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COMMUNICATION

Palladium-Catalyzed Direct Approch to α-Trifluoromethyl Alcohols by Selective Hydroxylfluorination of *gem*-Difluoroalkenes

Bin Zhang,[a,b] Xiaofei Zhang,[a] Jian Hao,[b] and Chunhao Yang*[a]

Abstract: A novel palladium-catalyzed selective hydroxylfluorination of *gem*-difluoroalkenes has been developed. By employing easily obtained *gem*-difluoroalkenes and NFSI as the fluorine source, the scope, advantages, and limitations of this reaction were well investigated. The reaction presents an efficient synthesis to afford a series of α-trifluoromethyl alcohols in good to excellent yields. Furthermore, this reaction probably proceeds via oxidation of Pd (0) to Pd (II) fluoride complex by NFSI, followed by fluoropalladation of *gem*-difluoroalkenes to generate an α-trifluoromethylbenzyl–Pd intermediate. And this strategy offers more possibilities for the constructing of other bonds, such as C-C, C-N and C-S.

Introduction

Because the trifluoromethyl (CF_3) group can dramatically modify the physical, chemical, and biological properties of molecules, CF_3-containing organic compounds have attracted significant attention from researchers in medicinal and agriculture chemistry.[1] In particular, the introduction of CF_3 into drug candidates is able to enhance chemical and metabolic stability, improve lipophilicity and bioavailability, and even increase the protein-binding a□nity.[2] Consequently, it is not surprising that numerous e□orts have been devoted to the development of new methodologies for the preparation of CF_3-containing compounds.[3] Furthermore, difunctionalization of alkenes, which involves the introduction of two functional groups across a double bond, represents a powerful method to construct diverse functionalized molecules. In the past decade, the development of methods for achieving difunctionalization of alkenes, including transition metal catalysis and visible-light photocatalysis, have been reported in organic synthesis.[4] It is need to be pointed that some pioneering and important works were reported by Liu and co-workers.[5] Among these methods of achieving difunctionalization of alkenes, the formation of a new C–CF_3 bond has become an important area and much effort has been made for the aim of developing novel and efficient methods.[6]

As an alternative CF_3 precursor, *gem*-difluoroalkenes have attracted more and more attention in organic chemistry. However, the further fluorination of *gem*-difluoroalkenes affording a CF_3 group was very difficult in the past. This is because the CF_3 carbanion formed from direct fluoride addition was found to be

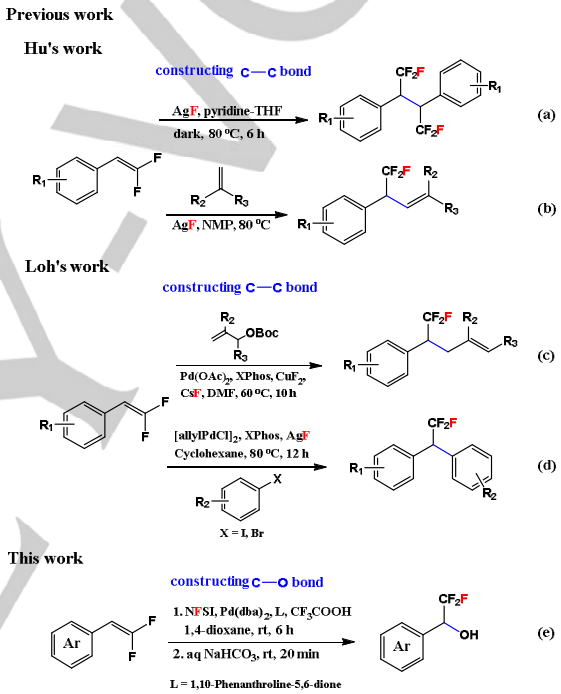

Figure 1. Synthesis of CF_3-containing compounds by difunctionalization of *gem*-difluoroalkenes

unstable and is spontaneously quenched by proton abstraction.[7,8] Recently, some novel methods for synthesis of CF_3-containing compounds by difunctionalization of *gem*-difluoroalkenes have been reported (Figure 1). In 2014, Hu and coworkers reported a novel silver(I)-fluoride-mediated homo-coupling reaction of *gem*-difluoroalkenes (Figure 1, a).[9] The key intermediate of this protocol is benzylsilver complex which was formed from nucleophilic addition of AgF to β, β-difluorostyrenes. This is the first example of the reactivity of α-trifluoromethylbenzyl-silver species. Later, Hu and coworkers carried out further exploration and developed an original route for the synthesis of α-CF_3 alkenes and β-CF_3 ketones via *gem*-difluoroalkenes fluorination and silver-mediated alkenyl C-H functionalization in 2015 (Figure 1, b).[10] In addition, Loh and coworkers presented a different and novel strategy based on palladium-catalyzed allylic alkylation by caesium fluoride nucleophilic addition of *gem*-difluoroalkenes in 2016 (Figure 1, c).[11] Furthermore, in 2017 Loh and coworkers

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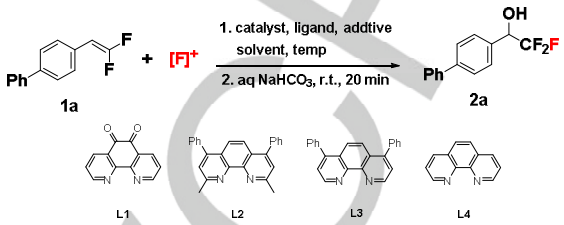
described the palladium-catalyzed fluoroarylation of *gem*-difluoroalkenes and arylation with aryl halides (Figure 1, d).[12] It is worthy to note that the in situ generated α-CF_3-benzylsilver, the key intermediate, derived from the nucleophilic addition of silver fluoride onto *gem*-difluoroalkenes. However, researches are still confronted with many potential challenges, such as the low stability of intermediates and their notorious reluctance to participate in the transmetalation. These academic problems are far less well investigated and required further study.

Inspired by our recent work in fluorine chemistry,[13] we designed a new strategy to construct α-trifluoromethyl alcohols via palladium-catalyzed selective hydroxylfluorination of *gem*-difluoroalkenes (Figure 1, e). As an effective fluorine source, N-Fluorobenzenesulfonimide (NFSI) could be served to oxidize Pd(0) to a Pd(II) fluoride complex. Different from the α-trifluoromethylbenzyl-Ag species (Hu and Lohs' work), the key intermediate of this strategy is probably the α-trifluoromethylbenzyl–Pd complex generated from fluoro-palladation of *gem*-difluoroalkenes. Furthermore, CF_3COOH, as an additive, involves ligand exchange and affords the C–O bond formation. As far as we know, α-trifluoromethyl alcohols can only be prepared from trifluoromethylation of aldehyde and carbonyl compounds or reduction of trifluoromethyl ketones.[14,15] Compared with existing methods, this new strategy has some significant advantages: (i) easily available fluorine source comes from NFSI, which serves as a good reagent ; (ii) only catalytic Pd is needed and no other metal is participated in hydroxylfluorination of *gem*-difluoroalkenes; (iii) based on the in-vestigation of the reaction mechanism, this strategy offers more possibilities for the constructing of other bonds, such as C-C, C-N and C-S. Therefore, we envisioned that this new strategy is important and significant.

Results and Discussion

As we know, *gem*-difluoroalkenes could be easily obtained from aldehydes or activated ketones in the presence of KI, Ph_3P, and methyl 2,2,-difluoro-2-(fluorosulfonyl)acetate (MDFA) under moderate conditions.[16] The study was initiated by exploring reaction conditions for the hydroxylfluorination of 4-(2,2-difluorovinyl)-1,1'-biphenyl (**1a**) (Table 1). Pleasingly, 68% yield of **2a** was found when **1a** was treated with 5 mol% of $PdCl_2$, 7.5 mol% of L1, 2 equiv of NFSI and 5 equiv of CF_3COOH at room temperature under argon in 1,4-dioxane (entry 1). Notably, only trace desired product was detected when CF_3COOH was replaced by CF_3COONa or CH_3COOH (entry 2 and entry 3) and it was implied that strong acid with weaker nucleophilicity was crucial for the formation of C–O bond. Then we investigated the fluorine sources and found that Selectfluor was a less effective fluorinating reagent for this tandem reaction (entry 4). Subsequently, the exploration of different Pd salts, such as $Pd(OAc)_2$, $Pd(OCOCF_3)_2$, $Pd(PPh_3)_4$ and $Pd(dba)_2$, led to the discovery that $Pd(dba)_2$ was the best choice for this process and the desired product **2a** could be obtained in 89% yield (entries 5-8). By screening the ligands, such as L2, L3 and L4, L1 was revealed to be the optimal ligand (entries 9-11). Although we obtained desired compound with a yield of 32% in NMP, the subsequent solvent screening indicated that this reaction did not work in other solvents such as CH_3CN, DMF and THF (entries 12-15). Furthermore, when the reaction mixture was warmed to 40 °C, the desired product **2a** was obtained in the same yield (entry 16 *vs* entry 8).

Table 1. Optimization of Reaction Conditions[a]



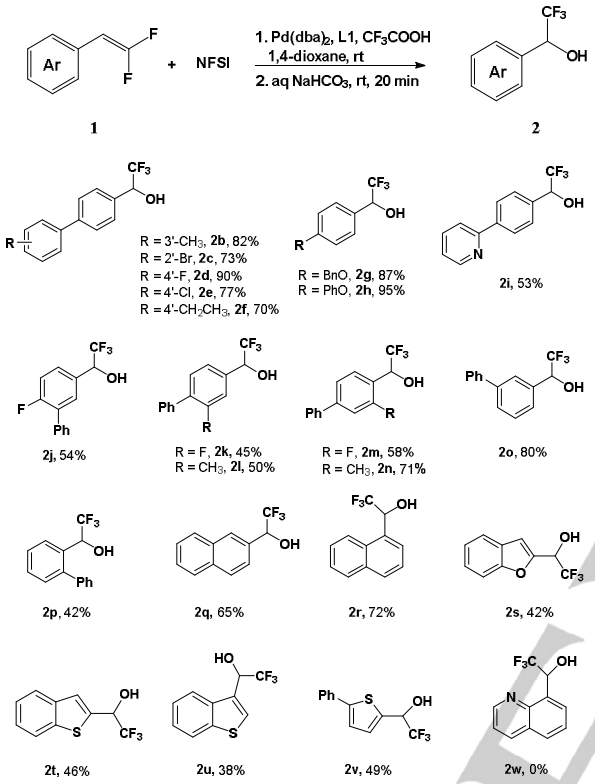
entry	[F]+	catalyst	ligand	additive	solvent	yield (%)[b]
1	NFSI	$PdCl_2$	L1	CF_3COOH	1,4-dioxane	68
2	NFSI	$PdCl_2$	L1	CH_3COOH	1,4-dioxane	trace
3	NFSI	$PdCl_2$	L1	CF_3COONa	1,4-dioxane	trace
4	Selectfluor	$PdCl_2$	L1	CF_3COOH	1,4-dioxane	20
5	NFSI	$Pd(OAc)_2$	L1	CF_3COOH	1,4-dioxane	40
6	NFSI	$Pd(OCOCF_3)_2$	L1	CF_3COOH	1,4-dioxane	63
7	NFSI	$Pd(PPh_3)_4$	L1	CF_3COOH	1,4-dioxane	48
8	**NFSI**	**$Pd(dba)_2$**	**L1**	**CF_3COOH**	**1,4-dioxane**	**89**
9	NFSI	$Pd(dba)_2$	L2	CF_3COOH	1,4-dioxane	21
10	NFSI	$Pd(dba)_2$	L3	CF_3COOH	1,4-dioxane	56
11	NFSI	$Pd(dba)_2$	L4	CF_3COOH	1,4-dioxane	60
12	NFSI	$Pd(dba)_2$	L1	CF_3COOH	CH_3CN	trace
13	NFSI	$Pd(dba)_2$	L1	CF_3COOH	NMP	32
14	NFSI	$Pd(dba)_2$	L1	CF_3COOH	DMF	trace
15	NFSI	$Pd(dba)_2$	L1	CF_3COOH	THF	0
16[c]	NFSI	$Pd(dba)_2$	L1	CF_3COOH	1,4-dioxane	88

[a] Reaction conditions: **1a** (0.5 mmol), $[F]^+$ (1.0 mmol), catalyst (5 mol%), ligand (7.5 mol%), additive (2.5 mmol) in solvent (3.0 mL) at r.t. for 6 h under Ar. [b] Isolated yields. [c] At 40 °C.

With the aforementioned optimized reaction conditions in hand (Table 1, entry 8), we firstly investigated the substrates prepared from aryl aldehydes, and the results are compiled in Scheme 1. Gratifyingly, the reaction showed broad substrate compatibility, and good functional group tolerance, including alkyl, fluoro, bromo, and chloro could react with NFSI under the standard conditions to a□ord the corresponding α-trifluoromethyl alcohols in moderate to excellent yields (**2b**-**2f**). Besides, *gem*-difluoroalkenes with the electron-donating groups such as benzyloxy and phenoxy worked well under the standard conditions (**2g** and **2h**, 87% and 95%

yields, respectively). However, the substrate with the 2-pyridyl group reacted with NFSI to deliver the corresponding product **2i** in 53% yield, which was lower than **2g** and **2h**. This result may be be caused by poisoning of the catalyst. Similar result was observed on **2W**. To better understand the substitution electron e□ect, more substituents were carried out. Among them,

Scheme 1. Palladium-Catalyzed Hydroxylfluorination of *gem*-difluoroalkenes from Aromatic Aldehydes

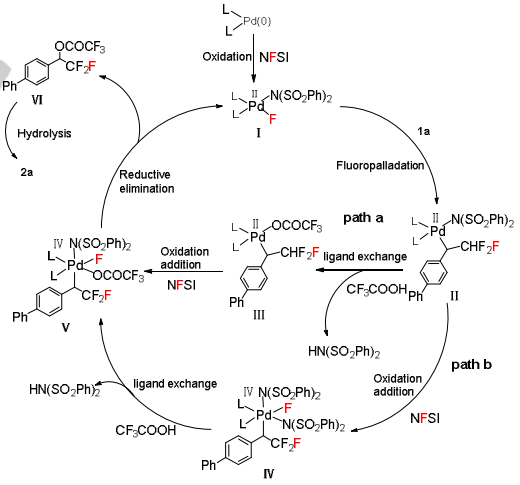


[a] Conditions: **1** (0.4 mmol), NFSI (0.8 mmol), $Pd(dba)_2$ (5 mol%), L1 (7.5 mol%), CF_3COOH (2.0 mmol), 1,4-Dioxane (2.0 mL), r.t., Ar. Isolated yields were presented.

when the fluoro group present at different positions on the aromatic ring, the lower yields were observed (**2j**, **2k**, and **2m**, 45%, 58% and 48% yields, respectively). Compared with the fluoro-substituted substrates, the methyl group substitutions showed higher yields (**2k** *vs* **2l**, 45% *vs* 50% and **2m** *vs* **2n**, 58% *vs* 71%). It is worth noting that whether the electron-donating group or the electron-withdrawing group, *ortho*-substituted substrates showed higher reactivity than meta isomer (**2k** *vs* **2m**, 45% *vs* 58% and **2l** *vs* **2n**, 50% *vs* 71%). Next, we investigated e□ect of steric hindrance. Comparable yields were obtained when we changed the substituents' location. For example, the *meta*-phenyl-substituted *gem*-difluorostyrene gave the corresponding products **2o** in 80% yields. However, the *ortho*-phenyl-substituted *gem*-difluorostyrene do not convert well in this transformation and only led to the formation of compound **2p** in 42% yield due to the bulky group's effect. In addition, reactions of the substrate bearing the naphthalene ring worked well under the standard conditions (**2q** and **2r**, 65% and 75% yields, respectively). Encouraged by the exciting results obtained from this Pd-catalyzed hydroxylfluorination of *gem*-difluorostyrenes, further application of the optimized reaction conditions to hetero-aromatic *gem*-difluoroalkenes were carried out. For example, the substrates with benzofuran, benzo[b]thiophene, and thiophene delivered the corresponding product **2s**, **2t**, and **2u** in acceptable yields. In order to reveal the practicability of this reaction, a gram-scale reaction between **1g** and NFSI was carried out, which gave product **2g** in 80% yield (Supporting Information).

On the basis of the literature reports on fluoroesterification of styrenes[17], a plausible reaction mechanism for palladium-catalyzed hydroxylfluorination of *gem*-difluoroalkenes has been proposed in Scheme 2. The reaction is initiated through oxidation of Pd (0) by NFSI to give Pd (II) fuoride complex I, and subsequence fuoropalladation of **1a** offers the intermediate II. Then, two possible paths are presented to address the transformation from complex II to the high-valent Pd intermediate V. The first pathway involves ligand exchange between II and CF_3COOH to yields intermediate III, and then subsequent oxidation of III by NFSI generates the high-valent Pd intermediate V (path a). For the second pathway, the transformation from Pd complex II to IV is firstly via oxidation of Pd (II) species II to the high-valent Pd interme-diate IV and subsequence undergoes ligand exchange be-tween IV and CF_3COOH (path b). Finally, intermediate V undergoes reductive elimination to form the C–O bond and get product VI, which is easily hydrolyzed to the compound **2a**.

Scheme 2. Possible Mechanism



Conclusions

In summary, we have developed a Pd-catalyzed selective hydroxylfluorination of *gem*-difluoroalkenes using NFSI as the fluoride source. The reaction tolerated a range of different substrates with a variety of functional groups. And the key intermediate of this strategy is probably the α-trifluoromethylbenzyl–Pd complex generated from fluoro-palladation of *gem*-difluoroalkenes. Meanwhile, the present protocol also offered more possibilities for constructing other bond,

such as C-C, C-N and C-S bonds, the relative studies are currently in progress.

Experimental Section

General Methods.

Unless otherwise noted, all solvents and other reagents are commercially available and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 300-400 mesh silica gel in petroleum ether. Nuclear magnetic resonance spectra (^{1}H, ^{13}C NMR and ^{19}F NMR) were recorded on Varian Mercury- 300/400 and Varian Mercury-400/500 spectrometers. High-resolution mass spectra (HRMS) were performed on a Finnigan MAT 95 spectrometer. Melting points were measured by Büchi 510 melting point apparatus without further corrected.

General experimental procedure for the synthesis of *gem*-difluoroalkenes[16,18,19].

A 5 mL, three necked round bottomed flask was equipped with a stir bar. The vessel was flamed dried and then allowed to cool to room temperature. Under the inert, nitrogen atmosphere, acetonitrile (2 mL) was added to the vessel, and the temperature was increased to 70 °C. Then triphenylphosphine (3 mmol), potassium iodide (2 mmol), and aldehyde (1 mmol) were added and let stir for 30 minutes. Methyl 2,2-difluoro-2-(fluorosulfonyl)acetate (MDFA) (1.75 mmol) was then added slowly over a period 10 minutes. The resulting mixture was stirred for three hours, a nitrogen atmosphere being maintained until the end of the reaction. Then the reaction was quenched with water and extracted with ethyl acetate. The ethyl acetate was then removed by rotary evaporation. Product was isolated from the slurry and separated from residual triphenylphosphine by extraction 5 times with hexane (5 mL). The combined hexane extracts were combined and concentrated. Additional impurities were removed via column chromatography using a mixture of petroleum ether and ethyl acetate to obtain pure product.

General experimental procedure for the synthesis of α-Trifluoromethyl Alcohols.

In a dried glass tube, $Pd(dba)_2$ (0.02 mmol, 5 mol%), L1 (0.03 mmol, 7.5 mol%), NFSI (0.8 mmol), *gem*-difluoroalkene (0.4 mmol) were dissolved in 1,4-dioxane (2.0 mL), and then CF_3COOH (2.0 mmol) was added. The reaction mixture was stirred at 25 ℃ for 6 h under an argon atmosphere. After the reaction completed, 10 drops of saturated aq. $NaHCO_3$ were added, and the reaction mixture was stirred for another 20 minutes. After that, the solvent was removed under vacuum, and the residue was purified by silica gel column chromatography with a gradient eluant of petroleum ether and ethyl acetate to afford product.

A gram-scale experimental procedure for the synthesis of 1g.

In a dried round bottomed flask glass, $Pd(dba)_2$ (0.25 mmol, 5 mol%), L1 (0.375 mmol, 7.5 mol%), NFSI (10 mmol, 3.15 g), *gem*-difluoroalkene **1g** (5 mmol, 1.23 g) were dissolved in 1,4-dioxane (25 mL), and then CF_3COOH (1.9 mL) was added. The reaction mixture was stirred at 25 ℃ for 10 h under an argon atmosphere. After the reaction completed, saturated aq. $NaHCO_3$ (5 mL) were added, and the reaction mixture was stirred for another 30 minutes. After that, the solvent was removed under vacuum, and the residue was purified by silica gel column chromatography with a gradient eluant of petroleum ether and ethyl acetate to afford white solid **2g** (1.12 g, 80%).

4-(2,2-difluorovinyl)-1,1'-biphenyl (1a)[18] White solid (164 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 4H), 7.50 – 7.30 (m, 5H), 5.32 (dd, *J* = 26.3, 3.8 Hz, 1H).

4'-(2,2-difluorovinyl)-3-methyl-1,1'-biphenyl (1b) Clear liquid (172 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.44 – 7.28 (m, 5H), 7.16 (d, *J* = 7.3 Hz, 1H), 5.31 (dd, *J* = 26.3, 3.6 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3 (dd, *J* = 298.5, 288.4 Hz), 140.5 (s), 140.0 (s), 138.4 (s), 129.3 (t, *J* = 6.4 Hz), 128.8 (s), 128.2 (s), 128.0 – 127.8 (m), 127.8 (s), 127.4 (s), 124.1 (s), 82.0 (dd, *J* = 29.2, 13.6 Hz), 21.6 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.97 (dd, *J* = 30.7, 26.5 Hz, 1F), -83.92 (dd, *J* = 31.0, 3.1 Hz, 1F). HRMS m/z (EI): calcd for [$C_{15}H_{12}F_2$], 230.0907; found 230.0900.

2-bromo-4'-(2,2-difluorovinyl)-1,1'-biphenyl (1c) Clear liquid (241 mg, 82%). 1H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.0 Hz, 1H), 7.45 – 7.26 (m, 6H), 7.26 – 7.09 (m, 1H), 5.32 (dd, *J* = 26.2, 3.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5 (dd, *J* = 298.7, 288.7 Hz), 142.02 (s), 139.8 (s), 133.2 (s), 131.2 (s), 129.8 (s), 128.9 (s), 127.5 (s), 127.2 (dd, *J* = 6.3, 3.5 Hz), 122.6 (s), 82.0 (dd, *J* = 29.3, 13.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.60 (dd, *J* = 29.7, 26.7 Hz, 1F), -83.55 (dd, *J* = 30.1, 3.0 Hz, 1F). HRMS m/z (EI): calcd for [$C_{14}H_9BrF_2$], 293.9856; found 293.9847.

4-(2,2-difluorovinyl)-4'-fluoro-1,1'-biphenyl (1d) White solid (204 mg, 87%). M.P. 86-88 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.32 (m, 6H), 7.12 (t, *J* = 8.6 Hz, 2H), 5.30 (dd, *J* = 26.3, 3.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, *J* = 246.7 Hz), 155.9 (dd, *J* = 298.5, 288.7 Hz), 138.4 (s), 136.2 (d, *J* = 3.1 Hz), 129.0 (t, *J* = 6.5 Hz), 128.1 (d, *J* = 8.0 Hz), 127.6 (dd, *J* = 6.3, 3.5 Hz), 126.8 (s), 115.3 (d, *J* = 21.5 Hz), 81.4 (dd, *J* = 29.3, 13.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.82 (dd, *J* = 30.1, 26.7 Hz, 1F), -83.70 (dd, *J* = 30.5, 3.0 Hz, 1F), -115.37 – -115.57 (m, 1F). HRMS m/z (EI): calcd for [$C_{14}H_9F_3$], 234.0656; found 234.0653.

4-chloro-4'-(2,2-difluorovinyl)-1,1'-biphenyl (1e) White solid (132 mg, 53%). M.P. 83-85 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.1, 5.3 Hz, 4H), 7.40 (d, *J* = 8.4 Hz, 4H), 5.31 (dd, *J* = 26.2, 3.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.4 (dd, *J* = 298.7, 288.9 Hz), 138.9 (s), 138.49 (s), 133.50 (s), 129.7 (t, *J* = 6.5 Hz), 129.0 (s), 128.1 (s), 128.0 (dd, *J* = 6.3, 3.5 Hz), 127.1 (s), 81.8 (dd, *J* =29.3, 13.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.47 – -81.73 (m, 1F), -83.46 (d, *J* = 29.8 Hz, 1F). HRMS m/z (EI): calcd for [$C_{14}H_9ClF_2$], 250.0361; found 250.0361.

4-(2,2-difluorovinyl)-4'-ethyl-1,1'-biphenyl (1f) White solid (161 mg, 66%). M.P. 113-115 °C.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.47 (m, 4H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.31 (dd, *J* = 26.3, 3.8 Hz, 1H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9 (dd, *J* = 298.4, 288.3 Hz), 143.2 (s), 139.4 (s), 137.5 (s), 128.7 (t, *J* = 6.4 Hz), 128.0 (s), 127.6 (dd, *J* = 6.3, 3.5 Hz), 126.8 (s), 126.5 (s), 81.5 (dd, *J* = 29.2, 13.6 Hz), 28.1 (s), 15.2 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -82.06 (dd, *J* = 31.0, 26.4 Hz, 1F), -84.01 (dd, *J* = 31.2, 3.0 Hz, 1F). HRMS m/z (EI): calcd for [$C_{16}H_{14}F_2$], 244.1064; found 244.1056.

1-(benzyloxy)-4-(2,2-difluorovinyl)benzene (1g)[17] White solid (160 mg, 57%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 5H), 7.28 – 7.19 (m, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 5.21 (dd, *J* = 26.3, 3.9 Hz, 1H), 5.06 (s, 2H).

1-(2,2-difluorovinyl)-4-phenoxybenzene (1h) Clear liquid (185 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 4H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.98 (dd, *J* = 12.4, 8.3 Hz, 4H), 5.23 (dd, *J* = 26.2, 3.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0 (s), 156.3 (s), 156.1(dd, *J* = 297.2, 287.5 Hz), 129.8 (s), 129.0 (dd, *J* = 6.3, 3.5 Hz), 125.3 (t, *J* = 6.3 Hz), 123.5 (s), 119.1 (s), 119.0 (s), 81.54 (dd, *J* = 29.4, 14.0 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -83.58 (dd, *J* = 34.1, 26.1 Hz, 1F), -85.25 (dd, *J* = 34.0, 3.3 Hz, 1F). HRMS m/z (EI): calcd for [$C_{14}H_{10}F_2O$], 232.0700; found 232.0694.

2-(4-(2,2-difluorovinyl)phenyl)pyridine (1i) Yellow solid (173 mg, 80%). M.P. 54-56 °C.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.5 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.79 – 7.66 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.17 (m, 1H), 5.33 (dd, *J* = 26.3, 3.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8 (s), 156.5 (dd, *J* = 299.1, 289.0 Hz), 149.7 (s), 137.2 (s), 136.8 (s), 131.1 (t, *J* = 6.5 Hz), 128.1 – 127.8 (m), 127.2 (s), 122.20 (s), 120.4 (s), 82.0 (dd, *J* = 29.3, 13.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.02 – -81.25 (m, 1F), -83.18 (dd, *J* = 29.0, 3.1 Hz, 1F). HRMS m/z (EI): calcd for [$C_{13}H_9F_2N$], 217.0703; found 217.0706.

5-(2,2-difluorovinyl)-2-fluoro-1,1'-biphenyl (1j) Clear liquid (140 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 2H), 7.49 – 7.31 (m, 4H), 7.32 – 7.21 (m, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.28 (dd, *J* = 25.9, 3.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7 (d, *J* = 249.0 Hz), 156.2 (ddd, *J* = 297.5, 288.3, 2.1 Hz), 135.4 (s), 130.2 – 129.9 (m), 129.4 (d, *J* = 14.2 Hz), 129.0 (d, *J* = 2.7 Hz), 128.5 (s), 128.1 (td, *J* = 8.1, 3.4 Hz), 127.9 (s), 126.7 (dd, *J* = 10.3, 6.2 Hz), 116.5 (d, *J* = 23.5 Hz), 81.3 (dd, *J* = 29.8, 13.9 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -82.95 (dd, *J* = 32.2, 26.0 Hz, 1F), -84.35 (d, *J* = 32.4 Hz, 1F), -119.47 (s, 1F). HRMS m/z (EI): calcd for [$C_{14}H_9F_3$], 234.0656; found 234.0650.

4-(2,2-difluorovinyl)-2-fluoro-1,1'-biphenyl (1k) Clear liquid (168 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.48 – 7.32 (m, 4H), 7.19 – 7.11 (m, 2H), 5.29 (dd, *J* = 25.8, 3.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8 (d, *J* = 247.6 Hz), 156.6 (dd, *J* = 299.2, 289.8 Hz), 135.3 (s), 131.5 (dd, *J* = 15.1, 7.0 Hz), 130.8 (d, *J* = 4.1 Hz), 128.9 (d, *J* = 2.9 Hz), 128.5 (s), 127.8 (s), 127.7 (d, *J* = 15.6 Hz), 123.7 (dd, *J* = 9.3, 3.5 Hz), 115.1 (ddd, *J* = 24.9, 7.0, 3.3 Hz), 81.5 (dd, *J* = 30.1, 13.4 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.35 (t, *J* = 26.6 Hz, IF), -82.52 (d, *J* = 28.1 Hz, 1F), -117.55 – -117.73 (m, 1F). HRMS m/z (EI): calcd for [$C_{14}H_9F_3$], 234.0656; found 234.0648.

4-(2,2-difluorovinyl)-2-methyl-1,1'-biphenyl (1l) Clear liquid (142 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2H), 7.37 – 7.28 (m, 3H), 7.24 – 7.20 (m, 3H), 5.28 (dd, *J* = 26.4, 3.9 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3 (dd, *J* = 294.7, 284.6 Hz), 141.4 (s), 140.8 (s), 135.7 (s), 130.2 (s), 129.6 (dd, *J* = 5.8, 3.7 Hz), 129.4 – 129.2 (m), 129.1 (s), 128.2 (s), 126.9 (s), 125.0 (dd, *J* = 6.4, 3.3 Hz), 81.9 (dd, *J* = 29.0, 13.6 Hz), 20.51 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -82.20 (dd, *J* = 31.5, 26.4 Hz, 1F), -84.13 (dd, *J* = 31.6, 3.2 Hz, 1F). HRMS m/z (EI): calcd for [$C_{15}H_{12}F_2$], 230.0907; found 230.0901.

4-(2,2-difluorovinyl)-3-fluoro-1,1'-biphenyl (1m) White solid (117 mg, 50%). M.P. 53-55 °C.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 3H), 7.49 – 7.41 (m, 2H), 7.41 – 7.33 (m, 2H), 7.30 (d, *J* = 11.5 Hz, 1H), 5.55 (dd, *J* = 26.2, 3.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.7 (dd, *J* = 247.8, 5.9 Hz), 156.5 (dd, *J* = 298.1, 289.7 Hz), 141.9 (d, *J* = 7.9 Hz), 139.3 (d, *J* = 1.5 Hz), 128.9 (s), 128.7 (d, *J* = 6.8 Hz), 128.0 (s), 126.8 (s), 122.8 (d, *J* = 3.0 Hz), 117.0 (dt, *J* = 13.3, 6.7 Hz), 113.8 (d, *J* = 22.7 Hz), 74.6 (ddd, *J* = 32.8, 13.3, 7.0 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.78 (td, *J* = 26.1, 4.2 Hz, 1F), -81.27 – -81.42 (m, 1F), -117.26 (td, *J* = 11.5, 4.4 Hz, 1F). HRMS m/z (EI): calcd for [$C_{14}H_9F_3$], 234.0656; found 234.0651.

4-(2,2-difluorovinyl)-3-methyl-1,1'-biphenyl (1n) Clear liquid (158 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.52 – 7.38 (m, 5H), 7.37 – 7.29 (m, 1H), 5.40 (dd, *J* = 25.5, 3.9 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3 (dd, *J* = 297.2, 288.1 Hz), 140.68 (s), 140.1 (s), 136.2 (d, *J* = 4.0 Hz), 128.9 (s), 128.8 (s), 128.5 (d, *J* = 8.8 Hz), 128.2 – 127.7 (m), 127.4 (s), 127.0 (s), 124.9 (s), 79.2 (dd, *J* = 28.9, 14.6 Hz), 20.2 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -83.46 (dd, *J* = 30.3, 3.4 Hz, 1F), -84.38 (dd, *J* = 29.8, 26.0 Hz, 1F). HRMS m/z (EI): calcd for [$C_{15}H_{12}F_2$], 230.0907; found 230.0901.

3-(2,2-difluorovinyl)-1,1'-biphenyl (1o) Clear liquid (168 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 3H), 7.52 – 7.32 (m, 6H), 5.37 (dd, *J* = 26.2, 3.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5 (dd, *J* = 298.4, 288.4 Hz), 141.8 (s), 140.9 (s), 130.9 (t, *J* = 6.4 Hz), 129.2 (s), 128.8 (s), 127.5 (s), 127.2 (s), 126.7 – 126.3 (m), 126.5 (s), 126.0 (s), 82.2 (dd, *J* = 29.1, 13.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.82 (dd, *J* = 30.7, 26.4 Hz, 1F), -83.78 (dd, *J* = 30.8, 3.1 Hz, 1F). HRMS m/z (EI): calcd for [$C_{14}H_{10}F_2$], 216.0751; found 216.0745.

2-(2,2-difluorovinyl)-1,1'-biphenyl (1p) Clear liquid (86 mg, 40%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 1H), 7.46 – 7.25 (m, 8H), 5.21 (dd, *J* = 26.1, 4.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8 (dd, *J* = 297.6, 287.1 Hz), 140.8 (d, *J* = 4.5 Hz), 140.3 (s), 129.7 (s), 129.1 (s), 127.9 (s), 127.7 (d, *J* = 9.4 Hz), 127.6 – 127.4 (m), 127.2 (s), 126.9 (s), 126.7 (s), 80.2 (dd, *J* = 30.2, 12.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -83.10 (dd, *J* = 31.7, 3.9 Hz, 1F), -84.91 (dd, *J* = 31.6, 26.3 Hz, 1F). HRMS m/z (EI): calcd for [$C_{14}H_{10}F_2$], 216.0751; found 216.0745.

2-(2,2-difluorovinyl)naphthalene (1q)[18] Clear liquid (126 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.69 (m, 4H), 7.54 – 7.39 (m, 3H), 5.43 (dd, *J* = 26.3, 3.9 Hz, 1H).

1-(2,2-difluorovinyl)naphthalene (1r) Clear liquid (116 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 1H), 7.84 (dd, *J* = 6.3, 3.2 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.62 – 7.40 (m, 4H), 5.85 (dd, *J* = 24.4, 3.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3 (dd, *J* = 300.1, 292.4 Hz), 133.2 (s), 131.0 (d, *J* = 3.3 Hz), 128.3 (s), 127.6 (s), 126.2 – 126.1 (m), 126.0 (s), 125.6 (s), 125.1 (s), 123.3 (s), 78.3 (dd, *J* = 29.2, 15.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -83.07 – -83.31 (m, 1F), -85.00 (dd, *J* = 29.1, 24.7 Hz, 1F). HRMS m/z (EI): calcd for [$C_{12}H_8F_2$], 190.0594; found 190.0586.

2-(2,2-difluorovinyl)benzofuran (1s)[18] Clear liquid (112 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.39 (m, 2H), 7.22 (pd, *J* = 7.1, 1.3 Hz, 2H), 6.64 (s, 1H), 5.41 (dd, *J* = 25.1, 1.9 Hz, 1H).

2-(2,2-difluorovinyl)benzo[b]thiophene (1t) Yellow solid (102 mg, 52%). M.P. 75-77 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 1H), 7.70 (dd, *J* = 6.8, 2.1 Hz, 1H), 7.39 – 7.26 (m, 2H), 7.19 (s, 1H), 5.62 (dd, *J* = 25.6, 2.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1 (dd, *J* = 299.3, 291.0 Hz), 139.1 (s), 131.9 (t, *J* = 7.1 Hz), 124.1 (s), 124.0 (s), 122.8 (s), 122.2 (dd, *J* = 7.1, 4.8 Hz), 121.6 (s), 77.9 (dd, *J* = 33.3, 16.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.70 – -78.99 (m, 1F), -84.74 (d, *J* = 22.9 Hz, 1F). HRMS m/z (EI): calcd for [$C_{10}H_6F_2S$], 196.0158; found 196.0161.

3-(2,2-difluorovinyl)benzo[b]thiophene (1u)[18] Clear liquid (123 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 1H), 7.73 – 7.65 (m, 1H), 7.49 – 7.32 (m, 3H), 5.58 (dd, *J* = 25.7, 2.4 Hz, 1H).

2-(2,2-difluorovinyl)-5-phenylthiophene (1v) Clear liquid (169 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.48 (m, 2H), 7.39 – 7.30 (m, 2H), 7.29 – 7.20 (m, 1H), 7.16 (dd, *J* = 3.7, 0.9 Hz, 1H), 6.91 (d, *J* = 3.7 Hz, 1H), 5.49 (dd, *J* = 25.8, 1.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0 (dd, *J* = 297.9, 289.8 Hz), 143.8 (dd, *J* = 6.3, 4.1 Hz), 134.0 (s), 131.7 – 131.1 (m), 129.0 (s), 127.6 (s), 127.2 – 126.7 (m), 125.6 (s), 123.2 (s), 77.9 (dd, *J* = 33.4, 17.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.09 (t, *J* = 26.3 Hz, 1F), -87.28 (d, *J* = 26.6 Hz, 1F). HRMS m/z (EI): calcd for [$C_{12}H_8F_2S$], 222.0315; found 222.0310.

8-(2,2-difluorovinyl)quinoline (1w)[19] Clear liquid (88 mg, 46%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.93 (d, *J* = 7.3 Hz, 1H), 7.72 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.75 (dd, *J* = 27.8, 4.2 Hz, 1H). ***1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethan-1-ol (2a)*** White solid (90 mg, 89%). M.P. 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.52 (m, 6H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 5.12 – 5.04 (m, 1H), 2.61 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1 (s), 139.9 (s), 132.5(s), 128.5 (s), 127.5 (s), 127.3 (s), 127.0 (s), 126.8 (s), 123.9 (q, *J* = 282.8 Hz), 72.2 (q, *J* = 32.0 Hz). ^{19}F NMR (471 MHz, $CDCl_3$)

δ -78.16 (d, *J* = 6.5 Hz). HRMS m/z (EI): calcd for [$C_{14}H_{11}F_3O$], 252.0762; found 252.0753.

2,2,2-trifluoro-1-(3'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-ol (2b) White solid (87 mg, 82%). M.P. 57-59 °C.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.27 (m, 3H), 7.17 (d, *J* = 6.6 Hz, 1H), 5.07 – 4.92 (m, 1H), 2.84 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7 (s), 140.3 (s), 138.5 (s), 132.8 (s), 128.7 (s), 128.5 (s), 128.0 (s), 127.9 (s), 127.4 (s), 125.1 (q, *J* = 281.0 Hz), 124.3 (s), 72.7 (q, *J* = 32.0 Hz), 21.5 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.16 (d, *J* = 6.5 Hz). HRMS m/z (EI): calcd for [$C_{15}H_{13}F_3O$], 266.0918; found 266.0920.

1-(2'-bromo-[1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethan-1-ol (2c) Clear liquid (96 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.28 (m, 2H), 7.27 – 7.17 (m, 1H), 5.08 (q, *J* = 6.4 Hz, 1H), 2.78 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3 (s), 141.8 (s), 133.3 (s), 133.2 (s), 131.2 (s), 129.7 (s), 129.1 (s), 127.4 (s), 127.1 (s), 124.9 (q, *J* = 280.0 Hz), 122.5 (s), 72.7 (q, *J* = 32.1 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.13 (d, *J* = 6.6 Hz). HRMS m/z (EI): calcd for [$C_{14}H_{10}BrF_3O$], 329.9867; found 329.9871.

2,2,2-trifluoro-1-(4'-fluoro-[1,1'-biphenyl]-4-yl)ethan-1-ol (2d) White solid (97 mg, 90%). M.P. 94-96 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 6H), 7.17 – 7.10 (m, 2H), 5.07 (q, *J* = 6.5 Hz, 1H), 2.80 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3 (d, *J* = 247.0 Hz), 141.1 (s), 136.0 (d, *J* = 3.2 Hz), 132.5 (s), 128.3 (d, *J* = 8.1 Hz), 127.5 (s), 126.8 (s), 123.8 (q, *J* = 282.2 Hz), 115.3 (d, *J* = 21.5 Hz), 72.2 (q, *J* = 32.1 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.28 (d, *J* = 6.4 Hz, 3F), -114.98 – -115.12 (m, 1F). M.P. 94-96 °C. HRMS m/z (EI): calcd for [$C_{14}H_{10}F_4O$], 270.0668; found 270.0662**.**

1-(4'-chloro-[1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethan-1-ol (2e) White solid (88 mg, 77%). M.P. 117-119 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.47 (m, 6H), 7.41 (d, *J* = 8.5 Hz, 2H), 5.07 (q, *J* = 6.4 Hz, 1H), 2.81 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2 (s), 138.8 (s), 133.9 (s), 133.3 (s), 129.1 (s), 128.4 (s), 128.0 (s), 127.2 (s), 124.3 (q, *J* = 282.1 Hz), 72.6 (q, *J* = 32.1 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.26 (d, *J* = 6.5 Hz). M.P. 117-119 °C. HRMS m/z (EI): calcd for [$C_{14}H_{10}ClF_3O$], 286.0372; found 286.0368.

1-(4'-ethyl-[1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethan-1-ol (2f) White solid (78 mg, 70%). M.P. 111-113 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.48 (m, 4H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.15 – 4.98 (m, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 2.64 (d, *J* = 4.4 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5 (s), 142.1 (s), 137.3 (s), 132.1 (s), 128.0 (s), 127.4 (s), 126.8 (s), 126.7 (s), 123.9 (q, *J* = 282.1 Hz), 72.3 (dd, *J* = 69.7, 26.5 Hz), 28.1 (s), 15.1 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.23 (d, *J* = 6.7 Hz). M.P. 111-113 °C. HRMS m/z (EI): calcd for [$C_{16}H_{15}F_3O$], 280.1075; found 280.1068.

1-(4-(benzyloxy)phenyl)-2,2,2-trifluoroethan-1-ol (2g) White solid (98 mg, 87%). M.P. 108-110 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 6H), 7.33 (dd, *J* = 8.3, 6.0 Hz, 1H), 7.03 – 6.97 (m, 2H), 5.07 (s, 2H), 4.99 – 4.91 (m, 1H), 2.53 (d, *J* = 3.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4 (s), 136.3 (s), 128.5 (s), 128.4 (s), 127.8 (s), 127.2 (s), 126.1 (s), 124.3 (d, *J* = 282.8 Hz), 114.7 (s), 72.2 (q, *J* = 32.1 Hz),69.8 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.50 (d, *J* = 6.6 Hz). HRMS m/z (EI): calcd for [$C_{15}H_{13}F_3O_2$], 282.0868; found 282.0862.

2,2,2-trifluoro-1-(4-phenoxyphenyl)ethan-1-ol (2h) White solid (102 mg, 95%). M.P. 79-81 °C.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 4H), 7.14 (ddd, *J* = 8.5, 2.2, 1.1 Hz, 1H), 7.06 – 6.97 (m, 4H), 5.03 – 4.92 (m, 1H), 2.73 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6 (s), 156.5 (s), 129.9 (s), 129.0 (s), 128.4 (s), 124.3 (q, *J* = 282.1 Hz), 123.9 (s), 119.5 (s), 118.4 (s), 72.4 (q, *J* = 32.1 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.45 (d, *J* = 6.7 Hz). HRMS m/z (EI): calcd for [$C_{14}H_{11}F_3O_2$], 268.0711; found 268.0705.

2,2,2-trifluoro-1-(4-(pyridin-2-yl)phenyl)ethan-1-ol (2i) White solid (54 mg, 53%). M.P. 141-143 °C.^{1}H NMR (300 MHz, DMSO) δ 8.73 – 8.63 (m, 1H), 8.12 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.90 (td, *J* = 7.7, 1.8 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.38 (ddd, *J* = 7.3, 4.8, 1.1 Hz, 1H), 6.91 (d, *J* = 5.6 Hz, 1H), 5.32 – 5.15 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 156.0 (s), 150.1 (s), 139.6 (s), 137.8 (s), 137 (s), 128.47 (s), 126.81 (s), 125.52 (q, *J* = 283.5 Hz), 123.22 (s), 120.87 (s), 70.66 (q, *J* = 30.5 Hz). ^{19}F NMR (471 MHz, DMSO) δ -76.63 (d, *J* = 7.4 Hz). HRMS m/z (EI): calcd for [$C_{13}H_{10}F_3NO$], 253.0714; found 253.0715.

2,2,2-trifluoro-1-(6-fluoro-[1,1'-biphenyl]-3-yl)ethan-1-ol (2j) Clear liquid (58 mg, 54%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 3H), 7.52 – 7.35 (m, 4H), 7.22 (dd, *J* = 17.4, 8.3 Hz, 1H), 5.06 (dd, *J* = 12.3, 6.2 Hz, 1H), 2.86 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3 (d, *J* = 250.4 Hz), 135.1 (s), 130.1 (d, *J* = 3.2 Hz), 129.5 (d, *J* = 14.2 Hz), 129.1 (d, *J* = 2.7 Hz), 128.6 (s), 128.1 (s), 128.0 (s), 124.2 (q, *J* = 282.1 Hz), 116.5 (d, *J* = 23.7 Hz), 72.2 (q, *J* = 32.2 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.47 (d, *J* = 6.5 Hz, 3F), -116.64 – -116.77 (m, 1F). HRMS m/z (EI): calcd for [$C_{14}H_{10}F_4O$], 270.0668; found 270.0668.

2,2,2-trifluoro-1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethan-1-ol (2k) Clear liquid (49 mg, 45%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.51 – 7.34 (m, 4H), 7.31 (d, *J* = 9.3 Hz, 2H), 5.10 – 4.98 (m, 1H), 2.86 (d, *J* = 4.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7 (d, *J* = 248.9 Hz), 135.1 (s), 135.0 (s), 130.9 (d, *J* = 3.7 Hz), 130.3 (d, *J* = 13.6 Hz), 129.0 (d, *J* = 2.8 Hz), 128.6 (s), 128.1 (s), 124.1 (q, *J* = 282.2 Hz), 123.4 (d, *J* = 2.8 Hz), 115.34 (d, *J* = 24.9 Hz), 72.05 (q, *J* = 32.1 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.24 (d, *J* = 6.4 Hz, 3F), -116.82 – -116.97 (m, 1F). HRMS m/z (EI): calcd for [$C_{14}H_{10}F_4O$], 270.0668; found 270.0656.

2,2,2-trifluoro-1-(2-methyl-[1,1'-biphenyl]-4-yl)ethan-1-ol (2l) Clear liquid (53 mg, 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.20 (m, 8H), 5.05 – 4.89 (m, 1H), 2.82 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3 (s), 141.2 (s), 136.0 (s), 132.9 (s), 130.1 (s), 129.4 (s), 129.1 (s), 128.2 (s), 127.2 (s), 124.9 (s), 124.4 (q, *J* = 282.1 Hz), 72.8 (q, *J* = 32.0 Hz), 20.5 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.06 (d, *J* = 6.6 Hz). HRMS m/z (EI): calcd for [$C_{15}H_{13}F_3O$], 266.0918; found 266.0918.

2,2,2-trifluoro-1-(3-fluoro-[1,1'-biphenyl]-4-yl)ethan-1-ol (2m) White solid (63 mg, 58%). M.P. 98-100 °C.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (t, *J* = 7.7 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.48 – 7.34 (m, 4H), 7.30 (dd, *J* = 11.4, 1.7 Hz, 1H), 5.42 (q, *J* = 6.3 Hz, 1H), 3.03 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7 (d, *J* = 248.4 Hz), 144.7 (d, *J* = 8.3 Hz), 139.1 (d, *J* = 1.4 Hz), 129.0 (s), 128.3 (s), 127.1 (s), 124.2 (q, *J* = 281.9 Hz), 123.2 (d, *J* = 2.9 Hz), 120.1 (d, *J* = 13.2 Hz), 114.1 (d, *J* = 22.8 Hz), 66.5 (qd, *J* = 33.5, 3.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.47 (t, *J* = 6.2 Hz, 3F), -117.82 (dt, *J* = 18.0, 6.0 Hz, 1F). HRMS m/z (EI): calcd for [$C_{14}H_{10}F_4O$], 270.0668; found 270.0663.

2,2,2-trifluoro-1-(3-methyl-[1,1'-biphenyl]-4-yl)ethan-1-ol (2n) Clear liquid (75 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.50 – 7.27 (m, 5H), 5.41 – 5.21 (m, 1H), 2.73 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2 (s), 140.4 (s), 137.0 (s), 131.5 (s), 129.4 (s), 128.9 (s), 127.7 (s), 127.6 (s), 127.2 (s), 125.2 (s), 124.8 (q, *J* = 282.5 Hz), 68.9 (q, *J* = 32.1 Hz), 19.5 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -77.57 (d, *J* = 5.0 Hz). HRMS m/z (EI): calcd for [$C_{15}H_{13}F_3O$], 266.0918; found 266.0918.

1-([1,1'-biphenyl]-3-yl)-2,2,2-trifluoroethan-1-ol (2o) Clear liquid (80 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.67 – 7.54 (m, 3H), 7.54 – 7.30 (m, 5H), 5.16 – 4.98 (m, 1H), 2.75 (d, *J* = 3.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8 (s), 140.5 (s), 134.5 (s), 129.1 (s), 128.9 (s), 128.4 (s), 127.7 (s), 127.2 (s), 126.3 (s), 124.2 (q, *J* = 282.5 Hz), 72.9 (q,

J = 32.0 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.20 (d, *J* = 6.8 Hz). HRMS m/z (EI): calcd for [$C_{14}H_{11}F_3O$], 252.0762; found 252.0750.

1-([1,1'-biphenyl]-2-yl)-2,2,2-trifluoroethan-1-ol (2p) Clear liquid (42 mg, 42%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 1H), 7.50 – 7.34 (m, 5H), 7.34 – 7.25 (m, 3H), 5.19 – 5.06 (m, 1H), 2.61 (d, *J* = 2.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0 (s), 140.0 (s), 131.9 (s), 130.4 (s), 129.3 (s), 129.2 (s), 128.4 (s), 128.1 (s), 127.6 (s), 127.3 (s), 124.6 (q, *J* = 284.2 Hz), 68.9 (q, *J* = 31.8 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -76.58 (d, *J* = 6.7 Hz). HRMS m/z (EI): calcd for [$C_{14}H_{11}F_3O$], 252.0762; found 252.0757.

2,2,2-trifluoro-1-(naphthalen-2-yl)ethan-1-ol (2q) Clear liquid (59 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.77 (m, 4H), 7.53 (dd, *J* = 11.3, 7.4 Hz, 3H), 5.17 (dt, *J* = 12.8, 6.5 Hz, 1H), 2.77 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.4 (s), 132.5 (s), 130.9 (s), 128.1 (s), 127.8 (s), 127.4 (s), 126.9 (s), 126.5 (s), 126.2 (s), 124.0(d, *J* = 282.4 Hz), 123.9 (s), 72.6 (q, *J* = 32.0 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.00 (d, *J* = 6.6 Hz). HRMS m/z (EI): calcd for [$C_{12}H_9F_3O$], 226.0605; found 226.0602.

2,2,2-trifluoro-1-(naphthalen-1-yl)ethan-1-ol (2r) Clear liquid (65 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.61 – 7.45 (m, 3H), 5.92 – 5.80 (m, 1H), 2.83 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.3 (s), 130.7 (s), 129.8 (s), 129.6 (s), 128.6 (s), 126.4 (s), 125.5 (s), 125.4 (s), 124.8 (s), 124.3 (q, *J* = 282.7 Hz), 122.4 (s), 68.5 (q, *J* = 32.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -76.84 (d, *J* = 6.2 Hz). HRMS m/z (EI): calcd for [$C_{12}H_9F_3O$], 226.0605; found 226.0600.

1-(benzofuran-2-yl)-2,2,2-trifluoroethan-1-ol (2s) Clear liquid (36 mg, 42%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 1H), 6.90 (s, 1H), 5.19 (q, *J* = 7.4 Hz, 1H), 3.03 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7 (s), 149.1 (s), 127.1 (s), 125.1 (s), 123.1 (s), 123.1 (q, *J* = 282.4 Hz), 121.3 (s), 111.3 (s), 106.6 (s), 67.5 (q, *J* = 34.2 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -77.54 (d, *J* = 6.5 Hz). HRMS m/z (EI): calcd for [$C_{10}H_7F_3O_2$], 216.0398; found 216.0393.

1-(benzo[b]thiophen-2-yl)-2,2,2-trifluoroethan-1-ol (2t) Yellow solid (42 mg, 46%). M.P. 79-81 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.73 (m, 2H), 7.47 – 7.32 (m, 3H), 5.42 – 5.29 (m, 1H), 2.90 (d, *J* = 3.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.91 (s), 138.89 (s), 136.67 (s), 125.23 (s), 124.70 (s), 124.34 (s), 124.11 (s), 123.69 (q, *J* = 282.2 Hz), 122.43 (s), 69.90 (q, *J* = 33.9 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.19 (d, *J* = 6.1 Hz). M.P. 79-81 °C. HRMS m/z (EI): calcd for [$C_{10}H_7F_3OS$], 232.0170; found 232.0159.

1-(benzo[b]thiophen-3-yl)-2,2,2-trifluoroethan-1-ol (2u) Yellow solid (35 mg, 38%). M.P. 77-79 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (t, *J* = 6.6 Hz, 2H), 7.67 (s, 1H), 7.45 – 7.36 (m, 2H), 5.48 – 5.39 (m, 1H), 2.76 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.9 (s), 136.7 (s), 128.6 (s), 126.4 (s), 124.5 (s), 124.2 (s), 123.9 (q, *J* = 282.0 Hz), 122.5 (s), 121.7 (s), 68.0 (q, *J* = 33.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -77.34 (d, *J* = 6.4 Hz). M.P. 77-79 °C. HRMS m/z (EI): calcd for [$C_{10}H_7F_3OS$], 232.0170; found 232.0169.

2,2,2-trifluoro-1-(5-phenylthiophen-2-yl)ethan-1-ol (2v) Clear liquid (35 mg, 49%).1H NMR (300 MHz, $CDCl^3$) δ 7.63 – 7.56 (m, 2H), 7.43 – 7.27 (m, 3H), 7.22 (d, *J* = 3.8 Hz, 1H), 7.16 (d, *J* = 3.7 Hz, 1H), 5.32 – 5.18 (m, 1H), 2.73 (d, *J* = 4.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9 (s), 134.7 (s), 133.3 (s), 128.6 (s), 128.1 (s), 127.7 (s), 125.5 (s), 123.3 (q, *J* = 282.1 Hz), 122.4 (s), 69.1 (q, *J* = 33.8 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.54 (d, *J* = 6.2 Hz). HRMS m/z (EI): calcd for [$C_{12}H_9F_3OS$], 258.0326; found 258.0314.

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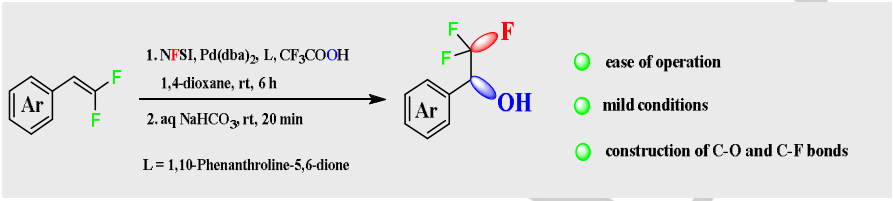

A mild and efficient synthesis of α-trifluoromethyl alcohols derivatives was achieved *via* Pd-catalyzed selective hydroxylfluorination of *gem*-difluoroalkenes using NFSI as the fluoride source.

gem*-difluoroalkenes *

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