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Nucleophilic Substitution of *gem*-Difluoroalkenes with TMSNu Promoted by Catalytic Amounts of Cs₂CO₃

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Supporting Information Placeholder



ABSTRACT

The efficient and practical nucleophilic cyanation and trifluoromethylation with appropriate trimethylsilyl nucleophiles were developed. Catalytic amounts of cheap and non-toxic Cs_2CO_3 was used to maintain a sufficiently high concentration of nucleophilic anion $(CN^{-} \text{ or } CF_3^{-})$ which could start up the catalytic cycle. The present methodologies provide diverse functionalized monofluoroalkenes bearing cyano and trifluoromethyl group with excellent to moderate stereoselectivities.

INTRODUCTION

Monofluoroalkenes, due to the unique properties, play a significant role in pharmaceutical/medicinal chemistry, synthetic organic chemistry and material sciences.¹ Consequently, a growing number of efficient methodologies for synthesis of monofluoroalkenes have been reported,^{2,3} and one of the most common methods is C-F functionalization of readily available *gem*-difluoroalkenes^{3,4} which can be mainly classified into transition metal catalysis (TMC) and nucleophilic vinylic substitution reaction (S_NV). Despite the great advances of this area, several drawbacks including requirement of transition metal as catalyst (for TMC) or excess quantities of base as additive (for S_NV) offered the attractive challenges for further exploration.

In general, a fluoride anion was displaced with nucleophilic anion (Nu⁻) via addition-elimination processes in S_NV reaction of *gem*-difluoroalkenes.^{3b} It is reasonable that trimethylsilyl nucleophiles (TMSNu)⁵ could assist the cleavage of C-F bond in the intermediate **A**, due to the high fluorophilicity of silicon,⁶ to form TMSF and product **B** as well as regenerate nucleophilic anion (Nu⁻) (Scheme 1, part 2b). Logically, a catalytic recycle could be realized if catalytic amounts of "Nu⁻" source was added in the system to start up the reaction. We postulated that only catalytic amounts of salts bearing oxoanion could dissociate TMSNu reversibly, due to high oxophilicity of silicon,⁷ to maintain a sufficiently high concentration of nucleophilic anion which is responsible for nucleophilic addition to *gem*-difluoroalkene (Scheme 1, part 2a). Notably, the related reports on catalytic nucleophilic substitution of *gem*-difluoroalkenes is still rare.⁸ In this context, we report herein that catalytic amounts of Cs₂CO₃⁹ promoted stereoselective nucleophilic cyanation and trifluoromethylation of *gem*-difluoroalkenes with appropriate trimethylsilyl nucleophiles for providing desired mono-fluoroalkenes, respectively.

Scheme 1. Nucleophilic Substitution of gem-Difluoroalkenes with TMSNu Promoted by Catalytic Amounts of Cs₂CO₃



RESULTS AND DISCUSSION

2-Fluoroacrylonitriles are an important and attractive type of structural scaffolds that form the basis of many biologically active molecules.¹⁰ However, very few related synthetic methodologies have been described in the literature.¹¹ In 2016, Cao's group developed an efficient method for the synthesis of 2-fluoroacrylonitriles by highly stereoselective cyanation of gem-difluoroalkenes using easily available benzyl nitrile as a cyanating reagent with assistance of excess lithium tert-butoxide under air atmosphere (Scheme 1, part 1a).^{11a} To the best of our knowledge, catalytic nucleophilic cyanation of gem-difluoroalkenes has been rarely developed.¹² Thus, we commenced our investigations using the cyanation of gem-difluoroalkene 1a with TMSCN as the model reaction to optimize the reaction conditions (Table 1). Initially, the reaction did not work when it was conducted in the presence of 10 mol % of CuCN in DMF under nitrogen atmosphere at 100 °C (Table 1, entry 1). Unexpectedly, the desired product 2a was obtained in 37% yield without any additive in DMF (Table 1, entry 2) and the product was also isolated in 10% yield employing MeCN as a solvent (Table 1, entry 3). Subsequently, adding catalytic amounts of alkali-metal salts could improve the reaction yields dramatically even the reaction was carried out at room temperature in MeCN (Table 1, entries 4-8). Cesium salts such as Cs₂CO₃, CsOAc and CsF turned out to be more effective, and Cs₂CO₃ provided the best yield (97%) with sole *E* configuration. In contrast, CsCl and CsBr proved to be unreactive (Table 1, entries 9 and 10), thus indicating that the counteranion played an important role on catalytic performance. Solvent screening showed that DMSO was also suitable for this reaction but got lower E/Z selectivity (Table 1, entry 12). Other solvents such as dioxane, EtOH, toluene, THF and DCM all resulted in no reaction (Table 1, entries 14-18). Excess amounts (3.0 equiv) of TMSCN were required for high yield. When the amount of TMSCN was changed to 2.0 equiv, the yield of product 2a was decreased to 82% (Table 1, entry 19). Finally, reducing the amount of Cs₂CO₃ to 5 mol % or 1 mol % still resulted in the product 2a with slightly lower yields (Table 1, entries 20 and 21). It is notable that the reaction of 1a with TMSCN could be scaled up to gram quantities smoothly and provided 2a (0.96 g) in 90% yield (Table 1, entry 22).

Table 1. Optimization of the Reaction Conditions of Cyanation^a

	٩	MeO ₂ C	TMSCN (3 equiv) cat. (10 mol %) solvent, rt MeO ₂	C CN	
		1a	time (h)	2a	F/ 7 ¢
entry	cat.	solvent	tille (li)	yield ^o (%)	E/Z
1	CuCN	DMF	48	\mathbf{NR}^{d}	n.d. ^e
2^{f}	^g	DMF	48	37	n.d. ^e
3 ^f	<i>g</i>	MeCN	48	10	n.d. ^e
4	Na ₂ CO ₃	MeCN	2	70	n.d. ^e
5	K_2CO_3	MeCN	2	76	n.d. ^e
6	Cs_2CO_3	MeCN	0.5	97^{h}	> 50:1
7	CsOAc	MeCN	2	90	> 50:1
8	CsF	MeCN	2	87	n.d. ^e

 9	CsCl	MeCN	12	NR^d	n.d. ^e
10	CsBr	MeCN	12	\mathbf{NR}^{d}	n.d. ^e
11	Cs ₂ CO ₃	DMF	0.5	70	11:1
12	Cs ₂ CO ₃	DMSO	2	90	16:1
13	Cs ₂ CO ₃	NMP	2	64	16:1
14	Cs ₂ CO ₃	dioxane	12	\mathbf{NR}^{d}	n.d. ^e
15	Cs ₂ CO ₃	EtOH	12	\mathbf{NR}^{d}	n.d. ^e
16	Cs_2CO_3	toluene	12	\mathbf{NR}^{d}	n.d. ^e
17	Cs ₂ CO ₃	THF	12	\mathbf{NR}^{d}	n.d. ^e
18	Cs ₂ CO ₃	DCM	12	\mathbf{NR}^{d}	n.d. ^e
19^{i}	Cs ₂ CO ₃	MeCN	2	82	n.d. ^e
20'	Cs ₂ CO ₃	MeCN	1	90	> 50:1
21^{k}	Cs ₂ CO ₃	MeCN	2	87	> 50:1
22^{l}	Cs ₂ CO ₃	MeCN	1	90	> 50:1

"Reactions were conducted with 1a (0.20 mmol), TMSCN (3.0 equiv), cat. (5 mol %) and solvent (1 mL) under an atmosphere of nitrogen at room temperature. ^bYields of isolated products. ^cThe ratio of E/Z isomer in the crude reaction mixture was determined by ¹H NMR, and the configuration of major isomer was established as *E* by comparison with the data in reference 6c. ^{*d*}No Reaction. "The compound was not detected. The reaction was conducted at 100 °C. "The reaction was conducted without any catalyst. "The isolated product was detemined as sole E configuration through analysis of NMR spectra. $^{i}2.0$ equiv of TMSCN was used. $^{i}5$ mol % of Cs₂CO₃ and 0.30 mmol of **1a** were used. ^k1 mol % of Cs₂CO₃ and 0.30 mmol of **1a** were used. ^lGram-scale reaction: 5.2 mmol of 1a was used and 0.96 g of 2a was obtained.

Scheme 2. Substrate Scope of Cyanation^{*a*, *b*}



^a Reactions were conducted with 1a (0.30 mmol), TMSCN (3.0 equiv), Cs₂CO₃ (10 mol %) and MeCN (1 mL) under the atmosphere of nitrogen at room temperature. ^b Yields of isolated products; the ratio of E/Z isomers was determined by ¹H NMR and ¹⁹F

NMR, and the configuration of major isomer was determined as *E* by comparison with the data in reference 11d. ^{*c*} The reaction was conducted at 40 °C. ^{*d*} The reaction was conducted at 60 °C. ^{*e*} 20 mol % of Cs₂CO₃ and 6.0 equiv of TMSCN were used.

With the optimal reaction conditions in hand (Table 1, entry 6), a range of monosubstituted *gem*-difluoroalkenes (**1b-q**) were reacted with TMSCN to examine the generality of the process (Scheme 2). It should be mentioned that in order to get satisfactory yields in a shortened time, the reactions of **1b**, **1c**, **1h-l**, and **1q** should be performed in higher temperature (40°C or 60°C). Generally, *gem*-difluoroalkenes bearing an electron-withdrawing group such as chloro, bromo, trifluoromethyl and cyano groups afforded the desired products in good to high yields (**2b-g**, 78%-93%), and the location of the substituent on the phenyl ring of *gem*-difluoroalkenes only effected the yields slightly (**2e**, **2f** and **2g**). Electron-donating substituents were unfavorable for the transformations, thus product **2i** with a *para*-methyl group and product **2j** with a *para-tert*-butyl group were obtained in 61% and 60% yields, respectively. These results indicated that the pathway of reaction probably involves a benzyl anion intermediate which was formed through cyanide anion attack. Other kind of groups on the aryl unit such as 4-phenyl (**1k**) and 4-thiomethyl (**1l**) substituents also afforded the product **2k** (78%) and **2l** (80%), respectively. 2-(2,2-Difluorovinyl)naphthalene was also a suitable substrate and afforded the corresponding product **2m** in 86% yield. To our delight, 1,3-dichloro-5-(2,2-difluorovinyl)benzene (**1n**) and sterically hindered substrates (**1o** and **1p**) were also tolerated under the optimized conditions and provided the desired products (**2n-p**) in high yields (86-92%). In addition, 1,4-bis(2,2-difluorovinyl)benzene (**1q**) also gave the desired product **2q** in a moderate yield (67 %).

To further evaluate the scope of the methods, several disubstituted *gem*-difluoroalkenes (**1r**-**w**) were subjected to the reaction (Scheme 2). Symmetrical *gem*-difluoroalkene **1r** got the desired product **2r** in 94% yield. In the case of unsymmetrical *gem*-difluoroalkenes as starting materials (**1s**-**v**), moderate E/Z selectivity (>= 7:1) was obtained. Finally, 2-fluoro-3-phenyl-3-(*p*-tolylthio)acrylonitrile (**2w**) was also obtained with moderate stereoselectivity.¹³

Scheme 3. Substrate Scope of Trifluoromethylation^{*a*, *b*}



^{*a*} Reactions were conducted with **1** (0.20 mmol), TMSCF₃ (2.5 equiv), Cs₂CO₃ (10 mol %) and DMF (1 mL) under an atmosphere of nitrogen at room temperature. ^{*b*} Yields of isolated products; the ratio of *E/Z* isomers was determined by ¹⁹F NMR sepectroscopy, and the configuration of major isomer was determined by analysis of NOESY(¹H-¹⁹F) spectrum.

Encouraged by the above results, we also explored the defluorinative trifluoromethylation of *gem*-difluoroalkenes (Scheme 3), which was few related investigations reported (Scheme 1, part 1b).¹⁴ After further optimization of the reaction conditions, DMF was found as the suitable solvent.¹⁵ In this transformation, disubstituted *gem*-difluoroalkenes¹⁶ reacted smoothly to deliver the corresponding products **3a-f** in good yields with moderate stereoselectivity (6:1). Monosubstituted *gem*-difluoroalkenes bearing electron-withdrawing groups generated the desired products **3g-h** in moderate yields with sole *Z* configuration.

As mentioned in Table 1, the presence of alkali-metal salts bearing oxoanions are crucial for the process. In order to verify the role of alkali-metal salts and understand the reaction mechanism, series of additional experiments were carried out as described in Table 2. The reaction of *gem*-difluoroalkene **1a** with NaCN was carried out partly (about 15% of **1a** was recovered) in the absence of Cs_2CO_3 to afford the desired product **2a** in 70% yield by prolonging the reaction time to 4 h (Table 2, entry 1), which demonstrated that the reaction probably proceeds through a S_NV pathway by using "CN-" as a nucleophile. Further screening salts found that K_3PO_4 , K_2HPO_4 and 'BuOK all showed high catalytic activities (Table 2, entries 2-4). In addition, the type of cation of salts also affected the reactivity obviously. The usage of 10 mol % of NaCN as a catalyst directly gave 52% yield, which is comparable to the results of NaOAc and Na₂CO₃ (Table 2, entries 5-6 and Table 1, entry 4). Zn(CN)₂ could not even catalyze the reaction (Table 2, entry 7); adding extra Zn(OAc)₂ (10 mol %), in which zinc ion probably coordinates with cyano anion generated *in situ* to reduce its concentration, restrained the reaction completely (Table 2, entry 8 *vs* Table 1, entry 8). Analysis of these data (including the data in Table 1) revealed that Cs_2CO_3 could dissociate TMSCN reversibly to maintain a sufficiently high concentration of cyano anion, which nucleophilically attacked *gem*-difluoroalkene **1** to form the intermediate **A**. Subsequently, the stereoselective elimination of fluoride^{11a} from the intermediate **A** with the assistance of TMSCN provided product **2** and regenerated cyano anion (Scheme 1, Nu = CN).

Table 2. Control Experiments for Mechanistic Investigations^a



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 1^c	NaCN (3.0 equiv)	4	70^d
2	K ₃ PO ₄ (10 mol %)	2	90
3	K ₂ HPO ₄ (10 mol %)	2	88
4	'BuOK (10 mol %)	12	96
5	NaCN (10 mol %)	20	52
6	NaOAc (10 mol %)	4	48
7	Zn(CN) ₂ (10 mol %)	2	NR ^e
8	$CsF (10 mol \%) + Zn(OAc)_2 (10 mol \%)$	24	Trace ^f

^{*a*}Reactions were conducted with **1a** (0.30 mmol), TMSCN (3.0 equiv), catalyst and MeCN (1 mL) under an atmosphere of nitrogen at room temperature. ^{*b*}Yields of isolated products. ^{*c*}3.0 equiv of NaCN was used instead of TMSCN, and without Cs₂CO₃. ^{*d*}15% of **1a** was recovered. ^{*e*}No reaction. ^{*f*}Only trace product **2a** was detected by TLC.

The conformational analysis of intermediate A (Scheme 1) could explain the different stereochemical outcomes of monosubstituted *gem*-difluoroalkenes between cyanation and trifluoromethylation (Figure 1). Rotation of the intermediate A would form two typically conformational intermediates. Intermediate A2 should be more stable than intermediate A1 because there might be no electronic repulsion between fluorine atom and aryl group.^{11a} However, intermediate A3 is less stable than intermediate A4 due to the electronic and stertical repulsions between CF_3 group and aryl group.¹⁷ Thus, favorable intermediates A2 and A4 could be transformed to the corresponding products with an excellent stereoselectivity, respectively.



Figure 1. Conformational Analysis of Intermediate A

CONCLUSIONS

We have developed an efficient and practical nucleophilic cyanation and trifluoromethylation of *gem*-difluoroalkenes with appropriate TMSNu under mild and convenient conditions by using catalytic amounts of Cs_2CO_3 as a promoter. The reaction can be readily scaled up to gram amounts and provides diverse monofluoroalkenes with excellent (for monosbustituted difluoroalkenes) to moderate (for disbustituted difluoroalkenes) *E/Z* selectivities. Preliminary mechanistic investigations suggested that catalytic amounts of Cs_2CO_3 is used to maintain the concentration of nucleophilic anion in the system to start up the catalytic recycle. Further studies on the mechanisms and the related applications are ongoing in our group.¹⁸

EXPERIMENTAL SECTION

General information. All manipulations were maintained under an atmosphere of nitrogen unless otherwise stated. Commercially available reagents were used without further purification. Solvents were predried over activated 4 Å molecular sieves and were refluxed over magnesium-iodine (methanol, ethanol), potassium (hexane), sodium-benzophenone (tetrahydrofurane) or calcium hydride (dichloroethane, acetonitrile, N, N-Dimethylformamide, dimethyl sulfoxide, N-Methyl pyrrolidone) under an argon atmosphere and collected by distillation. Column chromatography was performed on silica gel (200 - 300 mesh). NMR studies were performed on 400 Bruker spectrometers. Infrared spectra were prepared as KBr pellets and were recorded on a Varian Excalibur 3100 series F -IR spectrometer. Mass spectra were recorded by the mass spectrometry service of Shanghai Institute of Organic Chemistry.

Substrate preparation. The compounds 1a-1y were prepared according to the literatures, $^{4g, 4r, 19}$ and the known compounds spectra data are in agreement with the reports. The new compounds 10, 1w were prepared by the literature method^{4g, 19a, 19c} and the spectra data are shown in this paper.

1-bromo-2-(2,2-difluorovinyl)-4-(trifluoromethyl)benzene (10). Colorless liquid; 80% yield (1.6 g, 5.6 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 1.6 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.36 (dd, J = 8.4, 2.0 Hz, 1H), 5.71 (dd, J = 24.8, 3.4 Hz, 1H);

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 157.2 (dd, J = 299.9, 291.0 Hz), 133.7, 131.6 (dd, J = 8.3, 6.0 Hz), 130.5 (q, J = 32.9 Hz), 127.2 (dd, J = 3.7, 1.8 Hz), 126.0 (ddd, J = 9.7, 3.9, 1.5 Hz), 125.2 (q, J = 3.7 Hz), 123.8 (q, J = 273.4 Hz), 81.3 (dd, J = 33.6, 12.1 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -62.98 (s, 3F), -79.65 (dd, J = 22.0, 3.8 Hz, 1F), -80.94 (dd, J = 25.2, 21.6 Hz, 1F); IR ν (neat, cm⁻¹): 2926, 2856, 1729, 1610, 1282, 1085, 916, 827, 736; HRMS (ESI-TOF, m/z): calcd. For C₉H₄BrF₅H [M+H]⁺: 286.9489, found: 286.9493.

(2,2-*difluoro-1-phenylvinyl*)(*p-tolyl*)*sulfane* (*1w*). Colorless liquid; 50% yield for two steps (0.34 g, 1.3 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 7.8 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 2.26 (s, 3H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 157.0 (dd, J = 304.6, 289.6 Hz), 136.7, 132.7 (d, J = 4.2 Hz), 130.8 (t, J = 2.4 Hz), 129.9, 129.0, 128.9 (t, J = 3.5 Hz), 128.7, 128.5, 128.1, 21.1; ¹⁹F NMR (564 MHz, CDCl₃) δ -75.88 (d, J = 14.2 Hz, 1F), -78.07 (d, J = 14.2 Hz, 1F); IR v (neat, cm⁻¹): 3076, 3028, 1684, 1265, 1009, 814, 735, 687; HRMS (ESI-TOF, m/z): calcd. For C₉H₄BrF₅H [M+H]⁺: 263.0701, found: 263.0711.

General procedure for the synthesis of product 2 and gram-scale reaction. An oven-dried 10 mL Schlenk tube was charged with Cs_2CO_3 (0.03 mmol, 9.8 mg), TMSCN (0.90 mmol, 89 mg), 1 (0.30 mmol), and then anhydrous MeCN (1.0 mL) was added through syringe. After stirring in an oil bath preheated at a specified temperature for several hours, the solvent was removed in vacuo. Purification of the residue by silica gel column chromatography afforded the desired product 2.

(E)-methyl 4-(2-cyano-2-fluorovinyl)benzoate (2a).^{11c} Reaction temperature: rt; reaction time: 0.5 h; petroleum ether/ ethylacetate = 50:1; TLC: R_f = 0.5 (PE / EA = 10:1, UV); White solid; 97% yield (59.7 mg, 0.29 mmol); The same reaction has been carried on gram scale employing an oven-dried 50 mL Schlenk tube was charged with Cs₂CO₃ (0.52 mmol, 169 mg), TMSCN (15.6 mmol, 1.55 g), **1a** (5.2 mmol, 1.03 g), and then anhydrous MeCN (10 mL) was added through syringe. After stirring at rt for 1 h, the solvent was removed in vacuo. Purification of the residue by silica gel column chromatography (PE : EtOAc = 50 : 1) afforded the desired product **2a** (90%, 0.96 g); ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.09 (d, J=16.0 Hz, 1H), 3.94 (s, 3H).

(E)-3-(4-chlorophenyl)-2-fluoroacrylonitrile (2b).^{11a} Reaction temperature: 40 °C; reaction time: 16 h; petroleum ether; TLC: $R_f = 0.6$ (PE, UV); Colorless liquid; 78% yield (42.5 mg; 0.23 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 16.4 Hz, 1H).

(*E*)-3-(4-bromophenyl)-2-fluoroacrylonitrile (2c).^{11b} Reaction temperature: 40 °C; reaction time: 16 h; petroleum ether; TLC: $R_f = 0.6$ (PE, UV); Colorless liquid; 80% yield (54.2 mg, 0.24 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 16.2 Hz, 1H).

(*E*)-2-fluoro-3-(4-(trifluoromethyl)phenyl)acrylonitrile (2d). Reaction temperature: rt; reaction time: 0.5 h; petroleum ether; TLC: $R_f = 0.6$ (PE, UV); Colorless liquid; 89% yield (57.6 mg, 0.27 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 0.8 Hz, 4H), 7.10 (d, J = 15.8 Hz, 1H).

(*E*)-4-(2-cyano-2-fluorovinyl)benzonitrile (2e). Reaction temperature: rt; reaction time: 0.5 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 10:1, UV); White solid (mp:121 - 122 °C); 93% yield (48.1 mg 0.28 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 16.0 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 133.1, 133.0 (d, J = 246.8Hz), 132.9 (d, J = 7.1 Hz), 129.1 (d, J = 3.2 Hz), 124.3 (d, J = 25.6 Hz), 118.0 , 114.3, 111.8 (d, J = 46.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -115.73 (d, J = 15.6 Hz, 1F); IR ν (neat, cm⁻¹): 3043, 2922, 2225, 1646, 1502, 1260, 1222, 908, 834; HRMS (ESI-TOF, m/z): calcd. For C₁₀H₅FN₂H [M+H]⁺: 173.0510, found: 173.0509.

(*E*)-3-(2-cyano-2-fluorovinyl)benzonitrile (2f). Reaction temperature: rt; reaction time: 1 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 10:1, UV); White solid (mp: 87 - 88 °C); 91% yield (46.9 mg, 0.27 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.0 Hz, 1H), 7.79 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.06 (d, J = 15.4 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 133.7 (d, J = 1.6 Hz), 132.6 (d, J = 245.6 Hz), 132.2, 132.1 (d, J = 5.8 Hz), 130.3, 129.8 (d, J = 7.2 Hz), 123.9 (d, J = 25.6 Hz), 117.7, 113.9, 111.8 (d, J = 46.7 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -116.97 (d, J = 15.4 Hz, 1F); IR ν (neat, cm⁻¹): 3046, 2963, 2232, 1649, 1484, 1260, 1153, 917, 880; HRMS (ESI-TOF, m/z): calcd. For C₁₀H₅FN₂H [M+H]⁺: 173.0510, found: 173.0510.

(*E*)-2-(2-cyano-2-fluorovinyl)benzonitrile (2g). Reaction temperature: rt; reaction time: 1 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 10:1, UV); Colorless liquid; 87% yield (44.8 mg, 0.26 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 8.0 Hz, 1H), 7.76 (dd, J = 7.6, 0.8 Hz, 1H), 7.71 (td, J = 8.0, 1.2 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 14.8 Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 133.7, 133.7 (d, J = 249.0 Hz), 133.6, 131.7 (d, J = 7.1 Hz), 130.8 (d, J = 1.4 Hz), 127.8 (d, J = 1.8 Hz), 122.1 (d, J = 26.8 Hz), 116.6, 113.4 (d, J = 4.5 Hz), 111.6 (d, J = 46.7 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -113.79 (d, J = 14.8 Hz, 1F); IR v (neat, cm⁻¹): 3044, 2962, 2228, 1653, 1481, 1230. 891, 760; HRMS (ESI-TOF, m/z): calcd. For C₁₀H₃FN₂H [M+H]⁺: 173.0510, found: 173.0516.

(*E*)-2-fluoro-3-phenylacrylonitrile (2h).^{11b} Reaction temperature: 60 °C; reaction time: 2 h; petroleum ether; TLC: $R_f = 0.8$ (PE, UV); Colorless liquid; 73% yield (30.7 mg, 0.22 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.55 (m, 2H), 7.47 – 7.41 (m, 3H), 7.07 (d, J = 16.7 Hz, 1H).

(E)-2-fluoro-3-(p-tolyl)acrylonitrile (2i).^{11a} Reaction temperature: 60 °C; reaction time: 12 h; petroleum ether; TLC: $R_f = 0.8$ (PE, UV); Colorless liquid; 61% yield (29.6 mg, 0.18 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.03 (d, J = 17.0 Hz, 1H), 2.39 (s, 3H).

(*E*)-3-(4-(tert-butyl)phenyl)-2-fluoroacrylonitrile (2j).^{11a} Reaction temperature: 60 °C; reaction time: 12 h; petroleum ether; TLC: $R_f = 0.6$ (PE, UV); Colorless liquid; 60% yield (36.6 mg, 0.18 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 7.04 (d, J = 16.8 Hz, 1H), 1.33 (s, 9H).

(*E*)-3-([1,1'-biphenyl]-4-yl)-2-fluoroacrylonitrile (2k).^{11a} Reaction temperature: 60 °C; reaction time: 12 h; petroleum ether/ ethylacetate = 50:1; TLC: R_f = 0.6 (PE / EA = 10:1, UV); yellow solid; 78% yield (52.2 mg, 0.23 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.67 (s, 4H), 7.61 (d, *J* = 8.4, 2H), 7.49–7.45 (m, 2H), 7.41–7.37(m, 1H), 7.10 (d, *J* = 16.8 Hz, 1H).

(*E*)-2-fluoro-3-(4-(methylthio)phenyl)acrylonitrile (21).^{11a} Reaction temperature: 60 °C; reaction time: 12 h; petroleum ether/ ethylacetate = 50:1; TLC: R_f = 0.6 (PE / EA = 10:1, UV); light yellow liquid; 80% yield (46.4 mg, 0.24 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 16.9 Hz, 1H), 2.51 (s, 3H).

(*E*)-2-fluoro-3-(naphthalen-2-yl)acrylonitrile (2m).²⁰ Reaction temperature: rt; reaction time: 8 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 10:1, UV); White solid; 86% yield (50.9 mg, 0.26 mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.01 (s, 1H), 7.93 – 7.83 (m, 3H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.22 (d, *J* = 16.8 Hz, 1H).

(E)-3-(3,5-dichlorophenyl)-2-fluoroacrylonitrile (2n). Reaction temperature: rt; reaction time: 1 h; petroleum ether/ ethylacetate = 100:1; TLC: R_f = 0.6 (PE, UV); Colorless liquid; 90% yield (58.3 mg, 0.27 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 1.6 Hz, 2H), 7.43 (t, J = 1.6 Hz, 1H), 6.95 (d, J = 16.0 Hz, 1H); ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 136.1, 132.7 (d, J = 244.8 Hz), 131.2 (d, J = 7.1 Hz), 130.6 (d, J = 1.8 Hz), 126.7 (d, J = 3.2 Hz), 123.6 (d, J = 26.0 Hz), 111.7 (d, J = 46.7 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -116.93 (d, J = 15.5 Hz, 1F); IR ν (neat, cm⁻¹): 2960, 2925, 2230, 1651, 1561, 1289, 1152, 814, 667; HRMS (ESI-TOF, m/z): calcd. For C₉H₄Cl₂FNH [M+H]⁺: 215.9778, found: 215.9780.

(*E*)-3-(2-bromo-5-(trifluoromethyl)phenyl)-2-fluoroacrylonitrile (20). Reaction temperature: rt; reaction time: 1 h; petroleum ether/ ethylacetate = 100:1; TLC: R_f = 0.6 (PE, UV); Colorless liquid; 86% yield (76.2 mg, 0.26 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 2.0 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.56 (dd, J = 8.4, 1.8 Hz, 1H), 7.32 (d, J = 14.4 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 134.2, 133.8 (d, J = 248.8 Hz), 131.0 (q, J = 33.6 Hz), 130.2 (d, J = 7.6 Hz), 128.6 (dd, J = 4.5, 1.5 Hz), 128.3 (q, J = 3.7 Hz), 126.2 (qd, J = 3.8, 1.6 Hz), 124.2 (d, J = 26.9 Hz), 123.4 (q, J = 273.7 Hz), 111.2 (d, J = 46.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -62.97 (s, 3F), -114.97 (d, J = 14.2 Hz, 1F); IR ν (neat, cm⁻¹): 3053, 2925, 2232, 1654, 1469, 1337, 1215, 1084, 830; HRMS (ESI-TOF, m/z): calcd. For C₁₀H₄BrF₄NH [M+H]⁺: 293.9536, found: 293.9540.

(*E*)-3-(2-bromo-5-methoxyphenyl)-2-fluoroacrylonitrile (2p). Reaction temperature: rt; reaction time: 4 h; petroleum ether/ ethylacetate = 100:1; TLC: R_f = 0.6 (PE, UV); Colorless liquid; 92% yield (70.7mg, 0.28 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.8 Hz, 1H), 7.33 (d, J = 15.2 Hz, 1H), 7.27 (d, J = 2.8 Hz, 1H), 6.86 (dd, J = 8.8, 3.2 Hz, 1H), 3.83 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 159.3, 134.1, 132.8 (d, J = 243.6 Hz), 129.5 (d, J = 7.1 Hz), 125.6 (d, J = 26.2 Hz), 118.5 (d, J = 1.1 Hz), 115.2 (d, J = 4.7 Hz), 114.0 (d, J = 1.3 Hz), 112.0 (d, J = 47.0 Hz), 55.8, ¹⁹F NMR (376 MHz, CDCl₃) δ -118.08 (d, J = 15.4 Hz, 1F); IR ν (neat, cm⁻¹): 3049, 2939, 2229, 1651, 1592, 1466, 1243, 846, 657; HRMS (ESI-TOF, m/z): calcd. For C₁₀H₇BrFNOH [M+H]⁺: 255.9768, found: 255.9770.

(2E, 2'E)-3,3'-(1,4-phenylene)bis(2-fluoroacrylonitrile) (2q). Reaction temperature: 60 °C; reaction time: 4 h; petroleum ether/ ethylacetate = 50:1; TLC: R_f = 0.5 (PE / EA = 10:1, UV); White solid (mp: 120 - 121 °C); 67% yield (43.4 mg, 0.20 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 4H), 7.07 (d, J = 16.8 Hz, 2H); ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 132.1 (d, J = 242.5 Hz), 130.4 (dd, J = 5.9, 3.0 Hz), 129.3 (d, J = 2.3 Hz), 125.0 (d, J = 24.2 Hz), 112.3 (d, J = 46.8 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -118.95 (d, J = 16.4 Hz, 2F); IR ν (neat, cm⁻¹): 3046, 2957, 2225, 1697, 1489, 1295, 1234, 970, 878; HRMS (ESI-TOF, m/z): calcd. For C₁₂H₆F₂N₂Na [M+Na]⁺: 239.0391, found: 239.0397.

2-fluoro-3,3-diphenylacrylonitrile (2r).^{11a} Reaction temperature: 60 °C; reaction time: 3 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 10:1, UV); Colorless liquid; 94% yield (62.9 mg, 0.28 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.42 (m, 3H), 7.42 – 7.35 (m, 5H), 7.34-7.31 (m, 2H).

(*E*)-methyl 4-(1-cyano-1-fluoroprop-1-en-2-yl)benzoate (2s). Reaction temperature: 40 °C; reaction time: 6 h; petroleum ether/ ethylacetate = 50:1; TLC: R_f = 0.5 (PE / EA = 10:1, UV); Colorless liquid; 92% yield (60.5 mg, 0.28 mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 3.94 (s, 3H), 2.24 (d, J = 4.4 Hz, 3H, *E*), 2.32 (d, J = 4.4 Hz, 3H, *Z*), (E/Z = 7:1); ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 166.4, 139.0 (d, J = 3.9 Hz), 135.7 (d, J = 16.9 Hz), 131.5 (*E*), 130.0 (*Z*), 130.3 (d, J = 3.6 Hz), 130.3 (d, J = 242.3 Hz), 128.2 (d, J = 5.5 Hz, *Z*), 127.9 (d, J = 3.0 Hz, *E*), 112.3 (d, J = 4.6 6 Hz), 52.5, 18.2 (*Z*), 16.7 (d, J = 3.2 Hz, *E*); ¹⁹F NMR (376 MHz, CDCl₃) δ -121.70 (q, J = 4.3 Hz,1F, *E*), -124.59 (q, J = 3.8 Hz, 1F, *Z*), (E/Z = 7:1); IR ν (neat, cm⁻¹): 2956, 2918, 2224, 1728, 1610, 1436, 1277, 800, 727; HRMS (ESI-TOF, m/z): calcd. For C₁₂H₁₀FNO₂H [M+H]⁺: 220.0768, found: 220.0770.

(*E*)-4-(1-cyano-1-fluoroprop-1-en-2-yl)benzonitrile (2t). Reaction temperature: rt; reaction time: 5 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 10:1, UV); Colorless liquid; 94% yield (52.5 mg, 0.28 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 2.32 (d, J = 4.2 Hz, 3H, Z), 2.24 (d, J = 4.2 Hz, 3H, E), (E/Z = 7:1); ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 139.1 (d, J = 4.1 Hz), 135.0 (d, J = 18.2 Hz), 132.9 (E), 132.51 (Z), 130.5 (d, J = 243.4 Hz), 128.9 (d, J = 5.6 Hz, Z), 128.6 (d, J = 3.0 Hz, E), 118.1, 113.8, 112.0 (d, J = 46.5 Hz), 18.0 (Z), 16.6 (d, J = 3.1 Hz, E); ¹⁹F NMR (376 MHz, CDCl₃) δ -120.20 (q, J = 4.5 Hz, 1F, E); -123.16 (q, J = 3.8 Hz, 1F, Z), (E/Z = 7:1); IR v (neat, cm⁻¹): 2959, 2924, 2229, 1654, 1504, 1300, 1071, 870, 730; HRMS (ESI-TOF, m/z): calcd. For C₁₁H₇FN₂H [M+H]⁺: 187.0666, found: 187.0668.

(E)-2-fluoro-3-(3-nitrophenyl)but-2-enenitrile (2u). Reaction temperature: rt; reaction time: 12 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 10:1, UV); Colorless liquid; 92% yield (56.9 mg, 0.28 mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.35 – 8.27 (m, 2H), 7.78 (d, J = 7.8 Hz, 1H), 7.65 (m, 1H), 2.28 (d, J = 4.4 Hz, 3H, E), 2.37 (d, J = 4.0 Hz, 3H, Z), (E/Z = 7:1); ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 148.6, 136.2 (d, J = 4.3 Hz), 134.6 (d, J = 18.1 Hz), 133.8 (d, J = 2.6 Hz), 130.7 (d, J = 244.3 Hz), 130.4, 124.7 (*E*), 124.5 (*Z*), 123.1 (d, J = 5.4 Hz, *Z*), 123.0 (d, J = 3.5 Hz, *E*), 111.9 (d, J = 46.4 Hz), 18.1 (*Z*), 16.8 (d, J = 3.0 Hz, *E*); ¹⁹F NMR (376 MHz, CDCl₃) δ -120.41 (q, J = 4.2 Hz, 1F, *E*), -123.53 (q, J = 4.2 Hz, 1F, *Z*), (E/Z = 7:1); IR v (neat, cm⁻¹): 3086, 2926, 2225, 1654, 1531, 1210, 901, 806, 738; HRMS (ESI-TOF, m/z): calcd. For C₁₀H₇FN₂O₂H [M+H]⁺: 207.0564, found: 207.0560.

(E)-2-fluoro-3-(4-(trifluoromethyl)phenyl)pent-2-enenitrile (2v). Reaction temperature: 60 °C; reaction time: 12 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 10:1, UV); Colorless liquid; 75% yield (54.7 mg, 0.22 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 2.68 (qd, J = 7.6, 3.4 Hz, 2H), 1.07 (t, J = 7.6 Hz, 3H, Z), 1.02 (t, J = 7.6 Hz, 3H, E), (E/Z = 8:1); ¹³C {¹H} NMR (151 MHz, CDCl₃) δ 141.2 (d, J = 16.2 Hz), 137.1 (d, J = 3.9 Hz), 131.9 (q, J = 32.9 Hz), 130.0 (d, J = 242.5 Hz), 128.8 (d, J = 2.9 Hz), 126.1 (q, J = 3.7 Hz, E), 125.9 (q, J = 3.7 Hz, Z), 123.8 (q, J = 272.3 Hz), 112.1 (d, J = 47.0 Hz), 25.6 (Z), 24.0 (d, J = 1.9 Hz, E), 12.9 (d, J = 3.4 Hz, Z), 11.9 (d, J = 2.2 Hz, E); ¹⁹F NMR (376 MHz, CDCl₃) δ - 62.94 (s, 3F), -123.47 (t, 3.8Hz, 1F, E), -126.38 (Z) (E/Z = 8:1); IR ν (neat, cm⁻¹): 2962, 2927, 2228, 1540, 1260, 1098, 947, 842, 800; HRMS (ESI-TOF, m/z): calcd. For C₁₂H₉F₄NH [M+H]⁺: 244.0744, found: 244.0750.

(E)-2-fluoro-3-phenyl-3-(p-tolylthio)acrylonitrile (2w). Reaction temperature: rt; reaction time: 12 h; petroleum ether/ ethylacetate = 50:1; TLC: R_f = 0.6 (PE / EA = 10:1, UV); Light yellow liquid; 87% yield (70.3 mg, 0.26 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.21 (m, 5H), 7.13 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.2 Hz, 2H), 2.37 (s, 3H, Z), 2.23 (s, 3H, E), (E/Z = 9:1); ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 139.5, 134.3, 131.6 (Z), 130.1 (Z) 131.0 (d, J = 26.4 Hz), 130.4 (d, J = 0.8 Hz), 130.2 (E), 130.0 (d, J = 3.0 Hz), 129.9 (E), 128.7, 127.7 (d, J = 242.5 Hz) 125.4 (d, J = 2.2 Hz), 112.4 (d, J = 45.3 Hz), 21.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -117.82 (s, 1F, E); -112.02 (s, 1F, Z), (E/Z = 9:1); IR v (neat, cm⁻¹): 3024, 2923, 2220, 1597, 1459, 1492, 1207, 808, 756; HRMS (ESI-TOF, m/z): calcd. For C₁₆H₁₂FNSH [M+H]⁺: 270.0747, found: 270.0750.

General procedure for the synthesis of product 3. An oven-dried 10 mL Schlenk tube was charged with Cs_2CO_3 (0.02 mmol, 6.5 mg), TMSCF₃ (0.5 mmol), 1 (0.2 mmol), and then anhydrous DMF (1.0 mL) was added through syringe. After stirring at room temperature for 12 hours, the solvent was removed in vacuo. Purification of the residue by silica gel column chromatography afforded the desired product 3.

(*perfluoroprop-1-ene-1,1-diyl*)*dibenzene* (3a).^{3b} Reaction temperature: rt; reaction time: 12 h; petroleum ether; TLC: $R_f = 0.5$ (PE, UV); Colorless liquid; 74% yield (39.5 mg, 0.15 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.17 (m, 10H).

(*Z*)-*methyl* 4-(3,4,4,4-*tetrafluorobut-2-en-2-yl*)*benzoate* (3*b*). Reaction temperature: rt; reaction time: 12 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 20:1, UV); Colorless liquid; 51% yield (26.7 mg, 0.10 mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 3.93 (s, 3H), 2.18 (s, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 166.6 (s), 142.3 (dq, *J* = 255.0, 38.3 Hz), 140.7 (s), 130.1 (d, *J* = 60.7 Hz), 129.9 (s), 128.0 (d, *J* = 3.8 Hz), 122.5 (dq, *J* = 9.8, 2.6 Hz), 119.9 (qd, *J* = 273.2, 42.1 Hz), 52.4 (s), 16.1 (m); ¹⁹F NMR (376 MHz, CDCl₃) δ -64.94 – -65.07 (m), -128.06 – -128.08 (m) IR *v* (neat, cm⁻¹): 2957, 1728, 1611, 1340, 1311, 1276, 1137, 773,706; HRMS (ESI-TOF, m/z): calcd. For C₁₂H₁₀F₄O₂H [M+H]⁺: 263.0690, found: 263.0698.

(*Z*)-4-(3,4,4,4-tetrafluorobut-2-en-2-yl)benzonitrile (3c). Reaction temperature: rt; reaction time: 12 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 20:1, UV); Colorless liquid; 70% yield (32.1 mg, 0.14 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 2.18 (m, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 142.7 (dq, *J* = 260.2, 38.8 Hz), 140.8 (s), 132.5 (d, *J* = 1.3 Hz), 128.8 (d, *J* = 3.5 Hz), 121.7 (dq, *J* = 3.5, 2.6 Hz), 119.4 (dq, *J* = 274.4, 42.1 Hz), 118.5 (d, *J* = 4.7 Hz), 112.6 (d, *J* = 3.2 Hz), 15.9 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ -65.08 – 65.21 (m), -126.92 – -126.99 (m) IR *v* (neat, cm⁻¹): 2961, 2231, 1342, 1273, 1138, 1030, 877, 829, 623; HRMS (ESI-TOF, m/z): calcd. For C₁₁H₇F₄NH [M+H]⁺: 230.0587, found: 230.0580.

(*Z*)-1-nitro-3-(3,4,4,4-tetrafluorobut-2-en-2-yl)benzene (3d). Reaction temperature: rt; reaction time: 12 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 20:1, UV); Colorless liquid; 80% yield (39.9 mg, 0.16 mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 1H), 8.23 (d, *J* = 7.3 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 8.2 Hz, 1H), 2.26 (m, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 148.5 (s), 143.0 (dq, *J* = 256.8, 38.4 Hz), 137.7 (s), 134.1 (d, *J* = 4.3 Hz), 129.7 (s), 123.6 (s), 123.0 (d, *J* = 3.7 Hz), 121.2 (dq, *J* = 5.5, 2.4 Hz), 119.7 (dq, *J* = 273.3, 41.8 Hz), 16.0 (qd, *J* = 2.7, 1.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -65.05 – -65.18 (m), -127.13 – -127.16 (m) IR v (neat, cm⁻¹): 2962, 1536, 1304, 1179, 1140, 1030, 808, 739, 691; HRMS (ESI-TOF, m/z): calcd. For C₁₀H₇F₄NO₂H [M+H]⁺: 250.0486, found: 250.0490.

(*E*)-2,3,3-tetrafluoro-1-(naphthalen-2-yl)prop-1-en-1-yl benzoate (3e). Reaction temperature: rt; reaction time: 12 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 20:1, UV); Colorless liquid; 81% yield (49.2 mg, 0.16 mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 7.2 Hz, 2H), 8.13 (s, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.85 (dd, *J* = 7.8, 4.7 Hz, 2H), 7.70 (t, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 8.3 Hz, 4H); ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 164.1 (s), 141.8 (dq, *J* = 258.7, 38.6 Hz), 134.5 (s), 134.1 (s), 132.9 (s), 130.6 (s), 129.0 (s), 129.0 (s), 128.8 (s), 128.4 (s), 127.9 (s), 127.8 (s), 127.0 (s), 123.6 (d, *J* = 7.1 Hz), 123.9 (dq, *J* = 7.2, 2.5 Hz), 119.4 (dq, *J* = 273.9, 37.3 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -66.99 (d, *J* = 9.4 Hz), -150.88 (q, *J* = 9.3 Hz) IR v (neat, cm⁻¹): 2926, 1755, 1600, 1363, 1200, 1153, 1019, 852, 711; HRMS (ESI-TOF, m/z): calcd. For C₂₀H₁₆F₄NO₂ [M+NH₄]⁺: 378.1112, found: 378.1113.

(E)-2,3,3,3-tetrafluoro-1-phenylprop-1-en-1-yl 4-methyl benzenesulfonate (3f). Reaction temperature: rt; reaction time: 12 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 20:1, UV); Colorless liquid; 87% yield (62.8 mg, 0.17 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 8.1 Hz, 2H), 7.34 (t, J = 8.7 Hz, 3H), 7.25 (d, J = 10.9 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 2.39 (s, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 146.0 (d, J = 2.7 Hz), 143.0 (dq, J = 114.6, 38.7 Hz), 132.8 (d, J = 6.5 Hz), 130.7 (s), 129.8 (d, J = 1.1 Hz), 128.6 (s), 128.5 (s), 128.4 (s), 128.2 (s), 128.1 (qd, J = 4.3, 1.5Hz), 118.8 (qd, J = 273.5, 37.3 Hz), 21.8 (d, J = 3.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -66.64 (d, J = 9.9 Hz), -149.28 (q, J = 9.8 Hz); IR ν (neat, cm⁻¹): 2962, 1693, 1391, 1148, 1065, 917, 813, 763, 669; HRMS (ESI-TOF, m/z): calcd. For C₁₆H₁₆F₄NO₃S [M+NH₄]⁺: 378.0782, found: 378.0783.

(*Z*)-*methyl* 4-(2,3,3,3-*tetrafluoroprop-1-en-1-yl*)*benzoate* (3g).^{14a} Reaction temperature: rt; reaction time: 12 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 20:1, UV); Colorless liquid; 43% yield (21.3 mg, 0.09 mmol); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 6.41 (d, *J* = 35.0 Hz, 1H), 3.93 (s, 3H).

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(*Z*)-4-(2,3,3,3-tetrafluoroprop-1-en-1-yl)benzonitrile (3h).^{14a} Reaction temperature: rt; reaction time: 12 h; petroleum ether/ ethylacetate = 50:1; TLC: $R_f = 0.5$ (PE / EA = 20:1, UV); Colorless liquid; 44% yield (19.2 mg, 0.09 mmol); ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 7.8 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 6.41 (d, J = 34.3 Hz, 1H).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Reaction optimization for trifluoromethylation, NMR spectra for the products (PDF)

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Notes

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