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Synthesis of α-Trifluoromethylacrylates by Ligand-Free Palladium-Catalyzed Mirozoki-Heck Reaction

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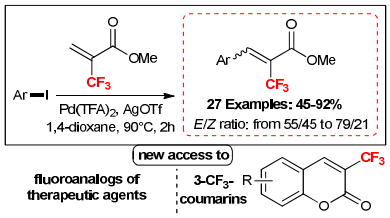
Supporting Information

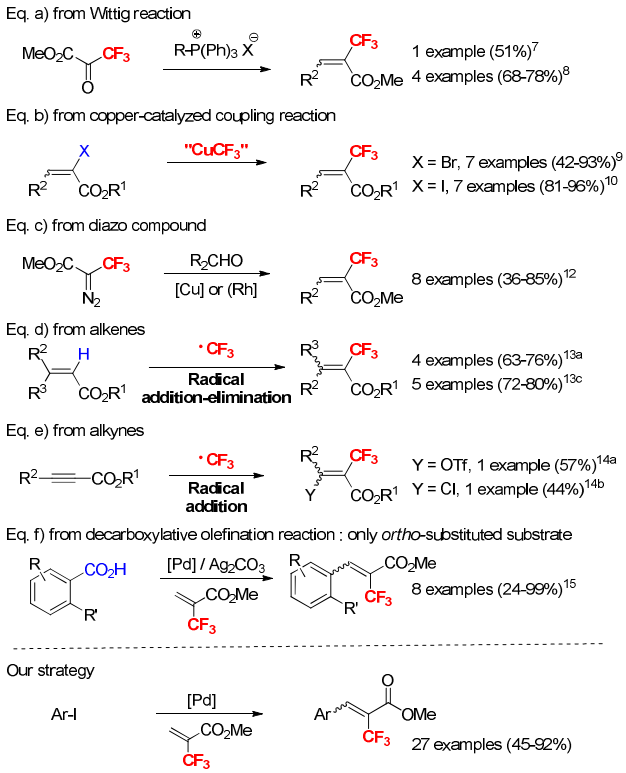


ABSTRACT: Efficient ligand-free palladium catalyzed Mizoroki-Heck reaction allowed the formation of trisubstituted α-trifluoromethylacrylates. The reaction showed good chemical tolerance and furnished good to excellent yields of reaction. Silver salt additive proved to be essential for the reaction. The reaction has been then applied to the formation of 3-trifluoromethyl coumarins and analogues of therapeutic agents.

Introduction

Organofluorine chemistry is a tremendous research area with plenty of different applications in materials, pharmaceuticals or agrochemical sciences.[1] Among the highly diversified groups containing one or more fluorine atoms, the trifluoromethyl moiety have received a lot of attention these last years.[2] Indeed, its impact on physical properties of molecules, ie. acidity, hydrophobicity, steric hindrance…, is spectacular. The trifluoromethylalkenes-containing molecules can be found, for instance, as therapeutic agents or agrochemicals.[3,4] Moreover, the trifluoromethylalkene group is known as an efficient peptide bond surrogate.[5,6] Among the various trifluoromethylalkene derivatives, α-trifluoromethyl-acrylate moiety is a valuable building block which can be found in various relevant molecules (materials, medicinal) or can serve as intermediate towards fine chemicals such as trifluoromethyl nucleosides or peptidomimetics for examples.[6] Despite obvious interest in such kind of scaffolds, there is very few general access to the α-trifluoromethylacrylates. Indeed, most of reported reactions gave only few examples of α-trifluoromethylacrylate synthesis (Scheme 1). In the early 2000s, Schlosser used the Wittig reaction with methyl 3,3,3-trifluoropyruvate to synthesize one specific α-trifluoromethylacrylate in 51% yield and low *E*/*Z* selectivity (60/40).[7] Later, Paleta *et al.* used the same reaction to get four α-trifluoromethylacrylates in good yields (68 to 78%) with selectivities depending of the substrate (*E*/*Z* from 43/57 to 92/8) (Scheme 1, Eq. a).[8] During the same time, Qing reported the synthesis of α-trifluoromethylacrylate via the *in-situ* formation of trifluoromethyl-copper species. The cross-coupling reaction between these latter and seven vinyl halides gave the corresponding products in fair to good yields (42-93%) and selectivities (*E*/*Z* from 61/39 to 89/11) starting from vinyl bromides.[5d,9]

Scheme 1. State of the art about the synthesis of α-trifluoromethylacrylates



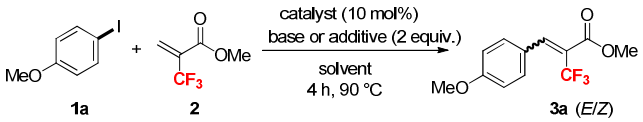
Yields and selectivities were improved using vinyl iodides as substrates (Scheme 1, Eq. b).[10] Nevertheless, these reactions required the multi-step pre-synthesis of the corresponding halophosphonoacetate and then the obtention of halogenoalkenes as

key intermediates for the reaction. Other authors used the same strategy later without improvement of yield or selectivity.[4c,11] Another strategy developed in 2006 by Jiang and Zhu involved the use of potentially explosive diazo compound (methyl 3,3,3-trifluoro-2-diazopropionate) in combination with aldehyde under transition metal-catalysis (Rh or Cu) to get the desired α-trifluoromethylacrylate in low to good yields and moderate selectivity (eight examples, 36-81% yield, *E/Z* from 24/76 to 84/16) (Scheme 1, Eq. c).[12] More recently, the radical trifluoromethylation (from Langlois's reagent, trifluoromethyl iodide or Togni's reagent) of acrylates through a radical addition-elimination process was developed but only few examples were dedicated to α-trifluoromethylacrylate and only fair to good yields (63-80%) were obtained in these cases (Scheme 1, Eq. d).[13] Even more recently, photoredox-catalyzed transformation of alkynes into α-(trifluoromethyl)alkenes were developed by Akita and then Han, respectively.[14] These reactions were only applied once to ethyl phenylpropiolate to furnish one example of α-trifluoromethylacrylate in good stereoselectivity, albeit in moderate yields (44[14b] and 57%,[14a] respectively) (Scheme 1, Eq. e). In 2018, we described the synthesis of trisubstituted α-trifluoromethylacrylates by a palladium-catalyzed decarboxylative olefination reaction in low to excellent yields (24-99%) with various selectivities (*E/Z* from 60/40 to 12/88) but this access allows only the formation of aromatic *ortho*-substituted α-trifluoromethylacrylates (Scheme 1, Eq. f).[15] Moreover good yields were only obtained starting from electron-rich benzoic acids. To resume, for the above-mentioned methods, most of them showed narrow substrate scope furnishing only moderate to good yields of α-trifluoromethylacrylate; moreover, some of them required pre-synthesis of substrates, used expensive fluorinated reagents or unstable starting materials. Herein, we propose an efficient and general straightforward access, in one step, to a large variety of α-trifluoromethylacrylates via a ligand-free palladium-catalyzed Mizoroki-Heck reaction. This methodology has then been applied to the synthesis of trifluororomethylated analogues of fine chemicals.

Results and discussion

We started the optimization of the reaction studying the Mizoroki-Heck reaction between *p*-methoxyphenyl iodide **1a** as model substrate and commercially available methyl α-trifluoromethylacrylate **2** (Table 1). To our knowledge, among the various fluorinated alkenes used in Mizoroki-Heck reaction, it was the first time that reagent **2** was used in such reaction.[16] We used our previous optimized experimental conditions reported for the synthesis of α-fluoroacrylates[17] (Table1, entry 1). These conditions furnished encouraging results and led to 86% yield of compound **3a** using 10 mol% of electrophilic catalyst, $Pd(TFA)_2$. We then tested several solvents and among them toluene allowed to slightly improve the yield of the reaction along with, nevertheless, a decrease of selectivity (Table 1, entry 2). Highly polar solvent such as DMF gave lower yield of compound **3a** (Table 1, entry 3). Other tested solvents did not give any improved results compared to those obtained with 1,4-dioxane.[18] Changing the nature of the catalyst proved to be detrimental for the reaction giving a poor 22% yield of **3a** with $Pd(OAc)_2$ and almost no reaction with $PdBr_2$ or $Pd(PPh_3)_4$, a Pd(0) catalyst. (Table 1, entries 4-6). In order to gain in selectivity, we used different common ligands such as monodentate or bidentate phosphines but the results were lower in terms of yield and selectivity.[18] The use of silver carbonate proved to be important for the reaction as without this base the yields dropped down to 17% and 19% in 4 and 24 h reaction, respectively (Table 1, entry 7). So, we then tested a plethora of other bases[18] and clearly, silver cation proved to be essential for the reaction (table 1, entries 8-11). At this stage, we decided to test other silver additives (Table 1, entries 12-16) and pleasingly, among them, silver triflate furnished the highest yield of **3a** (93%) using 2 (Table 1, entry 13) or even 1.5 equiv in 2 hours reaction time (Table 1, entry 17).

Table 1. Optimization of the trifluoromethylalkenylation reaction[a]



Entry	Solvent	Catalyst	Base or additive	Yield of **3a** (%)[b]	*E/Z* ratio
1	**1,4-Dioxane**	$Pd(TFA)_2$	Ag_2CO_3	86	77/23
2	**Toluene**	$Pd(TFA)_2$	Ag_2CO_3	93	66/34
3	**DMF**	$Pd(TFA)_2$	Ag_2CO_3	16	60/40
4	1,4-Dioxane	**$Pd(OAc)_2$**	Ag_2CO_3	22	74/26
5	1,4-Dioxane	**$PdBr_2$**	Ag_2CO_3	4	60/40
6	1,4-Dioxane	**$Pd(PPh_3)_4$**	Ag_2CO_3	3	-
7	**1,4-Dioxane**	$Pd(TFA)_2$	-	17 [19][c]	80/20
8	1,4-Dioxane	$Pd(PPh_3)_4$	**NEt_3**	13	75/25
9	1,4-Dioxane	**$Pd(TFA)_2$**	NEt_3	15	67/33
10	1,4-Dioxane	$Pd(TFA)_2$	**K_2CO_3**	17	67/33
11	1,4-Dioxane	$Pd(TFA)_2$	**CuOAc**	5	67/33
12	1,4-Dioxane	$Pd(TFA)_2$	**AgOAc**	74	74/26
13	1,4-Dioxane	$Pd(TFA)_2$	**AgOTf**	93	77/23
14	1,4-Dioxane	$Pd(TFA)_2$	**AgTFA**	86	77/23
15	1,4-Dioxane	$Pd(TFA)_2$	**Ag_3PO_4**	63	70/30
16	1,4-Dioxane	$Pd(TFA)_2$	**$AgNO_3$**	34	76/24
17[d]	1,4-Dioxane	$Pd(TFA)_2$	AgOTf	93 (86)[e]	76/24
18[d]	**Toluene**	$Pd(TFA)_2$	AgOTf	29	77/23
19[d]	**DMF**	$Pd(TFA)_2$	AgOTf	98	64/36
20[d]	1,4-Dioxane	**$Pd(OAc)_2$**	AgOTf	91 (84)[e]	76/24
21[d]	1,4-Dioxane	**$PdBr_2$**	AgOTf	90 (83)[e]	74/26
22[d]	1,4-Dioxane	**$Pd(PPh_3)_4$**	AgOTf	59	75/25
23[d]	1,4-Dioxane	**$Pd(dba)_2$**	AgOTf	traces	
24[d]	1,4-Dioxane	**$Pd_2(dba)_3$**	AgOTf	traces	
25[d]	1,4-Dioxane	-	AgOTf	0	
26[d,f]	1,4-Dioxane	$Pd(TFA)_2$	AgOTf	92 (86)[e]	76/24
27[d,g]	1,4-Dioxane	$Pd(TFA)_2$	AgOTf	90 (84)[e]	76/24

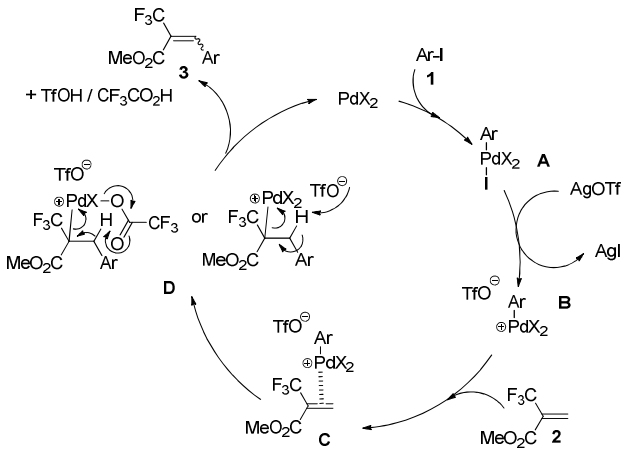
[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), [Pd] catalyst (10 mol%), base or additive (0.4 mmol, 2.0 equiv), solvent (1.0 mL), 4 h, 90 °C. [b]^{19}F NMR yields were obtained by using $PhCOCF_3$ as an internal standard. [c]24 h. [d]AgOTf (1.5 equiv), 2 h. [e]Isolated yield. [f]$Pd(TFA)_2$ (1.5 mol%). [g]$Pd(TFA)_2$ (0.5 mol%).

Taking into account that this silver triflate cannot be considered as a base but more as a halide abstracter allowing the formation of cationic palladium species,[19] we speculated that a highly polar solvent should stabilize it and favored the reaction. Indeed, with silver triflate, toluene gave only poor 29% yield (Table 1, entry 18) whereas DMF allowed us to reach 98% yield, albeit with lower selectivity (Table 1, entry 19). These

results clearly showed that the mechanism of the reaction is different when silver carbonate or silver triflate is employed (table 1, comparison entries 1-3 with entries 17-19). Another proof of this hypothesis is the possibility with silver triflate to use other palladium catalysts than the electrophilic $Pd(TFA)_2$ leading to good yield of **3a** (Table 1, entries 20-21). The yield was lower using Pd(0) catalyst in presence of phosphine ligand (entry 22) whereas without ligand stabilization, Pd(0) catalyst did afford only traces of product (entries 23-24). The absence of palladium in the reaction media proved to be detrimental as no reaction occured (Table 1, entry 25). Finally, it was possible to decrease the catalyst loading to 1.5 mol% or even 0.5 mol% still with good isolated yields (Table 1, entries 26 and 27). Nevertheless, it was not a general trend as some substrates required at least 5 or 10 mol% catalyst to go to completion.

Based on experimental findings, hereafter, we proposed the following mechanism for this trifluoromethylalkenylation reaction (Scheme 2). After an oxidative addition, the Pd(II) is transformed in Pd(IV), complex **A**. Silver triflate acted as an halide abstracter furnishing the cationic palladium **B**. This latter is stabilized in polar solvent as well as in the presence of electro-enriched substituent in the aryl moiety. Then a coordination of α-trifluoromethylacrylate **2** to complex **B** occurred to obtain intermediate **C**. This coordination is favored because the energy gap between the HOMO of the electron-deficient alkene **2** and the LUMO of palladium **B** is decreased by the electrophilic nature of **B**. Then an insertion of aryl into the double bond gave complex **D**. Deprotonation by the closed triflate counteranion or concerted deprotonation by TFA ligand regenerates PdX_2 and led to desired product **3** as well as the formation of triflic or trifluoroacetic acid. Indeed, at the end of the reaction, the pH in the reaction media appeared to be highly acidic (pH ≈1 with the presence of triflic acid and trifluoroacetic acid in ^{19}F NMR of the crude).

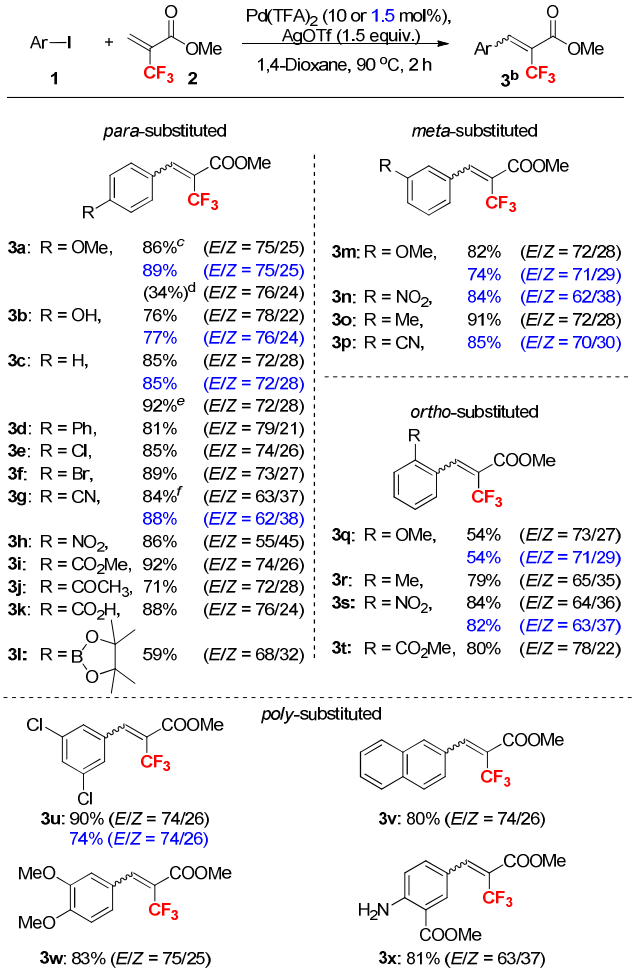
Scheme 2. Proposed mechanism.



A lot of other experimental conditions were tested[18] and worthy of note that depending on aryl iodides used, the reaction time can be reduced down to 5 min for some electron-rich substrates, which is consistant with stabilization of the cationic palladium. The reaction's temperature can also be decreased to 60°C in some cases. Nevertheless, in order to propose a general method, all the following scope has been obtained using the following experimental procedure: aryl iodide **1** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), [Pd] catalyst (10 or 1.5 mol%), AgOTf (0.3 mmol, 1.5 equiv), 1,4-dioxane (1.0 mL) in 2 h, at 90°C.

Various aryl iodides **1** were suitable for the reaction which proved to be highly tolerant in regards of substituents beared by the aryl moiety (Scheme 3). Interestingly, *para*-iodophenol did not need to be protected and furnished 76% yield of **3b**. The reaction was scaled up with iodobenzene **1c**, 3.5 mmol instead of usual 0.2 mmol, and the corresponding product **3c** was obtained with excellent 92% of isolated yield (740 mg). Other halogens (chlorine or bromine) did not interfer during the reaction which was regioselective at the iodine position leading to post-functionnalizable products **3e** and **3f** in very good 85% and 89% yield, respectively. Valuable withdrawing functional groups for further post-functionalizations such as cyano **1g**, nitro **1h**, ester **1i** or methylketone **1j**, displayed very good reactivities leading to high yields, (84 to 92%), albeit the yield was lower starting from **1j** (71%). Pleasingly, the carboxylic acid **1k** could also be used directly in the reaction giving high 88% yield of the corresponding **3k**. Finally, we succeeded using highly relevant 4-iodophenylboronic acid pinacol ester as substrate, albeit the yield was lower (59%) in this case. Replacing the *para*-iodoanisole by *para*-bromoanisole as substrate only led to 34% of **3a**.

Scheme 3. Scope of the reaction[a]

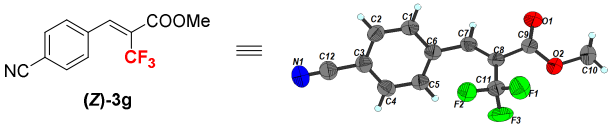


[a]General conditions: Ar-I **1** (0.2 mmol, 1.0 equiv), methyl 2-trifluoromethylacrylate **2** (0.3 mmol, 1.5 equiv), $Pd(TFA)_2$ (10 mol%), AgOTf (0.3 mmol, 1.5 equiv), 1,4-dioxane (1.0 mL), 2

h, 90 °C. [b]Yield based on isolated product after flash chromatography. [c]Reaction proceeded in 5 min. [d]with *para*-bromoanisole, ^{19}F NMR yield. [e]The reaction was scaled up: **1c** (3.5 mmol, 1.0 equiv), and 740 mg of **3c** was obtained. [f]1.2 equiv of **2**.

The stereoselectivity of the reaction was undoubtedly assigned by NMR spectroscopy (^{19}F NMR and HOESY experiments)[18] and X-ray diffraction analysis (Scheme 4). The less constrained *E*-product was always the major isomer obtained.

Scheme 4. X-ray of product (*Z*)-3g.



Then we submitted different *meta*- and *ortho*-substituted aryl iodides to our reaction conditions (Scheme 3). We always obtained good yields excepted with ortho-methoxy substituent leading to a fair 54% yield of **3q**.

The selectivity of the reaction was rather independent of the substituent whether it was electron-donating or electron-withdrawing group, *ie E*/*Z* ratio between 79/21 to 72/28, excepted for some substrates. Indeed, surprisingly, *para*-cyano **3g**, *para*-nitro **3h** and *meta*-nitro **3n** were obtained with a lower *E*/*Z* ratio of 63/37, 55/45 and 62/38 respectively whereas *ortho*-substituted **3r** (*o*-Me) and **3s** (*o*-NO_2) were obtained in the same range of *E*/*Z* ratio, 65/35 and 64/36 respectively, probably due for the latters of steric interaction close to the reaction center.

Polysubstituted aryl iodides could also be coupled efficiently with good yields. Among them, the valuable methyl 2-amino-5-iodobenzoate **1x** provided the corresponding product **3x** in high 81% yield without protection of the amine function.

Nevertheless, it has to be noted that whereas a lot of aryl iodides can be used in this reaction the use of heteroaryl iodides (azines, thiophen, furan) displayed only very low or no reactivity.[18]

We selected some substrates **1** and demonstrated that we can used only 1.5 mol% of catalyst affording, most of the time, the same selectivity and yield of **3** than obtained with 10 mol% catalyst (Scheme 3, results in blue).

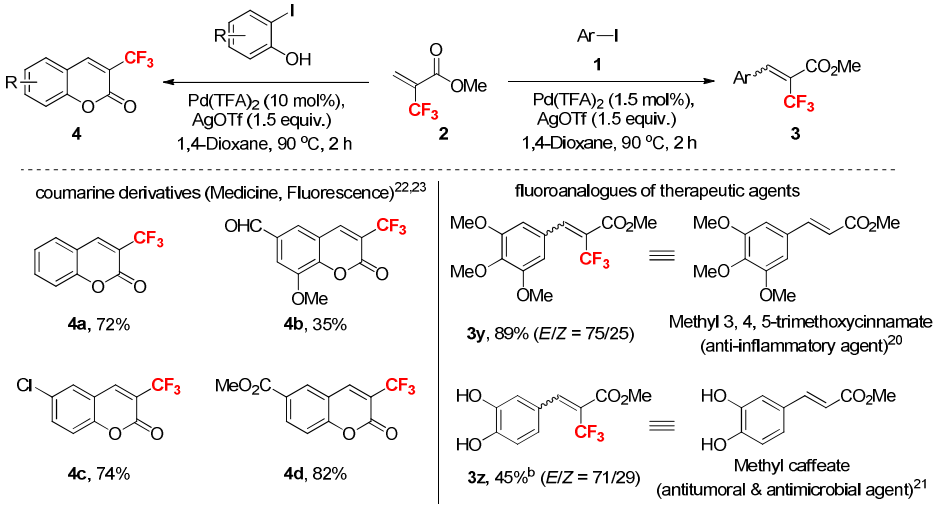
Then we decided to apply our methodology to the production of fine fluorinated chemicals (Scheme 5). Using our strategy, it was possible, in one step to obtain a fluorinated analogue **3y**, albeit in *E*/*Z* mixture, of methyl 3, 4, 5-trimethoxycinnamate, an anti-inflammatory agent in high 89% yield.[20] The reaction was then applied to the production of a fluorinated analogue **3z** (*E*/*Z* mixture) of the methyl caffeate, an antitumoral and antimicrobial agent,[21] in moderate 45% yield.[22]

Taking into account that we are in acid media at the end of the reaction, we wondered if it could be possible to use *ortho*-iodophenol and performed an *in-situ* cyclization between hydroxyl and ester function in order to get a direct access to 3-trifluoromethyl coumarin. So we submitted the *ortho*-iodophenol to the reaction conditions and we were pleased to obtain, as the sole product, the 3-trifluoromethyl coumarin **4a** in good 72% yield. We applied this methodology to the synthesis of three other relevant substituted 3-trifluoromethyl coumarins (**4b-d**) in moderate to very good yields. Usual synthesis of 3-trifluoromethyl coumarins involved the radical trifluoromethylation of coumarin scaffolds or specific designed substrates providing the desired coumarin in moderate yields.[23] So, this direct synthesis of 3-trifluoromethyl coumarins in one step by Mizoroki-Heck reaction represents a nice synthetic alternative obtaining this valuable scaffold with many application in fluorescence or medicine.[24]

Conclusion

To resume we described a general and efficient method to obtain valuables α-trifluoromethylacrylates. The reaction proved to be highly tolerant with respect to substituents beared by the aryl moiety. Indeed, substrates with non protected hydroxyl as well as carboxylic acid function displayed high reactivities. We then applied successfully our reaction to the synthesis of fluorinated therapeutic agents. Worthy of note that we also proposed, via this Mizoroki-Heck reaction, an efficient alternative to the production of highly relevant 3-trifluoromethyl coumarins.

Scheme 5. Applications to the synthesis of fine fluorinated chemicals.[a]



[a]Yields are based on isolated product after flash chromatography. [b]with $Pd(TFA)_2$ (0.5 mol%).

Experimental section

General Information: Commercially available reagents and anhydrous solvents were purchased from standard chemical suppliers (Fisher, Sigma-Aldrich, Fluorochem, Alfa Aesar) and used as received without further purification. Among them, methyl 2-(trifluoromethyl)acrylate (97% purity) was purchased from Sigma-Aldrich or Fluorochem. Thin layer chromatography (TLC) analyses were done using aluminium sheets coated with silica gel 60 F254; Flash column chromatography was carried out using Silicaflash P60 silica gel (40-60 μm). Melting points (Mp) were determined on a Fisher Scientific hot stage melting point apparatus and are uncorrected. NMR spectra were recorded using a Bruker Avance-300 spectrometer operating at 300 MHz (^{1}H), 282 MHz (^{19}F), and 75 MHz (^{13}C). ^{1}H and ^{13}C NMR chemical shifts (δ) were calibrated on residual proton and carbon resonances of $CDCl_3$ (^{1}H, δ = 7.26 ppm and ^{13}C, δ = 77.16 ppm) or CD_3OD (^{1}H, δ = 3.31 ppm and ^{13}C, δ = 49.00 ppm) or $(CD_3)_2SO$ (^{1}H, δ = 2.50 ppm and ^{13}C, δ = 39.52 ppm); ^{19}F NMR chemical shifts (δ) were determined relative to $CFCl_3$ as an internal standard (^{19}F, δ = 0.0 ppm). The multiplicity signals were indicated with the common abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) and the combinations thereof. IR spectra were recorded on Perkin Elmer Spectrum 100 FT IR spectrometer. High Resolution Mass Spectra (HRMS) were recorded on a JEOL AccuTof 4G spectrometer coupled to a GC HP Agilent 7890. Crystallographic data were collected using a Bruker SMART APEX diffractometer with a CCD area detector.

General Procedure for Heck Reaction: To a vial (2 mL) were added iodoarene (0.2 mmol, 1.0 equiv), AgOTf (0.3 mmol, 1.5 equiv), $Pd(TFA)_2$ (0.02 mmol, 10 mol%), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 1.5 equiv), and 1,4-dioxane (1.0 mL, 5 mL/mmol of iodoarene). The vial was then sealed. The reaction mixture was stirred at 90 °C for 2 hours and was then cooled to room temperature. The reaction mixture was transferred to a 50 mL flask (with the vial washed with 20 mL EtOAc) and was mixed with celite. After evaporation of solvents, the crude was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc or CH_3Cl/MeOH).

Characterization data for products 3:

Methyl (*E*)-3-(4-methoxyphenyl)-2-(trifluoromethyl)acrylate (*E*-3a) and **Methyl (*Z*)-3-(4-methoxyphenyl)-2-(trifluoromethyl)acrylate (*Z*-3a)**. 4-Iodoanisole (0.2 mmol, 46.8 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 5 minutes according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 30/1 to 15/1, v/v), affording compound **3a** in 86% yield [mixture of *E*/*Z* isomers (75/25), 44.5 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (s, 1H, *Z*), 7.51 – 7.29 (m, 2H, *Z* + 3H, *E*), 6.99 – 6.84 (m, 2H, *Z* + 2H, *E*), 3.88 (s, 3H, *Z*), 3.86 – 3.83 (m, 3H, *Z* + 3H, *E*), 3.82 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -63.8 (d, *J* = 1.7 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 164.5 – 164.3 (m), 161.70, 161.66, 148.3 (q, *J* = 3.0 Hz), 140.4 (q, *J* = 5.7 Hz), 132.4 (q, *J* = 2.7 Hz), 131.7, 124.7, 124.5, 122.6 (q, *J* = 271.0 Hz), 122.3 (q, *J* = 272.0 Hz), 120.4 (q, *J* = 31.0 Hz), 119.6 (q, *J* = 32.0 Hz), 114.2, 114.0, 55.4, 52.7, 52.6. IR: 2960, 2847, 1726, 1604, 1513, 1439, 1322, 1281, 1260, 1155, 1116, 1028, 832, 523 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{12}H_{11}F_3O_3$ (m/z): 260.0660 $[M]^+$, found: 260.0659.

Methyl (*E*)-3-(4-hydroxyphenyl)-2-(trifluoromethyl)acrylate (*E*-3b) and **Methyl (*Z*)-3-(4-hydroxyphenyl)-2-(trifluoromethyl)acrylate (*Z*-3b)**. 4-Iodophenol (0.2 mmol, 44.0 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 10/1 to 5/1, v/v), affording compound **3b** in 76% yield [mixture of *E*/*Z* isomers (78/22), 37.3 mg] as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (s, 1H, *Z*), 7.42 – 7.27 (m, 2H, *Z* + 3H, *E*), 6.91 – 6.73 (m, 2H, *Z* + 2H, *E*), 6.06 (s, 1H, *E*), 5.95 (s, 1H, *Z*), 3.89 (s, 3H, *Z*), 3.85 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -63.8 (d, *J* = 1.7 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 165.1 – 165.0 (m), 165.0 (q, *J* = 2.0 Hz), 158.22, 158.19, 148.7 (q, *J* = 2.7 Hz), 141.0 (q, *J* = 5.7 Hz), 132.7 (q, *J* = 2.7 Hz), 131.8, 124.7, 124.5, 122.5 (q, *J* = 271.1 Hz), 122.3 (q, *J* = 272.2 Hz), 120.2 (q, *J* = 31.1 Hz), 119.5 (q, *J* = 32.3 Hz), 115.9, 115.6, 53.0, 52.9. IR: 3292, 1699, 1608, 1515, 1438, 1383, 1279, 1250, 1210, 1157, 1126, 1109, 1019, 843, 493 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{11}H_9F_3O_3$ (m/z): 246.0504 $[M]^+$, found: 246.0496.

Methyl (*E*)-3-phenyl-2-(trifluoromethyl)acrylate (*E*-3c) and **Methyl (*Z*)-3-phenyl-2-(trifluoromethyl)acrylate (*Z*-3c)**. Iodobenzene (0.2 mmol, 40.8 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 60/1 to 30/1, v/v), affording compound **3c** in 85% yield [mixture of *E*/*Z* isomers (72/28), 39.3 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (s, 1H, *Z*), 7.53 – 7.34 (m, 5H, *Z* + 6H, *E*), 3.90 (s, 3H, *Z*), 3.79 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -64.4 (d, *J* = 1.4 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 163.9, 148.6 (q, *J* = 2.9 Hz), 140.6 (q, *J* = 5.7 Hz), 132.6, 132.3, 130.5, 130.3, 129.4 (q, *J* = 2.3 Hz), 129.2, 128.8, 128.4, 123.3 (q, *J* = 31.3 Hz), 122.5 (q, *J* = 31.9 Hz), 122.2 (q, *J* = 271.4 Hz), 122.0 (q, *J* = 272.6 Hz), 52.9, 52.7. IR: 2961, 1730, 1645, 1438, 1386, 1278, 1231, 1158, 1125, 1033, 1020, 755, 693 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{11}H_9F_3O_2$ (m/z): 230.0555 $[M]^+$, found: 230.0544.

Methyl (*E*)-3-([1,1'-biphenyl]-4-yl)-2-(trifluoromethyl)acrylate (*E*-3d) and **Methyl (*Z*)-3-([1,1'-biphenyl]-4-yl)-2-(trifluoromethyl)acrylate (*Z*-3d)**. 4-Iodobiphenyl (0.2 mmol, 56.0 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 60/1 to 30/1, v/v), affording compound **3d** in 81% yield [mixture of *E*/*Z* isomers (79/21), 49.4 mg. *E*/*Z* isomers were completely separated by column: compound ***E*-3d** 39.1 mg, yellow oil; impure *Z*-isomer was subsequently washed with petroleum ether (0.5 mL × 3) to obtain pure compound ***Z*-3d** 10.3 mg, white solid].

[*E*-isomer (major)] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 – 7.60 (m, 4H), 7.54 – 7.44 (m, 5H), 7.44 – 7.36 (m, 1H), 3.84 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -64.2 (d, *J* = 1.7 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 164.0, 143.4, 140.2 (q, *J* = 5.7 Hz), 140.0, 131.1, 130.0, 129.1, 128.2, 127.3, 127.2, 122.9

(q, *J* = 31.2 Hz), 122.3 (q, *J* = 271.4 Hz), 52.8. IR: 3034, 2954, 1730, 1645, 1492, 1439, 1384, 1322, 1293, 1280, 1230, 1158, 1124, 1018, 763, 696 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{17}H_{13}F_3O_2$ (m/z): 306.0868 $[M]^+$, found: 306.0868.

[*Z*-isomer (minor)] Mp 84-85 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.68 – 7.59 (m, 4H), 7.54 – 7.43 (m, 4H), 7.43 – 7.34 (m, 1H), 3.92 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -58.5 (s). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 164.1 (q, *J* = 2.0 Hz), 148.2 (q, *J* = 2.9 Hz), 143.2, 140.1, 131.4, 130.4 (q, *J* = 2.6 Hz), 129.1, 128.2, 127.3, 127.1, 122.2 (q, *J* = 32.0 Hz), 122.1 (q, *J* = 272.5 Hz), 53.0. IR: 3040, 2961, 2921, 2855, 1731, 1714, 1631, 1438, 1379, 1278, 1206, 1126, 1038, 845, 753, 701 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{17}H_{13}F_3O_2$ (m/z): 306.0868 $[M]^+$, found: 306.0855.

Methyl (*E*)-3-(4-chlorophenyl)-2-(trifluoromethyl)acrylate (*E*-3e) and **Methyl (*Z*)-3-(4-chlorophenyl)-2-(trifluoromethyl)acrylate (*Z*-3e)**. 1-Chloro-4-iodobenzene (0.2 mmol, 47.7 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 60/1 to 50/1, v/v), affording compound **3e** in 85% yield [mixture of *E*/*Z* isomers (74/26), 45.2 mg. *E*/*Z* isomers were completely separated by column: ***E*-3e** 33.5 mg, yellow oil; ***Z*-3e** 11.7 mg, yellow oil].

[*E*-isomer (major)] ^1H NMR (300 MHz, $CDCl_3$): δ 7.43 – 7.28 (m, 5H), 3.80 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -64.4 (d, *J* = 1.7 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 163.6 – 163.5 (m), 139.6 (q, *J* = 5.8 Hz), 136.7, 130.7, 130.6, 129.1, 123.8 (q, *J* = 31.4 Hz), 122.1 (q, *J* = 271.5 Hz), 52.9. IR: 2961, 1732, 1650, 1492, 1312, 1290, 1273, 1232, 1160, 1128, 1095, 1015, 842, 816, 502, 434 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{11}H_8{}^{35}ClF_3O_2$ (m/z): 264.0165 $[M]^+$, found: 264.0156.

[*Z*-isomer (minor)] ^1H NMR (300 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.43 – 7.30 (m, 4H), 3.90 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.6 (s). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 163.7 (q, *J* = 2.0 Hz), 147.2 (q, *J* = 2.9 Hz), 136.6, 131.0, 130.8 (q, *J* = 2.5 Hz), 128.8, 123.0 (q, *J* = 32.0 Hz), 121.8 (q, *J* = 272.7 Hz), 53.1. IR: 2961, 2921, 2855, 1731, 1640, 1491, 1438, 1392, 1279, 1257, 1131, 1091, 1041, 828, 788, 755 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{11}H_8{}^{35}ClF_3O_2$ (m/z): 264.0165 $[M]^+$, found: 264.0152.

Methyl (*E*)-3-(4-bromophenyl)-2-(trifluoromethyl)acrylate (*E*-3f) and **Methyl (Z)-3-(4-bromophenyl)-2-(trifluoromethyl)acrylate (*Z*-3f)**. 1-Bromo-4-iodobenzene (0.2 mmol, 56.6 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 60/1 to 50/1, v/v), affording compound **3f** in 89% yield [mixture of *E*/*Z* isomers (73/27), 55.0 mg] as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.92 (s, 1H, *Z*), 7.50 – 7.40 (m, 2H, *Z* + 2H, *E*), 7.27 (s, 1H, *E*), 7.17 (d, *J* = 8.4 Hz, 2H, *Z* + 2H, *E*), 3.81 (s, 3H, *Z*), 3.71 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -64.5 (d, *J* = 1.7 Hz, *E*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 163.7 (q, *J* = 1.9 Hz), 163.6 – 163.5 (m), 147.2 (q, *J* = 2.9 Hz), 139.6 (q, *J* = 5.8 Hz), 132.0, 131.7, 131.4, 131.2, 130.9 (q, *J* = 2.4 Hz), 130.8, 125.0, 124.9, 123.9 (q, *J* = 31.4 Hz), 123.1 (q, *J* = 32.0 Hz), 122.1 (q, *J* = 271.6 Hz), 121.8 (q, *J* = 272.7 Hz), 53.0, 52.8. IR: 2961, 1731, 1645, 1589, 1489, 1439, 1385, 1312, 1288, 1274, 1230, 1161, 1128, 1073, 1021, 1011, 839, 814, 498 cm^{-1}. HRMS (ES-TOF): Calcd for $C_{11}H_8{}^{79}BrF_3O_2Na$ (m/z): 330.9557 $[M+Na]^+$, found: 330.9554.

Methyl (*E*)-3-(4-cyanophenyl)-2-(trifluoromethyl)acrylate (*E*-3g) and **Methyl (*Z*)-3-(4-cyanophenyl)-2-(trifluoromethyl)acrylate (*Z*-3g)**. 4-Iodobenzonitrile (0.2 mmol, 45.8 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.24 mmol, 37.0 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 20/1 to 5/1, v/v), affording compound **3g** in 84% yield [mixture of *E*/*Z* isomers (63/37), 42.7 mg. *E*/*Z* isomers were completely separated by column: compound ***E*-3g** 27.1 mg, white solid; impure *Z*-isomer was subsequently washed with petroleum ether (0.5 mL × 5) to obtain pure compound ***Z*-3g** 15.6 mg, white solid].

[*E*-isomer (major)] Mp <44 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.52 – 7.42 (m, 3H), 3.78 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -64.7 (d, *J* = 1.4 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 162.9 – 162.7 (m), 139.2 (q, *J* = 5.8 Hz), 136.9, 132.4, 129.5, 126.2 (q, *J* = 31.7 Hz), 121.7 (q, *J* = 271.9 Hz), 118.2, 113.8, 53.0. IR: 2959, 2231, 1732, 1653, 1440, 1381, 1292, 1275, 1235, 1160, 1129, 1020, 554 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{12}H_8F_3NO_2$ (m/z): 255.0507 $[M]^+$, found: 255.0512.

[*Z*-isomer (minor)] Mp 120-121 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 3.92 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 163.1 (q, *J* = 1.8 Hz), 146.0 (q, *J* = 3.0 Hz), 137.3, 132.1, 129.4 (q, *J* = 2.3 Hz), 125.2 (q, *J* = 32.0 Hz), 121.5 (q, *J* = 273.0 Hz), 118.2, 113.6, 53.2. IR: 2230, 1716, 1639, 1440, 1386, 1289, 1225, 1149, 1127, 1041, 837, 657, 555 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{12}H_8F_3NO_2$ (m/z): 255.0507 $[M]^+$, found: 255.0511.

Methyl (*E*)-3-(4-nitrophenyl)-2-(trifluoromethyl)acrylate (*E*-3h) and **Methyl (*Z*)-3-(4-nitrophenyl)-2-(trifluoromethyl)acrylate (*Z*-3h)**. 1-Iodo-4-nitrobenzene (0.2 mmol, 49.8 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 15/1 to 7/1, v/v), affording compound **3h** in 86% yield [mixture of *E*/*Z* isomers (55/45), 47.6 mg; among which, partly pure compound ***Z*-3h** was obtained] as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ 8.25 (m, 2H, *Z* + 2H, *E*), 8.12 (s, 1H, *Z*), 7.63 – 7.43 (m, 2H, *Z* + 3H, *E*), 3.92 (s, 3H, *Z*), 3.78 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -64.8 (d, *J* = 1.1 Hz, *E*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 163.0 (q, *J* = 1.8 Hz), 162.8 – 162.6 (m), 148.6, 148.4, 145.6 (q, *J* = 3.0 Hz), 139.2, 139.0 (q, *J* = 5.9 Hz), 138.9, 129.8, 129.6 (q, *J* = 2.3 Hz), 126.7 (q, *J* = 31.7 Hz), 125.7 (q, *J* = 32.0 Hz), 123.8, 123.6, 121.6 (q, *J* = 272.1 Hz), 121.4 (q, *J* = 272.9 Hz), 53.3, 53.0. IR: 2963, 1732, 1600, 1522, 1439, 1347, 1277, 1132, 1042, 855, 691 cm^{-1}. HRMS (ES-TOF): Calcd for $C_{11}H_8F_3NO_4Na$ (m/z): 298.0303 $[M+Na]^+$, found: 298.0312.

[*Z*-isomer (minor)] White solid. Mp 78-79 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.7 Hz, 2H), 8.13 (s, 1H), 7.52

(d, *J* = 8.4 Hz, 2H), 3.93 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -58.5 (s). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 163.0 (q, *J* = 1.8 Hz), 148.4, 145.7 (q, *J* = 3.0 Hz), 139.2, 129.7 (q, *J* = 2.3 Hz), 125.8 (q, *J* = 32.0 Hz), 121.4 (q, *J* = 273.0 Hz), 53.3. IR: 3107, 2968, 1722, 1638, 1598, 1518, 1429, 1348, 1276, 1206, 1143, 1126, 1041, 856, 693 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{11}H_8F_3NO_4$ (m/z): 275.0405 $[M]^+$, found: 275.0396.

Methyl (*E*)-4-(3,3,3-trifluoro-2-(methoxycarbonyl)prop-1-en-1-yl)benzoate (*E*-3i) and **Methyl (*Z*)-4-(3,3,3-trifluoro-2-(methoxycarbonyl)prop-1-en-1-yl)benzoate (*Z*-3i)**. Methyl 4-iodobenzoate (0.2 mmol, 52.4 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 20/1 to 10/1, v/v), affording compound **3i** in 92% yield [mixture of *E*/*Z* isomers (74/26), 52.9 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (s, 1H, *Z*), 8.09 – 7.99 (m, 2H, *Z* + 2H, *E*), 7.46 (s, 1H, *E*), 7.41 (d, *J* = 8.1 Hz, 2H, *Z* + 2H, *E*), 3.92 (s, 3H, *Z* + 3H, *E*), 3.90 (s, 3H, *Z*), 3.75 (s, 3H, *Z*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -64.6 (d, *J* = 1.4 Hz, *E*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 166.34, 166.29, 163.4 (q, *J* = 1.9 Hz), 163.3 – 163.2 (m), 142.2 (q, *J* = 3.0 Hz), 139.7 (q, *J* = 5.7 Hz), 137.1, 136.7, 131.5, 131.3, 129.8, 129.5 128.9, 125.1 (q, *J* = 30.2 Hz), 124.2 (q, *J* = 32.0 Hz), 121.9 (q, *J* = 271.7 Hz), 121.6 (q, *J* = 272.9 Hz), 53.0, 52.8, 52.4. IR: 2961, 1721, 1650, 1437, 1384, 1272, 1234, 1131, 1108, 1020, 766, 698 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{13}H_{11}F_3O_4$ (m/z): 288.0609 $[M]^+$, found: 288.0599.

Methyl (*E*)-3-(4-acetylphenyl)-2-(trifluoromethyl)acrylate (*E*-3j) and **Methyl (*Z*)-3-(4-acetylphenyl)-2-(trifluoromethyl)acrylate (*Z*-3j)**. 1-(4-Iodophenyl)ethan-1-one (0.2 mmol, 49.2 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 15/1 to 8/1, v/v), affording compound **3j** in 71% yield [mixture of *E*/*Z* isomers (78/22), 38.9 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (s, 1H, *Z*), 8.01 – 7.91 (m, 2H, *Z* + 2H, *E*), 7.57 – 7.38 (m, 2H, *Z* + 3H, *E*), 3.89 (s, 3H, *Z*), 3.76 (s, 3H, *E*), 2.60 (s, 3H, *Z* + 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -64.6 (d, *J* = 1.7 Hz, *E*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 197.4, 197.3, 163.4 (q, *J* = 1.8 Hz), 163.3 – 163.2 (m), 147.1 (q, *J* = 2.8 Hz), 139.7 (q, *J* = 5.7 Hz), 138.0, 137.8, 137.2, 136.8, 129.5 – 128.9 (m), 128.5, 128.2, 125.2 (q, *J* = 31.5 Hz), 124.3 (q, *J* = 31.9 Hz), 121.9 (q, *J* = 271.7 Hz), 121.6 (q, *J* = 272.9 Hz), 53.1, 52.9, 26.8. IR: 2961, 1731, 1685, 1649, 1606, 1439, 1361, 1262, 1234, 1161, 1128, 1021, 835, 693, 598 cm^{-1}. HRMS (ES-TOF): Calcd for $C_{13}H_{11}F_3O_3Na$ (m/z): 295.0558 $[M+Na]^+$, found: 295.0562.

(*E*)-4-(3,3,3-trifluoro-2-(methoxycarbonyl)prop-1-en-1-yl)benzoic acid (*E*-3k) and **(*Z*)-4-(3,3,3-trifluoro-2-(methoxycarbonyl)prop-1-en-1-yl)benzoic acid (*Z*-3k)**. 4-Iodobenzoic acid (0.2 mmol, 49.6 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, 5/1, with 1% CH_3COOH, v/v), affording compound **3k** in 88% yield [mixture of *E*/*Z* isomers (76/24), 48.1 mg] as a white solid. ^{1}H NMR (300 MHz, CD_3OD): δ 8.20 (s, 1H, *Z*), 8.04 (d, *J* = 7.8 Hz, 2H, *Z* + 2H, *E*), 7.64 (s, 1H, *E*), 7.48 (d, *J* = 7.8 Hz, 2H, *Z* + 2H, *E*), 3.88 (s, 3H, *Z*), 3.75 (s, 3H, *E*). ^{19}F NMR (282 MHz, CD_3OD): δ -59.2 (s, *Z*), -65.5 (d, *J* = 0.8 Hz, *E*). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3OD): δ 169.0, 168.9, 164.8 – 164.7 (m), 164.5 (q, *J* = 1.9 Hz), 148.7 (q, *J* = 3.0 Hz), 141.0 (q, *J* = 5.8 Hz), 138.5, 138.1, 133.3, 133.0, 130.9, 130.5, 130.0, 129.9 (q, *J* = 2.3 Hz), 125.9 (q, *J* = 31.4 Hz), 124.9 (q, *J* = 31.5 Hz), 123.3 (q, *J* = 270.8 Hz), 123.1 (q, *J* = 272.1 Hz), 53.4, 533. IR: 2961, 2815, 2670, 2550, 1734, 1683, 1610, 1571, 1425, 1277, 1239, 1211, 1135, 1020, 929, 768, 696, 548 cm^{-1}. HRMS (ES-TOF): Calcd for $C_{12}H_9F_3O_4Na$ (m/z): 297.0351 $[M+Na]^+$, found: 297.0345.

Methyl (*E*)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2-(trifluoromethyl)acrylate (*E*-3l) and **Methyl (*Z*)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2-(trifluoromethyl)acrylate (*Z*-3l)**. 4-Iodobenzeneboronic acid pinacol ester (0.2 mmol, 66.0 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The reaction mixture was directly purified by flash silica gel column chromatography (petroleum ether/EtOAc, from 40/1 to 20/1, v/v), affording compound **3l** in 59% yield [mixture of *E*/*Z* isomers (68/32), 41.9 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (s, 1H, *Z*), 7.90 – 7.77 (m, 2H, *Z* + 2H, *E*), 7.44 (s, 1H, *E*), 7.42 – 7.28 (m, 2H, *Z* + 2H, *E*), 3.89 (s, 3H, *Z*), 3.76 (s, 3H, *E*), 1.35 (s, 12H, *Z* + 12H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -64.5 (d, *J* = 1.1 Hz, *E*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 163.9 – 163.7 (m), 148.5 (q, *J* = 2.9 Hz), 140.4 (q, *J* = 5.7 Hz), 135.2, 135.0, 134.9, 134.7, 128.4 (q, *J* = 2.3 Hz), 128.2, 124.0 (q, *J* = 31.2 Hz), 123.0 (q, *J* = 32.3 Hz), 122.1 (q, *J* = 271.4 Hz), 121.9 (q, *J* = 272.7 Hz), 84.24, 84.23, 52.9, 52.7, 25.0. IR: 2980, 1733, 1610, 1439, 1398, 1359, 1276, 1227, 1163, 1134, 1089, 1021, 858, 656 cm^{-1}. HRMS (AP-TOF): Calcd for $C_{17}H_{20}{}^{11}BF_3O_4$ (m/z): 356.1407 $[M]^-$, found: 356.1401.

Methyl (*E*)-3-(3-methoxyphenyl)-2-(trifluoromethyl)acrylate (*E*-3m) and **Methyl (*Z*)-3-(3-methoxyphenyl)-2-(trifluoromethyl)acrylate (*Z*-3m)**. 3-Iodoanisole (0.2 mmol, 46.8 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 30/1 to 15/1, v/v), affording compound **3m** in 82% yield [mixture of *E*/*Z* isomers (73/27), 42.7 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (s, 1H, *Z*), 7.30 (d, *J* = 0.9 Hz, 1H, *E*), 7.26 – 7.17 (m, 1H, *Z* + 1H, *E*), 6.94 – 6.79 (m, 3H, *Z* + 3H, *E*), 3.81 (s, 3H, *Z*), 3.78 – 3.67 (m, 3H, *Z* + 6H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.4 (s, *Z*), -64.4 (d, *J* = 1.7 Hz, *E*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 164.0 – 163.8 (m), 159.8, 159.4, 148.5 (q, *J* = 3.0 Hz), 140.1 (q, *J* = 5.7 Hz), 133.9, 133.6, 129.8, 129.5, 123.6 (q, *J* = 31.4 Hz), 122.8 (q, *J* = 31.8 Hz), 122.2 (q, *J* = 271.4 Hz), 121.9 (q, *J* = 272.7 Hz), 121.8 (q, *J* = 2.4 Hz), 121.6, 116.4, 116.0, 114.5 (q, *J* = 2.4 Hz), 114.3, 55.4, 52.9, 52.8. IR: 2958, 2845, 1731, 1581, 1436, 1302, 1254, 1227, 1125, 1203, 784, 690 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{12}H_{11}F_3O_3$ (m/z): 260.0660 $[M]^+$, found: 260.0650.

Methyl (*E*)-3-(3-nitrophenyl)-2-(trifluoromethyl)acrylate (*E*-3n) and **Methyl (*Z*)-3-(3-nitrophenyl)-2-(trifluoromethyl)acrylate (*Z*-3n)**. 1-Iodo-3-nitrobenzene (0.2 mmol, 49.8 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.003 mmol, 1.0 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 15/1 to 8/1, v/v), affording compound **3n** in 84% yield [mixture of *E*/*Z* isomers (62/38), 42.0 mg; among which, partly pure compound ***E*-3n** was obtained] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 – 8.20 (m, 2H, *Z* + 2H, *E*), 8.11 (s, 1H, *Z*), 7.69 (t, *J* = 6.6 Hz, 1H, *Z* + 1H, *E*), 7.65 – 7.55 (m, 1H, *Z* + 1H, *E*), 7.50 (s, 1H, *E*), 3.92 (2s, 3H, *Z*), 3.81 (2s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -64.7 (d, *J* = 1.4 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 163.0 (q, *J* = 1.8 Hz), 162.8, 148.3, 148.2, 145.4 (q, *J* = 3.0 Hz), 138.7 (q, *J* = 5.8 Hz), 134.9, 134.6 (q, *J* = 2.5 Hz), 134.3, 134.0, 129.8, 129.6, 126.1 (q, *J* = 31.7 Hz), 125.3 (q, *J* = 32.0 Hz), 124.8, 124.7, 123.9, 123.8 (q, *J* = 2.3 Hz), 121.7 (q, *J* = 272.0 Hz), 121.5 (q, *J* = 273.0 Hz), 53.2, 53.0. IR: 2958, 1731, 1531, 1439, 1352, 1274, 1236, 1163, 1130, 1025, 731, 678 cm^{-1}. HRMS (AP-TOF): Calcd for $C_{11}H_8F_3NO_4$ (m/z): 275.0405 [M]$^-$, found: 275.0411.

[*E*-isomer (minor)] Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 – 8.20 (m, 2H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.57 (m, 1H), 7.50 (s, 1H), 3.81 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.7 (d, *J* = 1.7 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.8, 148.4, 135.0 (q, *J* = 5.8 Hz), 134.9, 134.0, 129.8, 126.1 (q, *J* = 31.7 Hz), 124.9, 123.9, 121.7 (q, *J* = 272.0 Hz), 53.0. IR: 3093, 2960, 1731, 1531, 1439, 1353, 1302, 1274, 1236, 1163, 1130, 1023, 822, 736, 676 cm^{-1}. HRMS (AP-TOF): Calcd for $C_{11}H_8F_3NO_4$ (m/z): 275.0405 [M]$^-$, found: 275.0411.

Methyl (*E*)-3-(*m*-tolyl)-2-(trifluoromethyl)acrylate (*E*-3o) and **Methyl (*Z*)-3-(*m*-tolyl)-2-(trifluoromethyl)acrylate (*Z*-3o)**. 3-Iodotoluene (0.2 mmol, 43.6 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 50/1 to 40/1, v/v), affording compound **3o** in 91% yield [mixture of *E*/*Z* isomers (72/28), 44.3 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (s, 1H, *Z*), 7.30 (s, 1H, *E*), 7.25 – 7.05 (m, 4H, *Z* + 4H, *E*), 3.81 (s, 3H, *Z*), 3.70 (s, 3H, *E*), 2.39 – 2.21 (s, 3H, *Z* + 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -64.3 (d, *J* = 1.4 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 164.2 – 163.9 (m), 148.9 (q, *J* = 2.9 Hz), 140.6 (q, *J* = 5.7 Hz), 138.5, 138.1, 132.6, 132.3, 131.3, 131.1, 130.2 – 129.9 (m), 128.7, 128.3, 126.6 (q, *J* = 2.6 Hz), 126.2, 123.1 (q, *J* = 31.2 Hz), 122.29 (q, *J* = 31.7 Hz), 122.26 (q, *J* = 271.3 Hz), 122.0 (q, *J* = 272.7 Hz), 52.9, 52.7, 21.4. IR: 2958, 1731, 1647, 1438, 1383, 1284, 1224, 1152, 1126, 1032, 784, 694 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{12}H_{11}F_3O_2$ (m/z): 244.0711 [M]$^+$, found: 244.0714.

Methyl (*E*)-3-(3-cyanophenyl)-2-(trifluoromethyl)acrylate (*E*-3p) and **Methyl (*Z*)-3-(3-cyanophenyl)-2-(trifluoromethyl)acrylate (*Z*-3p)**. 3-Iodobenzonitrile (0.2 mmol, 45.8 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.003 mmol, 1.0 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 20/1 to 7/1, v/v), affording compound **3p** in 85% yield [mixture of *E*/*Z* isomers (70/30), 43.6 mg. *E*/*Z* isomers were completely separated by column: compound ***E*-3p** 30.4 mg, colorless oil; impure *Z*-isomer was subsequently washed with petroleum ether (0.3 mL × 3) to obtain pure compound ***Z*-3p** 13.2 mg, white solid].

[*E*-isomer (major)] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.64 – 7.48 (m, 2H), 7.44 (s, 1H), 3.79 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -64.7 (d, *J* = 1.7 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 162.8, 139.0 (q, *J* = 5.8 Hz), 133.8, 133.5, 133.1, 132.4, 129.6, 125.8 (q, *J* = 31.7 Hz), 121.7 (q, *J* = 271.9 Hz), 118.0, 113.2, 53.0. IR: 2958, 2234, 1731, 1654, 1440, 1379, 1296, 1282, 1229, 1129, 1024, 799, 686 cm^{-1}. HRMS (ES-TOF): Calcd for $C_{12}H_8F_3NO_2Na$ (m/z): 278.0405 [M+Na]$^+$, found: 278.0414.

[*Z*-isomer (minor)] Mp 45-46 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.64 (s, 1H), 7.62 – 7.48 (m, 2H), 3.92 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 163.1 (q, *J* = 1.9 Hz), 145.5 (q, *J* = 3.0 Hz), 134.0, 133.3, 133.0 (q, *J* = 2.3 Hz), 132.2 (q, *J* = 2.3 Hz), 129.4, 125.1 (q, *J* = 32.0 Hz), 121.5 (q, *J* = 272.9 Hz), 118.0, 113.1, 53.3. IR: 2958, 2237, 1731, 1648, 1439, 1391, 1282, 1125, 1131, 1042, 804, 688 cm^{-1}. HRMS (ES-TOF): Calcd for $C_{12}H_8F_3NO_2Na$ (m/z): 278.0405 [M+Na]$^+$, found: 278.0402.

Methyl (*E*)-3-(2-methoxyphenyl)-2-(trifluoromethyl)acrylate (*E*-3q) and **Methyl (*Z*)-3-(2-methoxyphenyl)-2-(trifluoromethyl)acrylate (*Z*-3q)**. 2-Iodoanisole (0.2 mmol, 46.8 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 40/1 to 20/1, v/v), affording compound **3q** in 54% yield [mixture of *E*/*Z* isomers (73/27), 28.2 mg; *E*/*Z* isomers were partly separated by column] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H, *Z*), 7.57 (s, 1H, *E*), 7.37 – 7.26 (m, 1H, *Z* + 1H, *E*), 7.24 – 7.15 (m, 1H, *Z* + 1H, *E*), 6.93 – 6.79 (m, 2H, *Z* + 2H, *E*), 3.81 (s, 3H, *Z*), 3.80 – 3.73 (m, 3H, *Z* + 3H, *E*), 3.65 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -59.3 (d, *J* = 0.6 Hz, *Z*), -64.2 (d, *J* = 1.7 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 164.1 – 164.0 (m), 163.9 (q, *J* = 2.1 Hz), 157.61, 157.57, 145.2 (q, *J* = 3.0 Hz), 137.5 (q, *J* = 5.9 Hz), 132.1, 132.0, 130.5 (q, *J* = 3.6 Hz), 130.0, 123.0 (q, *J* = 30.9 Hz), 122.4 (q, *J* = 271.2 Hz), 122.2 (q, *J* = 272.4 Hz), 122.1 (q, *J* = 31.5 Hz), 121.9, 121.7, 110.9, 110.5, 55.64, 55.58, 52.8, 52.4. IR: 2961, 2842, 1729, 1646, 1600, 1490, 1466, 1437, 1276, 1252, 1224, 1158, 1123, 1114, 1021, 752 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{12}H_{11}F_3O_3$ (m/z): 260.0660 [M]$^+$, found: 260.0661.

[*E*-isomer (major)] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.43 – 7.35 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 6.98 – 6.88 (m, 2H), 3.85 (s, 3H), 3.74 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.2 (d, *J* = 1.7 Hz).

[*Z*-isomer (minor)] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.44 – 7.36 (m, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -59.3 (d, *J* = 1.1 Hz).

Methyl (*E*)-3-(*o*-tolyl)-2-(trifluoromethyl)acrylate (*E*-3r) and **Methyl (*Z*)-3-(*o*-tolyl)-2-(trifluoromethyl)acrylate (*Z*-3r)**. 2-Iodotoluene (0.2 mmol, 43.6 mg), AgOTf (0.3 mmol,

77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 50/1 to 30/1, v/v), affording compound **3r** in 79% yield [mixture of *E*/*Z* isomers (65/35), 38.6 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (s, 1H, *Z*), 7.56 (s, 1H, *E*), 7.26 – 7.05 (m, 4H, *Z* + 4H, *E*), 3.82 (s, 3H, *Z*), 3.59 (s, 3H, *E*), 2.24 (s, 3H, *E*), 2.22 (s, 3H, *Z*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.9 (s, *Z*), -64.5 (d, *J* = 1.4 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 163.6 (q, *J* = 1.7 Hz), 163.6 – 163.4 (m), 148.5 (q, *J* = 3.0 Hz), 141.3 (q, *J* = 5.7 Hz), 136.7, 136.0, 132.6, 132.3, 130.3, 130.01, 129.95, 129.8, 128.3 (q, *J* = 3.1 Hz), 128.0, 125.9, 125.7, 124.6 (q, *J* = 30.9 Hz), 123.6 (q, *J* = 31.2 Hz), 122.1 (q, *J* = 271.4 Hz), 122.0 (q, *J* = 272.9 Hz), 52.9, 52.5, 20.0, 19.8. IR: 2961, 1732, 1647, 1438, 1379, 1294, 1276, 1238, 1216, 1160, 1129, 1032, 1021, 751 cm^{-1}. HRMS (ES-TOF): Calcd for $C_{12}H_{11}F_3O_2Na$ (m/z): 267.0609 $[M+Na]^+$, found: 267.0613.

Methyl (*E*)-3-(2-nitrophenyl)-2-(trifluoromethyl)acrylate (*E*-3s) and **Methyl (*Z*)-3-(2-nitrophenyl)-2-(trifluoromethyl)acrylate (*Z*-3s)**. 1-Iodo-2-nitrobenzene (0.2 mmol, 49.8 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 15/1 to 8/1, v/v), affording compound **3s** in 86% yield [mixture of *E*/*Z* isomers (64/36), 47.3 mg; among which, partly pure compound ***Z*-3s** was obtained] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (s, 1H, *Z*), 8.32 – 8.22 (m, 1H, *Z* + 1H, *E*), 8.04 (s, 1H, *E*), 7.75 – 7.55 (m, 2H, *Z* + 2H, *E*), 7.33 (t, *J* = 7.8 Hz, 1H, *Z* + 1H, *E*), 3.92 (s, 3H, *Z*), 3.61 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.6 (s, *Z*), -64.8 (d, *J* = 1.7 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 162.7 (q, *J* = 1.5 Hz), 162.1, 146.5, 146.2 (q, *J* = 3.2 Hz), 145.9, 142.9 (q, *J* = 6.3 Hz), 134.1, 133.9, 130.4 130.3, 130.2, 130.1 (q, *J* = 2.7 Hz), 129.9 – 129.8 (m), 124.98, 124.95, 124.0 (q, *J* = 31.4 Hz), 123.0 (q, *J* = 31.0 Hz), 121.73 (q, *J* = 271.5 Hz), 121.70 (q, *J* = 272.9 Hz), 53.1, 52.5. IR: 2961, 1731, 1524, 1439, 1343, 1277, 1236, 1131, 1045, 1024, 865, 789, 793 cm^{-1}. HRMS (CI-TOF): Calcd for $C_{11}H_9F_3NO_4$ (m/z): 276.0484 $[M+H]^+$, found: 276.0480.

[*Z*-isomer (minor)] Pale yellow solid. Mp 77-78 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.28 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.71 (td, *J* = 7.5, 1.5 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 3.93 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -58.6 (s). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.7 (q, *J* = 1.5 Hz), 146.2 (q, *J* = 3.2 Hz), 146.0, 134.0, 130.4, 130.1 (q, *J* = 2.7 Hz), 130.0, 125.0, 123.1 (q, *J* = 31.0 Hz), 121.7 (q, *J* = 272.9 Hz), 53.1. IR: 2974, 2921, 2855, 1731, 1611, 1525, 1440, 1386, 1338, 1284, 1265, 1154, 1126, 1052, 728 cm^{-1}. HRMS (CI-TOF): Calcd for $C_{11}H_9F_3NO_4$ (m/z): 276.0484 $[M+H]^+$, found: 276.0481.

Methyl (*E*)-2-(3,3,3-trifluoro-2-(methoxycarbonyl)prop-1-en-1-yl)benzoate (*E*-3t) and **Methyl (Z)-2-(3,3,3-trifluoro-2-(methoxycarbonyl)prop-1-en-1-yl)benzoate (*Z*-3t)**. Methyl 2-iodobenzoate (0.2 mmol, 52.4 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 20/1 to 10/1, v/v), affording compound **3t** in 80% yield [mixture of *E*/*Z* isomers (78/22), 46.0 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (s, 1H, *Z*), δ 8.07 (s, 1H, *E*), δ 8.02 (d, *J* = 7.8 Hz, 1H, *Z* + 1H, *E*), 7.53 – 7.35 (m, 2H, *Z* + 2H, *E*), 7.16 (d, *J* = 7.5 Hz, 1H, *Z* + 1H, *E*), 3.83 (s, 6H, *Z* + 3H, *E*), 3.51 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.2 (s, *Z*), -64.5 (d, *J* = 1.4 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 166.5, 166.4, 163.4 (q, *J* = 1.7 Hz), 163.0, 150.2 (q, *J* = 3.2 Hz), 145.5 (q, *J* = 6.0 Hz), 135.9, 135.7, 132.5, 132.4, 130.8, 130.6, 129.34, 129.29, 129.1 – 128.9 (m), 128.2, 127.7, 122.7 (q, *J* = 31.0 Hz), 122.2 (q, *J* = 271.3 Hz), 122.1 (q, *J* = 272.8 Hz), 121.4 (q, *J* = 30.6 Hz), 52.9, 52.5, 52.4, 52.3. IR: 2961, 1717, 1649, 1437, 1376, 1264, 1127, 1082, 1023, 755, 700 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{13}H_{11}F_3O_4$ (m/z): 288.0609 $[M]^+$, found: 288.0614.

Methyl (*E*)-3-(3,5-dichlorophenyl)-2-(trifluoromethyl)acrylate (*E*-3u) and **Methyl (*Z*)-3-(3,5-dichlorophenyl)-2-(trifluoromethyl)acrylate (*Z*-3u)**. 3,5-Dichloroiodobenzene (0.2 mmol, 54.6 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 60/1 to 50/1, v/v), affording compound **3u** in 90% yield [mixture of *E*/*Z* isomers (74/26), 54.1 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (s, 1H, *Z*), 7.35 – 7.29 (m, 1H, *Z* + 1H, *E*), 7.25 (s, 1H, *E*), 7.21 – 7.12 (m, 2H, *Z* + 2H, *E*), 3.83 (s, 3H, *Z*), 3.73 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.6 (s, *Z*), -64.7 (d, *J* = 1.7 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 163.1 (q, *J* = 1.7 Hz), 162.9 – 162.8 (m), 145.2 (q, *J* = 3.0 Hz), 138.1 (q, *J* = 5.8 Hz), 135.5, 135.4, 135.2, 130.1, 129.9, 127.3, 127.1 (q, *J* = 2.4 Hz), 126.0 (q, *J* = 31.7 Hz), 125.1 (q, *J* = 32.1 Hz), 121.7 (q, *J* = 271.9 Hz), 121.4 (q, *J* = 273.0 Hz), 53.2, 53.0. IR: 3087, 2954, 1734, 1653, 1587, 1562, 1439, 1377, 1285, 1216, 1167, 1134, 1025, 861, 802, 678 cm^{-1}. HRMS (ES-TOF): Calcd for $C_{11}H_7{}^{35}Cl_2F_3O_2Na$ (m/z): 320.9673 $[M+Na]^+$, found: 320.9666.

Methyl (*E*)-3-(naphthalen-2-yl)-2-(trifluoromethyl)acrylate (*E*-3v) and **methyl (*Z*)-3-(naphthalen-2-yl)-2-(trifluoromethyl)acrylate (*Z*-3v)**. 2-Iodonaphthalene (0.2 mmol, 50.8 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 60/1 to 50/1, v/v), affording compound **3v** in 80% yield [mixture of *E*/*Z* isomers (74/26), 44.7 mg; among which, partly pure compound ***E*-3v** was obtained] as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (s, 1H, *Z*), 7.93 – 7.79 (m, 4H, *Z* + 4H, *E*), 7.62 – 7.41 (m, 3H, *Z* + 4H, *E*), 3.94 (s, 3H, *Z*), 3.81 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.3 (s, *Z*), -64.2 (d, *J* = 1.4 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 164.1 – 164.0 (m), 148.7 (q, *J* = 2.9 Hz), 140.7 (q, *J* = 5.7 Hz), 134.1, 133.9, 133.0, 132.7, 130.4, 130.3 (q, *J* = 2.1 Hz), 130.0, 129.8, 128.8, 128.7, 128.4, 128.1, 127.85, 127.83, 127.8, 126.94, 127.89, 126.1 (q, *J* = 2.7 Hz), 125.4, 123.2 (q, *J* = 31.2 Hz), 122.39 (q, *J* = 31.8 Hz), 122.35 (q, *J* = 271.5 Hz), 122.1 (q, *J* = 272.6 Hz), 52.9, 52.7. IR: 2956, 2924, 1728, 1643, 1438, 1352, 1282, 1269, 1233, 1122, 1019, 815, 744, 475 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{15}H_{11}F_3O_2$ (m/z): 280.0711 $[M]^+$, found: 280.0707.

[*E*-isomer (major)] Mp <46 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 – 7.81 (m, 4H), 7.61 – 7.50 (m, 3H), 7.44 (dd, *J* = 8.7, 1.5 Hz, 1H), 3.81 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -64.2 (d, *J* = 1.4 Hz).

Methyl (*E*)-3-(3,4-dimethoxyphenyl)-2-(trifluoromethyl)acrylate (*E*-3w) and **Methyl (*Z*)-3-(3,4-dimethoxyphenyl)-2-(trifluoromethyl)acrylate (*Z*-3w)**. 4-Iodo-1,2-dimethoxybenzene (1.0 mmol, 264.1 mg), AgOTf (1.5 mmol, 385.4 mg), and $Pd(TFA)_2$ (0.015 mmol, 4.8 mg), methyl 2-(trifluoromethyl)acrylate (1.5 mmol, 231.1 mg) in 1,4-dioxane (5.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 10/1 to 5/1, v/v), affording compound **3w** in 83% yield [mixture of *E*/*Z* isomers (*E*/*Z* = 75/25), 242.2 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (s, 1H, *Z*), 7.30 (s, 1H, *E*), 7.10 – 6.96 (m, 2H, *Z* + 2H, *E*), 6.93 – 6.80 (m, 1H, *Z* + 1H, *E*), 3.93 – 3.89 (m, 3H, *Z* + 3H, *E*), 3.89 – 3.83 (m, 6H, *Z* + 3H, *E*), 3.81 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.3 (s, *Z*), -63.8 (d, *J* = 1.7 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 164.5 – 164.2 (m), 151.32, 151.29, 148.9, 148.6, 148.4 (q, *J* = 2.9 Hz), 140.4 (q, *J* = 5.7 Hz), 124.8, 124.8 – 124.6 (m), 124.1, 122.5 (q, *J* = 271.2 Hz), 122.3 (q, *J* = 272.2 Hz), 120.6 (q, *J* = 31.1 Hz), 119.8 (q, *J* = 32.0 Hz), 112.9 (q, *J* = 3.0 Hz), 112.1, 110.9, 110.7, 56.0, 56.9, 52.75, 52.66. IR: 2958, 2842, 1726, 1599, 1515, 1440, 1258, 1225, 1140, 1117, 1020, 808, 574 cm^{-1}. HRMS (AP-TOF): Calcd for $C_{13}H_{14}F_3O_4$ (m/z): 291.0844 $[M+H]^+$, found: 291.0851.

Methyl (*E*)-2-amino-5-(3,3,3-trifluoro-2-(methoxycarbonyl)prop-1-en-1-yl)benzoate (*E*-3x) and **Methyl (*Z*)-2-amino-5-(3,3,3-trifluoro-2-(methoxycarbonyl)prop-1-en-1-yl)benzoate (*Z*-3x)**. Methyl 2-amino-5-iodobenzoate (0.2 mmol, 55.4 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 10/1 to 5/1, v/v), affording compound **3x** in 81% yield [mixture of *E*/*Z* isomers (63/37), 49.3 mg] as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 – 7.95 (m, 1H, *Z* + 1H, *E*), 7.89 (s, 1H, *Z*), 7.41 (t, *J* = 8.0 Hz, 1H, *Z* + 1H, *E*), 7.23 (s, 1H, *E*), 6.76 – 6.55 (m, 1H, *Z* + 1H, *E*), 6.18 (br, 2H, *Z* + 2H, *E*), 3.92 – 3.78 (m, 6H, *Z* + 6H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.4 (s, *Z*), -63.4 (d, *J* = 1.7 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 168.0, 167.9, 164.6 (q, *J* = 2.3 Hz), 164.5, 152.4, 152.3, 148.1 (q, *J* = 2.7 Hz), 140.7 (q, *J* = 5.8 Hz), 136.3 (q, *J* = 2.2 Hz), 136.0 (q, *J* = 3.8 Hz), 135.3, 135.2, 122.8 (q, *J* = 270.8 Hz), 122.6 (q, *J* = 271.8 Hz), 119.8, 119.7, 118.3 (q, *J* = 30.9 Hz), 117.5 (q, *J* = 32.3 Hz), 116.7, 116.6, 110.2, 110.1, 52.6, 52.5, 51.92, 51.88. IR: 3477, 3364, 2961, 1722, 1694, 1610, 1499, 1440, 1278, 1256, 1202, 1152, 1116, 1024, 825, 546, 492 cm^{-1}. HRMS (ES-TOF): Calcd for $C_{13}H_{12}F_3NO_4Na$ (m/z): 326.0616 $[M+Na]^+$, found: 326.0622.

Methyl (*E*)-2-(trifluoromethyl)-3-(3,4,5-trimethoxyphenyl)acrylate (*E*-3y) and **Methyl (*Z*)-2-(trifluoromethyl)-3-(3,4,5-trimethoxyphenyl)acrylate (*Z*-3y)**. 5-Iodo-1,2,3-trimethoxybenzene (0.2 mmol, 58.8 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.003 mmol, 1 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 10/1 to 5/1, v/v), affording compound **3y** in 89% yield [mixture of *E*/*Z* isomers (75/25), 57.0 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (s, 1H, *Z*), 7.28 (s, 1H, *E*), 6.80 – 6.54 (m, 2H, *Z* + 2H, *E*), 3.99 – 3.67 (m, 12H, *Z* + 12H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.2 (s, *Z*), -64.1 (d, *J* = 1.4 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 164.3 – 164.1 (m), 164.0 (q, *J* = 2.2 Hz), 153.2, 153.0, 148.4 (q, *J* = 2.9 Hz), 140.2, 140.1, 139.9 (q, *J* = 5.7 Hz), 127.5, 127.4, 122.4 (q, *J* = 31.3 Hz), 122.2 (q, *J* = 271.4 Hz), 122.0 (q, *J* = 271.5 Hz), 121.5 (q, *J* = 32.1 Hz), 107.3 (q, *J* = 2.6 Hz), 106.8, 61.0, 60.98, 56.2, 56.18, 52.8, 52.77. IR: 2954, 2842, 1729, 1582, 1507, 1456, 1422, 1271, 1227, 1118, 1026, 1002 cm^{-1}. HRMS (ES+): Calcd for $C_{14}H_{15}F_3O_5Na$ (m/z): 343.0769 $[M+Na]^+$, found: 343.0766.

Methyl (*E*)-3-(3,4-dihydroxyphenyl)-2-(trifluoromethyl)acrylate (*E*-3z) and **Methyl (*Z*)-3-(3,4-dihydroxyphenyl)-2-(trifluoromethyl)acrylate (*Z*-3z)**. 1.0 mg $Pd(TFA)_2$ was dissolved in 3.0 mL 1,4-dioxane by ultrasound. 4-Iodobenzene-1,2-diol (0.2 mmol, 47.2 mg), AgOTf (0.3 mmol, 77.1 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg), and 1.0 mL the above prepared $Pd(TFA)_2$/1,4-dioxane solution [0.5 mol% $Pd(TFA)_2$] were reacted for 30 min. After evaporation of solvents, the crude was purified by silica gel column chromatography ($CHCl_3$/MeOH, from 100/1 to 60/1, v/v), affording compound **3z** in 45% yield [mixture of *E*/*Z* isomers (*E*/*Z* = 71/29), 23.7 mg] as a pale yellow solid. ^{1}H NMR (300 MHz, CD_3OD): δ 7.94 (s, 1H, *Z*), 7.28 ((d, *J* = 1.2 Hz, 1H, *E*), 7.00 (s, 1H, *Z*), 6.98 – 6.71 (m, 2H, *Z* + 3H, *E*), 3.84 (s, 3H, *Z*), 3.82 (s, 3H, *E*). ^{19}F NMR (282 MHz, CD_3OD): δ -59.2 (s, *Z*), -64.7 (d, *J* = 1.4 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ 166.2 – 166.0 (m), 165.7 (q, *J* = 2.3 Hz), 150.2 (q, *J* = 2.9 Hz), 150.0, 149.8, 146.5, 146.3, 141.2 (q, *J* = 5.8 Hz), 125.4 (q, *J* = 2.4 Hz), 125.0, 124.5, 124.1 (q, *J* = 269.9 Hz), 123.8 (q, *J* = 270.5 Hz), 120.2 (q, *J* = 31.1 Hz), 119.1 (q, *J* = 32.1 Hz), 118.3 (q, *J* = 3.2 Hz), 117.0, 116.3, 116.1, 53.1, 53.0. IR: 3508, 3338, 1694, 1602, 1524, 1443, 1255, 1112, 1023, 933 cm^{-1}. HRMS (ES-TOF): Calcd for $C_{11}H_8F_3O_4$ (m/z): 261.0375 $[M-H]^-$, found: 261.0365.

Synthesis of Iodoarenes 1w and 1z

Iodoarenes **1y** and **1z** were prepared according to a reported method.[25a] Analytical data of **1w** and **1z** are in agreement with those reported in the literature.

4-Iodo-1,2-dimethoxybenzene (1y).[25a] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.11 (d, *J* = 1.5 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H).

4-Iodobenzene-1,2-diol (1z).[25b] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (d, *J* = 1.8 Hz, 1H), 7.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 5.13 (s, 1H), 5.10 (s, 1H).

Characterization data for 3-CF_3-coumarins 4:

3-(Trifluoromethyl)-2*H*-chromen-2-one (4a). 2-Iodophenol (0.2 mmol, 44.0 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 20/1 to 10/1, v/v), affording compound **4** in 72% yield (30.8 mg) as a pale yellow solid. Mp 121-122 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.75 – 7.57 (m,

2H), 7.49 – 7.31 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -66.7 (s). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 156.1 – 155.9 (m), 154.7, 143.5 (q, *J* = 4.8 Hz), 134.6, 129.6, 125.4, 121.5 (q, *J* = 270.3 Hz), 118.0 (q, *J* = 33.1 Hz), 117.1, 116.9. IR: 3074, 2921, 1727, 1636, 1610, 1573, 1460, 1383, 1242, 1175, 1119, 975, 759, 733, 588, 464 cm^{-1}. HRMS (ES-TOF): Calcd for $C_{10}H_5F_3O_2Na$ (m/z): 237.0139 $[M+Na]^+$, found: 237.0132.

8-Methoxy-2-oxo-3-(trifluoromethyl)-2*H*-chromene-6-carbaldehyde (4b) 5-Iodovanillin (0.2 mmol, 55.6 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 5/1 to 3/1, v/v), and was subsequently washed with MeOH (0.5 mL × 2), affording compound **4b** in 35% yield (18.8 mg) as a white solid. Mp 162-163 °C. ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ 10.01 (s, 1H), 8.87 (s, 1H), 8.05 (s, 1H), 7.83 (s, 1H), 4.02 (s, 3H). ^{19}F NMR [282 MHz, $(CD_3)_2SO$]: δ -64.9 (s). ^{13}C{^{1}H} NMR [75 MHz, $(CD_3)_2SO$]: δ 191.3, 155.0 – 154.7 (m), 147.4, 147.1, 145.1 (q, *J* = 4.8 Hz), 132.8, 124.3, 121.5 (q, *J* = 269.9 Hz), 117.8, 116.8 (q, *J* = 32.4 Hz), 114.4, 56.3. IR: 3067, 2868, 1738, 1698, 1636, 1593, 1464, 1384, 1278, 1134, 1112, 952, 684 cm^{-1}. HRMS (AP-TOF): Calcd for $C_{12}H_7F_3O_4$ (m/z): 272.0296 $[M]^-$, found: 272.0301.

6-Chloro-3-(trifluoromethyl)-2*H*-chromen-2-one (4c) 4-Chloro-2-iodophenol (0.2 mmol, 50.9 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 20/1 to 10/1, v/v), affording compound **4c** in 74% yield (36.8 mg) as a white solid. Mp 167-168 °C. ^{1}H NMR (300 MHz, CD_3OD): δ 8.49 (s, 1H), 7.86 (d, *J* = 2.4 Hz, 1H), 7.72 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.42 (d, *J* = 9.0 Hz, 1H). ^{19}F NMR (282 MHz, CD_3OD): δ -67.7 (s). ^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ 157.0 – 156.9 (m), 154.5, 144.7 (q, *J* = 5.0 Hz), 135.3, 131.4, 130.3, 122.9 (q, *J* = 269.4 Hz), 119.7, 119.5, 119.2 (q, *J* = 33.0 Hz). IR: 3064, 1721, 1635, 1602, 1570, 1378, 1301, 1243, 1213, 1175, 1144, 1086, 980, 824, 679 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{10}H_4{}^{35}ClF_3O_2$ (m/z): 247.9852 $[M]^+$, found: 247.9853.

Methyl 2-oxo-3-(trifluoromethyl)-2*H*-chromene-6-carboxylate (4d) Methyl 4-hydroxy-3-iodobenzoate (0.2 mmol, 55.6 mg), AgOTf (0.3 mmol, 77.1 mg), and $Pd(TFA)_2$ (0.02 mmol, 6.5 mg), methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted for 2 hours according to the general procedure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, from 10/1 to 5/1, v/v), affording compound **4d** in 82% yield (44.7 mg) as a white solid. Mp 177-178 °C. ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ 8.89 (s, 1H), 8.55 (d, *J* = 1.8 Hz, 1H), 8.24 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 3.90 (s, 3H). ^{19}F NMR [282 MHz, $(CD_3)_2SO$]: δ -64.9 (s). ^{13}C{^{1}H} NMR [75 MHz, $(CD_3)_2SO$]: δ 164.8, 157.0, 155.4 – 155.2 (m), 144.9 (q, *J* = 4.9 Hz), 134.7, 132.0, 126.3, 121.6 (q, *J* = 270.0 Hz), 117.2, 117.1, 116.6 (q, *J* = 32.3 Hz), 52.6. IR: 3073, 2965, 2924, 2852, 1750, 1710, 1639, 1615, 1443, 1378, 1306, 1243, 1216, 1172, 1140, 965, 768 cm^{-1}. HRMS (EI-TOF): Calcd for $C_{12}H_7F_3O_4$ (m/z): 272.0296 $[M]^+$, found: 272.0294.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Optimization tables, NMR spectra of new compounds, X-ray crystallography data and CIF files (PDF).

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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