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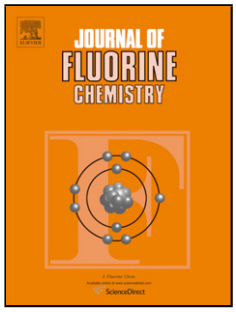

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Ligand-Free Palladium-Catalyzed Mizoroki-Heck Reaction to Synthesize Valuable α-Trifluoromethylacrylates

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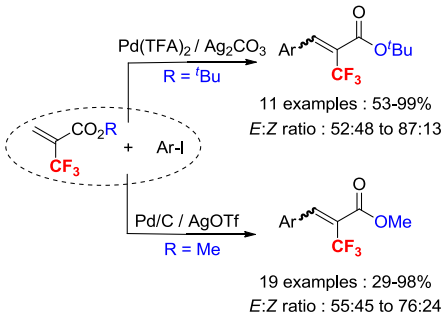
Table of contents:



Highlights

- α-Trifluoromethylacrylates synthesis
- Efficient ligand-free palladium catalyzed Mizoroki-Heck reaction
- Improvement to diastereomeric E:Z ratio
- Use of two different catalytic systems

Abstract: α-Trifluoromethylacrylates were synthesized using efficient ligand-free palladium catalyzed Mizoroki-Heck reaction. With the alkyl trifluoromethylacrylates used as substrates, different catalytic systems were explored including Pd/C as a catalyst. Good to excellent yields were obtained with good chemical tolerance

Keywords: fluoroalkenes; fluoroacrylates; olefination; Mizoroki-Heck; palladium

1. Introduction

Fluorinated organic compounds have become unavoidable in many fields such as medicine, pharmacy, agrochemistry and materials [1]. Among all the fluorinated building blocks, trifluoromethylacrylates proved to be very useful, as well as starting materials for the synthesis of relevant polymers [2], as intermediates towards fine chemicals [3]. To obtain these α-trifluoromethylacrylate scaffolds, some strategies have been described (Scheme 1) including double bond formation [4], trifluoromethylation of acrylates [5], radical addition to alkynes [6] and decarboxylation-olefination reaction [7].

Concerning the double bond formation reaction (Scheme 1, part a)): in 1991, Allmendinger and Lang reported the first general method for the preparation of α-trifluoromethylacrylates by using methyl 2,2-dichloro-3,3,3-trifluoropropanoate to react with aldehydes in the presence of zinc dust and copper(I) salt, affording the corresponding acrylates in low to good yields (20-88%) and low selectivities (*E*/*Z* from 47/53 to 34/66) [4a]. Then, in 2000, Schlosser and Volle utilized Wittig reaction to synthesize only one specific α-trifluoromethylacrylate with methyl 3,3,3-trifluoropyruvate as fluorinated reagent, and moderate yield (51%) with low selectivity (*E*/*Z* : 60/40) was obtained [4b]. Two years later, Paleta *et al.* used the same method to get four other α-trifluoromethylacrylates in good yields (69-78%) with selectivities depending on different substrates (*E*/*Z* from 43/57 to 92/8) [4c]. Inspired by the reaction involving ylide intermediate, Zhu and coworkers developed a copper (II)-catalyzed method for the construction of α-trifluoromethylacrylates with relatively unstable fluorinated diazo compound, providing the desired products in low to good yields (36-85%) and moderate selectivities (*E*/*Z* from 24/76 to 84/16) [4d].

The trifluoromethylation reaction of acrylates consists of two parts (Scheme 1, part b)): 1) coupling reaction between *in situ* generated $CuCF_3$ species and vinyl halides, 2) radical trifluoromethylation of acrylates. In early 2000s, Qing and coworkers reported the preparation of α-trifluoromethylacrylates through the coupling reaction between vinyl halides and $CuCF_3$ which was generated *in situ* from CuI and $FSO_2CF_2CO_2Me$. With vinyl bromides (*Z* major) as substrates, fair to good yields (42-93%) and selectivities (*E*/*Z* from 39/61 to 11/89) were obtained, but the yields (81-96%) and selectivities (*E*/*Z* from 18/82 to 5/95) were improved when vinyl iodides (*Z* major) were used as substrates [5a-b]. In this reaction, the *E*/*Z* mixtures of vinyl halides determined the *E*/*Z* selectivities of the products to some extent; therefore, the opposite selectivities (*E*/*Z* from 92/8 to 100/0) were observed when *E* major vinyl bromides were involved instead of the *Z* major ones [5c]. In addition to $FSO_2CF_2CO_2Me$, some other fluorinated reagents, such as $(CF_3)_2Hg$ [5d], $TMSCF_3$ [5e], HCF_3 [5f], were also used as the precursors of $CuCF_3$ species, but just few examples for the access to α-trifluoromethylacrylates were shown as a part of substrate scope [5d-f]. Recently, the methods for radical trifluoromethylation of alkenes through a radical addition-elimination process were developed. There are several sources of CF_3 radical such as Langlois reagent [5g], trifluoromethyl iodide [5h], and Togni's reagent [5i], which could release CF_3 radical in the presence of oxidant or reductant. But in these cases, α-trifluoromethylacrylates were not major target molecules.
More recently (Scheme 1, part c)), a method for stereoselective photoredox-catalyzed transformation of alkynes into α-trifluoromethylalkenes was developed by Akita [6a] and Han [6b], respectively. In both reaction systems, only one example was dedicated to tetrasubstituted α-trifluoromethylacrylate and good selectivity was obtained, albeit in moderate yield (57%, and 44%, respectively).
In 2018, our group has developed a method for palladium-catalyzed decarboxylative olefination reaction with methyl 2-(trifluoromethyl)acrylate (Scheme 1, part d)). Trisubstituted α-trifluoromethylacrylates were synthesized in low to excellent yields (24-99%) with various selectivities (*E*/*Z* from 60/40 to 12/88); however, the substrate scope was only limited to *ortho*-substituted benzoic acids and low yields were obtained when electron-deficient groups were involved in the substrates [7].
For the above-mentioned methods, most of them showed limited substrate scope. Some reactions proceeded with good stereoselectivity but not good yields. Some methods used expensive fluorinated reagents, unstable starting materials, or required multistep synthesis of substrates and/or reagents.
We recently proposed a general access to these products using a ligand-free Mizoroki-Heck reaction [8]. The reaction proved to be compatible with numerous active chemical moiety (cyano, amine, acid, alcohol, boronate…) and furnished good to excellent yields of desired α-trifluoromethylacrylate products. The major drawback of this reaction is the diastereomeric *E*:*Z* ratio ranging around 70:30 in most of the cases. Herein, we proposed a structural modification to increase the *E*:*Z* ratio of the reaction as well as a new relevant catalytic system to perform efficiently the reaction.

2. Results and Discussion

2.1 Synthesis of t-butyl α-trifluoromethylacrylates.

To begin the study about the stereoselectivity, we chose the *p*-methoxy-iodobenzene as model substrate. As coupling partner, we decided to increase the bulkiness of the ester group using *t*-butyl trifluoromethylacrylate **2a** instead of the methyl one **2b**. Unfortunately, using our previous optimal reaction conditions with **2b** [8], no product **3a** was obtained with **2a** (Table 1, entry 1).

Changing the silver triflate for the more basic silver acetate increased the yield to 76% (Table 1, entry 2). The use of silver carbonate allowed the formation of the desired product **3a** in good ^{19}F NMR and isolated yields (Table 1, entries 3-5), excepted for the case of reduced amount of catalyst loading (Table 1, entry 4). Using the potassium carbonate, a common base used in cross-coupling reaction, led to a poor 20% yield of **3a** (Table 1, entry 6). This last result pointed out the crucial role of silver cation serving as halide abstracter as already reported for this kind of reaction [8,9]. The use of other catalyst proved to be less efficient than the electrophilic $Pd(TFA)_2$ (Table 1, entries 7 and 8). We then used these reaction conditions to synthesize various *t*-butyl 2-(trifluoromethyl)acrylates **3** (Scheme 2).

Para-substituted *t*-butyl acrylates **3a** and **3b** were obtained in high yield and good diastereoselectivity (*E:Z* ratio of 85:15). The selectivity was lower for product **3c** bearing a *para*-cyano group whereas only fair yield with almost no selectivity was obtained for product **3d** bearing a *para*-nitro group. *Meta*- and *poly*-substituted products were obtained with high yields and selectivities. Probably due to the steric hindrance, the *E/Z* selectivity for the *ortho*-substituted products was decreased. These latter were synthesized in fair to quantitative yields (Scheme 2).

In a mechanistic point of view, this reaction is very interesting. Indeed, based on various experimental results, we recently proposed a Pd(II)/Pd(IV) catalytic cycle for the production of methyl trifluoromethylacrylates *via* the formation of a cationic palladium species [8], thanks to silver triflate acting as a halide abstracter [10], remaining a highly acidic media (pH ≈ 1) at the end of the reaction. In the case of *t*-butyl acrylate **2a** as reagent, the presence of silver was essential for the reaction to proceed but also the presence of base. In this case, we speculated that a "neutral" catalytic cycle proceeded with a classical role of silver carbonate, capturing the hydrogen iodide released at the end of the catalytic cycle by reductive elimination. The control pH at the end of the reaction was around 6 which is consistent with a neutral process. Nevertheless, for the moment, we have no explanation why the modification of the ester moiety from methyl to *t*-butyl group had such a huge influence on the mechanism of the reaction. Some calculation will be undertaken soon to better understand these mechanistic issues.

In the course of our optimization, we were wondering if the use of simple Pd/C catalyst, cheaper than common Pd(II) catalysts used in cross-coupling reaction, could be used in this reaction.

2.2 Use of Pd/C to synthesize the α-trifluoromethylacrylates.

The *t*-butyl trifluoromethylacrylate **2a** proved to be unreactive in the presence of Pd/C (Table 2, entries 1 and 2) or $Pd(OH)_2/C$ (Table 2, entry 3). Delighfully, the less hindered methyl trifluoromethylacrylate **2b** reacted using Pd/C catalyst furnishing a good isolated yield of 80% of **4a** using silver triflate as additive (Table 2, entry 4). The reaction was still efficient with a lower amount of catalyst albeit the yield was a little bit lower (Table 2, entries 5 and 6). The yield decreased using $Pd(OH)_2/C$ as catalyst (Table 2, entry 7) or carrying out the reaction for 2 h instead of 4 h (Table 2, entry 8). Using DMF as solvent dropped the yield of reaction (Table 2, entry 9). The use of silver carbonate was inefficient (Table 2, entry 10) as well as the use of sodium acetate in DMA, classical experimental conditions with Pd/C (Table 2, entry 11) [11]. The replacement of silver triflate by copper triflate failed (Table 2, entry 12). The reaction carried out without additive did not proceed (Table 2, entry 13).

With these new catalytic conditions in hand, we wondered if we could apply them to various substrates (Scheme 3). The reaction was efficient with various substrates and tolerated numerous chemical functional groups. We began the scope of the reaction with substituents in *para*-position. Electron-donating groups on aryl moiety gave fair to high yields of desired acrylates. Hydroxyl group could be used without protection to furnish compound **4b** in 67% isolated yield. 24 h of reaction was required to get **4c** bearing a methyl group in high 88% yield. Bromine atom proved to be unreactive in the reaction conditions furnishing the *para*-brominated product **4e** in 78% yield. It should be noted that with deactivated aromatic ring, *i.e.* bearing an electron-withdrawing group or a substituent with negative inductive effect, such as bromine, the reaction was necessary to be performed at 110°C to be efficient. This higher temperature allowed us to synthesize interesting products bearing a post-functionalizable function such as products **4f** (cyano), **4g** (ester), **4h** (nitro) and **4i** (ketone) in good yields from 62 to 88%. Increasing the reaction time with electron-withdrawing substituent was non effective to increase the yield of the reaction.
The reaction could be then applied to *meta*-substituted substrates, albeit the yield was slightly lower (42% to 71%). *Ortho*-substituted products bearing a methyl (**4m**), a cyano (**4n**) or a nitro moiety (**4o**) were obtained in excellent yields (83% to 98%). Poly-substituted products **4p** and **4q** were produced in good yields, 79% and 68%, respectively. An interesting functionnalized furan could also be obtained in these conditions but only in low 29% yield. Finally, starting from the *ortho*-iodophenol, the relevant 3-trifluoromethylcoumarin **5** could be obtained in fair 50% yield along with a small quantity of *Z* acrylate **4s**.
The *E:Z* ratio was, in most of the case, independent of the nature of the substrate ranging from 76:24 to 70:30, except for *para*-nitro **4h** (55:45) and *ortho*-substituted compounds **4m**, **4n** and **4o** (66:34 to 60:40).

Concerning the mechanism of the reaction, the usual question regarding the use of Pd/C is, does the reaction occur through a heterogeneous or homogeneous catalytic pathway? Does the reaction take place on the solid Pd surface (heterogeneous reaction) or does the active catalytic species come from a dissolution of Pd (homogeneous reaction), leaching from Pd/C? In the latter case, the Pd/C would act as a Pd reservoir [11]. Indeed, many research groups studied the mechanism of various cross-coupling reaction using Pd/C catalyst and it appears that no general conclusion can be drawn as the catalytic pathway depends on various

experimental parameters [11,12]. We carried out some control experiments to get insight in the mechanism with Pd/C. First, the reaction with Pd/C as catalyst was completely inhibited in the presence of mercury metal or CS_2, poisons for heterogeneous catalyst (Table 3, entries 2-4) [13]. Nevertheless, the reaction using homogeneous catalytic system based on $Pd(TFA)_2$ was also impacted by the presence of Hg or CS_2 leading to, on one hand, only half yield (Table 3, entries 6 and 7) or traces (Table 3, entry 8) of desired methyl acrylate product **4a** or, on the other hand, complete inhibition of the reaction producing *t*-butyl acrylate **3a** (Table 3, entries 10-12). ICP-AES measurements are inconclusive because they revealed a quantity of 58 ppm after 5 min of reaction and 11 ppm after completion of reaction. Even if these quantities are rather low, they cannot allow to exclude a homogeneous process [11]. Finally, we undertook a recycle study. Only the first round of recycle proved to be efficient whereas the yield dramatically dropped from the second recycle (reaction with **4a**: 80% isolated yield, recycle 1: 75% isolated yield; recycle 2: less than 20% ^{19}F NMR yield). These "recycle" results were in accordance with the report in the literature explaining that the structural change of Pd surface at the end of the reaction (by dissolution-reprecipitation) as well as co-precipitation of salt and base involving the fouling of the catalyst are responsible for rapid inactivation of recycled catalyst [11]. All these experiments cannot ruled out heterogeneous or homogeneous process.

From the acrylates, the obtention of relevant α-trifluoromethylacrylic acids, attractive compounds with numerous applications in medicinal chemistry or materials science [14], by simple hydrolysis could be envisioned. Taking into account that very few methods have been described to get these valuable scaffolds [15], this simple method could constitute an easy synthetic alternative. In this context, the *t*-butyl acrylates **3** proved to be suitable substrates to undergo hydrolysis compared to the methyl acrylates **4**. Indeed, whatever the basic or acidic conditions tested to hydrolyse the methyl acrylates **4**, the reaction proved to be unfruitful while the hydrolysis of the *t*-butyl α-trifluoromethylacrylates **3a,i** in acidic conditions, generating a stable *tert*-butyl carbocation, allowed the formation of the corresponding acids **6a,i** in good yields (Scheme 4).

3. Conclusions

To conclude, we described here an updated method to synthesize α-trifluoromethylacrylates by ligand-free Mirozoki-Heck reaction. The use of *t*-butyl trifluoromethylacrylate instead of methyl trifluoromethylacrylate allowed to improve the *E*:*Z* ratio of the reaction, albeit a complete stereoselectivity was not obtained. Worthy of note that the *t*-butyl acrylates were good substrates to reach relevant trifluoroacrylic acids by acid hydrolysis. Then we reported that the cheaper and useful Pd/C could be efficiently used to synthesize the methyl trifluoromethylacrylates, being a good alternative towards these relevant compounds.

4. Experimental Section

4.1. 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. Pd/C (Palladium, 10% on carbon, type 487, dry) was purchased from Alfa Aesar. Dry CH_2Cl_2 was distillated from calcium hydride. 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). NMR spectra were recorded using a Bruker Avance-300 spectrometer operating at 300 MHz (^1H), 282 MHz (^{19}F), and 75 MHz (^{13}C). ^1H and ^{13}C NMR chemical shifts (δ) were calibrated on residual proton and carbon resonances of $CDCl_3$ (^1H, δ = 7.26 ppm and ^{13}C, δ = 77.16 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.

4.2. General procedures for Heck reaction.

$Pd(TFA)_2$, Ag_2CO_3 catalytic system. To a vial (2 mL) were added iodoarene **1** (0.2 mmol, 1.0 equiv), Ag_2CO_3 (0.4 mmol, 2.0 equiv), $Pd(TFA)_2$ (0.02 mmol, 10 mol%), *t*-butyl 2-(trifluoromethyl)acrylate **2a** (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 CH_2Cl_2) and was mixed with celite. After evaporation of solvents, the crude was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc).
Pd/C, AgOTf catalytic system. To a vial (2 mL) were added iodoarene **1** (0.2 mmol, 1.0 equiv), AgOTf (0.3 mmol, 1.5 equiv), Pd/C (Palladium, 10% on carbon, type 487, dry) (0.02 mmol, 10 mol%), methyl 2-(trifluoro-methyl)acrylate **2b** (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 or 110 °C for 4 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 CH_2Cl_2) and was mixed with celite. After evaporation of solvents, the crude was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc).

***4.2.1. Tert*-butyl (*E*)-3-(4-methoxyphenyl)-2-(trifluoromethyl)acrylate (*E*-3a)** and ***tert*-butyl (*Z*)-3-(4-methoxyphenyl)-2-(trifluoromethyl)acrylate (*Z*-3a)**: 4-iodoanisole (0.2 mmol, 46.8 mg), Ag_2CO_3 (0.4 mmol, 110.3 mg), $Pd(TFA)_2$ (0.02 mmol, 6.4 mg), and *tert*-butyl 2-(trifluoromethyl)acrylate (0.3 mmol, 58.9 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 **3a** in 84% yield [mixture of *E*/*Z* isomers (85/15), 50.6 mg] as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.87 (s, 1H, *Z*), 7.50 – 7.37 (m, 2H, *Z* + 2H, *E*), 7.20 (s, 1H, *E*), 6.98 – 6.85

(m, 2H, *Z* + 2H, *E*), 3.83 (s, 3H, *Z* + 3H, *E*), 1.56 (s, 9H, *Z*), 1.50 (s, 9H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -64.0 (d, *J* = 1.7 Hz, *E*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 163.1 (q, *J* = 2.1 Hz), 163.0 – 162.9 (m), 161.4 – 161.3 (m), 146.8 (q, *J* = 2.9 Hz), 138.3 (q, *J* = 5.8 Hz), 132.1 (q, *J* = 2.7 Hz), 131.5, 125.0, 124.9, 122.8 (q, *J* = 271.1 Hz), 122.6 (q, *J* = 30.5 Hz), 122.5 (q, *J* = 272.0 Hz), 121.7 (q, *J* = 31.5 Hz), 114.0, 113.9, 83.4, 82.8, 55.4, 28.1, 27.9. IR (Neat): 2981, 2938, 2843, 1721, 1606, 1514, 1370, 1280, 1260, 1242, 1150, 1122, 1030, 1007, 828 cm^{-1}. HRMS (CI-TOF): Calcd for $C_{15}H_{18}F_3O_3$ (*m/z*): 303.1208 $[M+H]^+$, found: 303.1213.

***4.2.2. Tert*-butyl (*E*)-3-(4-bromophenyl)-2-(trifluoromethyl)acrylate (*E*-3b)** and ***tert*-butyl (*Z*)-3-(4-bromophenyl)-2-(trifluoromethyl)acrylate (*Z*-3b)**: 1-bromo-4-iodobenzene (0.2 mmol, 56.4 mg), Ag_2CO_3 (0.4 mmol, 110.3 mg), $Pd(TFA)_2$ (0.02 mmol, 6.4 mg), and *tert*-butyl 2-(trifluoromethyl)acrylate (0.3 mmol, 58.9 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 **3b** in 90% yield [mixture of *E*/*Z* isomers (85/15), 63.3 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (s, 1H, *Z*), 7.43 (d, *J* = 8.4 Hz, 2H, *Z* + 2H, *E*), 7.20 (d, *J* = 8.4 Hz, 2H, *Z* + 2H, *E*), 7.15 (s, 1H, *E*), 1.48 (s, 9H, *Z*), 1.37 (s, 9H, *E*). ^{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 162.3, 162.1, 145.7 – 145.5 (m), 137.5 (q, *J* = 5.7 Hz), 131.8, 131.6, 130.9 – 130.6 (m), 126.1 (q, *J* = 30.9 Hz), 125.1 (q, *J* = 30.9 Hz), 124.53, 124.46, 122.2 (q, *J* = 271.7 Hz), 122.0 (q, *J* = 272.3 Hz), 83.9, 83.4, 28.1, 27.8. IR (Neat): 2982, 2933, 1723, 1650, 1489, 1370, 1289, 1274, 1244, 1152, 1130, 1073, 1010, 915, 868, 839, 815 cm^{-1}. HRMS (CI-TOF): Calcd for $C_{14}H_{15}BrF_3O_2$ (*m/z*): 351.0208 $[M+H]^+$, found: 351.0192.

***4.2.3. Tert*-butyl (*E*)-3-(4-cyanophenyl)-2-(trifluoromethyl)acrylate (*E*-3c)** and ***tert*-butyl (*Z*)-3-(4-cyanophenyl)-2-(trifluoromethyl)acrylate (*Z*-3c)**: 4-iodobenzonitrile (0.2 mmol, 45.8 mg), Ag_2CO_3 (0.4 mmol, 110.3 mg), $Pd(TFA)_2$ (0.02 mmol, 6.4 mg), and *tert*-butyl 2-(trifluoromethyl)acrylate (0.3 mmol, 58.9 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 15/1, v/v), affording compound **3c** in 79% yield [mixture of *E*/*Z* isomers (75/25), 46.7 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (s, 1H, *Z*), 7.68 (d, *J* = 8.4 Hz, 2H, *Z* + 2H, *E*), 7.49 (d, *J* = 8.1 Hz, 2H, *E*), 7.43 (d, *J* = 8.1 Hz, 2H, *Z*), 7.34 (s, 1H, *E*), 1.55 (s, 9H, *Z*), 1.40 (s, 9H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.4 (s, *Z*), -64.9 (d, *J* = 1.4 Hz, *E*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 161.6 (q, *J* = l.7 Hz), 161.4 – 161.2 (m), 144.5 (q, *J* = 3.1 Hz), 137.6, 137.4, 137.1 (q, *J* = 5.8 Hz), 132.2, 132.0, 129.5, 129.3 (q, *J* = 2.3 Hz), 128.2 (q, *J* = 31.0 Hz), 127.0 (q, *J* = 31.4 Hz), 121.8 (q, *J* = 272.0 Hz), 121.6 (q, *J* = 272.8 Hz), 118.3, 118.2, 113.4, 113.2, 84.3, 83.8, 28.0, 27.7. IR (Neat): 2983, 2928, 2231, 1724, 1371, 1318, 1292, 1276, 1247, 1133, 1010, 915, 838 cm^{-1}. HRMS (CI-TOF): Calcd for $C_{15}H_{15}F_3NO_2$ (*m/z*): 298.1055 $[M+H]^+$, found: 298.1054.

***4.2.4. Tert*-butyl (*E*)-3-(4-nitrophenyl)-2-(trifluoromethyl)acrylate (*E*-3d)** and ***tert*-butyl (*Z*)-3-(4-nitrophenyl)-2-(trifluoromethyl)acrylate (*Z*-3d)**: 1-iodo-4-nitrobenzene (0.2 mmol, 49.8 mg), Ag_2CO_3 (0.4 mmol, 110.3 mg), $Pd(TFA)_2$ (0.02 mmol, 6.4 mg), and *tert*-butyl 2-(trifluoromethyl)acrylate (0.3 mmol, 58.9 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 15/1, v/v), affording compound **3d** in 54% yield [mixture of *E*/*Z* isomers (52/48), 34.0 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.7 Hz, 2H, *Z* + 2H, *E*), 7.98 (s, 1H, *Z*), 7.56 (d, *J* = 8.7 Hz, 2H, *E*), 7.50 (d, *J* = 8.7 Hz, 2H, *Z*), 7.39 (s, 1H, *E*), 1.57 (s, 9H, *Z*), 1.42 (s, 9H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.4 (s, *Z*), -65.0 (d, *J* = 1.4 Hz, *E*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 161.5 (q, *J* = l.7 Hz), 161.3, 148.4, 148.3, 144.1 (q, *J* = 2.9 Hz), 139.6, 139.3, 136.7 (q, *J* = 5.8 Hz), 129.8, 129.6 (q, *J* = 2.2 Hz), 128.7 (q, *J* = 31.1 Hz), 127.5 (q, *J* = 31.3 Hz), 123.7, 123.6, 121.8 (q, *J* = 272.1 Hz), 121.6 (q, *J* = 272.9 Hz), 84.5, 84.0, 28.1, 27.8. IR (Neat): 2983, 2934, 1724, 1602, 1523, 1371, 1347, 1278, 1248, 1134, 1013, 850, 692 cm^{-1}. HRMS (CI-TOF): Calcd for $C_{14}H_{15}F_3NO_4$ (*m/z*): 318.0953 $[M+H]^+$, found: 318.0940.

***4.2.5. Tert*-butyl (*E*)-3-(3-methoxyphenyl)-2-(trifluoromethyl)acrylate (*E*-3e)** and ***tert*-butyl (*Z*)-3-(3-methoxyphenyl)-2-(trifluoromethyl)-acrylate (*Z*-3e)**: 3-iodoanisole (0.2 mmol, 46.8 mg), Ag_2CO_3 (0.4 mmol, 110.3 mg), $Pd(TFA)_2$ (0.02 mmol, 6.4 mg), and *tert*-butyl 2-(trifluoromethyl)acrylate (0.3 mmol, 58.9 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 120/1 to 90/1, v/v), affording compound **3e** in 87% yield [mixture of *E*/*Z* isomers (87/13), 52.6 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (s, 1H, *Z*), 7.25 – 7.16 (m, 2H, *Z* + 2H, *E*), 6.93 – 6.80 (m, 2H, *Z* + 3H, *E*), 3.76 – 3.68 (m, 3H, *Z* + 3H, *E*), 1.48 (s, 9H, *Z*), 1.36 (s, 9H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.4 (s, *Z*), -64.5 (d, *J* = 1.4 Hz, *E*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 162.6 – 162.5 (m), 162.5 – 162.3 (m), 159.6, 159.3, 146.9 (q, *J* = 3.0 Hz), 138.4 (q, *J* = 5.8 Hz), 134.2, 134.0, 129.6, 129.4, 125.7 (q, *J* = 30.7 Hz), 124.7 (q, *J* = 31.4 Hz), 122.4 (q, *J* = 271.5 Hz), 122.0 (q, *J* = 272.5 Hz), 121.8 – 121.4 (m), 115.8, 115.7, 114.3, 83.6, 83.2, 55.40, 55.37, 28.1, 27.8. IR (Neat): 2982, 1724, 1600, 1581, 1489, 1458, 1370, 1300, 1241, 1149, 1127, 1043, 1011, 843, 689 cm^{-1}. HRMS (CI-TOF): Calcd for $C_{15}H_{18}F_3O_3$ (*m/z*): 303.1208 $[M+H]^+$, found: 303.1206.

***4.2.6. Tert*-butyl (*E*)-3-(3-nitrophenyl)-2-(trifluoromethyl)acrylate (*E*-3f)** and ***tert*-butyl (*Z*)-3-(3-nitrophenyl)-2-(trifluoromethyl)acrylate (*Z*-3f)**: 1-iodo-3-nitrobenzene (0.2 mmol, 49.8 mg), Ag_2CO_3 (0.4 mmol, 110.3 mg), $Pd(TFA)_2$ (0.02 mmol, 6.4 mg), and *tert*-butyl 2-(trifluoromethyl)acrylate (0.3 mmol, 58.9 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 (83/17), 56.4 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 – 8.19 (m, 2H, *Z* + 2H, *E*), 7.97 (s, 1H, *Z*), 7.74 – 7.64 (m, 1H, *Z* + 1H, *E*), 7.59 (t, *J* = 8.0 Hz, 1H, *Z* + 1H, *E*), 7.36 (s, 1H, *E*), 1.56 (s, 9H, *Z*), 1.45 (s, 9H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.4 (s, *Z*), -64.9 (d, *J* = 1.7 Hz, *E*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 161.6 (q, *J* = l.8 Hz), 161.5 – 161.4 (m), 148.3, 148.1, 143.9 (q, *J* = 3.0 Hz), 136.4 (q, *J* = 5.9 Hz), 135.0, 134.7 – 134.5 (m), 134.4, 129.7, 129.5, 128.1 (q, *J* = 31.1 Hz), 127.2 (q, *J* = 31.4 Hz), 124.5, 124.3, 123.7, 121.9 (q, *J* = 272.0 Hz), 121.7 (q, *J* = 272.8 Hz), 84.6, 83.9, 28.0, 27.8. IR (neat): 2983, 2934, 1723, 1532, 1352, 1300, 1274, 1247, 1133, 1014, 922, 840, 735, 675 cm^{-1}. HRMS (CI-TOF): Calcd for $C_{14}H_{15}F_3NO_4$ (*m/z*): 318.0953 $[M+H]^+$, found: 318.0940.

***4.2.7. Tert*-butyl (*E*)-3-(2-methoxyphenyl)-2-(trifluoromethyl)acrylate (*E*-3g)** and ***tert*-butyl (*Z*)-3-(2-methoxyphenyl)-2-(trifluoromethyl)-acrylate (*Z*-3g)**: 2-iodoanisole (0.2 mmol, 46.8 mg), Ag_2CO_3 (0.4 mmol, 110.3 mg), $Pd(TFA)_2$ (0.02 mmol, 6.4 mg), and *tert*-butyl 2-(trifluoromethyl)acrylate (0.3 mmol, 58.9 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 100/1 to 60/1, v/v), affording compound **3g** in 53% yield [mixture of *E*/*Z* isomers (69/31), 31.8 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (s, 1H, *Z*), 7.59 (s, 1H, *E*), 7.43 – 7.27 (m, 2H, *Z* + 2H, *E*), 6.99 – 6.86 (m, 2H, *Z* + 2H, *E*), 3.86 (s, 3H, *Z*), 3.85 (s, 3H, *E*), 1.57 (s, 9H, *Z*), 1.40 (s, 9H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -59.2 (s, *Z*), -64.4 (d, *J* = 1.4 Hz, *E*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 162.7 (q, *J* = l.8 Hz), 162.6 – 162.5 (m), 157.5, 143.7 (q, *J* = 3.0 Hz), 136.0 (q, *J* = 6.0 Hz), 131.7, 131.6, 130.5 (q, *J* = 3.5 Hz), 130.0, 125.0 (q, *J* = 30.3 Hz), 124.0 (q, *J* = 31.0 Hz), 122.6 (q, *J* = 271.4 Hz), 122.4 (q, *J* = 272.4 Hz), 122.2, 120.2, 110.7, 110.4, 83.0, 82.8, 55.6, 28.2, 27.8. IR (Neat): 2981, 1722, 1646, 1601, 1490, 1466, 1439, 1370, 1284, 1239, 1154, 1127, 1114, 1009, 843, 751 cm^{-1}. HRMS (CI-TOF): Calcd for $C_{15}H_{18}F_3O_3$ (*m/z*): 303.1208 $[M+H]^+$, found: 303.1206.

***4.2.8. Tert*-butyl (*E*)-3-(2-methylphenyl)-2-(trifluoromethyl)acrylate (*E*-3h)** and ***tert*-butyl (*Z*)-3-(2-methylphenyl)-2-(trifluoromethyl)acrylate (*Z*-3h)**: 2-iodotoluene (0.2 mmol, 43.6 mg), Ag_2CO_3 (0.4 mmol, 110.3 mg), $Pd(TFA)_2$ (0.02 mmol, 6.4 mg), and *tert*-butyl 2-(trifluoromethyl)acrylate (0.3 mmol, 58.9 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 100/1 to 60/1, v/v), affording compound **3h** in 77% yield [mixture of *E*/*Z* isomers (77/23), 44.3 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (s, 1H, *Z*), 7.46 (s, 1H, *E*), 7.23 – 7.16 (m, 1H, *Z* + 1H, *E*), 7.16 – 7.04 (m, 3H, *Z* + 3H, *E*), 2.22 (s, 3H, *Z* + 3H, *E*), 1.49 (s, 9H, *Z*), 1.21 (s, 9H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.8 (s, *Z*), -64.8 (d, *J* = 1.7 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 162.3 (q, *J* = l.6 Hz), 162.0 – 161.9 (m), 147.0 (q, *J* = 3.1 Hz), 139.9 (q, *J* = 5.7 Hz), 136.2, 136.0, 133.1, 132.9, 130.1, 129.9, 129.53, 129.50, 128.3 (q, *J* = 3.2 Hz), 128.2 – 128.1 (m), 126.8 (q, *J* = 30.3 Hz), 125.8, 125.7, 125.3 (q, *J* = 30.7 Hz), 122.2 (q, *J* = 271.5 Hz), 122.1 (q, *J* = 272.8 Hz), 83.14, 83.11, 28.1, 27.6, 20.1, 19.8. IR (Neat): 2981, 1725, 1649, 1370, 1296, 1278, 1247, 1155, 1132, 1011, 843, 749 cm^{-1}. HRMS (CI-TOF): Calcd for $C_{15}H_{18}F_3O_2$ (*m/z*): 287.1259 $[M+H]^+$, found: 287.1257.

4.2.9. (*E*)-methyl 2-(2-(tert-butoxycarbonyl)-3,3,3-trifluoroprop-1-en-1-yl)benzoate (*E*-3i) and **(*Z*)-methyl 2-(2-(tert-butoxycarbonyl)-3,3,3-trifluoroprop-1-en-1-yl)benzoate (*Z*-3i)**: methyl 2-iodobenzoate (0.2 mmol, 52.4 mg), Ag_2CO_3 (0.4 mmol, 110.3 mg), $Pd(TFA)_2$ (0.02 mmol, 6.4 mg), and *tert*-butyl 2-(trifluoromethyl)acrylate (0.3 mmol, 58.9 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 90/1 to 50/1, v/v), affording compound **3i** in 99% yield [mixture of *E*/*Z* isomers (67/33), 65.5 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (s, 1H, *Z*), 8.05 – 7.97 (m, 1H, *Z* + 1H, *E*), 7.96 (s, 1H, *E*), 7.51 – 7.42 (m, 1H, *Z* + 1H, *E*), 7.42 – 7.34 (m, 1H, *Z* + 1H, *E*), 7.21 – 7.13 (m, 1H, *Z* + 1H, *E*), 3.82 (s, 3H, *Z* + 3H, *E*), 1.50 (s, 9H, *Z*), 1.13 (s, 9H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.0 (s, *Z*), -64.7 (d, *J* = 1.4 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 166.5, 166.4, 162.1 (q, *J* = l.6 Hz), 161.5, 148.7 (q, *J* = 3.2 Hz), 143.3 (q, *J* = 6.1 Hz), 136.4, 135.9, 132.3, 130.7, 130.6, 129.4 – 129.1 (m), 129.1, 129.0, 128.2, 127.8, 124.7 (q, *J* = 30.0 Hz), 123.2 (q, *J* = 30.3 Hz), 122.3 (q, *J* = 271.4 Hz), 122.2 (q, *J* = 272.6 Hz), 82.9, 82.8, 52.4, 52.3, 28.1, 27.5. IR (Neat): 2982, 1718, 1650, 1370, 1292, 1281, 1264, 1156, 1130, 1082, 1013, 843, 753 cm^{-1}. HRMS (AP-TOF): Calcd for $C_{16}H_{17}F_3O_4$ (*m/z*): 330.1079 $[M]^+$, found: 330.1077.

***4.2.10. Tert*-butyl (*E*)-3-(naphthalen-2-yl)-2-(trifluoromethyl)acrylate (*E*-3j)** and ***tert*-butyl (*Z*)-3-(naphthalen-2-yl)-2-(trifluoromethyl)acrylate (*Z*-3j)**: 2-iodonaphthalene (0.2 mmol, 50.8 mg), Ag_2CO_3 (0.4 mmol, 110.3 mg), $Pd(TFA)_2$ (0.02 mmol, 6.4 mg), and *tert*-butyl 2-(trifluoromethyl)acrylate (0.3 mmol, 58.9 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 100/1 to 60/1, v/v), affording compound **3j** in less than 78% yield [mixture of *E*/*Z* isomers (86/14), 50.6 mg, not pure] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (s, 1H, *Z*), 7.94 – 7.78 (m, 4H, *Z* + 4H, *E*), 7.58 – 7.45 (m, 3H, *Z* + 4H, *E*), 1.62 (s, 9H, *Z*), 1.47 (s, 9H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.3 (s, *Z*), -64.4 (d, *J* = 1.1 Hz, *E*). IR (Neat): 3059, 2983, 2937, 1722, 1651, 1370, 1281, 1270, 1247, 1152, 1121, 1009, 842, 825, 750 cm^{-1}. HRMS (CI-TOF): Calcd for $C_{18}H_{18}F_3O_2$ (*m/z*): 323.1259 $[M+H]^+$, found: 323.1269.

***4.2.11. Tert*-butyl (*E*)-3-(3,5-dichlorophenyl)-2-(trifluoromethyl)acrylate (*E*-3k)** and ***tert*-butyl (*Z*)-3-(3,5-dichlorophenyl)-2-(trifluoromethyl)-acrylate (*Z*-3k)**: 3,5-dichloro-1-iodo-benzene (0.2 mmol, 54.6 mg), Ag_2CO_3 (0.4 mmol, 110.3 mg), $Pd(TFA)_2$ (0.02 mmol, 6.4 mg), and *tert*-butyl 2-(trifluoromethyl)acrylate (0.3 mmol, 58.9 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 100/1 to 60/1, v/v), affording compound **3k** in 81% yield [mixture of *E*/*Z* isomers (87/13), 55.5 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (s, 1H, *Z*), 7.33 – 7.28 (m, 1H, *Z* + 1H, *E*), 7.24 – 7.17 (m, 1H, *Z* + 2H, *E*), 7.15 – 7.09 (m, 1H, *Z* + 1H, *E*), 1.48 (s, 9H, *Z*), 1.38 (s, 9H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -65.0 (d, *J* = 1.7 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 161.6 (q, *J* = l.7 Hz), 161.6 – 161.4 (m), 143.7 (q, *J* = 3.1 Hz), 135.9, 135.6, 135.5 (q, *J* = 5.7 Hz), 135.3, 135.1, 129.7, 129.6, 128.1 (q, *J* = 31.1 Hz), 127.2, 126.9 (q, *J* = 2.3 Hz), 121.8 (q, *J* = 271.9 Hz), 121.6 (q, *J* = 272.4 Hz), 84.5, 83.8, 28.1, 27.8. IR (Neat): 2983, 1726, 1563, 1370, 1285, 1240, 1218, 1135, 1014, 841, 803 cm^{-1}. HRMS (CI-TOF): Calcd for $C_{14}H_{14}Cl_2F_3O_2$ (*m/z*): 341.0323 $[M+H]^+$, found: 341.0313.

4.2.12. Methyl (*E*)-3-(4-methoxyphenyl)-2-(trifluoromethyl)acrylate (*E*-4a) and **methyl (*Z*)-3-(4-methoxyphenyl)-2-(trifluoromethyl)acrylate (*Z*-4a)** [8]: 4-iodoanisole (0.2 mmol, 46.8 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 90 °C for 4 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 **4a** in 80% yield [mixture of *E*/*Z* isomers (76/24), 41.6 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*).

4.2.13. Methyl (*E*)-3-(4-hydroxyphenyl)-2-(trifluoromethyl)acrylate (*E*-4b) and **methyl (*Z*)-3-(4-hydroxyphenyl)-2-(trifluoromethyl)acrylate (*Z*-4b)** [8]: 4-Iodophenol (0.2 mmol, 44.0 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 90 °C for 4 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), and was subsequently washed with *n*-pentane (0.3 mL × 3), affording compound **4b** in 67% yield [mixture of *E*/*Z* isomers (73/27), 33.0 mg] as a white 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*), 5.77 (s, 1H, *E*), 5.70 (s, 1H, *Z*), 3.89 (s, 3H, *Z*), 3.84 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -63.8 (s, *E*).

4.2.14 Methyl (*E*)-3-(*p*-tolyl)-2-(trifluoromethyl)acrylate (*E*-4c) and **methyl (*Z*)-3-(p-tolyl)-2-(trifluoromethyl)acrylate (*Z*-4c)**: 1-iodo-4-methylbenzene (0.2 mmol, 43.6 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 90 °C for 24 hours according to the general procedure. When the reaction mixture was cooled to rt, ^{19}F NMR spectrum of the crude was tested with $PhCOCF_3$ (1.0 equiv) as an internal standard. ^{19}F NMR yield: 88% [according to the linear relationship, see SI], *E*/*Z* = 74/26. ^{19}F NMR (282 MHz, $CDCl_3$) for crude: δ -58.4 (s, *Z*), -64.1 (d, *J* = 1.7 Hz, *E*). We failed to obtain the pure isolated product.

4.2.15. Methyl (*E*)-3-phenyl-2-(trifluoromethyl)acrylate (*E*-4d) and **methyl (*Z*)-3-phenyl-2-(trifluoromethyl)acrylate (*Z*-4d)** [8]: iodobenzene (0.2 mmol, 40.8 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 90 °C for 4 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 **4d** in 63% yield [mixture of *E*/*Z* isomers (72/28), 29.0 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*).

4.2.16. Methyl (*E*)-3-(4-bromophenyl)-2-(trifluoromethyl)acrylate (*E*-4e) and **methyl (*Z*)-3-(4-bromophenyl)-2-(trifluoromethyl)acrylate (*Z*-4e)** [8]: 1-bromo-4-iodobenzene (0.2 mmol, 56.6 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoro-methyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 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 **4e** in 78% yield [mixture of *E*/*Z* isomers (73/27), 48.2 mg] as a yellow oil. ^{1}H 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*).

4.2.17. Methyl (*E*)-3-(4-cyanophenyl)-2-(trifluoromethyl)acrylate (*E*-4f) and **methyl (*Z*)-3-(4-cyanophenyl)-2-(trifluoromethyl)acrylate (*Z*-4f)** [8]: 4-iodobenzonitrile (0.2 mmol, 45.8 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 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 **4f** in 85% yield [mixture of *E*/*Z* isomers (67/33), 43.4 mg]. *E*/*Z* isomers were completely separated by column: compound ***E*-4f** 29.2 mg, white solid; impure *Z*-isomer was subsequently washed with *n*-pentane (0.2 mL × 3) to obtain pure compound ***Z*-4f** 14.2 mg, white solid. **[*E*-isomer (major)]** ^{1}H 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). **[*Z*-isomer (minor)]** ^{1}H 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).

4.2.18. Methyl (*E*)-4-(3,3,3-trifluoro-2-(methoxycarbonyl)prop-1-en-1-yl)benz-oate (*E*-4g) and **methyl (*Z*)-4-(3,3,3-trifluoro-2-(methoxy-carbonyl)-prop-1-en-1-yl)benzoate (*Z*-4g)** [8]: methyl 4-iodobenzoate (0.2 mmol, 52.4 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 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 **4g** in 75% yield [mixture of *E*/*Z* isomers (74/26), 43.2 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*).

4.2.19. Methyl (*E*)-3-(4-nitrophenyl)-2-(trifluoromethyl)acrylate (*E*-4h) and **methyl (*Z*)-3-(4-nitrophenyl)-2-(trifluoromethyl)acrylate (*Z*-4h)** [8]: 1-iodo-4-nitrobenzene (0.2 mmol, 49.8 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoro-methyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 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 **4h** in 88% yield [mixture of *E*/*Z* isomers (55/45), 48.4 mg] as a yellow oil. ^{1}H 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*).

4.2.20. Methyl (*E*)-3-(4-acetylphenyl)-2-(trifluoromethyl)acrylate (*E*-4i) and **methyl (*Z*)-3-(4-acetylphenyl)-2-(trifluoromethyl)acrylate (*Z*-4i)** [8]: 1-(4-iodophenyl)ethan-1-one (0.2 mmol, 49.2 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoro-methyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 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 **4i** in 62% yield [mixture of *E*/*Z* isomers (72/28), 33.8 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*).

4.2.21. Methyl (*E*)-3-(*m*-tolyl)-2-(trifluoromethyl)acrylate (*E*-4j) and **methyl (*Z*)-3-(*m*-tolyl)-2-(trifluoromethyl)acrylate (*Z*-4j)** [8]: 3-iodotoluene (0.2 mmol, 43.6 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 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 **4j** in 42% yield [mixture of *E*/*Z* isomers (72/28), 20.5 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*).

4.2.22. Methyl (*E*)-3-(3-cyanophenyl)-2-(trifluoromethyl)acrylate (*E*-4k) and **methyl (*Z*)-3-(3-cyanophenyl)-2-(trifluoromethyl)acrylate (*Z*-4k)** [8]: 3-iodobenzonitrile (0.2 mmol, 45.8 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 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 **4k** in 52% yield [mixture of *E*/*Z* isomers (70/30), 26.6 mg]. *E*/*Z* isomers were completely separated by column: compound ***E*-4k** 18.5 mg, colorless oil; impure *Z*-isomer was subsequently washed with petroleum ether (0.1 mL × 3) to obtain pure compound ***Z*-4k** 11.3 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). **[*Z*-isomer (minor)]** ^{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).

4.2.23. Methyl (*E*)-3-(3-nitrophenyl)-2-(trifluoromethyl)acrylate (*E*-4l) and **methyl (*Z*)-3-(3-nitrophenyl)-2-(trifluoromethyl)acrylate (*Z*-4l)** [8]: 1-iodo-3-nitrobenzene (0.2 mmol, 49.8 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoro-methyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 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 **4l** in 71% yield [mixture of *E*/*Z* isomers (70/30), 38.9 mg] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 – 8.21 (m, 2H, *Z* + 2H, *E*), 8.12 (s, 1H, *Z*), 7.45 – 7.66 (m, 1H, *Z* + 1H, *E*), 7.65 – 7.55 (m, 1H, *Z* + 1H, *E*), 7.51 (s, 1H, *E*), 3.93 (s, 3H, *Z*), 3.81 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.5 (s, *Z*), -64.7 (d, *J* = 1.4 Hz, *E*).

4.2.24. Methyl (*E*)-3-(*o*-tolyl)-2-(trifluoromethyl)acrylate (*E*-4m) and **methyl (*Z*)-3-(*o*-tolyl)-2-(trifluoromethyl)acrylate (*Z*-4m)**: 1-iodo-2-methylbenz-ene (0.2 mmol, 43.6 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 hours according to the general procedure. When the reaction mixture was cooled to rt, ^{19}F NMR spectrum of the crude was tested with $PhCOCF_3$ (1.0 equiv) as an internal standard. ^{19}F NMR yield: 83% [according to the linear relationship, see SI], *E*/*Z* = 66/34. ^{19}F NMR (282 MHz, $CDCl_3$) for crude: δ -58.8 (s, *Z*), -64.4 (d, *J* = 1.7 Hz, *E*). We failed to obtain the pure isolated product.

4.2.25. Methyl (*E*)-3-(2-cyanophenyl)-2-(trifluoromethyl)acrylate (*E*-4n) and **methyl (*Z*)-3-(2-cyanophenyl)-2-(trifluoromethyl)acrylate (*Z*-4n)**: 2-iodobenzonitrile (0.2 mmol, 45.8 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 hours according to the general procedure. When the reaction mixture was cooled to rt, ^{19}F NMR spectrum of the crude was tested with $PhCOCF_3$ (1.0 equiv) as an internal standard. ^{19}F NMR yield: 98% [according to the linear relationship, see SI], *E*/*Z* = 60/40. ^{19}F NMR (282 MHz, $CDCl_3$) for crude: δ -59.0 (s, *Z*), -64.8 (d, *J* = 1.7 Hz, *E*). We failed to obtain the pure isolated product.

4.2.26. Methyl (*E*)-3-(2-nitrophenyl)-2-(trifluoromethyl)acrylate (*E*-4o) and **methyl (*Z*)-3-(2-nitrophenyl)-2-(trifluoromethyl)acrylate (*Z*-4o)** [8]: 1-iodo-2-nitrobenzene (0.2 mmol, 49.8 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)-acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 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 **4o** in 88% yield [mixture of *E*/*Z* isomers (64/36), 48.4 mg] 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*).

4.2.27. Methyl (*E*)-3-(naphthalen-2-yl)-2-(trifluoromethyl)acrylate (*E*-4p) and **methyl (*Z*)-3-(naphthalen-2-yl)-2-(trifluoromethyl)acrylate (*Z*-4p)** [8]: 2-iodonaphthalene (0.2 mmol, 50.8 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 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 **4p** in 79% yield [mixture of *E*/*Z* isomers (74/26), 44.3 mg] 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*).

4.2.28. Methyl (*E*)-3-(3,5-dichlorophenyl)-2-(trifluoromethyl)acrylate (*E*-4q) and **methyl (*Z*)-3-(3,5-dichlorophenyl)-2-(trifluoromethyl)acrylate (*Z*-4q)** [8]: 3,5-dichloroiodobenzene (0.2 mmol, 54.6 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 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 **4q** in 68% yield [mixture of *E*/*Z* isomers (74/26), 40.7 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*).

4.2.29. Methyl (*E*)-3-(5-formylfuran-2-yl)-2-(trifluoromethyl)acrylate (*E*-4r) and **methyl (*Z*)-3-(5-formylfuran-2-yl)-2-(trifluoromethyl)acrylate (*Z*-4r)**: 5-iodofuran-2-carbaldehyde (0.2 mmol, 44.4 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 hours according to the general procedure. When the reaction mixture was cooled to rt, ^{19}F NMR spectrum of the crude was tested with $PhCOCF_3$ (1.0 equiv) as an internal standard. ^{19}F NMR yield: 29% [according to the linear relationship, see SI], *E*/*Z* = 83/17. ^{19}F NMR (282 MHz, $CDCl_3$) for crude: δ -60.2 (s, *Z*), -64.2 (s, *E*). We failed to obtain the pure isolated product.

4.2.30. 3-(Trifluoromethyl)-2*H*-chromen-2-one (5) [8]: 2-iodophenol (0.2 mmol, 44.0 mg), AgOTf (0.3 mmol, 77.1 mg), Pd/C (10%, dry) (0.02 mmol, 21.3 mg), and methyl 2-(trifluoromethyl)acrylate (0.3 mmol, 46.2 mg) in 1,4-dioxane (1.0 mL) were reacted at 110 °C for 4 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 **5** in 50% yield (21.3 mg) as a white solid. ^{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). The *Z* isomer **4s** was obtained in less than 13% yield (5.5 mg). **Methyl (*Z*)-3-(2-hydroxyphenyl)-2-(trifluoromethyl)-acrylate** (**4s**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.36 – 7.20 (m, 2H), 6.96 (t, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 5.41 (s, 1H), 3.91 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ -59.3 (s). We failed to obtain the pure isolated product.

4.3. General procedure for hydrolysis of t-butyl α-trifluoromethylacrylates.

To an oven-dried 10 mL reaction tube was added *tert*-butyl α-trifluoromethylacrylate **3** (0.2 mmol, 1.0 equiv), and the tube was then evacuated and filled with argon three times. Anhydrous CH_2Cl_2 (1.0 mL) was added, and the mixture was cooled to 0 °C. CF_3COOH (10.0 equiv) was added dropwisely at 0 °C and the reaction mixture was then allowed to stir at rt for 4 hours. Water (0.2 mL) was added and the two phase reaction mixture was further stirred at rt overnight. Water (5 mL) was added and the product was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of solvents, the crude was purified by silica gel column chromatography (eluent: CH_2Cl_2/MeOH (AcOH %)).

4.3.1. (*E*)-3-(4-methoxyphenyl)-2-(trifluoromethyl)acrylic acid (*E*-6a) and **(*Z*)-3-(4-methoxyphenyl)-2-(trifluoromethyl)acrylic acid (*Z*-6a)** [15d]: the crude was purified by silica gel column chromatography (CH_2Cl_2/MeOH (AcOH), from 100/1 (0.5%) to 60/1 (0.5%), v/v), affording compound **6a** in 77% yield (mixture of *E*/*Z* isomers, 37.8 mg, *E*/*Z* = 84/16) as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.30 (s, 1H, *Z* + 1H, *E*), 8.17 (s, 1H, *Z*), 7.58 – 7.43 (m, 2H, *Z* + 3H, *E*), 7.00 – 6.83 (m, 2H, *Z* + 2H, *E*), 3.87 (s, 3H, *Z*), 3.85 (s, 3H, *E*). ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.6 (s, *Z*), -63.7 (d, *J* = 1.4 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.4, 169.0, 162.2, 162.0, 150.8 (q, *J* = 2.4 Hz), 144.0 (q, *J* = 5.6 Hz), 133.1 (q, *J* = 2.7 Hz), 132.5, 124.4, 124.2, 122.6 (q, *J* = 271.3 Hz), 122.2 (q, *J* = 272.3 Hz), 119.0 (q, *J* = 31.1 Hz), 118.2 (q, *J* = 32.2 Hz), 114.2, 114.1, 55.6, 55.5. IR: 2850, 1698, 1599, 1514, 1424, 1268, 1154, 1134, 1019, 838, 527 cm^{-1}. HRMS (ES-TOF): Calcd for $C_{11}H_8F_3O_3$ (*m/z*): 245.0426 [M-H]$^-$, found: 245.0429.

4.3.2. (*E*)-3-(2-(methoxycarbonyl)phenyl)-2-(trifluoromethyl)acrylic acid (*E*-6i) and **(*Z*)-3-(2-(methoxycarbonyl)phenyl)-2-(trifluoromethyl)-acrylic acid (*Z*-6i)** [15d]: the crude was purified by silica gel column chromatography (CH_2Cl_2/MeOH (AcOH), 60/1 (0.5%), v/v), affording compound **6i** in 71% yield (mixture of *E*/*Z* isomers, 39.0 mg, *E*/*Z* = 67/33) as a white solid. ^{1}H NMR (300 MHz, CD_3OD): δ 8.56 (s, 1H, *Z*), 8.18 – 7.99 (m, 1H, *Z* + 2H, *E*), 7.68 – 7.42 (m, 2H, *Z* + 2H, *E*), 7.32 (d, *J* = 7.5 Hz, 1H, *E*), 7.28 (d, *J* = 7.8 Hz, 1H, *Z*), 3.89 (s, 3H, *Z*), 3.88 (s, 3H, *E*). ^{19}F NMR (282 MHz, CD_3OD): δ -59.3 (s, *Z*), -65.7 (d, *J* = 2.0 Hz, *E*). ^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ 167.9, 167.7, 165.5 – 165.3 (m), 165.2, 151.3 (q, *J* = 3.2 Hz), 145.6 (q, *J* = 6.2 Hz), 137.3, 137.1, 133.53, 133.51, 131.5, 131.4, 130.4 – 130.0 (m), 129.9 (q, *J* = 2.8 Hz), 129.5, 128.9, 124.4 (q, *J* = 30.2 Hz),

123.8 (q, *J* = 270.3 Hz), 123.7 (q, *J* = 271.9 Hz), 122.9 (q, *J* = 29.8 Hz), 52.8, 52.7. IR: 2954, 1699, 1635, 1438, 1270, 1135, 1088, 755, 695 cm^{-1}. HRMS (ES-TOF): Calcd for $C_{12}H_8F_3O_4$ (*m/z*): 273.0375 $[M-H]^-$, found: 273.0376.

Declaration of Competing Interest

The authors declare no conflict of interest.

Acknowledgements

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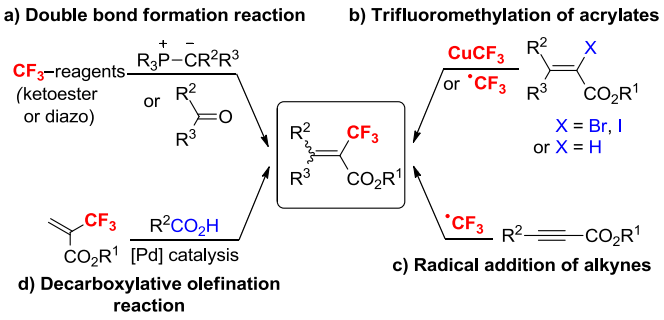
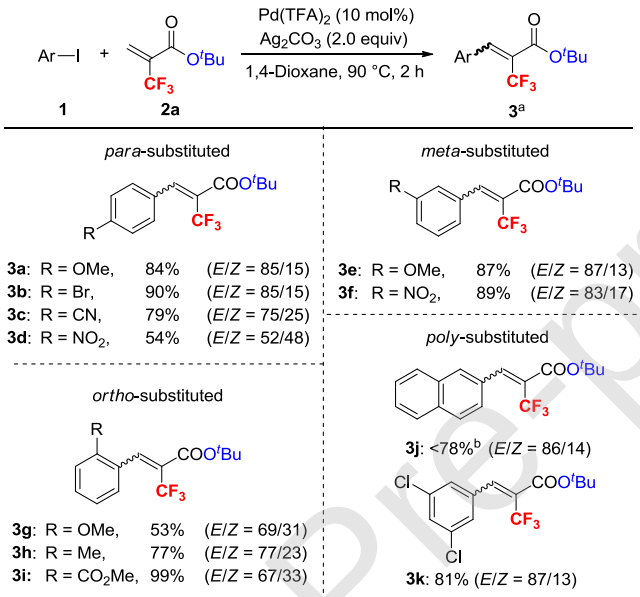
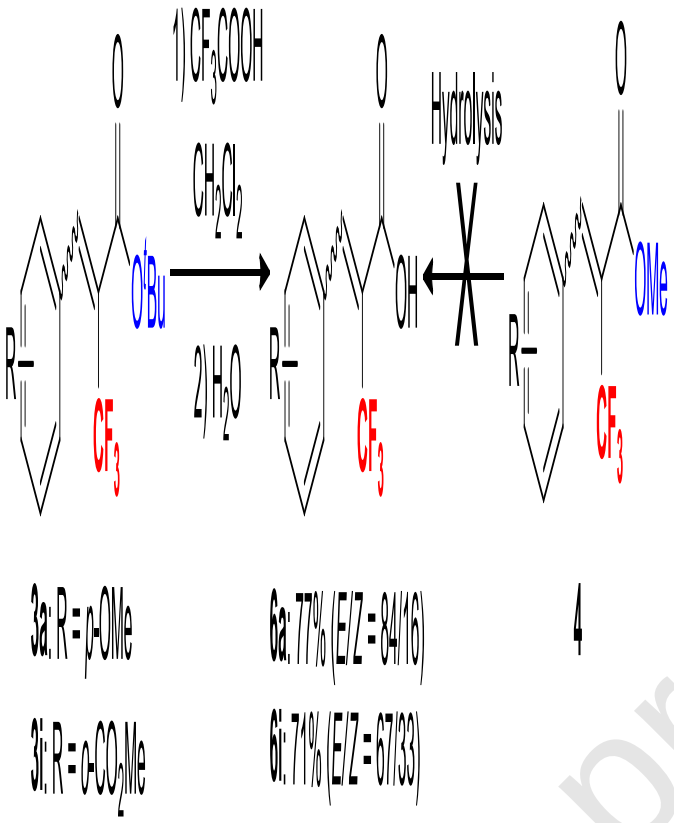


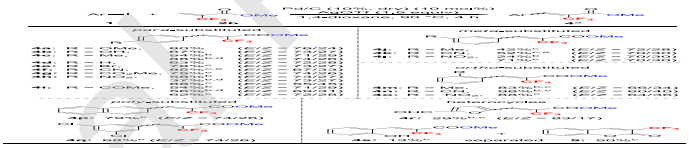
Scheme 1. Reported access to α-trifluoromethylacrylates.



Scheme 2. Scope of the alkenylation reaction with *t*-butyl 2-(trifluoromethyl)acrylate **2a**.
[a] Yields based on isolated product after flash chromatography. [b] Not pure.



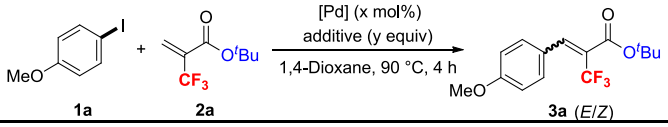
Scheme 3. Scope of the alkenylation reaction with methyl 2-(trifluoromethyl)acrylate **2b** using Pd/C catalyst.
[a] Yields based on isolated product after flash chromatography. [b] ^{19}F NMR yields were obtained by using $PhCOCF_3$ as an internal standard. [c] 110 °C. [d] 24 h. [e] Two *E/Z* isomers were separated.



Scheme 4. Hydrolysis of α-trifluoromethylacrylates.

Table

Table 1
Optimization of the alkenylation reaction with *t*-butyl 2-(trifluoromethyl)acrylate.

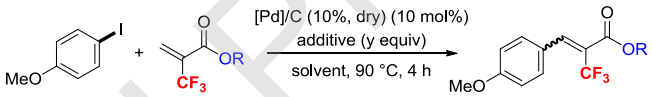


1a **2a** **3a** (*E*/*Z*)

Entry	[Pd]	$Pd(TFA)_2$ (x mol%)	Additive (y equiv)	Yield of **3a** (%)[a]	*E*/*Z* ratio
1	$Pd(TFA)_2$	10	AgOTf (1.5)	0	-
2	$Pd(TFA)_2$	10	AgOAc (2.0)	76	83/17
3	$Pd(TFA)_2$	10	Ag_2CO_3 (2.0)	88	84/16
4	$Pd(TFA)_2$	5	Ag_2CO_3 (2.0)	56	84/16
5[b]	$Pd(TFA)_2$	10	Ag_2CO_3 (2.0)	90 (84)[c]	85/15
6	$Pd(TFA)_2$	10	K_2CO_3 (2.0)	20	71/29
7	$Pd(OAc)_2$	10	Ag_2CO_3 (2.0)	14	76/24
8	$PdBr_2$	10	Ag_2CO_3 (2.0)	traces	-

[a] ^{19}F NMR yields were obtained by using $PhCOCF_3$ as an internal standard.
[b] 2 h.
[c] Isolated yield.

Table 2
Optimization of the alkenylation reaction with methyl or *t*-butyl 2-(trifluoromethyl)acrylate using Pd/C catalyst.



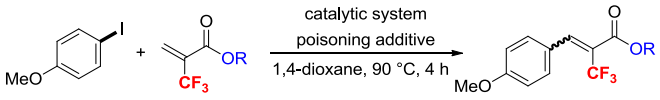
1a **2a**, R = ^{t}Bu; **2b**, R = Me **3a**, R = ^{t}Bu; **4a**, R = Me

Entry	**2**	[Pd]	Additive (y equiv)	Solvent	Yield of **3a**,**4a** (%)[a]	*E*/*Z* ratio
1	**2a**	Pd	AgOTf (1.5)	1,4-dioxane	traces	-
2	**2a**	Pd	Ag_2CO_3 (2.0)	1,4-dioxane	traces	-
3	**2a**	$Pd(OH)_2$[b]	Ag_2CO_3 (2.0)	1,4-dioxane	-	-
4	**2b**	Pd	AgOTf (1.5)	1,4-dioxane	87 (80)[c]	76/24
5[d]	**2b**	Pd	AgOTf (1.5)	1,4-dioxane	83 (76)[c]	73/27
6[e]	**2b**	Pd	AgOTf (1.5)	1,4-dioxane	80	76/24
7	**2b**	$Pd(OH)_2$[b]	AgOTf (1.5)	1,4-dioxane	76	76/24
8[f]	**2b**	Pd	AgOTf (1.5)	1,4-dioxane	78	76/24
9	**2b**	Pd	AgOTf (1.5)	DMF	18	68/32
10	**2b**	Pd	Ag_2CO_3 (2.0)	1,4-dioxane	-	-
11	**2b**	Pd	NaOAc (1.5)	DMA	-	-
12	**2b**	Pd	$Cu(OTf)_2$ (1.5)	1,4-dioxane	traces	-

13	**2b**	Pd	-	1,4-dioxane	-	-

[a] ^{19}F NMR yields were obtained by using $PhCOCF_3$ as an internal standard.
[b] $Pd(OH)_2$ (20%, dry)
[c] Isolated yield.
[d] 5 mol% of Pd
[e] 1 mol% of Pd
[f] 2 h.

Table 3
Control experiments to get insight in the mechanism with Pd/C



1a **2a**, R = ^{t}Bu; **2b**, R = Me **3a**, R = ^{t}Bu; **4a**, R = Me

Entry	**2**	Catalytic system	t (h)	Poisoning additive	Yield of **3a**,**4a** (%)[a]	*E*/*Z* ratio
1	**2b**	Pd/C (10 % dry) 10 mol% AgOTf (1.5 equiv)	4	-	87	76/24
2	**2b**	Pd/C (10 % dry) 10 mol% AgOTf (1.5 equiv)	4	Hg (one drop)	-	-
3	**2b**	Pd/C (10 % dry) 10 mol% AgOTf (1.5 equiv)	4	CS_2 (0.5 equiv per metal atom)	traces	-
4	**2b**	Pd/C (10 % dry) 10 mol% AgOTf (1.5 equiv)	4	CS_2 (2 equiv per metal atom)	-	-
5	**2b**	$Pd(TFA)_2$ 10 mol% AgOTf (1.5 equiv)	2	-	92	76/24
6	**2b**	$Pd(TFA)_2$ 10 mol% AgOTf (1.5 equiv)	2	Hg (one drop)	41	74/26
7	**2b**	$Pd(TFA)_2$ 10 mol% AgOTf (1.5 equiv)	2	CS_2 (0.5 equiv per metal atom)	38	78/22
8	**2b**	$Pd(TFA)_2$ 10 mol% AgOTf (1.5 equiv)	2	CS_2 (2 equiv per metal atom)	-	-
9	**2a**	$Pd(TFA)_2$ 10 mol% Ag_2CO_3 (2 equiv)	2	-	90	85/15
10	**2a**	$Pd(TFA)_2$ 10 mol% Ag_2CO_3 (2 equiv)	2	Hg (one drop)	-	-
11	**2a**	$Pd(TFA)_2$ 10 mol% Ag_2CO_3 (2 equiv)	2	CS_2 (0.5 equiv per metal atom)	5	83/17
12	**2a**	$Pd(TFA)_2$ 10 mol% Ag_2CO_3 (2 equiv)	2	CS_2 (2 equiv per metal atom)	-	-

[a] ^{19}F NMR yields were obtained by using $PhCOCF_3$ as an internal standard.

To conclude, we described here an updated method to synthesize α-trifluoromethylacrylates by ligand-free Mirozoki-Heck reaction. The use of *t*-butyl trifluoromethylacrylate instead of methyl trifluoromethylacrylate allowed to improve the *E*:*Z* ratio of the reaction, albeit a complete stereoselectivity was not obtained. Worthy of note that the *t*-butyl acrylates were good substrates to reach relevant trifluoroacrylic acids by acid hydrolysis. Then we reported that the cheaper and useful Pd/C could be efficiently used to synthesize the methyl trifluoromethylacrylates, being a good alternative towards these relevant compounds.