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FULL PAPER

Synthesis of α-Fluorinated Acrylates by Palladium-Catalyzed Decarboxylative Olefination Reaction

Ouafa Bouazzaoui,[a,b] Kevin Rousée,[a] Joseph Kajima Mulengi,[b] Xavier Pannecoucke,[a] Jean-Philippe Bouillon,[a]* and Samuel Couve-Bonnaire[a]*

Abstract: Ligand-free palladium-catalyzed subsequent decarboxylation/olefination reaction between 2-fluorinated acrylates and benzoic acids is reported. Valuables trisubstituted 2-fluoroacrylates and 2-trifluoromethylacrylates were produced in low to excellent yields, constituting a new interesting greener synthetic alternative to these fluorinated molecules.

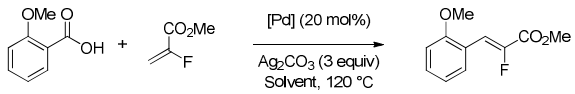
Introduction

Organofluorine chemistry has dramatically blossomed over the past decade and is now one of the most active research areas in organic synthesis. One of the main reasons of this impressive rise most certainly lies in the strong implications of fluorinated molecules in many areas of research and science (medicinal chemistry, medical imaging, agrochemistry, materials...).[1] Among the organofluorinated compounds, the fluoroacrylates family emerged as a relevant class of compounds with many different applications.[2] The fluoroacrylates are commonly synthesized by olefination reaction[3] and we recently reported the efficient Mizoroki-Heck reaction[4] between iodoarenes and α-fluoroacrylates as an effective synthetic alternative to these valuable compounds. In our program devoted to develop new routes to fluoroacrylates, we turned out our attention to the decarboxylative/olefination process which appeared as a new interesting greener way to obtain the targeted fluoroacrylates. Indeed, decarboxylative cross-coupling[5] usually involved carboxylic acids, which are common and available reagents, as coupling partners allowing to avoid a) the use of halogenated or "pseudo-halogenated" substrates or b) the use of expensive organometallic reagents or the preformation of sensitive organometallic partner. Moreover, the release of CO_2 as a by-product compared to possible toxic by-products generated by classical cross-coupling reactions makes the decarboxylative reaction a more "green" process. These last years carboxylic acids have been extensively used in various catalytic reactions such as arylation,[5,6] olefination[5,7]…In that context, the pioneering report of Myers,[8] a decade ago, about the decarboxylation/olefination reaction between aryl carboxylic acids and alkenes using simple catalytic system seemed interesting for the formation of fluorinated acrylates. We report herein, the ligand-free palladium-catalyzed decarboxylation/olefination reaction between 2-fluoroacrylates or 2-trifluoromethylacrylates and arylcarboxylic acids for the production of polysubstituted relevant fluorinated acrylates

Results and Discussion

Taking into account that at least one ortho-substituent was required for decarboxylation reaction to proceed,[5,7,8] we began to study the decarboxylative/olefination reaction with 2-methoxybenzoic acid as a model substrate.[9] We started the screening of experimental conditions using the Myers's conditions leading to poor 23% yield (Table 1, entry 1). The replacement of DMF by DMA allowed a slight increase of the reaction yield (Table 1, entry 2). The use of 1,4-dioxane in combination with DMSO enabled us to get a high 80% yield of **3a** (Table 1, entry 3). The use of 1,4-dioxane alone led to 55% yield whereas DMSO alone did not furnish the desired product (Table 1, entries 4-5).

Table 1. Optimization of the palladium-catalyzed decarboxylation/olefination reaction with methyl 2-fluoroacrylate **2**.



1a **2** (1.5 equiv) Time (h) **3a** (*Z*/*E*: > 95/5)

Entry	Solvent (95/5)	[Pd]	Time (h)	Yield[a]
1	DMF/DMSO	$Pd(TFA)_2$	4	23
2	**DMA**/DMSO	$Pd(TFA)_2$	4	31
3	**1,4-Dioxane**/DMSO	$Pd(TFA)_2$	4	80
4	**DMSO**	$Pd(TFA)_2$	4	0
5	**1,4-Dioxane**	$Pd(TFA)_2$	4	55
6	1,4-Dioxane/DMSO	$Pd(TFA)_2$	**12**	100 (92)
7[b]	1,4-Dioxane/DMSO	$Pd(TFA)_2$	12	68 (63)
8[c]	1,4-Dioxane/DMSO	$Pd(TFA)_2$	12	26
9[d]	1,4-Dioxane/DMSO	$Pd(TFA)_2$	12	7

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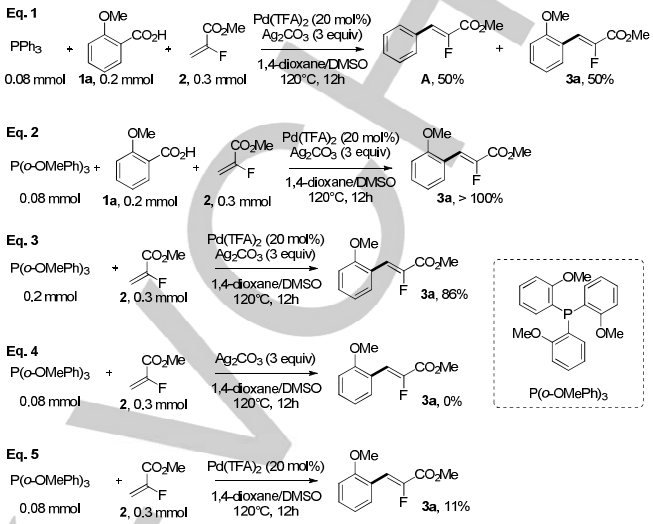
10	1,4-Dioxane/DMSO		12	0
11[e]	1,4-Dioxane/DMSO	$Pd(TFA)_2$	12	0
12	1,4-Dioxane/DMSO	**$Pd(OAc)_2$**	12	72 (66)
13	1,4-Dioxane/DMSO	**$PdCl_2$**	12	50
14	1,4-Dioxane/DMSO	**$PdBr_2$**	12	50
15	1,4-Dioxane/DMSO	**$Pd(acac)_2$**	12	20
16[f]	1,4-Dioxane/DMSO	$Pd(TFA)_2$	12	78 (71)
17[g]	1,4-Dioxane/DMSO	$Pd(TFA)_2$	12	30
18[h]	1,4-Dioxane/DMSO	$Pd(TFA)_2$	12	52 (48)

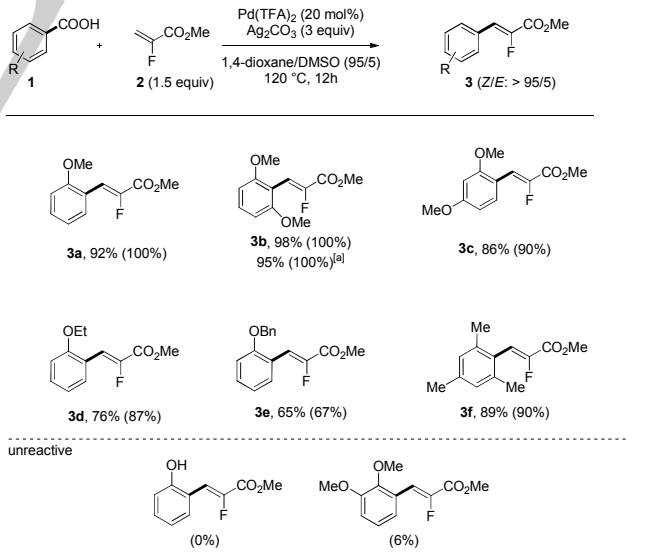
[a]^{19}F NMR yields, isolated yields in bracket. [b]1,4-Dioxane/DMSO (90:10). [c]2 equiv of Ag_2CO_3. [d]10 mol% of $Pd(TFA)_2$. [e]With K_2CO_3 as base. [f]Reaction carried out at 130°C. [g]Reaction carried out at 100°C. [h]Ratio **1a/2** = 1.5/1.

Extended reaction time to 12h allowed us to get a complete conversion with an excellent isolated yield of 92% in **3a** (Table 1, entry 6). The modification of 1,4-dioxane/DMSO ratio to 90:10 or the use of only 2 equivalents of base as well as the use of 10 mol% catalyst only led to lower yields (Table 1, entries 7-9). The presence of palladium catalyst as well as silver carbonate was crucial for the reaction to succeed (Table 1, entries 10-11). The change of palladium source (Table 1, entries 12-15) did not improve yields, giving evidence that palladium triflate was more adapted for this kind of reaction, as already demonstrated in Fu and Liu's report.[10] Finally, the modification of the reaction temperature (Table 1, entries 16-17) or the change of **1a/2** ratio (Table 1, entry 18) did not allow increasing the reaction yield. Then, we tried to add some common ligands in order to modify the catalytic sphere of the palladium to improve the former results. Nevertheless, the use of ligand proved to be detrimental to the reaction. The use of nitrogen-based ligand (phenanthroline) or trialkylphosphine (PCy_3, 1,2-bis(dicyclohexylphosphino)ethane (dcpe), P(*t*-Bu)$_3$) only led to non-reaction or poor NMR yield (<40%). The use of more common triphenylphosphine as a ligand led to an intriguish mixture of products, *i.e.* **3a** along with methyl 3-phenyl-2-fluoroacrylate **A** (Scheme 1, Eq. 1) whereas the use of tris(*o*-methoxyphenyl)phosphine as a ligand led to a NMR yield superior to 100% of **3a** (Scheme 1, Eq. 2). Regarding the literature precedent, it appears that our experimental conditions were closed to those used in palladium-catalyzed oxidative olefination reaction of triarylphosphines with alkenes via C-P bond cleavage. Indeed, this kind of reaction was already reported by several authors as early as the sixties[11] and more recently triarylphosphine was used in various catalytic reactions as a source of aryl moiety.[12] So, our side-product would come from the C-H activation of the aryl moiety of the phosphine ligand followed by phosphorous-carbon bond cleavage to give an aryl-palladium reactive intermediate. To confirm this hypothesis, we engaged only tris(*o*-methoxyphenyl)phosphine with 2-fluoroacrylate **2**, without any use of carboxylic acid **1a**. Under our experimental conditions we were able to obtain the corresponding product **3a** in good yield. (Scheme 1, Eq. 3). As expected, the absence of palladium did not allow the C-H activation step (Scheme 1, Eq. 4) whereas the absence of silver carbonate implied the non-reoxidation of palladium at the end of the catalytic cycle furnishing only 11% yield of **3a** (Scheme 1, Eq. 5). Although this side-reaction was not the heart of this manuscript, it seemed important to communicate about it.



Scheme 1. Effect of the addition of triarylphosphines on the decarboxylation/olefination reaction (NMR yields indicated).

Nevertheless, to prevent any undesired side reaction, we decided to use the ligand-free optimal experimental conditions (Table 1, entry 6) to study the scope of the reaction. It is worth noting that it was not necessary to carry out the reaction under inert atmosphere or using dry vials strongly simplifying the experimental procedure.

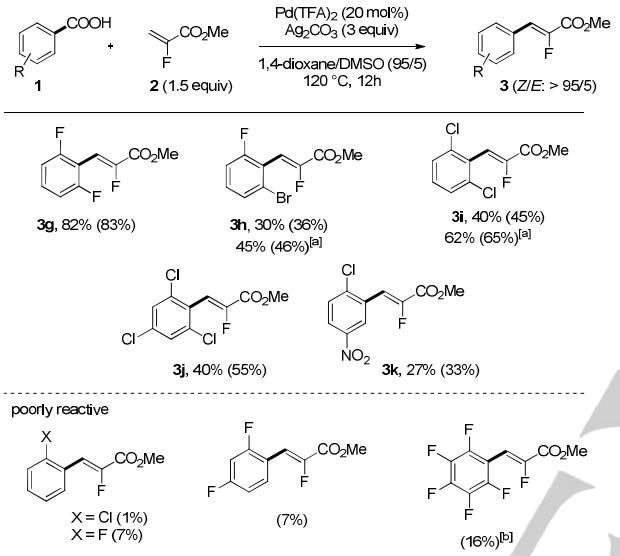


Scheme 2. Scope of decarboxylation/olefination reaction with electron rich carboxylic acids (isolated yields indicated, NMR yields under brackets). [a]On 1.2 mmol of acid **1b**.

First, we studied electron-rich benzoic acids (Scheme 2). Good results were obtained with 2-methoxy (**1a**), 2,6-dimethoxy (**1b**) and 2,4-dimethoxybenzoic acids (**1c**). The use of 2-ethoxy (**1d**)

as well as the valuable 2-benzyloxybenzoic acids (**1e**) proved to be compatible yielding products **3d** and **3e** in 76% and 65%, respectively. 2,4,6-Trimethylbenzoic acid (**1f**) proved also to be highly reactive furnishing product **3f** in 89% yield. Nevertheless, some enriched substrates revealed to be unreactive such as 2-hydroxy- or more surprisingly 2,3-dimethoxybenzoic acids.

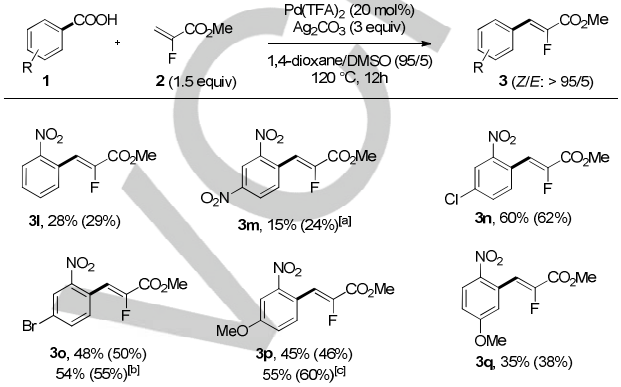
Next, we turned our attention to halogenated benzoic acids (Scheme 3). 2,6-Difluorobenzoic acid **1g** furnished the product **3g** in good 82% yield. To get fair yield with valuable 2-bromo-6-fluorobenzoic acid **1h**, it was necessary to decrease the reaction time to 6h at 140°C allowing us to get product **3h** in 45% yield. It has to be noted that no side-reaction occurred at the bromo position.



Scheme 3. Scope of decarboxylation/olefination reaction with halogenated carboxylic acids (isolated yields indicated, NMR yields under brackets). [a]At 140°C for 6h. [b]1h.

2,6-Dichlorobenzoic acid **1i** proved to be less reactive that the fluorinated acid **1g** giving 62% yield of **3g** at 140°C in 6h. Surprisingly, 2,4,6-trichlorobenzoic acid led to **3j** in only 40% yield and no improvement was observed modifying either the reaction time or the temperature. 2-Chloro-5-nitrobenzoic acid **1k** was less reactive furnishing 27% yield of **3k**. 2-Fluoro, 2-chloro and 2,4-difluorobenzoic acids proved to be almost unreactive in our experimental conditions. With 2-fluoro and 2,4-difluorobenzoic acids, we could monitor the reaction by ^{19}F NMR analysis. These experiments showed only poor conversion with the acid remaining almost unaffected by the decarboxylation step, *ie*. absence of fluorobenzene or 1,3-difluorobenzene at the end of the reaction. Pentafluorobenzoic acid gave only 16% NMR yield after 1h of reaction, whereas longer reaction times led to decreased yields.

Finally, some benzoic acids with electron-withdrawing groups were checked for the reaction (Scheme 4). Globally, all substrates gave poor to fair yields of reaction. As a matter of fact, compound nitro **1l** gave 28% yield of **3l**. Introduction of an additional nitro group in para-position of acid moiety (**1m**) decreased the yield of the reaction to 15%. Introducing a halogenated moiety (4-chloro **1n**, or 4-bromo **1o**) allowed us to get better yields with 60% of **3n** and 54% of **3o** respectively, without any side reactions at the halogenated position. Introducing an electron-donating methoxy group did not really increase the reaction yield producing the 2-fluoroacrylate **3p** in 55% yield at 140°C for 6h. Moving the methoxy group in position 5 gave the product **3q** in 35% yield. Taking into account, all these results, it was rather difficult to rationalize them in terms of steric or electronic effect.



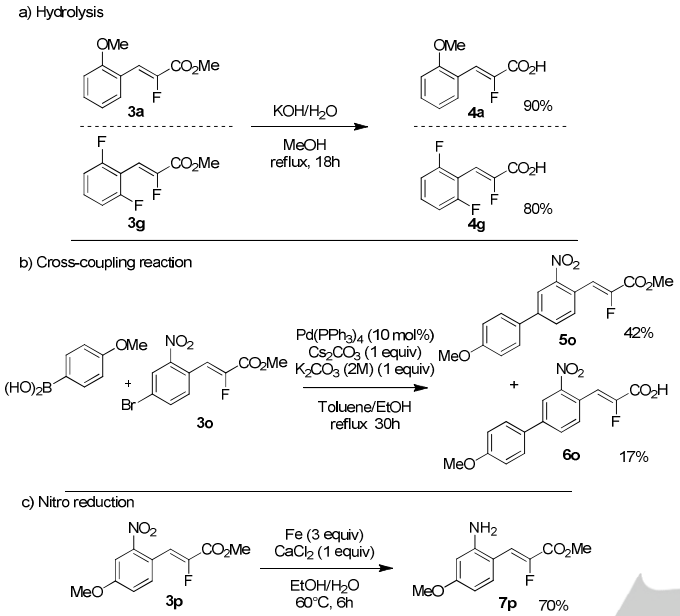
Scheme 4. Scope of decarboxylation/olefination reaction with electron-poor carboxylic acids (isolated yields indicated, NMR yields under brackets). [a](Z)/(E): 81:19. [b]On 0.8 mmol of acid **1m**, (Z)/(E): 90/10. [c]At 140°C for 6h.

While numerous catalytic systems were described to do such decarboxylation/olefination reaction,[4,7] with our ($Pd(TFA)_2$/Ag_2CO_3) system we assume that the mechanism should occur, as previously reported by Myers[8] and later supported by Fu and Liu's report[10], in four steps: a first decarboxylation step and concomitant formation of arylpalladium species, followed by olefin insertion, β-H elimination and regeneration of Pd(II) active catalyst by the oxidant (Ag_2CO_3). The latter being supported by the presence of metallic silver (Ag(0)-silver mirror) at the end of the reaction. The recent work published in 2016 by Jana[7g] pointed out two possible mechanistic pathways depending on the electronic nature of benzoic acids while these observations were only based on highly activated substrates, *i.e.* 2,6-dialkyloxy or 2,4,6-trimethoxybenzoic acids for electron rich substrates and pentafluorobenzoic acids for electron-poor substrates. Their study suggested that DMSO was not required with electron poor benzoic acids but this hypothesis was only demonstrated with pentafluorobenzoic acids; DMSO at high temperature (120°C) was required when using other perfluorobenzoic acids (2,4,5,6-tetrafluoro- and 2,6-difluorobenzoic acids). Moreover their reaction conditions were inefficient with activated alkenes such as methyl acrylate suggesting that their mechanistic proposition was inappropriate with our methyl 2-fluoroacrylate **2**.

Concerning the stereoselectivity, in all reactions presented above, the *Z*-stereoisomer was always the major one (>95%) and was easily detected by ^{19}F NMR with a characteristic coupling constant value ranging from 31 to 40 Hz. The *Z*-selectivity arised from the β-hydride elimination step where the Pd−C*α* and C*β*−H bonds needed to be aligned in a *syn* coplanar arrangement.[13] The formation of the *Z*-isomer was favoured by the steric hindrance of

the ester group with the aryl moiety implying a *trans* relationship between these two entities (see Scheme 7, Eq. 1).[4]

Then, to showcase the usefulness of our fluoroacrylates, we demonstrated the possible post-functionnalization into various relevant molecules (Scheme 5).

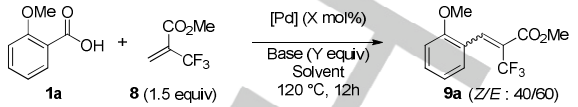


Scheme 5. Chemical transformations of various 2-fluoroacrylates (isolated yields indicated).

First, hydrolysis of 2-fluoroacrylates **3a** and **3g** with KOH in MeOH/H_2O afforded 2-fluoroacrylic acids **4a** and **4g** in 90% and 80% yields, respectively. These carboxylic acids could serve as starting materials for further decarboxylative/C-H fluoroalkenylation of heteroarenes.[14] Then, we submitted compound **3o** to a Suzuki cross-coupling[15] giving the coupling-product **5o** in 42% yield along with the corresponding acid **6o** in 17% yield, the latter arising from the *in situ* hydrolysis of **5o** during the course of the reaction. Finally, the reduction of the nitro group[16] of **3p** led to the corresponding free amine **7p** in 70% yield.

To expand the scope of decarboxylative/olefination process we decided to use the valuable 2-trifluoromethylacrylate **8** in order to get the corresponding relevant 3-aryl-2-trifluoromethyl-acrylates **9**. Very few methods are described in the literature to synthesize these compounds,[17] essentially by copper-mediated trifluoromethylation of halogenated alkenes; therefore, this decarboxylative/olefination reaction could be considered as a new interesting way to access to such compounds. Starting from our optimal procedure used with methyl 2-fluoroacrylate **2**, we tested different experimental conditions with the model substrate **1a** to find the best catalytic system in order to afford 3-aryl-2-trifluoromethylacrylates **9** in high yields (Table 2).

Table 2. Optimization of the palladium-catalyzed decarboxylation/olefination reaction with methyl 2-trifluoromethylacrylate **8**.



1a **8** (1.5 equiv) **9a** (*Z*/*E* : 40/60)

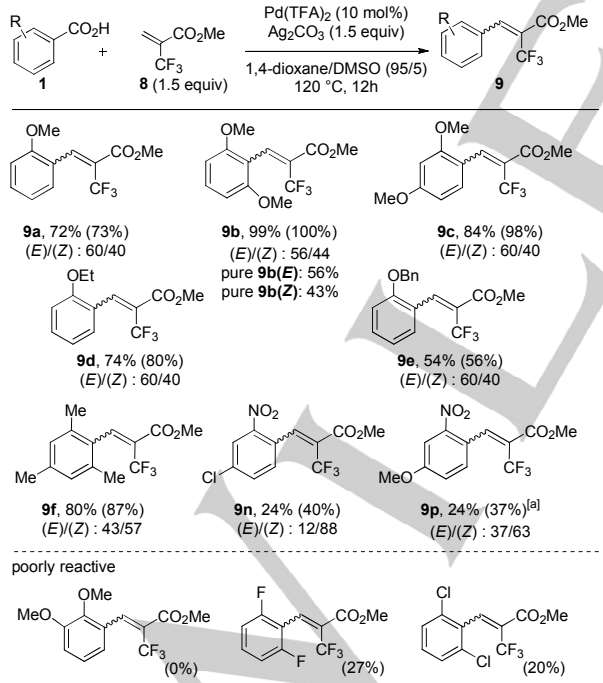
Entry	Ratio **1a/8**	Solvent (95/5)	[Pd] (X mol%)	Base (Y equiv)	Yield[a]
1	1/2	1,4-dioxane/DMSO	$Pd(TFA)_2$ (20)	Ag_2CO_3 (3)	75
2	**1/1.5**	1,4-dioxane/DMSO	$Pd(TFA)_2$ (20)	Ag_2CO_3 (3)	75 (74)
3	**1/1**	1,4-dioxane/DMSO	$Pd(TFA)_2$ (20)	Ag_2CO_3 (3)	67
4	**1.5/1**	1,4-dioxane/DMSO	$Pd(TFA)_2$ (20)	Ag_2CO_3 (3)	63
5	1/1.5	**1,4-dioxane**	$Pd(TFA)_2$ (20)	Ag_2CO_3 (3)	7
6	1/1.5	**DMSO**	$Pd(TFA)_2$ (20)	Ag_2CO_3 (3)	-
7	1/1.5	1,4-dioxane/DMSO	**$Pd(OAc)_2$** (20)	Ag_2CO_3 (3)	28
8	1/1.5	1,4-dioxane/DMSO	$Pd(TFA)_2$ (**10**)	Ag_2CO_3 (3)	73 (70)
9	1/1.5	1,4-dioxane/DMSO	$Pd(TFA)_2$ (**5**)	Ag_2CO_3 (3)	17
10	1/1.5	1,4-dioxane/DMSO	$Pd(TFA)_2$ (10)	Ag_2CO_3 (**2**)	73 (69)
11	1/1.5	1,4-dioxane/DMSO	$Pd(TFA)_2$ (10)	Ag_2CO_3 (**1.5**)	73 (72)
12	1/1.5	1,4-dioxane/DMSO	$Pd(TFA)_2$ (10)	Ag_2CO_3 (**1**)	65 (60)
13	1/1.5	1,4-dioxane/DMSO	$Pd(TFA)_2$ (10)	Ag_2CO_3 (**0.5**)	44 (40)
14[b]	1/1.5	1,4-dioxane/DMSO	$Pd(TFA)_2$ (10)	Ag_2CO_3 (2)	26
15	1/1.5	1,4-dioxane/DMSO	$Pd(TFA)_2$ (10)	**Cs_2CO_3** (2)	-

[a] ^{19}F NMR yields, isolated yields in bracket. [b] Reaction carried out at 100°C.

The optimal ratio between carboxylic acid and 2-trifluoromethylacrylate was found to be 1 equiv of **1a** for 1.5 equiv of **4** (Table 2, entries 1-4). Once again, the use of 1,4-dioxane along with DMSO proved to be crucial for the reaction to occur, the use of pure 1,4-dioxane or pure DMSO as a solvent giving poor yield or no reaction, respectively (Table 2, entries 5-6). Palladium acetate was not efficient giving only a poor 28% yield of product **9a** (Table 2, entry 7). We were pleased to see that the reaction could be as efficient with 10 mol% of $Pd(TFA)_2$ catalyst as with 20 mol% catalyst (Table 2, entry 8), this latter amount being required with 2-fluoroacrylate **2** (see Table 1). Decreasing the catalyst loading to 5 mol% led to poor yield of reaction (Table

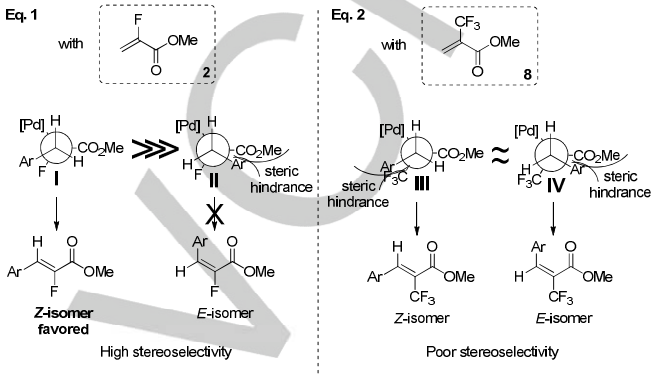
2, entry 9). Interestingly, we could decrease the number of equivalent of silver carbonate to 1.5 equivalent without loss of efficiency (Table 2, entries 10-11). The reaction with 1 or 0.5 equivalent of base proved to be less efficient (Table 2, entries 12-13). The decrease of temperature or the use of other base such as caesium carbonate was not suitable for the reaction to occur (Table 2, entries 14-15). Therefore, we decided to use 10 mol% of $Pd(TFA)_2$ and 1.5 equiv of Ag_2CO_3 in 1,4-dioxane/DMSO (95/5) as optimal conditions for the synthesis of 2-trifluoromethylacrylates **9** (Scheme 6).

The decarboxylation/olefination with 2-trifluoromethyl reagent **8**, gave only good yield with electron-rich carboxylic acids. Whereas product **9a** was isolated in 72% yield, more enriched carboxylic acid **1b** and **1c** allowed to increase the yield of **9b** and **9c** to 99% and 84%, respectively. From **9b**, it was possible to isolate each stereoisomer separately allowing us to assign without any doubt the configuration of the double bond, by HOESY experiments (see SI). 2-Ethoxy (**1d**) and 2-benzyloxy (**1e**) benzoic acids gave good (74%) to fair (54%) yields of **9d** and **9e**, respectively. The yield was also very good for **9f** (80%) starting from the 2,4,6-trimethylbenzoic acid **1f**. Switching to electron-poor carboxylic acid **1n** and **1p** bearing a nitro group in *ortho* position of the acid moiety led only to low 24% yield of products **9n** and **9p**. Interestingly, the diastereoselectivity was reversed in these cases probably because of electronic and steric repulsions between the nitro and the trifluoromethyl groups. Finally, as with methyl 2-fluoroacrylate **2**, the 2,3-dimethoxybenzoic acid did not react with fluorinated reagent **8** whereas dihalogenated benzoic acids were only poorly reactive giving less than 27% of NMR yield.



Scheme 6. Scope of decarboxylation/olefination reaction with carboxylic acids and methyl 2-trifluoromethylacrylate **8** (isolated yields indicated, NMR yields under brackets). [a]24h.

In the case of methyl 2-trifluoromethylacrylate **8**, the reaction was not as stereoselective as with methyl 2-fluoroacrylate **2**,[4] and the ratios of diastereoisomer (*E*)/(*Z*) were ranged from 60/40 to 12/88. This loss of stereoselectivity was probably due to lack of steric control between CF_3 and ester moieties implying a poor differenciation between both possible intermediates **III** and **IV** for the β-hydride elimination step (Scheme 7, Eq. 2).



Scheme 7. Intermediates (**I-IV**) for the β-hydride elimination reaction with both acrylates **2** and **8**.

Conclusions

We developed a decarboxylation/olefination reaction between carboxylic acids and methyl 2-fluoroacrylate **2** affording the desired trisubstituted fluoroalkenes in various yields depending on the electronic demand of the carboxylic acids. The use of phosphine ligand was inappropriate and led to undesired side-reaction. To prevent the latter, we used a ligand-free palladium-catalyzed decarboxylative olefination process enabling us to obtain excellent to good yields with electron-rich carboxylic acids and fair to low yields with electron-poor carboxylic acids. We then functionnalized some polysubstituted 2-fluoroacrylates by hydrolysis, reduction of nitro group or also cross-coupling reactions. Finally, we extended the reaction to the synthesis of highly valuable trisubstituted 2-trifluoromethylacrylates. Taking into account few reactions reported in the literature to get these compounds, the decarboxylative olefination reaction appeared as an interesting alternative. Excellent to moderate yields were only obtained with electron-rich carboxylic acids. The development of new effective catalytic reactions towards trifluoromethylalkenes are currently under study and will be reported in due course.

Experimental Section

General information: methyl 2-fluoroacrylate (**2**), methyl 2-trifluoro-methylacrylate (**8**), anhydrous solvents and other compounds were purchased from Sigma-Aldrich. Coupling reactions were carried out under air atmosphere, into a sealed tube. Flash chromatography was carried out using Silicaflash P60 silica gel (40-60 μm); solvents used: PE = petroleum ether, EA = ethyl acetate. Melting points (Mp) were determined on a Fisher Scientific hot stage melting point apparatus and are uncorrected. ^1H, ^{13}C

and ^{19}F NMR spectra were recorded using a Bruker Avance-300 spectrometer operating at 300 MHz (^{1}H), 75 MHz (^{13}C) and 282 MHz (^{19}F), using $CDCl_3$, CD_3OD, or DMSO-d_6 as NMR solvent. The chemical shifts (δ) were calibrated on residual proton and carbon resonances of $CDCl_3$ (^{1}H, δ = 7.26 ppm and ^{13}C, δ = 77.0 ppm) or relative to external $CFCl_3$ (^{19}F, δ = 0.0 ppm). In the ^{13}C NMR spectra, signals corresponding to CH, CH_2, or CH_3 groups were assigned from DEPT-135. The multiplicity signals were indicated with the common abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and 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 in electrospray ionization (ESI), chemical ionization (CI) or electron ionization (EI) mode.

Typical procedure for the synthesis of compounds 3: Methyl 2-fluoroacrylate (**2**) (31 mg, 0.30 mmol), 2-methoxybenzoic acid (**1a**) (30 mg, 0.20 mmol), $Pd(TFA)_2$ (14 mg, 0.04 mmol), Ag_2CO_3 (162 mg, 0.60 mmol) in a mixture DMSO (0.05 mL) and 1,4-dioxane (0.95 mL) were heated at 120°C for 12h (for compounds **3h, 3i, 3p**: at 140°C for 6h). The crude was filtrated over celite, washed with ethyl acetate (50 mL), then solvents were evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EA, 9/1) affording the desired compound **3a** in 92% yield (34 mg) as a white solid. The same procedure was applied for the synthesis of trifluoromethyl analogues **9**, except that $Pd(TFA)_2$ (10 mol %) and Ag_2CO_3 (1.5 equiv) were used.

(*Z*)-Methyl 2-fluoro-3-(2-methoxyphenyl)acrylate (3a):[4] Yellow solid. ^{19}F NMR (282 MHz, $CDCl_3$): δ -127.2 (d, *J* = 36.7Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 3.89 (s, 3H), 6.91 (d, *J* = 6.0 Hz, 1H), 7.00 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 7.43 (d, *J* = 36.7 Hz, 1H), 7.89 (dd, *J* = 7.7, 7.7 Hz, 1H).

(*Z*)-Methyl 2-fluoro-3-(2,6-dimethoxyphenyl)acrylate (3b): Yellow solid. Mp: 81-83 °C. IR: 2947, 1723, 1586, 1463, 1253, 1094, 969, 866, 779, 759 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -116.7 (d, *J* = 36.7 Hz).^{1}H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 6H), 3.88 (s, 3H), 6.57 (d, *J* = 9.0 Hz, 2H), 7.05 (d, *J* = 36.0 Hz, 1H), 7.30 (t, *J* = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.5 (d, *J* = 0.8 Hz, CH_3), 55.8 (s, 2*CH_3), 103.6 (s, 2*CH), 108.5 (d, *J* = 2.3 Hz, Cq), 110.5 (d, *J* = 9.8 Hz, CH), 130.7 (s, CH), 146.6 (d, *J* = 264.0 Hz, Cq), 158.3 (d, *J* = 0.7 Hz, 2*Cq), 161.9 (d, *J* = 35.3 Hz, Cq). HRMS (CI-TOF): calcd for $C_{12}H_{14}FO_4$ *m/z* 241.0876 $[M+H]^+$, found 241.0869. (*E*)-Isomer: ^{19}F NMR (282 MHz, $CDCl_3$): δ -117.3 (d, *J* = 19.7 Hz).

(*Z*)-Methyl 2-fluoro-3-(2,4-dimethoxyphenyl)acrylate (3c): Yellow solid. Mp: 109-111 °C. IR: 2954, 1720, 1604, 1505, 1436, 1273, 1211, 1114, 1027, 979, 837 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -130.0 (d, *J* = 36.7 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.848 (s, 3H), 3.852 (s, 3H), 3.87 (s, 3H), 6.44 (d, *J* = 2.8 Hz, 1H), 6.53 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 36.7 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.4 (s, CH_3), 55.4 (s, CH_3), 55.6 (s, CH_3), 98.1 (s, CH), 105.2 (s, CH), 111.4 (d, *J* = 3.0 Hz, CH), 113.0 (d, *J* = 5.3 Hz, Cq), 132.1 (d, *J* = 15.0 Hz, CH), 145.5 (d, *J* = 260.3 Hz, Cq), 158.9 (d, *J* = 2.3 Hz, Cq), 162.3 (d, *J* = 3.0 Hz, Cq), 162.3 (d, *J* = 34.5 Hz, Cq). HRMS (EI-TOF): calcd for $C_{12}H_{13}FO_4$ *m/z* 240.0798 $[M^+]$, found 240.0800. (*E*)-Isomer: ^{19}F NMR (282 MHz, $CDCl_3$): δ -120.0 (d, *J* = 22.6 Hz).

(*Z*)-Methyl 2-fluoro-3-(2-ethoxyphenyl)acrylate (3d): Yellow solid. Mp: 73-75 °C. IR: 2955, 1715, 1651, 1593, 1436, 1289, 1245, 1119, 1042, 975, 761 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -127.5 (d, *J* = 36.7 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.46 (t, *J* = 6.0 Hz, 3H), 3.90 (s, 3H), 4.09 (q, *J* = 6.0 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.98 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.32 (t, *J* = 6.0 Hz, 1H), 7.45 (d, *J* = 36.0 Hz, 1H), 7.89 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.7 (s, CH_3), 52.6 (s, CH_3), 64.1 (s, CH_2), 111.6 (d, *J* = 0.7 Hz, CH), 111.7 (d, *J* = 3.0 Hz, CH), 120.0 (d, *J* = 4.5 Hz, Cq), 120.6 (s, CH), 130.9 (s, CH), 131.1 (d, *J* = 2.3 Hz, CH), 146.7 (d, *J* = 264.0 Hz, Cq), 156.8 (d, *J* = 1.5 Hz, Cq), 162.1 (d, *J* = 34.3 Hz, Cq). HRMS (EI-TOF): calcd for $C_{12}H_{13}FO_3$ *m/z* 224.0850 $[M^+]$, found 224.0856. (*E*)-Isomer: ^{19}F NMR (282 MHz, $CDCl_3$): δ -118.3 (d, *J* = 22.6 Hz).

(*Z*)-Methyl 2-fluoro-3-(2-benzyloxyphenyl)acrylate (3e): Yellow liquid. IR: 2953, 1727, 1598, 1486, 1436, 1291, 1239, 1114, 1092, 973, 748 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -127.0 (d, *J* = 36.7 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): 3.90 (s, 3H), 5.20 (s, 2H), 6.95 (d, *J* = 6.0 Hz, 1H), 7.01 (t, *J* = 6.0 Hz, 1H), 7.35 (m, 6H), 7.51 (d, *J* = 36.0 Hz, 1H), 7.91 (dd, *J* = 9.0, 1.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.5 (s, CH_3), 69.4 (s, CH_2), 110.5 (d, *J* = 3.0 Hz, CH), 111.3 (s, CH), 119.4 (d, *J* = 5.3 Hz, Cq), 120.1 (s, CH), 126.1 (s, 2*CH), 127 (s, CH), 127.6 (s, 2*CH), 130.0 (d, *J* = 2.3 Hz, CH), 130.1 (d, *J* = 14.3 Hz, CH), 135.6 (s, Cq), 145.8 (d, *J* = 264.0 Hz, Cq), 155.5 (d, *J* = 2.3 Hz, Cq), 161.0 (d, *J* = 34.5 Hz, Cq). HRMS (EI-TOF): calcd for $C_{17}H_{15}FO_3$ *m/z* 286.1005 $[M^+]$, found 286.0994. (*E*)-Isomer: ^{19}F NMR (282 MHz, $CDCl_3$): -117.9 (d, *J* = 22.5 Hz).

(*Z*)-Methyl 2-fluoro-3-(2,4,6-trimethylphenyl)acrylate (3f):[4] Yellow liquid. IR: 2954, 1733, 1668, 1437, 1334, 1268, 1205, 1098, 974, 849 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -121.8 (d, *J* = 36.7 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23 (s, 6H), 2.28 (s, 3H), 3.92 (s, 3H), 6.90 (s, 2H), 7.06 (d, *J* = 36.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.5 (d, *J* = 3.0 Hz, 2*CH_3), 21.1 (s, CH_3), 52.8 (s, CH_3), 117.1 (d, *J* = 10.5 Hz, CH), 126.4 (s, Cq), 128.5 (s, 2*CH), 136.7 (d, *J* = 0.8 Hz, 2*Cq), 138.5 (s, Cq), 146.5 (d, *J* = 261.8 Hz, Cq), 162.6 (d, *J* = 35.3 Hz, Cq). HRMS (CI-TOF): calcd for $C_{13}H_{16}FO_2$ *m/z* 223.1134 $[M+H]^+$, found 223.1135.

(*Z*)-Methyl 2-fluoro-3-(2,6-difluorophenyl)acrylate (3g): Yellow liquid. IR: 2959, 1737, 1673, 1587, 1465, 1439, 1350, 1274, 1110, 975 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -107.7 (dt, *J* = 31.0, 8.5 Hz, 2F), -114.7 (dt, *J* = 33.8, 28.2 Hz, 1F). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92 (s, 3H), 6.9 - 7.0 (m, 2H), 6.96 (d, *J* = 33.0 Hz, 1H), 7.34 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.9 (s, CH_3), 105.3 (dt, *J* = 9.0, 1.5 Hz, CH), 108.5 (m, Cq), 111.5 (m, 2*CH), 131.1 (t, *J* = 9.8 Hz, CH), 148.3 (d, *J* = 271.5 Hz, Cq), 160.4 (ddd, *J* = 252.0, 6.7, 1.5 Hz, 2*Cq), 160.9 (d, *J* = 35.3 Hz, Cq). HRMS (ESI-TOF): calcd for $C_{10}H_7F_3O_2Na$ *m/z* 239.0296 $[M+Na]^+$, found 239.0303. (*E*)-Isomer: ^{19}F NMR (282 MHz, $CDCl_3$): -110.0 (m, 2F), -112.3 (dt, *J* = 16.9, 5.6 Hz, 1F).

(*Z*)-Methyl 2-fluoro-3-(2-bromo, 6-fluorophenyl)acrylate (3h): Yellow liquid. IR: 2956, 1737, 1673, 1565, 1459, 1438, 1345, 1287, 1100, 973, 884 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -104.7 (ddd, *J* = 39.5, 11.3, 5.6 Hz, 1F), -116.2 (dd, *J* = 39.5, 33.8 Hz, 1F). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93 (s, 3H), 6.95 (d, *J* = 33.0 Hz, 1H), 7.11 (t, *J* = 9.0 Hz, 1H), 7.24 (m, 1H), 7.43 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.9 (s, CH_3), 110.1 (dd, *J* = 9.0, 1.5 Hz, CH), 114.1 (d, *J* = 22.5 Hz, CH), 119.1 (dd, *J* = 18.7, 1.5 Hz, Cq), 123.3 (dd, *J* = 3.7, 1.5 Hz, Cq), 127.3 (d, *J* = 3.8 Hz, CH), 130.2 (d, *J* = 9.0 Hz, CH), 147.0 (dd, *J* = 270.7, 2.3 Hz, Cq), 159.2 (dd, *J* = 254.3, 1.5 Hz, Cq), 160.3 (d, *J* = 35.3 Hz, Cq). HRMS (EI-TOF): calcd for $C_{10}H_7{}^{81}BrF_2O_2$ *m/z* 277.9577 $[M^+]$, found 277.9572. (*E*)-Isomer: ^{19}F NMR (282 MHz, $CDCl_3$): -107.5 (m, 1F), -114.5 (dd, *J* = 16.9, 2.8 Hz, 1F).

(*Z*)-Methyl 2-fluoro-3-(2,6-dichlorophenyl)acrylate (3i): Yellow solid. Mp: 44-46 °C. IR: 2962, 1732, 1679, 1557, 1428, 1343, 1284, 1258, 1092, 972, 866 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -115.3 (d, *J* = 33.8 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93 (s, 3H), 7.02 (d, *J* = 33.0 Hz, 1H), 7.35 (m, 2H), 7.38 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.9 (s, CH_3), 111.8 (d, *J* = 9.8 Hz, CH), 127.0 (s, 2*CH), 127.8 (s, Cq), 129.2 (s, CH), 133.9 (d, *J* = 1.5 Hz, 2*Cq), 147.0 (d, *J* = 268.5 Hz, Cq), 159.8 (d, *J* = 34.5 Hz, Cq). HRMS (CI-TOF): calcd for $C_{10}H_8Cl_2FO_2$ *m/z* 248.9885 $[M+H]^+$, found 248.9892.

(*Z*)-Methyl 2-fluoro-3-(2,4,6-trichlorophenyl)acrylate (3j): Yellow solid. Mp: 99-101 °C. IR: 2963, 1736, 1683, 1577, 1437, 1349, 1286, 1099, 971, 857, 803, 787 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -114.2 (d, *J* = 31.0 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93 (s, 3H), 6.95 (d, *J* = 31.0 Hz, 1H), 7.39 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.9 (s, CH_3), 110.9 (d, *J* = 9.0 Hz, CH), 126.5 (d, *J* = 0.8 Hz, Cq), 127.1 (s, 2*CH), 134.40 (d, *J* = 0.8 Hz, 2*Cq), 134.42 (s, Cq), 147.3 (d, *J* = 270.0 Hz, Cq), 159.5 (d, *J* = 34.5 Hz, Cq). HRMS (CI-TOF): calcd for $C_{10}H_7{}^{35}Cl_3FO_2$ *m/z* 282.9496 $[M+H]^+$, found 282.9502.

(*Z*)-Methyl 2-fluoro-3-(2-chloro, 5-nitrophenyl)acrylate (3k): Yellow solid. Mp: 79-81 °C. IR: 2968, 1740, 1605, 1519, 1438, 1339, 1263, 1199, 1097, 971, 821, 738 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -120.3 (d, *J* = 31.0 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.95 (s, 3H), 7.35 (d, *J* = 30.0 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 8.17 (dd, *J* = 9.0, 3.0 Hz, 1H), 8.76 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.2 (s, CH_3), 111.3 (d, *J* = 3.0 Hz, CH), 124.9 (d, *J* = 1.5 Hz, CH), 126.0 (d, *J* = 14.3 Hz, CH), 130.5 (d, *J* = 3.8 Hz, Cq), 130.8 (s, CH), 140.6 (d, *J* = 2.3 Hz, Cq), 146.7 (s, Cq), 149.1 (d, *J* = 273.8 Hz, Cq), 160.7 (d, *J* = 34.5 Hz, Cq). HRMS (ESI-TOF): calcd for $C_{10}H_7ClFNO_4Na$ *m/z* 281.9945 $[M+Na]^+$, found 281.9951. (*E*)-Isomer: ^{19}F NMR (282 MHz, $CDCl_3$): δ -113.3 (d, *J* = 16.9 Hz).

(*Z*)-Methyl 2-fluoro-3-(2-nitrophenyl)acrylate (3l): Yellow solid. Mp: 91-93 °C. IR: 2919, 1731, 1669, 1518, 1433, 1342, 1282, 1096, 969, 867, 760 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -124.4 (d, *J* = 31.0 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93 (s, 3H), 7.42 (d, *J* = 30.0 Hz, 1H), 7.54 (t, *J* = 9.0 Hz, 1H), 7.68 (t, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 6.0 Hz, 1H), 8.08 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.0 (s, CH_3), 112.8 (d, *J* = 3.8 Hz, CH), 125.0 (s, CH), 125.6 (d, *J* = 2.3 Hz, Cq), 130.0 (s, CH), 131.8 (d, *J* = 9.0 Hz, CH), 133.4 (s, CH), 148.0 (d, *J* = 267.7 Hz, Cq), 148.1 (s, Cq), 161.0 (d, *J* = 35.3 Hz, Cq). HRMS (CI-TOF): calcd for $C_{10}H_9FNO_4$ *m/z* 226.0515 $[M+H]^+$, found 226.0510.

(*Z*)-Methyl 2-fluoro-3-(2,4-dinitrophenyl)acrylate (3m): Yellow solid. Mixture Z/E 81/19. IR: 2955, 1733, 1664, 1598, 1524, 1439, 1342, 1241, 1111, 1065, 1030, 972, 834 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -119.3 (d, *J* = 31.0 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.96 (s, 3H), 7.45 (d, *J* = 30.0 Hz, 1H), 8.05 (d, *J* = 9.0, 1H), 8.51 (dd, *J* = 9.0, 2.4 Hz, 1H), 8.92 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.4 (s, CH_3), 110.7 (d, *J* = 3.7 Hz, CH), 117.0 (s, Cq), 120.5 (s, CH), 127.4 (s, CH), 131.6 (d, *J* = 3.0 Hz, Cq), 133.2 (d, *J* = 9.7 Hz, CH), 147.7 (s, Cq), 149.6 (d, *J* = 274.5 Hz, Cq), 160.2 (d, *J* = 33.3 Hz, Cq). HRMS (EI-TOF): calcd for $C_{10}H_7FN_2O_6$ *m/z* 270.0288 $[M^+]$, found 270.0286. (*E*)-Isomer: ^{19}F NMR (282 MHz, $CDCl_3$): δ -114.7 (d, *J* = 22.6 Hz). Selected ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.71 (s, 3H), 7.21 (d, *J* = 18.0 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 9.01 (d, *J* = 3.0 Hz, 1H). Selected ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.8 (s, CH_3), 120.2 (s, CH), 127.1 (s, CH), 133.5 (d, *J* = 3.0 Hz, CH), 147.7 (d, *J* = 267.0 Hz, Cq), 148.1 (s, Cq).

(*Z*)-Methyl 2-fluoro-3-(4-chloro, 2-nitrophenyl)acrylate (3n): Yellow solid. Mp: 81-83 °C. IR: 2961, 1740, 1675, 1522, 1437, 1346, 1259, 1208, 1103, 968, 877, 763 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -123.0 (d, *J* = 31.0 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93 (s, 3H), 7.36 (d, *J* = 30.0 Hz, 1H), 7.65 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 8.07 (d, *J* = 3.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.1 (s, CH_3), 110.6 (d, *J* = 4.5 Hz, CH), 123.0 (d, *J* = 3.0 Hz, Cq), 124.2 (s, CH), 131.8 (d, *J* = 9.8 Hz, CH), 132.5 (s, CH), 134.9 (d, *J* = 1.5 Hz, Cq), 147.3 (s, Cq), 147.3 (d, *J* = 269.3 Hz, Cq), 159.7 (d, *J* = 35.3 Hz, Cq). HRMS (CI-TOF): calcd for $C_{10}H_8{}^{35}ClFNO_4$ *m/z* 260.0126 $[M+H]^+$, found 260.0124. (*E*)-Isomer: ^{19}F NMR (282 MHz, $CDCl_3$): δ -116.9 (d, *J* = 16.9 Hz). Selected ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.71 (s, 3H). Selected ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.6 (s, CH_3), 123.9 (s, CH), 130.9 (s, CH), 132.2 (s, CH), 132.7 (s, CH).

(*Z*)-Methyl 2-fluoro-3-(4-bromo, 2-nitrophenyl)acrylate (3o): Yellow solid. Mp: 91-93 °C. IR: 2957, 1738, 1667, 1528, 1438, 1344, 1242, 1210, 1093, 968, 878, 762 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -122.7 (d, *J* = 33.8 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.33 (d, *J* = 33.0 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.80 (dd, *J* = 9.0, 3.0 Hz, 1H), 8.20 (d, *J* = 3.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.1 (s, CH_3), 111.7 (d, *J* = 4.5 Hz, CH), 123.5 (d, *J* = 1.5 Hz, Cq), 124.5 (d, *J* = 1.5 Hz, Cq), 128.1 (s, CH), 133.0 (d, *J* = 9.8 Hz, CH), 136.5 (s, CH), 148.3 (s, Cq), 148.3 (d, *J* = 270.0 Hz, Cq), 160.7 (d, *J* = 35.3 Hz, Cq). HRMS (EI-TOF): calcd for $C_{10}H_7{}^{79}BrFNO_4$ *m/z* 302.9542 $[M^+]$, found 302.9540. (*E*)-Isomer: ^{19}F NMR (282 MHz, $CDCl_3$): δ -116.8 (d, *J* = 16.9 Hz). Selected ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.71 (s, 3H), 7.16 (d, *J* = 9.0 Hz, 1H), 8.37 (d, *J* = 3.0 Hz, 1H). Selected ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.6 (s, CH_3), 117.8 (d, *J* = 29.3 Hz, CH), 127.7 (s, CH), 132.0 (s, CH), 136.6 (s, CH).

(*Z*)-Methyl 2-fluoro-3-(4-methoxy, 2-nitrophenyl)acrylate (3p): Yellow solid. Mp: 111-113 °C. IR: 2957, 1722, 1613, 1523, 1494, 1318, 1249, 1241, 1067, 1030, 963, 873 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -125.9 (d, *J* = 31.0 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.91 (s, 6H), 7.19 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.34 (d, *J* = 33.0 Hz, 1H), 7.54 (d, *J* = 2.8 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.9 (s, CH_3), 56.0 (s, CH_3), 109.9 (s, CH), 112.3 (d, *J* = 3.7 Hz, CH), 117.6 (d, *J* = 3.7 Hz, Cq), 119.0 (s, CH), 132.9 (d, *J* = 10.5 Hz, CH), 147.3 (d, *J* = 265.5 Hz, Cq), 149.2 (s, Cq), 160.4 (d, *J* = 2.3 Hz, Cq), 161.2 (d, *J* = 34.5 Hz, Cq). HRMS (EI-TOF): calcd for $C_{11}H_{10}FNO_5$ *m/z* 255.0543 $[M^+]$, found 255.0528.

(*Z*)-Methyl 2-fluoro-3-(5-methoxy, 2-nitrophenyl)acrylate (3q): Beige solid. Mp: 107-109 °C. IR: 2968, 1730, 1671, 1575, 1512, 1435, 1326, 1230, 1088, 1032, 962, 893 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -125.2 (d, *J* = 31.0 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.91 (s, 3H), 3.93 (s, 3H), 7.00 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.21 (d, *J* = 3.0 Hz, 1H), 7.53 (d, *J* = 30.0 Hz, 1H), 8.17 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.0 (s, CH_3), 56.0 (s, CH_3), 113.9 (d, *J* = 3.7 Hz, CH), 114.9 (s, CH), 116.5 (d, *J* = 9.0 Hz, CH), 127.7 (s, CH), 128.3 (d, *J* = 2.3 Hz, Cq), 140.9 (s, Cq), 147.7 (d, *J* = 266.3 Hz, Cq), 161.0 (d, *J* = 35.3 Hz, Cq), 163.2 (s, Cq). HRMS (ESI-TOF): calcd for $C_{11}H_{10}FNO_5Na$ *m/z* 278.0441 $[M+Na]^+$, found 278.0443. (*E*)-Isomer: ^{19}F NMR (282 MHz, $CDCl_3$): δ -119.0 (d, *J* = 16.9 Hz).

Typical procedure for the saponification reaction: To a solution of methyl acrylate **3g** (47 mg, 0.21 mmol) in MeOH (1.5 mL) were added KOH (18 mg, 0.32 mmol) and H_2O (0.3 mL). The reaction was refluxed for 18 hours. After cooling at room temperature, the mixture was acidified to pH = 1 with 3 N HCl solution (~1.0 mL) and concentrated under vacuum. After extraction with ethyl acetate (3 x 5 mL), the organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting solid was purified over a pad of silica gel (5-6 cm, eluent: EtOAc) to afford the desired product **4g** in 80% yield (34 mg) as a white solid.

(*Z*)-2-Fluoro-3-(2-methoxyphenyl)acrylic acid (4a):[13] Colorless solid.^{19}F NMR (282 MHz, DMSO-d_6): δ -125.4 (d, *J* = 37.2 Hz). ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.86 (s, 3H), 7.03 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 7.26 (d, *J* = 37.2 Hz, 1H), 7.42 (td, *J* = 8.3, 1.6 Hz, 1H), 7.76 (dd, *J* = 7.8, 1.6 Hz, 1H), 13.62 (s, 1H).

(*Z*)-2-Fluoro-3-(2,6-difluorophenyl) acrylic acid (4g): White solid. Mp: 113-115 °C. IR: 2923, 2510, 1710, 1666, 1624, 1586, 1466, 1338, 1278, 1119, 1000, 779 cm^{-1}. ^{19}F NMR (282 MHz, CD_3OD): δ -110.5 (m, 2F), -115.3 (m, 1F). ^{1}H NMR (300 MHz, CD_3OD): δ 6.94 (d, *J* = 33.0 Hz, 1H), 7.05 (dd, *J* = 9.0, 6.0 Hz, 2H), 7.46 (m, 1H). ^{13}C NMR (75 MHz, CD_3OD): δ 105.3 (d, *J* = 9.8 Hz, CH), 109.7 (t, *J* = 19.5 Hz, Cq), 112.6 (m, 2*CH), 132.6 (t, *J* = 10.5 Hz, CH), 150.6 (d, *J* = 271.5 Hz, Cq), 161.7 (dd, *J* = 251.3, 6.7 Hz, 2*Cq), 163.0 (m, Cq). HRMS (ESI-TOF): calcd for $C_9H_4F_3O_2$ *m/z* 201.0163 $[M-H]^-$, found 201.0159.

Typical procedure for the Suzuki cross-coupling reaction of acrylate 3o with *p*-methoxyphenyl boronic acid: A mixture of methyl 2-fluoro-3-(4-bromo, 2-nitrophenyl)acrylate (**3o**) (40.0 mg, 0.13 mmol) , *p*-methoxyphenyl boronic acid (98.8 mg, 0.65 mmol), tetrakis(triphenyl-phosphine)palladium (14.5 mg, 0.013 mmol), cesium carbonate (42.4 mg, 0.13 mmol), aqueous solution of potassium carbonate (2M, 0.13 mmol), and ethanol (1 mL) in degassed toluene (15 mL) was refluxed under argon atmosphere for 30 hours. Then, the reaction mixture was cooled, diluted with a (1:1) mixture of water and ethyl acetate (20 mL) and the organic layer was separated. The aqueous phase was extracted with ethyl acetate (2 x 30 mL). The combined organic extracts were then dried over magnesium sulfate and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc) affording the desired compound **5o** in 42% yield (18 mg) as a brown solid and the corresponding acrylic acid **6o** in 17% yield (7 mg) as a brown solid.

(*Z*)-Methyl 2-fluoro-3-(4-(*p*-methoxyphenyl), 2-nitrophenyl) acrylate (5o): Brown solid. Mp: 78-80 °C. IR: 2961, 2840, 1735, 1605, 1515, 1438, 1345, 1299, 1247, 1179, 1102, 1023, 801 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -124.1 (d, *J* = 33.8 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 3.93 (s, 3H), 7.02 (d, *J* = 9.0 Hz, 2H), 7.42 (d, *J* = 33.0 Hz, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.84 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.91 (d, *J* = 6.0 Hz, 1H), 8.23 (d, *J* = 3.0 Hz, 1H). ^{13}C NMR (75 MHz, CD_3OD): δ 53.0 (s, CH_3), 55.5 (s, CH_3), 112.4 (d, *J* = 3.8 Hz, CH), 114.7 (s, 2*CH), 122.6 (s, CH), 123.2 (d, *J* = 3.0 Hz, Cq), 128.2 (s, 2*CH), 130.1 (s, Cq), 130.8 (s, CH), 132.2 (d, *J* = 10.5 Hz, CH), 143.0 (s, Cq), 148.0 (d, *J* = 267.8 Hz, Cq), 148.7 (s, Cq), 160.5 (s, Cq), 161.1 (d, *J* = 34.5 Hz, Cq). HRMS (ESI-TOF): calcd for $C_{17}H_{14}FNO_5Na$ *m/z* 354.0754 $[M+Na]^+$, found 354.0760.

(*Z*)-2-Fluoro-3-(4-(*p*-methoxyphenyl), 2-nitrophenyl) acrylic acid (6o): Brown solid. Mp: 174-176 °C. IR: 3208, 2918, 2850, 1726, 1668, 1605, 1516, 1342, 1293, 1253, 1180, 1063, 982 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -123.9 (d, *J* = 33.8 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 7.02 (d, *J* = 9.0 Hz, 2H), 7.41 (d, *J* = 33.0 Hz, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.84 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.91 (d, *J* = 6.0 Hz, 1H), 8.23 (d, *J* = 3.0 Hz, 1H).

Typical procedure for the reduction of nitroarene 3p: To a suspension of nitroarene **3p** (30 mg, 0.12 mmol) in a mixture of EtOH (1 mL) and H_2O (0.1 mL), iron powder (20 mg, 0.36 mmol), and $CaCl_2$ (16 mg, 0.14 mmol) were added. The resulting suspension was stirred at 60 °C for 6 hours (the progress of the reaction was monitored by TLC). After completion, the reaction mixture was filtered over celite to remove the iron residue, and the resulting pad was washed two times with EtOAc (2 x 10 mL). The combined organic extracts were washed with H_2O (3 × 10 mL), brine (2 × 10 mL), and dried over Na_2SO_4. After evaporation under reduced pressure, the crude product was purified by silica gel column chromatography (PE/EA, 70/30) affording the desired compound **7p** in 70% yield (19 mg) as a yellow solid.

(*Z*)-Methyl 2-fluoro-3-(2-amino, 4-methoxyphenyl) acrylate (7p): Yellow solid. Mp: 209-211 °C. IR: 3050, 2914, 2843, 1722, 1672, 1626, 1574, 1414, 1276, 1237, 1117, 1023, 906, 873 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -130.2 (d, *J* = 33.8 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H), 3.88 (s, 3H), 3.92 (br s, 2H), 6.24 (d, *J* = 3.0 Hz, 1H), 6.40 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.93 (d, *J* = 36.0 Hz, 1H), 7.62 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.5 (s, CH_3), 55.2 (s, CH_3), 101.2 (s, CH), 105.7 (s, CH), 109.4 (d, *J* = 4.5 Hz, Cq), 112.4 (d, *J* = 5.3 Hz, CH), 132.4 (d, *J* = 12.0 Hz, CH), 145.6 (d, *J* = 263.5 Hz, Cq), 146.9 (d, *J* = 1.5 Hz, Cq), 162.0 (d, *J* = 1.5 Hz, Cq), 162.2 (d, *J* = 33.8 Hz, Cq). HRMS (ESI-TOF): calcd for $C_{11}H_{13}FNO_3$ *m/z* 226.0879 $[M+H]^+$, found 226.0876.

Methyl 3-(2-methoxyphenyl)-2-trifluoromethylacrylate (9a):[16b] Yellow oil. Mixture *E/Z* 60/40. ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.8 (m, *Z*), -63.7 (m, *E*). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.71 (s, 3H, *E*), 3.83 (s, 3H, *E*), 3.84 (s, 3H, *Z*), 3.87 (s, 3H, *Z*), 6.9 – 7.0 (m, 2H, *E* + *Z*), 7.1 – 7.3 (m, 1H, *E* + *Z*), 7.3 – 7.4 (m, 1H, *E* + *Z*), 7.63 (s, 1H, *E*), 8.23 (s, 1H, *Z*).

Methyl 3-(2,6-dimethoxyphenyl)-2-trifluoromethylacrylate (9b): The two stereomers were fully separated by silica gel column chromatography. **(*E*)-Isomer**: Yellow solid. Mp: 125-127 °C. IR: 2962, 1735, 1650, 1593, 1476, 1436, 1258, 1110, 1018, 773, 734 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.63 (d, *J* = 1.7 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.68 (s, 3H), 3.81 (s, 6H), 6.54 (d, *J* = 9.0 Hz, 2H), 7.30 (t, *J* = 9.0 Hz, 1H), 8.01 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.7 (s, CH_3), 54.6 (s, 2*CH_3), 102.5 (s, 2*CH), 110.0 (s, Cq), 121.6 (q, *J* = 271.5 Hz, Cq), 122.9 (q, *J* = 30.0 Hz, Cq), 130.7 (s, CH), 132.4 (q, *J* = 6.0 Hz, CH), 157.0 (s, 2*Cq), 163.7 (m, Cq). HRMS (ESI-TOF): calcd for $C_{13}H_{13}F_3O_4Na$ *m/z* 313.0669 $[M+Na]^+$, found 313.0654. **(*Z*)-Isomer**: Yellow solid. Mp: 113-115 °C. IR: 2962, 1727, 1633, 1593, 1477, 1436, 1385, 1260, 1110, 1033, 963, 938, 765 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.67 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 6H), 3.88 (s, 3H), 6.54 (d, *J* = 9.0 Hz, 2H), 7.30 (m, 1H), 8.01 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.5 (s, CH_3), 55.6 (s, 2*CH_3), 103.3 (s, 2*CH), 111.0 (s, Cq), 122.2 (q, *J* = 272.3 Hz, Cq), 123.6 (q, *J* = 31.5 Hz, Cq), 131.5 (s, CH), 140.7 (q, *J* = 3.0 Hz, CH), 157.7 (m, 2*Cq), 163.7 (q, *J* = 1.5 Hz, Cq). HRMS (ESI-TOF): calcd for $C_{13}H_{13}F_3O_4Na$ *m/z* 313.0664 $[M+Na]^+$, found 313.0654.

Methyl 3-(2,4-dimethoxyphenyl)-2-trifluoromethylacrylate (9c): Yellow oil. Mixture *E/Z* 60/40. IR: 2955, 1725, 1605, 1504, 1438, 1320, 1289, 1265, 1209, 1112, 1028, 825 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.6 (d, *J* = 2.8 Hz, *Z*), -63.2 (d, *J* = 1.7 Hz, *E*). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.76 (s, 3H), 3.82 (s, 3H), 3.83 (s, 3H), 3.84 (s, 3H), 3.85 (s, 3H), 3.87 (s, 3H), 6.4-6.5 (m, 2H, *E* + *Z*), 7.2 – 7.3 (m, 1H, *E* + *Z*), 7.60 (m, 1H, *E*), 8.22 (s, 1H, *Z*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.2 (s, CH_3, *E*), 52.4 (s, CH_3, *Z*), 55.41 (s, CH_3), 55.43 (s, CH_3), 55.5 (s, CH_3), 55.6 (s, CH_3), 97.8 (s, CH, *Z*), 98.1 (s, CH, *E*), 104.8 (s, CH, *Z*), 104.9 (s, CH, *E*), 114.2 (s, Cq, *E*), 114.3 (s, Cq, *Z*), 119.3 (q, *J* = 31.5 Hz, Cq, *Z*), 120.2 (q, *J* = 30.8 Hz, Cq, *E*), 122.5 (q, *J* = 272.3 Hz, Cq, *Z*), 122.7 (q, *J* = 270.8 Hz, Cq, *E*), 132.1 (q, *J* = 3.8 Hz, CH, *Z*), 136.8 (q, *J* = 6.0 Hz, CH, *E*), 144.3 (q, *J* = 3.0 Hz, CH, *Z*), 159.3 (s, Cq, *E*), 159.5 (s, Cq, *Z*), 163.2 (s, Cq, *E*), 163.5 (s, Cq, *Z*), 164.3 (q, *J* = 1.5 Hz, Cq, *E*), 164.4 (m, Cq, *Z*). HRMS (ESI-TOF): calcd for $C_{13}H_{13}F_3O_4Na$ *m/z* 313.0664 $[M+Na]^+$, found 313.0668.

Methyl 3-(2-ethoxyphenyl)-2-trifluoromethylacrylate (9d): Yellow oil. Mixture *E/Z* 60/40. IR: 2987, 1729, 1643, 1599, 1455, 1438, 1251, 1219, 1158, 1119, 1036, 926, 750 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.7 (d, *J* = 1.4 Hz, *Z*), -63.8 (d, *J* = 1.7 Hz, *E*). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 – 1.46 (m, 3H, *E* + *Z*), 3.73 (s, 3H, *E*), 3.89 (s, 3H, *E* + *Z*), 4.04 - 4.13 (m, 2H, *E* + *Z*), 6.88 – 6.97 (m, 2H, *E* + *Z*), 7.26 – 7.39 (m, 2H, *E* + *Z*), 7.68 (s, 1H, *E*), 8.26 (s, 1H, *Z*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.59 (s, CH_3),14.62 (s, CH_3), 52.2 (s, OCH_3, *E*), 52.6 (s, OCH_3, *Z*), 64.0 (s, OCH_2, *Z*), 64.2 (s, OCH_2, *E*), 111.3 (s, CH, *Z*), 111.8 (s, CH, *E*), 120.0 (s, CH, *Z*), 120.2 (s, CH, *E*), 121.7 (s, Cq, *E*), 121.9 (s, Cq, *Z*), 122.2 (q, *J* = 271.5 Hz, Cq, *Z*), 122.4 (q, *J* = 272.3 Hz, Cq, *E*), 122.9 (q, *J* = 30.0 Hz, Cq, *Z*), 123.6 (q, *J* = 31.5 Hz, Cq, *E*), 129.8 (s, CH, *E*), 130.4 (q, *J* = 3.8 Hz, CH, *Z*), 131.84 (s, CH, *Z*), 131.88 (s, CH, *E*), 137.6 (q, *J* = 6.0 Hz, CH, *E*), 145.3 (q, *J* = 3.0 Hz, CH, *Z*), 156.9 (s, Cq, *Z*), 157.0 (s, Cq, *E*), 163.95 (q, *J* = 3.8 Hz, Cq, *E*), 163.98 (m, Cq, *Z*). HRMS (ESI-TOF): calcd for $C_{13}H_{13}F_3O_3Na$ *m/z* 297.0714 $[M+Na]^+$, found 297.0710.

Methyl 3-(2-benzyloxyphenyl)-2-trifluoromethylacrylate (9e): Yellow oil. Mixture *E/Z* 60/40. IR: 2955, 1728, 1642, 1600, 1487, 1437, 1257, 1217, 1159, 1113, 1042, 915, 750 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.4 (d, *J* = 1.1 Hz, *Z*). -63.7 (d, *J* = 1.7 Hz, *E*). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.70 (s, 3H), 3.89 (s, 3H), 5.14 (s, 2H), 5.17 (s, 2H), 6.97 (m, 2H), 7.2 – 7.4 (m, 7H), 7.75 (m, 1H, *E*), 8.34 (s, 1H, *Z*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.3 (s, CH_2), 52.7 (s, CH_2), 70.40 (s, CH_3), 70.49 (s, CH_3), 112.2 (s, CH),

112.6 (s, CH), 120.6 (s, CH), 120.8 (s, CH), 122.10 (s, Cq), 122.12 (q, *J* = 272.3 Hz, Cq), 122.29 (s, Cq,), 122.30 (q, *J* = 33.0 Hz, Cq), 122.32 (q, *J* = 271.5 Hz, Cq), 123.0 (q, *J* = 31.5 Hz, Cq), 126.99 (s, 2*CH), 127.03 (s, 2*CH), 128.04 (s, CH), 128.08 (s, CH), 128.66 (s, 2*CH), 128.67 (s, 2*CH), 129.8 (s, CH), 130.5 (q, *J* = 3.8 Hz, CH), 131.85 (s, CH), 131.89 (s, CH), 136.4 (s, Cq), 136.5 (s, Cq), 137.6 (q, *J* = 6.0 Hz, CH), 145.2 (q, *J* = 3.0 Hz, CH), 156.6 (s, Cq), 156.7 (s, Cq), 163.8 (m, Cq), 163.9 (m, Cq). HRMS (ESI-TOF): calcd for $C_{18}H_{15}F_3O_3Na$ *m/z* 359.0871 $[M+Na]^+$, found 359.0876.

Methyl 3-(2,4,6-trimethylphenyl)-2-trifluoromethylacrylate (9f): Yellow oil. Mixture *E/Z* 43/57. IR: 2957, 1733, 1648, 1438, 1379, 1271, 1229, 1167, 1132, 1044, 851 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -61.7 (s, *Z*), -64.0 (d, *J* = 2.8 Hz, *E*). ^1H NMR (300 MHz, $CDCl_3$): δ 2.15 (d, *J* = 3.0 Hz, 6H, *E* + *Z*), 2.28 (s, 3H, *E* + *Z*), 3.63 (s, 3H, *E*), 3.92 (s, 3H, *Z*), 6.87 (s, 2H, *E* + *Z*), 7.64 (s, 1H, *E*), 8.14 (s, 1H, *Z*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.8 (s, 2*CH_3), 19.0 (s, 2*CH_3), 19.9 (s, CH_3), 20.0 (s, CH_3), 51.2 (s, OCH_3, *E*), 51.7 (s, OCH_3, *Z*), 120.8 (q, *J* = 273.0 Hz, Cq, *Z*), 121.0 (q, *J* = 271.5 Hz, Cq, *E*), 124.1 (q, *J* = 30.8 Hz, Cq, *Z*), 125.1 (q, *J* = 30.0 Hz, Cq, *E*), 127.0 (s, 2*CH), 127.2 (s, 2*CH), 128.6 (s, Cq, *E*), 128.8 (s, Cq, *Z*), 132.8 (m, Cq, *Z*), 133.4 (s, Cq, *E*), 136.9 (s, Cq, *Z*), 137.0 (s, Cq, *E*), 143.8 (q, *J* = 5.3 Hz, CH, *E*), 148.3 (q, *J* = 3.0 Hz, CH, *Z*), 161.4 (s, Cq, *E*), 162.0 (m, Cq, *Z*). HRMS (ESI-TOF): calcd for $C_{14}H_{15}F_3O_2Na$ 295.0922 *m/z* $[M+Na]^+$, found 295.0914

Methyl 3-(4-chloro, 2-nitrophenyl)-2-trifluoromethylacrylate (9n): Yellow oil. Mixture *E/Z* 12/88. IR: 2959, 1732, 1655, 1561, 1531, 1438, 1384, 1344, 1289, 1267, 1134, 1043, 891 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.1 (s, *Z*), -64.3 (d, *J* = 1.7 Hz, *E*). ^1H NMR (300 MHz, $CDCl_3$): δ 3.66 (s, 3H, *E*), 3.94 (s, 3H, *Z*), 7.30 (d, *J* = 9.0 Hz, 1H, *Z*), 7.69 (dd, *J* = 9.0, 3.0 Hz, 1H, *Z*), 7.96 (s, 1H, *E*), 8.26 (d, *J* = 3.0 Hz, 1H, *E*), 8.28 (d, *J* = 3.0 Hz, 1H, *Z*), 8.36 (s, 1H, Z). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.6 (s, CH_3, *E*), 53.1 (s, CH_3, *Z*), 121.5 (q, *J* = 273.0 Hz, Cq, *Z*), 123.6 (q, *J* = 31.5 Hz, Cq, *Z*), 125.1 (s, CH, *E*), 125.2 (s, CH, *Z*), 128.1 (s, Cq, *Z*), 128.5 (s, Cq, *E*), 131.0 (m, CH, *E*), 131.1 (q, *J* = 3.0 Hz, CH, *Z*), 133.9 (s, CH, *E*), 134.0 (s, CH, *Z*), 136.2 (s, Cq, *E*), 136.4 (s, Cq, *Z*), 141.9 (m, Cq, *E*), 144.7 (q, *J* = 3.0 Hz, CH, *Z*), 146.3 (s, Cq, *Z*), 162.4 (m, Cq, *Z*). HRMS (ESI-TOF): calcd for $C_{11}H_7ClF_3NO_4Na$ *m/z* 331.9913 $[M+Na]^+$, found 331.9906.

Methyl 3-(4-methoxy, 2-nitrophenyl)-2-trifluoromethylacrylate (9p): Yellow oil. Mixture *E/Z* 37/63. IR: 2959, 1731, 1620, 1529, 1499, 1439, 1345, 1276, 1251, 1130, 1032, 843, 804 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ -58.0 (s, *Z*), -64.1 (d, *J* = 1.7 Hz, *E*). ^1H NMR (300 MHz, $CDCl_3$): δ 3.66 (s, 3H, *E*), 3.92 (s, 6H, *Z*), 3.93 (s, 3H, *E*), 7.1- 7.3 (m, 2H, *E* + *Z*), 7.75 (dd, *J* = 9.0, 3.0 Hz, 1H, *Z*), 7.95 (m, 1H, *E*), 8.38 (s, 1H, *Z*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.5 (s, CH_3, *E*), 52.9 (s, CH_3, *Z*), 56.0 (s, CH_3, *E*), 56.1 (s, CH_3, *Z*), 109.47 (s, CH, *E*), 109.52 (s, CH, *Z*), 120.2 (s, CH, *E*), 120.3 (s, CH, *Z*), 121.5 (s, Cq, *Z*), 121.7 (q, *J* = 273.0 Hz, Cq, *Z*), 121.78 (s, Cq, *E*), 121.79 (q, *J* = 271.5 Hz, Cq, *E*), 122.4 (q, *J* = 30.8 Hz, Cq, *Z*), 123.5 (q, *J* = 31.5 Hz, Cq, *E*), 131.2 (s, CH), 131.4 (q, *J* = 3.0 Hz, CH), 142.2 (q, *J* = 6.8 Hz, CH, *E*), 146.1 (q, *J* = 3.0 Hz, CH, *Z*), 147.0 (s, Cq, *Z*), 147.5 (s, Cq, *E*), 160.8 (s, Cq, *E*), 160.9 (s, Cq, *Z*), 162.4 (s, Cq, *E*), 162.9 (q, *J* = 1.5 Hz, Cq, *Z*). HRMS (ESI-TOF): calcd for $C_{12}H_{10}F_3NO_5Na$ *m/z* 328.0409 $[M+Na]^+$, found 328.0403.

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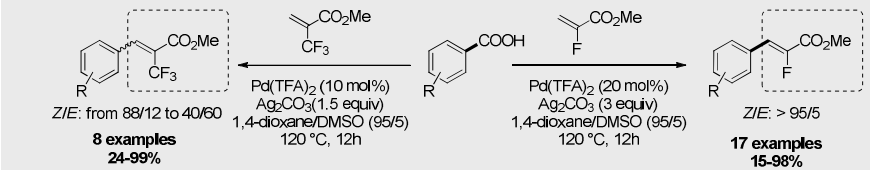

A ligand-free palladium-catalyzed decarboxylative olefination process is reported between carboxylic acids and valuables methyl 2-fluoroacrylate or methyl 2-trifluoromethylacrylate. The reaction affords the desired trisubstituted fluorinated alkenes in low to fair yields with electron-poor carboxylic acids and good to excellent yields with electron-rich carboxylic acids.

Decarboxylation/fluoroalkenylation*

Ouafa Bouazzaoui, Kevin Rousée, Joseph Kajima Mulengi, Xavier Pannecoucke, Jean-Philippe Bouillon, Samuel Couve-Bonnaire**

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Synthesis of α-Fluorinated Acrylates by Palladium-Catalyzed Decarboxylative Olefination Reaction