

# An industrially usable Pd-catalyzed carboalkoxylation of 1,2-dibromo-3,3,3-trifluoropropane to *tert*-butyl trifluoromethacrylate in the presence of an inorganic base

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## Abstract

Pd-catalyzed carboalkoxylation of 1,2-dibromo-3,3,3-trifluoropropane **1** with *tert*-butyl alcohol to provide *tert*-butyl trifluoromethacrylate was improved from a practical standpoint. The addition of an inorganic base, specifically  $\text{Li}_2\text{CO}_3$ , surmounted the previous disadvantages of low reactivity and selectivity.  $\text{Li}_2\text{CO}_3$  not only accelerated the reaction drastically but also suppressed the further reaction of the methacrylate and alcohol completely. It is suggested that the role of  $\text{Li}_2\text{CO}_3$  is to stabilize an acylpalladium *tert*-butoxide intermediate, while HBr and/or  $\text{H}^+$  were scarcely abstracted from the substrates by  $\text{Li}_2\text{CO}_3$ . Research on the optimal conditions resulted in a satisfactory yield (*ca.* 70%) of *tert*-butyl trifluoromethacrylate under mild conditions (CO 10 atm, 100 °C and 15 h) in ethyl acetate solvent with 0.05 mol%  $\text{PdCl}_2(\text{PPh}_3)_2$ . This carboalkoxylation was also usable for other bulky alcohols.

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**Keywords:** Carboalkoxylation; Palladium catalyst; Lithium carbonate; Trifluoromethacrylate; 1,2-Dibromo-3,3,3-trifluoropropane

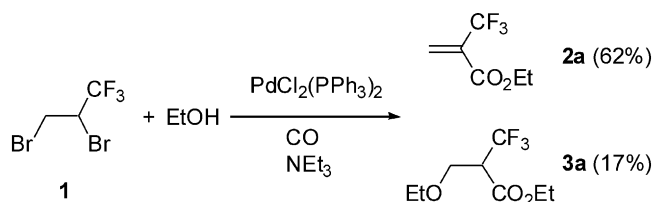
## 1. Introduction

Fluorinated organic compounds are valuable materials in the areas of medicinal, agricultural and material sciences. Several *tert*-alkyl trifluoromethacrylates are known to be important monomers, of which homo- and co-polymers are used as photoresists and optical fibers [1]. These trifluoromethacrylates can be synthesized through esterification of 2-(trifluoromethyl)acrylic acid and corresponding *tertiary* alcohols; the former is readily available by use of Pd-catalyzed carbohydroxylation of 1,2-dibromo-3,3,3-trifluoropropane **1** [2]. Recently, Matteoli et al. exploited carboalkoxylation of **1** with a palladium catalyst [3]. While this catalytic process enables the one-step formation of alkyl trifluoromethacrylates, it has two practical disadvantages. First, nucleophilicity of bulky alcohols is very low. Secondly, Michael addition of another alcohol to the olefinic bond of trifluoromethacrylate occurs smoothly, resulting in the low selectivity for trifluoromethacrylates. The high reactivity of the olefinic bond in trifluoromethacrylate may be due to the strong electron-withdrawing  $\text{CF}_3$  group [4].

We have found that the highly selective one-step formation of *tert*-butyl trifluoromethacrylate in a satisfactory yield was fulfilled by use of an inorganic base with a palladium catalyst. In addition, we refined various reaction conditions of this catalytic system from a practical standpoint.

## 2. Results and discussion

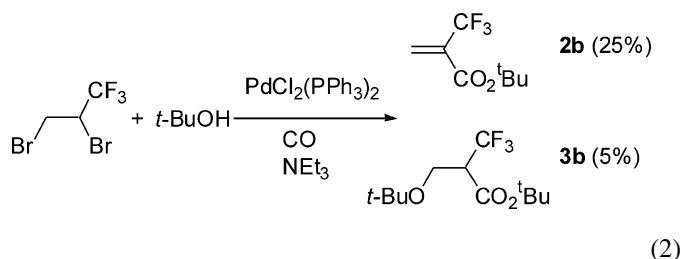
Keeping the temperature of a stainless steel autoclave containing **1** (1.0 mmol), ethanol (1.2 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.01 mmol, 1.0 mol% to **1**), triethylamine (2.2 mmol) and THF (5 mL) at 100 °C for 15 h in an atmosphere of carbon monoxide (20 atm) gave the moderate yield of **2a** with concomitant formation of **3a** (Eq. (1)); **2a** is the carboalkoxylated product of **1** and **3a** is presumably the Michael addition product of **2a**.



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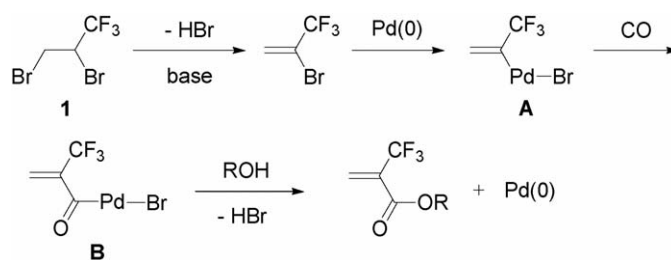
E-mail address: [yamakawa@sagami.or.jp](mailto:yamakawa@sagami.or.jp) (T. Yamakawa).

When ethanol was replaced by *tert*-butyl alcohol, the yields of both **2b** and **3b** drastically decreased to 25% and 5% (Eq. (2)). The relatively low reactivity of *tert*-butyl alcohol may be due to its steric hindrance [3]. Although an excess amount of *tert*-butyl alcohol provided **2b** in moderate yield, the formation of the undesired product **3b** was inevitable ( $[t\text{-BuOH}]/[\mathbf{1}] = 10$ , **2b** 66%, **3b** 15%;  $[t\text{-BuOH}]/[\mathbf{1}] = 20$ , **2b** 77%, **3b** 6%). Uneyama and co-workers reported a similar trend in Pd-catalyzed carboalkoxylation of fluorinated imidoyl halides [5]. Use of polar solvents furnished the desired products in high yields for the carboalkoxylation with bulky alcohols [6]. This report stimulated us to carry out the present reactions in polar solvents. However, we failed in the improvement of the catalytic process (see below).



Then, the addition of some inorganic bases to this catalytic process was performed in order to enhance the yield and selectivity for **2b**. As shown in Table 1, various inorganic bases promoted the carboalkoxylation and suppressed the formation of **3b** completely. Of the inorganic bases tested,  $\text{Li}_2\text{CO}_3$  gave the highest yield (run 1). Catalytic amount of  $\text{Li}_2\text{CO}_3$  (0.1 equiv. to **1**) was enough to obtain a satisfactory yield (run 2), while decreasing the amount of  $\text{Li}_2\text{CO}_3$  to less than 0.1 equiv. led to a rather low yield (run 3). The positive effect of  $\text{Li}_2\text{CO}_3$  also appeared in the reaction with ethanol (**2a**: 62%  $\rightarrow$  80%, **3a**: 17%  $\rightarrow$  5%).

Interestingly, even use of 2.2 equiv. of  $\text{Li}_2\text{CO}_3$  did not enhance the yield in the absence of triethylamine; rather, the carboalkoxylation did not proceed at all (run 4). The role of a

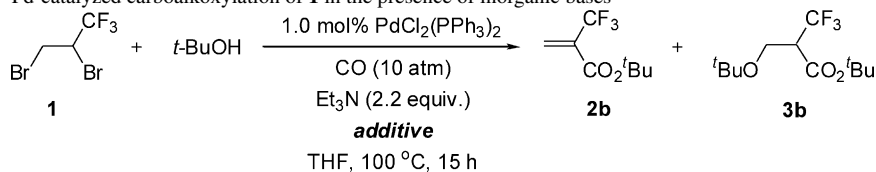


Scheme 1.

base in various Pd-catalyzed reactions is generally considered to be abstraction of HX (X = halogen) and/or  $\text{H}^+$  from substrates [7]. 2.2 equiv. of triethylamine is enough to eliminate HBr from **1** and  $\text{H}^+$  from *tert*-butyl alcohol. Therefore, the result of run 4 clearly proves that HBr and/or  $\text{H}^+$  were scarcely removed from **1** and/or *tert*-butyl alcohol by  $\text{Li}_2\text{CO}_3$ , and that the inorganic bases in Table 1 behave in a different manner from triethylamine. The reaction mechanism of the carboalkoxylation is considered to proceed as follows [8]: (i) HBr abstraction from **1** by triethylamine generates 2-bromo-3,3,3-trifluoropropene (BTP), (ii) oxidative addition of BTP to a palladium species produces a vinyl palladium intermediate A, (iii) CO insertion into the palladium-carbon bond of A forms an acylpalladium species B, and (iv) nucleophilic attack of an alcohol to the carbonyl group of B gives an alkyl trifluoromethacrylate (Scheme 1). Li and Yamamoto proposed that the last step takes place via an intermediate where an acyl, a bromido and an alkoxo ligands coordinate to the palladium [8b].

It is conceivable that the alkali carbonates in Table 1, especially  $\text{Li}_2\text{CO}_3$ , enable the formation of intermediate as depicted in Scheme 2 and facilitate the nucleophilic attack of *tert*-butoxide ion. Torisawa et al. reported a similar effect by  $\text{Cs}_2\text{CO}_3$  in the Pd-catalyzed carbohydroxylation of arylbromides, and concluded that it stabilizes the acylpalladium-aqua intermediate [9].

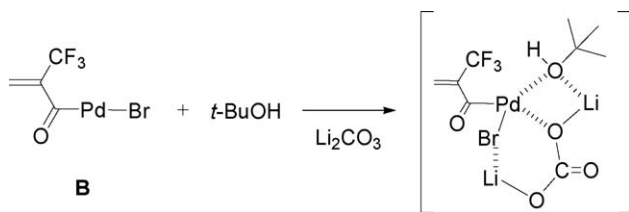
Table 1  
Pd-catalyzed carboalkoxylation of **1** in the presence of inorganic bases



Run	Additive	[Additive]/[ <b>1</b> ]	<b>2b</b> (%) <sup>a</sup>	<b>3b</b> (%) <sup>a</sup>
1	$\text{Li}_2\text{CO}_3$	1.0	85	0
2	$\text{Li}_2\text{CO}_3$	0.1	81	0
3	$\text{Li}_2\text{CO}_3$	0.05	53	0
4 <sup>b</sup>	$\text{Li}_2\text{CO}_3$	2.2	Trace	0
5	$\text{Na}_2\text{CO}_3$	0.1	78	0
6	$\text{K}_2\text{CO}_3$	0.1	41	0
7	$\text{Cs}_2\text{CO}_3$	0.1	40	0
8	<i>t</i> -BuONa	0.2	65	0
9	NaH	0.2	60	0
10	LiCl	0.2	60	0
11	LiBr	0.2	60	0

<sup>a</sup> GC yield.

<sup>b</sup> The reaction was carried out in the absence of triethylamine.



Scheme 2.

In addition, the complete suppression of the Michael addition pathway in the presence of an inorganic base might be due to the relative increase in the formation rate of **2b**.

Next, we investigated the various reaction conditions from the standpoint of practical use. Fig. 1 illustrates the conversion to **2b** from **1** under various pressures of carbon monoxide. When the initial carbon monoxide pressure was set to higher than 10 atm, the yield of **2b** increased linearly to ca. 80% until 4 h and then remained constant. It is probable that aggregation of Pd species to Pd black limited the yield to ca. 80%. Indeed, the formation of Pd black was observed after the reaction. Meanwhile **1** was completely consumed at over 6 h and BTP formed from **1** was not detected by GC and GC–MS. Therefore, polymerization of BTP and/or **2b** may also determine the limit of the yield, though any other products were not detected spectroscopically. The pressure of carbon monoxide (5 atm) lower than 10 atm afforded yields less than 80% after 10 h.

Reaction temperature was also important for the conversion to **2b**. Thus, a reaction time of 12 h was required to obtain 80% yield at 80 °C and an initial carbon monoxide pressure of 10 atm, while higher temperature (120 °C) leads to slightly diminished yields (75% for 10 h).

The catalytic activities of various palladium compounds are shown in Table 2. Pd(PPh<sub>3</sub>)<sub>4</sub> also provided **2b** in a satisfactory yield (run 2) as well as PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (run 1), suggesting that the catalytically active species in the carboalkoxylation is a Pd(0) species [7]. The combination of PdCl<sub>2</sub> and PPh<sub>3</sub> also gave satisfactory yields (runs 3 and 4). However, other phosphine ligands (P(*o*-tolyl)<sub>3</sub>, P(*n*-butyl)<sub>3</sub>, P(cyclohexyl)<sub>3</sub>) exhibited little activity (runs 5–7). When biden-

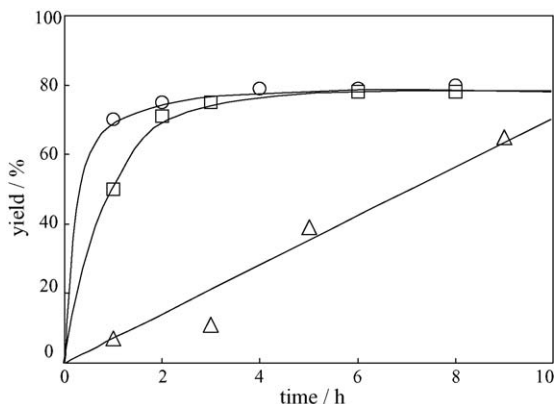


Fig. 1. Effect of CO pressure on the carboalkoxylation of **1** (○: 20 atm, □: 10 atm, △: 5 atm). Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1.0 mol%), **1** (1.0 mmol), *t*-BuOH (1.2 mmol), Et<sub>3</sub>N (2.2 mmol), Li<sub>2</sub>CO<sub>3</sub> (0.1 mmol), THF (2 mL) and 100 °C.

Table 2

Carboalkoxylation of **1** with *t*-BuOH with various palladium compounds<sup>a</sup>

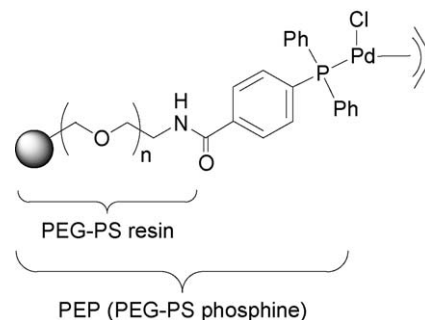
Run	Catalyst	Yield of <b>2b</b> (%) <sup>b</sup>
1	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	77
2	Pd(PPh <sub>3</sub> ) <sub>4</sub>	75
3	PdCl <sub>2</sub> /2PPh <sub>3</sub>	82
4	PdCl <sub>2</sub> /4PPh <sub>3</sub>	80
5	PdCl <sub>2</sub> /2P( <i>o</i> -tol) <sub>3</sub>	Trace
6	PdCl <sub>2</sub> /2P(cyclohexyl) <sub>3</sub>	3
7	PdCl <sub>2</sub> /2P( <i>n</i> -Bu) <sub>3</sub>	Trace
8	PdCl <sub>2</sub> /dppe	19
9	PdCl <sub>2</sub> /dppp	Trace
10	PdCl <sub>2</sub> /dppb	3
11	PdCl <sub>2</sub> / <i>rac</i> -BINAP	7
12	PdCl <sub>2</sub> /dppf	77
13	Pd/C + 2PPh <sub>3</sub>	56
14	Pd(OH) <sub>2</sub> /C + 4PPh <sub>3</sub>	70
15	Pd/Al <sub>2</sub> O <sub>3</sub> + 4PPh <sub>3</sub>	70
16	PdCl(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )(PEP)	54

<sup>a</sup> Reaction conditions: Pd compounds (0.5 mol%), **1** (1.0 mmol), *t*-BuOH (1.2 mmol), Et<sub>3</sub>N (2.2 mmol), THF solvent (5 mL), 100 °C, CO (10 atm) and 5 h.

<sup>b</sup> GC yield.

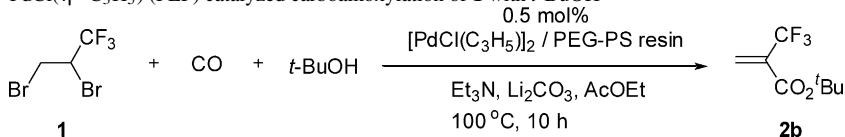
tate phosphine ligands such as dppe (diphenylphosphinoethane), dppp (diphenylphosphinopropane), dppb (diphenylphosphinobutane) and *rac*-BINAP (*rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) were employed, the yields of **2b** were rather low (runs 8–11). Only dppf (1,1'-diphenylphosphinoferrocene) showed an activity similar to that obtained with PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (run 12).

Heterogeneous palladium catalysts with triphenylphosphine also showed good activities (runs 13–16). The activity of the recovered monophosphine complex PdCl(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(PEP) (Scheme 3) [10] by filtration did not diminish as long as 2.0 equiv. of triphenylphosphine to palladium was added. Table 3 shows that the catalytic activity was retained after five iterative uses [11] by the extra addition of triphenylphosphine. In contrast the yield of **2b** decreased to less than 5% by use of the recovered catalyst alone. Phosphines accelerate the reduction of Pd(II) to catalytically active Pd(0) in general Pd-catalyzed reactions [7]. The extra phosphine here should reproduce active palladium species. However, as for the other reused heterogeneous palladium catalysts, great loss of the activity was observed despite the extra addition of triphenylphosphine. For example, the yield of **2b** with Pd/Al<sub>2</sub>O<sub>3</sub> + 4PPh<sub>3</sub> (run 15) decreased from



Scheme 3.

Table 3

PdCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>) (PEP) catalyzed carboalkoxylation of **1** with *t*-BuOH

Reuse time	<b>2b</b> (%) <sup>a</sup>
First	54
Second <sup>b</sup>	52
Third <sup>b</sup>	52
Fourth <sup>b</sup>	51
Fifth <sup>b</sup>	53

<sup>a</sup> GC yield.<sup>b</sup> 2.0 equiv. of PPh<sub>3</sub> was added.

77% in the first run to 5% in the second. The difference between PdCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(PEP) and the other heterogeneous catalysts in the reusability may be due to that the low solubility of the Pd complex, which is bound to the support chemically, in the former in the solvent compared to that of the Pd species in the latter.

In the carboalkoxylation, catalyst, triethylamine salt (triethylammonium bromide) and inorganic base were readily separated from the reaction mixture by filtration and/or distillation. Since the desired product **2b** is liquid at room temperature, it is practically significant to choose a solvent which can be separated from **2b** by distillation. Table 4 lists the yields of **2b** in various solvents. Toluene, which is an industrially convenient solvent, was suitable for the carboalkoxylation (run 1). Nevertheless, a small difference in boiling point between toluene (110 °C) and **2b** (*ca.* 120 °C) will make it difficult to separate them completely by distillation. THF and 1,4-dioxane are not appropriate industrially in terms of safety, though they also gave satisfactory yields (runs 2 and 3) and possess lower boiling point (64 °C for THF and 101 °C for 1,4-dioxane) than toluene. Ethyl acetate is expected to surmount two practical problems men-

Table 4

Pd-catalyzed carboalkoxylation in various solvents

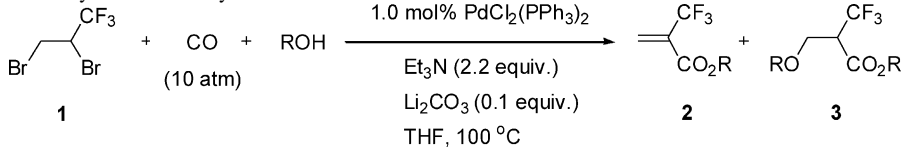
Run	Solvent	Yield of <b>2b</b> (%) <sup>a</sup>
1	THF	78
2	1,4-dioxane	77 (74) <sup>b</sup>
3	Toluene	73
4	Ethyl acetate	70
5	<i>p</i> -Xylene	43
6	Acetone	16
7	Acetonitrile	18
8	DMF	14

Reaction conditions: PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.5 mol%), **1** (1.0 mmol), *t*-BuOH (1.2 mmol), Et<sub>3</sub>N (2.2 mmol), solvent (5 mL), 100 °C, CO (10 atm) and 5 h.

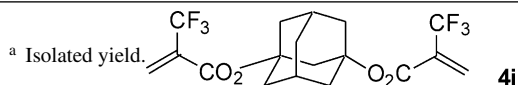
<sup>a</sup> GC yield.<sup>b</sup> An isolated yield.

tioned above due to its low boiling point (77 °C) and low toxicity. The use of ethyl acetate resulted in the exclusive formation of **2b** in moderate yield (run 4); no *trans*-esterification product was detected by GC and GC-MS. It can be concluded that ethyl acetate is a solvent adequate for an industrial synthesis of **2b**.

Table 5

Pd-catalyzed carboalkoxylation of **1** with various alcohols

Run	Alcohol	Yield		
		<b>2</b> (%) <sup>a</sup>	<b>3</b> (%) <sup>a</sup>	<b>4</b> (%) <sup>a</sup>
1	1-Octanol	88 ( <b>2c</b> )	0 ( <b>3c</b> )	
2	Cyclohexyl methanol	83 ( <b>2d</b> )	Trace ( <b>3d</b> )	
3	Cyclohexanol	89 ( <b>2e</b> )	0 ( <b>3e</b> )	
4	<i>l</i> -Menthol	85 ( <b>2f</b> )	0 ( <b>3f</b> )	
5	1-Adamantanol	90 ( <b>2g</b> )	0 ( <b>3g</b> )	
6	2-Methyl-2-adamantanol	75 ( <b>2h</b> )	0 ( <b>3h</b> )	
7	Adamantane-1,3-diol	64 ( <b>2i</b> )	0 ( <b>3i</b> )	25 ( <b>4i</b> )



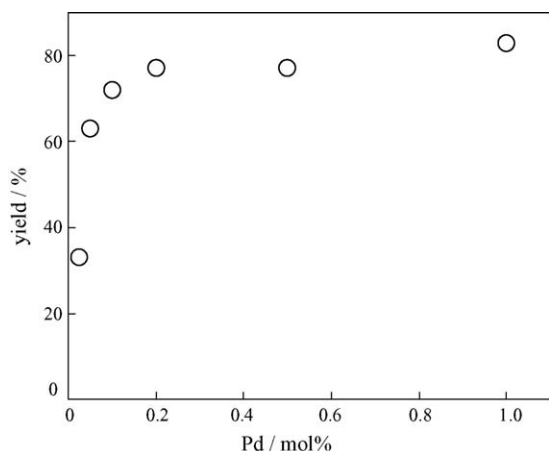


Fig. 2. Dependence of **2b** yield on the loaded amount of  $\text{PdCl}_2(\text{PPh}_3)_2$ . Reaction conditions: **1** (1.0 mmol), *t*-BuOH (1.2 mmol),  $\text{Et}_3\text{N}$  (2.2 mmol), AcOEt (5 mL),  $100^\circ\text{C}$ , CO (10 atm) and 15 h.

Non-polar and aprotic polar solvents afforded **2b** in poor yields (runs 6–8).

Fig. 2 displays the dependence of the **2b** yield on the loading of  $\text{PdCl}_2(\text{PPh}_3)_2$ . Satisfactory yields were obtained with 0.05 mol% of catalyst. The turnover number of palladium calculated from the initial slope in Fig. 2 reached 1300.

The carboalkoxylation here was applied to various alcohols. Representative results are given in Table 5. Satisfactory yields and selectivities of **2**, trifluoromethacrylates, were obtained for various *primary*, *secondary* and *tertiary* alcohols (runs 1–6). The reaction with adamantan-1,3-diol proceeded smoothly to furnish predominately **2i** and also **4i**, which was formed with two molecules of **1** (run 7).

### 3. Conclusion

In conclusion, we have disclosed the practical synthesis of trifluoromethacrylates in satisfactory yields and selectivities with a palladium catalyst and  $\text{Li}_2\text{CO}_3$ . The high activity and generality of this catalytic process under the practical conditions render it applicable to an industrial synthesis of a wide structural variety of fluorine containing  $\alpha,\beta$ -unsaturated alkyl esters.

## 4. Experimental

### 4.1. General techniques

IR spectra of thin films or solids of products were recorded on a Horiba FT-720 spectrometer.  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  on Bruker DRX-250 ( $^1\text{H}$  250 MHz and  $^{19}\text{F}$  235 MHz) and Bruker DRX-500 ( $^{13}\text{C}$  125 MHz) spectrometers using  $\text{CHCl}_3$  for  $^1\text{H}$  and  $^{13}\text{C}$  NMR and  $\text{CFCl}_3$  for  $^{19}\text{F}$  NMR as an internal reference. Chemical shifts are given in ppm ( $\delta$ ). Multiplicities are indicated by s (singlet), d (doublet), q (quartet), quint (quintet), m (multiplet), brs (broad singlet), brd (broad doublet) and dm (double of multiplet). GC analyses were performed on a Shimadzu GC-14A with FID using a ULBON HR-1 capillary column (50 m  $\times$  0.25 mm) (Shinwa

Chemical Industries, Ltd.). Melting points (mp) were recorded on a Yanako MP3 micro melting point apparatus without any correction. TLC analysis of a reaction mixture was performed on a Merck silica gel 60 F254 TLC plate. Flash chromatography was performed on silica gel (Merck C60). Ethanol was distilled over molecular sieve 3A under an argon atmosphere. Triethylamine, AcOEt, DMF and  $\text{CH}_3\text{CN}$  were distilled over  $\text{CaH}_2$  just before use under an argon atmosphere. THF and toluene were distilled over sodium/benzophenone under an argon atmosphere.  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and  $\text{Cs}_2\text{CO}_3$  were dried with a heating gun under a reduced pressure. Other commercially available reagents were used without further purification.

### 4.2. Typical procedure for the carboalkoxylation

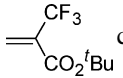
The carboalkoxylation using *tert*-butyl alcohol is given as an example of a typical procedure hereinafter. A stainless steel autoclave containing **1** (1.0 mmol), *tert*-butyl alcohol (1.2 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (1.0 mol% to **1**, 0.01 mmol),  $\text{Li}_2\text{CO}_3$  (0.1 mmol), triethylamine (2.2 mmol), tridecane (0.5 mmol, internal standard) and THF (5 mL) equipped with a stirring bar was purged with pressurized carbon monoxide three times. The initial pressure of carbon monoxide was set at 10 atm, and the autoclave was heated for 15 h at  $100^\circ\text{C}$ . After completion of the reaction, a 10  $\mu\text{L}$  aliquot of the reaction mixture was removed with a microsyringe. It was then analyzed by use of GC (GC yield). The residual reaction mixture was filtered through a Celite<sup>®</sup> (AcOEt, 20 mL). The obtained solution was poured into water (10 mL) and the mixture was extracted with ethyl acetate (5 mL  $\times$  2). Then the extract was washed with brine (10 mL  $\times$  2). The organic layer was dried over anhydrous magnesium sulfate. After the solvent was evaporated, the resulting crude products were purified with a silica gel column to give **2b** (81% yield, colorless oil).

### 4.3. Typical procedure for the carboalkoxylation with monophosphine complex $\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)(\text{PEP})$ resin catalyst

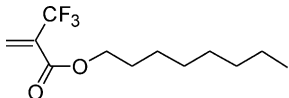
All the reactions with  $\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)(\text{PEP})$  catalyst were performed as follows. A stainless steel autoclave containing **1** (1.0 mmol), *tert*-butyl alcohol (1.2 mmol),  $\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)(\text{PEP})$  (0.5 mol% to **1**, 0.005 mmol),  $\text{Li}_2\text{CO}_3$  (0.1 mmol), triethylamine (2.2 mmol), tridecane (0.5 mmol, internal standard) and ethyl acetate (5 mL) equipped with a stirring bar was purged with pressurized carbon monoxide three times. The initial pressure of carbon monoxide was set at 10 atm, and the autoclave was heated for 10 h at  $100^\circ\text{C}$ . After completion of the reaction, a 10  $\mu\text{L}$  aliquot of the reaction mixture was removed with a microsyringe. It was then analyzed by use of GC. The residual reaction mixture was filtered, and the resin-supported palladium catalyst was washed with water (5 mL  $\times$  5), ethanol (5 mL  $\times$  2) and ether (5 mL  $\times$  2). Drying under a reduced pressure recovered the resin-supported palladium quantitatively. The second reaction was carried out under the same condition as above after the addition of triphenylphosphine (2.0 equiv. to Pd).

#### 4.4. Characterization of products

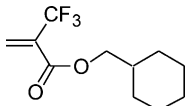
##### 4.4.1. *tert*-Butyl trifluoromethacrylate (**2b**)

 colorless oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 250 Hz)  $\delta$  1.53 (s, 9 H), 6.43 (q,  $J_{\text{HF}} = 1.2$  Hz, 1H), 6.73 (q,  $J_{\text{HF}} = 1.7$  Hz, 1H).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 Hz)  $\delta$  27.9, 83.0, 121.5 (q,  $J_{\text{CF}} = 272.3$  Hz), 131.6 (q,  $J_{\text{CF}} = 5.2$  Hz), 133.0 (q,  $J_{\text{CF}} = 31.5$  Hz), 160.5 (q,  $J_{\text{CF}} = 1.0$  Hz).  $^{19}\text{F}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 235 Hz)  $\delta$  -65.9. IR (neat) 2981, 2856, 1724, 1363, 1350, 1248, 1160, 1092, 1049  $\text{cm}^{-1}$ .

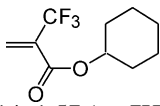
##### 4.4.2. 1-Octyl trifluoromethacrylate (**2c**)

 colorless oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 250 Hz)  $\delta$  0.81 (d,  $J_{\text{HH}} = 6.7$  Hz, 3H), 1.12–1.40 (m, 10H), 1.63 (quint,  $J_{\text{HH}} = 6.6$  Hz, 2H), 4.18 (t,  $J_{\text{HH}} = 6.6$  Hz, 2H), 6.35 (q,  $J_{\text{HF}} = 1.2$  Hz, 1H), 6.64 (q,  $J_{\text{HF}} = 1.7$  Hz, 1H).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 Hz)  $\delta$  13.1, 21.6, 24.7, 27.4, 28.1, 30.7, 65.0, 122.5 (q,  $J_{\text{CF}} = 272.4$  Hz), 130.6 (q,  $J_{\text{CF}} = 32.0$  Hz), 131.6 (q,  $J_{\text{CF}} = 5.1$  Hz), 160.4 (q,  $J_{\text{CF}} = 1.0$  Hz).  $^{19}\text{F}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 235 Hz)  $\delta$  -65.9. IR (neat) 2927, 1735, 1247, 1145, 1095  $\text{cm}^{-1}$ .

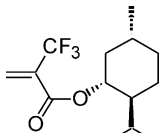
##### 4.4.3. Cyclohexylmethyl trifluoromethacrylate (**2d**)

 colorless oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 250 Hz)  $\delta$  0.84–1.15 (m, 2H), 1.15–1.37 (m, 3H), 1.58–1.82 (m, 6H), 4.07 (d,  $J_{\text{HH}} = 6.1$  Hz, 2H), 6.41 (q,  $J_{\text{HF}} = 1.2$  Hz, 1H), 6.72 (q,  $J_{\text{HF}} = 1.7$  Hz, 1H).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 Hz)  $\delta$  25.7, 26.3, 29.5, 37.0, 70.9, 121.4 (q,  $J_{\text{CF}} = 272.6$  Hz), 131.7 (q,  $J_{\text{CF}} = 32.0$  Hz), 132.6 (q,  $J_{\text{CF}} = 5.1$  Hz), 161.5 (q,  $J_{\text{CF}} = 1.0$  Hz).  $^{19}\text{F}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 235 Hz)  $\delta$  -65.9. IR (neat) 2927, 1736, 1245, 1143, 1093  $\text{cm}^{-1}$ .

##### 4.4.4. Cyclohexyl trifluoromethacrylate (**2e**)

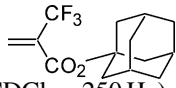
 colorless oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 250 Hz)  $\delta$  1.14–1.57 (m, 7H), 1.58–1.73 (m, 2H), 1.73–1.78 (m, 2H), 4.90 (tt,  $J_{\text{HH}} = 4.1$ , 11.9 Hz, 1H), 6.32 (q,  $J_{\text{HF}} = 1.2$  Hz, 1H), 6.62 (q,  $J_{\text{HF}} = 1.7$  Hz, 1H).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 Hz)  $\delta$  23.2, 25.3, 31.2, 74.2, 121.4 (q,  $J_{\text{CF}} = 272.5$  Hz), 121.4 (q,  $J_{\text{CF}} = 31.9$  Hz), 132.3 (q,  $J_{\text{CF}} = 5.1$  Hz), 160.7 (q,  $J_{\text{CF}} = 1.0$  Hz).  $^{19}\text{F}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 235 Hz)  $\delta$  -65.9. IR (neat) 2921, 2854, 1736, 1252, 1153, 1095  $\text{cm}^{-1}$ .

##### 4.4.5. *l*-Methyl trifluoromethacrylate (**2f**)

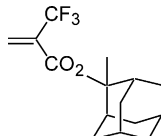
 colorless oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 250 Hz)  $\delta$  0.77 (d,  $J_{\text{HH}} = 7.0$  Hz, 3H), 0.81–1.19 (m, 3H), 0.90 (d,  $J_{\text{HH}} = 5.0$  Hz, 3H), 0.93 (d,  $J_{\text{HH}} = 4.5$  Hz, 3H), 1.40–1.59 (m, 2H), 1.64–1.77

(m, 2H), 1.88 (m, 1H), 2.06 (m, 1H), 4.85 (dt,  $J_{\text{HH}} = 4.4$ , 10.9 Hz, 1H), 6.39 (q,  $J_{\text{HF}} = 1.2$  Hz, 1H), 6.70 (q,  $J_{\text{HF}} = 1.7$  Hz, 1H).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 Hz)  $\delta$  16.2, 20.8, 22.0, 23.3, 26.2, 31.4, 40.5, 46.9, 76.2, 121.4 (q,  $J_{\text{CF}} = 272.6$  Hz), 132.0 (q,  $J_{\text{CF}} = 31.9$  Hz), 132.4 (q,  $J_{\text{CF}} = 5.2$  Hz), 161.0 (q,  $J_{\text{CF}} = 1.0$  Hz).  $^{19}\text{F}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 235 Hz)  $\delta$  -65.8. IR 2956, 1731, 1371, 1250, 1146, 1115, 1093  $\text{cm}^{-1}$ .

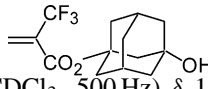
##### 4.4.6. 1-Adamantantyl trifluoromethacrylate (**2g**)

 white solid; mp 29.5–30.0 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 250 Hz)  $\delta$  1.61 (brs, 6H), 2.11 (brs, 9H), 6.25 (q,  $J_{\text{HF}} = 1.2$  Hz, 1H), 6.53 (q,  $J_{\text{HF}} = 1.7$  Hz, 1H).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 Hz)  $\delta$  30.9, 36.0, 41.2, 83.1, 121.4 (q,  $J_{\text{CF}} = 272.5$  Hz), 131.5 (q,  $J_{\text{CF}} = 5.1$  Hz), 133.0 (q,  $J_{\text{CF}} = 31.3$  Hz), 160.0 (q,  $J_{\text{CF}} = 1.0$  Hz).  $^{19}\text{F}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 235 Hz)  $\delta$  -65.8. IR 2950, 2856, 1724, 1363, 1350, 1248, 1160, 1092, 1049  $\text{cm}^{-1}$ .

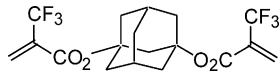
##### 4.4.7. 2-Methyl-2-adamantantyl trifluoromethacrylate (**2h**)

 colorless oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 Hz)  $\delta$  1.45–1.58 (m, 2H), 1.62 (s, 3H), 1.63–1.88 (m, 8H), 1.88–2.02 (m, 2H), 2.29 (brs, 2H), 6.27 (q,  $J_{\text{HF}} = 1.2$  Hz, 1H), 6.59 (q,  $J_{\text{HF}} = 1.7$  Hz, 1H).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 Hz)  $\delta$  22.2, 26.5, 27.3, 32.9, 34.6, 36.2, 38.1, 90.2, 121.5 (q,  $J_{\text{CF}} = 272.4$  Hz), 131.7 (q,  $J_{\text{CF}} = 5.2$  Hz), 133.0 (q,  $J_{\text{CF}} = 31.9$  Hz), 160.0 (q,  $J_{\text{CF}} = 0.9$  Hz).  $^{19}\text{F}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 235 Hz)  $\delta$  -65.5. IR (neat) 2914, 1726, 1650, 1348, 1250, 1144, 1086  $\text{cm}^{-1}$ .

##### 4.4.8. 3-Hydroxy-2-adamantantyl trifluoromethacrylate (**2j**)

 white solid; mp 82.5–82.8 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 Hz)  $\delta$  1.52 (dm,  $J_{\text{HH}} = 12.8$  Hz, 2H), 1.59 (dm,  $J_{\text{HH}} = 12.8$  Hz, 1H), 1.71 (m, 4H), 2.07 (m, 2H), 2.13 (brs, 1H), 2.16 (s, 3H), 2.37 (m, 2H), 6.35 (q,  $J_{\text{HF}} = 1.2$  Hz, 1H), 6.61 (q,  $J_{\text{HF}} = 1.7$  Hz, 1H).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 Hz)  $\delta$  31.2, 34.5, 39.7, 43.9, 48.9, 70.3, 83.5, 121.3 (q,  $J_{\text{CF}} = 272.5$  Hz), 131.9 (q,  $J_{\text{CF}} = 5.1$  Hz), 132.7 (q,  $J_{\text{CF}} = 31.6$  Hz), 159.9 (q,  $J_{\text{CF}} = 0.9$  Hz).  $^{19}\text{F}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 235 Hz)  $\delta$  -65.7. IR 3269, 2939, 1722, 1362, 1155, 1093, 991  $\text{cm}^{-1}$ .

##### 4.4.9. 1,3-Bis(trifluoromethacryloxy)adamantane (**4i**)

 white solid; mp 65.0–65.5 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 Hz)  $\delta$  1.62 (brs, 2H), 2.14 (brd,  $J_{\text{HH}} = 12.0$  Hz, 4H), 2.20 (brd,  $J_{\text{HH}} = 12.0$  Hz, 4H), 2.42 (m, 2H), 2.60 (brs, 2H), 6.36 (q,  $J_{\text{HF}} = 1.2$  Hz, 1H), 6.62 (q,  $J_{\text{HF}} = 1.7$  Hz, 1H).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 Hz)  $\delta$  31.1, 34.6, 39.8, 44.9, 82.9, 121.3 (q,  $J_{\text{CF}} = 272.5$  Hz), 132.6 (q,  $J_{\text{CF}} = 5.0$  Hz), 132.6 (q,  $J_{\text{CF}} = 31.6$  Hz), 159.9 (q,  $J_{\text{CF}} = 1.0$  Hz).  $^{19}\text{F}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ ,

235 Hz)  $\delta$   $-65.8$ . IR 2937, 1720, 1363, 1250, 1144, 1092, 1072  $\text{cm}^{-1}$ .

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