



## Short communication

Unusual  $\beta,\beta'$ -coupling and  $\beta$ -alkylation of methyl 2,3,3-trifluoropropenoate by lithium diorganocupratesJan Hajduch<sup>a,b</sup>, Oldřich Paleta<sup>a,\*</sup><sup>a</sup> Department of Organic Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic<sup>b</sup> Institute of Organic Chemistry and Biochemistry, Academy of Sciences, 166 10 Prague 6, Czech Republic

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## ABSTRACT

Methyl 2,3,3-trifluoroprop-2-enoate (**1**) reacts with lithium diorganocuprates in two ways, by fluorine substitution at C-3 with alkyl or aryl, or by  $\beta,\beta'$  C,C-coupling. The reaction product was strongly dependent on the organyl structure: while dibutyl- or diphenylcuprate reacted by C-3 substitution, dimethylcuprate afforded the product of the coupling, dimethyl (*Z,Z*)-2,3,4,5-tetrafluorohexa-2,4-dienedioate (**3**). (*Z*)-Configuration is highly prevailing in 3-alkylated 2,3-difluoropropenoates (77–90% rel.).

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## 1. Introduction

Trifluoroacrylates have been reported as useful building blocks in syntheses of lactones or 2,3-difluoro-2,3-unsaturated esters [1–6], which have been in turn exploited as convenient synthetic intermediates [7–9]. Recently,  $\beta$ -fluoroalkylation of benzyl trifluoroacrylate by fluorine vinylic substitution using Grignard reagents in the presence of copper(I) bromide has been reported [5,6]. In this paper, we report the results of the reaction of methyl 2,3,3-trifluoropropenoate (**1**) with lithium diorganocuprates. Depending on the organyl component in the cuprates, unusual  $\beta,\beta'$  C,C-coupling of the trifluoropropenoate **1** has been observed.

## 2. Results and discussion

We tested the reaction of methyl 2,2,3-trifluoroprop-2-enoate (**1**, methyl  $\alpha,\beta,\beta'$ -trifluoroacrylate – MTFA) with several organometallic reagents. The reaction of **1** with methylmagnesium iodide afforded a mixture of products, from which the dimer **2** was isolated in the 4.8% yield (Scheme 1). The dimer **2** was the same product as that obtained by the reaction of MTFA with the fluoride ion [10,11]. Very probably, fluoride ion was liberated by a reaction of methylmagnesium iodide with the substrate **1**. This result is in a contrast with the recently reported [5,6]  $\beta$ -fluoroalkylation of

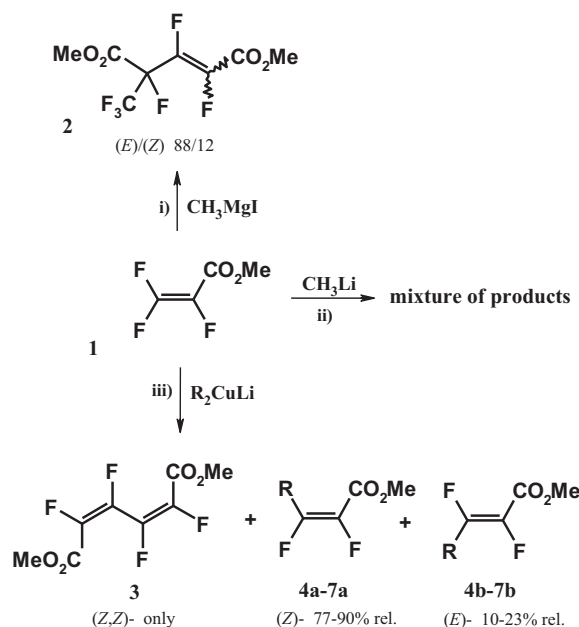
benzyl trifluoroacrylate by a mixture of a Grignard reagent and copper(I) bromide.

The reaction of MTFA with methyllithium (Scheme 1) was unsuccessful despite of very mild reaction conditions. A complex mixture of products was obtained, from which no individual product was isolated.

New results were found in the reaction of MTFA (**1**) with some lithium diorganocuprates (Scheme 1). The reaction of **1** with lithium dibutyl- or diphenylcuprates afforded only  $\beta$ -substituted products **6** or **7** with the *Z*-stereoisomer highly prevailing (Table 1, entry 3 and 5). Very close results to these were obtained in the reaction of benzyl 2,2,3-trifluoroprop-2-enoate with butyl- or phenylmagnesium bromide in the presence of copper(I) bromide (Table 1, entries 4 and 6) [6]. However, when the substrate **1** was reacted with lithium dimethylcuprate the substitution dimer **3**, dimethyl (*Z,Z*)-2,3,4,5-tetrafluorohexa-2,4-dienedioate was formed by a  $\beta,\beta'$  C,C-coupling in the 95% relative yield (Scheme 1; Table 1, entry 1). When a more bulky lithium di(*tert*-butyl)cuprate was involved in the reaction (Table 1, entry 2) the yield of the coupling product **3** was decreased to 56% rel.

A coupling of this type has not been observed so far. Several proposals for substitutions by organocuprates have been published [12] and the importance of tricoordinated copper compounds  $R_3Cu(III)$  in particular reactions has been recognized [12a,13] and their structure published [14]. The existence of  $Cu(III)$  intermediates in addition or substitution reactions involving dialkylcuprates was predicted by calculations [12b]. Probably, the  $\beta,\beta'$ -coupling of two molecules of MTFA (**1**) proceeds via an intermediate **8** (Scheme 2)

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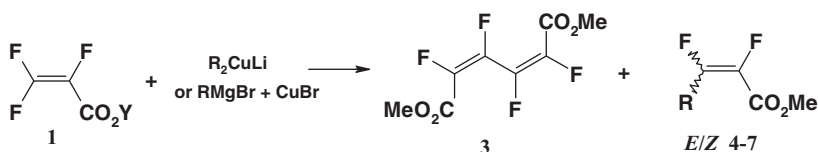
4a, 4b, R =  $\text{CH}_3$ ; 5a, 5b, R =  $\text{C}(\text{CH}_3)_3$ ; 6a, 6b, R =  $\text{C}_6\text{H}_9$ ; 7a, 7b, R =  $\text{C}_6\text{H}_5$ .

i)  $\text{Et}_2\text{O}$ , -10 to 0 °C, then  $\text{CF}_3\text{CO}_2\text{H}$ ; ii) THF, -100 °C, 1 h, then  $\text{CF}_3\text{CO}_2\text{H}$ , -100 °C to rt, 2 h; iii) THF, -100 to -70 °C, 3 h, then  $\text{CF}_3\text{CO}_2\text{H}$ , -70 °C to rt, 2 h

**Scheme 1.** Reactions of methyl 2,3,3-trifluoroprop-2-enoate with organometallic reagents.

**Table 1**

Overview of the reactions of trifluoroacrylates **1** with organometallic reagents.

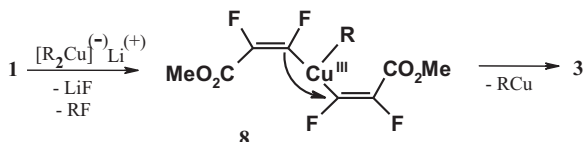


Entry	Reagent	Y	Product <b>3</b> Yield (% rel.)	Products <b>4-7</b>		Ref.
				Yield (%rel.)	E/Z	
1	$\text{Me}_2\text{CuLi}$	Me	95 (76) <sup>a</sup>	<b>4</b>	<b>5</b> 10/90	
2	$(t\text{-Bu})_2\text{CuLi}$	Me	56	<b>5</b>	<b>44</b> 23/77	
3	$\text{Bu}_2\text{CuLi}$	Me	0	<b>6</b>	<b>100 (81)<sup>a</sup></b> <b>7/93</b>	
4	$\text{BuMgBr}$ , $\text{CuBr}$	Bn	0		<b>(77)<sup>a</sup></b> <b>14/86</b>	[6]
5	$\text{Ph}_2\text{CuLi}$	Me	0	<b>7</b>	<b>100 (73)<sup>a</sup></b> <b>18/82</b>	
6	$\text{PhMgBr}$ , $\text{CuBr}$	Bn	0		<b>(90)<sup>a</sup></b> <b>14/86</b>	[6]

<sup>a</sup> Isolated yield.

possessing three-valent copper central atom combining two units of defluorinated substrate **1**. The coupling occurs only when the alkyl in a lithium cuprate is not sterically inconvenient. Both butyl and phenyl substituents coordinated with copper blocked the  $\beta, \beta'$ -coupling probably from steric reasons. A similar steric effect of these substituents caused limitations of the Wittig–Horner-type annulation to quinolinediones [15].

The  $^{19}\text{F}$  NMR of the product **3** contains only two signals for the four fluorine atoms attached to two double bonds (-120.3 and



**Scheme 2.** Proposed intermediate in the  $\beta, \beta'$ -coupling.

**Table 2**

Overview of  $^3J_{\text{F-F}}$  coupling constants for E–Z configurations of the structures.

Entry	Substituent		Compound	$^3J_{\text{F-F}}$ (Hz)		Ref.
	A	B		(Z)-	(E)-	
1	H	H		19.3	131.9	[16]
2	$\text{CH}_3$	$\text{CO}_2\text{Me}$	<b>4</b>	19.5	128.2	
3	$\text{CH}_3(\text{CH}_2)_3$	$\text{CO}_2\text{Me}$	<b>6</b>	2.4	129.4	
4	$\text{CH}_3(\text{CH}_2)_3$	$\text{CO}_2\text{Bn}$		4.4	–	[6]
5	$\text{C}(\text{CH}_3)_3$	$\text{CO}_2\text{Me}$	<b>5</b>	4.0	128.4	
6	$\text{C}_6\text{H}_5$	$\text{CO}_2\text{Me}$	<b>7</b>	3.4	128.4	
7	$\text{C}_6\text{H}_5$	$\text{CO}_2\text{Bn}$		6.6	127.6	[6]
8	Cl	$\text{CO}_2\text{Me}$		18.0	130.5	[17]
9	$\text{MeO}_2\text{C}(\text{CF}_3)\text{CF}$	$\text{CO}_2\text{Me}$		28.1	140.0	[10]
10	$\text{NC}(\text{CF}_3)\text{CF}$	CN		26.0	141.1	[11]

–137.4 ppm), which indicates a high symmetry of the molecule. Both signals appear as doublets cleaved by the same coupling constant  $^3J_{\text{FF}} = 3.7$ . Very low coupling constants indicate *Z*-configuration on the both double bonds as comes out from the data in Table 2: the coupling constants for the corresponding *E*-configurations are incomparably higher than those for *Z*-configurations.

### 3. Conclusions

A new  $\beta, \beta'$ -coupling of methyl 2,3,3-trifluorprop-2-enoate (**1**) by some lithium diorganylcuprates, in which  $\text{sp}^2$  C–F bonds are cleaved, afforded dimethyl (*Z,Z*)-2,3,4,5-tetrafluorohexa-2,4-dienedioate (**3**). The reagents possessing more bulky organyls (butyl, phenyl) afforded products of the  $\beta\text{C}$ –F substitution.

### 4. Experimental

#### 4.1. General comments

All starting organolithium reagents and CuI were purchased from Sigma–Aldrich and used without any further treatment. NMR spectra were recorded on a Bruker WP 80 SY ( $^1\text{H}$ , 80.13 MHz;  $^{19}\text{F}$ , 75.4 MHz) or a Varian 300 HC ( $^1\text{H}$ , 300.08 MHz;  $^{13}\text{C}$ , 75.46 MHz;  $^{19}\text{F}$ , 276.51 MHz) instrument in  $\text{CDCl}_3$ . Chemical shifts  $\delta$  (ppm) are relative to tetramethylsilane ( $^1\text{H}$ , 0.0 ppm),  $\text{CDCl}_3$  ( $^{13}\text{C}$ , 77.0 ppm) or  $\text{CFCl}_3$  ( $^{19}\text{F}$ , 0.0 ppm). For recording of  $^{13}\text{C}$  NMR spectra the pulse sequences APT or DEPT were used. Coupling constants  $J$  are given in Hz. Mass spectra were recorded using a combination of Hewlett Packard GC HP 5890 series II gas chromatograph and a Hewlett Packard MS HP 5971 mass spectrometer (70 eV, EI). The capillary column for GC was DB5–MS.

#### 4.2. Reaction of MTFA (1) with methylmagnesium iodide

Under argon, a solution of methylmagnesium iodide (6.2 mmol) in diethyl ether (30 mL) was added dropwise to a solution of MTFA (6 mmol) in diethyl ether (20 mL) placed in a flask, which was cooled in ice-salt bath while stirring (magnetic spinbar). The mixture was reacted for 2 h and then let to warm up to r.t. during 4 h and after that quenched by trifluoroacetic acid. The ethereal layer was washed with saturated water solution of  $\text{NH}_4\text{Cl}$  and dried over  $\text{MgSO}_4$ . Volatile components were distilled off (rotary evaporator) and the residue, a complex mixture (TLC) was chromatographed ( $\text{CH}_2\text{Cl}_2$ ). The only product isolated was dimer **2** of MTFA (20.1 mg, 14.4 mmol, 4.8%) as a mixture of (*E*)/(*Z*) = 88/12 isomers [10].

#### 4.3. Reaction of MTFA (1) with methyllithium

To a solution of MTFA (524 mg, 3.74 mmol) in THF (15 mL) in a flask (25 mL), which was cooled to  $-100^\circ\text{C}$  under argon, a solution of methyllithium in diethyl ether (2.9 mL, 1.4 M, 4.1 mmol) was added dropwise while stirring. The mixture was stirred for 1 h, then acidified with trifluoroacetic acid to pH = ~5 and then let to warm up to r.t. during 2 h. The mixture was neutralized by a solution of  $\text{NaHCO}_3$  and then filtered. Volatile components were distilled off (rotary evaporator) and the residue subjected to analysis ( $^{19}\text{F}$  NMR, TLC), which detected a rich mixture of compounds mostly of polar ones. The separation was not successful.

#### 4.4. Reaction of MTFA (1) with lithium dialkylcuprates

##### 4.4.1. General procedure

To a mixture of CuI (ca. 15 mmol) and dry THF (30 mL) in a flask (50 mL), which was cooled to  $-20^\circ\text{C}$  under argon, a solution of

commercially available organolithium reagent (ca. 29 mmol in organic solvent) was added dropwise while stirring. The mixture was warmed up to  $0^\circ\text{C}$  during 30 min and stirred for another 30 min. The mixture was then cooled to  $-100^\circ\text{C}$ , MTFA (ca. 15 mmol) was added dropwise and the resulting mixture warmed up to  $-70^\circ\text{C}$  during next 3 h. The reaction was quenched by addition of trifluoroacetic acid adjusting pH ca. 5. The crude final mixture was warmed up to r.t. during next 2 h and then filtered. Diethyl ether (50 mL) was added to the solution, which was washed three times with saturated water solution of  $\text{NH}_4\text{Cl}$  ( $3 \times 20$  mL). Organic layer was dried over  $\text{MgSO}_4$  and then filtered. The crude product was purified by column chromatography (50 g of silica gel,  $\text{CH}_2\text{Cl}_2$ ).

##### 4.4.2. Reaction of MTFA (1) with lithium dimethylcuprate

MTFA (2.13 g, 15.2 mmol), CuI (2.91 g, 15.3 mmol), methyl-lithium (22 mL, 30.4 mmol, 1.4 M in diethyl ether), product **3** (1.41 g, 5.81 mmol, 76.4%), ratio **3/4** = 95/5; product **4** (5% rel., **4a/4b** = 90/10).

Dimethyl (*Z,Z*)-2,3,4,5-tetrafluorohexa-2,4-dienedioate (**3**):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.88 (s, 6H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 53.2 (s,  $\text{OCH}_3$ ); 141.0 (dddd,  $^1J_{\text{CF}} = 273.1$ ,  $^2J_{\text{CF}} = 13.7$ ,  $^2J_{\text{CF}} = 12.3$ ,  $^3J_{\text{CF}} = 3.5$ , CF); 141.0 (dddd,  $^1J_{\text{CF}} = 273.1$ ,  $^2J_{\text{CF}} = 33.2$ ,  $^3J_{\text{CF}} = 22.0$ ,  $^4J_{\text{CF}} = 3.0$ , CF); 158.7 (d,  $^2J_{\text{CF}} = 29.5$ , C=O); ppm.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$ :  $-120.3$  (s, 1F,  $^3J_{\text{FF}} = 3.7$ );  $-137.4$  (s, 1F,  $^3J_{\text{FF}} = 3.7$ , CFC=O) ppm. GC–MS (EI): 243 ( $\text{M}^+ + 1$ ; 0.6), 243 ( $\text{M}^+$ , 4.1), 183 (100). Anal. Calcd for  $\text{C}_8\text{H}_6\text{F}_4\text{O}_4$ : C, 39.69; H, 2.50. Found: C, 39.58; H, 2.54.

Methyl (*Z*)-2,3-difluorobut-2-enoate (**4a**):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 2.38 (dd, 3H,  $^3J_{\text{HF}} = 19.5$ ,  $^4J_{\text{HF}} = 4.1$ ); 3.84 (s, 3H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 15.0 (d,  $^3J_{\text{CF}} = 1.3$ ,  $\text{CH}_3$ ); 52.2 (s,  $\text{OCH}_3$ ); 136.8 (dd,  $^1J_{\text{CF}} = 250.7$ ,  $^2J_{\text{CF}} = 18.9$ , CF); 156.8 (dd,  $^1J_{\text{CF}} = 268.9$ ,  $^2J_{\text{CF}} = 13.7$ , CF); 161.5 (dd,  $^2J_{\text{CF}} = 27.3$ ,  $^3J_{\text{CF}} = 10.3$ , C=O); ppm.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$ :  $-99.05$  (q, 1F,  $^3J_{\text{HF}} = 19.5$ );  $-154.3$  (s, 1F, CFC=O) ppm. GC–MS (EI): 137 ( $\text{M}^+ + 1$ ; 3.7), 136 ( $\text{M}^+$ ; 63.0), 135 ( $\text{M}^+ - 1$ ; 0.9), 105 (100).

Methyl (*E*)-2,3-difluorobut-2-enoate (**4b**):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 2.18 (dd, 3H,  $^3J_{\text{HF}} = 17.1$ ,  $^4J_{\text{HF}} = 5.8$ ); 3.86 (s, 3H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.4 (dd,  $^2J_{\text{CF}} = 44.7$ ,  $^3J_{\text{CF}} = 1.1$ ,  $\text{CH}_3$ ); 53.1 (s,  $\text{OCH}_3$ ); 139.2 (dd,  $^1J_{\text{CF}} = 233.0$ ,  $^2J_{\text{CF}} = 39.0$ , CF); 158.9 (dd,  $^1J_{\text{CF}} = 268.9$ ,  $^2J_{\text{CF}} = 49.3$ , CF); ppm.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$ :  $-110.2$  (dq, 1F,  $^3J_{\text{FF}} = 128.2$ ,  $^3J_{\text{HF}} = 17.1$ );  $-165.9$  (dq, 1F,  $^3J_{\text{FF}} = 128.2$ ,  $^4J_{\text{HF}} = 4.9$ , CFC=O) ppm. GC–MS (EI): 137 ( $\text{M}^+ + 1$ ; 3.7), 136 ( $\text{M}^+$ ; 56.5), 135 ( $\text{M}^+ - 1$ ; 0.5), 105 (100).

##### 4.4.3. Reaction of MTFA (1) with lithium di-tert-butylcuprate

MTFA (2.01 g, 14.4 mmol), CuI (2.81 g, 14.8 mmol), *tert*-butyllithium (16.9 mL, 28.7 mmol, 1.7 M in pentane), complex mixture of fluorinated products (2.56 g) was obtained,  $^{19}\text{F}$  NMR and GC–MS identified product **3** and product **5** (**5a/5b** = 77/23), the ratio of **5/3** = 44/56.

Methyl (*Z*)-3,3-difluoro-4,4-dimethylpent-2-enoate (**5a**):  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$ :  $-107.5$  (bs, 1F);  $-150.4$  (d, 1F,  $^3J_{\text{FF}} = 4.0$ , CFC=O) ppm. GC–MS (EI): 178 ( $\text{M}^+$ ; 3.3), 59 (100).

Methyl (*E*)-3,3-difluoro-4,4-dimethylpent-2-enoate (**5b**):  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$ :  $-128.1$  (d, 1F,  $^3J_{\text{FF}} = 130.8$ );  $-165.5$  (d, 1F,  $^3J_{\text{FF}} = 130.3$ , CFC=O) ppm. GC–MS (EI): 178 ( $\text{M}^+$ , 5.9), 131 (100).

##### 4.4.4. Reaction of MTFA (1) with lithium dibutylcuprate ( $\text{Bu}_2\text{CuLi}$ )

MTFA (1.95 g; 13.9 mmol), CuI (2.71 g, 14.2 mmol), butyllithium (14 mL, 27.9 mmol, 2 M in pentane), product **6** (2 g, 11.2 mmol, 80.9%, **6a/6b** = 93/7).

Anal. Calcd for  $\text{C}_8\text{H}_{12}\text{F}_2\text{O}_2$ : C, 53.93; H, 6.79. Found: C, 53.88; H, 6.85.

Methyl (*Z*)-2,3-difluorohept-2-enoate (**6a**):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.94 (t, 3H,  $^3J_{\text{HH}} = 7.4$ ); 1.33–1.45 (m, 2H); 1.55–1.65 (m, 2H); 2.77 (ddt, 2H,  $^3J_{\text{HF}} = 26.4$ ,  $^3J_{\text{HH}} = 7.4$ ,  $^4J_{\text{HF}} = 2.8$ ); 3.85 (s, 3H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 13.4 (s,  $\text{CH}_3$ ); 21.9 (s,  $\text{CH}_2$ ); 27.8 (d,  $^3J_{\text{CF}} = 2.3$ ,  $\text{CH}_2$ ); 28.0 (dd,  $^2J_{\text{CF}} = 20.2$ ,  $^4J_{\text{CF}} = 1.7$ ,  $\text{CH}_2$ ); 52.1 (s,  $\text{OCH}_3$ ); 135.8 (dd,

$^1J_{CF} = 251.9$ ,  $^2J_{CF} = 19.5$ , CF); 160.1 (dd,  $^1J_{CF} = 272.2$ ,  $^2J_{CF} = 11.8$ , CF); 161.6 (dd,  $^2J_{CF} = 27.8$ ,  $^3J_{CF} = 9.7$ , C=O); ppm.  $^{19}F$  NMR (CDCl<sub>3</sub>)  $\delta$ : -106.6 (dt, 1F,  $^3J_{HF} = 25.6$ ,  $^3J_{FF} = 2.4$ ); -155.6 (d, 1F,  $^3J_{FF} = 2.4$ , CFC=O) ppm. GC-MS (EI): 179 ( $M^+ + 1$ ), 149 (100).

Methyl (*E*)-2,3-difluorohept-2-enoate (**6b**):  $^1H$  NMR (CDCl<sub>3</sub>)  $\delta$ : 0.94 (t, 3H,  $^3J_{HH} = 7.4$ ); 1.33–1.45 (m, 2H); 1.55–1.65 (m, 2H); 2.50 (ddt, 2H,  $^3J_{HF} = 22.8$ ,  $^3J_{HH} = 7.2$ ,  $^4J_{HF} = 5.8$ ); 3.86 (s, 3H) ppm.  $^{13}C$  NMR (CDCl<sub>3</sub>)  $\delta$ : 13.4 (s, CH<sub>3</sub>); 21.9 (s, CH<sub>2</sub>); 27.1 (d,  $^3J_{CF} = 3.0$ , CH<sub>2</sub>); 27.4 (dd,  $^2J_{CF} = 21.7$ , CH<sub>2</sub>); 52.1 (s, OCH<sub>3</sub>); 162.1 (dd,  $^1J_{CF} = 272.0$ ,  $^2J_{CF} = 46.9$ , CF); ppm, other signals hidden in a noise.  $^{19}F$  NMR (CDCl<sub>3</sub>)  $\delta$ : -124.4 (dt, 1F,  $^3J_{FF} = 128.2$ ,  $^3J_{HF} = 23.2$ ); -166.8 (dt, 1F,  $^3J_{FF} = 129.4$ ,  $^4J_{HF} = 6.1$ , CFC=O) ppm. GC-MS (EI): 179 ( $M^+ + 1$ ), 100).

#### 4.4.5. Reaction of MTFA (1) with lithium diphenylcuprate (Ph<sub>2</sub>CuLi)

MTFA (2.25 g, 16.1 mmol), CuI (3.08 g, 16.2 mmol), phenyllithium (17.9 ml, 32.2 mmol, 1.8 M in diethyl ether), product **7** (2.34 g, 11.8 mmol, 73.4%, **7a/7b** = 82/8).

Anal. Calcd for C<sub>10</sub>H<sub>8</sub>F<sub>2</sub>O<sub>2</sub>: C, 60.61; H, 4.07. Found: C, 60.70; H, 4.00.

Methyl (*Z*)-2,3-difluoro-3-phenylprop-2-enoate (**7a**):  $^1H$  NMR (CDCl<sub>3</sub>)  $\delta$ : 3.77 (s, 3H); 7.34–7.81 (m, 5H, arom.) ppm.  $^{13}C$  NMR (CDCl<sub>3</sub>)  $\delta$ : 52.3 (s, OCH<sub>3</sub>); 137.2 (dd,  $^1J_{CF} = 256.9$ ,  $^2J_{CF} = 22.3$ , CF); 141.1 (m, arom. C); 156.1 (dd,  $^1J_{CF} = 249.0$ ,  $^2J_{CF} = 16.9$ , CF); 160.8 (dd,  $^2J_{CF} = 28.4$ ,  $^3J_{CF} = 8.3$ , C=O); ppm.  $^{19}F$  NMR (CDCl<sub>3</sub>)  $\delta$ : -101.0 (d, 1F,  $^3J_{FF} = 3.4$ ); -149.3 (d, 1F,  $^3J_{FF} = 4.9$ , CFC=O) ppm. GC-MS (EI): 198 ( $M^+$ , 100).

Methyl (*E*)-2,3-difluoro-3-phenylprop-2-enoate (**7b**):  $^1H$  NMR (CDCl<sub>3</sub>)  $\delta$ : 3.94 (s, 3H); 7.34–7.81 (m, 5H, arom.) ppm.  $^{13}C$  NMR (CDCl<sub>3</sub>)  $\delta$ : 52.5 (s, OCH<sub>3</sub>); 139.5 (dd,  $^1J_{CF} = 244.4$ ,  $^2J_{CF} = 44.1$ , CF); 141.2 (m, arom. C); 155.8 (dd,  $^1J_{CF} = 260.2$ ,  $^2J_{CF} = 39.5$ , CF); ppm. Signal C=O hidden in a noise.  $^{19}F$  NMR (CDCl<sub>3</sub>)  $\delta$ : -134.6 (d, 1F,  $^3J_{FF} = 128.4$ ); -162.4 (d, 1F,  $^3J_{FF} = 128.0$ , CFC=O) ppm. GC-MS (EI): 198 ( $M^+$ , 100).

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