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Fluorinated acrylates via alkoxycarbonylation of 1-alkynes with fluorinated alcohols

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ABSTRACT

The system formed by combining in situ $Pd(OAc)_2$ with (2-pyridyl)diphenylphosphine ($PyPPh_2$) and CH_3SO_3H catalyzes efficiently the carbonylation of terminal alkynes (phenylacetylene or 1-hexyne) with alcohols having perfluorinated segments of the type $CF_3(CF_2)_m(CH_2)_n$–OH (m=1 or 3, n=1, 2 or 3) or with pentafluorophenol. Good carbonylation rates accompanied by high regioselectivity towards acrylate ester formation are obtained under mild reaction conditions (T=60–80 °C, P(CO)=30 atm). The influence of the CO pressure, the catalyst composition, the temperature and the number (n) of protonated methylene groups on the catalysis has been studied.

1. Introduction

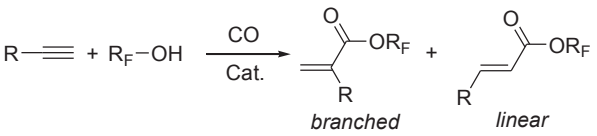
Fluorinated polymers have unique chemical and physical properties (low surface tensions, low friction coefficients, high transparency, water- and oil-repellency, high chemical stability), which continue to attract a great deal of attention from both the academic and the industrial community.[1]

Fluorinated acrylic esters are valuable intermediates as the corresponding polymers find a wide range of practical applications. Indeed, examples of application of fluorinated polymeric acrylates or methacrylates range from their use as sizing textile agents (they add water- and oil-repellency to natural or synthetic fabrics[2]) to the manufacture of optical devices (e.g., waveguides and interconnecting devices).[3] Other significant application fields are in lubricants manufacture and in coatings industry.[4]

A further peculiar application of fluorinated polyacrylates is in cultural heritage preservation owing to their optical properties and resistance to aging.[5]

The approaches employed to synthesize fluorinated (meth)acrylates usually entail a variety of esterification or transesterification processes based on the reaction of fluorinated alcohols with (meth) acrylic acid or some of its derivatives (halides, esters or anhydrides) in the presence of an acid or basic catalyst;[6] however, only the synthetic method developed by Yamaguchi[6d] appears of general applicability.

Terminal alkynes carbonylation (see Scheme 1) is a flexible synthetic approach, which allows to obtain in one step acrylic acid derivatives starting from easily accessible building blocks.[7] Since several years our research group has been interested in studying this reaction we successfully employed in the synthesis of some key intermediates in fine chemistry;[8] thus, we envisioned the carbonylation of 1-alkynes in the presence of fluorinated alcohols (see Scheme 1) as a new approach for the preparation of fluorinated acrylic esters.



R_F= $CF_3(CF_2)_m(CH_2)_n$, C_6F_5

R = phenyl, *n*-butyl

Cat.: $Pd(OAc)_2$ / $PyPPh_2$ / CH_3SO_3H

Scheme 1. Alkoxycarbonylation of 1-alkynes in the presence of fluorinated alcohols.

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The study appeared particularly intriguing since, at the best of our knowledge, in the literature there are no reports dealing with alkynes carbonylation in the presence of fluorinated alcohols.

2. Results and discussion

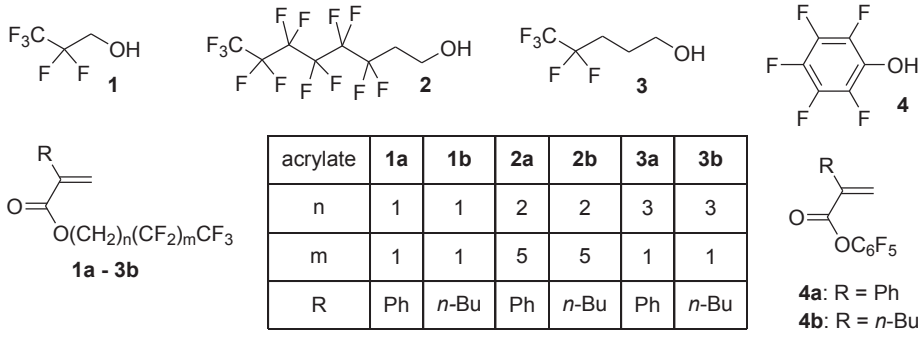
The carbonylation of phenylacetylene in the presence of 2,2,3,3,3-pentafluoropropanol (**1**) (Fig. 1) was chosen as model reaction for preliminary investigations (Scheme 1, R=phenyl, m=n=1). Phenylacetylene is an inexpensive, readily available, and easy to handle terminal alkyne, the reactivity of which is very similar to that of aliphatic alkynes in carbonylation reactions.[9] As for the fluorinated alcohol, we thought it interesting to first study the reactivity of **1**, which having a pK_a in water of 12.40 (compare with pK_a=12.39 for CF_3CH_2OH[10]), is one of the most acidic aliphatic alcohols and suffers from steric and conformational effects[11] brought about by the presence of the fluoro atoms on the carbon atom α to the CH_2OH moiety.

Owing to its high activity and selectivity, we decided to employ Drent's carbonylation catalyst, which is prepared combining in situ $Pd(OAc)_2$ with an excess of (2-pyridyl)diphenylphosphine ($PyPPh_2$) and methanesulfonic acid.[12]

Usually in alkyne alkoxycarbonylation the alkyne is the limiting reagent while the alcohol is present in large excess (e.g., most commonly as the reaction solvent); in our experiments only a moderate excess of the fluorinated alcohol was employed (alkyne/alcohol molar ratio in the 1:1.5–1:3 range) owing to its cost and dichloromethane was used as the reaction solvent. In preliminary experiments, the P(CO) was set at 30 atm and the palladium/phenylacetylene molar ratio was 1:1300. The data gathered in Table 1 show the influence of catalyst composition [$Pd(OAc)_2$/$PyPPh_2$/CH_3SO_3H molar ratios], temperature and alkyne/alcohol molar ratios on the reaction.

At 60 °C the reaction proceeds with reasonably good rates; after 3 h the alkyne conversion reaches the 83% and the sought acrylate ester (the branched isomer) forms with high regioselectivity (entry 1 of Table 1). The only side product formed by the reaction is the linear ester of (*E*) configuration as inferred from its ^{1}H NMR spectrum in which the vinyl protons appear as two doublets centered at 7.78 (=C*H*Ph) and 6.48 δ (=*CH*CO) having a coupling constant of 16.0 Hz.

Aiming to achieve complete substrate conversion, the reaction time was increased to 6 h (entry 2), but no improvement was observed. Usually in alkoxycarbonylations a large excess of the alcohol is present, thus we ascribed the incomplete alkyne conversion to the low amount of fluorinated alcohol employed. Hence, a further experiment (entry 3) was carried out doubling the alcohol to alkyne ratio, but no increase in substrate conversion was achieved.



acrylate	1a	1b	2a	2b	3a	3b
n	1	1	2	2	3	3
m	1	1	5	5	1	1
R	Ph	*n*-Bu	Ph	*n*-Bu	Ph	*n*-Bu

Fig. 1. Chemical structures of the starting fluorinated alcohols and the formed esters.

Table 1
Influence of the temperature and catalyst composition on the carbonylation of phenylacetylene with 2,2,3,3,3-pentafluoropropanol[a]

Entry	Pd/P/H$^+$[b]	T (°C)	Alcohol/alkyne	Conv. (%)[c]	Branched (%)	Linear (%)	TON[d]	TOF (h^{-1})[e]
1	1/30/60	60	1.5	83	96.6	3.4	1080	360
2[f]	1/30/60	60	1.5	83	97.0	3.0	1080	180
3	1/30/60	60	3	81	97.7	2.3	1050	350
4	1/30/60	70	3	89	97.0	3.0	1155	385
5	1/10/20	70	3	86	96.7	3.3	1125	375
6	1/30/60	80	3	91	96.8	3.2	1185	395
7	1/30/60	100	3	89	89.6	10.4	1155	385

[a] Reaction conditions: alkyne: phenylacetylene (4.5 mmol); alkyne/palladium molar ratio=1300; solvent: CH_2Cl_2 (10 mL); P(CO): 30 atm; reaction time: 3 h.
[b] $Pd(OAc)_2$/$PyPPh_2$/CH_3SO_3H (mol/mol/mol).
[c] Alkyne (limiting reagent) conversion determined by GLC with mesitylene as the internal standard.
[d] TON (turnover number): moles of substrate converted per mol of catalyst.
[e] TOF (turnover frequency): moles of substrate converted per mol of catalyst per hour.
[f] Reaction time: 6 h.

An enhancement of the catalytic activity without regioselectivity loss is observed on increasing the temperature from 60 to 80 °C, although at this temperature the reaction does not go to completion. On the other hand, a further raise of the reaction temperature from 80 to 100 °C leads to a small decrease in conversion, which is accompanied by a significant loss in regioselectivity. Detection of palladium black in the crude reaction mixture means that this latter result is likely caused by catalyst decomposition.

Finally it is worth to note that comparison of the data in entries 4 and 5 shows that the reaction course is practically unaffected by the palladium/phosphine/acid molar ratios employed in catalyst preparation.

On the basis of these experiments, we came to the conclusion that a maximum turnover number of about 1200 (entry 6) is achievable for the reaction and that likely there is some process leading to catalyst deactivation. In fact, it is worth to note that traces of palladium metal were sometimes observed in reaction crudes.

In Table 2 are reported the results obtained carrying out the reaction under different CO pressures, all other reaction conditions remaining the same employed in entry 1 of Table 1.

According to the results reported in Table 2 it appears that a minimum P(CO) of about 20 atm is necessary in order to obtain a satisfactory reaction rate accompanied by a good regioselectivity. The catalytic activity significantly increases by raising the P(CO) to 30 atm, while a further increase of P(CO) to 60 atm produces only a modest improvement.

With the optimized reaction conditions in hand, further experiments were carried out to highlight the influence of methylene groups spacing the CH_2OH from the carbon atoms bearing the fluorine substituents.

Table 2
Influence of the *P*(CO) on the carbonylation of phenylacetylene with 2,2,3,3,3-pentafluoropropanol[a]

Entry	*P*(CO)	Conv. (%)[b]	Branched (%)	Linear (%)	TON	TOF (h^{-1})
1	15	20	82.3	17.7	260	86
2	20	65	98.2	1.8	845	281
3	30	83	96.6	3.4	1080	360
4	60	85	96.6	3.4	1105	368

[a] Reaction conditions: $Pd(OAc)_2/PyPPh_2/CH_3SO_3H$: 1/30/60 (mol/mol/mol); alkyne: phenylacetylene (4.5 mmol); alkyne/palladium molar ratio: 1300; alcohol/alkyne molar ratio: 1.5; solvent: CH_2Cl_2 (10 mL); *T*: 60 °C; reaction time: 3 h.
[b] Alkyne (limiting reagent) conversion determined by GLC with mesitylene as the internal standard.

Accordingly, the carbonylation of phenylacetylene was carried out in the presence of the alcoholic substrates **2** and **3** (Fig. 1); the relevant data are presented in Table 3.

Table 3
Phenylacetylene carbonylation with different fluorinated alcohols[a]

Entry	Alcohol	Alkyne/Pd	Conv.[b] (%)	Branched (%)	Linear (%)	TON	TOF (h^{-1})
1	**1**	1300	86	96.7	3.3	1105	368
2	**2**	1300	95	96.7	3.3	1235	411
3	**2**	2600	73	96.5	3.5	1899	632
4	**3**	2600	72	97.0	3.0	1872	624
5[c]	**4**	400	70	97.3	2.7	280	12

[a] Reaction conditions: $Pd(OAc)_2/PyPPh_2/CH_3SO_3H$: 1/10/20 (mol/mol/mol); alkyne: phenylacetylene (4.5 mmol); solvent: CH_2Cl_2 (10 mL); *T*: 70 °C; *P*(CO): 30 atm; reaction time: 3 h.
[b] Alkyne (limiting reagent) conversion determined by GLC with mesitylene as the internal standard.
[c] *T*: 80 °C; reaction time: 24 h.

As surmised, the introduction of protonated methylene groups between the alcoholic carbon and the fluorinated segment of the substrates significantly mitigates the fluorine influence and increases the catalytic activity. For instance, carbonylation of phenylacetylene in the presence of **2** (alkyne/palladium molar ratio=1300:1) goes almost to completion in 3 h (entry 2 of Table 3). This result encouraged us to carry out a further experiment doubling the alkyne to catalyst molar ratio (entry 3).

The substrate conversion reaches 73% by 3 h, which corresponds to a good TON of 1900 (TOF >600 h^{-1}). Approximately the same conversion is achieved in the presence of alcohol **3** (entry 4) indicating that the introduction of a second methylene group does not further increase the alcohol reactivity.

Furthermore, in order to get a deeper insight on the scope of the reaction, some carbonylation experiments were carried out in the presence of pentafluorophenol **4**. In this connection it is worth to note that the effectiveness of poly(pentafluorophenylacrylates) as active ester polymers has been demonstrated by Théato and coworkers[13] and that the studies on alkynes phenoxycarbonylation are rare.[14]

With pentafluorophenol much lower reaction rates are observed, so it is necessary to increase the catalyst loading by about an order of magnitude in order to obtain reasonable alkyne conversion and yield in the sought acrylic ester (entry 5 of Table 3).

According to the data gathered in Table 3 the carbonylation rate appears to be inversely correlated with the acidity of the fluorinated alcohol since it increases when the fluorinated segment is moved away from the alcoholic moiety. This not only decreases the acidity of the alcoholic function but also alleviate the steric hindrance generated by the fluorine atoms.

Finally, it is interesting to remark that the regioselectivity of the reaction is practically unaffected by the nature of the fluorinated alcohol employed. This result is in keeping with the reaction mechanism proposed by us[15] in which alcoholysis of an acyl vinyl intermediate is the last step of the catalytic cycle.

In Table 4 are reported the results relevant to the carbonylation of 1-hexyne, we employed as the handy representative of the class of terminal aliphatic alkynes. The reaction conditions are the same employed in the experiments reported in Table 3, thus an immediate comparison is possible. According to the data gathered in Table 4, it appears that 1-hexyne is more reactive than phenylacetylene, whichever the alcohol. In particular, it is worth to note that, except with alcohol **3**, in all other cases almost complete alkyne conversion is obtained.

Table 4
n-Hexyne carbonylation in the presence of different fluorinated alcohols[a]

Entry	Alcohol	Alkyne/Pd	Conv.[b] (%)	Branched (%)	Linear (%)	TON	TOF (h^{-1})
1	**1**	1300	95	97.1	2.9	1235	410
2	**2**	2600	99	97.5	2.5	2574	860
3	**3**	2600	78	97.7	2.3	2028	680
4[c]	**4**	400	98	97.7	2.3	384	16

[a] Reaction conditions: $Pd(OAc)_2/PyPPh_2/CH_3SO_3H$: 1/10/20 (mol/mol/mol); alkyne: phenylacetylene (4.5 mmol); solvent: CH_2Cl_2 (10 mL); *T*: 70 °C; *P*(CO): 30 atm; reaction time: 3 h.
[b] Alkyne (limiting reagent) conversion determined by GLC with mesitylene as the internal standard.
[c] *T*: 80 °C; reaction time: 24 h.

The regioselectivity of the reaction is very close to that observed with phenylacetylene and, as found with the aromatic alkyne, it is almost unaffected by the nature of the fluorinated alcohol.

3. Conclusions

This study demonstrates that the carbonylation of terminal alkynes in the presence of fluorinated alcohols is a feasible methodology for the synthesis of fluorinated acrylates.

The $Pd(OAc)_2/PyPPh_2/CH_3SO_3H$ system emerges as an efficient and selective catalyst for the reaction; whichever the structure of the fluorinated alcohol, the regioselectivity towards the target branched ester is very high. Except with pentafluorophenol, very good reaction rates were obtained under relatively mild reaction conditions. The process is efficient and does not require of a stringent control of the reaction conditions working well over a wide range of temperatures and *P*(CO).

Finally, it should be emphasized that the disclosed synthetic approach represents a 'one pot', atom economical methodology of general applicability, allowing to obtain valuable high performance products starting from promptly available substrates.

4. Experimental section

4.1. General

All the operations were carried out under argon in Schlenk-type glassware.

Amylene stabilized dichloromethane (Sigma–Aldrich) was distilled from CaH_2 before use.

Pentafluorophenol, 2,2,3,3,3-pentafluoropropanol, 4,4,5,5,5-pentafluoropentan-1-ol, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol, (2-pyridyl)diphenylphosphine, and methanesulfonic acid were commercial products (Sigma–Aldrich) and used as received. $Pd(OAc)_2$ was purchased from Engelhard Industries. High purity CO was obtained by SIAD.

The ^{1}H and ^{13}C NMR spectra were registered in $CDCl_3$ solutions on a Bruker AVANCE 300 spectrometer operating at 300.11 and 75.44 MHz, respectively; ^{19}F NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 188.066 MHz. GLC analyses were performed on an Agilent 6850 gas chromatograph; GC–MS analyses were performed on a HP 5890 series II gas chromatograph interfaced to a HP 5971 quadrupole mass-detector. IR spectra (liquid film, KBr windows) were registered on a Perkin Elmer 'Spectrum One' FT-IR apparatus. High-resolution mass spectra were recorded on a Thermo Finnigan MAT 95 XP spectrometer.

4.2. Carbonylation experiments

The carbonylation experiments were carried out in a magnetically stirred stainless steel autoclave (total volume about 150 mL) connected to a thermostat in order to maintain the reaction temperature constant within ±1 °C.

As an example, the experimental details for entry 4 of Table 1 are reported. Under inert atmosphere, a Schlenk flask containing a small magnetic bar was charged with 10 mL of CH_2Cl_2, 460 mg (4.5 mmol) of phenylacetylene, 700 μL (1050 mg, 7.0 mmol) of $CF_3CF_2CH_2OH$, 29 mg (0.11 mmol) of PPh_2Py, 1.0 mL of a 3.46×10^{-3} M solution of $Pd(OAc)_2$ in dichloromethane (0.00346 mmol) and, finally, 14 μL (20.72 mg, 0.21 mmol) of methanesulfonic acid. The resulting yellow-orange solution was transferred via cannula into the autoclave. Then the reactor was pressurized with 30 atm of CO and heated at 70 °C. After 3 h the autoclave was cooled to −20 °C and the residual gas carefully vented off. Mesitylene (as the internal standard) was added to the raw reaction mixture, which was analyzed by GLC.

The reaction crudes were purified by flash-chromatography employing silica gel (Sigma–Aldrich, 60 Å, 70–230 mesh) and dichloromethane or dichloromethane/*n*-hexane mixtures to give mixtures of the regioisomers as clear colorless oils. We report below the spectroscopic characterization (^{1}H NMR, ^{13}C NMR, ^{19}F NMR, IR, and HRMS) together with the GC–MS fragmentation patterns relevant to the prevalent regioisomer (about 97% by GC) of the mixtures.

4.3. Acrylates characterization

*4.3.1. 2,2,3,3,3-Pentafluoropropyl 2-phenylacrylate (**1a**).* The crude carbonylation product was purified by flash chromatography (silica gel, *n*-hexane/Et_2O=70/30, R_f=0.65) to give the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47–7.35 (5H, m, arom), 6.49 (1H, d, J_{HH}=1.1 Hz, =CH*H*), 6.06 (1H, d, J_{HH}=1.1 Hz, =C*H*H), 4.70 (2H, t, J_{HF}=12.7 Hz, OCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.9 (*C*O), 139.8 (=*C*CO–), 135.9 (Ph-*ipso*), 129.1 (Ph-*para*), 128.7 (=CH_2), 128.41 (2C, Ph-*meta*), 128.37 (2C, Ph-*ortho*), 118.6 (qt, $^1J_{CF}$=286.2 Hz, $^2J_{CF}$=34.8 Hz, *C*F_3), 112.3 (tq, $^1J_{CF}$=255.2, $^2J_{CF}$=38.1 Hz, *C*F_2), 59.8 (t, $^2J_{CF}$=38.1 Hz, OCH_2). ^{19}F NMR (188 MHz, $CDCl_3$) δ: −83.99 (3F, s, C*F*$_3$), −123.44 (2F, t, $^3J_{FH}$=12.7 Hz, C*F*$_2$). MS (EI 70 eV) *m*/*z* (%): 280 (40, M^+), 131 (25), 103 (100), 77 (25). IR (liquid film, KBr) ν_{max}: 3070, 2968, 1750, 1607, 1496, 1450, 1205, 1146, 1110, 736 cm^{-1}. HRMS (EI): *m*/*z* $[M]^+$ calcd 280.0523 for $C_{12}H_9F_5O_2$, found 280.0528.

*4.3.2. 2,2,3,3,3-Pentafluoropropyl 2-methylenehexanoate (**1b**).* The crude carbonylation product was purified by flash chromatography (silica gel, *n*-hexane/Et_2O=99/1, R_f=0.47) to give the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.26–6.24 (1H, m, =C*H*H), 5.69–5.66 (1H, m, =CH*H*), 4.60 (2H, tq, $^3J_{HF}$=13.2, $^4J_{HF}$=0.98 Hz, OCH_2), 2.38–2.28 (2H, m, =CCH_2), 1.54–1.41 (2H, m, =CCH_2CH_2), 1.40–1.28 (2H, m, CH_2CH$_3$), 0.91 (3H, t, J_{HH}=7.1 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.6 (*C*O), 139.5 (=*C*CO–), 127.0 (=CH_2), 118.6 (qt, $^1J_{CF}$=284.0 Hz, $^2J_{CF}$=35.2 Hz, *C*F_3), 112.3 (tq, $^1J_{CF}$=252.3 Hz, $^2J_{CF}$=36.0 Hz, *C*F_2), 59.6 (t, $^2J_{CF}$=28.1 Hz, OCH_2), 31.6 (=CCH_2), 30.6 ($CH_2CH_2CH_3$), 22.4 (CH_2CH_3), 13.9 (*C*H$_3$). ^{19}F NMR (188 MHz, $CDCl_3$) δ: −83.87 (3F, s, C*F*$_3$), −123.42 (2F, t, $^3J_{FH}$=12.7 Hz, C*F*$_2$). MS (EI 70 eV) *m*/*z* (%): 260 (21, M^+), 219 (100), 191 (16), 111 (63), 69 (48). IR ν_{max} (liquid film, KBr): 2963, 2918, 1740, 1634, 1205, 1147, 1107, 812, 738 cm^{-1}. HRMS (EI, *m*/*z*): $[M]^+$, found 260.0840. $C_{10}H_{13}F_5O_2$ requires 260.0836.

*4.3.3. 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl 2-phenylacrylate (**2a**).* The crude carbonylation product was purified by flash chromatography (silica gel, *n*-hexane/CH_2Cl_2=70/30, R_f=0.60) to give the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46–7.34 (5H, m, arom), 6.41 (1H, d, J_{HH}=1.2 Hz, =C*H*H), 5.96 (1H, d, J_{HH}=1.2 Hz, =CH*H*), 4.54 (2H, t, J_{HH}=6.5 Hz, OCH_2), 2.55 (2H, tt, J_{HH}=6.5 Hz, J_{HF}=18.1 Hz, CH_2CF_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.3 (*C*O), 140.9 (=*C*CO), 136.5 (Ph-*ipso*), 128.45 (Ph-*para*), 128.43 (2C, Ph-*meta*), 128.3 (2C, Ph-*ortho*), 127.7 (=CH_2), 123.5–104.1 (overlapping m, CF_3 and CF_2), 57.1 (OCH_2), 30.7 (t, $^2J_{CF}$=21.7 Hz, CH_2CF_2). ^{19}F NMR (188 MHz, $CDCl_3$) δ: −81.09 (3F, t, $^2J_{FF}$=9.8 Hz, C*F*$_3$), −113.36 to −114.21 (2F, m, CH$_2$C*F*$_2$), −121.81 to −122.40 (2F, m, C*F*$_2$), −122.76 to −123.42 (2F, m, C*F*$_2$), −123.51 to −124.15 (2F, m, 2F, C*F*$_2$), −125.98 to −126.66 (2F, m, C*F*$_2$CF$_3$). MS (EI 70 eV) *m*/*z* (%): 494 (17, M^+), 147 (12), 131 (42), 103 (100), 77 (22). IR (liquid film, KBr) ν_{max}: 3058, 1741, 1240, 1194, 910, 732 cm^{-1}. HRMS (EI, *m*/*z*): $[M]^+$, found 494.2485. $C_{17}H_{11}F_{13}O_2$ requires 494.2473.

*4.3.4. 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl 2-methylenehexanoate (**2b**).* The crude carbonylation product was purified by flash chromatography (silica gel, *n*-hexane/ethyl acetate=98/2, R_f=0.44) to give the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.16–6.14 (1H, m, =C*H*H), 5.57–5.54 (1H, m, =CH*H*), 4.44 (2H, t, J_{HH}=6.5 Hz, OCH_2), 2.50 (2H, tt, J_{HH}=6.5 Hz, J_{HF}=18.1 Hz, CH_2CF_2), 2.29 (2H, t, J_{HH}=6.9 Hz, =CCH_2), 1.48–1.35 (2H, m, =CCH_2CH_2), 1.24 (2H, m, CH_2CH$_3$), 0.90 (3H, t, J_{HH}=7.0 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.0 (*C*O), 140.5 (=*C*CO), 125.4 (=CH_2), 123.5–104.2 (overlapping m, CF_3 and CF_2), 56.6 (t, $^3J_{CF}$=4.7 Hz, OCH_2), 31.6 (=CCH_2), 30.72 (t, $^2J_{CF}$=43.5 Hz, CH_2CF_2), 30.70 ($CH_2CH_2CH_3$), 22.4 (CH_2CH_3), 13.9 (*C*H$_3$). ^{19}F NMR (188 MHz, $CDCl_3$) δ: −81.58 (3F, t, $^3J_{FF}$=9.8 Hz, C*F*$_3$), −113.92 to −114.44 (2F, m, CH$_2$C*F*$_2$), −122.09 to −122.67 (2F, m, C*F*$_2$), −123.18 to −123.65 (2F, m, C*F*$_2$), −123.88 to −124.31 (2F, m, 2F, C*F*$_2$), −126.56 to −127.01 (2F, m, C*F*$_2$CF$_3$). MS (EI 70 eV) *m*/*z* (%): 474 (78, M^+), 433 (92), 111 (100), 81 (66), 69 (94). IR (liquid film, KBr) ν_{max}: 2963, 2924, 1726, 1633, 1239, 1197, 1138, 738 cm^{-1}. HRMS (EI, *m*/*z*): $[M]^+$, found 474.0879. $C_{15}H_{15}F_{13}O_2$ requires 474.0864.

*4.3.5. 4,4,5,5,5-Pentafluoropentyl 2-phenylacrylate (**3a**).* The crude carbonylation product was purified by flash chromatography (silica gel, *n*-hexane/Et_2O=70/30, R_f=0.50) to give the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46–7.35 (5H, m, arom), 6.38 (1H, d, J_{HH}=1.2 Hz, =CH*H*), 5.93 (1H, d, J_{HH}=1.2 Hz, =C*H*H), 4.31 (2H, t, J_{HH}=6.1 Hz, OCH_2), 2.27–2.10 (2H, m, CH_2CF_2), 2.10–1.97 (2H, m, OCH$_2$CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.6 (*C*O), 141.3 (=*C*CO–), 136.7 (Ph-*ipso*), 128.38 (Ph-*para*), 128.37 (2C, Ph-*meta*), 128.2 (2C, Ph-*ortho*), 127.2 (1C, =CH_2), 119.2 (qt, $^1J_{CF}$=283.5 Hz, $^2J_{CF}$=37.6 Hz, *C*F_3), 115.7 (tq, $^1J_{CF}$=250.5 Hz, $^2J_{CF}$=37.0 Hz, *C*F_2), 63.7, 27.7 (t, $^2J_{CF}$=22.2 Hz), 20.2 (t, $^3J_{CF}$=3.4 Hz). ^{19}F NMR (188 MHz, $CDCl_3$) δ: −85.63 (3F, s, C*F*$_3$), −118.38 (2F, t, $^3J_{FH}$=18.5 Hz, C*F*$_2$). MS (EI 70 eV) *m*/*z* (%): 308 (55, M^+), 147 (39), 131 (35), 103 (100), 77 (63). IR (liquid film, KBr) ν_{max}: 2960, 1726, 1452, 1202, 1190, 1019, 910, 740 cm^{-1}. HRMS (EI, *m*/*z*): $[M]^+$, found 308.0825. $C_{14}H_{13}F_5O_2$ requires 308.0836.

*4.3.6. 4,4,5,5,5-Pentafluoropentyl 2-methylenehexanoate (**3b**).* The crude carbonylation product was purified by flash chromatography (silica gel, *n*-hexane/ethyl acetate=98/2, R_f=0.77) to give the title

compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.14–6.12 (1H, m, =CH*H*), 5.56–5.53 (1H, m, =C*H*H), 4.21 (2H, t, J=6.1 Hz, OCH_2), 2.31 (2H, t, J=7.1 Hz, =CCH_2), 2.25–2.08 (2H, m, CH_2CF_2), 2.06–1.94 (2H, m, OCH_2CH_2), 1.51–138 (2H, m, =CCH_2CH_2), 1.37–1.27 (2H, m, CH_2CH_3), 0.91 (3H, t, J=7.2 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.2 (*C*O), 140.8 (=*C*CO), 125.0 (=CH_2), 119.2 (qt, $^1J_{CF}$=282.7 Hz, $^2J_{CF}$=36.1 Hz, *C*F_3), 115.7 (tq, $^1J_{CF}$=250.5 Hz, $^2J_{CF}$=37.5 Hz, *C*F_2), 63.1 (OCH_2), 31.7 (=CCH_2), 30.8 ($CH_2CH_2CH_3$), 27.8 (t, $^2J_{CF}$=22.7 Hz, CH_2CF_2), 22.4 (CH_2CH_3), 20.3 (t, $^3J_{CF}$=3.5 Hz, $CH_2CH_2CF_2$), 13.9 (CH_3). ^{19}F NMR (188 MHz, $CDCl_3$) δ: −85.89 (3*F*, s, C*F*$_3$), −118.74 (2F, t, $^3J_{FH}$=18.3 Hz, C*F*$_2$). MS (EI 70 eV) m/z (%): 288 (47, M^+), 247 (39), 127 (44), 111 (76), 87 (100). IR (liquid film, KBr) ν_{max}: 2962, 2929, 1721, 1633, 1200, 1160, 1007, 738 cm^{-1}. HRMS (EI, m/z): $[M]^+$, found 288.1168. $C_{12}H_{17}F_5O_2$ requires 288.1149.

*4.3.7. Perfluorophenyl 2-phenylacrylate (**4a**).* The crude carbonylation product was purified by flash chromatography (silica gel, cyclohexane/CH_2Cl_2=8/2, R_f=0.53) to give the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.57–7.51 (2H, m, arom), 7.49–7.40 (3H, m, arom), 6.74 (1H, s, =C*H*H), 6.25 (s, 1H, =CH*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 162.7 (*C*O), 141.4 (2C, ddq, $^1J_{CF}$=248.1, $^2J_{CF}$=12.9, $^3J_{CF}\approx{}^4J_{CF}$=4.2 Hz, *C*F-*ortho*), 139.7 (1C, dtt,, $^1J_{CF}$=251.7, $^2J_{CF}$=13.5, $^3J_{CF}$=4.0 Hz, *C*F-*para*), 138.9 (=*C*CO), 138.1 (2C, dtdd, $^1J_{CF}$=251.4, $^2J_{CF}$=13.5 Hz, $^3J_{CF}$=3.0 Hz, $^4J_{CF}$=6.2 Hz, *C*F-*meta*), 135.42 (Ph-*ipso*), 130.76 (Ph-*para*), 129.0 (=CH_2), 128.5 (2C, Ph-*meta*), 128.3 (2C, Ph-*ortho*), 125.4 (1C, ttd, $^2J_{CF}$=14.6 Hz, $^3J_{CF}$=2.0 Hz, $^4J_{CF}$=4.8 Hz, O*C*). ^{19}F NMR (188 MHz, $CDCl_3$) δ: −152.8 to −153.2 (2F, m, *F*-*ortho*), −158.40 (1F, t, $^3J_{FF}$=21.7 Hz, *F*-*para*), −162.66 to −162.93 (2F, m, *F*-*meta*). MS (EI 70 eV) m/z (%): 314 (5, M^+), 183 (8), 155 (17), 131 (38), 103 (100), 77 (37). IR ν_{max} (liquid film, KBr) ν_{max}: 3030, 1767, 1670, 1521, 1145, 1056, 995, 700 cm^{-1}. HRMS (EI, m/z): $[M]^+$, found 314.0371. $C_{15}H_7F_5O_2$ requires 314.0366.

*4.3.8. Perfluorophenyl 2-methylenehexanoate (**4b**).* The crude carbonylation product was purified by flash chromatography (silica gel, *n*-hexane/ethyl acetate=98/2, R_f=0.78) to give the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.47 (1H, s, =C*H*H), 5.88–5.85 (m, 1H, =CH*H*), 2.42 (1H, t, J_{HH}=7.5 Hz, =CCH_2), 1.60–1.48 (2H, m, =CCH_2CH_2), 1.46–1.32 (2H, m, CH_2CH_3), 0.94 (3H, t, J_{HH}=7.2, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 163.2 (*C*O), 141.5 (2C, ddq, $^1J_{CF}$=251.8, $^2J_{CF}$=12.6, $^3J_{CF}\approx{}^4J_{CF}$=4.2 Hz, *C*F-*ortho*), 139.6 (1C, dtt, $^1J_{CF}$=252.8, $^2J_{CF}$=13.7, $^3J_{CF}$=4.0 Hz, *C*F-*para*), 138.6 (=*C*CO), 138.1 (2C, dtdd, $^1J_{CF}$=251.8, $^2J_{CF}$=13.5 Hz, $^3J_{CF}$=3.0 Hz, $^4J_{CF}$=6.2 Hz, *C*F-*meta*), 128.9 (=CH_2), 125.6 (1C, ttd, $^2J_{CF}$=14.6 Hz, $^3J_{CF}$=2.1 Hz, $^4J_{CF}$=4.9 Hz, O*C*), 31.8 (=CCH_2), 30.6 ($CH_2CH_2CH_3$), 22.3 (CH_2CH_3), 13.8 (CH_3). ^{19}F NMR (188 MHz, $CDCl_3$) δ: −152.8 to −153.1 (2F, m, *F*-*ortho*), −158.87 (1F, t, $^3J_{FF}$=18.3 Hz, *F*-*para*), −162.62 to −163.01 (2F, m, *F*-*meta*). MS (EI 70 eV) m/z (%): 294 (4, M^+), 184 (32), 155 (51), 111 (100), 69 (94). IR (liquid film, KBr) ν_{max}: 2962, 2929, 1761, 1521, 1147, 1113, 1060, 997, 737 cm^{-1}. HRMS (EI, m/z): $[M]^+$, found 294.0669. $C_{13}H_{11}F_5O_2$ requires 294.0679.

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