ChemPubSoc Europe

DOI: 10.1002/ejoc.201901601

EurJOC European Journal of Organic Chemistry

Full Paper

Regioselective Hydroesterification

Pd-Catalyzed Regioselective Hydroesterification of Olefins with 2,2,2-Trifluoroethyl Formate

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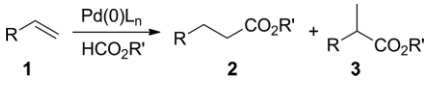
Abstract: A Pd-catalyzed regioselective hydroesterification of olefins with 2,2,2-trifluoroethyl formate (TFEF) is described. Either linear or branched esters can be selectively obtained with proper ligands in most cases. The reaction process is operationally simple and involves no toxic CO gas.

Introduction

Carboxylic esters are an important class of compounds and are of great significance for pharmaceuticals, fine chemicals, and organic synthesis. As an effective approach to this class of compounds, hydroesterification of olefins has been actively investigated with[1,2] or without CO gas.[3] Much efforts have been made in use of formates as CO surrogates primarily with Ru[4] and Pd[5] catalysts. For the Pd-catalyzed hydroesterification process, alkyl formates have been found to be generally much less effective than aryl formates for the reaction. For example, no ester products were observed for the hydroesterification reactions with alkyl formates such as HCO_2Bn,[5a,5c] $HCO_2C_2H_4Ph$,[5a] HCO_2Et,[5c] and HCO_2nBu.[5a,5e] As part of our continuing interest in hydroesterification process (Scheme 1), we have investigated a number of electronically different formates with aim of understanding the influencing factors for the reactivity and expanding the reaction to other esters. Our studies have shown that the electronic nature of the formate has profound impact on the reaction reactivity and selectivity. 2,2,2-Trifluoroethyl formate ($HCO_2CH_2CF_3$) has been found to be highly effective agent for the hydroesterification of olefins. Either linear or branched 2,2,2-trifluoroethyl esters can be obtained regioselectively with proper ligands. Herein, we wish to report our preliminary results on this subject.



Scheme 1. Pd-Catalyzed Hydroesterification of Olefins.

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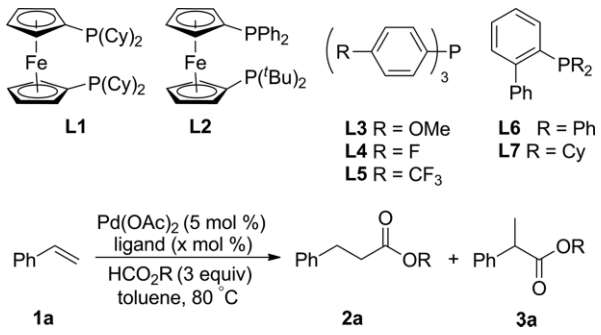
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejoc.201901601.

Results and Discussion

In our previous studies, we have shown that styrenes can be regioselectively hydroesterified with HCO_2Ph to give either linear or branched esters, respectively, with 1,1′-bis(dicyclohexylphosphino)-ferrocene or 2-(dicyclohexyl-phosphino)biphenyl as ligand.[5e] In current studies, several alkyl formates (**4a**–**g**) were first examined for the hydroesterification with styrene in the presence of 5 mol% $Pd(OAc)_2$ and 10 mol% 1,1′-bis(dicyclohexylphosphino)-ferrocene (**L1**)[5e,6] in toluene at 80 °C for 48 h (Table 1, entries 1–7). Poor reactivities were observed with HCO_2Me (**4a**) and HCO_2Et (**4b**) (Table 1, entries 1 and 2). A mixture of esters **2a** and **3a** were formed in 47 and 38 % yield, respectively, with HCO_2CH_2Ph (**4c**) and $HCO_2CH_2CO_2Me$ (**4d**) (Table 1, entries 3 and 4). Interestingly, with fluoroethyl formates (**4e**, **f**, **g**), both yield and regioselectivity were increased as more F was introduced (Table 1, entries 5–7). Linear ester **2a** was formed in 84 % yield with >20:1 l/b ratio when $HCO_2CH_2CF_3$ (**4g**) was used. The dramatic increase of l/b ratio from 1:1 to >20:1 with addition of F was particularly noteworthy. With $HCO_2CH_2CF_3$ (**4g**), additional ligands were investigated for the hydroesterification (Table 1, entries 8–18). Little hydroesterification reaction occurred with ligands such as dppe and tris(4-fluorophenyl)-phosphine (**L4**) (Table 1, entries 8 and 15). In other cases, a mixture of linear and branched esters were formed in varying yields (Table 1, entries 9–17). The regioselectivity was reversed with 2-(dicyclohexyl-phosphino)biphenyl (**L7**)[5e,7] (Table 1, entry 18). Branched ester **3a** was isolated in 32 % yield with l/b ratio <1:20. It was found that the reaction can be greatly boosted by adding small amounts of H_2O. The exact role of H_2O is not clear at this moment. Ester **3a** was formed in 94 % yield under proper reaction conditions (Table 1, entry 22).

The hydroesterification process with 2,2,2-trifluoroethyl formate ($HCO_2CH_2CF_3$) can be extended to a variety of substituted styrenes. With ligand **L1** (**Method A**), linear trifluoromethyl aryl propionates can be obtained in 38–82 % yields with >20:1 l/b ratio (Table 2, entries 1–13). The phenyl rings can bear various substituents including OMe, F, Cl, and CF_3 groups. 2-Vinylpyridine and *N*-vinylphthalimide were found to be effective substrates, giving the corresponding esters in 56 % and 90 % yield,

Table 1. Studies of the Reaction Conditions.[a]

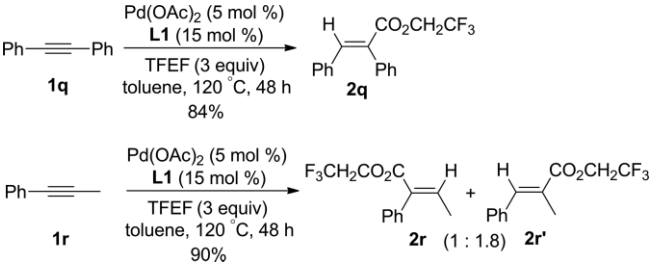


Entry	Ligand	HCO_2R	Yield (%)[b] (**2a**/**3a**)[c]
1	**L1**	HCO_2Me (**4a**)	trace
2	**L1**	HCO_2Et (**4b**)	0
3	**L1**	HCO_2CH_2Ph (**4c**)	47 (1:2)
4	**L1**	$HCO_2CH_2CO_2Me$ (**4d**)	38 (1:1)
5	**L1**	$HCO_2CH_2CH_2F$ (**4e**)	33 (1:1)
6	**L1**	$HCO_2CH_2CHF_2$ (**4f**)	76 (18:1)
7	**L1**	**$HCO_2CH_2CF_3$ (4g)**	**84 (> 20:1)**
8	dppe	**4g**	trace
9	dppp	**4g**	90 (2.5:1)
10	dppb	**4g**	83 (1.7:1)
11	dppf	**4g**	47 (1.6:1)
12	**L2**	**4g**	98 (1:1.4)
13	P(*p*-tolyl)$_3$	**4g**	73 (1.6:1)
14	**L3**	**4g**	70 (2.2:1)
15	**L4**	**4g**	trace
16	**L5**	**4g**	8 (1:1.3)
17	**L6**	**4g**	28 (1.1:1)
18	**L7**	**4g**	32 (< 1:20)
19[d]	**L7**	**4g**	37 (< 1:20)
20[d]	**L7**	**4g** (add 5 % HCOOH)	39 (< 1:20)
21[d]	**L7**	**4g** (add 10 μL H_2O)	80 (< 1:20)
22[d]	**L7**	**4g (add 15 μL H_2O)**	**94 (< 1:20)**
23[d]	**L7**	**4g** (add 30 μL H_2O)	80 (< 1:20)
24[d]	**L7**	**4g** (add 10 % F_3CCH_2OH)	37 (< 1:20)

[a] The reactions were carried out with **1a** (0.50 mmol), HCO_2R (1.50 mmol), $Pd(OAc)_2$ (0.025 mmol), ligand (0.050 or 0.10 mmol, P/Pd = 4:1) in toluene (0.10 mL) at 80 °C for 48 h unless otherwise stated. [b] The yield was determined from the crude reaction mixture by ^1H NMR with BnOMe as an internal standard. [c] The ratio of **2a**:**3a** was determined by ^1H NMR analysis of the crude reaction mixture. [d] **L7** (0.15 mmol) at 80 °C for 24 h.

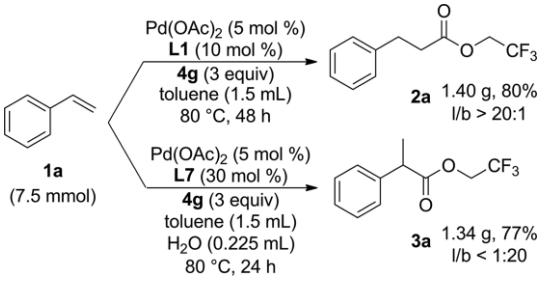
respectively, with >20:1 regioselectivity (Table 2, entries 14 and 15). For alkyl terminal olefin 1-pentadecene, the linear ester was obtained in 40 % yield with >20:1 l/b ratio (Table 2, entry 16). As shown in Scheme 2, the reaction can also apply to certain alkyne. α,β-Unsaturated trifluoroethyl ester **2q** was isolated in 84 % yield from diphenyl acetylene (**1q**).[8] A mixture of regioisomers (**2r**/**2r′** = 1:1.8) was obtained in 90 % yield with 1-phenylpropyne (**1r**).[9]

With ligand **L7** (**Method B**), branched trifluoromethyl aryl propionates were obtained in 32–91 % yields with 1:14 to <1:20 l/b ratio for styrenes (Table 2, entries 1–12). For sterically bulky 2,4,6-trimethylstyrene, a mixture of linear and branched esters was obtained in 30 % yield with 3.4:1 l/b ratio (Table 2, entry 13). No ester was obtained with 2-Vinylpyridine (Table 2, entry 14). For *N*-vinylphthalimide, the linear ester was isolated in 29 % yield (Table 2, entry 15). 1-Pentadecene was not effective substrate under the reaction conditions (Table 2, entry 16).



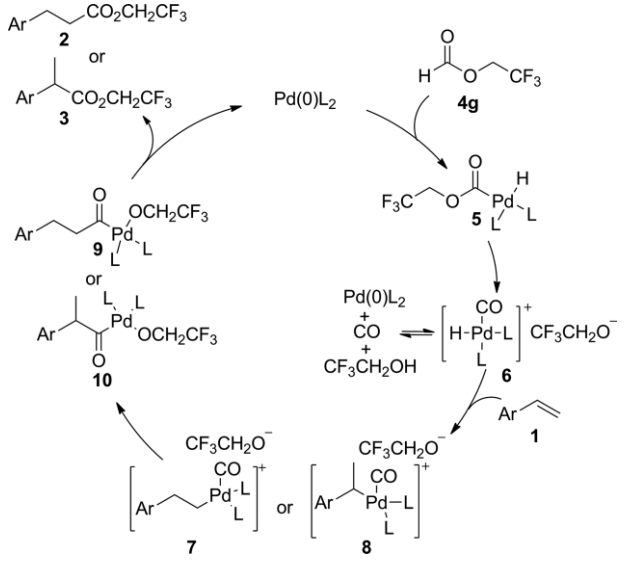
Scheme 2. Pd-Catalyzed Hydroesterification of Acetylenes.

As exemplified by styrene, the reaction process can be carried out on a gram scale with both **Method A** and **Method B** (Scheme 3). Linear ester **2a** and branched ester **3a** were obtained in 80 % and 77 % yield, respectively, with high regioselectivity.



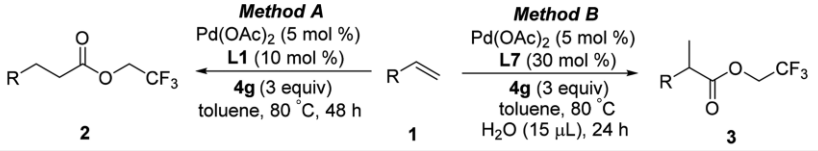
Scheme 3. Gram-Scale Hydroesterification of Olefin.

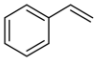
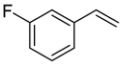
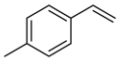
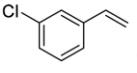
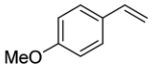
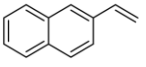
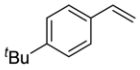
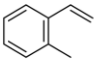
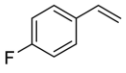
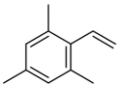
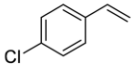
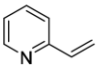
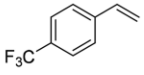
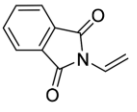
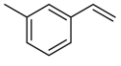
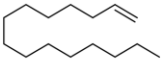
A precise reaction mechanism is not clear at this moment and await further study. One plausible catalytic cycle is shown in Scheme 4 as previously suggested for the hydroesterification with HCO_2Ph.[5e] The Pd^0 was first oxidatively added to $HCO_2CH_2CF_3$ (**4g**) to form complex **5**, which gave complex **6** after rearrangement. The hydropalladation of the olefin by **6** led to complexes **7** and **8**, which underwent migratory insertion to form acyl Pd complexes **9** and **10**. Upon reductive elimination, **9** and **10** were converted to esters **2** and **3**, respectively,



Scheme 4. Proposed Catalytic Pathways of Hydroesterification.

Table 2. Pd-Catalyzed Hydroesterification of Olefins with $HCO_2CH_2CF_3$ (TFEF) (**4g**).



Entry	1	Method[a]	Yield (%) (2:3)[b]	Entry	1	Method[a]	Yield (%) (2:3)[b]
1	 1a	A B	78 (> 20:1) 76 (< 1:20)	9	 1i	A B	75 (> 20:1) 65 (< 1:20)
2	 1b	A B	82 (> 20:1) 83 (< 1:20)	10	 1j	A B	47 (> 20:1) 69 (< 1:20)
3	 1c	A B	65 (> 20:1) 91 (< 1:20)	11	 1k	A B	38 (> 20:1) 32 (< 1:20)
4	 1d	A B	71 (> 20:1) 89 (< 1:20)	12	 1l	A B	81 (> 20:1) 82 (< 1:20)
5	 1e	A B	58 (> 20:1) 72 (< 1:20)	13	 1m	A B	80 (> 20:1) 30 (3.4:1)
6	 1f	A B	51 (> 20:1) 53 (1:17)	14	 1n	A[c] B	56 (> 20:1) 0
7	 1g	A B	40 (> 20:1) 55 (1:14)	15	 1o	A B	90 (> 20:1) 29 (**2o**)
8	 1h	A B	58 (> 20:1) 83 (< 1:20)	16	 1p	A B	40 (> 20:1) 0

[a] **Method A**: The reactions were carried out with **1** (0.50 mmol), $HCO_2CH_2CF_3$ (TFEF) (**4g**) (1.50 mmol), $Pd(OAc)_2$ (0.025 mmol), and **L1** (0.050 mmol) in toluene (0.1 mL) at 80 °C for 48 h unless otherwise stated. **Method B**: The reactions were carried out with **1** (0.50 mmol), $HCO_2CH_2CF_3$ (TFEF) (**4g**) (1.50 mmol), $Pd(OAc)_2$ (0.025 mmol), **L7** (0.15 mmol), and H_2O (15 μL) in toluene (0.1 mL) at 80 °C for 24 h unless otherwise stated. [b] Isolated yield. The ratio of **2**:**3** was determined by ^1H NMR analysis of the crude reaction mixture. [c] At 120 °C.

with the Pd^0 catalyst being regenerated. In general, $HCO_2CH_2CF_3$ displayed similar behavior to HCO_2Ph for the reaction process.

Conclusions

In summary, we have found that 2,2,2-trifluoroethyl formate (**4g**) is a highly effective reagent for hydroesterification of olefins. A variety of linear or branched 2,2,2-trifluoroethyl esters can be obtained with high regioselectivity by the choice of proper ligand. The reaction is operationally simple and involves no handling of toxic CO. The current reaction process provides a viable route for the synthesis of various 2,2,2-trifluoroethyl esters, which can serve as reactive intermediate in organic synthesis.[10] Further understanding of the reaction mechanism and development of more effective hydroesterification process with broad substrate scope will be pursued.

Experimental Section

General Methods: All commercially available reagents were used without further purification. All solvents used for the reaction were purified with solvent purification system. Column chromatography was performed on silica gel (300–400 mesh). ^1H NMR spectra were recorded on a 400 MHz NMR spectrometer, ^{13}C NMR spectra were recorded on a 100 MHz NMR spectrometer and ^{19}F NMR spectra were recorded on a 376 MHz NMR spectrometer. IR spectra were recorded on a FT-IR spectrometer. Melting points were uncorrected. HCO_2Me (**4a**), and HCO_2Et (**4b**) were purchased from commercial suppliers. Formates **4c** and **4d**, were prepared from HCO_2H, Ac_2O, the corresponding alcohols, and NaOAc based on the reported procedure.[11] For **4d** 1 mol-% Bu_4NI was also added after the addition of NaOAc. Formates **4e**, **4f**, and **4g** were prepared by heating HCO_2H and the corresponding alcohols at 80 °C for 18 h based on the reported procedure.[12]

Representative Procedure for Hydroesterification (Table 2)

Method A: To a mixture of $Pd(OAc)_2$ (0.0056 g, 0.025 mmol), ligand **L1** (0.0289 g, 0.050 mmol), and toluene (0.1 mL) in a sealed tube (2.0 mL) were added styrene (**1a**) (0.0521 g, 0.50 mmol) and 2,2,2-trifluoroethyl formate (**4g**) (0.192 g, 1.5 mmol) successively via syringe. Upon purging with Ar to remove the air, the tube was tightly sealed with a Teflon cap. The reaction mixture was stirred at 80 °C for 48 h, cooled to room temp., and purified by flash chromatography (silica gel, petroleum ether/diethyl ether = 100:3) to give ester **2a** as light yellow oil (0.0905 g, 78 % yield) (The solvent was evaporated in an ice water bath to reduce the loss of the ester product due to its volatility).

Method B: To a mixture of $Pd(OAc)_2$ (0.0056 g, 0.025 mmol), ligand **L7** (0.0526 g, 0.150 mmol), H_2O (15 μL), and toluene (0.1 mL) in a sealed tube (2.0 mL) were added styrene (**1a**) (0.0521 g, 0.50 mmol) and 2,2,2-trifluoroethyl formate (**4g**) (0.192 g, 1.5 mmol) successively via syringe. Upon purging with Ar to remove the air, the tube was tightly sealed with a Teflon cap. The reaction mixture was stirred at 80 °C for 24 h, cooled to room temp., quenched with 30 % H_2O_2 (0.20 mL), stirred at rt for 10 min to oxidize the ligand (**L7**), and purified by flash chromatography (silica gel, petroleum ether/diethyl ether = 100:3) to give ester **3a** as light yellow oil (0.0882 g, 76 % yield).

Ester 2a[13] (Table 2, entry 1): Light yellow oil; IR (film): 1758, 1171 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.32–7.26 (m, 2H), 7.24–7.16 (m, 3H), 4.44 (q, J = 8.5 Hz, 2H), 2.97 (t, J = 7.6 Hz, 2H), 2.73 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CCl_3) δ = 171.4, 140.0, 128.8, 128.4, 126.7, 123.1 (q, J = 275.5 Hz), 60.5 (q, J = 36.4 Hz), 35.4, 30.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ = –73.8; HRMS (EI) Calcd for $C_{11}H_{11}F_3O_2$ $[M]^+$: 232.0706, found 232.0709.

Ester 2b (Table 2, entry 2): Light yellow oil; IR (film): 1760, 1171 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.16–7.08 (m, 4H), 4.47 (q, J = 8.5 Hz, 2H), 2.96 (t, J = 7.5 Hz, 2H), 2.74 (t, J = 8.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.5, 136.9, 136.2, 129.5, 128.3, 123.1 (q, J = 275.7 Hz), 60.5 (q, J = 36.3 Hz), 35.6, 30.4, 21.2; HRMS (EI) Calcd for $C_{12}H_{13}F_3O_2$ $[M]^+$: 246.0862, found 246.0864.

Ester 2c (Table 2, entry 3): Light yellow oil; IR (film): 1760, 1175 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.16–7.10 (m, 2H), 6.87–6.82 (m, 2H), 4.45 (q, J = 8.5 Hz, 2H), 3.79 (s, 3H), 2.93 (t, J = 7.6 Hz, 2H), 2.72 (t, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.5, 158.4, 132.0, 129.4, 123.1 (q, J = 275.4 Hz), 114.1, 60.4 (q, J = 36.2 Hz), 55.4, 35.7, 29.9; HRMS (EI) Calcd for $C_{12}H_{13}F_3O_3$ $[M]^+$: 262.0811, found 262.0814.

Ester 2d (Table 2, entry 4): Light yellow oil; IR (film): 1762, 1173 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.37–7.31 (m, 2H), 7.19–7.12 (m, 2H), 4.47 (q, J = 8.5 Hz, 2H), 2.97 (t, J = 7.6 Hz, 2H), 2.75 (t, J = 7.4 Hz, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.6, 149.5, 136.9, 128.1, 125.7, 123.1 (q, J = 276.1 Hz), 60.5 (q, J = 36.5 Hz), 35.4, 34.6, 31.5, 30.3; HRMS (EI) Calcd for $C_{15}H_{19}F_3O_2$ $[M]^+$: 288.1332, found 288.1334.

Ester 2e (Table 2, entry 5): Light yellow oil; IR (film): 1760, 1259 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.21–7.13 (m, 2H), 7.02–6.94 (m, 2H), 4.45 (q, J = 8.5 Hz, 2H), 2.96 (t, J = 7.6 Hz, 2H), 2.73 (t, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.3, 161.8 (d, J = 242.8 Hz), 135.6 (d, J = 3.2 Hz), 129.9 (d, J = 7.8 Hz), 123.1 (q, J = 275.4 Hz), 115.6 (d, J = 21.1 Hz), 60.5 (q, J = 36.4 Hz), 35.5, 30.0; HRMS (EI) Calcd for $C_{11}H_{10}F_4O_2$ $[M]^+$: 250.0611, found 250.0614.

Ester 2f (Table 2, entry 6): Light yellow oil; IR (film): 1760, 1173 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.29–7.23 (m, 2H), 7.16–7.10 (m, 2H), 4.45 (q, J = 8.4 Hz, 2H), 2.95 (t, J = 7.6 Hz, 2H), 2.72 (t, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 138.4, 132.5, 129.8, 128.9, 123.1 (q, J = 275.5 Hz), 60.5 (q, J = 36.4 Hz), 35.2, 30.1; HRMS (EI) Calcd for $C_{11}H_{10}ClF_3O_2$ $[M]^+$: 266.0316, found 266.0318.

Ester 2g (Table 2, entry 7): Light yellow oil; IR (film): 1764, 1106 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.56 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.46 (q, J = 8.4 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2H), 2.78 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 144.1, 129.1 (q, J = 32.3 Hz), 128.9, 125.7 (q, J = 3.6 Hz), 124.4 (q, J = 270.0 Hz), 123.1 (q, J = 275.4 Hz), 60.6 (q, J = 36.4 Hz), 34.9, 30.5; HRMS (EI) Calcd for $C_{12}H_{10}F_6O_2$ $[M]^+$: 300.0580, found 300.0582.

Ester 2h (Table 2, entry 8): Light yellow oil; IR (film): 1758, 1169 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.22–7.14 (m, 1H), 7.06–6.95 (m, 3H), 4.43 (q, J = 8.5 Hz, 2H), 2.93 (t, J = 7.6 Hz, 2H), 2.71 (t, J = 8.0 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.4, 139.9, 138.4, 129.2, 128.7, 127.4, 125.4, 123.2 (q, J = 275.2 Hz), 60.4 (q, J = 36.3 Hz), 35.4, 30.7, 21.5; HRMS (EI) Calcd for $C_{12}H_{13}F_3O_2$ $[M]^+$: 246.0862, found 246.0864.

Ester 2i (Table 2, entry 9): Light yellow oil; IR (film): 1760, 1085 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.32–7.20 (m, 1H), 7.02–6.94 (m, 1H), 6.94–6.86 (m, 2H), 4.45 (q, J = 8.4 Hz, 2H), 2.97 (t, J = 7.6 Hz, 2H), 2.74 (t, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 163.1 (d, J = 244.3 Hz), 142.5 (d, J = 7.3 Hz), 130.3 (d, J = 8.2 Hz), 124.1 (d, J = 2.7 Hz), 123.1 (q, J = 275.4 Hz), 115.4 (d, J = 21.1 Hz), 113.6 (d, J = 20.8 Hz), 60.5 (q, J = 36.4 Hz), 35.0, 30.4 (d, J = 1.5 Hz); HRMS (EI) Calcd for $C_{11}H_{10}F_4O_2$ $[M]^+$: 250.0611, found 250.0613.

Ester 2j (Table 2, entry 10): Light yellow oil; IR (film): 1758, 1169 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.26–7.16 (m, 3H), 7.11–7.05 (m, 1H), 4.45 (q, J = 8.4 Hz, 2H), 2.95 (t, J = 7.6 Hz, 2H), 2.73 (t, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 142.0, 134.5, 130.0, 128.6, 126.9, 126.7, 123.1 (q, J = 275.4 Hz), 60.5 (q, J = 36.4 Hz), 35.0, 30.4; HRMS (EI) Calcd for $C_{11}H_{10}ClF_3O_2$ $[M]^+$: 266.0316, found 266.0318.

Ester 2k (Table 2, entry 11): White solid; mp. 49.0–49.7 °C; IR (film): 1760, 1169 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.90–7.75 (m, 3H), 7.67 (s, 1H), 7.53–7.42 (m, 2H), 7.35 (dd, J = 8.4, 1.6 Hz, 1H), 4.48 (q, J = 8.5 Hz, 2H), 3.17 (t, J = 7.6 Hz, 2H), 2.86 (t, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.4, 137.4, 133.7, 132.4, 128.5, 127.8, 127.7, 127.0, 126.7, 126.3, 125.7, 123.1 (q, J = 275.4 Hz), 60.5 (q, J = 36.4 Hz), 35.3, 30.9; HRMS (EI) Calcd for $C_{15}H_{13}F_3O_2$ $[M]^+$: 282.0862, found 282.0863.

Ester 2l (Table 2, entry 12): Light yellow oil; IR (film): 1762, 1184 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.21–7.13 (m, 4H), 4.49 (q, J = 8.4 Hz, 2H), 3.00 (t, J = 7.6 Hz, 2H), 2.72 (t, J = 7.5 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.6, 138.1, 136.1, 130.6, 128.6, 126.8, 126.4, 123.1 (q, J = 275.4 Hz), 60.5 (q, J = 36.4 Hz), 34.1, 28.2, 19.4; HRMS (EI) Calcd for $C_{12}H_{13}F_3O_2$ $[M]^+$: 246.0862, found 246.0865.

Ester 2m (Table 2, entry 13): Light yellow solid; mp. 45.3–45.6 °C; IR (film): 1746, 1271, 1163 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.87 (s, 2H), 4.52 (q, J = 8.5 Hz, 2H), 3.05–2.93 (m, 2H), 2.60–2.51 (m, 2H), 2.32 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.7, 136.2, 136.1, 133.6, 129.3, 123.2 (q, J = 275.3 Hz), 60.5 (q, J = 36.4 Hz), 33.1, 24.6, 21.0, 19.8; HRMS (EI) Calcd for $C_{14}H_{17}F_3O_2$ $[M]^+$: 274.1175, found 274.1176.

Ester 2n (Table 2, entry 14): Light yellow oil; IR (film): 1730, 1161 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.52–8.48 (m, 1H), 7.58 (td, J = 7.7, 1.8 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.13–7.08 (m, 1H), 4.44 (q, J = 8.5 Hz, 2H), 3.13 (t, J = 7.4 Hz, 2H), 2.92 (t, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.7, 159.4, 149.5, 136.6, 123.2, 123.1 (q, J = 275.6 Hz), 121.7, 60.4 (q, J = 36.4 Hz), 32.8, 32.6; HRMS (ESI) Calcd for $C_{10}H_{11}F_3NO_2$ $[M + H]^+$: 234.0736, found 234.0735.

Ester 2o (Table 2, entry 15): White solid; mp. 99.4–99.6 °C; IR (film): 1758, 1715, 1175 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.87–7.79 (m, 2H), 7.75–7.68 (m, 2H), 4.45 (q, J = 8.4 Hz, 2H), 4.01 (t, J = 7.0 Hz, 2H), 2.83 (t, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.5, 168.1, 134.3, 132.1, 123.6, 123.0 (q, J = 275.4 Hz), 60.8 (q, J = 36.5 Hz), 33.6, 32.6; HRMS (ESI) Calcd for $C_{13}H_{10}F_3KNO_4$ $[M + K]^+$: 340.0194, found 340.0193.

Ester 2p (Table 2, entry 16): Light yellow solid; mp. 27.3–27.5 °C; IR (film): 1760, 1173 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.45 (q, J = 8.5 Hz, 2H), 2.40 (t, J = 7.5 Hz, 2H), 1.72–1.57 (m, 2H), 1.32–1.21 (m,

24H), 0.87 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.4, 123.2 (q, J = 275.4 Hz), 60.3 (q, J = 36.2 Hz), 33.8, 32.2, 29.9, 29.89, 29.86, 29.8, 29.6, 29.59, 29.4, 29.2, 24.9, 22.9, 14.3; HRMS (EI) Calcd for $C_{18}H_{33}F_3O_2$ $[M]^+$: 338.2427, found 338.2429.

Ester 3a[14] (Table 2, entry 1): Light yellow oil; IR (film): 1756, 1167 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37–7.23 (m, 5H), 4.54–4.42 (m, 1H), 4.42–4.31 (m, 1H), 3.81 (q, J = 7.2 Hz, 1H), 1.53 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.2, 139.5, 128.9, 127.7, 127.65, 123.1 (q, J = 275.5 Hz), 60.6 (q, J = 36.3 Hz), 45.3, 18.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ = –73.8; HRMS (EI) Calcd for $C_{11}H_{11}F_3O_2$ $[M]^+$: 232.0706, found 232.0708.

Ester 3b (Table 2, entry 2): Light yellow oil; IR (film): 1760, 1169 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22–7.16 (m, 2H), 7.16–7.10 (m, 2H), 4.55–4.42 (m, 1H), 4.42–4.29 (m, 1H), 3.78 (q, J = 7.2 Hz, 1H), 2.32 (s, 3H), 1.52 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.3, 137.4, 136.6, 129.6, 127.5, 123.1 (q, J = 275.6 Hz), 60.6 (q, J = 36.3 Hz), 44.8, 21.2, 18.5; HRMS (EI) Calcd for $C_{12}H_{13}F_3O_2$ $[M]^+$: 246.0862, found 246.0863.

Ester 3c (Table 2, entry 3): Light yellow oil; IR (film): 1756, 1167 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25–7.18 (m, 2H), 6.89–6.82 (m, 2H), 4.53–4.41 (m, 1H), 4.41–4.29 (m, 1H), 3.76 (q, J = 7.2 Hz, 1H), 3.75 (s, 3H), 1.50 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.3, 159.1, 131.6, 128.6, 123.1 (q, J = 275.5 Hz), 114.2, 60.5 (q, J = 36.2 Hz), 55.2, 44.3, 18.4; HRMS (ESI) Calcd for $C_{12}H_{12}F_3O_3$ $[M - H]^-$: 261.0744, found 261.0741.

Ester 3d (Table 2, entry 4): Light yellow oil; IR (film): 1758, 1280 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 4.58–4.45 (m, 1H), 4.42–4.29 (m, 1H), 3.80 (q, J = 7.2 Hz, 1H), 1.53 (d, J = 7.2 Hz, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.4, 150.6, 136.4, 127.3, 125.9, 123.0 (q, J = 275.6 Hz), 60.6 (q, J = 36.4 Hz), 44.8, 34.7, 31.5, 18.5; HRMS (ESI) Calcd for $C_{15}H_{18}F_3O_2$ $[M - H]^-$: 287.1264, found 287.1262.

Ester 3e (Table 2, entry 5): Light yellow oil; IR (film): 1760, 1165 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31–7.24 (m, 2H), 7.06–6.98 (m, 2H), 4.55–4.45 (m, 1H), 4.45–4.34 (m, 1H), 3.81 (q, J = 7.2 Hz, 1H), 1.53 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.0, 162.3 (d, J = 244.4 Hz), 135.2 (d, J = 3.2 Hz), 129.3 (d, J = 8.0 Hz), 123.1 (q, J = 275.6 Hz), 115.8 (d, J = 21.3 Hz), 60.7 (q, J = 36.3 Hz), 44.5, 18.5; HRMS (ESI) Calcd for $C_{11}H_9F_4O_2$ $[M - H]^-$: 249.0544, found 249.0541.

Ester 3f (Table 2, entry 6): Light yellow oil; IR (film): 1758, 1173 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34–7.28 (m, 2H), 7.26–7.21 (m, 2H), 4.55–4.45 (m, 1H), 4.45–4.35 (m, 1H), 3.80 (q, J = 7.2 Hz, 1H), 1.53 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.8, 137.9, 133.6, 129.1, 129.07, 123.0 (q, J = 275.5 Hz), 60.7 (q, J = 36.3 Hz), 44.7, 18.5; HRMS (ESI) Calcd for $C_{11}H_9ClF_3O_2$ $[M - H]^-$: 265.0249, found 265.0247.

Ester 3g (Table 2, entry 7): Light yellow oil; IR (film): 1762, 1081 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 4.57–4.47 (m, 1H), 4.47–4.37 (m, 1H), 3.90 (q, J = 7.2 Hz, 1H), 1.58 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.5, 143.4, 130.1 (q, J = 32.6 Hz), 128.2, 126.0 (q, J = 3.7 Hz), 124.3 (q, J = 270.2 Hz), 123.0 (q, J = 275.5 Hz), 60.8 (q, J = 36.5 Hz), 45.1, 18.4; HRMS (ESI) Calcd for $C_{12}H_9F_6O_2$ $[M - H]^-$: 299.0512, found 299.0509.

Ester 3h (Table 2, entry 8): Light yellow oil; IR (film): 1764, 1165 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25–7.18 (m, 1H), 7.13–7.05 (m, 3H), 4.58–4.45 (m, 1H), 4.45–4.31 (m, 1H), 3.79 (q, J = 7.2 Hz, 1H), 2.34 (s, 3H), 1.53 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.3, 139.5, 138.6, 128.8, 128.5, 128.4, 124.7, 123.1 (q, J = 275.6 Hz), 60.6 (q, J = 36.2 Hz), 45.2, 21.6, 18.6; HRMS (ESI) Calcd for $C_{12}H_{12}F_3O_2$ $[M - H]^-$: 245.0795, found 245.0791.

Ester 3i (Table 2, entry 9): Light yellow oil; IR (film): 1762, 1173 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34–7.24 (m, 1H), 7.11–7.05 (m, 1H), 7.05–6.93 (m, 2H), 4.57–4.48 (m, 1H), 4.48–4.38 (m, 1H), 3.83 (q, J = 7.2 Hz, 1H), 1.54 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.6, 163.1 (d, J = 244.9 Hz), 141.8 (d, J = 7.3 Hz), 130.4 (d, J = 8.2 Hz), 123.4 (d, J = 2.9 Hz), 123.0 (q, J = 275.7 Hz), 114.8 (d, J = 3.8 Hz), 114.6 (d, J = 2.7 Hz), 60.8 (q, J = 36.5 Hz), 45.0, 18.4; HRMS (ESI) Calcd for $C_{11}H_9F_4O_2$ $[M - H]^-$: 249.0544, found 249.0541.

Ester 3j (Table 2, entry 10): Light yellow oil; IR (film): 1758, 1171 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.3 (s, 1H), 7.29–7.23 (m, 2H), 7.22–7.15 (m, 1H), 4.57–4.46 (m, 1H), 4.46–4.35 (m, 1H), 3.80 (q, J = 7.2 Hz, 1H), 1.54 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.6, 141.4, 134.7, 130.2, 128.0, 127.9, 125.9, 123.0 (q, J = 275.7 Hz), 60.7 (q, J = 36.4 Hz), 44.9, 18.4; HRMS (ESI) Calcd for $C_{11}H_9ClF_3O_2$ $[M - H]^-$: 265.0249, found 265.0245.

Ester 3k (Table 2, entry 11): Light yellow oil; IR (film): 1758, 1169 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89–7.81 (m, 3H), 7.78 (s, 1H), 7.55–7.44 (m, 3H), 4.63–4.50 (m, 1H), 4.49–4.36 (m, 1H), 4.02 (q, J = 7.2 Hz, 1H), 1.67 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.2, 136.9, 133.6, 132.9, 128.7, 128.0, 127.8, 126.5, 126.49, 126.2, 125.7, 123.1 (q, J = 275.6 Hz), 60.7 (q, J = 36.4 Hz), 45.4, 18.6; HRMS (ESI) Calcd for $C_{15}H_{12}F_3O_2$ $[M - H]^-$: 281.0795, found 281.0792.

Ester 3l (Table 2, entry 12): Light yellow oil; IR (film): 1760, 1169 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28–7.23 (m, 1H), 7.23–7.13 (m, 3H), 4.57–4.45 (m, 1H), 4.45–4.32 (m, 1H), 4.06 (q, J = 7.1 Hz, 1H), 2.38 (s, 3H), 1.52 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.4, 138.1, 136.0, 130.8, 127.5, 126.7, 126.6, 123.1 (q, J = 275.6 Hz), 60.5 (q, J = 36.3 Hz), 41.0, 19.7, 17.8; HRMS (EI) Calcd for $C_{12}H_{13}F_3O_2$ $[M]^+$: 246.0862, found 246.0866.

Ester 2q (Scheme 2): Light green solid; mp. 70.5–70.9 °C; IR (film): 1760, 1165 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.42–7.34 (m, 3H), 7.28–7.20 (m, 3H), 7.20–7.13 (m, 2H), 7.10–7.03 (m, 2H), 4.59 (q, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.3, 142.6, 135.1, 134.3, 131.0, 129.9, 129.8, 129.0, 128.5, 128.4, 123.3 (q, J = 275.7 Hz), 61.1 (q, J = 36.4 Hz); HRMS (EI) Calcd for $C_{17}H_{14}F_3O_2$ $[M + H]^+$: 307.0940, found 307.0939.

Esters 2r and **2r′** (Scheme 2): Light yellow liquid; IR (film): 1729, 1168 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (small amount of pure **2r′**) δ = 7.78 (q, J = 1.5 Hz, 1H), 7.45–7.32 (m, 5H), 4.60 (q, J = 8.4 Hz, 2H), 2.16 (d, J = 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (small amount of pure **2r′**) δ = 167.1, 141.3, 135.5, 130.0, 129.1, 128.7, 126.9, 123.4 (q, J = 275.4 Hz), 61.0 (q, J = 36.4 Hz), 14.2; HRMS (ESI) Calcd for $C_{12}H_{12}F_3O_2$ $[M + H]^+$: 245.0784, found 245.0782.

Acknowledgments

We gratefully acknowledge the National Natural Science Foundation of China (21632005, 21472083) and Changzhou University for financial support.

Keywords: Hydroesterification · Regioselectivity · 2,2,2-Trifluoroethyl formate · Olefins

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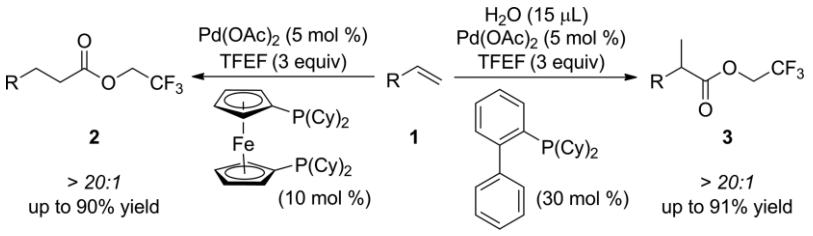
Received: October 31, 2019

Regioselective Hydroesterification



A Pd-catalyzed regioselective hydroesterification of olefins with 2,2,2-trifluoroethyl formate (TFEF) is described. Either linear or branched esters can be selectively obtained with proper ligands in most cases. The reaction process is operationally simple and involves no toxic CO gas.

DOI: 10.1002/ejoc.201901601