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Metal-free catalytic hydrocarboxylation of hexafluorobut-2-yne†

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An efficient method for stereoselective synthesis of trifluorinated enol esters catalyzed by base was introduced. The DFT calculations and experimental results both supported the nucleophilic addition process. The protocol featured mild reaction conditions and showed a wide functional group tolerance. The one-pot simultaneous etherification and esterification of the salicylic acids further demonstrated the prospective synthetic application.

Introduction

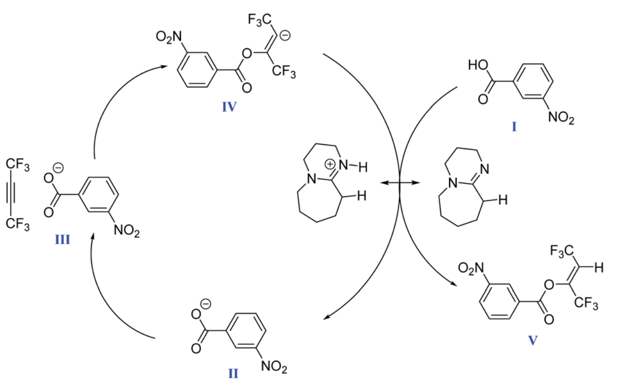
Enol esters are versatile building blocks in organic chemistry that serve as the intermediates in various synthetic transformations, including polymerization,[1] hydrogenation,[2] cycloaddition,[3] and cross-coupling reactions.[4] The hydrocarboxylation reaction is the most efficient and atom-economical route to prepare enol esters.[5] Hexafluorobut-2-yne (HFBY) is a cost-effective industrial intermediate for the production of *Z*-1,1,1,4,4,4-hexafluorobutene (*Z*-HFO-1336mzz).[6] As part of our ongoing research on fluorocarbon chemistry, the previous works demonstrated the hydrophenoxylation of HFBY.[7] Considering the electrophilicity,[8] it was speculated that HFBY reacted readily with nucleophiles to directly synthesize trifluorinated enol esters.

The classical methods to prepare trifluorinated enol esters rely on ruthenium catalysts,[9] and most are limited to the substrate scope and mild reaction conditions, while the hydrocarboxylation of HFBY is an exception.[10] Thus, it would be very appealing that the esterification reaction is carried out using a metal-free catalyst with high stereoselectivity. These experimental results strongly promoted the re-study of the hydrocarboxylation of HFBY. Herein, the stereoselective synthesis of trifluorinated enol esters under a mild reaction condition was reported.

Results and discussion

The studies were initiated using 3-nitrobenzoic acid (**1a**) as a model substrate (Table 1) Scheme 1. 3-Nitrobenzoic acid was treated with HFBY (**2**) in the presence of 10 mol% of either triethylamine (Et_3N) or tetramethylethylenediamine (TMEDA) in the DCM at room temperature for 10 hours (Table 1, entry 1 and 2), while there was no reaction. Unexpectedly, when the tertiary amine was converted to 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), the product (*Z*)-1,1,1,4,4,4-hexafluorobut-2-en-2-yl-3-nitrobenzoate (**3a**) was separated in 29% yield (Table 1, entry 3). DBU was the base of choice among the tested bases (entries 4–6). Unfortunately, the yield was not improved as the DBU loading increased to 20 mol% (entry 7). Acetone performed slightly better than other solvents, and 3a was generated in 62% yield (entries 8–12).

The generality of benzoic acid was examined by optimizing the reaction conditions. Carboxylic acids with electron-donating groups on the aromatic ring (**3b** and **3c**) participated in the reaction smoothly to produce enol esters with high stereoselectivity. The amine or amide groups in the acids had a slight effect on the reaction (**3d** and **3e**). The steric hinderance had little effect, and bulk **3f** and **3g** both worked well. The reaction with *p*-halo substrates gave products **3i** and **3j** in moderate yield. However, fluorobenzoic acid generated the desired product **3h** in only 43% yield, which was due to the electronic effect[11] and a low boiling point of the product. The scope was not limited to electron-rich



Scheme 1 Proposed reaction mechanism.

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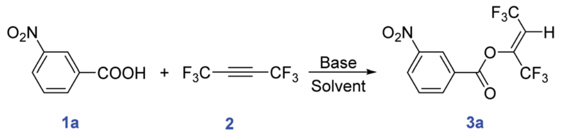
† Electronic supplementary information (ESI) available: Experimental procedures, characterization data, ^{1}H, ^{13}C, ^{19}F NMR, IR and HRMS spectra. See DOI: 10.1039/d1ra06526b

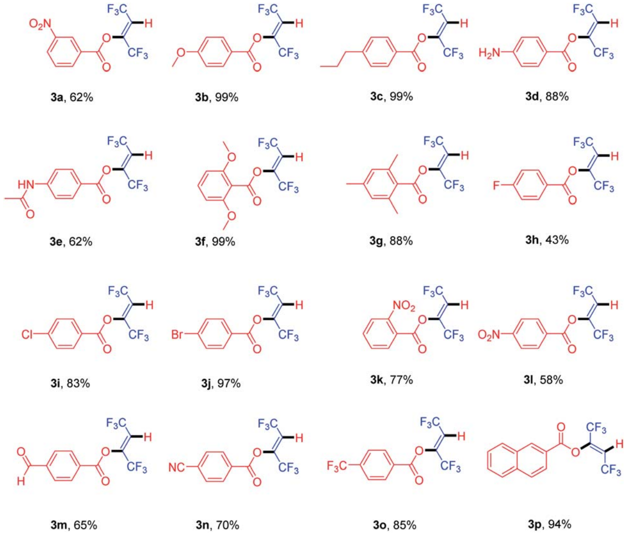
Table 1 Optimization for the hydrocarboxylation[a]



Entry	Catalyst	Loading (mol%)	Solvent	Yield[b] (%)
1	Et_3N	10	DCM	—
2	TMEDA	10	DCM	—
3	MTBD	10	DCM	32 (29[c])
4	DABCO	10	DCM	17
5	DBN	10	DCM	7
6	DBU	10	DCM	54
7	DBU	20	DCM	17
8	DBU	10	1,4-Dioxane	54
9	DBU	10	Acetone	62
10	DBU	10	HFIP	54
11	DBU	10	CH_3CN	58
12	DBU	10	Toluene	50

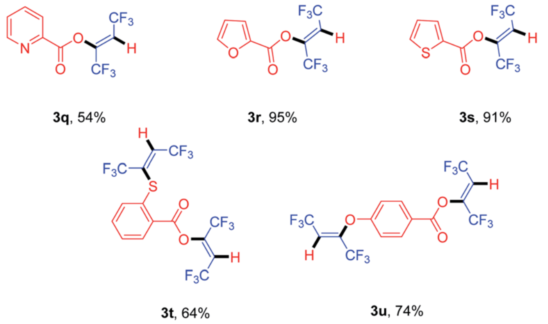
[a] Reaction conditions: **1** (1 mmol), **2** (2–3 mmol), solvent (2 mL), 25 °C, 10 h. [b] Yields determined by ^{1}H and ^{19}F NMR, 4′-fluoroacetophenone as internal standard. [c] Isolated yields.

Table 2 addition of benzoic acids into HFBY catalysed by DBU[a]a



[a] Reaction conditions: **1** (1 mmol), **2** (2–3 mmol), DBU (10 mol%), acetone (2 mL), 25 °C, 10 h, isolated yields.

Table 3 addition of heterocyclic acids into HFBY catalysed by DBU[a]



[a] Reaction conditions: **1** (1 mmol), **2** (2–3 mmol), DBU (10 mol%), acetone (2 mL), 25 °C, 10 h, isolated yields.

substrates, and a variety of electron-poor acids afforded enol esters in moderate yields (**3k**–**3o**). 2-Naphthoic acid proceeded smoothly, which furnished the corresponding products in a 94% yield (**3o**) (Tables 2 and 3).

The reactions of HFBY with heterocyclic acids were extended. Pyridine, furan, and thiophene substituents were well tolerated, furnishing the moderate to good yields under standard conditions (**3q**–**3s**). The one-pot difunctionalization of salicylic acids reacted well under standard conditions,[12] which indicated a broad application of the protocol.

A plausible reaction mechanism was proposed based on DFT calculations (Scheme 1). The nucleophilic addition and *Z* selectivity under DBU were well supported.[13] First, acid anion **II** was generated by the acid-base neutralization reaction between benzoic acid and DBU. Due to the high electrophilicity of the triple bonds, the anion was added to the hexafluorobut-2-yne to produce butenyl anion **IV**. Finally, **IV** abstracted a proton of [DBU-H]$^+$, selectively giving the desired product **3** with the regeneration of DBU.

Conclusions

In summary, a novel and practical method for the synthesis of enol esters was reported. The reactions were carried out by the base-catalyzed hydrogenation carboxylation process with industrially available substrates, even one-pot phenoxylation and carboxylation of salicylic acids was achieved. The mechanistic studies supported the nucleophilic addition reaction and explained the excellent stereoselectivity of the products. The metal-free catalysis with mild reaction conditions and simple operation endowed the alternative esterification strategy with broad application prospects in organic synthesis.

Experimental

General

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 500 MHz. ^{1}H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$(TMS) at δ 0.0 or to the signal of the residual protonated solvent: $CDCl_3$ δ 7.26. ^{13}C NMR chemical shifts were determined relative to internal TMS at δ 0.0. For the isolated compounds, ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.0. Data for ^{1}H, ^{13}C and ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad). High resolution mass spectra were recorded on an HRMS-TOF instrument using EI ionization. IR spectra were collected on a Nicolet IN10

FT-IR spectrometer, and reported in terms of frequency of absorption (cm^{-1}).

Reagents

Unless otherwise mentioned, solvents and reagents are purchased from commercial sources and used as received. 1,1,1,4,4,4-hexafluorobutyne (HFBY) is obtained by dehydrochlorination of 2-chloro-1,1,1,4,4,4-hexafluorobutene.[14]

Experimental procedure

The reaction was carried out in 25 mL Schlenk tube. To a solution of carboxylic acid (1 mmol) in acetone (2 mL), DBU was added. The tube was cooling in liquid nitrogen, then vacuumized and HFBY (2–3 mmol) was introduced into the tube, the reaction mixture was stirred at room temperature for 10 h. The crude product was purified by column chromatography.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-3-nitrobenzoate (3a). Yellow oil, 204 mg, 62%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.94 (m, 1H), 8.56 (m, 1H), 8.45 (m, 1H), 7.79 (m, 1H), 6.43 (q, 1H, $J_{HF} = 7$ Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 160.4, 148.6, 142.6 (qq, $^{2}J_{CF} = 38.5$ Hz, $^{3}J_{CF} = 5$ Hz), 136.0, 130.3, 129.1, 128.5, 125.5, 120.5 (q, $^{1}J_{CF} = 269.6$ Hz), 118.5 (q, $^{1}J_{CF} = 273.9$ Hz), 114.2 (qq, $^{2}J_{CF} = 36.9$ Hz, $^{3}J_{CF} = 3.6$ Hz). ^{19}F NMR (470.0 MHz, CDCl$_3$) δ −71.8 (s, CF$_3$), −61.2 (d, $J_{FH} = 6.1$ Hz, CF$_3$). IR (KBr): 2989, 1778, 1306, 1207, 1047, 987, 847 cm^{-1}. HRMS (EI-TOF): calcd for $C_{11}H_5F_6NO_4$ (M$^+$) 329.0123, found 352.0018.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-4-methoxybenzoate (3b). Yellow oil, 314 mg, 99%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.06 (d, 2H, $J_{HH} = 9$ Hz), 6.98 (d, 2H, $J_{HH} = 9$ Hz), 6.31 (q, 1H, $J_{HF} = 7$ Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 164.9, 161.8, 143.3 (qq, $^{2}J_{CF} = 37.6$ Hz, $^{3}J_{CF} = 5$ Hz), 132.9, 120.8 (q, $^{1}J_{CF} = 269.4$ Hz), 118.8, 118.7 (q, $^{1}J_{CF} = 274$ Hz), 114.2, 113.4 (qq, $^{2}J_{CF} = 36.6$ Hz, $^{3}J_{CF} = 3.5$ Hz), 55.8. ^{19}F NMR (470.0 MHz, CDCl$_3$) δ −71.9 (s, CF$_3$), −61.1 (d, $J_{FH} = 6.1$ Hz, CF$_3$). IR (KBr): 2842, 1765, 1612, 1273, 1146, 841, 648 cm^{-1}. HRMS (EI-TOF): calcd for $C_{12}H_8F_6O_3$ (M$^+$) 314.0378, found 314.0373.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-4-propylbenzoate (3c). Colorless oil, 326 mg, 99%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.01 (d, 2H, $J_{HH} = 8.5$ Hz), 7.31 (d, 2H, $J_{HH} = 8.5$ Hz), 6.33 (q, 1H, $J_{HF} = 6.5$ Hz), 2.68 (m, 2H), 1.68 (m, 2H), 0.96 (t, 3H, $J_{HH} = 7$ Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 162.2, 150.6, 143.3 (qq, $^{2}J_{CF} = 38$ Hz, $^{3}J_{CF} = 5$ Hz), 130.7, 129.0, 124.2, 120.7 (q, $^{1}J_{CF} = 269.5$ Hz), 118.7 (q, $^{1}J_{CF} = 274$ Hz), 113.5 (qq, $^{2}J_{CF} = 36.6$ Hz, $^{3}J_{CF} = 3.6$ Hz), 38.2, 24.1, 13.6. ^{19}F NMR (470.0 MHz, CDCl$_3$) δ −71.9 (s, CF$_3$), −61.1 (d, $J_{FH} = 7.1$ Hz, CF$_3$). IR (KBr): 2962, 1765, 1612, 1273, 1153, 994, 648 cm^{-1}. HRMS (EI-TOF): calcd for $C_{14}H_{12}F_6O_2$ (M$^+$) 326.0741, found 326.0736.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-4-aminobenzoate (3d). Yellow oil, 263 mg, 88%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.89 (d, 2H, $J_{HH} = 9$ Hz), 6.66 (d, 2H, $J_{HH} = 9$ Hz), 6.28 (q, 1H, $J_{HF} = 7.5$ Hz), 4.28 (s, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 162.1, 152.6, 143.5 (qq, $^{2}J_{CF} = 37.6$ Hz, $^{3}J_{CF} = 5$ Hz), 133.1, 120.9 (q, $^{1}J_{CF} = 269.5$ Hz), 118.9 (q, $^{1}J_{CF} = 274.1$ Hz), 115.4, 113.9, 113.1 (qq, $^{2}J_{CF} = 36.5$ Hz, $^{3}J_{CF} = 3.6$ Hz). ^{19}F NMR (470.0 MHz, CDCl$_3$) δ −71.9 (s, CF$_3$), −61.0 (d, $J_{FH} = 7.5$ Hz, CF$_3$). IR (KBr): 3394, 1745, 1605, 1279, 1153, 1053, 841 cm^{-1}. HRMS (EI-TOF): calcd for $C_{11}H_7F_6NO_2$ (M$^+$) 299.0381, found 299.0373.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-4-acetamidobenzoate (3e). White solid, 211 mg, 62%. ^{1}H NMR (500 MHz, DMSO) δ 10.45 (s, 1H), 8.02 (d, 2H, $J_{HH} = 8.5$ Hz), 7.84 (d, 2H, $J_{HH} = 8.5$ Hz), 7.38 (q, 1H, $J_{HF} = 7.5$ Hz), 2.12 (s, 3H). ^{13}C NMR (125 MHz, DMSO) δ 169.7, 162.1, 146.1, 142.2 (qq, $^{2}J_{CF} = 37.6$ Hz, $^{3}J_{CF} = 5.3$ Hz), 132.1, 121.4 (q, $^{1}J_{CF} = 269.4$ Hz), 119.8, 119.1, 119.1 (q, $^{1}J_{CF} = 273.9$ Hz), 115.1 (qq, $^{2}J_{CF} = 35.3$ Hz, $^{3}J_{CF} = 3.4$ Hz), 24.5. ^{19}F NMR (470.0 MHz, DMSO) δ −70.8 (s, CF$_3$), −60.5 (d, $J_{FH} = 7.1$ Hz, CF$_3$). IR (KBr): 3428, 1778, 1605, 1273, 1153, 854, 648 cm^{-1}. HRMS (EI-TOF): calcd for $C_{13}H_9F_6NO_3$ (M$^+$) 341.0487, found 342.0559.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-2,6-dimethoxybenzoate (3f). Yellow solid, 344 mg, 99%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 (t, 1H, $J_{HH} = 8.5$ Hz), 7.40 (d, 2H, $J_{HH} = 8.5$ Hz), 6.31 (q, 1H, $J_{HF} = 7$ Hz), 3.83 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 161.3, 158.4, 142.9 (qq, $^{2}J_{CF} = 37.7$ Hz, $^{3}J_{CF} = 5.3$ Hz), 139.2, 120.7 (q, $^{1}J_{CF} = 269.7$ Hz), 118.7 (q, $^{1}J_{CF} = 274.5$ Hz), 114.1 (qq, $^{2}J_{CF} = 37$ Hz, $^{3}J_{CF} = 3.7$ Hz), 109.6, 103.9, 56.0. ^{19}F NMR (470.0 MHz, CDCl$_3$) δ −71.6 (s, CF$_3$), −60.6 (d, $J_{FH} = 5.6$ Hz, CF$_3$). IR (KBr): 2982, 1785, 1599, 1486, 1160, 1000, 655 cm^{-1}. HRMS (EI-TOF): calcd for $C_{13}H_{10}F_6O_4$ (M$^+$) 344.0483, found 344.0477.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-2,4,6-trimethylbenzoate (3g). Yellow oil, 286 mg, 88%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.91 (s, 2H), 6.34 (q, 1H, $J_{HF} = 7$ Hz), 2.39 (s, 6H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 164.4, 142.7 (qq, $^{2}J_{CF} = 37.6$ Hz, $^{3}J_{CF} = 5.3$ Hz), 141.7, 137.8, 129.4, 126.2, 120.8 (q, $^{1}J_{CF} = 269.4$ Hz), 118.8 (q, $^{1}J_{CF} = 274.3$ Hz), 114.0 (qq, $^{2}J_{CF} = 36.7$ Hz, $^{3}J_{CF} = 3.7$ Hz), 21.1, 20.3. ^{19}F NMR (470.0 MHz, CDCl$_3$) δ −71.2 (s, CF$_3$), −60.4 (d, $J_{FH} = 6.1$ Hz, CF$_3$). IR (KBr): 2976, 1765, 1306, 1153, 987, 847, 648 cm^{-1}. HRMS (EI-TOF): calcd for $C_{14}H_{12}F_6O_4$ (M$^+$) 326.0741, found 326.0739.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-4-fluorobenzoate (3h). Colorless oil, 130 mg, 43%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.14 (m, 2H), 7.21 (m, 2H), 6.36 (q, 1H, $J_{HF} = 7$ Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.9 (d, $^{1}J_{CF} = 256.1$ Hz), 161.2, 143.0 (qq, $^{2}J_{CF} = 38.1$ Hz, $^{3}J_{CF} = 5$ Hz), 133.4 (d, $^{3}J_{CF} = 9.8$ Hz), 122.9 (d, $^{4}J_{CF} = 3$ Hz), 120.6 (q, $^{1}J_{CF} = 269.5$ Hz), 118.6 (q, $^{1}J_{CF} = 274$ Hz), 116.3 (d, $^{2}J_{CF} = 22.1$ Hz), 113.7 (qq, $^{2}J_{CF} = 36.7$ Hz, $^{3}J_{CF} = 3.6$ Hz). ^{19}F NMR (470.0 MHz, CDCl$_3$) δ −101.8 (s, 1F), −71.9 (s, CF$_3$), −61.2 (d, $J_{FH} = 6.6$ Hz, CF$_3$). IR (KBr): 3115, 1772, 1605, 1160, 1053, 854, 648 cm^{-1}. HRMS (EI-TOF): calcd for $C_{11}H_5F_7O_2$ (M$^+$) 302.0178, found 302.0181.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-4-chlorobenzoate (3i). Yellow oil, 264 mg, 83%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.05 (d, 2H, $J_{HH} = 9$ Hz), 7.50 (d, 2H, $J_{HH} = 8.5$ Hz), 6.36 (q, 1H, $J_{HF} = 7$ Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 161.4, 142.9 (qq, $^{2}J_{CF} = 38.1$ Hz, $^{3}J_{CF} = 5$ Hz), 141.7, 131.9, 129.4, 125.1, 120.6 (q, $^{1}J_{CF} = 269.5$ Hz), 118.6 (q, $^{1}J_{CF} = 274$ Hz), 113.8 (qq, $^{2}J_{CF} = 36.7$ Hz, $^{3}J_{CF} = 3.6$ Hz). ^{19}F NMR (470.0 MHz, CDCl$_3$) δ −71.9 (s, CF$_3$), −61.1 (d, $J_{FH} = 5.2$ Hz, CF$_3$). IR (KBr): 3115, 1778, 1592, 1160, 1007, 741, 648 cm^{-1}. HRMS (EI-TOF): calcd for $C_{11}H_5ClF_6O_2$ (M$^+$) 317.9882, found 317.9887.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-4-bromobenzoate (3j). Colorless oil, 351 mg, 97%. ^{1}H NMR (500 MHz, CDCl$_3$)

δ 7.96 (d, 2H, J_{HH} = 8.5 Hz), 7.68 (d, 2H, J_{HH} = 8.5 Hz), 6.36 (q, 1H, J_{HF} = 7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 143.0 (qq, $^{2}J_{CF}$ = 38.3 Hz, $^{3}J_{CF}$ = 5 Hz), 132.3, 131.9, 130.3, 125.7, 120.7 (q, $^{1}J_{CF}$ = 269.5 Hz), 118.6 (q, $^{1}J_{CF}$ = 273.9 Hz), 113.8 (qq, $^{2}J_{CF}$ = 36.7 Hz, $^{3}J_{CF}$ = 3.6 Hz). ^{19}F NMR (470.0 MHz, $CDCl_3$) δ −71.9 (s, CF_3), −61.1 (d, J_{FH} = 6.1 Hz, CF_3). IR (KBr): 3114, 1778, 1599, 1153, 1000, 741, 655 cm^{-1}. HRMS (EI-TOF): calcd for $C_{11}H_5BrF_6O_2$ (M^+) 361.9377, found 361.9375.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-2-nitrobenzoate (3k). Yellow solid, 271 mg, 77%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (m, 1H), 7.79 (m, 3H), 6.40 (q, 1H, J_{HF} = 7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 148.0, 142.3 (qq, $^{2}J_{CF}$ = 38.6 Hz, $^{3}J_{CF}$ = 5 Hz), 133.4, 130.1, 124.5, 124.4, 123.9, 120.6 (q, $^{1}J_{CF}$ = 269.6 Hz), 118.4 (q, $^{1}J_{CF}$ = 274.1 Hz), 113.8 (qq, $^{2}J_{CF}$ = 36.9 Hz, $^{3}J_{CF}$ = 3.6 Hz). ^{19}F NMR (470.0 MHz, $CDCl_3$) δ −71.5 (s, CF_3), −60.9 (d, J_{FH} = 6.6 Hz, CF_3). IR (KBr): 3115, 1792, 1539, 1153, 1047, 847, 641 cm^{-1}. HRMS (EI-TOF): calcd for $C_{11}H_5F_6NO_4$ (M^+) 329.0123, found 352.0018.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-4-nitrobenzoate (3l). Yellow solid, 191 mg, 58%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, 2H, J_{HH} = 9 Hz), 8.31 (d, 2H, J_{HH} = 9 Hz), 6.42 (q, 1H, J_{HF} = 7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 151.6, 142.6 (qq, $^{2}J_{CF}$ = 38.5 Hz, $^{3}J_{CF}$ = 5 Hz), 131.9, 131.8, 124.0, 120.4 (q, $^{1}J_{CF}$ = 269.7 Hz), 118.5 (q, $^{1}J_{CF}$ = 273.9 Hz), 114.2 (qq, $^{2}J_{CF}$ = 36.9 Hz, $^{3}J_{CF}$ = 3.6 Hz). ^{19}F NMR (470.0 MHz, $CDCl_3$) δ −71.5 (s, CF_3), −60.9 (d, J_{FH} = 6.6 Hz, CF_3). IR (KBr): 3115, 1765, 1539, 1273, 1080, 867, 714 cm^{-1}. HRMS (EI-TOF): calcd for $C_{11}H_5F_6NO_4$ (M^+) 329.0123, found 352.0017.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-4-formylbenzoate (3m). Yellow oil, 218 mg, 70%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.28 (d, 2H, J_{HH} = 8 Hz), 8.05 (d, 2H, J_{HH} = 8.5 Hz), 6.42 (q, 1H, J_{HF} = 6.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.1, 161.2, 142.8 (qq, $^{2}J_{CF}$ = 38.3 Hz, $^{3}J_{CF}$ = 5 Hz), 140.4, 131.4, 131.2, 129.8, 120.6 (q, $^{1}J_{CF}$ = 269.5 Hz), 118.5 (q, $^{1}J_{CF}$ = 273.9 Hz), 113.9 (qq, $^{2}J_{CF}$ = 36.9 Hz, $^{3}J_{CF}$ = 3.6 Hz). ^{19}F NMR (470.0 MHz, $CDCl_3$) δ −71.9 (s, CF_3), −61.3 (d, J_{FH} = 6.6 Hz, CF_3). IR (KBr): 3115, 2842, 1778, 1705, 1160, 847, 655 cm^{-1}. HRMS (EI-TOF): calcd for $C_{12}H_6F_6O_3$ (M^+) 312.0221, found 311.0146.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl 4-cyanobenzoate (3n). White solid, 216 mg, 70%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, 2H, J_{HH} = 8.5 Hz), 7.84 (d, 2H, J_{HH} = 8.5 Hz), 6.40 (q, 1H, J_{HF} = 6.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 142.7 (qq, $^{2}J_{CF}$ = 38.5 Hz, $^{3}J_{CF}$ = 5 Hz), 132.7, 131.1, 130.4, 120.5 (q, $^{1}J_{CF}$ = 269.7 Hz), 118.5 (q, $^{1}J_{CF}$ = 273.8 Hz), 118.3, 117.4, 114.2 (qq, $^{2}J_{CF}$ = 36.7 Hz, $^{3}J_{CF}$ = 3.6 Hz). ^{19}F NMR (470.0 MHz, $CDCl_3$) δ −71.9 (s, CF_3), −61.2 (d, J_{FH} = 5.6 Hz, CF_3). IR (KBr): 2244, 1759, 1273, 1153, 1000, 854, 648 cm^{-1}. HRMS (EI-TOF): calcd for $C_{12}H_5F_6NO_2$ (M^+) 309.0224, found 308.0153.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-4-(trifluoromethyl) benzoate (3o). White solid, 299 mg, 85%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, 2H, J_{HH} = 8 Hz), 7.80 (d, 2H, J_{HH} = 8 Hz), 6.39 (q, 1H, J_{HF} = 7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 142.8 (qq, $^{2}J_{CF}$ = 38.4 Hz, $^{3}J_{CF}$ = 5 Hz), 136.3 (q, $^{2}J_{CF}$ = 32.9 Hz), 131.1, 129.9, 126.0 (q, $^{3}J_{CF}$ = 3.8 Hz), 123.3 (q, $^{1}J_{CF}$ = 271.5 Hz), 120.6 (q, $^{1}J_{CF}$ = 269.6 Hz), 118.5 (q, $^{1}J_{CF}$ = 273.9 Hz), 114.0 (qq, $^{2}J_{CF}$ = 36.7 Hz, $^{3}J_{CF}$ = 3.5 Hz). ^{19}F NMR (470.0 MHz, $CDCl_3$) δ −71.9 (s, CF_3), −63.5 (s, 3F), −61.2 (d, J_{FH} = 6.6 Hz, CF_3). IR (KBr): 3115, 1778, 1333, 1160, 1007, 854, 648 cm^{-1}. HRMS (EI-TOF): calcd for $C_{12}H_5F_9O_2$ (M^+) 352.0146, found 351.0082.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-2-naphthoate (3p). White solid, 313 mg, 94%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.06–7.90 (m, 4H), 7.67–7.57 (m, 2H), 6.39 (q, 1H, J_{HF} = 7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 143.3 (qq, $^{2}J_{CF}$ = 38 Hz, $^{3}J_{CF}$ = 5 Hz), 136.0, 133.1, 132.4, 129.7, 129.4, 128.8, 127.9, 127.2, 125.2, 123.8, 120.8 (q, $^{1}J_{CF}$ = 269.6 Hz), 118.7 (q, $^{1}J_{CF}$ = 274.1 Hz), 113.7 (qq, $^{2}J_{CF}$ = 36.6 Hz, $^{3}J_{CF}$ = 3.5 Hz). ^{19}F NMR (470.0 MHz, $CDCl_3$) δ −71.8 (s, CF_3), −61.0 (d, J_{FH} = 6.1 Hz, CF_3). IR (KBr): 3069, 1765, 1306, 1160, 1060, 767, 648 cm^{-1}. HRMS (EI-TOF): calcd for $C_{15}H_8F_6O_2$ (M^+) 334.0428, found 334.0422.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-picolinate (3q). Yellow oil, 154 mg, 54%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (m, 1H), 8.22 (m, 1H), 7.94 (m, 1H), 7.61 (m, 1H), 6.40 (q, 1H, J_{HF} = 7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 150.5, 144.9, 143.1 (qq, $^{2}J_{CF}$ = 38.3 Hz, $^{3}J_{CF}$ = 4.9 Hz), 137.4, 128.3, 126.5, 120.6 (q, $^{1}J_{CF}$ = 269.6 Hz), 118.5 (q, $^{1}J_{CF}$ = 274 Hz), 113.8 (qq, $^{2}J_{CF}$ = 36.8 Hz, $^{3}J_{CF}$ = 3.6 Hz). ^{19}F NMR (470.0 MHz, $CDCl_3$) δ −71.8 (s, CF_3), −61.2 (d, J_{FH} = 7.1 Hz, CF_3). IR (KBr): 3062, 1772, 1306, 1160, 1073, 748, 655 cm^{-1}. HRMS (EI-TOF): calcd for $C_{10}H_5F_6NO_2$ (M^+) 285.0224, found 285.0215.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-furan-2-carboxylate (3r). Yellow oil, 260 mg, 95%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (m, 1H), 7.42 (m, 1H), 6.62 (m, 1H), 6.35 (q, 1H, J_{HF} = 7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 148.7, 143.1 (qq, $^{2}J_{CF}$ = 38.3 Hz, $^{3}J_{CF}$ = 4.9 Hz), 141.4, 121.9, 120.6 (q, $^{1}J_{CF}$ = 269.6 Hz), 118.5 (q, $^{1}J_{CF}$ = 273.9 Hz), 114.0 (qq, $^{2}J_{CF}$ = 36.9 Hz, $^{3}J_{CF}$ = 3.6 Hz), 112.6. ^{19}F NMR (470.0 MHz, $CDCl_3$) δ −72.1 (s, CF_3), −61.2 (d, J_{FH} = 6.6 Hz, CF_3). IR (KBr): 3115, 1778, 1473, 1300, 1160, 767, 648 cm^{-1}. HRMS (EI-TOF): calcd for $C_9H_4F_6O_3$ (M^+) 274.0065, found 274.0061.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-thiophene-2-carboxylate (3s). Yellow oil, 264 mg, 91%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (m, 1H), 7.76 (m, 1H), 7.20 (m, 1H), 6.34 (q, 1H, J_{HF} = 7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 142.6 (qq, $^{2}J_{CF}$ = 38.1 Hz, $^{3}J_{CF}$ = 5 Hz), 136.5, 135.6, 129.3, 128.4, 120.6 (q, $^{1}J_{CF}$ = 269.5 Hz), 118.6 (q, $^{1}J_{CF}$ = 274 Hz), 113.9 (qq, $^{2}J_{CF}$ = 36.8 Hz, $^{3}J_{CF}$ = 3.6 Hz). ^{19}F NMR (470.0 MHz, $CDCl_3$) δ −71.9 (s, CF_3), −61.1 (d, J_{FH} = 5.6 Hz, CF_3). IR (KBr): 3115, 1765, 1306, 1160, 1060, 734, 655 cm^{-1}. HRMS (EI-TOF): calcd for $C_9H_4F_6O_2S$ (M^+) 289.9836, found 289.9832.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-2-(((*Z*)-1,1,1,4,4,4-hexafluorobut-2-en-2-yl)thio)benzoate (3t). Yellow oil, 306 mg, 64%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (m, 1H), 7.58 (m, 1H), 7.41 (m, 1H), 7.35 (m, 1H), 7.00 (q, 1H, J_{HF} = 7 Hz), 6.38 (q, 1H, J_{HF} = 7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0, 142.7 (qq, $^{2}J_{CF}$ = 38.4 Hz, $^{3}J_{CF}$ = 5 Hz), 136.8, 136.2 (qq, $^{2}J_{CF}$ = 34.1 Hz, $^{3}J_{CF}$ = 4.9 Hz), 134.3, 133.0 (qq, $^{2}J_{CF}$ = 36.3 Hz, $^{3}J_{CF}$ = 4.6 Hz), 132.2, 130.5, 127.4, 125.8, 121.4 (q, $^{1}J_{CF}$ = 275.3 Hz), 121.0 (q, $^{1}J_{CF}$ = 271 Hz), 120.6 (q, $^{1}J_{CF}$ = 269.6 Hz), 118.5 (q, $^{1}J_{CF}$ = 273.9 Hz), 114.1 (qq, $^{2}J_{CF}$ = 36.9 Hz, $^{3}J_{CF}$ = 3.6 Hz). ^{19}F NMR (470.0 MHz, $CDCl_3$) δ −71.9 (s, CF_3), −65.5 (s, CF_3), −61.2 (d, J_{FH} = 5.6 Hz, CF_3), −59.5 (d, J_{FH} = 7.1 Hz, CF_3). IR (KBr): 3075, 1765, 1260. 1153, 1000, 748, 648 cm^{-1}. HRMS (EI-TOF): calcd for $C_{15}H_6F_{12}O_2S$ (M$^+$) 477.9897, found 477.9901.

(*Z*)-1,1,1,4,4,4-Hexafluorobut-2-en-2-yl-4-(((*Z*)-1,1,1,4,4,4-hexafluorobut-2-en-2-yl)oxy)benzoate (3u). White solid, 342 mg, 74%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, 2H, $J_{HH} = 9$ Hz), 7.14 (d, 2H, $J_{HH} = 9$ Hz), 6.34 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 160.5, 146.0 (qq, $^2J_{CF} = 36.5$ Hz, $^3J_{CF} = 5$ Hz), 136.8, 143.0 (qq, $^2J_{CF} = 33.1$ Hz, $^3J_{CF} = 5.1$ Hz), 133.1, 122.8, 120.7 (q, $^1J_{CF} = 269.9$ Hz), 120.6 (q, $^1J_{CF} = 269.5$ Hz), 118.8 (q, $^1J_{CF} = 276.3$ Hz), 118.6 (q, $^1J_{CF} = 274$ Hz), 116.3, 113.8 (qq, $^2J_{CF} = 36.7$ Hz, $^3J_{CF} = 3.6$ Hz), 113.1 (qq, $^2J_{CF} = 37.1$ Hz, $^3J_{CF} = 3.6$ Hz). ^{19}F NMR (470.0 MHz, $CDCl_3$) δ −71.9 (s, CF_3), −69.9 (s, CF_3), −61.1 (d, $J_{FH} = 6.1$ Hz, CF_3), −59.9 (d, $J_{FH} = 7.1$ Hz, CF_3). IR (KBr): 3122, 1605, 1266, 1153, 854, 648 cm^{-1}. HRMS (EI-TOF): calcd for $C_{15}H_6F_{12}O_3$ (M$^+$) 462.0125, found 462.0119.

Conflicts of interest

The authors declare no competing financial interest.

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