Supporting Information
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Supporting Information

Lewis acid-catalyzed rearrangement of fluoroalkylated propargylic alcohols: An alternative approach to β-fluoroalkyl-α,β-enones

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I. Synthetic procedure

General experimental information
All reactions were performed under an atmosphere of argon unless otherwise stated. All solvents and reagents were employed as received. Analytical thin layer chromatography was performed on SiO$_2$ 60 F-254 plates and flash column chromatography was carried out using SiO$_2$ 60 (particle size 0.040-0.055 mm, 230–400 mesh), both of which are available from E. Merck. Visualization was performed under UV irradiation at 254 nm followed by staining with aqueous potassium permanganate [KMnO$_4$ (3 g) and K$_2$CO$_3$ (20 g) in 300 mL of H$_2$O containing 5 mL of an aqueous solution of NaOH (5%, w/v)] and charring by heat gun. $^1$H and $^{13}$C NMR spectra were recorded on Bruker 500 and Inova 400 FT NMR. Chloroform-$d$ was used as the solvent and TMS ($\delta = 0.00$ ppm) as an internal standard. Chemical shifts are reported as $\delta$ values in ppm as referenced to TMS. Multiplicities are recorded as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), dd (doublet of doublets), dt (doublet of triplets), br (broad), m (multiplet). Coupling constants ($J$) are expressed in Hz. HRMS were measured by JEOL JMS-HX110 spectrometer and spectral data were recorded as m/z values. Melting points were measured using an Electrothermal instrument.

I-1. Synthesis of fluorinated propargylic alcohol 1a-s
The fluorinated propargylic alcohol 1a-i and 1s used for the current study were readily prepared via the sodium borohydride-induced reduction of the corresponding ynone S1a-i and S1s (Scheme 1, eq A). Compound 1r was synthesized via the sodium borohydride-induced reduction of ynone S2 (Scheme 1, eq B). Compound 1j-o were synthesized via the nucleophilic addition of lithium reagents or Grignard reagents with the corresponding fluorinated propargylic ynone S1j-o (Scheme 1, eq C). See Figure 1 for the structure of 1a-s.
Scheme S1. Synthetic scheme of compound 1a-s
I-2. General procedure for the synthesis of the compounds 1a-i and 1r-s

The general procedure is illustrated immediately below with compound 1a as a specific example.

To a stirred solution of S1a (1.000 g, 5.0 mmol) in MeOH (10 mL) was added NaBH₄ (0.270 g, 7.0 mmol) at 0 °C. The resulting solution was stirred at the same temperature for 1 hour. Water (8 mL) and saturated NH₄Cl solution (8 mL) were added to quench the reaction. The aqueous layer was separated and extracted with ethyl acetate (2x25 mL). The combined organic extracts were washed with brine, dried over MgSO₄, filtered and concentrated to give the crude product, which was purified by flash chromatography on silica gel with EtOAc/n-hexane (1:8) to afford compound 1a (0.980 g, >95%) as a yellow oil.
1,1,1-trifluoro-4-phenylbut-3-yn-2-ol (1a)

Yellow oil; Yield: >95%; $^1$H NMR (CDCl$_3$, 500 MHz)$\delta$ 7.48-7.45 (m, 2H), 7.38-7.30 (m, 3H), 4.90 (q, $J$ = 6.0 Hz, 1H), 2.81 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz)$\delta$ 131.8 (2xCH), 129.5 (t, $J$ = 25.0 Hz, 2xCH), 127.5 (2xCH), 120.9, 87.9, 80.4 (d, $J$ = 1.2 Hz), 63.0 (q, $J$ = 36.2 Hz); $^{19}$F NMR (CDCl$_3$, 470 MHz)$\delta$ 79.3; LRMS (ESI) calcd. for C$_{10}$H$_8$F$_3$O [M+H]$^+$ 201.1; found: 201.1.

I-3 General procedure for the synthesis of compound 1j-o

The general procedure is illustrated immediately below with compound 1o as a specific example.

To a stirred solution of S1o (200 mg, 0.9 mmol) in anhydrous THF (10 mL) was added p-ClPhMgBr (1.9 mL, 1.0 M in ether) at -60 °C. After reaction was complete (ca. 1h), water (8 mL) and saturated NH$_4$Cl solution (4 mL) was added. The aqueous layer was separated and extracted with ethyl acetate (2x20 mL). The combined organic extracts were washed with brine, dried over MgSO$_4$, filtered and concentrated to give the crude product, which was purified by flash chromatography on silica gel with EtOAc/n-hexane (1:10) to afford compound 1o (140 mg, 47%) as a yellow oil.

2-(4-chlorophenyl)-1,1,1-trifluoro-4-p-tolylbut-3-yn-2-ol (1o)

Yellow oil; Yield: 47%; $^1$H NMR (CDCl$_3$, 500 MHz)$\delta$ 7.75 (d, $J$ = 9.0 Hz, 2H), 7.45-7.42 (m, 4H), 7.21 (t, $J$ = 4.5 Hz, 2H), 3.21 (s, 1H), 2.41 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz)$\delta$ 140.1, 135.6, 134.0, 131.9 (2xCH), 129.2 (2xCH), 128.7, 128.4 (2xCH), 117.6, 88.6, 83.3, 73.1 (q, $J$ = 31.2 Hz), 21.5; $^{19}$F NMR (CDCl$_3$, 470 MHz)$\delta$ -80.4; LRMS (ESI) calcd. for C$_{11}$H$_{13}$F$_3$OCl [M+H]$^+$ 325.0; found: 325.0.

I-4. Procedure for sulfuric acid-induced rearrangement of compound 1l and 1m

The general procedure is illustrated immediately below with compound 1l as a specific example.
A stirred solution of compound 11 (100 mg, 0.39 mmol) and H₂SO₄ (191 mg, 1.95 mmol) in dichloroethane (2 mL) was heated at 50 °C under nitrogen for 6 hours. Then water (3 mL) and saturated Na₂CO₃ solution (2 mL) was added to quench the reaction at 0 °C. The aqueous layer was separated and extracted with CH₂Cl₂ (3 x 3 mL). The combined organic extracts were washed with brine, dried over MgSO₄, filtered and concentrated to give the crude residue, which was purified by flash chromatography on silica gel with EtOAc/n-hexane (1:20) to afford compound 2l (31 mg, 31% yield) as a yellow oil, compound 4l (15 mg, 15% yield) as a yellow oil and compound 5l (17 mg, 18% yield) as a yellow oil.

**(E)-1-phenyl-3-(trifluoromethyl)hept-2-en-1-one (2l)**

![Image of (E)-1-phenyl-3-(trifluoromethyl)hept-2-en-1-one](image)

Yellow oil; ¹H NMR (CDCl₃, 500 MHz) δ 7.93-7.91 (m, 2H), 7.60-7.57 (m, 1H), 7.49-7.46 (m, 2H), 7.20 (s, 1H), 2.52 (t, J = 8.5 Hz, 2H), 1.56-1.51 (m, 2H), 1.38-1.30 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 191.0, 143.7 (q, J = 29.8 Hz), 137.2, 133.7, 128.8, 128.5, 126.3 (q, J = 5.6 Hz), 123.7 (q, J = 272.6 Hz), 30.9, 27.0, 22.8, 13.6; ¹⁹F NMR (CDCl₃, 470 MHz) δ -68.3; HRMS (ESI) calcd. for C₁₄H₁₆F₃O [M+H]+ 257.1153; found: 257.1150.

**(Z)-1-phenyl-3-(trifluoromethyl)hept-2-en-1-one (4l)**

![Image of (Z)-1-phenyl-3-(trifluoromethyl)hept-2-en-1-one](image)

Yellow oil; ¹H NMR (CDCl₃, 500 MHz) δ 7.93 (d, J = 8.2 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 8.0 Hz, 2H), 6.53 (t, J = 1.4 Hz, 1H), 2.40 (t, J = 8.1 Hz, 2 H), 1.68-1.62 (m, 2H), 1.52-1.45 (m, 2H), 1.01 (t, J = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 193.0, 136.2 (q, J = 29.5 Hz), 135.8, 133.8, 131.3 (q, J = 3.7 Hz), 129.0, 128.7, 123.0 (q, J = 274.2 Hz), 30.5, 29.7, 22.2, 13.7; ¹⁹F NMR (CDCl₃, 470 MHz) δ -62.8; HRMS (ESI) calcd. for C₁₄H₁₆F₃O [M+H]+ 257.1153; found: 257.1160.

**(3-(trifluoromethyl)hept-3-en-1-yn-1-yl)benzene (5l)**

![Image of (3-(trifluoromethyl)hept-3-en-1-yn-1-yl)benzene](image)

Yellow oil; ¹H NMR (CDCl₃, 500 MHz) δ 7.54-7.52 (m, 2H), 7.40-7.37 (m, 3H), 6.64 (td, J = 7.6, 1.5 Hz, 1H), 2.50-2.45 (m, 2H), 1.62-1.55 (m, 2H), 1.03 (t, J = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 144.4 (t, J = 4.5 Hz), 131.7, 128.9, 128.3, 122.3, 121.9 (q, J = 270.8 Hz), 115.6 (q, J = 33.6 Hz), 96.5, 80.1, 31.9, 21.5, 13.7; ¹⁹F NMR (CDCl₃, 470 MHz) δ -66.2;
HRMS (ESI) calcd. for C_{14}H_{14}F_{3} [M+H]^+ 239.1048; found: 239.1045.

Characterization data for the synthetic compounds

4-(4-chlorophenyl)-1,1,1-trifluorobut-3-yn-2-ol (1b)

White solid; Yield: >95%; $^1$H NMR (CDCl$_3$, 500 MHz)$\delta$ 7.45-7.38 (m, 2H), 7.32-7.29 (m, 2H), 4.90-4.85 (m, 1H), 2.58 (d, $J = 8.0$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz)$\delta$ 135.8 (2xCH), 133.3 (2xCH), 128.8 (2xCH), 119.4 (2xCH), 86.8, 81.4, 63.1 (q, $J = 36.2$ Hz); $^{19}$F NMR (CDCl$_3$, 470 MHz)$\delta$ -81.5; LRMS (ESI) calcd. for C$_{11}$H$_7$F$_3$OCl [M+H]$^+$ 235.0; found: 235.0.

1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-yn-2-ol (1c)

Yellow oil; Yield: 87%; $^1$H NMR (CDCl$_3$, 500 MHz)$\delta$ 7.40-7.37 (m, 2H), 6.84-6.81 (m, 2H), 4.87 (q, $J = 6.0$ Hz, 1H), 3.80 (d, $J = 4.0$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz)$\delta$ 160.4 (2xCH), 133.7 (d, $J = 27.5$ Hz, 2xCH), 114.1 (2xCH), 88.1, 79.2 (d, $J = 1.2$ Hz), 63.1 (q, $J = 36.2$ Hz), 55.3; $^{19}$F NMR (CDCl$_3$, 470 MHz)$\delta$ -79.3; LRMS (ESI) calcd. for C$_{11}$H$_{10}$F$_3$O$_2$ [M+H]$^+$ 231.1; found: 231.1.

4-(4,4,4-trifluoro-3-hydroxybut-1-ynyl)benzonitrile (1d)

Yellow solid; Yield: >95%; $^1$H NMR (CDCl$_3$, 500 MHz)$\delta$ 7.58 (q, $J = 2.0$ Hz, 2H), 7.52 (t, $J = 2.0$ Hz, 2H), 4.90 (t, $J = 5.5$ Hz, 1H), 3.38 (t, $J = 9.5$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz)$\delta$ 132.5 (2xCH), 132.1 (2xCH), 125.9 (d, $J = 18.7$ Hz, 2xCH), 118.0, 112.9, 85.7, 84.6, 62.9 (q, $J = 36.2$ Hz); $^{19}$F NMR (CDCl$_3$, 470 MHz)$\delta$ -79.0; LRMS (ESI) calcd. for C$_{11}$H$_7$F$_3$NO [M+H]$^+$ 226.0; found: 226.1.

1,1,1-trifluoro-4-p-tolylbut-3-yn-2-ol (1e)
Yellow oil; Yield: 90%; $^1$H NMR (CDCl$_3$, 500 MHz)$\delta$ 7.36 (d, $J$ = 8.0 Hz, 2H), 7.12 (d, $J$ = 8.0 Hz, 2H), 4.89 (q, $J$ = 6.0 Hz, 1H), 2.34 (s, 3H); $^{13}$C NMR (CDCl$_3$,125 MHz)$\delta$ 139.8 (2xCH), 131.9 (t, $J$ = 28.7 Hz, 2xCH), 129.2 (t, $J$ = 23.7 Hz, 2xCH), 117.8, 88.1, 79.8 (d, $J$ = 1.2 Hz), 63.1 (q, $J$ = 36.2 Hz), 21.4; $^{19}$F NMR (CDCl$_3$, 470 MHz)$\delta$ -79.3; LRMS (ESI) calcd. for C$_{11}$H$_{10}$F$_3$O [M+H]$^+$ 215.1; found: 215.1.

1,1,1-trifluoro-4-(3-fluorophenyl)but-3-yn-2-ol (1f)

Yellow oil; Yield: 60%; $^1$H NMR (CDCl$_3$, 500 MHz)$\delta$ 7.29-7.22 (m, 2H), 7.15-7.13 (m, 1H), 7.08-7.04 (m, 1H), 4.88 (q, $J$ = 5.5 Hz, 1H), 3.20 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz)$\delta$ 163.2, 161.2, 130.1 (d, $J$ = 8.7 Hz), 127.9 (d, $J$ = 2.5 Hz), 122.7 (d, $J$ = 10.0 Hz), 118.8 (d, $J$ = 23.7 Hz), 116.9 (d, $J$ = 21.2 Hz), 86.5 (d, $J$ = 2.5 Hz), 81.3, 63.0 (q, $J$ = 36.2 Hz); $^{19}$F NMR (CDCl$_3$, 470 MHz)$\delta$ -79.2, -112.2; LRMS (ESI) calcd. for C$_{10}$H$_7$F$_4$O [M+H]$^+$ 219.1; found: 219.1.

edethyl 4-(4,4,4-trifluoro-3-hydroxybut-1-ynyl)benzoate (1g)

Colorless oil; Yield: 53%; $^1$H NMR (CDCl$_3$, 500 MHz)$\delta$ 7.98-7.96 (m, 2H), 7.48-7.41 (m, 2H), 4.91 (q, $J$ = 6.0 Hz, 1H), 4.38-4.34 (m, 2H), 3.28 (d, $J$ = 7.5 Hz, 1H), 1.37 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz)$\delta$ 166.0, 131.9 (2xCH), 130.9 (2xCH), 129.5 (2xCH), 125.4 (d, $J$ = 1.2 Hz), 86.8, 83.2, 63.0 (q, $J$ = 36.2 Hz), 61.7, 14.2; $^{19}$F NMR (CDCl$_3$, 470 MHz)$\delta$ -79.1; LRMS (ESI) calcd. for C$_{13}$H$_{12}$O$_3$F$_3$ [M+H]$^+$ 273.1; found: 273.1.

1,1,1-trifluoro-4-(naphthalen-5-yl)but-3-yn-2-ol (1i)
2-(trifluoromethyl)-4-phenylbut-3-yn-2-ol (1j)

Yellow oil; Yield: 48%; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.46-7.43 (m, 2H), 7.37-7.28 (m, 3H), 2.87 (s, 1H), 1.71 (d, $J = 0.5$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 131.9 (2xCH), 129.3 (2xCH), 128.4 (d, $J = 12.5$ Hz, 2xCH), 121.1, 86.2, 84.7, 69.2 (q, $J = 36.2$ Hz), 23.1; $^{19}$F NMR (CDCl$_3$, 470 MHz) $\delta$ -82.7; LRMS (ESI) calcd. for C$_{11}$H$_{10}$F$_3$O [M+H]$^+$ 215.1; found: 215.1.

3-(trifluoromethyl)-1-phenylpent-1-yn-3-ol (1k)

Yellow oil; Yield: 24%; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.47-7.45 (m, 2H), 7.38-7.30 (m, 3H), 2.69 (s, 1H), 1.96-1.90 (m, 2H), 1.22-1.18 (m, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 131.9 (2xCH), 129.3 (2xCH), 128.4 (2xCH), 121.2, 87.4, 83.4, 72.8 (q, $J = 31.2$ Hz), 28.2, 7.7; $^{19}$F NMR (CDCl$_3$, 470 MHz) $\delta$ -81.3; LRMS (ESI) calcd. for C$_{12}$H$_{12}$F$_3$O [M+H]$^+$ 229.1; found: 229.1.

3-(trifluoromethyl)-1-phenylhept-1-yn-3-ol (1l)
Yellow oil; Yield: 20%; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.46 (q, $J$ = 1.0 Hz, 2H), 7.37-7.30 (m, 3H), 2.61 (s, 1H), 1.88 (t, $J$ = 8.0 Hz, 2H), 1.69 (m, 2H), 1.45 (m, 2H), 0.97 (m, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 131.9 (2xCH), 129.2 (2xCH), 128.4 (2xCH), 87.3, 83.7, 72.5 (q, $J$ = 31.2 Hz), 34.5, 25.4, 22.6, 13.9; $^{19}$F NMR (CDCl$_3$, 470 MHz) $\delta$ -81.5; LRMS (ESI) calcd. for C$_{14}$H$_{16}$F$_3$O [M+Na]$^+$ 279.1; found: 279.1.

4,4,5,5,5-pentafluoro-1-phenylpent-1-yn-3-ol (1m)

Yellow oil; Yield: 23%; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.44 (q, $J$ = 1.0 Hz, 2H), 7.36-7.24 (m, 3H), 2.56 (d, $J$ = 3.5 Hz, 1H), 1.92 (q, $J$ = 3.5 Hz, 2H), 1.71-1.65 (m, 2H), 1.43 (q, $J$ = 5.0 Hz, 2H), 0.96 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 131.9 (2xCH), 129.3 (2xCH), 128.4 (2xCH), 121.4, 120.4, 118.1, 113.3, 88.3, 83.4, 72.5 (t, $J$ = 26.2 Hz), 34.5, 25.4, 22.6, 13.9; $^{19}$F NMR (CDCl$_3$, 470 MHz) $\delta$ -78.0; LRMS (ESI) calcd. for C$_{15}$H$_{16}$F$_5$O [M+H]$^+$ 307.1; found: 307.2.

1,1,1-trifluoro-2,4-diphenylbut-3-yn-2-ol (1n)

Colorless oil; Yield: 60%; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.80 (q, $J$ = 4.0 Hz, 2H), 7.54-7.52 (m, 2H), 7.45-7.33 (m, 6H), 3.18 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 135.5 (2xCH), 132.2 (d, $J$ = 27.5 Hz, 2xCH), 129.5 (d, $J$ = 3.7 Hz, 2xCH), 128.5 (d, $J$ = 20.0 Hz, 2xCH), 128.2 (2xCH), 127.2 (2xCH), 121.0, 88.1, 84.4, 73.5 (q, $J$ = 32.5 Hz); $^{19}$F NMR (CDCl$_3$, 470 MHz) $\delta$ -80.2; LRMS (ESI) calcd. for C$_{15}$H$_{16}$F$_3$O [M+H]$^+$ 277.1; found: 277.1.

1,1-difluoro-4-phenyl-1-(2-(trifluoromethyl)phenyl)but-3-yn-2-ol (1p)

Colorless oil; Yield: 93%; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.89-7.86 (m, 2H), 7.69-7.62 (m, 2H), 7.43-7.41 (m, 2H), 7.40-7.32 (m, 3H), 5.13 (q, $J$ = 10.1 Hz, 1H), 2.65 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 133.7, 131.4, 130.7, 130.3 (t, $J$ = 8.7 Hz), 129.1, 128.3, 127.5 (q, $J$ = 6.4 Hz), 121.4, 124.5, 121.4, 88.2, 82.8, 66.7 (t, $J$ = 30.8 Hz); $^{19}$F NMR (CDCl$_3$,}
470 MHz) δ -57.5, -104.6; HRMS (ESI) calcd. for C₁₇H₁₂F₅O [M+H]^+ 327.0808; found: 327.0805.

1-(2-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-ol (1q)

\[
\begin{align*}
\text{Colorless oil; Yield: 91%; } ^1\text{H NMR (CDCl}_3{\text{, 500 MHz}}) & \delta 7.75 \text{ (dd, } J = 7.7, \text{ 1.7 Hz, 1H),} \\
& \text{7.50-7.47 (m, 1H), 7.45-7.42 (m, 1H), 7.40-7.36 (m, 4H), 7.33-7.30 (m, 2H), 5.50-5.45 (m, 1H), 2.72 (s, 1H); } ^{13}\text{C NMR (CDCl}_3{\text{, 125 MHz}}) & \delta 136.2, 133.7, 132.9 \text{ (t, } J = 25.0 \text{ Hz, 130.5,} \\
& \text{130.2, 130.1, 129.8, 128.3, 128.2, 126.5 (t, } J = 6.2 \text{ Hz), 121.6, 119.5 (t, } J = 250.0 \text{ Hz, 88.2,} \\
& \text{84.6, 67.1 (t, } J = 37.5 \text{ Hz); } ^{19}\text{F NMR (CDCl}_3{\text{, 470 MHz}}) & \delta -105.3 \text{ (d, } J = 249.1 \text{ Hz), -107.8 (d, } J = 244.4 \text{ Hz); HRMS (ESI) calcd. for C}_{16}\text{H}_{12}\text{ClF}_2\text{O [M+H]}^+ 293.0545; \text{ found: 293.0543.}
\end{align*}
\]

3-(perfluoroethyl)-1-phenylhept-1-yn-3-ol (1r)

\[
\begin{align*}
\text{Yellow oil; Yield: 91%; } ^1\text{H NMR (CDCl}_3{\text{, 500 MHz}}) & \delta 7.46 \text{ (q, } J = 1.0 \text{ Hz, 2H),} \\
& 7.39-7.31 (m, 3H), 5.05-4.99 (m, 1H), 2.72 (d, } J = 8.5 \text{ Hz, 1H); } ^{13}\text{C NMR (CDCl}_3{\text{, 125 MHz}}) & \delta 132.0, 129.5, \\
& 128.4, 122.2, 119.9, 112.0, 88.9, 79.9, 62.3 (t, } J = 27.5 \text{ Hz); } ^{19}\text{F NMR (CDCl}_3{\text{, 470 MHz}}) & \delta -81.1; \text{ LRMS (ESI) calcd. for C}_{11}\text{H}_8\text{F}_5\text{O [M+H]}^+ 251.0; \text{ found: 251.1.}
\end{align*}
\]

\((E)-1-(4-chlorophenyl)-4,4,4-trifluorobut-2-en-1-one (2b)\)

\[
\begin{align*}
\text{The spectroscopic data were in good agreement with the literature data.\textsuperscript{1}} \\
\text{Yellow oil; } ^1\text{H NMR (CDCl}_3{\text{, 500 MHz}}) & \delta 7.90 \text{ (d, } J = 8.5 \text{ Hz, 2H),} \\
& 7.49 \text{ (d, } J = 8.5 \text{ Hz, 2H),} \\
& 7.45 \text{ (s, 1H), 6.81 (dq, } J = 15.5, 6.6 \text{ Hz, 1H); } ^{13}\text{C NMR (CDCl}_3{\text{, 125 MHz}}) & \delta 186.7, 140.8, \\
& 134.5, 130.5 (q, } J = 35.0 \text{ Hz), 130.1, 129.4, 122.4 (q, } J = 268.7 \text{ Hz); } ^{19}\text{F NMR (CDCl}_3{\text{, 470 MHz}}) & \delta -65.1; \text{ HRMS (ESI) calcd. for C}_{10}\text{H}_3\text{ClF}_3\text{O [M+H]}^+ 235.0138; \text{ found: 235.0133.}
\end{align*}
\]

\((E)-4,4,4-trifluoro-1-(4-methoxyphenyl)but-2-en-1-one (2c)\)
The spectroscopic data were in good agreement with the literature data.\textsuperscript{2}  
Colorless oil; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz)\(\delta\) 7.96 (dd, \(J = 7.0, 2.0\) Hz, 2H), 7.53-7.49 (m, 1H), 6.97 (d, \(J = 15.5\) Hz, 2H), 6.77 (dq, \(J = 15.5, 6.5\) Hz, 1H), 3.89 (s, 3H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz)\(\delta\) 186.1, 164.4, 131.3, 131.0 (q, \(J = 5.5\) Hz), 129.5 (q, \(J = 34.8\) Hz), 129.2, 114.2, 55.6; \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 470 MHz)\(\delta\) -64.9; HRMS (ESI) calcd. for C\textsubscript{11}H\textsubscript{10}F\textsubscript{3}O\textsubscript{2} [M+H]\(^+\) 231.0633; found: 231.0628.

\textit{(E)-4-(4,4,4-trifluorobut-2-enoyl)benzonitrile (2d)}

The spectroscopic data were in good agreement with the literature data.\textsuperscript{3}  
Colorless oil; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz)\(\delta\) 8.09 (dd, \(J = 6.7, 2.0\) Hz, 2H), 7.87 (dd, \(J = 6.5, 2.0\) Hz, 2H), 7.52 (d, \(J = 15.5\) Hz, 1H), 6.90 (dq, \(J = 15.5, 6.5\) Hz, 1H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz)\(\delta\) 186.7, 140.8, 134.5, 130.5 (q, \(J = 35.0\) Hz), 130.1, 129.4, 122.4 (q, \(J = 268.7\) Hz); \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 470 MHz)\(\delta\) -65.2; HRMS (ESI) calcd. for C\textsubscript{11}H\textsubscript{7}F\textsubscript{3}NO [M+H]\(^+\) 226.0480; found: 226.0471.

\textit{(E)-4,4,4-trifluoro-1-(p-tolyl)but-2-en-1-one (2e)}

The spectroscopic data were in good agreement with the literature data.\textsuperscript{4}  
Colorless oil; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz)\(\delta\) 7.91 (d, \(J = 8.2\) Hz, 2H), 7.55 (dq, \(J = 15.0, 2.0\) Hz, 1H), 7.34 (d, \(J = 8.4\) Hz, 2H), 6.83 (dq, \(J = 15.5, 6.6\) Hz, 1H), 2.47 (s, 3H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz)\(\delta\) 187.5, 145.3, 133.7, 131.2 (q, \(J = 6.2\) Hz), 129.1 (q, \(J = 35.0\) Hz), 129.7, 128.9, 21.7; \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 470 MHz)\(\delta\) -65.0; HRMS (ESI) calcd. for C\textsubscript{11}H\textsubscript{12}F\textsubscript{3}O\textsubscript{2} [M+H]\(^+\) 233.0789; found: 233.0789.

\textit{(E)-4,4,4-trifluoro-1-(3-fluorophenyl)but-2-en-1-one (2f)}

Colorless oil; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz)\(\delta\) 7.91 (d, \(J = 8.2\) Hz, 2H), 7.55 (dq, \(J = 15.0, 2.0\) Hz, 1H), 7.34 (d, \(J = 8.4\) Hz, 1H), 6.83 (dq, \(J = 15.5, 6.6\) Hz, 1H), 2.47 (s, 3H); \textsuperscript{13}C NMR
(CDCl₃, 125 MHz)δ 186.8, 162.9 (d, J = 247.7 Hz), 138.2 (d, J = 6.3 Hz), 131.0 (q, J = 35.2 Hz), 130.5 (q, J = 5.3 Hz), 124.5, 121.2 (d, J = 21.3 Hz), 115.5 (d, J = 22.5 Hz); ¹⁹F NMR (CDCl₃, 470 MHz)δ -65.2, -110.7; HRMS (ESI) calcd. for C₁₀H₃F₄O [M+H]^+ 217.0277; found: 217.0276.

**ethyl (E)-4-(4,4,4-trifluorobut-2-enoyl)benzoate (2g)**

![Structure of ethyl (E)-4-(4,4,4-trifluorobut-2-enoyl)benzoate (2g)](image)

Colorless oil; ¹H NMR (CDCl₃, 500 MHz)δ 8.21 (d, J = 8.6 Hz, 2H), 8.04 (d, J = 8.5 Hz, 2H), 7.55 (dq, J = 15.5, 2.0 Hz, 1H), 6.87 (dq, J = 15.5, 6.6 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 1.45 (q, J = 7.1 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz)δ 187.6, 165.4, 135.1, 131.1 (q, J = 35.1 Hz), 130.7 (q, J = 5.4 Hz), 130.0, 122.4 (q, J = 268.6 Hz), 61.6, 14.2; ¹⁹F NMR (CDCl₃, 470 MHz)δ -65.2; HRMS (ESI) calcd. for C₁₃H₁₂F₃O₃ [M+H]^+ 273.0739; found: 273.0738.

**methyl (E)-2-chloro-4-fluoro-5-(4,4,4-trifluorobut-2-enoyl)benzoate (2h)**

![Structure of methyl (E)-2-chloro-4-fluoro-5-(4,4,4-trifluorobut-2-enoyl)benzoate (2h)](image)

Colorless oil; ¹H NMR (CDCl₃, 500 MHz)δ 8.45 (d, J = 7.7 Hz, 1H), 7.43-7.37 (m, 2H), 6.89-6.82 (m, 1H), 1.59 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz)δ 184.2, 163.9, 162.4 (d, J = 262.1 Hz), 141.4, 134.9 (d, J = 3.7 Hz), 133.1, 131.0 (d, J = 35.4 Hz), 127.2, 123.4 (d, J = 12.9 Hz), 121.1, 120.1 (d, J = 26.7 Hz), 109.9, 52.8; ¹⁹F NMR (CDCl₃, 470 MHz)δ -65.3, -103.4; HRMS (ESI) calcd. for C₁₃H₁₂ClF₄NaO₃ [M+H]^+ 332.9917; found: 332.9920.

**(E)-4,4,4-trifluoro-1-(naphthalen-1-yl)but-2-en-1-one (2i)**

![Structure of (E)-4,4,4-trifluoro-1-(naphthalen-1-yl)but-2-en-1-one (2i)](image)

The spectroscopic data were in good agreement with the literature data.¹

Colorless oil; ¹H NMR (CDCl₃, 500 MHz)δ 8.51 (d, J = 8.7 Hz, 1H), 7.91-7.83 (m, 2H), 7.64-7.48 (m, 4H), 7.39 (dq, J = 15.5, 2.0 Hz, 1H), 6.80-6.70 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz)δ 191.4, 134.8 (q, J = 5.8 Hz), 134.1, 133.9, 133.9, 134.1, 130.4 (q, J = 35.0 Hz), 129.7, 129.2, 128.9, 128.6, 128.4, 126.9, 125.4, 124.5 (q, J = 268.5 Hz), 124.3; ¹⁹F NMR (CDCl₃, 470 MHz)δ -64.9; HRMS (ESI) calcd. for C₁₄H₁₀F₃O [M+H]^+ 251.0684; found: 251.0680.

**(E)-4,4,4-trifluoro-3-methyl-1-phenylbut-2-en-1-one (2j)**

![Structure of (E)-4,4,4-trifluoro-3-methyl-1-phenylbut-2-en-1-one (2j)](image)
The spectroscopic data were in good agreement with the literature data.\(^5\)

Colorless oil; \(^1\)H NMR (CDCl\(_3\), 500 MHz)\(\delta\) 7.98-7.96 (m, 2H), 7.66-7.63 (m, 1H), 7.55-7.52 (m, 2H), 7.26-7.25 (m, 1H), 2.19 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 125 MHz)\(\delta\) 191.1, 139.2 (q, \(J = 30.1\) Hz), 137.1, 133.8, 128.8, 128.5, 123.4 (q, \(J = 272.4\) Hz), 125.8 (q, \(J = 5.3\) Hz), 18.1; \(^{19}\)F NMR (CDCl\(_3\), 470 MHz)\(\delta\) -70.8; HRMS (ESI) calcd. for C\(_{11}\)H\(_9\)F\(_3\)NaO \([M+Na]^+\) 237.0503; found: 237.0510.

\((E)-1\)-phenyl-3-(trifluoromethyl)pent-2-en-1-one (2k)

Yellow oil; \(^1\)H NMR (CDCl\(_3\), 500 MHz)\(\delta\) 7.92-7.90 (m, 2H), 7.61-7.57 (m, 1H), 7.55-7.47 (m, 2H), 7.19 (s, 1H), 2.55 (q, \(J = 7.5\) Hz, 2H), 1.17 (t, \(J = 7.5\) Hz, 3H); \(^13\)C NMR (CDCl\(_3\), 125 MHz)\(\delta\) 191.0, 144.6 (q, \(J = 28.4\) Hz), 137.1, 133.8, 128.8, 128.5, 126.2 (q, \(J = 5.5\) Hz), 123.8 (q, \(J = 273.4\) Hz), 20.7, 13.4; \(^{19}\)F NMR (CDCl\(_3\), 470 MHz)\(\delta\) -68.4; HRMS (ESI) calcd. for C\(_{12}\)H\(_{12}\)F\(_3\)O \([M+H]^+\) 229.0840; found: 229.0852.

\((E)-3\)-(perfluoroethyl)-1-phenylhept-2-en-1-one (2m)

Yellow oil; \(^1\)H NMR (CDCl\(_3\), 500 MHz)\(\delta\) 7.91-7.87 (m, 2H), 7.62-7.58 (m, 1H), 7.52-7.48 (m, 2H), 7.17 (s, 1H), 2.49 (t, \(J = 8.1\) Hz, 2H), 1.55-1.48 (m, 2H), 1.38-1.30 (m, 2H), 0.87 (t, \(J = 7.3\) Hz, 3H); \(^13\)C NMR (CDCl\(_3\), 125 MHz)\(\delta\) 190.7, 143.6 (q, \(J = 20.2\) Hz), 137.2, 133.7, 129.5 (t, \(J = 7.9\) Hz), 128.8, 128.4, 118.9 (tq, \(J = 287.5, 38.1\) Hz), 113.4 (q, \(J = 37.5\) Hz), 31.7, 27.5, 22.9, 13.5; \(^{19}\)F NMR (CDCl\(_3\), 470 MHz)\(\delta\) -83.3, -116.4; HRMS (ESI) calcd. for C\(_{15}\)H\(_{16}\)F\(_5\)O \([M+H]^+\) 307.1121; found: 307.1129.

4,4,4-trifluoro-3-hydroxy-1,3-diphenylbutan-1-one (2n)

Colorless oil; \(^1\)H NMR (CDCl\(_3\), 500 MHz)\(\delta\) 7.81 (d, \(J = 8.3\) Hz, 2H), 7.58 (d, \(J = 7.5\) Hz, 2H), 7.35-7.30 (m, 3H), 7.24 (d, \(J = 6.9\) Hz, 2H), 5.77 (s, 1H), 3.97 (d, \(J = 17.2\) Hz, 1H), 3.58 (d, \(J = 10.7\) Hz, 2H).
\[ \delta = 17.2 \text{ Hz, 1H}, 2.40 \text{ (s, 3H)}; ^{13}C \text{ NMR (CDCl}_3, 125 \text{ MHz}) \delta 199.2, 145.6, 137.7, 133.8, 129.6, 128.6, 128.3, 126.3, 125.7 (t, J = 282.6 Hz), 39.9, 21.7; ^{19}F \text{ NMR (CDCl}_3, 470 \text{ MHz}) \delta -80.2; \text{ HRMS (ESI) calcd. for C}_{17}H_{16}F_{3}O_{2} [M+H]^+ 309.1102; \text{ found: 309.1100.} \]

3-(4-chlorophenyl)-4,4,4-trifluoro-3-hydroxy-1-(p-tolyl)butan-1-one (2o)

![Image of 2o structure]

Colorless oil; \(^1H \text{ NMR (CDCl}_3, 500 \text{ MHz}) \delta 7.80 \text{ (d, } J = 8.1 \text{ Hz, 2H), 7.51 \text{ (d, } J = 8.3 \text{ Hz, 2H), 7.31-7.26 \text{ (m, 4H), 5.78 \text{ (s, 1H), 3.93 \text{ (d, } J = 17.2 \text{ Hz, 1H), 3.56 \text{ (d, } J = 17.2 \text{ Hz, 1H), 2.41 \text{ (s, 3H)}; ^{13}C \text{ NMR (CDCl}_3, 125 \text{ MHz}) \delta 199.0, 145.9, 136.4, 134.8, 133.7, 129.6, 128.6, 128.3, 127.8, 125.5 (t, J = 282.5 Hz), 39.7, 21.7; ^{19}F \text{ NMR (CDCl}_3, 470 \text{ MHz}) \delta -80.3; \text{ HRMS (ESI) calcd. for C}_{17}H_{14}ClF_{3}NaO [M+Na]^+ 365.0532; \text{ found: 365.0523.} \]

\((E)-4,4-difluoro-1-phenyl-4-(2-(trifluoromethyl)phenyl)but-2-en-1-one (2p)\)

![Image of 2p structure]

Colorless oil; \(^1H \text{ NMR (CDCl}_3, 500 \text{ MHz}) \delta 7.91-7.90 \text{ (m, 2H), 7.82-7.81 \text{ (m, 1H), 7.75-7.73 \text{ (m, 1H), 7.67-7.63 \text{ (m, 1H), 7.60-7.57 \text{ (m, 2H), 7.49-7.46 \text{ (m, 2H), 7.26-7.23 \text{ (m, 1H), 7.04 \text{ (dt, } J = 15.5, 10.2 \text{ Hz, 1H}); ^{13}C \text{ NMR (CDCl}_3, 125 \text{ MHz}) \delta 189.3, 138.7 (t, J = 29.4 Hz), 136.7, 133.6, 132.2, 130.7, 128.8, 128.7, 128.1 (t, J = 8.6 Hz), 127.8 (q, J = 6.2 Hz), 121.2 (q, J = 272.0 Hz), 118.3, 109.9; ^{19}F \text{ NMR (CDCl}_3, 470 \text{ MHz}) \delta -57.7, -91.2; \text{ HRMS (ESI) calcd. for C}_{17}H_{12}F_{5}O [M+H]^+ 327.0808; \text{ found: 327.0800.} \]

\((E)-4-(2-chlorophenyl)-4,4-difluoro-1-phenylbut-2-en-1-one (2q)\)

![Image of 2q structure]

Colorless oil; \(^1H \text{ NMR (CDCl}_3, 500 \text{ MHz}) \delta 7.94-7.92 \text{ (m, 2H), 7.70-7.68 \text{ (m, 1H), 7.60-7.56 \text{ (m, 1H), 7.49-7.44 \text{ (m, 3H), 7.41-7.30 \text{ (m, 3H), 7.10 \text{ (dt, } J = 15.5, 10.6 \text{ Hz, 1H}); ^{13}C \text{ NMR (CDCl}_3, 125 \text{ MHz}) \delta 189.4, 137.7 \text{ (t, } J = 28.7 \text{ Hz), 136.8, 133.6, 132.8 \text{ (t, } J = 26.5 \text{ Hz), 132.0 \text{ (t, } J = 3.2 \text{ Hz), 131.7, 131.4, 128.8, 128.7, 128.6 \text{ (t, } J = 7.3 \text{ Hz), 127.3 \text{ (t, } J = 8.3 \text{ Hz), 127.0; ^{19}F \text{ NMR (CDCl}_3, 470 \text{ MHz}) \delta -94.3; \text{ HRMS (ESI) calcd. for C}_{16}H_{12}ClF_{2}O [M+H]^+ 293.0545; \text{ found: 293.0544.} \]

\((E)-4,4,5,5,5-pentafluoro-1-phenylpent-2-en-1-one (2r)\)
The spectroscopic data were in good agreement with the literature data.\(^7\)

**Colorless oil; \(^1\)H NMR (CDCl\(_3\), 500 MHz)\(\delta\) 7.97-7.95 (m, 2H), 7.62 (t, \(J = 7.5\) Hz, 1H), 7.58 (dt, \(J = 17.6, 2.2\) Hz, 1H), 7.51 (t, \(J = 8.0\) Hz, 2H), 6.83 (dt, \(J = 11.9, 14.1\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz)\(\delta\) 188.7, 136.1, 134.1, 133.0 (t, \(J = 7.2\) Hz), 129.3 (t, \(J = 23.5\) Hz), 129.0, 128.8, 118.6 (qt, \(J = 284.0, 36.4\) Hz), 112.1 (tq, \(J = 250.0, 38.9\) Hz); \(^{19}\)F NMR (CDCl\(_3\), 470 MHz)\(\delta\) -84.6, -116.7; HRMS (ESI) calcd. for C\(_{11}\)H\(_8\)F\(_5\)O [M+H]\(^+\) 251.0495; found: 251.0488.

**\((Z)-3-(\text{perfluoroethyl})-1-\text{phenylhept-2-en-1-one (4m)}\)**

Yellow oil; \(^1\)H NMR (CDCl\(_3\), 500 MHz)\(\delta\) 7.91 (d, \(J = 8.2\) Hz, 2H), 7.62 (t, \(J = 7.4\) Hz, 1H), 7.51 (t, \(J = 8.0\) Hz, 2H), 6.67 (t, \(J = 1.3\) Hz, 1H), 2.37 (t, \(J = 8.1\) Hz, 2H), 1.70-1.64 (m, 2H), 1.52-1.46 (m, 2H), 1.02 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz)\(\delta\) 192.9, 135.8, 134.6 (t, \(J = 20.0\) Hz), 134.5 (t, \(J = 5.0\) Hz), 133.8, 129.1, 128.6, 117.6 (qt, \(J = 250, 37.6\) Hz), 113.6 (q, \(J = 38.8\) Hz), 30.4, 29.7, 22.2, 13.8; \(^{19}\)F NMR (CDCl\(_3\), 470 MHz)\(\delta\) -82.3, -111.3; HRMS (ESI) calcd. for C\(_{15}\)H\(_{16}\)F\(_5\)O [M+H]\(^+\) 307.1121; found: 307.1120.

**\((3-(\text{perfluoroethyl})\text{hept-3-en-1-yn-1-yl})\text{benzene (5m)}\)**

Yellow oil; \(^1\)H NMR (CDCl\(_3\), 500 MHz)\(\delta\) 7.51-7.49 (m, 2H), 7.39-7.37 (m, 3H), 6.65 (t, \(J = 7.6\) Hz, 1H), 2.65-2.49 (m, 2H), 1.64-1.56 (m, 2H), 1.02 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz)\(\delta\) 147.0 (t, \(J = 25.2\) Hz), 131.5, 128.9, 128.3, 122.3, 118.9 (qt, \(J = 284.6, 38.4\) Hz), 114.0 (q, \(J = 24.8\) Hz), 97.0, 80.3 (t, \(J = 4.0\) Hz), 32.4, 21.5, 13.6; \(^{19}\)F NMR (CDCl\(_3\), 470 MHz)\(\delta\) -83.6, -114.6; HRMS (ESI) calcd. for C\(_{15}\)H\(_{14}\)F\(_5\) [M+H]\(^+\) 289.1016; found: 289.1011.
NMR Spectrum of new β-fluoroalkyl-α,β-enones and β-hydroxy-β-trifluoroalylated ketones

$^1$H spectrum of 2f

$^{13}$C spectrum of 2f
$^1$H spectrum of 2g

$^{13}$C spectrum of 2g
$^1$H spectrum of 2h

$^{13}$C spectrum of 2h
$^1$H spectrum of $2l$

$^{13}$C spectrum of $2l$
$^1$H spectrum of 2m

$^{13}$C spectrum of 2m
$^1$H spectrum of 2n

$^{13}$C spectrum of 2n
$^1$H spectrum of 2o

$^{13}$C spectrum of 2o
$^1$H spectrum of 2q

$^{13}$C spectrum of 2q
$^1$H spectrum of 4l

$^{13}$C spectrum of 4l
$^1$H spectrum of 4m

$^{13}$C spectrum of 4m
$^1$H spectrum of 5l

$^{13}$C spectrum of 5l
$^1$H spectrum of 5m

$^{13}$C spectrum of 5m
Reference: