Supporting Information

Visible-Light Photocatalytic Decarboxylation of \( \alpha, \beta \)-Unsaturated Carboxylic Acids: Facile access to Stereoselective Difluoromethylated Styrenes in Batch and Flow

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I. General information

All components as well as reagents and solvents were used as received without further purification, unless stated otherwise. Reagents and solvents were bought from Sigma Aldrich, Acros Organics, Alfa Aesar, and TCI Chemicals. Photocatalyst \( \text{fac-Ir(ppy)}_3(99\%) \) was bought from Sigma Aldrich and \( \text{fac-Ir(tBuppy)}_3 \) was synthesized according to a literature procedure (see section IV).[1] Technical solvents were bought from VWR International and used as received. Product isolation was performed using silica (60, F254, Merck™), and TLC analysis was performed using Silica on aluminum foils TLC plates (F254, Supelco Sigma-Aldrich™) with visualization under ultraviolet light (254 nm and 365 nm) or appropriate TLC staining. NMR (\(^1\text{H}, \text{^13C} \) and \(^{19}\text{F}\)) analyses were performed on a Bruker- Avance 400 (400 MHz) in solvent CDCl\(_3\) unless stated otherwise. \(^1\text{H}\)-NMR spectra are reported in parts per million (ppm) downfield relative to CDCl\(_3\) (7.27 ppm). All \(^{13}\text{C}\)-NMR spectra are reported in ppm relative to CDCl\(_3\) (77.00 ppm). NMR spectra uses the following abbreviations to describe the multiplicity; \( \text{s} = \text{singlet}, \text{d} = \text{doublet}, \text{t} = \text{triplet}, \text{q} = \text{quartet}, \text{m} = \text{multiplet}, \text{dd} = \text{double doublet}, \text{td} = \text{triple doublet}, \text{dt} = \text{double triplet} \). UV-Vis analyses were recorded on a Shimadzu (UV-2501PC). Infrared spectra were recorded on a Shimadzu IR Affinity-1 Fourier Transform Infrared Miracle 10 Single Reflection ATR Spectrometer.

Light Sources. The batch and flow reactions were carried out using Paulmann YourLED, stripe blue 97 cm, 78 Lumen, 3.12 Watt. The strips were wrapped on the inside of a 3D printed beaker.
II. General experimental procedures

A: General procedures for the photocatalytic decarboxylation in batch

An oven-dried reaction tube (7.5 mL) was charged with cinnamic acid (0.2 mmol, 1.0 equiv.), ethyl bromodifluoroacetate (0.6 mmol, 3.0 equiv.), \textit{fac}-Ir(ppy)$_3$ (1.3 mg, 1.0 mol%), NaHCO$_3$ (33.6 mg, 0.4 mmol, 2 equiv.) and a magnetic stirring bar in 1,4-dioxane (2.0 mL), sealed with a rubber septum and subsequently degassed 3 times (freeze-pump-thaw: cooled to –78 °C and degassed via vacuum evacuation (5 min), backfilled with argon, and warm to room temperature). Next the reaction mixture was irradiated with blue LEDs (at approximately 1 cm distance from the light source). The temperature in the reactor was kept at room temperature. After 24 hours, the mixture was transferred to a 50 mL flask with about 20 mL CH$_2$Cl$_2$. The solvent was subsequently removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate to give the desired product.

An oven-dried reaction tube (7.5 mL) was charged with \textit{o}-cinnamic acid (0.2 mmol, 1.0 equiv.), ethyl bromodifluoroacetate (0.6 mmol, 3.0 equiv.), \textit{fac}-Ir(ppy)$_3$ (3.9 mg, 3.0 mol%), NaHCO$_3$ (33.6 mg, 0.4 mmol, 2 equiv.), H$_2$O (3.0 mmol, 15 equiv.) and a magnetic stirring bar in 1,4-dioxane (0.4 mL), sealed with a rubber septum and subsequently degassed 3 times (freeze-pump-thaw: cooled to –78 °C and degassed via vacuum evacuation (5 min), backfilled with argon, and warm to room temperature). Next the reaction mixture was irradiated with blue LEDs (at approximately 1 cm distance from the light source). The temperature in the reactor was kept at room temperature. After 24 hours, the mixture was transferred to a 50 mL flask with about 20 mL CH$_2$Cl$_2$, then dried over MgSO$_4$. The solvent was subsequently removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate to give the desired product.

An oven-dried reaction tube (7.5 mL) was charged with aryl propiolic acids (0.2 mmol, 1.0 equiv.), ethyl bromodifluoroacetate (0.6 mmol, 3.0 equiv.), \textit{fac}-Ir(ppy)$_3$ (3.9 mg, 3.0 mol%), CsOAc (76.8 mg, 0.4 mmol, 2 equiv.), H$_2$O (2.0 mmol, 10 equiv.) and a magnetic stirring bar in 1,4-dioxane (1.0 mL), sealed with a rubber septum and subsequently degassed 3 times (freeze-pump-thaw: cooled to –78 °C and degassed via vacuum evacuation (5 min), backfilled with argon, and warm to room temperature). Next the reaction mixture was irradiated with blue LEDs (at approximately 1 cm distance from the light source). The temperature in the reactor was kept at room temperature. After 24 hours, the mixture was transferred to a 50 mL flask with about 20 mL CH$_2$Cl$_2$, then dried over MgSO$_4$. The solvent was subsequently removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate to give the desired product.
mL), sealed with a rubber septum and subsequently degassed 3 times (freeze-pump-thaw: cooled to –78 °C and degassed via vacuum evacuation (5 min), backfilled with argon, and warm to room temperature. Next the reaction mixture was irradiated with blue LEDs and a balloon with argon was sealed. The temperature in the reactor was kept at room temperature. After 24 hours, the mixture was transferred to a 50 mL flask with about 20 mL CH₂Cl₂. The solvent was subsequently removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate to give the desired product.

B: a: General procedures for the photocatalytic decarboxylation in flow

O-Cinnamic acid (1.0 mmol), fac-Ir(ppy)₃ (6.5 mg, 1 mol%), BrCF₂CO₂Et (609.0 mg, 3.0 mmol, 3 equiv.), 2,6-lutidine (214 mg, 2.0 mmol, 2 equiv.) was dissolved in 1,4-dioxane/EtOH = 5:1 (v/v, 6.7 mL) and subsequently degassed 3 times (freeze-pump-thaw: cooled to –78 °C and degassed via vacuum evacuation (5 min), backfilled with argon, and warm to room temperature). This reaction mixture was then transferred into a syringe (10 mL) and loaded onto a syringe pump. The reaction mixture was pumped through the microreactor with the desired flow rate (0.053 mL min⁻¹). The microreactor assembly was irradiated with a Blue LED array (1.5 × 3.12 Watts) at room temperature. The continuous reaction was allowed to reach steady state prior to collection of the product fractions. A standard residence time of 15 minutes was utilized. The crude product was collected at the end of the reactor. Workup and purification were done following the batch procedure.

b: Procedures for the recycling the starting material for photocatalytic decarboxylation in flow

O-Cinnamic acid (1.5 mmol), fac-Ir(ppy)₃ (9.8 mg, 1 mol%), BrCF₂CO₂Et (609.0 mg, 3.0 mmol, 3 equiv.), 2,6-lutidine (321 mg, 2.0 mmol, 2 equiv.) was dissolved in 1,4-dioxane/EtOH = 5:1 (v/v, 10.0 mL) and subsequently degassed 3 times (freeze-pump-thaw: cooled to –78 °C and degassed via vacuum evacuation (5 min), backfilled with argon, and warm to room temperature). This reaction mixture was then transferred into a syringe (10 mL) and loaded onto a syringe pump. The reaction mixture was pumped through the microreactor with the desired flow rate (0.053 mL min⁻¹). All the mixture was collected and 15 mL of HCl (1.0 M) was added, the aqueous phase and organic phase are dried separately. The two parts were combined together and purified to get the product and the α-cinnamic acid, which was used to be the starting material for the next run of the flow experiment.

C: Set-ups for the flow reactions

All microfluidic fittings were purchased from IDEX Health and Science. The syringes were connected to the capillary using ¼-28 flat-bottom flangeless fittings. A syringe pump (Fusion 200 Classic) equipped with a 10 mL syringe was used to infuse the liquid reagents into a reactor coil fabricated from a high purity perfluoroalkoxyalkane (PFA) capillary tubing (ID = 500 μm). The microreactor assembly was constructed of high purity PFA tubing (IDEX health and science, part
no. 1622L) (L = 3.9 meters, ID = 500 µm, V = 0.79 mL) in combination with 1.5 Blue LEDs (3.12 W). The outlet of the microreactor led to the collection vial which is protected by aluminum foil. The reactor was cooled with pressurized air to keep it at room temperature. The detail of the assembling the reactor is based on the literature.²

D: Pictures for the set-up.

Figure S1: Left) pieces for the set-ups for both batch and flow reactor; Middle) inside overview of the batch reactor; Right) inside overview of the flow reactor.

Figure S2: Left): Set-up for the batch reaction; 2) Right): Set-up for the flow reaction.
Figure S3: Schematic representations of decarboxylation of ortho-substituted cinnamic acid in flow.

III: Mechanistic Studies

A: Radical Trapping Experiment with TEMPO and BHT

An oven-dried reaction tube (7.5 mL) was charged with cinnamic acid 1a (0.2 mmol, 1.0 equiv.), diethyl bromodifluoroacetate (0.6 mmol, 3.0 equiv.), fac-Ir(ppy)₃ (1.3 mg, 1.0 mol%), NaHCO₃ (33.6 mg, 0.4 mmol, 2 equiv.), BHT or TEMPO (0.4 mmol, 2 equiv.) and a magnetic stirring bar in 1,4-dioxane (2.0 mL), sealed with a rubber septum. The mixture was subsequently degassed 3 times (freeze-pump-thaw method: cooled to −78 °C and degassed via vacuum evacuation (5 min), backfilled with argon, and warm to room temperature), then irradiated with blue LED (at approximately 1 cm distance from the light source). The temperature in the reactor was kept at room temperature. The reaction was kept for 24 hours. The target product could not be detected by HRMS. Instead the BHT-CF₂CO₂Et and TEMPO-CF₂CO₂Et adduct were observed in the HRMS and the BHT-CF₂CO₂Et was also isolated, which gave a direct evidence for the involvement of -CF₂CO₂Et radical in the reaction.
The HRMS spectra of BHT-CF₂CO₂Et and TEMPO-CF₂CO₂Et adduct are listed below.

**Figure S4: HRMS spectrum of the BHT trap experiment mixture**
Figure S5: HRMS spectrum of the TEMPO trap experiment mixture.
B: Time / Isomerization experiments

In order to determine the erosion of the E/Z-configuration during the decarboxylation reaction, the reaction was monitored by $^{19}$F-NMR over time. Two mixtures were prepared according to General procedure on a 2.0 mmol scale (10 mL) and irradiated with a Blue LED (1.5 × 3.12 W). Samples were collected and analyzed for every 30 minutes by $^{19}$F-NMR.

![Reaction Scheme]

Figure S6: $^{19}$F-NMR of the the substrates with 4a and 2, followed in time with Blue-LEDs light source.
C: UV-Vis absorption spectra:

![UV-Vis absorption spectra](image)

**Figure S7**: UV-Vis absorption spectra: The UV-Vis absorption spectra of ethyl bromodifluoroacetate and basic state of trans-cinnamic acid are below 330 nm in 1,4-dioxane, while fac-Ir(ppy)$_3$ exhibits moderate intense MLCT absorption in the range of 320-470 nm. These spectra indicate that the reaction is indeed initiated by photoexcitation of the fac-Ir(ppy)$_3$ complex.

D: Stern-Volmer experiments

All solutions were prepared in 1, 4-dioxane, the concentration of the fac-Ir(ppy)$_3$ is $7 \times 10^{-6}$ mol/L, the trans-cinnamic acid 0.01 mol/L with 2.0 equivalent of base NaHCO$_3$, the ethyl bromodifluoroacetate solution 0.0156 mol/L. All samples were bubbled with a stream of argon for 8 hours via a syringe needle prior to use. The fac-Ir(ppy)$_3$ solution and the quencher were irradiated at $\lambda = 410$ nm and the emission intensity was recorded between 540-600 nm in a quartz flow cuvette (Hellma analytics, quartz suprasil, art nr. 176-751-85-40). The spectra compose the average data of at least 5 times.

For each quenching experiment, the emission intensity of the solution of fac-Ir(ppy)$_3$ with different concentration of quencher, the quencher was : (a)trans-cinnamic acid with 2 equivalent of base NaHCO$_3$; (b) ethyl bromodifluoroacetate; (c)trans-cinnamic acid.(I$_0$: the intensity without quencher, I: the intensity with quencher, the rate constant was calculated according to $K_{SV} = k_q\tau_0$, $\tau_0 = 1.9$ $\mu$s).

**Table S1**: the rate constant of the compound.

| Entry | Quencher                               | Rate Constant(M$^{-1}$ s$^{-1}$) |
|-------|----------------------------------------|----------------------------------|
| a     | trans-cinnamic acid with 2 equiv. of NaHCO$_3$ | $1.24 \times 10^8$             |
| b     | ethyl bromodifluoroacetate             | $1.84 \times 10^8$             |
| c     | trans-cinnamic acid                    | $3.37 \times 10^8$             |
The rate constant of *trans*-cinnamic acid was much reduced by the addition of base (Entry a and c), indicating the necessity of adding base to this reaction. $k_q(a)$ is less than $k_q(b)$, this indicates that the reductive quenching of photoexcited $\text{fac-Ir(ppy)}_3$ by ethyl bromodifluoroacetate dominate. As the spectral overlap of absorption of ethyl bromodifluoroacetate 2 and photoluminescence of $\text{fac-Ir(ppy)}_3$ is rather small, the energy transfer from the excited $\text{fac-Ir(ppy)}_3$ to 2 would be negligible. The photoluminescence quenching is therefore attributed to the electron transfer from the excited $\text{fac-Ir(ppy)}_3$ to ethyl bromodifluoroacetate 2.

**Figure S8**: The Stern-Volmer plot with cinnamic acid with base. $y = 236.05x+1(R^2= 0.999)$

**Figure S9**: The Stern-Volmer plot with BrCF$_2$CO$_2$Et. $y= 350.05x+1(R^2=0.992)$
E: The electrochemistry of Cinnamic acid:

Electrochemical measurements (cyclic voltammetry) were performed under an inert atmosphere with an Eco Chemie Autolab PGSTAT 30 potentiostat/galvanostat using a three electrode microcell with a Pt working electrode, a platinum working electrode (2 mm in diameter), a silver counter electrode and a silver wire coated with silver chloride (Ag/AgCl) quasi-reference electrode. The reference electrode was calibrated against ferrocene/ferrocenium as an external standard.

From this figure, Cinnamic acid shows an irreversible reduction event in acetonitrile containing 0.1 mol.L⁻¹ tetrabutylammonium hexafluorophosphate. The reductive potential of cinnamic acid is $E^{\text{red}} = -1.09 \text{ V (vs SCE in CH}_3\text{CN)}$, with the addition of 2 equivalent of NaHCO₃, the reductive potential is $E^{\text{red}} = -1.20 \text{ V (vs SCE in CH}_3\text{CN)}$. As the $E^{1/2}_{1/2} [*\text{Ir}^{3+}/\text{Ir}^{4+}] = -1.72 \text{ V vs SCE}$, the reductive potential of ethyl bromodifluoroacetate is -0.57 V vs SCE², the possibility of first step initiated by ethyl bromodifluoroacetate is much higher. This result indicates that the addition of base is necessary to the reduction process which lower the reductive potential of cinnamic acid.
IV: Preparation of $\alpha,\beta$-Unsaturated Carboxylic Acids and photocatalyst $\text{fac-Ir(tBuppy)}_3$.

The alkene carboxylic acids $3\text{a-3b, 3d, 3g-3l, 3o-3q, 5a-5b, 5e-5h}$ were purchased and used directly from commercial sources, and other substrates were prepared in accordance with methods described in the reference.\(^4\)

The alkynyl carboxylic acids $6\text{a}$ was purchased and used directly from commercial sources, and substrates were prepared in accordance with methods described in the references.\(^5\)

The synthesis of the photocatalyst $\text{fac-Ir(tBuppy)}_3$ is performed according to a literature procedure:

Step 1: Iridium(III) chloride hydrate (0.3 g, 1.0 equiv.) and 2-(4-(tert-butyl)phenyl)pyridine (2.2 eq.) in 3:1 ethoxyethanol:H\(_2\)O were refluxed at 120 °C for 24 h. The resulting precipitate was cooled to room temperature, dilute with 20 mL deionized water, vacuum filtered, repeat this step for 3 times. Then use 10 mL anhydrous Et\(_2\)O wash the solid for 3 times, then use 10 mL pentane or hexane to wash the solid for 3 times. The powdery solid was transferred to a flask and dried in vacuum.\(^{1(a)}\)

\[
\text{IrCl}_3 \cdot x\text{H}_2\text{O} + \text{tBu} - \text{N} \quad \text{Step 1} \quad [\text{Ir(tBuppy)}_2\text{Cl}]_2 \quad \text{Step 2} \quad \text{fac-Ir(tBuppy)}_3
\]

Step 2: 2-phenylpyridine (5.0 equiv.), $[\text{Ir(tBuppy)}_2\text{Cl}]_2$ (280 mg, 1.0 equiv.), and silver triflate (2.0 equiv.) were dissolved in 2-ethoxyethanol (10 mL) and heated at 100 °C in an oil bath under an argon atmosphere overnight. The deep yellow solution was cooled and gravity-filtered to remove the gray AgCl precipitate. The solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel (CH\(_2\)Cl\(_2\)/n-hexane=1:2, v/v) to afford the product as a yellow solid (238 mg).\(^{1(b)}\)

V: Isolated Yields and Product Characterization

**Ethyl 2,2-difluoro-4-phenylbut-3-enolate (3a)**

Purification: Column chromatography (PE/Et\(_2\)O = 30:1) isolated as a colorless oil (68% yield).

E/Z: 94:6.

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): $\delta$ 7.48-7.45(m, 2H), \{Z: 7.09 (dt, $J = 16.0, 4.0$ Hz), E: 6.96 (dt, $J = 12.0, 4.0$ Hz), 1H\}, \{E: 6.32 (dt, $J = 16.0, 12.0$ Hz), Z: 5.77(q, $J = 12.0$ Hz), 1H\}, \{E:4.37 (q, $J = 8.0$ Hz), Z: 4.05(q, $J = 8.0$ Hz), 2H\}, \{E: 1.38 (t, $J = 8.0$ Hz), Z: 1.14 (t, $J = 8.0$ Hz), 3H\}. \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): $\delta$ 163.9 (t, $J = 35.0$ Hz), 136.8(t, $J = 9.0$ Hz), 134.1, 129.6, 128.8, 128.2, 127.4, 118.8 (t, $J = 25.0$ Hz), 112.7 (t, $J = 247.0$ Hz), 63.1, 14.0. \(^{13}\text{F NMR}\) (376 MHz, CDCl\(_3\)): $\delta$ -
93.99 (d, J = 13.6 Hz), -103.24 (dd, J = 11.5, 2.7 Hz). IR: v (cm⁻¹): 2970, 2927, 1767, 1655, 1454, 1296, 1976, 910, 732. **HRMS** (ESI) (m/z): [M+Na]⁺ calcd. for C₁₂H₁₂F₂NaO₂: 249.0703, found: 249.0700.

![Chemical structure of Ethyl (E)-2,2-difluoro-4-(p-tolyl)but-3-enoate (3b)](image)

**Ethyl (E)-2,2-difluoro-4-(p-tolyl)but-3-enoate (3b)**

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (75% yield). E/Z: 80:20.

**¹H NMR** (400 MHz, CDCl₃): δ 7.42 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.25-7.22 (m, 1H), 7.62-7.60 (m, 2H), {E: 7.57 (d, J = 8.0 Hz), Z: 7.48 (d, J = 12.0 Hz), 2H}, {E: 7.13 (dt, J = 16.0, 4.0 Hz), Z: 6.98 (d, J = 12.0 Hz), 1H}, {E: 6.33 (dt, J = 16.0, 12.0 Hz), Z: 5.90 (q, J = 12.0 Hz), 1H}, {E: 4.43 (q, J = 8.0 Hz), Z: 4.14 (q, J = 8.0 Hz), 2H}, {E: 2.45 (s), Z: 2.43 (s), 3H}, {E: 1.44 (t, J = 8.0 Hz), Z: 1.22 (t, J = 8.0 Hz), 3H}.

**¹³C NMR** (100 MHz, CDCl₃): δ 164.0 (t, J = 35.0 Hz), 139.9, 138.7 (t, J = 8.0 Hz), 136.7 (t, J = 10.0 Hz), 131.4, 131.3, 129.5, 129.0 (t, J = 3.0 Hz), 128.9, 127.4, 121.0 (t, J = 8.0 Hz), 117.7 (t, J = 25.0 Hz), 112.9 (t, J = 247.0 Hz), 63.1, 21.3, 14.0, 13.6. **¹³F NMR** (376 MHz, CDCl₃): δ -94.04, -103.00. **IR**: v (cm⁻¹) 2924, 1767, 1508, 1296, 910, 732. **HRMS** (ESI) (m/z): [M+Na]⁺ calcd. for C₁₃H₁₄F₂NaO₂: 263.0860, found: 263.0854.

![Chemical structure of Ethyl (E)-2,2-difluoro-4-(4-isopropylphenyl)but-3-enoate (3c)](image)

**Ethyl (E)-2,2-difluoro-4-(4-isopropylphenyl)but-3-enoate (3c)**

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (65% yield). E/Z: 84:16.

**¹H NMR** (400 MHz, CDCl₃): δ 7.33-7.48 (m), E: 7.39 (d, J = 8.0 Hz), 2H), 7.25-7.22 (m, 2H), {E: 7.57 (d, J = 16.0, 4.0 Hz), Z: 6.92 (d, J = 12.0 Hz), 1H}, {E: 6.26 (dt, J = 16.0, 12.0 Hz), Z: 5.83 (q, J = 12.0 Hz), 1H}, {E: 4.35 (q, J = 8.0 Hz), Z: 4.04 (q, J = 8.0 Hz), 2H}, 2.93 (heptet, J = 8.0 Hz, 1H), {E: 1.37 (t, J = 8.0 Hz), Z: 1.11 (t, J = 8.0 Hz), 3H}, {E: 1.27 (s), Z: 1.25 (s), 3H}.

**¹³C NMR** (100 MHz, CDCl₃): δ 150.8, 136.7 (t, J = 9.0 Hz), 131.7, 127.5, 126.9, 126.3, 117.9 (t, J = 15.0 Hz), 112.9, 63.1, 34.0, 29.7, 23., 14.0. **¹³F NMR** (376 MHz, CDCl₃): δ -94.04, -103.00. **IR**: v (cm⁻¹) 1697, 1508, 902, 725, 648. **HRMS** (ESI) (m/z): [M+Na]⁺ calcd. for C₁₅H₁₈F₂NaO₂: 291.1173, found: 291.1167.

![Chemical structure of Ethyl (E)-2,2-difluoro-4-(m-tolyl)but-3-enoate (3d)](image)

**Ethyl (E)-2,2-difluoro-4-(m-tolyl)but-3-enoate (3d)**
Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (73% yield).

**E/Z: 88:12.**

**1H NMR** (400 MHz, CDCl₃): δ 7.28-7.25 (m, 3H), 7.21-7.17 (m, 1H), {Z: 7.07 (dt, J = 16.0, 4.0Hz), E: 6.94 (d, J = 12.0 Hz), 1H}, {E: 6.30 (dt, J = 16.0, 12.0 Hz), Z: 5.87 (q, J = 8.0 Hz), 1H}, {E: 4.37 (q, J = 8.0 Hz), Z: 4.03 (q, J = 8.0 Hz), 2H}, {E: 2.38 (s), Z: 2.36 (s), 3H}, {E: 1.38 (t, J = 8.0 Hz), Z: 1.14 (t, J = 8.0 Hz), 3H}. **13C NMR** (100 MHz, CDCl₃): δ 164.0 (t, J = 35.0 Hz), 138.8 (t, J = 9.0 Hz), 138.5, 137.8, 136.9 (t, J = 10.0 Hz), 134.0, 130.4, 129.4, 128.7, 128.1, 128.0, 125.9, 124.6, 121.8 (t, J = 28.0 Hz), 118.6 (t, J = 25.0 Hz), 112.8 (t, J = 247.0 Hz), 63.1, 21.3, 14.0.

**13F NMR** (376 MHz, CDCl₃): δ -93.64 (dd, J = 11.3, 3.7 Hz), -103.18 (dd, J = 11.3, 3.7 Hz).

**IR:** \( \nu (cm^{-1}) \) 2982, 1763, 1655, 1373, 1296, 1219, 1168, 1072, 906, 686. **HRMS** (ESI) (m/z): [M+Na]+ calcd. for C₁₃H₁₄F₂NaO₂: 263.0860, found: 263.0859.

Ethyl (E)-4-([1,1'-biphenyl]-4-yl)-2,2-difluorobut-3-enoate (3e)

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (49% yield).

**E/Z: 81:19.**

**1H NMR** (400 MHz, CDCl₃): δ 7.64-7.58 (m, 5H), 7.56-7.53 (m, 2H), 7.49-7.44 (m, 1H), 7.41-7.36 (m, 1H), {E: 7.14 (dt, J = 16.0, 4.0 Hz), Z: 7.06-7.01 (m, 1H), {E: 6.36 (dt, J = 16.0, 12.0 Hz), Z: 5.91 (q, J = 12.0 Hz), 1H}, {E: 4.38 (q, J = 8.0 Hz), Z: 4.10 (d, J = 8.0 Hz), 2H}, {E: 1.39 (t, J = 8.0 Hz), Z: 1.17 (t, J = 7.1 Hz), 3H}. **13C NMR** (100 MHz, CDCl₃): δ 163.9 (t, J = 35.0 Hz), 142.4, 141.5, 140.3, 140.2, 138.3, 136.4 (t, J = 10.0 Hz), 129.5 (t, J = 3.0 Hz), 128.9, 128.8, 127.9, 127.7, 127.6, 127.5, 127.0, 126.8, 121.7 (t, J = 28.0 Hz), 118.7 (t, J = 25.0 Hz), 112.8 (t, J = 247.0 Hz), 63.1, 14.0. **13F NMR** (376 MHz, CDCl₃): δ -94.26 (d, J = 13.2 Hz), -103.12 (dd, J = 13.2 Hz). **IR:** \( \nu (cm^{-1}) \) 2978, 2885, 1762, 1384, 1153, 1076, 906, 729. **HRMS** (ESI) (m/z): [M+Na]+ calcd. for C₁₈H₁₆F₂NaO₂: 325.1016, found: 325.1016.

ethyl (E)-2,2-difluoro-4-(naphthalen-1-yl)but-3-enoate (3f)

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (37% yield).

**E/Z: 81:19.**

**1H NMR** (400 MHz, CDCl₃): δ 8.09 (d, J = 8.0 Hz, 1H), 7.93-7.86 (m, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.60-7.43 (m, 3H), {E: 6.39 (dt, J = 16.0, 12.0 Hz), Z: 6.21 (q, J = 12.0 Hz), 1H}, {E: 4.40 (q, J = 8.0 Hz), Z: 3.48 (q, J = 8.0 Hz), 2H}, {E: 1.40 (t, J = 8.0 Hz), Z: 0.74 (t, J = 8.0 Hz), 3H}. **13C NMR** (100 MHz, CDCl₃): δ 163.9, 134.3 (t, J = 10.0 Hz), 131.8, 131.1, 130.9, 129.9, 129.2, 128.7, 128.5, 126.7, 126.2, 125.4, 125.1, 124.7 (t, J = 2.0 Hz), 121.9 (t, J = 25.0 Hz), 112.6 (t, J = 248.0 Hz), 63.2, 14.0. **13F NMR** (376 MHz, CDCl₃): δ -92.89 (d, J = 11. Hz), -103.12, **IR:** \( \nu (cm^{-1}) \) 2980,
1800, 1380, 1250, 1080, 906. **HRMS (ESI) (m/z): [M+Na]^+ calcd. for C_{16}H_{14}F_{2}NaO_{2}: 299.0860, found: 299.0859.**

![Chemical structure](image)

**Ethyl (E)-2, 2-difluoro-4-(4-methoxyphenyl) but-3-enoate** (3g)

Purification: Column chromatography (PE/Et₂O = 8:1) isolated as a colorless oil (89% yield). E/Z: 88:12.

**¹H NMR** (400 MHz, CDCl₃): δ {E: 7.42-7.38 (m), Z: 7.35-7.33 (m), 2H}, 7.03 (dt, J = 16.0, 4.0 Hz, 1H), {Z: 6.94-6.88 (m), E: 6.87-6.82 (m), 2H}, {E: 6.17 (dt, J = 16.0, 12.0 Hz), Z: 5.77 (q, J = 12.0 Hz), 1H}, {E: 4.36 (q, J = 8.0 Hz), Z: 4.11 (q, J = 8.0 Hz), 2H}, {E: 3.84 (s), Z: 3.82 (s), 3H}, {E: 1.37 (t, J = 8.0 Hz), Z: 1.17 (t, J = 8.0 Hz), 3H}. **¹³C NMR** (100 MHz, CDCl₃): δ 164.1 (t, J = 35.0 Hz), 160.8, 160.0, 138.4 (t, J = 9.0 Hz), 136.3 (t, J = 9.0 Hz), 130.8, 128.9, 126.8 (t, J = 2.0 Hz), 119.8 (t, J = 28.0 Hz), 116.4 (t, J = 24.0 Hz), 114.2, 113.6, 112.9 (t, J = 247.0 Hz), 63.0, 14.0, 13.7. **¹³F NMR** (376 MHz, CDCl₃): δ -94.12 (d, J = 13.6 Hz), -102.67 (dd, J = 11.5, 2.7 Hz). IR: ν (cm⁻¹) 2978, 1762, 1512, 1253, 1076, 902, 725, 648. **HRMS (ESI) (m/z): [M+Na]^+ calcd. for C_{13}H_{14}F_{2}NaO_{3}: 279.0809, found: 279.0812.**

![Chemical structure](image)

**Ethyl (E)-2,2-difluoro-4-(4-(trifluoromethoxy)phenyl)but-3-enoate** (3h)

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (62% yield). E/Z: 94:6.

**¹H NMR** (400 MHz, CDCl₃): δ {E: 7.51-7.47 (m), Z: 7.41 (d, J = 8.0 Hz), 2H}, {E: 7.25-7.22 (m), Z: 7.20 (d, J = 8.0 Hz), 2H}, {E: 7.08 (dt, J = 16.0, 4.0 Hz), Z: 6.92 (d, J = 12.0 Hz), 1H}, {E: 6.30 (dt, J = 16.0, 12.0 Hz), Z: 5.91 (q, J = 12.0 Hz), 1H}, {E: 4.37 (q, J = 8.0 Hz), Z: 4.12 (d, J = 8.0 Hz), 2H}, {E: 1.38 (t, J = 8.0 Hz), Z: 1.18 (t, J = 8.0 Hz), 3H}. **¹³C NMR** (100 MHz, CDCl₃): δ 163.7 (t, J = 34.0 Hz), 150.0, 135.3 (t, J = 10.0 Hz), 132.8, 128.9, 121.2, 120.4 (q, J = 257.0 Hz), 119.9 (t, J = 25.0 Hz), 116.5, 112.4 (t, J = 248.0 Hz), 63.2, 14.0. **¹³F NMR** (376 MHz, CDCl₃): δ -57.83, -94.99 (d, J = 16.1 Hz), -103.47 (d, J = 14.9 Hz). IR: ν (cm⁻¹) 2978, 1767, 1508, 1257, 1211, 1168, 1076, 910, 733. **HRMS (ESI) (m/z): [M+Na]^+ calcd. for C_{13}H_{11}F_{5}NaO_{3}: 333.0526, found: 333.0521.**

![Chemical structure](image)

**Ethyl (E)-2,2-difluoro-4-(4-nitrophenyl)but-3-enoate** (3i)

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (73% yield). E/Z: 91:9.

**¹H NMR** (400 MHz, CDCl₃): δ {E: 8.26 (d, J = 12.0 Hz), Z: 8.22 (d, J = 8.0 Hz), 2H}, {E: 7.62 (d, J = 8.0 Hz), Z: 7.54 (d, J = 8.0 Hz), 2H}, {E: 7.16 (dt, J = 16.0, 4.0 Hz), Z: 6.99 (d, J = 16.0
Hz), 1H}, \{E: 6.48 (dt, J = 20.0, 8.0 Hz), Z: 6.09-5.99 (m), 1H\}, \{E: 4.38 (q, J = 8.0 Hz), Z: 4.21 (q, J = 8.0 Hz), 2H\}, \{E: 1.39 (t, J = 8.0 Hz), Z: 1.22 (t, J = 8.0 Hz), 3H\}. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 163.4 (t, J = 34.0 Hz), 148.3, 140.2, 134.5 (t, J = 10.0 Hz), 129.8, 128.2, 124.2, 123.4, 123.3 (t, J = 25.0 Hz), 112.1 (t, J = 248.0 Hz), 63.5, 14.0. $^{13}$F NMR (376 MHz, CDCl$_3$): δ -96.62 (dd, J = 13.8, 2.3 Hz), -103.95 (dd, J = 11.0, 2.6 Hz). IR: $\nu$ (cm$^{-1}$) 1550, 1380, 902, 725, 648. HRMS (ESI) (m/z): [M+Na]$^+$ calcd. for C$_{12}$H$_{11}$F$_2$NNaO$_4$: 294.0554, found: 294.0548.

**Ethyl (E)-2,2-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-enoate**

(E3j)

Purification: Column chromatography (PE/Et$_2$O = 30:1) isolated as a colorless oil (61% yield). E/Z: 93:7.

$^1$H NMR (400 MHz, CDCl$_3$): δ \{E: 7.65 (d, J = 8.0 Hz), Z: 7.62-7.60 (m), 2H\}, \{E: 7.57 (d, J = 8.0 Hz), Z: 7.48 (d, J = 12.0 Hz), 2H\}, \{E: 7.13 (d, J = 16.0, 4.0 Hz), Z: 6.03-5.93 (m), 1H\}, \{E: 4.38 (q, J = 8.0 Hz), Z: 4.13 (q, J = 8.0 Hz), 2H\}, \{E: 1.38 (t, J = 8.0 Hz), Z: 1.20 (t, J = 8.0 Hz), 3H\}. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 163.6 (t, J = 35.0 Hz), 136.2, 134.4 (t, J = 10.0 Hz), 134.1, 133.6, 133.2, 130.8, 129.1, 128.3, 126.5, 123.4 (t, J = 27.0 Hz), 120.8 (t, J = 25.0 Hz), 112.2 (t, J = 248.0 Hz), 63.5, 14.0. $^{13}$F NMR (376 MHz, CDCl$_3$): δ -62.84, -95.55, -103.73. IR: $\nu$ (cm$^{-1}$) 2978, 2885, 1770, 1458, 1384, 1153, 1130, 1064, 952. HRMS (ESI) (m/z): [M+Na]$^+$ calcd. for C$_{13}$H$_{11}$F$_5$NaO$_2$: 317.0577, found: 317.0573.

**Ethyl (E)-4-(3,4-dichlorophenyl)-2,2-difluorobut-3-enoate**

(E3k)

Purification: Column chromatography (PE/Et$_2$O = 30:1) isolated as a colorless oil (56% yield). E/Z: 86:14.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.55 (d, J = 2.0 Hz, 1H), \{E: 7.47 (d, J = 8.0 Hz), Z: 7.43 (d, J = 8.0 Hz), 1H\}, \{E: 7.30-7.27 (m), Z: 7.22 (dd, J = 12.0, 4.0 Hz), 1H\}, \{E: 7.00 (dt, J = 16.0, 4.0 Hz), Z: 6.83 (dt, J = 16.0, 4.0 Hz), 1H\}, \{E: 6.23 (dt, J = 16.0, 12.0 Hz), Z: 5.93 (q, J = 12.0 Hz), 1H\}, \{E: 4.37 (q, J = 8.0 Hz), Z: 4.20 (q, J = 8.0 Hz), 2H\}, \{E: 1.38 (t, J = 8.0 Hz), Z: 1.27 (t, J = 8.0 Hz), 3H\}. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 163.6 (t, J = 35.0 Hz), 136.2, 134.4 (t, J = 10.0 Hz), 134.1, 133.6, 133.2, 130.8, 129.1, 128.3, 126.5, 123.4 (t, J = 27.0 Hz), 120.8 (t, J = 25.0 Hz), 112.2 (t, J = 248.0 Hz), 63.5, 14.0. $^{13}$F NMR (376 MHz, CDCl$_3$): δ -62.84, -95.55, -103.73. IR: $\nu$ (cm$^{-1}$) 3649, 2978, 2885, 1770, 1458, 1384, 1327, 1153, 1130, 1064, 952. HRMS (ESI) (m/z): [M+Na]$^+$ calcd. for C$_{13}$H$_{11}$Cl$_2$F$_2$NaO$_2$: 316.9924, found: 316.9920.

**Ethyl (E)-4-(3-chlorophenyl)-2,2-difluorobut-3-enoate**

(E3l)
Purification: Column chromatography (PE/EtO₂ = 30:1) isolated as a colorless oil (58% yield).
E/Z: 91:9.

**1H NMR** (400 MHz, CDCl₃): δ 7.45 (s, 1H), 7.34-7.32 (m, 3H), {E: 7.04 (dt, J = 16.0, 4.0 Hz), Z: 6.89 (d, J = 12.0 Hz), 1H}, {E: 6.32 (dt, J = 16.0, 12.0 Hz), Z: 5.92 (q, J = 12.0 Hz), 1H}, {Z: 4.37 (q, J = 8.0 Hz), 2H}, {E: 1.38 (t, J = 8.0 Hz), Z: 1.22 (t, J = 8.0 Hz), 3H}.

**13C NMR** (100 MHz, CDCl₃): δ 163.7 (t, J = 35.0 Hz), 137.2, 135.9, 135.4 (t, J = 10.0 Hz), 134.9, 134.1, 130.1, 129.6, 129.5, 128.8, 128.7, 127.3, 125.7, 123.2 (t, J = 28.0 Hz), 120.4 (t, J = 25.0 Hz), 112.4 (t, J = 8.9 Hz), 63.2, 14.0.

**13F NMR** (376 MHz, CDCl₃); δ -95.00 (d, J = 13.4 Hz), -103.56 (d, J = 8.9 Hz). IR: υ (cm⁻¹) 2978, 2885, 1770, 1384, 1176, 1141, 1087, 906, 725, 651. HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₂H₁₁ClF₂NaO₂: 283.0313, found: 283.0308.

**Ethyl (E)-4-(3-bromophenyl)-2,2-difluorobut-3-enoate** (3m)

Purification: Column chromatography (PE/EtO₂ = 30:1) isolated as a colorless oil (46% yield).
E/Z: 82:18.

**1H NMR** (400 MHz, CDCl₃): δ 7.62 (s, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.32-7.22 (m, 1H), {E: 7.04 (dt, J = 16.0, 4.0 Hz), Z: 6.90 (d, J = 12.0 Hz), 1H}, {E: 6.33 (dt, J = 16.0, 12.0 Hz), Z: 5.94 (q, J = 12.0 Hz), 1H}, {E: 4.38 (q, J = 8.0 Hz), Z: 4.14 (q, J = 8.0 Hz), 2H}, {E: 1.39 (t, J = 8.0 Hz), Z: 1.23 (t, J = 8.0 Hz), 3H}.

**13C NMR** (100 MHz, CDCl₃): δ 163.7 (t, J = 35.0 Hz), 137.0 (t, J = 8.0 Hz), 136.2, 135.3 (t, J = 10.0 Hz), 132.5, 131.7, 131.6, 130.3, 130.2, 129.7, 127.5, 126.1, 123.5, 123.2, 123.0, 122.2, 120.4 (t, J = 25.0 Hz), 112.4 (t, J = 8.0 Hz), 63.2, 14.0.

**13F NMR** (376 MHz, CDCl₃); δ -95.12 (d, J = 15.0 Hz), -103.40 (dd, J = 11.3, 3.8 Hz). IR: υ (cm⁻¹) 3645, 2978, 2885, 1766, 1384, 1153, 1076, 906, 729. HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₂H₁₁BrF₂NaO₂: 326.9808, found: 326.9805.

**Ethyl (E)-4-(4-bromophenyl)-2,2-difluorobut-3-enoate** (3n)

Purification: Column chromatography (PE/EtO₂ = 30:1) isolated as a colorless oil (47% yield).
E/Z: 84:16.

**1H NMR** (400 MHz, CDCl₃): δ 7.53-7.47 (m, 2H), {E: 7.33-7.31 (m), Z: 7.25-7.23 (m), 2H}, {E: 7.03 (dt, J = 16.0, 4.0 Hz), Z: 6.88-6.85 (m), 1H}, {E: 6.31 (dt, J = 16.0, 8.0 Hz), Z: 5.95-5.85 (m), 1H}, {E: 4.37 (q, J = 8.0 Hz), Z: 4.14 (q, J = 8.0 Hz), 2H}, {E: 1.38 (t, J = 8.0 Hz), Z: 1.21 (t, J = 8.0 Hz), 3H}.

**13C NMR** (100 MHz, CDCl₃): δ 163.8 (t, J = 35.0 Hz), 137.5, 135.7 (t, J = 10.0 Hz), 133.0, 132.1, 131.4, 130.6 (t, J = 3.0 Hz), 123.8, 119.6 (t, J = 5.0 Hz), 112.5 (t, J = 248.0 Hz), 63.2, 14.0.

**13F NMR** (376 MHz, CDCl₃); δ -95.12 (d, J = 15.0 Hz), -103.40 (dd, J = 11.3, 3.8 Hz). IR: υ (cm⁻¹) 2978, 2885, 1762, 1489, 1072, 906, 729, 651. HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₂H₁₁BrF₂NaO₂: 326.9808, found: 326.9801.

**Ethyl (E)-2,2-difluoro-4-(pyridin-3-yl)but-3-enoate** (3o)
Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (33% yield).

E/Z > 99:1.

_{1}H NMR (400 MHz, CDCl₃): δ 8.68 (d, J = 40.0 Hz, 2H), 7.82 (dd, J = 8.0, 4.0 Hz, 1H), 7.37 (s, 1H), 7.11 (dt, J = 16.0, 4.0 Hz, 1H), 6.41 (dt, J = 16.0, 12.0 Hz, 1H), 4.38 (q, J = 8.0 Hz, 2H), 1.39 (t, J = 8.0 Hz, 3H).

_{13}C NMR (100 MHz, CDCl₃): δ 163.6, 150.2, 148.8, 134.1, 133.3, 133.2, 121.4 (t, J = 25.0 Hz), 112.2, 63.4, 14.0.

_{13}F NMR (376 MHz, CDCl₃): δ -103.74 (d, J = 14.7 Hz).

IR: ν (cm⁻¹) 2924, 1767, 1458, 1280, 972, 732.

HRMS (ESI) (m/z): [M+H]+ calcd. for C₁₁H₁₂F₂NO₂: 228.0836, found: 228.0845.

Ethyl 3-(thiophen-2-yl)acrylate

(3p)

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a pale yellow oil (61% yield).

E/Z: 61:39.

_{1}H NMR (400 MHz, CDCl₃): δ {Z: 7.41(d, J = 4.0 Hz), E: 7.32 (d, J = 4.0 Hz), 1H}, {Z: 7.31 (m), E: 7.20(dt, J = 16.0, 4.0 Hz), Z: 6.88(dt, J = 12.0, 4.0 Hz), 1H}, {E: 7.34(d, J = 4.0 Hz), Z:7.31(d, J = 4.0 Hz), 1H}, 7.18-7.16(m, 1H), 7.04-7.02(m, 1H), {Z: 7.07 (dt, J = 16.0, 4.0 Hz), E: 6.94 (d, J = 12.0 Hz), 1H}, {E: 6.12 (dt, J = 16.0, 12.0 Hz), Z: 5.73 (q, J = 8.0 Hz), 1H}, {E: 4.36 (q, J = 8.0 Hz), Z: 4.24 (q, J = 8.0 Hz), 2H}, {E: 1.38 (t, J = 8.0 Hz), Z: 1.25 (t, J = 8.0 Hz), 3H}.

_{13}C NMR (100 MHz, CDCl₃): δ 163.8, 163.3, 138.9, 138.5, 136.3, 131.1(t, J = 4.0 Hz), 130.1(t, J = 9.0 Hz), 129.8(t, J = 10.0 Hz), 129.4, 128.9(t, J = 2.0 Hz), 127.8, 127.6, 127.3, 118.6(t, J = 28.0 Hz), 117.6 (t, J = 25.0 Hz), 112.3, 112.4(t, J = 247.0 Hz), 63.1, 21.3, 14.0.

_{13}F NMR (376 MHz, CDCl₃): δ -98.32(s), -102.94(s).

IR: ν (cm⁻¹) 2986, 1763, 1647, 1307, 1199, 1072, 906, 729, 706.

HRMS (ESI) (m/z): [M+Na]+ calcd. for C₁₀H₁₀F₂NaO₂: 255.0267, found: 255.0260.

Ethyl (3E,5E)-2,2-difluoro-6-phenylhexa-3,5-dienoate

(3q)

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (81% yield).

E/Z > 99:1.

_{1}H NMR (400 MHz, CDCl₃): δ 7.46-7.43 (m, 2H), 7.38-7.34 (m, 2H), 7.32-7.28 (m, 1H), 6.90-6.82 (m, 1H), 6.81-6.78 (m, 2H), 5.91 (dt, J = 16.0, 12.0 Hz, 1H), 4.36 (q, J = 8.0Hz), 2H}, 1.38 (t, J = 8.0 Hz, 3H).

_{13}C NMR (100 MHz, CDCl₃): δ 163.9 (t, J = 35.0 Hz), 138.4 (t, J = 3.0 Hz), 136.8 (t, J = 10.0 Hz), 136.0, 128.8, 128.7, 126.9, 125.7(t, J = 2.0 Hz), 121.6(t, J = 25.0 Hz), 112.5 (t, J = 246.0 Hz), 63.1, 14.0.

_{13}F NMR (376 MHz, CDCl₃): δ -98.32(s), -102.94(s).

IR: ν (cm⁻¹) 3649, 2978, 1766, 1647, 1473, 1384, 1249, 1153, 1072, 952. HRMS (ESI) (m/z): [M+Na]+ calcd. for C₁₄H₁₄F₂NaO₂: 275.0860, found: 275.0858.
Ethyl 2,2-difluoro-4,4-diphenylbut-3-enoate

(3r)

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (81% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.30 - 7.27 (m, 3H), 7.26 - 7.22 (m, 3H), 7.20 - 7.17 (m, 2H), 7.14 - 7.12 (m, 2H), 6.20 (t, J = 12.0 Hz, 1H), 3.84 (q, J = 8.0 Hz, 2H), 1.10 (t, J = 8.0 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 163.4 (t, J = 34.0 Hz), 151.0 (t, J = 10.0 Hz), 140.5, 137.1, 129.8 (t, J = 2.0 Hz), 129.1, 128.6, 128.4, 128.0, 127.9, 119.5 (t, J = 28.0 Hz), 112.5 (t, J = 243.0 Hz), 62.7, 13.7.

¹³F NMR (376 MHz, CDCl₃): δ -90.99. IR: ν (cm⁻¹) 2978, 1766, 1103, 1068, 902, 725, 648.

HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₈H₁₆F₂NaO₂: 325.1016, found: 325.1008.

Ethyl (Z)-2,2-difluoro-4-(o-tolyl)but-3-enoate

(5a)-Z

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (77% yield).

E/Z: 6: 94.

¹H NMR (400 MHz, CDCl₃): δ {E: 7.48 (d, J = 8.0 Hz), Z: 7.02 (d, J = 8.0 Hz), 1H}, {E: 7.35 - 7.34 (m), Z: 7.26 - 7.14 (m), 4H}, 7.06 (d, J = 12.0 Hz, 2H), 6.99 - 6.85 (m, 2H), {E: 6.22 (dt, J = 16.0, 12.0 Hz), Z: 5.98 (q, J = 12.0 Hz), 1H}, {E: 4.37 (q, J = 8.0 Hz), Z: 3.88 (q, J = 8.0 Hz), 2H}, {E: 2.40 (s), Z: 2.27 (s), 3H}, {E: 1.38 (t, J = 8.0 Hz), Z: 1.13 (t, J = 8.0 Hz), 3H}.

¹³C NMR (100 MHz, CDCl₃): δ 164.0 (t, J = 35.0 Hz), 136.8, 134.7 (t, J = 10.0 Hz),

¹³F NMR (376 MHz, CDCl₃): δ -93.78 (d, J = 11.5 Hz), -103.05 (dd, J = 11.5, 2.8 Hz). IR: ν (cm⁻¹) 2978, 1766, 1311, 1153, 1095, 1072, 910, 767, 732. HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₃H₁₄F₂NaO₂: 263.0860, found: 263.0861.

ethyl (E)-2,2-difluoro-4-(o-tolyl)but-3-enoate

(5a)-E

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (62% yield).

E/Z: 92:8.

¹H NMR (400 MHz, CDCl₃): δ 7.48 (d, J = 8.0 Hz, 1H), 7.35 (dt, J = 16.0, 4.0 Hz, 1H), 7.29 - 7.19 (m, 3H), {E: 6.22 (dt, J = 16.0, 12.0 Hz), Z: 5.98 (q, J = 12.0 Hz), 1H}, {E: 4.37 (q, J = 8.0 Hz), Z: 3.88 (q, J = 8.0 Hz), 2H}, {E: 2.40 (s), Z: 2.27 (s), 3H}, {E: 1.38 (t, J = 8.0 Hz), E: 1.13 (t, J = 8.0 Hz), 3H}.

¹³C NMR (100 MHz, CDCl₃): δ 164.0 (t, J = 35.0 Hz), 136.8, 134.7 (t, J = 10.0 Hz),
133.2, 130.6, 129.4, 128.7, 126.3, 126.1 (t, J = 2.0 Hz), 125.5, 120.1 (t, J = 25.0 Hz), 112.7 (t, J = 253.0 Hz), 63.1, 19.6, 14.0. 13F NMR (376 MHz, CDCl3): δ -93.80 (d, J = 11.5 Hz), -103.05 (s).

IR: ν (cm⁻¹) 1751, 1076, 902, 725, 648.

**Ethyl (Z)-2,2-difluoro-4-(2-methoxyphenyl)but-3-enoate (5b)-Z**

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (69% yield).

E/Z: 9:91.

1H NMR (400 MHz, CDCl3): δ {E: 7.45-7.35 (m, Z: 7.33-7.29 (m), 2H), 7.06 (d, J = 12.0 Hz, 2H), 6.99-6.85 (m, 2H), {E: 6.42 (dt, J = 16.0, 12.0 Hz), Z: 6.02 (q, J = 12.0 Hz), 1H}, {E: 4.36 (q, J = 8.0 Hz), Z: 4.01 (q, J = 8.0 Hz), 2H}, {E: 3.88 (s), Z: 3.83 (s), 3H}, {E: 1.37 (t, J = 8.0 Hz), Z: 1.15 (t, J = 8.0 Hz), 3H}.

13C NMR (100 MHz, CDCl3): δ 163.4 (t, J = 34.0 Hz), 157.8, 156.9, 134.7 (t, J = 9.0 Hz), 132.2 (t, J = 9.0 Hz), 130.5 (t, J = 4.0 Hz), 130.3, 128.4, 123.5, 122.0 (t, J = 28.0 Hz), 120.7, 120.2, 119.4 (t, J = 25.0 Hz), 112.5 (t, J = 244.0 Hz), 111.0, 63.0, 62.74, 55.40, 13.6.

13F NMR (376 MHz, CDCl3): δ -94.33 (d, J = 12.9 Hz), -102.74 (dd, J = 11.3, 3.8 Hz). IR: ν (cm⁻¹) 2978, 1767, 1462, 1292, 1249, 1072, 906, 725, 648. HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₃H₁₄F₂NaO₃: 279.0809, found: 279.0808.

**ethyl (E)-2,2-difluoro-4-(2-methoxyphenyl)but-3-enoate (5b)-E**

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (63% yield).

E/Z: 87:13.

1H NMR (400 MHz, CDCl3): δ 7.45-7.35 (m, 3H), 7.08-6.85 (m, 2H), 6.99-6.85 (m, 2H), {E: 6.42 (dt, J = 16.0, 12.0 Hz), Z: 6.02 (q, J = 12.0 Hz), 1H}, {E: 4.36 (q, J = 8.0 Hz), Z: 4.00 (q, J = 8.0 Hz), 2H}, {E: 3.88 (s), Z: 3.84 (s), 3H}, {E: 1.38 (t, J = 8.0 Hz), Z: 1.15 (t, J = 8.0 Hz), 3H}.

13C NMR (100 MHz, CDCl3): δ 164.1 (t, J = 35.0 Hz), 157.7, 134.6, 132.2 (t, J = 10.0 Hz), 130.8, 130.5 (t, J = 4.0 Hz), 130.3, 128.3, 123.0, 121.9 (t, J = 28.0 Hz), 120.6, 119.6 (t, J = 56.0 Hz), 119.3, 113.1 (t, J = 247.0 Hz), 111.1, 110.0, 63.0, 55.40, 13.9.

13F NMR (376 MHz, CDCl3): δ -94.32 (d, J = 12.9 Hz), -102.74 (dd, J = 11.3, 3.8 Hz). IR: ν (cm⁻¹) 2978, 1767, 1462, 1292, 1249, 1072, 906, 725, 648.

**Ethyl (Z)-4-(2-(benzyloxy)phenyl)-2,2-difluorobut-3-enoate (5c)-Z**

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (69% yield).

E/Z: 9:91.

1H NMR (400 MHz, CDCl3): δ 7.45-7.35 (m, 3H), 7.08-6.85 (m, 2H), {E: 6.42 (dt, J = 16.0, 12.0 Hz), Z: 6.02 (q, J = 12.0 Hz), 1H}, {E: 4.36 (q, J = 8.0 Hz), Z: 4.00 (q, J = 8.0 Hz), 2H}, {E: 3.88 (s), Z: 3.84 (s), 3H}, {E: 1.38 (t, J = 8.0 Hz), Z: 1.15 (t, J = 8.0 Hz), 3H}.

13C NMR (100 MHz, CDCl3): δ 164.1 (t, J = 35.0 Hz), 157.7, 134.6, 132.2 (t, J = 10.0 Hz), 130.8, 130.5 (t, J = 4.0 Hz), 130.3, 128.3, 123.0, 121.9 (t, J = 28.0 Hz), 120.6, 119.6 (t, J = 56.0 Hz), 119.3, 113.1 (t, J = 247.0 Hz), 111.1, 110.0, 63.0, 55.40, 13.9.

13F NMR (376 MHz, CDCl3): δ -94.32 (d, J = 12.9 Hz), -102.74 (dd, J = 11.3, 3.8 Hz). IR: ν (cm⁻¹) 2978, 1767, 1489, 1458, 1296, 1249, 1076, 903, 725, 648.
**Purification:** Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (81% yield).

**1H NMR** (400 MHz, CDCl₃): δ 7.50-7.28(m, 7H), 7.16(dd, J = 16.0, 4.0 Hz, 1H), 6.99-6.91(m, 2H), {E: 6.46 (dt, J = 16.0, 12.0 Hz), Z: 5.92 (q, J = 12.0 Hz), 1H}, {E: 5.15(s), Z: 5.12(s), 2H}, {E: 4.33 (q, J = 8.0 Hz), Z: 4.01 (q, J = 8.0 Hz), 2H}, {Z: 1.33 (t, J = 8.0 Hz), E: 1.14 (t, J = 8.0 Hz), 3H}. ¹³C NMR (100 MHz, CDCl₃): δ 163.5 (t, J = 34.0 Hz), 156.9, 156.2, 136.8, 136.6, 134.9 (t, J = 9.0 Hz), 132.2 (t, J = 10.0 Hz), 130.8, 130.7(t, J = 4.0 Hz), 130.3, 128.7, 128.6, 128.1, 128.0, 127.3, 127.2, 124.0, 121.8 (t, J = 28.0 Hz), 121.1, 120.5, 119.6(t, J = 25.0 Hz), 115.0, 112.7, 112.6 (t, J = 244.0 Hz), 70.4, 70.2, 63.0, 62.8, 14.0, 13.6. ¹³F NMR (376 MHz, CDCl₃): δ -94.12 (d, J = 12.9 Hz), -102.63 (dd, J = 11.4, 2.8 Hz). IR: υ (cm⁻¹) 2245, 1770, 1273, 1145, 1080, 906, 729, 651. HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₉H₁₈F₂NaO₃: 355.1122, found: 355.1125.

**ethyl (E)-4-(2-(benzyloxy)phenyl)-2,2-difluorobut-3-enoate (5c)-E**

**Purification:** Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (55% yield).

**1H NMR** (400 MHz, CDCl₃): δ 7.49-7.29(m, 8H), 7.01-6.97(m, 2H), {E: 6.45 (dt, J = 16.0, 12.0 Hz), Z: 5.91 (q, J = 12.0 Hz), 1H}, {E: 5.15(s), Z:5.11(s), 2H}, {E: 4.32 (q, J = 8.0 Hz), Z: 4.00 (q, J = 8.0 Hz), 2H}, {Z: 1.32 (t, J = 8.0 Hz), E: 1.14 (t, J = 8.0 Hz), 3H}. ¹³C NMR (100 MHz, CDCl₃): δ 164.0 (t, J = 35.0 Hz), 156.8, 134.8, 132.2 (t, J = 10.0 Hz), 130.6, 130.2, 128.7, 128.6, 128.5, 128.4, 128.0, 127.9, 127.2, 127.1, 123.4, 121.8, 121.0, 120.4, 119.5(t, J = 25.0 Hz), 113.0 (t, J = 247.0 Hz), 112.6, 111.6, 70.4, 62.9, 13.9. ¹³F NMR (376 MHz, CDCl₃): δ -94.15 (d, J = 12.9 Hz), -102.63 (dd, J = 11.4, 2.8 Hz). IR: υ (cm⁻¹) 1763, 1770, 1273, 1145, 1080, 906, 729, 651. HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₉H₁₈F₂NaO₃: 355.1122, found: 355.1125.

**ethyl (Z)-4-(2-acetoxyphenyl)-2,2-difluorobut-3-enoate (5d)-Z**

**Purification:** Column chromatography (PE/Et₂O = 30:1) isolated as a colorless oil (73% yield).

**1H NMR** (400 MHz, CDCl₃): δ 7.57 (dd, J = 12.0, 4.0 Hz), Z: 7.40-7.34(m), 2H}, {E: 7.23 (dt, J = 8.0, 4.0 Hz), Z: 7.37 (t, J = 4.0 Hz), 1H}, 7.13-7.08 (m, 1H), 6.86 (d, J = 12.0, 1H), {E: 6.34 (dt, J = 16.0, 12.0 Hz), Z: 6.00 (q, J = 12.0 Hz), 1H}, {E: 4.36 (q, J = 8.0 Hz), Z: 4.06 (q, J = 8.0 Hz), 2H}, {E: 2.36 (s), Z: 2.30 (s), 3H}, {E: 1.37 (t, J = 8.0 Hz), Z: 1.19 (t, J = 8.0 Hz), 3H}. ¹³C NMR (100 MHz, CDCl₃): δ 168.7, 163.2 (t, J = 35.0 Hz), 154.7, 134.8, 132.2 (t, J = 10.0 Hz), 130.6, 130.2, 128.7, 128.6, 128.5, 128.4, 128.0, 127.9, 127.2, 127.1, 123.4, 121.8, 121.0, 120.4, 119.5(t, J = 25.0 Hz), 113.0 (t, J = 247.0 Hz), 112.6, 111.6, 70.4, 62.9, 13.9. ¹³F NMR (376 MHz, CDCl₃): δ -94.15 (d, J = 12.9 Hz), -102.65 (dd, J = 11.4, 2.8 Hz). IR: υ (cm⁻¹) 1763, 1296, 1246, 1076, 902, 725, 648.
ethyl (E)-4-(2-acetoxyphenyl)-2,2-difluorobut-3-enoate (5d)-E

Purification: Column chromatography (PE/Et2O = 30:1) isolated as a colorless oil (45% yield).

E/Z: 94:6.

$^1$H NMR (400 MHz, CDCl3): δ 7.57 (dd, $J = 8.0, 4.0$ Hz), 7.39 (t, $J = 8.0$ Hz, 1H), 7.27 (t, $J = 8.0$ Hz, 1H), 7.17-7.11 (m, 2H), {E: 6.34 (dt, $J = 16.0, 12.0$ Hz), Z: 5.97 (q, $J = 12.0$ Hz), 1H}, {E: 4.36 (q, $J = 8.0$ Hz), Z: 4.07 (q, $J = 8.0$ Hz), 2H}, {E: 2.36 (s), Z: 2.30 (s), 3H}, {E: 1.38 (t, $J = 8.0$ Hz), Z: 1.19 (t, $J = 8.0$ Hz), 3H}. $^{13}$C NMR (100 MHz, CDCl3): δ 169.0, 163.7 (t, $J = 34.0$ Hz), 148.8, 130.5 (t, $J = 10.0$ Hz), 129.9, 127.4, 126.8, 126.3, 123.0, 121.2 (t, $J = 24.0$ Hz), 112.4 (t, $J = 247.0$ Hz), 63.2, 20.9, 13.9.

$^{13}$F NMR (376 MHz, CDCl3): δ -95.47 (d, $J = 12.8$ Hz), -103.70. IR: $\nu$ (cm$^{-1}$) 1763, 1199, 1180, 1076, 906, 729, 648.

ethyl (E)-4-(2,4-bis(trifluoromethyl)phenyl)-2,2-difluorobut-3-enoate (5e)-E

Purification: Column chromatography (PE/Et2O = 30:1) isolated as a colorless oil (42% yield).

E/Z: 91:9.

$^1$H NMR (400 MHz, CDCl3): δ 7.96 (s, 1H), 7.86-7.83 (m, 2H), 7.51-7.46 (m, 1H), {E: 6.38 (dt, $J = 16.0, 12.0$ Hz), Z: 6.10 (q, $J = 12.0$ Hz), 1H}, {E: 4.39 (q, $J = 8.0$ Hz), Z: 4.20 (q, $J = 12.0$ Hz), 2H}, {Z: 1.39 (t, $J = 8.0$ Hz), E: 0.78 (t, $J = 8.0$ Hz), 3H}. $^{13}$C NMR (100 MHz, CDCl3): δ 163.2 (t, $J = 34.0$ Hz), 136.9, 131.9, 131.6, 131.2, 130.9, 129.4, 129.0, 128.7, 125.7 (t, $J = 25.0$ Hz), 124.5.
123.4, 121.7, 111.8 (t, J = 248.0 Hz), 63.5, 13.9. $^{13}$F NMR (376 MHz, CDCl$_3$): $\delta$ -94.15 (d, J = 12.9 Hz), -102.65 (dd, J = 11.4, 2.8 Hz). IR: $\nu$ (cm$^{-1}$) 2978, 1766, 1346, 1277, 1141, 906, 733.

![Structure](image)

**Ethyl (Z)-3-(2,6-difluorophenyl)acrylate**

**(5f)-Z**

Purification: Column chromatography (PE/Et$_2$O = 30:1) isolated as a colorless oil (80% yield).

E/Z: 10: 90.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ {E: 7.65-7.45 (m), Z: 6.68-6.78 (m), 2H}, 7.23-7.16(m, 1H), {E: 7.09 (dt, $J$ = 16.0, 4.0 Hz), Z: 6.08 (q, $J$ = 12.0 Hz), 1H}, {E: 4.29 (d, $J$ = 8.0 Hz), Z: 4.20 (q, $J$ = 8.0 Hz), 2H}, {E: 1.29 (t, $J$ = 8.0 Hz), Z: 1.25 (t, $J$ = 8.0 Hz), 3H}. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.0 (t, $J$ = 34.0 Hz), 161.0 (dt, $J$ = 7.0, 2.0 Hz), 158.50 (dt, $J$ = 7.0, 2.0 Hz), 130.9, 130.6 (t, $J$ = 11.0 Hz), 130.1 (t, $J$ = 10.0 Hz), 127.0 (t, $J$ = 26.0 Hz), 123.6 (tt, $J$ = 7.0, 2.0 Hz), 112.2, 112.0 (t, $J$ = 244.0 Hz), 111.9 (d, $J$ = 5.0 Hz), 111.7 (d, $J$ = 6.0 Hz), 111.2 (d, $J$ = 6.0 Hz), 110.0 (d, $J$ = 6.0 Hz), 63.0, 13.8. $^{13}$F NMR (376 MHz, CDCl$_3$): $\delta$ -102.5, -104.5, -111.1, -111.6. IR: $\nu$ (cm$^{-1}$) 2978, 1770, 1466, 1307, 1273, 1157, 1076, 729, 648. HRMS (ESI) (m/z): [M+Na]$^+$ calcd. for C$_{12}$H$_{10}$F$_4$NaO$_2$: 285.0515, found: 285.0510.

**ethyl (E)-4-(2,6-difluorophenyl)-2,2-difluorobut-3-enoate**

**(5f)-E**

Purification: Column chromatography (PE/Et$_2$O = 30:1) isolated as a colorless oil (37% yield).

E/Z: 99:1.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ {E: 7.34-7.29 (m, 1H), 7.19 (dt, $J$ = 16.0, 4.0 Hz), 6.99-6.92(m, 2H), 6.69 (dt, $J$ = 16.0, 4.0 Hz, 1H), 4.39 (q, $J$ = 8.0 Hz), 1.39 (t, $J$ = 8.0 Hz), 1H), {E: 7.22 (dt, $J$ = 16.0, 4.0 Hz), Z: 7.18-6.96(m, 2H), 1H), {E: 4.37 (q, $J$ = 8.0 Hz), Z: 4.12 (q, $J$ = 8.0 Hz), 2H}, {E: 1.38 (t, $J$ = 8.0 Hz), Z: 1.21 (t, $J$ = 8.0 Hz),

![Structure](image)

**Ethyl (E)-2,2-difluoro-4-(2-fluorophenyl)but-3-enoate**

**(5g)-Z**

Purification: Column chromatography (PE/Et$_2$O = 30:1) isolated as a colorless oil (62% yield).

E/Z: 14: 86.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ {E: 7.55-7.46 (m), Z: 7.42-7.29 (m), 2H}, {E: 7.22 (dt, $J$ = 16.0, 4.0 Hz), Z: 7.18-6.96(m, 3H), {E: 6.45 (dt, $J$ = 16.0, 12.0 Hz), Z: 6.01 (q, $J$ = 12.0 Hz), 1H}, {E: 4.37 (q, $J$ = 8.0 Hz), Z: 4.12 (q, $J$ = 8.0 Hz), 2H}, {E: 1.38 (t, $J$ = 8.0 Hz), Z: 1.21 (t, $J$ = 8.0 Hz),

![Structure](image)
\[ ^{13}\text{C NMR} \text{(100 MHz, CDCl}_3\):} \delta 163.3 \text{ (t, } J = 34.0 \text{ Hz)}, 159.9 \text{ (d, } J = 249.0 \text{ Hz)}, 131.4 \text{ (td, } J = 8.0, 4.0 \text{ Hz)}, 131.1 \text{ (d, } J = 9.0 \text{ Hz)}, 130.8 \text{ (q, } J = 4.0 \text{ Hz)}, 130.7 \text{ (d, } J = 8.0 \text{ Hz)}, 124.0 \text{ (dt, } J = 28.0, 1.0 \text{ Hz)}, 123.8 \text{ (d, } J = 4.0 \text{ Hz)}, 122.3 \text{ (d, } J = 14.0 \text{ Hz)}, 116.1 \text{ (d, } J = 22.0 \text{ Hz)}, 115.1 \text{ (d, } J = 21.0 \text{ Hz)}, 112.13 \text{ (t, } J = 247.0 \text{ Hz)}, 63.0, 13.6. \]

\[ ^{13}\text{F NMR} \text{(376 MHz, CDCl}_3\):} \delta -93.78 \text{ (d, } J = 11.5 \text{ Hz)}, -103.05 \text{ (dd, } J = 11.5, 2.8 \text{ Hz). IR:} \nu \text{ (cm}^{-1}) 3649, 2978, 1770, 1458, 1384, 1249, 1072, 952, 732. \]

**HRMS (ESI) (m/z):** \([M+Na]^+ \text{ calcd. for C}_{12}H_{11}F_{3}NaO_{2}: 267.0609, \text{ found: 267.0609.} \]

\[ \text{ethyl (E)-2,2-difluoro-4-(2-fluorophenyl)but-3-enoate} \]

**Purification:** Column chromatography (PE/Et2O = 30:1) isolated as a colorless oil (38% yield).

**E/Z:** 92:8.

\[ ^{1}\text{H NMR} \text{(400 MHz, CDCl}_3\):} \delta 7.48 \text{ (t, } J = 8.0 \text{ Hz, 1H)}, 7.37-7.30 \text{ (m, 1H)}, 7.22 \text{ (dt, } J = 16.0, 4.0 \text{ Hz, 1H)}, 7.18-6.97 \text{ (m, 2H)}, \{E: 6.44 \text{ (dt, } J = 16.0, 12.0 \text{ Hz, Z: 6.01 \text{ (q, } J = 12.0 \text{ Hz, 1H)}, \{E: 4.37 \text{ (q, } J = 8.0 \text{ Hz, Z: 4.12 \text{ (q, } J = 8.0 \text{ Hz, 2H), \{E: 1.38 \text{ (t, } J = 8.0 \text{ Hz, Z: 1.21 \text{ (t, } J = 8.0 \text{ Hz, 3H.}} \]

\[ ^{13}\text{C NMR} \text{(100 MHz, CDCl}_3\):} \delta 163.8 \text{ (t, } J = 34.0 \text{ Hz)}, 160.9 \text{ (d, } J = 252.0 \text{ Hz)}, 131.1 \text{ (d, } J = 7.0 \text{ Hz)}, 129.7 \text{ (td, } J = 8.0, 4.0 \text{ Hz)}, 128.6 \text{ (d, } J = 2.0 \text{ Hz)}, 124.4 \text{ (d, } J = 3.0 \text{ Hz)}, 123.8 \text{ (d, } J = 4.0 \text{ Hz)}, 122.0 \text{ (d, } J = 12.0 \text{ Hz)}, 121.7 \text{ (d, } J = 7.0 \text{ Hz)}, 121.4 \text{ (d, } J = 7.0 \text{ Hz)}, 121.2 \text{ (t, } J = 7.0 \text{ Hz)}, 116.1 \text{ (d, } J = 22.0 \text{ Hz)}, 115.0, 112.5, 110.1, 112.5 \text{ (t, } J = 247.0 \text{ Hz)}, 63.2, 13.9. \]

\[ ^{13}\text{F NMR} \text{(376 MHz, CDCl}_3\):} \delta -96.15 \text{ (d, } J = 11.5 \text{ Hz)}, -103.68 \text{ (dd, } J = 11.5, 2.8 \text{ Hz). IR:} \nu \text{ (cm}^{-1}) 1767, 1489, 1458, 1076, 903, 725, 648. \]

**Ethyl (Z)-4-(2-chlorophenyl)-2,2-difluorobut-3-enoate**

**Purification:** Column chromatography (PE/Et2O = 30:1) isolated as a colorless oil (81% yield).

**E/Z:** 8:92.

\[ ^{1}\text{H NMR} \text{(400 MHz, CDCl}_3\):} \delta \{E: 7.58-7.48 \text{ (m), Z: 7.43-7.35 \text{ (m, 2H), 7.32-7.23 \text{ (m, 2H), 7.04 \text{ (d, } J = 12.0, 1H), \{E: 6.33 \text{ (dt, } J = 16.0, 12.0 \text{ Hz), Z: 6.02 \text{ (q, } J = 12.0 \text{ Hz, 1H)}, \{E: 4.38 \text{ (q, } J = 8.0 \text{ Hz, Z: 4.03 \text{ (q, } J = 8.0 \text{ Hz, 2H), \{E: 1.39 \text{ (t, } J = 8.0 \text{ Hz, Z: 1.19 \text{ (t, } J = 8.0 \text{ Hz, 3H.}} \]

\[ ^{13}\text{C NMR} \text{(100 MHz, CDCl}_3\):} \delta 163.1 \text{ (t, } J = 34.0 \text{ Hz), 135.8 \text{ (t, } J = 9.0 \text{ Hz), 134.3, 133.3, 133.2 \text{ (t, } J = 2.0 \text{ Hz), 133.0, 131.0 \text{ (t, } J = 4.0 \text{ Hz), 130.6, 130.0, 129.0, 127.4, 127.1, 126.5, 123.7 \text{ (t, } J = 28.0 \text{ Hz), 121.6 \text{ (t, } J = 25.0 \text{ Hz), 112.1 \text{ (t, } J = 247.0 \text{ Hz), 63.0, 13.6.} ^{13}\text{F NMR} \text{(376 MHz, CDCl}_3\):} \delta -94.76 \text{ (d, } J = 12.3 \text{ Hz), -103.15 \text{ (dd, } J = 11.3, 3.8 \text{ Hz). IR:} \nu \text{ (cm}^{-1}) 1766, 1473, 1438, 1311, 1157, 1099, 1072, 906, 729, 648. \]

**HRMS (ESI) (m/z):** \([M+Na]^+ \text{ calcd. for C}_{12}H_{11}ClF_{2}NaO_{2}: 283.0313, \text{ found: 283.0314.} \]
ethyl (E)-4-(2-chlorophenyl)-2,2-difluorobut-3-enoate

(5h)-E

Purification: Column chromatography (PE/Et2O = 30:1) isolated as a colorless oil (61% yield).
E/Z: 90:10.

**1H NMR** (400 MHz, CDCl3): δ 7.58-7.48 (m, 2H), 7.43-7.37 (m, 1H), {E: 7.32-7.23 (m), Z: 7.05 (d, J = 12.0, 2H), {E: 6.33 (dt, J = 16.0, 12.0 Hz), Z: 6.02 (q, J = 12.0 Hz), 1H}, {E: 4.38 (q, J = 8.0 Hz), Z: 4.03 (q, J = 8.0 Hz), 2H}, {E: 1.39 (t, J = 8.0 Hz), Z: 1.19 (t, J = 8.0 Hz), 3H}. 13C NMR (100 MHz, CDCl3): δ 163.7 (t, J = 35.0 Hz), 135.8 (t, J = 9.0 Hz), 134.3, 133.2 (t, J = 10.0 Hz), 132.4, 131.0 (t, J = 3.0 Hz), 130.5, 130.0, 129.0, 127.4, 127.3, 126.4, 123.7 (t, J = 28.0 Hz), 121.6 (t, J = 2.0 Hz), 112.5 (t, J = 24.0 Hz), 63.2, 14.0. 13F NMR (376 MHz, CDCl3): δ -94.77 (d, J = 12.3 Hz), -103.16 (dd, J = 11.3, 3.8 Hz). IR: υ (cm⁻¹) 1771, 1697, 1508, 903, 725, 648.

Ethyl (Z)-4-(2-bromophenyl)-2,2-difluorobut-3-enoate

(5i)-Z

Purification: Column chromatography (PE/Et2O = 30:1) isolated as a colorless oil (85% yield).
E/Z: 6:94.

**1H NMR** (400 MHz, CDCl3): δ 7.58 (dd, J = 8.0, 1.2 Hz, 1H), {E: 7.47 (dt, J = 16.0, 4.0 Hz), Z: 7.37 (dd, J = 8.0, 4.0 Hz), 1H}, 7.30 (td, J = 8.0, 4.0 Hz, 1H), 7.20 (t, J = 8.0, 1H), 6.98 (d, J = 12.0 Hz, 1H), {E: 6.28 (dt, J = 16.0, 12.0 Hz), Z: 6.00 (q, J = 12.0 Hz), 1H}, {E: 4.38 (q, J = 8.0 Hz), Z: 4.02 (q, J = 8.0 Hz), 2H}, {E: 1.39 (t, J = 8.0 Hz), Z: 1.19 (t, J = 8.0 Hz), 3H}. 13C NMR (100 MHz, CDCl3): δ 163.1 (t, J = 34.0 Hz), 137.8 (t, J = 9.0 Hz), 134.8, 132.1, 131.0 (t, J = 3.0 Hz), 130.1, 127.1, 123.4 (t, J = 28.0 Hz), 123.0 (t, J = 2.0 Hz), 112.0 (t, J = 24.5 Hz), 63.0, 13.6. 13F NMR (376 MHz, CDCl3): δ -94.60 (d, J = 12.2 Hz), -103.08 (d, J = 8.3 Hz). IR: υ (cm⁻¹) 3649, 2978, 1767, 1392, 1157, 1072, 906, 729, 648. HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₂H₁₁BrF₂NaO₂: 326.9808, found: 326.9803.

ethyl (E)-4-(2-bromophenyl)-2,2-difluorobut-3-enoate

(5i)-E

Purification: Column chromatography (PE/Et2O = 30:1) isolated as a colorless oil (52% yield).
E/Z: 91:9.

**1H NMR** (400 MHz, CDCl3): δ {Z: 7.74-7.71 (m), E: 7.47 (dt, J = 16.0, 4.0 Hz), 1H}, 7.62-7.53 (m, 2H), {E: 7.22 (t, J = 8.0 Hz), Z: 6.98 (d, J = 12.0 Hz), 1H}, {E: 6.28 (dt, J = 16.0, 12.0 Hz), Z: 6.00 (q, J = 12.0 Hz), 1H}, {E: 4.38 (q, J = 8.0 Hz), Z: 4.02 (q, J = 8.0 Hz), 2H}, {E: 1.39 (t, J = 8.0 Hz), Z: 1.19 (t, J = 8.0 Hz), 3H}.
Hz), Z: 1.19 (t, J = 8.0 Hz), 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.1 (t, J = 34.0 Hz), 137.8 (t, J = 9.0 Hz), 134.8, 132.1, 131.0 (t, J = 3.0 Hz), 130.1, 127.1, 123.4 (t, J = 28.0 Hz), 123.0 (t, J = 2.0 Hz), 112.0 (t, J = 245.0 Hz), 63.0, 13.6. $^{13}$F NMR (376 MHz, CDCl$_3$): $\delta$ -94.60 (d, J = 12.2 Hz), -103.10 (d, J = 8.3 Hz).

IR: $\nu$ (cm$^{-1}$) 2978, 1766, 1292, 1076, 968, 906, 729.

ethyl (Z)-2,2-difluoro-4-(4-fluoro-2-methylphenyl)but-3-enoate (5j)-Z

Purification: Column chromatography (PE/Et$_2$O = 30:1) isolated as a colorless oil (76% yield). E/Z: 14: 86.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.47-7.43 (m, 1H), 7.28 (dt, J = 12.0, 4.0 Hz), Z: 7.21-7.17 (m, 1H), 7.28 (dt, J = 12.0, 4.0 Hz), Z: 7.21-7.17 (m, 1H), 6.94-6.89 (m, 2H), {E: 6.16 (dt, J = 16.0, 12.0 Hz), Z: 5.97 (q, J = 12.0 Hz), 1H}, {E: 4.37 (q, J = 8.0 Hz), Z: 3.97 (q, J = 8.0 Hz), 2H}, {E: 2.38 (s), Z: 2.26 (s), 3H}, {E: 1.38 (t, J = 8.0 Hz), Z: 1.17 (t, J = 8.0 Hz), 3H}. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.2 (t, J = 34.0 Hz), 162.8 (d, J = 249.0 Hz), 139.3 (d, J = 8.0 Hz), 133.6 (t, J = 9.0 Hz), 129.4 (t, J = 2.0 Hz), 128.0 (dt, J = 9.0, 2.0 Hz), 119.8 (dt, J = 25.0, 2.0 Hz), 117.2 (d, J = 21.0 Hz), 116.4 (d, J = 21.0 Hz), 113.4 (d, J = 22.0 Hz), 112.3 (d, J = 21.0 Hz), 112.2 (t, J = 245.0 Hz), 62.9, 20.0, 14.0.

$^{13}$F NMR (376 MHz, CDCl$_3$): $\delta$ -94.29 (d, J = 11.4 Hz), -103.01 (dd, J = 11.4, 3.8 Hz), -111.21 -112.14 (m).

IR: $\nu$ (cm$^{-1}$) 2978, 1770, 1492, 1072, 906, 733. HRMS (ESI) (m/z): [M+Na]$^+$ calcd. for C$_{13}$H$_{13}$F$_3$NaO$_2$: 281.0765, found: 281.0760.

ethyl (E)-2,2-difluoro-4-(4-fluoro-2-methylphenyl)but-3-enoate (5j)-E

Purification: Column chromatography (PE/Et$_2$O = 30:1) isolated as a colorless oil (52% yield). E/Z: 97:3.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.47-7.43 (m, 1H), 7.28 (dt, J = 12.0, 4.0 Hz), 6.94-6.89 (m, 2H), {E: 6.16 (dt, J = 16.0, 12.0 Hz), Z: 5.97 (q, J = 12.0 Hz), 1H}, {E: 4.37 (q, J = 8.0 Hz), Z: 3.97 (q, J = 8.0 Hz), 2H}, {E: 2.38 (s), Z: 2.26 (s), 3H}, {E: 1.38 (t, J = 8.0 Hz), Z: 1.17 (t, J = 8.0 Hz), 3H}. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.9 (t, J = 34.0 Hz), 163.2 (d, J = 249.0 Hz), 139.3 (d, J = 8.0 Hz), 133.6 (t, J = 9.0 Hz), 129.4 (t, J = 2.0 Hz), 128.0 (dt, J = 9.0, 2.0 Hz), 119.8 (dt, J = 25.0, 2.0 Hz), 117.2 (d, J = 21.0 Hz), 113.4 (d, J = 22.0 Hz), 112.2, 112.6 (t, J = 248.0 Hz), 63.1, 19.7, 14.0. $^{13}$F NMR (376 MHz, CDCl$_3$): $\delta$ -94.29 (d, J = 11.4 Hz), -103.01 (dd, J = 11.4, 3.8 Hz), -111.21 -112.14 (m). IR: $\nu$ (cm$^{-1}$) 2978, 1770, 1492, 1072, 906, 733. HRMS (ESI) (m/z): [M+Na]$^+$ calcd. for C$_{13}$H$_{13}$F$_3$NaO$_2$: 281.0765, found: 281.0760.
Ethyl (Z)-2,2-difluoro-4-(2,3,4,5,6-pentamethylphenyl)but-3-enoate

(5k)-Z

Purification: Column chromatography (PE/Et2O = 30:1) isolated as a colorless oil (55% yield).
E/Z: 1:99.

1H NMR (400 MHz, CDCl3): δ 7.23 (d, J = 16.0, 4.0 Hz, 1H), 5.75 (dt, J = 16.0, 12.0 Hz, 1H),
4.40 (q, J = 8.0 Hz, 2H), 2.24 (s, 6H), 2.21 (s, 6H), 1.39 (t, J = 8.0 Hz, 3H).

13C NMR (100 MHz, CDCl3): δ 164.0 (t, J = 35.0 Hz), 138.02 (t, J = 10.0 Hz), 134.9, 132.7, 132.3, 131.0 (d,
J = 1.0 Hz), 124.9 (t, J = 25.0 Hz), 112.4 (t, J = 248.0 Hz), 63.0, 17.6, 16.8, 16.5, 14.0.

13F NMR (376 MHz, CDCl3): δ -94.73 (d, J = 12.3 Hz), -103.79 (dd, J = 11.3, 3.8 Hz).

IR: υ (cm⁻¹) 2978, 2885, 1766, 1384, 1087, 729, 648.

HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C17H22F2NaO2: 319.1486, found: 319.1475.

ethyl (Z)-4-(2-chloro-6-methylphenyl)-2,2-difluorobut-3-enoate

(5l)-Z

Purification: Column chromatography (PE/Et2O = 30:1) isolated as a colorless oil (87% yield).
E/Z: 1:99.

1H NMR (400 MHz, CDCl3): δ 7.28-7.26 (m, 1H), 7.19-7.12 (m, 3H), 6.14 (dt, J = 16.0, 12.0 Hz,
1H), 4.39 (q, J = 8.0 Hz, 2H), 2.37 (s, 3H), 1.38 (t, J = 8.0 Hz, 3H).

13C NMR (100 MHz, CDCl3): δ 163.7 (t, J = 35.0 Hz), 138.2, 133.6, 132.9 (t, J = 10.0 Hz), 129.0, 127.5, 126.2 (t, J = 25.0 Hz),
112.3 (t, J = 248.0 Hz), 63.1, 21.0, 14.0.

13F NMR (376 MHz, CDCl3): δ -104.38 (dd, J = 11.4, 3.8 Hz).

IR: υ (cm⁻¹) 2982, 1767, 1261, 1076, 906, 733.

HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C13H13ClF2NaO2: 297.0470, found: 297.0460.

ethyl (Z)-2,2-difluoro-4-phenylpent-3-enoate

(5m)-Z

Purification: Column chromatography (Cyclohexane/EtOAc = 40:1) isolated as a colorless oil (71% yield).
E/Z: 10:90.

1H NMR (400 MHz, CDCl3): δ {E: 7.42-7.41(m), Z: 7.21-7.18(m), 2H}, 7.38-7.30(m, 3H), {E: 5.92 (t, J = 12.0 Hz), Z: 5.81 (t, J = 12.0 Hz), 1H}, {E: 4.38 (q, J = 8.0 Hz), Z: 3.88 (q, J = 8.0 Hz),
2H}, {E: 2.28-2.27(m), Z: 2.18-2.16(m), 3H}, {E: 1.37 (t, J = 8.0 Hz), Z: 1.20 (t, J = 8.0 Hz), 3H}.

13C NMR (100 MHz, CDCl3): δ 163.6 (t, J = 34.0 Hz), 148.7(t, J = 9.0 Hz), 139.1, 128.1, 128.0,
127.5(t, J = 2.0 Hz), 119.2 (t, J = 28.0 Hz), 112.3(t, J = 244.0 Hz), 62.6, 27.1, 13.6.

13F NMR (376
MHz, CDCl₃): δ -91.9 (d, J = 11.3 Hz), -97.7 (d, J = 11.3 Hz). HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₃H₁₄F₂NaO₂: 263.0860, found: 263.0857.

ethyl (E)-2,2-difluoro-4-phenylpent-3-enoate

(5m)-E

Purification: Column chromatography (Cyclohexane/EtOAc = 40:1) isolated as a colorless oil (51% yield). E/Z: 90: 10.

¹H NMR (400 MHz, CDCl₃): δ {E: 7.45-7.41(m), Z: 7.21-7.19(m), 2H}, 7.40-7.32(m, 3H), {E: 5.93 (dt, J = 12.0, 4.0 Hz), Z: 5.81 (t, J = 12.0, 4.0 Hz), 1H}, {E: 4.37 (q, J = 8.0 Hz), Z: 3.88(q, J = 8.0 Hz), 2H}, {E: 2.29-2.27(m), Z: 2.18-2.16(m), 3H}, {E: 1.37 (t, J = 8.0 Hz), Z: 1.16 (t, J = 8.0 Hz), 3H}. ¹³C NMR (100 MHz, CDCl₃): δ 164.3 (t, J = 35.0 Hz), 147.7(t, J = 7.0 Hz), 141.6, 128.7, 128.6, 128.0, 127.5(t, J = 2.0 Hz), 126.0, 118.7 (t, J = 27.0 Hz), 113.0(t, J = 247.0 Hz), 63.0, 17.4, 14.0. ¹³F NMR (376 MHz, CDCl₃): δ -91.9 (d, J = 11.3 Hz), -97.7 (d, J = 11.3 Hz).

Ethyl (Z)-4-(4-bromophenyl)-2,2-difluoropent-3-enoate

(5n)-Z

Purification: Column chromatography (Cyclohexane/EtOAc = 40:1) isolated as a colorless oil (88% yield). E/Z: 18: 82.

¹H NMR (400 MHz, CDCl₃): δ 7.51-7.49(m, 2H), {E: 7.30-7.28(m), Z: 7.09-7.06 (m), 2H}, {E: 5.92 (t, J = 12.0 Hz), Z: 5.81 (t, J = 12.0 Hz), 1H}, {E: 4.37 (q, J = 8.0 Hz), Z: 3.99 (q, J = 8.0 Hz), 2H}, {E: 2.26-2.24(m), Z: 2.15-2.13(m), 3H}, {E: 1.37 (t, J = 8.0 Hz), Z: 1.20 (t, J = 8.0 Hz), 3H}. ¹³C NMR (100 MHz, CDCl₃): δ 163.6 (t, J = 34.0 Hz), 147.4(t, J = 8.0 Hz), 138.0, 131.6, 131.4, 131.2, 129.4, 129.1, 127.7, 122.9, 122.2, 119.6 (t, J = 27.0 Hz), 119.2, 112.0(t, J = 246.0 Hz), 62.8, 27.0, 13.7. ¹³F NMR (376 MHz, CDCl₃): δ -92.9 (d, J = 11.3 Hz), -97.8 (d, J = 11.3 Hz). HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₃H₁₃BrF₂NaO₂: 340.9965, found: 340.9970.

Ethyl (E)-4-(4-bromophenyl)-2,2-difluoropent-3-enoate

(5n)-E

Purification: Column chromatography (Cyclohexane/EtOAc = 40:1) isolated as a colorless oil (43% yield). E/Z: 90: 10.

¹H NMR (400 MHz, CDCl₃): δ 7.51-7.46(m, 2H), {E: 7.31-7.27 (m), Z: 7.09-7.07 (m), 2H}, {E: 5.92(t, J = 12.0 Hz), Z: 5.81(t, J = 12.0 Hz), 1H} {E: 4.37 (q, J = 8.0 Hz), Z: 3.99(q, J = 8.0 Hz),
2H}, {E: 2.26-2.24(m), Z: 2.15-2.13(m), 3H}, {E: 1.37 (t, J = 8.0 Hz), Z: 1.16 (t, J = 8.0 Hz), 3H}. 

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 164.1 (t, J = 35.0 Hz), 146.6(t, J = 7.0 Hz), 140.4, 131.6, 131.2, 129.1(t, J = 2.0 Hz), 127.7, 122.8, 122.2, 119.2 (t, J = 27.0 Hz), 112.8(t, J = 248.0 Hz), 63.1, 17.3, 13.9. 

$^{13}$F NMR (376 MHz, CDCl$_3$): $\delta$ -92.9 (d, J = 11.3 Hz), -97.8 (d, J = 11.3 Hz).

**Ethyl (Z)-2,2-difluoro-4-(4-(methylthio)phenyl)pent-3-enoate**

(5o)-Z

Purification: Column chromatography (Cyclohexane/EtOAc = 40:1) isolated as a colorless oil (77% yield). E/Z: 1: 99.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.22-7.20(m, 2H), 7.14-7.11(m, 2H), Z: 5.78 (dt, J = 12.0, 4.0 Hz), 1H), 3.93 (q, J = 8.0 Hz), 2H, 2.49(s, 3H), 2.15-2.13(m, 3H), 1.37 (t, J = 8.0 Hz). 

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.7 (t, J = 34.0 Hz), 148.1(t, J = 10.0 Hz), 138.8, 135.6, 128.0(t, J = 2.0 Hz), 125.8, 119.2 (t, J = 27.0 Hz), 112.3(t, J = 244.0 Hz), 62.87, 26.9, 115.5, 13.6. 

$^{13}$F NMR (376 MHz, CDCl$_3$): $\delta$ -91.9 (d, J = 11.3 Hz), -97.4 (d, J = 11.3 Hz). 

**ethyl (E)-2,2-difluoro-4-(4-(methylthio)phenyl)pent-3-enoate**

(5o)-E

Purification: Column chromatography (Cyclohexane/EtOAc = 40:1) isolated as a colorless oil (53% yield). E/Z: 80: 20.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ {E: 7.37-7.34(m), Z: 7.14-7.12(m), 2H}, 7.25-7.20(m, 2H), {E: 5.96(t, J = 12.0 Hz), Z: 5.79(t, J = 12.0 Hz), 1H} {E: 4.36 (q, J = 8.0 Hz), Z: 3.92(q, J = 8.0 Hz), 2H}, {E:2.50(s), Z: 2.49(s), 3H}, {E: 2.26-2.24(m), Z: 2.15-2.13(m), 3H}, {E: 1.37 (t, J = 8.0 Hz), Z: 1.17 (t, J = 8.0 Hz), 3H}. 

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 164.3 (t, J = 35.0 Hz), 148.1, 146.9(t, J = 7.0 Hz), 139.6, 138.8, 138.0, 135.6, 128.0(t, J = 2.0 Hz), 126.4, 126.1, 125.7, 119.2 (t, J = 28.0 Hz), 126.4(t, J = 26.0 Hz), 113.0(t, J = 246.0 Hz), 63.0, 17.1, 13.6. 

$^{13}$F NMR (376 MHz, CDCl$_3$): $\delta$ -91.9 (d, J = 11.3 Hz), -97.4 (d, J = 11.3 Hz). 

**ethyl (E)-2,2-difluoro-4-(thiophen-2-yl)but-3-enoate**

(3p)-E
Purification: Column chromatography (PE/Et$_2$O = 30:1) isolated as a pale yellow oil (36% yield). 

E/Z: 91:9.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39-7.21 (m, 3H), {E: 7.09-7.07 (m), Z: 6.94 (d, $J = 12.0$ Hz), 1H} {E: 6.17 (dt, $J = 16.0$, 12.0 Hz), Z: 5.78 (q, $J = 8.0$ Hz), 1H}, {E: 4.41 (q, $J = 8.0$ Hz), Z: 4.29 (q, $J = 8.0$ Hz), 2H}, {E: 1.43 (t, $J = 8.0$ Hz), Z: 1.30 (t, $J = 8.0$ Hz), 3H}. 

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.8 (t, $J = 34.0$ Hz), 129.8 (t, $J = 11.0$ Hz), 129.4, 127.3, 117.6 (t, $J = 25.0$ Hz), 112.4 (t, $J = 248.0$ Hz), 63.1, 13.9.

$^{13}$F NMR (376 MHz, CDCl$_3$): $\delta$ -96.37 (d, $J = 15.0$ Hz), -102.97 (d, $J = 11.3$ Hz). IR: $\nu$ (cm$^{-1}$) 2986, 1763, 1647, 1307, 1199, 1072, 906, 729.

ethyl 2,2-difluoro-4-phenylbut-3-ynoate

(7a)

Purification: Column chromatography (PE/Et$_2$O = 30:1) isolated as colorless oil (60% yield). 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55 (d, $J = 8.0$ Hz), 7.48-7.44 (m, 1H), 7.41-7.36 (m, 2H), 4.42 (q, $J = 8.0$ Hz), 1.41 (t, $J = 8.0$ Hz), 2.82 (q, $J = 8.0$ Hz), 1.41 (t, $J = 8.0$ Hz), 1.26 (t, $J = 8.0$ Hz).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.6 (t, $J = 35.0$ Hz), 147.8, 133.0, 130.7, 128.3, 125.8, 118.4, 105.0 (t, $J = 241.0$ Hz), 88.8 (t, $J = 7.0$ Hz), 81.6 (t, $J = 38.0$ Hz), 63.8, 27.5, 14.8, 13.9. 

$^{13}$F NMR (376 MHz, CDCl$_3$): $\delta$ -89.96. IR(neat): $\nu$ (cm$^{-1}$) 2245, 1770, 1273, 1145, 1080, 906, 729, 652. HRMS (ESI) (m/z): [M+Na]$^+$ calcd. for C$_{12}$H$_{10}$F$_2$NaO$_2$: 247.0547, found: 247.0541.

ethyl 4-(2-ethylphenyl)-2,2-difluorobut-3-ynoate

(7b)

Purification: Column chromatography (PE/Et$_2$O = 100:1) isolated as a colorless oil (35% yield).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.51 (d, $J = 8.0$ Hz), 7.41-7.36 (m, 1H), 7.26-7.18 (m, 2H), 4.42 (q, $J = 8.0$ Hz), 2.47 (s, 3H), 1.41 (t, $J = 8.0$ Hz).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.6 (t, $J = 35.0$ Hz), 147.8 (J = 2.0 Hz), 133.0 (J = 2.0 Hz), 130.7, 128.3, 125.8, 118.4, 105.0 (t, J = 241.0 Hz), 88.8 (t, J = 7.0 Hz), 81.6 (t, J = 38.0 Hz), 63.8, 27.5, 14.8, 13.9. 

$^{13}$F NMR (376 MHz, CDCl$_3$): $\delta$ -89.79. HRMS (ESI) (m/z): [M+Na]$^+$ calcd. for C$_{14}$H$_{14}$F$_2$NaO$_2$: 275.0860, found: 275.0850.

ethyl 2,2-difluoro-4-(o-tolyl)but-3-ynoate

(7c)

Purification: Column chromatography (PE/Et$_2$O = 50:1) isolated as a colorless oil (48% yield).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.52-7.49 (m, 1H), 7.37-7.33 (m, 1H), 7.26-7.18 (m, 2H), 4.42 (q, $J = 8.0$ Hz), 2.47 (s, 3H), 1.41 (t, $J = 8.0$ Hz).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.6 (t, $J = 35.0$ Hz), 141.7, 132.7 (t, J = 2.0 Hz), 130.5, 129.7, 125.8, 119.1 (t, J = 3.0 Hz), 105.0 (t, J = 242.0 Hz), 88.8 (t, J = 7.0 Hz), 82.1 (t, J = 38.0 Hz), 63.8, 20.4, 13.9. 

$^{13}$F NMR (376 MHz, CDCl$_3$): $\delta$ -89.70. IR(neat): $\nu$ (cm$^{-1}$) 2978, 2241, 1770, 1385, 1269, 1149, 1076, 902, 725. HRMS (ESI) (m/z): [M+Na]$^+$ calcd. for C$_{13}$H$_{12}$F$_2$NaO$_2$: 261.0703, found: 261.0706.
ethyl 2,2-difluoro-4-(m-tolyl)but-3-ynoate

(7d)

Purification: Column chromatography (PE/Et₂O = 30:1) isolated as colorless oil (54% yield).

\( ^1H \text{ NMR} \) (400 MHz, CDCl₃): \( \delta \) 7.37-7.34(m, 2H), 7.27-7.26(m, 2H), 4.42 (q, \( J = 8.0 \text{ Hz}, 2H \)), 2.36(s, 3H), 1.41 (t, \( J = 8.0 \text{ Hz}, 3H \)).

\( ^13C \text{ NMR} \) (100 MHz, CDCl₃): \( \delta \) 161.6(t, \( J = 34.0 \text{ Hz} \)), 138.4, 132.9, 131.4, 129.5(t, \( J = 2.0 \text{ Hz} \)), 128.4, 119.1, 104.9(t, \( J = 241.0 \text{ Hz} \)), 63.8, 21.1, 13.9. 

\( ^13F \text{ NMR} \) (376 MHz, CDCl₃): \( \delta \) -89.84. 

IR(neat): \( \nu \) (cm\(^{-1}\)) 2245, 1770, 1508, 1284, 1199, 1134, 1080, 906, 729, 648. 

HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₃H₁₂F₂NaO₂: 261.0703, found: 261.0700.

ethyl 2,2-difluoro-4-(o-tolyl)but-3-ynoate

(7e)

Purification: Column chromatography (PE/Et₂O = 50:1) isolated as a colorless oil (34% yield).

\( ^1H \text{ NMR} \) (400 MHz, CDCl₃): \( \delta \) 7.44 (d, \( J = 8.0 \text{ Hz}, 2H \)), 7.19 (d, \( J = 8.0 \text{ Hz}, 2H \)), 4.42 (q, \( J = 8.0 \text{ Hz}, 2H \)), 2.39(s, 3H), 1.41 (t, \( J = 8.0 \text{ Hz}, 3H \)).

\( ^13C \text{ NMR} \) (100 MHz, CDCl₃): \( \delta \) 141.0, 132.3, 129.3, 116.2, 90.0, 63.8, 29.7, 13.9.

\( ^13F \text{ NMR} \) (376 MHz, CDCl₃): \( \delta \) -89.68. 

IR(neat): \( \nu \) (cm\(^{-1}\)) 2978, 1770, 1381, 1145, 1080, 903, 725. 

HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₃H₁₂F₂NaO₂: 261.0703, found: 261.0704.

ethyl 2,2-difluoro-4-(4-methoxyphenyl)but-3-ynoate

(7f)

Purification: Column chromatography (cyclohexane/EtOAc = 30:1) isolated as colorless oil (47% yield).

\( ^1H \text{ NMR} \) (400 MHz, CDCl₃): \( \delta \) 7.49 (d, \( J = 8.0 \text{ Hz}, 2H \)), 6.89 (d, \( J = 8.0 \text{ Hz}, 2H \)), 4.42 (q, \( J = 8.0 \text{ Hz}, 2H \)), 1.41 (t, \( J = 8.0 \text{ Hz}, 3H \)).

\( ^13C \text{ NMR} \) (100 MHz, CDCl₃): \( \delta \) 161.7(t, \( J = 35.0 \text{ Hz} \)), 161.3, 134.1, 130.9, 128.8, 114.2, 111.2, 105.1(t, \( J = 241.0 \text{ Hz} \)), 90.1, 63.7, 55.4, 13.9.

\( ^13F \text{ NMR} \) (376 MHz, CDCl₃): \( \delta \) -89.40. 

HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₃H₁₂F₂NaO₃: 277.0652, found: 277.0647.

ethyl 2,2-difluoro-4-(4-(methylthio)phenyl)but-3-ynoate

(7g)

Purification: Column chromatography (n-hexane/EtOAc = 50:1) isolated as colorless oil (62% yield).

\( ^1H \text{ NMR} \) (400 MHz, CDCl₃): \( \delta \) 7.44 (d, \( J = 8.0 \text{ Hz}, 2H \)), 7.21 (d, \( J = 8.0 \text{ Hz}, 2H \)), 4.42 (q, \( J = 8.0 \text{ Hz}, 2H \)), 1.41 (t, \( J = 8.0 \text{ Hz}, 3H \)).

\( ^13C \text{ NMR} \) (100 MHz, CDCl₃): \( \delta \) 161.6, 142.7, 135.5, 125.4, 115.2(t, \( J = 3.0 \text{ Hz} \)), 109.9, 107.2, 105.0(t, \( J = 242.0 \text{ Hz} \)), 89.7, 63.8, 31.9, 15.0.

\( ^13F \text{ NMR} \) (376 MHz, CDCl₃): \( \delta \) -89.71. 

IR(neat): \( \nu \) (cm\(^{-1}\)) 2253, 902, 721, 648. 

HRMS (ESI) (m/z): [M+Na]⁺ calcd. for C₁₃H₁₂F₂NaO₂S: 293.0424, found: 293.0414.
ethyl 2,2-difluoro-4-(naphthalen-1-yl)but-3-ynoate
(7h)

Purification: Column chromatography (n-hexane/EtOAc = 50:1) isolated as colorless oil (39% yield).

$^1$H NMR (400 MHz, CDCl$_3$): \(\delta 8.26 (dd, J = 12.0, 4.0 \text{ Hz}, 1H), 7.96(d, J = 8.0 \text{ Hz}, 1H), 7.90(d, J = 8.0 \text{ Hz}, 1H), 7.81(d, J = 8.0 \text{ Hz}, 1H), 7.66-7.56(m, 2H), 7.50-7.46(m, 1H), 4.47 (q, J = 8.0 \text{ Hz}, 2H), 1.45 (t, J = 8.0 \text{ Hz}, 3H). 1^3$C NMR (100 MHz, CDCl$_3$): \(\delta 133.0, 132.2, 131.2, 128.5, 127.6, 126.9, 125.5, 123.3, 63.9, 13.9. 1^3$F NMR (376 MHz, CDCl$_3$): \(\delta -89.65. IR(\text{neat}): \nu (\text{cm}^{-1}) 2978, 2885, 2233, 1770, 1384, 1149, 906, 732. HRMS (ESI) (m/z): [M+Na]$^+$ calcd. for C$_{18}$H$_{12}$F$_2$NaO$_2$: 297.0703, found: 297.0713.

ethyl 4-(3,5-dimethylphenyl)-2,2-difluorobut-3-ynoate
(7i)

Purification: Column chromatography (cyclohexane/EtOAc = 50:1) isolated as colorless oil (46% yield).

$^1$H NMR (400 MHz, CDCl$_3$): \(\delta 7.18 (s, 2H), 7.08(s, 1H), 4.42(q, J = 8.0 \text{ Hz}, 2H), 2.32(s, 6H), 1.41 (t, J = 8.0 \text{ Hz}, 3H). 1^3$C NMR (100 MHz, CDCl$_3$): \(\delta 161.6, 138.2, 132.4, 130.9, 130.0, 128.8, 118.9, 104.9, 90.2, 63.8, 21.0, 13.9. 1^3$F NMR (376 MHz, CDCl$_3$): \(\delta -89.73. HRMS (ESI) (m/z): [M+Na]$^+$ calcd. for C$_{14}$H$_{14}$F$_2$NaO$_2$: 275.0860, found: 275.0850.

ethyl 4-(3,5-dichlorophenyl)-2,2-difluorobut-3-ynoate
(7j)

Purification: Column chromatography (cyclohexane /EtOAc = 100:1) isolated as colorless oil (28% yield).

$^1$H NMR (400 MHz, CDCl$_3$): \(\delta 7.46-7.44 (m, 3H), 4.43(q, J = 8.0 \text{ Hz}, 2H), 1.42 (t, J = 8.0 \text{ Hz}, 3H). 1^3$C NMR (100 MHz, CDCl$_3$): \(\delta 161.0(t, J = 34.0 \text{ Hz}), 135.4, 131.0, 130.5(t, J = 2.0 \text{ Hz}), 122.1, 104.5(t, J = 243.0 \text{ Hz}), 86.3, 80.2, 64.1, 13.9. 1^3$F NMR (376 MHz, CDCl$_3$): \(\delta -90.75. HRMS (ESI) (m/z): [M+Na]$^+$ calcd. for C$_{12}$H$_8$Cl$_2$F$_2$NaO$_2$: 314.9767, found: 314.9757.

ethyl 4-(4-ethoxy-3,3-difluoro-4-oxobut-1-yn-1-yl)benzoate
(7k)

Purification: Column chromatography (cyclohexane /EtOAc = 50:1) isolated as colorless oil (27% yield).
1H NMR (400 MHz, CDCl3): δ 8.06 (d, J = 8.0 Hz, 2H), 7.62(d, J = 8.0 Hz, 2H), 4.42(q, J = 8.0 Hz, 2H), 4.41 (q, J = 8.0 Hz, 2H), 1.45 (t, J = 8.0 Hz, 6H). 13C NMR (100 MHz, CDCl3): δ 165.6, 161.3(t, J = 34.0 Hz), 132.3(t, J = 3.0 Hz), 132.1, 129.6, 123.6, 104.7(t, J = 242.0 Hz), 88.4(t, J = 7.0 Hz), 80.5(t, J = 38.0 Hz), 64.0, 61.5, 14.3, 13.9. 13F NMR (376 MHz, CDCl3): δ -90.41. HRMS (ESI) (m/z): [M+Na]+ calcd. for C15H14F2NaO4: 319.0758, found: 319.0754.

ethyl 4-(4-acetylphenyl)-2,2-difluorobut-3-ynoate

(7l)

Purification: Column chromatography (cyclohexane/EtOAc = 50:1) isolated as colorless oil (17% yield).

1H NMR (400 MHz, CDCl3): δ 7.97 (d, J = 8.0 Hz, 2H), 7.65(d, J = 8.0 Hz, 2H), 4.43(q, J = 8.0 Hz, 2H), 2.63(s, 3H), 1.42 (t, J = 8.0 Hz, 6H). 13C NMR (100 MHz, CDCl3): δ 197.0, 161.3, 138.1, 130.9, 104.7(t, J = 242.0 Hz), 88.2(t, J = 7.0 Hz), 80.8, 64.0, 26.7, 13.9. 13F NMR (376 MHz, CDCl3): δ -90.45. HRMS (ESI) (m/z): [M+Na]+ calcd. for C14H12F2NaO3: 289.0652, found: 289.0649.

ethyl 2-(2,6-di-tert-butyl-4-methylphenoxy)-2,2-difluoroacetate

BHT-CF2CO2Et

Purification: Column chromatography (PE/Et2O = 30:1) isolated as a colorless oil (35% yield).

1H NMR (400 MHz, CDCl3): δ 6.55 (s, 2H), 4.16 (q, J = 8.0 Hz, 2H), 1.41 (s, 3H), 1.27 (t, J = 4.0 Hz, 3H), 1.23 (s, 18H). 13C NMR (100 MHz, CDCl3): δ 185.3, 162.6, 149.1, 137.6, 130.9, 128.8, 116.0. 13F NMR (376 MHz, CDCl3): δ -113.01. IR: ν (cm⁻¹) 2963, 1763, 1647, 1458, 1373, 1307, 1180, 1126, 1030, 906, 733. HRMS (ESI) (m/z): [M+Na]+ calcd. for C19H28F2NaO3: 365.1904, found: 365.1904.

VI: References

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VII: $^1$H NMR, $^{13}$C NMR spectra

3a
3e

\[
\text{Ph}^+ \text{C} = \text{CF}_2 \text{CO}_2 \text{Et}
\]

\[
\text{Ph}^+ \text{C} = \text{CF}_2 \text{CO}_2 \text{Et}
\]
5b-E
5c-Z

![Diagram of chemical structure and NMR spectrum]

- O\text{Bn} \quad \text{CF}_2\text{CO}_2\text{Et}

- NMR spectrum with peaks at various ppm values.
5e-Z

[Chemical structure image]

[1H NMR spectrum image]

[Chemical structure image]
5g-E
5j-Z

\[ \text{Me} \quad \begin{array}{c}
\text{F} \\
\text{CF}_2\text{CO}_2\text{Et}
\end{array} \]

\[ \text{Me} \quad \begin{array}{c}
\text{F} \\
\text{CF}_2\text{CO}_2\text{Et}
\end{array} \]
5m-Z
5m-E

\[ \text{Formula Image} \]

\[ \text{Diagram Image} \]
5n-Z
5n-E
7a
$7d$
