Supporting Information

Copper-catalyzed direct monofluoroalkenylation of C(sp^3)–H bonds via decarboxylation of α-fluoroacrylic acids

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I. General Information

a. Materials

All the reactions were carried out in oven-dried schlenk tubes under argon atmosphere (purity ≥99.999%). CuI (CAS: 7681-65-4), CuCl (CAS: 7447-39-4), CuBr (CAS: 7787-70-4) was purchased from Adamas. CuTc (CAS: 7681-65-4), CuBr₂ (CAS: 7789-45-9) was purchased from Energy-Chemical. Oxane (CAS: 142-68-7), 1,3-dioxolane (CAS: 646-06-0), 1,2-dimethoxyethane (CAS: 110-71-4) was purchased from Adamas. The following chemicals were purchased and used as received: THF (Adamas), 1,4-Dioxane (Energy Chemical) were stored over 4 Å molecular sieves under an argon atmosphere in a septum-capped bottle.

All the other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

b. Analytical Methods

¹H-NMR, ¹³C-NMR and ¹⁹F-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in Chloroform-d unless otherwise noted; Data for ¹H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ¹³C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak IC, AD, AS, KM columns were purchased from Daicel Chemical Industries, LTD. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).
II. Preparation of Substrates

a. Synthesis of Z/E mixture α-fluoroacrylic acids

Table S1.

2-fluoro-triethylphosphonoacetate (2.42 g, 10 mmol, 1.0 equiv) was dissolved in dry THF (50 mL) at ambient temperature. Triethylamine (2.8 mL, 20 mmol, 2.0 equiv) was added, followed by magnesium bromide (1.84 g, 10 mmol, 1.0 equiv). An exotherm is observed, and while the reaction was hot (ca. 50 °C), benzaldehyde (10 mmol, 1.0 equiv) was added. The reaction was stirred and monitored by TLC. Upon completion, the reaction was diluted with 50 mL diethyl ether, then filtered on a medium porosity fritted funnel. The filtrate was washed with saturated ammonium chloride solution, which was then extracted with ether (2 x
50 mL). The organic layers were combined, washed with brine, dried over magnesium sulfate, filtered and concentrated to give 1.95g of colorless oil, ethyl 2-fluoro-3-phenylacrylate as a mixture of olefin isomers. Spectral data for this compound matched literature, and it was carried to the next step without further purification\textsuperscript{1-3}.

To a stirred solution of ethyl 2-fluoro-3-phenylacrylate in EtOH (20 mL) was added 1 M aqueous NaOH (15 mL) and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated in vacuo. 50 mL water was added. The aqueous phase was acidified with 2 N HCl and extracted with ethyl acetate. The combined organic layers were dried over NaSO\textsubscript{4}. The volatile compounds were removed in vacuo to afford 2-fluoro-3-phenylacrylic acid.

\textbf{b. Synthesis of (Z)-\(\alpha\)-fluoroacrylic acids}

\[
\begin{align*}
\text{F} & \quad \text{CO} - \text{O} - \text{CH}_2 \text{CHO} \quad \text{Cs}_2\text{CO}_3 \quad \text{CH}_3\text{CN} \quad \text{NaOH} \quad \text{HCl} \quad \text{COOH} \\
\text{F} & \quad \text{CO} - \text{O} - \text{CH}_2 \text{CHO} \quad \text{Cs}_2\text{CO}_3 \quad \text{CH}_3\text{CN} \quad \text{NaOH} \quad \text{HCl} \quad \text{COOH} \\
& \quad \text{Z/E > 50:1}
\end{align*}
\]

The reaction mixture of fluorinated substrates (5.5 mmol), aldehyde (5 mmol), cesium carbonate (10 mmol) and CH\textsubscript{3}CN (15 mL) was stirred at 40 °C for the indicated time until complete consumption of the starting material, which was monitored by TLC analysis (6-12 h). The solvents were removed by rotary evaporation to provide raw products. The residue was then chromatographed on silica gel, affording the desired fluorooletins\textsuperscript{4}.

\textbf{c. Synthesis of (Z)-\(\beta\)-fluoroacrylic acid}

Ethyl phenylpropiolate (1 mmol, 1 equiv) was dissolved in 2 mL acetonitrile in a flame dried Schlenk tube, silver fluoride (2 mmol, 2 equiv) was added before the flask was wrapped in aluminium foil and heated at 80 °C for 24 h. The resulting mixture was filtered through a pad of celite and silica, eluted with EtOAc before being concentrated in vacuo and purified by column chromatography to yield a colourless oil\textsuperscript{5}.
References

### III. General Experimental Procedures

**Experimental Procedures for Examples Described in Table 1.**

In air, 2-fluoro-3-phenylacrylic acid (0.2 mmol), catalyst (10 mol%) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Tetrahydrofuran (1.5 mL), and peroxide (3 equiv) were added in turn by syringe. The resulting reaction mixture was stirred at the indicated temperature for 18 h. The yield was determined by GC using biphenyl as internal standard.

Table S2.

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### Supporting Information

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**Experimental Procedures for Examples Described (General Procedure).**

In air, CuBr (10 mol%), and fluoro acrylic acids (0.2 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Solvent (1.5 mL), and DTBP (110 μL, 3 equiv) were added in turn by syringe. The resulting reaction mixture was stirred at 100 °C for 18 h. The residue was then purified by flash chromatography with a mixture of petroleum ether (PE) and ethyl acetate (EtOAc). The E/Z ratios were determined by ¹H NMR and ¹⁹F NMR analyses.
IV. Mechanism experiments and proposed catalytic cycle

A. Control experiments

(1) 
\[ \text{C}_{6}\text{H}_{5}\text{COOH} + \overset{\text{CuBr, 10 mol\% DTBP, 3 equiv}}{\text{1 equiv TEMPO}} \overset{100^\circ C, \text{Ac}, 18 \text{ h}}{\rightleftharpoons} \text{3a, trace} + \text{3aa detected by HRMS} \]

(2) 
\[ \text{C}_{6}\text{H}_{5}\text{COOH} + \overset{\text{CuBr, 10 mol\% DTBP, 3 equiv}}{\text{1.1-dichloroethylene}} \overset{100^\circ C, \text{Ac}, 18 \text{ h}}{\rightleftharpoons} \text{3a, trace} + \text{3aa, 65\%} \]

(3) 
\[ \text{C}_{6}\text{H}_{5}\text{COOH} \overset{\text{CuBr, 10 mol\% DTBP, 3 equiv}}{\text{Ac}, 18 \text{ h}} \overset{100^\circ C, \text{Ac}, 18 \text{ h}}{\rightleftharpoons} \text{3a + [D]-3a, 70\% yield} \]
\[ \text{K}_{\text{p}} = 3.7:1 \]
\[ \text{Z/E > 30:1} \]

(4) 
\[ \text{C}_{6}\text{H}_{5}\text{COOH} + \overset{\text{CuBr, 10 mol\% DTBP, 3 equiv}}{\text{Ac}, 18 \text{ h}} \overset{100^\circ C, \text{Ac}, 18 \text{ h}}{\rightleftharpoons} \text{3a, 75\%} \]
\[ \text{Z/E > 30:1} \]

B. Proposed mechanism 1

Proposed mechanism 2
V. Substrate Scope, Spectral Data and NMR Spectra

(Z)-2-(1-fluoro-2-phenylvinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, 3a, 30.1 mg, 78%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.54 – 7.43 (m, 2H), 7.35 – 7.25 (m, 2H), 7.26 – 7.18 (m, 1H), 5.77 (d, $J$ = 39.4 Hz, 1H), 4.52 (ddd, $J$ = 14.2, 7.5, 5.4 Hz, 1H), 4.02 (dt, $J$ = 8.0, 6.4 Hz, 1H), 3.93 – 3.83 (m, 1H), 2.21 – 1.89 (m, 4H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 159.30 (d, $J$ = 269.1 Hz), 133.05 (d, $J$ = 2.6 Hz), 128.66 (d, $J$ = 7.2 Hz), 128.44, 127.20 (d, $J$ = 2.4 Hz), 106.06 (d, $J$ = 6.5 Hz), 77.05 (d, $J$ = 31.8 Hz), 69.03, 29.54, 25.81. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -117.84. HRMS (ESI) calcd for C$_{12}$H$_{14}$FO (M+H$^+$): 193.1023; found: 193.1027.
(Z)-2-(1-fluoro-2-(4-methoxyphenyl)vinyl)tetrahydrofuran
Following the general procedure (pale-yellow liquid, 3b, 35.0 mg, 79%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (15:1) as an eluent.

**$^1$H NMR** (400 MHz, Chloroform-d) $\delta$ 7.44 (d, $J = 8.8$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 5.70 (d, $J = 39.5$ Hz, 1H), 4.49 (ddd, $J = 15.5, 7.3, 5.6$ Hz, 1H), 4.00 (dt, $J = 8.0, 6.4$ Hz, 1H), 3.90 – 3.84 (m, 1H), 3.80 (s, 3H), 2.21 – 1.86 (m, 4H). **$^{13}$C NMR** (101 MHz, Chloroform-d) $\delta$ 158.65 (d, $J = 2.9$ Hz), 157.82 (d, $J = 266.6$ Hz), 129.95 (d, $J = 7.3$ Hz), 125.74 (d, $J = 2.6$ Hz), 113.86, 105.81 (d, $J = 6.9$ Hz), 77.25 (d, $J = 31.3$ Hz), 68.96, 55.24, 29.42, 25.88. **$^{19}$F NMR** (376 MHz, Chloroform-d) $\delta$ -121.10. **HRMS** (ESI) calcd for C$_{13}$H$_{16}$FO$_2$ (M+H$^+$): 223.1129; found: 223.1128.
(Z)-2-(1-fluoro-2-(2-methoxyphenyl)vinyl)tetrahydrofuran
Following the general procedure (pale-yellow liquid, 3c, 33.3 mg, 75%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent.

^1H NMR (400 MHz, Chloroform-d) δ 7.78 (dd, J = 7.8, 1.7 Hz, 1H), 7.23 – 7.17 (m, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.85 (dd, J = 8.3, 1.1 Hz, 1H), 6.19 (d, J = 40.3 Hz, 1H), 4.53 (ddd, J = 16.5, 7.4, 5.7 Hz, 1H), 4.02 (dt, J = 8.2, 6.5 Hz, 1H), 3.93 – 3.84 (m, 1H), 3.82 (s, 3H), 2.14 – 1.91 (m, 4H).

^13C NMR (101 MHz, Chloroform-d) δ 159.10 (d, J = 268.8 Hz), 156.18, 129.92 (d, J = 12.4 Hz), 128.41 (d, J = 1.8 Hz), 121.75 (d, J = 3.1 Hz), 120.56, 110.41, 100.05 (d, J = 5.1 Hz), 77.55 (d, J = 31.2 Hz), 69.00, 55.51, 29.42, 25.95. ^19F NMR (376 MHz, CDCl3) δ -120.15. HRMS (ESI) calcd for C_{13}H_{16}FO_{2} (M+H^+): 223.1129; found: 223.1126.
(Z)-2-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)tetrahydrofuran
Following the general procedure (pale-yellow liquid, 3d, 37.8 mg, 75%, Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (15:1) as an eluent. 

**1H NMR** (400 MHz, Chloroform-d) δ 7.14 (d, J = 1.8 Hz, 1H), 7.01 (dd, J = 8.3, 2.0 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 5.70 (d, J = 39.3 Hz, 1H), 4.49 (ddd, J = 15.6, 7.4, 5.6 Hz, 1H), 4.05 – 3.97 (m, 1H), 3.88 (d, J = 2.3 Hz, 7H), 2.18 – 1.92 (m, 4H). 

**13C NMR** (101 MHz, Chloroform-d) δ 157.98 (d, J = 266.8 Hz), 148.64, 148.25 (d, J = 2.8 Hz), 125.99 (d, J = 2.7 Hz), 121.59 (d, J = 6.4 Hz), 111.56 (d, J = 8.8 Hz), 110.92, 106.05 (d, J = 6.6 Hz), 77.21 (d, J = 31.4 Hz), 68.96, 55.82, 55.75, 29.42, 25.88. 

**19F NMR** (376 MHz, CDCl3) δ -120.72. 

**HRMS** (ESI) calcd for C\textsubscript{14}H\textsubscript{18}FO\textsubscript{3} (M+H\textsuperscript{+}): 253.1234; found: 253.1230.
(Z)-2-(1-fluoro-2-(3-phenoxyphenyl)vinyl)tetrahydrofuran
Supporting Information

Following the general procedure (pale-yellow liquid, 3e, 43.1 mg, 76%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.29 (m, 2H), 7.28 – 7.22 (m, 2H), 7.17 (t, $J = 1.9$ Hz, 1H), 7.09 (t, $J = 7.4$ Hz, 1H), 7.00 (d, $J = 7.9$ Hz, 2H), 6.88 (ddd, $J = 7.9$, 2.5, 1.3 Hz, 1H), 5.73 (d, $J = 38.8$ Hz, 1H), 4.49 (ddd, $J = 13.3$, 7.5, 5.3 Hz, 1H), 4.04 – 3.94 (m, 1H), 3.86 (q, $J = 7.3$ Hz, 1H), 2.16 – 1.88 (m, 4H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 159.87 (d, $J = 270.2$ Hz), 157.21, 134.76 (d, $J = 2.4$ Hz), 129.75, 129.69, 123.73 (d, $J = 7.2$ Hz), 123.22, 119.10 (d, $J = 7.6$ Hz), 118.83, 117.84 (d, $J = 2.0$ Hz), 105.55 (d, $J = 6.1$ Hz), 76.92 (d, $J = 31.9$ Hz), 69.05, 29.56, 25.78. $^{19}$F NMR (376 MHz, Chloroform-d) δ -116.27. HRMS (ESI) calcd for C$_{18}$H$_{18}$FO$_{2}$ (M+H$^+$): 285.1285; found: 285.1282.
(Z)-2-(2-(4-(allyloxy)phenyl)-1-fluorovinyl)tetrahydrofuran
Following the general procedure (pale-yellow liquid, 3f, 30.2 mg, 61%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (20:1) as an eluent. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.43 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 6.05 (ddt, $J = 17.2$, 10.5, 5.3 Hz, 1H), 5.70 (d, $J = 39.6$ Hz, 1H), 5.49 – 5.37 (m, 1H), 5.28 (dq, $J = 10.5$, 1.4 Hz, 1H), 4.58 – 4.44 (m, 3H), 4.00 (dt, $J = 8.3$, 6.4 Hz, 1H), 3.92 – 3.79 (m, 1H), 2.21 – 1.89 (m, 4H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 157.87 (d, $J = 266.5$ Hz), 157.66 (d, $J = 2.8$ Hz), 133.18, 129.92 (d, $J = 7.3$ Hz), 125.89 (d, $J = 2.6$ Hz), 117.75, 114.67, 105.77 (d, $J = 6.9$ Hz), 77.23 (d, $J = 31.1$ Hz), 68.96, 68.76, 29.42, 25.87. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -120.92. HRMS (ESI) calcd for C$_{15}$H$_{18}$FO$_2$ (M+H$^+$): 249.1285; found: 249.1286.
(Z)-2-(1-fluoro-2-(4-fluorophenyl)vinyl)tetrahydrofuran
Following the general procedure (pale-yellow liquid, 3g, 31.9 mg, 76%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.53 – 7.37 (m, 2H), 7.00 (t, $J$ = 8.8 Hz, 2H), 5.73 (d, $J$ = 39.0 Hz, 1H), 4.49 (ddd, $J$ = 14.4, 7.5, 5.4 Hz, 1H), 4.00 (dt, $J$ = 8.3, 6.5 Hz, 1H), 3.87 (dddd, $J$ = 8.1, 6.7, 5.8, 1.1 Hz, 1H), 2.21 – 1.89 (m, 4H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 161.73 (dd, $J$ = 247.1, 3.4 Hz), 159.01 (dd, $J$ = 268.4, 2.3 Hz), 130.29 (t, $J$ = 7.7 Hz), 129.17 (t, $J$ = 3.0 Hz), 115.35 (d, $J$ = 21.5 Hz), 105.04 (d, $J$ = 6.6 Hz), 76.97 (d, $J$ = 31.7 Hz), 69.02, 29.50, 25.81.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.71, -102.58.

HRMS (ESI) calcd for C$_{12}$H$_{13}$F$_2$O (M+H$^+$): 211.0929; found: 211.0927.
(Z)-2-(2-(3,4-difluorophenyl)-1-fluorovinyl)tetrahydrofuran
Following the general procedure (pale-yellow liquid, 3h, 31.0 mg, 68%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent.

^1^H NMR (400 MHz, Chloroform-d) δ 7.38 (ddd, J = 12.1, 7.7, 2.1 Hz, 1H), 7.20 – 7.00 (m, 2H), 5.71 (d, J = 38.2 Hz, 1H), 4.50 (ddd, J = 13.1, 7.7, 5.2 Hz, 1H), 4.01 (dt, J = 8.9, 6.4 Hz, 1H), 3.93 – 3.81 (m, 1H), 2.16 (ddt, J = 14.1, 11.3, 7.0 Hz, 1H), 2.09 – 1.89 (m, 3H). ^1^C NMR (101 MHz, Chloroform-d) δ 160.02 (dd, J = 270.0, 2.5 Hz), 150.12 (dd, J = 246.5, 12.6 Hz), 149.31 (ddd, J = 248.9, 12.5, 3.1 Hz), 130.07 (dt, J = 6.4, 3.2 Hz), 124.85 (td, J = 6.4, 3.5 Hz), 117.30 (dd, J = 18.3, 8.9 Hz), 117.11 (d, J = 17.2 Hz), 104.24 (dt, J = 6.0, 1.9 Hz), 76.72 (d, J = 32.0 Hz), 69.10, 29.57, 25.75. ^19^F NMR (376 MHz, Chloroform-d) δ -116.84, -137.94 (d, J = 21.4 Hz), -139.00 (d, J = 21.4 Hz). HRMS (ESI) calcd for C_{12}H_{12}F_{3}O (M+H^+): 229.0835; found: 229.0832.
(Z)-2-(2-(4-chlorophenyl)-1-fluorovinyl)tetrahydrofuran
Following the general procedure (pale-yellow liquid, 3i, 32.1 mg, 71%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.45 – 7.40 (m, 2H), 7.27 (dd, \(J = 6.5, 4.6\) Hz, 2H), 5.73 (d, \(J = 38.9\) Hz, 1H), 4.50 (ddd, \(J = 13.4, 7.5, 5.3\) Hz, 1H), 4.00 (dt, \(J = 8.3, 6.4\) Hz, 1H), 3.88 (dddd, \(J = 8.0, 6.7, 5.8, 1.1\) Hz, 1H), 2.19 – 1.88 (m, 4H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 159.84 (d, \(J = 269.8\) Hz), 132.77 (d, \(J = 3.4\) Hz), 131.53 (d, \(J = 2.6\) Hz), 129.88 (d, \(J = 7.5\) Hz), 128.61, 104.98 (d, \(J = 6.3\) Hz), 76.91 (d, \(J = 32.0\) Hz), 69.08, 29.56, 25.80. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -116.70.

HRMS (ESI) calcd for C\(_{12}\)H\(_{13}\)ClFO (M+H\(^+\)): 227.0633; found: 227.0638.
(Z)-2-(2-(3-bromophenyl)-1-fluorovinyl)tetrahydrofuran
Following the general procedure (pale-yellow liquid, 3j, 37.8 mg, 70%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.66 (d, \(J = 1.8\) Hz, 1H), 7.45 – 7.30 (m, 2H), 7.18 (t, \(J = 7.9\) Hz, 1H), 5.72 (d, \(J = 38.6\) Hz, 1H), 4.51 (ddd, \(J = 13.0, 7.6, 5.2\) Hz, 1H), 4.00 (q, \(J = 6.9\) Hz, 1H), 3.88 (q, \(J = 7.0\) Hz, 1H), 2.20 – 2.09 (m, 1H), 2.09 – 1.87 (m, 3H).

\(^13\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 160.47 (d, \(J = 271.0\) Hz), 135.08 (d, \(J = 2.6\) Hz), 131.41 (d, \(J = 8.1\) Hz), 130.11 (d, \(J = 2.2\) Hz), 129.92, 127.18 (d, \(J = 7.1\) Hz), 122.52, 104.68 (d, \(J = 6.1\) Hz), 76.76 (d, \(J = 32.0\) Hz), 69.10, 29.63, 25.74.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -103.17.

HRMS (ESI) calcd for C\(_{12}\)H\(_{13}\)BrFO (M+H\(^+\)): 271.0128; found: 271.0129.
Following the general procedure (pale-yellow liquid, 3k, 37.8 mg, 70%, Z/E > 30:1). The residue
was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent. $^1\text{H}$ NMR (400 MHz, Chloroform-$d$) $\delta$ 7.49 – 7.39 (m, 2H), 7.35 (d, $J = 8.6$ Hz, 2H), 5.72 (d, $J = 38.8$ Hz, 1H), 4.49 (ddd, $J = 13.3$, 7.5, 5.3 Hz, 1H), 4.06 – 3.95 (m, 1H), 3.94 – 3.80 (m, 1H), 2.14 (tt, $J = 11.3$, 7.0 Hz, 1H), 2.09 – 1.89 (m, 3H). $^{13}\text{C}$ NMR (101 MHz, Chloroform-$d$) $\delta$ 160.03 (d, $J =$ 270.2 Hz), 132.00 (d, $J = 2.8$ Hz), 131.57, 130.19 (d, $J = 7.3$ Hz), 120.96 (d, $J = 3.5$ Hz), 104.99 (d, $J = 6.4$ Hz), 76.90 (d, $J = 32.0$ Hz), 69.05, 29.56, 25.79. $^{19}\text{F}$ NMR (376 MHz, CDCl$_3$) $\delta$ -116.29. HRMS (ESI) calcd for C$_{12}$H$_{13}$BrFO (M+H$^+$): 271.0128; found: 271.0126.
Supporting Information

(Z)-2-(1-fluoro-2-(3-iodophenyl)vinyl)tetrahydrofuran

S30
Following the general procedure (pale-yellow liquid, 3l, 43.1 mg, 68%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.94 – 7.83 (m, 1H), 7.62 – 7.53 (m, 1H), 7.45 (dd, $J = 8.2, 3.6$ Hz, 1H), 7.05 (td, $J = 8.0, 3.7$ Hz, 1H), 5.69 (dd, $J = 38.7, 3.6$ Hz, 1H), 4.61 (ddt, $J = 12.7, 7.8, 4.5$ Hz, 1H), 4.00 (dq, $J = 9.5, 6.0, 4.4$ Hz, 1H), 3.89 (dd, $J = 8.8, 4.7$ Hz, 1H), 2.21 – 1.91 (m, 4H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 160.37 (d, $J = 270.9$ Hz), 137.35 (d, $J = 7.7$ Hz), 136.05 (d, $J = 2.1$ Hz), 135.17 (d, $J = 2.7$ Hz), 130.09, 127.77 (d, $J = 7.4$ Hz), 104.55 (d, $J = 6.2$ Hz), 94.40, 76.77 (d, $J = 32.0$ Hz), 69.10, 29.63, 25.75. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ -115.42. HRMS (ESI) calcd for C$_{12}$H$_{13}$FIO (M+H$^+$): 318.9990; found: 318.9992.
(Z)-2-(2-((1,1'-biphenyl)-4-yl)-1-fluorovinyl)tetrahydrofuran
Following the general procedure (pale-yellow solid, 3m, 41.2 mg, 77%, Z/E > 30:1, m.p. = 81-83 °C). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.57 (d, \(J = 7.3\) Hz, 6H), 7.42 (t, \(J = 7.6\) Hz, 2H), 7.32 (t, \(J = 7.3\) Hz, 1H), 5.81 (d, \(J = 39.3\) Hz, 1H), 4.52 (ddd, \(J = 13.6, 7.4, 5.5\) Hz, 1H), 4.06 – 3.95 (m, 1H), 3.88 (qd, \(J = 6.7, 6.2, 3.1\) Hz, 1H), 2.19 – 1.85 (m, 4H). \(^1^3\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 159.61 (d, \(J = 269.5\) Hz), 140.72, 139.89 (d, \(J = 2.2\) Hz), 132.18 (d, \(J = 2.8\) Hz), 129.12 (d, \(J = 7.2\) Hz), 128.82, 127.35, 127.13, 126.99, 105.75 (d, \(J = 6.5\) Hz), 77.11 (d, \(J = 31.9\) Hz), 69.06, 29.61, 25.85. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -117.21. HRMS (ESI) calcd for C\(_{36}\)H\(_{18}\)FO (M+H\(^+\)): 269.1336; found: 269.1333.
(Z)-2-(1-fluoro-2-(4-(trifluoromethyl)phenyl)vinyl)tetrahydrofuran
Following the general procedure (pale-yellow liquid, 3n, 35.4 mg, 68%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent.

\[ \text{\textsuperscript{1}H NMR} \text{ (400 MHz, Chloroform-}d\text{)} \delta 7.64 – 7.52 (m, 4H), 5.83 (d, \text{ } J = 38.6 \text{ Hz, } 1H), 4.54 \text{ (ddd, } J = 12.8, 7.6, 5.2 \text{ Hz, } 1H), 4.02 \text{ (dt, } J = 8.0, 6.3 \text{ Hz, } 1H), 3.94 – 3.84 \text{ (m, } 1H), 2.22 – 2.12 \text{ (m, } 1H), 2.09 – 1.92 \text{ (m, } 3H). \]

\[ \text{\textsuperscript{13}C NMR} \text{ (101 MHz, Chloroform-}d\text{)} \delta 161.24 \text{ (d, } J = 272.2 \text{ Hz), 136.60, 128.78, 128.70, 125.34 \text{ (q, } J = 3.8 \text{ Hz), 124.15 \text{ (q, } J = 271.8 \text{ Hz), 104.73 \text{ (d, } J = 5.8 \text{ Hz), 76.71 \text{ (d, } J = 32.2 \text{ Hz), 69.15, 29.67, 25.74. \text{ \textsuperscript{19}F NMR} \text{ (376 MHz, CDCl}_3\text{)} \delta -62.60, -114.08.} \]

\[ \text{HRMS} \text{ (ESI) \text{ calcd for } C_{13}H_{13}F_4O \text{ (M+H}\text{"}^+\text{): 261.0897; found: 261.0895.} \]
(Z)-2-(1-fluoro-2-(3-(trifluoromethoxy)phenyl)vinyl)tetrahydrofuran
Following the general procedure (pale-yellow liquid, 3o, 40.3 mg, 73%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent.

\[ ^1H \text{NMR (400 MHz, Chloroform-}d\text{)} \delta 7.43 - 7.30 (m, 3H), 7.08 (ddt, J = 8.0, 2.3, 1.2 Hz, 1H), 5.78 (d, J = 38.4 Hz, 1H), 4.52 (ddd, J = 12.8, 7.6, 5.2 Hz, 1H), 4.02 (dt, J = 7.9, 6.3 Hz, 1H), 3.94 - 3.82 (m, 1H), 2.17 (tdd, J = 11.1, 8.2, 5.7 Hz, 1H), 2.10 - 1.92 (m, 3H). \]

\[ ^13C \text{NMR (101 MHz, Chloroform-}d\text{)} \delta 160.69 (d, J = 271.1 Hz), 149.33, 134.99 (d, J = 2.4 Hz), 129.66, 126.98 (d, J = 6.8 Hz), 121.02 (d, J = 8.3 Hz), 120.48 (q, J = 257.2 Hz), 119.55, 104.73 (d, J = 5.9 Hz), 76.72 (d, J = 32.1 Hz), 69.11, 29.63, 25.73. \]

\[ ^19F \text{NMR (376 MHz, CDCl}_3\text{)} \delta -57.76, -114.93. \]

\[ \text{HRMS (ESI) calcd for C}_{13}\text{H}_{13}\text{F}_4\text{O}_2\text{ (M+H)}^+: 277.0846; found: 277.0851. \]
(Z)-2-(1-fluoro-2-(4-(methylthio)phenyl)vinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, 3p, 28.7 mg, 60%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.45 – 7.38 (m, 2H), 7.23 – 7.13 (m, 2H), 5.72 (d, $J$ = 39.3 Hz, 1H), 4.49 (ddd, $J$ = 14.6, 7.4, 5.5 Hz, 1H), 4.00 (dt, $J$ = 8.0, 6.4 Hz, 1H), 3.92 – 3.81 (m, 1H), 2.47 (s, 3H), 2.15 – 1.91 (m, 4H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 159.18 ($J$ = 268.7 Hz), 137.48 (d, $J$ = 2.7 Hz), 129.95 (d, $J$ = 2.6 Hz), 129.11 (d, $J$ = 7.4 Hz), 126.45, 105.73 (d, $J$ = 6.6 Hz), 77.17 (d, $J$ = 31.6 Hz), 69.09, 29.58, 25.92, 15.77. $^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -117.89. HRMS (ESI) calcd for C$_{13}$H$_{16}$FOS (M+H$^+$): 239.0900; found: 239.0903.
(Z)-3-(2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)benzonitrile
Following the general procedure (pale-yellow liquid, 3q, 24.3 mg, 56%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (15:1) as an eluent.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.80 (d, $J = 1.7$ Hz, 1H), 7.68 (dt, $J = 7.8$, 1.5 Hz, 1H), 7.51 (dt, $J = 7.7$, 1.4 Hz, 1H), 7.42 (t, $J = 7.8$ Hz, 1H), 5.80 (d, $J = 38.2$ Hz, 1H), 4.53 (ddd, $J = 12.4$, 7.7, 5.1 Hz, 1H), 4.02 (dt, $J = 8.4$, 6.4 Hz, 1H), 3.96–3.81 (m, 1H), 2.23–2.14 (m, 1H), 2.07–1.90 (m, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 161.52 (d, $J = 272.2$ Hz), 134.29 (d, $J = 2.3$ Hz), 132.73 (d, $J = 7.0$ Hz), 131.94 (d, $J = 8.1$ Hz), 130.44 (d, $J = 2.2$ Hz), 129.26, 118.80, 112.66, 103.92 (d, $J = 5.8$ Hz), 76.55 (d, $J = 32.3$ Hz), 69.16, 29.69, 25.70. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -113.55. HRMS (ESI) calcd for C$_{13}$H$_{13}$FNO (M+H$^+$): 218.0976; found: 218.0975.
(Z)-4-(2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)phenyl-4-methylbenzenesulfonate
Following the general procedure (pale-yellow solid, 3r, 48.5 mg, 67%, Z/E > 30:1, m.p. = 119-121 °C). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent.  

**1H NMR** (400 MHz, Chloroform-d) δ 7.69 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 5.72 (d, J = 38.8 Hz, 1H), 4.48 (ddd, J = 13.2, 7.5, 5.1 Hz, 1H), 3.98 (q, J = 7.0 Hz, 1H), 3.91 – 3.82 (m, 1H), 2.43 (s, 3H), 2.16 – 1.85 (m, 4H).  

**13C NMR** (101 MHz, Chloroform-d) δ 159.97 (d, J = 270.2 Hz), 148.30 (d, J = 3.3 Hz), 145.43, 132.22, 132.12 (d, J = 2.5 Hz), 129.78, 129.78 (d, J = 7.4 Hz), 128.51, 122.37, 104.77 (d, J = 6.1 Hz), 76.82 (d, J = 31.8 Hz), 69.06, 29.54, 25.76, 21.72.  

**19F NMR** (376 MHz, Chloroform-d) δ -116.70.  

**HRMS** (ESI) calcd for C19H20FO4S (M+H+) 363.1061; found: 363.1066.
(Z)-N-(4-(2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)phenyl)acetamide

Following the general procedure (pale-yellow liquid, 3s, 30.4 mg, 61%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (5:1) as an eluent.

\[ \text{\textsuperscript{1}H NMR (400 MHz, Chloroform-\text{d}) } \delta 8.20 (s, 1H), 7.48 (d, J = 8.8 \text{ Hz, } 2H), 7.40 (d, J = 8.8 \text{ Hz, } 2H), 5.70 (d, J = 39.3 \text{ Hz, } 1H), 4.49 (ddd, J = 15.7, 7.4, 5.6 \text{ Hz, } 1H), 4.00 (dt, J = 8.5, 6.5 \text{ Hz, } 1H), 3.94 – 3.80 (m, 1H), 2.17 – 2.09 (m, 4H), 2.09 – 1.93 (m, 3H). \text{\textsuperscript{13}C NMR (101 MHz, Chloroform-\text{d}) } \delta 168.95, 158.61 (d, J = 268.3 \text{ Hz}), 137.12 (d, J = 2.9 \text{ Hz}), 129.24 (d, J = 7.3 \text{ Hz}), 128.93 (d, J = 2.6 \text{ Hz}), 119.85, 105.92 (d, J = 6.6 \text{ Hz}), 77.23 (d, J = 31.0 \text{ Hz}), 69.02, 29.41, 25.90, 24.45. \text{\textsuperscript{19}F NMR (376 MHz, CDCl\text{\textsubscript{3}) } } \delta -119.20. \text{ HRMS (ESI) calcd for C}_{14}H_{17}FNO\text{\textsubscript{2}} (M+H\textsuperscript{+}): 250.1238; found: 250.1239. \]
(Z)-2-(1-fluoro-2-(4-(methylsulfonyl)phenyl)vinyl)tetrahydrofuran
Following the general procedure (pale-yellow liquid, 3t, 33.5 mg, 62%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (5:1) as an eluent. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.88 (d, $J = 8.3$ Hz, 2H), 7.67 (d, $J = 8.3$ Hz, 2H), 5.88 (d, $J = 38.3$ Hz, 1H), 4.55 (ddd, $J = 12.2$, 7.7, 5.1 Hz, 1H), 4.06 – 3.99 (m, 1H), 3.95 – 3.87 (m, 1H), 3.05 (s, 3H), 2.24 – 2.15 (m, 1H), 2.10 – 1.93 (m, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 162.38 (d, $J = 274.3$ Hz), 138.61 (dd, $J = 14.2$, 2.5 Hz), 129.27, 129.19, 127.54, 104.27 (d, $J = 5.7$ Hz), 76.58 (d, $J = 35.0$ Hz), 69.17, 44.53, 29.76, 25.69. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -111.67.

HRMS (ESI) calcd for C$_{13}$H$_{16}$FO$_3$S (M+H$^+$): 271.0799; found: 271.0797.
(Z)-2-(1-fluoro-2-(naphthalen-2-yl)vinyl)tetrahydrofuran
Following the general procedure (pale-yellow solid, 3u, 34.3 mg, 71%, Z/E > 30:1, m.p. = 50-53 °C). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.91 (d, $J = 1.6$ Hz, 1H), 7.77 (dd, $J = 9.3, 4.6$ Hz, 3H), 7.66 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.50 – 7.33 (m, 2H), 5.91 (d, $J = 39.3$ Hz, 1H), 4.54 (ddd, $J = 13.9, 7.5, 5.7$ Hz, 1H), 4.02 (dt, $J = 8.2, 6.5$ Hz, 1H), 3.88 (dddd, $J = 8.2, 6.9, 6.0, 1.0$ Hz, 1H), 2.20 – 1.88 (m, 4H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 159.70 (d, $J = 269.6$ Hz), 133.47, 132.52 (d, $J = 1.7$ Hz), 130.67 (d, $J = 2.9$ Hz), 128.10, 128.01, 127.78 (d, $J = 7.2$ Hz), 127.60, 126.68 (d, $J = 7.6$ Hz), 126.17, 126.00, 106.28 (d, $J = 6.3$ Hz), 77.18 (d, $J = 31.7$ Hz), 69.10, 29.62, 25.90. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -117.40. HRMS (ESI) calcd for C$_{16}$H$_{16}$FO (M+H$^+$): 243.1180; found: 243.1183.
Following the general procedure (pale-yellow liquid, 3v, 32.5 mg, 70%, Z/E > 30:1). The residue was purified by silica gel-columun chromato graphy using PE/EtOAc (25:1) as an eluent.

\( ^1H \) NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.77 (d, \( J = 1.2 \) Hz, 1H), 7.60 (d, \( J = 2.2 \) Hz, 1H), 7.44 (d, \( J = 1.6 \) Hz, 2H), 6.74 (d, \( J = 2.2 \) Hz, 1H), 5.85 (d, \( J = 39.2 \) Hz, 1H), 4.53 (ddd, \( J = 15.1, 7.4, 5.6 \) Hz, 1H), 4.13 – 3.99 (m, 1H), 3.95 – 3.89 (m, 1H), 2.18 – 1.88 (m, 4H).

\( ^13C \) NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 158.29 (d, \( J = 267.1 \) Hz), 154.03 (d, \( J = 2.8 \) Hz), 145.39, 127.91 (d, \( J = 2.7 \) Hz), 127.65, 125.39 (d, \( J = 6.6 \) Hz), 121.35 (d, \( J = 8.2 \) Hz), 111.26, 106.73, 106.32 (d, \( J = 6.5 \) Hz), 77.23 (d, \( J = 32.0 \) Hz), 69.03, 29.50, 25.88.

\( ^{19}F \) NMR (376 MHz, CDCl\( _3 \)) \( \delta \) -120.20.

HRMS (ESI) calcd for C\(_{14}\)H\(_{14}\)FO\(_2\) (M+H\(^+\)): 233.0972; found: 233.0975.
Supporting Information

(Z)-2-(1-fluoro-2-(thiophen-2-yl)vinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, 3w, 28.1 mg, 71%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.31 – 7.21 (m, 1H), 7.11 – 7.02 (m, 1H), 6.98 (ddd, $J = 5.3$, 3.6, 1.9 Hz, 1H), 6.09 (d, $J = 38.2$ Hz, 1H), 4.52 (ddd, $J = 13.6$, 7.5, 5.4 Hz, 1H), 3.99 (dt, $J = 8.0$, 6.3 Hz, 1H), 3.91 – 3.74 (m, 1H), 2.18 – 1.88 (m, 4H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 158.01 (d, $J = 268.1$ Hz), 135.17 (d, $J = 3.8$ Hz), 126.76 (d, $J = 3.7$ Hz), 126.71, 125.73 (d, $J = 8.8$ Hz), 100.87 (d, $J = 10.3$ Hz), 76.51 (d, $J = 30.5$ Hz), 69.02, 29.50, 25.80. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -114.74. HRMS (ESI) calcd for C$_{10}$H$_{12}$FO$_2$: 199.0587; found: 199.0588.
Supporting Information

(Z)-6-(2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)-2,3-dihydrobenzo[b][1,4]dioxide

Following the general procedure (pale-yellow liquid, 3x, 31.0 mg, 62%, Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (20:1) as an eluent. ^1H NMR (400 MHz, Chloroform-d) δ 7.07 (d, J = 2.1 Hz, 1H), 6.96 (dd, J = 8.4, 2.0 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 5.64 (d, J = 39.1 Hz, 1H), 4.47 (ddd, J = 15.2, 7.4, 5.5 Hz, 1H), 4.23 (s, 4H), 4.03 – 3.95 (m, 1H), 3.91 – 3.81 (m, 1H), 2.15 – 1.84 (m, 4H). ^13C NMR (101 MHz, Chloroform-d) δ 158.19 (d, J = 267.4 Hz), 143.25, 142.85 (d, J = 2.8 Hz), 126.59 (d, J = 2.4 Hz), 122.19 (d, J = 6.8 Hz), 117.42 (d, J = 7.9 Hz), 117.13, 105.67 (d, J = 6.6 Hz), 77.15 (d, J = 31.4 Hz), 68.95, 64.45, 64.30, 29.44, 25.84. ^19F NMR (376 MHz, Chloroform-d) δ -120.09. HRMS (ESI) calcd for C_{14}H_{16}FO_3 (M+H^+): 251.1078; found: 251.1076.
(Z)-2-(2-(3,4-dimethoxyphenyl)-1-fluorovinyl)-1,4-dioxane

Following the general procedure (pale-yellow solid, 4a, 36.5 mg, 68%, Z/E > 20:1, m.p. = 72-73 °C). The residue was purified by silica gel-column chromatography using PE/EtOAc (15:1) as an eluent. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.12 (d, $J = 1.9$ Hz, 1H), 7.02 (dd, $J = 8.4$, 2.0 Hz, 1H), 6.82 (d, $J = 8.4$ Hz, 1H), 5.76 (d, $J = 40.4$ Hz, 1H), 4.29 – 4.20 (m, 1H), 4.02 – 3.96 (m, 1H), 3.91 – 3.84 (m, 7H), 3.83 – 3.60 (m, 4H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 154.55 (d, $J = 263.0$ Hz), 148.66, 148.54 (d, $J = 2.9$ Hz), 125.37 (d, $J = 2.6$ Hz), 121.86 (d, $J = 6.5$ Hz), 111.68 (d, $J = 8.7$ Hz), 110.93, 107.69 (d, $J = 5.1$ Hz), 74.06 (d, $J = 32.1$ Hz), 68.96, 66.57, 66.33, 55.81, 55.75. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -118.33. HRMS (ESI) calcd for C$_{14}$H$_{18}$FO$_4$ (M+H$^+$): 269.1184; found: 269.1189.
(Z)-2-(2-(3-chloro-4-fluorophenyl)-1-fluorovinyl)-1,4-dioxane

Following the general procedure (pale-yellow liquid, 4b, 32.7 mg, 63%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent.

$^1$H NMR (400 MHz, Chloroform-$_d$) $\delta$ 7.56 (dd, $J$ = 7.1, 2.2 Hz, 1H), 7.34 (ddd, $J$ = 8.7, 4.7, 2.2 Hz, 1H), 7.09 (t, $J$ = 8.7 Hz, 1H), 5.76 (d, $J$ = 39.4 Hz, 1H), 4.26 (td, $J$ = 9.7, 2.9 Hz, 1H), 4.00 (dd, $J$ = 11.4, 2.8 Hz, 1H), 3.92 (dd, $J$ = 11.6, 2.8 Hz, 1H), 3.86 – 3.75 (m, 2H), 3.68 (td, $J$ = 11.2, 2.9 Hz, 1H), 3.58 (dd, $J$ = 11.5, 9.7 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 157.14 (dd, $J$ = 250.3, 3.3 Hz), 156.47 (dd, $J$ = 265.7, 2.5 Hz), 130.74 (d, $J$ = 8.2 Hz), 129.68 (dd, $J$ = 4.1, 2.3 Hz), 128.55 (t, $J$ = 7.2 Hz), 121.00 (d, $J$ = 17.9 Hz), 116.57 (d, $J$ = 21.2 Hz), 106.10 – 104.24 (m), 73.57 (d, $J$ = 33.0 Hz), 68.99, 66.57, 66.34. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -115.08, -116.10. HRMS (ESI) calcd for C$_{12}$H$_{12}$ClF$_2$O$_2$ (M+H$^+$): 261.0488; found: 261.0485.
(Z)-2-(2-(3-bromophenyl)-1-fluorovinyl)-1,4-dioxane

Following the general procedure (pale-yellow liquid, 4c, 38.3 mg, 67%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (20:1) as an eluent.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.66 (t, $J$ = 1.8 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.19 (t, $J$ = 7.9 Hz, 1H), 5.78 (d, $J$ = 39.7 Hz, 1H), 4.27 (td, $J$ = 9.6, 2.8 Hz, 1H), 4.03 – 3.97 (m, 1H), 3.94 – 3.86 (m, 1H), 4.03 – 3.88 (m, 1H), 3.86 – 3.74 (m, 2H), 3.68 (ddd, $J$ = 11.7, 10.7, 2.9 Hz, 1H), 3.58 (dd, $J$ = 11.5, 9.7 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 156.85 (d, $J$ = 266.7 Hz), 134.49 (d, $J$ = 2.3 Hz), 131.58 (d, $J$ = 8.0 Hz), 130.50 (d, $J$ = 2.3 Hz), 130.00, 127.35 (d, $J$ = 7.2 Hz), 122.57, 106.27 (d, $J$ = 4.5 Hz), 73.65 (d, $J$ = 33.0 Hz), 69.05, 66.59, 66.37. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -113.54. HRMS (ESI) calcd for C$_{12}$H$_{13}$BrFO$_2$ (M+H$^+$): 287.0077; found: 287.0083.
(Z)-2-(1-fluoro-2-(thiophen-2-yl)vinyl)-1,4-dioxane

Following the general procedure (pale-yellow liquid, 4d, 27.8 mg, 65%; Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (20:1) as an eluent. 1H NMR (400 MHz, Chloroform- d) δ 7.29 (d, J = 5.1 Hz, 1H), 7.09 (d, J = 3.6 Hz, 1H), 6.99 (ddd, J = 5.3, 3.6, 1.9 Hz, 1H), 6.16 (d, J = 39.1 Hz, 1H), 4.28 (td, J = 10.1, 2.8 Hz, 1H), 3.98 (ddd, J = 11.5, 2.8 Hz, 1H), 3.90 (dt, J = 11.6, 2.0 Hz, 1H), 3.84 – 3.73 (m, 2H), 3.71 – 3.65 (m, 1H), 3.61 (dd, J = 11.5, 9.6 Hz, 1H). 13C NMR (101 MHz, Chloroform-d) δ 154.40 (d, J = 263.8 Hz), 134.49 (d, J = 3.7 Hz), 127.38 (d, J = 4.0 Hz), 126.79, 126.30 (d, J = 8.9 Hz), 102.47 (d, J = 8.9 Hz), 73.42 (d, J = 31.2 Hz), 68.90, 66.52, 66.38. 19F NMR (376 MHz, CDCl3) δ -113.32. HRMS (ESI) calcd for C_{10}H_{12}FO_{2}S (M+H^+): 215.0537; found: 215.0532.
(Z)-2-(1-fluoro-2-(4-methoxyphenyl)vinyl)-1,4-dioxane

Following the general procedure (pale-yellow liquid, 4e, 32.4 mg, 68%, Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (20:1) as an eluent.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.44 (d, $J = 8.9$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 5.76 (d, $J = 40.5$ Hz, 1H), 4.24 (ddd, $J = 12.2$, 9.7, 2.8 Hz, 1H), 4.01 – 3.81 (m, 3H), 3.80 (s, 3H), 3.78 – 3.59 (m, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 158.93 (d, $J = 2.9$ Hz), 154.41 (d, $J = 262.7$ Hz), 130.17 (d, $J = 7.4$ Hz), 125.12 (d, $J = 2.6$ Hz), 113.91, 107.46 (d, $J = 5.5$ Hz), 74.15 (d, $J = 31.9$ Hz), 69.00, 66.62, 66.35, 55.24. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -118.68. HRMS (ESI) calcd for C$_{13}$H$_{16}$FO$_3$ (M+H$^+$): 239.1078; found: 239.1073.
Following the general procedure (pale-yellow liquid, 4f, 32.2 mg, 72%, Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.46 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 5.65 (d, $J = 39.4$ Hz, 1H), 3.95 (dq, $J = 19.3$, 6.5 Hz, 1H), 3.81 (s, 3H), 3.70–3.59 (m, 1H), 3.51–3.40 (m, 1H), 1.42 (d, $J = 6.5$ Hz, 3H), 1.23 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 158.73 (d, $J = 3.0$ Hz), 157.90 (d, $J = 270.0$ Hz), 129.98 (d, $J = 7.4$ Hz), 125.60 (d, $J = 2.6$ Hz), 113.90, 106.44 (d, $J = 7.1$ Hz), 74.61 (d, $J = 28.8$ Hz), 64.26, 55.27, 19.00, 15.35. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -120.92. HRMS (ESI) calcd for C$_{13}$H$_{18}$FO$_2$ (M+H$^+$): 225.1285; found: 225.1280.
Following the general procedure (pale-yellow liquid, 4g, 36.6 mg, 73%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.44 (d, J = 7.4 Hz, 2H), 7.26 (t, J = 7.6 Hz, 2H), 7.21 – 7.13 (m, 1H), 5.62 (d, J = 39.3 Hz, 1H), 3.67 (dt, J = 18.7, 6.7 Hz, 1H), 3.55 (dt, J = 9.3, 6.6 Hz, 1H), 3.29 (dt, J = 9.3, 6.6 Hz, 1H), 1.65 (q, J = 7.5 Hz, 2H), 1.51 (dq, J = 8.7, 6.6 Hz, 2H), 1.44 – 1.26 (m, 4H), 0.95 – 0.78 (m, 6H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 157.88 (d, J = 273.2 Hz), 132.02 (d, J = 2.8 Hz), 127.63 (d, J = 7.6 Hz), 127.45, 126.21 (d, J = 2.2 Hz), 106.37 (d, J = 6.5 Hz), 77.88 (d, J = 28.3 Hz), 68.07, 34.15, 30.88, 18.34, 17.73, 12.86. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -116.79. HRMS (ESI) calcd for C$_{16}$H$_{24}$FO (M+H$^+$): 251.1806; found: 251.1809.
Following the general procedure (pale-yellow liquid, 4h, 38.3 mg, 72%, Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent.

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.15 (d, $J = 2.1$ Hz, 1H), 7.01 (dd, $J = 8.4$, 2.0 Hz, 1H), 6.82 (d, $J = 8.4$ Hz, 1H), 5.71 (d, $J = 40.1$ Hz, 1H), 4.14 – 4.08 (m, 1H), 4.00 – 3.95 (m, 1H), 3.88 (d, $J = 1.0$ Hz, 6H), 3.55 (td, $J = 11.6$, 2.3 Hz, 1H), 1.98 – 1.85 (m, 2H), 1.70 – 1.52 (m, 4H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 158.07 (d, $J = 264.2$ Hz), 148.58, 148.20 (d, $J = 2.9$ Hz), 125.98 (d, $J = 2.5$ Hz), 121.65 (d, $J = 6.4$ Hz), 111.62 (d, $J = 8.9$ Hz), 110.86, 105.68 (d, $J = 6.1$ Hz), 76.28 (d, $J = 31.3$ Hz), 68.77, 55.82, 55.75, 29.14, 25.68, 23.04. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -117.91. HRMS (ESI) calcd for C$_{15}$H$_{20}$FO$_3$ (M+H$^+$): 267.1391; found: 267.1396.
(Z)-2-(1-fluoro-2-phenylvinyl)-1,3-dioxolane

Following the general procedure (pale-yellow liquid, 4i, 21.7 mg, 56%, Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (20:1) as an eluent.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.56 – 7.49 (m, 2H), 7.34 (dd, $J = 8.3$, 6.6 Hz, 2H), 7.30 – 7.25 (m, 1H), 5.91 (d, $J = 38.0$ Hz, 1H), 5.50 (d, $J = 12.1$ Hz, 1H), 4.16 – 4.06 (m, 2H), 4.06 – 3.90 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 154.71 (d, $J = 272.1$ Hz), 132.08 (d, $J = 3.0$ Hz), 129.07 (d, $J = 7.2$ Hz), 128.55, 127.98 (d, $J = 2.3$ Hz), 108.98 (d, $J = 4.8$ Hz), 100.33 (d, $J = 31.3$ Hz), 65.52. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -124.46. HRMS (ESI) calcd for $C_{11}H_{12}FO_2$ (M+H$^+$): 195.0816; found: 195.0821.
Following the general procedure (pale-yellow liquid, 4j, 17.7 mg, 42%, Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (20:1) as an eluent. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.55 – 7.50 (m, 2H), 7.34 (dd, $J = 8.4$, 6.8 Hz, 2H), 7.26 (d, $J = 7.3$ Hz, 1H), 5.81 (d, $J = 39.5$ Hz, 1H), 3.94 (ddd, $J = 17.3$, 6.7, 4.7 Hz, 1H), 3.63 (dd, $J = 5.8$, 3.7 Hz, 2H), 3.46 (s, 3H), 3.42 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 155.72 (d, $J = 272.2$ Hz), 132.58 (d, $J = 2.8$ Hz), 128.82 (d, $J = 7.4$ Hz), 128.53, 127.60 (d, $J = 2.6$ Hz), 109.10 (d, $J = 5.4$ Hz), 79.95 (d, $J = 28.4$ Hz), 73.10, 59.40, 57.34. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -116.72. HRMS (ESI) calcd for C$_{12}$H$_{16}$FO$_2$ (M+H$^+$): 211.1129; found: 211.1135.
(Z)-(2-cyclohexyl-2-fluorovinyl)benzene

Following the general procedure (pale-yellow liquid, 4k, 27.2 mg, 67%, Z/E = 17:1). The residue was purified by silica gel-column chromatography using PE as an eluent. $^1\text{H NMR}$ (400 MHz, Chloroform-$d$) $\delta$ 7.52 (d, $J = 7.5$ Hz, 2H), 7.35 (t, $J = 7.7$ Hz, 2H), 7.24 (t, $J = 7.5$ Hz, 1H), 5.48 (d, $J = 40.7$ Hz, 1H), 2.28 (ddt, $J = 15.3, 7.6, 3.7$ Hz, 1H), 2.05 – 1.97 (m, 2H), 1.86 (dt, $J = 6.6, 3.0$ Hz, 2H), 1.80 – 1.73 (m, 1H), 1.44 – 1.24 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-$d$) $\delta$ 165.17 (d, $J = 268.0$ Hz), 134.07 (d, $J = 2.2$ Hz), 128.38, 128.38 (d, $J = 7.4$ Hz), 126.53 (d, $J = 2.3$ Hz), 103.58 (d, $J = 9.0$ Hz), 41.60 (d, $J = 24.6$ Hz), 30.09 (d, $J = 2.2$ Hz), 26.00, 25.94. $^{19}\text{F NMR}$ (376 MHz, CDCl3) $\delta$ -105.20. Spectral data match the reported literature values.
Following the general procedure (pale-yellow liquid, 4l, 21.5mg, 51%, Z/E = 11:1). The residue was purified by silica gel-column chromatography using PE as an eluent. $^1$H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.49 (m, 2H), 7.43 – 7.32 (m, 7H), 7.28 – 7.22 (m, 1H), 5.57 (d, $J = 38.7$ Hz, 1H), 3.70 (d, $J = 17.0$ Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 159.54 (d, $J = 267.3$ Hz), 136.22 (d, $J = 1.8$ Hz), 133.59 (d, $J = 2.8$ Hz), 129.01, 128.68, 128.44, 128.42 (d, $J = 7.4$ Hz), 127.01, 126.94 (d, $J = 2.4$ Hz), 107.35 (d, $J = 8.2$ Hz), 39.65 (d, $J = 28.0$ Hz). $^{19}$F NMR (376 MHz, CDCl3) δ -100.06. Spectral data match the reported literature values (Org. Lett., 2019, 21, 5645–5649)
(Z)-2-(1-fluoro-2-phenylvinyl)-1,4-oxathiane

Following the general procedure (pale-yellow liquid, 4m, 16.5 mg, 37%, Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (20:1) as an eluent. 

$^1$H NMR (400 MHz, Chloroform-d) δ 7.61 – 7.48 (m, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.31 – 7.19 (m, 1H), 5.93 (d, $J = 39.7$ Hz, 1H), 4.31 – 4.19 (m, 1H), 4.11 – 3.98 (m, 2H), 3.93 (ddd, $J = 11.7$, 7.2, 2.8 Hz, 1H), 3.64 – 3.51 (m, 1H), 2.91 – 2.82 (m, 1H), 2.78 – 2.68 (m, 1H). 

$^{13}$C NMR (101 MHz, Chloroform-d) δ 156.76 (d, $J = 266.5$ Hz), 132.88 (d, $J = 2.8$ Hz), 128.79 (d, $J = 7.5$ Hz), 128.49, 127.46 (d, $J = 2.4$ Hz), 108.50 (d, $J = 7.4$ Hz), 70.53 (d, $J = 3.2$ Hz), 68.37, 39.86 (d, $J = 27.1$ Hz), 25.99. 

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -104.66. 

HRMS (ESI) calcd for C$_{12}$H$_{14}$FOS (M+H$^+$): 225.0744; found: 225.0740.
(Z)-2-(1-fluoro-4-methylpenta-1,3-dien-1-yl)-1,4-dioxane

Following the general procedure (pale-yellow liquid, 5a, 21.6 mg, 58%, Z/E = 3:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (20:1) as an eluent. $^1$H NMR (400 MHz, Chloroform- $d$) $\delta$ 6.21 – 5.97 (m, 1H), 5.91 – 5.63 (m, 1H), 4.53 (ddd, $J$ = 23.3, 8.9, 4.2 Hz, 0.25H), 4.16 (ddd, $J$ = 12.5, 9.7, 2.8 Hz, 0.75H), 3.94 – 3.82 (m, 2H), 3.81 – 3.54 (m, 4H), 1.81 (d, $J$ = 1.5 Hz, 3H), 1.73 (d, $J$ = 10.1 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform- $d$) $\delta$ 153.86 (d, $J$ = 259.8 Hz), 137.18 (d, $J$ = 4.1 Hz), 115.20 (d, $J$ = 5.0 Hz), 105.31 (d, $J$ = 8.5 Hz), 73.89 (d, $J$ = 31.2 Hz), 68.88, 66.55, 66.31, 26.16, 18.44. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -121.25, -122.28. HRMS (ESI) calcd for C$_{10}$H$_{16}$FO$_2$ (M+H$^+$): 187.1129; found: 187.1126.
Supporting Information

(Z)-2-(2-fluoro-2-phenylvinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, 6a, 24.3 mg, 63%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent. 

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.47 – 7.37 (m, 2H), 7.33 – 7.24 (m, 3H), 5.43 (dd, $J = 37.0, 8.2$ Hz, 1H), 4.83 (q, $J = 7.5$ Hz, 1H), 3.91 – 3.82 (m, 1H), 3.74 (td, $J = 8.0, 6.1$ Hz, 1H), 2.17 – 2.07 (m, 1H), 1.98 – 1.82 (m, 2H), 1.60 (dq, $J = 12.2, 8.1$ Hz, 1H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) δ 157.59 (d, $J = 250.8$ Hz), 131.98 (d, $J = 28.5$ Hz), 129.08, 128.46 (d, $J = 1.8$ Hz), 124.35 (d, $J = 7.3$ Hz), 107.50 (d, $J = 13.8$ Hz), 72.86 (d, $J = 6.0$ Hz), 67.95, 32.70, 26.11.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -117.89. 

HRMS (ESI) calcd for C$_{12}$H$_{14}$FO (M+H$^+$): 193.1023; found: 193.1021.
(Z)-2-(2-fluoro-2-(4-fluorophenyl)vinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, 6b, 27.3 mg, 65%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.57 – 7.46 (m, 2H), 7.07 (t, $J$ = 8.6 Hz, 2H), 5.45 (dd, $J$ = 36.8, 8.2 Hz, 1H), 4.91 (q, $J$ = 7.6 Hz, 1H), 3.97 (q, $J$ = 7.3 Hz, 1H), 3.88 – 3.79 (m, 1H), 2.26 – 2.14 (m, 1H), 2.05 – 1.92 (m, 2H), 1.74 – 1.64 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 163.15 (d, $J$ = 249.1 Hz), 156.82 (d, $J$ = 250.5 Hz), 128.19 (dd, $J$ = 29.2, 3.4 Hz), 126.32 (dd, $J$ = 8.2, 7.3 Hz), 115.52 (dd, $J$ = 22.0, 1.8 Hz), 107.27 (dd, $J$ = 14.3, 1.9 Hz), 72.75 (d, $J$ = 6.2 Hz), 67.94, 32.66 (d, $J$ = 1.6 Hz), 26.10. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -113.64, -118.83. HRMS (ESI) calcd for C$_{12}$H$_{13}$F$_2$O (M+H$^+$): 211.0929; found: 211.0926.
(Z)-2-(2-(4-chlorophenyl)-2-fluorovinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, 6c, 29.8 mg, 66%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent. \textsuperscript{1}H NMR (400 MHz, Chloroform-\textit{d}) \(\delta\) 7.46 (d, \(J = 8.6\ \text{Hz},\ 2\text{H}\)), 7.35 (d, \(J = 8.4\ \text{Hz},\ 2\text{H}\)), 5.51 (dd, \(J = 36.8, 8.2\ \text{Hz},\ 1\text{H}\)), 4.96 – 4.83 (m, 1H), 4.02 – 3.93 (m, 1H), 3.84 (td, \(J = 8.0, 6.1\ \text{Hz},\ 1\text{H}\)), 2.29 – 2.15 (m, 1H), 2.08 – 1.94 (m, 2H), 1.74 – 1.63 (m, 1H). \textsuperscript{13}C NMR (101 MHz, Chloroform-\textit{d}) \(\delta\) 156.62 (d, \(J = 250.4\ \text{Hz}\)), 134.98, 130.45 (d, \(J = 29.2\ \text{Hz}\)), 128.70 (d, \(J = 2.0\ \text{Hz}\)), 125.63 (d, \(J = 7.1\ \text{Hz}\)), 108.10 (d, \(J = 14.2\ \text{Hz}\)), 72.72 (d, \(J = 6.0\ \text{Hz}\)), 67.97, 32.64 (d, \(J = 1.6\ \text{Hz}\)), 26.10.

HRMS (ESI) calcd for C\textsubscript{12}H\textsubscript{13}ClFO (M+H\textsuperscript{+}): 227.0633; found: 227.0631.
(Z)-2-(2-(4-bromophenyl)-2-fluorovinyl)tetrahydrofuran

Following the general procedure (pale-yellow liquid, 6d, 33.5 mg, 62%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (25:1) as an eluent. 

\( ^1H \) NMR (400 MHz, Chloroform-\( \text{d} \)) \( \delta \) 7.50 (d, \( J = 8.4 \) Hz, 2H), 7.40 (d, \( J = 8.6 \) Hz, 2H), 5.53 (dd, \( J = 36.8, 8.2 \) Hz, 1H), 4.90 (q, \( J = 7.5 \) Hz, 1H), 4.03–3.91 (m, 1H), 3.84 (td, \( J = 8.0, 6.1 \) Hz, 1H), 2.28–2.18 (m, 1H), 2.09–1.94 (m, 2H), 1.78–1.58 (m, 1H). 

\( ^{13}C \) NMR (101 MHz, Chloroform-\( \text{d} \)) \( \delta \) 156.66 (d, \( J = 250.4 \) Hz), 131.66 (d, \( J = 2.1 \) Hz), 130.90 (d, \( J = 29.1 \) Hz), 125.87 (d, \( J = 7.1 \) Hz), 123.21, 108.22 (d, \( J = 14.2 \) Hz), 72.72 (d, \( J = 6.1 \) Hz), 67.99, 32.62 (d, \( J = 1.4 \) Hz), 26.11. 

\( ^19F \) NMR (376 MHz, CDCl\( _3 \)) \( \delta \) -119.96. 

HRMS (ESI) calcd for C\(_{12}\)H\(_{13}\)BrFO (M+H\(^+\)): 271.0122; found: 271.0122.
Following the general procedure (pale-yellow liquid, 6e, 28.8 mg, 65%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE as an eluent. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.48 (dd, $J = 8.7, 5.4$ Hz, 2H), 7.05 (t, $J = 8.6$ Hz, 2H), 5.21 (dd, $J = 38.1, 9.2$ Hz, 1H), 2.69 – 2.58 (m, 1H), 1.78 (td, $J = 14.4, 3.5$ Hz, 5H), 1.40 – 1.13 (m, 5H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 162.69 (d, $J = 247.8$ Hz), 154.64 (d, $J = 245.1$ Hz), 129.16 (dd, $J = 30.2, 3.3$ Hz), 125.75 (dd, $J = 8.0, 7.1$ Hz), 115.34 (dd, $J = 21.8, 1.8$ Hz), 111.79 (dd, $J = 17.3, 1.8$ Hz), 33.80 (d, $J = 3.8$ Hz), 33.16 (d, $J = 1.5$ Hz), 26.01, 25.85. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -113.31, -120.75. HRMS (ESI) calcd for C$_{14}$H$_{17}$F$_2$ (M+H$^+$): 223.1293; found: 223.1288.
(8R,9S,13S,14S)-2-((Z)-2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)-3-methoxy-13-methyl-6, 7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one

Following the general procedure (pale-yellow liquid, 7a, 46.2 mg, 58%, Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.72 (s, 1H), 6.58 (s, 1H), 6.13 (d, $J = 40.4$ Hz, 1H), 4.51 (ddd, $J = 17.7, 7.3, 5.7$ Hz, 1H), 4.01 (q, $J = 6.7$ Hz, 1H), 3.88 (td, $J = 7.7, 5.4$ Hz, 1H), 3.79 (s, 3H), 2.93 – 2.87 (m, 2H), 2.55 – 2.41 (m, 2H), 2.27 – 2.23 (m, 1H), 2.17 – 1.94 (m, 9H), 1.63 – 1.52 (m, 3H), 1.49 – 1.40 (m, 2H), 0.90 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 158.56 (d, $J = 270.5$ Hz), 154.31, 136.91 (d, $J = 1.6$ Hz), 131.66, 126.94 (d, $J = 12.7$ Hz), 119.24 (d, $J = 3.2$ Hz), 110.72, 100.27 (d, $J = 5.1$ Hz), 77.67 (d, $J = 32.7$ Hz), 68.99, 55.59, 50.39, 48.06, 43.98 (d, $J = 3.7$ Hz), 38.39, 35.92, 31.56, 29.80, 29.36, 26.56, 26.03, 25.94, 21.61, 13.87. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -125.35. HRMS (APCI) calc'd for C$_{25}$H$_{32}$FO$_3$ (M+H$^+$): 399.2330; found: 399.2335.
(2R)-6-((4-(Z)-2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)benzyl)oxy)-2,5,7,8-tetramethyl-2-[(4R,8R)-4,8,12-trimethyltridecyl]chromane.

Following the general procedure (pale-yellow liquid, 7c, 86.1 mg, 68%, Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. 

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.58 (d, $J = 8.1$ Hz, 2H), 7.50 (d, $J = 8.0$ Hz, 2H), 5.85 (d, $J = 39.3$ Hz, 1H), 4.73 (s, 2H), 4.57 (ddd, $J = 13.6$, 7.4, 5.5 Hz, 1H), 4.07 (q, $J = 6.8$ Hz, 1H), 3.94 (q, $J = 7.1$ Hz, 1H), 2.64 (t, $J = 6.8$ Hz, 2H), 2.26 (s, 3H), 2.21 (s, 3H), 2.16 (s, 3H), 2.13 – 1.97 (m, 3H), 1.92 – 1.79 (m, 2H), 1.64 – 1.56 (m, 3H), 1.52 – 1.25 (m, 16H), 1.22 – 1.08 (m, 6H), 0.99 – 0.87 (m, 12H). 

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 159.40 (d, $J = 269.0$ Hz), 148.17, 147.94, 137.03 (d, $J = 2.2$ Hz), 132.57 (d, $J = 2.6$ Hz), 128.76 (d, $J = 7.2$ Hz), 127.95, 127.79, 125.97, 122.95, 117.61, 105.90 (d, $J = 6.4$ Hz), 77.11 (d, $J = 31.9$ Hz), 74.84, 74.48, 69.03, 40.07, 39.42, 37.53, 37.51, 37.47, 37.34, 32.85, 32.75, 31.38, 29.57, 28.03, 25.86, 24.86, 24.50, 23.93, 22.77, 22.68, 21.08, 20.73, 19.81, 19.72, 12.92, 12.05, 11.87. 

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -119.43.
HRMS (APCI) calcd for $\text{C}_{42}\text{H}_{64}\text{FO}_3$ (M+H$^+$): 635.4834; found: 635.4829.
(Z)-N-(4-(2-fluoro-2-(tetrahydrofuran-2-yl)vinyl)phenyl)-2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetamide

Following the general procedure (pale-yellow liquid, 7b, 55.7 mg, 61%, Z/E = 9:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (2:1) as an eluent. 

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.17 (d, $J = 2.3$ Hz, 1H), 7.92 – 7.84 (m, 2H), 7.56 (td, $J = 7.5, 1.4$ Hz, 1H), 7.52 – 7.33 (m, 7H), 7.04 (d, $J = 8.4$ Hz, 1H), 5.69 (d, $J = 39.3$ Hz, 1H), 5.17 (s, 2H), 4.49 (ddd, $J = 15.1, 7.3, 5.5$ Hz, 1H), 4.00 (q, $J = 6.9$ Hz, 1H), 3.88 (q, $J = 7.1$ Hz, 1H), 3.71 (s, 2H), 2.15 – 1.92 (m, 4H).$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 190.94, 169.08, 160.68, 158.78 (d, $J = 268.4$ Hz), 140.29, 136.77 (d, $J = 2.9$ Hz), 136.47, 135.56, 132.91, 132.46, 129.48, 129.30, 129.27, 129.19, 128.43, 127.89, 125.26, 121.56, 119.83, 105.73 (d, $J = 6.6$ Hz), 77.14 (d, $J = 31.4$ Hz), 73.62, 68.98, 43.47, 29.44, 25.86. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -118.77. HRMS (APCI) calcd for C$_{28}$H$_{25}$FNO$_4$ (M+H$^+$): 458.1762; found: 458.1758.
Supporting Information

2-(2,2-diphenylvinyl)tetrahydrofuran (3ba)

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.38 – 7.30 (m, 3H), 7.26 – 7.19 (m, 7H), 6.06 (d, $J$ = 9.0 Hz, 1H), 4.29 (td, $J$ = 8.2, 6.3 Hz, 1H), 3.93 (dt, $J$ = 8.4, 6.8 Hz, 1H), 3.72 (td, $J$ = 7.9, 5.8 Hz, 1H), 2.08 – 1.93 (m, 2H), 1.90 – 1.79 (m, 1H), 1.76 – 1.69 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.74, 142.05, 139.49, 130.01, 129.81, 128.14, 127.65, 127.48, 127.39, 76.70, 68.13, 33.14, 26.49. Spectral data match the reported literature values (Chem. Commun., 2020, 56, 2495–2498).
HRMS (ESI) calcd for C_{13}H_{26}NO (M+H^+): 228.1958; found: 228.1965.

Z/E mixture 0.2 mmol

1.5 mL

CuBr, 10 mol%
DTBP, 3 equiv
100 °C
Ar, 18 h
1 equiv TEMPO

3a, trace
detected by HRMS