Copper-Catalyzed Difluoromethylenation of C (sp$^2$) -H Bonds of Alkenes

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1. General information

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM400 and AM500 spectrometer. $^{19}$F NMR was recorded on a Bruker AM400 spectrometer ($\text{CFCl}_3$ as an external standard and low field is positive). Chemical shifts ($\delta$) are reported in ppm, and coupling constants ($J$) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: $s$ = singlet, $d$ = doublet, $t$ = triplet, $q$ = quartet, $m$ = multiplet, $br$ = broad. NMR yield was determined by $^{19}$F NMR using trifluorotoluene as an internal standard before working up the reaction. Infrared spectra (IR) were recorded on AVATAR 370 FT-IR spectrometer, absorbance frequencies are given at maximum of intensity in cm$^{-1}$. Melting points were obtained on a X-4 digital melting point apparatus without correction. High-resolution mass spectra (HRMS) were measured with JEOL JMX-SX 102A spectrometer (FAB) and electrospray (ESI). Some associative experiments were performed on a Varian Saturn 2200 GC-MS system.

Materials: All reagents were used as received from commercial sources.

2. Optimization of the reaction conditions

2.1 Optimization of reaction time

Table S1. Optimization of reaction time

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction time (h)</th>
<th>3a Yield (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>67</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>19</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>24</td>
<td>91</td>
</tr>
</tbody>
</table>

$^a$ Determined by $^{19}$F NMR spectroscopy using PhCF$_3$ as an internal standard

Conclusion: From above, the yield of desired product obviously increased when the reaction time changed from 8 hours to 10 hours. However, the yield was almost constant when the time prolonged from 10 h, 19 h to 24 h. Therefore, the reaction time was selected 10 h.
2.2 Optimization of the substrate ratio

**Table S2. Optimization of the substrate ratio**

<table>
<thead>
<tr>
<th>Entry</th>
<th>2a (equiv.)</th>
<th>1a (equiv.)</th>
<th>3a Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>1.0</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>1.0</td>
<td>67</td>
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<tr>
<td>3</td>
<td>3.0</td>
<td>1.0</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>1.0</td>
<td>87</td>
</tr>
</tbody>
</table>

<sup>a</sup> Determined by $^{19}$F NMR spectroscopy using PhCF<sub>3</sub> as an internal standard

Conclusion: From above, the yields of product 3a have obvious change when the amount of the substrate 2a increased from 2.0 to 3.0 equiv. Continue to increase the amount of substrate 2a to 5.0 equiv, the yield was slightly lower. Therefore, the substrate ratio (2/1a) = 2:1 was selected in the optimized reaction condition.

2.3 Optimization of reaction temperature

**Table S3. Optimization of reaction temperature**

<table>
<thead>
<tr>
<th>Entry</th>
<th>temperature (°C)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
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<tr>
<td>3</td>
<td>100</td>
<td>87</td>
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<tr>
<td>4</td>
<td>120</td>
<td>68</td>
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</tbody>
</table>

<sup>a</sup> Determined by $^{19}$F NMR spectroscopy using PhCF<sub>3</sub> as an internal standard

Conclusion: From above, the lower yield was observed when the reaction was carried at 120°C. Therefore, the 80°C was selected as the best reaction temperature.

2.4 Optimization of ratio between catalyst and ligand

**Table S4. Optimization of ratio between catalyst and ligand**

<table>
<thead>
<tr>
<th>Entry</th>
<th>CuI (equiv)</th>
<th>1,10-phen (equiv)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<td>49</td>
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<tr>
<td>4</td>
<td>0.01</td>
<td>0.01</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>0.01</td>
<td>0.03</td>
<td>90</td>
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</tbody>
</table>
3. Monitored the gem-difluoromethylation reaction by GC-MS

3.1 Exploring the reactions of 1l and 2a by GC-MS

Conclusion: From scheme S1, the peak at 8.445 min is attributed to the main product 3l, and the peak at 9.095 min is that of 4l.
3.2 Exploring the reaction of 1q and 2a by GC-MS

\[
\begin{align*}
1q + \text{ArCF}_2\text{Br} & \xrightarrow{\text{standard conditions}} 3q + 4q + 5q
\end{align*}
\]

**Scheme S2.** The results of the reaction of 1q and 2a by GC-MS

**Conclusion:** The desired product 3q, the peak at 9.340 min, was obtained in 35% isolated yield. The product 5q (GC-MS at 9.165 min) was formed through the active radical abstracting H. The product 4q, detected by $^{19}$F NMR and GC-MS (8.185 min), was a *gem*-difluoromethylenation/cyclizaion cascade product.
3.3 Exploring the reaction of 2a and 1k by GC-MS

![Scheme S3. The results of the reaction of 2 and 1k by GC-MS](image)

Conclusion: The alkane 5k (GC-MS 7.600 min) arisen from radical abstracting hydrogen atom. The formation of 5k was deduced that this reaction was to undergo a free radical process. The product 3k' was isolated and detected by $^{19}$F NMR and GC-MS (7.775 min).
4. Preliminary mechanistic study

4.1 The effect of TEMPO on the standard reaction

**Table S5.** The effect of TEMPO on the standard reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>TEMPO (equiv)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<td>2</td>
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<td>51</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>trace</td>
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</tbody>
</table>

<sup>a</sup> Determined by <sup>19</sup>F NMR spectroscopy using PhCF<sub>3</sub> as an internal standard

**Conclusion:** The yield of the desired product 3a was decreased from 94% to 51% when 1 equivalent TEMPO was added in the standard reaction system. Additionally, when 2 equivalents TEMPO was added, 3a was hardly observed. The results implied that the reaction could involve in a radical process.

4.2 The results of standard reaction by GC-MS

**Scheme S4.** The results of standard reaction by GC-MS
Conclusion: The product 3a'' was obtained in 8% isolated yields which was formed through the radical \( \text{ArCF}_2\cdot \) adding to 3a. Evidences of the formation of 3a and 3a'' further confirmed that the difluoromethenylation of alkenes was via intermediate difluoromethylene radical.

4.3 The results of the reaction of 1a, 2a and alkyne 6 by GC-MS
The mixture sample was prepared through the reaction of 6, 1a, and 2a under the standard conditions, then tested by the Instrument model Agilent 7890A-5975C. Gradient temperature was 190-280℃ (increasing speed: 3℃/min), and the volume injected was 1μL. The results see Scheme S5.

<table>
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<tr>
<th></th>
<th>t1 (min)</th>
<th>m/z</th>
<th>m/z 2</th>
<th>m/z 3</th>
<th>m/z 5</th>
<th>t3 (min)</th>
<th>m/z 6</th>
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<th>m/z 9</th>
<th>YIELD (%)</th>
<th>RET (%)</th>
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<td>15</td>
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<td>3451 BB</td>
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<td>4.87%</td>
<td>1.924%</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

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**Diagram 1:**

- Compound 3a
- **m/z:** 28, 63, 107, 133, 220, 251

**Diagram 2:**

- Compound 7
- **m/z:** 28, 51, 77, 100, 120, 169, 225, 245, 269, 289
Conclusion: Besides the products 3a and 3a'', the product 4, which formed by capturing radical A, was also isolated. The formation of those products further supported the speculated mechanism. The formation of hydroxyl adducts 7 and 8 (GC-MS 27.757 min and 28.236 min) could be further inferred that the carbocation was involved in this reaction. The product 9 observed through GC-MS monitoring of the reaction mixture after 8 hours was homo-coupled product of radical 1B.
5. $^1$H NOESY experiments of 3j and 3t

Scheme S6 $^1$H, $^1$H NOESY spectrum of 3j
From the NOESY spectrum, the $\alpha$-H ($\delta_{6.50}$) coupled with $\gamma$-H (an aromatic H), while the $\beta$-H ($\delta_{5.26}$) (displaying a single peak) had no couple with $\alpha$-H. These results deduced that the geometric configuration for the double bonds of 3j is indicated as $Z$.

Scheme S7 $^1$H, $^1$H NOESY spectrum of 3t
The NOESY spectrum showed that the $\alpha$-H ($\delta_{7.37}$, td) had no couple with $\beta$-H ($\delta_{2.39}$, s). Therefore, the geometric configuration for the double bonds of 3t is indicated as $E$. 
6. New compounds characterization

![Diagram of reaction](image)

A 25 mL round-bottom flask was charged with Cul (10 mol %), 1,10-phen (20 mol %), K$_2$CO$_3$ (2.0 equiv), 2 (0.6 mmol, 2.0 equiv), 1 (0.3 mmol) and DMF (2.5 mL) under air. The reaction mixture was stirred at 80 °C (oil bath) for 10 h. Then the reaction mixture was cooled to room temperature. The crude product was purified with silica gel chromatography (petroleum ether/ethyl acetate = 20/1) to give product 3.

(\textit{E})-2-(1,1-difluoro-3-phenylallyl)benzo[d]oxazole (3a)

Light yellow solid, 86%, mp: 52-54°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.85 (d, $J = 7.9$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.51-7.48 (m, 2H), 7.45 (td, $J = 7.4$, 1.5 Hz, 1H), 7.41 (td, $J = 7.5$, 1.3 Hz, 1H), 7.39-7.32 (m, 3H), 6.67 (dt, $J = 16.2$, 11.0 Hz, 1H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -94.63 (dd, $J = 11.0$, 2.4 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 158.0 (t, $^2$J$_{C-F} = 36.0$ Hz), 150.7, 140.1, 136.8 (t, $^3$J$_{C-F} = 9.0$ Hz), 134.1, 129.7, 128.9, 127.6, 126.9, 125.4, 121.3, 119.5 (t, $^2$J$_{C-F} = 25.1$ Hz), 113.5 (t, $^1$J$_{C-F} = 239.7$ Hz), 111.4. IR: 3060, 1652, 1610, 1443, 1193, 1054, 977, 749 cm$^{-1}$. HRMS (ESI) calcd. for C$_{16}$H$_{12}$F$_2$NO [M+H]$^+$ 272.0887, found: 272.0890.

2,2'(2-benzylidene-1,1,3,3-tetrafluoropropane-1,3-diyl)bis(benzo[d]oxazole) (3a'')

Colorless solid, 8%, mp: 109-110°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.94 (s, 1H), 7.87 (d, $J = 7.9$ Hz, 1H), 7.67 (d, $J = 8.1$ Hz, 2H), 7.54-7.44 (m, 3H), 7.43-7.38 (m, 1H), 7.38-7.30 (m, 3H), 7.21-7.08 (m, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -88.26 (t, $J = 7.4$ Hz), -93.56 (t, $J = 7.4$ Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 157.5 (t, $^2$J$_{C-F} = 35.2$ Hz), 156.5 (t, $^2$J$_{C-F} = 33.5$ Hz), 150.7, 150.3, 143.6-142.6 (m), 140.2, 139.8, 131.9, 129.2, 128.7, 127.9, 126.9, 126.9, 125.3, 125.2, 121.5, 112.8 (t, $^1$J$_{C-F} = 246.8$ Hz), 112.6 (t, $^1$J$_{C-F} = 246.8$ Hz). IR: 3024, 1651, 1449, 1184, 1082, 752 cm$^{-1}$. HRMS (ESI) calcd. for C$_{24}$H$_{15}$F$_4$N$_2$O$_2$ [M+H]$^+$ 438.0991, found: 438.0989.

2-(benzo[d]oxazol-2-yl)difluoromethyl)-5-methyl-3-phenyl-1H-inden-1-one (4)
Yellow solid, 16%, mp: 164-166°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.79 (d, $J$ = 7.8 Hz, 1H), 7.56 (d, $J$ = 8.0 Hz, 1H), 7.52 (d, $J$ = 7.1 Hz, 2H), 7.44 (m, 6H), 7.19 (d, $J$ = 7.3 Hz, 1H), 6.90 (s, 1H), 2.36 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -91.51 (s). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 157.4 (t, $^{3}$J$_{CF}$ = 34.3 Hz), 150.6, 145.1, 144.3, 140.1, 130.9, 130.8, 129.9, 128.3, 127.9, 126.7, 125.8, 125.2, 124.9 (t, $^{2}$J$_{CF}$ = 24.2 Hz), 124.6, 123.6, 121.5, 121.3, 112.4 (t, $^{1}$J$_{CF}$ = 241.6 Hz), 111.4, 22.0. IR: 3037, 2926, 1711, 1606, 1514, 1194, 1034, 743 cm$^{-1}$. HRMS (ESI) calcd. for C$_{24}$H$_{16}$F$_2$NO$_2$ [M+H]$^+$ 388.1149, found: 388.1153.

$(E)$-2-(1,1-difluoro-3-(p-tolyl)allyl)benzo[d]oxazole (3b)

Light yellow solid, 61%, mp: 38-40°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.88-7.85 (m, 1H), 7.67-7.64 (m, 1H), 7.51-7.41 (m, 4H), 6.62 (dt, $J$ = 16.1, 11.0 Hz, 1H), 2.39 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -94.24 (d, $J$ = 11.0 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 158.2 (t, $^{2}$J$_{CF}$ = 36.1 Hz), 150.7, 140.1, 139.9, 136.7 (t, $^{3}$J$_{CF}$ = 9.1 Hz), 131.3, 129.6, 127.6, 126.8, 125.3, 121.3, 118.3 (t, $^{2}$J$_{CF}$ = 24.8 Hz), 113.6 (t, $^{1}$J$_{CF}$ = 239.5 Hz), 111.4, 21.4. IR: 3013, 2916, 1609, 1448, 1190, 1043, 980, 748 cm$^{-1}$. HRMS (ESI) calcd. for C$_{17}$H$_{14}$F$_2$NO [M+H]$^+$ 286.1043, found: 286.1041.

$(E)$-2-(1,1-difluoro-3-(4-methoxyphenyl)allyl)benzo[d]oxazole (3c)

Yellow solid, 74%; mp: 81-82°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.86 (dd, $J$ = 7.7, 1.5 Hz, 1H), 7.65 (dd, $J$ = 7.7, 1.1 Hz, 1H), 7.52-7.41 (m, 4H), 7.16 (dt, $J$ = 16.1, 2.4 Hz, 1H), 6.96-6.89 (m, 2H), 5.25 (dt, $J$ = 16.1, 11.0 Hz, 1H), 3.85 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -93.88 (dd, $J$ = 11.0, 2.4 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 160.8, 158.3 (t, $^{2}$J$_{CF}$ = 36.4 Hz), 150.7, 140.1, 136.2 (t, $^{3}$J$_{CF}$ = 9.1 Hz), 129.1, 126.8, 125.3, 121.3, 117.0 (t, $^{2}$J$_{CF}$ = 25.1 Hz), 114.2, 113.7 (t, $^{1}$J$_{CF}$ = 239.5 Hz), 111.4, 55.4. IR: 3029, 2964, 1605, 1511, 1216, 1037, 969, 756 cm$^{-1}$. HRMS (ESI) calcd. for C$_{17}$H$_{14}$F$_2$NO [M+H]$^+$ 302.0993, found: 302.0995.

$(E)$-2-(3-(4-chlorophenyl)-1,1-difluoroallyl)benzo[d]oxazole (3d)
Light yellow solid, 89%, mp: 89-91°C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 8.1$ Hz, 1H), 7.66 (d, $J = 8.1$ Hz, 1H), 7.54-7.41 (m, 4H), 7.37 (m, 2H), 7.18 (dt, $J = 16.1$, 2.2 Hz, 1H), 6.65 (dt, $J = 16.1$, 10.9 Hz, 1H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -94.66 (d, $J = 10.9$ Hz).

$^{13}$C NMR (125 MHz, CDCl$_3$)$\delta$

157.8 (t, $^2J_{C-F} = 35.8$ Hz), 150.7, 140.0, 135.6, 135.4 (t, $^3J_{C-F} = 9.1$ Hz), 132.6, 129.1, 128.8, 127.0, 125.4, 121.3, 120.0 (t, $^2J_{C-F} = 25.3$ Hz), 113.3 (t, $^1J_{C-F} = 240.1$ Hz), 110.4. IR: 3035, 1658, 1489, 1189, 1077, 1044, 970, 811, 745 cm$^{-1}$. HRMS (ESI) calcd. for C$_{16}$H$_{11}$ClF$_2$NO [M+H]$^+$ 306.0497, found: 306.0495.

($E$)-2-(1,1-difluoro-3-(4-fluorophenyl)allyl)benzo[d]oxazole (3e)

Light yellow solid, 83%, mp: 67-68°C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.86 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.64 (dd, $J = 8.1$, 1.2 Hz, 1H), 7.59-7.34 (m, 4H), 7.19 (dt, $J = 16.2$, 2.3 Hz, 1H), 7.11-7.06 (m, 2H), 6.60 (dt, $J = 16.2$, 11.0 Hz, 1H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -94.41 (dd, $J = 11.0$, 2.3 Hz), -110.72 (ddd, $J = 13.6$, 8.5, 5.0 Hz).

$^{13}$C NMR (125 MHz, CDCl$_3$)$\delta$

163.5 (d, $^1J_{C-F} = 250.1$ Hz), 157.9 (t, $^2J_{C-F} = 35.9$ Hz), 150.7, 140.0, 135.5 (t, $^3J_{C-F} = 9.1$ Hz), 130.3, 129.4 (d, $^3J_{C-F} = 8.4$ Hz), 126.9, 125.4, 121.3, 119.2 (t, $^2J_{C-F} = 25.0$ Hz), 115.9 (d, $^2J_{C-F} = 21.9$ Hz), 112.4 (t, $^1J_{C-F} = 239.9$ Hz), 111.4. IR: 3040, 1605, 1059, 1223, 1161, 1044, 970, 746 cm$^{-1}$. HRMS (ESI) calcd. for C$_{16}$H$_{11}$F$_3$NO [M+H]$^+$ 290.0793, found: 290.0798.

($E$)-2-(1,1-difluoro-3-(4-nitrophenyl)allyl)benzo[d]oxazole (3f)

Light yellow solid, 49%, mp: 151-152°C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.26 (d, $J = 8.7$ Hz, 2H), 7.85 (d, $J = 7.9$ Hz, 1H), 7.67 (m, 3H), 7.56-7.39 (m, 2H), 7.31 (dt, $J = 16.1$, 2.3 Hz, 1H), 6.84 (dt, $J = 16.1$, 10.7 Hz, 1H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -95.37 (d, $J = 10.7$, 2.3 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$)$\delta$

157.3 (t, $^2J_{C-F} = 35.2$ Hz), 150.7, 148.3, 140.2, 139.9, 134.4 (t, $^3J_{C-F} = 9.0$ Hz), 128.3, 127.2, 125.5, 124.1, 123.8 (t, $^2J_{C-F} = 25.1$ Hz), 121.4, 112.8 (t, $^1J_{C-F} = 240.4$ Hz), 111.5. IR: 3024, 1602, 1518, 1343, 1192, 1061, 974, 747 cm$^{-1}$. HRMS (ESI) calcd. for C$_{16}$H$_{11}$F$_2$N$_2$O$_3$ [M+H]$^+$ 317.0738, found: 317.0741.

($E$)-2-(3-(2-bromophenyl)-1,1-difluoroallyl)benzo[d]oxazole (3g)

Light yellow solid, 67%, mp: 68-69°C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.85 (dd, $J = 7.5$, 1.0 Hz, 1H),
7.67 - 7.61 (m, 3H), 7.59 (dd, J = 8.0, 1.0 Hz, 1H), 7.47 (td, J = 7.5, 1.2 Hz, 1H), 7.43 (td, J = 7.6, 1.1 Hz, 1H), 7.32 (td, J = 7.2, 0.5 Hz, 1H), 7.20 (td, J = 7.9, 1.5 Hz, 1H), 6.65 (dt, J = 16.0, 10.9 Hz, 1H).

$^{19}$F NMR (470 MHz, CDCl$_3$) δ -94.82 (dd, J$_{CF}$ = 10.9, 2.5 Hz).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 157.7 (t, J$_{CF}$ = 35.6 Hz), 150.7, 140.0, 135.5 (t, J$_{CF}$ = 9.2 Hz), 134.1, 133.3, 130.8, 127.7, 127.7, 122.1 (t, J$_{CF}$ = 24.9 Hz), 121.3, 113.1 (t, J$_{CF}$ = 240.5 Hz), 111.4. IR: 3023, 1613, 1457, 1193, 1049, 960, 752, 658 cm$^{-1}$. HRMS (ESI) calcd. for C$_{16}$H$_{11}$BrF$_2$NO [M+H]$^+$ 349.9992, found: 349.9996.

(5-E)-2-(3-(3-bromophenyl)-1,1-difluoroallyl)benzodioxazole (3h)

Yellow oil, 54%; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.85 (dd, J = 8.0, 1.0 Hz, 1H), 7.67 - 7.61 (m, 2H), 7.51 - 7.46 (m, 2H), 7.44 (dd, J = 7.8, 1.2 Hz, 1H), 7.41 (dd, J = 7.9, 1.1 Hz, 1H), 7.25 (t, J = 7.9 Hz, 1H), 7.15 (dt, J = 16.1, 2.4 Hz, 1H), 6.68 (dt, J = 16.1, 10.8 Hz, 1H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -94.87 (dd, J = 10.8, 2.4 Hz).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 157.7 (t, J$_{CF}$ = 35.7 Hz), 150.7, 140.0, 136.1, 135.2 (t, J$_{CF}$ = 9.0 Hz), 132.6, 130.3, 127.0, 126.3, 125.4, 123.0, 121.4, 121.0 (t, J$_{CF}$ = 25.1 Hz), 113.1 (t, J$_{CF}$ = 240.2 Hz), 111.5. IR: 3023, 1659, 1565, 1187, 1045, 969, 744, 567 cm$^{-1}$. HRMS (ESI) calcd. for C$_{16}$H$_{11}$BrF$_2$NO [M+H]$^+$ 349.9992, found: 349.9987.

(E)-2-(3-(4-bromophenyl)-1,1-difluoroallyl)benzodioxazole (3i)

Yellow solid, 62%, mp: 111-112°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.86 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.57 - 7.52 (m, 2H), 7.50 (td, J = 7.6, 1.2 Hz, 1H), 7.45 (td, J = 7.6, 1.1 Hz, 1H), 7.39 (m, 2H), 7.17 (dt, J = 16.1, 2.4 Hz, 1H), 6.67 (dt, J = 16.1, 10.9 Hz, 1H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -94.77 (dd, J = 10.8, 2.4 Hz).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 157.7 (t, J$_{CF}$ = 35.9 Hz), 150.7, 140.0, 136.1, 135.5 (t, J$_{CF}$ = 9.0 Hz), 133.0, 132.1, 129.1, 127.0, 125.4, 123.9, 121.4, 120.2 (t, J$_{CF}$ = 25.2 Hz), 113.2 (t, J$_{CF}$ = 239.7 Hz), 111.5. IR: 3037, 1652, 1567, 1187, 1045, 969, 744, 562 cm$^{-1}$. HRMS (ESI) calcd. for C$_{16}$H$_{11}$BrF$_2$NO [M+H]$^+$ 349.9992, found: 349.9993.

(Z)-4-(benzodioxazol-2-yl)-4,4-difluoro-2-phenylbut-2-en-1-yl acetate (3j)

Yellow solid, 62%, mp: 111-112°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.86 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.57 - 7.52 (m, 2H), 7.50 (td, J = 7.6, 1.2 Hz, 1H), 7.45 (td, J = 7.6, 1.1 Hz, 1H), 7.39 (m, 2H), 7.17 (dt, J = 16.1, 2.4 Hz, 1H), 6.67 (dt, J = 16.1, 10.9 Hz, 1H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -94.73 (dd, J = 10.9, 2.4 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 157.7 (t, J$_{CF}$ = 35.9 Hz), 150.7, 140.0, 136.1, 135.5 (t, J$_{CF}$ = 9.0 Hz), 133.0, 132.1, 129.1, 127.0, 125.4, 123.9, 121.4, 120.2 (t, J$_{CF}$ = 25.2 Hz), 113.2 (t, J$_{CF}$ = 239.7 Hz), 111.5. IR: 3037, 1652, 1567, 1187, 1045, 969, 744, 562 cm$^{-1}$. HRMS (ESI) calcd. for C$_{16}$H$_{11}$BrF$_2$NO [M+H]$^+$ 349.9992, found: 349.9993.
Light yellow solid, 51%, mp: 127-129°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.86 (d, $J = 8.2$ Hz, 1H), 7.67 (d, $J = 8.2$ Hz, 1H), 7.51-7.46 (m, 3H), 7.47-7.39 (m, 4H), 6.50 (t, $J = 13.7$ Hz, 1H), 5.26 (s, 2H), 1.86 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -88.19 (d, $J = 13.7$ Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 170.4, 157.8 (t, $2J_{CF} = 35.4$ Hz), 150.8, 146.4 (t, $3J_{CF} = 6.1$ Hz), 140.0, 138.0, 129.2, 128.6, 127.0, 126.9, 125.4, 123.0 (t, $2J_{CF} = 26.9$ Hz), 121.4, 113.0 (t, $1J_{CF} = 240.2$ Hz), 111.5, 60.8 (t, $4J_{CF} = 2.4$ Hz), 20.5. IR: 3012, 2925, 1743, 1646, 1514, 1231, 1034, 745, 696 cm$^{-1}$. HRMS (ESI) calcd. for C$_{19}$H$_{16}$F$_2$NO $[M+H]^+$ 344.1098, found: 344.1201.

$(E)$-2-(1,1-difluoro-4-phenylbut-2-en-1-yl)benzo[d]oxazole (3k)

![Chemical structure of 3k](image)

Colorless oil, 40%; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.85 (d, $J = 8.0$ Hz, 1H), 7.64 (d, $J = 7.9$ Hz, 1H), 7.48 (td, $J = 7.2$, 1.2 Hz, 1H), 7.44 (td, $J = 7.5$, 1.1 Hz, 1H), 7.30-7.27 (m, 1H), 7.26-7.21 (m, 2H), 6.58 (dtt, $J = 15.7$, 6.9, 2.4 Hz, 1H), 6.08 (dtt, $J = 15.7$, 10.6, 1.5 Hz, 1H), 3.66-3.49 (m, 2H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -94.45 (dd, $J = 10.6$, 2.4 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 158.1 (t, $2J_{CF} = 35.6$ Hz), 150.7, 140.0, 138.3 (t, $1J_{CF} = 8.6$ Hz), 137.7, 128.8, 128.7, 126.8, 126.7, 125.3, 122.9 (t, $2J_{CF} = 25.3$ Hz), 121.3, 113.0 (t, $1J_{CF} = 239.2$ Hz), 111.4, 38.1. IR: 3030, 2910, 1610, 1491, 1210, 1041, 975, 750 cm$^{-1}$. HRMS (ESI) calcd. for C$_{17}$H$_{14}$F$_2$NO $[M+H]^+$ 286.1043, found: 286.1041.

$(E)$-2-(1,1-difluoro-4-phenylbut-3-en-1-yl)benzo[d]oxazole (3k’)

![Chemical structure of 3k’](image)

Light yellow oil, 15%; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.90 (d, $J = 7.5$ Hz, 1H), 7.64 (dd, $J = 7.2$, 1.2 Hz, 1H), 7.46 (m, 2H), 7.42 (d, $J = 7.4$ Hz, 2H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.33 – 7.25 (m, 1H), 6.71 (d, $J = 16.0$ Hz, 1H), 6.35 (td, $J = 15.9$, 7.2 Hz, 1H), 3.47 (td, $J = 16.0$, 7.2 Hz, 2H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -97.22 (t, $J = 16.0$ Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 157.85 (t, $2J_{CF} = 33.5$ Hz), 150.67 , 140.05 , 136.76 , 136.53 , 128.61 , 127.97 , 126.90 , 126.50 , 125.33 , 121.33 , 118.19 (t, $2J_{CF} = 4.8$ Hz), 115.91 (t, $1J_{CF} = 242.2$ Hz), 111.44 , 39.80 (t, $2J_{CF} = 24.3$ Hz). IR: 3008, 1606, 1485, 1206, 1030, 968,746 cm$^{-1}$. HRMS (ESI) calcd. for C$_{17}$H$_{14}$F$_2$NO $[M+H]^+$ 286.1043, found: 286.1047.

$(E)$-2-(1,1-difluoro-5-phenylpent-2-en-1-yl)benzo[d]oxazole (3l)
Light red oil, 58%; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.89 (dd, $J$ = 7.4, 1.5 Hz, 1H), 7.67-7.62 (dd, $J$ = 7.8, 1.5 Hz, 1H), 7.52-7.43 (m, 2H), 7.35-7.30 (m, 2H), 7.28-7.21 (m, 3H), 6.51 (dtt, $J$ = 15.8, 6.7, 2.3 Hz, 1H), 6.13 (dt, $J$ = 15.8, 10.5 Hz, 1H), 2.89-2.81 (m, 2H), 2.64-2.52 (m, 2H).

$^19$F NMR (470 MHz, CDCl$_3$) δ -94.77 (dd, $J$ = 10.9, 2.4 Hz).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 158.2 (t, $^2J_{C-F}$ = 35.9 Hz), 150.7, 140.8, 140.1, 138.9 (t, $^3J_{C-F}$ = 8.6 Hz), 128.5, 126.8, 126.2, 125.3, 122.4 (t, $^2J_{C-F}$ = 25.1 Hz), 121.3, 113.1 (t, $^1J_{C-F}$ = 239.1 Hz), 111.4, 34.6, 33.7. IR: 3029, 2931, 1676, 1448, 1213, 1032, 969, 749 cm$^{-1}$.

HRMS (ESI) calcd. for C$_{18}$H$_{16}$F$_2$NO [M+H$^+$] 300.1200, found: 300.1205.

2-(2-(2,3-dihydro-1H-inden-1-yl)-1,1-difluoroethyl)benzo[d]oxazole (4l)

Light yellow oil, 7%; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.84 (d, $J$ = 7.6 Hz, 1H), 7.65 (d, $J$ = 7.9 Hz, 1H), 7.52 – 7.26 (m, 1H), 7.22 (m, 3H), 4.32 (dtd, $J$ = 9.9, 6.7, 4.0 Hz, 1H), 3.25 (qd, $J$ = 15.9, 7.2 Hz, 1H), 3.17 – 3.04 (dtd, $J$ = 17.8, 12.1, 6.0 Hz, 1H), 2.96 (ddd, $J$ = 14.0, 9.1, 5.0 Hz, 1H), 2.82 (ddd, $J$ = 16.0, 9.0, 2.0 Hz, 1H), 2.37 – 2.17 (m, 2H).

$^{19}$F NMR (470 MHz, CDCl$_3$) δ -93.89 (ddd, $J$ = 278.2, 17.3, 12.1 Hz), -99.19 (dt, $J$ = 278.2, 16.5 Hz).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 157.11 (t, $^2J_{C-F}$ = 33.1 Hz), 150.58, 140.21, 139.90, 128.53, 128.49, 127.02, 126.25, 125.41, 121.36, 115.51 (t, $^1J_{C-F}$ = 243.1 Hz), 111.48, 45.40 (t, $^3J_{C-F}$ = 3.8 Hz), 45.02 (t, $^2J_{C-F}$ = 24.0 Hz), 40.60, 33.32. IR: 3022, 2927, 1688, 1469, 1223, 1068, 747 cm$^{-1}$. HRMS (ESI) calcd. for C$_{18}$H$_{16}$F$_2$NO [M+H$^+$] 300.1200, found: 300.1204.

2-(1,1-difluoro-5-phenylpentyl)benzo[d]oxazole (5l)

Light yellow oil, 9%; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.85 (d, $J$ = 7.9 Hz, 1H), 7.65 (d, $J$ = 7.8 Hz, 1H), 7.49 (d, $J$ = 22.0, 7.8, 1.1 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.22 (m, 3H), 4.32 (dtd, $J$ = 9.9, 6.7, 4.0 Hz, 1H), 3.25 (qd, $J$ = 15.9, 7.2 Hz, 1H), 3.17 – 3.04 (dtd, $J$ = 17.8, 12.1, 6.0 Hz, 1H), 2.96 (ddd, $J$ = 14.0, 9.1, 5.0 Hz, 1H), 2.82 (ddd, $J$ = 16.0, 9.0, 2.0 Hz, 1H), 2.37 – 2.17 (m, 2H).

$^{19}$F NMR (470 MHz, CDCl$_3$) δ -98.20 (t, $J$ = 16.7 Hz).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 158.17 (t, $^2J_{C-F}$ = 33.9 Hz), 150.58, 140.21, 139.90, 128.53, 128.49, 127.02, 126.25, 125.41, 121.36, 115.51 (t, $^1J_{C-F}$ = 243.1 Hz), 111.48, 45.40 (t, $^3J_{C-F}$ = 3.8 Hz), 45.02 (t, $^2J_{C-F}$ = 24.0 Hz), 40.60, 33.32. IR: 3022, 2927, 1688, 1469, 1223, 1068, 978, 747 cm$^{-1}$. HRMS (ESI) calcd. for C$_{18}$H$_{18}$F$_2$NO [M+H$^+$] 302.1356, found: 302.1360.

2-(2-(2,3-dihydro-1H-inden-1-yl)-1,1-difluoroethyl)benzo[d]oxazole (4l)

Light yellow oil, 58%; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.83 (dd, $J$ = 7.9, 1.3 Hz, 1H), 7.63-7.60 (m, 1H), 7.52 – 7.43 (m, 2H), 7.31 – 7.27 (m, 2H), 7.20 (t, $J$ = 7.8 Hz, 3H), 2.68 (t, $J$ = 7.7 Hz, 2H), 2.58 – 2.44 (m, 2H), 1.77 (m, 2H), 1.69 (m, 2H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -98.20 (t, $J$ = 16.7 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 158.17 (t, $^2J_{C-F}$ = 33.9 Hz), 150.57, 141.87, 139.98, 128.35, 126.77, 125.85, 125.26, 121.24, 116.88 (t, $^1J_{C-F}$ = 241.2 Hz), 114.56, 111.40, 35.77 (t, $^2J_{C-F}$ = 23.5 Hz), 35.55, 30.91, 21.37 (t, $^1J_{C-F}$ = 3.9 Hz). IR: 3021, 2918, 1648, 1490, 1212, 1049, 972,750 cm$^{-1}$. HRMS (ESI) calcd. for C$_{18}$H$_{18}$F$_2$NO [M+H$^+$] 302.1356, found: 302.1360.

(E)-2-(1,1-difluoroundec-2-en-1-yl)benzo[d]oxazole (3m)

Yellow oil, 94%; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.83 (dd, $J$ = 7.9, 1.3 Hz, 1H), 7.63-7.60 (m, 1H),
7.49-7.37 (m, 2H), 6.46-6.34 (m, 1H), 6.09-5.98 (m, 1H), 2.28-2.16 (m, 2H), 1.47 (p, $J = 7.4$ Hz, 2H), 1.39-1.19 (m, 10H), 0.89 (t, $J = 7.0$ Hz, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -94.32 (dd, $J = 10.6$, 2.8 Hz).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 158.2 (t, $J_{C-F} = 36.4$ Hz), 150.6, 140.06, 139.8 (t, $J_{C-F} = 7.7$ Hz), 126.6, 125.1, 121.6 (t, $J_{C-F} = 25.0$ Hz), 121.2, 113.0 (t, $J_{C-F} = 238.9$ Hz), 111.2, 31.9, 31.8, 29.3, 29.2, 29.1, 28.1, 22.6, 14.0. IR: 3032, 2926, 1676, 1457, 1228, 1040, 972, 749 cm$^{-1}$. HRMS (ESI) calc'd. for C$_{18}$H$_{24}$F$_2$NO [M+H]$^+$ 308.1826, found: 308.1832.

2-(1,1-difluoro-2-(4-phenylcyclohexylidene)ethyl)benzo[d]oxazole (3n)

Light yellow solid, 95%, mp: 99-101°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.87 (dd, $J = 7.9$, 1.1 Hz, 1H), 7.67 (d, $J = 7.9$ Hz, 1H), 7.50 (td, $J = 7.6$, 1.3 Hz, 1H), 7.46 (td, $J = 7.6$, 1.3 Hz, 1H), 7.34-7.28 (m, 2H), 7.25–7.19 (m, 3H), 5.77 (s, 1H), 3.18 (t, $J = 17.0$ Hz, 2H), 2.84–2.69 (m, 1H), 2.39–2.26 (m, 2H), 2.25–2.10(m, 2H), 2.00–1.93(m, 1H), 1.87–1.73(m, 1H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -96.75 (td, $J = 17.0$, 3.4 Hz).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 158.3 (t, $J_{C-F} = 33.9$ Hz), 150. 6, 146.6, 140. 1, 128.4, 128.3 (t, $J_{C-F} = 2.8$ Hz), 126.8, 126.7, 126.1, 125.3, 121.3, 116.4 (t, $J_{C-F} = 243.8$ Hz), 111.4, 44.0 (t, $J_{C-F} = 23.7$ Hz), 39.4, 33.6, 30.0, 29.9. IR: 3026, 2918, 1609, 1489, 1445, 1198, 1022, 754 cm$^{-1}$. HRMS (ESI) calc'd. for C$_{21}$H$_{20}$F$_2$NO [M+H]$^+$ 340.1513, found: 340.1515.

(E)-2-(1,1-difluoro-7-(naphthalen-2-yloxy)hept-2-en-1-yl)benzo[d]oxazole (3o)

Light yellow solid, 52%, mp: 70-72°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.87 (d, $J = 7.4$ Hz, 1H), 7.83-7.73 (m, 3H), 7.65 (d, $J = 7.7$ Hz, 1H), 7.52-7.42 (m, 3H), 7.37 (t, $J = 7.4$ Hz, 1H), 7.22-7.12 (m, 2H), 6.48 (dt, $J = 15.7$, 6.8 Hz, 1H), 6.13 (dt, $J = 15.7$, 10.7 Hz, 1H), 4.12 (t, $J = 6.4$Hz, 2H), 2.39-2.33 (m, 2H), 1.93 (m, 2H), 1.75 (m, 2H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -94.79 (dd, $J = 10.8$, 2.1 Hz).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 158.2 (t, $J_{C-F} = 36.0$ Hz), 157.0, 150.7, 140.1, 139.4 (t, $J_{C-F} = 8.5$ Hz), 134.6, 129.4, 129.0, 127.7, 126.8, 126.8, 126.4, 125.3, 123.6, 122.1 (t, $J_{C-F} = 25.0$ Hz), 121.3, 119.0, 113.1 (t, $J_{C-F} = 238.7$ Hz), 111.4, 106.6, 67.5, 31.7, 28.7, 24.9. IR: 3024, 2939, 1625, 1508, 1176, 1132, 1059,970, 750 cm$^{-1}$. HRMS (ESI) calc'd. for C$_{24}$H$_{22}$F$_2$NO$_2$ [M+H]$^+$ 394.1619, found: 394.1621.

(E)-2-(1,1-difluoro-5-(p-tolyloxy)pent-2-en-1-yl)benzo[d]oxazole (3p)
Yellow oil, 44%; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.87 (d, J = 8.0 \text{ Hz}, 1H), 7.65 (d, J = 7.9 \text{ Hz}, 1H), 7.49 (\text{td}, J = 7.8, 1.4 \text{ Hz}, 1H), 7.45 (\text{td}, J = 7.8, 1.4 \text{ Hz}, 1H), 7.11 (d, J = 8.6 \text{ Hz}, 2H), 6.84-6.82 (m, 2H), 6.54 (dt, J = 15.8, 6.8, 2.3 \text{ Hz}, 1H), 6.22 (dt, J = 15.8, 10.6 \text{ Hz}, 1H), 4.09 (t, J = 6.4 \text{ Hz}, 2H), 2.87-2.61 (m, 2H), 2.32 (s, 3H). \(^1^9\)F NMR (470 MHz, CDCl\(_3\)) \(\delta -94.90 (d, J = 10.6 \text{ Hz}).\) \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 158.0 (t, J_{C-F} = 35.7 \text{ Hz}), 156.5, 150.7, 140.0, 135.7 (t, J_{C-F} = 8.8 \text{ Hz}), 130.2, 129.9, 126.9, 125.3, 123.8 (t, J_{C-F} = 25.0 \text{ Hz}), 121.3, 114.5, 112.9 (t, J_{C-F} = 239.3 \text{ Hz}), 111.4, 66.2, 31.9, 20.5. IR: 3024, 2924, 1681, 1513, 1237, 1039, 968, 745 \text{ cm}^{-1}.\) HRMS (ESI) calcd. for C\(_{19}\)H\(_{18}\)F\(_2\)NO\(_2\) [M+H]\(^+\) 330.1306, found: 330.1311.

2-[1,1-Difluoro-2-(6-methyl-chroman-4-yl)-ethyl]-benzooxazole (4p)

Yellow oil, 14%; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.87 (d, J = 8.0 \text{ Hz}, 1H), 7.65 (d, J = 7.9 \text{ Hz}, 1H), 7.51 (\text{td}, 1H), 7.47 (\text{td}, J = 7.4, 1.1 \text{ Hz}, 1H), 7.01 (s, 1H), 6.93 (dd, J = 8.3, 1.5 \text{ Hz}, 1H), 6.74 (d, J = 8.3 \text{ Hz}, 1H), 4.26–4.15 (m, 2H), 3.42–3.30 (m, 1H), 3.01 (dtd, J = 22.3, 15.8, 2.9 \text{ Hz}, 1H), 2.74 (m, 1H), 2.27 (s, 3H), 2.26–2.19 (m, 1H), 2.11–2.00 (m, 1H). \(^{1^9}\)F NMR (470 MHz, CDCl\(_3\)) \(\delta -94.22 (ddd, J = 276.2, 22.4, 10.9 \text{ Hz}), -98.61 (ddd, J = 276.1, 21.2, 16.4 \text{ Hz}).\) \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 157.9 (t, J_{C-F} = 33.6 \text{ Hz}), 152.4, 150.6, 139.9, 129.7, 129.3, 128.7, 127.0, 125.4, 123.9, 121.3, 116.9, 116.8 (t, J_{C-F} = 242.9 \text{ Hz}), 111.4, 62.9, 42.6 (t, J_{C-F} = 22.3 \text{ Hz}), 28.2 (t, J_{C-F} = 2.7 \text{ Hz}), 27.8, 20.6. IR: 3012, 2929, 1691, 1502, 1098, 1046, 745 \text{ cm}^{-1}.\) HRMS (ESI) calcd. for C\(_{18}\)H\(_{18}\)F\(_2\)NO\(_2\) [M+H]\(^+\) 330.1306, found: 330.1310.

(E)-2-(1,1-difluoro-4-(p-tolyloxy)but-2-en-1-yl)benzo[d]oxazole (3q)

Light yellow solid, 35%, mp: 76-78 \text{ °C}; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.86 (dd, J = 8.0, 1.1 \text{ Hz}, 1H), 7.66 (d, J = 7.9 \text{ Hz}, 1H), 7.66 (d, J = 8.1 \text{ Hz}, 1H), 7.50 (td, J = 7.5, 1.3 \text{ Hz}, 1H), 7.45 (td, J = 7.7, 1.2 \text{ Hz}, 1H), 7.15–7.10 (m, 2H), 6.90–6.83 (m, 2H), 6.68–6.60 (m, 1H), 6.49 (dtt, J = 15.8, 10.4, 1.5 \text{ Hz}, 1H), 4.78–4.56 (m, 2H), 2.32 (s, 3H). \(^{19}\)F NMR (470 MHz, CDCl\(_3\)) \(\delta -95.52 (dd, J = 10.4, 3.1 \text{ Hz} ).\) \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 157.6 (t, J_{C-F} = 35.4 \text{ Hz}), 156.0, 150.7, 140.4, 134.2 (t, J_{C-F} = 8.5 \text{ Hz}), 130.7, 130.0, 126.9, 125.4, 122.7 (t, J_{C-F} = 25.5 \text{ Hz}), 121.3, 114.6, 112.9 (t, J_{C-F} = 239.7 \text{ Hz}), 111.4, 66.3, 20.5. IR: 3025, 2918, 1609, 1488, 1197, 1058, 1022, 936, 755 \text{ cm}^{-1}.\) HRMS (ESI) calcd. for C\(_{18}\)H\(_{18}\)F\(_2\)NO\(_2\) [M+H]\(^+\) 316.1149, found: 316.1152.

(E)-6-(benzo[d]oxazol-2-yl)-6,6-difluorohex-4-en-1-yl 4-iodobenzoate (3r)
2-(benzo[d]oxazol-2-yldifluoromethyl)-3-methylbut-2-en-1-yl 4-bromobenzoate (3s)

(E)-p-tolyl -4-(benzo[d]oxazol-2-yl)-4,4-difluoro-2-methylbut-2-enoate (3t)

(E)-3-(2-(benzo[d]oxazol-2-yl)-2,2-difluoroethyl)-1,3-dimethylindolin-2-one (4u)
Light yellow solid, 96%, mp: 167-168 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.66 (d, $J$ = 7.3 Hz, 1H), 7.47 (d, $J$ = 7.7 Hz, 1H), 7.39 (dd, $J$ = 7.4, 1.2 Hz, 1H), 7.35 (dd, $J$ = 7.5, 1.1 Hz, 1H), 7.04 (td, $J$ = 7.7, 1.1 Hz, 1H), 6.95 (d, $J$ = 7.3 Hz, 1H), 6.77 (d, $J$ = 7.8 Hz, 1H), 6.57 (td, $J$ = 7.5, 0.8 Hz, 1H), 3.25 (td, $J$ = 15.5, 11.5 Hz, 1H), 3.19 (s, 3H), 3.09 (dt, $J$ = 20.9, 14.3 Hz, 1H), 1.42 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -90.46 (dt, $J$ = 277.6, 12.4 Hz), -101.16 (ddd, $J$ = 277.6, 20.9, 16.4 Hz).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 178.7, 157.3 (t, $J_{C-F}$ = 33.5 Hz), 150.4, 142.9, 139.9, 130.6, 128.1, 126.6, 125.1, 123.2, 121.9, 121.0, 115.4 (t, $J_{C-F}$ = 244.6 Hz), 111.2, 108.3, 44.6, 43.1 (t, $J_{C-F}$ = 24.1 Hz), 26.4, 25.6. IR: 3021, 2928, 1708, 1610, 1483, 1190, 1047, 748 cm$^{-1}$. HRMS (ESI) calcd. for C$_{19}$H$_{17}$F$_2$N$_2$O$_2$ [M+H]$^+$ 343.1258, found: 343.1261.

2-(benzofuran-3-yldifluoromethyl)benzo[d]oxazole (3v)

Light yellow solid, 48%, mp: 97-99 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.89 (dd, $J$ = 7.4, 0.9 Hz, 1H), 7.70 (d, $J$ = 7.8 Hz, 1H), 7.67 (d, $J$ = 8.0 Hz, 1H), 7.58 (dd, $J$ = 8.3, 0.8 Hz, 1H), 7.51 (m, 1H), 7.46 (m, 1H), 7.44–7.40 (m, 1H), 7.36–7.31 (m, 2H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -96.10 (d, $J$ = 4.6 Hz).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 156.4 (t, $J_{C-F}$ = 34.8 Hz), 155.6, 150.8, 146.7 (t, $J_{C-F}$ = 33.8 Hz), 140.1, 127.2, 126.6, 126.51, 125.5, 123.8, 122.4, 121.6, 112.1, 111.5, 109.9 (t, $J_{C-F}$ = 240.8 Hz), 108.6 (t, $J_{C-F}$ = 3.7 Hz). IR: 3015, 1609, 1447, 1158, 1004, 750 cm$^{-1}$. HRMS (ESI) calcd. for C$_{16}$H$_{10}$F$_2$NO$_2$ [M+H]$^+$ 286.0680, found: 286.0677.

(E)-2-(1,1-difluoro-3-phenylallyl)-5-methylbenzo[d]oxazole (3w)

Light yellow solid, 85%, mp: 71-73 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.64 (s, 1H), 7.55-7.49 (m, 3H), 7.44-7.34 (m, 3H), 7.29 (d, $J$ = 8.1 Hz, 1H), 7.22 (d, $J$ = 16.1 Hz, 1H), 6.67 (dt, $J$ = 16.1, 10.8 Hz, 1H), 2.52 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -94.44 (d, $J$ = 10.7 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 158.1 (t, $J_{C-F}$ = 35.7 Hz), 149.0, 140.3, 136.7 (t, $J_{C-F}$ = 8.9 Hz), 135.3, 134.1, 129.7, 128.8, 128.1, 127.6, 121.0, 119.6 (t, $J_{C-F}$ = 25.3 Hz), 113.5 (t, $J_{C-F}$ = 239.4 Hz), 110.8, 21.5. IR: 3010, 1661, 1612, 1453, 1214, 1067, 979 cm$^{-1}$. HRMS (ESI) calcd. for C$_{17}$H$_{14}$F$_2$NO [M+H]$^+$ 286.1043, found: 286.1047.
\((E)-2-(1,1\text{-difluoro-3-phenylallyl})\text{benzo}[d]\text{thiazole} \ (3x)\)

\[
\begin{align*}
\text{Yellow oil, 49%; } &\text{ } ^1\text{H NMR (500 MHz, CDCl}_3\text{) } \delta 8.18 (d, J = 8.3 \text{ Hz, } 1\text{H}), 7.99 (d, J = 8.0 \text{ Hz, } 1\text{H}), 7.59 (m, 1\text{H}), 7.55-7.49 (m, 3\text{H}), 7.43-7.36 (m, 3\text{H}), 7.21 (dt, J = 16.1, 2.5 \text{ Hz, } 2\text{H}), 6.75 (dt, J = 16.1, 11.0 \text{ Hz, } 1\text{H}). &\text{ } ^19\text{F NMR (470 MHz, CDCl}_3\text{) } \delta -86.68 (dd, J = 11.0, 2.5 \text{ Hz}). &\text{ } ^{13}\text{C NMR (125 MHz, CDCl}_3\text{) } \delta 164.6 (t, J_{\text{C-F}} = 36.4 \text{ Hz}), 152.8, 135.9 (t, J_{\text{C-F}} = 9.3 \text{ Hz}), 135.0, 134.4, 129.5, 128.8, 127.6, 126.8, 126.6, 124.4, 122.0, 120.9 (t, J_{\text{C-F}} = 26.2 \text{ Hz}), 116.6 (t, J_{\text{C-F}} = 239.9 \text{ Hz}). \text{ IR: } 3011, 1647, 1598, 1436, 1186, 1029, 974, 741 \text{ cm}^{-1}. &\text{HRMS (ESI) calcd. for C}_{16}\text{H}_{12}\text{F}_{2}\text{NS} [M+H]^+ 288.0659, \text{ found: 288.0663.}
\end{align*}
\]

\((E)-2-(1,1\text{-difluoroundec-2-en-1-yl})\text{-5-methylbenzo}[d]\text{oxazole} \ (3y)\)

\[
\begin{align*}
\text{Yellow oil, 90%; } &\text{ } ^1\text{H NMR (500 MHz, CDCl}_3\text{) } \delta 7.61 (s, 1\text{H}), 7.48 (d, J = 8.5 \text{ Hz, } 1\text{H}), 7.26 (dd, J = 8.5, 1.2 \text{ Hz,1H}), 6.39 (dtt, J = 15.7, 6.9, 2.5 \text{ Hz, } 1\text{H}), 6.02 (dtt, J = 15.7, 10.6, 1.5 \text{ Hz,1H}), 2.50 (s, 3\text{H}), 2.27-2.18 (m, 2\text{H}), 1.52-1.43 (m, 2\text{H}), 1.37-1.23 (m, 10\text{H}), 0.90 (t, J = 7.0 \text{ Hz, } 3\text{H}). &\text{ } ^19\text{F NMR (470 MHz, CDCl}_3\text{) } \delta -94.23 (dd, J = 10.6, 2.9 \text{ Hz}). &\text{ } ^{13}\text{C NMR (125 MHz, CDCl}_3\text{) } \delta 158.3 (t, J_{\text{C-F}} = 35.7 \text{ Hz}), 148.93, 140.3, 139.9 (t, J_{\text{C-F}} = 8.6 \text{ Hz}), 135.2, 127.9, 121.7 (t, J_{\text{C-F}} = 25.1 \text{ Hz}), 121.0, 113.1 (t, J_{\text{C-F}} = 238.8 \text{ Hz}), 110.7, 31.9, 31.8, 29.3, 29.2, 29.1, 28.1, 22.7, 21.43, 14.1. \text{ IR: } 3018, 2930, 1679, 1461, 1232, 1044, 975, 953 \text{ cm}^{-1}. &\text{HRMS (ESI) calcd. for C}_{16}\text{H}_{26}\text{F}_{2}\text{NO} [M+H]^+ 322.1982, \text{ found: 322.1986.}
\end{align*}
\]
7. Copies of $^1$H NMR, $^{19}$F NMR, $^{13}$C NMR spectra of product 3, 4

$(E)$-2-(1,1-difluoro-3-phenylallyl)benzo[$d$]oxazole (3a)
2,2′-(2-benzylidene-1,1,3,3-tetrafluoropropane-1,3-diyl)bis(benzo[d]oxazole) (3a′′)
2-(benzo[d]oxazol-2-yl)difluoromethyl)-5-methyl-3-phenyl-1H-inden-1-one (4)
(E)-2-(1,1-difluoro-3-(p-toly)allyl)benzo[d]oxazole (3b)
(E)-2-(1,1-difluoro-3-(4-methoxyphenyl)allyl)benzo[d]oxazole (3c)
(E)-2-(3-(4-chlorophenyl)-1,1-difluoroallyl)benzo[d]oxazole (3d)
(E)-2-(1,1-difluoro-3-(4-fluorophenyl)allyl)benzo[d]oxazole (3e)
(E)-2-(1,1-difluoro-3-(4-nitrophenyl)allyl)benzo[d]oxazole (3f)
(E)-2-(3-(2-bromophenyl)-1,1-difluoroallyl)benzo[d]oxazole (3g)
\((E)\)-2-(3-(3-bromophenyl)-1,1-difluorallyl)benzo[\text{d}]oxazole (3h)
(E)-2-(3-(4-bromophenyl)-1,1-difluoroallyl)benzo[d]oxazole (3i)
(Z)-4-(benzo[d]oxazol-2-yl)-4,4-difluoro-2-phenylbut-2-en-1-yl acetate (3j)
(E)-2-(1,1-difluoro-4-phenylbut-2-en-1-yl)benzo[d]oxazole (3k)
(E)-2-(1,1-difluoro-4-phenylbut-3-en-1-yl)benzo[d]oxazole (3k')
(E)-2-(1,1-difluoro-5-phenylpent-2-en-1-yl)benzo[d]oxazole (3l)
2-(2-(2,3-dihydro-1H-inden-1-yl)-1,1-difluoroethyl)benzo[d]oxazole (4l)
2-(1,1-difluoro-5-phenylpentyl)benzo[d]oxazole (5l)
(E)-2-(1,1-difluoroundec-2-en-1-yl)benzo[d]oxazole (3m)
2-(1,1-difluoro-2-(4-phenylcyclohexylidene)ethyl)benzo[d]oxazole (3n)
(E)-2-(1,1-difluoro-7-(naphthalen-2-yloxy)hept-2-en-1-yl)benzo[d]oxazole (3o)
(E)-2-(1,1-difuoro-5-(p-tolyloxy)pent-2-en-1-yl)benzo[d]oxazole (3p)
(E)-2-(1,1-difluoro-4-(p-tolyloxy)but-2-en-1-yl)benzo[d]oxazole (3q)
(E)-6-(benzo[d]oxazol-2-yl)-6,6-difluorohex-4-en-1-yl 4-iodobenzoate (3r)
2-(benzo[d]oxazol-2-yl)fluoromethyl)-3-methylbut-2-en-1-yl 4-bromobenzoate (3s)
p-tolyl (E)-4-(benzo[d]oxazol-2-yl)-4,4-difluoro-2-methylbut-2-enoate (3t)
3-(2-(benzo[d]oxazol-2-yl)-2,2-difluoroethyl)-1,3-dimethylindolin-2-one (4u)
2-(benzofuran-3-ylidifluoromethyl)benzo[d]oxazole (3v)
(E)-2-(1,1-difluoro-3-phenylallyl)-5-methylbenzo[d]oxazole (3w)
(E)-2-(1,1-difluoro-3-phenylallyl)benzo[d]thiazole  (3x)
(E)-2-(1,1-difluoroundec-2-en-1-yl)-5-methylbenzo[d]oxazole (3y)