Supporting Information

Visible-light-mediated radical oxydifluoromethylation of olefinic amides for the synthesis of CF₂H-containing heterocycles

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Table of contents

General ................................................................. 2
General Procedures for Experiments and Analytical Data ................ 2-12
X-ray diffraction analysis of compound 3n ..................................... 13
The ¹H NMR, ¹³C NMR and ¹⁹F NMR Spectra of compounds 3a-s .... 14-70
The ¹H NMR, ¹³C NMR and ¹⁹F NMR Spectra of compounds 5a-e ....... 71-85
**General:** Solvents were purified or dried in a standard manner. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. $^1$H NMR, $^{13}$C NMR and $^{19}$F$^{1}	ext{H}$ NMR spectra were recorded on a 500 MHz NMR spectrometers with TMS as an internal standard. Chemical shifts ($\delta$) are reported in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. HRMS analyses was recorded on Waters Q-TOF Global mass spectrometer. All of olefinic amides 1 and N-allylamides 4 were synthesized according to the literature.$^1$

**General experimental details**

To a mixture of olefinic amides 1 (0.20 mmol), 2-((difluoromethyl)sulfonyl)benzo[d]thiazole (0.24 mmol) and Na$_2$CO$_3$ (0.24 mmol) in 2.0 mL of CH$_3$CN was added fac-Ir(ppy)$_3$ (0.004 mmol, 2.0 mol%) under N$_2$ atmosphere. The solution was stirred at room temperature under 5 W blue LED irradiation for 10 h. Then the reaction mixture was diluted by adding EtOAc and brine. The aqueous layer was extracted with EtOAc The combined organic layer was dried over MgSO$_4$, filtered and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 25:1 as the eluant) on silica gel to give the desired benzoxazine 3.

![Chemical structure](image_url)

4-(2,2-difluoroethyl)-4-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (3a):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.18 (d, $J$ = 7.1 Hz, 2H), 7.56-7.53 (m, 1H), 7.51-7.48 (m, 2H), 7.40-7.36 (m, 2H), 7.29-7.25 (m, 1H), 7.15 (d, $J$ = 7.4 Hz, 1H), 6.05 (tdd, $J$ = 55.8 Hz, $J$ = 5.2 Hz, $J$ = 4.0 Hz, 1H), 2.71-2.49 (m, 2H), 1.83 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 155.8, 138.4, 132.5, 131.6, 129.2, 128.5, 128.4, 127.9, 127.0, 125.7,
122.6, 115.0 (t, \( J = 238.0 \) Hz), 77.5 (t, \( J = 5.8 \) Hz), 45.0(t, \( J = 21.0 \) Hz), 27.5. \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): \( \delta \) -112.2 (d, \( J = 291.0 \) Hz, 1F), -113.0 (d, \( J = 291.0 \) Hz, 1F). HRMS (ESI): calcd for [M+H]\(^+\) C\(_{17}\)H\(_{16}\)F\(_2\)NO: 288.1195, found: 288.1197.

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\text{CF}_2H
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4-(2,2-difluoroethyl)-4-methyl-2-p-tolyl-4H-benzo[d][1,3]oxazine (3b):

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.06 (d, \( J = 8.2 \) Hz, 2H), 7.36 (dd, \( J = 5.1 \) Hz, \( J = 1.2 \) Hz, 2H), 7.29 (d, \( J = 8.1 \) Hz, 2H), 7.26-7.23 (m, 1H), 7.14 (d, \( J = 7.6 \) Hz, 1H), 6.04 (tdd, \( J = 55.9 \) Hz, \( J = 5.1 \) Hz, \( J = 4.1 \) Hz, 1H), 2.69-2.48 (m, 2H), 2.45 (s, 3H), 1.82 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 156.0, 142.1, 138.6, 129.7, 129.2, 129.1, 128.5, 127.8, 126.7, 125.5, 122.6, 114.9 (t, \( J = 238.0 \) Hz), 77.4 (t, \( J = 5.5 \) Hz), 44.9 (t, \( J = 21.3 \) Hz), 27.3, 21.6. \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): \( \delta \) -112.2 (d, \( J = 291.0 \) Hz, 1F), -113.0 (d, \( J = 290.0 \) Hz, 1F). HRMS (ESI): calcd for [M+H]\(^+\) C\(_{18}\)H\(_{18}\)F\(_2\)NO: 302.1351, found: 302.1354.

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\text{CF}_2H
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4-(2,2-difluoroethyl)-2-(4-methoxyphenyl)-4-methyl-4H-benzo[d][1,3]oxazine (3c):

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.11 (d, \( J = 8.9 \) Hz, 2H), 7.36-7.34 (m, 2H), 7.25-7.21 (m, 1H), 7.13 (d, \( J = 7.4 \) Hz, 1H), 6.98 (d, \( J = 8.9 \) Hz, 2H), 6.03 (tdd, \( J = 55.8 \) Hz, \( J = 5.0 \) Hz, \( J = 4.1 \) Hz, 1H), 3.89 (s, 3H), 2.68-2.46 (m, 2H), 1.81 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 162.5, 155.8, 138.7, 129.7, 129.2, 128.4, 126.5, 125.4, 124.9, 122.5, 115.0 (t, \( J = 238.0 \) Hz), 113.7, 77.3 (t), 55.4, 44.8 (t, \( J = 21.2 \) Hz), 27.2. \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): \( \delta \) -112.2 (d, \( J = 291.0 \) Hz, 1F), -113.0 (d, \( J = 290.0 \) Hz, 1F). HRMS (ESI): calcd for [M+H]\(^+\) C\(_{18}\)H\(_{18}\)F\(_2\)NO\(_2\): 318.1300, found: 318.1297.
4-(2,2-difluoroethyl)-2-(4-fluorophenyl)-4-methyl-4H-benzo[d][1,3]oxazine (3d):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.17 (dd, $J = 8.8$ Hz, $J = 5.5$ Hz, 2H), 7.39-7.34 (m, 2H), 7.28-7.24 (m, 1H), 7.18-7.14 (m, 3H), 6.01 (tt, $J = 55.7$ Hz, $J = 4.3$ Hz, 1H), 2.69-2.47 (m, 2H), 1.83 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 165.0 (d, $J = 250.8$ Hz), 154.9, 138.3, 130.1 (d, $J = 8.7$ Hz), 129.3, 128.6, 128.3, 127.0, 125.6, 122.6, 115.9 (t, $J = 238.0$ Hz), 115.4 (d, $J = 21.8$ Hz), 77.7 (t, $J = 5.9$ Hz), 45.0 (t, $J = 21.2$ Hz), 27.5. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -118.1 (s, 1F), -112.3 (d, $J = 290.9$ Hz, 1F), -113.0 (d, $J = 290.6$ Hz, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{17}$H$_{15}$F$_3$NO: 306.1100, found: 306.1105.

2-(4-chlorophenyl)-4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (3e):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.10 (d, $J = 8.6$ Hz, 2H), 7.45 (d, $J = 8.7$ Hz, 2H), 7.39-7.34 (m, 2H), 7.29-7.25 (m, 1H), 7.14 (d, $J = 7.9$ Hz, 1H), 6.12-5.88 (m, 1H), 2.68-2.46 (m, 2H), 1.82 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 154.9, 138.2, 137.8, 131.0, 129.3, 129.2, 128.6, 128.3, 127.2, 125.7, 122.7, 114.9 (t, $J = 237.8$ Hz), 77.8 (t, $J = 5.9$ Hz), 45.0 (t, $J = 21.1$ Hz), 27.5. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -112.3 (d, $J = 291.0$ Hz, 1F), -112.9 (d, $J = 290.8$ Hz, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{17}$H$_{15}$ClF$_2$NO: 322.0805, found: 322.0804.

2-(4-bromophenyl)-4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (3f):
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.02 (d, $J = 8.6$ Hz, 2H), 7.60 (d, $J = 8.6$ Hz, 2H), 7.39-7.34 (m, 2H), 7.29-7.25 (m, 1H), 7.14 (d, $J = 7.3$ Hz, 1H), 5.99 (tt, $J = 55.2$ Hz, $J = 4.9$ Hz, 1H), 2.67-2.46 (m, 2H), 1.82 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 155.0, 138.1, 131.6, 131.4, 129.4, 129.3, 128.3, 127.2, 126.4, 125.7, 122.7, 114.9 (t, $J = 238.1$ Hz), 77.8 (t, $J = 5.7$ Hz), 45.0 (t, $J = 21.2$ Hz), 27.5. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -112.3 (d, $J = 290.9$ Hz, 1F), -113.0 (d, $J = 291.0$ Hz, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{17}$H$_{18}$BrF$_2$NO: 366.0300, found: 366.0304.

![Structure](image)

4-(2,2-difluoroethyl)-2-(4-(trifluoromethyl)phenyl)-4-methyl-4H-benzo[d][1,3]oxazine (3g):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.24 (d, $J = 8.2$ Hz, 2H), 7.69 (d, $J = 8.3$ Hz, 2H), 7.35-7.34 (m, 2H), 7.27-7.24 (m, 1H), 7.12 (d, $J = 7.6$ Hz, 1H), 5.96 (tdd, $J = 55.6$ Hz, $J = 5.0$ Hz, $J = 4.3$ Hz, 1H), 2.65-2.44 (m, 2H), 1.81 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 154.4, 138.0, 135.8, 133.0 (q, $J = 32.4$ Hz), 129.4, 128.3, 128.1, 127.6, 126.0, 125.3 (q, $J = 3.5$ Hz), 123.9 (q, $J = 270.9$ Hz), 122.7, 114.8 (t, $J = 237.9$ Hz), 78.0 (t, $J = 5.7$ Hz), 45.1 (t, $J = 21.3$ Hz), 27.6. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -62.8 (s, 3F), -112.70 (s, 1F), -112.72 (s, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{18}$H$_{15}$F$_5$NO: 356.1069, found: 356.1075.

![Structure](image)

4-(4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazin-2-yl)benzonitrile (3h):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.26 (d, $J = 8.6$ Hz, 1H), 7.76 (d, $J = 8.6$ Hz, 1H), 7.40-7.35 (m, 2H), 7.30 (td, $J = 7.6$ Hz, $J = 1.9$ Hz, 1H), 7.16 (d, $J = 7.9$ Hz, 1H), 5.98 (tdd, $J = 55.7$ Hz, $J = 5.0$ Hz, $J = 4.3$ Hz, 1H), 2.68-2.47 (m, 2H), 1.84 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 153.9, 137.8, 136.6, 132.1, 129.4, 128.24, 128.16, 127.9,
126.1, 122.8, 118.4, 114.8 (t, $J = 238.1$ Hz), 114.7, 78.2 (t, $J = 6.1$ Hz), 45.2 (t, $J = 21.3$ Hz), 27.8. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -112.7 (s, 2F). HRMS (ESI): calcd for [M+H]$^+$ C$_{18}$H$_{15}$F$_2$N$_2$O: 313.1147, found: 313.1152.

4-(2,2-difluoroethyl)-4-methyl-2-o-tolyl-4H-benzo[d][1,3]oxazine (3i):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.80 (d, $J = 7.9$ Hz, 1H), 7.40-7.33 (m, 3H), 7.31-7.26 (m, 3H), 7.14 (d, $J = 7.8$ Hz, 1H), 5.99 (tdd, $J = 55.9$ Hz, $J = 5.1$ Hz, $J = 4.1$ Hz, 1H), 2.74-2.54 (m, 2H), 2.67 (s, 3H), 1.82 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 157.5, 138.3, 138.2, 132.4, 131.5, 130.5, 129.4, 129.2, 127.8, 127.1, 125.8, 125.7, 122.6, 115.0 (t, $J = 237.6$ Hz), 77.9 (t, $J = 6.1$ Hz), 45.1 (t, $J = 21.2$ Hz), 28.0, 21.6. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -112.3 (d, $J = 290.9$ Hz, 1F), -113.0 (d, $J = 290.3$ Hz, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{18}$H$_{18}$F$_2$NO: 302.1351, found: 302.1350.

4-(2,2-difluoroethyl)-2-(2-fluorophenyl)-4-methyl-4H-benzo[d][1,3]oxazine (3j):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.97 (td, $J = 8.9$ Hz, $J = 1.8$ Hz, 1H), 7.48-7.31 (m, 4H), 7.26-7.20 (m, 2H), 7.15-7.10 (m, 2H), 6.06 (tdd, $J = 56.0$ Hz, $J = 5.5$ Hz, $J = 3.5$ Hz, 1H), 2.69-2.48 (m, 2H), 1.79 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 161.5 (d, $J = 255.4$ Hz), 154.6 (d, $J = 2.9$ Hz), 138.0, 132.9 (d, $J = 8.8$ Hz), 131.1, 129.2, 128.5, 127.4, 125.8, 124.1 (d, $J = 3.6$ Hz), 122.6, 121.1 (d, $J = 9.7$ Hz), 116.8 (d, $J = 22.1$ Hz), 115.0 (t, $J = 237.4$ Hz), 78.1 (dd, $J = 7.9$ Hz, $J = 4.5$ Hz), 44.9 (t, $J = 21.5$ Hz), 27.3. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -111.4 (s, 1F), -112.1 (d, $J = 290.9$ Hz, 1F), -113.2 (d, $J = 290.8$ Hz, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{17}$H$_{15}$F$_3$NO: 306.1100, found: 306.1103.
2-(2-chlorophenyl)-4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (3k):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.75 (dd, $J = 7.6$ Hz, $J = 1.7$ Hz, 1H), 7.45 (dd, $J = 8.0$ Hz, $J = 1.2$ Hz, 1H), 7.39 (td, $J = 7.4$ Hz, $J = 1.8$ Hz, 1H), 7.35-7.30 (m, 3H), 7.28-7.25 (m, 1H), 7.11 (d, $J = 7.8$ Hz, 1H), 6.03 (tdd, $J = 55.9$ Hz, $J = 5.3$ Hz, $J = 3.9$ Hz, 1H), 2.73-2.54 (m, 2H), 1.81 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 156.3, 137.8, 133.1, 132.5, 131.4, 131.2, 130.7, 129.2, 127.9, 127.5, 126.8, 125.8, 122.7, 115.0 (t, $J = 237.6$ Hz), 78.9 (t, $J = 5.3$ Hz), 45.2 (t, $J = 21.6$ Hz), 28.2. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -112.4 (d, $J = 290.9$ Hz, 1F), -113.2 (d, $J = 290.5$ Hz, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{17}$H$_{15}$ClF$_2$NO: 322.0805, found: 322.0891.

4-(2,2-difluoroethyl)-4-methyl-2-m-tolyl-4H-benzo[d][1,3]oxazine (3l):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.99 (s, 1H), 7.94 (d, $J = 7.1$ Hz, 1H), 7.39-7.34 (m, 4H), 7.27-7.24 (m, 1H), 7.14 (d, $J = 7.6$ Hz, 1H), 6.03 (tt, $J = 55.8$ Hz, $J = 5.1$ Hz, 1H), 2.69-2.49 (m, 2H), 2.46 (s, 3H), 1.83 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 156.0, 138.5, 138.1, 132.4, 132.3, 129.2, 128.5, 128.4, 128.2, 126.9, 125.6, 125.0, 122.6, 114.9 (t, $J = 238.0$ Hz), 77.5 (t, $J = 5.8$ Hz), 44.9 (t, $J = 21.3$ Hz), 27.4, 21.4. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -112.3 (d, $J = 290.8$ Hz, 1F), -113.0 (d, $J = 290.8$ Hz, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{18}$H$_{18}$F$_2$NO: 302.1351, found: 302.1352.

2-(3-bromophenyl)-4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (3m):
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.26 (s, 1H), 8.05 (d, $J$ = 7.9 Hz, 1H), 7.62 (dd, $J$ = 7.9 Hz, $J$ = 0.6 Hz, 1H), 7.35-7.29 (m, 3H), 7.25-7.22 (m, 1H), 7.11 (d, $J$ = 7.6 Hz, 1H), 5.96 (tt, $J$ = 60.5 Hz, $J$ = 4.8 Hz, 1H), 2.64-2.44 (m, 2H), 1.79 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 154.4, 138.0, 134.5, 134.4, 130.8, 129.9, 129.3, 128.2, 127.4, 126.4, 125.8, 122.7, 122.5, 114.9 (t, $J$ = 238.1 Hz), 77.9 (t, $J$ = 6.1 Hz), 45.0 (t, $J$ = 21.5 Hz), 27.6. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -112.3 (d, $J$ = 291.0 Hz, 1F), -113.0 (d, $J$ = 291.1 Hz, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{17}$H$_{15}$BrF$_2$NO: 366.0300, found: 366.0303.

2-(2,6-dichlorophenyl)-4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (3n):
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.40 (d, $J$ = 1.2 Hz, 1H), 7.38 (s, 1H), 7.37-7.35 (m, 1H), 7.34-7.32 (m, 2H), 7.31-7.29 (m, 1H), 7.14 (d, $J$ = 7.4 Hz, 1H), 6.10 (tt, $J$ = 55.9 Hz, $J$ = 4.1 Hz, 1H), 2.85-2.75 (m, 1H), 2.59-2.49 (m, 1H), 1.85 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 153.6, 136.8, 134.1, 132.9, 131.0, 129.3, 128.1, 127.9, 127.7, 126.0, 123.1, 114.8 (t, $J$ = 237.7 Hz), 79.5 (t, $J$ = 5.4 Hz), 45.7 (t, $J$ = 21.4 Hz), 29.1. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -112.4 (d, $J$ = 290.8 Hz, 1F), -113.7 (d, $J$ = 289.7 Hz, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{17}$H$_{14}$Cl$_2$F$_2$NO: 356.0415, found: 356.0417.

4-(2,2-difluoroethyl)-4-methyl-2-(thiophen-2-yl)-4H-benzo[d][1,3]oxazine (3o):
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.75 (dd, $J$ = 3.7 Hz, $J$ = 1.2 Hz, 1H), 7.53 (dd, $J$ = 5.0 Hz, $J$ = 1.2 Hz, 1H), 7.37-7.31 (m, 2H), 7.25-7.22 (m, 1H), 7.15-7.12 (m, 2H), 6.04 (tdd, $J$ = 55.8 Hz, $J$ = 5.2 Hz, $J$ = 4.0 Hz, 1H), 2.69-2.44 (m, 2H), 1.82 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 152.5, 138.3, 136.8, 130.5, 123.0, 129.2, 128.5, 127.8, 126.8, 125.4, 122.6, 114.8 (t, $J$ = 237.7 Hz), 77.9 (dd, $J$ = 6.6 Hz, $J$ = 5.2 Hz), 44.8 (t, $J$ = 21.2 Hz), 27.1. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -112.2 (d, $J$ = 290.9 Hz, 1F), -
113.1 (d, J = 290.9 Hz, 1F). HRMS (ESI): calcd for [M+H]+ C_{15}H_{14}F_{2}NO: 294.0759, found: 294.0764.

2-cyclopropyl-4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (3p):

^1^H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta \) 7.27-7.23 (m, 1H), 7.15-7.11 (m, 2H), 7.00 (d, \( J = 7.6 \) Hz, 1H), 5.95-5.71 (m, 1H), 2.51-2.32 (m, 2H), 1.71-1.66 (m, 1H), 1.62 (s, 3H), 1.04-1.02 (m, 2H), 0.87-0.83 (m, 2H). \(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}): \( \delta \) 162.4, 138.2, 129.1, 127.7, 126.1, 124.4, 122.5, 114.9 (t, \( J = 237.9 \) Hz), 77.1 (t), 44.9 (t, \( J = 21.2 \) Hz), 27.6, 14.6, 6.8, 6.7. \(^{19}\)F NMR (470 MHz, CDCl\textsubscript{3}): \( \delta \) -112.2 (d, \( J = 290.5 \) Hz, 1F), -112.9 (d, \( J = 291.0 \) Hz, 1F). HRMS (ESI): calcd for [M+H]+ C_{14}H_{16}F_{2}NO: 252.1195, found: 252.1191.

4-(2,2-difluoroethyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine (3r):

^1^H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta \) 8.27 (dd, \( J = 8.1 \) Hz, 2H), 7.57-7.49 (m, 3H), 7.44-7.37 (m, 4H), 7.34-7.26 (m, 5H), 6.09 (tt, \( J = 55.7 \) Hz, \( J = 4.3 \) Hz, 1H), 3.06 (td, \( J = 15.1 \) Hz, \( J = 4.2 \) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}): \( \delta \) 155.9, 142.0, 139.2, 132.1, 131.7, 129.5, 128.6, 128.4, 128.3, 127.9, 126.7, 126.5, 125.9, 125.5, 124.4, 115.2 (t, \( J = 238.7 \) Hz), 80.9 (t, \( J = 6.4 \) Hz), 44.9 (t, \( J = 22.2 \) Hz). \(^{19}\)F NMR (470 MHz, CDCl\textsubscript{3}): \( \delta \) -111.0 (d, \( J = 289.1 \) Hz, 1F), -112.0 (d, \( J = 289.1 \) Hz, 1F). HRMS (ESI): calcd for [M+H]+ C_{22}H_{18}BrF_{2}NO: 350.1351, found: 350.1356.

6-chloro-4-(2,2-difluoroethyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine (3s):
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.26 (d, $J = 7.7$ Hz, 2H), 7.59-7.56 (m, 1H), 7.53-7.50 (m, 2H), 7.39-7.36 (m, 5H), 7.35-7.32 (m, 2H), 7.23 (d, $J = 1.6$ Hz, 1H), 6.08 (tt, $J = 59.9$ Hz, $J = 4.3$ Hz, 1H), 3.06-2.99 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 156.1, 141.2, 137.8, 131.9, 131.8, 131.7, 129.7, 128.8, 128.7, 128.5, 128.2, 128.0, 127.2, 125.4, 124.5, 115.0 (t, $J = 238.7$ Hz), 80.7 (t, $J = 5.6$ Hz), 44.7 (t, $J = 22.4$ Hz). $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -111.1 (d, $J = 289.6$ Hz, 1F), -112.2 (d, $J = 290.8$ Hz, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{22}$H$_{17}$ClF$_2$NO: 384.0961, found: 384.0967.

![Image of 4-ethyl-4-(2,2-difluoroethyl)-2-phenyl-4H-benzo[d][1,3]oxazine (3t):](image)

4-ethyl-4-(2,2-difluoroethyl)-2-phenyl-4H-benzo[d][1,3]oxazine (3t):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.18 (d, $J = 8.2$ Hz, 2H), 7.56-7.48 (m, 3H), 7.38-7.34 (m, 2H), 7.27-7.23 (m, 1H), 7.08 (d, $J = 7.5$ Hz, 1H), 5.98 (tt, $J = 60.4$ Hz, $J = 4.5$ Hz, 1H), 2.61 (td, $J = 15.9$ Hz, $J = 4.5$ Hz, 2H), 2.16-2.07 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 156.0, 139.2, 132.5, 131.5, 129.1, 128.3, 127.8, 126.8, 125.8, 125.7, 123.3, 115.2 (t, $J = 237.9$ Hz), 80.8 (t, $J = 5.8$ Hz), 44.6 (t, $J = 21.1$ Hz), 34.1, 7.7. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -112.4 (s, 2F). HRMS (ESI): calcd for [M+H]$^+$ C$_{18}$H$_{16}$F$_2$NO: 302.1351, found: 302.1350.

![Image of 5-(2,2-difluoroethyl)-4,5-dihydro-5-phenyl-2-p-tolyloxazole (5a):](image)

5-(2,2-difluoroethyl)-4,5-dihydro-5-phenyl-2-p-tolyloxazole (5a):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.96 (d, $J = 8.1$ Hz, 2H), 7.43-7.42 (m, 4H), 7.39-7.32 (m, 1H), 7.29 (d, $J = 8.3$ Hz, 2H), 5.83 (tt, $J = 55.7$ Hz, $J = 4.7$ Hz, 1H), 4.33 (d, $J = 14.7$ Hz, 1H), 4.19 (d, $J = 14.8$ Hz, 1H), 2.68-2.61 (m, 2H), 2.45 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 163.0, 142.9, 142.2, 129.2, 128.9, 128.2, 128.0, 124.6, 124.3, 115.0 (t, $J = 238.2$ Hz), 85.4 (t, $J = 5.9$ Hz), 68.0, 45.3 (t, $J = 21.5$ Hz), 21.6. $^{19}$F NMR
(470 MHz, CDCl$_3$): $\delta$-113.11 (s, 1F), -113.13 (s, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{18}$H$_{18}$F$_2$NO: 302.1351, found: 302.1352.

5-(2,2-difluoroethyl)-2-(4-fluorophenyl)-4,5-dihydro-5-phenyloxazole (5b):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.04 (dd, $J$ = 8.8 Hz, $J$ = 5.4 Hz, 2H), 7.42-7.37 (m, 4H), 7.34-7.31 (m, 1H), 7.14 (t, $J$ = 8.6 Hz, 2H), 5.78 (tt, $J$ = 55.7 Hz, $J$ = 4.7 Hz, 1H), 4.31 (d, $J$ = 14.8 Hz, 1H), 4.19 (d, $J$ = 14.8 Hz, 1H), 2.65-2.58 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 164.9 (d, $J$ = 250.9 Hz), 161.9, 142.7, 130.5 (d, $J$ = 8.7 Hz), 129.0, 128.0, 124.3, 123.7 (d, $J$ = 3.3 Hz), 115.7 (d, $J$ = 22.1 Hz), 115.0 (t, $J$ = 238.3 Hz), 85.8 (t, $J$ = 5.6 Hz), 68.1, 45.3 (t, $J$ = 21.2 Hz). $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -107.5 (s, 1F), -113.19 (s, 1F), -113.20 (s, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{17}$H$_{15}$F$_3$NO: 306.1100, found: 306.1104.

2-(4-chlorophenyl)-5-(2,2-difluoroethyl)-4,5-dihydro-5-phenyloxazole (5c):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.99 (d, $J$ = 8.6 Hz, 2H), 7.47-7.43 (m, 3H), 7.42-7.39 (m, 3H), 7.37-7.34 (m, 1H), 5.80 (tt, $J$ = 55.7 Hz, $J$ = 4.7 Hz, 1H), 4.34 (d, $J$ = 14.9 Hz, 1H), 4.21 (d, $J$ = 14.9 Hz, 1H), 2.68-2.61 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 162.0, 142.6, 138.0, 129.6, 129.0, 128.9, 128.1, 125.9, 124.3, 114.9 (t, $J$ = 238.4 Hz), 85.8 (t, $J$ = 5.6 Hz), 68.1, 45.2 (t, $J$ = 21.4 Hz). $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -113.22 (s, 1F), -113.23 (s, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{17}$H$_{15}$ClF$_2$NO: 322.0805, found: 322.0809.
2-(4-bromophenyl)-5-(2,2-difluoroethyl)-4,5-dihydro-5-phenyloxazole (5d): 

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.89 (d, $J = 8.5$ Hz, 2H), 7.59 (d, $J = 8.6$ Hz, 2H), 7.42-7.36 (m, 4H), 7.34-7.31 (m, 1H), 5.77 (tt, $J = 55.7$ Hz, $J = 4.7$ Hz, 1H), 4.31 (d, $J = 15.0$ Hz, 1H), 4.18 (d, $J = 14.9$ Hz, 1H), 2.65-2.58 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 162.1, 142.6, 131.8, 129.8, 129.0, 128.1, 126.4, 126.3, 124.3, 114.9 (t, $J = 238.4$ Hz), 85.8 (t, $J = 5.8$ Hz), 68.1, 45.2 (t, $J = 21.4$ Hz). $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -113.2 (s, 1F), -113.2 (s, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{17}$H$_{15}$BrF$_2$NO: 366.0300, found: 366.0306.

2-(3-bromophenyl)-5-(2,2-difluoroethyl)-4,5-dihydro-5-phenyloxazole (5e): $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.20 (d, $J = 1.6$ Hz, 1H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.68 (d, $J = 8.1$ Hz, 1H), 7.45-7.40 (m, 4H), 7.38-7.35 (m, 2H), 5.81 (tt, $J = 55.7$ Hz, $J = 4.6$ Hz, 1H), 4.36 (d, $J = 15.0$ Hz, 1H), 4.23 (d, $J = 14.9$ Hz, 1H), 2.68-2.61 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 161.5, 142.6, 134.7, 131.2, 130.1, 129.4, 129.0, 128.1, 126.8, 124.3, 122.6, 114.9 (t, $J = 238.4$ Hz), 86.0 (t, $J = 5.8$ Hz), 68.0, 45.3 (t, $J = 21.5$ Hz). $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -113.2 (s, 1F), -113.2 (s, 1F). HRMS (ESI): calcd for [M+H]$^+$ C$_{17}$H$_{15}$BrF$_2$NO: 366.0300, found: 366.0304.

References:
Figure 1 The ORTEP drawing of 3n (Thermal ellipsoids are set at 30% probability level)
NO2

CF2H

116.6972

114.7925

114.704

112.8867

78.216

78.2130

78.1650

117 116 115 114 ppm

78.2 ppm

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
\[
\begin{align*}
\text{Ph} & \quad \text{CF}_2\text{H} \\
\end{align*}
\]