Supporting Information

Light-mediated copper-catalyzed phosphorus/halogen exchange
in 1,1-difluoroalkylphosphonium salts

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Content

<table>
<thead>
<tr>
<th></th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>General Methods</td>
<td>S2</td>
</tr>
<tr>
<td>Compounds 5a-r</td>
<td>S3-S8</td>
</tr>
<tr>
<td>Compounds 6a-f</td>
<td>S8-S11</td>
</tr>
<tr>
<td>Compounds 7a-g</td>
<td>S11-S14</td>
</tr>
<tr>
<td>NMR spectra</td>
<td>S15-S75</td>
</tr>
<tr>
<td>UV-vis spectra</td>
<td>S76</td>
</tr>
</tbody>
</table>
Experimental

General Methods. All reactions were performed under an argon atmosphere. 1,2-Dichloroethane was distilled from CaH₂. MeCN was distilled twice: from P₂O₅ and CaH₂ successively and stored over MS 3Å. Column chromatography was carried out employing silica gel (230-400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or acidic aq. KMnO₄ solution. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and time-of-flight (TOF) mass analyzer. The measurements were done in a positive ion mode (interface capillary voltage – 4500 V) or in a negative ion mode (3200 V); mass range from m/z 50 to m/z 3000. For the irradiation, 400 nm LED, the strip of diodes smd 3528, 50 cm (3528-120LED-1M, 12 V, IP 33) was used. Reactions were performed in a glass tube (outer diameter 16 mm, inner diameter 13.4 mm). The reaction tube was placed in a glass jacket, which was wrapped by a strip of LEDs. The distance between the reaction vessel and diodes was about 1 cm. Absorption spectra were recorded at SF-2000 UV/Vis spectrophotometer (OKB Spectr) in 1 cm quartz cuvettes at room temperature. Phosphobetaine 1 was obtained according to a literature procedure. ¹

Synthesis of iododifluoromethylated alcohols 5
(General procedure 1).

A reaction tube equipped with a magnetic stirring bar was charged with betaine 1 (428 mg, 1.2 mmol, 1.2 equiv), evacuated and backfilled with argon. Dichloroethane (2 mL), aldehyde (1 mmol) and Me₃SiCl (190 μL, 1.5 mmol, 1.5 equiv) were added successively. The suspension was stirred at 45–50 °C until complete dissolution of betaine 1 (2–5 h). Methyl iodide (155 μL, 2.5 mmol, 2.5 eq) was added, and the mixture was stirred for additional 5 min. Then, CuI (19 mg, 0.1 mmol, 0.1 eq) was added and the reaction vessel was irradiated with 400 nm LED for 18 h; during irradiation the mixture was cooled with room temperature water. For the desilylative work-up, ethanol (750 μL) and trifluoroacetic acid (250 μL) were added and the mixture was stirred at room temperature for 5 h. The mixture was diluted with water (5 mL) and extracted with EtOAc/hexane (1/2, 3×10 mL). The combined organic phases were filtered through Na₂SO₄, concentrated under vacuum, and the residue was purified by column chromatography on silica gel eluting with hexane/EtOAc.

1-(4-Chlorophenyl)-2,2-difluoro-2-iodoethan-1-ol (5a).\(^2\)

Yield 254 mg (80%). Light yellow crystals. Mp 43-45 °C. Chromatography: hexane/EtOAc, 5/1 \(R_f\) 0.32 (hexane/EtOAc 5/1).

\(^1\)H NMR (300 MHz, CDCl\(_3\)), \(\delta\): 7.51-7.33 (m, 4H), 4.68 (ddd, \(J = 10.6, 7.5, 4.4\) Hz, 1H), 2.84 (d, \(J = 4.4\) Hz, 1H).

4-(2,2-Difluoro-1-hydroxy-2-iodoethyl)benzonitrile (5b).\(^3\)

Yield 263 mg (85%). White crystals. Mp 106-107 °C. Chromatography: hexane/EtOAc, 3/1 \(R_f\) 0.26 (hexane/EtOAc 3/1).

\(^1\)H NMR (300 MHz, CDCl\(_3\)), \(\delta\): 7.85-7.54 (m, 4H), 4.75 (ddd, \(J = 10.5, 7.2, 4.1, 1H\), 3.04 (d, \(J = 4.1\) Hz, 1H).

Methyl 4-(2,2-difluoro-1-hydroxy-2-iodoethyl)benzoate (5c).\(^2\)

Yield 308 mg (90%). White crystals. Mp 82-83 °C. Chromatography: hexane/EtOAc, 4/1 \(R_f\) 0.25 (hexane/EtOAc 4/1).

\(^1\)H NMR (300 MHz, CDCl\(_3\)), \(\delta\): 8.01 (d, \(J = 8.2\) Hz, 2H), 7.57 (d, \(J = 8.2\) Hz, 2H), 4.74 (ddd, \(J = 10.0, 7.8, 4.8\) Hz, 1H), 4.17 (d, \(J = 4.8\) Hz, 1H), 3.91 (s, 3H).

2,2-Difluoro-2-iodo-1-(4-methoxyphenyl)ethan-1-ol (5d).\(^2\)

Yield 235.5 mg (75%). White crystals. Mp 63-65 °C. Chromatography: hexane/EtOAc, 5/1. \(R_f\) 0.18 (hexane/EtOAc 7/1).

\(^1\)H NMR (300 MHz, CDCl\(_3\)), \(\delta\): 7.42 (d, \(J = 8.7\) Hz, 2H), 6.93 (d, \(J = 8.7\) Hz, 2H), 4.65 (ddd, \(J = 12.9, 8.7, 4.7\) Hz, 1H), 3.85 (s, 3H), 2.81 (br, 1H).


2,2-Difluoro-2-iodo-1-(3,4,5-trimethoxyphenyl)ethan-1-ol (5e).\(^4\)

![Chemical Structure of 5e](image)

Yield 303 mg (81%). White crystals. Mp 174-175 °C. Chromatography: hexane/EtOAc, 1/1 \(R_f\) 0.36 (hexane/EtOAc 1/1).

\(^1\)H NMR (300 MHz, CDCl\(_3\)), \(\delta\): 6.72 (s, 2H), 4.70–4.59 (m, 1H), 3.90 (s, 6H), 3.89 (s, 3H), 2.89 (br, 1H).

1-(2,4-Dichlorophenyl)-2,2-difluoro-2-iodoethan-1-ol (5f).\(^4\)

![Chemical Structure of 5f](image)

Yield 300 mg (85%). Light yellow oil. Chromatography: hexane/EtOAc, 7/1. \(R_f\) 0.34 (hexane/EtOAc 7/1).

\(^1\)H NMR (300 MHz, CDCl\(_3\)), \(\delta\): 7.69 (d, \(J = 8.5\) Hz, 1H), 7.45 (d, \(J = 2.1\) Hz, 1H), 7.36 (dd, \(J = 8.5, 2.1\) Hz, 1H), 5.36 (dd, \(J = 11.2, 6.9\) Hz, 1H), 2.90 (br, 1H).

1-[4-(2,2-Difluoro-1-hydroxy-2-iodoethyl)phenyl]ethanone (5g).

![Chemical Structure of 5g](image)

Yield 267 mg (82%). White crystals. Mp 109-111 °C. Chromatography: hexanes/EtOAc, 2/1. \(R_f\) 0.29 (hexanes/EtOAc, 2/1).

\(^1\)H NMR (300 MHz, CDCl\(_3\)), \(\delta\): 7.98 (d, \(J = 8.3\) Hz, 1H), 7.60 (d, \(J = 8.3\) Hz, 2H), 4.75 (ddd, \(J = 11.1, 7.3, 4.5\) Hz, 1H), 3.16 (d, \(J = 4.5\) Hz, 1H), 2.62 (s, 3H).

\(^13\)C\(_{\text{1H}}\) NMR (75 MHz, CDCl\(_3\)), \(\delta\): 198.6, 140.2 (d, \(J = 3.3\) Hz), 137.6, 128.41, 128.35, 107.3 (dd, \(J = 319.5, 317.6\) Hz), 79.4 (t, \(J = 23.6\) Hz), 26.8.

\(^19\)F NMR (282 MHz, CDCl\(_3\)), \(\delta\): –48.8 (dd, \(J = 183.3, 7.3\) Hz, 1F), –54.0 (dd, \(J = 183.3, 11.1\) Hz, 1F).

HRMS (ESI): Calcd for C\(_{10}\)H\(_{10}\)F\(_2\)IO\(_2\) (M+H) 326.9688; found 326.9691.

2,2-Difluoro-2-iodo-1-phenylethan-1-ol (5h).\(^2\)

![Chemical Structure of 5h](image)
Yield 230 mg (81%). Light yellow oil. Chromatography: hexane/EtOAc, 5/1. $R_f$ 0.40 (hexane/EtOAc 5/1).

$^1$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.65-7.33 (m, 5H), 4.70 (dd, $J = 10.6$, 7.8 Hz, 1H), 3.00 (br, 1H).

$^{1}$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.71-7.54 (m, 6H), 7.53-7.33 (m, 3H), 4.77 (dd, $J = 10.7$, 7.6 Hz, 1H), 2.82 (br, 1H).

$^{13}$C{$_{^1}$H} NMR (75 MHz, CDCl$_3$), $\delta$: 137.7 (d, $J = 2.8$ Hz), 134.8, 127.4, 107.7 (dd, $J = 319.6$, 317.3 Hz), 84.2, 80.0 (t, $J = 23.3$ Hz), 25.0.

$^{19}$F NMR (282 MHz, CDCl$_3$), $\delta$: −48.5 (dd, $J = 181.2$, 7.7 Hz, 1F), −53.5 (dd, $J = 181.2$, 10.4 Hz, 1F).

HRMS (ESI): Calcd for C$_{14}$H$_{18}$BF$_2$IO$_3$Na (M+Na) 433.0256; found 433.0253.

Yield 287 mg (70%). White crystals. Mp 117-119 °C. Chromatography: hexanes/EtOAc, 5/1. $R_f$ 0.22 (hexanes/EtOAc, 5/1).

$^1$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.82 (d, $J = 8.0$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 4.66 (dd, $J = 10.4$, 7.7 Hz, 1H), 3.15 (br, 1H), 1.35 (s, 12H).

C$_{14}$H$_{18}$BF$_2$IO$_3$Na (M+Na) 433.0256; found 433.0253.

$^{1}$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.65-7.33 (m, 5H), 4.70 (dd, $J = 10.6$, 7.8 Hz, 1H), 3.00 (br, 1H).

$^{1}$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.71-7.54 (m, 6H), 7.53-7.33 (m, 3H), 4.77 (dd, $J = 10.7$, 7.6 Hz, 1H), 2.82 (br, 1H).

$^{1}$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.82 (d, $J = 8.0$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 4.66 (dd, $J = 10.4$, 7.7 Hz, 1H), 3.15 (br, 1H), 1.35 (s, 12H).

C$_{14}$H$_{18}$BF$_2$IO$_3$Na (M+Na) 433.0256; found 433.0253.

$^{1}$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.82 (d, $J = 8.0$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 4.66 (dd, $J = 10.4$, 7.7 Hz, 1H), 3.15 (br, 1H), 1.35 (s, 12H).

$^{13}$C{$_{^1}$H} NMR (75 MHz, CDCl$_3$), $\delta$: 137.7 (d, $J = 2.8$ Hz), 134.8, 127.4, 107.7 (dd, $J = 319.6$, 317.3 Hz), 84.2, 80.0 (t, $J = 23.3$ Hz), 25.0.

$^{19}$F NMR (282 MHz, CDCl$_3$), $\delta$: −48.5 (dd, $J = 181.2$, 7.7 Hz, 1F), −53.5 (dd, $J = 181.2$, 10.4 Hz, 1F).

HRMS (ESI): Calcd for C$_{14}$H$_{18}$BF$_2$IO$_3$Na (M+Na) 433.0256; found 433.0253.

Yield 250 mg (75%). Yellow oil. Chromatography: hexane/EtOAc, 20/1. $R_f$ 0.21 (hexane/EtOAc 20/1).

$^1$H NMR (300 MHz, CDCl$_3$), $\delta$: 8.03 (d, $J = 7.8$ Hz, 1H), 7.99-7.84 (m, 3H), 7.68-7.42 (m, 3H), 5.58 (ddd, $J = 10.7$, 6.7, 4.1 Hz, 1H), 3.35 (d, $J = 4.1$ Hz, 1H).

2,2-Difluoro-1-(2-furyl)-2-iodoethanol (5l).$^3$

Yield 219 mg (80%). Light yellow oil. Chromatography: hexane/EtOAc, 8/1. $R_f$ 0.23 (hexane/EtOAc 8/1)

$^1$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.49 (d, $J = 1.9$ Hz, 1H), 6.56 (d, $J = 3.4$ Hz, 1H), 6.44 (dd, $J = 3.4$, 1.9 Hz, 1H), 4.80 (t, $J = 9.1$ Hz, 1H), 3.37 (br, 1H).

2,2-Difluoro-2-iodo-1-thien-2-ylethanol (5m).$^4$

Yield 203 mg (70%). Light yellow oil. Chromatography: hexane/EtOAc, 6/1. $R_f$ 0.20 (hexane/EtOAc 6/1)

$^1$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.42 (dd, $J = 5.1$, 1.1 Hz, 1H), 7.23 (d, $J = 3.6$ Hz, 1H), 7.08 (dd, $J = 5.1$, 3.6 Hz, 1H), 4.93 (td, $J = 8.7$, 5.3 Hz, 1H), 3.25 (d, $J = 5.3$ Hz, 1H).

2,2-Difluoro-2-iodo-1-{1-[(4-methylphenyl)sulfonyl]-1H-indol-3-yl}ethanol (5n).$^3$

Yield 357 mg (75%). Yellow oil. Chromatography: CH$_2$Cl$_2$. $R_f$ 0.26 (CH$_2$Cl$_2$).

$^1$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.96 (d, $J = 8.0$ Hz, 1H), 7.82 (s, 1H), 7.77 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.34 (t, $J = 8.0$ Hz, 1H), 7.20-7.30 (m, 3H), 4.93 (ddd, $J = 13.2$, 8.8, 5.0 Hz, 1H), 3.19 (d, $J = 4.0$ Hz, 1H), 2.33 (s, 3H).

2,2-Difluoro-2-iodo-1-(pyridine-2-yl)ethanol (5o).

Yield 157 mg (55%). Yellow oil. Chromatography: hexanes/EtOAc, 2/1. $R_f$ 0.23 (hexanes/EtOAc, 2/1).
\( ^1 \)H NMR (300 MHz, CDCl\(_3\)), \( \delta \): 8.68-8.63 (m, 1H), 7.79 (td, \( J = 7.7, 1.6 \) Hz, 1H), 7.48-7.35 (m, 2H), 4.53 (dd, \( J = 9.0, 6.1 \) Hz, 1H).

\( ^{13} \)C\{\( ^1 \)H\} NMR (75 MHz, CDCl\(_3\)), \( \delta \): 152.1 (d, \( J = 6.5 \) Hz), 148.2, 137.2, 124.6, 123.4 (dd, \( J = 3.9, 1.1 \) Hz), 107.9 (dd, \( J = 320.1, 317.5 \) Hz), 77.4 (dd, \( J = 25.2, 22.8 \) Hz).

\( ^{19} \)F NMR (282 MHz, CDCl\(_3\)), \( \delta \): –46.5 (dd, \( J = 184.5, 6.1 \) Hz, 1F), –54.0 (dd, \( J = 184.5, 9.0 \) Hz, 1F).

HRMS (ESI): Calcd for C\(_7\)H\(_7\)F\(_2\)INO (M+H) 285.9535; found 285.9540.

1,1-Difluoro-1-iodo-4-phenylbutan-2-ol (5p). \(^5\)

Yield 200 mg (64%). Colorless oil. Chromatography: hexane/EtOAc, 5/1 \( R_f \) 0.43 (hexane/EtOAc 5/1).

\( ^1 \)H NMR (300 MHz, CDCl\(_3\)), \( \delta \): 7.41-7.30 (m, 2H), 7.30-7.18 (m, 3H), 3.53-3.24 (m, 1H), 2.98 (ddd, \( J = 14.0, 9.0, 5.1 \) Hz, 1H), 2.79 (dt, \( J = 14.0, 8.3 \) Hz, 1H), 2.38 (d, \( J = 6.0 \) Hz, 1H), 2.26-1.99 (m, 1H), 2.00-1.76 (m, 1H).

(3E)-1,1-Difluoro-1-iodo-4-phenylbut-3-en-2-ol (5q). \(^5\)

Yield 232 mg (75%). Yellow oil. Chromatography: hexane/EtOAc, 7/1 \( R_f \) 0.30 (hexane/EtOAc 7/1).

\( ^1 \)H NMR (300 MHz, CDCl\(_3\)), \( \delta \): 7.54-7.43 (m, 2H), 7.43-7.30 (m, 3H), 6.91 (d, \( J = 15.9 \) Hz, 1H), 6.18 (dd, \( J = 16.0, 5.9 \) Hz, 1H), 4.24-4.13 (m, 1H), 2.46 (br, 1H).

(E)-1,1-Difluoro-1-iodohept-3-en-2-ol (5r).

Yield 188 mg (68%). Yellow oil. Chromatography: hexanes/EtOAc, 5/1. \( R_f \) 0.38 (hexanes/EtOAc 5/1).

\( ^1 \)H NMR (300 MHz, CDCl\(_3\)), \( \delta \): 5.98 (dt, \( J = 15.4, 6.8, 1.3 \) Hz, 1H), 5.45 (ddq, \( J = 15.4, 6.3, 1.3 \) Hz, 1H), 3.90 (br, 1H), 2.75 (br, 1H), 2.07 (q, \( J = 6.8 \) Hz, 2H), 1.44 (sext, \( J = 7.4 \) Hz, 2H), 0.91 (t, \( J = 7.4 \) Hz, 3H).

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$^{13}$C/$^1$H NMR (75 MHz, CDCl$_3$), $\delta$: 138.8, 124.1 (dd, $J = 3.9$, 1.1 Hz), 108.8 (t, $J = 318.4$ Hz), 78.7 (dd, $J = 24.3$, 22.7 Hz), 34.5, 21.9, 13.7.

$^{19}$F NMR (282 MHz, CDCl$_3$), $\delta$: –49.8 (dd, $J = 178.2$, 9.2 Hz, 1F), –53.7 (dd, $J = 178.2$, 7.5 Hz, 1F).

HRMS (ESI): Calcd for C$_7$H$_{11}$F$_2$IONa (M+Na) 298.9715; found 298.9708.

Synthesis of bromodifluoromethylated alcohols 6a,b,d-f (General procedure 2).

A reaction tube equipped with a magnetic stirring bar was charged with betaine 1 (428 mg, 1.2 mmol, 1.2 equiv), evacuated and backfilled with argon. Acetonitrile (2 mL), aldehyde (1 mmol) and Me$_3$SiCl (190 $\mu$L, 1.5 mmol, 1.5 equiv) were added successively. The suspension was stirred at 45–50 °C until complete dissolution of betaine 1 (2–5 h). Then, dimethylsulfate (117 $\mu$L, 1.2 mmol, 1.2 equiv) was added. The mixture was stirred for 5 min, then cooled to room temperature, and the solvent was evaporated under vacuum (8 Torr). Then, acetonitrile (2 mL), CuBr (15 mg, 0.1 mmol, 0.1 equiv), tetrabutylammonium bromide (644 mg, 2 mmol, 2 equiv) were added [for the synthesis of compound 6f, N,N,N',N''-pentamethyldiethylenetriamine (21 $\mu$L, 0.1 mmol, 0.1 equiv) was added]. The reaction vessel was irradiated with 400 nm LED overnight; during irradiation the mixture was cooled with room temperature water. The work-up is the same as in General procedure 1.

2-Bromo-1-(4-chlorophenyl)-2,2-difluoroethanol (6a).$^2$

![Image](https://via.placeholder.com/150)

Yield 223 mg (82%). Colorless oil. Chromatography: hexane/EtOAc, 5/1 R$_f$ 0.35 (hexane/EtOAc 5/1).

$^1$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.52-7.30 (m, 4H), 5.01 (t, $J = 7.5$ Hz, 1H), 3.00 (s, 1H).

4-(2-Bromo-2,2-difluoro-1-hydroxyethyl)benzonitrile (6b).

![Image](https://via.placeholder.com/150)

After column chromatography (hexanes/EtOAc, 3/1, R$_f$ 0.35), the obtained material was purified by preparative HPLC (reversed-phase column C$_{18}$, 21.2×250 mm, 5 $\mu$m, flow rate 12 mL/min, 5% water in acetonitrile, retention time 4.31 min). Yield 173 mg (66%). White crystals. Mp 103-105 °C.
$^1$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.73 (d, $J = 8.2$ Hz, 2H), 7.66 (d, $J = 8.2$ Hz, 2H), 5.08 (ddd, $J = 10.1, 6.4, 4.0$ Hz, 1H), 3.34 (d, $J = 4.0$ Hz, 1H).

$^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$), $\delta$: 139.9 (d, $J = 1.7$ Hz), 132.1, 130.2, 128.9, 123.6 (t, $J = 311.0$ Hz), 118.5, 112.9, 77.5 (t, $J = 25.2$ Hz).

$^{19}$F NMR (282 MHz, CDCl$_3$), $\delta$: −56.6 (dd, $J = 165.3, 6.4$ Hz, 1F), −60.1 (dd, $J = 165.3, 10.1$ Hz, 1F).

HRMS (ESI): Calcd for C$_9$H$_6$$_{79}$BrF$_2$NONa (M+Na) 283.9493; found 283.9501; Calcd for C$_9$H$_6$$_{81}$BrF$_2$NONa (M+Na) 285.9473; found 285.9483.

2-Bromo-1-(3,4-dimethoxyphenyl)-2,2-difluoroethanol (6c).

![Chemical Structure](image)

A reaction tube equipped with a magnetic stirring bar was charged with betaine 1 (428 mg, 1.2 mmol, 1.2 equiv), evacuated and backfilled with argon. Dichloroethane (2 mL), 3,4-dimethoxybenzaldehyde (166 mg, 1 mmol) and Me$_3$SiCl (190 $\mu$L, 1.5 mmol, 1.5 equiv) were added successively. The suspension was heated at 45–50 °C for 5 h until complete dissolution of betaine 1. Then, allyl bromide (171 $\mu$L, 2 mmol, 2 equiv) was added. The mixture was cooled to room temperature, and the solvent was evaporated under vacuum (8 Torr). Then, dichloroethane (2 mL), CuBr (15 mg, 0.1 mmol, 0.1 equiv), tetrabutylammonium bromide (322 mg, 1 mmol, 1 equiv) were added, and the reaction vessel was irradiated with 400 nm LED for 18 h; during irradiation the mixture was cooled with room temperature water. Then, ethanol (750 $\mu$L) and trifluoroacetic acid (250 $\mu$L) were added, and the mixture was stirred at room temperature for 2 h. The mixture diluted with water (5 mL) and extracted with EtOAc/hexane (1/2, 3×10 mL). The combined organic phases were filtered through Na$_2$SO$_4$, concentrated under vacuum, and the residue was purified by column chromatography on silica gel eluting with hexane/EtOAc, 2/1. Yield 211 mg (71%). Colorless oil. $R_f$ 0.27 (hexanes/EtOAc, 2/1).

$^1$H NMR (300 MHz, CDCl$_3$), $\delta$: 6.98 (d, $J = 7.9$ Hz, 2H), 6.83 (d, $J = 8.2$ Hz, 1H), 4.92 (dd, $J = 10.2, 7.3$ Hz, 1H), 3.84 (s, 6H), 3.25 (br, 1H).

$^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$), $\delta$: 149.9, 148.9, 127.0 (d, $J = 2.1$ Hz), 124.4 (t, $J = 311.0$ Hz), 120.9, 119.8, 110.8, 78.3 (t, $J = 25.0$ Hz), 56.0, 55.9.

$^{19}$F NMR (282 MHz, CDCl$_3$), $\delta$: −56.6 (dd, $J = 161.9, 7.3$ Hz, 1F), −59.9 (dd, $J = 161.9, 10.2$ Hz, 1F).

HRMS (ESI): Calcd for C$_{10}$H$_{11}$$_{79}$BrF$_2$O$_3$Na (M+Na) 318.9752; found 318.9758; Calcd for C$_{10}$H$_{11}$$_{81}$BrF$_2$O$_3$Na (M+Na) 320.9732; found 320.9740.
2-Bromo-2,2-difluoro-1-(4-isopropylphenyl)ethanol (6d).

Yield 209 mg (75%). Colorless oil. Chromatography: hexanes/EtOAc, 8/1. R_f 0.25 (hexanes/EtOAc, 8/1).

\[
\begin{align*}
^1H \text{ NMR (300 MHz, CDCl}_3\text{), } &\delta: 7.42 (d, J = 8.0 \text{ Hz}, 2H), 7.30 (d, J = 8.0 \text{ Hz}, 2H), 4.97 (ddd, J = 10.4, 7.2, 4.7 \text{ Hz}, 1H), 3.02-2.90 (m, 2H), 1.30 (d, J = 6.9 \text{ Hz}, 6H). \\
^{13}C\{^1H\} \text{ NMR (75 MHz, CDCl}_3\text{), } &\delta: 150.5, 132.4 (d, J = 10.8 \text{ Hz}), 131.8 (d, J = 1.7 \text{ Hz}), 128.7 (d, J = 12.7 \text{ Hz}), 128.0, 126.6, 124.3 (dd, J = 311.8, 310.2 \text{ Hz}), 78.6 (t, J = 25.0 \text{ Hz}), 34.0, 24.0. \\
^{19}F \text{ NMR (282 MHz, CDCl}_3\text{), } &\delta: -56.5 (dd, J = 161.5, 7.2 \text{ Hz}, 1F), -59.8 (dd, J = 161.5, 10.4 \text{ Hz}, 1F). \\
\end{align*}
\]

Calcd for C_{11}H_{13}BrF_2O (279.12): C, 47.33; H, 4.69. Found: C, 47.35; H, 4.65.

2-Bromo-2,2-difluoro-1-(2-fluorophenyl)ethanol (6e).

\[
\begin{align*}
^1H \text{ NMR (300 MHz, CDCl}_3\text{), } &\delta: 7.65 (t, J = 7.4 \text{ Hz}, 1H), 7.48-7.34 (m, 1H), 7.24 (t, J = 7.6 \text{ Hz}, 1H), 7.17-7.07 (m, 1H), 5.50-5.37 (m, 1H), 3.22 (br, 1H). \\
^{13}C\{^1H\} \text{ NMR (75 MHz, CDCl}_3\text{), } &\delta: 160.6 (d, J = 248.8 \text{ Hz}), 131.3 (d, J = 8.6 \text{ Hz}), 129.2, 124.5 (d, J = 3.6 \text{ Hz}), 123.6 (td, J = 311.8, 1.7 \text{ Hz}), 121.8 (d, J = 13.0 \text{ Hz}), 115.6 (d, J = 21.9 \text{ Hz}), 72.4 (td, J = 26.2, 25.8, 3.4 \text{ Hz}). \\
^{19}F \text{ NMR (282 MHz, CDCl}_3\text{), } &\delta: -57.8 (dt, J = 162.1, 7.8 \text{ Hz}, 1F), -60.3 (dt, J = 162.1, 10.1 \text{ Hz}, 1F), -117.7 (m, 1F). \\
\end{align*}
\]

Calcd for C_{8}H_{8}BrF_3O (255) C, 37.68; H, 2.37. Found: C, 37.54; H, 2.31.

1-Bromo-1,1-difluoro-4-phenylbutan-2-ol (6f).

\[
\begin{align*}
^1H \text{ NMR (300 MHz, CDCl}_3\text{), } &\delta: 7.65 (t, J = 7.4 \text{ Hz}, 1H), 7.48-7.34 (m, 1H), 7.24 (t, J = 7.6 \text{ Hz}, 1H), 7.17-7.07 (m, 1H), 5.50-5.37 (m, 1H), 3.22 (br, 1H). \\
^{13}C\{^1H\} \text{ NMR (75 MHz, CDCl}_3\text{), } &\delta: 160.6 (d, J = 248.8 \text{ Hz}), 131.3 (d, J = 8.6 \text{ Hz}), 129.2, 124.5 (d, J = 3.6 \text{ Hz}), 123.6 (td, J = 311.8, 1.7 \text{ Hz}), 121.8 (d, J = 13.0 \text{ Hz}), 115.6 (d, J = 21.9 \text{ Hz}), 72.4 (td, J = 26.2, 25.8, 3.4 \text{ Hz}). \\
^{19}F \text{ NMR (282 MHz, CDCl}_3\text{), } &\delta: -57.8 (dt, J = 162.1, 7.8 \text{ Hz}, 1F), -60.3 (dt, J = 162.1, 10.1 \text{ Hz}, 1F), -117.7 (m, 1F). \\
\end{align*}
\]

Calcd for C_{8}H_{8}BrF_3O (255) C, 37.68; H, 2.37. Found: C, 37.54; H, 2.31.

1-Bromo-1,1-difluoro-4-phenylbutan-2-ol (6f).

Yield 159 mg (60%). Colorless oil. Chromatography: hexanes/EtOAc, 5/1. R_f 0.44 (hexanes/EtOAc, 5/1).
$^1$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.54-7.03 (m, 5H), 3.93-3.78 (m, 1H), 3.12-2.89 (m, 1H), 2.79 (dt, $J = 13.9, 8.3$ Hz, 1H), 2.52 (d, $J = 6.0$ Hz, 1H), 2.23-2.07 (m, 1H), 2.05-1.89 (m, 1H).

$^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$), $\delta$: 140.6, 128.8, 128.6, 126.5, 125.7 (t, $J = 310.5$ Hz), 75.7 (t, $J = 23.4$ Hz).

$^{19}$F NMR (282 MHz, CDCl$_3$), $\delta$: –56.9 (dd, $J = 162.3$, 8.2 Hz, 1F), –59.8 (dd, $J = 162.3$, 8.2 Hz, 1F).

HRMS (ESI): Calcd for C$_{10}$H$_{11}$Br$_2$F$_2$ONa (M+Na) 286.9854; found 286.9860; Calcd for C$_{10}$H$_{11}$Br$_2$F$_2$ONa (M+Na) 288.9833; found 288.9843.

**Synthesis of chlorodifluoromethylated alcohols 7 (General procedure 3).**

A reaction tube equipped with magnetic stirring bar was charged with betaine 1 (428 mg, 1.2 mmol, 1.2 equiv), evacuated and backfilled with argon. Dichloroethane (2 mL), aldehyde (1 mmol) and Me$_3$SiCl (190 $\mu$L, 1.5 mmol, 1.5 equiv) were added successively. The suspension was heated at 45–50 °C until complete dissolution of betaine 1 (2–5 h). Then, benzyltriethylammonium chloride (113.5 mg, 0.5 mmol, 0.5 equiv) and CuCl (10 mg, 0.1 mmol, 0.1 equiv) were added [for 7g, $N,N,N',N''$-pentamethyldiethylenetriamine (21 $\mu$L, 0.1 mmol, 0.1 equiv) was added]. The reaction vessel was irradiated with 400 nm LED for 18 h; during irradiation the mixture was cooled with room temperature water. The work-up is the same as in General procedure 1.

**2-Chloro-1-(4-chlorophenyl)-2,2-difluoroethanol (7a).**

![2-Chloro-1-(4-chlorophenyl)-2,2-difluoroethanol](image)

Yield 191 mg (84%). Colorless oil. Chromatography: hexane/EtOAc, 10/1 R$_f$ 0.27 (hexane/EtOAc 10/1).

$^1$H NMR (300 MHz, CDCl$_3$), $\delta$: 7.59-7.30 (m, 4H), 5.04 (t, $J = 7.8$ Hz, 1H), 3.43 (br, 1H).

$^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$), $\delta$: 135.6, 132.8 (d, $J = 2.2$ Hz), 129.3 (t, $J = 1.5$ Hz), 128.9 (t, $J = 296.9$ Hz), 128.8, 76.7 (t, $J = 27.8$ Hz).

$^{19}$F NMR (282 MHz, CDCl$_3$), $\delta$: –63.1 (dd, $J = 165.9$, 7.8 Hz, 1F), –64.9 (dd, $J = 165.9$, 7.8 Hz, 1F).

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Methyl 4-(2-chloro-2,2-difluoro-1-hydroxyethyl)benzoate (7b).

Yield 215 mg (86%). Colorless oil. Chromatography: hexanes/EtOAc, 5/1. R$_f$ 0.16 (hexanes/EtOAc, 5/1).

$^1$H NMR (300 MHz, CDCl$_3$), δ: 7.99 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 5.12 (td, J = 7.5, 3.1 Hz, 1H), 4.28 (br, 1H), 3.88 (s, 3H).

$^{13}$C{^1}H NMR (75 MHz, CDCl$_3$), δ: 167.7 (d, J = 3.3 Hz), 140.3, 131.1, 129.9, 129.2 (t, J = 296.4 Hz), 128.4, 77.5 (t, J = 27.9 Hz), 52.9.

$^{19}$F NMR (282 MHz, CDCl$_3$), δ: –63.3 (dd, J = 165.8, 7.5 Hz, 1F), –65.2 (dd, J = 165.8, 7.5 Hz, 1F).

HRMS (ESI): Calcd for C$_{10}$H$_9$Cl$_3$F$_2$O$_3$Na (M+Na) 273.0100; found 273.0104; calcd for C$_{10}$H$_9$Cl$_3$F$_2$O$_3$Na (M+Na) 275.0072; found 275.0078.

2-Chloro-1-(4-chlorophenyl)-2,2-difluoroethanol (7c).

Yield 164 mg (74%). Colorless oil. Chromatography: hexanes/EtOAc, 5/1. R$_f$ 0.32 (hexanes/EtOAc, 5/1).

$^1$H NMR (300 MHz, CDCl$_3$), δ: 7.41 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 5.00 (td, J = 8.1, 4.1 Hz, 1H), 3.83 (s, 3H), 3.16 (d, J = 4.1 Hz, 1H).

$^{13}$C{^1}H NMR (75 MHz, CDCl$_3$), δ: 160.5, 129.2 (t, J = 296.5), 129.2, 126.6, 114.0, 77.1 (t, J = 27.7 Hz), 55.4.

$^{19}$F NMR (282 MHz, CDCl$_3$), δ: –63.9 (dd, J = 164.6, 8.1 Hz, 1F), –65.7 (dd, J = 164.6, 8.1 Hz, 1F).

HRMS (ESI): Calcd for C$_9$H$_9$Cl$_3$F$_2$O$_2$Na (M+Na) 245.0151; found 245.0158; calcd for C$_9$H$_9$Cl$_3$F$_2$O$_2$Na (M+Na) 247.0122; found 247.0129.

1-(1,1'-Biphenyl-4-yl)-2-chloro-2,2-difluoroethanol (7d).

Yield 230 mg (86%). White crystals. Mp 107-109 °C. Chromatography: hexanes/EtOAc, 5/1. R$_f$ 0.30 (hexanes/EtOAc, 5/1).
1H NMR (300 MHz, CDCl3), δ: 7.76-7.51 (m, 6H), 7.51-7.30 (m, 3H), 5.13 (ddd, J = 8.7, 7.2, 4.3 Hz, 1H), 2.76 (d, J = 4.3 Hz, 1H).

13C{1H} NMR (75 MHz, CDCl3), δ: 142.6, 140.5, 133.3 (d, J = 1.1 Hz), 129.1 (t, J = 297.3 Hz), 129.0, 128.4, 127.8, 127.3, 77.3 (t, J = 27.4 Hz).

19F NMR (282 MHz, CDCl3), δ: –63.5 (dd, J = 165.3, 7.2 Hz, 1F), –65.6 (dd, J = 165.3, 8.7 Hz, 1F).

HRMS (ESI): Calcd for C14H1135ClF2ONa (M+Na) 291.0359; found 291.0360; Calcd for C14H1137ClF2ONa (M+Na) 293.0330; found 293.0334.

2-Chloro-2,2-difluoro-1-thien-2-ylethanol (7e).

Yield 150 mg (76%). Light yellow oil. Chromatography: hexanes/EtOAc, 5/1. Rf 0.34 (hexanes/EtOAc).

1H NMR (300 MHz, CDCl3), δ: 7.40 (dd, J = 5.0, 1.3 Hz, 1H), 7.22 (d, J = 3.6 Hz, 1H), 7.06 (dd, J = 5.0, 3.6 Hz, 1H), 5.33 (td, J = 7.6, 5.0 Hz, 1H), 2.83 (d, J = 5.0 Hz, 1H).

13C{1H} NMR (75 MHz, CDCl3), δ: 136.6 (d, J = 1.6 Hz), 128.5 (t, J = 296.8 Hz), 127.9, 127.2, 127.0, 74.2 (t, J = 29.2 Hz).

19F NMR (282 MHz, CDCl3), δ: –64.3 (dd, J = 165.3, 7.6 Hz, 1F), –65.8 (dd, J = 165.3, 7.6 Hz, 1F).

HRMS (ESI): Calcd for C6H535ClF2OSNa (M+Na) 220.9610; found 220.9621; calcd for C6H537ClF2OSNa (M+Na) 222.9580; found 222.9551.

(3E)-1-Chloro-1,1-difluoro-4-phenylbut-3-en-2-ol (7f).

Yield 137 mg (63%). Light yellow oil. Chromatography: hexanes/EtOAc, 7/1. Rf 0.32 (hexanes/EtOAc, 7/1).

1H NMR (300 MHz, CDCl3), δ: 7.61-7.29 (m, 5H), 6.87 (d, J = 16.0 Hz, 1H), 6.24 (dd, J = 16.0, 7.0 Hz, 1H), 4.68 (q, J = 7.0 Hz, 1H), 2.77 (br, 1H).

13C{1H} NMR (75 MHz, CDCl3), δ: 136.5, 135.6, 127.2 (t, J = 296.8 Hz), 128.8, 127.0, 121.5, 76.2 (t, J = 27.9 Hz).

19F NMR (282 MHz, CDCl3), δ: –64.2 (dd, J = 164.3, 7.0 Hz, 1F), –65.6 (dd, J = 164.3, 7.0 Hz, 1F).
HRMS (ESI): Calcd for C$_{10}$H$_9$ClF$_2$ONa (M+Na) 241.0202; found 241.0203; Calcd for C$_{10}$H$_9$ClF$_2$ONa (M+Na) 243.0173; found 243.0186.

1-Chloro-1,1-difluoro-4-phenylbutan-2-ol (7g).

Yield 132 mg (60%). Colorless oil. Chromatography: hexane/EtOAc, 10/1. R$_f$ 0.32 (hexane/EtOAc 10/1).

$^1$H NMR (300 MHz, CDCl$_3$), δ: 7.47-7.33 (m, 2H), 7.32-7.24 (m, 3H), 4.07-3.80 (m, 1H), 3.00 (ddd, $J = 14.0$, 9.0, 5.1 Hz, 1H), 2.80 (dt, $J = 13.9$, 8.3 Hz, 1H), 2.52 (d, $J = 6.0$ Hz, 1H), 2.21-2.08 (m, 1H), 2.07-1.86 (m, 1H).

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$^1$H NMR
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CDCl$_3$
$^1$H NMR
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CDCl$_3$
\( ^1H\text{ NMR} \)

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\( \text{CDCl}_3 \)
$^1$H NMR
300 MHz
CDCl$_3$
**1H NMR**

300 MHz

CDCl₃
$^{13}$C\textsubscript{\textit{H}} NMR
75 MHz
CDCl\textsubscript{3}
$^{19}$F NMR
282 MHz
CDCl$_3$
$^1$H NMR
300 MHz
CDCl$_3$
$^1$H NMR
300 MHz
CDCl$_3$
^1H NMR
300 MHz
CDCl₃
$^{13}$C-$^1$H NMR
75 MHz
CDCl$_3$
$^{19}$F NMR
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$^{13}$C-$^1$H NMR
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$^19$F NMR
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$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C{\textsuperscript{'}}H\textsubscript{NMR}

75 MHz

CDCl\textsubscript{3}
$^{19}$F NMR
282 MHz
CDCl$_3$
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C\{$^1$H} NMR
75 MHz
CDCl$_3$

**Chemical Structure**

![Chemical Structure Image]

- ppm Values: 142.5712, 140.4907, 133.2676, 133.0552, 129.1139, 128.9894, 128.3594, 127.8173, 127.3045, 125.1800, 77.7021, 77.5849, 77.3431, 77.1600, 76.9769, 76.7351

**CDCl$_3$**
$^{19}$F NMR
282 MHz
CDCl$_3$
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C{$^1$H} NMR
75 MHz
CDCl$_3$
\(^{19}\text{F NMR}\)

282 MHz

CDCl\(_3\)
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C{$^1$H} NMR
75 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$
$^1$H NMR
300 MHz
CDCl$_3$
**Figure S1.** Spectrum of the light emitting diode.

**Figure S2.** Spectrum of salt $3\text{a-}I$. $1\times10^{-4}$ M in dichloroethane. The salt was obtained according to General procedure 1.

**Figure S3.** Spectrum of the reaction mixture of salt $3\text{a-}I + \text{CuI (0.1 equiv)}$ after 1.5 h of irradiation; $1\times10^{-5}$ M in dichloroethane. The mixture was obtained according to General procedure 1.