Supporting Information

Novel photoredox-active group for the generation of fluorinated radicals from difluorostyrenes

Mikhail O. Zubkov, Mikhail D. Kosobokov, Vitalij V. Levin, Vladimir A. Kokorekin, Alexander A. Korlyukov, Jinbo Hu and Alexander D. Dilman*
Table of Contents

Experimental Procedures........................................................................................................3
  General methods ..................................................................................................................3
  Synthesis of 2,3,5,6-tetrafluoropyridine-4-thiol 2................................................................3
  Synthesis of gem-difluorostyrenes 1 .................................................................................4
  Addition of thiol 2 to the gem-difluorostyrenes ...............................................................6
  Reactions of sulfides 3 with silyl enol ethers .................................................................10
  Reactions of sulfides 3 with electron-withdrawing alkenes .............................................14
  Reactions of sulfides 3 with nitrones .............................................................................15
  Synthesis of (3,3-difluorobut-1-ene-1,4-diyl)dibenzene 11 ...........................................17
  Synthesis of 9-phenylacridin-10-i um 2,3,5,6-tetrafluoropyridine-4-thiolate A ............18

Results and Discussions ......................................................................................................19
  Optimization of Reactions Parameters ........................................................................19
  Mechanistic Studies .........................................................................................................22
  Cyclic Voltammetry .........................................................................................................23
  EPR experiment ...............................................................................................................24
  X-Ray Crystallographic Data ..........................................................................................25

References ..........................................................................................................................26

NMR Spectra .......................................................................................................................27
Experimental Procedures

General methods

All reactions were performed under an argon atmosphere. MeCN was distilled twice: from P₂O₅ and CaH₂ 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 irradiation, a strip of light emitting diodes (2835-120LED 1M-Blue, 12V) was used.

Starting compounds

Silyl enol ethers 4 were prepared according to a literature procedure[1] and were used without purification. Acrylonitrile 6d and tert-butyl acrylate 6f were purchased from Acros Organics. Nitrones 8a-e[2-6], acrylamides 6a-c[7-9] were prepared according to literature procedures:

Diethyl vinylphosphonate (6e) was prepared according to modified literature procedure.[10]

(a) Triethylphosphite (10 mL, 84.8 mmol) was mixed with 1,2-dibromoethane (30 mL, 340 mmol) in a round-bottom flask equipped with a reflux condenser, heated at 160 °C and stirred for 4 h at 160 °C. The reaction mixture was cooled to room temperature, and the product was purified by distillation at reduced pressure affording 8.8 g (42%) of diethyl 2-bromoethylphosphonate as a colorless liquid. Bp 92–95 °C (1.2 Torr).

(b) Diethyl 2-bromoethylphosphonate (8.8 g, 35.9 mmol) was slowly added to a solution of K₂CO₃ (5.45 g, 39.5 mmol) in ethanol (50 mL, ethanol contains 4% of water). The reaction mixture was stirred at room temperature for 6 h. The formed solid was filtered off and washed with ethanol. The solvent was removed under vacuum and the remaining oil was distilled under reduced pressure affording 3.71 g (63%) of diethyl vinylphosphonate 6e as a colorless liquid. Bp 46–48 °C (0.22 Torr).

Synthesis of 2,3,5,6-tetrafluoropyridine-4-thiol (2) [11]

A flask containing a solution of sodium hydrosulfide hydrate NaSH·H₂O (109 g, 1.47 mol) in 200 mL of MeOH was immersed into a room temperature water bath. Pentfluoropyridine (100 g, 0.59 mol) was added dropwise, maintaining the temperature below 30 °C. The resulting cloudy viscous solution was stirred for 20 minutes and volatile components were evaporated under reduced pressure. The solid residue was carefully quenched with concentrated HCl (150 mL) (Caution: H₂S evolution). The product was extracted with petroleum ether (100 mL and twice 50 mL). The combined organic phases were evaporated under ambient pressure, and the residue was distilled at 56 Torr collecting the fraction boiling at 70–72 °C (56 Torr) to afford 104 g (96%) of colorless fluid liquid, which solidifies at room temperature. Mp 27–29 °C. Colorless crystals.

1H NMR (300 MHz, CDCl₃) δ 4.17 (s, 1H)
13C{¹H} NMR (126 MHz, CDCl₃) δ 143.25 (ddddd, J = 244.6 Hz, 16.6 Hz, 13.9 Hz, 2.4 Hz), 138.6 (dddm, J = 255.1 Hz), 129.1 (tt, J = 19.2, 3.3 Hz)
19F NMR (282 MHz, CDCl₃) δ -92.0 – -92.5 (m, 2F), -140.7 – -140.1 (m, 2F)
Potassium bromodifluoroacetate (2.56 g, 12 mmol) was placed in a 100 mL 2-neck round-bottom flask and dried under vacuum (ca. 0.5 Torr) at 90°C for 5 hours. The flask was cooled to room temperature, then aldehyde (10 mmol), triphenylphosphine (3.28 g, 12.5 mmol) and Bu$_2$NBr (32 mg, 0.1 mmol), and dry DMF (20 mL) were added successively. Thermometer and bubble counter were attached to the reaction flask. The mixture was slowly heated up until gas evolution begins (around 40-45 °C). The reaction temperature was adjusted to maintain the gas evolution rate around 1 bubble per second (in case of acceleration, the reaction mixture should be cooled a little bit with tap water bath). As reaction progresses, the bath temperature was slowly increased up to 70 °C (for 1a-i,k) (or 45 °C for 1j) and kept at this temperature until the gas evolution ceased (around 3 hours).

Workup for 1a,d,i,j: the reaction mixture was entirely re-condensed under vacuum of 1 Torr into a trap cooled with liquid nitrogen; during this, the reaction flask was slowly heated from room temperature to 70 °C. The distillate containing DMF and the product was diluted with 60 mL of water. The bottom layer of difluorostyrene was collected, and the aqueous phase was extracted with pentane (5 mL). The combined organic phases were dried over Na$_2$SO$_4$, the solvent was removed under reduced pressure, and the residue was distilled under vacuum on Hickman still.

Workup for 1b,c,e,f,h,k: the reaction mixture was cooled to room temperature, quenched with water (60 mL) and extracted with EtOAc (3×10 mL). The combined organic layers were washed with H$_2$O$_2$ (30 wt% in water, 5 mL) brine (4×10 mL) and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel.

### (2,2-Difluorovinyl)benzene (1a) [12,13]

![Image of (2,2-Difluorovinyl)benzene (1a)](image)

Yield 12.75 g (85%) [107 mmol scale]. Colorless liquid. Bp 114 – 116 °C.

- $^{1}$H NMR (300 MHz, CDCl$_3$) δ 7.43 – 7.31 (m, 4H), 7.30 – 7.22 (m, 1H), 5.30 (dd, $J = 26.8, 3.8$ Hz, 1H).
- $^{13}$C{[H]} NMR (75 MHz, CDCl$_3$) δ 156.5 (dd, $J = 298.1, 288.0$ Hz), 130.5 (t, $J = 6.3$ Hz), 128.8, 127.8 (dd, $J = 6.2, 3.5$ Hz), 127.2, 82.3 (dd, $J = 28.0, 13.6$ Hz).
- $^{19}$F NMR (282 MHz, CDCl$_3$) δ -83.2 (dd, $J = 31.1, 26.8$, 1F), -85.1 (dd, $J = 31.1, 3.8$ Hz, 1F).

### 4-(2,2-Difluorovinyl)-1,1′-biphenyl (1b) [12]

![Image of 4-(2,2-Difluorovinyl)-1,1′-biphenyl (1b)](image)

Yield 1.62 g (75%). Colorless crystals. Mp 83–85 °C.

Chromatography: hexanes/EtOAc, 20/1. $R_f = 0.36$ (hexanes/EtOAc, 20/1).

- $^{1}$H NMR (300 MHz, CDCl$_3$) δ 7.65 – 7.55 (m, 4H), 7.51 – 7.32 (m, 5H), 5.34 (dd, $J = 26.3, 3.7$ Hz, 1H).
- $^{13}$C{[H]} NMR (75 MHz, CDCl$_3$) δ 156.5 (dd, $J = 298.5, 288.6$ Hz), 140.7, 140.0 (t, $J = 1.8$ Hz), 129.5 (t, $J = 6.4$ Hz), 129.0, 128.2 (dd, $J = 6.3, 3.6$ Hz), 127.6, 127.5, 127.1, 82.1 (dd, $J = 29.2, 13.7$ Hz).

### 2-{4-[2,2-Difluorovinyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1c)

![Image of 2-{4-[2,2-Difluorovinyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1c)](image)

Yield 1.44 g (54%). Colorless oil.

Chromatography: hexanes/EtOAc, 20/1. $R_f = 0.26$ (hexanes/EtOAc, 20/1). The compound is slightly unstable on silica gel.

- $^{1}$H NMR (300 MHz, CDCl$_3$) δ 7.79 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 5.29 (dd, $J = 27.1, 3.8$ Hz, 1H), 3.15 (s, 12H).
- $^{13}$C{[H]} NMR (75 MHz, CDCl$_3$) δ 156.6 (dd, $J = 299.6, 289.0$ Hz), 135.2, 133.3 (t, $J = 6.6$ Hz), 127.0 (dd, $J = 6.2, 3.5$ Hz), 84.0, 82.5 (dd, $J = 29.1, 13.3$ Hz), 25.0.

- $^{19}$F NMR (282 MHz, CDCl$_3$) δ -81.5 (t, $J = 27.1$ Hz, 1F), -83.7 (d, $J = 27.1$ Hz, 1F).

HRMS (ESI): calcd for C$_{14}$H$_{13}$BF$_2$O$_2$ (M+H) 267.1365, found 267.1365; calcd for C$_{14}$H$_{13}$BF$_2$O$_2$Na (M+Na) 289.1184, found 289.1179.

### 1-(2,2-Difluorovinyl)-4-methoxybenzene (1d) [12]

![Image of 1-(2,2-Difluorovinyl)-4-methoxybenzene (1d)](image)

Yield 1.33 g (78%). Colorless oil. Bp 75-76 °C (15 Torr).

- $^{1}$H NMR (300 MHz, CDCl$_3$) δ 7.35 (d, $J = 8.8$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 5.30 (dd, $J = 26.7, 3.9$ Hz, 1H), 3.87 (s, 3H).
- $^{13}$C{[H]} NMR (75 MHz, CDCl$_3$) δ 156.7, 156.0 (dd, $J = 296.3, 286.3$ Hz), 128.9 (dd, $J = 6.2, 3.5$ Hz), 122.7 (t, $J = 6.2$ Hz), 114.2, 81.6 (dd, $J = 28.2, 14.2$ Hz), 55.1.

- $^{19}$F NMR (282 MHz, CDCl$_3$) δ -85.7 (dd, $J = 36.8, 26.7$ Hz, 1F), -87.4 (dd, $J = 36.8, 3.9$ Hz, 1F).

S4
Methyl 4-(2,2-difluorovinyl)benzoate (1e) \[^{13}\]

Yield 793 mg (40%). Colorless oil.

\[^1\]H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.99 (d, \(J = 8.4\) Hz, 2H), 7.38 (d, \(J = 8.4\) Hz, 2H), 5.32 (dd, \(J = 26.0, 3.6\) Hz, 1H), 3.91 (s, 3H).

\[^{13}\]C{[\(^1\)H]} NMR (75 MHz, CDCl\(_3\)) \(\delta\) 166.6, 165.8 (dd, \(J = 300.4, 290.6\) Hz), 135.1 (t, \(J = 6.7\) Hz), 130.0, 128.6, 127.4 (dd, \(J = 6.4, 3.5\) Hz), 82.0 (dd, \(J = 29.8, 13.1\) Hz), 52.0.

3-(2,2-Difluorovinyl)-1-tosyl-1H-indole (1f) \[^{14}\]

\[\text{Ts} \]

Yield 2.43 g (73%). Colorless crystals. \(\text{Mp} \) 106–108 °C.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.03 (d, \(J = 8.2\) Hz, 1H), 7.80 (d, \(J = 8.3\) Hz, 2H), 7.65 (s, 1H), 7.50 (d, \(J = 7.8\) Hz, 1H), 7.38 (t, \(J = 7.4\) Hz, 1H), 7.32 – 7.19 (m, 3H), 5.40 (d, \(J = 26.7\) Hz, 1H), 2.35 (s, 3H).

\[^{13}\]C{[\(^1\)H]} NMR (75 MHz, CDCl\(_3\)) \(\delta\) 156.9 (dd, \(J = 296.0, 289.9\) Hz), 145.2, 135.3, 134.9, 130.0, 129.5 (d, \(J = 3.3\) Hz), 127.0, 125.3, 123.5, 123.4 (dd, \(J = 9.6, 3.9\) Hz), 119.2 (s), 113.9, 111.9 (dd, \(J = 6.5, 5.4\) Hz), 72.52 (dd, \(J = 32.1, 18.5\) Hz), 21.6 (s).

1-[3-(2,2-Difluorovinyl)-1H-indol-1-yl]ethanone (1g) \[^{12}\]

\[\text{Ac} \]

Yield 1.04 g (47%). Colorless crystals.

Chromatography: hexanes/\(\text{EtOAc}\), 1/1. \(R_f = 0.5\) (hexanes/\(\text{EtOAc}\), 1/1).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.47 (d, \(J = 8.1\) Hz, 1H), 7.54 (d, \(J = 7.7\) Hz, 1H), 7.48 (s, 1H), 7.42 (t, \(J = 7.4\) Hz, 1H), 7.34 (t, \(J = 7.4\) Hz, 1H), 5.47 (d, \(J = 27.0\) Hz, 1H), 2.67 (s, 3H).

\[^{13}\]C{[\(^1\)H]} NMR (75 MHz, CDCl\(_3\)) \(\delta\) 168.5, 156.9 (dd, \(J = 295.6, 290.2\) Hz), 135.5, 129.1, 125.9, 123.9, 122.4 (dd, \(J = 9.9, 3.9\) Hz), 118.5, 116.3, 111.8 (t, \(J = 5.9\) Hz), 72.7 (dd, \(J = 31.7, 18.4\) Hz), 24.1.

6-(2,2-Difluorovinyl)-2,3-dihydrobenzo[b][1,4]dioxine (1h) \[^{17}\]

\[\text{O} \]

Yield 1.35 g (68%). Colorless oil. Bp (bath temperature) 160–167°C (4 Torr).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 6.92 – 6.79 (m, 3H), 5.18 (dd, \(J = 26.1, 3.8\) Hz, 4), 4.27 (s, 3H).

\[^{13}\]C{[\(^1\)H]} NMR (75 MHz, CDCl\(_3\)) \(\delta\) 156.0 (dd, \(J = 297.0, 286.8\) Hz), 143.7, 142.8, 123.8 (t, \(J = 6.1\) Hz), 121.1 (dd, \(J = 5.9, 3.7\) Hz), 117.6, 116.5 (dd, \(J = 6.7, 3.4\) Hz), 81.7 (dd, \(J = 29.5, 13.8\) Hz), 64.5, 64.5.

2-(2,2-Difluorovinyl)thiophene (1i) \[^{13}\]

\[\text{S} \]

Yield 906 mg (62%). Colorless liquid. Bp 83-84 °C (183 Torr).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.29 (t, \(J = 3.2\) Hz, 1H), 7.06 – 7.00 (m, 2H), 5.58 (dd, \(J = 27.0, 2.0\) Hz, 1H).

\[^{13}\]C{[\(^1\)H]} NMR (75 MHz, CDCl\(_3\)) \(\delta\) 156.2 (dd, \(J = 297.2, 289.0\) Hz), 132.2 (t, \(J = 6.8\) Hz), 127.3, 126.1 (t, \(J = 5.3\) Hz), 125.0 (dd, \(J = 6.0, 3.7\) Hz), 77.7 (dd, \(J = 33.5, 17.3\) Hz).

\(^3\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -81.5 (t, \(J = 27.0\) Hz, 1F), -88.7 (d, \(J = 27.0\) Hz, 1F).

2-(2,2-Difluorovinyl)furan (1j) \[^{13,16}\]

Yield 637 mg (49%). Colorless liquid. Bp 42-44 °C (170 Torr). The compound is prone to explosive polymerization in pure form. It must be kept at temperatures below –30 °C under argon atmosphere. It was used immediately after vacuum distillation (after distillation, the apparatus was filled with argon). NMR spectra were recorded immediately after distillation. The distilled product contained around 5% of pentane. Similar observations concerning the instability of 1j were reported. \[^{16}\]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.39 (d, \(J = 1.8\) Hz, 1H), 6.43 (dd, \(J = 3.3, 1.8\) Hz, 1H), 6.33 (d, \(J = 3.3\) Hz, 1H), 5.36 (dd, \(J = 25.4, 1.8\) Hz, 1H).

\[^{13}\]C{[\(^1\)H]} NMR (75 MHz, CDCl\(_3\)) \(\delta\) 156.3 (dd, \(J = 297.8, 288.2\) Hz), 145.6 – 144.7 (m), 142.0 – 141.8 (m), 111.5, 108.2 – 107.8 (m), 74.6 (dd, \(J = 34.7, 16.6\) Hz).

S5
(1,1-Difluorohept-1-en-2-yl)benzene (1k) [15]

Yield 1.91 g (91%). Colorless oil.

\[ \begin{align*}
{ }_1^1H \text{ NMR} (300 \text{ MHz, CDCl}_3) & \delta 7.43 - 7.22 \text{ (m, 5H)}, 2.46 - 2.35 \text{ (m, 2H)}, 1.46 - 1.21 \text{ (m, 6H)}, 0.88 \text{ (t, } J = 6.4 \text{ Hz, 3H)}. \\
{ }_{13}^1C{ }_1^1H \text{ NMR} (75 \text{ MHz, CDCl}_3) & \delta 153.8 \text{ (t, } J = 288.0 \text{ Hz)}, 134.1, 128.5, 128.4 \text{ (t, } J = 3.2 \text{ Hz), 127.3, 92.7 \text{ (dd, } J = 18.0, 16.5 \text{ Hz), 31.4, 27.8, 27.6, 22.5, 14.1}. \\
\end{align*} \]

Addition of thiol 2 to the gem-difluorostyrenes 1 (General procedure)

A Schlenk tube containing a stirring bar and 9-phenylacridine (13 mg, 1 mol%) was evacuated and filled with argon. Then, freshly distilled cyclohexane (5 mL), difluorostyrene 1 (5 mmol) and 2,3,5,6-tetrafluoropyridine-4-thiol 2 (1 g, 5.5 mmol) were added successively. The reaction mixture was irradiated for 18 hours with 465 nm LED. For 3c,e, another portion of 9-phenylacridine (13 mg, 1 mol%) was added, and irradiation was continued for additional 18 hours. During irradiation, the mixture was cooled with tap water (see Figure S1 for the reaction setup). For the workup, saturated aqueous solution of Zn(OAc)\(_2\) (1 mL) and water (10 mL) were added. The mixture was extracted with ethyl acetate/hexane (1/3, 3×4 mL). The combined organic phases were dried over Na\(_2\)SO\(_4\) and concentrated under vacuum. The crude material was purified by flash column chromatography on silica gel [for 3a,b,d,f,h,i,j,k] or by recrystallization [for 3e,c] or by high vacuum distillation [for 3l].

The procedure for synthesis of 3a was also performed on 20 mmol scale of styrene 1a with the same setup (5 runs). Isolated yields of 3a were 92 – 99%.

Figure S1. Setup for 5 to 20 mmol scale reactions.
4-[(1,1-Difluoro-2-phenylethyl)thio]-2,3,5,6-tetrafluoropyridine (3a)

Yield 1.53 g (95%). Colorless crystals. Mp 67-69 °C.
Chromatography: hexanes/EtOAc, 10/1. R_f = 0.5 (hexanes/EtOAc, 10/1).
\(^1\)H NMR (300 MHz, CDCl_3) δ 7.45 – 7.31 (m, 5H), 3.57 (t, \(J = 14.6 \) Hz, 2H).
\(^13\)C{\(^1\)H} NMR (126 MHz, CDCl_3) δ 144.8 – 144.3 (m), 142.8 – 142.2 (m), 130.6, 128.9, 128.6, 128.5 (t, \(J = 287.5 \) Hz), 121.1 – 120.7 (m), 45.7 (t, \(J = 22.8 \) Hz).
\(^19\)F NMR (282 MHz, CDCl_3) δ -67.4 (tt, \(J = 14.6, 7.0 \) Hz, 2F), -89.4 – -89.8 (m, 2F), -132.24 – -132.60 (m, 2F).
HRMS (ESI): calcd for C_{13}H_{10}F_6NS (M+H) 324.0276, found 324.0275.

Figure S2. OLEX diagram of compound 3a (CCDC 1947115).

4-((2-(1,1'-Biphenyl)-4-yl)-1,1-difluorooethyl)thio)-2,3,5,6-tetrafluoropyridine (3b)

Yield 1.82 g (91%). Colorless crystals. Mp 105 – 107 °C.
Chromatography: hexanes/EtOAc, 20/1. R_f = 0.27 (hexanes/EtOAc, 20/1).
\(^1\)H NMR (300 MHz, CDCl_3) δ 7.67 – 7.57 (m, 4H), 7.52 – 7.34 (m, 5H), 3.62 (t, \(J = 14.5 \) Hz, 2H).
\(^13\)C{\(^1\)H} NMR (75 MHz, CDCl_3) δ 145.7 – 144.7 (m), 142.5 – 141.5 (m), 141.5, 140.5, 131.0, 129.5 (t, \(J = 3.6 \) Hz), 129.0, 128.5 (t, \(J = 287.0 \) Hz), 127.7, 127.6, 127.2, 121.3 – 120.4 (m), 45.3 (t, \(J = 22.9 \) Hz).
\(^19\)F NMR (282 MHz, CDCl_3) δ -67.3 (tt, \(J = 14.5, 7.0 \) Hz, 2F), -89.3 – -89.7 (m, 2F), -132.00 – -132.54 (m, 2F).
HRMS (ESI): calcd for C_{19}H_{12}F_6NS (M+H) 400.0589, found 400.0587.

4-((1,1-Difluoro-2-(4-methoxyphenyl)ethyl)thio)-2,3,5,6-tetrafluoropyridine (3d)

Yield 1.55 g (88%). Colorless oil.
Chromatography: hexanes/EtOAc, 10/1. R_f = 0.23 (hexanes/EtOAc, 10/1).
\(^1\)H NMR (300 MHz, CDCl_3) δ 7.29 (d, \(J = 8.5 \) Hz, 2H), 6.93 (d, \(J = 8.6 \) Hz, 2H), 3.85 (s, 3H), 3.52 (t, \(J = 14.5 \) Hz, 2H).
\(^13\)C{\(^1\)H} NMR (75 MHz, CDCl_3) δ 159.9, 145.6 – 144.8 (m), 142.3 – 141.3 (m), 131.7, 128.8 (t, \(J = 287.2 \) Hz), 122.5 (t, \(J = 3.8 \) Hz), 121.5 – 120.6 (m), 114.3, 55.4, 44.9 (t, \(J = 22.9 \) Hz).
\(^19\)F NMR (282 MHz, CDCl_3) δ -67.6 (tt, \(J = 14.5, 7.0 \) Hz, 2F), -89.6 – -90.0 (m, 2F), -132.2 – -132.7 (m, 2F).
HRMS (ESI): calcd for C_{14}H_{10}F_6NS (M+H) 354.0382, found 354.0372.
4-[(1,1-Difluoro-2-phenylethyl)thio]-2,3,5,6-tetrafluoropyridine (3k)

![Structure](image)

Yield 1.63 g (83%). Colorless oil.

Chromatography: hexanes/CH₂Cl₂, 5/1. Rf = 0.25 (hexanes/CH₂Cl₂, 5/1).

H NMR (300 MHz, CDCl₃) δ 7.46 – 7.31 (m, 5H), 3.49 – 3.26 (m, 1H), 2.16 – 2.00 (m, 1H) 1.99 – 1.83 (m, 1H), 1.38 – 1.11 (m, 6H), 0.92 – 0.78 (m, 3H).

Yield 1.24 g (73%). Colorless crystals. Mp 59 – 61 °C.

Chromatography: hexanes/EtOAc, 5/1. Rf = 0.33 (hexanes/EtOAc, 5/1).

H NMR (300 MHz, CDCl₃) δ 8.06 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 3.93 (s, 3H), 3.62 (t, J = 14.5 Hz, 2H).

C¹H NMR (75 MHz, CDCl₃) δ 166.7, 145.6 (m), 144.9 (m), 144.2 (m), 135.5 (t, J = 3.6 Hz), 130.7, 130.5, 130.1, 128.0 (t, J = 287.3 Hz), 121.1 – 119.9 (m), 52.4, 45.5 (t, J = 23.0 Hz).

HRMS (ESI): calcd for C₁₈H₁₂F₄NS (M+H) 314.0069, found 314.0074; calcd for C₁₈H₁₂F₄NO (M+H) 335.9888, found 335.9875.

Yield 1.64 g (73%). Colorless crystals. Mp 160 – 162 °C.

The compound was unstable on silica or alumina, purified by recrystallization from methanol.

H NMR (300 MHz, CDCl₃) δ 7.83 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 3.57 (t, J = 14.5 Hz, 3H), 1.36 (s, 12H).

C¹H NMR (75 MHz, CDCl₃) δ 145.6 – 144.9 (m), 142.3 – 141.4 (m), 135.3, 133.5 (t, J = 3.6 Hz), 129.9, 128.4 (t, J = 287.6 Hz), 121.3 – 120.5 (m), 84.1, 45.8 (t, J = 22.8 Hz), 25.0.

Yield 157 mg (10%). Colorless crystals. Mp 30 – 32 °C.

Chromatography: hexanes/EtOAc, 10/1. Rf = 0.41 (hexanes/EtOAc, 10/1).

H NMR (300 MHz, CDCl₃) δ 7.45 – 7.42 (m, 1H), 6.42 – 6.37 (m, 2H), 3.63 (t, J = 13.4 Hz, 2H).

C¹H NMR (75 MHz, CDCl₃) δ 145.6 – 144.9 (m), 144.7 (t, J = 5.2 Hz), 143.5, 142.3 – 141.4 (m), 127.4 (t, J = 287.8 Hz), 121.0 – 120.3 (m), 111.1 (s), 111.0, 38.7 (t, J = 25.5 Hz).

F NMR (282 MHz, CDCl₃) δ -67.5 (tt, J = 13.4, 6.8 Hz, 2F), -89.3 – -89.7 (m, 2F), -132.1 – -132.6 (m, 2F).

HRMS (ESI): calcd for C₁₉H₁₈F₄NO (M+H) 472.0951, found 472.0958; calcd for C₁₉H₁₈F₄NO²Sm (M+K) 508.0722, found 508.0721.

Yield 1.63 g (73%). Colorless crystals. Mp 30 – 32 °C.

Chromatography: hexanes/EtOAc, 10/1. Rf = 0.41 (hexanes/EtOAc, 10/1).

H NMR (300 MHz, CDCl₃) δ 7.45 – 7.42 (m, 1H), 6.42 – 6.37 (m, 2H), 3.63 (t, J = 13.4 Hz, 2H).

C¹H NMR (75 MHz, CDCl₃) δ 145.6 – 144.9 (m), 144.7 (t, J = 5.2 Hz), 143.5, 142.3 – 141.4 (m), 127.4 (t, J = 287.8 Hz), 121.0 – 120.3 (m), 111.1 (s), 111.0, 38.7 (t, J = 25.5 Hz).

F NMR (282 MHz, CDCl₃) δ -67.5 (tt, J = 13.4, 6.8 Hz, 2F), -89.3 – -89.7 (m, 2F), -132.1 – -132.6 (m, 2F).

HRMS (ESI): calcd for C₁₉H₁₈F₄NOS (M+H) 335.9888, found 335.9875.
3-(2,2-Difluoro-2-[(perfluoropyridin-4-yl)thio]ethyl)-1-tosyl-1H-indole (3f)

Yield 2.40 g (93%). Colorless crystals. Mp 91 – 93 °C.

Chromatography: hexanes/EtOAc, 10/1. Rf = 0.18 (hexanes/EtOAc, 10/1).

1H NMR (300 MHz, CDCl3) δ 8.02 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.2 Hz, 2H), 7.70 (s, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.42 – 7.27 (m, 2H), 7.25 (d, J = 8.2 Hz, 2H), 3.69 (t, J = 14.0 Hz, 2H), 2.35 (s, 3H).

19F NMR (282 MHz, CDCl3) δ -66.7 (tt, J = 14.0, 6.7 Hz, 2F), -89.2 – -89.5 (m, 2F), -132.0 – -132.7 (m, 2F).

HRMS (ESI): calcd for C28H17F3N2OsNa (M+Na) 539.0293, found 539.0295; calcd for C28H17F3N2OsK (M+K) 555.0032, found 555.0035.

4-[(1,1-Difluoro-2-(thiophen-2-yl)ethyl]thio)-2,3,5,6-tetrafluoropyridine (3i)

Yield 971 mg (59%). Colorless crystals. Mp 26 – 28 °C.

Compound was purified by distillation on Hickman still head. Bath temperature 134 – 140 °C, 0.28 Torr.

1H NMR (300 MHz, CDCl3) δ 7.34 (d, J = 5.0 Hz, 1H), 7.09 (d, J = 3.2 Hz, 1H), 7.04 (dd, J = 5.0, 3.2 Hz, 1H), 3.79 (t, J = 13.8 Hz, 2H).

19F NMR (282 MHz, CDCl3) δ -68.3 (tt, J = 13.8, 6.6 Hz, 2F), -89.3 – -89.7 (m, 2F), -132.1 – -132.5 (m, 2F).

HRMS (ESI): calcd for C13H17F3N2SNa (M+Na) 351.9660, found 351.9644.

4-[2-(2,3-Dihydrobenzo[b][1,4]dioxin-5-yl)-1,1-difluoroethyl]thio)-2,3,5,6-tetrafluoropyridine (3h)

Yield 1.62 g (85%). Colorless crystals. Mp 84 – 86 °C.

Chromatography: hexanes/EtOAc, 5/1. Rf = 0.32 (hexanes/EtOAc, 5/1).

1H NMR (300 MHz, CDCl3) δ 6.91 – 6.75 (m, Hz, 3H), 4.27 (s, 4H), 3.44 (t, J = 14.4 Hz, 2H).

19F NMR (282 MHz, CDCl3) δ -67.3 (tt, J = 14.4, 6.9 Hz, 2F), -89.5 – -89.9 (m, 2F), -132.1 – -132.6 (m, 2F).

HRMS (ESI): calcd for C15H17F3N2O2SNa (M+Na) 404.0150, found 404.0148.

1-(3-(2,2-Difluoro-2-[(perfluoropyridin-4-yl)thio]ethyl)-1H-indol-1-yl)ethanone (3g)

Yield 1.09 g (54%). Colorless crystals. Mp 125 – 127 °C. Reaction was conducted in CH2Cl2.

Chromatography: hexanes/EtOAc, 3/1. Rf = 0.37 (hexanes/EtOAc, 3/1).

1H NMR (300 MHz, CDCl3) δ 8.44 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.51 (s, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 3.69 (t, J = 14.2 Hz, 2H), 2.66 (s, 3H).

19F NMR (282 MHz, CDCl3) δ -66.6 (tt, J = 14.2, 6.8 Hz, 2F), -89.2 – -89.6 (m, 2F), -132.2 – -132.6 (m).

HRMS (ESI): calcd for C21H12F3N2O2SNa (M+Na) 405.0491, found 405.0487; calcd for C21H12F3N2O2SNa (M+Na) 427.0306, found 427.0306.
Synthesis of (1,1-difluoro-2-phenylethyl)(perfluorophenyl)sulfane (3l) \([18]\]

The Schlenk tube containing a stirring bar and 7H-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (13.5 mg, 1 mol%) was evacuated and filled with argon. Then, freshly distilled cyclohexane (10 mL), difluorostyrene 1a (701 mg, 5 mmol) and pentafluorobenzenethiol (1.1 g, 5.5 mmol) were added successively. The reaction mixture was irradiated for 18 hours with 465 nm LED; during irradiation the mixture was cooled with room temperature water (see Figure S1 for the reaction setup). For the workup, saturated aqueous solution of Zn(OAc)_2 (1 mL) and water (10 mL) were added. The mixture was extracted with ethyl acetate/hexane (1/3, 3×4 mL). The combined organic phases were dried with Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel. Yield 1.565 g (92%). Colorless crystals. Mp 51 – 52 °C.

Chromatography: hexanes/EtOAc, 20/1. R_f = 0.41 (hexanes/EtOAc, 20/1).

Reactions of sulfides 3 with silyl enol ethers 4 (General procedure)

Figure S3. Setup for small scale reactions.

Method A

A screw capped tube containing a stirring bar, triphenylphosphine (26 mg, 0.1 mmol) and 12-phenyl-12H-benzo[b]phenothiazine (8 mg, 0.025 mmol, 5 mol%) was evacuated and backfilled with argon. Anhydrous DMF (1 mL) was added. The mixture was subjected to a vacuum of 10 Torr for 1 min at room temperature, and then the flask was filled with argon. Dry zinc acetate (55 mg, 0.3 mmol), sulfide 3 (0.5 mmol) and silyl enol ether 4 (0.665 mmol) were added successively. The tube was tightly closed with the screw cap and irradiated (irradiation time: 12 h for 5aa,ak,af,ab; 48 h for 5ah,aj) using 465 nm LED 4W; during irradiation the mixture was cooled with room temperature water (see Figure S3 for the reaction setup). For the workup, water (3 mL) was added, the mixture was
extracted with ethyl acetate/hexane (1/3, 3×3 mL). The combined organic phases were dried over Na₂SO₄ and concentrated under vacuum. The residue was purified by chromatography (see characterization data for details).

**Method B**

A screw capped tube containing a stirring bar, triphenylphosphine (26 mg, 0.1 mmol), [Ir(ppy)₂(dtbppy)]PF₆ (2.2 mg, 0.0025 mmol, 0.5 mol%), tetrabutylammonium iodide (92 mg, 0.25 mmol) and anhydrous DMF (1 mL). The mixture was subjected to a vacuum of 10 Torr for 1 min at room temperature, and then the flask was filled with argon. Sulfide 3 (0.5 mmol) and silyl enol ether 4 (0.665 mmol) were added, the tube was tightly closed with the screw cap and irradiated (irradiation time: 12 h for 5aa.ac.bg.cf; 48 h for 5ah.aj.ae; 60 h for 5ab) using 465 nm LED 4W strips; during irradiation the mixture was cooled with room temperature water (see Figure S3 for the reaction setup). For the workup, saturated aqueous solution of Zn(OAc)₂ (1 mL) and water (2 mL) were added, and the mixture was extracted with ethyl acetate/hexane (1/3, 3×3 mL). The combined organic phases were dried over Na₂SO₄ and concentrated under vacuum. The residue was purified by chromatography (see characterization data for details).

3,3-Difluoro-1,4-diphenylbutan-1-one (5aa) [19]

![3,3-Difluoro-1,4-diphenylbutan-1-one (5aa)](image)

**Method A:** yield 108 mg (83%). **Method B:** yield 114 mg (85%). Colorless crystals. Mp 54–56 °C.

**Chromatography:** hexane/EtOAc, 20/1. Rₜ = 0.20 (hexane/EtOAc, 20/1).

**¹H NMR (300 MHz, CDCl₃)** δ 7.92 (d, J = 7.7 Hz, 2H), 7.60 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.39 – 7.27 (m, 5H), 3.53 (t, J = 16.8 Hz, 2H), 3.43 (d, J = 14.2 Hz, 2H).

**¹³C{¹H} NMR (75 MHz, CDCl₃)** δ 193.9 (t, J = 243.7 Hz), 44.3 (t, J = 244.2 Hz), 42.5 (t, J = 243.7 Hz), 43.3 (t, J = 244.2 Hz), 42.4 (t, J = 246.6 Hz).

3,3-Difluoro-1-(naphthalen-2-yl)-4-phenylbutan-1-one (5ah) [20]

![3,3-Difluoro-1-(naphthalen-2-yl)-4-phenylbutan-1-one (5ah)](image)

**Method A:** yield 99 mg (64%). **Method B:** yield 112 mg (72 %). Colorless crystals. Mp 69–71 °C.

**Chromatography:** hexane/EtOAc, 10/1. Rₜ = 0.25 (hexane/EtOAc, 10/1).

**¹H NMR (400 MHz, CDCl₃)** δ 8.36 (s, 1H), 8.00 (dd, J = 8.6, 1.6 Hz, 1H), 7.96 – 7.85 (m, 3H), 7.62 (t, J = 7.0 Hz, 1H), 7.56 (t, J = 7.0 Hz, 1H), 7.38 – 7.27 (m, 5H), 3.57 (t, J = 13.2 Hz, 2H), 3.54 (t, J = 16.7 Hz, 2H).

**¹³C{¹H} NMR (75 MHz, CDCl₃)** δ 186.5 (t, J = 186.5 Hz, 1H), 136.8, 133.8, 133.4 (t, J = 5.0 Hz), 130.5, 128.8, 128.6, 128.4, 127.5, 122.7 (t, J = 243.7 Hz), 43.3 (t, J = 26.4 Hz), 42.4 (t, J = 24.6 Hz).

3,3-Difluoro-4-phenyl-1-(thiophen-2-yl)butan-1-one (5aj) [20]

![3,3-Difluoro-4-phenyl-1-(thiophen-2-yl)butan-1-one (5aj)](image)

**Method A:** yield 77 mg (58%). **Method B:** yield 32 % (¹⁹F NMR). Colorless crystals. Mp 47–49 °C.

**Chromatography:** hexane/EtOAc, 12/1. Rₜ = 0.17 (hexane/EtOAc, 12/1).

**¹H NMR (300 MHz, CDCl₃)** δ 7.69 (dd, J = 4.9, 0.8 Hz, 1H), 7.64 (dd, J = 3.8, 0.8 Hz, 1H), 7.38 – 7.27 (m, 5H), 7.13 (dd, J = 4.9, 3.8 Hz, 1H), 3.46 (t, J = 16.7 Hz, 2H), 3.37 (t, J = 14.3 Hz, 2H).

**¹³C{¹H} NMR (75 MHz, CDCl₃)** δ 186.5 (t, J = 244.2 Hz), 144.4, 135.1, 133.3, 133.2 (t, J = 5.0 Hz), 130.7, 128.7, 128.5, 127.6, 122.3 (t, J = 244.2 Hz), 44.3 (t, J = 26.8 Hz), 42.5 (t, J = 24.6 Hz).

2-(1,1-Difluoro-2-phenylethyl)-3,4-dihydronaphthalen-1(2H)-one (5ak) [20]

![2-(1,1-Difluoro-2-phenylethyl)-3,4-dihydronaphthalen-1(2H)-one (5ak)](image)

**Method A:** yield 97 mg (68%). Pale yellow crystals. Mp 71–73 °C.

**Chromatography:** hexane/EtOAc, 20/1. Rₜ = 0.29 (hexane/EtOAc, 20/1).

**¹H NMR (300 MHz, CDCl₃)** δ 8.13 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.45 – 7.23 (m, 7H), 3.86 (dd, J = 27.4, 13.7 Hz, 1H), 3.84 – 3.43 (dd, J = 21.3, 14.2, 8.9 Hz, 1H), 3.09 (dt, J = 16.8, 4.6 Hz, 1H), 3.02 – 2.83 (m, 2H), 2.49 – 2.35 (m, J = 13.7, 4.6 Hz, 1H), 2.31 – 2.14 (m, 1H).

**¹³C{¹H} NMR (75 MHz, CDCl₃)** δ 194.2 (d, J = 6.2 Hz), 144.0, 133.9, 133.7 (d, J = 9.1 Hz), 132.8 (d, J = 3.7 Hz), 130.4, 128.8, 128.5, 127.8, 127.4, 126.9, 123.4 (t, J = 246.0 Hz), 51.2 (t, J = 25.0 Hz), 42.3 (dd, J = 25.9, 23.7 Hz), 28.2, 22.8 (dd, J = 7.9, 1.4 Hz).
3,3-Difluoro-2-methyl-1,4-diphenylbutan-1-one (5ai)

Method A: yield 121 mg (88%). Colorless oil.
The crude product was passed through 3 cm silica gel pad using hexane/EtOAc (10/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21x250 mm, 5 μm), flow rate 12 mL·min⁻¹; mobile phase: isocratic, acetonitrile/water, 17% water; tᵣ = 12.17 min.

1H NMR (500 MHz, CDCl₃) δ 7.86 (d, J = 7.4 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.36 – 7.22 (m, 5H), 4.06 – 3.94 (m, 1H), 3.51 – 3.26 (m, 2H), 1.42 (d, J = 7.2 Hz, 3H).

13C{1H} NMR (125 MHz, CDCl₃) δ 198.75 (s, 1C), 130.7, 128.8, 128.6, 128.5, 127.5, 123.4 (dd, J = 249.2, 244.6 Hz), 45.8 (t, J = 24.5 Hz), 40.6 (t, J = 24.9 Hz), 12.4 (t, J = 4.8 Hz).

Methyl 4-(3,3-difluoro-4-phenylbutanoyl)benzoate (5ab)

Method A: yield 125 mg (87%). Colorless oil.
Chromatography: hexane/EtOAc, 7/1. Rᵣ = 0.24 (hexane/EtOAc, 20/1).
1H NMR (500 MHz, CDCl₃) δ 7.75 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 7.34 – 7.27 (m, J = 7.4 Hz, 5H), 3.46 (t, J = 16.6 Hz, 2H), 3.38 (t, J = 14.2 Hz, 2H).

13C{1H} NMR (125 MHz, CDCl₃) δ 193.6 (s, 1C), 136.2, 133.3, 132.2, 130.0, 129.2, 128.7, 127.7, 122.5 (t, J = 244.2 Hz), 43.4 (t, J = 26.5 Hz), 42.5 (t, J = 24.7 Hz).

12F NMR (282 MHz, CDCl₃) δ -90.7 (tt, J = 16.6, 14.2 Hz, 2F).
HRMS (ESI): calcd for C₁₉H₁₄F₂O₃Na (M+Na) 341.0960, found 341.0960; calcd for C₁₉H₁₄F₂O₃K (M+K) 357.0699, found 357.0698.

1-(4-Bromophenyl)-3,3-difluoro-4-phenylbutan-1-one (5ad)

Method A: yield 125 mg (87%). Colorless oil.
Chromatography: hexane/EtOAc, 7/1. Rᵣ = 0.26 (hexane/EtOAc, 20/1).
1H NMR (500 MHz, CDCl₃) δ 7.43 (d, J = 8.0 Hz, 2H), 7.35 – 7.27 (m, 5H), 7.08 (s, 1H), 7.04 (d, J = 8.0 Hz, 1H), 3.49 (t, J = 16.8 Hz, 2H), 3.35 (t, J = 14.3 Hz, 2H), 2.53 (s, 3H), 2.35 (s, 2H).

13C{1H} NMR (125 MHz, CDCl₃) δ 196.8 (s, 1C), 142.8, 139.3, 134.7 (t, J = 1.5 Hz), 133.6 (t, J = 5.1 Hz), 133.2, 130.6, 129.5, 128.7, 127.6, 126.5, 122.8 (t, J = 243.6 Hz), 45.7 (t, J = 26.2 Hz), 42.5 (t, J = 24.7 Hz), 21.7, 21.5.

12F NMR (282 MHz, CDCl₃) δ -90.8 (tt, J = 16.8, 14.3 Hz, 2F).
HRMS (ESI): calcd for C₁₉H₁₄BrF₂O₃Na (M+Na) 362.9990, found 362.9990; calcd for C₁₉H₁₄BrF₂O₃ (M+K) 385.0526, found 388.0540.

1-(2,4-Dimethylphenyl)-3,3-difluoro-4-phenylbutan-1-one (5af)

Method A: yield 125 mg (87%). Colorless oil.
Chromatography: hexane/EtOAc, 7/1. Rᵣ = 0.26 (hexane/EtOAc, 20/1).
1H NMR (500 MHz, CDCl₃) δ 7.43 (d, J = 8.0 Hz, 2H), 7.35 – 7.27 (m, 5H), 7.08 (s, 1H), 7.04 (d, J = 8.0 Hz, 1H), 3.49 (t, J = 16.8 Hz, 2H), 3.35 (t, J = 14.3 Hz, 2H), 2.53 (s, 3H), 2.35 (s, 2H).

13C{1H} NMR (125 MHz, CDCl₃) δ 196.8 (s, 1C), 142.8, 139.3, 134.7 (t, J = 1.5 Hz), 133.6 (t, J = 5.1 Hz), 133.2, 130.6, 129.5, 128.7, 127.6, 126.5, 122.8 (t, J = 243.6 Hz), 45.7 (t, J = 26.2 Hz), 42.5 (t, J = 24.7 Hz), 21.7, 21.5.

12F NMR (282 MHz, CDCl₃) δ -90.8 (tt, J = 16.8, 14.3 Hz, 2F).
HRMS (ESI): calcd for C₁₉H₁₄BrF₂O₃Na (M+Na) 362.9990, found 362.9990; calcd for C₁₉H₁₄BrF₂O₃ (M+K) 385.0526, found 388.0540.
1H NMR (300 MHz, CDCl₃) δ 7.61 (d, J = 7.6 Hz, 1H), 7.43 – 7.26 (m, 8H), 3.48 (t, J = 16.7 Hz, 2H), 3.44 (t, J = 14.1 Hz, 2H).

13C{[1H]} NMR (75 MHz, CDCl₃) δ 197.2 (t, J = 5.9 Hz), 141.1 (t, J = 1.6 Hz), 134.0, 133.2 (t, J = 5.0 Hz), 132.3, 130.6, 128.9, 128.7, 127.7, 127.7, 122.2 (t, J = 24.2 Hz), 118.8, 47.2 (t, J = 26.6 Hz), 42.5 (t, J = 24.6 Hz).

19F NMR (282 MHz, CDCl₃) δ -91.1 (tt, J = 16.7, 14.1 Hz, 2F).

HRMS (ESI): calcd for C₁₈H₁₃BrF₂O₆ Na⁺ (M+Na) 361.0010, found 361.0003; calcd for C₁₈H₁₃BrF₂O₆ Na⁺ (M+Na) 362.9990, found 362.9984.

1-(4-Chlorophenyl)-3,3-difluoro-4-phenylbutan-1-one (5ac)

Method B: yield 136 mg (92%). Colorless crystals. Mp 57-59 °C.

Chromatography: hexane/EtOAc, 15/1, Rf = 0.29 (hexane/EtOAc, 15/1).

1H NMR (300 MHz, CDCl₃) δ 7.83 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.36 – 7.26 (m, 5H), 3.47 (t, J = 16.7 Hz, 2H), 3.39 (t, J = 14.2 Hz, 2H).

13C{[1H]} NMR (75 MHz, CDCl₃) δ 192.8 (t, J = 5.8 Hz), 140.4, 135.2, 133.3 (t, J = 5.0 Hz), 130.6, 129.9, 129.2, 128.7, 127.7, 122.6 (t, J = 244.1 Hz), 43.4 (t, J = 26.5 Hz), 42.5 (t, J = 24.6 Hz).

19F NMR (282 MHz, CDCl₃) δ -90.8 (tt, J = 16.7, 14.1 Hz, 2F).

HRMS (ESI): calcd for C₁₈H₁₃ClF₂O Na⁺ (M+Na) 295.0696, found 295.0703; calcd for C₁₈H₁₃BrF₂O Na⁺ (M+H) 297.0630, found 297.0667; calcd for C₁₈H₁₃BrF₂O Na⁺ (M+Na) 317.0515, found 317.0521; calcd for C₁₈H₁₃BrF₂O Na⁺ (M+Na) 319.0487, found 319.0494.

6-([1,1'-Biphenyl]-4-yl)-5,5-difluoro-2,2-dimethylhexan-3-one (5bg)

Method B: yield 90 mg (57%). Colorless crystals. Mp 61-63 °C.

The crude product was passed through 3 cm silica gel pad using hexane/EtOAc (20/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 12 mL·min⁻¹; mobile phase: isocratic, acetonitrile/water, 5% water; tₘ = 7.64 min.

1H NMR (300 MHz, CDCl₃) δ 7.64 – 7.53 (m, 4H), 7.46 (t, J = 7.5 Hz, 2H), 7.41 – 7.32 (m, 3H), 3.53 (t, J = 17.0 Hz, 2H), 3.01 (t, J = 13.9 Hz, 2H), 1.14 (s, 9H).

13C{[1H]} NMR (75 MHz, CDCl₃) δ 209.5, 140.8, 140.4, 132.8 (t, J = 5.2 Hz), 131.0, 128.9, 127.5, 127.3, 127.1, 123.0 (t, J = 242.9 Hz), 44.9, 41.8 (t, J = 24.7 Hz), 41.2 (t, J = 26.7 Hz), 26.1.

19F NMR (282 MHz, CDCl₃) δ -90.3 (tt, J = 17.0, 13.9 Hz, 2F).

HRMS (ESI): calcd for C₂₀H₂₃F₂O Na⁺ (M+H) 317.1711, found 317.1714; calcd for C₂₀H₂₃F₂O Na⁺ (M+Na) 339.1531, found 339.1529.

Methyl 4-[4-(2,4-dimethylphenyl)-2,2-difluoro-4-oxobutyl]benzoate (5ef)

Method B: yield 138 mg (80%). Colorless oil.

Chromatography: hexane/EtOAc, 10/1, Rf = 0.20 (hexane/EtOAc, 10/1).

1H NMR (300 MHz, CDCl₃) δ 7.97 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.06 (s, 1H), 7.03 (d, J = 8.1 Hz, 1H), 3.89 (s, 3H), 5.94 (t, J = 16.8 Hz, 2H), 3.35 (t, J = 14.2 Hz, 2H), 2.52 (s, 3H), 2.33 (s, 3H).

13C{[1H]} NMR (75 MHz, CDCl₃) δ 196.3 (t, J = 5.8 Hz), 166.8, 142.9, 139.3, 138.6 (s, t, J = 4.8 Hz), 134.4, 133.2, 130.6, 129.8, 129.4, 126.5, 125.6, 122.3 (t, J = 243.8 Hz), 52.1, 45.6 (t, J = 26.0 Hz), 42.3 (t, J = 24.9 Hz), 21.6, 21.4.

19F NMR (282 MHz, CDCl₃) δ -90.6 (tt, J = 16.8, 14.2 Hz, 2F).

HRMS (ESI): calcd for C₂₀H₂₃F₂O Na⁺ (M+H) 347.1453 found, 347.1455, calcd for C₂₀H₂₃F₂O Na⁺ (M+Na) 369.1273, found 369.1274.

1-(2,4-Dimethylphenyl)-3,3-difluoro-4-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]butan-1-one (5cf)

Method B: yield 83 mg (40%). ¹⁹F NMR yield 76%. Colorless oil.

The crude product was passed through 3 cm silica gel pad using hexane/EtOAc (5/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 11 mL·min⁻¹; mobile phase: isocratic, acetonitrile/water, 5% water; tₘ = 10.24 min.

1H NMR (300 MHz, CDCl₃) δ 7.77 (d, J = 7.8 Hz, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.07 (s, 1H), 7.03 (d, J = 8.0 Hz, 2H), 3.51 (t, J = 16.7 Hz, 2H), 3.34 (t, J = 14.3 Hz, 2H), 2.53 (s, 3H), 2.35 (s, 3H), 1.35 (s, 12H).

13C{[1H]} NMR (75 MHz, CDCl₃) δ 196.6 (t, J = 5.6 Hz), 142.8, 139.2, 136.7 (t, J = 5.0 Hz), 135.1, 134.6, 133.2, 130.0, 129.4, 126.5, 122.7 (t, J = 243.7 Hz), 83.9 (s), 45.6 (t, J = 26.0 Hz), 42.7 (t, J = 24.8 Hz), 25.0, 21.7, 21.5.

¹⁹F NMR (282 MHz, CDCl₃) δ -90.5 (tt, J = 16.7, 14.3 Hz, 2F).

HRMS (ESI): calcd for C₄₀H₃₀BF₂O₃ Na⁺ (M+H) 415.2255 found, 415.2262, calcd for C₄₀H₃₀BF₂O₃ Na⁺ (M+Na) 437.2074, found 437.2085.
Reactions of sulfides 3 with electron-withdrawing alkenes 6 (General procedure)

The tube containing a stirring bar was evacuated and filled with argon. Then, methanol (1.0 mL), sulfide 3 (0.50 mmol), alkene 6 (0.6 mmol), fac-Ir(ppy)$_3$ (1.6 mg, 0.0025 mmol, 0.5 mol%) and pyridine (59 mg, 0.75 mmol) were added successively. The tube was tightly closed with a screw cap and the reaction mixture was irradiated for 18 h using a strip of blue LED; during irradiation the mixture was cooled with room temperature water (see Figure S3 for the reaction setup). For the work-up, water (3 mL) was added, and the mixture was extracted with ethyl acetate (3×4 mL). The combined organic phases were dried with Na$_2$SO$_4$, concentrated under vacuum, and the residue was purified by column chromatography on silica gel.

4,4-Difluoro-N,N-diisopropyl-5-(4-methoxyphenyl)pentanamide (7da)

Yield 123 mg (75%). Colorless oil.
Chromatography: hexane/EtOAc, 3/1. R$_f$ = 0.35 (hexane/EtOAc, 3/1).

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.17 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 4.03–3.86 (m, 1H), 3.77 (s, 3H), 3.56–3.34 (m, 1H), 3.09 (t, J = 15.9 Hz, 2H), 2.51–2.41 (m, 2H), 2.23–2.01 (m, 2H), 1.33 (d, J = 6.8 Hz, 6H), 1.16 (d, J = 6.8 Hz, 6H).

$^{13}$C{$_1$H} NMR (75 MHz, CDCl$_3$) δ 170.0, 159.0, 131.4, 125.3 (t, J = 5.0 Hz), 124.2 (t, J = 242.1 Hz), 114.0, 55.3, 48.2, 45.7, 43.0 (t, J = 26.2 Hz), 31.4 (t, J = 24.0 Hz), 27.3 (t, J = 3.4 Hz), 20.9, 20.7.

$^{19}$F NMR (282 MHz, CDCl$_3$) δ -99.4 (tt, J = 16.8, 15.9 Hz, 2F).

HRMS (ESI): calcd for C$_{18}$H$_{28}$F$_2$NO$_2$ (M+H) 328.2083, found 328.2090; calcd for C$_{18}$H$_{27}$F$_2$NO$_2$Na (M+Na) 350.1902, found 350.1903.

tert-Butyl 4,4-difluoro-5-phenylpentanoate (7af)

Yield 95 mg (70%). Colorless oil.
Chromatography: hexanes/EtOAc, 10/1. R$_f$ = 0.29 (hexanes/EtOAc, 10/1).

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.40–7.24 (m, 5H), 3.18 (t, J = 16.0 Hz, 2H), 2.47 (t, J = 7.9 Hz, 2H), 2.11 (tt, J = 17.0, 7.9 Hz, 2H), 1.46 (s, 9H).

$^{13}$C{$_1$H} NMR (75 MHz, CDCl$_3$) δ 171.8, 133.2 (t, J = 4.7 Hz), 130.4, 128.6, 127.5, 123.5 (t, J = 242.6 Hz), 80.8, 43.5 (t, J = 25.9 Hz), 31.3 (t, J = 25.1 Hz), 28.3 (t, J = 4.4 Hz), 28.2.

4,4-Difluoro-5-phenyldecanitrile (7kd)

Yield 111 mg (84%). Colorless oil.
Chromatography: hexanes/EtOAc, 10/1. R$_f$ = 0.3 (hexanes/EtOAc, 10/1).

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.42–7.29 (m, 3H), 7.29–7.21 (m, 2H), 2.97 (dddd, J = 23.4, 11.7, 8.6, 3.5 Hz, 1H), 2.60–2.37 (m, 2H), 2.19–1.74 (m, 4H), 1.38–1.03 (m, 6H), 0.92–0.76 (m, 3H).

$^{13}$C{$_1$H} NMR (75 MHz, CDCl$_3$) δ 171.2, 133.2 (t, J = 17.0 Hz, 2H), 118.7, 52.8 (dd, J = 23.4, 22.7 Hz), 31.8 (t, J = 25.7 Hz, 2H), 31.6, 28.1 (t, J = 3.9 Hz, 2H), 28.6, 22.4, 14.0, 10.4 (t, J = 6.3 Hz).

$^{19}$F NMR (282 MHz, CDCl$_3$) δ -103.2 (ddddd, J = 224.3, 246.1 Hz), -108.5, -114.5 (ddddd, J = 224.3, 23.4, 9.2, 4.0 Hz, 1F).

HRMS (ESI): calcd for C$_{16}$H$_{21}$F$_2$NNa (M+Na) 288.1534, found 288.1546; calcd for C$_{16}$H$_{21}$F$_2$NK (M+K) 304.1274, found 304.1284.

Diethyl (3,3-difluoro-4-phenylbutyl)phosphonate (7ae)

Yield 103 mg (67%). Colorless oil.
Chromatography: EtOAc, R$_f$ = 0.22 (EtOAc).

S14
During irradiation the mixture was cooled with room temperature water (see Figure S3 for the reaction setup). For the work-up, the mixture was treated with water (3 mL) and extracted with EtOAc (3×4 mL). The combined organic phases were dried with Na₂SO₄, concentrated under vacuum, and the residue was purified by column chromatography.

4,4-Difluoro-N-phenethyl-5-phenylpentanamide (7ac)

Yield 97 mg (61%). Pale yellow crystals. Mp 112–114°C.

Chromatography: hexanes/EtOAc, 3/1. Rₚ = 0.38 (hexanes/EtOAc, 1/1).

1H NMR (300 MHz, CDCl₃) δ 7.39 – 7.20 (m, 5H), 4.16 – 3.97 (m, 4H), 3.16 (t, J = 15.9 Hz, 2H), 2.18 – 1.82 (m, 4H), 1.28 (t, J = 7.1 Hz, 6H).

13C{1H} NMR (75 MHz, CDCl₃) δ 132.9 (t, J = 4.7 Hz), 130.3, 128.6, 127.6, 123.1 (dt, J = 243.1, 18.9 Hz), 61.9, 61.8, 43.2 (t, J = 25.9 Hz), 29.4 (td, J = 26.1, 3.8 Hz), 18.6 (dt, J = 145.4, 4.4 Hz), 16.5, 16.4.

HRMS (ESI): calcd for C₁₉H₁₈FNOSNa (M+Na) 358.1048, found 358.1043.

1-(3,4-Dihydroquinolin-1(2H)-yl)-4,4-difluoro-5-(thiophen-2-yl)pentan-1-one (7ib)

Yield 97 mg (58%). Colorless oil.

Chromatography: hexanes/EtOAc, 3/1. Rₚ = 0.22 (hexanes/EtOAc, 3/1).

1H NMR (300 MHz, CDCl₃) δ 7.36 – 7.07 (m, 5H), 7.03 – 6.88 (m, 2H), 3.79 (t, J = 6.5 Hz, 2H), 3.37 (t, J = 15.4 Hz, 2H), 2.83 – 2.62 (m, 4H), 2.44 – 2.10 (m, 2H), 1.97 (pent, J = 6.6 Hz, 2H).

13C{1H} NMR (75 MHz, CDCl₃) δ 171.0, 138.8, 134.0 (t, J = 5.4 Hz), 128.6, 128.0, 127.0, 126.2, 125.4, 124.6, 123.1 (t, J = 242.9 Hz), 44.1 – 42.6 (broad), 37.8 (t, J = 28.2 Hz), 31.7 (t, J = 24.4 Hz), 27.2 (t, J = 3.9 Hz), 26.8, 24.0.

19F NMR (282 MHz, CDCl₃) δ -99.20 (lt, J = 16.1, 15.4 Hz, 2F).

HRMS (ESI): calcd for C₁₈H₁₇F₂NO (M+H) 336.1228, found 336.1228; calcd for C₁₈H₁₇F₂NO-Na (M+Na) 358.1043, found 358.1043.

5-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-4,4-difluoropentanenitrile (7hd)

Yield 108 mg (85%). Colorless oil.

Chromatography: hexanes/EtOAc, 3/1. Rₚ = 0.24 (hexanes/EtOAc, 3/1).

1H NMR (300 MHz, CDCl₃) δ 6.82 (d, J = 8.2 Hz, 1H), 6.75 (s, 1H), 6.69 (d, J = 8.3 Hz, 1H), 4.24 (s, 4H), 3.06 (t, J = 15.8 Hz, 2H), 2.51 (t, J = 7.7 Hz, 2H), 2.24 – 2.00 (m, 2H).

13C{1H} NMR (75 MHz, CDCl₃) δ 143.6, 143.3, 125.3 (t, J = 5.3 Hz), 123.1, 122.4 (t, J = 243.8 Hz), 118.9, 118.6, 117.5, 64.4, 42.5 (t, J = 25.5 Hz), 31.7 (t, J = 25.5 Hz), 10.4 (t, J = 6.0 Hz).

19F NMR (282 MHz, CDCl₃) δ -100.17 (lt, J = 16.0, 15.8 Hz, 2F).

HRMS (ESI): calcd for C₁₃H₁₂F₂NOSNa (M+Na) 376.0807, found 376.0800.

Reactions of sulfides 3 with nitrones 8 (General procedure)

Fac-Ir(ppy)₃ (1.6 mg, 0.0025 mmol, 0.5 mol%), sulfide 3 (0.5 mmol), nitrone 6 (0.75 mmol), and ascorbic acid (132 mg, 0.75 mmol) were placed in a tube containing a stirring bar. The tube was evacuated and backfilled with argon. DMSO (1 mL) was added followed by 2,4,6-collidine (91 mg, 0.75 mmol). The reaction vessel was irradiated 6 hours by a strip of blue LEDs; during irradiation the mixture was cooled with room temperature water (see Figure S3 for the reaction setup). For the work-up, the mixture was treated with water (3 mL) and extracted with EtOAc (3×4 mL). The combined organic phases were dried with Na₂SO₄, concentrated under vacuum, and the residue was purified by column chromatography.
N-(2,2-Difluoro-1,3-diphenylpropyl)-N-methylhydroxylamine (9ac)

Yield 111 mg (80%). Colorless crystals. Mp 138–140 °C.

Chromatography: hexanes/EtOAc, 4/1. Rf = 0.24 (hexanes/EtOAc, 4/1).

1H NMR (300 MHz, CDCl3) δ 7.47 – 7.17 (m, 10H), 5.62 (s, 1H), 3.82 (t, J = 13.6 Hz, 1H), 3.50 – 3.07 (m, 2H), 2.56 (s, 3H).

13C{H} NMR (75 MHz, CDCl3) δ 131.3 (t, J = 4.3 Hz), 132.1, 131.3, 130.8, 128.8, 128.4, 128.3, 127.4, 123.5 (t, J = 248.7 Hz), 74.3 (t, J = 23.4 Hz), 46.4, 41.9 (t, J = 24.9 Hz).

N-(2,2-Difluoro-1,5-diphenylpentan-3-yl)-N-methylhydroxylamine (9fe)

Yield 99 mg (65%). Colorless crystals. Mp 62–64°C.

Chromatography: hexanes/EtOAc, 5/1. Rf = 0.31 (hexanes/EtOAc, 5/1).

1H NMR (300 MHz, CDCl3) δ 7.42 – 7.17 (m, 7H), 7.13 (d, J = 7.0 Hz, 2H), 5.10 (s, 1H), 3.53 – 3.20 (m, 2H), 2.91 – 2.61 (m, 3H), 2.60 (s, 3H), 2.18 – 2.03 (m, 2H).

13C{H} NMR (75 MHz, CDCl3) δ 141.9, 133.7 (d, J = 8.1 Hz), 130.7, 128.7, 128.5, 125.2 (dd, J = 266.3, 261.7 Hz), 67.0 (dd, J = 27.2, 22.6 Hz), 45.1 (t, J = 1.8 Hz), 41.3 (dd, J = 26.2, 23.6 Hz), 34.3 (d, J = 3.5 Hz), 23.7.

19F NMR (282 MHz, CDCl3) δ -100.7 (dt, J = 254.1, 20.7 Hz), -106.0 (dt, J = 254.1, 22.9 Hz).

HRMS (ESI): calcd for C19H13FNO Na+ (M+Na) 306.1664, found 306.1658.

N-(2,2-Difluoro-1-(4-fluorophenyl)-3-(furan-2-yl)propyl)-N-methylhydroxylamine (9ja)

Yield 123 mg (86%). Colorless oil.

Chromatography: hexanes/EtOAc, 4/1. Rf = 0.23 (hexanes/EtOAc, 4/1).

1H NMR (300 MHz, CDCl3) δ 7.50 – 7.33 (m, 3H), 7.17 – 6.96 (m, 2H), 6.44 – 6.28 (m, 1H), 6.21 (d, J = 3.1 Hz, 1H), 5.75 (s, 1H), 3.87 (dd, J = 15.3, 10.8 Hz, 1H), 3.45 (q, J = 15.3 Hz, 1H), 3.25 (q, J = 15.3 Hz, 1H), 2.53 (s, 3H).

13C{H} NMR (75 MHz, CDCl3) δ 163.1 (d, J = 247.6 Hz), 147.4 (t, J = 5.9 Hz), 144.2, 133.0 (d, J = 8.1 Hz), 127.8, 122.3 (dd, J = 250.4, 248.1 Hz), 115.3 (d, J = 21.3 Hz), 110.8, 109.6, 73.4 (dd, J = 24.7, 21.8 Hz), 46.4, 35.1 (t, J = 27.3 Hz).

19F NMR (282 MHz, CDCl3) δ -100.3 (dd, J = 251.1, 10.8 Hz), -102.3 (dq, J = 251.1, 15.3 Hz), -114.03 (s).

HRMS (ESI): calcd for C18H12F3N2O2 Na+ (M+Na) 308.0869, found 308.0866.

1-[1,1-Difluoro-2-(4-methoxyphenyl)ethyl]-3,4-dihydroisoquinolin-2[1H]-ol (9dd)

Yield 125 mg (78%). Colorless oil.

Chromatography: hexanes/EtOAc, 4/1. Rf = 0.21 (hexanes/EtOAc, 4/1).

1H NMR (300 MHz, CDCl3) δ 7.39 (d, J = 8.2 Hz, 1H), 7.33 – 7.15 (m, 5H), 6.90 (d, J = 8.6 Hz, 2H), 6.20 (s, 1H), 4.52 (dd, J = 12.8, 9.8 Hz, 1H), 3.56 (s, 3H), 3.56 (dt, J = 11.4, 5.6 Hz, 1H), 3.42 – 3.20 (m, 2H), 3.10 – 2.79 (m, 3H).

13C{H} NMR (75 MHz, CDCl3) δ 158.9, 135.7, 131.8, 129.8, 129.3 (t, J = 3.7 Hz), 128.4, 127.6, 126.3, 125.1 (t, J = 2.9 Hz), 123.9 (t, J = 247.7 Hz), 113.8, 70.2 (t, J = 24.8 Hz), 55.3, 51.8, 38.6 (t, J = 24.2 Hz), 26.2.

19F NMR (282 MHz, CDCl3) δ -100.3 – -102.6 (m, 2F).

HRMS (ESI): calcd for C18H12F3N2O2 Na+ (M+Na) 320.1457, found 320.1458; calcd for C18H12F3N2O2 Na+ (M+Na) 342.1276, found 342.1275.

N-[3-[[1,1'-Biphenyl]-4-yl]-1-(3,4-dimethoxyphenyl)-2,2-difluoropropyl]-N-methylhydroxylamine (9bb)

Yield 161 mg (78%). Colorless oil.

Crude was passed through 3 cm silica gel pad using 1/1 hexane/EtOAc mixture and final purification was performed by preparative HPLC (reversed-phase column C18, 21250 mm, 5 μm, flow rate 12 mL·min⁻1; mobile phase: isocratic, acetonitrile/water, 5% water; tR = 6.64 min).

1H NMR (300 MHz, CDCl3) δ 7.63 (d, J = 7.4 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H), 7.47 (t, J = 7.4 Hz, 2H), 7.38 (d, J = 7.4 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.04 (s, 1H), 6.99 – 6.93 (dd, J = 8.3, 1.2 Hz, 1H), 6.90 (d, J = 8.2 Hz, 1H), 5.99 – 5.40 (br, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 3.82 (t, J = 13.7 Hz, 1H), 3.53 – 3.11 (m, 2H), 2.59 (s, 3H).

516
15C{[H] NMR (75 MHz, CDCl₃) δ 149.4, 148.7, 140.7, 140.2, 132.1 (t, J = 4.1 Hz), 131.2, 128.8, 127.4, 127.0, 127.0, 124.5, 124.0, 123.5 (t, J = 248.9 Hz), 114.1, 110.6, 73.9 (t, J = 23.1 Hz), 56.0, 55.8, 46.3, 41.6 (t, J = 25.0 Hz).

15F NMR (282 MHz, CDCl₃) δ -99.8 – -102.0 (m, 2F).

HRMS (ESI): calcd for C₂₀H₂₁F₁₅N₂O₇Na (M+Na) 436.1695, found 436.1690.

1-[3-(2,2-Difluoro-3-[hydroxy(methyl)amino]-3-phenylpropyl]-1H-indol-1-yl]ethanone (9gc)

Yield 145 mg (81%). White crystals. Mp 143 – 145 °C.

Chromatography: hexanes/EtOAc, 1/1. Rf = 0.35 (hexanes/EtOAc, 1/1).
1H NMR (300 MHz, DMSO-d₆) δ 8.39 – 8.30 (m, 2H), 7.72 – 7.62 (m, 2H), 7.58 – 7.48 (m, 2H), 7.41 – 7.23 (m, 5H), 4.06 (dd, J = 18.7, 8.4 Hz, 1H), 3.78 – 3.50 (m, 2H), 2.63 (s, 3H), 2.41 (s, 3H).

15C{[H] NMR (75 MHz, CDCl₃) δ 169.1, 134.9, 133.2, 131.3, 130.9, 127.9, 127.6, 126.3, 124.6, 123.6 (dd, J = 250.3, 242.4 Hz), 123.1 (s), 119.8, 115.7, 113.5 (dd, J = 4.2, 1.3 Hz), 73.36 (dd, J = 28.0, 22.3 Hz), 46.3, 30.2 (t, J = 25.6 Hz), 23.8.

15F NMR (282 MHz, DMSO-d₆) δ -94.8 (d, J = 247.7 Hz, 1F), -100.8 (dm, J = 247.7 Hz, 1F).

HRMS (ESI): calcd for C₂₀H₁₇F₄N₂O₇Na (M+H) 359.1566, found 359.1564; calcd for C₂₀H₁₇F₄N₂O₇Na (M+Na) 381.1385, found 381.1381.

N-[2,2-Difluoro-1-phenyl-3-(thiophen-2-yl)propyl]-N-methylhydroxylamine (9ic)

Yield 113 mg (80%). White crystals. Mp 132 – 134 °C.

Chromatography: hexanes/EtOAc, 5/1. Rf = 0.18 (hexanes/EtOAc, 5/1).
1H NMR (300 MHz, CDCl₃) δ 7.50 – 7.35 (m, 5H), 7.27 (d, J = 5.3 Hz, 1H), 7.27 (dd, J = 5.3, 3.1 Hz, 1H), 6.93 (d, J = 3.1 Hz, 1H), 5.84 – 5.47 (br, 1H), 3.92 (t, J = 13.7 Hz, 1H), 3.63 (td, J = 16.5, 15.5 Hz, 1H), 3.44 (td, J = 15.6, 15.5 Hz, 1H), 2.57 (s, 3H).

15C{[H] NMR (75 MHz, CDCl₃) δ 134.1 (t, J = 9.8 Hz), 132.0, 131.3, 128.8, 128.5, 128.3, 127.0, 125.6, 122.8 (dd, J = 250.0, 248.0 Hz), 73.8 (dd, J = 24.6, 22.0 Hz), 46.4, 36.5 (t, J = 27.1 Hz).

15F NMR (282 MHz, CDCl₃) δ -100.7 (d, J = 249.7 Hz, 1F), -102.3 (dm, J = 249.7 Hz, 1F).

HRMS (ESI): calcd for C₁₄H₁₅F₄N₂O₇Na (M+H) 284.0915, found 284.0925; calcd for C₁₄H₁₅F₄N₂OSNa (M+Na) 306.0735, found 306.0745.

Synthesis of (3,3-difluorobut-1-ene-1,4-diyldibenzene (11) [2]

A screw capped tube containing a stirring bar, triphenylphosphine (13 mg, 0.05 mmol), fac-Ir(ppy)₃ (0.82 mg, 0.00125 mmol, 0.5% mol), sulfide 3a (81 mg, 0.25 mmol) and potassium (E)-trifluorostyryl)borate 10 (70 mg,0.333 mmol) and anhydrous DMF (1 mL). The mixture was subjected to a vacuum of 10 Torr for 1 min at room temperature, and then the flask was filled with argon. Dry zinc acetate (28 mg, 0.15 mmol) was added, tube was tightly closed with the screw cap and irrigated for 15 hours using 465 nm LED; during irradiation the mixture was cooled with room temperature water (see Figure S3 for the reaction setup). For the workup, the reaction mixture was diluted with water (3 mL), and the mixture was extracted with hexane (3×3 mL). The combined organic phases were dried over Na₂SO₄, concentrated under vacuum, and the residue was purified by column chromatography on silica gel. Yield 45 mg (74%). Mixture of isomers, E/Z = 1:4.1. Colorless oil.

Chromatography: hexanes/EtOAc, 30/1. Rf = 0.26 (hexanes/EtOAc, 30/1).
1H NMR (300 MHz, CDCl₃) δ 7.47 – 7.20 (m, 10H, Ph-Z Et), 6.88 (dt, J = 16.2, 2.5 Hz, 1H, E), 6.78 (dt, J = 12.9, 1.7 Hz, 1H, Z), 6.19 (dt, J = 16.2, 11.4 Hz, 1H, Z), 5.72 (dd, J = 27.1, 13.8 Hz, 1H, E), 3.35 (t, J = 14.6 Hz, 2H, E), 3.25 (t, J = 15.9 Hz, 2H, Z).

15C{[H] NMR (75 MHz, CDCl₃) δ 137.4, 137.3, 136.3 (t, J = 7.3 Hz, 1Z), 135.4, 135.1, 134.1 (t, J = 9.3 Hz, E), 134.0, 133.8, 133.0 (t, J = 9.9 Hz, Z), 132.9 (t, J = 4.4 Hz, E), 130.7, 130.7, 129.2 (t, J = 3.5 Hz), 129.0, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2 (d, J = 2.5 Hz), 127.5, 127.5, 127.2, 125.5 (t, J = 28.2 Hz), 123.2 (t, J = 26.2 Hz, E), 120.9 (t, J = 240.8 Hz, Z), 120.8 (t, J = 240.6, E) 44.7 (t, J = 28.0 Hz, E), 43.7 (t, J = 27.0 Hz, Z).

15F NMR (282 MHz, CDCl₃) δ -85.9 (td, J = 15.3, 15.2 Hz, 2F, Z), -94.8 (td, J = 14.2, 13.0 Hz, 2F, E).

S17
Synthesis of 9-phenylacridin-10-lum 2,3,5,6-tetrafluoropyridine-4-thiolate (A)

A screw capped 20 mL vial containing a stirring bar was charged with 9-phenylacridine (127.5 mg, 0.5 mmol) and dichloromethane (3 mL). Thiol 2 (91.5 mg, 0.5 mmol) was added dropwise to deliver crimson red solution. The reaction mixture was stirred for 30 min at room temperature. Then, the stirring was discontinued, and pentane (15 mL) was carefully added to form a separate layer. The reaction vial was kept in a fridge (ca. 5 °C) overnight for slow solvent diffusion. Red needle crystals formed were filtered off and dried under vacuum. Yield 160 mg (73 %). Mp 126-140 °C (dec).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 14.20 – 13.70 (broad singlet, 1H), 8.79 (d, J = 8.8 Hz, 2H), 8.07 – 7.94 (m, 2H), 7.86 (d, J = 8.7 Hz, 2H), 7.75 – 7.56 (m, 5H), 7.53 – 7.44 (m, 2H).

\(^13\)C{\(^1\)H} NMR (75 MHz, CDCl\(_3\)) \(\delta\) 155.0, 145.5 – 144.9 (m), 143.9 – 143.6 (m), 143.5, 142.3 – 141.6 (m), 140.7 – 140.0 (m), 134.3, 130.1, 129.8, 129.0, 127.8, 127.3, 125.4, 124.1.

\(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -96.5 – -97.9 (broad singlet, 2F), -140.7 – -141.9 (broad singlet, 2F).

Figure S4. OLEX diagram of compound A (CCDC 1947116).
Results and Discussions

Optimization of Reactions Parameters

Optimization reactions were carried out on 0.50 mmol scale, unless mentioned otherwise. The reaction mixtures were analyzed by GC-FID (mesitylene as an internal standard) and/or $^{19}$F NMR (trifluorotoluene as an internal standard).

| Entry | Photocatalyst | Solvent | Deviation | Yield (%)$^a$ |
|-------|---------------|---------|-----------|---------------|
| 1     | cat-I         | MeCN    | none      | 36            |
| 2     | cat-I         | DCM     | none      | 71            |
| 3     | cat-I         | DCM     | 352 nm    | 52            |
| 4     | cat-II        | MeCN    | none      | 17            |
| 5     | cat-II        | DCM     | none      | 67            |
| 6     | none          | cyclohexane | none      | 34            |
| 7     | cat-I         | cyclohexane | none      | 99            |
| 8     | cat-II        | cyclohexane | none      | 99            |
| 9     | cat-III       | cyclohexane | none      | 92            |
| 10    | cat-IV        | cyclohexane | none      | 88            |
| 11    | cat-II        | cyclohexane | 1 h       | 55            |
| 12    | cat-II        | cyclohexane | 1 h, 465 nm | 47      |
| 13    | cat-II        | cyclohexane | 465 nm    | 99 (95)       |
| 14$^{b}$ | cat-II   | cyclohexane | 465 nm    | 99 (95)       |

$^a$ Determined by GC-FID. Isolated yields are shown in parenthesis.

$^b$ 20 mmol scale.

Unsuccessful substrates:
Table S2. Reactions of sulfides 3 with silyl enol ethers 4 (Method A).

| Entry | Photocatalyst | Solvent | Deviation | Wavelength | Yield (%)[^a] |
|-------|--------------|---------|-----------|------------|---------------|
| 1     | cat-V (0.5%) | MeCN    | no Zn(OAc)$_2$ | 400 nm     | 14            |
| 2     | cat-V (0.5%) | MeCN    | none      | 400 nm     | 87            |
| 3     | none         | MeCN    | none      | 400 nm     | 0             |
| 4     | cat-VI (5%)  | MeCN    | none      | 400 nm     | 43            |
| 5     | cat-VII (5%) | MeCN    | no PPh$_3$ | 400 nm     | 71            |
| 6     | cat-VII (5%) | MeCN    | 2 h       | 400 nm     | 0             |
| 7     | cat-VII (5%) | MeCN    | none      | 400 nm     | 85            |
| 8     | cat-VII (5%) | MeCN    | none      | 465 nm     | 0             |
| 9     | cat-VIII (5%)| MeCN    | DCM       | 465 nm     | 49            |
| 10    | cat-VIII (5%)| DCM     | cyclohexane| 465 nm     | 0             |
| 11    | cat-VIII (5%)| DMSO    | none      | 465 nm     | 86 (83)       |
| 12    | cat-VIII (5%)| DMF     | none      | 465 nm     | 87 (83)       |
| 13    | none         | DMF     | 24 h, 40W LED[^b] | 465 nm | 33            |
| 14    | cat-VIII (5%)| DMF     | 1.0 equiv Zn(OAc)$_2$ | 465 nm | 74            |
| 15    | cat-VIII (5%)| DMF     | 0.6 equiv PPh$_3$ | 465 nm | 62            |
| 16    | cat-VIII (5%)| DMF     | ZnF$_2$ instead of Zn(OAc)$_2$ | 465 nm | 80            |
| 17    | cat-VIII (5%)| DMF     | ZnI$_2$ instead of Zn(OAc)$_2$ | 465 nm | 66            |
| 18    | cat-VIII (5%)| DMF     | CuF$_2$ instead of Zn(OAc)$_2$ | 465 nm | 74            |
| 19    | cat-VIII (5%)| DMF     | MnF$_2$ instead of Zn(OAc)$_2$ | 465 nm | 87            |
| 20    | cat-V (0.5%) | DMF     | none      | 465 nm     | 79            |
| 21    | cat-IX (0.5%)| DMF     | none      | 465 nm     | 48            |

[^a]: Yield determined by $^{19}$F NMR. Isolated yields are shown in parentheses.
[^b]: 40W Blue Kessil LED lamp.
Table S3. Reactions of sulfides 3 with silyl enol ethers 4 containing EWG group (Method B).

| Entry | X       | Photocatalyst     | Deviation | Yield (%) [a] |
|-------|---------|-------------------|-----------|---------------|
| 1     | CO₂Me   | cat-VIII (5%)     | Zn(OAc)₂ (0.6 equiv) | 0             |
| 2     | CO₂Me   | cat-X (0.5%)      | Zn(OAc)₂ (0.6 equiv) | 0             |
| 3     | CO₂Me   | cat-XI (0.5%)     | Zn(OAc)₂ (0.6 equiv) | 0             |
| 4     | CO₂Me   | cat-V (0.5%)      | Zn(OAc)₂ (0.6 equiv) | 35 (25)       |
| 5     | CO₂Me   | cat-IX (0.5%)     | 0.5 equiv TBAI | 31            |
| 6     | CO₂Me   | cat-X (0.5%)      | 0.5 equiv TBAI | 35            |
| 7     | CO₂Me   | cat-XII (0.5%)    | 0.5 equiv TBAI | 32            |
| 8     | CO₂Me   | cat-X (0.5%)      | 0.5 equiv TBAI, 60 h | 53 (45)     |
| 9     | Cl      | cat-VIII (5%)     | Zn(OAc)₂ (0.6 equiv) | 57            |
| 10    | Cl      | cat-XII (0.5%)    | 0.5 equiv TBAI | 79            |
| 11    | Cl      | cat-IX (0.5%)     | 0.5 equiv TBAI | 99 (92)       |

[a] Yield determined by 19F NMR. Isolated yields are shown in parentheses.

Reaction of sulfide 3I with silyl enol ether 4a under optimal conditions proceeded with low conversion. A by-product resulting from the hydrodefluorination of 3I was also observed (Scheme S1). Yields were determined by 19F NMR with internal standard.

Scheme S1. Reaction of compound 3I.
Mechanistic Studies

Figure S5. Stern-Volmer studies. Plots of relative fluorescence intensities of the photocatalyst \([\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6]\) depending on concentration of the quencher – (i) Bu\(\text{N}\)I (TBAI), (ii) sulfide 3a, (iii) silyl enol ether 4a. Solvent - MeCN.

Figure S6. UV-vis spectra of solutions of compound A in MeCN: 1 – 5 \(\times\) 10\(^{-1}\) mM, 2 – 5 \(\times\) 10\(^{-2}\) mM, 3 – 5 \(\times\) 10\(^{-3}\) mM.

Figure S7. Intermittent light irradiation experiment. The reaction conditions are identical to Method A in Table 2 except for irradiation with 40W blue Kessil LED lamp (A160WE).

Figure S8. Comparison of the colors of cyclohexane solutions: (i) PfySH, (ii) 9-phenylacridine (cat-II), (iii) mixture of PfySH and cat-II prior to irradiation, (iv) reaction mixture after addition of PfySH with 18 h irradiation.
Cyclic Voltammetry studies.

Voltammetric studies were carried out using potentiostat P30JM with a scan rates of 1.0 and 8.0 V s⁻¹ in a temperature-controlled (25 °C) glass cell (V = 10 mL) under a nitrogen atmosphere. Software IR compensation using ferrocene (R = 600 Ω) was used in all experiments. A glassy carbon disk (d = 2.9 mm) was used as the working electrode (carefully polished before each measurement). A saturated calomel electrode (SCE) separated from the solution being studied by a salt bridge filled with the supporting electrolyte (0.1 M Et₄NClO₄ in MeCN) was used as the reference electrode. A platinum plate (S = 3 cm²) was used as the counter electrode. All experiments were performed with the concentration of a studied compounds of 1 mM in MeCN.

Intensity of the cathodic peak of 3a is comparable to that of single-electron wave of ferrocene (see Figures S9 and S10). This suggests that compound 3a may follow single-electron reduction pathway. At scan rate of 1.0-8.0 V s⁻¹ (see Figures S10 and S14) the reduction of 3a is irreversible. Presumably, after the reduction, the resulting anion-radical undergoes fragmentation with the formation of stable thiolate-anion and a radical species. On the reversed scan (scan rate of 1.0-8.0 V s⁻¹, see Figures S10 and S14), there are two irreversible anodic peaks at +0.45 and +0.80 V, which correspond to thiolate—anion (cf. with Figure S12). The first peak may relate to the oxidative transformation of thiolate-anion to the thyl radical, the second peak – to the oxidation of thyl radical followed by fragmentation. Corresponding thiol (see Figure S13) is electrochemically inactive in the studied potential range.
EPR experiment

Procedure: Sulfide 3a (400 µmol) and 5,5-dimethyl-1-pyrroline-N-oxide (800 µmol) were added to the solution of Ir(ppy)$_3$ in benzene (10$^{-3}$ M, 2 mL) under argon. 300 µL of the resulted mixture was taken into an EPR tube. The tube was placed under light (455 nm, 60W) for 15 seconds. The EPR spectrum was immediately recorded at 298 K on EPR spectrometer SPINSCAN X (ADANI).

Figure S15. The X-band EPR spectrum (blue line) of the radical 12. Simulated EPR spectrum (orange line) based on hyperfine coupling constants of $a_N = 12.98$ G, $a_H = 17.25$ G and $a_F = 2.01$ G ($g$-factor = 2.0065).

Experiment parameters:

- Center Field: 3360 G
- Width: 100 G
- Points: 5000
- Scans: 5
- Modulation Amplitude: 100 µT
- Modulation Frequency: 9.432985 GHz
- Microwave Power: 1.0 mW
- Time constant: 0.009 s
### X-Ray Crystallographic Data

**Table S4. Crystallographic data for compounds 3a and A**

| Compound | 3a | A |
|----------|----|----|
| **Formula moiety** | C₁₃H₇F₆NS | C₉F₄NS, C₁₅H₄₄N |
| **Formula** | C₁₃H₇F₆NS | C₂₄H₁₄F₄NS, C₁₉H₁₄ |
| **Formula weight** | 323.26 | 438.43 |
| **Diffractometer** | Bruker APEX-II CCD | Bruker APEX-II CCD |
| **Scan mode** | ω and ϕ scans | ω and ϕ scans |
| **Anode [Wavelength, Å]** | MoKα [0.71073] sealed tube | MoKα [0.71073] sealed tube |
| **Crystal dimensions, mm** | 0.24 × 0.29 × 0.32 | 0.25 × 0.25 × 0.25 |
| **Crystal color** | yellow | yellow |
| **Crystal system** | monoclinic | monoclinic |
| **a, Å** | 9.5947(11) | 8.6198(3) |
| **b, Å** | 4.8799(6) | 7.7249(3) |
| **c, Å** | 13.6316(16) | 29.3919(11) |
| **α, °** | 90 | 90 |
| **β, °** | 94.414(2) | 91.2010(10) |
| **γ, °** | 90 | 90 |
| **Volume, Å³** | 636.35(13) | 1956.69(13) |
| **Density, gcm⁻³** | 1.687 | 1.488 |
| **Temperature, K** | 120 | 120 |
| **T_min/T_max** | 0.6745/0.7465 | 0.6448/0.7461 |
| **μ, mm⁻¹** | 0.319 | 0.217 |
| **Space group** | P2₁ | P2₁/c |
| **Z** | 2 | 4 |
| **F(000)** | 324 | 896 |
| **Reflections collected** | 9856 | 26990 |
| **Independent reflections** | 4591 | 6204 |
| **Reflections (I>2σ(I))** | 4107 | 4804 |
| **Parameters** | 190 | 280 |
| **R_int** | 0.0254 | 0.0349 |
| **2Θ_min - 2Θ_max, °** | 4.258 - 65.552 | 4.726 - 61.850 |
| **wR₂ (all reflections)** | 0.0790 | 0.1097 |
| **R₁(I>σ(I))** | 0.0352 | 0.0408 |
| **GOF** | 1.041 | 1.013 |
| **ρ_min/ρ_max, eÅ⁻³** | -0.215/0.333 | -0.308/0.402 |
| **Restraints** | 1 | 0 |

The structures were solved by direct method and refined in anisotropic approximation for non-hydrogen atoms. Hydrogens atoms of methyl, methylene and aromatic fragments were calculated according to those idealized geometry and refined with constraints applied to C-H and N-H bond lengths and equivalent displacement parameters (U_eq(H) = 1.2U_eq(X), X - central atom of XH₂ group; U_eq(H) = 1.5U_eq(Y), Y - central atom of YH₂ group. All structures were solved with the ShelXT[23] program and refined with the ShelXL[24] program. Molecular graphics was drawn using OLEX2[25] program.

CCDC contains the supplementary crystallographic data for 3a (# 1947115) and A (# 1947116). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.
References

[1] O. V. Fedorov, M. D. Kosobokov, V. V. Levin, M. I. Struchkova and A. D. Dilman, J. Org. Chem. 2015, 80, 5870-5876.
[2] M. Cordier and A. Archambeau, Org. Lett. 2018, 20, 2265-2268.
[3] G. Wagner and T. Garland, Tetrahedron Lett. 2008, 49, 3596-3599.
[4] E. Tyrrell, J. Allen, K. Jones and R. Beauchet, Synthesis 2005, 2005, 2393-2399.
[5] S. Murahashi, H. Mitsui, T. Shiota, T. Tsuda and S. Watanabe, J. Org. Chem. 1990, 55, 1736-1744.
[6] H. Zheng, R. McDonald and D. G. Hall, Chem. Eur. J. 2010, 16, 5454-5460.
[7] N. Kuhl, N. Schröder and F. Glorius, Org. Lett. 2013, 15, 3860-3863.
[8] J. Eriksson, O. Åberg and B. Långström, Eur. J. Org. Chem. 2007, 2007, 455-461.
[9] C. G. Frost, S. D. Penrose and R. Gleave, Org. Biomol. Chem. 2008, 6, 4340-4347.
[10] M. Lukáč, M. Garajová, M. Mrva, F. Devínsky, F. Ondriska and J. Kubincová, J. Fluorine Chem. 2014, 164, 10-17.
[11] R. E. Banks, R. N. Haszeldine, D. R. Karsa, F. E. Rickett and I. M. Young, J. Chem. Soc. C 1969, 1660–1662.
[12] H. Sakaguchi, Y. Uetake, M. Ohashi, T. Niwa, S. Ogoshi and T. Hosoya, J. Am. Chem. Soc. 2017, 139, 12855-12862.
[13] C. S. Thompson, H. Martinez and W. R. Dobbier, J. Fluorine Chem. 2013, 150, 53-59.
[14] D. L. Orsi, B. J. Easley, A. M. Lick and R. A. Altman, Org. Lett. 2017, 19, 1570-1573.
[15] J.-P. Bégué, D. Bonnet-Delpon and M. H. Rock, J. Chem. Soc., Perkin Trans. 1 1996, 1409-1413.
[16] S. A. Fuqua, W. G. Duncan and R. M. Silverstein, J. Org. Chem. 1965, 30, 1027-1029.
[17] H.-J. Tang, L.-Z. Lin, C. Feng and T.-P. Loh, Angew. Chem. Int. Ed. 2017, 56, 9872-9876.
[18] S. S. Ashirbaev, V. V. Levin, M. I. Struchkova and A. D. Dilman, Fluorine Notes 2017, 115, 1-2.
[19] G. N. Chernov, V. V. Levin, V. A. Kokorekin, M. I. Struchkova and A. D. Dilman, Adv. Synth. Catal. 2017, 359, 3063-3067.
[20] V. I. Supranovich, V. V. Levin, M. I. Struchkova, J. Hu and A. D. Dilman, Beilstein J. Org. Chem. 2018, 14, 1637-1641.
[21] V. I. Supranovich, V. V. Levin, M. I. Struchkova and A. D. Dilman, Org. Lett. 2018, 20, 840-843.
[22] N. S. Kondratyev, V. V. Levin, A. A. Zemtsov, M. I. Struchkova and A. D. Dilman, J. Fluorine Chem. 2015, 176, 89-92.
[23] G. M. Sheldrick, Acta Crystallogr. Sect. A. 2015, 71, 3-8.
[24] G. M. Sheldrick, Acta Crystallogr. Sect. C. 2015, 71, 3-8.
[25] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Cryst. 2009, 42, 339-341.
$^{1}$H NMR
300 MHz
CDCl$_3$
$^{13}\text{C}[^1\text{H}]$ NMR
75 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$
$^{1}H$ NMR
300 MHz
CDCl$_3$
$^{13}$C$^1$H NMR
75 MHz
CDCl$_3$
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C\textsuperscript{1H} 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$_3$
19F NMR
282 MHz
CDCl₃

S37
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}\text{C}^{(1\text{H})}$ NMR
75 MHz
CDCl$_3$
$^{1}H$ NMR
300 MHz
CDCl$_3$

Structure: 1f

ppm

1.03
2.02
1.01
1.01
3.39
1.00
3.05
$^{13}$C($^1$H) NMR
75 MHz
CDCl$_3$
$^{13}$C{H$^1$} NMR
75 MHz
CDCl$_3$
$^{1}$H NMR
300 MHz
CDCl$_3$
$^{13}$C\textsuperscript{1}H NMR
75 MHz
CDCl$_3$
$\text{F}$

$\text{F}$

$\text{1H NMR}$

$\text{300 MHz}$

$\text{CDCl}_3$
$\text{^{13}C(}^1\text{H)} \text{ NMR}$

75 MHz

CDCl$_3$

S47
$^{19}$F NMR
282 MHz
CDCl$_3$
$^{13}$C\text{\text{\text{\text{\text{\text{H}}}_1}}}\text{NMR}$

75 MHz

CDCl$_3$

Pentane
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C($^1$H) NMR
75 MHz
CDCl$_3$
$1^1$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$_3$
$^{13}$C({$^1$}H) NMR
126 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$
$^{13}$C{\(^1\)H} NMR
75 MHz
CDCl\textsubscript{3}
$^{19}$F NMR
282 MHz
CDC$_3$
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C($^1$H) NMR
75 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$
$^1\text{H NMR}$

300 MHz

CDCl$_3$

$3k$
$^{13}$C{\textit{H}} NMR
75 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$
\[ \text{MeO}_2\text{C} \] 3e

\( ^1\text{H NMR} \)

300 MHz

CDCl\textsubscript{3}

ppm
$^{13}$C($^1$H) NMR
75 MHz
CDCl$_3$
\[ ^{19}\text{F NMR} \]

282 MHz

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

282 MHz

CDCl$_3$
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C($^1$H) NMR
75 MHz
CDCl$_3$
^19F NMR
282 MHz
CDCl₃

3f

-66.65
-89.22
-89.32
-89.41
-89.45
-132.31
-132.34
-132.36
-132.39
-132.42
-132.45

Ts

0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210

ppm
$^{1}H$ 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$_3$
$^{13}\text{C}^{1\text{H}}\text{NMR}$

75 MHz

CDCl$_3$

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

5aa
\(^1\)H NMR
300 MHz
CDCl\(_3\)

5ah

H\(_2\)O
$^{13}\text{C}^{(1)}\text{H}$ NMR
75 MHz
CDCl$_3$

5ah
'H NMR
300 MHz
CDCl₃
$^{13}$C{H} NMR
75 MHz
CDCl$_3$
$^{1}$H NMR
300 MHz
CDCl$_3$

5ak
$^{13}$C($^1$H) NMR
75 MHz
CDCl$_3$
$^{1}H$ NMR
300 MHz
CDCl$_3$
$^{13}$C($^1$H) NMR
75 MHz
CDCl$_3$
$^{1}H$ NMR
300 MHz
CDCl$_3$
$^{13}$C-$^1$H NMR

75 MHz

CDCl$_3$
\(^{19}\text{F} \text{NMR}\)

282 MHz

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

5ad
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C($^1$H) NMR
75 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$

5af
$^{1}$H NMR
300 MHz
CDCl$_3$
$^{13}$C($^1$H) NMR
75 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$
\[ \text{Ph} \quad \text{FF} \quad \text{O} \]

\[ 5bg \]

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

5cf
$^1$H NMR
300 MHz
CDCl$_3$
19F NMR
282 MHz
CDCl₃

7da
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C\textsuperscript{1}{H} NMR
75 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$_3$
$\text{^1H NMR}$

$300$ MHz

$\text{CDCl}_3$
$^{13}$C{'H) NMR
75 MHz
CDCl$_3$
$^{13}$C($^1$H) NMR
75 MHz
CDCl$_3$
$^{19}$F NMR
g282 MHz
CDCl$_3$
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C\(^{1}H\) NMR
75 MHz
CDCl\(_3\)

7ib
$^{19}$F NMR
282 MHz
CDCl$_3$
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C($^1$H) NMR
75 MHz
CDCl$_3$
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C\NMR
75 MHz
CDCl$_3$
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C\textsuperscript{1}H NMR
75 MHz
CDCl\textsubscript{3}
$^{19}$F NMR
282 MHz
CDCl$_3$
$^{13}$C\(^{1}H\) NMR
75 MHz
CDCl\(_3\)

9ja
$^{19}$F NMR
282 MHz
CDCl$_3$
$^1$H NMR
300 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$
\[ ^1H \text{NMR} \]

300 MHz

CDCl\textsubscript{3}

9bb
$^{13}$C$^1$H NMR
75 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$
$^{1}H$ NMR
300 MHz
DMSO-$d_6$
$^{13}$C($^1$H) NMR
75 MHz
DMSO-$d_6$
$^{19}$F NMR
282 MHz
DMSO-$d_6$

$9_{gc}$
$^{13}$C{$_{^1}$H} NMR
75 MHz
CDCl$_3$
$\text{H NMR}$
$300 \text{ MHz}$
$\text{CDCl}_3$

$11, E:Z = 1.4:1$
$^{13}$C{$^1$H} NMR
75 MHz
CDCl$_3$

11, $E:Z = 1.4:1$
$^{19}$F NMR
282 MHz
CDCl$_3$

11, $E:Z = 1.4:1$
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C\textsuperscript{(1}H\textsuperscript{) NMR
75 MHz
CDCl\textsubscript{3}
$^{19}$F NMR
282 MHz
CDCl$_3$