Supporting Information

Photoredox Generation of the Trifluoromethyl Radical from Borate Complexes via Single Electron Reduction

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General Methods: All reactions were performed under an argon atmosphere. 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.

Reagents. The following starting compounds were prepared according to literature procedures: potassium trifluoromethyltrifluoroborate ([CF₃BF₃]K),¹ potassium pentafluoroethyltrifluoroborate (CF₂CF₂BF₃K),² potassium heptafluoropropyltrifluoroborate ([n-C₃F₇BF₃]K),³ borate complexes 1a-c,⁴ 1,2-dihydronaphthalene,⁵ 1-phenylcyclopetene,⁶ 1-phenylcyclohexene,⁷ 1-phenylcycloheptene,⁸ 1-methylene-1,2,3,4-tetrahydronaphthalene,⁹ 1-vinylnaphthalene,¹⁰ 4-vinyl-1,1'-biphenyl,¹¹ methyl 4-vinylbenzoate,¹² 4-vinylbenzyl acetate,¹³ O-(tert-butyl)dimethylsilyl(4-vinylphenyl)methanol,¹⁴ 1-(azidomethyl)-4-vinylbenzene,¹⁵ tert-butyl 4-vinylbenzylcarbamate,¹⁶ 1-(phthalimidomethyl)-4-vinylbenzene,¹⁷ photocatalyst Cu(dap)₂PF₆.¹⁸

p-Vinylbenzyl alcohol.\textsuperscript{14}

A solution of methyl p-vinylbenzoate (5.64 g, 34.8 mmol) in THF (12 mL) was added to a stirred suspension of LiAlH\textsubscript{4} (1.41 g, 37.1 mmol) in THF (25 mL) within 10 minutes by cooling the mixture with ice-water bath (the reaction is strongly exothermic, and the solvent may even boil despite external cooling). When the addition is complete, the cooling bath was removed, and mixture was stirred at room temperature for 30 minutes. Then, the flask was again cooled with an ice-water bath, and the mixture was quenched by careful dropwise addition of 40% aqueous KOH (15 mL) (CAUTION! Gas evolution). The mixture was extracted with hexane (2 × 50 mL), the combined organic layers were concentrated, and the residue was purified by column chromatography (silica gel, from CH\textsubscript{2}Cl\textsubscript{2} to MTBE/CH\textsubscript{2}Cl\textsubscript{2}, 4/1) to afford 4.26 g (91% yield) of the product as a colorless oil. \textit{Rf} 0.22 (CH\textsubscript{2}Cl\textsubscript{2}).

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \): 7.43 (d, \( J = 8.1 \) Hz, 2H), 7.33 (d, \( J = 8.1 \) Hz, 2H), 6.74 (dd, \( J = 17.6 \) Hz, 10.8 Hz, 1H), 5.78 (d, \( J = 17.6 \) Hz, 1H), 5.27 (d, \( J = 11.0 \) Hz, 1H), 4.68 (br s, 2H), 1.96 (br s, 1H).

2-[(4-vinylbenzyl)oxy]tetrahydro-2H-pyran.

A mixture of p-vinylbenzyl alcohol (468 mg, 3.49 mmol), dihydropyran (0.50 mL, 0.48 g, 5.48 mmol, 1.6 eq.) and NH\textsubscript{2}SO\textsubscript{3}H (65 mg, 0.67 mmol, 0.19 equiv) was stirred for 24 hours at room temperature. The mixture was diluted with hexane (10 mL), filtered, the precipitate was washed with additional hexane (10 mL). The filtrates were combined and subjected to column chromatography (silica gel, from CH\textsubscript{2}Cl\textsubscript{2}/hexane 1/2 to CH\textsubscript{2}Cl\textsubscript{2}). The product was obtained as a pale yellow oil (717 mg, 94 % yield). \textit{Rf} 0.53 (CH\textsubscript{2}Cl\textsubscript{2}).

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \): 7.42 (d, \( J = 7.5 \) Hz, 2H), 7.36 (d, \( J = 7.9 \) Hz, 2H), 6.74 (dd, \( J = 17.6 \) Hz, 10.8 Hz, 1H), 5.77 (d, \( J = 17.6 \) Hz, 1H), 5.26 (d, \( J = 11.0 \) Hz, 1H), 4.80 (d, \( J = 12.1 \) Hz, 1H), 4.73 (br s, 1H), 4.53 (d, \( J = 12.1 \) Hz, 1H), 4.01–3.88 (m, 1H), 3.63–3.51 (m, 1H), 2.00–1.48 (m, 6H).

\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}), \( \delta \): 138.0, 136.9, 136.6, 128.1, 126.2, 113.7, 97.7, 68.5, 62.1, 30.6, 25.5, 19.4. HRMS (ESI): Calcd for C\textsubscript{14}H\textsubscript{18}NaO\textsubscript{2} (M+Na): 241.1199. Found: 241.1203.
**Methyl nicotinate N-oxide.**<sup>19</sup>

![Methyl nicotinate N-oxide](image)

m-Chloroperbenzoic acid (20.3 g of 75% by weight, 88 mmol, 1.1 equiv) was added portionwise to a stirred solution of methyl nicotinate (10.96 g, 80 mmol) in CH₂Cl₂ (80 mL) with external cooling with water bath at room temperature, and the resulting mixture was kept at room temperature for 60 hours. Then, K₂CO₃ (21.5 g, 156 mmol, 1.95 equiv) was added portionwise with stirring, and the mixture was stirred until in turns into thick paste which is hard to stir with a magnetic stirrer (about 15 min). The paste was diluted with CH₂Cl₂ (200 mL), filtered, and the precipitate was washed with CH₂Cl₂ (5×50 mL). The filtrates were combined, and the solvent was removed on a rotary evaporator. The obtained crystalline residue was recrystallized from toluene (40 mL) to afford 11.48 g (94 % yield) of the product as off-white crystals. Mp 102–104 °C. <sup>1</sup>H NMR (300 MHz, CDCl₃) δ: 8.73 (s, 1H), 8.31 (d, J = 6.6 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.35 (dd, J = 7.9 Hz, 6.6 Hz, 1H), 3.93 (s, 3H).

**[3-(Methoxycarbonyl)pyridinium-1-yloxy](trifluoromethyl)difluoroborate (1d).**

Boron trifluoride etherate (4.45 g, 31.36 mmol, 1.03 equiv) was added to a stirred suspension of CF₃BF₃K (5.55 g, 31.55 mmol, 1.04 equiv) and methyl nicotinate N-oxide (4.64 g, 30.33 mmol) in CH₂Cl₂ (31 mL) with cooling in an ice bath, and the reaction mixture was stirred at room temperature for 15 hours. Fine white precipitate was filtered off and washed with CH₂Cl₂ (3×30 mL). The combined filtrates were evaporated, the residue was dissolved in hot CH₂Cl₂ (35 mL), and the solution was kept in a freezer (−20 °C). The mother liquor was removed from the deposited crystals, and the crystals were dried under vacuum to afford the product (7.09 g, 86 %). Colorless crystals. Mp 99–100 °C with decomp (CH₂Cl₂).

<sup>1</sup>H NMR (300 MHz, acetone-d₆) δ: 9.22 (s, 1H), 9.12 (d, J = 6.2 Hz, 1H), 9.04 (d, J = 8.1 Hz, 1H), 8.38 (dd, J = 8.1, 6.2 Hz, 1H), 4.09 (s, 3H).

<sup>13</sup>C NMR (75 MHz, acetone-d₆) δ: 162.4, 146.6, 144.0, 143.0, 132.2, 129.5, 54.1.

<sup>19</sup>F NMR (282 MHz, acetone-d₆) δ: −76.5 (q, J = 32.5 Hz, 3F), −162.0 (q, J = 44.5, 2F).

<sup>11</sup>B (96 MHz, acetone-d₆): 0.4 (tq, J = 43.4, 34.7 Hz).


**Figure S1.** X-ray structure of complex 1d.

**Methyl isonicotinate N-oxide.**

\[
\begin{align*}
| & | \\
\text{O} & \text{OMe} \\
\end{align*}
\]

\(m\)-Chloroperbenzoic acid (9.15 g of 75% by weight, 39.8 mmol, 1.1 equiv) was added portionwise to a stirred solution of methyl isonicotinate (4.93 g, 36.0 mmol) in \(\text{CH}_2\text{Cl}_2\) (36 mL) with external cooling with water bath at room temperature, and the resulting mixture was heated at reflux for 6 hours. Then, \(\text{K}_2\text{CO}_3\) (8.39 g, 60.8 mmol, 1.69 equiv) was added portionwise with stirring and the reaction mixture was stirred until in turns into thick paste which is hard to stir with magnetic stirrer (about 15 min). The paste was diluted with \(\text{CH}_2\text{Cl}_2\) (108 mL), filtered, and the precipitate was washed with \(\text{CH}_2\text{Cl}_2\) (3×100 mL). The filtrates were combined, and the solvent was removed on a rotary evaporator. The obtained crystalline residue was recrystallized from toluene (20 mL) to afford 5.00 g (91% yield) of the product as off-white crystals. \(\text{Mp} 121–123 \degree \text{C.}\) \(^1\text{H}\) NMR (300 MHz, \(\text{CDCl}_3\)) \(\delta\): 8.22 (d, \(J = 7.2\) Hz, 2H), 7.87 (d, \(J = 7.2\) Hz, 2H), 3.95 (s; 3H).

**[4-(Methoxycarbonyl)pyridinium-1-yloxy](trifluoromethyl)difluoroborate (1e).**

\[
\begin{align*}
| & | \\
\text{O} & \text{OMe} \\
\end{align*}
\]

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Boron trifluoride etherate (935 mg, 6.59 mmol, 1.10 equiv) was added to a stirred suspension of CF<sub>3</sub>BF<sub>3</sub>K (1.13 g, 6.42 mmol, 1.07 equiv) and methyl isonicotinate N-oxide (918 mg, 6.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6.0 mL) with cooling in an ice bath, and the reaction mixture was stirred at room temperature for 16 hours. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (15 mL), fine white precipitate was filtered off and washed with CH<sub>2</sub>Cl<sub>2</sub> (3×20 mL). The combined filtrates were evaporated, the crystalline residue was dissolved in hot CH<sub>2</sub>Cl<sub>2</sub> (24 mL), and the solution was kept in a freezer (−20 °C). The mother liquor was removed from the deposited crystals, and the crystals were dried under vacuum to afford the product (1.285 g, 79 % yield). Colorless crystals. Mp 95–99 °C (dec.).

<sup>1</sup>H NMR (300 MHz, acetone-d6) δ: 9.04 (d, J = 6.8 Hz, 2H), 8.58 (d, J = 6.8 Hz, 2H), 4.06 (s; 3H).

<sup>13</sup>C NMR (75 MHz, acetone-d6) δ: 163.2, 144.6, 142.6, 128.7, 54.2.

<sup>19</sup>F NMR (282 MHz, acetone-d6) δ: −76.6 (q, J = 33.2 Hz, 3F), −161.9 (q, J = 43.8, 2F).

<sup>11</sup>B NMR (96 MHz, acetone-d6) δ: 0.4 (tq; J = 43.8, 33.2 Hz).


[3-(Methoxycarbonyl)pyridinium-1-yloxy](pentfluoroethyl)difluoroborate (1f).

Boron trifluoride etherate (715 mg, 5.04 mmol, 1.01 equiv) was added to a stirred suspension of C<sub>2</sub>F<sub>5</sub>BF<sub>3</sub>K (1.16 g, 5.14 mmol, 1.03 equiv) and methyl nicotinate N-oxide (765 mg, 5.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) with cooling in an ice bath, and the reaction mixture was stirred at room temperature for 15 hours and diluted with CH<sub>2</sub>Cl<sub>2</sub> (15 mL). Fine white precipitate was filtered off and washed with CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The combined filtrates were evaporated, and the residue was subjected to column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) to afford the product (1.31 g, 82 %).

Colorless crystals. Mp 100–102 °C (CHCl<sub>3</sub>). Rf 0.27 (CH<sub>2</sub>Cl<sub>2</sub>).

<sup>1</sup>H NMR (300 MHz, acetone-d6) δ: 9.21 (s, 1H), 9.12 (d, J = 6.2 Hz, 1H), 9.04 (d, J = 8.1 Hz, 1H), 8.40 (dd, J = 8.1, 6.2 Hz, 1H), 4.09 (s, 3H).

<sup>13</sup>C NMR (75 MHz, acetone-d6) δ: 162.5, 146.7, 144.1, 143.1, 132.2, 129.6, 121.9 (qt, J = 283.6, 31.5 Hz), 54.1.

<sup>19</sup>F NMR (282 MHz, acetone-d6) δ: −85.0 (t, J = 5.3 Hz, 3F), −137.3 (m, 2F), −159.5 (q, J = 45.9, 2F).

<sup>11</sup>B (96 MHz, acetone-d6): 1.2 (tt, J = 47.1, 21.7 Hz).

[3-\{\text{Methoxycarbonyl}\text{pyridinium-1-yloxy}\}n-\text{heptafluoropropyl}difuoroborate (1g).

Boron trifluoride etherate (752 mg, 5.30 mmol, 1.03 equiv) was added to a stirred suspension of \(n\)-C\(_3\)F\(_7\)BF\(_3\)K (1.453 g, 5.26 mmol, 1.03 equiv) and methyl nicotinate N-oxide (783 mg, 5.12 mmol) in CH\(_2\)Cl\(_2\) (5 mL) with cooling in an ice bath, and the reaction mixture was stirred at room temperature for 15 hours and diluted with CH\(_2\)Cl\(_2\) (15 mL). Fine white precipitate was filtered off and washed with CH\(_2\)Cl\(_2\) (15 mL). The combined filtrates were evaporated, and the residue was subjected to column chromatography (silica gel, CH\(_2\)Cl\(_2\)) to afford the product (1.755 g, 92 % yield).

Colorless crystals. Mp 89–90 °C. R\(_f\) 0.28 (CH\(_2\)Cl\(_2\)).

\(^1\)H NMR (300 MHz, acetone-d\(_6\)) \(\delta\): 9.21 (s, 1H), 9.11 (d, \(J = 6.2\) Hz, 1H), 9.04 (d, \(J = 8.1\) Hz, 1H), 8.38 (dd, \(J = 8.1, 6.2\) Hz, 1H), 4.09 (s, 3H).

\(^{13}\)C NMR (75 MHz, acetone-d\(_6\)) \(\delta\): 162.5, 146.7, 144.1, 143.1, 132.2, 129.6, 119.6 (qt, \(J = 287.2, 35.1\) Hz), 111.5 (m), 54.1.

\(^{19}\)F NMR (282 MHz, acetone-d\(_6\)) \(\delta\): –82.5 (t, \(J = 9.5\) Hz, 3F), –129.2 (t, \(J = 5.3\) Hz, 2F), –135.0 (br.s, 2F), –158.6 (q, \(J = 42.4, 2F\)).

\(^{11}\)B (96 MHz, acetone-d\(_6\)): 1.2 (tt, \(J = 46.7, 21.0\) Hz).


Figure S2. X-ray structure of complex 1f.
Methoxytrifluoromethylation of alkenes (General procedure).

Degassed methanol (3.0 mL) was added to a mixture of KHCO₃ (160 mg, 1.6 mmol, 2.67 equiv), Cu(dap)₂PF₆ (6.0 mg, 0.006 mmol, 0.01 equiv) and alkene (0.60 mmol) in the Schlenk tube. [Dichloromethane was added in reactions of 1,2-diphenylethylene (2 mL of CH₂Cl₂) and 1-(phthalimidomethyl)-4-vinylbenzene (1 mL of CH₂Cl₂) to improve their solubility in the reaction mixture.] Complex 1d (203 mg, 0.75 mmol, 1.25 equiv) was added, and the vessel was irradiated for 1 hour with a strip of blue LED with stirring; during irradiation the mixture was cooled with tap water. The mixture was diluted [for 3a-g,j,l,m,o,p,t,u, with MTBE (3 mL); for 3i,k,n,q,r,s, with hexane (3 mL)], and water (6 mL) was added with stirring, minor frothing may occur at this step. Organic layer was separated and aqueous layer was extracted with the corresponding solvent (3×3 mL). The combined organic layers were dried over Na₂SO₄, concentrated, and the residue was subjected to column chromatography on silica gel.

Photo S1. Reaction setup.

Photo S2. Reaction setup with LED irradiation.
(3,3,3-Trifluoro-1-methoxy-1-phenylpropyl)benzene (3a).\(^{21}\)

\[
\begin{array}{c}
\text{MeO} \\
\text{CF}_3 \\
\end{array}
\]

Yield 160 mg (95%). Colorless crystals. Mp 61–62 °C. R\(_f\) 0.14 (CH\(_2\)Cl\(_2\)/hexane, 1/10).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 7.28–7.08 (m, 10H), 3.13 (q, \(J = 10.0\); 2H), 3.03 (s, 3H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)), \(\delta\): 144.0, 128.3, 127.4, 126.7, 125.8 (q, \(J = 278.2\) Hz), 79.9 (q, \(J = 1.7\) Hz), 51.1, 38.9 (q, \(J = 26.2\) Hz).

\(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\): –60.6 (t, \(J = 10.1\) Hz).


1-Methoxy-2-(trifluoromethyl)indane (3b).

\[
\begin{array}{c}
\text{OMe} \\
\text{CF}_3 \\
\end{array}
\]

Yield 109 mg (84%). Mixture of two isomers (ratio 1.5:1). Colorless oil. R\(_f\) 0.35 and 0.41 (CH\(_2\)Cl\(_2\)/hexane, 1/1) (both spots were collected together).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 7.52–7.23 (m, 4H), 5.08 (d, \(J = 3.7\) Hz, major) and 4.84 (d, \(J = 5.5\) Hz, minor) (1H), 3.56 (s, major) and 3.45 (s, minor) (3H), 3.43–3.29 (m, 1H), 3.25–3.00 (m, 2H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)), \(\delta\): 141.6, 140.8, 140.5, 140.3, 129.4, 129.3, 127.7 (q, \(J = 277.5\) Hz, major), 127.4, 126.9, 126.5 (q, \(J = 277.5\) Hz, minor), 125.44, 125.37, 125.32, 124.9, 84.8 (q, \(J = 2.8\) Hz, major), 82.5 (q, \(J = 2.0\) Hz, minor), 57.2 (major), 57.0 (minor), 49.0 (q, \(J = 26.5\) Hz, major), 47.9 (q, \(J = 27.3\) Hz, minor), 31.06 (q, \(J = 2.8\) Hz, major), 30.96 (q, \(J = 2.6\) Hz, minor).

\(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\): –60.4 (d, \(J = 10.6\) Hz, minor), –71.1 (d, \(J = 8.5\) Hz, major).


1-Methoxy-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene (3c).

\[
\begin{array}{c}
\text{OMe} \\
\text{CF}_3 \\
\end{array}
\]

Yield 109 mg (79%). Mixture of two isomers (ratio 1:1). Colorless oil. R\(_f\) 0.33 and 0.42 (CH\(_2\)Cl\(_2\)/hexane, 1/1) (both spots collected together).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 7.45–7.15 (m, 2x4H), 4.62 (d, \(J = 5.1\) Hz, 1H), 4.47 (s, 1H), 3.42 (s, 3H), 3.38 (s, 3H), 3.10 (dd, \(J = 17.4, 6.4\) Hz, 1H), 2.96–2.74 (m, 4H), 2.58–2.19 (m, 3H), 2.10–1.96 (m, 1H), 1.93–1.76(m, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$), δ: 137.8, 136.3, 134.4, 134.0, 130.0, 129.6, 129.1, 128.9, 128.5, 128.2, 127.5 (q, $J = 279.7$ Hz), 127.3 (q, $J = 279.2$ Hz), 126.4, 125.6, 75.9 (q, $J = 2.4$ Hz), 75.1 (q, $J = 2.9$ Hz), 56.9, 55.9, 44.3 (q, $J = 26.5$ Hz), 43.3 (q, $J = 24.9$ Hz), 27.6, 26.8, 20.9 (q, $J = 2.8$ Hz), 16.8 (q, $J = 2.4$ Hz).

$^{19}$F NMR (282 MHz, CDCl$_3$) δ: −69.6 (d, $J = 8.5$ Hz), −70.7 (d, $J = 8.5$ Hz). HRMS (ESI): Calcd for C$_{12}$H$_{13}$F$_3$NaO (M+Na): 253.0811. Found: 253.0819.

**[1-Methoxy-2-(trifluoromethyl)cyclopentyl]benzene (3d).**

![Image](image)

Yield 91 mg (62%). Mixture of two isomers (ratio 11:1). Colorless oil. R$_f$ 0.24 (CH$_2$Cl$_2$/hexane, 1/4).

$^1$H NMR (300 MHz, CDCl$_3$) δ: 7.55–7.30 (m, 5H both isomers), 3.21 (s, minor) and 2.98 (s, major) (3H), 2.96–2.82 (m, major) and 2.77–2.65 (m, minor) (1H), 2.42–2.19 (m, 3H both isomers), 2.12–1.81 (m, 3H both isomers).

$^{13}$C NMR (75 MHz, CDCl$_3$), δ: major isomer: 138.3, 128.06 (br), 128.02, 127.96, 126.7 (q, $J = 278.6$ Hz), 88.6 (q, $J = 1.5$ Hz), 54.9 (q, $J = 24.3$ Hz), 49.4, 30.4 (q, $J = 1.5$ Hz), 25.0 (q, $J = 2.6$ Hz), 21.0. minor isomer (observed peaks only): 128.5, 127.4, 126.5 (br), 55.3 (q, $J = 25.4$ Hz), 51.4, 34.8 (br), 25.1 (q, $J = 2.2$ Hz), 22.0.

$^{19}$F NMR (282 MHz, CDCl$_3$) δ: −64.6 (d, $J = 10.6$ Hz, minor), −66.9 (d, $J = 10.6$ Hz, major). HRMS (ESI): Calcd for C$_{13}$H$_{15}$F$_3$NaO (M+Na): 267.0967. Found: 267.0967.

**[1-Methoxy-2-(trifluoromethyl)cyclohexyl]benzene (3e).**

![Image](image)

Yield 101 mg (65%). Mixture of two isomers (ratio 3.8:1). Colorless oil. R$_f$ 0.29 (CH$_2$Cl$_2$/hexane, 1/4).

$^1$H NMR (300 MHz, CDCl$_3$) δ: 7.47–7.26 (m, 5H both isomers), 3.31 (s, minor) and 2.92 (s, major) (3H), 2.76–2.58 (m) and 2.40–1.38 (m) (9H, both isomers).

$^{13}$C NMR (75 MHz, CDCl$_3$), δ: major isomer: 142.6, 128.23, 127.7, 127.14 (br), 126.79 (q, $J = 280.9$ Hz), 76.9 (q, $J = 1.1$ Hz), 50.4 (q, $J = 22.7$ Hz), 48.5, 25.7 (q, $J = 1.7$ Hz), 22.2 (q, $J = 2.8$ Hz), 20.7, 20.6 (br), minor isomer: 142.8, 128.21, 127.08, 126.85 (q, $J = 282.5$ Hz), 126.6 (br), 78.4, 52.9 (q, $J = 23.2$ Hz), 50.3, 33.4 (br), 25.1, 22.4 (q, $J = 2.8$ Hz), 21.5.

$^{19}$F NMR (282 MHz, CDCl$_3$) δ: −60.9 (d, $J = 12.7$ Hz, major), −64.4 (d, $J = 8.5$ Hz, minor). HRMS (ESI): Calcd for C$_{14}$H$_{17}$F$_3$NaO (M+Na): 281.1124. Found: 281.1114.
(1R*,2S*)-1-Methoxy-1-phenyl-2-(trifluoromethyl)cycloheptane (3f).

Yield 155 mg (95%). Colorless oil. Mp 70–71 °C. Rf 0.24 (CH3Cl2/hexane, 1/4). Stereochemistry was determined by 2D 1H–1H NOESY and 1H–19F HOESY experiments.

1H NMR (300 MHz, CDCl3) δ: 7.44–7.22 (m, 5H), 3.34 (s, 3H), 2.60–2.44 (m, 1H), 2.25–1.83 (m, 6H), 1.82–1.51 (m, 4H).

13C NMR (75 MHz, CDCl3), δ: 144.9 (br), 128.0, 127.4 (q, J = 282.5 Hz), 126.9, 126.5 (br), 81.1 (br), 56.0 (q, J = 22.1 Hz), 51.2, 37.5 (br), 27.8, 26.6, 22.6 (q, J = 3.0 Hz), 21.6.

19F NMR (282 MHz, CDCl3) δ: –63.8 (d, J = 10.6 Hz).


1-Methoxy-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydronaphthalene (3g).

Yield 133 mg (91%). Colorless oil. Rf 0.61 (CH3Cl2/hexane, 1/4).

1H NMR (300 MHz, CDCl3) δ: 7.54–7.45 (m, 1H), 7.33–7.21 (m, 2H), 7.20–7.12 (m, 1H), 3.11 (s; 3H), 2.95–2.75 (m, 2H), 2.75–2.57 (m, 2H), 2.33–2.14 (m, 2H), 2.12–1.82 (m, 2H).

13C NMR (75 MHz, CDCl3), δ: 138.5, 137.9, 129.3, 127.8, 126.7, 126.4, 125.8 (q, J = 278.8 Hz), 75.9 (q, J = 1.8 Hz), 50.4, 45.2 (q, J = 26.4 Hz), 29.6, 29.3 (br), 20.6.

19F NMR (282 MHz, CDCl3) δ: –60.2 (t; J = 10.6 Hz).


1-Methoxy-4-(3,3,3-trifluoro-1-methoxy-2-methylpropyl)benzene (3h).

Yield 125 mg (84%). Mixture of two isomers (ratio 1:1). Colorless oil. Rf 0.67 (CH3Cl2).

1H NMR (300 MHz, CDCl3) δ: 7.22 (d, J = 8.2 Hz, 2x2H), 6.92 (d, J = 8.2 Hz, 2x2H), 4.47 (d, J = 3.7 Hz, 1H), 4.21 (d, J = 7.8 Hz, 1H), 3.83 (s, 2x3H), 3.27 (s, 3H), 3.18 (s, 3H), 2.63 (octet, J = 7.9 Hz, 1H), 2.47–2.26 (m, 1H), 1.12 (d, J = 7.3 Hz, 3H), 0.87 (d, J = 6.9 Hz, 3H).

13C NMR (75 MHz, CDCl3), δ: 159.8, 159.4, 131.4, 130.5, 129.0, 127.9, 114.0, 113.9, 127.6 (q, J = 280.5 Hz), 82.3 (q, J = 1.9 Hz), 80.2 (q, J = 2.7 Hz), 57.2, 56.6, 55.31, 55.29, 45.5 (q, J = 24.9 Hz), 44.2 (q, J = 24.7 Hz), 10.3 (q, J = 3.1 Hz), 7.2 (q, J = 2.7 Hz).

19F NMR (282 MHz, CDCl3) δ: –69.6 (d, J = 8.5 Hz), –70.6 (d, J = 8.5 Hz).

\{2,2,2-Trifluoro-1-[methoxy(phenyl)methyl]ethyl\}benzene (3i).\textsuperscript{20}

\begin{center}
\includegraphics[width=0.2\textwidth]{image1.png}
\end{center}

Yield 109 mg (65%). Mixture of two isomers (4:1). Colorless oil. R\(_f\) 0.14 and 0.25 (CH\(_2\)Cl\(_2\)/hexane, 1/4) (both spots collected together).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 7.35–7.05 (m, 10H), 4.90 (d, \(J = 5.0\) Hz, minor) and 4.71 (d, \(J = 9.4\) Hz, major) (1H), 3.76 (quintet, \(J = 9.1\) Hz, major) and 3.64–3.49 (m, minor) (1H), 3.32 (s, major) and 3.28 (s, minor) (3H).

\(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\): –63.9 (d, \(J = 8.5\) Hz, major), –66.2 (d, \(J = 8.5\) Hz, minor).

1-(3,3,3-Trifluoro-1-methoxypropyl)naphthalene (3j).

\begin{center}
\includegraphics[width=0.2\textwidth]{image2.png}
\end{center}

Yield 116 mg (76%). Colorless oil. R\(_f\) 0.61 (CH\(_2\)Cl\(_2\)/hexane, 1/1).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 8.20 (d, \(J = 8.1\) Hz, 1H), 7.99–7.86 (m, 2H), 7.70–7.52 (m, 4H), 5.29 (dd, \(J = 9.1\), 2.8 Hz, 1H), 3.39 (s, 3H), 2.94–2.73 (m, 1H), 2.72–2.52 (m, 1H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)), \(\delta\): 135.5, 134.2, 130.6, 129.3, 129.0, 126.7, 126.2 (q, \(J = 277.5\) Hz), 126.0, 125.6, 124.4, 122.7, 75.9 (q, \(J = 3.1\) Hz), 57.1, 41.8 (q, \(J = 27.6\) Hz).

\(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\): –65.0 (t, \(J = 10.6\) Hz).


3,3,3-Trifluoro-2-[methoxy(phenyl)methyl]propan-1-ol (3k).

\begin{center}
\includegraphics[width=0.2\textwidth]{image3.png}
\end{center}

Yield 83 mg (59%). Mixture of two isomers (ratio 1.5:1). Colorless oil. R\(_f\) 0.42 (EtOAc/hexane, 1/3).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 7.51–7.30 (m, 5H), 4.70 (d, \(J = 4.8\) Hz, minor) and 4.64 (d, \(J = 7.5\) Hz, 1H, major) (1H), 4.09–3.78 (m) and 3.56–3.43 (m) (2H), 3.31 (s, minor) and 3.26 (s, major) (3H), 2.95 (t, \(J = 6.1\) Hz, minor) and 2.82–2.64 (m, major) (1H), 2.61–2.44 (m, minor) and 2.22 (t, \(J = 5.6\) Hz, major) (1H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)), \(\delta\): 138.8, 137.7, 128.9, 128.74, 128.71, 128.5, 127.7, 126.8, 126.5 (q, \(J = 281.4\), major), 126.4 (q, \(J = 280.9\), minor), 81.4 (q, \(J = 2.4\) Hz, minor), 80.7 (q, \(J = 2.0\) Hz, major), 58.3 (q, \(J = 3.3\) Hz, major), 58.1 (q, \(J = 2.9\) Hz, minor), 57.5 (minor), 57.1 (major), 51.9 (q, \(J = 23.2\) Hz, minor), 51.5 (q, \(J = 23.2\) Hz, major).

\(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\): –65.0 (d, \(J = 8.5\) Hz, major), –67.2 (d, \(J = 8.5\) Hz, minor).

1-(1,1'-Biphenyl-4-yl)-3,3,3-trifluoropropyl methyl ether (3l).

\[
\text{Yield 158 mg (94%). Colorless crystals. Mp 40–41 °C. Rf 0.18 (CH}_2\text{Cl}_2/\text{hexane, 1/4).}
\]

\[ ^1\text{H NMR (300 MHz, CDCl}_3\] \( \delta \) : 7.75–7.60 (m, 4H), 7.56–7.37 (m, 5H), 4.57 (dd, \( J = 8.2, 4.0 \) Hz, 1H), 3.32 (s, 3H), 2.85–2.65 (m, 1H), 2.56–2.36 (m, 1H).

\[ ^{13}\text{C NMR (75 MHz, CDCl}_3\] \( \delta \) : 140.73, 140.72, 139.2, 129.0, 127.65, 127.63, 127.23, 127.08, 125.9 (q; \( J = 277.3 \) Hz), 77.7 (q; \( J = 3.3 \) Hz), 57.1, 42.4 (q; \( J = 27.5 \) Hz).

\[ ^{19}\text{F NMR (282 MHz, CDCl}_3\] \( \delta \) : –64.4 (t, \( J = 10.6 \) Hz).


1-Methoxy-4-(3,3,3-trifluoro-1-methoxypropyl)benzene (3m).

\[
\text{Yield 121 mg (86%). Colorless oil. Rf 0.50 (CH}_2\text{Cl}_2).}
\]

\[ ^1\text{H NMR (300 MHz, CDCl}_3\] \( \delta \) : 7.27 (d, \( J = 8.6 \) Hz, 2H), 6.94 (d, \( J = 8.6 \) Hz, 2H), 4.44 (dd, \( J = 8.4, 4.4 \) Hz, 1H), 3.84 (s, 3H), 3.22 (s, 3H), 2.78–2.57 (m, 1H), 2.48–2.28 (m, 1H).

\[ ^{19}\text{F NMR (282 MHz, CDCl}_3\] \( \delta \) : –64.5 (t, \( J = 10.6 \) Hz).


2-{(4-(3,3,3-Trifluoro-1-methoxypropyl)benzyl)oxy}tetrahydro-2H-pyran (3n).

\[
\text{Yield 181 mg (95%). Colorless oil. Rf 0.33 (CH}_2\text{Cl}_2). Only one set of signals is observed in NMR spectra, since two stereocenters are located far away from each other.}
\]

\[ ^1\text{H NMR (300 MHz, CDCl}_3\] \( \delta \) : 7.41 (d, \( J = 8.0 \) Hz, 2H), 7.31 (d, \( J = 8.0 \) Hz, 2H), 4.82 (d, \( J = 12.1 \) Hz, 1H), 4.74 (t, \( J = 3.0 \) Hz, 1H), 4.51 (d, \( J = 12.1 \) Hz, 1H), 4.47 (dd, \( J = 8.6, 4.0 \) Hz, 1H), 4.02–3.86 (m, 1H), 3.64–3.50 (m, 1H), 3.23 (s, 3H), 2.77–2.53 (m, 1H), 2.47–2.26 (m, 1H), 2.01–1.46 (m, 6H).

\[ ^{13}\text{C NMR (75 MHz, CDCl}_3\] \( \delta \) : 139.3, 138.8, 128.2, 126.6, 125.8 (q, \( J = 277.4 \) Hz), 98.0, 77.6 (q, \( J = 3.9 \) Hz), 68.6, 62.2, 56.7, 42.3 (q, \( J = 27.5 \) Hz), 30.6, 25.5, 19.4.

\[ ^{19}\text{F NMR (282 MHz, CDCl}_3\] \( \delta \) : –64.5 (t, \( J = 10.6 \) Hz).


---

**4-(3,3,3-Trifluoro-1-methoxypropyl)benzyl acetate (3o).**

![Chemical Structure]

Yield 144 mg (87%). Colorless oil. Rf 0.17 (CH2Cl2).

\(^1\)H NMR (300 MHz, CDCl3) δ: 7.39 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5.12 (s, 2H), 4.47 (dd, J = 8.5, 4.1 Hz, 1H), 3.23 (s, 3H), 2.75–2.55 (m, 1H), 2.45–2.25 (m, 1H), 2.12 (s, 3H).

\(^13\)C NMR (75 MHz, CDCl3), δ: 170.9, 140.2, 136.3, 128.7, 126.8, 125.7 (q, J = 277.3 Hz), 77.6 (q, J = 3.3 Hz), 65.9, 56.8, 42.3 (q, J = 27.5 Hz), 21.0.

\(^19\)F NMR (282 MHz, CDCl3) δ: –64.5 (t, J = 10.6 Hz).


**tert-Butyl(dimethyl){[4-(3,3,3-trifluoro-1-methoxypropyl)benzyl]oxy}silane (3p).**

![Chemical Structure]

Yield 177 mg (85%). Colorless oil. Rf 0.24 (CH2Cl2/hexane, 1/3).

\(^1\)H NMR (300 MHz, CDCl3) δ: 7.36 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 4.77 (s, 2H), 4.47 (dd, J = 8.4, 4.0 Hz, 1H), 3.23 (s, 3H), 2.77–2.55 (m, 1H), 2.47–2.27 (m, 1H), 0.97 (s, 9H), 0.13 (s, 6H).

\(^13\)C NMR (75 MHz, CDCl3), δ: 141.9, 138.7, 126.6, 125.8 (q, J = 277.2 Hz), 77.7 (q, J = 3.3 Hz), 64.8, 56.7, 42.4 (q, J = 27.6 Hz), 26.1, 18.6, –5.2.

\(^19\)F NMR (282 MHz, CDCl3) δ: –64.5 (t, J = 10.6 Hz).


**[4-(3,3,3-Trifluoro-1-methoxypropyl)phenyl]methanol (3q).**

![Chemical Structure]

Yield 122 mg (87%). Colorless oil. Rf 0.18 (EtOAc/hexane = 1/3).

\(^1\)H NMR (300 MHz, CDCl3) δ: 7.39 (d, J = 7.5 Hz, 2H), 7.32 (d, J = 7.5 Hz, 2H), 4.70 (d, J = 4.7 Hz, 2H), 4.47 (dd, J = 8.2, 4.1 Hz, 1H), 3.22 (s, 3H), 2.77-2.57 (m, 1H), 2.47–2.27 (m, 1H), 2.18 (t, J = 4.7 Hz, 1H).

\(^13\)C NMR (75 MHz, CDCl3), δ: 141.3, 139.4, 127.5, 126.9, 125.7 (q, J = 277.2 Hz), 77.7 (q, J = 2.9 Hz), 65.0, 56.7, 42.2 (q, J = 27.6 Hz).

\(^19\)F NMR (282 MHz, CDCl3) δ: –64.5 (t, J = 10.6 Hz).

2-[4-{3,3,3-Trifluoro-1-methoxypropyl}benzyl]-1H isoindole-1,3(2H)-dione (3r).

Yield 198 mg (91%). Colorless crystals. Mp 85–87 °C. Rf 0.45 (CH$_2$Cl$_2$).
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.89–7.79 (m, 2H), 7.76–7.65 (m, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 4.85 (s, 2H), 4.43 (dd, $J = 8.5$, 3.8 Hz, 1H), 3.19 (s, 3H), 2.71–2.48 (m, 1H), 2.41–2.20 (m, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$), $\delta$: 168.0, 139.8, 136.7, 134.1, 132.2, 129.1, 126.9, 125.7 (q, $J = 277.0$ Hz), 123.4, 77.5 (q, $J = 3.3$ Hz), 56.7, 42.2 (q, $J = 27.6$ Hz), 41.3.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$: –64.5 (t, $J = 10.6$ Hz).


tert-Butyl 4-{3,3,3-trifluoro-1-methoxypropyl}benzylcarbamate (3s).

Yield 168 mg (84%). Colorless oil. Rf 0.39 (EtOAc/hexane = 1/3).
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.33–7.24 (m, 4H), 5.06 (br s, 1H), 4.44 (dd, $J = 8.4$, 4.2 Hz, 1H), 4.32 (br s, 2H), 3.20 (s, 3H), 2.73–2.51 (m, 1H), 2.44–2.22 (m, 1H), 1.46 (br. s, 9H).

$^{13}$C NMR (75 MHz, CDCl$_3$), $\delta$: 156.1, 139.5, 139.1, 127.9, 126.8, 125.7 (q, $J = 277.3$ Hz), 79.6 (br), 77.6 (q, $J = 3.3$ Hz), 56.6, 44.3 (br), 42.2 (q, $J = 27.5$ Hz), 28.5.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$: –64.5 (t, $J = 10.6$ Hz).

HRMS (ESI): Calcd for C$_{16}$H$_{22}$F$_3$NNaO$_3$ (M+Na): 356.1444. Found: 356.1436.

1-[4-(Azidomethyl)phenyl]-3,3,3-trifluoropropyl methyl ether (3t).

Yield 129 mg (83%). Colorless oil. Rf 0.52 (CH$_2$Cl$_2$).
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.37 (s, 4H), 4.50 (dd, $J = 8.4$, 4.2 Hz, 1H), 4.38 (s, 2H), 3.25 (s, 3H), 2.78–2.57 (m, 1H), 2.48–2.28 (m, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$), $\delta$: 140.3, 135.8, 128.7, 127.1, 125.7 (q, $J = 277.4$ Hz), 77.6 (q, $J = 3.3$ Hz), 56.8, 54.5, 42.3 (q, $J = 27.6$ Hz).

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$: –64.5 (t, $J = 10.6$ Hz).

1-[4-(Chloromethyl)phenyl]-3,3,3-trifluoropropyl methyl ether (3u).

Yield 102 mg (67%). Colorless oil. R$_f$ 0.70 (CH$_2$Cl$_2$).

$^1$H NMR (300 MHz, CDCl$_3$) δ: 7.45 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.62 (s, 2H), 4.50 (dd, J = 8.4, 4.0 Hz, 1H), 3.25 (s, 3H), 2.78–2.55 (m, 1H), 2.48–2.27 (m, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$), δ: 140.5, 137.8, 129.1, 127.0, 125.7 (q, J = 277.5 Hz), 77.6 (q, J = 2.8 Hz), 56.8, 45.8, 42.3 (q, J = 27.1 Hz).

$^{19}$F NMR (282 MHz, CDCl$_3$) δ: –64.5 (t, J = 10.6 Hz).


(3,3,4,4,4-Pentafluoro-1-methoxy-1-phenylbutyl)benzene (4a).

According to the General procedure using complex 1f; for the work-up, hexane was used. Yield 186 mg (94%). Colorless crystals, Mp 80–81 °C. R$_f$ 0.33 (CH$_2$Cl$_2$/hexane = 1/10).

$^1$H NMR (300 MHz, CDCl$_3$) δ: 7.61–7.25 (m, 10H), 3.30 (t, J = 17.6 Hz, 2H), 3.26 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$), δ: 144.2, 128.3, 127.4, 126.7, 119.3 (qt, J = 286.4, 35.9 Hz), 115.3 (tq, J = 257.4, 36.8 Hz), 80.4, 51.1, 34.4 (t, J = 19.1 Hz).

$^{19}$F NMR (282 MHz, CDCl$_3$) δ: –87.5 (s, 3F), –117.6 (t, J = 18.0 Hz, 2F).

HRMS (ESI): Calcd for C$_{17}$H$_{15}$F$_5$NaO$_3$ (M+Na): 353.0935. Found: 353.0931.

(3,3,4,4,5,5,5-Heptafluoro-1-methoxy-1-phenylpentyl)benzene (4b).

According to the General procedure using complex 1g; for the work-up, hexane was used. Yield 217 mg (95%). Colorless crystals. Mp 72–73 °C. R$_f$ 0.25 (CH$_2$Cl$_2$/hexane = 1/10).

$^1$H NMR (300 MHz, CDCl$_3$) δ: 7.55–7.29 (m, 10H), 3.33 (t, J = 18.2 Hz, 2H), 3.25 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$), δ: 144.3, 128.3, 127.4, 126.7, 118.1 (qt, J = 287.5, 34.0 Hz), 117.5 (tt, J = 258.7, 30.1 Hz), 109.0 (ts, J = 264.3, 37.6 Hz), 80.5, 51.1, 34.1 (t, J = 19.1 Hz).

$^{19}$F NMR (282 MHz, CDCl$_3$) δ: –80.9 (t, J = 9.5 Hz, 3F), –114.4 (m, 2F), –128.6 (m, 2F).

Trapping experiments.

Complex 1d (42.5 mg, 0.157 mmol, 1.31 equiv) was added to a stirred mixture of Cu(dap)2PF6 (121 mg, 0.122 mmol, 1.01 equiv), KHCO3 (40 mg, 0.40 mmol, 3.3 equiv), and TEMPO (18.8 mg, 0.120 mmol) in MeOH (1.2 mL), and the reaction mixture was irradiated with blue LED with stirring and cooling with tap water for 1 hour. Then, PhCF3 was added (22.5 mg, 0.154 mmol) as an internal standard, the precipitate was allowed to settle down and a part of solution (ca. 0.6 mL) was taken, and analyzed by 19F NMR. Compound 6 (79% yield), 19F NMR (282 MHz, MeOH) δ: –57.1 (s).23

1,3-Dimethyl-3-(2,2,2-trifluoroethyl)-1,3-dihydro-2H-indol-2-one.24
According to the General procedure (see page S8) using N-methacryloyl-N-methylaniline instead of arylalkene).
Yield 33 mg (23 %). Colorless oil. Chromatography (CH2Cl2 to EtOAc/CH2Cl2, 1/10). Rf = 0.45 (EtOAc/CH2Cl2, 1/19).
1H NMR (300 MHz, CDCl3) δ: 7.37–7.24 (m, 2H), 7.10 (t, J = 7.5 Hz, 2H), 6.89 (d, J = 7.7 Hz, 2H), 3.24 (s, 3H), 2.92–2.57 (m, 2H), 1.41 (s, 3H).
19F NMR (282 MHz, CDCl3) δ: –62.7 (t, J = 10.6 Hz; 3F).

Cyclic voltammetry.
Voltammetric studies were carried out using with the scan rate 0.1 V·s⁻¹ in a temperature-controlled (25 °C) cell (V = 5 mL) under a nitrogen atmosphere. A glassy-carbon (GC) disk (d = 2 mm) was used as the working electrode. A saturated calomel electrode (SCE) separated from the solution being studied by a salt bridge filled with the supporting electrolyte (0.05 M Et₄NClO₄ in methanol) was used as the reference electrode. A platinum plate (S = 3 cm²) was used as the counter electrode. The GC electrode was polished before each measurement. All experiments were performed with the concentration of a studied compound of 1 mM in methanol.

Figure S3. Methyl nicotinate (initial cathodic scan). \( E_{\text{red}} < -1.7 \) V (supporting electrolyte discharge) (lit. ~ \(-2.4 \) V\(^\text{25}\)).

Figure S4. 3-(Methoxycarbonyl)pyridine 1-oxide (initial cathodic scan). \( E_{\text{red}} = -1.45 \) V.

Figure S5. Compound 1a (initial cathodic scan). \( E_{\text{red}} = -1.22 \) V.

Figure S6. Compound 1c (initial cathodic scan). \( E_{\text{red}} = -1.18 \) V.

Figure S7. Compound 1d (initial cathodic scan). $E_{\text{red}} = -1.01$ V.

Figure S8. Compound 1g (initial cathodic scan). $E_{\text{red}} = -1.11$ V.

Figure S9. Potassium trifluoro(trifluoromethyl)borate (initial cathodic scan). $E_{\text{red}} < -1.70$ V (supporting electrolyte discharge).

Figure S10. Potassium trifluoro(trifluoromethyl)borate (initial cathodic scan). $E_{\text{ox}} > +1.70$ V (supporting electrolyte discharge).

Figure S11. Potassium trimethoxy(trifluoromethyl)borate (initial cathodic scan). $E_{\text{red}} < -1.70$ V (supporting electrolyte discharge).

Figure S12. Potassium trimethoxy(trifluoromethyl)borate (initial anodic scan). $E_{\text{ox}} > +1.70$ V (supporting electrolyte discharge).
For Cu(dap)$_2^{+}$, the potential of Cu(II)/Cu(I) is determined by the mean value of oxidation and reoxidation peaks. For Cu(dap)$_2$PF$_6$, the initial oxidation potential is significantly shifted owing to solubility issues. Therefore, data for Cu(dap)$_2$Cl were taken for the description of electrochemical properties of the cation Cu(dap)$_2^{+}$. The determined potential of Cu(II)/Cu(I) couple of 0.65 V (in methanol) is very close to the literature value of 0.62 V in acetonitrile.$^{26}$ This also suggests that electrochemical properties of Cu(dap)$_2^{+}$ should not depend on solvent.

![Graph S13](image1.png)  
**Figure S13.** Cu(dap)$_2$Cl (initial anodic scan). $E_{\text{ox}} = +0.68$ V, $E_{\text{reox}} = +0.62$ V.

![Graph S14](image2.png)  
**Figure S14.** Cu(dap)$_2$PF$_6$ (initial anodic scan). $E_{\text{ox}} = +0.82$ V, $E_{\text{reox}} = +0.64$ V.

Quantum yield determination

Calibration of the light source.
The photon flux of the light source for quantum yield determination was determined by standard ferrioxalate actinometry with 0.15 M solution in 0.05 M aqueous sulfuric acid as actinometer. A buffered solution of 1,10-phenanthroline was prepared by dissolution of phenanthroline hydrate (200 mg, 1.0 mmol), sodium acetate (246 mg, 3.0 mmol) and acetic acid (0.23 mL, 4.0 mmol) in water (adjusted to 6 mL). Solutions were stored in the dark, and all manipulations with ferrioxalate solution were performed in dull red light. To determine the photon flux, ferrioxalate solution (2.5 mL) was irradiated with stirring in a standard 1-cm quartz cuvette for 600 seconds with blue 10W LED ($\lambda_{\text{max}}$ = 460 nm, spectra is given in Figure S15). Light from LED was passed through 8-mm round aperture in a screen placed right before the cuvette. After irradiation, the content of the cuvette was transferred to a 100-mL measuring flask and the cuvette was rinsed with distilled water (ca 50 mL). Then, phenanthroline buffered solution was added (0.50 mL) and total volume was adjusted to 100 mL with water. The resulting solution was allowed to stand for 20 minutes in the dark, and its absorbance at 510 nm was measured. Control measurement after 15 hours in the dark showed no change in absorbance indicating that under the applied conditions: (a) developing with phenanthroline was complete within 20 minutes, and (b) no Fe(phen)$_3^{2+}$ is formed as a result of side dark reactions of unreacted ferrioxalate. Additionally, the determined content of Fe(phen)$_3^{2+}$ indicated that phenanthroline was indeed used in excess and is not exhausted in the complexation reaction. Control dark sample was prepared in the same way excluding exposure to the light source.

Data processing

Correction for non-monochromaticity of the light source and for incomplete absorption
The quantum yield of the light-induced ferrioxalate decomposition was reported to vary insignificantly over the wavelength region that was used, and it was taken as a constant value of 1.1. Figure S15 illustrates the derivation of the correction for incomplete absorption. The fraction of photons from the light source absorbed by the sample (f) can be derived from the areas under black ($S_{\text{black}}$) and green ($S_{\text{green}}$) lines: $f = 1 - (S_{\text{green}}/S_{\text{black}})$, $f = 0.835$.

Figure S15. Correction for incomplete absorption. Black line shows the spectrum of the light source normalized to its maximum. Blue line is the transmittance (T) of the sample. Green line shows the spectrum of the light from the light source passed through the sample.

Photon flux determination

With the known molar absorptivity for Fe(phen)$_3^{2+}$ $\varepsilon$(510)=11100 (M$^{-1}$ cm$^{-1}$), the amount of Fe$^{2+}$ formed under irradiation was determined as

$$n(Fe^{2+}) = (\Delta A^*V)/(L^*\varepsilon)$$

where $\Delta A$ is the difference between absorbances of irradiated and dark samples, V is the measuring flask volume (0.100 L), and L is the light path length (1.00 cm), and photon flux was determined as

$$\text{flux} = n(Fe^{2+})/(\Phi^*t*f)$$

where $\Phi$ is quantum yield of ferrioxalate decomposition (1.1), t is the irradiation time (10 min = 600 sec) and $f = 0.835$ is the correction for incomplete absorption. The results of three independent experiments are summarized in Table S1.

Table S1. Photon flux determination.

<table>
<thead>
<tr>
<th>run</th>
<th>$A$[510]</th>
<th>$\Delta A$</th>
<th>Fe$^{2+}$, mol/L</th>
<th>Fe$^{2+}$ amount (μmole)</th>
<th>flux, μeinstein/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>dark</td>
<td>0.100224</td>
<td>0</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>#1</td>
<td>0.493101</td>
<td>0.392877</td>
<td>3.53943E-05</td>
<td>3.539430756</td>
<td>0.38548</td>
</tr>
<tr>
<td>#2</td>
<td>0.5114</td>
<td>0.411176</td>
<td>3.70429E-05</td>
<td>3.704288978</td>
<td>0.403435</td>
</tr>
<tr>
<td>#3</td>
<td>0.514276</td>
<td>0.414052</td>
<td>3.7302E-05</td>
<td>3.730197242</td>
<td>0.406256</td>
</tr>
<tr>
<td>mean</td>
<td></td>
<td></td>
<td></td>
<td>3.657972325</td>
<td>0.39839</td>
</tr>
<tr>
<td>deviation</td>
<td></td>
<td></td>
<td></td>
<td>0.10347409</td>
<td>0.011269</td>
</tr>
</tbody>
</table>
Quantum yield for the perfluoroalkylation reaction.
The following process was studied:

\[
\begin{align*}
\text{Ph} & \quad + \quad n-C_3F_7B(\text{dap})_{2}PF_6 (1\%) \\
\text{2a} & \quad \rightarrow \quad \text{Ph}OMe \\
\text{1g} & \quad \text{MeOH, blue LED, rt}
\end{align*}
\]

Then reaction was performed in a sealed screw-capped quartz cuvette under argon using triacetoneamine as a proton scavenger and in the presence of menthol as internal standard for GC yield determination. The complete light absorption (> 99%) over the whole light source spectrum was checked prior to irradiation.

Borate complex 1g (230 mg, 0.620 mmol), menthol (80.1 mg, 0.512 mmol), triacetoneamine (110.4 mg, 0.638 mmol), 1,1-diphenylethylene (81.6 mg, 0.453 mmol), Cu(dap)2PF6 (4.8 mg, 0.0048 mmol) and MeOH (3.0 ml) were mixed under argon with stirring in the dark and the resulting mixture was transferred under argon with a syringe into 1-cm quartz cuvette containing a stirring bar. The cuvette was sealed with a silicon cap and irradiated with light source of known photon flux with stirring. To determine the amount of the product formed, aliquots (approximately 50 μL) of the reaction mixture were taken with a microsyringe every 30 minutes and quenched by pouring into a mixture of saturated aqueous sodium bicarbonate (0.150 ml) and hexane (1.2 ml). After vigorous shaking, hexane layer was analyzed by GC, and the product yield was determined by comparison with menthol. The dependence of the product yield from time (in minutes) is shown in Figure S16.

![Figure S16. The slope parameter is equal to the reaction rate of 0.246 μmol·min⁻¹.](image)

Quantum yield is derived as follows:

\[
\Phi = \frac{\text{moles of product formed}}{\text{einstein of light absorbed}} = \frac{0.246 \mu \text{mol·min}^{-1}}{0.398 \mu \text{einstein·min}^{-1}} = 0.62
\]
$^1$H NMR
300 MHz
CDCl$_3$
$^{1}H$ NMR
300 MHz
CDCl$_3$
$^{13}\text{C}^{1\text{H}}$ NMR
75 MHz
CDCl$_3$
$^1$H NMR
300 MHz
CDCl$_3$
$^1$H NMR  
300 MHz  
$(CD_3)_2CO$
$^{13}$C NMR
75 MHz
$(CD_3)_2CO$
$^{19}$F NMR
282 MHz
(CD$_3$)$_2$CO
$^{11}$B NMR
96 MHz
$(\text{CD}_3)_2\text{CO}$
$\text{O} \quad \text{O}$

**$^1$H NMR**

300 MHz

CDCl$_3$

integral

ppm
$^1$H NMR
300 MHz
(CD$_3$)$_2$CO
$^{13}$C NMR
75 MHz
$(\text{CD}_3)_2\text{CO}$
$^{19}$F NMR
282 MHz
(CD$_3$)$_2$CO
$^{11}$B NMR
96 MHz
$(\text{CD}_3)_2\text{CO}$
$^{1}H$ NMR
300 MHz
$(CD_{3})_{2}CO$
$^{19}$F NMR
282 MHz
$(CD_3)_2CO$
$^{11}$B NMR
96 MHz
(CD$_3$)$_2$CO
$^1$H NMR
300 MHz
(CD$_3$)$_2$CO

D-solv. residual peak
$^{13}$C NMR
75 MHz
$(CD_3)_2CO$
$^{19}$F NMR
282 MHz
(CD$_3$)$_2$CO

$^{19}$F NMR data:
- $\delta = -82.4498$ ppm
- $\delta = -129.1571$ ppm
- $\delta = -134.9881$ ppm

Chemical shifts:
- $\delta = -156$ ppm
- $\delta = -158.4093$ ppm
- $\delta = -158.5294$ ppm
- $\delta = -158.7095$ ppm
- $\delta = -158.8520$ ppm

Compound 1g
$^{11}$B NMR
96 MHz
$(\text{CD}_3)_2\text{CO}$

1.8908
1.6927
1.4337
1.2051
0.9766
0.7175
0.5042

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

![Chemical Structure](image)
$^{19}$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$_3$

3b, mixture of isomers 1.5:1
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C{${}^1$H} NMR
75 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$

$3c$, mixture of isomers 1:1
$^{1}$H NMR
300 MHz
CDCl$_3$

3d, mixture of isomers 11:1

$\text{MeO}$

$\text{CF}_3$

Integral

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

3d, mixture of isomers 11:1
$^{19}$F NMR
282 MHz
CDCl$_3$

3d, mixture of isomers 11:1
3e, mixture of isomers 3.8:1

$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C\{$^1$H\} NMR
75 MHz
CDCl$_3$

3e, mixture of isomers 3.8:1
19F NMR
282 MHz
CDCl₃

3e, mixture of isomers 3.8:1
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C\text{\textsuperscript{1}H} NMR
75 MHz
CDCl\textsubscript{3}
$^{19}$F NMR
282 MHz
CDCl$_3$
$^1$H-$^1$H NOESY

\[ \text{ppm} \]

![Chemical Structure](image-url)
1H-19F HOESY
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C{$_1^1$H} NMR
75 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$

![Compound Structure](image)
$^{1}$H NMR
300 MHz
CDCl$_3$
$^{13}C\{^1H\}$ NMR
75 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$

3h, mixture of isomers 1:1
$^1$H NMR
300 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$

3i, mixture of isomers 4:1
$^{1}$H NMR
300 MHz
CDCl$_3$
$^{13}$C\textsuperscript{1H} NMR
75 MHz
CDCl\textsubscript{3}
$^{19}$F NMR
282 MHz
CDCl$_3$
3k, mixture of isomers 1.5:1

$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C{$_{1H}$} NMR
75 MHz
CDCl$_3$

3k, mixture of isomers 1.5:1
$^{19}$F NMR
282 MHz
CDCl$_3$

3k, mixture of isomers 1.5:1
\(^1\)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$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$

$\text{MeO}$

$\text{OMe}$

$\text{CF}_3$

3m
$^{1}H$ 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$_3$
$^{13}\text{C}\{^1\text{H}\}$ 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$_3$

![Chemical Structure](image)
$^1$H NMR
300 MHz
CDCl$_3$
$^{13}$C-$^1$H NMR
75 MHz
CDCl$_3$

$^3$q

OMe

CF$_3$

HO

S94
$^{19}$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$_3$
$^{13}$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{$_{1}^1$}H NMR
75 MHz
CDCl$_3$
$^{19}$F NMR
282 MHz
CDCl$_3$
\textbf{\textsuperscript{1}H NMR} \\
300 MHz \\
CDCl\textsubscript{3}
$^{13}$C{$_{1}^{1}$H} NMR
75 MHz
CDCl$_3$

- 140.4761
- 137.8315
- 129.1432
- 127.5755
- 127.0115
- 123.8980
- 77.5776
- 77.5409
- 77.1600
- 76.7351
- 56.8458
- 45.8409
- 42.4241
- 42.0918
- 41.7256

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

![Chemical Structure](image)

![NMR Spectrum](image)

-80.8289 ppm
-80.8664 ppm
-80.8965 ppm
-114.3586 ppm
-114.3886 ppm
-114.4186 ppm
-114.4486 ppm
-114.4786 ppm

-81.0 ppm
-114 ppm

-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 (ppm)
1H NMR
300 MHz
CDCl₃
$^{19}$F NMR
282 MHz
CDCl₃