Supporting Information for

Synthesis of Fluorinated Amide Derivatives via a Radical N-Perfluoroalkylation - Defluorination Pathway

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1. General Information

All reactions were carried out under air unless otherwise stated. Nitrosoarenes 1c-l and 1n-q, and the sodium perfluoroalkanesulfonates were prepared according to literature procedures using commercial reagents (Section 2.1). All other starting materials and solvents were purchased from commercial suppliers and were used as received.

$^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded at room temperature in CDCl$_3$ on a Bruker 400 or 500 MHz spectrometer unless otherwise stated. Chemical shifts (δ) are reported in ppm with the following abbreviations used for the observed multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), bs (broad singlet), m (multiplet for unresolved lines). $^1$H NMR chemical shifts were referenced to the residual solvent signal in CDCl$_3$ (7.26 ppm), DMSO-$d_6$ (2.50 ppm) or acetone-$d_6$ (2.05 ppm). $^{13}$C NMR chemical shifts were referenced to the solvent signal of CDCl$_3$ (77.16 ppm) or acetone-$d_6$ (29.84 ppm) and $^{19}$F NMR chemical shifts were referenced to the external standard α,α,α-trifluorotoluene (-63.72 ppm). Analytical TLC was performed on pre-coated silica gel plates. After elution, the plates were visualized by UV illumination at 254−360 nm, and by staining with ethanolic KMnO$_4$. Column chromatography was performed using Davisil or Merck 60 Å silica gel (35–70 μm). HRMS data were recorded on a Bruker micrOTOF instrument using ESI technique. GC/MS analyses were performed on a Shimadzu GCMS-QP2020 equipped with an HP-5MS column (30m×0.25mm×0.25μm) with a quadrupole mass analyzer using helium as the carrier gas.
2. Experimental Procedures and Spectral Data

2.1 Preparation of starting materials

Nitrosobenzenes 1 were synthesized according to adapted versions of the following literature procedures: oxidation of the corresponding anilines\(^\text{[1]}\) (1c-e, 1g, 1i-k, 1n-q), direct halogenation of the corresponding nitrosobenzene\(^\text{[2]}\) (1f, 1h) and direct nitrosation\(^\text{[3]}\) (1l). Spectral data for the compounds above can be found in the following references: 1c,\(^\text{[4]}\) 1d,\(^\text{[5]}\) 1e,\(^\text{[6]}\) 1f,\(^\text{[2]}\) 1g,\(^\text{[7]}\) 1h,\(^\text{[2]}\) 1i,\(^\text{[8]}\) 1j,\(^\text{[9]}\) 1l,\(^\text{[10]}\) 1n,\(^\text{[11]}\) 1o,\(^\text{[12]}\) and 1q.\(^\text{[13]}\) Sodium perfluoroalkanesulfonates were prepared from the corresponding perfluoro-1-iodoalkanes with sodium dithionite under argon in degassed solvent according to an adapted version of a literature procedure\(^\text{[14]}\) and were stored under argon. Sodium dithionite was recrystallized according to a literature procedure\(^\text{[15]}\) prior to use. Spectral data for the sodium perfluoroalkanesulfonates can be found in the following references.\(^\text{[14, 16]}\)

2.2 In situ preparation of N-perfluoroalkylated hydroxylamines 2

**Method A:**

\[
\text{NaSO}_2\text{CF}_2\text{RF} (3.0 \text{ equiv}) \quad \text{Cu(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O} (1 \text{ mol\%}) \quad \text{tBuOOH (70\% aqueous, 3.0 \text{ equiv})} \quad \text{hydroquinone (1.1 \text{ equiv})} \\
\text{EtOAc, rt, 1 h} \quad \text{See Sections 2.3-2.9 for transformations into products 3-7} \\
\begin{array}{c}
\text{N=O} \\
\text{R} \\
\end{array} \quad \text{2 (not isolable)} \\
\begin{array}{c}
\text{CF}_2\text{RF} \\
\text{R} \\
\end{array}
\]

**Scheme S-1:** Reaction conditions for the N-perfluoroalkylation (Method A).

To a screw-cap vial equipped with a magnetic stirring bar were added 1 (0.50 mmol, 1.0 equiv), sodium perfluoroalkanesulfonate (1.50 mmol, 3.0 equiv), hydroquinone (60.6 mg, 0.55 mmol, 1.1 equiv), ethyl acetate (3.05 mL), a solution of copper(II) perchlorate hexahydrate in ethyl acetate (0.95 mL, 0.0054 M, 1 mol%), and tert-butyl hydroperoxide (70% solution in water, 210 µL, 1.50 mmol, 3.0 equiv). The reaction mixture was stirred for 1 h at room temperature during which the color changed from blue or green to brown or orange. 1,1,2,2-Tetrachloroethane was added as an internal standard and a crude sample was taken out and analyzed by \(^1\text{H} \text{NMR. The yields of 2 (Table S-1) were determined by } \text{1H NMR analysis of the crude reaction mixture in CDCl}_3 \text{ or DMSO-d6. Attempted isolation of hydroxylamines 2 led to decomposition.}
Method B:

Scheme S-2: Reaction conditions for the N-perfluoroalkylation (Method B).

To a dry screw-cap vial equipped with a magnetic stirring bar were added 1 (0.50 mmol, 1.0 equiv), sodium perfluoroalkanesulfinate (1.50 mmol, 3.0 equiv), hydroquinone (60.6 mg, 0.55 mmol, 1.1 equiv), copper(II) chloride (3.4 mg, 0.025 mmol, 5 mol%), anhydrous ethyl acetate (3.05 mL) and tert-butyl hydroperoxide (5.5 M in decane, 273 µL, 1.50 mmol, 3.0 equiv). The reaction mixture was stirred under argon for 1 h at room temperature during which the color changed from blue or green to brown or orange. 1,1,2,2-Tetrachloroethane was added as an internal standard and a crude sample was taken out and analyzed by 1H NMR. The yields of 2 (Table S-1) were determined by 1H NMR analysis of the crude reaction mixture in CDCl₃ or DMSO-d₆. Attempted isolation of hydroxylamines 2 led to decomposition.
Table S-1: N-Perfluoroalkylation of nitroso compounds

| Compound | Method | Yield | Additional Conditions |
|----------|--------|-------|-----------------------|
| 2a       | Method A | 79%<sup>a</sup>, 73%<sup>b</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2b       | Method B | 85%<sup>a</sup>, 75%<sup>b</sup>, 81%<sup>c</sup> | 1H NMR yield using Method B; Performed on 1.0 mmol scale using Method B; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2c       | Method A | 86%<sup>a</sup>, 85%<sup>b</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2d       | Method A | 80%<sup>a</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2e       | Method A | 57%<sup>a</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2f       | Method A | 78%<sup>a</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2g       | Method A | 78%<sup>a</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2h       | Method A | 81%<sup>a</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2i       | Method A | 86%<sup>a</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2j       | Method A | 79%<sup>a</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2k       | Method A | 57%<sup>a</sup>, 70%<sup>b</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2l       | Method A | 61%<sup>a</sup>, 72%<sup>b</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2m       | Method A | 56%<sup>a</sup>, 56%<sup>b</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2n       | Method A | 67%<sup>a</sup>, 75%<sup>b</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2o       | Method A | 83%<sup>a</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2p       | Method A | 61%<sup>a</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2q       | Method A | 70%<sup>a</sup>, 66%<sup>b</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2r       | Method A | 61%<sup>a</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2s       | Method A | 80%<sup>a</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2t       | Method A | 75%<sup>a</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
| 2u       | Method A | 68%<sup>a</sup>, 68%<sup>b</sup> | 1H NMR yield using Method A; Performed on 1.0 mmol scale using Method A; The HCl salt was used; After 1 h, Ac<sub>2</sub>O (1.0 mL) and NaHCO<sub>3</sub> (3.0 mmol) were added and the reaction mixture was stirred for an additional 24 h; Reaction time: 24 h. Isolated yield; Performed on 0.20 mmol scale. |
\[{}^{1}\text{H} \text{NMR shift data for the perfluoroalkylated hydroxylamines } 2 \text{ (as obtained from analysis of the crude reaction mixture), are given below.}\]

**N-(Perfluorobutyl)-N-phenylhydroxylamine (2a)**

\[
\text{N}-(\text{Perfluorobutyl})-\text{N}-\text{phenylhydroxylamine (2a)}
\]

\[
\begin{array}{c}
\text{N}-(\text{Perfluorobutyl})-\text{N}-\text{phenylhydroxylamine (2a)}
\end{array}
\]

2a: (Method A: 79% \(^1\text{H} \text{ NMR yield};\) Method B: 73% \(^1\text{H} \text{ NMR yield});\)

\text{\(^1\text{H} \text{ NMR (400 MHz, CDCl}_3\text{ with EtOAc, data obtained from analysis of the crude reaction mixture): } \delta \text{ ppm } 7.43–7.39 \text{ (m, } 2\text{H}), 7.38–7.33 \text{ (m, } 2\text{H}), 7.31–7.28 \text{ (m, } 1\text{H}), \text{OH-proton was not observed.}\)

\text{MS (EI): } m/z \text{ calcd for } C_{10}H_6F_9NO \ [M]^{+} 327, \text{ found 327. Fragments: } 307 \text{ [M - HF]}^{+}, 291 \text{ [M - F - OH]}^{+}, 158 \text{ [M - CF}_2\text{CF}_2\text{CF}_3]^{+}, 141 \text{ [M - CF}_2\text{CF}_2\text{CF}_3 - \text{OH]}^{+}, 108 \text{ [M - CF}_2\text{CF}_2\text{CF}_2\text{CF}_3^{+}, \text{ see Section 2.11.}\)

**N-(Perfluorobutyl)-N-(o-tolyl)hydroxylamine (2b)**

\[
\text{N}-(\text{Perfluorobutyl})-\text{N}-(\text{o-tolyl})\text{hydroxylamine (2b)}
\]

2b: (Method A: 85% \(^1\text{H} \text{ NMR yield};\) Method B: 75% \(^1\text{H} \text{ NMR yield});\)

\text{\(^1\text{H} \text{ NMR (400 MHz, DMSO-}d_6\text{ with EtOAc, data obtained from analysis of the crude reaction mixture): } \delta \text{ ppm } 10.24 \text{ (s, } 1\text{H}), 7.57–7.55 \text{ (m, } 1\text{H}), 7.32–7.28 \text{ (m, } 3\text{H}), 2.28 \text{ (s, } 3\text{H}).\)

\text{MS (EI): } m/z \text{ calcd for } C_{11}H_8F_9NO \ [M]^{+} 341, \text{ found 341. Fragments: } 321 \text{ [M - HF]}^{+}, 305 \text{ [M - F - OH]}^{+}, 172 \text{ [M - CF}_2\text{CF}_2\text{CF}_3]^{+}, 155 \text{ [M - CF}_2\text{CF}_2\text{CF}_3 - \text{OH]}^{+}, 122 \text{ [M - CF}_2\text{CF}_2\text{CF}_2\text{CF}_3^{+}, \text{ see Section 2.11.}\)

**N-(Perfluorobutyl)-N-(2-(trifluoromethyl)phenyl)hydroxylamine (2c)**

\[
\text{N}-(\text{Perfluorobutyl})-\text{N}-(\text{2-(trifluoromethyl)phenyl})\text{hydroxylamine (2c)}
\]

2c: (Method A: 86% \(^1\text{H} \text{ NMR yield};\) Method B: 88% \(^1\text{H} \text{ NMR yield});\)

\text{\(^1\text{H} \text{ NMR (400 MHz, CDCl}_3\text{ with EtOAc, data obtained from analysis of the crude reaction mixture): } \delta \text{ ppm } 7.87 \text{ (d, } J = 8.2 \text{ Hz, } 1\text{H}), 7.71–7.64 \text{ (m, } 2\text{H}), 7.51 \text{ (t, } J = 7.7 \text{ Hz, } 1\text{H}), \text{OH-proton was not observed.}\)

**N-([1,1'-Biphenyl]-2-yl)-N-(perfluorobutyl)hydroxylamine (2d)**

\[
\text{N-([1,1'-Biphenyl]-2-yl)-N-(perfluorobutyl)hydroxylamine (2d)}
\]

2d: (Method A: 80% \(^1\text{H} \text{ NMR yield);\) \text{\(^1\text{H} \text{ NMR (400 MHz, DMSO-}d_6\text{ with EtOAc, data obtained from analysis of the crude reaction mixture): } \delta \text{ ppm } 10.27 \text{ (s, } 1\text{H}), 7.76 \text{ (dd, } J = 7.3, 2.0 \text{ Hz, } 1\text{H}), 7.57–7.30 \text{ (m, } 8\text{H}).\)

**N-(2,6-Dimethylphenyl)-N-(perfluorobutyl)hydroxylamine (2e)**

\[
\text{N-(2,6-Dimethylphenyl)-N-(perfluorobutyl)hydroxylamine (2e)}
\]

2e: (Method A: 57% \(^1\text{H} \text{ NMR yield);\) \text{\(^1\text{H} \text{ NMR (400 MHz, DMSO-}d_6\text{ with EtOAc, data obtained from analysis of the crude reaction mixture): } \delta \text{ ppm } 10.11 \text{ (s, } 1\text{H}), 7.20–7.16 \text{ (m, } 1\text{H}), 7.12–7.10 \text{ (m, } 2\text{H}), 2.36 \text{ (s, } 6\text{H}).\)
N-(4-Chloro-2-methylphenyl)-N-(perfluorobutyl)hydroxylamine (2f)

2f: (Method A: 78% \(^1\)H NMR yield); \(^1\)H NMR (400 MHz, CDCl\(_3\) with EtOAc, data obtained from analysis of the crude reaction mixture): \(\delta\) ppm 7.55 (d, \(J = 8.5\) Hz, 1H), 7.22–7.15 (m, 2H), 2.26 (s, 3H), OH-proton was not observed.

N-(2-Fluorophenyl)-N-(perfluorobutyl)hydroxylamine (2g)

2g: (Method A: 78% \(^1\)H NMR yield); \(^1\)H NMR (400 MHz, CDCl\(_3\) with EtOAc, data obtained from analysis of the crude reaction mixture): \(\delta\) ppm 7.65 (td, \(J = 7.8, 1.7\) Hz, 1H), 7.33–7.28 (m, 1H), 7.20–7.15 (m, 1H), 7.11–7.06 (m, 1H), OH-proton was not observed.

N-(4-Bromo-2-methylphenyl)-N-(perfluorobutyl)hydroxylamine (2h)

2h: (Method A: 81% \(^1\)H NMR yield); \(^1\)H NMR (400 MHz, CDCl\(_3\) with EtOAc, data obtained from analysis of the crude reaction mixture): \(\delta\) ppm 7.49–7.45 (m, 1H), 7.37–7.33 (m, 2H), 2.25 (s, 3H), OH-proton was not observed.

N-(3-Bromophenyl)-N-(perfluorobutyl)hydroxylamine (2i)

2i: (Method A: 86% \(^1\)H NMR yield); \(^1\)H NMR (400 MHz, CDCl\(_3\) with EtOAc, data obtained from analysis of the crude reaction mixture): \(\delta\) ppm 7.60–7.59 (m, 1H), 7.42–7.40 (m, 1H), 7.35–7.32 (m, 1H), 7.24–7.22 (m, 1H), OH-proton was not observed.

N-(3-Chlorophenyl)-N-(perfluorobutyl)hydroxylamine (2j)

2j: (Method A: 79% \(^1\)H NMR yield); \(^1\)H NMR (400 MHz, CDCl\(_3\) with EtOAc, data obtained from analysis of the crude reaction mixture): \(\delta\) ppm 7.41–7.39 (m, 1H), 7.25–7.18 (m, 3H), OH-proton was not observed.

N-(Perfluorobutyl)-N-(3-(trifluoromethyl)phenyl)hydroxylamine (2k)

2k: (Method A: 57% \(^1\)H NMR yield; Method B: 70% \(^1\)H NMR yield); \(^1\)H NMR (400 MHz, CDCl\(_3\) with EtOAc, data obtained from analysis of the crude reaction mixture): \(\delta\) ppm 7.68 (s, 1H), 7.59 (d, \(J = 7.8\) Hz, 1H), 7.54–7.46 (m, 2H), OH-proton was not observed.
N-(4-Methoxyphenyl)-N-(perfluorobutyl)hydroxylamine (2l)

\[ \text{MeO} \]
\[ \begin{array}{c}
\text{N} \\
\text{HO}
\end{array} \]
\[ \text{CF}_3 \]
\[ \text{CF}_2 \]

2l: (Method A: 61\% \textsuperscript{1}H NMR yield; Method B: 72\% \textsuperscript{1}H NMR yield; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3} with EtOAc, data obtained from analysis of the crude reaction mixture): \( \delta \) ppm 7.34 (d, \( J = 9.0 \) Hz, 2H), 6.86 (d, \( J = 9.0 \) Hz, 2H), 3.78 (s, 3H), OH-proton was not observed.

4-(Hydroxy(perfluorobutyl)amino)-N,N-dimethylaniline hydrochloride (2m)

The hydrochloride salt of N,N-dimethyl-4-nitrosoaniline 1m (0.50 mmol, 1.0 equiv) was prepared \textit{in situ} by treating a solution of 1m in ethyl acetate (3.1 mL) with HCl (37\%, 0.050 mL, 0.60 mmol, 1.20 equiv). The mixture was stirred at room temperature for 20 min. Then, NaSO\textsubscript{2}(CF\textsubscript{2})\textsubscript{3}CF\textsubscript{3}, hydroquinone, Cu(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O in EtOAc and \textsuperscript{t}BuOOH were added sequentially, according to the general procedure of Method A.

\[ \begin{array}{c}
\text{MeN} \\
\text{N} \text{HCl} \\
\text{OH}
\end{array} \]
\[ \text{CF}_2 \]
\[ \text{CF}_3 \]

2m: (Method A: 56\% \textsuperscript{1}H NMR yield; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3} with EtOAc, data obtained from analysis of the crude reaction mixture): \( \delta \) ppm 9.93 (s, 1H), 7.87 (d, \( J = 9.0 \) Hz, 2H), 7.59 (d, \( J = 9.0 \) Hz, 2H), 3.22 (s, 6H), OH-proton was not observed.

N-(4-Chlorophenyl)-N-(perfluorobutyl)hydroxylamine (2n)

\[ \begin{array}{c}
\text{Cl} \\
\text{N} \\
\text{HO}
\end{array} \]
\[ \text{CF}_3 \]
\[ \text{CF}_2 \]

2n: (Method A: 67\% \textsuperscript{1}H NMR yield; Method B: 75\% \textsuperscript{1}H NMR yield; \textsuperscript{1}H NMR (400 MHz, DMSO-\textsubscript{d}\textsubscript{6} with EtOAc, data obtained from analysis of the crude reaction mixture): \( \delta \) ppm 10.53 (bs, 1H), 7.50 (d, \( J = 8.9 \) Hz, 2H), 7.42 (d, \( J = 8.9 \) Hz, 2H).

Methyl 4-(hydroxy(perfluorobutyl)amino)benzoate (2o)

\[ \begin{array}{c}
\text{MeOOC} \\
\text{N} \\
\text{HO}
\end{array} \]
\[ \text{CF}_2 \]
\[ \text{CF}_3 \]

2o: (Method A: 83\% \textsuperscript{1}H NMR yield; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3} with EtOAc, data obtained from analysis of the crude reaction mixture): \( \delta \) ppm 7.98 (d, \( J = 8.8 \) Hz, 2H), 7.43 (d, \( J = 8.7 \) Hz, 2H), 3.86 (s, 3H), OH-proton was not observed.

3-Ethyl-3-(4-(hydroxy(perfluorobutyl)amino)phenyl)piperidine-2,6-dione (2p)

\[ \begin{array}{c}
\text{Et} \\
\text{N} \\
\text{HO}
\end{array} \]
\[ \text{CF}_2 \]
\[ \text{CF}_3 \]

2p: (Method A: 61\% \textsuperscript{1}H NMR yield; \textsuperscript{1}H NMR (500 MHz, DMSO-\textsubscript{d}\textsubscript{6} with EtOAc, data obtained from analysis of the crude reaction mixture): \( \delta \) ppm 10.89 (s, 1H), 10.38 (s, 1H), 7.41 (d, \( J = 8.7 \) Hz, 2H), 7.37 (d, \( J = 8.8 \) Hz, 2H), 0.76 (t, \( J = 7.5 \) Hz, 3H), other aliphatic protons were not distinguishable due to overlap with EtOAc.

S-8
**N-(4-Nitrophenyl)-N-(perfluorobutyl)hydroxylamine (2q)**

2q: (Method A: 70% $^1$H NMR yield; Method B: 66% $^1$H NMR yield); 
$^1$H NMR (400 MHz, CDCl$_3$ with EtOAc, data obtained from analysis of the crude reaction mixture): $\delta$ ppm 8.23 (d, $J = 9.2$ Hz, 2H), 7.56 (d, $J = 9.2$ Hz, 2H), OH-proton was not observed.

**N-(Perfluoropropyl)-N-(o-tolyl)hydroxylamine (2s)**

2s: (Method A: 80% $^1$H NMR yield); $^1$H NMR (400 MHz, DMSO-$d_6$ with EtOAc, data obtained from analysis of the crude reaction mixture): $\delta$ ppm 10.23 (bs, 1H), 7.58–7.54 (m, 1H), 7.33–7.27 (m, 3H), 2.27 (s, 3H).

**N-(Perfluorohexyl)-N-(o-tolyl)hydroxylamine (2t)**

2t: (Method A: 75% $^1$H NMR yield); $^1$H NMR (400 MHz, DMSO-$d_6$ with EtOAc, data obtained from analysis of the crude reaction mixture): $\delta$ ppm 10.21 (s, 1H), 7.57–7.55 (m, 1H), 7.31–7.27 (m, 3H), 2.28 (s, 3H).

**N-(8H-Perfluorooctyl)-N-(o-tolyl)hydroxylamine (2u)**

The reaction was performed on a 0.20 mmol scale. 
2u: (Method A: 68% $^1$H NMR yield); $^1$H NMR (400 MHz, DMSO-$d_6$ with EtOAc, data obtained from analysis of the crude reaction mixture): $\delta$ ppm 10.19 (s, 1H), 7.57–7.55 (m, 1H), 7.32–7.27 (m, 3H), 7.20–7.16 (m, 1H), 2.28 (s, 3H).
O-Acetyl-N-(4-nitrophenyl)-N-(perfluorobutyl)hydroxylamine (6q)

Compound 6q was obtained by a sequential one-pot reaction from 1q. The perfluoroalkylation of 1q was performed on 0.5 mmol scale according to the general procedure using Method A. Subsequently, acetic anhydride (1.0 mL) and NaHCO₃ (252.0 mg, 3.00 mmol, 6.0 equiv) were added, and the reaction mixture was allowed to stir for 24 h at room temperature before water (30 mL) and EtOAc (30 mL) were added. The layers were separated and the organic layer was washed with water (2 x 30 mL) and the combined aqueous layers were extracted with EtOAc (1 x 30 mL). The combined organic layers were dried (MgSO₄) and reduced in vacuo and the crude product was purified by column chromatography (pentane:DCM = 2:1) to obtain product 6q as a white solid in 61% yield.

6q: (126.3 mg, 61% yield, white solid, pentane:DCM = 2:1); ¹H NMR (400 MHz, CDCl₃): δ ppm 8.29 (d, J = 9.0 Hz, 2H), 7.63 (d, J = 8.9 Hz, 2H), 2.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ ppm 165.9, 147.8, 145.4, 126.2, 124.8, 117.4 (qt, J = 288.2, 33.3 Hz), 114.7 (tt, J = 269.9, 39.8 Hz), 113.5–105.6 (m, 2C), 18.4; ¹⁹F NMR (376 MHz, CDCl₃): δ ppm (-81.24)–(-80.88) (m, 3F), -98.92 (s, 2F), -112.82 (q, J = 9.0 Hz, 2F), -123.77 (s, 2F); HRMS (ESI): m/z calcd for C₁₂H₇F₉N₂NaO₄ [M+Na]⁺ 437.0154, found 437.0156.

N-(tert-Butyl)-2,2,3,3,4,4,4-heptafluoro-N-hydroxybutanamide (7r)

The perfluoroalkylation of 1r was performed on 0.5 mmol scale according to the general procedure using Method A. The reaction mixture was stirred for 24 h. Thereafter, water (30 mL) and EtOAc (30 mL) were added and the layers separated. The organic layer was washed with water (2 x 30 mL) and the combined aqueous layers were extracted with EtOAc (1 x 30 mL). The combined organic layers were dried (MgSO₄) and reduced in vacuo. The crude product was purified by column chromatography (pentane:DCM = 1:1) to obtain product 7r as a white solid in 54% yield.

7r: (76.4 mg, 54% isolated yield, white solid, pentane:DCM = 1:1); ¹H NMR (400 MHz, CDCl₃): δ ppm 7.03 (bs, 1H), 1.46 (s, 9H); ¹³C NMR (126 MHz, CDCl₃): δ ppm 158.9 (t, J = 24.7 Hz), 117.8 (qt, J = 287.8, 34.4 Hz), 112.8–106.9 (m, 2C), 63.8, 26.4; ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -81.24 (t, J = 9.2 Hz, 3F), -112.82 (q, J = 9.0 Hz, 2F), -123.77 (s, 2F); HRMS (ESI): m/z calcd for C₈H₉F₇NO₂ [M-H]⁻ 284.0527 found 284.0518.
2.3 Screening of reaction conditions for the oxydefluorination of 2b

Scheme S-3: Screening of reaction conditions for the oxydefluorination of hydroxylamine 2b.

The perfluoroalkylation of 1b was performed on 0.1 mmol scale according to the general procedure using Method A or Method B described in section 2.2. Subsequently, additional reagents were added to the reaction mixture and stirring was continued according to the conditions in Table S-2. Hexafluoroisopropanol was added as an internal standard and the crude sample was analyzed by 19F NMR to determine the yields of 7b, 4b and 3b in CDCl3.

Table S-2: Screening of reaction condition for the oxydefluorination of 2b[a].

| Entry | Method A or B | Conditions for oxydefluorination | Unreacted 2b (%) | Yield of 7b (%) | Yield of 4b (%) | Yield of 3b (%) |
|-------|---------------|----------------------------------|-----------------|----------------|----------------|----------------|
| 1     | A             | -                                | 85              | -              | -              | -              |
| 2     | A             | 50 °C, 24 h                       | trace           | 25             | -              | -              |
| 3     | A             | HCl (37%, 5 equiv), rt, 6 h       | 56              | 11             | -              | -              |
| 4     | A             | HCl (37%, 20 equiv), rt, 6 h      | -               | 36             | -              | -              |
| 5     | A             | HCl (37%, 20 equiv), AcOH (1.0 mL), 0 °C, 6 h | - 41 (35)[b] | -              | -              | -              |
| 6     | A             | HCl (37%, 20 equiv), AcOH (1.0 mL), 65 °C, 2 h | - 38          | -              | -              | -              |
| 7     | A             | TsOH·H2O (3 equiv), 50 °C, 6 h    | -              | 26             | -              | -              |
| 8     | A             | TfOH (3 equiv), 50 °C, 6 h        | -              | 24             | -              | -              |
| 9     | A             | InCl3 (3 equiv), 50 °C, 6 h       | trace           | 26             | -              | -              |
| 10    | A             | (TMS)2O (3 equiv), 50 °C, 6 h     | trace           | 25             | -              | -              |
| 11    | A             | Zn (20 equiv), HCl (37%, 20 equiv), rt, 6 h | 36          | -              | -              | 16             |
Table S-2: (Continued)

| Entry | Method A or B | Conditions for oxydefluorination | Unreacted of 2b (%) | Yield of 7b (%) | Yield of 4b (%) | Yield of 3b (%) |
|-------|---------------|---------------------------------|---------------------|----------------|----------------|----------------|
| 12 A  | Zn (20 equiv), HCl (37%, 20 equiv), AcOH (1.0 mL), rt, 6 h | 21 | - | - | 28 |
| 13 A  | Zn (40 equiv), HCl (37%, 40 equiv), AcOH (1.0 mL), rt, 6 h | 5 | - | - | 38 |
| 14 A  | Zn (40 equiv), HCl (37%, 40 equiv), AcOH (1.0 mL), 65 °C, 6 h | - | - | - | 72(70) [b] |
| 15 A  | Pd/C (10% Pd), H₂ (1 atm), rt, 6 h | 81 | - | - | - |
| 16 A  | Pd(OH)₂/C (20% Pd), H₂ (1 atm), rt, 6 h | 80 | - | - | - |
| 17 A  | NaOAc (6 equiv), rt, 16 h | - | - | 69 (64) [b] | - |
| 18 A  | NaOAc (3 equiv), rt, 16 h | 5 | - | 45 | - |
| 19 A  | K₂CO₃ (3 equiv), rt, 6 h | trace | - | - | - |
| 20 A  | Pyridine (3 equiv), rt, 6 h | 25 | - | - | - |
| 21 B  | H₂O (10 equiv), 50 °C, 12 h | trace | 23 | - | - |
| 22 B  | HCl (37%, 20 equiv), rt, 6 h | - | 35 | - | - |
| 23 B  | InCl₃ (3 equiv), 50 °C, 6 h | trace | 24 | - | - |
| 24 B  | BF₃·OEt₂ (10 equiv), rt, 6 h | trace | 23 | - | - |
| 25 B  | NaOAc (6 equiv), rt, 16 h | - | - | 68 (64) [b] | - |

[a] The yields of 7b, 4b and 3b were determined by ¹H NMR analysis of the crude reaction mixture in CDCl₃; [b] Isolated yield.
2.4 N-perfluoroalkylation and subsequent oxydefluorination with HCl/HOAc (7b)

Scheme S-4: Synthesis of hydroxamic acid 7b.

Hydroxylamine 2b was prepared in situ on 0.5 mmol scale according to the general procedure of Method A described in section 2.2. Subsequently, the reaction mixture was cooled to 0 °C (ice bath) before acetic acid (1.0 mL) and HCl (37%, 0.83 mL, 10.0 mmol, 20.0 equiv) were added. The mixture was stirred at 0 °C for 6 h. Water (20 mL) was added and the mixture was extracted with EtOAc (10 mL) five times. The combined organic layers were washed with a saturated aqueous solution of NaHCO₃, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography (pentane:EtOAc:formic acid = 5:1:0.1) to yield hydroxamic acid 7b.

2,2,3,3,4,4,4-Heptafluoro-N-hydroxy-N-(o-tolyl)butanamide (7b)

7b: (55.7 mg, 35% yield, brown oil, pentane:EtOAc:formic acid = 5:1:0:1); ¹H NMR (400 MHz, CDCl₃): δ ppm 7.91 (bs, 1H), 7.44–7.40 (m, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.30–7.27 (m, 2H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ ppm 153.9 (t, J = 27.3 Hz), 137.5, 135.3, 131.6, 131.4, 128.9, 126.9, 117.6 (qt, J = 286.1, 33.3 Hz), 112.5–105.3 (m, 2C), 17.1; ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -80.22 (t, J = 9.4 Hz, 3F), -113.04 (q, J = 9.5 Hz, 2F), -125.37 (d, J = 9.1 Hz, 2F); HRMS (ESI): m/z calcd for C₁₁H₈F₇NNaO₂ [M+Na]⁺ 342.0335, found 342.0333.
2.5 General procedure for the oxydefluorination and N-O bond reduction with Zn/HCl (Scheme 3)

Scheme S-5: Synthesis of amides 3.

Hydroxylamines 2 were prepared \textit{in situ} on 0.5 mmol scale according to the general procedure using Method A described in section 2.2. Subsequently, the reaction mixture was transferred into a 25 mL round-bottom flask using acetic acid (5.0 mL). Zn powder (1.30 g, 20.0 mmol, 40.0 equiv) and HCl (37%, 1.67 mL, 20.0 mmol, 40.0 equiv) were added at room temperature. The mixture was stirred vigorously at 65 °C (oil bath) for 2 h. Water (20 mL) was added and the mixture was extracted with EtOAc (10 mL) five times. The combined organic layers were washed with a saturated aqueous solution of NaHCO$_3$, dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The crude products were purified by column chromatography (pentane:DCM or pentane:EtOAc) to yield amides 3 as white solids.

2,2,3,3,4,4,4-Heptafluoro-N-phenylbutanamide (3a)$^{[17]}$

![Image](Image1.png)

3a: (79.4 mg, 55% yield, white solid, pentane:DCM = 5:1); NMR data are in accordance with literature values$^{[17]}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.99 (bs, 1H), 7.56 (d, $J = 7.7$ Hz, 2H), 7.40 (t, $J = 8.0$ Hz, 2H), 7.28–7.23 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 155.3 (t, $J = 25.7$ Hz), 135.2, 129.5, 126.7, 120.7, 117.6 (qt, $J = 285.9$, 33.1 Hz), 111.7–105.6 (m, 2C); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ ppm -80.52 (t, $J = 8.8$ Hz, 3F), -120.31 (qd, $J = 8.8$, 2.0 Hz, 2F), -126.74 (s, 2F); HRMS (ESI): $m/z$ calcd for C$_{10}$H$_5$F$_7$NO [M-H]$^- 288.0265$, found 288.0278.

2,2,3,3,4,4,4-Heptafluoro-N-(o-tolyl)butanamide (3b)

![Image](Image2.png)

3b: (30.2 mg, 70% yield, white solid, pentane:DCM = 5:1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.85 (bs, 1H), 7.69 (d, $J = 7.5$ Hz, 1H), 7.28–7.19 (m, 1H), 2.28 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 155.6 (t, $J = 25.6$ Hz), 132.9, 131.1, 130.5, 127.4, 127.3, 123.7, 117.6 (qt, $J = 287.7$, 33.5 Hz), 111.8–105.6 (m, 2C), 17.4; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ ppm -80.51 (t, $J = 8.8$ Hz, 3F), -120.36 (qd, $J = 8.8$, 1.8 Hz, 2F), -126.79 (s, 2F); HRMS (ESI): $m/z$ calcd for C$_{11}$H$_8$F$_7$NNaO [M+Na]$^+$ 326.0386, found 326.0391.
2,2,3,3,4,4,4-Heptafluoro-N-(2-(trifluoromethyl)phenyl)butanamide (3c)

3c: (30.4 mg, 42% yield, white solid, pentane:DCM = 3:1); \[^1\text{H}\] NMR (400 MHz, CDCl\(_3\)): \(\delta\) ppm 8.27 (bs, 1H), 8.12 (d, \(J = 8.2\) Hz, 1H), 7.70 (d, \(J = 8.2\) Hz, 1H), 7.65 (t, \(J = 7.9\) Hz, 1H), 7.40 (t, \(J = 7.7\) Hz, 1H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\)): \(\delta\) ppm 155.8 (t, \(J = 26.2\) Hz), 133.4, 132.4, 126.9, 126.7 (q, \(J = 5.2\) Hz), 124.9, 123.7 (q, \(J = 272.9\) Hz), 121.9 (q, \(J = 30.4\) Hz), 117.5 (qt, \(J = 287.5, 33.1\) Hz), 111.6–105.5 (m, 2C); \[^{19}\text{F}\] NMR (376 MHz, CDCl\(_3\)): \(\delta\) ppm -60.75 (s, 3F), -80.62 (t, \(J = 8.7\) Hz, 3F), -120.75 (qd, \(J = 8.7, 2.1\) Hz, 2F), -126.96 (s, 2F); HRMS (ESI): m/z calcd for C\(_{11}\)H\(_{5}\)F\(_{10}\)NNaO [M+Na\(^+\)] 380.0104, found 380.0110.

N-(2,6-Dimethylphenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (3e)

3e: (97.8 mg, 62%, white solid, pentane:DCM = 5:1); \[^1\text{H}\] NMR (400 MHz, CDCl\(_3\)): \(\delta\) ppm 7.72 (bs, 1H), 7.18 (dd, \(J = 8.3, 6.7\) Hz, 1H) 7.09 (d, \(J = 7.6\) Hz, 2H), 2.18 (s, 6H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\)): \(\delta\) ppm 156.0 (t, \(J = 25.8\) Hz), 135.4, 130.9, 128.7, 128.7, 117.6 (qt, \(J = 285.9, 33.3\) Hz), 112.1–105.2 (m, 2C), 18.0; \[^{19}\text{F}\] NMR (376 MHz, CDCl\(_3\)): \(\delta\) ppm -80.43 (t, \(J = 9.1\) Hz, 3F), -119.89 (q, \(J = 9.0\) Hz, 2F), -126.55 (s, 2F); HRMS (ESI): m/z calcd for C\(_{12}\)H\(_{9}\)F\(_{7}\)NO [M-H\(^-\)] 316.0578, found 316.0574.

2,2,3,3,4,4,4-Heptafluoro-N-(2-fluorophenyl)butanamide (3g)

3g: (81.3 mg, 53% white solid, pentane:DCM = 5:1); \[^1\text{H}\] NMR (400 MHz, CDCl\(_3\)): \(\delta\) ppm 8.26-8.22 (m; 1H), 8.16 (bs, 1H), 7.25–7.14 (m, 3H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\)): \(\delta\) ppm 155.3 (t, \(J = 26.2\) Hz), 153.0 (d, \(J = 244.2\) Hz), 127.1 (d, \(J = 7.8\) Hz), 125.1 (d, \(J = 3.9\) Hz), 123.9 (d, \(J = 10.3\) Hz), 122.2, 117.6 (qt, \(J = 286.2, 33.1\) Hz), 115.5 (d, \(J = 18.8\) Hz), 111.6–105.5 (m, 2C); \[^{19}\text{F}\] NMR (376 MHz, CDCl\(_3\)): \(\delta\) ppm -80.52 (t, \(J = 8.8\) Hz, 3F), -120.29 (qd, \(J = 8.8, 1.9\) Hz, 2F), -126.74 (s, 2F), -129.93–(-130.04) (m, 1F); HRMS (ESI): m/z calcd for C\(_{10}\)H\(_{4}\)F\(_{8}\)NO [M-H\(^-\)] 306.0170, found 306.0171.

N-(4-Bromo-2-methylphenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (3h)

3h: (134.0 mg, 70% yield, white solid, pentane:DCM = 6:1); \[^1\text{H}\] NMR (400 MHz, CDCl\(_3\)): \(\delta\) ppm 7.75 (bs, 1H), 7.61 (d, \(J = 8.4\) Hz, 1H), 7.41–7.37 (m, 2H), 2.26 (s, 3H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\)): \(\delta\) ppm 155.6 (t, \(J = 25.8\) Hz), 133.9, 132.5, 132.0, 130.4, 125.1, 120.7, 117.6 (qt, \(J = 286.1, 33.3\) Hz), 111.8–105.6 (m, 2C), 17.3; \[^{19}\text{F}\] NMR (376 MHz, CDCl\(_3\)): \(\delta\) ppm -80.44 (t, \(J = 8.8\) Hz, 3F), -120.30 (qd, \(J = 8.8, 1.9\) Hz, 2F), -126.71 (s, 2F); HRMS (ESI): m/z calcd for C\(_{11}\)H\(_{6}\)BrF\(_{7}\)NO [M-H\(^-\)] 379.9526, found 379.9510.
**N-(3-Bromophenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (3i)**

[Chemical structure image]

3i: (106.0 mg, 58% yield, white solid, pentane:DCM = 6:1); 
\( ^1\text{H NMR} \)(400 MHz, CDCl\(_3\)): \( \delta \) ppm 7.94 (bs, 1H), 7.82 (t, \( J = 2.0 \) Hz, 1H), 7.49 (ddd, \( J = 8.1, 2.1, 0.9 \) Hz, 1H), 7.40 (ddd, \( J = 8.0, 1.8, 1.0 \) Hz, 1H), 7.27 (t, \( J = 8.1 \) Hz, 1H); 
\( ^{13}\text{C NMR} \)(100 MHz, CDCl\(_3\)): \( \delta \) ppm 155.4 (t, \( J = 26.1 \) Hz), 136.4, 130.8, 129.8, 123.7, 123.2, 119.2, 121.7–111.2 (m), 108.8–103.7 (m, 2C); 
\( ^{19}\text{F NMR} \)(376 MHz, CDCl\(_3\)): \( \delta \) ppm -80.44 (t, \( J = 8.8 \) Hz, 3F), -120.24 (qd, \( J = 8.7, 1.9 \) Hz, 2F), -126.66 (s, 2F); 
\( \text{HRMS (ESI)} \): m/z calcd for C\(_{10}\)H\(_4\)BrF\(_7\)NO [M-H]\(- 365.9370\), found 365.9379.

**2,2,3,3,4,4,4-Heptafluoro-N-(3-chlorophenyl)butanamide (3j)**

[Chemical structure image]

3j: (92.1 mg, 57% yield, white solid, pentane:DCM = 3:1); 
\( ^1\text{H NMR} \)(400 MHz, CDCl\(_3\)): \( \delta \) ppm 8.03 (bs, 1H), 7.67 (d, \( J = 2.2 \) Hz, 1H), 7.43 (dd, \( J = 8.1, 0.8 \) Hz, 1H), 7.32 (td, \( J = 8.1, 2.4 \) Hz, 1H), 7.23 (dd, \( J = 8.0, 1.3 \) Hz, 1H); 
\( ^{13}\text{C NMR} \)(100 MHz, CDCl\(_3\)): \( \delta \) ppm 155.5 (t, \( J = 25.9 \) Hz), 136.2, 135.3, 130.5, 126.9, 121.0, 118.8, 117.5 (qt, \( J = 285.9, 33.3 \) Hz), 111.5–105.1 (m, 2C); 
\( ^{19}\text{F NMR} \)(376 MHz, CDCl\(_3\)): \( \delta \) ppm -80.50 (t, \( J = 8.8 \) Hz, 3F), -120.30 (qd, \( J = 9.1, 1.5 \) Hz, 2F), -126.71 (s, 2F); 
\( \text{HRMS (ESI)} \): m/z calcd for C\(_{10}\)H\(_5\)ClF\(_7\)NNaO [M+Na]\(^+\) 345.9840, found 345.9845.

**2,2,3,3,4,4,4-Heptafluoro-N-(3-(trifluoromethyl)phenyl)butanamide (3k)**

[Chemical structure image]

3k: (Method A: 58.0 mg, 31%; Method B: 67.8 mg, 38%, yellow solid, pentane:DCM = 6:1); NMR data are in accordance with literature values;\(^{[18]}\) 
\( ^1\text{H NMR} \)(400 MHz, CDCl\(_3\)): \( \delta \) ppm; 8.14 (bs, 1H), 7.86 (s, 1H), 7.81–7.78 (m, 1H), 7.56–7.50 (m, 2H); 
\( ^{13}\text{C NMR} \)(100 MHz, CDCl\(_3\)): \( \delta \) ppm 155.9 (t, \( J = 26.2 \) Hz), 135.7, 132.2 (q, \( J = 33.0 \) Hz), 130.2, 124.0, 123.6 (q, \( J = 270.7 \) Hz), 123.4 (q, \( J = 3.7 \) Hz), 117.7 (q, \( J = 3.9 \) Hz), 117.5 (qt, \( J = 285.9, 33.2 \) Hz), 111.5–105.6 (m, 2C); 
\( ^{19}\text{F NMR} \)(376 MHz, CDCl\(_3\)): \( \delta \) ppm -62.98 (s, 3F), -80.49 (t, \( J = 8.8 \) Hz, 3F), -80.49 (t, \( J = 8.8 \) Hz, 3F), -120.29 (qd, \( J = 8.8, 1.9 \) Hz, 2F), -126.68 (s, 2F); 
\( \text{HRMS (ESI)} \): m/z calcd for C\(_{11}\)H\(_4\)F\(_{10}\)NO [M-H]\(- 356.0139\), found 356.0154.

**2,2,3,3,4,4,4-Heptafluoro-N-(4-methoxyphenyl)butanamide (3l)**

[Chemical structure image]

3l: (95.9 mg, 60% yield, white solid, pentane:DCM = 3:1); 
\( ^1\text{H NMR} \)(400 MHz, CDCl\(_3\)): \( \delta \) ppm 7.94 (bs, 1H), 7.46 (d, \( J = 9.0 \) Hz, 2H), 6.90 (d, \( J = 9.0 \) Hz, 2H), 3.81 (s, 3H); 
\( ^{13}\text{C NMR} \)(100 MHz, CDCl\(_3\)): \( \delta \) ppm 158.1, 155.2 (t, \( J = 25.6 \) Hz), 128.1, 122.6, 117.6 (qt, \( J = 285.7, 33.2 \) Hz), 114.6, 111.7–105.7 (m, 2C), 55.7; 
\( ^{19}\text{F NMR} \)(376 MHz, CDCl\(_3\)): \( \delta \) ppm -80.55 (t, \( J = 8.8 \) Hz, 3F), -120.32 (qd, \( J = 8.7, 1.5 \) Hz, 2F), -126.78 (s, 2F); 
\( \text{HRMS (ESI)} \): m/z calcd for C\(_{11}\)H\(_4\)BrF\(_7\)NO [M-H]\(- 342.0335\), found 342.0339.
2,2,3,3,4,4,4-Heptafluoro-N-(4-(dimethylamino)phenyl)butanamide (3m)

For work-up, a saturated aqueous solution of Na₂CO₃ was used in place of NaHCO₃.

3m: (81.3 mg, 49% yield, grey solid, pentane:EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃): δ ppm 7.91 (bs, 1H), 7.39 (d, J = 9.1 Hz, 2H), 6.69 (d, J = 9.1 Hz, 2H), 2.95 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ ppm 154.9 (t, J = 25.3 Hz), 149.2, 124.4, 122.3, 117.6 (qt, J= 285.9, 33.2 Hz), 112.7, 111.7–105.6 (m, 2C), 40.7; ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -80.58 (t, J= 8.8 Hz, 3F), -120.29 (qd, J = 8.8, 2.0 Hz, 2F), -126.81 (s, 2F); HRMS (ESI): m/z calecd for C₁₂H₁₁F₇N₂NaO [M+Na]⁺ 355.0652, found 355.0655.

2,2,3,3,4,4,4-Heptafluoro-N-(4-chlorophenyl)butanamide (3n)

3n: (101.7 mg, 63% yield, white solid, pentane:DCM = 3:1; ¹H NMR (400 MHz, CDCl₃): δ ppm 8.02 (bs, 1H), 7.51 (d, J = 8.8 Hz, 2H), 7.36 (d, J = 8.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ ppm 155.5 (t, J= 25.8 Hz), 133.7, 132.1, 129.6, 122.1, 117.5 (qt, J= 286.0, 33.4 Hz), 111.6–105.2 (m, 2C); ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -80.58 (t, J= 8.5 Hz, 3F), -120.29 (qd, J = 8.8, 1.8 Hz, 2F), -126.80 (s, 2F); HRMS (ESI): m/z calecd for C₁₀H₅ClF₇NNaO [M+Na]⁺ 345.9840, found 345.9848.

Methyl 4-(2,2,3,3,4,4,4-heptafluorobutanamido)benzoate (3o)

3o: (105.6 mg, 61% yield, white solid, pentane:EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃): δ ppm 8.39 (bs, 1H), 8.06 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.7 Hz, 2H), 3.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ ppm 166.4, 155.6 (t, J= 26.0 Hz), 139.4, 131.1, 128.0, 120.1, 117.5 (qt, J= 286.0, 33.4 Hz), 111.5–105.2 (m, 2C), 52.4; ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -80.53 (t, J= 8.8 Hz, 3F), -120.22 (qd, J = 8.8, 1.2 Hz, 2F), -126.68 (s, 2F); HRMS (ESI): m/z calecd for C₁₂H₈F₇NNaO₃ [M+Na]⁺ 370.0285, found 370.0289.

N-(4-(3-Ethyl-2,6-dioxopiperidin-3-yl)phenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (3p)

3p: (118.3 mg, 55% yield, brown solid, pentane:EtOAc = 3:1; ¹H NMR (400 MHz, (CD₃)₂CO): δ ppm 10.37 (bs, 1H), 9.64 (bs, 1H), 7.78 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.9 Hz, 2H), 2.60–2.44 (m, 2H), 2.36–2.26 (m, 2H), 2.04–1.87 (m, 2H), 0.85 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, (CD₃)₂CO): δ ppm 176.0, 172.9, 156.2 (t, J = 25.7 Hz), 138.5, 136.4, 128.1, 122.1, 118.5 (qt, J= 285.2, 33.3 Hz), 112.6–106.2 (m, 2C), 51.5, 33.5, 30.0, 27.5, 9.3; ¹⁹F NMR (376 MHz, (CD₃)₂CO): δ ppm -81.50 (t, J= 8.8 Hz, 3F), -120.54 (q, J = 8.8 Hz, 2F), -127.55 (s, 2F); HRMS (ESI): m/z calecd for C₁₇H₁₅F₇N₂NaO₃ [M+Na]⁺ 451.0863, found 451.0874.
2,2,3,3-Pentafluoro-N-(o-tolyl)propanamide (3s)

3s: (81.2 mg, 64% yield, white solid, pentane:DCM = 5:1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.96 (bs, 1H), 7.66–7.63 (m, 1H), 7.27–7.18 (m, 3H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 155.8 (t, $J = 25.4$ Hz), 132.9, 131.0, 130.7, 127.5, 127.2, 123.8, 118.0 (qt, $J = 286.6$, 34.6 Hz), 107.2 (tq, $J = 266.8$, 39.1 Hz), 17.4; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ ppm -82.75 (s, 3F), -122.74 (s, 2F); HRMS (ESI): $m/z$ calcd for C$_{10}$H$_8$F$_5$NNaO [M+Na]$^+$ 276.0418, found 276.0413.

2,2,3,3,4,4,5,5,6,6,6-Undecafluoro-N-(o-tolyl)hexanamide (3t)

3t: (122.9 mg, 61% yield, white solid, pentane:DCM = 3:1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.86 (bs, 1H), 7.70–7.68 (m, 1H), 7.28–7.19 (m, 3H), 2.28 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 155.9 (t, $J = 25.6$ Hz), 132.9, 131.1, 131.0, 127.5, 127.1, 124.1, 117.4 (qt, $J = 286.4$, 32.8 Hz), 113.7–106.4 (m, 4C), 17.3; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ ppm (-80.79)–(-80.86) (m, 3F), -119.39 (t, $J = 12.9$ Hz, 2F), (-122.39)–(-122.59) (m, 4F), (-126.15)–(-126.25) (m, 2F); HRMS (ESI): $m/z$ calcd for C$_{13}$H$_8$F$_{11}$NNaO [M+Na]$^+$ 426.0322, found 426.0337.

2,2,3,3,4,4,5,5,6,6,7,7,8,8-Tetradecafluoro-N-(o-tolyl)octanamide (3u)

The reaction was performed on 0.2 mmol scale. 3u: (56.3 mg, 58% yield, white solid, pentane:DCM = 5:1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.82 (bs, 1H), 7.73–7.71 (m, 1H), 7.28–7.18 (m, 3H), 6.06 (tt, $J = 51.8$, 5.1 Hz, 1H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 155.6 (t, $J = 25.5$ Hz), 133.0, 131.1, 130.4, 127.4, 127.3, 123.7, 113.8–106.4 (m, 6C), 107.7 (tt, $J = 253.5$, 31.2 Hz), 17.5; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ ppm (-119.27)–(-119.34) (m, 2F), -121.47 (s, 2F), -122.02 (s, 2F), -122.32 (s, 2F), -123.34 (s, 2F), -129.34 (s, 2F), (-136.90)–(-137.12) (m, 2F); HRMS (ESI): $m/z$ calcd for C$_{15}$H$_{14}$F$_{14}$NNaO [M+Na]$^+$ 508.0353, found 508.0354.
2.6 N-perfluoroalkylation of nitrosoarene 1b and subsequent oxydefluorination and N-O bond reduction with Zn/HCl on 1.0 mmol scale (Scheme 3)

To a screw-cap vial equipped with a magnetic stirring bar were added 1b (121.1 mg, 1.00 mmol, 1.0 equiv), sodium 1,1,2,2,3,3,4,4,4-nonafluoro-1-butanesulfinate (917.8 mg, 3.00 mmol, 3.0 equiv), hydroquinone (121.1 mg, 1.10 mmol, 1.1 equiv), ethyl acetate (6.10 mL), a solution of copper(II) perchlorate hexahydrate in ethyl acetate (1.90 mL, 0.0054 M, 1 mol%), and tert-butyl hydroperoxide (70% solution in water, 420 µL, 3.00 mmol, 3.0 equiv). The reaction mixture was stirred for 1 h at room temperature during which the color changed from green to brown. Subsequently, the reaction mixture was transferred into a 100 mL round-bottom flask using acetic acid (10.0 mL). Zn powder (2.60 g, 40.0 mmol, 40.0 equiv) and HCl (37%, 3.33 mL, 40.0 mmol, 40.0 equiv) were added at room temperature. The mixture was stirred vigorously at 65 °C (oil bath) for 2 h. Water (40 mL) was added and the mixture was extracted with EtOAc (5 x 15 mL). The combined organic layers were washed with a saturated aqueous solution of NaHCO3, dried over anhydrous NaSO4, and concentrated under reduced pressure. The crude product was purified by column chromatography (pentane: DCM, 5:1) to yield amide 3b in 68% isolated yield (206.1 mg, 0.68 mmol) as a white solid. For spectral data of 3b, see page S-14.
2.7 General procedure for the N-perfluoroalkylation and subsequent oxydefluorination with NaOAc (Scheme 4)

\[ \text{Scheme S-6: Synthesis of } O\text{-acyl hydroxamic acids 4 and 8b.} \]

Hydroxylamines 2b–f were prepared in situ on 0.5 mmol scale according to the general procedure using Method A. Hydroxylamines 2a, 2j, 2k and 2n were prepared in situ according to the general procedure using Method B described in section 2.2. Subsequently, NaOAc (246.1 mg, 3.00 mmol, 6.0 equiv) or sodium propionate (for 8b, 336.2 mg, 3.50 mmol, 7.0 equiv) was added. For products 4a, 4f, 4j, 4k and 4n, dichloromethane (4 mL) or 1,1,2,2-tetrachloroethane (4 mL) was added as co-solvent to improve the yields. The resulting reaction mixture was stirred for 16 h at room temperature before water (30 mL) and EtOAc (30 mL) were added. The layers were separated and the organic layer was washed with water (2 x 30 mL) and the combined aqueous layers were extracted with EtOAc (1 x 30 mL). The combined organic layers were dried (MgSO₄) and reduced in vacuo and the crude products were purified by column chromatography. For products 4b–f and 8b, pentane: DCM was used as eluent; for products 4a, 4j, 4k and 4n, pentane:DCM or pentane:EtOAc with 3% formic acid was used as eluent. Products 4a–f, 4j, 4k, 4n and 8b were obtained as mixtures of rotamers in a near 1:1 ratio.

**N-Acetoxy-2,2,3,3,4,4,4-heptafluoro-N-phenylbutanamide (4a)**

4a: (Dichloromethane (4.0 mL) was added before the addition of NaOAc, 118.2 mg, 68% yield, brown oil, obtained as a 1:1:1 mixture of two rotamers, pentane:DCM = 4:1 with 3% formic acid); \[^1H\text{ NMR}\] (400 MHz, CDCl₃): δ ppm 7.52–7.44 (m, 5H, both rotamers), 2.19 (s, 3H, both rotamers); \[^1^3C\text{ NMR}\] (100 MHz, CDCl₃), both rotamers: δ ppm 167.3, 166.4, 155.8, 153.9, 138.1, 137.3, 131.5 (2C), 129.6, (2C), 124.9 (2C), 117.6 (qt, \( J = 286.2, 33.4 \text{ Hz, 2C} \)), 112.3–105.5 (m, 4C), 17.9 (2C); \[^1^9F\text{ NMR}\] (376 MHz, CDCl₃): δ ppm rotamer A: -80.25 (s, 3F), -111.57 (s, 2F), -125.27 (s, 2F), rotamer B: -80.61 (s, 3F), -115.07 (s, 2F), -124.98 (s, 2F); \[^{HRMS}\text{ (ESI)}\]: \( m/z \) calcd for C₁₂H₈F₇NNaO₃ \([\text{M+Na}^+]\) 370.0285, found 370.0269.
N-Acetoxy-2,2,3,3,4,4,4-heptafluoro-N-(o-tolyl)butanamide (4b)

4b: (119.2 mg, 66% yield, colorless oil, obtained as a 1.3:1 mixture of two rotamers, pentane:DCM = 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) ppm 7.52–7.25 (m, 4H, both rotamers), 2.38 and 2.36 (s, 3H, both rotamers), 2.19 and 2.16 (s, 3H, both rotamers); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)), both rotamers: \(\delta\) ppm 167.3, 166.2, 155.9 (t, \(J = 26.4\) Hz), 154.4 (t, \(J = 27.7\) Hz), 138.3, 136.9, 136.6, 136.1, 131.7, 131.40, 131.37, 130.6, 127.8, 127.01, 126.95, 121.1–114.2 (m, 2C), 112.3–105.9 (m, 4C), 18.1, 17.9, 17.7, 17.5; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): rotamer A: -80.11 (t, \(J = 9.3\) Hz, 3F), (-112.19)–(-114.05) (m, 2F), -125.30 (d, \(J = 6.7\) Hz, 2F), rotamer B: -80.47 (t, \(J = 9.2\) Hz, 3F), -115.14 (s, 2F), -124.81 (s, 2F); HRMS (ESI): \(m/z\) calcd for C\(_{13}\)H\(_{10}\)F\(_7\)NNaO\(_3\) [M+Na]\(^+\) 384.0445, found 384.0441.

N-Acetoxy-2,2,3,3,4,4,4-heptafluoro-N-(2-(trifluoromethyl)phenyl)butanamide (4c)

4c: (134.9 mg, 65% yield, colorless oil, obtained as a 1.4:1 mixture of two rotamers, pentane:DCM = 2:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) ppm 7.84–7.76 (m, 2H, both rotamers), 7.71–7.58 (m, 2H, both rotamers), 2.19 and 2.16 (s, 3H, both rotamers); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)), both rotamers: \(\delta\) ppm 167.9, 166.4, 156.4 (t, \(J = 27.1\) Hz), 153.9 (t, \(J = 27.1\) Hz), 134.4, 134.2, 133.4, 133.2, 132.7, 132.3, 132.2, 131.3, 129.4 (q, \(J = 31.6\) Hz, 128.5 (q, \(J = 32.3\) Hz), 128.1–127.9 (m), 122.79 (q, \(J = 273.0\) Hz), 122.76 (q, \(J = 273.4\) Hz), 121.4–113.8 (m, 2C), 112.2–105.9 (m, 4C), 17.9, 17.7; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) ppm rotamer A: -60.90 (s, 3F), (-80.35)–(-80.47) (m, 3F), -112.92 (s, 2F), -125.48 (s, 2F), rotamer B: -61.59 (s, 3F), (-80.35)–(-80.47) (m, 3F), -115.73 (bs, 2F), -125.52 (s, 2F); HRMS (ESI): \(m/z\) calcd for C\(_{13}\)H\(_7\)F\(_{10}\)NNaO\(_3\) [M+Na]\(^+\) 438.0158, found 438.0164.

N-([1,1’-Biphenyl]-2-yl)-N-acetoxy-2,2,3,3,4,4,4-heptafluorobutanamide (4d)

4d: (164.3 mg, 78% yield, colorless oil, obtained as a 1.4:1 mixture of two rotamers, pentane:DCM = 3:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 7.74 and 7.71 (d, \(J = 7.8\) and 7.9 Hz, 1H, both rotamers) 7.61–7.41 (m, 8H, both rotamers), 2.22 and 2.06 (s, 3H, both rotamers); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)), both rotamers: \(\delta\) ppm 167.6, 166.2, 156.3 (t, \(J = 26.5\) Hz), 153.8 (t, \(J = 26.9\) Hz), 142.8, 141.3, 138.0, 137.1, 135.3, 135.2, 131.8, 131.5, 131.4, 130.7, 130.4, 129.6, 129.1, 128.7, 128.62, 128.57, 128.43, 128.39, 128.1, 121.2–113.8 (m, 2C), 112.0–106.1 (m, 4C), 18.1, 17.8; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) ppm rotamer A: -80.25 (t, \(J = 9.3\) Hz, 3F), (-113.52)–(-113.61) (m, 2F), -125.43 (s, 2F), rotamer B: -80.31 (t, \(J = 9.8\) Hz, 3F), -115.47 (s, 2F), -125.24 (bs, 2F); HRMS (ESI): \(m/z\) calcd for C\(_{18}\)H\(_{12}\)F\(_7\)NNaO\(_3\) [M+Na]\(^+\) 446.0598, found 446.0605.
N-Acetoxy-N-(2,6-dimethylphenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (4e)

4e: (110.7 mg, 59% yield, colorless oil, obtained as a 1:1 mixture of two rotamers, pentane:DCM = 2:1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.31 and 7.24 (t, $J = 7.6$ Hz, 1H, both rotamers), 7.15 and 7.12 (d, $J = 7.7$ Hz, 2H, both rotamers), 2.39 (s, 6H, both rotamers), 2.20 and 2.15 (s, 3H, both rotamers); $^{13}$C NMR (100 MHz, CDCl$_3$), both rotamers: $\delta$ ppm 166.4, 165.6, 156.0 (t, $J = 26.9$ Hz), 155.8 (t, $J = 26.3$ Hz), 139.0, 137.3, 135.4, 135.2, 131.5, 130.5, 129.10, 129.09, 122.4–113.0 (m, 2C), 113.8–105.5 (m, 4C), 18.3, 18.2, 17.9; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ ppm rotamer A: -80.25 (t, $J = 9.6$ Hz, 3F), -114.83 (q, $J = 8.9$ Hz, 2F), -125.51 (s, 2F), rotamer B: -79.97 (t, $J = 9.5$ Hz, 3F), -115.09 (q, $J = 9.2$ Hz, 2F), -124.51 (s, 2F); HRMS (ESI): $m/z$ calcd for C$_{14}$H$_{12}$F$_7$NNaO$_3$ [M+Na]$^+$ 398.0598, found 398.0590.

N-Acetoxy-N-(4-chloro-2-methylphenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (4f)

4f: (1,1,2,2-tetrachloroethane (4.0 mL) was added before the addition of NaOAc, 122.7 mg, 62% yield, colorless oil, obtained as a 1.1:1 mixture of two rotamers, pentane:DCM = 3:1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.45 and 7.39 (d, $J = 8.0$ and 8.2 Hz, both rotamers), 7.32 (d, $J = 10.9$ Hz, 1H, both rotamers), 7.26 and 7.24 (d, $J = 1.5$ and 2.4 Hz, 1H, both rotamers) 2.35 and 2.33 (s, 3H, both rotamers), 2.19 and 2.17 (s, 3H, both rotamers); $^{13}$C NMR (126 MHz, CDCl$_3$), both rotamers: $\delta$ ppm 167.2, 166.2, 156.0 (t, $J = 27.1$ Hz), 154.2 (t, $J = 25.7$ Hz), 140.3, 138.9, 137.7, 136.4, 135.1, 134.6, 131.9, 131.4, 129.3, 127.3, 121.4–113.9 (m, 2C), 113.9–104.0 (m, 4C), 18.1, 17.9, 17.7, 17.5; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ ppm rotamer A: -80.04 (t, $J = 8.9$ Hz, 3F), -114.83 (q, $J = 8.9$ Hz, 2F), -125.51 (s, 2F), rotamer B: -79.97 (t, $J = 9.5$ Hz, 3F), -115.09 (q, $J = 9.2$ Hz, 2F), -124.51 (s, 2F); HRMS (ESI): $m/z$ calcd for C$_{13}$H$_{10}$ClF$_7$NNaO$_3$ [M+Na]$^+$ 418.0051, found 418.0057.

N-Acetoxy-N-(3-chlorophenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (4j)

4j: (Dichloromethane (4.0 mL) was added before the addition of NaOAc, 97.1 mg, 51% yield, brown oil, obtained as a 1:1.5 mixture of two rotamers, pentane:EtOAc = 10:1 with 3% formic acid); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.43–7.37 (m, 3H, both rotamers), 7.43–7.37 (m, 3H, both rotamers), 7.43–7.37 (m, 3H, both rotamers), 2.22 (s, 3H, both rotamers); $^{13}$C NMR (100 MHz, CDCl$_3$), both rotamers: $\delta$ ppm 167.1 (2C), 155.7, 154.0, 138.9, 135.2, 131.8, 130.5, 129.5, 127.7, 124.6, 122.7, 117.6 (qt, $J = 286.2$, 33.2 Hz, 2C), 112.4–105.8 (m, 4C), 17.9 (2C); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ ppm rotamer A: -80.21 (s, 3F), -111.55 (s, 2F), -125.27 (s, 2F), rotamer B: -80.55 (s, 3F), -115.07 (s, 2F), -124.95 (2F); HRMS (ESI): $m/z$ calcd for C$_{12}$H$_2$ClF$_7$NNaO$_3$ [M+Na]$^+$ 403.9895, found 403.9890.
N-Acetoxy-2,2,3,3,4,4,4-heptafluoro-N-(3-(trifluoromethyl)phenyl)butanamide (4k)

4k: (Dichloromethane (4.0 mL) was added before the addition of NaOAc, 92.3 mg, 44% yield, brown oil, obtained as a 1:1.7 mixture of two rotamers, pentane:DCM = 3:1 with 3% formic acid);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.76–7.59 (m, 4H, both rotamers), 2.24 (s, 3H, both rotamers);

$^{13}$C NMR (100 MHz, CDCl$_3$), both rotamers: $\delta$ ppm 167.0 (2C), 155.9, 153.8, 138.5 (2C), 132.4 (q, $J = 33.2$ Hz, 2C), 130.3 (2C), 127.9 (2C), 126.0 (2C), 123.3 (q, $J = 270.8$ Hz, 2C), 121.3 (2C), 117.6 (qt, $J = 286.2$, 33.2 Hz, 2C), 112.2–105.7 (4C), 17.9 (2C);

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ ppm rotamer A: -62.95 (s, 3F), -80.24 (s, 3F), -111.49 (s, 2F), -125.30 (s, 2F), rotamer B: -62.95 (s, 3F), -80.52 (s, 3F), -115.08 (s, 2F), -124.94 (s, 2F);

HRMS (ESI): $m/z$ calcld for C$_{13}$H$_7$F$_{10}$NNaO$_3$ [M+Na]$^+$ 438.0158, found 438.0155.

N-Acetoxy-N-(4-chlorophenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (4n)

4n: (Dichloromethane (4.0 mL) was added before the addition of NaOAc, 114.8 mg, 60% yield, brown oil, obtained as a 1:1.1 mixture of two rotamers, pentane:DCM = 3:1 with 3% formic acid);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.46–7.41 (m, 4H, both rotamers), 2.20 (s, 3H, both rotamers);

$^{13}$C NMR (100 MHz, CDCl$_3$), both rotamers: $\delta$ ppm 167.2, 166.5, 155.8, 153.8, 137.8, 136.5, 135.7, 135.3, 130.9, 129.9, 126.3, 117.6 (qt, $J = 286.2$, 33.2 Hz, 2C), 112.4–105.8 (m, 4C), 17.9 (2C);

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ ppm rotamer A: -80.22 (s, 3F), -111.53 (s, 2F), -125.30 (s, 2F), rotamer B: -80.60 (s, 3F), -115.11 (s, 2F), -125.00 (2F);

HRMS (ESI): $m/z$ calcld for C$_{12}$H$_7$ClF$_7$NNaO$_3$ [M+Na]$^+$ 403.9899, found 403.9899.

2,2,3,3,4,4,4-Heptafluoro-N-(propionyloxy)-N-(o-tolyl)butanamide (8b)

8b: (82.6 mg, 44% yield, colorless oil, obtained as a 1.2:1 mixture of two rotamers, pentane:DCM = 3:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.53–7.25 (m, 4H, both rotamers), 2.56–2.37 (m, 5H, both rotamers), 1.23–1.17 (m, 3H, both rotamers);

$^{13}$C NMR (126 MHz, CDCl$_3$), both rotamers: $\delta$ ppm 171.0, 170.0, 155.9 (t, $J = 26.6$ Hz), 154.4 (t, $J = 26.9$ Hz), 138.3, 136.9, 136.7, 136.2, 131.7, 131.4, 131.3, 130.6, 130.5, 127.7, 127.0, 126.9, 121.4–113.9 (m, 2C), 112.7–106.0 (m, 4C), 24.9, 17.7, 17.5, 8.7, 8.5;

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ ppm rotamer A: -80.14 (t, $J = 9.3$ Hz, 3F), (-112.16)–(-114.03) (m, 2F), -125.31 (d, $J = 8.5$ Hz, 2F), rotamer B: -80.45 (t, $J = 9.2$ Hz, 3F), -115.17 (s, 2F), -124.91 (s, 2F); HRMS (ESI): $m/z$ calcld for C$_{14}$H$_{12}$F$_7$NNaO$_3$ [M+Na]$^+$ 398.0598, found 398.0584.
2.8 Coalescence experiment of acylated hydroxamic acid 4c

$^1$H NMR spectra of 4c in CDCl$_3$ were recorded at 25, 50, 75, 90, and 25 °C again, and the results are shown in Figure S-1. At 25 °C two sets of signals were observed, while at higher temperatures (75 and 90 °C) one set of signals was observed. Upon cooling down the sample to 25 °C again, the two original sets of signals were observed. These results indicate that the two sets of signals originate from two rotamers of 4c.

**Figure S-1:** Coalescence of the aromatic signals of 4c at higher temperatures.
2.9 General procedure for the N-perfluoroalkylation and subsequent defluorination with KSAc (Scheme 5)

Scheme S-7: Synthesis of thioamides 5.

Hydroxylamines 2 were prepared in situ on 0.5 mmol scale according to the general procedure using Method B described in section 2.2. Subsequently, KSAc (342.6 mg, 3.00 mmol, 6.0 equiv) was added. For products 5a, 5j, 5k, and 5o, dichloromethane (4 mL) was added as co-solvent to improve the yields. The resulting reaction mixture was stirred for 16 h at room temperature before water (20 mL) and EtOAc (20 mL) were added. The layers were separated and the organic layer was washed with water (2 x 20 mL) and the combined aqueous layers were extracted with EtOAc (2 x 20 mL). The combined organic layers were dried (MgSO\(_4\)) and reduced in vacuo and the crude products were purified by column chromatography (pentane:DCM and/or pentane:EtOAc) to yield thioamides 5a–c, 5j, 5k, and 5o.

2,2,3,3,4,4,4-Heptafluoro-N-phenylbutanethioamide (5a)

5a: (Dichloromethane (4.0 mL) was added before the addition of KSAc, 86.9 mg, 57% yield, yellow oil, pentane:DCM = 8:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) ppm 9.24 (bs, 1H), 7.72 (d, \(J = 7.9\) Hz, 2H), 7.47 (t, \(J = 7.6\) Hz, 2H), 7.37 (t, \(J = 7.5\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) ppm 180.0 (t, \(J = 24.8\) Hz), 136.8, 129.5, 128.3, 123.4, 117.8 (qt, \(J = 288.5, 33.9\) Hz), 112.9–105.9 (m, 2C); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) ppm -80.11 (t, \(J = 9.3\) Hz, 3F), -111.08 (qd, \(J = 9.6, 2.8\) Hz, 2F), -124.42 (s, 2F); HRMS (ESI): \(m/z\) calcd for C\(_{10}\)H\(_5\)F\(_7\)NS [M-H]- 304.0036, found 304.0042.

2,2,3,3,4,4,4-Heptafluoro-N-(o-tolyl)butanethioamide (5b)

5b: (108.5 mg, 68% yield, yellow oil, pentane:DCM = 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) ppm 9.07 (bs, 1H), 7.52–7.49 (m, 1H), 7.35–7.29 (m, 3H), 2.27 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) ppm 181.8 (t, \(J = 24.7\) Hz), 135.0, 133.9, 131.5, 129.1, 127.2, 125.9, 117.8 (qt, \(J = 286.4, 33.8\) Hz), 113.8–104.9 (m, 2C), 17.6; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) ppm -80.05 (t, \(J = 9.6\) Hz, 3F), -110.71 (qd, \(J = 10.0, 2.6\) Hz, 2F), -124.45 (s, 2F); HRMS (ESI): \(m/z\) calcd for C\(_{11}\)H\(_7\)F\(_7\)NS [M-H]- 318.0193, found 318.0198.
2,2,3,3,4,4,4-Heptafluoro-N-(2-(trifluoromethyl)phenyl)butanethioamide (5c)

5c: (117.4 mg, 63% yield, yellow oil, pentane:DCM = 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) ppm 9.27 (bs, 1H), 7.97 (d, \(J = 8.0\) Hz, 1H), 7.78 (d, \(J = 7.9\) Hz, 1H), 7.68 (t, \(J = 7.8\) Hz, 1H), 7.51 (t, \(J = 7.7\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) ppm 182.8 (t, \(J = 25.0\) Hz), 134.3, 133.0, 128.7, 128.4, 127.1 (q, \(J = 5.0\) Hz), 125.2 (q, \(J = 30.4\) Hz), 123.3 (q, \(J = 271.2\) Hz), 117.7 (qt, \(J = 286.1, 33.4\) Hz), 111.6–105.2 (m, 2C); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) ppm -61.27 (s, 3F), -80.10 (t, \(J = 9.5\) Hz, 3F), -110.82 (qd, \(J = 9.6, 2.7\) Hz, 2F), -124.58 (s, 2F); HRMS (ESI): \(m/z\) calcd for C\(_{11}\)H\(_4\)F\(_{10}\)NS [M-H]- 371.9910, found 371.9918.

N-(3-Chlorophenyl)-2,2,3,3,4,4,4-heptafluorobutanethioamide (5j)

5j: (Dichloromethane (4.0 mL) was added before the addition of KSAc, 79.8 mg, 47% yield, yellow oil, pentane:DCM = 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) ppm 9.22 (bs, 1H), 7.83 (s, 1H), 7.57 (d, \(J = 8.0\) Hz, 1H), 7.39 (t, \(J = 8.1\) Hz, 1H), 7.33 (d, \(J = 7.8\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) ppm 180.4 (t, \(J = 24.7\) Hz), 137.8, 135.2, 130.5, 128.4, 123.6, 121.6, 121.6, 117.7 (qt, \(J = 286.3, 33.5\) Hz), 113.1–105.2 (m, 2C); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) ppm -80.06 (t, \(J = 9.6\) Hz, 3F), -111.08 (qd, \(J = 9.6, 2.7\) Hz, 2F), -124.40 (s, 2F); HRMS (ESI): \(m/z\) calcd for C\(_{10}\)H\(_4\)ClF\(_7\)NS [M-H]- 337.9647, found 337.9654.

2,2,3,3,4,4,4-Heptafluoro-N-(3-(trifluoromethyl)phenyl)butanethioamide (5k)

5k: (Dichloromethane (4.0 mL) was added before the addition of KSAc, 93.3 mg, 50% yield, yellow oil, pentane:DCM = 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) ppm 9.29 (bs, 1H), 8.02 (s, 1H), 7.96–7.93 (m, 1H), 7.64–7.58 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) ppm 180.7 (t, \(J = 24.9\) Hz), 137.2, 132.1 (q, \(J = 33.0\) Hz), 130.2, 126.7, 124.9 (q, \(J = 3.6\) Hz), 123.5 (q, \(J = 270.8\) Hz), 120.5 (q, \(J = 3.8\) Hz), 117.7 (qt, \(J = 286.1, 33.5\) Hz), 115.5–105.2 (m, 2C); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) ppm -62.95 (s, 3F), -80.13 (t, \(J = 9.5\) Hz, 3F), -110.95 (qd, \(J = 9.6, 3.4\) Hz, 2F), -124.46 (s, 2F); HRMS (ESI): \(m/z\) calcd for C\(_{11}\)H\(_4\)F\(_{10}\)NS [M-H]- 371.9910, found 371.9914.

Methyl 4-(2,2,3,3,4,4,4-heptafluorobutanethioamido)benzoate (5o)

5o: (Dichloromethane (4.0 mL) was added before the addition of KSAc, 112.0 mg, 62% yield, yellow oil, pentane:DCM = 3:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) ppm 9.49 (bs, 1H), 8.11 (d, \(J = 8.8\) Hz, 2H), 7.88 (d, \(J = 8.7\) Hz, 2H), 3.92 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) ppm 180.1 (t, \(J = 24.8\) Hz), 166.2, 140.7, 131.0, 129.4, 122.7, 117.7 (qt, \(J = 286.1, 33.7\) Hz), 113.4–105.2 (m, 2C), 52.5; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) ppm -80.11 (t, \(J = 9.5\) Hz, 3F), -110.95 (qd, \(J = 9.3, 2.8\) Hz, 2F), -124.39 (s, 2F); HRMS (ESI): \(m/z\) calcd for C\(_{12}\)H\(_7\)F\(_7\)NO\(_2\)S [M-H]- 362.0091, found 362.0093.
2.10 Synthesis applications of 3b and 5c (Scheme 6)

2.10.1 Reduction of amide 3b to amine 9

To a solution of 3b (60.6 mg, 0.20 mmol, 1.0 equiv) in anhydrous THF (3 mL) was added LiAlH₄ (34.2 mg, 0.90 mmol, 4.5 equiv) at 0 °C (ice bath) and the mixture was refluxed (oil bath) under stirring for 12 h. After cooling to 0 °C again, an additional portion of LiAlH₄ (11.4 mg, 0.30 mmol, 1.5 equiv) was added and the mixture was refluxed for 18 h. After cooling to room temperature, water (10 mL) was added carefully. The resulting mixture was extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography (pentane:DCM = 10:1) to yield amine 9.

N-(2,2,3,3,4,4,4-Heptafluorobutyl)-2-methylaniline (9)

9: (37.6 mg, 65% yield, colorless oil, pentane:DCM = 10:1); ¹H NMR (400 MHz, CDCl₃): δ ppm 7.17 (td, J = 7.8, 1.6 Hz, 1H), 7.11 (d, J = 7.3 Hz, 1H), 6.77 (td, J = 7.4, 1.1 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 3.93 (td, J = 15.3, 6.8 Hz, 2H), 3.75 (bs, 1H), 2.21 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ ppm 144.5, 130.7, 127.4, 122.8, 118.9, 117.9 (qt, J = 285.7, 33.6 Hz), 115.9 (t, J = 253.9, 30.4 Hz), 110.3, 109.2 (qd, J = 34.7, 3.5 Hz), 44.2 (t, J = 23.2 Hz), 17.5; ¹⁹F NMR (376 MHz, CDCl₃): δ ppm -80.73 (t, J = 9.4 Hz, 3F), (-118.93)–(-119.10) (m, 2F), -127.60 (d, J = 4.1 Hz, 2F); HRMS (ESI): m/z calcd for C₁₁H₉F₇N [M-H]- 288.0629, found 288.0621.

2.10.2 Transformation of thioamide 5c to benzothiazole 10

Benzothiazole 10 was synthesized using a literature method: A mixture of thioamide 5c (59.7 mg, 0.16 mmol, 1.0 equiv), CAN (184.2 mg, 0.34 mmol, 2.1 equiv) and NaHCO₃ (56.5 mg, 0.67 mmol, 4.2 equiv) in MeCN (2 mL) was stirred at 80 °C (oil bath) for 2 h. Then water (10 mL) was added and the mixture was extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was then purified by column chromatography (pentane:DCM = 5:1) to yield benzothiazole 10.
2-(Perfluoropropyl)-4-(trifluoromethyl)benzo[d]thiazole (10)

\[
\begin{align*}
\text{CF}_3 & \quad \text{N} \quad \text{(CF}_2\text{)}_2\text{CF}_3 \\
\end{align*}
\]

\(10\): (41.8 mg, 70% yield, white solid, pentane:DCM = 5:1);
\(\text{\textsuperscript{1}H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) ppm 8.22 (d, \(J = 8.2\) Hz, 1H), 7.93 (d, \(J = 7.5\) Hz, 1H), 7.67 (t, \(J = 7.9\) Hz, 1H); \(\text{\textsuperscript{13}C NMR}\) (126 MHz, CDCl\(_3\)): \(\delta\) ppm 157.7 (t, \(J = 30.6\) Hz), 148.8, 137.3, 127.0, 126.5 (q, \(J = 33.2\) Hz), 126.0, 125.2 (q, \(J = 5.0\) Hz), 123.2 (q, \(J = 273.7\) Hz), 117.9 (qt, \(J = 288.2, 33.7\) Hz), 114.3–106.1 (m, 2C); \(\text{\textsuperscript{19}F NMR}\) (376 MHz, CDCl\(_3\)): \(\delta\) ppm -61.51 (s, 3F), -79.97 (t, \(J = 9.3\) Hz, 3F), -106.76 (qd, \(J = 9.2, 4.3\) Hz, 2F), -125.66 (s, 2F); \(\text{HRMS}\) (ESI): \(m/z\) calcd for C\(_{11}\)H\(_2\)F\(_{10}\)NS [M-H]- 369.9754, found 369.9744.

2.10.3 S-Arylation of thioamide 5c to phenyl thioimidate 11

Phenyl thioimidate 11 was synthesized using a literature method\[^{[20]}\]. Thioamide 5c (44.8 mg, 0.12 mmol, 1.0 equiv), diphenyliodonium triflate (56.7 mg, 0.13 mmol, 1.1 equiv) and LiO\(_{t}\)Bu (10.6 mg, 0.13 mmol, 1.1 equiv) were weighed into an oven dried screw-cap vial. The reaction vessel was evacuated and backfilled with argon three times, and degassed, anhydrous toluene (1.9 mL) was added under argon. The mixture was stirred at 80 °C (oil bath) for 2 h. After cooling to room temperature, the resulting mixture was concentrated under reduced pressure and transferred directly onto a silica gel column with a small amount of DCM. The mixture was purified by column chromatography (pentane: DCM = 10:1) to yield phenyl thioimidate 11.

Phenyl (Z)-2,2,3,3,4,4,4-heptafluoro-N-(2-(trifluoromethyl)phenyl)butanimidothioate (11)

\[
\begin{align*}
\text{PhS} & \quad \text{N} \quad \text{(CF}_2\text{)}_2\text{CF}_3 \\
\end{align*}
\]

\(11\): (47.8 mg, 88% yield, pale yellow oil, pentane:DCM = 10:1); \(\text{\textsuperscript{1}H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) ppm 7.46 (d, \(J = 7.9\) Hz, 1H), 7.32–7.28 (m, 3H), 7.24–7.19 (m, 1H), 7.17–7.12 (m, 2H), 7.08 (t, \(J = 7.7\) Hz, 1H), 6.83 (d, \(J = 8.0\) Hz, 1H); \(\text{\textsuperscript{13}C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta\) ppm 153.2 (t, \(J = 27.9\) Hz), 143.4, 135.2, 132.1, 129.9, 129.3, 126.4 (q, \(J = 5.0\) Hz), 125.7 (t, \(J = 2.1\) Hz), 125.3, 123.4 (q, \(J = 271.4\) Hz), 120.0 (q, \(J = 31.1\) Hz), 118.8, 118.0 (qt, \(J = 286.3, 33.4\) Hz), 114.4–105.8 (m, 2C); \(\text{\textsuperscript{19}F NMR}\) (376 MHz, CDCl\(_3\)): \(\delta\) ppm -61.82 (s, 3F), -80.10 (t, \(J = 9.7\) Hz, 3F), -109.21 (q, \(J = 9.7\) Hz, 2F), -124.50 (s, 2F); \(\text{HRMS}\) (ESI): \(m/z\) calcd for C\(_{17}\)H\(_9\)F\(_{10}\)NNaS [M+Na]\(^+\) 472.0188, found 472.0193.
2.11 GC-MS (EI) study

2.11.1 GC-MS (EI) analysis of hydroxylamines 2a and 2b

Hydroxylamines 2a and 2b were prepared in situ on 0.1 mmol scale according to the general procedure using Method B described in section 2.2. Subsequently, the resulting mixture were diluted 10 times with anhydrous EtOAc and filtered. The solutions of the filtrates were used freshly for GC-MS analysis (GC-MS conditions: 60 °C for 2 min; gradient from 60 °C to 260 °C during 10 min; 260 °C for 4 min. Column: HP-5MS (30m×0.25mm×0.25μm). The results are shown in Figure S-2 and Figure S-3.

**Figure S-2: GC-MS spectra for the detection of hydroxylamine 2a**

![GC-MS spectra for the detection of hydroxylamine 2a](image-url)
Figure S-3: GC-MS spectra for the detection of hydroxylamine 2b
2.11.2 GC-MS traces of the defluorination of hydroxylamines 2a and 2b by KSAc

Hydroxylamines 2a and 2b were prepared in situ on 0.1 mmol scale according to the general procedure using Method B described in section 2.2. Subsequently, KSAc (68.5 mg, 0.6 mmol, 6.0 equiv) was added. For hydroxylamine 2a, dichloromethane (0.8 mL) was added as co-solvent. The resulting reaction mixtures were stirred for 4 h at room temperature. The suspensions were diluted 10 times with anhydrous EtOAc and filtered. The filtrates were directly used for GC-MS analysis (GC-MS conditions: 60 °C for 2 min; gradient from 60 °C to 260 °C during 10 min; 260 °C for 4 min. Column: HP-5MS (30m×0.25mm×0.25μm)). The results are shown in Figure S-4 and Figure S-5.
Figure S-4: GC-MS traces of the KSAc promoted defluorination of hydroxylamine 2a
Figure S-5: GC-MS traces of the KSAc promoted defluorination of hydroxylamine 2b
3. $^1$H, $^{13}$C and $^{19}$F NMR Spectra

$3a$ $^1$H NMR (CDCl$_3$, 400 MHz)

$3a$ $^{13}$C NMR (CDCl$_3$, 100 MHz)
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3b^{19}F NMR (CDCl₃, 376 MHz)
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3c $^{19}$F NMR (CDCl$_3$, 376 MHz)
$^{19}$F NMR (CDCl$_3$, 376 MHz)
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3H $^{19}$F NMR (CDCl$_3$, 376 MHz)
$^{31}\text{F NMR (CDCl}_3, 376 \text{ MHz)}$
$3\text{J}^\text{19F}$ NMR (CDCl$_3$, 376 MHz)
$^{31}\text{F} \text{NMR (CDCl}_3, \text{376 MHz)}$
Zhiyao Zheng, Angela van der Werf, Marie Deliaval, and Nicklas Selander*
Zhiyao Zheng, Angela van der Werf, Marie Deliaval, and Nicklas Selander*
Zhiyao Zheng, Angela van der Werf, Marie Deliaval, and Nicklas Selander*

$\text{O} - (\text{CF}_2)_3 \text{CF}_3$

$\text{Me}$

$3^1\text{H}^1\text{F NMR (CDCl}_3 \text{ 376 MHz)}$

![NMR Spectrogram](Image)
Zhiyao Zheng, Angela van der Werf, Marie Deliaval, and Nicklas Selander*

$\text{Me}$

$\text{O} = (\text{CF}_2) = \text{H}$

$\text{NMR (CDCl}_3 \, 376 \text{ MHz})$

$\delta$ ppm
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4b $^{19}$F NMR (CDCl$_3$, 376 MHz)
$\text{O}^{\text{CF}}\text{CF}_2\text{CF}_3$

$\text{N}^\text{Me}$

$\text{OAc}$

4e $^{19}$F NMR (CDCl$_3$, 376 MHz)
$^{1}H$ NMR (CDCl$_3$, 400 MHz)

$^{13}C$ NMR (CDCl$_3$, 100 MHz)
$4^J \text{F-NMR (CDCl}_3 \text{, } 376 \text{ MHz)}$
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$\text{S-87}$

Zhiyao Zheng, Angela van der Werf, Marie Deliaval, and Nicklas Selander*

$\text{5a}^{19}\text{F-NMR (CDCl}_3\text{, 376 MHz)}$
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$\text{S=}(\text{CF}_2)_2\text{CF}_3$

$5b$ $^1\text{H NMR (CDCl}_3$, 400 MHz)

$\text{S=}(\text{CF}_2)_2\text{CF}_3$

$5b$ $^{13}\text{C NMR (CDCl}_3$, 100 MHz)
5b $^1$F NMR (CDCl$_3$, 376 MHz)
Zhiyao Zheng, Angela van der Werf, Marie Deliaval, and Nicklas Selander*

$\text{S-(CF}_2\text{)}_2\text{CF}_3$

$\text{N}$

$\text{F}_3$

$5\text{c}^{19}\text{F NMR (CDCl}_3\text{ 376 MHz)}$

$\delta$ (ppm)
$^{19}$F NMR (CDCl$_3$, 376 MHz)
Zhiyao Zheng, Angela van der Werf, Marie Deliaval, and Nicklas Selander*
Zhiyao Zheng, Angela van der Werf, Marie Deliaval, and Nicklas Selander*
Zhiyao Zheng, Angela van der Werf, Marie Deliaval, and Nicklas Selander*

$\text{O}_2\text{N} \quad \text{(CF}_2\text{)}_3\text{CF}_3 \quad \text{N} \quad \text{OAc}$

$^1\text{H}^\text{NMR (CDCl}_3\text{, }376\text{MHz}}$

$\delta$ NMR (CDCl$_3$, 376 MHz)
Zhiyao Zheng, Angela van der Werf, Marie Deliaval, and Nicklas Selander*

$\text{O} - (\text{CF}_2)_{2} \text{CF}_3$

Me

7b $^1$H NMR (CDCl$_3$, 400 MHz)

$\text{O} - (\text{CF}_2)_{2} \text{CF}_3$

Me

7b $^{13}$C NMR (CDCl$_3$, 100 MHz)
\[ \text{O} \quad (\text{CF}_2)_2\text{CF}_3 \]
\[ \text{i}^\text{Bu} \quad \text{NOH} \]

7r \[^1H\text{NMR (CDCl}_3, 400\text{MHz)}\]

\[ \text{O} \quad (\text{CF}_2)_2\text{CF}_3 \]
\[ \text{i}^\text{Bu} \quad \text{NOH} \]

7r \[^{13}\text{C NMR (CDCl}_3, 126\text{MHz)}\]
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$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
9 $^1^F$ NMR (CDCl$_3$, 376 MHz)
$^{11}$F NMR (CDCl$_3$, 376 MHz)
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