Supporting Online Material

Mechanistic Studies on Intramolecular C-H Trifluoromethoxylation of (Hetero)arenes via OCF₃-Migration

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### Spectroscopic Data

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Materials and Methods

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere, magnetically stirred, and monitored by thin layer chromatography (TLC) using Agela Technologies TLC plates pre-coated with 250 μm thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. Flash chromatography was performed on SiliaFlash® Silica Gel 40-63μm 60Å particle size using a forced flow of eluent at 0.3–0.5 bar pressure. All air- and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen. Diethyl ether and THF were distilled from deep purple sodium benzophenone ketyl. Methylene chloride, chloroform and acetonitrile were dried over CaH₂ and distilled. Nitromethane was dried over 4Å molecular sieves. All other chemicals were used as received. All deuterated solvents were purchased from Cambridge Isotope Laboratories. NMR spectra were recorded on either a Bruker Ascend 700 spectrometer operating at 700 MHz for ¹H acquisitions and 175 MHz for ¹³C acquisitions, a Bruker 500 Advance spectrometer operating at 500 MHz, 125 MHz, and 470 MHz for ¹H, ¹³C, and ¹⁹F acquisitions, respectively, a Bruker 400 Nanobay spectrometer operating at 400 MHz, 100 MHz, and 376 MHz for ¹H, ¹³C, and ¹⁹F acquisitions, respectively. Chemical shifts were referenced to the residual proton solvent peaks (¹H: CDCl₃, δ 7.26; (CD₃)₂SO, δ 2.50; CD₂OD, δ 3.31; CD₂CN, δ 1.94), solvent ¹³C signals (CDCl₃, δ 77.16; (CD₃)₂SO, δ 39.52; CD₂OD, δ 49.00), dissolved or external neat PhCF₃ (¹⁹F, δ – 63.3 relative to CFCl₃). Signals are listed in ppm, and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. High-resolution mass spectra were performed at Mass Spectrometry Services at the Univ. of Illinois at Urbana-Champaign and were obtained using Waters Q-TOF Ultima ESI mass spectrometer. Concentration under reduced pressure was performed by rotary evaporation at 25–30 °C at appropriate pressure. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds.

Experimental Data

Standard procedure for the synthesis of $N$-aryl-$N$-hydroxylamines

Under N$_2$ atmosphere, a suspension of aryl nitro compound (1.00 equiv) and Rh/C (5 mol%) in THF (0.20 M) was cooled to 0 °C. Hydrazine monohydrate (1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C until the TLC analysis indicated a complete consumption of the starting material. The reaction mixture was filtered through a short pad of celite and concentrated in vacuo. The residue was used directly for the next step without further purification unless otherwise stated.

Standard procedure for the synthesis of protected $N$-aryl-$N$-hydroxylamines

To a stirred suspension of $N$-aryl-$N$-hydroxylamine (1.00 equiv) and NaHCO$_3$ (1.20 equiv) in Et$_2$O (0.20 M) at 0 °C under N$_2$ was slowly added a solution of protecting group precursor (1.20 equiv) in Et$_2$O (0.24 M) via a syringe pump (at a rate of 10 mL/h). The reaction was stirred at 0 °C until the TLC analysis indicated a complete consumption of the starting material. The reaction mixture was filtered through a short pad of celite and concentrated in vacuo. The residue was purified by chromatography on silica gel.

Standard procedure for $O$-trifluoromethylation of protected $N$-aryl-$N$-hydroxylamines

Under N$_2$ atmosphere, to a mixture of protected $N$-aryl-$N$-hydroxylamine (1.00 equiv) and Cs$_2$CO$_3$ (10 mol%) in CHCl$_3$ (0.100 M) was added Togni reagent II (1.20 equiv) and the reaction mixture was stirred at rt for 14–23h. The reaction mixture was then washed with sat. aq. NaHCO$_3* \text{ and the organic layer was collected, dried (MgSO}_3\text{), filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel.}$

*The wash with sat. aq. NaHCO$_3$ was not necessary in case of compounds of low polarity, which could be easily separated from 2-iodobenzoic acid by means column chromatography.

Standard procedure for the synthesis of ortho-OCF$_3$ aniline derivatives via OCF$_3$-migration

A solution of protected $N$-aryl-$N$-(trifluoromethoxy)amine (0.400 mmol) in MeNO$_2$ (0.400 mL, 1.00 M) was heated at an appropriate temperature (50 °C, 80 °C, 120 °C or 140 °C) under N$_2$ atmosphere for 11–48h. The reaction mixture was concentrated in vacuo. The residue was purified by chromatography on silica gel.
Reaction procedures

Methyl 4-(hydroxyamino)benzoate (S1)

\[ \text{MeO} \quad \text{H}_2\text{NNH}_2 \quad \text{H}_2\text{O} \quad \text{RH/C} \quad \text{THF, 0 °C} \quad \text{quant.} \]

Under N₂ atmosphere, a suspension of methyl 4-nitrobenzoate (5.00 g, 27.6 mmol, 1.00 equiv) and Rh/C (159 mg, 1.38 mmol, 5 mol%) in THF (300 mL, 0.0920 M) was cooled to 0 °C. Hydrazine monohydrate (1.52 g, 30.4 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 5 h. The reaction mixture was filtered through a short pad of celite, the celite was washed with EtOAc and the combined organic layers were concentrated in vacuo to afford 4.62 g of the title compound as a yellow solid (quant yield).

R_f = 0.23 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (500 MHz, (CD₃)₂SO, δ): 8.95 (s, 1H), 8.64 (d, J = 1.5 Hz, 1H), 7.76 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 3.77 (s, 3H). \(^{13}\)C NMR (125 MHz, (CD₃)₂SO, δ): 166.2, 156.0, 130.4, 119.1, 111.2, 51.4. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₈H₁₀NO₃ ([M + H]⁺), 168.0661, found, 168.0667.

Methyl 4-(N-hydroxyacetamido)benzoate (S2)

To a stirred suspension of methyl 4-(hydroxyamino)benzoate (S1) (0.900 g, 5.38 mmol, 1.00 equiv) and NaHCO₃ (0.540 g, 6.46 mmol, 1.20 equiv) in Et₂O (30.0 mL, 0.179 M) at 0 °C under N₂ was slowly added a solution of acetyl chloride (0.510 g, 6.46 mmol, 1.20 equiv) in Et₂O (30.0 mL, 0.215 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 1:1 (v/v)), to afford 0.910 g of the title compound as a light yellow solid (81% yield).

R_f = 0.13 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (400 MHz, (CD₃)₂SO, δ): 10.83 (s, 1H), 7.96 (d, J = 9.0 Hz, 2H), 7.83 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H), 2.26 (s, 3H). \(^{13}\)C NMR (100 MHz, (CD₃)₂SO, δ): 170.8, 165.7, 145.4, 129.8, 124.6, 118.4, 52.0, 22.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₁₀H₁₂NO₄ ([M + H]⁺), 210.0766, found, 210.0766.
Methyl 4-(N-(trifluoromethoxy)acetamido)benzoate (2a)

Under N\textsubscript{2} atmosphere, to a mixture of methyl 4-(N-hydroxyacetamido)benzoate (S2) (335 mg, 1.60 mmol, 1.00 equiv) and Cs\textsubscript{2}CO\textsubscript{3} (52.1 mg, 0.160 mmol, 10 mol\%) in CHCl\textsubscript{3} (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 16 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:CH\textsubscript{2}Cl\textsubscript{2} (7:3 to 0:1 (v/v)), to afford 428 mg of the title compound a slightly yellow oil (97\% yield).

R\textsubscript{f} = 0.44 (CH\textsubscript{2}Cl\textsubscript{2}). NMR Spectroscopy: \textsuperscript{1}H NMR (700 MHz, CDCl\textsubscript{3}, 25 \degree C, \delta): 8.13–8.09 (m, 2H), 7.49–7.45 (m, 2H), 3.93 (s, 3H), 2.33 (s, 3H). \textsuperscript{13}C NMR (175 MHz, CDCl\textsubscript{3}, 25 \degree C, \delta): 172.3, 166.2, 143.9, 130.6, 129.9, 124.0, 122.8 (q, J = 264.1 Hz), 52.5, 21.9. \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}, 25 \degree C, \delta): –65.00 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\textsubscript{11}H\textsubscript{11}NO\textsubscript{4}F\textsubscript{3} ([M + H]\textsuperscript{+}), 278.0640, found, 278.0637.

Methyl 4-acetamido-3-(trifluoromethoxy)benzoate (3a)

A solution of methyl 4-(N-(trifluoromethoxy)acetamido)benzoate (2a) (111 mg, 0.400 mmol) in MeNO\textsubscript{2} (0.400 mL, 1.00 M) was heated at 120 \degree C under N\textsubscript{2} atmosphere for 20 h. The reaction mixture was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 7:3 (v/v)), to afford 428 mg of the title compound as a white solid (87\% yield).

R\textsubscript{f} = 0.51 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: \textsuperscript{1}H NMR (700 MHz, CDCl\textsubscript{3}, 25 \degree C, \delta): 8.56 (d, J = 8.6 Hz, 1H), 7.97 (d, J = 8.6 Hz, 1H), 7.93 (s, 1H), 7.56 (br. s, 1H), 3.92 (s, 3H), 2.27 (s, 3H). \textsuperscript{13}C NMR (175 MHz, CDCl\textsubscript{3}, 25 \degree C, \delta): 168.5, 165.6, 137.2, 134.7, 129.3, 125.8, 121.5, 120.8, 120.6 (q, J = 258.9 Hz), 52.5, 25.2. \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}, 25 \degree C, \delta): –58.1 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\textsubscript{11}H\textsubscript{11}NO\textsubscript{4}F\textsubscript{3} ([M + H]\textsuperscript{+}), 278.0640, found, 278.0643.
**N-Phenyl-N-hydroxylamine (S3)**

![Chemical structure of N-phenyl-N-hydroxylamine (S3)]

Under N₂ atmosphere, a suspension of nitrobenzene (1.00 g, 8.10 mmol, 1.00 equiv) and Rh/C (40.5 mg, 0.352 mmol, 5 mol%) in THF (25.0 mL, 0.324 M) was cooled to 0 °C. Hydrazine monohydrate (0.487 g, 9.72 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 1 h and then slowly warmed up to rt and stirred at rt for 4 h. The reaction mixture was filtered through a short pad of celite and concentrated in vacuo. Recrystallization from CH₂Cl₂/hexanes at −20 °C afforded 0.740 g of the title compound as a white solid (84% yield).

R <sub>f</sub> = 0.25 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, (CD₃)₂SO, δ): 8.25 (s, 1H), 8.21 (s, 1H), 7.14 (t, J = 7.9 Hz, 2H), 6.81 (d, J = 7.9 Hz, 2H), 6.72 (t, J = 7.9 Hz, 1H). ¹³C NMR (125 MHz, (CD₃)₂SO, δ): 152.1, 128.4, 119.2, 112.9.

**N-Hydroxy-N-phenylacetamide (S4)**

![Chemical structure of N-hydroxy-N-phenylacetamide (S4)]

To a stirred suspension of N-phenylhydroxylamine (S3) (0.500 g, 4.58 mmol, 1.00 equiv) and NaHCO₃ (0.462 g, 5.50 mmol, 1.20 equiv) in Et₂O (15.0 mL, 0.305 M) at 0 °C under N₂ was slowly added a solution of acetyl chloride (0.432 g, 5.50 mmol, 1.20 equiv) in Et₂O (15.0 mL, 0.367 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The combined organic layers were washed with water, dried with MgSO₄, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 3:2 (v/v)), to afford 0.59 g of the title compound as a white solid (86% yield).

R <sub>f</sub> = 0.27 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, (CD₃)₂SO, δ): 10.61 (s, 1H), 7.59 (d, J = 6.0 Hz, 2H), 7.35 (t, J = 6.0 Hz, 2H), 7.13 (t, J = 6.0 Hz, 1H), 2.18 (s, 3H). ¹³C NMR (125 MHz, (CD₃)₂SO, δ): 169.9, 141.7, 128.4, 124.7, 120.3, 22.5.
Under N\textsubscript{2} atmosphere, to a mixture of N-hydroxy-N-phenylacetamide (S4) (400 mg, 2.65 mmol, 1.00 equiv) and Cs\textsubscript{2}CO\textsubscript{3} (86.2 mg, 0.265 mmol, 10 mol\%) in CHCl\textsubscript{3} (26.5 mL, 0.100 M) was added Togni reagent II (1.00 g, 3.18 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 21 h. The reaction mixture concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (19:1 to 9:1 (v/v)), to afford 420 mg of the title compound a slightly yellow oil (72% yield).

R\textsubscript{f} = 0.63 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 25 °C, \(\delta\)): 7.49–7.41 (m, 2H), 7.41–7.31 (m, 3H), 2.22 (s, 3H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}, 25 °C, \(\delta\)): 172.4, 140.4, 129.5, 129.4, 126.3, 122.9 (q, \(J = 263.0\) Hz), 22.0. \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}, 25 °C, \(\delta\)): −64.8 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\textsubscript{9}H\textsubscript{9}NO\textsubscript{2}F\textsubscript{3} ([M + H]\textsuperscript{+}), 220.0585, found, 220.0580.

N-(2-(Trifluoromethoxy)phenyl)acetamide (3b) and N-(4-(trifluoromethoxy)phenyl)acetamide (3b-II)

A solution of N-phenyl-N-(trifluoromethoxy)acetamide (2b) (128 mg, 100 μL, 0.584 mmol) in MeNO\textsubscript{2} (0.584 mL, 1.00 M) was heated at 80 °C under N\textsubscript{2} atmosphere for 19 h. The reaction mixture was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 1:1 (v/v)), to afford 105 mg of 3b (82% yield) and 11.2 mg of 3b-II (9% yield).

Data for 3b: white solid; R\textsubscript{f} = 0.36 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: \textsuperscript{1}H NMR (700 MHz, CDCl\textsubscript{3}, 25 °C, \(\delta\)): 8.39 (d, \(J = 8.2\) Hz, 1H), 7.39 (br. s, 1H), 7.28 (t, \(J = 7.7\) Hz, 1H), 7.25–7.24 (m, 1H), 7.12–7.08 (m, 1 H), 2.23 (s, 3H). \textsuperscript{13}C NMR (175 MHz, CDCl\textsubscript{3}, 25 °C, \(\delta\)): 168.4, 138.1, 130.7, 127.7, 124.3, 122.1, 120.7 (q, \(J = 257.7\) Hz), 120.4, 25.0. \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}, 25 °C, \(\delta\)): −58.4 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\textsubscript{9}H\textsubscript{9}NO\textsubscript{2}F\textsubscript{3} ([M + H]\textsuperscript{+}), 220.0585, found, 220.0583.

Data for 3b-II: white solid; R\textsubscript{f} = 0.33 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 25 °C, \(\delta\)): 7.53 (d, \(J = 8.9\) Hz, 2H), 7.18 (app d, \(J = 8.9\) Hz, 3H), 2.19 (s, 3H). \textsuperscript{13}C NMR (175 MHz, CDCl\textsubscript{3}, 25 °C, \(\delta\)): 168.4, 145.4, 136.6, 121.9, 121.1, 120.6 (q, \(J = 255.5\) Hz), 24.7. \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}, 25 °C, \(\delta\)): −58.8 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for
C₉H₈NO₂F₁ ([M + H]⁺), 220.0585, found, 220.0583.

**N-(3-Methoxyphenyl)hydroxylamine (S5)**

\[
\text{OMe} \quad \xrightarrow{\text{H₂NNH₂ H₂O (1.20 equiv)}} \quad \text{OMe} \quad \text{NHOH}
\]

Under N₂ atmosphere, a suspension of 1-methoxy-3-nitrobenzene (1.00 g, 6.53 mmol, 1.00 equiv) and Rh/C (50 mg, mmol, 5 mmol%) in THF (25.0 mL, 0.261 M) was cooled to 0 °C. Hydrazine monohydrate (0.360 g, 7.19 mmol, 1.10 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 2 h. The reaction mixture was filtered through a short pad of celite, the celite was washed with EtOAc and the combined organic layers were concentrated in vacuo to afford 0.89 g of the title compound as a white solid (98% yield).

R_f = 0.47 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, (CD₃)₂SO, 25 °C, δ): 8.26 (d, J = 2.2 Hz, 1H), 8.23 (s, 1H), 7.04 (t, J = 8.0 Hz, 1H), 6.38–6.41 (m, 2H), 6.30 (dd, J = 8.0, 2.3 Hz, 1H), 3.68 (s, 3H). ¹³C NMR (125 MHz, (CD₃)₂SO, 25 °C, δ): 159.8, 153.5, 129.1, 105.5, 104.6, 98.5, 54.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₇H₁₀NO₂ ([M + H]⁺), 140.0712, found, 140.0714.

**N-Hydroxy-N-(3-methoxyphenyl)acetamide (S6)**

\[
\text{OMe} \quad \xrightarrow{\text{AcCl (1.20 equiv)}} \quad \text{OMe} \quad \text{N OH}
\]

To a stirred suspension of N-(3-methoxyphenyl)hydroxylamine (S5) (0.900 g, 6.47 mmol, 1.00 equiv) and NaHCO₃ (0.650 g, 7.76 mmol, 1.20 equiv) in Et₂O (30.0 mL, 0.216 M) at 0 °C under N₂ was slowly added a solution of acetyl chloride (0.610 g, 7.76 mmol, 1.20 equiv) in Et₂O (30.0 mL, 0.259 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (5:1 to 4:1 (v/v)), to afford 0.810 g of the title compound as a brown liquid (69% yield).

R_f = 0.26 (hexanes/EtOAc 5:1 (v/v)). ¹H NMR (500 MHz, (CD₃)₂SO, δ): 10.61 (s, 1H), 7.30–7.20 (m, 3H), 6.74–6.71 (m, 1H), 3.74 (s, 3H), 2.19 (s, 3H). ¹³C NMR (125 MHz, (CD₃)₂SO, δ): 169.9, 159.2, 142.8, 129.2, 112.3, 109.8, 106.0, 55.1, 22.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₉H₁₂NO₃ ([M + H]⁺), 182.0817, found, 182.0816.
N-(3-Methoxyphenyl)-N-(trifluoromethoxy)acetamide (2c)

Under N\textsubscript{2} atmosphere, to a mixture of N-hydroxy-N-(3-methoxyphenyl)acetamide (S6) (290 mg, 1.60 mmol, 1.00 equiv) and Cs\textsubscript{2}CO\textsubscript{3} (52.1 mg, 0.160 mmol, 10 mol\%) in CHCl\textsubscript{3} (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 19 h. The reaction mixture was concentrated \textit{in vacuo}. The residue was purified by chromatography on silica gel, eluting with hexanes:CH\textsubscript{2}Cl\textsubscript{2} (1:1 to 3:7 (v/v)), to afford 290 mg of the title compound as a yellow oil (76\% yield).

R\textsubscript{f} = 0.34 (hexanes/CH\textsubscript{2}Cl\textsubscript{2} 1:1 (v/v)). NMR Spectroscopy: \textsuperscript{1}H NMR (700 MHz, CDCl\textsubscript{3}, 25 °C, \textit{\delta}): 7.35 (t, J = 8.2 Hz, 1H), 6.99–6.96 (m, 1H), 6.94 (dd, J = 8.4, 1.9 Hz, 1H), 6.93–6.90 (m, 1H), 3.83 (s, 3H), 2.21 (s, 3H).

\textsuperscript{13}C NMR (175 MHz, CDCl\textsubscript{3}, 25 °C, \textit{\delta}): 172.4, 160.4, 141.4, 130.2, 122.9 (q, J = 262.7 Hz), 118.5, 115.2, 112.0, 55.6, 22.0.

\textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}, 25 °C, \textit{\delta}): –64.8 (s).

Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\textsubscript{10}H\textsubscript{11}NO\textsubscript{3}F\textsubscript{3} ([M + H]\textsuperscript{+}), 250.0691, found, 250.0687.

N-(5-Methoxy-2-(trifluoromethoxy)phenyl)acetamide (3c) and N-(3-methoxy-2-(trifluoromethoxy)phenyl)acetamide (3c-II)

A solution of N-(3-methoxyphenyl)-N-(trifluoromethoxy)acetamide (2c) (99.7 mg, 0.400 mmol) in MeNO\textsubscript{2} (0.400 mL, 1.00 M) was heated at 80 °C under N\textsubscript{2} atmosphere for 15 h. The reaction mixture was purified by preparative TLC using hexanes:EtOAc (4:1 (v/v)) for development (prep TLC was developed four times). The purification afforded 55.3 mg of 3c and 14.9 mg of 3c-II (70\% overall yield).

Data for 3c: white solid; R\textsubscript{f} = 0.77 (hexanes/ETOAc 3:2 (v/v)). NMR Spectroscopy: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 25 °C, \textit{\delta}): 8.02 (d, J = 2.0 Hz, 1H), 7.48 (br. s, 1H), 7.12 (dd, J = 9.2, 1.1 Hz, 1H), 6.59 (dd, J = 9.0, 3.0 Hz, 1H), 3.79 (s, 3H), 2.21 (s, 3H). \textsuperscript{13}C NMR (175 MHz, CDCl\textsubscript{3}, 25 °C, \textit{\delta}): 168.5, 158.5, 131.8, 131.6, 121.7, 120.8 (q, J = 256.8 Hz), 109.9, 106.8, 55.8, 24.9. \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}, 25 °C, \textit{\delta}): –58.7 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\textsubscript{10}H\textsubscript{11}NO\textsubscript{3}F\textsubscript{3} ([M + H]\textsuperscript{+}), 250.0691, found, 250.0690.

Data for 3c-II: white solid; R\textsubscript{f} = 0.70 (hexanes/ETOAc 3:2 (v/v)). NMR Spectroscopy: \textsuperscript{1}H NMR (700 MHz, CDCl\textsubscript{3}, 25 °C, \textit{\delta}): 7.93 (d, J = 8.2 Hz, 1H), 7.40 (br. s, 1H), 7.23 (t, J = 8.4 Hz, 1H), 6.73 (d, J = 8.2
12 Hz, 1H), 3.87 (s, 3H), 2.21 (s, 3H). $^{13}$C NMR (175 MHz, CDCl$_3$, 25 ºC, $\delta$): 168.4, 152.7, 132.9, 128.2, 127.6, 121.1 (q, $J = 258.7$ Hz), 113.8, 108.0, 56.3, 24.9. $^{19}$F NMR (376 MHz, CDCl$_3$, 25 ºC, $\delta$): −57.9 (s).

Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C$_{10}$H$_{11}$NO$_3$F$_3$ ([M + H]+), 250.0691, found, 250.0692.

$N$-(4-Iodophenyl)hydroxylamine (S7)

![Diagram of $N$-(4-Iodophenyl)hydroxylamine (S7)]

Under N$_2$ atmosphere, a suspension of 1-iodo-4-nitrobenzene (2.00 g, 8.03 mmol, 1.00 equiv) and Rh/C (46.1 mg, 0.400 mmol, 5 mol%) in THF (30.0 mL, 0.268 M) was cooled to 0 ºC. Hydrazine monohydrate (0.482 g, 9.64 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 ºC for 2 h. The reaction mixture was filtered through a short pad of celite and concentrated in vacuo. Recrystallization from CH$_2$Cl$_2$/hexanes at −20 ºC afforded 1.20 g of the title compound as a yellow solid (64% yield). $R_f = 0.26$ (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: $^1$H NMR (500 MHz, (CD$_3$)$_2$SO, $\delta$): 8.41 (s, 2H), 7.46 (d, $J = 2.7$ Hz, 1H), 7.44 (d, $J = 2.7$ Hz, 1H), 6.67 (d, $J = 2.6$ Hz, 1H), 6.65 (d, $J = 2.6$ Hz, 1H). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO, $\delta$): 152.4, 137.3, 115.8, 88.4, 81.1.

$N$-Hydroxy-$N$-(4-iodophenyl)acetamide (S8)

![Diagram of $N$-Hydroxy-$N$-(4-iodophenyl)acetamide (S8)]

To a stirred suspension of $N$-(4-iodophenyl)hydroxylamine (S7) (1.00 g, 4.25 mmol, 1.00 equiv) and NaHCO$_3$ (0.430 g, 5.11 mmol, 1.20 equiv) in Et$_2$O (30.0 mL, 0.412 M) at 0 ºC under N$_2$ was slowly added a solution of acetyl chloride (0.400 g, 5.11 mmol, 1.20 equiv) in Et$_2$O (20.0 mL, 0.256 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, water was added and the aqueous layer was extracted with EtOAc (4 $\times$ 15 mL). The combined organic layers were dried (MgSO$_4$), filtered, and concentrated in vacuo. Recrystallization from Et$_2$O/hexanes afforded 0.980 g of the title compound as light brown solid (83% yield). $R_f = 0.18$ (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: $^1$H NMR (400 MHz, (CD$_3$)$_2$SO, $\delta$): 10.69 (s, 1H), 7.72–7.67 (m, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 2.21 (s, 3H). $^{13}$C NMR (100 MHz, (CD$_3$)$_2$SO, $\delta$): 170.1, 141.4, 137.0, 121.8, 88.4, 22.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C$_8$H$_9$NO$_2$I ([M + H]+), 277.9678, found, 277.9684.
**N-(4-Iodophenyl)-N-(trifluoromethoxy)acetamide (2d)**

![Structural formula of 2d](image)

Under N\(_2\) atmosphere, to a mixture of N-hydroxy-N-(4-iodophenyl)acetamide (S8) (200 mg, 0.722 mmol, 1.00 equiv) and Cs\(_2\)CO\(_3\) (23.5 mg, 0.0720 mmol, 10 mol\%) in CHCl\(_3\) (7.20 mL, 0.100 M) was added Togni reagent II (274 mg, 0.867 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 18 h. The reaction mixture was filtered and the filtrate was concentrated \textit{in vacuo}. The residue was purified by chromatography on silica gel, eluting with hexanes:CH\(_2\)Cl\(_2\) (1:1 (v/v)), to afford 205 mg of the title compound a slightly yellow oil (82% yield).

R\(_f\) = 0.48 (hexanes/CH\(_2\)Cl\(_2\) 1:1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (700 MHz, CDCl\(_3\), 25 °C, \(\delta\)): 7.79–7.76 (m, 2H), 7.14–7.11 (m, 2H), 2.27 (s, 3H). \(^{13}\)C NMR (175 MHz, CDCl\(_3\), 25 °C, \(\delta\)): 172.5, 140.1, 138.6, 127.2, 122.8 (q, \(J = 263.5\) Hz), 94.4, 21.9. \(^{19}\)F NMR (376 MHz, CDCl\(_3\), 25 °C, \(\delta\)): –64.9 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\(_9\)H\(_8\)NO\(_2\)F\(_3\)I ([M + H]\(^+\)), 345.9552, found, 345.9549.

**N-(4-Iodo-2-(trifluoromethoxy)phenyl)acetamide (3d)**

A solution of N-(4-iodophenyl)-N-(trifluoromethoxy)acetamide (2d) (138 mg, 0.400 mmol) in MeNO\(_2\) (0.400 mL, 1.00 M) was heated at 80 °C under N\(_2\) atmosphere for 13 h. The reaction mixture was concentrated \textit{in vacuo}. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 2:3 (v/v)), to afford 108 mg of the title compound as a beige solid (78% yield).

R\(_f\) = 0.46 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (700 MHz, CDCl\(_3\), 25 °C, \(\delta\)): 8.19 (d, \(J = 8.6\) Hz, 1H), 7.59 (dd, \(J = 8.8, 1.5\) Hz, 1H), 7.56 (s, 1H), 7.36 (br. s, 1H), 2.22 (s, 3H). \(^{13}\)C NMR (175 MHz, CDCl\(_3\), 25 °C, \(\delta\)): 168.3, 138.0, 136.8, 130.7, 129.2, 123.4, 120.6 (q, \(J = 259.1\) Hz), 85.6, 25.0. \(^{19}\)F NMR (376 MHz, CDCl\(_3\), 25 °C, \(\delta\)): –58.3 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\(_9\)H\(_8\)NO\(_2\)F\(_3\)I ([M + H]\(^+\)), 345.9552, found, 345.9548.

**N-(4-Bromophenyl)hydroxylamine (S9)**

![Structural formula of S9](image)

A solution of N-(4-bromophenyl)-N-hydroxyacetamide (S9) (138 mg, 0.400 mmol) in THF/H\(_2\)O (9:1, 4.00 mL) was stirred under N\(_2\) atmosphere at rt for 24 h. The reaction mixture was filtered and the filtrate was concentrated \textit{in vacuo}. The residue was purified by chromatography on silica gel, eluting with hexanes:CH\(_2\)Cl\(_2\) (1:1 (v/v)), to afford 108 mg of the title compound as a white solid (78% yield).

R\(_f\) = 0.46 (hexanes/CH\(_2\)Cl\(_2\) 1:1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (700 MHz, CDCl\(_3\), 25 °C, \(\delta\)): 7.93 (d, \(J = 8.6\) Hz, 1H), 7.51 (dd, \(J = 8.8, 1.5\) Hz, 1H), 7.43 (t, \(J = 7.2\) Hz, 1H), 7.27 (br. s, 1H), 2.22 (s, 3H). \(^{13}\)C NMR (175 MHz, CDCl\(_3\), 25 °C, \(\delta\)): 168.3, 138.0, 136.8, 130.7, 129.2, 123.4, 120.6 (q, \(J = 259.1\) Hz), 85.6, 25.0. \(^{19}\)F NMR (376 MHz, CDCl\(_3\), 25 °C, \(\delta\)): –58.3 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\(_9\)H\(_8\)NO\(_2\)F\(_3\)I ([M + H]\(^+\)), 345.9552, found, 345.9548.
Under N₂ atmosphere, a suspension of 1-bromo-4-nitrobenzene (3.00 g, 14.9 mmol, 1.00 equiv) and Rh/C (85.3 mg, 0.740 mmol, 5 mol%) in THF (100 mL, 0.149 M) was cooled to 0 °C. Hydrazine monohydrate (0.892 g, 16.2 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 2.5 h. The reaction mixture was filtered through a short pad of celite and concentrated in vacuo to afford 2.78 g of the title compound as a brown solid (99% yield).

\[ R_f = 0.30 \text{ (hexanes/EtOAc 5:1 (v/v))} \]

NMR Spectroscopy: \(^{1}H\text{ NMR (500 MHz, (CD}_3\text{)SO, } \delta): 8.42 \text{ (s, 1H), 8.40 \text{ (s, 1H), 7.30 \text{ (d, } J = 8.8 \text{ Hz, 2H), 6.78 \text{ (d, } J = 8.8 \text{ Hz, 2H).} } ^{13}C\text{ NMR (125 MHz, (CD}_3\text{)SO, } \delta): 151.4, 131.1, 114.8, 110.1. \]


\( N-(4-\text{Bromophenyl})-\text{N-hydroxyacetamide (S10)} \)

To a stirred suspension of \( N-(4-\text{bromophenyl})-\text{N-hydroxyacetamide (S9)} \) (1.00 g, 5.32 mmol, 1.00 equiv) and NaHCO₃ (0.540 g, 6.38 mmol, 1.20 equiv) in Et₂O (25.0 mL, 0.213 M) at 0 °C under N₂ was slowly added a solution of acetyl chloride (0.500 g, 6.38 mmol, 1.20 equiv) in Et₂O (30.0 mL, 0.213 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated in vacuo to afford 1.23 g of the title compound as a brown solid (quant yield).

\[ R_f = 0.14 \text{ (hexanes/EtOAc 4:1 (v/v))} \]

NMR Spectroscopy: \(^{1}H\text{ NMR (400 MHz, (CD}_3\text{)SO, } \delta): 10.72 \text{ (s, 1H), 7.61 \text{ (d, } J = 9.0 \text{ Hz, 2H), 7.54 \text{ (d, } J = 9.0 \text{ Hz, 2H), 2.21 \text{ (s, 3H).} } ^{13}C\text{ NMR (100 MHz, (CD}_3\text{)SO, } \delta): 170.2, 140.9, 131.2, 121.6, 116.2, 22.5. \]


\( N-(4-\text{Bromophenyl})-\text{N-(trifluoromethoxy)acetamide (2e)} \)

Under N₂ atmosphere, to a mixture of \( N-(4-\text{bromophenyl})-\text{N-hydroxyacetamide (S10)} \) (368 mg, 1.60 mmol, 1.00 equiv) and Cs₂CO₃ (52.1 mg, 0.160 mmol, 10 mol%) in CHCl₃ (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 18 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:CH₂Cl₂ (1:1 to 1:3 (v/v)), to afford 384 mg of the title compound as a brown solid (99% yield).
compound a slightly yellow oil (81% yield).

\[ R_f = 0.47 \] (hexanes/CH\(_2\)Cl\(_2\) 1:1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (700 MHz, CDCl\(_3\), 25 °C, \(\delta\)): 7.59–7.55 (m, 2H), 7.23–7.28 (m, 2H), 2.26 (s, 3H). \(^13\)C NMR (175 MHz, CDCl\(_3\), 25 °C, \(\delta\)): 172.5, 139.3, 132.6, 127.2, 122.9, 122.8 (q, \(J = 263.3\) Hz), 21.8. \(^19\)F NMR (376 MHz, CDCl\(_3\), 25 °C, \(\delta\)): –64.9 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\(_9\)H\(_8\)NO\(_2\)F\(_3\)Br ([M + H]+), 297.9690, found, 297.9694.

**N-(4-Bromo-2-(trifluoromethoxy)phenyl)acetamide (3e)**

A solution of N-(4-bromophenyl)-N-(trifluoromethoxy)acetamide (2e) (119 mg, 0.400 mmol) in MeNO\(_2\) (0.400 mL, 1.00 M) was heated at 80 °C under N\(_2\) atmosphere for 14 h. The reaction mixture was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (17:1 to 7:3 (v/v)), to afford 107 mg of the title compound as a beige solid (90% yield).

\[ R_f = 0.42 \] (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C, \(\delta\)): 8.32 (d, \(J = 9.2\) Hz, 1H), 7.42–7.41 (m, 1H), 7.40 (s, 1H), 7.37 (br. s, 1H), 2.22 (s, 3H). \(^13\)C NMR (125 MHz, CDCl\(_3\), 25 °C, \(\delta\)): 168.3, 138.2, 130.8, 129.9, 123.6, 123.1, 120.6 (q, \(J = 259.2\) Hz), 115.9, 25.0. \(^19\)F NMR (376 MHz, CDCl\(_3\), 25 °C, \(\delta\)): –58.2 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\(_9\)H\(_8\)NO\(_2\)F\(_3\)Br ([M + H]+), 297.9690, found, 297.9692.

**N-(3-Fluorophenyl)hydroxylamine (S11)**

Under N\(_2\) atmosphere, a suspension of 1-fluoro-3-nitrobenzene (1.00 g, 7.09 mmol, 1.00 equiv) and Rh/C (50.0 mg, 0.435 mmol, 6 mol%) in THF (25.0 mL, 0.284 M) was cooled to 0 °C. Hydrazine monohydrate (0.390 g, 7.80 mmol, 1.10 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 1 h. The reaction mixture was filtered through a short pad of celite. The celite was washed with EtOAc and the combined organic layers were concentrated in vacuo to afford 0.87 g of the title compound as a white solid (97% yield).

\[ R_f = 0.28 \] (hexanes/EtOAc 4:1 (v/v)). \(^1\)H NMR (400 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)): 8.50 (s, 1H), 8.45 (d, \(J = 2.1\) Hz, 1H), 7.17–7.14 (m, 1H), 6.61–6.58 (m, 2H), 6.50–6.48 (m, 1H). \(^13\)C NMR (100 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)): 163.0 (d, \(J = 238.8\) Hz), 154.4 (d, \(J = 10.2\) Hz), 130.0 (d, \(J = 9.6\) Hz), 108.7 (d, \(J = 2.3\) Hz), 105.1 (d, \(J = 21.4\) Hz), 99.3 (d, \(J = 25.5\) Hz). \(^19\)F NMR (376 MHz, (CD\(_3\))\(_2\)SO, 25 °C, \(\delta\)): –117.3 (s). Mass Spectrometry:
HRMS (ESI-TOF) (m/z): calcd for C₇H₈NOF ([M + H]⁺), 128.0512, found, 128.0513.

N-(3-Fluorophenyl)-N-hydroxyacetamide (S12)

![Chemical structure of S11 and S12]

To a stirred suspension of N-(3-fluorophenyl)hydroxylamine (S11) (0.800 g, 6.29 mmol, 1.00 equiv) and NaHCO₃ (0.634 g, 7.55 mmol, 1.20 equiv) in Et₂O (35.0 mL, 0.180 M) at 0 °C under N₂ was slowly added a solution of acetyl chloride (0.593 g, 7.55 mmol, 1.20 equiv) in Et₂O (30.0 mL, 0.252 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 1:1 (v/v)), to afford 0.830 g of the title compound as a yellow liquid (78% yield).

Rₜ = 0.52 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, (CD₃)₂SO, δ): 10.77 (s, 1H), 7.54–7.50 (m, 2H), 7.50–7.37 (m, 1H), 7.00–7.6.94 (m, 1H), 2.23 (s, 3H).

¹³C NMR (125 MHz, (CD₃)₂SO, δ): 170.4, 161.80 (d, J = 240.2 Hz), 143.1 (d, J = 10.7 Hz), 130.1 (d, J = 9.2 Hz), 115.0, 110.7 (d, J = 20.9 Hz), 106.3 (d, J = 27.7 Hz), 22.7. ¹⁹F NMR (376 MHz, (CD₃)₂SO, 25 °C, δ): –114.5 (s).


N-(3-Fluorophenyl)-N-(trifluoromethoxy)acetamide (2f)

![Chemical structure of S12, 1.2 equiv, and 2f]

Under N₂ atmosphere, to a mixture of N-(3-fluorophenyl)-N-hydroxyacetamide (S12) (243 mg, 1.44 mmol, 1.00 equiv) and Cs₂CO₃ (46.9 mg, 0.144 mmol, 10 mol%) in CHCl₃ (14.4 mL, 0.100 M) was added Togni reagent II (546 mg, 1.73 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 22 h. The reaction mixture was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:CH₂Cl₂ (1:1 to 1:3 (v/v)), to afford 287 mg of the title compound as a slightly yellow oil (76% yield).

Rₜ = 0.55 (hexanes/CH₂Cl₂ 1:1 (v/v)). NMR Spectroscopy: ¹H NMR (700 MHz, CDCl₃, 25 °C, δ): 7.41 (td, J = 8.2, 6.0 Hz, 1H), 7.19 (d, J = 8.2 Hz, 1H), 7.13 (dt, J = 9.4, 2.2 Hz, 1H), 7.08 (td, J = 8.2, 1.7 Hz, 1H), 2.28 (s, 3H). ¹³C NMR (175 MHz, CDCl₃, 25 °C, δ): 172.5, 162.7 (d, J = 246.8 Hz), 141.6 (d, J = 9.8 Hz), 130.5 (d, J = 8.8 Hz), 122.8 (q, J = 263.4 Hz), 121.0, 115.9 (d, J = 20.9 Hz), 112.9 (d, J = 24.0 Hz),
19F NMR (376 MHz, CDCl3, 25 °C, δ): –65.0 (s), –111.2 (s). Mass Spectrometry: HRMS (EI-TOF) (m/z): calcd for C9H7NO2F4 ([M+]†), 237.0413, found, 237.0417.

N-(5-Fluoro-2-(trifluoromethoxy)phenyl)acetamide (3f) and N-(3-fluoro-2-(trifluoromethoxy)phenyl)acetamide (3f-II)

A solution of 2f (95.9 mg, 0.400 mmol) in MeNO2 (0.400 mL, 1.00 M) was heated at 120 °C under N2 atmosphere for 20 h. The reaction mixture was purified by preparative TLC using hexanes:EtOAc (7:3 (v/v)) for development. The purification afforded 51.2 mg of 3f and 31.5 mg of 3f-II (87% overall yield).

Data for 3f: white solid; Rf = 0.67 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: 1H NMR (700 MHz, CDCl3, 25 °C, δ): 8.25 (d, J = 9.0 Hz, 1H), 7.47 (br. s, 1H), 7.23–7.18 (m, 1H), 6.83–6.73 (m, 1H), 2.23 (s, 3H). 13C NMR (175 MHz, CDCl3, 25 °C, δ): 168.4, 161.0 (d, J = 243.9 Hz), 133.7, 132.2 (d, J = 12.1 Hz), 121.8 (d, J = 9.7 Hz), 120.7 (q, J = 258.0 Hz), 110.6 (d, J = 24.1 Hz), 109.1 (d, J = 29.6 Hz), 25.0. 19F NMR (376 MHz, CDCl3, 25 °C, δ): –58.5 (s), –111.9 (q). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C9H8NO2F4 ([M + H]+), 238.0491, found, 238.0492.

Data for 3f-II: white solid; Rf = 0.56 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: 1H NMR (700 MHz, CDCl3, 25 °C, δ): 8.15 (d, J = 7.7 Hz, 1H), 7.41 (br. s, 1H), 7.29–7.23 (m, 1H), 6.93 (t, J = 9.0 Hz, 1H), 2.23 (s, 3H). 13C NMR (175 MHz, CDCl3, 25 °C, δ): 168.4, 155.2 (d, J = 250.3 Hz), 133.5, 128.6 (d, J = 8.5 Hz), 126.3 (d, J = 13.8 Hz), 121.0 (q, J = 259.9 Hz), 117.3, 111.9 (d, J = 18.3 Hz), 24.9. 19F NMR (376 MHz, CDCl3, 25 °C, δ): –58.9 (d), –127.3 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C9H8NO2F4 ([M + H]+), 238.0491, found, 238.0490.

Methyl 3-(hydroxyamino)benzoate (S13)

Under N2 atmosphere, a suspension of methyl 3-nitrobenzoate (2.00 g, 11.0 mmol, 1.00 equiv) and Rh/C (63.0 mg, 0.550 mmol, 5 mol%) in THF (40.0 mL, 0.275 M) was cooled to 0 °C. Hydrazine monohydrate (0.663 g, 13.3 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 2.5 h. The reaction mixture was filtered through a short pad of celite, the celite was washed with EtOAc and the
combined organic layers were concentrated *in vacuo* to afford 1.82 g of the title compound as a light yellow solid (99% yield).

\[ R_f = 0.19 \text{ (hexanes/EtOAc 4:1 (v/v))}. \]

NMR Spectroscopy: \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)) 8.51 (s, 1H), 8.49 (d, \(J = 2.1\) Hz, 1H), 7.45 (s, 1H), 7.35–7.28 (m, 2H), 7.07–7.04 (m, 1H), 3.82 (s, 3H). 13C NMR (125 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)) 166.6, 152.4, 130.0, 128.9, 119.9, 117.5, 113.2, 52.1.

Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\(_{10}\)H\(_8\)NO\(_3\) ([M + H]\(^+\)), 168.0661, found, 168.0666.

**Methyl 3-(N-hydroxyacetamido)benzoate (S14)**

![Reaction Scheme](image URL)

To a stirred suspension of methyl 3-(hydroxyamino)benzoate (S13) (1.00 g, 5.98 mmol, 1.00 equiv) and NaHCO\(_3\) (0.600 g, 7.18 mmol, 1.20 equiv) in Et\(_2\)O (30.0 mL, 0.199 M) at 0 °C under N\(_2\) was slowly added a solution of acetyl chloride (0.560 g, 7.18 mmol, 1.20 equiv) in Et\(_2\)O (30.0 mL, 0.239 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated *in vacuo* to afford 1.25 g of the title compound as a yellow solid (quant yield).

\[ R_f = 0.10 \text{ (hexanes/EtOAc 4:1 (v/v))}. \]

NMR Spectroscopy: \(^1\)H NMR (400 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)) 10.80 (s, 1H), 8.26 (s, 1H), 7.95–7.90 (m, 1H), 7.72 (d, \(J = 7.6\) Hz, 1H), 7.51 (t, \(J = 7.9\) Hz, 1H), 3.86 (s, 3H), 2.24 (s, 3H). 13C NMR (100 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)) 170.4, 166.0, 141.9, 129.8, 124.9, 124.2, 120.1, 52.3, 22.5.


**Methyl 3-(N-(trifluoromethoxy)acetamido)benzoate (2g)**

![Reaction Scheme](image URL)

Under N\(_2\) atmosphere, to a mixture of methyl 3-(N-hydroxyacetamido)benzoate (S14) (335 mg, 1.60 mmol, 1.00 equiv) and Cs\(_2\)CO\(_3\) (52.1 mg, 0.160 mmol, 10 mol%) in CHCl\(_3\) (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 15 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:CH\(_2\)Cl\(_2\) (1:3 to 0:1 (v/v)), to afford 298 mg of the title compound as a slightly yellow oil (67% yield).
\( R_f = 0.50 \) (CH₂Cl₂). NMR Spectroscopy: \(^1\)H NMR (500 MHz, CDCl₃, 25 °C, \( \delta \)): 8.07–8.04 (m, 2H), 7.59–7.56 (m, 1H), 7.55–7.50 (m, 1H), 3.94 (s, 3H), 2.29 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl₃, 25 °C, \( \delta \)): 172.7, 166.0, 140.6, 131.7, 130.0, 129.5, 126.5, 122.8 (q, \( J = 263.7 \) Hz), 52.6, 21.8. \(^{19}\)F NMR (376 MHz, CDCl₃, 25 °C, \( \delta \)): –64.9 (s).

Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₁₁H₁₁NO₄F₃ ([M + H]⁺), 278.0640, found, 278.0640.

**Methyl 3-acetamido-4-(trifluoromethoxy)benzoate (3g) and methyl 3-acetamido-2-(trifluoromethoxy)benzoate (3g-II)**

A solution of methyl 3-(N-(trifluoromethoxy)acetamido)benzoate (2g) (111 mg, 0.400 mmol) in MeNO₂ (0.400 mL, 1.00 M) was heated at 120 °C under N₂ atmosphere for 20 h. The reaction mixture was purified by preparative TLC using Et₂O for development. The purification afforded 90.4 mg of a 1.14:1 mixture of 3g and 3g-II (81% overall yield).

Compounds 3g and 3g-II were further separated for characterization by preparative TLC (eluting twenty times with hexanes:EtOAc 7:3 (v/v)).

Data for 3g: white solid; \( R_f = 0.59 \) (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: \(^1\)H NMR (400 MHz, CDCl₃, 25 °C, \( \delta \)): 9.02 (br. s, 1H), 7.82 (dd, \( J = 8.5, 2.0 \) Hz, 1H), 7.41 (br. s, 1H), 7.31 (dd, \( J = 8.7, 1.6 \) Hz, 1H), 3.92 (s, 3H), 2.25 (s, 3H). \(^{13}\)C NMR (175 MHz, CDCl₃, 25 °C, \( \delta \)): 168.4, 166.0, 141.2, 130.3, 129.4, 125.9, 123.4, 120.5 (q, \( J = 259.1 \) Hz), 119.5, 52.6, 24.9. \(^{19}\)F NMR (376 MHz, CDCl₃, 25 °C, \( \delta \)): –57.8 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₁₁H₁₁NO₄F₃ ([M + H]⁺), 278.0640, found, 278.0640.

Data for 3g-II: white solid; \( R_f = 0.56 \) (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: \(^1\)H NMR (700 MHz, CDCl₃, 25 °C, \( \delta \)): 8.56 (d, \( J = 8.2 \) Hz, 1H), 7.66 (d, \( J = 7.7 \) Hz, 1H), 7.51 (br. s, 1H), 7.39 (t, \( J = 8.0 \) Hz, 1H), 3.93 (s, 3H), 2.24 (s, 3H). \(^{13}\)C NMR (175 MHz, CDCl₃, 25 °C, \( \delta \)): 168.5, 165.0, 136.5, 132.8, 128.1, 126.6, 126.2, 126.1, 120.8 (q, \( J = 258.6 \) Hz), 52.7, 24.9. \(^{19}\)F NMR (376 MHz, CDCl₃, 25 °C, \( \delta \)): –57.5 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₁₁H₁₁NO₄F₃ ([M + H]⁺), 278.0640, found, 278.0639.

\( N-(3-(\text{Trifluoromethyl})\text{phenyl})\text{hydroxylamine (S15)} \)
Under N₂ atmosphere, a suspension of 1-nitro-3-(trifluoromethyl)benzene (1.00 g, 5.21 mmol, 1.00 equiv) and Rh/C (50 mg, 0.225 mmol, 5 mol%) in THF (25.0 mL, 0.208 M) was cooled to 0 °C. Hydrazine monohydrate (0.314 g, 5.73 mmol, 1.10 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 2 h. The reaction mixture was filtered through a short pad of celite, the celite was washed with EtOAc and the combined organic layers were concentrated in vacuo to afford 0.88 g of the title compound as a yellow solid (95% yield).

Rf = 0.30 (hexanes/EtOAc 4:1 (v/v)). ¹H NMR (400 MHz, (CD₃)₂SO, δ): 8.66 (s, 1H), 8.58 (s, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.09 (s, 1H), 7.07–7.03 (m, 2H). ¹³C NMR (175 MHz, (CD₃)₂SO, δ): 152.7, 129.4 (q, J = 30.6 Hz), 124.4 (q, J = 270.6 Hz), 116.3, 115.2 (d, J = 3.8 Hz), 111.9, 108.5 (q, J = 4.0 Hz). ¹⁹F NMR (376 MHz, (CD₃)₂SO, 25 °C, δ): –63.4 (s).

N-Hydroxy-N-(3-(trifluoromethyl)phenyl)acetamide (S16)

To a stirred suspension of N-(3-(trifluoromethyl)phenyl)hydroxylamine (S15) (0.720 g, 4.06 mmol, 1.00 equiv) and NaHCO₃ (0.410 g, 4.88 mmol, 1.20 equiv) in Et₂O (20.0 mL, 0.203 M) at 0 °C under N₂ was slowly added a solution of acetyl chloride (0.380 g, 4.88 mmol, 1.20 equiv) in Et₂O (25.0 mL, 0.192 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 1:1 (v/v)), to afford 0.760 g of the title compound as a yellow solid (85% yield).

Rf = 0.19 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, (CD₃)₂SO, δ): 10.88 (s, 1H), 8.03 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 2.08 (s, 3H). ¹³C NMR (125 MHz, (CD₃)₂SO, δ): 170.7, 142.2, 129.8, 129.1 (q, J = 31.6 Hz), 126.2 (d, J = 270.9 Hz), 122.9 (d, J = 9.6 Hz), 120.6 (d, J = 29.7 Hz), 115.5, 22.6. ¹⁹F NMR (376 MHz, (CD₃)₂SO, 25 °C, δ): –63.1 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₉H₉NO₂F₃ ([M + H]⁺), 220.0585, found, 220.0589.

N-(Trifluoromethoxy)-N-(3-(trifluoromethyl)phenyl)acetamide (2h)

N-(Trifluoromethoxy)-N-(3-(trifluoromethyl)phenyl)acetamide (2h)
Under N₂ atmosphere, to a mixture of N-hydroxy-N-(3-(trifluoromethyl)phenyl)acetamide (S16) (351 mg, 1.60 mmol, 1.00 equiv) and Cs₂CO₃ (52.1 mg, 0.160 mmol, 10 mol%) in CHCl₃ (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 15 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:CH₂Cl₂ (1:1 to 0:1 (v/v)), to afford 378 mg of the title compound as a slightly yellow oil (82% yield).

Rᵣ = 0.50 (hexanes/CH₂Cl₂ 1:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 25 °C, δ): 7.66 (s, 1H), 7.64–7.60 (m, 1H), 7.60–7.56 (m, 2H), 2.33 (s, 3H). ¹³C NMR (125 MHz, CDCl₃, 25 °C, δ): 172.8, 140.8, 132.0 (q, J = 33.0 Hz), 129.9, 128.3, 125.4 (q, J = 3.1 Hz), 123.5 (q, J = 271.1 Hz), 122.8 (q, J = 264.0 Hz), 121.7, 21.8. ¹⁹F NMR (376 MHz, CDCl₃, 25 °C, δ): −63.3 (s), −65.0 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₁₀H₇NO₂F₆ ([M + H]⁺), 287.0381, found, 287.0389.

**N-(2-(Trifluoromethoxy)-5-(trifluoromethyl)phenyl)acetamide (3h) and N-(2-(trifluoromethoxy)-3-(trifluoromethyl)phenyl)acetamide (3h-II)**

A solution of N-(trifluoromethoxy)-N-(3-(trifluoromethyl)phenyl)acetamide (2h) (115 mg, 0.400 mmol) in MeNO₂ (0.400 mL, 1.00 M) was heated at 140 °C under N₂ atmosphere for 20 h. The reaction mixture was purified by preparative TLC using hexanes:EtOAc (4:1 (v/v)) for development (prep TLC was developed twice). The purification afforded 53.5 mg of 3h and 37.4 mg of 3h-II (80% overall yield).

Data for 3h: white solid; Rᵣ = 0.66 (hexanes/ EtOAc 7:3 (v/v)). NMR Spectroscopy: ¹H NMR (700 MHz, CDCl₃, 25 °C, δ): 8.79 (br. s, 1H), 7.55 (br. s, 1H), 7.32–7.39 (m, 2H), 2.26 (s, 3H). ¹³C NMR (175 MHz, CDCl₃, 25 °C, δ): 168.6, 139.9, 131.1, 129.9 (q, J = 33.1 Hz), 123.5 (q, J = 270.8 Hz), 121.1, 120.5 (q, J = 259.6 Hz), 120.1, 119.2, 24.9. ¹⁹F NMR (376 MHz, CDCl₃, 25 °C, δ): −58.0 (s), −63.2 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₁₀H₈NO₂F₆ ([M + H]⁺), 288.0459, found, 288.0457.

Data for 3h-II: white solid; Rᵣ = 0.43 (hexanes/ EtOAc 7:3 (v/v)). NMR Spectroscopy: ¹H NMR (700 MHz, CDCl₃, 25 °C, δ): 8.52 (br. s, 1H), 7.50 (br. s, 1H), 7.39–7.46 (m, 2H), 2.23 (s, 3H). ¹³C NMR (175 MHz, CDCl₃, 25 °C, δ): 168.5, 135.7, 133.1, 128.3, 126.7, 125.2 (q, J = 32.0 Hz), 122.6 (d, J = 5.3 Hz), 122.5 (q, J = 271.6 Hz), 120.7 (q, J = 260.3 Hz), 24.7. ¹⁹F NMR (376 MHz, CDCl₃, 25 °C, δ): −55.7 (d), −61.1 (q). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₁₀H₈NO₂F₆ ([M + H]⁺), 288.0459, found, 288.0463.
1-(4-(Hydroxyamino)phenyl)ethan-1-one (S17)

\[
\begin{align*}
\text{Me} & \quad \text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O} \ (1.20 \text{ equiv}) \quad \text{Rh/C} \ (5 \text{ mol}%) \\
\text{O} & \quad \text{THF, 0 }^\circ\text{C} \\
\text{NO}_2 & \quad \text{quant.} \\
\end{align*}
\]

Under N\textsubscript{2} atmosphere, a suspension of 1-(4-nitrophenyl)ethan-1-one (3.00 g, 18.2 mmol, 1.00 equiv) and Rh/C (104 mg, 0.908 mmol, 5 mol\%) in THF (90.0 mL, 0.202 M) was cooled to 0 °C. Hydrazine monohydrate (1.09 g, 21.8 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 3.5 h. The reaction mixture was filtered through a short pad of celite and concentrated \textit{in vacuo} to afford 2.80 g of the title compound as a yellow solid (quant yield).

\[ R_f = 0.27 \text{ (hexanes/EtOAc 5:1 (v/v))}. \]
NMR Spectroscopy: \(^1\)H NMR (400 MHz, (CD\textsubscript{3})\textsubscript{2}SO, \(\delta\)): 8.99 (s, 1H), 8.67 (s, 1H), 7.79 (d, \(J = 8.7\) Hz, 2H), 6.82 (d, \(J = 8.7\) Hz, 2H), 2.44 (s, 3H). \(^{13}\)C NMR (100 MHz, (CD\textsubscript{3})\textsubscript{2}SO, \(\delta\)): 195.6, 155.9, 129.8, 127.7, 110.9, 26.1.

N-(4-Acetylphenyl)-N-hydroxyacetamide (S18)

To a stirred suspension of 1-(4-(hydroxyamino)phenyl)ethan-1-one (S17) (0.200 g, 1.32 mmol, 1.00 equiv) and NaHCO\textsubscript{3} (0.130 g, 1.59 mmol, 1.20 equiv) in Et\textsubscript{2}O (10.0 mL, 0.132 M) at 0 °C under N\textsubscript{2} was slowly added a solution of acetyl chloride (0.130 g, 1.59 mmol, 1.20 equiv) in Et\textsubscript{2}O (5.00 mL, 0.318 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated \textit{in vacuo}. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (2:1 to 1:1 (v/v)), to afford 0.230 g of the title compound as a white solid (91% yield).

\[ R_f = 0.13 \text{ (hexanes/EtOAc 2:1 (v/v))}. \]
NMR Spectroscopy: \(^1\)H NMR (400 MHz, (CD\textsubscript{3})\textsubscript{2}SO, \(\delta\)): 10.84 (s, 1H), 7.96 (d, \(J = 8.9\) Hz, 2H), 7.82 (d, \(J = 8.9\) Hz, 2H), 2.54 (s, 3H), 2.27 (s, 3H). \(^{13}\)C NMR (100 MHz, (CD\textsubscript{3})\textsubscript{2}SO, \(\delta\)): 196.6, 170.8, 145.3, 132.2, 128.9, 118.3, 26.5, 22.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\textsubscript{10}H\textsubscript{12}NO\textsubscript{3} ([M + H]\textsuperscript{+}), 194.0817, found, 194.0820.
**N-(4-Acetylphenyl)-N-(trifluoromethoxy)acetamide (2i)**

![Chemical Structure](image)

Under N₂ atmosphere, to a mixture of methyl N-(4-acetylphenyl)-N-hydroxyacetamide (S18) (309 mg, 1.60 mmol, 1.00 equiv) and Cs₂CO₃ (52.1 mg, 0.160 mmol, 10 mol%) in CHCl₃ (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 16 h. The reaction mixture was then washed with sat. aq. NaHCO₃ (30 mL) and the layers were separated. The organic layer was dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 7:3 (v/v)), to afford 314 mg of the title compound a slightly yellow oil (75% yield).

Rᶠ = 0.62 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ¹H NMR (700 MHz, CDCl₃, 25 ºC, δ): 8.03–8.00 (m, 2H), 7.50–7.48 (m, 2H), 2.61 (s, 3H), 2.33 (s, 3H). ¹³C NMR (175 MHz, CDCl₃, 25 ºC, δ): 196.9, 172.3, 143.9, 136.5, 129.3, 124.0, 122.7 (q, J = 264.2 Hz), 26.8, 21.9. ¹⁹F NMR (376 MHz, CDCl₃, 25 ºC, δ): −65.00 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₁₁H₁₁NO₃F₃ ([M + H]+), 262.0691, found, 262.0691.

**N-(4-Acetyl-2-(trifluoromethoxy)phenyl)acetamide (3i)**

![Chemical Structure](image)

A solution of N-(4-acetylphenyl)-N-(trifluoromethoxy)acetamide (2i) (104 mg, 0.400 mmol) in MeNO₂ (0.400 mL, 1.00 M) was heated at 120 ºC under N₂ atmosphere for 20 h. The reaction mixture was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 3:2 (v/v)), to afford 93.6 mg of the title compound as a white solid (90% yield).

Rᶠ = 0.46 (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: ¹H NMR (700 MHz, CDCl₃, 25 ºC, δ): 8.59 (d, J = 8.6 Hz, 1H), 7.89–7.86 (m, 2H), 7.58 (br. s, 1H), 2.59 (s, 3H), 2.27 (s, 3H). ¹³C NMR (175 MHz, CDCl₃, 25 ºC, δ): 195.7, 168.6, 137.6, 134.8, 132.9, 128.4, 120.8, 120.6 (q, J = 259.1 Hz), 119.8, 26.5, 25.1. ¹⁹F NMR (376 MHz, CDCl₃, 25 ºC, δ): −58.0 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₁₁H₁₁NO₃F₃ ([M + H]+), 262.0691, found, 262.0692.
4-(Hydroxyamino)benzonitrile (S19)

\[
\begin{align*}
\text{NC} & \quad \text{H}_2\text{NNH}_2 \quad \text{H}_2\text{O} \quad (1.20 \text{ equiv}) \\
& \quad \text{Rh/C} \quad (5 \text{ mol%}) \\
\text{THF} & \quad 0 \, ^\circ\text{C} \\
& \quad 99\%
\end{align*}
\]

Under N\textsubscript{2} atmosphere, a suspension of 4-nitrobenzonitrile (2.00 g, 13.5 mmol, 1.00 equiv) and Rh/C (77.6 mg, 0.680 mmol, 5 mol%) in THF (40.0 mL, 0.338 M) was cooled to 0 °C. Hydrazine monohydrate (0.810 g, 16.2 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 1 h and then slowly warmed up to rt and stirred at rt for 1 h. The reaction mixture was filtered through a short pad of celite and concentrated in vacuo to afford 1.80 g of the title compound as a yellow solid (99% yield).

\[R_f = 0.14 \text{ (hexanes/EtOAc 5:1 (v/v)).} \]

NMR Spectroscopy:

- \(^1\text{H NMR} (400 \text{ MHz}, (\text{CD}_3)_2\text{SO}, \delta): 9.10 \text{ (s, 1H)}, 8.76 \text{ (s, 1H)}, 7.57–7.52 \text{ (m, 2H)}, 7.85 \text{ (d, } J = 8.6 \text{ Hz, 2H)}.
- \(^{13}\text{C NMR} (100 \text{ MHz}, (\text{CD}_3)_2\text{SO}, \delta): 155.4, 133.1, 120.1, 111.8, 90.1.

\(N\)-(4-Cyanophenyl)-\(N\)-hydroxyacetamide (S20)

\[
\begin{align*}
\text{NC} & \quad \text{AcCl} \quad (1.20 \text{ equiv}) \\
& \quad \text{NaHCO}_3 \quad (1.20 \text{ equiv}) \\
\text{Et}_2\text{O} & \quad 0 \, ^\circ\text{C} \\
& \quad 78\%
\end{align*}
\]

To a stirred suspension of 4-(hydroxyamino)benzonitrile (S19) (0.500 g, 3.73 mmol, 1.00 equiv) and NaHCO\textsubscript{3} (0.380 g, 4.47 mmol, 1.20 equiv) in Et\textsubscript{2}O (25.0 mL, 0.149 M) at 0 °C under N\textsubscript{2} was slowly added a solution of acetyl chloride (0.350 g, 4.47 mmol, 1.20 equiv) in Et\textsubscript{2}O (10.0 mL, 0.447 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined, concentrated in vacuo. Recrystallization from Et\textsubscript{2}O/hexanes afforded 0.510 g of the title compound as a light pink solid (78% yield).

\[R_f = 0.32 \text{ (hexanes/EtOAc 1:1 (v/v)).} \]

NMR Spectroscopy:

- \(^1\text{H NMR} (400 \text{ MHz}, (\text{CD}_3)_2\text{SO}, \delta): 10.92 \text{ (s, 1H)}, 7.88 \text{ (d, } J = 9.0 \text{ Hz, 2H)}, 7.82 \text{ (d, } J = 9.0 \text{ Hz, 2H)}, 2.27 \text{ (s, 3H)}.
- \(^{13}\text{C NMR} (100 \text{ MHz}, (\text{CD}_3)_2\text{SO}, \delta): 171.1, 145.1, 132.9, 118.9, 118.8, 105.7, 22.9.

Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\textsubscript{9}H\textsubscript{9}N\textsubscript{2}O\textsubscript{2} ([M + H]\textsuperscript{+}), 177.0664, found, 177.0665.

\(N\)-(4-Cyanophenyl)-\(N\)-(trifluoromethoxy)acetamide (2j)

\[
\begin{align*}
\text{NC} & \quad \text{F}_3\text{C} & \quad \text{Cs}_2\text{CO}_3 \quad (10 \text{ mol%}) \\
& \quad \text{CHCl}_3, \text{rt}, 23 \text{ h} \\
& \quad 84\%
\end{align*}
\]

\(N\)-(4-Cyanophenyl)-\(N\)-(trifluoromethoxy)acetamide (2j)
Under \( N_2 \) atmosphere, to a mixture of \( N-(4\text{-cyanophenyl})-N\text{-hydroxyacetamide} \) (S20) (200 mg, 1.14 mmol, 1.00 equiv) and \( \text{Cs}_2\text{CO}_3 \) (37.0 mg, 0.114 mmol, 10 mol%) in \( \text{CHCl}_3 \) (11.4 mL, 0.100 M) was added Togni reagent II (432 mg, 1.37 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 23 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:CH\(_2\)Cl\(_2\) (1:2 to 0:1 (v/v)), to afford 234 mg of the title compound as an off-white solid (84\% yield).

\( \text{R}_f = 0.66 \) (CH\(_2\)Cl\(_2\)). NMR Spectroscopy: \(^1\text{H} \text{NMR} \) (700 MHz, CDCl\(_3\), 25 °C, \( \delta \)): 7.74–7.70 (m, 2H), 7.55–7.51 (m, 2H), 2.38 (s, 3H).

\(^13\text{C} \text{NMR} \) (175 MHz, CDCl\(_3\), 25 °C, \( \delta \)): 172.4, 143.6, 133.1, 123.8, 122.7 (q, \( J = 265.2 \text{ Hz} \)), 118.1, 111.6, 21.9. \(^{19}\text{F} \text{NMR} \) (376 MHz, CDC\(_3\)l, 25 °C, \( \delta \)): –65.2 (s).

Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\(_{10}\)H\(_8\)N\(_2\)O\(_2\)F\(_3\) ([M + H]\(^+\)), 245.0538, found, 245.0541.

\( N-(4\text{-cyanophenyl})-N-(\text{trifluoromethoxy})acetamide \) (3j)

Under \( N_2 \) atmosphere, a suspension of \( N-(4\text{-cyanophenyl})-N\text{-hydroxyacetamide} \) \( 2j \) (97.7 mg, 0.400 mmol) in MeNO\(_2\) (0.400 mL, 1.00 M) was heated at 120 °C under \( N_2 \) atmosphere for 48 h. The reaction mixture was purified by preparative TLC using hexanes:EtOAc (7:3 (v/v)) for development. The purification afforded 61.4 mg of the title compound as a white crystalline solid (63\% yield). 20.0 mg (20\%) of the starting material was recovered.

Data for \( 3j \): \( \text{R}_f = 0.64 \) (hexanes/EtOAc 3:2 (v/v)). NMR Spectroscopy: \(^1\text{H} \text{NMR} \) (700 MHz, CDCl\(_3\), 25 °C, \( \delta \)): 8.66 (d, \( J = 8.6 \text{ Hz} \), 1H), 7.61 (br. s, 1H), 7.58 (d, \( J = 8.6 \text{ Hz} \), 1H), 7.54 (s, 1H), 2.28 (s, 3H).

\(^13\text{C} \text{NMR} \) (175 MHz, CDCl\(_3\), 25 °C, \( \delta \)): 168.6, 137.1, 135.0, 132.0, 123.7, 121.8, 120.5 (q, \( J = 260.2 \text{ Hz} \)), 117.6, 107.2, 25.2. \(^{19}\text{F} \text{NMR} \) (376 MHz, CDCl\(_3\), 25 °C, \( \delta \)): –58.4 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\(_{10}\)H\(_8\)N\(_2\)O\(_2\)F\(_3\) ([M + H]\(^+\)), 245.0538, found, 245.0539.

\( N-(3,5\text{-bis(Trifluoromethyl)phenyl})\text{hydroxylamine} \) (S21)

Under \( N_2 \) atmosphere, a suspension of 1-nitro-3,5-bis(trifluoromethyl)benzene (1.00 g, 3.86 mmol, 1.00 equiv) and Rh/C (30.00 mg, 0.261 mmol, 5 mol%) in THF (25 mL, 0.154 M) was cooled to 0 °C. Hydrazine monohydrate (0.232 g, 4.63 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 2h. The reaction mixture was filtered through a short pad of celite, the celite was
washed with EtOAc and the combined organic layers were concentrated in vacuo to afford 0.940 g of the title compound as a yellow solid (quant yield).

\[
R_f = 0.48 \text{ (hexanes/EtOAc 4:1 (v/v))}. \text{ NMR Spectroscopy: } ^1H \text{ NMR (400 MHz, (CD}_3\text{)SO, } \delta): 9.11 \text{ (s, 1H), 8.94 (s, 1H), 7.31 (s, 3H). }  ^{13}C \text{ NMR (100 MHz, (CD}_3\text{)SO, } \delta): 153.5, 130.7 \text{ (q, } J = 25.7 \text{ Hz ), 123.5 (q, } J = 216.9 \text{ Hz ), 111.8, 111.0 (q, } J = 3.0 \text{ Hz ). } ^{19}F \text{ NMR (376 MHz, (CD}_3\text{)SO, 25 }^\circ\text{C, } \delta): -63.8 \text{ (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C}_{18}H_{16}NOF_6 \text{ ([M + H]+), 246.0354, found, 246.0363.}
\]

\[\text{N-(3,5-bis(Trifluoromethyl)phenyl)-N-hydroxyacetamide (S22)}\]

\[
\text{To a stirred suspension of methyl N-(3,5-bis(trifluoromethyl)phenyl)hydroxylamine (S21) (1.00 g, 4.08 mmol, 1.00 equiv) and NaHCO}_3 \text{ (0.411 g, 4.90 mmol, 1.20 equiv) in Et}_2\text{O (20.0 mL, 0.204 M) at 0 }^\circ\text{C under N}_2 \text{ was slowly added a solution of acetyl chloride (0.384 g, 4.09 mmol, 1.20 equiv) in Et}_2\text{O (25.0 mL, 0.196 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 3:1 (v/v)), to afford 0.890 g of the title compound as a light white long needle solid (76% yield).} \]

\[
R_f = 0.36 \text{ (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: } ^1H \text{ NMR (400 MHz, (CD}_3\text{)SO, } \delta): 11.17 \text{ (s, 1H), 8.32 (s, 2H), 7.84 (s, 1H), 2.30 (s, 3H). }  ^{13}C \text{ NMR (100 MHz, (CD}_3\text{)SO, } \delta): 171.6, 143.0, 130.6 \text{ (q, } J = 26.5 \text{ Hz), 123.2 (q, } J = 217.0 \text{ Hz), 118.5, 116.9, 22.7. } ^{19}F \text{ NMR (376 MHz, CDC}_1\text{, (376 MHz, CDC}_3\text{, 25 }^\circ\text{C, } \delta): -63.6 \text{ (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C}_{10}H_{8}NO_2F_6 \text{ ([M + H]+), 288.0459, found, 288.0457.} \]

\[\text{N-(3,5-bis(Trifluoromethyl)phenyl)-N-(trifluoromethoxy)acetamide (2k)}\]

\[
\text{Under N}_2 \text{ atmosphere, to a mixture of N-(3,5-bis(trifluoromethyl)phenyl)-N-hydroxyacetamide (S22) (459 mg, 1.60 mmol, 1.00 equiv) and Cs}_2\text{CO}_3 \text{ (52.1 mg, 0.160 mmol, 10 mol%) in CHCl}_3 \text{ (16.0 mL, 0.100 M) was added Togni reagent II (607 g, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred} \]

26
at rt for 19 h. The reaction mixture was then washed with sat. aq. NaHCO₃ (30 mL) and the layers were separated. The organic layer was dried (MgSO₄), filtered and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (19:1 to 9:1 (v/v)), to afford 454 mg of the title compound a slightly yellow oil (80% yield).

**N-(p-Tolyl)hydroxylamine (S23)**

![Chemical structure](image)

Under N₂ atmosphere, a suspension of 1-methyl-4-nitrobenzene (2.50 g, 18.3 mmol, 1.00 equiv) and Rh/C (104.8 mg, 0.910 mmol, 0.30 mol%) in THF (91.0 mL, 0.200 M) was cooled to 0 °C. Hydrazine monohydrate (1.11 g, 21.9 mmol, 1.20 equiv) was added dropwise. The reaction mixture was stirred at 0 °C for 2.5 h, filtered through a short pad of celite and concentrated in vacuo to afford 2.25 g of the title compound as a brown solid (quant yield).

**N-Hydroxy-N-(p-tolyl)acetamide (S24)**

![Chemical structure](image)

To a stirred suspension of N-(p-tolyl)hydroxylamine (S23) (0.200 g, 1.62 mmol, 1.00 equiv) and NaHCO₃ (164 mg, 1.95 mmol, 1.20 equiv) in Et₂O (10.0 mL, 0.162 M) at 0 °C under N₂ was slowly added a solution of acetyl chloride (153 mg, 1.95 mmol, 1.20 equiv) in Et₂O (5.00 mL, 0.390 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 2:1 (v/v)), to afford 0.156 g of the title compound as a yellow solid (58% yield).

**NMR Spectroscopy:** ¹H NMR (400 MHz, (CD₃)₂SO, δ): 10.51 (s, 1H).
1H), 7.47 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 2.28 (s, 3H), 2.16 (s, 3H). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO, $\delta$): 169.5, 139.3, 133.8, 128.8, 120.3, 22.3, 20.4. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C$_9$H$_{12}$NO$_2$ ([M + H$^+$]), 166.0868, found, 166.0867.

$N$-(4-Methyl-2-(trifluoromethoxy)phenyl)acetamide (3l)

![Chemical Structure](image)

Under N$_2$ atmosphere, to a mixture of $N$-hydroxy-$N$-(p-tolyl)acetamide ($S24$) (78.2 mg, 0.473 mmol, 1.00 equiv) and NaH (13.6 mg, 0.568 mmol, 1.20 equiv) in CH$_2$Cl$_2$ (4.73 mL, 0.100 M) was added Togni reagent II (179 mg, 0.568 mmol, 1.2 equiv) and the reaction mixture was stirred at rt for 23 h. The reaction mixture diluted with CH$_2$Cl$_2$ (30 mL) and washed with water (30 mL). The layers were separated, the organic layer was dried (MgSO$_4$), filtered and concentrated in vacuo. The residue was purified by preparative TLC using hexanes:EtOAc (4:1 (v/v)) for development (prep TLC was developed twice). The purification afforded 76.8 mg of the title compound as a white solid (70% yield).

$R_F$ = 0.42 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: $^1$H NMR (700 MHz, CDCl$_3$, 25 $^\circ$C, $\delta$): 8.21 (d, J = 8.2 Hz, 1H), 7.31 (br. s, 1H), 7.08 (d, J = 8.2 Hz, 1H), 7.05 (br. s, 1H), 2.33 (s, 3H), 2.21 (s, 3H). $^{13}$C NMR (175 MHz, CDCl$_3$, 25 $^\circ$C, $\delta$): 168.3, 138.2, 134.7, 128.2, 128.0, 122.2, 120.9, 120.7 (q, J = 257.4 Hz), 24.8, 21.0. $^{19}$F NMR (376 MHz, CDCl$_3$, 25 $^\circ$C, $\delta$): $-$58.0 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C$_{10}$H$_{11}$NO$_2$F$_3$ ([M + H$^+$]), 234.0742, found, 234.0737.

Methyl 4-(N-hydroxybenzamido)benzoate (S25)

![Chemical Structure](image)

To a stirred suspension of methyl 4-(hydroxyamino)benzoate ($S1$) (1.00 g, 5.98 mmol, 1.00 equiv) and NaHCO$_3$ (0.603 g, 7.18 mmol, 1.20 equiv) in Et$_2$O (30.0 mL, 0.199 M) at 0 $^\circ$C under N$_2$ was slowly added a solution of acetyl chloride (1.01 g, 7.18 mmol, 1.20 equiv) in Et$_2$O (30.0 mL, 0.239 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 (v/v)), to afford 1.47 g of the title compound as a light yellow solid (91% yield).

$R_F$ = 0.20 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: $^1$H NMR (500 MHz, (CD$_3$)$_2$SO, $\delta$): 10.93 (s, 1H), 8.00 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 7.4 Hz, 2H), 7.52–7.44 (m, 3 H), 3.85
(s, 3H). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO, δ): 168.6, 165.7, 145.9, 135.2, 130.6, 129.8, 128.4, 127.9, 125.5, 120.0, 52.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C$_{15}$H$_{14}$NO$_4$ ([M + H$^+$]), 272.0923, found, 272.0925.

**Methyl 4-(N-(trifluoromethoxy)benzamido)benzoate (2m)**

![Chemical Structure]

Under N$_2$ atmosphere, to a mixture of methyl 4-(N-hydroxybenzamido)benzoate (S25) (434 mg, 1.60 mmol, 1.00 equiv) and Cs$_2$CO$_3$ (52.1 mg, 0.160 mmol, 10 mol%) in CHCl$_3$ (16.0 mL, 0.100 M) was added Togni reagent II (607 mg, 1.92 mmol, 1.20 equiv) and the reaction mixture was stirred at rt for 19 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:CH$_2$Cl$_2$ (1:1 to 0:1 (v/v)), to afford 521 mg of the title compound as a slightly yellow oil (96% yield).

R$_f$ = 0.67 (CH$_2$Cl$_2$). NMR Spectroscopy: $^1$H NMR (700 MHz, CDCl$_3$, 25 °C, δ): 8.03 (d, $J = 8.6$ Hz, 2H), 7.65–7.61 (m, 2H), 7.47–7.41 (m, 3H), 7.32 (t, $J = 7.7$ Hz, 2H), 3.90 (s, 3H). $^{13}$C NMR (175 MHz, CDCl$_3$, 25 °C, δ): 170.7, 165.9, 145.2, 132.5, 132.1, 131.1, 131.0, 129.2, 128.6, 127.2, 122.8 (q, $J = 265.8$ Hz), 52.6. $^{19}$F NMR (376 MHz, CDCl$_3$, 25 °C, δ): –64.4 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C$_{16}$H$_{13}$NO$_4$F$_3$ ([M + H$^+$]), 340.0797, found, 340.0801.

**Methyl 4-benzamido-3-(trifluoromethoxy)benzoate (3m)**

![Chemical Structure]

A solution of methyl 4-(N-(trifluoromethoxy)benzamido)benzoate (2m) (136 mg, 0.400 mmol) in MeNO$_2$ (0.400 mL, 1.00 M) was heated at 120 °C under N$_2$ atmosphere for 20 h. The reaction mixture was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 7:3 (v/v)), to afford 107 mg of the title compound as a white solid (79% yield). The reaction also afforded methyl methyl 2-phenylbenzo[d]oxazole-6-carboxylate (3m’) as a white solid (4% yield).

Data for 3m: R$_f$ = 0.72 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: $^1$H NMR (700 MHz, CDCl$_3$, 25 °C, δ): 8.74 (d, $J = 8.6$ Hz, 1H), 8.37 (br. s, 1H), 8.04 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.98 (s, 1H), 7.90–7.84 (m, 2H), 7.63–7.58 (m, 1H), 7.56–7.51 (m, 2H), 3.93 (s, 3H). $^{13}$C NMR (175 MHz, CDCl$_3$, 25 °C, δ):
165.6, 165.5, 137.7, 135.0, 134.2, 132.8, 129.5, 129.3, 127.2, 126.0, 121.7, 120.8, 120.7 (q, J = 259.1 Hz), 52.5. $^{19}$F NMR (376 MHz, CDCl$_3$, 25 °C, δ): −58.1 (s). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C$_{16}$H$_{13}$NO$_2$F$_2$ ([M + H]$^+$), 340.0797, found, 340.0793.

Data for 3m': $R_f$ = 0.73 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: $^1$H NMR (700 MHz, CDCl$_3$, 25 °C, δ): 8.36–8.25 (m, 3H), 8.10 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.65–7.49 (m, 3H), 3.97 (s, 3 H).

$^{13}$C NMR (175 MHz, CDCl$_3$, 25 °C, δ): 166.8, 165.7, 150.6, 146.2, 132.4, 129.2, 128.1, 127.3, 126.8, 126.6, 119.7, 112.4, 52.5. These spectroscopic data correspond to previously reported data.$^4$

**N-(4-Chlorophenyl)hydroxylamine (S26)**

\[
\begin{align*}
\text{Cl} \quad \text{NO}_2 \quad \overset{H_2NNH_2 \; H_2O (1.20 \text{ equiv})}{\text{Rh/C (5 mol\%)} \atop \text{THF, 0 °C}} \quad \overset{95\%}{\text{S26}}
\end{align*}
\]

Under N$_2$ atmosphere, a suspension of 1-chloro-4-nitrobenzene (2.00 g, 12.7 mmol, 1.00 equiv) and Rh/C (72.9 mg, 0.635 mmol, 5 mol%) in THF (40.0 mL, 0.318 M) was cooled to 0 °C. Hydrazine monohydrate (0.762 g, 15.2 mmol, 1.20 equiv) was added dropwise. The reaction mixture stirred at 0 °C for 2.5 h. The reaction mixture was filtered through a short pad of celite and concentrated in vacuo to afford 1.72 g of the title compound as a yellow solid (95% yield).

$R_f$ = 0.27 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: $^1$H NMR (500 MHz, (CD$_3$)$_2$SO, δ): 8.43 (d, J = 2.2 Hz, 1H), 8.40 (s, 1H), 7.19 (d, J = 8.8 Hz, 2H), 6.87–6.83 (m, 2H). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$SO, δ): 151.0, 128.3, 122.6, 114.4.

**N-(4-Chlorophenyl)-N-hydroxyacetamide (S27)**

\[
\begin{align*}
\text{Cl} \quad \text{NH}_2 \quad \overset{\text{AcCl (1.20 equiv)} \atop \text{Et}_2O, 0 °C \atop 89\%}{\text{NaHCO}_3 (1.20 \text{ equiv})} \quad \overset{\text{S27}}{\text{S26}}
\end{align*}
\]

To a stirred suspension of N-(4-chlorophenyl)hydroxylamine (S26) (1.00 g, 6.97 mmol, 1.00 equiv) and NaHCO$_3$ (0.700 g, 8.36 mmol, 1.20 equiv) in Et$_2$O (20.0 mL, 0.349 M) at 0 °C under N$_2$ was slowly added a solution of acetyl chloride (0.660 g, 8.36 mmol, 1.20 equiv) in Et$_2$O (20.0 mL, 0.418 M) via a syringe pump (at a rate of 10.0 mL/h). After the addition was complete, the reaction mixture was filtered through a short pad of celite and the celite was washed with EtOAc. The organic layers were combined and concentrated in vacuo. Recrystallization from Et$_2$O/hexanes afforded 1.15 g of the title compound.

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as a yellow solid (89% yield).

\( R_f = 0.13 \) (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (400 MHz, (CD\(_3\))\(_2\)SO, \( \delta \)): 10.72 (s, 1H), 7.67 (d, \( J = 8.9 \) Hz, 2H), 7.44–7.38 (m, 2H), 2.21 (s, 3H). \(^{13}\)C NMR (100 MHz, (CD\(_3\))\(_2\)SO, \( \delta \)): 170.1, 140.5, 128.3, 128.1, 121.4, 22.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\(_8\)H\(_9\)NO\(_2\)Cl ([M + H]\(^+\)), 186.0322, found, 186.0321.

**N-(4-Chlorophenyl)-N-(perfluoroethoxy)acetamide (6)**

![Chemical Structure of N-(4-Chlorophenyl)-N-(perfluoroethoxy)acetamide (6)](image)

Under N\(_2\) atmosphere, to a mixture of N-(4-chlorophenyl)-N-hydroxyacetamide (S27) (177 mg, 0.956 mmol, 1.00 equiv) and Cs\(_2\)CO\(_3\) (31.1 mg, 0.0956 mmol, 10 mol%) in CHCl\(_3\) (9.56 mL, 0.100 M) was added 1-(perfluoroethyl)-1H-[1,2,3]iodoxybenzene (700 mg, 1.91 mmol, 2.00 equiv) and the reaction mixture was stirred at rt for 16 h. The reaction mixture was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:CH\(_2\)Cl\(_2\) (19:1 to 1:1 (v/v)), to afford the title compound as a yellow oil (173 mg, 0.570 mmol, 60% yield).

\( R_f = 0.51 \) (hexanes/CH\(_2\)Cl\(_2\) 1:1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (700 MHz, CDCl\(_3\), 25 \(^\circ\)C, \( \delta \)): 7.45–7.38 (m, 2H), 7.36–7.28 (m, 2H), 2.25 (s, 3H). \(^{13}\)C NMR (175 MHz, CDCl\(_3\), 25 \(^\circ\)C, \( \delta \)): 172.8, 139.3, 135.0, 129.7, 127.0, 116.4 (qt, \( J = 283.5, 40.3 \) Hz), 116.2 (tq, \( J = 276.6, 40.8 \) Hz), 21.8. \(^{19}\)F NMR (376 MHz, CDCl\(_3\), 25 \(^\circ\)C, \( \delta \)): –85.0, –93.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C\(_{10}\)H\(_8\)Cl\(_3\)F\(_5\)NO \( ([M + H]^{+})\), 304.0164, found, 304.0151.

**N-(4-Chloro-2-(perfluoroethoxy)phenyl)acetamide (8)**

![Chemical Structure of N-(4-Chloro-2-(perfluoroethoxy)phenyl)acetamide (8)](image)

A solution of N-(4-chlorophenyl)-N-(perfluoroethoxy)acetamide (6) (50.0 mg, 0.165 mmol) in MeNO\(_2\) (0.165 mL, 1.00 M) was heated at 80 \(^\circ\)C under N\(_2\) atmosphere for 17 h. The reaction mixture was purified by preparative TLC using hexanes:EtOAc (9:1 (v/v)) for development (the PLC was developed twice). The purification afforded the title compound as a beige solid (86.2 mg, 0.340 mmol, 85% yield).

\( R_f = 0.30 \) (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (700 MHz, CDCl\(_3\), 25 \(^\circ\)C, \( \delta \)): 8.33 (d, 5

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\(^5\) The reagent was prepared according to the procedure described in Li, Y.; Studer, A. Angew. Chem. Int. Ed. **2012**, 51, (33), 8221-8224.
$J = 9.54$ Hz, 1H), 7.32–7.26 (m, 2H), 2.18 (s, 3H). $^1$H NMR (175 MHz, CDCl$_3$, 25 °C, δ): 168.2, 137.3, 129.9, 129.1, 128.2, 123.0, 122.0, 116.7 (qt, $J = 283.2$, 43.1 Hz), 114.4 (tq, $J = 278.3$, 43.0 Hz), 24.7. $^1$H NMR (376 MHz, CDCl$_3$, 25 °C, δ): –86.4, –88.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{10}\text{H}_8\text{ClF}_5\text{NO}_2 ([M + H]^+)$, 304.0164, found, 304.0151.
Mechanistic studies

*O*-trifluoromethylation in the presence of a radical trap (TEMPO)

Under N\textsubscript{2} atmosphere, to a mixture of methyl 4-(N-hydroxyacetamido)benzoate (1a) (10.5 mg, 0.0502 mmol, 1.00 equiv), TEMPO (7.8 mg, 0.0500 mmol, 1.00 equiv) and Cs\textsubscript{2}CO\textsubscript{3} (1.60 mg, 5.00 μmol, 10 mol%) in CHCl\textsubscript{3} (0.500 mL) was added Togni reagent II (19.0 mg, 0.0600 mmol, 1.2 equiv) and the reaction mixture was stirred at rt for 15 h. Trifluorotoluene (6.14 μL, 0.0500 mmol, 1.00 equiv) and CDCl\textsubscript{3} (0.250 mL) were added and the reaction mixture was analyzed by \textsuperscript{19}F NMR. The \textsuperscript{19}F NMR analysis indicated that the yield of *O*-trifluoromethylation of 1a in the presence of TEMPO (37%) was much lower than in the absence of the radical trap (97%). In addition, the formation of 2,2,6,6-tetramethyl-1-(trifluoromethoxy)piperidine (80%) resulting from recombination of TEMPO and CF\textsubscript{3}· was observed (Figure S1).

![Figure S1. \textsuperscript{19}F NMR spectrum of the reaction mixture.](image-url)
**O-trifluoromethylation in the presence of a radical trap (BHT)**

![Chemical structures](image)

Under N₂ atmosphere, to a mixture of methyl 4-(N-hydroxyacetamido)benzoate (1a) (10.5 mg, 0.0502 mmol, 1.00 equiv), BHT (11.0 mg, 0.0500 mmol, 1.00 equiv) and Cs₂CO₃ (1.60 mg, 5.00 μmol, 10 mol%) in CHCl₃ (0.500 mL) was added Togni reagent II (19.0 mg, 0.0600 mmol, 1.2 equiv) and the reaction mixture was stirred at rt for 15 h. Trifluorotoluene (6.14 μL, 0.0500 mmol, 1.00 equiv) and CDCl₃ (0.250 mL) were added and the reaction mixture was analyzed by ¹⁹F NMR. The ¹⁹F NMR analysis indicated that the yield of O-trifluoromethylation of 1a in the presence of BHT (28%) was much lower than in the absence of the radical trap (97%). In addition, the formation of 2,6-di-tert-butyl-4-(2,2,2-trifluoroethyl)phenol (56%) resulting from benzylic trifluoromethylation of BHT was observed. (Figure S2).

![Figure S2. ¹⁹F NMR spectrum of the reaction mixture.](image)
**O-CF₃ migration in the presence of a radical trap**

**w/o BHT:**

\[
\begin{align*}
\text{N-phenyl-N-(trifluoromethoxy)acetamide} & \quad \text{MeNO}_2 \\
2b & \quad 80 \degree C \\
& \quad 81\% (\alpha:\beta = 13:1)
\end{align*}
\]

**with BHT:**

\[
\begin{align*}
\text{BHT (1.0 equiv)} & \quad \text{MeNO}_2 \\
2b & \quad 80 \degree C \\
& \quad 80\% (\alpha:\beta = 15:1)
\end{align*}
\]

**Reaction without BHT:** Under N₂ atmosphere, a solution of N-phenyl-N-(trifluoromethoxy)acetamide (11.0 mg, 50.2 μmol) (2b) in MeNO₂ (50.0 μL, 1.00 M) was heated at 80 °C for 12 h. Trifluorotoluene (6.14 μL, 50.0 μmol, 1.00 equiv) and CDCl₃ (0.350 mL) were added and the reaction mixture was analyzed by ¹⁹F NMR (Figure S3).

**Figure S3.** ¹⁹F NMR spectrum of the reaction mixture w/o BHT.
**Reaction with BHT**: Under N$_2$ atmosphere, a solution of N-phenyl-N-(trifluoromethoxy)acetamide (2b) (11.0 mg, 50.2 μmol, 1.00 equiv) and BHT (11.0 mg, 50.0 μmol, 1.00 equiv) in MeNO$_2$ (50.0 μL, 1.00 M) was heated at 80 °C for 12 h. Trifluorotoluene (6.14 μL, 50.0 μmol, 1.00 equiv) and CDCl$_3$ (0.350 mL) were added and the reaction mixture was analyzed by $^{19}$F NMR (Figure S4).

---

**Figure S4.** $^{19}$F NMR spectrum of the reaction mixture with BHT.
Crossover experiments

A mixture of N-(4-chlorophenyl)-N-(perfluoroethoxy)acetamide (6) (7.6 mg, 0.025 mmol, 1.0 equiv) and N-(4-bromophenyl)-N-(trifluoromethoxy)acetamide (2e) (7.5 mg, 0.025 mmol, 1.0 equiv) was heated at 80 °C for 6h (i) in MeNO₂ (25 μL); (ii) neat. Trifluorotoluene (3.1 μL, 0.025 mmol, 1.0 equiv) and CDCl₃ (0.400 mL) were added and the reaction mixture was analyzed by ¹⁹F NMR and GCMS. No crossover products were observed (Figure S5 and S6).

*Figure S5. ¹⁹F NMR spectrum of the crossover experiment (i) in MeNO₂.*
Figure S6. $^{19}$F NMR spectrum of the crossover experiment (ii) neat.
Decomposition of trifluoromethoxide

While running the rearrangement reactions, in certain cases we observed that trifluoromethoxide was underwent decomposition as evidenced by detection of fluorophosgene and BF$_4^-$ by $^{19}$F NMR (Figure S7).

Figure S7. $^{19}$F NMR spectrum of the rearrangement reaction showing the decomposition of trifluoromethoxide.
Possible mechanisms for the OCF$_3$-migration reaction

a. Intramolecular mechanism: tight ion pair

b. Intermolecular mechanisms

i. Counterion swap: nitrenium ions exchange OCF$_3$ anions (expect formation of crossover products)

ii. Trifluoromethoxide attack on O-trifluoromethylated N-hydroxylamine derivative (expect formation of crossover products)

Figure S8. Possible OCF$_3$-migration mechanisms.
Kinetic Experiments

Sample Preparation

All samples were prepared inside a glovebox under nitrogen atmosphere. N-Aryl-N-(trifluoromethoxy)-acetamides were weighed into a 5 mm thin wall precision screw-cap NMR tube (purchased from Wilmad-labglass) and dissolved in degassed anhydrous nitromethane (0.7 mL, at 0.01 – 0.1 M). PhCF₃ (4 μL) was used as internal standard which was added into NMR tubes with a 10 μL micro-syringe outside of glovebox. PhCF₃ (4 μL) in deuterium MeNO₂-d₃ (0.7 mL) was prepared for pre-shimming the ¹⁹F probe.

General methods for data acquisition

All kinetic experiments (¹⁹F NMR) were performed on a Bruker 400 Nanobay spectrometer (400 MHz without proton decoupling). The ¹⁹F probe was pre-shimmed with the standard sample prior to data acquisition. Raw data from the spectra were processed using TopSpin 3.1 and plots for kinetic were generated and analyzed with SigmaPlot 12.0. All kinetic experiments were performed in triplicate.

Method A (substrates with fast-kinetic)

The sample was inserted into the pre-shimmed NMR spectrometer at 25 °C and the signal collected was named as the initial concentration. Then, the NMR spectrometer was warmed up to 80 °C, tuned and shimmed with the standard sample at 80 °C. The sample was inserted into the spectrometer and at the same time a digital stopwatch was used to record the time. Data was acquired right after the sample was inserted into the NMR spectrometer, each data point was collected manually with an interval time between 15 s up to 5 minutes and the reaction was monitored for at least three half-lives.

The data were fitted with the equation:

\[ \ln [S] = \text{constant} - kt \]

whereas the \([S]\) is the concentration of the substrates at different time, \(k\) is the rate constant, \(t\) is the time.

Method B (substrates with slow-kinetic)

The sample was inserted into the pre-shimmed NMR spectrometer at 25 °C and the signal collected was named as the initial concentration. Then, the sample was heated in an oil bath at 80 °C. Every 0.5-3 hours, the reaction was cooled in an ice-bath and ¹⁹F NMR data was acquired. This procedure was repeated for at least 6 times until 10-15 % of the substrate was converted.

The data were fitted with the equation:

\[ [P] = k[S]₀t \]

whereas the \([P]\) is the concentration of products, \([S]₀\) is the concentration of the
substrate before the reaction begins, $k$ is the rate constant, $t$ is time.
Substrates and Data collected with Method A

*N*-Phenyl-N-(trifluoromethoxy)acetamide (2b)

<table>
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<tr>
<th>Trial</th>
<th>Concentration mole/L</th>
<th>k s⁻¹</th>
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<tr>
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<td>0.0013</td>
</tr>
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</table>

Trial 1: ln[S] = -2.7065 – 0.0013 t  
\[ R^2 = 0.9969 \]

Trial 2: ln[S] = -2.8432 – 0.0013 t  
\[ R^2 = 0.9955 \]

Trial 3: ln[S] = -3.0350 – 0.0013 t  
\[ R^2 = 0.9947 \]
**N-(4-Bromophenyl)-N-(trifluoromethoxy)acetamide (2e)**

<table>
<thead>
<tr>
<th>Trial</th>
<th>Concentration mole/L</th>
<th>( k ) s(^{-1} )</th>
</tr>
</thead>
<tbody>
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<td>0.0022</td>
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<tr>
<td>2</td>
<td>0.049</td>
<td>0.0023</td>
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<tr>
<td>3</td>
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<td>0.0023</td>
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<tr>
<td>average</td>
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</tr>
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</table>

Trial 1: \( \ln[S] = -3.1249 - 0.0022t \)
\( R^2 = 0.9962 \)

Trial 2: \( \ln[S] = -3.7676 - 0.0023t \)
\( R^2 = 0.9957 \)

Trial 3: \( \ln[S] = -3.7676 - 0.0023t \)
\( R^2 = 0.9957 \)
N-(4-Iodophenyl)-N-((trifluoromethoxy)acetamide (2d)

<table>
<thead>
<tr>
<th>Trial</th>
<th>Concentration mole/L</th>
<th>k s⁻¹</th>
</tr>
</thead>
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<td>2</td>
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<tr>
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<tr>
<td>average</td>
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</table>

Trial 1: \[ \ln[S] = -2.9864 - 0.0045 \cdot t \]
\[ R^2 = 0.9986 \]

Trial 2: \[ \ln[S] = -3.1016 - 0.0046 \cdot t \]
\[ R^2 = 0.9941 \]

Trial 3: \[ \ln[S] = -4.4443 - 0.0042 \cdot t \]
\[ R^2 = 0.9891 \]
**N-(3-Methoxyphenyl)-N-(trifluoromethoxy)acetamid (2c)**

<table>
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<td>0.0028</td>
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Trial 1: \( \ln[S] = -2.9146 - 0.00028t \)
\[ R^2 = 0.9962 \]

Trial 2: \( \ln[S] = -2.9631 - 0.00028t \)
\[ R^2 = 0.9966 \]

Trial 3: \( \ln[S] = -3.1884 - 0.00026t \)
\[ R^2 = 0.9912 \]

---

### Graph

![Graph showing the relationship between ln(S) and time for different concentrations.](image)

---

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<thead>
<tr>
<th>Time, s</th>
<th>Integrals [S], mol/L</th>
<th>( \ln [S] )</th>
<th>Time, s</th>
<th>Integrals [S], mol/L</th>
<th>( \ln [S] )</th>
<th>Time, s</th>
<th>Integrals [S], mol/L</th>
<th>( \ln [S] )</th>
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</thead>
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<td>Trial 1, 0.063 M</td>
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<td></td>
<td>Trial 2, 0.061 M</td>
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<td>Trial 3, 0.059 M</td>
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</table>
Substrates and Data collected with Method B

**N-(3-Fluorophenyl)-N-(trifluoromethoxy)acetamide (2f)**

<table>
<thead>
<tr>
<th>Trial</th>
<th>Concentration mole/L</th>
<th>$k[S_o]$ mole·L$^{-1}$s$^{-1}$</th>
<th>$k$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.064</td>
<td>7.2084×10$^{-7}$</td>
<td>1.13×10$^{-5}$</td>
</tr>
<tr>
<td>2</td>
<td>0.058</td>
<td>5.5806×10$^{-7}$</td>
<td>9.62×10$^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>0.052</td>
<td>4.7753×10$^{-7}$</td>
<td>9.18×10$^{-6}$</td>
</tr>
<tr>
<td>average</td>
<td></td>
<td></td>
<td>9.64×10$^{-6}$</td>
</tr>
</tbody>
</table>

Trial 1: $[P] = 7.2084×10^{-7}t$
$R^2 = 0.9943$
Trial 2: $[P] = 5.5806×10^{-7}t$
$R^2 = 0.9960$
Trial 3: $[P] = 4.7753×10^{-7}t$
$R^2 = 0.9974$

---

**Trial 1, 0.064 M**
Time, s: 5755.52, Integrals [P], mol/L: 0.0722, [P], mol/L: 0.003362
Time, s: 1591.08, Integrals [P], mol/L: 0.0187, [P], mol/L: 0.000871
Time, s: 1591.08, Integrals [P], mol/L: 0.0164, [P], mol/L: 0.000764

**Trial 2, 0.058 M**
Time, s: 9237.92, Integrals [P], mol/L: 0.1428, [P], mol/L: 0.00665
Time, s: 5064.33, Integrals [P], mol/L: 0.067, [P], mol/L: 0.00312
Time, s: 5064.33, Integrals [P], mol/L: 0.0576, [P], mol/L: 0.002683

**Trial 3, 0.052 M**
Time, s: 10819.75, Integrals [P], mol/L: 0.2316, [P], mol/L: 0.01076
Time, s: 10412.92, Integrals [P], mol/L: 0.124, [P], mol/L: 0.005775
Time, s: 10412.92, Integrals [P], mol/L: 0.1091, [P], mol/L: 0.005081

**Trial 4, 0.029 M**
Time, s: 14586.48, Integrals [P], mol/L: 0.3178, [P], mol/L: 0.0148
Time, s: 15597.7, Integrals [P], mol/L: 0.1907, [P], mol/L: 0.008881
Time, s: 15597.7, Integrals [P], mol/L: 0.1612, [P], mol/L: 0.007507

---

**Graph**

- Trial 1: blue, 0.064 M
- Trial 2: red, 0.058 M
- Trial 3: green, 0.052 M
- Trial 4: black, 0.029 M

---

47
**N-(Trifluoromethoxy)-N-(3-(trifluoromethyl)phenyl)acetamide (2h)**

<table>
<thead>
<tr>
<th>Trial</th>
<th>Concentration mole/L</th>
<th>$k[S_o]$ mole·L$^{-1}$s$^{-1}$</th>
<th>$k$ s$^{-1}$</th>
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</thead>
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<td>$4.6687 \times 10^{-8}$</td>
<td>$7.08 \times 10^{-7}$</td>
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<tr>
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<td>$7.30 \times 10^{-7}$</td>
</tr>
<tr>
<td>average</td>
<td></td>
<td></td>
<td>$7.26 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

**Trial 1:** $[P] = 4.6687 \times 10^{-8}t$

$R^2 = 0.9991$

**Trial 2:** $[P] = 4.6767 \times 10^{-8}t$

$R^2 = 0.9942$

**Trial 3:** $[P] = 3.8088 \times 10^{-8}t$

$R^2 = 0.9934$

**Trial 1, 0.066 M**

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<th>Time, s</th>
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<th>Time, s</th>
<th>Integrals</th>
<th>$[P]$, mol/L</th>
<th>Time, s</th>
<th>Integrals</th>
<th>$[P]$, mol/L</th>
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**Trial 2, 0.063 M**

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<th>Time, s</th>
<th>Integrals</th>
<th>$[P]$, mol/L</th>
<th>Time, s</th>
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<td>0.000238</td>
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<td>0.000745</td>
<td>58082.14</td>
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<td>0.0021795</td>
<td>58082.14</td>
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<td>0.001951</td>
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<td>0.00394</td>
<td>81401.94</td>
<td>0.0803</td>
<td>0.0037397</td>
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<td>0.002859</td>
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<td>149657.9</td>
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**Trial 3, 0.052 M**

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<td>0.0101</td>
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<tr>
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<td>0.016</td>
<td>0.000745</td>
<td>58082.14</td>
<td>0.0468</td>
<td>0.0021795</td>
<td>58082.14</td>
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<td>0.0037397</td>
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Methyl 3-(N-(trifluoromethoxy)acetamido)benzoate (2g)

<table>
<thead>
<tr>
<th>Trial</th>
<th>Concentration mole/L</th>
<th>(k[S_o]) mole·L(^{-1})·s(^{-1})</th>
<th>(k) s(^{-1})</th>
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<tbody>
<tr>
<td>1</td>
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<td>3.63×10(^{-7})</td>
<td>9.33×10(^{-6})</td>
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<tr>
<td>2</td>
<td>0.035</td>
<td>3.43×10(^{-7})</td>
<td>9.80×10(^{-6})</td>
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<tr>
<td>3</td>
<td>0.029</td>
<td>2.41×10(^{-7})</td>
<td>8.30×10(^{-6})</td>
</tr>
<tr>
<td>average</td>
<td></td>
<td></td>
<td>9.1×10(^{-6})</td>
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</tbody>
</table>

Trial 1: \([P] = 3.6334×10^{-7}t\)  
\(R^2 = 0.9902\)

Trial 2: \([P] = 3.4299×10^{-7}t\)  
\(R^2 = 0.9898\)

Trial 3: \([P] = 2.4121×10^{-7}t\)  
\(R^2 = 0.9838\)

![Graph of Methyl 3-(N-(trifluoromethoxy)acetamido)benzoate (2g)]
The Hammett Plot

<table>
<thead>
<tr>
<th>substituent</th>
<th>log ((k_R/k_H))</th>
<th>(\sigma_p^+) or (\sigma_m)</th>
</tr>
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<tbody>
<tr>
<td>(m)-MeO</td>
<td>0.333214679</td>
<td>0.12</td>
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<tr>
<td>(p)-I</td>
<td>0.529509324</td>
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<tr>
<td>(p)-Br</td>
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<tr>
<td>(m)-F</td>
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<td>-2.15490196</td>
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<tr>
<td>(m)-CF₃</td>
<td>-3.253006732</td>
<td>0.43</td>
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</table>

\[ y = -11.86x + 1.99 \]
\[ R^2 = 0.99 \]

Activation Energy of OCF3 Migration of 2b

N-Phenyl-N-(trifluoromethoxy)acetamide (2b) at 60 °C

<table>
<thead>
<tr>
<th>Trial</th>
<th>Concentration mole/L</th>
<th>$k[S_0]$ mole·L⁻¹s⁻¹</th>
<th>$k$ s⁻¹</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.104</td>
<td>1.02×10⁻⁵</td>
<td>1.08×10⁻⁴</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>7.05×10⁻⁶</td>
<td>8.81×10⁻⁵</td>
</tr>
<tr>
<td>3</td>
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<td>5.05×10⁻⁶</td>
<td>9.27×10⁻⁵</td>
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<tr>
<td>average</td>
<td></td>
<td></td>
<td>9.30×10⁻⁵</td>
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</tbody>
</table>

Trial 1: $[P] = 1.02×10^{-5}t$
$R^2 = 0.9971$

Trial 2: $[P] = 7.05×10^{-6}t$
$R^2 = 0.9954$

Trial 3: $[P] = 5.05×10^{-6}t$
$R^2 = 0.9963$

![Graph showing concentration-time data for trials 1, 2, and 3](image)

### Trial 1, 0.104 M

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<th>Integrals</th>
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<tr>
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<td>0.1122</td>
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<tr>
<td>784.6</td>
<td>0.1753</td>
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<tr>
<td>1133.2</td>
<td>0.2443</td>
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<tr>
<td>1583.2</td>
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### Trial 2, 0.080 M

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### Trial 3, 0.0545 M

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<tr>
<td>2336.3</td>
<td>0.0118811</td>
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### Charts

- **Trial 1** (0.104 M)
- **Trial 2** (0.080 M)
- **Trial 3** (0.0545 M)
The experimental activation energy for the OCF$_3$-migration process of substrate 2b was calculated using Arrhenius equation and based on the kinetic data of substrate 2b at 80 °C and 60 °C.

Arrhenius equation:

\[ k = A e^{-\frac{E_a}{RT}} \]

Where \( k \) is the rate constant of the reaction, \( R \) is the universal gas constant, 1.987 cal K$^{-1}$ mol$^{-1}$, \( T \) is the absolute temperature, \( A \) is constant.

\( k_1 = 0.0013 \text{ s}^{-1} \) at \( T_1 = 353 \text{ K} \)

\( k_2 = 9.3 \times 10^{-5} \text{ s}^{-1} \) at \( T_2 = 333 \text{ K} \)

\[ E_a = \left[ \frac{RT_1T_2}{(T_1-T_2)} \right] \times \ln(\frac{k_1}{k_2}) = 30.8 \text{ kcal/mol} \]
Computational Details

All DFT calculations were performed with the Gaussian 09 software package. Geometries were optimized using the M06-2X functional and the 6-31+G(d) basis set in solution. The SMD solvation model and MeNO$_2$ solvent were used in the calculations. Single point energies were calculated using M06-2X and 6-311++G(d,p) and the SMD solvation model in MeNO$_2$. Reported Gibbs free energies and enthalpies in solution include thermal corrections computed at 298 K.

Complete Reference of Gaussian 09

Reaction Energy Profile of the OCF₃ Migration of 2a

a. Reaction energy profile of the OCF₃-migration of 2a

ΔG

(ΔH)
kcal/mol

[301x61]54

[72x698]Reaction

[116x698]Energy

[153x698]Profile

[188x698]of

[200x698]the

[217x698]OCF₃

[240x697]Migration

[247x698]of

[297x698]2a

TS3

0.0

(0.0)

2a

O

N

OCF₃

R

R

26.4

(28.1)

TS4

-4.1

(-4.6)

14

O

Me

R

R

24.4

(27.5)

13

32.2

(33.2)

O

Me

N

OCF₃

b. Optimized geometries of the ion-pair intermediate 13 and the transition states of N–O cleavage (TS3) and C–O formation (TS4)

R = CO₂Me
Reaction Energy Profile of the OCF₃ Migration of 2b

a. Reaction energy profile of the OCF₃-migration of 2b

\[ \Delta G \ (\Delta H) \text{ kcal/mol} \]

\[ \begin{array}{c}
\text{TS1} \\
27.6 \\
20.4 \\
19.2 \\
27.6 \\
20.4 \\
\end{array} \]

\[ \begin{array}{c}
\text{10} \\
10.4 \\
19.2 \\
10.4 \\
19.2 \\
\end{array} \]

\[ \begin{array}{c}
\text{TS2} \\
0.0 \\
10.4 \\
0.0 \\
10.4 \\
0.0 \\
\end{array} \]

\[ \begin{array}{c}
\text{2b} \\
27.6 \\
20.4 \\
19.2 \\
27.6 \\
20.4 \\
\end{array} \]

b. Optimized geometries of the ion-pair intermediate 10 and the transition states of N-O cleavage (TS1) and C-O formation (TS2)
Potential Energy Surface of OCF$_3$ Migration of 2b

The concerted OCF$_3$ migration transition state that directly connects 2b and the dearomatized intermediate 11 cannot be located in the geometry optimization. To evaluate if such concerted pathway exists and competes with the stepwise process, the potential energy surface of the OCF$_3$ migration was constructed at the M06-2X/6-31+G(d)/SMD(MeNO$_2$) level of theory and is shown in Fig. S9. The stationary points in the stepwise pathway (2b, TS1, 10, TS2, and 11) are labeled on the surface. The potential energy surface clearly indicates that the concerted reaction pathway, in which the C-O bond formation and the N-O bond cleavage take place simultaneously, requires a much higher barrier than the stepwise pathway (TS1 and TS2). The stepwise pathway described in Fig. 4 in the main text is thus more favorable than the concerted process.

Figure S9. Potential Energy Surface of OCF$_3$ Migration from 2b to Form 11.
### Cartesian Coordinates and Energies of Optimized Structures

**2b**

\[
\begin{align*}
\text{M06-2X/6-31+G(d) SCF energy:} & \quad -852.18829646 \text{ a.u.} \\
\text{M06-2X/6-31+G(d) enthalpy:} & \quad -852.009108 \text{ a.u.} \\
\text{M06-2X/6-31+G(d) free energy:} & \quad -852.065810 \text{ a.u.} \\
\text{M06-2X/6-311++G(d,p) SCF energy:} & \quad -852.41585217 \text{ a.u.} \\
\text{M06-2X/6-311++G(d,p) enthalpy:} & \quad -852.236664 \text{ a.u.} \\
\text{M06-2X/6-311++G(d,p) free energy:} & \quad -852.293366 \text{ a.u.}
\end{align*}
\]

**Cartesian coordinates**

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<th>Z</th>
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</table>

**TS1**

\[
\begin{align*}
\text{M06-2X/6-31+G(d) SCF energy:} & \quad -852.13763527 \text{ a.u.} \\
\text{M06-2X/6-31+G(d) enthalpy:} & \quad -851.962090 \text{ a.u.} \\
\text{M06-2X/6-31+G(d) free energy:} & \quad -852.019775 \text{ a.u.} \\
\text{M06-2X/6-311++G(d,p) SCF energy:} & \quad -852.36722909 \text{ a.u.} \\
\text{M06-2X/6-311++G(d,p) enthalpy:} & \quad -852.191684 \text{ a.u.} \\
\text{M06-2X/6-311++G(d,p) free energy:} & \quad -852.249369 \text{ a.u.} \\
\text{Imaginary frequency:} & \quad -225.7874 \text{ cm}^{-1}
\end{align*}
\]

**Cartesian coordinates**

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<th>Z</th>
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M06-2X/6-31+G(d) enthalpy: -851.971486 a.u.
M06-2X/6-31+G(d) free energy: -852.032054 a.u.
M06-2X/6-31++G(d,p) SCF energy: -852.37577142 a.u.
M06-2X/6-31++G(d,p) enthalpy: -852.199276 a.u.
M06-2X/6-31++G(d,p) free energy: -852.259844 a.u.
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M06-2X/6-31+G(d) enthalpy: -851.971587 a.u.
M06-2X/6-31+G(d) free energy: -852.030645 a.u.
M06-2X/6-311++G(d,p) SCF energy: -852.37715583 a.u.
M06-2X/6-311++G(d,p) enthalpy: -852.201773 a.u.
M06-2X/6-311++G(d,p) free energy: -852.260831 a.u.

Imaginary frequency: -91.6548 cm⁻¹

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M06-2X/6-31+G(d) enthalpy: -852.015340 a.u.
M06-2X/6-31+G(d) free energy: -852.074457 a.u.
M06-2X/6-311++G(d,p) SCF energy: -852.42276525 a.u.
M06-2X/6-311++G(d,p) enthalpy: -852.243784 a.u.
M06-2X/6-311++G(d,p) free energy: -852.302901 a.u.

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12a
M06-2X/6-31+G(d) SCF energy: -852.63294428 a.u.
M06-2X/6-31+G(d) enthalpy: -852.440587 a.u.
M06-2X/6-31+G(d) free energy: -852.497443 a.u.
M06-2X/6-311++G(d,p) SCF energy: -852.86314667 a.u.
M06-2X/6-311++G(d,p) enthalpy: -852.670789 a.u.
M06-2X/6-311++G(d,p) free energy: -852.727645 a.u.

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M06-2X/6-31+G(d) free energy: -851.655866 a.u.
M06-2X/6-31++G(d,p) SCF energy: -851.99322525 a.u.
M06-2X/6-31++G(d,p) enthalpy: -851.827109 a.u.
M06-2X/6-31++G(d,p) free energy: -851.882981 a.u.

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M06-2X/6-31+G(d) free energy: -852.132194 a.u.
M06-2X/6-311++G(d,p) SCF energy: -852.48453400 a.u.
M06-2X/6-311++G(d,p) enthalpy: -852.304074 a.u.
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Spectroscopic Data

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$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S2
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$^{19}$F NMR (CDCl$_3$, 25 °C) of 3a
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S3
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 ºC) of S3
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S4
$^{13}$C NMR ((CD$_3$)$_2$SO, 25°C) of S4
$^1$H NMR (CDCl$_3$, 25 °C) of 2b
$^{13}$C NMR (CDCl$_3$, 25 °C) of 2b
$^{19}$F NMR (CDCl$_3$, 25 °C) of 2b
$^{1}$H NMR (CDCl$_3$, 25 °C) of 3b
$^{13}$C NMR (CDCl$_3$, 25 °C) of 3b
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3b
$^1$H NMR (CDCl$_3$, 25 °C) of 3b-II
$^{13}$C NMR (CDCl₃, 25 °C) of 3b-II
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3b-II
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S5
$\textsuperscript{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S5
\(^1\)H NMR ((CD\(_3\))\(_2\)SO, 25 °C) of S6
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S6
$^1$H NMR (CDCl$_3$, 25 °C) of 2c
\(^{13}\text{C} \text{NMR} (\text{CDCl}_3, 25 ^\circ \text{C})\) of 2c

\[
\text{OMe} \\
\text{N} \\
\text{OCF}_3 \\
2c
\]
$^{19}$F NMR (CDCl$_3$, 25 $^\circ$C) of 2c
$^1$H NMR (CDCl$_3$, 25 °C) of 3c
$^{13}$C NMR (CDCl$_3$, 25 °C) of 3c
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3c
$^1$H NMR (CDCl$_3$, 25 ºC) of 3c-II
$^{13}$C NMR (CDCl$_3$, 25 °C) of 3c-II
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3c-II
$^1$H NMR ((CD$_3$)$_2$SO, 25 $^\circ$C) of S7

![NMR Spectrum of S7](image-url)
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S7
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S8
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 $^\circ$C) of S8
$^1$H NMR (CDCl$_3$, 25 °C) of 2d
$^{13}$C NMR (CDCl$_3$, 25 °C) of 2d
$^{19}$F NMR (CDCl$_3$, 25 °C) of 2d
$^1$H NMR (CDCl$_3$, 25 °C) of 3d
$^{13}$C NMR (CDCl$_3$, 25 °C) of 3d
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3d
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S9
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S9
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S10
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S10
$^{1}$H NMR (CDCl$_3$, 25 °C) of 2e
$^{13}$C NMR (CDCl$_3$, 25 °C) of 2e
$^{19}$F NMR (CDCl$_3$, 25 °C) of 2e
$^1$H NMR (CDCl$_3$, 25 °C) of 3e
$^{13}$C NMR (CDCl$_3$, 25 °C) of 3e
$^{19}$F NMR (CDCl$_3$, 25 °C) of $3e$
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S11
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S11
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S12
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S12
$^1$H NMR (CDCl$_3$, 25 °C) of 2f
$^{13}$C NMR (CDCl$_3$, 25 °C) of 2f
$^{19}$F NMR (CDCl$_3$, 25 °C) of 2f
$^1$H NMR (CDCl$_3$, 25 °C) of 3f
$^{13}$C NMR (CDCl$_3$, 25 °C) of $3f$
$^{19}$F NMR (CDCl$_3$, 25 ºC) of 3f
$^1$H NMR (CDCl$_3$, 25 ºC) of 3f-II
\(^{13}\)C NMR (CDCl\(_3\), 25 °C) of 3f-II
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3f-II
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S13
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S13
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S14
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S14
$^1$H NMR (CDCl$_3$, 25 °C) of 2g
$^{13}$C NMR (CDCl$_3$, 25 °C) of 2g
$^{19}\text{F NMR (CDCl}_3, 25 \, ^\circ\text{C) of 2g}$
$^1$H NMR (CDCl$_3$, 25 °C) of 3g
$^{13}$C NMR (CDCl$_3$, 25 °C) of 3g
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3g
$^1$H NMR (CDCl$_3$, 25 ºC) of 3g-II
$^{13}$C NMR (CDCl$_3$, 25 °C) of 3g-II
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3g-II
$^1$H NMR ((CD$_3$)$_2$SO, 25 ºC) of S15
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S15
$^{19}$F NMR ((CD$_3$)$_2$SO, 25 °C) of S15
$^1$H NMR ((CD$_3$)$_2$SO, 25 ºC) of S16
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S16
$^{19}$F NMR ((CD$_3$)$_2$SO, 25 °C) of S16
$^1$H NMR (CDCl$_3$, 25 °C) of 2h
$^{13}\text{C} \text{ NMR (CDCl}_3, \ 25 \ ^\circ\text{C}) \ of \ 2h$
$^{19}$F NMR (CDCl$_3$, 25 °C) of 2h
$^1$H NMR (CDCl$_3$, 25 °C) of 3h
$^{13}$C NMR (CDCl$_3$, 25 °C) of 3h
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3h
$^1$H NMR (CDCl$_3$, 25 °C) of 3h-II
$^{13}$C NMR (CDCl$_3$, 25 $^\circ$C) of 3h-II
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3h-II
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S17
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S17
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S18
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S18
$^1$H NMR (CDCl$_3$, 25 °C) of 2i
$^{13}$C NMR (CDCl$_3$, 25 °C) of 2i
$^{19}$F NMR (CDCl$_3$, 25 °C) of 2i
$^1$H NMR (CDCl$_3$, 25 °C) of 3i

![Chemical structure of 3i with NMR spectrum]
$^{13}$C NMR (CDCl$_3$, 25 °C) of 3i
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3i
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S19

![NMR Spectrum of S19]
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S19
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S20
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S20
$^1$H NMR (CDCl$_3$, 25 °C) of 2j
$^{13}$C NMR (CDCl$_3$, 25 °C) of 2j
$^{19}$F NMR (CDCl$_3$, 25 °C) of 2j
$^1$H NMR (CDCl$_3$, 25 °C) of 3j
$^{13}$C NMR (CDCl$_3$, 25 °C) of 3j
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3j
$^1$H NMR ((CD$_3$)$_2$SO, 25 ºC) of S21
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S21
$^{19}$F NMR ((CD$_3$)$_2$SO, 25 °C) of S21
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S22
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S22
$^{19}$F NMR ((CD$_3$)$_2$SO, 25 °C) of S22
$^1$H NMR (CDCl$_3$, 25 °C) of 2k
$^{13}$C NMR (CDCl$_3$, 25 °C) of 2k
$^{19}$F NMR (CDCl$_3$, 25 °C) of 2k
$^1$H NMR ((CD$_3$)$_2$SO, 25 ºC) of S23
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S23
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S24
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 ºC) of S24
$^1$H NMR (CDCl$_3$, 25 °C) of 3I
$^{13}$C NMR (CDCl$_3$, 25 °C) of 3l
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3l
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S25
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S25
$^1$H NMR (CDCl$_3$, 25 °C) of 2m
$^{13}$C NMR (CDCl$_3$, 25 °C) of $2m$
$^{19}$F NMR (CDCl$_3$, 25 °C) of 2m
$^1$H NMR (CDCl$_3$, 25 °C) of 3m
$^{13}$C NMR (CDCl$_3$, 25 °C) of 3m

![Chemical structure of 3m]
$^{19}$F NMR (CDCl$_3$, 25 °C) of 3m
$^{1}H$ NMR (CDCl$_3$, 25 °C) of 3m’
$^{13}$C NMR (CDCl$_3$, 25 ºC) of 3m'}
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S26
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S26
$^1$H NMR ((CD$_3$)$_2$SO, 25 °C) of S27
$^{13}$C NMR ((CD$_3$)$_2$SO, 25 °C) of S27
$^1$H NMR (CDCl$_3$, 25 ºC) of 6
$^{13}$C NMR (CDCl$_3$, 25 °C) of 6
$^{19}$F NMR (CDCl$_3$, 25 °C) of 6
$^1$H NMR (CDCl$_3$, 25 °C) of 8
$^{13}$C NMR (CDCl$_3$, 25 °C) of 8
$^{19}$F NMR (CDCl₃, 25 °C) of 8