Supporting Information

Silver-Mediated Trifluoromethoxylation of (Hetero) Aryldiazonium Tetrafluoroborates

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1. General Information

All commercially available compounds were purchased from Energy Chemical, Tansoole or Bide Pharmatech Ltd, and used without further purification, unless otherwise noted. NMR spectra were recorded on Bruker 400 (400 MHz for $^1$H; 376 MHz for $^{19}$F; 100 MHz for $^{13}$C) spectrometer. The chemical shifts (δ) are given in parts per million relative to CDCl$_3$ (7.26 ppm for $^1$H), TMS (0 ppm for $^1$H) and CDCl$_3$ (77.0 ppm for $^{13}$C), DMSO-d$_6$ (2.50 ppm for $^1$H). High-resolution mass spectra were obtained on Thermo Fisher LTQ Orbitrap Velos Pro ETD mass spectrometer, Electron Ionization mass spectra were obtained on Shimadzu GCMS-QP2010 Ultra mass spectrometer at Advanced Research Center, Central South University. $^{19}$F NMR chemical shifts were determined relative to 1, 3, 5-trifluorobenzene (-108.0 ppm) as internal standard. $^1$H and $^{19}$F multiplicities are reported as following: singlet (s), doublet (d), doublet of doublets (dd), quartet (q), multiplet (m), and broad resonance (br). The CH$_3$CN-solvated AgOCF$_3$ was prepared according to the known procedures.$^{[S3][S4]}$ Flash column chromatography was performed on silica gel (particle size 200-300 mesh).

2. Experimental Section

2.1 Synthesis of TFMS

2.1.1 Trifluoromethyl 4-fluorobenzenesulfonate (TFMS) $^1$

\[
\begin{align*}
\text{F} & \quad \text{SO}_2 \quad \text{Cl} \\
\text{S} & \quad \text{O} \\
\text{1. dioxane: H}_2\text{O, 100°C} & \\
\text{2. Togni’s Reagent} & \\
\text{CHCl}_3: \text{tBuOH, rt} & \\
\rightarrow & \\
\text{F} & \quad \text{SO}_2 \quad \text{OCF}_3
\end{align*}
\]

Dissolve 4-Fluorobenzenesulfonyl chloride (5.0 g, 25.7 mmol) in solvent of dioxane (12.5 mL) and water (12.5 mL), then heated under refluxing for 5 h. The solvent was removed under reduced pressure to afford 4-fluorobenzenesulfonic acid (4.30 g) as a white solid (95% yield). Dissolve 4-fluorobenzenesulfonic acid (3.90 g, 22.2 mmol, 2.0 equiv) and Togni’s reagent (3.49 g, 11.1 mmol, 1.0 equiv) in solvent of CHCl$_3$ (15.0 mL) and tBuOH (3.0 mL) under an atmosphere of argon, room temperature overnight. Neutralize the reaction with NaHCO$_3$ (1.0 M) and extracted 3 times with CH$_2$Cl$_2$ (20
mL). The combined organic layers were dried over Na$_2$SO$_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with petroleum ether to afford 2.17 g trifluoromethyl 4-fluorobenzenesulfonate (TFMS) as a clear oil (80% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.06 (m, 2H), 7.32 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -53.96 (s, 3F), -99.08 (s, 1F).

2.1.2 Methoxy 4-(trifluoromethyl)benzenesulfonate (TFMS3)

\[
\begin{align*}
\text{MeC} & \quad \text{S} \quad \text{Cl} & \quad \text{1. dioxane:H$_2$O, 100°C} & \quad \text{MeC} & \quad \text{S} \quad \text{OCF}_3 \\
\text{1. dioxane:H$_2$O, 100°C} & \quad \text{2. Togni's Reagent} & \quad \text{CHCl$_3$:tBuOH, rt} & \quad \text{1. dioxane:H$_2$O, 100°C} & \quad \text{2. Togni's Reagent} & \quad \text{CHCl$_3$:tBuOH, rt}
\end{align*}
\]

Dissolve 4-Methoxy-benzenesulfonyl chloride (5.0 g, 20.4 mmol) in solvent of dioxane (12.5 mL) and water (12.5 mL), then heated under reflux for 5 h. The solvent was removed under reduced pressure to afford 4-Methoxy-benzenesulfonic acid (4.5 g) as a white solid (98% yield). Dissolve 4-Methoxy-fluorobenzenesulfonic acid (4.2 g, 22.2 mmol, 2.0 equiv) and Togni’s reagent (3.49 g, 11.1 mmol, 1.0 equiv) in solvent of CHCl$_3$ (15.0 mL) and tBuOH (3.0 mL) under an atmosphere of argon, room temperature overnight. Neutralize the reaction with NaHCO$_3$ (1.0 M) and extracted 3 times with CH$_2$Cl$_2$ (20 mL). The combined organic layers were dried over Na$_2$SO$_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with petroleum ether to afford 2.56 g Methoxy 4-(trifluoromethyl)benzenesulfonate (TFMS3) as a clear oil (90% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J = 9.0$ Hz, 2H), 7.06 (d, $J = 9.0$ Hz, 2H), 3.92 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -54.08 (s, 3F).

2.1.3 Trifluoromethyl 2, 4, 6-triisopropylbenzenesulfonate (TFMS2)

\[
\begin{align*}
\text{iPr} & \quad \text{O} \quad \text{SO} & \quad \text{1. dioxane: H$_2$O, 100°C} & \quad \text{iPr} & \quad \text{O} \quad \text{SO} \\
\text{iPr} & \quad \text{O} \quad \text{SO} & \quad \text{2. Togni's Reagent} & \quad \text{iPr} & \quad \text{O} \quad \text{SO} \\
\text{iPr} & \quad \text{O} \quad \text{SO} & \quad \text{CHCl$_3$:tBuOH, rt} & \quad \text{iPr} & \quad \text{O} \quad \text{SO} \\
\text{iPr} & \quad \text{O} \quad \text{SO} & \quad \text{CHCl$_3$:tBuOH, rt} & \quad \text{iPr} & \quad \text{O} \quad \text{SO} \\
\text{iPr} & \quad \text{O} \quad \text{SO} & \quad \text{CHCl$_3$:tBuOH, rt} & \quad \text{iPr} & \quad \text{O} \quad \text{SO} \\
\text{iPr} & \quad \text{O} \quad \text{SO} & \quad \text{CHCl$_3$:tBuOH, rt} & \quad \text{iPr} & \quad \text{O} \quad \text{SO} \\
\text{iPr} & \quad \text{O} \quad \text{SO} & \quad \text{CHCl$_3$:tBuOH, rt} & \quad \text{iPr} & \quad \text{O} \quad \text{SO} \\
\text{iPr} & \quad \text{O} \quad \text{SO} & \quad \text{CHCl$_3$:tBuOH, rt} & \quad \text{iPr} & \quad \text{O} \quad \text{SO} \\
\end{align*}
\]
Dissolve 2, 4, 6-Triisopropylbenzenesulfonyl chloride (5.0 g, 16.5 mmol) in solvent of dioxane (12.5 mL) and water (12.5 mL), then heated under reflux for 5 h. The solvent was removed under reduced pressure to afford 2, 4, 6-Triisopropylbenzenesulfonic acid (4.66 g) as a white solid (99% yield). Dissolve 2, 4, 6-Triisopropylbenzenesulfonic acid (3.16 g, 11.1 mmol, 2.0 equiv) and Togni’s reagent (1.75 g, 5.05 mmol, 1.0 equiv) in solvent of CHCl$_3$ (15.0 mL) and tBuOH (3.0 mL) under an atmosphere of argon, room temperature overnight. Neutralize the reaction with NaHCO$_3$ (1.0 M) and extracted 3 times with CH$_2$Cl$_2$ (20 mL). The combined organic layers were dried over Na$_2$SO$_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with hexanes to afford 1.6 g trifluoromethyl 2, 4, 6-triisopropylbenzenesulfonate (TFMS2) as a clear oil (90% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24 (s, 2H), 4.05 (dt, $J = 13.5$, 6.7 Hz, 2H), 2.94 (dt, $J = 13.8$, 6.9 Hz, 1H), 1.28 (dd, $J = 6.8$, 3.0 Hz, 18H).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -53.51 (s, 3F).

2.2 Synthesis of CF$_3$SO$_2$OFCF$_3$$_2$, 3

CF$_3$SO$_3$H (205.0 g, 120 mL, 1.37 mol) was added to a three-necked flask equipped a condenser under vigorous stirring. Anhydrous P$_2$O$_5$ (32.0 g, 0.23 mol) was added portion-wise and the mixture was heated to 120°C in about 3 hours, keep temperature at 130 °C for 1 hour and at 150°C for another 2 hours. The product (CF$_3$SO$_2$OFCF$_3$, TFMT) was collected by bubbling into aqueous NaOH solution (50.0 g NaOH in 800 mL water ) at -10°C. The bottom layer was separated from the NaOH solution and distilled with anhydrous P$_2$O$_5$ to give 45 mL of CF$_3$SO$_2$OFCF$_3$ as a colorless liquid (80.6 g, 54%, b.p. 21°C), which was stored over anhydrous P$_2$O$_5$ for further use in a freezer (-30°C). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -53.0 (s, 3F), -73.6 (s, 3F).

2.3 Synthesis of AgOCF$_3$ (1.0 M in MeCN) 3, 4

The AgOCF$_3$ stock solution was prepared according to the known procedure reported by Vivic[S3] with slight modification: 2.53 g of AgF was added into a 100 mL Schlenk flask (The Schlenk flask was evacuated and backfilled with argon for three
times) and 20 mL of dry CH$_3$CN was then added. The mixture was cooled in a CH$_3$CN/dry ice bath (ca. -40 °C). CF$_3$SO$_2$OCF$_3$ (7.2 mL) was introduced into the reaction mixture in one shot by syringe. The mixture was violently stirring at -40 °C and warmed gradually to room temperature overnight. After all the AgF solid was dissolved, the solution was degassed with argon. The obtained colorless (or light yellow) solution was stored in the Schlenk flask (100 mL) in darkness at -20 °C for use. AgOCF$_3$ solution in CH$_3$CN (~1.0 mol/L, 20 mL) was obtained as colorless liquid. $^{19}$F NMR (376 MHz, CD$_3$CN) δ -24.8 (s, 3F).

2.4 Syntheses of Substrates

2.4.1 Synthesis of 3-(2-phenylethynyl)benzenamine 15a

To a Schlenk flask containing diisopropylamine (7.0 mL) was added with 3-iodobenzenamine (500 mg, 2.89 mmol), CuI (55 mg, 0.29 mmol), Pd(dppf)$_2$Cl$_2$ (85 mg, 0.17 mmol) and phenylacetylene (0.95 mL, 884 mg, 8.67 mmol) under argon. The flask was sealed and stirred at 60 °C for 72 hours. A solution of 3:1 CHCl$_3$/IPA (100 mL) and aqueous 0.1 M EDTA/NH$_4$OH solution (100 mL) were added and stirred for one hour. The organic layer was washed with water (50 mL), brine (50 mL) and dried over Na$_2$SO$_4$, filtered, and the solvent was removed under vacuum. The resultant solid was purified by column chromatography (1:6 ethyl acetate / petroleum ether) to give the product as a brown solid (523 mg, 2.71 mmol, 94%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (dd, $J = 7.4$, 2.2 Hz, 1H), 7.34 (dd, $J = 4.9$, 2.2 Hz, 1H), 7.13 (t, $J = 7.8$ Hz, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 6.87 (d, $J = 1.8$ Hz, 1H), 6.71 – 6.61 (m, 1H), 3.68 (s, 1H).

2.4.2 Synthesis of 5-p-tolylpyridin-3-amine 12a

2.5
5-Bromopyridin-3-amine (6 mmol) and 4-methylphenylboronic acid (7 mmol) were dissolved in toluene/ethanol (30 mL/3 mL) in a 100 mL Schlenk flask at room temperature under argon. Na$_2$CO$_3$ solution (2 N, 6 mL) was added. The mixture was stirred for 30 minutes at room temperature and then treated with tetrakis(triphenylphosphine) palladium (0) (277 mg, 0.24 mmol) and refluxed for 24 hours. The reaction was cooled to room temperature and partitioned between EtOAc and water, the organic layer was separated and dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. The residue was purified by flash chromatography to give the desired product (670 mg, 3.66 mmol, 61%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 (d, $J$ = 1.6 Hz, 1H), 8.05 (d, $J$ = 2.5 Hz, 1H), 7.44 (d, $J$ = 8.0 Hz, 2H), 7.25 (d, $J$ = 6.8 Hz, 3H), 7.21 (d, $J$ = 6.8 Hz).

2.4.3 Synthesis of 3-(Allyloxy)aniline 14a

To a solution of 3-aminophenol (8.12 g, 74.4 mmol) in EtOAc (80 mL) was added Ac$_2$O (16.3 mL, 168 mmol) dropwise at 0 °C, and the mixture was stirred at room temperature for 4 h. The reaction mixture was concentrated in vacuo, and the residual solid was recrystallized from MeOH: acetone (1:1) and CH$_2$Cl$_2$ at 0°C. 3-hydroxyacetanilide (9.45 g, 62.6 mmol, 84%) was isolated as a light yellow powder (9.2 g, 6.1 mmol, 82%).

To a solution of 3-hydroxyacetanilide (4.53 g, 30 mmol) and K$_2$CO$_3$ (4.20 g, 30 mmol) in anhydrous acetone (11 mL) was added allyl bromide (2.60 mL, 30 mmol) dropwise at 0 °C. The reaction was refluxing for 20 hours. The reaction mixture was quenched with water and extracted with Et$_2$O (2 × 50 mL), washed with water (50
mL), and NaOH (aq., 10%) and dried under anhydrous MgSO₄. The crude product was purified by flash column chromatography (3.9 g, 20.7 mmol, 69%).

A solution of N-(2-(allyloxy)phenyl)acetamide (1.91 g, 10 mmol) in 6 M HCl (2.4 mL) was refluxed for 4 h. The mixture was basified with 4 N sodium hydroxide solution until pH = 14. This basified solution was extracted with EtOAc (2 × 20 mL) and dried over anhydrous MgSO₄. The organic solvent was evaporated and the crude product purified by flash column chromatography to give the desired product (1.2 g, 8 mmol, 80%).

\(^1\)H NMR (400 MHz, CDCl₃) δ 7.06 (t, \(J = 8.0\) Hz, 1H), 6.35 (dd, \(J = 8.2, 1.7\) Hz, 1H), 6.29 (dt, \(J = 4.2, 1.7\) Hz, 1H), 6.05 (tdt, \(J = 15.8, 10.5, 5.3\) Hz, 1H), 5.41 (dd, \(J = 17.3, 1.5\) Hz, 1H), 5.28 (dd, \(J = 10.5, 1.3\) Hz, 1H), 4.50 (dd, \(J = 4.0, 1.3\) Hz, 1H), 3.47 (s, 1H).

2.4.4 Synthesis of (1R, 2S, 4S)-2-isopropyl-4-methylcyclohexyl 3-aminobenzoate 49a

To a mixture of L-Menthol (3.2 g, 20.0 mmol, 1.0 equiv) and Et₃N (2.2 g, 22.0 mmol, 1.1 equiv) in DCM (16 mL) was added a solution of 3-nitrobenzoyl chloride (4.08 g, 22.0 mmol, 1.1 equiv.) in DCM (100 mL) at 0°C. The reaction was allowed to reflux for 20 hours. After the reaction was complete, the reaction mixture was diluted with EtOAc (60 mL) and filtrated through a pad of silica gel. The solvent was removed under reduced pressure with a rotary evaporator and the crude residue was purified by a silica gel column chromatography (DCM) to give L-Menthol 3-nitrobenzoate (5.4 g, 90%) as a yellow oil.

To 5% palladium-on-carbon (10% wet with water, 291 mg) under a nitrogen atmosphere was added L-Menthol 3-nitro benzoate (3.0 g, 10 mmol, 1.0 equiv)
dissolved in MeOH (20 mL) and EtOAc (20 mL). The reaction mixture was stirred under a hydrogen atmosphere (1 atm in balloon) for 24 hours. The catalyst was removed by filtration through Celite. The solvent was removed under reduced pressure with a rotary evaporator and the crude residue was purified by silica gel column chromatography (PE: EtOAc = 5:1) to give L-Menthol 3-amino benzoate (2.5 g, 9 mmol, 90%).

1H NMR (400 MHz, CDCl₃) δ 7.72 – 7.58 (m, 2H), 7.35 (t, J = 8.1 Hz, 1H), 7.22 – 7.12 (m, 1H), 5.35 (s, 1H), 4.93 (td, J = 10.9, 4.4 Hz, 1H), 2.12 (d, J = 11.6 Hz, 1H), 1.95 (ddt, J = 13.9, 7.0, 2.7 Hz, 1H), 1.73 (d, J = 11.6 Hz, 2H), 1.54 (dd, J = 11.9, 2.4 Hz, 2H), 1.27 (d, J = 10.3 Hz, 2H), 1.17 – 1.07 (m, 2H), 0.97 – 0.89 (m, 8H), 0.79 (d, J = 6.9 Hz, 3H).

13C NMR (100 MHz, CDCl₃) δ 166.2, 150.0, 131.5, 128.9, 123.2, 118.7, 115.3, 75.0, 47.2, 40.9, 34.3, 31.4 (d, J = 4.2 Hz), 26.4, 23.6, 22.0, 20.7, 16.4.

2.4.5 Synthesis of (R)-2, 5, 7, 8-tetramethyl-2-((4R, 8R)-4, 8, 12-trimethyltridecyl)chroman-6-yl 3-aminobenzoate 50a

![Chemical Structure](image)

To a mixture of D-α-tocopherol (4.31 g, 10.0 mmol, 1.0 equiv) and Et₃N (1.11 g, 11.0 mmol, 1.1 equiv) in DCM (16 mL) was added a solution of 3-nitro-benzoyl chloride (2.04 g, 11.0 mmol, 1.1 equiv) in DCM (100 mL) at 0 ℃. The reaction was allowed to reflux for 20 hours. After the reaction was complete, the reaction mixture was diluted with EtOAc (60 mL) and filtrated through a pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography (PE: EtOAc = 9:1) to give D-α-tocopherol 4-nitro benzoate (5.25 g, 90%) as a yellow oil. To 5% palladium-
on-carbon (10% wet with water, 291 mg) under a nitrogen atmosphere was added D-α-tocopherol 4-nitro benzoate (3.50 g, 6.04 mmol, 1.0 equiv) dissolved in MeOH (20 mL) and EtOAc (20 mL). The reaction mixture was stirred under a hydrogen atmosphere (1 atm in balloon) for 24 hours. The catalyst was removed by filtration through Celite. The solvent was removed under reduced pressure with a rotary evaporator and the crude residue was purified by silica gel column chromatography (PE:EtOAc = 5:1) to give D-α-tocopherol 3-amino benzoate (2.72 g, 82%) as a pale yellow solid.

\[
\begin{array}{c}
\text{1H NMR (400 MHz, DMSO)} \delta 9.51 \text{ (s, 1H), 8.98 (d, } J = 8.3 \text{ Hz, 1H), 8.91 (d, } J = 8.1 \text{ Hz, 1H), 8.21 (t, } J = 8.2 \text{ Hz, 1H), 3.57 (s, 12H), 2.61 (d, } J = 6.6 \text{ Hz, 2H), 2.07 (s, 4H), 1.98 (s, 4H), 1.96 (s, 4H), 1.79 (t, } J = 6.7 \text{ Hz, 3H), 1.59 – 1.44 (m, 5H), 1.40 (d, } J = 5.4 \text{ Hz, 4H), 1.24 (d, } J = 14.1 \text{ Hz, 13H), 1.16 – 1.02 (m, 8H), 0.83 (t, } J = 6.1 \text{ Hz, 14H).}
\end{array}
\]

\[
\begin{array}{c}
\text{13C NMR (100 MHz, CDCl}_3\text{) } \delta 165.3, 149.4, 146.7, 140.6, 130.5, 129.4, 126.9, 125.1, 123.0, 120.1, 119.7, 117.4, 116.1, 75.0, 39.3, 37.4, 37.3, 32.8, 32.7, 27.9, 24.8, 24.4, 22.7, 22.6, 21.0, 20.6, 19.7, 19.6, 13.0, 12.10, 11.80.
\end{array}
\]

2.5 Preparation of Diazonium Salts

In a 50 mL Schlenk flask, the aniline (10 mmol) was dissolved in absolute ethanol (5.0 mL). An aqueous solution of HBF₄ (48%, 2.5 mL) was added, followed by dropwise addition of tBuONO (2.7 mL) at 0°C. After stirring at room temperature for 1 hour, diethyl ether (20 mL) was added to precipitate the (Hetero) aryl diazonium tetrafluoroborate. After filtration and washing with diethyl ether (3×10 mL), the product was dried in vacuo and stored in refrigerator.

2.6 Optimization of the Reaction Conditions

The process of conditional optimization is as follows. All reaction scale was 0.1 mmol of aryl diazonium salts. After completion of the reaction, yield were determined by ¹⁹F NMR with 1, 3, 5-trifluoroszene as an internal standard. The results were listed in Table S1-S9.
Table S1. Trifluoromethoxylation by different trifluoromethoxylation reagents

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{N}_2^+\text{BF}_4^- + \text{AgF} + [\text{OCF}_3]^+ \\
& \quad \text{MeCN (0.2 M)} \quad -40^\circ\text{C to rt, Ar} \\
& \quad \text{overnight} \\
\hline
\text{Entry} & [\text{OCF}_3]^+ & \text{Yield (\%)}^b \\
1 & \text{MeO} & 53 \\
2 & \text{Pr}^+ \quad \text{MeO} & 38 \\
3 & \text{Pr}^+ \quad \text{Pr}^+ & 41 \\
4 & \text{Pr}^+ \quad \text{Pr}^+ & 51 \\
\hline
\end{align*}
\]

\(^a\) The reaction scale was 0.1 mmol. \(^b\) Yield were determined by \(^{19}\text{F}\) NMR with 1, 3, 5-trifluoroszene as an internal standard.

Table S2. Effects of Anions of the Diazonium Salt

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{N}_2^+\text{X}^- + \text{AgF} + \text{CF}_3\text{OSO}_2\text{CF}_3^- \\
& \quad \text{MeCN (0.2 M)} \\
& \quad -40^\circ\text{C to rt, Ar} \\
& \quad \text{overnight} \\
\hline
\text{Entry} & (\text{X}^-) & \text{Yield (\%)}^b \\
1 & \text{Cl}^- & 21 \\
2 & \text{Br}^- & 27 \\
3 & \text{BF}_4^- & 51 \\
4 & \text{HSO}_4^- & 7 \\
5 & \text{CF}_3\text{COO}^- & 25 \\
6 & \text{CF}_3\text{SO}_3^- & 50 \\
7 & \text{tBuO}^- & 0 \\
\hline
\end{align*}
\]

\(^a\) The reaction scale was 0.1 mmol. \(^b\) Yield were determined by \(^{19}\text{F}\) NMR with 1, 3, 5-trifluoroszene as an internal standard.
Table S3. Solvent effects $^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Acetone</td>
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<td>4</td>
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<td>5</td>
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<td>0</td>
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<tr>
<td>6</td>
<td>Ether</td>
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</tr>
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<td>CH$_3$OH</td>
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<td>8</td>
<td>CH$_3$CN</td>
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</tr>
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<td>THF/CH$_3$CN=1/3</td>
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<td>Ether/CH$_3$CN=1/3</td>
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</tr>
<tr>
<td>11</td>
<td>CH$_3$CN/CH$_3$O=300/1</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$The reaction scale was 0.1 mmol. $^b$Yield were determined by $^{19}$F NMR with 1, 3, 5-trifluoroszene as an internal standard.

Table S4. Temperature effects $^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>T/°C</th>
<th>Yield (%) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-40 → rt</td>
<td>51</td>
</tr>
<tr>
<td>2</td>
<td>0 → rt</td>
<td>19</td>
</tr>
<tr>
<td>3</td>
<td>-40 → rt → 50</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>-40 → 0</td>
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<td>5</td>
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<td>0</td>
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<tr>
<td>7</td>
<td>-40</td>
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</tbody>
</table>

$^a$The reaction scale was 0.1 mmol. $^b$Yield were determined by $^{19}$F NMR with 1, 3, 5-trifluoroszene as an internal standard.
Table S5. Effects of different inorganic salts

<table>
<thead>
<tr>
<th>Entry</th>
<th>F⁻</th>
<th>Ag⁺</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>KF</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>CsF</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>TBAF</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>Ag₂O</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>Ag₂CO₃</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>AgBF₄</td>
<td>0</td>
</tr>
<tr>
<td>8ᵇ</td>
<td>CsF</td>
<td>AgBF₄</td>
<td>0</td>
</tr>
<tr>
<td>9ᵇ</td>
<td>AgF</td>
<td></td>
<td>51</td>
</tr>
<tr>
<td>10ᵇ</td>
<td>AgF</td>
<td>Ag₂O</td>
<td>43</td>
</tr>
<tr>
<td>11ᵇ</td>
<td>KF</td>
<td>AgBF₄</td>
<td>7</td>
</tr>
</tbody>
</table>

ᵃ The reaction scale was 0.1 mmol. ᵇ Yield were determined by ¹⁹F NMR with 1, 3, 5-trifluoroszene as an internal standard.

Table S6. Ratio effects

<table>
<thead>
<tr>
<th>Entry</th>
<th>X:Y</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:1</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>2:4</td>
<td>43</td>
</tr>
<tr>
<td>3</td>
<td>3:3</td>
<td>47</td>
</tr>
<tr>
<td>4</td>
<td>3:5</td>
<td>51</td>
</tr>
<tr>
<td>5</td>
<td>3:8</td>
<td>52</td>
</tr>
<tr>
<td>6</td>
<td>4:2</td>
<td>28</td>
</tr>
</tbody>
</table>

ᵃ The reaction scale was 0.1 mmol. ᵇ Yield were determined by ¹⁹F NMR with 1, 3, 5-trifluoroszene as an internal standard.
Table S7. Concentration effects \(^a\)

\[
\text{N}_2\text{BF}_4^- + \text{AgF} + \text{CF}_3\text{OSO}_2\text{CF}_3 \xrightarrow{-40^\circ \text{C to rt, Ar overnight}} \text{O}_2\text{N} + \text{OCF}_3
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Concentration/X</th>
<th>Yield (%) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>51</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>0.067</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>31</td>
</tr>
</tbody>
</table>

\(^a\) The reaction scale was 0.1 mmol. \(^b\) Yield were determined by \(^{19}\)F NMR with 1, 3, 5-trifluoroszene as an internal standard.

Table S8. Effects of additives \(^a\)

\[
\text{N}_2\text{BF}_4^- + \text{AgF} + \text{CF}_3\text{OSO}_2\text{CF}_3 + \text{Additive} \xrightarrow{-40^\circ \text{C to rt, Ar overnight}} \text{O}_2\text{N} + \text{OCF}_3
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additives</th>
<th>Yield (%) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0 eq. Cu(^+) (CuI, CuCl, Cu(_2)OAc, CuSCN, CuOTf, Cu(CH(_3)CN)(_4)PF(_6))</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1.0 equiv Selectfluor</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>1.2 equiv NaHCO(_3)</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>3 mmol% bipyridine</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>1.0 equiv NaOH</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>1.0 equiv BQ</td>
<td>27</td>
</tr>
</tbody>
</table>

\(^a\) The reaction scale was 0.1 mmol 1a. \(^b\) Yield were determined by \(^{19}\)F NMR with 1, 3, 5-trifluoroszene as an internal standard.

Table S9. AgOCF\(_3\) ratio effects \(^a\)

\[
\text{N}_2\text{BF}_4^- + \text{AgOCF}_3^- \xrightarrow{-40^\circ \text{C to rt, Ar overnight}} \text{O}_2\text{N} + \text{OCF}_3
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>AgOCF(_3)</th>
<th>Yield (%) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>8</td>
</tr>
</tbody>
</table>
2.7 General experimental procedure

To a 25 mL Schlenk flask with a magnetic stirring bar were added (hetero)aryl diazonium salts (1 mmol, 1.0 equiv.) The Schlenk flask was evacuated and backfilled with argon for three times, and the previously prepared AgOCF₃(1.0 M in MeCN, 5 mL, 5 mmol) was added by syringe in one shot at -40°C. The mixture was vigorously stirring at -40°C and gradually warmed to room temperature overnight. The reaction mixture was diluted with water (40 mL) and rinsed with DCM (2×20 mL) and brine (10 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated. The residue was further purified by flash column chromatography to afford the corresponding aryl trifluoromethyl ether products.

2.8 One-pot trifluoromethoxylation procedure

\[
\begin{align*}
&\text{Br} \quad \text{BF}_3 \text{Et}_2\text{O (1.5 equiv)} \quad \text{t-BuONO (1.5 equiv)} \\
&\text{Et}_2\text{O, 0 °C, 30 min} \\
\end{align*}
\]

To a 25 mL Schlenk flask with a magnetic stirring bar were added 3-bromobenzenamine (86.0 mg, 0.5 mmol), BF₃Et₂O (0.75 mmol) and diethyl ether (3 mL). The mixture was cooled to 0 °C and tBuONO (0.75 mmol) was added via syringe. After stirring at 0 °C for 30 minutes, the reaction is completed, monitored by TLC. After removed solvent by vacuum, flask was evacuated and backfilled with argon for three time. The flask was cooled at - 40°C and the previously prepared AgOCF₃ solution (5 mL, 1 mmol) was added. The mixture was vigorously stirring at -40°C and warmed up to room temperature gradually overnight. The reaction mixture was diluted with water (40 ml), followed by extracting with DCM (20 mL× 2). The...
combined organic extracts dried over anhydrous sodium sulfate and concentrated in vacuo. The crude product was purified by flash column chromatography (PE) to afford the product 5 (64.8 mg, 54% yield).

2.9 Gram-scale reaction

To a 100 mL Schlenk flask with a magnetic stirring bar were added 3-nitrobenzene diazonium salts (1.185 g, 5 mmol, 1.0 equiv.) The Schlenk flask was evacuated and backfilled with argon for three times, and the previously prepared AgOCF₃(1.0 M in MeCN, 25 mL, 25 mmol) was added by syringe in one shot at -40°C. The mixture was vigorously stirring at -40°C and gradually warmed to room temperature overnight. The reaction mixture was diluted with water (100 mL) and rinsed with DCM (2×50 mL) and brine (30 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated. The residue was further purified by flash column chromatography (petroleum ether: DCM = 10:1) to afford the corresponding aryl trifluoromethyl ether products 3 (0.82 g, 79% yield).

3 Mechanism Studies

To a 5 mL Schlenk flask with a magnetic stirring bar were added TEMPO and 3-nitro benzene diazonium salts (0.1 mmol, 1.0 equiv) The Schlenk flask was evacuated and backfilled with argon for three times, AgOCF₃(0.1 M in MeCN, 0.5 mL, 0.5 mmol) was added. The reaction mixture was cooled at -40°C. The mixture was
vigorously stirring at -40°C and warmed to room temperature gradually overnight.
The yields were determined by $^{19}$F NMR using 1, 3, 5-trifluorobenzene (-108ppm) as internal standard.

$^{19}$F NMR Spectrum, TEMPO (0.5equiv), product(40%, $^{19}$F NMR yield)

$^{19}$F NMR Spectrum, TEMPO(0.0equiv), product(85%, $^{19}$F NMR yield)
To a 25 mL Schlenk flask with a magnetic stirring bar was added TEMPO (2, 2, 6, 6-tetramethyl-1-piperidinyloxy) (2 mmol, 2.0 equiv) and aryldiazonium salts (1 mmol, 1.0 equiv). The Schlenk flask was evacuated and backfilled with argon for three times, and AgOCF$_3$(5 mL, 5 mmol). The mixture was cooled at -40°C. The mixture was violently stirring at -40 °C and warmed to room temperature gradually overnight. The reaction mixture was diluted with water (40 mL), followed by extracting with DCM (20 mL×2). The combined organic extracts dried over anhydrous sodium sulfate and concentrated in vacuo. The crude product was purified by flash column chromatography (PE: EA= 50:1) to afford the product 51 (178.2 mg, 64% yield).

To a 25 mL Schlenk flask with a magnetic stirring bar was added TEMPO (2, 2, 6, 6-tetramethyl-1-piperidinyloxy) (2 mmol, 2.0 equiv) and aryldiazonium salt (1 mmol, 1.0 equiv). The Schlenk flask was evacuated and backfilled with argon for three times, and CH$_3$CN (5 mL). The mixture was cooled at -40°C. The mixture was violently stirring at -40 °C and warmed to room temperature gradually overnight. The reaction mixture was diluted with water (40 mL), followed by extracting with DCM (20 mL×2). The combined organic extracts dried over anhydrous sodium sulfate and concentrated in vacuo. The crude product was purified by flash column chromatography (PE: EA= 50:1) to afford the product 51 (181 mg, 65% yield).

4 Compounds of Characterization

1-nitro-3-trifluoromethoxy-benzene (3)
176 mg (85%) colorless oil isolated. \( R_f = 0.6 \) (PE/DCM 10:1 (v/v)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.20 (d, \( J = 12.0 \) Hz, 1H), 8.11 (s, 1H), 7.63 (t, \( J = 8.0 \) Hz, 1H), 7.58 (d, \( J = 8.0 \) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 149.3 (d, \( J = 2.0 \) Hz), 148.9, 130.7, 126.9, 121.8, 120.2 (q, \( J = 258.0 \) Hz), 116.5 (d, \( J = 0.7 \) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.1.

1-chloro-3-(trifluoromethoxy)benzene (4)

This compound is highly volatile. The yield (71%) is based on \(^{19}\)F NMR with 1, 3, 5-trifluorobenzene as internal standard. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -57.9.

1-bromo-3-(trifluoromethoxy)benzene (5)

152 mg (63%) colorless oil isolated. \( R_f = 0.8 \) (PE). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.45 (d, \( J = 8.0 \) Hz, 1H), 7.40 (s, 1H), 7.28 (t, \( J = 8.0 \) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 149.5 (d, \( J = 1.8 \) Hz), 130.7, 130.1, 124.4, 121.6, 120.3 (q, \( J = 256.7 \) Hz), 119.6. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -57.9.

1-fluoro-3-(trifluoromethoxy)benzene (6)

This compound is highly volatile. The yield (67%) is based on \(^{19}\)F NMR based on 1, 3, 5-Trifluorobenzene as reference. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.3, -110.3.

1-(trifluoromethyl)-3-(trifluoromethoxy)benzene (7)

This compound is highly volatile. The yield (65%) is based on \(^{19}\)F NMR based on 1, 3, 5-Trifluorobenzene as reference. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.2, -62.8.

3-(trifluoromethoxy)benzonitrile (8)
138 mg (74%) colorless oil isolated. \( R_f = 0.7 \) (PE/DCM 10:1 (v/v)).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.62 (d, \( J = 7.6 \) Hz, 1H), 7.55 (t, \( J = 8.0 \) Hz, 1H), 7.52 (s, 1H), 7.48 (d, \( J = 8.0 \) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 149.2(d, \( J = 2.0 \) Hz), 131.0, 130.5, 125.6, 124.5, 120.2 (q, \( J = 257.7 \) Hz), 117.3, 114.1. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.0.

1-(trifluoromethoxy)benzene (9) \(^{10}\)

This compound is highly volatile. The yield (41%) is based on \(^{19}\)F NMR based on 1, 3, 5-trifluorobenzene as reference. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.2.

1-methoxy-3-(trifluoromethoxy)benzene (10)

98 mg (51%) colorless oil isolated. \( R_f = 0.5 \) (PE/DCM 10:1 (v/v)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.28 (t, \( J = 8.4 \) Hz, 1H), 6.83 (t, \( J = 7.6 \) Hz, 2H), 6.76 (s, 1H), 3.82 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 160.6, 150.1, 130.1, 120.4 (q, \( J = 255.5 \) Hz), 112.8, 112.4, 107.1, 59.5. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -57.7. HRMS: m/z (ESI) calculated [M+H]\(^+\):193.0476, measured:193.0471.

methyl(3-(trifluoromethoxy)phenyl)sulfane (11)

96 mg (46%) colorless oil isolated. \( R_f = 0.6 \) (PE/DCM 10:1 (v/v)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.29 (t, \( J = 8.0 \) Hz, 1H), 7.16 (d, \( J = 8.0 \) Hz, 1H), 7.07 (s, 1H), 6.98 (d, \( J = 8.0 \) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 149.6, 141.0, 129.8, 124.4, 120.4 (q, \( J = 255.8 \) Hz), 118.4, 117.1, 15.5. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -57.7. HRMS: m/z (ESI) calculated [M+H]\(^+\):209.0248, measured:209.0241.

1-(benzyloxy)-2-(trifluoromethoxy)benzene (12)

180 mg (67%) colorless oil isolated. \( R_f = 0.5 \) (PE/DCM 10:1 (v/v)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.41 (q, \( J = 8.0 \) Hz, 4H), 7.34 (t, \( J = 8.0 \) Hz, 1H), 7.29
(t, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 8.0 Hz, 2H), 5.06 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.7, 150.1, 136.2, 130.2, 128.7, 128.2, 127.5, 120.4 (q, J = 255.7 Hz), 113.2, 113.1, 108.1, 70.3. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -57.7. HRMS: m/z (ESI) calculated [M+H]$^+$: 269.0783, measured: 269.0783.

**methyl 3-(trifluoromethoxy)benzoate (13)**

\[
\text{MeC}_2\text{C} = \text{OCF}_3
\]

90 mg (41%) colorless oil isolated. R$_f$ = 0.5 (PE/DCM 5:1 (v/v)). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, J = 7.7 Hz, 1H), 7.82 (s, 1H), 7.42 (t, J = 7.9 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 3.87 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.7, 149.2, 132.6, 130.1, 119.9 (d, J = 255.6 Hz), 118.1, 113.1, 113.0, 107.9, 69.1. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -57.9. HRMS: m/z (ESI) calculated [M+H]$^+$: 221.0426, measured: 221.0419.

**1-(allyloxy)-3-(trifluoromethoxy)benzene (14)**

\[
\text{C} = \text{OCF}_3
\]

157 mg (72%) colorless oil isolated. R$_f$ = 0.7 (PE/DCM 10:1 (v/v)). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.28 (t, J = 8.0 Hz, 1H), 6.84 (t, J = 10.0 Hz, 2H), 6.78 (s, 1H), 6.00–6.09 (m, J = 5.6 Hz, 1H), 5.43 (d, J = 17.2 Hz, 1H), 5.32 (d, J = 10.4 Hz, 1H), 4.54(d, J = 4.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.6, 150.1, 132.6, 130.1, 119.9 (d, J = 255.6 Hz), 118.1, 113.1, 113.0, 107.9, 69.1. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -57.8. HRMS: m/z (ESI) calculated [M+H]$^+$: 219.0633, measured: 219.0627.

**1-phenylethynyl-3-trifluoromethoxy-benzene (15)**

\[
\text{Ph} = \text{OCF}_3
\]

128 mg (49%) colorless oil isolated. R$_f$ = 0.9 (PE/DCM 10:1 (v/v)). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.54 (m, 2H), 7.46(d, J = 7.6 Hz, 1H), 7.37(m, 5H), 7.20(d, J = 7.6 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.1,133.1, 131.7,131.6, 130.0, 129.8, 128.7, 128.5,128.4,125.2, 123.9, 122.6, 120.9, 120.4(q, J = 256.1 Hz) 90.7, 87.7. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -57.8. HRMS: m/z (ESI) calculated [M+H]$^+$: 263.0684, measured: 263.0681.
4-(trifluoromethoxy)benzonitrile (16)  

\[
\begin{align*}
&\text{NC} \\
&\text{OCF}_3
\end{align*}
\]

80 mg (43%) colorless oil isolated. \( R_f = 0.7 \) (PE/DCM 10:1 (v/v)).

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.73 (d, \( J = 8.8 \) Hz, 2H), 7.33 (d, \( J = 8.0 \) Hz, 2H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 152.2, 134.2, 121.2, 120.0 (q, \( J = 258.2 \) Hz), 117.7, 110.8. \( ^{19}F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -57.7.

1-bromo-4-(trifluoromethoxy)benzene (17)  

\[
\begin{align*}
&\text{Br} \\
&\text{OCF}_3
\end{align*}
\]

This compound is highly volatile and evaporated with pentane. The yield (41%) is based on \( ^{19}F \) NMR based on 1, 3, 5-trifluorobenzene as reference. \( ^{19}F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.5.

1-fluoro-4-(trifluoromethoxy)benzene (18)  

\[
\begin{align*}
&\text{F} \\
&\text{OCF}_3
\end{align*}
\]

This compound is highly volatile and evaporated with pentane. The yield (47%) is based on \( ^{19}F \) NMR based on 1, 3, 5-trifluorobenzene as reference. \( ^{19}F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.2, -115.4.

1-(methylsulfonyl)-4-(trifluoromethoxy)benzene (19)  

\[
\begin{align*}
&\text{MeO}_2\text{S} \\
&\text{OCF}_3
\end{align*}
\]

110 mg (46%) colorless oil isolated. \( R_f = 0.8 \) (PE/DCM 1:1 (v/v)). \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.01 (d, \( J = 8.8 \) Hz, 2H), 7.40 (d, \( J = 8.4 \) Hz, 2H), 3.07 (s, 3H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 153.0, 138.8, 129.7, 121.2, 120.0 (q, \( J = 258.16 \) Hz), 44.6. \( ^{19}F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -57.7. HRMS: m/z (ESI) calculated [M+H]\(^+\):241.0146, measured:241.0141.

1-bromo-2-(trifluoromethoxy)benzene (20)  

\[
\begin{align*}
&\text{Br} \\
&\text{OCF}_3
\end{align*}
\]

This compound is highly volatile. The yield (45%) is based on \( ^{19}F \) NMR based on 1, 3, 5-Trifluorobenzene as reference. \( ^{19}F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.3.
1-bethoxy-2-(trifluoromethoxy)benzene (21) \(^{13}\)

\[
\begin{align*}
\text{O}_{\text{CF}_3} & \quad \text{OMe}
\end{align*}
\]

This compound is highly volatile. The yield (31%) is based on \(^{19}\)F NMR based on 1, 3, 5-trifluorobenzene as reference. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -57.7.

1-bromo-4-methoxy-2-(trifluoromethoxy)benzene (22)

\[
\begin{align*}
\text{MeC} & \quad \text{OCF}_3
\end{align*}
\]

84 mg (31%) colorless oil isolated. \(R_f = 0.6\) (PE/DCM 20:1 (v/v)).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43 (d, \(J = 8.9\) Hz, 1H), 6.80 (dd, \(J = 2.5, 1.2\) Hz, 1H), 6.67 (dd, \(J = 8.9, 2.8\) Hz, 1H), 3.73 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.7, 146.9, 133.9, 120.4 (q, \(J = 259.2\) Hz), 113.8, 108.7, 106.3, 55.8. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -57.5. HRMS: m/z (ESI) calculated [M+H]\(^+\):270.9582, 272.9561, measured:270.9576, 272.9558.

2-chloro-1-methoxy-4-(trifluoromethoxy)benzene (23)

\[
\begin{align*}
\text{Cl} & \quad \text{MeC} \quad \text{OCF}_3
\end{align*}
\]

167 mg (75%) colorless oil isolated. \(R_f = 0.5\) (PE/DCM 20:1 (v/v)).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.28 (s, 1H), 7.11 (d, \(J = 8.8\) Hz, 1H), 6.91 (d, \(J = 9.2\) Hz, 1H), 3.91 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 153.9, 142.2, 123.6, 123.0, 120.5, 120.4 (q, \(J = 255.6\) Hz), 112.1, 56.5. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -58.5; HRMS: m/z (ESI) calculated [M+H]\(^+\):227.0087, 229.0057, measured:227.0080, 229.0050.

1, 2-dichloro-4-(trifluoromethoxy)benzene (24)

\[
\begin{align*}
\text{Cl} & \quad \text{MeC} \quad \text{OCF}_3
\end{align*}
\]

150 mg (65%) colorless oil isolated. \(R_f = 0.8\) (PE). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.48 (d, \(J = 8.8\) Hz, 1H), 7.35 (s, 1H), 7.10 (d, \(J = 8.8\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 147.7, 133.6, 131.2, 123.3, 120.4, 120.2 (q, \(J = 257.2\) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -58.2. EI-MS (m/z, relative intensity): 230(M\(^+\),100), 211(0.3), 161(29), 147(5), 133(42), 129(7), 109(7), 97(6), 83(3), 69(29), 63(27).

1-chloro-2-nitro-4-trifluoromethoxy-benzene (25)
99 mg (41%) colorless oil isolated. \( R_f = 0.4 \) (PE/DCM 10:1 (v/v)).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \)

- 7.78 (s, 1H), 7.62 (d, \( J = 8.8 \) Hz, 2H), 7.42 (d, \( J = 8.8 \) Hz, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \)

- 148.1, 147.4, 133.2, 125.7, 125.5, 120.1 (q, \( J = 258.6 \) Hz), 118.5.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.3. EI-MS (m/z, relative intensity): 241(M\(^+\),81), 225(3), 211(4), 183(45), 129(100), 79(6), 109(19), 98(22), 69(61), 63(66).

**2-chloro-4-(trifluoromethoxy)benzonitrile (26)**

124 mg (56%) colorless oil isolated. \( R_f = 0.6 \) (PE).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \)

- 7.74 (d, \( J = 8.6 \) Hz, 1H), 7.40 (s, 1H), 7.25 (d, \( J = 8.7 \) Hz, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \)

- 152.3, 138.6, 135.3, 122.1, 120.0 (q, \( J = 260.9 \) Hz), 119.2, 114.9, 111.8.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -57.8. HRMS: m/z (ESI) calculated [M+H]\(^+\):221.9934, 223.9904, measured:221.9928, 223.9898.

**1-methoxy-2-nitro-4-(trifluoromethoxy)benzene (27)**

107 mg (45%) colorless oil isolated. \( R_f = 0.4 \) (PE/DCM 10:1 (v/v)).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \)

- 7.76 (d, \( J = 2.0 \) Hz, 1H), 7.44 (dd, \( J = 9.2, 2.0 \)Hz, 1H), 7.12 (d, \( J = 9.2 \) Hz, 1H), 3.98 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \)

- 151.7, 141.2, 139.3, 127.1, 120.4 (q, \( J = 256.7 \)Hz), 119.1, 114.5, 56.9.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.7. HRMS: m/z (ESI) calculated [M+H]\(^+\):238.0327 measured:238.0321.

**1, 3-dichloro-5-trifluoromethoxy-benzene (28)**

180 mg (78%) colorless oil isolated. \( R_f = 0.9 \) (PE).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \)

- 7.32 (s, 1H), 7.15 (s, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \)

- 149.6, 135.8, 127.3, 120.2 (q, \( J = 257.8 \)Hz), 129.9.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.0. EI-MS (m/z, relative intensity): 230(M\(^+\),84), 164(12), 145(5), 133(15), 109(3), 98(3), 73(4), 69(35), 63(13), 40(100).
1, 3-dibromo-5-trifluoromethoxy-benzene (29)

\[
\begin{align*}
\text{Br} & \quad \text{OCF}_3 \\
\text{Br} \\
\end{align*}
\]

253 mg (79%) colorless oil isolated. \( R_f = 0.8 \) (PE). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.62 (s, 1H), 7.35 (s, 2H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 149.7, 149.6, 132.8, 123.2, 120.2 (q, \( J = 257.8 \) Hz). \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.0. El-MS (m/z, relative intensity): 320(\( M^+ \), 76), 301(1), 254(3), 239(4), 223(5), 173(14), 94(9), 74(5), 69(18), 63(21), 50(2), 40(100).

1, 3-dinitro-5-trifluoromethoxy-benzene (30)

\[
\begin{align*}
\text{C}_2\text{N} & \quad \text{OCF}_3 \\
\end{align*}
\]

192 mg (76%) colorless oil isolated. \( R_f = 0.8 \) (PE/DCM 10:1 (v/v)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.03 (s, 1H), 8.44 (s, 2H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 149.6, 149.1, 121.5, 120.0 (q, \( J = 260.7 \) Hz), 117.0. \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.1. El-MS (m/z, relative intensity): 252(\( M^+ \),92), 236(3), 222(1), 206,(12), 176(15), 160(39), 123(1), 94(9), 82(12), 74(7), 69(25), 63(42), 51(5), 40(100).

1-bromo-3-chloro-5-(trifluoromethoxy)benzene (31)

\[
\begin{align*}
\text{Cl} & \quad \text{OCF}_3 \\
\text{Br} \\
\end{align*}
\]

196 mg (71%) colorless oil isolated. \( R_f = 0.8 \) (PE). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.47 (s, 1H), 7.30 (s, 1H), 7.20 (s, 1H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 149.7, 134.0, 130.1, 123.0, 122.7, 120.4, \( J = 257.8 \). \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -58.0. El-MS (m/z, relative intensity): 276(\( M^+ \),53), 210(3), 191(2), 179(5), 167(2), 129(16), 109(2), 98(2), 69(18), 63(13), 50(1), 40(100).

2-methoxy-3-trifluoromethoxy-pyridine (32)

\[
\begin{align*}
\text{N} & \quad \text{OCF}_3 \\
\text{OMe} \\
\end{align*}
\]

166 mg (86%) colorless oil isolated. \( R_f = 0.5 \) (PE/DCM 10:1 (v/v)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.15 (d, \( J = 5.6 \) Hz, 1H), 6.72 (d, \( J = 5.6 \) Hz, 1H), 6.54 (s, 1H), 3.95(s, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 165.8, 157.7, 148.7, 120.1(q, \( J = 258.7 \) Hz, 1H).
Hz) 108.3, 101.0. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -57.6. HRMS: m/z (ESI) calculated [M+H]$^+$: 194.0429, measured: 194.0422.

2-methoxy-5-trifluoromethoxy-pyridine (33)

![Structural formula of 2-methoxy-5-trifluoromethoxy-pyridine](image)

91 mg (47%) colorless oil isolated. $R_f = 0.5$ (PE/DCM 10:1 (v/v)).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J = 5.6$ Hz, 1H), 6.73 (d, $J = 6.0$ Hz, 1H), 6.55 (s, 1H) 3.95 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.8, 157.7, 148.7, 120.1 (q, $J = 258.7$ Hz) 108.3, 101.0, 54.0. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.6. HRMS: m/z (ESI) calculated [M+H]$^+$: 194.0429, measured: 194.0424.

3-chloro-5-trifluoromethoxy-pyridine (34)

![Structural formula of 3-chloro-5-trifluoromethoxy-pyridine](image)

124 mg (63%) colorless oil isolated. $R_f = 0.6$ (PE/DCM 10:1 (v/v)).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.55 (s, 1H), 8.47 (s, 1H), 7.60 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.2, 145.7, 140.7, 132.2, 128.5, 120.2 (q, $J = 258.6$ Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -58.2. HRMS: m/z (ESI) calculated [M+H]$^+$: 197.9934, 199.9904, measured: 197.9927, 199.9897.

3-bromo-5-trifluoromethoxy-pyridine (35)

![Structural formula of 3-bromo-5-trifluoromethoxy-pyridine](image)

126 mg (52%) colorless oil isolated. $R_f = 0.5$ (PE/DCM 10:1 (v/v)).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.65 (s, 1H), 8.51 (s, 1H), 7.75 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.3, 145.8, 141.0, 131.3, 120.3, 120.2 (q, $J = 258.6$ Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -58.2. HRMS: m/z (ESI) calculated [M+H]$^+$: 241.9428, 243.9408, measured: 241.9424, 243.9402.

3-methyl-5-trifluoromethoxy-pyridine (36)

![Structural formula of 3-methyl-5-trifluoromethoxy-pyridine](image)

This compound is highly volatile. The yield (31%) is based on $^{19}$F NMR based on 1, 3, 5-trifluorobenzene as reference; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -58.0
3-p-toly-5-trifluoromethoxy-pyridine (37)

\[
\begin{align*}
\text{OCF}_3 \\
\text{N} \\
\text{OCF}_3
\end{align*}
\]

142 mg (56%) colorless oil isolated. R_f = 0.3 (PE/DCM 10:1 (v/v)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.78 (s, 1H), 8.51 (s, 1H), 8.0 (s, 1H), 7.71 (s, 1H), 7.48 (d, \(J = 8.0\) Hz, 2H), 7.31 (d, \(J = 7.6\) Hz, 2H), 2.42 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.4, 146.3, 141.0, 139.0, 138.1, 133.2, 130.0, 127.1, 126.4, 120.5 (q, \(J = 257.4\) Hz), 21.2. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -58.0. HRMS: m/z (ESI) calculated \([M+H]^+\): 254.0793, measured: 254.0788.

2-chloro-3-(trifluoromethoxy)pyridine (38)

\[
\begin{align*}
\text{OCF}_3 \\
\text{Cl}
\end{align*}
\]

This compound is highly volatile and evaporated with pentane. The yield (50%) is based on \(^{19}\)F NMR based on 1, 3, 5-trifluorobenzene as reference; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -57.7.

2-bromo-3-(trifluoromethoxy)pyridine (39)

\[
\begin{align*}
\text{OCF}_3 \\
\text{Br}
\end{align*}
\]

This compound is highly volatile and evaporated with pentane. The yield (70%) is based on \(^{19}\)F NMR based on 1, 3, 5-trifluorobenzene as reference; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -58.1.

2, 5-dibromo-3-trifluoromethoxy-pyridine (40)

\[
\begin{align*}
\text{Br} \\
\text{OCF}_3 \\
\text{Br}
\end{align*}
\]

125 mg (39%) colorless oil isolated. R_f = 0.5 (PE/DCM 10:1 (v/v)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.41 (s, 1H), 6.89 (s, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.47, 162.08, 155.73 (d, \(J = 11.2\) Hz), 150.89 (q, \(J = 17.1\) Hz), 120.04 (q, \(J = 258.7\) Hz), 101.17 (q, \(J = 44.2\), 2.2 Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -57.6. HRMS: m/z (ESI) calculated \([M+H]^+\): 319.8533, 321.8513, 323.8493, measured: 319.8526, 321.8504, 323.8483.

2-chloro-5-methyl-3-trifluoromethoxy-pyridine (41)
This compound is highly volatile and evaporated with pentane. The yield (41%) is based on $^{19}$F NMR based on 1, 3, 5-trifluorobenzene as reference; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.7.

2-bromo-5-chloro-3-trifluoromethoxy-pyridine (42)

This compound is highly volatile and evaporated with pentane. The yield (50%) is based on $^{19}$F NMR based on 1, 3, 5-trifluorobenzene as reference; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.8.

5-bromo-2-methoxy-3-trifluoromethoxy-pyridine (43)

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.30 (s, 1H), 6.67 (d, $J = 2$ Hz, 1H), 3.94(s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.6, 154.2, 150.1, 120.5 (q, $J = 260.5$ Hz) 104.2, 102.0, 54.3. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.6. HRMS: m/z (ESI) calculated [M+H]$^+$: 271.9534, 273.9514, measured: 271.9529, 273.9507.

2-chloro-3-methyl-5-trifluoromethoxy-pyridine (44)

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.30 (s, 1H), 6.67 (d, $J = 2$ Hz, 1H), 3.94(s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.6, 154.2, 150.1, 120.5 (q, $J = 260.5$ Hz) 104.2, 102.0, 54.3. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.6. HRMS: m/z (ESI) calculated [M+H]$^+$: 271.9534, 273.9514, measured: 271.9529, 273.9507.

3-bromo-2-chloro-5-trifluoromethoxy-pyridine (45)

160 mg (58%) colorless oil isolated. $R_f$ = 0.7 (PE/DCM 10:1 (v/v)). $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 (s, 1H), 7.90 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.9, 156.6, 143.5, 138.9 (d, $J = 14.5$ Hz), 137.0, 120.2 (q, $J = 260.0$ Hz).
\[^{19}\text{F NMR (376 MHz, CDCl}_3\) \delta -58.7. HRMS: m/z (ESI) calculated [M+H]^+: 275.9039, 277.9018, measured: 275.9031, 277.9010.\]

3-bromo-2-methoxy-5-trifluoromethoxy-pyridie (46)

\[
\begin{align*}
\text{Br} & \quad \text{OCF}_3 \\
\text{Me} & \quad \text{N}
\end{align*}
\]

139 mg (51%) colorless oil isolated. \(R_f = 0.5 \) (PE/DCM 10:1 (v/v)). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta 8.06 (d, J = 1.6 \text{ Hz, 1H}), 7.74 (d, J = 1.2 \text{ Hz, 1H}), 4.01 (s, 3H).\) \(^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta 158.7, 140.1, 138.3, 135.3, 120.4 (q, J = 256.9 \text{ Hz}) 106.6, 55.0.\) \(^{19}\text{F NMR (376 MHz, CDCl}_3\) \(\delta -59.0. HRMS: m/z (ESI) calculated [M+H]^+: 271.9534, 273.9514, measured: 271.9525, 273.9505.\)

3-trifluoromethoxy-quinoline (47)

\[
\begin{align*}
\text{OCF}_3 \\
\text{N}
\end{align*}
\]

171 mg (80%) colorless oil isolated. \(R_f = 0.5 \) (PE/DCM 10:1 (v/v)). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta 8.84 (s, 1H), 8.16 (d, J = 8.8 \text{ Hz, 1H}), 8.0 (s, 1H), 7.85(d, J = 8.0 \text{ Hz, 1H}), 7.76 (t, J = 8.0 \text{ Hz, 1H}), 7.63 (t, J = 7.6 \text{ Hz, 1H}).\) \(^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta 146.5, 144.8, 142.7, 129.8, 129.5, 127.9, 127.7, 125.5, 120.6(q, J = 257.3 \text{ Hz}).\) \(^{19}\text{F NMR (376 MHz, CDCl}_3\) \(\delta -58.1. HRMS: m/z (ESI) calculated [M+H]^+: 214.0480, measured: 214.0480.\)

4-trifluoromethoxy-isoquinoline (48)

\[
\begin{align*}
\text{OCF}_3 \\
\text{N}
\end{align*}
\]

173 mg (81%) colorless oil isolated. \(R_f = 0.4 \) (PE/DCM 10:1 (v/v)). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta 9.21 (s, 1H), 8.53 (s, 1H), 8.12(s, J = 8.4 \text{ Hz, 1H}), 8.05(d, J = 8.4 \text{ Hz, 1H}), 7.83(t, J = 7.6 \text{ Hz, 1H}), 7.71 (t, J = 7.6 \text{ Hz, 1H}).\) \(^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta 151.2, 141.4, 134.5, 131.4, 129.8, 129.7, 128.4, 127.4, 120.8. (q, J = 257.4 \text{ Hz}),120.5.\) \(^{19}\text{F NMR (376 MHz, CDCl}_3\) \(\delta -57.8. HRMS: m/z (ESI) calculated [M+H]^+: 214.0480, measured: 214.0473.\)

(1R, 2S, 5R)-2-isopropyl-5-methycyclohexyl3-(trifluoromethoxy)benzoate (49)
169 mg (49%) colorless oil isolated. R<sub>f</sub> = 0.5 (PE/DCM 10:1 (v/v)). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, <i>J</i> = 7.7 Hz, 1H), 7.88 (s, 1H), 7.48 (t, <i>J</i> = 7.9 Hz, 1H), 7.40 (d, <i>J</i> = 8.2 Hz, 1H), 4.95 (td, <i>J</i> = 10.9, 4.4 Hz, 1H), 2.12 (d, <i>J</i> = 11.9 Hz, 1H), 1.93 (dtd, <i>J</i> = 13.9, 7.0, 2.7 Hz, 1H), 1.74 (d, <i>J</i> = 12.3 Hz, 2H), 1.61 – 1.51 (m, 1H), 1.13 (t, <i>J</i> = 11.7 Hz, 2H), 0.93 (dd, <i>J</i> = 6.7, 4.9 Hz, 6H), 0.80 (d, <i>J</i> = 7.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.7, 149.2, 132.9, 129.8, 127.9, 125.1, 122.1, 120.4 (q, <i>J</i> = 257.4 Hz), 75.6, 47.2, 40.9, 34.3, 31.5, 26.6, 23.7, 22.0, 20.7, 16.6. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -57.9. HRMS: m/z (ESI) calculated [M+H]<sup>+</sup>: 345.1678, measured: 345.1673.

(R)-2, 5, 7, 8-tetramethyl-2-((4R, 8R)-4, 8, 12-trimethyltridecyl)chroman-6-yl 3-(trifluoromethoxy)benzoate (50)

217 mg (39%) colorless oil isolated. R<sub>f</sub> = 0.4 (PE/DCM 10:1 (v/v)). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (d, <i>J</i> = 7.7 Hz, 1H), 8.09 (s, 1H), 7.57 (t, <i>J</i> = 8.0 Hz, 2H), 7.50 (d, <i>J</i> = 8.2 Hz, 2H), 2.63 (t, <i>J</i> = 6.7 Hz, 2H), 2.13 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.90 – 1.79 (m, 2H), 1.57 – 1.49 (m, 4H), 1.39 (d, <i>J</i> = 6.1 Hz, 2H), 1.19 – 1.13 (m, 10H), 1.10 (d, <i>J</i> = 9.7 Hz, 6H), 0.87 (t, <i>J</i> = 6.6 Hz, 14H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.8, 150.1, 149.5, 140.7, 131.3, 130.3, 128.5, 128.0, 127.5, 126.1, 124.4, 122.7, 120.4 (q, <i>J</i> = 257.0 Hz), 118.1, 75.7, 39.4, 38.2, 37.5, 37.3, 33.02 – 32.88 (m), 28.0, 24.8, 24.5, 22.7, 22.6, 21.0, 19.8, 19.6, 19.3, 13.2, 12.3. HRMS: m/z(ESI) calculated[M+H]<sup>+</sup>: 619.3974, 620.4008, measured: 619.3967, 620.3999.

1-(3-nitrophenoxy)-2, 2, 6, 6-tetramethyloipiperidine (51)
178 mg (64%) light yellow oil isolated. R_f = 0.7 (PE/EA 50:1 (v/v)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.09 (s, 1H), 7.72 (d, \(J = 8.1\) Hz, 1H), 7.45 (s, 1H), 7.34 (t, \(J = 8.2\) Hz, 1H), 1.62 (ddd, \(J = 17.6, 9.6, 3.1\) Hz, 6H), 1.24 (s, 6H), 1.00 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.1, 149.0, 129.2, 120.1, 115.1, 109.2, 60.7, 39.6, 32.3, 20.4, 16.8. HRMS: m/z (ESI) calculated [M+H]\(^+\): 279.1709, measured: 279.1700.

5. Reference


S30
6. NMR Spectra

$^{19}$F NMR (376 MHz, CDCl$_3$) of TFMS

$^1$H NMR (400 MHz, CDCl$_3$) of TFMS

![TFMS 1H NMR spectrum](image1)

$^{19}$F NMR (376 MHz, CDCl$_3$) of TFMS3

![TFMS3 19F NMR spectrum](image2)
$^1$H NMR (400 MHz, CDCl$_3$) of TFMS3

$^{19}$F NMR (376 MHz, CDCl$_3$) of TFMS2
$^1$H NMR(400 MHz, CDCl$_3$) of TFMS2

TFMS2

$^1$H NMR(400 MHz, CDCl$_3$) of 14a

14a

S34
$^1$H NMR (400 MHz, CDCl$_3$) of 15a

$^1$H NMR (400 MHz, CDCl$_3$) of 37a
$^1$H NMR (400 MHz, CDCl$_3$) of 49a

$^{13}$C NMR (100 MHz, CDCl$_3$) of 49a
$^1$H NMR (400 MHz, DMSO-$d_6$) of 50a

$^{13}$C NMR (100 MHz, CDCl$_3$) of 50a

50a
$^{13}$C NMR (100 MHz, CDCl$_3$) of 3

$^{19}$F NMR (376 MHz, CDCl$_3$) of 5
$^1$H NMR(400 MHz, CDCl$_3$) of 5

$^{13}$C NMR (100 MHz, CDCl$_3$) of 5
$^{19}$F NMR (376 MHz, CDCl$_3$) of $8$

$^{1}$H NMR (400 MHz, CDCl$_3$) of $8$
$^{13}$C NMR (100 MHz, CDCl$_3$) of 8

$^{19}$F NMR (376 MHz, CDCl$_3$) of 10
$^1$H NMR (400 MHz, CDCl$_3$) of 10

$^{13}$C NMR (100 MHz, CDCl$_3$) of 10
$^{19}$F NMR (376 MHz, CDCl$_3$) of 11

$^1$H NMR (400 MHz, CDCl$_3$) of 11
$^{13}$C NMR (100 MHz, CDCl$_3$) of 11

$^{19}$F NMR (376 MHz, CDCl$_3$) of 12
$^1$H NMR (400 MHz, CDCl$_3$) of 12

$^{13}$C NMR (100 MHz, CDCl$_3$) of 12
\[^{19}F \text{ NMR (376 MHz, CDCl}_3\text{) of 13}\]

\[\text{MeC}_2\text{C} - \text{OCF}_3\]

\[13\]

\[^{1}H \text{ NMR (400 MHz, CDCl}_3\text{) of 13}\]

\[\text{MeC}_2\text{C} - \text{OCF}_3\]

\[13\]
$^{13}$C NMR (100 MHz, CDCl$_3$) of 13

$^{19}$F NMR (376 MHz, CDCl$_3$) of 14
$^1$H NMR (400 MHz, CDCl$_3$) of 14

$^{13}$C NMR (100 MHz, CDCl$_3$) of 14
$^{19}$F NMR (376 MHz, CDCl$_3$) of 15

$^1$H NMR (400 MHz, CDCl$_3$) of 15
$^{13}$C NMR (100 MHz, CDCl$_3$) of 15

**15**

$^{19}$F NMR (376 MHz, CDCl$_3$) of 16

**16**
$^1$H NMR (400 MHz, CDCl$_3$) of 16

$^{13}$C NMR (100 MHz, CDCl$_3$) of 16
$^{19}$F NMR (376 MHz, CDCl$_3$) of 19

$^1$H NMR (400 MHz, CDCl$_3$) of 19
$^{13}$C NMR (100 MHz, CDCl$_3$) of 19

$^{19}$F NMR (376 MHz, CDCl$_3$) of 22

S54
$^1$H NMR (400 MHz, CDCl$_3$) of 22

$^{13}$C NMR (100 MHz, CDCl$_3$) of 22
\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) of 23

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) of 23
$^{13}$C NMR (100 MHz, CDCl$_3$) of 23

![13C NMR spectrum of 23](image)

$^{19}$F NMR (376 MHz, CDCl$_3$) of 24

![19F NMR spectrum of 24](image)
$^1$H NMR (400 MHz, CDCl$_3$) of 24

$^{13}$C NMR (100 MHz, CDCl$_3$) of 24
Mass Spectrum of 24

\[ \text{Mass Spectrum of 24} \]

\[ \text{19}^F \text{ NMR (376 MHz, CDCl}_3\text{) of 25} \]

\[ \text{19}^F \text{ NMR (376 MHz, CDCl}_3\text{) of 25} \]
$^1$H NMR (400 MHz, CDCl$_3$) of 25

$^{13}$C NMR (100 MHz, CDCl$_3$) of 25
Mass Spectrum of 25

\[ \text{Mass Spectrum of 25} \]

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{OCF}_3 \\
\text{Cl} & \quad \text{25}
\end{align*}
\]

\[^{19}\text{F} \text{NMR (376 MHz, CDCl}_3) \text{ of 26} \]

\[
\begin{align*}
\text{Cl} & \quad \text{OCF}_3 \\
\text{NC} & \quad \text{26}
\end{align*}
\]
$^1$H NMR (400 MHz, CDCl$_3$) of 26

$^{13}$C NMR (100 MHz, CDCl$_3$) of 26
$^{19}$F NMR (376 MHz, CDCl$_3$) of 27

$^1$H NMR (400 MHz, CDCl$_3$) of 27
$^{13}$C NMR (100 MHz, CDCl$_3$) of 27

$^{19}$F NMR (376 MHz, CDCl$_3$) of 28
$^1$H NMR (400 MHz, CDCl$_3$) of 28

$^{13}$C NMR (100 MHz, CDCl$_3$) of 28
Mass Spectrum of 28

19F NMR (376 MHz, CDCl3) of 29
$^1$H NMR (400 MHz, CDCl$_3$) of 29

$^{13}$C NMR (100 MHz, CDCl$_3$) of 29
Mass Spectrum of 29

$^{19}$F NMR (376 MHz, CDCl$_3$) of 30
$^1$H NMR (400 MHz, CDCl$_3$) of 30

$^{13}$C NMR (100 MHz, CDCl$_3$) of 30
Mass Spectrum of 30

$^{19}$F NMR (376 MHz, CDCl$_3$) of 31
$^1$H NMR (400 MHz, CDCl$_3$) of 31

$^{13}$C NMR (100 MHz, CDCl$_3$) of 31
Mass Spectrum of 31

19F NMR (376 MHz, CDCl3) of 32
$^1$H NMR (400 MHz, CDCl$_3$) of 32

$^{13}$C NMR (100 MHz, CDCl$_3$) of 32
$^{19}\text{F} \text{NMR (376 MHz, CDCl}_3\text{)} \text{ of 33}$

$^{1}\text{H} \text{NMR(400 MHz, CDCl}_3\text{)} \text{ of 33}$
$^{13}$C NMR (100 MHz, CDCl$_3$) of 33

$^{19}$F NMR (376 MHz, CDCl$_3$) of 34
$^1$H NMR (400 MHz, CDCl$_3$) of 34

$^{13}$C NMR (100 MHz, CDCl$_3$) of 34
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$ of 35

$^{1}\text{H NMR (400 MHz, CDCl}_3\text{)}$ of 35
$^{13}$C NMR (100 MHz, CDCl$_3$) of 35

$^{19}$F NMR (376 MHz, CDCl$_3$) of 37
$^1$H NMR (400 MHz, CDCl$_3$) of 37

$^{13}$C NMR (100 MHz, CDCl$_3$) of 37
$^{19}$F NMR (376 MHz, CDCl$_3$) of 40

$^1$H NMR (400 MHz, CDCl$_3$) of 40
$^{13}$C NMR (100 MHz, CDCl$_3$) of 40

$^{19}$F NMR (376 MHz, CDCl$_3$) of 43
$^1$H NMR (400 MHz, CDCl$_3$) of 43

$^1$C NMR (100 MHz, CDCl$_3$) of 43
$^{19}$F NMR (376 MHz, CDCl$_3$) of 45

$^1$H NMR (400 MHz, CDCl$_3$) of 45
$^{13}$C NMR (100 MHz, CDCl$_3$) of 45

$^{19}$F NMR (376 MHz, CDCl$_3$) of 46
$^1$H NMR (400 MHz, CDCl$_3$) of 46

$^{13}$C NMR (100 MHz, CDCl$_3$) of 46
$^{19}$F NMR (376 MHz, CDCl$_3$) of 47

$^1$H NMR (400 MHz, CDCl$_3$) of 47
\[ \text{\( ^{13}\text{C} \text{ NMR (100 MHz, CDCl}_3 \text{) of } 47 \)} \]

\[ \text{\( ^{19}\text{F} \text{ NMR (376 MHz, CDCl}_3 \text{) of } 48 \)} \]
$^1$H NMR (400 MHz, CDCl$_3$) of 48

$^{13}$C NMR (100 MHz, CDCl$_3$) of 48
$^{19}$F NMR (376 MHz, CDCl$_3$) of 49

$^1$H NMR (400 MHz, CDCl$_3$) of 49
$^{13}$C NMR (100 MHz, CDCl$_3$) of 49

\[
\begin{align*}
&16.555 \\
&20.700 \\
&23.691 \\
&31.452 \\
&40.889 \\
&47.213 \\
&75.568 \\
&76.683 \\
&77.000 \\
&77.318 \\
&116.587 \\
&119.149 \\
&121.712 \\
&122.068 \\
&124.275 \\
&125.073 \\
&127.869 \\
&129.796 \\
&132.949 \\
&149.238 \\
&164.707 \\
&-57.848
\end{align*}
\]

$^{19}$F NMR (376 MHz, CDCl$_3$) of 50

\[
\begin{align*}
&-57.848
\end{align*}
\]
$^1$H NMR (400 MHz, CDCl$_3$) of 50

$^{13}$C NMR (100 MHz, CDCl$_3$) of 50
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 51

$^{13}C$ NMR (100 MHz, CDCl$_3$) of 51