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## **Supporting Information**

## Trifluoromethylation of Haloarenes with a New Trifluoromethylating

## Reagent Cu(O<sub>2</sub>CCF<sub>2</sub>SO<sub>2</sub>F)<sub>2</sub>

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#### **General information**

NMR spectra were obtained on a 400 MHz spectrometer using CDCl<sub>3</sub> or CD<sub>3</sub>CN as deuterated solvents, with proton, carbon and fluorine resonances at 400 MHz, 100 MHz and 376 MHz, respectively. Chemical shifts were reported in parts per million (ppm) relative to TMS as an internal standard ( $\delta_{TMS} = 0$  ppm) for <sup>1</sup>H and <sup>13</sup>C NMR spectra and CFCl<sub>3</sub> as an external standard (negative for upfield) for <sup>19</sup>F NMR spectra. GC-MS (EI) data were determined on an Agilent 5975C. HRMS (EI) data were tested on a Water Micromass GCT Premier. Element analysis data were determined on Elementar VARIO EL apparatus. DMF was distilled from CaH<sub>2</sub>. All the other solvents or reagents were used as commercial sources without purification if not noted. All reactions were performed in standard sealed tubes and monitored by thin-layer chromatography (TLC), <sup>19</sup>F NMR or GC-MS. Flash column chromatography was carried out using 300-400 mesh silica gel.

#### Procedures for the preparation of Cu(O<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F)<sub>2</sub>

Synthesis of FSO<sub>2</sub>CF<sub>2</sub>COOH and FSO<sub>2</sub>CF<sub>2</sub>COOMe

$$F_2C-CF_2 \longrightarrow FSO_2CF_2COF \xrightarrow{H_2O} FSO_2CF_2COH$$

An oven-dried 1000 mL three-necked round-bottom flask was equipped with a magnetic stir bar, addition constant pressure funnel with nitrogen (N<sub>2</sub>) inlet and gas outlet. The gas outlet was connected to an empty 500 ml backup trap and then to an inverted glass funnel outlet positioned just above a 1000 mL beaker, which contained 120 g of NaOH in 600 ml of water. The flask was successively charged with dry petroleum ether (400 mL) and tetrafluoroethane  $\beta$ -sultone (440 g, 2.44 mol), and deionized water (44g, 2.44 mol) was added dropwise via addition funnel, with stirring and cooling with an ice bath over a 2 h period. Upon completion of addition, the reaction mixture was warmed stepwise to room temperature, and then the mixture was stirred at room temperature overnight. After blown by nitrogen flow for 1 h to completely remove HF remained in the system, the resulting reaction mixture was collected and directly distilled in vacuum to afford pure product FSO<sub>2</sub>CF<sub>2</sub>COOH as colorless liquid (340 g, 78% yield, 92-94 °C/50 mmHg).

**FSO<sub>2</sub>CF<sub>2</sub>COOH:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  5.47 (s, 1H) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  41.47 (t, *J* = 5.0 Hz), -104.00 (d, *J* = 5.1 Hz) ppm.<sup>[1]</sup>

$$F_2C-CF_2$$
  $\longrightarrow$  FSO<sub>2</sub>CF<sub>2</sub>COF  $\xrightarrow{\text{MeOH}}$  FSO<sub>2</sub>CF<sub>2</sub>COOMe

An oven-dried 1000 mL three-necked round-bottom flask was equipped with a magnetic stir bar, addition constant pressure funnel and gas outlet. The gas outlet was connected to an empty 500 ml backup trap and then to an inverted glass funnel outlet positioned just above a 1000 mL beaker, which contained 120 g of NaOH in 600 ml of water. The flask was charged with dry methanol (160 g, 5 mol). Tetrafluoroethane  $\beta$ -sultone (440 g, 2.44 mol) was added dropwise via addition funnel, with stirring and cooling with an ice bath over a 3 h period. Upon completion of addition, the reaction mixture was warmed stepwise to room temperature, and then the mixture was stirred

at room temperature overnight. After blown by nitrogen flow for 1 h to completely remove HF remained in the system, the resulting reaction mixture was washed with water (2\*400 mL) and brine (2\*400 mL) to remove the residual methanol, and the organic phase was collected and dried with anhydrous sodium sulfate. After filtration, the filtrate with crude product was purified by distillation to afford pure product FSO<sub>2</sub>CF<sub>2</sub>COOMe as colorless liquid (398 g, 85% yield, 116-118 °C).

**FSO<sub>2</sub>CF<sub>2</sub>COOMe:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  4.08 (s, 1H) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  41.17 (t, *J* = 5.0 Hz), -103.39 (d, *J* = 4.8 Hz) ppm.<sup>[2]</sup>

Synthesis of  $Cu(O_2CF_2SO_2F)_2$ 

$$FSO_2CF_2COOH \xrightarrow{Cu_2(OH)_2CO_3} Cu(O_2CF_2SO_2F)_2$$
  
Et<sub>2</sub>O, r.t.

An oven-dried 250 mL three-necked round-bottom flask equipped with a stir bar was charged with dry Et<sub>2</sub>O (100 mL) and Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> (66.3 g, 0.3 mol). FSO<sub>2</sub>CF<sub>2</sub>COOH (53.4 g, 0.3 mol) was added dropwise during a period of 1 h. The reaction mixture was stirred at room temperature for 24 h. The resulting reaction mixture was filtered via Celite pad. The filtrate was concentrated under reduced pressure to dryness. The residue was then completely dried in vacuum at 50 °C to provide a blue solid (59.1 g, 97% yield).

**Cu**(**O**<sub>2</sub>**CF**<sub>2</sub>**SO**<sub>2</sub>**F**)<sub>2</sub>: Anal. Calcd for C<sub>4</sub>CuF<sub>6</sub>O<sub>8</sub>S<sub>2</sub>: C, 11.50; S, 15.35. Found: C, 11.15; S, 15.27.

X-ray crystallographic studies of Cu(FSO<sub>2</sub>CF<sub>2</sub>COO)<sub>2</sub>·4H<sub>2</sub>O



Suitable crystals were mounted on grass fibers or sealed in thin-walled glass capillaries. X-ray intensity data of Cu(FSO<sub>2</sub>CF<sub>2</sub>COO)<sub>2</sub>·4H<sub>2</sub>O was collected on a Bruker SMART CCD-APEX diffractometer employing graphite monochromated Mo-K $\alpha$  radiation ( $\lambda$ =0.71073 Å) and using the  $\omega$ -2 $\theta$  scan technique. The intensity data were corrected for Lorentz and polarization effects. Refinement was by full-matrix least-squares techniques based on *F* to minimize the quantity  $\sum w(|Fo|-|Fc|)^2$  with  $w = 1/\sigma^2(F)$ . Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. Crystal data and data collection parameters are summarized in Table S1.

	Cu(FSO <sub>2</sub> CF <sub>2</sub> COO) <sub>2</sub> ·4H <sub>2</sub> O
CCDC No.	1450534
empirical formula	C4 H8 Cu F6 O12 S2
formula mass	489.76
crystallization	Et <sub>2</sub> O/Hexane
dimensions [mm <sup>3</sup> ]	0.265 x 0.211 x 0.145
crystal system	Triclinic
space group	P-1
a [Å]	5.4169(10)
b [Å]	6.2821(12)
c [Å]	11.269(2)
α[°]	88.143(4)

Table S1. Crystallographic Data for Cu(FSO<sub>2</sub>CF<sub>2</sub>COO)<sub>2</sub>:4H<sub>2</sub>O

β[°]	84.561(4)
γ[°]	87.540(4)
V [Å <sup>3</sup> ]	381.26(13)
Z	1
d <sub>calcd</sub> [Mg m <sup>-3</sup> ]	2.133
absorption coefficient [mm <sup>-1</sup> ]	1.834
T [k]	293(2)
2θ <sub>max</sub> [°]	26
measured reflections	2189
unique reflections	1448
R <sub>int</sub>	0.0397
R1 [I>2σ(I)]	0.0647
wR2 [I>2σ(I)]	0.1687
R1(all data)	0.0654
wR2(all data)	0.1697



Figure S1. CuCF<sub>3</sub> species region of the <sup>19</sup>F NMR spectrum of the reaction mixture of Cu(O<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F)<sub>2</sub> in DMF under nitrogen at room temperature

#### General procedures for trifluoromethylation of various (hetero)aryl iodides

A Schleck tube was charged with Cu (39.2 mg, 0.6 mmol), Cu(O<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F)<sub>2</sub> (250 mg, 0.6 mmol) and aryl iodide (0.4 mmol) under nitrogen. DMF (4 mL) was added under N<sub>2</sub> atmosphere while keeping the Schleck tube at -78 °C. The reaction mixture was then warmed stepwise to room temperature. The resulting mixture was stirred at room temperature for 3 h. An internal standard (trifluorotoluene) was added into the resulting mixture to calculate the <sup>19</sup>F NMR yield. Or the reaction mixture was filtered. The filtrate was washed with water (2\*5 mL) and brine (2\*5 mL), and the organic phase was dried with anhydrous sodium sulfate. After removal of the solvent under reduced pressure with a rotary evaporator, the crude product was purified by column chromatography on silica gel with an ethyl acetate/petroleum ether mixture as eluent to afford the desired trifluoromethylated product.



**1-(trifluoromethyl)naphthalene** (**2a**).<sup>[3]</sup> Obtained as colorless oil in 84% yield (66 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.25 (d, J = 8 Hz, 1H),  $\delta$  8.03 (d, J = 8.0 Hz, 1H),  $\delta$  7.92 (q, J = 8.0 Hz, 2H),  $\delta$  7.67-7.58 (m, 2H),  $\delta$  7.51 (t, J = 8 Hz, 1H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  134.0, 132.9, 129.1, 128.9, 127.8, 126.7, 126.2 (q, J = 30 Hz), 124.8 (q, J = 6 Hz), 124.4 (q, J = 3 Hz), 124.3, 124.9 (q, J = 271 Hz) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -59.72 (s, 3F) ppm.



**1-methoxy-2-(trifluoromethyl)benzene** (2b).<sup>[4]</sup> 94% <sup>19</sup>F NMR yield. Characterization of 2b in the reaction solution: m/z = 176.1 (GC–MS; EI). Crude <sup>19</sup>F NMR (unlocked):  $\delta$  –62.44 (s, 3F) ppm.



**1-methoxy-3-(trifluoromethyl)benzene** (2c).<sup>[4]</sup> 70% <sup>19</sup>F NMR yield. Characterization of 2c in the reaction solution: m/z = 176.1 (GC–MS; EI). Crude <sup>19</sup>F NMR (unlocked):  $\delta$  –62.83 (s, 3F) ppm.



**1-methoxy-4-(trifluoromethyl)benzene** (2d).<sup>[4]</sup> 65% <sup>19</sup>F NMR yield. Characterization of 2d in the reaction solution: m/z = 176.1 (GC–MS; EI). Crude <sup>19</sup>F NMR (unlocked):  $\delta$  –61.49 (s, 3F) ppm.



**1-methyl-2-(trifluoromethyl)benzene (2e).**<sup>[4]</sup> 91% <sup>19</sup>F NMR yield. Characterization of **2e** in the reaction solution: m/z = 160.0 (GC–MS; EI). Crude <sup>19</sup>F NMR (unlocked):  $\delta$ –61.79 (s, 3F) ppm.



**1-methyl-3-(trifluoromethyl)benzene (2f).**<sup>[4]</sup> 62% <sup>19</sup>F NMR yield. Characterization of **2f** in the reaction solution: m/z = 160.1 (GC–MS; EI). Crude <sup>19</sup>F NMR (unlocked):  $\delta$  –62.73 (s, 3F) ppm.



**1-methyl-4-(trifluoromethyl)benzene (2g).**<sup>[4]</sup> 57% <sup>19</sup>F NMR yield. Characterization of **2g** in the reaction solution: m/z = 160.1 (GC–MS; EI). Crude <sup>19</sup>F NMR (unlocked):  $\delta$  –62.39 (s, 3F) ppm.



**1-nitro-2-(trifluoromethyl)benzene (2h).**<sup>[5]</sup> Obtained as a white solid in 82% yield (63 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.88-7.82 (m, 2H), 7.77-7.73 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.4, 133.3, 132.7, 128.1 (q, *J* = 5.0 Hz), 125.1, 123.8 (q, *J* = 34.0 Hz), 122.1 (q, *J* = 272.0 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -60.13 (s, 3F) ppm.



**1-nitro-4-(trifluoromethyl)benzene (2i).**<sup>[6]</sup> Obtained as a white solid in 78% yield (60 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.38 (d, J = 8.0 Hz, 2H) ppm,  $\delta$  7.86 (d, J = 8.0 Hz, 2H) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -63.18 (s, 3F) ppm.



4-(trifluoromethyl)benzonitrile (2j).<sup>[3]</sup> Obtained as colorless oil in 90% yield (62

mg).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.81 (d, J = 8.0 Hz, 2 H), 7.76 (d, J = 8.0 Hz, 2 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  134.7 (q, J = 33 Hz), 132.8, 126.3, 123.2 (q, J = 272 Hz), 117.5, 116.2 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -63.61 (s, 3F) ppm.



**2-(trifluoromethyl)benzonitrile (2k)**.<sup>[3]</sup> Obtained as colorless oil in 78% yield (53 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.86-7.68 (m, 4H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  134.8, 133.1, 132.7, 132.4, 126.8 (q, *J* = 3 Hz), 122.5 (q, *J* = 272 Hz), 115.6, 110.2 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -62.05 (s, 3F) ppm.



**1,3-dimethoxy-2-(trifluoromethyl)benzene** (**2l).** <sup>[7]</sup> Obtained as a light yellow viscous solid in 70% yield (57mg). <sup>1</sup>H NMR (400M, CDCl<sub>3</sub>):  $\delta$  7.38 (t, *J* = 8.0 Hz, 1H),  $\delta$  6.61 (d, *J* = 8.0 Hz, 2H),  $\delta$  3.86 (s, 6H) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -54.90 (s, 3F) ppm.



**1-chloro-4-(trifluoromethyl)benzene (2m).**<sup>[3]</sup> 70% <sup>19</sup>F NMR yield. Characterization of P2-7 in the reaction solution: m/z = 180.1 (GC–MS; EI). Crude <sup>19</sup>F NMR (unlocked):  $\delta$  –62.77 (s, 3F) ppm.



**1-(2-(trifluoromethyl)phenyl)ethanone** (**2n**).<sup>[8]</sup> Obtained as colorless oil in 80% yield (60 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.69 (d, J = 8.0 Hz, 1H),  $\delta$  7.61-7.52 (m, 2H),  $\delta$  7.45 (d, J = 8.0 Hz, 1H),  $\delta$  2.56 (s, 3H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  201.9, 140.5, 132.0, 130.2, 127.1, 127.0, 126.7 (q, J = 5 Hz), 123.7 (q, J = 272 Hz), 30.6 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -58.25 (s, 3F) ppm.



**1-(4-(trifluoromethyl)phenyl)ethanone** (**20).**<sup>[9]</sup> Obtained as colorless oil in 73% yield (55 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.03 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 2.62 (s, 3H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  197.0, 139.8, 134.5 (q, J = 33 Hz), 128.7, 125.8 (q, J = 4 Hz), 123.7 (q, J = 271 Hz), 26.9 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -63.23 (s, 3F) ppm.



methyl 2-(trifluoromethyl)benzoate (2p).<sup>[3]</sup> Obtained as colorless oil in 81% yield (66 mg).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78-7.72 (m, 2H), 7.60-7.58 (m, 2H), 3.93 (s, 3H) ppm. <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>): δ 167.3, 131.8, 131.2, 130.2, 128.8 (q, J = 32.0 Hz), 126.7 (q, J = 5.0 Hz), 123.5 (q, J = 271.0 Hz), 52.8 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -59.79 (s, 3F) ppm.

F<sub>3</sub>C COOMe

**methyl 4-(trifluoromethyl)benzoate** (**2q**).<sup>[3]</sup> Obtained as colorless oil in 86% yield (70 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.14 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 3.94 (s, 3H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.9, 134.5 (q, J = 33 Hz), 133.5, 130.1, 125.5 (q, J = 4 Hz), 123.8 (q, J = 271 Hz), 52.6 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -63.21 (s, 3F) ppm.



**2-(trifluoromethyl)pyridine** (**2r**).<sup>[4]</sup> 80% <sup>19</sup>F NMR yield. Characterization of **2r** in the reaction solution: m/z = 147.1 (GC–MS; EI). Crude <sup>19</sup>F NMR (unlocked):  $\delta$  –62.77 (s, 3F) ppm.



**2-fluoro-4-(trifluoromethyl)pyridine (2s).** 90% <sup>19</sup>F NMR yield. Characterization of **2s** in the reaction solution: m/z = 165.1 (GC–MS; EI). Crude <sup>19</sup>F NMR (unlocked): $\delta = -65.12$  (s, 3F),  $\delta - 66.52$  (s, F) ppm.



**2-methoxy-3-(trifluoromethyl)pyridine (2t).** Obtained as a yellow liquid in 75% (53 mg). <sup>1</sup>H NMR (400M, CDCl<sub>3</sub>):  $\delta$  8.32 (d, J = 4.0 Hz, 1H) ppm,  $\delta$  7.84 (d, J = 8.0 Hz, 1 H),  $\delta$  6.95 (dd, J = 4.0 Hz, 1H) ppm,  $\delta$  4.03 (s, 3H) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -64.03 (s, 3F) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  161.0, 150.6, 136.4 (q, J = 5 Hz), 123.2 (q, J = 270 Hz), 116.0, 113.4 (q, J = 33 Hz), 54.1 ppm. HRMS-EI m/z Anal. Calculated for C<sub>7</sub>H<sub>6</sub>NOF<sub>3</sub>: 177.0401, Found: 177.0403.



4-methoxy-2-(trifluoromethyl)pyrimidine (2u). Obtained as a yellow liquid in 74%

yield (53 mg). <sup>1</sup>H NMR (400M, CDCl<sub>3</sub>):  $\delta$  8.52 (d, *J* = 4.0 Hz, 1H) ppm,  $\delta$  6.86 (d, *J* = 4.0 Hz, 1 H) ppm,  $\delta$  4.04 (s, 3 H) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -71.09 (s, 3F) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.4, 157.5, 156.5 (q, *J* = 37 Hz), 119.4 (q, *J* = 274 Hz), 110.7, 54.6 ppm. HRMS-EI m/z Anal. Calculated for C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>OF<sub>3</sub>: 178.0354, Found: 178.0350.

**5-chloro-2-(trifluoromethyl)pyrimidine (2v)**. Obtained as yellow oil in 71% yield (52 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.96 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 156.7, 154.6 (q, J = 37 Hz), 134.1, 119.4 (q, J = 274 Hz) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -70.04 (s, 3F). HRMS-EI m/z Anal. Calculated for C<sub>5</sub>H<sub>2</sub>N<sub>2</sub>F<sub>3</sub>Cl: 181.9859, Found: 181.9858.



**1-methyl-2-(trifluoromethyl)-1H-imidazole** (2w).<sup>[10]</sup> 50% <sup>19</sup>F NMR yield. Characterization of 2w in the reaction solution: m/z = 150.0 (GC–MS; EI). Crude <sup>19</sup>F NMR (unlocked):  $\delta$  –61.47 (s, 3F) ppm.



**3-(trifluoromethyl)thiophene (2x).**<sup>[11]</sup> 69% <sup>19</sup>F NMR yield. Characterization of **2x** in the reaction solution: m/z = 152.0 (GC–MS; EI). Crude <sup>19</sup>F NMR (unlocked):  $\delta$  –59.45 (s, 3F) ppm.

#### General procedures for trifluoromethylation of various benzyl bromides

A Schleck tube was charged with  $Cu(O_2CF_2SO_2F)_2$  (418 mg, 1.0 mmol) and benzyl bromide (0.5 mmol). DMF (4 mL) was added under N<sub>2</sub> atmosphere while keeping the Schleck tube at -78 °C. The reaction mixture was then warmed stepwise to room temperature, heated to 60 °C and stirred for 3 h. An internal standard (trifluorotoluene) was added to calculate the <sup>19</sup>F NMR yield. Or the reaction mixture was washed by water (2\*5 mL) and brine (2\*5 mL), and the organic phase was dried with anhydrous sodium sulfate. After removal of the solvent under reduced pressure with a rotary evaporator, the crude product was purified by column chromatography on silica gel with an ethyl acetate/petroleum ether mixture as eluent to afford the desired trifluoromethylated product.



**1-nitro-4-(2,2,2-trifluoroethyl)benzene (2aa).**<sup>[12]</sup> Obtained as a white solid in 67% yield (69 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.24 (d, J = 12.0 Hz, 2H), 7.50 (d, J = 12.0 Hz, 2H), 3.50 (q, J = 10.7 Hz, 3H) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -65.47 (t, J = 11.3, 3F) ppm. CN

**4-(2,2,2-trifluoroethyl)benzonitrile (2bb).**<sup>[12]</sup> Obtained as a white solid in 78% yield (72 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.65 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.44 (q, *J* = 10.7 Hz, 3H) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -65.57 (t, *J* = 9.4, 3F) ppm.



**methyl 4-(2,2,2-trifluoroethyl)benzoate (2cc).**<sup>[12]</sup> Obtained as a white solid in 72% yield (78 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.02 (d, J = 12.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 3.91 (s, 3H), 3.42 (q, J = 10.7 Hz, 2H) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -65.65 (t, J = 9.4, 3F) ppm.

F<sub>3</sub>C

**1-(2,2,2-trifluoroethyl)naphthalene (2dd).**<sup>[13]</sup> Obtained as a white solid in 70% yield (74 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.05 (d, *J* = 8.0 Hz, 2H), 7.93-7.88 (m, 2H), 7.63-7.48 (m, 4H), 3.88 (q, *J* = 10.7 Hz, 2H) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -64.68 (t, *J* = 9.4, 3F) ppm.



**1,3-dimethoxy-5-(2,2,2-trifluoroethyl)benzene (2ee).**<sup>[12]</sup> Obtained as a white solid in 64% yield (70 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.45 (s, 3H), 3.80 (s, 6H), 3.31 (q, J = 10.7 Hz, 2H) ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -65.67 (t, J = 11.3, 3F) ppm.

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70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 f1 (ppm)







Crude <sup>19</sup>F NMR spectrum of 1-methoxy-3-(trifluoromethyl)benzene (2c)



70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 f1 (ppm)

Crude <sup>19</sup>F NMR spectrum of 1-methyl-2-(trifluoromethyl)benzene (2e)









S22





![](_page_24_Figure_0.jpeg)

![](_page_25_Figure_0.jpeg)

![](_page_26_Figure_0.jpeg)

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 f1 (ppm)

Crude <sup>19</sup>F NMR spectrum of 1-chloro-4-(trifluoromethyl)benzene (2m)

![](_page_27_Figure_1.jpeg)

<sup>1</sup>H NMR spectrum of 1-(2-(trifluoromethyl)phenyl)ethanone (2n)

![](_page_27_Figure_3.jpeg)

![](_page_28_Figure_0.jpeg)

![](_page_28_Figure_1.jpeg)

![](_page_29_Figure_0.jpeg)

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 f1 (ppm)

![](_page_30_Figure_0.jpeg)

![](_page_31_Figure_0.jpeg)

![](_page_32_Figure_0.jpeg)

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 f1 (ppm)

![](_page_33_Figure_0.jpeg)

![](_page_34_Figure_0.jpeg)

S35

![](_page_35_Figure_0.jpeg)

![](_page_36_Figure_0.jpeg)

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 f1 (ppm)

![](_page_37_Figure_0.jpeg)

![](_page_37_Figure_1.jpeg)

![](_page_38_Figure_0.jpeg)

![](_page_38_Figure_1.jpeg)

![](_page_39_Figure_0.jpeg)

![](_page_39_Figure_1.jpeg)

![](_page_40_Figure_0.jpeg)

![](_page_41_Figure_0.jpeg)

![](_page_42_Figure_0.jpeg)

![](_page_43_Figure_0.jpeg)

![](_page_44_Figure_0.jpeg)

![](_page_44_Figure_1.jpeg)

<sup>19</sup>F NMR spectrum of 1,3-dimethoxy-5-(2,2,2-trifluoroethyl)benzene (4e)

![](_page_44_Figure_3.jpeg)