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## **Transition-Metal-Free C-H Oxidative Activation:**

## Persulfate-Promoted Selective Benzylic Mono- and

## Difluorination

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## (A) General

All the reagents were commercially available and used without any further purification. The solvents were dried before use. GC-MS analyses were performed on an Thermo Trace 1300 and ISQLT instrument (Column: TR-35 MS: 30 m ×0.25 mm × 0.25  $\mu$ m, ionization mode: EI, carrier gas: He, MS transfer temp: 250 °C, ion source temp: 280 °C, detection detector: initial temperature 50 °C, temperature program: 10 °C/min, final temperature 260 °C, He: 60 mL/min). <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, <sup>19</sup>F-NMRwas recorded on Bruker DRX 500 and tetramethylsilane (TMS) was used as a reference Mass.

#### **(B) Experimental Procedures**

#### **Method A: Monofluorination**

A reaction tube was charged with 4'-Methyl-2-cyanobiphenyl (**1a**) (38.6 mg, 0.2 mmoLl) at room temperature, then  $K_2S_2O_8$  (81mg, 0.3 mmoL), Selectfluor (106.2 mg, 0.3 mmoL) and MeCN/H<sub>2</sub>O (4 mL, v/v = 1:1) were added. The resulting mixture was stirred at 80 °C in this sealed tube equipped with a Teflon plug. After cooling to room temperature, the reaction mixture was quenched and extracted with dichloromethane (5 mL x 3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered, and all of the volatiles were removed under reduced pressure. The resulting residue was purified by flash silica gel column chromatography (eluent: hexane/EtOAc) to afford the desired products.

#### **Method B: Difluorination**

A reaction tube was charged with 4'-Methyl-2-cyanobiphenyl (**1a**) (38.6mg, 0.2mmoL) at room temperature, then  $K_2S_2O_8$  (162 mg, 0.6 mmoL), Selectfluor (212.4 mg, 0.6 mmoL) and MeCN/H<sub>2</sub>O (6 mL, v/v = 1:1) were added. The resulting mixture was stirred at 80 °C in this sealed tube equipped with a Teflon plug. After cooling to room temperature, the reaction mixture was quenched and extracted with dichloromethane (10 mL x 3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered, and all of the volatiles were removed under reduced pressure. The resulting residue was purified by flash silica gel column chromatography (eluent: hexane/EtOAc) to afford the desired products.

### (C) Spectra Analytical data for products

#### 1. Monofluorination:



4'- (fluoromethyl)-[1, 1'-biphenyl]-2-carbonitrile

(2a): The product was obtain as a white solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 (dd, J = 7.7, 0.8 Hz, 1H), 7.66 (dd, J = 7.7, 1.2 Hz, 1H), 7.60 (d, J = 7.7 Hz, 2H), 7.52 (t, J = 6.7 Hz, 3H), 7.46 (td, J = 7.7, 1.0 Hz, 1H), 5.46 (d, J = 47.6 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  144.92 (s), 138.52 (s), 136.85 (s), 133.79 (s), 132.90 (s), 130.05 (s), 129.04 (s), 127.89 – 127.51 (m), 118.59 (s), 111.32 (s), 84.76 (s), 83.43 (s), 77.29 (s), 77.03 (s), 76.78 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -209.02 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>10</sub>FN: 211.23, found 211.11.



#### 2-(fluoromethyl)-1, 1'-biphenyl

(2b): The product was obtained as a colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.79 (d, J = 7.2 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.55–7.48 (m, 2H), 7.47 –7.39 (m, 4H), 7.38 –7.31 (m, 3H), 6.54 (t, J = 54.9 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  141.24 (s), 139.04 (s), 132.36 (d, J = 15.9 Hz), 129.15 (s), 128.32 (t, J = 46.1 Hz), 127.27 (s), 126.66 (s), 126.48 (s), 82.46 (s), 81.15 (s), 76.15 (d, J = 31.9 Hz), 75.96 – 75.89 (m), 75.77 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -215.67 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>11</sub>F: 186.22, found 186.08.



3-(fluoromethyl)-1, 1'-biphenyl

(2c): The product was obtained as a colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  10.10 (s, 1H), 8.11 (d, *J* = 1.6 Hz, 2H), 7.87 (dd, *J* = 7.7, 1.5 Hz, 4H), 7.67 – 7.56 (m, 8H), 7.47 (dt, *J* = 15.9, 7.6 Hz, 6H), 7.43 – 7.32 (m, 3H), 5.45 (d, *J* = 47.8 Hz, 2H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -207.28 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>11</sub>F: 186.22, found 186.12.



#### 1-(tert-butyl)-4-(fluoromethyl)benzene

(2d)<sup>[1]</sup>: The product was obtained as a light yellow oil (this product is challenging to get purification due to high volatility with high reactivity, so it is hard to get pure mono- and difluorination products, we obtained the mixed compounds and the yield was detected by GC-MS, the ratio of these two compounds > 5.5 :1, determinate by <sup>19</sup>F); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) -204.27 (s)(); MS (EI) [M]<sup>+</sup> Calcd for C<sub>11</sub>H<sub>15</sub>F: 166.24, found 166.11.



#### 1- (4- (fluoromethyl) phenyl)ethanone

(2e): The product was obtained as a colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (d, *J* = 7.7 Hz, 2H), 7.56 – 7.32 (m, 2H), 5.44 (d, *J* = 47.2 Hz, 2H), 2.60 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  134.39 (s), 128.53 (s), 126.85 (d, *J* = 17.6 Hz), 124.89 (s), 81.95 (s), 80.58 (s), 77.26 (s), 77.01 (s), 76.75 (s), 29.70 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -213.08 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>9</sub>FO: 152.17, found 152.08.



#### 1-(3-(fluoromethyl)phenyl)ethanone

(2f): The product was obtained as a yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 5.44 (d, *J* = 47.5 Hz, 2H), 2.62 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  196.68 (s), 137.14 – 134.67 (m), 135.03 (d, *J* = 90.0 Hz), 130.76 (s), 127.97 (s), 127.37 (d, *J* = 54.4 Hz), 127.13 – 127.08 (m), 126.00 (s), 83.60 (s), 82.27 (s), 76.29 (s), 76.04 (s), 75.79 (s), 25.65 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -209.33 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>9</sub>FO: 152.17, found 152.12.



#### (4-(fluoromethyl)phenyl)(phenyl)methanone

(2g): The product was obtained as a yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (dd, J = 16.7, 7.8 Hz, 4H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 4H), 5.48 (d, J = 47.2 Hz, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  195.25 (s), 139.66 (d, J = 16.3 Hz), 136.74 (s), 136.45 (s), 131.59 (s), 129.82 (s), 129.20 (d, J = 37.8 Hz), 127.37 (s), 125.64 (s), 83.43 (s), 82.09 (s), 76.31 (s), 76.06 (s), 75.80 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -212.32 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>11</sub>FO: 214.08, found 214.10.



#### 1-chloro-2-(fluoromethyl)-4-nitrobenzene

(2h): The product was obtained as a light yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.38 (d, J = 2.2 Hz, 1H), 8.17 (dd, J = 8.7, 2.3 Hz, 1H), 7.56 (d, J = 8.7 Hz, 1H), 5.56 (d, J = 46.6 Hz, 2H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -116.41 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>5</sub>ClFNO<sub>2</sub>: 189.00, found 189.03.



(2i): The product was obtained as a colorless oil (this product is challenging to get purification due to high volatility and the reported yields are the average GC yields of three trials and determined by <sup>19</sup>F NMR); <sup>19</sup>F NMR



#### 1-bromo-4-(fluoromethyl)benzene

 $(2j)^{[2]}$ : The product was obtained as a red solid (this product is challenging to get purification due to high volatility and the reported yields are the average GC yields of three trials and determined by <sup>19</sup>F NMR ); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -207.86 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>6</sub>BrF: 187.96, found 187.97.



#### 4- (fluoromethyl)benzoic acid

(2k): The product was obtained as a light yellow solid; <sup>1</sup>H NMR (500 MHz, MeOD)  $\delta$  8.03 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 2H), 5.44 (d, *J* = 47.4 Hz, 2H); <sup>13</sup>C NMR (126 MHz, MeOD)  $\delta$  166.99 (s), 140.72 (d, *J* = 17.0 Hz), 129.63 (s), 128.60 (s), 125.48 (s), 82.98 (s), 81.66 (s), 46.95 (s), 46.78 (s), 46.61 (s), 46.44 (s), 46.27 (s); <sup>19</sup>F NMR (470 MHz, MeOD)  $\delta$  -214.22 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>7</sub>FO<sub>2</sub>: 154.04, found 155.07.



#### 3- (fluoromethyl)benzoic acid

(21): The product was obtained as a white solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.12 (d, *J* = 7.3 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 5.45 (d, *J* = 47.5 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  170.63 (s), 135.85 (d, *J* = 17.4 Hz), 131.57 (s), 130.26 - 127.32 (m), 83.48 (s), 82.15 (s), 76.77 - 75.74 (m), 75.74 - 75.23 (m). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -209.43 (s). MS (EI) [M]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>7</sub>FO<sub>2</sub>: 154.04, found 155.06.



#### 4-(fluoromethyl)benzamide

(2m): The product was obtained as a yellow soild; <sup>1</sup>H NMR (500 MHz, MeOD)  $\delta$  7.90 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 5.44 (d, *J* = 47.4 Hz, 2H);<sup>13</sup>C NMR (126 MHz, MeOD)  $\delta$  169.52 (s), 139.53 (d, *J* = 17.0 Hz), 126.55 (s), 125.69 (s), 83.01 (s), 81.69 (s), 46.78 (s), 46.61 (s), 46.44 (s); <sup>19</sup>F NMR (470 MHz, MeOD)  $\delta$  -213.21 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>8</sub>FNO: 153.06, found 153.10.



#### methyl 4-(fluoromethyl)benzoate

(2n): The product was obtained as a colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 5.44 (d, *J* = 47.2 Hz, 2H), 3.92 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  165.71 (s), 140.21 (d, *J* = 17.1 Hz), 129.31 (s), 128.89 (s), 125.63 (s), 83.38 (s), 82.04 (s), 76.29 (s), 76.29 (s), 76.38 – 75.30 (m), 51.20 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -212.85 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>9</sub>FO<sub>2</sub>: 168.06, found 168.10.



#### 1- (fluoromethyl)-4-nitrobenzene

(**2q**): The product was obtained as a yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.26 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 5.51 (d, J = 46.8 Hz, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 146.98 (s), 142.40 (d, J = 17.3 Hz), 126.05 (d, J = 5.8 Hz), 122.86 (s), 82.56 (s), 81.20 (s), 76.16 (d, J = 31.9 Hz), 75.77 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -215.66 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>6</sub>FNO<sub>2</sub>: 155.04, found 155.04.



#### 1- (fluoromethyl)-3-nitrobenzene

(2r): the product was obtained as a yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.33 – 8.13 (m, 2H), 7.70 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.9 Hz, 1H), 5.49 (d, J = 47.0 Hz, 2H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -212.33 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>6</sub>FNO<sub>2</sub>: 155.04, found 155.07.



# (2s): The product was obtained as a yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) $\delta$ 8.22 (d, *J* = 8.2 Hz, 1H), 7.78 (dd, *J* = 28.4, 7.7 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 5.87 (d, *J* = 47.9 Hz, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) $\delta$ 134.39 (s), 128.53 (s), 126.85 (d, *J* = 17.6 Hz), 124.89 (s), 81.95 (s), 80.58 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) $\delta$ -219.15 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>6</sub>FNO<sub>2</sub>: 155.04, found 138.05.



#### 1-(1-fluoroethyl)-4-nitrobenzene

(2t): The product was obtained as a yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 5.73 (dd, *J* = 47.4, 6.5 Hz, 1H), 1.69 (d, *J* = 6.5 Hz, 1H), 1.64 (d, *J* = 6.5 Hz, 2H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -172.69 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>8</sub>FNO<sub>2</sub>: 169.05, found 169.04.



#### (fluoromethylene)dibenzene

(2u): The product was obtained as a colorless oil (because of hydrolysis issues, we got the crude 1H NMR and 1H NMR of hydrolysis product ); <sup>19</sup>F NMR (470 MHz, CDCl3)  $\delta$  -166.51 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>11</sub>F: 185.09, found 186.08.



#### 1-(4-(1-fluoroethyl)phenyl) ethanone

(2v): The product was obtained as a yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 5.68 (dq, *J* = 47.6, 6.5 Hz, 1H), 2.61 (s, 3H), 1.64 (dd, *J* = 24.0, 6.5 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  197.76 (s), 146.78 (d, *J* = 19.6 Hz), 136.94 (s), 128.69 (s), 125.20 (d, *J* = 6.1 Hz), 91.05 (s), 89.70 (s), 77.38 (s), 77.00 (d, *J* = 31.9 Hz), 76.49 – 76.31 (m), 26.73 (s), 23.17 (s), 22.97 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -171.32 (d, *J* = 8.8 Hz), -171.62 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>10</sub>H<sub>11</sub>FO: 166.08, found 166.08.



#### 2- (fluoromethyl)anthracene-9, 10-dione

(**2w**): The product was obtained as a yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.40 – 8.25 (m, 4H), 7.82 (td, *J* = 7.4, 4.0 Hz, 3H), 5.57 (d, *J* = 46.9 Hz, 2H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -215.27 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>9</sub>FO<sub>2</sub>: 240.06, found 240.06.



#### 8- (fluoromethyl)quinoline

(2x): The product was obtained as a yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.93 (dd, J = 4.1, 1.4 Hz, 1H), 8.19 (dd, J = 8.3, 1.4 Hz, 1H), 7.83 (t, J = 6.6 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.45 (dd, J = 8.3, 4.2 Hz, 1H), 6.15 (d, J = 47.5 Hz, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  148.79 (s), 144.28 (s), 135.44 (s), 133.67 (d, J = 16.5 Hz), 126.81 (dd, J = 74.4, 15.1 Hz), 125.39 (s), 120.38 (s), 81.41 (s), 80.10 (s), 76.71 – 75.49 (m); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -219.22 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>10</sub>H<sub>8</sub>FN: 161.06, found 161.07.

#### 2. Difluorination:



#### 4'-(difluoromethyl)- [1, 1'-biphenyl]-2-carbonitrile

(**3a**): The product was obtained as a white solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.79 (d, J = 7.7 Hz, 1H), 7.72 – 7.61 (m, 5H), 7.55 – 7.46 (m, 2H), 6.72 (t, J = 56.4 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  144.37 (s), 140.54 (s), 134.66 (s), 133.85 (s), 133.04 (s), 130.08 (s), 129.19 (s), 128.18 (s), 126.05 (t, J = 6.0 Hz), 118.44 (s), 116.32 (s), 114.42 (s), 112.52 (s), 111.31 (s), 77.35 (s), 77.09 (s), 76.84 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -111.24 (s); MS (EI) [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>9</sub>F<sub>2</sub>N: 229.07, found 229.10.



#### 1- (tert-butyl)-4- (difluoromethyl)benzene

 $(3b)^{[3]}$ : The product was obtained as a yellow oil (this product is challenging to get purification due to high volatility and the reported yields are the average GC yields of three trials and determined by crude <sup>19</sup>F NMR, BF<sub>4</sub>- $\delta$  -151.22 (s) ); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -109.53 (s) (); MS (EI) [M]<sup>+</sup> Calcd for C<sub>11</sub>H<sub>11</sub>F<sub>2</sub>: 184.11, found 184.13.

#### 1-(4-(difluoromethyl)phenyl)ethanone

(3c): The product was obtained as a yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H), 6.69 (t, J = 56.1 Hz, 1H), 2.63 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  197.62 (s), 141.36 (d, J = 17.2 Hz), 137.15 (s), 128.61 (s), 126.78 (d, J = 6.6 Hz), 84.30 (s), 82.96 (s), 77.31 (s), 77.05 (s), 76.80 (s), 26.65 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -112.30 (s); [M]<sup>+</sup> Calcd for C<sub>11</sub>H<sub>11</sub>F<sub>2</sub>: 184.11, found 184.13.



#### 1- (2- (difluoromethyl)phenyl)ethanone

(3d): The product was obtained as a yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 – 7.80 (m, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 55.6 Hz, 1H), 2.64 (s, 3H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -113.46 (s); [M]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>8</sub>F<sub>2</sub>O: 170.05, found 170.03.



#### (4- (difluoromethyl)phenyl) (phenyl)methanone

(**3e**): The product was obtained as a white solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.63 (dd, J = 13.2, 7.6 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 6.73 (t, J = 56.2 Hz, 1H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -112.04 (s); [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>10</sub>F<sub>2</sub>O: 232.07, found 232.11.



#### 1- (difluoromethyl)-4-fluorobenzene

(3f)<sup>[1]</sup>: The product was obtained as a red oil (this product is challenging to get purification due to high volatility and the reported yields are the average GC yields of three trials and determined by crude <sup>19</sup>F NMR,); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -103.37(s),  $\delta$  -109.74(t) (1-fluoro-4-methylbenzene as stanrdard  $\delta$  -116.48 (s)); [M]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>5</sub>F<sub>3</sub>: 146.03, found 145.05.

Br CF<sub>2</sub>H

1-bromo-4- (difluoromethyl)benzene

 $(3g)^{[4]}$ : The product was obtained as a red oil (this product is challenging to get purification due to high volatility and the reported yields are the average GC yields of three trials and determined by crude <sup>19</sup>F NMR,); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -111.11 (s); [M]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>5</sub>BrF<sub>2</sub>: 205.95, found 205.98.



HOOC

#### 4- (difluoromethyl)benzoic acid

(**3h**): The product was obtained as a white solid; <sup>1</sup>H NMR (500 MHz, MeOD)  $\delta$  8.11 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 6.82 (t, J = 55.9 Hz, 1H); <sup>13</sup>C NMR (126 MHz, MeOD)  $\delta$  166.41 (s), 137.81 (t, J = 22.7 Hz), 131.90 (s), 128.73 (s), 124.41 (s), 113.35 (s), 46.95 (s), 46.78 (s), 46.61 (s), 46.44 (s), 46.27 (s); <sup>19</sup>F NMR (470 MHz, MeOD)  $\delta$  -113.47 (s); [M]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>6</sub>F<sub>2</sub>O<sub>2</sub>: 172.03, found 172.04.



(**3i**): The product was obtained as a white solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.32 – 8.20 (m, 2H), 7.78 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 6.72 (t, J = 56.2 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  169.52 (s), 134.13 (d, J = 23.0 Hz), 131.39 (s), 129.69 (s), 128.57 (d, J = 104.3 Hz), 128.05 – 127.41 (m), 126.58 (s), 112.98 (s), 76.14 (d, J = 31.9 Hz), 75.76 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -110.63 (s); [M]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>6</sub>F<sub>2</sub>O<sub>2</sub>: 172.03, found 172.05.



#### 4-(difluoromethyl)benzamide

(**3j**): The product was obtained as a yellow solid; <sup>1</sup>H NMR (500 MHz, MeOD)  $\delta$  7.97 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 6.83 (t, J = 56.0 Hz, 1H); <sup>19</sup>F NMR (470 MHz, MeOD)  $\delta$  -113.22 (s); [M]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>7</sub>F<sub>2</sub>NO: 171.05, found 171.05.



#### methyl 4-(difluoromethyl)benzoate

(**3k**): The product was obtained as a light yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.13 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 6.69 (t, *J* = 56.1 Hz, 1H), 3.95 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  166.36 (s), 132.44 (s), 130.06 (s), 125.74 (s), 114.09 (s), 77.23 (d, *J* = 31.9 Hz), 76.85 (s), 52.48 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -112.25 (s); [M]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>8</sub>F<sub>2</sub>O<sub>2</sub>: 186.05, found 184.03.



4-(difluoromethyl)benzenesulfonamide 4-(difluoromethyl)benzenesulfonamide

(31): The product was obtained as a yellow solid; <sup>1</sup>H NMR (500 MHz, MeOD)  $\delta$  7.93 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 6.78 (t, J = 55.8 Hz, 1H);<sup>19</sup>F NMR (470 MHz, MeOD)  $\delta$  -113.54 (s); [M]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>7</sub>NF<sub>2</sub>O<sub>2</sub>S: 207.20, found 207.01.



#### 4- (difluoromethyl)-1, 1'-bipheny

(**3n**):The product was obtained as a white solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (d, *J* = 8.1 Hz, 2H), 7.65 (dd, *J* = 10.2, 8.1 Hz, 4H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 6.75 (t, *J* = 56.5 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  143.75 (s), 140.23 (s), 133.47 (s), 133.29 (s), 133.11 (s), 129.00 (s), 127.99 (s), 127.49 (s), 127.31 (s), 126.11 (t, *J* = 6.0 Hz), 116.76 (s), 114.86 (s), 112.96 (s), 77.38 (s), 77.12 (s), 76.87 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -110.14 (s); [M]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>10</sub>F<sub>2</sub>: 204.08, found 204.09.



3- (difluoromethyl)-1, 1'-bipheny

(**30**): The product was obtained as a purple solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.68 – 7.61 (m, 2H), 7.56 – 7.50 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.40 (dd, *J* = 15.8, 8.3 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.64 (t, *J* = 56.5 Hz, 1H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -110.63 (s); [M]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>10</sub>F<sub>2</sub>: 204.08, found 204.11.



#### 2-(difluoromethyl)-1, 1'-bipheny

(**3p**): The product was obtained as a colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.79 (d, J = 7.2 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.55 – 7.48 (m, 2H), 7.48 – 7.40 (m, 4H), 7.36 (dd, J = 5.2, 3.0 Hz, 3H), 6.54 (t, J = 54.9 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  141.24 (s), 139.04 (s), 132.36 (d, J = 15.9 Hz), 129.15 (s), 128.32 (t, J = 46.1 Hz), 127.27 (s), 126.66 (s), 126.48 (s), 82.46 (s), 81.15 (s), 76.15 (d, J = 31.9 Hz), 75.96 – 75.89 (m), 75.77 (s); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -107.40 (s); [M]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>10</sub>F<sub>2</sub>: 204.08, found 204.05.



1-(1, 1-difluoroethyl)-4-nitrobenzene

(**3q**): The product was obtained as a yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.29 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.7 Hz, 2H), 5.35 (t, J = 4.7 Hz, 1H), 5.17 – 5.07 (m, 1H), 1.95 (t, J = 18.2 Hz, 4H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -89.01 (s); [M]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>7</sub>F<sub>2</sub>NO: 187.04, found 187.08.



#### $1-(4-(1,\,1-difluoroethyl) phenyl) ethanone$

(**3r**): The product was obtained as a yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl3)  $\delta$  7.97 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 2.56 (s, 3H), 1.92 (t, J = 6.5 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl3)  $\delta$  128.61 (s), 125.09 (s), 77.24 (d, J = 31.9 Hz), 77.24 (d, J = 31.9 Hz), 77.58 – 76.38 (m), 26.81 (s), 25.99 (s); <sup>19</sup>F NMR (470 MHz, CDCl3)  $\delta$  -88.75 (s); [M]<sup>+</sup> Calcd for C<sub>10</sub>H<sub>10</sub>F<sub>2</sub>O: 184.07, found 184.10.



#### 8-(difluoromethyl)quinoline

(**3t**): The product was obtained as a colorless oil;<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.98 (dd, J = 4.1, 1.6 Hz, 1H), 8.22 (dd, J = 8.3, 1.5 Hz, 1H), 8.06 (d, J = 7.1 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.84 (s, 1H), 7.73 (s, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.53 – 7.43 (m, 1H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -115.84 (s); [M]<sup>+</sup> Calcd for C<sub>10</sub>H<sub>7</sub>F<sub>2</sub>N: 179.05, found 179.05.

## References

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- [2] K. Shing, Tetrahedron 2004, 60, 6923-6930
- [3] F. Kenichi, Org. Lett. 2011, 13, 5560-5563
- [4] H. Alois, Chem. Beri. 1988, 121,1329-1340.

## <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>1</sup>9F NMR and GC-MS Spectra

#### 1. monofluorintion

<sup>1</sup>H NMR of 4'-( fluoromethyl)-[ 1,1'-biphenyl]-2-carbonitrile (1a)





<sup>13</sup>C NMR of 4'- (fluoromethyl) - [1, 1'-biphenyl]-2-carbonitrile (1a)





## MS of 4'- (fluoromethyl) - [1, 1'-biphenyl]-2-carbonitrile (1a)





<sup>1</sup>H NMR of 2- (fluoromethyl)-1, 1'-biphenyl (2b)





<sup>13</sup>C NMR of 2- (fluoromethyl) - 1, 1'-biphenyl (2b)





<sup>19</sup>F NMR of 2- (fluoromethyl) -1, 1'-biphenyl (2b)





MS of 2-(fluoromethyl)-1,1'-biphenyl (2b)





<sup>1</sup>H NMR of 3- (fluoromethyl)-1, 1'- biphenyl (2c)



<sup>19</sup>F NMR of 3- (fluoromethyl)-1, 1'- biphenyl (2c)





MS of 3- (fluoromethyl)-1, 1'- biphenyl (2c)





#### MS of 1- (tert-butyl)-4- (fluoromethyl) benzene (2d):



<sup>19</sup>F NMR of 1- (*tert*-butyl)-4- (fluoromethyl) benzene (2d):



<sup>1</sup>H NMR of 1- (4- (fluoromethyl) phenyl) ethanone (2e)



 $^{13}\mathrm{C}$  NMR of 1- (4- (fluoromethyl) phenyl) ethanone (2e)





 $^{19}\mathrm{F}\,\mathrm{NMR}$  of 1- (4- (fluoromethyl) phenyl) ethanone (2e)





MS of 1- (4- (fluoromethyl) phenyl) ethanone (2e)





<sup>1</sup>H NMR of 1-(3-(fluoromethyl)phenyl)ethanone (2f)





 $^{19}\mathrm{F}$  NMR of 1-(3-(fluoromethyl)phenyl)ethanone (2f)





MS of 1-(3-(fluoromethyl)phenyl)ethanone (2f)



 $^{1}H\ NMR\ of\ (4-(fluoromethyl)phenyl)(phenyl)methanone\ (2g)$ 



 $^{13}\mathrm{C}$  NMR of (4 (fluoromethyl)phenyl)(phenyl)methanone (2g)





 $^{19}\mbox{F}$  NMR of (4-(fluoromethyl)phenyl)(phenyl)methanone (2g)





MS of (4-(fluoromethyl)phenyl)(phenyl)methanone (2g)







<sup>19</sup>F NMR of 1-chloro-2-(fluoromethyl)-4-nitrobenzene (2h)





MS of 1-chloro-2-(fluoromethyl)-4-nitrobenzene (2h)





 $^{19}\mathrm{F}$  NMR of 1-chloro-2- (fluoromethyl) benzene ( 2i)





MS of 1-chloro-2- (fluoromethyl) benzene (2i)









MS of 1-bromo-4- (fluoromethyl) benzene ( 2j)



 $^1\mathrm{H}$  NMR of 4- (fluoromethyl) benzoic acid ( 2k)



 $^{13}\mathrm{C}$  NMR of 4- (fluoromethyl) benzoic acid ( 2k)





<sup>19</sup>F NMR of 4- (fluoromethyl) benzoic acid ( 2k)





#### MS of 4- (fluoromethyl) benzoic acid ( 2k)










 $^{19}\mathrm{F}$  NMR of 3-(fluoromethyl)benzoic acid ( 2l)



MS of 3- (fluoromethyl)benzoic acid (2l)





<sup>13</sup>C NMR of 4- (fluoromethyl) benzamide (2m)



## <sup>1</sup>H NMR of 4- (fluoromethyl) benzamide (2m)



<sup>19</sup>F NMR of 4- (fluoromethyl) benzamide (2m)





## MS of 4- (fluoromethyl) benzamide (2m)











<sup>13</sup>C NMR of methyl 4-( fluoromethyl )benzoate ( 2n)



 $^{19}\mathrm{F}$  NMR of methyl 4-( fluoromethyl ) benzoate (  $2\mathrm{n})$ 





MS of methyl 4-( fluoromethyl )benzoate ( 2n)





<sup>1</sup>H NMR of 1- (fluoromethyl)-4-nitrobenzene (2q)





MS of 1- (fluoromethyl)-4-nitrobenz)ene (2q)



<sup>1</sup>H NMR of 1- (fluoromethyl)-3-nitrobenzene (2r)





<sup>13</sup>C NMR of 1- (fluoromethyl)-3-nitrobenzene (2r)



 $^{19}\mathrm{F}$  NMR of 1-(fluoromethyl)-3-nitrobenzene (2r)





MS of 1- (fluoromethyl)-3-nitrobenzene (2r)





<sup>1</sup>H NMR of 1- (fluoromethyl)-2-nitrobenzene (2s)



 $^{19}\mathrm{F}\,\mathrm{NMR}$  of 1- (fluoromethyl)-2-nitrobenzene (2s)





MS of 1- (fluoromethyl)-2-nitrobenzene (2s)









<sup>19</sup>F NMR of 1- (1-fluoroethyl)-4-nitrobenzene (2t)





MS of 1- (1-fluoroethyl)-4-nitrobenzene (2t)





Crude <sup>1</sup>H NMR of (fluoromethylene)dibenzene (2u)



<sup>1</sup>H NMR of hydrolysis (fluoromethylene)dibenzene ( 2u)



<sup>19</sup>F NMR of (fluoromethylene)dibenzene ( 2u)





## <sup>1</sup>H NMR of 1- (4- (1-fluoroethyl)phenyl)ethanone (2v)





<sup>13</sup>C NMR 1- (4- (1-fluoroethyl)phenyl)ethanone of (2v)









MS of 1- (4- (1-fluoroethyl)phenyl)ethanone (2v)





<sup>1</sup>H NMR of 2- (fluoromethyl)anthracene-9, 10-dione (2w)



 $^{19}\mathrm{F}$  NMR of 2- (fluoromethyl)anthracene-9, 10-dione ( 2w)





MS of 2- (fluoromethyl)anthracene-9, 10-dione ( 2w)











<sup>13</sup>C NMR of 8- (fluoromethyl)quinoline (2x)



<sup>19</sup>F NMR of 8-(fluoromethyl)quinoline (2x)





MS of 8- (fluoromethyl)quinoline (2x)





## 2. Difluorination:



<sup>13</sup>C NMR of 4'- (difluoromethyl)- [1, 1'-biphenyl]-2-carbonitrile ( 3a)





 $^{19}\mathrm{F}$  NMR of 4'- (difluoromethyl)- [1, 1'-biphenyl]-2-carbonitrile ( 3a)





MS of 4'- (difluoromethyl)- [1, 1'-biphenyl]-2-carbonitrile ( 3a)



100-

90-

80-

70-

60-

50-

40

30-

20-

10-

0-

50

100





m/z



MS of 1- (tert-butyl)-4- (difluoromethyl)benzene (3b)



<sup>19</sup>F NMR of 1- (*tert*-butyl)-4- (difluoromethyl)benzene (3b)



 $^1\!H$  NMR of 1- (4- (difluoromethyl)phenyl)ethanone (3c)



<sup>13</sup>C NMR of 1- (4- (difluoromethyl)phenyl)ethanone (3c)



<sup>19</sup>F NMR of 1- (4- (difluoromethyl)phenyl)ethanone (3c)





MS of 1- (4- (difluoromethyl)phenyl)ethanone (3c)







∠CF<sub>2</sub>H





MS of 1- (2- (difluoromethyl)phenyl)ethanone (3d)




<sup>1</sup>H NMR of (4- (difluoromethyl)phenyl) (phenyl)methanone (3e)



 $^{19}\mathrm{F}\,\mathrm{NMR}$  of (4- (difluoromethyl)phenyl) (phenyl)methanone (3e)





MS of (4- (difluoromethyl)phenyl) (phenyl)methanone (3e)







MS of 1- (difluoromethyl)-4-fluorobenzene (3f)





## <sup>19</sup>F NMR of 1-bromo-4- (difluoromethyl)benzene (3g)







MS of 1- (difluoromethyl)-4-fluorobenzene (3g)



<sup>19</sup>F NMR of4- (difluoromethyl)benzoic acid (3h)





MS of 4- (difluoromethyl)benzoic acid (3h)

.CF<sub>2</sub>H





<sup>1</sup>H NMR of 3- (difluoromethyl)benzoic acid (3i)



<sup>13</sup>C NMR of 3- (difluoromethyl)benzoic acid (3i)





<sup>19</sup>F NMR of 3- (difluoromethyl)benzoic acid (3i)





MS of 3- (difluoromethyl)benzoic acid (3i)











<sup>13</sup>C NMR of 4- (difluoromethyl)benzamide (3j)



<sup>19</sup>F NMR of 4- (difluoromethyl)benzamide (3j)





MS of 4- (difluoromethyl)benzamide (3j)





<sup>1</sup>H NMR of methyl 4- (difluoromethyl)benzoate (3k)



<sup>13</sup>C NMR of methyl 4- (difluoromethyl)benzoate (3k)



<sup>19</sup>F NMR of methyl 4- (difluoromethyl)benzoate (3k)





MS of methyl 4- (difluoromethyl)benzoate (3k)



<sup>1</sup>H NMR of 4-(difluoromethyl)benzenesulfonamide (3l)



<sup>19</sup>F NMR of 4-(difluoromethyl)benzenesulfonamide (3l)





MS of 4-(difluoromethyl)benzenesulfonamide (3l)



<sup>1</sup>H NMR of 4- (difluoromethyl)-1, 1'-bipheny (3n)









<sup>19</sup>F NMR of 4-(difluoromethyl)-1,1'-bipheny (3n)



MS of 4- (difluoromethyl)-1, 1'-bipheny (3n)











<sup>19</sup>F NMR of 3- (difluoromethyl)-1, 1'-biphenyl (30)





MS of 3- (difluoromethyl)-1, 1'-biphenyl (30)













<sup>19</sup>F NMR of 2- (difluoromethyl)-1, 1'- biphenyl (3p)





MS of 2- (difluoromethyl)-1, 1'- biphenyl (3p)





<sup>1</sup>H NMR of 1- (1, 1- difluoroethyl)-4-nitrobenzene (3q)





<sup>19</sup>F NMR of 1- (1, 1- difluoroethyl)-4-nitrobenzene (3q)





MS of 1- (1, 1- difluoroethyl)-4-nitrobenzene (3q)





<sup>1</sup>H NMR of 1- (4- (1, 1-difluoroethyl)phenyl)ethanone (3r)





 $^{13}\mathrm{C}$  NMR of 1- (4- (1, 1-difluoroethyl)phenyl)ethanone (3r)





<sup>19</sup>F NMR of 1- (4- (1, 1-difluoroethyl)phenyl)ethanone (3r)





MS of 1- (4- (1, 1-difluoroethyl)phenyl)ethanone (3r)





## <sup>1</sup>H NMR of 8- (difluoromethyl)quinoline (3t)





<sup>19</sup>F NMR of 8- (difluoromethyl)quinoline (3t)



MS of 8- (difluoromethyl)quinoline (3t)



