

# Microwave-assisted Silver-catalyzed protodecarboxylation and decarboxylative iodination of aromatic carboxylic acids

## Supporting Information

### General Information

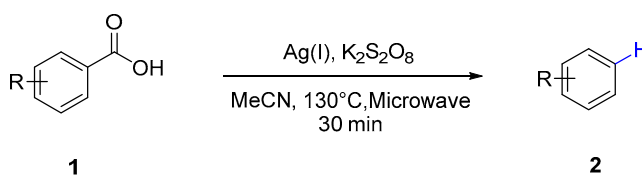
Anhydrous solvents and deuterated solvents were bought from Energy Chemical Company and used as received. All other chemicals were purchased from a chemical supplier and used as received, unless otherwise stated. TLC was performed on Merck Kieselgel 60 (particle size 40-63  $\mu\text{m}$ ) silica under positive pressure.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were determined by Bruker Ava 400 (400 MHz) instrument with chemical shift values reported in ppm residual solvent peaks: proton,  $\text{CDCl}_3$ : 7.26 ppm and carbon,  $\text{CDCl}_3$ : 77.0 ppm.  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR are obtained as follows: chemical shift (in ppm on the  $\delta$  scale), multiplicity (bs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), the coupling constant ( $J$ , in Hertz) and integration.  $^{13}\text{C}$  NMR data were obtained as the ppm on the  $\delta$  scale followed by the interpretation and multiplicity where appropriate.

Microwave heating experiments were performed on CEM Discover-SP Microwave Reactor with max microwave power of 300 W and magnetic frequency of 2.45GHz. Standard Method: Temperature: 100-150°C; Microwave Power: 150 W; Stirring: high.

Gas Chromatography-Mass Spectrometry (GC-MS) was performed on Agilent 5975C Triple Axis GC-MS (EI/CI), equipped with J&W 122-5532 (325°C, 30m $\times$ 250 $\mu\text{m}$  $\times$ 0.25 $\mu\text{m}$ ) column.

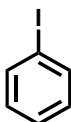
### General procedures for microwave-assisted protodecarboxylation reaction of aromatic carboxylic acid



An oven-dried microwave reaction vial (35 mL) was charged with carboxylic acid (0.50 mmol), silver(I) carbonate (15 mol%), potassium persulfate (2 equiv.) in 4 mL of acetonitrile. The mixture was heated in microwave reactor at 130°C for 30 minutes, then allowed to cool down.

For the measurement of volatile products, chlorobenzene (0.50 mmol) was added into the reaction mixture, and analysis was carried out on GC/MS. Otherwise the reaction mixture was diluted with Et<sub>2</sub>O (10 mL) and washed with saturated aqueous NaHCO<sub>3</sub> (10 mL). The aqueous layer was extracted with Et<sub>2</sub>O (2×10 mL) and the combined organic layers were dried with anhydrous MgSO<sub>4</sub>, then filtered and concentrated under reduced pressure. The crude product was purified by the short silica column and eluted with n-Hexane.

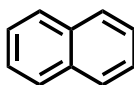
### **2c, iodobenzene**



Prepared following the general procedure using 2-iodobenzoic acid (124.0 mg, 0.5 mmol) to afford the product as the colorless oil (65.0 mg, 65%).

<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 2H). <sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>): δ 137.5 (C-H), 130.3 (C-H), 127.5 (C-H), 94.4 (C). Mass spectrum: found 204[M], 77[M-I].

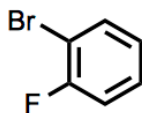
### **2g, naphthalene,**



Prepared following the general procedure using 1-Nipthoic acid (86.09 mg, 0.5 mmol) to afford naphthalene as white solid (50.0 mg, 77%).

<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 7.86-7.84 (m, 4H), 7.749-7.47 (m, 4H). <sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>): δ 133.4 (C), 127.9 (C-H), 125.8 (C-H). Mass spectrum: found 128[M].

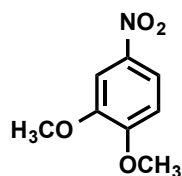
### **2i, 2-fluoro bromobenzene**



Prepared following the general procedure using 3-bromo-4-fluoro benzoic acid (109.50 mg, 0.5 mmol) to afford 2-fluoro bromobenzene as a colorless oil (52.3 mg, 60%)

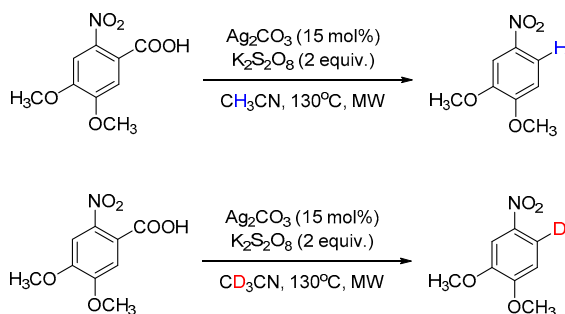
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.63-7.53 (m, 1H), 7.35-7.29 (m, 1H), 7.15 (td,  $J$  = 8.6, 1.4 Hz, 1H), 7.06 (td,  $J$  = 7.9, 1.0 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.37, 157.91, 133.61, 128.95, 125.27, 116.67, 116.45, 109.18, 108.97. Mass spectrum: found 175[M], 95[M-Br].

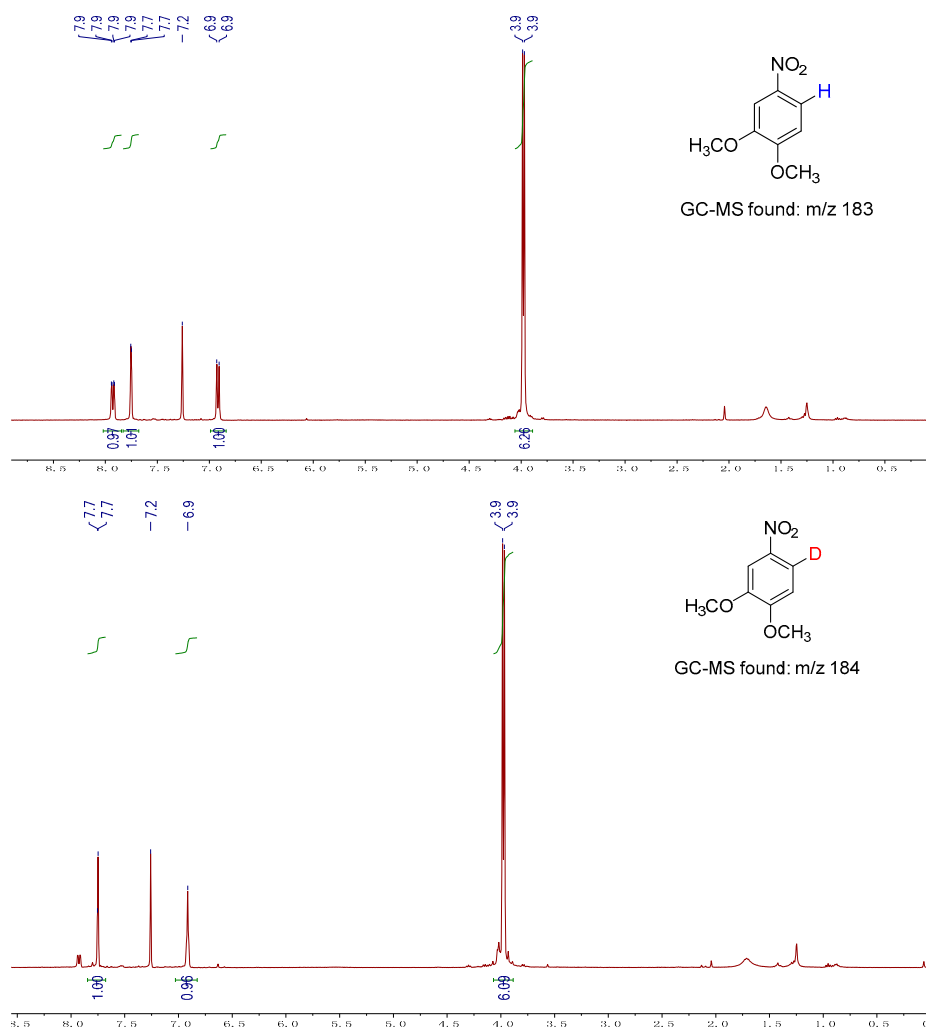
### 2k, 3, 4-Dimethoxy nitrobenzene



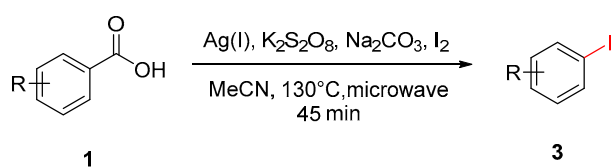
Prepared following the general procedure using 2-nitrobenzoic acid (124.0 mg, 0.5 mmol) to afford as a yellow solid (84.5 mg, 92%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J$  = 8.9 Hz, 1H), 7.75 (s, 1H), 6.92 (d,  $J$  = 8.9 Hz, 1H), 3.99 (s, 3H), 3.97 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.5 (C-O), 148.9 (C-O), 141.5 (C-H), 117.8 (C-H), 109.8 (C-H), 106.5 (C-N). Mass spectrum: found 183[M], 137[M-NO<sub>2</sub>], 107[M-NO<sub>2</sub>-OCH<sub>3</sub>].

### Protodecarboxylation reaction, deuterium exchange reaction



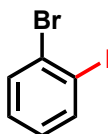


### General procedures for microwave-assisted decarboxylative iodination of aromatic carboxylic acid



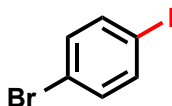
An oven-dried microwave reaction vial (35 mL) was charged with benzoic acid (0.50 mmol), silver (I) carbonate (25 mol %), potassium persulfate (2 equiv.), sodium carbonate (2 equiv.) and iodine (2 equiv.) in 4 mL acetonitrile. The mixture was heated in microwave reactor at 130°C for 45 minutes, then allowed to cool down, diluted with EtOAc (10 mL) and washed with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (10 mL). The resulting mixture was extracted with EtOAc (2×10 mL) and the combined organic layers were dried with anhydrous MgSO<sub>4</sub>, then filtered and concentrated under reduced pressure. The crude product was purified by the short silica column and eluted with n-hexane.

### 3a, 2-Bromo Iodobenzene



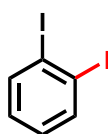
Prepared following the general procedure using 2-bromobenzoic acid (100.0 mg, 0.5 mmol) to afford 2-bromo iodobenzene as yellow oil (137mg, 97%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J$  = 7.9 Hz, 1H), 7.63 (d,  $J$  = 8.0 Hz, 1H), 7.21 (t,  $J$  = 7.7 Hz, 1H), 7.00 (t,  $J$  = 7.6 Hz, 1H).  $^{13}\text{C}$  NMR (101MHz,  $\text{CDCl}_3$ ):  $\delta$  140.4 (C-H), 132.8 (C-H), 129.8 (C-H), 129.5 (C-H), 128.4 (C-Br), 101.2(C-I). Mass spectrum: 283[M], 156[M-I].

### 3b, 4-Bromo Iodobenzene



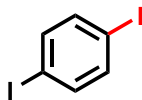
Prepared following the general procedure using 4-bromobenzoic acid (100.0 mg, 0.5 mmol) to afford 4-bromo iodobenzene as yellow oil (102mg, 72%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J$  = 7.9 Hz, 2H), 7.23 (d,  $J$  = 8.0 Hz, 2H).  $^{13}\text{C}$  NMR (101MHz,  $\text{CDCl}_3$ ):  $\delta$  139.1 (C-H), 133.5 (C-H), 122.2 (C-H), 92.0 (C-I). Mass spectrum: 283[M], 156[M-I].

### 3c, 1,2-Diiodobenzene



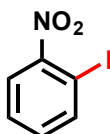
Prepared following the general procedure using 2-iodobenzoic acid (124.0 mg, 0.5 mmol) to afford 1,2-diiodobenzene as brown oil (163mg, 99%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99-7.77 (m, 2H), 7.11-6.89 (m, 2H).  $^{13}\text{C}$  NMR (101MHz,  $\text{CDCl}_3$ ):  $\delta$  139.5 (C-H), 129.2 (C-H), 107.9 (C-I). Mass spectrum: 330[M], 203[M-I].

### 3d, 1, 4-Diiodobenzene



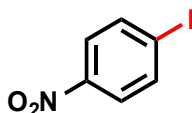
Prepared following the general procedure using 4-iodobenzoic acid (124.0 mg, 0.5 mmol) to afford 1,4-diiodobenzene as brown oil (124 mg, 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (s, 4H)  $^{13}\text{C}$  NMR (101MHz,  $\text{CDCl}_3$ ):  $\delta$  139.3 (C-H), 93.3 (C-I). Mass spectrum: 330[M], 203[M-I].

### 3e, 2-Nitro Iodobenzene



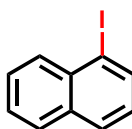
Prepared following the general procedure using 2-nitrobenzoic acid (83.5 mg, 0.5 mmol) to afford 2-nitroiodobenzene as yellow solid (114 mg, 92%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J$  = 7.9 Hz, 1H), 7.89 (d,  $J$  = 8.1 Hz, 1H), 7.52 (t,  $J$  = 7.7 Hz, 1H), 7.30 (t,  $J$  = 7.8 Hz, 1H).  $^{13}\text{C}$  NMR (101MHz,  $\text{CDCl}_3$ ):  $\delta$  141.9 (C-H), 133.4 (C-H), 129.0 (C-H), 128.5 (C-H), 125.4 (C- $\text{NO}_2$ ), 86.2 (C-I). Mass spectrum: 249[M], 203[M- $\text{NO}_2$ ], 76[M-I- $\text{NO}_2$ ].

### 3f, 4-Nitro Iodobenzene



Prepared following the general procedure using 4-nitrobenzoic acid (83.5 mg, 0.5 mmol) to afford 2-nitroiodobenzene as white solid (84 mg, 68%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J$  = 9.0 Hz, 2H), 7.94 (d,  $J$  = 8.9 Hz, 2H).  $^{13}\text{C}$  NMR (101MHz,  $\text{CDCl}_3$ ):  $\delta$  146.9 (C-N), 138.7 (C-H), 124.9 (C-H), 102.2 (C-I). Mass spectrum: 249[M], 203[M- $\text{NO}_2$ ], 76[M-I- $\text{NO}_2$ ].

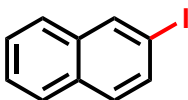
### 3g, 1-Iodonaphthalene



Prepared following the general procedure using 1-Nipthoic acid (86.1 mg, 0.5 mmol) to afford 2-iodonaphthalene as colorless oil (92 mg, 73%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J$  = 7.7 Hz, 2H), 7.84 (d,  $J$  = 8.2 Hz, 1H), 7.77 (d,  $J$  = 7.7 Hz, 1H), 7.58 (t,  $J$  = 7.5 Hz, 1H), 7.52 (t,  $J$  = 7.4 Hz, 1H).  $^{13}\text{C}$  NMR

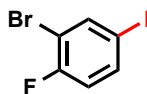
(101MHz. CDCl<sub>3</sub>):  $\delta$  137.5 (C-H), 134.4 (C-H), 134.2 (C-H), 132.2 (C-H), 129.0 (C-H), 128.6 (C-H), 127.7 (C-H), 126.9 (C-H), 126.7 (C-H), 99.6 (C-I). Mass spectrum: 254[M], 127[M-I].

### 3h, 2-Iodonaphthalene



Prepared following the general procedure using 2-Nipthoic acid (86.1 mg, 0.5 mmol) to afford 2-iodonaphthalene as brown oil (71 mg, 56%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (s, 1H), 7.80 (m, 1H), 7.78 (d,  $J$  = 7.7 Hz, 2H), 7.57 (d,  $J$  = 7.5 Hz, 1H), 7.49 (m, 2H). <sup>13</sup>C NMR (101MHz. CDCl<sub>3</sub>):  $\delta$  136.6 (C-H), 135.0 (C-H), 134.4 (C-H), 132.1 (C-H), 129.5 (C-H), 127.9 (C-H), 126.8 (C-H), 126.7 (C-H), 126.5 (C-H), 91.5 (C-I). Mass spectrum: 254[M], 127[M-I].

### 3i, 3-bromo-4-fluoro-iodobenzene

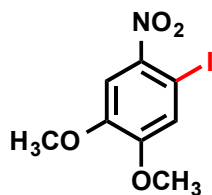


Prepared following the general procedure using 3-bromo-4-fluoro-benzoic acid (109.5 mg, 0.5 mmol) to afford 3-bromo-4-fluoro-iodobenzene as yellow oil (120 mg, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d,  $J$  = 6.2 Hz, 1H), 7.57 (s, 1H), 6.88 (t,  $J$  = 8.4 Hz, 1H). <sup>13</sup>C NMR (101MHz. CDCl<sub>3</sub>):  $\delta$  160.5 (C-H), 158.0 (C-H), 141.5 (C-H), 137.9 (C-H), 118.3 (C-F), 110.5 (C-Br), 87.1 (C-I). Mass spectrum: 300[M], 173[M-I], 94[M-I-Br].

### 3j, 3-chloro-4-fluoro-iodobenzene

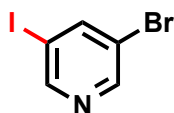
Prepared following the general procedure, using 3-chloro-4-fluoro-benzoic acid (87.0 mg, 0.5mmol). Yield of 83% was measured by GC/MS.

### 3k, 2-Nitro-3,4-dimethoxy Iodobenzene



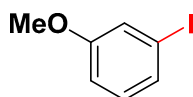
Prepared following the general procedure using 2-nitro-3,4-dimethoxy benzoic acid (113.6 mg, 0.5 mmol) to afford 2-nitro-3,4-dimethoxy iodobenzene as yellow solid (131 mg, 85%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63(s, 1H), 7.42 (s, 1H), 3.98(s, 3H), 3.96(s, 3H).  $^{13}\text{C}$  NMR (101MHz,  $\text{CDCl}_3$ ):  $\delta$  152.8 (C-O), 149.1 (C-O), 145.1 (C-N), 123.1 (C-H), 109.0 (C-H), 77.2(C-I), 56.7 (C-3H), 56.4 (C-3H). Mass spectrum: 309[M], 263[M- $\text{NO}_2$ ], 236[M- $\text{NO}_2\text{-OCH}_3$ ].

### 3l, 3-Iodo-5-bromopyridine



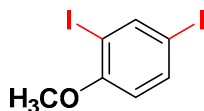
Prepared following the general procedure using 5-Bromonicotinic acid (100.0 mg, 0.5 mmol). The yield of 63% was measured by GC/MS.

### 3m, 1-iodo-3-methoxybenzene



Prepared following the general procedure using 3-methoxybenzoic acid (76.0 mg, 0.5 mmol). The product was analyzed by GC/MS, as a mixture of di-, triiodo substituted products, and the combined yield was 97%.

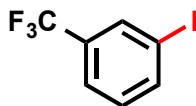
### 3n, 2,4-diiodo-1-methoxybenzene



Prepared following the general procedure using 4-methoxybenzoic acid (76.0 mg, 0.5 mmol). The product was analyzed by GC/MS to give the yield of 86%.

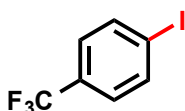
### 3o, 3-Trifluoromethyl Iodobenzene





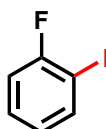
Prepared following the general procedure using 3-trifluoromethyl benzoic acid (95.0 mg, 0.5 mmol) to afford 3-trifluoromethyl iodobenzene as brown solid (125 mg, 92%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.41 (d,  $J$  = 7.9 Hz, 1H), 8.33 (d,  $J$  = 8.0 Hz, 1H), 7.91 (t,  $J$  = 7.7 Hz, 1H), 7.67 (t,  $J$  = 7.6 Hz, 1H). Mass spectrum: 272[M], 145[M-I].

### 3p, 4-Trifluoromethyl iodobenzene



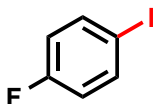
Prepared following the general procedure using 4-trifluoromethyl benzoic acid (95.0 mg, 0.5 mmol) to afford 4-trifluoromethyl iodobenzene as brown solid (102 mg, 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d,  $J$  = 7.9 Hz, 2H), 7.78 (d,  $J$  = 8.0 Hz, 2H). Mass spectrum: 272[M], 145[M-I].

### 3q, 2-Fluoro iodobenzene



Prepared following the general procedure using 2-fluorobenzoic acid (70.1 mg, 0.5 mmol) to afford 2-fluoro iodobenzene as brown solid (100 mg, 90%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J$  = 7.9 Hz, 1H), 7.58 (d,  $J$  = 8.0 Hz, 1H), 7.23 (t,  $J$  = 7.7 Hz, 1H), 7.21-7.09 (t,  $J$  = 7.6 Hz, 1H). Mass spectrum: 222[M], 95[M-I].

### 3r, 4-Fluoro iodobenzene



Prepared following the general procedure using 4-fluorobenzoic acid (70.1 mg, 0.5 mmol) to afford 2-fluoro iodobenzene as brown solid (72 mg, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (dd,  $J$  = 7.4 Hz, 2H), 7.18 (t,  $J$  = 8.3 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.7 (C-F), 132.9 (C-H), 115.9 (C-H), 84.3 (C-I). Mass spectrum: 222[M], 95[M-I].