

## Electronic Supplementary Information (ESI)

### An Effective and Catalytic Oxidation Using Recyclable Fluorous IBX.

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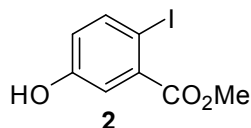
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$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured with a JEOL AL 400 spectrometer (400 MHz for  $^1\text{H}$  NMR and 100 MHz for  $^{13}\text{C}$  NMR), or JEOL ECA 500 spectrometer (500 MHz for  $^1\text{H}$  NMR and 125 MHz for  $^{13}\text{C}$  NMR). The chemical shifts are expressed in ppm downfield from tetramethylsilane ( $\delta = 0.00$ ) as an internal standard. The high-resolution Mass spectra (HRMS) of the compounds were recorded using a JEOL JMS-SX102A spectrometer. For thin layer chromatographic (TLC) analyses, Merck precoated TLC plates (silica gel 60 F<sub>254</sub>, Art 5715) were used.

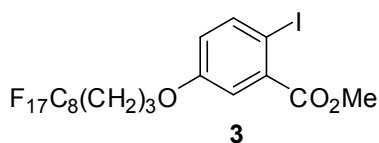
## 2. Preparation of fluorous IBX

### Methyl 5-hydroxy-2-iodobenzoate (**2**)

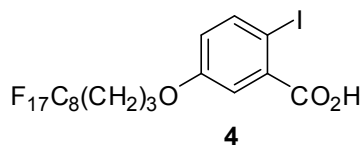


5-Hydroxy-2-iodobenzoic acid<sup>1</sup> (**1**, 4.39 g, 16.0 mmol) was added to a solution of hydrochloric acid in methanol, which was prepared by the slow addition of acetyl chloride (7 mL) to methanol (45 mL) at 0 °C. After stirring for 5 h at reflux temperature, the reaction mixture was evaporated. The residue was purified by flash column chromatography on silica gel with  $\text{CHCl}_3$  to afford pure methyl 5-hydroxy-2-iodobenzoate (**2**, 4.16 g, 90%) as a pale yellow powder.

### Fluorous methyl ester **3**

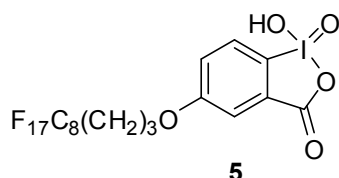


Potassium carbonate (2.07 g, 15.0 mmol) was added to a solution of **2** (1.98 g, 7.12 mmol) in dry acetonitrile (150 mL) under an argon atmosphere. The mixture was stirred for 10 min at 70 °C, then cooled to room temperature. Fluorous tosylate<sup>2</sup> was added to the reaction mixture under an argon atmosphere. After stirring for 19 h at 70 °C, the reaction mixture was added to water, and the mixture was extracted three times with EtOAc. The EtOAc layers were combined, washed with brine, dried over anhydrous  $\text{MgSO}_4$ , and evaporated. The residue was purified by flash column chromatography on silica gel with a 20:1 mixture of hexane and EtOAc to afford the pure **3** (5.13 g, 98%) as a colorless powder. mp 66–68 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.13 (m, 2H), 2.31 (m, 2H), 3.94 (s, 3H), 4.05 (t,  $J$  = 5.8 Hz, 2H), 6.78 (dd,  $J$  = 8.6, 2.9 Hz, 1H), 7.36 (d,  $J$  = 2.9 Hz, 1H), 7.85 (d,  $J$  = 8.6 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 20.5, 27.8 (t,  $^2J_{\text{C-F}}$  = 22.1 Hz), 52.5, 66.7, 82.9, 107.0–121.0 (complex signals of  $-\text{CF}_2-$  or  $-\text{CF}_3$ ), 117.0, 119.7, 135.9, 142.0, 158.4, 166.6. HRMS (FAB) Calcd for  $\text{C}_{19}\text{H}_{14}\text{O}_3\text{F}_{17}\text{I}$  ( $\text{M}+\text{H}$ )<sup>+</sup>: 738.9639. Found: 738.9634.



To a solution of compound **3** (5.13 g, 6.96 mmol) in 1,4-dioxane (100 mL) was added 10% aq. NaOH (34 mL) at room temperature. After stirring for 4 h at 70 °C, 2 M aq. HCl was added, and the reaction mixture was adjusted to pH 3. The mixture was extracted three times with EtOAc. The EtOAc layers were combined, washed with brine, dried over anhydrous MgSO<sub>4</sub>, and concentrated. The residue was purified by flash column chromatography on silica gel with a 1:2 mixture of hexane and EtOAc to afford the pure **4** (4.95 g, 98%) as a colorless powder. mp 100-101 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 2.13 (m, 2H), 2.32 (m, 2H), 4.07 (t, *J* = 6.3 Hz, 2H), 6.81 (dd, *J* = 8.6, 3.4 Hz, 1H), 7.57 (d, *J* = 3.4 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 20.4, 27.8 (t, <sup>2</sup>*J*<sub>C-F</sub> = 22.0 Hz), 66.7, 83.6, 107.0-121.0 (complex signals of -CF<sub>2</sub>- or -CF<sub>3</sub>), 117.8, 120.8, 133.9, 142.7, 158.5, 170.8; Anal. Calcd for C<sub>18</sub>H<sub>10</sub>F<sub>17</sub>IO<sub>3</sub>: C, 29.85; H, 1.39. Found: C, 29.70; H, 1.51.

#### Fluorous IBX (**5**):



To a solution of compound **4** (1.11 g, 1.53 mmol) in MeCN (20 mL) and H<sub>2</sub>O (10 mL) was added Oxone (4.69 g, 7.64 mmol) at room temperature. After stirring for 10 h at 70 °C, the reaction mixture was cooled to 0 °C. The precipitated fluorous IBX (**5**) was filtered, and washed with cool water. The collected **5** was dried *in vacuo*, and reasonably pure compound **5** (1.15 g, 100%) was obtained as a colorless powder, then used in the next step without further purification. mp 196-198 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sup>6</sup>): δ = 2.02 (m, 2H), 2.44 (m, 2H), 4.23 (t, *J* = 6.3 Hz, 2H), 7.46 (m, 2H), 7.99 (d, *J* = 9.2 Hz, 1H).

#### 3. Procedure for recycling and reusing fluorous organocatalyst **4** (Table 3):

A typical procedure of oxidation using fluorous organocatalyst **4** is as follows: To a colorless solution of diphenylmethanol (**6a**, 100 mg, 0.543 mmol) and the organocatalyst **4** (39.3 mg, 0.054 mmol) in MeNO<sub>2</sub> (1.6 mL) and H<sub>2</sub>O (0.6 mL) were added Oxone (334 mg, 0.543 mmol) and Bu<sub>4</sub>NHSO<sub>4</sub> (18.4 mg, 0.054 mmol) at room temperature. The reaction mixture was stirred at 70 °C for 8 h, and then was cooled to room temperature. The precipitated fluorous IBA (**9**) was filtered, and washed with water and ether. The collected **9** was dried *in vacuo*, and was used in the next step without further purification. The filtrate was extracted three times with AcOEt. The AcOEt layers were combined, washed with brine, dried over anhydrous MgSO<sub>4</sub>, and evaporated. The residue was purified by flash column chromatography on silica gel with a 5:1 mixture of hexane and AcOEt to afford pure benzophenone (**7a**, 86.4 mg, 87%).

Supplementary Material (ESI) for Chemical Communications  
fluorinated BA (9) can be used as a solid, clear, colorless oil. HRMS (FAB) Calcd for C<sub>18</sub>H<sub>11</sub>O<sub>4</sub>F<sub>17</sub>I (M+H)<sup>+</sup>: 740.9431. Found: 740.9439.

Compounds **2**<sup>3</sup>, **7a**<sup>4</sup>, **7b**<sup>5</sup>, **7c**<sup>5</sup>, **7d**<sup>5</sup>, **7e**<sup>6</sup>, **7f**<sup>7</sup>, **7g**<sup>8</sup>, **7h**<sup>5</sup>, **7i**<sup>4</sup>, **7j**<sup>5</sup>, **7k**<sup>4</sup>, and **8**<sup>9</sup> are known compounds that exhibited spectroscopic data identical to those reported in the literature.

## 5. References

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