

**Supporting Information for**

**Esters of 2-Iodoxybenzoic Acid (IBX-Esters):**

**Hypervalent Iodine Oxidizing Reagents with a**

**Pseudobenziodoxole Structure**

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**General.** All reactions were performed under dry nitrogen atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. Methylene chloride was distilled from  $\text{CaH}_2$  immediately prior to use. Diethyl ether was distilled from Na/benzophenone. All other reagents and solvents were of commercial quality from freshly opened containers. Methyl 2-iodobenzoate **7a** was purchased from commercial sources. 2-Iodobenzene-1,3-benzenedicarbonyl dichloride **9** was prepared by known method (Denmark, S. E.; Stavenger, R. A.; Faucher, A.-M.; Edwards, J. P. *J. Org. Chem.* **1997**, 62, 3375). Infrared spectra were recorded as a KBr or NaCl pellet; NMR spectra were recorded at 300 MHz ( $^1\text{H}$  NMR) and 75.5 MHz ( $^{13}\text{C}$  NMR). Chemical shifts are reported in parts per million (ppm).  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are referenced relative to the residual nondeuteriated solvent. Benzaldehyde, cyclohexanone, cycloheptanone, and cyclooctanone (GC standards for oxidation of alcohols) were purchased from commercial sources.

**General procedure for preparation of 2-iodobenzoate esters.** The appropriate alcohol (20 mmol) in dry ether (30 mL) was placed into a 50 mL round bottom flask equipped with magnetic stirrer and rubber septum. The 2.5M hexane solution of BuLi (8.0 mL, 20 mmol) was added into the flask dropwise at 0 °C in 5 minutes and the mixture was stirred for 30 min at room temperature under nitrogen. In a separate 25 mL flask, 2-iodobenzoyl chloride (5.05 g, 19 mmol) was dissolved in 5 mL of dry ether and added dropwise at room temperature to the reaction flask. Immediate reaction takes place and the formation of a precipitate of lithium chloride is observed. The nitrogen line was disconnected, the reaction stirred overnight at room temperature, and then quenched with 10 mL of water. The top ethereal layer was separated, dried with  $\text{MgSO}_4$ , and the solvent removed *in vacuo*. Crude esters of 2-iodobenzoic acid were purified by column chromatography (hexanes/ethyl acetate, 4:1, as eluent).

### **Alternative Procedure for the Preparation of Isopropyl 2-iodobenzoate 7c.**

2.8 g (10 mmol) of 2-iodobenzoyl chloride was placed into a 50 mL round bottom flask equipped with magnetic stirrer and 20 mL of isopropyl alcohol was added. The mixture was stirred under reflux for 30 minutes and concentrated on a rotary evaporator. Crude isopropyl 2-iodobenzoate was purified by filtration through silica gel (dichloromethane as eluent). Reaction afforded 2.7 g (93%) of pure **7c**.

### **ethyl 2-iodobenzoate 7b:**

Reaction of 2-iodobenzoyl chloride with ethanol according to general procedure afforded 4.45 g (85%) of product **7b**. IR (KBr): 3065, 2981, 2904, 1727, 1290, 1251  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.00 (d,  $J = 7.9$  Hz, 1H), 7.78 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.8$  Hz, 1H), 7.40 (td,  $J_1 = 7.6$  Hz,  $J_2 = 1.0$  Hz, 1H), 7.14 (td,  $J_1 = 7.8$  Hz,  $J_2 = 1.7$  Hz, 1H), 4.40 (q,  $J = 7.1$  Hz, 2H), 1.41 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  166.6, 141.2, 135.5, 132.5, 130.8, 127.9, 94.0, 61.7, 14.2. Anal. Calcd for  $\text{C}_9\text{H}_9\text{IO}_2$ : C, 39.16; H, 3.29; I, 45.97. Found: C, 38.90; H, 3.34; I, 45.67.

### **isopropyl 2-iodobenzoate 7c:**

Reaction of 2-iodobenzoyl chloride with 2-propanol according to general procedure afforded 4.6 g (84%) of product **7c**. IR (KBr): 3065, 2981, 2877, 1724, 1291, 1254  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.97 (d,  $J = 7.9$  Hz, 1H), 7.75 (dd,  $J_1 = 7.8$  Hz,  $J_2 = 1.5$  Hz, 1H), 7.39 (td,  $J_1 = 7.7$  Hz,  $J_2 = 1.1$  Hz, 1H), 7.13 (td,  $J_1 = 7.7$  Hz,  $J_2 = 1.8$  Hz, 1H), 5.28 (m, 1H), 1.40 (d,  $J = 7.3$  Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  166.3, 141.2, 136.0, 132.5, 130.8, 128.0, 94.0, 69.7, 22.0. Anal. Calcd for  $\text{C}_{10}\text{H}_{11}\text{IO}_2$ : C, 41.40; H, 3.82; I, 43.75. Found: C, 41.23; H, 3.85; I 43.57.

### **tert-butyl 2-iodobenzoate 7d:**

Reaction of 2-iodobenzoyl chloride with 2-methyl-2-propanol according to general procedure afforded 4.85 g (84%) of product **7d**. IR (KBr): 3064, 2978, 2932, 1726, 1252  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR

(CDCl<sub>3</sub>):  $\delta$  7.93 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 0.7$  Hz, 1H), 7.68 (d,  $J_1 = 7.6$  Hz,  $J_2 = 1.7$  Hz, 1H), 7.37 (td,  $J_1 = 7.6$  Hz,  $J_2 = 1.0$  Hz, 1H), 7.11 (td,  $J_1 = 7.6$  Hz,  $J_2 = 1.7$  Hz, 1H), 1.62 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  166.2, 140.9, 137.4, 131.9, 130.4, 127.8, 93.4, 82.6, 28.1. Anal. Calcd for C<sub>11</sub>H<sub>13</sub>IO<sub>2</sub>: C, 43.44; H, 4.31; I, 41.73. Found: C, 43.83; H, 4.33; I, 41.35.

**(-)-menthyl 2-iodobenzoate 7e:**

Reaction of 2-iodobenzoyl chloride with (-)-menthol according to general procedure afforded 4.62 g (66%) of product **7e**. IR (KBr): 3066, 2955, 2869, 1724, 1290, 1252 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.98 (d,  $J = 7.9$  Hz, 1H), 7.74 (dd,  $J_1 = 7.8$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.39 (t,  $J = 7.5$  Hz, 1H), 7.13 (t,  $J = 7.7$  Hz, 1H), 4.97 (td,  $J_1 = 11$  Hz,  $J_2 = 4.4$  Hz, 1H), 2.18 (d,  $J = 12.7$  Hz, 1H), 2.02 (m, 1H), 1.73 (m, 2H), 1.54 (m, 2H), 1.17 (m, 2H), 1.14 (m, 1H), 0.93 (m, 6H), 0.82 (d,  $J = 7$  Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  166.2, 141.2, 136.0, 132.3, 130.4, 127.8, 93.9, 75.9, 47.1, 40.8, 34.3, 31.5, 26.3, 23.3, 22.1, 20.8, 16.3. Anal. Calcd for C<sub>17</sub>H<sub>23</sub>IO<sub>2</sub>: C, 52.86; H, 6.0. Found: C, 53.02; H, 6.10.

**(+)-menthyl 2-iodobenzoate 7f:**

Reaction of 2-iodobenzoyl chloride with (+)-menthol according to general procedure afforded 4.33 g (62%) of product **7f**. IR (KBr): 3066, 2956, 2868, 1724, 1290, 1251 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.98 (d,  $J = 7.9$  Hz, 1H), 7.74 (dd,  $J_1 = 7.8$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.39 (t,  $J = 7.5$  Hz, 1H), 7.13 (t,  $J = 7.7$  Hz, 1H), 4.97 (td,  $J_1 = 11$  Hz,  $J_2 = 4.4$  Hz, 1H), 2.19 (d,  $J = 12.7$  Hz, 1H), 2.02 (m, 1H), 1.73 (m, 2H), 1.55 (m, 2H), 1.17 (m, 2H), 1.14 (m, 1H), 0.93 (m, 6H), 0.82 (d,  $J = 7$  Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  166.2, 141.2, 136.0, 132.3, 130.5, 127.8, 93.9, 75.9, 47.1, 40.8, 34.3, 31.5, 26.3, 23.3, 22.1, 20.8, 16.3. Anal. Calcd for C<sub>17</sub>H<sub>23</sub>IO<sub>2</sub>: C, 52.86; H, 6.0; I, 32.85. Found: C, 53.04; H, 6.08; I, 32.60.

**(±)-menthyl 2-iodobenzoate 7g:**

Reaction of 2-iodobenzoyl chloride with (±)-menthol according to general procedure afforded 5.17 g (74%) of product **7g**. IR (KBr): 3066, 2955, 2869, 1724, 1290, 1252 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.97 (dd, J<sub>1</sub> = 8.1 Hz, J<sub>2</sub> = 1.2, 1H), 7.74 (dd, J<sub>1</sub> = 7.8 Hz, J<sub>2</sub> = 1.8 Hz, 1H), 7.39 (td, J<sub>1</sub> = 7.5 Hz, J<sub>2</sub> = 1.2, 1H), 7.13 (td, J<sub>1</sub> = 7.7 Hz, J<sub>2</sub> = 1.8, 1H), 4.97 (td, J<sub>1</sub> = 11 Hz, J<sub>2</sub> = 4.4 Hz, 1H), 2.19 (m, 1H), 2.02 (m, 1H), 1.72 (m, 2H), 1.54 (m, 2H), 1.17 (m, 2H), 1.13 (m, 1H), 0.93 (m, 6H), 0.82 (d, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 166.3, 141.3, 136.2, 132.5, 130.6, 128.0, 94.1, 76.0, 47.3, 41.0, 34.4, 31.7, 26.4, 23.5, 22.2, 21.0, 16.5. Anal. Calcd for C<sub>17</sub>H<sub>23</sub>IO<sub>2</sub>: C, 52.86; H, 6.0; I, 32.85. Found: C, 53.02; H, 6.09; I, 32.58.

**[(1S)-endo]-(-)-bornyl 2-iodobenzoate 7h:**

Reaction of 2-iodobenzoyl chloride with [(1S)-endo]-(-)-borneol according to general procedure afforded 6.49 g (89%) of product **7h**, mp 64-65 °C (recryst. from CH<sub>2</sub>Cl<sub>2</sub>/hexanes). IR (KBr): 2995, 2876, 1726, 1290, 1253 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.99 (dd, J<sub>1</sub> = 7.9 Hz, J<sub>2</sub> = 1.1 Hz, 1H), 7.80 (dd, J<sub>1</sub> = 7.9 Hz, J<sub>2</sub> = 1.5 Hz, 1H), 7.42 (td, J<sub>1</sub> = 7.6 Hz, J<sub>2</sub> = 1.2 Hz, 1H), 7.15 (td, J<sub>1</sub> = 7.8 Hz, J<sub>2</sub> = 1.7 Hz, 1H), 5.15 (m, 1H), 2.50 (m, 1H), 1.75 (m, 2H), 1.35 (m, 4H), 0.96 (s, 3H), 0.94 (s, 3H), 0.91 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 166.9, 141.3, 135.8, 132.4, 130.8, 127.9, 93.9, 81.8, 49.0, 48.0, 44.9, 36.7, 28.0, 27.4, 19.7, 18.9, 13.7. Anal. Calcd for C<sub>17</sub>H<sub>21</sub>IO<sub>2</sub>: C, 53.14; H, 5.51; I, 33.03. Found: C, 53.31; H, 5.59; I, 32.82.

**2-adamantyl 2-iodobenzoate 7i:**

Reaction of 2-iodobenzoyl chloride with 2-adamantanol according to general procedure afforded 6.02 g (83%) of product **7i**, mp 90-91 °C (recryst. from Et<sub>2</sub>O). IR (KBr): 2925, 2854, 1717, 1292, 1264 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.99 (dd, J<sub>1</sub> = 7.9 Hz, J<sub>2</sub> = 1.1 Hz, 1H), 7.86 (dd, J<sub>1</sub> = 8.0 Hz, J<sub>2</sub> = 1.7 Hz, 1H), 7.41 (td, J<sub>1</sub> = 7.6 Hz, J<sub>2</sub> = 1.2 Hz, 1H), 7.15 (td, J<sub>1</sub> = 7.7 Hz, J<sub>2</sub> = 1.8 Hz, 1H), 5.22 (m, 1H), 2.18 (m, 4H), 1.89 (m, 6H), 1.77 (m, 2H), 1.65 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ

165.9, 141.3, 135.7, 132.4, 130.9, 127.9, 94.1, 78.8, 37.4, 36.4, 32.0, 27.2, 27.0. Anal. Calcd for  $C_{17}H_{19}IO_2$ : C, 53.42; H, 5.01; I, 33.20. Found: C, 53.40; H, 5.05; I, 33.17.

**1-adamantyl 2-iodobenzoate **7j**:**

Reaction of 2-iodobenzoyl chloride with 1-adamantanol according to general procedure afforded 6.39 g (88%) of product **7j**, mp 95-96 °C (recryst. from  $Et_2O$ ). IR (KBr): 3060, 2851, 1717, 1290, 1270  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.93 (d,  $J$  = 6.3 Hz, 1H), 7.70 (d,  $J$  = 6.7 Hz, 1H), 7.37 (t,  $J$  = 6.5 Hz, 1H), 7.11 (t,  $J$  = 6.8 Hz, 1H), 2.30 (m, 6H), 2.23 (m, 3H), 1.72 (m, 6H).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  165.9, 140.9, 137.3, 131.9, 130.5, 127.8, 93.5, 82.8, 41.3, 36.2, 30.9. Anal. Calcd for  $C_{17}H_{19}IO_2$ : C, 53.42; H, 5.01; I, 33.20. Found: C, 53.44; H, 5.02; I, 33.38.

**General procedure for oxidation of alcohols with ester **4c**:** To a solution of IBX-ester **4c** (0.161 g, 0.5 mmol) in methylene chloride (5 mL) a solution of the appropriate alcohol (0.5 mmol) in methylene chloride (2 mL) was added, and then the trifluoroacetic acid (0.06 g, 0.5 mmol) (or  $BF_3 \cdot Et_2O$ , 0.07 g, 0.5 mmol) in entries 3 and 8) was added dropwise. The reaction mixture was stirred at 40 °C for 2 hours (unless specified in the table). A portion of the crude reaction mixture (1.5 mL) was passed through 1 cm of silica gel suspended in a pasteur pipet and eluted with  $CH_2Cl_2$  (2-3 mL); then diluted to 10 mL and analyzed by GCMS.

Entry 1. Benzyl alcohol was reacted with reagent **4c** according to general procedure to produce benzaldehyde (100% conversion according to GC analysis).

Entry 2. Oxidation of alcohols with ester **4c** in the presence of KBr: To a solution of IBX-ester **4c** (0.01 g, 0.031 mmol) in  $CDCl_3$  (0.5 mL) benzyl alcohol (5  $\mu$ l, 0.048 mmol) was added, and then an excess of KBr and 18-crown-6 (2 mg, 0.0075 mmol) were added. The reaction mixture was heated in NMR tube for 4 h at 50 °C to afford benzaldehyde in quantitative yield as judged by the integration of the area of the  $^1H$  NMR signal at 10.03 ppm.

Entry 3. Benzyl alcohol was reacted with reagent **4c** in the presence of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  at r.t. for 30 min. according to general procedure to produce benzaldehyde in quantitative yield as judged by the integration of the area of the  $^1\text{H}$  NMR signal at 10.03 ppm.

Entry 4. Cyclohexanol was reacted with reagent **4c** at r.t. for 11 hrs according to general procedure to produce cyclohexanone (95% conversion according to GC analysis).

Entry 5. Cyclohexanol was reacted with reagent **4c** according to general procedure to produce cyclohexanone (95% conversion according to GC analysis).

Entry 6. Cycloheptanol was reacted with reagent **4c** according to general procedure to produce cycloheptanone (90% conversion according to GC analysis).

Entry 7. Cyclooctanol was reacted with reagent **4c** according to general procedure to produce cyclooctanone (95% conversion according to GC analysis).

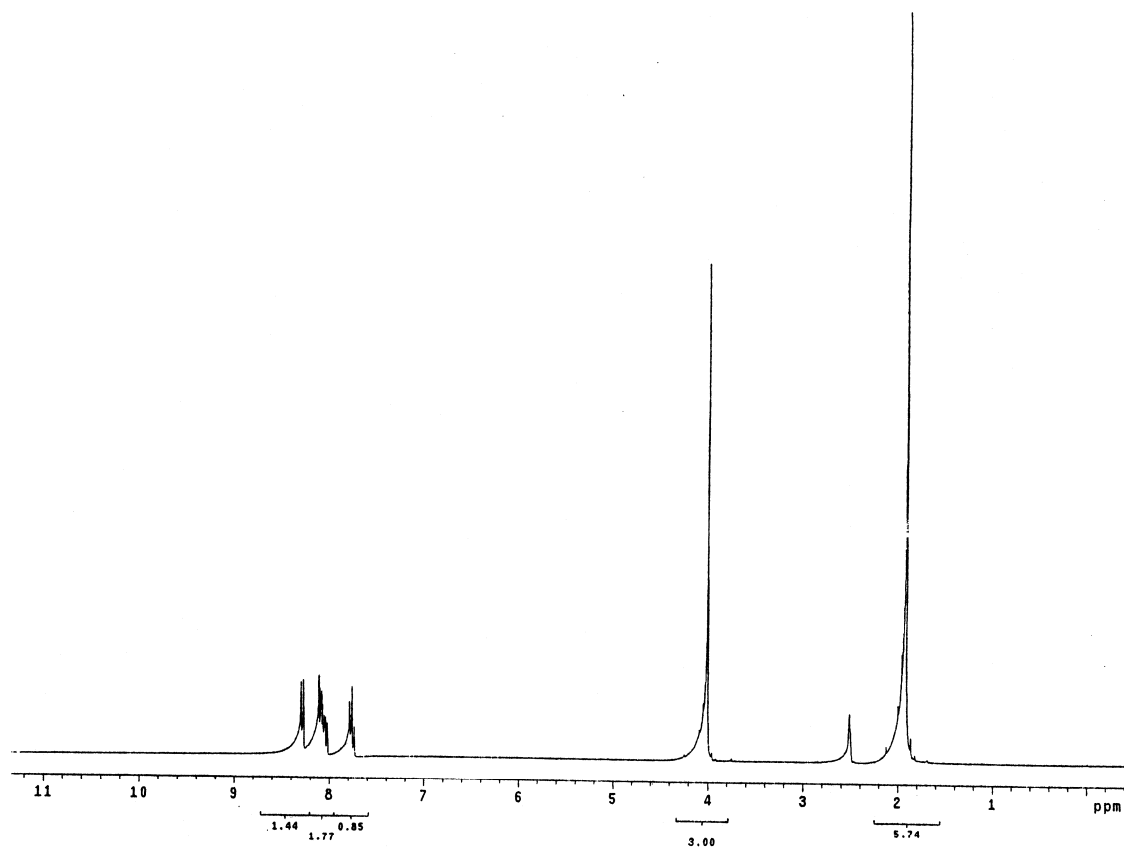
Entry 8. Cyclooctanol was reacted with reagent **4c** in the presence of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  at r.t. for 30 min. according to general procedure to produce cyclooctanone (95% conversion according to GC analysis).

Entry 9. Oxidation of alcohols with trifluoroacetate **8b**: To a solution of trifluoroacetate **8b** (0.04 mg, 0.1 mmol) in  $\text{CDCl}_3$  (0.5 mL) benzyl alcohol (10  $\mu\text{L}$ , 0.096 mmol) was added. The reaction mixture was stored at r.t. for 0.5 h to afford benzaldehyde in quantitative yield as judged by the integration of the area of the  $^1\text{H}$  NMR signal at 10.03 ppm.

Entry 10. Oxidation of alcohols with acetate **8a** in the presence of trifluoroacetic acid: To a solution of acetate **8a** (0.04 mg, 0.1 mmol) in  $\text{CDCl}_3$  (0.5 mL) benzyl alcohol (10  $\mu\text{L}$ , 0.096 mmol) was added. The reaction mixture was stored at 40 °C for 1 h to afford benzaldehyde in quantitative yield as judged by the integration of the area of the  $^1\text{H}$  NMR signal at 10.03 ppm.

Entry 11. Oxidation of alcohols with ester **6b** in the presence of trifluoroacetic acid: To a solution of acetate **6b** (0.04 mg, 0.1 mmol) in CDCl<sub>3</sub> (0.5 mL) benzyl alcohol (10 µl, 0.096 mmol) was added. The reaction mixture was stored at 40 °C for 2 h to afford benzaldehyde in quantitative yield as judged by the integration of the area of the <sup>1</sup>H NMR signal at 10.03 ppm.





$^1\text{H}$  NMR of compound **8a** in  $\text{DMSO-d}_6$

