Supporting Information

FACILE PREPARATION OF 1-HYDROXY-1,2-BENZIODOXOL-3(1*H*)-ONE 1-OXIDE (IBX) AND DESS–MARTIN REAGENT USING SODIUM HYPOCHLORITE UNDER CARBON DIOXIDE

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1. Experimental details

General: IR spectra were recorded on a JASCO FR/IR-4700 spectrometer. ^{1}H NMR spectra were recorded on a BRUKER AVANCE III HD 500 spectrometer (TMS or CHD_2SOCD_3 as an internal standard). Melting points were determined with SRS MPA 100 OptiMelt Automated Melting Point System and were uncorrected.

Sodium hypochlorite pentahydrate, 13% aqueous sodium hypochlorite, and 4% aqueous sodium hypochlorite were purchased from Fujifilm Wako Pure Chemical Industries, Co. Ltd. The concentration of aqueous sodium hypochlorite was determined by iodometric titration prior to use. Other materials were purchased from Tokyo Chemical Industry Co., Ltd., Sigma-Aldrich Co., LLC., Fujifilm Wako Pure Chemical Industries, Co. Ltd.

CAUTION: Although we have never encountered any safety-related issue during the synthesis of **1** or **4**, Plumb and Harper cautioned that even analytically pure IBX (>99%) has an explosive character based on in-house impact sensitivity tests.[1] Therefore, great care should be taken during large-scale operations. See also the section 3. Property of IBX obtained with NaClO-$5H_2O$–CO_2 system.

General Procedure for Synthesis of IBX 1 (2 mmol scale)

To a stirred solution of NaClO-$5H_2O$ (724 mg, 4.4 mmol) in H_2O (1.3 mL) was added 2-iodobenzoic acid **2** (496 mg, 2.0 mmol) under CO_2 at room temperature and the mixture was vigorously stirred for 12 hours. The resulting suspension was acidified with 1.0 M aq. HCl (final pH: about 1–2) to give a white slurry, which was filtered through a sintered-glass funnel and rinsed with water (4 X 5 mL) and acetone (3 X 5 mL). The solid thus collected was dried under reduced pressure (0.3 Torr) for 2 hours to give IBX **1** (493 mg, 88%) as a white microcrystalline solid.[2] Mp. 232–236 °C (decomp.); IR (ATR): 3300–2600 (br), 1632, 1331, 1140, 1296, 775, 598 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.13 (d, J = 7.5 Hz, 1H), 8.03 (dd, J = 7.5, 1.0 Hz, 1H), 8.00 (t, J = 7.5 Hz, 1H), 7.84 (td, J = 7.5, 1.0 Hz, 1H).

Large-scale (100 mmol) Synthesis of 1

A 500 mL round-bottomed flask was charged with NaClO-$5H_2O$ (36.1 g, 0.22 mol) and H_2O (67 mL). The resulting pale yellow solution was cooled to 2–3 °C in an ice-water bath, and iodoarene **2** (24.8 g, 0.10 mol) was added portionwise to the solution. The flask was flushed with CO_2 and vigorously stirred in the ice bath. After 30 minutes, remaining ice in the bath was removed and the flask was allowed to warm gradually to

room temperature. After 12 hours, the resulting suspension was acidified with 3.0 M aq. HCl (final pH: about 1–2). The slurry was filtered through a sintered-glass funnel and rinsed with water (6 X 50 mL) and acetone (3 X 50 mL). The solid thus collected was dried under reduced pressure (0.3 Torr) for 2 hours to give IBX **1** (26.0 g, 93%) as a white microcrystalline solid. ^{1}H NMR, IR analyses, and iodometric titration showed that this batch had the same purity as that obtained in the 2 mmol scale experiment.

One-pot Synthesis of Dess-Martin Reagent 4 from 2

To a stirred solution of NaClO-5H_2O (724 mg, 4.4 mmol) in H_2O (1.3 mL) was added 2-iodobenzoic acid (496 mg, 2.0 mmol) under CO_2 at room temperature and the mixture was vigorously stirred for 12 hours. The reaction mixture was acidified with 3 M HCl (final pH: about 1–2) and the resulting suspension was washed several times with water by decantation to give a white solid. This solid was then dried under reduced pressure (0.3 Torr) for 2 hours to give almost pure IBX as a white powder (checked by NMR). The flask was flushed with argon, and acetic anhydride (1.7 mL, 18 mmol) and acetic acid (1.5 mL, 26 mmol) were added to it. The resulting suspension was warmed to 85 °C for 0.5–1.5 hours (until almost all the solid was dissolved - dependent on the batch). The mixture was allowed to cool to room temperature and left at this temperature for 12 h. The colorless prisms that formed were separated from the supernatant by decantation and washed several times with dry ether under argon to give **4** (710–760 mg, 84–90%) as a white solid.[3] Mp. 132–135 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 (d, J = 8.5 Hz, 1H), 8.28 (m, 1H), 8.02 (m, 1H), 7.93 (m, 1H), 2.31 (s, 3H), 2.10 (s, 6H).

2. Attempted one-pot synthesis of Dess-Martin reagent using Oxone

To a stirred solution of Oxone (1.37 g, 4.4 mmol) in H_2O (0.4 mL) was added 2-iodobenzoic acid **2** (250 mg, 2.0 mmol) under air at room temperature and the mixture was vigorously stirred at 70 °C for 3 hours. The reaction mixture was acidified with 3 M HCl (final pH: about 1–2) and the resulting suspension was washed several times with water by decantation to give a white solid. This solid was then dried under reduced pressure (0.3 Torr) for 2 hours. The flask was flushed with argon, and acetic anhydride (1.7 mL, 18 mmol) and acetic acid (1.5 mL, 26 mmol) were added to it. The resulting suspension was warmed to 85 °C for 1.5 hours. ^{1}H NMR spectrum of the resulting solution showed the absence of desired product **4**.

3. Property of IBX obtained with NaClO-5H_2O–CO_2 system

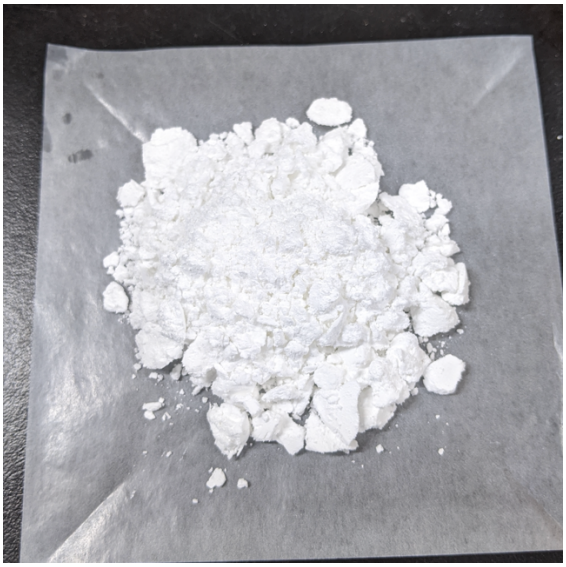


Fig. S1 Appearance of IBX obtained with large-scale (100 mmol) reaction.

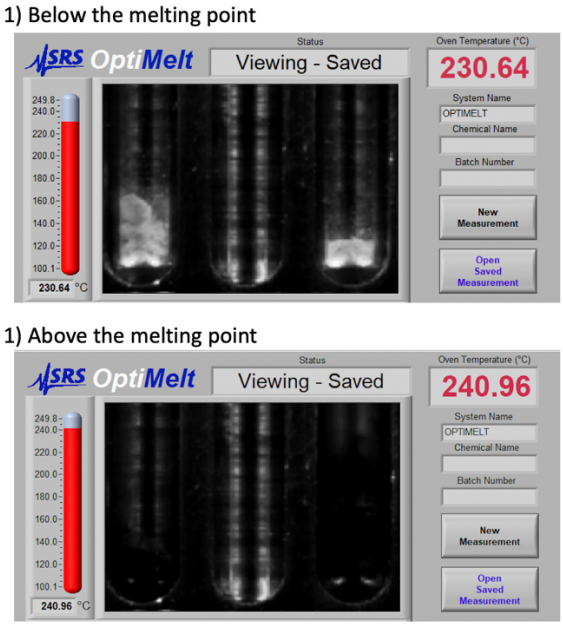


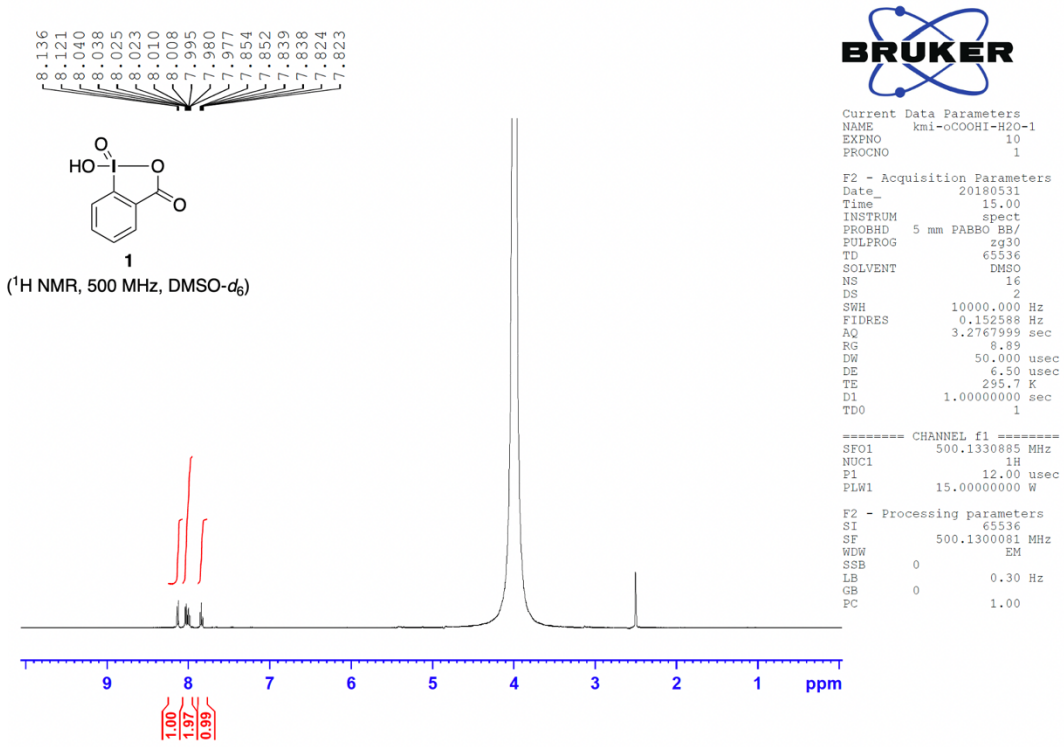
Fig. S2 IBX below and above melting points (two batches (left and right side) were decomposed in the same way at ca. 232–236 °C).

A white microcrystalline solid of IBX **1** that obtained after ordinally work-up was not shock-/heat-sensitive. A piece of **1** did not exhibit impact sensitiveness when impact it with iron hammer. Heating of a piece of crystal of **1** above melting point resulted in the rapid evolution of gas but was not explosive.

4. References

1. J. B. Plumb and D. J. Harper, *Chem. Eng. News*, 1990, **68**, July 16, 3.
2. M. Frigerio and M. Santagostino, *Tetrahedron Lett.*, 1994, **35**, 8019.
3. D. B. Dess and J. C. Martin, *J. Am. Chem. Soc.*, 1991, **113**, 7277.

5. Spectra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O
O
O
1
(1H NMR, 500 MHz, DMSO-d6)
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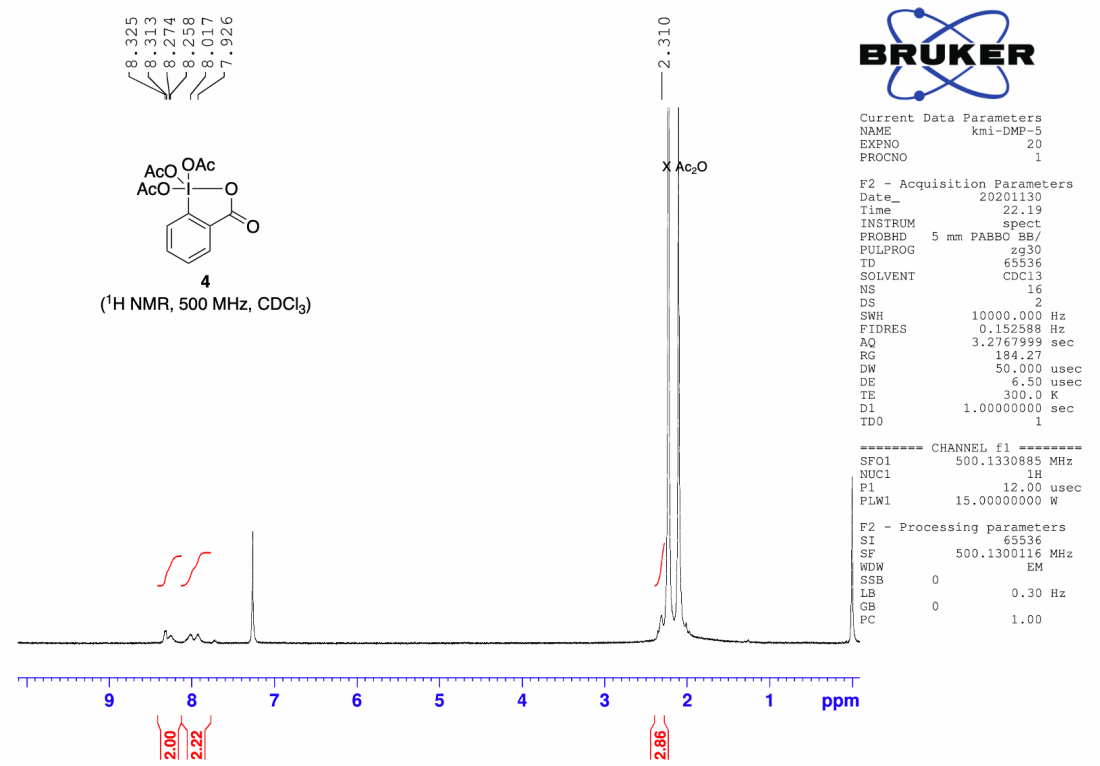
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