Practical Synthesis of 2-Iodosobenzoic Acid (IBA) without Contamination by Hazardous 2-Iodoxybenzoic Acid (IBX) under Mild Conditions

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Abstract: We report a convenient and practical method for the preparation of nonexplosive cyclic hypervalent iodine(III) oxidants as efficient organocatalysts and reagents for various reactions using Oxone® in aqueous solution under mild conditions at room temperature. The thus obtained 2-iodosobenzoic acids (IBAs) could be used as precursors of other cyclic organoiodine(III) derivatives by the solvolytic derivatization of the hydroxy group under mild conditions of 80 °C or lower temperature. These sequential procedures are highly reliable to selectively afford cyclic hypervalent iodine compounds in excellent yields without contamination by hazardous pentavalent iodine(III) compound.

Keywords: cyclic organoiodine(III) compounds; Oxone®; water, solvolytic functionalization, mild condition, metal-free, 2-iodosobenzoic acid

1. Introduction

Cyclic hypervalent iodine reagents, such as 2-iodosobenzoic acid (IBA) and 2-iodoxybenzoic acid (IBX) are nonmetallic green oxidants with excellent recyclability [1–3]. IBA and IBX can be regenerated from 2-iodobenzoic acid (2-IB) without requiring an external ligand except for water in this reoxidation step. This is because the carboxy group adjacent to the iodine atom serves as an endogenous ligand. Recently, IBA, a representative trivalent cyclic hypervalent iodine oxidant, has been used as a catalyst and reagent in various reactions, i.e., decarboxylative alkynylation [4,5], decarboxylative acylarylation [6], oxyalkenylation [7], oxyarylation [8], oxidative C–H arylation [9], C–H hydroxylation [10], C–H oxidation [11,12], ring-opening hydrazinilation [13], and asymmetric intramolecular α-cyclopropanation [14]. IBA derivatives containing OAc [15–28], OMe [29–32], OTs [33–35], OTf [36,37], Cl [38–42], F [43–45], CN [46], N3 [47–54], CF3 [55,56], OCOCF3 [57], alkynyl [58–62] ligands instead of the hydroxy group have also found application in various reactions (Figure 1).

Figure 1. 2-Iodosobenzoic acid (IBA) and its precursor 2-iodobenzoic acid (2-IB).

Although IBAs can be prepared from 2-IBs by existing methods (Figure 2) [63–66], the development of a safer and more efficient method for their synthesis is highly desirable.
As shown in Figure 2, IBAs can be further oxidized to pentavalent cyclic hypervalent IBXs [67], which need to be prevented for the preparation of IBAs [68–70], mainly due to the explosive nature of IBXs on heating and impact, while IBXs are useful in some small-scale reactions [71–76]. Thus, contamination by IBX in the IBA products should be avoided for long-term safe storage or large-scale use.

![Figure 2](image.png)

**Figure 2.** Synthesis of 2-iodosobenzoic acids (IBAs) and 2-iodoxybenzoic acids (IBXs) from 2-iodobenzoic acids (2-IBs).

In recent decades, many reactions using Oxone®, which is an inexpensive and commercially available stable triple salt (2KHSO₄/KHSO₄/K₂SO₄), have been developed for practical synthetic purposes [77]. In particular, the use of Oxone® as a re-oxidant for pentavalent hypervalent iodine reagents is drawing attention for catalytic oxidation reactions [78–92]. The reaction systems for alcohol oxidations [78–84] involving in situ generated active hypervalent iodine(V) species are optimized on the basis of the preparative conditions of IBX from 2-IB at 70 °C [93]. Meanwhile, oxidative lactonizations from modified 2-IBs using Oxone® occur at room temperature [85–87]. In this context, the generation of nonexplosive trivalent cyclic hypervalent iodines, i.e., IBA and its analogs, using Oxone® can be expected to provide a convenient and safe synthetic procedure; however, to best of our knowledge, the selective preparation of IBAs using Oxone® has not been reported so far.

Recently, we reported that IBAs generated in a reaction system containing 2-IB and Oxone® play a catalytic role in the selective oxidation of alkoxybenzenes to p-quinones [94]. This resulted in the development of the practical method herein reported for the selective preparation of IBAs under mild conditions.

2. Results and Discussion

2.1. Selective Synthesis of IBA and Its Analogs

We started our investigation on the selective preparation of IBAs by evaluating the solvent effects on the oxidation of 2-IB 1a using 1.0 equivalent of Oxone® to obtain IBA 2a as a representative compound, and the results are summarized in Figure 3. First, the reaction in water led to the successful production of IBA 2a in 82% yield (Figure 3, entry 2), whereas IBA 2a was not produced in organic solvent in the absence of water (no reaction because Oxone® was not dissolved) (see entry 1). This result indicates that water plays an essential role in the formation of IBA. Therefore, we assumed that an aqueous system similar to the selective formation of p-quinone from alkoxybenzenes catalyzed by 2-IB 1a with Oxone® [94] could be suitable for the present reaction. We then investigated in detail the effect of a series of organic solvents on the aqueous preparation of IBA 2a using Oxone®.
Various water-miscible organic solvents were investigated to dissolve 2-IB 1a in this reaction. The preparation of IBA 2a using acetonitrile (MeCN) in aqueous condition (Figure 3, entry 3) was similar to that performed in the absence of organic solvents (Figure 3, entry 2). Tetrahydrofuran (THF), dioxane, benzene and N,N-dimethylformamide (DMF) were also examined, finding that the use of highly polar dioxane and DMF led to excellent yields of IBA 2a (Figure 3, entries 5 and 7), whereas benzene, the least polar solvent among these aprotic solvents, significantly reduced the yield of the desired product (Figure 3, entry 6). The reason for this very low yield IBA formation was interpreted as being due to that benzene forms a two-phase system and interferes with the dissolution of 2-IB into water. Protic solvents such as MeOH, EtOH and 2,2,2-trifluoroethanol (TFE) gave IBA 2a in high yields; however, they also worked as a ligand for IBA, causing the formation of very small amounts of ligand-exchanged byproducts 3a–c (Figure 3, entries 8–10). The white solid IBA 2a obtained after the water and acetone washings did not contain any other byproducts. Although this result indicated that protic organic solvents were not suitable for the selective preparation of IBAs, it also revealed that the IBA hydroxyl group could undergo substitution reactions under mild conditions (vide infra). The yields indicated in Figure 3 are almost equal to the conversion of 2-IB 1a.

Next, we investigated the substrate scope for the synthesis of IBAs using Oxone® under aqueous conditions with MeCN, and the results are shown in Figure 4. MeCN was used as a component of the solvent to dissolve substrates 1. By oxidation of 5-substituted 2-IBs, IBAs 2b–d containing fluoro-, chloro-, and bromo-substituents were smoothly obtained in excellent yields from the corresponding halo-substituted 2-IBs 1b–d. From 2-IBs 1e–j with electron-donating groups such as methyl-, methoxy-, and acethoxy-substituents (1e–g) and electron-withdrawing groups such as trifluoromethyl-, nitro- and cyano-substituents (1h–j), the desired IBAs 2e–j were also produced in good yields. However, 2-IB bearing a hydroxy-substituent 1k afforded the desired product 2k in a moderate yield under the same conditions. In the oxidation of 4-substituted 2-IBs, fluoro-, chloro-, bromo-, trifluoromethyl-, and carboxy-substituted IBAs 2l–p were obtained in excellent yields from the corresponding 2-IBs 1l–p. In addition, the oxidized products of 4,5-disubstituted 2-IBs containing difluoro-substituents 2q and dimethoxy-substituents 2r were obtained in high yields. Meanwhile, with regard to 3-substituted 2-IBs, the reaction of methyl-substituted 1t with a slight excess of Oxone® afforded the expected IBA 2t in a good yield, whereas...
the yield of bromo-substituted IBA 2s was lower even at the elevated temperature and in the presence of a large excess of Oxone®. Steric effects are probably important in the formation of the cyclic $\lambda^3$-iodanes. Indeed, the presence of a substituent at the ortho position of the iodine atom (3-position) interfered in the synthesis of the corresponding product for 3-bromo-substituted 2-IB 1s. In the case of 6-substituted 2-IBs, fluoro-substituted IBA 2u and methyl-substituted 2v were obtained in good yields. Finally, the reaction of 3-iodonaphthalene-2-carboxylic acid 3 under the present conditions led to the expected tricyclic hypervalent iodine 4 in an excellent yield (Scheme 1).

![Scheme 1. Synthesis of tricyclic hypervalent iodine compound 4.](image)

2.2. IBAs Synthesis Using Ferric Effect

As mentioned in Section 2.1, our present method can selectively afford trivalent cyclic hypervalent iodine IBA at room temperature without contamination by pentavalent iodine byproduct. The mild conditions used contributed favorably to this product selectivity. Interestingly, we further found that iron ion in tap water (TW), which contained iron ion (5.8 μM or less), contribute to the IBA formation, whereas calcium and magnesium ions as main minerals in TW do not affect the selectivity. Indeed, IBA 2a was selectively produced from 2-IB 1a by heating even at 100 °C in DW containing 5 mol% FeCl₃ (Scheme 2, left). On the other hand, IBX was instead formed as a main product in the absence of FeCl₃ in

![Figure 4. Substrate scope of the selective preparation of IBAs 2b–v using Oxone® under aqueous conditions. (a) This reaction was performed at 30 °C in the presence of 1.2 equivalents of Oxone®. (b) Performed using 5 equivalents of Oxone® at 40 °C.](image)
deionized water (DW) [93]. Other ferric salts such as Fe(NO₃)₃, Fe(OTf)₃, and FeSO₄ had similar effects. In addition, it was found that pentavalent IBX 5 was converted to IBA 2a in the presence of a catalytic amount of FeCl₃ at 100 °C (Scheme 2, right), while the formation of unidentified high- and low-polar decomposition products were detected in the water and the acetone washing solution, respectively. Here, 2-IB 1a was not produced. These results would indicate that overoxidation of IBA 2a to pentavalent IBX 5 was strongly prevented by ferric salts. Thus, the effect of the metal ion in the decomposition of hazardous IBX 5 is also a significant key factor to ensure the safety for our trivalent cyclic hypervalent iodine synthesis under heating conditions.

**Scheme 2.** Effect of a ferric salt on the selective synthesis of IBA 2a.

The reaction time in the synthesis of IBAs was significantly shortened by heating. In the investigation of the heating conditions for the synthesis of IBA 2a in 0.2 M 2-IB 1a in the presence of 2.5 mol% FeCl₃ for 10 min, the required amount of Oxone® and the reaction temperature were thus optimized to 60 °C (Figure 5a) and 1.0 equivalent (Figure 5b), respectively. The yield of IBA 2a was very sensitive to the reaction time, which dropped from 83% for 10 min to 70% for 1 h. IBA may be decomposed to small molecules in the presence of excess Oxone®; it has been reported that Oxone® causes oxidative cleavage of the aromatic ring [95]. Without Oxone®, we also confirmed that IBA 2a was hardly decomposed under the conditions of Scheme 2 in the presence of 1.0 equivalent of H₂SO₄ and 10 mol% FeCl₃ at 100 °C for 10 min, while only 64% of IBA 2a was recovered by replacing H₂SO₄ in the presence of Oxone® under the same conditions. Thus, the excess uses of Oxone® and performing the reaction at high temperature would decrease the IBA yield as shown in Figure 5a,b.

**Figure 5.** Optimization of (a) temperature using 1.0 equivalent of Oxone® and (b) amount of Oxone® at 60 °C for the synthesis of IBA 2a from 2-IB 1a in the presence of 2.5 mol% FeCl₃ (MeCN/DW (1/1)).
This optimized heating method could be applied to the synthesis of IBAs 2a–j (Scheme 3). 2-IB 1a as well as the substrates 1b–d and 1g–j that are tolerable to over-oxidation at this temperature were successfully converted to the desired IBAs 2a–d and 2g–j in high yields. However, the transformation of 2-IB having an electron-rich functional group, i.e., methoxy-substituted 2-IB 1f, resulted in low yield of the corresponding IBA 2f due to the formation of 2-carboxy-p-benzoquinone by the oxidation with Oxone®. Therefore, in order to apply the heating conditions, the stability of the product to oxidation must be considered.

![Scheme 3. Short-time selective synthesis of IBAs 2a–j in the presence of ferric salt.](image)

2.3. IBA Derivatives

As previously mentioned, when IBA 2a was synthesized in an aqueous solution with alcohols, alkoxy-substituted derivatives 3a–c were obtained as byproducts by substitution of the hydroxyl ligand of IBA 2a (see Figure 3), implying the potential of the solvolytic ligand exchange of IBA 2a under mild conditions. For the ligand derivatization of IBAs, the water molecule is an obstacle because the ligand exchanges of the IBA hydroxy group are reversible. Thus, molecular sieves with a pore diameter of 3 Å (MS3Å) was used for the solvolytic functionalization of IBA 2a in dehydrated protic solvent (Figure 6). The quantitative derivatization to benziodoxole methoxide (IB-OMe) 6a was achieved by heating IBA 2a at 60 °C in MeOH (Figure 6, entry 1). Upon treatment at 80 °C, benziodoxole ethoxide (IB-OEt) 6b and benziodoxole 2,2,2-trifluoroethoxide (IB-OCH2CF3) 6c were also produced in high yields by the ligand exchange reaction with EtOH and TFE, respectively (Figure 6, entries 2 and 3). Benziodoxole n-propoxide (IB-O–Pr) 6d was obtained in 98% yield using PrOH at 70 °C (Figure 6, entry 4), and benziodoxole isopropoxide (IB-O–Pr) 6e was produced in 52% yield at 60 °C in the presence of tPrOH (Figure 6, entry 5). In the cases of IB-O–Pr 6d and IB-O–Pr 6e, the temperature control was essential to suppress the formation of a 2-IB-IBA condensate as a byproduct; here, the formation of 2-IB 1a can be explained in terms of the alcohol oxidation by IBA. It is known that secondary alcohols are readily oxidized by IBA [83]. No unwanted byproduct was found during the transformation to benziodoxole hexafluoroisopropoxide (IB-OCH(CF3)2) 6f using hexafluoroisopropanol (HFIP) at 80 °C (Figure 6, entry 6), which is most likely due to the stability of HFIP against oxidation. Indeed, the condensate between 2-IB and IBA appeared during the reaction for benziodoxole n-buthoxide (IB-O–Bu) 6g using an oxidizable primary alcohol, tBuOH, at 80 °C, whereas such byproduct was not observed in the synthesis of benziodoxole tert-buthoxide (IB-O–Bu) 6h using tBuOH as a solvent inert to oxidation. Nevertheless, IB-O–Bu 6g could be selectively obtained by heat treatment at 60 °C without the formation of the condensate.

Using AcOH as a solvent, the solvolytic method was further applied to the synthesis of benziodoxole acetate (IB-OAc) 7a and its analogs (R-IB-OAc) 7b–i from the corresponding IBAs 2a–i (Scheme 4). IB-OAc 7a was easily produced in good yield by ligand exchange of IBA 2a with AcOH at room temperature. Similarly, these transformations successfully afforded R-IB-OAc 7b–d containing fluoro-, chloro-, and bromo-substituents; 7e–g with electron-donating methyl-, methoxy-, and acethoxy-groups; and 7h and 7i bearing an electron-withdrawing trifluoromethyl- and nitro-substituent, respectively.
Figure 6. Benziodoxole alkoxides 6a–h by solvolytic functionalization of IBA 2a.

| Entry | Solvent | Time (h) | Temperature (°C) | Product | Yield (%) |
|-------|---------|----------|------------------|---------|-----------|
| 1     | MeOH    | 2        | 60               | R = Me (6a) | 100       |
| 2     | EtOH    | 1        | 80               | R = Et (6b) | 96        |
| 3     | TFE     | 1        | 80               | R = CH₂CF₃ (6c) | 94       |
| 4     | PrOH    | 3        | 70               | R = Pr (6d) | 96        |
| 5     | PhOH    | 15       | 60               | R = Ph (6e) | 52        |
| 6     | HFIP    | 1        | 80               | R = CH(CF₃)₂ (6f) | 83       |
| 7     | tertBuOH | 18     | 60               | R = tertBu (6g) | 75        |
| 8     | tertBuOH | 2       | 80               | R = tertBu (6h) | 49        |

Scheme 4. Transformation of IBAs 2a–i to benziodoxole acetates 7a–i.

3. Materials and Methods

3.1. General Information

Substrates 1i [96], 1k [97], 1m [98], 1o [98], 1p [99], 1q [100], 1s [101], 1t [98], 1v [102], and 3i [65] were prepared by Sandmeyer reaction of the corresponding anthranilic acids. Substrate 1g [84] was synthesized by acetylation of compound 1k. Substrate 1j [103] is derived from 5-bromo-anthranilic acid methyl ester. 1H, 13C, and 19F nuclear magnetic resonance (NMR) spectra were recorded on ECS 400 and ECX 500 NMR spectrometers (JEOL Ltd., Tokyo, Japan) using deuterated dimethyl sulfoxide (DMSO-d₆) or chloroform (CDCl₃) as a solvent. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (δ = 0 ppm) as an internal standard for 1H and 13C NMR spectra and hexafluoroacetone (δ = -84.6 ppm) as an internal standard for 19F NMR spectra. Coupling constants (J) are reported in Hertz (Hz), and the multiplicity is reported according to the following convention: singlet (s), doublet (d), double doublet (dd), double double double (ddd), double triplet (dt), triplet (t), double triplet (td), quartet (q), quintet (quin), sextet (sext), septet (sep), and multiplet (m). Data are reported as follows: Chemical shift (number of protons, multiplicity, coupling constants). Infrared (IR) spectra were recorded on a JASCO FT/IR-4200 spectrometer (JASCO Co., Tokyo, Japan) on diffuse reflectance method using KBr powder. Absorptions are expressed in reciprocal centimeter (cm⁻¹). High resolution mass spectra (HRMS) obtained by the direct analysis in real time (DART) method were recorded on a Thermo Scientific Exactive Plus Orbitrap (Thermo Fisher Scientific, Inc., Waltham, MA, USA).

3.2. Synthesis of IBA Analogues

3.2.1. General Procedure for the Synthesis of IBAs 2a–v and 4

To a solution of 2-IBs (1.0 mmol) in MeCN (5 mL) was added Oxone® (738 mg, 1.2 mmol) and H₂O (TW for Figure 3; Figure 4, Scheme 1 or DW for Scheme 2; Scheme 3, 5 mL). After the mixture was stirred at room temperature for the appropriate time (see Figure 4 and Scheme 1), the product was filtered under reduced pressure. The residue was washed with water and acetone to obtain the corresponding IBAs 2a–v and 4 (see Supplementary Materials for 1H NMR spectroscopic data) as a white powder.
3.2.2. 1-Hydroxy-1λ3-benzo[d][1,2]iiodaoxol-3(1H)-one (2a)

1H NMR (400 MHz, DMSO-d6): δ 7.72 (1H, td, J = 7.3, 0.9 Hz, H5), 7.86 (1H, d, J = 8.2 Hz, H3), 7.97 (1H, d, J = 8.7, 1.4 Hz, H4), 8.03 (1H, d, J = 7.8, 1.4 Hz, H6), 8.08 (1H, s) ppm. 13C NMR (100 MHz, DMSO-d6): δ 120.3 (C2), 126.2 (C3), 130.3 (C5), 131.0 (C1), 131.4 (C6), 134.4 (C4), 167.7 (COOH) ppm. IR (ATR, KBr): ν 2936 (OH), 1616 (C=O), 1566 (C=O) cm−1. Mp: 243–244 ºC. 1H and 13C NMR data are consistent with those reported in the literature [33].

3.2.3. 5-Fluoro-1-hydroxy-1λ3-benzo[d][1,2]iiodaoxol-3(1H)-one (2b)

1H NMR (500 MHz, DMSO-d6): δ 7.76 (1H, dd, J = 8.7, 2.3 Hz), 7.79–7.88 (2H, m), 8.21 (1H, s) ppm. 13C NMR (125 MHz, DMSO-d6): δ 114.2, 117.3 (d, J = 22.7 Hz), 121.7 (d, J = 23.8 Hz), 128.3 (d, J = 8.4 Hz), 134.1 (d, J = 7.2 Hz), 163.9 (d, J = 246.8 Hz), 166.4 (d, J = 2.4 Hz) ppm. 19F NMR (470 MHz, DMSO-d6): δ −116.2 (dt, J = 5.7, 8.6 Hz) ppm. IR (ATR, KBr): ν 2904 (OH), 1635 (C=O), 1577 (C=O) cm−1. Mp: 212–214 ºC. 1H and 13C NMR data are consistent with those reported in the literature [105].

3.2.4. 5-Bromo-1-hydroxy-1λ3-benzo[d][1,2]iiodaoxol-3(1H)-one (2c)

1H NMR (400 MHz, DMSO-d6): δ 7.74 (1H, d, J = 8.7 Hz), 7.95 (1H, d, J = 2.3 Hz), 8.03 (1H, d, J = 8.7, 2.3 Hz), 8.28 (1H, s) ppm. 13C NMR (100 MHz, DMSO-d6): δ 118.6, 128.1, 130.3, 133.5, 134.0, 135.8, 166.3 ppm. IR (ATR, KBr): ν 2905 (OH), 1624 (C=O), 1560 (C=O) cm−1. Mp: 294–295 ºC. 1H and 13C NMR data are consistent with those reported in the literature [104].

3.2.5. 5-Chloro-1-hydroxy-1λ3-benzo[d][1,2]iiodaoxol-3(1H)-one (2d)

1H NMR (400 MHz, DMSO-d6): δ 7.81 (1H, d, J = 8.7 Hz), 7.95 (1H, d, J = 2.3 Hz), 8.15 (1H, d, J = 8.7, 2.3 Hz), 8.27 (1H, s) ppm. 13C NMR (100 MHz, DMSO-d6): δ 119.5, 124.2, 128.3, 133.3, 133.7, 136.8, 166.2 ppm. IR (ATR, KBr): ν 2884 (OH), 1617 (C=O), 1557 (C=O) cm−1. Mp: 236–238 ºC. 1H and 13C NMR data are consistent with those reported in the literature [106].

3.2.6. 1-Hydroxy-5-methyl-1λ3-benzo[d][1,2]iiodaoxol-3(1H)-one (2e)

1H NMR (400 MHz, DMSO-d6): δ 2.48 (3H, s), 7.70 (1H, d, J = 8.2 Hz), 7.79 (1H, dd, J = 8.7, 1.8 Hz), 7.85 (1H, s), 8.01 (1H, s) ppm. 13C NMR (100 MHz, DMSO-d6): δ 20.1, 116.7, 125.9, 131.3, 131.4, 135.2, 140.4, 167.7 ppm. IR (ATR, KBr): ν 3054 (OH), 1622 (C=O), 1569 (C=O) cm−1. Mp: 212–214 ºC. 1H and 13C NMR data are consistent with those reported in the literature [105].

3.2.7. 1-Hydroxy-5-methoxy-1λ3-benzo[d][1,2]iiodaoxol-3(1H)-one (2f)

1H NMR (400 MHz, DMSO-d6): δ 3.89 (3H, s), 7.52 (1H, d, J = 2.7 Hz), 7.55 (1H, dd, J = 8.7, 2.8 Hz), 7.67 (1H, d, J = 9.2 Hz), 8.04 (1H, s) ppm. 13C NMR (100 MHz, DMSO-d6): δ 55.8, 108.9, 114.8, 121.5, 127.0, 132.9, 161.4, 167.4 ppm. IR (ATR, KBr): ν 2953 (OH), 1620 (C=O), 1577 (C=O) cm−1. Mp: 217–218 ºC. 1H and 13C NMR data are consistent with those reported in the literature [105].

3.2.8. 1-Hydroxy-3-oxo-1,3-dihydro-1λ3-benzo[d][1,2]iiodaoxol-5-yl acetate (2g)

1H NMR (500 MHz, DMSO-d6): δ 2.33 (3H, s), 7.74 (1H, dd, J = 8.6, 2.3 Hz), 7.77 (1H, d, J = 2.3 Hz), 7.84 (1H, d, J = 8.6 Hz), 8.16 (1H, s) ppm. 13C NMR (125 MHz, DMSO-d6): δ 20.8, 116.1, 124.2, 127.4, 127.9, 133.0, 152.5, 166.8, 169.0 ppm. IR (ATR, KBr): ν 2891 (OH), 1759 (C=O), 1604 (C=O), 1559 (C=O) cm−1. Mp: 207–208 ºC. HRMS (DART, m/z) calcd for C9H8IO3 [M + H]+: 322.9411; found: 322.9413.
3.2.9. 1-Hydroxy-5-(trifluoromethyl)-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (2h)

1H NMR (500 MHz, DMSO-d6): δ 8.08 (1H, d, J = 8.0 Hz), 8.21 (1H, s), 8.33 (1H, d, J = 8.1 Hz), 8.38 (1H, s) ppm. 13C NMR (125 MHz, DMSO-d6): δ 123.4 (q, J = 271.0 Hz), 125.5, 127.1 (d, J = 3.6 Hz), 127.9, 130.6 (d, J = 2.4 Hz), 131.6 (q, J = 32.6 Hz), 132.9, 166.3 ppm. 19F NMR (470 MHz, DMSO-d6): δ −64.5 ppm. IR (ATR, KBr): ν 2854 (OH), 1597 (C=O), 1559 (C=O) cm⁻¹. Mp: 233–235 °C. HRMS (DART, m/z) calcd for C₉H₅F₃IO₃ [M + H⁺]: 332.9230; found: 332.9227.

3.2.10. 1-Hydroxy-5-nitro-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (2i)

1H NMR (400 MHz, DMSO-d6): δ 8.10 (1H, d, J = 8.7 Hz), 8.54 (1H, s), 8.57 (1H, d, J = 2.3 Hz), 8.73 (1H, dd, J = 8.7, 2.8 Hz) ppm. 13C NMR (100 MHz, DMSO-d6): δ 124.8, 127.7, 128.1, 128.2, 133.4, 149.7, 165.9 ppm. IR (ATR, KBr): ν 2834 (OH), 1617 (C=O), 1572 (C=O), 1541 (C=O) cm⁻¹. Mp: 214–216 °C. 1H and 13C NMR data are consistent with those reported in the literature [107].

3.2.11. 1-Hydroxy-3-oxo-1,3-dihydro-1λ3-benzo[d][1,2]iodaoxole-5-carbonitrile (2j)

1H NMR (500 MHz, DMSO-d6): δ 8.01 (1H, d, J = 8.6 Hz), 8.32–8.41 (3H, m) ppm. 13C NMR (125 MHz, DMSO-d6): δ 113.5, 117.3, 126.4, 127.7, 132.9, 134.2, 137.0, 166.0 ppm. IR (ATR, KBr): ν 2903 (OH), 1625 (C=O), 1582 (C=O), 1561 (C=O) cm⁻¹. Mp: 234–236 °C. HRMS (DART, m/z) calcd for C₉H₅NO₃ [M + H⁺]: 289.9309; found: 289.9310.

3.2.12. 1,5-Dihydroxy-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (2k)

1H NMR (400 MHz, DMSO-d6): δ 7.36 (1H, dd, J = 8.7, 2.7 Hz), 7.40 (1H, d, J = 2.3 Hz), 7.57 (1H, d, J = 9.2 Hz), 7.94 (1H, s) ppm. 13C NMR (100 MHz, DMSO-d6): δ 106.6, 117.1, 122.0, 127.0, 132.8, 159.7, 167.6 ppm. IR (ATR, KBr): ν 3447 (OH), 3234 (OH), 1576 (C=O) cm⁻¹. Mp: 230–232 °C. HRMS (DART, m/z) calcd for C₇H₇IO₃ [M + H⁺]: 280.9305; found: 280.9304.

3.2.13. 6-Fluoro-1-hydroxy-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (2l)

1H NMR (500 MHz, DMSO-d6): δ 7.53–7.60 (2H, m), 8.01 (1H, dd, J = 8.0, 5.2 Hz), 8.21 (1H, s) ppm. 13C NMR (125 MHz, DMSO-d6): δ 113.5 (d, J = 27.4 Hz), 118.0 (d, J = 22.7 Hz), 122.8 (d, J = 8.4 Hz), 128.3, 132.9 (d, J = 8.4 Hz), 166.0 (d, J = 254.0 Hz), 166.7 ppm. 19F NMR (470 MHz, DMSO-d6): δ −109.0 (dt, J = 5.8, 8.6 Hz) ppm. IR (ATR, KBr): ν 3091 (OH), 1636 (C=O), 1586 (C=O) cm⁻¹. Mp: 206–208 °C. 1H and 13C NMR data are consistent with those reported in the literature [105].

3.2.14. 6-Chloro-1-hydroxy-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (2m)

1H NMR (400 MHz, DMSO-d6): δ 7.75 (1H, d, J = 1.8 Hz), 7.78 (1H, dd, J = 7.8, 1.8 Hz), 7.96 (1H, d, J = 8.2, 2.3 Hz), 8.27 (1H, s) ppm. 13C NMR (100 MHz, DMSO-d6): δ 122.1, 125.7, 130.6, 130.7, 132.2, 139.3, 166.7 ppm. IR (ATR, KBr): ν 2854 (OH), 1607 (C=O), 1557 (C=O) cm⁻¹. Mp: 212–214 °C. 1H NMR data is consistent with those reported in the literature [94].

3.2.15. 6-Bromo-1-hydroxy-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (2n)

1H NMR (500 MHz, DMSO-d6): δ 7.80–7.98 (3H, m), 8.23 (1H, s) ppm. 13C NMR (125 MHz, DMSO-d6): δ 122.1, 127.9, 128.5, 131.0, 132.5, 133.5, 166.8 ppm. IR (ATR, KBr): ν 2844 (OH), 1602 (C=O), 1556 (C=O) cm⁻¹. Mp: 222–224 °C. HRMS (DART, m/z) calcd for C₇H₅BrIO₃ [M + H⁺]: 342.8461; found: 342.8460.

3.2.16. 1-Hydroxy-6-(trifluoromethyl)-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (2o)

1H NMR (400 MHz, DMSO-d6): δ 8.06 (1H, s), 8.10 (1H, d, J = 8.1 Hz), 8.20 (1H, d, J = 8.0 Hz), 8.38 (1H, s) ppm. 13C NMR (100 MHz, DMSO-d6): δ 121.7, 123.1 (d, J = 3.6 Hz), 123.4 (d, J = 270.7 Hz), 127.6 (d, J = 3.6 Hz), 131.9, 133.9 (q, J = 32.2 Hz), 135.4, 166.4 ppm. 19F NMR (370 MHz, DMSO-d6): δ −64.6 ppm. IR (ATR, KBr): ν 2871 (OH), 1616 (C=O), 1560
(C=O) cm⁻¹. Mp: 216–217 ºC. ¹H and ¹³C NMR data are consistent with those reported in the literature [12].

3.2.17. 1-Hydroxy-3-oxo-1,3-dihydro-1λ³-benzo[d][1,2]iodaoxole-6-carboxylic acid (2p)
¹H NMR (500 MHz, DMSO-d6): δ ppm. ¹³C NMR (125 MHz, DMSO-d6): δ ppm. IR (ATR, KBr): ν 2832 (OH), 1704 (C=O), 1616 (C=O), 1558 (C=O) cm⁻¹. Mp: 291–293 ºC. HRMS (DART, m/z) calcd for C₉H₉IO₃ [M + H]⁺: 308.9254; found: 308.9252.

3.2.18. 5,6-Difluoro-1-hydroxy-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (2q)
¹H NMR (500 MHz, DMSO-d6): δ 7.73 (1H, dd, J = 9.2, 6.9 Hz), 7.97 (1H, dd, J = 9.7, 7.4 Hz), 8.37 (1H, s) ppm. ¹³C NMR (125 MHz, DMSO-d6): δ 115.5 (d, J = 22.7 Hz), 119.2 (d, J = 19.1 Hz), 129.16 (d, J = 2.4 Hz), 129.20 (d, J = 3.6 Hz), 151.3 (dd, J = 263.5, 13.1 Hz), 153.7 (dd, J = 256.4, 14.3 Hz), 165.9 ppm. ¹⁹F NMR (470 MHz, DMSO-d6): δ −138.7–138.5 (m), −132.6–132.4 (m) ppm. IR (ATR, KBr): ν 2895 (OH), 1624 (C=O), 1591 (C=O) cm⁻¹. Mp: 201–203 ºC. HRMS (DART, m/z) calcd for C₇H₇F₂IO₃ [M + H]⁺: 300.9168; found: 300.9170.

3.2.19. 1-Hydroxy-5,6-dimethoxy-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (2r)
¹H NMR (500 MHz, DMSO-d6): δ 3.89 (6H, s), 7.24 (1H, s), 7.46 (1H, s), 7.95 ppm. ¹³C NMR (125 MHz, DMSO-d6): δ 55.9, 56.0, 107.4, 110.7, 112.4, 123.9, 150.6, 154.1, 167.8 ppm. IR (ATR, KBr): ν 3016 (OH), 1592 (C=O), 1559 (C=O) cm⁻¹. Mp: 201–203 ºC. ¹H and ¹³C NMR data are consistent with those reported in the literature [46].

3.2.20. 7-Bromo-1-hydroxy-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (2s)
¹H NMR (500 MHz, DMSO-d6): δ 7.60 (1H, t, J = 7.7 Hz), 7.97 (1H, dd, J = 7.7, 1.5 Hz), 8.02 (1H, dd, J = 7.5, 1.2 Hz) ppm. ¹³C NMR (125 MHz, DMSO-d6): δ 119.6, 130.0, 133.1, 135.4, 140.5, 146.1, 167.0 ppm. IR (ATR, KBr): ν 3273 (OH), 1647 (C=O) cm⁻¹. Mp: 154–155 ºC. HRMS (DART, m/z) calcd for C₇H₇BrIO₃ [M + H]⁺: 342.8461; found: 342.8462.

3.2.21. 1-Hydroxy-7-methyl-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (2t)
¹H NMR (400 MHz, DMSO-d6): δ 2.79 (3H, s), 7.57–7.73 (2H, m), 7.90 (1H, d, J = 6.9 Hz) ppm. ¹³C NMR (100 MHz, DMSO-d6): δ 19.6, 128.7, 132.0, 132.6, 137.9, 139.1, 147.4, 167.9 ppm. IR (ATR, KBr): ν 1672 (C=O) cm⁻¹. Mp: 164–166 ºC. ¹H NMR data are consistent with those reported in the literature [106].

3.2.22. 4-Fluoro-1-hydroxy-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (2u)
¹H NMR (400 MHz, DMSO-d6): δ 7.51 (1H, dd, J = 10.1, 8.2 Hz), 7.71 (1H, d, J = 7.7 Hz), 7.90 (1H, td, J = 8.2, 4.6 Hz), 8.24 (1H, s) ppm. ¹³C NMR (100 MHz, DMSO-d6): δ 118.6 (d, J = 22.0 Hz), 119.2 (d, J = 11.5 Hz), 122.5 (d, J = 3.8 Hz), 128.3, 134.3 (d, J = 8.6 Hz), 163.8 (d, J = 4.8 Hz), 163.8 (d, J = 264.4 Hz) ppm. ¹⁹F NMR (375 MHz, DMSO-d6): δ −114.7 (dd, J = 15.2, 4.9 Hz) ppm. IR (ATR, KBr): ν 3091 (OH), 1625 (C=O), 1586 (C=O) cm⁻¹. Mp: 213–214 ºC. ¹H and ¹³C NMR data are consistent with those reported in the literature [106,108].

3.2.23. 1-Hydroxy-4-methyl-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (2v)
¹H NMR (400 MHz, DMSO-d6): δ 2.70 (3H, s), 7.48–7.55 (1H, m), 7.72–7.80 (2H, m), 7.94 (1H, s) ppm. ¹³C NMR (100 MHz, DMSO-d6): δ 20.4, 122.2, 124.2, 128.2, 133.3, 133.4, 144.3, 168.0 ppm. IR (ATR, KBr): ν 2926 (OH), 1625 (C=O), 1584 (C=O) cm⁻¹. Mp: 212–213 ºC. ¹H and ¹³C NMR data are consistent with those reported in the literature [106].

3.2.24. 1-Hydroxy-1λ³-naphtho[2,3-d][1,2]iodaoxol-3(1H)-one (4)
¹H NMR (400 MHz, DMSO-d6): δ 7.76 (2H, m), 8.14–8.33 (2H, m), 8.29 (1H, d, J = 8.2 Hz), 8.39 (1H, s), 8.69 (1H, s) ppm. ¹³C NMR (100 MHz, DMSO-d6): δ 115.9, 126.3, 127.8, 127.9, 128.1, 128.9, 129.3, 131.7, 132.8, 135.8, 167.7 ppm. IR (ATR, KBr): ν 3053 (OH),
1698 (C=O), 1607 (C=O), 1559 (C=O) cm$^{-1}$. Mp: 164–165 °C. $^1$H and $^{13}$C NMR data are consistent with those reported in the literature [107].

3.3. Synthesis of Benziodoxole Alkoxides

3.3.1. General Procedure for the Synthesis of Benziodoxole Alkoxides (6)

To a suspension of IBA 2a (264 mg, 1.0 mmol) in an appropriate alcohol (10 mL) was added MS3Å (1 g). After the mixture was stirred under the appropriate conditions (see Figure 6), MS3Å was filtered using CH$_2$Cl$_2$, and the solvents were then removed by evaporation. The residue was washed with hexane and filtered to remove the corresponding alcohol completely. The residue was dissolved with CH$_2$Cl$_2$, and after the mixture was stirred under the appropriate conditions (see Figure 6), the solvent was removed by evaporation giving the corresponding benziodoxole alkoxides 6a-h as a white powder.

3.3.2. 1-Methoxy-1$^3$-benzo[d][1,2]iodaoxol-3(1H)-one (6a)

$^1$H NMR (500 MHz, CDCl$_3$): δ 4.29 (3H, s), 7.70 (1H, t, $J$ = 7.7 Hz), 7.78 (1H, d, $J$ = 8.1 Hz), 7.91 (1H, ddd, $J$ = 8.6, 6.9, 1.2 Hz), 8.28 (1H, dd, $J$ = 7.5, 1.2 Hz) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 62.3, 118.6, 126.0, 130.6, 131.0, 132.9, 135.1, 168.0 ppm. IR (ATR, KBr): ν 1698 (C=O), 1607 (C=O), 1559 (C=O) cm$^{-1}$. Mp: 161–163 °C. $^1$H and $^{13}$C NMR data are consistent with those reported in the literature [28,109].

3.3.3. 1-Ethoxy-1$^3$-benzo[d][1,2]iodaoxol-3(1H)-one (6b)

$^1$H NMR (500 MHz, CDCl$_3$): δ 1.35 (3H, t, $J$ = 6.9 Hz), 4.30 (2H, q, $J$ = 6.9 Hz), 7.70 (1H, t, $J$ = 7.4 Hz), 7.79 (1H, d, $J$ = 8.9 Hz), 7.89 (1H, td, $J$ = 8.6, 1.8 Hz), 8.28 (1H, dd, $J$ = 7.2, 2.0 Hz) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 19.0, 69.9, 118.8, 125.9, 130.7, 131.0, 132.9, 135.0, 168.0 ppm. IR (ATR, KBr): ν 1655 (C=O) cm$^{-1}$. Mp: 123–125 °C. $^1$H and $^{13}$C NMR data are consistent with those reported in the literature [109].

3.3.4. 1-(2,2,2-trifluoroethoxy)-1$^3$-benzo[d][1,2]iodaoxol-3(1H)-one (6c)

$^1$H NMR (500 MHz, CDCl$_3$): δ 4.52 (2H, q, $J$ = 8.6 Hz), 7.74 (1H, t, $J$ = 7.5 Hz), 7.86 (1H, d, $J$ = 8.0 Hz), 7.97 (1H, ddd, $J$ = 8.0, 6.9, 1.2 Hz), 8.27 (1H, dd, $J$ = 7.5, 1.2 Hz) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 69.7 (q, $J$ = 34.2 Hz), 119.0, 123.5 (q, $J$ = 278.2 Hz), 126.5, 129.5, 131.4, 133.2, 135.9, 167.9 ppm. $^{19}$F NMR (470 MHz, CDCl$_3$): δ −77.2 (q, $J$ = 9.1 Hz) ppm. IR (ATR, KBr): ν 1646 (C=O) cm$^{-1}$. Mp: 139–141 °C. HRMS (DART, m/z) calcd for C$_9$H$_3$F$_3$O$_3$ [M + H]$^+$: 346.9386; found: 346.9383.

3.3.5. 1-Propoxy-1$^3$-benzo[d][1,2]iodaoxol-3(1H)-one (6d)

$^1$H NMR (500 MHz, CDCl$_3$): δ 1.02 (3H, t, $J$ = 7.5 Hz), 1.72 (2H, sext, $J$ = 7.1 Hz), 4.20 (2H, t, $J$ = 6.6 Hz), 7.70 (1H, t, $J$ = 7.2 Hz), 7.79 (1H, d, $J$ = 8.6 Hz), 7.89 (1H, t, $J$ = 7.2 Hz), 8.28 (1H, d, $J$ = 7.5 Hz) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 10.1, 26.5, 76.0, 118.9, 125.9, 130.7, 130.9, 132.8, 135.0, 167.9 ppm. IR (ATR, KBr): ν 1651 (C=O) cm$^{-1}$. Mp: 146–148 °C. HRMS (DART, m/z) calcd for C$_{10}$H$_3$IO$_3$ [M + H]$^+$: 306.9826; found: 306.9823.

3.3.6. 1-Isoproxy-1$^3$-benzo[d][1,2]iodaoxol-3(1H)-one (6e)

$^1$H NMR (500 MHz, CDCl$_3$): δ 1.36 (6H, d, $J$ = 6.3 Hz), 4.33 (1H, sep, $J$ = 6.1 Hz), 7.69 (1H, t, $J$ = 7.4 Hz), 7.82 (1H, d, $J$ = 7.5 Hz), 7.88 (1H, td, $J$ = 7.8, 1.5 Hz), 8.28 (1H, dd, $J$ = 7.5, 1.7 Hz) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 25.2, 75.6, 119.1, 126.0, 130.8, 130.9, 132.7, 134.8, 168.0 ppm. IR (ATR, KBr): ν 1653 (C=O) cm$^{-1}$. Mp: 253–254 °C. $^1$H and $^{13}$C NMR data are consistent with those reported in the literature [109].

3.3.7. 1-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-1$^3$-benzo[d][1,2]iodaoxol-3(1H)-one (6f)

$^1$H NMR (500 MHz, CDCl$_3$): δ 4.80 (1H, sep, $J$ = 5.8 Hz), 7.74 (1H, ddd, $J$ = 8.0, 7.5, 1.4 Hz), 7.97–8.04 (2H, m), 8.24 (1H, dd, $J$ = 7.4, 1.2 Hz) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 76.1 (quin, $J$ = 32.5 Hz), 119.4, 122.2 (q, $J$ = 283.8 Hz), 127.3, 128.5, 131.6, 133.3, 136.4,
168.1 ppm. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ –76.0 (d, $J = 5.7$ Hz) ppm. IR (ATR, KBr): $\nu$ 1661 (C=O) cm$^{-1}$. Mp: 148–149 °C. HRMS (DART, m/z) calcd for C$_{10}$H$_8$F$_3$IO$_3$ [M + H]$^+$: 414.9260; found: 414.9258.

3.3.8. 1-Butoxy-1$^3$-benzo[d][1,2]iodoxol-3(1H)-one (6g)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.98 (3H, t, $J = 7.5$ Hz), 1.46 (2H, sext, $J = 7.4$ Hz), 1.68 (2H, quin, $J = 7.2$ Hz), 4.24 (2H, t, $J = 6.6$ Hz), 7.70 (1H, t, $J = 7.5$ Hz), 7.78 (1H, d, $J = 8.0$ Hz), 7.89 (1H, t, $J = 7.5$ Hz), 8.28 (1H, d, $J = 7.5$ Hz) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 13.9, 19.0, 35.4, 74.2, 118.9, 125.9, 130.7, 131.0, 132.9, 135.0, 167.9 ppm. IR (ATR, KBr): $\nu$ 1661 (C=O) cm$^{-1}$. Mp: 143–144 °C. $^1$H and $^{13}$C NMR data are consistent with those reported in the literature [110].

3.3.9. 1-(tert-Butoxy)-1$^3$-benzo[d][1,2]iodoxol-3(1H)-one (6h)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.41 (9H, s), 7.67 (1H, ddd, $J =$ 8.1, 7.5, 1.8 Hz), 7.83–7.91 (2H, m), 8.26 (1H, dd, $J =$ 8.1, 1.8 Hz) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 30.4, 78.6, 119.6, 126.2, 130.8, 131.0, 132.4, 134.7, 168.0 ppm. IR (ATR, KBr): $\nu$ 1659 (C=O) cm$^{-1}$. Decomp: 265 °C. HRMS (DART, m/z) calcd for C$_{11}$H$_{13}$IO$_3$ [M + H]$^+$: 320.9982; found: 320.9980.

3.4. Synthesis of Benziodoxole Acetates

3.4.1. General Procedure for the Synthesis of Benziodoxole Acetates (7)

MS3Å (0.5 g) was added to a suspension of IBAs 2a–i (0.50 mmol) in AcOH (5 mL), and the mixture was stirred under the appropriate conditions (see Scheme 4). Then, MS3Å was filtered using CH$_2$Cl$_2$, and the solvents were removed by evaporation. The residue was washed with ether and filtered to remove AcOH completely. The resulting acetates were obtained as a white powder.

3.4.2. 3-Oxo-1$^3$-benzo[d][1,2]iodoxol-1(3H)-yl acetate (7a)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.27 (3H, s), 7.72 (1H, td, $J =$ 7.5, 1.2 Hz), 7.94 (1H, ddd, $J =$ 8.6, 6.9, 1.2 Hz), 8.01 (1H, d, $J =$ 8.6 Hz), 8.25 (1H, d, $J =$ 7.5, 1.2 Hz) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 20.2, 118.3, 128.9, 129.2, 131.2, 133.1, 136.1, 168.1, 176.3 ppm. IR (ATR, KBr): $\nu$ 1684 (C=O) cm$^{-1}$. Mp: 220–222 °C. $^1$H and $^{13}$C NMR data are consistent with those reported in the literature [109].

3.4.3. 5-Fluoro-3-oxo-1$^3$-benzo[d][1,2]iodoxol-1(3H)-yl acetate (7b)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.26 (3H, s), 7.64 (1H, ddd, $J =$ 8.6, 7.7, 2.9 Hz), 7.94–8.00 (2H, m) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 20.2, 111.3, 120.0 (d, $J =$ 23.8 Hz), 123.7 (d, $J =$ 22.7 Hz), 131.0 (d, $J =$ 8.3 Hz), 131.8 (d, $J =$ 7.2 Hz), 165.0 (d, $J =$ 252.8 Hz), 166.8, 176.4 ppm. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ –110.8 (td, $J =$ 7.2, 4.3 Hz) ppm. IR (ATR, KBr): $\nu$ 1696 (C=O) cm$^{-1}$. Mp: 225–226 °C. $^1$H and $^{13}$C NMR data are consistent with those reported in the literature [111].

3.4.4. 5-Chloro-3-oxo-1$^3$-benzo[d][1,2]iodoxol-1(3H)-yl acetate (7c)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.27 (3H, s), 7.87 (1H, ddd, $J =$ 8.6, 2.3 Hz), 7.93 (1H, d, $J =$ 9.2 Hz), 8.22 (1H, d, $J =$ 1.7 Hz) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 20.2, 115.5, 130.4, 130.9, 133.0, 136.0, 138.8, 166.7, 176.4 ppm. IR (ATR, KBr): $\nu$ 1698 (C=O) cm$^{-1}$. Mp: 244–245 °C. $^1$H and $^{13}$C NMR data are consistent with those reported in the literature [105].

3.4.5. 5-Bromo-3-oxo-1$^3$-benzo[d][1,2]iodoxol-1(3H)-yl acetate (7d)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.27 (3H, s), 7.85 (1H, d, $J =$ 9.2 Hz), 8.01 (1H, ddd, $J =$ 8.6, 2.3 Hz), 8.37 (1H, d, $J =$ 1.8 Hz) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 20.2, 116.5, 126.6, 130.7,
131.0, 136.1, 138.9, 166.6, 176.4 ppm. IR (ATR, KBr): ν 1680 (C=O) cm⁻¹. Mp: 226–228 °C.

3.4.6. 5-Methyl-3-oxo-1λ³-benzo[d][1,2]iodaoxol-1(3H)-yl acetate (7e)

1H NMR (500 MHz, CDCl₃): δ 2.25 (3H, s), 2.56 (3H, s), 7.73 (1H, dd, J = 8.6, 1.7 Hz), 7.84 (1H, d, J = 8.6 Hz), 8.07 (1H, d, J = 1.8 Hz) ppm. 13C NMR (125 MHz, CDCl₃): δ 20.3, 20.8, 114.6, 128.9, 133.6, 137.1, 142.3, 168.3, 176.4 ppm. IR (ATR, KBr): ν 1692 (C=O), 1647 (C=O) cm⁻¹.

3.4.7. 5-Methoxy-3-oxo-1λ³-benzo[d][1,2]iodaoxol-1(3H)-yl acetate (7f)

1H NMR (500 MHz, CDCl₃): δ 2.25 (3H, s), 3.94 (3H, s), 7.46 (1H, dd, J = 9.2, 2.9 Hz), 7.74 (1H, d, J = 2.9 Hz), 7.81 (1H, d, J = 8.6 Hz) ppm. 13C NMR (125 MHz, CDCl₃): δ 20.3, 56.2, 106.8, 115.9, 124.5, 129.7, 130.6, 162.7, 168.1, 176.4 ppm. IR (ATR, KBr): ν 1681 (C=O), 1656 (C=O) cm⁻¹. Mp: 207–209 °C.

3.4.8. 3-Oxo-1λ³-benzo[d][1,2]iodaoxole-1,5(3H)-diyl diacetate (7g)

1H NMR (500 MHz, CDCl₃): δ 2.26 (3H, s), 2.37 (3H, s), 7.68 (1H, dd, J = 8.9, 2.6 Hz), 7.96–8.02 (2H, m) ppm. 13C NMR (125 MHz, CDCl₃): δ 20.3, 21.1, 113.6, 126.2, 129.8, 130.3, 130.9, 153.6, 167.2, 168.7, 176.5 ppm. IR (ATR, KBr): ν 1690 (C=O) cm⁻¹. Mp: 153–154 °C.

3.4.9. 3-Oxo-5-(trifluoromethyl)-1λ³-benzo[d][1,2]iodaoxol-1(3H)-yl acetate (7h)

1H NMR (500 MHz, CDCl₃): δ 2.29 (3H, s), 8.14 (1H, dd, J = 8.6, 1.7 Hz), 8.20 (1H, d, J = 8.6 Hz), 8.52 (1H, d, J = 1.7 Hz) ppm. 13C NMR (125 MHz, CDCl₃): δ 20.2, 121.9, 122.8 (q, J = 271.4 Hz), 130.1 (d, J = 3.6 Hz), 130.4 (d, J = 9.5 Hz), 132.4 (d, J = 2.4 Hz), 134.5 (q, J = 33.8 Hz), 166.7, 176.5 ppm. 19F NMR (470 MHz, CDCl₃): δ −64.9 ppm. IR (ATR, KBr): ν 1692 (C=O), 1647 (C=O) cm⁻¹. Mp: 212–213 °C.

3.4.10. 5-Nitro-3-oxo-1λ³-benzo[d][1,2]iodaoxol-1(3H)-yl acetate (7i)

1H NMR (500 MHz, CDCl₃): δ 2.30 (3H, s), 8.27 (1H, d, J = 9.2 Hz), 8.71 (1H, dd, J = 9.0, 2.5 Hz), 9.04 (1H, d, J = 2.3 Hz) ppm. 13C NMR (125 MHz, CDCl₃): δ 20.2, 124.1, 127.6, 129.8, 131.0, 131.5, 150.8, 165.7, 176.6 ppm. IR (ATR, KBr): ν 1705 (C=O), 1665 (C=O) cm⁻¹. Mp: 209–210 °C.

4. Conclusions

We have presented a practical synthetic method for IBA from 2-IB without contamination by hazardous pentavalent IBX using cost-effective Oxone® in aqueous solution. This highly safe, convenient method operates under mild conditions such as room temperature, which contrasts with traditional method using reflux conditions and expensive NaIO₄ in AcOH solution. The use of mild conditions circumvents the problem of the formation of byproducts such as potentially explosive pentavalent cyclic hypervalent iodine compound, i.e., IBX; the contamination of IBX into IBA is generally not desired for safety reasons. The reaction time can be shortened by heating; in this case, addition of a ferric salt in our reaction system can effectively suppress the formation of IBX as byproducts. In addition, a convenient derivatization of the hydroxy group of IBAs by solvolytic treatment is presented. These derivatizations were generally achieved under mild conditions below 80 °C. Our methods, which do not require any chromatography technique, can be performed safely and would be suitable for large-scale synthesis.

Supplementary Materials: Supplementary materials are available online, 1H NMR spectroscopic data for the compounds 2a–v and 4.
Author Contributions: H.C. found the selective reaction to obtain IBAs using Oxone® and the solvolytic functionalization for IBA and drafted the manuscript; N.K., H.Y., and N.T. also contributed to the experiments; T.D. directed this study as a project and finalized the manuscript with critical discussion. All authors have read and agreed to the published version of the manuscript.

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Sample Availability: Samples of the compounds are not available from the authors.

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