Supporting Information***In Situ* Generation of *o*-Iodoxybenzoic Acid (IBX) and the Catalytic Use of it in
Oxidation Reactions in Presence of Oxone® as a Co-Oxidant**

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General.

All oxidation reactions were carried out on 1.5 mmol scale in 2:1 v/v mixture of acetonitrile and water at 70⁰C for 6 h. The ratios of the catalytic oxidant and the co-oxidant used in the two optimization studies, results of which are reported in Table 1 and 2, are different and are noted in the respective Tables. The ratios of 2-iodobenzoic acid (2IBAcid) and Oxone used in the oxidation of different substrates varied with the nature of the substrate and the ratios used are reported in Table 3. Thin layer chromatography of the reaction mixtures were performed on commercially prepared silica gel 60 F₂₅₄ plates. Flash chromatography, for the purification of oxidized products, was carried out using silica gel 60-200 purchased from Fisher Scientific. IR spectra were recorded in the range of 4000-600 cm⁻¹ using a Shimadzu FTIR-8400 spectrometer with internal calibration. Mass spectra were recorded using a Shimadzu-QP5050 GC-MS instrument. GC column in this instrument is a DB-5 coated capillary column 30 m long and with 0.25 mm i.d. The following GC program was used for all the experiments: Oven temperature 80°C (2 min), 80 to 250°C at 20°C /min, injector temperature 250°C, GC-MS interface temperature 250°C. The mass spectrometer was set to operate in the positive ion mode

S2

with electron impact as the ionization method. The mass range was scanned from 80-600 daltons (Da) with a 3.00-min solvent delay. ^1H spectra were recorded on JEOL 300 Eclipse spectrometer operating at 300 MHz for protons.

General Procedure for Oxidation of Alcohols.

To a solution of the alcohol substrate (1.5 mmol) in acetonitrile:water (20 mL, 2:1 v/v) was added the required amount of the catalytic oxidant (IBX, IBA or 2IBAcid) and the required amount of Oxone. The mixture was then maintained at 70⁰C for 6h and subsequently cooled in an ice bath to completely precipitate the insoluble hypervalent iodine by-product which was then removed by filtration. The precipitate was successively washed with water (2 x 10 mL) and dichloromethane (2x 10mL) and the combined filtrate was subsequently extracted with dichloromethane (40 mL). The organic extract was then treated as follows depending on whether a primary or secondary alcohol was being oxidized. The organic extract obtained from the work-up of a primary alcohol oxidation reaction was dried (MgSO_4) and evaporated to yield the carboxylic acid product, sometimes contaminated with ~2-5% of 2-iodobenzoic acid derivatives, requiring column chromatographic purification. The organic extract obtained from the oxidation of secondary alcohols was subsequently washed with aq. sodium bicarbonate (15 % solution, 30 mL) to remove the acidic impurities and dried (MgSO_4) and evaporated to yield ketones in essentially pure form.

Spectral Data :

Spectral properties of oxidized products reported in Table 3 match those reported in the Aldrich library NMR and IR spectra. Spectral data for 5-hexenoic acid (entry 4), 4-

benzyloxybutyric acid (entry 6) and 3-phthalimidopropionic acid (entry 7) are not available in the Aldrich libraries and are thus reported here. Copies of the ^1H NMR spectra of these compounds are also attached with the supplementary material.

5-Hexenoic acid (entry 4, Table 3): Isolated in 80% yield as a thick oil. IR (CHCl_3 , NaCl , cm^{-1}) 3380, 3018, 1705, 1280; LRMS (70 eV, EI) m/z 114 $[\text{M}^+]$, 96 $[\text{M}^+-\text{H}_2\text{O}]$, 73 $[\text{M}^+-\text{C}_3\text{H}_5]$, 60; ^1H NMR (CDCl_3 , 300 MHz), δ 5.77 (m, 1H), 5.02 (m, 2H), 2.39 (t, $J=7.6$ Hz, 2H), 2.12 (m, 2H), 1.75 (t, $J=7.6$ Hz, 2H).

4-Benzyloxybutyric acid (entry 6, Table 3): Isolated in 87% yield as a thick oil. IR (CHCl_3 , NaCl , cm^{-1}) 3450, 3031, 2933, 2864, 2798, 1705, 1452, 1413, 1105; LRMS (70 eV, EI) m/z 194 $[\text{M}^+]$, 176 $[\text{M}^+-\text{H}_2\text{O}]$, 107 $[\text{M}^+-\text{C}_3\text{H}_6-\text{CO}_2\text{H}]$, 91 $[\text{C}_6\text{H}_5\text{CH}_2^+]$; ^1H NMR (CDCl_3 , 300 MHz), δ 7.33 (m, 5H), 4.51 (s, 2H), 3.53 (t, $J=6.3$ Hz, 2H), 2.40 (t, $J=6.3$ Hz, 2H), 1.97 (q, $J=6.3$ Hz, 2H).

3-Phthalimidopropionic acid (entry 7, Table 3): Isolated in 92% yield, mp 144-146 $^\circ\text{C}$. LRMS (70 eV, EI) m/z 219 $[\text{M}^+]$, 201 $[\text{M}^+-\text{H}_2\text{O}]$, 173 $[\text{M}^+-\text{H}-\text{CO}_2\text{H}]$, 160 $[\text{M}^+-\text{CH}_2-\text{CO}_2\text{H}]$; ^1H NMR (CDCl_3 , 300 MHz), δ 7.84 (AA'BB, m, 2H), 7.72 (AA'BB, m, 2H), 4.02 (t, $J=9.0$ Hz, 2H), 2.08 (t, $J=9.0$ Hz, 2H).

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(Millions)

S4

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5.7389

0.414

5.0

5.0696
5.0229
5.0192
5.0128

0.864

4.0

3.0

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2.0

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7.7103

7.2571

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3.9919

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X : parts per Million : 1H