Catalytic Hypervalent Iodine Oxidation Using 4-Iodophenoxyacetic Acid and Oxone®: Oxidation of *p*-Alkoxyphenols to *p*-Benzoquinones

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A catalytic hypervalent iodine oxidation of *p*-alkoxyphenols using 4-iodophenoxyacetic acid (1a) and Oxone® was developed. Reaction of *p*-alkoxyphenol (2) with a catalytic amount of 1a in the presence of Oxone® as a co-oxidant in 2,2,2-trifluoroethanol–water (1 : 2) gave the corresponding *p*-quinone (3) in excellent yield without special operation. The substituent effect on iodobenzene ring in the oxidation was observed; *p*-alkoxy is the most effective, with the series following the approximate order *p*-RO>*p*-Me, *o*-MeO, *m*-MeO>H>*o*-CO_2H. And remarkable solvent effects were observed.

Key words hypervalent iodine; 4-iodophenoxyacetic acid; Oxone®; *p*-alkoxyphenol; *p*-benzoquinone

Hypervalent iodine compounds, trivalent iodine compounds such as phenyliodine(III) diacetate (PIDA) and phenyliodine(III) trifluoroacetate (PIFA) and pentavalent iodine reagents such as Dess–Martin periodinane (DMP) and *o*-iodoxybenzoic acid (IBX), have been used extensively in recent organic synthesis because of their low toxicity, ready availability and easy handling.[1—15] However, these reagents are highly expensive. And stoichiometric amounts of iodine reagents are required to produce equimolar amounts of organic iodine waste. Moreover, pentavalent iodine reagents are potentially explosive. To overcome these disadvantages, catalytic hypervalent iodine oxidations[16—18] using *m*-chloroperbenzoic acid (*m*-CPBA),[19—27] Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$),[28,29] and H_2O_2[30] as a co-oxidant have been reported recently.

Development of efficient methods for synthesis of *p*-quinone and *p*-quinone derivatives is an important subject in synthetic organic chemistry because they are structural components of numerous natural products and useful synthetic intermediates.[31—36] A convenient procedure for *p*-quinones was hypervalent iodine oxidation of *p*-alkoxyphenols using PIFA.[37] Reactions of *p*-alkoxyphenols with an equimolar amount of PIFA in a 2 : 1 mixture of acetonitrile and water at room temperature gave the corresponding *p*-quinones in excellent yield.

As part of our study for development of practical and environmentally benign oxidation, we report a mild, efficient and practical procedure for catalytic hypervalent iodine oxidation of *p*-alkoxyphenols to *p*-quinones using a catalytic amount of 4-iodophenoxyacetic acid (**1a**) and Oxone® as a co-oxidant[38] in 2,2,2-trifluoroethanol–water.

Results and Discussion

We chose Oxone® as an environmentally safe co-oxidant for a catalytic hypervalent iodine oxidation of *p*-alkoxyphenols because Oxone® is an inorganic and water-soluble oxidant with a low order of toxicity, moreover, it is commercially available and inexpensive.[39] Oxone® has been already used as a co-oxidant under heating conditions in the catalytic IBX oxidation by Vinod[28] and Giannis[29] groups, independently. Because alkoxyphenols have high reactivity under oxidation conditions, we first investigated the oxidative ability of Oxone® itself.[40] A mixture of 2-pivaloyloxymethyl-4-methoxyphenol (**2a**) and an equimolar amount of Oxone® in acetonitrile–water (2 : 1) at room temperature gave the corresponding *p*-benzoquinone (**3a**), but the reaction was sluggish and the yield of **3a** was only 13% along with 78% of recovered starting **2a** after 24 h. Next, we examined reactions of **2a** in the presence of several iodoarenes as a catalyst (Chart 1). Table 1 presents the results. According to the procedure reported by Vinod,[28] a mixture of **2a**, 0.2 equivalents (eq) of 2-iodobenzoic acid, and 1 eq of Oxone® in acetonitrile–water was heated at 70 °C for 19 h to give a complicated mixture (entry 2). However, a similar reaction at room temperature suggested catalytic activity of iodoarene to give **3a** in 39% yield (entry 3). Iodobenzene gave better result (entry 4). Methyl and methoxy groups on the benzene ring showed

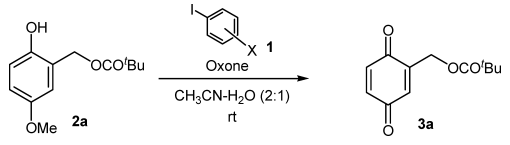

Chart 1

Table 1. Oxidation of **2a** with **1** and Oxone®[a]

Entry	1		Time (h)	Yield of **3a** (%)
	X	(eq)		
1	none		24	13 (78)[b]
2[c]	*o*-CO_2H	0.2	19	6 (4)[b]
3	*o*-CO_2H	0.2	24	39 (6)[b]
4	H	0.2	24	64 (24)[b]
5	*p*-Me	0.2	24	77 (14)[b]
6	*o*-OMe	0.2	24	71 (14)[b]
7	*m*-OMe	0.2	24	77 (4)[b]
8	*p*-OMe	0.2	17	90
9	*p*-$OCOCH_3$	0.2	24	54 (40)[b]
10	*p*-OMOM	0.2	22	92
11	*p*-OCH_2CO_2Me	0.2	21	94
12	*p*-$O(CH_2)_3CO_2Me$	0.2	40	86
13	*p*-OMe	0.1	24	73 (18)[b]
14	*p*-OMe	0.5	9	92
15	*p*-OMe	1.0	5	94
16	*p*-OCH_2CO_2H	0.2	19	99

a) Reactions were carried out in the presence of 1 eq of Oxone® in CH_3CN–H_2O (2 : 1) at room temperature. *b*) Parentheses are recovery of **2a**. *c*) Reaction was carried out at 70 °C.

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Table 2. Oxidation of **2a** with **1a** and Oxone®[a)]

Entry	**1a** (eq)	Oxone (eq)	Solvent	Time (h)
1	0.2	1	CH_3CN–H_2O (2 : 1)	19
2	0.2	0.7	CH_3CN–H_2O (2 : 1)	48
3	0.2	0.5	CH_3CN–H_2O (2 : 1)	8 d[b)]
4	0.2	2	CH_3CN–H_2O (2 : 1)	10
5	0.2	4	CH_3CN–H_2O (2 : 1)	6
6	0.2	4	CH_3CN–H_2O (1 : 2)	1
7	0.2	4	Acetone–H_2O (1 : 2)	4
8	0.2	4	THF–H_2O (1 : 2)	4
9	0.2	4	1,4-Dioxane–H_2O (1 : 2)	1
10	0.2	4	TFE–H_2O (1 : 2)	0.33
11	0.2	4	TFE–H_2O (1 : 5)	2
12	0.05	4	TFE–H_2O (1 : 2)	0.75
13	0.05	1	TFE–H_2O (1 : 2)	28[b)]
14	0.01	4	TFE–H_2O (1 : 2)	13

a) Reactions were carried out at room temperature. *b*) Reaction was not finished.

enhanced reactivity of iodoarene (entries 5—8). Especially, when 0.2 eq of 4-iodoanisole was used as a catalyst, the reaction was completed within 17 h to give **2a** in 90% yield (entry 8). Acetoxy group, however, decreased reactivity of iodoarene (entry 9). Other iodobenzenes having *p*-alkoxy group such as *p*-OMOM, *p*-OCH_2CO_2Me, and *p*-$O(CH_2)_3CO_2Me$ are also effective to catalyze the oxidation of **2a** to **3a** (entries 10—12). These results show that the electron-donating alkoxy group at the *para* position on the benzene ring would increase the catalytic efficiency of iodoarene, in contrast to the reported results using *m*-CPBA[19,20)] and H_2O_2[30)] as a co-oxidant. Slower reaction was observed using 0.1 eq of 4-iodoanisole (entry 13). However, larger amounts (0.5—1 eq) led to decreased reaction times with similar yields of **3a** (entries 14, 15).

Although *p*-alkoxyiodobenzenes gave satisfactory results, the reactions unfortunately required careful purification by column chromatography to separate the product quinone and the recovered catalyst. Therefore, we selected 4-iodophenoxyacetic acid (**1a**), which is prepared easily from 4-iodophenol[41)] and which is commercially available, in the hope of finding more practical catalyst because **1a** has an electron-donating group at the *para* position and is soluble in alkaline solution. A similar reaction of **2a** with 0.2 eq of **1a** in the presence of 1 eq of Oxone® proceeded smoothly to afford pure **3a** in 99% yield and 75% of recovered **1a** without column chromatography (entry 16).

We next investigated influences of the amounts of Oxone®, **1a**, and solvent systems (Table 2). In all cases, except for entries 3 and 13, starting **2a** was completely consumed and quinone **3a** was given in quantitative yield. The reactions were monitored by thin-layer chromatography. The reaction was completed within longer 48 h when 0.2 eq of **1a** and 0.7 eq of Oxone® was used in the reaction of **2a** (entry 2). A similar reaction using 0.5 eq of Oxone® was not finished after several days (entry 3). On the other hand, use of 2 or 4 eq of Oxone® decreased the reaction times to 10 and 6 h, respectively (entries 4, 5). Remarkable solvent effects[42)] were observed in this catalytic hypervalent iodine oxidation system (entries 6—10). The reaction was accelerated by addition of water. The reaction of **2a** with 0.2 eq of **1a** and 4 eq of Oxone® in CH_3CN–H_2O (1 : 2) was completed within 1 h (entry 6). Although acetone, tetrahydrofuran (THF), and 1,4-dioxane gave almost similar results (entries 7—9), 2,2,2-trifluoroethanol (TFE) was found to be the best co-solvent (entries 10—14).[22,30,42)] In TFE–H_2O (1 : 2) the completion of a similar reaction of **2a** required only 20 min (entry 10), although 1 : 5 mixture of TFE and H_2O lengthened the reaction time longer (entry 11). Using 0.05 eq of **1a** with 4 eq of Oxone® gave a satisfactory result (entry 12), although a similar reaction with 1 eq of Oxone® was not completed after 28 h (entry 13). With only 0.01 eq of **1a** and 4 eq of Oxone®, the reaction was finished after 13 h to give **3a** in quantitative yield in TFE–H_2O (1 : 2) (entry 14).

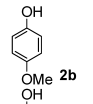
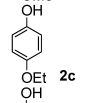
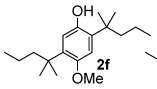
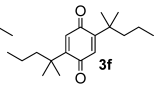
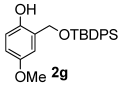
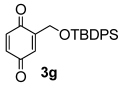
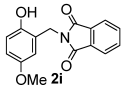
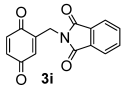
Variety of *p*-alkoxyphenols (**2b**—**i**) were oxidized with 0.05 eq of **1a** and 4 eq of Oxone® in TFE–H_2O (1 : 2) to the corresponding *p*-quinones. Results are presented in Table 3 with our preliminary results reported in ref. 38. In all cases TFE–H_2O was suprerior to CH_3CN–H_2O as a solvent system. Reactions of simple *p*-methoxy, *p*-ethoxy, and *p*-butoxyphenols (**2b**—**d**) respectively gave *p*-benzoquinone (**3b**) in high yield (entries 1—3). This oxidation system was also effective for phenols bearing a bulky substituent at the *ortho* position (entries 4, 5). *tert*-Butyldiphenylsilyloxy (TBDPSO) and azide groups were tolerable under the reaction conditions (entries 6, 7). Oxidation of phenol having succinimide group (**2i**) proceeded with high yield (entry 8). In all cases, **1a** was recovered in good yield (75—85%) and it can be used for the oxidation again after recrystallization.

Based on the remarkable acceleration of the oxidation of phenols by addition of only a small amount of iodoarene and documented examples of the reactions of iodoarene and Oxone®, which produce pentavalent iodine species,[43—48)] it was suggested that iodine(V) species, generated *in situ*, was included in this oxidation as the active catalyst. However, formation of pentavalent iodine species requires a higher temperature (70 °C) than that in the oxidation of **2** with **1a** and Oxone®. Therefore, it would be possible that trivalent iodine species is formed and acts as an oxidant. Both pentavalent and trivalent iodines react with phenols, but oxidized products were different in some cases.[49—52)] For example, reaction of *p*-methoxyphenol with IBX provided 4-methoxy-1,2-benzoquinone,[53)] in contrast to the reaction with PIFA giving *p*-quinone.[37)] Although it remains unclear whether iodine(V) or iodine(III) species was formed during the reaction,[54)] a possible catalytic cycle for this oxidation is shown in Chart 2. Oxone® oxidizes **1a** to a hypervalent species; chemical behaviors suggest that trivalent species would be more likely than pentavalent one. It oxidizes *p*-alkoxyphenol to give the *p*-quinone and **1a**. Iodoarene (**1a**) would be re-oxidized by Oxone® to a hypervalent species. Iodoarenes with electron-donating substituents such as alkoxy and methyl groups may be more easily oxidized by Oxone® to cause rapid reactions, whereas an electron-withdrawing substituent such as carboxyl group may decrease the reactivity of iodoarene against the oxidant.

Conclusion

A novel and practical catalytic method was developed for hypervalent iodine oxidation of phenol derivatives using **1a**. Reaction of *p*-alkoxyphenol (**2**) with a catalytic amount of **1a** in the presence of Oxone® as a co-oxidant in TFE–water (1 : 2) gave the corresponding *p*-quinones (**3**) in excellent yield without special operation. The substituent effect on

Table 3. Catalytic Hypervalent Iodine Oxidation of **2** with **1a** and Oxone®[a)]

Entry	Phenol	Quinone	in TFE–H_2O (1 : 2)		in CH_3CN–H_2O (2 : 1)[b,c)]	
			Time (h)	Yield (%)	Time (h)	Yield (%)
1	 **2b**	**3b**	0.5	78	16	80
2	 **2c**	**3b**	0.5	97	17	79
3	 **2d**	**3b**	0.5	88	17	77
4	 **2e**	 **3e**	1	Quant	24	53
5	 **2f**	 **3f**	3	Quant	23	80
6	 **2g**	 **3g**	3	Quant	24	96
7	 **2h**	 **3h**	0.5	95	22	92
8	 **2i**	 **3i**	2	98	40	89[d)]

a) Reactions were carried out using 0.05 eq of **1a** and 4 eq of Oxone® at room temperature. *b*) Our preliminary results in ref. 38. *c*) 0.2 eq of **1a** and 1 eq of Oxone® were used. *d*) 0.4 eq of **1a** was used.

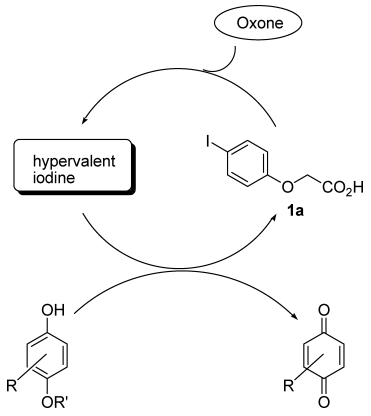


Chart 2

iodobenzene ring in the oxidation was observed; *p*-alkoxy is the most effective, with the series following the approximate order *p*-RO>*p*-Me, *o*-MeO, *m*-MeO>H>*o*-CO_2H. And remarkable solvent effects were observed. This oxidation system has the following features. The first is that reaction proceeds under mild conditions. The second is that Oxone® is an inorganic, water-soluble, commercially available, and inexpensive with low toxicity. The third is that solubility of **1a** in alkaline solution facilitates its recovery.

Experimental

Melting points are uncorrected. IR spectra were recorded using JASCO FT/IR-460 Plus spectrophotometer. ^{1}H-NMR spectra were determined with Varian Gemini 300 (300 MHz) and JEOL JNM-FX270 (270 MHz) spectrometers, tetramethylsilane as an internal standard. ^{13}C-NMR spectra were determined with Varian Gemini 300 (75 MHz) and JEOL JNM-FX270 (67.5 MHz) spectrometers. All ^{13}C-NMR spectra were determined with complete proton decoupling. High resolution MS were determined with JEOL JMS-GCmate and JEOL JMS-AX505HAD instruments. 4-Iodophenoxyacetic acid (**1a**) was purchased from Tokyo Chemical Industry (TCI) Co., Ltd. and used after recrystallization from diethyl ether–hexane, and Oxone® was available from Wako Pure Chemical Industries, Ltd. and used as received. Phenols (**2b**—**g**) were commercially available. Other phenols (**2a**, **2g**, **2h**, **2i**) were prepared from 2-hydroxymethyl-4-methoxyphenol by the usual methods.

2-Hydroxy-5-methoxybenzyl 2,2-Dimethylpropanoate (**2a**): Colorless crystals, mp 66.5—67 °C (ethyl acetate–hexane). IR (KBr) cm^{-1}: 3363, 1686, 1510, 1469, 1432. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.19 (9H, s), 3.77 (3H, s), 5.07 (2H, s), 6.78—6.96 (3H, m), 7.50 (1H, s). ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 27.1 (3), 38.9, 55.8, 63.4, 116.5 (2), 118.6, 122.5, 149.3, 153.3, 180.9. *Anal.* Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.46; H, 7.33. HR-MS *m*/*z*: 238.11718 (Calcd for $C_{13}H_{18}O_4$ (M^+): 238.12051).

2-(*tert*-Butyldiphenylsilyloxymethyl)-4-methoxyphenol (**2g**): A colorless oil. IR (neat) cm^{-1}: 3399, 1499, 1465, 1428. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.07 (9H, s), 3.68 (3H, s), 4.84 (2H, s), 6.34 (1H, d, J=2.7 Hz), 6.75 (1H, dd, J=8.6, 2.9 Hz), 6.85 (1H, d, J=8.6 Hz), 7.35—7.50 (6H, m), 7.61 (1H, s), 7.65—7.72 (4H, m). ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 19.1, 26.7 (3), 55.7, 66.5, 112.4, 114.1, 117.2, 124.6, 127.9 (4), 130.1 (2), 132.0 (2), 135.5 (4), 150.2, 152.8. HR-MS *m*/*z*: 392.17912 (Ccalcd for $C_{24}H_{28}O_3Si$ (M^+): 392.18078).

2-Azidomethyl-4-methoxyphenol (**2h**): A colorless oil. IR (neat) cm^{-1}: 3331, 1514, 1446, 1435. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 3.77 (3H, s), 4.39 (2H, s), 5.11 (1H, br s), 6.75—6.80 (3H, m). ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 51.0, 55.8, 114.9, 115.4, 116.9, 122.6, 148.0, 153.7. HR-MS *m*/*z*: 179.06662 (Calcd for $C_8H_9N_3O_2$ (M^+): 179.06948).

2-(2-Hydroxy-5-methoxybenzyl)isoindole-1,3-dione (**2i**): Pale yellow crystals, mp 161—162 °C (ethyl acetate–ether). IR (KBr) cm^{-1}: 3328, 1765, 1697, 1617, 1501, 1434, 1400. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.75 (3H, s),

4.80 (2H, s), 6.79 (1H, dd, J=8.8, 3.0 Hz), 6.91 (1H, d, J=8.8 Hz), 6.94 (1H, t, J=3.0 Hz), 7.51 (1H, s), 7.70—7.75 (2H, m), 7.82—7.88 (2H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 37.2, 55.8, 115.9, 116.1, 119.2, 122.9, 123.6 (2), 131.6, 134.3 (3), 148.6, 153.4, 168.8 (2). *Anal.* Calcd for $C_{16}H_{13}NO_4$: C, 67.84; N, 4.94; H, 4.63. Found: C, 67.53; N, 5.25; H, 4.66. HR-MS *m/z*: 283.08138 (Calcd for $C_{16}H_{13}NO_4$ (M^+): 283.08446).

Catalytic Hypervalent Iodine Oxidation of 2a, General Procedure A suspension of **2a** (1.0 g, 4.2 mmol), **1a** (58 mg, 0.2 mmol) and Oxone® (1.03 g, 16.8 mmol) in TFE–H_2O (1 : 2, 42 ml) was stirred at room temperature for 45 min. The mixture was diluted with ethyl acetate and washed with water. The organic layer was then washed with aqueous saturated sodium bicarbonate solution and dried, concentrated to give pure 3,6-dioxocyclohexa-1,4-dienylmethyl 2,2-dimethylpropanoate (**3a**) (931 mg, quant) as yellow crystals; mp 71—72 °C (ethyl acetate–hexane). IR (KBr) cm^{-1}: 1735, 1658, 1484, 1459, 1440. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.27 (9H, s), 4.99 (2H, d, J=1.9 Hz), 6.64—6.68 (1H, m), 6.74—6.88 (2H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 27.2 (3), 38.9, 59.4, 131.1, 136.5, 136.6, 143.6, 177.5, 186.1, 186.9. *Anal.* Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.71; H, 5.86. HR-MS *m/z*: 222.08846 (Calcd for $C_{12}H_{14}O_4$ (M^+): 222.08921). The alkaline solution was acidified by 10% hydrochloric acid solution and extracted with ethyl acetate. The organic layer was dried and concentrated to give recovered **1a** (44 mg, 76%). It can be used after recrystallization from diethyl ether–hexane.

Catalytic Hypervalent Iodine Oxidation of 2b Following the general procedure, **2b** (124 mg, 1 mmol) was treated with **1a** (14 mg, 0.05 mmol) and Oxone® (2.46 g, 4 mmol) in TFE–H_2O (1 : 2, 10 ml) to give 1,4-benzoquinone (**3b**) (84 mg, 78%) as yellow crystals, which was directly identical to the commercial sample supplied by Nacalai Chemicals, Ltd.

Catalytic Hypervalent Iodine Oxidation of 2c Following the general procedure, **2c** (41 mg, 0.3 mmol) was treated with **1a** (4 mg, 0.015 mmol) and Oxone® (738 mg, 1.2 mmol) in TFE–H_2O (1 : 2, 3 ml) to give **3b** (31 mg, 97%) as yellow crystals.

Catalytic Hypervalent Iodine Oxidation of 2d Following the general procedure, **2d** (50 mg, 0.3 mmol) was treated with **1a** (4 mg, 0.015 mmol) and Oxone® (738 mg, 1.2 mmol) in TFE–H_2O (1 : 2, 3 ml) to give **3b** (29 mg, 88%) as yellow crystals.

Catalytic Hypervalent Iodine Oxidation of 2e Following the general procedure, **2e** (180 mg, 1 mmol) was treated with **1a** (14 mg, 0.05 mmol) and Oxone® (2.46 g, 4 mmol) in TFE–H_2O (1 : 2, 10 ml) to give 2-*tert*-butyl-1,4-benzoquinone (**3e**) (163 mg, quant) as orange crystals, which was directly identical to the commercial sample supplied by TCI CO., Ltd.

Catalytic Hypervalent Iodine Oxidation of 2f Following the general procedure, **2f** (292 mg, 1 mmol) was treated with **1a** (14 mg, 0.05 mmol) and Oxone® (2.46 g, 4 mmol) in TFE–H_2O (1 : 2, 10 ml) to give 2,5-bis-(1,1-dimethylbutyl)-1,4-benzoquinone (**3f**) (276 mg, quant) as yellow crystals, mp 61—62 °C (hexane). IR (KBr) cm^{-1}: 1648, 1597, 1470, 1461, 1449, 1366. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.84 (6H, t, J=7.0 Hz), 0.97—1.15 (4H, m), 1.22 (12H, s), 1.65—1.74 (4H, m), 6.42 (2H, s). ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 14.6 (2), 18.4 (2), 27.4 (4), 38.1 (2), 43.1 (2), 134.9 (2), 153.5 (2), 188.3 (2). *Anal.* Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.41; H, 10.14. HR-MS *m/z*: 276.20919 (Calcd for $C_{18}H_{28}O_2$ (M^+): 276.20893).

Catalytic Hypervalent Iodine Oxidation of 2g Following the general procedure, **2g** (59 mg, 0.15 mmol) was treated with **1a** (2 mg, 0.0075 mmol) and Oxone® (369 mg, 0.6 mmol) in TFE–H_2O (1 : 2, 1.5 ml) to give 2-(*tert*-butyldiphenylsilyloxymethyl)-1,4-benzoquinone (**3g**) (57 mg, quant) as yellow solid, mp 76—79 °C (ethyl acetate–hexane). IR (KBr) cm^{-1}: 1656, 1598, 1470, 1428. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.10 (9H, s), 4.58 (2H, d, J=2.4 Hz), 6.68 (1H, d, J=10.0 Hz), 6.73 (1H, dd, J=10.0, 2.2 Hz), 7.04 (1H, q, J=2.4 Hz), 7.36—7.49 (6H, m), 7.60—7.73 (4H, m). ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 19.4, 26.9 (3), 59.9, 127.8 (4), 129.9 (2), 130.5, 132.4 (2), 135.3 (4), 136.3, 136.4, 147.9, 186.9, 187.5. HR-MS *m/z*: 376.14506 (Calcd for $C_{23}H_{24}O_3Si$ (M^+): 376.14948).

Catalytic Hypervalent Iodine Oxidation of 2h Following the general procedure, **2h** (48 mg, 0.27 mmol) was treated with **1a** (4 mg, 0.013 mmol) and Oxone® (659 mg, 1.07 mmol) in TFE–H_2O (1 : 2, 2.7 ml) to give 2-azidomethyl-1,4-benzoquinone (**3h**) (42 mg, 95%) as yellow needles, mp 65—66.5 °C (ethyl acetate–hexane). IR (KBr) cm^{-1}: 1661, 1637, 1602, 1425, 1361. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 4.29 (2H, d, J=1.4 Hz), 6.75—6.84 (3H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 48.5, 132.6, 136.3, 136.7, 142.6, 186.1, 186.6. *Anal.* Calcd for $C_7H_5N_3O_2$: C, 51.54; H, 3.09; N, 25.76. Found: C, 51.63; H, 3.45; N, 24.99; HR-MS *m/z*: 163.03585 (Calcd for $C_7H_5N_3O_2$ (M^+): 163.03818).

Catalytic Hypervalent Iodine Oxidation of 2i Following the general procedure, **2i** (50 mg, 0.18 mmol) was treated with **1a** (2.5 mg, 0.0088 mmol) and Oxone® (434 mg, 0.71 mmol) in TFE–H_2O (1 : 2, 2 ml) to give 2-(3,6-dioxocyclohexa-1,4-dienylmethyl)isoindole-1,3-dione (**3i**)[55] (46 mg, 98%) as yellow needles, mp 169—172 °C (ethyl acetate–hexane). IR (neat) cm^{-1}: 1767, 1711, 1659, 1467, 1419, 1391. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 4.72 (2H, d, J=1.9 Hz), 6.37 (1H, q, J=2.2 Hz), 6.75 (1H, dd, J=10.3, 2.2 Hz), 6.83 (1H, d, J=10.3 Hz), 7.75—7.93 (2H, m), 7.87—7.93 (2H, m). ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 28.9, 123.6 (2), 131.1, 131.6, 134.4 (3), 136.4 (2), 142.4, 167.3 (2), 186.0, 186.5. HR-MS *m/z*: 267.04932 (Calcd for $C_{15}H_9NO_4$ (M^+): 267.05316).

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