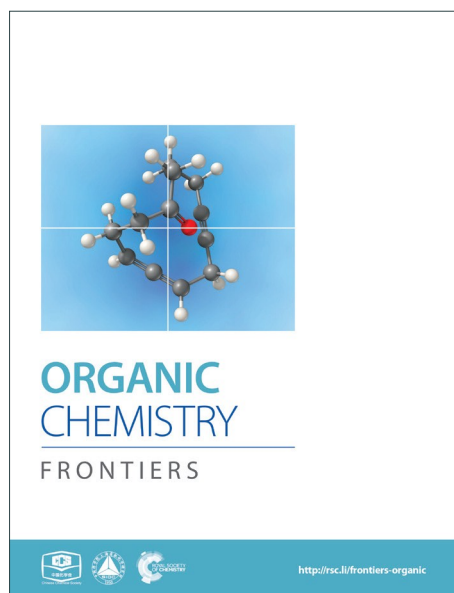
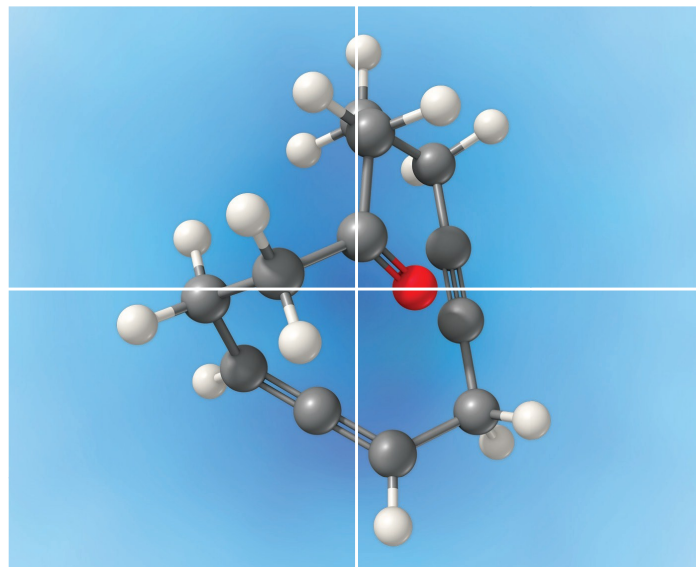


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ARTICLE

## Manganese-catalysed hydroperoxidation of carbon–carbon double bonds using molecular oxygen present in air and hydroxylamine under ambient conditions

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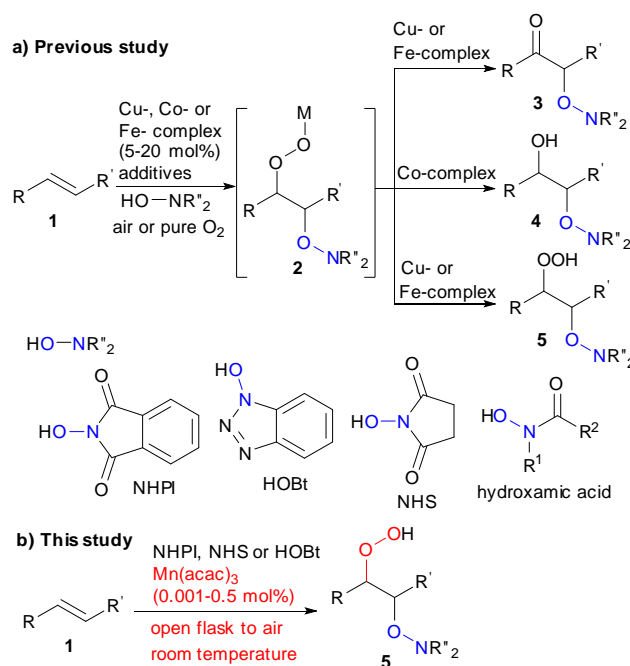
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Daisuke Yamamoto, Masayuki Soga, Hiromasa Ansai and Kazuishi Makino\*

A highly efficient manganese-catalysed hydroperoxidation of carbon–carbon double bonds of enynes as well as styrene derivatives using *N*-hydroxyphthalimide, *N*-hydroxybenzotriazole or *N*-hydroxysuccinimide was developed. This reaction proceeded at room temperature through the direct incorporation of molecular oxygen present in air. The required catalytic loading of manganese (III) acetylacetonate is extremely low (generally 0.02–0.5 mol%, and a minimum of 0.001 mol%).

### Introduction

Developing a new methodology for transition metal-catalysed oxidation reactions has been extensively studied in the recent decade, and molecular oxygen is essentially recognised as an ideal oxidant.<sup>1</sup> Despite developing several elegant oxidation processes involving molecular oxygen as a sole oxidant,<sup>2</sup> methodologies for directly incorporating molecular oxygen into organic substrates remains a major challenge in synthetic chemistry. The incorporation of an oxygen atom into substrates, such as C–H oxidation and epoxidation, has been observed in several biological processes,<sup>3</sup> and aerobic epoxidation is used as an elegant strategy in organic chemistry.<sup>4</sup> Recently, several aerobic difunctionalisations of carbon–carbon double bonds, such as oxyazidation,<sup>5</sup> oxytrifluoromethylation,<sup>6</sup> oxysulfonylation,<sup>7</sup> oxysulfoxidation,<sup>8</sup> oxysulfurization<sup>9</sup> and oxyphosphorylation,<sup>10</sup> were demonstrated. In addition, metal-free or transition metal-catalysed aerobic dioxygenation<sup>11–13</sup> of carbon–carbon double bonds using hydroxylamine derivatives, such as *N*-hydroxyphthalimide (NHPI), *N*-hydroxybenzotriazole (HOBt), *N*-hydroxysuccinimide (NHS) and hydroxamic acids, has witnessed significant progress (Scheme 1). The transition metal-catalysed oxidative *N*-hydroxyphthalimidation using molecular oxygen was originally reported by Ozaki *et al.*<sup>13a</sup> in 1989 as a side reaction occurring during the manganese (III) tetraphenylporphyrin chloride-catalysed epoxidation of carbon–carbon double bonds present in styrene, 2-norbornene or indene, which resulted in a mixture of  $\beta$ -keto-*N*-alkoxyphthalimides and  $\beta$ -hydroxy-*N*-



**Scheme 1** Aerobic hydroperoxidation of a carbon–carbon double bond with *N*-hydroxyphthalimide.

alkoxyphthalimides in moderate yield. Recently, Punniyamurthy *et al.*<sup>13b</sup> demonstrated that 10 mol% Cu(OAc)<sub>2</sub>·H<sub>2</sub>O-catalysed direct dioxygenation of carbon–carbon double bonds in styrene derivatives using NHPI and molecular oxygen in air at room temperature yields  $\beta$ -keto-*N*-alkoxyphthalimides in good yield (Scheme 1). Woerpel *et al.*<sup>13c</sup> suggested that in addition to NHPI, HOBt added to a carbon–carbon double bond in styrene derivatives or conjugated enynes in the presence of 5–20 mol% [Cu(MeCN)<sub>4</sub>]ClO<sub>4</sub> under a pure O<sub>2</sub> atmosphere. Furthermore, Lei *et al.*<sup>13d,e</sup> reported that using 10 mol% of CuCl or Co(OAc)<sub>2</sub>·4H<sub>2</sub>O promoted the oxidative addition of hydroxamic acids to styrene derivatives under a

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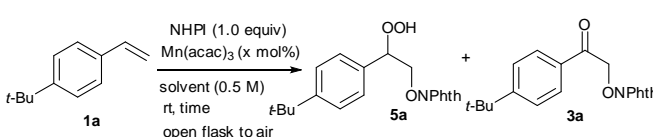
pure O<sub>2</sub> atmosphere to selectively yield β-keto or β-hydroxy compounds. Xia's group<sup>13f</sup> reported that the combination of 10 mol% CuBr<sub>2</sub> and 4.0 equivalent di-*tert*-butyl peroxide worked as a catalysis for direct dioxygenation of styrene derivatives in air to afford β-keto-*N*-alkoxyphthalimides in moderate to good yield. On the other hand, Tang *et al.*<sup>13g</sup> have demonstrated that 10 mol% of FeCl<sub>3</sub> is an effective catalyst for the oxidative *N*-hydroxyphthalimidation of styrene derivatives to afford β-keto-*N*-alkoxyphthalimides under a pure O<sub>2</sub> atmosphere. In the methodologies described above involving the direct incorporation of an oxygen atom into a carbon-carbon double bond using *N*-hydroxylamine derivatives, the existence of metal hydroperoxide **2** is suggested as an intermediate. However, the corresponding hydroperoxide could not be isolated in acceptable yields due to the instability of the intermediate metal hydroperoxide **2** in metal-catalysed dioxygenation reactions. More recently, Woerpel *et al.*<sup>13h</sup> reported a 20 mol% of [Cu(MeCN)<sub>4</sub>]ClO<sub>4</sub>-catalysed hydroperoxidation of conjugated enynes using NHPI or HOBt under a pure O<sub>2</sub> atmosphere to obtain propargyl hydroperoxides in good yields by lowering the reaction temperature to 0 °C. Furthermore, Punniyamurthy *et al.*<sup>13i</sup> also described the hydroperoxidation of styrene derivatives catalysed by 20 mol% Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. While these pioneering research efforts provided new methods for incorporating oxygen atom(s) derived from gaseous dioxygen into organic substrates, several challenges still remain. In particular, developing highly active and robust catalysts capable of directly incorporating molecular oxygen present in air into organic substrates without cooling or heating conditions is in high demand.

Herein, we report a highly efficient manganese-catalysed hydroperoxidation of a carbon-carbon double bond using hydroxylamine and molecular oxygen in air (open flask) under ambient conditions.

## Results and discussion

The reaction between 4-*tert*-butylstyrene **1a** (1.0 equiv) and NHPI (1.0 equiv) in the presence of a metal complex in air at room temperature was initially investigated (Table 1). Using 1.0 mol% of Mn(acac)<sub>3</sub> in MeCN as a catalyst for 5 h offered a mixture of hydroperoxide **5a** and β-keto-*N*-alkoxyphthalimide **3a** in good yield (61%, **5a** : **3a** = 4 : 1, entry 1). Decreasing the amount of Mn(acac)<sub>3</sub> to 0.02 mol% improved the yield and product ratio of hydroperoxide **5a** and ketone **3a** (92%, **5a** : **3a** = >20 : 1, entry 3). We interpreted this result as being indicative of the fact that the further decomposition of hydroperoxide **5a** to ketone **3a** and other side products by manganese complex was effectively suppressed due to reduced catalyst loading. To test the scalability of the hydroperoxidation reaction, a gram-scale reaction was performed at 0.02 mol% catalyst loading in air (entry 4). The reaction proceeded in >99% yield at room temperature. Although a further reduction of catalyst loading to 0.001 mol% required a longer reaction time under air at room temperature, the desirable hydroperoxide **5a** was obtained in high yield at an excellent product ratio (84% yield, **5a** : **3a** =

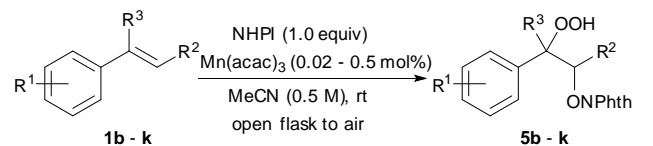
**Table 1** Optimisation of manganese-catalysed aerobic hydroperoxidation of 4-*tert*-butylstyrene.<sup>a</sup>



Entry	Mn(acac) <sub>3</sub> (mol%)	Solvent	Time (h)	Yield <sup>b</sup> (%) ( <b>5a</b> : <b>3a</b> ) <sup>c</sup>
1	1.0	MeCN	5	61 (4 : 1)
2	0.1	MeCN	16	90 (4 : 1)
3	0.02	MeCN	24	92 (>20 : 1)
4 <sup>d</sup>	0.02	MeCN	72	>99% (>20 : 1)
5	0.01	MeCN	31	83 (>20 : 1)
6	0.001	MeCN	46	84 (>20 : 1)
7	0.01	EtCN	24	5 (17 : 1)
8	0.01	CH <sub>2</sub> Cl <sub>2</sub>	24	7 (>20 : 1)
9	0.01	benzene	24	Trace -
10	0.01	THF	24	11 (>20 : 1)
11	0.01	DMF	24	Trace -
12	0.01	DMSO	24	Trace -
13	0.01	MeOH	24	Trace -
14	none	MeCN	24	no reaction

<sup>a</sup> Reaction conditions: **1a** (0.50 mmol), metal salt (0.001–1.0 mol%), O<sub>2</sub> in air at room temperature. <sup>b</sup> Isolated yield. <sup>c</sup> The ratio was determined by <sup>1</sup>H NMR analysis of crude sample. <sup>d</sup> The reaction was conducted at 1.04 g (6.50 mmol) scale of **1a**.

**Table 2** Styrene derivatives as potential substrates for aerobic hydroperoxidation styrene derivatives.



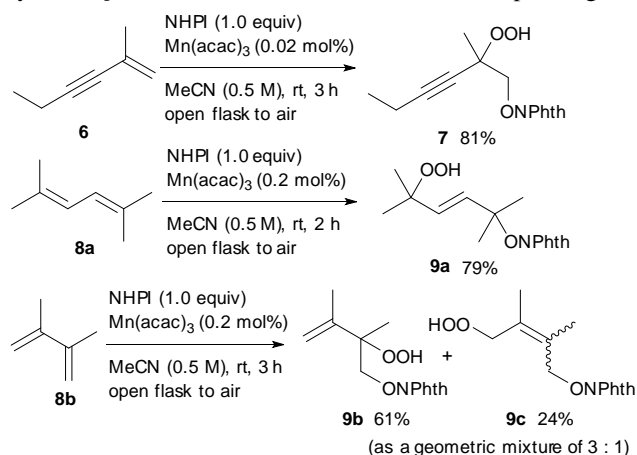
R<sup>1</sup> = EWG, EDG, R<sup>2</sup> = H, alkyl, aryl, R<sup>3</sup> = H, alkyl

<b>5b</b> 24 h, 64% <sup>a</sup>	<b>5c</b> 24 h, 96% <sup>a</sup>	<b>5d</b> 24 h, >99% <sup>b</sup>
<b>5e</b> 24 h, 91% <sup>b</sup>	<b>5f</b> 24 h, 94% <sup>b</sup>	<b>5g</b> 24 h, 88% <sup>c</sup>
<b>5h</b> 48 h, 60% <sup>b</sup>	<b>5i</b> 24 h, >99% <sup>a</sup>	<b>5j</b> 36 h, 69% <sup>a,d</sup> (anti : syn = 4 : 1)
<b>5k</b> 24 h, 80% <sup>b,d</sup> (anti : syn = 2 : 1)		

<sup>a</sup> Mn(acac)<sub>3</sub> (0.02 mol%). <sup>b</sup> Mn(acac)<sub>3</sub> (0.2 mol%). <sup>c</sup> Mn(acac)<sub>3</sub> (0.5 mol%). <sup>d</sup> The diastereomeric ratio (dr) was determined by <sup>1</sup>H-NMR analysis of crude sample.

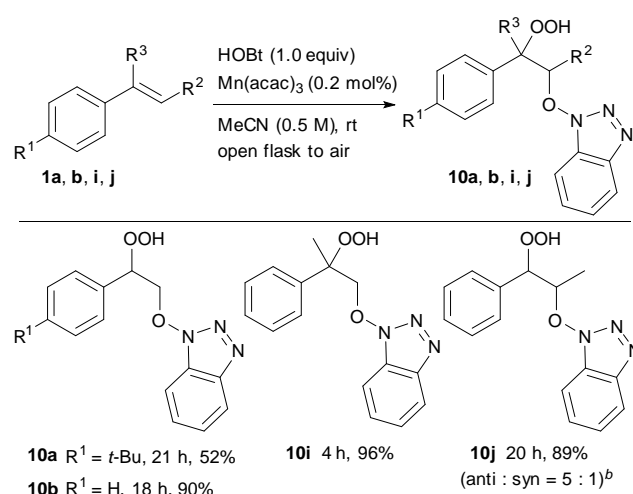
>20 : 1, entry 6). A series of solvents were screened, and it was observed that MeCN was essential for this reaction, while EtCN, CH<sub>2</sub>Cl<sub>2</sub>, benzene, THF, DMF, DMSO and MeOH afforded poor yields (entries 7–13).<sup>14</sup>

Using these optimal reaction conditions, potential substrates for this manganese-catalysed aerobic hydroperoxidation reaction were evaluated (Table 2). The reaction with styrene **1b** offered the hydroperoxide **5b** in 64% yield. Styrenes substituted with a methyl group at the 4- or 3-position **1c** and **1d** was transformed into the corresponding hydroperoxides **5c** and **5d**, respectively, in excellent yield without the oxidation of the methyl group at the benzylic position. The reaction of the styrene derivatives bearing a 4-fluoro, 4-chloro or 4-bromo moiety on the aromatic ring produced the corresponding hydroperoxide **5e**, **5f** or **5g**, respectively, in high yield (88%–94%). The electron-rich styrene derivative **1h** with a methoxy group at 4-position was effective under these oxidation conditions to provide the hydroperoxide **5h** in good yield (60%). Sterically hindered  $\alpha$ -methylstyrene **1i** could be efficiently oxidised in >99% yield. In addition,  $\beta$ -substituted styrenes **1j** and **1k** were transformed to the corresponding



**Scheme 2** Aerobic hydroperoxidation of conjugated enyne and dienes.

**Table 3** Aerobic hydroperoxidation of styrene derivatives with HOBT.<sup>a</sup>

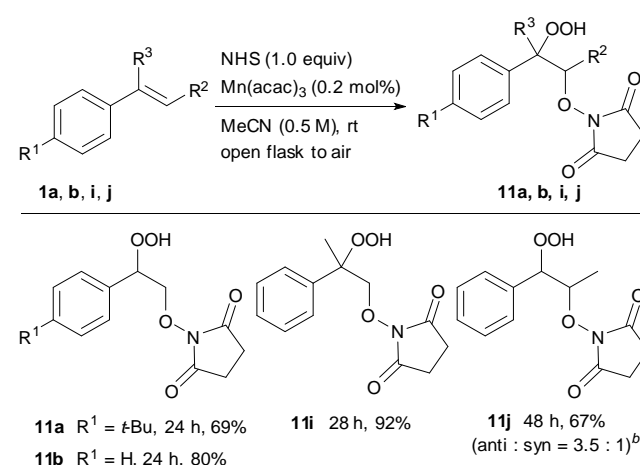


<sup>a</sup> Styrene derivatives **1a**, **b**, **i** and **j** (0.50 mmol). <sup>b</sup> The diastereomeric ratio (dr) was determined by <sup>1</sup>H-NMR analysis of crude sample.

hydroperoxides **5j** and **5k**, respectively, in good yields with moderate diastereoselectivity.

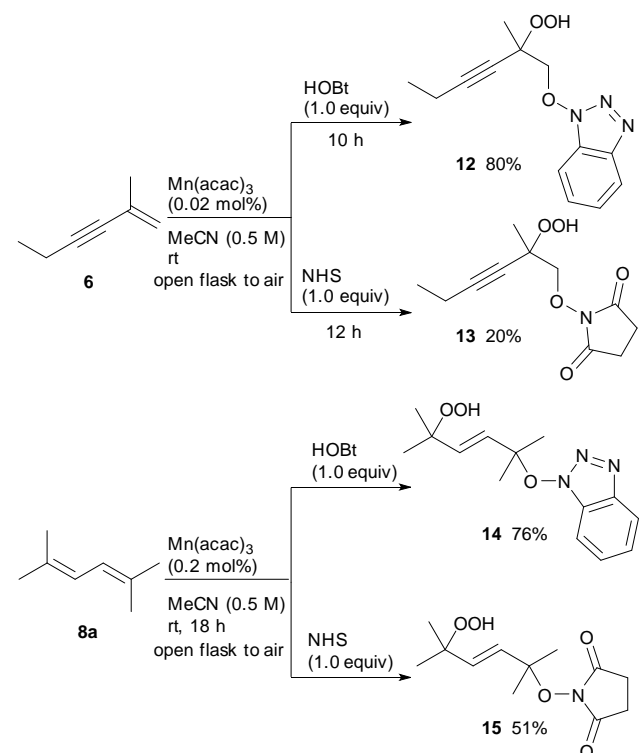
Furthermore, we investigated the hydroperoxidation of the conjugated enyne and dienes (Scheme 2).<sup>15</sup> Treatment of enyne **6** with 0.02 mol% of Mn(acac)<sub>3</sub> in air at room temperature for 3 h offered the hydroperoxide **7** in 81% yield, while the carbon–carbon triple bond remained intact under these oxidation conditions. The conjugated dienes **8a** and **8b** were also viable substrates. The dioxygenation of 2,5-dimethyl-2,4-hexadiene **8a** in the presence of 0.2 mol% of Mn(acac)<sub>3</sub> provided the 1,4-dioxygenated product **9a** in 79% yield as a single *E*-isomer. On the other hand, when 2,3-dimethyl-1,3-butadiene **8b** was used

**Table 4** Aerobic hydroperoxidation of styrenes derivatives with NHS.<sup>a</sup>



<sup>a</sup> Styrene derivatives **1a**, **b**, **i** and **j** (0.50 mmol). <sup>b</sup> The diastereomeric ratio (dr) was determined by <sup>1</sup>H-NMR analysis of crude sample.

**Scheme 3** Aerobic hydroperoxidation of conjugated enyne **6** and diene **8a**.



as a substrate, the 1,2-dioxygenated product **9b** and the 1,4-dioxygenated product **9c** were obtained in 61% and 24% yield (as a geometric mixture of 3 : 1), respectively.

Subsequently, we evaluated the incorporation of molecular oxygen into a carbon–carbon double bond using HOBt or NHS instead of NHPI (Tables 3 and 4). The oxidative addition of HOBt to styrene **1b** in the presence of 0.2 mol% of Mn(acac)<sub>3</sub> occurred at room temperature in air to offer the hydroperoxide **10b** in excellent yield (90%). On the other hand, the reaction of 4-substituted styrene derivatives, such as 4-*tert*-butylstyrene **1a**, resulted in moderate yield (52%). Both  $\alpha$ - and  $\beta$ -alkyl-substituted styrene derivatives **1i** and **1j** performed well as substrates providing the corresponding hydroperoxides **10i** and **10j** in 96% and 89% yield (anti : syn = 5 : 1), respectively. In addition, the oxidative addition of NHS to styrene derivatives, such as **1a**, **1b**, **1i** and **1j**, led to similar results yielding the corresponding hydroperoxides **11a**, **11b**, **11i** and **11j**.

Moreover, the manganese-catalysed oxidative addition of HOBt or NHS to conjugated enyne **6** and diene **8a** was also examined (Scheme 3). The dioxygenation of both enyne **6** and diene **8a** using HOBt under air proceeded at low catalyst loading to afford the hydroperoxides **12** and **14**, respectively, in high yields compared to the reaction using NHS.

## Conclusions

To summarise our study, we have developed a manganese-catalysed aerobic hydroperoxidation method for conjugated alkenes. Notably, the unprecedentedly low catalyst loading of Mn(acac)<sub>3</sub> promoted the oxidative addition of NHPI, HOBt or NHS to conjugated alkenes through the direct incorporation of molecular oxygen from air (pure oxygen is not required) without any other additives. Considering the desirable features, such as the simplicity of operation, inexpensive catalyst, a wide range of substrates and mild reaction conditions, this novel reaction provides an attractive synthetic approach to produce hydroperoxides. The investigation of reaction mechanism involved in the manganese-catalysed aerobic hydroperoxidation reactions is currently ongoing in our laboratory.

## Experimental

### Representative procedure for the manganese-catalyzed hydroperoxidation with NHPI

To a stirred solution of 4-*tert*-butylstyrene (80.1 mg, 0.500 mmol) and *N*-hydroxyphthalimide (81.6 mg, 0.500 mmol) in MeCN (0.9 mL) at room temperature was added a solution of Mn(acac)<sub>3</sub> in MeCN (100  $\mu$ L, 0.10  $\mu$ mol, 1.0 mM in MeCN) under air (open flask). The solution was stirred for 24 h at room temperature and quenched with saturated aqueous NaCl solution (0.5 mL). The resulting mixture was extracted with ethyl acetate (3 x 1.0 mL). The combined organic phases were washed with brine (1.0 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The obtained crude material was purified by column chromatography (silica gel, hexane : EtOAc = 3 : 1) to afford **5a** (163 mg, 0.459 mmol, 92%).

### Gram-scale synthesis

To a stirred solution of 4-*tert*-butylstyrene (1.04 g, 6.50 mmol) and *N*-hydroxyphthalimide (1.06 g, 6.50 mmol) in MeCN (13.0 mL) at room temperature was added a solution of Mn(acac)<sub>3</sub> in MeCN (1.0 mL, 1.3  $\mu$ mol, 1.3 mM in MeCN) under air (open flask). The solution was stirred for 72 h at room temperature and quenched with saturated aqueous NaCl solution (10 mL). The resulting mixture was extracted with ethyl acetate (3 x 14 mL). The combined organic phases were washed with brine (14 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The obtained crude material was purified by column chromatography (silica gel, hexane : EtOAc = 3 : 1) to afford **5a** (2.31 g, 6.50 mmol, >99% yield).

### 2-(2-(4-(*tert*-Butyl)phenyl)-2-hydroperoxyethoxy)isoindoline-1,3-dione (**5a**)

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.37 (OOH), 7.89-7.84 (m, 2H, Ar-H), 7.80-7.75 (m, 2H, Ar-H), 7.39 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.33 (d, *J* = 8.8 Hz, 2H, Ar-H), 5.40 (dd, *J* = 7.7, 3.8 Hz, 1H, CHOOH), 4.55 (dd, *J* = 11.6, 3.8 Hz, 1H, CH(OOH)CH<sub>2</sub>O), 4.50 (dd, *J* = 11.6, 7.7 Hz 1H, CH(OOH)CH<sub>2</sub>O), 1.30 (s, 9H, Ar-C<sub>4</sub>H<sub>9</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 163.8, 152.0, 134.7, 132.6, 128.7, 126.9, 125.7, 123.8, 85.3, 78.9, 34.6, 31.2; IR (neat) 3402, 3098, 3062, 3032, 2962, 2359, 2248, 1789, 1730, 1466, 1375, 1186, 1132, 1081, 1018, 997, 877, 701 cm<sup>-1</sup>; HRMS (FAB, NBA) *m/z* calcd for C<sub>20</sub>H<sub>21</sub>NNaO<sub>5</sub> [M+Na]<sup>+</sup> 378.1317, found 378.1319.

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