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AMMONIUM HYPOIODITE-CATALYZED PEROXIDATIVE DEAROMATIZATION OF PHENOLS

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Abstract – Here, we report the first transition metal-free peroxidative dearomatization of phenols using hypoiodite catalysis with TBHP. Hypoiodite salts are generated *in situ* from the corresponding quaternary ammonium iodides in the presence of TBHP, and the oxidative coupling reaction proceeds efficiently under mild conditions. The dearomatized products are versatile synthetic intermediates for further synthetic transformations to various complex structures including heterocycles. As a demonstration, the further oxidation of the unsaturated peroxide with TBHP afforded the corresponding peroxy epoxide in good yield.

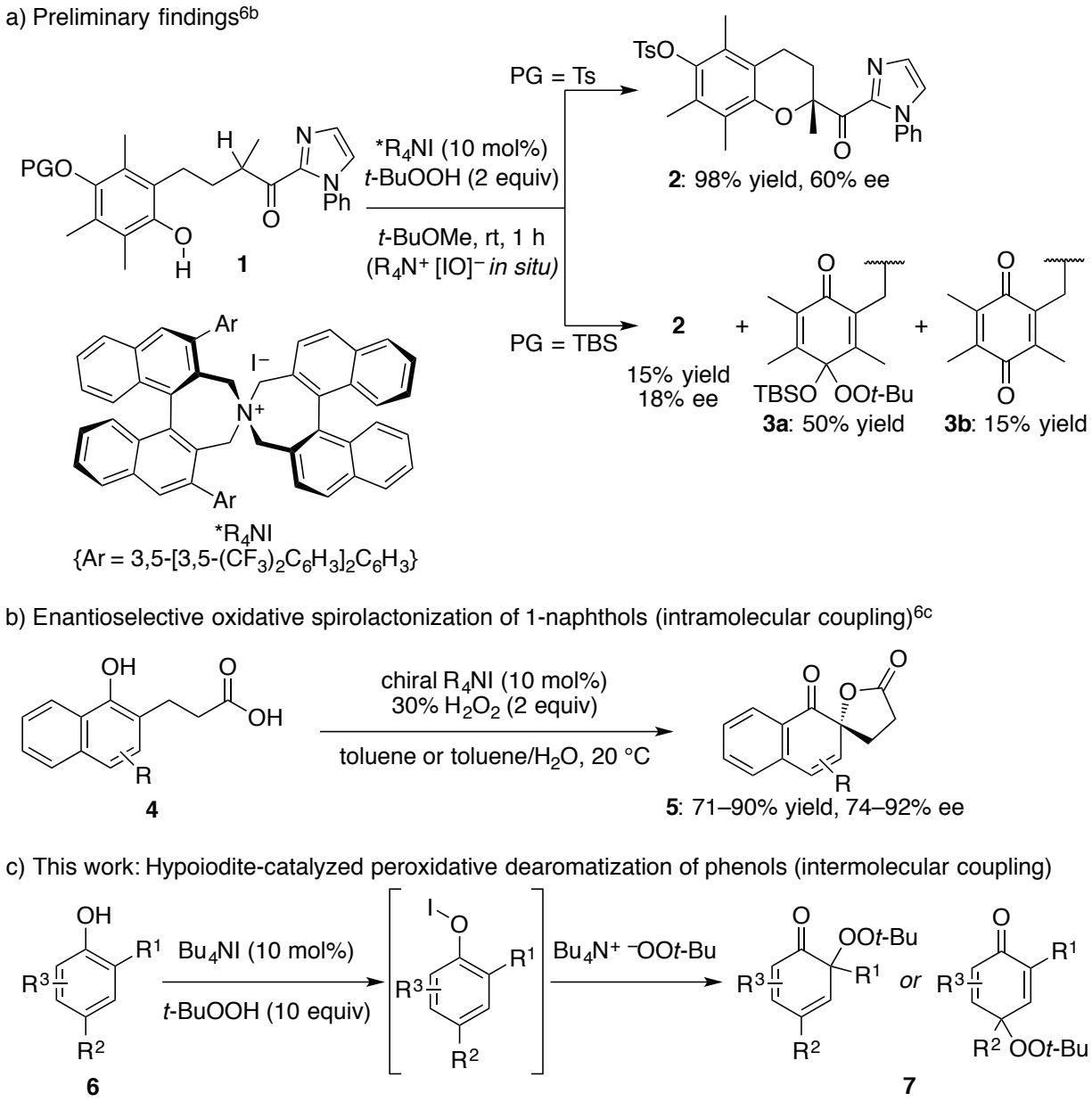
INTRODUCTION

The oxidative dearomatization of phenols has emerged as a promising tool for the synthesis of various natural products and biologically active compounds.[1] Several different compounds can be generated depending on the nature of the reagents and oxidants used. Various nucleophiles, such as water, alcohols, carboxylic acids and their derivatives, and electron-rich (hetero)aromatics, can be used in either an inter- or intramolecular fashion.[1] In this context, the peroxidative dearomatization of electron-rich phenols has been developed using *tert*-butyl hydroperoxide (TBHP) as an oxidant and coupling reagent.[2–4] Murahashi's group and Doyle's group independently reported a transition metal-catalyzed peroxidative dearomatization of electron-rich phenols at the *para*-position with TBHP by using ruthenium or rhodium complexes, respectively.[2,3] Very recently, Prabhu's group reported a copper bromide-catalyzed peroxidative dearomatization of 1-substituted 2-naphthols at the *ortho*-position.[4] The dearomatized products, (2- or 4-peroxy)cyclohexa-2,4- or 2,5-dienones, are versatile synthons for further synthetic transformations to various complex structures including heterocycles. Murahashi's group achieved the Lewis acid-promoted rearrangement of 4-(*tert*-butylperoxy)cyclohexadienones into 2-substituted

Dedicated to Prof. Dr. Masakatsu Shibasaki on the occasion of his 70th birthday

1,4-benzoquinones.[2] Meanwhile, Doyle's group developed a tandem oxidation–Michael addition to furnish various heterocycles.[3b] After the Rh-catalyzed peroxidative dearomatization of phenols tethered to alcohols, ketones, amides, carboxylic acids, and *N*-Boc-protected amines at the 4-position was complete, Brønsted acid-catalyzed intramolecular Michael addition in one-pot afforded oxo- and -aza-heterocycles in moderate to good yields.[3b]

On the other hand, Ochiai's group reported a transition metal-free peroxidation of phenols with TBHP.[5] However, the use of stoichiometric quantities of a highly reactive and potentially explosive hypervalent iodine(III) reagent, 1-(*tert*-butylperoxy)-1,2-benziodoxol-3(1*H*)-one, as a radical precursor was required. Here, we report a transition metal-free catalytic peroxidative dearomatization of phenols using hypoiodite catalysis[6,7] with TBHP as an oxidant and coupling reagent.



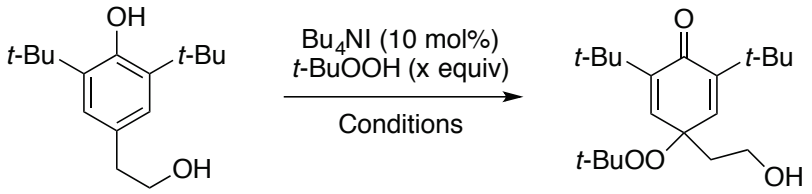
Scheme 1. Hypoiodite-catalyzed oxidation of phenols

Recently, we developed an in situ-generated chiral quaternary ammonium hypoiodite catalysis for the enantioselective oxidative cyclization of ketophenols to 2-acyl-2,3-dihydrobenzofurans or 2-acyl-chromans with the use of hydrogen peroxide or TBHP as an oxidant.[6a,b] In these reactions, the chemoselective α-oxidation of carbonyl moieties proceeded preferentially, and hydroxyphenyl moieties served as intramolecular nucleophiles. However, in the course of our studies on six-membered oxidative cyclization to chromans using TBHP, we found that tuning of the acidity of the hydroxyphenyl of substrates with electron-withdrawing protective groups is crucial for chemoselective oxidative carbon–oxygen coupling (i.e., **1** to **2**), since electron-rich hydroxyphenyl moieties are easily dearomatized (i.e., **1** to **3**, Scheme 1a).[6b] Based on these preliminary findings, we developed a chiral ammonium hypoiodite-catalyzed enantioselective oxidative dearomatizative intramolecular coupling of 1-naphthols **4** tethered to a hydroxycarbonyl group at the 2-position (Scheme 1b).[6c] Since the development of intermolecular coupling reactions is generally more challenging than that of intramolecular reactions, we next focused our attention on the hypoiodite-catalyzed peroxidative dearomatization of phenols **6** with TBHP as an oxidant and intermolecular coupling reagent (Scheme 1c).

RESULTS AND DISCUSSION

A mixture of 2,6-di-*tert*-butyl-4-(2-hydroxyethyl)phenol (**6a**) with TBHP (10 equivalents) in methyl *tert*-butyl ether in the presence of 10 mol% of tetrabutylammonium iodide at room temperature gave the desired 4-(*tert*-butylperoxy)cyclohexa-2,5-dienone **7a** in 60% yield along with unidentified byproducts (Table 1, entry 1). A brief screening of solvents revealed that a clean reaction in non-polar solvents such as toluene and dichloroethane gave **7a** quantitatively (entries 2–5). However, the partial oxidation of toluene also proceeded in the presence of an excess amount of TBHP (entry 4). A decrease in the amount of TBHP from 10 to 5 equivalents resulted in incomplete conversion (entry 6). The use of an aqueous solution of TBHP instead of an anhydrous solution gave similar results (entry 7). Moreover, the reaction was compatible with open-air conditions (entry 8). Notably, no reaction occurred in the presence of tetrabutylammonium chloride or bromide instead of the corresponding iodide (entries 9 and 10).

Table 1. Peroxidative dearomatization of phenol 6a[a]



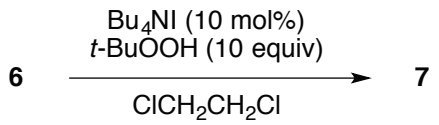
6a **7a**

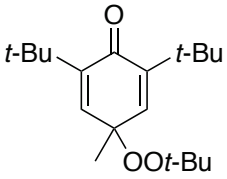
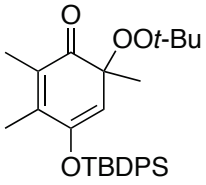
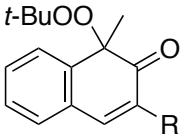
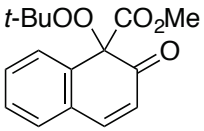
Entry	TBHP (x/equiv)	Solvent	Time/h	**6a**, Conv./%[b]	**7a**, Yield/%[b]
1	10	*t*-BuOMe	48	>99	60
2	10	MeCN	24	20	10
3	10	EtOAc	24	>99	81[c]
4	10	toluene[d]	24	>99	99
5	10	$ClCH_2CH_2Cl$	24	>99	99 (96)[c,e]
6	5	$ClCH_2CH_2Cl$	48	45	45
7	10[f]	$ClCH_2CH_2Cl$	24	>99	97
8[g]	10	$ClCH_2CH_2Cl$	24	>99	97
9[h]	10	$ClCH_2CH_2Cl$	24	<5	0
10[h]	10	$ClCH_2CH_2Cl$	24	<5	0

[a] Unless otherwise noted, a solution of **6a** (0.1 mmol), Bu_4NI (10 mol%) and TBHP (in nonane solution) in the solvent described was stirred at room temperature under N_2. [b] Determined by ^1H NMR analysis. [c] Isolated yield. [d] Oxidation of toluene was observed by *in situ* NMR analysis. [e] Reaction was performed with 1 mmol of **6a** for 36 h. [f] A 70-wt% aqueous solution of TBHP was used. [g] Reaction was performed under open-air conditions. [h] Bu_4NBr (entry 10) or Bu_4NCl (entry 11) was used instead of Bu_4NI.

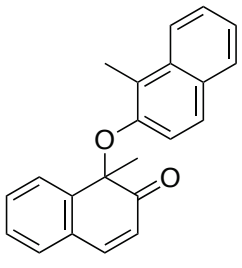
To explore the scope of the hypoiodite-catalyzed peroxidative dearomatization reaction, several electron-rich phenols and 2-napthols **6** were examined as substrates under the optimized conditions (Table 2). The oxidation of 2,6-di-*tert*-butyl-4-methylphenol (**6b**) at room temperature gave *para*-peroxide **7b** quantitatively (entry 1). The peroxidation reaction occurred at the less-hindered *ortho*-position of unsymmetric phenol **6c** (entry 2). On the other hand, the oxidation of 1-methyl-2-naphthol (**6d**) at room temperature afforded the desired peroxide **7d** in only moderate yield along with dearomatized dimeric ether **8**. Control experiments revealed that **7d** was obtained *via* the direct peroxidation of **6d** or nucleophilic substitution of **8** with TBHP. To our delight, **7d** was obtained exclusively at 50 °C due to acceleration of both the direct peroxidation and nucleophilic substitution reactions (entry 3). Peroxidative dearomatization of various 3-substituted 1-methyl-2-naphthols **6e–k** gave the corresponding dearomatized products **7e–k** in good to high yields (entries 4–10). Notably, several functional groups such as chloride, bromide, iodide, alkyne, ester, and primary alcohol were found to be compatible with these mild conditions. Oxidation of methyl 2-hydroxy-1-naphthoate (**6l**) afforded peroxide **7l** in good yield, albeit after a long reaction time (entry 11). In contrast, the oxidation of 2- or 4-substituted 1-naphthols gave a complex mixture. No reaction occurred for the oxidation of less-substituted phenols such as *p*-cresol.

Table 2. Peroxidative dearomatization of phenols and 2-naphthols 6



Entry	Product **7**		Conditions	**7**, Yield/%[a]
1		**7b**	RT, 24 h	99
2		**7c**	RT, 30 h	74
3		**7d** (R = H)	50 °C, 12 h	91[b]
4		**7e** (R = Cl)	50 °C, 12 h	89
5		**7f** (R = Br)	50 °C, 12 h	64
6		**7g** (R = I)	50 °C, 12 h	74
7		**7h** (R = Ph)	50 °C, 6 h	71
8		**7i** (R = C≡CPh)	50 °C, 6 h	78
9		**7j** (R = $(CH_2)_2CO_2Me$)	RT, 24 h	86
10		**7k** (R = $(CH_2)_2OH$)	RT, 12 h	76
11		**7l**	50 °C, 72 h	76

[a] Isolated yield. [b] When the reaction was conducted at room temperature for 12 h, **7d** and **8** were obtained in 41% and 40% yields, respectively. After 108 h at room temperature, the yields of **7d** and **8** were 65% and 26%, respectively.



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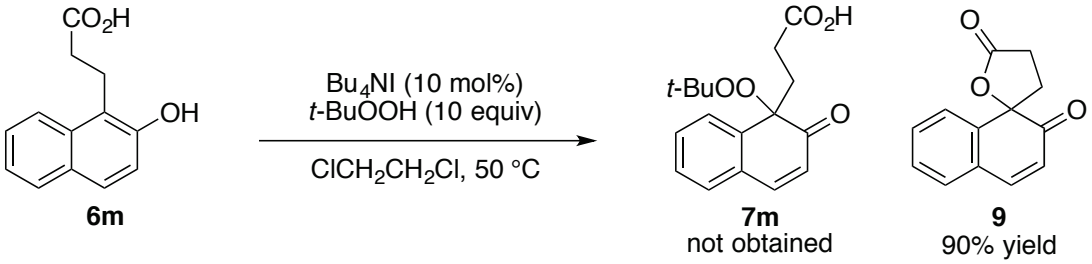
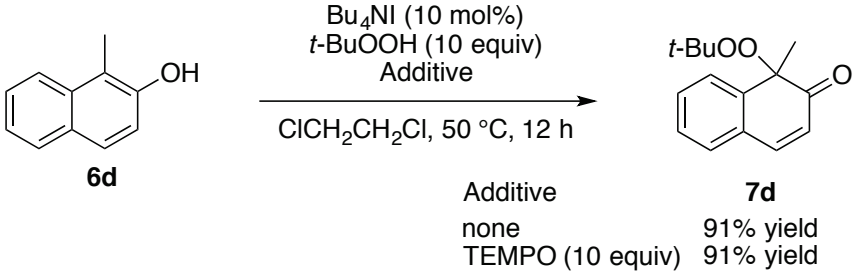
Intramolecular oxidative coupling proceeded in preference to intermolecular coupling, even in the presence of an excess amount of TBHP. For instance, the reaction of 2-naphthol **6m** tethered to carboxylic acid at the 1-position gave spirolactone **9** in 90% yield, and peroxide **7m** was not obtained (Scheme 2).



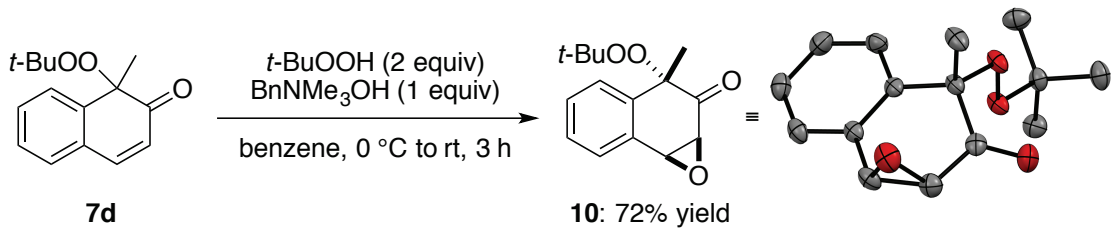
Scheme 2. Oxidative intramolecular versus intermolecular coupling

We proposed that the peroxidative dearomatization reaction might proceed *via* an aryl hypoiodite intermediate, which gives the dearomatized product **7** *via* intermolecular S_N2' addition of ammonium *tert*-butylperoxide at the 2- or 4-position (Scheme 1c).[6c] The addition of an excess amount of TEMPO as a radical scavenger did not influence the yield in the oxidation of **6d** (Scheme 3). These results suggested that a free radical pathway might be unlikely.



Scheme 3. Control experiment with radical scavenger

The further oxidation of unsaturated peroxide **7h** with TBHP in the presence of Triton B[8] afforded the *trans*-epoxide **10** in 72% yield along with unidentified byproducts (Scheme 4). Only one diastereomer could be isolated, and the relative stereochemistry of **10** was confirmed by single-crystal X-ray diffraction analysis.



Scheme 4. Synthesis of epoxide **10**

In summary, we have developed the first transition metal-free peroxidative dearomatization of phenols using hypoiodite catalysis with TBHP as an oxidant and a coupling reagent. Hypoiodite salts are generated *in situ* from the corresponding quaternary ammonium iodides in the presence of TBHP. The

intermolecular oxidative coupling reaction proceeds efficiently under mild conditions, and is compatible with various functional groups such as chloride, bromide, iodide, alkyne, ester, and primary alcohol. The dearomatized products are highly useful synthons for further synthetic transformations to various complex structures including heterocycles. As a demonstration, the further oxidation of the unsaturated peroxide with TBHP afforded the corresponding peroxy epoxide in good yield with high diastereoselectivity.

EXPERIMENTAL

Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. ^{1}H NMR spectra were measured on a JEOL ECS-400 (400 MHz) and Bruker AVANCE III HD (500 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; quin = quintet; m = multiplet; brs = broad singlet), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on a JEOL ECS-400 (100 MHz) and Bruker AVANCE III HD (126 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.00 ppm). For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254} 0.25 mm) were used. The products were purified by column chromatography on silica gel (E. Merck Art. 9385). High-resolution mass spectral analysis (HRMS) was performed at Chemical Instrument Center, Nagoya University (JEOL JMS-700). In experiments that required dry solvents, toluene, benzene, *tert*-butyl methyl ether, ethyl acetate, acetonitrile, and dichloromethane were purchased from Wako Pure Chemical Industries, Ltd., as the "anhydrous" and stored over 4Å molecular sieves. Other solvents were purchased from Kanto Chemical Co., Inc., Aldrich Chemical Co., Inc., Tokyo Chemical Industry (TCI) Co. Ltd., Nacalai Tesque, Inc. or Wako Pure Chemical Industries, Ltd., and used without further purification. Tetrabutylammonium iodide was purchased from TCI and used without further purification. 70-wt% aqueous TBHP was purchased from Wako. Anhydrous TBHP (5.5 M nonane solution) was purchased from Aldrich Chemical Co., Inc. and used without further purification. Other simple chemicals were analytical-grade and obtained commercially and used without further purification.

Starting Materials. 2,6-Di-*tert*-butyl-4-methylphenol (**6b**) and methyl 2-hydroxy-1-naphthoate (**6l**) were purchased from TCI and used without further purification. **6a**,[9] **6c**–**h**,[10,11] **6m**[12] were prepared by previously reported procedures.

2,6-Di-*tert*-butyl-4-(2-hydroxyethyl)phenol (6a). White solid; TLC, R_f = 0.34 (Hexane–EtOAc = 4:1); IR (KBr) 3490, 2952, 1593, 1433, 1194, 1076, 847 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.37–1.41 (m, 1H), 1,44 (s, 18H), 2.79 (t, J = 6.4 Hz, 2H), 3.83 (q, J = 6.4 Hz, 2H), 5.10 (s, 1H), 7.02 (s, 2H); ^{13}C NMR

($CDCl_3$, 100 MHz) δ 30.3, 34.3, 39.1, 64.0, 125.5, 128.7, 136.1, 152.4; HRMS (FAB+) *m*/*z* calcd for $[C_{16}H_{26}O_2+H]^+$ 251.2011, found 251.2014.

4-[(*tert*-Butyldiphenylsilyl)oxy]-2,3,6-trimethylphenol (6c).[10] Colorless oil; TLC, R_f = 0.29 (Hexane–EtOAc = 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.09 (s, 9H), 1.85 (s, 3H), 2.18 (s, 3H), 2.29 (s, 3H), 4.14 (s, 1H), 6.07 (s, 1H), 7.33–7.43 (m, 6H), 7.70–7.73 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 12.4, 13.0, 15.8, 19.6, 26.7, 117.6, 119.7, 123.2, 125.1, 127.7, 129.7, 133.4, 135.5, 145.8, 146.9.

1-Methylnaphthalen-2-ol (6d).[11] White solid; TLC, R_f = 0.40 (Hexane–EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.54 (s, 3H), 4.81 (s, 1H), 7.07 (d, *J* = 8.7 Hz, 1H), 7.32–7.34 (m, 1H), 7.49–7.51 (m, 1H), 7.63 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.4, 115.2, 117.5, 123.1, 126.3, 127.3, 128.4, 129.2, 133.8, 150.4.

3-Chloro-1-methylnaphthalen-2-ol (6e).[11] White solid; TLC, R_f = 0.29 (Hexane–EtOAc = 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.60 (s, 3H), 5.77 (s, 1H), 7.34–7.38 (m, 1H), 7.47–7.51 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.75 (s, 1H), 7.90 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.3, 117.8, 121.7, 123.4, 124.1, 125.2, 126.4, 127.5, 128.7, 132.7, 146.0.

3-Bromo-1-methylnaphthalen-2-ol (6f).[11] White solid; TLC, R_f = 0.39 (Hexane–EtOAc = 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.62 (s, 3H), 5.70 (s, 1H), 7.33–7.37 (m, 1H), 7.48–7.52 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.88–7.91 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 11.5, 112.6, 117.5, 123.2, 123.8, 126.4, 127.3, 128.5, 129.2, 133.0, 146.3.

3-Iodo-1-methylnaphthalen-2-ol (6g).[11] Yellow solid; TLC, R_f = 0.38 (Hexane–EtOAc = 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.63 (s, 3H), 5.39 (s, 1H), 7.31–7.35 (m, 1H), 7.48–7.52 (m, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 8.15 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 12.0, 89.2, 116.6, 123.3, 123.7, 126.7, 127.2, 130.2, 133.8, 135.8, 148.2.

1-Methyl-3-phenylnaphthalen-2-ol (6h).[11] White solid; TLC, R_f = 0.39 (Hexane–EtOAc = 10:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.62 (s, 3H), 5.33 (s, 1H), 7.34–7.38 (m, 1H), 7.45–7.60 (m, 7H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.9, 116.2, 123.1, 123.4, 126.2, 127.1, 128.2, 128.4, 128.7, 129.3, 129.4, 130.1, 133.6, 137.2, 147.9.

1-Methyl-3-(phenylethynyl)naphthalen-2-ol (6i).[11] Brown oil; TLC, R_f = 0.44 (Hexane–EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.59 (s, 3H), 6.02 (s, 1H), 7.33–7.37 (m, 1H), 7.40–7.41 (m, 3H), 7.48–7.52 (m, 1H), 7.58–7.60 (m, 2H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.89–7.91 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.8, 83.7, 96.4, 111.3, 115.6, 122.2, 123.2, 123.6, 127.1, 128.2, 128.3, 128.5, 128.9, 129.9, 131.7, 134.1, 149.6.

3-(2-Hydroxynaphthalen-1-yl)propanoic acid (6m). White solid; TLC, R_f = 0.52 (Hexane–EtOAc–$CHCl_3$ = 1:2:1 with a few drops of AcOH); IR (KBr) 3500–3000, 1714, 1517, 1406, 1319, 1193 cm^{-1}; ^{1}H

NMR ($CDCl_3$, 400 MHz) δ 2.95 (t, *J* = 6.4 Hz, 2H), 3.33 (t, *J* = 6.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.35 (t, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.4, 33.5, 117.9, 119.4, 122.0, 123.2, 126.7, 128.7, 128.9, 129.5, 132.7, 151.6, 180.4; HRMS (FAB) *m*/*z* calcd for $[C_{13}H_{13}O_3+H]^+$ 217.0865, found 217.0868.

Methyl 3-(3-hydroxy-4-methylnaphthalen-2-yl)propanoate (6j). To a solution of 3-(methoxymethoxy)-4-methyl-2-naphthaldehyde[13] (0.283 g, 1.23 mmol) in toluene (2.50 mL) was added methyl (triphenylphosphoranylidene)acetate (0.495 g, 1.48 mmol) at room temperature. The reaction mixture was stirred at 80 ºC for 2 h. The resulting mixture was cooled to 0 ºC and the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (eluent: Hexane-EtOAc = 20:1) to give desired ester. To a stirring mixture of unsaturated ester in MeOH (4.10 mL) was added 10% palladium on carbon (0.0150 g) at room temperature. The flask was shortly evacuated and a balloon filled with hydrogen put on it. The reaction mixture was stirred at 25 °C for 3 h. The resulting mixture was filtered through a plug of tightly packed celite on a sintered glass funnel, which was successively washed with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo*. Without further purification, the residue was dissolved in EtOH (4.10 mL) and $TsOH{\cdot}H_2O$ (0.117 g, 0.615 mmol) was added. After stirring for 12 h at 50 ºC, the resulting mixture was poured into water (15.0 mL), and the aqueous layers were extracted with EtOAc. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvents were removed in *vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: Hexane-EtOAc = 10:1 to 4:1) to give **6j** (0.105 g, 0.431 mmol, 35% yield for 3 steps). White solid; TLC, R_f = 0.26 (Hexane–EtOAc = 4:1); IR (KBr) 3462, 1718, 1627, 1400, 1308, 1188, 1150 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.58 (s, 3H), 2.82 (t, *J* = 6.9 Hz, 2H), 3.10 (t, *J* = 6.9 Hz, 2H), 3.69 (s, 3H), 7.09 (s, 1H), 7.28–7.33 (m, 1H), 7.41–7.45 (m, 1H), 7.48 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 10.6, 25.4, 34.6, 51.7, 116.6, 122.8, 122.9, 125.3, 126.6, 127.6, 128.8, 129.3, 132.6, 149.8, 175.4; HRMS (FAB+) *m*/*z* calcd for $[C_{15}H_{16}O_3+Na]^+$ 267.0997, found 267.1002.

3-(2-Hydroxyethyl)-1-methylnaphthalen-2-ol (6k). To a solution of 3-bromo-2-(methoxymethoxy)-1-methylnaphthalene[11] (0.281 g, 1.00 mmol) in Et_2O (5.00 mL) was added *n*-BuLi (0.688 mL, 1.10 mmol, 1.60 *M* in hexane) at –78 ºC. After stirring for 1 h, to the resulting mixture was added oxirane (2.00 mL, 2.00 mmol, 1.0 *M* in toluene) at –78 ºC. The reaction mixture was allowed to room temperature. After stirring for 12 h, the resulting mixture was quenched by aqueous ammonium chloride, and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed *in vacuo*. Without further purification, the residue was dissolved in EtOH (4.00 mL) was added $TsOH{\cdot}H_2O$ (0.0951

g, 0.500 mmol). After stirring for 12 h at 50 ºC, the resulting mixture was poured into water (15.0 mL), and the aqueous layers were extracted with EtOAc. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvents were removed in *vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: Hexane-EtOAc = 4:1) to give **6k** (0.0890 g, 0.440 mmol, 44% yield for 2 steps). White solid; TLC, R_f = 0.45 (Hexane–EtOAc = 1:1); IR (KBr) 3377, 2925, 1629, 1456, 1367, 1241, 1033 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.48 (brs, 1H), 2.57 (s, 3H), 3.05–3.11 (m, 2H), 4.02–4.07 (m, 2H), 7.28–7.32 (m, 1H), 7.42–7.46 (m, 2H), 7.70 (d, J = 7.4 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 8.01 (brs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.9, 35.2, 65.0, 117.7 123.0, 123.1, 125.6, 127.4, 127.8, 128.8, 129.1, 133.3, 150.8; HRMS (FAB+) m/z calcd for $[C_{13}H_{14}O_2+H]^+$ 203.1072, found 203.1077.

Typical Procedure for the Peroxidative Dearomatization of 6 to 7.

2,6-Di-*tert*-butyl-4-(2-hydroxyethylidene)cyclohexa-2,5-dien-1-one (7a). To a solution of **6a** (0.250 g, 1.00 mmol) and tetrabutylammonium iodide (0.0369 g, 0.100 mmol, 10 mol%) in 1,2-dichloroethane (100 mL) was added *tert*-butyl hydroperoxide (1.81 mL, 10.0 mmol, 5.5 *M* in nonane) at room temperature. The reaction was monitored by TLC analysis. After 36 h, the resulting mixture was cooled to 0 °C and quenched by saturated aqueous $NaHSO_3$ (20 mL). The aqueous layers were separated and extracted with $CHCl_3$ (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, and then the solvents were removed in *vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: Hexane–EtOAc = 10:1 to 4:1) to give desired **7a** (0.325 g, 0.960 mmol, 96% yield). Pale yellow oil; TLC, R_f = 0.43 (Hexane–EtOAc = 4:1); IR (neat) 3486, 2368, 1667, 1646, 1363, 1196, 1047 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.21 (s, 9H), 1.24 (s, 18H), 1.72–7.75 (m, 1H), 1.98 (t, J = 6.4 Hz, 2H), 3.63–3.68 (m, 2H), 6.63 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.4, 29.3, 34.8, 40.2, 58.4, 78.3, 79.8, 140.3, 147.4, 186.6; HRMS (FAB+) m/z calcd for $[C_{20}H_{34}O_4+H]^+$ 339.2535, found 339.2531.

2,6-Di-*tert*-butyl-4-(*tert*-butylperoxy)-4-methylcyclohexa-2,5-dien-1-one (7b).[3b] Typical procedure (1 mmol scale, room temperature). Yellow solid; TLC, R_f = 0.35 (Hexane–EtOAc = 10:1); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.19 (s, 9H), 1.23 (s, 18H), 1.33 (s, 3H), 6.56 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.2, 26.5, 29.4, 34.7, 76.2, 79.3, 141.8, 146.6, 186.7.

4-[(*tert*-Butyldiphenylsilyl)oxy]-6-(*tert*-butylperoxy)-2,3,6-trimethylcyclohexa-2,4-dien-1-one (7c). Typical procedure (0.1 mmol scale, room temperature). Only one regiomer was observed. An NOE interaction between H5 and protons of 6-Me group confirmed the regioselectivity of the peroxidative dearomatization reaction. Colorless oil; TLC, R_f = 0.41 (Hexane–EtOAc = 10:1); IR (neat) 2976, 1650, 1428, 1362, 1195, 1112cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.04 (s, 9H), 1.29 (s, 9H), 1.42 (s, 3H), 1.61 (s, 3H), 2.03 (s, 3H), 6.66 (s, 1H), 7.24 (t, J = 6.9 Hz, 2H), 7.32–7.46 (m, 4H), 7.52 (d, J = 8.2 Hz, 2H),

7.84 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.8, 14.2, 15.4, 19.6, 26.7, 27.0, 80.6, 95.8, 127.1, 127.2, 129.6, 129.9, 131.9, 132.7, 133.4, 133.9, 135.6, 135.9, 139.0, 147.1, 184.9; HRMS (FAB+) *m*/*z* calcd for $[C_{29}H_{38}O_4Si+H]^+$ 479.2618, found 479.2608.

1-(*tert*-Butylperoxy)-1-methylnaphthalen-2(1*H*)-one (7d). Typical procedure (0.1 mmol scale, 50 °C). White solid; TLC, R_f = 0.33 (Hexane–EtOAc = 10:1); IR (KBr) 2980, 1684, 1619, 1447, 1363, 1242cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16 (s, 9H), 1.44 (s, 3H), 6.17 (d, *J* = 10.1 Hz, 1H), 7.29–7.35 (m, 2H), 7.39 (d, *J* = 9.6 Hz, 1H), 7.43 (dd, *J* = 2.3, 7.8 Hz, 1H), 7.63–7.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.5, 26.7, 79.9, 82.4, 124.9, 126.9, 127.7, 129.0, 129.8, 129.9, 144.4, 144.7, 199.5; HRMS (FAB+) *m*/*z* calcd for $[C_{15}H_{18}O_3+H]^+$ 247.1334, found 247.1339.

1-(*tert*-Butylperoxy)-3-chloro-1-methylnaphthalen-2(1*H*)-one (7e). Typical procedure (0.1 mmol scale, 50 °C). Yellow solid; TLC, R_f = 0.43 (Hexane–EtOAc = 10:1); IR (KBr) 2998, 1687, 1363, 1248, 1190, 1081 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16 (s, 9H), 1.48 (s, 3H), 7.27 (dd, *J* = 0.9, 7.8 Hz, 1H), 7.34 (dt, *J* = 1.4, 7.3 Hz, 1H), 7.45 (dt, *J* = 1.4, 7.3 Hz, 1H), 7.60 (s, 1H), 7.61 (dd, *J* = 0.9, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.5, 27.0, 80.4, 84.1, 127.0, 128.2, 128.7, 128.8, 129.4, 130.1, 142.1, 143.3, 192.6; HRMS (FAB+) *m*/*z* calcd for $[C_{15}H_{17}ClO_3+H]^+$ 281.0944, found 281.0944.

3-Bromo-1-(*tert*-butylperoxy)-1-methylnaphthalen-2(1*H*)-one (7f). Typical procedure (0.1 mmol scale, 50 °C). Brown solid; TLC, R_f = 0.42 (Hexane–EtOAc = 10:1); IR (KBr) 2981, 1685, 1604, 1553, 1458, 1356 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16 (s, 9H), 1.48 (s, 3H), 7.27 (dd, *J* = 0.9, 7.8 Hz, 1H), 7.34 (dt, *J* = 1.4, 7.3 Hz, 1H), 7.46 (dt, *J* = 1.4, 7.3 Hz, 1H), 7.62 (dd, *J* = 0.9, 7.8 Hz, 1H), 7.85 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.5, 27.1, 80.4, 84.0, 121.1, 127.0, 128.2, 128.7, 129.6, 130.3, 143.6, 146.2, 192.5; HRMS (FAB+) *m*/*z* calcd for $[C_{15}H_{17}BrO_3+H]^+$ 325.0439, 327.0419, found 325.0436, 327.0395.

1-(*tert*-Butylperoxy)-3-iodo-1-methylnaphthalen-2(1*H*)-one (7g). Typical procedure (0.1 mmol scale, 50 °C). Yellow solid; TLC, R_f = 0.49 (Hexane–EtOAc = 10:1); IR (KBr) 2980, 1688, 1440, 1368, 1188 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16 (s, 9H), 1.47 (s, 3H), 7.23–7.25 (m, 1H), 7.33 (dt, *J* = 1.4, 7.8 Hz, 1H), 7.46 (dt, *J* = 1.4, 7.8 Hz, 1H), 7.61–7.64 (m, 1H), 8.15 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.5, 27.2, 80.4, 82.9, 100.4, 126.9, 128.0, 128.5, 130.4, 130.9, 144.2, 153.7, 193.5; HRMS (FAB+) *m*/*z* calcd for $[C_{15}H_{17}IO_3+H]^+$ 373.0301, found 373.0307.

1-(*tert*-Butylperoxy)-1-methyl-3-phenylnaphthalen-2(1*H*)-one (7h). Typical procedure (0.1 mmol scale, room temperature). Pale yellow oil; TLC, R_f = 0.48 (Hexane–EtOAc = 10:1); IR (neat) 2979, 1685, 1491, 1363, 1195, 1082, 759 cm^{-1}; ^{1}H NMR (CD_3OD, 400 MHz) δ 1.17 (s, 9H), 1.51 (s, 3H), 7.35–7.43 (m, 4H), 7.45–7.52 (m, 4H), 7.65–7.68 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.6, 80.0, 83.5, 126.6, 127.9, 128.1, 128.2, 128.6, 129.2, 129.5, 130.2, 135.1, 135.5, 141.5, 143.6, 198.1; HRMS (FAB+)

m/*z* calcd for $[C_{21}H_{22}O_3+H]^+$ 323.1647, found 323.1653.

1-(*tert*-Butylperoxy)-1-methyl-3-(phenylethynyl)naphthalen-2(1*H*)-one (7i). Typical procedure (0.1 mmol scale, room temperature). Pale yellow oil; TLC, R_f = 0.41 (Hexane–EtOAc = 4:1); IR (neat) 2979, 2207, 1692, 1490, 1363, 1195, 757 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.19 (s, 9H), 1.49 (s, 3H), 7.31–7.37 (m, 5H), 7.42–7.47 (m, 1H), 7.56–7.58 (m, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.70 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.5, 27.0, 80.2, 83.1, 84.3, 95.0, 120.3, 122.8, 126.8, 128.0, 128.3, 128.6, 129.2, 129.6, 130.3, 131.9, 144.1, 147.0, 195.9; HRMS (FAB+) *m*/*z* calcd for $[C_{23}H_{22}O_3+H]^+$ 347.1647, found 347.1642.

Methyl 3-[4-(*tert*-butylperoxy)-4-methyl-3-oxo-3,4-dihydronaphthalen-2-yl]propanoate (7j). Typical procedure (0.1 mmol scale, room temperature). Pale yellow oil; TLC, R_f = 0.19 (Hexane–EtOAc = 10:1); IR (neat) 2980, 1739, 1679, 1438, 1363, 1245, 1198 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.13 (s, 9H), 1.41 (s, 3H), 2.53–2.60 (m, 2H), 2.64–2.82 (m, 2H), 3.65 (s, 3H), 7.23–7.32 (m, 3H), 7.38 (dt, *J* = 1.8, 7.3 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.4, 26.5, 26.6, 32.7, 51.5, 79.9, 82.4, 126.6, 127.7, 128.5, 129.1, 129.9, 134.3, 141.5, 143.6, 173.4, 198.9; HRMS (FAB+) *m*/*z* calcd for $[C_{19}H_{24}O_5+H]^+$ 333.1702, found 333.1709.

1-(*tert*-Butylperoxy)-3-(2-hydroxyethyl)-1-methylnaphthalen-2(1*H*)-one (7k). Typical procedure (0.1 mmol scale, room temperature). Pale yellow oil; TLC, R_f = 0.38 (Hexane–EtOAc = 1:1); IR (neat) 3429, 2979, 1675, 1363, 1197, 1042, 758 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.15 (s, 9H), 1.45 (s, 3H), 2.13 (brs, 1H), 2.63–2.74 (m, 2H), 3.75–3.84 (m, 2H), 7.25–7.28 (m, 2H), 7.31 (dt, *J* = 1.4, 7.4 Hz, 1H), 7.39 (dt, *J* = 1.4, 7.4 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.3, 26.5, 33.7, 61.9, 80.1, 82.4, 126.8, 127.9, 128.6, 129.2, 133.3, 142.8, 143.4, 200.3; HRMS (FAB+) *m*/*z* calcd for $[C_{17}H_{22}O_4+H]^+$ 291.1596, found 291.1586.

Methyl 1-(*tert*-butylperoxy)-2-oxo-1,2-dihydronaphthalene-1-carboxylate (7l).[4] Typical procedure (1 mmol scale, room temperature). White solid; TLC, R_f = 0.33 (Hexane–EtOAc = 4:1); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.14 (s, 9H), 3.64 (s, 3H), 6.23 (d, *J* = 10.1 Hz, 1H), 7.32–7.35 (m, 1H), 7.38–7.44 (m, 3H), 7.61–7.63 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.3, 52.9, 81.1, 83.9, 125.0, 128.2, 129.3, 129.4, 130.0, 130.6, 137.4, 145.2, 166.3, 193.3.

1-Methyl-1-[(1-methylnaphthalen-2-yl)oxy]naphthalen-2(1*H*)-one (8). Pale yellow solid; TLC, R_f = 0.38 (Hexane–EtOAc = 4:1); IR (KBr) 3439, 2920, 1690, 1238, 1149, 1082 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.83 (s, 3H), 2.76 (s, 3H), 6.01 (d, *J* = 9.2 Hz, 1H), 6.38 (d, *J* = 10.3 Hz, 1H), 7.23–7.33 (m, 4H), 7.41–7.46 (m, 3H), 7.58–7.62 (m, 2H), 7.96 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.1, 31.7, 82.0, 115.7, 119.8, 123.2, 123.4, 125.0, 125.7, 126.0, 126.2, 128.1, 128.2, 128.7, 129.3, 129.8, 130.9, 133.8, 144.5, 145.0, 150.2, 200.0; HRMS (FAB+) *m*/*z* calcd for $[C_{22}H_{18}O_2+H]^+$ 315.1385, found

315.1384.

Procedure for Oxidative Spirolactonization of 6m.

2'*H*,3*H*-Spiro[furan-2,1'-naphthalene]-2',5(4*H*)-dione (9). To a solution of **6m** (0.0216 g, 0.100 mmol) and tetrabutylammonium iodide (0.00369 g, 0.0100 mmol, 10 mol%) in 1,2-dichloroethane (10.0 mL) was added *tert*-butyl hydroperoxide (0.181 mL, 10.0 mmol, 5.5 *M* in nonane) at room temperature. The reaction mixture was stirred at 50 °C for 6 h. The resulting mixture was cooled to 0 °C and quenched by saturated aqueous $NaHSO_3$ (5 mL). The aqueous layers were separated and extracted with $CHCl_3$ (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, and then the solvents were removed in *vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: Hexane–EtOAc = 4:1) to give desired **9** (0.0325 g, 0.0900 mmol, 90% yield). White solid; TLC, R_f = 0.70 (Hexane–EtOAc = 1:2); IR (film) 1786, 1685, 1210, 1171, 1039 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.11–2.20 (m, 1H), 2.62–2.70 (m, 2H), 2.81–2.91 (m, 1H), 6.18 (d, *J* = 9.6 Hz, 1H), 7.36 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.41 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.46–7.50 (m, 2H), 7.56 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.5, 35.7, 85.8, 122.4, 125.6, 129.0, 129.1, 129.7, 131.0, 140.4, 146.0, 176.4, 197.5; HRMS (FAB+) *m*/*z* calcd for $[C_{13}H_{11}O_3+H]^+$ 215.0708, found 215.0712.

Procedure for Epoxidation of 7d with TBHP.

(1a*R,3*R**,7b*R**)-3-(*tert*-Butylperoxy)-3-methyl-3,7b-dihydronaphtho[1,2-*b*]oxiren-2(1a*H*)-one (10).** To a solution of **7d** (0.246 g, 1.00 mmol) in benzene (20 mL) was added benzyltrimethylammonium hydroxide (Triton B, 0.220 mL, 0.500 mmol, 40% MeOH solution) and *tert*-butyl hydroperoxide (0.138 mL, 1.00 mmol, 70% aqueous solution) at 0 ºC. The resulting mixture was stirred at 0 °C for 30 min. The reaction mixture was allowed to warm to room temperature and stirred continually for an additional 1 h followed by another addition of benzyltrimethylammonium hydroxide (0.220 mL, 0.500 mmol, 40% MeOH solution) and *tert*-butyl hydroperoxide (0.138 mL, 1.00 mmol, 70% aqueous solution). After stirring for 1 h at room temperature, the resulting mixture was cooled to 0 °C and quenched by saturated aqueous $NaHSO_3$ (50 mL). The aqueous layers were separated and extracted with CH_2Cl_2 (twice). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, and then the solvents were removed in *vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: Hexane–EtOAc = 10:1) to give desired **10** (0.189 g, 0.720 mmol, 72% yield). White solid; TLC, R_f = 0.48 (Hexane–EtOAc = 10:1); IR (KBr) 2983, 1731, 1462, 1362, 1194, 1151, 1013 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.19 (s, 9H), 1.56 (s, 3H), 3.76 (d, *J* = 4.0 Hz, 1H), 4.23 (d, *J* = 4.0 Hz, 1H), 7.34 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.44 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.50 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.59 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 26.4, 27.6, 53.5, 58.3, 79.9, 83.1, 127.4, 127.5, 128.8, 129.2, 130.2, 141.2, 202.9; HRMS (FAB+) *m*/*z* calcd for $[C_{15}H_{18}O_4+Na]^+$ 285.1103, found 285.1098.

X-Ray Diffraction Analysis of (±)-10. X-Ray crystallographic analysis was performed with a Rigaku PILATUS-200K diffractometer (graphite monochromator, MoKa radiation, λ = 0.71075 Å) and the structure was solved by direct methods and expanded using Fourier techniques (Sir97 and SHELXL).[14] Recrystallization of **10** was carried out in the solution of CH_2Cl_2/pentane at –20 °C. Mp 114 °C. Formula $C_{15}H_{18}O_4$, colorless, crystal dimensions 0.70 × 0.50 × 0.20 mm^3, triclinic, space group *P-1 (#2)*, a = 8.341(6) Å, b = 9.193(7) Å, c = 9.821(7) Å, α = 107.601(11) °, β = 91.434(14) °, γ = 107.800(7) °, V = 677.7(9) $Å^3$, Z = 2, ρ_{calc} = 1.285 g cm^{-3}, F(000) = 280, μ(MoKα) = 0.0924 mm^{-1}, T = 123 K. 5831 reflections collected, 2905 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 27.51°), and 176 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0522 and wR_2 = 0.1553. GOF = 0.999. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 1506176 for **10**. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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