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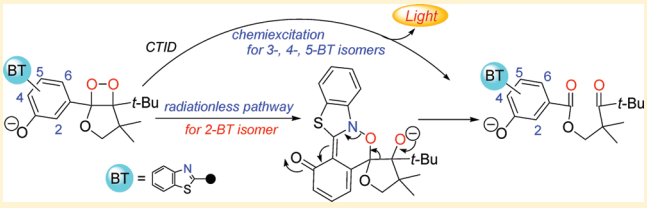
Base-Induced Chemiluminescent Decomposition of Bicyclic Dioxetanes Bearing a (Benzothiazol-2-yl)-3-hydroxyphenyl Group: A Radiationless Pathway Leading to Marked Decline of Chemiluminescence Efficiency

Masatoshi, Tanimura, Nobuko Watanabe, Hisako K. Ijuin, and Masakatsu Matsumoto*

Department of Chemistry, Kanagawa University, Tsuchiya, Hiratsuka, Kanagawa 259-1293, Japan

Supporting Information

ABSTRACT: Charge-transfer-induced decomposition (CTID) of bicyclic dioxetanes **1b–d** bearing a 3-hydroxylphenyl moiety substituted with a benzothiazol-2-yl group at the 2-, 6-, or 5-position was investigated, and their chemiluminescence properties were compared to each other, based on those for a 4-benzothiazolyl analogue **1a**. Dioxetanes **1c** and **1d** underwent CTID to give the corresponding oxido anions of keto esters **8c** or **8d** in the singlet excited state with high efficiencies similarly to the case of **1a**. On the other hand, **1b** showed chemiluminescence with quite low efficiency, though it gave exclusively keto ester **2b**. The marked decline of chemiluminescence efficiency for **1b** was attributed to **1b** mainly being decomposed to **8b** through a radiationless pathway, in which intramolecular nucleophilic attack of nitrogen in the benzothiazolyl group to dioxetane O–O took place to give cyclic intermediate *cis*-**11**.



INTRODUCTION

Dioxetanes substituted with an aromatic electron donor such as the phenoxide anion undergo intramolecular charge-transfer-induced decomposition (CTID) with an accompanying emission of bright light.[1−4] The phenomenon has received considerable attention from the viewpoints of mechanistic interest related to bioluminescence and application to clinical and biological analysis.[5−7] Thus, up to the present, a wide variety of CTID-active dioxetanes have been designed and synthesized. One such dioxetane is bicyclic dioxetane **1a** bearing a 4-(benzothiazol-2-yl)-3-hydroxyphenyl group, which effectively emits light even in an aqueous system.[8,9] To understand how the benzothiazol-2-yl group functioned to achieve high-performance chemiluminescence, we investigated CTID of three isomeric dioxetanes **1b–d**, in which a benzothiazolyl group was attached at the 2-, 6-, or 5-position on the 3-hydroxyphenyl group. We report here that these isomeric dioxetanes **1b–d** showed characteristic chemiluminescence depending on the structure of the aromatic electron donor, and that a radiationless decomposition of dioxetane **1b** concurrently took place with the chemiluminescent CTID, though both decompositions gave the same keto ester **2b** (Chart 1).

RESULTS AND DISCUSSION

Synthesis of Bicyclic Dioxetanes 1b–d Bearing a 3-Hydroxyphenyl Moiety Substituted with a Benzothiazol-2-yl Group. All of the dioxetanes **1b–d** investigated here were prepared by singlet oxygenation of the corresponding 4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofurans **3b–d** bearing a 5-(3-hydroxyphenyl) group, to which a benzothiazolyl group was attached at the 2-, 5-, or 6-position. These precursors **3b–d** were synthesized according to the synthetic process of **1a**[9] through several steps starting from the corresponding 4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofurans **4b–d** bearing a 5-(formyl-3-methoxyphenyl) group, as illustrated in Scheme 1. The initial step was condensation of **4b–d** with 2-aminobenzenethiol to give exclusively the corresponding benzothiazolinyl derivatives **5b–d**, which were used for the next reaction without further purification. The oxidation of benzothiazolines **5b–d** was achieved by the use of 2,3-dichoro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene to give dihydrofurans **6b–d** in high yields. Dihydrofurans **6b–d** were finally demethylated with sodium methanethiolate in hot DMF to give the desired precursors **3b–d** in 95, 85, and 89% yields, respectively. All of **3b–d** underwent 1,2-addition of singlet oxygen to selectively give the corresponding dioxetanes **1b–d** in 69 (conversion yield 97%), 100, and 98% yields. The structures of dioxetanes **1b–d** were determined by ^{1}H NMR, ^{13}C NMR, IR, mass spectral data, and elemental analyses. Furthermore, X-ray single crystallographic analysis was successfully achieved for all dioxetanes **1b–d**. ORTEP views of dioxetanes **1b–d** are shown in the Supporting Information. All of these benzothiazolyl-substituted dioxetanes **1b–d** were thermally stable enough to permit handling at room temperature, though they decomposed into the corresponding keto esters **2b–d** when heated in refluxing *p*-xylene.

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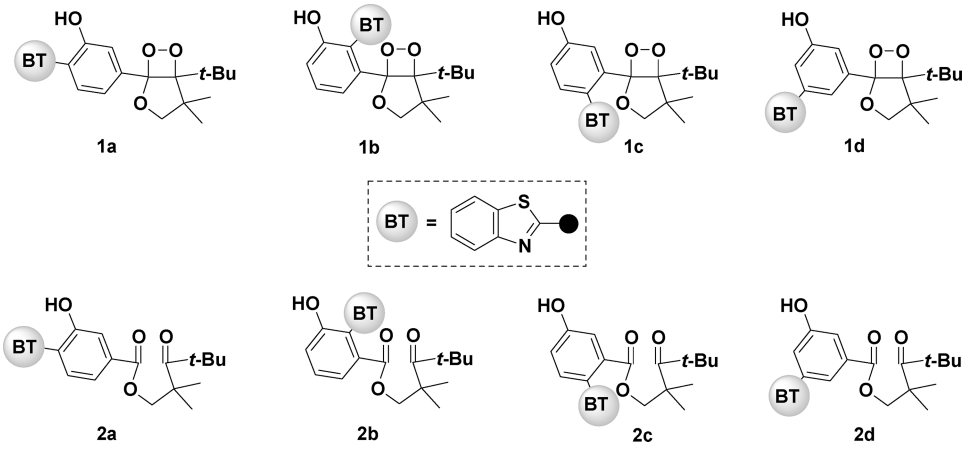
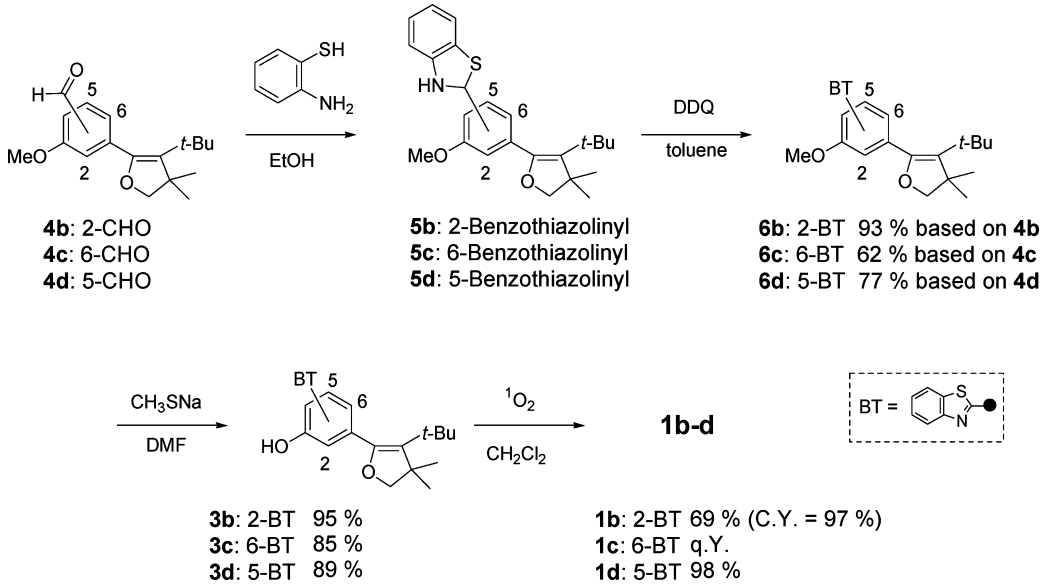
Chart 1. Bicyclic Dioxetanes 1a–d Bearing a 3-Hydroxyphenyl Moiety Substituted with a Benzothiazol-2-yl Group and Their Decomposition Products 2a–d



Scheme 1. Synthetic Pathway of Dioxetanes 1b–d



4b: 2-CHO
4c: 6-CHO
4d: 5-CHO

5b: 2-Benzothiazolinyl
5c: 6-Benzothiazolinyl
5d: 5-Benzothiazolinyl

6b: 2-BT 93 % based on **4b**
6c: 6-BT 62 % based on **4c**
6d: 5-BT 77 % based on **4d**

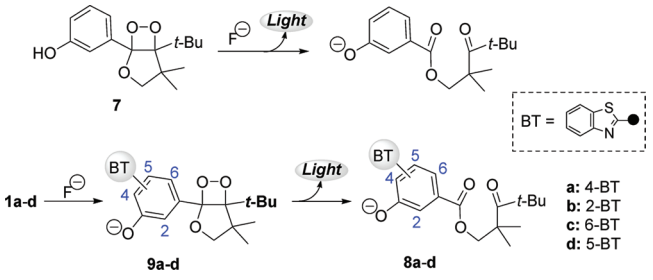
3b: 2-BT 95 %
3c: 6-BT 85 %
3d: 5-BT 89 %

1b: 2-BT 69 % (C.Y. = 97 %)
1c: 6-BT q.Y.
1d: 5-BT 98 %

Chemiluminescent Decomposition of Bicyclic Dioxetanes Bearing a 3-Hydroxyphenyl Moiety Substituted with a Benzothiazol-2-yl Group in a TBAF/Acetonitrile System. Dioxetane **1a** has been reported to decompose according to the pseudo-first-order kinetics to give bright green light (maximum wavelength λ_{max}^{CL} = 492 nm) with chemiluminescence efficiency Φ^{CL} = 0.28 and rate constant of CTID $k^{CTID} = 4.2 \times 10^{-4}$ s^{-1} at 45 °C (half-life $t_{1/2}$ = ln 2/k^{CTID} = 1600 s) when treated with a large excess of tetrabutylammonium fluoride (TBAF) in acetonitrile.[8,9] Comparing chemiluminescence properties for **1a** with those for parent dioxetane **7** bearing an unsubstituted 3-hydroxyphenyl group (λ_{max}^{CL} = 467 nm, Φ^{CL} = 0.11, and $t_{1/2}$ = 25 s in TBAF/acetonitrile at 25 °C) (Scheme 2),[10] we can see that the benzothiazolyl group acts to considerably improve Φ^{CL}, while decreasing $t_{1/2}$ by 2 orders.

Dioxetane **1b** has a π-electron system of *o*-(benzothiazol-2-yl)phenol formally the same as that of **1a**, though the benzothiazolyl group suffers the steric hindrance of the adjacent dioxetane ring and a hydroxy group at the opposite side. On treatment with TBAF (large excess) in acetonitrile at 25 °C, dioxetane **1b** decomposed far more rapidly than **1a** with the

Scheme 2. Base-Induced Decomposition of Dioxetanes 1b–d and 7



accompanying chemiluminescence, the λ_{max}^{CL} of which was the same as that for **1a**, as shown in Table 1, though the spectrum was broader than that for **1a**, as shown in Figure 1. However, Φ^{CL} for **1b** was unexpectedly low (Φ^{CL} = 0.0036)[11,12] and only 1/80 of that for **1a**.

Careful neutralization of the spent reaction mixture of **1b** gave selectively keto ester **2b** as in the case of **1a** giving **2a**. Oxido anion **8b** generated from **2b** in situ in TBAF/acetonitrile showed fluorescence, the spectrum of which practically

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Table 1. TBAF-Induced Chemiluminescence of Dioxetanes 1a–d and 7[a]

dioxetane	λ_{max}^{CL}/nm	Φ^{CL}[b]	Φ^{fl}	Φ_S	k^{CTID}/s^{-1}	$t_{1/2}$/s
1a[c]	492	0.28	0.66	0.42	4.2×10^{-4}	1600
1b	493	0.0036	0.67	0.0054	2.0×10^{-2}	34
1c	528	0.011	0.024	(0.46)	6.9×10^{-5}	11000
1d	535	0.044	0.060	0.73	7.2×10^{-3}	96
7[d]	467	0.11	0.24[e]	0.46	2.8×10^{-2}	25

[a]Unless otherwise stated, reactions were carried out in a TBAF/acetonitrile system at 45 °C. [b]Based on a value reported for the chemiluminescent decomposition of 3-adamantylidene-4-(3-*tert*-butyldimethylsiloxyphenyl)-4-methoxy-1,2-dioxetane in TBAF/DMSO.[11,12] [c]From ref 9. [d]From ref 10. Chemiluminescent decomposition was carried out at 25 °C. [e]From ref 13.

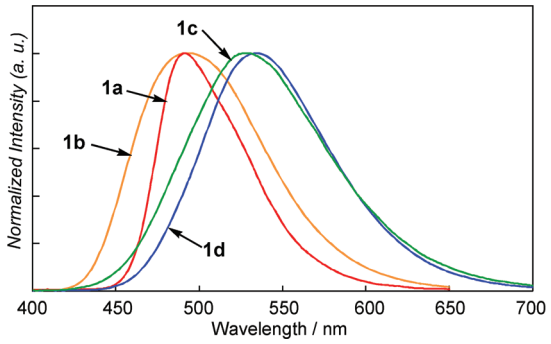

Figure 1. Chemiluminescence spectra of dioxetanes **1a–d**.

coincided with chemiluminescence spectrum of **1b** (Figure 2). This result showed that **8b** was the emitter produced through

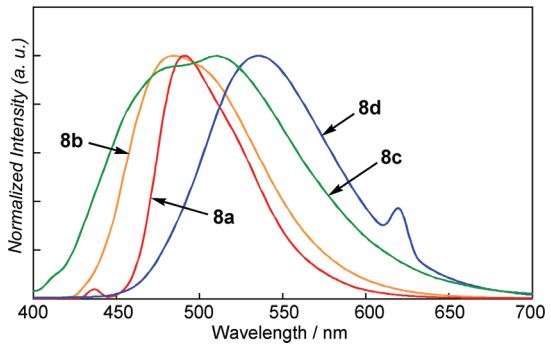

Figure 2. Fluorescence spectra of authentic **8a–d** generated from **2a–d** in TBAF/acetonitrile.

9b from **1b** (Scheme 2). On the basis of fluorescence efficiency Φ^{fl} = 0.67 measured for **8b**, singlet chemiexcitation efficiency Φ_S (=Φ^{CL}/Φ^{fl}) for **1b** was estimated to be only 0.0054 and 1/80 of that for **1a**. Therefore, unexpected decline of Φ^{CL} for **1b** was attributed to quite low Φ_S. Thus, we decided to investigate TBAF-induced decomposition of analogous dioxetanes **1c** and **1d** to understand why **1b** gave such a poor chemiluminescence.

Benzothiazolyl group of dioxetane **1c** lies in a π-conjugation system with a hydroxy group, though at the *para*-position differently from the case of **1a** and **1b**, and receives steric effect of the adjacent dioxetane ring as **1b**. When **1c** was treated in a TBAF/acetonitrile system similarly to the case of **1b**, **1c** showed chemiluminescence, the spectrum of which shifted to a longer wavelength region from the case of **1a** and **1b**, as shown in Figure 1 and Table 1. Value of Φ^{CL} for **1c** was considerably higher than that for **1b**, though the rate of CTID markedly decreased.

Benzothiazolyl group of dioxetane **1d** does not directly lie in π-conjugation system with a hydroxy group and receives steric effect from neither a dioxetane ring nor a hydroxyl group since these three groups are in *meta*-relation among each other. Therefore, the aromatic system of **1d** lies in a different situation from those for **1a**, **1b**, and **1c**. Dioxetane **1d** also underwent TBAF-induced decomposition to give light, the spectrum of which is shown in Figure 1. As shown in Table 1 and Figure 1, comparing that for dioxetane **7** rather than **1a**, the chemiluminescence spectrum shifted to a longer wavelength region, but both Φ^{CL} and k^{CTID} decreased for **1d**: low Φ^{CL} was attributed to low Φ^{fl} of the emitter (vide infra). Such a tendency has been observed for various dioxetanes bearing a 5-aryl-3-hydroxyphenyl group (1,3,5-trisubstitution pattern).[14]

Both dioxetanes **1c** and **1d** gave also the corresponding keto esters **2c** and **2d** in high yields after careful neutralization of spent reaction mixtures, as in the case of **1a** and **1b**. Fluorescence spectrum of authentic emitter **8d** generated from **2d** coincided with the chemiluminescence spectrum of dioxetane **1d** (Figure 2). On the basis of fluorescence efficiency Φ^{fl} (0.060) for **8d**, singlet chemiexcitation efficiency Φ_S for **1d** was estimated to be as high as or rather higher than for **1a**, as shown in Table 1. On the other hand, authentic emitter **8c** generated from **2c** showed fluorescence (Φ^{fl} = 0.024), the spectrum of which did not coincide with the chemiluminescence spectrum of **1c** and showed two peaks, differently from the case of **8a**, **8b**, and **8d** (Figure 2). Notably, the concentration of **8c** did not affect the shape of the spectrum. Thus, the fluorescence spectrum of **8c** was analyzed to comprise two fluorescence spectra: the first coincided with the chemiluminescence spectrum of **1c** (λ_{max}^{fl} = 528 nm), and the second was one with λ_{max}^{fl} = 466 nm (Figure 2 and the Supporting Information). This finding suggests that **8c** should exist as an equilibrium mixture of at least two species.[15] Here, chemiexcitation efficiency Φ_S for **1c** was formally estimated to be as high as that for **1a** (Table 1), though it could not reliably be estimated because of a discrepancy in the spectrum between chemiluminescence of **1c** and the fluorescence of **8c**.

As described above, singlet chemiexcitation effectively occurred for CTID of **1a**, **1c**, and **1d** but not for **1b**. Considering that **1a** and **1b** both have an *ortho*-benzothiazolyl-substituted phenol group as an important aromatic electron donor as well as a fluorophore and that the authentic emitters **8a** and **8b** both effectively show fluorescence, the marked decrease in Φ_S for CTID of **1b** was unexpected. Thus, we thought that **1b** may decompose to keto ester **8b** through a new concurrent pathway(s) that did not lead to chemiluminescence. A clue to understanding this radiationless decomposition was found when we measured the melting point of **1b**.

After a sample of crystalline **1b** was heated to melting (100 °C), we found the unusual decomposition product *trans*-**10** in addition to intact dioxetane **1b** and keto ester **2b**. Chromatographic purification (SiO_2) gave crystalline *trans*-**10**, the structure of which was determined by X-ray single crystallographic analysis (Supporting Information). However, the ^{1}H NMR and ^{13}C NMR spectra of pure *trans*-**10** could not be measured because of its instability: *trans*-**10** was contaminated by ca. 10% of keto ester **2b**. Notably, crystalline **1a**, **1c**, and **1d** exclusively gave the corresponding keto esters **2a**, **2c**, and **2d** when heated to melting.

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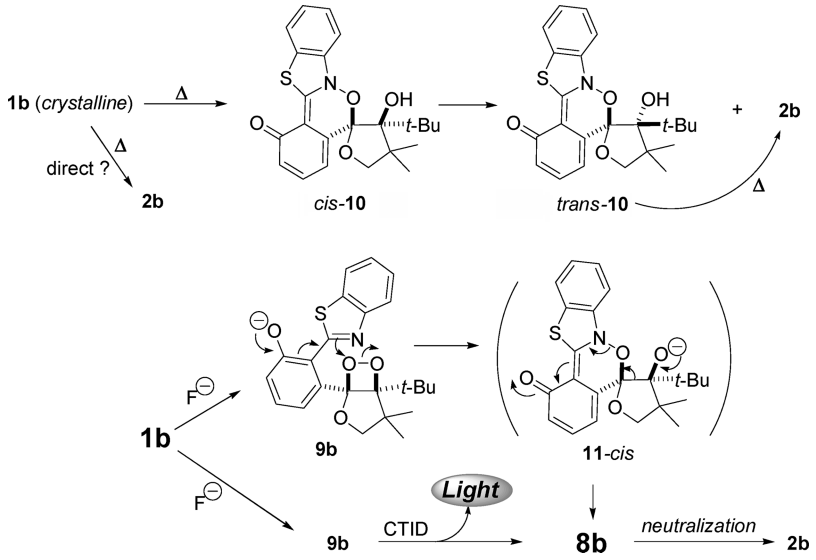
Scheme 3. Radiationless Decomposition of Dioxetane 1b to Keto Ester 2b



The unusual decomposition product *trans*-**10** was thought to be derived from an intramolecular redox reaction between the benzothiazolyl nitrogen and the O−O in dioxetane **1b**. A redox reaction between an amine and a dioxetane has been reported by Adam and his co-workers: a *primary* or *secondary* amine attacks a dioxetane to give the corresponding 2-aminooxyethanol, while *tertiary* amine catalyzes the decomposition of dioxetane to two carbonyl fragments through an as-yet-undetected aminooxy intermediate.[16] Thus, *trans*-**10** was the first example of an aminooxy intermediate for the *tert*-amine-catalyzed decomposition of dioxetane. In fact, when heated at >100 °C, *trans*-**10** changed exclusively to **2b**. However, such a redox reaction would directly give isomeric *cis*-**10** but not *trans*-**10**. Although product *cis*-**10** could not be isolated in pure form after thermolysis of crystalline **1b** (vide infra),[17] its structure was fortunately determined by X-ray single crystallographic analysis of a eutectic crystal of **1b** and *cis*-**10** (1:1) obtained during the recrystallization of **1b** (Supporting Information).

The results described above encouraged us to investigate whether or not **1b** produced **10** or its anion *cis*-**11** even in TBAF/acetonitrile. Upon treatment with even only 1 equiv of TBAF in acetonitrile at 45 °C, **1b** exclusively gave **2b** after 30 min. However, when the amount of TBAF was further decreased to 0.3 equiv, **1b** was found to produce *cis*-**10** (29%) and **2b** (64%) along with a trace amount of **1b** and *trans*-**10** after 10 h. Thus, *cis*-**10** contaminated with ca. 10% of **2b** was obtained as yellow crystals by rinsing from a reaction mixture after usual workup. The product *cis*-**10** was, of course, rapidly and exclusively transformed to **2b** on further treatment with TBAF.

The results described above showed that the decomposition of **9b** (oxido anion of **1b**) to **8b** (isolated as **2b**) through intermediate *cis*-**11** (isolated as *cis*-**10**) should occur concurrently with chemiluminescent CTID to give **8b** in TBAF/acetonitrile. Scheme 3 offers a plausible process, in which nucleophilic attack of the nitrogen in the benzothiazolyl group takes place on O−O of dioxetane **9b** to give intermediate *cis*-**11**, which spontaneously undergoes cleavage of a C−C bond of the tetrahydrofuran ring to finally give keto ester **8b**. This process would not cause chemiexcitation of any carbonyl fragment, in contrast to CTID of **9b**. Hence, the base-induced decomposition of **1b** gave only weak light.

CONCLUSION

CTID of bicyclic dioxetanes **1b−d** bearing a benzothiazolyl-substituted 3-hydroxylphenyl group was investigated, and their chemiluminescence properties were compared, based on those for **1a**. While dioxetanes **1c** and **1d** underwent CTID to give the corresponding keto esters **8c** and **8d** in a singlet excited state with high efficiencies as with **1a**, **1b** led to singlet chemiexcitation with quite low efficiency. The unusually low singlet chemiexcitation efficiency for **1b** was attributed to the decomposition of oxido anion **9b** to **8b** mainly through a radiationless pathway in which intramolecular nucleophilic attack of the nitrogen of benzothiazolyl group took place on the dioxetane O−O to give *cis*-**11**.

EXPERIMENTAL SECTION

General. Melting points were uncorrected. IR spectra were taken on a FT/IR infrared spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a 400 and 500 MHz spectrometers. Mass spectra were obtained by using double-focusing mass spectrometers and an ESI-TOF mass spectrometer. X-ray diffraction data were collected on a CCD diffrectometer with graphite monochromated MoKα (λ=0.71070 Å) radiation. Column chromatography was carried out using silica gel.

4-*tert*-Butyl-5-(2-formyl-3-methoxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (4b): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.01 (s, 9H), 1.35 (s, 6H), 3.92 (s, 2H), 3.93 (s, 3H), 6.94 (dd, J = 7.6 and 1.0 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 7.48 (dd, J = 8.4 and 7.6 Hz, 1H), 10.35 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 27.0, 32.0, 32.5, 47.2, 55.9, 83.5, 112.1, 123.5, 124.0, 127.1, 134.1, 140.0, 146.1, 160.6, 190.8 ppm; IR (liquid film) ν 2957, 2867, 2762, 1698, 1652, 1587, 1577 cm^{-1}; mass (m/z, %) 288 (M^+, 8), 273 (12), 232 (16), 231 (100), 217 (24), 201 (17), 189 (11), 163 (11); HRMS (ESI) 311.1656, calcd for $C_{18}H_{24}O_3Na$ [M + Na^+] 311.1623.

4-*tert*-Butyl-5-(2-formyl-5-methoxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (4c): Colorless plates, mp 61.5−62.0 °C (from hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 1.03 (s, 9H), 1.37 (s, 6H), 3.89 (s, 3H), 3.94 (s, 2H), 6.84 (d, J = 2.4 Hz, 1H), 6.97 (dd, J = 8.8 and 2.4 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 10.04 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 27.1, 32.1, 32.5, 47.4, 55.5, 83.4, 114.7, 116.1, 128.0, 129.0, 129.1, 141.7, 144.9, 163.5, 190.5 ppm; IR (KBr) ν 2981, 2861, 2763, 1655, 1690, 1601 cm^{-1}; mass (m/z, %) 288 (M^+, 7),

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233 (58), 232 (16), 231 (68), 217 (35), 201 (17), 189 (17), 163 (100); HRMS (ESI) 311.1613, calcd for $C_{18}H_{24}O_3Na$ [M + Na^+] 311.1623.

4-*tert*-Butyl-5-(3-formyl-5-methoxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (4d): Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.06 (s, 9H), 1.35 (s, 6H), 3.87 (s, 3H), 3.89 (s, 2H), 7.11 (s with fine coupling, 1H), 7.35 (s with fine coupling, 1H), 7.41 (s, 1H), 9.96 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 27.3, 32.5, 32.6, 47.3, 55.6, 83.3, 112.0, 122.8, 125.2, 126.8, 137.4, 138.4, 148.2, 159.8, 191.8 ppm; IR (liquid film) ν 2958, 2868, 2729, 1700, 1463, 1335, 1054 cm^{-1}; mass (*m*/*z*, %) 288 (M^+, 24), 274 (19), 273 (100), 217 (14), 163 (32); HRMS (ESI) 311.1653, calcd for $C_{18}H_{24}O_3Na$ [M + Na^+] 311.1623.

Synthesis of 5-[2-(Benzothiazol-2-yl)-3-methoxyphenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (6b). Typical Procedure: A solution of 4-*tert*-butyl-5-(2-formyl-3-methoxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (**4b**) (7.12 g, 24.7 mmol) and 2-aminobenzenethiol (2.90 mL, 27.2 mmol, 1.1 equiv) in dry EtOH (140 mL) was mixed under a nitrogen atmosphere at room temperature and stirred for 5 h. The reaction mixture was concentrated in vacuo to give 10.5 g of crude 4-*tert*-butyl-5-[2-(2,3-dihydrobenzothiazol-2-yl)-3-methoxyphenyl]-3,3-dimethyl-2,3-dihydrofuran **5b** as a pale yellow oil. The crude **5b** was used for the next reaction without further purification.

A solution of crude **5b** and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (5.60 g, 24.7 mmol, 1.00 equiv) in dry toluene (80 mL) was refluxed for 50 min. After cooling, the reaction mixture was filtered and concentrated in vacuo. The residue was chromatographed on silica gel and eluted with AcOEt−hexane (1:4) to give 9.01 g of 5-[2-(benzothiazol-2-yl)-3-methoxyphenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**6b**) as a colorless solid in 93% yield based on **4b**.

According to the procedure described above, 5-[2-(benzothiazol-2-yl)-5-methoxyphenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**6c**) and 5-[3-(benzothiazol-2-yl)-5-methoxyphenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**6d**) were synthesized by using the corresponding benzaldehydes **4c** and **4d** instead of **4b** in 62 and 77% yield, respectively.

6b: Colorless granules, mp 120.0−120.5 °C (from AcOEt−hexane); ^1H NMR (400 MHz, $CDCl_3$) δ_H 0.88 (s, 9H), 0.75−1.40 (m, 6H), 3.77 (s, 2H), 3.82 (s, 3H), 6.98−7.04 (m, 2H), 7.38 (ddd, *J* = 7.9, 7.2, and 1.2 Hz, 1H), 7.41 (dd, *J* = 8.3 and 7.8 Hz, 1H), 7.47 (ddd, *J* = 8.2, 7.2, and 1.2 Hz, 1H), 7.92 (d with fine coupling, *J* = 7.9 Hz, 1H), 8.09 (d with fine coupling, *J* = 8.2 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 26.9 (broad), 31.7, 32.4, 46.7, 56.0, 82.8, 111.3, 121.1, 123.1, 123.2, 123.6, 124.7, 125.5, 126.1, 130.4, 136.4, 137.9, 146.7, 152.9, 157.5, 162.6 ppm; IR (KBr) ν 3434, 2989, 2924, 2864, 1654, 1577, 1468, 1429 cm^{-1}; mass (*m*/*z*, %) 393 (M^+, 0.2), 378 (16), 337 (22), 336 (100), 322 (15); HRMS (ESI) 394.1852, calcd for $C_{24}H_{28}NO_2S$ [M + H^+] 394.1841, 416.1673, calcd for $C_{24}H_{27}NO_2SNa$ [M + Na^+] 416.1660. Anal. Calcd for $C_{24}H_{27}NO_2S$: C, 73.25; H, 6.92; N, 3.56. Found: C, 73.18; H, 7.07; N, 3.67.

6c: Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ_H 0.94 (s, 9H), 1.37 (s, 6H), 3.88 (s, 3H), 3.92−4.20 (m, 2H), 6.89 (d, *J* = 2.7 Hz, 1H), 7.01 (dd, *J* = 8.8 and 2.7 Hz, 1H), 7.36 (ddd, *J* = 7.9, 7.2, and 1.2 Hz, 1H), 7.47 (ddd, *J* = 8.2, 7.2, and 1.2 Hz, 1H), 7.90 (d with fine coupling, *J* = 7.9 Hz, 1H), 8.06 (d with fine coupling, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 26.2 (broad), 28.4 (broad), 31.8, 32.6, 47.2, 55.5, 83.3, 114.6, 117.2, 121.2, 123.0, 124.6, 125.9, 126.5, 126.6, 131.5, 136.1, 136.4, 147.2, 153.1, 160.5, 166.1 ppm; IR (liquid film) ν 2957, 2934, 2868, 1602, 1566, 1482, 1463, 1433 cm^{-1}; mass (*m*/*z*, %) 393 (M^+, 0.7), 378 (15), 337 (22), 336 (100), 322 (15), 268 (9). HRMS (ESI): 394.1854, calcd for $C_{24}H_{28}NO_2S$ [M + H^+] 394.1841, 416.1673, calcd for $C_{24}H_{27}NO_2SNa$ [M + Na^+] 416.1660.

6d: Pale yellow granules, mp 139.0−140.0 °C (from AcOEt−hexane); ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.10 (s, 9H), 1.37 (s, 6H), 3.91 (s, 2H), 3.92 (s, 3H), 6.98 (dd, *J* = 2.6 and 1.3 Hz, 1H), 7.39 (ddd, *J* = 7.9, 7.2, and 1.2 Hz, 1H), 7.49 (ddd, *J* = 8.2, 7.2, and 1.3 Hz, 1H), 7.59 (dd, *J* = 1.6 and 1.3 Hz, 1H), 7.64 (dd, *J* = 2.6 and 1.6 Hz, 1H), 7.90 (d with fine coupling, *J* = 7.9 Hz, 1H), 8.08 (d with fine coupling, *J* = 8.2 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 27.4, 32.5, 32.5, 47.2, 55.6, 83.2, 112.0, 118.6, 121.5, 121.8, 123.2, 125.2, 126.3, 126.3, 134.5, 135.0, 138.2, 148.8, 154.0, 159.6, 167.6 ppm; IR (KBr) ν 3442, 2982, 2955, 2924, 2854, 1605, 1584, 1508, 1458, 1422, 1337 cm^{-1}; mass (*m*/*z*, %) 394 (M^+ + 1, 7), 393 (M^+, 25), 379 (24), 378 (100), 322 (26). HRMS (ESI): 394.1844, calcd for $C_{24}H_{28}NO_2S$ [M + H^+] 394.1841, 416.1666, calcd for $C_{24}H_{27}NO_2SNa$ [M + Na^+] 416.1660. Anal. Calcd for $C_{24}H_{27}NO_2S$: C, 73.25; H, 6.92; N, 3.56. Found: C, 73.25; H, 7.08; N, 3.57.

Synthesis of 5-[2-(Benzothiazol-2-yl)-3-hydroxyphenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (3b). Typical Procedure: A solution of 5-[2-(benzothiazol-2-yl)-3-methoxyphenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**6b**) (537 mg, 1.36 mmol) and sodium thiomethoxide (200 mg, 2.85 mmol, 2.09 equiv) in dry DMF (5 mL) was stirred under a nitrogen atmosphere at 140 °C for 10 min. The reaction mixture was poured into saturated aqueous NH_4Cl and extracted with AcOEt. The organic layer was washed three times with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel and eluted with AcOEt−hexane (1:9) to give 493 mg of 5-[2-(benzothiazol-2-yl)-3-hydroxyphenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**3b**) as a pale yellow solid in 95% yield.

(Benzothiazol-2-yl)-3-methoxyphenyl-substituted dihydrofurans **6c** and **6d** were similarly demethylated with sodium thiomethoxide to give 5-[2-(benzothiazol-2-yl)-5-hydroxyphenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**3c**) and 5-[3-(benzothiazol-2-yl)-5-hydroxyphenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**3d**) in 85 and 89% yield, respectively.

3b: Pale yellow granules, mp 171.0−171.5 °C (from AcOEt−hexane); ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.05 (s, 9H), 1.42 (s, 3H), 1.51 (s, 3H), 4.03 (d, *J* = 8.3 Hz, 1H), 4.17 (d, *J* = 8.3 Hz, 1H), 6.87 (dd, *J* = 7.3 and 1.3 Hz, 1H), 7.13 (dd, *J* = 8.3 and 1.3 Hz, 1H), 7.33 (dd, *J* = 8.3 and 7.3 Hz, 1H), 7.42 (ddd, *J* = 7.9, 7.2, and 1.2 Hz, 1H), 7.51 (ddd, *J* = 8.2, 7.2, and 1.2 Hz, 1H), 7.93 (d with fine coupling, *J* = 7.9 Hz, 1H), 8.01 (d with fine coupling, *J* = 8.2 Hz, 1H), 13.93 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 25.7, 29.0, 31.7, 32.9, 47.6, 83.4, 116.2, 118.7, 121.1, 121.9, 123.5, 125.4, 126.5, 127.7, 131.3, 133.9, 135.4, 147.7, 149.4, 159.4, 167.3 ppm; IR (KBr) ν 3435, 2984, 2952, 2928, 2866, 2700, 2586, 1575, 1466, 1454, 1444 cm^{-1}; mass (*m*/*z*, %) 379 (M^+, 0.3), 364 (20), 323 (21), 322 (100), 308 (17), 254 (10), 57 (12). HRMS (ESI): 380.1682, calcd for $C_{23}H_{26}NO_2S$ [M + H^+] 380.1684, 402.1512, calcd for $C_{23}H_{25}NO_2SNa$ [M + Na^+] 402.1504. Anal. Calcd for $C_{23}H_{25}NO_2S$: C, 72.79; H, 6.64; N, 3.69. Found: C, 72.79; H, 6.75; N, 3.78.

3c: Colorless columns, mp 206.5−207.0 °C (from AcOEt−hexane); ^1H NMR (400 MHz, $CDCl_3$) δ_H 0.94 (s, 9H), 1.36 (s, 6H), 3.90−4.20 (m, 2H), 5.77 (s, 1H), 6.85 (d, *J* = 2.7 Hz, 1H), 6.91 (dd, *J* = 8.5 and 2.7 Hz, 1H), 7.37 (ddd, *J* = 7.9, 7.2, and 1.2 Hz, 1H), 7.47 (ddd, *J* = 8.2, 7.2, and 1.2 Hz, 1H), 7.90 (d with fine coupling, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 8.06 (d with fine coupling, *J* = 8.2 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 26.1 (broad), 28.4 (broad), 31.8, 32.6, 47.2, 83.2, 116.3, 119.0, 121.3, 122.8, 124.8, 126.0, 126.0, 127.0, 131.6, 135.9, 136.6, 146.8, 152.7, 157.4, 166.7 ppm; IR (KBr) ν 3388, 3058, 2966, 2929, 2908, 2864, 2777, 2677, 2586, 1608, 1568, 1465, 1432 cm^{-1}; mass (*m*/*z*, %) 379 (M^+, 0.3), 364 (14), 323 (20), 322 (100), 308 (15), 254 (11). HRMS (ESI): 380.1696, calcd for $C_{23}H_{26}NO_2S$ [M + H^+] 380.1684, 402.1517, calcd for $C_{23}H_{25}NO_2SNa$ [M + Na^+] 402.1504. Anal. Calcd for $C_{23}H_{25}NO_2S$: C, 72.79; H, 6.64; N, 3.69. Found: C, 72.79; H, 6.83; N, 3.75.

3d: Colorless granules, mp 190.0−191.0 °C (from CH_2Cl_2−hexane); ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.06 (s, 9H), 1.33 (s, 6H), 3.89 (s, 2H), 6.95 (t, *J* = 1.8 Hz, 1H), 7.32 (s, 1H), 7.34 (ddd, *J* = 8.0, 7.3, and 1.1 Hz, 1H), 7.44 (ddd, *J* = 8.2, 7.3, and 1.1 Hz, 1H), 7.53 (d, *J* = 1.8 Hz, 2H), 7.82 (d with fine coupling, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 27.3, 32.5, 32.5, 47.2, 83.1, 114.2, 120.3, 121.5, 121.6, 123.0, 125.3, 126.4, 126.6, 134.2, 134.8, 138.3, 148.5, 153.6, 156.3, 168.1 ppm; IR (KBr) ν 3494, 2980, 2967, 2910, 2869, 1608, 1597, 1465, 1438, 1429 cm^{-1}; mass (*m*/*z*, %) 380 (M^+ + 1, 7), 379 (M^+, 26), 365 (25), 364 (100), 308 (27), 254 (10), 226 (8); HRMS (ESI) 380.1691, calcd for $C_{23}H_{26}NO_2S$ [M +

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H^+] 380.1684, 402.1509, calcd for $C_{23}H_{25}NO_2SNa$ [M + Na^+] 402.1504. Anal. Calcd for $C_{23}H_{25}NO_2S$: C, 72.79; H, 6.64; N, 3.69. Found: C, 72.79; H, 6.77; N, 3.72.

Singlet Oxygenation of 5-[2-(Benzothiazol-2-yl)-3-hydroxyphenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (3b). Typical Procedure: A solution of dihydrofuran **3b** (202 mg, 0.532 mmol) and tetraphenylporphyrin (TPP) (1.5 mg) in CH_2Cl_2 (10 mL) was irradiated externally with a 940 W Na lamp under an oxygen atmosphere at 0 °C for 8.5 h. After the concentration of the photolysate in vacuo, the residue was chromatographed on silica gel and eluted with CH_2Cl_2–hexane (4:1) and then with AcOEt–hexane (1:1) to give intact **3b** (60 mg, 30%) and 1-[2-(benzothiazol-2-yl)-3-hydroxyphenyl]-5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]-heptane (**1b**) as a pale yellow solid (150 mg, 69% yield (CY = 97%)).

Dihydrofurans **3c** and **3d** were similarly oxygenated with singlet oxygen to give the corresponding dioxetanes **1c** and **1d** in 100 and 98% yields, respectively.

1b: Colorless granules, mp 100.5–101.0 °C (dec) (from CH_2Cl_2–hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.95 (s, 9H), 1.03 (broad s, 3H), 1.06 (s, 3H), 3.81 (d, J = 8.2 Hz, 1H), 4.55 (d, J = 8.2 Hz, 1H), 7.14 (dd, J = 8.2 and 1.1 Hz, 1H), 7.28–7.36 (m, 1H), 7.42 (dd, J = 8.2 and 7.8 Hz, 1H), 7.43 (ddd, J = 8.0, 7.3, and 1.1 Hz, 1H), 7.52 (ddd, J = 8.0, 7.3, and 1.1 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.36 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 19.0, 24.6, 26.9, 36.7, 45.1, 80.4, 106.1, 117.0, 118.1, 118.7, 121.2, 122.2, 123.0, 125.4, 126.1, 130.5, 135.1, 136.8, 151.8, 155.4, 165.5 ppm; IR (KBr) ν 3493, 3314, 3218, 3065, 2974, 2919, 2806, 2681, 1586, 1463 cm^{-1}; mass (m/z, %) 412 (M^+ + 1, 14), 411 (M^+, 57), 271 (13), 255 (17), 254 (100), 253 (33), 227 (27), 198 (12), 57 (15); HRMS (ESI) 412.1597, calcd for $C_{23}H_{26}NO_4S$ [M + H^+] 412.1583, 434.1422, calcd for $C_{23}H_{25}NO_4SNa$ [M + Na^+] 434.1402. Anal. Calcd for $C_{23}H_{25}NO_4S{\cdot}1/2CH_2Cl_2$: C, 62.17; H, 5.77; N, 3.09. Found: C, 62.19; H, 6.08; N, 3.19.

1c: Colorless granules, mp 181.0–181.5 °C (dec) (from AcOEt–hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.89 (broad s, 3H), 1.00 (s, 3H), 1.01 (s, 9H), 3.61 (d, J = 8.2 Hz, 1H), 4.42 (d, J = 8.2 Hz, 1H), 6.85 (dd, J = 8.5 and 2.7 Hz, 1H), 7.25 (d, J = 8.5 Hz, 1H), 7.31 (broad s, 1H), 7.40 (ddd, J = 8.0, 7.3, and 1.1 Hz, 1H), 7.47 (ddd, J = 8.0, 7.3, and 1.1 Hz, 1H), 7.63 (broad s, 1H), 7.87 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 19.1, 24.4 (broad), 27.0, 36.7, 45.2, 80.3, 106.1, 116.5, 116.8, 117.9, 121.1, 123.0, 125.1, 125.1, 126.0, 133.7, 136.3, 136.5, 151.9, 157.1, 169.3 ppm; IR (KBr) ν 3441, 3067, 3007, 2982, 2959, 2896, 1605, 1479, 1432, 1306 cm^{-1}; mass (m/z, %) 411 (M^+, 8), 355 (11), 255 (17), 254 (100), 227 (40), 57 (16); HRMS (ESI) 412.1594, calcd for $C_{23}H_{26}NO_4S$ [M + H^+] 412.1583, 434.1420, calcd for $C_{23}H_{25}NO_4SNa$ [M + Na^+] 434.1402. Anal. Calcd for $C_{23}H_{25}NO_4S$: C, 67.13; H, 6.12; N, 3.40. Found: C, 67.11; H, 6.23; N, 3.45.

1d: Colorless columns, mp 141.0–141.5 °C (dec) (from CH_2Cl_2–hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.02 (s, 9H), 1.17 (s, 3H), 1.39 (s, 3H), 3.84 (d, J = 8.3 Hz, 1H), 4.60 (d, J = 8.3 Hz, 1H), 6.35 (s, 1H), 7.27 (dd, J = 2.4 and 1.5 Hz, 1H), 7.40 (ddd, J = 8.1, 7.2, and 1.2 Hz, 1H), 7.49 (ddd, J = 8.2, 7.2, and 1.3 Hz, 1H), 7.71 (dd, J = 2.4 and 1.5 Hz, 1H), 7.84 (dd, J = 1.5 and 1.5 Hz, 1H), 7.89 (d with fine coupling, J = 8.1 Hz, 1H), 8.08 (d with fine coupling, J = 8.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 18.5, 25.2, 27.0, 36.8, 45.7, 80.3, 105.2, 115.1, 116.0, 118.3, 120.2, 121.6, 123.2, 125.4, 126.4, 134.5, 135.0, 138.7, 153.7, 156.1, 167.3 ppm; IR (KBr) ν 3388, 3073, 2979, 2967, 2696, 1600, 1488, 1433, 1346 cm^{-1}; mass (m/z, %) 411 (M^+, 5), 355 (39), 354 (10), 272 (10), 271 (19), 255 (15), 254 (100), 227 (30), 226 (28), 57 (20); HRMS (ESI) 412.1598, calcd for $C_{23}H_{26}NO_4S$ [M + H^+] 412.1583, 434.1409, calcd for $C_{23}H_{25}NO_4SNa$ [M + Na^+] 434.1402. Anal. Calcd for $C_{23}H_{25}NO_4S$: C, 67.13; H, 6.12; N, 3.40. Found: C, 67.03; H, 6.19; N, 3.43.

Thermal Decomposition of 1-[2-(Benzothiazol-2-yl)-3-hydroxyphenyl]-5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo-[3.2.0]heptane (1b). Typical Procedure: A solution of dioxetane **1b** (168 mg, 0.408 mmol) in *p*-xylene (4 mL) was refluxed under a nitrogen atmosphere for 4 h. After cooling, the reaction mixture was concentrated in vacuo. The residue was chromatographed on silica gel and eluted with AcOEt–hexane (1:9) to give 2,2,4,4-tetramethyl-3-oxopentyl 2-(benzothiazol-2-yl)-3-hydroxybenzoate (**2b**) as a pale yellow oil (165 mg, 98% yield).

Dioxetanes **1c** and **1d** were similarly decomposed to give the corresponding keto esters **2c** and **2d** in 98 and 97% yields, respectively.

2b: Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 1.12 (s, 9H), 1.28 (s, 6H), 4.40 (s, 2H), 7.10 (dd, J = 7.4 and 1.4 Hz, 1H), 7.22 (dd, J = 8.4 and 1.4 Hz, 1H), 7.38 (dd, J = 8.4 and 7.4 Hz, 1H), 7.45 (ddd, J = 7.8, 7.3, and 1.2 Hz, 1H), 7.53 (ddd, J = 8.1, 7.3, and 1.4 Hz, 1H), 7.93 (d with fine coupling, J = 7.8 Hz, 1H), 8.04 (d with fine coupling, J = 8.1 Hz, 1H), 12.68 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 23.5, 27.8, 45.7, 48.7, 73.7, 114.7, 120.3, 120.6, 121.3, 122.3, 125.8, 126.7, 131.7, 133.1, 134.2, 150.4, 158.1, 166.1, 168.7, 215.6 ppm; IR (liquid film) ν 3351, 2974, 2872, 1724, 1685, 1579, 1477, 1454 cm^{-1}; mass (m/z, %) 412 (M^+ + 1, 11), 411 (M^+, 40), 255 (17), 254 (100), 253 (32), 227 (29), 198 (12), 57 (20); HRMS (ESI) 412.1598, calcd for $C_{23}H_{26}NO_4S$ [M + H^+] 412.1583, 434.1415, calcd for $C_{23}H_{25}NO_4SNa$ [M + Na^+] 434.1402.

2c: Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 1.04 (s, 6H), 1.10 (s, 9H), 4.23 (s, 2H), 6.92 (dd, J = 8.4 and 2.6 Hz, 1H), 7.13 (d, J = 2.6 Hz, 1H), 7.39 (ddd, J = 8.0, 7.2, and 1.1 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.48 (ddd, J = 8.1, 7.2, and 1.2 Hz, 1H), 7.88 (d with fine coupling, J = 8.0 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 8.76 (broad s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 23.1, 27.9, 45.7, 48.7, 72.8, 117.1, 118.5, 121.5, 122.9, 124.3, 125.2, 126.3, 132.1, 133.0, 135.6, 153.1, 158.6, 167.5, 167.7, 217.0 ppm; IR (liquid film) ν 3355, 3060, 2976, 2934, 2873, 2793, 2683, 2607, 1726, 1685, 1605, 1576, 1479, 1434, 1367 cm^{-1}; mass (m/z, %) 411 (M^+, 6), 355 (10), 255 (16), 254 (100), 227 (42), 57 (23); HRMS (ESI) 434.1414, calcd for $C_{23}H_{25}NO_4SNa$ [M + Na^+] 434.1402.

2d: Colorless needles, mp 185.5–186.0 °C (from AcOEt–hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.33 (s, 9H), 1.43 (s, 6H), 4.44 (s, 2H), 6.01 (s, 1H), 7.41 (ddd, J = 8.1, 7.2, and 1.2 Hz, 1H), 7.50 (ddd, J = 8.2, 7.2, and 1.2 Hz, 1H), 7.56 (dd, J = 2.6 and 1.3 Hz, 1H), 7.86 (dd, J = 2.6 and 1.6 Hz, 1H), 7.91 (d with fine coupling, J = 8.1 Hz, 1H), 8.06 (d with fine coupling, J = 8.2 Hz, 1H), 8.16 (dd, J = 1.6 and 1.3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 23.7, 28.1, 46.0, 49.2, 72.6, 118.1, 119.2, 120.9, 121.6, 123.1, 125.6, 126.5, 132.1, 134.7, 134.9, 153.4, 157.0, 165.4, 167.1, 216.7 ppm; IR (KBr) ν 3434, 2973, 1696, 1685, 1614, 1601, 1437, 1374, 1334 cm^{-1}; mass (m/z, %) 411 (M^+, 5), 355 (39), 354 (10), 272 (10), 271 (19), 255 (16), 254 (100), 227 (28), 226 (25), 57 (22); HRMS (ESI) 412.1605, calcd for $C_{23}H_{26}NO_4S$ [M + H^+] 412.1583, 434.1411, calcd for $C_{23}H_{25}NO_4SNa$ [M + Na^+] 434.1402. Anal. Calcd for $C_{23}H_{25}NO_4S$: C, 67.13; H, 6.12; N, 3.40. Found: C, 67.06; H, 6.11; N, 3.44.

Time Course of Thermal Decomposition of Crystalline 1b at 80 °C. Crystalline **1b** (20.0 mg) was heated at 80 °C, and after 1, 2, 3, and 4 h, product distribution was monitored by ^{1}H NMR in $CDCl_3$ (Figure S1).

Thermal Decomposition of Crystalline 1b To Isolate *trans*-10. Crystalline **1b** (21.5 mg) was heated at 90 °C for 45 min to give a mixture of **2b** and *trans*-**10**. After cooling, the crude product was chromatographed on NH–silica gel and eluted with AcOEt–MeOH (9: 1) to give a mixture of **2b** and *trans*-**10** (37:63) as a pale yellow oil (13.2 mg), which was crystallized from $CHCl_3$–hexane to give colorless plates of *trans*-**10** including 10% of **1b**. Further purification of *trans*-**10** was unsuccessful because of its thermal and chemical (silica gel) instability: *trans*-**10** gradually decomposed to **2b** during isolation and purification process even though at low temperature.

***trans*-10:** ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 1.19 (s, 9H), 1.38 (s, 3H), 1.89 (s, 3H), 2.47 (s, 1H), 3.88 (d, J = 8.7 Hz, 1H), 4.01 (d, J = 8.7 Hz, 1H), 6.84 (d, J = 8.9 Hz, 1H), 7.13 (d, J = 7.3 Hz, 1H), 7.34 (dd, J = 8.9 and 7.3 Hz, 1H), 7.47 (dd with fine coupling, J = 8.0 and 7.3 Hz, 1H), 7.61 (dd with fine coupling, J = 8.0 and 7.3 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 25.2, 28.7, 29.1, 39.3, 46.8, 82.2, 90.9, 107.5, 110.8, 111.4, 117.5, 123.9, 124.0, 125.5, 126.3, 127.9, 130.0, 135.3, 136.7, 151.0, 174.4 ppm.

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TBAF-Induced Decomposition of Crystalline 1b To Isolate *cis*-10. A solution of **1b** (61.4 mg) and TBAF (0.3 equiv) in acetonitrile (15 mL) was heated at 45 °C for 10 h. The reaction mixture was poured in aqueous NH_4Cl and extracted with AcOEt. The organic layer was washed with aqueous NaCl, dried over $MgSO_4$, and concentrated in vacuo. The residue was rinsed with CH_2Cl_2 to give *cis*-**10** as a yellow solid (14.0 mg).

***cis*-10:** ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.68 (broad s, 9H), 1.25 (s, 3H), 1.51 (s, 3H), 2.61 (s, 1H), 3.76 (d, J = 8.6 Hz, 1H), 4.33 (d, J = 8.6 Hz, 1H), 6.61 (d, J = 7.1 Hz, 1H), 6.85 (d, J = 9.0 Hz, 1H), 7.35 (dd, J = 9.0 and 7.1 Hz, 1H), 7.47 (dd with fine coupling, J = 8.0 and 7.3 Hz, 1H), 7.61 (dd with fine coupling, J = 8.2 and 7.3 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 21.3, 25.9, 27.8 (broad), 39.5, 49.3, 80.4, 91.9, 107.9, 110.5, 111.7, 119.3, 123.7, 125.1, 125.5, 125.7, 128.1, 131.6, 134.8, 136.4, 153.0, 174.3 ppm.

Measurement of Chemiluminescence and Time Course of the Charge-Transfer-Induced Decomposition of Dioxetanes 1. General Procedure: Chemiluminescence was measured using a JASCO FP-750 and/or FP-6500 spectrometer and/or Hamamatsu Photonics PMA-11 multichannel detector.

A freshly prepared solution (2.0 mL) of TBAF (1.0×10^{-2} mol/L) in acetonitrile was transferred to a quartz cell ($10 \times 10 \times 50$ mm) and was placed in the spectrometer, which was thermostatted with stirring at an appropriate temperature range of 45 °C. After 3−5 min, a solution of the dioxetane **1** in acetonitrile (1.0×10^{-5} mol/L, 1.0 mL) was added by means of a syringe and measurement was started immediately. The intensity of the light emission time-course was recorded and processed according to first-order kinetics. The total light emission was estimated by comparing it with that of an adamantylidene dioxetane, whose chemiluminescent efficiency Φ^{CL} has been reported to be 0.29 and was used here as a standard.[11,12]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR/^{13}C NMR spectra of **1b−d**, **2b−d**, **3b−d**, **4b−d**, **6b−d**, *trans*-**10**, *cis*-**10**, and ORTEP views and crystallographic information files for **1b−d**, *trans*-**10**, and *cis*-**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: matsumo-chem@kanagawa-u.ac.jp.

Notes

The authors declare no competing financial interest.

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