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Synthesis and fluoride-induced chemiluminescent decomposition of bicyclic dioxetanes substituted with a 2-hydroxynaphthyl group

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Abstract—Five bicyclic dioxetanes bearing a 2-hydroxynaphthyl group, **1aA**–**1eA**, were synthesized and their chemiluminescent decomposition was examined by the use of tetrabutylammonium fluoride (TBAF) as a base in DMSO. It was found that these dioxetanes hold completely the '*odd*/*even*' relationship between the substitution pattern of hydroxy as a trigger on the naphthalene ring and their chemiluminescent efficiency, and that dioxetane **1aA** exhibited chemiluminescence with the highest efficiency among those for the oxynaphthyl-substituted dioxetanes hitherto known. The significant change in chemiluminescent efficiency depending on the substitution pattern was clarified to be attributed to the marked change in singlet-chemiexcitation efficiency for charge-transfer-induced chemiluminescence (CTICL) of **1aA**–**1eA**. In respect of the rate of CTICL-decomposition, '*odd*/*even*' relationship was observed for **1aA**–**1dA**.

1. Introduction

Dioxetanes substituted with an aromatic electron donor such as the phenoxide anion or naphthoxide anion undergo intramolecular charge-transfer-induced chemiluminescence (CTICL). The phenomenon has received much attention from the viewpoints of mechanistic interest related to bioluminescence and application to modern chemiluminescent biological analysis.[1–4] As a very recent development, it has been reported that the atropisomeric 2-hydroxy-1,1′-binaphthyl-5-yl moiety also acts as an electron donor after deprotonation, and dioxetanes bearing such substituent display CTICL, the spectrum of which varies depending on the microenvironment.[5] In the course of our further investigation to design such type of dioxetanes, we synthesized various dioxetanes substituted with the 2-hydroxynaphthyl moiety and examined their base-induced decomposition to know what kind of substitution pattern, namely, the position of a dioxetane ring relative to the 2-hydroxy group on the naphthalene ring, leads to effective chemiluminescence.

There are five types of dioxetane bearing a 2-hydroxynaphthyl moiety, **1a**–**1e** (Y=H) that relate to dioxetanes bearing a 2-hydroxy-1,1′-binaphthyl group **2** except one with a sterically too congested 2-hydroxy-1,1′-binaphthyl-8-yl group (Fig. 1). Among them, three analogs having a 3,3-diisopropyl-4-methoxy-1,2-dioxetane skeleton (**1aB**, **1bB**, **1eB**; Y=t-BuMe$_2$Si) have already been reported to exhibit '*odd*/*even*' relationship between the chemiluminescent properties and substitution pattern of a trigger (YO group).[6–9] On the other hand, a bicyclic dioxetane skeleton, namely, 5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane, substituted with various aryl groups at the 1-position, has been known to exhibit marked thermal stability[10] and synthetic versatility of its precursor.[11] Thus, we synthesized bicyclic dioxetanes **1cA** and **1dA** with new substitution pattern and examined their chemiluminescent decomposition in tetrabutylammonium fluoride (TBAF)/DMSO system. Bicyclic dioxetanes **1aA**, **1bA**, and **1eA** were also synthesized and their chemiluminescent properties were compared with those of **1cA**, **1dA**, as well as with those for diisopropyldioxetanes **1aB**, **1bB**, and **1eB**, and their related dioxetanes.

Keywords: Dioxetane; Chemiluminescence; 'Odd/even' relationship.

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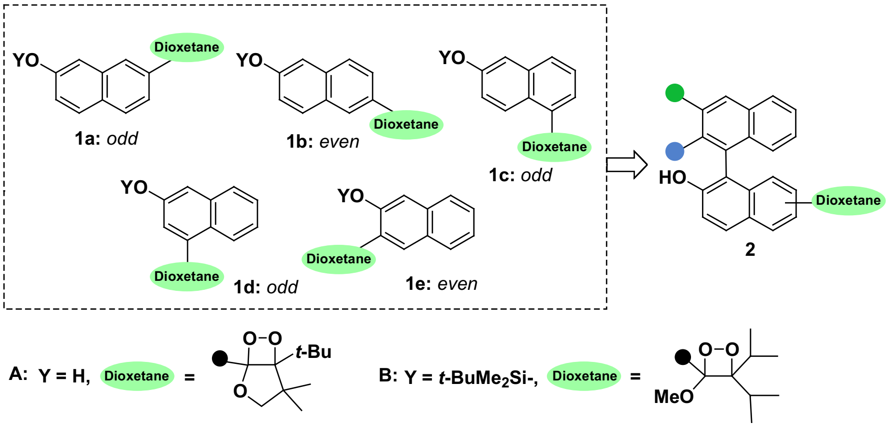
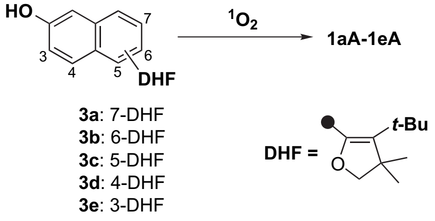


Figure 1.

2. Results and discussion

2.1. Synthesis of bicyclic dioxetanes substituted with a 2-hydroxynaphthyl group

Sensitized photooxygenation has been reported to be very effective to transform 5-aryl-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofurans into the corresponding bicyclic dioxetanes, namely, 1-aryl-5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptanes.[3,4,10,11] The precursors leading to dioxetanes **1aA–1eA** were 4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofurans **3a–3e** bearing a 2-hydroxynaphthyl group at the 5-position (Scheme 1).

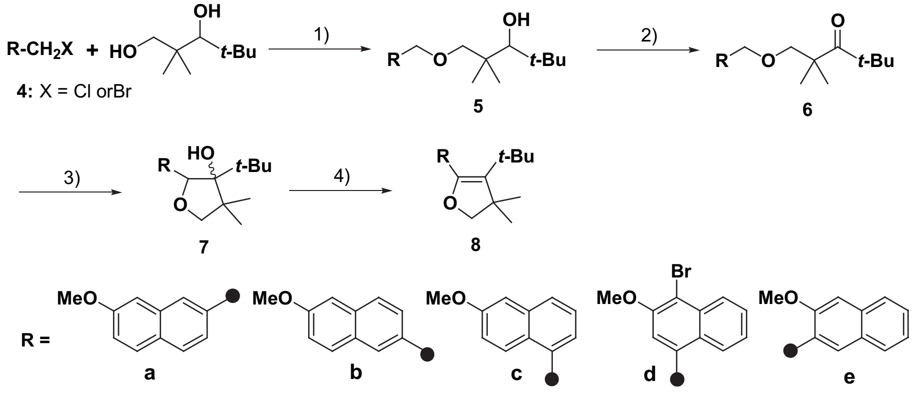


Scheme 1.

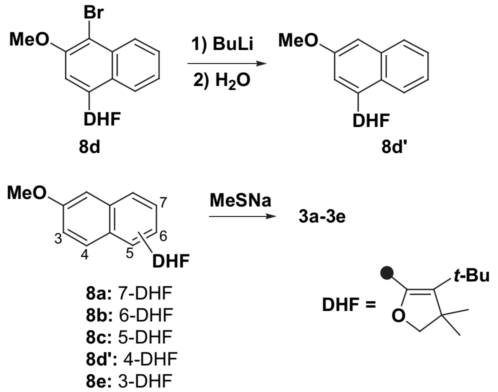
Synthesis of the precursors **3a–3e** started from the Williamson synthesis of 2-methoxynaphthylmethyl halides **4a–4e** with 2,2,4,4-tetramethylpentane-1,3-diol to afford the corresponding hydroxy ethers **5a–5e**. Successive oxidation of **5a–5e** with pyridinium chlorochromate (PCC) gave the corresponding ketones **6a–6e** in high yields. On treatment with a base such as lithium diisopropylamide (LDA) in tetrahydrofuran (THF) or *t*-BuOK in DMSO, the ketones **6a–6e** underwent intramolecular cyclization smoothly to yield 3-hydroxytetrahydrofurans **7a–7e**, respectively. Dehydration of **7a–7e** into the corresponding dihydrofurans **8a–8e** was effectively attained on heating with an acid catalyst or on treatment with $SOCl_2$/pyridine (Scheme 2).

Dihydrofuran **8d** was treated with butyllithium in THF to give debrominated product **8d′**. Demethylation of the methoxy group in (methoxynaphthyl)dihydrofurans **8a–8c**, **8d′**, and **8e** took place on heating with sodium methanethiolate in hot dimethylformamide (DMF) to give dihydrofurans **3a–3e**, respectively (Scheme 3).

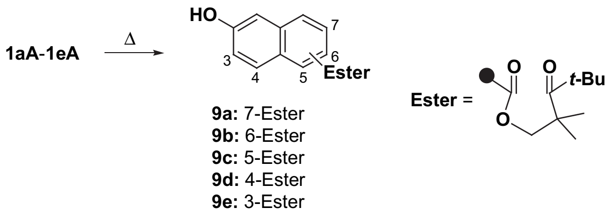
When dihydrofurans **3a–3e** were irradiated in the presence of tetraphenylporphin (TPP) (catalytic amount) in dichloromethane with Na lamp under an oxygen atmosphere at −78–0 °C for 0.5–1 h, the corresponding dioxetanes **1aA–1eA** were produced exclusively. The structures of these dioxetanes were determined by ^{1}H NMR, ^{13}C NMR, IR, Mass, and HR mass spectral analysis. All dioxetanes synthesized here were thermally stable enough to permit handling at room temperature, though they decomposed into the corresponding keto esters **9a–9e** on heating in xylene (Scheme 4).



Scheme 2. *Reagents*: (1) NaH/THF–DMF; (2) PCC/CH_2Cl_2; (3) LDA/THF or *t*-BuOK/DMSO; (4) TsOH/toluene or pyridine/$SOCl_2$/CH_2Cl_2.



Scheme 3.



Scheme 4.

2.2. Fluoride-induced chemiluminescent decomposition of bicyclic dioxetanes substituted with a 2-hydroxynaphthyl group

A dioxetane bearing a siloxyaryl or hydroxyaryl group is triggered with TBAF in an aprotic solvent such as DMSO and acetonitrile; its desilylation or deprotonation with fluoride affords an unstable oxidoaryl-substituted dioxetane, which decomposes rapidly by the intramolecular CTICL process. Such fluoride-triggered decomposition has been reported to proceed following the pseudo-first-order kinetics independent of the TBAF concentration, when a large excess of fluoride concentration is used.[12] Thus, we used a large excess of TBAF to examine the fluoride-induced decomposition of dioxetanes **1aA–1eA** for simplifying the system, so that we could estimate the rate of decomposition of intermediary oxidonaphthyldioxetanes **10a–10e** into keto esters **11a–11e** in the singlet-excited state (Scheme 5).

When a solution of **1aA** in DMSO ($1.0\times10^{-5}\ \mathrm{mol\,dm^{-3}}$, 1 mL) was added to a TBAF solution in DMSO ($1.0\times10^{-2}\ \mathrm{mol\,dm^{-3}}$, 2 mL) at 25 °C, **1aA** underwent the CTICL-decomposition accompanied with emission of light: maximum wavelength $\lambda_{\max}^{\mathrm{CTICL}}=559$ nm, chemiluminescent efficiency $\Phi^{\mathrm{CTICL}}=0.11$, the rate of CTICL-decomposition $k^{\mathrm{CTICL}}=5.8\times10^{-3}\ \mathrm{s}^{-1}$, and half-life $t_{1/2}=\log_e 2/k^{\mathrm{CTICL}}=120$ s. On treatment with TBAF in DMSO similarly to the case of **1aA**, dioxetanes **1bA–1eA** displayed chemiluminescence, the spectra of which are illustrated in Figure 2. The chemiluminescent properties for **1aA–1eA** are summarized in Table 1, in which those for diisopropyldioxetanes **1aB**, **1bB**, **1eB**, and **1c′B**, **1d′B** (Scheme 5, vide infra) are also cited.[6]

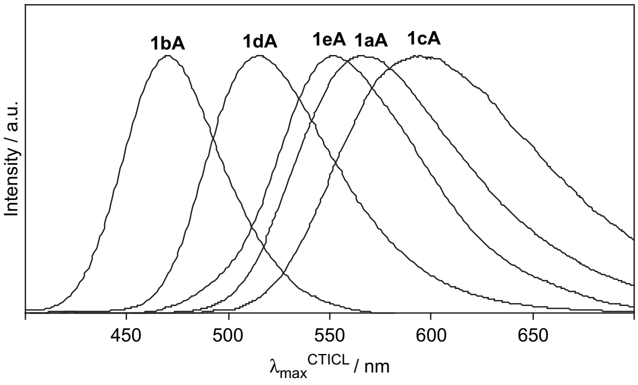
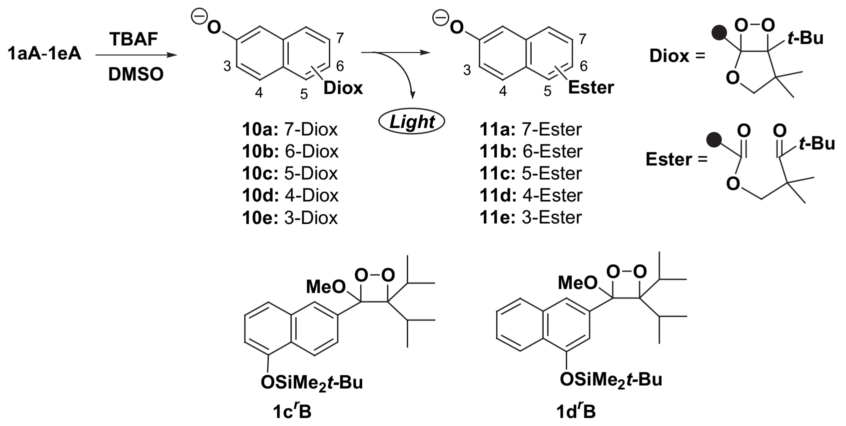


Figure 2. Chemiluminescent spectra of dioxetanes **1aA–1eA** in TBAF/DMSO system.

The results in Table 1 exhibit several characteristic features for the CTICL of dioxetanes **1aA–1eA**, as follows. First, dioxetane **1aA** gave light in very high yield: Φ^{CTICL} for **1aA** was twice higher than that for **1aB**, and was the highest among those for hitherto-known dioxetanes bearing a naphtholic group ($\Phi^{\mathrm{CTICL}}<0.06$).[6,8,9] Second, bicyclic dioxetanes (group **1A**) appeared to give higher Φ^{CTICL} than the corresponding diisopropyldioxetanes (group **1B**). Third, dioxetanes **1aA**, **1cA**, and **1dA** with ‘*odd*’ substitution pattern afforded far higher Φ^{CTICL} than isomers **1bA** and **1eA** with ‘*even*’ substitution pattern. Thus, bicyclic dioxetanes (group **A**) are completely in the category of the ‘*odd/even*’



Scheme 5.

Table 1. Chemiluminescent decomposition of dioxetanes substituted with 2-hydroxynaphthyl group in TBAF/DMSO system[a]

Dioxetane[b]	$\lambda_{\mathrm{max}}^{\mathrm{CTICL}}$/nm	$\Phi^{\mathrm{CTICL}c}$	$t_{1/2}$/s	k^{CTICL}/s^{-1}	Substitution pattern
1aA	559	0.11	120	5.8×10^{-3}	*Odd*
1aB	558	5.6×10^{-2}	250	2.8×10^{-3}	*Odd*
1bA	470	1.7×10^{-5}	0.04	18	*Even*
1bB	470	3.2×10^{-6}	0.15	4.6	*Even*
1cA	582	1.7×10^{-2}	19	3.7×10^{-2}	*Odd*
1c′B	628	7.4×10^{-3}	4.8	0.14	*Odd*
1dA	516	6.8×10^{-2}	220	3.2×10^{-3}	*Odd*
1d′B	496	5.2×10^{-2}	0.076	9.1	*Odd*
1eA	551	6.6×10^{-4}	170	4.2×10^{-3}	*Even*
1eB	548[d]	1.6×10^{-4}[d]	46[d]	1.5×10^{-2}[d]	*Even*

[a] A solution of dioxetane in DMSO (1.0×10^{-5} mol dm^{-3}, 1 mL) was added into a TBAF solution in DMSO (1.0×10^{-2} mol dm^{-3}, 2 mL) at 25 °C, for **1aA**, **1cA**, **1dA**, and **1eA**. Similarly, a solution of dioxetane (1.0×10^{-4} mol dm^{-3}) and a solution of TBAF (1.0×10^{-2} mol dm^{-3}) were used for **1bA**.

[b] Chemiluminescent properties for a class of dioxetanes **1B** summarized here are the values reported already (Ref. 6).

[c] Chemiluminescent efficiencies (Φ^{CTICL}) were based on the reported value for 3-(3-*tert*-butyldimethylsiloxyphenyl)-3-methoxy-4-(2′-spiro-adamantane)-1,2-dioxetane ($\Phi^{\mathrm{CTICL}}=0.29$) (Ref. 12).

[d] Revised value after the reexamination.

Table 2. Fluorescence of 2-oxidonaphthoates **11a**–**11e** and singlet-chemiexcitation efficiency for CTICL of dioxetanes **1aA**–**1eA**

Naphthoate[a]	$\lambda_{\mathrm{max}}^{\mathrm{fl}}$/nm	Φ^{fl}	Dioxetane	Φ_{S}[b]	Substitution pattern
11a	558	0.23	**1aA**	0.49	*Odd*
11b	471	0.74	**1bA**	2.3×10^{-5}	*Even*
11c	586	0.078	**1cA**	0.22	*Odd*
11d	513	0.77	**1dA**	8.8×10^{-2}	*Odd*
11e	550	0.21	**1eA**	3.2×10^{-3}	*Even*

[a] Fluorescence of **11a**–**11e** generated from the corresponding keto esters **9a**–**9e** in TBAF/DMSO.

[b] Singlet-chemiexcitation efficiency: $\Phi_{\mathrm{S}}=\Phi^{\mathrm{CTICL}}/\Phi^{\mathrm{fl}}$.

relationship in respect of Φ^{CTICL} as illustrated in Figure 3A. Although similar '*odd*/*even*' relationship has been observed also for diisopropyldioxetanes (group **1B**) as shown in Figure 3B, it has been little known whether this '*odd*/*even*' relationship is based on the difference in fluorescent efficiency of emitters and/or the difference in singlet-chemiexcitation efficiency of dioxetanes.

Authentic emitters **11a**–**11e** were prepared by dissolving the corresponding neutral keto esters **9a**–**9e** in TBAF/DMSO. They displayed fluorescence with maximum wavelength ($\lambda_{\mathrm{max}}^{\mathrm{fl}}$) and efficiency ($\Phi^{\mathrm{fl}}$) as summarized in Table 2, and their fluorescence spectra coincided substantially with the chemiluminescent spectra of the corresponding dioxetanes **1aA**–**1eA**, as shown in Figure 4. Since Φ^{CTICL} is described as the product of $\Phi^{\mathrm{fl}}\times\Phi_{\mathrm{S}}$ (singlet-chemiexcitation efficiency) for CTICL of the dioxetanes, Φ_{S} for **1aA**–**1eA** are estimated as summarized in Table 2. The results reveal that the significant change in Φ^{CTICL} among **1aA**–**1eA** is attributed predominantly to the difference in Φ_{S} but not to that in Φ^{fl} of emitters **11a**–**11e**, as illustrated in Figure 5.

The '*odd*/*even*' relationship in respect of k^{CTICL} has been reported to hold for diisopropyldioxetanes **1aB**, **1bB**, and **1c′B**, but for neither **1d′B** nor **1eB**, as shown in Figure 6B.[6] On the other hand, such relationship held even for dioxetane **1dA** as well for **1aA**–**1cA** as illustrated in Table 1 and Figure 6A. It should be noted here that dioxetane **1dA** has the '*odd*' substitution pattern (2-OH/4-dioxetane on naphthalene ring), whereas **1d′B** has the reverse '*odd*' substitution pattern (4-OH/2-dioxetane) (Scheme 5). Considering that k^{CTICL} is smaller for bicyclic dioxetanes **1dA** and **1eA** than for the respective diisopropyldioxetanes **1d′B** and **1eB**, significant difference in k^{CTICL} between **1dA** and **1d′B** is presumably attributed to the difference in the ease of oxidation between the 2-oxidonaphthalene anion and 1-oxidonaphthalene anion, which act as an electron donor for the CTICL, but not to the structural difference in the dioxetane skeleton. In fact, 1-oxidonaphthalene anion has been reported to possess formal oxidation potential (E vs $\mathrm{Ag/Ag^+}$ in DMSO=−498 mV) considerably lower than that of the 2-oxidonaphthalene anion (E=−369 mV).[6] Such tendency was observed also between dioxetanes with the reverse substitution pattern **1cA** (2-OH/5-dioxetane) and **1c′B** (5-OH/2-dioxetane).

It has been suggested that the rate of CTICL-decomposition is affected also by the conformation of the aromatic electron donor relative to the dioxetane ring,[3] and that such steric

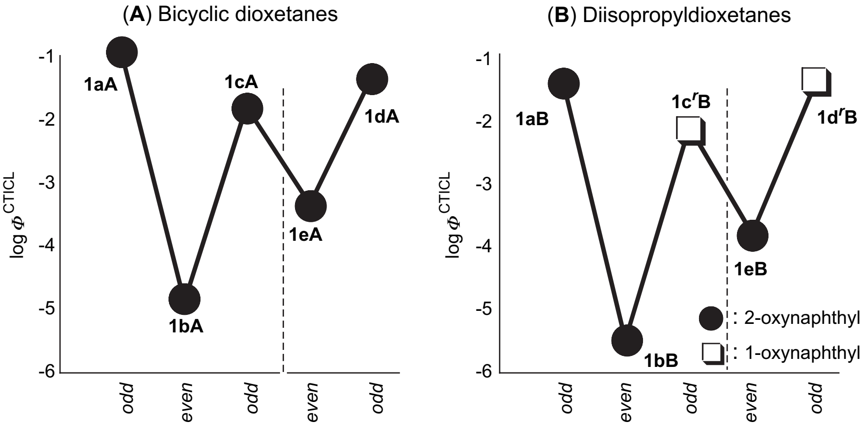


Figure 3. '*Odd*/*even*' relationship between substitution pattern and chemiluminescent efficiency Φ^{CTICL} for dioxetanes **1aA**–**1eA** (group A) and **1aB**–**1d′B** (group B).

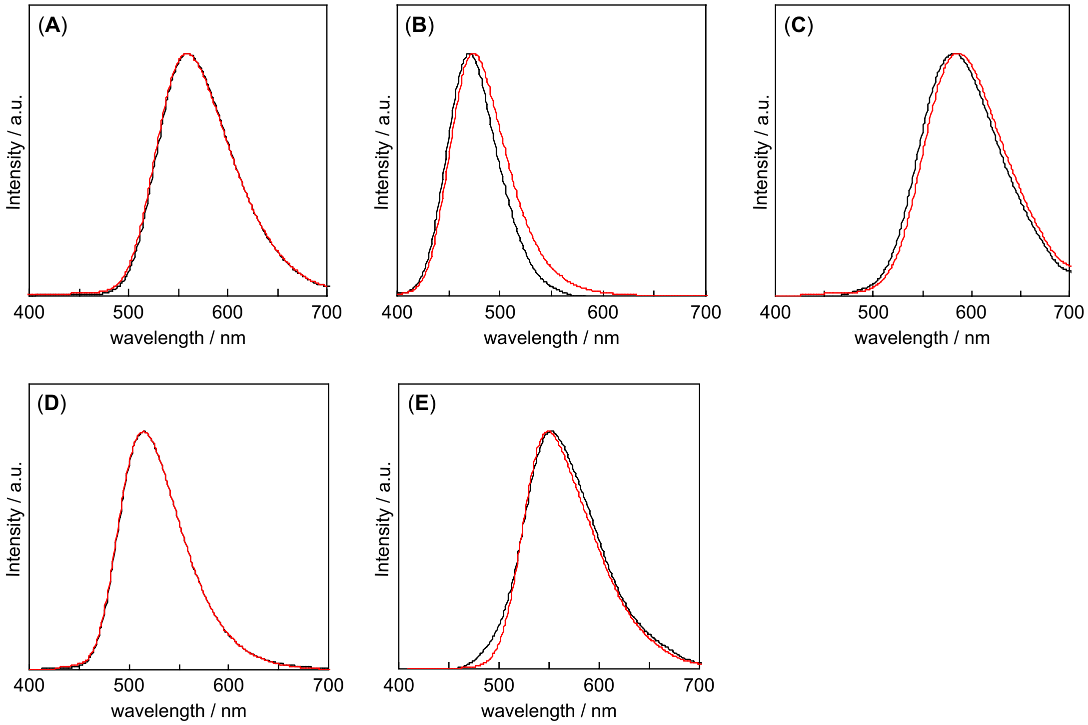


Figure 4. Chemiluminescent spectra of **1aA**–**1eA** and fluorescence spectra of 2-oxidonapthoates **11a**–**11e** prepared from keto esters **9a**–**9e** in TBAF/DMSO. Black line: chemiluminescence, red line: fluorescence spectra, (A) **1aA** versus **11a** (B) **1bA** versus **11b**, (C) **1cA** versus **11c**, (D) **1dA** versus **11d**, (E) **1eA** versus **11e**.

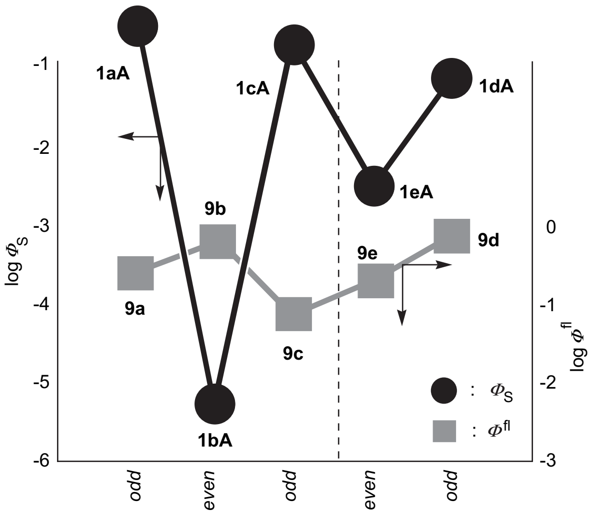


Figure 5. '*Odd*/*even*' relationship between substitution pattern and singlet-chemiexcitation efficiency Φ_{S} and fluorescent efficiency Φ^{fl} for chemiluminescence of dioxetanes **1aA**–**1eA**.

factor causes presumably the unusual thermal stability of 2-methoxyphenyl-substituted bicyclic dioxetane.[10] This suggestion should be also applied to account for the fact that dioxetane **1eA** as well as **1eB** decompose slowly, even though they have the '*even*' substitution pattern, in TBAF/DMSO.

3. Conclusion

It was found that bicyclic dioxetanes **1aA**–**1eA** bearing a 2-hydroxynaphthyl moiety hold completely the '*odd*/*even*' relationship between the substitution pattern on the naphthalene ring and their chemiluminescent efficiency in TBAF/DMSO system, and **1aA** exhibited chemiluminescence with the highest efficiency among those for the oxynaphthyl-substituted dioxetanes hitherto known. The significant change of Φ^{CTICL} among **1aA**–**1eA** was found to be attributed mainly to the difference in Φ_{S} but not to that in Φ^{fl} of emitters **11a**–**11e**. Difference in the oxidation potential between the 1-oxidonaphthyl and 2-oxidonaphthyl moieties, which act as an electron donor for the intramolecular CTICL of dioxetanes **1**, was suggested to cause significant difference in the rate of CTICL-decomposition between dioxetane **1dA** (2-OH/4-dioxetane) and **1d′B** with the reverse substitution pattern (4-OH/2-dioxetane).

4. Experimental

4.1. General

Melting points were measured with a Yanako MP-S3 melting point apparatus and are uncorrected. IR spectra were taken on a JASCO FT/IR-300 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on JEOL EX-400 and JEOL EPC-500 spectrometers. Mass spectra were obtained by using JEOL JMS-AX-505H and JEOL JMS-T-100LC mass spectrometers. Reagents were purchased from Aldrich, Tokyo Chemical Industries, Wako Pure Chemical Industries, and/or Kanto Chemical Industries. Column chromatography was carried out with silica gel, unless otherwise stated.

4.1.1. Preparation of (halomethyl)methoxynaphthalenes 4a–4e. 1-Bromo-4-bromomethyl-2-methoxynaphthalene (**4d**)

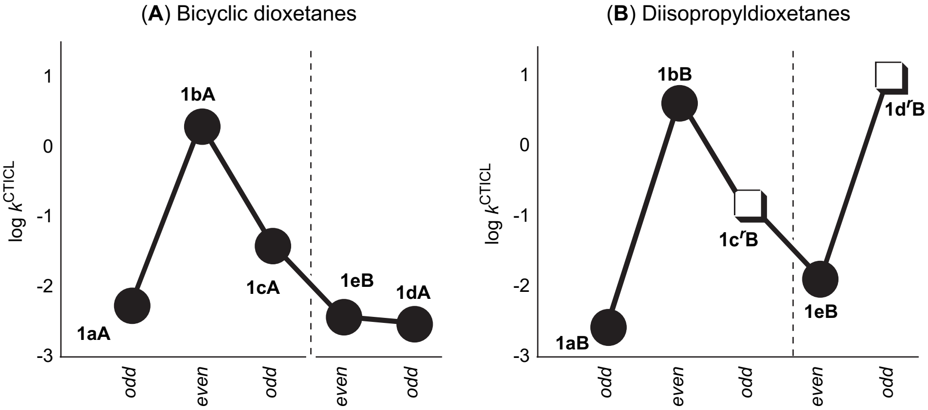


Figure 6. '*Odd/even*' relationship between substitution pattern and rate of CT-induced chemiluminescent decomposition (k^{CTICL}) for dioxetanes **1aA–1eA** (group A) and **1aB–1eB**.

was synthesized by bromination of 3-methoxy-1-methylnaphthalene with *N*-bromosuccinimide (NBS) in the presence of azobisisobutyronitrile (AIBN) in hot CCl_4: 79.8% yield.

4d: Pale yellow needles melted at 151.0–153.0 °C (from AcOEt–hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.04 (s, 3H), 4.93 (s, 2H), 7.35 (s, 1H), 7.53 (dd with fine coupling, J=8.5 and 6.8 Hz, 1H), 7.60 (dd with fine coupling, J=8.5 and 6.8 Hz, 1H), 8.07 (d with fine coupling, J=8.5 Hz, 1H), 8.20 (d with fine coupling, J=8.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 30.9, 57.1, 110.3, 115.3, 123.9, 125.0, 127.1, 127.4, 128.1, 133.7, 134.4, 153.0 ppm. IR (KBr): 3037, 3019, 2965, 2936, 2844, 1597 cm^{-1}. Mass (m/z, %): 332 (M^++4, 20), 330 (M^++2, 41), 328 (M^+, 22), 266 (34), 264 (27), 252 (33), 251 (99), 250 (34), 249 (100), 208 (25), 206 (26), 140 (51), 139 (37), 127 (82), 126 (36). Anal. Calcd for $C_{12}H_{10}Br_2O$: C, 43.67; H, 3.05%. Found: C, 43.78; H, 2.68%.

2-Chloromethyl-7-methoxynaphthalene (**4a**),[13] 2-chloromethyl-6-methoxynaphthalene (**4b**),[14] 1-chloromethyl-6-methoxynaphthalene (**4c**),[15] and 2-chloromethyl-3-methoxynaphthalene (**4e**)[16] were synthesized by chlorination of the corresponding (hydroxymethyl)naphthalenes with $CCl_4/(C_6H_5)_3P$.

4.1.2. Synthesis of 1-(7-methoxynaphthalen-2-yl)methoxy-2,2,4,4-tetramethylpentan-3-ol (5a); typical procedure. A solution of 2,2,4,4-tetramethyl-1,3-pentanediol (904 mg, 5.64 mmol) in dry THF (5.0 mL) was added dropwise over 5 min to a suspension of sodium hydride (60% in oil, 236 mg, 5.90 mmol) in dry DMF (30 mL) and dry THF (30 mL) at 0 °C under a nitrogen atmosphere and was stirred at 0 °C for 30 min. 2-Chloromethyl-7-methoxynaphthalene (**4a**) (1.06 g, 5.13 mmol) was added to the solution and was stirred for 3 h at room temperature. The reaction mixture was poured into satd aq NH_4Cl and then extracted with AcOEt. The organic layer was washed twice with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:9) to give 1-(7-methoxynaphthalen-2-yl)methoxy-2,2,4,4-tetramethylpentan-3-ol (**5a**) (1.53 g, 4.63 mmol, 90.3%) as a colorless solid.

5a: Colorless needles melted at 90.0–91.0 °C (from AcOEt). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.03 (s, 9H), 1.05 (s, 3H), 1.08 (s, 3H), 3.25 (d, J=4.4 Hz, 1H), 3.30 (d, J=8.9 Hz, 1H), 3.44 (d, J=8.9 Hz, 1H), 3.51 (d, J=4.4 Hz, 1H), 3.92 (s, 3H), 4.64 (s, 2H), 7.12 (s, 1H), 7.12–7.14 (m, 1H), 7.29 (d, J=8.3 Hz, 1H), 7.65 (s, 1H), 7.72 (d, J=9.2 Hz, 1H), 7.74 (d, J=8.3 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.8, 25.8, 28.7, 37.3, 40.6, 55.3, 73.7, 82.2, 84.8, 105.9, 118.7, 123.3, 125.3, 128.0, 128.5, 129.2, 134.4, 135.8, 157.9 ppm. IR (KBr): 3487, 2959, 2870, 1632 cm^{-1}. Mass (m/z, %): 330 (M^+, 12), 188 (41), 172 (34), 171 (100), 128 (14). HRMS (ESI): 353.2099, calcd for $C_{21}H_{30}O_3Na$ (M+Na$^+$) 353.2093. Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.33; H, 9.15%. Found: C, 76.48; H, 9.46%.

After following the above procedure using the corresponding (halomethyl)methoxynaphthalene **4b**–**4e**, 1-(methoxynaphthyl)methoxy-2,2,4,4-tetramethylpentan-3-ol **5b**–**5e** were obtained; **5b**: 91.9%, **5c**: 97.9%, **5d**: 94.8%, **5e**: 80.7%.

5b: Colorless amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.03 (s, 9H), 1.04 (s, 3H), 1.07 (s, 3H), 3.24 (d, J=4.9 Hz, 1H), 3.28 (d, J=8.8 Hz, 1H), 3.42 (d, J=8.8 Hz, 1H), 3.50 (br d, J=4.9 Hz, 1H), 3.91 (s, 3H), 4.61 (s, 2H), 7.12 (d, J=2.4 Hz, 1H), 7.15 (dd, J=8.7 and 2.4 Hz, 1H), 7.41 (dd, J=8.5 and 1.7 Hz, 1H), 7.66 (br s, 1H), 7.70–7.73 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.9, 25.9, 28.7, 37.3, 40.6, 55.3, 73.7, 82.0, 84.8, 105.9, 118.9, 126.2, 126.4, 127.0, 128.5, 129.3, 132.8, 134.1, 157.6 ppm. IR (KBr): 3437, 2954, 2865, 1610 cm^{-1}. Mass (m/z, %): 330 (M^+, 28), 278 (11), 188 (89), 187 (27), 186 (33), 172 (55), 171 (100), 128 (19). HRMS (ESI): 353.2090, calcd for $C_{21}H_{30}O_3Na$ (M+Na$^+$) 353.2093. Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.33; H, 9.15%. Found: C, 76.61; H, 8.96%.

5c: Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.99 (s, 12H), 1.04 (s, 3H), 3.20–3.22 (m, 1H), 3.26 (d, J=4.8 Hz, 1H), 3.28 (d, J=8.7 Hz, 1H), 3.45 (d, J=8.7 Hz, 1H), 3.93 (s, 3H), 4.90 (q_{AB}, J=12.0 Hz, 2H), 7.16 (d, J=2.5 Hz, 1H), 7.19 (dd, J=9.2 and 2.5 Hz, 1H), 7.30 (d with fine coupling, J=7.0 Hz, 1H), 7.38 (dd, J=8.2 and 7.0 Hz, 1H), 7.71 (d, J=8.2 Hz, 1H), 8.00 (d, J=9.2 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.7, 25.7, 28.6, 37.2, 40.6, 55.2, 72.1, 81.9, 84.4, 106.5, 118.7, 124.3, 125.5, 125.7, 127.1, 127.6, 133.2, 135.0, 157.4 ppm. IR (liquid film): 3500, 2954, 1626 cm^{-1}. Mass (*m/z*, %): 330 (M$^+$, 15), 188 (49), 172 (33), 171 (100), 128 (18). HRMS (ESI): 353.2076, calcd for $C_{21}H_{30}O_3Na$ (M+Na$^+$) 353.2093.

5d: Pale yellow granules melted at 71.0–71.5 °C (from hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.01 (s, 9H), 1.03 (s, 3H), 1.09 (s, 3H), 3.01 (d, *J*=5.1 Hz, 1H), 3.26 (d, *J*=5.1 Hz, 1H), 3.32 (d, *J*=8.5 Hz, 1H), 3.52 (d, *J*=8.5 Hz, 1H), 4.05 (s, 3H), 4.95 (q_{AB}, *J*=12.7 Hz, 2H), 7.34 (s, 1H), 7.44 (dd with fine coupling, *J*=8.5 and 6.8 Hz, 1H), 7.58 (dd with fine coupling, *J*=8.5 and 6.8 Hz, 1H), 7.96 (d, *J*=8.5 Hz, 1H), 8.28 (d, *J*=8.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.8, 25.7, 28.6, 37.2, 40.8, 57.0, 71.3, 82.0, 84.2, 108.6, 113.7, 123.7, 124.6, 126.8, 127.7, 133.3, 134.9, 134.9, 153.1 ppm. IR (KBr): 3474, 3071, 2955, 2870, 1619 cm^{-1}. Mass (*m/z*, %): 410 (M$^+$+2, 16), 408 (M$^+$, 18), 268 (47), 266 (61), 252 (25), 251 (99), 250 (26), 249 (100), 127 (19), 57 (16). HRMS (ESI): 431.1213, calcd for $C_{21}H_{29}^{79}BrO_3Na$ (M+Na$^+$) 431.1198 and 433.1199, calcd for $C_{21}H_{29}^{81}BrO_3Na$ (M+Na$^+$) 433.1177. Anal. Calcd for $C_{21}H_{29}BrO_3$: C, 61.61; H, 7.14%. Found: C, 61.61; H, 7.20%.

5e: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.03 (s, 9H), 1.06 (s, 3H), 1.11 (s, 3H), 3.26 (s, 1H), 3.32 (d, *J*=8.8 Hz, 1H), 3.52 (d, *J*=8.8 Hz, 1H), 3.65 (br s, 1H), 3.94 (s, 3H), 4.65 (s, 2H), 7.11 (s, 1H), 7.31–7.36 (m, 1H), 7.40–7.45 (m, 1H), 7.72 (d, *J*=8.3 Hz, 1H), 7.75 (s, 1H), 7.77 (d, *J*=8.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.7, 26.0, 28.6, 37.2, 40.6, 55.2, 69.3, 82.4, 84.4, 105.0, 123.7, 126.2, 126.3, 127.6, 127.7, 127.9, 128.4, 134.1, 155.7 ppm. IR (liquid film): 3484, 2954, 2864, 1635, 1604 cm^{-1}. Mass (*m/z*, %): 330 (M$^+$, 19), 188 (66), 172 (35), 171 (100), 141 (31), 91 (7), 57 (8). HRMS (ESI): 353.2064, calcd for $C_{21}H_{30}O_3Na$ (M+Na$^+$) 353.2093.

4.1.3. Synthesis of 1-(7-methoxynaphthalen-2-yl)methoxy-2,2,4,4-tetramethylpentan-3-one (6a); typical procedure. 1-(7-Methoxynaphthalen-2-yl)methoxy-2,2,4,4-tetramethylpentan-3-ol (**5a**) (1.53 g, 4.63 mmol) was added to a suspension of Celite (2.41 g) and PCC (1.20 g, 5.57 mmol) in CH_2Cl_2 (20 mL) at room temperature under a nitrogen atmosphere. The reaction mixture was stirred overnight. 2-Propanol (3.0 mL) was added to the reaction mixture and stirred for 30 min, then diethyl ether (ca. 200 mL) was added to the reaction mixture and was stirred for 30 min. The reaction mixture was filtered twice through Celite and was concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:6) to give 1-(7-methoxynaphthalene-2-yl)methoxy-2,2,4,4-tetramethylpentan-3-one (**6a**) (1.38 g, 4.20 mmol, 90.7%) as colorless solid.

6a: Colorless needles melted at 82.0–82.5 °C (from AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.24 (s, 9H), 1.29 (s, 6H), 3.54 (s, 2H), 3.92 (s, 3H), 4.62 (s, 2H), 7.10–7.14 (m, 1H), 7.11 (s, 1H), 7.25–7.28 (m, 1H), 7.63 (br s, 1H), 7.71 (d, *J*=9.5 Hz, 1H), 7.72 (d, *J*=8.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 24.1, 28.2, 45.8, 50.2, 55.3, 73.4, 78.6, 105.8, 118.4, 123.3, 125.0, 127.6, 128.3, 129.1, 134.3, 136.5, 157.7, 217.2 ppm. IR (KBr): 3440, 2966, 2914, 2864, 1684, 1633 cm^{-1}. Mass (*m/z*, %): 328 (M$^+$, 20), 272 (6), 188 (11), 172 (25), 171 (100), 157 (6), 128 (13), 57 (20). HRMS (ESI): 351.1940, calcd for $C_{21}H_{28}O_3Na$ (M+Na$^+$) 351.1936. Anal. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59%. Found: C, 76.39; H, 8.31%.

After following the above procedure using the corresponding 1-(methoxynaphthyl)methoxy-2,2,4,4-tetramethylpentan-3-ol **5b**–**5e**, 1-(methoxynaphthyl)methoxy-2,2,4,4-tetramethylpentan-3-one **6b**–**6e** were obtained; **6b**: 91.3%, **6c**: 91.8%, **6d**: 94.1%, **6e**: 94.7%.

6b: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.23 (s, 9H), 1.28 (s, 6H), 3.52 (s, 2H), 3.91 (s, 3H), 4.60 (s, 2H), 7.11–7.15 (m, 1H), 7.12 (s, 1H), 7.38 (dd, *J*=8.4 and 1.6 Hz, 1H), 7.65 (br s, 1H), 7.68–7.71 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 24.1, 28.1, 45.8, 50.2, 55.3, 73.4, 78.5, 105.7, 118.7, 126.1, 126.4, 126.7, 128.6, 129.2, 133.6, 133.9, 157.5, 217.2 ppm. IR (KBr): 2966, 1677, 1608 cm^{-1}. Mass (*m/z*, %): 328 (M$^+$, 51), 272 (13), 188 (26), 187 (74), 172 (61), 171 (100), 128 (25), 57 (36). HRMS (ESI): 351.1940, calcd for $C_{21}H_{28}O_3Na$ (M+Na$^+$) 351.1936.

6c: Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.19 (s, 9H), 1.24 (s, 6H), 3.54 (s, 2H), 3.92 (s, 3H), 4.86 (s, 2H), 7.14 (d, *J*=2.4 Hz, 1H), 7.16 (dd, *J*=8.9 and 2.4 Hz, 1H), 7.29 (d, *J*=7.1 Hz, 1H), 7.37 (dd, *J*=8.1 and 7.1 Hz, 1H), 7.69 (d, *J*=8.1 Hz, 1H), 7.98 (d, *J*=8.9 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 24.0, 28.0, 45.7, 50.0, 55.2, 72.0, 78.6, 106.3, 118.5, 124.1, 125.7, 126.0, 127.1, 127.3, 133.9, 134.9, 157.3, 217.4 ppm. IR (liquid film): 2964, 1684, 1473 cm^{-1}. Mass (*m/z*, %): 328 (M$^+$, 49), 272 (24), 188 (22), 172 (54), 171 (100), 128 (33), 57 (32). HRMS (ESI): 351.1924, calcd for $C_{21}H_{28}O_3Na$ (M+Na$^+$) 351.1936.

6d: Pale yellow granules melted at 77.0–77.5 °C (from AcOEt–hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.22 (s, 9H), 1.30 (s, 6H), 3.62 (s, 2H), 4.04 (s, 3H), 4.92 (s, 2H), 7.35 (s, 1H), 7.41 (dd with fine coupling, *J*=8.5 and 6.8 Hz, 1H), 7.56 (dd with fine coupling, *J*=8.5 and 6.8 Hz, 1H), 7.90 (d, *J*=8.5 Hz, 1H), 8.26 (d, *J*=8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 24.0, 28.0, 45.8, 50.1, 57.0, 71.1, 79.3, 108.0, 113.2, 123.8, 124.4, 126.7, 127.5, 133.2, 135.6, 135.6, 153.2, 217.2 ppm. IR (KBr): 2977, 2852, 1682 cm^{-1}. Mass (*m/z*, %): 408 (M$^+$+2, 30), 406 (M$^+$, 30), 352 (14), 350 (13), 268 (14), 266 (16), 252 (22), 251 (99), 250 (23), 249 (100), 127 (19), 85 (15), 57 (59). HRMS (ESI): 429.1059, calcd for $C_{21}H_{27}^{79}BrO_3Na$ (M+Na$^+$) 429.1041 and 431.1042, calcd for $C_{21}H_{27}^{81}BrO_3Na$ (M+Na$^+$) 431.1021. Anal. Calcd for $C_{21}H_{27}BrO_3$: C, 61.92; H, 6.68%. Found: C, 62.06; H, 6.68%.

6e: Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.25 (s, 9H), 1.32 (s, 6H), 3.64 (s, 2H), 3.90 (s, 3H), 4.64 (s, 2H), 7.07 (s, 1H), 7.30–7.33 (m, 1H), 7.38–7.41 (m, 1H), 7.70 (d, *J*=8.1 Hz, 1H), 7.74 (d, *J*=8.1 Hz, 1H), 7.76 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 24.1, 28.1, 45.8, 50.3, 55.2, 68.5, 79.0, 104.6, 123.6, 125.9, 126.3, 126.9, 127.6, 128.58, 128.64, 133.8, 155.4, 217.4 ppm. IR (liquid film): 2963, 2865, 1685, 1635 cm^{-1}. Mass (*m/z*, %): 328 (M$^+$, 25), 272 (9), 188 (16), 187 (19), 172 (28), 171 (100), 141 (31), 128 (9), 57 (18). HRMS (ESI): 351.1930, calcd for $C_{21}H_{28}O_3Na$ (M+Na$^+$) 351.1936.

4.1.4. Synthesis of 3-*tert*-butyl-*r*-3-hydroxy-*c*-2-(7-methoxynaphthalen-2-yl)-4,4-dimethyl-tetrahydrofuran (7a). A solution of 1-(7-methoxynaphthalen-2-yl)methoxy-tetramethylpentane-3-one (**6a**) (1.00 g, 3.04 mmol) in dry DMSO (5 mL) was added dropwise over 5 min to a suspension of *t*-BuOK (682 mg, 6.08 mmol) in DMSO (10 mL) at 0 °C under a nitrogen atmosphere and stirred for 2 h at room temperature. The reaction mixture was poured into satd aq NH_4Cl and then extracted with AcOEt. The organic layer was washed twice with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:5) to give 3-*tert*-butyl-*r*-3-hydroxy-*c*-2-(7-methoxynaphthalen-2-yl)-4,4-dimethyltetrahydrofuran (**7a**-*cis*) (879 mg, 2.68 mmol, 88.1%) as a colorless solid.

7a-*cis*: Colorless needles melted at 110.5–111.0 °C (from AcOEt–hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.98 (s, 9H), 1.20 (s, 3H), 1.44 (s, 3H), 1.63 (s, 1H), 3.55 (d, J=7.3 Hz, 1H), 3.92 (s, 3H), 4.21 (d, J=7.3 Hz, 1H), 5.58 (s, 1H), 7.12–7.14 (m, 1H), 7.15 (s, 1H), 7.43 (dd, J=8.3 and 1.6 Hz, 1H), 7.71–7.73 (m, 1H), 7.75 (d, J=8.3 Hz, 1H), 7.82 (br s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 20.2, 26.6, 28.1, 38.1, 48.3, 55.3, 82.0, 84.2, 85.0, 105.9, 118.9, 124.7, 127.0, 127.5, 128.6, 129.0, 134.3, 138.2, 157.7 ppm. IR (KBr): 3456, 2963, 2870, 1631, 1515 cm^{-1}. Mass (*m*/*z*, %): 328 (M$^+$, 61), 272 (18), 188 (25), 187 (59), 172 (30), 171 (100), 159 (20), 85 (40), 57 (31). HRMS (ESI): 351.1939, calcd for $C_{21}H_{28}O_3Na$ (M+Na$^+$) 351.1936. Anal. Calcd for $C_{21}H_{28}O_3$+hexane (3.2 w/w %): C, 77.00; H, 8.94%. Found: C, 76.88; H, 9.34.

4.1.5. Synthesis of 3-*tert*-butyl-3-hydroxy-2-(6-methoxynaphthalen-2-yl)-4,4-dimethyltetrahydrofuran (7b); typical procedure. BuLi (1.62 M in hexane) (47.0 mL, 76.1 mmol) was added to a solution of diisopropylamine (11.2 mL, 7.99 mmol) in dry THF (70 mL) under a nitrogen atmosphere at room temperature and stirred for 0.5 h. To the solution, 1-(6-methoxynaphthalen-2-yl)methoxy-2,2,4,4-tetramethylpentan-3-one (**6b**) (12.5 g, 38.1 mmol) in dry THF (24 mL) was added dropwise under a nitrogen atmosphere at −78 °C and stirred and then stirred at 0 °C for 2.5 h. The solution was poured into satd aq NH_4Cl and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:4) to give 3.35 g of **7b** as a mixture of 3-*tert*-butyl-*r*-3-hydroxy-*c*-2-(6-methoxynaphthalen-2-yl)-4,4-dimethyltetrahydrofuran (**7b**-*cis*) and 3-*tert*-butyl-*r*-3-hydroxy-*t*-2-(6-methoxynaphthalen-2-yl)-4,4-dimethyltetrahydrofuran (**7b**-*trans*) in 91.1%.

7b-*trans*: Colorless needles melted at 125.0–125.5 °C (from AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.87 (br s, 9H), 1.22 (s, 3H), 1.45 (s, 3H), 1.98 (s, 1H), 3.74 (d, J=8.3 Hz, 1H), 3.91 (s, 3H), 3.96 (d, J=8.3 Hz, 1H), 5.17 (s, 1H), 7.11–7.15 (m, 1H), 7.12 (s, 1H), 7.63 (dd, J=8.7 and 1.5 Hz, 1H), 7.68 (d, J=8.7 Hz, 1H), 7.71 (d, J=8.9 Hz, 1H), 7.88 (br s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 22.5, 26.2, 28.3, 39.2, 47.9, 55.3, 80.9, 88.7, 94.7, 105.5, 118.7, 125.9, 127.5, 127.7, 128.3, 129.5, 134.0, 136.4, 157.6 ppm. IR (KBr): 3487, 2964, 2875, 1605 cm^{-1}. Mass (*m*/*z*, %): 328 (M$^+$, 25), 310 (35), 296 (28), 295 (100), 239 (33), 188 (19), 187 (99), 186 (49), 185 (78), 172 (14), 171 (75), 157 (26), 57 (20). HRMS (ESI): 351.1937, calcd for $C_{21}H_{28}O_3Na$ (M+Na$^+$) 351.1936. Anal. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59%. Found: C, 76.89; H, 9.10%.

7b-*cis*: Colorless plates melted at 126.0–126.5 °C (from AcOEt–hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.97 (s, 9H), 1.19 (s, 3H), 1.43 (s, 3H), 1.61 (s, 1H), 3.54 (d, J=7.1 Hz, 1H), 3.90 (s, 3H), 4.20 (d, J=7.1 Hz, 1H), 5.57 (s, 1H), 7.11 (d, J=2.3 Hz, 1H), 7.14 (dd, J=9.0 and 2.3 Hz, 1H), 7.54 (d with fine coupling, J=8.2 Hz, 1H), 7.71–7.75 (m, 2H), 7.83 (br s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.2, 26.5, 28.0, 38.0, 48.2, 55.3, 81.9, 84.2, 84.9, 105.6, 119.0, 126.7, 127.6, 128.0, 128.6, 129.6, 134.4, 135.3, 157.9 ppm. IR (KBr): 3547, 2960, 1631, 1604 cm^{-1}. Mass (*m*/*z*, %): 328 (M$^+$, 53), 272 (9), 188 (20), 187 (100), 172 (14), 171 (68), 85 (19), 57 (12). HRMS (ESI): 351.1934, calcd for $C_{21}H_{28}O_3Na$ (M+Na$^+$) 351.1936. Anal. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59%. Found: C, 76.99; H, 8.81%.

After following the above procedure using the corresponding 1-(methoxynaphthyl)methoxy-2,2,4,4-tetramethylpentan-3-one **6c**, **6d**, and **6e**, 3-*tert*-butyl-3-hydroxy-2-(methoxynaphthyl)-4,4-dimethyltetrahydrofurans **7c**, **7d**, and **7e** were obtained as mixture of cis- and trans-isomers; **7c**: 90.1%, **7d**: 99.2%, **7e**: 98.1%.

7c-*trans*: Colorless needles melted at 100.5–101.0 °C (from AcOEt–hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.78 (br s, 9H), 1.32 (s, 3H), 1.43 (s, 3H), 1.98 (s, 1H), 3.84 (q_{AB}, J=3.8 Hz, 2H), 3.91 (s, 3H), 5.80 (s, 1H), 7.12 (d, J=2.7 Hz, 1H), 7.16 (dd, J=9.3 and 2.7 Hz, 1H), 7.43 (dd, J=8.1 and 7.3 Hz, 1H), 7.67 (d, J=8.1 Hz, 1H), 7.86 (d, J=7.3 Hz, 1H), 8.23 (d, J=9.3 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 24.7, 25.9, 28.2, 39.6, 48.7, 55.1, 79.7, 88.0, 88.5, 106.3, 118.3, 124.2, 125.5, 126.5, 126.7, 127.6, 134.7, 136.9, 156.7 ppm. IR (KBr): 3571, 2964, 1473, 1251 cm^{-1}. Mass (*m*/*z*, %): 328 (M$^+$, 58), 310 (36), 295 (89), 280 (28), 239 (24), 187 (37), 186 (20), 172 (31), 171 (100), 157 (26), 115 (29), 85 (25), 57 (41). HRMS (ESI): 351.1919, calcd for $C_{21}H_{28}O_3Na$ (M+Na$^+$) 351.1936. Anal. Calcd for $C_{21}H_{28}O_3$+hexane (4.2 w/w %): C, 77.08; H, 8.92%. Found: C, 76.96; H, 9.20%.

7c-*cis*: Colorless needles melted at 102.5–103.0 °C (from AcOEt–hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.88 (s, 9H), 1.22 (s, 3H), 1.49 (s, 3H), 1.98 (s, 1H), 3.57 (d, J=7.1 Hz, 1H), 3.90 (s, 3H), 4.26 (d, J=7.1 Hz, 1H), 6.15 (s, 1H), 7.13 (d, J=2.7 Hz, 1H), 7.18 (d, J=9.2 Hz, 1H), 7.44 (dd, J=7.8 and 6.4 Hz, 1H), 7.60 (d, J=6.4 Hz, 1H), 7.70 (d, J=7.8 Hz, 1H), 8.22 (d, J=9.2 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.3, 27.0, 27.9, 38.2, 48.3, 55.2, 80.6, 81.9, 85.9, 106.7, 118.6, 125.8, 126.0, 126.0, 127.4, 127.7, 135.6, 136.3, 157.0 ppm. IR (KBr): 3560, 2964, 1473 cm^{-1}. Mass (*m*/*z*, %): 328 (M$^+$, 90), 272 (29), 188 (26), 187 (62), 172 (40), 171 (100), 85 (40), 57 (34). HRMS (ESI): 351.1927, calcd for $C_{21}H_{28}O_3Na$ (M+Na$^+$) 351.1936. Anal. Calcd for $C_{21}H_{28}O_3$+hexane (4.2 w/w %): C, 77.08; H, 8.92%. Found: C, 77.00; H, 9.18%.

7d-*trans*: Colorless prisms melted at 151.5–153.0 °C (from AcOEt–hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.79 (br s, 9H), 1.37 (s, 3H), 1.42 (s, 3H), 1.99 (s, 1H), 3.90 (s, 2H), 4.04 (s, 3H), 5.87 (s, 1H), 7.41 (dd with fine coupling, J=8.5 and 6.8 Hz, 1H), 7.54 (dd with fine coupling, J=8.5 and 6.8 Hz, 1H), 7.79 (s, 1H), 8.27 (d, J=8.5 Hz, 1H), 8.31 (d, J=8.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 25.6, 25.7, 27.9, 39.7, 48.7, 57.0, 79.7, 86.8, 88.5, 108.4, 114.2, 124.3, 125.1, 126.7, 127.2, 128.8, 132.9, 138.7, 153.1 ppm. IR (KBr): 3614, 2972, 2936, 2881, 1596 cm^{-1}. Mass (*m/z*, %): 408 (M^++2, 60), 406 (M^+, 60), 390 (11), 388 (11), 375 (27), 373 (27), 352 (28), 350 (28), 266 (44), 251 (100), 249 (99), 158 (29), 127 (22), 85 (66), 57 (72). HRMS (ESI): 461.1356, calcd for $C_{22}H_{31}{}^{79}BrO_4Na$ (M+Na$^+$+MeOH) 461.1303, 463.1332, calcd for $C_{22}H_{31}{}^{81}BrO_4Na$ (M+Na$^+$+MeOH) 463.1283. Anal. Calcd for $C_{21}H_{27}BrO_3$: C, 61.92; H, 6.68%. Found: C, 62.15; H, 7.15%.

7d-*cis*: Colorless granules melted at 126.5–128.0 °C (from AcOEt–hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.89 (s, 9H), 1.24 (s, 3H), 1.52 (s, 3H), 1.65 (br s, 1H), 3.60 (d, J=7.3 Hz, 1H), 4.06 (s, 3H), 4.26 (d, J=7.3 Hz, 1H), 6.22 (s, 1H), 7.42–7.46 (m, 1H), 7.54–7.58 (m, 1H), 7.65 (s, 1H), 8.21 (d, J=8.7 Hz, 1H), 8.31 (d, J=8.7 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.5, 27.2, 28.0, 38.2, 48.4, 57.0, 79.0, 82.0, 86.2, 109.4, 116.0, 123.9, 124.4, 127.1, 127.3, 128.3, 133.3, 137.7, 152.9 ppm. IR (KBr): 3548, 3507, 2965, 2879, 1596 cm^{-1}. Mass (*m/z*, %): 408 (M^++2, 20), 406 (M^+, 20), 390 (11), 388 (11), 375 (27), 373 (27), 352 (28), 350 (28), 267 (27), 266 (41), 265 (38), 264 (36), 252 (24), 251 (100), 250 (25), 249 (99), 158 (29), 85 (75), 57 (87). HRMS (ESI): 429.1079, calcd for $C_{21}H_{27}{}^{79}BrO_3Na$ (M+Na$^+$) 429.1041. Anal. Calcd for $C_{21}H_{27}BrO_3$: C, 61.92; H, 6.68%. Found: C, 61.47; H, 6.89%.

7e-*trans*: Colorless needles melted at 102.0–103.0 °C (from AcOEt–hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.96 (br s, 9H), 1.34 (s, 3H), 1.37 (s, 3H), 3.87 (br s, 1H), 3.88 (d, J=8.2 Hz, 1H), 4.00 (s, 3H), 4.01 (d, J=8.2 Hz, 1H), 5.54 (s, 1H), 7.10 (s, 1H), 7.33–7.37 (m, 1H), 7.41–7.40 (m, 1H), 7.71 (d, J=8.2 Hz, 1H), 7.79 (d, J=7.8 Hz, 1H), 8.09 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 25.4, 28.7, 29.0, 40.1, 48.8, 55.6, 80.1, 84.5, 86.4, 105.1, 124.1, 126.2, 126.3, 127.1, 128.0, 129.0, 131.4, 133.4, 155.0 ppm. IR (KBr): 3502, 2967, 2875, 1631, 1468 cm^{-1}. Mass (*m/z*, %): 328 (M^+, 40), 295 (28), 188 (26), 187 (100), 172 (28), 171 (80), 141 (18), 57 (29). HRMS (ESI): 351.1919, calcd for $C_{21}H_{28}O_3Na$ (M+Na$^+$) 351.1936. Anal. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59%. Found: C, 76.81; H, 9.11%.

7e-*cis*: Colorless granules melted at 113.5–114.5 °C (from AcOEt–hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.98 (s, 9H), 1.21 (s, 3H), 1.44 (s, 3H), 3.51 (d, J=7.1 Hz, 1H), 3.96 (s, 3H), 4.23 (d, J=7.1 Hz, 1H), 6.02 (s, 1H), 7.13 (s, 1H), 7.32–7.36 (m, 1H), 7.41–7.45 (m, 1H), 7.71 (d, J=8.3 Hz, 1H), 7.79 (d, J=8.1 Hz, 1H), 7.94 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.3, 26.8, 27.6, 38.2, 48.5, 55.1, 82.0, 82.0, 85.6, 105.6, 123.9, 126.2, 126.5, 128.0, 128.6, 130.4, 130.7, 134.1, 155.5 ppm. IR (KBr): 3455, 2963, 2874, 1631, 1470 cm^{-1}. Mass (*m/z*, %): 328 (M^+, 38), 272 (15), 188 (29), 187 (100), 172 (29), 171 (77), 141 (16), 85 (19), 57 (22). HRMS (ESI): 351.1918, calcd for $C_{21}H_{28}O_3Na$ (M+Na$^+$) 351.1936. Anal. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59%. Found: C, 76.79; H, 9.17%.

4.1.6. Synthesis of 4-*tert*-butyl-5-(7-methoxynaphthalen-2-yl)-3,3-dimethyl-2,3-dihydrofuran (8a). $SOCl_2$ (0.24 mL, 3.29 mmol) was added to a solution of 3-*tert*-butyl-*r*-3-hydroxy-*c*-2-(7-methoxynaphthalen-2-yl)-4,4-dimethyltetrahydrofuran (**8a**) (879 mg, 2.68 mmol) and pyridine (2.17 mL, 26.8 mmol) in dry CH_2Cl_2 (10 mL) at 0 °C under a nitrogen atmosphere and the solution was stirred for 30 min. The reaction mixture was allowed to warm from 0 °C to room temperature and was stirred at room temperature for 2 h. The reaction mixture was poured into satd aq NaCl and then extracted with AcOEt. The organic layer was washed with 1 N HCl, washed twice with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:5) to give 4-*tert*-butyl-5-(7-methoxynaphthalen-2-yl)-3,3-dimethyl-2,3-dihydrofuran (**8a**) (749 mg, 2.41 mmol, 89.9%) as colorless viscous oil.

8a: Colorless viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.07 (s, 9H), 1.37 (s, 6H), 3.91 (s, 3H), 3.92 (s, 2H), 7.12 (d, J=2.3 Hz, 1H), 7.14 (dd, J=8.9 and 2.3 Hz, 1H), 7.26 (dd, J=8.3 and 1.7 Hz, 1H), 7.68 (br s, 1H), 7.72 (d, J=8.9 Hz, 1H), 7.73 (d, J=8.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 27.5, 32.5, 32.7, 47.3, 55.2, 83.1, 105.9, 118.9, 125.4, 125.9, 127.1, 127.9, 128.3, 129.0, 133.9, 134.1, 150.1, 157.6 ppm. IR (KBr): 3330, 2961, 2871, 1628, 1516 cm^{-1}. Mass (*m/z*, %): 310 (M^+, 30), 296 (23), 295 (100), 239 (16), 185 (21), 171 (20), 157 (10), 57 (13). HRMS (ESI): 333.1829, calcd for $C_{21}H_{26}O_2Na$ (M+Na$^+$) 333.1831.

4.1.7. Synthesis of 4-*tert*-butyl-5-(6-methoxynaphthalen-2-yl)-3,3-dimethyl-2,3-dihydrofuran (8b); typical procedure. $TsOH\cdot H_2O$ (457 mg, 2.40 mmol) was added to a solution of tetrahydrofuran **7b**-*trans* (7.98 g, 21.8 mmol) in toluene (80 mL) under a nitrogen atmosphere at room temperature and stirred for 1.5 h at refluxed temperature. The reaction mixture was poured into satd aq $NaHCO_3$ and extracted with AcOEt. The organic layer was washed twice with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:6) to afford 4-*tert*-butyl-5-(6-methoxynaphthalen-2-yl)-3,3-dimethyl-2,3-dihydrofuran (**8b**) (6.46 g, 20.8 mmol, 85.7%) as a colorless solid.

8b: Colorless needles melted at 95.0–96.0 °C (from AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.06 (s, 9H), 1.36 (s, 6H), 3.90 (s, 3H), 3.91 (s, 2H), 7.11 (d, J=2.4 Hz, 1H), 7.13 (dd, J=8.8 and 2.4 Hz, 1H), 7.36 (dd, J=8.3 and 1.7 Hz, 1H), 7.67–7.72 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 27.5, 32.6, 32.7, 47.3, 55.3, 83.1, 105.6, 118.8, 125.9, 126.2, 128.2, 128.3, 128.7, 129.5, 131.3, 134.0, 150.1, 157.8 ppm. IR (KBr): 2958, 1861, 1627, 1599 cm^{-1}. Mass (*m/z*, %): 310 (M^+, 61), 296 (41), 295 (100), 253 (10), 239 (22), 185 (33), 157 (10), 57 (15). HRMS (ESI): 333.1830, calcd for $C_{21}H_{26}O_2Na$ (M+Na$^+$) 333.1831. Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44%. Found: C, 81.26; H, 8.95%.

After following the above procedure using the corresponding 3-*tert*-butyl-*r*-3-hydroxy, *tert*-2-methoxynaphthyl-4,4-dimethyltetrahydrofurans **7c–7e**, 4-*tert*-butyl-5-methoxynaphthyl-3,3-dimethyl-2,3-dihydrofurans **8c–8e** were obtained; **8c**: 98.9%, **8d**: 90.8%, **8e**: 85.3%

8c: Colorless plates melted at 83.5–84.0 °C (from AcOEt–hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.99 (s, 9H), 1.40 (s, 3H), 1.46 (s, 3H), 3.89 (s, 3H), 3.97 (q_{AB}, J=7.8 Hz, 2H), 7.10 (d, J=2.7 Hz, 1H), 7.16 (dd, J=9.2 and 2.7 Hz, 1H), 7.28 (d with fine coupling, J=8.1 Hz, 1H), 7.38 (d, J=8.3 and 8.1 Hz, 1H), 7.70 (d, J=8.3 Hz, 1H), 7.85 (d, J=9.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 27.4, 27.7, 32.0, 32.7, 47.3, 55.2, 83.3, 105.8, 118.9, 125.5, 125.8, 127.3, 127.4, 127.6, 127.7, 133.4, 134.5, 147.9, 157.4 ppm. IR (KBr): 2959, 1625, 1469 cm^{-1}. Mass (*m*/*z*, %): 310 (M^+, 35), 296 (23), 295 (100), 280 (33), 239 (25), 185 (11), 157 (13), 57 (11). HRMS (ESI): 333.1822, calcd for $C_{21}H_{26}O_2Na$ ($M+Na^+$) 333.1831. Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44%. Found: C, 81.41; H, 8.94%.

8d: Amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.01 (s, 9H), 1.43 (s, 3H), 1.48 (s, 3H), 4.00 (q_{AB}, J=7.8 Hz, 2H), 4.03 (s, 3H), 7.22 (s, 1H), 7.41 (dd with fine coupling, J=7.8 and 6.8 Hz, 1H), 7.54 (dd with fine coupling, J=8.5 and 6.8 Hz, 1H), 7.88 (d, J=7.8 Hz, 1H), 8.22 (d, J=8.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 27.4, 27.6, 32.0, 32.7, 47.4, 57.2, 83.4, 109.3, 115.8, 124.7, 126.1, 126.3, 127.7, 128.6, 128.8, 133.0, 134.7, 146.8, 152.8 ppm. IR (KBr): 2958, 2931, 2862, 1590 cm^{-1}. Mass (*m*/*z*, %) 390 (M^++2, 43), 388 (M^+, 43), 376 (25), 375 (100), 374 (26), 373 (99), 360 (27), 358 (28), 238 (19), 128 (11), 57 (37). HRMS (ESI): 443.1234, calcd for $C_{22}H_{29}^{79}BrO_3Na$ ($M+Na^++MeOH$) 443.1198 and 445.1220, calcd for $C_{22}H_{29}^{81}BrO_3Na$ ($M+Na^++MeOH$). Anal. Calcd for $C_{21}H_{25}BrO_2$+hexane (3.6 w/w %): C, 65.46; H, 6.82%. Found: C, 65.52; H, 6.83%.

8e: Colorless amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.03 (s, 9H), 1.37 (s, 6H), 3.92 (q_{AB}, J=7.6 Hz, 2H), 3.93 (s, 3H), 7.11 (s, 1H), 7.30–7.34 (m, 1H), 7.40–7.45 (m, 1H), 7.67 (s, 1H), 7.72 (d, J=7.8 Hz, 1H), 7.74 (d. J=7.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.2, 31.9, 32.5, 47.1, 55.6, 83.1, 105.3, 123.6, 126.4, 126.5, 126.9, 127.0, 127.8, 128.2, 131.3, 134.6, 145.9, 155.9 ppm. IR (KBr): 2955, 2866, 1654, 1466 cm^{-1}. Mass (*m*/*z*, %): 310 (M^+, 31), 296 (23), 295 (100), 239 (23), 185 (28). HRMS (ESI): 333.1812, calcd for $C_{21}H_{26}O_2Na$ ($M+Na^+$) 333.1831. Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44%. Found: C, 81.09; H, 8.94%.

4.1.8. Synthesis of 4-*tert*-butyl-5-(3-methoxynaphthalen-1-yl)-3,3-dimethyl-2,3-dihydrofuran (8d′). Butyllithium (1.61 mol L^{-1} in hexane, 4.0 mL, 6.44 mmol) was added to a solution of 5-(4-bromo-3-methoxynaphthalen-1-yl)-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**8d**) (2.11 g, 5.42 mmol) in THF (20 mL) under a nitrogen atmosphere at −78 °C. After stirring for 10 min, the reaction mixture was poured into satd aq NH_4Cl and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel and eluted with AcOEt–hexane (1:10) to give 4-*tert*-butyl-5-(3-methoxynaphthalen-1-yl)-3,3-dimethyl-2,3-dihydrofuran (**8d′**) (1.67 g, 5.38 mmol, 99.3%) as a colorless solid.

8d′: Colorless granules melted at 83.0–84.0 °C (from hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.02 (s, 9H), 1.41 (s, 3H), 1.47 (s, 3H), 3.92 (s, 3H), 3.97 (q_{AB}, J=7.8 Hz, 2H), 7.12 (s, 2H), 7.35 (dd with fine coupling, J=8.1 and 6.8 Hz, 1H), 7.42 (dd with fine coupling, J=8.1 and 6.8 Hz, 1H), 7.71 (d, J=8.1 Hz, 1H), 7.85 (d, J=8.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 27.3, 27.7, 32.0, 32.7, 47.3, 55.3, 83.3, 106.4, 120.7, 123.9, 125.7, 126.3, 126.9, 127.8, 127.9, 134.6, 135.1, 147.2, 156.5 ppm. IR (KBr): 3062, 2955, 2863, 1598 cm^{-1}. Mass (*m*/*z*, %): 310 (M^+, 34), 296 (20), 295 (100), 280 (20), 265 (11), 239 (22). HRMS (ESI): 333.1856, calcd for $C_{21}H_{26}O_2Na$ ($M+Na^+$) 333.1831. Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44%. Found: C, 81.32; H, 8.87%.

4.1.9. Synthesis of 4-*tert*-butyl-5-(7-hydroxynaphthalen-2-yl)-3,3-dimethyl-2,3-dihydrofuran (3a); typical procedure. CH_3SNa (338 mg, 4.82 mmol) was added to a solution of 4-*tert*-butyl-5-(7-methoxynaphthalen-2-yl)-3,3-dimethyl-2,3-dihydrofuran (**8a**) (749 mg, 2.41 mmol) in dry DMF (10 mL) at room temperature under a nitrogen atmosphere and was refluxed for 2 h. The reaction mixture was poured into satd aq NH_4Cl and then extracted with AcOEt. The organic layer was washed twice with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:3) to give 4-*tert*-butyl-5-(7-hydroxynaphthalen-2-yl)-3,3-dimethyl-2,3-dihydrofuran (**3a**) (664 mg, 2.24 mmol, 92.9%) as a colorless solid.

3a: Colorless granules melted at 196.0–197.0 °C (from CH_2Cl_2–hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.06 (s, 9H), 1.38 (s, 6H), 3.93 (s, 2H), 5.15 (s, 1H), 7.03–7.07 (m, 1H), 7.06 (s, 1H), 7.24 (dd, J=8.3 and 1.6 Hz, 1H), 7.59 (br s, 1H), 7.69 (d, J=8.5 Hz, 1H), 7.70 (d, J=8.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 27.5, 32.6, 32.6, 47.3, 83.2, 109.7, 118.0, 125.5, 126.1, 127.2, 127.5, 128.3, 129.4, 133.9, 134.1, 149.9, 153.4 ppm. IR (KBr): 3330, 2961, 2871, 1628, 1518 cm^{-1}. Mass (*m*/*z*, %): 296 (M^+, 29), 282 (24), 281 (100), 225 (17), 171 (23), 143 (10), 115 (4), 57 (12). HRMS (ESI): 319.1672, calcd for $C_{20}H_{24}O_2Na$ ($M+Na^+$) 319.1674. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16%. Found: C, 80.70; H, 8.63%.

After following the above procedure using the corresponding 4-*tert*-butyl-5-methoxynaphthyl-3,3-dimethyl-2,3-dihydrofurans **8b–8c**, **8d′**, and **8e**, 4-*tert*-butyl-5-hydroxynaphthyl-3,3-dimethyl-2,3-dihydrofurans **3b–3e** were obtained; **3b**: 88.1%, **3c**: 84.8%, **3d**: 95.1%, **3e**: 85.0%.

3b: Colorless plates melted at 202.5–203.0 °C (from AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.06 (s, 9H), 1.37 (s, 6H), 3.93 (s, 2H), 5.54 (s, 1H), 6.94 (d, J=2.4 Hz, 1H), 6.98 (dd, J=8.8 and 2.4 Hz, 1H), 7.31 (dd, J=8.5 and 1.6 Hz, 1H), 7.49 (d, J=8.5 Hz, 1H), 7.60 (d, J=8.8, 1H), 7.65 (br s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 27.5, 32.6, 32.7, 47.3, 83.0, 109.4, 118.0, 125.9, 126.2, 128.1, 128.2, 128.9, 129.8, 130.9, 134.0, 149.9, 153.7 ppm. IR (KBr): 3385, 2956, 1856, 1655, 1628, 1478, 1600 cm^{-1}. Mass (*m*/*z*, %): 296 (M$^+$, 50), 282 (32), 281 (100), 225 (19), 171 (32). HRMS (ESI): 319.1693, calcd for $C_{20}H_{24}O_2Na$ (M+Na$^+$) 319.1674. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16; O, 10.80. Found: C, 81.12; H, 8.63.

3c: Colorless needles melted at 197.5–198.0 °C (from AcOEt–hexane). ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 0.99 (s, 9H), 1.41 (s, 3H), 1.46 (s, 3H), 4.00 (q$_{AB}$, *J*=8.0 Hz, 2H), 5.97 (s, 1H), 6.83 (d, *J*=2.4 Hz, 1H), 6.95 (d, *J*=9.0 and 2.4 Hz, 1H), 7.26 (d with fine coupling, *J*=7.0 Hz, 1H), 7.32 (d, *J*=8.2 and 2.4 Hz, 1H), 7.34 (d, *J*=8.2 Hz, 1H), 7.77 (d, *J*=9.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 27.3, 27.7, 32.0, 32.7, 47.3, 83.1, 109.6, 118.2, 125.4, 125.7, 127.1, 127.5, 127.5, 128.0, 133.1, 134.6, 147.6, 153.3 ppm. IR (KBr): 3330, 2959, 1633, 1433 cm^{-1}. Mass (*m*/*z*, %): 296 (M$^+$, 35), 282 (21), 281 (100), 266 (29), 225 (23), 171 (17), 143 (15), 57 (22). HRMS (ESI): 297.1877, calcd for $C_{20}H_{25}O_2$ (M+H$^+$) 297.1855 and 319.1671, calcd for $C_{20}H_{24}O_2Na$ (M+Na$^+$) 319.1674. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16%. Found: C, 81.38; H, 8.63%.

3d: Pale yellow granules melted at 152.5–154.0 °C (from AcOEt–hexane). ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 1.02 (s, 9H), 1.41 (s, 3H), 1.47 (s, 3H), 3.98 (q$_{AB}$, *J*=8.1 Hz, 2H), 5.05 (s, 1H), 7.07 (d, *J*=2.4 Hz, 1H), 7.10 (br d, *J*=2.4 Hz, 1H), 7.34 (dd with fine coupling, *J*=8.3 and 6.8 Hz, 1H), 7.41 (dd with fine coupling, *J*=8.1 and 6.8 Hz, 1H), 7.64 (d, *J*=8.1 Hz, 1H), 7.85 (d, *J*=8.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 27.3, 27.5, 31.9, 32.7, 47.3, 83.2, 110.3, 120.1, 123.9, 125.6, 126.3, 126.6, 127.8, 128.2, 134.6, 135.1, 146.8, 152.3 ppm. IR (KBr): 3344, 2958, 2870, 1600 cm^{-1}. Mass (*m*/*z*, %): 296 (M$^+$, 46), 282 (23), 281 (100), 266 (39), 251 (23), 225 (29), 171 (13), 115 (14). HRMS (ESI): 319.1718, calcd for $C_{20}H_{24}O_2Na$ (M+Na$^+$) 319.1674. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16%. Found: C, 81.06; H, 8.76%.

3e: Colorless columns melted at 133.5–134.0 °C (from AcOEt–hexane). ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 1.11 (s, 9H), 1.41 (s, 6H), 3.96 (s, 2H), 5.55 (s, 1H), 7.28 (s, 1H), 7.31 (dd with fine coupling, *J*=8.1 and 6.8 Hz, 1H), 7.42 (dd with fine coupling, *J*=7.8 and 6.8 Hz, 1H), 7.69 (d, *J*=7.8 Hz, 1H), 7.71 (s, 1H), 7.74 (d, *J*=8.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 27.4, 32.0, 32.8, 47.5, 83.1, 110.0, 123.7, 124.4, 126.4, 126.8, 127.9, 128.1, 130.6, 131.3, 135.0, 144.4, 151.4 ppm. IR (KBr): 3372, 2962, 1659, 1452 cm^{-1}. Mass (*m*/*z*, %): 296 (M$^+$, 42), 282 (23), 281 (100), 225 (55), 171 (41), 115 (15), 57 (22). HRMS (ESI): 319.1665, calcd for $C_{20}H_{24}O_2Na$ (M+Na$^+$) 319.1674. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16%. Found: C, 81.08; H, 8.60%.

4.1.10. Singlet oxygenation of 4-*tert*-butyl-5-(7-hydroxynaphthalen-2-yl)-3,3-dimethyl-2,3-dihydrofuran (3a); typical procedure. A solution of a 4-*tert*-butyl-5-(7-hydroxynaphthalen-2-yl)-3,3-dimethyl-2,3-dihydrofuran (**3a**) (100 mg, 0.337 mmol) and tetraphenylporphin (TPP) (1.0 mg) in CH$_2$Cl$_2$ (10 mL) was irradiated externally with 940 W Na lamp under an oxygen atmosphere at 0 °C for 1 h. The photolysate was concentrated in vacuo. The residue was chromatographed on silica gel with CH$_2$Cl$_2$ to give a 5-*tert*-butyl-1-(7-hydroxynaphthalen-2-yl)-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (**1aA**) (91.1 mg, 0.277 mmol, 82.2%) as a colorless solid.

1aA: Colorless needles melted at 122.0–123.0 °C (from CH$_2$Cl$_2$–hexane). ^{1}H NMR (500 MHz, CDCl$_3$): δ_H 0.99 (s, 9H), 1.19 (s, 3H), 1.43 (s, 3H), 3.87 (d, *J*=8.2 Hz, 1H), 4.63 (d, *J*=8.2 Hz, 1H), 4.95 (s, 1H), 7.16 (dd, *J*=8.7 and 2.5 Hz, 1H), 7.21 (d, *J*=2.5 Hz, 1H), 7.48 (d with fine coupling, *J*=8.7 Hz, 1H), 7.77 (d, *J*=8.7 Hz, 1H), 7.78 (d, *J*=8.7 Hz, 1H), 8.02 (s, 1H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ_C 18.5, 25.1, 26.8, 36.8, 45.7, 80.4, 105.2, 110.4, 117.0, 119.1, 122.9, 126.9, 127.5, 129.0, 129.5, 133.6, 133.7, 153.9 ppm. IR (KBr): 3744, 3421, 2966, 1692, 1609 cm^{-1}. Mass (*m*/*z*, %): 328 (M$^+$, 9), 296 (2), 272 (19), 188 (29), 172 (16), 171 (100), 143 (18), 115 (8), 57 (21). HRMS (ESI): 351.1558, calcd for $C_{20}H_{24}O_4Na$ (M+Na$^+$) 351.1572. Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37%. Found: C, 72.83; H, 7.75%.

After following the above procedure using the corresponding 4-*tert*-butyl-5-hydroxynaphthyl-3,3-dimethyl-2,3-dihydrofurans **3b–3e**, 5-*tert*-butyl-1-(hydroxynaphthalen-2-yl)-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptanes **1bA–1eA** were obtained; **1bA**: 53.7%, **1cA**: 88.2%, **3d**: 80.5%, **3e**: 83.5%.

1bA: Colorless needles melted at 158.0–159.0 °C (CH$_2$Cl$_2$–hexane). ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 0.99 (s, 9H), 1.18 (s, 3H), 1.43 (s, 3H), 3.86 (d, *J*=8.1 Hz, 1H), 4.62 (d with fine coupling, *J*=8.1 Hz, 1H), 5.07 (s, 1H), 7.12 (d, *J*=2.4 Hz, 1H), 7.14–7.16 (m, 1H), 7.59 (dd, *J*=8.6 and 1.7 Hz, 1H), 7.69 (d, *J*=8.6 Hz, 1H), 7.81 (d, *J*=8.8 Hz, 1H), 8.09 (d, *J*=1.7 Hz, 1H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ_C 18.5, 25.1, 26.8, 36.7, 45.6, 80.3, 104.9, 109.3, 117.0, 118.3, 125.9, 126.1, 127.9, 128.4, 130.7, 130.9, 134.9, 154.5 ppm. IR (KBr): 3368, 2972, 1631, 1482 cm^{-1}. Mass (*m*/*z*, %): 328 (M$^+$, 11), 272 (17), 188 (24), 172 (13), 171 (100), 143 (14), 57 (14). HRMS (ESI): 351.1584, calcd for $C_{20}H_{24}O_4Na$ (M+Na$^+$) 351.1572. Anal. Calcd for $C_{20}H_{24}O_4$+CH$_2$Cl$_2$ (1.0 w/w %): C, 72.62; H, 7.32%. Found: C, 72.78; H, 6.80%.

1cA: Colorless needles melted at 162.5–163.0 °C (from CH$_2$Cl$_2$–hexane). ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 0.89 (s, 9H), 1.29 (s, 3H), 1.61 (s, 3H), 4.06 (d, *J*=8.7 Hz, 1H), 4.79 (d, *J*=8.7 Hz, 1H), 5.12 (s, 1H), 7.10 (dd, *J*=9.4 and 2.6 Hz, 1H), 7.14 (d, *J*=2.6 Hz, 1H), 7.43–7.47 (m, 1H), 7.72 (d, *J*=8.2 Hz, 1H), 8.06 (br s, 1H), 8.50 (br s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 20.0, 26.1, 26.7, 36.8, 45.6, 80.5, 106.0, 110.5, 117.7, 125.2, 126.6, 127.8, 128.3, 129.6, 131.3, 135.8, 152.8 ppm. IR (KBr): 3363, 2975, 1633, 1514 cm^{-1}. Mass (*m*/*z*, %): 328 (M$^+$, 20), 278 (12), 272 (20), 188 (34), 172 (13), 171 (100), 143 (18), 115 (8), 57 (26). HRMS (ESI): 351.1590, calcd for $C_{20}H_{24}O_4Na$ (M+Na$^+$) 351.1572. Anal. Calcd for $C_{20}H_{24}O_4$+CH$_2$Cl$_2$ (6.1 w/w %): C, 69.56; H, 7.06%. Found: C, 69.61; H, 7.18%.

1dA: Pale yellow granules melted at 157.5–158.0 °C (from CH$_2$Cl$_2$–hexane). ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 0.91 (s, 9H), 1.30 (s, 3H), 1.63 (s, 3H), 4.07 (d, *J*=8.4 Hz, 1H), 4.68 (d, *J*=8.4 Hz, 1H), 4.97 (s, 1H), 7.24 (d, *J*=2.7 Hz, 1H), 7.34 (dd with fine coupling, J=8.3 and 6.8 Hz, 1H), 7.41 (dd with fine coupling, J=8.1 and 6.8 Hz, 1H), 7.70 (d with fine coupling, J=8.1 Hz, 1H), 7.87 (br s, 1H), 8.47 (br d, J=8.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 20.0, 26.1, 26.8, 36.9, 45.6, 80.7, 106.5, 112.6, 117.2, 122.0, 123.7, 126.1, 126.1, 126.7, 127.6, 133.2, 135.8, 152.0 ppm. IR (KBr): 3461, 2970, 2907, 1512 cm^{-1}. Mass (*m/z*, %): 328 (M^+, 24), 272 (18), 188 (44), 172 (14), 171 (100), 115 (17), 57 (37). HRMS (ESI): 351.1589, calcd for $C_{20}H_{24}O_4Na$ ($M+Na^+$) 351.1572. Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37%. Found: C, 73.36; H, 7.21%.

1eA: Colorless needles melted at 159.5–160.0 °C (from CH_2Cl_2–hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.00 (s, 9H), 1.22 (s, 3H), 1.46 (s, 3H), 3.97 (d, J=8.7 Hz, 1H), 4.68 (d, J=8.7 Hz, 1H), 7.29 (s, 1H), 7.35 (dd with fine coupling, J=8.2 and 6.9 Hz, 1H), 7.47 (dd with fine coupling, J=8.2 and 6.9 Hz, 1H), 7.70 (d, J=8.2 Hz, 1H), 7.82 (d, J=8.2 Hz, 1H), 7.86 (br s, 1H), 8.22 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 18.7, 25.0, 26.4, 36.6, 45.7, 80.3, 105.8, 112.5, 117.2, 121.9, 124.0, 126.1, 127.7, 127.7, 128.6, 131.5, 135.7, 152.3 ppm. IR (KBr): 3398, 2970, 1636, 1458 cm^{-1}. Mass (*m/z*, %): 328 (M^+, 48), 296 (3), 188 (38), 172 (13), 171 (100), 170 (97), 141 (61), 115 (34), 57 (66). HRMS (ESI): 351.1578, calcd for $C_{20}H_{24}O_4Na$ ($M+Na^+$) 351.1572. Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37%. Found: C, 73.22; H, 7.34%.

4.1.11. Thermal decomposition of 5-*tert*-butyl-1-(7-hydroxynaphthalen-2-yl)-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (1aA); typical procedure. A solution of 5-*tert*-butyl-1-(7-hydroxynaphthalen-2-yl)-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane **1aA** (53.8 mg, 0.164 mmol) in xylene (3 mL) was refluxed for 6.5 h. After cooling, the reaction mixture was concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:10) to give 2,2,4,4-tetramethyl-3-oxopentyl 7-hydroxynaphthalene-2-carboxylate (**9a**) (46.7 mg, 0.142 mmol, 86.6%) as a colorless solid.

9a: Colorless columns melted at 157.0–158.0 °C (from AcOEt–hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.31 (s, 9H), 1.43 (s, 6H), 4.48 (s, 2H), 6.10 (s, 1H), 7.22 (dd, J=8.7 and 2.3 Hz, 1H), 7.25 (d, J=2.3 Hz, 1H), 7.73 (d, J=8.7 Hz, 1H), 7.75 (d, J=8.7 Hz, 1H), 7.80 (dd, J=8.7 Hz, 1H), 8.36 (br s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.8, 28.2, 46.0, 49.3, 72.2, 110.7, 120.5, 122.7, 127.6, 128.0, 129.5, 129.6, 130.9, 133.7, 154.3, 166.8, 216.7 ppm. IR (KBr): 3415, 2973, 1695, 1605 cm^{-1}. Mass (*m/z*, %): 328 (M^+, 16), 278 (18), 272 (23), 188 (28), 172 (16), 171 (100), 143 (17), 57 (24). HRMS (ESI): 351.1569, calcd for $C_{20}H_{24}O_4Na$ ($M+Na^+$) 351.1572. Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37%. Found: C, 73.04; H, 7.78%.

9b: Colorless granules melted at 126.0–126.5 °C (from AcOEt–hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.32 (s, 9H), 1.43 (s, 6H), 4.48 (s, 2H), 7.08 (br s, 1H), 7.15 (d with fine coupling, J=8.7 Hz, 1H), 7.16 (s, 1H), 7.54 (d, J=8.7 Hz, 1H), 7.71 (d, J=8.7 Hz, 1H), 7.84 (d with fine coupling, 1H), 8.38 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.7, 28.2, 46.0, 49.4, 72.0, 109.5, 118.9, 124.5, 125.5, 126.5, 127.5, 131.0, 131.3, 137.2, 156.2, 167.0, 217.3 ppm. IR (KBr): 3402, 2976, 1697, 1623, 1484 cm^{-1}. Mass (*m/z*, %): 328 (M^+, 16), 272 (23), 188 (26), 172 (14), 171 (100), 143 (13), 57 (12). HRMS (ESI): 351.1572, calcd for $C_{20}H_{24}O_4Na$ ($M+Na^+$) 351.1572. Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37%. Found: C, 72.96; H, 7.67%.

9c: Colorless needles melted at 109.0–109.5 °C (from AcOEt–hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.28 (s, 9H), 1.42 (s, 6H), 4.48 (s, 2H), 6.65 (s, 1H), 7.71 (d, J=2.7 Hz, 1H), 7.19 (dd, J=9.4 and 2.7 Hz, 1H), 7.34 (dd, J=8.2 and 7.3 Hz, 1H), 7.75 (d, J=8.2 Hz, 1H), 7.89 (d with fine coupling, J=7.3 Hz, 1H), 8.72 (d, J=9.4 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.7, 28.1, 46.0, 49.2, 72.3, 110.1, 119.7, 125.0, 126.4, 126.7, 127.6, 127.7, 131.9, 135.4, 153.9, 167.6, 217.0 ppm. IR (liquid film): 3331, 2973, 1707, 1669 cm^{-1}. Mass (*m/z*, %): 328 (M^+, 23), 278 (3), 272 (22), 188 (36), 172 (14), 171 (100), 143 (18), 115 (7), 57 (17). HRMS (ESI): 351.1573, calcd for $C_{20}H_{24}O_4Na$ ($M+Na^+$) 351.1572. Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37%. Found: C, 73.22; H, 7.44%.

9d: Colorless needles melted at 158.0–159.0 °C (from AcOEt–hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.27 (s, 9H), 1.41 (s, 6H), 4.49 (s, 2H), 7.11 (br s, 1H), 7.36–7.42 (m, 3H), 7.61–7.64 (m, 1H), 7.73 (d, J=2.7 Hz, 1H), 8.71–8.73 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.6, 28.1, 46.0, 49.3, 72.3, 115.3, 121.9, 125.2, 125.6, 126.6, 126.7, 127.0, 128.3, 135.3, 152.3, 167.0, 217.5 ppm. IR (KBr): 3409, 2968, 1716, 1671, 1576 cm^{-1}. Mass (*m/z*, %): 328 (M^+, 26), 278 (16), 272 (21), 188 (47), 172 (14), 171 (100), 115 (21), 57 (27). HRMS (ESI): 351.1572, calcd for $C_{20}H_{24}O_4Na$ ($M+Na^+$) 351.1572. Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37%. Found: C, 72.96; H, 7.67%.

9e: Pale yellow needles melted at 89.0–90.0 °C (from MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.32 (s, 9H), 1.44 (s, 6H), 4.48 (s, 2H), 7.28–7.32 (m, 1H), 7.29 (s, 1H), 7.46–7.49 (m, 1H), 7.66 (d, J=8.2 Hz, 1H), 7.74 (d, J=8.2 Hz, 1H), 8.32 (s, 1H), 10.4 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.6, 28.0, 45.9, 49.1, 72.6, 111.7, 114.1, 123.9, 126.2, 126.9, 129.1, 129.1, 132.0, 137.8, 156.3, 169.4, 215.7 ppm. IR (liquid film): 3239, 2968, 1681, 1637, 1514 cm^{-1}. Mass (*m/z*, %): 328 (M^+, 44), 188 (38), 171 (97), 170 (100), 141 (68), 142 (26), 141 (61), 115 (28), 57 (53). HRMS (ESI): 351.1558, calcd for $C_{20}H_{24}O_4Na$ ($M+Na^+$) 351.1572. Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37%. Found: C, 73.19; H, 7.56%.

4.1.12. Chemiluminescence measurement; general procedure. Chemiluminescence was measured using a Hitachi FP-750 spectrometer and/or Hamamatsu Photonics PMA-11 multi-channel detector.

Freshly prepared solution (2 mL) of TBAF (1.0×10^{-2} mol L^{-1}) in DMSO was transferred to a quartz cell (10×10×50 mm) and the latter placed in the spectrometer, which was thermostated with stirring at 25 °C. After 3–5 min, a solution of the dioxetane in DMSO (1.0×10^{-4} mol L^{-1}–1.0×10^{-6} mol L^{-1}, 1 mL) was added by means of a syringe with immediate starting of measurement. 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^{CTICL} has been reported to be 0.29 and was used here as a standard.[11]

4.1.13. Fluorescence measurement; general procedure. Freshly prepared solution of 2.05–2.10×10^{-5} mol dm^{-3} of **9a**–**9e** and of 1.0×10^{-2} mol dm^{-3} of TBAF in DMSO was transferred to a quartz cell (10×10×50 mm) and the latter placed in the spectrometer, which was thermostated with stirring at 25 °C. Thus, the fluorescence spectra of **11a**–**11e** were measured and their fluorescence efficiencies (Φ^{fl}) were estimated using fluorescein as a standard.

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