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Fluoride-induced chemiluminescent decomposition of dioxetanes bearing a siloxyaryl moiety to produce an alkyl aryl ketone as an emitter

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Abstract—Tetrabutylammonium fluoride induces the decomposition of 1-*tert*-butyl-4,4-dimethyl-5-(3-siloxyphenyl)-2,6,7-trioxabicyclo[3.2.0]heptane (**4a**) in DMSO to form an oxyanion of aromatic ketone (**14a**) as an emitter with high singlet-chemiexcitation yield comparable with that for a chemically initiated electron exchange luminescence (CIEEL) active dioxetane producing an oxyanion of aromatic ester as an emitter. A 7-siloxynaphthalen-2-yl analog (**4b**) was found on similar treatment to emit light with the maximum wavelength the longest among CIEEL-active dioxetanes hitherto known.

Since the discovery of 1,2-dioxetanes their chemistry has been extensively studied. These high-energy molecules have been established to generate mainly triplet-excited carbonyl fragments on thermal decomposition.[1] In contrast, dioxetanes substituted with an aromatic electron donor display intramolecular chemically initiated electron exchange luminescence (CIEEL),[2–4] in which a charge transfer from an aromatic electron donor to the dioxetane ring occurs to induce its decomposition with light emission. A representative of such CIEEL-active dioxetane is a thermally stable 3-methoxy-3-(3-siloxyphenyl)-1,2-dioxetane (**1**). A siloxyphenyl of **1** is deprotected with fluoride to produce an unstable dioxetane (**2**) bearing a *m*-oxyphenyl anion, CIEEL-decay of which affords a singlet-excited aromatic ester (**3**).[4,5] After the reports on dioxetane (**1**) and related peroxides, a variety of 3-alkoxy-4,4-dialkyl-3-aryl-1,2-dioxetanes have been synthesized and examined from the viewpoints of understanding the chemiluminescent and bioluminescent mechanisms and of application to biological analysis.[6,7]

One structural characteristic of the hitherto-known CIEEL-active dioxetanes is that they consist of an alkoxy and an aromatic electron donor at the geminal position so that they afford, after the above deprotection, an aromatic ester as an emitter. For example, **1** produces an excited aromatic ester (**3**) while a dialkyl ketone fragment, namely, adamantanone formed concomitantly, gives little light so that the adamantylidene part in dioxetane (**1**) has been regarded chiefly as a stabilizer to improve thermal persistency of the dioxetane ring. On the other hand, there has been little known of the CIEEL-active dioxetanes producing an oxyphenyl ketone as an emitter[8,9] though the base-induced chemiluminescent decomposition of benzofuran-dioxetanes[10] and indole-dioxetanes[11] as rather special examples and spirodioxetanes producing an excited acridone[12] or an excited xanthone[13] have been known. These facts prompted us to synthesize 3-alkoxy-4-(siloxyaryl)-1,2-dioxetanes, which would give a rather simple aromatic ketone fragment, and to examine whether their fluoride-induced decomposition occurs to afford effectively an excited anion of the oxyaryl ketone as an emitter. The realized dioxetanes were 1-*tert*-butyl-4,4-dimethyl-5-(siloxyaryl)-2,6,7-trioxabicyclo[3.2.0]heptanes (**4a**–**4c**) which were then examined (Scheme 1).

An isomeric bicyclic dioxetane of **4a**, namely, 5-*tert*-butyl-4,4-dimethyl-1-(3-siloxyphenyl)-2,6,7-trioxabicyclo[3.2.0]-heptane (**5**), possesses marked thermal stability, which is likely attributed to the steric repulsion between a 4-methyl(s) and a 5-substituent (*tert*-butyl) as well as to the inhibition of twisting of a dioxetane ring by a fused five-membered ring. The dioxetane (**5**) is, furthermore, an effective precursor to form at will a CIEEL-active dioxetane bearing an oxyanion of the phenolic moiety on treatment with tetrabutylammonium fluoride (TBAF) in an aprotic solvent such as DMSO and acetonitrile.[14] Hence, we planned to synthesize 4,4-dimethyl-2,6,7-trioxabicyclo-[3.2.0]heptanes (**4**) in which both *tert*-butyl and siloxy-substituted aryl groups exist as in the case of **5** except the positions of these two substituents are exchanged. We chose

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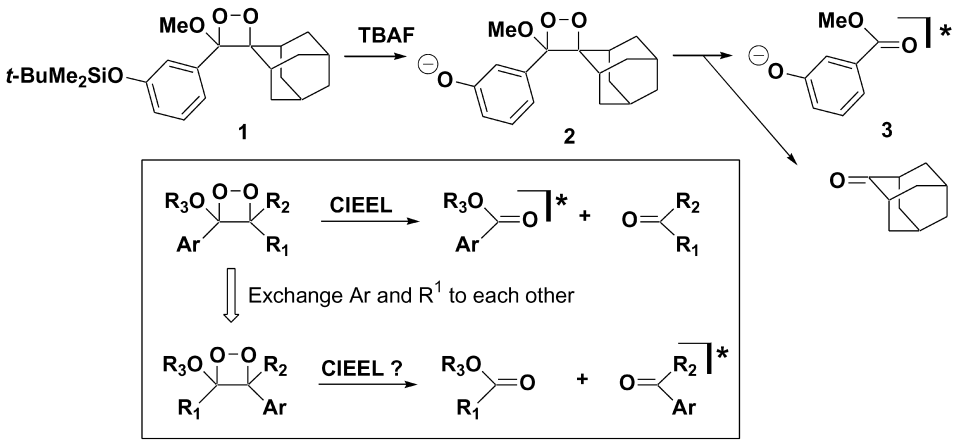
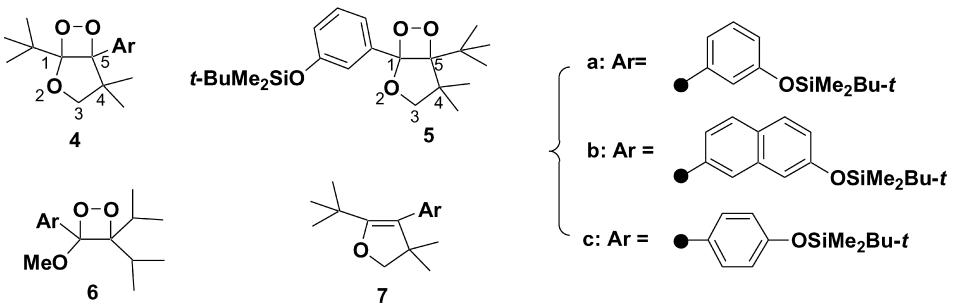


Scheme 1.



3-siloxyphenyl (**4a**), 7-siloxynaphthalen-2-yl (**4b**), and 4-siloxyphenyl (**4c**) as representatives for a siloxy-substituted aryl group for **4**, since the behavior of these dioxetanes can presumably be easily compared with those of the known CIEEL-active dioxetanes (**1**), (**5**), (**6a**)[15] (**6b**)[16] and (**6c**)[17] bearing the corresponding aromatic electron donor for CIEEL in the TBAF/DMSO system.

1. Results and discussion

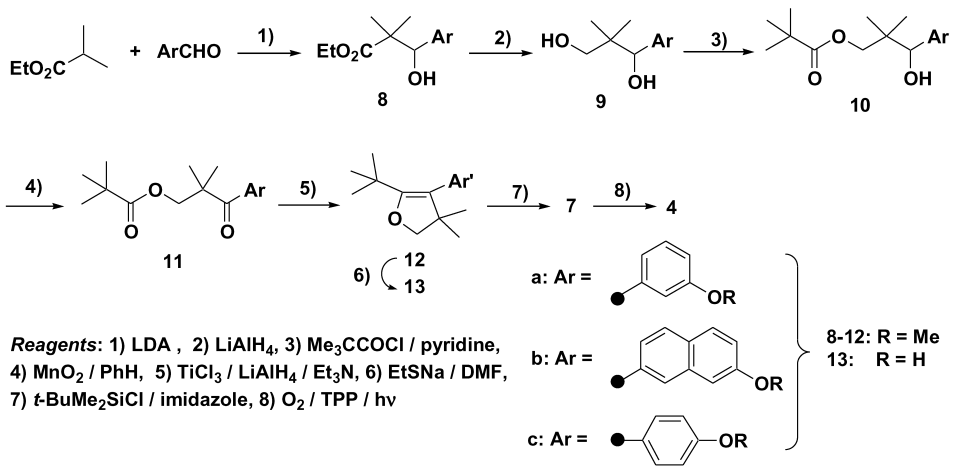
1.1. Synthesis of 1-*tert*-butyl-4,4-dimethyl-5-(siloxyaryl)-2,6,7-trioxabicyclo[3.2.0]heptanes

The sensitized photooxygenation would be an effective tool to prepare the desired dioxetanes (**4a**–**4c**) from the corresponding 4-aryl-5-*tert*-butyl-3,3-dimethyl-2,3-dihydrofurans (**7a**–**7c**) similarly to the case of a dioxetane (**5**). Thus, the dihydrofurans (**7a**–**7c**) were synthesized from their methoxyaryl-analogs (**12**) by means of their demethylation yielding hydroxyaryl-analogs (**13**) with EtSNa/dimethylformamide (DMF) and successive silylation with *tert*-butyldimethylsilyl chloride. Methoxyaryl-substituted dihydrofurans (**12**) as a key intermediate were synthesized by the McMurry reductive coupling[18] of the corresponding 2,2-dimethylpropanoic acid (pivalic acid) esters of a 3-(methoxyaryl)-2,2-dimethyl-3-oxo-1-propanol (**11**), which were synthesized in several steps starting from ethyl 2-methylpropanoate and aromatic aldehydes as illustrated in Scheme 2. The first step was the coupling of a lithium enolate of ethyl 2-methylpropanoate with an aromatic aldehyde to afford a 3-aryl-3-hydroxy-2,2-dimethylpropanoate (**8**), which was reduced, in turn, with $LiAlH_4$ to a propanediol (**9**). The primary OH group of a diol (**9**) was selectively esterified with pivaloyl chloride to yield a monoester (**10**) of **9**, which was successively oxidized into the desired ketoester (**11**).

When a solution of dihydrofuran (**7a**) (100 mg) and a catalytic amount of tetraphenylporphin (TPP) in dichloromethane (10 mL) was irradiated externally with 940 W Na-lamp under an oxygen atmosphere at −78°C for 1 h, **7a** was transformed exclusively to a dioxetane (**4a**), which was isolated as colorless granules in 83.0% yield after chromatographic purification. The structure of **4a** was characterized by ^{1}H NMR, ^{13}C NMR, IR, Mass, and HRMS spectral analysis. The other dihydrofurans (**7b** and **7c**) were similarly oxygenated to give the corresponding 1,2-dioxetanes (**4b** and **4c**) in high yields. These dioxetanes (**4a**–**4c**) were sufficiently thermally stable to permit handling at room temperature.

1.2. TBAF-induced CIEEL-decay of 1-*tert*-butyl-4,4-dimethyl-5-(siloxyaryl)-2,6,7-trioxabicyclo[3.2.0]heptanes

A siloxyphenyl-substituted dioxetane (**1**) is triggered with TBAF in an aprotic solvent such as DMSO and acetonitrile; its desilylation with fluoride affords an unstable phenolate-substituted dioxetane, which decomposes rapidly by the CIEEL process. It has been reported very recently for the fluoride-triggered CIEEL process of a siloxyphenyl-substituted dioxetane that the CIEEL-decay rate of dioxetane follows pseudo-first-order kinetics independent of the TBAF concentration when an excess of fluoride concentration is used.[5] Therefore, we used a large excess of



Scheme 2.

Table 1. F^--Induced chemiluminescence of 5-aryl-1-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptanes (**4**) and their related dioxetanes in DMSO

Dioxetane	λ_{max}^{CIEEL} (nm)	Φ_{CIEEL}[a]	Φ_S	k (s^{-1})	$t_{1/2}$ (s)
4a	549	1.5×10^{-2}	0.21	2.8×10^{-4}	2500
5[b]	466	0.20	0.63	0.15	4.6
6a[c]	463	0.24	0.48	0.11	6.3
4b	642	5.6×10^{-3}	0.31	1.3×10^{-4}	5500
6b[d]	558	6.3×10^{-2}	–	2.8×10^{-3}	250
4c	[e]	[e]	[e]	[e]	[e]
6c[f]	463	5.8×10^{-4}	–	>0.7	<1

A solution of a dioxetane in DMSO (1.0×10^{-5} M, 1 mL) was added to a solution of TBAF in DMSO (1.0×10^{-2} M, 2 mL) at 25°C.

[a] Relative chemiluminescent efficiency based on the value for **1** (Ref. 5): λ_{max}=466 nm, Φ^{CIEEL}=0.29, $t_{1/2}$=5 s.

[b] Ref 14.

[c] Ref 15.

[d] Ref 16.

[e] No chemiluminescence could be detected.

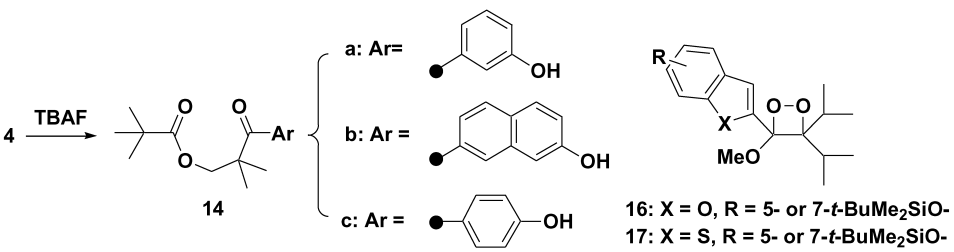
[f] Ref. 17.

TBAF to examine the fluoride-induced decomposition of dioxetanes (**4**) for simplifying the system.

When a solution of **4a** in DMSO (1.0×10^{-5} mol dm^{-3}, 1 mL) was added to a TBAF solution in DMSO (1.0×10^{-2} mol dm^{-3}, 2 mL) at 25°C, **4a** underwent CIEEL-decay to emit light with maximum wavelength λ_{max}^{CIEEL}=549 nm, chemiluminescent efficiency $\Phi^{CIEEL}=1.5\times10^{-2}$, CIEEL-decay rate $k=2.8\times10^{-4}$ s^{-1}, and half-life $t_{1/2}(=\log_e 2/k)$=2500 s. These chemiluminescent properties are shown together with those for a naphthyl-analog (**4b**), 4-siloxyphenyl-analog (**4c**), and related dioxetanes (**5**, and **6a**–**6c**) in Table 1. Comparing the chemiluminescent properties of **4a** with those for dioxetanes **5** and **6a**, in which an aromatic electron donor is a 3-oxyphenyl anion equally to the case of **4a**, one realizes that (a) fluoride-induced CIEEL-decay for **4a** occurs far more slowly than for **5** and **6a**, (b) emission from **4a** is yellow light, while that from **5** and **6a** is blue (λ_{max}^{CIEEL}=463–466 nm), and (c) chemiluminenscent efficiency Φ^{CIEEL} is considerably lower for **4a** than for **5** and **6a**.

The ease of intramolecular CIEEL-decay depends on the ease of electron transfer from an aromatic electron donor to O–O of the dioxetane ring. Therefore, a dioxetane bearing an aryl moiety, which is oxidized the more easily, would undergo the CIEEL-decay the more rapidly.[19] However, both dioxetanes (**4a**) and (**5**) bear a 3-oxyphenyl moiety, so that the ease of electron transfer for **4a** might be little different in an electronic factor from that for **5**. On the other hand, it has been suggested very recently for a CIEEL-active dioxetane bearing a phenolic moiety that an intramolecular electron transfer occurs preferentially from the phenolic electron donor to O–O of the dioxetane, when the phenolic ring lies in a certain conformation(s).[20] According to the suggestion, the electron transfer should become difficult to occur when the aromatic ring is prevented from rotating freely by the proximal substituent(s) on the dioxetane ring. Such steric interaction of the aromatic ring with the neighboring entities would be larger for **4a** than for **5**: the neighboring entities are the 1-*tert*-butyl and the methyl(s) at the 4-position for **4a**, while the 5-*tert*-butyl and oxygen of the tetrahydrofuran ring for **5**. This is likely the reason why **4a** undergoes the CIEEL-decay far more slowly than **5**.

The maximum wavelength of CIEEL emission (λ_{max}^{CIEEL}) of **4a** coincided with fluorescence maximum (λ_{max}^{fl}) of the corresponding spent reaction mixture, from which a



3-hydroxyphenyl ketone (**14a**) was isolated in high yield. The fluorescence maximum (λ_{max}^{fl}) of an oxyanion produced from **14a** by treatment with TBAF in DMSO coincided also with λ_{max}^{CIEEL} of **4a**. Hence, an oxyanion of **14a** is undoubtedly an emitter for the CIEEL of **4a**, of which fluorescence efficiency Φ^{fl} was estimated to be 7.2×10^{-2}. Since the chemiluminenscent yield (Φ^{CIEEL}) is equal to the product of $\Phi_S\times\Phi^{fl}$, Φ_S was estimated to be 0.21 for **4a**. The results reveal that a CIEEL-active dioxetane, such as **4a**, producing an aromatic ketone as the emitter causes singlet-chemiexcitation in high yield which bears comparison with that for dioxetanes (**1**, **5**, and **6a**) giving an aromatic ester as the emitter (Table 1).

The result that a dioxetane (**4a**) affords light with λ_{max}^{CIEEL} considerably longer than that for **1**, **5**, and **6a**, and the reported result that **6b**, which produces an excited oxyanion of a 7-hydroxynaphthalene-2-carboxylate emitting yellow light (λ_{max}^{CIEEL}=558 nm), suggest that a 7-siloxynaphthalen-2-yl analog (**4b**) should become a new chemiluminescent substrate emitting red light. Treatment of **4b** with TBAF similarly to the case of **4a** afforded light with λ_{max}^{CIEEL}=642 nm, $\Phi^{CIEEL}=5.6\times10^{-3}$, $k=1.3\times10^{-4}$ s^{-1}, and $t_{1/2}$=5500 s. The result was gratifying beyond expectation: (a) **4b** emits red light with the longest λ_{max}^{CIEEL} among the CIEEL-active dioxetanes hitherto known, such as **6b** and its phosphate-analog (λ_{max}^{CIEEL}=550–560 nm),[21] a benzofuran-substituted dioxetane (**16**) (λ_{max}^{CIEEL}=615–620 nm, $\Phi^{CIEEL}=1.6\times10^{-4}$–$2.1\times10^{-4}$)[22] and a benzothiophene-substituted dioxetane (**17**) (λ_{max}^{CIEEL}=615–628 nm, $\Phi^{CIEEL}=1.4\times10^{-4}$–$2.1\times10^{-4}$),[22] and (b) chemiluminescent efficiency is rather better than that for **16** and **17** (Table 1). The maximum wavelength of CIEEL emission (λ_{max}^{CIEEL}) of **4b** coincided not only with fluorescence maximum (λ_{max}^{fl}) of the corresponding spent mixture but also with λ_{max}^{fl} of an oxyanion of 7-hydroxynaphthalen-2-yl ketone (**14b**) in the TBAF–DMSO system. Thus, Φ^{fl} and Φ_s for **4b** were estimated to be 0.018 and 0.31, respectively.

A 4-oxyphenyl-substituted dioxetane such as **6c** has been known also to emit light though far less effectively than its 3-oxyphenyl-analog such as **1**, **5**, and **6a** on CIEEL-decay.[17,23] From the analogy of the results for **4a** and **4b**, it is inferred a dioxetane bearing a 4-siloxyphenyl moiety (**4c**) was expected also to emit light though weak. However, no light emission was observed for **4c** on treatment with TBAF in DMSO, though the expected decomposition of **4c** proceeded to give the corresponding ketoester (**14c**), an oxyanion of which showed little fluorescence in TBAF/DMSO.

2. Conclusion

Treatment of 1-*tert*-butyl-4,4-dimethyl-5-(3-siloxyphenyl)-2,6,7-trioxabicyclo[3.2.0]heptane (**4a**) with TBAF in DMSO generates a CIEEL-active dioxetane, which decomposes smoothly to form an oxyanion of aromatic ketone (**14a**) as an emitter with high singlet-chemiexcitation yield comparable with that for a CIEEL-active dioxetane producing an oxyanion of aromatic ester as an emitter. A 7-siloxynaphthalen-2-yl analog (**4b**) was found on treatment with TBAF to emit light with the maximum wavelength the longest among CIEEL-active dioxetanes hitherto known. On the other hand, a 4-siloxyphenyl-analog (**4c**) gave no detectable light emission in the TBAF/DMSO system.

3. Experimental

3.1. 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 spectrometer. Mass spectra were obtained by using JEOL JMS-AX-505H, JEOL JMS-T-100LC (AccuTOF), and/or Hitachi M80B mass spectrometers. Chemiluminescences were measured by Hitachi F-4010 spectrometer, JASCO FP-750 spectrometer, and/or Hamamatsu Photonics PMA-11 multi-channel detector. 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.

3.1.1. Ethyl 3-hydroxy-3-(3-methoxyphenyl)-2,2-dimethylpropanoate (8a). Ethyl 2-methylpropanoate (13.7 mL, 0.102 mol) was added to a solution of lithium diisopropylamide (0.104 mol) in THF (100 mL) at −78°C and stirred for 30 min under nitrogen atmosphere. To the solution, 3-methoxybenzaldehyde (10.0 mL, 0.082 mol) was added and stirred for 1.5 h. The reaction mixture was poured into NH_4Cl aq. solution and extracted with ethyl acetate (AcOEt). The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel and eluted with hexane–AcOEt (5:1–2:1) to give **8a** as a colorless oil in quantitative yield (20.9 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.12 (s, 3H), 1.15 (s, 3H), 1.28 (t, J=7.1 Hz, 3H), 3.15 (d with fine coupling, J=4.3 Hz, 1H), 3.80 (s, 3H), 4.19 (q, J=7.1 Hz, 2H), 6.82 (ddd, J=8.1, 2.6, 0.9 Hz, 1H), 6.86–6.90 (m, 2H), 7.23 (t, J=8.1 Hz, 1H). IR (liquid film): 3494, 2980, 1717, 1602, 1259 cm^{-1}. Mass (EI) (*m*/*z*, %): 252 (M^+, 9), 137 (28), 116 (100), 109 (40), 88 (48). HRMS (ESI): 275.1282, calcd for $C_{14}H_{20}O_4Na$ ($M+Na^+$) 275.1259.

3.1.2. Ethyl 3-hydroxy-3-(7-methoxynaphthalen-2-yl)-2,2-dimethylpropanoate (8b). Similarly to the preparation of **8a** from 3-methoxybenzaldehyde, the coupling reaction of an enolate of ethyl 2-methylpropanoate with 7-methoxynaphthalene-2-carbaldehyde was carried out to give **8b** as a colorless oil in 86.9% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.16 (s, 3H), 1.19 (s, 3H), 1.28 (t, J=7.1 Hz, 3H), 3.26 (d, J=4.4 Hz, 1H), 3.92 (s, 3H), 4.21 (q, J=7.1 Hz, 2H), 5.04 (d, J=4.4 Hz, 1H), 7.11–7.15 (m, 2H), 7.30 (dd, J=8.3, 1.5 Hz, 1H), 7.68 (broad s, 1H), 7.69–7.74 (m, 2H). IR (liquid film): 3500, 2979, 2938, 1717, 1607, 1514, 1216 cm^{-1}. Mass (EI) (*m*/*z*, %): 302 (M^+, 22), 187 (91), 186 (48), 159 (47), 144 (27), 116 (100). HRMS (EI): 302.1510, calcd for $C_{18}H_{22}O_4$ 302.1518.

3.1.3. Ethyl 3-hydroxy-3-(4-methoxyphenyl)-2,2-dimethylpropanoate (8c). Similarly to the preparation of **8a** from 3-methoxybenzaldehyde, the coupling reaction of

an enolate of ethyl 2-methylpropanoate with 4-methoxybenzaldehyde was carried out to give **8c** as colorless granules, melted at 72.0–72.5°C (from hexane–AcOEt), in 87.3% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.09 (s, 3H), 1.13 (s, 3H), 1.28 (t, J=7.1 Hz, 3H), 3.10 (d, J=4.2 Hz, 1H), 3.81 (s, 3H), 4.18 (q, J=7.1 Hz, 2H), 4.85 (d, J=4.2 Hz, 1H), 6.86 (d with fine coupling, J=8.5 Hz, 2H), 7.23 (t, d with fine coupling, J=8.5 Hz, 2H). IR (KBr): 3455, 2975, 1704, 1514, 1244, 1026 cm^{-1}. Mass (EI) (*m/z*, %): 252 (M^+, 2), 207 (2), 137 (100), 116 (20). HRMS (EI): 252.1349, calcd for $C_{14}H_{20}O_4$ 252.1362.

3.1.4. 1-(3-Methoxyphenyl)-2,2-dimethyl-1,3-propanediol (9a). A solution of ethyl 3-hydroxy-3-(3-methoxyphenyl)-2,2-dimethylpropanoate (**8a**) (6.11 g, 24.2 mmol) in THF (20 mL) was added drop by drop to a suspension of lithium aluminum hydride (LAH) (902 mg, 23.8 mmol) in THF (40 mL) under nitrogen atmosphere at 0°C and stirred for 1 h. After the usual work-up, the crude product was purified by column chromatography on silica gel with hexane–AcOEt (5:1–1:1) to give **9a** as a colorless oil in 67.8% yield (3.45 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.87 (s, 3H), 0.89 (s, 3H), 2.70 (dd, J=5.6, 4.9 Hz, 1H), 2.95 (d, J=2.9 Hz, 1H), 3.52 (dd, J=10.7, 4.9 Hz, 1H), 3.60 (dd, J=10.7, 5.6 Hz, 1H),3.82 (s, 3H), 4.64 (d, J=2.9 Hz, 1H), 6.83 (ddd, J=8.2, 2.4, 1.1 Hz, 1H), 6.89–6.93 (m, 2H), 7.25 (t, J=8.2 Hz, 1H). IR (liquid film): 3367, 2959, 2873, 1602, 1585, 1258 cm^{-1}. Mass (EI) (*m/z*, %): 210 (M^+, 3), 192 (14), 136 (100), 109 (23). HRMS (ESI): 233.1165, calcd for $C_{12}H_{18}O_3Na$ (M+Na^+) 233.1154.

3.1.5. 1-(7-Methoxynaphthalen-2-yl)-2,2-dimethyl-1,3-propanediol (9b). Similarly to the preparation of **9a** from **8a**, the reduction of ethyl 3-hydroxy-3-(7-methoxynaphthalen-2-yl)-2,2-dimethylpropanoate (**8b**) with LAH was carried out to give **9b** as colorless needles, melted at 122.0–123.0°C (from dichloromethane), in 55.4% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.91 (s, 3H), 0.95 (s, 3H), 3.56 (d, J=10.7 Hz, 1H), 3.66 (d, J=10.7 Hz, 1H), 3.93 (s, 3H), 4.82 (s, 1H), 7.12–7.16 (m, 2H), 7.33 (dd, J=8.3, 1.7 Hz, 1H), 7.69–7.75 (m, 3H). IR (KBr): 3368, 2965, 2871, 1605, 1514, 1215, 1174 cm^{-1}. Mass (EI) (*m/z*, %): 260 (M^+, 5), 186 (100), 159 (21), 144 (15). HRMS (EI): 260.1406, calcd for $C_{16}H_{20}O_3$ 260.1412.

3.1.6. 1-(4-Methoxyphenyl)-2,2-dimethyl-1,3-propanediol (9c). Similarly to the preparation of **9a** from **8a**, the reduction of ethyl 3-hydroxy-3-(4-methoxyphenyl)-2,2-dimethylpropanoate (**8c**) with LAH was carried out to give **9c** as colorless granules, melted at 78.0–79.0°C (from hexane), in 63.5% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.85 (s, 3H), 0.87 (s, 3H), 2.70 (dd, J=5.9, 5.4 Hz, 1H), 2.75 (d, J=2.7 Hz, 1H), 3.52 (dd, J=10.7, 5.9 Hz, 1H), 3.82 (s, 3H), 4.63 (d, J=2.7 Hz, 1H), 6.88 (d with fine coupling, J=8.8 Hz, 2H), 7.26 (d with fine coupling, J=8.8 Hz, 2H). IR (KBr): 3351, 3234, 2967, 1612, 1518, 125, 1035 cm^{-1}. Mass (EI) (*m/z*, %): 210 (M^+, trace), 192 (4), 137 (100), 109 (17). HRMS (EI): 210.1269, calcd for $C_{12}H_{18}O_3$ 210.1256.

3.1.7. 3-Hydroxy-3-(3-methoxyphenyl)-2,2-dimethyl-1-propyl 2,2-dimethylpropanoate (10a). Pivaloyl chloride (2.1 mL, 17.1 mmol) was added to a solution of 1-(3-methoxyphenyl)-2,2-dimethyl-1,3-propanediol (**9a**) (3.17 g, 15.1 mmol) and pyridine (3.5 mL, 43.3 mmol) in 1,2-dichloroethane (25 mL) under nitrogen atmosphere at room temperature and then heated at refluxing temperature for 45 min. The reaction mixture was poured into NaCl aq. solution and extracted with AcOEt. The organic layer was washed with NaCl aq. solution, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with hexane–AcOEt (4:1) to afford **10a** as a colorless oil in 74.9% yield (3.32 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.88 (s, 3H), 0.97 (s, 3H), 1.25 (s, 9H), 3.74 (d, J=11.0 Hz, 1H), 3.81 (s, 3H), 4.18 (d, J=11.0 Hz, 1H), 4.55 (s, 1H), 7.30 (ddd, J=8.2, 2.5, 0.9 Hz, 1H), 6.86–6.89 (m, 2H), 7.23 (t, J=8.2 Hz, 1H). IR (liquid film): 3488, 2973, 2873, 1705, 1608, 1583 cm^{-1}. Mass (EI) (*m/z*, %): 294 (M^+, 3), 174 (11), 136 (100), 109 (12). HRMS (ESI): 317.1763, calcd for $C_{17}H_{26}O_4Na$ (M+Na^+) 317.1729.

3.1.8. 3-Hydroxy-3-(7-methoxynaphthalen-2-yl)-2,2-dimethyl-1-propyl 2,2-dimethylpropanoate (10b). Similarly to the preparation of **10a** from **9a**, the esterification of 1-(7-methoxynaphthalen-2-yl)-2,2-dimethyl-1,3-propanediol (**9b**) with pivaloyl chloride was carried out to give **10b** as colorless granules, melted at 133.0–134.0°C (from hexane–AcOEt), in 72.4% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.92 (s, 3H), 1.01 (s, 3H), 1.27 (s, 9H), 2.45 (broad s, 1H), 3.79 (d, J=10.7 Hz, 1H), 3.92 (s, 3H), 4.25 (d, J=10.7 Hz, 1H), 4.72 (s, 1H), 7.11–7.15 (m, 2H), 7.30 (d with fine coupling, J=8.3 Hz, 1H), 7.66 (s, 1H), 7.70–7.74 (m, 2H). IR (KBr): 3496, 3056, 2972, 2937, 2872, 1701, 1607, 1514, 1217 cm^{-1}. Mass (EI) (*m/z*, %): 344 (M^+, 2), 186 (100), 159 (15). HRMS (ESI): 344.1991, calcd for $C_{21}H_{28}O_4$ 344.1998.

3.1.9. 3-Hydroxy-3-(4-methoxyphenyl)-2,2-dimethyl-1-propyl 2,2-dimethylpropanoate (10c). Similarly to the preparation of **10a** from **9a**, the esterification of 1-(4-methoxyphenyl)-2,2-dimethyl-1,3-propanediol (**9c**) with pivaloyl chloride was carried out to give **10c** as colorless granules, melted at 78.0–79.0°C (from hexane), in 68.5% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.85 (s, 3H), 0.95 (s, 3H), 1.25 (s, 9H), 2.28 (d, J=2.9 Hz, 1H), 3.73 (d, J=10.7 Hz, 1H), 3.81 (s, 3H), 4.16 (d, J=10.7 Hz, 1H), 4.53 (d, J=2.9 Hz, 1H), 6.86 (d with fine coupling, J=8.8 Hz, 2H), 6.86 (d with fine coupling, J=8.8 Hz, 2H). IR (KBr): 3484, 2967, 1702, 1512, 1253, 1193 cm^{-1}. Mass (EI) (*m/z*, %): 294 (M^+, trace), 136 (100), 135 (39). HRMS (EI): 294.1837, calcd for $C_{17}H_{26}O_4$ 294.1831.

3.1.10. 3-(3-Methoxyphenyl)-2,2-dimethyl-3-oxopropan-1-yl 2,2-dimethylpropanoate (11a). 3-Hydroxy-3-(3-methoxyphenyl)-2,2-dimethyl-1-propyl 2,2-dimethylpropanoate (**10a**) (2.98 g, 10.1 mmol) was stirred together with MnO_2 (20.5 g) in benzene (30 mL) at refluxing temperature for 30 min. The reaction mixture was filtered through celite to remove the inorganic oxide and the benzene solution was concentrated in vacuo. The residue was chromatographed on silica gel with hexane–AcOEt (4:1) to give **11a** as a colorless oil in 70.0% yield (2.07 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.14 (s, 9H), 1.37 (s, 6H), 3.83 (s, 3H), 4.25 (s, 2H), 7.01 (ddd, J=8.2, 2.6, 0.9 Hz, 1H), 7.12 (dd, J=2.6, 1.6 Hz, 1H), 7.20 (ddd, J=7.6, 1.6, 0.9 Hz, 1H), 7.31 (dd, J=8.2, 7.6 Hz, 1H). IR (liquid film): 2973, 1731, 1683, 1582 cm^{-1}. Mass (EI) (*m/z*, %): 292 (M^+, 4), 236 (33), 135

(100), 107 (9). HRMS (ESI): 315.1609, calcd for $C_{17}H_{24}O_4Na$ ($M+Na^+$) 315.1572.

3.1.11. 3-(7-Methoxynaphthalen-2-yl)-2,2-dimethyl-3-oxopropan-1-yl 2,2-dimethylpropanoate (11b). Similarly to the preparation of **11a** from **10a**, the oxidation of 3-hydroxy-3-(7-methoxynaphthalen-2-yl)-2,2-dimethyl-1-propyl 2,2-dimethylpropanoate (**10b**) with MnO_2 was carried out to give **11b** as a colorless oil in 83.8% isolated yield. ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.14 (s, 9H), 1.45 (s, 6H), 3.94 (s, 3H), 4.33 (s, 2H), 7.17 (d, J=2.4 Hz, 1H), 7.23 (dd, J=8.8, 2.4 Hz, 1H), 7.57 (dd, J=8.3, 2.0 Hz, 1H), 7.75 (d, J=8.8 Hz, 1H), 7.78 (d, J=8.3 Hz, 1H), 8.04 (broad s, 1H). IR (liquid film): 2973, 2936, 2872, 1604, 1509, 1460, 1218 cm^{-1}. Mass (EI) (*m/z*, %): 342 (M^+, 10), 286 (17), 185 (100), 157 (18). HRMS (EI): 342.1818, calcd for $C_{21}H_{26}O_4$ 342.1831.

3.1.12. 3-(4-Methoxyphenyl)-2,2-dimethyl-3-oxopropan-1-yl 2,2-dimethylpropanoate (11c). Similarly to the preparation of **11a** from **10a**, the oxidation of 3-hydroxy-3-(4-methoxyphenyl)-2,2-dimethyl-1-propyl 2,2-dimethylpropanoate (**10c**) with MnO_2 was carried out to give **11c** as a colorless oil in 83.8% isolated yield. ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.12 (s, 9H), 1.40 (s, 6H), 3.85 (s, 3H), 4.29 (s, 2H), 6.90 (d with fine coupling, J=9.3 Hz, 2H), 7.78 (d with fine coupling, J=9.3 Hz, 2H). IR (liquid film): 2972, 1730, 1603, 1258, 1035 cm^{-1}. Mass (EI) (*m/z*, %): 236 [M^+-56 ($Me_2C{=}CH_2$), trace], 135 (100). CIMS MH^+: 293. HRMS (EI): 236.1039, calcd for $C_{13}H_{16}O_4$ 236.1049.

3.1.13. 5-*tert*-Butyl-4-(3-methoxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (12a). Titanium (III) chloride (80%, 6.12 g, 31.8 mmol) was stirred in dry THF (100 mL) at ice-cooled temperature for 30 min. To the solution, LAH (630 mg, 16.6 mmol) was added and stirred for 30 min, and successively triethylamine (3.0 mL, 21.6 mmol) was added and stirred at refluxing temperature for 30 min. To this solution of low-valent titanium, a solution of 3-(3-methoxyphenyl)-2,2-dimethyl-3-oxopropan-1-yl 2,2-dimethylpropanoate (**11a**) (1.01 g, 3.45 mmol) in THF (20 mL) was added dropwise for 1 h and the mixture was refluxed for 1 h. After cooling, the reaction mixture was poured carefully into NaCl aq. solution and extracted with AcOEt. The organic layer was washed with $NaHCO_3$ aq. solution, dried over $MgSO_4$, and concentrated in vacuo. The crude mixture of 6-hydroxy-4-(3-methoxyphenyl)-2,2,5,5-tetramethyl-3-hexanone was dissolved in dichloromethane (10 mL) and to the solution pyridinium *p*-tolylsulfonate (PPTS) (75 mg, 0.30 mmol) was added and stirred at room temperature for 1 h. The reaction mixture was concentrated in vacuo and the residue was chromatographed on silica gel and eluted with AcOEt–hexane (1:20) to afford **12a** as colorless crystals, melted at 46.5–47.0°C (from MeOH), in 75.4% isolated yield. ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.97 (s, 9H), 1.01 (s, 6H), 3.81 (s, 3H), 3.97 (s, 2H), 6.66 (s with fine coupling, 1H), 6.70 (d with fine coupling, J=7.3 Hz, 1H), 6.80 (dd with fine coupling, J=8.3, 2.4 Hz, 1H), 7.19 (dd, J=8.3, 7.3 Hz, 1H). IR (KBr): 2959, 2872, 1665, 1589, 1266 cm^{-1}. Mass (EI) (*m/z*, %): 260 (M^+, 41), 245 (100), 189 (30), 187 (11). HRMS (EI): 260.1769, calcd for $C_{17}H_{24}O_2$ 260.1776.

3.1.14. 5-*tert*-Butyl-4-(7-methoxynaphthalen-2-yl)-3,3-dimethyl-2,3-dihydrofuran (12b). Similarly to the preparation of **12a** from **11a**, the McMurry coupling of 3-(7-methoxynaphthalen-2-yl)-2,2-dimethyl-3-oxopropan-1-yl 2,2-dimethylpropanoate (**11b**) was carried out to give **12b** as colorless crystals melted at 103.0–105.0°C (from hexane–AcOEt), in 66.3% yield. ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.97 (s, 9H), 1.05 (s, 6H), 2.93 (s, 3H), 4.02 (s, 2H), 7.09–7.14 (m, 3H), 7.47 (broad s, 1H), 7.68 (d, J=8.3 Hz, 1H), 7.72 (d, J=9.8 Hz, 1H). IR (KBr): 3051, 2958, 2930, 2864, 1604, 1509, 1215 cm^{-1}. Mass (EI) (*m/z*, %): 310 (M^+, 59), 295 (100), 239 (30). HRMS (EI): 310.1926, calcd for $C_{21}H_{26}O_2$ 310.1933.

3.1.15. 5-*tert*-Butyl-4-(4-methoxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (12c). Similarly to the preparation of **12a** from **11a**, the McMurry coupling of 3-(4-methoxyphenyl)-2,2-dimethyl-3-oxopropan-1-yl 2,2-dimethylpropanoate (**11c**) was carried out to give **12c** as colorless crystals melted at 49.0–50.0°C (from hexane–AcOEt), in 79.0% yield. ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.95 (s, 9H), 0.99 (s, 6H), 3.81 (s, 3H), 3.96 (s, 2H), 6.82 (d with fine coupling, J=8.8 Hz, 2H), 7.01 (d with fine coupling, J=8.8 Hz, 2H). IR (KBr): 2959, 2870, 1607, 1508, 1243, 1114 cm^{-1}. Mass (EI) (*m/z*, %): 260 (M^+, 58), 245 (100), 189 (31). HRMS (EI): 260.1773, calcd for $C_{17}H_{24}O_2$ 260.1776.

3.1.16. 5-*tert*-Butyl-4-(3-hydroxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (13a). 5-*tert*-Butyl-4-(3-methoxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (**12a**) (361 mg, 1.39 mmol) was stirred together with sodium ethanethiolate (4.6 mmol, prepared from ethanethiol and NaH) in DMF (4 mL) under nitrogen atmosphere at refluxing temperature for 2 h. The reaction mixture was poured into NaCl aq. solution and extracted with AcOEt. The organic layer was washed with water, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel and eluted with AcOEt–hexane (1:5) to give **13a** as colorless crystals melted at 130.5–132.0°C (from hexane–AcOEt), in 80.2% yield. ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.97 (s, 9H), 1.01 (s, 6H), 3.96 (s, 2H), 4.67 (s, 1H), 6.60 (s with fine coupling, 1H), 6.69 (d, J=7.3 Hz, 1H), 6.73 (dd, J=8.3, 2.7 Hz, 1H), 7.14 (dd, J=8.3, 7.3 Hz, 1H). IR (KBr): 3406, 2962, 1671, 1611, 1577 cm^{-1}. Mass (EI) (*m/z*, %): 246 (M^+, 47), 231 (100), 175 (24). HRMS (EI): 246.1618, calcd for $C_{16}H_{22}O_2$ 246.1620.

3.1.17. 5-*tert*-Butyl-4-(3-hydroxynaphthalen-2-yl)-3,3-dimethyl-2,3-dihydrofuran (13b). Similarly to the preparation of **13a** from **12a**, the demethylation of 5-*tert*-butyl-4-(7-methoxynaphthalen-2-yl)-3,3-dimethyl-2,3-dihydrofuran (**12b**) was carried out to give **13b** as colorless crystals, melted at 186.0–188.0°C, in 93.0% isolated yield. ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.97 (s, 9H), 1.04 (s, 6H), 4.02 (s, 2H), 7.07 (dd, J=8.8, 2.4 Hz, 1H), 7.09–7.12 (m, 2H), 7.40 (broad s, 1H), 7.68 (d, J=8.3 Hz, 1H), 7.74 (d, J=8.8 Hz, 1H). IR (KBr): 3358, 3058, 2862, 2869, 1509, 1216 cm^{-1}. Mass (EI) (*m/z*, %): 296 (M^+, 57), 281 (100), 225 (27). HRMS (EI): 296.1773, calcd for $C_{20}H_{24}O_2$ 296.1776.

3.1.18. 5-*tert*-Butyl-4-(4-hydroxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (13c). Similarly to the preparation of **13a** from **12a**, the demethylation of 5-*tert*-butyl-4-(4-methoxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (**12c**) was

carried out to give **13c** as colorless granules, melted at 195.0–196.0°C (from hexane–AcOEt), in 93.0% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.95 (s, 9H), 0.98 (s, 6H), 3.96 (s, 2H), 4.59 (s, 1H), 6.75 (d with fine coupling, J=8.5 Hz, 2H), 6.96 (d with fine coupling, J=8.5 Hz, 2H). IR (KBr): 3377, 2970, 2871, 1610, 1512, 1259, 1098 cm^{-1}. Mass (EI) (*m/z*,%): 246 (M^+, 55), 231 (100), 175 (28). HRMS (EI): 246.1609, calcd for $C_{16}H_{22}O_2$ 246.1620.

3.1.19. 5-*tert*-Butyl-4-[(3-*tert*-butyldimethylsiloxy)phenyl]-3,3-dimethyl-2,3-dihydrofuran (7a). 5-*tert*-Butyl-4-(3-hydroxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (**13a**) (212 mg, 0.86 mmol) was stirred together with imidazole (120 mg, 1.77 mmol) and *tert*-butyldimethylsilyl chloride (285 mg, 1.89 mmol) in DMF (3 mL) under nitrogen atmosphere at 0°C for 1 h. The reaction mixture was poured into NaCl aq. solution and extracted with AcOEt. The organic layer was washed with water, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel and eluted with AcOEt–hexane (1:20) to give **7a** as a colorless oil in 94.7% yield (293 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.18 (s, 6H), 0.96 (s, 9H), 0.98 (s, 9H), 1.00 (s, 6H), 3.96 (s, 2H), 6.60 (s with fine coupling, 1H), 6.70 (d with fine coupling, J=7.3 Hz, 1H), 6.74 (ddd, J=8.3, 2.4, 1.0 Hz, 1H), 7.12 (dd, J=8.3, 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C −4.3, 18.3, 25.7, 26.0, 29.1, 33.4, 46.9, 81.2, 116.4, 118.4, 123.4, 124.9, 128.2, 137.1, 154.8, 157. IR (liquid film): 2957, 2860, 1575, 1477, 1273, 1117 cm^{-1}. Mass (EI) (*m/z*, %): 360 (M^+, 35), 345 (100), 289 (17). HRMS (EI): 360.2470, calcd for $C_{22}H_{36}O_2Si$ 360.2485.

3.1.20. 5-*tert*-Butyl-4-[(7-*tert*-butyldimethylsiloxy)naphthalen-2-yl]-3,3-dimethyl-2,3-dihydrofuran (7b). Similarly to the preparation of **7a** from **13a**, the silylation of 5-*tert*-butyl-4-(7-hydroxynaphthalen-2-yl)-3,3-dimethyl-2,3-dihydrofuran (**13b**) was carried out to give **7b** as colorless granules, melted at 101–102°C (from MeOH), in 97.7% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.26 (s, 6H), 0.97 (s, 9H), 1.03 (s, 9H), 1.05 (s, 6H), 4.02 (s, 2H), 7.04 (dd, J=8.8, 2.4 Hz, 1H), 7.10 (dd, J=8.3, 1.7 Hz, 1H), 7.15 (d, J=2.4 Hz, 1H), 7.41 (broad s, 1H), 7.67 (d, J=8.3 Hz, 1H), 7.70 (d, J=8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C −4.1, 18.4, 25.8, 26.2, 29.4, 33.6, 47.2, 81.3, 114.7, 116.6, 121.5, 126.3, 127.8, 128.2, 128.6, 128.8, 133.6, 134.1, 153.3, 157.8. IR (KBr): 2956, 2862, 1668, 1630, 1599, 1248 cm^{-1}. Mass (EI) (*m/z*, %): 410 (M^+, 65), 395 (100), 353 (12), 339 (21). HRMS (EI): 410.2624, calcd for $C_{26}H_{38}O_2Si$ 410.2641.

3.1.21. 5-*tert*-Butyl-4-[(4-*tert*-butyldimethylsiloxy)phenyl]-3,3-dimethyl-2,3-dihydrofuran (7c). Similarly to the preparation of **7a** from **13a**, the silylation of 5-*tert*-butyl-4-(4-hydroxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (**13c**) was carried out to give **7c** as a colorless oil in 89.5% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.20 (s, 6H), 0.94 (s, 9H), 0.98 (s, 15H), 3.96 (s, 2H), 6.75 (d with fine coupling, J=8.5 Hz, 2H), 6.93 (d with fine coupling, J=8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C −4.2, 18.4, 25.8, 26.0, 29.3, 33.5, 46.7, 81.1, 116.1, 118.9, 128.4, 132.4, 154.1, 157.5. IR (liquid film): 2955, 2929, 1507, 1259, 1118 cm^{-1}. Mass (EI) (*m/z*, %): 360 (M^+, 83), 345 (100), 289 (21). HRMS (EI): 360.2481, calcd for $C_{22}H_{36}O_2Si$ 360.2485.

3.1.22. 1-*tert*-Butyl-5-[(3-*tert*-butyldimethylsiloxy)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (4a). A solution of 5-*tert*-butyl-4-[(3-*tert*-butyldimethylsiloxy)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**7a**) (100 mg) and TPP (1 mg) in dichloromethane (10 mL) was irradiated with 940 W Na-lamp under oxygen atmosphere at −78°C for 1 h. The photolysate was concentrated and chromatographed on silica gel (Fuji silisia, NH-DM1020). Elution with hexane gave the desired dioxetane **4a** as colorless granules, melted at 42.0–43.0°C (from hexane–AcOEt), in 83.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.18 (s, 3H), 0.19 (s, 3H), 0.84 (s, 3H), 0.95 (s, 9H), 0.98 (s, 9H), 1.07 (s, 3H), 3.93 (d, J=8.3 Hz, 1H), 4.54 (d, J=8.3 Hz, 1H), 6.80 (ddd, J=8.3, 2.4, 1.0 Hz, 1H), 6.89 (broad s, 1H), 6.94 (broad d, J=7.8 Hz, 1H), 7.22 (dd, J=8.3, 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C −4.3, 15.5, 18.2, 24.0, 24.4, 25.7, 36.2, 45.6, 77.6, 101.6, 118.8, 119.4, 120.0, 121.0, 128.3, 136.8, 155.1. IR (KBr): 2959, 2893, 2861, 1583, 1248 cm^{-1}. Mass (EI) (*m/z*, %): 360 (M^+−32, 13), 345 (11), 335 (14), 279 (100), 235 (885), 159 (69). CIMS: MH^+ 393. HRMS (EI): 360.2467, calcd for $C_{22}H_{36}O_2Si$ 360.2485.

3.1.23. 1-*tert*-Butyl-5-[(7-*tert*-butyldimethylsiloxy)naphthalen-2-yl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (4b). Similarly to the preparation of **4a** from **7a**, the singlet oxygenation of 5-*tert*-butyl-4-[(7-*tert*-butyldimethylsiloxy)naphthalen-2-yl]-3,3-dimethyl-2,3-dihydrofuran (**7b**) was carried out to give as colorless granules, melted at 110.0–111.0°C (from MeOH), in 93.6% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.27 (s, 6H), 0.88 (s, 3H), 0.97 (s, 9H), 1.03 (s, 9H), 1.13 (s, 3H), 3.98 (d, J=8.1 Hz, 1H), 4.60 (d, J=8.1 Hz, 1H), 7.10 (dd, J=8.8, 2.1 Hz, 1H), 7.10 (dd, J=8.8, 2.1 Hz, 1H), 7.21 (d, J=2.1 Hz, 1H), 7.29 (broad d, J=8.2 Hz, 1H), 7.70–7.75 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C −4.1, 15.7, 18.4, 24.3, 24.7, 25.8, 36.4, 46.0, 77.8, 102.2, 115.2, 121.2, 122.6, 124.8, 126.1, 128.1, 128.8, 133.0, 133.8, 153.8. IR (KBr): 2959, 2895, 2861, 1630, 1603, 1255 cm^{-1}. Mass (EI) (*m/z*, %): 442 (M^+, 15), 329 (17), 285 (100). HRMS (EI): 442.2526, calcd for $C_{26}H_{38}O_4Si$ 442.2539.

3.1.24. 1-*tert*-Butyl-5-[(4-*tert*-butyldimethylsiloxy)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (4c). Similarly to the preparation of **4a** from **7a**, the singlet oxygenation of 5-*tert*-butyl-4-[(4-*tert*-butyldimethylsiloxy)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**7c**) was carried out to give **4c** as colorless granules, melted at 79.0–80.0°C (from MeOH), in 74.7% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.21 (s, 6H), 0.83 (s, 3H), 0.93 (s, 9H), 0.99 (s, 9H), 1.06 (s, 3H), 3.92 (d, J=8.3 Hz, 1H), 4.53 (d, J=8.3 Hz, 1H), 6.84 (d, J=8.8 Hz, 2H), 6.93 (d, J=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C −4.2, 15.6, 18.4, 24.1, 24.6, 25.8, 36.3, 45.5, 77.5, 101.8, 119.0, 120.7, 127.7, 127.9, 154.9. IR (KBr): 2957, 2891, 1610, 1263 cm^{-1}. Mass (EI) (*m/z*, %): 336 (M^+−56 (Me_2-C=CH_2, 56), 235 (100). CIMS: MH^+ 393. HRMS (EI): 336.1762, calcd for $C_{18}H_{28}O_4Si$ 336.1757.

3.2. Isolation of an emitter as a neutral form from the spent reaction mixture of CIEEL-decay of 1-*tert*-butyl-5-[(*tert*-butyldimethylsiloxy)aryl]-4,4-dimethyl-2,6,7-trioxabicyclo [3.2.0]heptane (4a–4c)

General procedure. To a solution of 1-*tert*-butyl-5-[(*tert*-

butyldimethylsiloxy)aryl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (**4a**–**4c**) (0.1 mmol) in DMSO (2 mL), TBAF in DMSO (1.0×10^{-1} mol dm^{-3}, 4 mL) was added and stirred at room temperature. The reaction mixture was poured into NaCl aq. solution and extracted with AcOEt. The organic layer was washed with water, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel and eluted with AcOEt–hexane (1:4) to give the corresponding ketoester (**14a**–**14c**): 89% yield for **14a**, 93% yield for **14b**, and 49% yield for **14c**.

3.2.1. 3-(3-Hydroxyphenyl)-2,2-dimethyl-3-oxopropan-1-yl 2,2-dimethylpropanoate (14a). As colorless granules melted at 69.0–70.0°C (from hexane–AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.14 (s, 9H), 1.37 (s, 6H), 4.26 (s, 2H), 6.95 (dd, J=8.1, 2.6 Hz, 1H), 7.09 (s with fine coupling, 1H), 7.19 (d with fine coupling, J=7.7 Hz, 1H), 7.27 (dd, J=8.1, 7.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.2, 27.0, 38.8, 47.9, 70.5, 114.4, 118.5, 119.3, 129.5, 139.6, 155.9, 178.6, 207.0. IR (KBr): 3319, 2981, 1730, 1668, 1594, 1266 cm^{-1}. Mass (EI) (*m*/*z*, %): 278 (M^+, 6), 222 (17), 121 (100), 57 (27). HRMS (ESI): 301.1408, calcd for $C_{16}H_{22}O_4Na$ ($M+Na^+$) 301.1416.

3.2.2. 3-(7-Hydroxynaphthalen-2-yl)-2,2-dimethyl-3-oxopropan-1-yl 2,2-dimethylpropanoate (14b). Colorless granules, melted at 137.0–138.0°C (from hexane–AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.14 (s, 9H), 1.43 (s, 6H), 4.32 (s, 2H), 5.31 (s, 1H), 7.16–7.21 (m, 1H), 7.19 (s, 1H), 7.54 (dd, J=8.5, 1.7 Hz, 1H), 7.76 (d, J=8.1 Hz, 1H), 7.78 (d, J=8.5 Hz, 1H), 7.96 (s with fine coupling, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.4, 27.1, 38.8, 48.0, 70.6, 110.5, 119.9, 121.8, 126.2, 127.9, 129.5, 129.7, 133.6, 136.4, 154.4, 178.4, 207.3. IR (KBr): 3363, 2970, 2873, 1708, 1667, 1629, 1600 cm^{-1}. Mass (EI) (*m*/*z*, %): 328 (M^+, 15), 272 (30), 171 (100), 143 (17), 57 (10). HRMS (ESI): 351.1588, calcd for $C_{20}H_{24}O_4Na$ ($M+Na^+$) 351.1572.

3.2.3. 3-(4-Hydroxyphenyl)-2,2-dimethyl-3-oxopropan-1-yl 2,2-dimethylpropanoate (14c). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.12 (s, 9H), 1.42 (s, 6H), 4.31 (s, 2H), 6.78 (s, 1H), 6.84 (d, J=8.8 Hz, 2H), 7.72 (d, J=8.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.6, 27.0, 38.9, 47.6, 70.9, 115.1, 129.9, 130.6, 159.2, 178.8, 204.2. IR (liquid film): 3365, 2974, 2937, 1730, 1705, 1664, 1583 cm^{-1}. Mass (EI) (*m*/*z*, %): 278 (M^+, 1), 223 (4), 121 (100), 93 (10). HRMS (ESI): 301.1413, calcd for $C_{16}H_{22}O_4Na$ ($M+Na^+$) 301.1416.

3.3. Chemiluminescence measurement of 1-*tert*-butyl-5-[(3-*tert*-butyldimethylsiloxy)aryl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (4a–4c)

Freshly prepared solution (2 mL) of 1.0×10^{-2} mol dm^{-3} of TBAF in DMSO was transferred to a quartz cell ($10\times10\times50$ mm^3) 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^{-5} mol dm^{-3}, 1 mL), which was thermostated at the same temperature as that of the above TBAF solution, was added with 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 (**1**), whose chemiluminescent efficiency Φ^{CIEEL} has been reported to be 0.29 and was used here as a standard.[5]

3.5. Fluorescence measurement of 3-(3-hydroxyaryl)-2,2-dimethyl-3-oxopropan-1-yl 2,2-dimethylpropanoate (14a and 14b)

Freshly prepared solution of $2.05-2.10\times10^{-5}$ mol dm^{-3} of **14a** or **14b** and of 1.0×10^{-2} mol dm^{-3} of TBAF in DMSO was transferred to a quartz cell ($10\times10\times50$ mm^3) and the latter placed in the spectrometer, which was thermostated with stirring at 25°C. Thus, the fluorescence spectra of **14a** and **14b** were measured and their fluorescence efficiencies (Φ^{fl}) were estimated using quinine bisulfate for **14a** or using fluorescein for **14b** as a standard.[24]

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