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SYNTHESIS OF TRICYCLIC DIOXETANES THAT EXHIBIT INTRAMOLECULAR CHARGE-TRANSFER-INDUCED DECOMPOSITION: RELATIONSHIP BETWEEN STRUCTURE AND CHEMILUMINESCENCE EFFICIENCY

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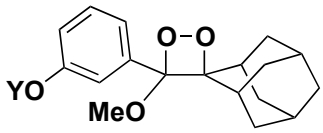
Abstract – Tricyclic dioxetanes bearing a 3-oxyphenyl group **3**–**5** were stereoselectively synthesized in high yields by the singlet oxygenation of three types of 5-(3-oxyphenyl)-2,3-dihydrofurans fused with a cyclopentane ring **6b**–**8b**. Upon treatment with tetrabutylammonium fluoride (TBAF) in DMSO or acetonitrile at 25 °C, these dioxetanes underwent charge-transfer-induced decomposition (CTID) accompanied by the emission of bright blue light. Although all of these dioxetanes gave excited oxyanions of 3-hydroxybenzoate as an emitter, their chemiluminescence efficiencies were significantly different and depended on their structures.

INTRODUCTION

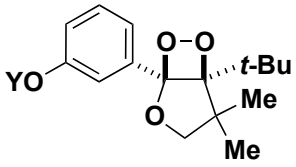
Intramolecular charge-transfer-induced decomposition (CTID) of a 1,2-dioxetane bearing an aromatic electron donor may lead to highly efficient chemiluminescence and is now believed to play a key role in the bioluminescence of various organisms such as the firefly.[1-3] Extensive research has been conducted to elucidate the chemiexcitation processes in both chemiluminescence and bioluminescence. CTID has also stimulated the development of high-performance dioxetane-based chemiluminescence systems that can be used in modern biological and clinical analysis, as represented by AMPPD® (**1**) and DIFURAT® (**2a**) (Figure 1).[4,5]

In the course of our investigation to develop a high-performance chemiluminescence system, we attempted to modify the parent dioxetane **2b** to determine whether or not further stereochemical

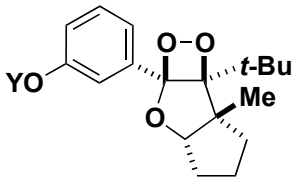
regulation of the dioxetane skeleton fused to a dihydrofuran ring leads to an increase in chemiluminescence efficiency (Φ^{CL}). The thus-realized dioxetanes were 3-oxyphenyl-substituted tricyclic dioxetanes **3–5**, in which a tetrahydrofuran ring was further fused with a cyclopentane ring (Figure 1). We report here the synthesis of **3–5** and their CTID, for which the Φ^{CL} values differed from the value for **2b** depending on their structures, though they gave quite similar esters of 3-oxidobenzoic acid as an emitter.[6,7]



1: Y = $(NaO)_2P(O)^-$



2a: Y = $(NaO)_2P(O)$-
2b: Y = *t*-Bu$(Me)_2$Si-



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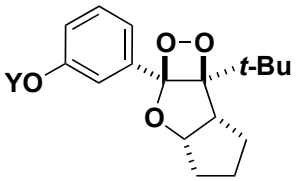
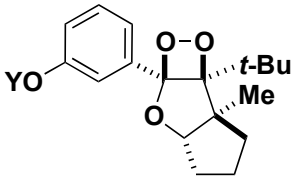


4: Y = *t*-Bu$(Me)_2$Si-



5: Y = *t*-Bu$(Me)_2$Si-

Figure 1. AMPPD® (**1**), DIFURAT® (**2a**) and tricyclic dioxetanes **3**, **4** and **5**

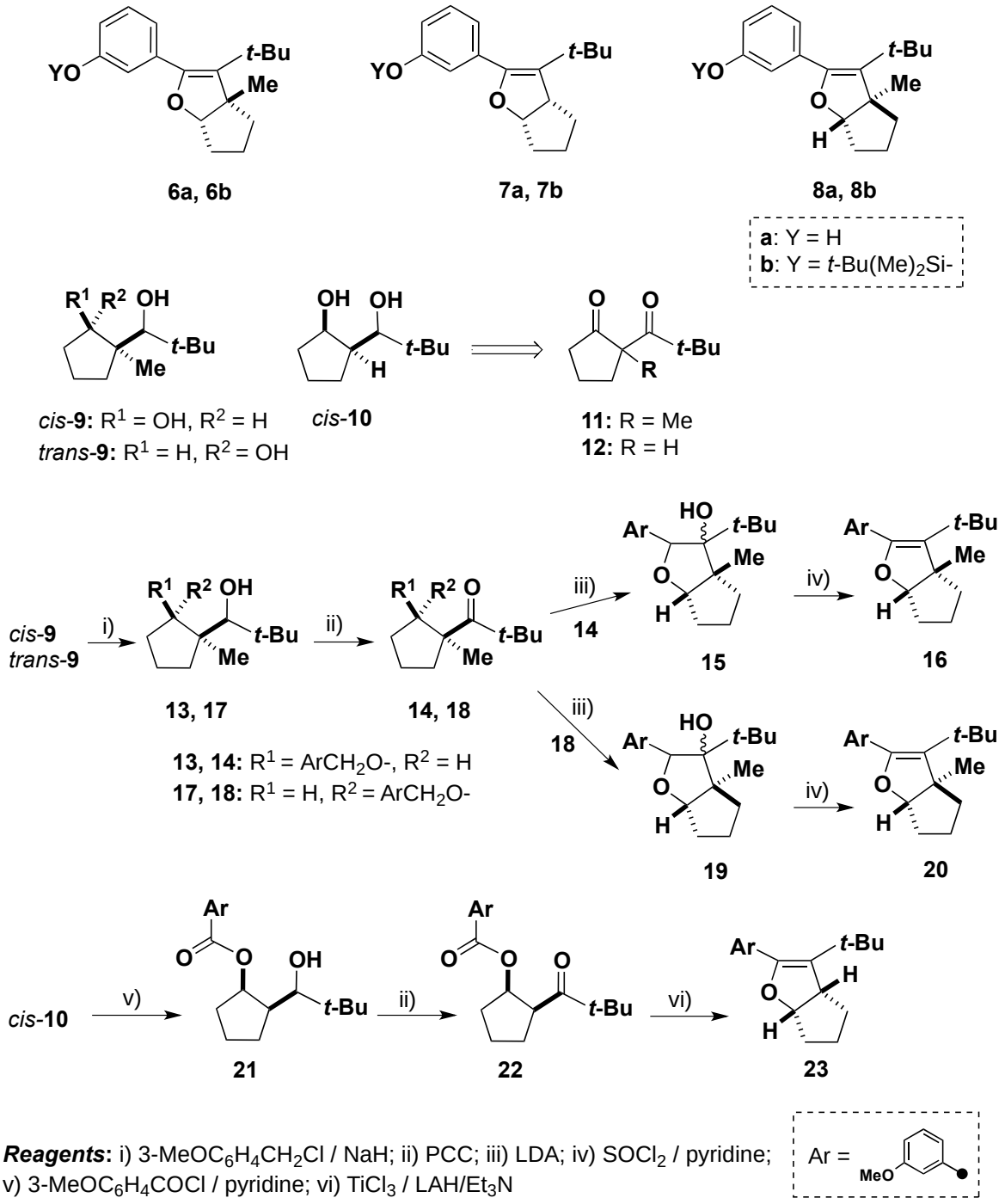
RESULTS AND DISCUSSION

Synthesis of tricyclic dioxetanes bearing a 3-(*tert*-butyldimethylsiloxy)phenyl group

Tricyclic dioxetanes bearing a 3-(*tert*-butyldimethylsiloxy)phenyl group **3**, **4** and **5** were prepared by singlet oxygenation of the corresponding 3-(*tert*-butyldimethylsiloxy)phenyl-substituted 2,3-dihydrofurans **6b**, **7b** and **8b** fused with a cyclopentane ring. These precursors were synthesized through several steps starting from *t*-2-methyl-*c*-2-(2,2-dimethyl-1-hydroxypropyl)cyclopentan-*r*-1-ol (*cis*-**9**), *c*-2-(2,2-dimethyl-1-hydroxypropyl)cyclopentan-*r*-1-ol (*cis*-**10**) and the *trans*-isomer (*trans*-**9**) of *cis*-**9**. These diols were prepared from pivaloylcyclopentanone **11** or **12** by reduction with $LiAlH_4$ or DIBAL.

Williamson ether synthesis using diol *cis*-**9** and 3-methoxybenzyl chloride selectively gave cyclopentyl ether **13**, the remaining OH group of which was in turn oxidized with PCC to give benzyloxycyclopentyl *tert*-butyl ketone **14** in high yield. LDA-mediated cyclization[8] of ketone **14** effectively took place to give hydroxytetrahydrofuran fused with a cyclopentane ring **15**, which was successively dehydrated with $SOCl_2$/pyridine to give 3-methoxyphenyl-substituted bicyclic dihydrofuran **16** in good yield. Finally, deprotection of the methoxy group in **16** with MeSNa/DMF followed by silylation with

t-butyldimethylsilyl chloride gave the precursor **6b**. As shown in Scheme 1, the precursor **8b** was similarly synthesized starting from *trans*-**9** through the steps **17** → **18** → **19** → **20**. On the other hand, this synthetic pathway could not be applied to the synthesis of **7b** from *cis*-**10** because of the instability of the intermediary benzyloxycyclopentane related to **14** and **18** under basic conditions. Thus, dihydrofuran **23** was synthesized by the McMurry coupling of keto benzoate **22**, which was prepared by the oxidation of alcohol **21** with PCC (Scheme 1).



Scheme 1. Synthesis of bicyclic dihydrofurans bearing a 3-siloxyphenyl group

When dihydrofuran fused with a *cis*-cyclopentane **6b** was irradiated in the presence of a small amount of tetraphenylporphin (TPP) with a 940 W Na lamp in CH_2Cl_2 under an O_2 atmosphere at 0 °C for 1.5 h, dioxetane **3** was the sole product.

A similar singlet oxygenation of dihydrofuran **7b** proceeded smoothly to exclusively give dioxetane **4**. The structures of **3** and **4** were determined by ^{1}H NMR, ^{13}C NMR, IR, and HR Mass spectral analysis. Thus, we know that singlet oxygenation proceeded with quite high π-face selectivity: both **3** and **4** were products due to the attack by $^1O_2$ of the sterically less-congested π-face of dihydrofuran, which was opposite a fused cyclopentane ring. On the other hand, singlet oxygenation of dihydrofuran **8b** proceeded sluggishly even at 40 °C, albeit with high stereoselectivity: $^1O_2$ attacked the π-face opposite the 3-methyl group to selectively give dioxetane **5**. The structure of **5** was determined by X-ray single crystallographic analysis in addition to ^{1}H NMR, ^{13}C NMR, IR, and HR Mass spectral analysis: an ORTEP view is shown in Figure 2.

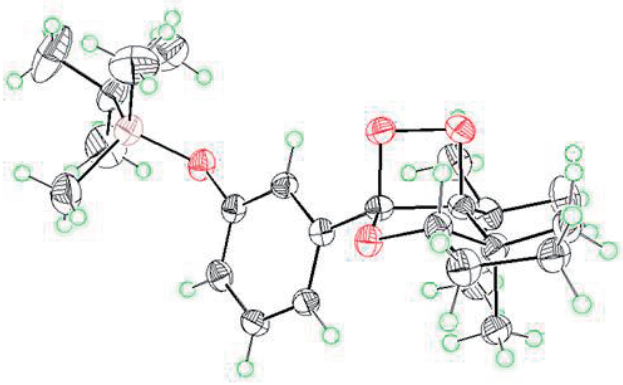
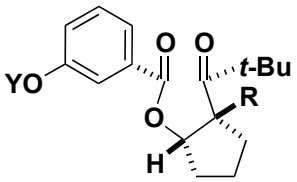


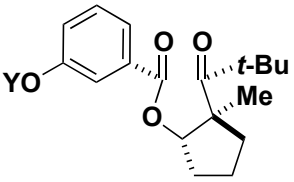
Figure 2. ORTEP view of dioxetane **5**

Chemiluminescent decomposition of tricyclic dioxetanes bearing a 3-(*tert*-butyldimethylsiloxy)-phenyl group

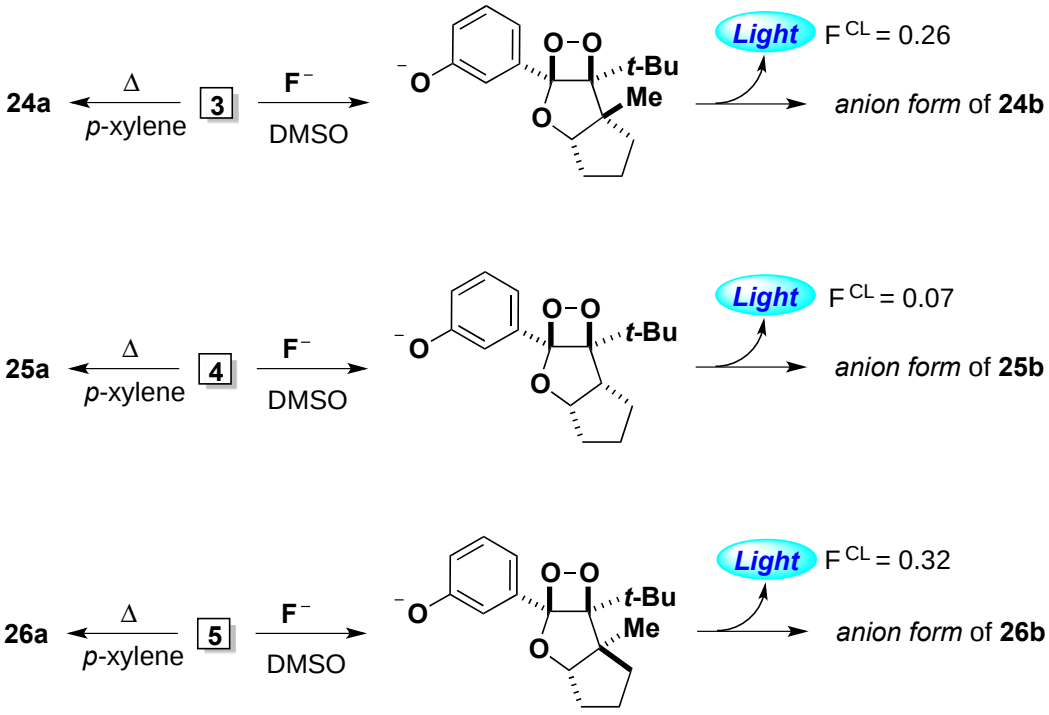
Tricyclic dioxetanes **3**, **4** and **5** were thermally stable enough to permit handling at room temperature, though they decomposed exclusively into the corresponding ketoesters **24a**, **25a** and **26a** in refluxing *p*-xylene (Scheme 2). When dioxetane **3** was treated with a large excess of tetrabutylammonium fluoride (TBAF) in DMSO at 25 °C, **3** decomposed rapidly to emit intense blue light (maximum wavelength: λ_{max}^{CL} = 466 nm, rate constant of CTID: k^{CTID} = 0.039 s^{-1}, and half-life: $t_{1/2}$ = 18 s) with chemiluminescence efficiency Φ^{CL} = 0.26,[9,10] the value of which was considerably higher than that for the parent dioxetane **2b** (Φ^{CL} = 0.20)[6a] as shown in Table 1 (Scheme 2). Dioxetanes **4** and **5** also decomposed in TBAF/DMSO to emit blue light (λ_{max}^{CL} = 466–467 nm), though their Φ^{CL} values diverged from those for the parent **2b** and **3**. Thus, Φ^{CL} for **4** decreased to only 0.07 (relative Φ^{CL} was 2/5 of that for **2b** and 1/4 of that for **3**), whereas Φ^{CL} for **5** increased to 0.32, the value of which was the highest among the three dioxetanes presented here and 1.6 times higher than that for **2b** (Table 1, Scheme 2).



24a: R = Me, Y = *t*-BuMe$_2$Si-
24b: R = Me, Y = H
25a: R = H, Y = *t*-BuMe$_2$Si-
25b: R = H, Y = H



26a: Y = *t*-BuMe$_2$Si-
26b: Y = H



Scheme 2. Thermal- and base-induced decomposition of tricyclic dioxetanes

Table 1. Chemiluminescence properties of dioxetanes **3**, **4**, **5** and **2b** in a TBAF/DMSO system and in a TBAF/MeCN system

Dioxetane	TBAF/DMSO system [a]				TBAF/MeCN system [a]			
	λ_{max}/nm	Φ^{CL}	Φ_S [b]	$t_{1/2}$ /s	λ_{max}/nm	Φ^{CL}	Φ_S [b]	$t_{1/2}$ /s
3	466	0.26	0.79	18	470	0.13	0.54	64
4	466	0.07	0.21	7.7	470	0.035	0.15	33
5	467	0.32	0.97	0.56	470	0.19	0.79	2.1
2b	466 [c]	0.20 [c]	0.63 [c]	4.6 [c]	469 [d]	0.10 [d]	0.42 [d]	19 [d]

a) The reaction was carried out at 25 °C. b) $\Phi_S = \Phi^{CL} / \Phi^{fl}$, Φ^{fl} = 0.33 for **3**, **4** and **5**, and 0.32 for **2b** in a TBAF/DMSO system; Φ^{fl} = 0.24 for **3**, **4**, **5** and **2b** in a TBAF/MeCN system. c) ref. 6b. d) ref. 6a.

The spent reaction mixtures of **3**, **4** and **5** afforded the corresponding ketoesters **24b**, **25b** and **26b** after neutralization followed by the usual work-up.[11] The fluorescence spectra of oxido anions generated from authentic **24b**, **25b** and **26b** in TBAF/DMSO (MeCN) coincided with the chemiluminescence spectra for **3**, **4** and **5**, respectively. Thus, these oxido anions of ketoesters **24b**–**26b** were undoubtedly the emitters for the present CTID of dioxetanes **3**–**5**. The fluorescence efficiencies (Φ^{fl}) of the oxido anions of ketoesters **24b**–**26b** were all estimated to be 0.33, which was practically the same as the value for an emitter from **2b** (Φ^{fl} = 0.32) in a TBAF/DMSO system.[6a] Thus, the efficiencies of singlet-chemiexcitation ($\Phi_S = \Phi^{CL}/\Phi^{fl}$) in TBAF/DMSO were calculated to be 0.79 for **3**, 0.21 for **4** and 0.97 for **5**. These results showed that tricyclic dioxetanes **3** and **5** were excellent chemiluminescence compounds with singlet-chemiexcitation efficiency that was markedly high among oxyphenyl-substituted dioxetanes known to date.[1,2,12,13]

TBAF-induced chemiluminescent decomposition of these dioxetanes was also carried out in acetonitrile and the results are summarized in Table 1. When we compared the chemiluminescence properties of **3**, **4** and **5** in acetonitrile to those in DMSO, we found that λ_{max}^{CL} was practically the same and $t_{1/2}$ was increased *ca*. 4-fold, while Φ^{CL} decreased to *ca*.1/2. However, the magnitude of Φ^{CL} was in the order of **5** > **3** > **2b** >> **4** both in DMSO and in MeCN. Thus, the efficiencies of singlet-chemiexcitation Φ_S were estimated similarly to the case of TBAF/DMSO and are summarized in Table 1.

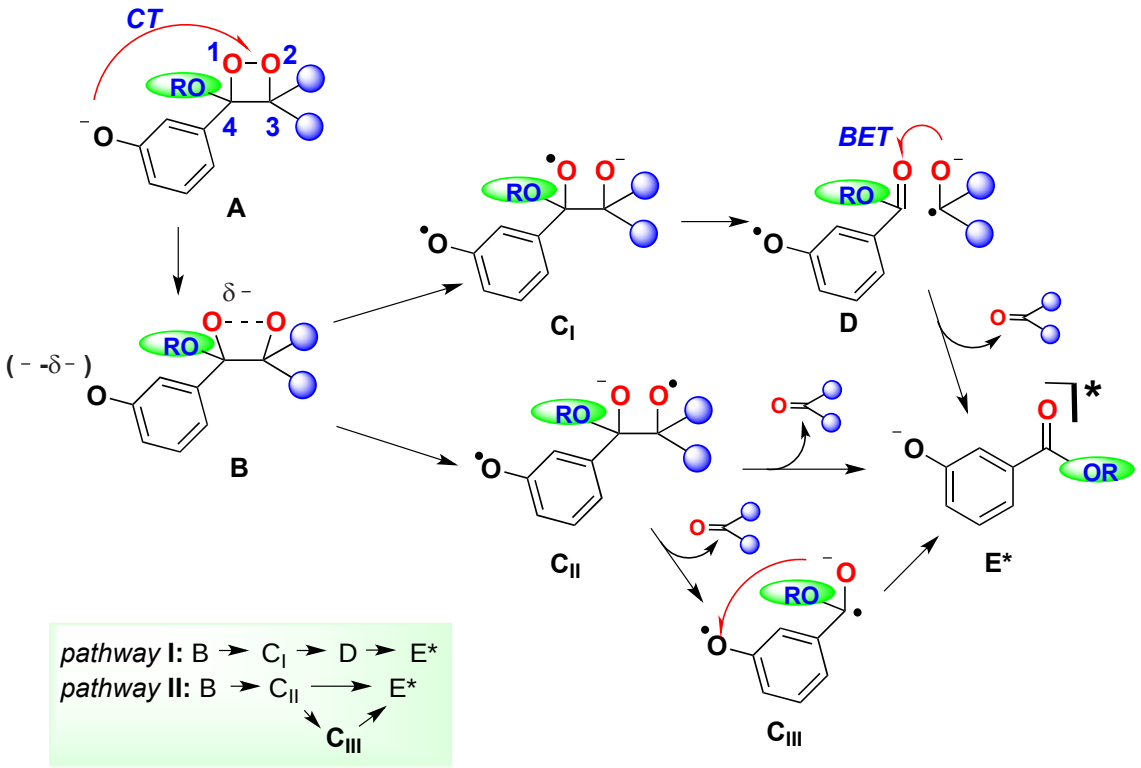
As described above, both stereoisomeric tricyclic dioxetanes **3** and **5** fused with a cyclopentane ring showed effective singlet-chemiexcitation that was 25–50% (in DMSO) or 30–90% (in MeCN) higher than that for the parent dioxetane **2b**. However, singlet-chemiexcitation for dioxetane **4** was far less effective than in the case of **3**, though the structural features of **4** and **3** resembled each other except regarding the presence of a bridge-head methyl group. Thus, we will finally discuss how the chemiexcitation process was affected by the skeleton of the dioxetane bearing an oxidophenyl group.

Plausible mechanisms for singlet-chemiexcitation that have typically been proposed for CTID of oxidophenyl-substituted dioxetane **A** are illustrated in Scheme 3, where the reaction proceeds as follows:[2,3,14,15]

i) Intramolecular CT takes place from an oxidophenyl anion to O-O for dioxetane **A** to give **B**, which causes O-O bond cleavage to give two types of transient biradical anion, $\mathbf{C_I}$ and/or $\mathbf{C_{II}}$, as an extreme structure.

ii) Cleavage of the C-C bond in biradical anion $\mathbf{C_I}$ gives pair **D** of neutral radical/ketyl radical anion, which is annihilated by intermolecular backward electron transfer (BET) to form singlet-excited oxidobenzoate **E*** and neutral ketone (*pathway* **I**) [CIEEL[16] (chemically initiated electron exchange luminescence) mechanism]. On the other hand, biradical anion $\mathbf{C_{II}}$ extrudes a neutral ketone

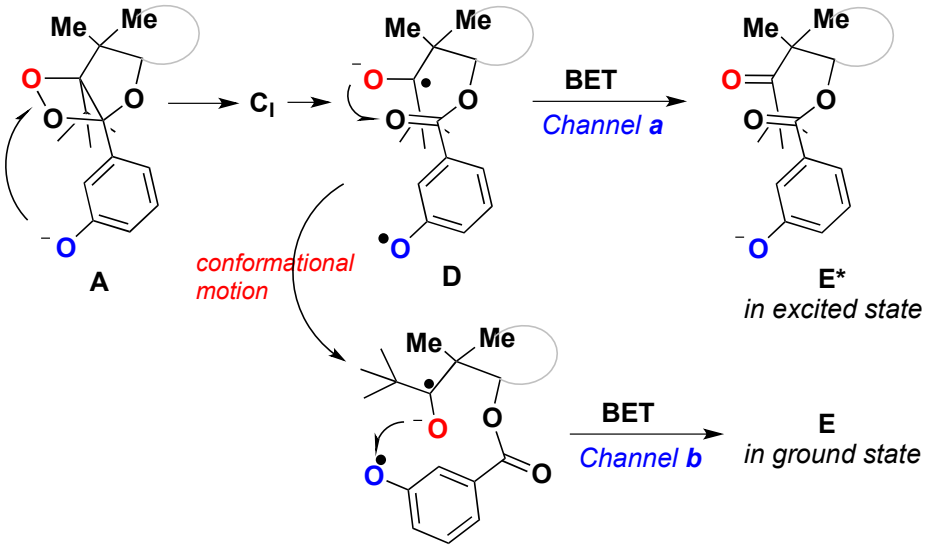
molecule in the ground state to give **E*** directly or through intramolecular BET[14] of diradical anion **C**III (*pathway* **II**) [CT/direct mechanism].[17]



Scheme 3. Singlet-chemiexcitation mechanism for CTID of oxidophenyl-substituted dioxetane

If the CIEEL mechanism is operative, Φ_S of dioxetane **A** depends on the efficiency of BET (*channel* ***a***, *vide infra*) which occurs in a solvent cage. Therefore, difusion of a ketyl radical anion would decisively decrease Φ_S for dioxetanes such as **1**.[4c] On the other hand, this possibility can be excluded for bicyclic dioxetanes **2**, since a ketyl radical anion is tethered to an oxybenzoate radical by a $-CH_2C(Me)_2-$ chain for **D**. However, another BET (*channel* ***b***) has been proposed to occur from ketyl radical anion to ·O-Ar radical of a benzoate moiety with an accompanying conformational change to directly give a benzoate in the ground state (Scheme 4).[18] According to this mechanism, the fact that Φ_S for tricyclic dioxetanes **3** and **5** were markedly higher than that for bicyclic dioxetane **2b** may be accounted for as follows. Since the conformational change of both the neutral radical of oxybenzoate and the ketyl radical anion is considerably regulated by the cyclopentane ring joining them for **D** produced from **3** or **5**, BET through *channel* ***b*** becomes more difficult to occur than in the case of **2b**. If we consider that the structural features of **25** with a *cis-vicinal*-disubstitution pattern on a cyclopentane ring are the same as those of **24** except that the latter has a 3-methyl group, radical pair **D** for dioxetane **4** would have a steric environment similar to that for **3**. Therefore, while Φ_S for **4** was expected to be as high as that for **3**, it was only 1/4

of that for **3**. In conclusion, CIEEL (*pathway* **I**) cannot well describe the relationship between structure and Φ_S for the chemiluminescent CTID of dioxetanes **2**–**5**.



Scheme 4. Two BET channels leading to **E*** or **E** for a bicyclic dioxetane

On the other hand, for the CT/direct mechanism (*pathway* **II**), singlet-chemiexcitation occurs through $\mathbf{C_{II}}$, which undergoes homolytic C-C bond cleavage to give excited ester **E*** either directly or through $\mathbf{C_{III}}$. Thus, $\mathbf{C_{II}}$, once produced, is presumed to effectively give **E***. Since a transient species **B** can give both $\mathbf{C_I}$ and $\mathbf{C_{II}}$, effective singlet-chemiexcitation seems to depend on how $\mathbf{C_{II}}$ is preferentially produced for CTID of dioxetane **A**.[19-22] This notion suggests that CTID of dioxetanes **2b** and **3**–**5** proceeded preferentially through $\mathbf{C_{II}}$ (*pathway* **II**) in the order **5** > **3** > **2b** >> **4**. Note that this order apparently coincides with the order of steric congestion around the carbon at the 3-position of dioxetane **A**, i.e., **5** ≥ **3** > **2b** > **4**. These results suggest that the steric environment such as congestion around the carbon of dioxetane presumably affects singlet-chemiexcitation for oxyphenyl-substituted dioxetanes. Thus, we are now investigating chemiluminescent CTID of various oxyphenyl-substituted dioxetanes to determine how their singlet-chemiexcitation efficiencies relate to their structures mainly based on X-ray single crystallographic analysis.

CONCLUSION

Three types of 5-oxyphenyl-2,3-dihydrofurans fused with a cyclopentane ring **6b**–**8b** were oxygenated with $^1O_2$ to stereoselectively give the corresponding tricyclic dioxetanes bearing an 3-oxyphenyl group **3**–**5** in high yields. TBAF induced CTID of **3**–**5** accompanied by the emission of a flash of blue light. Although all of these dioxetanes gave excited 3-oxidobenzoates as emitters with the very same

fluorescence efficiency, their chemiluminescence efficiencies diverged from that for the parent **2b** (Φ^{CL} = 0.20) to within the range 0.07-0.32 depending on their structures. The results suggested that chemiluminescent CTID for these dioxetanes could not be well described by an intramolecular CIEEL mechanism through *pathway* **I**. Alternatively, effective singlet-chemiexcitation was presumed to take place through *pathway* **II** (CT/direct mechanism), where the preferred destination was affected by the steric conditions around the carbon of dioxetane.

EXPERIMENTAL

General Melting points were uncorrected. IR spectra were taken on a FT/IR infrared spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz, 400 MHz and 500 MHz spectrometers. Mass spectra were obtained using double-focusing mass spectrometers and an ESI-TOF mass spectrometer. Column chromatography was carried out using silica gel.

Synthesis of *r*-1-(3-methoxybenzyloxy)-*t*-2-methyl-*c*-2-(1-hydroxy-2,2-dimethylpropyl)cyclopentane (13): typical procedure. *t*-2-Methyl-*c*-2-(2,2-dimethyl-1-hydroxypropyl)cyclopentan-*r*-1-ol (*cis*-**9**) (2.10 g, 11.3 mmol) was added to a suspension of NaH (60% in oil, 510 mg, 12.8 mmol) in dry DMF (40 mL) under N_2 atmosphere at room temperature and stirred for 1 h. To the solution, 3-methoxybenzyl chloride (1.70 mL, 11.7 mmol,) was added and stirred for overnight. The reaction mixture was poured into sat. aq. NH_4Cl and extracted twice with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane–AcOEt (10:1) to give 3.068 g of **13**. The stereoisomer **17** of **13** was similarly synthesized.

13: 89% yield. colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 0.94 (s, 3H), 1.03 (s, 9H), 1.37-1.45 (m, 1H), 1.55-1.92 (m, 4H), 2.15-2.27 (m, 1H), 3.26 (d, *J* = 3.2 Hz, 1H), 3.59 (dd, *J* = 4.6 and 1.8 Hz, 1H), 3.67 (d, *J* = 3.2 Hz, 1H), 3.81 (s, 3H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 6.82 (dd, *J* = 8.2 and 2.4 Hz, 1H), 6.87-6.90 (m, 2H), 7.25 (dd, *J* = 8.2 and 7.9 Hz, 1H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 21.3, 23.3, 28.5, 29.4, 33.3, 36.7, 52.3, 55.1, 70.5, 80.6, 91.1, 112.4, 113.1, 119.4, 129.3, 140.0, 159.7 ppm. IR (liquid film): $\tilde{\nu}$ 3495, 2955, 2907, 2836, 1602 cm^{-1}. Mass (*m/z*, %): 306 (M^+, 1), 185 (8), 138 (80), 121 (100). HRMS (ESI) (*m/z*): 329.2088, calcd for $C_{19}H_{30}O_3Na$ [M + Na^+] 329.2093.

17: 87% yield. colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 0.98 (s, 9H), 1.05 (s, 3H), 1.43-1.65 (m, 4H), 1.69-1.81 (m, 1 H), 1.96-2.04 (m, 1H), 3.21 (s, 1H), 3.78 (t, *J* = 8.7 Hz, 1H), 3.81 (s, 3H), 4.28 (s, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.55 (d, *J* = 11.7 Hz, 1H), 6.82 (dd, *J* = 8.3 and 2.6 Hz, 1H), 6.87 (s with fine coupling, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 7.24 (dd, *J* = 8.3 and 7.6 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C 13.9, 19.0, 26.1, 28.3, 35.6, 37.0, 49.0, 55.2, 71.6, 88.7, 90.6, 113.0, 113.2, 119.8, 129.4,

139.4, 159.7 ppm. IR (liquid film): $\tilde{\nu}$ 3490, 2956, 2871, 1602 cm^{-1}. Mass (*m/z*, %): 306 (M^+, 11), 249 (8), 138 (62), 121 (100). HRMS (ESI) (*m/z*): 329.2099, calcd for $C_{19}H_{30}O_3Na$ [M + Na^+] 329.2093.

Synthesis of *r*-1-(3-methoxybenzyloxy)-*t*-2-methyl-*c*-2-pivaloylcyclpentane (14): typical procedure. Celite (10.4 g) and PCC (5.20 g, 24.1 mmol) was added to a solution of **13** (4.74 g, 15.5 mmol) in dry CH_2Cl_2 (50 mL) under N_2 atmosphere at room temperature and stirred overnight. To the reaction mixture, 2-propanol (5 mL) was added and stirred for 30 min, and then ether was added. The reaction mixture was filtered through celite and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane–AcOEt (10:1) to give of 4.46 g of **14**. The stereoisomer **18** of **14** was similarly synthesized from **17**.

14: 95% yield. colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.14 (s, 3H), 1.19 (s, 9H), 1.55-1.95 (m, 5H), 2.52-2.63 (m, 1H), 3.79 (s, 3H), 4.08 (d, *J* = 3.8 Hz, 1H), 4.31 (d, *J* = 11.9 Hz, 1H), 4.46 (d, *J* = 11.9 Hz, 1H), 6.75-6.84 (m, 3H), 7.20 (t, *J* = 8.0 Hz, 1H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 20.2, 22.6, 27.6, 28.1, 33.3, 45.0, 55.1, 62.1, 69.8, 87.4, 112.4, 112.9, 119.4, 129.0, 140.3, 159.5, 216.8 ppm. IR (liquid film): $\tilde{\nu}$ 2961, 2875, 1685, 1601 cm^{-1}. Mass (*m/z*, %): 304 (M^+, 8), 168 (13), 121 (100). HRMS (ESI) (*m/z*): 327.1934, calcd for $C_{19}H_{28}O_3Na$ [M + Na^+] 327.1936.

18: 86% yield. colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.25 (s, 9H), 1.39 (s, 3H), 1.46-1.79 (m, 4H), 1.83-2.03 (m, 2H), 3.81 (s, 3H), 4.41 (t, *J* = 7.1 Hz, 1H), 4.46 (d, *J* = 12.7 Hz, 1H), 4.52 (d, *J* = 12.7 Hz, 1H), 6.80 (d with fine coupling, *J* = 8.1 Hz, 1H), 6.89-6.93 (m, 2H), 7.23 (t, *J* = 8.1 Hz, 1H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 18.6, 20.4, 28.6, 29.4, 36.3, 45.4, 55.1, 58.8, 71.6, 83.6, 112.7, 112.8, 119.5, 129.1, 140.8, 159.5, 217.4 ppm. IR (liquid film): $\tilde{\nu}$ 2957, 2873, 1682, 1603 cm^{-1}. Mass (*m/z*, %): 304 (M^+, 14), 183 (8), 121 (100). HRMS (ESI) (*m/z*): 327.1941, calcd for $C_{19}H_{28}O_3Na$ [M + Na^+] 327.1936.

Synthesis of *cis*-2-(1-hydroxy-2,2-dimethylpropyl)cyclopentyl 3-methoxybenzoate (21). 3-Methoxybenzoyl chloride (2.23 mL, 15.9 mmol) was added to a solution of 2 *cis*-2-(2,2-dimethyl-1-hydroxypropyl)cyclopentan-1-ol (*cis*-**10**) (2.74 g, 15.9 mmol) and pyridine (3.2 mL, 39.6 mmol) in dry CH_2Cl_2 (30 mL) under argon atmosphere at 0 °C and stirred at room temperature for overnight. The reaction mixture poured into sat. aq. NaCl and extracted with AcOEt. The organic layer was washed with 1M HCl and then with sat. aq. NaCl, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane–AcOEt (10:1) to give 3.40 g of **21**.

21: 70% yield. colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 0.93 (s, 9H), 1.66-1.75 (m, 1H), 1.79-2.14 (m, 6H), 2.24-2.30 (m, 1H), 3.61-3.64 (m, 1H), 3.85 (s, 3H), 5.44-5.47 (m, 1H), 7.10 (dd, *J* = 8.0 and 2.8 Hz, 1H), 7.35 (*t*, *J* = 8.0 Hz, 1H), 7.53 (s with fine coupling, 1H), 7.56 (d, *J* = 8.0 Hz, 1H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ_C 22.4, 22.4, 26.5, 32.7, 35.4, 44.8, 55.4, 77.6, 81.8, 114.1, 119.3, 121.6, 129.6, 131.9, 159.7, 165.9 ppm. IR (liquid film): $\tilde{\nu}$ 3551, 2957, 2871, 1714, 1602 cm^{-1}. Mass (*m/z*, %): 306 (M^+, 6), 249 (26), 153 (38), 135 (100). HRMS (ESI) (*m/z*): 329.1728, calcd for $C_{18}H_{26}O_4Na$ [M + Na^+] 329.1729.

***cis*-2-Pivaloylcyclopentyl 3-methoxybenzoate (22).** Similarly to the case of **13**, alcohol **21** was oxidized with PCC to give **22**.

22: 90% yield. colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.13 (s, 9H), 1.60-1.83 (m, 2H), 1.91-2.02 (m, 2H), 2.11-2.31 (m, 2H), 3.50 (ddd, *J* = 8.9, 7.9 and 6.2 Hz, 1H), 3.85 (s, 3H), 5.55-5.60 (m, 1H), 7.08 (ddd, *J* = 8.3, 2.7 and 1.0 Hz, 1H), 7.32 (dd, *J* = 8.3 and 7.7 Hz, 1H), 7.49 (s with fine coupling, 1H), 7.56 (d with fine coupling, *J* = 7.7 Hz, 1H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 22.6, 26.0, 28.2, 33.6, 44.7, 48.9, 55.3, 77.6, 113.7, 119.7, 122.0, 129.3, 131.4, 159.5, 165.6, 213.5 ppm. IR (liquid film): $\tilde{\nu}$ 2966, 2873, 1716, 1587 cm^{-1}. Mass (*m/z*, %): 304 (M^+, 7), 247 (26), 136 (11), 135 (100). HRMS (ESI) (*m/z*): 327.1574, calcd for $C_{18}H_{24}O_4Na$ [M + Na^+] 327.1572.

Synthesis of *cis*-4-*tert*-butyl-4-hydroxy-3-(3-methoxyphenyl)-5-methyl-2-oxabicyclo[3.3.0]octane (15): typical procedure. Butyllithium (1.6 M in hexane, 19.4 mL, 31.0 mmol) was added to a solution of diisopropylamine (4.44 mL, 33.9 mmol) in dry THF (50 mL) and stirred for 30 min under N_2 atmosphere at room temperature. To the solution, **14** (4.30 g, 14.1 mmol) in dry THF (10 mL) was added at –78 °C and stirred for 1 h and then at room temperature for 3 h. The reaction mixture was poured into sat. aq. NH_4Cl and extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane–AcOEt (5:1) to give 3.30 g of **15**.

15: 77% yield. colorless columns, mp 105.5–106.5 °C (from AcOEt–hexane). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 0.92 (br-s, 9H), 1.34 (s, 3H), 1.30-1.38 (m, 1H), 1.70-1.91 (m, 3H), 2.03 (s, 1H), 2.00-2.10 (m, 1H), 2.53-2.62 (m, 1H), 3.80 (s, 3H), 4.46 (dd, *J* = 5.7 and 3.0 Hz, 1H), 5.05 (s, 1H), 6.79 (d with fine coupling, *J* = 8.1 Hz, 1H), 7.04-7.08 (m, 2H), 7.21 (dd, *J* = 8.1 and 7.5 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C 25.3, 25.7, 28.5, 35.1, 38.4, 38.6, 55.2, 58.6, 87.8, 90.1, 91.0, 112.7, 113.1, 120.0, 128.9, 142.7, 159.4 ppm. IR (KBr): $\tilde{\nu}$ 3556, 3017, 2963, 2881, 1604 cm^{-1}. Mass (m/z, %): 304 (M^+, 20), 247 (9), 168 (33), 137 (19), 121 (61), 111 (100). HRMS (ESI) (*m/z*): 327.1938, calcd for $C_{19}H_{28}O_3Na$ [M + Na^+] 327.1936. Anal. Calcd for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 74.90; H, 9.34.

19: 21% yield. colorless columns, mp 128.0–128.5 °C (from hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 1.00-1.15 (m, 9H), 1.20-1.40 (m, 3H), 1.43 (ddd, *J* = 12.0, 9.2 and 1.9 Hz, 1H), 1.60-1.73 (m, 2H), 1.94-2.21 (m, 3H), 3.81 (s, 3H), 4.18 (dd, *J* = 11.7 and 7.3 Hz, 1H), 5.47 (s, 1H), 6.83 (d with fine coupling, *J* = 8.1 Hz, 1H), 7.08-7.12 (m, 2H), 7.29 (t, *J* = 8.1 Hz, 1H) ppm. ^{13}C-NMR (125 MHz,

$CDCl_3$): δ_C 17.4, 20.6, 24.9, 25.5, 27.4, 28.1, 29.0, 39.2, 55.2, 57.8, 83.7, 86.5, 92.1, 113.2, 114.2, 120.6, 129.4, 139.5, 159.6 ppm. IR (KBr): $\tilde{\nu}$ 3555, 2994, 2958, 2904, 2885, 1601, 1492, 1463 cm^{-1}. Mass (m/z, %): 304 (M^+, 23), 247 (13), 183 (17), 168 (15), 137 (31), 121 (100). HRMS (ESI) (*m*/*z*): 327.1937, calcd for $C_{19}H_{28}O_3Na$ [M + Na^+] 327.1936.

Synthesis of *cis*-4-*tert*-butyl-3-(3-methoxyphenyl)-5-methyl-2-oxabicyclo[3.3.0]oct-3-ene (16): typical procedure. Thionyl chlolide (1.00 mL, 13.7 mmol) was added to a solution of **15** (2.74 g, 8.99 mmol) and pyridine (7.0 mL) in dry THF (40 mL) at 0 °C and stirred for 1 h. The reaction mixture was poured into sat. aq. $NaHCO_3$ and then extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with hexane–AcOEt (10:1) to give 2.37 g of **16**.

16: 92% yield. colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 1.05 (s, 9H), 1.39 (s, 3H), 1.54-1.67 (m, 2H), 1.74-1.86 (m, 2H), 1.89-1.98 (m, 1H), 2.02-2.11 (m, 1H), 3.80 (s, 3H), 4.35 (dd, *J* = 6.1 and 3.1 Hz, 1H), 6.83-6.87 (m, 2H), 6.90 (d with fine coupling, *J* = 7.6 Hz, 1H), 7.24 (dd with fine coupling, *J* = 8.0 and 7.6 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C 24.5, 28.4, 31.8, 32.5, 34.6, 41.5, 55.2, 58.2, 92.9, 113.8, 115.3, 122.4, 122.7, 128.9, 137.3, 149.5, 159.1 ppm. IR (liquid film): $\tilde{\nu}$ 2953, 2867, 1655, 1596 cm^{-1}. Mass (*m/z*, %): 286 (M^+, 46), 271 (100), 257 (30), 135 (30). HRMS (ESI) (*m/z*): 309.1839, calcd for $C_{19}H_{26}O_2Na$ [M + Na^+] 309.1831.

20: 20% yield. colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.11 (s, 3H), 1.47-1.54 (m, 1H), 1.65-1.76 (m, 3H), 2.03-2.20 (m, 2H), 3.80 (s, 3H), 4.02 (dd, *J* = 12.0 and 7.8 Hz, 1H), 6.84-6.88 (m, 2H), 6.92 (d with fine coupling, *J* = 7.6 Hz, 1H), 7.23 (dd with fine coupling, *J* = 8.9 and 7.6 Hz, 1H) ppm. ^{13}C-NMR (125MHz, $CDCl_3$): δ_C 18.5, 19.6, 25.4, 29.1, 32.0, 32.3, 55.2, 56.4, 91.6, 114.1, 115.1, 122.4, 128.8, 133.4, 136.8, 155.3, 159.0 ppm. IR (liquid film): $\tilde{\nu}$ 2963, 2902, 2871, 1591 cm^{-1}. Mass (*m/z*, %): 286 (M^+, 31), 271 (100), 215 (34), 135 (98). HRMS (ESI) (*m/z*): 309.1838, calcd for $C_{19}H_{26}O_2Na$ [M + Na^+] 309.1831.

Synthesis of *cis*-4-*tert*-butyl-3-(3-methoxyphenyl)-2-oxabicyclo[3.3.0]oct-3-ene (23).

$TiCl_3$ (5.19 g, 33.7 mmo1) was suspended in dry THF (100 mL) under nitrogen atmosphere at room temperature and stirred for 30 min. To the solution, $LiAlH_4$ (729 mg, 19.2 mmol) was added at 0 °C and stirred at room temperature for 40 min, and then triethylamine (2.50 mL, 17.9 mmo1) was added and refluxed for 1 h. To the solution, **22** (1.243 g, 4.08 mmo1) in dry THF (20 mL) was added dropwise over 30 min at refluxing temperature and then stirred for 1.5 h. The reaction mixture was poured into chilled sat. aq. Na_2CO_3 and extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue (1.339 g) was dissolved together with pyridinium *p*-toluenesulfonate (PPTS) (101 mg, 0.402 mmol) in CH_2Cl_2 (15 mL) and stirred at refluxing

temperature for 4h. The reaction mixture was poured into sat. aq. $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel and eluted with hexane−AcOEt (20:1) to give of 751 mg of **23**.

23: 68% yield. colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.03 (s, 9H), 1.57-1.99 (m, 6H), 3.39-3.45 (m, 1H), 3.80 (s, 3H), 4.95 (ddd, *J* = 8.6, 4.8 and 2.0 Hz, 1H), 6.85 (ddd, *J* = 8.2, 2.6 and 0.9 Hz, 1H), 6.88 (s with fine coupling, 1H), 6.94 (d with fine coupling, *J* = 7.5 Hz, 1H), 7.23 (dd, *J* = 8.2 and 7.5 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C 23.9, 30.8, 31.7, 34.4, 35.3, 51.0, 55.2, 85.2, 114.0, 115.1, 120.3, 122.3, 128.8, 136.2, 148.9, 159.1 ppm. IR (liquid film): $\tilde{\nu}$ 2956, 2865, 1664, 1601 cm^{-1}. Mass (*m/z*, %): 272 (M^+, 27), 257 (100), 135 (37). HRMS (ESI) (*m/z*): 295.1681, calcd for $C_{18}H_{24}O_2Na$ [M + Na^+] 295.1674.

Synthesis of *cis*-4-*tert*-butyl-3-(3-hydroxyphenyl)-5-methyl-2-oxabicyclo[3.3.0]oct-3-ene (6a): typical procedure. 3-(3-Methoxyphenyl)-2-oxabicyclooct-3-ene **16** (2.12 g, 7.41 mmol) and sodium methanethiolate (95 %, 1.09 g, 14.8 mmol) in dry DMF (25 mL) was stirred under N_2 atmosphere at 140 °C for 4 h. The reaction mixture was poured into 1M HCl and extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane−AcOEt (4:1) to give 1.872 g of **6a**.

6a: 93% yield. colorless needles, mp 113.0–114.0 °C (from AcOEt–hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 1.05 (s, 9H), 1.38 (s, 3H), 1.54-1.67 (m, 2H), 1.73-1.85 (m, 2H), 1.89-1.97 (m, 1H), 2.04-2.10 (m, 1H), 4.34 (dd, *J* = 6.1 and 3.1 Hz, 1H), 4.78 (s, 1H), 6.74-6.78 (m, 2H), 6.89 (d with fine coupling, *J* = 7.6 Hz, 1H), 7.19 (dd, *J* = 7.8 and 7.6 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C 24.5, 28.4, 31.8, 32.5, 34.6, 41.5, 58.2, 92.9, 115.2, 117.0, 122.4, 123.0, 129.1, 137.1, 149.1, 155.2 ppm. IR (KBr): $\tilde{\nu}$ 3397, 2984, 2953, 2901, 1665, 1597 cm^{-1}. Mass (*m/z*, %): 272 (M^+, 37), 257 (100), 243 (28), 121 (31). HRMS (ESI) (*m/z*): 295.1677, calcd for $C_{18}H_{24}O_2Na$ [M + Na^+] 295.1674. Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.39; H, 8.99.

7a: 78% yield. colorless columns, mp 146.5–147.0 °C (from AcOEt–hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 1.03 (s, 9H), 1.58-1.65 (m, 1H), 1.70-1.86 (m, 4H), 1.91-1.98 (m, 1H), 3.39-3.44 (m, 1H), 4.77 (s, 1H), 4.92-4.96 (m, 1H), 6.77 (dd, *J* = 8.2 and 2.6 Hz, 1H), 6.81 (s with fine coupling, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 7.18 (dd, *J* = 8.2 and 7.6 Hz, 1H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 23.9, 30.8, 31.7, 34.3, 35.3, 50.9, 85.3, 115.4, 117.0, 120.7, 122.3, 129.0, 135.9, 148.4, 155.1 ppm. IR (KBr): $\tilde{\nu}$ 3355, 2953, 2903, 1680, 1599 cm^{-1}. Mass (m/z, %): 258 (M^+, 27), 243 (100), 121 (37). HRMS (ESI) (*m/z*): 281.1515, calcd for $C_{17}H_{22}O_2Na$ [M + Na^+] 281.1518. Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.19; H, 8.73.

8a: 97% yield. colorless needles melted at 95.0–96.0 ºC (from CH_2Cl_2–hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.10 (br-s, 3H), 1.50 (ddd, *J* = 11.6, 8.2 and 2.4 Hz, 1H), 1.64-1.75 (m, 3H), 2.04-2.18 (m, 2H), 4.01 (dd, *J* = 12.1 and 7.8 Hz, 1H), 4.76-4.84 (m, 1H), 6.76-6.80 (m, 2H), 6.90 (d with fine coupling, *J* = 7.6 Hz, 1H), 7.19 (dd, *J* = 8.0 and 7.6 Hz, 1H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 18.6, 19.6, 25.5, 29.1, 32.0, 32.3, 56.3, 91.6, 115.5, 116.9, 122.2, 128.9, 133.7, 136.4, 154.7, 155.0 ppm. IR (KBr): $\tilde{\nu}$ 3347, 2958, 1590 cm^{-1}. Mass (*m/z*, %): 272 (M^+, 34), 257 (98), 201 (32), 121 (100). HRMS (ESI) (*m/z*): 295.1680, calcd for $C_{18}H_{24}O_2Na$ [M + Na^+] 295.1674. Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.31; H, 9.00.

Synthesis of *cis*-4-*tert*-butyl-3-[(3-*tert*-butyldimethylsiloxy)phenyl]-5-methyl-2-oxabicyclo[3.3.0]-oct-3-ene (6b): typical procedure. Phenol **6a** (869 mg, 3.19 mmol), imidazole (519 mg, 7.62 mmol) and *tert*-butyldimethylsilyl chloride (986 mg, 6.54 mmol) in dry DMF (10 mL) was stirred under nitrogen atmosphere at room temperature for 3 h. The reaction mixture was poured into sat. aq. NaCl and extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane–AcOEt (20:1) to give 1.231 g of **6b**.

6b: quantitative yield. colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 0.18 (s, 6H), 0.98 (s, 9H), 1.04 (s, 9H), 1.38 (s, 3H), 1.53-1.66 (m, 2H), 1.73-1.85 (m, 2H), 1.89-1.97 (m, 1H), 2.04-2.10 (m, 1H), 4.34 (dd, *J* = 6.0 and 3.2 Hz, 1H), 6.76-6.80 (m, 2H), 6.89 (d with fine coupling, *J* = 7.5 Hz, 1H), 7.17 (dd with fine coupling, *J* = 8.8 and 7.5 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C -4.4, 18.2, 24.5, 25.7, 28.4, 31.8, 32.5, 34.7, 41.6, 58.2, 92.8, 119.7, 121.7, 122.5, 123.0, 128.9, 137.3, 149.5, 155.2 ppm. IR (liquid film): $\tilde{\nu}$ 2954, 2930, 2860, 1654, 1596 cm^{-1}. Mass (*m/z*, %): 418 (M^+, 0.2), 361 (33), 235 (100), 195 (28). Mass (*m/z*, %): 387 (M^++1, 18), 386 (M^+, 53), 372 (34), 371 (100), 357 (14), 329 (12), 235 (15). HRMS (ESI) (*m/z*): 409.2531, calcd for $C_{24}H_{38}O_2SiNa$ [M + Na^+] 409.2539.

7b: 90% yield. colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 0.18 (s, 6H), 0.98 (s, 9H), 1.02 (s, 9H), 1.52-1.99 (m, 6H), 3.38-3.45 (m, 1H), 4.94 (ddd, *J* = 8.6, 4.7 and 2.2 Hz, 1H), 6.78 (ddd, *J* = 8.1, 2.4 and 1.1 Hz, 1H), 6.81 (s with fine coupling, 1H), 6.93 (ddd, *J* = 7.6, 1.5 and 1.1 Hz, 1H), 7.17 (dd with fine coupling, *J* = 8.1 and 7.6 Hz, 1H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C -4.4, 18.1, 23.9, 25.7, 30.8, 31.7, 34.3, 35.3, 50.9, 85.1, 119.9, 120.1, 121.6, 122.9, 128.8, 136.3, 148.9, 155.1 ppm. IR (liquid film): $\tilde{\nu}$ 2956, 2901, 2861, 1663, 1598 cm^{-1}. Mass (*m/z*, %): 372 (M^+, 25), 358 (31), 357 (100), 249 (7), 235 (20). HRMS (ESI) (*m/z*): 395.2379, calcd for $C_{23}H_{36}O_2SiNa$ [M + Na^+] 395.2382.

8b: 98% yield. colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 0.18 (s, 6H), 0.98 (s, 9H), 1.03 (s, 9H), 1.10 (s, 3H), 1.46-1.57 (m, 1H), 1.65-1.75 (m, 3H), 2.02-2.19 (m, 2H), 4.01 (dd, *J* = 12.0 and 8.1Hz, 1H), 6.77-6.79 (m, 2H), 6.91 (d with fine coupling, *J* = 7.6 Hz, 1H), 7.17 (dd with fine coupling, *J* = 8.8 and

7.6 Hz, 1H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C -4.3, 18.2, 18.6, 19.7, 25.5, 25.7, 29.2, 32.0, 32.3, 56.4, 91.6, 119.9, 121.6, 123.0, 128.7, 133.2, 136.8, 155.0, 155.2 ppm. IR (liquid film): $\tilde{\nu}$ 2958, 2930, 2898, 2859, 1588 cm^{-1}. Mass (*m/z*, %): 386 (M^+, 24), 371 (100), 315 (26), 235 (65). HRMS (ESI) (*m/z*): 409.2535, calcd for $C_{24}H_{38}O_2SiNa$ [M + Na^+] 409.2539.

Synthesis of *cis*-1-*transoid*-1,3-*cis*-3-(6-*tert*-butyl)-7-methyl-3-[3-(*tert*-butyldimethylsiloxy)phenyl]-2,4,5-trioxatricyclo[5.3.0.0^{3,6}]decane (3): typical procedure. A solution of **6b** (350 mg, 0.905 mmol) and TPP (1.2 mg) in CH_2Cl_2 (25 mL) was irradiated with Na lamp (940W) under O_2 atmosphere at 0 °C for 1.5 h. The photolysate was concentrated and chromatographed on silica gel with hexane–Et_2O (20:1) to give 367 mg of **3**.

3: 97% yield. colorless granules, mp 67.5–68.5 °C (from MeOH). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 0.18 (s, 6H), 0.97 (s, 9H), 0.98 (s, 9H), 1.12 (s, 3H), 1.53-1.64 (m, 1H), 1.90-2.18 (m, 5H), 4.91 (d, *J* = 5.4 Hz, 1H), 6.85 (ddd, *J* = 8.0, 2.4 and 1.0 Hz, 1H), 7.06 (s with fine coupling, 1H), 7.13 (br-d, *J* = 7.8 Hz, 1H), 7.23 (dd, *J* = 8.0 and 7.8 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C -4.4, 16.2, 18.2, 24.7, 25.7, 26.9, 27.1, 34.0, 36.9, 57.6, 90.6, 106.0, 115.6, 119.8, 121.0, 121.1, 128.9, 137.5, 155.4 ppm. IR (KBr): $\tilde{\nu}$ 2956, 2931, 2860, 1603, 1585 cm^{-1}. Mass (*m/z*, %): 418 (M^+, 3), 386 (M^+-32, 0.4), 361 (17), 235 (100). HRMS (ESI) (*m/z*): 441.2432, calcd for $C_{24}H_{38}O_4SiNa$ [M + Na^+] 441.2437. Anal. Calcd for $C_{24}H_{38}O_4Si$: C, 68.86; H, 9.15. Found: C, 68.59; H, 9.35.

4: 80% yield. pale yellow oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 0.18 (s, 3H), 0.18 (s, 3H), 0.95 (s, 9H), 0.98 (s, 9H), 1.67-1.87 (m, 3H), 1.94-2.03 (m, 1H), 2.07-2.22 (m, 2H), 2.64-2.70 (m, 1H), 5.42-5.45 (m, 1H), 6.85 (ddd, *J* = 8.0, 2.5 and 0.9 Hz, 1H), 7.07 (s with fine coupling, 1H), 7.13 (d with fine coupling, *J* = 7.8 Hz, 1H), 7.24 (dd, *J* = 8.0 and 7.8 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C -4.4, 18.2, 25.7, 25.8, 27.6, 29.7, 35.4, 53.9, 85.7, 106.5, 115.2, 119.7, 121.0, 121.1, 129.0, 136.8, 155.4 ppm. IR (liquid film): $\tilde{\nu}$ 2958, 2934, 2860, 1604, 1586 cm^{-1}. Mass (*m/z*, %): 404 (M^+, 17), 372 (M^+-32, 0.8), 347 (67), 235 (100). HRMS (ESI) (*m/z*): 427.2273, calcd for $C_{23}H_{36}O_4SiNa$ [M + Na^+] 427.2281.

5: 93% yield. pale yellow granules, mp 95.0–96.0 °C (from hexane–CH_2Cl_2). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 0.18 (s, 3H), 0.19 (s, 3H), 0.97 (s, 9H), 0.98 (s, 9H), 1.10 (s, 3H), 1.19-1.25 (m, 1H), 1.68-1.84 (m, 2H), 1.90-1.98 (m, 1H), 2.16-2.23 (m, 2H), 5.32 (dd, *J* = 12.8 and 7.1 Hz, 1H), 6.84-6.89 (m, 1H), 7.17 (s with fine coupling, 1H), 7.23-7.28 (m, 2H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C -4.4, -4.4, 16.1, 18.2, 19.4, 24.1, 24.3, 25.7, 26.8, 36.3, 54.8, 85.6, 104.2, 119.6, 120.9, 121.4, 122.3, 129.1, 136.9, 155.5 ppm. IR (KBr): $\tilde{\nu}$ 2957, 2932, 2897, 2861, 1604, 1586 cm^{-1}. Mass (m/z, %): 418 (M^+, 0.9), 386 (M^+-32, 0.2), 361 (38), 235 (100). HRMS (ESI) (*m/z*): 441.2440, calcd for $C_{24}H_{38}O_4SiNa$ [M + Na^+] 441.2437. Anal. Calcd for $C_{24}H_{38}O_4Si$: C, 68.86; H, 9.15. Found: C, 68.84; H, 9.34.

Thermolysis of tricyclic dioxetanes: typical procedure. Dioxetane **3** (53 mg) was stirred in *p*-xylene (2 mL) under N_2 atmosphere at 140 °C for 2 h. The reaction mixture was concentrated *in vacuo*. ^{1}H NMR spectral analysis showed that the residue included the desired keto ester exclusively. The residue was chromatographed on silica gel with hexane–AcOEt (10:1) to give 47.5 mg of *t*-methyl-*c*-2-pivaloylcyclopentyl *r*-3-(*tert*-butyldimethylsiloxy)benzoate (**24a**).

24a: 89% yield. colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 0.21 (s, 3H), 0.21 (s, 3H), 0.98 (s, 9H), 1.19 (s, 9H), 1.27 (s, 3H), 1.67-1.92 (m, 4H), 2.19-2.28 (m, 1H), 2.59-2.68 (m, 1H), 5.51 (d, *J* = 4.8 Hz, 1H), 7.01 (ddd, *J* = 8.0, 2.5 and 0.9 H, 1H), 7.26 (dd, *J* = 8.0 and 7.8 Hz, 1H), 7.39 (s with fine coupling, 1H), 7.52 (d with fine coupling, *J* = 7.8 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C -4.5, -4.5, 18.1, 19.6, 21.6, 25.6, 28.4, 30.8, 33.9, 45.1, 60.9, 82.6, 120.8, 122.5, 124.9, 129.4, 131.5, 155.7, 165.2, 215.6 cm^{-1}. IR (liquid. film): $\tilde{\nu}$ 2957, 2931, 2859, 1720, 1688, 1600 cm^{-1}. Mass (*m/z*, %): 418 (M^+, 3), 361 (16), 279 (6), 235 (100). HRMS (ESI) (*m/z*): 441.2432, calcd for $C_{24}H_{38}O_4SiNa$ [M + Na^+] 441.2437.

25a: 90% yield. colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 0.22 (s, 3H), 0.23 (s, 3H), 0.99 (s, 9H), 1.12 (s, 9H), 1.60-1.69 (m, 1H), 1.74-1.81 (m, 1H), 1.91-2.00 (m, 2H), 2.11-2.29 (m, 2H), 3.48 (ddd, *J* = 9.0, 7.9 and 6.3 Hz, 1H), 5.57 (ddd, *J* = 6.3, 5.7 and 3.0 Hz, 1H), 7.01 (ddd, *J* = 8.0, 2.5 and 0.9 Hz, 1H), 7.27 (dd, *J* = 8.0 and 7.8 Hz, 1H), 7.42 (s with fine coupling, 1H), 7.55 (d with fine coupling, *J* = 7.8 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C -4.5, -4.5, 18.2, 22.6, 25.6, 26.1, 28.2, 33.6, 44.7, 48.9, 77.5, 120.9, 122.6, 124.9, 129.4, 131.5, 155.6, 165.6, 213.3 ppm. IR (liquid film): $\tilde{\nu}$ 2957, 2931, 2860, 1719, 1601 cm^{-1}. Mass (*m/z*, %): 404 (M^+, 17), 347 (62), 235 (100). HRMS (ESI) (*m/z*): 427.2276, calcd for $C_{23}H_{36}O_4SiNa$ [M + Na^+] 427.2281.

26a: quantitative yield. colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 0.21 (s, 6H), 0.99 (s, 9H), 1.27 (s, 9H), 1.45 (s, 3H), 1.60-1.90 (m, 4H), 2.12-2.24 (m, 2H), 5.78 (t, *J* = 6.3 Hz, 1H), 7.02 (ddd, *J* = 8.0, 2.5 and 0.9 Hz, 1H), 7.28 (dd, *J* = 8.0 and 7.8 Hz, 1H), 7.48 (s with fine coupling, 1H), 7.61 (d with fine coupling, *J* = 7.8 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C -4.5, -4.4, 18.2, 19.0, 20.8, 25.6, 28.6, 30.1, 35.7, 45.4, 58.9, 79.0, 120.9, 122.5, 124.7, 129.3, 131.9, 155.7, 165.6, 216.0 ppm. IR (liquid film): $\tilde{\nu}$ 2957, 2931, 2859, 1721, 1685, 1601, 1585 cm^{-1}. Mass (*m/z*, %): 418 (M^+, 1), 362 (14), 361 (50), 279 (13), 235 (100). HRMS (ESI) (*m/z*): 441.2428, calcd for $C_{24}H_{38}O_4SiNa$ [M + Na^+] 441.2437.

Isolation of ketoester of 3-hydroxybenzoic acid from the spent reaction mixture after chemiluminescent decomposition of dioxetane 3: typical procedure. A solution of TBAF (1 M in THF, 0.70 mL) in dry DMSO (2.0 mL) was added to a solution of dioxetane **3** (56.0 mg, 0.134 mmol) in dry THF– DMSO (1:10, 3.3 mL) and stirred for 1 h at room temperature under N_2 atmosphere. The reaction mixture was poured into sat. aq. NH_4Cl and extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by

column chromatograpy on silica gel with hexane–AcOEt (4:1) to give 40.5 mg of *t*-2-methyl-*c*-2-pivaloylcyclopentyl *r*-3-hydroxybenzoate (**24b**).

24b: quantitative yield. colorless columns melted at 116.5–117.0 ºC (from AcOEt–hexane). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 1.19 (s, 9H), 1.29 (s, 3H), 1.65-1.94 (m, 4H), 2.20-2.31 (m, 1H), 2.58-2.72 (m, 1H), 5.51 (d, *J* = 5.0 Hz, 1H), 6.16 (s, 1H), 7.05 (ddd, *J* = 8.1, 2.6 and 0.9 Hz, 1H), 7.28 (dd, *J* = 8.1 and 7.7 Hz, 1H), 7.41 (s with fine coupling, 1H), 7.49 (d with fine coupling, *J* = 7.7 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C 19.5, 21.3, 28.4, 30.9, 33.9, 45.3, 61.0, 82.8, 116.2, 120.6, 121.5, 129.7, 131.1, 156.3, 165.6, 217.5 ppm. IR (KBr): $\tilde{\nu}$ 3456, 3081, 2988, 2968, 2882, 1694, 1602, 1481, 1457. Mass (m/z, %): 304 (M^+, 0.1), 247 (33), 122 (9), 121 (100), 57 (9). HRMS (ESI) (*m*/*z*): 327.1571, calcd for $C_{18}H_{24}O_4Na$ [M + Na^+] 327.1572. Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 70.89; H, 7.91.

25b: 86% yield. pale yellow granules, mp 94.5–96.0 °C (from AcOEt–hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 1.14 (s, 9H), 1.61-1.70 (m, 1H), 1.74-1.82 (m, 1H), 1.91-2.01 (m, 2H), 2.11-2.32 (m, 2H), 3.51 (ddd, *J* = 9.3, 7.9 and 6.2 Hz, 1H), 5.54-5.58 (m, 1H), 6.73 (s, 1H), 7.04 (ddd, *J* = 8.2, 2.6 and 1.0 Hz, 1H), 7.27 (dd, *J* = 8.2 and 7.6 Hz, 1H), 7.42 (dd, *J* = 2.6 and 1.6 Hz, 1H), 7.52 (d with fine coupling, *J* = 7.6 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C 22.7, 26.0, 28.2, 33.7, 44.9, 49.2, 77.7, 116.2, 120.4, 121.5, 129.6, 131.1, 156.2, 165.8, 215.4 ppm. IR (KBr): $\tilde{\nu}$ 3183, 2971, 2873, 1699, 1587 cm^{-1}. Mass (*m/z*, %): 290 (M^+, 2), 233 (31), 138 (6), 121 (100). HRMS (ESI) (*m*/*z*): 313.1419, calcd for $C_{17}H_{22}O_4Na$ [M + Na^+] 313.1416.

26b: quantitative yield. colorless oil, ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 1.26 (s, 9H), 1.44 (s, 3H), 1.62-1.90 (m, 4H), 2.12-2.24 (m, 2H), 5.78 (t, *J* = 6.5 Hz, 1H), 5.93 (br-s, 1H), 7.05 (ddd, *J* = 8.1, 2.6 and 0.9 Hz, 1H), 7.29 (dd, *J* = 8.1 and 7.7 Hz, 1H), 7.52 (s with fine coupling, 1H), 7.56 (d with fine coupling, *J* = 7.7 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C 19.1, 20.8, 28.6, 30.0, 35.6, 45.4, 58.9, 79.2, 116.3, 120.1, 121.8, 129.6, 131.9, 155.8, 165.8, 216.4 ppm. IR (KBr): $\tilde{\nu}$ 3408, 2971, 2877, 1717, 1686, 1601 cm^{-1}. Mass (*m/z*, %): 304 (M^+, trace), 247 (41), 121 (100). HRMS (ESI) (*m*/*z*): 327.1584, calcd for $C_{18}H_{24}O_4Na$ [M + Na^+] 327.1572.

Chemiluminescence measurement: general procedure. Chemiluminescence was measured by using a JASCO FP-750, FP-6500 spectrometer and/or Hamamatsu Photonics PMA-11 multi-channel detector. Freshly prepared solution (2 mL) of TBAF (1.0 x 10^{-2} mol dm^{-3}) in DMSO (or MeCN) was transferred to a quartz cell (10 x 10 x 50 mm) and the latter placed in the spectrometer, which was thermostated with stirring at 25 °C. After 3-5 min, a solution (1 mL) of the dioxetane (1.0 x 10^{-5} mol dm^{-3} or 1.0 x 10^{-6} mol dm^{-3}) in DMSO (or MeCN), 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 adamantylidene dioxetane **1b**, whose chemiluminescent efficiency Φ^{CL} has been reported to be 0.29 and was used here as a standard.[10]

X-Ray Single Crystallographic Analysis. X-Ray diffraction data were collected on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71070 Å) radiation. Data were processed using CrystalClear.*1 The structures were solved by direct method (SIR92)*2 and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 5379 observed reflections and 300 variable parameters (for **compound 5**). All calculations were performed using the CrystalStructure crystallographicsoftware package.*3,4

Crystal data for **5**: $C_{24}H_{38}O_4Si$, (M_r = 418.65), colorless platelet, 0.50 x 0.50 x 0.20 mm, triclinic, space group *P*-1 (#2), *a* = 10.000(9) Å, *b* = 11.334(5) Å, *c* = 12.6982(4) Å, α = 64.46(12) °, β = 69.80(13)°, γ = 78.20(2) °, *V* = 1216.0(12) Å ^{3}, *Z* = 2, ρ_{calcd} = 1.143 g cm^{-3}, *T* = 173 K, *F*(000) = 456.00, reflections collected/unique 25846 / 5380 (R_{int} = 0.024), μ(MoKα) = 1.215 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.859 - 0.976. The data were corrected for Lorentz and polarization effects. *R*1 = 0.0673 [$I > 2\sigma(I)$], *wR*2 = 0.1806 (all data), GOF on F^2 = 1.792, and residual electron density 0.76 / -0.34 e$^-$Å $^{-3}$. Crystallographic data for the structural analysis of compound **5** has been deposited at the Cambridge Crystallographic Data Center, CCDC-265173. Free Copies of the data can be obtained, via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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