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SYNTHESIS OF BICYCLIC DIOXETANES BEARING A 4-(BENZIMIDAZOL-2-YL)-3-HYDROXYPHENYL GROUP AND THEIR BASE-INDUCED CHEMILUMINESCENT DECOMPOSITION IN AN APROTIC MEDIUM AND IN AN AQUEOUS MEDIUM

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Abstract – Bicyclic dioxetane, 5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane, bearing a 4-(benzimidazol-2-yl)-3-hydroxyphenyl group at the 1-position and its *N*-substituted benzimidazolyl-analogs were synthesized. *N*-Methylbenzimidazolyl-analog and *N*-phenylbenzimidazolyl-analog were found to undergo charge-transfer-induced decomposition (CTID) to effectively give light in both TBAF/MeCN and in NaOH/H_2O. The CTID of *N*-(4-carboxybutyl)benzimidazolyl-analog gave also effectively light both in MeCN and in H_2O. On the other hand, chemiluminescent CTID of the unsubstituted benzimidazolyl-analog changed depending on the base used: TBAF/MeCN induced weak emission of yellow light due to a dianion of the dioxetane, while TMG(tetramethylguanidine)/MeCN induced strong emission of blue light due to a monoanion of the dioxetane.

INTRODUCTION

Upon treatment with a base, a hydroxyphenyl-substituted dioxetane is deprotonated to give an unstable oxidophenyl-substituted dioxetane which rapidly decomposes with an accompanying emission of light by intramolecular charge-transfer-induced decomposition (CTID) mechanism. This phenomenon has received considerable attention from the viewpoints of application to clinical and biological analysis as well as of mechanistic interest related to bioluminescence and chemiluminescence.[1–7] One of such CTID-active dioxetanes is bicyclic compound **1** bearing a 4-(benzothiazol-2-yl)-3-hydroxyphenyl group, which effectively emits light in an aqueous system as well as in an aprotic polar solvent.[8] Furthermore,

dioxetane **1** has very recently been found to undergo solvent-promoted decomposition, which is an entropy-controlled reaction leading to effective chemiluminescence.[9]

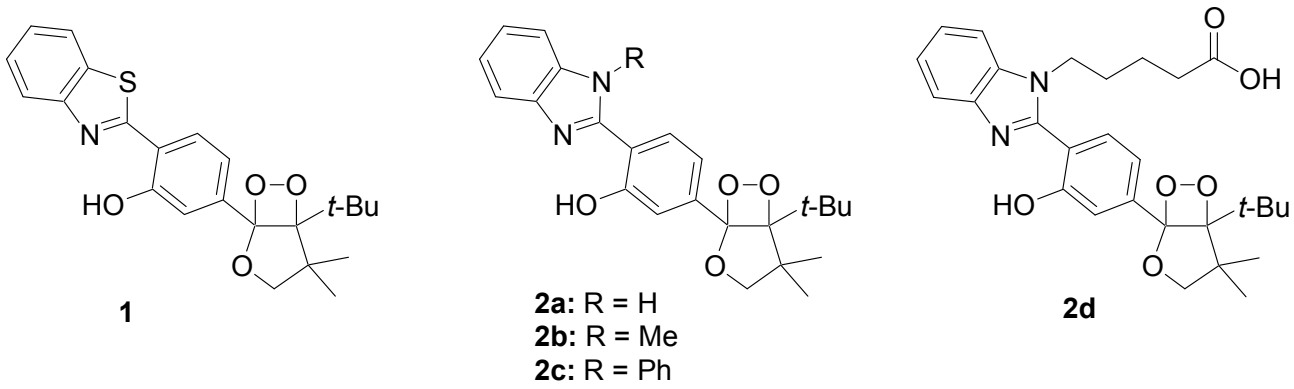


Figure 1. Dioxetanes bearing a 3-hydroxyphenyl group substituted with a 4-(benzothizol-2-yl) **1** or 4-(benzimidazol-2-yl) group **2a**–**d**

These facts prompted us to realize bicyclic dioxetanes **2** bearing a 4-(benzimidazol-2-yl)-3-hydroxyphenyl group with expectation that the skeleton of **2** could be developed to novel chemiluminescence substrates bearing various auxiliaries, since a saturated nitrogen of benzimidazolyl group could be easily functionalized or tethered, differently from benzothiazolyl or benzoxazolyl group. Thus, we basically investigated here whether or not dioxetanes **2** showed effective chemiluminescence in an aqueous medium as well as in an aprotic medium. Dioxetanes investigated here were parent **2a** bearing a 4-(benzimidazol-2-yl)-3-hydroxyphenyl group and its *N*-methylbenzimidazolyl- **2b**, *N*-phenylbenzimidazolyl- **2c** and *N*-(4-carboxybutyl)benzimidazolyl-analog **2d** (Figure 1).

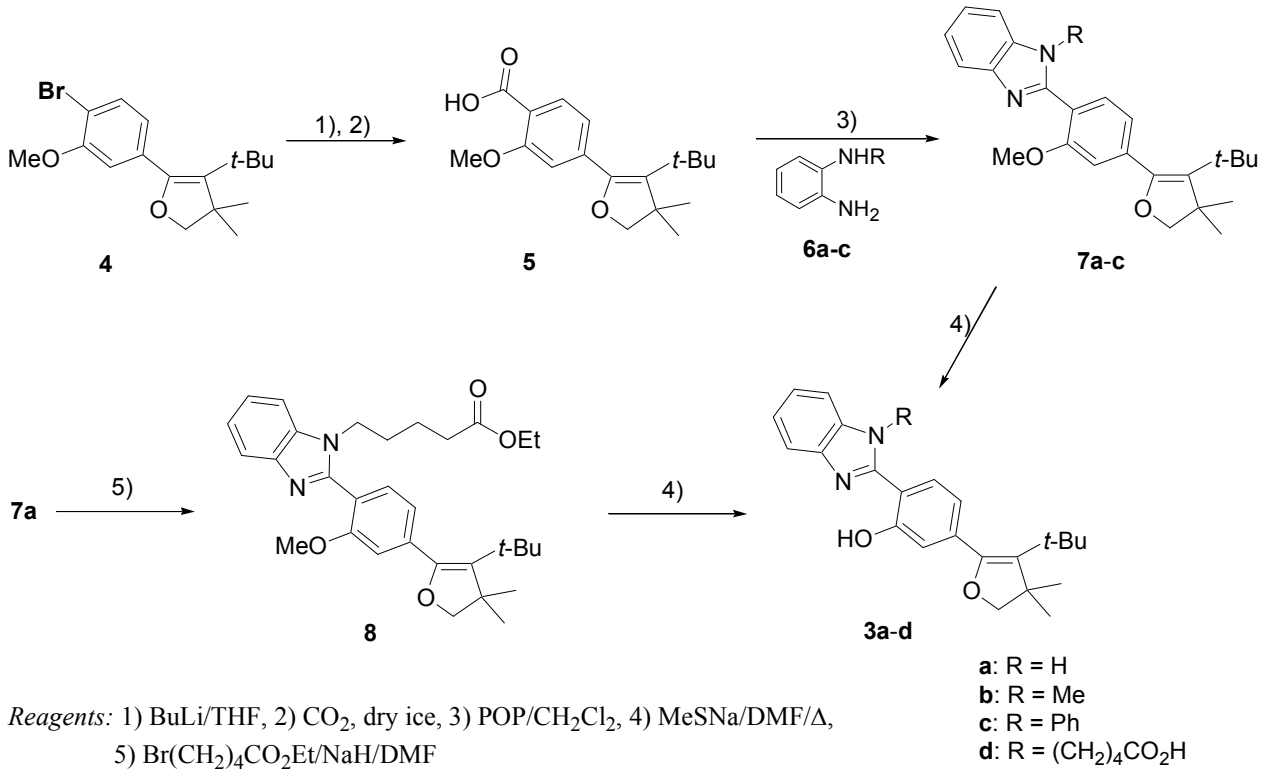
RESULTS AND DISCUSSION

Synthesis of bicyclic dioxetanes bearing a 4-(benzimidazol-2-yl)-3-hydroxyphenyl group

All of the dioxetanes **2a**–**d** investigated here were prepared by singlet oxygenation of the corresponding 5-[4-(benzimidazol-2-yl)-3-hydroxyphenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofurans **3a**–**d**. These precursors were synthesized through several steps starting from 4-*tert*-butyl-5-(4-carboxy-3-methoxyphenyl)-3,3-dimethyl-2,3-dihydrofuran (**5**), which was synthesized from 5-(4-bromo-3-methoxyphenyl)-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**4**),[10] as illustrated in Scheme 1.

The initial step was condensation of carboxylic acid **5** with benzene-1,2-diamines **6a**–**c**, which smoothly proceeded by using triphenylphosphonium anhydride trifluoromethanesulfonate (POP)[11] in CH_2Cl_2 at room temperature to give the corresponding benzimidazoles **7a**–**c**. Nucleophilic substitution of benzimidazole **7a** with ethyl 5-bromopentanoate gave ester **8**. These 4-benzimidazolyl-3-methoxyphenyl-substituted dihydrofurans **7a**–**c** and **8** were demethylated effectively with sodium methylthiolate to give the desired precursors **3a**–**d**: for the case of **8**, saponification of the ester function

also proceeded. All of dihydrofurans **3a**−**d** were individually irradiated with Na-lamp in the presence of catalytic amount of tetraphenylporphin (TPP) in acetone or CH_2Cl_2 under O_2 atmosphere at 0 ºC to selectively give the corresponding dioxetanes **2a**−**d**. The structures of dioxetanes **2a**−**d** were determined by ^{1}H NMR, ^{13}C NMR, IR, MS and HRMass spectral analyses.



Reagents: 1) BuLi/THF, 2) CO_2, dry ice, 3) POP/CH_2Cl_2, 4) MeSNa/DMF/Δ, 5) $Br(CH_2)_4CO_2Et$/NaH/DMF

Scheme 1. Synthetic pathway of dihydrofurans **3a**−**d** bearing a 4-(benzimidazol-2-yl)-3-hydroxyphenyl group

Base-induced chemiluminescent decomposition of dioxetanes bearing a 4-(benzimidazol-2-yl)-3-hydroxyphenyl group

When a solution of dioxetane **2a** in MeCN was added to a solution of tetrabutylammonium fluoride (TBAF, large excess) in MeCN at 45 ºC, **2a** decomposed according to the pseudo-first order kinetics independent of the TBAF concentration to emit yellow light, the spectrum of which is shown in Figure 2(A). The chemiluminescence properties of **2a** were as follows: maximum wavelength λ_{max}^{CL} = 510 nm, chemiluminescence efficiency Φ^{CL} = 0.065,[12,13] rate of CTID k^{CTID} = 4.6 x 10^{-3} s^{-1}, and half-life $t_{1/2}^{CTID}$ = 150 s (Table 1). On similar treatment with TBAF, **2b** and **2c** showed bright chemiluminescence, the properties of which are shown in Table 1 (Figure 2(A)). We can see from Table 1 that **2b** and **2c** emitted light as effectively as benzothiazolyl-analog **1**, while, in contrast, parent **2a** gave light in poor yield, and the λ_{max}^{CL} was considerably longer for **2a** than those for **2b** and **2c**.

Next, we carried out CTID of dioxetanes **2a**–**c** in an aqueous system. When dioxetanes **2a**–**c** were individually treated with 0.1 M NaOH aqueous solution at 45 ºC, they decomposed with the accompanying chemiluminescence. Their chemiluminescence properties and spectra are summarized in Table 1 and Figure 2(B), respectively. Table 1 shows that all of three dioxetanes **2a**–**c** emitted light in high yields, which were >1000 times higher than that for simple bicyclic dioxetane, 5-*tert*-butyl-1-(3-hydroxyphenyl)-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (**9**),[14] though they were somewhat lower than that for **1**. If we compare here features of CTID for **2a**–**c** in a NaOH/H_2O system to those in a TBAF/MeCN, we can see that only parent dioxetane **2a** showed the noticeable differences in λ_{max}^{CL} and in Φ^{CL} between these two systems. The λ_{max}^{CL} for **2a** was 33 nm shorter in an aqueous system than in an MeCN system, though those for **2b** and **2c** were not so much different between in these two systems. Chemiluminescence efficiency for **2a** was unexpectedly higher in the aqueous system than in the MeCN system, while those for **2b** and **2c** somewhat decreased in an aqueous system. Notably, **2a** was the first example that a CTID-active dioxetane emitted light more effectively in an aqueous system than in an aprotic polar solvent system.

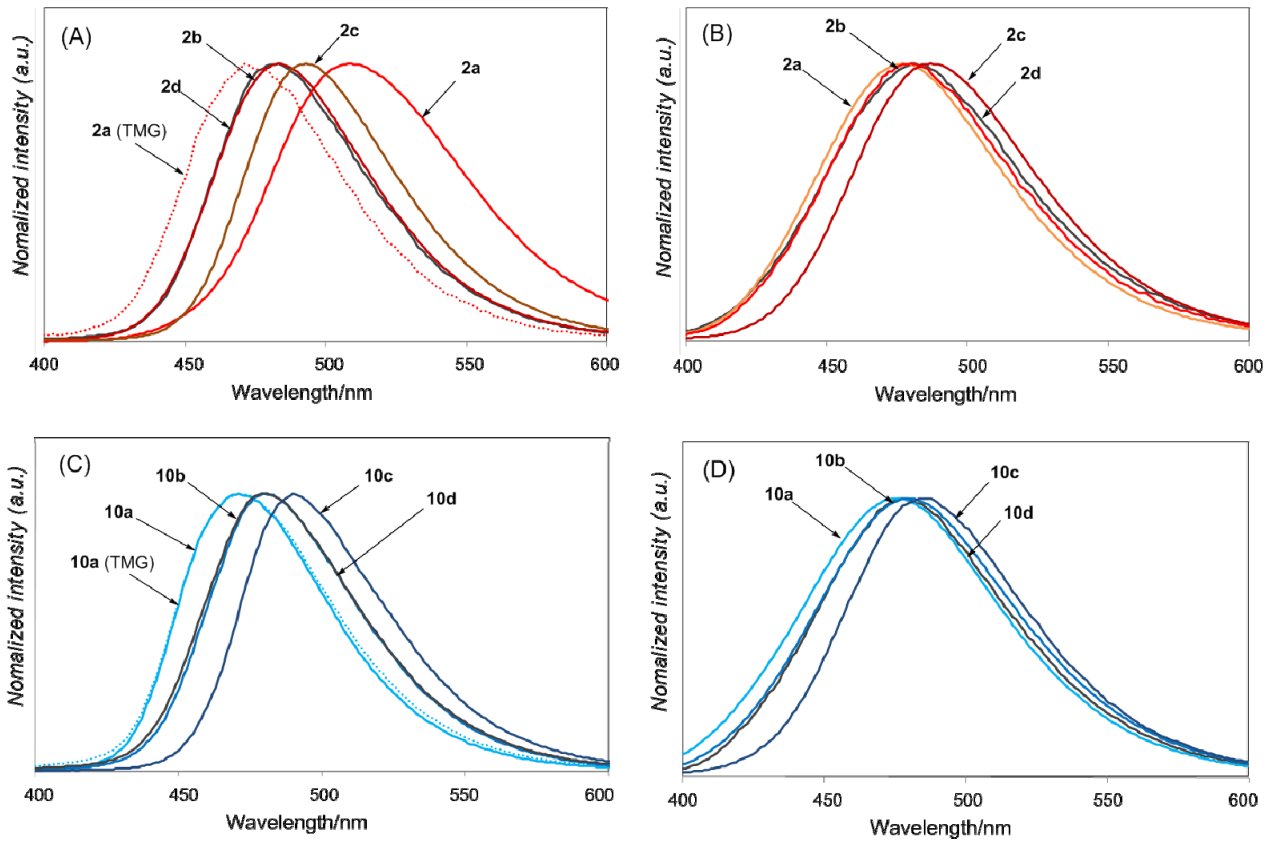
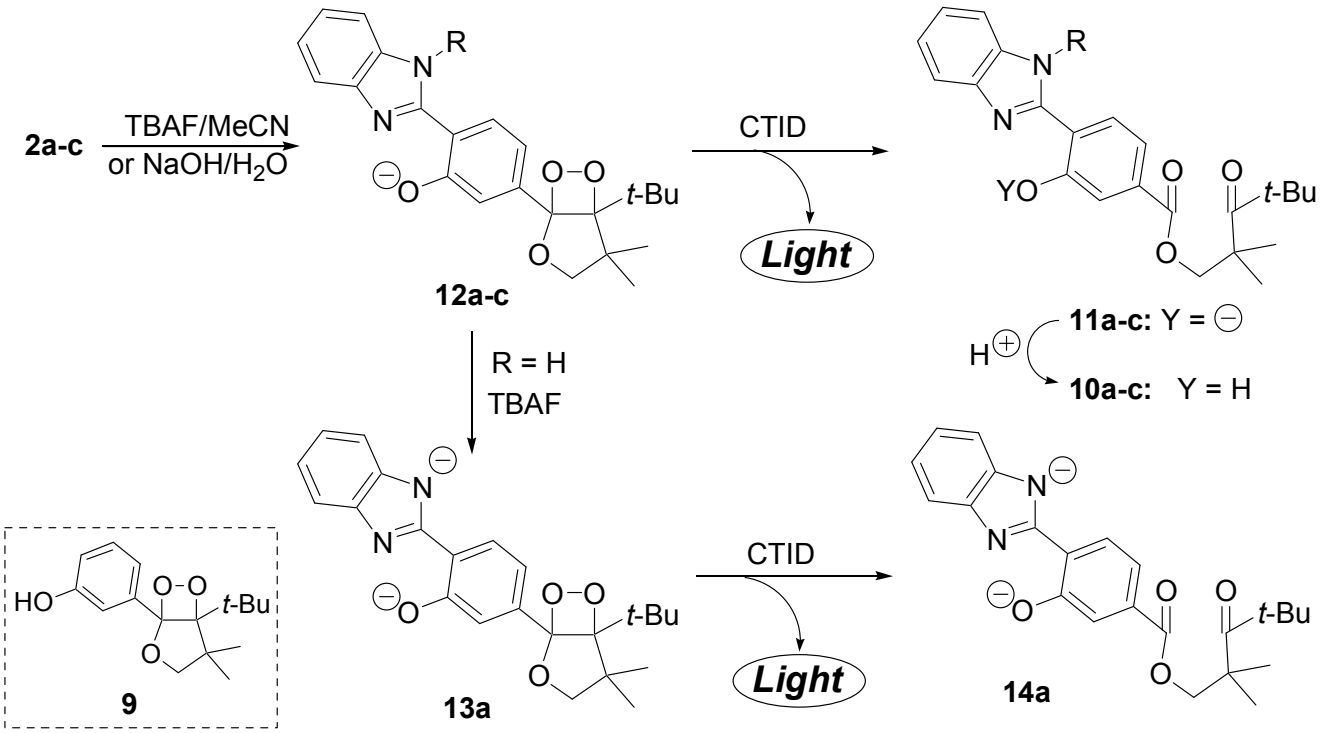


Figure 2. Chemiluminescence spectra of dioxetanes **2a**–**d** in TBAF/MeCN (A) and in NaOH/H_2O (B) and fluorescence spectra of keto esters **10a**–**d** in TBAF/MeCN (C) and in NaOH/H_2O (D)

The freshly spent reaction mixture for **2a**–**c** in both base systems effectively gave the corresponding keto

ester **10a**–**c** after careful neutralization. Authentic oxido anions **11a**–**c** generated by dissolving **10a**–**c** in NaOH/H_2O gave fluorescences, the spectra of which coincided with the corresponding chemiluminescence spectra of **2a**–**c** (Figure 2(D)). The results suggest that **11a**–**c** were undoubtedly emitters for CTID of the corresponding dioxetanes **2a**–**c** in a NaOH/H_2O system (Scheme 2). On the other hand, in a TBAF/MeCN system, fluorescence spectrum of **11a** generated from **10a** did not coincide with chemiluminescence spectrum from **2a**, though fluorescence spectra of authentic **11b** and **11c** coincided with the corresponding chemiluminescence spectra of **2b** and **2c** (Figure 2(C)).



Scheme 2. Base-Induced decomposition of dioxetanes **2a**–**c**

We carried out several experiments to understand the discrepancy between fluorescence spectrum of **11a** and chemiluminescence spectrum of **2a** in a TBAF/MeCN. Prominent difference in the structure between **2a** and **2b** or **2c** was that only benzimidazolyl group in **2a** possesses a weakly acidic NH. This structural difference suggested that **2a** would decompose in different manner depending on a base system. Thus, we attempted to use tetramethylguanidine (TMG, p*K*a = 13.6) as a base far weaker than TBAF (p*K*a >> 15) though strong enough for CTID of **2a** in MeCN. When a solution of **2a** in MeCN was added to a solution of MeCN including a large excess of TMG instead of TBAF at 45 °C, **2a** showed chemiluminescence with λ_{max}^{CL} = 471 nm, Φ^{CL} = 0.22, k^{CTID} = 1.9 x 10^{-4} and $t_{1/2}$ = 3700 s.

This λ_{max}^{CL} was 39 nm shorter than that in a TBAF/MeCN, and coincided with λ_{max}^{fl} of fluorescence from

authentic **11a** in TBAF/MeCN as well as in TMG/MeCN (Figure 2(C)). We can understand from Table 1 that Φ^{CL} of **2a** in a TMG/MeCN system increased more than 3 times from that in a TBAF/MeCN system, and was same as that for **2b** in a TBAF/MeCN. These results suggested that a strong base TBAF produced dianion **14a** of keto ester in the excited state through dianion **13a** of dioxetane **2a**, whereas TMG could abstract only a phenolic proton of **2a** to produce monoanion of dioxetane **12a** which decomposed into monoanion **11a** in the excited state (Scheme 2).

Table 1. Base-induced chemiluminescent decomposition of bicyclic dioxetanes **2a**−**2d** bearing a 4-(benzimidazol-2-yl)-3-hydroxyphenyl moiety in TBAF/MeCN and in NaOH/H_2O[a)]

Dioxetane	TBAF/MeCN			$NaOH/H_2O$		
	λ_{max}^{CL} / nm	Φ^{CL} [b)]	$t_{1/2}$ / s	λ_{max}^{CL} / nm	Φ^{CL} [b)]	$t_{1/2}$ / s
2a	510	0.065	150	477	0.070	246
2b	483	0.22	90	480	0.024	361
2c	492	0.23	36	485	0.086	164
2d	483	0.20	63	483	0.017	396
1	492	0.28	1600	492	0.12	280
9[c)]	467	0.11	25	467	1.1×10^{-5}	810
2a[d)]	471	0.22	3700	-----	-----	-----

a) Reactions were carried out at 45 °C. b) Chemiluminescence efficiencies were based on the reported value for 3-(3-*tert*-butyldimethylsiloxyphenyl)-3-methoxy-4-(2'-spiroadamantane)-1,2-dioxetane (Φ^{CL} = 0.29).[13] c) ref. 14 d) TMG was used as a base instead of TBAF.

As described above, dioxetane **2b** bearing a 3-hydroxy-4-(*N*-methylbenzimidazol-2-yl)phenyl group underwent CTID to effectively give light in both TBAF/MeCN and $NaOH/H_2O$ systems. Thus, we investigated whether or not the substitution with *ω*-functionalized alkyl group instead of *N*-methyl in **2b** could keep up chemiluminescence properties, especially high Φ^{CL}, for base-induced decomposition. As a representative of *ω*-functionalized alkyl group, we selected 4-carboxybutyl group, which could tether various auxiliaries or pendants (Figure 1). Dioxetane bearing an 4-[*N*-(4-carboxybutyl)-benzimidazol-2-yl]-3-hydroxyphenyl group **2d** decomposed to effectively emit light in both TBAF/MeCN and $NaOH/H_2O$ systems (Figure 2). The results summarized in Table 1 show that chemiluminescence properties for **2d** were practically similar to those for **2b**.

CONCLUSION

Bicyclic dioxetane bearing a 4-(benzimidazol-2-yl)-3-hydroxyphenyl group **2a** and its *N*-substituted benzimidazolyl-analogs **2b**−**2d** were synthesized. *N*-Methylbenzimidazolyl-analog **2b** and *N*-phenylbenzimidazolyl-analog **2c** were found to undergo CTID to effectively give light in both

TBAF/MeCN and in NaOH/H_2O. On the other hand, Φ^{CL}, $\lambda_{max}{}^{CL}$ and k^{CTID} for CTID of unsubstituted benzimidazolyl-analog **2a** changed depending on the base used: especially Φ^{CL} in TBAF/MeCN system was quite low and was only <1/3 of Φ^{CL} in TMG/MeCN system. CTID of *N*-(4-carboxybutyl)-benzimidazolyl-analog **2d** gave also effectively light both in MeCN and in H_2O. The results presented here show that design of new CTID-dioxetanes tethering various auxiliaries through an *N*-spacer can become possible.

EXPERIMENTAL

General

Melting points were uncorrected. IR spectra were taken on a FT/IR infrared spectrometer. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz and 500 MHz spectrometers. Mass spectra were obtained by using a double-focusing mass spectrometer and an ESI-TOF mass spectrometer. Column chromatography was carried out using SiO_2.

Synthesis of 5-(4-carboxy-3-methoxyphenyl)-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (5): BuLi (4.30 mL, 1.62 M in hexane, 6.97 mmol) was added to a solution of 5-(4-bromo-3-methoxyphenyl)-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**4**) (2.22 g, 6.56 mmol) in dry THF (20 mL) under a nitrogen atmosphere at -78 °C. After stirring for 30 min, dry ice was added to the solution and the reaction mixture was warmed slowly to room temperature. The reaction mixture was poured into 1 M HCl and extracted with AcOEt. The organic layer was washed twice with sat. aq. NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel and eluted with AcOEt−hexane (1:9~1:1) to give **5** (1.73 g, 5.69 mmol, 87%). **5**: colorless needles, mp 103.0−10.4.0 °C (from AcOEt−hexane). ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.07 (s, 9H), 1.35 (s, 6H), 3.90 (s, 2H), 4.09 (s, 3H), 6.98 (d, J = 1.1 Hz, 1H), 7.11 (dd, J = 7.9 and 1.1 Hz, 1H), 8.15 (d, J = 7.9 Hz, 1H), 10.60 (br s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.3, 32.5, 32.5, 47.4, 56.8, 83.4, 113.2, 117.1, 124.1, 127.2, 133.4, 143.4, 148.0, 157.5, 165.0 ppm. IR (KBr): 3448, 2956, 1687, 1604, 1561 cm^{-1}. Mass (m/z, %): 304 (M^+, 22), 289 (100), 245 (22), 215 (30), 179 (29), 52 (21). HRMS (ESI): 327.1554 calcd for $C_{18}H_{24}O_4Na$ [M+Na^+] 327.1572.

Synthesis of 5-[4-(benzimidazol-2-yl)-3-methoxyphenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (7a): Typical procedure. Triphenylphosphonium anhydride trifluoromethanesulfonate (POP) was prepared by adding trifluoromethanesulfonic anhydride (2.19 mL, 13.0 mmol) to a solution of triphenylphosphine oxide (7.26 g, 26.1 mmol) in dry CH_2Cl_2 (15 mL) under a nitrogen atmosphere at room temperature and stirring for 20 min. To the POP solution, 5-(4-carboxy-3-methoxyphenyl)-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**5**) (1.00 g, 3.29 mmol) and 1,2-phenylenediamine (353 mg, 3.26 mmol) in dry CH_2Cl_2 (10 mL) were added and stirred at room temperature over night. The reaction mixture was poured into sat. aq. $NaHCO_3$ and extracted with AcOEt. The organic layer was washed twice

with sat. aq. NaCl, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with AcOEt−hexane (1:2) to give **7a** (753 mg, 2.00 mmol, 62%) as a pale yellow solid. **7a**: colorless needles, mp 233.5−234.0 °C (from AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.09 (s, 9H), 1.36 (s, 6H), 3.92 (s, 2H), 4.11 (s, 3H), 7.01 (s with fine coupling, 1H), 7.12 (d with fine coupling, J = 7.9 Hz, 1H), 7.23−7.30 (m, 2H), 7.42−7.58 (m, 1H), 7.72−7.90 (m, 1H), 8.56 (d, J = 7.9 Hz, 1H), 10.60 (br s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 27.3, 32.3, 32.5, 47.0, 56.1, 82.5, 112.2, 113.4, 118.1, 118.7, 121.8, 122.4, 122.8, 125.8, 129.5, 134.9, 139.0, 142.9, 148.7, 149.1, 156.3 ppm. IR (KBr): 3435, 3056, 2962, 2870, 1646, 1611, 1570 cm^{-1}. Mass (m/z, %): 377 (M^++1, 13), 376 (M^+, 43), 362 (28), 361 (100), 305 (30), 251 (13). HRMS (ESI): 377.2206 calcd for $C_{24}H_{29}N_2O_2$ [M+H$^+$] 377.2229. Anal. Calcd for $C_{24}H_{28}N_2O_2$: C, 76.56; H, 7.50; N, 7.44. Found: C, 76.32; H, 7.69; N, 7.42.

4-*tert*-Butyl-5-[3-methoxy-4-(*N*-methylbenzimidazol-2-yl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (7b): 79% yield. Colorless plates, mp 158.0–158.5 °C (from CH_2Cl_2–hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.10 (s, 9H), 1.37 (s, 6H), 3.64 (s, 3H), 3.83 (s, 3H), 3.93 (s, 2H), 6.96 (d, J = 1.2 Hz, 1H), 7.07 (dd, J = 7.6 and 1.2 Hz, 1H), 7.26−7.35 (m, 2H), 7.38−7.41 (m, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.80−7.83 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.3, 30.8, 32.4, 32.5, 47.3, 55.6, 83.2, 109.3, 112.5, 119.4, 119.7, 121.9, 122.4, 122.7, 126.4, 131.8, 136.0, 139.6, 143.1, 149.1, 151.7, 157.0 ppm. IR (KBr): 3049, 2958, 2871, 1655, 1609, 1563 cm^{-1}. Mass (m/z, %): 391 (M^++1, 16), 390 (M^+, 53), 376 (29), 375 (100), 319 (35), 265 (8). HRMS (ESI) : 391.2401 calcd for $C_{25}H_{31}N_2O_2$ [M+H$^+$] 391.2386. Anal. Calcd for $C_{25}H_{30}N_2O_2$: C, 76.89; H, 7.74; N, 7.17. Found: C, 76.98; H, 7.93; N, 7.19.

4-*tert*-Butyl-5-[3-methoxy-4-(*N*-phenylbenzimidazol-2-yl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (7c): 56% yield. Colorless amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.33 (s, 6H), 3.33 (s, 3H), 3.89 (s, 2H), 6.66 (d, J = 1.2 Hz, 1H), 7.01 (dd, J = 7.6 and 1.2 Hz, 1H), 7.20−7.40 (m, 8H), 7.63 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.3, 32.4, 32.4, 47.2, 54.7, 83.2, 110.2, 112.4, 119.7, 119.9, 122.5, 123.1, 125.8, 126.3, 127,5, 129.0, 131.6, 136.0, 137.1, 139.3, 143.1, 149.1, 150.9, 156.4 ppm. IR (KBr): 3057, 2956, 2865, 1652, 1604, 1565, 1499 cm^{-1}. Mass (m/z, %): 453 (M^++1, 24), 452 (M^+, 70), 438 (34), 437 (100), 381 (29), 327 (13), 298 (12). HRMS (ESI): 453.2520 calcd for $C_{30}H_{33}N_2O_2$ [M+H$^+$] 453.2542.

Synthesis of 4-*tert*-butyl-5-{4-[*N*-(4-ethoxycarbonylbutyl)benzimidazol-2-yl]-3-methoxyphenyl}-3,3-dimethyl-2,3-dihydrofuran (8): 4-*tert*-Butyl-5-[4-(benzimidazol-2-yl)-3-methoxyphenyl]-3,3-dimethyl-2,3-dihydrofuran (**7a**) (500 mg, 1.33 mmol) was added to a suspension of NaH (60% in oil, 70.2 mg, 1.76 mmol) in dry DMF (10 mL) under a nitrogen atmosphere at room temperature. After stirring for 30 min, ethyl 5-bromopentanoate (0.32 mL, 2.0 mmol) was added to the solution at room temperature and stirred for 2 days. The reaction mixture was poured into sat. aq. NH_4Cl and extracted with AcOEt. The organic layer was washed twice with sat. aq. NaCl, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with AcOEt−hexane (1:1) to give **8**

(666 mg, 1.32 mmol, 99%). **8:** Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.09 (s, 9H), 1.21 (t, J = 7.1 Hz, 3H), 1.37 (s, 6H), 1.42−1.52 (m, 2H), 1.69−1.79 (m, 2H), 2.16 (t, J = 7.3 Hz, 2H), 3.81 (s, 3H), 3.93 (s, 2H), 4.01−4.11 (m, 4H), 6.96 (s, 1H), 7.06 (dd, J = 7.6 and 1.2 Hz, 1H), 7.23−7.33 (m, 2H), 7.38−7.43 (m, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.78−7.84 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 14.1, 22.0, 27.3, 28.7, 32.4, 32.5, 33.6, 44.1, 47.3, 55.6, 60.3, 83.2, 109.8, 112.6, 119.7, 120.0, 121.9, 122.4, 122.7, 126.5, 131.7, 135.0, 139.5, 143.3, 149.0, 151.2, 156.9, 172.8 ppm. IR (liquid film): 3055, 2957, 2868, 1732, 1651, 1609, 1563 cm^{-1}. Mass (m/z, %): 505 (M^++1, 23), 504 (M^+, 60), 490 (37), 489 (100), 459 (11). HRMS (ESI): 505.3039 calcd for $C_{31}H_{41}N_2O_4$ [M+H$^+$] 505.3066.

Synthesis of 5-[4-(benzimidazol-2-yl)-4-*tert*-butyl-3-hydroxyphenyl]-3,3-dimethyl-2,3-dihydrofuran (3a): Typical procedure. MeSNa (95%, 120 mg, 1.63 mmol) was added to a solution of **7a** (210 mg, 0.56 mmol) in dry DMF (5 mL) under a nitrogen atmosphere at room temperature and stirred for 30 min at 140 °C. The reaction mixture was poured into 1 M aq. HCl and sat. aq. NaCl, and extracted with AcOEt. The organic layer was washed twice with sat. aq. NaCl, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with AcOEt−hexane (1:4) to give **3a** (200 mg, 0.552 mmol, 99%) as a pale yellow solid. **3a**: Colorless needles, mp 284.5−285.0 °C (from AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.09 (s, 9H), 1.35 (s, 6H), 3.90 (s, 2H), 6.91 (dd, J = 8.0 and 1.5 Hz, 1H), 7.08 (d, J = 1.5 Hz, 1H), 7.28−7.34 (m, 2H), 7.46−7.53 (m, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.71−7.78 (m, 1H), 9.45 (br s, 1H), 13.09 (br s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 27.2, 32.3, 32.4, 47.0, 82.5, 111.7 (br), 112.6, 118.1 (br), 118.5, 121.0, 122.7 (br), 123.4 (br), 125.6, 126.0, 133.4 (br), 139.5, 141.1 (br), 149.0, 151.5, 157.5 ppm. IR (KBr): 3302, 2958, 2868, 2630, 1630, 1580 cm^{-1}. Mass (m/z, %): 363 (M^++1, 11), 362 (M^+, 39), 348 (27), 347 (100), 291 (38). HRMS (ESI): 363.2043 calcd for $C_{23}H_{27}N_2O_2$ [M+H$^+$] 363.2073. Anal. Calcd for $C_{23}H_{26}N_2O_2$: C, 76.21; H, 7.23; N, 7.73. Found: C, 76.47; H, 7.43; N, 7.72.

4-*tert*-Butyl-5-[3-hydroxy-4-(*N*-methylbenzimidazol-2-yl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (3b): 97% yield. Colorless columns, mp 136.0−137.0 °C (from AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.11 (s, 9H), 1.35 (s, 6H), 3.90 (s, 2H), 4.07 (s, 3H), 6.93 (dd, J = 8.1 and 1.7 Hz, 1H), 7.13 (d, J = 1.7, 1H), 7.31−7.39 (m, 2H), 7.41−7.44 (m, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.75−7.78 (m, 1H), 12.92 (br s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.3, 32.5, 32.5, 33.0, 47.3, 83.2, 109.5, 112.7, 118.8, 119.6, 120.2, 123.0, 123.3, 126.1, 126.5, 135.6, 139.6, 140.3, 149.0, 151.4, 158.6 ppm. IR (KBr): 3417, 2956, 2867, 1624, 1566, 1466 cm^{-1}. Mass (m/z, %): 377 (M^++1, 14), 376 (M^+, 48), 362 (28), 361 (100), 305 (40). HRMS (ESI): 377.2212 calcd for $C_{24}H_{29}N_2O_2$ [M+H$^+$] 377.2229 Anal. Calcd for $C_{24}H_{28}N_2O_2$: C, 76.56; H, 7.50; N, 7.44. Found: C, 76.52; H, 7.68; N, 7.46.

4-*tert*-Butyl-5-[3-hydroxy-4-(*N*-phenylbenzimidazol-2-yl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (3c): 82% yield. Pale yellow plates, mp 180.5-181.5 °C (from CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.05 (s, 9H), 1.30 (s, 6H), 3.83 (s, 2H), 6.49 (dd, J = 8.3 and 1.7 Hz, 1H), 6.79 (d, J = 8.3 Hz, 1H), 7.06 (d, J = 1.7 Hz, 1H), 7.08 (d, J = 8.1 Hz, 1H), 7.23−7.29 (m, 1H), 7.32−7.42 (m, 3H), 7.56−7.63 (m, 3H), 7.80

(d, J = 8.1 Hz, 1H), 13.48 (br s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.2, 32.4, 32.4, 47.2, 83.1, 110.3, 111.9, 118.6, 119.5, 119.7, 123.4, 123.8, 126.0, 126.7, 127.9, 129.5, 130.3, 136.5, 137.1, 139.4, 140.0, 149.0, 150.6, 159.1 ppm. IR (KBr): 3431, 3065, 2955, 2867, 1623, 1596, 1565 cm^{-1}. Mass (m/z, %): 439 (M^++1, 20), 438 (M^+, 60), 424 (33), 423 (100), 381 (13), 368 (11), 367 (40), 285 (12). HRMS (ESI): 439.2363 calcd for $C_{29}H_{31}N_2O_2$ [M+H$^+$] 439.2386.

4-*tert*-Butyl-5-{4-[*N*-(4-carboxybutyl)benzimidazol-2-yl]-3-hydroxyphenyl}-3,3-dimethyl-2,3-dihydrofuran (3d): 89% yield. Pale yellow columns, mp 174.0−175.0 °C (from CH_2Cl_2−hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.11 (s, 9H), 1.35 (s, 6H), 1.73−1.82 (m, 2H), 1.99−2.09 (m, 2H), 2.44 (t, J = 7.1 Hz, 2H), 3.90 (s, 2H), 4.39−4.48 (m, 2H), 6.94 (dd, J = 8.1 and 1.7 Hz, 1H), 7.13 (d, J = 1.7 Hz, 1H), 7.30−7.38 (m, 2H), 7.40−7.45 (m, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.73−7.80 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.8, 27.3, 29.1, 32.5, 32.5, 33.2, 45.2, 47.2, 83.2, 109.7, 112.8, 118.9, 119.9, 120.5, 123.1, 123.4, 125.9, 126.3, 134.9, 139.6, 140.3, 148.8, 150.7, 158.4, 178.4 ppm. IR (KBr): 3386, 3061, 2955, 2865, 1723, 1654, 1618, 1558 cm^{-1}. Mass (m/z, %): 463 (M^++1, 25), 462 (M^+, 77), 448 (36), 447 (100), 445 (21), 403 (17), 391 (30), 389 (20), 347 (32), 291 (18), 57 (18). HRMS (ESI): 463.2591 calcd for $C_{28}H_{35}N_2O_4$ [M+H$^+$] 463.2597.

Synthesis of 1-[4-(benzimidazol-2-yl)-3-hydroxyphenyl]-5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (2a): Typical procedure. A solution of **3a** (164 mg, 0.45 mmol) and tetraphenylporphine (TPP) (2.0 mg) in acetone (10 mL) was irradiated externally with 940W Na lamp under an oxygen atmosphere for 1.5 h at 0 °C. The reaction mixture was concentrated *in vacuo*. The photolysate was rinsed with CH_2Cl_2 to give dioxetane **2a** (139 mg, 78%). **2a**: Pale yellow granules, mp 284.0−285.0 °C (dec.) (from THF−hexane). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 0.99 (s, 9H), 1.10 (s, 3H), 1.38 (s, 3H), 3.92 (d, J = 8.1 Hz, 1H), 4.38 (d, J = 8.1 Hz, 1H), 7.18 (d, J = 1.5, 1H), 7.22 (dd, J = 8.3 and 1.5 Hz, 1H), 7.26−7.34 (m, 2H), 7.60−7.77 (m, 2H), 8.14 (d, J = 8.3 Hz, 1H), 13.24 (br s, 1H) ppm. ^{13}C NMR (125 MHz, THF-d_8): δ_C 18.7, 25.2, 27. 3, 37.5, 46.4, 80.9, 105.7, 111.7, 114.4, 117.0, 118.8, 119.3, 119.5, 123.4, 124.3, 125.5, 134.3, 140.6, 142.7, 152.5, 159.7 ppm. IR (KBr) : 3417, 3288, 2969, 2901, 1630, 1588, 1543 cm^{-1}. Mass (m/z, %) : 395 (M^++1, 19), 394 (M^+, 67), 338 (20), 294 (15), 255 (11), 254 (27), 238 (19), 237 (100), 210 (27), 209 (28), 181 (19), 57 (22). HRMS (ESI) : 395.1947 calcd for $C_{23}H_{27}N_2O_4$ [M+H$^+$] 395.1971. Anal. Calcd for $C_{23}H_{26}N_2O_4$: C, 70.03; H, 6.64; N, 7.10. Found: C, 69.98; H, 6.75; N, 7.02.

5-*tert*-Butyl-1-[3-hydroxy-4-(*N*-methylbenzimidazol-2-yl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo-[3.2.0]heptane (2b): 94% yield. Pale yellow needles, mp 162.5−163.0 °C (dec.) (from CH_2Cl_2−hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.05 (s, 9H), 1.17 (s, 3H), 1.41 (s, 3H), 3,85 (d, J = 8.3 Hz, 1H), 4.09 (s, 3H), 4.61 (d, J = 8.3 Hz, 1H), 7.28 (dd, J = 8.5 and 1.8 Hz, 1H), 7.33−7.46 (m, 4H), 7.76−7.80 (m, 2H), 13.07 (br s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 18.4, 25.0, 26.9, 33.1, 36.7, 45.6, 80.3, 105.2, 109.6, 113.9, 116.2, 118.2, 118.4, 118.9, 123.1, 123.5, 126.4, 135.6, 139.2, 140.2, 150.9, 158.7 ppm. IR (KBr): 3428, 2969, 2893, 1625, 1577 cm^{-1}. Mass (m/z, %): 409 (M^++1, 23), 408 (M^+, 97), 352 (10), 308

(21), 278 (12), 268 (14), 267 (23), 252 (19), 251 (100), 224 (37), 223 (39), 195 (18), 57 (36). HRMS (ESI): 409.2114 calcd for $C_{24}H_{29}N_2O_4$ [M+H$^+$] 409.2127. Anal. Calcd for $C_{24}H_{28}N_2O_4$: C, 70.57; H, 6.91; N, 6.86. Found: C, 70.26; H, 7.01; N, 6.85.

5-*tert*-Butyl-1-[3-hydroxy-4-(*N*-phenylbenzimidazol-2-yl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo-[3.2.0]heptane (2c): 96% yield. Colorless plates, mp 164.0−165.0 °C (dec.) (from CH_2Cl_2−hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.99 (s, 9H), 1.13 (s, 3H), 1.34 (s, 3H), 3.78 (d, *J* = 8.4 Hz, 1H), 4.54 (d, *J* = 8.4 Hz, 1H), 6.81 (dd, *J* = 8.5 and 1.7 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.25−7.30 (m, 5H), 7.58−7.64 (m, 3H), 7.81 (d, *J* = 7.9 Hz, 1H), 13.61 (br s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 18.4, 25.0, 26.9, 36.7, 45.6, 80.3, 105.1, 110.4, 113.1, 116.1, 117.9, 118.1, 118.7, 123.6, 124.0, 126.6, 127.8, 129.7, 130.4, 136.5, 136.9, 139.1, 139.9, 150.1, 159.2 ppm. IR (KBr): 3433, 3065, 2993, 2969, 2898, 1631, 1595, 1574 cm^{-1}. Mass (m/z, %): 471 (M$^+$+1, 36), 470 (M$^+$, 100), 414 (13), 370 (17), 330 (15), 329 (16), 314 (19), 313 (77), 286 (40), 285 (47), 257 (12), 256 (22), 255 (14), 57 (23). HRMS (ESI): 471.2279 calcd for $C_{29}H_{31}N_2O_4$ [M+H$^+$] 471.2284.

5-*tert*-Butyl-1-{4-[*N*-(4-carboxybutyl)benzimidazol-2-yl]-3-hydroxyphenyl}-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (2d): 99% yield. Pale yellow amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.05 (s, 9H), 1.17 (s, 3H), 1.41 (s, 3H), 1.74−1.83 (m, 2H), 2.01−2.10 (m, 2H), 2.44 (t, *J* = 7.3 Hz, 2H), 3.84 (d, *J* = 8.2 Hz, 1H), 4.41−4.49 (m, 2H), 4.60 (d, *J* = 8.2 Hz, 1H), 7.28 (dd, *J* = 8.2 and 1.8 Hz, 1H), 7.32−7.39 (m, 2H), 7.41−7.46 (m, 2H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.76−7.79 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 18.4, 21.7, 25.0, 26.9, 29.1, 33.1, 36.7, 45.3, 45.6, 80.3, 105.3, 109.8, 114.0, 116.2, 118.5, 118.6, 119.0, 123.3, 123.7, 125.8, 135.0, 139.4, 140.2, 150.3, 158.6, 178.4 ppm. IR (KBr): 3448, 2965, 1716, 1625, 1542 cm^{-1}. Mass (m/z, %): 495 (M$^+$+1, 31), 494 (M$^+$, 100), 478 (17), 477 (49), 435 (36), 422 (24), 421 (67), 409 (23), 408 (30), 394 (27), 338 (29), 337 (78), 319 (40), 310 (46), 309 (61), 281 (45), 254 (27), 237 (56), 181 (47), 57 (88). HRMS (ESI): 495.2485 calcd for $C_{28}H_{35}N_2O_6$ [M+H$^+$] 495.2495.

Thermal decomposition of 2a to 2,2,4,4-tetramethyl-3-oxopentyl 4-(benzimidazol-2-yl)-3-hydroxybenzoate (10a): Typical procedure. A solution of **2a** (48.0 mg, 0.12 mmol) in *p*-xylene was stirred under a nitrogen atmosphere at 140 °C for 3 h. After cooling, the reaction mixture was concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with hexane−AcOEt to give **10a** (47.4 mg, 99%). **10a**: Colorless granules, mp 285.0−286.0 °C (dec.) (from THF−hexane). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 1.23 (s, 9H), 1.35 (s, 6H), 4.35 (s, 2H), 7.28−7.35 (m, 2H), 7.48 (d, *J* = 1.5 Hz, 1H), 7.53 (dd, *J* = 8.1 and 1.5 Hz, 1H), 7.66−7.74 (m, 2H), 8.21 (d, *J* = 8.1 Hz, 1H), 13.34 (br s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 23.3, 28.0, 45.4, 48.8, 71.9, 112.3 (br), 117.1, 117.6, 118.2 (br), 119.6, 123.4 (br), 126.9, 131.9, 133.7 (br), 140.9 (br), 150.5, 157.8, 164.9, 215.5 ppm. IR (KBr) : 3347, 3318, 2969, 1709, 1681, 1612, 1582 cm^{-1}. Mass (m/z, %) 395 (M$^+$+1, 19), 394 (M$^+$, 70), 338 (18), 294 (14), 255 (11), 254 (27), 238 (18), 237 (100), 210 (25), 209 (25), 181 (19), 57 (24). HRMS (ESI) : 395.1980 calcd for $C_{23}H_{27}N_2O_4$ [M+H$^+$] 395.1971. Anal. Calcd for $C_{23}H_{26}N_2O_4$: C, 70.03; H, 6.64; N, 7.10. Found:

C, 70.02; H, 6.78; N, 7.08.

2,2,4,4-Tetramethyl-3-oxopentyl 3-hydroxy-4-(*N*-methylbenzimidazol-2-yl)benzoate (10b): 94% yield. Pale yellow columns, mp 174.0−175.0 °C (from CH_2Cl_2−hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.31 (s, 9H), 1.41 (s, 6H), 4.09 (s, 3H), 4.43 (s, 2H), 7.34−7.47 (m, 3H), 7.59 (dd, *J* = 8.3 and 1.7 Hz, 1H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.76−7.82 (m, 2H), 13.13 (br s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.6, 28.1, 33.1, 45.9, 49.1, 72.2, 109.6, 116.7, 118.9, 119.0, 119.3, 123.2, 123.8, 126.7, 132.3, 135.6, 140.0, 150.4, 158.9, 165.5, 215.9 ppm. IR (KBr) : 3423, 3071, 2961, 1712, 1680, 1573 cm^{-1}. Mass (m/z, %) : 409 (M^++1, 29), 408 (M^+, 100), 352 (11), 308 (17), 268 (12), 267 (19), 252 (16), 251 (87), 224 (27), 223 (30), 195 (11), 57 (16). HRMS (ESI) : 409.2139 calcd for $C_{24}H_{29}N_2O_4$ [M+H$^+$] 409.2127. Anal. Calcd for $C_{24}H_{28}N_2O_4$: C, 70.57; H, 6.91; N, 6.86. Found: C, 70.28; H, 6.98; N, 6.91.

2,2,4,4-Tetramethyl-3-oxopentyl 3-hydroxy-4-(*N*-phenylbenzimidazol-2-yl)benzoate (10c): 97% yield. Pale yellow columns, mp 180.5−181.0 °C (from CH_2Cl_2−hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.27 (s, 9H), 1.37 (s, 6H), 4.37 (s, 2H), 6.89 (d, *J* = 8.4 Hz, 1H), 7.10−7.15 (m, 2H), 7.28−7.44 (m, 4H), 7.62−7.66 (m, 3H), 7.68 (d, *J* = 1.6 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 13.67 (br s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.6, 28.2, 45.8, 49.1, 72.1, 110.5, 116.1, 118.8, 118.9, 119.0, 123.7, 124.3, 127.1, 127.8, 129.8, 130.5, 132.2, 136.5, 136.8, 139.8, 149.7, 159.4, 165.6, 215.9 ppm. IR (KBr) : 3431, 3060, 2971, 2874, 1724, 1685, 1579 cm^{-1}. Mass (m/z, %): 471 (M^++1, 36), 470 (M^+, 100), 414 (14), 370 (24), 330 (18), 329 (22), 314 (21), 313 (86), 287 (11), 286 (53), 285 (64), 257 (20), 256 (34), 255 (20), 57 (30). HRMS (ESI): 471.2278 calcd for $C_{29}H_{31}N_2O_4$ [M+H$^+$] 471.2284.

2,2,4,4-Tetramethyl-3-oxopentyl 4-[*N*-(4-carbonylbutyl)benimidazol-2-yl]-3-hydroxybenzoate (10d): 82% yield. Pale yellow amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.30 (s, 9H), 1.41 (s, 6H), 1.75−1.83 (m, 2H), 2.02−2.10 (m, 2H), 2.45 (t, *J* = 7.1 Hz, 2H), 4.42 (s, 2H), 4.42−4.49 (m, 2H), 7.33−7.40 (m, 2H), 7.43−7.47 (m, 1H), 7.59 (dd, *J* = 8.2 and 1.8 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.77−7.80 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.7, 23.6, 28.1, 29.1, 33.1, 45.3, 45.9, 49.1, 72.2, 109.9, 116.9, 119. 1, 119.2, 119.6, 123.4, 123.9, 126.4, 132.4, 135.0, 140.0, 149.8, 158.7, 165.5, 178.1, 216.1 ppm. IR (KBr) : 2970, 2932, 2877, 1719, 1704, 1684, 1525, cm^{-1}. Mass (m/z, %) : 495 (M^++1, 34), 494 (M^+, 100), 493 (41), 477 (54), 435 (36), 421 (64), 408 (25), 337 (58), 319 (84), 309 (37), 292 (39), 237 (34), 57 (60). HRMS (ESI) : 495.2481 calcd for $C_{28}H_{35}N_2O_6$ [M+H$^+$] 495.2495.

Measurement of chemiluminescence and time-course of the base-induced decomposition of dioxetanes; General Procedure: Chemiluminescence was measured using a JASCO FP-750 and/or FP-6500 spectrometer, and a Hamamatsu Photonics PMA-11 multi-channel detector.

TBAF/MeCN system. A freshly prepared solution (2.00 mL) of TBAF (1.0 x 10^{-2} mol/L) in MeCN was transferred to a quartz cell (10 x 10 x 50 mm), which was placed in a spectrometer that was thermostated with stirring at 45 °C. After 3−5 min, a solution of dioxetane **2** in MeCN (1.0 x 10^{-5} mol/L, 1.00 mL)

was added by means of a syringe, and measurement was started immediately. The time-course of the intensity of light emission was recorded and processed according to first-order kinetics. The total light emission was estimated by comparing it with that of an adamantylidene dioxetane, the chemiluminescent efficiency Φ^{CL} of which has been reported to be 0.29 and which was used here as a standard.[12,13]

NaOH/H_2O system. A solution of NaOH (0.1 M, 2.90 mL) in H_2O was transferred to a quartz cell (10 x 10 x 50 mm), which was placed in a spectrometer that was thermostated with stirring at 45 °C. After 3−5 min, a solution of dioxetane **2** in MeCN (1.0×10^{-4} mol/L, 0.10 mL) was added by means of a syringe, and measurement was started immediately. The time-course of the intensity of light emission was recorded and processed according to first-order kinetics.

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