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Synthesis of bicyclic dioxetanes bearing a 2-hydroxy-1,1′-binaphthyl-5-yl moiety active toward intramolecular charge-transfer-induced chemiluminescent decomposition

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Abstract—Five pairs of diastereoisomeric dioxetanes, *cis*- and *trans*-**2a**–**2e**, were synthesized. These dioxetanes underwent intramolecular charge-transfer-induced decomposition with accompanying emission of orange light in TBAF in DMSO (*system **A***) as a complete homogeneous system and in [K⊂(18C6)]$^+$*t*-BuO$^-$ in PhH–THF (*system **B***) as a sterically anisotropic environment. Maximum wavelength (λ_{max}^{CTICL}) of chemiluminescence did not vary practically with the triggering system. The λ_{max}^{CTICL} was little affected also by substituents on the *upper-Nap* of dioxetanes **2**, nor by the difference in their stereochemistry, namely, *cis*- or *trans*-isomer. On the other hand, chemiluminescent efficiency was found to split up depending on stereochemistry of **2**. Dioxetane **2b** bearing a methoxycarbonyl group on the *upper-Nap* gave significantly weak light, while its free carboxylic acid analog **2c** afforded light effectively.

1. Introduction

A 2-substituted 1,1′-binaphthyl is a most promising functionality to construct optically active molecules and its fluorescence properties, which vary depending on the change of the dihedral angle between the two naphthyl groups is of much interest.[1] Such binaphthyl functionality should become a unique electron donor as well as the most influential part of an emitter, when introduced into a dioxetane active toward intramolecular charge-transfer-induced chemiluminescence (CTICL).[2–5] Thus, we attempted here to synthesize racemic dioxetanes bearing a 2-hydroxy-1,1′-binaphthyl-5-yl moiety and examined their CTICL decomposition as a fundamental investigation leading to studies of optically active dioxetanes.[6,7] Our design was based on an idea that a naphthyl group was introduced to the 2-hydroxynaphthyl moiety in a parent dioxetane, namely, 5-*tert*-butyl-1-(2-hydroxynaphthalen-5-yl)-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane **1**, which has very recently been found to exhibit chemiluminescence in high efficiency.[8] The thus-realized substrates were dioxetane **2a** bearing a rather simple 2-hydroxy-1,1′-binaphthyl-5-yl, dioxetane **2b** bearing a 2-hydroxy-2′-methoxy-3′-methoxycarbonyl-1,1′-binaphthyl, dioxetane **2c** bearing a 3′-carboxy-2-hydroxy-2′-methoxy-1,1′-binaphthyl moiety, and two 2′,3′-disubstituted 2-hydroxy-1,1′-binaphthyl analogs, **2d** and **2e**, which were synthesized from a precursor of **2b** (Fig. 1). The CTICL decomposition of these dioxetanes **2a**–**2e** was examined by the use of tetrabutylammonium fluoride (TBAF) in DMSO as a complete homogeneous system and by the use of a potassium *t*-butoxide complex of 18-crown-6 ether as a sterically anisotropic microenvironment in benzene (PhH)–THF.

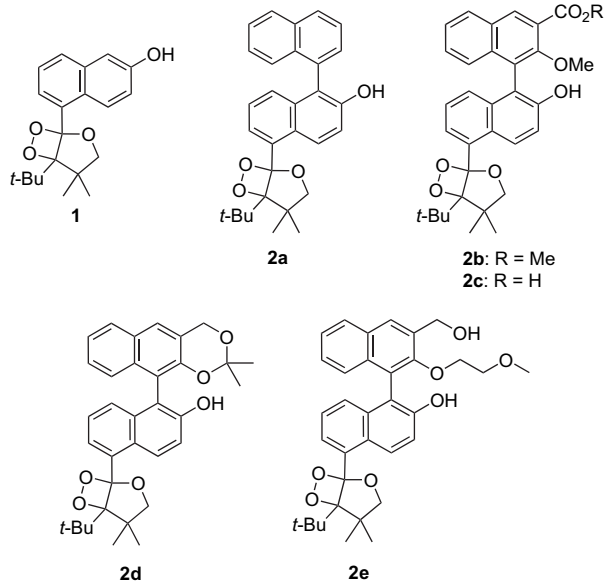

Figure 1.

Keywords: Dioxetane; Chemiluminescence; Binaphthyl; Crown ether.
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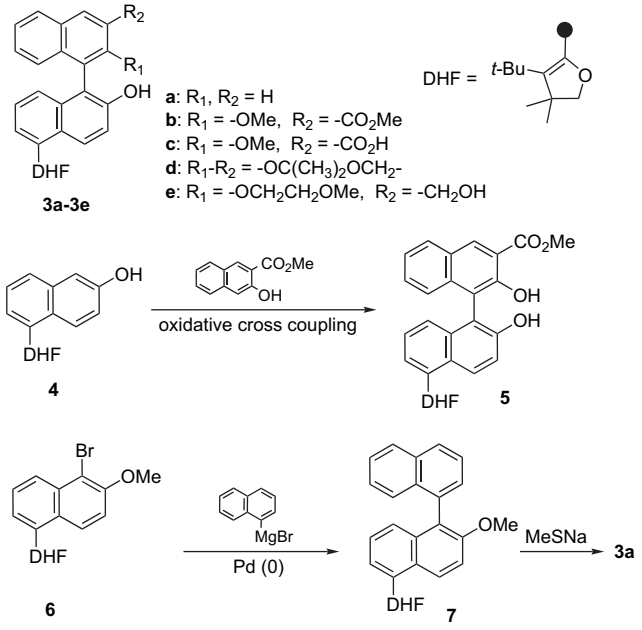
2. Results and discussion

2.1. Synthesis of bicyclic dioxetanes bearing a 2-hydroxy-1,1′-binaphthyl-5-yl moiety

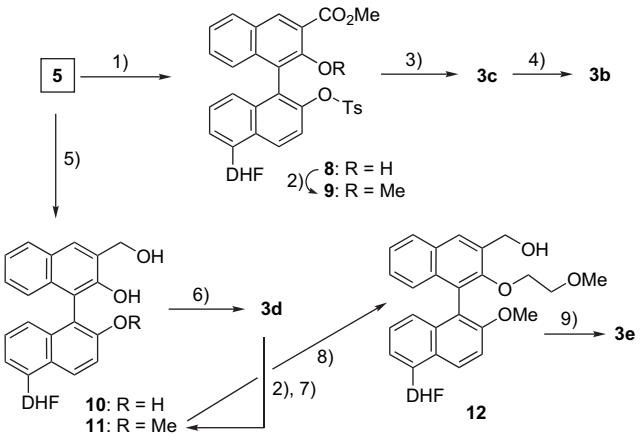
Synthesis of dioxetanes **2a–2e** was based on singlet oxygenation of the corresponding binaphthyl-substituted 4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofurans **3a–3e**. Since 5-aryl-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofurans have been known to undergo effectively 1,2-cycloaddition of singlet oxygen,[4,5] the synthesis of precursor dihydrofurans **3a–3e** was the step to be contrived carefully. Our synthetic strategy was to utilize dihydrofuran **5** bearing a 2,2′-dihydroxy-3′-methoxycarbonyl-1,1′-binaphthyl-5-yl moiety as a key intermediate, since **5** has very recently been found to be effectively produced from 2-hydroxynaphthalen-5-yl-substituted dihydrofuran **4** by means of copper-catalyzed oxidative cross-coupling with methyl 3-hydroxynaphthalene-2-carboxylate (Scheme 1).[9] Thus, dihydrofurans **3b–3e** except **3a** were synthesized from **5** in several steps (vide infra).



Scheme 1.

Dihydrofuran **3a** substituted with a simple 2-hydroxy-1,1′-binaphthyl-5-yl group was synthesized by Pd-catalyzed cross-coupling[10] of dihydrofuran **6** bearing a 1-bromo-2-methoxynaphthalen-5-yl group with 1-naphthylmagnesium bromide giving dihydrofuran **7** bearing a 2-methoxy-1,1′-binaphthyl-5-yl group, and successive demethylation of the 2-methoxy group in **7** (Scheme 1).

The first step to synthesize **3b** bearing a 2-hydroxy-2′-methoxy-3′-methoxycarbonyl-1,1′-binaphthyl-5-yl moiety from **5** was selective protection of the 2-hydroxy group into *p*-toluenesulfonate **8**. Next, the 2′-hydroxy group of **8** was methylated to give 2′-methoxy-derivative **9**, which was hydrolyzed into dihydrofuran **3c** bearing a 3′-carboxy-2-hydroxy-2′-methoxy-1,1′-binaphthyl-5-yl moiety. Finally, **3c** was esterified with methyl iodide and $NaHCO_3$ to afford **3b** (Scheme 2).



Scheme 2. Reagents and conditions: (1) TsCl/pyridine, (2) MeI/K_2CO_3, (3) NaOH, (4) MeI/$NaHCO_3$, (5) $LiAlH_4$, (6) $Me_2C(OMe)_2$/PPTS, (7) H_2O/TsOH/THF, (8) $MeOCH_2CH_2Br/K_2CO_3$, (9) MeSNa/DMF.

On the other hand, dihydrofuran **5** was reduced with $LiAlH_4$ to give dihydrofuran **10** bearing a 2,2′-dihydroxy-3′-hydroxymethyl-1,1′-binaphthyl-5-yl moiety, which was further treated with 2,2-dimethoxypropane to afford cyclic acetal **3d**. Williamson synthesis of **3d** with MeI followed by hydrolysis of acetal group gave dihydrofuran **11**, which was treated with 2-methoxyethyl bromide–K_2CO_3 to give dihydrofuran **12** bearing a 3′-hydroxymethyl-2-methoxy-2′-(2-methoxyethoxy)-1,1′-binaphthyl-5-yl moiety.[11] Demethylation of the 2-methoxy group with MeSNa gave dihydrofuran **3e** bearing a 2-hydroxy-3′-hydroxymethyl-2′-(2-methoxyethoxy)-1,1′-binaphthyl-5-yl moiety.

All dihydrofurans **3a–3e** synthesized here were obtained as a mixture of diastereomers, which could not be separated from each other. Therefore, 1,2-addition of singlet oxygen to **3** should afford the corresponding dioxetanes **2** also as a mixture of diastereomers, namely, *cis*-**2** in which both long wing of 1′-naphthyl (called *upper-Nap* for the sake of convenience) and O_7 of dioxetane O–O lie in the same side of the π-face of central hydroxynaphthyl ring, and *trans*-**2** in which the long wing of *upper-Nap* and the O_7 lie in the opposite side of the π-face to each other (Fig. 2). When a solution of dihydrofuran **3a** in CH_2Cl_2 was irradiated in the presence of a catalytic amount of tetraphenylporphin (TPP) with Na lamp under O_2 atmosphere at 0 °C for 1 h, dioxetane **2a** was selectively produced as a mixture of diastereomers (cis:trans=64:36), from which *cis*-**2a**, as the first fraction, and *trans*-**2a**, as the second fraction, were separated in pure form by column chromatography (SiO_2/hexane–AcOEt). Similar singlet oxygenation of dihydrofurans **3b–3e** gave the corresponding dioxetanes, **2b–2e** as a mixture of diastereomers (cis:trans=42:58 for **2b**, 48:52 for **2c**, 43:57 for **2d**, and 46:54 for **2e**). Chromatographic separation of the diastereomers afforded also *cis*-**2b–2e** and *trans*-**2b–2e** in pure form. The structures of these dioxetanes were determined by ^1H NMR, ^{13}C NMR, IR, mass spectral analyses and elemental analysis. Furthermore, X-ray single crystallographic analysis was successfully attained for *cis*-**2a**, *cis*-**2b**, *cis*-**2c**, *trans*-**2d**, and *cis*-**2e**. ORTEP views illustrated in Figure 3 show that two naphthyl rings lie in seriously twisted conformation for all these dioxetanes: dihedral angles θ (C_2–C_1–$C_{1'}$–$C_{2'}$) were 86.7° for *cis*-**2a**,

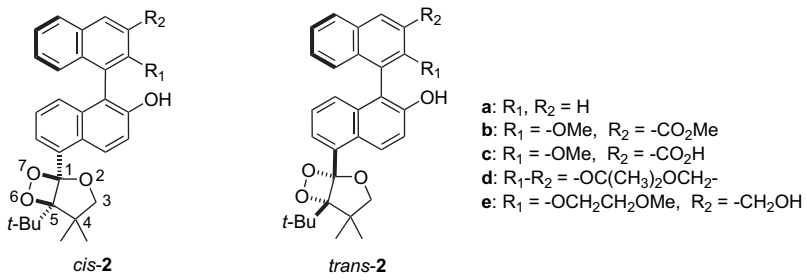


Figure 2.

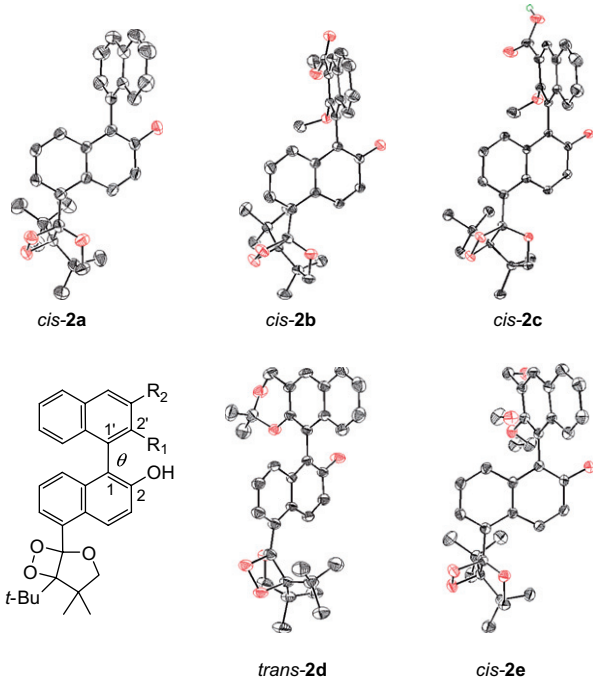


Figure 3. ORTEP views of dioxetane *cis*-**2a**, *cis*-**2b**, *cis*-**2c**, *trans*-**2d**, and *cis*-**2e**.

109.1° for *cis*-**2b**, 75.1° for *cis*-**2c**, 96.5° for *trans*-**2d**, and 76.5° for *cis*-**2e**.

2.2. Base-induced chemiluminescent decomposition of bicyclic dioxetanes bearing a 2-hydroxy-1,1′-binaphthyl-5-yl moiety

The parent dioxetane **1** bearing a 2-hydroxynaphthalen-5-yl moiety has been reported to undergo CTICL decomposition followed by a pseudo-first-order kinetics to give yellow light with maximum wavelength λ_{max}^{CTICL}=582 nm, when treated with a large excess of TBAF in DMSO.[8] Thus, we carried out first the CTICL decomposition of dioxetanes **2a**–**2e** in the TBAF in DMSO system (*system* ***A***) to evaluate their chemiluminescent properties in comparison with those of dioxetane **1**. When solutions of dioxetanes, *cis*-**2a** and *trans*-**2a** in DMSO (1.0×10^{-5} mol cm^{-3}, 1 mL) were added to solutions of TBAF in DMSO (1.0×10^{-2} mol cm^{-3}, 2 mL) at 25 °C, these diastereomeric dioxetanes decomposed rapidly to emit orange light with the same λ_{max}^{CTICL} (597 nm), though chemiluminescent efficiency (Φ^{CTICL}) and pseudo-first-order rate constant (k^{CTICL}) were somewhat different from each other. Then, the fluoride-induced chemiluminescent decomposition of dioxetanes, *cis*-**2b**–**2e** and *trans*-**2b**–**2e**, were carried out similarly. The results are summarized in Table 1, which reveals characteristic features for CTICL of **2** as follows. First, the introduction of the *upper-Nap* on the 2-hydroxynaphthyl ring of the parent dioxetane **1** caused a little red-shift of λ_{max}^{CTICL}s, which were observed at ca. 600 nm regardless of substituents on the *upper-Nap* ring. Secondly, Φ^{CTICL}s tended to decrease as substituent(s) was introduced into the *upper-Nap* ring of **2**, and the extreme was that for **2b**, Φ^{CTICL} of which was only 1/500–1/1000 of those for **1** and

Table 1. Base-induced chemiluminescent decomposition of bicyclic dioxetanes bearing a 2-hydroxy-1,1′-binaphthyl-5-yl moiety **2**[a]

Dioxetane		*System A*			*System B*		
		TBAF in DMSO			[K⊂(18C6)]$^+$*t*-BuO$^-$ in PhH–THF		
		λ_{max}^{CTICL}/nm	Φ^{CTICL} [b]	k^{CTICL}/s^{-1}	λ_{max}^{CTICL}/nm	Φ^{CTICL} [b]	k^{CTICL}/s^{-1}
2a	*cis*	597	1.6×10^{-2}	5.0×10^{-2}	594	9.2×10^{-3}	3.1×10^{-2}
	trans	597	1.8×10^{-2}	4.8×10^{-2}	594	8.8×10^{-3}	3.4×10^{-2}
2b	*cis*	600	2.0×10^{-5}	2.2×10^{-2}	600	9.7×10^{-3}	1.9×10^{-1}
	trans	600	1.8×10^{-5}	2.2×10^{-2}	600	7.5×10^{-3}	2.0×10^{-1}
2c	*cis*	609	8.5×10^{-3}	4.0×10^{-1}	600	9.4×10^{-3}	1.9×10^{-1}
	trans	609	9.3×10^{-3}	3.6×10^{-1}	600	7.4×10^{-3}	1.9×10^{-1}
2d	*cis*	600	9.2×10^{-3}	1.8×10^{-1}	595	6.9×10^{-3}	1.3×10^{-1}
	trans	600	1.1×10^{-2}	1.8×10^{-1}	595	6.2×10^{-3}	9.0×10^{-2}
2e	*cis*	600	1.7×10^{-2}	5.1×10^{-2}	595	7.2×10^{-3}	1.3×10^{-1}
	trans	600	1.2×10^{-2}	5.5×10^{-2}	595	5.5×10^{-3}	1.1×10^{-1}
1		582[c]	1.7×10^{-2}	3.7×10^{-2}	614	4.2×10^{-3}	4.5×10^{-2}

[a] Base-induced decompositions were carried out at 25 °C.
[b] Chemiluminescent efficiencies (Φ^{CTICL}) were based on the reported value for 3-(3-*tert*-butyldimethylsiloxyphenyl)-3-methoxy-4-(2′-spiroadamantane)-1,2-dioxetane (Φ^{CTICL}=0.29) (Ref. 12).
[c] Chemiluminescent properties for **1** in TBAF in DMSO summarized here are the values reported (Ref. 8).

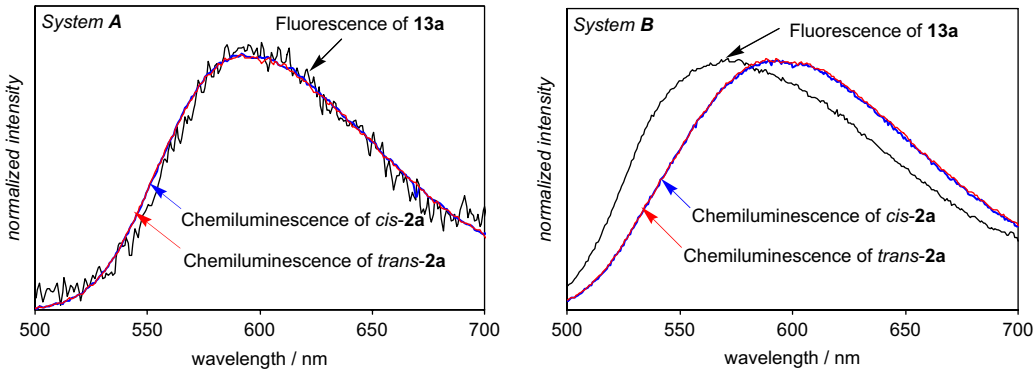
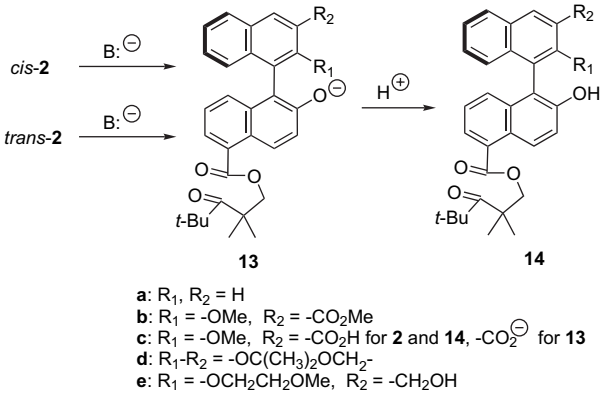


Figure 4. Chemiluminescent spectra of dioxetane **2a** and fluorescence spectra of keto ester **13a**.

the other dioxetanes **2a** and **2c**–**2e**. It should be noted that dioxetane **2c**, which is simply a carboxylic acid analog of **2b**, displayed chemiluminescence as effective as **2a**, **2d**, and **2e**. Thirdly, difference in configuration of the dioxetane, namely, cis- or trans-type, did not affect λ_{max}^{CTICL}, but caused apparently a split of Φ^{CTICL} and k^{CTICL} to some extent.

All spent mixtures of fluoride-induced decomposition of **2** in DMSO gave the corresponding keto esters of 1,1′-binaphthyl-5-carboxylic acid **14a**–**14e** in high isolated yields after neutralization; both *cis*-**2** and *trans*-**2** gave the same **14**. This fact shows that fluoride-induced decomposition of **2** produced undoubtedly oxido anion **13**. For instance, **13a** generated from the corresponding authentic keto esters, **14a** in TBAF in DMSO displayed fluorescence (efficiency $\Phi^{fl}=5.9\times10^{-2}$), the spectra of which coincided with the chemiluminescence spectra of the corresponding dioxetanes, *cis*-**2a** and *trans*-**2a** (Fig. 4). However, keto ester **14b** exhibited little observable fluorescence under similar conditions. This is a reason why Φ^{CTICL} was extremely low for **2b**, implying that Φ^{CTICL} is proportional to fluorescence efficiency of the emitter produced. On the other hand, keto ester **14c** would exist in TBAF in DMSO as a dianion form, and displayed fluorescence differently from **14b**. Conclusively, an electron-withdrawing ester function attached at the 3′-position of *upper-Nap* decreased fluorescence of **14b**, so that decreased significantly Φ^{CTICL} of **2b**, whereas its carboxylate anion did not deteriorate the fluorescence property of **13c** (Scheme 3).

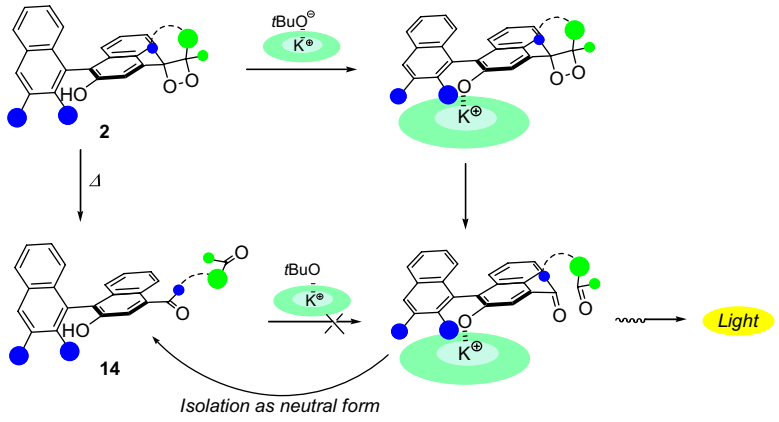


Scheme 3.

A complex of 18-crown-6 ether with *t*-BuOK, $[K\subset(18C6)]^{+}t\text{-}BuO^{-}$, provides a sterically anisotropic microenvironment to a ligand such as phenol and naphthol as they coordinate to it.[13–16] When dioxetane **1** was treated as a reference with a large excess of $[K\subset(18C6)]^{+}t\text{-}BuO^{-}$ in PhH–THF (1:1) (*system* ***B***) at 25 °C, **1** decomposed with accompanying emission of light with λ_{max}^{CTICL} at 614 nm, though Φ^{CTICL} decreased to 1/4 of the value in *system* ***A***. Chemiluminescent decomposition of **2a**–**2e** was examined similarly in *system* ***B***. The results are summarized in Table 1, which shows that the behavior of dioxetanes **2a**–**2e** in *system* ***B*** was considerably different from the case of **1**. Thus, λ_{max}^{CTICL}s did not change or rather shifted slightly to blue for **2**, whereas that for **1** shifted to red considerably as the base system changed from *system* ***A*** to *system* ***B***. Decrease of Φ^{CTICL}s was smaller for **2** than for **1** in *system* ***B***, and Φ^{CTICL}s were rather higher than that of **1**. Structural difference between diastereomers, *cis*-**2** and *trans*-**2**, caused difference in Φ^{CTICL} but not in λ_{max}^{CTICL} also for *system* ***B***. It should be noted here that difference in Φ^{CTICL} tended to expand in *system* ***B***, and its magnitude increased in the order of **2a**, **2c**≤**2d**<**2e**. Furthermore, weak diastereomeric recognition is apparently reflected in the singlet-chemiexcitation process for CTICL decomposition of **2**.

Table 1 shows that Φ^{CTICL} of **2b** appeared to increase surprisingly when the triggering system changed from *system* ***A*** to *system* ***B***. However, the spent reaction mixture after neutralization afforded free carboxylic acid **14c** but not ester **14b**. This fact suggests that hydrolysis of **2b** to dianion of **2c** took place far more rapidly than decomposition of **2b** into excited **13b**, and successive decomposition of **2c** occurred to emit light in *system* ***B***. The hydrolysis is presumably caused by a trace amount of water existing as hydroxide anion, which could hardly be excluded from *system* ***B*** in spite of careful experiment even under N_2 atmosphere, though such sensitivity was little observed for the other CTICLs.

Spent reaction mixtures from **2a**–**2e** except **2b** in *system* ***B*** gave the corresponding keto esters **14a** and **14c**–**14e** in high yields after neutralization. Therefore, emitters produced from dioxetanes were believed to be anionic keto esters **13** as in the case of *system* ***A***. However, all authentic anionic keto esters **13** generated from **14** displayed fluorescence spectra with λ_{max}^{fl}s at ca. 560 nm, which was considerably shorter than λ_{max}^{CTICL}s of chemiluminescent spectra from the corresponding dioxetanes **2** in *system* ***B***, as illustrated in Figure 4, where the case of **2a** and **13a** is shown as a



Scheme 4.

representative. The discrepancy between λ_{max}^{CTICL} and λ_{max}^{fl} suggests that excited keto ester **13** produced from dioxetane **2** lies presumably in conformation different from that of authentic **13** under the coordination to $[K\subset(18C6)]^+$. That is, dioxetane **2** produces most likely, in the coordination sphere, excited **13** retaining afterimage of stereochemistry of **2**, which could never be reproduced from authentic **14**, as illustrated in Scheme 4.

An AM1 MO calculation was indicative for the change of excitation energy depending on the conformational change of binaphthyl. Figure 5 illustrates the relationship of energy gap ($\Delta E=E_{LUMO}-E_{HOMO}$) with the dihedral angle (θ) for 2-oxido-1,1′-binaphthyl-5-carboxylic acid methyl ester as a model of **13a**. The calculation suggested for the model emitter that, as θ decreased from ca. 100°, ΔE increased so that emission shifted to blue more and more. Thus, the coordination to $[K\subset(18C6)]^+$ causes most likely decrease of θ larger for authentic **13** generated from **14** than for excited **13** produced from **2**.

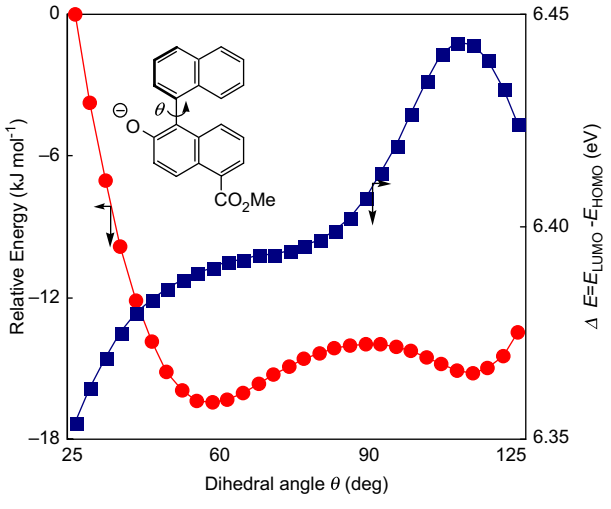


Figure 5. Relationship between ΔE and dihedral angle θ for 2-oxido-1,1′-binaphthyl-5-carboxylic acid methyl ester.

3. Conclusion

It was disclosed for CTICL decomposition of diastereoisomeric dioxetanes, *cis*-**2** and *trans*-**2**, in TBAF in DMSO (*system* ***A***) and in $[K\subset(18C6)]^+t$-BuO^- in PhH–THF (*system* ***B***) that λ_{max}^{CTICL} of chemiluminescence was little affected practically by the triggering system, the substituents on *upper-Nap*, nor their stereochemistry, whereas Φ^{CTICL} and k^{CTICL} split up depending on the stereochemistry of **2**. The bulk of substituents on *upper-Nap* was suggested to influence the magnitude of the split in Φ^{CTICL} between diastereoisomeric dioxetanes **2**. These findings provide a promising possibility that structural modification of dioxetanes **2d** and **2e** should lead to optically active dioxetanes that undergo CTICL decomposition responding to anisotropic microenvironment. The rather unexpected finding that very rapid hydrolysis of the ester function in **2b** into **2c** caused most likely significant increase of Φ^{CTICL} in *system* ***B*** may be useful to monitor hydrolysis of the ester function.

4. Experimental

4.1. General

Melting points were measured with a Yanako MP-S3 melting point apparatus and are uncorrected. IR spectra were taken on a JASCO FT/IR-300 infrared spectrometer. ^1H and ^{13}C NMR spectra were recorded on JEOL EX-400 and JEOL EPC-500 spectrometers. Mass spectra were obtained by using JEOL JMS-AX-505H and JEOL JMS-T-100LC mass spectrometers. Elemental analysis was performed by means of Perkin–Elmer 2400II. Reagents were purchased from Aldrich, Tokyo Chemical Industries, Wako Pure Chemical Industries, and/or Kanto Chemical Industries. Column chromatography was carried out with silica gel, unless otherwise stated.

4.1.1. Synthesis of 4-*tert*-butyl-5-(2-methoxy-1,1′-binaphthyl-5-yl)-3,3-dimethyl-2,3-dihydrofuran (7). A solution of naphthalen-1-yl magnesium bromide, prepared from 1-bromonaphthalene (0.61 mL, 4.4 mmol) in dry THF (8 mL) was added dropwise to a suspension of 5-(5-bromo-6-methoxynaphthalen-1-yl)-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**6**) (1.42 g, 3.65 mmol) and $Pd(PPh_3)_4$ (380 mg, 0.33 mmol) in dry THF (14 mL) under a nitrogen atmosphere for 20 min at refluxing temperature and then stirred for 7.5 h. The mixture was worked up as usual and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated

in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:40) to give dihydrofuran **7** (510 mg, 32.1%, conversion: 61.9%) as a colorless solid. Compound **7**: colorless plates melted at 137.0–137.5 °C (from AcOEt–hexane); (63:37 mixture of diastereomers) ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.07 (s, 9H×0.63), 1.08 (s, 9H×0.37), 1.43 (s, 3H), 1.51 (s, 3H), 3.72 (s, 3H), 4.01 (q_{AB}, J=6.4 Hz, 2H×0.37), 4.06 (q_{AB}, J=8.2 Hz, 2H×0.63), 7.09–7.16 (m, 2H), 7.20–7.46 (m, 6H), 7.56–7.61 (m, 1H), 7.89–7.93 (m, 2H), 8.10 (d with fine coupling, J=9.2 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.3 and 27.4, 27.6 and 27.7, 32.1, 32.7, 47.4, 56.6, 83.3, 114.0 and 114.1, 123.2, 125.4 and 125.5, 125.6, 125.6 and 125.7, 125.8, 125.8 and 125.9, 126.2, 126.2 and 126.3, 127.4, 127.7, 127.7 and 127.8, 127.8 and 127.9, 128.1 and 128.2, 128.3 and 128.6, 132.9 and 133.0, 133.4 and 133.5, 133.6 and 133.7, 134.3 and 134.4, 134.5 and 134.6, 148.2, 154.5 ppm. IR (KBr): $\tilde{\nu}$ 2956, 2857, 1610, 1589, 1508, 1260, 1090, 1048 cm^{-1}. Mass (*m*/*z*, %): 436 (M^+, 80), 422 (36), 421 (100), 406 (16), 375 (19), 365 (17), 239 (10), 57 (19). HRMS (ESI): 459.2254, calcd for $C_{31}H_{32}O_2Na$ (M+Na$^+$) 459.2300. Anal. Calcd for $C_{31}H_{32}O_2$: C, 85.28; H, 7.39. Found: C, 84.90; H, 7.29.

4.1.2. Synthesis of 4-*tert*-butyl-5-(2-hydroxy-1,1′-binaphthyl-5-yl)-3,3-dimethyl-2,3-dihydrofuran (3a). Sodium methanethiolate (95%, 145 mg, 1.97 mmol) was added to a solution of 4-*tert*-butyl-5-(2-methoxy-1,1′-binaphthyl-5-yl)-3,3-dimethyl-2,3-dihydrofuran (**7**) (409 mg, 0.937 mmol) in dry DMF (4 mL) under a nitrogen atmosphere at room temperature and stirred for 1 h at 140 °C. The reaction mixture was poured into satd aq NH_4Cl and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:4) to give dihydrofuran **3a** (363 mg, 91.7%) as a colorless solid. Compound **3a**: colorless granules melted at 199.5–200.0 °C (from AcOEt–hexane); (63:37 mixture of diastereomers) ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.06 (s, 9H×0.63), 1.08 (s, 9H×0.37), 1.44 (s, 3H), 1.52 (s, 3H), 4.01 (q_{AB}, J=7.8 Hz, 2H×0.37), 4.03 (q_{AB}, J=8.1 Hz, 2H×0.63), 4.86 (s, 1H×0.37), 4.90 (s, 1H×0.62), 7.04–7.08 (m, 1H), 7.15–7.20 (m, 1H), 7.26 (d with fine coupling, J=7.0 Hz, 1H), 7.30–7.41 (m, 3H), 7.47–7.55 (m, 1H), 7.58 (d with fine coupling, J=7.0 Hz, 1H), 7.63–7.68 (m, 1H), 7.96 (d, J=7.8 Hz, 1H), 7.98–8.03 (m, 1H), 8.02 (d, J=7.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.3 and 27.4, 27.6 and 27.7, 32.1, 32.7, 47.4, 83.3, 117.7, 118.7 and 118.8, 125.6 and 125.7, 125.7, 125.7 and 125.9, 125.9 and 126.0, 126.4 and 126.5, 126.7 and 126.8, 127.6 and 127.7, 127.8, 127.8, 128.3 and 128.5, 129.1 and 129.2, 129.4 and 129.8, 131.5, 132.8, 132.9, 133.6 and 133.7, 133.9 and 134.0, 134.1, 148.1, 150.9 ppm. IR (KBr): $\tilde{\nu}$ 3512, 2955, 2865, 1614, 1590, 1469, 1386, 1300, 1197, 1050 cm^{-1}. Mass (*m*/*z*, %): 422 (M^+, 61), 408 (34), 407 (100), 392 (22), 377 (14), 351 (17), 239 (13), 57 (22). HRMS (ESI): 423.2334, calcd for $C_{30}H_{31}O_2$ (M+H$^+$) 423.2324. Anal. Calcd for $C_{30}H_{30}O_2$: C, 85.27; H, 7.16. Found: C, 85.06; H, 7.06.

4.1.3. Synthesis of 4-*tert*-butyl-5-[2′-hydroxy-3′-methoxycarbonyl-2-(4-methylphenylsulfonyloxy)-1,1′-binaphthyl-5-yl]-3,3-dimethyl-2,3-dihydrofuran (8). *p*-Toluenesulfonyl chloride (944 mg, 4.95 mmol) was added to a solution of 4-*tert*-butyl-5-(2,2′-dihydroxy-3′-methoxycarbonyl-1,1′-binaphthyl-5-yl)-3,3-dimethyl-2,3-dihydrofuran (**5**)[9] (2.03 g, 4.09 mmol) and triethylamine (2.9 mL, 21 mmol) in dry THF (10 mL) under a nitrogen atmosphere at room temperature and stirred for 25 h. The reaction mixture was added to satd aq NH_4Cl and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with CH_2Cl_2–hexane (1:1) to give dihydrofuran **8** (2.00 g, 75.1%) as a pale yellow solid. Compound **8**: pale yellow amorphous solid; (64:36 mixture of diastereomers) ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.05 (s, 9H), 1.44 (s, 3H), 1.52 (s, 3H), 2.25 (s, 3H×0.64), 2.29 (s, 3H×0.36), 3.99 (d, J=7.8 Hz, 1H×0.36), 4.00 (d, J=7.8 Hz, 1H×0.64), 4.04–4.07 (m, 1H), 4.05 (s, 3H×0.36), 4.07 (s, 3H×0.64), 6.72 (d, J=8.7 Hz, 1H×0.64), 6.76–6.87 (m, 2H), 6.96 (d, J=7.8 Hz, 1H×0.36), 7.10–7.14 (m, 4H), 7.18–7.23 (m, 1H), 7.27–7.33 (m, 1H), 7.38–7.41 (m, 1H), 7.79–7.84 (m, 2H), 8.12 (s, 1H×0.64), 8.14 (s, 1H×0.36), 8.53 (s, 1H×0.36), 8.55 (s, 1H×0.64), 10.1 (s, 1H×0.36), 10.5 (s, 1H×0.64) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.5, 27.2 and 27.3, 27.5 and 27.6, 32.0 and 32.1, 32.7, 47.3 and 47.4, 52.5 and 52.6, 83.3, 113.4 and 113.5, 115.6 and 115.7, 121.9 and 122.0, 123.6 and 123.7, 124.6 and 124.7, 124.9 and 125.2, 125.9 and 126.0, 126.4 and 126.5, 126.9 and 127.0, 127.4 and 127.6, 127.9 and 128.0, 128.2 and 128.3, 128.5, 128.9 and 129.0, 129.1 and 129.3, 129.2 and 129.4, 130.9 and 131.1, 132.9 and 133.0, 133.1 and 133.2, 133.2, 133.9 and 134.0, 136.8 and 136.9, 144.1 and 144.2, 145.9 and 146.1, 147.4 and 147.6, 154.0 and 154.1, 170.0 and 170.1 ppm. IR (KBr): $\tilde{\nu}$ 3448, 2955, 2865, 1684, 1628, 1438, 1322, 1213, 1173, 1051 cm^{-1}. Mass (*m*/*z*, %): 650 (M^+, 69), 637 (13), 636 (49), 635 (100), 603 (28), 547 (31), 496 (21), 482 (19), 481 (51), 480 (25), 465 (30), 433 (19), 393 (18), 363 (14), 226 (19), 91 (45), 57 (29). HRMS (ESI): 673.2212, calcd for $C_{39}H_{38}O_7SNa$ (M+Na$^+$) 673.2236. Anal. Calcd for $C_{39}H_{38}O_7S$: C, 71.98; H, 5.89. Found: C, 71.77; H, 5.77.

4.1.4. Synthesis of 4-*tert*-butyl-5-[2′-methoxy-3′-methoxycarbonyl-2-(4-methyl-phenylsulfonyloxy)-1,1′-binaphthyl-5-yl]-3,3-dimethyl-2,3-dihydrofuran (9). MeI (0.10 mL, 1.6 mmol) was added to a solution of 4-*tert*-butyl-5-[2′-hydroxy-3′-methoxycarbonyl-2-(4-methylphenylsulfonyloxy)-1,1′-binaphthyl-5-yl]-3,3-dimethyl-2,3-dihydrofuran (**8**) (204 mg, 0.313 mmol) and K_2CO_3 (65 mg, 0.47 mmol) in dry DMF (2 mL) under a nitrogen atmosphere at room temperature and stirred for 1.5 h. The reaction mixture was poured into satd aq NH_4Cl and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with CH_2Cl_2 to give dihydrofuran **9** (193 mg, 92.6%) as a pale yellow solid. Compound **9**: colorless plates melted at 189.0–189.5 °C (from EtOH–hexane); (64:36 mixture of diastereomers) ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.02 (s, 9H×0.64), 1.08 (s, 9H×0.36), 1.44 (s, 3H), 1.53 (s, 3H), 2.23 (s, 3H×0.64), 2.26 (s, 3H×0.36), 3.32 (s, 3H×0.36), 3.41 (s, 3H×0.64), 3.99 (s, 3H×0.36), 4.00 (s, 3H×0.64), 4.01–4.09 (m, 2H), 6.71–6.91 (m, 3H), 7.02–7.25 (m, 5H), 7.35–7.43 (m, 2H), 7.83 (d, J=8.7 Hz, 1H), 7.87 (d, J=9.6 Hz, 1H), 8.16 (d, J=9.6 Hz, 1H), 8.39 (s, 1H×0.36), 8.41 (s, 1H×0.64) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.5, 27.3, 27.6, 31.9 and 32.1, 32.6 and 32.7,

47.5, 52.5, 61.8 and 61.9, 83.4 and 83.5, 121.8 and 121.9, 124.4 and 124.5, 124.6, 124.7 and 124.8, 125.2 and 125.3, 126.0 and 126.2, 126.3, 126.9 and 127.0, 127.1, 127.2, 128.2, 128.3 and 128.4, 128.5 and 128.6, 128.7, 129.0, 129.1 and 129.3, 130.7 and 130.8, 133.0 and 133.2, 133.4 and 133.5, 133.6, 134.0 and 134.1, 135.3, 144.2, 145.9 and 146.0, 147.3 and 147.4, 154.3 and 154.4, 166.8 ppm. IR (KBr): $\tilde{\nu}$ 2954, 2866, 1734, 1624, 1468, 1445, 1361, 1292, 1207, 1173, 1092 cm^{-1}. Mass (*m/z*, %): 664 (M^+, 79), 651 (17), 650 (43), 649 (100), 617 (21), 561 (19), 510 (19), 469 (12), 495 (32), 463 (19), 448 (13), 447 (33), 407 (13). HRMS (ESI): 687.2383, calcd for $C_{40}H_{40}O_7SNa$ (M+Na^+) 687.2392. Anal. Calcd for $C_{40}H_{40}O_7S$: C, 72.27; H, 6.06. Found: C, 72.23; H, 6.09.

4.1.5. Synthesis of 4-*tert*-butyl-5-(3′-carboxy-2-hydroxy-2′-methoxy-1,1′-binaphthyl-5-yl)-3,3-dimethyl-2,3-dihydrofuran (3c). NaOH (364 mg, 9.10 mmol) was added to a solution of 4-*tert*-butyl-5-[2′-methoxy-3′-methoxycarbonyl-2-(4-methylphenylsulfonyloxy)-1,1′-binaphthyl-5-yl]-3,3-dimethyl-2,3-dihydrofuran (**9**) (840 mg, 1.26 mmol) in MeOH (5 mL) under a nitrogen atmosphere at room temperature and stirred at refluxing temperature for 4 h. The reaction mixture was poured into 1 N HCl and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:1) to give dihydrofuran **3c** (577 mg, 92%) as a colorless solid. Compound **3c**: colorless granules melted at 235.5–236.5 °C (from AcOEt–hexane); (54:46 mixture of diastereomers) ^1H NMR (500 MHz, $CDCl_3$): δ_H 1.03 (s, 9H×0.54), 1.07 (s, 9H×0.46), 1.44 (s, 3H), 1.52 (s, 3H), 3.45 (s, 3H×0.46), 3.46 (s, 3H×0.54), 4.00 (d, *J*=7.8 Hz, 1H×0.46), 4.01 (d, *J*=7.3 Hz, 1H×0.54), 4.05 (d, *J*=7.3 Hz, 1H×0.54), 4.06 (d, *J*=7.8 Hz, 1H×0.46), 5.66 (br s, 1H), 7.00–7.03 (m, 1H), 7.21–7.31 (m, 3H), 7.37–7.53 (m, 3H), 7.99 (br s, 1H), 8.09 (d, *J*=8.7 Hz, 1H), 8.81 (br s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.3, 27.6 and 27.7, 31.9 and 32.0, 32.7, 47.4, 62.1 and 62.4, 83.3 and 83.4, 113.5, 118.3 and 118.4, 120.9, 123.3, 125.1, 125.3 and 125.6, 126.1 and 126.2, 126.5, 126.6 and 126.7, 127.9, 128.2 and 128.3, 129.0, 129.8, 129.9, 130.3 and 130.4, 133.6, 134.0, 136.4, 136.4, 147.7, 151.7, 154.1 and 154.2, 166.3 ppm. IR (KBr): $\tilde{\nu}$ 3357, 3181, 2957, 2864, 1729, 1687, 1620, 1449, 1298, 1230, 1044 cm^{-1}. Mass (*m/z*, %): 496 (M^+, 56), 495 (30), 482 (37), 481 (100), 466 (15), 453 (16), 407 (34), 371 (14), 277 (14), 266 (12), 57 (14). HRMS (ESI): 519.2166, calcd for $C_{32}H_{32}O_5Na$ (M+Na^+) 519.2147. Anal. Calcd for $C_{32}H_{32}O_5$: C, 77.40; H, 6.50. Found: C, 77.06; H, 6.41.

4.1.6. Synthesis of 4-*tert*-butyl-5-(2-hydroxy-2′-methoxy-3′-methoxycarbonyl-1,1′-binaphthyl-5-yl)-3,3-dimethyl-2,3-dihydrofuran (3b). MeI (0.10 mL, 1.6 mmol) was added to a solution of 4-*tert*-butyl-5-(3′-carboxy-2-hydroxy-2′-methoxy-1,1′-binaphthyl-5-yl)-3,3-dimethyl-2,3-dihydrofuran (**3c**) (520 mg, 1.05 mmol) and $NaHCO_3$ (94 mg, 1.1 mmol) in dry DMF (5 mL) under a nitrogen atmosphere at room temperature and stirred overnight. The reaction mixture was poured into satd aq NH_4Cl and extracted with AcOEt. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo to give dihydrofuran **3b** (486 mg, 90.8%) as a colorless solid. Compound **3b**: colorless needles melted at 178.5–179.5 °C (from EtOH–hexane); (58:42 mixture of diastereomers) ^1H NMR (500 MHz, $CDCl_3$): δ_H 1.03 (s, 9H×0.58), 1.07 (s, 9H×0.42), 1.43 (s, 3H), 1.51 (s, 3H), 3.41 (s, 3H×0.42), 3.42 (s, 3H×0.58), 3.90 (s, 3H×0.42), 3.91 (s, 3H×0.58). 4.00 (d, *J*=8.2 Hz, 1H×0.42), 4.01 (d, *J*=7.8 Hz, 1H×0.58), 4.05 (d, *J*=7.8 Hz, 1H×0.58), 4.06 (d, *J*=8.2 Hz, 1H×0.42), 5.37 (s, 1H), 7.00–7.04 (m, 1H), 7.14–7.20 (m, 2H), 7.27 (d, *J*=6.9 Hz, 1H), 7.29–7.35 (m, 1H), 7.36 (d, *J*=9.2 Hz, 1H), 7.42–7.46 (m, 1H), 7.93 (d, *J*=8.2 Hz, 1H×0.58), 7.94 (d, *J*=7.8 Hz, 1H×0.42), 8.06 (d, *J*=9.2 Hz, 1H), 8.50 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 27.3, 27.5 and 27.6, 31.8 and 32.0, 32.6 and 32.7, 47.3, 52.4, 61.7 and 62.0, 83.2 and 83.3, 114.5, 118.3, 124.2 and 124.2, 125.1 and 125.3, 125.3, 125.4, 125.6 and 125.7, 125.8 and 125.9, 125.9 and 126.0, 127.8, 127.9 and 127.9, 128.3, 128.9, 129.1 and 129.2, 129.9 and 130.0, 133.7 and 133.8, 133.8, 133.9, 135.5 and 135.6, 147.9 and 148.0, 151.4, 155.0 and 155.1, 166.6 and 166.7 ppm. IR (KBr): $\tilde{\nu}$ 3427, 2954, 1678, 1618, 1452, 1365, 1307, 1237, 1052, 1006 cm^{-1}. Mass (*m/z*, %): 510 (M^+, 59), 496 (37), 495 (100), 480 (11), 407 (24). HRMS (ESI): 533.2292, calcd for $C_{33}H_{34}O_5Na$ (M+Na^+) 533.2304. Anal. Calcd for $C_{33}H_{34}O_5$: C, 77.62; H, 6.71. Found: C, 77.32; H, 6.71.

4.1.7. Synthesis of 4-*tert*-butyl-5-(2,2′-dihydroxy-3′-hydroxymethyl-1,1′-binaphthyl-5-yl)-3,3-dimethyl-2,3-dihydrofuran (10). A solution of 4-*tert*-butyl-5-(2,2′-dihydroxy-3′-methoxycarbonyl-1,1′-binaphthyl-5-yl)-3,3-dimethyl-2,3-dihydrofuran (**5**) (501 mg, 1.01 mmol) in dry THF (2 mL) was added dropwise to a suspension of $LiAlH_4$ (61.3 mg, 1.62 mmol) in dry THF (5 mL) under a nitrogen atmosphere at 0 °C and stirred for 2 h at room temperature. The reaction mixture was poured into 2 N HCl and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–CH_2Cl_2 (20:1) to give dihydrofuran **10** (411 mg, 86.9%) as a colorless solid. Compound **10**: colorless granules melted at 233.0–233.5 °C (from AcOEt); (55:45 mixture of diastereomers) ^1H NMR (500 MHz, $CDCl_3$): δ_H 1.06 (s, 9H), 1.43 (s, 3H×0.55), 1.44 (s, 3H×0.45), 1.50 (s, 3H×0.55), 1.52 (s, 3H×0.45), 2.52 (m, 1H), 3.92 (d, *J*=8.0 Hz, 1H×0.55), 3.97 (d, *J*=8.0 Hz, 1H×0.55), 4.00 (d, *J*=7.8 Hz, 1H×0.45), 4.05 (d, *J*=7.8 Hz, 1H×0.45), 4.84 (dd, *J*=13.3 and 6.0 Hz, 1H×0.45), 4.89 (d, *J*=10.1 Hz, 1H×0.55), 4.90 (d, *J*=10.1 Hz, 1H×0.55), 4.94 (dd, *J*=13.3 and 5.3 Hz, 1H×0.45), 5.16 (s, 1H×0.55), 5.19 (s, 1H×0.45), 7.04 (m, 2H), 7.21–7.24 (m, 2H), 7.28–7.38 (m, 2H), 7.38 (d, *J*=9.2 Hz, 1H×0.55), 7.39 (d, *J*=9.2 Hz, 1H×0.45), 7.82–7.85 (m, 1H), 7.86 (s, 1H×0.45), 7.88 (s, 1H×0.55), 8.08 (d, *J*=9.2 Hz, 1H×0.55), 8.08 (d, *J*=9.2 Hz, 1H×0.45) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.3, 27.6 and 27.7, 32.0 and 32.1, 32.7, 47.4, 62.6 and 62.9, 83.2 and 83.3, 111.2 and 111.4, 111.6 and 112.0, 118.1 and 118.2, 124.1 and 124.3, 124.4 and 124.5, 124.9 and 125.0, 126.3 and 126.4, 126.6 and 126.7, 127.3, 128.1, 128.1 and 128.3, 128.2 and 128.4, 128.5, 129.0, 129.1 and 129.2, 129.3, 133.0 and 133.3, 133.5 and 133.6, 134.1 and 134.1, 147.6 and 147.8, 151.2 and 151.4, 152.5 and 152.6 ppm. IR (KBr): $\tilde{\nu}$ 3405, 2957, 1618, 1391, 1208, 1047 cm^{-1}. Mass (*m/z*, %): 468 (M^+, 60), 454 (36), 453 (100), 451 (13), 420 (14), 403 (14), 379 (26). HRMS (ESI): 491.2185, calcd for

$C_{31}H_{32}O_4Na$ ($M+Na^+$) 491.2198. Anal. Calcd for $C_{31}H_{32}O_4$: C, 79.46; H, 6.88. Found: C, 79.27; H, 6.75.

4.1.8. Synthesis of 4-*tert*-butyl-5-[2-hydroxy-1-(2,2,-dimethyl-1,3-dioxa-1,2,3,4-tetrahydroanthracen-9-yl)-naphthalen-5-yl]-3,3-dimethyl-2,3-dihydrofuran (3d). Pyridinium *p*-toluenesulfonate (PPTS) (54.1 mg, 0.215 mmol) was added to a solution of 4-*tert*-butyl-5-(2,2′-dihydroxy-3′-hydroxymethyl-1,1′-binaphthyl-5-yl)-3,3-dimethyl-2,3-dihydrofuran (**10**) (1.01 g, 2.16 mmol) and acetone dimethyl acetal (0.32 mL, 2.6 mmol) in acetone (10 mL) under a nitrogen atmosphere at 0 °C and stirred for 1 h at refluxing temperature. The reaction mixture was poured into satd aq $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–CH_2Cl_2 (1:30) to give dihydrofuran **3d** (1.03 g, 93.5%) as a colorless solid. Compound **3d**: yellow plates melted at 182.5–183.0 °C (from AcOEt–hexane); (55:45 mixture of diastereomers) ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.04 (s, 9H×0.45), 1.07 (s, 9H×0.55), 1.35 (s, 3H), 6.38 (s, 3H×0.45), 1.40 (s, 3H×0.55), 1.43 (s, 3H), 1.51 (s, 3H), 4.00 (d, J=8.2 Hz, 1H×0.45), 4.00 (d, J=7.8 Hz, 1H×0.55), 4.05 (d, J=7.8 Hz, 1H×0.55), 4.06 (d, J=8.2 Hz, 1H×0.45), 4.97 (s, 1H), 5.10 (q_{AB}, J=15.8 Hz, 2H×0.55), 5.10 (q_{AB}, J=15.1 Hz, 2H×0.45), 7.02–7.05 (m, 1H), 7.11–7.17 (m, 2H), 7.19–7.23 (m, 1H), 7.24 (d, J=6.9 Hz, 1H), 7.30–7.32 (m, 1H), 7.34 (d, J=9.2 Hz, 1H), 7.61 (s, 1H), 7.76 (d, J=8.2 Hz, 1H×0.45), 7.77 (d, J=8.2 Hz, 1H×0.55), 8.01 (d, J=9.2 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 24.1 and 24.3, 25.2 and 25.3, 27.3 and 27.4, 27.5 and 27.6, 31.9 and 32.0, 32.7, 47.3 and 47.3, 61.1 and 61.2, 83.2 and 83.3, 100.2 and 100.3, 114.3 and 114.4, 114.8 and 115.0, 117.8 and 117.8, 121.3 and 121.3, 124.2 and 124.3, 124.6 and 124.7, 124.8 and 124.8, 125.3 and 125.4, 125.5, 125.5 and 125.7, 126.7, 127.6 and 127.6, 127.7 and 127.7, 127.7, 127.9 and 127.9, 128.6, 133.1 and 133.2, 133.5, 133.8, 148.2 and 148.2, 148.7 and 148.8, 151.2 and 151.3 ppm. IR (KBr): $\tilde{\nu}$ 2955, 1614, 1371, 1275, 1051 cm^{-1}. Mass (*m*/*z*, %): 508 (M^+, 33), 451 (42), 450 (100), 436 (29), 435 (63), 420 (16), 403 (20), 379 (14). HRMS (ESI): 531.256, calcd for $C_{34}H_{36}O_4Na$ ($M+Na^+$) 531.2511. Anal. Calcd for $C_{34}H_{36}O_4$: C, 80.28; H, 7.13. Found: C, 79.94; H, 7.10.

4.1.9. Synthesis of 4-*tert*-butyl-5-(2′-hydroxy-3′-hydroxymethyl-2-methoxy-1,1′-binaphthyl-5-yl)-3,3-dimethyl-2,3-dihydrofuran (11). MeI (0.60 mL, 9.6 mmol) was added to a solution of 4-*tert*-butyl-5-[2-hydroxy-1-(2,2,-dimethyl-1,3-dioxa-1,2,3,4-tetrahydroanthracen-9-yl)naphthalen-5-yl]-3,3-dimethyl-2,3-dihydrofuran (**3d**) (4.03 g, 7.92 mmol) and K_2CO_3 (1.64 g, 11.9 mmol) in dry DMF (40 mL) under a nitrogen atmosphere at room temperature and stirred for 9 h. The reaction mixture was poured into satd aq NH_4Cl and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:1) to give 4.13 g of 4-*tert*-butyl-5-[2-methoxy-1-(2,2,-dimethyl-1,3-dioxa-1,2,3,4-tetrahydroanthracen-9-yl)naphthalen-5-yl]-3,3-dimethyl-2,3-dihydrofuran as a colorless solid. The solid (4.13 g), ethylene glycol (5.0 mL, 90 mmol), and $TsOH\cdot H_2O$ (150 mg, 0.789 mmol) was dissolved in dry THF (40 mL) under a nitrogen atmosphere at room temperature and refluxed for 3 h. The reaction mixture was poured into satd aq $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:1) to give dihydrofuran **11** (3.54 g, 92.8%) as a colorless solid. Compound **11**: pale yellow granules melted at 206.0–207.0 °C (from MeOH–CH_2Cl_2); (52:48 mixture of diastereomers) ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.06 (s, 9H×0.48), 1.07 (s, 9H×0.52), 1.43 (s, 3H×0.48), 1.44 (s, 3H×0.52), 1.50 (s, 3H×0.48), 1.52 (s, 3H×0.52), 2.65 (br s, 1H), 3.74 (s, 3H×0.48), 3.75 (s, 3H×0.52), 3.95 (q_{AB}, J=8.0 Hz, 2H×0.48), 4.02 (q_{AB}, J=8.4 Hz, 2H×0.52), 4.86 (q_{AB}, J=13.3 Hz, 1H×0.52), 4.89 (q_{AB}, J=12.8 Hz, 1H×0.48), 5.70 (br s, 1H×0.48), 5.84 (br s, 1H×0.52), 6.95 (d, J=8.2 Hz, 1H×0.48), 7.10 (d, J=8.7 Hz, 1H×0.52), 7.10–7.23 (m, 3H), 7.25–7.31 (m, 2H), 7.48 (d, J=9.2 Hz, 1H×0.48), 7.49 (d, J=9.6 Hz, 1H×0.52), 7.77–7.81 (m, 2H), 8.17 (d, J=9.2 Hz, 1H×0.48), 8.18 (d, J=9.6 Hz, 1H×0.52) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.3 and 27.3, 27.6 and 27.7, 32.0 and 32.1, 32.7, 47.4, 56.5 and 56.6, 62.9 and 63.1, 83.2 and 83.3, 114.1, 115.5 and 115.6, 115.8, 123.4 and 123.5, 124.5 and 124.9, 125.5 and 125.7, 126.2 and 126.3, 126.4, 126.4 and 126.5, 127.6, 127.9 and 128.1, 128.1 and 128.2, 128.2 and 128.3, 128.6 and 128.7, 128.8 and 128.9, 133.4 and 133.5, 133.8, 133.8, 134.0 and 134.1, 147.8 and 147.9, 149.9 and 150.0, 155.7 and 155.8 ppm. IR (KBr): $\tilde{\nu}$ 3364, 2954, 2866, 1613, 1508, 1395, 1264, 1215, 1085, 1049 cm^{-1}. Mass (*m*/*z*, %): 482 (M^+, 97), 481 (11), 480 (13), 468 (37), 467 (100), 466 (12), 465 (21), 452 (10), 449 (12), 434 (11), 403 (20), 394 (12), 393 (30), 374 (15), 370 (11), 279 (13), 239 (11), 57 (21). HRMS (ESI): 505.2330, calcd for $C_{32}H_{34}O_4Na$ ($M+Na^+$) 505.2355. Anal. Calcd for $C_{32}H_{34}O_4$: C, 79.64; H, 7.10. Found: C, 79.39; H, 7.07.

4.1.10. Synthesis of 4-*tert*-butyl-5-[3′-hydroxymethyl-2-methoxy-2′-(2-methoxyethoxy)-1,1′-binaphthyl-5-yl]-3,3-dimethyl-2,3-dihydrofuran (12). 2-Methoxyethyl bromide (0.65 mL, 6.9 mmol) was added to a solution of 4-*tert*-butyl-5-(2′-hydroxy-3′-hydroxymethyl-2-methoxy-1,1′-binaphthyl-5-yl)-3,3-dimethyl-2,3-dihydrofuran (**11**) (2.78 g, 5.76 mmol) and K_2CO_3 (1.30 g, 9.41 mmol) in dry DMF (30 mL) under a nitrogen atmosphere at room temperature and stirred for 12 h. The reaction mixture was poured into satd aq NH_4Cl and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:1) to give dihydrofuran **12** (2.87 g, 92.2%) as a colorless solid. Compound **12**: colorless granules melted at 150.5–151.0 °C (from AcOEt–hexane); (52:48 mixture of diastereomers) ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.02 (s, 9H×0.52), 1.06 (s, 9H×0.48), 1.44 (s, 3H), 1.51 (s, 3H×0.52), 1.52 (s, 3H×0.42), 3.12–3.30 (m, 2H), 3.23 (s, 3H×0.52), 3.27 (s, 3H×0.48), 3.34–3.43 (m, 1H), 3.48–3.56 (m, 1H), 3.75 (s, 3H), 4.03 (q_{AB}, J=8.0 Hz, 2H×0.52), 4.04 (q_{AB}, J=7.3 Hz, 2H×0.48), 4.36 (t, J=7.1 Hz, 1H×0.48), 4.67 (t, J=7.1 Hz, 1H×0.52), 4.81–4.90 (m, 2H), 7.04–7.22 (m, 4H), 7.27 (d, J=6.4 Hz, 1H), 7.32–7.35 (m, 1H), 7.46 (d, J=9.6 Hz, 1H), 7.82 (d, J=8.2 Hz, 1H), 7.84 (s, 1H×0.48), 7.85 (s, 1H×0.52), 8.14 (d, J=9.2 Hz,

1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.2, 27.6 and 27.7, 31.8 and 31.9, 32.6 and 32.6, 47.3, 56.4 and 56.5, 58.5 and 58.6, 62.6 and 62.7, 71.3, 71.7 and 71.9, 83.3 and 83.3, 113.7 and 113.9, 119.3 and 119.4, 123.1 and 123.4, 124.5 and 124.6, 124.9 and 125.2, 126.0, 126.0, 126.0, 126.1 and 126.1, 127.8, 127.8 and 127.9, 128.0 and 128.1, 128.1, 128.9 and 129.1, 133.4 and 133.4, 133.9, 133.9 and 133.9, 134.0 and 134.2, 148.0 and 148.0, 154.3 and 154.8, 154.9, 154.9 ppm. IR (KBr): $\tilde{\nu}$ 3488, 2955, 2865, 1648, 1611, 1509, 1361, 1263, 1104, 1050 cm^{-1}. Mass (*m*/*z*, %): 540 (M^+, 100), 526 (16), 525 (37), 492 (15), 462 (10), 403 (18), 59 (16), 57 (12). HRMS (ESI): 563.2753, calcd for $C_{35}H_{40}O_5Na$ (M+Na^+) 563.2773. Anal. Calcd for $C_{35}H_{40}O_5$: C, 77.75; H, 7.46. Found: C, 77.67; H, 7.38.

4.1.11. Synthesis of 4-*tert*-butyl-5-[2-hydroxy-3′-hydroxymethyl-2′-(2-methoxyethoxy)-1,1′-binaphthyl-5-yl]-3,3-dimethyl-2,3-dihydrofuran (3e). Sodium methanethiolate (95%, 750 mg, 10.2 mmol) was added to a solution of 4-*tert*-butyl-5-[3′-hydroxymethyl-2-methoxy-2′-(2-methoxyethoxy)-1,1′-binaphthyl-5-yl]-3,3-dimethyl-2,3-dihydrofuran (**12**) (2.87 g, 5.33 mmol) in dry DMF (30 mL) under a nitrogen atmosphere at room temperature and stirred at 135 °C for 1 h. The reaction mixture was poured into satd aq $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1:1) to give dihydrofuran **3e** (1.65 g, 58.8%) as a colorless solid. Compound **3e**: colorless granules melted at 178.0–179.0 °C (from MeOH–CH_2Cl_2); (50:50 mixture of diastereomers) ^1H NMR (500 MHz, $CDCl_3$): δ_H 1.00 (s, 9H×0.50), 1.05 (s, 9H×0.50), 1.43 (s, 3H), 1.51 (s, 3H×0.50), 1.52 (s, 3H×0.50), 3.11–3.15 (m, 1H×0.50), 3.20–3.27 (m, 1H×0.50), 3.21 (s, 3H×0.50), 3.24 (s, 3H×0.50), 3.29–3.39 (m, 1H), 3.42–3.52 (m, 2H), 4.03 (q_{AB}, J=7.8 Hz, 2H×0.5), 4.04 (q_{AB}, J=7.8 Hz, 2H×0.50), 4.50 (t, J=7.1 Hz, 1H×0.50), 4.75 (t, J=7.1 Hz, 1H×0.50), 4.78–4.84 (m, 2H), 5.64 (s, 1H×0.50), 5.65 (s, 1H×0.50), 7.09–7.28 (m, 5H), 7.34 (d, J=9.2 Hz, 1H), 7.37–7.40 (m, 1H), 7.83 (d, J=8.2 Hz, 1H), 7.86 (d, J=2.7 Hz, 1H), 8.04 (d, J=9.2 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.3, 27.6 and 27.7, 31.8 and 31.9, 32.6 and 32.7, 47.3, 58.6 and 58.7, 62.3 and 62.4, 71.5 and 71.6, 71.7 and 71.8, 83.3 and 83.4, 115.0 and 115.2, 118.0 and 118.1, 121.0 and 120.3, 124.6 and 125.0, 125.2 and 125.3, 125.6, 125.8 and 125.9, 126.1 and 126.2, 126.8 and 126.9, 127.7 and 127.8, 128.0 and 128.2, 128.1, 128.3 and 128.4, 130.2 and 130.5, 130.7 and 130.8, 133.6, 133.7, 133.8, 134.3 and 134.5, 147.9 and 148.0, 151.5 and 151.6, 155.5 and 155.9 ppm. IR (KBr): $\tilde{\nu}$ 3379, 3284, 2955, 2865, 1647, 1617, 1468, 1396, 1300, 1237, 1129, 1105 cm^{-1}. Mass (*m*/*z*, %): 526 (M^+, 100), 512 (26), 511 (66), 493 (10), 478 (17), 448 (10), 435 (11), 420 (16), 419 (12), 405 (14), 403 (19), 239 (10), 59 (36), 57 (17). HRMS (ESI): 549.2612, calcd for $C_{34}H_{38}O_5Na$ (M+Na^+) 549.2617. Anal. Calcd for $C_{34}H_{38}O_5$: C, 77.54; H, 7.27. Found: C, 77.83; H, 7.44.

4.2. Synthesis of bicyclic dioxetanes 2: general procedure

A solution of 5-(1,1′-binaphthyl-5-yl)-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran **3** (50–200 mg) and TPP (ca. 1 mg) in CH_2Cl_2 (3–10 mL) was irradiated externally with 940 W Na lamp under an oxygen atmosphere at 0 °C for 1–4 h. The photolysate was concentrated in vacuo. The residue was chromatographed on silica gel with CH_2Cl_2 to give a stereoisomeric mixture of 1-(1,1′-binaphthyl-5-yl)-5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane *cis*-**2** and *trans*-**2** as a colorless solid (cis:trans=64:36 for **2a**, 42:58 for **2b**, 48:52 for **2c**, 43:57 for **2d**, and 46:54 for **2e**) in 90–96% yields. The mixture was further separated into pure *cis*-**2** and pure *trans*-**2** by means of column chromatography (SiO_2).

4.2.1. 5-*tert*-Butyl-1-(2-hydroxy-1,1′-binaphthyl-5-yl)-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (2a). Compound *cis*-**2a**: colorless granules melted at 163.5–164.0 °C (from THF–AcOEt). ^1H NMR (500 MHz, $CDCl_3$): δ_H 0.96 (s, 9H), 1.33 (s, 3H), 1.69 (s, 3H), 4.13 (d, J=8.2 Hz, 1H), 4.73 (d, J=8.2 Hz, 1H), 4.90 (s, 1H), 7.17 (d, J=8.7 Hz, 1H), 7.23–7.33 (m, 3H), 7.35 (d, J=8.5 Hz, 1H), 7.51 (dd with fine coupling, J=8.3 and 6.9 Hz, 1H), 7.57 (d, J=6.9 Hz, 1H), 7.66 (dd, J=8.3 and 6.9 Hz, 1H), 7.97 (d, J=8.3 Hz, 1H), 8.03 (d, J=8.3 Hz, 1H), 8.06–8.07 (m, 1H), 8.67 (br d, J=8.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.1, 26.3, 26.8, 36.9, 45.7, 80.6, 106.0, 117.2, 117.7, 119.5, 125.2, 125.8, 125.9, 126.6, 127.0, 127.4, 128.0, 128.2, 128.4, 129.4, 129.6, 131.5, 131.5, 132.9, 134.2, 134.9, 150.5 ppm. IR (KBr): $\tilde{\nu}$ 3512, 2978, 2893, 1613, 1473, 1385, 1264, 1203, 1038, 994 cm^{-1}. Mass (*m*/*z*, %): 454 (M^+, 44), 398 (30), 314 (33), 298 (22), 297 (100), 269 (23), 268 (15), 252 (12), 251 (13). HRMS (ESI): 477.2032, calcd for $C_{30}H_{30}O_4Na$ (M+Na^+) 477.2042. Anal. Calcd for $C_{30}H_{30}O_4$: C, 79.27; H, 6.65. Found: C, 79.00; H, 6.66. Compound *trans*-**2a**: colorless granules melted at 163.0–164.0 °C (from THF–AcOEt). ^1H NMR (500 MHz, $CDCl_3$): δ_H 0.98 (s, 9H), 1.32 (s, 3H), 1.69 (s, 3H), 4.11 (d, J=8.3 Hz, 1H), 4.73 (d, J=8.3 Hz, 1H), 4.87 (s, 1H), 7.18 (d, J=8.3 Hz, 1H), 7.25 (dd, J=8.3 and 7.3 Hz, 1H), 7.31–7.39 (m, 3H), 7.50 (d, J=6.7 Hz, 1H), 7.54 (dd, J=7.8 and 7.3 Hz, 1H), 7.66 (dd, J=8.3 and 6.7 Hz, 1H), 7.99 (d, J=8.3 Hz, 1H), 8.04 (d, J=7.8 Hz, 1H), 8.04–8.06 (m, 1H), 8.68–8.70 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.1, 26.2, 26.8, 36.9, 45.7, 80.6, 106.0, 117.2, 118.7, 119.4, 125.2, 125.6, 126.1, 126.6, 126.7, 127.0, 127.4, 127.9, 128.2, 128.6, 129.4, 129.8, 131.5, 131.5, 132.8, 134.2, 135.0, 150.5 ppm. IR (KBr): $\tilde{\nu}$ 3412, 2979, 2902, 1616, 1599, 1473, 1387, 1211, 1038 cm^{-1}. Mass (*m*/*z*, %): 454 (M^+, 35), 398 (26), 314 (31), 298 (24), 297 (100), 269 (24), 268 (13), 251 (12), 250 (13), 239 (23), 57 (22). HRMS (ESI): 509.2339, calcd for $C_{31}H_{34}O_5Na$ (M+Na^++MeOH) 509.2304. Anal. Calcd for $C_{30}H_{30}O_4$: C, 79.27; H, 6.65. Found: C, 78.98; H, 6.60.

4.2.2. 5-*tert*-Butyl-1-(2-hydroxy-2′-methoxy-3′-methoxycarbonyl-1,1′-binaphthyl-5-yl)-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (2b). Compound *cis*-**2b**: colorless plate melted at 170.0–171.0 °C (from AcOEt–hexane). ^1H NMR (500 MHz, $CDCl_3$): δ_H 0.91 (s, 9H), 1.32 (s, 3H), 1.68 (s, 3H), 3.42 (s, 3H), 3.96 (s, 3H), 4.14 (d, J=8.2 Hz, 1H), 4.75 (d, J=8.2 Hz, 1H), 5.14 (s, 1H), 7.13–7.17 (m, 2H), 7.25 (m, 1H), 7.36 (dd with fine coupling, J=9.6 and 6.9 Hz, 1H), 7.38 (d, J=9.6 Hz, 1H), 7.48 (dd with fine

coupling, J=8.3 and 6.9 Hz, 1H), 7.97 (d, J=8.3 Hz, 1H), 8.06–8.09 (m, 1H), 8.54 (s, 1H), 8.74–8.76 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.0, 26.1, 26.7, 36.8, 45.7, 52.5, 61.7, 80.6, 106.0, 115.1, 117.7, 117.7, 124.1, 125.2, 125.4, 125.5, 126.2, 126.8, 127.6, 127.7, 128.6, 129.1, 129.2, 130.0, 131.5, 134.1, 134.8, 135.5, 151.0, 155.1, 166.6 ppm. IR (KBr): $\tilde{\nu}$ 3406, 2960, 1704, 1620, 1269, 1224, 1003 cm^{-1}. Mass (*m*/*z*, %): 542 (M^+, 56), 510 (M^+-32, trace), 486 (12), 454 (13), 386 (28), 385 (100), 370 (23), 326 (19), 294 (15), 266 (24), 239 (13), 226 (12). HRMS (ESI): 565.2182, calcd for $C_{33}H_{34}O_7Na$ (M+Na^+) 565.2202. Anal. Calcd for $C_{33}H_{34}O_7$: C, 73.04; H, 6.32. Found: C, 72.76; H, 6.31. Compound *trans*-**2b**: colorless granules melted at 163.5–164.0 °C (from CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.97 (s, 9H), 1.33 (s, 3H), 1.69 (s, 3H), 3.43 (s, 3H), 3.98 (s, 3H), 4.13 (d, J=8.7 Hz, 1H), 4.74 (d, J=8.7 Hz, 1H), 5.10 (s, 1H), 7.12 (d, J=8.2 Hz, 1H), 7.16 (d, J=8.5 Hz, 1H), 7.20 (dd, J=8.5 and 7.0 Hz, 1H), 7.38 (d, J=9.6 Hz, 1H), 7.39 (dd, J=8.2 and 6.9 Hz, 1H), 7.50 (dd, J=8.2 and 6.9 Hz, 1H), 7.99 (d, J=8.2 Hz, 1H), 8.05–8.08 (m, 1H), 8.55 (s, 1H), 8.71–8.75 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.0, 26.2, 26.8, 36.9, 45.7, 52.5, 62.0, 80.6, 106.0, 115.1, 117.7, 124.0, 125.2, 125.4, 125.5, 126.1, 126.9, 127.6, 127.7, 128.7, 129.1, 129.3, 130.1, 131.6, 134.1, 134.8, 135.5, 151.0, 155.2, 166.6 ppm. IR (KBr): $\tilde{\nu}$ 3406, 2960, 1704, 1621, 1224, 1003 cm^{-1}. Mass (*m*/*z*, %): 542 (M^+, 45), 510 (M^+-32, trace), 486 (13), 454 (14), 386 (26), 385 (100), 326 (21), 297 (13), 294 (14), 278 (13), 266 (29), 239 (18), 226 (17), 57 (66). HRMS (ESI): 565.2199, calcd for $C_{33}H_{34}O_7Na$ (M+Na^+) 565.2202. Anal. Calcd for $C_{33}H_{34}O_7$+CH_2Cl_2 (3.0% w/w): C, 71.26; H, 6.20. Found: C, 70.97; H, 6.50.

4.2.3. 5-*tert*-Butyl-1-(3′-carboxy-2-hydroxy-2′-methoxy-1,1′-binaphthyl-5-yl)-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (2c). Compound *cis*-**2c**: colorless granules melted at 179.5–180.5 °C (from THF–hexane). ^{1}H NMR (400 MHz, acetone-d_6): δ_H 0.93 (s, 9H), 1.31 (s, 3H), 1.72 (s, 3H), 3.50 (s, 3H), 4.21 (d, J=8.2 Hz, 1H), 4.65 (d, J=8.2 Hz, 1H), 7.16–7.20 (m, 2H), 7.34 (dd, J=8.5 and 7.3 Hz, 1H), 7.42 (dd with fine coupling, J=8.3 and 6.8 Hz, 1H), 7.46 (d, J=9.3 Hz, 1H), 7.52 (dd with fine coupling, J=8.1 and 6.8 Hz, 1H), 7.99–8.02 (m, 1H), 8.12 (d, J=8.1 Hz, 1H), 8.61 (s, 1H), 8.79 (br d, J=9.3 Hz, 1H) ppm. ^{13}C NMR (125 MHz, acetone-d_6): δ_C 20.2, 26.2, 27.1, 37.5, 46.3, 61.7, 81.1, 106.6, 116.3, 118.4, 119.0, 125.8, 126.1, 126.2, 126.5, 126.9, 127.3, 127.6, 128.4, 129.2, 129.3, 130.0, 130.9, 132.6, 133.9, 136.2, 136.7, 153.5, 155.8, 167.3 ppm. IR (KBr): $\tilde{\nu}$ 3412, 3126, 2976, 2911, 1735, 1619, 1590, 1446, 1355, 1224, 1038 cm^{-1}. Mass (*m*/*z*, %): 528 (M^+, 25), 500 (14), 472 (14), 386 (15), 385 (42), 372 (28), 371 (100), 370 (19), 356 (15), 343 (26), 327 (18), 326 (28), 294 (17), 267 (20), 266 (27), 255 (16), 239 (26), 226 (23), 57 (55). HRMS (ESI): 551.2059, calcd for $C_{32}H_{32}O_7Na$ (M+Na^+) 551.2046. Anal. Calcd for $C_{32}H_{32}O_7$: C, 72.71; H, 6.10. Found: C, 72.32; H, 6.50. Compound *trans*-**2c**: colorless granules melted at 175.0–175.5 °C (from AcOEt–hexane). ^{1}H NMR (500 MHz, acetone-d_6): δ_H 0.96 (s, 9H), 1.31 (s, 3H), 1.73 (s, 3H), 3.54 (s, 3H), 4.18 (d, J=8.2 Hz, 1H), 4.63 (d, J=8.2 Hz, 1H), 7.15 (d, J=8.7 Hz, 1H), 7.19 (d, J=8.7 Hz, 1H), 7.33 (dd, J=8.7 and 7.3 Hz, 1H), 7.40 (dd with fine coupling, J=8.7 and 6.7 Hz, 1H), 7.46 (d, J=9.6 Hz, 1H), 7.52 (dd, J=7.8 and 6.7 Hz, 1H), 7.98–8.01 (m, 1H), 8.12 (d, J=7.8 Hz, 1H), 8.60 (s, 1H), 8.76–8.79 (m, 1H) ppm. ^{13}C NMR (125 MHz, acetone-d_6): δ_C 20.2, 26.3, 27.1, 37.5, 46.4, 61.9, 81.1, 106.7, 116.4, 117.3, 119.0, 125.8, 125.9, 126.3, 126.5, 127.0, 127.3, 127.6, 128.4, 129.2, 129.4, 130.1, 131.0, 132.8, 133.9, 136.2, 136.8, 153.5, 155.8, 167.3 ppm. IR (KBr): $\tilde{\nu}$ 3421, 3200, 2976, 2892, 1717, 1620, 1591, 1447, 1400, 1370, 1274, 1225, 1038 cm^{-1}. Mass (*m*/*z*, %): 528 (M^+, 37), 500 (23), 472 (17), 444 (15), 386 (23), 385 (68), 372 (26), 371 (100), 370 (31), 356 (14), 343 (46), 327 (23), 326 (34), 294 (22), 267 (19), 266 (40), 255 (21), 239 (30), 226 (30), 57 (95). HRMS (ESI): 551.2039, calcd for $C_{32}H_{32}O_7Na$ (M+Na^+) 551.2046. Anal. Calcd for $C_{32}H_{32}O_7$+H_2O (1.7% w/w): C, 71.49; H, 6.19. Found: C, 71.17; H, 6.30.

4.2.4. 5-*tert*-Butyl-1-[2-hydroxy-1-(2,2-dimethyl-1,3-dioxa-1,2,3,4-tetrahydro-anthracen-9-yl)naphthalen-5-yl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (2d). Compound *cis*-**2d**: colorless needles melted at 145.0–146.0 °C (from AcOEt–hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.91 (s, 9H), 1.32 (s, 3H), 1.35 (s, 3H), 1.38 (s, 3H), 1.67 (s, 3H). 4.13 (d, J=8.5 Hz, 1H), 4.75 (d, J=8.5 Hz, 1H), 4.84 (s, 1H), 5.16 (q_{AB} with fine coupling, J=15.1 Hz, 2H), 7.14–7.19 (m, 2H), 7.21–7.28 (m, 2H), 7.34 (d, J=9.3 Hz, 1H), 7.36 (dd with fine coupling, J=8.1 and 6.8 Hz, 1H), 7.69 (s, 1H), 7.82 (d, J=8.1 Hz, 1H), 8.02–8.05 (m, 1H), 8.69–8.73 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.0, 24.3, 25.2, 26.1, 26.7, 36.8, 45.7, 61.2, 80.6, 100.2, 106.0, 114.9, 115.0, 117.3, 117.8, 121.3, 124.4, 124.6, 124.8, 124.9, 126.8, 127.0, 127.3, 127.8, 127.9, 127.9, 128.6, 131.1, 133.0, 134.8, 148.8, 150.8 ppm. IR (KBr): $\tilde{\nu}$ 3500, 2993, 1617, 1371, 1135, 1039 cm^{-1}. Mass (*m*/*z*, %): 540 (M^+, 10), 539 (27), 482 (35), 481 (100), 425 (17), 382 (13), 341 (19), 326 (23), 325 (91), 324 (31), 297 (11), 296 (11), 239 (11), 57 (22). HRMS (ESI): 563.2413, calcd for $C_{34}H_{36}O_6Na$ (M+Na^+) 563.2410. Anal. Calcd for $C_{34}H_{36}O_4$+H_2O (2.5% w/w): C, 73.62; H, 6.82. Found: C, 73.26; H, 6.91. Compound *cis*-**2d**: colorless granules melted at 165.0–165.5 °C (from AcOEt–hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.97 (s, 9H), 1.33 (s, 3H), 1.36 (s, 3H), 1.41 (s, 3H), 1.70 (s, 3H), 4.13 (d, J=8.3 Hz, 1H), 4.74 (d, J=8.3 Hz, 1H), 4.88 (s, 1H), 5.16 (q_{AB} with fine coupling, J=15.4 Hz, 2H), 7.09 (d, J=8.3 Hz, 1H), 7.15 (d, J=8.4 Hz, 1H), 7.24 (dd, J=8.3 and 7.3 Hz, 1H), 7.26 (dd with fine coupling, J=8.4 and 7.3 Hz, 1H), 7.34 (d, J=9.5 Hz, 1H), 7.36 (dd with fine coupling, J=8.1 and 6.8 Hz, 1H), 7.69 (s, 1H), 7.82 (d, J=8.1 Hz, 1H), 8.00–8.04 (m, 1H), 8.66–8.68 (br d, J=9.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.1, 24.2, 25.3, 26.2, 26.8, 36.9, 45.7, 61.4, 80.6, 100.4, 105.9, 114.7, 115.1, 117.3, 117.8, 121.4, 124.3, 124.4, 124.9, 125.0, 126.8, 127.3, 127.8, 127.9, 128.0, 128.7, 131.3, 133.2, 134.8, 148.9, 150.8 ppm. IR (KBr): $\tilde{\nu}$ 3416, 2979, 1617, 1371, 1268, 1133, 1046 cm^{-1}. Mass (*m*/*z*, %): 540 (M^+, 9), 539 (24), 507 (10), 482 (34), 481 (95), 449 (35), 434 (23), 425 (17), 382 (14), 341 (20), 325 (27), 324 (100), 323 (35), 298 (10), 297 (15), 295 (11), 239 (12), 162 (12), 57 (33). HRMS (ESI): 595.2686, calcd for $C_{35}H_{40}O_7Na$ (M+Na^++MeOH) 595.2672. Anal. Calcd for $C_{34}H_{36}O_4$+AcOEt (2.0% w/w): C, 75.11; H, 6.76. Found: C, 74.81; H, 6.75.

4.2.5. 5-*tert*-Butyl-1-[2-hydroxy-3′-hydroxymethyl-2′-(2-methoxyethoxy)-1,1′-binaphthyl-5-yl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (2e). Compound *cis*-**2e**: colorless granules melted at 165.5–166.0 °C (from THF–MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.89 (s, 9H), 1.32 (s, 3H), 1.67 (s, 3H), 3.20 (ddd, *J*=10.8, 6.2, and 2.3 Hz, 1H), 3.05 (s, 3H), 3.30 (ddd, *J*=10.8, 6.0, and 2.3 Hz, 1H), 3.37 (ddd, *J*=10.8, 6.2, and 2.3 Hz, 1H), 3.45 (ddd, *J*=10.8, 6.0, and 2.3 Hz, 1H), 4.15 (br d, *J*=8.2 Hz, 1H), 4.48 (br s, 1H), 4.75 (d, *J*=8.2 Hz, 1H), 4.87 (m, 2H), 5.11 (s, 1H), 7.17 (d, *J*=8.2 Hz, 1H), 7.25 (dd, *J*=8.2 and 6.9 Hz, 1H), 7.30 (dd, *J*=8.2 and 6.9 Hz, 1H), 7.32 (d, *J*=8.2 Hz, 1H), 7.36 (d, *J*=9.6 Hz, 1H), 7.44 (dd with fine coupling, *J*=8.2 and 6.9 Hz, 1H), 7.90 (d, *J*=8.2 Hz, 1H), 7.95 (s, 1H), 8.08–8.10 (m, 1H), 8.75–8.78 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.0, 26.1, 26.8, 36.8, 45.7, 58.8, 62.5, 71.6, 71.7, 80.7, 105.9, 115.8, 117.5, 120.0, 124.8, 125.6, 125.8, 126.8, 127.2, 127.7, 127.9, 128.3, 128.7, 128.8, 130.7, 130.8, 131.4, 133.5, 134.6, 134.7, 151.1, 155.7 ppm. IR (KBr): $\tilde{\nu}$ 3307, 2961, 1618, 1516, 1400, 1335, 1234, 1104, 1040, 1020 cm^{-1}. Mass (*m*/*z*, %): 558 (M^+, 68), 540 (15), 402 (18), 401 (71), 339 (14), 372 (14), 342 (19), 325 (33), 324 (31), 297 (16), 296 (17), 269 (19), 239 (31), 59 (100), 57 (58). HRMS (ESI): 581.2503, calcd for $C_{34}H_{38}O_7Na$ (M+Na^+) 581.2515. Anal. Calcd for $C_{34}H_{38}O_7$: C, 73.10; H, 6.86. Found: C, 72.91; H, 6.70. Compound *trans*-**2e**: colorless granules melted at 165.0–166.0 °C (from THF–MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.96 (s, 9H), 1.33 (s, 3H), 1.69 (s, 3H), 3.25 (ddd, *J*=10.8, 5.8, and 2.3 Hz, 1H), 3.31 (s, 3H), 3.34 (ddd, *J*=10.8, 6.4, and 2.3 Hz, 1H), 3.27 (ddd, *J*=10.8, 6.4, and 2.3 Hz, 1H), 3.48 (ddd, *J*=10.8, 5.8, and 2.3 Hz, 1H), 4.13 (d, *J*=8.5 Hz, 1H), 4.69 (br s, 1H), 4.75 (d, *J*=8.5 Hz, 1H), 4.86 (s, 2H), 5.11 (s, 1H), 7.90 (d, *J*=8.7 Hz, 1H), 7.25–7.32 (m, 3H), 7.36 (d, *J*=9.6 Hz, 1H), 7.43 (dd with fine coupling, *J*=7.8 and 7.3 Hz, 1H), 7.90 (d, *J*=7.8 Hz, 1H), 7.95 (s, 1H), 8.07–8.10 (m, 1H), 8.73–8.75 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.0, 26.1, 26.8, 36.9, 45.7, 58.8, 62.5, 71.7, 71.8, 80.6, 106.0, 115.8, 117.5, 117.7, 119.9, 124.6, 125.4, 125.7, 126.8, 127.1, 127.7, 128.0, 128.3, 128.7, 130.8, 130.9, 131.5, 133.6, 134.7, 134.7, 151.1, 155.9 ppm. IR (KBr): $\tilde{\nu}$ 3421, 2976, 1618, 1474, 1400, 1370, 1234, 1106, 1038 cm^{-1}. Mass (*m*/*z*, %): 558 (M^+, 50), 402 (18), 401 (56), 339 (17), 372 (13), 342 (18), 325 (28), 324 (26), 298 (13), 297 (20), 296 (12), 269 (19), 252 (12), 239 (31), 141 (13), 59 (100). HRMS (ESI): 581.2511, calcd for $C_{34}H_{38}O_7Na$ (M+Na^+) 581.2515. Anal. Calcd for $C_{34}H_{38}O_7$+CH_3OH (2.1% w/w): C, 72.35; H, 6.98. Found: C, 72.02; H, 7.07.

4.3. Chemiluminescence measurement: general procedure

Chemiluminescence were measured using a Hamamatsu Photonics PMA-11 multi-channel detector and/or JASCO FP-750 spectrometer.

TBAF in DMSO (*system* ***A***): freshly prepared solution (2 mL) of TBAF (1.0×10^{-2} mol cm^{-3}) in DMSO was transferred to a quartz cell (10×10×50 mm) and the latter placed in the spectrometer, which was thermostated with stirring at 25 °C. After 3–5 min, a solution of the dioxetane in DMSO (1.0×10^{-5} mol cm^{-3}, 1 mL) was added by means of a syringe with immediate starting of measurement. The intensity of the light emission time-course was recorded and processed according to first-order kinetics. The total light emission was estimated by comparing it with that of an adamantylidene dioxetane, whose chemiluminescent efficiency Φ^{CTICL} has been reported to be 0.29 and was used here as a standard.[12]

[K⊂(18C6)]$^+$*t*-BuO$^-$ in PhH–THF (1:1) (*system* ***B***): *t*-BuOK (1.0 mol cm^{-3} in THF, 2 mL, 2 mmol) was added to a solution of 18-crown-6 ether (555 mg, 2.10 mmol) in dry benzene (10 mL) and dry THF (8 mL) at room temperature under a nitrogen atmosphere and stirred for 10 min. Chemiluminescence measurement using the solution of 18-crown–ether complex of *t*-BuOK in PhH–THF was carried out similarly to the case of *system* ***A***.

4.4. Isolation of keto esters 14 from the spent reaction mixture after chemiluminescent decomposition of dioxetanes 2: general procedure

A solution of the dioxetane **2** (20–30 mg) in DMSO (3 mL) was added to a solution of TBAF (1 M in THF, 0.1 mL) in DMSO (0.9 mL) at room temperature under nitrogen atmosphere. After stirring for 1 h, the reaction mixture was poured into satd aq NH_4Cl and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. ^{1}H NMR spectral analysis showed that the residue was comprised of keto ester **14** without detectable amount of other products. The residue was purified by column chromatography on silica gel with AcOEt–hexane to give the corresponding keto ester **14**.

4.4.1. 2,2,4,4-Tetramethyl-3-oxopentyl 2-hydroxy-1,1′-binaphthyl-5-carboxylate (14a). Colorless granules melted at 174.0–174.5 °C (from AcOEt–hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.29 (s, 9H), 1.43 (s, 6H), 4.50 (s, 2H), 5.06 (br s, 1H), 7.19–7.22 (m, 1H), 7.25–7.35 (m, 3H), 7.43 (d, *J*=9.6 Hz, 1H), 7.49–7.52 (m, 2H), 7.61–7.65 (m, 1H), 7.89 (d with fine coupling, *J*=6.9 Hz, 1H), 7.95 (d, *J*=8.2 Hz, 1H), 8.01 (d, *J*=8.2 Hz, 1H), 8.95 (d, *J*=9.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.7, 28.2, 45.9, 49.2, 72.3, 119.0, 119.1, 125.2, 125.6, 126.0, 126.6, 126.7, 126.9, 127.2, 127.3, 127.7, 128.5, 129.4, 129.6, 130.1, 131.2, 132.8, 134.1, 134.5, 151.1, 167.5, 216.1 ppm. IR (KBr): $\tilde{\nu}$ 3411, 2974, 1719, 1685, 1668, 1512, 1366, 1262, 1136 cm^{-1}. Mass (*m*/*z*, %): 454 (M^+, 56), 399 (10), 398 (33), 314 (39), 298 (33), 297 (100), 269 (27), 268 (16), 252 (13), 251 (14), 250 (18), 239 (29), 57 (39). HRMS (ESI): 509.2292, calcd for $C_{31}H_{34}O_5Na$ (M+Na^++MeOH) 509.2304. Anal. Calcd for $C_{30}H_{30}O_4$: C, 79.27; H, 6.65. Found: C, 78.86; H, 6.59.

4.4.2. 2,2,4,4-Tetramethyl-3-oxopentyl 2-hydroxy-2′-methoxy-3′-methoxycarbonyl-1,1′-binaphthyl-5-carboxylate (14b). Colorless granules melted at 149.0–149.5 °C (from AcOEt–hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.30 (s, 9H), 1.44 (s, 6H), 3.46 (s, 3H), 3.96 (s, 3H), 4.50 (q_{AB}, *J*=11.0 Hz, 2H), 5.31 (br s, 1H), 7.15 (d, *J*=8.7 Hz, 1H), 7.21–7.26 (m, 2H), 7.36 (dd with fine coupling, *J*=7.8 and 7.7 Hz, 1H), 7.47 (d, *J*=9.2 Hz, 1H), 7.48 (dd, *J*=7.7 and 6.9 Hz, 1H), 7.90 (d with fine coupling,

J=6.9 Hz, 1H), 7.97 (d, J=7.8 Hz, 1H), 8.55 (s, 1H), 8.78 (d, J=9.2 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.7, 23.8, 28.2, 45.9, 49.2, 52.5, 62.0, 72.3, 114.9, 119.5, 123.8, 125.2, 125.2, 125.5, 126.2, 126.9, 127.5, 127.5, 128.2, 129.1, 129.3, 129.8, 130.0, 134.2, 134.3, 135.5, 151.6, 155.2, 166.6, 167.4, 216.1 ppm. IR (KBr): $\tilde{\nu}$ 3431, 2955, 1716, 1687, 1620, 1446, 1365, 1308, 1251, 1136, 1061 cm^{-1}. Mass (*m*/*z*, %): 542 (M^+, 63), 486 (11), 454 (10), 386 (28), 385 (100), 370 (19), 326 (16), 294 (12), 266 (16), 57 (31). HRMS (ESI): 565.2186, calcd for $C_{33}H_{34}O_7Na$ (M+Na^+) 565.2202. Anal. Calcd for $C_{33}H_{34}O_7$: C, 73.04; H, 6.32. Found: C, 72.97; H, 6.30.

4.4.3. 2,2,4,4-Tetramethyl-3-oxopentyl 3′-carboxy-2-hydroxy-2′-methoxy-1,1′-binaphthyl-5-carboxylate (14c). Colorless amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.30 (s, 9H), 1.45 (s, 6H), 3.50 (s, 3H), 4.51 (s, 2H), 5.32 (br s, 1H), 7.22 (d, J=8.5 Hz, 1H), 7.25–7.31 (m, 2H), 7.45 (dd, J=8.1 and 6.8 Hz, 1H), 7.47 (d, J=9.5 Hz, 1H), 7.56 (dd, J=8.1 and 6.8 Hz, 1H), 7.93 (d with fine coupling, J=6.8 Hz, 1H), 8.05 (d, J=8.1 Hz, 1H), 8.93 (s, 1H), 9.04 (d, J=9.5 Hz, 1H), 11.2 (br s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 23.7, 23.7, 28.2, 45.9, 49.2, 62.5, 72.5, 113.8, 119.5, 121.0, 122.8, 125.2, 126.0, 126.9, 127.0, 127.7, 127.8, 129.0, 129.4, 130.1, 130.2, 130.5, 134.0, 136.2, 136.7, 151.7, 154.2, 165.6, 167.3, 216.1 ppm. IR (KBr): $\tilde{\nu}$ 3422, 3293, 2983, 1711, 1686, 1624, 1516, 1458, 1366, 1259, 1219, 1105 cm^{-1}. Mass (*m*/*z*, %): 528 (M^+, 39), 500 (25), 472 (17), 444 (14), 385 (79), 372 (25), 371 (100), 370 (25), 360 (17), 356 (14), 344 (23), 343 (47), 327 (29), 326 (32), 294 (20), 267 (20), 266 (34), 255 (26), 239 (22), 226 (34), 57 (82). HRMS (ESI): 551.2037, calcd for $C_{32}H_{32}O_7Na$ (M+Na^+) 551.2046. Anal. Calcd for $C_{32}H_{32}O_7$: C, 72.71; H, 6.10. Found: C, 72.39; H, 6.29.

4.4.4. 2,2,4,4-Tetramethyl-3-oxopentyl 6-hydroxy-5-(2,2-dimethyl-1,3-dioxa-1,2,3,4-tetrahydroanthracen-9-yl)-naphthalene-1-carboxylate (14d). Pale yellow amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.30 (s, 9H), 1.37 (s, 3H), 1.42 (s, 3H), 1.44 (s, 6H), 4.50 (q_{AB}, J=10.5 Hz, 2H), 5.05–5.06 (m, 1H), 5.12 (q_{AB}, J=15.3 Hz, 2H), 7.09 (d, J=8.5 Hz, 1H), 7.19 (dd, J=8.5 and 7.0 Hz, 1H), 7.21 (d with fine coupling, J=7.9 Hz, 1H), 7.26 (dd, J=8.2 and 7.0 Hz, 1H), 7.33 (dd, J=7.9 and 7.1 Hz, 1H), 7.44 (d, J=9.4 Hz, 1H), 7.65 (s, 1H), 7.79 (d, J=8.2 Hz, 1H), 7.88 (d with fine coupling, J=7.1 Hz, 1H), 8.94 (d, J=9.4 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.7, 23.7, 24.4, 25.1, 28.2, 45.9, 49.2, 61.1, 72.2, 100.4, 114.4, 114.7, 119.1, 121.3, 124.4, 124.5, 124.9, 125.0, 126.8, 127.0, 127.2, 127.3, 127.5, 127.8, 128.6, 130.0, 133.2, 134.4, 148.8, 151.5, 167.6, 216.0 ppm. IR (KBr): $\tilde{\nu}$ 3448, 2983, 2865, 1715, 1685, 1612, 1438, 1259, 1178, 1138, 1115 cm^{-1}. Mass (*m*/*z*, %): 540 (M^+, 20), 483 (34), 482 (88), 426 (21), 383 (12), 343 (20), 326 (26), 325 (100), 324 (33), 297 (14), 269 (12), 239 (13), 57 (15). HRMS (ESI): 563.2379, calcd for $C_{34}H_{36}O_6Na$ (M+Na^+) 563.2409. Anal. Calcd for $C_{34}H_{36}O_6$: C, 75.53; H, 6.71. Found: C, 75.21; H, 6.64.

4.4.5. 2,2,4,4-Tetramethyl-3-oxopentyl 2-hydroxy-3′-hydroxymethyl-2′-(2-methoxyethoxy)-1,1′-binaphthyl-5-carboxylate (14e). Colorless amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.30 (s, 9H), 1.44 (s, 3H), 1.45 (s, 3H), 3.23–3.28 (m, 1H), 3.25–3.26 (m, 3H), 3.33 (ddd, J=11.0, 6.0, and 2.3 Hz, 1H), 4.43 (ddd, J=11.0, 6.0, and 1.8 Hz, 1H), 3.51 (ddd, J=11.0, 6.4, and 2.3 Hz, 1H), 4.50 (s, 2H), 4.64 (dd, J=7.3 and 6.9 Hz, 1H), 4.79 (dd with fine coupling, J=12.4 and 7.3 Hz, 1H), 4.84 (dd, J=12.4 and 6.9 Hz, 1H), 5.7 (br s, 1H), 7.11 (d, J=8.2 Hz, 1H), 7.22–7.27 (m, 2H), 7.32 (d, J=8.7 Hz, 1H), 7.39–7.46 (m, 1H), 7.45 (d, J=9.6 Hz, 1H), 7.89 (d, J=8.2 Hz, 1H), 7.89–7.90 (m, 1H), 7.91 (s, 1H), 8.97 (d, J=9.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.7, 23.8, 28.2, 45.9, 49.2, 58.7, 62.4, 71.8, 71.8, 72.3, 115.5, 119.4, 119.9, 124.7, 125.4, 125.6, 126.9, 127.1, 127.4, 127.5, 128.2, 128.3, 130.1, 130.7, 130.8, 133.6, 134.3, 134.5, 151.8, 155.9, 167.5, 216.1 ppm. IR (KBr): $\tilde{\nu}$ 3422, 2958, 2874, 1716, 1685, 1514, 1475, 1254, 1198, 1254, 1143, 1107, 1047 cm^{-1}. Mass (*m*/*z*, %): 558 (M^+, 61), 540 (12), 402 (19), 401 (61), 372 (12), 343 (10), 342 (15), 326 (13), 325 (29), 324 (27), 297 (10), 296 (11), 269 (11), 268 (11), 239 (18), 59 (100), 57 (45). HRMS (ESI): 581.2480, calcd for $C_{34}H_{38}O_7Na$ (M+Na^+) 581.2515. Anal. Calcd for $C_{34}H_{38}O_7$: C, 73.10; H, 6.86. Found: C, 73.17; H, 6.63.

4.5. Fluorescence measurement: general procedure

Freshly prepared solution of 2.05–2.10×10^{-5} mol dm^{-3} of **14a**–**14e** and of 1.0×10^{-2} mol dm^{-3} of TBAF in DMSO was transferred to a quartz cell (10×10×50 mm) and the latter placed in the spectrometer, which was thermostated with stirring at 25 °C. Thus, the fluorescence spectra of **14a**–**14e** were measured by means of JASCO FP-750. The fluorescence of **14a**–**14e** in 18-crown- ether complex of *t*-BuOK in PhH–THF system was measured similarly to the case of TBAF in DMSO.

4.6. X-ray single crystallographic analysis of dioxetanes

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.[†] The structure was solved by direct method (SHELX97)[‡] 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 6532 observed reflections and 390 variable parameters (for **2a**), on 6312 observed reflections and 395 variable parameters (for **2b**), on 7001 observed reflections and 446 variable parameters (for **2c**), on 13,200 observed reflections and 846 variable parameters (for **2d**), and on 7345 observed reflections and 461 variable parameters (for **2e**). All calculations were performed using the CrystalStructure crystallographic software package.[§,¶]

[†] Rigaku Corporation, 1999.
[‡] Sheldrick, G. M. University of Gottingen, Gottingen, Germany, 1997.
[§] CrystalStructure 3.6.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC(2000–2003). 9009 New Trails Dr. The Woodlands, TX 77381, USA.
[¶] CRYSTALS Issue 10: Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. Chemical Crystallography Laboratory, Oxford, UK, 1996.

Crystal data for compound *cis*-**2a**: $C_{30}H_{30}O_4 \cdot C_4H_8O$ (M_r=526.67), colorless platelet (recrystallized from THF), 0.30×0.20×0.08 mm, orthorhombic, space group *Pccn* (#56), a=23.64(3) Å, b=22.72(1) Å, c=10.635(8) Å, V=5712.5(89) Å^3, Z=8, ρ_{calcd}=1.225 g cm^{-3}, T=150 K, $2\theta_{max}$=55.0°, F(000)=2256.00, reflections collected/unique 58,346/6532 (R_{int}=0.083), μ(Mo Kα)=0.81 cm^{-1}. An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.8818 to 1.0000. The data were corrected for Lorentz and polarization effects. Final R indices $R1$=0.093 [$I>2\sigma(I)$], $wR2$=0.208 (all data), GOF on F^2=0.768, and residual electron density 0.35/−0.32 eÅ^{-3}.

Crystal data for compound *cis*-**2b**: $C_{33}H_{34}O_7$ (M_r=542.63), colorless platelet (recrystallized from dioxane), 0.30×0.20×0.15 mm, monoclinic, space group $C2/c$ (#15), a=29.96(2) Å, b=12.904(6) Å, c=14.57(2) Å, β=96.138(8)°, V=5601.5(76) Å^3, Z=8, ρ_{calcd}=1.287 g cm^{-3}, T=150 K, $2\theta_{max}$=55.0°, F(000)=2304.00, reflections collected/unique 29,440/6312 (R_{int}=0.038), μ(Mo Kα)=0.90 cm^{-1}. An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.8452 to 1.0000. The data were corrected for Lorentz and polarization effects. Final R indices $R1$=0.063 [$I>2\sigma(I)$], $wR2$=0.196 (all data), GOF on F^2=1.002, and residual electron density 0.40/−0.39 eÅ^{-3}.

Crystal data for compound *cis*-**2c**: $C_{32}H_{32}O_7 \cdot C_4H_8O_2$ (M_r=616.71), colorless prism (recrystallized from dioxane), 0.20×0.10×0.10 mm, triclinic, space group P-1 (#2), a=8.12(2) Å, b=13.40(2) Å, c=15.06(2) Å, α=89.43(9)°, β=77.95(8)°, γ=82.12(8)°, V=1587.1(46) Å^3, Z=2, ρ_{calcd}=1.290 g cm^{-3}, T=120 K, $2\theta_{max}$=55.0°, F(000)=656.00, reflections collected/unique 16,809/7001 (R_{int}=0.046), μ(Mo Kα)=0.92 cm^{-1}. An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.8462 to 1.0000. The data were corrected for Lorentz and polarization effects. Final R indices $R1$=0.059 [$I>2\sigma(I)$], $wR2$=0.151 (all data), GOF on F^2=1.003, and residual electron density 0.62/−0.70 eÅ^{-3}.

Crystal data for compound *trans*-**2d**: $C_{34}H_{36}O_6 \cdot 0.5(C_4H_8O)$ (M_r=576.71), colorless prism (recrystallized from THF), 0.30×0.25×0.10 mm, triclinic, space group P-1 (#2), a=10.930(11) Å, b=16.31(2) Å, c=18.60(3) Å, α=107.22(3)°, β=98.74(3)°, γ=102.62(3)°, V=3004.5(66) Å^3, Z=4, ρ_{calcd}=1.275 g cm^{-3}, T=150 K, $2\theta_{max}$=55.0°, F(000)=1232.00, reflections collected/unique 31,765/13,200 (R_{int}=0.039), μ(Mo Kα)=0.86 cm^{-1}. An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.8740 to 1.0000. The data were corrected for Lorentz and polarization effects. Final R indices $R1$=0.065 [$I>2\sigma(I)$], $wR2$=0.162 (all data), GOF on F^2=1.017, and residual electron density 0.38/−0.30 eÅ^{-3}.

Crystal data for compound *cis*-**2e**: $C_{34}H_{38}O_7 \cdot C_4H_8O$ (M_r=630.78), colorless prism (recrystallized from THF), 0.20×0.10×0.10 mm, triclinic, space group P-1 (#2), a=10.193(5) Å, b=11.647(12) Å, c=14.59(2) Å, α=88.59(8)°, β=77.07(7)°, γ=85.02(8)°, V=1681.9(31) Å^3, Z=2, ρ_{calcd}=1.245 g cm^{-3}, T=150 K, $2\theta_{max}$=55.0°, F(000)=676.00, reflections collected/unique 17,692/7345 (R_{int}=0.038), μ(Mo Kα)=0.86 cm^{-1}. An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.8324 to 1.0000. The data were corrected for Lorentz and polarization effects. Final R indices $R1$=0.067 [$I>2\sigma(I)$], $wR2$=0.173 (all data), GOF on F^2=1.013, and residual electron density 0.51/−0.46 eÅ^{-3}.

Crystallographic data for the structural analysis of compounds *cis*-**2a**, *cis*-**2b**, *cis*-**2c**, *trans*-**2d**, and *cis*-**2e** have been deposited at the Cambridge Crystallographic Data Center, CCDC-617817 (for *cis*-**2a**), −617818 (for *cis*-**2b**), −620734 (for *cis*-**2c**), −617819 (for *trans*-**2d**), and −617820 (for *cis*-**2e**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033 or deposit@ccdc.cam.au.uk).

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