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Synthesis of 3,3-Diisopropyl-4-methoxy-4-(siloxy-2-naphthyl)-1,2-dioxetanes and their F$^-$-Induced Chemiluminescent Decomposition

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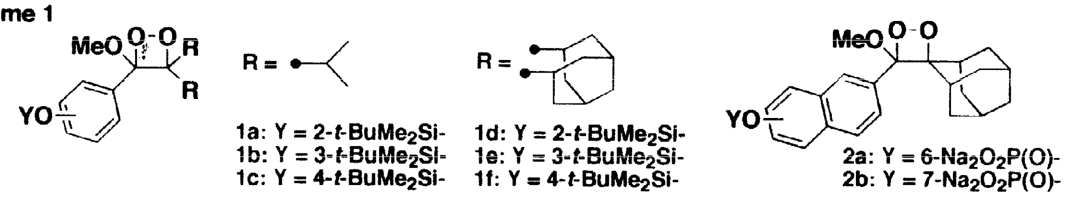
Abstract: Six isomeric 3,3-diisopropyl-4-methoxy-4-(siloxy-2-naphthyl)-1,2-dioxetanes (**3**) were synthesized and their F$^-$-induced chemiluminescencent decomposition were examined in DMSO. The '*odd/even*' relationship in Φ_{CL} holds for all the dioxetanes (**3**). On the other hand, the '*odd/even*' relationship in emission half-lives $t_{1/2}$ is observed for dioxetanes (**3c**-**3f**) with a trigger on the ring **B** but not for dioxetanes (**3a** and **3b**) with a trigger on the ring **A**. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: 3-(2-naphtyl)-1,2-dioxetane, CIEEL, odd / even relationship

Charge transfer-induced decomposition of a 1,2-dioxetane bearing an electron donor has recently received considerable attention because of its potential leading to highly efficient chemiluminescence.[1-3] A dioxetane substituted with a phenolic group forms after deprotonation or deprotection an unstable dioxetane bearing an oxyphenyl anion which acts as an electron donor for the chemiluminescent decomposition[2,3] by the CIEEL (chemically initiated electron exchange luminescence) mechanism.[4,5] The position of an oxyanion on the aryl ring relative to the attachment point to the dioxetane influences significantly the chemiluminescent properties and an '*odd/even*' relationship[6,7] has been observed for dioxetanes bearing a phenolic moiety (**1**); **1b** and **1e** with an *odd(meta)*-pattern give more intense but longer half-life emission than **1c** and **1f** with an *even (para)*-pattern and its *ortho* (*even*)-isomer.[3,8-11] The '*odd/even*' relationship has been reported to hold also for dioxetanes (**2a**, **2b**) bearing a naphthol moiety.[7,12] These facts bring on a rather simple but important aspect of the synthesis, namely whether a CIEEL-active dioxetane emitting light with high efficiency as well as short half-life can be realized by designing a fluorescent electron donor. To know more detailed features of the relationship between the chemiluminescent properties of a dioxetane bearing an oxyphenyl and the position of an oxyanion on the aryl ring, we attempted to synthesize various 3-[(*tert*-butyldimethylsiloxy)-2-naphthyl]-4,4-diisopropyl-3-methoxy-1,2-dioxetanes (**3**) and examine their F$^-$-induced chemiluminescent decomposition.[13,14]

Scheme 1



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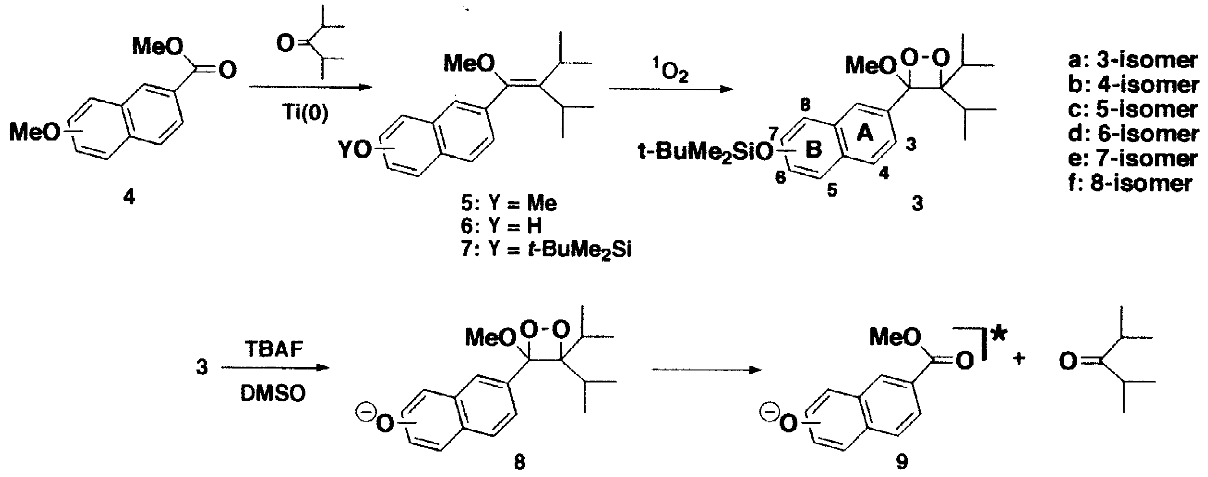
Results and Discussion

First, we planned to synthesize all seven isomers of 3,3-diisopropyl-4-methoxy-1,2-dioxetanes (**3**) bearing a *tert*-butyldimethylsiloxy-2-naphthyl group from the corresponding naphthylethylenes (**7**) by means of the low temperature-singlet oxygenation, which has been recently proven to be effective for the transformation of the phenyl-analogue of **7** to dioxetanes (**1a** - **1c**).[8-10] The ethylenes (**7**) were easily synthesized in three steps starting from methyl methoxy-2-naphthoates (**4**); McMurry reductive coupling[15,16] of **4** with diisopropyl ketone afforded ethylenes (**5**), which were, in turn, demethylated and the resulting naphthols (**6**) were silylated successively to give **7** as illustrated in **Scheme 2**. Thus, all the desired key intermediates (**7**) were successfully synthesized, except the 1-siloxy-2-naphthyl analogue, whose synthesis could not be attained, because McMurry coupling of 1-methoxy-analogue of **4** with diisopropyl ketone afforded little of the corresponding ethylene but gave an ethylene bearing an unsubstituted 2-naphthyl. When a solution of ethylene (**7a**) (100 mg) and tetraphenylporphin (TPP) (1.5 mg) in CH_2Cl_2 (10 mL) was externally irradiated with a Na lamp (180 W) under an oxygen atmosphere at - 78 °C for 2 h, a dioxetane (**3a**) was produced and isolated by chromatography on silica gel in 58 % yield. The other ethylenes (**7b**-**7f**) were similarly oxygenated with singlet oxygen to give the corresponding dioxetanes (**3b**-**3f**) in 42 - 78 % yield.

Scheme 2



The siloxyphenyl-substituted dioxetanes (**1**) are triggered with tetrabutylammonium fluoride (TBAF) in aprotic solvent such as DMSO and acetonitrile; desilylation of **1** with fluoride affords an unstable phenolate-substituted dioxetane, which decomposes rapidly by CIEEL process.[3, 8-10] It has been very recently reported for the fluoride-triggered CIEEL process of a siloxyphenyl-substituted dioxetane (**1e**) that the CIEEL decay rate of dioxetane depends on both the TBAF concentration and the substrate concentration, though it follows pseudo-first-order kinetics independent of the TBAF concentration when an excess of fluoride concentration is used.[17] Naphthyl-substituted dioxetanes (**3**) decomposed also in TBAF / DMSO system through unstable naphtholate-substituted dioxetanes (**8**) into esters (**9**) to emit light. To know half-life $t_{1/2}$ = ln 2 / k (k: rate constant) as well as emission maximum λ_{max} and chemiluminescent efficiency Φ_{CL} for CIEEL decay of **3**, F$^-$-induced decomposition of **3** were carried out under the conditions using a large excess of TBAF where the decomposition of **3** follows pseudo-first-order process. Among the dioxetanes synthesized here, **3a** and **3b** possess a trigger (*tert*-butyldimethylsiloxy group) on the benzene ring (ring **A**) attached directly to the dioxetane and their formal structures resemble that of **1a** and **1b** with respect to the positional relationship between a trigger and the attachment point to the dioxetane ring. When solutions of **3a** or **3b** in DMSO (1.0×10^{-5} mol dm^{-3}, 1mL) were added to a TBAF solution in DMSO (1.0×10^{-2} mol dm^{-3}, 2mL) at 25 °C, **3a** decomposed to emit weak blue light with λ_{max} = 460 nm, $\Phi_{CL} = 2.7 \times 10^{-4}$, and $t_{1/2}$ = 7.3 s, while **3b** afforded intense flash light with λ_{max} = 496 nm, $\Phi_{CL} = 5.2 \times 10^{-2}$, and $t_{1/2}$ = 0.076 s. These results show that the '*odd/even*' relationship as observed for **1a** and **1b**[8-10] does not hold for **3a** and **3b**; the reverse tendency was observed for $t_{1/2}$: **1b** >> **1a**, but **3b** << **3a**, though a similar tendency was observed for Φ_{CL}: **1b** >> **1a**, and **3b** >> **3a**.

Table 1 F⁻-Induced chemiluminescence of 3,3-diisopropyl-4-methoxy-4-(siloxy-2-naphthyl)-1,2-dioxetanes (3)[a)]

Dioxetane	Substitution pattern	λ_{max} / nm	Φ_{CL}[b)]	$t_{1/2}$ / s	k / s^{-1}	HOMO Electron density at Cα[c)]
3a	*even*	460	2.7×10^{-4}	7.3	0.095	0.275
3b	*odd*	496	5.2×10^{-2}	0.076	9.1	0.059
3c	*odd*	628[d)]	7.4×10^{-3}	4.8	0.14	0.056
3d	*even*	470[e)]	3.2×10^{-6}	0.15	4.6	0.358
3e	*odd*	558	5.6×10^{-2}	250	0.0028	0.014
3f	*even*	560	3.7×10^{-4}	0.24	2.9	0.297

a) Measured at 25 °C. Unless otherwise stated, a solution of a dioxetane (**3**) in DMSO (1.0×10^{-5} mol dm^{-3}, 1mL) was added to a TBAF solution in DMSO (1.0×10^{-2} mol dm^{-3}, 2 mL). b) Relative quantum yield based on the value for **1e** (ref 3): λ_{max} = 470 (465) nm, Φ_{CL} = 0.25, $t_{1/2}$ = 5 (5) s; values in parentheses were obtained in the present work. A very recent work has reported Φ_{CL} = 0.29 for **1e**.[17] c) AM1 calculation reported for oxy-anions of 1- and 2-naphthols in ref 18. d) A value reported in ref 14 is revised. e) A dioxetane (**3d**) (1.0×10^{-3} mol dm^{-3}, 1 mL) and TBAF (1.0×10^{-1} mol dm^{-3}, 2mL) were used.

Next, the remaining four isomeric dioxetanes (**3c** - **3f**) having a trigger on the remote benzene ring (ring **B**) were decomposed similarly on treatment with TBAF in DMSO. The chemiluminescent properties for **3c** - **3f** are shown in **Table 1** where those for **3a** and **3b** are also cited. Based on the results in **Table 1**, the relations between the substitution pattern of the trigger and log Φ_{CL}, log k (k = ln 2 / $t_{1/2}$), and λ_{max} are illustrated in

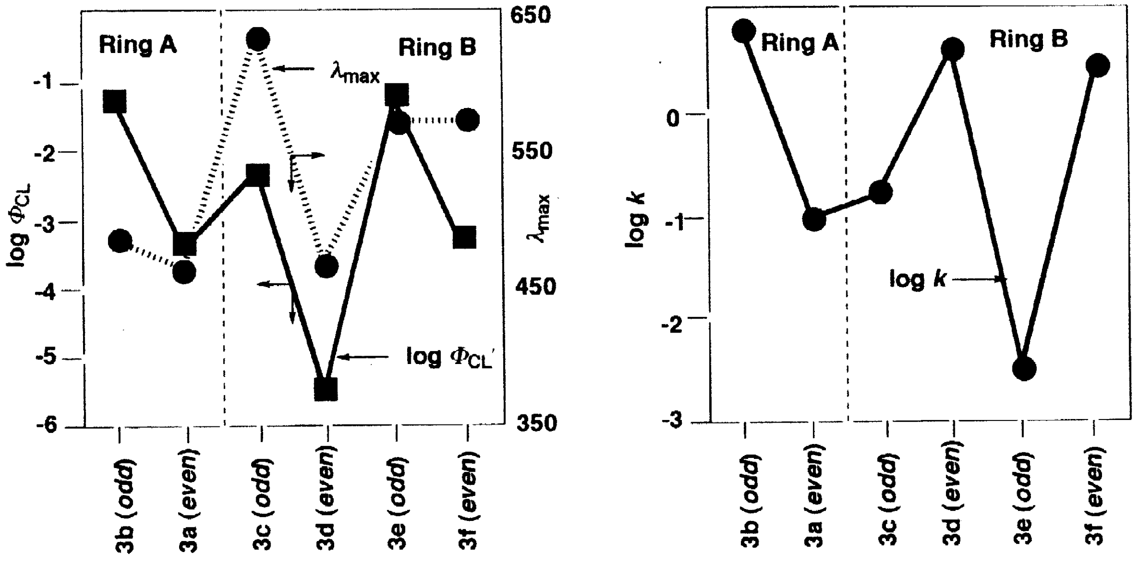


Figure 1 '*Odd / even*' relationship in Φ_{CL}, k, and λ_{max} for naphthyldioxetanes (**3**)

Figure 1, which shows that 1) chemiluminescent efficiencies Φ_{CL} of **3** are classified into two groups; **3b**, **3c** and **3e** exhibit high efficiency while **3a**, **3d** and **3f**, especially **3d**, emit very weak light, 2) for decomposition rates of **3**, a group of **3b**, **3d**, and **3f** giving flash-like light is distinguished from a group of **3a**, **3c** and **3e** affording glow light, and 3) **3c**, **3e**, and **3f** emit light with λ_{max} longer than those for **3a**, **3b**, and **3d**. In conclusion, all the dioxetanes examined here are completely in the category of the '*odd/even*' relationship in Φ_{CL}, whereas the '*odd/even*' relationship in the decomposition rate constant *k* (or emission half-lives $t_{1/2}$) is observed for dioxetanes (**3c** - **3f**) with a trigger on the ring **B** but not for dioxetanes (**3a** and **3b**) with a trigger on the ring **A**. The '*odd/even*' relationship in λ_{max} of emission is also observed for **3** except **3f**.

The chemiluminescent efficiency Φ_{CL} for dioxetanes depends on the yield of singlet-excited state and the fluorescencent quantum yield of an emitter. McCapra[11] and Bronstein[7] have suggested for the '*odd/even*' relationship in Φ_{CL} that a singlet-excited state is effectively formed when an oxyanion on the aromatic ring stabilizes a charge transfer transition in thermal decomposition of intermediary aryloxide-substituted dioxetanes formed after triggering, and this explanation fits to **1e** and **2b** (*odd* pattern) but not to **1d**, **1f** nor **2a** (*even* pattern). The classification of chemiluminescent efficiency Φ_{CL} for **3** into the '*odd/even*' pattern is probably rationalized as the cases of **1** and **2**.

On the other hand, little attempt has been made to account for the relationship between the substitution pattern and decomposition rates of intermediary aryloxide-substituted dioxetanes.[19] According to the intramolecular CIEEL mechanism,[1-5] where a charge-transfer (CT) from an aromatic electron donor to a dioxetane induces the decomposition of dioxetane, the ease of intramolecular CT from an O^--substituted aromatic ring to the dioxetane ring should be reflected in the half-life of emission, that is, the rate of decomposition of the dioxetane as **8**. Thus, the oxidation potential of an aromatic electron donor should affect the rate of CT-induced decomposition of a dioxetane, as already suggested.[20,21] Naphthyldioxetanes (**8**) discussed here are classified into two groups, dioxetanes (**8a**, **8d**, **8e**) bearing a β-naphtholate and dioxetanes (**8b**, **8c**, **8f**) having an α-naphtholate. The latter dioxetanes were expected to have tendency to decompose more rapidly than the former, since α-naphtholate anion possesses lower oxidation potential than an anion of β-isomer: formal oxidation potential *vs* Ag / Ag^+ in DMSO was -498 mV for α-naphtholate and -369 mV for β-naphtholate. However, little marked relation between the oxidation potential of naphtholates and the decomposition rates was observed for above two groups as shown in **Table 1** and **Figure 1**.

It has been very recently reported for dioxetanes bearing an aminophenyl as an electron donor that a *p*-aminophenyl-derivative decomposes thermally far more rapidly than its *m*-analogue.[20-22] This phenomenon is most likely rationalized by an idea that the HOMO electron density at the aromatic carbon (Cα) attached to the dioxetane ring participates in the CT-induced decomposition of a dioxetane. Providing that the idea is also the case for dioxetanes (**8**), the evaluation of the HOMO electron density at Cα is expected to offer explanation for the relation between rates of decomposition (half-lives) and the substitution patterns in a series of the dioxetanes **3**. As shown in **Table 1**, an AM1 calculation reported for α- and β-naphtholates[18], which are the parent oxy-anions for the aromatic electron donors of **8**, reveals that the order of the HOMO electron density at Cα is in good agreement with the order of the decomposition rates *k* of dioxetanes bearing a trigger on the ring **B** (**3d** > **3f** > **3c** > **3e**). However, the reason why the rate for **3b** is unexpectedly rapid and deviated from the '*odd / even*' relationship is little clear at present. The decomposition rate for a dioxetane (**3a**) may be decreased by steric factor(s), considering a reported suggestion[8,9,23] that the rate of CT-induced decomposition of a dioxetane is affected by the conformation of an aromatic electron donor.

Conclusion

The '*odd/even*' relationship holds completely in Φ_{CL} for all the naphthyldioxetanes (**3**) examined here. This type of relationship is also observed in λ_{max} of emission for **3** except **3f**. On the other hand, the '*odd/even*' relation in emission half-lives $t_{1/2}$ (or decomposition rate constant k) is observed for dioxetanes (**3c** - **3f**) with a trigger on the ring **B** but not for dioxetanes (**3a** and **3b**) with a trigger on the ring **A**.

Experimental

Melting points were measured with a Yanako MP-S3 melting point apparatus and are uncorrected. IR spectra were taken on a Hitachi 270-30 fourier transform infrared spectrometer. ^{1}H and ^{13}CNMR spectra were recorded on Varian Unity Inova 400 or JEOL EX-400 spectrometers. Deuteriochloroform (99.8 atom% enriched, Merck or Isotec) was used for the NMR solvent. ^{1}HNMR and ^{13}CNMR chemical shifts were reported in δ value based on internal TMS (δH = 0) or solvent signal ($CDCl_3$ δC = 77.0) as reference, and coupling constants (J) were reported by the use of Hz as a unit. Mass spectra were obtained by using JEOL JMS-SX-102A mass spectrometers. Chemiluminescences were measured by Hitachi F-4010 spectrometer and/or Hamamatsu Photonics PMA-11 multi-channel detector. Formal oxidation potentials were measured by using Bioanalytical Systems CV-50W voltammetric analyzer. Reagents were purchased from Aldrich, Tokyo Chemical Industries, and/or Wako Pure Chemical Industries. Column chromatography was carried out with Wako gel C-200.

Methyl methoxy-2-naphthoate (4) Methyl 3-methoxy-2-naphthoates (**4a**) and its 6-methoxy analogue (**4d**) were prepared by the usual methylation of commercially available 3-hydroxy-2-naphthoic acid or 6-hydroxy-2-naphthoic acid with methyl iodide. The other methyl methoxy-2-naphthoates (**4b**, **4c**, **4e** and **4f**) were synthesized by the methods reported[24-26] or as modified.

4a: Colorless oil. ^{1}HNMR: 3.95 (s, 3H), 3.98 (s, 3H), 7.18 (s, 1H), 7.36 (ddd, J = 8.1, 7.0 and 1.3, 1H), 7.50 (ddd, J = 8.2, 7.0 and 1.3, 1H), 7.72 (dd, J = 8.2 and 0.7, 1H), 7.80 (dd, J = 8.1 and 0.7, 1H), 8.29 (s, 1H). IR (liq. film): 2952, 1732, 1634, 1589, 1216, 1074 cm^{-1}. Mass: 216 (M^+, 100), 185 (88), 183 (37), 127(61). HRMS: 216.0771, calcd for $C_{13}H_{12}O_3$ 216.0786. **4b**: Colorless needles (from ethanol) melted at 43.0 - 43.5 °C (oil, ref 24). ^{1}HNMR: 3.98 (s, 3H), 4.06 (s, 3H), 7.39 (d, J = 1.3, 1H), 7.52 - 7.61 (m, 2H), 7.90 (d with fine coupling, J = 7.5, 1H), 8.21 (s, 1H), 8.26 (d with fine coupling, J = 7.5, 1H). IR(KBr): 2964, 1724, 1598, 1580, 1410, 1378, 1298, 1252, 1100 cm^{-1}. Mass: 216 (M^+, 100), 185 (34), 157 (28), 143 (18). HRMS: 216.0785, calcd for $C_{13}H_{12}O_3$ 216.0786. **4c**: Colorless granules (from hexane-AcOEt) melted at 72.0 - 72.5 °C (67 - 69 °C, ref 25). ^{1}HNMR: 3.97 (s, 3H), 4.01 (s, 3H), 6.91 (dd, J = 7.7 and 0.7, 1H), 7.44 (dd, J = 8.4 and 7.7, 1H), 7.52 (d, J = 8.4, 1H), 8.04 (dd, J = 8.8 and 1.6, 1H), 8.30 (dd, J = 8.8 and 0.7, 1H), 8.55 (d, J = 1.6, 1H). IR(KBr): 2956, 1714, 1632, 1598, 1296, 1198 cm^{-1}. Mass: 216 (M^+, 100), 185 (93), 157 (30). HRMS: 216.0777, calcd for $C_{13}H_{12}O_3$ 216.0786. **4d**: Colorless needles (from hexane -AcOEt) melted at 129.0 - 129.5 °C (128 - 129 °C, ref 26). ^{1}HNMR: 3.94 (s, 3H), 3.96 (s, 3H), 7.15 (d, J = 2.5, 1H), 7.19 (dd, J = 9.0 and 2.5, 1H), 7.76 (d, J = 8.6, 1H), 7.84 (d, J = 9.0, 1H), 8.02 (dd, J = 8.6 and 1.8, 1H), 8.52 (s with fine coupling, 1H). IR(KBr): 2952, 1712, 1630, 1604, 1488, 1292, 1208, 1126, 1098 cm^{-1}. Mass: 216 (M^+, 100), 185 (78), 157 (24). HRMS: 216.0820, calcd for $C_{13}H_{12}O_3$ 216.0786. **4e**: Colorless plates (from hexane-AcOEt) melted at 91.0 - 91.5 °C (91.5 - 92 °C, ref 26). ^{1}HNMR: 3.94 (s, 3H), 3.97 (s, 3H), 7.21 - 7.24 (m, 1H), 7.25 - 7.27 (m, 1H), 7.77 (d, J = 9.0, 1H), 7.80 (d, J = 8.6, 1H), 7.92 (dd, J = 8.6 and 1.6, 1H), 8.51 (s with fine coupling, 1H). IR(KBr): 2952, 1718, 1634, 1608, 1286, 1242, 1220, 1098 cm^{-1}. Mass: 216 (M$^+$, 100), 185 (52), 157 (28). HRMS: 216.0774, calcd for $C_{13}H_{12}O_3$ 216.0786. **4f**: Colorless needles (from hexane) melted at 55.5 - 56.5 °C (oil, ref 24, 25). ^{1}HNMR: 3.98 (s, 3H), 4.03 (s, 3H), 6.86 (dd, *J* = 7.5 and 0.7, 1H), 7.42 - 7.53 (m, 2H), 7.82 (d, *J* = 8.6, 1H), 8.07(dd, *J* = 8.6 and 1.7, 1H), 9.02 (d, *J* = 1.7, 1H). IR(KBr): 2952, 1720, 1630, 1578, 1278, 1242, 1124 cm^{-1}. Mass: 216(M$^+$, 100), 201 (19), 185 (93), 127 (42). HRMS: 216.0814, calcd for $C_{13}H_{12}O_3$: 216.0786.

Synthesis of 1,1-diisopropyl-2-methoxy-2-(methoxy-2-naphthyl)ethylenes (5); general procedure: $LiAlH_4$ (0.608 g, 16 mmol) was added to a solution of titanium (III) trichloride (5.0 g, 32.4 mmol) in dry THF (100 mL) under Ar atmosphere at ice-cooled temperature. To the solution, triethylamine (2.3 mL, 16.5 mmol) was added at room temperature, and then stirred at refluxing temperature for 30 min. Under refluxing, a solution of methyl methoxy-2-naphthoate (**4**) (0.690 g, 3.19 mmol) and diisopropyl ketone (0.95 mL, 6.71 mmol) in dry THF (30 mL) was added dropwise for 30 min to the solution of low valent titanium prepared above. After refluxing for 1.5 h, the reaction mixture was poured into ice water, and extracted with ethyl acetate. The organic layer was washed successively with water, aq. $NaHCO_3$, and saturated aq. NaCl, dried over $MgSO_4$, and then concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with hexane-CH_2Cl_2 (10 : 1) to give 1,1-diisopropyl-2-methoxy-2-(methoxy-2-naphthyl)ethylene (**5**).

5a: 52.1 %. Colorless granules (from hexane) melted at 95.0 - 96.0 °C. ^{1}HNMR: 0.86 (d, *J* = 7.0, 3H), 0.88 (d, *J* = 6.8, 3H), 1.29 (d, *J* = 7.0, 3H), 1.31 (d, *J* = 6.8, 3H), 2.14 (sept, *J* = 6.8, 1H), 2.38 (sept, *J* = 7.0, 1H), 3.22 (s, 3H), 3.91 (s, 3H), 7.14 (s, 1H), 7.32 - 7.37 (m, 1H), 7.42 - 7.47 (m, 1H), 7.60 (s, 1H), 7.73-7.80 (m, 2H). IR(KBr): 2956, 1630, 1596, 1464, 1206, 1122 cm^{-1}. Mass: 298 (M$^+$, 66), 283 (63), 255 (100), 208 (23), 127 (13). HRMS: 298.1954, calcd for $C_{20}H_{26}O_2$ 298.1933. **5b**: 44.2 %. Colorless granules (from methanol) melted at 65.0 - 65.5 °C. ^{1}HNMR: 0.95 (d, *J* = 7.0, 6H), 1.30 (d, *J* = 7.0, 6H), 2.37 (sept, *J* = 7.0, 1H), 2.58 (sept, *J* = 7.0, 1H), 3.24 (s, 3H), 4.01 (s, 3H), 6.73 (d, *J* = 0.8, 1H), 7.30 (s, 1H), 7.42 - 7.54 (m, 2H), 7.74 - 7.82 (m, 1H), 8.20 - 8.28 (m,1H). IR (liq.film) 2968, 1594, 1402, 1232, 1110 cm^{-1}. Mass 298 (M$^+$, 100), 283 (55), 255 (46). HRMS 298.1958, calcd for $C_{20}H_{26}O_2$ 298.1933. **5c**: 47.7 %. Colorless plates (from hexane) melted at 93.5 - 94.0 °C. ^{1}HNMR: 0.94 (d, *J* = 7.0, 6H), 1.29 (d, *J* = 7.0, 6H), 2.37 (sept, *J* = 7.0, 1H), 2.50 (sept, *J* = 7.0, 1H), 3.20 (s, 3H), 4.01(s, 3H), 6.82 (dd, *J* = 6.6 and 1.9, 1H), 7.34 - 7.42 (m, 3H), 7.67 (d, *J* = 1.1, 1H), 8.23 (d, *J* = 8.6, 1H). IR(KBr) 2956, 1600, 1274, 1110, 1066 cm^{-1}. Mass: 298(M$^+$, 86), 283(100), 255(97). HRMS: 298.1955, calcd for $C_{20}H_{26}O_2$ 298.1933. **5d**: 47.7%. Colorless granules (from hexane) melted at 96.0 - 96.5 °C. ^{1}HNMR: 0.94 (d, *J* = 6.8, 6H), 1.29 (d, *J* = 7.0, 6H), 2.36 (sept, *J* = 7.0, 1H), 2.51 (sept, *J* = 6.8, 1H), 3.20 (s, 3H), 3.93 (s, 3H), 7.13 - 7.18 (m, 2H), 7.35 (dd, *J* = 8.2 and 1.6, 1H), 7.63 (d, *J* = 1.6, 1H), 7.71 (d, *J* = 8.4, 1H), 7.73 (d, *J* = 8.4, 1H). IR (KBr) 2964, 1600, 1272, 1250, 1204, 1114, 1066 cm^{-1}. Mass: 298 (M$^+$, 81), 283 (100), 255 (81). HRMS: 298.1937, calcd for $C_{20}H_{26}O_2$ 298.1933. **5e**: 28.2%. Colorless granules (from hexane) melted at 58.0 - 59.0 °C. ^{1}HNMR: 0.96 (d, *J* = 6.8, 6H), 1.30 (d, *J* = 7.0, 6H), 2.38 (sept, *J* = 7.0,1H), 2.54 (sept, *J* = 6.8, 1H), 3.22 (s, 3H), 3.94 (s, 3H), 7.14 (s, 1H), 7.13 - 7.18 (m, 1H), 7.23 - 7.28 (m, 1H), 7.63 (s, 1H), 7.75 (d with fine coupling, *J* = 8.6, 2H). IR (KBr): 2960, 1630, 1604, 1218, 1068 cm^{-1}. Mass: 298 (M$^+$, 86), 283 (100), 255 (97). HRMS: 298.1922, calcd for $C_{20}H_{26}O_2$ 298.1933. **5f**: 34.9%. Colorless oil. ^{1}HNMR: 0.94 (d, *J* = 6.8, 6H), 1.30 (d, *J* = 7.0, 6H), 2.37 (sept, *J* = 7.0, 1H), 2.51 (sept, *J* = 6.8, 1H), 3.20 (s, 3H), 4.01(s, 3H), 6.83 (dd, *J* = 7.3 and 1.3, 1H), 7.35 - 7.44 (m, 3H), 7.77 (d, *J* = 8.4, 1H), 8.14 (s with fine coupling, 1H). IR(liq film): 2960, 1604, 1574, 1270, 1104 cm^{-1}. Mass: 298 (M$^+$, 78), 283 (100), 255 (94). HRMS: 298.1942, calcd for $C_{20}H_{26}O_2$ 298.1933.

1-(Hydroxy-2-naphthyl)-2,2-diisopropyl-1-methoxyethylene (6); general procedure:

Ethanethiol (0.19 mL, 2.57 mmol) was added to a solution of a methoxynaphthylethylene (**5**) (405 mg, 1.36 mmol) and NaH (60 % in oil, 106 mg, 2.65 mmol) in dry DMF (5 mL) under Ar atmosphere at ice-cooled temperature, stirred for 10 min, and then for 2 h at refluxing temperature. The reaction mixture was poured into brine and extracted with ethyl acetate. The organic layer was washed successively with water, aq. $NaHCO_3$, and saturated aq. NaCl, dried over $MgSO_4$, and then concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with hexane-ethyl acetate (10 : 1) to afford 1-(hydroxy-2-naphthyl)-2,2-diisopropyl-1-methoxyethylene(**6**).

6a: 50.4 %. Colorless amorphous solid. ^{1}HNMR: 0.6 - 1.0 (m, 3H), 1.0 - 1.4 (m, 3H), 1.31 (d, *J* = 7.0, 6H), 2.43 (sept, *J* = 7.0, 1H), 2.57 (sept, *J* = 6.8, 1H), 3.31 (s, 3H), 6.51 (s, 1H), 7.29 (s, 1H), 7.29 - 7.36 (m, 1H), 7.39 - 7.47 (m, 1H), 7.59 (s, 1H), 7.69 - 7.78 (m, 2H). IR (KBr): 3456, 2960, 1636, 1278, 1168 cm^{-1}. Mass: 284 (M$^+$, 81), 269 (63), 241 (100), 209 (30). HRMS: 284.1793, calcd for $C_{19}H_{24}O_2$ 284.1776. **6b:** 90.4 %. Colorless granules (from hexane) melted at 119.0 - 120.0 °C. ^{1}HNMR: 0.94 (d, *J* = 6.8, 6H), 1.28 (d, *J* = 7.0, 6H), 2.37 (sept, *J* = 7.0, 1H), 2.57 (sept, *J* = 6.8, 1H), 3.23 (s, 3H), 5.43 (s, 1H), 6.77 (d, *J* = 1.3, 1H), 7.32 (s, 1H), 7.46 - 7.55 (m, 2H), 7.77 - 7.82 (m, 1H), 8.15 - 8.20 (m, 1H). IR (KBr): 3336, 2964, 1594, 1404, 1264, 1226, 1084, 1060, 1030 cm^{-1}. Mass: 284 (M$^+$, 100), 269 (68), 241 (72), 209 (22). HRMS: 284.1774, calcd for $C_{19}H_{24}O_2$: 284.1776. **6c:** 95.9 %. Colorless granules (from hexane-CH_2Cl_2) melted at 121.0 - 122.0 °C. ^{1}HNMR: 0.95 (d, *J* = 6.8, 6H), 1.30 (d, *J* = 7.0, 6H), 2.37 (sept, *J* = 7.0, 1H), 2.51 (sept, *J* = 6.8, 1H), 3.21 (s, 3H), 5.26 (s, 1H), 6.82 (d, *J* = 7.3, 1H), 7.28 -7.36 (m, 1H), 7.38 - 7.46 (m, 2H), 7.68 (s with fine coupling, 1H), 8.06 (d, *J* = 5.7, 1H). IR (KBr): 3432, 2960, 1282 cm^{-1}. Mass: 284 (M$^+$, 89), 269 (95), 241 (100), 209 (19). HRMS: 284.1765, calcd for $C_{19}H_{24}O_2$ 284.1776. **6d:** 97.1 %. Colorless needles (from hexane-CH_2Cl_2) melted at 110.5 - 111.5 °C. ^{1}HNMR: 0.94 (d, *J* = 6.8, 6H), 1.29 (d, *J* =7.0, 6H), 2.36 (sept, *J* = 7.0, 1H), 2.51 (sept, *J* = 6.8, 1H), 3.20 (s, 3H), 4.93 (s, 1H), 7.11 (dd, *J* = 8.4 and 1.7, 1H), 7.16 (d, *J* = 2.4, 1H), 7.34 (dd, *J* = 8.4 and 1.7, 1H), 7.61 - 7.68 (m, 2H), 7.74 (d, *J* = 8.7, 1H). IR (KBr): 3184, 2960, 1636, 1608, 1222, 1114, 1068 cm^{-1}. Mass: 284 (M$^+$, 78), 269 (100), 241 (93). HRMS: 284.1758, calcd for $C_{19}H_{24}O_2$ 284.1776. **6e:** 93.3 %. Colorless granules (from hexane-ethyl acetate) melted at 131.0 - 132.0 °C. ^{1}HNMR: 0.94 (d, *J* = 7.0, 6H), 1.29 (d, *J* = 7.0, 6H), 2.36 (sept, *J* = 7.0, 1H), 2.51 (sept, *J* = 7.0, 1H), 3.21 (s, 3H), 4.93 (s, 1H), 7.10 (dd, *J* = 8.7 and 2.6, 1H), 7.13 - 7.16 (m, 1H), 7.22 - 7.26 (m, 1H), 7.55 (s, 1H), 7.74 (d, *J* = 8.4, 1H), 7.75 (d, *J* = 8.7, 1H). IR (KBr): 3400, 2960, 1634, 1602, 1204 cm^{-1}. Mass: 284 (M$^+$, 82), 269 (96), 241 (100). HRMS: 284.1754, calcd for $C_{19}H_{24}O_2$ 284.1776. **6f:** 91.3 %. Pale yellow granules (from hexane-CH_2Cl_2) melted at 125.0 - 126.0 °C. ^{1}HNMR: 0.95 (d, *J* = 6.8, 6H), 1.30 (d, *J* = 7.1, 6H), 2.38 (sept, *J* = 7.1, 1H), 2.52 (sept, *J* = 6.8, 1H), 3.22 (s, 3H), 5.26 (s, 1H), 6.84 (dd, *J* = 7.3 and 1.0, 1H), 7.31 (dd, *J* = 8.4 and 7.3, 1H), 7.41 (dd, *J* = 8.4 and 1.6, 1H), 7.44 (d, *J* = 8.3, 1H), 7.79 (d, *J* = 8.4, 1H), 8.05 (s with fine coupling, 1H). IR (KBr): 3320, 2964, 1632, 1576, 1282, 1054 cm^{-1}. Mass: 284 (M$^+$, 78), 269 (93), 241 (100), 209 (19), 171 (31). HRMS: 284.1800, calcd for $C_{19}H_{24}O_2$ 284.1776.

2-[(*tert*-Butyldimethylsiloxy)-2-naphthyl]-1,1-diisopropyl-2-methoxyethylene (7); general procedure: *tert*-Butyldimethylsilyl chloride (250 mg, 1.66 mmol) was added to a solution of a hydroxynaphthylethylene(**6**) (262 mg, 0.922 mmol) and imidazole (132 mg, 1.94 mmol) in dry DMF (3 mL) and stirred over night at room temperature. The reaction mixture was diluted with ethyl acetate, washed with water, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with hexane-CH_2Cl_2 (40 : 1) and then with (20 : 1) to give 2-[(*tert*-butyldimethylsiloxy)-2-naphthyl]-1,1-diisopropyl-2-methoxyethylene.

7a: 72.2 %. Pale yellow oil. ^{1}HNMR: 0.29 (s, 3H), 0.30 (s, 3H), 0.86 (d, J = 7.0, 3H), 0.92 (d, J = 7.0, 3H), 1.03 (s, 9H), 1.28 (d, J = 6.8, 3H), 1.29 (d, J = 6.8, 3H), 2.24 (sept, J = 6.8, 1H), 2.36 (sept, J = 7.0, 1H), 3.19 (s, 3H), 7.14 (s, 1H), 7.33 (t with fine coupling, J = 7.5, 1H), 7.42 (t with fine coupling, J = 7.5, 1H), 7.58 (s, 1H), 7.68 (d, J = 8.2, 1H), 7.75 (d, J = 8.2, 1H). ^{13}CNMR: -4.4, -4.2, 20.7, 20.7, 21.1, 22.1, 25.6, 26.6, 30.8, 55.1, 112.9, 123.6, 126.1, 126.1, 127.6, 128.3, 128.8, 130.8, 131.9, 134.3, 147.0, 152.6. IR(liq.film): 2956, 1632, 1594, 1466, 1262, 1178 cm^{-1}. Mass: 398 (M$^+$, 100), 383 (96), 355 (61), 341 (76), 298 (10). HRMS: 398.2617, Calcd for $C_{25}H_{38}O_2Si$ 398.2641. **7b:** 80.4%. Colorless oil. ^{1}H-NMR: 0.29 (s, 6H), 0.94 (d, J = 7.0, 6H), 1.10 (s, 9H), 1.29 (d, J = 7.0, 6H), 2.36 (sept, J = 7.0, 1H), 2.56 (sept, J = 7.0, 1H), 3.22 (s, 3H), 6.77 (d, J = 1.3, 1H), 7.35 (s, 1H), 7.42 - 7.50 (m, 2H), 7.76 - 7.80 (m, 1H), 8.14 - 8.18 (m, 1H). ^{13}CNMR: -4.4, 18.4, 20.9, 22.0, 25.8, 26.7, 30.4, 56.2, 114.4, 121.9, 122.4, 125.2, 126.2, 127.2, 127.7, 132.7, 134.0, 134.4, 149.8, 151.2. IR(liq.film): 2960, 1594, 1574, 1398, 1288, 1234, 1102 cm^{-1}. Mass: 398 (M$^+$, 100), 383 (34), 355 (21). HRMS: 398.2663, Calcd for $C_{25}H_{38}O_2Si$ 398.2641. **7c:** 95.1%. Colorless plates (from methanol) melted at 84.5 - 85.0 °C. ^{1}HNMR: 0.31 (s, 6H), 0.94 (d, J = 7.0, 6H), 1.11(s, 9H), 1.29 (d, J = 7.0, 6H), 2.37 (sept, J = 7.0, 1H), 2.52 (sept, J = 7.0, 1H), 3.20 (s, 3H), 6.85 (dd, J = 7.5 and 0.9, 1H), 7.32 (d, J = 8.2, 1H), 7.36 (dd, J = 8.6 and 1.5, 1H), 7.43 (d, J = 8.2, 1H), 7.66 (d, J = 1.5, 1H), 8.15 (d, J = 8.6, 1H). ^{13}CNMR: -4.4, 20.9, 22.0, 25.8, 26.7, 30.4, 56.3, 112.4, 120.8, 122.2, 126.0, 126.9, 127.0, 128.3, 133.1, 134.1, 134.5, 149.8, 151.5. IR(KBr): 2960, 1592, 1272, 1118 cm^{-1}. Mass: 398 (M$^+$, 100), 383 (86), 355 (69). HRMS: 398.2661, calcd for $C_{25}H_{38}O_2Si$ 398.2641. **7d:** 74.3%. Colorless needles (from MeOH) melted at 84.0 - 85.0 °C. ^{1}HNMR: 0.26 (s, 6H), 0.94 (d, J = 6.8, 6H), 1.03 (s, 9H), 1.29 (d, J = 7.0, 6H), 2.36 (sept, J = 7.0, 1H), 2.52 (sept, J = 6.8, 1H), 3.20 (s, 3H), 7.08 (dd, J = 8.8 and 2.4, 1H), 7.18 (d, J = 2.4, 1H), 7.32 (dd, J = 8.4 and 1.6, 1H), 7.63 (s, 1H), 7.66 (d, J = 8.4, 1H), 7.71 (d, J = 8.8, 1H). ^{13}CNMR: -4.4, 18.2, 21.0, 22.0, 25.6, 26.7, 30.4, 56.3, 114.6, 122.1, 126.2, 127.9, 128.3, 128.6, 129.3, 131.6, 132.8, 133.8, 149.9, 153.6. IR(KBr): 2960, 2928, 1602, 1270, 1114, 1068 cm^{-1}. Mass: 398 (M$^+$, 81), 383 (100), 355 (71). HRMS: 398.2647, calcd for $C_{25}H_{38}O_2Si$ 398.2641. **7e:** 76.8%. ^{1}HNMR: 0.26 (s, 6H), 0.94 (d, J = 6.8, 6H), 1.03 (s, 9H), 1.29 (d, J = 7.0, 6H), 2.36 (sept, J = 7.0, 1H), 2.52 (sept, J = 6.8, 1H), 3.21 (s, 3H), 7.07 (dd, J = 8.8 and 2.6, 1H), 7.17 (d, J = 2.6, 1H), 7.23 (dd, J = 8.4 and 1.6, 1H), 7.56 (s with fine coupling, 1H), 7.71 (d, J = 8.2, 1H), 7.73 (d, J = 8.2, 1H). ^{13}CNMR: -4.4, 18.2, 20.9, 22.0, 25.6, 26.7, 30.4, 56.3, 114.9, 122.0, 125.6, 127.1, 127.4, 128.4, 128.9, 133.0, 134.1, 134.2, 149.9, 153.6. IR(liq.film): 2956, 1628, 1600, 1507, 1458, 1362, 1240 cm^{-1}. Mass: 398 (M$^+$, 1), 316 (46), 259 (100). HRMS: 398.2661, calcd for $C_{25}H_{38}O_2Si$ 398.2641. **7f:** 91.9%. Colorless needles (from MeOH-CH_2Cl_2) melted at 58.0 - 59.0 °C. ^{1}HNMR: 0.29 (s, 6H), 0.93 (d, J = 6.8, 6H), 1.08 (s, 9H), 1.29 (d, J = 7.1, 6H), 2.37 (sept, J = 7.1, 1H), 2.54 (sept, J = 6.8, 1H), 3.18 (s, 3H), 6.87 (dd, J = 7.5 and 0.9, 1H), 7.32 (t, J = 7.5, 1H), 7.38 (dd, J = 8.2 and 1.6, 1H), 7.45 (d, J = 8.2, 1H), 7.78 (d, J = 8.4, 1H), 8.03 (s with fine coupling, 1H). ^{13}CNMR: -4.3, 18.4, 21.0, 22.0, 25.8, 26.8, 30.4, 56.2, 112.9, 120.5, 123.6, 125.9, 127.2, 127.4, 127.7, 132.9, 133.0, 134.1, 150.1, 151.7. IR(KBr): 2956, 1596, 1572, 1280, 1116 cm^{-1}. Mass: 398 (M$^+$, 100), 383 (92), 355 (91). HRMS: 398.2639, calcd for $C_{25}H_{38}O_2Si$ 398.2641.

3-[(*tert*-Butyldimethylsiloxy)-2-naphthyl]-4,4-diisopropyl-3-methoxy-1,2-dioxetane (3); general procedure: A solution of a siloxynaphthalene (**7**) (60 - 200 mg) and TPP (1 - 5 mg) in CH_2Cl_2 (10 - 20 mL) was externally irradiated with a Na-lamp (180 W) under O_2 atmosphere at -78 - 0 °C for 1 - 2 h. The photolysate was concentrated and chromatographed on silica gel. Elution with hexane-ethyl acetate (100 : 1) gave 3-(*tert*-butyldimethylsiloxy-2-naphthyl)-4,4-diisopropyl-3-methoxy-1,2-dioxetane (**3**).

3a: 58.1%. Pale yellow amourphous solid. ^{1}HNMR: 0.31 (s, 3H), 0.36 (s, 3H), 0.73 (d, *J* = 7.1, 3H), 0.87 (d, *J* = 7.1, 3H), 1.07 (s, 9H), 1.17 (d, *J* = 7.1, 3H), 1.32 (d, *J* = 7.1, 3H), 2.39 (sept, *J* = 7.1, 1H), 2.98 (sept, *J* = 7.1, 1H), 3.07 (s, 3H), 7.14 (s, 1H), 7.38 (ddd, *J* = 8.2, 7.0 and 1.3, 1H), 7.47 (ddd, *J* = 8.2, 7.0 and 1.3, 1H), 7.68 (d, *J* = 8.2, 1H), 7.87 (d, *J* = 8.2, 1H), 8.32 (s, 1H). ^{13}CNMR: -4.5, -3.7, 16.9, 17.3, 18.0, 18.9, 19.7, 26.2, 30.3, 33.7, 49.3, 98.7, 113.0, 114.9, 124.1, 125.9, 126.8, 127.1, 128.1, 128.4, 132.5, 134.6, 151.0. IR(KBr): 2960, 2932, 1634, 1596, 1464, 1258, 1180, 1118 cm^{-1}. Mass: 430 (M$^+$, 0.4), 398 (37), 260 (85), 259 (100). HRMS: 430.2511, calcd for $C_{25}H_{38}O_4Si$ 430.2539. **3b:** 63.7%. Colorless viscous oil. ^{1}HNMR: 0.27 (s, 3H), 0.30 (s, 3H), 0.46 (d, *J* = 7.0, 3H), 0.93 (d, *J* = 7.0, 3H), 1.10 (s, 9H), 1.23 (d, *J* = 7.0, 3H), 1.35 (d, *J* = 7.0, 3H), 2.50 (sept, *J* = 7.0, 1H), 2.64 - 2.76 (m, 1H), 3.15 (s, 3H), 6.76 - 6.94 (m, 1H), 7.48 - 7.56 (m, 2H), 7.72 - 7.84 (m, 1H), 7.84 - 7.91 (m, 1H), 8.15 - 8.22 (m, 1H). ^{13}CNMR: -4.4, -4.4, 16.4, 17.3, 18.3, 18.5, 19.3, 25.8, 29.0, 33.3, 49.3, 98.3, 110.4, 114.6, 122.4, 126.2, 126.7, 127.9, 128.4, 132.9, 134.1, 151.8. IR(liq. film): 2932, 1598, 1580, 1406, 1294, 1256, 1104 cm^{-1}. Mass: 430 (M$^+$, 3), 398 (31), 316 (100), 259 (94). HRMS: 430.2556. Calcd for $C_{25}H_{38}O_4Si$ 430.2539. **3c**: 42.3%. Pale yellow amorphous solid. ^{1}HNMR: 0.31 (s, 6H), 0.41 (d, *J* = 7.0, 3H), 0.91 (d, *J* = 7.0, 3H), 1.10 (s, 9H), 1.23 (d, *J* = 7.0, 3H), 1.36 (d, *J* = 7.0, 3H), 2.53 (sept, *J* = 7.0, 1H), 2.62 (sept, *J* = 7.0, 1H), 3.14 (s, 3H), 6.92 (dd, *J* = 7.5 and 0.7, 1H), 7.34 - 7.58 (m, 3H), 8.04 - 8.26 (m, 2H). ^{13}CNMR: -4.4, -4.4, 16.4, 17.2, 18.3, 18.5, 19.4, 25.8, 29.2, 33.4, 49.4, 98.3, 113.4, 114.6, 121.4, 122.7, 124.3, 126.5, 130.7, 134.2, 151.5. IR(KBr): 2960, 2936, 1598, 1572, 1276, 1112, 1092 cm^{-1}. MS: 430 (M$^+$, 0.7), 398 (3), 317 (25), 316 (100), 259 (27). HRMS: 430.2511, calcd for $C_{25}H_{38}O_4Si$ 430.2539. **3d**: 78.2%. Pale yellow viscous oil. ^{1}HNMR: 0.27 (s, 6H), 0.41 (d, *J* = 7.1, 3H), 0.92 (d, *J* = 7.0, 3H), 1.02 (s, 9H), 1.22 (d, *J* = 7.0, 3H), 1.35 (d, *J* = 7.1, 3H), 2.52 (sept, *J* = 7.1, 1H), 2.62 (sept, *J* = 7.0, 1H), 3.13 (s, 3H), 7.12 (dd, *J* = 8.8 and 2.4, 1H), 7.20 (d, *J* = 2.4, 1H), 7.28 - 7.52 (m, 1H), 7.70 (d with fine coupling, *J* = 8.4, 1H), 7.80 (d, *J* = 8.8, 1H), 7.96 - 8.20 (m,1H). ^{13}CNMR: -4.4, 16.4, 17.2, 18.2, 18.5, 19.4, 25.6, 29.2, 33.4, 49.3, 98.3, 114.5, 114.7, 122.5, 124.8, 126.7, 128.3, 128.8, 130.0, 134.7, 154.4. IR(liq.film): 2960, 1634, 1606, 1274, 1184, 1026 cm^{-1}. Mass: 430 (M$^+$, 0.3), 316 (100), 259 (49). HRMS: 430.2550, calcd for $C_{25}H_{38}O_4Si$: 430.2539. **3e**: 73.3%. ^{1}HNMR: 0.27 (s, 3H), 0.28 (s, 3H), 0.42 (d, *J* = 7.1, 3H), 0.92 (d, *J* = 7.0, 3H), 1.03 (s, 9H), 1.23 (d, *J* = 7.1, 3H), 1.35 (d, *J* = 7.0, 3H), 2.52 (sept, *J* = 7.1, 1H), 2.62 (sept, *J* = 7.0, 1H), 3.13 (s, 3H), 7.13 (dd, *J* = 8.8 and 2.4, 1H), 7.22 - 7.36 (m, 1H), 7.74 (d, *J* = 8.8, 1H), 7.72 - 7.80 (m, 2H), 7.94 - 8.12 (m, 1H). ^{13}CNMR: -4.4, -4.4, 16.4, 17.2, 18.1, 18.5, 19.4, 25.6, 29.2, 33.4, 49.4, 98.3, 114.7, 115.4, 122.2, 123.0, 127.7, 128.0, 128.9, 132.9, 133.9, 154.0. IR(KBr): 2960, 1608, 1514, 1462, 1254, 1224, 1112 cm^{-1}. Mass: 430 (M$^+$, 0.5), 316 (100), 259 (41). HRMS: 430.2541, calcd for $C_{25}H_{38}O_4Si$ 430.2539. **3f:** 72.1%. Pale yellow oil. ^{1}HNMR: 0.27 (s, 3H), 0.29 (s, 3H), 0.39 (d, *J* = 7.0, 3H), 0.90 (d, *J* = 7.0, 3H), 1.10 (s, 9H), 1.22 (d, *J* = 7.0, 3H), 1.35 (d, *J* = 7.0, 3H), 2.45 - 2.56 (m, 1H), 2.63 (sept, *J* = 7.0, 1H), 3.14 (bs, 3H), 6.82 - 7.00 (m, 1H), 7.30 - 7.46 (m, 3H), 7.70 - 7.96 (m, 1H), 8.20 - 8.64 (m, 1H). IR(liq.film): 2964, 1598, 1574, 1388, 1278, 1114 cm^{-1}. Mass: 430 (M$^+$, 0.5), 398 (2), 317 (24), 316 (100), 243 (31). HRMS: 430.2534, calcd for $C_{25}H_{38}O_4Si$ 430.2539.

Formal oxidation potential measurement of α- and β-naphtholate anions; The measurement was carried out under the following conditions; 0.1 M Bu_4NClO_4, 0.01 M MeONa, and 0.001 M hydroxyarene (α-, β-naphthol, or 2,6-di-*tert*-butyl-4-methylphenol) in DMSO, and scan rate v = 100 mv / s. As a control experiment, 2,6-di-*tert*-butyl-4-methylphenol was measured to give a quasi-reversible curve as reported.[27] On the other hand, both naphthols did not afford quasi-reversible curves, so that their formal potentials were based on the first oxidation peak potentials; formal potential *vs* Ag / Ag^+ for α-naphtholate = -498 mV, and for β-naphtholate = -369 mV.

Chemiluminescence measurement of 3-[(*tert*-butyldimethylsiloxy)-2-naphthyl]-4,4-diisopropyl-3-methoxy-1,2-dioxetane (3); general Procedure: From a freshly prepared solution of 1.0 x 10^{-2} M TBAF in DMSO was transferred 2 mL into a quartz cell (10 x 10 x 50 mm) and the latter placed into the spectrometer, which was thermostated at 25 °C. After 3 - 5 min, a solution of the dioxetane in DMSO (1.0 x 10^{-5} M, 1 mL) was added by means of a syringe with immediate starting of measurement. The intensity of light emission - time-courses was recorded and processed according to first-order kinetics. The total light emission was estimated by comparing with that of an adamantylidene dioxetane (**1e**) as a standard.[3]

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