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Intramolecular charge-transfer-induced chemiluminescent decomposition of 1,2-dioxetanes bearing a phenylmethanide anion

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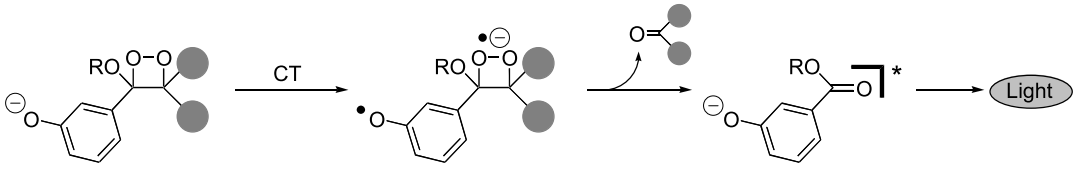
Abstract—Dioxetanes (**1**) bearing a phenyl moiety substituted with a methylene or methine having an electron-withdrawing group(s) (–CH_2-Ew or –CH(X)-Ew) and dioxetane (**2**) bearing a 3-(1-cyanoethenyl)phenyl group were synthesized. Treatment of dioxetanes (**1**) with tetrabutylammonium fluoride (TBAF) caused their decomposition with accompanying emission of light with maximum wavelength at 530–758 nm. The Michael addition of a bis(methoxycarbonyl)methanide anion to dioxetane (**2**) produced initially an unstable dioxetane bearing a phenylmethanide anion, decomposition of which gave light with maximum wavelength at 710–740 nm. Intramolecular cyclopropanation without decomposition of the dioxetane ring took place concurrently for the Michael reaction-induced decomposition of **2** with the bis(methoxycarbonyl)chloromethanide anion.

1. Introduction

Dioxetanes substituted with an aromatic electron donor such as an arenoxide anion (aryl-O^-) undergo intramolecular charge-transfer (CT)-induced decomposition with accompanying luminescence (Scheme 1).[1–4] The phenomenon has received much attention from the viewpoints of mechanistic interests related to bioluminescence and application to chemiluminescent bioassays, and extensive research efforts have been made to elucidate the chemiexcitation pathways as well as to develop efficient chemiluminescent systems.[5–7] However, there has been little known of dioxetanes bearing a carbanion such as an arenemethanide anion (aryl-C^-) instead of the arenoxide anion (aryl-O^-), though an arenemethanide anion would play the role of electron donor similarly to an arenoxide anion for the intramolecular CT-induced chemiluminescent decomposition. One advantage of such type of chemiluminescent substrate would be that a phenylmethanide anion can be generated not only by proton-abstraction from a benzylic methylene or methine but also by conjugate addition of an anion to an ethenylphenyl moiety (Scheme 2).

This situation stimulated us to design a stable dioxetane, which can be easily transformed into an unstable dioxetane bearing a phenylmethanide anion. Thus-designed were dioxetanes bearing a phenyl moiety substituted with a methylene or methine having electron-withdrawing group(s) (–CH_2-Ew or –C*H*(X)-Ew) and their 3-(1-cyanoethenyl)phenyl-analog. We report here the synthesis of these dioxetanes and their chemiluminescent decomposition induced by various bases such tetrabutylammonium fluoride (TBAF), and bis(methoxycarbonyl)methanide anions.[8,9]



Scheme 1.

Keywords: Dioxetane; Chemiluminescence; Carbanion; Michael addition; Cyclopropanation.
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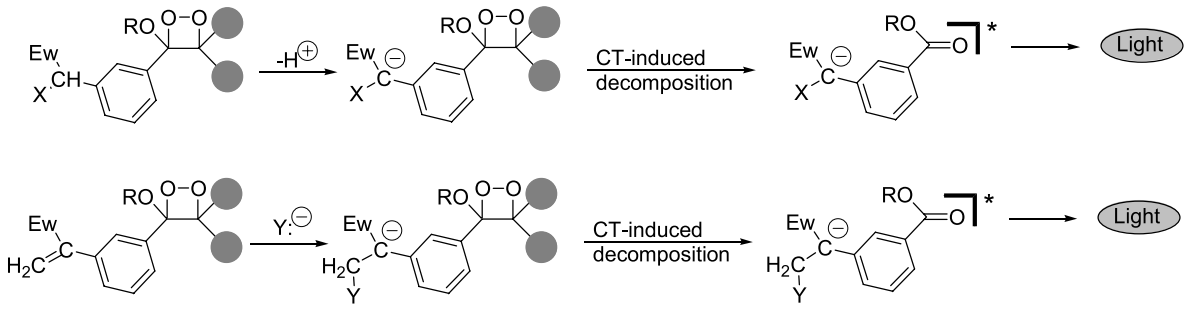
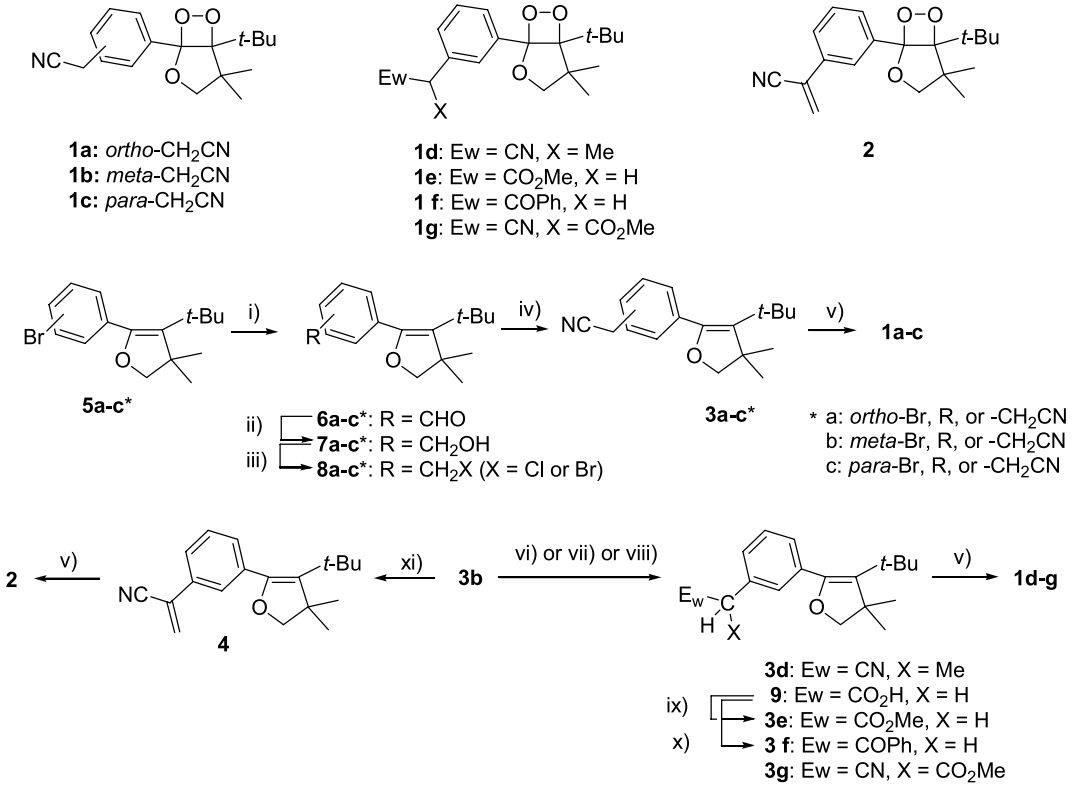


Scheme 2.

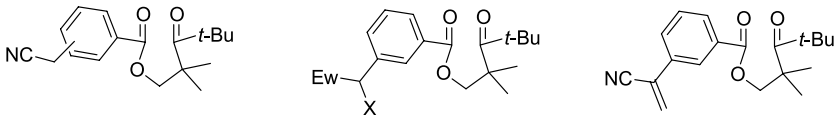
2. Results and discussion

2.1. Synthesis of 1,2-dioxetanes

Dioxetanes realized were 1-aryl-5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptanes (**1**),[10,11] the aryl moiety of which was substituted with a cyanomethyl group at the *ortho*-(**a**), *meta*-(**b**), or *para*-position (**c**). Bicyclic dioxetanes bearing a 3-(1-cyanoethyl)phenyl (**1d**), 3-(methoxycarbonylmethyl)phenyl (**1e**), 3-(benzoylmethyl)phenyl (**1f**), 3-[cyano(methoxycarbonyl)methyl]phenyl (**1g**) or 3-(1-cyanoethenyl)phenyl (**2**) were also realized. Synthesis of these dioxetanes was effectively attained by means of singlet oxygenation of the corresponding dihydrofurans (**3a**–**g** to **4**). Dihydrofurans (**3a**–**g** to **4**) were synthesized from 5-bromophenyl-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**5a**–**5c**)[12] in several steps, as shown in Scheme 3. For example, 3-bromophenyl in (**5b**) easily underwent metal–halogen exchange reaction with butyllithium in THF to give a lithio derivative, to which *N*-methylformanilide added to afford formylphenyl derivative (**6b**). Reduction of (**6b**) with $NaBH_4$, followed by halogenation with CBr_4/PPh_3/THF, gave 3-(bromomethyl)phenyl-derivative (**8b**), which was, in turn, converted to the desired dihydrofuran bearing a 3-(cyanomethyl)phenyl moiety (**3b**) on treatment with NaCN. Dihydrofurans (**3a**, **3c**) were synthesized in a similar manner to the case of **3b**. The other dihydrofurans were prepared from 3-(cyanomethyl)phenyl-derivative (**3b**) as a key precursor. Methylation of the benzylic position in **3b** with MeI/NaH gave 3-(1-cyanoethyl)phenyl-dihydrofuran (**3d**). Hydrolysis of the nitrile group in **3b** gave 3-(carboxymethyl)phenyl-dihydrofuran (**9**), which was successively esterified into 3-(methoxycarboxylmethyl)-phenyl-derivative (**3e**). Lithiation of **9** with butyllithium followed by treatment with benzoyl chloride afforded 3-(benzoylmethyl)phenyl-dihydrofuran (**3f**). 3-[Cyano-(methoxycarbonyl)methyl]phenyl-dihydrofuran (**3g**) was synthesized by the Claisen condensation of **3b** with dimethyl



Scheme 3. Reagents: (i) BuLi/PhNMeCHO; (ii) $NaBH_4$; (iii) TsCl/DMAP or CBr_4/PPh_3; (iv) NaCN/TBA-HS; (v) O_2/TPP/*hv*; (vi) NaH/MeI; (vii) NaOH; (viii) NaH/$CO(OMe)_2$; (ix) $NaHCO_3$/MeI; (x) BuLi/PhCOCl; (xi) K_2CO_3/$(CHO)_n$/TBA-HS.



Scheme 4.

carbonate. Dihydrofuran bearing a 3-(1-cyanoethenyl)phenyl (**4**) was synthesized by the base-catalyzed condensation of **3b** with paraformaldehyde.

Singlet oxygenation of dihydrofurans (**3a**–**3g** to **4**) to the corresponding dioxetanes (**1a**–**1g** to **2**) was easily attained by the irradiation of a solution of dihydrofuran (**3a**–**3g** to **4**) and a catalytic amount of tetraphenylporphin (TPP) in CH_2Cl_2 with a 940 W Na lamp under O_2 atmosphere at $-78\sim0$ °C. All dioxetanes synthesized here except **2** were fairly stable thermally at room temperature, though they decomposed to give the corresponding ketoesters (**10a**–**10g**, **11**) exclusively in refluxing *p*-xylene (Scheme 4). On the other hand, dioxetane bearing a 3-(1-cyanoethenyl)phenyl moiety (**2**) polymerized gradually on standing for a long period at room temperature.

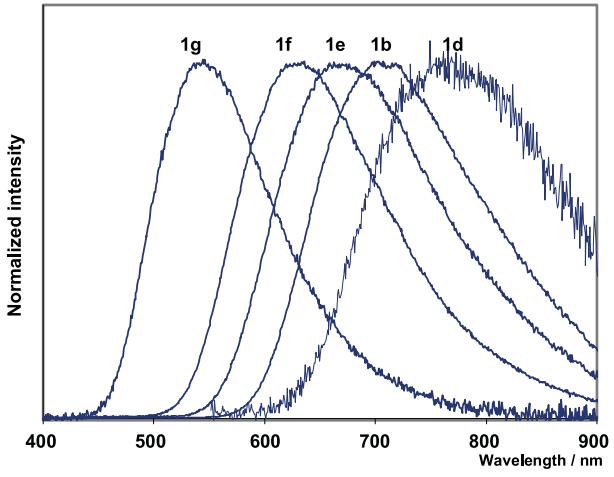


Figure 1. Chemiluminescene spectra for TBAF-induced decomposition of dioxetanes (**1b**, **1d**–**1g**) in DMSO.

2.2. Base-induced chemiluminescent decomposition of 1,2-dioxetanes bearing a phenyl moiety substituted with a methyl having an electron-withdrawing group

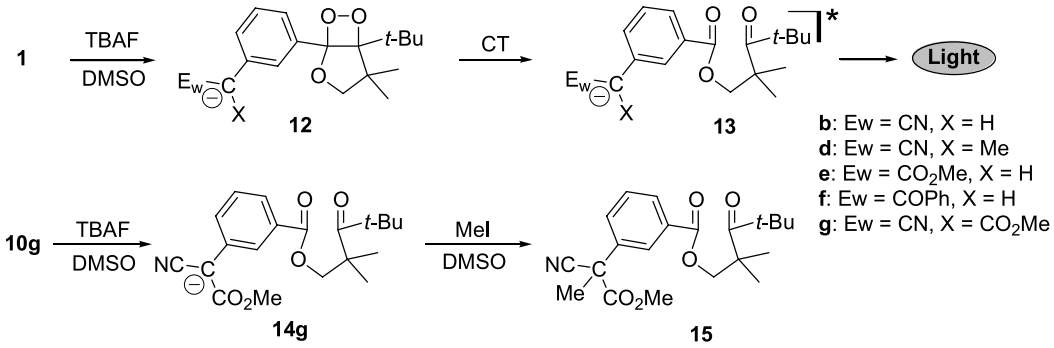
When a solution of dioxetane bearing a *meta*-(cyanomethyl) phenyl group (**1b**) in DMSO (1×10^{-4} mol dm^{-3}, 1 mL) was added to a solution of tetrabutylammonium fluoride (TBAF)[13,14] in DMSO (0.1 mol dm^{-3}, 2 mL) at 25 °C, **1b** decomposed rapidly to emit flash crimson light (maximum wavelength: $\lambda_{max}^{CL}=702$ nm, chemiluminescence efficiency: $\Phi^{CL}=3.3\times10^{-5}$).[15,16] The fresh spent reaction mixture was confirmed to include keto ester (**10b**) exclusively. Dioxetane bearing an *ortho*-(cyanomethyl)phenyl group (**1a**) and its *para*-isomer (**1c**) decomposed also easily to give the corresponding keto esters (**10a**) and (**10c**), though they gave little light. Such phenomenon has been observed as 'odd/even' relationship for dioxetanes bearing a phenoxide anion, among which the *meta*-oxidophenyl-isomer (odd-pattern) gives light in far higher yield than the *ortho*-oxidophenyl- and *para*-oxidophenyl isomer (even-pattern).[7,17–19]

Similarly to the case of **1b**, the other dioxetanes (**1d**–**1g**) bearing a phenyl substituted with a 3-methyl bearing an electron-withdrawing group(s) underwent the TBAF-induced decomposition in DMSO to afford light as shown in Figure 1. The chemiluminescent properties, namely, λ_{max}^{CL}, $t_{1/2}$ (half-life of chemiluminescent decomposition), k^{DICT} (rate constant of chemiluminescent decomposition: $k^{DICT}=\log_e 2/t_{1/2}$), Φ^{CL}, are summarized together with those for **1b** in Table 1. It is noteworthy that, dioxetane bearing a 3-(1-cyanoethyl)phenyl (**1d**) displayed light with λ_{max}^{CL} at 56 nm longer region than that for **1b**, while dioxetane bearing a 3-[cyano(methoxycarbonyl)methyl]phenyl (**1g**) exhibited chemiluminescence with prominent efficiency Φ^{CL}, though with far slower decomposition rate (rate constant: k^{DICT}) and far shorter λ_{max}^{CL} than those for the others (**1b**, **1d**–**1f**). It was confirmed that dioxetanes (**1d**–**1g**) were transformed exclusively into the corresponding keto ester (**10d**–**10g**) for TBAF-induced decomposition. However, fluorescence of

Table 1. TBAF-induced chemiluminescent decomposition of dioxetanes (**1b**, **1d**–**1g**) in DMSO[a]

Dioxetane (**1**)			λ_{max}^{CL}/nm	$t_{1/2}$/s	k^{DICT}/s^{-1}	Φ^{CL} [b]	pK_a of CH_2(X)Ew[c]	HOMO energy[d]/ev
	Ew	X						
1b	–CN	H	702	<0.02	>35	3.3×10^{-5}	25	−2.58
1d	–CN	Me	758	<0.05	>14	2.0×10^{-6}	—	−2.58
1e	–CO_2Me	H	666	0.42	1.7	4.0×10^{-5}	24.5	−2.88
1f	–COPh	H	622	0.43	1.6	4.4×10^{-4}	19	−2.99
1g	–CN	–CO_2Me	530	2300	3.0×10^{-4}	5.7×10^{-3}	9	−3.61

[a] A solution of a dioxetane (**1**) in DMSO (1×10^{-4} mol dm^{-3}, 1 mL) was added to a solution of TBAF in DMSO (0.1 mol dm^{-3}, 2 mL) at 25 °C.
[b] Chemiluminescent yields (Φ^{CL}) were based on the reported value for TBAF-induced chemiluminescent decomposition of 3-(2′-spiroadamantane)-4-methoxy-4-(3′-*tert*-butyldimethylsiloxy)phenyl-1,2-dioxetane in DMSO: $\Phi^{CL}=0.29$ (Ref. 16).
[c] pK_a of the corresponding parent carbon acid, CH_2(X)Ew (Ref. 21).
[d] Based on an AM1 MO calculation for model phenymethanides, PhC$^-$(X)Ew as a model of respective dioxetanes (**12**).



Scheme 5.

these spent reaction mixtures for dioxetane (**1**) was unfortunately not observed except that for dioxetane **1g**. The authentic keto ester (**10g**), prepared by thermolysis of **1g**, showed fluorescence with maximum wavelength (λ_{max}^{fl}), which coincided with λ_{max}^{CL} of **1g** in TBAF/DMSO, and its efficiency (Φ^{fl}) was estimated to be 0.018.[20] Furthermore, when a solution of keto ester (**10g**) in TBAF/DMSO was treated with methyl iodide, a methylation to an intermediary benzylic anion (**14g**) took place to give product (**15**) in 77% yield (Scheme 5). These facts reveal that the emitter produced from **1g** in TBAF/DMSO is undoubtedly a carbanion of **10g**, namely **13g**. Hence, the singlet-chemiexcitation efficiency ($\Phi_S = \Phi^{CL}/\Phi^{fl}$) is estimated to be 0.32 for the TBAF-induced decomposition of dioxetane (**1g**) in DMSO. The emitters would be the corresponding benzylic carbanions of keto esters (**13b**, **13d–13f**) also for the chemiluminescent decomposition of the other dioxetanes (**1b**, **1d–1f**), though little fluorescence was observed even for the authentic keto esters (**10b**, **10d–10f**) in TBAF/DMSO.

Chemiluminescent decomposition did not occur for all dioxetanes (**1a–1g**), when TBAF was absent in DMSO, while it took place easily on treatment with *tert*-BuOK as well as with TBAF. Considering this fact and that phenylmethanide anion (**13**) would be an emitter, it is reasonable to assume that proton-abstraction from **1** with TBAF generates an unstable dioxetane **12** bearing a phenymethanide anion, from which the intramolecular CT occurs to induce decomposition of the dioxetane producing excited carbanion **13** of keto ester by the mechanism similar to the case of a dioxetane bearing an arenoxide anion.[5–7] It is worth to point out that the singlet-chemiexcitation efficiency compares favorably with the value for dioxetanes bearing a *meta*-phenoxide anion, as observed for dioxetane (**1g**).[5–7]

In analogy with the CT-induced decomposition of a dioxetane bearing an arenoxide anion, it is inferring that chemiluminescent decomposition of dioxetane (**12**) bearing a phenylmethanide anion produced from **1** occurs the more easily, as the phenylmethanide anion becomes the less stable and the more easily oxidized. This idea is apparently consistent with the fact that the rate of chemiluminescent decomposition (k^{DICT}) increases in the order of **1g**<**1f**<**1e**<**1b** (**1d**) (Table 1). Considering the order of acidity for the parent carbon acids,[21] namely $CH_2(CN)CO_2Me \gg CH_3COPh > CH_3CO_2Me > CH_3CN$ (Table 1), the acidity of a benzylic position for **1** is presumed to decrease in the order of **1g**>**1f**>**1e**>**1b** (**1d**), so that stability of their conjugate carbanions decreases in the same order as illustrated in Figure 2. A similar tendency was observed also in the relationship between $\log_e k^{DICT}$ and HOMO energy estimated by an AM1 MO calculation for model phenymethanides, $PhC^-(X)Ew$ (Fig. 2).

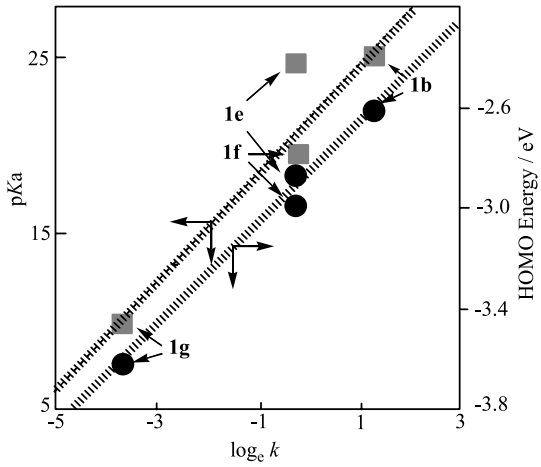
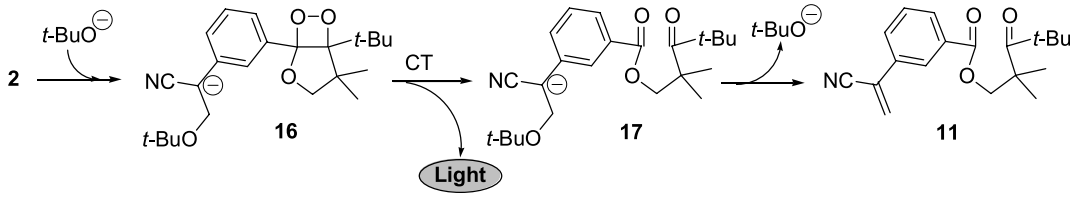


Figure 2. Relationship of $\log_e k^{DICT}$ for TBAF-induced decomposition of **1** with pK_a of parent carbon acids, X-CH_2-Ew and with HOMO energy of Ph-CH^-(X)-Ew.

2.3. Chemiluminescent decomposition of a dioxetane bearing a 3-(1-cyanoethenyl)phenyl moiety induced by the conjugate addition of a nucleophile

As described in the previous section, 3-(1-cyanoethyl) phenyl-substituted dioxetane (**1d**) underwent chemiluminescent decomposition through an intermediary dioxetane bearing a phenylmethanide anion (**12d**). Such type of phenylmethanide anion would be generated by the conjugate addition of a nucleophile to a (1-cyanoethenyl)-phenyl moiety. Thus, we attempted to react dioxetane (**2**) bearing a 3-(1-cyanoethenyl)phenyl group with the *tert*-BuO^- anion as a preliminary experiment. When dioxetane (**2**) was treated with 18-crown-6 ether complex of *tert*-BuOK in benzene, emission of light (λ_{max}^{CL}=706 nm) was observed, though the spent reaction mixture was found to include little product due to the conjugate addition of *tert*-BuO^-, but only 14% of keto ester (**11**) along with a complex mixture (Scheme 6). These results suggest for *tert*-BuO^--induced decomposition of **2** that dioxetane (**16**) bearing a phenylmethanide anion produced initially might



Scheme 6.

decompose to an excited keto ester (**17**), from which the *tert*-BuO$^-$ anion is eliminated to afford keto ester (**11**) after the emission of light (Scheme 6), though the intermediacy of neither **16** nor **17** was clear.

The next examination was to react dioxetane (**2**) with an anion of dimethyl methylmalonate, namely, 1,1-bis(methoxycarbonyl)ethanide anion (**18a**), which would add irreversibly to an electron-deficient olefin. An anion of ester (**18a**) (1.0×10^{-1} mol dm^{-3}) was prepared by dissolving malonate (**18a**) together with an equimolar amount of 18-crown-6 ether and *tert*-BuOK in benzene: the abbreviation [K⊂(18-crown-6)]$^+$(**18a**)$^-$ is used here for this anionic system. When a solution of a dioxetane (**2**) in benzene (1.0×10^{-3} mol dm^{-3}, 1 mL) was added to a solution of [K⊂(18-crown-6)]$^+$(**18a**)$^-$ in benzene (1.0×10^{-1} mol dm^{-3}, 2 mL) at 25 °C, dioxetane (**2**) decomposed rapidly to emit flash crimson light ($\lambda_{max}^{CL}=740$ nm, $\Phi^{CL}=5.6\times10^{-6}$) as shown in Figure 3. The maximum wavelength of chemiluminescence (λ_{max}^{CL}) was between that for dioxetane (**1b**) and that for dioxetane (**1d**) (Table1).

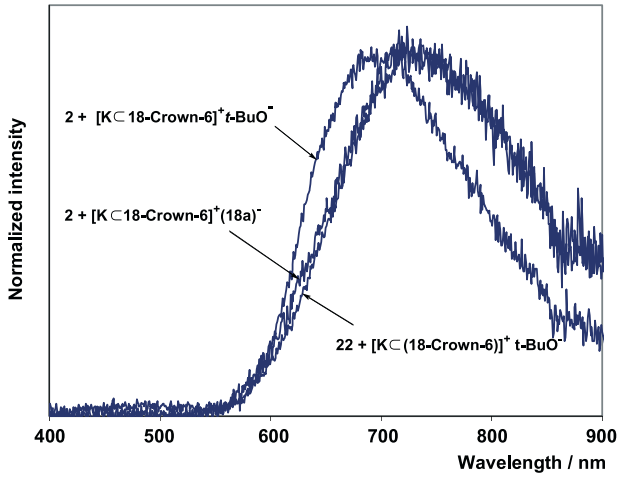
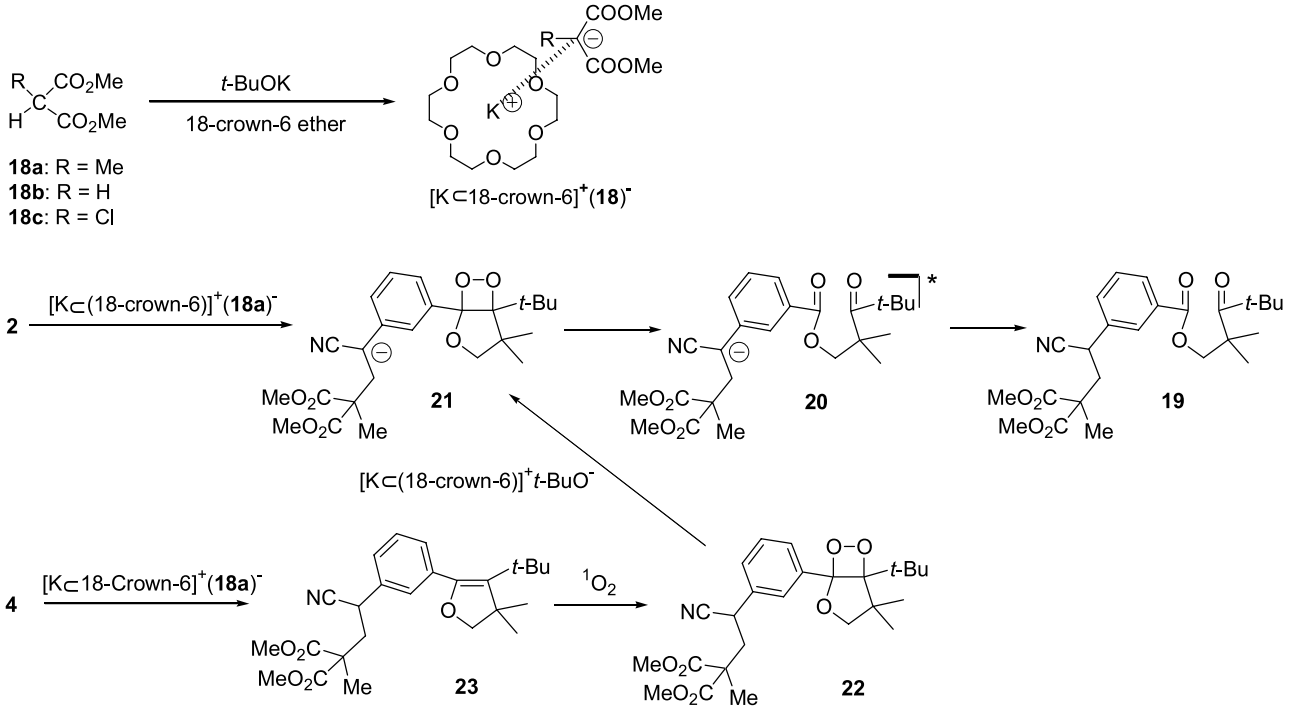


Figure 3. Chemiluminescene spectra for base-induced decomposition of dioxetane (**2**) and (**22**) in benzene.

The spent reaction mixture of **2** with [K⊂18-crown-6]$^+$(**18a**)$^-$ after neutralization gave exclusively keto ester (**19**). The result suggested that the emitter was carbanion (**20**), which was produced from an unstable Michael adduct, namely, dioxetane bearing a phenylmethanide anion (**21**). Thus, we synthesized authentic dioxetane (**22**), which was a neutral form of **21**, as a reference: the singlet oxygenation of dihydrofuran (**23**), which was prepared from dihydrofuran (**4**) and an anion of **18a**, gave **22** in high yield. On treatment with [K⊂(18-crown-6)]$^+$*t*-BuO$^-$ in benzene (1.0×10^{-1} mol dm^{-3}, 2 mL) at 25 °C, dioxetane (**22**) (1.0×10^{-3} mol dm^{-3}, 1 mL) decomposed rapidly to emit light with



Scheme 7.

chemiluminescent properties: $\lambda_{max}^{CL}=740$ nm, $\Phi^{CL}=5.7\times10^{-6}$, and the rate constant $k^{DICT}=8.1\ s^{-1}$.[22] Keto ester (**19**) was also obtained from the neutralized spent reaction mixture exclusively. These results are in good agreement with those for the decomposition of **2** with [K⊂18-crown-6]$^+$(**18a**)$^-$. Therefore, anionic dioxetane (**21**) is undoubtedly produced as an intermediate for the chemiluminescent decomposition of **2** induced by [K⊂18-crown-6]$^+$(**18a**)$^-$ (Scheme 7).

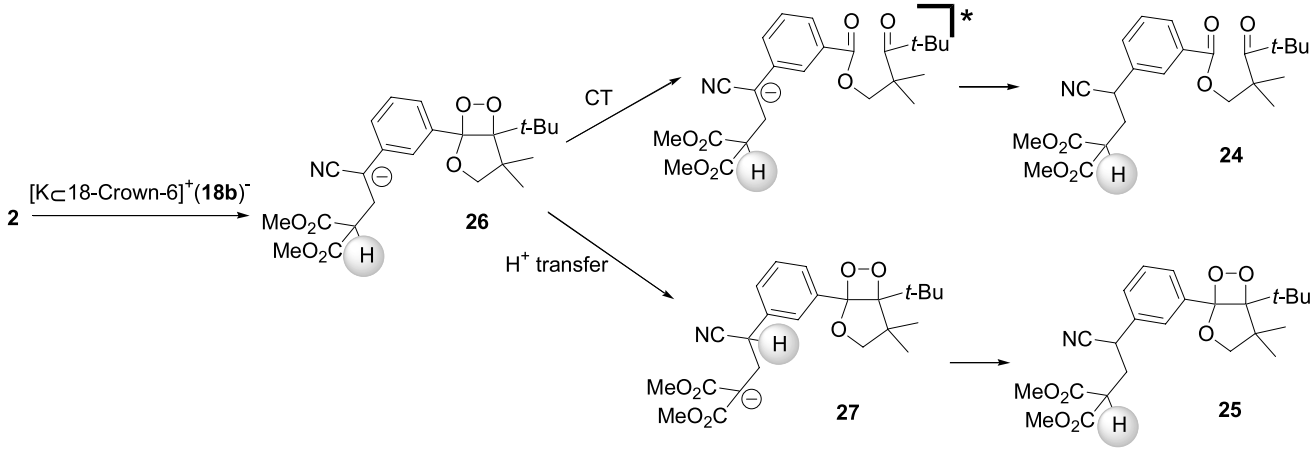
When dioxetane (**2**) was treated with a solution of bis(methoxycarbonyl)methanide complex (**18b**), [K⊂18-crown-6]$^+$(**18b**)$^-$, in benzene, **2** decomposed also to display crimson light ($\lambda_{max}=737$ nm, $\Phi^{CL}=1.5\times10^{-6}$) as in the case of anion (**18a**)$^-$ (Scheme 8). The spent reaction mixture gave the expected product **24** (39% yield), derived from the Michael addition of anion (**18b**)$^-$ to **2** followed by the CT-induced decomposition, and dioxetane (**25**) (28% yield), produced only by the Michael addition of (**18b**)$^-$ to **2**. The formation of dioxetane (**25**) reveals that a considerable quantity of initially-produced phenylmethanide anion (**26**) would change into a more stable anion (**27**) without causing the CT-induced decomposition to **24**. This means surely that the change of the phenylmethanide anion (**26**) into a bis(methoxycarbonyl)methanide anion (**27**) takes place as rapidly as the CT-induced decomposition of **26**, and should explain the fact that the chemiluminescent efficiency was considerably lower for the triggering with the (**18b**)$^-$ anion than for that with the (**18a**)$^-$ anion.

The results described above suggest a possibility that, when an intermediary phenylmethanide anion such as **26** undergoes another reaction competing with the intramolecular CT-induced chemiluminescent decomposition, its rate can be estimated by examining the chemiluminescent decomposition rate for the system of dioxetane (**2**), if the stoichiometry of products is clear and accurate. Thus, we attempted further to examine a reaction of dioxetane (**2**) that leads both to the CT-induced decomposition and a competitive reaction to extinguish it without causing the decay of the dioxetane ring.

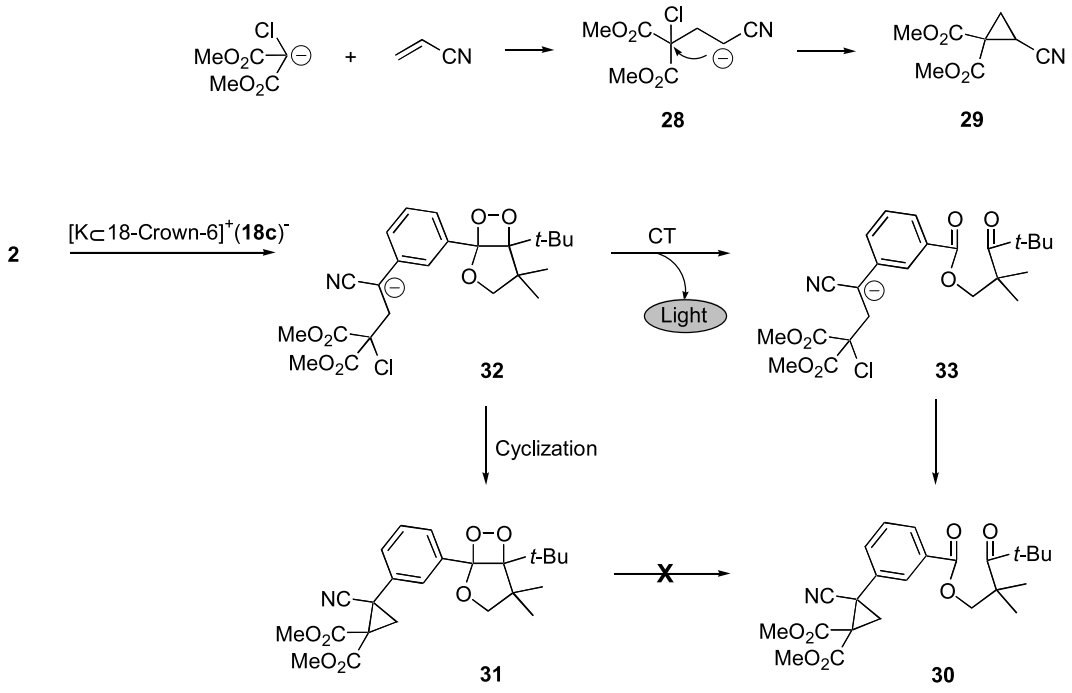
Dimethyl chloromalonate (**18c**) has been reported to undergo base-induced reaction with an α,β-unsaturated nitrile to give a cyclopropanedicarboxylate.[23,24] The reaction proceeds through the Michael addition of (**18c**)$^-$ to acrylonitrile giving an intermediary carbanion (**28**), whose intramolecular nucleophilic attack to an adjacent carbon bearing a chlorine furnishes a cyclopropanedicarboxylate (**29**). One mechanistically interesting point of this cyclopropanation is that the intramolecular nucleophilic attack of (**18c**)$^-$ should be more rapid than the quenching of the anion by protonation, since the reaction proceeds effectively even under weak basic conditions where anion (**28**) is hardly expected to form from a conjugate acid of **28**.

Thus, we carried out the reaction of dioxetane (**2**) with an anion of dimethyl chloromalonate, namely, bis(methoxycarbonyl)chloromethanide anion (**18c**). When **2** was treated with an anion of dimethyl chloromalonate (**18c**), [K⊂18-crown-6]$^+$(**18c**)$^-$, in benzene, emission of crimson light ($\lambda_{max}=710$ nm, $\Phi^{CL}=2.4\times10^{-6}$) was observed. After neutralization, the spent reaction mixture afforded ester (**30**) of a benzoic acid bearing a cyclopropyl group at the 3-position (71% yield) together with a cyclopropane derivative (**31**), in which the dioxetane ring remained intact (29% yield) (Scheme 9).

Dioxetane (**31**) was stable and hardly decomposed into ketoester (**30**) under the conditions similar to the case of **2** with [K⊂18-crown-6]$^+$(**18c**)$^-$. Therefore, a reasonable explanation of the formation of **30** is that an intermediary phenylmethanide anion **32**, produced by the Michael addition of an anion of **18c** to **2**, undergoes the CT-induced decomposition into phenylmethanide anion (**33**) with accompanying light, and, thereafter, **33** is transformed into a cyclopropane **30** through intramolecular cyclization. According to this explanation, the ratio of (rate for CT-induced decomposition of **32**) versus (rate for the reaction of **32** leading to a dioxetane **31**) equals the product ratio of **30** to **31**. Thus, the rate for intramolecular cyclopropanation of **32** is estimated roughly to be $k=3.3\ s^{-1}$, since the rate for CT-induced decomposition of **32** is presumably not so much different from the rate for the case of **22** with [K⊂18-crown-6]$^+$*t*-BuO$^-$.



Scheme 8.



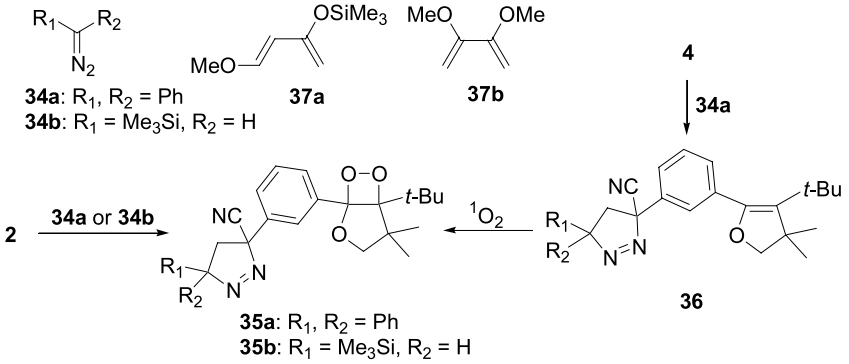
Scheme 9.

2.4. 1,3-Dipolar cycloaddition of diazomethanes to the (1-cyanoethenyl)phenyl moiety attached to a dioxetane ring

The results described earlier show a possibility that the chemiluminescent decomposition of dioxetane (**2**) induced by the conjugate addition of an anion provides a new probe to know a feature of an intramolecular reaction competing with the CT-induced chemiluminescent decomposition of an intermediary dioxetane. Thus, we dared finally to apply dioxetane (**2**) to a pericyclic reaction such as 1,3-dipolar cycloaddition and Diels–Alder reaction, which proceeds generally by a concerted mechanism and not by a stepwise ionic mechanism. 1,3-Dipoles chosen here were diphenyldiazomethane (**34a**) and trimethylsilyldiazomethane (**34b**). When dioxetane (**2**) was treated with diazomethane (**34a**) in CH_3CN at room temperature, 1,3-dipolar addition proceeded smoothly and completed within 120 min to afford dihydropyrazole (**35a**) without accompanying decomposition of the dioxetane ring. Adduct (**35a**) was synthesized also by the singlet oxygenation of dihydrofuran (**36**), which was prepared by the 1,3-dipolar addition of **34a** to **4**. The reaction of **2** with **34b** proceeded similarly to give dihydropyrazole (**35b**). These results are consistent with an idea that the reaction of **2** with **34** proceeds presumably by the concerted mechanism. On the other hand, Diels–Alder reaction of dioxetane (**2**) with a diene such as Danishefsky's diene (**37a**) and 2,3-dimethoxy-1,3-butadiene (**37b**) took place sluggishly at room temperature, though these dienes are well known to be very reactive to various dienophiles (Scheme 10).

3. Conclusion

Dioxetanes (**1**) bearing a phenyl moiety substituted with a methyl having an electron-withdrawing group(s) (–C*H*$_2$-Ew or –C*H*(X)-Ew) were effectively triggered with a base such as fluoride to decompose rapidly with accompanying emission of light ranging in color from yellow to crimson. The base-induced reaction of dioxetane (**1**) was clarified to proceed through dioxetanes bearing a phenymethanide anion, from which the intramolecular CT causes chemiluminescent decomposition of the dioxetane. The rate of



Scheme 10.

CT-induced decomposition for dioxetanes (**1**) in TBAF/DMSO was found to relate with the acidity of the parent carbon acids (CH_2(X)-Ew). This relationship provides a possibility to estimate the acidity of carbon acids by the use of chemiluminescent decomposition of dioxetanes.

Dioxetane (**2**) bearing a 3-(1-cyanoethenyl)phenyl group underwent the Michael addition of a bis(methoxycarbonyl)methanide anion to generate unstable dioxetane bearing a phenylmethanide anion, which decomposed with accompanying emission of light. When bis(methoxycarbonyl)-methanide anion or bis(methoxycarbonyl) chloromethanide anion was used, the CT-induced decomposition of an intermediary dioxetane competed with the intramolecular proton transfer or cyclopropanation. These findings suggest that the chemiluminescent properties, especially the rate, for the Michael addition-induced decomposition of **2** should become a probe to know the features of the intramolecular reactions, which occur concurrently.

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. ^{1}H and ^{13}C NMR spectra were recorded on JEOL EX-400 and JEOL EPC-500 spectrometer. Mass spectra were obtained by using JEOL JMS-AX-505H, JEOL JMS-T-100LC mass spectrometers. 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. 4-*tert*-Butyl-5-(3-formylphenyl)-3,3-dimethyl-2,3-dihydrofuran (6b): typical procedure. BuLi (1.61 M in hexane, 30.1 mL, 48.5 mmol) was added to a solution of 5-(3-bromophenyl)-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**5b**)[12] (14.3 g, 46.2 mmol) in THF (100 mL) at −78 °C under nitrogen atmosphere and was stirred for 30 min. To the solution, *N*-methylformanilide (6.27 mL, 50.8 mmol) was added and was stirred for 30 min. The reaction mixture was poured into 1 N HCl and then extracted with ethyl acetate (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 11.5 g of **6b** as a pale yellow oil in 96.3% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.35 (s, 6H), 3.90 (s, 2H), 7.51 (t, J=7.6 Hz, 1H), 7.57 (d with fine coupling, J=7.6 Hz, 1H), 7.82 (s with fine coupling, 1H), 7.84 (d with fine coupling, J=7.6 Hz, 1H), 10.0 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.3, 32.5, 32.6, 47.3, 83.2, 127.0, 128.6, 129.2, 131.3, 135.9, 136.1, 137.3, 148.4, 192.0 ppm. IR (liquid film): 2959, 2868, 2723, 1702 cm^{-1}. Mass (*m*/*z*, %): 259 (M^++1, 14), 258 (M^+, 69), 244 (81), 243 (100), 187 (78), 159 (38), 133 (95). HRMS (ESI): 281.1538, calcd for $C_{17}H_{22}O_2Na$ ($M+Na^+$) 281.1518.

Similarly to the case of **6b**, 4-*tert*-butyl-5-(2-formylphenyl)-3,3-dimethyl-2,3-dihydrofuran (**6a**) was synthesized from 2-bromphenyl isomer (**5a**) as a yellow oil in 90.1% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.01 (s, 9H), 1.38 (s, 6H), 3.94 (s, 2H), 7.38 (d with fine coupling, J=7.6 Hz, 1H), 7.48 (t, J=7.6 Hz, 1H), 7.58 (td, J=7.6, 1.3 Hz, 1H), 7.95 (dd, J=7.6, 1.3 Hz, 1H), 10.2 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.2, 32.3, 32.5, 47.5, 83.4, 126.7, 128.9, 129.5, 131.5, 133.4, 134.4, 139.4, 145.0, 192.0 ppm. IR (liquid film): 2959, 2868, 2745, 1699 cm^{-1}. Mass (*m*/*z*, %): 258 (M^+, 17), 243 (38), 202 (18), 201 (100), 187 (45), 171 (25), 159 (28), 149 (40), 133 (45), 105 (30), 85 (27), 77 (26), 57 (44). HRMS (ESI): 281.1525, calcd for $C_{17}H_{22}O_2Na$ ($M+Na^+$) 281.1518.

Similarly to the case of **6b**, 4-*tert*-butyl-5-(4-formylphenyl)-3,3-dimethyl-2,3-dihydrofuran (**6c**) was synthesized from 4-bromphenyl isomer (**5c**) as a colorless columns, melted at 41.6–42.2 °C (from hexane) in 78.4% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.05 (s, 9H), 1.35 (s, 6H), 3.90 (s, 2H), 7.48 (d, J=8.2 Hz, 2H), 7.86 (d, J=8.2 Hz, 2H), 10.0 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.2, 32.4, 32.5, 47.4, 83.3, 127.1, 129.2, 130.6, 135.8, 142.6, 148.5, 191.9 ppm. IR (KBr): 2962, 2865, 1696 cm^{-1}. Mass (*m*/*z*, %): 258 (M^+, 18), 244 (18), 243 (100), 187 (33), 133 (40), 105 (12), 57 (16).

4.1.2. 4-*tert*-Butyl-5-[3-(hydroxymethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (7b): typical procedure. $NaBH_4$ (870 mg, 23.0 mmol) was added to a solution of 4-*tert*-butyl-5-(3-formylphenyl)-3,3-dimethyl-2,3-dihydrofuran (**6b**) (11.8 g, 45.6 mmol) in CH_2Cl_2 (100 mL) at 0 °C under nitrogen atmosphere. To the solution MeOH (10 mL) was added and stirred for 30 min. 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 11.4 g of **7b** as a colorless oil in 96.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.05 (s, 9H), 1.34 (s, 6H), 3.87 (s, 2H), 4.69 (s, 2H), 7.21–7.25 (m, 1H), 7.29–7.34 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 27.4, 32.4, 32.6, 47.1, 64.8, 83.0, 125.7, 126.4, 127.9, 128.1, 128.9, 136.1, 140.5, 149.6 ppm. IR (liquid film): 3415, 2957, 2869, 1653 cm^{-1}. Mass (*m*/*z*, %): 260 (M^+, 20), 246 (17), 245 (100), 243 (23), 171 (19), 135 (45). HRMS (ESI): 283.1662, calcd for $C_{17}H_{24}O_2Na$ ($M+Na^+$) 283.1674.

Similarly to the case of **7b**, 4-*tert*-butyl-5-[2-(hydroxymethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**7a**) was synthesized from 2-formylphenyl isomer (**6a**) as a colorless granules, melted at 59.3–60.0 °C (from hexane–CH_2Cl_2) in 97.1% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.03 (s, 9H), 1.37 (s, 6H), 2.65 (t, J=6.5 Hz, 1H), 3.89 (s, 2H), 4.60 (broad s, 2H), 7.27–7.38 (m, 3H), 7.42 (d, J=7.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.1, 32.1, 32.5, 47.1, 64.2, 82.8, 127.3, 127.3, 128.7, 129.0, 131.0, 134.7, 139.9, 147.7 ppm. IR (KBr): 3475, 2957, 2872, 1647 cm^{-1}. Mass (*m*/*z*, %): 261 (M^++1, 11), 260 (M^+, 56), 246 (20), 245 (100), 227 (26), 173 (46), 171 (72), 135 (66), 133 (27), 57 (20). HRMS (ESI): 283.1665, calcd for $C_{17}H_{24}O_2Na$ ($M+Na^+$) 283.1674.

Similarly to the case of **7b**, 4-*tert*-butyl-5-[4-(hydroxymethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**7c**) was synthesized from 4-formylphenyl isomer (**6c**) as a colorless columns melted at 56.1–57.0 °C (from hexane) in 96.6% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.33 (s, 6H), 1.66 (t, J=6.0 Hz, 1H), 3.87 (s, 2H), 4.70 (d, J=6.0 Hz, 2H), 7.29 (d, J=8.1 Hz, 2H), 7.33 (d, J=8.1 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.4, 32.4, 32.6, 47.2, 65.1, 83.1, 125.9, 126.4, 130.1, 135.6, 140.6, 149.8 ppm. IR (KBr): 3272, 2957, 2867, 1648 cm^{-1}. Mass (*m*/*z*, %): 260 (M^+, 20), 246 (18), 245 (100), 243 (18), 171 (25), 135 (30), 77 (11), 57 (17). HRMS (ESI): 283.1671, calcd for $C_{17}H_{24}O_2Na$ ($M+Na^+$) 283.1674.

4.1.3. 4-*tert*-Butyl-5-[2-(chloromethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (8a). 4-(*N*,*N*-Dimethylamino)-pyridine (DMAP) (382 mg, 3.13 mmol) and *p*-toluenesulfonyl chloride (TsCl) (658 mg, 3.45 mmol) were added to a solution of 4-*tert*-butyl-5-[2-(hydroxymethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**7a**) (739 mg, 2.84 mmol) in THF (5 mL) at room temperature under nitrogen atmosphere and refluxed for 6 h. The reaction mixture was poured into satd aq NH_4Cl and then 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 (9/1) to give 411 mg of **8a** as a pale yellow oil in 51.8% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.36 (s, 6H), 3.88 (s, 2H), 4.65 (broad s, 2H), 7.23–7.30 (m, 2H), 7.36 (ddd, J=7.6, 7.1, 2.0 Hz, 1H), 7.50 (d, J=7.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.2, 32.1, 32.6, 43.6, 47.2, 83.0, 127.6, 127.7, 129.0, 129.5, 130.8, 135.1, 136.3, 147.0 ppm. IR (liquid film): 2957, 2867, 1648 cm^{-1}. Mass (20 eV, *m*/*z*, %): 280 (M^+, 9), 278 (M^+, 32), 265 (33), 264 (13), 263 (100), 171 (29), 57 (13). HRMS (ESI): 303.1316, calcd for $C_{17}H_{23}ClONa$ ($M+Na^+$) 303.1306 and 301.1341, calcd for $C_{17}H_{23}ClONa$ ($M+Na^+$) 301.1335.

4.1.4. 5-[3-(Bromomethyl)phenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (8b); typical procedure. CBr_4 (3.94 g, 11.8 mmol) was added to a solution of PPh_3 (3.65 g, 13.9 mmol) and 4-*tert*-butyl-5-[3(-hydroxymethyl)-phenyl]-3,3-dimethyl-2,3-dihydrofuran (**7b**) (3.03 g, 11.6 mmol) in THF (30 mL) at room temperature under nitrogen atmosphere and stirred for 50 min. The reaction mixture was poured into satd aq NaCl and then 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 (1/9) to give 3.55 g of **8b** as a pale yellow oil in 94.3% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.34 (s, 6H), 3.87 (s, 2H), 4.48 (s, 2H), 7.23 (d with fine coupling, J=7.2 Hz, 1H), 7.28–7.36 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 27.4, 32.4, 32.6, 33.2, 47.2, 83.1, 126.1, 128.2, 128.5, 129.8, 130.5, 136.6, 137.2, 149.1 ppm. IR (liquid film): 2958, 2867, 1653, 1597 cm^{-1}. Mass (*m*/*z*, %): 324 (M^+, 17), 322 (M^+, 17), 310 (18), 309 (100), 308 (17), 307 (97), 243 (25), 228 (38), 199 (44), 197 (44), 172 (16), 171 (23), 90 (22), 57 (50). HRMS (ESI): 345.0841, calcd for $C_{17}H_{23}BrONa$ ($M+Na^+$) 345.0830 and 347.0819, calcd for $C_{17}H_{23}BrONa$ ($M+Na^+$) 347.0810.

Similarly to the case of **8b**, 4-*tert*-butyl-5-[4-(bromomethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**8c**) was synthesized from 4-(hydroxymethyl)phenyl isomer (**7c**) as pale yellow oil and crude product was used to the next reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.33 (s, 6H), 3.87 (s, 2H), 4.49 (s, 2H), 7.27 (d, J=8.1 Hz, 2H), 7.35 (d, J=8.1 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.4, 32.4, 32.6, 33.2, 47.2, 83.1, 126.2, 128.6, 130.3, 136.4, 137.5, 149.3 ppm. IR (liquid film): 2957, 2868, 1651 cm^{-1}. Mass (*m*/*z*, %): 324 (M^+, 20), 322 (M^+, 21), 310 (17), 309 (99), 308 (19), 307 (100), 263 (26), 243 (32), 228 (20), 199 (25), 197 (24), 171 (43), 118 (27), 90 (29), 57 (72).

4.1.5. 4-*tert*-Butyl-5-[3-(cyanomethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (3a); typical procedure. A solution of 5-[3-(bromomethyl)phenyl]-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**8b**) (3.81 g, 11.8 mmol), NaCN (804 mg, 16.4 mmol) and tetra-*n*-butylammonium hydrogen sulfate (804 mg, 2.37 mmol) in THF–H_2O (5/1) (36 mL) was stirred under nitrogen atmosphere at refluxing temperature for 28 h. The reaction mixture was poured into satd aq NaCl and extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel and eluted with AcOEt–hexane (1/9) to give 2.43 g of **3a** as a colorless oil in 76.4% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.34 (s, 6H), 3.76 (s, 2H), 3.88 (s, 2H), 7.26–7.31 (m, 3H), 7.35 (t, J=7.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 23.5, 27.4, 32.5, 32.6, 47.3, 83.2, 117.6, 126.3, 127.4, 128.6, 129.2, 129.4, 129.6, 137.2, 148.8 ppm. IR (liquid film): 2957, 2869, 2251 cm^{-1}. Mass (*m*/*z*, %): 269 (M^+, 11), 255 (16), 254 (100), 144 (42), 116 (16), 57 (14). HRMS (ESI): 292.1663, calcd for $C_{18}H_{23}NONa$ ($M+Na^+$) 292.1677.

Similarly to the case of **3b**, 4-*tert*-butyl-5-[2-(cyanomethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**3a**) was synthesized from 2-(chloromethyl)phenyl isomer (**8a**) as a colorless oil in 78.9% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.03 (s, 9H), 1.36 (s, 6H), 3.78 (s, 2H), 3.88 (s, 2H), 7.28–7.41 (m, 3H), 7.50 (d, J=7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 21.2, 27.3, 32.1, 32.6, 47.3, 83.1, 117.8, 127.5, 127.9, 128.0, 129.2, 129.2, 131.1, 135.0, 146.8 ppm. IR (liquid film): 2958, 2869, 2250 cm^{-1}. Mass (*m*/*z*, %): 269 (M^+, 19), 255 (17), 254 (100), 198 (40), 171 (19), 144 (30), 130 (60), 91 (66), 57 (30). HRMS (ESI): 292.1675, calcd for $C_{18}H_{23}NONa$ ($M+Na^+$) 292.1677.

Similarly to the case of **3b**, 4-*tert*-butyl-5-[4-(cyanomethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**3c**) was synthesized from 4-(bromomethyl)phenyl isomer (**8c**) as pale yellow plates, melted at 68.7–69.1 °C (from hexane–CH_2Cl_2) in 62.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.33 (s, 6H), 3.76 (s, 2H), 3.87 (s, 2H), 7.28–7.34 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.4, 27.3, 32.4, 32.6, 47.2, 83.1, 117.7, 126.3, 127.4, 129.6, 130.7, 136.2, 149.0 ppm. IR (KBr): 2959, 2924, 2869, 2250 cm^{-1}. Mass (*m*/*z*, %): 269 (M^+, 18), 255 (20), 254 (100), 171 (11), 144 (41), 116 (13), 57 (22). HRMS (ESI): 292.1662, calcd for $C_{18}H_{23}NONa$ ($M+Na^+$) 292.1677.

4.1.6. 4-*tert*-Butyl-5-[3-(1-cyanoethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (3d). A solution of

4-*tert*-butyl-5-[3-(cyanomethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**3b**) (497 mg, 1.84 mmol) in dry THF (2.5 mL) was added to a suspension of NaH (60% in oil, 74.9 mg, 1.87 mmol) in dry THF (2.5 mL) under nitrogen atmosphere at 0 °C. To the solution MeI (0.13 mL, 2.09 mmol) was added and stirred at room temperature for 2 h. The reaction mixture was poured into saturated aq NH_4Cl and extracted with AcOEt. The organic layer was washed with saturated aq NaCl, dried over $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel with hexane–AcOEt (9/1) to give 337 mg of **3d** as a pale yellow oil in 64.5% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.34 (s, 6H), 1.64 (d, J=7.3 Hz, 3H), 3.88 (s, 2H), 3.90 (q, J=7.3 Hz, 1H), 7.25–7.38 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.5, 27.3, 31.1, 32.4, 32.5, 47.2, 83.2, 121.4, 126.3, 126.4, 128.2, 128.7, 129.6, 136.6, 137.2, 149.1 ppm. IR (liquid film): 2957, 2870, 2243 cm^{-1}. Mass (*m*/*z*, %): 283 (M^+, 11), 268 (63), 243 (26), 228 (26), 159 (15), 158 (100), 57 (55). HRMS (ESI): 306.1804, calcd for $C_{19}H_{25}NONa$ ($M+Na^+$) 306.1834.

4.1.7. 4-*tert*-Butyl-5-[3-(carboxymethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (9). 4-*tert*-butyl-5-[3-(cyanomethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**3b**) (8.52 g, 31.6 mmol) was added to a solution of NaOH (6.31 g, 158 mmol) in EtOH (80 mL) and H_2O (8 mL) and refluxed for 2 h. The reaction mixture was poured into 1 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–hexane (1/1) to give 8.44 g of **9** as a colorless leaflets melted at 95.5–96.1 °C (from hexane–CH_2Cl_2) in 97.4% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.03 (s 9H), 1.33 (s, 6H), 3.64 (s, 2H), 3.87 (s, 2H), 7.20–7.25 (m, 3H), 7.29 (t, J=7.3 Hz, 1H ppm). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.4, 32.4, 32.5, 40.9, 47.2, 83.1, 126.0, 128.1, 128.8, 129.0, 130.9, 132.8, 136.5, 149.6. 177.3 ppm. IR (KBr): 2983, 2955, 2916, 2869, 1711 cm^{-1}. Mass (*m*/*z*, %): 288 (M^+, 18), 274 (19), 273 (100), 171 (14), 163 (35), 57 (16). HRMS (ESI, negative): 287.1629, calcd for $C_{18}H_{23}O_3$ 287.1647.

4.1.8. 4-*tert*-Butyl-5-[3-(methoxycarbonylmethyl)-phenyl]-3,3-dimethyl-2,3-dihydrofuan (3e). $NaHCO_3$ (512 mg, 6.09 mmol) was added to a solution of 4-*tert*-butyl-5-[3-(carboxymethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**9**) (1.17 g, 4.06 mmol) in dry DMF (10 mL) at room temperature under nitrogen atmosphere and stirred for 20 min. To the solution methyl iodide (0.51 mL, 8.19 mmol) was added and stirred overnight. The reaction mixture was poured into satd aq NH_4Cl and then extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel and eluted with AcOEt–hexane (1/4) to give 1.10 g of **3e** as a colorless oil in 89.7% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.04 (s 9H), 1.33 (s, 6H), 3.62 (s, 2H), 3.67 (s, 3H), 3.87 (s, 2H), 7.18–7.30 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 27.4, 32.4, 32.6, 41.1, 47.2, 51.9, 83.1, 125.8, 128.0, 128.5, 128.8, 130.7, 133.4, 136.3, 149.7, 171.6 ppm. IR (liquid film): 2955, 2870, 1742 cm^{-1}. Mass (*m*/*z*, %): 302 (M^+, 18), 288 (20), 287 (100), 177 (46), 171 (29), 57 (25). HRMS (ESI): 325.1787, calcd for $C_{19}H_{26}O_3Na$ ($M+Na^+$) 325.1780.

4.1.9. 4-*tert*-Butyl-5-[3-(benzoylmethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (3f). A solution of 4-*tert*-butyl-5-[3-(carboxymethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**9**) (304 mg, 1.05 mmol) in dry THF (2 mL) was added dropwise over 10 min to a solution of butyllithium (1.62 M in hexane, 1.35 mL, 2.19 mmol) in dry THF (1.5 mL) at −78 °C under nitrogen atmosphere and was stirred for 30 min. Benzoyl chloride (0.13 mL, 1.12 mmol) was added to the solution and stirred for 1 h. The reaction mixture was poured into 1 N HCl and then extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel and eluted with AcOEt–hexane (1/9) to give 96 mg of **3f** as a yellow oil in 26.2% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.99 (s, 9H), 1.32 (s, 6H), 3.86 (s, 2H), 4.27 (s, 2H), 7.17 (d, J=7.6 Hz, 1H), 7.21 (s, 1H), 7.21 (d, J=7.6 Hz, 1H), 7.28 (t, J=7.6 Hz, 1H), 7.43 (t, J=7.4 Hz, 2H), 7.53 (t with fine coupling, J=7.4 Hz, 1H), 7.98 (d, J=7.4 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.4, 32.3, 32.5, 45.5, 47.1, 83.1, 125.8, 128.2, 128.3, 128.6, 128.6, 129.0, 131.0, 133.0, 134.1, 136.5, 136.5, 149.7, 197.4 ppm. IR (liquid film): 2957, 2869, 1720, 1683 cm^{-1}. Mass (*m*/*z*, %): 348 (M^+, 22), 334 (27), 333 (100), 277 (17), 223 (38), 105 (67), 91 (13), 77 (27), 57 (29). HRMS (ESI): 371.1987, calcd for $C_{24}H_{28}O_2Na$ ($M+Na^+$) 371.1987.

4.1.10. 4-*tert*-Butyl-5-{3-[cyano(methoxycarbonyl) methyl]phenyl}-3,3-dimethyl-2,3-dihydrofuran (3g). A solution of 4-*tert*-butyl-5-[3-(cyanomethy)lphenyl]-3,3-dimethyl-2,3-dihydrofuran (**3b**) (511 mg, 1.90 mmol) and dimethyl carbonate (0.24 mL, 2.85 mmol) in toluene (4 mL) was added dropwise over 5 min to a suspension of NaH (60% in oil, 161 mg, 4.03 mmol) in toluene (4 mL) under nitrogen atmosphere and stirred for 1 h. The reaction mixture was poured into 1 N HCl and then extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel and eluted with AcOEt–hexane (1/9) to give 582 mg of **3g** as a pale orange oil in 93.7% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.03 (s, 9H), 1.34 (s, 6H), 3.79 (s, 3H), 3.88 (s, 2H), 4.73 (s, 1H), 7.34 (d with fine coupling, J=7.1 Hz, 1H), 7.37–7.45 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 27.4, 32.5, 32.6, 43.4, 47.3, 53.9, 83.2, 115.3, 126.7, 127.4, 128.8, 129.2, 129.5, 130.7, 137.3, 148.6, 165.1 ppm. IR (liquid film): 2957, 2869, 2252, 1753 cm^{-1}. Mass (*m*/*z*, %): 327 (M^+, 13), 313 (21), 312 (100), 202 (42), 115 (10), 57 (56), 55 (11). HRMS (ESI): 350.1725, calcd for $C_{20}H_{25}NO_3Na$ ($M+Na^+$) 350.1732.

4.1.11. 4-*tert*-Butyl-5-[3-(1-cyanoethenyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (4). A solution of 4-*tert*-butyl-5-[3-(cyanomethyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**3b**) (521 mg, 1.93 mmol), paraformaldehyde (87.8 mg, 2.92 mmol), K_2CO_3 (429 mg, 3.10 mmol) and Bu_4NI (14.7 mg, 0.0398 mmol) in toluene (10 mL) was stirred under nitrogen atmosphere at 80 °C for 15 min. The reaction mixture was poured into satd aq NaCl and then 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 hexane–AcOEt (9/1) to give 441 mg of (**4**) as a yellow oil in 81.3% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.05 (s, 9H), 1.35 (s, 6H), 3.89 (s, 2H), 6.12 (s, 1H), 6.35 (s, 1H), 7.35 (d with fine coupling, J=7.6 Hz, 1H), 7.40 (t, J=7.6 Hz, 1H), 7.52 (s with fine coupling, 1H), 7.56 (d with fine coupling, J=7.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 27.4, 32.5, 32.6, 47.3, 83.2, 117.6, 122.7, 125.4, 126.7, 127.1, 128.3, 128.6, 131.5, 132.0, 137.2, 148.8 ppm. IR (liquid film): 2957, 2868, 2228 cm^{-1}. Mass (*m*/*z*, %): 281 (M^+, 20), 267 (22), 266 (100), 210 (19), 156 (69), 128 (22), 101 (12), 57 (64). HRMS (ESI): 304.1654, calcd for $C_{19}H_{23}NONa$ ($M+Na^+$) 304.1677.

4.1.12. 4-*tert*-Butyl-5-{3-[1-cyano-3,3-bis(methoxycarbonyl)butyl]pheny}-3,3-dimethyl-2,3-dihydrofuran (23). Dimethyl methylmalonate (**18a**) (203 mg, 1.39 mmol) was added to 18-crown-6 (331 mg, 1.25 mmol) and *tert*-BuOK (1.0 M in THF, 1.2 mL, 1.20 mmol) in dry toluene (15 mL) at room temperature under nitrogen atmosphere. To the solution 4-*tert*-butyl-5-[3-(1-cyanoethenyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**4**) (339 mg, 1.20 mmol) in dry toluene (5 mL) was added at room temperature under nitrogen atmosphere and stirred for 8 min. 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 hexane–ethyl ether (3/1) to give 272 mg of **23** as a colorless viscous oil in 52.8% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.04 (s, 9H), 1.34 (s, 6H), 1.57 (s, 3H), 2.35 (dd, J=14.6, 3.7 Hz, 1H), 2.50 (dd, J=14.6, 10.3 Hz, 1H), 3.77 (s, 6H), 3.88 (s, 2H), 4.04 (dd, J=10.3, 3.7 Hz, 1H), 7.25–7.38 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.9, 27.4, 27.4, 32.4, 32.6, 33.2, 42.1, 47.3, 52.8, 52.9, 52.9, 83.2, 120.4, 126.5, 127.0, 128.7, 128.8, 129.9, 136.0, 137.3, 149.0, 171.3, 171.6 ppm. IR (liquid film): 2956, 2870, 2243, 1734 cm^{-1}. Mass (*m*/*z*, %): 427 (M^+, 17), 413 (31), 412 (100), 410 (10), 302 (11), 266 (13), 236 (12), 57 (12). HRMS (ESI): 450.2257, calcd for $C_{25}H_{33}NO_5Na$ ($M+Na^+$) 450.2256.

4.1.13. 4-*tert*-Butyl-5-[3-(3-cyano-4,5-dihydro-5,5-diphenyl-3*H*-pyrazole-3-yl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (36a). A solution of (diphenyl)diazomethane (1.0 mmol: prepared from benzophenone hydrazone and mercury oxide in hexane and ethanol in the presence of catalytic amount of EtONa and used crude product) in acetonitrile (1.0 mL) was added to a solution of 4-*tert*-butyl-5-[3-(1-cyanoethenyl)phenyl]-3,3-dimethyl-2,3-dihydrofuran (**4**) (184 mg, 0.65 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (2.5 mg) in acetonitlile (2 mL) at room temperature under nitrogen atmosphere and stirred for 3.5 h. The reaction mixture was concentrated in vacuo and chromatographed on silica gel with hexane–AcOEt (10/1–5/1) to give 298 mg of **36a** as colorless viscous oil in 96.0% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.90 (s, 9H), 1.31 (s, 3H), 1.31 (s, 3H), 2.45 (d, J=6.2 Hz, 1H), 2.62 (d, J=6.2 Hz, 1H), 3.84 (s 2H), 6.97–7.16 (m, 8H), 7.18 (s with fine coupling, 1H), 7.28 (d with fine coupling, J=7.3 Hz, 1H), 7.35–7.40 (m, 2H), 7.58–7.62 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 24.6, 27.3, 27.3, 27.4, 32.3, 32.6, 47.0, 47.1, 83.1, 121.3, 126.1, 127.2, 127.5, 127.8, 127.8, 128.3, 128.8, 129.1, 129.2, 129.3, 129.7, 132.4, 136.6, 138.0, 141.1, 149.1 ppm. IR (liquid film): 2957, 2868, 2233, 1652 cm^{-1}. Mass (*m*/*z*, %): 475 (M^+, trace), 447 (22), 433 (37), 432 (100), 376 (16), 322 (20). HRMS (ESI): 470.2455, calcd for $C_{32}H_{33}NONa$ ($M-N_2+Na^+$) 470.2460.

4.2. Synthesis of bicyclic dioxetanes (1): general procedure

A solution of 5-aryl-4-*tert*-butyl-3,3-dimethyl-2,3-dihydrofuran (**3**) (100–300 mg) and tetraphenylporphin (TPP) (ca.1 mg) in CH_2Cl_2 (10 mL) was irradiated externally with 940 W Na lamp under oxygen atmosphere at 0 °C for 1–2 h, except the case of dihydrofuran (**4**), singlet oxygenation of which was carried out at −78 °C. The photolysate was concentrated in vacuo. The residue was chromatographed on silica gel to give the corresponding 5-*tert*-butyl-1-aryl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]-heptane (**1**).

4.2.1. 5-*tert*-Butyl-1-[3-(cyanomethyl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (1b). Pale yellow granules melted at 99.8–100.6 °C (from hexane–CH_2Cl_2), 88.9% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.98 (s, 9H), 1.16 (s, 3H), 1.39 (s, 3H), 3.79 (s, 2H), 3.83 (d, J=8.2 Hz, 1H), 4.59 (broad d, J=8.2 Hz, 1H), 7.39 (d, J=7.6 Hz, 1H), 7.44 (t, J=7.6 Hz, 1H), 7.59 (broad s, 1H), 7.62 (d, J=7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 18.5, 23.7, 25.2, 26.8, 36.7, 45.7, 80.3, 104.9, 116.2, 117.4, 127.8, 128.1, 128.7, 128.9, 129.7, 137.1 ppm. IR (KBr): 3000, 2966, 2902, 2251 cm^{-1}. Mass (20 eV, *m*/*z*, %): 302 (M^++1, 2), 269 (7), 246 (15), 244 (40), 218 (52), 216 (23), 162 (48), 144 (89), 125 (11), 111 (14), 97 (12), 85 (66), 57 (100), 56 (39). HRMS (ESI): 324.1587, calcd for $C_{18}H_{23}NO_3Na$ ($M+Na^+$) 324.1576. Anal. Calcd for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.86; H, 8.08; N, 4.73.

4.2.2. 5-*tert*-Butyl-1-[2-(cyanomethyl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (1a). Pale yellow columns melted at 98.3–99.0 °C (from hexane–CH_2Cl_2), 94.8% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.98 (s, 9H), 1.22 (s, 3H), 1.44 (s, 3H), 3.89 (d, J=8.3 Hz, 1H), 3.98 (d, J=18.8 z, 1H), 4.29 (d, J=18.8 Hz, 1H), 4.57 (d, J=8.3 Hz, 1H), 7.38–7.48 (m, 2H), 7.58 (d, J=7.3 Hz, 1H), 7.86 (d, J=7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 19.3, 23.1, 25.8, 26.4, 36.7, 45.5, 80.2, 106.0, 117.3, 118.1, 127.7, 129.2, 130.3, 130.5, 131.3, 133.4 ppm. IR (KBr): 2978, 2905, 2251 cm^{-1}. Mass (20 eV, *m*/*z*, %): 301 (M^+, 1), 269 (7), 254 (11), 246 (36), 244 (50), 218 (34), 216 (27), 163 (11), 162 (100), 145 (13), 144 (86), 134 (14), 85 (32), 57 (69), 56 (17). HRMS (ESI): 324.1583, calcd for $C_{18}H_{23}NO_3Na$ ($M+Na^+$) 324.1576.

4.2.3. 5-*tert*-Butyl-1-(4-cyanomethyl)phenyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (1c). Pale yellow granules melted at 69.3–70.2 °C (from hexane–CH_2Cl_2), 80.3% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.97 (s, 9H), 1.16 (s, 3H), 1.38 (s, 3H), 3.79 (s, 2H), 3.83 (d, J=8.1 Hz, 1H), 4.58 (d, J=8.1 Hz, 1H), 7.37 (d, J=8.5 Hz, 2H), 7.65 (d, J=8.5 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 18.4, 23.4, 25.0, 26.7, 36.6, 45.6, 80.2, 104.9,

116.3, 117.5, 127.5, 129.1, 131.3, 136.0 ppm. IR (KBr): 2969, 2897, 2251 cm^{-1}. Mass (20 eV, *m/z*, %): 302 (M^+ + 1, 1), 269 (2), 246 (13), 244 (56), 216 (19), 177 (21), 162 (24), 145 (11), 144 (100), 85 (79), 57 (73), 56 (24). HRMS (ESI): 324.1584, calcd for $C_{18}H_{23}NO_3Na$ ($M+Na^+$) 324.1576.

4.2.4. 5-*tert*-Butyl-1-[3-(1-cyanoethyl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (1d). Pale yellow plates melted at 134.7–135.5 °C (from hexane–CH_2Cl_2), 78.6% yield. ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.97 (s, 9H), 1.16 (s, 3H), 1.39 (s, 3H), 1.64 (d, $J=7.3$ Hz, 3H), 3.84 (d, $J=8.1$ Hz, 1H), 3.95 (q, $J=7.3$ Hz, 1H), 4.59 (d, $J=8.1$ Hz, 1H), 7.40–7.46 (m, 2H), 7.59–7.62 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 18.4, 21.3, 21.5, 25.1, 26.7, 31.2, 31.3, 36.7, 45.6, 80.2, 80.3, 104.9, 116.3, 121.2, 126.8, 126.9, 127.7, 127.8, 128.1, 128.2, 128.8, 136.8, 136.9, 137.1 ppm. IR (KBr): 2992, 2966, 2890, 2242 cm^{-1}. Mass (20 eV, *m/z*, %): 283 (M^+-32, 4), 260 (15), 258 (33), 232 (57), 230 (26), 177 (12), 176 (63), 159 (11), 158 (100), 85 (38), 57 (72). HRMS (ESI): 338.1752, calcd for $C_{19}H_{25}NO_3Na$ ($M+Na^+$) 338.1732.

4.2.5. 5-*tert*-Butyl-1-[3-(methoxycarbonylmethyl)-phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (1e). Pale yellow oil, 85.6% yield. ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.97 (s 9H), 1.16 (s, 3H), 1.38 (s, 3H), 3.66 (s, 2H), 3.67 (s, 3H), 3.82 (d, $J=8.1$ Hz, 1H), 4.59 (broad d, $J=8.1$ Hz, 1H), 7.30 (d with fine coupling, $J=7.6$ Hz, 1H), 7.35 (dd, $J=7.8$, 7.6 Hz, 1H), 7.52–7.56 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 18.5, 25.1, 26.7, 36.7, 41.1, 45.6, 52.0, 80.2, 104.8, 116.5, 127.1, 128.1, 129.3, 130.3, 133.7, 136.2, 171.6 ppm. IR (liquid film): 2962, 2896, 1740 cm^{-1}. Mass (20 eV, *m/z*, %): 334 (M^+, trace), 302 (trace), 277 (18), 195 (13), 178 (10), 177 (100), 57 (12). HRMS (ESR): 357.1686, calcd for $C_{19}H_{26}O_5Na$ ($M+Na^+$) 357.1678.

4.2.6. 5-*tert*-Butyl-1-[3-(benzoylmethyl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (1f). Pale yellow granules, melted at 110.0–110.9 °C (from hexane–CH_2Cl_2), 90.2% yield. ^1H NMR (500 MHz, $CDCl_3$): δ_H 0.92 (s, 9H), 1.14 (s, 3H), 1.35 (s, 3H), 3.81 (d, $J=8.2$ Hz, 1H), 4.32 (s, 2H), 4.57 (d, $J=8.2$ Hz, 1H), 7.30 (d, $J=7.6$ Hz, 1H), 7.36 (dd, $J=8.2$, 7.6 Hz, 1H), 7.44 (dd, $J=8.3$, 7.3 Hz, 2H), 7.51–7.57 (m, 3H), 7.99 (d with fine coupling, $J=$ 8.3 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 18.5, 25.1, 26.7, 36.6, 45.5, 45.6, 80.2, 104.9, 116.6, 126.9, 128.2, 128.6, 128.6, 129.5, 130.5, 133.2, 134.3, 136.3, 136.5, 197.2 ppm. IR (KBr): 2971, 2906, 1688 cm^{-1}. Mass (20 eV, *m/z*, %): 348 (M^+-32, 1), 323 (20), 241 (21), 224 (17), 223 (100), 105 (24). HRMS (ESI): 403.1894, calcd for $C_{24}H_{28}O_4Na$ ($M+Na^+$) 403.1885.

4.2.7. 5-*tert*-Butyl-1-[3-cyano(methoxycarbonyl)methyl-phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (1g). Pale yellow oil in 88.9% yield (1:1 mixture of diastereoisomers). ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.96 (s, 9H), 1.17 (s, 3H), 1.38 (s, 1.5H), 1.39 (s, 1.5H), 3.78 (s, 1.5H), 3.79 (s, 1.5H), 3.85 (d, $J=8.2$ Hz, 1H), 4.59 (d, $J=$ 8.2 Hz, 1H), 4.78 (s, 1H), 7.45–7.55 (m, 2H), 7.65–7.76 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 18.4, 25.1, 26.7, 36.7, 43.4, 45.6, 54.0, 80.3, 80.3, 105.0, 115.2, 115.2, 116.0, 128.2, 128.2, 128.9, 128.9, 129.0, 129.0, 129.3, 129.3, 129.6, 137.4, 137.4, 165.1, 165.1 ppm. IR (liquid film): 2962, 2898, 2254, 1753 cm^{-1}. Mass (20 eV, *m/z*, %): 360 (M^+ + 1, 1), 327 (4), 304 (12), 302 (26), 287 (29), 276 (63), 274 (23), 220 (63), 203 (11), 202 (100), 85 (43), 57 (69), 56 (23). HRMS (ESI): 382.1626, calcd for $C_{20}H_{25}NO_5Na$ ($M+Na^+$) 382.1630.

4.2.8. 5-*tert*-Butyl-1-[3-(1-cyanoethenyl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (2). Pale yellow granules melted at 123.3–124.0 °C (from hexane–CH_2Cl_2), 89.7% yield. ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.98 (s, 9H), 1.17 (s, 3H), 1.39 (s, 3H), 3.85 (d, $J=8.2$ Hz, 1H), 4.60 (d, $J=8.2$ Hz, 1H), 6.16 (s, 1H), 6.38 (s, 1H), 7.48 (t, $J=7.8$ Hz, 1H), 7.64 (d with fine coupling, $J=7.8$ Hz, 1H), 7.68 (d with fine coupling, $J=7.8$ Hz, 1H), 7.86 (s with fine coupling, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 18.4, 25.1, 26.8, 36.7, 45.6, 80.3, 105.0, 116.2, 117.4, 122.6, 125.5, 127.0, 128.7, 128.8, 129.8, 132.2, 137.1 ppm. IR (KBr): 2998, 2959, 2902, 2226 cm^{-1}. Mass (20 eV, *m/z*, %): 281 (M^+-32, 8), 258 (22), 256 (33), 230 (40), 228 (26), 174 (41), 157 (13), 156 (100), 85 (40), 57 (75). HRMS (ESI): 336.1593, calcd for $C_{19}H_{23}NO_3Na$ ($M+Na^+$) 336.1576. Anal. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.52; H, 7.80; N, 4.17.

4.2.9. 5-*tert*-Butyl-1-{3-[1-cyano-3,3-bis(methoxycarbonyl)butyl]phenyl}-4,4-dimethyl-2,6,7-trioxabicyclo-[3.2.0]heptane (22). Pale yellow oil, 82.8% yield (1:1 mixture of diastereoisomers). ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.97 (s, 4.5H), 0.97 (s, 4.5H), 1.16 (s, 3H), 1.39 (s, 1.5H), 1.40 (s, 1.5H), 1.57 (s, 1.5H), 1.57 (s, 1.5H), 2.32 (dd, $J=$ 14.5, 3.5 Hz, 0.5H), 2.35 (dd, $J=14.5$, 3.5 Hz, 0.5H), 2.49 (dd, $J=14.5$, 7.6 Hz, 0.5H), 2.52 (dd, $J=14.5$, 7.6 Hz, 0.5H), 3.77 (broad s, 6H), 3.84 (d, $J=8.1$ Hz, 0.5H), 3.84 (d, $J=8.1$ Hz, 0.5H), 4.04–4.12 (m, 1H), 4.59 (d, $J=8.1$ Hz, 1H), 7.42–7.46 (m, 2H), 7.57–7.68 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 18.4, 18.4, 20.8, 20.9, 25.1, 26.7, 33.2, 33.3, 36.7, 41.9, 42.1, 45.6, 52.8, 52.8, 52.9, 52.9, 80.2, 80.3, 105.0, 116.2, 120.2, 120.2, 127.3, 127.3, 128.3, 128.3, 128.4, 128.4, 128.8, 128.9, 136.1, 136.2, 137.2, 171.2, 171.2, 171.5, 171.5 ppm. IR (liquid film): 2958, 2898, 2243, 1731 cm^{-1}. Mass (20 eV, *m/z*, %): 427 (M^+- 32, 6), 320 (24), 303 (18), 302 (100), 57 (10). HRMS (ESI): 482.2143, calcd for $C_{25}H_{33}NO_7Na$ ($M+Na^+$) 482.2155.

4.2.10. 5-*tert*-Butyl-1-[3-(3-cyano-4,5-dihydro-5,5-diphenyl-3*H*-pyrazol-3-yl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (35a). Pale yellow granules melted at 151.0–153.0 °C (from MeOH–CH_2Cl_2), 99.3% yield (45:55 mixture of diastereoisomers). ^1H NMR (500 MHz, $CDCl_3$): δ_H 0.81 (s, 4.95H), 0.87 (s. 4.05H), 1.13 (s, 1.65H), 1.13 (s, 1.35H), 1.32 (s, 1.35H), 1.33 (s, 1.65H), 2.48 (d, $J=6.2$ Hz, 0.55H), 2.49 (d, $J=6.2$ Hz, 0.45H), 2.62 (d, $J=6.2$ Hz, 0.45H), 2.65 (d, $J=6.2$ Hz, 0.55H), 3.78 (d, $J=8.2$ Hz, 0.55H), 3.82 (d, $J=8.2$ Hz, 0.45H), 4.54 (d, $J=8.2$ Hz, 0.55H), 4.56 (d, $J=8.2$ Hz, 0.45H), 6.98–7.11 (m, 5H), 7.18–7.41 (m, 5.55H), 7.48 (d, $J=7.8$ Hz, 0.45H), 7.53–7.62 (m, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 18.4 (CH_3), 24.7, 24.9, 25.0, 25.0, 26.7, 26.8, 27.4, 36.5, 36.5, 45.5, 46.9, 47.2, 80.1, 80.2, 104.9, 104.9, 116.2, 116.3, 121.1, 121.1, 126.5, 127.2, 127.2, 127.7, 127.8, 127.8, 128.0, 128.4, 128.4, 128.4,

128.8, 128.9, 129.0, 129.1, 129.5, 129.6, 129.6, 132.7, 136.4, 136.5, 137.9, 138.0, 141.0 ppm. IR (KBr): 2968, 2894, 2234 cm^{-1}. Mass (*m/z*, %): 479 (M^+-N_2, 3), 452 (8), 339 (16), 338 (15), 323 (26), 322 (100), 321 (21), 312 (14), 295 (16), 294 (22), 293 (68), 217 (11), 216 (14), 165 (22), 141 (51), 57 (42). HRMS (ESI): 502.2352, calcd for $C_{32}H_{33}NO_3Na$ ($M-N_2+Na^+$) 502.2358.

4.3. Thermolysis of bicyclic dioxetanes (1a–1g); general procedure

A solution of 5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane bearing a substituted phenyl (**1**) (30 mg) in *p*-xylene (5 mL) was stirred under nitrogen atmosphere for 2 h at 140 °. After cooling, the reaction mixture was concentrated in vacuo. ^1H NMR Spectral analysis showed that the residue included the desired ester (**10**) exclusively. Chromatographic purification [silica gel/AcOEt–hexane (1/4)] of the residue gave the corresponding 2,2,4,4-tetramethyl-3-oxopentyl benzoate (**10**).

4.3.1. 2-(Cyanomethyl)benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (10a). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.28 (s, 9H), 1.40 (s, 6H), 4.23 (s, 2H), 4.39 (s, 2H), 7.41 (td, $J=7.3$, 2.0 Hz, 1H), 7.54–7.62 (m, 2H), 7.95 (d with fine coupling, $J=7.3$ Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.0, 23.5, 28.1, 45.8, 49.0, 72.3, 117.8, 128.1, 128.3, 130.1, 131.1, 132.2, 133.1, 165.9, 215.8 ppm. IR (liquid film): 2979, 2246, 1714, 1681 cm^{-1}. Mass (20 eV, *m/z*, %): 301 (M^+, 1), 246 (35), 244 (45), 218 (31), 216 (28), 163 (11), 162 (100), 145 (14), 144 (94), 85 (18), 57 (56), 56 (13). HRMS (ESI): 324.1533, calcd for $C_{18}H_{23}NO_3Na$ ($M+Na^+$) 324.1576.

4.3.2. 3-(Cyanomethyl)benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (10b). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.29 (s, 9H), 1.39 (s, 6H), 3.79 (s, 2H), 4.41 (s, 2H), 7.46 (t, $J=7.8$ Hz, 1H), 7.55 (d with fine coupling, $J=7.8$ Hz, 1H), 7.92–7.95 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 23.5, 23.7, 28.2, 45.9, 49.2, 72.4, 117.1, 128.9, 129.1, 129.3, 130.3, 131.0, 132.2, 165.3, 215.7 ppm. IR (liquid film): 2972, 2874, 2250, 1721, 1685 cm^{-1}. Mass (20 eV, *m/z*, %): 302 ($M^+ +1$, trace), 246 (13), 244 (35), 218 (43), 216 (31), 162 (48), 145 (11), 144 (100) 85 (46), 57 (85), 56 (32). HRMS (ESI): 324.1581, calcd for $C_{18}H_{23}NO_3Na$ ($M+Na^+$) 324.1576.

4.3.3. 4-(Cyanomethyl)benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (10c). Colorless needles, melted at 66.1–66.5 °C (from hexane–ether). ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.28 (s, 9H), 1.39 (s, 6H), 3.81 (s, 2H), 4.41 (s, 2H), 7.41 (d, $J=8.4$ Hz, 2H), 7.99 (d, $J=8.4$ Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 23.7, 23.7, 28.2, 45.9, 49.2, 72.2, 117.0, 127.9, 129.9, 130.2, 134.8, 165.4, 215.7 ppm. IR (KBr): 2978, 2929, 2873, 2246, 1719, 1683 cm^{-1}. Mass (20 eV, *m/z*, %): 246 (M^+-55, 14), 244 (M^+, 46), 216 (13), 162 (24), 145 (11), 144 (100), 85 (46), 57 (59), 56 (23). HRMS (ESI): 324.1530, calcd for $C_{18}H_{23}NO_3Na$ ($M+Na^+$) 324.1576.

4.3.4. 3-(1-Cyanoethyl)benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (10d). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.29 (s, 9H), 1.39 (s, 3H), 1.40 (s, 3H), 1.66 (d, $J=7.3$ Hz, 3H), 3.95 (q, $J=7.3$ Hz, 1H), 4.42 (s, 2H), 7.47 (t, $J=7.8$ Hz, 1H), 7.58 (d with fine coupling, $J=7.8$ Hz, 1H), 7.93 (d with fine coupling, $J=7.8$ Hz, 1H), 7.96 (s with fine coupling, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.3, 23.6, 23.7, 28.1, 31.1, 45.9, 49.1, 72.4, 121.0, 127.8, 129.2, 129.4, 131.0, 131.2, 137.5, 165.5, 215.9 ppm. IR (liquid film): 2980, 2875, 2243, 1722, 1686 cm^{-1}. Mass (20 eV, *m/z*, %): 316 ($M^+ +1$, 2), 260 (12), 258 (26), 232 (36), 230 (20), 177 (12), 176 (48), 159 (11), 158 (100), 85 (25), 57 (59). HRMS (ESI): 338.1737, calcd for $C_{19}H_{25}NO_3Na$ ($M+Na^+$) 338.1732.

4.3.5. 3-(Methoxycarbonylmethyl)benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (10e). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.28 (s, 9H), 1.38 (s, 6H), 3.66 (s, 2H), 3.70 (s, 3H), 4.41 (s, 2H), 7.39 (t, $J=7.8$ Hz, 1H), 7.48 (d, $J=7.8$ Hz, 1H), 7.86–7.90 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 23.8, 28.2, 40.9, 45.9, 49.2, 52.2, 72.1, 128.2, 128.6, 130.3, 130.3, 133.8, 134.3, 165.9, 171.3, 215.7 ppm. IR (liquid film): 2958, 2874, 1741, 1722, 1686 cm^{-1}. Mass (20 eV, *m/z*, %): 334 (M^+, trace), 277 (18), 195 (16), 178 (11), 177 (100), 57 (11). HRMS (ESI): 357.1673, calcd for $C_{19}H_{26}O_5Na$ ($M+Na^+$) 357.1678.

4.3.6. 3-(Benzoylmethyl)benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (10f). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.27 (s, 9H), 1.37 (s, 6H), 4.33 (s, 2H), 4.40 (s, 2H), 7.39 (t, $J=7.6$ Hz, 1H), 7.44–7.50 (m, 3H), 7.58 (t with fine coupling, $J=7.4$ Hz, 1H), 7.85–7.90 (m, 2H), 7.98–8.03 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 23.8, 28.2, 45.1, 45.9, 49.2, 72.1, 128.0, 128.4, 128.6, 128.7, 130.3, 130.6, 133.3, 134.2, 134.8, 136.3, 165.9, 196.7, 215.8 ppm. IR (liquid film): 2973, 2873, 1721, 1684 cm^{-1}. Mass (20 eV, *m/z*, %): 381 ($M^+ +1$, trace), 323 (17), 241 (22), 224 (17), 223 (100), 105 (35), 57 (10). HRMS (ESI): 403.1873, calcd for $C_{24}H_{28}O_4Na$ ($M+Na^+$) 403.1885.

4.3.7. 3-[Cyano(methoxycarbonyl)methyl]benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (10g). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.29 (s, 9H), 1.40 (s, 3H), 1.40 (s, 3H), 3.82 (s, 3H), 4.41 (s, 2H), 4.79 (s, 1H), 7.51 (t, $J=7.8$ Hz, 1H), 7.68 (d with fine coupling, $J=7.8$ Hz, 1H), 8.01 (d with fine coupling, $J=7.8$ Hz, 1H), 8.06 (s with fine coupling, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.7, 23.7, 28.2, 43.3, 45.9, 49.2, 54.1, 72.5, 114.9, 129.0, 129.5, 130.3, 130.3, 131.3, 132.2, 164.8, 165.0, 215.7 ppm. IR (liquid film): 2960, 2252, 1754, 1723, 1685 cm^{-1}. Mass (20 eV, *m/z*, %): 360 ($M^+ +1$, trace), 304 (11), 302 (28), 277 (12), 276 (66), 274 (20), 220 (74), 203 (12), 202 (100), 85 (38), 57 (71), 56 (25). HRMS (ESI): 382.1609, calcd for $C_{20}H_{25}NO_5Na$ ($M+Na^+$) 382.1630.

4.3.8. 3-(1-Cyanoethenyl)benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (11). A solution of 5-*tert*-butyl-1-[3-(1-cyanoethenyl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (**2**) (17.5 mg, 0.056 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (3 mg) in *p*-xylene (1.5 mL) was stirred under nitrogen atmosphere for 8 h at 120 °C. After cooling, the reaction mixture was concentrated in vacuo and chromatographed on silica gel with hexane–AcOEt (5/1) to give 10.5 mg of **11** as colorless oil in 60.0%

yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.29 (s, 9H), 1.40 (s, 6H), 4.42 (s, 2H), 6.18 (s, 1H), 6.40 (s, 1H), 7.51 (t, J= 7.8 Hz, 1H), 7.79 (d with fine coupling, J=7.8 Hz, 1H), 8.00 (d with fine coupling, J=7.8 Hz, 1H), 8.21 (s with fine coupling, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.7, 28.2, 45.9, 49.2, 72.5, 117.2, 122.2, 126.5, 129.1, 129.2, 130.2, 130.6, 131.0, 132.7, 165.2, 215.6 ppm. IR (liquid film): 2972, 2875, 2229, 1724, 1685 cm^{-1}. Mass (20 eV, *m/z*, %): 256 (M^+-57, 14), 230 (15), 228 (16), 174 (28), 157 (14), 156 (100), 128 (17), 101 (11), 85 (21), 57 (69). HRMS (ESI): 336.1578, calcd for $C_{19}H_{23}NO_3Na$ ($M+Na^+$) 336.1576.

4.4. Chemiluminescence measurement: general procedure

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

Freshly prepared solution (2 mL) of TBAF (1.0×10^{-1} mol/L) in DMSO was transferred to a quartz cell ($10\times10\times$ 50 mm) and the latter placed into the spectrometer, which was thermostated with stirring at 25 °C. After 3–5 min, a solution of the dioxetane in DMSO (1.0×10^{-3} mol/L or 1.0×10^{-4} mol/L 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^{CL} has been reported to be 0.29 and was used here as standard[16].

Chemiluminescence measurement using a 18-crown-6 ether complex of *tert*-BuOK or potassium bis(methoxycarbonyl) methanide as a base was carried out in benzene similarly to the case of TBAF/DMSO. Complex of 18-crown-6 ether with a base was prepared in benzene as follows.

[K⊂(18-crown-6)]$^+$t-BuO$^-$: *tert*-BuOK (1 M in THF, 1.10 mL, 1.10 mmol) was added to a solution of 18-crown-6 ether (294 mg, 1.11 mmol) in benzene (30 mL) at room temperature under nitrogen atmosphere, and stirred for 10 min.

[K⊂(18-crown-6)]$^+$(**18a**)$^-$: *tert*-BuOK (1 M in THF, 1.10 mL, 1.10 mmol) was added to a solution of 18-crown-6 ether (291 mg, 1.10 mmol) and dimethyl methylmalonate, $CH_3CH(CO_2CH_3)_2$ (**18a**) (0.16 mL, 1.2 mmol) in benzene (30 mL) and stirred at room temperature under nitrogen atmosphere for 10 min.

[K⊂(18-crown-6)]$^+$(**18b**)$^-$: *tert*-BuOK (1 M in THF, 1.10 mL, 1.10 mmol) was added to a solution of 18-crown-6 ether (291 mg, 1.10 mmol), and dimethyl malonate, $CH_2(CO_2CH_3)_2$ (**18b**), (0.12 mL, 1.2 mmol) in benzene (30 mL) and stirred at room temperature under nitrogen atmosphere for 10 min.

[K⊂(18-crown-6)]$^+$(**18c**)$^-$: dimethyl chloromalonate, $ClCH(CO_2CH_3)_2$ (**18c**), (0.077 mL) was added to a solution of 18-crown-6 (148 mg, 0.56 mmol), and *tert*-BuOK (1 M in THF, 0.55 mL, 0.55 mmol) in benzene (4.4 mL) and stirred at room temperature under nitrogen atmosphere for 10 min.

4.5. Isolation of ketoesters (10) from the spent reaction mixture after chemiluminescent decomposition of dioxetanes (1): typical procedure

A solution of TBAF (1 M in THF, 0.1 mL) in DMSO (0.9 mL) was added to a solution of the dioxetane (**1g**) (20 mg) in DMSO (3 mL) at room temperature under nitrogen atmosphere. After stirring for 1 h, H_2O (1 mL) was added to the solution, and then, 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 ketoester (**10g**) without detectable amount of other products. The residue was purified by column chromatograpy on silica gel with AcOEt–hexane (1/4) to give the corresponding ketoester (**10g**) as a colorless oil in 78.6% yield.

4.5.1. 3-[1-Cyano-1-(methoxycarbonyl)ethyl]benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (15). TBAF (1 M in THF, 0.5 mL) was added to a solution of 3-[cyano(methoxycarbonyl)methyl]benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (**10g**) (82.9 mg, 0.231 mmol) in DMSO (2 mL) at room temperature under nitrogen atmosphere. After 5 min, MeI (0.05 mL, 0.80 mmol) was added to the solution. After stirring for 5 min, 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. The residue was chromatographed on silica gel and eluted with AcOEt–hexane (1/4) to give **15** as a colorless oil in 76.6% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.29 (s, 9H), 1.40 (s, 3H), 1.40 (s, 3H), 1.98 (s, 3H), 3.80 (s, 3H), 4.41 (s, 2H), 7.50 (t, J= 7.8 Hz, 1H), 7.75 (ddd, J=7.8, 2.1, 1.2 Hz, 1H), 7.99 (d with fine coupling, J=7.8 Hz, 1H), 8.13 (s with fine coupling, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.6, 23.7, 24.8, 28.1, 45.9, 47.9, 49.1, 54.1, 72.6, 118.9, 126.8, 129.4, 130.0, 130.4, 131.2, 136.1, 165.2, 168.0, 215.8 ppm. IR (liquid film): 2962, 2875, 2246, 1751, 1724, 1686, cm^{-1}. Mass (20 eV, *m/z*, %): 374 (M^++1, trace), 316 (25), 318 (10), 290 (56), 288 (15), 234 (71), 217 (14), 216 (100), 85 (23), 57 (42). HRMS (ESI): 396.1798, calcd for $C_{21}H_{27}NO_5Na$ ($M+Na^+$) 396.1787.

4.5.2. Chemiluminescent decomposition of a dioxetane (2) with [K⊂(18-crown-6)]$^+$*t*-BuO$^-$: isolation of 3-(1-cyanoethenyl)benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (11). To a solution of 5-*tert*-butyl-1-[3-(1-cyanoethenyl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo-[3.2.0]heptane (**2**) (31.4 mg, 0.10 mmol) in benzene (1 mL), a solution of [K⊂(18-crown-6)]$^+$*t*-BuO$^-$ (3 mL, 0.1 mmol) in benzene was added with a syringe at 25 °C under nitrogen atmosphere for 1 min, during which emission of orange light was observed. The reaction mixture was poured into satd aq NH_4Cl and then extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. Chromatographic purification (silica gel) of the residue with hexane–AcOEt (4/1–1/1) gave **11** in 14% yield.

4.5.3. Chemiluminescent decomposition of a dioxetane (2) with $[K\subset 18\text{-crown-6}]^+(18a)^-$: isolation of 3-[1-cyano-3,3-bis(methoxycarbonyl)butyl]benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (19). To a solution of 5-*tert*-butyl-1-[3-(1-cyanoethenyl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (**2**) (31.4 mg, 0.10 mmol) in benzene (1 mL), a solution of $[K\subset(18\text{-crown-6})]^+(\mathbf{18a})^-$ (3 mL, 0.10 mmol) in benzene was added with a syringe at 25 °C under nitrogen atmosphere for 1 min, during which emission of crimson light was observed. The reaction mixture was poured into satd aq NH_4Cl and then extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. ^{1}H NMR spectrum of the residue showed that 3-[1-cyano-3,3-bis(methoxycarbonyl)butyl]benzoic acid 2,2,4,4-tetramethyl-3-oxo-pentyl ester (**19**) was produced exclusively. Chromatographic purification of the residue on silica gel with CH_2Cl_2:hexane–AcOEt (4/5/1) gave **19** as a pale yellow oil in 39.1% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.29 (s, 9H), 1.40 (s, 3H), 1.40 (s, 3H), 1.56 (s, 3H), 2.36 (dd, J=14.7, 3.7 Hz, 1H), 2.50 (dd, J=14.7, 10.1 Hz, 1H), 3.76 (s, 3H), 3.77 (s, 3H), 4.12 (dd, J=10.1, 3.7 Hz, 1H), 4.41 (s, 2H), 7.47 (t, J=7.8 Hz, 1H), 7.61 (broad d, J=7.8 Hz, 1H), 7.94 (broad d, J=7.8 Hz, 1H), 8.01 (broad s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.9, 23.6, 23.7, 28.1, 33.1, 42.0, 45.9, 49.1, 52.7, 52.9, 52.9, 72.4, 120.0, 128.4, 129.4, 129.4, 131.1, 131.8, 136.8, 165.4, 171.2, 171.4, 215.9 ppm. IR (liquid film): 2956, 2875, 2242, 1730, 1686 cm^{-1}. Mass (20 eV, *m/z*, %): 402 (M^+-57, 11), 376 (12), 320 (27), 303 (19), 302 (100), 270 (9), 57 (17). HRMS (ESI): 482.2143, calcd for $C_{25}H_{33}NO_7Na$ ($M+Na^+$) 482.2155.

4.5.4. Chemiluminescent decomposition of a dioxetane (2) with $[K\subset 18\text{-crown-6}]^+(18b)^-$: isolation of 3-[1-cyano-3,3-bis(methoxycarbonyl)propyl]benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (24) and 5-*tert*-butyl-1-{3-[1-cyano-3,3-bis(methoxycarbonyl)propyl]-phenyl}-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (25). To a solution of 5-*tert*-butyl-1-[3-(1-cyanoethenyl)-phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (**2**) (31.4 mg, 0.10 mmol) in benzene (1 mL), a solution of $[K\subset(18\text{-crown-6})]^+(\mathbf{18b})^-$ (3 mL, 0.1 mmol) in benzene was added with a syringe at 25 °C under nitrogen atmosphere for 1 min, during which emission of red light was observed. The reaction mixture was poured into satd aq NH_4Cl and then extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. ^{1}H NMR spectrum of the residue showed that 3-[1-cyano-3,3-bis(methoxycarbonyl)propyl]benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (**24**) (39%) was produced along with 5-*tert*-butyl-1-{3-[1-cyano-3,3-bis(methoxycarbonyl) propyl]phenyl}-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (**25**) (28%). Chromatographic purification of the residue with hexane–AcOEt (4/1–1/1) gave **24** as a colorless viscous oil in 26.9% yield and **25** as a colorless oil in 16.2% yield.

Compound **24**. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.29 (s, 9H), 1.40 (s, 3H), 1.40 (s, 3H), 2.48 (t, J=7.8 Hz, 2H), 3.57 (t, J=7.8 Hz, 1H), 3.75 (s, 3H), 3.79 (s, 3H), 4.04 (t, J=7.8 Hz, 1H), 4.41 (s, 2H), 7.48 (t, J=7.8 Hz, 1H), 7.57 (d with fine coupling, J=7.8 Hz, 1H), 7.93–7.98 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.6, 23.7, 28.1, 34.4, 34.9, 45.9, 48.9, 49.1, 53.0, 53.0, 72.5, 119.2, 128.5, 129.6, 129.7, 131.3, 131.8, 135.1, 165.3, 168.3, 168.4, 215.9 ppm. IR (liquid film): 2958, 2875, 2243, 1734, 1685 cm^{-1}. Mass (20 eV, *m/z*, %): 414 (M^+-31, 1), 388 (7), 306 (23), 289 (33), 288 (100), 256 (17), 165 (21), 133 (35), 113 (68), 85 (27), 57 (64). HRMS (ESI): 468.2002, calcd for $C_{24}H_{31}NO_7Na$ ($M+Na^+$) 468.1998.

Compound **25** (1:1 mixture of diastereisomers). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.97 (s, 4.5H), 0.97 (s, 4.5H), 1.16 (s, 3H), 1.38 (s, 1.5H), 1.39 (s, 1.5H), 2.43–2.50 (m, 2H), 3.50–3.57 (m, 1H), 3.75 (s, 1.5H), 3.75 (s, 1.5H), 3.78 (s, 1.5H), 3.79 (s, 1.5H), 3.84 (d, J=8.3 Hz, 0.5H), 3.84 (d, J=8.3 Hz, 0.5H), 4.00–4.05 (m, 1H), 4.59 (d, J=8.3 Hz, 1H), 7.40–7.48 (m, 2H), 7.58–7.66 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 18.4, 25.1, 26.7, 34.3, 34.4, 35.1, 35.1, 36.7, 45.6, 48.9, 53.0, 53.0, 80.3, 80.3, 105.0, 116.2, 119.4, 119.4, 127.4, 128.5, 128.5, 128.7, 128.7, 129.0, 134.3, 134.4, 137.4, 137.4, 168.4, 168.4, 168.5, 168.5 ppm. IR (liquid film): 2960, 2892, 2243, 1736 cm^{-1}. Mass (20 eV, *m/z*, %): 445 (M^+, trace), 413 (3), 373 (21), 306 (11), 289 (19), 288 (100), 143 (12), 113 (21), 85 (11), 57 (45). HRMS (ESI): 468.1983, calcd for $C_{24}H_{31}NO_7Na$ ($M+Na^+$) 468.1998.

4.5.5. Chemiluminescent decomposition of a dioxetane (2) with $[K\subset 18\text{-crown-6}]^+(18c)^-$: isolation of 3-[1-cyano-2,2-bis(methoxycarbonyl)cyclopropyl]benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (30) and 1-{3-[1-cyano-2,2-bis(methoxycarbonyl)cyclopropyl]phenyl}-5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo-[3.2.0]heptane (31). To a solution of 5-*tert*-butyl-1-[3-(1-cyanoethenyl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo-[3.2.0]heptane (**2**) (31.4 mg, 0.10 mmol) in benzene (1 mL), a solution of $[K\subset(18\text{-crown-6})]^+(\mathbf{18c})^-$ (3 mL, 0.1 mmol) in benzene was added by means of a syringe at 25 °C under nitrogen atmosphere for 1 min, during which emission of red light was observed. The reaction mixture was poured into satd aq NH_4Cl and then extracted with AcOEt. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. ^{1}H NMR spectrum of the residue showed that 3-[1-cyano-2,2-bis(methoxycarbonyl)cyclopropyl]benzoic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (**30**) (71%) and was produced along with 1-{3-[1-cyano-2,2-bis(methoxycarbonyl)propyl]phenyl}-5-*tert*-butyl-4,4-dimethyl-2,6,7-trioxabicyclo-[3.2.0]heptane (**31**) (29%). Chromatographic purification of the residue on silica gel with hexane–AcOEt (4/1–1/1) gave **30** as a colorless viscous oil in 52% yield and **31** as a colorless oil in 23% yield.

Compound **30**. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.30 (s, 9H), 1.39 (s, 3H), 1.40 (s, 3H), 2.41 (t, J=6.2 Hz, 1H), 2.58 (d, J=6.2 Hz, 1H), 3.39 (s, 3H), 3.92 (s, 3H), 4.40 (s, 2H), 7.45 (t, J=7.8 Hz, 1H), 7.63 (d with fine coupling, J=7.8 Hz, 1H), 7.94–7.98 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 22.8, 23.6, 23.7, 27.5, 28.1, 41.9, 45.9, 49.1, 53.1, 53.7, 72.5, 117.7, 129.1, 129.7, 130.4, 130.8, 131.2, 133.5, 164.1, 165.1, 165.7, 215.8 ppm. IR (liquid film): 2958, 2875, 2240, 1746, 1731, 1685 cm^{-1}. Mass (20 eV, *m/z*, %): 386 (M^+-57, 17), 360 (23), 305 (14), 304 (74),

287 (16), 286 (100), 272 (12), 57 (14). HRMS (ESI): 466.1828, calcd for $C_{24}H_{31}NO_7Na$ ($M+Na^+$) 466.1842.

Compound **31** (1:1 mixture of diastereoisomers). ^1H NMR (500 MHz, $CDCl_3$): δ_H 0.96 (s, 9H), 1.16 (s, 3H), 1.37 (s, 1.5H), 1.39 (s, 1.5H), 2.38 (d, $J=6.1$ Hz, 0.5H), 2.39 (d, $J=6.1$ Hz, 0.5H), 2.58 (d, $J=6.1$ Hz, 0.5H), 2.59 (d, $J=6.1$ Hz, 0.5H), 3.36 (s, 3H), 3.83 (d, $J=8.2$ Hz, 1H), 3.91 (s, 1.5H), 3.91 (s, 1.5H), 4.58 (d, $J=8.2$ Hz, 1H), 7.38–7.46 (m, 2H), 7.60–7.72 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 18.4, 18.4, 22.8, 22.9, 25.0, 25.1, 26.7, 26.7, 27.7, 27.8, 36.6, 41.9, 41.9, 45.6, 53.0, 53.1, 53.7, 80.2, 80.3, 105.0, 116.0, 116.0, 117.8, 117.9, 128.4, 128.5, 128.9, 129.4, 129.5, 129.8, 130.1, 130.5, 130.5, 137.0, 137.1, 164.1, 164.1, 165.9 ppm. IR (liquid film): 2961, 2241, 1743 cm^{-1}. Mass (20 eV, *m/z*, %): 411 (M^+-32, 2), 386 (14), 360 (23), 327 (11), 305 (13), 304 (70), 287 (19), 286 (100), 272 (12), 57 (17). HRMS (ESI): 466.1828, calcd for $C_{24}H_{29}NO_7Na$ ($M+Na^+$) 466.1842.

4.5.6. 5-*tert*-Butyl-1-[3-(3-cyano-4,5-dihydro-5,5-diphenyl-3*H*-pyrazole-3-yl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (35a). A solution of (diphenyl)diazomethane (0.50 mmol: prepared from benzophenone hydrazone and HgO in hexane–ethanol in the presence of catalytic amount of EtONa and used crude product) in acetonitrile (0.5 mL) was added to a solution of 5-*tert*-butyl-1-[3-(1-cyanoethenyl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (**2**) (92 mg, 0.29 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (2 mg) in acetonitlile (3 mL) at room temperature under nitrogen atmosphere and stirred for 2 h. The reaction mixture was concentrated in vacuo and chromatographed on silica gel with hexane–AcOEt (10/1–5/1) to give 142 mg of **35a** as pale yellow granules in 95.2% yield (45:55 mixture of diastereoisomers).

4.5.7. 5-*tert*-Butyl-1-[3-(3-cyano-4,5-dihydro-5-trimethylsilyl-3*H*-pyrazole-3-yl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (35b). A solution of (trimethylsilyl)diazomethane (2.0 M in hexane, 1 mL, 2 mmol) was added to a solution of 5-*tert*-butyl-1-[3-(1-cyanoethenyl)phenyl]-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]-heptane (**2**) (52.4 mg, 0.17 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (2 mg) in acetonitlile (2 mL) at room temperature under nitrogen atmosphere and stirred for 1.5 h. The reaction mixture was concentrated in vacuo and chromatographed on silica gel with hexane–AcOEt (10/1–5/1) to give 41.4 mg of **35b** as colorless viscous oil in 58.0% yield (1:1 mixture of diastereoisomers). ^1H NMR (500 MHz, $CDCl_3$): δ_H 0.22 (s, 4.5H), 0.23 (s. 4.5H), 0.57 (dd, $J=10.7$, 5.8 Hz, 0.5H), 0.59 (dd, $J=10.7$, 5.8 Hz, 0.5H), 0.96 (s, 9H), 1.16 (s, 3H), 1.39 (s, 3H), 1.59 (dd, $J=5.8$, 4.6 Hz, 0.5H), 1.60 (dd, $J=5.8$, 4.6 Hz, 0.5H), 1.66 (dd, $J=10.7$, 4.6 Hz, 0.5H), 1.69 (dd, $J=10.7$, 4.6 Hz, 0.5H), 3.83 (d, $J=8.1$ Hz, 1H), 4.58 (d, $J=8.1$ Hz, 1H), 7.35–7.43 (m, 2H), 7.49–7.55 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C −2.08, 17.5, 18.4, 19.9, 20.2, 21.4, 21.5, 25.0, 25.1, 26.7, 36.7, 45.6, 80.2, 80.2, 104.9, 104.9, 116.3, 116.3, 121.7, 121.8, 125.1, 125.4, 127.1, 127.2, 127.4, 127.4, 128.4, 136.7, 137.6, 137.7 ppm. IR (liquid film): 2961, 2897, 2232 cm^{-1}. Mass (*m/z*, %): 399 (M^+-N_2, 3), 343 (20), 342 (15), 314 (10), 260 (21), 259 (19), 244 (13), 243 (32), 242 (100), 169 (30), 73 (38), 57 (46). HRMS (ESI): 422.2116, calcd for $C_{23}H_{33}NO_3SiNa$ ($M-N_2+Na^+$) 422.2127.

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