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Application and details of photoinduced oxidative cyclization of 5-(4′,9′-methanocycloundeca-2′,4′,6′,8′,10′-pentaenylidene)-pyrimidine-2,4,6(1,3,5*H*)-triones and related compounds

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Abstract

As novel methodology for synthesizing the furan ring, a photoinduced oxidative cyclization of 5-(4′,9′-methanocycloundeca-2′,4′,6′,8′,10′-pentaenylidene)pyrimidine-2,4,6(1,3,5*H*)-triones (**7a**–**c**) and related compounds **9a**–**c** was accomplished to give 5,10-methanocycloundeca[4,5]furo[2,3-*d*]pyrimidine-2,4(1,3*H*)-dionylium tetrafluoroborates (**8a**–**c**$^{+}\cdot\mathbf{BF_4^-}$) and related compounds **2a**–**c**$^{+}\cdot\mathbf{BF_4^-}$, respectively. In the photoinduced oxidative cyclization, the molecular oxygen in air is used as oxidant and the reaction proceeds under mild conditions to give desired products without byproducts, and thus, it is interesting from the viewpoint of the green chemistry. On the reactions of the mono-substituted derivatives **7d**,**e** and **9e**,**f**, the selectivity of the photoinduced cyclizations were reversed as compared with those of the DDQ-promoted oxidative cyclizations. By the NMR monitoring of the reactions of **7a** and deuterated compound **7a-*D*$_2$** under degassed conditions, the details of the reaction pathway were clarified and rationalized on the basis of the MO calculation by the 6-31G* basis set of the MP2 levels as well.

Keywords: Photoinduced oxidative cyclization; 5-(4′,9′-Methanocycloundeca-2′,4′,6′,8′,10′-pentaenylidene)-pyrimidine-2,4,6(1,3,5*H*)-trione; Heptafulvene; Furo[2,3-*d*]pyrimidine

1. Introduction

Construction of the furan ring, which is found in many natural and biologically important molecules,[1–3] has been the focus of much research attention.[4] Among these, the synthesis of furo[2,3-*d*]pyrimidine systems as formal isoelectronic compounds of purine is interesting in developing novel medicinal and agrochemical agents namely antimalarials,[5] antifolates,[6] and antivirus,[7] as well as potential radiation protection agents.[8] Recently, some furo[2,3-*d*]pyrimidines were shown to be potent VEGFR2 (vascular endothelial growth factor receptor 2) and EGFR (epidermal growth factor receptor) inhibitors,[9] and the environment-friendly synthesis of furo[2,3-*d*]pyrimidine derivatives (**1**) (Fig. 1) was also reported.[10] As the investigation of the compounds containing the furo[2,3-*d*]pyrimidine-ring system, we have previously reported the synthesis, properties, and reactivity of cyclohepta[4,5]furo[2,3-*d*]pyrimidine-2,4(1,3*H*)-dionylium ions (**2a**–**c**$^{+}\cdot\mathbf{BF_4^-}$).[11] Furthermore, as the model of flavin-type reaction,[12] their novel photoinduced autorecycling oxidizing reactions toward some alcohols and amines were clarified.[11,13] In this relation, the alternative synthesis of **2a**–**c**$^{+}\cdot\mathbf{BF_4^-}$ from heptafulvene derivatives (**9a**–**c**) (Scheme 1) was accomplished by the novel oxidative cyclization using DDQ.[14] While several methodologies for synthesizing furo[2,3-*d*]pyrimidine derivatives have been developed due to their high potential and unique characteristics,[15] to our best knowledge, this is the first example of synthesizing methodology starting from the pyrimidine derivatives containing the heptafulvene-ring system.

On the other hand, heptafulvenes have intrigued chemists for several decades, especially in the context of the concept

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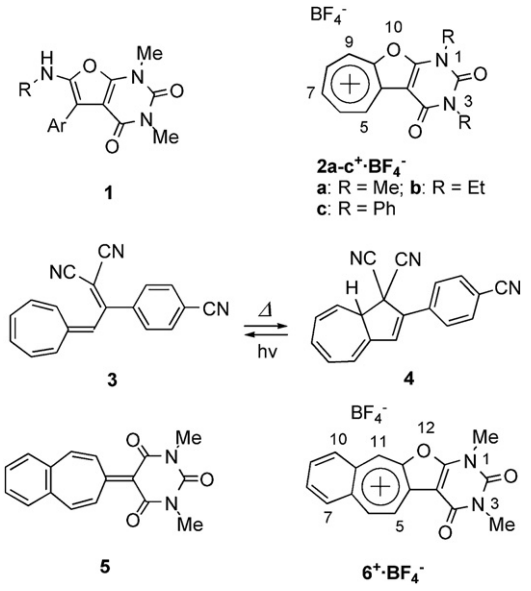
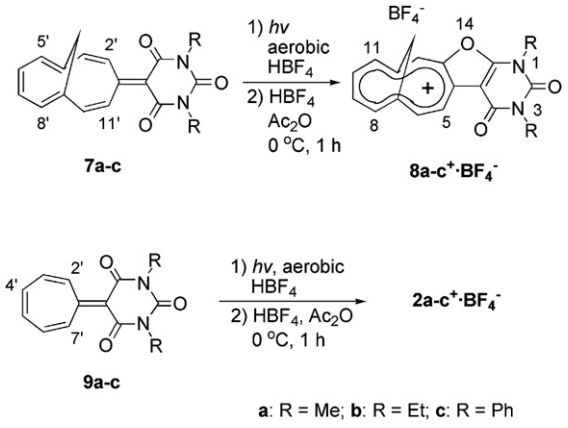


Figure 1. Furo[2,3-*d*]pyrimidine derivatives and heptafulvenes.



Scheme 1. Photoinduced oxidative cyclization of disubstituted compounds **7a**–**c** and **9a**–**c**.

of aromaticity.[16] The chemistry of the heptafulvenes derived by insertion of more complex conjugated π-systems has also been studied relative to the molecular design of organic dyes, highly polarized compounds, and electron acceptors or electron donors.[17] Recently, the synthesis and photochemical properties of vinylheptafulvene **3** have been studied to demonstrate that compound **3** possesses a remarkable property of multimode-switching arising from the ring-closure and ring-opening process: a very fast photoreversible switch and a thermal switch.[18] While it is well known that the 10π-electrocyclization of vinylheptafulvenes gives dihydroazulenes,[19] there are few reports of the oxa 10π-electrocyclization using carbonyl-moiety of heptafulvenes.[20] Thus, the studies on the properties and reactivity of carbonyl-substituted heptafulvenes are interesting from the viewpoint of molecular function. In this relation, we have recently reported that the oxidative cyclization of benzo-annulated derivative **5** afforded the corresponding compound $\mathbf{6}^{+}\cdot\mathbf{BF_4^-}$.[21] In the study, the reaction of **5** by using only DDQ did not proceed. By adding $Sc(OTf)_3$ to activate DDQ[22] and under higher temperature and long reaction time, the reaction of **5** with DDQ proceeded to afford compound $\mathbf{6}^{+}\cdot\mathbf{BF_4^-}$, although the yield was still low (20%). Thus, we accomplished the photoinduced oxidative cyclization of **5** by the photoirradiation (RPR-100, 350 nm lamps) under aerobic conditions in the presence of 42% aq HBF_4 to result in the formation of compound $\mathbf{6}^{+}\cdot\mathbf{BF_4^-}$ in quantitative yield. In the photoinduced oxidative cyclization, the molecular oxygen in air was used as oxidant, and thus, byproducts derived from oxidant such as hydroquinone and heavy metal ions were not generated. Furthermore, the reaction proceeded under room temperature, and the hard reaction conditions were not required. Consequently, the photoinduced oxidative cyclization is environmentally-friendly synthetic method, and thus, it is interesting from the viewpoint of the green chemistry. Furthermore, in the synthesis of tropylium ions annulated with two 2,4-dimethylfuro[2,3-*d*]pyrimidine-1,3(2,4*H*)-diones, we have clarified that the photoinduced oxidative cyclization exhibits a complete selectivity.[23] In addition, we have carried out the similar reaction on a large scale to obtain the desired product at gram scale. Thus, the further application of the reaction and its details are very attractive to explore the novel methodology for synthesizing furan-ring systems. We have recently reported that the DDQ-promoted oxidative cyclization of 5-(4′,9′-methanocycloundeca-2′,4′,6′,8′,10′-pentaenylidene)pyrimidine-2,4,6(1,3,5*H*)-triones **7a**–**c** (Scheme 1), which are vinylogous compounds of **9a**–**c**, afforded the compounds $\mathbf{8a}\text{–}\mathbf{c}^{+}\cdot\mathbf{BF_4^-}$.[24] In the present study, photoinduced oxidative cyclization of **7a**–**c** and related compounds **9a**–**c** was investigated. In addition, the selectivity of the cyclization of monosubstituted derivatives **7d**,**e** and **9d**–**f** was studied as well. Furthermore, by the NMR monitoring of the reactions of **7a** and deuterated compound **7a-*D*$_2$** under degassed conditions, the details of the reaction were clarified and rationalized on the basis of the MO calculation by the 6-31G* basis set of the MP2 levels. We report herein the results in detail.

2. Results and discussion

2.1. Application of photoinduced oxidative cyclization

In order to clarify the scope and limitation of photoinduced oxidative cyclization, the reaction of **7a**–**c**[24] and related compounds **9a**–**c**[14] was investigated (Scheme 1). The photoirradiation (RPR-100, 350 nm lamps) of **7a**–**c** was carried out under aerobic condition in CH_3CN and $(CH_2Cl)_2$ in the presence of 42% aq HBF_4 (Table 1, runs 1–3). By irradiation for 2–3 h, the oxidative cyclization of **7a**–**c** proceeded more smoothly to give $\mathbf{8a}\text{–}\mathbf{c}^{+}\cdot\mathbf{BF_4^-}$ in good yields (94–100%) as compared with the reaction of **5** (irradiation time: 36 h).[21] Moreover, the reaction of related compounds **9a**–**c** was carried out under similar conditions (Table 1, runs 4–6). Although the reaction of compounds **9a**–**c** was relatively slow, the oxidative cyclization was completed by photoirradiation for 7–21 h to give $\mathbf{2a}\text{–}\mathbf{c}^{+}\cdot\mathbf{BF_4^-}$ quantitatively. The feature shows that the oxidative cyclization of 11-membered ring proceeded more effectively as compared with that of 7-membered

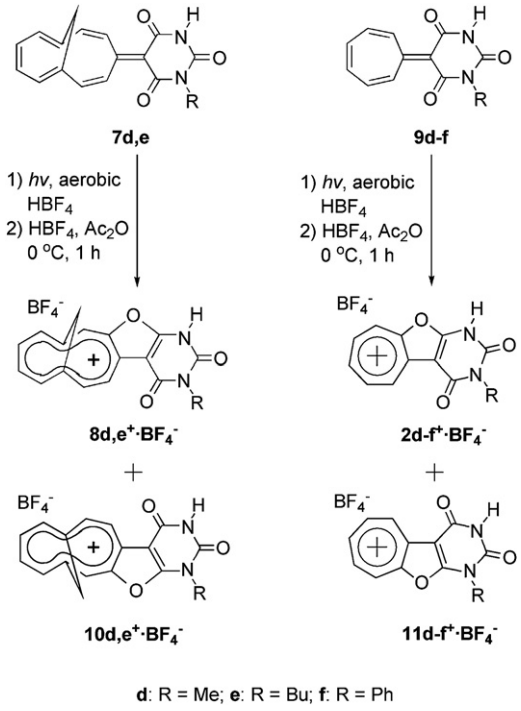
Table 1
Results for the photoinduced oxidative cyclization of disubstituted compounds **7a–c** and **9a–c**

Run[a]	Compound	Time/h	Product (yield/%)
1	**7a** (R=Me)	2	**8a**$^+\cdot$**BF$_4^-$** (94)
2	**7b** (R=Et)	2	**8b**$^+\cdot$**BF$_4^-$** (100)
3	**7c** (R=Ph)	3	**8c**$^+\cdot$**BF$_4^-$** (97)
4	**9a** (R=Me)	7	**2a**$^+\cdot$**BF$_4^-$** (100)
5	**9b** (R=Et)	5	**2b**$^+\cdot$**BF$_4^-$** (100)
6	**9c** (R=Ph)	21	**2c**$^+\cdot$**BF$_4^-$** (100)

[a] A solution of **7a–c** or **9a–c** (0.1 mmol) and 42% aq HBF_4 (0.4 mL) in CH_3CN (10 mL) and $(CH_2Cl)_2$ (10 mL) in a Pyrex tube was irradiated by RPR-100, 350 nm lamps under aerobic conditions at room temperature.

ring. In addition, the reaction of **7c** and **9c** having phenyl-substituent required longer irradiation time, while the spectroscopic properties of **7c** and **9c** such as ^{1}H and ^{13}C NMR spectra and UV–vis spectra seemed similar to those of **7a**,**b** and **9a**,**b**, respectively.[14,24] The products **2a–c**$^+\cdot$**BF$_4^-$** and **8a–c**$^+\cdot$**BF$_4^-$** were confirmed by inspection of the spectroscopic data.[14,24]

Furthermore, the photoinduced oxidative cyclization of mono-substituted derivatives **7d**,**e**[25] and **9d–f**[14] was also accomplished (Scheme 2). Since **7d**,**e** and **9d–f** have two kinds of reactive carbonyl groups (–CONR– and –CONH–), these reactions could afford two types of products. The fast reaction of **7d**,**e** proceeded to give possible mixtures of **8d,e**$^+\cdot$**BF$_4^-$** and **10d,e**$^+\cdot$**BF$_4^-$**, respectively, in good combined yields (Table 2, runs 1 and 2). Similarly, the relatively slow reaction of **9d–f** gave mixtures of **2d–f**$^+\cdot$**BF$_4^-$** and **11d–f**$^+\cdot$**BF$_4^-$**, respectively (Table 2, runs 3–5). On the reaction of phenyl-substituted derivative **9f**, longer irradiation time was also required (vide supra). The products **8d,e**$^+\cdot$**BF$_4^-$** and **10d,f**$^+\cdot$**BF$_4^-$** as well as **2d–f**$^+\cdot$**BF$_4^-$** and **11d–f**$^+\cdot$**BF$_4^-$** were confirmed by inspection of the spectroscopic data.[14,25] The ratios of **8d,e**$^+\cdot$**BF$_4^-$** and **10d,e**$^+\cdot$**BF$_4^-$** as well as **2d–f**$^+\cdot$**BF$_4^-$** and **11d–f**$^+\cdot$**BF$_4^-$** were determined from ^{1}H NMR spectra of the mixtures. We have previously reported that the DDQ-promoted oxidative cyclization of **7d**,**e** and **9d–f** also affords similar mixtures.[14,25] However, in the photoinduced oxidative cyclization, the different selectivity was observed as compared with the DDQ-promoted reaction. In the photoinduced reaction of **7d**,**e**, compound **8d,e**$^+\cdot$**BF$_4^-$** was obtained as major product, while the DDQ-promoted reaction gave **10d,e**$^+\cdot$**BF$_4^-$** preferentially (Table 2, runs 1 and 2). Similarly,



Scheme 2. Photoinduced oxidative cyclization of mono-substituted compounds **7d**,**e** and **9d–f**.

the photoinduced reaction of **9e**,**f** showed a different selectivity, and compounds **11e,f**$^+\cdot$**BF$_4^-$** became major products (Table 2, runs 4 and 5). Moreover, the reverse in the selectivity between the reaction of **7d**,**e** and **9e**,**f** was also observed. While the DDQ-promoted reaction proceeds via intramolecular radical addition on the radical cations generated by oxidation of starting compounds,[14,24] the photoinduced oxidative cyclization would be initiated by the photoinduced electrocyclization (vide infra). Moreover, in contrast to the planar 7-membered ring of **9e**,**f**, the 11-membered ring of **7d**,**e** has the bending structure.[25] However, MO calculations of reactants and possible intermediates such as **12** (Scheme 3) could not rationalize the different selectivity, and thus, further investigations are required.

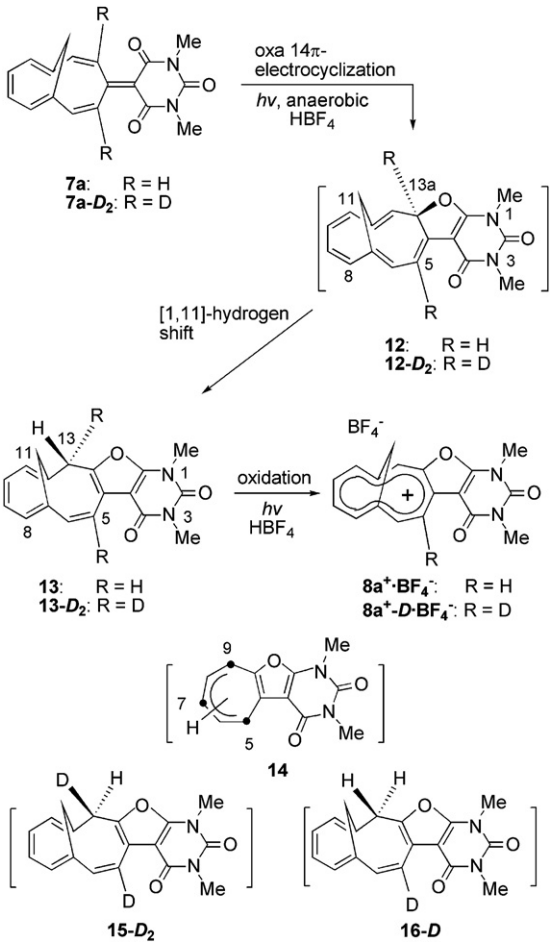
2.2. Reaction pathway

In order to clarify the details of the reaction, ^{1}H NMR monitoring of reactions of **7a** and **9a** as well as 2′,11′-deuterated

Table 2
Results for the photoinduced oxidative cyclization of mono-substituted compounds **7d**,**e** and **9d–f**

Run[a]	Compound	Time/h	Product (yield/%)	Ratio[b] of **8**$^+$/**10**$^+$ or **2**$^+$/**11**$^+$	Ratio[c] of **8**$^+$/**10**$^+$ or **2**$^+$/**11**$^+$
1	**7d** (R=Me)	3	**8d**$^+\cdot$**BF$_4^-$** (63), **10d**$^+\cdot$**BF$_4^-$** (37)	1.7:1	1:2.0
2	**7e** (R=Bu)	3	**8e**$^+\cdot$**BF$_4^-$** (68), **10e**$^+\cdot$**BF$_4^-$** (32)	2.1:1	1:2.0
3	**9d** (R=Me)	9	**2d**$^+\cdot$**BF$_4^-$** (50), **11d**$^+\cdot$**BF$_4^-$** (50)	1:1	1:1
4	**9e** (R=Bu)	9	**2e**$^+\cdot$**BF$_4^-$** (39), **11e**$^+\cdot$**BF$_4^-$** (61)	1:1.6	2.5:1
5	**9f** (R=Ph)	26	**2f**$^+\cdot$**BF$_4^-$** (39), **11f**$^+\cdot$**BF$_4^-$** (61)	1:1.6	3.3:1

[a] A solution of **7d**,**e** or **9d–f** (0.1 mmol) and 42% aq HBF_4 (0.4 mL) in CH_3CN (10 mL) and $(CH_2Cl)_2$ (10 mL) in a Pyrex tube was irradiated by RPR-100, 350 nm lamps under aerobic conditions at room temperature.
[b] Photoinduced oxidative cyclization.
[c] DDQ-promoted oxidative cyclization (Refs. 14 and 25).



Scheme 3. Reaction pathway for the photoinduced oxidative cyclization.

compound **7a-*D*$_2$** prepared by the reaction of **7a** with CD_3OD and D_2O[26] were carried out (Scheme 3). Under degassed conditions in NMR tubes, solutions of **7a** and **9a** in CD_3CN and $CDCl_3$ in the presence of 42% aq HBF_4 were irradiated by RPR-100, 350 nm lamps. Before irradiation, the addition of 42% aq HBF_4 caused no change of the ^1H NMR spectra of **7a** and **9a**. In addition, the visible region of the UV–vis spectra of **7a** and **9a** was not changed by adding 42% aq HBF_4, suggesting that the protonation would not occur under the ground states. By irradiation for 2 h, compound **7a** was converted completely to compound **13**. After additional irradiation for 6 h, compound **8a**$^+\cdot$**BF$_4^-$** was generated by the oxidation of **13** using the stray oxygen in the solvent. In the independent reaction, the compound **13** prepared by $NaBH_4$ reduction of **8a**$^+\cdot$**BF$_4^-$**, was oxidized by photoirradiation under aerobic conditions in the presence of 42% aq HBF_4 to give **8a**$^+\cdot$**BF$_4^-$** quantitatively. Thus, the present photoinduced oxidative cyclization of **7a** would proceed as shown in Scheme 3. The photoinduced oxa 14π-electrocyclization[27] of **7a** gives intermediate **12**, which would undergo [1,11]-hydrogen shift to give **13** as similar to the photochemical [1,7]-hydrogen shift of 1,3,5-cycloheptatriene.[28] Under photoirradiation and aerobic conditions, oxidation of **13** in the presence of 42% aq HBF_4 affords **8a**$^+\cdot$**BF$_4^-$**. In contrast, the irradiation of **9a** under degassed conditions afforded compound **2a**$^+\cdot$**BF$_4^-$** directly, and thus, intermediates such as compound **14** were not observed. Since the photoinduced oxa 10π-electrocyclization of **9a** is relatively slow, the oxidation of intermediate **14** would proceed fast to give compound **2a**$^+\cdot$**BF$_4^-$**. Under similar conditions, irradiation of **7a-*D*$_2$** afforded **13-*D*$_2$** having two deuterium atoms at C5- and C13*endo*-position, while the *exo*-isomer **15-*D*$_2$** and mono-deuterated compound **16-*D*** were not observed. We have previously clarified the bending structure of the 11-membered ring of **7a** on the basis of the ^1H and ^{13}C NMR spectra.[24] On the MO calculation of two possible structures **7a-*syn*** and **7a-*anti*** by the 6-31G* basis set of the MP2 levels,[29] the former structure is more stable by 10.486 kcal mol^{-1} than the latter structure (Fig. 2). Thus, the photoinduced oxa 14π-electrocyclization of **7a** and **7a-*D*$_2$** would proceed from the structure **7a-*syn*** and **7a-*D*$_2$-*syn***, respectively, to give intermediate **12** and **12-*D*$_2$**, the C13a-proton and the C13a-deuterium of which are located at *endo*-position. In compound **13-*D*$_2$**, the deuterium located at the C13*endo*-position shows that suprafacial [1,11]-deuterium shift of **12-*D*$_2$** would proceed to give **13-*D*$_2$** as a photochemically allowed process.[28,30] Furthermore, oxidation of **13-*D*$_2$** gave mono-deuterated cation **8a**$^+$**-*D*·BF$_4^-$**, suggesting that the oxidative deuterium abstraction occurred at the C13*endo*-position of **13-*D*$_2$** as similar to the oxidation by using DDQ.[24] The feature would be due to the higher reactivity of *endo*-position as compared with that of *exo*-position in this ring system,[24,25] however, the details are unclear at this stage. It is well known that the photoinduced oxidation of various olefins by using molecular oxygen proceeds through a charge transfer (CT) complex. In a reaction pathway proceeding through the CT complex, the intermediate would be the radical cation as similar to the DDQ-promoted reaction. Thus, the similar selectivity to the DDQ-promoted reaction would be expected to be observed on the reaction of the mono-substituted derivatives. However, the selectivity of the photoinduced cyclizations was reversed as compared with those of the DDQ-promoted oxidative cyclizations. Consequently, the present photoinduced oxidative cyclization would consist of photoinduced oxa 14π-electrocyclization and suprafacial [1,11]-hydrogen shift and subsequent photoinduced oxidation by the molecular oxygen. There is a possibility that the photoinduced oxidation proceeds through CT complex, and thus, further investigations are required. The compounds **7a-*D*$_2$**, **13**, and **13-*D*$_2$** as well as

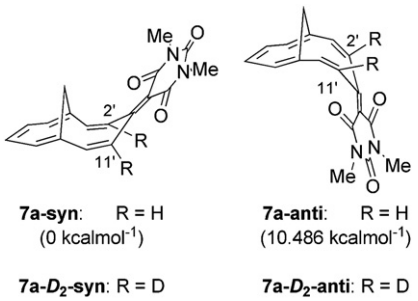


Figure 2. Two possible conformations of **7a** and **7a-*D*$_2$**.

8a$^+$-*D*·BF$_4^-$ were confirmed by inspection of the spectroscopic data.[24]

3. Conclusion

A photoinduced oxidative cyclization of **7a–c** and related compounds **9a–c** was accomplished to give **8a–c$^+$·BF$_4^-$** and **2a–c$^+$·BF$_4^-$** in almost quantitative yields, respectively. The reactions of the mono-substituted derivatives **7d**,**e** and **9d–f** afforded mixtures of **8d,e$^+$·BF$_4^-$** and **10d,e$^+$·BF$_4^-$** and mixtures of **2d–f$^+$·BF$_4^-$** and **11d–f$^+$·BF$_4^-$**, respectively. The selectivity of photoinduced cyclizations of **7d**,**e** and **9e**,**f** was reversed as compared with that of DDQ-promoted oxidative cyclization, respectively. On the basis of the NMR monitoring of reactions of **7a** and deuterated compound **7a-*D*$_2$** under degassed conditions, the details of the reaction pathway were clarified and rationalized on the basis of the MO calculation by the 6-31G* basis set of the MP2 levels. In the photoinduced oxidative cyclization, the molecular oxygen in air is used as oxidant to give desired products without byproducts, and thus, it is interesting from the viewpoint of the green chemistry. Further studies concerning application of the photoinduced oxidative cyclization are currently underway.

4. Experimental

4.1. General

IR spectra were recorded on a HORIBA FT-710 spectrometer. Mass spectra and high-resolution mass spectra were run on JMS-AUTOMASS 150 and JMS-SX102A spectrometers. ^{1}H NMR spectra were recorded on a JNM-lambda500 spectrometer, and the chemical shifts are given relative to internal $SiMe_4$ standard, *J* values are given in hertz. Photoirradiation was carried out by using RPR-100 fitted with 350 nm lamps though a Pyrex filter.

*4.2. General procedure for the oxidative cyclization of **7a–c** and **9a–c***

A solution of **7a–c** or **9a–c** (0.1 mmol) and 42% aq HBF_4 (0.4 mL) in CH_3CN (10 mL) and $(CH_2Cl)_2$ (10 mL) in a Pyrex tube was irradiated by RPR-100, 350 nm lamps under aerobic conditions at room temperature until the reaction was completed. The mixture was concentrated in vacuo, and the resulting residue was dissolved in a mixture of acetic anhydride (2 mL) and 42% aq HBF_4 (0.4 mL) at 0 °C, and stirred for 1 h. To the resulting mixture was added Et_2O (100 mL) and the precipitate was collected by filtration to give compound **8a–c$^+$·BF$_4^-$** or **2a–c$^+$·BF$_4^-$** (Table 1).

*4.3. General procedure for the oxidative cyclization of **7d**,**e** and **9d–f***

A solution of **7d**,**e** or **9d–f** (0.1 mmol) and 42% aq HBF_4 (0.4 mL) in CH_3CN (10 mL) and $(CH_2Cl)_2$ (10 mL) in a Pyrex tube was irradiated by RPR-100, 350 nm lamps under aerobic conditions at room temperature until the reaction was completed. The mixture was concentrated in vacuo, and the resulting residue was dissolved in a mixture of acetic anhydride (2 mL) and 42% aq HBF_4 (0.4 mL) at 0 °C, and stirred for 1 h. To the resulting mixture was added Et_2O (100 mL) and the precipitate was collected by filtration to give a mixture of **8d,e$^+$·BF$_4^-$** and **10d,e$^+$·BF$_4^-$** or a mixture of **2d–f$^+$·BF$_4^-$** and **11d–f$^+$·BF$_4^-$** (Table 2).

*4.4. Preparation of deuterated derivative **7a-D$_2$***

To a solution of **7a** (15 mg, 0.05 mmol) in CD_3OD (5 mL) and D_2O (2 mL) was added a drop of TFA-*D*, and the mixture was heated in a sealed tube at 130 °C for 72 h. The resulting mixture was poured into saturated aq $NaHCO_3$, and extracted with CH_2Cl_2. The combined organic layer was washed with water, and dried over $MgSO_4$. The solution was concentrated in vacuo, and purified through column chromatography on Al_2O_3 using hexane–AcOEt (2:1) as the eluent to give product **7a-*D*$_2$** (8 mg, 53%).

*4.4.1. 2′,11′-Dideuterio-1,3-dimethyl-5-(4′,9′-methanocycloundeca-2′,4′,6′,8′,10′-pentaenylidene)pyrimidine-2,4,6(1,3,5H)-trione (**7a-D$_2$**)*

^{1}H NMR (500 MHz, DMSO-d_6) δ −0.38 (1H, d, *J*=11.0 Hz, H_E), 1.79 (1H, d, *J*=11.0 Hz, H_Z), 3.18 (6H, s, NMe), 6.86 (2H, br s, H-3′, 10′), 7.06 (4H, m, H-5′, 8′), 7.35 (2H, m, H-6′, 7′); IR ($CHCl_3$) ν_{max} 1655 cm^{-1}; MS (FAB) *m*/*z* 311 (M^++H); HRMS calcd for $C_{18}H_{15}D_2N_2O_3$: 311.1450 (M+H), found: 311.1326 (M^++H).

*4.5. ^{1}H NMR monitoring of the photoirradiation of **7a** and **7a-D$_2$***

Under degassed conditions, a solution of compound **7a** or **7a-D$_2$** (3.1 mg, 0.01 mmol) in CD_3CN (0.25 mL) and $CDCl_3$ (0.25 mL) in the presence of 42% aq HBF_4 (0.01 mL) was irradiated by RPR-100, 350 nm lamps at room temperature in an NMR tube. After 2 h, the NMR measurement confirmed the formation of **13** or **13-D$_2$**. After additional irradiation for 6 h, oxidation of **13** or **13-D$_2$** to **8a$^+$·BF$_4^-$** or **8a-D$^+$·BF$_4^-$** was observed, respectively.

*4.5.1. 5,13-Dideuterio-1,13-dihydro-7,12-methanocycloundeca[4,5]furo[2,3-d]pyrimidine-2,4(1,3H)-dione (**13-D$_2$**)*

^{1}H NMR (500 MHz, CD_3CN–$CDCl_3$) δ 1.62 (1H, d, *J*=11.0 Hz, H_E), 3.20 (3H, s, N_3Me), 3.35 (3H, s, N_1Me), 4.02 (1H, br s, H-13*exo*), 4.15 (1H, d, *J*=11.0 Hz, H_Z), 6.06 (1H, m, H-8), 6.17 (1H, m, H-11), 6.30 (1H, br s, H-6), 6.53–6.63 (2H, m, H-9, 10); IR (KBr) ν_{max} 1703, 1662, 1525, 1254 cm^{-1}; MS (FAB) *m*/*z* 310 (M^+); HRMS calcd for $C_{18}H_{14}D_2N_2O_3$: 310.1310 (M), found: 310.1280 (M^+).

*4.5.2. 5-Deuterio-7,12-methanocycloundeca[4,5]furo[2,3-d]pyrimidine-2,4(1,3H)-dionylium tetrafluoroborate (**8a-D$^+$·BF$_4^-$**)*

^{1}H NMR (500 MHz, CD_3CN–$CDCl_3$) δ −1.24 (1H, d, *J*=11.5 Hz, H_E), −0.47 (1H, d, *J*=11.5 Hz, H_Z), 3.40 (3H, s,

N_3Me), 3.72 (3H, s, N_1Me), 8.32–8.62 (2H, m, H-9, 10), 8.50 (1H, d, J=8.0 Hz, H-8), 8.57 (1H, d, J=8.0 Hz, H-11), 9.15 (1H, br s, H-6), 9.72 (1H, s, H-13); IR (KBr) ν_{max} 1726, 1673, 1646, 1574, 1084 cm^{-1}; MS (FAB) *m/z* 308 (M^+-BF_4); HRMS calcd for $C_{18}H_{14}DN_2O_3$: 308.1170 ($M-BF_4$), found: 308.1202 (M^+-BF_4).

4.6. ^1H NMR monitoring of the photoirradiation of **9a**

Under degassed conditions, a solution of compound **9a** (2.4 mg, 0.01 mmol) in CD_3CN (0.25 mL) and $CDCl_3$ (0.25 mL) in the presence of 42% aq HBF_4 (0.01 mL) was irradiated by RPR-100, 350 nm lamps at room temperature in an NMR tube. The NMR measurement was carried out at intervals, however, intermediates such as compound **14** were not observed, and compound **9a** was transformed to $\mathbf{2a}^+\cdot\mathbf{BF_4^-}$ gradually. After 24 h, the NMR measurement confirmed the exclusive formation of $\mathbf{2a}^+\cdot\mathbf{BF_4^-}$.

4.7. Photoinduced oxidation of **13**

A solution of **13** (31 mg, 0.1 mmol) and 42% aq HBF_4 (0.4 mL) in CH_3CN (10 mL) and $(CH_2Cl)_2$ (10 mL) in a Pyrex tube was irradiated by RPR-100, 350 nm lamps under aerobic conditions at room temperature for 2 h. The mixture was concentrated in vacuo, and the resulting residue was dissolved in a mixture of acetic anhydride (2 mL) and 42% aq HBF_4 (0.4 mL) at 0 °C, and stirred for 1 h. To the resulting mixture was added Et_2O (100 mL) and the precipitates were collected by filtration to give compound $\mathbf{8a}^+\cdot\mathbf{BF_4^-}$ (39 mg, 100%).

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