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The Paternò–Büchi Reaction of 1,3-Dimethyluracil and 1,3-Dimethylthymine with 4,4′-Disubstituted Benzophenones

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The photochemical [2+2] cycloadditions (the Paternò–Büchi reaction) of 1,3-dimethylthymine (DMT) or 1,3-dimethyluracil (DMU) with benzophenone and its six 4,4′-disubstituted derivatives (BPs) generate two series of regioisomeric oxetanes, the *head-to-head* (*hh*) oxetanes **2** or **4** and the *head-to-tail* (*ht*) oxetanes **3** or **5**. The PB reactions reveal notable substituent effects on their regioselectivity, photochemical efficiency as well as their stability and the mode of ring-opening. The regioselectivity and the photochemical efficiency correlate clearly with the electronic properties of the substituents of the BPs, that is, the BPs with electron-withdrawing groups (EWGs) give more efficient PB reactions with a lower proportion of the *hh* oxetane and less efficient PB reactions with a higher proportion of the *hh* oxetane for BPs with electron-donating groups (EDGs). The oxetanes from DMT, **2** and **3**, are more stable than the corresponding oxetanes from DMU, **4** and **5**. The oxetanes from the BPs with EWGs are more stable than the corresponding oxetanes formed from the BPs with EDGs. The ring-opening modes of the oxetanes are also dependent on the DMT/DMU and BPs in the presence of acid.

Introduction

The Paternò–Büchi (PB) reaction, which is a photochemical [2+2] cycloaddition of carbonyl compounds with alkenes, has been developed into a reliable method for the construction of substituted oxetanes,[1] taking advantage of the propensity of oxetanes to undergo ring-opening in different fashions depending on the reaction conditions used to furnish products with delicate structures.[1d,2–5] For the synthetic and mechanistic points of view, the dependence of the regio- and stereo-selectivity on various factors has attracted considerable attention[6–10] such as solvent, substituent, the excited state of the carbonyls (singlet- vs. triplet-excited state) and temperature effects. However, in contrast to the extensive studies carried out on the stereoselectivity, studies on the effects of these factors on the regioselectivity are scarce. For example, no information for the effect of substituents of carbonyl compounds on the regioselectivity is available.

The (6–4) photoproduct, which is the second major lesion induced in DNA by UV radiation, is formed from the ring-opening of an oxetane (or azetidine). It is generated from a PB reaction of the 5, 6 double bond of the 5′ thymine with the C4 carbonyl (or amino) of the 3′ thymine (cytosine) at a temperature above –80 °C.[11] To determine whether the cycloreversion of the intermediate oxetane (6–4) in photolyase occur via the proposed electron transfer mechanism,[12] *head-to-head* (*hh*) oxetane adducts of DMT,[13,14] thymine covalently linked flavin[15] and 1,3-dimethyluracil (DMU)[16,17] with carbonyl compounds were prepared as model compounds of the intermediate oxetane formed during the repair process of the (6–4) photoproduct. Recently, the PB reactions of DMT with benzophenone[18] and its derivatives[10] were found to give two series of regioisomeric oxetanes, *hh* oxetanes and *ht* oxetanes. The formation of similar regioisomeric oxetanes was also observed from the photolysis of thymidine with benzophenone.[19] However, information about the stability and the ring opening mode of the oxetane adducts is very rare.[10]

In this work, we have investigated the photochemical reactions of DMU and DMT with benzophenone (**1d**) and its 4,4′-disubstituted derivatives (BPs); 4,4′-dimethoxybenzophenone (**1a**), 4,4′-dimethylbenzophenone (**1b**), 4,4′-di-*tert*-butylbenzophenone (**1c**), 4,4′-difluorobenzophenone (**1e**), 4,4′-dichlorobenzophenone (**1f**) and 4,4′-dicyanobenzophenone (**1g**), and observed notable substituent effects on the regioselectivity, the photochemical efficiency as well as the stability and the ring-opening mode of the oxetane photoproducts in the PB reactions.

Results and Discussion

The Photochemical Reactions of BPs with DMT and DMU

In our previous paper, we investigated the photochemical reactions of DMT with four BPs, **1a**, **1c**, **1d** and **1e** in deaer-

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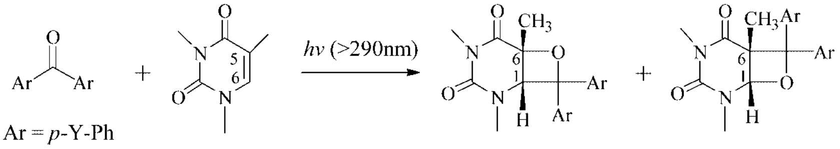
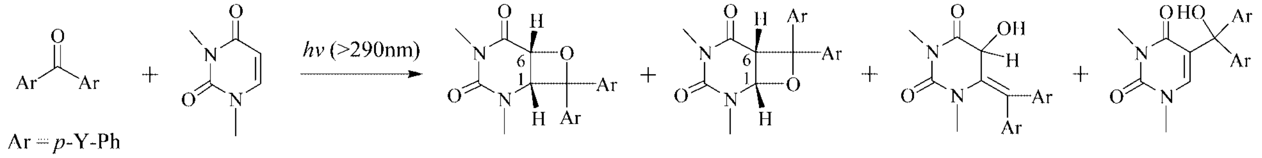


1a: Y = CH_3O	DMT	**2a**: Y = CH_3O	**3a**: Y = CH_3O
1b: Y = CH_3		**2b**: Y = CH_3	**3b**: Y = CH_3
1c: Y = *t*Bu		**2c**: Y = *t*Bu	**3c**: Y = *t*Bu
1d: Y = H		**2d**: Y = H	**3d**: Y = H
1e: Y = F		**2e**: Y = F	**3e**: Y = F
1f: Y = Cl		**2f**: Y = Cl	[**3f**: Y = Cl]
1g: Y = CN		**2g**: Y = CN	**3g**: Y = CN

Scheme 1.



1a: Y = CH_3O	DMU	**4a**: Y = CH_3O		**4'a**: Y = CH_3O	
1b: Y = CH_3		**4b**: Y = CH_3	[**5b**: Y = CH_3]	**4'b**: Y = CH_3	
1c: Y = *t*Bu		**4c**: Y = *t*Bu	[**5c**: Y = *t*Bu]	**4'c**: Y = *t*Bu	**5'c**: Y = *t*Bu
1d: Y = H		**4d**: Y = H	[**5d**: Y = H]	**4'd**: Y = H	**5'd**: Y = H
1e: Y = F		**4e**: Y = F	[**5e**: Y = F]	**4'e**: Y = F	**5'e**: Y = F
1f: Y = Cl		**4f**: Y = Cl	[**5f**: Y = Cl]	**4'f**: Y = Cl	**5'f**: Y = Cl
1g: Y = CN		**4g**: Y = CN	**5g**: Y = CN		

Scheme 2.

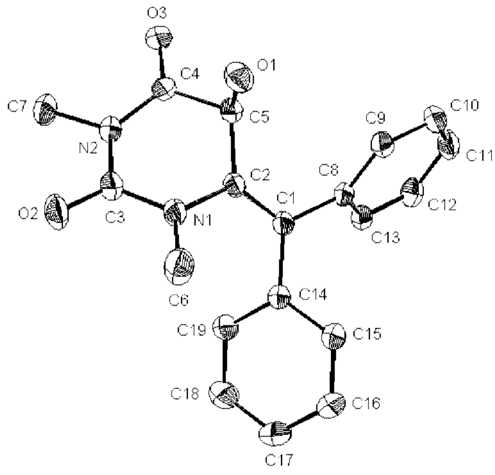
ated acetonitrile solutions and obtained two series of regioisomers, *hh* oxetanes **2a** and **2c–e** and *ht* oxetanes **3a** and **3c–e**.[10] The photochemical reaction was further performed with DMT and three additional 4,4′-disubstituted benzophenones, **1b**, **1f** and **1g**. Two series of regioisomeric oxetanes, **2b**, **2f**, **2g** and **3b**, **3g** were isolated. **3f** was not obtained due to decomposition to the starting materials during the separation process. Although **3f** was not isolated, its formation in an [D$_3$]acetonitrile solution of DMT and **1f** was clearly observed by the ^{1}H NMR spectrum of the crude product mixture (Scheme 1).

The PB reactions of DMT with all seven BPs uniformly generate two regioisomeric oxetanes, while the products isolated from the photolysis systems of DMU-BPs include four series of compounds. The oxetanes in brackets, shown in Scheme 2, were not obtained. For the DMU and **1a** photochemical system, only the 5-hydroxy-6-vinyluracil **4′a** was isolated and one series of the *hh* oxetanes, **4b–f**, and one series of 5-hydroxymethyluracils, **5′c–f** were obtained from the DMU with **1b–f** systems. Besides **4b**, **4c** and **5′c**, 5-hydroxy-6-vinyluracils **4′b** and **4′c** were also obtained from DMU systems with **1b** and **1c**, respectively. The photoproducts from the DMU and **1g** system are two regioisomeric oxetanes, **4g** and **5g** and are similar to the DMT system. Compounds **4′d**, **5′d** and **5′e** were further confirmed by their X-ray crystal structure determination (Figure 1).

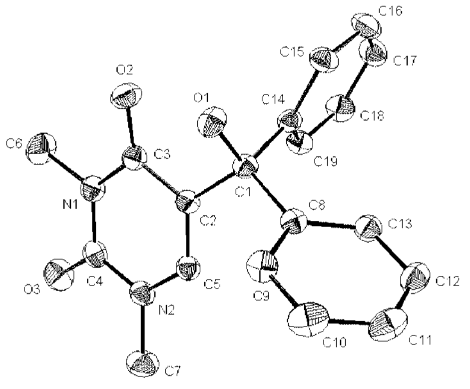
Compounds **4′a–c** may be rearrangements of the products of the *hh* oxetanes **4a–c**. This was confirmed by the ^{1}H NMR spectra of the crude product mixtures for photolysis of DMU and **1a–c** in [D$_3$]acetonitrile. The initial photoproducts **4a–c**, rather than **4′a–c**, were clearly observed from the ^{1}H NMR spectra. In the region of chemical shift 4–6 ppm on the ^{1}H NMR spectra, the characteristic peaks of two protons (H-1 and H-6) for the oxetanes, **4a–c**, are two groups of double peaks, and one or two single peaks for two protons (C5-H and C5-OH) of the 5-hydroxy-6-vinyluracils **4′a–c**. At a lower temperature the same preparative procedure of the DMU with **1a** system was performed and **4a** was obtained. In the absence of acid **4a** is stable at room temperature.

To test whether compounds **4d–g** undergo the same rearrangement, a trace of hydrochloric acid was added to the acetonitrile solutions of **4d–g**. The oxetanes **4d–f** easily rearranged to form the 5-hydroxy-6-vinyluracils **4′d–f** at room temperature (Scheme 3), while **4g** is stable. The *hh* oxetane from DMT, **2a**, easily isomerizes to form **2′a** by the same rearrangement in acid solution. Although the experiment was not performed further, we can expect that other **2**-type oxetanes such as **2b** and **2c** can also undergo the rearrangement to form **2′b** and **2′c**.

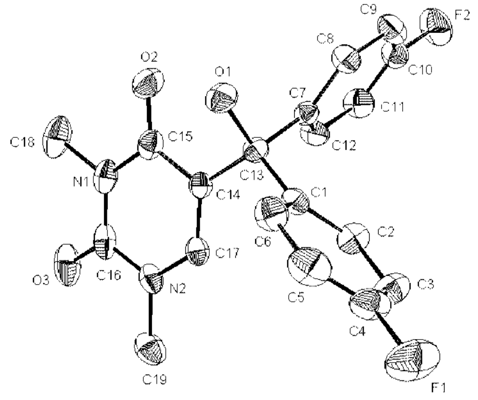
Similarly, compounds **5′c–f** are inferred to be the rearrangement products of possible *ht* oxetanes **5c–f**. The ^{1}H NMR spectra of the crude product mixtures showed that the initial photoproducts are the *ht* oxetanes **5b–f** for DMU systems with **1b–f**, and both **5a** and **5′a** are not detected in the DMU system with **1a**. A respresentative set of ^{1}H NMR



4’d

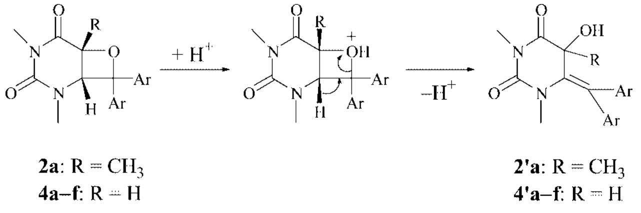


5’d



5’e

Figure 1. X-ray crystal structures of **4′d**, **5′d** and **5′e**. ORTEP plots of the molecular structures. Displacement ellipsoids are shown at the 30% probability level. CCDC-281758, -281759 and -281760, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Scheme 3.

spectra for the DMU system with **1d** show the initial photoproduct is *ht* oxetane **5d**, and **5′d** appears in the solution after two days resulting from rearrangement of **5d** (Figure 2). These results confirmed that compounds **5′c**–**f** are rearrangement products of the unisolated *ht* oxetanes **5c**–**f**.

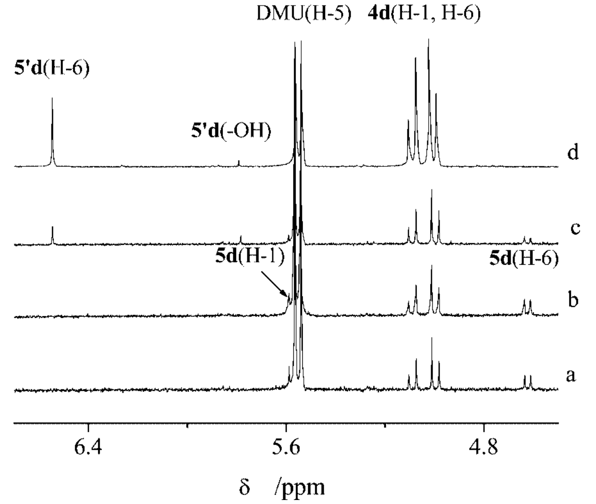


Figure 2. ^{1}H NMR spectra of the crude product mixture of DMU with **1d** in [D$_3$]acetoniltrile irradiated for (a) 10 min, (b) 30 min, (c) 30 min (determined again after 2 day) and (d) mixture of compounds **4d**, **5′d** and DMU in [D$_3$]acetonitrile.

The PB Reaction vs. Energy and Electron Transfer Processes in the Photochemical Reactions

By HPLC chromatography and ^{1}H NMR spectroscopy, the photochemical reactions of DMT or DMU with BPs were observed to be clean PB reactions and generate only two regioisomeric oxetanes as well as side products in very small amounts except for the DMT system with **1g**. The side products are mainly from the photo-degeneration of the BPs themselves.

Using the Rehm–Weller equation (1),[20] the free energy changes (ΔG) for the proposed electron-transfer reactions from DMT or DMU to triplet BPs were estimated.

$$\Delta G\ (\mathrm{kJ\cdot mol^{-1}}) = 96.5\ [E_{\mathrm{ox}}(\mathrm{D}) - E_{\mathrm{red}}(\mathrm{A}) - \mathrm{e}_0^2/\varepsilon R_{\mathrm{D+A-}}] - \Delta E_{0,0} \quad (1)$$

Where E_{ox} of DMU and DMT in acetonitrile was 1.69 V and 1.45 V vs. Ag/AgCl,[21] and the coulomb term $-\mathrm{e}_0^2/\varepsilon R_{\mathrm{D+A-}}$ was –0.06 eV in acetonitrile.[22] Although $-E_{\mathrm{red}}$ value of **1g** is not available, it is expected that the the value is lower than 1.42 eV of *p*-cyanobenzophenone [i.e. E_{red}(**1g**) > –1.42 eV].[23]

Except for the DMT system with **1g**, the other calculated values of ΔG are positive (Table 1). This implies that the proposed electron-transfer reactions would not easily occur

Table 1. Substituents of BPs dependence on the regioselectivity (*hh*:*ht*) and the efficiency of the PB reactions[a] and the calculated free energy changes (ΔG) for the proposed electron transfer from triplet BPs to DMT or DMU.

BPs	$\Delta E_{0,0}$ [b] kJ·mol^{-1}	$-E_{1/2}$red[b] /V	ΔG_{DMT} kJ·mol^{-1}	DMT[c] **2/3**	Yield (mb[e])%	ΔG_{DMU} kJ·mol^{-1}	DMU[d] **4/5**	Yield (mb[e]) %
1a	290	2.02	+34.7	44:56	10 (96)	+57.9	>95:5 [f]	7 (93)
1b	289	1.90	+24.1	48:52	18 (96)	+47.3	77:23	13 (91)
1c	289	1.87	+21.2	52:48	20 (95)	+44.4	76:24	21 (97)
1d	289	1.83	+17.4	54:46	29 (97)	+40.5	65:35	39 (95)
1e	294	1.78	+7.6	53:47	25 (98)	+30.7	63:37	49 (95)
1f	287	1.67	+3.9	32:68	27 (100)	+27.1	54:46	49 (96)
1g	276[g]	<1.42	< –9.2	8:92	26 (81)	< +14.0	38:62	51 (100)

[a] Average of three measurements, DMU(DMT)/BPs = 20:20 mM, in [D$_3$]acetonitrile, irradiation at 25 °C with 125-W high-pressure Hg lamp, values determined by ^{1}H NMR (300 MHz) of the crude product mixture, the experimental error <5%. [b] From ref.[23] unless otherwise indicated. [c] Irradiation for 10 min. [d] Irradiation for 30 min. [e] mb = mass balance. [f] The value was not determined due to the low yield of the product. [g] From ref.[24]

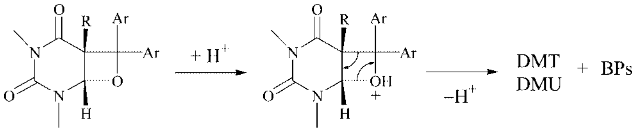
between DMT/DMU and the triplet BPs in acetonitrile except for the DMT system with **1g**. The calculation results are in accordance with experimental observations. Side products in larger amounts observed from the DMT system with **1g** may be from an electron transfer reaction. A clean PB reaction for the DMU system with **1g** is observed.

The regioselectivity (regioisomeric ratio, *hh*:*ht*) for the PB reaction is unchanged for various reactant ratios (DMT/DMU:BPs) and in a broad concentration range in 1:2 ratio. This clearly shows that the photochemical reactions are the PB reactions initiated purely by the triplet states of BPs. No significant photodimerization of DMT or DMU was detected under the reactant ratio (DMT/DMU:BPs = 1:2), that is, the energy transfer between triplet BPs and DMT or DMU appears unlikely. Although the formation of a thymidine dimer was detected in a photolysis system with a large excess of thymidine (benzophenone:thymidine = 1:3, in quartz tube and irradiation with a medium-pressure Hg lamp),[19] we prefer to think the dimerization is due to the direct excitation of the thymidine rather than triplet-triplet energy transfer from triplet benzophenone because most photons are absorbed by thymidine. Other authors' observations have also shown that triplet-triplet energy transfer between triplet benzophenone and thymidine 5′-monophosphate does not occur.[25]

The PB reaction, an energy or electron transfer process in the photosensitization of thymine in the nucleoside, oligonucletides or DNA by benzophenone derivatives would cause different photoproducts or DNA damages. In a deaerated solution the prevailing mechanism of the photosensitization of thymidine by benzophenone is the PB reaction, rather than energy transfer leading to cyclobutane pyrimidine dimers.[19] This is in accordance with the photochemical behavior of DMT with BPs. In sharp contrast, in an aerated aqueous solution the main process is an electron transfer reaction for thymidine and for the thymine base in thymidylyl-(3′→5′)-thymidine (TpT), the energy transfer mechanism dominates, leading to an intramolecular dimerization, rather than the PB reaction, in the benzophenone photosensitization.[26] As the triplet energy of a thymine base in DNA is lowered due to π-stacking interactions, the formation of cyclobutane pyrimidine dimers via energy transfer were further observed by the irradiation of DNA in the presence of benzophenone and ketoprofen.[27–29] Although no data about the triplet energy of the thymine base in an oligonucleotide or DNA is available, it is expected that a PB reaction is a likely reaction pathway for DNA and BPs with a low triplet energy level under UV light, and its biological significance is worth noting.

Substituent Effects on the Stability and the Ring-Opening Mode of the Oxetanes

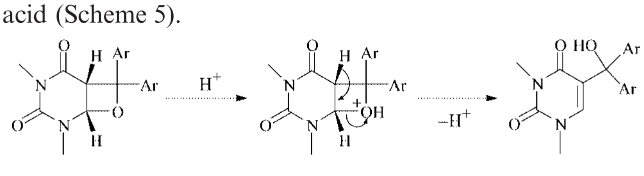
For two regioisomeric oxetanes from DMT, *hh* oxetanes **2** are more stable than the corresponding *ht* oxetanes **3**, which are acid-labile and easily decompose to the starting materials DMT and the corresponding BPs in the presence of silica gel or a trace of acid (Scheme 4).



3a–g: R = CH$_3$
5g: R = H

Scheme 4.

Similarly, *hh* oxetanes from DMU **4** are relatively stable compared to the corresponding *ht* oxetanes **5**. The oxetanes from DMT, **2** and **3**, are more stable than the corresponding oxetanes from DMU, **4** and **5**. The *hh* oxetanes from DMU **4a–f** can easily rearrange to form **4′a–f**, and most *hh* oxetanes from DMT **2** are stable, in acid solutions. In contrast to **3**, **5c–f** isomerize to give 5-(hydroxymethyl)uracils **5′c–f**, and **5g** is stable in the presence of silica gel or a trace of acid (Scheme 5).



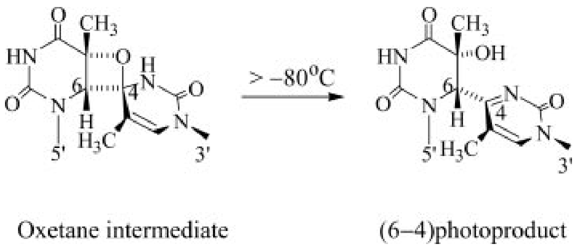
5c–f **5′c–f**

Scheme 5.

The stability of the oxetanes is strongly dependent on the substituents of the BPs. The oxetanes formed from BPs with electron-withdrawing groups (EWGs) are more stable than the corresponding oxetanes from BPs with electron-donating groups (EDGs). The *hh* oxetanes **2** are the most stable amongst the four kinds of oxetanes (**2**–**5**), but the oxetanes formed from the BPs with EDGs such as **2a** can easily rearrange to form **2′a**, whereas the oxetane **4g** from the BPs with EWGs is stable in acid solution. The *ht* oxetanes **5** are the most unstable amongst the four kinds of oxetanes, but the one isolable *ht* oxetane **5g** from DMU and the BPs with EWGs (CN, **1g**) are stable in the presence of silica gel. In acid solution, **5g** decomposes to its starting materials, like *ht* oxetanes **3** from DMT. The oxetanes **3** from the BPs with EDGs such as **3a** and **3b** are very unstable in the presence of silica gel or acidic media.

The mode of ring-opening for the oxetanes is also dependent on the olefin (DMU/DMT) and the substituents of BPs. Among the *hh* oxetanes **2** and **4**, the oxetanes from the BPs with EDGs, **2a** and **4a**–**f**, can isomerize to form 5-hydroxy-6-vinyluracils **2′a** and **4′a**–**f**, and most **2**-type oxetanes and **4g** are stable in the presence of silica gel or in acidic solutions. The *ht* oxetanes from DMU, **5c**–**f**, can quickly isomerize to 5-hydroxymethyluracils **5′c**–**f**, while **5g** and **3** decompose to their starting materials, in the presence of silica gel or in acidic solution. The oxetane **3** from DMT does not isomerize according to Scheme 5 due to the difficult formation of a methyl cation from heterolysis of C5-CH_3.

The (6–4) photoproduct is thought to form in DNA by a PB reaction between two adjacent pyrimidines and generates an oxetane (or azetidine) intermediate, which at temperature above –80 °C undergoes ring-opening by C4-O bond cleavage accompanied by a proton shift from N3 to generate the "open form" of the (6–4) photoproduct (Scheme 6).[11] The ring-opening mode of the natural oxetane is similar to that of *hh* oxetanes **2** and **4** isomerizing to **2′** and **4′**.



Scheme 6.

Substituent Effects on Regioselectivity and Efficiency in the PB Reactions

To further investigate the regioselectivity and the efficiency in the PB reactions, deaerated [D_3]acetonitrile solutions containing BPs and DMT or DMU in Pyrex NMR tubes were irradiated for 15 min (for DMT system) or 30 min (for DMU system) and the ^{1}H NMR spectra of the crude product mixtures were measured immediately. Yields and mass balances were calculated in reference to the sum of the aromatic signals and the regioisomeric ratios (*hh*:*ht*) were obtained from the peak area of the H-1 of the oxetanes and are listed in Table 1.

The photochemical efficiencies of the PB reactions of DMT systems are 1–3 times higher than the corresponding DMU systems. The proportions of **3** in the oxetanes from DMT (**2** and **3**) are higher than the corresponding **5** in the oxetanes from DMU (**4** and **5**). The results show that the 5-methyl group of DMT in the PB reaction plays the role of stabilizing the intermediates, the 1,4-diradicals especially C6-DR, rather than sterically hindering the ring closure for C6-DR (Figure 3). The former enhances the efficiencies of the PB reactions and the latter would lead to a decrease. In addition, if an exciplex intermediate[1d] formed via charge transfer prior to the formation of the diradicals occurred in the PB reaction, a high efficiency for the formation of the exciplex would also be an important factor for the high efficiency of the DMT system due to a lower oxidative potential for DMT.

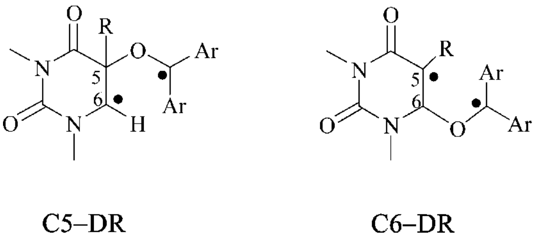


Figure 3. Two diradicals from the PB reaction of DMU/DMT with BPs.

In contrast with the PB reaction, the role of the 5-methyl group should be steric hindrance in the photochemical [2+2] cycloaddition between two DMT molecules to form a cyclobutane dimer via a triplet pathway, because the efficiency for DMT[30] is lower than DMU,[31] using acetone as photosensitizer. Thus, the 5-methyl group of DMT plays very different roles in the two-step [2+2] cycloaddition (the PB reaction) and in the concerted [2+2] cycloaddition (the photodimerization).

Data in Table 1 shows that the regioselectivity (*hh*:*ht*) in the PB reactions correlates well with the free energy changes (ΔG) of the proposed electron-transfer reactions from DMT or DMU to triplet BPs. The systems with large values of ΔG are less efficient photochemical reactions with higher proportions of *hh* oxetanes (**2** and **4**), and more efficient reactions with high proportions of *ht* oxetanes (**3** and **5**) for the systems with small ΔG. The regioselectivities for the DMT system with **1a** and the DMT system with **1b** are not in good agreement with the calculated ΔG values. This may indicate the existence of other factors that strongly influence the regioselectivity, such as temperature.[9] The mechanism for substituent effects on the regioselectivity remain to be clarified after further investigation.

The efficiency of the PB reactions dependence on the free energy change, ΔG, can be discussed in terms of frontier molecular orbital (FMO) theory. To a certain extent, the value of ΔG reflects the energy gap between the low singlyoccupied molecular orbital (SOMO) of triplet BPs and the HOMO of DMT/DMU. The interaction between two molecular orbitals in the [2+2] cycloaddition may generate an exciplex intermediate[1d] via charge transfer prior to the formation of the triplet diradicals, and its efficiency depends on the energy gap. A small energy gap (or ΔG) implies a strong interaction, and would induce a higher efficiency in the PB reaction.

Photochemical Reaction of Thymidine and Uridine with Benzophenone

Recently, two pairs of diastereomic regioisomers were detected from the photolysis of a system of thymidine and benzophenone in a deaerated acetonitrile-water (80:20) binary solvent by HPLC/MS chromatography, and two diastereomic *ht* oxetanes were well characterized.[19] We further observed the PB reaction of benzophenone with thymidine and uridine in both a deaerated [D$_3$]acetonitrile solution (Figure 4) and CD$_3$CN/D$_2$O (1:1) binary solvent (not shown) by ^{1}H NMR spectra. The characteristic ^{1}H NMR spectra show the formation of oxetane products, and the ratio of the two regioisomers, *hh*:*ht* = 35:65 for thymidine in a deaerated [D$_3$]acetonitrile solution. The efficiency of the photoreaction of thymidine with benzophenone is 3–4 times as high as for uridine. Hence, if the photoreaction occurs in nucleic acids, DNA would be more sensitive than RNA.

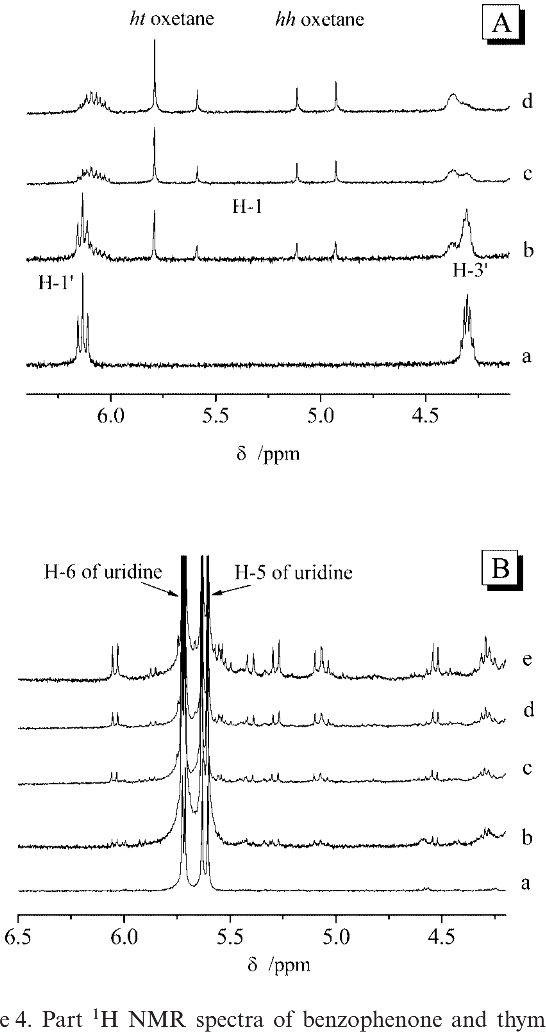


Figure 4. Part ^{1}H NMR spectra of benzophenone and thymidine (A) irradiation for (a) 0 min, (b) 5 min, (c) 15 min, (d) 25 min; uridine (B) irradiation for (a) 0 min, (b) 10 min, (c) 30 min, (d) 60 min, (e) 120 min, in [D$_3$]acetoniltrile.

Conclusion

In summary, the PB reactions of 4,4′-disubstituted benzophenones with DMT or DMU reveal notable substituent effects on the regioselectivity and the efficiency as well as the stability and the mode of the ring-opening of oxetanes. The regioselectivity and the efficiency correlate well with the electronic properties of the substituents of BPs. The PB reactions of DMU and the BPs with EDGs gave higher proportions of *hh* oxetanes, and higher proportions of *ht* oxetanes for the BPs with EWGs. The oxetanes from DMT are more stable than the corresponding oxetanes from DMU. The oxetanes from the BPs with EWGs are more stable than the corresponding oxetanes from the BPs with EDGs. The mode of ring-opening of the *hh* oxetanes from the BPs with EDGs, such as **2a** and **4a**–**f**, is a rearrangement to 5-hydroxy-6-vinyluracils **2′a** and **4′a**–**f**, and *ht* oxetanes from DMT **3** and the oxetane from DMU and a BPs with EWGs **5g** decompose to their starting materials, and **5c**–**f** isomerize to 5-hydroxymethyluracils **5′c**–**f**, in the presence of silica gel or acidic media.

Experimental Section

General Remarks: Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a Bruker AV 300 spectrometer operating at 300 and 75 MHz, respectively. The chemical shifts were referenced to CHCl$_3$ (δ = 77.16) in CDCl$_3$, acetone (δ = 29.84) in [D$_3$]acetone and DMSO (δ = 39.52) in [D$_6$]DMSO for ^{13}C NMR spectra, and CH$_3$CN (δ = 2.19) in CD$_3$CN for ^{1}H NMR spectra. IR spectra were recorded in KBr and measured in cm^{-1} using a Bruker Vector22 Infrared Spectrometer. Mass spectra were obtained with a Micromass GCF TOF mass spectrometer. 1,3-Dimethyluracil (DMU), 1,3-dimethylthymine (DMT), 4,4′-dimethoxybenzophenone,[32] 4,4′-di-*tert*-butylbenzophenone,[33] 4,4′-dichlorobenzophenone and 4,4′-dicyanobenzophenone[34] were prepared by literature methods. Other materials were obtained from commercial suppliers and were used as received without further purification. Solvents of technical quality were distilled prior to use.

Photoproduct Assay: The photochemical reactions of DMT, DMU, thymidine and uridine with BPs were performed in CD$_3$CN and/or CD$_3$CN/D$_2$O. The solution of reactants was placed in a Pyrex NMR tube (> 290 nm), bubbled with high purity N$_2$ for 15 min, and then irradiated with a 125-W high-pressure Hg lamp. The yields of photoproducts were assessed by ^{1}H NMR spectroscopy (300 MHz) of the crude product mixture, using the sum of the aromatic signals as an internal standard. The ratios of two regioisomeric oxetanes were obtained from the peak areas of the H-1 for the two oxetanes from the ^{1}H NMR spectra.

General Procedure for Preparative Photolysis Reactions: DMT or DMU and BPs were dissolved in acetonitrile (DMT/DMU/BPs = 100 mM:200 mM). The solution was placed in a Pyrex tube, sealed, bubbled for 15 min with high pure nitrogen, and irradiated at room temperature (unless otherwise indicated) with a 300-W high-pressure Hg lamp for 5–10 h. The solvent was removed by rotary evaporation, and products were separated by column chromatography.

X-ray Crystal Structure Data of 4′d: Orange needles. $C_{19}H_{18}N_2O_3$, $M = 322.35$; triclinic, space group $P\bar{1}$: $D_c = 1.244$ g cm^{-1}, $Z = 2$, $a = 5.9027(12)$ Å, $b = 10.727(2)$ Å, $c = 14.720(3)$ Å, $\alpha = 109.711(2)°$, $\beta = 95.385(3)°$, $\gamma = 97.506(3)°$, $V = 860.4(3)$ Å^3, $T = 293(2)$ K, μ(Mo-$K\alpha$) = 0.085 mm mm^{-1}, 5904 reflections collected, 4020 unique ($R_{int} = 0.0233$), $R_1 = 0.0437$, $wR_2 = 0.1164$ [$I > 2\sigma(I)$].

X-ray Crystal Structure Data of 5′d: Colorless needles. $C_{19}H_{18}N_2O_3$, $M = 322.35$; monoclinic, space group $P21/c$: $D_c = 1.322$ g cm^{-1}, $Z = 4$, $a = 12.7184(16)$ Å, $b = 7.8745(10)$ Å, $c = 16.285(2)$ Å, $\beta = 96.727(2)°$, $V = 1619.8(4)$ Å^3, $T = 293(2)$ K, μ(Mo-$K\alpha$) = 0.090 mm^{-1}, 10643 reflections collected, 3889 unique ($R_{int} = 0.0237$), $R_1 = 0.0393$, $wR_2 = 0.1031$ [$I > 2\sigma(I)$].

X-ray Crystal Structure Data of 5′e: Colorless needles. $C_{19}H_{16}F_2N_2O_3$, $M = 358.34$; monoclinic, space group $P21/c$: $D_c = 1.397$ g cm^{-1}, $Z = 4$, $a = 5.6908(14)$ Å, $b = 18.498(5)$ Å, $c = 16.278(3)$ Å, $\beta = 95.961(6)°$, $V = 1704.3(7)$ Å^3, $T = 293(2)$ K, μ(Mo-$K\alpha$) = 0.110 mm^{-1}, 8756 reflections collected, 3004 unique ($R_{int} = 0.0523$), $R_1 = 0.0447$, $wR_2 = 0.1005$ [$I > 2\sigma(I)$].

(Z)-8,8-Bis(4-methoxyphenyl)-2,4,6-trimethyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (2a):[10] Yield 18%; $R_f = 0.14$ (EtOAc/cyclohexane, 1:4). ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ = 1.69 (s, 3 H, CH_3), 2.84 (s, 3 H, NCH_3), 3.06 (s, 3 H, NCH_3), 3.78 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 4.88 (s, 1 H, NCH), 6.92–7.39 (m, 8 H, $H_{benzene}$). ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 23.4 (CH_3), 26.9 (NCH_3), 34.8 (NCH_3), 55.0 (OCH_3), 59.6 (OCH_3), 64.3 (NCH), 75.8 (*C*CH_3), 90.7 (OC), 113.3, 113.6, 126.7, 126.8, 131.5, 136.6, 151.0 (NCON), 158.5 (*C*OCH_3), 158.6 (*C*OCH_3), 169.4 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 1714 s, 1676 s, 1250 s, 832 m, 747 m cm^{-1}. TOFMS (CI) calcd. for $(M + 1)^+$ $C_{22}H_{25}N_2O_5$: 397.1763, found 397.1776.

(Z)-7,7-Bis(4-methoxyphenyl)-2,4,6-trimethyl-8-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (3a):[10] Yield 10%; $R_f = 0.34$ (EtOAc/cyclohexane, 1:4). ^{1}H NMR (300 MHz, $(CD_3)_2CO$, TMS): δ = 1.41 (s, 3 H, CH_3), 2.70 (s, 3 H, NCH_3), 3.11 (s, 3 H, NCH_3), 3.74 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 5.41 (s, 1 H, NCH), 6.82 (d, J = 8.9 Hz, 2 H, $H_{benzene}$), 6.97 (d, J = 8.8 Hz, 2 H, $H_{benzene}$), 7.42 (d, J = 8.9 Hz, 2 H, $H_{benzene}$), 7.48 (d, J = 8.8 Hz, 2 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $(CD_3)_2CO$): δ = 21.0 (CH_3), 28.7 (NCH_3), 33.9 (NCH_3), 54.5 (*C*CH_3), 56.5 (OCH_3), 56.6 (OCH_3), 89.6 (OC), 91.5 (OC), 114.8, 115.1, 115.3, 115.4, 128.2, 128.5, 129.0, 135.9, 136.8, 139.8 (C), 153.7 (C), 160.8 (NCON), 171.4 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 1707 s, 1666 s, 1250 s, 832 s cm^{-1}. TOFMS (EI) calcd. for (M^+) $C_{22}H_{24}N_2O_5$: 396.1685, found 396.1681.

6-[2,2-Bis(4-methoxyphenyl)vinyl]-5-hydroxy-1,3,5-trimethyluracil (2′a): An acetonitrile solution (100 mL) of DMT (0.30 mg, 2 mmol) and **1a** (0.48 g, 2 mmol) in a nitrogen atmosphere was placed in a Pyrex reactor (transmitted light >290 nm) and irradiated at 5 °C with a 300-W high-pressure Hg lamp for 7 h. The solvent was removed in vacuo, and separation of crude products by flash chromatography on silica gel (EtOAc/petroleum ether, 1:8→1:4) gave a mixture containing **2a** and DMT. After removal of the solvent in vacuo, the mixture containing **2a** and DMT was dissolved in acetonitrile (20 mL) and hydrochloric acid (1 M, 0.05 mL) was added. After stirring for 10 min, **2a** disappeared, and the elution of the residual material over silica (EtOAc/petroleum ether, 1:6) gave **2′a** (80 mg, 10%) as white crystals. $R_f = 0.23$ (EtOAc/cyclohexane, 1:4); m.p. 139–140 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO, TMS): δ = 1.35 (s, 3 H, CH_3), 2.57 (s, 3 H, NCH_3), 3.08 (s, 3 H, NCH_3), 3.74 (ss, 6 H, OCH_3), 5.54 (s, 1 H, OH), 6.80–6.88 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 25.8 (CH_3), 28.0 (NCH_3), 37.2 (NCH_3), 54.9 (*C*CH_3), 55.1 (OCH_3), 73.1 (*C*CH_3OH), 112.6, 113.9, 130.8, 131.3, 131.8, 133.9, 134.8, 152.0 (NCON), 158.2 (*C*OCH_3), 158.5 (*C*OCH_3), 172.3 (N*C*OC) ppm. IR (KBr): 3441 s, 1716 s, 1675 s, 834 s cm^{-1}. TOFMS (EI) calcd. for (M^+) $C_{22}H_{24}N_2O_5$: 396.1685, found 396.1687.

6-[2,2-Bis(4-methoxyphenyl)vinyl]-5-hydroxy-1,3-dimethyluracil (4′a): A deaerated acetonitrile solution (10 mL) of DMU (0.14 g, 1 mmol) and **1a** (0.48 g, 2 mmol) was irradiated for 10 h. TLC showed the formation of only one photoproduct. After the removal of the solvent in vacuo and separation by flash chromatography on silica gel (EtOAc/petroleum ether, 1:6) **4′a** was obtained in the form of a yellowish oil (20 mg, 5%). $R_f = 0.40$ (EtOAc/cyclohexane, 1:2). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.79 (s, 3 H, NCH_3), 3.24 (s, 3 H, NCH_3), 3.82 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 4.70 (s, 1 H, C*H*OH), 6.84–7.04 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.6 (NCH_3), 36.7 (NCH_3), 55.2 (2C, OCH_3), 67.5, 67.6, 113.8 ($HC_{benzene}$), 114.0 ($HC_{benzene}$), 131.1 ($HC_{benzene}$), 131.2 ($HC_{benzene}$), 131.9, 132.0, 132.7, 151.9 (NCON), 158.9 (*C*OCH_3), 159.2 (*C*OCH_3), 168.2 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 3329 m, 1716 m, 1656 s, 836 w, 813 w cm^{-1}. TOFMS (EI) calcd. for $(M)^+$ $C_{21}H_{22}N_2O_5$: 382.1529, found: 382.1538.

(*Z*)-8,8-Bis(4-methoxyphenyl)-2,4,6-trimethyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (4a): The preparative procedure of **4′a** was performed at a lower temperature such as < 5 °C and the removal of solvents in vacuo and separation using silica gel (EtOAc/petroleum ether, 1:5→1:3) at < 10 °C. **4a** was isolated as a yellowish powder (50 mg, 13%). $R_f = 0.25$ (EtOAc/cyclohexane, 1:2). ^{1}H NMR (300 MHz, [D$_6$]DMSO, TMS): δ = 2.83 (s, 3 H, NCH_3), 2.88 (s, 3 H, NCH_3), 3.73 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 5.04 (d, J = 8.8 Hz, 1 H, NCH), 5.15 (d, J = 8.8 Hz, 1 H, OCH), 6.90 (d, J = 8.7 Hz, 2 H, $H_{benzene}$), 6.99 (d, J = 8.6 Hz, 2 H, $H_{benzene}$), 7.10 (d, J = 8.7 Hz, 2 H, $H_{benzene}$), 7.33 (d, J = 8.6 Hz, 2 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 26.9 (NCH_3), 34.7 (NCH_3), 55.1 (OCH_3), 55.2 (OCH_3), 59.3 (NCH), 70.0 (OCH), 94.8 (OC), 113.4 ($HC_{benzene}$), 113.7 ($HC_{benzene}$), 127.0 ($HC_{benzene}$), 127.2 ($HC_{benzene}$), 131.7 ($C_{benzene}$), 135.8 ($C_{benzene}$), 151.3 (NCON), 158.7 (*C*OCH_3), 158.8 (*C*OCH_3), 167.1 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 1715 m, 1673 s, 835 m, 746 w cm^{-1}. TOFMS (EI) calcd. for $(M)^+$ $C_{21}H_{22}N_2O_5$: 382.1529, found: 382.1521.

(Z)-2,4,6-Trimethyl-8,8-bis(4-methylphenyl)-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (2b) and (Z)-2,4,6-Trimethyl-7,7-bis(4-methylphenyl)-8-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (3b): A deaerated acetonitrile solution (10 mL) of DMT (0.15 g, 1 mmol) and **1b** (0.42 g, 2 mmol) was irradiated for 5 h. The solvent in the reaction mixture was removed in vacuo. Elution of the residual material over silica with 6:1 and 4:1 petroleum ether/EtOAc gave successively **3b** (0.12 g, 33%) and **2b** (0.06 g, 17%) as colorless oils. **2b:** $R_f = 0.34$ (EtOAc/cyclohexane, 1:4). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.43 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.90 (s, 3 H, NCH_3), 3.08 (s, 3 H, NCH_3), 4.54 (s, 1 H, NCH), 6.98–7.27 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 21.2 (2C, CH_3), 24.2 (CH_3), 27.5 (NCH_3), 35.8 (NCH_3), 66.6 (NCH), 76.4 (*C*CH_3), 91.7 (OC), 125.1, 125.7, 129.1, 129.4, 136.1, 137.8, 141.7, 151.9 (NCON), 170.1 (C*C*ON) ppm. TOFMS (EI) calcd. for $(M)^+$ $C_{22}H_{24}N_2O_3$: 364.1787, found:

364.1778. **3b:** R_f = 0.60 (EtOAc/cyclohexane, 1:4). ^{1}H NMR (300 MHz, CD_3CN): δ = 1.35 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 2.23 (s, 3 H, NCH_3), 2.64 (s, 3 H, NCH_3), 3.03 (s, 3 H, NCH_3), 5.23 (s, 1 H, NCH), 7.03–7.38 (m, 8 H, $H_{benzene}$) ppm. TOFMS (EI) calcd. for $(M)^+$ $C_{22}H_{24}N_2O_3$: 364.1787, found: 364.1776.

(*Z*)-2,4,6-Trimethyl-8,8-bis(4-methylphenyl)-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (4b) and 6-[2,2-Bis(4′-methylphenyl)vinyl]-5-hydroxy-1,3-dimethyluracil (4′b): A deaerated acetonitrile solution (10 mL) of DMU (0.14 g, 1 mmol) and **1b** (0.42 g, 2 mmol) was irradiated for 10 h. The solvent in the reaction mixture was removed in vacuo. Elution of the residual material over silica (EtOAc/petroleum ether, 1:10→1:4) gave **4′b** (18 mg, 5%) as yellowish crystals and **4b** (0.12 g, 34%) as a white powder. **4b**: R_f = 0.18 (EtOAc/cyclohexane, 1:4); m.p. 63–64 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.29 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 2.93 (s, 3 H, NCH_3), 3.05 (s, 3 H, NCH_3), 4.86 (d, J = 8.7 Hz, 1 H, NCH), 5.15 (d, J = 8.7 Hz, 1 H, OCH), 7.10–7.30 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 21.2 (2C, CH_3), 27.5 (NCH_3), 35.4 (NCH_3), 60.7 (NCH), 70.5 (OCH), 96.0 (OC), 125.3, 126.0, 129.1, 129.3, 136.0, 138.1, 138.2, 140.6, 151.9 (NCON), 167.2 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 1716 s, 1675 s, 815 m, 746 m cm^{-1}. TOFMS (EI) calcd. for $(M)^+$ $C_{21}H_{22}N_2O_3$: 350.1630, found: 350.1639. **4′b**: R_f = 0.25 (EtOAc/cyclohexane, 1:4); m.p. 180 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.35 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 2.77 (s, 3 H, NCH_3), 3.23 (s, 3 H, NCH_3), 4.69 (C*H*OH), 6.97–7.14 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR ($(CD_3)_2CO$, 75 MHz): δ = 21.2 (2C, CH_3), 28.0 (NCH_3); 37.3 (NCH_3), 69.1 (CHOH), 129.8, 130.0, 130.9, 133.6, 134.8, 138.1, 138.3, 138.7, 153.1 (NCON), 169.1 (C*C*ON) ppm. IR (KBr): $\tilde{\nu}$ = 3289 s, 1714 s, 1665 s, 1621, 826 m cm^{-1}. TOFMS (EI) calcd. for $(M)^+$ $C_{21}H_{22}N_2O_3$: 350.1630, found: 350.1628.

(*Z*)-8,8-Bis(4-*tert*-butylphenyl)-2,4,6-trimethyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (2c):[10] Yield 28%; R_f = 0.43 (EtOAc/cyclohexane, 1:4); m.p. 152–154 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.27 (s, 9 H, $C(CH_3)_3$), 1.30 (s, 9 H, $C(CH_3)_3$), 1.73 (s, 3 H, CH_3), 2.77 (s, 3 H, NCH_3), 3.15 (s, 3 H, NCH_3), 4.53 (s, 1 H, NCH), 7.20–7.40 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.9 (CH_3), 27.3 (NCH_3), 31.3 [$C(CH_3)_3$], 34.6 [$C(CH_3)_3$], 35.9 (NCH_3), 67.0 (NCH), 76.7 (*C*CH_3), 91.8 (OC), 124.7, 125.2, 125.4, 125.6, 135.9, 141.4, 150.8 (2C), 151.8 (NCON), 170.3 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 2963 s, 1717 s, 1685 s, 748 s cm^{-1}. TOFMS (EI) calcd. for (M^+) $C_{28}H_{36}N_2O_3$: 448.2726, found: 448.2731.

(*Z*)-7,7-Bis(4-*tert*-butylphenyl)-2,4,6-trimethyl-8-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (3c):[10] Yield 22%; R_f = 0.60 (EtOAc/cyclohexane, 1:4); m.p. 135–136 °C. ^{1}H NMR (300 MHz, $(CD_3)_2CO$, TMS): δ = 1.25 [s, 9 H, $C(CH_3)_3$], 1.29 [s, 9 H, $C(CH_3)_3$], 1.45 (s, 3 H, CH_3), 2.61 (s, 3 H, NCH_3), 3.12 (s, 3 H, NCH_3), 5.42 (s, 1 H, NCH), 7.29–7.51 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $(CD_3)_2CO$): δ = 20.0 (CH_3), 27.6 (NCH_3), 31.4 [$C(\mathit{CH}_3)_3$], 31.5 [$C(\mathit{CH}_3)_3$], 32.9 [*C*$(CH_3)_3$], 34.9 (NCH_3), 53.6 (*C*CH_3), 88.6 (NCH), 90.5 (OC), 125.2, 125.7, 125.8, 125.9, 139.9, 140.8, 150.8 (2C), 152.6 (NCON), 170.1 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 2962 s, 1713 s, 1680 s, 835 m cm^{-1}. TOFMS (CI) calcd. for $(M + 1)^+$ $C_{28}H_{37}N_2O_3$: 449.2804, found: 449.2812.

(*Z*)-8,8-Bis(4-*tert*-butylphenyl)-2,4,6-trimethyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (4c), 6-[2,2-Bis(4-*tert*-butylphenyl)vinyl]-5-hydroxy-1,3-dimethyluracil (4′c) and 5-[Bis(4-*tert*-butylphenyl)hydroxymethyl)-1,3-dimethyluracil (5′c): A deaerated acetonitrile solution (10 mL) of DMU (0.14 g, 1 mmol) and **1c** (0.59 g, 2 mmol) was irradiated for 10 h. The solvent was removed by rotary evaporation, and elution of the residual material over silica (EtOAc/petroleum ether, 1:12→1:8) gave successively **5′c** (32 mg, 7%) as white crystals and **4′c** (25 mg, 6%) and **4c** (0.18 g, 0.41 mmol, 41%) as white solids. **4c:** R_f = 0.30 (EtOAc/cyclohexane, 1:4); m.p. 158–160 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.27 [s, 9 H, $C(CH_3)_3$], 1.32 [s, 9 H, $C(CH_3)_3$], 2.97 (s, 3 H, NCH_3), 2.99 (s, 3 H, NCH_3), 4.87 (d, J = 8.7 Hz, 1 H, NCH), 5.13 (d, J = 8.7 Hz, 1 H, OCH), 7.25–7.45 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 27.3 (NCH_3), 31.3 [$C(\mathit{CH}_3)_3$], 31.4 [$C(\mathit{CH}_3)_3$], 34.6 [*C*$(CH_3)_3$], 34.7 [*C*$(CH_3)_3$], 35.5 (NCH_3), 61.1 (NCH), 70.8 (OCH), 96.1 (OC), 125.0, 125.3, 125.6, 125.8, 135.9, 140.6, 151.2 (C), 151.3 (C), 151.8 (NCON), 167.31 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 2961 s, 1717 s, 1677 s, 844 m, 824 m, 746 m cm^{-1}. TOFMS (EI) calcd. for $(M)^+$ $C_{27}H_{34}N_2O_3$: 434.2569, found: 434.2561. **4′c:** R_f = 0.37 (EtOAc/cyclohexane, 1:4); m.p. 190 °C (decomp.). ^{1}H NMR (300 MHz, $(CD_3)_2CO$, TMS): δ = 1.32 [d, 18 H, $C(CH_3)_3$], 2.75 (s, 3 H, NCH_3), 3.25 (s, 3 H, NCH_3), 4.73 (s, 1 H, C*H*OH), 7.01–5.35 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.2 (NCH_3), 31.4 [$C(CH_3)_3$], 37.5 (NCH_3), 68.6 (CHOH), 125.4, 125.6, 129.9, 130.0, 130.5, 136.5, 136.6, 136.7, 151.7, 152.4 (NCON), 169.2 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 3413 s, 2962 s, 1726 s, 1658 s, 825 w, 805 w cm^{-1}. TOFMS (EI) calcd. for (M^+) $C_{27}H_{34}N_2O_3$: 434.2569, found: 434.2565. **5′c**: R_f = 0.51 (EtOAc/cyclohexane, 1:4); m.p. 163–165 °C. ^{1}H NMR (300 MHz, $(CD_3)_2CO$, TMS): δ = 1.31 [s, 18 H, $C(CH_3)_3$], 3.29 (s, 3 H, NCH_3), 3.34 (s, 3 H, NCH_3), 6.45 (s, 1 H, NCH), 7.19–7.35 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.1 (NCH_3), 31.5 [$C(\mathit{CH}_3)_3$], 34.6 [*C*$(CH_3)_3$], 37.6 (NCH_3), 79.4 (HOC), 118.8, 125.2, 127.1, 141.4, 141.8, 150.5, 151.4 (NCON), 164.3 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 3441 s, 2961 s, 1708 s, 1651 s, 834 w cm^{-1}. TOFMS (EI) calcd. for (M^+) $C_{27}H_{34}N_2O_3$: 434.2569, found: 434.2560.

(*Z*)-2,4,6-Trimethyl-8,8-diphenyl-7-oxa-2,4-diazabicyclo[4.2.0]-octane-3,5-dione (2d):[13] Yield 25%; R_f = 0.27 (EtOAc/cyclohexane, 1:4); m.p. 149–151 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.78 (s, 3 H, CH_3), 2.90 (s, 3 H, NCH_3), 3.17 (s, 3 H, NCH_3), 4.62 (s, 1 H, NCH), 7.30–7.44 (m, 10 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.9 (CH_3), 27.3 (NCH_3), 35.7 (NCH_3), 66.5 (NCH), 76.5 (*C*CH_3), 91.6 (OC), 124.9, 125.5, 128.3, 128.6, 138.8 (C), 144.1 (C), 151.6 (N*C*ON), 169.8 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 1717 s, 1678 s, 744 s, 712 s cm^{-1}. TOFMS (EI) calcd. for $(M)^+$ $C_{20}H_{20}N_2O_3$: 336.1474, found: 336.1469.

(*Z*)-2,4,6-Trimethyl-7,7-diphenyl-8-oxa-2,4-diazabicyclo[4.2.0]-octane-3,5-dione (3d):[18] Yield 32%; R_f = 0.54 (EtOAc/cyclohexane, 1:4); mM p. 116–117 °C. ^{1}H NMR (300 MHz, $(CD_3)_2CO$, TMS): δ = 1.44 (s, 3 H, CH_3), 2.64 (s, 3 H, NCH_3), 3.11 (s, 3 H, NCH_3), 5.43 (s, 1 H, NCH), 7.24–7.60 (m, 10 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $(CD_3)_2CO$): δ = 20.1 (CH_3), 27.7 (NCH_3), 32.9 (NCH_3), 53.5 (*C*CH_3), 88.7 (NCH), 90.4 (OC), 125.9, 126.2, 128.1, 128.2, 128.5, 129.0, 142.7 (C), 143.7 (C), 152.5 (N*C*ON), 169.9 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 1713 s, 1673 s, 705 s cm^{-1}. TOFMS (CI) calcd. for $(M + 1)^+$ $C_{20}H_{21}N_2O_3$: 337.1552, found: 337.1542.

(*Z*)-2,4-Dimethyl-8,8-diphenyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (4d)[16,17] **and 5-(Hydroxydiphenylmethyl)-1,3-dimethyluracil (5′d):** In a nitrogen atmosphere, an acetonitrile solution (50 mL) of DMU (0.7 g, 5 mmol) and **1d** (1.82 g, 10 mmol) was placed in a Pyrex reactor (transmitted light >290 nm) and irradiated with a 300-W high-pressure Hg lamp for 10 h. After the solvent was removed in vacuo, elution of the residual material over silica with EtOAc/EtOAc, 6:1 and 4:1, gave successively **5′d** (0.11 g, 5%) and **4d** (0.35 g, 15%) as white crystals. **4d**: R_f = 0.16 (EtOAc/cyclohexane, 1:4); m.p. 134–135 °C. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 2.81 (s, 3 H, NCH_3), 2.92 (s, 3 H, NCH_3), 5.12 (d, J = 8.8 Hz, 1 H, NCH), 5.19 (d, J = 8.8 Hz, 1 H, OCH), 7.23–7.44 (m, 10 H,

$H_{benzene}$) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 26.7 (NCH_3), 34.9 (NCH_3), 59.3 (NCH), 70.8 (OCH), 95.3 (OC), 125.2, 125.4, 127.8, 128.1, 128.4, 139.6, 143.6, 151.2 (NCON), 167.1 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 1718 s, 1683 s, 744 s cm^{-1}. TOFMS (EI) calcd. for (M^+) $C_{19}H_{18}N_2O_3$: 322.1317, found: 322.1320. **5′d**: R_f = 0.32 (EtOAc/cyclohexane, 1:4); m.p. 203–205 °C. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.28 (s, 3 H, NCH_3), 3.34 (s, 3 H, NCH_3), 5.71 (s, 1 H, OH), 6.41 (s, 1 H, =CH), 7.29–7.35 (m, 10 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.1 (NCH_3), 37.5 (NCH_3), 79.5 (CHOH), 118.5, 127.4, 127.9, 128.4, 141.9, 144.3, 151.3 (NCON), 164.2 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 3464 s, 1710 s, 1650 s, 1625 s,706 s cm^{-1}. TOFMS (EI) calcd. for (M^+) $C_{19}H_{18}N_2O_3$: 322.1317, found: 322.1319.

6-(2,2-Diphenylvinyl)-5-hydroxy-1,3-dimethyluracil (4′d): (*Z*)-2,4-Dimethyl-8,8-diphenyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (**4d**, 180 mg, 0.56 mmol) was dissolved in acetonitrile (10 mL) and concentrated hydrochloric acid (0.04 mL) was added to the solution. The oxetane **4d** disappeared after 5 h at room temperature. The solvent was removed by rotary evaporation, and **4′d** was separated by elution over silica gel using petroleum ether/EtOAc, 3:1. The fractions containing **4′d** were collected, and concentrated in vacuo to give **4′d** (62 mg, 34%) as orange crystals. R_f = 0.25 (EtOAc/cyclohexane, 1:4); m.p. 156–157 °C. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.76 (s, 3 H, NCH_3), 3.24 (s, 3 H, NCH_3), 4.70 (s, 1 H, C*H*OH), 7.09–7.35 (m, 10 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.3 (NCH_3), 37.6 (NCH_3), 68.6 (CHOH), 128.5, 128.6, 128.8, 130.2, 130.4, 131.4, 136.2, 139.6, 139.7, 152.3 (NCON), 169.0 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 3414 s, 1715 s, 1665 s, 1625 s, 702 s cm^{-1}. TOFMS (EI) calcd. for (M^+) $C_{19}H_{18}N_2O_3$: 322.1317, found: 322.1321.

(*Z*)-2,4,6-Trimethyl-8,8-bis(4-fluorophenyl)-7-oxa-2,4-diazabicyclo-[4.2.0]octane-3,5-dione (2e):[10] Yield 33%; R_f = 0.15 (EtOAc/cyclohexane, 1:4); m.p. 128–129 °C. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.74 (s, 3 H, CH_3), 2.91 (s, 3 H, NCH_3), 3.10 (s, 3 H, NCH_3), 4.52 (s, 1 H, NCH), 7.01–7.36 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.1 (CH_3), 27.6 (NCH_3), 35.8 (NCH_3), 66.9 (NCH), 76.6 (*C*CH_3), 91.0 (OC), 115.5, 115.6, 115.7, 116.0, 127.0, 127.1, 127.6, 127.8, 134.6 (C), 140.0 (C), 151.6 (N*C*ON), 160.8 (CF), 164.1 (CF), 169.8 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 1709 s, 1673 s, 1221 s, 1156 m, 839 m cm^{-1}. TOFMS (CI) calcd. for $(M + 1)^+$ $C_{20}H_{19}N_2O_3F_2$: 373.1364, found 373.1371.

(*Z*)-7,7-Bis(4-fluorophenyl)-2,4,6-trimethyl-8-oxa-2,4-diazabicyclo-[4.2.0]octane-3,5-dione (3e):[10] Yield 32%; R_f = 0.35 (EtOAc/cyclohexane, 1:4); m.p. 120–121 °C. ^1H NMR (300 MHz, $(CD_3)_2CO$, TMS): δ = 1.45 (s, 3 H, CH_3), 2.72 (s, 3 H, NCH_3), 3.14 (s, 3 H, NCH_3), 5.49 (s, 1 H, NCH), 7.04–7.67 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $(CD_3)_2CO$): δ = 19.7 (CH_3), 27.8 (NCH_3), 33.2 (NCH_3), 54.2 (*C*CH_3), 88.8 (OC), 89.3 (OC), 112.4, 112.5, 118.9, 127.1, 127.4, 132.7, 133.3, 146.5 (CF), 147.6 (CF), 152.3 (NCON), 169.4 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 1712 s, 1674 s, 1230 s, 1162 m, 837 s cm^{-1}. TOFMS (CI) calcd. for $(M + 1)^+$ $C_{20}H_{19}N_2O_3F_2$: 373.1364, found 373.1360.

(*Z*)-8,8-Bis(4-fluorophenyl)-2,4-dimethyl-7-oxa-2,4-diazabicyclo-[4.2.0]octane-3,5-dione (4e) and 5-[Bis(4-fluorophenyl)hydroxymethyl]-1,3-dimethyluracil (5′e): A deaerated acetonitrile solution (10 mL) of DMU (0.14 g, 1 mmol) and **1e** (0.44 g, 2 mmol) was irradiated for 10 h. The solvent was removed in vacuo, the residual material was dissolved in dichloromethane, and elution of over silica with petroleum ether/EtOAc, 5:1 and 3:1, gave successively **5′e** (0.013 g, 4%) as white crystals and **4e** (0.12 g, 33%) as white solid. **4e**: R_f = 0.11 (EtOAc/cyclohexane, 1:4); m.p. 176–177 °C. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.96 (s, 3 H, NCH_3), 3.06 (s, 3 H, NCH_3), 4.86 (d, *J* = 8.7 Hz, 1 H, NCH), 5.18 (d, *J* = 8.7 Hz, 1 H, OCH), 7.01–7.40 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.5 (NCH_3), 35.4 (NCH_3), 60.9 (NCH), 70.5 (OCH), 95.2 (OC), 115.5, 115.7, 116.0, 127.2, 127.3, 128.0, 128.1, 134.5 (C), 139.0 (C), 151.7 (NCON), 161.1 (CF), 164.3 (CF), 166.8 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 1716 s, 1670 s, 1221 s, 832 s, 748 m cm^{-1}. TOFMS (EI) calcd. for (M^+) $C_{19}H_{16}N_3O_3F_2$: 358.1129, found 358.1128. **5′e**: R_f = 0.30 (EtOAc/cyclohexane, 1:4); m.p. 187–188 °C. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.30 (s, 3 H, NCH_3), 3.34 (s, 3 H, NCH_3), 5.72 (s, 1 H, OH), 6.39 (s, 1 H, NCH), 6.99–7.30 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.1 (NCH_3), 37.6 (NCH_3), 78.8 (CHOH), 115.2, 115.4, 118.2, 129.1, 129.2, 140.1, 141.9, 151.2 (NCON), 160.8, 164.1 (2C) ppm. IR (KBr): $\tilde{\nu}$ = 3361 s, 1708 s, 1655 s, 1625 s, 1227 s, 1215 s, 838 s, 751 s cm^{-1}. TOFMS (EI) calcd. for (M^+) $C_{19}H_{16}N_2O_3F_2$: 358.1129, found 358.1134.

6-[2,2-Bis(4-fluorophenyl)vinyl]-5-hydroxy-1,3-dimethyluracil (4′e): (*Z*)-8,8-Bis(4-fluorophenyl)-2,4-dimethyl-7-oxa-2,4-diazabicyclo-[4.2.0]octane-3,5-dione (**4e**, 116 mg, 0.32 mmol) was dissolved in acetonitrile (10 mL), and concentrated hydrochloric acid (0.04 mL) was added to the solution. After 5 h at room temperature, the solvent was removed in vacuo. Elution of the residual material over silica with petroleum ether/EtOAc, 3:1, gave **4′e** (46 mg, 40%) as white crystals. R_f = 0.21 (EtOAc/cyclohexane, 1:4); m.p. 193–194 °C. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.78 (s, 3 H, NCH_3), 3.25 (s, 3 H, NCH_3), 4.66 (s, 1 H, C*H*OH), 5.61 (s, 1 H, OH), 7.02–7.23 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.3 (NCH_3), 37.6 (NCH_3), 68.3 (CHOH), 115.8, 116.2, 131.6, 132.0, 132.2, 133.7, 135.3, 135.5, 152.3 (NCON), 161.3 (CF), 164.6 (CF), 169.2 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 3409 s, 1727 s, 1651 s, 1226 s, 839 s cm^{-1}. TOFMS (EI) calcd. for (M^+) $C_{19}H_{16}N_2O_3F_2$: 358.1129, found: 358.1121.

(*Z*)-8,8-Bis(4-chlorophenyl)-2,4,6-trimethyl-7-oxa-2,4-diazabicyclo-[4.2.0]octane-3,5-dione (2f): A deaerated acetonitrile solution (10 mL) of DMT (0.15 g, 1 mmol) and **1f** (0.50 g, 2 mmol) was irradiated for 5 h. The solvent in the reaction mixture was removed in vacuo. Separation of the mixture, containing **2f** and **3f**, was performed on silica gel column chromatography (petroleum ether/EtOAc, 3:1). Only **2f** was isolated as white crystals (0.025 g, 62%). **2f**: R_f = 0.62 (EtOAc/cyclohexane, 1:4); m.p. 173–174 °C. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 1.61 (s, 3 H, CH_3), 2.72 (s, 3 H, NCH_3), 3.01 (s, 3 H, NCH_3), 4.99 (s, 1 H, NCH), 7.20–7.49 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.1 (CH_3), 27.6 (NCH_3), 35.9 (NCH_3), 66.7 (NCH), 76.7 (*C*CH_3), 90.9 (OC), 126.4, 127.1, 128.8, 129.1, 134.3, 134.5, 137.0, 142.3, 151.5 (NCON), 169.6 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 1703 s, 1672 s, 820 m, 747 m cm^{-1}. TOFMS (CI) calcd. for $(M + 1)^+$ $C_{20}H_{19}N_2O_3Cl_2$: 405.0773, found 405.0775.

(*Z*)-8,8-Bis(4-chlorophenyl)-2,4-dimethyl-7-oxa-2,4-diazabicyclo-[4.2.0]octane-3,5-dione (4f) and 5-[Bis(4-chlorophenyl)hydroxymethyl]-1,3-dimethyluracil (5′f): A deaerated acetonitrile solution (10 mL) of DMU (0.14 g, 1 mmol) and **1f** (0.50 g, 2 mmol) was irradiated for 10 h. After the solvent in the reaction mixture was removed in vacuo, elution of the residual material over silica with petroleum ether/EtOAc, 5:1 and 3:1, gave successively **5′f** (42 mg, 11%) as a white solid and **4f** (90 mg, 22%) as white crystals. **4f**: R_f = 0.15 (EtOAc/cyclohexane, 1:4); m.p. 193–194 °C. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.98 (s, 3 H, NCH_3), 3.05 (s, 3 H, NCH_3), 4.85 (d, *J* = 8.7 Hz, 1 H, NCH), 5.18 (d, *J* = 8.7 Hz, 1 H, OCH), 7.21–7.43 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.6 (NCH_3), 35.6 (NCH_3), 60.9 (NCH), 70.7 (OCH), 95.1 (OC), 126.7, 127.4, 128.9, 129.1, 134.6, 134.9, 137.0, 141.4, 151.6 (NCON), 166.7 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 1714 s, 1670 s, 822 m, 748 m cm^{-1}. TOFMS (EI) calcd. for (M)$^+$ $C_{19}H_{16}N_2O_3Cl_2$: 390.0538, found 390.0540. **5′f**: R_f = 0.37 (EtOAc/cyclohexane, 1:4); m.p. 193–194 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.30 (s, 3 H, NCH_3), 3.33 (s, 3 H, NCH_3), 5.71 (s, 1 H, OH), 6.42 (s, 1 H, NCH), 7.24 (d, J = 8.6 Hz, 4 H, $H_{benzene}$), 7.31 (d, J = 8.6 Hz, 4 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.1 (NCH_3), 37.6 (NCH_3), 78.7 (CHOH), 117.6, 128.5, 128.6, 128.7, 128.8, 134.0, 141.9, 142.5, 151.1 (NCON), 164.0 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 3455 s, 1714 s, 1647 s, 1631 s, 825 w, 806 w cm^{-1}. TOFMS (EI) calcd. for (M$^+$) $C_{19}H_{16}N_2O_3Cl_2$: 390.0538, found: 390.0541.

6-[2,2-Bis(4-chlorophenyl)vinyl]-5-hydroxy-1,3-dimethyluracil (4′f): (*Z*)-8,8-Bis(4-chlorophenyl)-2,4-dimethyl-7-oxa-2,4-diazabicyclo-[4.2.0]octane-3,5-dione (**4f**, 120 mg, 0.31 mmol) was dissolved in acetonitrile (10 mL), and concentrated hydrochloric acid (0.04 mL) was added to the solution. After 5 h at room temperature, the solvent was removed by rotary evaporation, and elution of the residual material over silica with petroleum ether/EtOAc, 3:1, gave **4′f** (37 mg, 31%) as white crystals. R_f = 0.37 (EtOAc/cyclohexane, 1:4); m.p. 204–205 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.77 (s, 3 H, NCH_3), 3.21 (s, 3 H, NCH_3), 3.95 (s, 1 H, OH), 4.59 (s, 1 H, C*H*OH), 7.02–7.35 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.3 (NCH_3), 37.8 (NCH_3), 68.3 (CHOH), 128.9, 129.3, 131.5, 131.7, 132.4, 133.3, 134.8, 135.0, 137.6, 137.8, 152.2 (NCON), 169.0 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 3417 s, 1727 s, 1650 s, 831 m, 801 m cm^{-1}. TOFMS (EI) calcd. for (M$^+$) $C_{19}H_{16}N_2O_3Cl_2$: 390.0538, found: 390.0541.

(*Z*)-8,8-Bis(4-cyanophenyl)-2,4,6-trimethyl-7-oxa-2,4-diazabicyclo-[4.2.0]octane-3,5-dione (2g) and (*Z*)-7,7-Bis(4-cyanophenyl)-2,4,6-trimethyl-8-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (3g): A deaerated acetonitrile solution (10 mL) of DMT (0.15 g, 1 mmol) and **1 g** (0.46 g, 2 mmol) was irradiated for 5 h. After the solvent in the reaction mixture was removed in vacuo, elution of the residual material over silica with petroleum ether/EtOAc, 4:1 and 3:1, gave **3g** (0.12 g, 31%) and **2g** (0.07 g, 18%) as white crystals. **2g**: R_f = 0.11 (EtOAc/cyclohexane, 1:2); m.p. 196–198 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO, TMS): δ = 1.63 (s, 3 H, CH_3), 2.67 (s, 3 H, NCH_3), 3.09 (s, 3 H, NCH_3), 5.12 (s, 1 H, NCH), 7.43–7.91 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0 (C*C*H$_3$), 27.6 (NCH_3), 36.1 (NCH_3), 67.1 (NCH), 77.6 (*C*CH$_3$), 90.8 (OC), 112.7, 112.8, 118.0, 125.6, 126.4, 132.6, 133.0, 143.2, 147.9, 151.4 (NCON), 169.0 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 2228 s, 1676 s, 828 m, 745 s cm^{-1}. TOFMS (CI) calcd. for (M + 1)$^+$ $C_{22}H_{19}N_4O_3$: 387.1457, found 387.1458. **3g**: R_f = 0.30 (EtOAc/cyclohexane, 1:2); m.p. 185–187 °C. ^{1}H NMR (300 MHz, $(CD_3)_2CO$, TMS): δ = 1.52 (s, 3 H, CH_3), 2.72 (s, 3 H, NCH_3), 3.15 (s, 3 H, NCH_3), 5.59 (s, 1 H, NCH), 7.77–7.92 (m, 8 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $(CD_3)_2CO$): δ = 19.8 (C*C*H$_3$), 27.8 (NCH_3), 33.2 (NCH_3), 54.2 (*C*CH$_3$), 88.9 (NCH), 89.4 (OC), 112.5, 119.0, 126.9, 127.5, 132.8, 133.3, 146.5, 147.6, 152.3 (NCON), 169.5 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 2228 s, 1716 s, 1676 s, 842 s cm^{-1}. TOFMS (CI) calcd. for (M + 1)$^+$ $C_{22}H_{19}N_4O_3$: 387.1457, found 387.1459.

(*Z*)-8,8-Bis(4-cyanophenyl)-2,4-dimethyl-7-oxa-2,4-diazabicyclo-[4.2.0]octane-3,5-dione (4g) and (*Z*)-7,7-Bis(4-cyanophenyl)-2,4-dimethyl-8-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (5g): A deaerated acetonitrile solution (10 mL) of DMU (0.14 g, 1 mmol) and **1g** (0.46 g, 2 mmol) was irradiated for 10 h. The solvent in the reaction mixture was removed in vacuo. Elution of the residual material over silica with petroleum ether/EtOAc, 4:1 and 3:1, gave successively **5g** (0.04 g, 11%) and **4g** (0.06 g, 16%) as white crystals. **4g**: R_f = 0.07 (EtOAc/cyclohexane, 1:2); m.p. 119–120 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.00 (s, 3 H, NCH_3), 3.08 (s, 3 H, NCH_3), 4.94 (d, J = 8.8 Hz, 1 H, NCH), 5.24 (d, J = 8.8 Hz, 1 H, OCH), 7.46 (d, J = 8.2 Hz, 2 H, $H_{benzene}$), 7.54 (d, J = 8.2 Hz, 2 H, $H_{benzene}$), 7.68 (d, J = 8.2 Hz, 2 H, $H_{benzene}$), 7.76 (d, J = 8.2 Hz, 2 H, $H_{benzene}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.6 (NCH_3), 35.9 (NCH_3), 61.2 (NCH), 71.2 (OCH), 95.1 (OC), 113.0, 113.2, 117.9, 118.0, 125.8, 126.6, 132.6, 133.0, 143.0, 147.0, 151.4 (NCON), 166.2 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 2228 s, 1718 s, 1664 s, 834 m, 746 m cm^{-1}. TOFMS (EI) calcd. for (M)$^+$ $C_{21}H_{16}N_4O_3$: 372.1222, found: 372.1221. **5g**: R_f = 0.19 (EtOAc/cyclohexane, 1:2); m.p. 161–162 °C. ^{1}H NMR (300 MHz, $(CD_3)_2CO$, TMS): δ = 2.74 (s, 3 H, NCH_3), 3.16 (s, 3 H, NCH_3), 4.88 (d, J = 7.3 Hz, 1 H, CHC), 5.88 (d, J = 7.3 Hz, 1 H, NCH), 7.57–7.94 (m, 8 H) ppm. ^{13}C NMR (75 MHz, $(CD_3)_2CO$): δ = 27.3 (NCH_3), 33.3 (NCH_3), 51.1 (CH), 83.1 (NCH), 87.6, 112.9, 118.9, 127.4, 127.6, 132.9, 133.5, 146.2, 149.7, 152.3 (NCON), 165.9 (N*C*OC) ppm. IR (KBr): $\tilde{\nu}$ = 2231 s, 1719 s, 1672 s, 831 m cm^{-1}. TOFMS (EI) calcd. for (M)$^+$ $C_{21}H_{16}N_4O_3$: 372.1222, found: 372.1223.

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