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# Regioselectivity and Competition of the Paternò–Büchi Reaction and Triplet–Triplet Energy Transfer between Triplet Benzophenones and Pyrimidines: Control by Triplet Energy Levels

Xiu-Ling Liu, Jian-Bo Wang, Yao Tong, and Qin-Hua Song\*<sup>[a]</sup>

**Abstract:** The photochemical reaction of a pyrimidine and a ketone occurs either as a Paternò–Büchi (PB) reaction or as energy transfer (ET) from the triplet ketone to the pyrimidine. It is rare for the two types of reactions to occur concurrently, and their competitive mechanism remains unknown. In this work, two classes of products, regioisomeric oxetane(s) (**2**, **3**) from a PB reaction and three isomeric dimers of 5-fluoro-1,3-dimethyl uracil (FDMU) (**4**–**6**) from a photosensitized dimerization of FDMU, are obtained through the UV irradiation of FDMU with various benzophenones (BPs). The ratio of the two products (oxetanes to dimers) reveals that the two competitive reactions depend strongly on the triplet energy levels ( $E_T$ ) of the BPs. The BPs with higher  $E_T$  values lead to

higher proportions of dimers, whereas those with lower  $E_T$  values give higher proportions of oxetane(s), with the generation of just two regioisomeric oxetanes for the BP with the lowest  $E_T$  of the eight BPs investigated. The ratio of the two oxetanes (**2**:**3**) decreases with the BP  $E_T$  value. The competitive mechanism for the two types of photochemical reactions is demonstrated through quenching experiments and investigation of temperature effects. Kinetic analysis shows that the rate constants of the two [2+2] photocycloadditions are comparable. Furthermore, in combination with the results of previ-

ous studies, we have gained insight into the dependence of the photochemical type and the regioselectivity in the PB reaction on the triplet energy gaps ( $\Delta E$ ) between the pyrimidines and ketones. For ketones with higher  $E_T$  values than the pyrimidines, the photochemical reaction is a photosensitized dimerization of the pyrimidine. In the opposite case, a PB reaction occurs, and the lower the  $E_T$  of the ketones, the lower the ratio of oxetanes (**2**:**3**). When the  $E_T$  of values of the ketones are close to those of the pyrimidines, the two reactions occur concurrently, and the higher the  $E_T$  of the ketones, the higher the proportion of the dimers. The ratio of oxetanes (**2**:**3**) decreases with the  $E_T$  value of the BPs.

**Keywords:** cycloaddition • energy transfer • kinetics • photochemistry • reaction mechanisms

## Introduction

The far-UV component (UV 280–320 nm) of solar light has mutagenic, carcinogenic, and lethal effects on living organisms. DNA is the most significant cellular target for far-UV light. The two major DNA lesions are the cyclobutane pyrimidine dimers (CPDs), which are in *cis-syn* form for double-stranded DNA (as well as *trans-syn* forms to a much lesser extent for single-stranded DNA), and pyrimidine (6-4) pyrimidone photoproducts in dipyrimidine sequences of double-stranded DNA. These two photoproducts are responsible for the harmful effects of UV radiation on organisms, such as growth delay, mutagenesis, and killing, and constitute 70–80 % and 20–30 % of the total photoproducts,

respectively.<sup>[1]</sup> Taking thymine (T) as an example, the (6-4) photoproducts are derived from an oxetane intermediate formed through the Paternò–Büchi (PB) reaction of the C4 carbonyl of the 3' thymine across the 5,6-double bond of the 5' thymine. The oxetane undergoes ring opening through C4–O bond cleavage accompanied by a proton shift from N3 to generate the observed (6-4) photoproduct (Figure 1).<sup>[2]</sup>

The two types of [2+2] photocycloadditions can be observed in simple systems containing pyrimidines and ketones. In the presence of acetone, only CPDs from photosensitized dimerization were observed (except for cytosine and uracil),<sup>[3]</sup> and in the presence of benzophenones, only oxetanes from the PB reaction through a triplet pathway were observed for monomeric pyrimidines<sup>[4]</sup> except for high-concentration thymidine (Thd).<sup>[5]</sup> However, in the presence of acetone or benzophenones, only CPDs in DNA were observed owing to the low triplet energy level of thymine in DNA of approximately 267 kJ mol<sup>−1</sup>.<sup>[6]</sup>

In our previous papers,<sup>[4]</sup> we reported that the photochemical reactions of various uracils including 1,3-dimethyluracil (DMU), 1,3-dimethylthymine (DMT), and 1,3,6-trimethylthymine (TMT) with various 4,4'-substituted benzophenones

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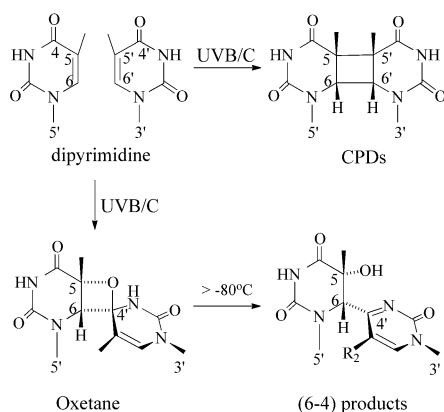
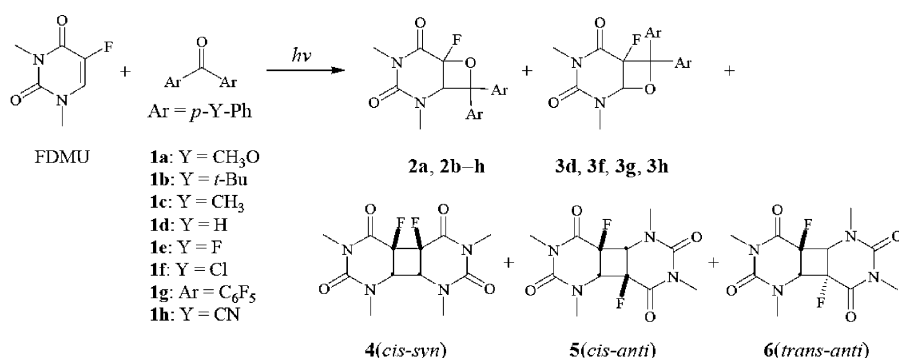


Figure 1. Formation of the two major photoproducts in DNA under UV light (CPDs and (6-4) photoproducts) using thymine as an example.

(BPs) generate two regioisomeric oxetanes through the PB reaction, and no CPDs from the photosensitized dimerization are formed. The regioselectivity of the PB reaction depends on the substituents of the 4,4'-sites on the BPs<sup>[4]</sup> and 5,6-sites on the pyrimidines.<sup>[4b,e]</sup> For example, the electronic properties of the substituents on the BPs influence the regioselectivity strongly, that is, BPs with electron-donating groups give a higher proportion of *head-to-head* (i.e., 2-type in the text) oxetanes, whereas BPs with electron-withdrawing groups lead to a higher proportion of *head-to-tail* (i.e., 3-type) oxetanes. In this work, we observed a competition of the PB reaction with triplet energy transfer (ET) in the photochemical reactions of 5-fluoro-1,3-dimethyluracil (FDMU) and eight BPs (**1a–h**). Some new insights into two types of [2+2] photocycloadditions were gained from the photochemical reactions of FDMU and BPs.

## Results and Discussion

**Photoproducts and reaction pathways:** Ultraviolet irradiation of FDMU and various BPs (**1a–h**) dissolved in acetonitrile in a Pyrex reactor with a high-pressure mercury arc yielded two classes of photoproducts: regioisomeric oxetanes (**2**, **3**) and three isomeric dimers of FDMU (**4–6**), as shown in Scheme 1. Most of the photoproducts were well



Scheme 1. Photochemical reactions of FDMU and BPs.

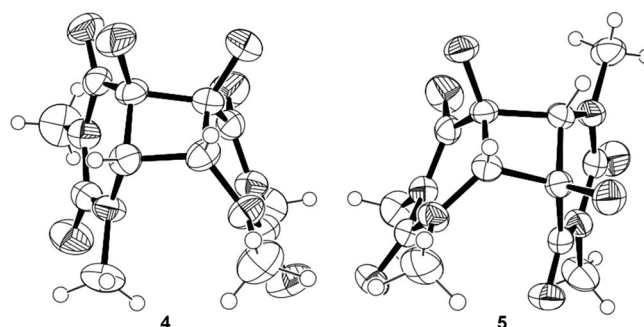
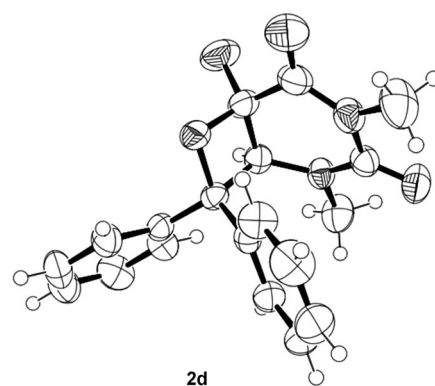
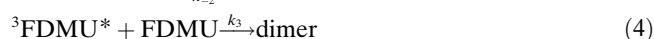


Figure 2. X-ray crystal structures of **2d**, **4**, and **5**. ORTEP plots of the molecular structures. Displacement ellipsoids are shown at the 50% probability level.

characterized by NMR and HRMS, and crystal data of **2d**, **4**, and **5** were obtained (Figure 2). Photoproducts **2a** and **3d**, **3f**, and **3g** were observed through <sup>1</sup>H NMR spectroscopy of the crude product mixtures, but were not isolated because of their very low yields and instability.<sup>[4b]</sup>

The two classes of photoproducts may be derived from two types of [2+2] photocycloadditions: the PB reaction and photosensitized dimerization. The oxetanes (**2**, **3**) come from the PB reaction between triplet BPs and FDMU, and the dimers of FDMU (**4–6**) may result from the [2+2] cycloaddition between a triplet FDMU and a ground-state FDMU. The formation of the triplet FDMU should undergo a triplet–triplet (T–T) excitation energy transfer from triplet BPs to FDMU. Thus, the formation of dimers allows the estimation of the efficiency of the ET process. The crystal structures of **4** and **5** and the NMR data of **4–6** show that the FDMU dimers **4**, **5**, and **6** have the *cis-syn*, *cis-anti*, and *trans-anti* forms, respectively; the *trans-syn* isomer was not obtained, possibly owing to its low yield. Previous studies<sup>[7,8]</sup> also showed that the *trans-syn* form accounted for the smallest isomer proportion among the four dimers in the photosensitized dimerization of DMT.

As confirmation of the formation pathway of the FDMU dimers, a control experiment involving direct irradiation of FDMU in acetonitrile without BPs was performed, and no photoproduct was observed after irradiation for a prolonged time. Hence, the [2+2] photocycloaddition cannot occur through the direct excitation of FDMU owing to the very short lifetime and low intersystem crossing efficiency ( $\Phi_{ISC}$ ) of the singlet excited state of FDMU. In other words, the formation of FDMU dimers cannot follow the singlet pathway, that is, the [2+2] cycloaddition of a singlet excited state of FDMU and its ground-state molecule. Thus, the formation of FDMU dimers should occur through photosensitized dimerization along a triplet pathway. Therefore, several essential processes in photochemical systems of FDMU and BPs can be identified, as illustrated by Equations (1)–(4).



The Paternò–Büchi reaction, which is a well-studied photochemical reaction,<sup>[9]</sup> is usually accompanied by hydrogen abstraction by the triplet ketone from the olefin or electron transfer from the olefin to the triplet ketone, and triplet energy transfer from the triplet ketone to the olefin. In acetone–olefin reaction systems, acetone can act as a partner in the PB reaction, and also as a photosensitizer that sensitizes the dimerization<sup>[10]</sup> or *cis–trans* isomerization<sup>[11]</sup> of olefins.

Banlrop and Carless<sup>[10]</sup> reported photochemical reactions of acetone with electron-deficient olefins and dienes. Besides the photocycloaddition of acetone to olefins leading to oxetanes through a singlet pathway, the photosensitized dimerization of olefins also occurs through an excitation energy transfer from triplet acetone to the olefin.<sup>[10]</sup> In addition, the reactions of excited acetone with olefins can lead to cycloaddition to oxetane and *cis–trans* isomerization of olefins via a 1,4-biradical intermediate<sup>[11a]</sup> or through triplet energy transfer.<sup>[11b]</sup> These studies focused on the mechanisms of the photocycloaddition and *cis–trans* isomerization between excited acetone and olefins, but no attention was paid to the factors controlling these competitive reactions, that is, the PB reaction versus sensitized dimerization and the PB reaction versus *cis–trans* isomerization, and their kinetics.

In our previous papers,<sup>[4]</sup> we reported single PB reactions between BPs with 5,6-substituted pyrimidines including DMU, DMT, thymidine (Thd), and TMT, except for a few cases involving electron transfer or hydrogen abstraction. For example, non-oxetane products from the **1h**–DMT and **1h**–TMT systems were observed besides oxetanes. Herein, two photochemical reactions, both the PB reaction and sensitized dimerization following a triplet pathway, occur concurrently in the photochemical systems of FDMU and BPs.

These excellent systems allow the investigation of the competition between the PB reaction and triplet energy transfer.

**Photochemical reactions and triplet energy levels:** To investigate the relationship of the photochemical reactions with the triplet energy levels of the BPs, we measured the ratio of two photoproducts, oxetanes and dimers, from the photochemical reactions of FDMU with various BPs in CD<sub>3</sub>CN, by using <sup>1</sup>H NMR spectroscopy. As one example, <sup>1</sup>H NMR spectra of **1f**–FDMU solutions before and after irradiation are shown in Figure 3. From these spectra of the crude prod-

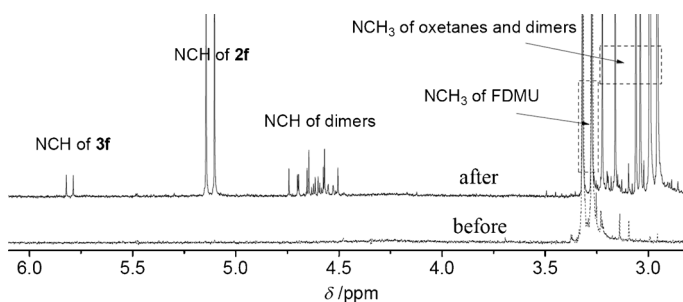


Figure 3. <sup>1</sup>H NMR spectra of **1f**–FDMU (15 mm:15 mm) acetonitrile solution before and after irradiation.

uct mixtures from photochemical reactions, the yields and ratios of oxetane(s) to dimers were obtained on the basis of the peak area of NCH<sub>3</sub> or NCH of oxetane(s) and dimers, and are listed in Table 1. As shown in Table 1, the ratio of

Table 1. The photochemical reactions of FDMU and BPs in acetonitrile; ratios of photoproducts and triplet energy levels of BPs.<sup>[a]</sup>

BPs, Y	Oxetane(2:3):dimer	Yield [%]	$E_T$ [kJ mol <sup>-1</sup> ] <sup>[b]</sup>
<b>1a</b> , CH <sub>3</sub> O	31(100:0):69	53	293/292/291
<b>1b</b> , <i>t</i> Bu	62(100:0):38	49	290/–/295
<b>1c</b> , CH <sub>3</sub>	51(100:0):49	55	288/290/291
<b>1d</b> , H	56(>98:2):44	42	287/289/288
<b>1e</b> , F	52(100:0):48	43	294/294/293
<b>1f</b> , Cl	75(96:4):25	49	285/286/286
<b>1g</b> , C <sub>6</sub> F <sub>5</sub> <sup>[c]</sup>	92(95:5):8	39	282/292/291
<b>1h</b> , CN	100(91:9):0	60	–/276/276

[a] FDMT/BPs = 10 mm:10 mm, acetonitrile solution, 125 W high-pressure Hg lamp, 15 min, unless other indicated. Average of two measurements, from <sup>1</sup>H NMR (300 MHz) directly on the crude product mixture; experimental error within 5%. [b]  $E_T(n)/E_T(p)/E_T(\text{ethanol})$ , the former two values from nonpolar and polar solvents,<sup>[13]</sup> and the latter from ethanol solution at 77 K in this work. [c] Reaction time = 60 min.

products (oxetanes to dimers) depends on the triplet energy levels of the BPs. On the whole, with decreasing triplet energy level, the ratio of oxetane/dimer increases. The ratio value (31:69) from **1a**–FDMU is lower than the expected value. This may be because **2a** decomposes partially to its starting materials owing to its instability. In the case of **1h** with the lowest triplet energy level (276 kJ mol<sup>-1</sup>), only PB products (**2h**, **3h**) were observed (Figure S1, Supporting Information),<sup>[12]</sup> and the ratio of **2h/3h** is 91:9. Another exam-

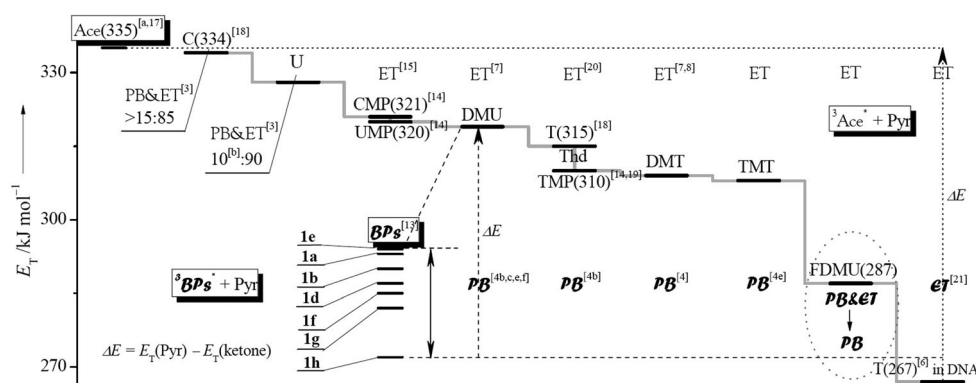


Figure 4. Dependence of photochemical types (PB, ET) of triplet ketones with pyrimidines on their triplet energy gaps ( $\Delta E$ ). [a] Values in brackets are triplet energies; unit:  $\text{kJ mol}^{-1}$ . [b] 2-type oxetane > 90 %.

ple, **1g**, with a lower triplet energy level, gave regioisomeric oxetanes 95:5 (**2g/3g**) besides the dimers. For other BPs with lower triplet energy levels, two regioisomeric oxetanes were observed, for instance, **2f/3f** = 96:4 for **1f** and **2d/3d** > 98:2 for **1d**. In the system of FDMU and BPs with higher triplet energy levels (**1a–c** and **1e**), only 2-type oxetanes were observed besides the dimers. The regioselectivity (**2:3**) is in agreement with the previous observation,<sup>[4b–f]</sup> that is, that BPs with higher triplet energy levels lead to higher proportions of 2-type oxetanes in the PB reactions with various 5,6-substituted uracils.

With a very low triplet energy level ( $253 \text{ kJ mol}^{-1}$ ), 4-phenylbenzophenone can react with DMT only through the PB process to yield a single 3-type oxetane.<sup>[4d]</sup> This result supports the above conclusion about the photochemical types and the regioselectivity in the PB reaction.

With acetone used as a photosensitizer, the triplet energy level of FDMU was obtained as  $287 \text{ kJ mol}^{-1}$  from its phosphorescence spectrum in ethanol at 77 K (Figure S2, Supporting Information). This energy level is much lower than those of UMP ( $321 \text{ kJ mol}^{-1}$ )<sup>[14]</sup> and TMP ( $310 \text{ kJ mol}^{-1}$ ).<sup>[14]</sup> Although there are no available data on the triplet energy levels of some pyrimidines, their relative levels can be inferred on the basis of reported experimental<sup>[15]</sup> and theoretical<sup>[16]</sup> studies. Figure 4 shows the triplet energy levels of pyrimidines and ketones, as well as their photochemical reaction types and product ratios. When the triplet energy levels of the ketones ( $E_T(\text{ketone})$ ) are much higher than those of the pyrimidines ( $E_T(\text{Pyr})$ ), that is,  $\Delta E (= E_T(\text{Pyr}) - E_T(\text{ketone}))$  is a large negative value, their photochemical process is single sensitized dimerization through T–T energy transfer from triplet ketones to pyrimidines. On the contra-

ry, if  $\Delta E$  is a large positive value, the photochemical reaction is the PB reaction, and the ratios of the two oxetanes (**2:3**) increase with the triplet energy levels of the pyrimidines<sup>[4e]</sup> or with the decreasing triplet energy levels of the BPs.<sup>[4b–f]</sup> When their energy levels are close, that is,  $\Delta E$  is small, such as in the cytosine- and uracil–acetone systems<sup>[3]</sup> and FDMU–BPs systems, the two types of reactions (PB and ET) occur concurrently. The proportion of dimers increases with the triplet energy levels. In addition, uracil (U) with a lower  $E_T$  generates a higher proportion of dimers than cytosine (C) for the two acetone–pyrimidine systems.<sup>[3]</sup> In this situation, major or exclusive regioisomeric 2-type oxetanes are observed for both acetone systems and BP–FDMU systems, and the ratio of the two oxetanes (**2:3**) decreases with the  $E_T$  values of the BPs. These results are summarized in Table 2. Clearly, the relative triplet energy gaps determine the photochemical reaction type, that is, the PB reaction or ET. However, the two ways of increasing the energy gap (by increasing the ET of pyrimidines or by decreasing of BPs) lead to different changes in the ratio of **2:3**. The regioselectivity in PB reactions between 5,6-substituted pyrimidine and 4,4'-substituted BPs was discussed in terms of the stability<sup>[4a,c]</sup> and formation rate<sup>[4e]</sup> of two regioisomeric biradicals from theoretical studies in our previous papers.

**Quenching experiments:** For further investigation of this pair of competition reactions, quenching experiments were performed with the photochemical reactions of three BPs (**1a**, **1d**, and **1f**) in the presence of different concentrations of FDMU in  $\text{CD}_3\text{CN}$ . Under the same irradiation conditions, the crude product mixtures were analyzed by  $^1\text{H}$  NMR spectroscopy. The data show that with increasing concentration

Table 2. Dependence of the photoproducts on triplet energy gaps ( $\Delta E$ ) between pyrimidines and ketones.

Sign of $\Delta E$ <sup>[a]</sup>	Reaction type	Change in product ratios with increasing $\Delta E$
+	PB	1) <b>2:3</b> increases with increasing $E_T(\text{Pyr})$ <sup>[4e]</sup> 2) <b>2:3</b> decreases with decreasing $E_T(\text{BPs})$ <sup>[4b,c,e]</sup>
±	PB & ET	1) increase in ratio of oxetane/dimer (O/D) and decrease in <b>2:3</b> with decreasing $E_T(\text{BPs})$ 2) increase in O/D with increasing $E_T(\text{Pyr})$ <sup>[3]</sup>
–	ET	Only dimers

[a]  $\Delta E = E_T(\text{Pyr}) - E_T(\text{ketone})$ .

of FDMU, the concentration of dimers increases uniformly and rapidly for all three BPs, but not for the oxetanes. Hence, the ratio of oxetanes to dimers (O/D) decreases gradually. As an example, the analysis data of the crude reaction mixture of **1a** in the presence of different concentrations of FDMU are listed in Table 3. The analysis data for the other two systems are listed in Tables S1 and S2 in the Supporting information.

Table 3. Analysis data of the crude reaction mixture of **1a** with different concentrations of FDMU.<sup>[a]</sup>

Entry	[ <b>1a</b> ]	[FDMU]	[oxetane]	[dimer]	O:D <sup>[b]</sup>
1	14.12	1.57	0.72	0.90	44:56
2	13.60	2.41	1.09	2.10	34:66
3	13.39	3.70	1.38	3.80	26:74
4	13.67	6.79	1.19	4.91	19:81
5	13.40	7.37	1.46	7.09	17:83
6	13.70	13.3	1.03	7.82	12:88

[a] [**1a**] = 15 mM, [FDMU] = 5–30 mM, 125 W high-pressure Hg lamp, 10 min, 10 °C. [b] O:D = oxetane/dimers.

Equations (1)–(4) can explain the above data. Two photochemical reactions follow the triplet pathway: the PB reaction of triplet BPs with FDMU, and photosensitized dimerization induced by triplet BPs. The equations lead to the expression given by Equation (5).

$$\frac{[\text{oxetane}]}{[\text{dimer}]} = \frac{1}{K} \frac{k_1}{k_3} \frac{[\text{BPs}]}{[\text{FDMU}]} + \frac{k_1}{k_{+2}} \quad (5)$$

Clearly, the product ratio [oxetane]/[dimer] depends on the ratio of the reactants [BPs]/[FDMU]. Because the ratio of reactants is changing through the two photochemical processes, the ratio of products will be different at different irradiation times (see irradiation-time effects in Supporting Information). According to Equation (5), the analysis data are plotted as the concentration ratios of [oxetane]/[dimer] versus [BPs]/[FDMU], as shown in Figure 5. The linear fits show good linear relationships, with  $R > 0.99$ , between the two pairs of concentration ratios of products and reactants, and their slopes ( $k_1/(Kk_3)$ ) and intercepts ( $k_1/k_{+2}$ ) are listed

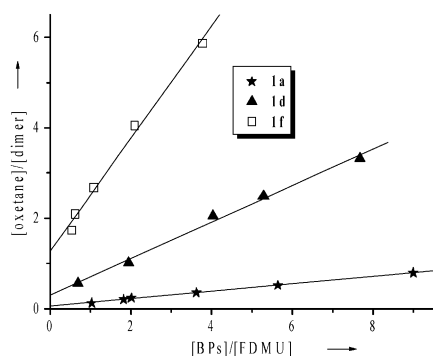


Figure 5. Plots of [oxetane]/[dimer] versus [BPs]/[FDMU] from quenching experiments.

Table 4. Parameters obtained from fitting straight lines of Figure 5.

BPs	$k_1/(Kk_3)$	$k_1/k_{+2}$	R	$K^{[a]}$	$k_1/k_3^{[b]}$
<b>1a</b>	0.082	0.059	0.999	8.40	0.69
<b>1d</b>	0.402	0.311	0.997	2.34	0.94
<b>1f</b>	1.242	1.277	0.996	0.65	0.81

[a] From Eq. (7) at 283 K. [b] From calculated  $K$  values and the slopes.

in Table 4. This implies that the mechanism proposed in Equations (1)–(4) is reasonable.

In a T–T energy-transfer process, the energy-transfer rate constant ( $k_{ET}$ ) between the BPs (donor) and FDMU (acceptor) depends on the energy gap ( $\Delta E$ ), as shown by Sandos' equation [Eqs. (6) and (7)],<sup>[22]</sup> in which  $k_D$  is the diffusion rate constant in liquid solutions, and  $\Delta E$  is the gap of triplet energies between an energy acceptor and a donor.

$$k_{ET} = k_D (e^{-\Delta E/RT} + 1)^{-1} \quad (6)$$

$$\Delta E = -RT \ln K \quad (7)$$

From Equation (6), a large energy gap of donor over acceptor would result in a fast  $k_{ET}$  (i.e.,  $k_{+2}$ ). According to Equation (7), the BPs with higher  $E_T$  values give higher  $K$  values for the ET process; the calculated values for  $T = 283$  K are listed in Table 4, and are supported by experiment results. With increasing  $E_T$  of BPs, both the slopes ( $k_1/(Kk_3)$ ) and intercepts ( $k_1/k_{+2}$ ) of the straight lines decrease, possibly owing to the increase in  $K$  and  $k_{+2}$  values.

On the basis of the slopes and calculated  $K$  values, the  $k_1/k_3$  values were obtained. As shown in Table 4,  $k_1$  and  $k_3$  are of the same order of magnitude; in other words, the two different types of [2+2] photocycloadditions have comparable rate constants.

**Temperature effects:** For the investigation of the effects of temperature on the two types of photochemical reactions, three BPs (**1d**, **1e**, and **1f**) were reacted with FDMU in  $\text{CD}_3\text{CN}$  at different temperatures ranging from  $-30$  to  $50$  °C. The ratios of the photoproducts (oxetane/dimer) were measured, and are listed in Table 5. With increasing reaction temperature, the proportion of oxetanes decreases and the proportion of dimers increases for all three systems. In other words, a high temperature is favorable for the photosensi-

Table 5. Temperature effects on photochemical reactions of FDMU and three BPs.<sup>[a]</sup>

$T$ [°C]	<b>1f</b>		<b>1d</b>		<b>1e</b>	
	O:D <sup>[b]</sup>	Yield [%]	O:D	Yield [%]	O:D	Yield [%]
$-30$	79:21	20.1	62:38	17.0	54:46	19.7
$-10$	75:25	15.3	54:46	13.5	44:56	11.9
10	73:27	22.0	48:52	19.7	39:61	18.8
30	70:30	25.0	44:56	20.4	36:64	15.7
50	51:49	44.7	42:58	13.1	33:67	13.3

[a] FDMT/BPs = 10 mm:10 mm, 125 W high-pressure Hg lamp, 10 min. [b] O:D = oxetane/dimers; no detectable **3** owing to very low concentration.



tized dimerization, but not for the PB reaction. This is easy to understand from the results. The formation of ET products occurs through two bimolecular reactions [Eqs. (3) and (4)], but only one occurs for the PB reaction [Eq. (2)]. Hence, a high viscosity of the reaction system at a low temperature would suppress the molecular diffusion to slow the intermolecular reaction. In addition, a high reaction temperature is unfavorable for the ring-closing of biradicals to form oxetanes.<sup>[4a,c,f]</sup>

In terms of Equation (7), if  $\Delta E \geq 11 \text{ kJ mol}^{-1}$  at 283 K, the equilibrium constant,  $K(=k_{+2}/k_{-2}) \leq 0.01$ , and the energy transfer can be negligible. In the case of **1h**, with the lowest  $E_T$  among the BPs, no dimer from energy transfer was observed. This implies that the  $E_T$  value of FDMU is at least  $11 \text{ kJ mol}^{-1}$  higher than that ( $276 \text{ kJ mol}^{-1}$ ) of **1h** (i.e.,  $E_T \geq 287 \text{ kJ mol}^{-1}$ ), which matches the experimental value for <sup>3</sup>FDMU\*.

## Conclusion

In summary, two photochemical reactions, the PB reaction and triplet energy transfer (ET), were observed in systems of FDMU and various 4,4'-substituted benzophenones (BPs). These competition reactions are controlled by the triplet energy levels of the BPs, that is, a high  $E_T$  is favorable for ET and a low  $E_T$  favors the PB reaction. The regioselectivity (**2:3**) also depends on the  $E_T$  values of the BPs, that is, BPs with lower  $E_T$  give lower ratios of **2** to **3**. Besides the triplet energy levels, the influence of external causes (including the ratio of reactants and the temperature) on these competition reactions was demonstrated through experiments on quenching and temperature effects. The kinetic analysis showed that the rate constants of the two [2+2] photocycloadditions are comparable. Furthermore, a picture of the photochemical reaction types and the regioselectivity in the PB reaction versus the triplet energy levels was obtained. The picture shows that the triplet energy gaps between the pyrimidines and ketones control the photochemical types. When the triplet energy level of a ketone is much higher than that of a pyrimidine, their photochemical reaction is ET. In the opposite case, the PB reaction prevails. The two reactions occur concurrently when the triplet energy levels are close.

## Experimental Section

**Materials and general methods:** 5-Fluoro-1,3-dimethyluracil (FDMU) was prepared with 5-fluorouracil according to the literature procedure.<sup>[23]</sup> 4,4'-Dimethoxybenzophenone (**1a**), 4,4'-di-tert-butylbenzophenone, 4,4'-dichlorobenzophenone, and 4,4'-dicyanobenzophenone were prepared through routine 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.

Melting points were uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV spectrometer (300 MHz for <sup>1</sup>H, 75 MHz for <sup>13</sup>C). FTIR spectra were obtained on a Bruker Vector22 infrared spectrometer. UV/

Vis absorption spectra were recorded at room temperature with a Shimadzu UV-2401PC UV/Vis absorption spectrometer. Mass spectra were obtained with a Micromass GCF time-of-flight (TOF) mass spectrometer. X-ray diffraction data were collected at 290(2) K on a Gemini S Ultra CCD diffractometer (Oxford diffraction Ltd.) equipped with MoK $\alpha$  monochromated radiation ( $\lambda = 0.71073 \text{ \AA}$ ).

**Irradiation and photoproduct assay:** The photochemical reactions of FDMU with BPs were performed in [D<sub>3</sub>]acetonitrile. The solution of reactants was placed in a Pyrex NMR tube (transmitted light > 290 nm), and bubbled with high-purity N<sub>2</sub> for 15 min, then irradiated with a 125 W high-pressure Hg lamp. The sample tubes were placed on merry-go-round equipment moving around the Hg lamp. Photoproducts **2**, **3**, **4**, **5**, and **6** have no significant absorption for the light at above 290 nm. Hence, a secondary photolysis of these photoproducts would not occur without prolonged irradiation. Photoproduct assay was performed directly on the crude product mixture through <sup>1</sup>H NMR spectroscopy (300 MHz) on the basis of the peak areas of NCH and NCH<sub>3</sub> for the oxetane(s) and dimers.

**Measurements of triplet energy levels:** BPs were dissolved in ethanol, and FDMU was dissolved in the ethanol solution containing acetone (0.1 M). The FDMU solution in a quartz tube was degassed through three freeze-pump-thaw cycles. The sample solutions were placed in a quartz tube, and measured with low-temperature equipment on a Perkin–Elmer LS55 luminescence spectrometer at 77 K.

**General procedure for preparative photolysis reactions:** Under a nitrogen atmosphere, an acetonitrile solution of FDMU (100 mm) and benzophenone derivatives (200 mm) was placed in a Pyrex reactor (transmitted light > 290 nm), bubbled for 15 min with high-purity nitrogen, sealed, and irradiated with a 300 W high-pressure Hg lamp for 3–5 h. The solvent in the reaction mixture was removed in vacuo, and the residual material was subjected to flash chromatography with silica-H gel as absorbent. The photoproducts **2**, **3**, **4**, **5**, and **6** were obtained.

**Crystal structure data:** CCDC-791437 (**2d**), CCDC-791439 (**4**), and CCDC-791438 (**5**) 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](http://www.ccdc.cam.ac.uk/data_request/cif).

**X-ray crystal structure data of 2d:** Colorless needles; C<sub>19</sub>H<sub>17</sub>FN<sub>2</sub>O<sub>3</sub>,  $M_r = 340.35$ ; monoclinic; space group *Pbca*;  $\rho_{\text{calcd}} = 1.348 \text{ g cm}^{-3}$ ;  $Z = 4$ ;  $a = 12.5372(18)$ ,  $b = 8.6128(16)$ ,  $c = 16.238(2) \text{ \AA}$ ;  $\beta = 106.972(2)^\circ$ ;  $V = 1677.0(5) \text{ \AA}^3$ ;  $T = 298(2) \text{ K}$ ;  $\mu(\text{MoK}\alpha) = 0.100 \text{ mm}^{-1}$ ; 8138 reflections collected, 2957 unique ( $R_{\text{int}} = 0.0310$ );  $R_1 = 0.0381$ ,  $wR_2 = 0.1027$  [ $I > 2\sigma(I)$ ].

**X-ray crystal structure data of 4:** Colorless needles; C<sub>12</sub>H<sub>14</sub>F<sub>2</sub>N<sub>4</sub>O<sub>4</sub>,  $M_r = 316.27$ ; orthorhombic; space group *Pbca*;  $\rho_{\text{calcd}} = 1.522 \text{ g cm}^{-3}$ ;  $Z = 8$ ;  $a = 7.8072(10)$ ,  $b = 13.9458(14)$ ,  $c = 25.356(2) \text{ \AA}$ ;  $\beta = 90.00^\circ$ ;  $V = 2760.7(5) \text{ \AA}^3$ ;  $T = 298(2) \text{ K}$ ;  $\mu(\text{MoK}\alpha) = 0.133 \text{ mm}^{-1}$ ; 12858 reflections collected, 2434 unique ( $R_{\text{int}} = 0.0453$ );  $R_1 = 0.0447$ ,  $wR_2 = 0.1283$  [ $I > 2\sigma(I)$ ].

**X-ray crystal structure data of 5:** Colorless needles; C<sub>12</sub>H<sub>14</sub>F<sub>2</sub>N<sub>4</sub>O<sub>4</sub>,  $M_r = 316.27$ ; orthorhombic; space group *Pbca*;  $\rho_{\text{calcd}} = 1.554 \text{ g cm}^{-3}$ ;  $Z = 8$ ;  $a = 14.4986(14)$ ,  $b = 12.6769(11)$ ,  $c = 14.7086(15) \text{ \AA}$ ;  $\beta = 90.00^\circ$ ;  $V = 2703.4(5) \text{ \AA}^3$ ;  $T = 298(2) \text{ K}$ ;  $\mu(\text{MoK}\alpha) = 0.136 \text{ mm}^{-1}$ ; 10979 reflections collected, 2383 unique ( $R_{\text{int}} = 0.0295$ );  $R_1 = 0.0365$ ,  $wR_2 = 0.1066$  [ $I > 2\sigma(I)$ ].

### Characterization data

**4a,4b-Difluoro-1,3,6,8-tetramethyl-hexahydro-1,3,6,8-tetraaza-biphenylene-2,4,5,7-tetraone (4):**  $R_f = 0.18$  (ethyl acetate/petroleum ether 1:2); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 3.08$  (s, 6H, NCH<sub>3</sub>), 3.18 (s, 6H, NCH<sub>3</sub>), 4.38–4.48 ppm (m, 2H, CH); TOFMS(CI) calcd for C<sub>12</sub>H<sub>15</sub>N<sub>4</sub>O<sub>4</sub>F<sub>2</sub> [ $M+H$ ]<sup>+</sup>: 317.1061; found: 317.1069.

**4a,8a-Difluoro-1,3,5,7-tetramethyl-tetrahydro-1,3,5,7-tetraaza-biphenylene-2,4,6,8-tetraone (5):**  $R_f = 0.57$  (ethyl acetate/petroleum ether = 1:2); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 3.12$  (s, 6H, NCH<sub>3</sub>), 3.24 (s, 6H, NCH<sub>3</sub>), 4.33 ppm (dd, <sup>3</sup>J<sub>(H,H)</sub> = 18 Hz, <sup>3</sup>J<sub>(H,H)</sub> = 16 Hz, 2H, CH); TOFMS(CI) calcd for C<sub>12</sub>H<sub>15</sub>N<sub>4</sub>O<sub>4</sub>F<sub>2</sub> [ $M+H$ ]<sup>+</sup>: 317.1061; found: 317.1065.

**4a,8a-Difluoro-1,3,5,7-tetramethyl-tetrahydro-1,3,5,7-tetraaza-biphenylene-2,4,6,8-tetraone (6):**  $R_f = 0.57$  (ethyl acetate/petroleum ether = 1:2); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 3.14$  (s, 6H, NCH<sub>3</sub>), 3.32 (s, 6H,

NCH<sub>3</sub>), 4.23–4.32 ppm (m, 2H, CH); TOFMS(CI) calcd for C<sub>12</sub>H<sub>15</sub>N<sub>4</sub>O<sub>4</sub>F<sub>2</sub> [M+H]<sup>+</sup>: 317.1061; found: 317.1064.

**8,8-Bis-(4-tert-butylphenyl)-6-fluoro-2,4-dimethyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (2b)**: Yield: 31%; R<sub>f</sub>=0.59 (ethyl acetate/petroleum ether, 2:1); m.p. 122–123°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): δ=1.28 (s, 9H, CH<sub>3</sub>), 1.32 (s, 9H, CH<sub>3</sub>), 2.95 (s, 3H, NCH<sub>3</sub>), 3.03 (s, 3H, NCH<sub>3</sub>), 4.84 (d, <sup>3</sup>J(H,H)=16.5 Hz, 1H, CH), 7.17–7.46 ppm (m, 8H, CH, H<sub>Ar</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS): δ=27.8 (NCH<sub>3</sub>), 31.3 (C(CH<sub>3</sub>)<sub>3</sub>), 34.7 (C(CH<sub>3</sub>)<sub>3</sub>), 35.5 (NCH<sub>3</sub>), 66.4 (CF), 66.7 (CF), 89.2 (NCH), 104.1 (CO), 125.3, 125.4, 125.8, 133.8, 138.9, 150.9, 151.9 (NCON), (162.3, 162.9) ppm (NCOC); IR (Nujol):  $\tilde{\nu}$ =3407 (w), 2963 (s), 2870 (s), 1728 (s), 1693 (s), 1463 (s), 1283 (s), 1053 (s), 937 (s), 757 cm<sup>-1</sup> (m); TOFMS(EI) calcd for C<sub>27</sub>H<sub>33</sub>N<sub>2</sub>O<sub>3</sub>F [M]<sup>+</sup>: 452.2475; found 452.2479.

**6-Fluoro-2,4-dimethyl-8,8-di-p-tolyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (2c)**: Yield: 33%; R<sub>f</sub>=0.42 (ethyl acetate/petroleum ether 2:1); m.p. 127–128°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): δ=2.31 (s, 3H, CH<sub>3</sub>), 2.37 (s, 3H, CH<sub>3</sub>), 2.98 (s, 3H, NCH<sub>3</sub>), 3.04 (s, 3H, NCH<sub>3</sub>), 4.84 (d, <sup>3</sup>J(H,H)=16.5 Hz, 1H, CH), 7.12–7.31 ppm (m, 8H, CH, H<sub>Ar</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS): δ=21.2 (CH<sub>3</sub>), 27.8 (NCH<sub>3</sub>), 35.3 (NCH<sub>3</sub>), 66.0 (CF), 66.3 (CF), 89.7 (NCH), 104.0 (CO), 125.6, 126.0, 129.3, 129.5, 134.1, 138.8, 139.0, 150.9 ppm; IR (Nujol):  $\tilde{\nu}$ =3404 (w), 2956 (w), 1728 (s), 1695 (s), 1464 (m), 1279 (s), 1047 (s), 916 (m), 739 cm<sup>-1</sup> (m); TOFMS(EI) calcd for C<sub>21</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub>F [M]<sup>+</sup>: 368.1536; found: 368.1534.

**6-Fluoro-2,4-dimethyl-8,8-diphenyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (2d)**: Yield: 38%; R<sub>f</sub>=0.35 (ethyl acetate/petroleum ether 2:1); m.p. 123–124°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): δ=3.01 (s, 3H, NCH<sub>3</sub>), 3.03 (s, 3H, NCH<sub>3</sub>), 4.88 (d, <sup>3</sup>J(H,H)=16.5 Hz, 1H, CH), 7.25–7.40 ppm (m, 10H, H<sub>Ar</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS): δ=27.9 (NCH<sub>3</sub>), 35.5 (NCH<sub>3</sub>), 66.1 (CF), 66.4 (CF), 89.5 (NCH), 100.6 (CO), 104.0, 125.5, 125.9, 128.7, 128.8, 128.9, 136.8, 141.7, 150.8 (NCON), (162.2, 162.7) ppm (NCOC); IR (Nujol):  $\tilde{\nu}$ =3400 (w), 3033 (w), 1731 (s), 1691 (s), 1447 (m), 1286 (s), 1057 (s), 916 (m), 745 cm<sup>-1</sup> (m); TOFMS(EI) calcd for C<sub>19</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub>F [M]<sup>+</sup>: 340.1223; found: 340.1216.

**6-Fluoro-8,8-bis-(4-fluorophenyl)-2,4-dimethyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (2e)**: Yield: 35%; R<sub>f</sub>=0.29 (ethyl acetate/petroleum ether 2:1); m.p. 191–192°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): δ=3.01 (s, 3H, NCH<sub>3</sub>), 3.05 (s, 3H, NCH<sub>3</sub>), 4.83 (d, <sup>3</sup>J(H,H)=16.5 Hz, 1H, CH), 7.04–7.41 ppm (m, 8H, H<sub>Ar</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS): δ=27.9 (NCH<sub>3</sub>), 35.4 (NCH<sub>3</sub>), 66.2 (CF), 66.5 (CF), 88.9 (NCH), 100.5 (CO), 103.9, 115.7, 115.9, 116.0, 116.2, 127.6, 127.7, 128.0, 128.1, 132.6, 137.4, 150.7 (NCON), (161.2, 161.9) (NCOC), 162.4, 164.5 ppm; IR (Nujol):  $\tilde{\nu}$ =3409 (w), 3065 (w), 1738 (s), 1686 (s), 1511 (s), 1232 (s), 1051 (m), 921 (m), 745 cm<sup>-1</sup> (m); TOFMS(EI) calcd for C<sub>19</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>F<sub>3</sub> [M]<sup>+</sup>: 376.1035; found: 376.1029.

**8,8-Bis-(4-chlorophenyl)-6-fluoro-2,4-dimethyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (2f)**: Yield: 67%; R<sub>f</sub>=0.36 (ethyl acetate/petroleum ether 2:1); m.p. 118–120°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): δ=3.01 (s, 3H, NCH<sub>3</sub>), 3.05 (s, 3H, NCH<sub>3</sub>), 4.81 (d, <sup>3</sup>J(H,H)=16.2 Hz, 1H, CH), 7.16–7.44 ppm (m, 10H, H<sub>Ar</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS): δ=28.0 (NCH<sub>3</sub>), 35.5 (NCH<sub>3</sub>), 66.2 (CF), 66.5 (CF), 88.7 (NCH), 100.4 (CO), 103.9, 127.0, 127.4, 129.1, 129.3, 135.0, 135.2, 135.4, 139.7, 150.6 ppm; IR (Nujol):  $\tilde{\nu}$ =3398 (w), 2927 (w), 1735 (s), 1689 (s), 1472 (m), 1282 (s), 1092 (s), 928 (m), 747 cm<sup>-1</sup> (m); TOFMS(EI) calcd for C<sub>19</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub>Cl<sub>2</sub>F [M]<sup>+</sup>: 408.0444; found: 408.0447.

**6-Fluoro-2,4-dimethyl-8,8-bis-pentafluorophenyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (2g)**: Yield: 90%; R<sub>f</sub>=0.62 (ethyl acetate/petroleum ether 2:1); m.p. 190–191°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): δ=3.12 (s, 3H, NCH<sub>3</sub>), 3.16 (s, 3H, NCH<sub>3</sub>), 5.50 ppm (d, <sup>3</sup>J(H,H)=16.5 Hz, 1H, CH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS): δ=28.4 (NCH<sub>3</sub>), 36.3 (NCH<sub>3</sub>), 65.3 (CF), 65.7 (CF), 83.2, 88.0, 88.4, 101.7, 105.2, 113.3, 136.5, 136.7, 139.8, 140.6, 142.7, 144.0, 144.4, 146.0, 151.1 (NCON), (160.4, 160.9) ppm (NCOC); IR (Nujol):  $\tilde{\nu}$ =3422 (w), 2924 (w), 1737 (s), 1698 (s), 1499 (s), 1284 (m), 1094 (m), 946 (m), 747 cm<sup>-1</sup> (m); TOFMS(EI) calcd for C<sub>19</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>F<sub>11</sub> [M+H]<sup>+</sup>: 521.0359; found: 521.0362.

**6-Fluoro-8,8-bis-(4-cyanophenyl)-2,4-dimethyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (2h)**: Yield: 64%; R<sub>f</sub>=0.41 (ethyl acetate/petroleum ether 1:2); m.p. 180–181°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): δ=3.03 (s, 3H, NCH<sub>3</sub>), 3.09 (s, 3H, NCH<sub>3</sub>), 4.87 (d, <sup>3</sup>J(H,H)=15.9 Hz, 1H,

CH), 7.41 (d, <sup>3</sup>J(H,H)=8.4 Hz, 2H, H<sub>Ar</sub>), 7.55 (d, <sup>3</sup>J=8.1 Hz, 2H, H<sub>Ar</sub>), 7.71 (d, <sup>3</sup>J(H,H)=8.4 Hz, 2H, H<sub>Ar</sub>), 7.78 ppm (d, <sup>3</sup>J(H,H)=8.1 Hz, 2H, H<sub>Ar</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS): δ=28.0 (NCH<sub>3</sub>), 35.7 (NCH<sub>3</sub>), (66.3, 66.6) (CF), 88.4 (NCH), 100.4 (CO), 103.8, 113.3, 113.5, 117.8, 126.1, 126.5, 132.7, 133.0, 140.9, 145.1, 150.3 (NCON), (161.2, 161.7) ppm (NCOC); IR (Nujol):  $\tilde{\nu}$ =3398 (w), 2952 (w), 2229 (m) (CN), 1734 (s), 1692 (s), 1473 (s), 1286 (s), 1051 (m), 932 (m), 746 cm<sup>-1</sup> (m); TOFMS(EI) calcd for C<sub>21</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub>F [M+H]<sup>+</sup>: 391.1206; found: 391.1210.

**6-Fluoro-7,7-bis-(4-cyanophenyl)-2,4-dimethyl-8-oxa-2,4-diaza-bicyclo[4.2.0]octane-3,5-dione (3h)**: Yield: 5%; R<sub>f</sub>=0.62 (ethyl acetate/petroleum ether 1:2); m.p. 148–150°C; <sup>1</sup>H NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, TMS): δ=2.78 (s, 3H, NCH<sub>3</sub>), 3.23 (s, 3H, NCH<sub>3</sub>), 6.08 (d, <sup>3</sup>J(H,H)=13.2 Hz, 1H, CH), 7.72–7.92 ppm (m, 8H, H<sub>Ar</sub>); <sup>13</sup>C NMR (75 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, TMS): δ=27.2 (NCH<sub>3</sub>), 33.4 (NCH<sub>3</sub>), (86.8, 87.2) (CF), 89.4 (NCH), 92.5 (CO), 112.5, 117.8, 117.9, 126.3, 127.1, 127.2, 132.3, 132.4, 142.8, 143.5, 151.2 ppm; IR (Nujol):  $\tilde{\nu}$ =3436 (s), 2960 (w), 2232 (m) (CN), 1733 (s), 1691 (s), 1477 (m), 1285 (m), 1082 (m), 922 (m), 829 cm<sup>-1</sup> (m); TOFMS(EI) calcd for C<sub>21</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub>F [M+H]<sup>+</sup>: 391.1206; found: 391.1209.

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