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NEW RESULTS ON THE PHOTOREACTIVITY OF 5-FLUORO-1,3-DIMETHYLURACIL WITH METHOXYLATED NAPHTHALENES

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Abstract – Photocycloaddition of 5-fluoro-1,3-dimethyluracil (5-FDMU) with various methoxy and dimethoxynaphthalenes was investigated. Reaction of 5-FDMU with 1,x-dimethoxynaphthalenes (x = 4-7) gave rise to the selective formation of cycloadducts, conjugated arylpropenylidene-1,3-diazin-2-ones, which were derived from an initially formed oxetane moiety via the Paterno-Büchi reaction cycloadduct. The present study shows that the presence of a methoxy substituent on the α-position in naphthalene is essential for the formation of products through the Paterno-Büchi reaction. This unique photoreaction involving formation of an oxetane between 5-FDMU and a naphthalene ring, followed by a concomitant disruption of the initially formed oxetane moiety and an aromatic ring of naphthalene moiety, can be regarded as a novel aromatic Paterno-Büchi reaction.

INTRODUCTION

Photoreaction of nucleic bases has received much attention from both organic chemistry and biological perspectives. The formation of thymine-adenine photoadducts[1] or of pyrimidine-pyrimidine cyclobutane dimers and bipyrimidine [6-4]-photoadducts[2] between adjacent pyrimidine bases play important roles in the direct induction of DNA damage. The former two reactions result through [2 + 2]-addition of olefinic double bonds, while the [6-4]-photoadducts derive from oxetane or azetidine intermediates formed by photoaddition of the C4-carbonyl of thymine or the C4-imino tautomer of cytosine[3] across the C5 = C6 double bond of the adjacent base.

This paper is Dedicated to Professor Ei-ichi Negishi on the occasion of his 77th birthday.

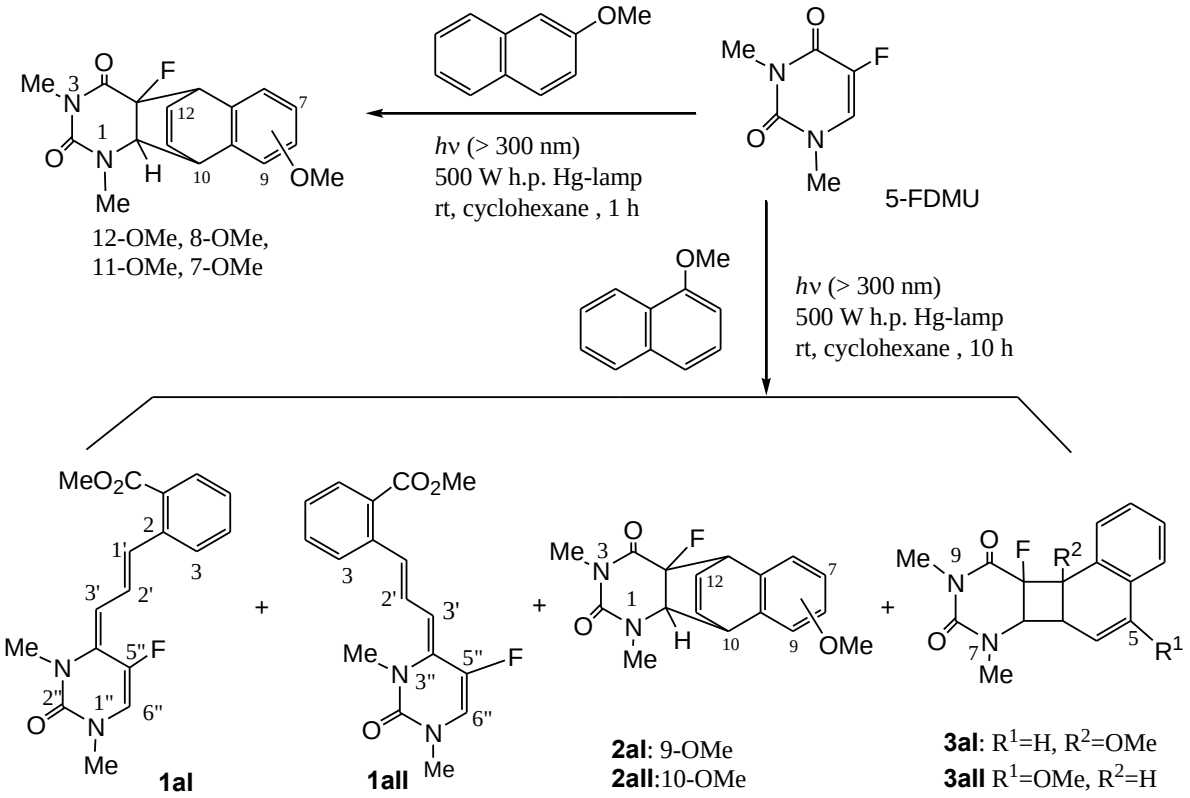
At the same time, photochemical coupling reactions involving the C = C or C = O double bonds have attracted much attention from a synthetic view point, since the chemical modification of nucleic bases has been recognized as one of the most promising approaches for developing bioactive substances such as anticancer and antiviral agents.[4] In this context, we have intensively studied the photochemical modification of halogenated pyrimidines that occurs when they are irradiated in presence of aromatic hydrocarbons such as benzene and naphthalene derivatives. We have thus successfully demonstrated that upon UV-irradiation, 6-chloro-1,3-dimethyluracil undergoes a variety of photocycloaddition reactions with benzene derivatives[5] and naphthalenes,[6] to give a structurally diverse range of photoproducts. We recently reported that UV-irradiation of 5-FDMU with naphthalene and its derivatives substituted with electron withdrawing groups, or an electron donating methyl group, proceeded mode-selectively by 1,2- and 1,4-cycloaddition, to afford naphthocyclobutapyrimidines and ethenobenzoquinazolines (barrelene), respectively, depending on the irradiation conditions.[7] The cycloadditions with aromatic hydrocarbons hitherto reported, however, are limited only to the couplings or substitutions on the C5=C6 double bond of the pyrimidine ring. No cycloaddition involving the carbonyl group and an aromatic ring has yet been discovered. The occurrence of a Paterno-Büchi type reaction would provide a new aspect for the photochemical modification of pyrimidine rings with aromatic compounds.

In order to explore further the scope of this reaction, we aimed to extend our work to the photochemistry of 5-FDMU with methoxynaphthalenes (MN). In the present paper[8] we report that the photoreaction of 5-FDMU with naphthalenes with a methoxy group at the α-position proceeds by way of Paterno-Büchi cycloaddition, followed by concomitant disruption of the resulting oxetane ring to yield highly conjugated arylpropenylidene-1,3-diazin-2-ones, while the 1,4-cycloaddition reaction occurs exclusively with naphthalenes without a methoxy group at the α-position.

RESULTS AND DISCUSSION

In contrast to the photoreaction of 5-FDMU with 2-methoxynaphthalene (2-MN), whereby 1,4-cyclo-adducts were furnished exclusively,[7b] external irradiation of a degassed solution of 5-FDMU and 1-methoxynaphthalene (1-MN) in cyclohexane with a 500 W high-pressure mercury lamp in a Pyrex tube (λ>300 nm) for 10 h afforded methyl 2-[(1*E*)-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)prop-1-enyl]benzoates as a mixture of the (1′*E*,3′*E*)-isomer (**1aI**) (24%) and the (1′*E*,3′*Z*)-stereoisomer (**1aII**) (14%), together with a conventional regio-isomeric mixture of 1,4-cycloadducts (**2aI**, **2aII**) and 1,2-cycloadducts (**3aI**, **3aII**) as the minor components (yields are given based on 47% of 5-FDMU consumed) (Scheme 1). Compound **1aII** isomerized spontaneously into the (1′*E*,3′*E*)-isomer (**1aI**) when kept at room temperature in the dark (**1aII**; half-life time = 6.5 h at room temperature). Upon irradiation, **1aI** isomerized into **1aII**, to yield a 1:1 mixture of **1aI** and **1aII** at the equilibrium state. The

(1′*E*,3′*Z*)-stereoisomer (**1aII**) is too unstable to isolate in sufficient amounts as a pure form, so spectral analyses for **1aII** were made on the mixture with **1aI**.



Scheme 1

The stereochemistry of **1aI** and **1aII** was determined with the aid of NOE experiments (Figure 1). Irradiation of the H-3′ proton of **1aI** significantly affected the H-1′ vinyl proton, as well as N3″-Me. Also irradiation at N3″-Me showed enhancement of signal for the H-3′ vinyl proton. On the other hand, the (1′*E*,3′*Z*) isomer (**1aII**) showed no NOE correlation for H-3′–N3″-Me, while significant correlation was observed between N3″-Me–H-2′. These differences in the NOE′s conclusively determined the stereochemistry of **1aI** as (1*E*′,3*E*′) and **1aII** to be (1*E*′,3*Z*′), respectively.[8]

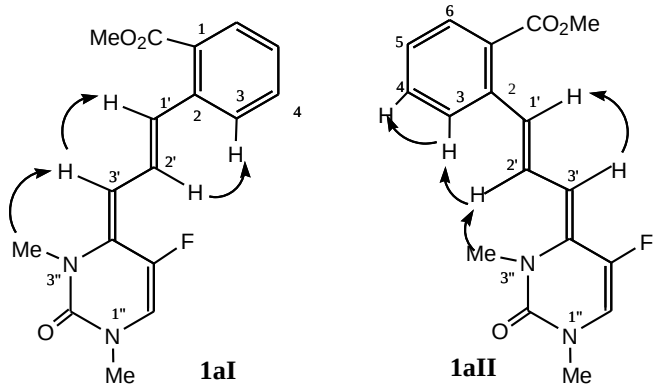
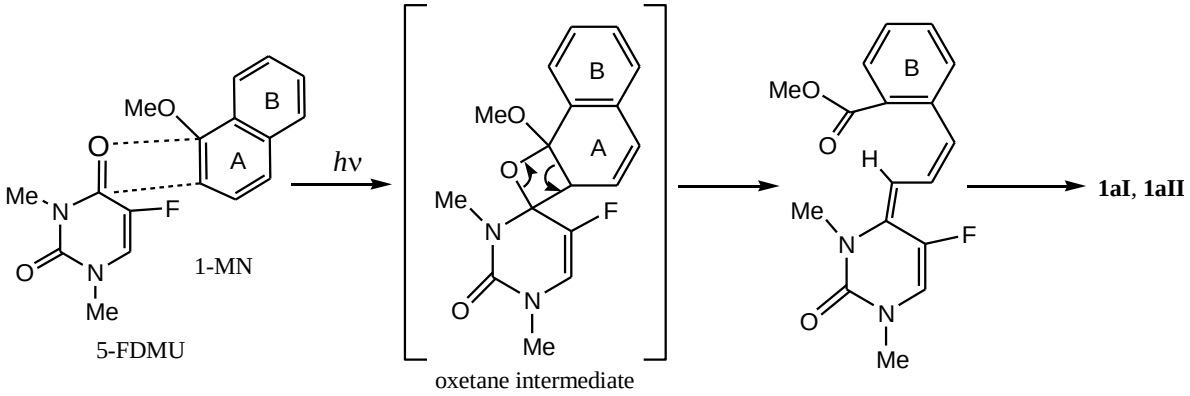


Figure 1. NOE correlations for **1aI** and **1aII**

The formation of 4-(3-phenylprop-2-enylidene)-5-fluoropyrimidin-2-ones (**1aI**, **1aII**) is rationally explained in terms of [2 + 2]-addition between the uracil C4 = O carbonyl group and the C1 = C2 double bond of the naphthalene ring (i.e., Paterno-Büchi reaction), giving rise to the corresponding oxetane

intermediate (Scheme 2), which is followed by the subsequent ring opening of the highly strained oxetane moiety, accompanied by the concomitant cleavage of the naphthalene A-ring in the manner shown in Scheme 2.



Scheme 2

It is noted that in most cases, enones undergo [2 + 2]-photocycloaddition with olefins, leading to the formation of cyclobutanes via π-π*excited states, in competition with oxetane formation from then π-π* triplet state of the carbonyl moiety.[9] In order to gain more insight into the mechanism underlying the present reaction, UV-irradiation of 5-FDMU and 1-MN was conducted in varying ratios. Thus, it is demonstrated that the ratio of Paterno-Büchi adducts vs. (1,2-adducts + 1,4-adducts) increases as the molar ratios of 1-MN vs. 5-FDMU decreased (Table 1). These results suggested that the present Paterno-Büchi reaction is initiated by the n-π* excited 5-FDMU. Addition of triplet quencher *trans*-piperylene was inefficient on the formation of Paterno-Büchi product, suggesting the participation of an n-π* singlet state or extremely short-lived n-π* triplet state of 5-FDMU.

Table 1. Photoreaction of 5-FDMU with various amounts of 1-MN in benzene for 3 h

Molar Ratio	Yield based on 5-FDMU consumed (%)					Product Ratio	
1MN/5-FDMU	Paterno-Büchi Product (**1a**)	1,4-Adduct (**2aI**, **2aII**)		1,2-Adduct (**3aI**, **3aII**)		(**1a**) vs. (**2a**+**3a**)	1,4-Adduct (**2a**) vs. 1,2-Adduct (**3a**)
10	52	20	14	8.5		1.2	4.0
2	42	15	12	5.8		1.3	4.7
1	62	14	11	5.7		1.9	4.4
0.5	49	7.5	5.6	7.5		2.3	1.7
0.1	29	3.5	2.3	4.2	1.7	2.5	1.0

Interestingly, the ratio of 1,4-adduct vs. 1,2-adduct increases as the molar ratio of 1-MN vs. 5FDMU increases from 0.1 to 2 (Table 1), implying that the participation of a charge-transfer complex (CT) or exciplex formation may participate in the 1,4-addition. However, no spectroscopic evidence supporting the presence of any intermolecular interaction was obtained.

We then carried out the photoreaction of 5-FDMU with 1-MN in various solvents. As shown in Table 2, the Paterno-Büchi reaction proceeds preferentially in such a non- (or weakly-)-polar solvents, such as cyclohexane, benzene or toluene. In a polar solvent, acetonitrile, the Paterno-Büchi reaction was suppressed significantly and 1,4-cyloadducts were formed only in sparing yield, while in a protic solvent, methanol, the substitution reaction occurs exclusively.

Presumably, in a polar solvent, acetonitrile, photo-induced electron transfer (PET) from electron donating 1-MN prevails, to disrupt the oxetane intermediate[10] and probably 1,2-adducts, cyclobutane derivatives,[11] to restore the starting 5-FDMU and 1-MN, resulting in the lowest consumption of the starting 5-FDMU; only trace amounts of 1,4-cycloadducts produced were detected.

Table 2. Photoreaction of 5-FDMU with 1-MN in various solvents (3 h)

Solvent	Paterno-Büchi Product (%)	1,4-Adduct (%)	1,2-Adduct (%)	ArDMU (%)	DMU (%)	Consumed 5-FDMU(%)
cyclohexane	13 (43)	8 (27)	3 (10)	---		30
benzene	13 (62)	5 (24)	1 (5)	---		21
toluene	9 (45)	6 (30)	---	---		20
MeCN	---	trace (<0.5)	---	---		10
MeOH	---	---		9 (38)	4 (17)	24

( ): Yields are given based on 5-FDMU consumed. DMU: 1,3-dimethyluracil.
ArDMU: aryl 1,3-dimethyluracil (Substitution product).

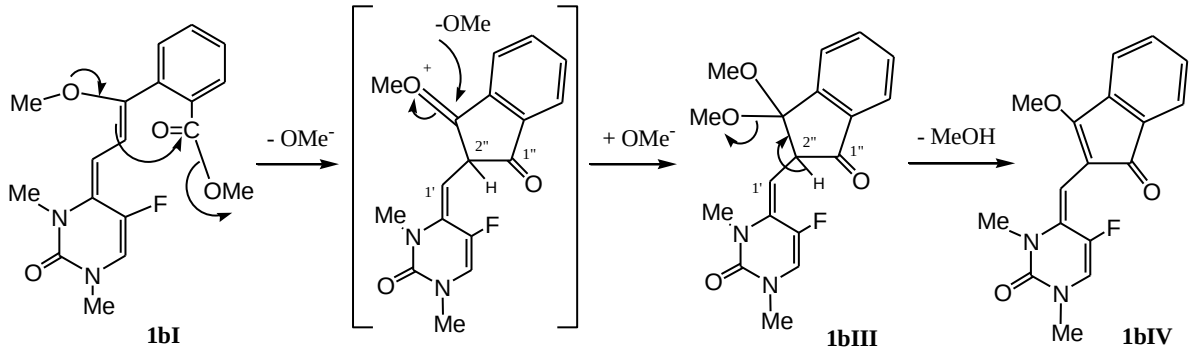
In a protic solvent, methanol, conventional substitution reaction and hydrogen subtraction were observed, as has been found in the reaction with 5-FDMU and benzene or naphthalene.[7a,7b,12] The substitution reaction can be explained in terms of PET, and subsequent protonation to the resulting radical anion of 5-FDMU, followed by the radical-radical coupling between 5-FDMU and 1-MN.

Thus, the precise mechanisms participating in the present Paterno-Büchi reaction remain unclear. The generation of the products through Paterno-Büchi reaction can be explained in terms of the electronic effects of a methoxy group incorporated in the α-position on the oxetane intermediate which serves importantly in the disruption of the oxetane moiety in the way to produce conjugated arylpropenylidenepyrimidines, whereas the oxetane intermediates from the β-MN, if ever derived, with no such driving force to furnish propenylidenepyrimidine derivatives, would only revert to the original 5-FDMU and β-MN.

In order to explore the important role of a methoxy group on the naphthalene ring in yielding Paterno-Büchi reaction involved products, photoreaction of 5-FDMU with naphthalenes with methoxy groups at varying positions was examined. UV-irradiation of 5-FDMU and 1,4-dimethoxynaphthalene (1,4-MN) under analogous conditions furnished methyl 2-[(1*E*)-1-methoxy-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)-1-propenyl]benzoate as a separable mixture of the (1′*E*,3′*E*)-isomer (**1bI**) (44%) and the (1′*Z*,3′*E*)-stereoisomer (**1bII**) (15%), together with a novel valence isomer **1bIII**, in 20% yield (yields are given based on 82% of 5-FDMU consumed). Upon being allowed to stand in the dark at 25 °C, 4-[(3,3-dimethoxy-1-oxoindan-2-yl)methylene]-5-fluoro-1,3-dimethyl-1,3-dihydropyrimidin-2-one (**1bIII)** transformed into the oxoindenyl derivative **1bIV** with a half-life time of *ca*. 5 h.

The stereochemistry of **1bI** was determined with the aid of NOE experiments. Irradiation of the H-3′ proton significantly affected the 1′-OMe proton, as well as N3″-Me. Also irradiation at H-2′ showed enhancement of the signal for the H-3 aromatic proton. On the other hand, the (1′*Z*,3′*E*) isomer (**1bII**) showed NOE correlation for H-3′– N3″-Me and aromatic H-3. Also significant correlation was observed between H-2′– 1′-OMe. These differences in the NOE′s conclusively determined the stereochemistry of **1bI** as (1′*E*,3′*E*) and **1bII** to be (1′*Z*,3′*E*), respectively. The structure of the novel adduct **1bIII** was deduced by means of MS (M + H^+, *m/z* 347) and NMR spectroscopy. The ^{1}H-NMR spectrum showed two OMes, H-2″ and aromatic protons in the dimethoxy-1-oxoindan-2-yl methylene moiety. Also the ^{13}C-NMR spectrum showed peaks due to C-1″ carbons at 201.5 ppm and C-1′ at 92.6 ppm in oxoindanyl methylene part. Indene derivative **1bIV** was easily conformed by means of MS (M + H^+, *m/z* 315) and NMR spectroscopy.

The formation of indene derivatives **1bIII** and **1bIV** is rationally explained in terms of intramolecular ring closure of **1bIII** or **1bIV** produced from the Paterno-Büchi reaction, followed by the subsequent ring opening of the resulting oxetane moiety in the manner shown in Scheme 3.



Scheme 3

Photoreaction of 1,5-MN under the conditions employed above (in cyclohexane, 10 h) furnished methyl 3-methoxy-2-[(1′*E*,3′*E*)-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)prop-1-enyl]-

benzoate (**1cI**) in high yield (59%) together with small amounts of the (1′*E*,3′*Z*)-isomer (**1cII**) (16%) (at the stage where 54% of the 5-FDMU was consumed).

Photoreaction of 1,6-MN afforded methyl 4-methoxy-2-[(1′*E*)-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)-1-propenyl]benzoate as a mixture of the (1′*E*,3′*E*)-isomer (**1dI**) (39%) and the (1′*E*,3′*Z*)-stereoisomer (**1dII**) (9%) (yields are given based on 46% of 5-FDMU consumed).

Similarly, 1,7-MN afforded the (5-methoxy-phenylpropenylidene)-1,3-diazin-2-ones as a mixture of the (1′*E*,3′*E*)-isomer (**1eI**) (44%) and the (1′*E*,3′*Z*)-stereoisomer (**1eII**) (3%) together with the conventional 1,2-cycloadduct (**3e**) in 6% yield (yields are given based on 39% of 5-FDMU consumed).

Next, the photoreaction with naphthalenes with methoxy groups at both of α and β-positions was examined: Irradiation of 1,2-MN (10 h) furnished 1,2-adduct, cyclobutapyrimidine (**3f**) (24%) as a major product together with the conventional 1,4-cycloadduct (**2f**) in 7% yield (yields are given based on 38% of 5-FDMU consumed).

In the case of 1,3-MN (10 h), the conventional 1,2-cycloadducts (**3gI**, **3gII**) were obtained as a stereoisomeric mixture in 24% and 18% yields, respectively (yields are given based on 40% of 5-FDMU consumed).

Then the photoreaction with naphthalenes bearing methoxy groups at the β-position was conducted: Photoreaction of 2,6-MN in cyclohexane (10 h) afforded the 1,4-adduct, 8,12-dimethoxyethenobenzo-quinazoline (**2h**), exclusively (88% yield at the stage where 25% of 5-FDMU consumed). In the case of 2,7-MN (3 h), 1,4-adduct (**2iI**) (8,11-dimethoxy derivative) was also yielded as the major product (36%), together with the regioisomer (**2iII**) (7,12-dimethoxy derivative) (2%) as a minor component (yields are given based on 42% of 5-FDMU consumed). These results are summarized in Chart 1 and Table 3.

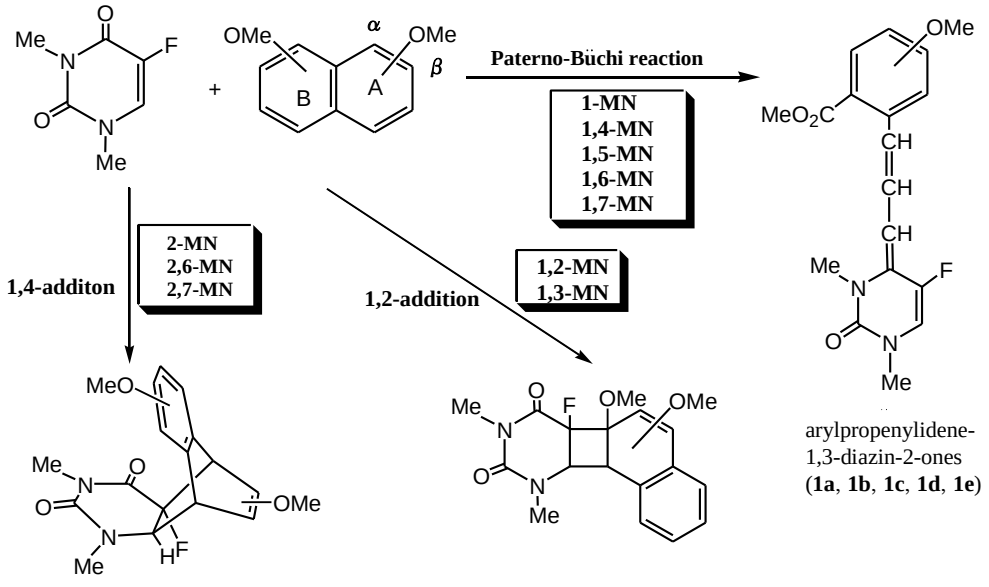


Chart 1

These results demonstrate that UV- irradiation of a mixture of 5-FDMU and MNs undergoes photocycloaddition which can be classified into three categories of cycloaddition depending on the site of the methoxy substituents on the naphthalene ring: 1) Naphthalenes with methoxy groups at the α or α,α-position in the A ring, or at the α-position in the A ring and either the α- or, β-position in the B ring, effected Paterno-Büchi cycloaddition preferentially.

Table 3. The mode selectivity on the photoreaction of 5-FDMU with methoxynaphthalenes

Methoxy-naphthalene	Position in A ring	Position in B ring	Reaction Mode
1-MN	α		Paterno-Büchi Reaction
1,4-MN	α, α		
1,5-MN	α	α	
1,6-MN	α	β	
1,7-MN	α	β	
1,2-MN	α, β		1,2-Addition
1,3-MN	α, β		
2-MN	β		1,4-Addition
2,6-MN	β	β	
2,7-MN	β	β	

2) In the case of naphthalenes having methoxy groups at the α,β-position in A ring, 1,2-cycloaddition proceeds favorably. 3) Mono- and dimethoxynaphthalenes with no methoxy group at the α-position exclusively underwent conventional 1,4-cycloaddition.

The 1,2- and 1,3-MNs, which have an α-methoxy group as well as the β-methoxy group on the A-ring of naphthalene, underwent 1,2-cycloaddition exclusively. Although the precise mechanisms involved in the reaction remain unclear, we have previously reported[7c,7d] that upon UV-irradiation of 5-FDMU with naphthalene, 1,4-addition took place through triplet excited states while 1,2-cycloaddition proceeded via the singlet excited state. Based on these findings, it is surmised that 1,2- and 1,3-MNs may serve as a singlet sensitizer or a singlet quencher of 5-FDMU in the n-π* singlet states, to generate excited MNs in the π-π* singlet states.

In the case of naphthalenes with methoxy groups only at β, the conventional 1,4-cycloaddition observed in our serial studies on the photoreaction of 5-FDMU with naphthalenes took place exclusively.[7]

Thus, the present work demonstrates the significant role of the presence of a methoxy group at the α-position for yielding Paterno-Büchi cycloaddition involved adducts.

CONCLUSION

Despite a large number of examples involving oxetane formation,[13] only a few papers on the aromatic Paterno-Büchi cycloaddition have appeared,[14] except for the reaction with five-membered heteroaromatics.[15] It is noteworthy that our present study provides a new example of an aromatic-Paterno-Büchi reaction which involves the synthesis of an intermediate oxetane, followed by concomitant ring opening of the oxetane moiety and disruption of the original aromatic ring, giving rise

to highly conjugated methyl 2-[-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)-1-propenyl]benzoates.

EXPERIMENTAL

NMR spectra were measured with a JEOL JNM-ECA500 (500 MHz) spectrometer. Chemical shifts are given on the δ (ppm) scale based onthe residual deuterated solvent signals as reference. MS spectra and high-resolution EIMS and FABMS (HRMS) spectra were recorded with a JEOL FABmate and a JEOL JMS-HX110, respectively. HPLC was conducted on a Shim-pac PREP-Sil (H) (25 cm x 20 mm *i. d.*) (silica gel), using a LC-6A apparatus (Shimadzu, Kyoto) with monitoring at 254 nm. UV-Irradiation was carried out externally with a 500 W high-pressure mercury lamp (Eiko-sha, Osaka) in a degassed Pyrex tube (> 300 nm) on a merry-go-round apparatus. Yields are determined by means of ^{1}H-NMR spectroscopy with *p*-dinitrobenzene as an internal standard.

Photoreaction of 5-FDMU with methoxynaphthalenes. — Typically, an equivalent molar solution (1.5 mM) of 5-FDMU and methoxynaphthalene in cyclohexane (160 mL) was introduced portionwise (5 mL each) into 32 degassed Pyrex tubes, and irradiated externally at rt (10 h unless cited therein). The reaction mixture was concentrated *in vacuo*, and the residual oil was submitted to HPLC with appropriate solvent systems as follows: 5% AcOEt in CH_2Cl_2 for adducts **1a**, **1b**, **1e**, **3f**, and **2h** 20-30% AcOEt in hexane for adducts **1c**, **1d**, **3g** and **2i**.

Methyl 2-[(1*E*,3*E*)-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)-1-propenyl]-benzoate (1aI): Yellow oil. ^{1}H-NMR (C_6D_6) δ: 2.43 (3H, s, N1″-Me), 2.76 (3H, s, N3″-Me), 3.50 (3H, s, C1-CO_2Me), 5.25 (1H, d, *J* = 8.6 Hz, H-6″), 5.54 (1H, d, *J* = 11.0 Hz, H-3′), 6.90 (1H, dd, *J* = 7.4, 8.0 Hz, H-5), 7.07 (1H, dd, *J* = 7.4, 8.0 Hz, H-4), 7.73 (1H, d, *J* = 8.0 Hz, H-3), 7.82 (1H, dd, *J* = 11.0, 15.0 Hz, H-2′), 7.90 (1H, d, *J* = 8.0 Hz, H-6), 7.92 (1H, dd, *J* = 4.4, 15.0 Hz, H-1′). NOE: H-3′ with N3″-Me (14.1%), H-1′ (6.4%); H-6″ with N1″-Me (7.1%); H-2′ with H-3 (2.0%); H-3 with H-2′ (3.2%), H-4 (5.8%). FAB-MS *m/z*: 317 $[M+H]^+$. HRFAB-MS: Calcd for $C_{17}H_{18}N_2O_3F$: 317.1301. Found: 317.1316. UV λ_{max} ($CHCl_3$) nm (ε): 376 (21290).

Methyl 2-[(1*E*,3*Z*)-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)-1-propenyl]-benzoate (1aII): ^{1}H-NMR (C_6D_6) δ: 2.44 (3H, s, N1″-Me), 3.20 (3H, s, N3″-Me), 3.46(3H, s, C1-CO_2Me), 5.25 (1H, d, *J* = 6.9 Hz, H-6′), 5.86 (1H, d, *J* = 12.0 Hz, H-3′), 6.94 (1H, dd, *J* = 7.4, 8.0 Hz, H-5), 7.12 (1H, dd, *J* = 7.4, 8.0 Hz, H-4), 7.12 (1H, dd, *J* = 12.0, 15.0 Hz, H-2′), 7.43 (1H, d, *J* = 8.0 Hz, H-3), 7.71 (1H, d, *J* = 15.0 Hz, H-1′), 7.90 (1H, d, *J* = 8.0 Hz, H-6). NOE: H-3′ with H-1′ (20.4%), H-2′ (5.4%); H-6″ with N1″-Me (7.1%); H-2′ with N3″-Me (3.2%), H-3 (4.0%). HRFAB-MS: Calcd for $C_{17}H_{18}N_2O_3F$: 317.1301. Found: 317.1296.

4a-Fluoro-4a,5,10,10a-tetrahydro-10-methoxy-1,3-dimethyl-*cis*-5,10-ethenobenzo[*f*]quinazoline-2,4-

dione (2aI): Colorless crystals, mp 134-135 °C (hexane). ^{1}H-NMR ($CDCl_3$) δ: 2.59 (3H, s, N3-Me), 3.20 (3H, s, N1-Me), 3.66 (1H, d, J = 31.7 Hz, H-10a), 3.71 (3H, s, C10-OMe), 4.51 (1H, dt, J = 1.7, 6.0 Hz, H-5), 6.68 (1H, dd, J = 6.0, 8.2 Hz, H-12), 6.88 (1H, dd, J = 1.7, 8.2 Hz, H-11), 7.15-7.17 (3H, H-6, H-7, H-8), 7.42 (1H, d, J = 7.7 Hz, H-9). HRFAB-MS: Calcd for $C_{17}H_{18}N_2O_3F$: 317.1301. Found: 317.1324.

4a-Fluoro-4a,5,10,10a-tetrahydro-9-methoxy-1,3-dimethyl-*cis*-5,10-ethenobenzo[*f*]quinazoline-2,4-dione (2aII): Colorless crystals, mp 149-151 °C (hexane). ^{1}H-NMR (C_6D_6) δ: 2.69 (3H, s, N1-Me), 2.77 (3H, s, N3-Me), 3.13 (1H, dd, J = 2.9, 31.0 Hz, H-10a), 3.18 (3H, s, C9-OMe), 4.46 (1H, ddd, J = 1.2, 2.9, 6.3 Hz, H-10), 4.66 (1H, ddd, J = 1.7, 4.6, 6.3 Hz, H-5), 6.19 (1H, ddd, J = 1.7, 6.3, 7.5 Hz, H-11), 6.22 (1H, d, J = 8.0 Hz, H-8), 6.32 (1H, ddd, J = 1.2, 5.8, 7.5 Hz, H-12), 6.79 (1H, dd, J = 7.5, 8.0 Hz, H-7), 6.92 (1H, d, J = 7.5 Hz, H-6). HRFAB-MS: Calcd for $C_{17}H_{18}N_2O_3F$: 317.1301. Found: 317.1328.

10a-Fluoro-6a,6b,10a,10b-tetrahydro-5-methoxy-7,9-dimethylnaphtho[1′,2′:3,4]cyclobuta[1,2-*d*]-pyrimidine-8,10-dione (3aI): Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 2.94 (3H, d, J = 1.1 Hz, N9-Me), 3.11 (3H, s, N7-Me), 3.67 (3H, s, C5-OMe), 3.83 (1H, ddd, J = 3.7, 7.3, 10.8 Hz, H-6a), 3.96 (1H, dd, J = 10.8, 18.1 Hz, H-10b), 4.34 (1H, dd, J = 7.3, 20.7 Hz, H-6b), 4.44 (1H, d, J = 3.7 Hz, H-6), 7.11-7.15 (4H, m, H1-H4). NOE: H-6 with H-6a, N7-Me, C5-Me; H-6b with N1-Me; H-10b with H-6a, H-1. FAB-MS *m/z*: 317 $[M+H]^+$. HRFAB-MS: Calcd for $C_{17}H_{17}N_2O_3F$: 317.1301. Found: 317.1284.

10a-Fluoro-6a,6b,10a,10b-tetrahydro-10b-methoxy-7,9-dimethylnaphtho[1′,2′:3,4]cyclobuta[1,2-*d*]-pyrimidine-8,10-dione (3aII): Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 2.75 (3H, d, J = 1.1Hz, N9-Me), 3.03 (3H, s, N7-Me), 3.16 (3H, s, C10b-OMe), 3.80 (1H, ddd, J = 1.1, 5.0, 9.7 Hz, H-6a), 4.47 (1H, dd, J = 9.7, 22.9 Hz, H-5), 5.74 (1H, dd, J = 5.0, 9.7 Hz, H-6), 7.05-7.44 (4H, m, H1-H4). NOE: H-6b with H-6a, N7-Me; H-6a with H-6b, H-6, C10b-OMe; H-6 with H-5, H-6a; N7-Me with H-6b, H-6. FAB-MS *m/z*: 317 $[M+H]^+$. HRFAB-MS: Calcd for $C_{17}H_{17}N_2O_3F$:317.1301. Found: 317.1306.

Methyl 2-[(1*E*,3*E*)-1-methoxy-3-(5-fluoro-2,4-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)prop-1-enyl]benzoate (1bI): Yellow oil. ^{1}H-NMR (acetone-d_6) δ: 2.86 (3H, s, N3″-Me), 3.12 (3H, s, N1″-Me), 3.44 (3H, s, C1′-OMe), 3.79 (3H, s, C1-CO_2Me), 5.70 (1H, d, J = 12.0 Hz, H-3′), 6.23 (1H,d, J = 12.0 Hz, H-2′), 6.75 (1H, d, J = 9.7 Hz, H-6”), 7.39 (1H, dt, J = 1.2, 7.5 Hz, H-4), 7.49 (1H, dd, J = 1.2, 7.5 Hz, H-5), 7.51 (1H, dt, J = 1.2, 7.5 Hz, H-3), 7.60 (1H, dd, J = 1.2, 7.5 Hz, H-6). NOE: H-3′ with C1′-OMe (4.4%), N3″-Me (19%), H-2′ (11%); H-6″ with N1″-Me (9.2%); H-2′ with H-3′ (8.8%), H-3 (5.2%); N1″-Me with H-5″ (16%). ^{13}C-NMR (acetone-d_6) δ: 31.1 (N3″-Me), 35.5 (N1″-Me), 51.0 (OMe), 58.0 (OMe), 95.2 (3′), 110.7 (2′), 117.3 (6″), 127.9 (4), 128.4 (5), 128.7 (3), 130.3 (4″), 130.8 (2), 135.2 (6), 142.3 (5″), 151.8 (2″), 151.8 (1′), 170.0 (1). HMBC：H-1 with C1-CO, C-2; H-3 with C-1′, C-4; H-4 with C-2, C-5; H-5 with C-1, C-5; H-6 with C-1, C-4; H-2′ with C-2, C-1′, C-4″; H-3′with C-6”, C-2′, C-4″; N1″-Me with C-2″; N1″-Me with C-2″,C-6″; H-6″ with C-5″, C-2″, C-4″. FAB-MS *m/z*: 347 $[M+H]^+$. HRFAB-MS: Calcd for $C_{18}H_{20}N_2O_4F$: 347.1409. Found: 347.1409.

Methyl 2-[(1*Z*,3*E*)-1-methoxy-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)-prop-1-enyl]benzoate (1bII): Yellow oil. ^{1}H-NMR (acetone-d_6) δ: 2.90 (3H, s, N3″-Me), 3.09 (3H, s, N1″-Me), 3.64 (3H, s, C1′-OMe), 3.77 (3H, s, C1-CO_2Me), 5.15 (1H, d, J = 12.0 Hz, H-3′), 6.15 (1H,d, J = 12.0 Hz, H-2′), 6.79 (1H, d, J = 9.7 Hz, H-5″), 7.50 (1H, dd, J = 7.5, 8.0 Hz, H-5), 7.56 (1H, d, J = 8.0 Hz, H-3), 7.60 (1H, dd, J = 1.0, 7.7 Hz, H-4), 7.78 (1H, d, J = 7.5 Hz, H-6). NOE: H-3′ with N3″-Me (14.0%), H-3 (6.4%), H-6″ with N1″-Me (7.1%), H-2′ with H-3′ (2.0%), C1′-OMe (10.0%), N1″-Me with H-6″ (4.6%). ^{13}C-NMR (acetone-d_6) δ: 30.7 (N3″-Me), 35.3 (N1″-Me), 52.0 (OMe), 55.0 (OMe), 97.4 (3′), 98.2 (2′), 116.0 (6″), 127.2 (1″), 128.2 (4), 129.9 (5), 131.3 (4), 132.2 (2), 143,0 (5″), 150.3 (3′), 155.2 (1′), 168.0 (1). HMBC : H-1 with C1-CO, C-2; H-3 with C-1′, C-4; H-4 with C-2, C-5; H-5 with C-1, C-5; H-2 with C-1, C-4; H-2′ with C-2, C-1′, C-1″; H-3′ with C-5″, C-2′, C-1″; N1″-Me with C-2″; N3″-Me with C-2″, C-6″; H-6″ with C-5″, C-2″, C-4″. FAB-MS *m/z*: 347 $[M+H]^+$. HRFAB-MS: Calcd for $C_{18}H_{20}N_2O_4F$: 347.1409. Found: 347.1390.

4-[(3,3-dimethoxy-1-oxoindan-2-yl)methylene]-5-fluoro-1,3-dimethyl-1,3-dihydroprymidine-2-one (1bIII): Light yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 3.15 (3H, s, N1-Me), 3.18 (3H, s, N3-Me), 3.28 (3H, s, C3′-OMe), 3.40 (3H, s, C3″-OMe), 4.29 (1H, dd, J = 3.5, 9.8 Hz, H-2″), 4.69 (1H, d, J = 9.8 Hz, H-1′), 6.31 (1H, d, J = 9.2 Hz, H-6), 7.51 (1H, dd, J = 7.5, 8.0 Hz, H-5″), 7.65 (1H, dd, J = 7.5, 8.0 Hz, H-6″), 7.70 (1H, d, J = 8.0 Hz, H-4″), 7.78 (1H, d, J = 7.5 Hz, H-7″). NOE: H-1′ with N3-Me (12.6%); H-6 with N3-Me (21.3%); H-1″ with C3″-OMe (7.1%). ^{13}C-NMR ($CDCl_3$) δ: 32.2 (N3-Me), 36.5 (N1-Me), 50.2 (OMe), 51.5 (OMe), 57.4 (1″), 92.6 (1′), 104.1 (3″), 116.6 (6), 124.2 (4″), 125.2 (7″), 130.4 (5″), 132.9 (4), 134.2 (6″), 135.2 (3″a), 142.0 (5), 149.0 (7″a), 150.9 (2), 201.5 (1″). HMBC: H-1′ with C-1″, C-4, C-5, C-3″; H-2″ with C-1″, C-1′, C-3″, C-4; H-6 with C-5, C-2, C-4; H-5″ with C-7″, C-3″a; H-6″ with C-4″, C-7″a; H-4″ with C-3″, C-3″a; H-7″ with C-7″a, C-1″ C-6″; N3-Me with C-2, C-4; N1-Me with C-6, C-2; OMe with C-3″. FAB-MS *m/z*: 347 $[M+H]^+$. HRFAB-MS: Calcd for $C_{18}H_{20}N_2O_4F$: 347.1396. Found: 347.1439.

5-Fluoro-4-[(3-methoxy-1-oxoinden-2-yl)methylene]-1,3-dimethyl-1,3-dihydroprymidine-2-one (1bIV): Light red oil. ^{1}H-NMR ($CDCl_3$) δ: 3.16 (3H, s, N1-Me), 3.28 (3H, s, N3-Me), 4.22 (3H, s, C3″-OMe), 4.98 (1H, s, H-1'), 6.28 (1H, d, J = 9.2 Hz, H-6), 7.15 (1H, d, J = 7.4 Hz, H-4″), 7.22 (1H, dd, J = 0.9, 7.5 Hz, H-6″), 7.31(1H, dd, J = 1.2, 7.4 Hz, H-5″), 7.38 (1H, d, J = 7.5 Hz, H-7″). NOE: H-1'with N3-Me (17.5%), C3″-OMe (5.3%); H-6 with N3-Me (13.0%); C3″-OMe with H-1' (3.4%), H-4″ (1.2%). ^{13}C-NMR ($CDCl_3$) δ: 31.7 (N3-Me), 36.5 (N1-Me), 59.2 (OMe), 86.4 (1'), 107.2 (1″), 116.5 (6), 118.3 (4″), 121.1 (7″), 129.2 (6″), 132.0 (7″a), 132.4 (5″), 140.9 (3″a), 142.0 (5), 150.5 (2), 170.5 (3″), 194.6 (1″). HMBC: H-1' with C-1″, C-4, C-5, C-3″; H-6 with C-5, C-2, C-6; H-5″ with C-4″, C-7″, C-3″a; H-6″ with C-4″, C-7″a; H-4″ with C-3″, C-3″a; H-7″ with C-7″a, C-1″ C-6″; N1-Me with C-2,

C-6; N3-Me with C-4, C-2; OMe with C-3″. FAB-MS *m/z*: 315 $[M+H]^+$. HRFAB-MS: Calcd for $C_{17}H_{16}N_2O_3F$: 315.1145. Found: 315.1168.

Methyl 3-methoxy-2-[(1*E*,3*E*)-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)-1-propenyl]benzoate (1cI): Yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 3.17 (3H, s, N1″-Me), 3.27 (3H, s, N3″-Me), 5.46 (1H, d, *J* = 12.0 Hz, H-3'), 6.30 (1H, dd, *J* = 0.9, 8.4 Hz, H-6″), 6.77 (1H, dd, *J* = 4.4, 15.4 Hz, H-1'), 6.96 (1H, dd, *J* = 1.0, 7.9 Hz, H-4), 7.15 (1H, dd, *J* = 7.7, 7.9 Hz, H-5), 7.22 (1H, dd, *J* = 1.0, 7.7 Hz, H-6), 7.49 (1H, dd, *J* = 12.0, 15.4 Hz, H-2'). NOE: H-3′ with H-1′ (20.8%), N3”-CH_3 (15.3%); H-6″ with N1″-Me (11.5%); H-1' with H-3' (13.9%); N1″-Me with H-6″ (4.3%); N3″-Me with H-3′ (6.1%); C5-OMe with H-4 (2.2%), H-2′ (0.8%). FAB-MS *m/z*: 347 $[M+H]^+$. HRFAB-MS: Calcd for $C_{18}H_{20}N_2O_4F$: 347.1407. Found: 347.1390.

Methyl 3-methoxy-2-[(1*E*,3*Z*)-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)-1-propenyl]benzoate (1cII): ^{1}H-NMR (C_6D_6) δ: 2.42 (3H, s, N1″-Me), 2.78 (3H, s, N3″-Me), 3.15 (3H, s, C3-OMe), 3.46 (3H, s, C1-CO_2Me), 5.24 (1H, d, *J* = 12.0 Hz, H-2″), 5.88 (1H, dd, *J* = 0.9, 8.4 Hz, H-6″), 6.46 (1H, d, *J* = 8.0 Hz, H-4), 6.86 (1H, t, *J* = 8.0 Hz, H-5), 7.26 (1H, d, *J* = 15 Hz, H-5), 7.40 (1H, d, *J* = 8.0 Hz, H-6), 7.71 (1H, dd, *J* = 12.0, 15.0 Hz, H-2′). NOE: N3″-Me with H-4 (9.8%); H-2′ with N3″-Me (10.4%), H-1′ (3.8%), H-3’ (1.4%); H-1′ with H-2′ (9.7%), H-3′ (10.5%); N1″-Me with H-6″ (4.4%), N3″-Me with H-2′ (6.1%); H-3′ with H-1′ (10.6%); C3-OMe with H-4 (11.6%). FAB-MS *m/z*: 347 $[M+H]^+$. HRFAB-MS: Calcd for $C_{18}H_{20}N_2O_4F$: 347.1407. Found: 347.1394.

Methyl 4-methoxy-2-[(1*E*,3*E*)-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)-1-propenyl]benzoate (1dI): Yellow oil.^{1}H-NMR (C_6D_6) δ: 2.42 (3H, s, N1″-Me), 2.78 (3H, s, N3″-Me), 3.23(3H, s, C4-OMe), 3.54 (3H, s, C1-CO_2Me), 5.27 (1H, dd, *J* = 1.2, 8.6 Hz, H-6″), 5.41 (1H, d, *J* = 12.0 Hz, H-3′), 6.57 (1H, dd, *J* = 2.6, 8.7 Hz, H-5), 7.38 (1H, d, *J* = 2.6 Hz, H-3), 7.81 (1H, dd, *J* = 12.0, 15.0 Hz, H-2′), 8.02 (1H, d, *J* = 8.7 Hz, H-6), 8.09 (1H, dd, *J* = 4.4, 15.0 Hz, H-1′). NOE: H-3′ with H-1′ (20.8%), N3″-Me (15.3%); H-6″ with N1″-Me (11.5%); H-1′ with H-3′ (13.9%); C4-OMe with H-4 (2.2%), H-2′ (0.8%). ^{13}C-NMR (C_6D_6) δ: 31.3 (N3″-Me), 35.5 (N1″-Me), 51.3 (OMe), 54.6 (OMe), 103.3 (3′), 110.9 (3), 112.4 (5), 116.5 (6″), 120.7 (1), 128 (1′-2′), 133.5 (6), 132.0 (4″), 143.0 (5″), 144.9 (2″), 162.8 (4), 167.37 (C1-CO). HMBC: H-1 with CO; H-3 with C-5, C-1, C-4; H-4 with C-4; H-5 with C-1, C-3; H-6 with C-2, C-4, CO; H-1′ with C-3, C-3′; H-2′ with C-2; H-3′ with C-5″, C-6″, C-4″; N3″-Me with C-2″, C-4″; N1″-Me with C-3″, C-6″; H-6″ with C-5″, C-2″, C-4″. FAB-MS *m/z*: 347 $[M+H]^+$. HRFAB-MS: Calcd for$C_{18}H_{20}N_2O_4F$: 347.1407. Found: 347.1390. UV λ_{max}($CHCl_3$) nm (ε): 376 (19400).

Methyl 4-methoxy-2-[(1*E*,3*Z*)-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)-1- propenyl]benzoate (1dII): ^{1}H-NMR (C_6D_6) δ: 2.43 (3H, s, N1″-Me), 3.15 (3H, s, N3″-Me), 3.24 (3H, s, C4-OCH_3), 3.51 (3H, s, C1-CO_2Me), 5.24 (1H, d, *J* = 6.9 Hz, H-6″), 5.90 (1H, d, *J* = 12.0 Hz, H-3′), 6.53 (1H, dd, *J* = 2.3, 8.6 Hz, H-5), 7.12 (1H, dd, *J* = 12.0, 15.0 Hz, H-2′), 7.40 (1H, d, *J* =2.3 Hz, H-3),

7.90 (1H, d, *J* =15.0 Hz, H-1′), 8.04 (1H, d, *J* = 8.6 Hz, H-6). NOE: N3″-Me with H-2′; H-1′ with H-3′, H-2′; H-3′ with H-1′; C4-OMe with H-3, H-5.

Methyl 5-methoxy-2-[(1*E*,3*E*)-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)-1-propenyl]benzoate (1eI): Yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 3.16 (3H, s, N1″-Me), 3.24 (3H, s, N3″-Me), 3.38 (3H, s, C5-OMe), 3.89 (3H, s, C1-CO_2Me), 5.50 (1H, d, *J* = 10.4 Hz, H-3′), 6.30 (1H, dd, *J* = 1.0, 8.3 Hz, H-6"), 6.98 (1H, dd, *J* = 2.8, 9.0 Hz, H-4), 7.17 (1H, dd, *J* = 4.2, 15.4 Hz, H-1′), 7.27 (1H, dd, *J* = 10.4, 15.4 Hz, H-2′), 7.32 (1H, d, *J* = 2.8 Hz, H-6), 7.54 (1H, d, *J* = 9.0 Hz, H-5). NOE: H-3′ with N3″-Me (20.0%), H-1′(23%); H-6″ with N1″-Me (8.5%); H-2′ with H-3 (8.8%). ^{13}C-NMR ($CDCl_3$) δ: 31.9 (N3″-Me), 36.3 (N1″-Me), 52.1 (OMe), 55.5 (OMe), 103.4 (3′), 114.0 (6), 116.0 (6″), 118.9 (4), 126.0 (2′), 127.2 (1′), 127.5 (3), 128.4 (1), 130.7 (4″), 132.5 (2) ,143.0 (5″), 150.7 (2″), 169.7 (C1-CO). HMBC: H-1 with CO; H-3 with C-5, C-1; H-4 with C-3, C-2, C-5; C5-OMe with C-5; H-6 with C-1, C-3; H-2′ with C-2, C-1′, C-3′; H-3′ with C-6″, C-2′, C-1″; N3″-Me with C-2″, C-4″, N1″-Me with C-2″, C-6″, C-5″, H-6″ with C-5″, C-2″, C-4″. FAB-MS *m/z*: 347 $[M+H]^+$. HRFAB-MS: Calcd for $C_{18}H_{20}N_2O_4F$: 347.1407. Found: 347.1386. UV λ_{max} ($CHCl_3$) nm (ε): 376 (21070).

Methyl 5-methoxy-2-[(1*E*,3*Z*)-3-(5-fluoro-1,3-dimethyl-2-oxo-1,3-dihydropyrimidin-4-ylidene)-1-propenyl]benzoate (1eII): ^{1}H-NMR (C_6D_6) δ: 2.55 (3H, s, N1″-Me), 3.25 (3H, s, N3″-Me), 3.25 (3H, s, C5-OMe), 3.46 (3H, s, C1-CO_2Me), 5.27 (1H, d, *J* = 6.9 Hz, H-6″), 5.90 (1H, d, *J* = 12.0 Hz, H-3′), 6.89 (1H, dd, *J* = 2.9, 8.6 Hz, H-4), 7.09 (1H, dd, *J* = 12.0, 15.0 Hz, H-2′), 7 .41 (1H, d, *J* = 8.6 Hz, H-3), 7.53 (1H, d, *J* = 2.9 Hz, H-6), 7.68 (1H, d, *J* = 15.0 Hz, H-1′). NOE: H-2′ with H-3 (15.5%), N3″-Me (11.3%).

6b-Fluoro-6a,6b,10a,10b-tetrahydro-1,6a-dimethoxy-8,10-dimethylnaphtho[1′,2′:3,4]cyclobuta-[1,2-*d*]pyrimidine-7,9-dione (3e): Colorless crystals, mp 156-158 °C. ^{1}H-NMR (C_6D_6) δ: 2.18 (3H, s, N10-Me), 3.11 (3H, s, N8-Me), 3.12 (3H, s, C1-OMe), 3.25 (3H, s, C6a-OMe), 3.87 (1H, dd, *J* = 9.2, 25.2 Hz, H-10a), 4.43 (1H, d, *J* = 9.2 Hz, H-10b), 5.69 (1H, dd, *J* = 1.1, 10.3 Hz, H-6), 6.24 (1H, d, *J* = 8.1 Hz, H-2), 6.26 (1H, d, *J* = 10.3 Hz, H-5), 6.44 (1H, d, *J* = 7.5 Hz, H-4), 6.88 (1H, dd, *J* = 7.5, 8.1 Hz, H-3). NOE: H-10a with H-10b, N10-CH_3; H-6 with H-5 (14.9%), C6a-OMe (7.7%); C6a-OMe with H-6 (5.3%).

6b-Fluoro-6a,6b,10a,10b-tetrahydro-6a,10b-dimethoxy-*cis*-8,10-dimethylnaphtho[1′,2′:3,4]cyclobuta-[1,2-*d*]pyrimidine-7,9-dione (3f): Colorless crystals, mp 161-162 °C (hexane). ^{1}H-NMR ($CDCl_3$) δ: 2.60 (3H, s, N8-Me), 3.05 (3H, s, C10b-OMe), 3.17 (3H, s,N10-Me), 3.78 (3H, s, C6a-OMe), 4.64 (1H, dd, *J* = 0.8, 24.6 Hz, H-10a), 6.35 (1H, d, *J* = 10.1 Hz, H-6), 6.53 (1H, d, *J* = 10.1 Hz, H-5), 7.13 (1H, m, H-4), 7.25 (1H, m, H-1), 7.30-7.34 (2H, H-2, H-3). NOE: H-10a with N10-Me (7.1%); H-6 with H-5 (15.7%), C6a-OMe (9.1%); H-5 with H-6 (8.9%), H-4 (8.7%), C6a-OMe with H-6 (4.0%), N10-Me with H-10a (4.1%), H-1 (2.7%). FAB-MS *m/z*: 347 $[M+H]^+$. HRFAB-MS: Calcd for $C_{18}H_{20}N_2O_4F$: 347.1402. Found:

347.1395. UV λ_{max} (cyclohexane) nm (ε): 267 (2020).

4a-Fluoro-4a,5,10,10a-tetrahydro-8,9-dimethoxy-1,3-dimethyl-*cis*-5,10-ethenobenzo[*f*]quinazoline-2,4-dione (2f): Colorless crystals, mp 115-117 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.57 (3H, s, N3-Me), 3.21 (3H, s, N1-Me), 3.72 (3H, s, C8-OMe), 3.83 (3H, s, C9-OMe), 3.71 (1H, d, *J* = 30.0 Hz, H-10a), 4.34 (1H, dd, *J* = 6.4, 6.9 Hz, H-5), 5.30 (1H, d, *J* = 6.9 Hz, H-12), 7.12-7.26 (3H, H-6, H-7, H-8), 7.43 (1H, d, *J* = 7.1 Hz, H-9). NOE: H-10a with N1-Me (7.8%), H-11 (2.7%), H-10 (7.2%); H-5 with H-6 (7.2%), H-12 (7.9%); H-12 with H-5 (11.2%), C11-OMe (7.1%); C10-OMe with H-9 (2.2%); C11-OMe with H-12 (3.2%), H-7 (1.2%); N1-Me with H-10a (3.5%), C10-OMe (0.5%). FAB-MS *m/z*: 347 $[M+H]^+$. HRFAB-MS: Calcd for $C_{18}H_{20}N_2O_4F$: 347.1402. Found: 347.1393. UV λ_{max} (cyclohexane) nm (ε): 240 (3300), 283 (720).

6a-Fluoro-6a,6b,10a,10b-tetrahydro-5,6a-dimethoxy-*cis*-8,10-dimethylnaphtho[1',2':3,4]cyclobuta-[1,2-*d*]pyrimidine-7,9-dione (3gI): Colorless oil. ^{1}H-NMR (C_6D_6) δ: 1.96 (3H, s, N10-Me), 3.09 (3H, s, N8-CH_3), 3.12 (3H, s, C5-OMe), 3.26 (3H, s, C6a-OMe), 3.50 (1H, dd, *J* = 8.7, 24.6 Hz, H-10a), 3.81 (1H, d, *J* = 10.1 Hz, H-10b), 4.61 (1H, s, H-6), 6.65 (1H, d, *J* = 7.5 Hz, H-1), 6.92 (1H, t, *J* = 7.5 Hz, H-2), 7.01 (1H, t, *J* = 7.5 Hz, H-3), 7.71 (1H, d, *J* = 7.5 Hz, H-4). NOE: H-10a with N10-Me (7.2%), H-10b (9.6%); H-10b with H-10a (14.7%), H-1 (10.0%), C6a-OMe (9.1%); H-6 with C5-OMe (8.4%), C6a-OMe (6.3%); C6a-OMe with H-6 (3.3%), H-10b (2%); N10-Me with H-10a (3.4%), H-1 (1.5%). FAB-MS *m/z*: 347 $[M+H]^+$. HRFAB-MS: Calcd for $C_{18}H_{20}N_2O_4F$: 347.1407. Found: 347.1382. UV λ_{max} (cyclohexane) nm (ε): 223 (7960), 270 (2080).

6a-Fluoro-6a,6b,10a,10b-tetrahydro-5,6a-dimethoxy-*trans*-8,10-dimethylnaphtho[1′,2′:3,4]cyclobuta-[1,2-*d*]pyrimidine-7,9-dione (3gII): Light yellow oil. ^{1}H-NMR (C_6D_6) δ:1.95 (3H, s, N10-CH_3), 3.09 (3H, s, N8-CH_3), 3.12 (3H, s, C5-OCH_3), 3.26 (3H, s, C6a-OCH_3), 2.89 (1H, d, *J* = 7.9 Hz, H-10b), 3.17 (1H, dd, *J* = 17.5 Hz, 10.1 Hz, H-10a), 4.86 (1H, s, H-6), 6.57 (1H, d, *J* = 7.5 Hz, H-1), 6.94 (1H, dd, *J* = 7.5, 7.7 Hz, H-2), 7.05 (1H, dd, *J* = 7.2, 7.7 Hz, H-3), 7.78 (1H, d, *J* = 7.2 Hz, H-4). NOE: H-10a with N10-CH_3 (1.2%); H-10b with H-1 (9.0%), N10-CH_3 (1.2%), C6a-OCH_3 (2.1%); H-6 with C5-OCH_3 (3.4%), C6a-OCH_3 (9.3%), C5-OCH_3 with H-6 (6.7%), H-4 (0.1%), H-1 with H-10b (10.2%), N10-CH_3 (2.6%). FAB-MS m/z: 347 $[M+H]^+$. HRFAB-MS: Calcd for $C_{18}H_{20}N_2O_4F$: 347.1407. Found: 347.1398. UV λ_{max} (cyclohexane) nm (ε): 235 (5020) 280 (1040).

4a-Fluoro-4a,5,10,10a-tetrahydro-8,12-dimethoxy-1,3-dimethyl-*cis*-5,10-ethenobenzo[*f*]quinazoline-2,4-dione (2h): Degradative colorless crystals. ^{1}H-NMR (C_6D_6) δ: 2.59 (3H, s, N3-CH_3), 2.77 (3H, s, N1-Me), 3.17 (3H, s, C12-OMe), 3.21 (3H, s, C8-OMe), 3.31(1H, dd, *J* = 2.5, 31.7 Hz, H-10a), 3.49 (1H, dd, *J* = 2.5, 6.9 Hz, H-10), 4.64 (1H, dd, *J* = 2.4, 4.8 Hz, H-5), 4.73 (1H, dd, *J* = 2.4, 6.9 Hz, H-11), 6.30 (H, dd, *J* = 2.7, 8.3 Hz, H-7), 6.65 (1H, d, *J* = 2.7 Hz, H-9), 6.81 (1H, d, *J* = 8.3 Hz, H-6). NOE: H-10a with N1-Me (7.3%), H-10 (5.2%), H-11 (2.0%); H-5 with H-6(8.8%); H-10 with H-9 (9.7%), H-11

(10.6%), H-10a (6.6%), N1-CH_3 (7.1%), H-11 with H-10a (7.2%), H-10 (9.2%). FAB-MS *m/z*: 347 $[M+H]^+$. HRFAB-MS: Calcd for $C_{18}H_{20}N_2O_4F$: 347.1407. Found: 347.1431.

4a-Fluoro-4a,5,10,10a-tetrahydro-8,11-dimethoxy-1,3-dimethyl-*cis*-5,10-ethenobenzo[*f*]quinazoline-2,4-dione (2iI): Colorless crystals, mp 61-62 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.77 (3H, d, J = 0.8 Hz, N3-Me), 3.10 (3H, s, N1- Me), 3.61 (3H, s, C11-OMe), 3.74 (3H, s, C8-OMe), 3.75 (1H, dd, J = 2.7, 30.4 Hz, H-10a), 3.95 (1H, dd, J = 2.2, 2.7 Hz, H-10), 4.44 (1H, dd, J = 5.3, 6.4 Hz, H-5), 5.23 (1H, dd, J = 2.2, 6.4 Hz, H-12), 6.62 (1H, dd, J = 2.4, 8.2 Hz, H-7), 6.77 (1H, d, J = 2.4 Hz, H-9), 7.04 (1H, d, J = 8.2 Hz, H-6). NOE: H-10a with N1-Me, H-10, H-11, H-5 with H-6, H-12, H-10 with C11-OMe, H-9, C11-OMe with H-10, H-12. FAB-MS *m/z*: 347 $[M+H]^+$. HRFAB-MS: Calcd for $C_{18}H_{20}N_2O_4F$: 347.1407. Found: 347.1387.

4a-Fluoro-4a,5,10,10a-tetrahydro-7,12-dimethoxy-1,3-dimethyl-*cis*-5,10-ethenobenzo[*f*]quinazoline-2,4-dione (2iII): Colorless crystals. ^{1}H-NMR (acetone-d_6) δ: 2.65 (3H, d, J = 0.8 Hz, N3-Me), 3.08 (3H, s, N1-Me), 3.59 (3H, s, C12-OMe), 3.73 (3H, s, C7-OMe), 3.76 (1H, dd, J = 2.7, 32.4 Hz, H-10a), 4.20 (1H, dd, J = 2.4, 5.1 Hz, H-10), 4.31 (1H, dd, J = 2.7, 7.0 Hz, H-5), 5.37 (1H, dd, J = 2.4, 7.0 Hz, H-11), 6.68 (1H, dd, J = 2.6, 8.1 Hz, H-8), 6.79 (1H, d, J = 2.6 Hz, H-6), 7.21 (1H, d, J = 8.1 Hz, H-9). FAB-MS *m/z*: 347 $[M+H]^+$. HRFAB-MS: Calcd for $C_{18}H_{20}N_2O_4F$: 347.1407. Found: 347.1494.

Photoreaction of 5-FDMU with1-methoxynaphthalene in the presence of piperylene. An equivalent molar solution (1.5 mM) of 5FDMU and 1-methoxynaphthalene in cyclohexane containing *trans*-piperylene (1.5 mM) was irradiated.

Photoreaction of 5-FDMUwith 1-methoxynaphthalene in various solvents. Equivalent molar solutions (1.5 mM) of 5FDMU and 1-methoxynaphthalene in cyclohexane, benzene, toluene, MeCN, and MeOH, respectively, were irradiated.

Substitution products: 1,3-dimethyl-5-(4-methoxy-1-naphtyl)uracil (4aI): Colorless crystals, mp 217-218 °C (hexane). ^{1}H-NMR (acetone-d_6) δ: 3.31 (3H, s, N3-Me), 3.48 (3H, s, N1-Me), 4.03 (3H, C4′-OMe), 6.94 (1H, d, J = 8.0 Hz, H-3′), 7.30 (1H, d, J = 8.0 Hz, H-2′), 7.45 (1H, dt, J = 1.7, 6.9 Hz, H-7′), 7.47 (1H, dt, J = 2.3, 6.9 Hz, H-6′), 7.62 (1H, s, H-6), 7.73 (1H, dd, J = 2.3, 6.9 Hz, H-8′), 8.24 (1H, dd, J = 1.7, 6.9 Hz, H-5′). NOE: H-6 with H-2′ (22.0%), N1-Me (16.8%), C4′-Me with H-3′, H-5′. FAB-MS *m/z*: 297 $[M+H]^+$. HRFAB-MS: Calcd for $C_{17}H_{17}N_2O_3$: 297.1239. Found: 297.1248.

1,3-Dimethyl-5-(5-methoxy-1-naphthyl)uracil (4aII): Colorless oil. ^{1}H-NMR (acetone-d_6) δ: 3.31 (3H, s, N3-Me), 3.49 (3H, s, N1-Me), 4.02 (3H, C4′-OMe), 6.94 (1H, dd, J = 1.2, 6.9 Hz, H-6′), 7.32-7.37 (2H, H-7′, H-8′), 7.39 (1H, dd, J = 1.7, 6.9 Hz, H-2′), 7.47 (1H, dd, J = 6.9, 8.6 Hz, H-3′), 7.65 (1H, s, H-6), 8.25 (1H, d, J = 8.6 Hz, H-4′). NOE: H-6 with H-2′ (3.7%), N1-Me (30.0%), C5′-Me with H-6' (19.0%); H-4′ with H-3′ (4.3%); H-3′ with H-2′ (5.9%), H-4′ (4.7%); H-6′ with H-7′ (20.0%). FAB-MS *m/z*: 297 $[M+H]^+$. HRFAB-MS: Calcd for $C_{17}H_{17}N_2O_3$: 297.1239. Found: 297.1260.

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