

Photochemical reaction of bis-aromatic systems: a novel photocycloaddition of pyridine with furan



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The photochemical reaction of the bis-aromatic system pyridine–furan was investigated. Irradiation of a benzene solution containing 3-cyano-2-methoxypyridines **1** (0.02 M) and furan (0.2 M) resulted in the formation of a 1 : 1 adduct, 11-cyano-10-methoxy-8-methyl-4-oxa-9-azapentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{5,8}]undec-9-ene and 10-cyano-9-methoxy-7-methyl-5-oxa-8-azatricyclo[5.4.0.0^{2,6}]undeca-3,8,10-triene in 30 and 16% yield, accompanied by the transpositional pyridine, 5-cyano-2-methoxy-6-methylpyridine, and the pyridine dimer, in 2 and 44% yield, respectively, when the reaction conversion reached 48% yield. The cage and the face-to-face structures were established by X-ray structural analyses. The cage adduct was stable under neutral conditions; however, it easily converted to a face-to-face structure in acidic conditions. On the other hand, though the face-to-face structure was stable at rt, the starting pyridine **1** and furan were easily regenerated quantitatively by heating (>100 °C) or irradiation (>290 nm). The 4 + 4 adduct of pyridine with furan was detected by ¹H NMR spectroscopy, and subsequently transformed to a cage structure on irradiation.

Introduction

The photochemical reactions of bis-aromatic systems have received much attention from both mechanistic and synthetic perspectives.^{1–3} Naphthalenes, and anthracene and its derivatives, undergo [4 + 4] photodimerization^{4–8} and cycloaddition with furan.^{9–11} It has, however, been reported that benzene and its derivatives display a very diverse range of photochemical reactions, such as cycloaddition with both alkenes^{12,13} and furan,^{14–19} although the cycloaddition with heteroaromatic systems is an underdeveloped area.^{20,21} Now we provide the first example of photocycloaddition of the pyridine–furan system.

Results and discussion

Recently, we reported that 2-alkoxy-3-cyanopyridines show high photochemical reactivity, promoting a variety of photochemical reactions, such as transpositional isomerization, dimerization,^{22,23} and 2 + 2 cycloaddition with methacrylonitrile.²⁴ The high reactivity of these pyridines compared with that of pyridine itself is dependent on the polarization within the pyridine ring from the conjugate relationship of the cyano and alkoxy groups.

Irradiation of a benzene solution of 3-cyano-2-methoxy-6-methylpyridine **1a** (0.02 M) containing a large excess of furan (0.2 M) through a Pyrex filter with a high-pressure mercury lamp followed by separation with chromatography on silica gel gave two types of 1 : 1 adducts of furan and substrate **1a** (**2a**, 30%; **3a**, 16%) accompanied with the transpositional isomer **4a** and the pyridine dimer **5a**, in 2 and 44% yield, respectively, when the reaction conversion reached 48% yield (Table 1).

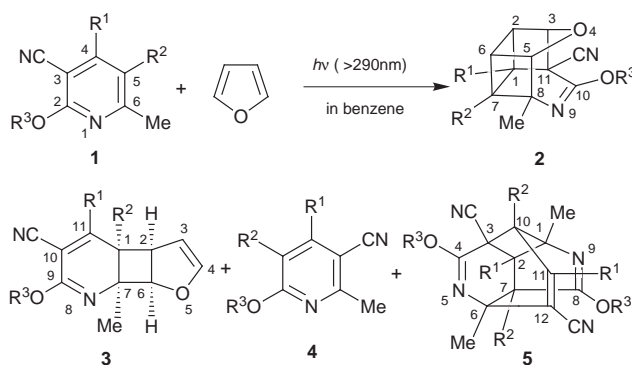
The structures of the adducts **2a** and **3a** were determined on the basis of spectral data. The assignment was performed by chemical-shift-correlation spectroscopy (COSY) techniques. For the transpositional isomer **4a** and the dimer **5a**, we have already reported their formation by the direct irradiation of compound **1a**.²² Irradiation of other pyridines **1b–e** also gave 1 : 1 adducts in moderate yields as shown in Table 1.

Finally, the cage structure of compound **2d** was established by X-ray structural analysis (Fig. 1). The cage product **2d** gave prismatic crystals of formula C₁₃H₁₄N₂O₂, monoclinic, space group *P*2₁/*n*, *a* = 8.6634(8), *b* = 13.649(2), *c* = 10.3163(9) Å, β = 97.503(7)°, *V* = 1209.4(2) Å³, *Z* = 4, ρ = 1.265 g cm⁻³, μ(CuKα) = 7.06 cm⁻¹, *F*_w ('formula weight') = 230.27. The structure was solved by direct methods and refined by full-matrix least-squares, where the final *R*- and *R*_w-value were 0.038 and 0.033 for 2030 reflections.† The cage compound **2d** has three cyclobutane rings. The four-membered rings show a range of bond lengths: 1.532 (C-2–C-5 bond) to 1.595 Å (C-3–C-9 bond), and bond angles of 88.0 to 90.7°. The reported bond length for other cyclobutane rings shows a range of 1.540 to 1.567 Å.²⁵ It is interesting that compound **2d** has a much longer bond length than do previously reported cyclobutanes.

The face-to-face structure of adduct **3b** was also confirmed by X-ray structural analysis (Fig. 2). The compound gave prismatic crystals, formula C₁₃H₁₄N₂O₂, triclinic, space group *P*2₁/*c*, *a* = 7.781(2), *b* = 8.649(2), *c* = 17.850(1) Å, α = 91.75(1)°, β = 105.73(2)°, γ = 92.33(1)°, *V* = 1200.2(4) Å³, *Z* = 4, ρ = 1.274 g cm⁻³, μ(CuKα) = 7.12 cm⁻¹, *F*_w = 230.27. The structure was also solved by direct methods and refined by full-matrix least-squares, where the final *R*- and *R*_w-value were 0.053 and 0.055 for 2485 reflections.† In adduct **3b**, two rings derived from furan and the pyridine chromophore are positioned wing-like on the upper face of the cyclobutane ring. The bond length of the cyclobutane ring is in the range 1.538 (C-2–C-6) to 1.569 (C-1–C-7) Å, and the bond angles are in the range 88.3 to 90.9°.

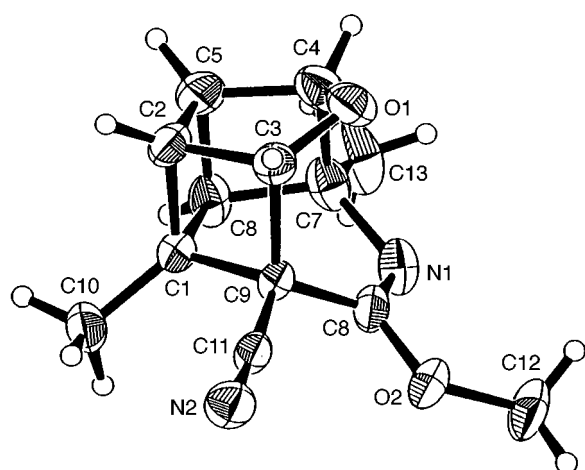
The pyridine–furan adducts **3** are stable at rt; however, the starting pyridines **1** and furan were easily regenerated quanti-

† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available via the RSC web page (<http://www.rsc.org/authors>). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/286.

Table 1 Photoreaction of the pyridine–furan system

Entry	Pyridine	R ¹	R ²	R ³	Conv. (%)	Yield (%) ^a			
						2	3	4	5
1	1a	H	H	Me	48	30	16	2 ^b	44
2	1b	H	H	Et	52	45	18	2 ^b	34
3	1c	H	H	Pr ⁱ	51	28	18	4 ^b	44
4	1d	Me	H	Me	64	23	15	46	0
5	1e	Me	Me	Me	67	42	25	0	0

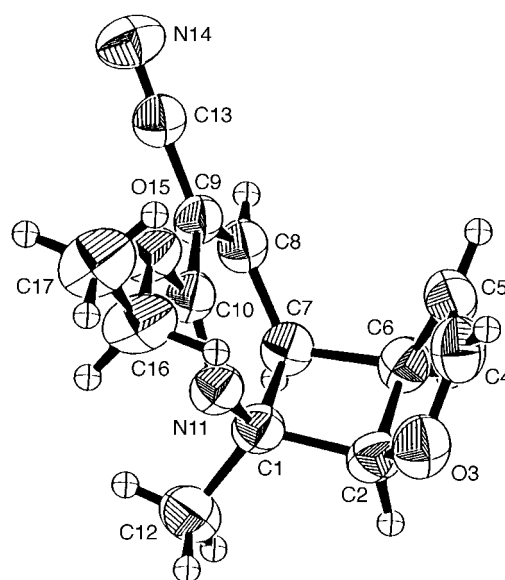
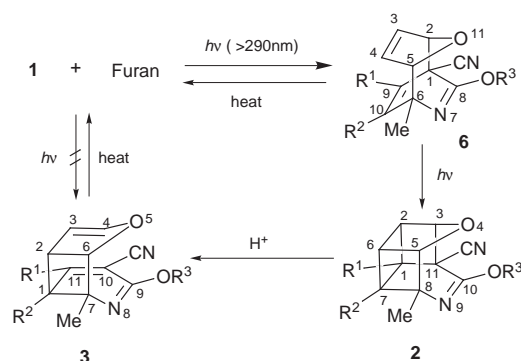
^a Isolated yield. A 0.02 M benzene solution of pyridine **1** and 0.2 M furan was irradiated with a high-pressure mercury lamp. ^b Pyridines **4a–c** could not be isolated in a pure state, and were obtained as mixtures with **1a–c**. The chemical yields were determined by ¹H-NMR spectroscopy.

**Fig. 1** ORTEP drawing of pyridine–furan adduct **2d**, with crystallographic numbering scheme.

tatively by heating (>100 °C) or irradiation (>290 nm). All cage products **2** were quite sensitive toward acidic conditions, such as exposure on silica gel; thus slow handling during the separation of photoproducts did not give cage products **2a–e** but afforded open tricycles **3a–e** as the isolable adducts.

The formation of the adduct is dependent on the concentration of both starting pyridine **1** and furan. When the concentrations of starting pyridine **1** and furan are 0.02 M and 0.1 M, respectively, the chemical yield of the adduct, the dimer, and the transpositional isomer increased linearly at an early stage of the reaction. After the reaction conversion reached ~50%, the formation of the adduct accelerated in contrast to the suppression of the formation of dimer, because the dimerization strongly depends on the concentration of pyridine **1**, and the dimer did not form under a low concentration of the starting pyridine. On the other hand, irradiation of a benzene solution of substrate **1a** (0.02 M) containing a higher concentration of furan (0.5 M) gave a 44% yield of cage **2a** and a 25% yield of tricycle **3a** accompanied by products **4a** (2%) and **5a** (18%) at 60% conversion yield.

We postulate a 4 + 4 photocycloaddition of pyridine with furan leading to an intermediate adduct **6** as shown in Scheme 1. The 4 + 4 cycloadduct **6** subsequently absorbs a light quan-

**Fig. 2** ORTEP drawing of pyridine–furan adduct **3b**, with crystallographic numbering scheme.**Scheme 1** A mechanism for the photochemical addition of pyridines to furan.

tum, leading to cage adduct **2**. The formation of the 4 + 4 adduct **6** was detected spectroscopically. Irradiation of a C₆D₆ solution of the pyridine **1a** (0.02 M) and furan (0.2 M) in a

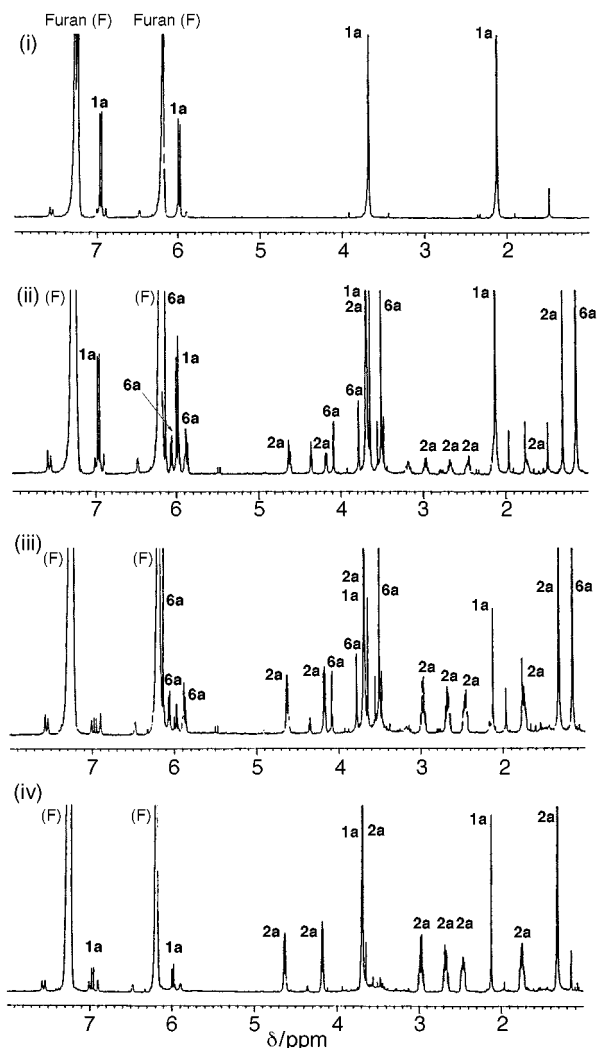


Fig. 3 ^1H NMR spectra of a photolyzed C_6D_6 solution of pyridine **1a** (0.02 M) and furan (0.2 M) in an NMR tube. (i) Before irradiation. (ii) Irradiated for 10 min. (iii) Irradiated for 1 h. (iv) Irradiated for 1 h and subsequently heated at 80°C for 1 h.

Pyrex NMR tube was followed by ^1H NMR spectroscopy. Fig. 3(i) shows the spectrum of a C_6D_6 solution of compound **1a** (0.02 M) and furan (0.2 M). When the solution was irradiated for 10 min [Fig. 3(ii)], new peaks assignable to 4 + 4 adduct **6a** appeared in addition to the peaks derived from cage adduct **2a**. New peaks derived from the methine and olefinic protons of 4 + 4 adduct **6a** exhibited at δ 3.78 (d, J 1.9 Hz, 1H, 2- or 5-CH), 4.09 (d, J 1.7 Hz, 1H, 5- or 2-CH), 5.88 (dd, J 1.9 and 5.9 Hz, 1H, 3- or 4 CH), 6.05 (dd, J 1.7 and 5.9 Hz, 1H, 4- or 3-CH) and 6.13 (br, 2H, 9- and 10-CH) in addition to the peaks of the methyl group at δ 1.15 (s, 3H, 6- CH_3) and 3.50 (s, 3H, OCH_3). After irradiation for 60 min [Fig. 3(iii)], yields of adducts (**6a** and **2a**) increased; however, the ratio was reversed. Prolonged irradiation gave only cage compound **2a**. The 4 + 4 adduct **6a** was unstable; a solution irradiated for 1 h, subsequently followed by heating for 1 h at 80°C , showed the spectrum in Fig. 3(iv), which indicated that 4 + 4 adduct **6a** easily regenerated the starting pyridine **1a**. On the other hand, the cage product **2a** was stable under neutral conditions, and the same spectrum was observed after two weeks. The ^1H NMR spectrum of the crude photolysate did not show the peaks derived from tricycle **3a**. The adduct **3a** was not generated immediately after irradiation, whereas it was obtained in 16% yield after separation of the photoproducts by column chromatography on silica gel as shown in Table 1. These results strongly supported the contention that the adducts **3** are not

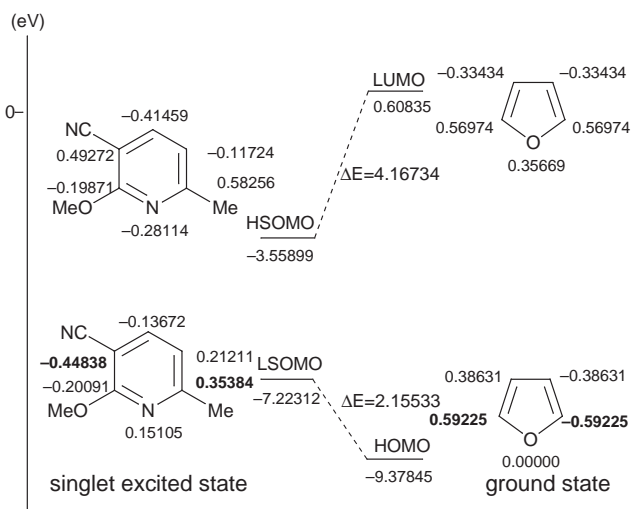


Fig. 4 Estimated energies and coefficients of 3-cyano-2-methoxy-6-methylpyridine **1a** and furan obtained from the PM3 Hamiltonian contained within the MOPAC program.

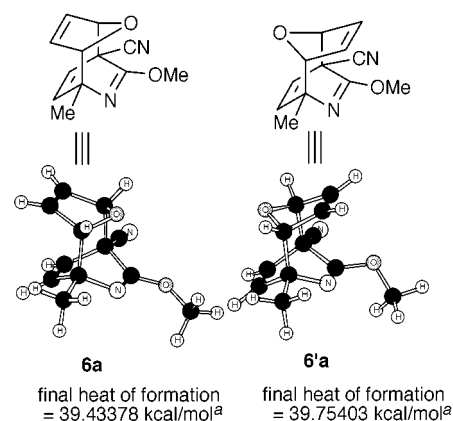


Fig. 5 Minimized conformation and the heat of formation of 4 + 4 adducts **6a** and **6'a**. a 1 Cal = 4.184 J.

photoproducts but are formed by acid-catalyzed ring opening of the cage adducts **2**.

The 4 + 4 cycloaddition was not quenched by triplet quenchers, such as 2,5-dimethylhexa-2,4-diene or penta-1,3-diene. These results indicate that the cycloaddition of the pyridine-furan system proceeds from its singlet excited state.

For the formation of 4 + 4 adduct **6**, a mechanism is postulated which involves $4\pi + 4\pi$ photocycloaddition between the C-3-C-6 positions of the pyridine ring and the C-2-C-4 positions of furan. The high selectivity for the addition is supported by Frontier-MO calculations using the PM3 Hamiltonian contained within the MOPAC program. The orbital energies and coefficients of the singlet excited state for substrate **1a** (HSOMO and LSOMO) and those of the ground state of furan (LUMO and HOMO) were obtained^{26,27} (Fig. 4). The energy gap (ΔE) between LSOMO and HOMO is smaller than that between HSOMO and LUMO, and this frontier orbital interaction is the most important in this photocycloaddition. The coefficients at the 3- and 6-position in the LSOMO of the singlet excited state of the pyridine ring and those at the 2- and 5-position of the HOMO in the ground state of furan are larger than those at any other positions. We conclude that the initial bond formation between the C-3-C-6 positions of the pyridine and the C-2-C-4 positions of the furan occurs and leads to intermediate **6a**.

There are two possible routes for 4 + 4 cycloadditions leading to intermediates **6** or **6'** (Fig. 5). What determines the diastereoselectivity? The final heat of formation of these two 4 + 4 adducts was calculated by the PM3 method contained

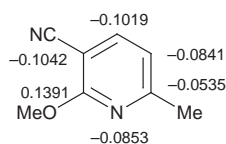


Fig. 6 Net atomic charges of the singlet excited state of pyridine **1a**.

within the MOPAC program. Each optimized structure and the final heat of formation are shown in Fig. 5. The ΔH -value of compound **6a** was 39.43378 kcal mol⁻¹, which is smaller than that of compound **6a'**, $\Delta H = 39.75403$ kcal mol⁻¹. This small difference is not sufficient to control the diastereoselectivity. Furthermore, the secondary overlapping effect of the orbital is considered; however, it is not an important factor in controlling the selectivity.²⁷ Gilbert and co-workers reported the photocycloaddition of furan to benzonitrile, and control of the diastereoselectivity was discussed in terms of the substituent stabilization of the developing polarity in the excited aromatic ring on approach of the addends.¹⁹ The net atomic charge of the singlet excited state of the pyridine **1a** was calculated by the PM3 method and is shown in Fig. 6. The pyridine has a strong positive charge at the 2-C position. In the formation of the 4 + 4 cycloadduct, control to give adduct **6** may be provided by the interaction of the lone pair on the oxygen of furan with the developing positive charge in the electronically excited pyridine.

In conclusion, we have provided the first example of a photochemical reaction of a bis-aromatic system, the pyridine–furan system, leading to three types of 1:1 cycloadducts. Attempted photoaddition of the 2-alkoxy-3-cyanopyridines **1** to thiophene and 1-methylpyrrole proved unsuccessful, and pyridine itself, 2-methoxypyridine and 3-cyanopyridine did not give any adducts. Only 2-alkoxy-3-cyanopyridines showed high photochemical reactivity toward cycloaddition; it seems that the polarization within the pyridine ring from the conjugative relationship of the cyano and alkoxy groups is the dominant feature and promotes the high reactivity of the 2,3-positions of the pyridine ring. We are continuing to explore the details and scope of the photochemical reaction of bis-aromatic systems containing heteroaromatics.

Experimental

General methods

NMR spectra were recorded on CDCl₃ solutions on a JEOL GSX-400 and Bruker-300, respectively, for ¹H- and ¹³C-NMR spectroscopy unless otherwise noted. Chemical shifts are reported in parts per million (ppm) relative to TMS as internal standard. Elemental analyses were made using a Perkin-Elmer-240 instrument. Ultraviolet (UV) spectra were determined with a JASCO model V-570 UV/VIS/NIR spectrophotometer. IR spectra were recorded on a JASCO FT/IR-230 spectrometer for samples as KBr disks, unless otherwise noted. An Eikohsya 500 W or a 1 kW high-pressure mercury lamp was used as irradiation source.

Preparation of alkylated 2-alkoxy-3-cyanopyridines **1a–e**

These pyridines were obtained by alkylation of the corresponding pyridones according to the method in the literature;^{28–31} They were also prepared from the corresponding 2-chloro-3-cyanopyridines according to the method in the literature by a substitution reaction with the corresponding sodium alkoxides.^{30,31}

3-Cyano-2-methoxy-6-methylpyridine 1a. Mp 87–88 °C; UV (C₆H₁₂) 231 (ε 10 100), 284 (8400), 289 (10 700), 294 (10 700) and 299 nm (9200); IR (CHCl₃) 2220 cm⁻¹; ¹H-NMR (CDCl₃) δ 2.51 (s, 3H, CH₃), 4.03 (s, 3H, OCH₃), 6.81 (d, *J* 7.7 Hz, 1H, 5-CH) and 7.73 (d, *J* 7.7 Hz, 1H, 4-CH); ¹³C-NMR (CDCl₃)

δ 23.7 (q, CH₃), 53.2 (q, OCH₃), 92.3 (s, 3-C), 114.7 (s, CN), 114.8 (d, 5-C), 141.7 (d, 4-C), 161.1 (s, 2-C) and 162.6 (s, 6-C) (Calc. for C₈H₈N₂O: C, 64.85; H, 5.44; N, 18.90%. Found: C, 64.96; H, 5.44; N, 18.94%).

3-Cyano-2-ethoxy-6-methylpyridine 1b. Mp 91–92 °C; UV (C₆H₁₂) 232 (ε 12 100), 290 (11 900), 295 (11 900) and 299 nm (9900); IR (CHCl₃) 2220 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.42 (t, *J* 7.1 Hz, 3H, CH₂CH₃), 2.49 (s, 3H, CH₃), 4.48 (q, *J* 7.1 Hz, 2H, OCH₂), 6.79 (d, *J* 7.4 Hz, 1H, 5-CH) and 7.73 (d, *J* 7.4 Hz, 1H, 4-CH); ¹³C-NMR (CDCl₃) δ 14.4 (q, CH₂CH₃), 24.8 (q, CH₃), 62.9 (q, OCH₂), 93.3 (s, 3-C), 115.6 (d, 5-C), 115.9 (s, CN), 142.8 (d, 4-C), 162.1 (s, 2-C) and 163.5 (s, 6-C) (Calc. for C₉H₁₀N₂O: C, 66.65; H, 6.21; N, 17.27%. Found: C, 66.66; H, 6.27; N, 17.30%).

3-Cyano-2-isopropoxy-6-methylpyridine 1c. Mp 40–41 °C; UV (C₆H₁₂) 232 (ε 9200), 286 (7100), 291 (8900), 296 (8900) and 302 nm (7400); IR (CHCl₃) 2220 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.37 (d, *J* 6.3 Hz, 6H, CH₃ × 2), 2.48 (s, 3H, CH₃), 5.44 (sep, *J* 6.3 Hz, 1H, OCH), 6.75 (d, *J* 7.7 Hz, 1H, 5-CH) and 7.70 (d, *J* 7.7 Hz, 1H, 4-CH); ¹³C-NMR (CDCl₃) δ 21.8 (q, CH₃ × 2), 24.8 (q, CH₃), 69.9 (d, OCH), 93.5 (s, 3-C), 115.2 (d, 5-C), 115.9 (s, CN), 142.8 (d, 4-C), 161.9 (s, 2-C) and 163.1 (s, 6-C) (Calc. for C₁₀H₁₂N₂O: C, 68.16; H, 6.86; N, 15.90%. Found: C, 67.98; H, 7.18; N, 15.83%).

3-Cyano-2-methoxy-4,6-dimethylpyridine 1d. Mp 94–95 °C; UV (C₆H₁₂) 234 (ε 11 500), 291 (12 200), 294 (10 600) and 338 nm (65); IR (CHCl₃) 2220 cm⁻¹; ¹H-NMR (CDCl₃) δ 2.44 (s, 3H, 4-CH₃), 2.45 (s, 3H, 6-CH₃), 4.01 (s, 3H, OCH₃) and 6.69 (s, 1H, 5-CH); ¹³C-NMR (CDCl₃) δ 20.0 (q, CH₃), 24.5 (q, CH₃), 54.2 (q, OCH₃), 93.8 (s, 3-C), 115.1 (s, CN), 117.4 (d, 5-C), 154.2 (s, 4-C), 160.6 (s, 2-C) and 164.3 (s, 6-C) (Calc. for C₉H₁₀N₂O: C, 66.65; H, 6.21; N, 17.27%. Found: C, 66.44; H, 6.26; N, 17.16%).

3-Cyano-2-methoxy-4,5,6-trimethylpyridine 1e. Mp 78–79 °C; UV (C₆H₁₂) 233 (ε 7700) and 297 nm (7800); IR (CHCl₃) 2220 cm⁻¹; ¹H-NMR (CDCl₃) δ 2.14 (s, 3H, 5-CH₃), 2.42 (s, 3H, 4-CH₃), 2.46 (s, 3H, 6-CH₃) and 3.98 (s, 3H, OCH₃); ¹³C-NMR (CDCl₃) δ 14.2 (q, 5-CH₃), 18.5 (q, 4-CH₃), 23.5 (q, 6-CH₃), 53.9 (q, OCH₃), 94.4 (s, 3-C), 115.7 (s, CN), 123.0 (s, 5-C), 152.0 (s, 4-C), 158.5 (s, 2-C) and 161.9 (s, 6-C) (Calc. for C₁₀H₁₂N₂O: C, 68.16; H, 6.86; N, 15.90%. Found: C, 68.27; H, 6.95; N, 15.94%).

General procedure for the photochemical reaction of 2-alkoxy-3-cyanopyridines **1a–e** in the presence of furan

A benzene solution of a 2-alkoxy-3-cyanopyridine (0.02 M) containing 0.1 M furan was deaerated by bubbling argon for 15 min and was irradiated by Pyrex-filtered light with a 1 kW high-pressure mercury lamp at 15–20 °C for 2 h. After irradiation, the solvent was removed *in vacuo* and the residual mixture was subjected to chromatography on silica gel (eluant: *n*-hexane–ethyl acetate 9:1). The crystalline photoproducts were recrystallized from a mixture of chloroform and hexane.

11-Cyano-10-methoxy-8-methyl-4-oxa-9-azapentacyclo-[5.4.0.0^{2,6}.0^{3,11}.0^{5,8}]undec-9-ene 2a. Mp 113–114 °C; IR (KBr) 2229 and 1645 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.48 (s, 3H, 8-CH₃), 2.46 (dddd, *J* 1.9, 2.9, 5.8 and 7.7 Hz, 1H, 7-CH), 3.18 (dddd, *J* 1.5, 2.9, 5.4 and 7.7 Hz, 1H, 1-CH), 3.55 (dddd, *J* 1.5, 4.8, 5.4 and 7.3 Hz, 1H, 6-CH), 3.82 (dddd, *J* 1.9, 2.9, 5.8 and 7.7 Hz, 1H, 2-CH), 3.83 (s, 3H, OCH₃), 4.47 (dd, *J* 2.9 and 4.8 Hz, 1H, 5-CH) and 4.91 (dd, *J* 2.9 and 5.3 Hz, 1H, 3-CH); ¹³C-NMR (CDCl₃) δ 26.0 (q, 8-CH₃), 35.9 (d, 1-C), 36.3 (d, 7-C), 40.0 (d, 6-C), 43.7 (s, 11-C), 43.9 (d, 2-C), 53.4 (q, OCH₃), 61.0 (s, 8-C), 82.6 (d, 3-C), 88.5 (d, 5-C), 118.1 (s, CN) and 159.6 (s, 10-C);

MS(FAB) m/z 217 (MH⁺) (Calc. for C₁₂H₁₂N₂O₂: C, 66.65; H, 5.59; N, 12.96%. Found: C, 66.46; H, 5.50; N, 12.83%).

10-Cyano-9-methoxy-7-methyl-5-oxa-8-azatricyclo[5.4.0.0^{2,6}]-undeca-3,8,10-triene 3a. Mp 100–101 °C; IR (KBr) 2224, 1675 and 1605 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.43 (s, 3H, CH₃), 3.07 (dddd, *J* 1.3, 3.0, 7.3 and 7.8 Hz, 1H, 2-CH), 3.79 (s, 3H, OCH₃), 3.86 (ddd, *J* 1.0, 5.5 and 7.8 Hz, 1H, 1-CH), 4.85 (dd, *J* 2.7 and 3.0 Hz, 1H, 3-CH), 4.95 (dd, *J* 1.0 and 7.3 Hz, 1H, 6-CH), 6.46 (dd, *J* 1.3 and 2.7 Hz, 1H, 4-CH) and 6.86 (d, *J* 5.5 Hz, 1H, 11-CH); ¹³C-NMR (CDCl₃) δ 29.8 (q, CH₃), 42.3 (d, 2-C), 48.3 (d, 1-C), 53.4 (q, OCH₃), 61.5 (s, 7-C), 90.8 (d, 6-C), 100.1 (d, 3-C), 106.2 (s, 10-C), 115.2 (s, CN), 149.8 (d, 4-C), 151.5 (d, 11-C) and 151.7 (s, 9-C); MS(FAB) m/z 217 (MH⁺) (Calc. for C₁₂H₁₂N₂O₂: C, 66.65; H, 5.59; N, 12.96%. Found: C, 66.51; H, 5.48; N, 12.78%).

3-Cyano-6-methoxy-2-methylpyridine **4a** was obtained as a mixture with the starting material **1a** and could not be isolated in a pure state; IR (KBr) 2220 and 1592 cm⁻¹; ¹H-NMR (CDCl₃) δ 2.66 (s, 3H, CH₃), 3.97 (s, 3H, OCH₃), 6.66 (d, *J* 8.5 Hz, 1H, 5-CH) and 7.69 (d, *J* 8.5 Hz, 1H, 4-CH); ¹³C-NMR (CDCl₃) δ 23.4 (q, CH₃), 54.0 (q, OCH₃), 101.1 (s, 3-C), 108.7 (d, 5-C), 115.9 (s, CN), 141.6 (d, 4-C), 161.8 (s, 6-C) and 164.6 (s, 2-C).

3,12-Dicyano-4,8-dimethoxy-1,6-dimethyl-5,9-diazatetracyclo[4.3.3.0^{2,7}.0^{3,10}]dodeca-4,8,11-triene 5a. Mp 150–151 °C; IR (CHCl₃) 1650 and 2200 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.82 (s, 3H, CH₃), 1.92 (s, 3H, CH₃), 2.74 (d, *J* 9.4 Hz, 1H, 7-CH), 3.24 (dd, *J* 4.7 and 9.4 Hz, 1H, 2-CH), 3.59 (dd, *J* 4.7 and 8.8 Hz, 1H, 10-CH), 3.77 (s, 3H, OCH₃), 3.89 (s, 3H, OCH₃) and 6.37 (d, *J* 8.8 Hz, 1H, 11-CH); ¹³C-NMR (CDCl₃) δ 24.5 (q, CH₃), 28.6 (q, CH₃), 33.0 (s, 1-C), 53.7 (d, 7-C), 54.0 (d, 2-C), 54.3 (d, 10-C), 54.5 (q, OCH₃), 56.9 (q, OCH₃), 59.4 (s, 3-C), 74.2 (s, 6-C), 116.3 (s, CN), 119.2 (s, CN), 127.1 (s, 12-C), 142.3 (d, 11-C), 157.8 (s, 4-C) and 177.2 (s, 8-C); MS(FAB) m/z 297 (MH⁺) (Calc. for C₁₆H₁₆N₄O₂: C, 64.85; H, 5.44; N, 18.90%. Found: C, 64.94; H, 5.45; N, 19.05%).

11-Cyano-10-ethoxy-8-methyl-4-oxa-9-azapentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{5,8}]undec-9-ene 2b. Mp 126–127 °C; IR (KBr) 2233 and 1647 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.35 (t, *J* 7.0 Hz, 3H, CH₂CH₃), 1.47 (s, 3H, 8-CH₃), 2.46 (dddd, *J* 1.9, 2.9, 5.8 and 7.7 Hz, 1H, 7-CH), 3.18 (dddd, *J* 1.5, 2.9, 5.4 and 7.7 Hz, 1H, 1-CH), 3.46 (dddd, *J* 1.5, 4.9, 5.4 and 7.3 Hz, 1H, 6-CH), 3.82 (dddd, *J* 1.9, 5.3, 5.4, 7.3 Hz, 1H, 2-CH), 4.14–4.34 (m, 2H, OCH₂), 4.46 (dd, *J* 2.9 and 4.9 Hz, 1H, 5-CH) and 4.91 (dd, *J* 2.9 and 5.1 Hz, 1H, 3-CH); ¹³C-NMR (CDCl₃) δ 19.3 (q, CH₂CH₃), 26.1 (q, 8-CH₃), 35.8 (d, 1-C), 36.2 (d, 7-C), 39.9 (d, 6-C), 43.8 (s, 11-C), 43.9 (d, 2-C), 60.9 (s, 8-C), 62.4 (q, OCH₂), 82.6 (d, 3-C), 88.6 (d, 5-C), 118.2 (s, CN) and 159.0 (s, 10-C); MS(FAB) m/z 231 (MH⁺) (Calc. for C₁₃H₁₄N₂O₂: C, 67.81; H, 6.13; N, 12.17%. Found: C, 67.68; H, 5.99; N, 12.16%).

10-Cyano-9-ethoxy-7-methyl-5-oxa-8-azatricyclo[5.4.0.0^{2,6}]-undec-3,8,10-triene 3b. Mp 95–96 °C; IR (KBr) 2226, 1667 and 1596 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.32 (t, 3H, OCH₂CH₃), 1.42 (s, 3H, CH₃), 3.05 (dddd, *J* 1.2, 2.7, 7.3 and 7.8 Hz, 1H, 2-CH), 3.87 (ddd, *J* 1.2, 5.5 and 7.8 Hz, 1H, 1-CH), 4.20 (m, 2H, OCH₂), 4.85 (t, *J* 2.7 Hz, 1H, 3-CH), 4.94 (dd, *J* 1.2 and 7.3 Hz, 1H, 6-CH), 6.46 (dd, *J* 1.2 and 2.7 Hz, 1H, 4-CH) and 6.84 (d, *J* 5.5 Hz, 1H, 11-CH); ¹³C-NMR (CDCl₃) δ 13.9 (q, OCH₂CH₃), 29.9 (q, CH₃), 42.2 (d, 2-C), 48.3 (d, 1-C), 61.5 (s, 7-C), 61.9 (t, OCH₂), 90.9 (d, 6-C), 100.1 (d, 3-C), 106.6 (s, 10-C), 115.2 (s, CN), 149.8 (d, 11-C), 151.0 (d, 4-C) and 151.2 (s, 9-C); MS(FAB) m/z 231 (MH⁺) (Calc. for C₁₃H₁₄N₂O₂: C, 67.81; H, 6.13; N, 12.17%. Found: C, 67.57; H, 6.09; N, 12.10%).

3-Cyano-6-ethoxy-1-methylpyridine **4b** was obtained as a mixture with the starting material **1b** and could not be isolated in a pure state; IR (KBr) 2221 and 1593 cm⁻¹; ¹H-NMR

(CDCl₃) δ 1.39 (t, *J* 6.2 Hz, 3H, OCH₂CH₃), 2.65 (s, 3H, CH₃), 4.36 (q, *J* 6.6 Hz, 2H, OCH₂), 6.60 (d, *J* 7.8 Hz, 1H, 5-CH) and 7.69 (d, *J* 7.8 Hz, 1H, 4-CH); ¹³C-NMR (CDCl₃) δ 14.4 (q, CH₃), 23.5 (q, CH₃), 62.6 (t, OCH₂), 100.7 (s, 3-C), 108.7 (d, 5-C), 117.8 (s, CN), 141.6 (d, 4-C), 161.8 (s, 6-C) and 164.9 (s, 2-C).

3,12-Dicyano-4,8-diethoxy-1,6-dimethyl-5,9-diazatetracyclo[4.3.3.0^{2,7}.0^{3,10}]dodeca-4,8,11-triene 5b. Mp 148–149 °C; IR (CHCl₃) 2200 and 1650 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.3–1.4 (m, 6H, CH₃), 1.81 (s, 3H, CH₃), 1.91 (s, 3H, CH₃), 2.72 (d, *J* 9.6 Hz, 1H, 7-CH), 3.20 (dd, *J* 4.6 and 9.6 Hz, 1H, 2-CH), 3.57 (dd, *J* 4.6 and 8.9 Hz, 1H, 10-CH), 4.0–4.4 (m, 4H, OCH₂) and 6.37 (d, *J* 8.9 Hz, 1H, 11-CH); ¹³C-NMR (CDCl₃) δ 13.8 (q, CH₂CH₃), 14.2 (q, CH₂CH₃), 24.6 (q, CH₃), 28.7 (q, CH₃), 33.2 (s, 1-C), 53.3 (d, 7-C), 53.8 (d, 2-C), 54.0 (d, 10-C), 59.3 (s, 3-C), 63.2 (t, OCH₂), 65.9 (t, OCH₂), 74.5 (s, 6-C), 116.5 (s, CN), 119.3 (s, CN), 127.2 (s, 12-C), 142.3 (d, 11-C), 157.2 (s, 4-C) and 176.4 (s, 8-C) (Calc. for C₁₈H₂₀N₄O₂: C, 66.64; H, 6.21; N, 17.30%. Found: C, 66.50; H, 6.20; N, 17.27%).

The dimeric structure was established by X-ray crystallographic analysis (see ref. 23).

11-Cyano-10-isopropoxy-8-methyl-4-oxa-9-azapentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{5,8}]undec-9-ene 2c. Mp 139–140 °C; IR (KBr) 2231 and 1645 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.26 (d, *J* 6.3 Hz, 3H, CHCH₃), 1.35 (d, *J* 6.3 Hz, 3H, CHCH₃), 1.45 (s, 3H, 8-CH₃), 2.45 (dddd, *J* 1.7, 2.9, 6.3 and 7.5 Hz, 1H, 7-CH), 3.16 (dddd, *J* 1.5, 2.9, 5.3 and 7.5 Hz, 1H, 1-CH), 3.46 (dddd, *J* 1.5, 5.1, 6.3 and 7.3 Hz, 1H, 6-CH), 3.80 (dtd, *J* 1.7, 5.3 and 7.3 Hz, 1H, 2-CH), 4.45 (dd, *J* 2.9 and 5.1 Hz, 1H, 5-CH) and 4.90 (dd, *J* 2.9 and 5.3 Hz, 1H, 3-CH) and 5.18 (sep, *J* 6.3 Hz, 1H, OCH); ¹³C-NMR (CDCl₃) δ 21.4 (q, CHCH₃), 21.6 (q, CHCH₃), 26.2 (q, 8-CH₃), 35.8 (d, 1-C), 36.1 (d, 7-C), 39.9 (d, 6-C), 44.0 (s, 11-C), 44.0 (d, 2-C), 60.9 (s, 8-C), 69.2 (d, OCH), 82.6 (d, 3-C), 88.6 (d, 5-C), 118.3 (s, CN) and 158.2 (s, 10-C); MS(FAB) m/z 245 (MH⁺) (Calc. for C₁₄H₁₆N₂O₂: C, 68.83; H, 6.60; N, 11.47%. Found: C, 68.68; H, 6.49; N, 11.35%).

10-Cyano-9-isopropoxy-7-methyl-5-oxa-8-azatricyclo[5.4.0.0^{2,6}]undeca-3,8,10-triene 3c. Mp 96–97 °C; IR (KBr) 2223, 1669 and 1607 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.29 (d, *J* 6.1 Hz, 3H, CH₃), 1.30 (d, *J* 6.1 Hz, 3H, CH₃), 1.39 (s, 3H, 7-CH₃), 3.04 (dddd, *J* 1.4, 2.9, 5.6 and 7.8 Hz, 1H, 2-CH), 3.86 (ddd, *J* 1.0, 5.6 and 7.8 Hz, 1H, 1-CH), 4.85 (t, *J* 2.9 Hz, 1H, 3-CH), 4.96 (dd, *J* 1.0 and 7.3 Hz, 1H, 6-CH), 5.09 (sep, *J* 6.1 Hz, 1H, OCHMe₂), 6.45 (dd, *J* 1.4 and 2.9 Hz, 1H, 4-CH) and 6.83 (d, *J* 5.6 Hz, 1H, 11-CH); ¹³C-NMR (CDCl₃) δ 21.2 (q, CH₃), 21.6 (q, CH₃), 30.0 (q, CH₃), 41.9 (d, 2-C), 48.3 (d, 1-C), 61.7 (s, 7-C), 68.6 (d, OCH), 90.1 (d, 6-C), 100.4 (d, 3-C), 106.8 (s, 10-C), 115.4 (s, CN), 149.8 (d, 11-C), 150.2 (s, 9-C) and 151.0 (d, 4-C); MS(FAB) m/z 245 (MH⁺) (Calc. for C₁₄H₁₆N₂O₂: C, 68.83; H, 6.60; N, 11.47%. Found: C, 68.63; H, 6.55; N, 11.47%).

3-Cyano-6-isopropoxy-1-methylpyridine **4c** was obtained as a mixture with the starting material **1c** and could not be isolated in a pure state; IR (KBr) 2221 and 1593 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.34 (d, *J* 6.3 Hz, 6H, 2 × CH₃), 2.64 (s, 3H, 2-CH₃), 5.39 (sep, *J* 6.3 Hz, 1H), 6.54 (d, *J* 8.5 Hz, 1H, 5-CH) and 7.67 (d, *J* 8.5 Hz, 1H, 4-CH); ¹³C-NMR (CDCl₃) δ 21.9 (q, CH₃), 23.7 (q, CH₃), 69.4 (d, OCH), 100.4 (s, 3-C), 109.3 (d, 5-C), 118.0 (s, CN), 141.7 (d, 4-C), 161.9 (s, 6-C) and 164.7 (s, 2-C).

3,12-Dicyano-4,8-diisopropoxy-1,6-dimethyl-5,9-diazatetracyclo[4.3.3.0^{2,7}.0^{3,10}]dodeca-4,8,11-triene 5c. Mp 132–133.0 °C; IR (CHCl₃) 1650 and 2200 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.25 (d, *J* 6.3 Hz, 3H, CH₃), 1.28 (d, *J* 6.3 Hz, 3H, CH₃), 1.32 (d, *J* 6.3 Hz, 3H, CH₃), 1.36 (d, *J* 6.3 Hz, 3H, CH₃), 1.80 (s, 3H, CH₃), 1.90 (s, 3H, CH₃), 2.67 (d, *J* 9.6 Hz, 1H, 7-CH), 3.17 (dd, *J* 4.4

and 9.6 Hz, 1H, 2-CH), 3.55 (dd, *J* 4.4 and 8.8 Hz, 1H, 10-CH), 4.99 (sep, *J* 6.3 Hz, 1H, OCH), 5.06 (sep, *J* 6.3 Hz, 1H, OCH) and 6.37 (d, *J* 8.8 Hz, 1H, 11-CH); ¹³C-NMR (CDCl₃) δ 21.3 (q, CH₃), 21.4 (q, CH₃), 21.4 (q, CH₃), 21.7 (q, CH₃), 24.7 (q, CH₃), 28.9 (q, CH₃), 33.4 (s, 1-C), 52.9 (d, 7-C), 53.8 (d, 2-C), 54.0 (d, 10-C), 59.2 (s, 3-C), 73.3 (d, OCH), 74.0 (d, OCH), 74.7 (s, 6-C), 116.6 (s, CN), 119.4 (s, CN), 127.4 (s, 12-C), 142.2 (d, 11-C), 156.5 (s, 4-C) and 175.5 (s, 8-C) (Calc. for C₂₀H₂₄N₄O₂: C, 68.16; H, 6.86; N, 15.90%. Found: C, 67.90; H, 7.12; N, 15.81%).

11-Cyano-10-methoxy-1,8-dimethyl-4-oxa-9-azapentacyclo-[5.4.0.0^{2,6}.0^{3,11}.0^{5,8}]undec-9-ene 2d. Mp 95–97 °C; IR (KBr) 2237 and 1651 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.40 (s, 3H, 1-CH₃), 1.46 (s, 3H, 8-CH₃), 2.15 (ddd, *J* 1.8, 2.7 and 4.8 Hz, 1H, 7-CH), 3.42 (ddd, *J* 4.8, 5.5 and 7.3 Hz, 1H, 6-CH), 3.49 (ddd, *J* 1.8, 5.5 and 7.3 Hz, 1H, 2-CH), 3.50 (s, 3H, OCH₃), 4.42 (dd, *J* 2.7 and 5.5 Hz, 1H, 5-CH) and 4.81 (d, *J* 5.5 Hz, 1H, 3-CH); ¹³C-NMR (CDCl₃) δ 20.0 (1-CH₃), 26.5 (q, 8-CH₃), 38.0 (d, 7-C), 41.7 (s, 11-C), 43.4 (d, 6-C), 47.6 (d, 2-C), 50.1 (s, 1-C), 54.2 (q, OCH₃), 60.6 (s, 8-C), 80.4 (d, 3-C), 88.5 (d, 5-C), 116.9 (s, CN) and 159.7 (s, 10-C); MS(FAB) *m/z* 231 (MH⁺) (Calc. for C₁₃H₁₄N₂O₂: C, 67.81; H, 6.13; N, 12.17%. Found: C, 67.58; H, 5.96; N, 11.98%).

10-Cyano-9-methoxy-7,11-dimethyl-5-oxa-8-azatricyclo-[5.4.0.0^{2,6}]undeca-3,8,10-triene 3d. Mp 126–127 °C; IR (CHCl₃) 2221 and 1607 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.41 (s, 3H, 7-CH₃), 1.98 (s, 3H, 11-CH₃), 2.91 (dd, *J* 1.0 and 7.8 Hz, 1H, 1-CH), 3.78 (s, 3H, OCH₃), 3.82 (dddd, *J* 1.2, 3.0, 7.3 and 7.8 Hz, 1H, 2-CH), 4.76 (dd, *J* 2.7 and 3.0 Hz, 1H, 3-CH), 4.90 (dd, *J* 1.0 and 7.3 Hz, 1H, 6-CH) and 6.44 (dd, *J* 1.2 and 2.7 Hz, 1H, 4-CH); ¹³C-NMR (CDCl₃) δ 21.1 (q, CH₃), 30.0 (q, CH₃), 47.2 (d, 2-C), 47.5 (d, 1-C), 53.5 (q, OCH₃), 61.8 (s, 7-C), 89.6 (d, 6-C), 98.9 (d, 3-C), 102.1 (s, 10-C), 114.6 (s, CN), 150.2 (d, 4-C), 151.5 (s, 11-C) and 162.7 (s, 9-C); MS(FAB) *m/z* 231 (MH⁺) (Calc. for C₁₃H₁₄N₂O₂: C, 67.81; H, 6.13; N, 12.17%. Found: C, 67.68; H, 6.02; N, 12.00%).

3-Cyano-2,4-dimethyl-6-methoxypyridine 4d. Mp 94–95 °C; IR (CHCl₃) 2220 cm⁻¹; ¹H-NMR (CDCl₃) δ 2.44 (s, 3H, CH₃), 2.64 (s, 3H, CH₃), 3.94 (s, 3H, CH₃) and 6.47 (s, 1H, 5-CH); ¹³C-NMR (CDCl₃) δ 20.3 (q, CH₃), 23.5 (q, CH₃), 53.8 (q, OCH₃), 102.5 (s, 3-C), 108.8 (d, 5-C), 117.0 (s, CN), 152.7 (s, 4-C), 161.8 (s, 6-C) and 165.1 (s, 2-C) (Calc. for C₉H₁₀N₂O: C, 66.65; H, 6.21; N, 17.27%. Found: C, 66.48; H, 6.20; N, 17.21%).

11-Cyano-10-methoxy-1,7,8-trimethyl-4-oxa-9-azapentacyclo-[5.4.0.0^{2,6}.0^{3,11}.0^{5,8}]undec-9-ene 2e. Mp 114–115 °C; IR (KBr) 2233 and 1654 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.06 (s, 3H, 7-CH₃), 1.34 (s, 3H, 1-CH₃), 1.38 (s, 3H, 8-CH₃), 3.15 (dd, *J* 5.3 and 7.5 Hz, 1H, 6-CH), 3.44 (dd, *J* 5.3 and 7.5 Hz, 1H, 2-CH), 3.81 (s, 3H, OCH₃), 4.35 (d, *J* 5.3 Hz, 1H, 5-CH) and 4.80 (d, *J* 5.3 Hz, 1H, 3-CH); ¹³C-NMR (CDCl₃) δ 13.0 (q, 7-CH₃), 16.7 (1-CH₃), 23.9 (q, 8-CH₃), 43.2 (s, 7-C), 43.3 (d, 6-C), 43.4 (s, 11-C), 46.3 (d, 2-C), 50.0 (s, 1-C), 53.7 (q, OCH₃), 62.2 (s, 8-C), 79.8 (d, 3-C), 86.9 (d, 5-C), 117.2 (s, CN) and 158.7 (s, 10-C); MS(FAB) *m/z* 245 (MH⁺) (Calc. for C₁₄H₁₆N₂O₂: C, 68.83; H, 6.60; N, 11.47%. Found: C, 68.65; H, 6.61; N, 11.32%).

10-Cyano-9-methoxy-1,7,11-trimethyl-5-oxa-8-azatricyclo-[5.4.0.0^{2,6}]undeca-3,8,10-triene 3e. Mp 101–102 °C; IR (KBr) 2222, 1677 and 1603 cm⁻¹; ¹H-NMR (CDCl₃) δ 1.38 (s, 3H, 1-CH₃), 1.39 (s, 3H, 7-CH₃), 2.00 (s, 3H, 11-CH₃), 3.44 (ddd, *J* 1.2, 2.7 and 7.6 Hz, 1H, 2-CH), 3.77 (s, 3H, OCH₃), 4.82 (t, *J* 2.7 Hz, 1H, 3-CH), 4.87 (d, *J* 7.6 Hz, 1H, 6-CH) and 6.43 (dd, *J* 1.2 and 2.7 Hz, 1H, 4-CH); ¹³C-NMR (CDCl₃) δ 19.2 (q, 1-CH₃), 20.4 (q, 7-CH₃), 25.1 (q, 11-CH₃), 47.9 (s, 1-C), 53.3 (d, 2-C), 56.5 (q, OCH₃), 63.6 (s, 7-C), 89.1 (d, 6-C), 100.1 (d, 3-C), 102.8 (s, 10-C), 115.0 (s, CN), 150.2 (d, 4-C), 152.3 (s, 11-C) and

166.7 (s, 9-C); MS(FAB) *m/z* 245 (MH⁺) (Calc. for C₁₄H₁₆N₂O₂: C, 68.83; H, 6.60; N, 11.47%. Found: C, 68.69; H, 6.63; N, 11.55%).

Photochemical reaction of 2-alkoxy-3-cyanopyridine 1a with furan in C₆D₆

A deuterated benzene solution of the 2-alkoxy-3-cyanopyridine **1a** (0.02 M) containing 0.2 M furan in an NMR tube was deaerated by bubbling argon for 10 min and was then irradiated with a 500 W high-pressure mercury lamp at 15–20 °C from 10 min to 1 h with monitoring by ¹H-NMR spectroscopy. After irradiation for 10 min, new peaks appeared assignable to 1-cyano-8-methoxy-6-methyl-11-oxa-7-azatricyclo[4.2.2.1^{2,5}]-undeca-3,7,9-triene **6a**. ¹H-NMR (C₆D₆) showed peaks at δ 1.15 (s, 3H, 6-CH₃), 3.50 (s, 1H, OCH₃), 3.78 (d, *J* 1.9 Hz, 1H, 2- or 5-CH), 4.09 (d, *J* 1.7 Hz, 1H, 5- or 2-CH), 5.88 (dd, *J* 1.9 and 5.9 Hz, 1H, 3- or 4-CH), 6.05 (dd, *J* 1.7 and 5.9 Hz, 1H, 4- or 3-CH) and 6.13 (br, 2H, 9- and 10-CH).

Frontier-MO calculations using the PM3 Hamiltonian

Frontier MO calculations were achieved by the PM3 method contained in the MOPAC program (version 6.601) available from Power Macintosh.^{26,27} The keywords GEO-OK, SINGLET, EXCITED, PM3, VECTOR, C.I.=4 and DENSITY, were added for calculation of the singlet excited state of 3-cyano-2-methoxy-6-methylpyridine **1a**. The keywords PM3, SYMMETRY, DENSITY and GEO-OK were used for the calculation of furan.

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