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Tetrahedron 60 (2004) 10887–10898

Photoreactions of β-aziridinylacrylonitriles and acrylates with alkenes: formation of head-to-head adducts and application to the preparation of pyrrolizidine alkaloid

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Received 3 July 2004; revised 10 September 2004; accepted 13 September 2004

Available online 1 October 2004

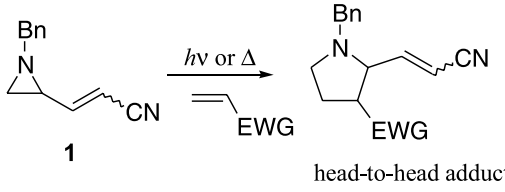
Abstract—The photochemical C,C-bond cleavage of *N*-benzyl β-aziridinylacrylonitrile **1** and acrylate **2** and the subsequent [3+2] cycloaddition with electron-deficient alkenes afforded head-to-head adducts selectively and efficiently. Irradiation of *N*-phenyl aziridine **3** with acrylonitrile gave adducts, but photoreaction of *N*-benzoyl aziridine **4** and thermal reactions of **3** and **4** with alkenes yielded C(γ),N-cleaved products instead of cycloadducts. *N*-trityl aziridine **5** also reacted with electron-deficient alkenes, affording 2,3-*cis*-pyrrolidine derivatives exclusively. A formal synthesis of a pyrrolizidine alkaloid, isoretronecanol (**27**), starting from **5** was achieved in a convenient manner.

1. Introduction

The 1,3-dipolar cycloaddition of azomethine ylides with alkenes is an important and useful strategy for the construction of nitrogen-containing five-membered heterocycles.[1] One of the method for the generation of azomethine ylide is the heating or irradiation of aziridines, most of which bear an adjacent electron-withdrawing or phenyl group.[2] However, mild and efficient methods for the C,C-bond cleavage of aziridines have not been widely studied.

We have investigated photochemical reactions of α,β-unsaturated γ,δ-epoxy nitriles systematically.[3] These studies have revealed that carbonyl ylides photochemically generated from epoxy nitriles undergo 1,3-diporlar cycloaddition with electron-rich alkenes to afford tetrahydrofurans.[3d] On the basis of these studies, we became interested in extending the photochemistry of epoxy nitriles to that of β-aziridinylacrylonitrile.

As part of these studies, we reported in a previous letter that direct irradiation or heating of β-aziridinylacrylonitrile **1** with electron-deficient alkenes causes the ring-opening of **1** and subsequent cycloaddition reactions, leading to head-to-head adducts selectively and efficiently (Scheme 1).[4] In this paper, we describe the details of the reactions of nitrile **1**, the photochemical behavior of β-aziridinylacrylate **2**, and the effects of N-substituents in the aziridine ring [*N*-phenyl, *N*-benzoyl and *N*-trityl aziridines **3**–**5** (Fig. 1)] on the cycloaddition with alkenes. Furthermore, we describe that using the cycloadducts **5**, the formal preparation of a pyrrolizidine alkaloid, isoretronecanol (**27**),[5] was achieved conveniently.



Scheme 1.

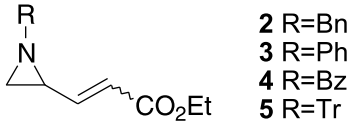


Figure 1.

Keywords: Aziridine; Photolysis; [3+2] Cycloaddition; Pyrrolidine; Pyrrolizidine.
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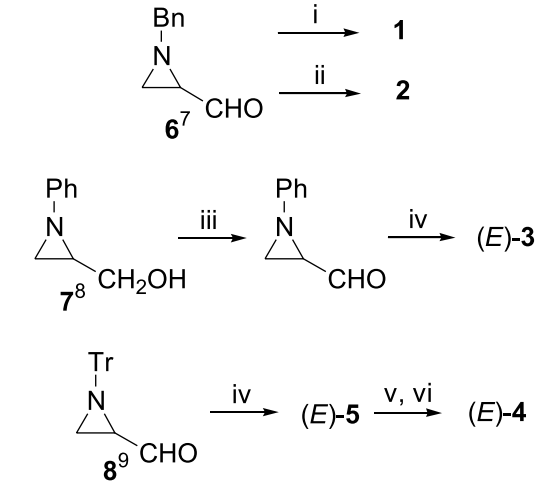
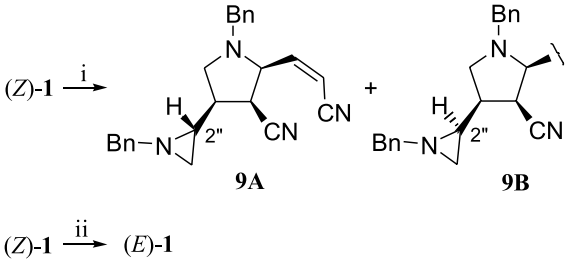
doi:10.1016/j.tet.2004.09.031

2. Results and discussion

The *N*-benzylnitrile **1** and ester **2** were prepared from aldehyde **6**[6] with diethyl cyanomethylphosphonate and diethyl ethoxycarbonylmethylphosphonate in 75% yield (*E*/*Z*=44:31) and 75% yield (*E*/*Z*=68:7), respectively. *N*-phenyl ester (*E*)-**3** and *N*-trityl ester (*E*)-**5** were synthesized from the corresponding alcohol **7**[7] and aldehyde **8**,[8] respectively, as shown in Scheme 2. *N*-Benzoyl ester (*E*)-**4** was prepared in 58% yield by the detritylation and benzoylation of (*E*)-**5** (Scheme 2).



Scheme 2. Reagents and conditions: (i) $(EtO)_2P(O)CH_2CN$, NaH, THF, 0 °C; (ii) $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF, 0 °C; (iii) oxalyl chloride, DMSO, CH_2Cl_2, −78 °C; (iv) $(EtO)_2P(O)CH_2CO_2Et$, NaH, CH_2Cl_2, 0 °C; (v) TFA, MeOH, $CHCl_3$; (vi) $(PhCO)_2O$, NEt_3, $CHCl_3$.



Scheme 3. Reagents and conditions: (i) $\lambda=254$ nm, acetonitrile, rt; (ii) $\lambda>280$ nm, acetone, rt.

Direct irradiation of a solution of (*Z*)-**1** in acetonitrile with a low-pressure mercury lamp in a quartz test tube at rt (conversion 83%) afforded dimers **9A** (32%[9]) and **9B** (14%) (Scheme 3). On triplet sensitization, the nitrile (*Z*)-**1** in acetone with a high-pressure mercury lamp in a Pyrex test tube at rt (conversion 58%) selectively underwent (*E*/*Z*)-isomerization of the side chain leading to (*E*)-**1** (64%[9]) (Scheme 3).

Since the photolysis of nitrile **1** had given cycloadducts **9** in moderate yield, the reactions of **1** and electron-deficient alkenes or an alkyne were studied. The results are summarized in Table 1 and Figure 2. No significant differences in reactivity between (*E*)- and (*Z*)-**1** were observed (entries 1–4).

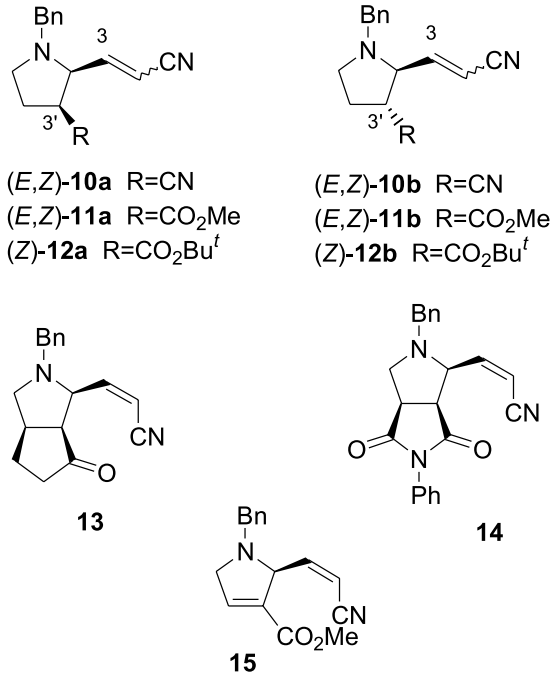


Figure 2.

Table 1. Photochemical and thermal reactions of aziridine **1** with alkenes or an alkyne[a]

Entry	(*E*)/(*Z*)-**1**	Alkene or alkyne	Reaction time (h)	Conversion (%)	Products and yields (%)[9,b]
1	(*E*)	Acrylonitrile	6	100	(*E*)-**10a** (52) and (*E*)-**10b** (26)
2	(*Z*)	Acrylonitrile	7	100	(*Z*)-**10a** (52) and (*Z*)-**10b** (15)
3	(*E*)	Methyl acrylate	2	87	(*E*)-**11a** (37) and (*E*)-**11b** (25)
4	(*Z*)	Methyl acrylate	4	98	(*Z*)-**11a** (38) and (*Z*)-**11b** (48)
5	(*Z*)	*tert*-Butyl acrylate	2 [3][c]	90 [86]	**12a** (23) [21] and **12b** (49) [13]
6	(*Z*)	2-Cyclopentenone	2.5	91	**13** (39)
7	(*Z*)	*N*-Phenylmaleimide	2 [2]	84 [81]	**14** (39) [42]
8	(*Z*)	Methyl propiolate	0.75	66	**15** (49)

[a] A 0.060 mol L^{-1} solution of **1** in acetonitrile with 10 equiv of alkene or alkyne was irradiated at rt.
[b] Isolated yield.
[c] Values in square brackets are yields of thermal reactions of **1** with 10 equiv of alkene in refluxing xylene.

The reactions **1** and mono-substituted alkenes selectively afforded 3-substituted pyrrolidines in moderate yields (62–86%[9]) (entries 1–5). The photoreactions of nitrile **1** and dimethyl fumarate or dimethyl acetylenedicarboxylate gave only dimethyl maleate and a complex mixture, respectively.

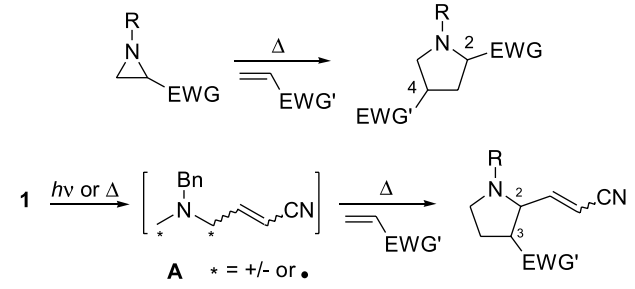


Figure 3.

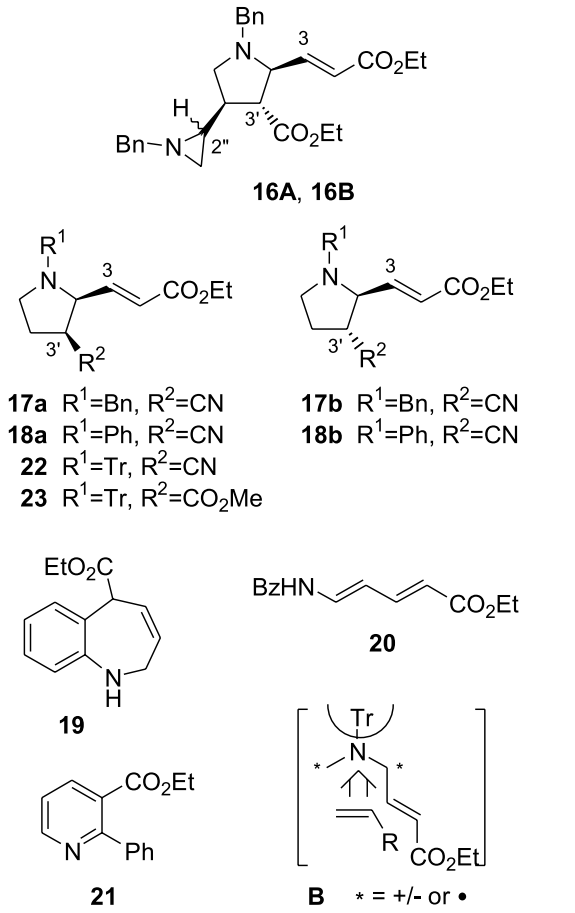


Figure 4.

On the other hand, the reactions of **1** and non-activated (bicyclo[2.2.1]hept-2-ene and cyclohexene) or electron-rich alkenes (ethyl vinyl ether) gave only dimers **9** instead of the adducts with alkenes.

The thermal 1,3-dipolar cycloaddition of an azomethine ylide derived from an aziridine bearing an ester function and electron-deficient alkenes normally affords products possessing the electron-withdrawing group (EWG) at the C(4) position in the pyrrolidine (Fig. 3).[2b] However, the position of the EWG in our cycloadducts was at C(3). In order to investigate the mechanism of the cycloaddition step between electron-deficient alkenes and ring-cleaved intermediate **A** (Fig. 3), thermal reactions of **1** and alkenes were performed. A solution of (*Z*)-**1** with *tert*-butyl acrylate or *N*-phenylmaleimide was heated in refluxing xylene and gave the same adducts **12** (**a** 21% and **b** 13%[9]) and **14** (42%[9]) as yielded by the photoreactions, respectively. The results may suggest that the C,C-bond cleavage of aziridine **1** proceeds photochemically or thermally and the cycloaddition occurs thermally.

We next investigated ethyl β-aziridinylacrylate **2** possessing an ester group, which is easily transformed to other functional groups. Direct irradiation of a solution of (*E*)-**2** in acetonitrile with a low-pressure mercury lamp in a quartz test tube at rt (conversion 98%) afforded dimers **16A** (19%[9]) and **16B** (7%[9]) (Fig. 4).

On triplet sensitization, ester (*E*)-**2** in acetone with a high-pressure mercury lamp in a Pyrex test tube at rt (conversion 84%) selectively underwent (*E*/*Z*)-isomerization of the side chain leading to (*Z*)-**2** (25%[9]).

Since the photochemical behavior of ester **2** was similar to that of nitrile **1**, the reactions of **2** and acrylonitrile were studied (Table 2, Fig. 4).

The structures of the cycloadducts **9**–**15** were deduced mainly on the basis of their spectral data and were discussed in the previous communication.[4] Particularly, in the ^{1}H NMR spectra of the *N*-benzyl pyrrolidines **9**–**12**, the signals due to H-(3′) for 2,3-*cis*-pyrrolidines appear in a lower field (δ 3.18–3.46) than those of 2,3-*trans*-pyrrolidines (δ 2.74–2.85) (Table 3).

The molecular ion peak in the mass spectrum (MS) of **17** indicates the 1:1 adducts of **2** and acrylonitrile. The regio- and stereochemistries of **17a** and **17b** were determined by the H–H and C–H COSY spectra. In particular, the configurations at the 2′,3′-positions of **17a** and **17b** were deduced from a comparison of the chemical shifts

Table 2. Photochemical reactions of aziridines **2**–**5** with alkenes[a]

Entry	Aziridine	Alkene	Reaction time (h)	Conversion (%)	Products and yields (%)[9,b]
1	(*E*)-**2**	Acrylonitrile	3	100	**17a** (42) and **17b** (21)
2	(*E*)-**3**	Acrylonitrile	2	52	**18a** (10) and **18b** (6)
3	(*E*)-**4**	Acrylonitrile	5	74	**20** (30)
4	(*E*)-**5**	Acrylonitrile	1.3	40	**22** (43)
5	(*E*)-**5**	Methyl acrylate	4	57	**23** (61)

[a] A 0.060 mol L^{-1} solution of **2**–**5** in acetonitrile with 10 equiv of alkene was irradiated at rt.
[b] Isolated yield.

Table 3. The chemical shift of H–C(3′) in the ^{1}H NMR spectra for **9–12**, **16** and **17**

cis-Adduct	δ	*trans*-Adduct	δ
(*E*)-**10a**	3.18–3.25 m	(*E*)-**10b**	2.82 ddd
(*Z*)-**10a**[a]	3.29 ddd	(*Z*)-**10b**[a]	2.85 ddd
(*E*)-**11a**[a]	3.20–3.28 m	(*E*)-**11b**	2.81 ddd
(*Z*)-**11a**[a]	3.29–3.37 m	(*Z*)-**11b**	2.83 ddd
12a[a]	3.18–3.24 m	**12b**[a]	2.74 ddd
17a	3.16–3.21 m	**17b**	2.84 ddd
9A[a]	3.46 dd	**16A**[a]	2.49 dd
9B[a]	3.36 dd	**16B**	2.62 dd

[a] The stereochemistry was also determined by phase-sensitive NOESY spectrum.

(δ 3.16–3.21 for **17a** and δ 2.84 for **17b**) with those of the compounds described in Table 3.

The molecular ion peak in the mass spectrum (MS) of **16A** and **16B** shows that they are the dimers of **2**. The regio- and stereochemistries of **16A** and **16B** were determined from the H–H and C–H COSY spectra and from a comparison of the spectral data with those of **9A** and **9B**. In particular, in the ^{1}H NMR spectrum, the 2′,3′-*trans* configuration in the pyrrolidine ring was deduced from a comparison of the chemical shifts at the 3′-position of **16A** (δ 2.49) and **16B** (δ 2.62) with the data described in Table 3. Furthermore, in the NOESY spectrum of **16A**, the cross-peaks showed 2′,3′-*trans* and 3′,4′-*trans* configurations in the pyrrolidine ring (Fig. 5). However, the stereochemistries at C(2″) for **16A** and **16B** could not be determined.

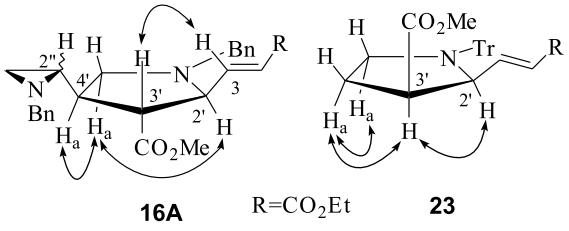


Figure 5. Phase-sensitive NOESY for **16A** and **23**.

As the photochemical reactions of *N*-benzyl aziridines **1** and **2** with electron-deficient alkenes afforded the cycloadducts in moderate yields, the effects of other N-substituents in the aziridine ring on the cycloaddition were studied. Aziridines substituted with phenyl or benzoyl groups, which possess stronger electron-withdrawing characteristics than the benzyl group, were supposed to react with electron-rich or non-activated alkenes.[2b]

Irradiation of a solution of (*E*)-**3** and acrylonitrile in acetonitrile with a low-pressure mercury lamp in a quartz test tube afforded the adducts **18a** and **18b** (Table 2, Fig. 4). The yields of adducts from **3** were reduced in comparison with those from the *N*-benzyl aziridine **2**. Aziridine (*E*)-**3** also did not react with electron-rich alkene (ethyl vinyl ether) photochemically giving a complex mixture. On the other hand, the thermal reaction of (*E*)-**3** and 3,4-dihydro-2*H*-pyran in refluxing xylene yielded no adducts but underwent an electrocyclic reaction leading to benzazepine **19** (Fig. 4). This type of rearrangement is also observed by thermal reaction[10] or treatment with silica gel[11] of 1-phenyl-2-vinylaziridines.

The structures of **18a** and **18b** were deduced from the chemical shifts for H–(C3′) in the ^{1}H NMR spectra in comparison with those of the adducts shown in Table 3; the signal (δ 3.28) for **18a** appears in a lower field than that for **18b** (δ 3.06–3.11). Furthermore, in the phase-sensitive NOESY spectrum of **18a** the crosspeak between H-2′ and H-3′ was observed. The structure of **19** was determined on the basis of its spectral data. In particular, the molecular ion peak in MS indicates that **19** is an isomer of **3**, and the ^{1}H NMR spectrum shows the signals due to four aromatic protons, two isolated alkenic protons and amino moiety (see Section 4).

An acetonitrile solution of **4** and acrylonitrile was irradiated with a low-pressure mercury lamp in a quartz test tube affording the C(γ),N-bond-cleaved product **20** (Table 2, Fig. 4). The thermal reaction of (*E*)-**4** and *tert*-butyl acrylate in refluxing xylene yielded no adducts but a mixture of C(γ),N-bond-cleaved compounds (mainly isomers of **20**) and pyridine derivative **21** (4%[9]) (Fig. 4).[12]

The structure of **20** was deduced from the spectral data (see Section 4). The structure of **21** was determined by a comparison of the spectral data with those of reference 12. The *N*-benzoyl substituent indicated a tendency to cleave the C(γ),N-bond on thermal and photochemical reactions.

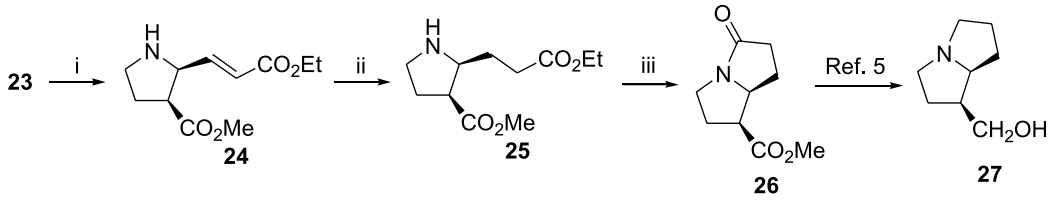
In order to improve the stereoselectivity at the 2,3-position of the pyrrolidine ring on the cycloaddition, we chose trityl group, which is more bulky than benzyl group, as the N-substituent of aziridine. Acetonitrile solutions of *N*-trityl aziridine **5** with acrylonitrile and methyl acrylate were irradiated with a low-pressure mercury lamp in quartz test tubes affording the adducts **22** and **23**, respectively (Table 2, Fig. 4).

The regio- and stereochemistries of **22** and **23** were determined by the H–H COSY and the phase-sensitive NOESY spectra. In particular, the crosspeaks between H-2′ and H-3′, between H-3′ and H_a-4′ and between H_a-4′ and H_a-5′ are observed in the NOESY spectra of **23** (Fig. 5).

In the case of the reaction of *N*-trityl aziridine **5**, the relative configuration between C(2′) and C(3′) in the isolated adducts was absolutely *cis*. In the transition state **B** for the formation of **22** and **23**, both the acrylate moiety of the aziridine-ring-cleaved intermediate and the substituent R of alkenes were presumably orientated on the opposite side of the trityl group because of the steric hindrance (Fig. 4).

Since the photolysis of *N*-trityl aziridine **5** and methyl acrylate gave 2,3-*cis*-pyrrolidine **23** in moderate yield, we were interested in the synthesis of a pyrrolizidine alkaloid, isoretronecanol (**27**), using the stereochemistry of **23**. Hydrogenolysis of the side chain in **23** over Pd/C gave no reduced product. After detritylation of **23** with trifluoroacetic acid, reduction of the double bond in **24** over Pd/C proceeded successfully, affording propionate **25** (64%). Cyclization of **25** in toluene gave pyrrolizidine **26**[5] in 87% yield, which can be transformed by authentic methods[5] into **27** (Scheme 4).

To clarify the chemical behavior and the utility of



Scheme 4. Reagents and conditions: (i) TFA, rt; (ii) 10% Pd/C, H_2 (1 bar), AcOEt; (iii) toluene, 110 °C.

β-aziridinylacrylates, further work with 2,3-disubstituted aziridines and the synthetic application of the cycloadducts is currently in progress.

3. Summary

In conclusion, the photoreactions of *N*-benzyl β-aziridinylacrylonitrile **1** and acrylate **2** with electron-deficient alkenes afforded novel head-to-head adducts selectively and efficiently. Aziridines **3** and **4**, possessing the N-conjugated substituent had a tendency to cleave the C(γ),N-bond. *N*-trityl aziridine **5** also reacted with electron-deficient alkenes, yielding 2,3-*cis*-pyrrolidine derivatives selectively. A formal synthesis of a pyrrolizidine alkaloid, isoretronecanol (**27**), starting from the pyrrolidine **23** was achieved in a convenient manner.

4. Experimental

4.1. General

Melting points and boiling points are uncorrected. Melting points were measured with a Yanaco MP-3 apparatus and boiling points were measured with a Büchi Kugel Rohr GKR-50 apparatus. UV spectra were recorded on a Hitachi 124 spectrometer and IR spectra on a Hitachi 215 spectrometer. NMR spectra were obtained with a JEOL JNM-AL300 (300 MHz; AL3), a JEOL JNM-AL400 (400 MHz; AL4) or JEOL JNM-LA500 (500 MHz; LA) spectrometers in $CDCl_3$ using tetramethylsilane as an internal standard. Mass spectra (MS) and high-resolution MS (HRMS) were taken on a JEOL JMS-700 spectrometer. Column chromatography was performed with Merck silica gel 60 (230–400 mesh) and Chromatorex NH (Fuji Silysia Chemical LTD.), and preparative TLC with Wakogel B-5F.

An Eikosha 60 W low-pressure mercury lamp and a Riko 400 W high-pressure mercury lamp were used for irradiation. The photolysis solutions were purged with argon both before and during irradiation.

4.2. Preparations of aziridines

4.2.1. (*E*)-3-(1-Benzylaziridin-2-yl)acrylonitrile (*E*)-1 and (*Z*)-3-(1-benzylaziridin-2-yl)acrylonitrile (*Z*)-1. To a suspension of NaH [1.48 g, 61.8 mmol; prepared from a NaH dispersion (60%, 2.47 g) by washing it twice with hexane (30 mL)] in dry THF (125 mL) was added dropwise a solution of diethyl cyanomethylphosphonate (10.9 g, 61.8 mmol) in dry THF (125 mL) at 0 °C. After the mixture had been stirred for 10 min at 0 °C, a solution of *N*-benzylaziridinecarbaldehyde **6**[6] (6.64 g, 41.2 mmol) in dry THF (40 mL) was added dropwise, and stirring was continued for 1.5 h at 0 °C. Ice/water was added to the mixture, and the organic phase was extracted with diethyl ether. The ethereal extract was washed with brine, dried with $MgSO_4$, and concentrated in vacuo, giving a residue that was subjected to flash column chromatography [hexane–ethyl acetate (9:1)] to afford (*E*)-**1** (3.30 g, 44%) and (*Z*)-**1** (2.34 g, 31%).

Compound (*E*)-**1**. Bp 130 °C at 0.35 mm Hg; IR (film): 2300 cm^{-1} (C≡N); ^1H NMR (AL4): δ 1.84 (d, 1H, J=6.4 Hz, H-3′), 1.92 (d, 1H, J=3.2 Hz, H-3′), 2.09–2.14 (m, 1H, H-2′), 3.47, 3.58 (each d, 2H, J=13.6 Hz, CH_2Ph), 5.59 (dd, 1H, J=16.4, 0.8 Hz, H-2), 6.55 (dd, 1H, J=16.4, 6.8 Hz, H-3), 7.26–7.42 (m, 5H, Ph); ^{13}C NMR (AL4): δ 37.7 (t, C-3′), 39.0 (d, C-2′), 64.0 (t, *C*H_2Ph), 99.8 (d, C-2), 117.1 (s, C-1), 127.2, 127.6 128.3 (3d, 5 C in Ph), 137.9 (s, C in Ph), 153.9 (d, C-3); EI-MS *m*/*z* 184 (M^+, 19%), 104 (4), 91 (100), 77 (3), 65 (10), 51 (3), 39 (7). Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.20%. Found: C, 78.01; H, 6.72; N, 14.85%.

Compound (*Z*)-**1**. An oil; IR ($CHCl_3$): 2220 cm^{-1} (C≡N); ^1H NMR (AL4): δ 1.94 (d, 1H, J=6.4 Hz, H-3′), 2.02 (d, 1H, J=3.6 Hz, H-3′), 2.56–2.62 (m, 1H, 2′-H), 3.46, 3.66 (each d, 2H, J=13.2 Hz, CH_2Ph), 5.39 (dd, 1H, J=10.8, 0.8 Hz, H-2), 6.10 (dd, 1H, J=16.4, 9.3 Hz, H-3), 7.26–7.42 (m, 5H, Ph); ^{13}C NMR (AL4): δ 36.1 (t, C-3′), 39.0 (d, C-2′), 64.1 (t, *C*H_2Ph), 99.7 (d, C-2), 115.6 (s, C-1), 127.2, 127.8, 128.3 (3d, 5C in Ph), 137.8 (s, C in Ph), 154.2 (d, C-3); EI-MS *m*/*z* 184 (M^+, 15%), 104 (4), 91 (100), 77 (3), 65 (9), 51 (3), 39 (6); HRMS calcd for $C_{12}H_{12}N_2$: 184.1000. Found: 184.1004.

4.2.2. Ethyl (*E*)-3-(1-benzylaziridin-2-yl)acrylate (*E*)-2 and ethyl (*Z*)-3-(1-benzylaziridin-2-yl)acrylate (*Z*)-2. By analogy with the synthesis of **1**, aldehyde **6** (6.79 g, 42.1 mmol) was treated with NaH (1.52 g, 63.2 mmol) and diethyl ethoxycarbonylmethylphosphonate (14.2 g, 63.2 mmol) in dry THF at 0 °C, and the resulting mixture was stirred for 1 h at 0 °C. Flash column chromatography [hexane–ethyl acetate (9:1)] of the reaction mixture afforded esters (*E*)-**2** (6.61 g, 68%) and (*Z*)-**2** (680 mg, 7%).

Compound (*E*)-**2**. An oil; IR (film): 1710 cm^{-1} (C=O); ^1H NMR (AL4): δ 1.27 (t, 3H, J=6.9 Hz, CH_3), 1.84 (d, 1H, J=6.6 Hz, H-3′), 1.95 (d, 1H, J=3.0 Hz, H-3′), 2.09–2.17 (m, 1H, H-2′), 3.51, 3.54 (each d, 2H, J=13.5 Hz, CH_2Ph), 4.18 (q, 2H, J=6.9 Hz, OCH_2), 6.05 (d, 1H, J=15.8 Hz, H-2), 6.69 (dd, 1H, J=15.8, 7.9 Hz, H-3), 7.24–7.34 (m, 5H, Ph); ^{13}C NMR (AL4): δ 14.3 (q, CH_3), 36.8 (t, C-3′), 39.3 (d, C-2′), 60.3, 64.3 (2t, O*C*H_2, *C*H_2Ph), 121.8 (d, C-2), 127.0, 127.6, 128.2 (3d, 5C in Ph), 138.3 (s, C in Ph), 147.8 (d, C-3), 165.8 (s, C-1); EI-MS *m*/*z* 231 (M^+, 2%), 186 (9),

158 (98), 140 (36), 112 (47), 96 (19), 91 (100), 83 (27); HRMS calcd for $C_{14}H_{17}NO_2$: 231.1259. Found: 231.1259.

Compound (*Z*)-**2**. An oil; IR (film): 1705 cm^{-1} (C═O); ^1H NMR (AL4): δ 1.30 (t, 3H, J=7.1 Hz, CH_3), 1.87 (d, 1H, J=6.6 Hz, H-3′), 1.92 (d, 1H, J=3.2 Hz, H-3′), 3.43, 3.65 (each d, 2H, J=13.4 Hz, CH_2Ph), 3.43–3.48 (m, 1H, H-2′), 4.20 (q, 2H, J=7.1 Hz, OCH_2), 5.80 (dd, 1H, J=11.5, 8.5 Hz, H-3), 5.86 (d, 1H, J=11.5 Hz, H-2), 7.24–7.34 (m, 5H, Ph); ^{13}C NMR (AL4): δ 14.4 (q, CH_3), 36.1 (t, C-3′), 37.4 (d, C-2′), 60.7, 64.2 (2t, OCH_2, CH_2Ph), 120.9 (d, C-2), 126.9, 127.8, 128.2 (3d, 5C in Ph), 138.5 (s, C in Ph), 149.7 (d, C-3), 166.2 (s, C-1); EI-MS *m*/*z* 231 (M^+, 3%), 186 (6), 158 (90), 140 (31), 112 (38), 96 (18), 91 (100), 83 (28); HRMS calcd for $C_{14}H_{17}NO_2$: 231.1259. Found: 231.1250.

4.2.3. Ethyl (*E*)-3-(1-phenylaziridin-2-yl)acrylate 3. To a solution of oxalyl chloride (410 mg, 3.2 mmol) in dry CH_2Cl_2 (7.0 mL) was added dropwise a solution of DMSO (440 mg, 5.6 mmol) in dry CH_2Cl_2 (7.0 mL) at −70 °C. After the mixture had been stirred for 20 min at −70 °C, a solution of alcohol **7**[7] (404 mg, 2.8 mmol) in dry CH_2Cl_2 (5.0 mL) was added dropwise, and stirring was continued for 15 min at −70 °C. Triethylamine (1.9 mL, 14 mmol) was added slowly to the reaction mixture, which was stirred for 10 min at −70 °C, warmed to 0 °C and further stirred for 2 h. Water was added to the mixture, and the organic phase was extracted with CH_2Cl_2. The organic extract was washed with brine, dried with $MgSO_4$, and concentrated in vacuo, giving a aldehyde that was used for the next step without further purification. By analogy with the synthesis of **1**, the aldehyde (1.03 g, 7.0 mmol) was treated with NaH (202 mg, 8.4 mmol) and diethyl ethoxycarbonylmethylphosphonate (1.88 g, 8.4 mmol) in dry CH_2Cl_2 at 0 °C, and the resulting mixture was stirred for 10 min at 0 °C. Flash column chromatography [hexane–ethyl acetate (3:1)] of the reaction mixture afforded ester (*E*)-**3** (679 mg, 45%). An oil; IR (film): 1710 cm^{-1} (C═O); ^1H NMR (AL3): δ 1.29 (t, 3H, J=7.2 Hz, CH_3), 2.35 (d, 1H, J=3.3 Hz, H-3′), 2.42 (d, 1H, J=6.3 Hz, H-3′), 2.70–2.77 (m, 1H, H-2′), 4.21 (q, 2H, J=7.2 Hz, OCH_2), 6.19 (d, 1H, J=15.6 Hz, H-2), 6.78 (dd, 1H, J=15.6 Hz, 7.8, H-3), 6.95–7.05, 7.21–7.29 (m, 5H, Ph); ^{13}C NMR (AL4): δ 14.3 (q, CH_3), 35.9 (t, C-3′), 39.6 (d, C-2′), 60.4 (t, OCH_2), 120.3, 122.7, 128.8 (3d, 5C in Ph), 122.5 (d, C-2), 146.7 (d, C-3), 152.9 (s, C in Ph), 165.6 (s, C-1); EI-MS *m*/*z* 217 (M^+, 16%), 172 (6), 144 (100), 112 (13), 104 (13), 91 (6), 84 (14), 77 (20), 51 (5); HRMS calcd for $C_{15}H_{15}NO_2$: 217.1103. Found: 217.1104.

4.2.4. Ethyl (*E*)-3-(1-tritylaziridin-2-yl)acrylate (*E*)-5. By analogy with the synthesis of **1**, aldehyde **8**[8] (4.0 g, 12.8 mmol) was treated with NaH (460 mg, 19 mmol) and diethyl ethoxycarbonylmethylphosphonate (4.3 g, 19 mmol) in dry CH_2Cl_2 at 0 °C, and the resulting mixture was stirred for 10 min at 0 °C. Flash column chromatography [hexane–ethyl acetate (9:1)] of the reaction mixture afforded ester (*E*)-**5** (4.26 g, 87%). Colorless crystals; mp 82–83 °C (hexane–ethyl acetate); IR ($CHCl_3$): 1710 cm^{-1} (C═O); ^1H NMR (AL4): δ 1.29 (t, 3H, J=7.3 Hz, CH_3), 1.48 (d, 1H, J=6.4 Hz, H-3′), 1.80–1.85 (m, 1H, H-2′), 1.92 (d, 1H, J=2.4 Hz, H-3′), 4.20 (q, 2H, J=7.3 Hz, OCH_2), 6.04 (d, 1H, J=15.6 Hz, H-2), 6.94 (dd, 1H, J=15.6, 8.0 Hz, H-3), 7.18–7.45 (m, 9H, Ph), 7.47 (d, 6H, J=1.2 Hz, Ph); ^{13}C NMR (AL4): δ 14.4 (q, CH_3), 30.8 (t, C-3′), 33.2 (d, C-2′), 60.3 (t, OCH_2), 74.4 (s, CPh_3) 121.9 (d, C-2), 127.2, 127.4, 129.0 (3d, 15C in Ph), 143.8 (s, 3C in Ph), 149.0 (d, C-3), 166.0 (s, C-1); EI-MS *m*/*z* 383 (M^+, 0.1%), 257 (4), 243 (100), 228 (8), 215 (4), 180 (3), 165 (52), 154 (2), 115 (2), 91 (3), 77 (4). Anal. Calcd for $C_{26}H_{25}NO_2$: C, 81.43; H, 6.57; N, 3.65%. Found: C, 81.30; H, 6.50; N, 3.59%.

4.2.5. Ethyl (*E*)-3-(1-benzoylaziridin-2-yl)acrylate (*E*)-4. To a solution of **5** (897 mg, 2.34 mmol) in $CHCl_3$ (2.3 mL) and MeOH (1.8 mL) was added dropwise trifluoroacetic acid (3.5 mL) at 0 °C. After the mixture had been stirred for 30 min at 0 °C, water was added to the mixture, and the organic phase was extracted with $CHCl_3$. The organic extract was washed with sat. aqueous $NaHCO_3$ solution and brine, dried with Na_2SO_4, and concentrated in vacuo. To a solution of the residue (236 mg) in $CHCl_3$ (3 mL) was added triethylamine (0.47 mL) and then benzoic anhydride (378 mg, 1.67 mmol) at 0 °C. After the mixture had been stirred for 2 h at 0 °C, water was added to the mixture, the organic phase was extracted with $CHCl_3$. The extract was subjected to the same workup as used for the synthesis of **1**. The residue was subjected to flash column chromatography [hexane–ethyl acetate (3:1)] to yield ester (*E*)-**4** (334 mg, 58% from **5**). A colorless oil; IR (film): 1710 cm^{-1} (C═O); ^1H NMR (AL4): δ 1.31 (t, 3H, J=7.2 Hz, CH_3), 2.43 (d, 1H, J=3.2 Hz, H-3′), 2.85 (d, 1H, J=5.6 Hz, H-3′), 3.11–3.17 (m, 1H, H-2′), 4.22 (q, 2H, J=7.2 Hz, OCH_2), 6.21 (d, 1H, J=16.0 Hz, H-2), 6.74 (dd, 1H, J=16.0, 8.0 Hz, H-3) 7.45 (t, 2H, J=7.6 Hz, Ph), 7.54–7.59 (m, 1H, Ph), 7.99 (d, 2H, J=7.6 Hz, Ph); ^{13}C NMR (AL4): δ 14.3 (q, CH_3), 33.6 (t, C-3′), 38.0 (d, C-2′), 60.7 (t, OCH_2), 124.4 (d, C-2), 128.4, 129.0, 132.9 (3d, 5C in Ph), 132.3 (s, C in Ph), 144.0 (d, C-3), 165.3 (s, C-1), 177.9 (s, NC═O); EI-MS *m*/*z* 245 (M^+, 7%), 200 (2), 140 (3), 117 (20), 105 (100), 95 (2), 77 (22), 51 (3); HRMS calcd for $C_{14}H_{15}NO_3$: 245.1052. Found: 245.1053.

4.3. Irradiation of acrylonitrile 1

4.3.1. (2*Z*,2′*RS*,3′*RS*,4′*SR*,2″*SR*)-3-[1-Benzyl-4-(1-benzylaziridin-2-yl)-3-cyanopyrrolidin-2-yl]acrylonitrile 9A and (2*Z*,2′*RS*,3′*RS*,4′*SR*,2″*RS*)-3-[1-Benzyl-4-(1-benzylaziridin-2-yl)-3-cyanopyrrolidin-2-yl]acrylonitrile 9B. A solution of (*Z*)-**1** (733 mg, 3.98 mmol) in acetonitrile (66 mL) was irradiated with a low-pressure mercury lamp in a quartz test tube (conversion 83%) for 6.5 h at rt. After removal of the solvent, flash column chromatography [hexane–ethyl acetate (7:3)] of the residue afforded dimers **9A** (197 mg, 32%) and **9B** (83.8 mg, 14%).[9]

Compound **9A**. Colorless crystals, mp 113–114 °C (hexane/ethyl acetate); IR ($CHCl_3$): 2240, 2230 cm^{-1} (C≡N); ^1H NMR (LA): δ 1.65 (d, 1H, J=6.1 Hz, H-3″), 1.75 (d, 1H, J=3.4 Hz, H-3″), 1.84–1.89 (m, 1H, H-2″), 1.96–2.02 (m, 1H, H-4′), 2.45 (dd, 1H, J=10.1, 7.9 Hz, H-5′), 2.73 (dd, 1H, J=10.1, 4.3 Hz, H-5′), 3.31, 3.50 (each d, 2H, J=12.8 Hz, 1″-CH_2Ph), 3.36 (dd, 1H, J=8.5, 7.0 Hz, H-3′), 3.40, 3.69 (each d, 2H, J=13.4 Hz, 1′-CH_2Ph), 3.72 (dd, 1H, J=9, 7.0 Hz, H-2′), 5.53 (dd, 1H, J=11.0, 0.6 Hz, H-2), 6.59 (dd, 1H, J=11.0, 9.2 Hz, H-3), 7.16–7.33 (m, 10H, Ph); ^{13}C NMR (LA): δ 33.9 (t, C-3″), 37.5 (d, C-3′),

40.5 (d, C-2″), 42.5 (d, C-4′), 56.0 (t, C-5′), 57.1 (t, 1′-*C*H$_2$Ph), 64.5 (t, 1″-*C*H$_2$Ph), 65.0 (d, C-2′), 103.6 (d, C-2), 114.9, 116.9 (2s, C-1, CN), 127.3, 127.4, 128.29, 128.31, 128.4, 128.5 (6d, 10C in Ph), 137.4, 138.6 (2s, 2C in Ph), 151.9 (d, C-3); EI-MS *m/z* 368 (M^+, 0.9%), 277 (4), 261 (12), 210 (23), 158 (8), 120 (27), 91 (100), 65 (5). Anal. Calcd for $C_{24}H_{24}N_4$: C, 78.23; H, 6.57; N, 15.20%. Found: C, 78.17; H, 6.63; N, 15.10%.

Compound **9B**. Colorless crystals, mp 58–60 °C (hexane/ethyl acetate); IR ($CHCl_3$): 2260, 2240 cm^{-1} (C≡N); ^1H NMR (LA): δ 1.48 (d, 1H, *J*=6.1 Hz, H-3″), 1.68 (d, 1H, *J*=3.4 Hz, H-3″), 1.85–1.89 (m, 1H, H-2″), 2.11–2.18 (m, 1H, H-4′), 2.49 (dd, 1H, *J*=10, 9.2 Hz, H-5′), 2.98 (ddd, 1H, *J*=10, 5.2, 4.9 Hz, H-5′), 3.07, 4.03 (each d, 2H, *J*=13.4 Hz, 1″-C*H*$_2$Ph), 3.40, 3.83 (each d, 2H, *J*=13.4 Hz, 1′-C*H*$_2$Ph), 3.46 (dd, 1H, *J*=8, 6.1 Hz, H-3′), 3.75 (dd, 1H, *J*=9.2, 6.1 Hz, H-2′), 5.59 (dd, 1H, *J*=11.0, 0.6 Hz, H-2), 6.65 (dd, 1H, *J*=11.0, 9.2 Hz, H-3), 7.25–7.33 (m, 10H, Ph); ^{13}C NMR (LA): δ 33.4 (t, C-3″), 38.8 (d, C-3′), 40.0 (d, C-2″), 43.1 (d, C-4′), 54.4 (t, C-5′), 57.3 (t, 1′-*C*H$_2$Ph), 64.2 (t, 1″-*C*H$_2$Ph), 65.3 (d, C-2′), 104.0 (d, C-2), 114.8, 117.4 (2s, C-1, CN), 127.1, 127.5, 128.1, 128.38, 128.43, 128.44 (6d, 10C in Ph), 137.5, 138.6 (2s, 2C in Ph), 151.9 (d, C-3); EI-MS *m/z* 368 (M^+, 0.8%), 277 (4), 261 (15), 210 (31), 158 (6), 120 (31), 91 (100), 65 (5); HRMS calcd for $C_{24}H_{24}N_4$: 368.2001. Found: 368.2007.

4.3.2. Triplet sensitization of 1. A solution of (*Z*)-**1** (794 mg, 4.31 mmol) in acetone (80 mL) was irradiated with a high-pressure mercury lamp in a Pyrex test tube (conversion 58%) for 20 h at rt. After removal of the solvent, flash column chromatography [hexane–ethyl acetate (7:3)] of the residue afforded (*E*)-**1** (295 mg, 64%[9]).

4.4. General procedure for the irradiation of acrylonitrile 1 with various alkenes

A 0.060 mol L^{-1} solution of (*E*)- or (*Z*)-**1** in dry acetonitrile with 10 equiv of alkene was irradiated with a low-pressure mercury lamp in a quartz test tube at 0 °C. After removal of the solvent, flash column chromatography afforded the adducts. The results are summarized in Table 1.

4.4.1. (2*E*,2′*RS*,3′*RS*)-3-(1-Benzyl-3-cyanopyrrolidin-2-yl)acrylonitrile (*E*)-10a. An oil; IR ($CHCl_3$): 2240 cm^{-1} (C≡N); ^1H NMR (AL4): δ 2.04–2.20, 2.21–2.30 (each m, 2H, H_2-4′), 2.37–2.43 (m with td character, 1H, *J*=9.5, 7 Hz, H-5′), 3.13 (ddd, 1H, *J*=9.5, 7.0, 2.9 Hz, H-5′), 3.18–3.25 (m, 1H, H-3′), 3.34–3.39 (m, 1H, overlapped with d at δ 3.36, H-2′), 3.36, 3.86 (each d, 2H, *J*=13.6 Hz, 1′-C*H*$_2$Ph), 5.77 (dd, 1H, *J*=16.1, 1.1 Hz, H-2), 6.78 (dd, 1H, *J*=16.1, 7.3 Hz, H-3), 7.24–7.38 (m, 5H, Ph); ^{13}C NMR (AL4): δ 28.5 (t, C-4′), 33.4 (d, C-3′), 51.6 (t, C-5′), 57.5 (t, 1′-*C*H$_2$Ph), 65.5 (d, C-2′), 103.7 (d, C-2), 116.2, 118.8 (2s, C-1, CN), 127.2, 128.17, 128.20 (3d, 5C in Ph), 137.1 (s, C in Ph), 151.1 (d, C-3); EI-MS *m/z* 237 (M^+, 30%), 197 (6), 184 (17), 160 (5), 146 (8), 91 (100), 65 (9); HRMS calcd for $C_{15}H_{15}N_3$: 237.1266. Found: 237.1271.

4.4.2. (2*E*,2′*RS*,3′*SR*)-3-(1-Benzyl-3-cyanopyrrolidin-2-yl)acrylonitrile (*E*)-10b. An oil; IR ($CHCl_3$): 2220 cm^{-1} (C≡N); ^1H NMR (AL4): δ 2.07–2.16, 2.20–2.30 (each m, 2H, H_2-4′), 2.47–2.55 (m with q character, 1H, *J*=9 Hz, H-5′), 2.82 (ddd, 1H, *J*=10.3, 7.7, 5.9 Hz, H-3′), 3.08 (ddd, 1H, *J*=9.5, 8, 2.9 Hz, H-5′), 3.32 (t, 1H, *J*=7.7 Hz, H-2′), 3.37, 3.86 (each d, 2H, *J*=12.8 Hz, 1′-C*H*$_2$Ph), 5.77 (dd, 1H, *J*=16.1, 0.7 Hz, H-2), 6.58 (dd, 1H, *J*=16.1, 7.7 Hz, H-3), 7.23–7.38 (m, 5H, Ph); ^{13}C NMR (AL4): δ 27.8 (t, C-4′), 34.0 (d, C-3′), 52.0 (t, C-5′), 57.9 (t, 1′-*C*H$_2$Ph), 69.6 (d, C-2′), 103.5 (d, C-2), 116.0, 119.8 (2s, C-1, CN), 127.5, 128.3, 128.4 (3d, 5C in Ph), 137.0 (s, C in Ph), 151.9 (d, C-3); EI-MS *m/z* 237 (M^+, 27%), 197 (6), 184 (16), 160 (6), 146 (10), 91 (100), 65 (9); HRMS calcd for $C_{15}H_{15}N_3$: 237.1266. Found: 237.1270.

4.4.3. (2*Z*,2′*RS*,3′*RS*)-3-(1-Benzyl-3-cyanopyrrolidin-2-yl)acrylonitrile (*Z*)-10a. Colorless crystals; mp 105–106 °C (hexane–ethyl acetate); IR ($CHCl_3$): 2230, 2210 cm^{-1} (C≡N); ^1H NMR (LA): δ 2.16–2.24, 2.25–2.30 (each m, 2H, H_2-4′), 2.31–2.36, 3.12–3.16 (each m, 2H, H_2-5′), 3.29 (ddd, 1H, *J*=8.8, 7.3, 5.5 Hz, H-3′), 3.43, 3.83 (each d, 2H, *J*=13.4 Hz, 1′-C*H*$_2$Ph), 3.68 (dd, 1H, *J*=9.2, 7.3 Hz, H-2′), 5.59 (dd, 1H, *J*=11.0, 0.6 Hz, H-2), 6.61 (dd, 1H, *J*=11.0, 9.2 Hz, H-3), 7.24–7.36 (5H, m, Ph); ^{13}C NMR (LA): δ 28.5 (t, C-4′), 33.3 (d, C-3′), 51.8 (t, C-5′), 57.4 (t, 1′-*C*H$_2$Ph), 64.9 (d, C-2′), 103.8 (d, C-2), 114.9, 119.3 (2s, C-1, CN), 127.5, 128.4, 128.6 (3d, 5C in Ph), 137.5 (s, C in Ph), 151.9 (d, C-3); EI-MS *m/z* 237 (M^+, 35%), 197 (5), 184 (20), 160 (7), 146 (10), 91 (100), 65 (9). Anal. Calcd for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71%. Found: C, 75.71; H, 6.48; N, 17.61%.

4.4.4. (2*Z*,2′*RS*,3′*SR*)-3-(1-Benzyl-3-cyanopyrrolidin-2-yl)acrylonitrile (*Z*)-10b. A colorless oil; IR ($CHCl_3$): 2260, 2240 cm^{-1} (C≡N); ^1H NMR (LA): δ 2.12–2.19, 2.26–2.35 (each m, 2H, H_2-4′), 2.48–2.55 (m with q character, 1H, *J*=9 Hz, H-5′), 2.85 (ddd, 1H, *J*=10.1, 8.9, 6.7 Hz, H-3′), 3.05–3.10 (m with td character, 1H, *J*=9, 3 Hz, H-5′), 3.44, 3.83 (each d, 2H, *J*=12.8 Hz, 1′-C*H*$_2$Ph), 3.75 (dd, 1H, *J*=9.5, 8.9 Hz, H-2′), 5.56 (d, 1H, *J*=11.0 Hz, H-2), 6.28 (dd, 1H, *J*=11.0, 9.5 Hz, H-3), 7.25–7.33 (m, 5H, Ph); ^{13}C NMR (LA): δ 27.8 (t, C-4′), 33.6 (d, C-3′), 52.1 (t, C-5′), 57.8 (t, 1′-*C*H$_2$Ph), 68.3 (d, C-2′), 104.2 (d, C-2), 114.7, 119.5 (2s, C-1, CN), 127.6, 128.4, 128.7 (3d, 5C in Ph), 137.5 (s, C in Ph), 151.2 (d, C-3); EI-MS *m/z* 237 (M^+, 35%), 197 (7), 184 (17), 160 (8), 146 (14), 91 (100), 65 (10); HRMS calcd for $C_{15}H_{15}N_3$: 237.1266. Found: 237.1270.

4.4.5. Methyl (2*RS*,3*RS*)-1-benzyl-2-[(*E*)-2-cyanovinyl]-pyrrolidine-3-carboxylate (*E*)-11a. An oil; IR ($CHCl_3$): 2210 (C≡N), 1725 cm^{-1} (C=O); ^1H NMR (AL4): δ 1.95–2.14, 2.15–2.26 (each m, 2H, H_2-4), 2.40–2.47 (m with td character, 1H, *J*=9.5, 6 Hz, H-5), 3.04–3.10 (m with ddd character, 1H, *J*=9, 7.5, 2 Hz, H-5), 3.20–3.28 (m with q character, 1H, *J*=9 Hz, H-3), 3.41, 3.80 (each d, 2H, *J*=13.2 Hz, 1-C*H*$_2$Ph), 3.51 (ddd, 1H, *J*=9.2, 7.0, 1.1 Hz, H-2), 3.68 (s, 3H, OCH_3), 5.53 (dd, 1H, *J*=16.1, 1.1 Hz, H-2′), 6.78 (dd, 1H, *J*=16.1, 7.0 Hz, H-1′), 7.24–7.35 (m, 5H, Ph); ^{13}C NMR (AL3): δ 26.7 (t, C-4), 48.1 (d, C-3), 52.0 (q, OCH_3), 52.4 (t, C-5), 58.1 (t, 1-*C*H$_2$Ph), 66.0 (d, C-2), 101.6 (d, C-2′), 116.9 (s, CN), 127.2, 128.3, 128.4 (3d, 5C in Ph), 137.9 (s, C in Ph), 152.8 (d, C-1′), 171.8 (s, CO_2); EI-MS *m/z* 270 (M^+, 18%), 230 (15), 211 (22), 179 (51), 91

(100), 65 (11); HRMS calcd for $C_{16}H_{18}N_2O_2$: 270.1368. Found: 270.1371.

4.4.6. Methyl (2*RS*,3*SR*)-1-benzyl-2-[(*E*)-2-cyanovinyl]-pyrrolidine-3-carboxylate (*E*)-11b. An oil; IR ($CHCl_3$): 2210 (C≡N), 1725 cm^{-1} (C=O); ^1H NMR (AL4): δ 2.01–2.14 (m, 2H, H_2-4), 2.34–2.42 (m with q character, 1H, J=9 Hz, H-5), 2.81 (ddd, 1H, J=9.9, 7.7, 5.5 Hz, H-3), 2.98–3.03 (m with ddd character, 1H, J=9.5, 7.3, 2.9 Hz, H-5), 3.30, 3.85 (each d, 2H, J=12.8 Hz, 1-CH_2Ph), 3.34–3.39 (m with t character, 1H, J=7 Hz, 2-H), 3.72 (s, 3H, OCH_3), 5.69 (dd, 1H, J=16.3, 1.1 Hz, H-2′), 6.70 (dd, 1H, J=16.3, 7.2 Hz, H-1′), 7.24–7.35 (m, 5H, Ph); ^{13}C NMR (AL4): δ 27.2 (t, C-4), 49.2 (d, C-3), 52.2 (q, OCH_3), 52.7 (t, C-5), 58.5 (t, 1-CH_2Ph), 68.6 (d, C-2), 101.3 (d, C-2′), 116.9 (s, CN), 127.2, 128.3, 128.5 (3d, 5C in Ph), 138.1 (s, C in Ph), 155.0 (d, C-1′), 173.5 (s, CO_2); EI-MS *m*/*z* 270 (M^+, 17%), 230 (27), 211 (26), 179 (75), 91 (100), 65 (11); HRMS calcd for $C_{16}H_{18}N_2O_2$: 270.1368. Found: 270.1364.

4.4.7. Methyl (2*RS*,3*RS*)-1-benzyl-2-[(*Z*)-2-cyanovinyl]-pyrrolidine-3-carboxylate (*Z*)-11a. An oil; bp 160 °C at 0.40 mm Hg; IR ($CHCl_3$): 2220 (C≡N) and 1730 cm^{-1} (C=O); ^1H NMR (AL4): δ 2.01–2.09, 2.23–2.89 (each m, 2H, H_2-4), 2.45 (dt, 1H, J=9.5, 7.0 Hz, H-5), 3.04–3.09 (m, 1H, H-5), 3.29–3.37 (m with q character, 1H, J=9 Hz, H-3), 3.54, 3.76 (each d, 2H, J=13.2 Hz, 1-CH_2Ph), 3.66 (s, 3H, OCH_3), 3.86–3.91 (m with dd character, 1H, J=9.5, 9.2 Hz, H-2), 5.35 (dd, 1H, J=11.0, 0.7 Hz, H-2′), 6.42 (dd, 1H, J=11.0, 9.5 Hz, H-1′), 7.29–7.31 (5H, m, Ph); ^{13}C NMR (AL3): δ 27.1 (t, C-4), 47.7 (d, C-3), 51.8 (q, OCH_3), 52.4 (t, C-5), 57.7 (t, 1-CH_2Ph), 65.2 (d, C-2), 101.0 (d, C-2′), 115.3 (s, CN), 127.2, 128.2, 128.7 (3d, 5C in Ph), 138.1 (s, C in Ph), 153.3 (d, C-1′), 172.6 (s, CO_2); EI-MS *m*/*z* 270 (M^+, 33%), 230 (16), 211 (24), 184 (15), 179 (62), 91 (100), 65 (8). Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36%. Found: C, 70.94; H, 6.70; N, 10.30%.

4.4.8. Methyl (2*RS*,3*SR*)-1-benzyl-2-[(*Z*)-2-cyanovinyl]-pyrrolidine-3-carboxylate (*Z*)-11b. Colorless crystals; mp 45–48 °C; IR ($CHCl_3$): 2220 (C≡N), 1730 cm^{-1} (C=O); ^1H NMR (AL4): δ 2.05–2.23 (m, 2H, H_2-4), 2.37–2.45 (m, 1H, H-5), 2.83 (ddd, 1H, J=10.6, 8.4, 5.5 Hz, H-3), 3.00–3.05 (m with ddd character, 1H, J=9.5, 8.1, 2 Hz, H-5), 3.40, 3.80 (each d, 2H, J=13.2 Hz, 1-CH_2Ph), 3.61–3.67 (m with t character, 1H, J=9 Hz, H-2), 3.75 (s, 3H, OCH_3), 5.42 (dd, 1H, J=11.0, 0.7 Hz, H-2′), 6.38 (dd, 1H, J=11.0, 9.2 Hz, H-1′), 7.25–7.32 (m, 5H, Ph); ^{13}C NMR (AL4): δ 26.8 (t, C-4), 49.0 (d, C-3), 52.3 (q, OCH_3), 53.1 (t, C-5), 58.4 (t, 1-CH_2Ph), 68.3 (d, C-2), 101.8 (d, C-2′), 115.2 (s, CN), 127.1, 128.1, 128.6 (3d, 5C in Ph), 138.2 (s, C in Ph), 154.3 (d, C-1′), 173.0 (s, CO_2); EI-MS *m*/*z* 270 (M^+, 23%), 230 (34), 211 (29), 179 (100), 91 (82), 65 (9); HRMS calcd for $C_{16}H_{28}N_2O_2$: 270.1368. Found: 270.1367.

4.4.9. *tert*-Butyl (2*RS*,3*RS*)-1-benzyl-2-[(*Z*)-2-cyanovinyl]pyrrolidine-3-carboxylate 12a. Colorless crystals; mp 54–55 °C; IR ($CHCl_3$): 2230 (C≡N), 1725 cm^{-1} (C=O); ^1H NMR (LA): δ 1.42 (s, 9H, CMe_3), 1.96–2.03, 2.16–2.26 (each m, 2H, H_2-4), 2.46 (dt, 1H, J=9.2, 7.0 Hz, H-5), 3.02 (ddd, 1H, J=9.2, 8, 2 Hz, H-5), 3.18–3.24 (m with q character, 1H, J=9 Hz, H-3), 3.55, 3.75 (each d, 2H, J=13.4 Hz, 1-CH_2Ph), 3.88–3.92 (m with t character, 1H, J=9.5 Hz, 2-H), 5.34 (dd, 1H, J=11.0, 0.9 Hz, H-2′), 6.45 (dd, 1H, J=11.0, 10 Hz, H-1′), 7.22–7.31 (m, 5H, Ph); ^{13}C NMR (LA): δ 27.0 (t, C-4), 28.1 (q, CMe_3), 48.5 (d, C-3), 52.4 (t, C-5), 57.7 (t, 1-CH_2Ph), 65.2 (d, C-2), 81.1 (s, CMe_3), 100.7 (d, C-2′), 115.5 (s, CN), 127.2, 128.3, 128.7 (3d, 5C in Ph), 138.4 (s, C in Ph), 153.7 (d, C-1′), 171.2 (s, CO_2); EI-MS *m*/*z* 312 (M^+, 11%), 255 (21), 239 (17), 221 (19), 211 (11), 184 (9), 165 (37), 133 (14), 91 (100), 41 (9); HRMS calcd for $C_{19}H_{24}N_2O_2$: 312.1838. Found: 312.1834.

4.4.10. *tert*-Butyl (2*RS*,3*SR*)-1-benzyl-2-[(*Z*)-2-cyanovinyl]pyrrolidine-3-carboxylate 12b. Colorless needles; mp 78–79 °C (hexane/ethyl acetate); IR ($CHCl_3$): 2230 (C≡N), 1725 cm^{-1} (C=O); ^1H NMR (LA): δ 1.48 (s, 9H, CMe_3), 1.99–2.08, 2.12–2.18 (each m, 2H, H_2-4), 2.37–2.43 (m with q character, 1H, J=9 Hz, H-5), 2.74 (ddd, 1H, J=10.3, 8, 5 Hz, H-3), 2.97–3.02 (m with ddd character, 1H, J=9, 8, 2 Hz, H-5), 3.38, 3.82 (each d, 2H, J=13.1 Hz, 1-CH_2Ph), 3.57–3.61 (m with dd character, 1H, J=9, 8 Hz, H-2), 5.40 (dd, 1H, J=11.0, 0.6 Hz, H-2′), 6.37 (dd, 1H, J=11.0, 9.5 Hz, H-1′), 7.21–7.31 (m, 5H, Ph); ^{13}C NMR (LA): δ 26.6 (t, C-4), 27.9 (q, CMe_3), 50.2 (d, C-3), 53.2 (t, C-5), 58.3 (t, 1-CH_2Ph), 68.3 (d, C-2), 81.4 (s, CMe_3), 101.6 (d, C-2′), 115.6 (s, CN), 127.2, 128.2, 128.7 (3d, 5C in Ph), 138.5 (s, C in Ph), 154.9 (d, C-1′), 172.0 (s, CO_2); EI-MS *m*/*z* 312 (M^+, 4%), 255 (39), 239 (15), 216 (10), 165 (48), 91 (100), 41 (6). Anal. Calcd for $C_{19}H_{24}N_2O_2$: C, 73.05; H, 7.74; N, 8.97%. Found: C, 73.14; H, 7.81; N, 8.92%.

4.4.11. (2*Z*,1′*RS*,2′*RS*,5′*SR*)-3-(3-Benzyl-8-oxo-3-azabicyclo[3.3.0]oct-2-yl)acrylonitrile 13. Colorless crystals; mp 91–92 °C (hexane/ethyl acetate); IR ($CHCl_3$): 2220 (C≡N), 1730 cm^{-1} (C=O); ^1H NMR (AL4): δ 1.80–1.89, 2.03–2.14 (each m, 2H, H_2-6′), 2.21–2.30 (m with dddd character, 1H, J=18, 8, 5, 1 Hz, H-7′), 2.35–2.46 (m, 1H, H-7′), 2.54 (dd, 1H, J=9.8, 8 Hz, H-4′), 2.78–2.83 (m with t character, 1H, J=8 Hz, H-1′), 2.89 (dd, 1H, J=9.8, 1.4 Hz, H-4′), 2.90–2.98 (m, 1H, H-5′), 3.17, 3.79 (each d, 2H, J=13.8 Hz, 3′-CH_2Ph), 3.68 (dd, 1H, J=9.8, 7.3 Hz, H-2′), 5.51 (dd, 1H, J=11.0, 0.7 Hz, H-2), 6.46 (dd, 1H, J=11.0, 9.8 Hz, H-3), 7.22–7.32 (5H, m, Ph); ^{13}C NMR (AL3): δ 28.3 (t, C-6′), 38.0 (d, C-5′), 39.4 (t, C-7′), 55.2 (d, C-1′), 57.9, 61.0 (2t, C-4′, 1-CH_2Ph), 68.3 (d, C-2′), 102.1 (d, C-2), 115.3 (s, C-1), 127.0, 128.1, 128.2 (3d, 5C in Ph), 138.2 (s, C in Ph), 153.0 (d, C-3), 217.9 (s, C-8′); EI-MS *m*/*z* 266 (M^+, 33%), 226 (5), 210 (20), 184 (13), 175 (16), 91 (100), 65 (9). Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52%. Found: C, 76.71; H, 6.86; N, 10.46%.

4.4.12. (2*Z*,1′*RS*,2′*RS*,5′*SR*)-3-(3-Benzyl-6,8-dioxo-7-phenyl-3,7-diazabicyclo[3.3.0]oct-2-yl)acrylonitrile 14. Colorless crystals; mp 49–51 °C; IR ($CHCl_3$): 2230 (C≡N), 1720 cm^{-1} (C=O); ^1H NMR (LA): δ 2.56 (dd, 1H, J=10.1, 7.9 Hz, H-4′), 3.33, 3.83 (each d, 2H, J=13.4 Hz, 3′-CH_2Ph), 3.36 (td, 1H, J=7.9, 0.6 Hz, H-5′), 3.47 (d, 1H, J=10.1 Hz, H-4′), 3.54 (t, 1H, J=7.9 Hz, H-1′), 3.79 (dd, 1H, J=9.8, 7.9 Hz, H-2′), 5.59 (dd, 1H, J=11.0, 0.6 Hz, H-2), 6.45 (dd, 1H, J=11.0, 9.8 Hz, H-3), 7.20–7.23, 7.24–7.32, 7.39–7.43, 7.47–7.51 (4m, 10H, Ph); ^{13}C NMR (LA): δ 43.4 (d, C-5′), 48.8 (d, C-1′), 55.9 (t, C-4′), 56.8 (t, 3′-CH_2Ph), 66.4 (d, C-2′), 103.5 (d, C-2), 115.2 (s, C-1), 126.3, 127.6, 128.4, 128.5, 128.8, 129.2 (6d, 10C in Ph), 131.7, 136.8 (2s, 2C in Ph), 151.1 (d, C-3),

174.4, 177.4 (2s, C-6′, C-8′); EI-MS *m/z* 357 (M^+, 55%), 317 (21), 266 (21), 184 (19), 119 (8), 91 (100), 65 (8); HRMS calcd for $C_{22}H_{19}N_3O_2$: 357.1477. Found: 357.1479.

4.4.13. Methyl (*Z*)-1-benzyl-2-(2-cyanovinyl)-3-pyrroline-3-carboxylate 15. An oil; bp 160 °C at 0.20 mm Hg; IR ($CHCl_3$): 2230 (C≡N), 1720 cm^{-1} (C=O); ^1H NMR (LA): δ 3.50 (ddd, 1H, *J*=17, 5, 2 Hz, H-5), 3.74 (s, 3H, OCH_3), 3.74, 3.97 (each d, 2H, *J*=13.4 Hz, 1-CH_2Ph), 3.87 (ddd, 1H, *J*=17, 5.5, 2 Hz, H-5), 4.82–4.87 (m, 1H, 2-H), 5.39 (dd, 1H, *J*=10.7, 0.6 Hz, H-2′), 6.37 (dd, 1H, *J*=10.7, 9.2 Hz, H-1′), 6.89 (q, 1H, *J*=2.1 Hz, H-4), 7.23–7.33 (m, 5H, Ph); ^{13}C NMR (LA): δ 51.7 (q, OCH_3), 57.5 (t, 1-*C*H_2Ph), 59.0 (t, C-5), 68.8 (d, C-2), 100.7 (d, C-2′), 115.7 (s, CN), 127.3, 128.4, 128.6 (3d, 5C in Ph), 133.5 (s, C-3), 138.3 (s, C in Ph), 141.8 (d, C-4), 153.2 (d, C-1′), 163.0 (s, CO_2); EI-MS *m/z* 268 (M^+, 8%), 216 (17), 177 (15), 91 (100), 65 (14); HRMS calcd for $C_{16}H_{16}N_2O_2$: 268.1212. Found: 268.1218.

4.5. Thermal reactions of nitrile 1 with alkenes

By analogy with the photoreactions of (*Z*)-**1**, a 0.060 mol L^{-1} solution of (*Z*)-**1** in xylene with 10 equiv of *tert*-butyl acrylate or *N*-phenylmaleimide was heated under reflux. Flash column chromatography afforded the adducts. The results are summarized in Table 1.

4.6. Irradiation of ethyl acrylate 2

4.6.1. Ethyl (2*E*,2′*RS*,3′*SR*,4′*SR*)-3-[1-benzyl-4-(1-benzylaziridin-2-yl)-3-ethoxycarbonylpyrrolidin-2-yl]acrylate 16A and ethyl (2*E*,2′*RS*,3′*SR*,4′*SR*)-3-[1-benzyl-4-(1-benzylaziridin-2-yl)-3-ethoxycarbonylpyrrolidin-2-yl]acrylate 16B. By analogy with the photolysis of **1**, a solution of (*E*)-**2** (51.8 mg, 0.223 mmol) in acetonitrile was irradiated (conversion 98%) for 2 h at rt. Preparative TLC [hexane–ethyl acetate–diethylamine (9:1:0.5)] of the reaction mixture afforded dimers **16A** (9.8 mg, 19%[9]) and **16B** (3.3 mg, 7%[9]).

Compound **16A**. An oil; IR ($CHCl_3$): 1720 cm^{-1} (C=O); ^1H NMR (LA): δ 1.22, 1.31 (2t, 6H, *J*=7.0 Hz, 2CH_3), 1.36 (d, 1H, *J*=6.1 Hz, H-3″), 1.63–1.67 (m, 2H, H-2″, H-3″), 2.16–2.22 (m, 1H, H-4′), 2.38 (dd, 1H, *J*=9.7, 8 Hz, H-5′), 2.49 (dd, 1H, *J*=8.2, 5.2 Hz, H-3′), 2.77 (dd, 1H, *J*=9.7, 2.4 Hz, H-5′), 3.14, 3.88 (each d, 2H, *J*=13.1 Hz, 1″-CH_2Ph), 3.23, 3.56 (each d, 2H, *J*=12.8 Hz, 1′-CH_2Ph), 3.25 (m, 1H, H-2′), 4.21, 4.22 (2q, 4H, *J*=7.0 Hz, 2OCH_2), 6.00 (dd, 1H, *J*=15.6, 0.6 Hz, H-2), 6.80 (dd, 1H, *J*=15.6, 7.9 Hz, H-3), 7.22–7.33 (m, 10H, 2Ph); ^{13}C NMR (LA): δ 14.2, 14.3 (2q, 2CH_3), 33.2 (t, C-3″), 42.8 (d, C-2″), 43.5 (d, C-4′), 54.2 (d, C-3′), 55.6 (t, C-5′), 58.0 (t, 1″-*C*H_2Ph), 60.4, 60.8 (2t, 2OCH_2), 64.7 (t, 1′-*C*H_2Ph), 69.0 (d, C-2′), 123.2 (d, C-2), 127.0, 127.1, 128.26, 128.34, 128.5 (5d, 10C in Ph), 138.7, 139.2 (2s, 2C in Ph), 148.2 (d, C-3), 166.2, 173.3 (2s, C-1, 3′-CO_2); EI-MS *m/z* 462 (M^+, 2%), 417 (6), 342 (41), 282 (17), 233 (17), 120 (7), 91 (100); HRMS calcd for $C_{28}H_{34}N_2O_4$: 462.2518. Found: 462.2527.

Compound **16B**. An oil; IR ($CHCl_3$): 1730 cm^{-1} (C=O); ^1H NMR (LA): δ 1.22, 1.30 (2t, 6H, *J*=7.0 Hz, 2CH_3), 1.44 (d, 1H, *J*=6.4 Hz, H-3″), 1.68–1.73 (m, 2H, H-2″, H-3″), 1.99–2.05 (m, 1H, H-4′), 2.40 (dd, 1H, *J*=9.8, 7.9 Hz, H-5′), 2.62 (dd, 1H, *J*=8.5, 5.8 Hz, H-3′), 2.73 (dd, 1H, *J*=9.8, 2.7 Hz, H-5′), 3.16, 3.86 (each d, 2H, *J*=13.4 Hz, 1″-CH_2Ph), 3.19, 3.50 (each d, 2H, *J*=12.8 Hz, 1′-CH_2Ph), 3.34 (m with t character, 1H, *J*=8 Hz, H-2′), 4.11, 4.20 (2q, 4H, *J*=7.0 Hz, 2OCH_2), 6.05 (dd, 1H, *J*=15.6, 0.6 Hz, H-2), 6.87 (dd, 1H, *J*=15.6, 7.9 Hz, H-3), 7.15–7.31 (m, 10H, 2Ph); ^{13}C NMR (LA): δ 14.17, 14.23 (2q, 2CH_3), 33.0 (t, C-3″), 43.5 (d, C-2″), 44.5 (d, C-4′), 53.5 (d, C-3′), 57.0 (t, C-5′), 57.8 (t, 1″-*C*H_2Ph), 60.4, 60.8 (2t, 2OCH_2), 64.7 (t, 1′-*C*H_2Ph), 68.5 (d, C-2′), 123.5 (d, C-2), 127.0, 127.1, 128.2, 128.3, 128.5 (5d, 10C in Ph), 138.6, 138.9 (2s, 2C in Ph), 148.2 (d, C-3), 166.2, 172.9 (2s, C-1, 3′-CO_2); EI-MS *m/z* 462 (M^+, 2%), 417 (12), 342 (100), 282 (20), 233 (23), 120 (6), 91 (77); HRMS calcd for $C_{28}H_{34}N_2O_4$: 462.2518. Found: 462.2516.

4.6.2. Triplet sensitization of 2. By analogy with the photolysis of **1**, a solution of (*E*)-**2** (424 mg, 1.83 mmol) in acetone (31 mL) was irradiated with a high-pressure mercury lamp in a Pyrex test tube (conversion 84%) for 11.5 h at rt. After removal of the solvent, flash column chromatography [hexane–ethyl acetate (3:2)] of the residue afforded (*Z*)-**2** (67 mg, 25%[9]).

4.6.3. Ethyl (2*E*,2′*RS*,3′*RS*)-3-(1-benzyl-3-cyanopyrrolidin-2-yl)acrylate 17a and ethyl (2*E*,2′*RS*,3′*SR*)-3-(1-benzyl-3-cyanopyrrolidin-2-yl)acrylate 17b. By analogy with the photoreactions of **1**, a 0.060 mol L^{-1} solution of (*E*)-**2** in dry acetonitrile with 10 equiv of acrylonitrile was irradiated. Preparative TLC [hexane–ethyl acetate (3:1)] afforded the adducts. The results are summarized in Table 2.

Compound **17a**. An oil; bp 180 °C at 0.20 mm Hg (decomp.); IR ($CHCl_3$): 2250 (C≡N), 1715 cm^{-1} (C=O); ^1H NMR (LA): δ 1.31 (t, 3H, *J*=7.0 Hz, CH_3), 2.13–2.27 (m, 2H, H_2-4′), 2.28–2.34 (m with dt character, 1H, *J*=9, 8 Hz, H-5′), 3.07–3.12 (m with ddd character, 1H, *J*=9, 8, 3 Hz, H-5′), 3.16–3.21 (m with ddd character, 1H, *J*=8.5, 7, 6.1 Hz, H-3′), 3.27, 3.92 (each d, 2H, *J*=13.1 Hz, 1′-CH_2Ph), 3.27–3.31 (m, 1H, H-2′), 4.22 (q, 2H, *J*=7.0 Hz, OCH_2), 6.14 (dd, 1H, *J*=15.6, 0.9 Hz, H-2), 6.98 (dd, 1H, *J*=15.6, 8.2 Hz, H-3), 7.22–7.33 (m, 5H, Ph); ^{13}C NMR (LA): δ 14.2 (q, CH_3), 28.4 (t, C-4′), 33.7 (d, C-3′), 51.3 (t, C-5′), 57.1 (t, 1′-*C*H_2Ph), 60.7 (t, OCH_2), 65.8 (d, C-2′), 119.6 (s, CN), 126.2 (d, C-2), 127.3, 128.3, 128.5 (3d, 5C in Ph), 137.9 (s, C in Ph), 144.0 (d, C-3), 165.3 (s, C-1); EI-MS *m/z* 284 (M^+, 10%), 255 (11), 239 (10), 211 (35), 193 (68), 158 (38), 140 (14), 112 (19), 91 (100); HRMS calcd for $C_{17}H_{20}N_2O_2$: 284.1525. Found: 284.1529.

Compound **17b**. An oil; IR ($CHCl_3$): 2240 (C≡N), 1715 cm^{-1} (C=O); ^1H NMR (LA): δ 1.31 (t, 3H, *J*=7.0 Hz, CH_3), 2.05–2.12, 2.26–2.30 (2m, 2H, H_2-4′), 2.38–2.44 (m with q character, 1H, *J*=9 Hz, H-5′), 2.84 (ddd, 1H, *J*=10.7, 8.2, 6.4 Hz, H-3′), 3.03 (ddd, 1H, *J*=9.5, 8.2, 2.7 Hz, H-5′), 3.25, 3.93 (each d, 2H, *J*=12.8 Hz, 1′-CH_2Ph), 3.27 (t, 1H, *J*=8.2 Hz, 2′-H), 4.22 (q, 2H, *J*=7.0 Hz, OCH_2), 6.20 (dd, 1H, *J*=15.9, 0.6 Hz, H-2), 6.79 (dd, 1H, *J*=15.9, 8.2 Hz, H-3), 7.23–7.33 (m, 5H, Ph); ^{13}C NMR (LA): δ 14.2 (q, CH_3), 27.7 (t, C-4′), 33.8 (d, C-3′), 51.8 (t, C-5′), 57.6 (t, 1′-*C*H_2Ph), 60.7 (t, OCH_2), 69.5 (d, C-2′), 120.5 (s, CN), 125.6 (d, C-2), 127.4, 128.4, 128.6 (3d,

5C in Ph), 137.7 (s, C in Ph), 145.1 (d, C-3), 165.5 (s, C-1); EI-MS *m/z* 284 (M^+, 5%), 255 (11), 239 (15), 211 (25), 193 (67), 158 (27), 140 (12), 112 (15), 91 (100); HRMS calcd for $C_{17}H_{20}N_2O_2$: 284.1525. Found: 284.1523.

4.7. Reaction of *N*-phenylaziridine (*E*)-3

4.7.1. Ethyl (2*E*,2′*RS*,3′*RS*)-3-(3-cyano-1-phenylpyrrolidin-2-yl)acrylate 18a and ethyl (2*E*,2′*RS*,3′*SR*)-3-(3-cyano-1-phenylpyrrolidin-2-yl)acrylate 18b. By analogy with the photoreactions of (*Z*)-**1**, a 0.060 mol L^{-1} solution of (*E*)-**3** in dry acetonitrile with 10 equiv of acrylonitrile was irradiated. Preparative TLC [SiO_2; hexane–ethyl acetate (3:1)] afforded the adducts. The results are summarized in Table 2.

Compound **18a**. An oil; IR ($CHCl_3$): 2240 (C≡N), 1720 cm^{-1} (C=O); ^1H NMR (AL3): δ 1.28 (t, 3H, J=7.2 Hz, CH_3), 2.26–2.41, 2.44–2.53 (2m, 2H, H_2-4′), 3.28 (ddd, 1H, J=12.0, 7.8, 6.3 Hz, H-3′), 3.34–3.43 (m with td character, 1H, J=9, 7 Hz, H-5′), 3.60–3.67 (m with td character, 1H, J=9, 2 Hz, H-5′), 4.19 (q, 2H, J=7.2 Hz, OCH_2), 4.55–4.60 (m, 1H, H-2′), 6.00 (dd, 1H, J=15.6, 1.5 Hz, H-2), 6.51–6.54 (m with d character, 2H, J=7.9 Hz, H-2″, H-6″), 6.75–6.80 (m with t character, 1H, J=7.3 Hz, H-4″), 7.04 (dd, 1H, J=15.6, 4.8 Hz, H-3), 7.21–7.26 (m, 2H, H-3″, H-5″); ^{13}C NMR (AL4): δ 14.3 (q, CH_3), 27.9 (t, C-4′), 33.1 (d, C-3′), 47.0 (t, C-5′), 59.9 (d, C-2′), 60.8 (t, OCH_2), 112.1 (d, C-2″, C-6″), 117.5 (s, CN), 117.7 (d, C-4″), 125.3 (d, C-2), 129.2 (d, C-3″, C-5″), 142.4 (d, C-3), 145.4 (s, C-1″), 165.1 (s, C-1); EI-MS *m/z* 270 (M^+, 68%), 241 (70), 225 (34), 197 (50), 171 (18), 144 (100), 112 (16), 104 (11), 84 (13), 77 (24); HRMS calcd for $C_{17}H_{20}N_2O_2$: 270.1368. Found: 270.1371.

Compound **18b**. An oil; IR ($CHCl_3$): 2240 (C≡N), 1720 cm^{-1} (C=O); ^1H NMR (AL3): δ 1.27 (t, 3H, J=7.2 Hz, CH_3), 2.32–2.39 (m, 2H, H_2-4′), 3.06–3.11 (m, 1H, H-3′), 3.57–3.72 (m, 2H, H_2-5′), 4.18 (q, 2H, J=7.2 Hz, OCH_2), 4.58–4.62 (m, 1H, H-2′), 5.99 (dd, 1H, J=15.3, 1.7 Hz, H-2), 6.54–6.58 (m with d character, 2H, J=9 Hz, H-2″, H-6″), 6.76–6.82 (m with t character, 1H, J=7.3 Hz, H-4″), 6.86 (dd, 1H, J=15.3, 4.8 Hz, H-3), 7.20–7.28 (m, 2H, H-3″, H-5″); ^{13}C NMR (AL4): δ 14.3 (q, CH_3), 27.8 (t, C-4′), 34.7 (d, C-3′), 47.2 (t, C-5′), 60.9 (t, OCH_2), 63.3 (d, C-2′), 112.6 (d, C-2″, C-6″), 117.8 (d, C-4″), 119.7 (s, CN), 124.0 (d, C-2), 129.2 (d, C-3″, C-5″), 144.3 (d, C-3), 145.6 (s, C-1″), 165.4 (s, C-1); EI-MS *m/z* 270 (M^+, 67%), 241 (72), 225 (32), 197 (53), 171 (24), 144 (100), 112 (15), 104 (12), 84 (13), 77 (28); HRMS calcd for $C_{17}H_{20}N_2O_2$: 270.1368. Found: 270.1365.

4.7.2. Ethyl 2,5-dihydro-1*H*-1-benzazepine-5-carboxylate 19. A solution of (*E*)-**3** (100 mg, 0.46 mmol) in xylene (7.6 mL) with 10 equiv of 3,4-dihydro-2*H*-pyrane (386 mg, 4.6 mmol) was heated under reflux for 1.5 h (conversion 98%). After removal of the solvent, preparative TLC [hexane–ethyl acetate (3:1)] of the residue afforded benzazepine **19** (41.2 mg, 42%[9]). An oil; IR ($CHCl_3$): 3340 (N–H), 1720 cm^{-1} (C=O); ^1H NMR (AL4): δ 1.22 (t, 3H, J=7.2 Hz, CH_3), 3.30 (br s, 1H, NH), 3.66–3.73 (m with ddd character, 1H, J=17.2, 4.8, 2.8 Hz, H-2), 3.75–3.82 (m with d character, 1H, J=17.2 Hz, H-2), 4.19 (q, 2H, J=7.2 Hz, OCH_2), 4.42–4.44 (m with d character, 1H, J=7.2 Hz, H-5), 5.61–5.66 (m, 1H, H-3), 5.97–6.04 (m, 1H, H-4), 6.87 (dd, 1H, J=7.6, 1 Hz, H-9), 6.96 (td, 1H, J=7.6, 1.2 Hz, H-7), 7.04 (dd, 1H, J=7.6, 1.6 Hz, H-6), 7.16 (td, 2H, J=7.6, 1.6 Hz, H-8); ^{13}C NMR (AL4): δ 14.3 (q, CH_3), 48.4 (t, C-2), 49.2 (d, C-5), 61.0 (t, OCH_2), 121.8 (d, C-9), 122.5 (d, C-7), 124.3 (d, C-4), 128.1 (d, C-8), 128.6 (d, C-6), 129.1 (d, C-3), 134.3 (s, C-5a), 147.9 (s, C-9a), 172.5 (s, 5-CO); EI-MS *m/z* 217 (M^+, 28%), 188 (3), 172 (5), 144 (100), 127 (4), 115 (7), 72 (2); HRMS calcd for $C_{13}H_{15}NO_2$: 217.1103. Found: 217.1099.

4.8. Reaction of *N*-benzoylaziridine (*E*)-4

4.8.1. Ethyl (2*E*,4*E*)-5-benzamido-2,4-pentadienoate 20. By analogy with the photoreactions of **1**, a solution of (*E*)-**4** (124 mg, 0.51 mmol) in dry acetonitrile (8.5 mL) with 10 equiv of acrylonitrile (270 mg, 5.1 mmol) was irradiated for 5 h at rt (conversion 74%). After removal of the solvent, preparative TLC [hexane–ethyl acetate (3:1)] of the residue afforded dienoate **20** (27.9 mg, 30%[9]). Colorless plates; mp 124–127 °C (hexane/ethyl acetate); IR ($CHCl_3$): 1690 cm^{-1} (C=O); ^1H NMR (AL4): δ 1.27 (t, 3H, J=7.2 Hz, CH_3), 4.19 (q, 2H, J=7.2 Hz, OCH_2), 5.74 (d, 1H, J=15.2 Hz, H-2), 6.09 (dd, 1H, J=14.0, 11.6 Hz, H-4), 7.31 (dd, 1H, J=15.2, 11.6 Hz, H-3), 7.45 (t, 2H, J=7.2 Hz, H-3′, H-5), 7.49–7.54 (m with d character, 1H, J=14.0 Hz, H-2), 7.56 (t, 1H, J=7.2 Hz, H-4′), 7.86 (d, 2H, J=7.2 Hz, H-2′, H-6′), 8.78 (br d, 1H, J=11 Hz, NH); ^{13}C NMR (AL4): δ 14.3 (q, CH_3), 60.2 (t, OCH_2), 111.3, 111.8 (2d, C-2, C-4), 127.3, 128.5 (2d, 4C in Ph), 132.5, 133.2 (2d, C-5, C in Ph), 132.8 (s, C in Ph), 143.4 (d, C-3), 164.7, 167.2 (2s, C-1, CONH); EI-MS *m/z* 245 (M^+, 19%), 200 (4), 140 (7), 105 (100), 77 (26), 51 (4); HRMS calcd for $C_{14}H_{15}NO_3$: 245.1052. Found: 245.1046.

4.8.2. Thermal reactions of (*E*)-4. A solution of (*E*)-**4** (300 mg, 1.22 mmol) in xylene (20 mL) with 10 equiv of *tert*-butyl acrylate (1.54 g, 12 mmol) was heated under reflux for 3.5 h (conversion 83%). After removal of the solvent, flash column chromatography [hexane–ethyl acetate (6:1)] of the residue afforded pyridine **21**[12] (9.1 mg, 4%[9]) and a mixture of isomers of dienoate **20** (134 mg).

4.9. Reaction of *N*-trityl aziridine (*E*)-5

4.9.1. Ethyl (2*E*,2′*RS*,3′*RS*)-3-(3-cyano-1-tritylpyrrolidin-2-yl)acrylate 22. By analogy with the photoreactions of (*Z*)-**1**, a 0.060 mol L^{-1} solution of (*E*)-**5** in dry acetonitrile with 10 equiv of acrylonitrile was irradiated. Preparative TLC [hexane–ethyl acetate (5:1)] afforded the adduct **22**. The results are summarized in Table 2. An oil; IR ($CHCl_3$): 2240 (C≡N), 1710 cm^{-1} (C=O); ^1H NMR (AL4): δ 1.27–1.34 (m, 1H, H-3′) 1.36 (t, 3H, J=7.2 Hz, CH_3), 1.62–1.70, 1.75–1.87 (2m, 2H, H_2-4′), 3.07 (td, 1H, J=13, 8.4 Hz, H-5′), 3.48 (ddd, 1H, J=13, 10.0, 4.0 Hz, H-5′), 4.19 (t, 1H, J=6.4 Hz, H-2′) 4.28 (q, 2H, J=7.2 Hz, OCH_2), 6.34 (d, 1H, J=15.6 Hz, H-2), 7.09 (dd, 1H, J=15.6, 6.4 Hz, H-3), 7.18–7.57 (m, 15H, Tr); ^{13}C NMR (AL4): δ 14.4 (q, CH_3), 29.1 (t, C-4′), 31.3 (d, C-3′), 48.3 (t, C-5′), 60.8 (t, OCH_2), 63.0 (d, C-2′), 78.0 (s, *C*Ph_3), 118.9 (s, CN), 123.7 (d, C-2), 126.6 (d, 3C in Ph), 127.9 (d, 6C in Ph), 128.8 (d, 6C in Ph), 143.8 (s, 3C in Ph), 144.8 (d, C-3),

165.8 (s, C-1); EI-MS *m/z* 436 (M^+, 0.4%), 359 (1), 243 (100), 165 (2); HRMS calcd for $C_{29}H_{28}N_2O_2$: 436.2151. Found: 436.2150.

4.9.2. Ethyl (2*E*,2′*RS*,3′*RS*)-3-(3-methoxycarbonyl-1-tritylpyrrolidin-2-yl)acrylate 23. By analogy with the photoreactions of (*Z*)-**1**, a solution of (*E*)-**5** in dry acetonitrile with 10 equiv of methyl acrylate was irradiated. Preparative TLC [hexane–ethyl acetate (7:1)] afforded the adduct **23**. The results are summarized in Table 2. Colorless crystals; mp 134–135 °C (hexane/ethyl acetate); IR ($CHCl_3$): 1720 (C═O), 1710 cm^{-1} (C═O); ^1H NMR (AL4): δ 1.33 (t, 3H, J=7.1 Hz, OCH_2CH_3), 1.34–1.40, 1.86–1.97 (2m, 2H, H_2-4′), 1.59 (dt, 1H, J=10.5, 8.3 Hz, H-3′), 2.97–3.06, 3.41–3.49 (m, 2H, H_2-5′), 3.49 (s, 3H, OCH_3), 4.19–4.23 (m, 1H, overlapping with q at δ 4.23, H-2′) 4.23 (q, 2H, J=7.1 Hz, OCH_2), 6.14 (d, 1H, J=15.6 Hz, H-2), 6.86 (dd, 1H, J=15.6, 6.4 Hz, H-3), 7.12–7.29 (m, 9H, Tr), 7.56 (d, 6H, J=7.6 Hz, Tr); ^{13}C NMR (AL4): δ 14.3 (q, OCH_2CH_3), 26.6 (t, C-4′), 47.6 (d, C-3′), 48.3 (t, C-5′), 51.5 (q, OCH_3), 60.4 (t, OCH_2), 63.4 (d, C-2′), 78.0 (s, CPh_3), 122.1 (d, C-2), 126.3 (d, 3C in Ph), 127.7 (d, 6C in Ph), 129.0 (d, 6C in Ph), 144.2 (s, 3C in Ph), 146.6 (d, C-3), 166.2 (s, C-1), 171.6 (s, CO_2CH_3); EI-MS *m/z* 469 (M^+, 1%), 392 (3), 243 (100), 228 (4), 198 (2), 165 (23), 154 (2), 91 (2); HRMS calcd for $C_{30}H_{31}NO_4$: 469.2253. Found: 469.2252.

4.10. Application to the synthesis of (±)-isoretronecanol 27

4.10.1. Ethyl (2*E*,2′*RS*,3′*RS*)-3-(3-methoxycarbonylpyrrolidin-2-yl)acrylate 24. To a solution of **23** (430 mg, 0.86 mmol) in chloroform (0.7 mL) and methanol (0.7 mL) was trifluoroacetic acid (1.3 mL) at rt. After being stirred for 1 h at rt, the reaction mixture was extracted with water (2× 3 mL). The aqueous phase was neutralized with aqueous saturated $NaHCO_3$ and extracted with chloroform (3× 5 mL). The organic phase was washed with brine, dried with $MgSO_4$, and concentrated in vacuo to yield **24** (168 mg, 83%).

An oil; IR ($CHCl_3$): 3510 (N–H), 1710 cm^{-1} (C═O); ^1H NMR (AL4): δ 1.28 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.77 (brs, 1H, NH), 2.01–2.20 (m, 2H, H_2-4′), 2.91–2.99 (m with ddd-character, 1H, J=11, 8.3, 7.8 Hz, H-5′), 3.11–3.17 (m, 1H, H-3′), 3.29 (ddd, 1H, J=11.2, 8.6, 4.4 Hz, H-5′), 3.64 (s, 3H, OCH_3), 3.87–3.92 (m, 1H, H-2′) 4.19 (q, 2H, J=7.2 Hz, OCH_2), 5.99 (dd, 1H, J=15.6, 1.5 Hz, H-2), 6.89 (dd, 1H, J=15.6, 6.3 Hz, H-3); ^{13}C NMR (AL4): δ 14.3 (q, OCH_2CH_3), 29.3 (t, C-4′), 46.3 (t, C-5′), 48.5 (d, C-3′), 51.7 (q, OCH_3), 60.4 (t, OCH_2), 62.8 (d, C-2′), 122.3 (d, C-2), 144.5 (d, C-3), 165.7 (s, C-1), 173.4 (s, CO_2CH_3); EI-MS *m/z* 227 (M^+, 21%), 198 (100), 181 (40), 154 (41), 128 (38), 116 (80), 100 (48), 56 (42); HRMS calcd for $C_{11}H_{17}NO_4$: 227.1158. Found: 227.1160.

4.10.2. Ethyl (2′*RS*,3′*RS*)-3-(3-methoxycarbonylpyrrolidin-2-yl)propanate 25. A solution of **24** (18.1 mg, 0.08 mmol) in ethyl acetate (0.5 mL) with 10% Pd/C (5.2 mg) under hydrogen was stirred for 21 h at rt. The reaction mixture was filtered with celite, and the filtrate was concentrated in vacuo, giving a residue that was subjected to NH-silica gel column chromatography [hexane–ethyl acetate (1:5)] to afford **25** (11.7 mg, 64%).

An oil; IR ($CHCl_3$): 3410 (N–H), 1720 cm^{-1} (C═O); ^1H NMR (AL4): δ 1.25 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.62–1.85 (m, 3H, NH and H_2-3), 1.93–2.10 (m, 2H, H_2-4′), 2.44–2.50 (m, 2H, H_2-2), 2.79–2.87 (m, 1H, H-5′), 2.92–2.97 (m, 1H, H-3′), 3.04–3.11 (m, 1H, H-2′), 3.18–3.25 (m, 1H, H-5′), 3.68 (s, 3H, OCH_3), 4.13 (q, 2H, J=7.2 Hz, OCH_2); ^{13}C NMR (AL4): δ 14.4 (q, OCH_2CH_3), 26.4 (t, C-3), 30.3 (t, C-4′), 32.5 (t, C-2), 46.4 (t, C-5′), 47.6 (d, C-3′), 51.5 (q, OCH_3), 60.4 (t, OCH_2), 63.0 (d, C-2′), 173.0, 174.9 (2s, C-1, CO_2CH_3); EI-MS *m/z* 229 (M^+, 4%), 183 (34), 155 (29), 152 (24), 128 (100), 97 (76), 69 (26); HRMS calcd for $C_{11}H_{19}NO_4$: 229.1314. Found: 229.1314.

4.10.3. Methyl (4*RS*,5*RS*)-8-oxo-1-azabicyclo[3.3.0]oct-4-ylcarboxylate 26. A solution of **25** (14.6 mg, 0.065 mmol) in toluene (1.0 mL) was refluxed for 15.5 h. The reaction mixture was concentrated in vacuo, giving a residue that was subjected to flush column chromatography [ethyl acetate] to afford **26**[5] (10.3 mg, 87%).

An oil; IR ($CHCl_3$): 1730 (C═O), 1695 cm^{-1} (C═O); ^1H NMR (AL4): δ 1.69–1.78 (m, 1H, H-6), 2.16–2.43 (m, 4H, H_2-3, H-6, H-7), 2.61–2.70 (m, 1H, H-7), 3.02 (td, 1H, J=7.1, 3.4 Hz, H-4), 3.04–3.11 (m, 1H, H-2), 3.70 (s, 3H, OCH_3), 3.82 (td, 1H, J=11.2, 7.6 Hz, H-2), 4.16 (q, 1H, J=7 Hz, H-5); ^{13}C NMR (AL4): δ 22.6 (t, C-6), 30.4 (t, C-3), 34.0 (t, C-7), 41.3 (t, C-2), 45.5 (d, C-4), 51.9 (q, OCH_3), 63.2 (d, C-5), 172.6, 175.2 (2s, C-8, CO_2CH_3); EI-MS *m/z* 183 (M^+, 37%), 183 (34), 155 (45), 152 (26), 97 (100), 69 (44); HRMS calcd for $C_9H_{13}NO_3$: 183.0895. Found: 183.0892.

Compound **26**.[5b] ^1H NMR (250 MHz): δ 1.5–1.75 (m, 1H), 2.0–2.4 (m, 4H), 2.45–2.7 (m, 1H), 2.85–3.1 (m, 2H), 3.6 (s, 3H), 3.5–3.8 (m, 1H), 4.08 (q, 1H, J=7 Hz); ^{13}C NMR (62.5 MHz): δ 22.3, 30.2, 33.6, 41.0, 45.2, 51.8, 63.1, 172.9, 175.4.

Acknowledgements

This work was partially supported by the Grant-in-Aid for Scientific Research (C) (No. 13672239) administered by Japan Society for the Promotion of Science and by Bio Venture Center of Meiji Pharmaceutical University. The authors wish to thank the staff of the Analysis Center of Meiji Pharmaceutical University for performing the elemental analysis and measurements of LA-NMR (HMBC and NOESY spectra) (Miss S. Kubota) and mass spectra (Miss T. Koseki). We are also grateful to Mr. N. Goi for his technical assistance.

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