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Photoreactions of β-aziridinylacrylonitriles and acrylates with alkenes: the substituent effects on the formation of [3+2] cycloadducts

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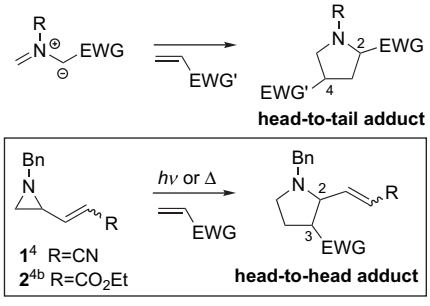
Abstract—The photochemical C,C-bond cleavage of trisubstituted aziridines **3**–**6** and consequent [3+2] cycloaddition with electron-deficient alkenes afforded the novel head-to-head adducts (1,2,3,5-tetrasubstituted pyrrolidines) selectively and efficiently. The aziridines **3** and **5** reacted with molecular oxygen, affording dioxazolidine **26** and cleaved products, respectively. The results may suggest that the C,C-bond of aziridine cleaves biradically. The photoreactions of *N*-tritylaziridines **7**–**9** possessing diester, dinitrile, and butadiene groups in the side chain with electron-deficient alkenes yielded 2,3-*cis*-pyrrolidine derivatives **29**, **30**, and **33** exclusively. In particular, the dinitrile **8** also reacted with non-electron-deficient alkenes. The formal synthesis of the indolizidine fragment **10** of stellettamides starting from the pyrrolidine (*E*)-**33** 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 pyrrolidines.[1] On irradiation or under thermal conditions the aziridine ring is cleaved to give the corresponding azomethine ylide.[2] In general, the 1,3-dipolar cycloaddition of the azomethine ylide possessing one electron withdrawing group (EWG) at the ylide carbon and electron-deficient alkenes affords head-to-tail adducts (1,2,4-trisubstituted pyrrolidines; Scheme 1). The regiochemistries of the adducts have been explained by the frontier MO interaction of azomethine ylides and alkenes.[2b,3]



Scheme 1.

We have reported previously that direct irradiation (via singlet state) or heating of β-aziridinylacrylonitrile **1** or acrylate **2** with electron-deficient alkenes undergoes ring opening and subsequent [3+2] cycloaddition leading to head-to-head adducts (1,2,3-trisubstituted pyrrolidines; Scheme 1) selectively and efficiently (Scheme 1).[4] The regiochemistry of the head-to-head adducts could not be clearly rationalized by the interaction between HOMO of azomethine ylide generated from **1** or **2** and LUMO of electron-deficient alkenes. Therefore, in order to study the scope and limitations of the cycloaddition, the reactions of various aziridines (di- and trisubstituted aziridines and aziridines bearing diester, dinitrile, and butadiene groups in the side chain) **1**–**9** and alkenes were performed. Furthermore, we describe a convenient synthetic application of **9** to indolizidine part **10** of stellettamides A–C[5] (Fig. 1).

2. Results and discussion

2.1. Preparations of aziridines

The δ-methyl γ,δ-epimino α,β-unsaturated nitriles **3a** and (*E*)-**3b** were synthesized by the Horner–Emmons reaction of aldehydes **12a**[8,9] and **12b**[9] obtained by Swern oxidation of the *cis*-alcohol **11a**[6,7] and *trans*-alcohol **11b**[6,7] with diethyl cyanomethylphosphonate in 87% yield (*E*:*Z*=51:36) and 34% yield from **11a** and **11b**, respectively. Similarly, the aldehydes **12a** and **12b** were treated with (carbethoxymethylene)triphenylphosphorane and triethyl phosphonoacetate affording the ester **4a** in 67% yield (*E*:*Z*=46:21) and (*E*)-**4b** in 52% yield from **11a** and **11b**, respectively.

Keywords: Aziridine; Photolysis; [3+2] Cycloaddition; Pyrrolidine; Indolizidine.
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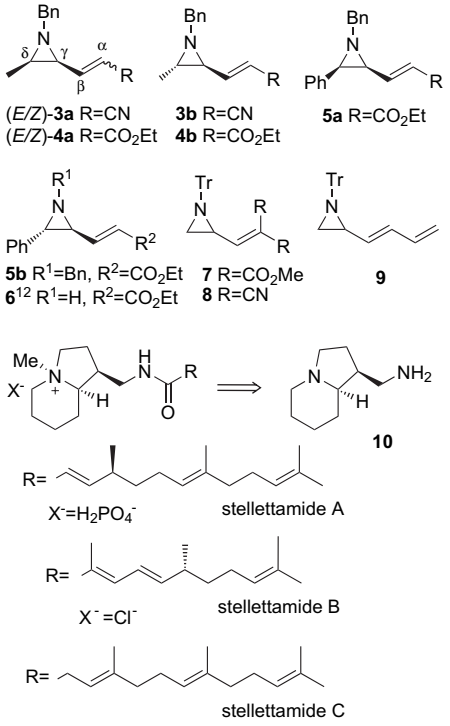
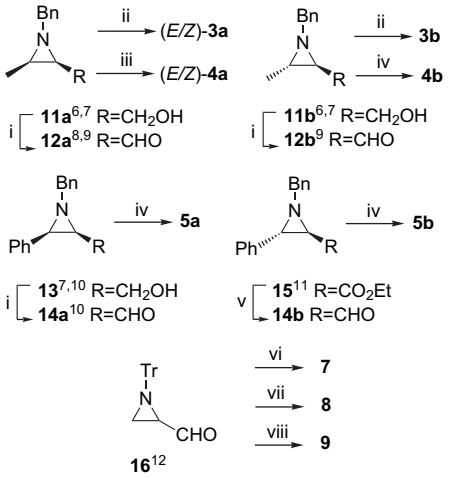


Figure 1.

Each 2,3-*trans* aziridine, **3b** and **4b**, was obtained as a 1:0.7 mixture of two invertomers at nitrogen in the aziridine (Scheme 2).[7]



Scheme 2. Reagents and conditions: (i) $(COCl)_2$, Me_2SO, NEt_3, CH_2Cl_2, −70 °C; (ii) $(EtO)_2P(O)CH_2CN$, NaH, THF, 0 °C; (iii) $Ph_3P{=}CHCO_2Et$, CH_2Cl_2, −40 °C; (iv) $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF or CH_2Cl_2, 0 °C; (v) DIBAL-H, CH_2Cl_2, −70 °C; (vi) $CH_2(CO_2Me)_2$, pyrrolidine, CH_2Cl_2; (vii) $CH_2(CN)_2$, toluene, 110 °C; (viii) $Ph_2(PO)CH_2CH{=}CH_2$, *n*BuLi, THF, −70 °C.

In a similar manner, the δ-phenyl γ,δ-epimino α,β-unsaturated esters **5a** and **5b** were obtained by the Horner–Emmons reaction of the aldehyde **14a**[10] with triethyl phosphonoacetate in 26% yield and in 53% yield from *cis*-alcohol **13**[7,10] and ester **15**,[11] respectively. The compound **6** was prepared according to the literature procedure.[12] The *N*-trityl diester **7**, dinitrile **8**, and butadiene **9** were synthesized from *N*-trityl aldehyde **16**[13] as shown in Scheme 2 (see Section 4).

2.2. Reactions of aziridine (*Z*)-1 with disubstituted alkenes

The disubstituted aziridine (*Z*)-**1** reacts with cyclic alkenes (e.g., 2-cyclopentenone and *N*-phenylmaleimide), affording the adducts in moderate yields.[4] The stereochemistries at 2-, 3-, and 4-position of these pyrrolidines were all cis. Therefore, we investigated the cycloaddition of acyclic 1,2-disubstituted alkenes and (*Z*)-**1**. Direct irradiation of a solution of (*Z*)-**1** with 10 equiv of (*Z*)-2-pentenenitrile in acetonitrile with a low-pressure mercury lamp in a quartz test tube at room temperature (conversion 78%) afforded adduct **17** (56%)[14] (Fig. 2). Ethyl crotonate reacted also with (*Z*)-**1** (conversion 56%), yielding a 1:2 mixture of adducts **18a** and **18b** (50%).[14] The structures of adducts **17**, **18a**, and **18b** were deduced on the basis of their spectral data. Especially, the stereochemistries of **17**, **18a**, and **18b** were determined by the phase-sensitive NOESY spectra (see Supplementary data). The stereochemistries of the 3,4-positions in adducts **17**, **18a**, and **18b** conserve the stereochemistries of the corresponding alkenes.

2.3. Reactions of 3-substituted aziridines 3–6 with alkenes

The effects of the substituent at the 3-position in the aziridine ring on the [3+2] cycloaddition with alkenes were studied. Irradiation and heating of 3-methylaziridine (*E*)-**3a** with acyclic 1,2-disubstituted alkenes [e.g., (*Z*)-2-pentenenitrile] afforded no pentasubstituted pyrrolidines owing to the steric hindrance between five substituents in the aziridine and the alkene. The photochemical and thermal reactions of 3-methyl and 3-phenylaziridines **3**–**6** with *tert*-butyl acrylate were performed, and the results are summarized in Tables 1 and 2 and Schemes 3 and 4. The cycloaddition of *cis*-methylaziridine **3a** gave *a mixture of* 2,5-*cis*- and -*trans*-pyrrolidines **19a** and **19b** photochemically and thermally, and *trans*-aziridine **3b** afforded the same products without (*E*/*Z*)-isomerization at the side chain (entries 1–6 in Table 1). The results show that stereochemistries of aziridines **3a** and **3b** were not reflected in stereochemistries at 2- and 5-positions in the cycloadducts. The same tendency was also observed on the photocycloaddition of the esters **4a** (2,3-*cis*) and **4b** (2,3-*trans*) (entries 7 and 9 in Table 1). In the thermal reactions of aziridines, the *cis*-aziridines (*E*)- and (*Z*)-**3a** gave the adducts (entries 2 and 6 in Table 1). However, the *trans*-aziridines **3b** and *cis*- and *trans*-aziridines **4a** and **4b** yielded no adducts (entries 4, 8, and 10 in Table 1). In particular, **4b** underwent homosigmatropic rearrangement of vinyl aziridine moiety[15] to afford imine **21** (Scheme 3).

The photoreactions of *trans*-phenylaziridines **6** with methyl acrylate yielded the 2,5-*trans*-pyrrolidines (*E*)-**24b** (entry 5

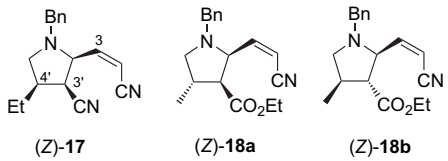


Figure 2.

Table 1. Photochemical and thermal reactions of aziridines **3** and **4** with *tert*-butyl acrylate

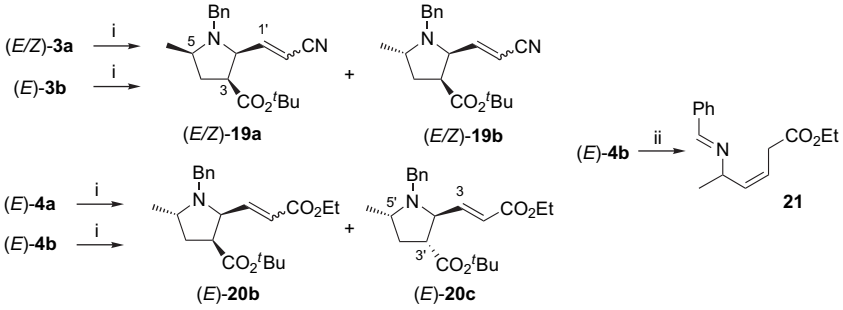
Entry	Aziridine	Reaction conditions	Reaction time (h)	Conversion (%)	Products and yields (%)[14,a]
1	(*E*)-**3a**	hν[b]	2.5	88	(*E*)-**19a** (14) and (*E*)-**19b** (27)
2	(*E*)-**3a**	Δ[c]	3	81	(*E*)-**19a** (35) and (*E*)-**19b** (12)
3	(*E*)-**3b**	hν	0.75	78	(*E*)-**19a** (21) and (*E*)-**19b** (21)
4	(*E*)-**3b**	Δ	0.5	100	Complex mixture
5	(*Z*)-**3a**	hν	2	93	(*Z*)-**19a** (12) and (*Z*)-**19b** (59)
6	(*Z*)-**3a**	Δ	3	83	(*Z*)-**19a** (26) and (*Z*)-**19b** (17)
7	(*E*)-**4a**	hν	2.5	91	(*Z*)-**20b** (26) and (*Z*)-**20c** (26)
8	(*E*)-**4a**	Δ	2	0	No reaction
9	(*E*)-**4b**	hν	1.5	69	(*Z*)-**20b** (17) and (*Z*)-**20c** (17)
10	(*E*)-**4b**	Δ	0.5	100	**21** (33)

[a] Isolated yield.
[b] A 0.060 mol L^{-1} solution of aziridine in acetonitrile with 10 equiv of *tert*-butyl acrylate was irradiated at rt.
[c] A 0.060 mol L^{-1} solution of aziridine in xylene with 10 equiv of *tert*-butyl acrylate was heated under reflux.

Table 2. Photochemical and thermal reactions of aziridines **5** and **6** with alkyl acrylate

Entry	Aziridine	Reaction conditions	Reaction time (h)	Conversion (%)	Products and yields (%)[14,a]
1	(*E*)-**5a**	hν[b,c]	2	58	(*E*)-**22b** (18) and (*E*)-**22d** (9)
2	(*E*)-**5a**	Δ[c,d]	1.5	100	(*E*)-**22d** (21) and (*E*)-**23b** (11)
3	(*E*)-**5b**	hν	0.5	100	(*E*)-**22b** (20) and (*E*)-**22d** (7)
4	(*E*)-**5b**	Δ	0.75	100	(*E*)-**22a** (14), (*E*)-**22c** (19), and (*E*)-**23a** (5)
5	**6**	hν[b,e]	1	92	(*E*)-**24b** (26)
6[f]	**6**	Δ	—	—	(*E*)-**24a** (28) and (*E*)-**25** (16)

[a] Isolated yield.
[b] A 0.060 mol L^{-1} solution of aziridine in acetonitrile with 10 equiv of *tert*-butyl acrylate was irradiated at rt.
[c] *tert*-Butyl acrylate (3 equiv) was used.
[d] A 0.060 mol L^{-1} solution of aziridine in xylene with 10 equiv of *tert*-butyl acrylate was heated under reflux.
[e] Methyl acrylate (10 equiv) was used.
[f] See Ref. 12.

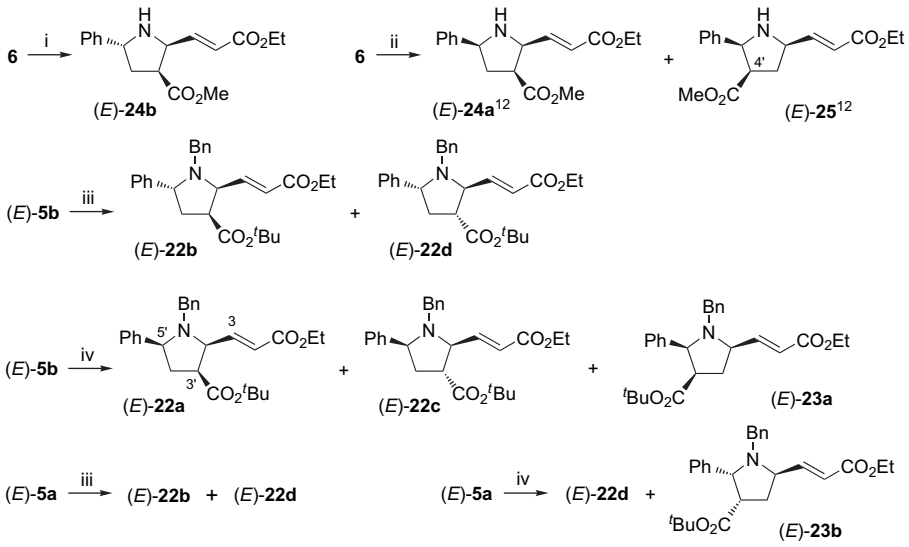


Scheme 3. Reagents and conditions: (i) λ=254 nm, CH_2=$CHCO_2{}^tBu$, MeCN, rt; (ii) CH_2=$CHCO_2{}^tBu$, xylene, 145 °C.

in Table 2) and those thermal reactions afforded the 2,5-*cis*-pyrrolidines (*E*)-**24a** and (*E*)-**25**[12] exclusively (entry 6 in Table 2). The photochemical cycloaddition of *trans*-aziridine **5b** with *tert*-butyl acrylate similarly afforded the 2,5-*trans*-pyrrolidines (*E*)-**22b** and (*E*)-**22d** (entry 3 in Table 2) and the thermal reactions gave the 2,5-*cis*-pyrrolidines (*E*)-**22a**, (*E*)-**22c**, and (*E*)-**23a** exclusively (entry 4 in Table 2). From the results, the ring opening of 3-phenylaziridine **6** and **5b** and cycloaddition with alkenes seems to proceed based on the Woodward–Hoffmann prediction.[2a] On the other hand, both photochemical and thermal reactions of *cis*-phenylaziridine **5a** afforded only the 2,5-*trans*-pyrrolidines [(*E*)-**22b**, (*E*)-**22d**, and (*E*)-**23b**] (entries 1 and 2 in Table 2; Scheme 4). Therefore, in the reactions of 3-phenylaziridines **5** and **6** with alkenes, the stereochemistries of aziridines were not strictly reflected in stereochemistries of the cycloadducts.

Especially, the 3-phenylaziridines **5** and **6** react with *tert*-butyl acrylate thermally, also affording head-to-tail adducts (*E*)-**23a**, (*E*)-**23b**, and (*E*)-**25**, whose formation is discussed later in this paper.

The structures of adducts **19**, **20**, and **22**–**24** were deduced on the basis of their spectral data. Especially, the stereochemistries of (*E*)-**19a**,**b**, (*E*)-**20b**,**c**, (*E*)-**22a**,**d**, (*E*)-**23a**,**b**, and (*E*)-**24b** were determined by the phase-sensitive NOESY spectra (see Supplementary data). The regio- and stereochemistries of (*Z*)-**19a** and (*Z*)-**19b** were determined from the H–H and C–H COSY spectra and from a comparison of the spectral data with those of (*E*)-**19a** and (*E*)-**19b**. In particular, the configuration in the pyrrolidine ring was deduced from the comparison of the ^{1}H NMR chemical shifts at the 3-position of (*Z*)-**19a** (δ 2.64–2.71) and (*Z*)-**19b** (δ 3.28–3.36) with those of (*E*)-**19a** (δ 2.64) and (*E*)-**19b** (δ 3.20–3.28).



Scheme 4. Reagents and conditions: (i) λ=254 nm, CH_2=$CHCO_2Me$, MeCN, rt; (ii) Ref. 12; (iii) λ=254 nm, CH_2=$CHCO_2{}^tBu$, MeCN, rt; (iv) CH_2=$CHCO_2{}^tBu$, xylene, 145 °C.

2.4. Reactions of aziridines 3 and 5 with molecular oxygen

The reactions of aziridines **1**–**6** and electron-deficient alkenes mainly gave head-to-head adducts. The regiochemistries for the adducts could not be clearly rationalized by the interaction between HOMO of the azomethine ylide **A** generated from **1**–**6** and LUMO of the electron-deficient alkenes. Therefore, we assumed that the intermediates for the reaction possess a biradical character (e.g., **B**; Fig. 3) and attempted to trap the chemical species with molecular oxygen.[16] Direct irradiation of a solution of (*Z*)-**3a** in acetonitrile under bubbling oxygen with a low-pressure mercury lamp in a quartz test tube at room temperature (conversion 83%) afforded dioxazolidine **26** (56%). By analogy with the photoreactions of (*Z*)-**3a**, the ester (*E*)-**5b** gave (conversion 100%) benzaldehyde (30%), *N*-benzylbenzamide (28%), and crotonate **27** (20%), which would be afforded by decomposition of dioxazolidine **28** (Scheme 5). Reactions of disubstituted aziridines **1** and **2** under oxygen were also performed, and the corresponding dioxazolidines could not be observed.

The aziridines **1**–**6** underwent photochemical and thermal C,C-bond cleavage giving mainly the biradical intermediate **B** (Fig. 3), followed by [3+2] cycloaddition to alkene to afford the head-to-head adducts presumably. The azomethine ylide intermediate **A** (Fig. 3) generated from 3-phenylaziridines **5** and **6** simultaneously was especially stabilized by the phenyl substituent, and then cyclized with alkenes yielding the head-to-tail adducts (*E*)-**23a**, (*E*)-**23b**, and (*E*)-**25** by heating. The formation of the head-to-tail adducts occurred only in the thermal conditions. The results may show the

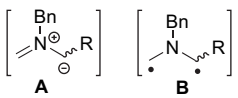
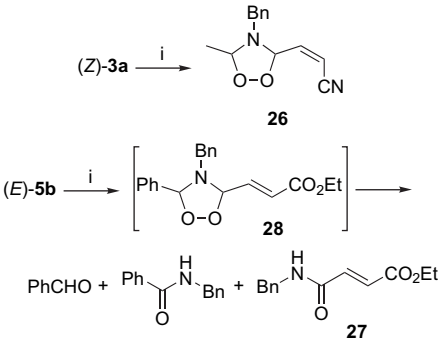


Figure 3.



Scheme 5. Reagents and conditions: (i) λ=254 nm, O_2, MeCN, rt.

transition state for the cyclization step lies much higher than those of the head-to-head adducts.

The structures of benzaldehyde and *N*-benzylbenzamide were identified by a comparison of their ^1H and ^{13}C NMR spectra with those of commercial products. The structures of **26** and **27** were deduced on the basis of their spectral data. The molecular ion peak in the mass spectrum (MS) of **26** indicates the 1:1 adducts of intermediate **B** and oxygen. The ^{13}C NMR spectrum of **26** shows characteristic signals at δ_C 93.8 and 95.3 due to the dioxazolidine moiety. The compound **26** was obtained as a single stereoisomer, and the stereochemistry could not be determined due to the instability. The molecular ion peak in MS of **27** shows 233 [M^+ of **28** (339) minus M^+ of benzaldehyde (106)], and the IR bands at 3430, 1720, and 1670 cm^{-1} reveal amine, ester, and amide moieties, respectively.

2.5. Reactions of aziridines 7–9 possessing diester, dinitrile, and butadiene functional groups at the 2-position with various alkenes

The aziridines **1**–**6** bearing one electron-withdrawing group (e.g., ester or nitrile) underwent [3+2] cycloaddition with only electron-deficient alkenes to give adducts.

Table 3. Photochemical reactions of aziridines **7–9** with various alkenes[a]

Entry	Aziridine	Alkene	Reaction time (h)	Conversion (%)	Products and yields (%)[14,b]
1	**7**	Acrylonitrile	1	56	**29** (18)
2	**7**	Vinyl acetate	3.5	—	—[c]
3	**8**	Acrylonitrile	2	49	**30** (31)
4	**8**	Vinyl acetate	3	100	**31** (7)
5	**8**	Isoprene[d]	3.5	37	**32** (19)
6	**9**	Acrylonitrile	1	72	(*E*)-**33** (54) and (*Z*)-**33** (12)

[a] A 0.060 mol L^{-1} solution of aziridine in acetonitrile with 10 equiv of alkene was irradiated at rt.
[b] Isolated yield.
[c] The reaction gave complex mixture.
[d] Isoprene (3 equiv) was used.

The electron-withdrawing inductive effects at the 2-position in the aziridine ring on the [3+2] cycloaddition with alkenes were studied. In earlier studies of the 1,3-dipolar cycloaddition of carbonyl ylide and alkenes, the carbonyl ylides possessing stronger electron-withdrawing substituents (e.g., dinitrile) reacted with electron-rich alkenes better than the ylides possessing weaker ones (e.g., diester and mononitrile).[17] Therefore, we became interested in the reactivity of the [3+2] cycloaddition of aziridines **7–9** with various alkenes. The results are summarized in Table 3 and Fig. 4. The reactions of aziridines **7–9** and acrylonitrile afforded adducts **29**, **30**, and (*E*/*Z*)-**33** in moderate yields (entries 1, 3, and 6). With the decreasing electron-withdrawing inductive effects of the substituent, the reaction proceeded more efficiently. Only the most electron-deficient aziridine **8** reacted with non-electron-deficient alkenes (vinyl acetate and isoprene) to give the adducts (entries 4 and 5).

The stereo- and regiochemistries of **29–33** were determined by the mean of the ^{1}H and ^{13}C NMR spectra and/or H–H COSY and phase-sensitive NOESY spectra. In particular, the phase-sensitive NOESY spectra of **30–32** and (*Z*)-**33** show the cis-orientation at C-2 and C-3 in the pyrrolidine ring (see Supplementary data).

The photoreactions of *N*-tritylaziridines **7–9** and alkenes exclusively gave the cis-adducts **29–33** owing to the steric hindrance of the trityl group.[4b]

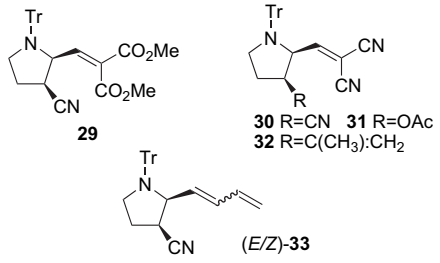


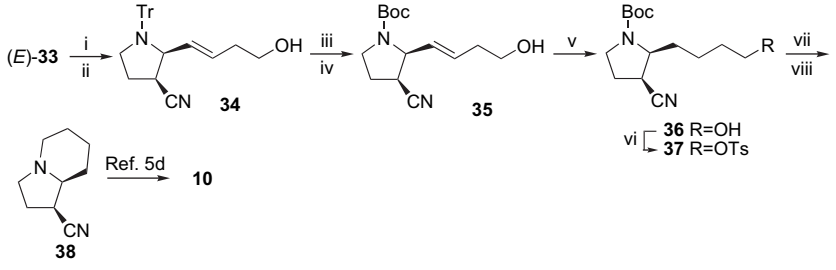
Figure 4.

2.6. Application to the synthesis of indolizidine fragment of stellettamides 10

Since the photoreaction of *N*-tritylaziridine **9** and acrylonitrile gave 2,3-*cis*-pyrrolidine **33** in a moderate yield, we focused on preparing the indolizidine core **10**[5] of stellettamides, using the substituents and the stereochemistry of **33**. Hydroboration of the side chain in (*E*)-**33** with 9-BBN and H_2O_2 gave alcohol **34** in 25% yield. Detritylation of **34**, *N*-Boc protection (79%), and reduction of the double bond in **35** proceeded successfully, yielding butanol **36** (95%). After tosylation of **36** (76%), deprotection of *N*-Boc for **37** occurred in HCl–dioxane and cyclization by treatment of NaOH afforded indolizidine **38**,[5d,18] which had been transformed by authentic methods[5d] into **10**, in 89% yield (Scheme 6).

3. Conclusions

The reactions of β-aziridinylacrylonitrile **1** with disubstituted electron-deficient alkene and photoreactions of 3-substituted aziridines **3–6** with electron-deficient alkenes afforded the novel head-to-head adducts (1,2,3,5-tetrasubstituted pyrrolidines) selectively and efficiently. However, the thermal reactions of 3-phenylaziridines **5** and **6** with electron-deficient alkenes gave head-to-tail adducts **23** and **25** in addition to head-to-head adducts. The trisubstituted aziridines **3** and **5** reacted with molecular oxygen, affording dioxazolidine **26** and cleaved products, respectively. From the result, the [3+2] cycloaddition of aziridines and alkenes may occur via an intermediate **B** with a biradical character. The photoreaction of *N*-tritylaziridines **7–9** bearing diester, dinitrile, and butadiene groups in the side chain with electron-deficient alkenes yielded 2,3-*cis*-pyrrolidine derivatives **29**, **30**, and **33** exclusively. In particular, the dinitrile **8** reacted also with non-electron-deficient alkenes. The formal synthesis of the indolizidine fragment of stellettamides **10** starting from the pyrrolidine (*E*)-**33** was achieved in a convenient manner.



Scheme 6. Reagents and conditions: (i) 9-BBN, THF, rt; (ii) H_2O_2, THF, rt; (iii) TFA, $CHCl_3$, MeOH, 0 °C; (iv) Boc_2O, NaOH, THF–H_2O, 0 °C; (v) H_2, Pd/C, EtOH, rt; (vi) TsCl, pyridine, −20 °C; (vii) HCl, dioxane, rt; (viii) NaOH aq, rt.

4. Experimental

4.1. General

Mps are uncorrected. Mps were measured with a Yanaco MP-3 apparatus. IR spectra were recorded on a Hitachi 215 spectrometer. ^{1}H NMR spectra were obtained with a JEOL JNM-AL300 (300 MHz), a JEOL JNM-AL400 (400 MHz) or a JEOL JNM-LA500 (500 MHz) spectrometer. ^{13}C NMR spectra were recorded on a JEOL JNM-AL300 (75 MHz), a JEOL JNM-AL400 (100 MHz) or a JEOL JNM-LA500 (125 MHz) spectrometer. Unless otherwise noted, NMR spectra were measured in $CDCl_3$ using tetramethylsilane as an internal standard at room temperature. 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 preparative TLC with Wakogel B-5F.

An Eikosha 60 W low-pressure mercury lamp was used for irradiation. The photolysis solutions were purged with argon before and during irradiation.

4.2. Preparations of aziridines

4.2.1. (*E*,2′*RS*,3′*SR*)-3-(1′-Benzyl-3′-methylaziridin-2′-yl)acrylonitrile [(*E*)-3a] and (*Z*,2′*RS*,3′*SR*)-3-(1′-benzyl-3′-methylaziridin-2′-yl)acrylonitrile [(*Z*)-3a]. To a solution of oxalyl chloride (1.80 g, 14.2 mmol) in dry methylene chloride (33 mL) was added dropwise a solution of DMSO (2.00 g, 25.6 mmol) in dry methylene chloride (26 mL) at −70 °C. After the mixture had been stirred for 20 min at −70 °C, a solution of alcohol **11a**[6,7] (2.28 g, 12.9 mmol) in dry methylene chloride (13 mL) was added dropwise, and stirring was continued for 15 min at −70 °C. Triethylamine (9.0 mL, 65 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 methylene chloride. The organic extract was washed with brine, dried with $MgSO_4$, and concentrated in vacuo, giving aldehyde **12a**[8,9] that was used for the next step without further purification. To a suspension of NaH [680 mg, 17.0 mmol; prepared from an NaH dispersion (60%, 1.13 g) by washing it twice with hexane (12 mL)] in dry THF (10 mL) was added dropwise a solution of diethyl cyanomethylphosphonate (3.01 g, 17.0 mmol) in dry THF (15 mL) at 0 °C. After the mixture had been stirred for 10 min at 0 °C, a solution of aldehyde **12a** (12.9 mmol) in dry THF (15 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 (7:3)] to afford (*E*)-**3a** (1.29 g, 51%) and (*Z*)-**3a** (914 mg, 36%).

Compound (*E*)-**3a**, an oil; IR (film): 2200 cm^{-1} (C≡N); ^{1}H NMR (400 MHz): δ 1.14 (d, 3H, J=5.9 Hz, CH_3), 1.98–2.04 (m with quintet character, 1H, J=6 Hz, H-3′), 2.13–2.17 (m with t-character, 1H, J=6 Hz, H-2′), 3.49, 3.62 (each d, 2H, J=13.7 Hz, CH_2Ph), 5.58 (dd, 1H, J=16.1, 0.8 Hz, H-2), 6.60 (dd, 1H, J=16.1, 6.4 Hz, H-3), 7.25–7.36 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ 13.3 (q, CH_3), 43.5, 43.8 (2d, C-2′, C-3′), 63.8 (t, *C*H$_2$Ph), 101.2 (d, C-2), 117.1 (s, C-1), 126.9, 127.4, 128.1 (3d, 5C in Ph), 138.1 (s, C in Ph), 151.4 (d, C-3); EI-MS *m*/*z* 198 (M$^+$, 5%), 107 (100), 91 (51), 80 (12); HRMS calcd for $C_{13}H_{14}N_2$: 198.1157, found: 198.1157.

Compound (*Z*)-**3a**, an oil; IR (film): 2200 cm^{-1} (C≡N); ^{1}H NMR (400 MHz): δ 1.21 (d, 3H, J=5.9 Hz, CH_3), 2.05–2.11 (m with quintet character, 1H, J=6 Hz, H-3′), 2.55 (dd, 1H, J=9, 7 Hz, H-2′), 3.53, 3.66 (each d, 2H, J=13.7 Hz, CH_2Ph), 5.45 (dd, 1H, J=11.2, 1 Hz, H-2), 6.28 (dd, 1H, J=11.2, 9 Hz, H-3), 7.26–7.36 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ 14.6 (q, CH_3), 43.2, 43.5 (2d, C-2′, C-3′), 64.0 (t, *C*H$_2$Ph), 100.7 (d, C-2), 115.8 (s, C-1), 127.1, 127.6, 128.3 (3d, 5C in Ph), 138.1 (s, C in Ph), 152.3 (d, C-3); EI-MS *m*/*z* 198 (M$^+$, 7%), 107 (100), 91 (53), 80 (15); HRMS calcd for $C_{13}H_{14}N_2$: 198.1157, found: 198.1165.

4.2.2. Ethyl (*E*,2′*RS*,3′*SR*)-3-(1′-benzyl-3′-methylaziridin-2′-yl)acrylate [(*E*)-4a] and ethyl (*Z*,2′*RS*,3′*SR*)-3-(1′-benzyl-3′-methylaziridin-2′-yl)acrylate [(*Z*)-4a]. To a solution of oxalyl chloride (584 mg, 4.6 mmol) in dry methylene chloride (9.1 mL) was added dropwise a solution of DMSO (440 mg, 7.6 mmol) in dry methylene chloride (7.6 mL) at −70 °C. After the mixture had been stirred for 20 min at −70 °C, a solution of alcohol **11a**[6,7] (675 mg, 3.81 mmol) in dry methylene chloride (3.8 mL) was added dropwise, and stirring was continued for 25 min at −70 °C. Triethylamine (2.7 mL, 19 mmol) was added slowly to the reaction mixture, which was stirred for 10 min at −70 °C, warmed to −40 °C and further stirred for 40 min. To the mixture was added dropwise a solution of (carbethoxymethylene)triphenylphosphorane (3.3 g, 9.48 mmol) in methylene chloride (4.6 mL) at −40 °C. After the mixture had been stirred for 1.5 h at −40 °C, ice/water (30 mL) was added to the mixture, and the organic phase was extracted with methylene chloride. The organic 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 (2:3)] to afford (*E*)-**4a** (443 mg, 46%) and (*Z*)-**4a** (191 mg, 21%).

Compound (*E*)-**4a**, an oil; IR (film): 1710 cm^{-1} (C=O); ^{1}H NMR (400 MHz): δ 1.19 (d, 3H, J=5.6 Hz, 3′-CH_3), 1.28 (t, 3H, J=7.2 Hz, OCH$_2$CH_3), 1.92–1.98 (m with quintet character, 1H, J=6 Hz, H-3′), 2.13–2.17 (m with t-character, 1H, J=7 Hz, H-2′), 3.53, 3.60 (each d, 2H, J=13.6 Hz, CH_2Ph), 4.18 (q, 2H, J=7.2 Hz, OCH$_2$), 6.05 (dd, 1H, J=15.8, 0.7 Hz, H-2), 6.81 (dd, 1H, J=15.6, 7.3 Hz, H-3), 7.24–7.32 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ 14.0, 14.5 (2q, 2CH_3), 43.2, 44.3 (2d, C-2′, C-3′), 60.6, 64.5 (2t, OCH$_2$, *C*H$_2$Ph), 124.0 (d, C-2), 127.5, 128.1, 129.0 (3d, 5C in Ph), 139.3 (s, C in Ph), 146.1 (d, C-3), 166.7 (s, C-1); EI-MS *m*/*z* 245 (M$^+$, 7%), 200 (11), 172 (88), 154 (100), 126 (9), 108 (10), 91 (61), 80 (16); HRMS calcd for $C_{15}H_{19}NO_2$: 245.1416, found: 245.1418.

Compound (*Z*)-**4a**, an oil; IR (film): 1715 cm^{-1} (C=O); ^{1}H NMR (400 MHz): δ 1.21 (d, 3H, J=5.6 Hz, 3′-CH_3), 1.30 (t, 3H, J=7.2 Hz, OCH$_2$CH_3), 2.00–2.07 (m, 1H, H-3′),

3.31–3.35 (m with t-character, 1H, J=8 Hz, H-2′), 3.53, 3.67 (each d, 2H, J=13.7 Hz, CH_2Ph), 4.20 (q, 2H, J=7.2 Hz, OCH_2), 5.93 (dd, 1H, J=11.5, 0.8 Hz, H-2), 6.04 (dd, 1H, J=11.5, 8.5 Hz, H-3), 7.23–7.34 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ 14.3, 14.6 (2q, $2CH_3$), 42.3, 43.0 (2d, C-2′, C-3′), 60.2, 64.3 (2t, OCH_2, CH_2Ph), 122.4 (d, C-2), 127.3, 128.1, 128.7 (3d, 5C in Ph), 139.4 (s, C in Ph), 148.2 (d, C-3), 166.8 (s, C-1); EI-MS m/z 245 (M^+, 1%), 200 (2), 172 (18), 154 (22), 133 (13), 112 (20), 91 (100); HRMS calcd for $C_{15}H_{19}NO_2$: 245.1416, found: 245.1413.

4.2.3. (*E*,2′*RS*,3′*RS*)-3-(1′-Benzyl-3′-methylaziridin-2′-yl)acrylonitrile (3b). By analogy with the synthesis of **3a**, oxidation of alcohol **11b**[6,7] (180 mg, 1.02 mmol) with oxalyl chloride and DMSO gave aldehyde **12b**,[9] which was consequently treated with NaH (60%, 48 mg, 1.2 mmol) and diethyl cyanomethylphosphonate (213 mg, 1.2 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 (2:1)] of the reaction mixture afforded esters **3b** (68.7 mg, 34%) as a 1:0.7 mixture of invertomers at nitrogen; an oil; IR (film): 2210 cm^{-1} (C≡N); ^{1}H NMR (400 MHz): δ 1.14 (d, 3H, J=6.0 Hz, CH_3), 1.29 (d, 2.1H, J=5.2 Hz, CH_3), 1.90–1.94 (m, 1H, H-2′), 1.97–2.03 (m, 0.7H, H-3′), 2.18–2.23 (m, 1H, H-3′), 2.41–2.46 (m with d-character, 0.7H, J=10.0 Hz, H-2′), 3.62, 3.83 (each d, 2H, J=14.0 Hz, CH_2Ph), 3.70, 3.81 (each d, 1.4H, J=14.0 Hz, CH_2Ph), 5.54 (d, 1H, J=16.0 Hz, H-2), 5.58 (d, 0.7H, J=16.0 Hz, H-2), 6.57–6.66 (m, 1+0.7H, H-3), 7.25–7.36 (m, 5+3.5H, Ph); ^{13}C NMR (100 MHz): δ major invertomer 11.3 (q, CH_3), 43.8, 45.8 (2d, C-2′, C-3′), 54.8 (t, CH_2Ph), 98.9 (d, C-2), 117.4 (s, C-1), 126.9, 127.5, 128.3 (3d, 5C in Ph), 138.9 (s, C in Ph), 154.3 (d, C–3); EI-MS m/z 198 (M^+, 10%), 107 (100), 91 (40), 80 (8); HRMS calcd for $C_{13}H_{14}N_2$: 198.1157, found: 198.1156.

4.2.4. Ethyl (*E*,2′*RS*,3′*RS*)-3-(1′-benzyl-3′-methylaziridin-2′-yl)acrylate (4b). By analogy with the synthesis of **3a**, oxidation of alcohol **11b**[6,7] (335 mg, 1.89 mmol) with oxalyl chloride and DMSO gave aldehyde **12b**,[9] which was consequently treated with NaH (60%, 90.8 mg, 2.3 mmol) and triethyl phosphonoacetate (515 mg, 2.3 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 (4:1)] of the reaction mixture afforded esters **4b** (241 g, 52%) as a 1:0.7 mixture of invertomers at nitrogen; an oil; IR (film): 1710 cm^{-1} (C═O); ^{1}H NMR (400 MHz): δ 1.24–1.32 (m, 6+2.1H, 3′-CH_3 and OCH_2CH_3), 1.38 (d, 2.1H, J=5.9 Hz, CH_3), 1.92–2.01 (m, 1+0.7H, H-3′), 2.26–2.29 (m, 0.7H, H-2′), 2.49 (dd, 1H, J=10.3, 2.7 Hz, H-2′), 3.66, 3.83 (each d, 1.4H, J=14.2 Hz, CH_2Ph), 3.68, 3.90 (each d, 2H, J=13.8 Hz, CH_2Ph), 4.11–4.23 (m, 2+1.4H, OCH_2), 6.01 (d, 0.7H, J=15.6 Hz, H-2), 6.13 (d, 1H, J=15.4 Hz, H-2), 6.75 (dd, 0.7H, J=15.6, 7.6 Hz, H-3), 6.89 (dd, 1H, J=15.4, 10.3 Hz, H-3), 7.24–7.34 (m, 5+3.5H, Ph); ^{13}C NMR (100 MHz): δ major invertomer 14.2, 18.1 (2q, $2CH_3$), 44.5, 44.8 (2d, C-2′, C-3′), 57.2, 60.3 (2t, OCH_2, CH_2Ph), 124.2 (d, C-2), 126.7, 127.4, 128.1 (3d, 5C in Ph), 138.9 (s, C in Ph), 144.1 (d, C-3), 165.4 (s, C-1); minor invertomer 11.1, 14.2 (2q, $2CH_3$), 42.1, 46.1 (2d, C-2′, C-3′), 54.8, 60.1 (2t, OCH_2, CH_2Ph), 121.0 (d, C-2), 126.5, 127.3, 128.1 (3d, 5C in Ph), 139.1 (s, C in Ph), 148.3 (d, C-3), 165.9 (s, C-1); EI-MS m/z 245 (M^+, 5%), 200 (14), 172 (85), 154 (100), 126 (10), 108 (12), 91 (63), 80 (20); HRMS calcd for $C_{15}H_{19}NO_2$: 245.1416, found: 245.1421.

4.2.5. Ethyl (*E*,2′*RS*,3′*SR*)-3-(1′-benzyl-3′-phenylaziridin-2′-yl)acrylate (5a). By analogy with the synthesis of **3a**, oxidation of alcohol **13**[7,10] (1.07 mg, 4.48 mmol) with oxalyl chloride and DMSO gave aldehyde **14a**,[10] which was consequently treated with NaH (60%, 215 mg, 5.4 mmol) and triethyl phosphonoacetate (1.20 g, 5.4 mmol) in dry methylene chloride at 0 °C, and the resulting mixture was stirred for 12 h at room temperature. Flash column chromatography [hexane–ethyl acetate (4:1)] of the reaction mixture afforded esters **5a** (361 mg, 26%); an oil; IR (film): 1720 cm^{-1} (C═O); ^{1}H NMR (300 MHz): δ 1.20 (t, 3H, J=7.2 Hz, CH_3), 2.51 (dd, 1H, J=7.9, 6.5 Hz, H-2′), 3.06 (d, 1H, J=6.5 Hz, H-3′), 3.72, 3.80 (each d, 2H, J=13.6 Hz, CH_2Ph), 4.08 (q, 2H, J=7.2 Hz, OCH_2), 6.01 (d, 1H, J=15.8 Hz, H-2), 6.49 (dd, 1H, J=15.8, 7.9 Hz, H-3), 7.20–7.39 (m, 10H, 2Ph); ^{13}C NMR (100 MHz): δ 14.3 (q, CH_3), 47.3, 49.5 (2d, C-2′, d C-3′), 60.2, 64.2 (2t, OCH_2, CH_2Ph), 123.7 (d, C-2), 127.0, 127.5, 127.7, 128.0, 128.3 (5d, 10C in 2Ph), 135.8, 138.2 (2s, 2C in 2Ph), 144.4 (d, C-3), 165.5 (s, C-1); EI-MS m/z 307 (M^+, 18%), 234 (100), 216 (20), 91 (63); HRMS calcd for $C_{20}H_{21}NO_2$: 307.1572, found: 307.1576.

4.2.6. Ethyl (*E*,2′*RS*,3′*RS*)-3-(1′-benzyl-3′-phenylaziridin-2′-yl)acrylate (5b). To a solution of the ester **15**[11] (480 mg, 1.71 mmol) in dry methylene chloride (8.5 mL) was added dropwise a 0.97 M solution of DBAL-H (3.5 mL, 3.4 mmol) in hexane at −70 °C. After the mixture had been stirred for 15 min at −70 °C, sodium fluoride (1.43 g, 34 mmol) was added to the mixture. The reaction was quenched by the addition of water (1.0 mL), and the reaction mixture was allowed to reach room temperature. The white precipitate was filtered off and washed with diethyl ether. The organic extract was washed with brine, dried with $MgSO_4$, and concentrated in vacuo giving an aldehyde **14b** that was used for the next step without further purification. To a suspension of NaH [41 mg, 1.71 mmol; prepared from an NaH dispersion (60%, 68 mg) by washing it twice with hexane (0.5 mL)] in dry methylene chloride (2 mL) was added dropwise a solution of triethyl phosphonoacetate (383 mg, 1.71 mmol) dry methylene chloride (2 mL) at 0 °C. After the mixture had been stirred for 10 min at 0 °C, a solution of aldehyde **14b** in dry methylene chloride (4 mL) was added dropwise, and stirring was continued for 0.5 h at 0 °C. Ice/water (20 mL) was added slowly to the mixture, and the organic phase was extracted with methylene chloride. The organic 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 (2:1)] to afford **5b** (277 mg, 53% from **15**); an oil; IR (film): 1720 cm^{-1} (C═O); ^{1}H NMR (400 MHz): δ 1.30 (t, 3H, J=7.2 Hz, CH_3), 2.78 (dd, 1H, J=10, 2.8 Hz, H-2′), 2.94 (br s, 1H, H-3′), 3.91, 4.07 (each br d, 2H, J=14.0 Hz, CH_2Ph), 4.21 (q, 2H, J=7.2 Hz, OCH_2), 6.13 (d, 1H, J=15.6 Hz, H-2), 7.02 (dd, 1H, J=15.6, 10 Hz, H-3), 7.22–7.52 (m, 10H, 2Ph); ^{13}C NMR (100 MHz): δ 14.3 (q, CH_3), 48.6 (d, C-2′), 51.0 (d, C-3′), 57.4 (t, OCH_2), 60.5 (t, CH_2Ph), 124.9 (d, C-2), 125.9, 126.9, 127.2, 127.6, 128.3, 128.4 (6d, 10C in 2Ph), 138.5, 138.7 (2s, 2C in

2Ph), 142.9 (d, C-3), 165.5 (s, C-1); EI-MS *m/z* 307 (M^+, 12%), 262 (10), 234 (58), 216 (100), 142 (10), 129 (10), 105 (18), 91 (42); HRMS calcd for $C_{20}H_{21}NO_2$: 307.1572, found: 307.1573.

4.2.7. Dimethyl 1-tritylaziridin-2-ylmethlylenemalonate (7). To a solution of the aldehyde **16**[13] (932 mg, 3.0 mmol) in dry methylene chloride (18 mL) was added dimethyl malonate (367 mg, 2.8 mmol). Pyrrolidine (five drops) was added to the mixture at −70 °C, which stirred for 5 h at −70 °C and was warmed to room temperature and further stirred for 30 h. The reaction was quenched with 5% citric acid and the organic phase was extracted with methylene chloride. The organic 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 (3:1)] to afford **7** (596 mg, 47%) as colorless needles; mp 165–168 °C (hexane–ethyl acetate); IR ($CHCl_3$): 1720 cm^{-1} (C=O); ^1H NMR (400 MHz): δ 1.58 (d, 1H, *J*=6.1 Hz, H-3′), 2.07 (d, 1H, *J*=2.7 Hz, H-3′), 2.20 (ddd, 1H, *J*=9.5, 6.1 Hz, 2.7, H-2′), 3.62, 3.81 (2s, 6H, 2Me), 7.00 (d, 1H, *J*=9.5 Hz, H-3), 7.19–7.30 (m, 9H, 3Ph), 7.42–7.45 (m, 6H, 3Ph); ^{13}C NMR (100 MHz): δ 30.7 (t, C-3′), 31.8 (d, C-2′), 52.1, 52.5 (2q, 2OMe), 74.4 (s, *C*Ph_3), 126.8, 127.4, 129.2 (3d, 15C in 3Ph), 128.4 (s, C-2), 143.6 (s, 3C in 3Ph), 151.4 (d, C-3), 163.9, 164.9 (2s, $2CO_2$); EI-MS *m/z* 427 (M^+, 1%), 257 (1), 243 (100), 228 (3), 165 (22); Anal. Calcd for $C_{27}H_{25}NO_4$: C, 75.86; H, 5.89; N, 3.28%. Found: C, 75.99; H, 5.98; N, 3.24%.

4.2.8. 1-Tritylaziridin-2-ylmethlylenemalononitrile (8). To a solution of the malononitrile (793 mg, 11.9 mmol) in dry toluene (15 mL) was added aldehyde **16**[13] (3.1 g, 9.9 mmol). The reaction mixture was stirred for 10 min at 110 °C and concentrated in vacuo, giving a residue that was subjected to flash column chromatography [hexane–ethyl acetate (5:1)] to afford **8** (1.72 g, 56%) as colorless prisms; mp 85–87 °C (hexane–chloroform); IR ($CHCl_3$): 2210 cm^{-1} (C≡N); ^1H NMR (400 MHz): δ 1.80 (d, 1H, *J*=6.0 Hz, H-3′), 2.28 (br s, 1H, H-3′), 2.28–2.33 (m, 1H, H-2′), 7.21–7.47 (m, 16H, H-3, 3Ph); ^{13}C NMR (100 MHz): δ 32.6 (t, C-3′), 33.8 (d, C-2′), 74.7 (s, *C*Ph_3), 89.4 (s, C-2), 110.3, 111.8 (2s, 2CN), 127.2, 127.8, 128.9 (3d, 15C in 3Ph), 142.7 (s, 3C in 3Ph), 169.4 (d, C-3); EI-MS *m/z* 361 (M^+, 1%), 260 (3), 245 (100), 183 (5), 165 (25), 105 (4), 77 (4); HRMS calcd for $C_{25}H_{19}N_3$: 361.1578, found: 361.1570.

4.2.9. 2-[(*E*)-1,3-Butadien-1-yl]-1-tritylaziridine (9). To a solution of allyldiphenylphosphine oxide (1.0 g, 4.2 mmol) and HMPA (1.5 g, 8.4 mmol) in dry THF (15 mL) was added dropwise butyl lithium (2.6 mL, 1.6 M in hexane) at −70 °C. After the mixture had been stirred for 10 min at −70 °C, a solution of aldehyde **16**[13] (1.1 g, 3.5 mmol) in dry THF (5 mL) was added dropwise at −70 °C. The mixture was stirred for 1 h, warmed to room temperature, and further stirred for 3 h. Ice/water (20 mL) was added slowly to the mixture, the organic phase was extracted with ether. The organic extract was washed with satd aqueous $NaHCO_3$ and brine, dried with $MgSO_4$, and concentrated in vacuo, giving a residue that was subjected to flash column chromatography [hexane–ethyl acetate (10:1)] to afford **9** (666 mg, 56%) as colorless oil; IR ($CHCl_3$): 1590 cm^{-1} (C=C); ^1H NMR (400 MHz): δ 1.38 (d, 1H, *J*=6.1 Hz, H-3), 1.68–1.73 (m, 1H, H-2), 1.82 (d, 1H, *J*=2.7 Hz, H-3), 5.03 (d, 1H, *J*=10.0 Hz, H-4′), 5.13 (d, 1H, *J*=6.8 Hz, H-4′), 5.71 (dd, 1H, *J*=15.1, 7.8 Hz, H-1′), 6.24 (dd, 1H, *J*=15.1, 10.5 Hz, H-2′), 6.34–6.44 (m with dt-character, 1H, *J*=16.8 Hz, 10, H-3′), 7.15–7.29, 7.46–7.48 (2m, 15H, 3Ph); ^{13}C NMR (100 MHz): δ 29.6 (t, C-3), 34.3 (d, C-2), 74.4 (s, *C*Ph_3), 115.9 (t, C-4′), 126.5, 127.3, 129.4 (3d, 15C in 3Ph), 132.2, 134.8, 136.5 (3d, C-1′, C-2′, C-3′), 144.2 (s, 3C in 3Ph); EI-MS *m/z* 337 (M^+, 2%), 257 (1), 243 (100), 228 (3), 165 (23), 94 (2), 77 (2); HRMS calcd for $C_{25}H_{23}N$: 337.1831, found: 337.1834.

4.3. Reactions of aziridines (*Z*)-1 with disubstituted alkenes

4.3.1. (*Z*)-1 and (*Z*)-2-Pentenenitrile. A solution of aziridine (*Z*)-**1** (510 mg, 2.77 mmol) in dry acetonitrile (45 mL) with (*Z*)-2-pentenenitrile (2.19 g, 27.7 mmol) was irradiated with a low-pressure mercury lamp (conversion 78%) in a quartz test tube for 1.5 h at room temperature. After removal of the solvent, flash column chromatography [hexane–ethyl acetate (4:1)] of the residue afforded (*Z*)-**17** (320 mg, 56%[14]).

(2*Z*,2′*RS*,3′*RS*,4′*SR*)-3-(1-Benzyl-3-cyano-4-ethylpyrrolidin-2-yl)acrylonitrile [(*Z*)-**17**], an oil; IR (film): 2210 cm^{-1} (C≡N); ^1H NMR (500 MHz): δ 0.93 (t, 3H, *J*=7.3 Hz, 4′-CH_2CH_3), 1.55–1.73 (m, 2H, *J*=7.3 Hz, 4′-CH_2), 2.30–2.37 (m, 1H, H-4′), 2.64 (t, 1H, *J*=9.8 Hz, H-5′), 2.87 (dd, 1H, *J*=9.8, 7.0 Hz, H-5′), 3.29 (dd, 1H, *J*=7.3, 5.5 Hz, H-3′), 3.48, 3.83 (each d, 2H, *J*=13.7 Hz, CH_2Ph), 3.87 (dd, 1H, *J*=9.2, 5.5 Hz, H-2′), 5.55 (d, 1H, *J*=11.0 Hz, H-2), 6.63 (dd, 1H, *J*=11.0, 9.2 Hz, H-3), 7.24–7.32 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ 12.4 (q, 4′-CH_2CH_3), 24.8 (t, 4′-CH_2), 39.9 (d, C-3′), 41.1 (d, C-4′), 56.3 (t, C-5′), 57.5 (t, *C*H_2Ph), 65.4 (d, C-2′), 103.4 (d, C-2), 114.9, 114.9 (2s, 2CN), 127.3, 128.3, 128.4 (3d, 5C in Ph), 137.9 (s, C in Ph), 152.7 (d, C-3); EI-MS *m/z* 265 (M^+, 26%), 225 (5), 184 (37), 174 (9), 91 (100), 65 (10); HRMS calcd for $C_{17}H_{19}N_3$: 265.1579, found: 265.1575.

4.3.2. (*Z*)-1 and (*E*)-Ethyl crotonate. A solution of aziridine (*Z*)-**1** (44.7 mg, 0.24 mmol) in dry acetonitrile (4.0 mL) with (*E*)-ethyl crotonate (275 mg, 2.4 mmol) was irradiated with a low-pressure mercury lamp (conversion 56%) in a quartz test tube for 1.5 h at room temperature. After removal of the solvent, flash column chromatography [hexane–ethyl acetate (2:1)] of the residue afforded a 1:2 mixture of **18a** and **18b** (20.1 mg, 50%[14]).

Ethyl (2*RS*,3*RS*,4*RS*)-1-benzyl-2-[(*Z*)-2-cyanovinyl]-4-methylpyrrolidine-3-carboxylate [(*Z*)-**18a**]; ^1H NMR (500 MHz): δ 1.04 (d, 3H, *J*=6.4 Hz, 4-Me), 1.24 (t, 3H, *J*=7 Hz, OCH_2CH_3), 2.12 (t, 1H, *J*=9.5 Hz, H-5), 2.62–2.70 (m, 1H, H-4), 2.87 (t, 1H, *J*=9.8 Hz, H-3), 3.11 (dd, 1H, *J*=9, 6.7 Hz, H-5), 3.53, 3.75 (each d, 2H, *J*=13.1 Hz, CH_2Ph), 3.96 (t, 1H, *J*=9.8 Hz, H-2), 4.11 (q, 2H, *J*=7 Hz, OCH_2), 5.27 (d, 1H, *J*=11.0 Hz, H-2′), 6.41–6.46 (m with t-character, 1H, *J*=10 Hz, H-1′), 7.22–7.31 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ 14.4 (q, 4-Me), 17.2 (q, OCH_2CH_3), 36.0 (d, C-4), 55.6 (d, C-3), 58.1 (t, C-5), 60.5 (t, *C*H_2Ph), 60.8 (t, OCH_2), 65.4 (d, C-2), 100.2 (d, C-2′), 115.4 (s,

CN), 127.0, 128.1, 128.7 (3d, 5C in Ph), 138.1 (s, C in Ph), 153.7 (d, C-1′), 171.4 (s. CO_2).

Ethyl (2*RS*,3*SR*,4*SR*)-1-benzyl-2-[(*Z*)-2-cyanovinyl]-4-methylpyrrolidine-3-carboxylate [(*Z*)-**18b**]; ^{1}H NMR (500 MHz): δ 1.13 (d, 3H, *J*=6.7 Hz, 4-Me), 1.29 (t, 3H, *J*=7 Hz, OCH_2CH_3), 2.40 (dd, 1H, *J*=9, 7 Hz, H-3), 2.52–2.61 (m, 1H, H-4), 2.62–2.70 (m, 2H, 2H-5), 3.40, 3.81 (each d, 2H, *J*=13.1 Hz, CH_2Ph), 3.79 (t, 1H, *J*=9 Hz, H-2), 4.19 (q, 2H, *J*=7 Hz, OCH_2), 5.39 (d, 1H, *J*=11.0 Hz, H-2′), 6.37 (dd, 1H, *J*=11.0, 9.8 Hz, H-1′), 7.22–7.31 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ 14.3 (q, 4-Me), 20.8 (q, OCH_2CH_3), 35.5 (d, C-4), 57.7 (d, C-3), 58.2 (t, C-5), 60.2 (t, CH_2Ph), 61.2 (t, OCH_2), 68.6 (d, C-2), 101.7 (d, C-2′), 115.2 (s, CN), 127.0, 128.1, 128.4 (3d, 5C in Ph), 138.5 (s, C in Ph), 154.7 (d, C-1′), 172.0 (s, CO_2).

4.4. Reactions of 3-methyl aziridines 3 and 4 with alkenes

4.4.1. (*E*)-3a and (*Z*)-2-pentenenitrile. A solution of aziridine (*E*)-**3a** (220 mg, 1.10 mmol) in dry acetonitrile (18.3 mL) with 10 equiv of (*Z*)-2-pentenenitrile was irradiated with a low-pressure mercury lamp in a quartz test tube for 1.5 h at room temperature. The reactant was recovered quantitatively.

A solution of aziridine (*E*)-**3a** (54 mg, 0.27 mmol) in xylene (4.5 mL) with 10 equiv of (*Z*)-2-pentenenitrile was heated under reflux for 4 h affording a complex mixture.

4.4.2. Aziridines 3 and 4 with *tert*-butyl acrylate. A 0.060 mol L^{-1} solution of aziridines **3** and **4** in dry acetonitrile with 10 equiv of *tert*-butyl acrylate was irradiated with a low-pressure mercury lamp in a quartz test tube at room temperature. After removal of the solvent, flash column chromatography afforded the adducts. A 0.060 mol L^{-1} solution of aziridines **3** and **4** in xylene with 10 equiv of *tert*-butyl acrylate was heated under reflux. The results are summarized in Table 1.

4.4.3. *tert*-Butyl (2*RS*,3*RS*,5*SR*)-1-benzyl-2-[(*E*)-2-cyanovinyl]-5-methylpyrrolidine-3-carboxylate [(*E*)-19a]. An oil; IR ($CHCl_3$): 2220 (C≡N), 1720 cm^{-1} (C=O); ^{1}H NMR (300 MHz): δ 1.03 (d, 3H, *J*=6.4 Hz, 5′-Me), 1.45 (s, 9H, CMe_3), 1.86 (ddd, 1H, *J*=13.0, 5.0, 4.4 Hz, H-4), 2.29 (ddd, 1H, *J*=13.0, 10.3, 7.4 Hz, H-4), 2.64 (m with quintet character, 1H, *J*=5 Hz, H-3), 3.15–3.28 (m, 1H, H-5), 3.51, 3.76 (each d, 2H, *J*=13.9 Hz, CH_2Ph), 3.73 (dd, 1H, *J*=8.4, 5.5 Hz, H-2), 5.42 (dd, 1H, *J*=16.2, 0.7 Hz, H-2′), 6.64 (dd, 1H, *J*=16.2, 8.4 Hz, H-1′), 7.21–7.33 (m, 5H, Ph); ^{13}C NMR (125 MHz): δ 16.3 (q, 5-Me), 28.0 (q, CMe_3), 34.7 (t, C-4), 48.9 (d, C-3), 51.4 (t, CH_2Ph), 54.9 (d, C-5), 65.6 (d, C-2), 81.1 (s, CMe_3), 101.2 (d, C-2′), 117.0 (s, CN), 127.0, 128.2, 128.3 (3d, 5C in Ph), 138.8 (s, C in Ph), 155.5 (d, C-1′), 172.5 (s, CO_2); EI-MS *m*/*z* 326 (M^+, 7%), 269 (32), 253 (11), 179 (33), 91 (100); HRMS calcd for $C_{20}H_{26}N_2O_2$: 326.1994, found: 326.1999.

4.4.4. *tert*-Butyl (2*RS*,3*RS*,5*RS*)-1-benzyl-2-[(*E*)-2-cyanovinyl]-5-methylpyrrolidine-3-carboxylate [(*E*)-19b]. Colorless crystals; mp 115–116 °C (hexane–ethyl acetate); IR ($CHCl_3$): 2220 (C≡N), 1720 cm^{-1} (C=O); ^{1}H NMR (300 MHz): δ 1.10 (d, 3H, *J*=6.1 Hz, 5-Me), 1.39 (s, 9H, CMe_3), 1.70 (ddd, 1H, *J*=13.2, 9.2, 4.2 Hz, H-4), 2.48 (ddd, 1H, *J*=13.2, 9.9, 8.6 Hz, H-4), 3.15–3.25 (m, 1H, H-5), 3.20–3.28 (m, 1H, H-3), 3.46, 3.83 (each d, 2H, *J*=13.9 Hz, CH_2Ph), 3.66 (dd, 1H, *J*=9.7, 7.9 Hz, H-2), 5.25 (d, 1H, *J*=16.2 Hz, H-2′), 6.66 (dd, 1H, *J*=16.2, 9.7 Hz, H-1′), 7.21–7.34 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ 19.2 (q, 5-Me), 28.2 (q, CMe_3), 33.7 (t, C-4), 46.8. (d, C-3), 52.0 (t, CH_2Ph), 55.3 (d, C-5), 64.7 (d, C-2), 81.2 (s, CMe_3), 102.6 (d, C-2′), 116.5 (s, CN), 126.9, 128.1, 128.2 (3d, 5C in Ph), 138.6 (s, C in Ph), 151.9 (d, C-1′), 170.5 (s, CO_2); EI-MS *m*/*z* 326 (M^+, 7%), 269 (19), 253 (31), 179 (41), 91 (100); Anal. Calcd for $C_{20}H_{26}N_2O_2$: C, 73.59; H, 8.03; N, 8.58%. Found: C, 73.66; H, 7.99; N, 8.61%.

4.4.5. *tert*-Butyl (2*RS*,3*RS*,5*SR*)-1-benzyl-2-[(*Z*)-2-cyanovinyl]-5-methylpyrrolidine-3-carboxylate [(*Z*)-19a]. Colorless crystals; mp 77–78 °C (hexane–ethyl acetate); IR ($CHCl_3$): 2220 (C≡N), 1720 cm^{-1} (C=O); ^{1}H NMR (400 MHz): δ 1.05 (d, 3H, *J*=6.6 Hz, 5-Me), 1.48 (s, 9H, CMe_3), 1.92 (ddd, 1H, *J*=12.9, 5.1, 3.7 Hz, H-4), 2.28 (ddd, 1H, *J*=12.9, 10.5, 7.5 Hz, H-4), 2.64–2.71 (m, 1H, H-3), 3.24–3.32 (m, 1H, H-5), 3.61, 3.73 (each d, 2H, *J*=13.9 Hz, CH_2Ph), 4.07 (dd, 1H, *J*=10, 6.6 Hz, H-2), 5.37 (d, 1H, *J*=10.7 Hz, H-2′), 6.36 (dd, 1H, *J*=10.7, 10 Hz, H-1′), 7.22–7.33 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ 15.8 (q, 5-Me), 28.0 (q, CMe_3), 34.6 (t, C-4), 49.5 (d, C-3), 51.7 (t, CH_2Ph), 55.3 (d, C-5), 64.6 (d, C-2), 81.3 (s, CMe_3), 101.3 (d, C-2′), 115.2 (s, CN), 126.8, 128.1, 128.2 (3d, 5C in Ph), 138.9 (s, C in Ph), 154.9 (d, C-1′), 172.0 (s, CO_2); EI-MS *m*/*z* 326 (M^+, 3%), 269 (29), 253 (11), 179 (41), 91 (100); HRMS calcd for $C_{20}H_{26}N_2O_2$: 326.1994, found: 326.1988.

4.4.6. *tert*-Butyl (2*RS*,3*RS*,5*RS*)-1-benzyl-2-[(*Z*)-2-cyanovinyl]-5-methylpyrrolidine-3-carboxylate [(*Z*)-19b]. Colorless crystals; mp 104–106 °C (hexane–ethyl acetate); IR ($CHCl_3$): 2220 (C≡N), 1720 cm^{-1} (C=O); ^{1}H NMR (400 MHz): δ 1.09 (d, 3H, *J*=6.3 Hz, 5-Me), 1.40 (s, 9H, CMe_3), 1.70 (ddd, 1H, *J*=13, 9.0, 3.9 Hz, H-4), 2.49 (ddd, 1H, *J*=13, 10, 8.5 Hz, H-4), 3.19–3.27 (m, 1H, H-5), 3.28–3.36 (m, 1H, H-3), 3.54, 3.78 (each d, 2H, *J*=13.9 Hz, CH_2Ph), 4.18 (dd, 1H, *J*=10.7, 8.1 Hz, H-2), 5.41 (dd, 1H, *J*=11.0, 0.7 Hz, H-2′), 6.46 (dd, 1H, *J*=11.0, 10.7 Hz, H-1′), 7.22–7.34 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ 19.1 (q, 5-Me), 28.2 (q, CMe_3), 33.9 (t, C-4), 46.7 (d, C-3), 52.5 (t, CH_2Ph), 55.7 (d, C-5), 63.2 (d, C-2), 81.2 (s, CMe_3), 102.0 (d, C-2′), 114.9 (s, CN), 126.9, 128.2, 128.3 (3d, 5C in Ph), 138.7 (s, C in Ph), 151.7 (d, C-1′), 170.9 (s, CO_2); EI-MS *m*/*z* 326 (M^+, 3%), 269 (17), 255 (28), 235 (28), 179 (30), 107 (23) and 91 (100); Anal. Calcd for $C_{20}H_{26}N_2O_2$: C, 73.59; H, 8.03; N, 8.58%. Found: C, 73.57; H, 7.98; N, 8.48%.

4.4.7. Ethyl (*E*,2′*RS*,3′*RS*,5′*RS*)-3-(1-benzyl-3-*tert*-butyloxycarbonyl-5-methylpyrrolidin-2-yl)acrylate [(*E*)-20b] and ethyl (*E*,2′*RS*,3′*SR*,5′*RS*)-3-(1-benzyl-3-*tert*-butyloxycarbonyl-5-methylpyrrolidin-2-yl)acrylate [(*E*)-20c]. An oily 5:4 mixture; ^{1}H NMR (400 MHz): δ 1.03 (d, 3H, *J*=6.4 Hz, 5′-Me for **c**), 1.09 (d, 3H, *J*=6.4 Hz, 5′-Me for **b**), 1.27 (t, 3H, *J*=7.3 Hz, OCH_2CH_3 for **b**), 1.29 (t, 3H,

J=7.4 Hz, OCH_2CH_3 for **c**), 1.34 (s, 9H, CMe_3 for **b**), 1.44 (s, 9H, CMe_3 for **c**), 1.65 (ddd, 1H, J=13.1, 4.3, 4.0 Hz, H-4′ for **b**), 1.83–1.88 (m with dt-character, 1H, J=12.8, 5 Hz, H-4′ for **c**), 2.30 (ddd, 1H, J=12.8, 10.4, 7.6 Hz, H-4′ for **c**), 2.53 (td, 1H, J=13.1, 9.2 Hz, H-4′ for **b**), 2.64–2.69 (m with quintet character, 1H, J=5 Hz, H-3′ for **c**), 3.19–3.25 (m, 3H, H-3′ for **b** and H-5′ for **b** and **c**), 3.50, 3.79 (each d, 4H, J=14 Hz, CH_2Ph for **b** and **c**), 3.72 (dd, 1H, J=10, 7.6 Hz, H-2′ for **b**), 3.75 (dd, 1H, J=8.9, 5.2 Hz, H-2′ for **c**), 4.19 (q, 4H, J=7.3 Hz, OCH_2 for **b** and **c**), 5.75 (d, 1H, J=15.6 Hz, H-2 for **b**), 5.88 (d, 1H, J=15.6 Hz, H-2 for **c**), 6.84 (dd, 1H, J=15.6, 10 Hz, H-3 for **b**), 6.87 (dd, 1H, J=15.6, 8.9 Hz, H-3 for **c**), 7.19–7.32 (m, 10 H, Ph for **b** and **c**); ^{13}C NMR (100 MHz): δ 14.4 (q, OCH_2CH_3 for **b** and **c**), 16.7 (q, 5′-Me for **c**), 19.6 (q, 5′-Me for **b**), 28.1 (q, CMe_3 for **b** and **c**), 33.6 (t, C-4′ for **b**), 34.8 (t, C-4′ for **c**), 46.9 (d, C-3′ for **b**), 49.1 (d, C-3′ for **c**), 51.3, 51.9 (t, CH_2Ph for **b** and **c**), 54.7, 55.3 (d, C-5′ for **b** and **c**), 60.3, 60.4 (t, OCH_2 for **b** and **c**), 64.2, 65.1 (d, C-2′ for **b** and **c**), 80.7 (s, CMe_3 for **b** and **c**), 123.2 (d, C-2 for **c**), 124.9 (d, C-2 for **b**), 126.6, 127.9, 128.0, 128.1, 128.3 (5d, 10C in Ph for **b** and **c**), 139.3 (s, 2C in Ph for **b** and **c**), 144.3 (d, C-3 for **b**), 148.1 (d, C-3 for **c**), 165.4, 166.0 (s, C-1 for **b** and **c**), 170.9, 172.8 (s, CO_2 for **b** and **c**).

4.4.8. Ethyl (*Z*)-5-[(*E*)-*N*-benzylideneamino]-3-hexenoate (21). An oil; IR ($CHCl_3$): 1720 (C=O), 1635 cm^{-1} (C=N); ^{1}H NMR (400 MHz): δ 1.24 (t, 3H, J=7.1 Hz, OCH_2CH_3), 1.35 (d, 3H, J=6.6 Hz, 3H-3), 3.17 (ddd, 2H, J=7.3, 3.4, 1.7 Hz, 2H-2), 4.13 (q, 2H, J=7.1 Hz, OCH_2), 4.25–4.33 (m, 1H, H-5), 5.66 (dtd, 1H, J=11.0, 7.3, 1.0 Hz, H-3), 5.78–5.85 (m with ddt-character, 1H, J=11, 8, 2 Hz, H-4), 7.37–7.42, 7.71–7.74 (each m, 5H, Ph), 8.31 (s, 1H, N=CH); ^{13}C NMR (100 MHz): δ 14.3 (q, OCH_2CH_3), 23.2 (q, C-6), 33.6 (t, C-2), 60.7 (t, OCH_2), 62.9 (d, C-5), 120.9 (d, C-3), 128.0, 128.4, 130.4 (3, 5C in Ph), 135.9 (d, C-4), 136.1 (s, C in Ph), 159.3 (d, N=C), 171.2 (s, C-1); EI-MS m/z 245 (M^+, 16%), 230 (6), 200 (16), 172 (31), 158 (100), 131 (11), 106 (23), 91 (27), 67 (15), 55 (11); HRMS calcd for $C_{15}H_{19}NO_2$: 245.1416, found: 245.1417.

4.5. Reactions of 3-phenylaziridines 5 and 6 with alkenes

A 0.060 mol L^{-1} solution of aziridines **5** and **6** in dry acetonitrile with 10 equiv of *tert*-butyl acrylate was irradiated with a low-pressure mercury lamp in a quartz test tube at room temperature. After removal of the solvent, flash column chromatography afforded the adducts. A 0.060 mol L^{-1} solution of aziridines **5** and **6** in xylene with 10 equiv of *tert*-butyl acrylate was heated under reflux. The results are summarized in Table 2.

4.5.1. Ethyl (*E*,2′*RS*,3′*RS*,5′*RS*)-3-(1-benzyl-3-*tert*-butyloxycarbonyl-5-phenylpyrrolidin-2-yl)acrylate [(*E*)-22a]. An oil; IR ($CHCl_3$): 1710 cm^{-1} (C=O); ^{1}H NMR (500 MHz): δ 1.26 (t, 3H, J=7.0 Hz, OCH_2CH_3), 1.39 (s, 9H, CMe_3), 2.17 (t, 2H, J=8.5 Hz, H-4′), 2.99–3.06 (m with q-character, 1H, J=9 Hz, H-3′), 3.45, 3.75 (each d, 2H, J=14.0 Hz, CH_2Ph), 3.67–3.73 (m with q-character, 2H, J=8 Hz, H-2′, H-5′), 4.15 (q, 2H, J=7.0 Hz, OCH_2), 5.87 (dd, 1H, J=15.6, 0.6 Hz, H-2), 6.78 (dd, 1H, J=15.6, 8 Hz, H-3), 7.03–7.47 (m, 10H, 2Ph); ^{13}C NMR (100 MHz): δ 14.4 (q, OCH_2CH_3), 28.1 (q, CMe_3), 37.7 (t, C-4′), 47.8 (d, C-3′), 54.1 (t, CH_2Ph), 60.2 (t, OCH_2), 64.2, 66.9 (2d, C-2′, C-5′), 81.0 (s, CMe_3), 122.6 (d, C-2), 126.9, 127.3, 127.6, 127.8, 128.4, 129.8 (6d, 10C in 2Ph), 136.3 (s, C in CH_2Ph), 141.9 (s, C in 5′-Ph), 147.3 (d, C-3), 165.8 (C-1), 170.8 (s, CO_2); EI-MS m/z 435 (M^+, 6%), 378 (10), 362 (6), 344 (24), 334 (7), 288 (34), 216 (11), 104 (8), 91 (100), 57 (13); HRMS calcd for $C_{27}H_{33}NO_4$: 435.2410, found: 435.2415.

4.5.2. Ethyl (*E*,2′*RS*,3′*RS*,5′*SR*)-3-(1-benzyl-3-*tert*-butyloxycarbonyl-5-phenylpyrrolidin-2-yl)acrylate [(*E*)-22b]. An oil; IR ($CHCl_3$): 1715 cm^{-1} (C=O); ^{1}H NMR (500 MHz): δ 1.29 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.34 (s, 9H, CMe_3), 1.97 (ddd, 1H, J=13.7, 9.8, 5.5 Hz, H-4′), 2.84 (td, 1H, J=13.7, 9.8 Hz, H-4′), 3.38–3.42 (m, 1H, H-3′), 3.40, 3.60 (each d, 2H, J=13.7 Hz, CH_2Ph), 3.93 (dd, 1H, J=10.5, 7.0 Hz, H-2′), 4.14 (dd, 1H, J=9.8, 5.5 Hz, H-5′), 4.22 (q, 2H, J=7.2 Hz, OCH_2), 5.72 (d, 1H, J=15.6 Hz, H-2), 6.97 (dd, 1H, J=15.6, 10.5 Hz, H-3), 7.20–7.50 (10H, m, 2Ph); ^{13}C NMR (100 MHz): δ 14.4 (q, OCH_2CH_3), 28.1 (q, CMe_3), 35.3 (t, C-4′), 47.4 (d, C-3′), 51.7 (t, CH_2Ph), 60.4 (t, OCH_2), 63.4, 65.0 (2d, C-2′, C-5′), 80.9 (s, CMe_3), 125.8 (d, C-2), 126.7, 127.1, 127.4, 128.0, 128.3, 128.4 (6d, 10C in 2Ph), 138.7 (s, C in CH_2Ph), 142.8 (d, C-3), 144.0 (s, C in 5′-Ph), 165.3 (C-1), 170.5 (s, CO_2); EI-MS m/z 435 (M^+, 6%), 378 (41), 362 (14), 344 (100), 288 (86), 216 (15), 91 (80); HRMS calcd for $C_{27}H_{33}NO_4$: 435.2410, found: 435.2412.

4.5.3. Ethyl (*E*,2′*RS*,3′*SR*,5′*RS*)-3-(1-benzyl-3-*tert*-butyloxycarbonyl-5-phenylpyrrolidin-2-yl)acrylate [(*E*)-22c]. An oil; IR ($CHCl_3$): 1710 cm^{-1} (C=O); ^{1}H NMR (400 MHz): δ 1.28 (t, 3H, J=7.1 Hz, OCH_2CH_3), 1.39 (s, 9H, CMe_3), 1.88–1.96 (m, 1H, H-4′), 2.35 (ddd, 1H, J=12.5, 8, 5 Hz, H-4′), 2.72–2.79 (m, 1H, H-3′), 3.47, 3.76 (each d, 2H, J=13.7 Hz, CH_2Ph), 3.53–3.56 (m with t-character, 1H, J=8 Hz, H-2′), 3.78–3.82 (m with t-character, 1H, J=8 Hz, H-5′), 4.16 (q, 2H, J=7.1 Hz, OCH_2), 5.90 (d, 1H, J=15.6 Hz, H-2), 6.79 (dd, 1H, J=15.6, 7.8 Hz, H-3), 7.07–7.47 (m, 10H, 2Ph); ^{13}C NMR (100 MHz): δ 14.4 (q, OCH_2CH_3), 28.2 (q, CMe_3), 37.8 (t, C-4′), 49.0 (d, C-3′), 54.9 (t, CH_2Ph), 60.3 (t, OCH_2), 66.8, 67.3 (2d, C-2′, C-5′), 80.9 (s, CMe_3), 121.9 (d, C-2), 126.9, 127.2, 127.4, 127.8, 128.4, 129.7 (6d, 10C in 2Ph), 136.5 (s, C in CH_2Ph), 142.6 (s, C in 5′-Ph), 149.3 (d, C-3), 166.0 (C-1), 172.6 (s, CO_2); EI-MS m/z 435 (M^+, 37%), 378 (68), 362 (21), 344 (44), 334 (9), 306 (26), 288 (48), 202 (9), 91 (100); HRMS calcd for $C_{27}H_{33}NO_4$: 435.2410, found: 435.2404.

4.5.4. Ethyl (2*E*,2′*RS*,3′*SR*,5′*SR*)-3-(1-benzyl-3-*tert*-butyloxycarbonyl-5-phenylpyrrolidin-2-yl)acrylate [(*E*)-22d]. An oil; IR ($CHCl_3$): 1720, 1715 cm^{-1} (C=O); ^{1}H NMR (500 MHz): δ 1.30 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.45 (s, 9H, CMe_3), 2.33 (ddd, 1H, J=13.4, 7.5, 5 Hz, H-4′), 2.59 (ddd, 1H, J=13.4, 9.5, 8.2 Hz, H-4′), 2.74 (ddd, 1H, J=9.5, 5, 2.7 Hz, H-3′), 3.33, 3.60 (each d, 2H, J=14.0 Hz, CH_2Ph), 4.01–4.05 (m with t-character, 1H, J=8 Hz, H-5′), 4.08 (dd, 1H, J=9.8, 2.7 Hz, H-2′), 4.22 (q, 2H, J=7.2 Hz, OCH_2), 5.74 (d, 1H, J=15.6 Hz, H-2), 7.00 (dd, 1H, J=15.6, 9.8 Hz, H-3), 7.20–7.40 (m, 10H, 2Ph);

^{13}C NMR (100 MHz): δ 14.4 (q, OCH_2CH_3), 28.2 (q, CMe_3), 36.4 (t, C-4′), 48.5 (d, C-3′), 50.9 (t, CH_2Ph), 60.5 (t, OCH_2), 64.0, 65.3 (2d, C-2′, C-5′), 80.8 (s, CMe_3), 124.1 (d, C-2), 126.5, 127.3, 127.8, 127.9, 128.0, 128.3 (6d, 10C in 2Ph), 138.8 (s, C in CH_2Ph), 142.6 (s, C in 5′-Ph), 145.5 (d, C-3), 165.8 (C-1), 172.4 (s, CO_2); EI-MS *m*/*z* 435 (M^+, 49%), 378 (66), 362 (20), 344 (33), 334 (10), 306 (37), 288 (51), 216 (10), 91 (100); HRMS calcd for $C_{27}H_{33}NO_4$: 435.2410, found: 435.2414.

4.5.5. Ethyl (*E*,2′*RS*,4′*RS*,5′*SR*)-3-(1-benzyl-4-*tert*-butyloxycarbonyl-5-phenylpyrrolidin-2-yl)acrylate [(*E*)-23a]. An oil contaminated with ca. 65% of (*E*)-**22a**; ^{1}H NMR (500 MHz): δ 0.97 (s, 9H, CMe_3), 1.30 (t, 3H, J=7.0 Hz, OCH_2CH_3), 1.99 (ddd, 1H, J=12.8, 8.2, 6 Hz, H-3′), 2.25 (dt, 1H, J=12.8, 10.1 Hz, H-3′), 3.09 (td, 1H, J=10, 8.2 Hz, H-4′), 3.37–3.42 (m, 1H, H-2′), 3.52, 3.76 (each d, 2H, J=14.0 Hz, CH_2Ph), 4.04 (d, 1H, J=10.4 Hz, H-5′), 4.20 (q, 2H, J=7.0 Hz, OCH_2), 5.97 (d, 1H, J=15.6 Hz, H-2), 6.91 (dd, 1H, J=15.6, 8.2 Hz, H-3), 7.03–7.53 (m, 10H, 2Ph); ^{13}C NMR (100 MHz): δ 14.4 (q, OCH_2CH_3), 27.5 (q, CMe_3), 34.2 (t, C-3′), 48.7 (d, C-4′), 54.1 (t, CH_2Ph), 60.3 (t, OCH_2), 63.1, 68.0 (2d, C-2′, C-5′), 80.2 (s, CMe_3), 122.0 (d, C-2), 126.9, 127.2, 127.8, 128.4, 129.0, 129.8 (6d, 10C in 2Ph), 135.8 (s, C in CH_2Ph), 139.9 (s, C in 5′-Ph), 150.1 (d, C-3), 166.0 (C-1), 170.8 (s, CO_2).

4.5.6. Ethyl (*E*,2′*RS*,4′*SR*,5′*RS*)-3-(1-benzyl-4-*tert*-butyloxycarbonyl-5-phenylpyrrolidin-2-yl)acrylate [(*E*)-23b]. An oil; IR ($CHCl_3$): 1710 cm^{-1} (C=O); ^{1}H NMR (300 MHz): δ 0.97 (s, 9H, CMe_3), 1.31 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.88 (ddd, 1H, J=13.2, 8.8, 2.4 Hz, H-3′), 2.77 (ddd, 1H, J=13.2, 10.6, 8.1 Hz, H-3′), 3.33, 3.63 (each d, 2H, J=13.8 Hz, CH_2Ph), 3.47–3.57 (m, 1H, H-4′), 3.82–3.90 (m, 1H, H-2′), 4.21 (q, 2H, J=7.2 Hz, OCH_2), 4.33 (d, 1H, J=9.7 Hz, H-5′), 5.81 (dd, 1H, J=15.6, 0.6 Hz, H-2), 6.98 (dd, 1H, J=15.6, 9.0 Hz, H-3), 7.16–7.31 (m, 10H, 2Ph); ^{13}C NMR (75 MHz): δ 14.4 (q, OCH_2CH_3), 27.5 (q, CMe_3), 32.6 (t, C-3′), 48.1 (d, C-4′), 51.9 (t, CH_2Ph), 60.5 (t, OCH_2), 60.9 (d, C-2′), 67.2 (d, C-5′), 80.3 (s, CMe_3), 122.8 (d, C-2), 126.7, 127.4, 127.8, 128.0, 128.4, 129.2 (6d, 10C in 2Ph), 138.8, 139.4 (2s, 2C in CH_2Ph, 5′-Ph), 147.9 (d, C-3), 166.0 (C-1), 170.8 (s, CO_2); EI-MS *m*/*z* 435 (M^+, 3%), 378 (28%), 362 (10), 344 (76), 288 (100), 216 (10), 91 (54); HRMS calcd for $C_{27}H_{33}NO_4$: 435.2410, found: 435.2412.

4.5.7. Ethyl (*E*,2′*RS*,3′*RS*,5′*SR*)-3-(3-methyloxycarbonyl-5-phenylpyrrolidin-2-yl)acrylate [(*E*)-24b]. An oil; IR ($CHCl_3$): 3400 (N–H), 1720 cm^{-1} (C=O); ^{1}H NMR (400 MHz): δ 1.29 (t, 3H, J=7.1 Hz, OCH_2CH_3), 1.94 (br s, 1H, NH), 1.96–2.06 (m, 1H, H-4′), 2.68 (ddd, 1H, J=13.7, 8, 6 Hz H-4′), 3.33–3.39 (m, 1H, H-3′), 3.67 (s, 3H, OCH_3), 4.20 (q, 2H, J=7.1 Hz, OCH_2), 4.27–4.31 (m with t-character, 1H, J=7 Hz, H-2′), 4.66–4.70 (m with t-character, 1H, J=8 Hz, H-5′), 6.02 (dd, 1H, J=15.6 Hz, 1.0, H-2), 6.95 (dd, 1H, J=15.6, 7.1 Hz, H-3), 7.22–7.37 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ 14.4 (q, OCH_2CH_3), 37.2 (t, C-4′), 48.6 (d, C-3′), 51.8 (q, OCH_3), 60.3, 61.5 (2d, C-2′, C-5′), 60.5 (t, OCH_2), 122.3 (d, C-2), 126.0, 126.8, 128.4 (3d, 5C in Ph), 144.7 (s, C in Ph), 145.2 (d, C-3), 165.8 (C-1), 172.6 (s, CO_2); EI-MS *m*/*z* 303 (M^+, 16%), 274 (21), 258 (12), 230 (16), 199 (15), 144 (29), 126 (12), 119 (100), 112 (17), 104 (10); HRMS calcd for $C_{17}H_{21}NO_4$: 303.1471, found: 303.1465.

4.6. Reactions of aziridines 3 and 5 with molecular oxygen

4.6.1. Aziridine (*Z*)-3a and oxygen. A solution of (*Z*)-**3a** (200 mg, 1.01 mmol) in acetonitrile was irradiated with a low-pressure mercury lamp (conversion 83%) in a quartz test tube under bubbling oxygen for 2 h at room temperature. After removal of the solvent, flash column chromatography [hexane–ethyl acetate (3:1)] of the residue afforded adducts **26** (46.1 mg, 24%).[14]

(*Z*)-(4-Benzyl-5-methyl-1,2,4-dioxazolidin-3-yl)acrylonitrile (**26**), an oil; IR ($CHCl_3$): 2220 cm^{-1} (C≡N); ^{1}H NMR (400 MHz): δ 1.24 (d, 3H, J=5.4 Hz, 5′-CH_3), 4.01, 4.11 (each d, 2H, J=12.9 Hz, CH_2Ph), 4.72 (q, 1H, J=5.4 Hz, H-5′), 5.37 (d, 1H, J=11.0 Hz, H-2), 5.43 (d, 1H, J=7.8 Hz, H-3′), 6.48 (dd, 1H, J=11.0, 7.8 Hz, H-3), 7.26–7.38 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ 18.5 (q, 5′-CH_3), 57.8 (t, CH_2Ph), 93.8 (d, C-3′), 95.3 (d, C-5′), 100.9 (d, C-2), 114.5 (s, C-1), 127.7, 128.6, 128.7 (3d, 5C in Ph), 136.8 (s, C in Ph), 149.4 (d, C-3); EI-MS *m*/*z* 230 (M^+, 1%), 198 (33), 149 (6), 107 (63), 91 (100), 77 (9), 65 (12), 50 (9); HRMS calcd for $C_{13}H_{14}N_2O_2$: 230.1055, found: 230.1057.

4.6.2. Aziridine (*E*)-5b and oxygen. By analogy with the photoreactions of (*Z*)-**3a**, a solution of (*E*)-**5b** (41.2 mg, 0.13 mmol) in acetonitrile (3 mL) was irradiated (conversion 100%) under bubbling oxygen for 1.5 h. Preparative TLC [hexane–ethyl acetate (5:1)] of the reaction mixture afforded benzaldehyde (4.1 mg, 30%), *N*-benzylbenzamide (7.5 mg, 28%), and ester **27** (6.1 mg, 20%).[14]

Ethyl 4-benzylamino-4-oxocrotonate (**27**), as colorless crystals; mp 110–111 °C (hexane–ethyl acetate); IR ($CHCl_3$): 3430 (N–H), 1720 (C=O), 1670 cm^{-1} (C=O); ^{1}H NMR (400 MHz): δ 1.25 (d, 3H, J=7.2 Hz, OCH_2CH_3), 4.15 (q, 2H, J=7.2 Hz, OCH_2), 4.52 (d, 2H, J=5.6 Hz, CH_2Ph), 6.15 (br s, 1H, NH), 6.89 (d, 1H, J=15.6 Hz, H-2), 6.92 (d, 1H, J=15.6 Hz, H-3), 7.21–7.39 (m, 5H, Ph); ^{13}C NMR (100 MHz): δ 14.3 (q, OCH_2CH_3), 44.1 (t, CH_2Ph), 61.2 (t, OCH_2), 127.7, 127.8, 128.7 (3d, 5C in Ph), 130.7 (d, C-2), 135.8 (d, C-3), 137.2 (s, C in Ph), 163.2 (s, C-4), 165.3 (s, C-1); EI-MS *m*/*z* 233 (M^+, 19%), 187 (11), 128 (8), 106 (100), 99 (11), 91 (20), 79 (5); HRMS calcd for $C_{13}H_{15}NO_3$: 233.1052, found: 233.1057.

4.7. Reactions of aziridines 7–9 possessing diester, dinitrile, and butadiene functional groups with various alkenes

A 0.060 mol L^{-1} solution of aziridines **7–9** in dry acetonitrile with 10 equiv of alkenes was irradiated with a low-pressure mercury lamp in a quartz test tube at room temperature. After removal of the solvent, flash column chromatography afforded the adducts. The results are summarized in Table 3.

4.7.1. Diester 7 and acrylonitrile. Dimethyl (2′*RS*,3′*RS*)-(3-cyano-1-tritylpyrrolidin-2-yl)methylenemalonate (**29**), an oil;

IR ($CHCl_3$): 2240 (C≡N), 1720 cm^{-1} (C=O); ^1H NMR (400 MHz): δ 1.38–1.48 (m, 1H, H-4), 1.81–1.91 (m, 1H, H-4), 1.97–2.05 (m with q-character, 1H, J=9 Hz, H-3), 3.07 (ddd, 1H, J=12.7, 8.3, 6.1 Hz, H-5), 3.53–3.60 (m, 1H, H-5), 3.56, 3.84 (each s, 6H, $2OCH_3$), 4.69 (dd, 1H, J=10.0, 7.6 Hz, H-2), 7.15 (d, 1H, J=10.0 Hz, 2-CH), 7.18–7.28 (m, 9H, 3Ph), 7.46–7.49 (m, 6H, 3Ph); ^{13}C NMR (100 MHz): δ 29.9 (t, C-4), 33.1 (d, C-3), 48.7 (t, C-5), 52.1, 52.7 (2q, $2OCH_3$), 61.1 (d, C-2), 77.5 (s, CPh_3), 118.5 (s, CN), 126.5, 127.8, 128.9 (3d, 15C in 3Ph), 127.0 [s, $C(CO_2Me)_2$], 143.4 (s, 3C in 3Ph), 163.9, 164.3 (2s, $2CO_2$); EI-MS m/z 480 (M^+, 1%), 449 (1), 362 (14), 403 (1), 243 (100), 237 (15), 205 (5), 165 (41), 91 (4), 83 (5), 77 (4); HRMS calcd for $C_{30}H_{28}N_2O_4$: 480.2049, found: 480.2055.

4.7.2. Dinitrile 8 and acrylonitrile. (2*RS*,3*RS*)-(3-Cyano-1-tritylpyrrolidin-2-yl)methylenemalononitrile (**30**), colorless crystals, mp 201–203 °C (hexane–ethyl acetate); IR ($CHCl_3$): 2210 cm^{-1} (C≡N); ^1H NMR (400 MHz): δ 1.52–1.61 (m, 1H, H-4), 1.85–1.95 (m, 1H, H-4), 2.18–2.26 (m, 1H, H-3), 3.06 (ddd, 1H, J=12.2, 7.6, 6.8 Hz, H-5), 3.56 (ddd, 1H, J=12.2, 7.8, 5.9 Hz, H-5), 4.45–4.50 (m with dd-character, 1H, J=10, 8 Hz, H-2), 7.23–7.38, 7.47–7.50 (2m, 16H, 2-CH, 15H in 3Ph); ^1H NMR (400 MHz; acetone-d_6): δ 1.71–1.80 (m with dtd-character, 1H, J=13, 8, 5 Hz, H-4), 1.99–2.10 (m with dtd-character, 1H, J=13, 9, 7 Hz, H-4), 2.40–2.48 (m with q-character, 1H, J=8.5 Hz, H-3), 3.14 (ddd, 1H, J=12.0, 8.1, 6.8 Hz, H-5), 3.66 (ddd, 1H, J=12.0, 8.5, 5.3 Hz, H-5), 4.63 (dd, 1H, J=9.8, 7.8 Hz, H-2), 7.20–7.29 (m, 9H, 3Ph), 7.57–7.60 (m, 6H, 3Ph), 7.93 (d, 1H, J=9.8 Hz, 2-CH); ^{13}C NMR (100 MHz; acetone-d_6): δ 29.7 (t, C-4), 33.7 (d, C-3), 49.2 (t, C-5), 63.8 (d, C-2), 78.0 (s, CPh_3), 89.7 [s, $C(CN)_2$], 111.1, 112.9, 118.7 (3s, 3CN), 127.9, 129.0, 130.1 (3d, 15C in 3Ph), 144.1 (s, 3C in 3Ph), 167.0 [d, C(2)*C*H]; EI-MS m/z 414 (M^+, 1%), 337 (9), 243 (100), 228 (10), 215 (7), 165 (67), 117 (5), 91 (5); HRMS calcd for $C_{28}H_{22}N_4$: 414.1845, found: 414.1841.

4.7.3. Dinitrile 8 and vinyl acetate. (2*RS*,3*RS*)-2-(2,2-Dicyanovinyl)-1-tritylpyrrolidin-3-yl acetate (**31**), colorless crystals, mp 154–157 °C (hexane–ethyl acetate); IR ($CHCl_3$): 2230 (C≡N), 1740 cm^{-1} (C=O); ^1H NMR (500 MHz): δ 1.27–1.35 (m, 1H, H-4), 1.52–1.59 (m, 1H, H-4), 1.99 (s, 3H, CH_3), 2.97 (ddd, 1H, J=11.9, 7.9, 5.5 Hz, H-5), 3.45 (dt, 1H, J=11.9, 7.3 Hz, H-5), 4.49 (dd, 1H, J=9.5, 7.0 Hz, H-2) 4.63–4.68 (m, 1H, H-3), 7.19–7.33, 7.47–7.51 (2m, 16H, H-1′, 15H in 3Ph); ^{13}C NMR (125 MHz): δ 20.7 (q, CH_3), 30.7 (t, C-4), 47.5 (t, C-5), 62.8 (d, C-2), 75.9 (d, C-3), 76.8 (s, CPh_3), 88.4 [s, $C(CN)_2$], 110.0, 112.1 (2s, 2CN), 127.1, 128.1, 129.4 (3d, 15C in 3Ph), 142.8 (s, 3C in 3Ph), 167.8 (d, C-1′), 169.5 (s, CO_2); EI-MS m/z 447 (M^+, 1%), 404 (1), 370 (6), 243 (100), 228 (8), 215 (4), 165 (48), 91 (4), 43 (6); HRMS calcd for $C_{29}H_{25}N_3O_2$: 447.1947, found: 447.1954.

4.7.4. Dinitrile 8 and isoprene. (2*RS*,3*RS*)-(3-Isopropenyl-1-tritylpyrrolidin-2-yl)methylenemalononitrile (**32**), an oil; IR ($CHCl_3$): 2230 cm^{-1} (C≡N); ^1H NMR (400 MHz): δ 1.25–1.39 (m, 1H, H-3), 1.42 (s, 3H, CH_3), 1.48–1.55 (m, 1H, H-4), 1.71–1.80 (m, 1H, H-4), 2.75–2.83 (m with td-character, 1H, J=10, 7 Hz, H-5), 3.43–3.48 (m with t-character, 1H, J=9 Hz, H-5), 4.21–4.26 (m with dd-character, 1H, J=10, 8 Hz, H-2), 4.51, 4.69 (each br s, 2H, $C(CH_3)$:CH_2), 7.06 (d, 1H, J=9.8 Hz, 2-CH), 7.10–7.25 (m, 9H, 3Ph), 7.46–7.49 (m, 6H, 3Ph); ^{13}C NMR (100 MHz; C_6D_6; 65 °C): δ 23.2 (q, CH_3), 28.0 (t, C-4), 49.2 (t, C-5), 50.6 (d, C-3), 63.8 (d, C-2), 78.3 (s, CPh_3), 88.5 [s, $C(CN)_2$], 111.4, 113.0 (2s, 2CN), 112.8 (t, $C(CH_3)$:CH_2), 127.3, 128.3, 130.1 (3d, 15C in 3Ph), 141.6, 142.8 (s, $C(CH_3)$:CH_2 and 3C in 3Ph), 168.3 [d, C(2)*C*H]; EI-MS m/z 429 (M^+, 1%), 352 (4), 243 (100), 228 (9), 215 (5), 165 (53), 146 (4), 91 (4), 77 (2); HRMS calcd for $C_{30}H_{27}N_3$: 429.2204, found: 429.2202.

4.7.5. Butadinene 9 and acrylonitrile. (2*RS*,3*RS*,1′*E*)-2-(1,3-Butadienyl)-1-tritylpyrrolidine-3-carbonitrile [(*E*)-**33**], an oil; IR ($CHCl_3$): 2210 cm^{-1} (C≡N); ^1H NMR (400 MHz): δ 1.24 (ddd, 1H, J=10.7, 8.5, 6.8 Hz, H-3), 1.60–1.69 (m, with dtd-character, 1H, J=13, 9, 4 Hz, H-4), 1.76–1.87 (m with dtd-character, 1H, J=13, 10, 8 Hz, H-4), 3.00 (ddd, 1H, J=2.7, 8.8, 7.6 Hz, H-5), 3.44 (ddd, 1H, J=12.7, 9.8, 3.9 Hz, H-5), 4.03–4.06 (m with t-character, 1H, J=7 Hz, H-2), 5.17–5.20 (m with d-character, 1H, J=10 Hz, H-4′), 5.31–5.36 (m with d-character, 1H, J=17 Hz, H-4′), 5.89 (dd, 1H, J=14.4, 6.1 Hz, 1′-H), 6.42–6.57 (m, 2H, H-2′, H-3′), 7.16–7.32 (m, 9H, 3Ph), 7.54–7.56 (6H, m, 3Ph); ^{13}C NMR (100 MHz): δ 29.1 (t, C-4), 31.8 (d, C-3), 48.3 (t, C-5), 63.4 (d, C-2), 78.0 (s, CPh_3), 117.6 (t, C-4′), 119.7 (s, CN), 126.5, 127.7, 128.9 (3d, 15C in 3Ph), 129.1, 133.1, 136.2 (3d, C-1′, C-2′, C-3′), 144.1 (s, 3C in 3Ph); EI-MS m/z 390 (M^+, 1%), 313 (3), 243 (100), 228 (4), 183 (5), 165 (33), 105 (5), 91 (2), 77 (4); HRMS calcd for $C_{28}H_{26}N_2$: 390.2096, found: 390.2090.

(2*RS*,3*RS*,1′*Z*)-2-(1,3-Butadienyl)-1-tritylpyrrolidine-3-carbonitrile [(*Z*)-**33**], an oil; ^1H NMR (400 MHz): δ 1.40–1.48 (m with td-character, 1H, J=10, 7 Hz, H-3), 1.62–1.72 (m with dtd-character, 1H, J=13, 9.0, 4.6 Hz, H-4), 1.84–1.95 (m with dtd-character, 1H, J=13, 9.5, 7.1 Hz, H-4), 3.00 (ddd, 1H, J=12.7, 8.9, 7.1 Hz, H-5), 3.50 (ddd, 1H, J=12.7, 9.5, 4.6 Hz, H-5), 4.35 (dd, 1H, J=10.0, 7.1 Hz, H-2), 5.07–5.10 (m with d-character, 1H, J=10 Hz, H-4′), 5.23–5.28 (m with d-character, 1H, J=14 Hz, H-4′), 5.61–5.67 (m with t-character, 1H, J=10 Hz, 1′-H), 6.16–6.27 (m, 2H, H-2′, H-3′), 7.15–7.27 (m, 9H, 3Ph), 7.52–7.55 (m, 6H, 3Ph); ^{13}C NMR (100 MHz): δ 29.7 (t, C-4), 32.6 (d, C-3), 48.1 (t, C-5), 60.1 (d, C-2), 77.9 (s, CPh_3), 119.2 (t, C-4′), 119.8 (s, CN), 126.3, 127.8, 128.9 (3d, 15C in 3Ph), 128.0, 130.1, 131.3 (3d, C-1′, C-2′, C-3′), 144.0 (s, 3C in 3Ph).

4.8. Application to the synthesis of indolizidine fragment of stellettamides 10

4.8.1. (2*RS*,3*RS*,1′*E*)-2-(4-Hydroxy-1-butenyl)-1-tritylpyrrolidine-3-carbonitrile (34). To a solution of butadiene (*E*)-**33** (606 mg, 1.55 mmol) in dry THF (3 mL) was added dropwise 9-BBN (4.7 mL, 0.5 M in THF) at 0 °C. After the mixture had been stirred for 4 h at room temperature, the reaction mixture was cooled to 0 °C. Water (0.1 mL), 30% aqueous H_2O_2 (0.68 mL), and 3 M aqueous NaOH (0.68 mL) were added, the resulting mixture was stirred for 2 h at room temperature and extracted with ether. The organic 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 (2:1)] to afford **34** (159 mg, 25%) as a white amorphous solid: IR ($CHCl_3$): 3530 (O–H), 2240 cm^{-1} (C≡N); ^1H NMR (400 MHz): δ 1.28–1.36 (m with ddd-character, 1H, J=10, 9, 6 Hz, H-3), 1.61–1.70 (m with dtd-character, 1H, J=13, 9, 4 Hz, H-4), 1.75 (br s, 1H, OH), 1.85 (dtd, 1H, J=12.6, 10.0, 7.6 Hz, H-4), 2.40–2.45 (m, 2H, 2H-3′), 2.99 (ddd, 1H, J=12.5, 8.8, 7.6 Hz, H-5), 3.45 (ddd, 1H, J=12.5, 9.8, 4.2 Hz, H-5), 3.69–3.75 (m, 2H, 2H-4′), 3.93–3.97 (m with t-character, 1H, J=6 Hz, H-2), 5.69–5.81 (m, 2H, H-1′, H-2′), 7.16–7.28 (m, 9H, 3Ph), 7.53–7.57 (m, 6H, 3Ph); ^{13}C NMR (100 MHz): δ 29.1 (t, C-4), 32.5 (d, C-3), 36.0 (t, C-3′), 48.3 (t, C-5), 61.9 (t, C-4′), 64.4 (d, C-2), 77.9 (s, CPh_3), 120.8 (s, CN), 126.4, 127.7, 129.0 (3d, 15C in 3Ph), 129.7, 131.0 (2d, C-1′, C-2′), 144.0 (s, 3C in 3Ph); FAB-MS (magic bullet) m/z 409 [(M+1)$^+$]; HRMS (FAB) calcd for $C_{28}H_{29}N_2O$ (M+H): 409.2280, found: 409.2282.

4.8.2. *tert*-Butyl (2*RS*,3*RS*,1′*E*)-3-cyano-2-(4-hydroxy-1-butenyl)pyrrolidine-1-carboxylate (35). To a solution of butene **34** (147 mg, 0.36 mmol) in chloroform (0.36 mL) and methanol (0.36 mL) was added dropwise trifluoroacetic acid (TFA; 0.55 mL, 7.2 mmol) at 0 °C. After the mixture had been stirred for 2 h at 0 °C, the reaction mixture was evaporated under reduced pressure giving a detritylated compound that was used for the next step without further purification. To a solution of the compound in THF/H_2O=2:1 (0.72 mL) was added 10% aqueous NaOH (0.36 mL) at 0 °C, the resulting mixture was stirred for 15 min at 0 °C and then di-*tert*-butyl dicarbonate (0.127 mL, 0.53 mmol) was added dropwise. After the mixture was stirred for 38 h at room temperature, the reaction was quenched with H_2O and extracted with ether. The organic 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 (1:1)] to afford **35** (75.5 mg, 79%) as a colorless oil: IR (neat): 3460 (O–H), 2250 (C≡N), 1685 cm^{-1} (C=O); ^1H NMR (400 MHz): δ 1.44 [s, 9H, C(CH_3)$_3$], 2.16–2.34 (m, 3H, OH, 2H-4), 2.34–2.40 (m with q-character, 2H, J=6 Hz, 2H-3′), 3.13–3.20 (m with dt-character, 1H, J=11, 7 Hz, H-3), 3.37–3.45, 3.53–3.60 (each m, 2H, 2H-5), 3.65–3.69 (m with t-character, 2H, J=6 Hz, 2H-4′), 4.47–4.54 (m, 1H, H-2), 5.53–5.60 (m with dd-character, 1H, J=15, 7 Hz, H-1′), 5.66–5.74 (m with dt-character, 1H, J=15, 7 Hz, H-2′); ^{13}C NMR (100 MHz): δ 28.4 [q, C(CH_3)$_3$], 28.4 (t, C-4), 33.7 (d, C-3), 35.6 (t, C-3′), 44.9 (t, C-5), 59.6 (d, C-2), 61.4 (t, C-4′), 80.3 [s, C(CH$_3$)$_3$], 118.3 (s, CN), 128.2, 131.9 (2d, C-1′, C-2′), 153.5 (s, CO); FAB-MS (glycerol) m/z 267 [(M+1)$^+$]; HRMS (FAB) calcd for $C_{14}H_{23}N_2O_3$ (M+H): 267.1708, found: 267.1716.

4.8.3. *tert*-Butyl (2*RS*,3*RS*)-3-cyano-2-(4-hydroxybutyl)-pyrrolidine-1-carboxylate (36). A solution of butenol **35** (74.1 mg, 0.28 mmol) in ethanol (1.7 mL) with 10% Pd/C (37 mg) under hydrogen was stirred for 21 h at room temperature. The reaction mixture was filtered with Celite, and the filtrate was concentrated in vacuo, giving a residue that was subjected to flash column chromatography (hexane) to afford **36** (70.9 mg, 95%) as a colorless oil: IR (neat): 3400 (O–H), 2245 (C≡N), 1690 cm^{-1} (C=O); ^1H NMR (400 MHz): δ 1.46 [s, 9H, C(CH_3)$_3$], 1.45–1.79 (m, 7H, 5H in the side chain, H-4, OH), 2.16–2.34 (m, 2H, 1H in the side chain, H-4), 2.34–2.40 (m with q-character, 2H, J=6 Hz, 2H-3′), 3.13 (dt, 1H, J=9.8, 7.3 Hz, H-3), 3.40–3.53 (m, 2H, 2H-5), 3.62–3.68 (m, 2H, 2H-4′), 4.02–4.13 (m, 1H, H-2); ^{13}C NMR (100 MHz): δ 22.5, 28.5, 28.6, 32.4 (4t, C-1′, C-2′, C-3′, C-4), 28.5 [q, C(CH_3)$_3$], 32.4 (d, C-3), 44.7 (t, C-5), 57.5 (d, C-2), 62.3 (t, C-4′), 80.2 [s, C(CH$_3$)$_3$], 118.7 (s, CN), 154.0 (s, CO); FAB-MS (glycerol) m/z 269 [(M+1)$^+$]; HRMS (FAB) calcd for $C_{14}H_{25}N_2O_3$ (M+H): 269.1865, found: 269.1861.

4.8.4. *tert*-Butyl (2*RS*,3*RS*)-3-cyano-2-[4-(*p*-toluenesulfonyl)oxybutyl]pyrrolidine-1-carboxylate (37). A solution of *p*-toluenesulfonyl chloride (42 mg, 0.22 mmol) in dry pyridine (0.6 mL) under argon was added to a solution of butanol **36** (48.6 mg, 0.18 mmol) in dry pyridine (0.6 mL) at −20 °C. After 12 h, a solution of *p*-toluenesulfonyl chloride (27 mg, 0.14 mmol) in dry pyridine (0.4 mL) was added moreover, and the mixture was stirred for 17 h at −20 °C and for 23 h at −10 °C. Furthermore, a solution of *p*-toluenesulfonyl chloride (17 mg, 0.09 mmol) in dry pyridine (0.25 mL) was added, and the mixture was stirred for 33 h at −5 °C. The reaction was quenched with H_2O and extracted with methylene chloride. The combined organic extract was washed with brine, dried over $MgSO_4$, and concentrated in vacuo, giving a residue that was subjected to flash column chromatography [hexane–ethyl acetate (2:1)] to afford **37** (57.8 mg, 79%) as a colorless oil: IR (neat): 2240 (C≡N), 1685 cm^{-1} (C=O); ^1H NMR (400 MHz): δ 1.25–1.48, 1.60–1.78, 2.12–2.30 (3m, 8H, 2H-1′, 2H-2′, 2H-3′, 2H-4), 1.46 [s, 9H, C(CH_3)$_3$], 2.45 (s, 3H, Me), 3.08 (dt, 1H, J=10.0, 7.3 Hz, H-3), 3.37–3.51 (m, 2H, 2H-5), 4.01–4.09 (m, 3H, H-2, 2H-4′), 7.35, 7.79 (each d, 4H, J=8 Hz, Ar); ^{13}C NMR (100 MHz): δ 21.8 (q, Me), 22.4, 28.5, 28.9, 31.9 (4t, C-1′, C-2′, C-3′, C-4), 28.5 [q, C(CH_3)$_3$], 32.6 (d, C-3), 44.6 (t, C-5), 57.4 (d, C-2), 70.2 (t, C-4′), 80.4 [s, C(CH$_3$)$_3$], 118.5 (s, CN), 127.7, 129.7 (2d, 4C in Ar), 133.0, 144.5 (2s, 2C in Ar), 153.9 (s, CO); FAB-MS (glycerol) m/z 423 [(M+1)$^+$]; HRMS (FAB) calcd for $C_{21}H_{31}N_2O_5S$ (M+H): 423.1953, found: 423.1952.

4.8.5. (1*RS*,8a*RS*)-1,2,3,5,6,7,8,8a-Octahydroindolizine-1-carbonitrile (38). A solution of **37** (15.0 mg, 0.036 mmol) in 4 M HCl–dioxane solution (0.07 mL) was stirred for 4 h at room temperature. After methylene chloride was added, the mixture was extracted with H_2O (two times). The combined aqueous layer was adjusted to pH 14 with 1 M aqueous NaOH and stirred for 2.5 h at room temperature. The reaction mixture was extracted with methylene chloride. The combined organic extract was washed with brine, dried over $MgSO_4$, and concentrated, giving **38** (4.7 mg, 89%) as a colorless oil: IR (neat): 2240 cm^{-1} (C≡N); ^1H NMR (400 MHz): δ 1.20–1.34 (m, 1H,), 1.52–1.67 (m, 3H), 1.80–1.99 (m, 4H), 2.05–2.17 (m, 3H), 2.96–3.02 (m, 1H), 3.11–3.17 (m, 2H); ^{13}C NMR (100 MHz): δ 24.0, 25.0, 27.4, 28.5 (4t), 32.6 (d, C-1), 52.9, 53.2 (2t, C-3, C-5), 64.4 (d, C-8a), 121.1 (s, CN); EI-MS m/z 150 (M$^+$, 28%), 121 (8), 97 (100), 83 (6), 69 (25), 55 (10), 41 (16); HRMS calcd for $C_9H_{14}N_2$: 150.1157, found: 150.1155.

Compound **38**[18]—^1H NMR: δ 1.16–1.29 (m, 1H), 1.42–1.62 (m, 3H), 1.73–2.14 (m, 7H), 2.94–3.16 (m, 3H); δ_C 23.9, 24.9, 27.3, 28.4, 32.5, 52.9, 53.1, 64.4, 121.2.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.08.098.

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