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[3+2] Cycloadditions and Nucleophilic Additions of Aziridines under C-C and C-N Bond Cleavage¹

Carsten Gaebert and Jochen Mattay*

Institut für Organische Chemie der Universität Kiel, Olshausenstr. 40, D-24098 Kiel, Germany.

Abstract: Under PET conditions (photoinduced electron transfer) aziridines react with dipolarophiles in a [3+2] cycloaddition to form five-membered heterocycles. In this study we used mono- and disubstituted N-alkyl and N-arylaziridines. We noticed that the radical cation as intermediate reacts in a different manner to the classical azomethine ylide. Furthermore, under mild thermal conditions, aziridines react in acetonitrile in a formal [3+2] cycloaddition with activated acetylene derivatives under C-N bond cleavage. Using methanol as solvent, the intermediate is trapped leading to highly substituted enamines. A mechanism for this unexpected thermal reaction is proposed. © 1997 Elsevier Science Ltd.

Aziridines and their reactions are of great interest because of their synthetic and pharmacological importance.² The [3+2] cycloaddition represents one of the most intensively studied conversions.³ On irradiation or under thermal conditions the aziridine ring opens to the corresponding azomethine ylide which can be trapped in a [3+2] cycloaddition with various dipolarophiles, e. g. dimethyl acetylenedicarboxylate (DMAD), to form nitrogen-containing five-membered heterocycles.⁴ Under PET conditions (photoinduced electron transfer)⁵ the aziridine is oxidized to the corresponding radical cation which can react in a similar manner. Only reactions of (Z)-1-alkyl-2,3-diphenylaziridines are documented so far.^{6,7,8} In this study we enlarge the synthetic application of the PET transformations and present a new thermal reaction under formal C-N bond cleavage of the aziridines.

The substrates examined in the present study are 1-butyl-2-phenylaziridine (1), (E)-1-butyl-2,3diphenylaziridine (2), 1,2-diphenylaziridine (3), 1-(p-methoxyphenyl)-2-phenylaziridine (4), 1-(p-cyanophenyl)-2-phenylaziridine (5) and 1-butyl-2-(p-cyanophenyl)aziridine (6).



Scheme 1. Aziridines investigated in this study

Fax: +49-431-880-7410. E-mail: mattay@oc.uni-kiel.de

Photochemical Reactions

Concerning the [3+2] cycloadditions of aziridines under PET conditions (acetonitrile, 9,10-dicyanoanthracene (DCA), $\lambda = 419$ nm), we first studied a monosubstituted N-alkylaziridine (Scheme 2).⁹



Scheme 2. [3+2] Cycloadditions of 1-butyl-2-phenylaziridine (1) with DMAD

The reaction of 1-butyl-2-phenylaziridine (1) with DMAD under PET conditions revealed an unexpected result. Four products were formed. We isolated 7 in a yield of 2 % and the corresponding oxidation product 8 in yields of 10 %. The expected cleavage of the C-C bond of the aziridine is responsible for the formation of these heterocycles. Futhermore, we obtained 9 in a yield of 9 % and the corresponding oxidation product 10 in yields of 4 %. These products are formed in a formal [3+2] cycloaddition under cleavage of the C-N bond of the aziridine. At room temperature and without irradiation, we observed the same product 9 in a similar yield in the transformation of aziridine 1 with DMAD.

In accordance with the results of Laurent et al.⁷, who investigated the reaction of the *trisubstituted* aziridine 15, the reaction of the *disubstituted* aziridine 1 with dimethyl fumarate or dimethyl maleate as dipolarophile indicates a concerted reaction pathway (Scheme 3). In these cases a back electron transfer is postulated, i. e., the initially generated aziridine radical cation is converted to the corresponding azomethine ylide which reacts in a concerted manner. In the case of dimethyl fumarate, the two pyrrolidines 11 and 12 were built up in yields of 4 % each, retaining the stereochemistry of the alkene. In analogy, the reaction with dimethyl maleate afforded the pyrrolidines 13 and 14 in yields of 5 and 1 %. In both cases, traces of the pyrrol 8 were detected as oxidation product (GC).



Scheme 3. [3+2] Cycloadditions of 1-butyl-2-phenylaziridine (1) with dimethyl fumarate and maleate

Because of the diminished reactivity of monosubstituted N-alkylaziridines compared with disubstituted N-alkylaziridines we used (E)-1-butyl-2,3-diphenylaziridine (2) for further investigations.

Under direct photolysis aziridine 2 undergoes isomerization (Scheme 4). In yields of almost 50 % the *cis* isomer 15 is formed beside the starting material (20 %). Longer irradiation time reduced the amount of the starting material but also decreased the yields of the *cis* isomer. Starting with the latter isomer, Laurent and coworkers⁶ did not observe any isomerization due to the higher stability of the corresponding intermediate, the *cis* azomethine yilde^{8c}.



Scheme 4. Direct photolysis of (E)-1-butyl-2,3-diphenylaziridine (2)

The reaction of aziridine 2 with DMAD under PET conditions (Scheme 5) led to the unexpected dihydropyrrole 16 (5%) under formal C-N bond cleavage of the aziridine. We also observed the expected dihydropyrrole 17 (31%) and the corresponding pyrrole 18 (18%) as oxidation product. Using direct photolysis, we got the same products in different yields. The dihydropyrrole 17 under C-C bond cleavage is built up in yields of 8% and the corresponding pyrrole 18 in yields of 21%. Only the yield of the unexpected dihydropyrrole 16, based on a formal C-N bond cleavage, did not change. Because of the higher yields, in this case the aziridine radical cation, formed under PET conditions, is superior to the classical azomethine ylide generated under direct photolysis. Further investigations proved that the dihydropyrrole 16 is formed in a thermal side reaction. Without irradiation the yield of this product increased up to 13%.



Scheme 5. [3+2] Cycloadditions of (E)-1-butyl-2,3-phenylaziridine (2) with DMAD

The conversion of (Z)-1-butyl-2,3-diphenylaziridine (15) with DMAD under PET conditions has been published by Laurent and coworkers.⁶ In a ratio of 1:1 they obtained the dihydropyrrole 17 and the corresponding *cis* isomer. The authors proposed an aziridine radical cation as intermediate without any favoured stereochemistry. In contrast, the conversion of the *(E)*-aziridine 2 with DMAD under PET conditions is stereospecific, provided the pyrrole 18 is formed exclusively by oxidation of the dihydropyrrole 17 and not on the oxidation of the corresponding *cis* isomer.



Scheme 6. [3+2] Cycloadditions of (E)-1-butyl-2,3-phenylaziridine (2) with acrylonitrile

Further investigations proved that, for the thermal side reaction, an activated triple bond is necessary. Therefore, with acrylonitrile as dipolarophile, we did not observe any thermal reaction (Scheme 6). Under direct photolysis we found two isomeric pyrrolidines 19 and 20 in yields of 40 and 18 %. In both products the phenyl groups are in the *trans* position. In pyrrolidine 19 the cyano group is standing *cis* to the phenyl group at C 2, in the case of pyrrolidine 20 it is in *trans* position. Using PET conditions we observed all possible isomeric pyrrolidines. The main products 19 and 20 were formed in yields of 29 and 17 % and the side products 21 and 22 in yields of about 4 % each. The side products are characterized by a *cis* position of the phenyl groups.

In accordance with Laurent et al.⁶, we propose the following mechanism (Scheme 7). Under direct photolysis, the aziridine ring is opened in a disrotatory manner to build up the azomethine ylide 23 with the phenyl groups in the *trans* position. The *trans* azomethine ylide 23 is trapped with acrylonitrile in a stereospecific [3+2] cycloaddition leading to the corresponding pyrrolidines 19 and 20 with *trans*-configurated phenyl groups. Under PET conditions, first the sensitizer, 9,10-dicyanoanthracene, is electronically excited into its singlet state which then oxidizes the aziridine 2 to its radical cation 24. 24 reacts under back electron transfer and [3+2] cycloaddition with acrylonitrile to give the four isomeric pyrrolidines 19 - 22. The sequence of these steps is still unknown. However, the radical cation 24 has different properties compared to the azomethine ylide 23 and, consequently, the pyrrolidines 21 and 22 with the *cis* position of the phenyl groups are formed as well. Therefore, an isomerization step has to be involved. In the case of the azomethine ylide 23 this isomerization step is not observed.

In order to elucidate the influence of the back electron transfer we applied both, salt effects and the cosensitization process.^{5c} However, when using a saturated lithium perchlorate solution in acetonitrile, no change of the product ratio was observed. The same is true with biphenyl as cosensitizer. Therefore, we assume that dissociation into separated radical ions is favoured even under standard PET conditions.

Under PET conditions no reaction is detected in the cases of 1-aryl-2-phenylaziridines 3 and 4. The radical cations, formed of these aziridines under PET conditions, probably have a ring closed structure.¹⁰ Therefore, a cycloaddition cannot take place.



Scheme 7. Proposed mechanism for the transformations under PET conditions

Thermal Reactions

In acetonitrile as solvent aziridines 1 and 2 also afforded the corresponding dihydropyrroles 9 and 16 based on a formal C-N bond cleavage up to 13 %. In the case of aziridine 2 the *trans* position of the phenyl substituents is retained in the five-membered heterocycle.

To elucidate the mechanism of this reaction, we used methanol as solvent (Table). In this case a 1:1:1 aziridine-acetylene-solvent addition product is formed. Aziridine 1 and DMAD in methanol gave 25a in yields of 70 % (Entry a). Using methyl propiolate instead of DMAD (Entry b), the analogous product 25b is formed in almost quantitative yields. In the case of the trisubstituted aziridine 2 the reaction occurred with similar efficiency (Entry c and d). In order to change the electron density at the nitrogen atom of the aziridine, we synthesized 1-aryl-2-phenyl substituted aziridines. The aziridine 3 reacted with both acetylene derivatives (Entry e and f) in yields of 84 % and 64 %, respectively. The reactions of aziridine 4 with enlarged electron density at the nitrogen atom only led to increased yields with methyl propiolate compared to the phenyl derivate (Entry h). Using aziridine 5 the electron density at the nitrogen atom is reduced. The reaction time is increased and the yields of the reaction with DMAD were diminished to 42 % (Entry i). The transformation with methyl propiolate (Entry k) led to yields lower than 10 %.

Due to the longer reaction times the nucleophilic addition of the 1-aryl-2-phenylaziridines compete with the nucleophilic ring opening of the aziridine ring by methanol. Nevertheless, the nucleophilic ring opening took place in yields about 10%. The same amount is obtained in the reaction of the aziridines in methanol without any acetylenic component. Only in the case of the transformation of aziridine 5 with methyl propiolate, the reactivity of the aziridine is reduced in such a manner, that the nucleophilic ring opening is favoured.

Table: Thermal reactions of aziridines with acetylene derivatives in different solvents at r.t.



Entry	Compd.	Solvent	\mathbf{R}^1	R ²	R ³	R ⁴	Yield (%)
a	1	MeOH	Bu	Н	E	Me	70
b	1	MeOH	Bu	Н	Н	Me	95
c	2	MeOH	Bu	Ph	E	Me	74
d	2	MeOH	Bu	Ph	Н	Me	83
e	3	MeOH	Ph	Н	Е	Me	84
f	3	MeOH	Ph	Н	Н	Me	64
g	4	MeOH	p-MeOC ₆ H ₄	Н	E	Me	85
h	4	MeOH	p-MeOC ₆ H ₄	Н	Н	Me	80
i	5	MeOH	p-CNOC ₆ H ₄	Н	Е	Me	42
k	5	MeOH	p-CNOC ₆ H ₄	Н	Н	Me	<10
1	1	$CH_3CN:H_2O = 1:1$	Bu	Н	Н	Н	18
m	2	$CH_3CN:H_2O = 9:1$	Bu	Ph	Н	Н	29

In the cases of methyl propiolate ($\mathbb{R}^3 = H$) as acetylenic compound, the coupling constant of the olefinic protones (J = 13 Hz) and increment calculations ($\delta_{trans} > 7.23$ ppm vs. $\delta_{cis} > 6.60$ ppm, measured $\delta = 7.35$ -7,85 ppm for 3-H) indicate a *trans* configuration. In analogy, the corresponding products formed with DMAD ($\mathbb{R}^3 = E$) are supposed to be maleate derivatives.

The products of the reactions with 1-aryl-2-phenyl substituted aziridines are less stable than in the case of 1-alkyl substitution. On silica gel we observed the decomposition of the highly substituted enamines 25e-k to (2-methoxy)-2-(phenylethyl)arylamines (26a-c), however, the products are stable on neutral aluminium oxide (Scheme 8).



Scheme 8. Decomposition of the enamines 25 on silica gel

Changing the solvent to a mixture of acetonitrile and water (1:1) the reaction of aziridine 1 led to 25l in yields of 18 % (Entry I). With a mixture of acetonitrile and water (9:1) aziridine 2 afforded 25m in yields of 29 % (Entry m). The reaction conditions have not been optimized so far. Nevertheless, this method provides the opportunity to introduce further functionalizations.

Concerning the mechanism we propose a nucleophilic attack of the lone electron pair at the nitrogen atom of the aziridine 1 to one of the acetylenic carbon centers (Scheme 9). The resulting intermediate has a positive charge at the nitrogen atom and a negative charge on the acetylenic unit. Because of the retention of the relative stereochemistry during product formation we assume that the aziridine ring has not been opened in this step. In acetonitrile as solvent the negative center opens the aziridine ring by intramolecular nucleophilic substitution forming the corresponding five-membered heterocycle 9. In presence of methanol (or in a mixture of water and acetonitrile), the negative charge is trapped by a proton while the methoxy group (or hydroxyl group) opens the aziridine ring by intermolecular nucleophilic substitution. The 1:1:1 aziridine-acetylenesolvent adduct **25a** is formed in high up to quantitative yields.



Scheme 9. Proposed mechanism for the formal [3+2] cycloaddition of aziridines to acetylenic derivatives

This mechanism is in agreement with an early investigation of Winterfeldt and Dillinger.¹¹ They observed a *single* analogous reaction of aziridine 27 with DMAD in *tert*-butanol (Scheme 10) leading to the ring opened butyl ether 28. The corresponding dihydropyrrole 29 was not observed at that time. In this paper we provide an access to the corresponding dihydropyrrole by changing the solvent from an alcohol to acetonitrile.



Scheme 10. Winterfeldt-Dillinger reaction¹¹

The key step of the mechanism is the nucleophilic attack of the lone pair at the nitrogen to the acetylenic compound. This step is also involved during the formation of azetidines from azabicyclobutanes and DMAD.¹² Guimanini proposed an analogeous mechanism concerning the reaction of *N*-benzylaziridine with aryne.¹³ The cycloaddition of 1,2-disubstituted aziridines to heterocumulenes by organoantimony halides is explained with a nucleophilic attack of the lone electron pair at the nitrogen atom of the aziridine to the heterocumulene.¹⁴

In order to increase the yields of the dihydropyrrole, we synthesized aziridine 6. The electronwithdrawing cyano group should facilitate the second step of the mechanism, the intramolecular nucleophilic substitution. Interestingly, we obtained the corresponding dihydropyrrole 30 only as side product in yields of 4%. As main product the pyrrole 31 is formed in yields of 7%. The rationalization of the formation of the main product is given by an insertion step (Scheme 11). First the lone pair attacks the acetylenic compound. Then an insertion of another acetylenic unit takes place followed by an intramolecular substitution of the aziridine. The negative charge is located at the carbon center with the electron-withdrawing aryl substituent. Finally the pyrrole 31 is formed under elemination of p-cyanostyrole, which could be identified by gas chromatography.



Scheme 11. Reaction of aziridine 6 with DMAD in acetonitrile

In conclusion, we have shown that the formation of products during the [3+2] cycloaddition of aziridines depends on the reaction conditions. Direct photolysis generates the azomethine ylide. With reactive dipolarophiles, this intermediate reacts in a stereospecific conversion. Under PET conditions the corresponding radical cation is formed. Contrasting the azomethine ylide, the radical cation undergoes isomerization. In addition we have presented a new formal [3+2] cycloaddition of aziridines to DMAD under mild conditions (r.t.) which occurs under C-N bond cleavage of the aziridine ring instead of the normal C-C bond cleavage. Changing the solvent from acetonitrile to more protic solvents, such as methanol, we observed the formation of an 1:1:1 addition product consisting of the aziridine, the dipolarophile and the solvent. The products are highly substituted enamines which may be simply functionalized at least in the case of the hydroxy substituted species. The use of activated acetylene derivatives seems to be important for this conversions because 1,2-diphenyl acetylene or cyclooctyne do not undergo any reaction. Further investigations are in progress.

EXPERIMENTAL

¹H and ¹³C NMR spectra were recorded on a Bruker AC 200 P, Bruker AM 300, Bruker WM 300 or Bruker AM 360 spectrometer using CDCL₃ as solvent and TMS as internal standard. IR spectra were conducted on a Perkin-Elmer 298 or a FTIR Perkin-Elmer 1600 spectrometer. UV spectra were run on a Shimadzu UV-2100 spectrophotometer. GC-MS spectra were performed on a Varian MAT CH 7A with GC Varian 1400, Finnigan MAT 8230 with GC Varian 3400 or a Varian Saturn 2 spectrometer. Elemental analyses were carried out by the Analytische Abteilung, Organisch-Chemisches Institut, Universität Münster, Germany. Column chromatography was executed using Merck silica gel or ICN aluminium oxide. Solvents were dried using standard procedures. The irradiations were performed in a Rayonet photoreactor (Southern New England) fitted with 253.7 nm or 419.0 nm lamps using quartz or pyrex tubes of ca. 12 mL volume.

Due to the conformational flexibility of nitrogen-containing five-membered heterocycles, it is difficult to base structural conclusions on J values alone.¹⁵ Important for the assignment is the anisotropic effect of the phenyl group. A ring substituent is shielded by *cis-vic*-phenyl, but deshilded by *trans-vic*-phenyl groups.^{15,16}

1-Butyl-2-phenylaziridine (1)

Starting with commercial available 2-phenyloxirane the corresponding β -amino alcohol is prepared according to the procedure of Chapman and Triggle in yields of 44 %.¹⁷ The formation of 1-butyl-2-phenyl-aziridine (1) occurred as described by Okada et al. in yields of 56 %.¹⁸

(E)-1-Butyl-2,3-diphenylaziridine (2)

Using *trans*-stilbene as starting material, epoxidation with MCPBA formed the corresponding (E)-1,2diphenyloxirane in yields of 84 %. Following the procedure of Deyrup and Moyer¹⁹, the epoxide is opened to the β -amino alcohol²⁰ in yields of 88 %. The cyclization as described above formed (E)-1-butyl-2,3diphenylaziridine (2) as a colorless liquid in yields of 58 %, b.p. 103°C/0.1 Torr. ¹H NMR (CDCl₃): $\delta = 0.79$ (t, J = 7.3 Hz, 3 H, 4'-H), 1.26 (sex, J = 7.3 Hz, 2 H, 3'-H), 1.49 (quint, J = 7.3 Hz, 2 H, 2'-H), 2.07 (dt, J =7.3, 11.9 Hz, 1 H, 1'-H_a), 2.46 (dt, J = 7.3, 11.9 Hz, 1 H, 1'-H_b), 2.99 (br, 1 H, 1/2-H), 3.23 (br, 1 H, 2/1-H), 7.20-7.41 (m, 10 H, H_{arom.}). ¹³C NMR (CDCl₃): $\delta = 13.90$ (C-4'), 20.42 (C-3'), 32.10 (C-2'), 45.59 (C-1/2), 50.41 (C-2/1), 52.32 (C-1'), 126.41, 126.62, 127.49, 128.12, 128.57, 129.88 (CH_{arom.}), 134.27 (C-1''/1'''), 140.24 (C-1''/1'''). IR (KBr): $\tilde{v} = 2956$ cm⁻¹, 2929, 1602, 1496, 1449, 1029, 751, 698. UV (CH₃CN): λ_{max} (lg ε): 230 nm (4.07), 265 (2.99). GC-MS m/z (%): 252 (12) [M^+ + H], 251 (69) [M^+], 250 (58) [M^+ - H], 208 (92) [M^+ - C₃H₇], 194 (100, [M^+ - C₄H₉], 174 (21), 165 (31), 130 (13), 116 (31), 104 (20), 91 (66), 77 (19), 65 (21), 57 (20), 41 (35). C₁₈H₂₁N (251.4): calcd. C 86.01, H 8.42, N 5.57; found C 85.48, H 8.49, N 5.53.

3 and 4 were prepared by reported procedures.²¹

1-(p-Cyanophenyl)-2-phenylaziridine (5)

Starting with 4-benzylideneamino-benzonitrile,²² aziridine 5 is synthesized following the procedure of Franzen and Driesen²¹ as a yellow oil in yields of 26 %. ¹H NMR (CDCl₃): $\delta = 2.50$ (dd, J = 1.0, 3.4 Hz, 1 H, 3-H_a), 2.54 (dd, J = 1.0, 6.4 Hz, 1 H, 3-H_b), 3.19 (dd, J = 3.4, 6.4 Hz, 1 H, 2-H), 7.08 (dm, J = 8.6 Hz, 2 H,

2''-H), 7.25-7.40 (m, 5 H, H_{arom.}), 7.53 (dm, J = 8.6 Hz, 2 H, 3''-H). ¹³C NMR (CDCl₃): $\delta = 37.71$ (C-3), 41.76 (C-2), 105.46 (C-4'), 119.27 (CN), 121.15 (2'-C), 126.05 (C-4''), 127.76 (C-3''), 128.61 (C-2''), 133.29 (C-3'), 138.08 (C-1''), 158.49 (C-1'). IR (kap.): $\tilde{\nu} = 2222 \text{ cm}^{-1}$, 1603, 1500, 1464, 1418, 1394, 1319, 1281, 1177, 1151, 988, 842, 759, 699, 558. UV (CH₃CN) λ_{max} (lg ε): 213 nm (4.09), 266 (4.25). GC-MS m/z (%): 220 (53) [M^+], 219 (100) [M^+ - H], 129 (76), 116 (18), 102 (44), 92 (20), 91 (26), 77 (8). CI (*Isobutane*): m/z (%): 221 (100, MH^+). C₁₅H₁₂N₂ (220.3): calcd. C 81.79, H 5.49, N 12.72; found C 81.57, H 5.49, N 12.63.

1-Butyl-2-(p-cyanophenyl)aziridine (6)

3.96 g (40 mmol) 1-azidobutane²³ were added to 5 g (38.8 mmol) *p*-cyanostyrole dissolved in 100 mL cyclohexane. After refluxing for 14 d the solvent was removed and the crude product was separated on silica gel with 10% ethyl acetate/cyclohexane. The aziridine 6 was obtained as pale yellow oil in yields of 17%. ¹H NMR (CDCl₃): $\delta = 0.92$ (t, J = 7.3 Hz, 3 H, 4'-H), 1.41 (m, 2 H, 3'-H), 1.58 (m, 2 H, 2'-H), 1.75 (dd, J = 0.9, 6.6 Hz, 1 H, 3-H_a), 1.86 (dd, J = 0.9, 3.2 Hz, 1 H, 3-H_b), 2.33 (dd, J = 3.1, 6.5 Hz, 1 H, 2-H), 2.36 (dt, J = 7.0, 11.6 Hz, 1 H, 1'-H_a), 2.49 (ddd, J = 7.0, 7.1, 11.5 Hz, 1 H, 1'-H_b), 7.32 (d, J = 8.4 Hz, 2 H, 2''-H), 1.75 (dd, J = 7.0, 11.6 Hz, 1 H, 1'-H_a), 2.49 (ddd, J = 7.0, 7.1, 11.5 Hz, 1 H, 1'-H_b), 7.32 (d, J = 8.4 Hz, 2 H, 2''-H), 7.54 (d, J = 8.4 Hz, 2 H, 3''-H). ¹³C NMR (CDCl₃): $\delta = 14.06$ (C-4'), 20.55 (C-3'), 31.88 (C-2'), 38.81 (C-3), 40.65 (C-2), 61.21 (C-1'), 110.37 (C-4''), 119.04 (CN), 126.88 (C-2''), 132.06 (C-3''), 146.55 (C-1''). IR (kap.): $\tilde{\nu} = 2957$ cm⁻¹, 2937, 2869, 2227, 1610, 1506, 1208, 1077, 850, 562. GC-MS *m/z* (%): 200 (12) [*M*⁺], 199 (42) [*M*⁺ - H], 157 (100) [*M*⁺ - C₃H₇], 143 (42) [*M*⁺ - C₄H₉], 129 (8) [*M*⁺ - NC₄H₉], 116 (64), 98 (48), 89 (18), 41 (26). C₁₃H₁₆N₂ (200.3): calcd. C 77.96, H 8.05, N 13.99; found C 77.52, H 8.21, N 13.45.

PET conversion of aziridine 1 with DMAD ^{9a}

1.192 g (8.4 mmol) DMAD and 37 mg (0.16 mmol) DCA were added to 490 mg (2.8 mmol) aziridine 1 dissolved in 140 mL acetonitrile. The argon-saturated solution was irradiated for 3.5 h at $\lambda = 419$ nm. The solvent was removed and the products were separated by HPLC with 10% ethyl acetate/cyclohexane. We obtained 7, 8, 9 and 10 in yields of 2%, 10%, 9% and 4%.

Dimethyl 1-butyl-2-phenyl-2,5-dihydro-1H-pyrrole-3,4-dicarboxylate (7). ¹H NMR (CDCl₃): $\delta = 0.77$ (t, J = 7.4 Hz, 3 H, 4'-H), 1.10-1.45 (m, 4 H, 2',3'-H), 2.50 (m, 2 H, 1'-H), 3.52 (s, 3 H, CO₂C<u>H₃</u>), 3.75 (s, 3 H, CO₂C<u>H₃</u>), 3.78 (dd, J = 5.7, 14.6 Hz, 1 H, 5-H_a), 4.22 (dd, J = 5.7, 14.6 Hz, 1 H, 5-H_b), 4.79 (dd, J = 5.7, 5.8 Hz, 1 H, 2-H), 7.23-7.40 (m, 5 H, H_{arom.}). ¹³C NMR (CDCl₃): $\delta = 13.83$ (C-4'), 19.53 (C-3'), 32.84 (C-2'), 47.21 (C-1'), 51.44 (CO₂CH₃), 52.08 (CO₂CH₃), 52.63 (C-5'), 76.32 (C-2), 126.36, 128.29, 130.33 (CH_{arom.}), 132.86 (C-4/3), 136.91 (C-3/4), 139.78 (C_{arom.}), 164.28 (C=O), 165.72 (C=O). IR (kap.): $\tilde{\nu} = 3020 \text{ cm}^{-1}$, 2940, 1720, 1570, 1440, 1370, 1270, 1235, 1200, 1170, 1145, 1095, 1060, 700. GC-MS *m/z* (%): 317 (10) [*M*⁺], 286 (10) [*M*⁺ - OCH₃], 274 (100) [*M*⁺ - C₃H₇], 258 (8) [*M*⁺ - CO₂CH₃], 226 (10), 208 (15), 91 (11), 42 (12). C₁₈H₂₃NO₄ (317.4).

Dimethyl 1-butyl-2-phenyl-1H-pyrrole-3,4-dicarboxylate (8). ¹H NMR (CDCl₃): $\delta = 0.71$ (t, J = 7.4 Hz, 3 H, 4'-H), 1.09 (sex, J = 7.4 Hz, 2 H, 3'-H), 1.48 (quint, J = 7.4 Hz, 2 H, 2'-H), 3.56 (s, 3 H, CO₂C<u>H₃</u>), 3.67 (t, J = 7.4 Hz, 2 H, 1'-H), 3.74 (s, 3 H, CO₂C<u>H₃</u>), 7.16-7.36 (m, 5 H, H_{arom}), 7.33 (s, 1 H, 5-H). ¹³C NMR (CDCl₃): $\delta = 13.33$ (C-4'), 19.46 (C-3'), 32.79 (C-2'), 47.17 (C-1'), 51.30 (CO₂C<u>H₃</u>), 51.52

 (CO_2CH_3) , 114.46 (C-4/3), 115.21 (C-3/4), 126.27 (C-5), 128.18, 128.62, 130.31 ($CH_{arom.}$), 136.75, 138.94 ($C_{arom.}$), 164.12 (C=O), 165.52 (C=O). **IR** (kap.): $\tilde{\nu} = 2940 \text{ cm}^{-1}$, 1710, 1570, 1520, 1480, 1430, 1375, 1280, 1230, 1200, 1165, 1150, 1060, 755, 700. **GC-MS** m/z (%): 315 (100) [M^+], 284 (80) [M^+ - OCH₃], 272 (71) [M^+ - C₃H₇], 254 (8) [M^+ - CO₂CH₃], 240 (37), 228 (19), 214 (27), 196 (21), 182 (19), 169 (12), 115 (11), 41 (26). C₁₈H₂₁NO₄ (315.4).

Dimethyl 1-butyl-4-phenyl-4,5-dihydro-1H-pyrrole-2,3-dicarboxylate (9). ¹H NMR (CDCl₃): $\delta = 0.87$ (t, J = 7.3 Hz, 3 H, 4'-H), 1.10-1.52 (m, 4 H, 2',3'-H), 3.00 (tq, J = 7.0, 13.8 Hz, 2 H, 1'-H), 3.40 (dd, J = 5.5, 10.5 Hz, 1 H, 4-H), 3.48 (s, 3 H, CO₂CH₃), 3.88 (dd, J = 10.5, 11.7 Hz, 1 H, 5-H_a), 3.92 (s, 3 H, CO₂CH₃), 4.22 (dd, J = 5.5, 11.7 Hz, 1 H, 5-H_b), 7.14-7.30 (m, 5 H, H_{arom}). ¹³C NMR (CDCl₃): $\delta = 13.56$ (C-4'), 19.71 (C-3'), 29.91 (C-2'), 45.58 (C-4), 48.01 (C-5), 50.54 (CO₂CH₃), 52.84 (CO₂CH₃), 60.52 (C-1'), 103.15 (C-3), 126.62, 127.00, 128.52 (CH_{arom}), 144.52 (C_{arom}), 153.99 (C-2), 163.97 (C=O), 165.15 (C=O). IR (kap.): $\tilde{\nu} = 2940$ cm⁻¹, 2850, 1720, 1700, 1500, 1440, 1430, 1370, 1255, 1195, 1120, 1085, 695. GC-MS m/z (%): 317 (40) [M⁺], 286 (19) [M⁺ - OCH₃], 274 (100) [M⁺ - C₃H₇], 258 (12) [M⁺ - CO₂CH₃], 226 (12), 115 (13), 91 (12), 45 (14). C₁₈H₂₃NO₄ (317.4).

Dimethyl 1-butyl-4-phenyl-1H-pyrrole-2, 3-dicarboxylate (10). ¹H NMR (CDCl₃): $\delta = 0.92$ (t, J = 7.4 Hz, 3 H, 4'-H), 1.34 (sex, J = 7.4 Hz, 2 H, 3'-H), 1.75 (tquint, J = 2.4, 7.4 Hz, 2 H, 2'-H), 3.80 (s, 3 H, CO₂CH₃), 3.82 (s, 3 H, CO₂CH₃), 4.27 (t, J = 7.4 Hz, 2 H, 1'-H), 6.89 (s, 1 H, 5-H), 7.21-7.40 (m, 5 H, H_{arom.}). ¹³C NMR (CDCl₃): $\delta = 13.65$ (C-4'), 19.83 (C-3'), 33.48 (C-2'), 49.38 (C-1'), 51.76 (CO₂CH₃), 52.37 (CO₂CH₃), 121.93 (C-3), 123.41 (C-4), 125.50 (C-5), 126.82, 127.26, 128.57 (CH_{arom.}), 133.40, 142.09 (C_{arom.}), 160.58 (C=O), 167.49 (C=O). **IR** (kap.): $\tilde{\nu} = 2940$ cm⁻¹, 1735, 1680, 1580, 1485, 1430, 1340, 1300, 1270, 1210, 1185, 1130, 1090, 695. **GC-MS** m/z (%): 315 (82) [M^+], 284 (42) [M^+ - OCH₃], 273 (24) [M^+ + H - C₃H₇], 256 (100) [M^+ - CO₂CH₃], 240 (21), 224 (70), 214 (25), 196 (28), 182 (13), 169 (17), 140 (25), 115 (12), 41 (29). C₁₈H₂₁NO₄ (315.4).

PET conversion of aziridine 1 with dimethyl fumarate

1.728 g (12 mmol) dimethyl fumarate and 54 mg (0.24 mmol) DCA were added to 700 mg (4 mmol) aziridine 1 dissolved in 200 mL acetonitrile. The argon-saturated solution was irradiated for 60 h at $\lambda = 419$ nm. The solvent was removed and the products were separated by HPLC with 5% ethyl acetate/cyclohexane. We obtained 11 and 12 in yields of 4% each as yellow oils.

 $(2S^*, 3S^*, 4S^*)$ -Dimethyl 1-butyl-2-phenylpyrrolidine-3, 4-dicarboxylate (11). ¹⁶ ¹H NMR (CDCl₃): $\delta = 0.78$ (t, J = 7.2 Hz, 3 H, 4'-H), 1.10-1.70 (m, 4 H, 2',3'-H), 1.95 (ddd, J = 4.7, 6.9, 11.7 Hz, 1 H, 1'-H_a), 2.37 (dt, J = 7.8, 11.7 Hz, 1 H, 1'-H_b), 2.55 (dd, J = 8.8, 9.0 Hz, 1 H, 5-H_a), 3.35 (m, 2 H), 3.58 (m, 1 H), 3.59 (s, 3 H, CO₂CH₃), 3.70 (m, 1 H), 3.72 (s, 3 H, CO₂CH₃), 7.20-7.35 (m, 5 H, H_{arom.}). ¹³C NMR (CDCl₃): $\delta = 13.88$ (C-4'), 20.70 (C-3'), 30.26 (C-2'), 44.94 (C-4), 52.00 (CO₂CH₃), 52.32 (CO₂CH₃), 52.74 (C-1'), 54.86 (C-3), 55.13 (C-5), 73.43 (C-2), 127.71, 127.95, 128.39 (CH_{arom.}), 140.90 (C_{arom.}), 173.43 (C=O), 174.07 (C=O). IR (KBr): $\tilde{\nu} = 2940$ cm⁻¹, 2900, 1725, 1650, 1425, 1285, 1240, 1200, 1160. GC-MS m/z (%): 318 (1) [M^{+} - H], 288 (9) [M^{+} - OCH₃], 276 (100) [M^{+} - C₃H₇], 262 (12) [M^{+} - C₄H₉], 244 (14), 91 (11), 42 (12). C₁₈H₂₅NO₄ (319.4).

 $(2S^*, 3R^*, 4R^*)$ -Dimethyl 1-butyl-2-phenylpyrrolidine-3,4-dicarboxylate (12).¹⁶ ¹H NMR (CDCl₃): $\delta = 0.78$ (t, J = 7.2 Hz, 3 H, 4'-H), 1.10-1.70 (m, 4 H, 2',3'-H), 2.05 (ddd, J = 4.4, 8.3, 12.1 Hz, 1 H, 1'-H₈), 2.37

(dd, J = 8.2, 10.0 Hz, 1 H, 5-H_a), 2.47 (dt, J = 8.3, 11.9 Hz, 1 H, 1'-H_b), 3.04 (s, 3 H, CO₂CH₃), 3.53 (dd, J = 7.5, 10.2 Hz, 1 H, 3-H), 3.63 (m, 1 H, 5-H_b/4-H), 3.68 (s, 3 H, CO₂CH₃), 3.71 (dd, J = 7.5, 10.0 Hz, 1 H, 5-H_b/4-H), 3.76 (d, J = 10.2 Hz, 1 H, 2-H), 7.18-7.27 (m, 5 H, H_{arom}). ¹³C NMR (CDCl₃): $\delta = 13.71$ (C-4'), 20.18 (C-3'), 29.49 (C-2'), 43.78 (C-4), 50.86, 51.90 (CO₂CH₃), 52.98 (C-1'), 53.17 (C-3), 54.82 (C-5), 71.11 (C-2), 127.23, 127.74, 128.18 (CH_{arom}), 136.77 (C_{arom}), 173.87 (C=O), 174.20 (C=O). IR (KBr): $\tilde{\nu} = 2925$ cm⁻¹, 2895, 1720, 1240, 1115, 1080, 1000, 780. GC-MS m/z (%): 318 (2) [M^{+} - H], 288 (8) [M^{+-} OCH₃], 276 (100) [M^{+} - C₃H₇], 262 (15) [M^{+} - C₄H₉], 244 (15), 91 (12), 42 (12). C₁₈H₂₅NO₄ (319.4).

PET conversion of aziridine 1 with dimethyl maleate

1.728 g (12 mmol) dimethyl maleate and 54 mg (0.24 mmol) DCA were added to 700 mg (4 mmol) aziridine 1 dissolved in 200 mL acetonitrile. The argon-saturated solution was irradiated for 48 h at $\lambda = 419$ nm. The solvent was removed and the products were purified by HPLC with 15% ethyl acetate/cyclohexane. We obtained 13 and 14 in yields of 5% and 1% as yellow oils. We could not completely separate the two isomers.

 $(2S^*, 3S^*, 4R^*)$ -Dimethyl 1-butyl-2-phenylpyrrolidine-3, 4-dicarboxylate (13).¹⁶ ¹H NMR (CDCl₃): $\delta = 0.78$ (t, J = 7.2 Hz, 3 H, 4'-H), 1.10-1.42 (m, 4 H, 2',3'-H), 2.11 (ddd, J = 5.2, 7.4, 12.4 Hz, 1 H, 1'-H_a), 2.46 (dt, J = 8.0, 12.4 Hz, 1 H, 1'-H_b), 2.70 (t, J = 9.3 Hz, 1 H, 5-H_a), 3.08 (dd, J = 8.1, 10.5 Hz, 1 H, 3-H), 3.40 (ddd, J = 7.6, 9.3, 10.5 Hz, 1 H, 4-H), 3.53 (dd, J = 7.6, 9.0 Hz, 1 H, 5-H_b), 3.59 (s, 3 H, CO₂CH₃), 3.64 (s, 3 H, CO₂CH₃), 3.69 (d, J = 8.1 Hz, 1 H, 2-H), 7.18-7.38 (m, 5 H, H_{arom.}). ¹³C NMR (CDCl₃): $\delta = 13.85$ (C-4'), 20.35 (C-3'), 30.40 (C-2'), 44.58 (C-4), 51.76, 51.86 (CO₂CH₃), 53.24 (C-1'), 54.56 (C-3), 55.00 (C-5), 71.98 (C-2), 127.65, 128.09, 128.42 (CH_{arom.}), 141.50 (C_{arom.}), 172.60 (C=O), 172.70 (C=O). IR (KBr): mixture of the two isomers 13 and 14: $\tilde{\nu} = 2940$ cm⁻¹, 2850, 1730, 1455, 1440, 1430, 1350, 1315, 1260, 1200, 1165, 1025, 755, 600. GC-MS m/z (%): 318 (3) [M^+ - H], 288 (10) [M^+ - OCH₃], 276 (100) [M^+ - C₃H₇], 262 (10) [M^+ - C₄H₉], 244 (12), 91 (12), 40 (34). C₁₈H₂₅NO₄ (319.4).

 $(2S^*, 3R^*, 4S^*)$ -Dimethyl 1-butyl-2-phenylpyrrolidine-3, 4-dicarboxylate (14).¹⁶ ¹H NMR (CDCl₃): $\delta = 0.82$ (t, J = 7.1 Hz, 3 H, 4'-H), 1.10-1.52 (m, 4 H, 2',3'-H), 2.06 (ddd, J = 4.1, 8.3, 11.7 Hz, 1 H, 1'-H_a), 2.52 (dt, J = 7.9, 11.7 Hz, 1 H, 1'-H_b), 2.75 (t, J = 9.5 Hz, 1 H, 5-H_a), 3.16 (s, 3 H, CO₂CH₃), 3.29 (ddd, J = 6.3, 7.6, 10.1 Hz, 1 H, 4-H), 3.40 (dd, J = 6.0, 7.6 Hz, 1 H, 3-H), 3.62 (s, 3 H, CO₂CH₃), 3.89 (d, J = 6.4 Hz, 1 H, 2-H), 3.92 (dd, J = 6.7, 9.5 Hz, 1 H, 5-H_b), 7.18-7.38 (m, 5 H, H_{arom}). ¹³C NMR (CDCl₃): $\delta = 14.02$ (C-4'), 28.88 (C-3'), 30.87 (C-2'), 43.98 (C-4), 51.02 (2 CO₂CH₃), 52.64 (C-1'), 53.51 (C-3), 53.98 (C-5), 72.28 (C-2), 127.65, 128.09, 128.42 (CH_{arom}), 138.88 (C_{arom}), 171.19 (C=O), 172.36 (C=O). GC-MS *m*/z (%): 320 (10) [M^+ + H], 319 (1) [M^+], 318 (4) [M^+ - H], 288 (8) [M^+ -OCH₃], 276 (100) [M^+ - C₃H₇], 262 (16) [M^+ - C₄H₉], 42 (15). C₁₈H₂₅NO₄ (319.4).

Direct photolysis of aziridine 2

100 mg (0.4 mmol) aziridine 2 dissolved in 20 mL argon-saturated cyclohexane were irradiated for 3 h at $\lambda = 253.7$ nm. The solvent was removed and the products were separated by HPLC with 5% ethyl acetate/cyclohexane. We obtained (Z)-1-butyl-2,3-diphenylaziridine (15)⁶ in yields of 49% and aziridine 2 in yields of 20%.

PET conversion of aziridine 2 with DMAD

852 mg (6 mmol) DMAD and 25 mg (0.12 mmol) DCA were added to 502 mg (2 mmol) aziridine 2 dissolved in 70 mL acetonitrile. The argon-saturated solution was irradiated for 5 h at $\lambda = 419$ nm. The solvent was removed and the products were separated by HPLC with 10% ethyl acetate/cyclohexane. We obtained 16, 17 and 18 in yields of 5 %, 31 % and 18 %. 16 and 17 were pale yellow oils whereas 18 was a colorless solid.

 $(4S^*, 5S^*)$ -Dimethyl 1-butyl-4,5-diphenyl-4,5-dihydro-1H-pyrrole-2,3-dicarboxylate (16). ¹H NMR (CDCl₃): $\delta = 0.81$ (t, J = 7.1 Hz, 3 H, 4'-H), 1.10-1.27 (m, 2 H, 3'-H), 1.29-1.48 (m, 2 H, 2'-H), 2.88 (dt, J = 7.0, 14.5 Hz, 1 H, 1'-Ha), 3.08 (dt, J = 7.7, 14.4 Hz, 1 H, 1'-Hb), 3.49 (s, 3 H, CO₂CH₃), 4.01 (s, 3 H, CO₂CH₃), 4.09 (d, J = 5.8 Hz, 1 H, 4-H), 4.52 (d, J = 5.8 Hz, 1 H, 5-H), 7.18-7.43 (m, 10 H, Harom.). ¹³C NMR (CDCl₃): $\delta = 13.56$ (C-4'), 19.75 (C-3'), 29.99 (C-2'), 45.82 (C-1'), 50.68 (CO₂CH₃), 53.00 (CO₂CH₃), 56.37 (C-5), 75.49 (C-8), 99.91 (C-2), 126.39, 126.81, 127.12, 128.20, 128.70, 129.06 (CH_{arom}.), 140.81, 144.36 (C_{arom}.), 153.84 (C-3), 163.96 (C=O), 165.36 (C=O). IR (kap.): $\tilde{v} = 2955$ cm⁻¹, 1747, 1682, 1592, 1435, 1101, 1031. GC-MS m/z (%): 394 (21) [M^+ + H], 393 (56) [M^+], 362 (18) [M^+ -OCH₃], 350 (100) [M^+ - C₃H₇], 334 (12), 318 (11), 302 (18), 290 (12), (16). C₂₄H₂₇NO₄ (393.5).

 $(2R^*, 5R^*)$ -Dimethyl 1-butyl-2,5-diphenyl-2,5-dihydro-1H-pyrrole-3,4-dicarboxylate (17).⁶ ¹H NMR (CDCl₃): $\delta = 0.62$ (t, J = 7.0 Hz, 3 H, 4'-H), 0.90-1.30 (m, 4 H, 2',3'-H), 2.27 (m, 2 H, 1'-H), 3.60 (s, 6 H, CO₂C<u>H₃</u>), 5.35 (s, 2 H, 2,5-H), 7.20-7.40 (m, 10 H, H_{arom}). ¹³C NMR (CDCl₃): $\delta = 13.71$ (C-4'), 19.92 (C-3'), 30.49 (C-2'), 45.90 (C-1'), 51.98 (CO₂CH₃), 66.94 (C-2,5), 128.02, 128.36, 128.40 (CH_{arom}), 138.73, 140.27 (C_{arom}), 163.84 (C=O). **IR** (kap.): $\tilde{v} = 2953$ cm⁻¹, 1724, 1484, 1453, 1436, 1276, 1225, 1200, 1169, 1101, 733, 701. **GC-MS** m/z (%): 393 (8) [M^+], 362 (5) [M^+ - OCH₃], 350 (100) [M^+ -C₃H₇], 316 (16), 284 (16), 91 (11). CI (*Iso*butane) m/z (%): 394 (100) [MH⁺]. C₂₄H₂₇NO₄ (393.5): calcd. C 73.26, H 6.92, N 3.56; found C 73.04, H 7.07, N 3.88.

Dimethyl 1-butyl-2,5-diphenyl-1H-pyrrole-dicarboxylate (18).^{6,24} ¹H NMR (CDCl₃): $\delta = 0.49$ (t, J = 7.4 Hz, 3 H, 4'-H), 0.83 (sex, J = 7.3 Hz, 2 H, 3'-H), 1.16 (m, 2 H, 2'-H), 3.65 (s, 6 H, CO₂CH₃), 3.67 (m, 2 H, 1'-H), 7.40-7.49 (m, 10 H, H_{arom}). ¹³C NMR (CDCl₃): $\delta = 13.06$ (C-4'), 19.30 (C-3'), 32.36 (C-2'), 44.68 (C-1'), 51.43 (CO₂CH₃), 114.45 (C-3,4), 128.17, 128.60, 130.51 (CH_{arom}), 131.08 (C-2,5), 136.52 (C_{arom}), 165.33 (C=0). IR (KBr): $\tilde{\nu} = 1731$ cm⁻¹, 1709, 1482, 1438, 1255, 1197, 1168, 1058, 772, 702. GC-MS *m*/*z* (%): 391 (100) [*M*⁺], 360 (26) [*M*⁺ - OCH₃], 348 (10) [*M*⁺ - C₃H₇], 316 (19), 304 (13), 290 (31), 271 (13), 258 (11). C₂₄H₂₅NO₄ (391.5): calcd. C 73.64, H 6.44, N 3.58; found C 73.94, H 6.50, N 3.82. The X-ray crystallographic data of 18 are also available.

Direct photolysis of aziridine 2 with DMAD

170 mg (1.2 mmol) DMAD were added to 100 mg (0.4 mmol) aziridine 2 dissolved in 20 mL acetonitrile. The argon-saturated solution was irradiated for 24 h at $\lambda = 253.7$ nm. The solvent was removed and the products were separated by HPLC with 10% ethyl acetate/cyclohexane. We obtained 16, 17 and 18 in yields of 5 %, 8 % and 21 %.

Direct photolysis of aziridine 2 with acrylonitrile

65 mg (1.2 mmol) acrylonitrile were added to 100 mg (0.4 mmol) aziridine 2 dissolved in 20 mL acetonitrile. The argon-saturated solution was irradiated for 24 h at $\lambda = 253.7$ nm. The solvent was removed

and the products were separated by HPLC with 5% ethyl acetate/cyclohexane. We obtained 19 and 20 in yields of 40 % and 18 %.

 $(2S^*, 3R^*, 5S^*)$ -1-Butyl-3-cyano-2,5-diphenylpyrrolidine (19). ¹H NMR (CDCl₃): $\delta = 0.71$ (t, J = 7.2 Hz, 3 H, 4'-H), 1.00-1.40 (m, 4 H, 2',3'-H), 2.26 (ddd, J = 3.6, 8.9, 12.5 Hz, 1 H, 4-H_a), 2.37 (m, 2 H, 1'-H), 2.84 (ddd, J = 9.3, 9.5, 13.2 Hz, 1 H, 4-H_b), 3.61 (ddd, J = 7.3, 9.0, 9.5 Hz, 1 H, 3-H), 4.48 (dd, J = 3.6, 9.2 Hz, 1 H, 5-H), 4.65 (d, J = 7.2 Hz, 1 H, 2-H), 7.25-7.50 (m, 10 H, H_{arom}.). ¹³C NMR (CDCl₃): $\delta = 13.78$ (C-4'), 20.20 (C-3'), 30.43 (C-2'), 33.56 (C-3), 37.69 (C-4), 47.00 (C-1'), 64.93 (C-5), 67.40 (C-2), 119.66 (CN), 127.13, 127.34, 128.19, 128.37, 128.48, 128.53 (CH_{arom}.), 138.25, 143.67 (C_{arom}.). IR (kap.): $\tilde{\nu} = 2956$ cm⁻¹, 2861, 2242, 1454, 754, 702. GC-MS m/z (%): 304 (1) [M^+], 303 (2) [M^+ - H], 261 (100) [M^+ - C₃H₇], 227 (3) [M^+ - C₆H₅], 91 (19). C₂₁H₂₄N₂ (304.4).

 $(2S^*, 3S^*, 5S^*)$ -1-Butyl-3-cyano-2,5-diphenylpyrrolidine (20). ¹H NMR (CDCl₃): $\delta = 0.72$ (t, J = 7.3 Hz, 3 H, 4'-H), 1.00-1.40 (m, 4 H, 2',3'-H), 2.09 (m, 1 H, 1'-H_a), 2.22 (dt, J = 8.0, 12.5 Hz, 1 H, 1'-H_b), 2.28 (ddd, J = 5.3, 6.1, 13.3 Hz, 1 H, 4-H_a), 2.92 (ddd, J = 8.1, 9.9, 13.2 Hz, 1 H, 4-H_b), 3.04 (ddd, J = 5.7, 5.9, 9.9 Hz, 1 H, 3-H), 4.41 (dd, J = 5.4, 8.2 Hz, 1 H, 5-H), 4.54 (d, J = 5.7 Hz, 1 H, 2-H), 7.25-7.55 (m, 10 H, H_{arom}). ¹³C NMR (CDCl₃): $\delta = 13.83$ (C-4'), 20.04 (C-3'), 29.93 (C-2'), 36.07 (C-3), 37.55 (C-4), 45.75 (C-1'), 64.87 (C-5), 69.70 (C-2), 121.82 (<u>C</u>N), 127.54, 127.62, 128.12, 128.17, 128.53, 128.76 (<u>CH_{arom}</u>), 139.69, 142.12 (C_{arom}). **IR** (kap.): $\tilde{\nu} = 2956$ cm⁻¹, 2861, 2240, 1493, 1454, 755, 701. **GC-MS** m/z (%): 303 (3) [M^+ - H], 261 (100) [M^+ - C₃H₇], 227 (4) [M^+ - C₆H₅]. C₂1H₂₄N₂ (304.4).

PET conversion of aziridine 2 with acrylonitrile

636 mg (12 mmol) acrylonitrile were added to 1 g (4 mmol) aziridine 2 dissolved in 140 mL acetonitrile. The argon-saturated solution was irradiated for 4 h at $\lambda = 419$ nm. The solvent was removed and the products were separated by HPLC with 7% ethyl acetate/cyclohexane. We obtained 19, 20, 21 and 22 in yields of 29 %, 17 %, 4 % and 4 %. All compounds were pale yellow oils.

 $(2R^*, 3S^*, 5S^*)$ -*1-Butyl-3-cyano-2,5-diphenylpyrrolidine (21).* ¹H NMR (CDCl₃): $\delta = 0.59$ (t, J = 7.1 Hz, 3 H, 4'-H), 0.80-1.70 (m, 4 H, 2',3'-H), 2.16 (ddd, J = 6.6, 8.1, 13.1 Hz, 1 H, 4-H_a), 2.46 (t, J = 8.1 Hz, 2 H, 1'-H), 2.62 (ddd, J = 7.6, 8.5, 13.1 Hz, 1 H, 4-H_b), 3.31 (ddd, J = 6.5, 7.6, 8.5 Hz, 1 H, 3-H), 3.80 (t, J = 7.8 Hz, 1 H, 5-H), 4.02 (d, J = 7.7, 1 H, 2-H), 7.20-7.62 (m, 10 H, H_{arom.}). ¹³C NMR (CDCl₃): $\delta = 13.65$ (C-4'), 20.36 (C-3'), 27.85 (C-2'), 35.29 (C-3), 38.75 (C-4), 51.38 (C-1'), 67.44 (C-5), 69.24 (C-2), 120.16 (CN), 127.60, 127.65, 128.17, 128.38, 128.44, 128.58 (CH_{arom.}), 139.23, 142.80 (C_{arom.}). IR (kap.): $\tilde{\nu} = 2959$ cm⁻¹, 2223, 1637, 1449, 700. GC-MS m/z (%): 303 (3) [M^+ - H], 302 (12), 261 (13) [M^+ - C₃H₇], 189 (13), 105 (100), 91 (12), 77 (43), 51 (13). C₂₁H₂₄N₂ (304.4).

 $(2R^*, 3R^*, 5S^*)$ -*1-Butyl-3-cyano-2,5-diphenylpyrolidine (22).* ¹**H** NMR (CDCl₃): $\delta = 0.61$ (t, J = 7.1 Hz, 3 H, 4'-H), 0.92-1.13 (m, 4 H, 2',3'-H), 2.17 (ddd, J = 7.5, 9.6, 13.0 Hz, 1 H, 4-H_a), 2.46 (dd, J = 6.9, 9.5 Hz, 2 H, 1'-H), 2.52 (ddd, J = 6.7, 8.2, 13.0 Hz, 1 H, 4-H_b), 2.92 (ddd, J = 6.7, 8.1, 9.6 Hz, 1 H, 3-H), 3.99 (d, J = 8.1 Hz, 1 H, 2-H), 4.01 (dd, J = 7.4, 8.1 Hz, 1 H, 5-H), 7.26-7.58 (m, 10 H, H_{arom}). ¹³C NMR (CDCl₃): $\delta = 13.66$ (C-4'), 20.37 (C-3'), 27.85 (C-2'), 36.56 (C-3), 38.34 (C-4), 51.18 (C-1'), 66.82 (C-5), 72.22 (C-2), 121.09 (CN), 127.17, 127.22, 127.56, 128.33, 128.60, 128.84 (CH_{arom}), 140.68, 143.27 (C_{arom}). **IR** (kap.): $\tilde{\nu} = 3029$ cm⁻¹, 2956, 2861, 2241, 1493, 1453, 1170, 753, 701. **GC-MS** *m/z* (%): 261 (100) [M^{+} - C₃H₇], 227 (3) [M^{+} - C₆H₅], 205 (12), 154 (10), 91 (18). C₂₁H₂₄N₂ (304.4).

1.278 mg (12 mmol) DMAD were added to 525 mg (3 mmol) aziridine 1 dissolved in 200 mL acetonitrile. After 2 d the solvent was removed and separation occurred by HPLC with 15% ethyl acetate/cyclohexane. We obtained 9 in yields of 13%.

Thermal reaction of aziridine 2 with DMAD in acetonitrile

85 mg (0.6 mmol) DMAD were added to 250 mg (0.2 mmol) aziridine 2 dissolved in 10 mL acetonitrile. After several days the solvent was removed and the products separated by HPLC with 10% ethyl acetate/cyclohexane. We obtained 16 in yields of 13%.

General procedures of the thermal transformations in methanol

In 54 mL absolute methanol 1 mmol of the aziridine was treated with 3 mmol of the dipolarophile and stirred at room temperature for several hours. After complete conversion (GC monitored) the solvent was removed by distillation under reduced pressure and the crude product is purified on silica gel. In the case of 1-aryl aubstituted aziridines neutral aluminium oxide is used due to decomposition on silica gel.

Dimethyl 2-[butyl-(2'-methoxy-2'-phenylethyl)amino]maleate (25a). The conversion of aziridine 1 with DMAD in methanol afforded 25a as a yellow oil in 70 % yield. ¹H NMR (CDCl₃): $\delta = 0.86$ (t, J = 7.3 Hz, 3 H, 4''-H), 1.22 (sex, J = 7.3 Hz, 2 H, 3''-H), 1.50 (quint, J = 7.7 Hz, 2 H, 2''-H), 2.95 (dt, J = 7.5, 14.6 Hz, 1 H, 1''-Ha), 3.14 (dd, J = 3.8, 15.0 Hz, 1 H, 1'-Ha), 3.19 (s, 3 H, CH-OCH₃), 3.23 (dt, J = 7.5, 14.6 Hz, 1 H, 1''-Hb), 3.30 (dd, J = 8.3, 15.0 Hz, 1 H, 1'-Hb), 3.62 (s, 3 H, CO₂CH₃), 3.88 (s, 3 H, CO₂CH₃), 4.43 (dd, J = 3.8, 8.3 Hz, 1 H, 2'-H), 4.64 (s, 1 H, 3-H), 7.24-7.38 (m, 5 H, Harom.). ¹³C NMR (CDCl₃): $\delta = 13.63$ (C-4''), 19.86 (C-3''), 28.71 (C-2''), 50.59 (CO₂CH₃), 52.18 (C-1'/1''), 52.71 (CO₂CH₃), 56.83 (CH-OCH₃), 57.29 (C-1''/1'), 82.12 (C-3/2'), 84.22 (C-2'/3), 126.34 (2 CH_{arom}), 128.17 (CH_{arom}), 128.64 (2 CH_{arom}), 139.15 (C_{arom}), 154.15 (C-2), 165.97 (C-4), 168.10 (C-1). IR (kap.): $\tilde{\nu} = 2940$ cm⁻¹, 2860, 1730, 1690, 1565, 1435, 1420, 1360, 1250, 1150, 1100, 1040, 1020, 700. GC-MS m/z (%): 350 (1) [M^+ + H], 349 (2) [M^+], 318 (7) [M^+ - OCH₃], 290 (2) [M^+ - CO₂CH₃], 258 (2) [M^+ - 91], 228 (100) [M^+ - PhCHOCH₃], 186 (52), 140 (14), 121 (12) [PhCHOCH₃⁺], 112 (13), 91 (10), 77 (12). C₁₉H₂₇NO₅ (349.4).

(*E*)-Methyl 3-[butyl-(2'-methoxy-2'-phenylethyl)amino]acrylate (25b). The conversion of aziridine 1 with methyl propiolate in methanol afforded 25b as a yellow oil in 95 % yield. ¹H NMR (CDCl₃): $\delta = 0.80$ (t, J = 7.4 Hz, 3 H, 4''-H), 1.17 (sex, J = 7.6 Hz, 2 H, 3''-H), 1.40 (quint, J = 7.6 Hz, 2 H, 2''-H), 2.90 (dt, J = 7.4, 14.1 Hz, 1 H, 1''-H_a), 3.05 (m, 2 H, 1'-H_a, 1''-H_b), 3.10 (s, 3 H, CH-OC<u>H</u>₃), 3.25 (dd, J = 8.2, 14.4 Hz, 1 H, 1'-H_b), 3.55 (s, 3 H, CO₂C<u>H</u>₃), 4.25 (br, 1 H, 2'-H), 4.50 (d, J = 13.1 Hz, 1 H, 2-H), 7.16-7.30 (m, 5 H, H_{arom.}), 7.35 (d, J = 13.1 Hz, 1 H, 3-H). ¹³C NMR (CDCl₃): $\delta = 14.35$ (C-4''), 19.84 (C-3''), 29.58 (C-2''), 50.34 (CO₂C<u>H</u>₃), 51.25 (C-1'/1''), 56.81 (CH-OCH₃), 57.50 (C-1'/1''), 82.78 (C-2'), 83.86 (C-2), 126.49 (2 CH_{arom.}), 128.16 (CH_{arom.}), 128.62 (2 CH_{arom.}), 139.12 (C_{arom.}), 151.95 (C-3), 170.07 (C-1). IR (kap.): $\tilde{\nu} = 2920$ cm⁻¹, 2860, 2810, 1680, 1600, 1450, 1415, 1350, 1240, 1180, 1140, 1100, 1045, 1015, 780, 750, 700. GC-MS *m*/*z* (%): 292 (2) [*M*⁺ + H], 260 (12) [*M*⁺ -OCH₃], 248 (1) [*M*⁺ - C₃H₇], 170 (88) [*M*⁺ - PhCHOCH₃], 128 (100), 121 (16) [PhCHOCH₃⁺], 91 (11), 82 (19), 77 (12), 41 (13). C₁₇H₂₅NO₃ (291.4).

Dimethyl 2-[butyl-(2'-methoxy-1', 2'-diphenylethyl)amino]maleate (25c). The conversion of aziridine 2 with DMAD in methanol afforded 25c as a yellow oil in 78 % yield. ¹H NMR (CDCl₃): $\delta = 0.60$ (m, 1 H, 2''-H_a), 0.71 (t, J = 7.3 Hz, 3 H, 4''-H), 1.00 (m, 2 H, 3''-H), 1.40 (m, 1 H, 2''-H_b), 3.03 (ddd, J = 4.6, 10.8, 14.7 Hz, 1 H, 1''-H_a), 3.21 (ddd, J = 5.0, 10.9, 14.6 Hz, 1 H, 1''-H_b), 3.31 (s, 3 H, CH-OCH₃), 3.59 (s, 3 H, CO₂CH₃), 3.86 (s, 3 H, CO₂CH₃), 4.51 (s, 1 H, 3-H), 4.56 (d, J = 6.5 Hz, 1 H, 1''-H), 4.87 (d, J = 6.5 Hz, 1 H, 2''-H), 7.20-7.60 (m, 10 H, H_{arom}). ¹³C NMR (CDCl₃): $\delta = 13.48$ (C-4''), 20.09 (C-3''), 27.40 (C-2''), 47.07 (C-1''), 50.68 (CO₂CH₃), 52.77 (CO₂CH₃), 57.25 (CH-OCH₃), 68.25 (C-1'), 84.71 (C-3/2'), 85.56 (C-2'/3), 127.25, 127.96, 128.09, 128.23, 128.28, 129.74 (CH_{arom}), 135.9, 137.89 (C_{arom}), 153.39 (C-2), 166.30 (C-4), 168.02 (C-1) IR (kap.): $\tilde{\nu} = 2949$ cm⁻¹, 2869, 1736, 1697, 1567,1437, 1420, 1374, 1151, 1104, 1046, 795, 761, 701. GC-MS m/z (%): 394 (5) [M^+ -OCH₃], 304 (100) [M^+ - PhCHOCH₃], 156 (12), 142 (12), 121 (44), 105 (10), 91 (16), 77 (18), 57 (48), 41 (13). C₂₅H₃₁NO₅ (425.5).

(E)-Methyl 3-[butyl-(2'-methoxy-1', 2'-diphenylethyl)amino]acrylate (25d). The conversion of aziridine 2 with methyl propiolate in methanol afforded 25d as a pale yellow oil in 83 % yield. ¹H NMR (CDCl₃): $\delta = 0.74$ (t, J = 7.2 Hz, 3 H, 4''-H), 1.00 (m, 3 H, 3''-H, 2''-H_a), 1.24 (m, 1 H, 2''-H_b), 2.63 (m, 1 H, 1''-H_a), 2.78 (m, 1 H, 1''-H_b), 3.20 (s, 3 H, CH-OCH₃), 3.63 (s, 3 H, CO₂CH₃), 4.34 (d, J = 8.7 Hz, 1 H, 1'-H), 4.43 (d, J = 13.1 Hz, 1 H, 2-H), 4.72 (d, J = 8.3 Hz, 1 H, 2'-H), 7.20-7.35 (m, 10 H, H_{arom.}), 7.56 (d, J = 13.1 Hz, 1 H, 3-H). ¹³C NMR (CDCl₃): $\delta = 13.59$ (C-4''), 19.04 (C-3''), 28.19 (C-2''), 49.61 (C-1''), 50.39 (CO₂CH₃), 56.68 (CH-OCH₃), 72.43 (1'), 83.60 (C-2'/2), 84.57 (C-2/2'), 127.55, 127.97, 128.40 (CH_{arom.}), 137.47, 138.56 (C_{arom.}), 150.01 (C-3), 170.04 (C-1). IR (kap.): $\tilde{\nu} = 2956$ cm⁻¹, 2949, 1693, 1606, 1454, 1422, 1360, 1241, 1147, 1098, 790, 701. GC-MS m/z (%): 336 (8) [M^+ -OCH₃], 246 (100) [M^+ - PhCHOCH₃], 163 (25), 131 (33), 121 (38) [PhCHOCH₃⁺], 91 (15), 77 (19), 57 (23), 41 (12). C₂₃H₂₉NO₃ (367.5).

Dimethyl 2-[(2'-methoxy-2'-phenylethyl)phenylamino]maleate (25e). The conversion of aziridine 3 with DMAD in methanol afforded 25e as a yellow oil in 81 % yield. As a side product 26a was isolated in yields of 10 %. ¹H NMR (CDCl₃): δ = 3.19 (s, 3 H, OC<u>H</u>₃), 3.60 (m, 1 H, 1'-H_a), 3.65 (s, 3 H, CO₂C<u>H</u>₃), 3.67 (s, 3 H, CO₂C<u>H</u>₃), 3.78 (dd, J = 8.7, 14.8 Hz, 1 H, 1'-H_b), 4.43 (dd, J = 3.8, 8.7 Hz, 1 H, 2'-H), 4.89 (s, 1 H, 3-H), 7.14-7.36 (m, 10 H, H_{arom}). ¹³C NMR (CDCl₃): δ = 50.84 (CO₂CH₃), 52.48 (CO₂CH₃), 56.81 (CH-O<u>C</u>H₃), 59.89 (C-1'), 80.86 (C-2'), 88.82 (C-3), 126.69 (C-2''), 127.46 (C-4''), 127.84 (C-2'''), 128.29 (C-4'''), 128.67 (C-3'''), 129.21 (C-3''), 138.95 (C-1'''), 143.67 (C-1''), 154.26 (C-2), 165.29 (C-4/1), 167.78 (C-1/4). IR (kap.): $\tilde{\nu}$ = 2950 cm⁻¹, 1731, 1714, 1596, 1574, 1494, 1453, 1435, 1258, 1173, 1106, 1023, 755, 700. GC-MS *m/z* (%): 338 (1) [*M*⁺ - OCH₃], 248 (100) [*M*⁺ - PhCHOCH₃], 144 (31), 121 (13) [PhCHOCH₃⁺], 91 (18), 77 (43), 51 (14). CI (NH₃) *m/z* (%): 370 (100) [*M*H⁺]. C₂₁H₂₃NO₅ (369.4).

(2-Methoxy-2-phenylethyl)phenylamine (26a).²⁵ ¹H NMR (CDCl₃): δ = 1.59 (br, 1 H, NH), 3.28 (s, 3 H, OCH₃), 3.30 (m, 2 H, 1-H), 4.40 (dd, J = 4.8, 7.9 Hz, 1 H, 2-H), 6.65 (dd, J = 1.0, 8.6 Hz, 2 H, 3'-H), 6.73 (tt, J = 1.0, 7.4 Hz, 1 H, 4'-H), 7.18 (dd, J = 7.4, 8.6 Hz, 2 H, 2'-H), 7.33-7.42 (m, 5 H, H_{arom}). ¹³C NMR (CDCl₃): δ = 50.75 (C-1), 56.84 (OCH₃), 82.22 (C-2), 113.34 (C-2'), 117.69 (C-4'), 126.73 (C-2''), 128.06 (C-4''), 128.58 (C-3''), 129.23 (C-3'), 139.87 (C-1''), 148.02 (C-1'). **IR** (kap.): $\tilde{\nu}$ = 1603 cm⁻¹, 1504, 1454, 1317, 1249, 1106, 750, 701. **GC-MS** m/z (%): 227 (2) [M^+], 121 (12) [PhCHOCH₃⁺], 106 (100) [M^+ - PhCHOCH₃], 91 (13), 77 (39), 51 (16). CI (NH₃) m/z (%): 228 (100) [M^+]. C₁₅H₁₇NO (227.3).

(E)-Methyl 3-[(2'-methoxy-2'-phenylethyl)phenylamino]acrylate (25f). The conversion of aziridine 3 with methyl propiolate in methanol afforded 25f as a yellow oil in 64 % yield. As a side product 26a was isolated in yields of 7 %. ¹H NMR (CDCl₃): $\delta = 3.21$ (s, 3 H, CH-OCH₃), 3.69 (dd, J = 4.2, 14.8 Hz, 1 H, 1'-H_a), 3.72 (s, 3 H, CO₂CH₃), 3.87 (dd, J = 8.8, 14.9 Hz, 1 H, 1'-H_b), 4.52 (dd, J = 3.9, 8.8 Hz, 1 H, 2'-H), 4.97 (d, J = 13.3 Hz, 1 H, 2-H), 7.13-7.37 (m, 10 H, H_{arom.}), 7.85 (d, J = 13.3 Hz, 1 H, 3-H). ¹³C NMR (CDCl₃): $\delta = 50.72$ (CO₂CH₃), 57.06 (CH-OCH₃), 58.08 (C-1'), 80.02 (C-2'), 89.94 (C-2), 122.53, 125.05, 126.63, 128.30, 128.72, 129.33 (CH_{arom.}), 139.09, 146.03 (C_{arom.}), 149.12 (C-3), 169.59 (C-1). IR (kap.): $\tilde{\nu} = 2985$ cm⁻¹, 2928, 1694, 1614, 1585, 1495, 1454, 1435, 1343, 1262, 1156, 1107, 1023, 979, 801, 756, 700. GC-MS m/z (%): 280 (5) [M⁺ - OCH₃], 190 (100) [M⁺ - PhCHOCH₃], 177 (22), 158 (23), 130 (12), 121 (23) [PhCHOCH₃⁺], 104 (22), 91 (23), 77 (58), 45 (42). CI (NH₃) m/z (%): 312 (100) [MH⁺]. C₁₉H₂₁NO₃ (311.4).

Dimethyl 2-[(p-methoxyphenyl)-(2'-methoxy-2'-phenylethyl)amino]maleate (25g). The conversion of aziridine 4 with DMAD in methanol afforded 25g as a yellow oil in 85 % yield. As a side product 26b was isolated in yields of 10 %. ¹H NMR (CDCl₃): $\delta = 3.19$ (s, 3 H, CH-OCH₃), 3.55 (dd, J = 3.8, 14.7 Hz, 1 H, 1'-H_a), 3.64 (s, 3 H, CO₂CH₃), 3.68 (s, 3 H, CO₂CH₃), 3.73 (dd, J = 8.8, 14.7 Hz, 1 H, 1'-H_b), 3.81 (s, 3 H, Ar-OCH₃), 4.43 (dd, J = 3.8, 8.8 Hz, 1 H, 2'-H), 4.83 (s, 1 H, 3-H), 6.84 (d, J = 9.1 Hz, 2 H, 3''-H), 7.08 (d, J = 9.1 Hz, 2 H, 2''-H), 7.23-7.38 (m, 5 H, 2''',3''',4'''-H). ¹³C NMR (CDCl₃): $\delta = 50.85$ (CO₂CH₃), 55.39 (Ar-OCH₃), 56.79 (CH-OCH₃), 59.97 (C-1'), 80.73 (C-2'), 87.47 (C-3), 114.31 (C-3''), 126.70 (C-2''), 128.30 (C-4'''), 128.68 (C-2'''), 129.33 (C-3'''), 136.14 (C-1''), 138.90 (C-1'''), 154.82 (C-2), 158.70 (C-4''), 165.43 (C-4/1), 167.96 (C-1/4). IR (kap.): $\tilde{\nu} = 1745$ cm⁻¹, 1698, 1574, 1510, 1249, 1149. GC-MS m/z (%): 278 (100) [M^+ - PhCHOCH₃], 248 (14), 174 (47), 146 (14), 121 (26) [PhCHOCH₃⁺], 104 (23), 77 (31), 63 (16). CI (NH₃) m/z (%): 400 (100) [MH⁺]. C₂₂H₂₅NO₆ (399.4).

(*p*-Methoxyphenyl)-(2-methoxy-2-phenylethyl)amine (26b). ¹H NMR (CDCl₃): $\delta = 3.20$ (m, 2 H, 1-H), 3.27 (s, 3 H, CH-OC<u>H</u>₃), 3.75 (s, 3 H, Ar-OC<u>H</u>₃), 4.38 (dd, J = 5.4, 7.5 Hz, 1 H, 2-H), 6.63 (d, J = 9.1 Hz, 2 H, 3'-H), 6.78 (d, J = 9.1 Hz, 2 H, 2'-H), 7.25-7.41 (m, 5 H, 2'',3'',4''-H). ¹³C NMR (CDCl₃): $\delta = 51.95$ (C-1), 55.79 (O<u>C</u>H₃), 56.88 (O<u>C</u>H₃), 82.20 (C-2), 114.85 (C-2'), 114.93 (C-3'), 126.77 (C-4''), 128.07 (C-2''), 128.60 (C-3''), 139.96 (C-1'), 142.21 (C-1''), 152.44 (C-4'). **IR** (kap.): $\tilde{\nu} = 1513$ cm⁻¹, 1454, 1235, 1180, 1109, 1037, 821, 702. **GC-MS** *m/z* (%): 258 (2) [*M*⁺ + H], 257 (8) [*M*⁺], 136 (100) [*M*⁺ - PhCHOCH₃], 121 (12) [PhCHOCH₃⁺]. CI (NH₃) *m/z* (%): 258 (100) [*M*H⁺]. C₁₆H₁₉NO₂ (257.3).

(E)-Methyl 3-[(p-methoxyphenyl)-(2'-methoxy-2'-phenylethyl)amino]acrylate (25h). The conversion of aziridine 4 with methyl propiolate in methanol afforded 25h as a yellow oil in 80 % yield. As a side product 26b was isolated in yields of 8 %. ¹H NMR (CDCl₃): $\delta = 3.21$ (s, 3 H, CH-OC<u>H₃</u>), 3.62 (dd, J = 4.0, 14.6 Hz, 1 H, 1'-H_a), 3.68 (s, 3 H, CO₂C<u>H₃</u>), 3.78 (dd, J = 8.6, 14.4 Hz, 1 H, 1'-H_b), 3.81 (s, 3 H, Ar-OC<u>H₃</u>), 4.45 (br, d, J = 4.9 Hz, 1 H, 2'-H), 4.81 (br, d, J = 12.3 Hz, 1 H, 3-H), 6.86 (d, J = 9.1 Hz, 2 H, 3''-H), 7.11 (d, J = 9.1 Hz, 2 H, 2''-H), 7.26-7.39 (m, 5 H, 2''',3''',4'''-H), 7.74 (d, J = 13.2 Hz, 1 H, 2-H). ¹³C NMR (CDCl₃): $\delta = 50.68$ (CO₂CH₃), 55.50 (2 OCH₃), 57.02 (C-1'), 80.17 (C-2'), 88.37 (C-2), 114.71 (C-3''), 126.72 (C-2''), 126.77 (C-1''), 128.32 (C-4'''), 128.75 (C-2''',3'''), 139.06 (C-1'''), 150.53 (C-3), 157.51 (C-4''), 169.85 (C-1). IR (kap.): $\tilde{\nu} = 3031$ cm⁻¹, 2932, 1682, 1614, 1514, 1441, 1107. GC-MS m/z (%): 341 (1) [M⁺], 310 (5) [M⁺ - OCH₃], 220 (100) [M⁺ - PhCHOCH₃], 190 (18), 134 (23), 121 (17) [PhCHOCH₃⁺], 91 (16), 77 (28), 45 (30). CI (NH₃) m/z (%): 342 (100) [MH⁺]. C₂₀H₂₃NO₄ (341.4).

Dimethyl 2-[(*p*-cyanophenyl)-(2'-methoxy-2'-phenylethyl)amino]maleate (25i). The conversion of aziridine 5 with DMAD in methanol afforded 25i as a yellow oil in 42 % yield. As a side product 26c was isolated in yields of 18 %. ¹H NMR (CDCl₃): $\delta = 3.03$ (s, 3 H, OCH₃), 3.61 (s, 3 H, OCH₃), 3.72 (s, 3 H, OCH₃), 3.74 (dd, J = 4.5, 7.5 Hz, 2 H, 1'-H), 4.39 (dd, J = 4.2, 7.3 Hz, 1 H, 2'-H), 6.71 (d, J = 9.0 Hz, 2 H, 2''-H), 6.74 (s, 1 H, 3-H), 7.29-7.33 (m, 5 H, H_{arom.}), 7.42 (d, J = 9.0 Hz, 2 H, 3''-H). ¹³C NMR (CDCl₃): $\delta = 52.02$, 53.13 (CO₂CH₃), 56.50 (OCH₃), 59.23 (C-1'), 82.49 (C-2'), 101.83 (C-4''), 114.89 (C-3), 119.30 (CN), 122.03, 126.54, 128.44, 128.84, 133.44 (CH_{arom.}), 138.74 (C-1'''), 144.61 (C-1''), 150.40 (C-2), 164.01 (C-4/1), 164.60 (C-1/4). **IR** (kap.): $\tilde{v} = 2951$ cm⁻¹, 2218, 1732, 1603, 1513, 1435, 1392, 1336, 1258, 1174, 1105, 1054, 1022, 825, 784, 760, 733, 703. **GC-MS** m/z (%): 394 (3) [M^+], 363 (3) [M^+ - OCH₃], 273 (100) [M^+ - Ph-CH-OCH₃], 169 (13), 121 (53) [Ph-CH-OCH₃⁺], 77 (12). C₂₂H₂₂N₂O₅ (394.4).

(*p*-Cyanophenyl)-(2-methoxy-2-phenylethyl)amine (26c). ¹H NMR (CDCl₃): $\delta = 3.28$ (s, 3 H, OCH₃), 3.32 (dd, J = 4.5, 7.7 Hz, 2 H, 1-H), 4.37 (dd, J = 5.1, 7.5 Hz, 1 H, 2-H), 6.56 (dm, J = 8.9 Hz, 2 H, 2'-H), 7.30-7.45 (m, 7 H, H_{arom}). ¹³C NMR (CDCl₃): $\delta = 49.62$ (C-1), 56.89 (OCH₃), 81.82 (C-2), 98.88 (CN), 112.48 (C-2'), 120.44 (C-4'), 126.68 (C-2''), 128.44 (C-4''), 128.77 (C-3''), 133.67 (C-3'), 138.96 (C-1''), 151.13 (C-1'). IR (kap.): $\tilde{\nu} = 3372$ cm⁻¹, 2932, 2211, 1606, 1525, 1454, 1338, 1173, 1110, 824, 763, 702, 545. GC-MS m/z (%): 252 (7) [M^+], 131 (29), 121 (100) [Ph-CH-OCH₃⁺], 77 (13). CI (*Iso*butane) m/z (%): 253 (100) [MH^+]. C₁₆H₁₆N₂O (252.3).

(E)-Methyl 3-[(p-cyanophenyl)-(2'-methoxy-2'-phenylethyl)amino]acrylate (25k). On the conversion of aziridine 5 with methyl propiolate in methanol 25i was afforded only as a side product. It was identified by the GC-MS spectrum. As main product 26c was detected. GC-MS m/z (%): 336 (4) $[M^+]$, 305 (4) $[M^+ - \text{OCH}_3]$, 215 (40), 121 (100) [PhCHOCH₃⁺], 91 (9), 77 (13). CI (Isobutane) m/z (%): 337 (100) $[MH^+]$. C₂₀H₂₀N₂O₃ (336.4).

(E)-Methyl 3-[butyl-(2'-hydroxy-2'-phenylethyl)amino]acrylate (25l). 2.016 g (24 mmol) methyl propiolate and 90 mL water were added to 1.4 g (8 mmol) aziridine 1 dissolved in 90 mL acetonitrile. After 5 d the organic layer was extracted with pentane and dried over magnesium sulfate. The solvent was removed and the product was purified on silica gel with 20% ethyl acetate/cyclohexane. 25l was afforded in yields of 18 % as a yellow oil. ¹H NMR (CDCl₃): $\delta = 0.90$ (t, J = 7.3 Hz, 3 H, 4''-H), 1.26 (sex., J = 7.3 Hz, 2 H, 3''-H), 1.51 (m, 2 H, 2''-H), 2.55 (br, 1 H, OH), 3.03 (m, 1 H, 1''-H_a), 3.18 (m, 1 H, 1''-H_b), 3.28 (dd, J = 4.5, 14.3 Hz, 1 H, 1'-H_a), 3.35 (dd, J = 8.0, 14.4 Hz, 1 H, 1'-H_b), 3.65 (s, 3 H, CO₂CH₃), 4.64 (d, J = 13.2 Hz, 1 H, 2-H), 4.93 (br, 1 H, 2'-H), 7.28-7.38 (m, 5 H, H_{arom}), 7.48 (d, J = 13.2 Hz, 1 H, 3-H). ¹³C NMR (CDCl₃): $\delta = 13.71$ (C-4''), 19.96 (C-3''), 29.53 (C-2''), 50.44 (CO₂CH₃), 52.75 (C-1'/1''), 59.45 (C-1''/1'), 71.84 (C-2/2'), 84.21 (C-2'/2), 125.82 (2 CH_{arom}), 128.02 (CH_{arom}), 128.58 (2 CH_{arom}), 141.70 (C_{arom}), 152.15 (C-3), 170.20 (C-1). IR (kap.): $\tilde{\nu} = 3408$ cm⁻¹, 2956, 2872, 1672, 1614, 1423, 1360, 1257, 1152, 1113, 1060, 788, 701. GC-MS m/z (%): 246 (12) [M^+ -OCH₃], 204 (15), 176 (11), 170 (68) [M^+ - PhCHOH], 158 (21), 128 (100), 105 (48), 98 (38), 91 (11), 82 (47), 77 (76), 70 (10), 51 (32), 41 (28). C₁₆H₂₃NO₃ (277.4).

(E)-Methyl 3-[butyl-(1',2'-diphenyl-2'-hydroxyethyl)amino]acrylate (25m). 2.016 g (24 mmol) methyl propiolate were added to 2 g (8 mmol) aziridine 2 dissolved in a mixture of 90 mL acetonitrile and 10 mL water. After 4 d the solvent was removed and the product was purified on silica gel with 50% diethyl ether/pentane. 25m was isolated in yields of 29 % as a yellow oil. ¹H NMR (CDCl₃): $\delta = 0.74$ (t, J = 7.6 Hz,

3 H, 4'-H), 0.94-1.10 (m, 2 H, 3'-H), 1.15-1.35 (m, 2 H, 2'-H), 2.25 (br, s, 1 H, O<u>H</u>), 2.60-2.90 (m, 2 H, 1'-H), 3.62 (s, 3 H, CO₂C<u>H₃</u>), 4.34 (d, J = 8.5 Hz, 1 H, 1''-H), 4.45 (d, J = 13.1 Hz, 1 H, 2-H), 5.27 (d, J =8.5 Hz, 1 H, 2''-H), 7.29-7.40 (m, 10 H, H_{arom}), 7.67 (d, J = 13.0 Hz, 1 H, 3-H). ¹³C NMR (CDCl₃): $\delta =$ 13.62 (C-4'), 19.99 (C-3'), 27.94 (C-2'), 49.71 (C-1'), 50.47 (CO₂CH₃), 73.16 (C-2''), 74.13 (C-2), 84.39 (C-1''), 126.78, 128.30, 128.33, 128.47, 128,52, 128.73 (CH_{arom}), 137.01, 141.07 (C_{arom}), 149.80 (C-3), 170.19 (C-1). IR (kap.): $\tilde{\nu} = 3406$ cm⁻¹, 2956, 2236, 1682, 1614, 1496, 1454, 1360, 1250, 1151, 1096, 791, 756, 701, 606. GC-MS m/z (%): 335 (6) [M^+ - H₂O], 280 (16), 247 (78) [M^+ -PhCHO], 246 (33) [M^+ PhCHOH], 204 (33), 188 (21), 174 (100) [M^+ - Ph - OH - CH=CHCO₂CH₃], 158 (16), 132 (32), 117 (22), 106 (49) [PhCHO⁺], 91 (72), 77 (59). CI (*Iso*butane) m/z (%): 354 (100) [MH⁺]. C₂₂H₂₇NO₃ (353.5).

Thermal conversion of aziridine 6 with DMAD in acetonitrile

852 mg (6 mmol) DMAD were added to 200 mg (1 mmol) aziridine 6 dissolved in 50 mL acetonitrile. After 24 h refluxing the solvent was removed and the products were separated by HPLC with 25 % ethyl acetate/cyclohexane. 30 and 31 were isolated in yields of 4 % and 7 % as yellow oils.

Dimethyl 1-butyl-4-(p-cyanophenyl)-4,5-dihydro-1H-pyrrole-2,3-dicarboxylate (30). ¹H NMR (CDCl₃): $\delta = 0.84$ (t, J = 7.3 Hz, 3 H, 4'-H), 1.15 (sex, J = 7.3 Hz, 2 H, 3'-H), 1.30-1.43 (m, 2 H, 2'-H), 2.50 (ddd, J = 5.7, 9.7, 15.1 Hz, 1 H, 1'-H_a), 2.94 (ddd, J = 5.7, 9.8, 15.1 Hz, 1 H, 1'-H_b), 3.58 (dd, J = 8.6, 15.1 Hz, 1 H, 5-H_a), 3.66 (s, 3 H, CO₂CH₃), 3.86 (dd, J = 6.1, 15.1 Hz, 1 H, 5-H_b), 4.66 (s, 3 H, CO₂CH₃), 5.17 (dd, J = 6.1, 8.6 Hz, 1 H, 4-H), 7.56 (dm, J = 8.4 Hz, 2 H, 2''-H), 7.66 (dm, J = 8.4 Hz, 2 H, 3''-H). ¹³C NMR (CDCl₃): $\delta = 13.64$ (C-4'), 19.79 (C-3'), 26.88 (C-2'), 51.06 (CO₂CH₃), 52.33 (C-5), 53.18 (CO₂CH₃), 58.19 (C-1'), 86.59 (C-4), 109.56 (C-4''), 112.85 (CN), 118.09 (C-3), 128.80 (C-2''), 132.66 (C-3''), 144.01 (C-1''), 153.18 (C-2), 165.64, 167.69 (CO₂CH₃). **IR** (KBr, CH₂Cl₂): $\tilde{\nu} = 2229$ cm⁻¹, 1741, 1697, 1577, 1438, 1417, 1254, 1150. **GC-MS** m/z (%): 342 (31) [M^+], 311 (15) [M^+ - OCH₃], 299 (100) [M^+ - C₃H₇], 283 (12) [M^+ - CO₂CH₃], 140 (13). CI (*Iso*butane) m/z (%): 343 (100) [MH⁺]. C₁9H₂₂N₂O₄ (342.4).

Teteramethyl 1-butyl-1H-pyrrole-2,3,4,5-tetracarboxylate (31). ¹**H** NMR (CDCl₃): $\delta = 0.92$ (t, J = 7.4 Hz, 3 H, 4'-H), 1.23-1.43 (m, 2 H, 3'-H), 1.63-1.79 (m, 2 H, 2'-H), 3.86 (s, 6 H, CO₂C<u>H₃</u>), 3.89 (s, 6 H, CO₂C<u>H₃</u>), 4.39 (m, 2 H, 1'-H). ¹³**C** NMR (CDCl₃): $\delta = 17.53$ (C-4'), 19.74 (C-3'), 33.46 (C-2'), 47.63 (C-1'), 52.40, 52.65 (CO₂CH₃), 119.76 (C-3), 133.11 (C-2), 160.60, 163.84 (<u>CO₂CH₃</u>). **IR** (kap.): $\tilde{\nu} = 2956$ cm⁻¹, 1724, 1507, 1456, 1314, 1242, 1120. **GC-MS** *m/z* (%): 355 (17) [*M*⁺], 324 (36) [*M*⁺ - OCH₃], 313 (17), 296 (63) [*M*⁺ - CO₂CH₃], 254 (55), 236 (100) [*M*⁺ + H - 2 x CO₂CH₃], 206 (30), 178 (19), 93 (10). CI (*Iso*butane) *m/z* (%): 356 (100) [*M*H⁺]. C₁₆H₂₁NO₈ (355.3).

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