Pergamon

Tetrahedron 55 (1999) 9535–9558

TETRAHEDRON

# Nonstereospecific 1,3-Dipolar Cycloadditions of Azomethine Ylides and Enamines

**Thomas Böhm, Andreas Weber, and Jürgen Sauer***

*Institut für Organische Chemie der Universität Regensburg, D-93040 Regensburg, Germany*

Received 27 April 1999; accepted 10 June 1999

**Abstract:** The combination of electron-poor azomethine ylides **3** (AMY-I) or **4** (AMY-II) with electron-rich enamines **5** results in nonstereospecific 1,3-dipolar cycloadditions, which are $LUMO_{dipole}$-$HOMO_{dipolarophile}$ controlled reactions. This phenomenon can be explained only by a two-step mechanism via zwitterionic intermediates. 

**Keywords:** *Nonstereospecific cycloadditions; 1,3-Dipolar cycloadditions; Azomethine ylides; Enamines*

## INTRODUCTION

According to the Woodward-Hoffmann rules 1,3-dipolar cycloadditions are expected to occur in a stereospecific suprafacial manner due to the symmetry of the participating molecular orbitals [1,2,3]. Nonconcerted nonstereospecific cycloadditions are not excluded completely but until 1986 there was lack of experimental evidence. Earlier reports on nonstereospecific cycloadditions of azomethine imines [4] had to be revised [5,6]. The first examples proved were reported by Huisgen's group [7,8,9], who found that electron-rich thiocarbonyl ylides combine with the electron-poor dipolarophiles dicyanomaleate and dicyanofumarate in a nonstereospecific manner. A zwitterionic intermediate in the course of a two-step, nonconcerted cycloaddition was offered as an explanation.

Quite recently we reported on the synthesis of two new classes of coloured, stable azomethine ylides **3** and **4** derived from 3,4-diazanorcaradienes **1** and 1-aza-1,3-cyclopentadienes [10,11,12]. These electron-poor 1,3-dipoles combine, as kinetic studies prove [10], in a $LUMO_{dipole}$-$HOMO_{dipolarophile}$ controlled reaction preferentially with electron-rich

* Fax: (internat.) +49 941-943-4946, E-mail: elisabeth.liebl@chemie.uni-regensburg.de

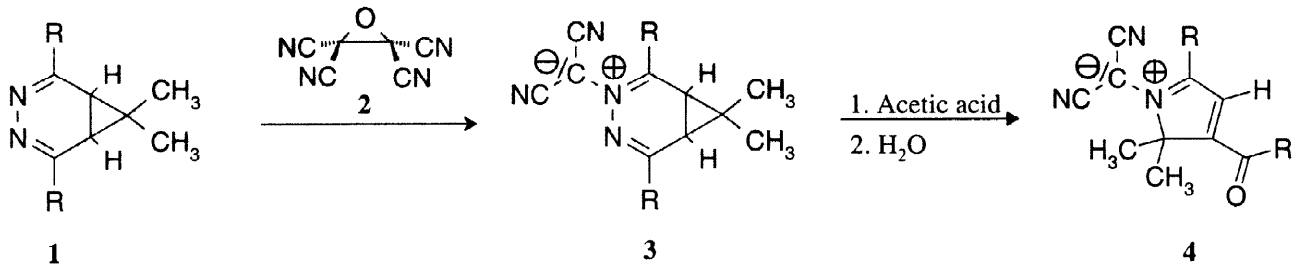
0040-4020/99/$ - see front matter 
*PII:* S0040-4020(99)00517-7

dipolarophiles such as enolethers, enamines, ynamines and ketene aminals. These 1,3-dipolar cycloadditions, the electronic counterpart of Huisgen's system, turned out to occur in a nonstereospecific manner, too, as could be shown when *(E)*-1-*N*,*N*-dimethylamino-1-propene was used as a dipolarophile [13].

In this communication we show that for all 1,3-dipoles **3** (AMY-I) and **4** (AMY-II) nonstereospecific cycloadditions are observed when *(E)*-enamines **5** were used as dipolarophiles.

## RESULTS

Azomethine ylides **3** are easily obtained when 3,4-diazanorcaradienes **1** are treated with tetracyanoethylene oxide **2** in inert solvents [10,14] in good to excellent yields (Scheme 1).



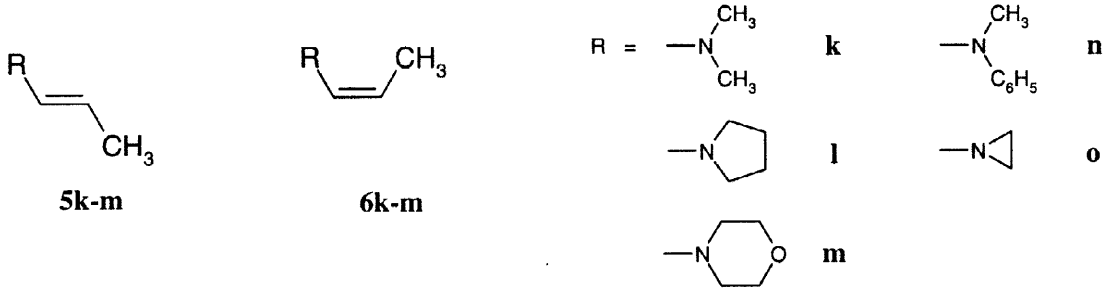

**1** **3** **4**

| 1/3/4 | a | b | c | d | e |
|---|---|---|---|---|---|
| R | 4-$CH_3O$-$C_6H_4$ | 4-$CH_3$-$C_6H_4$ | $C_6H_5$ | 4-Cl-$C_6H_4$ | 4-$CF_3$-$C_6H_4$ |

**Scheme 1.** Reactions of 2,5-disubstituted 3,4-diazanorcaradienes **1** with tetracyanoethylene oxide (TCNEO) **2** and acid triggered transformation of the 2,5-disubstituted AMY-I **3** in acetic acid to azacyclopentadiene-ylides AMY-II **4**.

These coloured 1,3-dipoles **3** are transformed by heating in acetic acid and following hydrolysis again to coloured 1,3-dipoles **4** (AMY-II) in a multistep sequence passing different coloured intermediates (Scheme 2). Mechanistic studies are still lacking [11,14].

*(E)*-1-Propenyl-amines **5k-o** are obtained in high purity from N-allylamines by base catalyzed double bond migration; the *(Z)*-enamines **6** are the primary products [15], but can be readily isomerized to the *(E)*-isomers by mild acid catalysis.

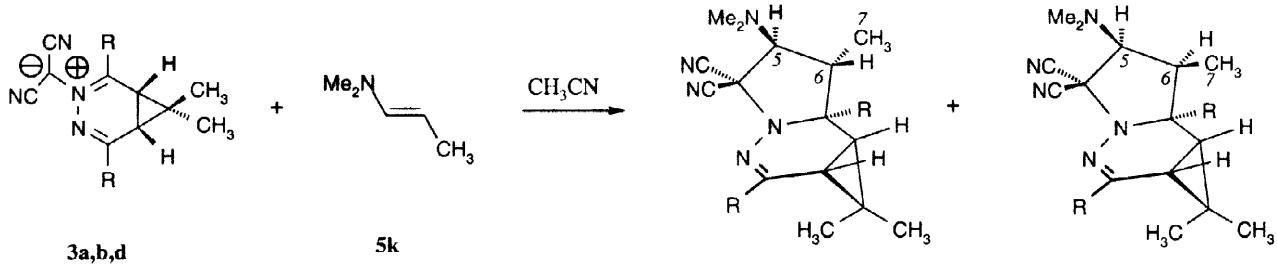



**5k-m** **6k-m**

**Figure 1.** 1-N-propenyl-substituted enamines with *(E)*-configuration (**5**) and *(Z)*-configuration (**6**) used in cycloaddition reactions.

The reaction of AMY-I **3b** with approximately one equivalent enamine **5k** in acetonitrile at 20°C results in almost quantitative formation of *two* diastereomeric cycloadducts **7b** and **8b**, which can be separated by flash column chromatography. NMR data and X-ray analysis (vide infra) prove the trans-configuration for **7b** and the cis-configuration for **8b**, in both adducts the dimethylamino group appears in endo-position.

Table 1 summarizes all results for the combination of AMY-I **3a,b,d** with the *(E)*-enamine **5k** (Scheme 2). The yields as well as the isomer ratio were obtained by NMR technique or HPLC analysis (see Experimental Section).




**Scheme 2.** Nonstereospecific 1,3-dipolar cycloadditions of AMY-I **3a,b,d** with *(E)*-1-*N,N*-dimethylamino-1-propene (**5k**).

**Table 1.** Data for the reaction of AMY-I **3a,b,d** with *(E)*-1-*N,N*-dimethylamino-1-propene (**5k**) in acetonitrile at ambient conditions.

| AMY-I [µmol] | | R | 5k [µmol] | t [h] | % 7 + 8 | 7 : 8 |
|---|---|---|---|---|---|---|
| **3a** | 300 | 4-$CH_3O$-$C_6H_4$ | 364 | 116 | 99 | 45 : 55 [a] |
| **3b** | 287 | 4-$CH_3$-$C_6H_4$ | 349 | 3 | 100 | 48 : 52 [a] |
| **3d** | 430 | 4-Cl-$C_6H_4$ | 539 | 3 | 100 | 45 : 55 [b] |

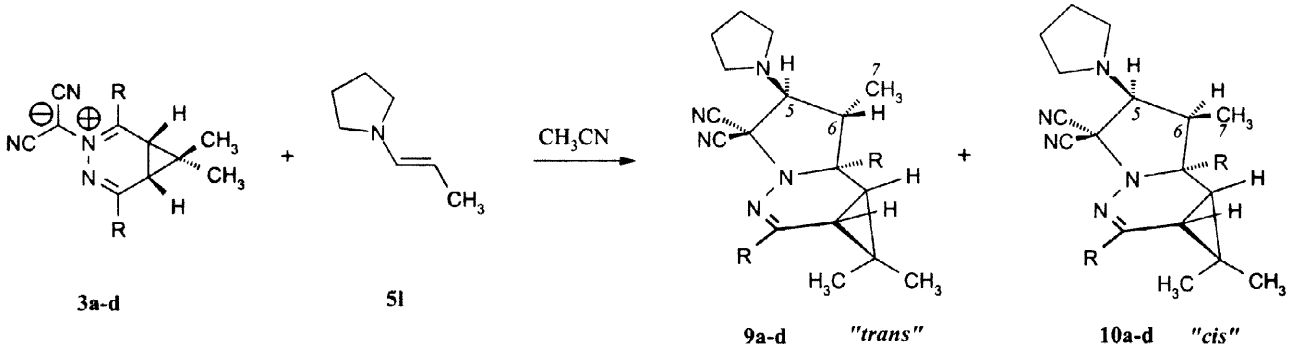
a) Yield and ratio from HPLC analysis (conditions see Table 11); b) Yield and ratio from $^1$H NMR: only signals of the two isomers, no quantitative internal standard.

The isomer ratio **7b** (trans-adduct) : **8b** (cis-adduct) depends only scarcely on the polarity of the solvent used ($CH_3CN$: 48 : 52, $CHCl_3$: 52 : 48, acetone: 56 : 44, dioxane: 65 : 35, toluene: 54 : 46). Acetonitrile is the top solvent with regard to the product yield obtainable; the yield **7b** + **8b** drops considerably passing to $CHCl_3$ (73%), acetone (43%), dioxane (80%), toluene (22%). For this reason all further cycloadditions were performed in acetonitrile.

Within the limit of error use of higher temperature (70°C; **7b** : **8b** = 46 : 54) and pressure (20°C, 7 kbar; **7b** : **8b** = 49 : 51) do not influence the isomer ratio. Also changing substituent R in the dipole **3** is negligible with regard to the isomer ratio (Scheme 2, Table 1).

All 1,3-dipolar cycloadditions presented in Table 1 are kinetically controlled reactions. Between 10-95 percentage conversion the isomer ratios do not change within the limit of error (HPLC). Even at 70°C the adducts **7** and **8** are stable in acetonitrile for 116 hours (**7b, 8b**) respectively 210 hours (**7a,d**, **8a,d**). In the presence of the highly reactive dipolarophile cyclooctyne [13] no trace of a trapping product of dipole **3b** could be detected by HPLC.

The approximate 1 : 1 - ratio for the diastereomeric cycloadducts formed when enamine **5k** is used as dipolarophile is also observed for the combination of AMY-I with the pyrrolidino enamine **5l** (Scheme 3, Table 2) and the morpholino enamine **5m** (Scheme 4, Table 3). All cycloadditions with **5m** are much slower compared to those of **5k** and **5l**.




**Scheme 3.** Nonstereospecific 1,3-dipolar cycloadditions of AMY-I **3a-d** with (*E*)-1-*N*-propenyl-pyrrolidine (**5l**).

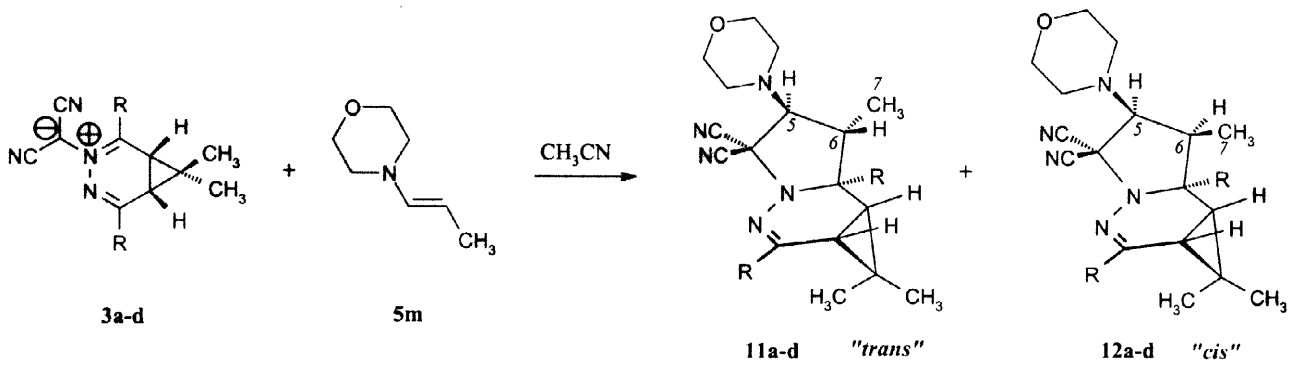
**Table 2.** Data for the reaction of AMY-I **3a-d** with (*E*)-1-*N*-propenyl-pyrrolidine (**5l**) in acetonitrile at ambient conditions.

| AMY-I [μmol] | | R | 5l [μmol] | t [h] | % 9 + 10 | 9 : 10 |
|---|---|---|---|---|---|---|
| **3a** | 444 | 4-$CH_3O$-$C_6H_4$ | 705 | 72 | 100 | 45 : 55 [a] |
| **3b** | 461 | 4-$CH_3$-$C_6H_4$ | 705 | 36 | 100 | 44 : 56 [a] |
| **3c** | 473 | $C_6H_5$ | 676 | 24 | 63 | 53 : 47 [b] |
| **3d** | 171 | 4-Cl-$C_6H_4$ | 214 | 10 | 89 | 54 : 46 [c] |

a) Yield and ratio from $^1$H NMR: only signals of the two isomers, no quantitative internal standard; b) Yield and ratio from $^1$H NMR: OMS as quantitative internal standard; c) Yield: isolated mixture of isomers, ratio from $^1$H NMR.

When we tried to prove the kinetic control for the systems of Scheme 4 (Table 3) quite unexpected but fully reproducable results were obtained which are not yet completely understood. As Figure 2 shows, only for the combination of **3a** with the *(E)*-morpholino enamine **5m** the adduct ratio trans : cis (**11a** : **12a**) is constant between 5 and 95 percent conversion. In contrast, using the dipoles **3b** and **3d**, the amount of cis-adduct **12b** and **12d** increases by about 20 percent as the reaction proceeds. Under the conditions of the reaction both cycloadducts **12b** and **12d** are stable.

The regiochemistry and stereochemistry could be proved beyond doubt by X-ray analysis for **7b** and **8b** [16]. The coupling constants of the tertiary protons H-5 and H-6 in **7b** (12.4 Hz) for the trans-adduct and **8b** (4.7 Hz) for the cis-adduct are in accordance with the Karplus rule. Table 4 and Table 5 summarize the corresponding coupling constants for all trans-adducts **7**, **9**, and **11** as well as for the cis-isomers **8**, **10**, and **12**. The constancy of the chemical shifts and the coupling constants within the whole series offers an excellent structure proof for all adducts compared.




**Scheme 4.** Nonstereospecific 1,3-dipolar cycloadditions of AMY-I **3a-d** with (*E*)-1-*N*-propenyl-morpholine (**5m**).

**Table 3.** Data for the reaction of AMY-I **3a-d** with (*E*)-1-*N*-propenyl-morpholine (**5m**) in acetonitrile at ambient conditions.

| AMY-I [μmol] | | R | **5m** [μmol] | t [d] | % **11** + **12** | **11** : **12** [a] |
|---|---|---|---|---|---|---|
| **3a** | 427 | 4-$CH_3O$-$C_6H_4$ | 500 | 6 | 100 | 45 : 55 |
| **3b** | 447 | 4-$CH_3$-$C_6H_4$ | 500 | 6 | 100 | 47 : 53 |
| **3c** | 575 | $C_6H_5$ | 722 | 20 | 100 | 45 : 55 |
| **3d** | 493 | 4-Cl-$C_6H_4$ | 644 | 6 | 100 | 46 : 54 |

a) Yield and ratio from $^1$H NMR: only signals of the two isomers, no quantitative internal standard.

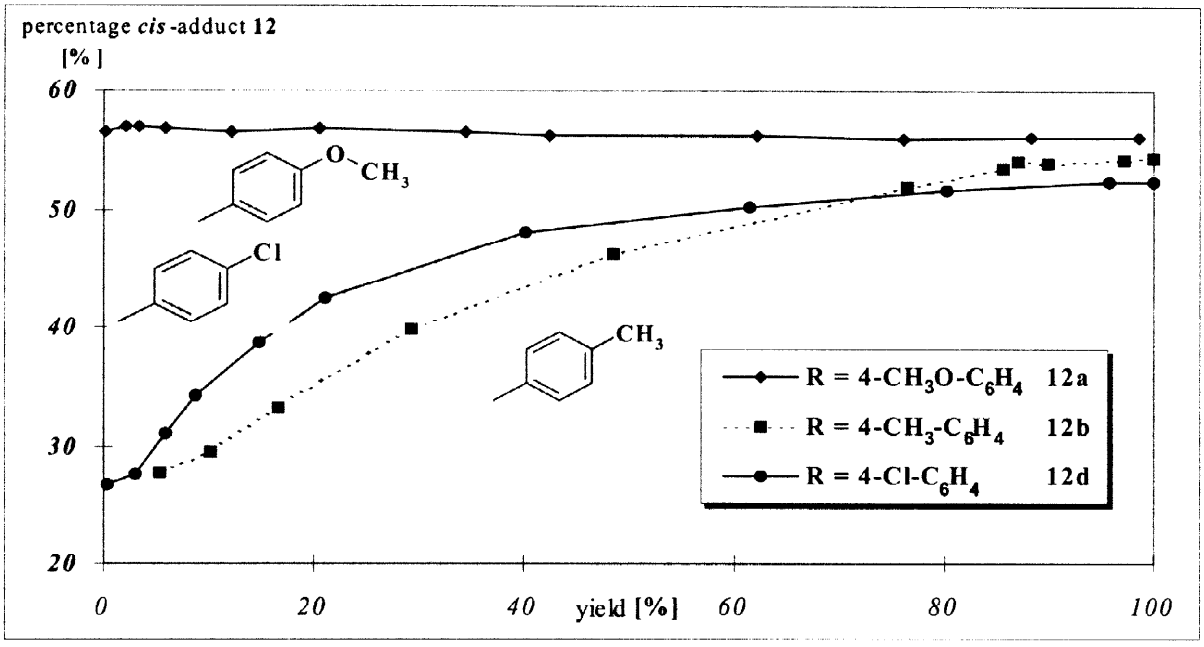



**Figure 2.** Percentage of the cis-adducts **12a**, **12b**, **12d** for the cycloadditions of dipoles **3a**, **3b**, **3d** with enamine **5m**.

All 1,3-dipoles AMY-II tested in our laboratory undergo nonstereospecific [3+2]-cycloadditions, too (Scheme 5-7; Table 6-8). In contrast to the cycloadducts of AMY-I described above, not all cycloadducts **13-18** are stable in solution, especially at higher temperature. Therefore, all yields and product ratios presented in Table 6-8 were obtained by quantitative NMR analysis with help of a tracer (see Experimental Section) or by HPLC analysis. Both cycloadducts **13b** and **14b**, the isomers with the dimethylamino group, could be separated by flash column chromatography and isolated as colourless crystalline substances.

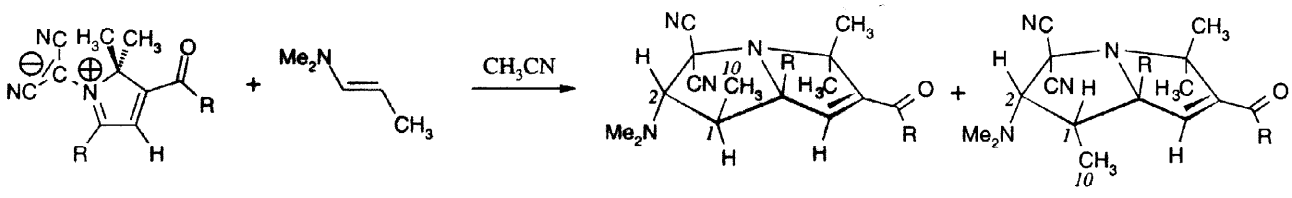
**Table 4.** $^1$H NMR data for the *trans*-cycloadducts of AMY-I **3a-d**: chemical shifts δ [ppm], coupling constants *J* [Hz], $CDCl_3$, TMS, 250 or 400 MHz.

| No. | R | δ (H-5) | δ (H-6) | δ (H-7) | $^3J$ (H-5,H-6) | $^3J$ (H-6,H-7) |
|---|---|---|---|---|---|---|
| **7a** | 4-$CH_3O$-$C_6H_4$ | 3.52 (d) | 2.63 (dq) | 0.96 (d) | 12.3 | 6.7 |
| **7b** | 4-$CH_3$-$C_6H_4$ | 3.54 (d) | 2.65 (dq) | 0.96 (d) | 12.4 | 6.7 |
| **7d** | 4-Cl-$C_6H_4$ | 3.48 (d) | 2.66 (dq) | 0.97 (d) | 12.4 | 6.7 |
| **9a** | 4-$CH_3O$-$C_6H_4$ | 3.76 (d) | 2.66 (dq) | 0.97 (d) | 12.2 | 6.6 |
| **9b** | 4-$CH_3$-$C_6H_4$ | 3.78 (d) | 2.67 (dq) | 0.97 (d) | 12.3 | 6.6 |
| **9c** | $C_6H_5$ | 3.79 (d) | 2.70 (dq) | 0.99 (d) | 12.3 | 6.5 |
| **9d** | 4-Cl-$C_6H_4$ | 3.72 (d) | 2.69 (dq) | 0.98 (d) | 12.3 | 6.6 |
| **11a** | 4-$CH_3O$-$C_6H_4$ | 3.45 (d) | 2.66 (dq) | 1.01 (d) | 12.4 | 6.6 |
| **11b** | 4-$CH_3$-$C_6H_4$ | 3.47 (d) | 2.67 (dq) | 1.01 (d) | 12.4 | 6.6 |
| **11c** | $C_6H_5$ | 3.48 (d) | 2.70 (dq) | 1.03 (d) | 12.4 | 6.7 |
| **11d** | 4-Cl-$C_6H_4$ | 3.41 (d) | 2.69 (dq) | 1.03 (d) | 12.5 | 6.6 |

**Table 5.** $^1$H NMR data for the *cis*-cycloadducts of AMY-I **3a-d**: chemical shifts δ [ppm], coupling constants *J* [Hz], $CDCl_3$, TMS, 250 or 400 MHz .

| No. | R | δ (H-5) | δ (H-6) | δ (H-7) | $^3J$ (H-5,H-6) | $^3J$ (H-6,H-7) |
|---|---|---|---|---|---|---|
| **8a** | 4-$CH_3O$-$C_6H_4$ | 2.94 (d) | 2.73 (dq) | 1.20 (d) | 4.8 | 6.9 |
| **8b** | 4-$CH_3$-$C_6H_4$ | 2.94 (d) | 2.75 (dq) | 1.20 (d) | 4.7 | 7.0 |
| **8d** | 4-Cl-$C_6H_4$ | 2.90 (d) | 2.74 (dq) | 1.21 (d) | 4.8 | 7.0 |
| **10a** | 4-$CH_3O$-$C_6H_4$ | 3.06 (d) | 2.69 (dq) | 1.21 (d) | 4.8 | 7.0 |
| **10b** | 4-$CH_3$-$C_6H_4$ | 3.06 (d) | 2.72 (dq) | 1.22 (d) | 4.7 | 7.0 |
| **10c** | $C_6H_5$ | 3.06 (d) | 2.75 (dq) | 1.24 (d) | 4.7 | 7.0 |
| **10d** | 4-Cl-$C_6H_4$ | 3.02 (d) | 2.70 (dq) | 1.23 (d) | 4.8 | 7.1 |
| **12a** | 4-$CH_3O$-$C_6H_4$ | 3.12 (d) | 2.77 (dq) | 1.18 (d) | 4.6 | 7.0 |
| **12b** | 4-$CH_3$-$C_6H_4$ | 3.12 (d) | 2.79 (dq) | 1.18 (d) | 4.7 | 6.9 |
| **12c** | $C_6H_5$ | 3.11 (d) | 2.83 (dq) | 1.21 (d) | 4.7 | 7.0 |
| **12d** | 4-Cl-$C_6H_4$ | 3.07 (d) | 2.78 (dq) | 1.19 (d) | 4.7 | 6.9 |

Furthermore could be isolated the trans-adducts **13a** and **17a-d** as stable compounds, whereas the corresponding cis-adducts **14a** and **18a-d** gave labile oils. By combination of X-ray analysis for **13b** [16] with the coupling constants for the tertiary protons H-1 and H-2 in **13b** and **14b** the regiochemistry and stereochemistry could be verified for both adducts unequivocally. In Table 9 and 10 the conclusive coupling constants H-1/H-2 are listed for all trans-adducts **13**, **15**, **17** and cis-adducts **14**, **16**, **18** as well. The Karplus rule is obeyed again, as shown by the X-ray analysis for adduct **13b** [16].



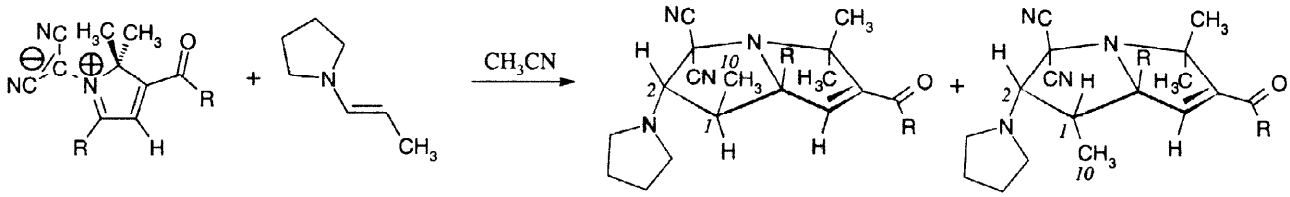
**4a,b** **5k** **13a,b** *"trans"* **14a,b** *"cis"*

**Scheme 5.** Nonstereospecific 1,3-dipolar cycloadditions of AMY-II **4a,b** with (*E*)-1-*N*,*N*-dimethylamino-1-propene (**5k**).

**Table 6.** Data for the reaction of AMY-II **4a,b** with (*E*)-1-*N*,*N*-dimethylamino-1-propen (**5k**) in acetonitrile at ambient conditions.

| AMY-I [µmol] | | **R** | **5k** [mmol] | **t** [h] | %yield **13** + **14** | **13** : **14** |
|---|---|---|---|---|---|---|
| **4a** | 783 | 4-$CH_3O$-$C_6H_4$ | 1.56 | 168 | 100 | 66 : 34 [a] |
| **4b** | 829 | 4-$CH_3$-$C_6H_4$ | 1.76 | 4.5 | 98 | 45 : 55 [b] |

a) Yield and ratio from $^1$H NMR: OMS as quantitative internal standard; b) Yield and ratio from HPLC analysis.



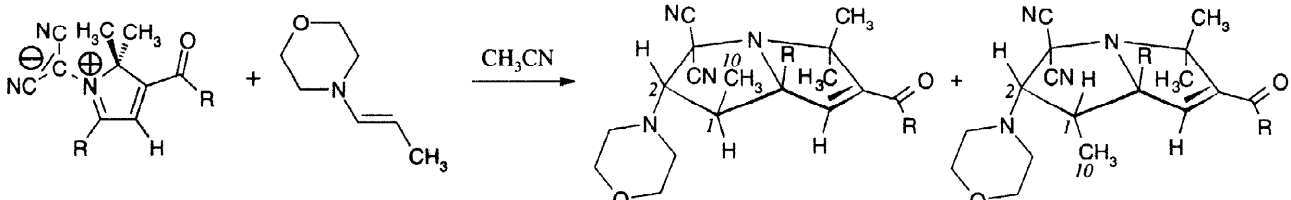
**4a-d** **5l** **15a-d** *"trans"* **16a-d** *"cis"*

**Scheme 6.** Nonstereospecific 1,3-dipolar cycloadditions of AMY-II **4a-d** with (*E*)-1-*N*-propenyl-pyrrolidine (**5l**).

**Table 7.** Data for the reaction of AMY-II **4a-d** with (*E*)-1-*N*-propenyl-pyrrolidine (**5l**) in acetonitrile at ambient conditions.

| AMY-I [µmol] | | **R** | **5l** [mmol] | **t** [h] | %yield **15** + **16** | **15** : **16** [a] |
|---|---|---|---|---|---|---|
| **4a** | 247 | 4-$CH_3O$-$C_6H_4$ | 427 | 288 | 71 | 78 : 22 |
| **4b** | 395 | 4-$CH_3$-$C_6H_4$ | 498 | 28 | 100 | 49 : 51 |
| **4c** | 318 | $C_6H_5$ | 498 | 51 | 83 | 50 : 50 |
| **4d** | 335 | 4-Cl-$C_6H_4$ | 498 | 24 | 100 | 44 : 56 |

a) Yield and ratio from $^1$H NMR: OMS as quantitative internal standard.



**4a-d** **5m** **17a-d** *"trans"* **18a-d** *"cis"*

**Scheme 7.** Nonstereospecific 1,3-dipolar cycloadditions of AMY-II **4a-d** with (*E*)-1-*N*-propenyl-morpholine (**5m**).

**Table 8.** Data for the reaction of AMY-II **4a-d** with (*E*)-1-*N*-propenyl-morpholine (**5m**) in acetonitrile at ambient conditions.

| AMY-I [µmol] | | **R** | **5m** [µmol] | **t** [d] | %yield **17** + **18** | **17** : **18** [a] |
|---|---|---|---|---|---|---|
| **4a** | 418 | 4-$CH_3O$-$C_6H_4$ | 500 | 28 | 95 | 67 : 33 |
| **4b** | 473 | 4-$CH_3$-$C_6H_4$ | 625 | 33 | 100 | 70 : 30 |
| **4c** | 345 | $C_6H_5$ | 460 | 39 | 96 | 62 : 38 |
| **4d** | 458 | 4-Cl-$C_6H_4$ | 601 | 2 | 87 | 69 : 31 |

a) Yield and ratio from $^1$H NMR: OMS as quantitative internal standard.

**Table 9.** $^1$H NMR data for the *trans*-cycloadducts of AMY-II **4a-d**: chemical shifts δ [ppm], coupling constants *J* [Hz], $CDCl_3$, TMS, 250 or 400 MHz .

| No. | R | δ (H-1) | δ (H-2) | δ (H-10) | $^3J$ (H-1,H-2) | $^3J$ (H-1,H-10) |
|---|---|---|---|---|---|---|
| **13a** | 4-$CH_3O$-$C_6H_4$ | 2.90 (dq) | 3.69 (d) | 0.61 (d) | 12.3 | 6.7 |
| **13b** | 4-$CH_3$-$C_6H_4$ | 2.90 (dq) | 3.69 (d) | 0.59 (d) | 12.3 | 6.7 |
| **15a** | 4-$CH_3O$-$C_6H_4$ | 2.95 (dq) | 3.92 (d) | 0.60 (d) | 12.2 | 6.7 |
| **15b** | 4-$CH_3$-$C_6H_4$ | 2.96 (dq) | 3.94 (d) | 0.59 (d) | 12.3 | 6.6 |
| **15c** | $C_6H_5$ | 2.99 (dq) | 3.95 (d) | 0.58 (d) | 12.1 | 6.7 |
| **15d** | 4-Cl-$C_6H_4$ | 2.96 (dq) | 3.89 (d) | 0.59 (d) | 12.2 | 6.7 |
| **17a** | 4-$CH_3O$-$C_6H_4$ | 2.93 (dq) | 3.60 (d) | 0.67 (d) | 12.3 | 6.7 |
| **17b** | 4-$CH_3$-$C_6H_4$ | 2.92 (dq) | 3.60 (d) | 0.65 (d) | 12.3 | 6.7 |
| **17c** | $C_6H_5$ | 2.96 (dq) | 3.63 (d) | 0.66 (d) | 12.3 | 6.7 |
| **17d** | 4-Cl-$C_6H_4$ | 2.94 (dq) | 3.57 (d) | 0.67 (d) | 12.3 | 6.7 |

**Table 10.** $^1$H NMR data for the *cis*-cycloadducts of AMY-II **4a-d**: chemical shifts δ [ppm], coupling constants *J* [Hz], $CDCl_3$, TMS, 250 or 400 MHz .

| No. | R | δ (H-1) | δ (H-2) | δ (H-10) | $^3J$ (H-1,H-2) | $^3J$ (H-1,H-10) |
|---|---|---|---|---|---|---|
| **14a** | 4-$CH_3O$-$C_6H_4$ | 2.55 (dq) | 3.27 (d) | 1.39 (d) | 5.5 | 7.5 |
| **14b** | 4-$CH_3$-$C_6H_4$ | 2.57 (dq) | 3.27 (d) | 1.39 (d) | 5.4 | 7.3 |
| **16a** | 4-$CH_3O$-$C_6H_4$ | 2.51 (dq) | 3.37 (d) | 1.39 (d) | 5.5 | 7.5 |
| **16b** | 4-$CH_3$-$C_6H_4$ | 2.53 (dq) | 3.38 (d) | 1.40 (d) | 5.5 | 7.1 |
| **16c** | $C_6H_5$ | 2.56 (dq) | 3.37 (d) | 1.41 (d) | 5.5 | 7.3 |
| **16d** | 4-Cl-$C_6H_4$ | 2.50 (dq) | 3.32 (d) | 1.39 (d) | 5.5 | 7.3 |
| **18a** | 4-$CH_3O$-$C_6H_4$ | 2.60 (dq) | 3.45 (d) | 1.36 (d) | 5.5 | 7.3 |
| **18b** | 4-$CH_3$-$C_6H_4$ | 2.61 (dq) | 3.44 (d) | 1.36 (d) | 5.5 | 7.3 |
| **18c** | $C_6H_5$ | 2.64 (dq) | 3.44 (d) | 1.38 (d) | 5.6 | 7.2 |
| **18d** | 4-Cl-$C_6H_4$ | ---[a)] | 3.66 (d) | 1.53 (d) | 5.6 | 7.5 |

a) H-1 signal covered by signals of the morpholino group

The endo-configuration for the dimethylamino group is verified for **13b** by X-ray analysis [16] and is assumed for all cis-adducts **14**, **16**, **18** by analogy to the reaction of AMY-I (vide supra).

HPLC investigations showed for the combination of 1,3-dipole **4b** + enamine **5k** at 20°C that this cycloaddition is kinetically controlled, too (up to 98 % conversion). At longer reaction times and higher temperature the isomerization of the cis-adduct (**14**, **16**, **18**) to the trans adduct (**13**, **15**, **17**) occurs slowly. In acetonitrile at 50°C the splitting of cycloadducts **13b** and **14b** occurs in the presence of a large excess of the highly reactive dipolarophile cyclooctyne in a

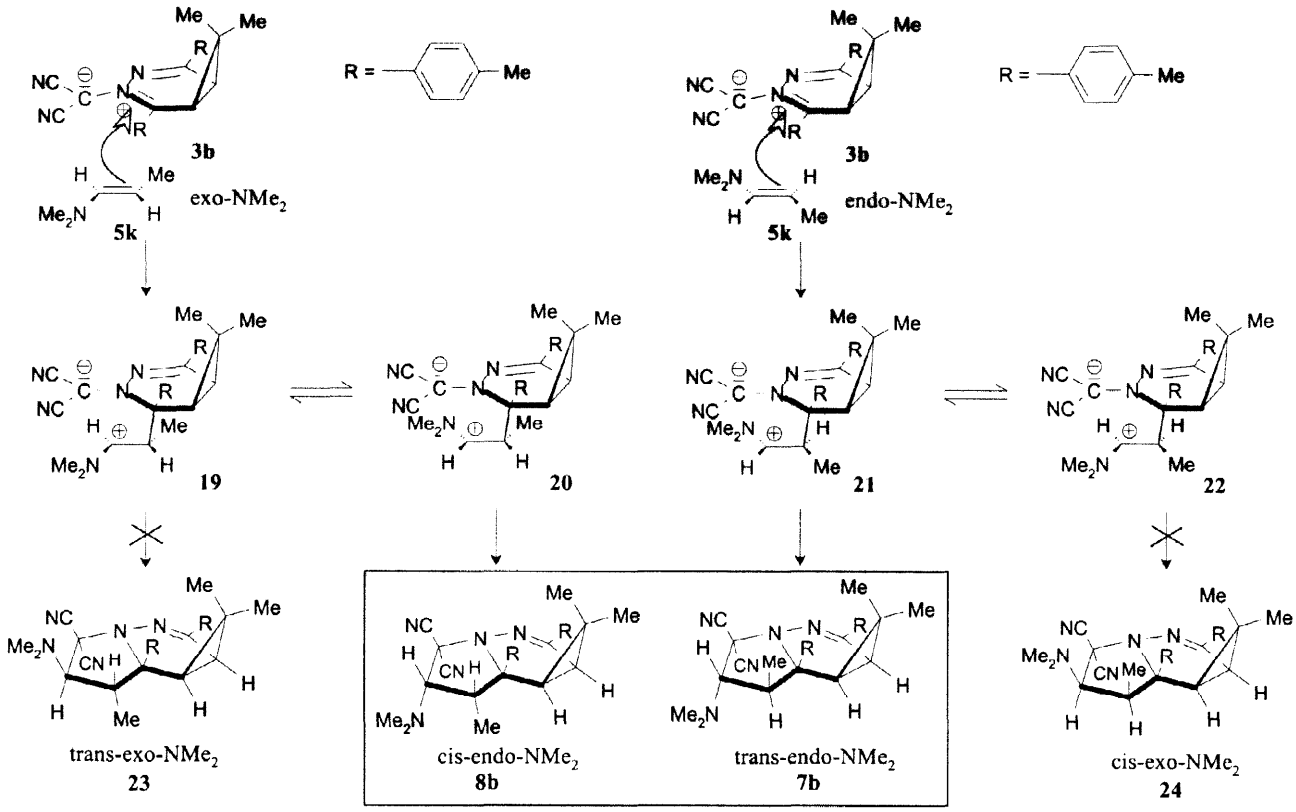
clean first order reaction with rate constants of $1.06 \cdot 10^{-6}$ $s^{-1}$ (for trans-adduct **13b**) and $4.21 \cdot 10^{-5}$ $s^{-1}$ (for cis-adduct **14b**).

Finally, HPLC analysis showed that the trans (**13b**) : cis (**14b**) - ratio depends only little on the solvent used, but due to the reversibility of the cycloaddition the isomer ratios obtained are not too accurate (20°C, $CH_3CN$: 45 : 55, $CH_2Cl_2$: 25 : 75, $CH_3CO_2C_2H_5$: 23 : 77, dioxane: 16 : 84, toluene: 10 : 90). Again product yields are the highest in acetonitrile and the lowest in toluene (40-50%).

## Discussion

In analogy to the excellent mechanistic studies obtained in Huisgen's group for the electron-rich thiocarbonyl ylides as dipoles when combined with electron-poor dipolarophiles dicyanofumarate and dicyanomaleate [1,3,7,8,9] we also tend to explain the nonstereospecific cycloadditions of the electron-poor azomethine ylides **3** and **4** with *(E)*-enamines **5** by a two-step reaction via zwitterionic intermediates. Scheme 8 offers a reaction network for the cycloaddition of AMY-I **3b** and **5k**, pars pro toto. This mechanistic approach is also applicable for the reaction of dipoles **4** (AMY-II) in principle. Some aspects of this mechanistic scheme are worthwhile to be discussed briefly.

1. In all cases studied, the 1,3-dipolar cycloaddition of the thermodynamically more stable *(E)*-enamines **5** yields *two* diastereomeric cycloadducts, dipole **3b** for instance leading to the trans-endo-$NMe_2$ adduct **7b** and the cis-endo-$NMe_2$ adduct **8b** in almost equal amounts. An in situ isomerization of *(E)*-enamine **5** to the *(Z)*-isomer **6** before the cycloaddition step can be excluded [15]. For the cycloadducts of AMY-II (**4**) experimental results prove, that the trans-adducts are thermodynamically more stable than the corresponding cis-adducts.
2. Any attempt for a mechanistic explanation must be in accord with the experimental result, that the $NR_2$ group always appears in the endo-position of the cycloadduct.
3. Scheme 8 shows a way to rationalize the experimental findings. Enamine **5k** approaches the dipole **3b** from the less hindered side in two modes, either an endo-orientation of the $NMe_2$-group or an exo-orientation of the $NMe_2$ group forming the two dipoles **21** and **19** with an excellent stabilization of the positive and negative charge.
4. A free rotation of the CC bond in the dipoles **21** and **19** should be possible and compete with the ring closure to form the cycloadducts. Thus, four adducts **23**, **8b**, **7b**, and **24** should be possible in principle. Experimentally we could not detect any cycloadducts besides **7b** and **8b** by HPLC in measurable amounts.




**Scheme 8.** Mechanistic approach for the nonstereospecific 1,3-dipolar cycloaddition of AMY-I **3b** with (*E*)-enamine **5k**.

5. The formation of trans-adduct **7b** could also be explained without postulating a zwitterionic intermediate **21**. A competing concerted stereospecific cycloaddition of enamine **5k** to 1,3-dipole **3b** would lead directly to the trans-adduct **7b**, when the $NMe_2$ group approaches the dipole in an endo-orientation. Non covalent interactions between the lone pair of the amine function and the π-system of the dipole could be responsible for this result [17].
6. The isolation of the cis-adduct **8b** makes an intermediate zwitterion **19** compelling. But there is no convincing argument and explanation at hand why dipole **19** only isomerizes to **20** before ring-closure to **8b** and does not directly close the five-membered ring to form adduct **23**.
7. All attempts to introduce enamine **5n** or **5o** into 1,3-dipolar cycloadditions with AMY-I and AMY-II failed because of the extreme low reactivity of the 2π-components. In dioxane at 20°C the aziridino enamine **5o** turned out to be less reactive by a factor of approximately $10^4$ in rate constants compared with enamine **5k** using 3,6-diphenyl-1,2,4,5-tetrazine as diene component. In comparison with the electron-poor 3,6-bis(methoxycarbonyl)-1,2,4,5-tetrazine enamine **5n** was less reactive by almost a factor of $10^8$ than 1-*N*,*N*-dimethylaminocyclohexene [18].

## CONCLUSION

The electron-poor azomethine ylides AMY-I **3** and AMY-II **4** combine with *(E)*-enamine **5** in a nonstereospecific 1,3-dipolar cycloaddition to form *two* diastereomeric cycloadducts, both bearing the dialkylamino group in endo-arrangement in the cycloadduct. These 1,3-dipolar cycloadditions are the electronic counterpart to the combination of the electron-rich thiocarbonyl ylides with electron-poor dipolarophiles studied by Huisgen [3,7,8,9], which also occur in a nonstereospecific manner.

## EXPERIMENTAL SECTION

*General:* IR spectra were recorded with a Beckmann Acculab I. - NMR spectra were obtained with a Bruker AC250 and ARX400 (250 MHz / 400 MHz for $^{1}H$ and 63 MHz / 101 MHz for $^{13}C$). The degree of substitution of the C atoms was determined by the DEPT-135/90/45 methods. All NMR spectra were taken in $CDCl_3$ with TMS respectively octamethylsiloxane (OMS) for quantitative analyses as an internal standard. - Mass spectra were recorded either with an ionizing voltage of 70 eV by electron impact with a Varian CH90 instrument or by field desorption with a Varian 311A instrument. - Melting points were determined with a Büchi melting point apparatus and are uncorrected. - Elemental analysis were performed in the microanalytical laboratory of the University of Regensburg. - For analytical thin layer chromatography (tlc) precoated plastic sheets (POLYGRAM SIL G/UV254, Macherey-Nagel) were used. - Silica gel 60 (particle size 0.040 - 0.063 mm, Merck) was used for flash column chromatography (fcc). The preparative high pressure liquid chromatography (HPLC) was performed with an Orlita MS 30/10 pump, 8300 UVICORD II detector, and a Polygosil column ($SiO_2$, 7 µm). - The HPLC-analysis were carried out with a Bromma LKB 2150 pump, a Spectra 100 UV-detector (Thermo Separation Products), recorded with a Spectra-Physics Data Jet Integrator and after data transfer via Labnet treated with the program „Winner on Windows" (Thermo Separation Products). - Cycloaddition reactions were carried out under an atmosphere of argon in acetonitrile dried according to standard procedures.

All azomethinylides AMY-I **3**, AMY-II **4** [14], and enamines **5/6** [15] were prepared according to literature procedures. Spectroscopic data of Tables 4,5,9, and 10 are not repeated anymore below.

*General procedure for the cycloaddition of AMY-I* **3a-d** *and AMY-II* **4a-d** *with enamines* **5k-m** *:* To a solution of **3a-d** (0.2 - 0.6 mmol) respectively **4a-d** (0.2 - 0.8 mmol) in dry acetonitrile was added the dipolarophile (0.2 - 1.8 mmol) under an atmosphere of argon at ambient temperature and allowed to react until no azomethine ylide could be detected anymore by tlc. After removal of the solvent in vacuo, the crude reaction products were analyzed by NMR and then worked up as described for the different reactions.

*r-5-Dimethylamino-2,c-6a-bis-(4-methoxy-phenyl)-1,1,t-6-trimethyl-1,1a,5,6,6a,6b-hexa-hydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**7a**) *and r-5-Dimethylamino-2,t-6a-bis-(4-methoxy-phenyl)-1,1,c-6-trimethyl-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopropa-[e]indene-4,4-dicarbonitrile* (**8a**)*:* Following the *general procedure* **3a** (119.5 mg, 300 µmol) and **5k** (31.0 mg, 364 µmol) in 25 ml acetonitrile yielded after fcc ($CH_2Cl_2$ : ethyl acetate 40 : 1) and recrystallization from $CH_2Cl_2$/hexane 36.1 mg (74.6 µmol, 25 %) of **7a**, colourless crystals, m.p. 192-193°C (decomp.). - IR

(KBr): $\tilde{\nu}$ = 3010, 2980, 2950, 2930, 2840, 1605, 1505, 1455, 1445, 1295, 1170, 1025, 830 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 400 MHz): δ = 0.11 (s, 3 H), 1.32 (s, 3 H), 1.72 (d, 1 H, $^3J$ = 8.2 Hz), 1.77 (d, 1 H, $^3J$ = 8.2 Hz), 2.70 (s, 6 H), 3.81 (s, 3 H), 3.83 (s, 3 H), 6.85-6.94 (m, 4 H), 7.29-7.35 (m, 2 H), 7.71-7.77 (m, 2 H) ppm. - $^{13}C$ NMR ($CDCl_3$, 63 MHz): δ = 13.36 (1 C), 16.70 (1 C), 20.26 (1 C), 23.68 (1 C), 26.99 (1 C), 27.07 (1 C), 41.14 (2 C), 46.60 (1 C), 55.26 (1 C), 55.36 (1 C), 60.29 (1 C), 62.22 (1 C), 75.32 (1 C), 113.01 (2 C), 113.43 (1 C), 113.88 (2 C), 116.40 (1 C), 127.14 (2 C), 128.55 (2 C), 130.17 (1 C), 134.50 (1 C), 149.00 (1 C), 158.78 (1 C), 160.66 (1 C) ppm. - EI MS (70 eV); m/z (%): 483 (2) [$M^+$], 398 (100) [ylid$^+$], 265 (25) [ylid$^+$ - $CH_3O$-$C_6H_4CN$], 250 (4) [ylid$^+$ - $CH_3O$-$C_6H_4CN$ - $CH_3$], 201 (8), 187 (14), 133 (5) [$CH_3O$-$C_6H_4CN^+$], 85 (14) [$C_3H_5N(CH_3)_2^+$], 42 (5) [$C_3H_5N(CH_3)_2^+$ - $N(CH_3)_2$ + H]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ (ε) = 226 (20800), 254 (11000), 293 (14600) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{29}H_{33}N_5O_2$ (483.6): calcd. C 72.03, H 6.88, N 14.48; found C 71.89, H 7.01, N 14.44. Furthermore could be obtained 50.1 mg (104 μmol, 35 %) of **8a**, colourless crystals, m.p. 208-209 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3050, 2980, 2940, 2860, 2820, 2780, 1600, 1500, 1450, 1290, 1240, 1160, 1025, 1010, 830, 810 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 400 MHz): δ = 0.35 (s, 3 H), 1.17 (s, 3 H), 2.33 (s, 6 H), 3.828 (s, 3 H), 3.832 (s, 3 H), 6.83-6.97 (m, 4 H), 7.22 (m, 1 H), 7.62 (m, 1 H), 7.72-7.78 (m, 2H) ppm. - $^{13}C$ NMR ($CDCl_3$, 63 MHz, DEPT 45): δ = 9.20 (1 C, +), 16.74 (1 C, +), 21.14 (1 C, +), 24.11 (1 C, 0), 26.67 (1 C, +), 27.26 (1 C, +), 44.86 (2 C, +), 50.45 (1 C, +), 55.29 (1 C, +), 55.39 (1 C, +), 64.16 (1 C, 0), 64.64 (1 C, 0), 74.91 (1 C, +), 111.69 (1 C, 0), 111.79 (1 C, +), 113.95 (2 C, +), 115.41 (1 C, +), 116.58 (1 C, 0), 125.46 (1 C, +), 127.07 (2 C, +), 127.87 (1 C, +), 130.58 (1 C, 0), 138.10 (1 C, 0), 145.04 (1 C, 0), 158.58 (1 C, 0), 160.45 (1 C, 0) ppm. - EI MS (70 eV); m/z (%): 483 (1) [$M^+$], 398 (100) [ylid$^+$], 265 (23) [ylid$^+$ - $CH_3O$-$C_6H_4CN$], 250 (5) [ylid$^+$ - $CH_3O$-$C_6H_4CN$ - $CH_3$], 201 (10), 187 (17), 133 (7) [$CH_3O$-$C_6H_4CN^+$], 85 (16) [$C_3H_5N(CH_3)_2^+$], 42 (7) [$C_3H_5N(CH_3)_2^+$ - $N(CH_3)_2$ + H]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ (ε) = 227 (18500), 253 (10100), 285 (20400) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{29}H_{33}N_5O_2$ (483.6): calcd. C 72.03, H 6.88, N 14.48; found C 71.63, H 6.86, N 14.46.

*r-5-Dimethylamino-1,1,t-6-trimethyl-2,c-6a-di-p-tolyl-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**7b**) *and r-5-Dimethylamino-1,1,c-6-trimethyl-2,t-6a-di-p-tolyl)-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**8b**)*:* Following the *general procedure* **3b** (105 mg, 287 μmol) and **5k** (29.7 mg, 349 μmol) in 25 ml acetonitrile yielded after fcc ($CH_2Cl_2$) and recrystallization from $CH_2Cl_2$/hexane 51.3 mg (113 μmol, 40 %) of **7b**, colourless crystals, m.p. 208-209°C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3040, 2990, 2960, 2930, 2820, 1450, 1130, 1110, 1070, 1010, 815 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 250 MHz): δ = 0.08 (s, 3 H), 1.31 (s, 3 H), 1.73 (d, 1 H, $^3J$ = 8.3 Hz), 1.78 (d, 1 H, $^3J$ = 8.3 Hz), 2.34 (s, 3 H), 2.36 (s, 3 H), 2.69 (s, 6 H), 7.09-7.24 (m, 4 H), 7.27-7.31 (m, 2 H), 7.67-7.70 (m, 2 H) ppm. - $^{13}C$ NMR ($CDCl_3$, 63 MHz): δ = 13.40 (1 C), 16.76 (1 C), 20.24 (1 C), 20.92 (1 C), 21.32 (1 C), 23.69 (1 C), 26.92 (1 C), 27.03 (1 C), 41.11 (2 C), 46.49 (1 C), 60.32 (1 C), 62.55 (1 C), 75.33 (1 C), 113.41 (1 C), 116.36 (1 C), 125.67 (2 C), 127.42 (2 C), 128.33 (2 C), 129.13 (2 C), 134.64 (1 C), 136.92 (1 C), 139.19 (1 C), 139.44 (1 C), 149.05 (1 C) ppm. - EI MS (70 eV); m/z (%): 452 (3) [$M^+$], 367 (28), 366 (100) [ylide$^+$], 365 (14), 250 (12), 249 (63) [ylide$^+$ - $C_7H_7CN$], 234 (10) [ylide$^+$ - $C_7H_7CN$ - $CH_3$], 185 (15) [ylide$^+$ - $C_7H_7CN$ - $C(CN)_2$], 171 (10), 85 (25) [$C_3H_5N(CH_3)_2^+$], 84 (12). - UV/VIS (1,4-dioxane): $\lambda_{max}$ (ε) = 220 (27300), 295 (14500) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{29}H_{33}N_5$ (451.6): calcd. C 77.13, H 7.37, N 15.51; found C 76.89, H 7.41, N 15.41. Furthermore could be obtained 59.4 mg (131 μmol, 46 %) of **8b**, colourless crystals, m.p. 215-216 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3010, 2970, 2940, 2890, 2850, 2800, 1510, 1455, 1120, 1020, 815 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 250 MHz): δ = 0.32 (s, 3 H), 1.17 (s, 3 H), 1.70 (d, 1 H, $^3J$ = 8.2 Hz), 1.78 (d, 1 H, $^3J$ = 8.2 Hz), 2.32 (s, 6 H), 2.357 (s, 3 H), 2.364 (s, 3 H),7.11-7.36 (m, 5 H), 7.57-7.60 (m, 1 H), 7.69-7.72 (m, 2 H) ppm. - $^{13}C$ NMR ($CDCl_3$, 63 MHz): δ = 9.16 (1 C), 16.76 (1 C), 20.95 (1 C), 21.07 (1 C), 21.28 (1 C), 24.08 (1 C, 0), 26.54 (1 C), 27.21 (1 C), 44.81 (2 C), 50.39 (1 C, +), 64.08 (1 C, 0), 64.99 (1 C), 74.81 (1 C), 111.76 (1 C, 0), 116.52 (1 C, 0), 124.34 (1 C), 125.61 (2 C), 126.61 (1 C),

128.19 (1 C), 129.15 (2 C), 129.53 (1 C), 135.00 (1 C), 136.71 (1 C), 138.88 (1 C), 143.09 (1 C), 145.20 (1 C) ppm. - EI MS (70 eV); m/z (%): 452 (3) [$M^+$], 367 (28), 366 (100) [ylide$^+$], 365 (13), 250 (12), 249 (60) [ylide$^+$ - $C_7H_7CN$], 234 (10) [ylide$^+$ - $C_7H_7CN$ - $CH_3$], 185 (14) [ylide$^+$ - $C_7H_7CN$ - $C(CN)_2$], 171 (10), 85 (24) [$C_3H_5N(CH_3)_2^+$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 222 (22200), 290 (15500) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{29}H_{33}N_5$ (451.6): calcd. C 77.13, H 7.37, N 15.51; found C 76.92, H 7.49, N 15.34.

*r-5-Dimethylamino-2,c-6a-bis-(4-chloro-phenyl)-1,1,t-6-trimethyl-1,1a,5,6,6a,6b-hexa-hydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**7d**) *and r-5-Dimethylamino-2,t-6a-bis-(4-chloro-phenyl)-1,1,c-6-trimethyl-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopropa-[e]indene-4,4-dicarbonitrile* (**8d**)*:* Following the *general procedure* **3d** (175.0 mg, 430 µmol) and **5k** (45.9 mg, 539 µmol) in 25 ml acetonitrile yielded after fcc (petroleum ether 40/60 : $CH_2Cl_2$ from 1 : 2 to 0 : 1) and recrystallization from $CH_2Cl_2$/hexane 58.0 mg (118 µmol, 27 %) of **7d**, colourless crystals, m.p. 220-222 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3070, 3040, 3010, 2960, 2930, 2880, 2860, 2820, 2780, 2760, 1590, 1470, 1440, 1120, 1105, 1070, 1055, 995, 835, 815, 805 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 250 MHz): $\delta$ = 0.09 (s, 3 H), 1.32 (s, 3 H), 1.76 (d, 1 H, $^3J$ = 8.4 Hz), 1.78 (d, 1 H, $^3J$ = 8.4 Hz), 2.70 (s, 6 H), 7.33-7.39 (m, 6 H), 7.70-7.75 (m, 2 H) ppm. - $^{13}C$ NMR ($CDCl_3$, 63 MHz, DEPT 135/90): $\delta$ = 13.34 (1 C, +/0), 16.85 (1 C, +/0), 19.99 (1 C, +/+), 23.85 (1 C, 0/0), 26.60 (1 C, +/+), 26.89 (1 C, +/0), 41.00 (2 C, +/0), 46.35 (1 C, +/+), 59.88 (1 C, 0/0), 62.36 (1 C, 0/0), 75.28 (1 C, +/+), 113.03 (1 C, 0/0), 115.94 (1 C, 0/0), 126.90 (2 C, +/+), 127.93 (2 C, +/+), 128.68 (2 C, +/+), 128.69 (2 C, +/+), 133.42 (1 C, 0/0), 135.32 (1 C, 0/0), 135.35 (1 C, 0/0), 140.75 (1 C, 0/0), 148.12 (1 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 491 (1) [$M^+$], 406 (17) [ylid$^+$], 269 (20) [ylid$^+$ - Cl-$C_6H_4CN$], 254 (2) [ylid$^+$ - Cl-$C_6H_4CN$ - $CH_3$], 242 (3) [ylid$^+$ - Cl-$C_6H_4CN$ - HCN], 205 (4), 137 (7) [Cl-$C_6H_4CN^+$], 85 (100) [$C_3H_5N(CH_3)_2^+$], 70 (14) [$C_3H_5N(CH_3)_2^+$ - $CH_3$], 42 (11) [$C_3H_5N(CH_3)_2^+$ - $N(CH_3)_2$ +H]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 223 (6400), 297 (3400) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{27}H_{27}N_5Cl_2$ (492.5): calcd. C 65.85, H 5.53, N 14.22; found C 65.84, H 5.69, N 14.09. Furthermore could be obtained 47.0 mg (95.4 µmol, 22 %) of **8d**, colourless crystals, m.p. 234-235 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3080, 3050, 2980, 2950, 2920, 2850, 2820, 2780, 1595, 1480, 1450, 1445, 1260, 1105, 1080, 1000, 830, 810, 725 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 250 MHz): $\delta$ = 0.32 (s, 3 H), 1.19 (s, 3 H), 1.72 (d, 1 H, $^3J$ = 8.1 Hz), 1.79 (d, 1 H, $^3J$ = 8.1 Hz), 2.34 (s, 6 H), 7.27-7.29 (m, 1 H), 7.33-7.42 (m, 4 H), 7.62-7.66 (m, 1 H), 7.71-7.75 (m, 2H) ppm. - $^{13}C$ NMR ($CDCl_3$, 63 MHz, DEPT 135/90): $\delta$ = 9.12 (1 C, +/0), 16.78 (1 C, +/0), 20.71 (1 C, +/+), 24.24 (1 C, 0/0), 26.15 (1 C, +/+), 27.08 (1 C, +/0), 44.78 (2 C, +/0), 50.32 (1 C, +/+), 63.78 (1 C, 0/0), 64.83 (1 C, 0/0), 74.55 (1 C, +/+), 111.43 (1 C, 0/0), 116.09 (1 C, 0/0), 125.79 (1 C, +/+), 126.86 (2 C, +/+), 127.84 (1 C, +/+), 128.00 (1 C, +/+), 128.69 (2 C, +/+), 129.13 (1 C, +/+), 133.10 (1 C, 0/0), 135.03 (1 C, 0/0), 135.72 (1 C, 0/0), 144.36 (1 C, 0/0), 144.40 (1 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 491 (1) [$M^+$], 406 (17) [ylid$^+$], 343 (4), 269 (24) [ylid$^+$ - Cl-$C_6H_4CN$], 254 (2) [ylid$^+$ - Cl-$C_6H_4CN$ - $CH_3$], 243 (3) [ylid$^+$ - Cl-$C_6H_4CN$ - HCN], 205 (5), 138 (4) [Cl-$C_6H_4CN^+$], 85 (100) [$C_3H_5N(CH_3)_2^+$], 70 (13) [$C_3H_5N(CH_3)_2^+$ - $CH_3$], 42 (7) [$C_3H_5N(CH_3)_2^+$ - $N(CH_3)_2$ + H]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 224 (21500), 293 (14700) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{27}H_{27}N_5Cl_2$ (492.5): calcd. C 65.85, H 5.53, N 14.22; found C 65.66, H 5.58, N 14.16.

*2,c-6a-Bis-(4-methoxy-phenyl)-1,1,t-6-trimethyl-r-5-pyrrolidin-1-yl-1,1a,5,6,6a,6b-hexa-hydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**9a**) *and 2,t-6a-Bis-(4-methoxy-phenyl)-1,1,c-6-trimethyl-r-5-pyrrolidin-1-yl-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopro-pa[e]indene-4,4-dicarbonitrile* (**10a**)*:* Following the *general procedure* **3a** (177.0 mg, 444 µmol) and **5l** (78.4 mg, 705 µmol) in 20 ml acetonitrile yielded after preparative HPLC (hexane : $CH_2Cl_2$ : methanol 80 : 20 : 0.17) and recrystallization from acetonitrile 72.0 mg (141 µmol, 32 %) of **9a**, colourless crystals, m.p. 224 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3030, 2960, 2930, 2870, 2830, 1600, 1500, 1445, 1360, 1290, 1245, 1165, 1115, 1100, 1025, 835, 820 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 0.12 (s, 3 H), 1.32 (s, 3 H),

1.71 (d, 1 H, $^3J$ = 8.4 Hz), 1.76 (d, 1 H, $^3J$ = 8.4 Hz), 1.76-1.83 (m, 4 H), 3.03-3.11 (m, 2 H), 3.13-3.21 (m, 2 H), 3.81 (s, 3 H), 3.83 (s, 3 H), 6.86-6.94 (m, 4 H), 7.30-7.36 (m, 2 H), 7.71-7.77 (m, 2 H) ppm. - $^{13}$C NMR ($CDCl_3$, 101 MHz, DEPT 135/90): δ = 13.75 (1 C, +/0), 16.70 (1 C, +/0), 20.12 (1 C, +/+), 23.63 (1 C, 0/0), 24.78 (2 C, -/0), 26.81 (1 C, +/+), 27.01 (1 C, +/0), 47.13 (1 C, +/+), 48.91 (2 C, -/0), 55.20 (1 C, +/0), 55.31 (1 C, +/0), 61.65 (1 C, 0/0), 62.53 (1 C, 0/0), 72.22 (1 C, +/+), 112.85 (2 C, +/+), 113.40 (1 C, 0/0), 113.76 (2 C, +/+), 116.58 (1 C, 0/0), 127.06 (2 C, +/+), 128.48 (2 C, +/+), 130.08 (1 C, 0/0), 134.41 (1 C, 0/0), 148.62 (1 C, 0/0), 158.57 (1 C, 0/0), 160.47 (1 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 510 (2) [$M^+$], 483 (1) [$M^+$- HCN], 425 (1), 413 (2), 398 (100) [ylid$^+$], 370 (8), 320 (17), 305 (13), 292 (4), 279 (7), 265 (45) [ylid$^+$ - $CH_3O$-$C_6H_4CN$], 250 (9), 238 (15), 225 (21), 200 (17), 187 (13), 172 (10), 159 (8), 133 (28) [$CH_3O$-$C_6H_4CN^+$], 111 (51) [$C_3H_5NC_4H_8^+$], 96 (45) [$C_3H_5NC_4H_8^+$ - $CH_3$], 90 (11), 82 (13), 68 (19), 55 (22) [$C_3H_5NC_4H_8^+$ - $C_4H_8$], 41 (32) [$C_3H_5NC_4H_8^+$ - $NC_4H_8$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ (ε) = 226 (7800), 254 (4200), 292 (5600) nm (l·mol$^{-1}$·cm$^{-1}$). - $C_{29}H_{33}N_5O_2$ (509.7): calcd. C 73.05, H 6.92, N 13.74; found C 72.97, H 6.91, N 13.66. Furthermore could be obtained 47.0 mg (92.2 μmol, 21 %) of **10a**, colourless crystals, m.p. 227 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3040, 2970, 2950, 2930 2870, 2830, 2800, 1600, 1500, 1240, 1165, 1100, 1025, 835, 820 cm$^{-1}$. - $^1$H NMR ($CDCl_3$, 400 MHz): δ = 0.34 (s, 3 H), 1.17 (s, 3 H), 1.69 (d, 1 H, $^3J$ = 8.2 Hz), 1.77 (d, 1 H, $^3J$ = 8.2 Hz), 1.77-1.85 (m, 4 H), 2.54-2.69 (m, 4 H), 3.82 (s, 3 H), 3.83 (s, 3 H), 6.83-6.86 (m, 1 H), 6.91-6.96 (m, 3 H), 7.20-7.24 (m, 1 H), 7.59-7.63 (m, 1 H), 7.73-7.77 (m, 2H) ppm. - $^{13}$C NMR ($CDCl_3$, 101 MHz, DEPT 135/90): δ = 9.61 (1 C, +/0), 16.70 (1 C, +/0), 20.95 (1 C, +/+), 23.26 (2 C, -/0), 23.98 (1 C, 0/0), 26.41 (1 C, +/+), 27.19 (1 C, +/0), 51.27 (1 C, +/+), 53.04 (2 C, -/0), 55.22 (1 C, +/0), 55.33 (1 C, +/0), 64.43 (1 C, 0/0), 64.59 (1 C, 0/0), 73.47 (1 C, +/+), 111.47 (1 C, +/+), 111.82 (1 C, 0/0), 113.82 (2 C, +/+), 115.26 (1 C, +/+), 116.40 (1 C, 0/0), 125.43 (1 C, +/+), 126.98 (2 C, +/+), 127.73 (1 C, +/+), 130.51 (1 C, 0/0), 138.18 (1 C, 0/0), 144.94 (1 C, 0/0), 158.34 (1 C, 0/0), 160.27 (1 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 510 (2) [$M^+$], 483 (5) [$M^+$ - HCN], 431 (6), 398 (100) [ylid$^+$], 383 (10), 370 (15), 355 (11), 334 (7) [ylid$^+$ -], 320 (23), 305 (27), 292 (5), 279 (8), 265 (45) [ylid$^+$ - $CH_3O$-$C_6H_4CN$], 250 (10) [ylid$^+$ - $CH_3O$-$C_6H_4CN$ - $CH_3$], 238 (22), 225 (14), 200 (21), 187 (28), 172 (13), 159 (11), 133 (42), 121 (10), 111 (79) [$C_3H_5NC_4H_8^+$], 110 (88) [$C_3H_5NC_4H_8^+$ - H], 96 (85), 90 (18) , 82 (25), 68 (36), 55 (44) [$C_3H_5NC_4H_8^+$ - $C_4H_8$], 41 (67) [$C_3H_5NC_4H_8^+$ - $NC_4H_8$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ (ε) = 224 (20700), 248 (9200), 286 (18900) nm (l·mol$^{-1}$·cm$^{-1}$). - $C_{29}H_{33}N_5O_2$ (509.7): calcd. C 73.05, H 6.92, N 13.74; found C 72.80, H 7.05, N 13.62.

*1,1,t-6-Trimethyl-r-5-pyrrolidin-1-yl-2,c-6a-di-p-tolyl-1,1a,5,6,6a,6b-hexahydro-3,3a-di-aza-cyclopropa[e]indene-4,4-dicarbonitrile* (**9b**) *and 1,1,c-6-Trimethyl-r-5-pyrrolidin-1-yl-2,t-6a-di-p-tolyl-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**10b**)*:* Following the *general procedure* **3b** (169.0 mg, 461 μmol) and **5l** (78.4 mg, 705 μmol) in 20 ml acetonitrile yielded after preparative HPLC (hexane : $CH_2Cl_2$ : methanol 70 : 30 : 0.025) and recrystallization from acetonitrile 65.7 mg (138 μmol, 30 %) of **9b**, colourless crystals, m.p. 237 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3020, 2960, 2940, 2920, 2860, 2810, 1610, 1500, 1445, 1405, 1360, 1260, 1115, 1010, 810 cm$^{-1}$. - $^1$H NMR ($CDCl_3$, 400 MHz): δ = 0.09 (s, 3 H), 1.31 (s, 3 H), 1.71-1.82 (m, 4 H), 1.73 (d, 1 H, $^3J$ = 8.3 Hz), 1.77 (d, 1 H, $^3J$ = 8.3 Hz), 2.34 (s, 3 H), 2.36 (s, 3 H), 3.03-3.10 (m, 2 H), 3.14-3.21 (m, 2 H), 7.14-7.16 (m, 2 H), 7.18-7.20 (m, 2 H), 7.29-7.31 (m, 2 H), 7.68-7.71 (m, 2 H) ppm. - $^{13}$C NMR ($CDCl_3$, 101 MHz, DEPT 135/90): δ = 13.79 (1 C, +/0), 16.76 (1 C, +/0), 20.10 (1 C, +/+), 20.91 (1 C, +/0), 21.32 (1 C, +/0), 23.65 (1 C, 0/0), 24.79 (2 C, -/0), 26.73 (1 C, +/+), 26.98 (1 C, +/0), 47.02 (1 C, +/+), 48.87 (2 C, -/0), 61.64 (1 C, 0/0), 62.85 (1 C, 0/0), 72.21 (1 C, +/+), 113.38 (1 C, 0/0), 116.52 (1 C, 0/0), 125.57 (2 C, +/+), 127.34 (2 C, +/+), 128.24 (2 C, +/+), 129.07 (2 C, +/+), 134.54 (1 C, 0/0), 136.78 (1 C, 0/0), 139.11 (1 C, 0/0), 139.34 (1 C, 0/0), 148.66 (1 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 477 (3) [$M^+$], 366 (100) [ylid$^+$], 339 (4) [ylid$^+$ - HCN], 324 (4) [ylid$^+$ - HCN - $CH_3$], 303 (19), 288 (5), 272 (4), 265 (2), 249 (55) [ylid$^+$ - $C_7H_7CN$], 234 (9) [ylid$^+$ - $C_7H_7CN$ - $CH_3$], 222 (9), 209 (9), 196

(5), 185 (15), 171 (10), 157 (6), 143 (7), 111 (58) [$C_3H_5NC_4H_8^+$], 105 (5), 96 (25) [$C_3H_5NC_4H_8^+$ - $CH_3$], 82 (5), 68 (8), 55 (8) [$C_3H_5NC_4H_8^+$ - $C_4H_8$], 41 (13) [$C_3H_5NC_4H_8^+$ - $NC_4H_8$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 220 (9500), 295 (5600) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{31}H_{35}N_5$ (477.7): calcd. C 77.94, H 7.39, N 14.66; found C 77.93, H 7.45, N 14.63. Furthermore could be obtained 58.9 mg (123 µmol, 27 %) of **10b**, colourless crystals, m.p. 247 °C (decomp.). - IR (KBr): $\bar{\nu}$ = 3020, 3000 2970, 2940, 2920 2860, 2800, 1600, 1500, 1445, 1355, 1325, 1110, 1100, 1010, 905, 805 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 0.32 (s, 3 H), 1.17 (s, 3 H), 1.70 (d, 1 H, $^3J$ = 8.3 Hz), 1.77 (d, 1 H, $^3J$ = 8.3 Hz), 1.74-1.86 (m, 4 H), 2.35 (s, 3 H), 2.37 (s, 3 H) 2.54-2.64 (m, 4 H), 7.12-7.14 (m, 1 H), 7.17-7.21 (m, 4 H), 7.56-7.58 (m, 1 H), 7.69-7.71 (m, 2 H) ppm. - $^{13}C$ NMR ($CDCl_3$, 101 MHz, DEPT 135/90): $\delta$ = 9.60 (1 C, +/0), 16.75 (1 C, +/0), 20.89 (1 C, +/+), 20.95 (1 C, +/0), 21.30 (1 C, +/0), 23.28 (2 C, -/0), 23.96 (1 C, 0/0), 26.31 (1 C, +/+), 27.18 (1 C, +/0), 51.25 (1 C, +/+), 53.00 (2 C, -/0), 64.37 (1 C, 0/0), 64.95 (1 C, 0/0), 73.40 (1 C, +/+), 111.81 (1 C, 0/0), 116.35 (1 C, 0/0), 124.31 (1 C, +/+), 125.54 (2 C, +/+), 126.54 (1 C, +/+), 128.12 (1 C, +/+), 129.12 (2 C, +/+), 129.41 (1 C, +/+), 134.95 (1 C, 0/0), 136.55 (1 C, 0/0), 138.84 (1 C, 0/0), 143.19 (1 C, 0/0), 145.09 (1 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 477 (3) [$M^+$], 366 (100) [ylid$^+$], 339 (4) [ylid$^+$ - HCN], 324 (3) [ylid$^+$ - HCN - $CH_3$], 303 (19), 288 (4), 272 (3), 265 (2), 249 (50) [ylid$^+$ - $C_7H_7CN$], 234 (8) [ylid$^+$ - $C_7H_7CN$ - $CH_3$], 222 (10), 209 (6), 196 (3), 185 (13), 171 (9), 157 (5), 143 (6), 111 (51) [$C_3H_5NC_4H_8^+$], 105 (4), 96 (19) [$C_3H_5NC_4H_8^+$ - $CH_3$], 82 (4), 68 (5), 55 (6) [$C_3H_5NC_4H_8^+$ - $C_4H_8$], 41 (9) [$C_3H_5NC_4H_8^+$ - $NC_4H_8$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 220 (19300), 289 (13600) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{31}H_{35}N_5$ (477.7): calcd. C 77.94, H 7.39, N 14.66; found C 77.86, H 7.41, N 14.60.

*1,1,t-6-Trimethyl-2,c-6a-diphenyl-r-5-pyrrolidin-1-yl-1,1a,5,6,6a,6b-hexa-hydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**9c**) *and 1,1,c-6-Trimethyl-2,t-6a-diphenyl-r-5-pyrrolidin-1-yl-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**10c**)*:* Following the *general procedure* **3c** (160.0 mg, 473 µmol) and **5l** (75.2 mg, 676 µmol) in 20 ml acetonitrile yielded after fcc ($CH_2Cl_2$) and recrystallization from acetonitrile 134 mg (298 µmol, 63 %) of a mixture of the two diastereomeres **9c/10c**, colourless crystals, m.p. 217-218 °C (decomp.). - IR (KBr): $\bar{\nu}$ = 3070, 3030, 3020, 2970, 2950, 2860, 2820, 2800, 1600, 1590, 1485, 1440, 1400, 1385, 1360, 1325, 1260, 1110, 1060, 1005, 910, 760, 695, 685 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 250 MHz): **9c**: $\delta$ = 0.10 (s, 3 H), 1.33 (s, 3 H), 3.02-3.12 (m, 2 H), 3.14-3.22 (m, 2 H); **10c**: 0.31 (s, 3 H), 1.18 (s, 3 H), 2.52-2.66 (m, 4 H); **9c/10c**: 1.7-1.9 (m, 12 H), 7.23-7.46 (m, 16 H), 7.68-7.73 (m, 2 H), 7.78-7.84 (m, 4 H) ppm. - $^{13}C$ NMR ($CDCl_3$, 101 MHz, DEPT 135/90): **9c**: $\delta$ = 13.82 (1 C, +/0), 16.76 (1 C, +/0), 20.31 (1 C, +/+), 23.76 (1 C, 0/0), 24.85 (2 C, -/0), 26.91 (1 C, +/+), 26.98 (1 C, +/0), 47.12 (1 C, +/+), 48.92 (2 C, -/0), 61.71 (1 C, 0/0), 63.17 (1 C, 0/0), 72.37 (1 C, +/+), 113.37 (1 C, 0/0), 116.32 (1 C, 0/0), 142.35 (1 C, 0/0), 148.73 (1 C, 0/0); **10c**: 9.62 (1 C, +/0), 16.76 (1 C, +/0), 21.10 (1 C, +/+), 23.36 (2 C, -/0), 24.05 (1 C, 0/0), 26.36 (1 C, +/+), 27.17 (1 C, +/0), 51.33 (1 C, +/+), 53.03 (2 C, -/0), 64.37 (1 C, 0/0), 65.27 (1 C, 0/0), 73.33 (1 C, +/+), 111.81 (1 C, 0/0), 116.50 (1 C, 0/0), 124.57 (1 C, +/+), 145.26 (1 C, 0/0), 146.26 (1 C, 0/0); **9c/10c**: 125.70 (2 C, +/+), 125.73 (2 C, +/+), 126.64 (1 C, +/+), 127.06 (1 C, +/+), 127.27 (1 C, +/+), 127.51 (2 C, +/+), 127.63 (2 C, +/+), 128.26 (1 C, +/+), 128.43 (2 C, +/+), 128.47 (2 C, +/+), 128.70 (1 C, +/+), 128.91 (1 C, +/+), 129.16 (1 C, +/+), 137.27 (1 C, 0/0), 137.67 (1 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 450 (3) [$M^+$], 338 (40) [ylid$^+$], 275 (20), 235 (24) [ylid$^+$ - $C_6H_5CN$], 220 (4) ) [ylid$^+$ - $C_6H_5CN$ - $CH_3$], 208 (2) ) [ylid$^+$ - $C_6H_5CN$ - HCN], 195 (4), 156 (4), 129 (5), 111 (100) [$C_3H_5NC_4H_8^+$], 96 (16) [$C_3H_5NC_4H_8^+$ - $CH_3$], 91 (3), 77 (3), 70 (3) [$C_3H_5NC_4H_8^+$ - $C_3H_5$], 55 (5) [$C_3H_5NC_4H_8^+$ - $C_4H_8$], 41 (11) [$C_3H_5NC_4H_8^+$ - $NC_4H_8$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 291 (4800) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{29}H_{31}N_5$ (449.6): calcd. C 77.47, H 6.95, N 15.58; found C 77.47, H 7.16, N 15.53.

*2,c-6a-Bis-(4-chloro-phenyl)-1,1,t-6-trimethyl-r-5-pyrrolidin-1-yl-1,1a,5,6,6a,6b-hexahy-dro-3,3a-diaza-cyclopropa[e]-indene-4,4-dicarbonitrile* (**9d**) *and 2,t-6a-Bis-(4-chloro-phenyl)-1,1,c-6-trimethyl--r-5-pyrrolidin-1-yl-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopro-pa[e]-indene-4,4-*

*dicarbonitrile* (**10d**)*:* Following the *general procedure* **3d** (69.5 mg, 171 µmol) and **5l** (23.8 mg, 214 µmol) in 5 ml acetonitrile yielded after fcc (petroleum ether 40/60 : $CH_2Cl_2$ 1 : 4) and recrystallization from acetonitrile 79.5 mg (153 µmol, 89 %) of a mixture of the two diastereomeres **9d/10d**, colourless crystals, m.p. 223-224 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3040, 3000, 2940, 2920, 2840, 2800, 1595, 1480, 1440, 1110, 1080, 1000, 830, 810, 725 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 250 MHz): **9d**: δ = 0.10 (s, 3 H), 1.32 (s, 3 H), 3.00-3.11 (m, 2 H), 3.14-3.22 (m, 2 H); **10d**: 0.31 (s, 3 H), 1.19 (s, 3 H), 2.52-2.66 (m, 4 H); **9d/10d**: 1.7-1.9 (m, 12 H), 7.25-7.41 (m, 9 H), 7.61-7.66 (m, 1 H), 7.70-7.75 (m, 4 H) ppm. - EI MS (70 eV); m/z (%): 517 (1) [$M^+$], 406 (3) [ylid$^+$], 365 (1), 343 (3), 269 (9) [ylid$^+$ - Cl-$C_6H_4CN$], 242 (4) [ylid$^+$ - Cl-$C_6H_4CN$ - HCN], 229 (5), 204 (6), 190 (4), 139 (5), 137 (5) [Cl-$C_6H_4CN^+$], 128 (5), 111 (100) [$C_3H_5NC_4H_8^+$], 96 (26) [$C_3H_5NC_4H_8^+$ - $CH_3$], 82 (6), 68 (10), 55 (11) [$C_3H_5NC_4H_8^+$ - $C_4H_8$], 41 (23) [$C_3H_5NC_4H_8^+$ - $NC_4H_8$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ (ε) = 223 (23700), 295 (13600) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{29}H_{29}N_5Cl_2$ (518.5): calcd. C 67.18, H 5.64, N 13.51; found C 66.98, H 5.71, N 13.68.

*2,c-6a-Bis-(4-methoxy-phenyl)-1,1,t-6-trimethyl-r-5-morpholin-4-yl-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**11a**) *and 2,t-6a-Bis-(4-methoxy-phenyl)-1,1,c-6-trimethyl-r-5-morpholin-4-yl-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**12a**)*:* Following the *general procedure* **3a** (170.0 mg, 427 µmol) and **5m** (63.6 mg, 500 µmol) in 17 ml acetonitrile yielded after fcc (petroleum ether 40/60 : diethyl ether 1 : 1) and recrystallization from $CH_2Cl_2$/hexane 56.0 mg (107 µmol, 25 %) of **11a**, colourless crystals, m.p. 198-199 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3050, 3020, 2990, 2950, 2890, 2870, 2840, 2820, 1495, 1450, 1435, 1280, 1235, 1155, 1100, 1015, 1000, 820, 810 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 400 MHz): δ = 0.11 (s, 3 H), 1.32 (s, 3 H), 1.70 (d, 1 H, $^3J$ = 8.2 Hz), 1.77 (d, 1 H, $^3J$ = 8.2 Hz), 2.89-2.94 (m, 2 H), 3.15-3.20 (m, 2 H), 3.63-3.72 (m, 4 H), 3.81 (s, 3 H), 3.83 (s, 3 H), 6.88-6.94 (m, 4 H), 7.30-7.33 (m, 2 H), 7.72-7.76 (m, 2 H) ppm. - $^{13}C$ NMR ($CDCl_3$, 101 MHz, DEPT 135): δ = 13.75 (1 C, +), 16.66 (1 C, +), 20.08 (1 C, +), 23.70 (1 C, 0), 26.72 (1 C, +), 26.98 (1 C, +), 45.49 (1 C, +), 50.45 (2 C, -), 55.20 (1 C, +), 55.31 (1 C, +), 61.68 (1 C, 0), 62.32 (1 C, 0), 67.54 (2 C, -), 75.08 (1, +) 112.95 (2 C, +), 113.26 (1 C, 0), 113.79 (2 C, +), 116.03 (1 C, 0), 127.08 (2 C, +), 128.45 (2 C, +), 129.87 (1 C, 0), 134.15 (1 C, 0), 149.22 (1 C, 0), 158.70 (1 C, 0), 160.58 (1 C, 0) ppm. - EI MS (70 eV); m/z (%): 525 (1) [$M^+$], 498 (2) [$M^+$ - HCN], 398 (55) [ylid$^+$], 383 (8) [ylid$^+$ - $CH_3$], 370 (5), 355 (5), 331 (6), 320 (20), 305 (31), 290 (5), 279 (7), 265 (33) [ylid$^+$ - $CH_3O$-$C_6H_4CN$], 250 (9) [ylid$^+$ - $CH_3O$-$C_6H_4CN$ - $CH_3$], 238 (11), 225 (26), 212 (7), 201 (21), 187 (37), 172 (13), 159 (12), 133 (31) [$CH_3O$-$C_6H_4CN^+$], 127 (55) [$C_3H_5NC_4H_8O^+$], 112 (25) [$C_3H_5NC_4H_8O^+$ - $CH_3$], 103 (12), 90 (18), 82 (27), 68 (100), 54 (21), 41 (82) [$C_3H_5NC_4H_8O^+$ - $NC_4H_8O$]. - FD MS ($CH_2Cl_2$); *m/z* (%): 525 (100) [$M^+$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ (ε) = 210 (28200), 227 (27000), 253 (13300), 293 (16600) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{31}H_{35}N_5O_3$ (525.7): calcd. C 70.82, H 6.71, N 13.32; found C 70.65, H 6.89, N 13.18. Furthermore could be obtained 63.0 mg (120 µmol, 28 %) of **12a**, colourless crystals, m.p. 204 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3060, 3020, 2980, 2940, 2920 2820, 2800, 2780, 1595, 1495, 1450, 1440, 1290, 1255, 1235, 1165, 1105, 1015, 900, 830, 810 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 400 MHz): δ = 0.35 (s, 3 H), 1.17 (s, 3 H), 1.68 (d, 1 H, $^3J$ = 7.9 Hz), 1.78 (d, 1 H, $^3J$ = 7.9 Hz), 2.44-2.49 (m, 2 H), 2.57 (s, 2 H), 3.73-3.79 (m, 4 H), 3.83 (s, 3 H), 3.84 (s, 3 H), 6.85-6.88 (m, 1 H), 6.93-6.96 (m, 3 H), 7.19-7.22 (m, 1 H), 7.58-7.61 (m, 1 H), 7.73-7.77 (m, 2H) ppm. - $^{13}C$ NMR ($CDCl_3$, 101 MHz, DEPT 135): δ = 9.20 (1 C, +), 16.69 (1 C, +), 21.01 (1 C, +), 24.13 (1 C, 0), 26.52 (1 C, +), 27.18 (1 C, +), 49.08 (1 C, +), 52.49 (2 C, -), 55.24 (1 C, +), 55.33 (1 C, +), 63.45 (1 C, 0), 64.40 (1 C, 0), 66.19 (2 C, -), 73.18 (1 C, +), 111.31 (1 C, 0), 111.59 (1 C, +), 113.85 (2 C, +), 115.41 (1 C, +), 116.35 (1 C, 0), 125.37 (1 C, +), 127.00 (2 C, +), 127.70 (1 C, +), 130.37 (1 C, 0), 137.66 (1 C, 0), 145.18 (1 C, 0), 158.49 (1 C, 0), 160.35 (1 C, 0) ppm. - EI MS (70 eV); m/z (%): 525 (1) [$M^+$], 498 (6) [$M^+$ - HCN], 446 (6), 398 (66) [ylid$^+$], 383 (10) [ylid$^+$ - $CH_3$], 370 (11), 355 (13), 331 (9), 320 (38), 305 (21), 290 (5), 279 (11), 265 (27) [ylid$^+$ - $CH_3O$-$C_6H_4CN$], 250 (14) [ylid$^+$ - $CH_3O$-$C_6H_4CN$ - $CH_3$], 238 (12), 225 (38), 212 (9), 200 (24), 187 (61), 172 (22), 158 (19),

145 (12), 133 (44) [$CH_3O$-$C_6H_4CN^+$], 127 (49) [$C_3H_5NC_4H_8O^+$], 121 (18), 112 (21) [$C_3H_5NC_4H_8O^+$ - $CH_3$], 103 (15), 90 (19), 82 (27), 77 (20), 68 (100), 63 (11), 55 (20) [$C_3H_5NC_4H_8O^+$ - $C_4H_8O$], 41 (88) [$C_3H_5NC_4H_8O^+$ - $NC_4H_8O$]. - FD MS ($CH_2Cl_2$); *m/z* (%): 525 (100) [$M^+$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 210 (25400), 227 (23600), 286 (19200) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{31}H_{35}N_5O_3$ (525.7): calcd. C 70.82, H 6.71, N 13.32; found C 70.52, H 6.80, N 13.24.

*1,1,t-6-Trimethyl-r-5-morpholin-4-yl-2,c-6a-di-p-tolyl-1,1a,5,6,6a,6b-hexahydro-3,3a-di-aza-cyclopropa[e]indene-4,4-dicarbonitrile* (**11b**) *and 1,1,c-6-Trimethyl-r-5-morpholin-4-yl-2,t-6a-di-p-tolyl-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**12b**)*:* Following the *general procedure* **3b** (164.0 mg, 447 µmol) and **5m** (63.6 mg, 500 µmol) in 25 ml acetonitrile yielded after fcc (petroleum ether 40/60 : diethyl ether 1 : 1) and recrystallization from $CH_2Cl_2$/hexane 38.0 mg (77.0 µmol, 17 %) of **11b**, colourless crystals, m.p. 234-235 °C (decomp.). - IR (KBr): $\bar{\nu}$ = 3020, 2950, 2880, 2850, 2820, 1605, 1505, 1455, 1445, 1250, 1175, 1110, 1010, 810 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 250 MHz): $\delta$ = 0.08 (s, 3 H), 1.32 (s, 3 H), 1.72 (d, 1 H, $^3J$ = 8.2 Hz), 1.76 (d, 1 H, $^3J$ = 8.2 Hz), 2.34 (s, 3 H), 2.37 (s, 3 H), 2.87-2.95 (m, 2 H), 3.13-3.21 (m, 2 H), 3.65-3.69 (m, 4 H), 7.14-7.21 (m, 4 H), 7.27-7.30 (m, 2 H), 7.67-7.70 (m, 2 H) ppm. - $^{13}C$ NMR ($CDCl_3$, 63 MHz): $\delta$ = 13.81 (1 C), 16.77 (1 C), 20.19 (1 C), 20.92 (1 C), 21.33 (1C), 23.74 (1 C), 26.83 (1 C), 27.02 (1 C), 45.51 (1 C), 50.55 (2 C), 61.81 (1 C), 62.75 (1 C), 67.62 (2 C), 75.22 (1 C) 113.33 (1 C), 116.06 (1 C), 125.69 (2 C), 127.41 (2 C), 128.42 (2 C), 129.16 (2 C), 134.50 (1 C), 137.09 (1 C), 139.23 (1 C), 139.34 (1 C), 149.33 (1 C) ppm. - EI MS (70 eV); m/z (%):493 (1) [$M^+$], 366 (100) [ylid$^+$], 288 (5) 249 (88) [ylid$^+$ - $C_7H_7CN$], 234 (13) [ylid$^+$ - $C_7H_7CN$- $CH_3$], 209 (11) [ylid$^+$ -$C_7H_7CN$ - HCN], 185 (17), 171 (14), 143 (10), 127 (18), [$C_3H_5NC_4H_8O^+$], 118 (11) [$(C_7H_7CN+H)^+$], 105 (8), 91 (7), 69 (13), 42 (6) [$C_3H_5NC_4H_8O^+$ - $NC_4H_8O$ + H]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 210 (23400), 220 (21100), 294 (12200) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{31}H_{35}N_5O_3$ (493.7): calcd. C 75.75, H 7.15, N 14.19; found C 75.49, H 7.26, N 13.92. Furthermore could be obtained 57.0 mg (115 µmol, 26 %) of **12b**, colourless crystals, m.p. 226 °C (decomp.). - IR (KBr): $\bar{\nu}$ = 3030, 2980, 2950, 2930, 2880, 2860, 2820, 1610, 1510, 1445, 1260, 1110, 1020, 1010, 900, 805 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 250 MHz): $\delta$ = 0.32 (s, 3 H), 1.17 (s, 3 H), 1.69 (d, 1 H, $^3J$ = 8.2 Hz), 1.79 (d, 1 H, $^3J$ = 8.2 Hz), 2.36 (s, 3 H), 2.37 (s, 3 H), 2.42-2.56 (m, 4 H), 3.74-3.77 (m, 4 H), 7.13-7.25 (m, 5 H), 7.55-7.58 (m, 1 H), 7.68-7.72 (m, 2H) ppm. - $^{13}C$ NMR ($CDCl_3$, 63 MHz): $\delta$ = 9.21 (1 C), 16.76 (1 C), 20.96 (1 C), 21.11 (1 C), 21.30 (1 C), 24.13 (1 C), 26.55 (1 C), 27.23 (1 C), 49.17 (1 C), 52.56 (2 C), 63.47 (1 C), 64.86 (1 C), 66.26 (2 C), 73.19 (1 C), 111.37 (1 C), 116.39 (1 C), 124.29 (1 C), 125.62 (2 C), 126.59 (1 C), 128.30 (1 C), 129.19 (2 C), 129.60 (1 C), 134.95 (1 C), 136.87 (1 C), 138.99 (1 C), 142.82 (1 C), 145.41 (1 C) ppm. - EI MS (70 eV); m/z (%):493 (1) [$M^+$], 466 (2), 366 (100) [ylid$^+$], 288 (5), 249 (88) [ylid$^+$ - $C_7H_7CN$], 234 (13) [ylid$^+$ - $C_7H_7CN$ - $CH_3$], 223 (5), 209 (11), 185 (17), 171 (14), 143 (10), 127 (18) [$C_3H_5$- $NC_4H_8O^+$], 118 (11) [$(C_7H_7CN+H)^+$], 105 (8), 91 (7), 69 (13), 42 (6) [$C_3H_5NC_4H_8O^+$ - $NC_4H_8O$ + H]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 203 (13600), 210 (23400), 221 (21000) nm, 289 (16600) ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{31}H_{35}N_5O$ (493.7): calcd. C 75.75, H 7.15, N 14.19; found C 75.66, H 7.20, N 14.11.

*1,1,t-6-Trimethyl-r-5-morpholin-4-yl-2,c-6a-diphenyl-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**11c**) *and 1,1,c-6-Trimethyl-r-5-morpholin-4-yl-2,t-6a-diphenyl-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**12c**)*:* Following the *general procedure* **3c** (194.5 mg, 575 µmol) and **5m** (91.8 mg, 722 µmol) yielded after fcc (petroleum ether 40/60 : diethyl ether 1 : 1) and recrystallization from diethyl ether/hexane 21.0 mg (45.1 µmol, 8 %) of **11c**, colourless crystals, m.p. 228 °C (decomp.). - IR (KBr): $\bar{\nu}$ = 3060, 3040, 3010, 2960, 2950, 2900, 2880, 2830, 1595, 1585, 1435, 1280, 1245, 1180, 1100, 1000, 845, 690, 675 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 250 MHz): $\delta$ = 0.07 (s, 3 H), 1.34 (s, 3 H), 1.77 (d, 1 H, $^3J$ = 8.2 Hz), 1.81 (d, 1 H, $^3J$ = 8.2 Hz), 2.88-2.95 (m, 2 H), 3.14-3.21 (m, 2 H), 3.64-3.72 (m, 4 H), 7.27-7.31 (m, 1 H), 7.34-7.44 (m, 7 H), 7.78-7.82 (m, 2 H) ppm. - $^{13}C$ NMR ($CDCl_3$, 63 MHz): $\delta$ = 13.84 (1 C), 16.72 (1

C), 20.15 (1 C), 23.83 (1 C), 26.64 (1 C), 26.91 (1 C), 45.37 (1 C), 50.40 (2 C), 61.61 (1 C), 62.83 (1 C), 67.52 (2 C), 75.06 (1 C), 113.17 (1 C), 115.87 (1 C), 125.67 (2 C), 127.38 (2 C), 127.70 (2 C), 128.43 (2 C), 129.31 (2 C), 136.95 (1 C), 142.03 (1 C), 149.30 (1 C) ppm. - EI MS (70 eV); m/z (%): 465 (2) [$M^+$], 338 (86) [ylid$^+$], 323 (5), 275 (5), 235 (100) [ylid$^+$ - $C_6H_5CN$], 220 (12) [ylid$^+$ - $C_6H_5CN$ - $CH_3$], 209 (6), 195 (11), 171 (14), 156 (14), 141 (11), 127 (33) [$C_3H_5NC_4H_8O^+$], 115 (9), 104 (12) [$(C_6H_5CN+H)^+$], 91(11), 82 (6), 69 (20), 42 (9) 41 (10) [$C_3H_5NC_4H_8O^+$ - $NC_4H_8O$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 293 (9700) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{29}H_{31}N_5O$ (465.6): calcd. C 74.81, H 6.71, N 15.04; found C 74.88, H 7.00, N 14.76. Furthermore could be obtained 24.5 mg (52.6 µmol, 9 %) of **12c**, colourless crystals, m.p. 233-234 °C (decomp.). - IR (KBr): $\bar{\nu}$ = 3060, 3020, 2980, 2950, 2910, 2890, 2850, 1585, 1430, 1260, 1155, 1110, 1020, 900, 760, 690 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 250 MHz): $\delta$ = 0.32 (s, 3 H), 1.18 (s, 3 H), 1.74 (d, 1 H, $^3J$ = 8.2 Hz), 1.82 (d, 1 H, $^3J$ = 8.2 Hz), 2.43-2.50 (m, 2 H), 2.57 (s, 2 H), 3.72-3.79 (m, 4 H), 7.27-7.43 (m, 7 H), 7.68-7.71 (m, 1 H), 7.79-7.82 (m, 2H) ppm. - $^{13}C$ NMR ($CDCl_3$, 63 MHz, DEPT 135/90): $\delta$ = 9.19 (1 C, +/0), 16.72 (1 C, +/0), 21.02 (1 C, +/+), 24.21 (1 C, 0/0), 26.33 (1 C, +/+), 27.12 (1 C, +/0), 49.05 (1 C, +/+), 52.45 (2 C, -/0), 63.30 (1 C, 0/0), 64.97 (1 C, 0/0), 66.18 (2 C, -/0), 72.99 (1 C, +/+), 111.23 (1 C, 0/0), 116.18 (1 C, 0/0), 124.43 (1 C, +/+), 125.64 (2 C, +/+), 126.48 (1 C, +/+), 127.23 (1 C, +/+), 127.76 (1 C, +/+), 128.48 (2 C, +/+), 128.80 (1 C, +/+), 129.01 (1 C, +/+), 137.42 (1 C, 0/0), 145.46 (1 C, 0/0), 145.64 (1 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 466 (2) [$M^+$], 338 (75) [ylid$^+$], 275 (5), 235 (100) [ylid$^+$- $C_6H_5CN$], 220 (12) [ylid$^+$ - $C_6H_5CN$ - $CH_3$], 209 (5), 195 (9), 170 (12), 156 (14), 141 (12), 127 (30) [$C_3H_5NC_4H_8O^+$], 115 (10), 104 (11) [$(C_6H_5CN+H)^+$], 91(12), 69 (22), 42 (11) [$C_3H_5$-$NC_4H_8O^+$ - $C_4H_8O$ + H]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 220 (15100), 289 (12200) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{29}H_{31}N_5O$ (465.6): calcd. C 74.81, H 6.71, N 15.04; found C 74.90, H 7.09, N 14.94.

*2,c-6a-Bis-(4-chloro-phenyl)-1,1,t-6-trimethyl-r-5-morpholin-4-yl-1,1a,5,6,6a,6b-hexahy-dro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**11d**) *and 2,t-6a-Bis-(4-chloro-phenyl)-1,1,c-6-trimethyl-r-5-morpholin-4-yl-1,1a,5,6,6a,6b-hexahydro-3,3a-diaza-cyclopropa[e]indene-4,4-dicarbonitrile* (**12d**)*:* Following the *general procedure* **3d** (200.6 mg, 493 µmol) and **5m** (81.9 mg, 644 µmol) in 20 ml acetonitrile yielded after fcc (petroleum ether 40/60 : diethyl ether 1 : 2) and recrystallization from diethyl ether/hexane 64.8 mg (121 µmol, 25 %) of **11d**, colourless crystals, m.p. 237-238 °C (decomp.). - IR (KBr): $\bar{\nu}$ = 3100, 3070, 3010, 2980, 2950, 2920, 2890, 2860, 1605, 1485, 1445, 1250, 1195, 1110, 1085, 1005, 855, 835, 820 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 250 MHz): $\delta$ = 0.09 (s, 3 H), 1.33 (s, 3 H), 1.74 (d, 1 H, $^3J$ = 8.3 Hz), 1.78 (d, 1 H, $^3J$ = 8.3 Hz), 2.85-2.97 (m, 2 H), 3.10-3.22 (m, 2 H), 3.60-3.74 (m, 4 H), 7.31-7.42 (m, 6 H), 7.68-7.75 (m, 2 H) ppm. - $^{13}C$ NMR ($CDCl_3$, 63 MHz, DEPT 135/90): $\delta$ = 13.74 (1 C, +/0), 16.85 (1 C, +/0), 20.02 (1 C, +/+), 23.87 (1 C, 0/0), 26.65 (1 C, +/+), 26.89 (1 C, +/0), 45.45 (1 C, +/+), 50.46 (2 C, -/0), 61.48 (1 C, 0/0), 62.65 (1 C, 0/0), 67.52 (2 C, -/0), 75.27 (1 C, +/+), 112.98 (1 C, 0/0), 115.69 (1 C, 0/0), 126.95 (2 C, +/+), 128.04 (2 C, +/+), 128.73 (2 C, +/+), 128.75 (2 C, +/+), 133.67 (1 C, 0/0), 135.31 (1 C, 0/0), 135.51 (1 C, +/+) 140.60 (1 C, 0/0), 148.41 (1 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 533 (3) [$M^+$], 406 (54) [ylid$^+$], 343 (5), 269 (33) [ylid$^+$ - Cl-$C_6H_4CN$], 242 (5) [ylid$^+$ - Cl-$C_6H_4CN$ - HCN], 205 (8), 127 (100) [$C_3H_5NC_4H_8O^+$], 69 (13), 41 (6) [$C_3H_5NC_4H_8O^+$ - $NC_4H_8O$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 223 (24400), 297 (12600) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{29}H_{29}N_5Cl_2O$ (534.5): calcd. C 65.16, H 5.46, N 13.10; found C 65.17, H 5.63, N 13.10. Furthermore could be obtained 38.4 mg (71.8 µmol, 15 %) of **12d**, colourless crystals, m.p. 237-238 °C (decomp.). - IR (KBr): $\bar{\nu}$ = 3070, 3040, 2970, 2950, 2905, 2880, 2850, 2820, 1595, 1480, 1440, 1390, 1260, 1155, 1110, 1080, 1000, 900, 810, 730 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 250 MHz): $\delta$ = 0.32 (s, 3 H), 1.19 (s, 3 H), 1.71 (d, 1 H, $^3J$ = 8.1 Hz), 1.80 (d, 1 H, $^3J$ = 8.1 Hz), 2.41-2.52 (m, 2 H), 2.56 (s, 2 H), 3.68-3.84 (m, 4 H), 7.23-7.30 (m, 1 H), 7.32-7.43 (m, 4 H), 7.59-7.66 (m, 1 H), 7.69-7.76 (m, 2 H) ppm. - $^{13}C$ NMR ($CDCl_3$, 63 MHz, DEPT 135/90): $\delta$ = 9.17 (1 C, +/0), 16.77 (1 C, +/0), 20.85 (1 C, +/+), 24.26 (1 C, 0/0), 26.27 (1 C, +/+), 27.11 (1 C, +/0), 49.16 (1 C, +/+), 52.53 (2 C, -/0),

63.21 (1 C, 0/0), 64.75 (1 C, 0/0), 66.17 (2 C, -/0), 73.00 (1 C, +/+), 111.06 (1 C, 0/0), 116.01 (1 C, 0/0), 125.77 (1 C, +/+), 126.90 (2 C, +/+), 127.98 (1 C, +/+), 128.03 (1 C, +/+), 128.75 (2 C, +/+), 129.22 (1 C, +/+), 133.33 (1 C, 0/0), 135.18 (1 C, 0/0), 135.73 (1 C, 0/0), 144.22 (1 C, 0/0), 144.59 (1 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 533 (3) [$M^+$], 506 (2) [$M^+$ - HCN], 406 (52) [ylid$^+$], 343 (6), 269 (32) [ylid$^+$ - Cl-$C_6H_4CN$], 254 (3) [ylid$^+$ - Cl-$C_6H_4CN$ - $CH_3$], 205 (7), 191 (5), 137 (6) [Cl-$C_6H_4CN^+$], 127 (100) [$C_3H_5NC_4H_8O^+$], 112 (8), 74 (29), 69 (11), 59 (45), 45 (32), 41 (8) [$C_3H_5NC_4H_8O^+$ - $NC_4H_8O$], 36 (8). - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 224 (21600), 292 (14700) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{29}H_{29}N_5Cl_2O$ (534.5): calcd. C 65.16, H 5.46, N 13.10; found C 65.14, H 5.62, N 13.03.

*t-2-Dimethylamino-6-(4-methoxy-benzoyl)-c-7a-(4-methoxy-phenyl)-r-1,5,5-trimethyl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-dicarbonitrile* (**13a**) *and c-2-Dimethylamino-6-(4-methoxy-benzoyl)-t-7a-(4-methoxy-phenyl)-r-1,5,5-trimethyl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-dicarbonitrile* (**14a**)*:* Following the *general procedure* **4a** (313 mg, 783 µmol) and **5k** (133 mg, 1.56 mmol) in 10 ml acetonitrile yielded after fcc (petroleum ether 40/60 : ethyl acetate from 2 : 1 to 1 : 1 to 1 : 2) and recrystallization from acetonitrile 235 mg (485 µmol, 62 %) of **13a**, colourless crystals, m.p. 187 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3060, 3040, 2990, 2960, 2930, 2880, 2840, 2800, 1635, 1560, 1500, 1450, 1300, 1245, 1185, 1015, 830, 755 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.15 (s, 3 H), 1.91 (s, 3 H), 2.78 (s, 6 H), 3.79 (s, 3 H), 3.89 (s, 3 H), 6.77 (s, 1 H), 6.83-6.85 (m, 2 H), 6.97-7.19 (m, 4 H), 7.90-7.93 (m, 2 H) ppm. - $^{13}C$ NMR ($CDCl_3$, 101 MHz): $\delta$ = 14.76 (1 C), 20.36 (1 C), 31.20 (1 C), 41.85 (2 C), 42.11 (1 C), 54.54 (1 C), 55.20 (1 C), 55.48 (1 C), 70.41 (1 C), 77.82 (1 C), 79.52 (1 C), 113.59 (2 C), 113.77 (2 C), 116.84 (1 C), 116.97 (1 C), 127.68 (2 C), 131.44 (1 C), 131.54 (2 C), 134.38 (1 C), 141.31 (1 C), 146.69 (1 C), 158.95 (1 C), 163.50 (1 C), 191.78 (1 C) ppm. - FD MS ($CH_2Cl_2$); *m/z* (%): 484 (100) [$M^+$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 227 (19100), 292 (11500) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{29}H_{32}N_4O_3$ (484.6): calcd. C 71.88, H 6.66, N 11.56; found C 71.72, H 6.84, N 11.35. As the cycloadduct **14a** is very unstable - it splits almost completely during fcc into the starting compounds - only 11 mg (22.7 µmol, 3 %) could be obtained as a purple oil. - $^1H$ NMR ($CDCl_3$, 250 MHz): $\delta$ = 1.53 (s, 3 H), 2.03 (s, 3 H), 2.40 (s, 6 H), 3.80 (s, 3 H), 3.88 (s, 3 H), 6.57 (s, 1 H), 6.83-6.90 (m, 2 H), 6.91-6.98 (m, 2 H), 7.23-7.30 (m, 2 H), 7.71-7.78 (m, 2H) ppm.

*t-2-Dimethylamino-r-1,5,5-trimethyl-6-(4-methyl-benzoyl)-c-7a-p-tolyl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-dicarbonitrile* (**13b**) *and c-2-Dimethylamino-r-1,5,5-trimethyl-6-(4-methyl-benzoyl)-t-7a-p-tolyl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-dicarbonitrile* (**14b**)*:* Following the *general procedure* **4b** (305 mg, 829 µmol) and **5k** (150 mg, 1.76 mmol) in 10 ml acetonitrile yielded after fcc (petroleum ether 40/60 : ethyl acetate 1 : 2) and recrystallization from ethyl acetate/hexane 143 mg (315 µmol, 38 %) of **13b**, colourless crystals, m.p. 152-153 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3030, 2980, 2940, 2880, 2810, 1640, 1600, 1450, 1325, 1310, 1250, 1180 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.13 (s, 3 H), 1.93 (s, 3 H), 2.32 (s, 3 H), 2.44 (s, 3 H), 2.77 (s, 6 H), 6.80 (s, 1 H), 6.80-7.26 (m, 4 H), 7.27-7.33 (m, 2 H), 7.76-7.84 (m, 2 H) ppm. - $^{13}C$ NMR ($CDCl_3$, 63 MHz): $\delta$ = 14.69 (1 C), 20.49 (1 C), 20.95 (1 C), 21.61 (1 C), 31.23 (1 C), 41.85 (2 C), 42.07 (1 C), 54.70 (1 C), 70.38 (1 C), 77.93 (1 C), 79.79 (1 C), 116.92 (1 C), 116.99 (1 C), 126.55 (2 C), 129.01 (2 C), 129.22 (2 C), 129.36 (2 C), 136.26 (1 C), 137.42 (1 C), 139.40 (1 C), 142.36 (1 C), 143.56 (1 C), 146.90 (1 C), 192.77 (1 C) ppm. - EI MS (70 eV); m/z (%): 452 (2) [$M^+$], 368 (10), 367 (36) [ylide$^+$], 303 (5) [$M^+$ - $(CN)_2C$-$C_3H_5NMe_2$], 288 (10) [$M^+$ - $(CN)_2CC_3H_5NMe_2$ - $CH_3$], 119 (65) [$C_7H_7CO^+$], 91 (8) [$C_7H_7^+$], 85 (100) [$C_3H_5NMe_2^+$], 84 (12). - UV/VIS (1,4-dioxane): $\lambda_{max}$ ($\varepsilon$) = 262 (16350) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{29}H_{32}N_4O$ (452.6): calcd. C 76.96, H 7.13, N 12.38; found C 76.96, H 7.21, N 12.32. Furthermore could be obtained 158 mg (349 µmol, 42 %) of **14b**, colourless crystals, m.p. 142-143 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3080, 3060, 3020, 2980, 2940, 2880, 2840, 2800, 1635, 1600, 1455, 1445, 1380, 1320, 1265, 1255, 1205, 1190, 1175, 815, 750 $cm^{-1}$. - $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.53 (s, 3 H), 2.05 (s, 3 H), 2.33 (s, 3 H), 2.39

(s, 6 H), 2.43 (s, 3 H), 6.62 (s, 1 H), 7.14-7.16 (m, 2 H), 7.21-7.30 (m, 4 H), 7.59-7.66 (m, 2H) ppm. - $^{13}$C NMR ($CDCl_3$, 63 MHz, DEPT 135): δ = 11.32 (1 C, +), 20.92 (1 C, +), 21.57 (1 C, +), 22.82 (1 C, +), 30.08 (1 C, +), 44.96 (2 C, +) 47.44 (1 C, +), 55.05 (1 C, 0), 69.78 (1 C, 0), 76.76 (1 C, +), 83.73 (1 C, 0), 115.26 (1 C, 0), 117.30 (1 C, 0), 125.07 (2 C, +), 129.12 (2 C, +), 129.19 (2 C, +), 129.45 (2 C, +), 136.24 (1 C, 0), 137.18 (1 C, 0), 141.50 (1 C, +), 142.80 (1 C, 0), 143.55 (1 C, 0), 147.51 (1 C, 0), 192.35 (1 C, 0) ppm. - EI MS (70 eV); m/z (%): 904 (3) [$M_2^+$], 452 (100) [$M^+$], 367 (3) [ylide$^+$]. - UV/VIS (1,4-dioxane): $\lambda_{max}$ (ε) = 262 (15500) nm (l·mol$^{-1}$·cm$^{-1}$). - $C_{29}H_{32}N_4O$ (452.6): calcd. C 76.96, H 7.13, N 12.38; found C 76.92, H 7.25, N 12.32.

*6-(4-Methoxy-benzoyl)-c-7a-(4-methoxy-phenyl)-r-1,5,5-trimethyl-t-2-pyrrolidin-1-yl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**15a**) *and 6-(4-Methoxy-benzoyl)-t-7a-(4-methoxy-phenyl)-r-1,5,5-trimethyl-c-2-pyrrolidin-1-yl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**16a**)*:* Following the *general procedure* **4a** (98.8 mg, 247 μmol) and **5l** (47.5 mg, 427 μmol) were combined in 5 ml acetonitrile. The cycloadducts were not isolated, but analyzed by a $^1$H NMR spectroscopy. - $^1$H NMR ($CDCl_3$, 250 MHz): δ (**15a**) = 1.14 (s, 3 H), 1.90 (s, 3 H), 3.15-3.26 (m, 4 H), 6.76 (s, 1 H), 7.88-7.94 (m, 2 H) ppm; δ (**16a**) = 1.51 (s, 3 H), 2.02 (s, 3 H), 2.58-2.71 (m, 4 H), 6.57 (s, 1 H), 7.72-7.77 (m, 2 H) ppm; δ (**15a/16a**) = 1.70-1.90 (m, 8 H), 3.78 (s, 6 H), 3.87 (s, 6 H), 6.80-7.30 (m, 12 H) ppm.

*r-1,5,5-Trimethyl-6-(4-methyl-benzoyl)-t-2-pyrrolidin-1-yl-c-7a-p-tolyl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**15b**) *and r-1,5,5-Trimethyl-6-(4-methyl-benzoyl)-c-2-pyrrolidin-1-yl-t-7a-p-tolyl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**16b**)*:* Following the *general procedure* **4b** (145 mg, 395 μmol) and **5l** (55.4 mg, 498 μmol) in 6 ml acetonitrile yielded after fcc (petroleum ether 40/60 : diethyl ether from 3 : 1 to 1 : 1) 53.4 mg (112 μmol, 28 %) of **15b**, colourless unstable oil, that splits back into starting compunds. - $^1$H NMR ($CDCl_3$, 250 MHz): δ = 1.13 (s, 3 H), 1.77-1.85 (m, 4 H), 1.93 (s, 3 H), 2.32 (s, 3 H), 2.44 (s, 3 H), 3.17-3.26 (m, 4 H), 6.81 (s, 1 H), 7.05-7.20 (m, 4 H), 7.26-7.32 (m, 2 H), 7.77-7.85 (m, 2 H) ppm. - $^{13}$C NMR ($CDCl_3$, 101 MHz, DEPT 135/90): δ = 15.01 (1 C, +/0), 20.43 (1 C, +/0), 21.00 (1 C, +/0), 21.67 (1 C, +/0), 24.70 (2 C, -/0), 31.13 (1 C, +/0), 42.28 (1 C, +/+), 49.80 (2 C, -/0), 56.29 (1 C, 0/0), 70.26 (1 C, 0/0), 75.32 (1 C, +/+), 80.30 (1 C, 0/0), 117.20 (1 C, 0/0), 126.16 (1 C, 0/0), 126.53 (2 C, +/+), 128.99 (2 C, +/+), 129.22 (2 C, +/+), 129.38 (2 C, +/+), 136.18 (1 C, 0/0), 137.33 (1 C, 0/0), 139.51 (1 C, 0), 142.77 (1 C, +/+), 143.59 (1 C, 0/0), 146.72 (1 C, 0/0), 192.88 (1 C, 0/0) ppm. Furthermore could be obtained 40.3 mg (84.2 μmol, 21 %) of **16b**, colourless oil, that splits back into starting compunds. - $^1$H NMR ($CDCl_3$, 250 MHz): δ = 1.52 (s, 3 H), 1.77-1.87 (m, 4 H), 2.05 (s, 3 H), 2.32 (s, 3 H), 2.43 (s, 3 H), 2.60-2.70 (m, 4 H), 6.63 (s, 1 H), 7.10-7.16 (m, 2 H), 7.20-7.30 (m, 4 H), 7.60-7.65 (m, 2H) ppm. - $^{13}$C NMR ($CDCl_3$, 101 MHz, DEPT 135/90): δ = 11.70 (1 C, +/0), 20.90 (1 C, +/0), 21.56 (1 C, +/0), 22.75 (1 C, +/0), 23.42 (2 C, -/0), 30.22 (1 C, +/0), 48.39 (1 C, +/+), 53.14 (2 C, -/0), 55.73 (1 C, 0/0), 69.58 (1 C, 0/0), 75.37 (1 C, +/+), 83.92 (1 C, 0/0), 115.41 (1 C, 0/0), 117.28 (1 C, 0/0), 125.08 (2 C, +/+), 129.13 (2 C, +/+), 129.17 (2 C, +/+), 129.39 (2 C, +/+), 136.28 (1 C, 0/0), 137.08 (1 C, 0/0), 141.55 (1 C, +/+), 142.94 (1 C, 0/0), 143.50 (1 C, 0/0), 147.54 (1 C, 0/0), 192.39 (1 C, 0/0) ppm.

*6-Benzoyl-r-1,5,5-trimethyl-c-7a-phenyl-t-2-pyrrolidin-1-yl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**15c**) *and 6-Benzoyl-r-1,5,5-trimethyl-t-7a-phenyl-c-2-pyrrolidin-1-yl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**16c**)*:* Following the *general procedure* **4c** (108 mg, 318 μmol) and **5l** (55.4 mg, 498 μmol) were combined in 5 ml acetonitrile. The cycloadducts were not isolated, but analyzed by a $^1$H NMR spectroscopy. - $^1$H NMR ($CDCl_3$, 250 MHz): δ (**15c**) = 1.11 (s, 3 H), 1.95 (s, 3 H), 3.14-3.27 (m, 4 H), 6.85 (s, 1 H), 7.84-7.90 (m, 2 H) ppm; δ (**16c**) = 1.52 (s, 3 H), 2.07 (s, 3 H), 2.58-2.71 (m, 4 H), 6.66 (s, 1 H), 7.67-7.73 (m, 2 H) ppm; δ (**15c/16c**) = 1.70-1.90 (m, 8 H), 7.17-7.60 (m, 16 H) ppm.

*6-(4-Chloro-benzoyl)-c-7a-(4-chloro-phenyl)-r-1,5,5-trimethyl-t-2-pyrrolidino-1-yl-1,2,5,*

*7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**15d**) *and 6-(4-Chloro-benzoyl)-t-7a-(4-chloro-phenyl)-r-1,5,5-trimethyl-c-2-pyrrolidin-1-yl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**16d**): Following the *general procedure* **4d** (137 mg, 335 µmol) and **5l** (55.4 mg, 498 µmol) were combined in 5 ml acetonitrile. The cycloadducts were not isolated, but analyzed by a $^1$H NMR spectroscopy. - $^1$H NMR ($CDCl_3$, 250 MHz): δ (**15d**) = 1.11 (s, 3 H), 1.92 (s, 3 H), 3.13-3.28 (m, 4 H), 6.77 (s, 1 H), 7.79-7.84 (m, 2 H) ppm; δ (**16d**) = 1.48 (s, 3 H), 2.05 (s, 3 H), 2.60-2.70 (m, 4 H), 6.59 (s, 1 H), 7.63-7.69 (m, 2 H) ppm; δ (**15d/16d**) = 1.70-1.90 (m, 8 H), 7.15-7.52 (m, 12 H) ppm.

*6-(4-Methoxy-benzoyl)-c-7a-(4-methoxy-phenyl)-r-1,5,5-trimethyl-t-2-morpholin-4-yl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**17a**) *and 6-(4-Methoxy-benzoyl)-t-7a-(4-methoxy-phenyl)-r-1,5,5-trimethyl-c-2-morpholin-4-yl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**18a**): Following the *general procedure* **4a** (167 mg, 418 µmol) and **5m** (63.6 mg, 500 µmol) in 15 ml acetonitrile yielded after fcc (petroleum ether 40/60 : diethyl ether 1 : 2, 1 : 1) and recrystallization from $CH_2Cl_2$/hexane 50.0 mg (94.9 µmol, 23 %) of **17a**, colourless crystals, m.p. 163 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3070, 3000, 2980, 2960, 2930, 2910, 2850, 2830, 1590, 1500, 1325, 1300, 1245, 1165, 1110, 1020, 835 cm$^{-1}$. - $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.15 (s, 3 H), 1.91 (s, 3 H), 3.02-3.07 (m, 2 H), 3.19-3.24 (m, 2 H), 3.69-3.77 (m, 4 H), 3.79 (s, 3 H), 3.88 (s, 3 H), 6.75 (s, 1 H), 6.80-7.26 (m, 6 H), 7.89-7.92 (m, 2 H) ppm. - $^{13}$C NMR ($CDCl_3$, 101 MHz, DEPT 135): δ = 15.20 (1 C, +), 20.43 (1 C, +), 31.08 (1 C, +), 41.23 (1 C, +), 51.15 (2 C, -), 55.22 (1 C, +), 55.49 (1 C, +), 56.15 (1 C, 0), 67.66 (2 C, -), 70.40 (1 C, 0), 77.73 (1 C, +), 79.76 (1 C, 0), 113.68 (1 C, +), 113.77 (2 C, +), 116.55 (1 C, 0), 116.87 (1 C, 0), 127.57 (1 C, 0), 127.81 (2 C, 0), 131.36 (1 C, 0), 131.53 (2 C, +), 134.15 (1 C, 0), 141.02 (1 C, +), 146.70 (1 C, 0), 159.03 (1 C, 0), 163.54 (1 C, 0), 191.64 (1 C, 0) ppm. - FD MS ($CH_2Cl_2$); *m/z* (%): 526 (100) [M$^+$], 499 (20) [M$^+$ - HCN]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ (ε) = 227 (27200), 286 (19800) nm (l·mol$^{-1}$·cm$^{-1}$). - $C_{31}H_{34}N_4O_4$ (526.6): calcd. C 70.71, H 6.51, N 10.64; found C 70.66, H 6.72, N 10.49. As the cycloadduct **18a** is very unstable - it splits almost completely during fcc into the starting compounds - only 20.0 mg (38.0 µmol, 9 %) could be obtained as a purple oil. - $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.52 (s, 3 H), 2.03 (s, 3 H), 2.53-2.63 (m, 4 H), 3.77-3.81 (m, 4 H), 3.80 (s, 3 H), 3.88 (s, 3 H), 6.57 (s, 1 H), 6.86-6.90 (m, 2 H), 6.93-6.97 (m, 2 H), 7.24-7.29 (m, 2 H), 7.73-7.77 (m, 2H) ppm. - $^{13}$C NMR ($CDCl_3$, 101 MHz, DEPT 135): δ = 11.38 (1 C, +), 22.77 (1 C, +), 30.11 (1 C, +), 46.25 (1 C, +), 52.55 (2 C, -), 54.25 (1 C, 0), 55.31 (1 C, +), 55.52 (1 C, +), 66.26 (2 C, -), 69.86 (1 C, 0), 75.04 (1 C, +), 83.25 (1 C, 0), 113.76 (2 C, +), 114.12 (2 C, +), 114.81 (1 C, 0), 117.08 (1 C, 0), 126.16 (2 C, +), 131.29 (2 C, +), 131.36 (1 C, 0), 137.55 (1 C, 0), 140.08 (1 C, +), 147.29 (1 C, 0), 158.82 (1 C, 0), 163.49 (1 C, 0), 191.34 (1 C, 0) ppm.

*r-1,5,5-Trimethyl-6-(4-methyl-benzoyl)-t-2-morpholin-4-yl-c-7a-p-tolyl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**17b**) *and r-1,5,5-Trimethyl-6-(4-methyl-benzoyl)-c-2-morpholin-4-yl-t-7a-p-tolyl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**18b**): Following the *general procedure* **4b** (174 mg, 473 µmol) and **5m** (79.5 mg, 625 µmol) in 15 ml acetonitrile yielded after fcc (petroleum ether 40/60 : diethyl ether from 5 : 1 to 2 : 1) and recrystallization from $CH_2Cl_2$/hexane 75.0 mg (152 µmol, 32 %) of **17b**, colourless crystals, m.p. 158 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3060, 3010, 2960, 2910, 2840, 1630, 1590, 1440, 1370, 1310, 1245, 1165, 1100, 740 cm$^{-1}$. - $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.13 (s, 3 H), 1.93 (s, 3 H), 2.32 (s, 3 H), 2.44 (s, 3 H), 3.02-3.07 (m, 2 H), 3.19-3.24 (m, 2 H), 3.69-3.78 (m, 4 H), 6.79 (s, 1 H), 6.85-7.26 (m, 4 H), 7.28-7.30 (m, 2 H), 7.77-7.80 (m, 2 H) ppm. - $^{13}$C NMR ($CDCl_3$, 101 MHz, DEPT 135): δ = 15.15 (1 C, +), 20.45 (1 C, +), 20.97 (1 C, +), 21.64 (1 C, +), 31.06 (1 C, +), 41.09 (1 C, +), 51.14 (2 C, -), 56.18 (1 C, 0), 67.67 (2 C, -), 70.27 (1 C, 0), 77.67 (1 C, +), 79.93 (1 C, 0), 116.57 (1 C, 0), 116.82 (1 C, 0), 126.41 (1 C, 0), 128.81 (1 C, 0), 129.06 (2 C, +), 129.20 (2 C, +), 129.31 (2 C, +), 136.05 (1 C, 0), 137.53 (1 C, 0), 139.05 (1 C, 0), 142.21 (1 C, +), 146.65 (1 C, 0), 146.75 (1 C, 0), 192.65 (1 C, 0) ppm. - FD MS ($CH_2Cl_2$); *m/z* (%): 494 (100) [M$^+$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ (ε) = 220 (21600), 265 (14800) nm (l·mol$^{-1}$·cm$^{-1}$). - $C_{31}H_{34}N_4O_2$ (494.6): calcd.

C 75.28, H 6.93, N 11.33; found C 74.98, H 7.13, N 11.07. As the cycloadduct **18b** is very unstable - it splits almost completely during fcc into the starting compounds - only 43.0 mg (38.0 µmol, 9 %) could be obtained as a purple oil. - $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.53 (s, 3 H), 2.05 (s, 3 H), 2.33 (s, 3 H), 2.44 (s, 3 H), 2.52-2.68 (m, 4 H), 3.73-3.82 (m, 4 H), 6.62 (s, 1 H), 7.14-7.16 (m, 2 H), 7.19-7.24 (m, 2 H), 7.25-7.29 (m, 2 H), 7.62-7.64 (m, 2H) ppm. - $^{13}$C NMR ($CDCl_3$, 101 MHz, DEPT 135): δ = 11.32 (1 C, +), 20.92 (1 C, +), 21.59 (1 C, +), 22.77 (1 C, +), 30.02 (1 C, +), 46.20 (1 C, +), 52.52 (2 C, -), 54.25 (1 C, 0), 66.25 (2 C, -), 69.72 (1 C, 0), 74.98 (1 C, +), 83.49 (1 C, 0), 114.78 (1 C, 0), 117.05 (1 C, 0), 124.95 (2 C, +), 129.06 (2 C, +), 129.17 (2 C, +), 129.48 (2 C, +), 136.08 (1 C, 0), 137.27 (1 C, 0), 141.43 (1 C, +), 142.44 (1 C, +), 143.60 (1 C, 0), 147.41 (1 C, 0), 192.30 (1 C, 0) ppm.

*6-(Benzoyl)-r-1,5,5-trimethyl-t-2-morpholin-4-yl-c-7a-phenyl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**17c**) *and 6-(Benzoyl)-r-1,5,5-trimethyl-c-2-morpholin-4-yl-t-7a-phenyl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**18c**)*:* Following the *general procedure* **4c** (117 mg, 345 µmol) and **5m** (58.5 mg, 460 µmol) in 15 ml acetonitrile yielded after fcc (petroleum ether 40/60 : diethyl ether 1 : 1) and recrystallization from diethyl ether/hexane 37.2 mg (79.7 µmol, 23 %) of **17c**, colourless crystals, m.p. 207 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3060, 3020, 2970, 2950, 2930, 2910, 2850, 2820, 1640, 1590, 1440, 1380, 1315, 1250, 1175, 1110, 850, 710, 695 cm$^{-1}$. - $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.13 (s, 3 H), 1.96 (s, 3 H), 3.02-3.08 (m, 2 H), 3.18-3.25 (m, 2 H), 3.69-3.78 (m, 4 H), 6.84 (s, 1 H), 6.90-7.55 (m, 7 H), 7.58-7.63 (m, 1 H), 7.86-7.90 (m, 2 H) ppm. - $^{13}$C NMR ($CDCl_3$, 101 MHz, DEPT 135/90): δ = 15.14 (1 C, +/0), 20.44 (1 C, +/0), 31.00 (1 C, +/0), 41.04 (1 C, +/+), 51.12 (2 C, -/0), 56.16 (1 C, 0/0), 67.65 (2 C, -/0), 70.28 (1 C, 0/0), 77.63 (1 C, +/+), 80.06 (1 C, 0/0), 116.47 (1 C, 0/0), 116.77 (1 C, 0/0), 126.47 (2 C, 0/0), 127.83 (2 C, +/+) 128.41 (1 C, +/+), 128.53 (2 C, +/+), 129.12 (2 C, +/+), 132.82 (1 C, +/+), 138.62 (1 C, 0/0), 141.98 (1 C, 0/0), 142.72 (1 C, +/+), 146.92 (1 C, 0/0), 192.89 (1 C, 0/0) ppm. - FD MS ($CH_2Cl_2$); *m/z* (%): 466 (100) [M$^+$]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ (ε) = 251 (13900) nm (l·mol$^{-1}$·cm$^{-1}$). - $C_{29}H_{30}N_4O_2$ (494.6): calcd. C 74.65, H 6.48, N 12.00; found C 74.51, H 6.56, N 11.91. As the cycloadduct **18c** is very unstable - it splits almost completely during fcc into the starting compounds - only 50.0 mg (107 µmol, 31 %) could be obtained as a purple oil. - $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.53 (s, 3 H), 2.08 (s, 3 H), 2.52-2.59 (m, 2 H), 2.60-2.71 (m, 2 H), 3.74-3.82 (m, 4 H), 6.67 (s, 1 H), 7.24-7.28 (m, 1 H), 7.33-7.37 (m, 4 H), 7.44-7.49 (m, 2 H), 7.56-7.60 (m, 1 H), 7.70-7.74 (m, 2 H) ppm. - $^{13}$C NMR ($CDCl_3$, 101 MHz, DEPT 135): δ = 11.34 (1 C, +/0), 22.73 (1 C, +/0), 30.03 (1 C, +/0), 46.20 (1 C, +/+), 52.53 (2 C, -/0), 54.28 (1 C, 0/0), 66.24 (2 C, -/0), 69.78 (1 C, 0/0), 74.87 (1 C, +/+), 83.66 (1 C, 0/0), 114.75 (1 C, 0/0), 116.98 (1 C, 0/0), 125.02 (2 C, +/+), 127.55 (1 C, +/+), 128.53 (2 C, +/+), 128.89 (2 C, +/+), 128.90 (2 C, +/+), 132.76 (1 C, +/+), 138.65 (1 C, 0/0), 141.96 (1 C, +/+), 145.27 (1 C, 0/0), 147.60 (1 C, 0/0), 192.52 (1 C, 0/0) ppm.

*6-(4-Chloro-benzoyl)-c-7a-(4-chloro-phenyl)-r-1,5,5-trimethyl-t-2-morpholin-4-yl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**17d**) *and 6-(4-Chloro-benzoyl)-t-7a-(4-chloro-phenyl)-r-1,5,5-trimethyl-c-2-morpholin-4-yl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-carbonitrile* (**18d**)*:* Following the *general procedure* **4d** (187 mg, 458 µmol) and **5m** (76.5 mg, 601 µmol) in 20 ml acetonitrile yielded after fcc (petroleum ether 40/60 : diethyl ether 1 : 1) and recrystallization from acetonitrile 43.2 mg (80.7 µmol, 18 %) of **17d**, colourless crystals, m.p. 184-185 °C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3090, 3060, 2960, 2920, 2870, 2840, 1650, 1580, 1480, 1445, 1390, 1290, 1250, 1170, 1080, 1000, 830 cm$^{-1}$. - $^1$H NMR ($CDCl_3$, 400 MHz): δ = 1.12 (s, 3 H), 1.94 (s, 3 H), 3.01-3.08 (m, 2 H), 3.17-3.24 (m, 2 H), 3.69-3.78 (m, 4 H), 6.76 (s, 1 H), 6.90-7.44 (m, 4 H), 7.46-7.49 (m, 2 H), 7.80-7.83 (m, 2 H) ppm. - $^{13}$C NMR ($CDCl_3$, 101 MHz, DEPT 135/90): δ = 15.22 (1 C, +/0), 20.38 (1 C, +/0), 31.06 (1 C, +/0), 40.96 (1 C, +/+), 51.10 (2 C, -/0), 56.02 (1 C, 0/0), 67.61 (2 C, -/0), 70.52 (1 C, 0/0), 77.67 (1 C, +/+), 79.74 (1 C, 0/0), 116.21 (1 C, 0/0), 116.66 (1 C, 0/0), 127.74 (2 C, 0/0), 128.72 (2 C, +/+) 128.96 (2 C, +/+), 130.50 (2 C, +/+), 133.94 (1 C, 0/0), 136.72 (1 C, 0/0), 139.48 (1 C, 0/0), 140.49 (1 C, 0/0),

141.81 (1 C, +/+), 147.24 (1 C, 0/0), 191.51 (1 C, 0/0) ppm. - FD MS ($CH_2Cl_2$); *m/z* (%): 534 (100) [$M^+$], 507 (40) [$M^+$ - HCN]. - UV/VIS ($CH_3CN$): $\lambda_{max}$ ($\varepsilon$) = 218 (21700), 263 (17400) nm ($l \cdot mol^{-1} \cdot cm^{-1}$). - $C_{29}H_{28}N_4Cl_2O_2$ (535.5): calcd. C 65.05, H 5.27, N 10.46; found C 64.79, H 5.36, N 10.50. As the cycloadduct **18d** is very unstable - it splits almost completely during fcc into the starting compounds - only 4.00 mg (7.47 µmol, 2 %) could be obtained as a purple oil. - $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.39 (s, 3 H), 2.03 (s, 3 H), 2.48-2.63 (m, 2 H), 2.79-2.87 (m, 2 H), 3.70-3.82 (m, 4 H), 6.67 (s, 1 H), 7.28-7.33 (m, 4 H), 7.42-7.49 (m, 2 H), 7.72-7.79 (m, 2 H) ppm.

*HPLC Experiments:* The analysis for the isomers **7b/8b** and **13b/14b** were performed with a 250 x 4mm Lichrospher Si 60 (5 µm) column, eluents: $CH_3CN$, hexane, $CH_2Cl_2$-mixtures, 2 ml/min, UV detection: 290 nm. The analysis for the systems **7a/8a**, **7d/8d**, **11a/12a**, **11b/12b**, **11d/12d** were carried out on a LiChroCART 250-4 HPLC-Cartridge Purospher RP-18 endcapped (5 µm), eluents: water, acetonitrile-mixtures, 1 ml/min, UV detection: 221-227 nm. Internal standard was always 1,2-diphenyl-acetylene (concentration: 0.26 mg/ml).

*Dependence of Isomer Ratio* **7b/8b** *and* **13b/14b** *on the Solvent Polarity:* Analogous to the general procedure for the cycloaddition (see above) azomethine ylides **3b** and **4b** were combined with enamine **5k**. After evaporation of the solvent the residue was dissolved in $CH_2Cl_2$. To 100 µl of this solution were added 100 µl solution of the internal standard, and these samples were analyzed (data Table 11, conditions Table 12).

*General Procedure of the Stability Tests for the Cycloadducts* **7a,b,d/8a,b,d**, *and* **11a,b,d/12a,b,d**, *and* **13b/14b**: A solution of the cycloadducts in acetonitrile (1.9-4.1 µmol/ml) was prepared and heated to 70°C (50°C for **13b/14b**). After a period of 116 to 288 hours a sample of 100 µl was added to 100 µl internal standard and then analyzed by HPLC [19] (vide supra). The concentration of the cycloadducts of AMY-I remained constant, whereas the adducts **13b/14b** are not stable.

**Table 11.** Data for the reaction of AMY-I **3b** with enamine **5k** in various solvents

| | acetonitrile | chloroform | acetone | dioxane | toluene |
|---|---|---|---|---|---|
| **3b** [mg] | 105 | 22.8 | 24.5 | 20.6 | 23.4 |
| ([µmol]) | (287) | (62.3) | (66.9) | (56.1) | (63.9) |
| **5k** [mg] | 29.7 | 7.04 | 9.12 | 156 | 7.01 |
| ([µmol]) | (349) | (82.7) | (107) | (1830) | (82.3) |
| volume [ml] | 25 | 5 | 5 | 100 | 50 |
| reaction time | 3 h | 70 h | 11 h | 26 h | 49 d |
| **7b + 8b** [%] | 100 | 73 | 73 | 80 | 22 |
| **7b : 8b** | 48 : 52 | 52 : 48 | 56 : 44 | 65 : 35 | 54 : 46 |

**Table 12.** Data for the reaction of AMY-II **4b** with enamine **5k** in various solvents.

| | acetonitrile | $CH_2Cl_2$ | ethyl acetate | dioxane | toluene |
|---|---|---|---|---|---|
| **4b** [mg] | 305 | 14.4 | 14.1 | 14.5 | 13.8 |
| ([µmol]) | (829) | (39.2) | (38.5) | (39.3) | (37.5) |
| **5k** [mg] | 150 | 4.52 | 4.38 | 4.89 | 6.01 |
| ([µmol]) | (1760) | (53.1) | (51.4) | (57.4) | (70.6) |
| volume [ml] | 10 | 10 | 10 | 10 | 10 |
| reaction time | 4.5 h | 165 h | 165 h | 384 h | 384 h |
| **13b + 14b** [%] | 98 | 50 | 61 | 34 | 38 |
| **13b : 14b** | 45 : 55 | 25 : 75 | 23 : 77 | 16 : 84 | 10 : 90 |

*Procedure for Trapping Experiments with Cyclooctyne:* A solution of the cycloadducts **7b**, **8b**, **13b**, respectively **14b** together with cyclooctyne in acetonitrile is put under inert gas into 1 ml ampoules. These are heated to 70°C (**7b**, **8b**) respectively 50°C (**13b**, **14b**). For analysis these ampoules are opened, the solvent is evaporated, the residue is solved in $CH_2Cl_2$, and the internal standard (100 µl) is added to 100 µl of these samples. For the compounds **7b** and **8b** no cycloadduct of AMY-I **3b** with cyclooctyne could be detected within 144 hours, whereas **13b** and **14b** form these cyclooctyne adducts. Using the data for the decrease of the adduct concentrations with time the rate constants for the splitting of **13b** and **14b** were calculated. The concentrations of the compounds were: $1.629 \cdot 10^{-9}$ mol/l (**7b**) + $3.80 \cdot 10^{-9}$ mol/l cyclooctyne, $1.645 \cdot 10^{-9}$ mol/l (**8b**) + $3.80 \cdot 10^{-9}$ mol/l cyclooctyne, $4.000 \cdot 10^{-9}$ mol/l (**13b**) + $3.69 \cdot 10^{-8}$ mol/l cyclooctyne, : $3.940 \cdot 10^{-9}$ mol/l (**14b**) + $3.70 \cdot 10^{-9}$ mol/l cyclooctyne.

## ACKNOWLEDGEMENTS

We are grateful to the Deutsche Forschungsgemeinschaft (DFG), the Fonds der Chemischen Industrie and the BASF AG for financial support of this research. Furthermore, we thank Dr. E. Eibler and R. Vasold for sharing their HPLC equipment and their aid.

## REFERENCES

[1] Huisgen R. 1,3-Dipolar Cycloaddtions - Introduction, Survey, Mechanism. In 1,3-Dipolar Cycloaddition Chemistry; Padwa A. editor, New York: John Wiley, 1984; 35-42.
[2] Huisgen R. Pure & Appl. Chem. 1981; 53: 171-187.
[3] Huisgen R. Steric Course and Mechanism of 1,3-Dipolar Cycloadditions. In Advances in Cycloaddition, Vol. 1; Curran DP, editor, New York: JAI Press, 1988; 1-31.
[4] Dorn H, Ozegowski R, Gründemann E. J. Prakt. Chem. 1979; 321: 555-564.
[5] Huisgen R, Weinberger R. Tetrahedron Lett. 1985; 26: 5119-5122.
[6] Dorn H. Tetrahedron Lett. 1985; 26: 5123-5126.
[7] Huisgen R, Mloston G, Langhals E. J. Am. Chem. Soc. 1986; 108: 6401-6402.
[8] Huisgen R, Langhals E, Nöth H. Tetrahedron Lett. 1986; 27: 5475-5478.
[9] Huisgen R, Mloston G, Langhals E. J. Org. Chem. 1986; 51: 4085-4087.
[10] Riebel P, Weber A, Troll T, Sauer J, Breu J. Tetrahedron Lett. 1996, 37: 1583-1586.
[11] Riebel P, Weber A, Troll T, Sauer J, Breu J, Nöth H. Tetrahedron Lett. 1996, 37: 1587-1590.
[12] Breu J, Range KJ, Riebel P, Weber A, Sauer J. Acta Cryst. Section C 1996; 52: 2053-2056.
[13] Weber A, Sauer J. Tetrahedron Lett. 1998: 39: 807-810.
[14] Böhm T, Elender K, Riebel P, Troll T, Weber A, Sauer J. Tetrahedron, preceeding publication.
[15] Sauer J, Prahl H. Chem. Ber. 1969; 102: 1917-1927.
[16] Breu J. Range KJ, Weber A, Sauer J. Acta Cryst. Section C 1998; 54: 509-513.
[17] Cioslowski J, Sauer J, Hetzenegger J, Karcher T, Hierstetter T. J. Am. Chem. Soc. 1993; 115: 1353-1359.
[18] Böhm, T. Stereo*un*spezifische 1,3-dipolare Cycloadditionen von Azomethinyliden mit Enaminen, Ph.D.-Thesis, University of Regensburg, 1999.