Cope Rearrangements versus Retro Diels–Alder Reactions**

Karin Beck, Petra Hoffman, and Siegfried Hünig*

Dedicated to Professor Dr. Dieter Seebach on the occasion of his 60th birthday

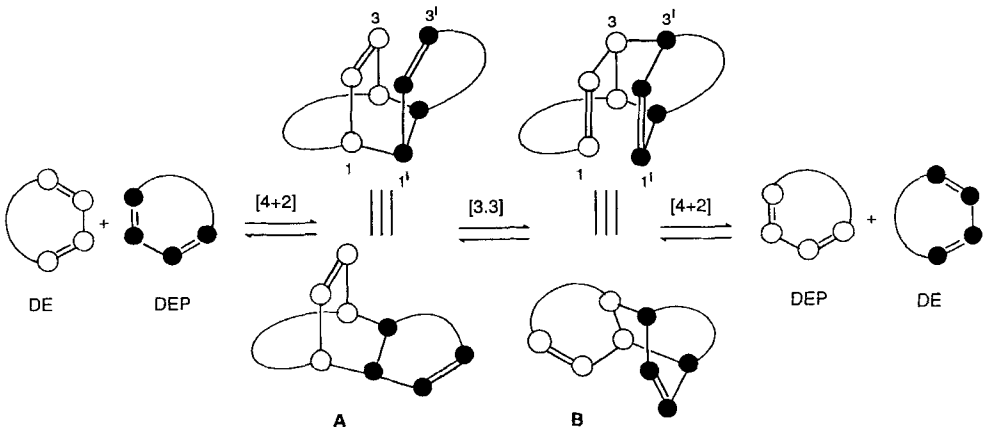
Abstract: The two isomeric [4+2] cycloadducts from two different 1,3-dienes may result from direct cycloadditions as well as from Cope rearrangements (Scheme 1). This general question is tackled by employing two energetically different types of dienes, protonated pyrazolines ($\mathbf{1}H^+$, $\mathbf{2}H^+$) or dihydropyridazines ($\mathbf{3}H^+$), prepared in situ from their trimers and alicyclic (**4**–**6**) or aliphatic (**7**–**9**) 1,3-dienes. Depending on structural features and conditions (amount of acid, reaction time), various ratios of the two isomeric [4+2] cycloadducts **A** and **B** are obtained; **A** and **B** are azo compounds **10**, **14**, **16**, **20**, **22**, **24**, **27**, **32**, **34**, **36**–**39**, **41**, **42**, pyrazolines *endo*-**11**, *endo*-**13**, *endo*-**15**, *endo-endo*-**17**, *endo*-**18**, *endo*-**19**, **21**, **23**, **25**, **26**, **28**, and hydropyridazines **31**, *endo*-**33**, *endo*-**35**, **40** and **43** (Schemes 3, 4). These results were backed by others from acid-catalyzed isomerizations, trapping experiments, and calculations of the equilibria ($\Delta\Delta H$) between the isomers (by analogy with the corresponding olefins). A critical discussion reveals: a) Azo compounds **20**, **22**, **24**, **27**, **34**, **38**, and **42** must result from a [4⁺+2] cycloaddition with inverse electron demand, whereas hydropyridazines *endo*-**33**, *endo*-**35**, **40**, and **43** originate from a [4+2⁺] cycloaddition with normal electron demand. b) All isomerizations occur by a [3,3] sigmatropic rearrangement; [4+2] cycloreversion is energetically disfavored. c) A clear-cut distinction between the [4⁺+2] or [4+2⁺] cycloaddition reaction routes to the energetically well-balanced systems **10**⇌*endo*-**11** and **12**⇌*endo*-**13** is not possible. d) The two cycloadditions may well favor a nonconcerted reaction through an allylic cationic intermediate which also governs the [3,3] rearrangements (Scheme 8).

Keywords
azo compounds · cycloadditions · hydropyridazines · pyrazolines · rearrangements

Introduction

In Diels–Alder type [4+2] cycloadditions diene (DE) and dienophile (DEP) are normally unequivocally defined. However, the situation becomes much more complex if both components are 1,3-diene systems. As depicted in Scheme 1, two products, **A** and **B**, are possible. Starting with two dienes of different HOMO/LUMO energies, **A** and **B** could arise from a Diels–Alder [4+2] cycloaddition with either normal or inverse[1] electron demand,[2] or from a [3,3] rearrangement, since both products **A** and **B** contain 1,5-diene systems in the correct geometry for Cope rearrangements. As both [4+2] cycloadditions and [3,3] rearrangements have been proven to be reversible, products **A** and/or **B** may result from different reaction routes.

The problems outlined in Scheme 1 were first tackled in 1959 by Woodward and Katz. They clearly demonstrated [3,3] rearrangement between α-1-hydroxydicyclopentadiene and *syn*-8-hydroxydicyclopentadiene at only 140 °C.[3] Despite these results, the thermal decomposition of *endo*-dicyclopentadiene at ca. 200 °C into cyclopentadiene is still quoted as a typical example for the reversibility of a classical Diels–Alder reaction.[4]



Scheme 1. Relationship between Diels–Alder reactions and Cope rearrangements starting with two different 1,3-dienes.

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[**] Azo Bridges from Azines, Part 25; for Part 24 see U. Brand, S. Hünig, K. Peters, F. Prokschy, H. G. von Schnering, *Liebigs Ann.* **1997**, 785–789.

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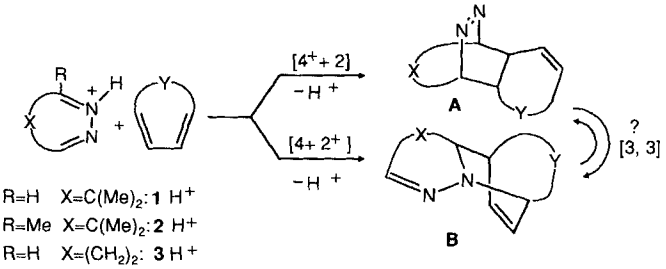
To the best of our knowledge the general consequences of the interconnected reactions in Scheme 1 have not been explicitly expressed so far. However, a series of isomerizations of type **A** or **B** products have been attributed to Cope rearrangements, although their intramolecular character has been demonstrated in only a few cases.[2, 5]

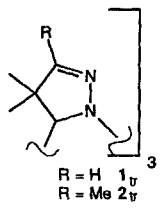
We now present new results starting from cyclic azines **1**–**3** and (cyclic) 1,3-dienes as 4π and/or 2π systems with greatly differing HOMO and LUMO energies.[6] Formation and interconversion of products of type **A** and/or **B** will be considered with respect to the ring size[7] of the components and the presence of acid.

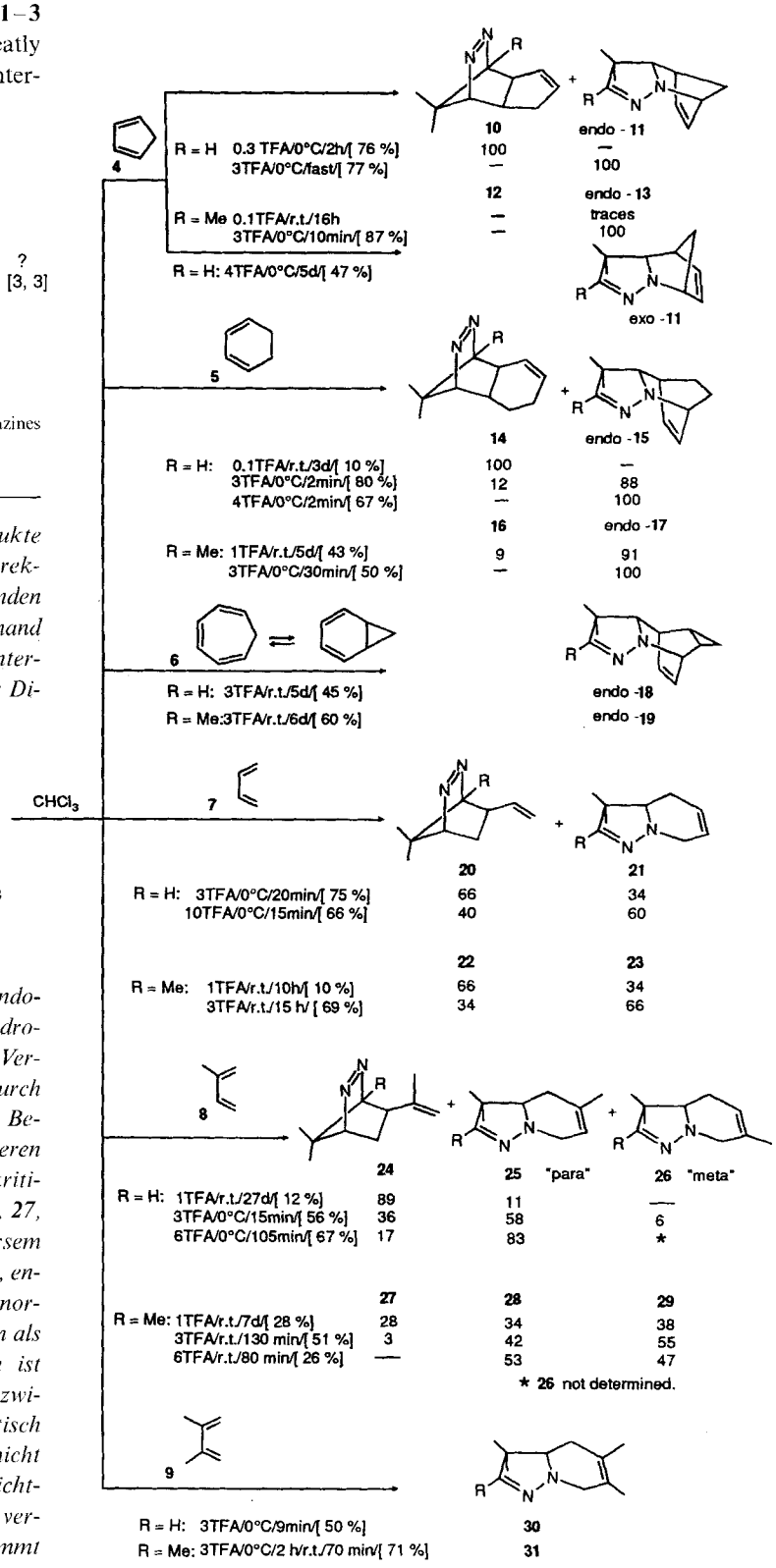
Azines **1**–**3** have to be prepared in situ from their trimers by acid catalysis. The protonated monomers act as highly reactive dienes with a variety of alkenes in a $[4^+ + 2]$ cycloaddition, that



Scheme 2. General reaction scheme for [4 + 2] cycloadditions of protonated azines **1**–**3** with 1,3-dienes.

Abstract in German: *Die beiden isomeren [4+2]-Cycloaddukte aus zwei unterschiedlichen 1,3-Dienen können sowohl durch direkte Cycloaddition als auch durch Cope-Umlagerung entstanden sein (Schema 1). Dieses allgemeine Problem wird hier anhand zweier energetisch unterschiedlicher Typen von 1,3-Dienen untersucht, der protonierten Pyrazoline* ***1*** H^+ *und* ***2*** H^+ *sowie des Dihydropyridazins* ***3*** H^+ *(in situ hergestellt aus ihren Trimeren) einerseits und der alicyclischen und aliphatischen 1,3-Diene* ***4***–***6*** *bzw.* ***7***–***9*** *andererseits. In Abhängigkeit von den Struktureigenschaften und den Reaktionsbedingungen (Menge an Säure, Reaktionszeit) erhält man die isomeren [4+2]-Cycloaddukte – die Azoverbindungen* ***10***, ***14***, ***16***, ***20***, ***22***, ***24***, ***27***, ***32***, ***34***, ***36***–***39***, ***41*** *und* ***42***, *die Pyrazoline endo-****11***, *endo-****13***, *endo-****15***, *endo-****17***–*endo-****19***, ***21***, ***23***, ***25***, ***26*** *und* ***28***–***31*** *sowie die Hydropyridazine endo-****33***, *endo-****35***, ***40*** *und* ***43***—*in unterschiedlichen Verhältnissen (Schema 3·4). Diese Ergebnisse werden vertieft durch säurekatalysierte Isomerisierungen, Abfangexperimente und Berechnungen der Gleichgewichte (ΔΔH) zwischen den Isomeren anhand der Analogie zu den entsprechenden Olefinen. Eine kritische Diskussion ergibt: a) Die Azoverbindungen* ***20***, ***22***, ***24***, ***27***, ***34***, ***38*** *und* ***42*** *werden durch [4⁺ + 2]-Cycloaddition mit inversem Elektronenbedarf gebildet, und die Hydropyridazine endo-****33***, *endo-****35***, ***40*** *und* ***43*** *entstehen durch [4 + 2⁺]-Cycloaddition mit normalem Elektronenbedarf. b) Alle Isomerisierungen verlaufen als [3,3]-sigmatrope Umlagerung, die [4+2]-Cycloreversion ist energetisch stark benachteiligt. c) Eine klare Entscheidung zwischen [4⁺ + 2]- und [4 + 2⁺]-Cycloaddition ist in den energetisch ausbalancierten Systemen* ***10*** ⇌ *endo-****11*** *und* ***12*** ⇌ *endo-****13*** *nicht möglich. d) Die beiden Cycloadditionen könnten bevorzugt nichtkonzertiert über eine allylische, kationische Zwischenstufe verlaufen, die dann auch den Verlauf der Umlagerung bestimmt (Schema 8).*





Scheme 3. Cycloadditions of isopyrazolium ions **1** H^+ and **2** H^+ (generated from $\mathbf{1}_{tr}$ and $\mathbf{2}_{tr}$ by TFA in $CHCl_3$) with dienes **4**–**9**.

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is, a Diels–Alder reaction with inverse electron demand;[8] however, a [4+2⁺] cycloaddition with **1**–**3**H⁺ acting as dienophiles must also be considered.

These protonated azines were subjected to reactions with cyclic 1,3-dienes as shown in Scheme 3, and also with some 1,3-butadiene derivatives. Taking thermal and acid-catalyzed rearrangements of the products into account, we expected to gain a deeper understanding of the ambiguous reaction path. Formation of products **A** and/or **B** has already been observed with cyclopentadiene[6, 9] and cyclohexadiene.[6, 9, 10]

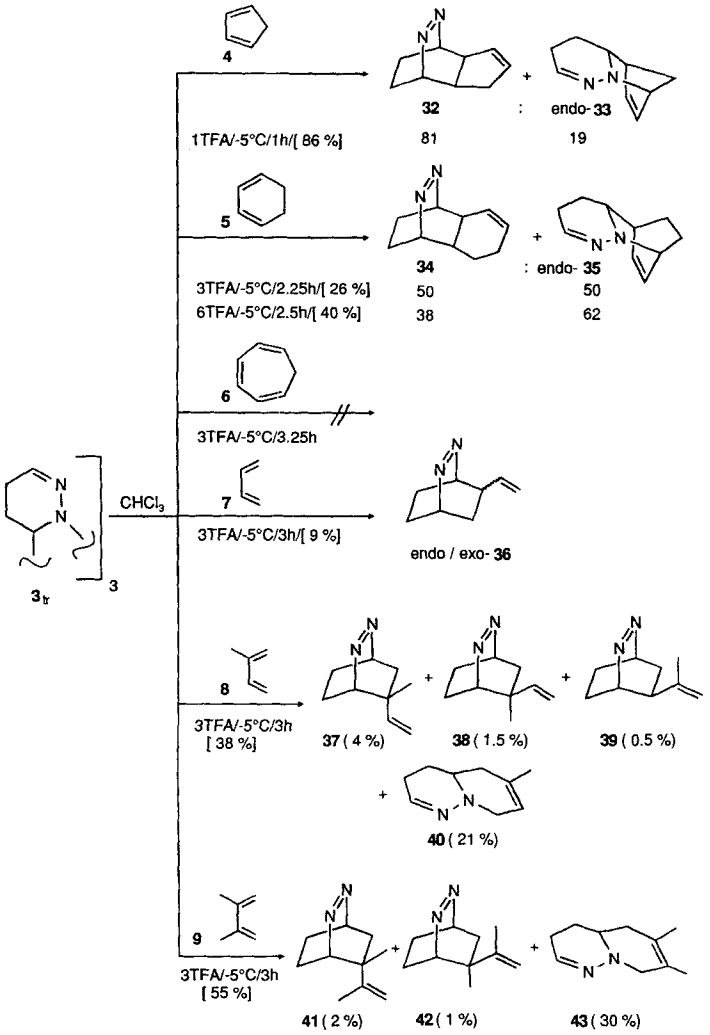
Results

1. Cycloadditions with isopyrazolium ions 1H⁺ and 2H⁺: The protonated cyclic azines **1**H⁺ and **2**H⁺ were liberated from the corresponding trimers in chloroform solution by trifluoroacetic acid (TFA) in either catalytic (0.1 equiv)[8a–d] or at least stoichiometric (1–10 equiv) amounts in the presence of 1,3-dienes **4**–**9** at 0–25 °C for a period varying from minutes to days. The results collected in Scheme 3 allow the following generalizations:

a) In accordance with earlier observations,[8a–d] introduction of a methyl group (**1**H⁺ → **2**H⁺) was found to diminish the reactivity of these cyclic azines.
b) The reactivities of 1,3-dienes ranked in the order cyclopentadiene (**4**) ≫ cyclohexa-1,3-diene (**5**) > 2,3-dimethyl-1,3-butadiene (**9**) > isoprene (**8**) > 1,3-butadiene (**7**) > cycloheptatriene (**6**).
c) Increasing amounts of TFA (0.1 → 10 equiv) enhanced the cycloadditions dramatically.
d) With dienes **6** and **9**, only one cycloaddition product, the pyrazolines *endo*-**18**/*endo*-**19** (R = H or Me) or **30**/**31**, respectively, were obtained.
e) With dienes **4**, **5**, **7**, and **8**, both the azo-bridged compounds **10**/**12**, **14**/**16**, **20**/**22**, and **24**/**27** and the isomeric pyrazolines *endo*-**11**/*endo*-**13**, *endo*-**15**/*endo*-**17**, **21**/**23**, and **25** + **26**/**28** + **29**, respectively, could be isolated.
f) With small amounts of TFA the azo-bridged cycloadducts were formed exclusively (**10**[8a–c], **14**[10]) or predominantly (**20**, **22**, **24**) whereas with excess TFA the isomeric pyrazolines were the only cycloaddition products (*endo*-**11**,[10] *endo*-**13**, *endo*-**15**,[10] *endo*-**17**) or at least the preferred ones (**22**, **23**, **25**, **28**).
g) Cycloadditions to give the azo-bridged compounds **16**, **22**, and **27** occurred highly regioselectively, since only the isomers with R = Me close to the olefinic bond could be detected.
h) Reaction of **1**H⁺ and **2**H⁺ with isoprene (**8**) interestingly yielded two isomeric pyrazolines (**25** + **26**/**28** + **29**).
i) Isomerization of *endo*- into *exo*-pyrazolines by prolonged treatment with TFA was only successful in the case of *endo*-**11** → *exo*-**11**.

2. Cycloadditions with 4,5-dihydropyridaziniumion 3H⁺: From earlier experiences the much-diminished reactivity of **3**H⁺, prepared from its trimer $\mathbf{3}_{tr}$ in situ, was already known. Only the highly reactive dienophiles norbornene and norbornadiene furnished the [4+2] cycloaddition products (Scheme 1), and then only in yields of 7% and 5%. However, with cyclopentadiene the azo-bridged product **32** was isolated in 67% yield.[8] Only fast cycloadditions with **3**H⁺ can succeed, since the acid also triggers the well-known imine–enamine tautomerism between 4,5- and 1,4-dihydropyridazines with subsequent polymerization.[11]

Scheme 4 shows the results obtained from $\mathbf{3}_{tr}$ and the dienes **4**–**9**. Again cyclopentadiene turned out to be the reactive diene,



Scheme 4. Cycloadditions of 4,5-dihydropyridazinium ion **3**H⁺ (generated from $\mathbf{3}_{tr}$ by TFA in $CHCl_3$) with 1,3-dienes **4**–**9**.

yielding appreciable amounts of the isomeric hydropyridazine *endo*-**33** besides the already known azo compound **32**.[8b] The two classes of cycloadducts were also found with olefins **5**, **8**, and **9**. Cycloheptatriene (**6**) was not attacked by **3**H⁺, in sharp contrast to **1**H⁺ and **2**H⁺ (Scheme 3). Due to the very low reactivity of butadiene (**7**) the reaction with **3**H⁺ afforded a mixture of undefined products from which only *endo*/*exo*-**36** could be isolated.

3. Cycloadditions and synthesis of a seven-membered azine (44H⁺): Given the disappointing experiences with **3**H⁺, use of a still larger ring, the seven-membered azine **44**H⁺, seemed not to be very promising. Indeed, **44**H⁺ is special in several regards (Scheme 5). Even with the highly reactive cyclopentadiene (**4**)

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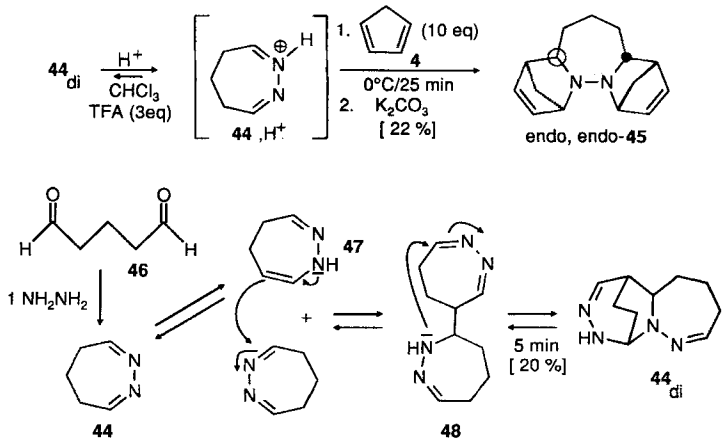


Scheme 5. Cycloaddition between $\mathbf{44}H^+$ (generated from its dimer $\mathbf{44}_{di}$ by TFA in $CHCl_3$) with cyclopentadiene.

only 22% of a cycloadduct could be isolated; it differed from all the others by its 2:1 stochiometry (*endo,endo*-**45**). In addition, the precursor of $\mathbf{44}H^+$ is not a trimer but the previously unknown dimer $\mathbf{44}_{di}$. A published procedure for the treatment of 1,5-diphenyl-1,5-dioxopentane to obtain monomeric 3,7-diphenyl-4 *H*,5,6-dihydro-1,2-diazepine[12] was adapted for the treatment of dialdehyde **46** with one equivalent of hydrazine in aqueous solution. After only 5 min a white solid precipitated, from which $\mathbf{44}_{di}$ was isolated by sublimation. The reaction is assumed to pass through the monomer **44** and its tautomer **47**, forming **48** by the aldol reaction and finally collapsing to $\mathbf{44}_{di}$.[13]

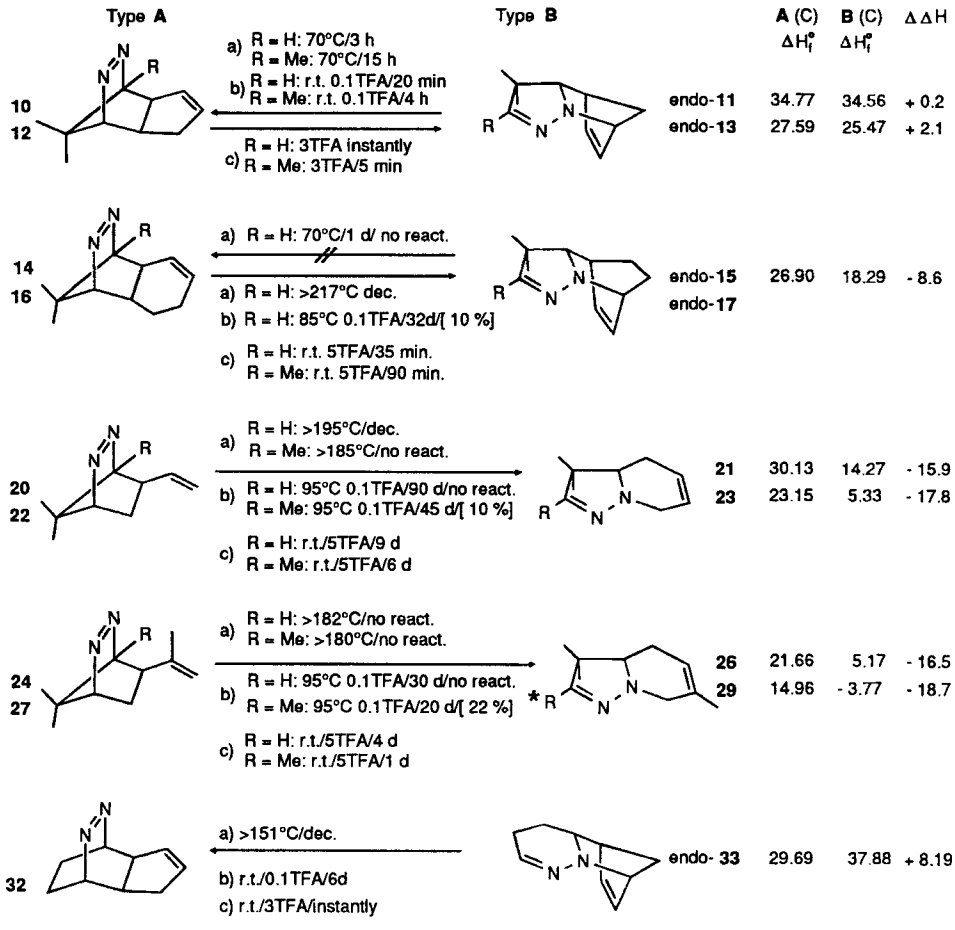
4. [3,3] Rearrangements: The isomeric cycloaddition products from azines **1**–**3** and several 1,3-dienes were tested for interconversion under three conditions: a) thermal treatment as usual for pericyclic [3,3] rearrangements,[14] b) acid-catalyzed reactions, already used in aza-Cope rearrangements,[15] and finally c) treatment with excess acid, since pyrazolines of type **B** are stronger bases than azo compounds of type **A** and therefore should be removed from the equilibrating systems $\mathbf{A} \rightleftharpoons \mathbf{B}$ by protonation (Scheme 2).

Calculation of the equilibrium $\mathbf{A} \rightleftharpoons \mathbf{B}$ ($\Delta\Delta H$) met with difficulties due to the lack of reliable data for azo and azino groups even nowadays.[16] Therefore W. R. Roth[17] suggested the calculation of ΔH_{ff}° of the corresponding hydrocarbons **A**(C) and **B**(C) for estimating $\Delta\Delta H$ of $\mathbf{A} \rightleftharpoons \mathbf{B}$, since in all cases the difference in energy for the transformation of the moieties azo $\rightleftharpoons$ azine should be very similar. The data obtained with the refined force-field program MMEVBH[17] together with the experimental data are collected in Scheme 6, the main points of which can be summarized as follows:

a) Equilibration $\mathbf{A} \rightleftharpoons \mathbf{B}$ was possible only with the closely related systems **10** $\rightleftharpoons$ *endo*-**11** and **12** $\rightleftharpoons$ *endo*-**13**. Thereby the pyrazolines *endo*-**11** (but not *exo*-**11**) and *endo*-**13** were very rapidly formed from their isomers if they were fully protonated (vide infra). The thermal equilibrium was way over towards the azo isomers **10** and **12**. Calculated $\Delta\Delta H$ values for the corresponding olefins are in reasonable agreement with this finding. The rate of isomerization in both directions was faster for R = H than for R = Me. Exothermic rearrangement of *endo*-**11** to **10** was observed by differential thermoanalysis (DTA) between 72 and 135 °C. Assuming a first-order reaction,[18] isomerization occurs with $\Delta H^{+} \approx 26$ kcal mol^{-1} and $\Delta S^{+} \approx 0$ kcal mol^{-1}.

b) All other isomerizations were irreversible, in accordance with strongly negative or positive $\Delta\Delta H$ values. These results were backed by DTA data.

c) Despite a strong driving force for starting materials **14**, **16**, **20**, **22**, **24** and **27**, excess TFA was needed to achieve isomer-



Scheme 6. Experimental data for [3,3] rearrangements of systems **A** and/or **B**. a) Thermal reaction without solvent; b) reaction in $CHCl_3$ with 0.1 equiv TFA; c) reaction in $CHCl_3$ with 3–5 equiv TFA. ΔH_{ff}° was calculated for the corresponding hydrocarbons **A**(C) and **B**(C) (MMEVBH force field[20]).

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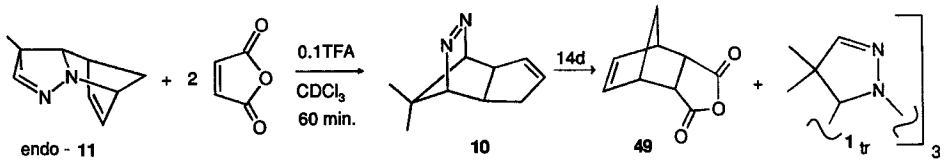
ization within a reasonable time. In examples **14** and **16**, which differ from **10** and **12** only by the six-membered carbocyclic ring, R = Me again diminished the rate of isomerization. By contrast, in the monocyclic systems both bridgehead CH_3 (**22**, **27**) and side-chain CH_3 groups (**24**, **27**) enhanced the isomerization.

d) In the case of *endo*-**33**, catalytic amounts of TFA accelerated isomerization to azo compound **32**, but 3 equivalents of TFA had a greater effect, despite the higher basicity of *endo*-**33**. This behavior is in accordance with the strongly positive $\Delta\Delta H$ of $+8.19\ \mathrm{kcal\,mol^{-1}}$ for the corresponding olefins.

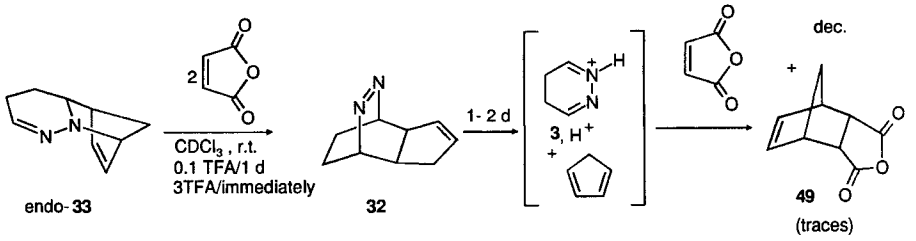
c) Only with **27** → **29** and not with the very similar system **22** → **23** were small amounts of cycloreversion products observed.

f) Rearrangements of **24** and **27** yielded the "*meta*" isomers **26** and **29** exclusively, and not the closely related "*para*" isomers **25** and **28**.

g) In sharp contrast to the rearrangements **24**/**27** → **26**/**29** and *endo*-**33** → **32**, the interconversions **34**/*endo*-**35**, **38**/**40**, and **42**/**43** failed from both sides, even in the presence of 4–21 equivalents of TFA, and over up to eight days (not included in Scheme 6).



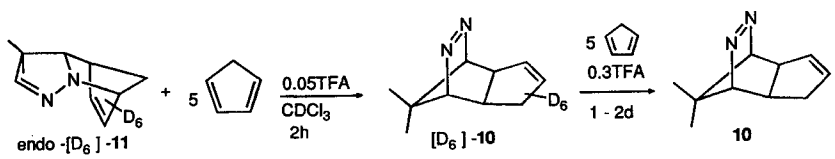
Scheme 8.



Scheme 9.

5. [4+2] Cycloreversions: In principle the interconversion of the isomeric [4+2] cycloadducts collected in Scheme 6 could occur by [4+2] cycloreversion (cf. Scheme 1). This problem was addressed by systems **24** → **26** and **27** → **29** (see discussion) and by the following trapping experiments.

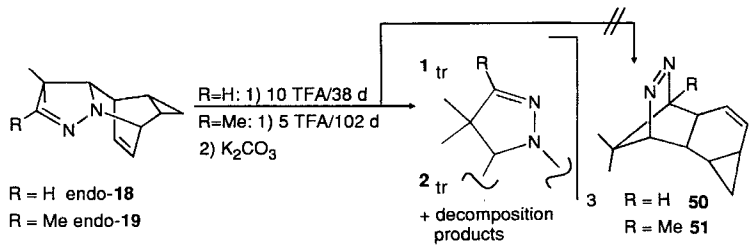
endo-[D_6]**11**, obtained from $\mathbf{1}_{tr}$ and perdeuterated cyclopentadiene, was treated with a catalytic amount of trifluoroacetic acid in the presence of excess cyclopentadiene. As with *endo*-**11**, rapid isomerization occurred, yielding [D_6]**10** exclusively within 2 h. Only after addition of more acid was the C_5D_6 moiety exchanged for undeuterated cyclopentadiene over 1–2 days (Scheme 7).



Scheme 7.

In a complementary experiment, *endo*-**11** was isomerized by acid catalysis in the presence of maleic anhydride. The isomer **10** was formed within 1 h, and only traces of the cycloadduct **49** could be detected. After two weeks, however, **10** was completely converted into **49** and the heterocyclic part of **10** was found as trimer $\mathbf{1}_{tr}$ (Scheme 8). The corresponding experiment with *endo*-**33** again yielded the isomeric product **32** (Scheme 9) without any interference from the added maleic acid anhydride. On extended treatment with acid for 1–2 days the mixture turned dark brown, containing mainly products of decomposition and some traces of cycloadduct **49**. In the absence of the trapping agent the reaction took the same course, probably owing to the already mentioned instability of intermediate protonated 4,5-dihydropyridazine $\mathbf{3}H^+$.

Finally the reversibility of the [4+2] cycloaddition was checked with *endo*-**18** and *endo*-**19**, obtained as the only cycloadducts from cycloheptatriene and $\mathbf{1}_{tr}$ or $\mathbf{2}_{tr}$, respectively (Scheme 3). The anticipated isomers **50** and **51** were formed neither thermally nor by treatment with excess trifluoroacetic acid (Scheme 10). The reaction mixtures developed an increasing brown color and after neutralization the trimeric pyrazolines $\mathbf{1}_{tr}$ and $\mathbf{2}_{tr}$ could be separated from the decomposition products by Kugelrohr distillation.



Scheme 10.

Discussion

The experimental results presented for azo compounds [D_6]**10**, **10**, and **32** and for pyrazolines *endo*-**18** and *endo*-**19** clearly demonstrate that these systems and probably all the others—can undergo [4+2] cycloreversion. However, in all cases, despite fairly severe conditions the reaction times were much too long to compete with the rather fast [3,3] rearrangements such as *endo*-**11** → **10** or *endo*-**33** → **32**. Besides, any isomerization of the cycloadducts **32**–**35** by a [4+2] cycloreversion is highly improbable because of the instability of the intermediate 4,5-dihydropyridazine **3** ($\mathbf{3}H^+$).

Very valuable information is obtained from the isomerization of azo-bridged compounds **24** and **27**. As shown in Scheme 3,

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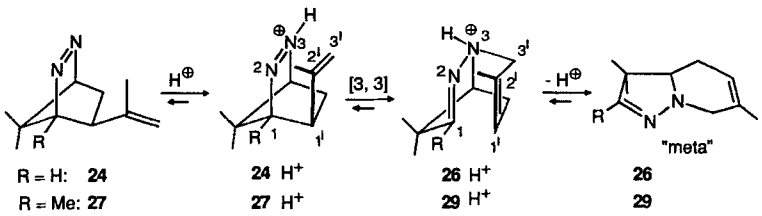
these cycloadducts are formed together with their isomers **25** ("*para*") + **26** ("*meta*") and **28** ("*para*") + **29** ("*meta*"), respectively, with equal or greater proportions of the *para* isomers **25** and **28** due to poor regioselectivity of these Diels–Alder reactions. On acid-catalyzed isomerization of both **24** and **27**, however, the "*meta*" isomers **26** and **29** are formed exclusively. These results clearly indicate a concerted [3,3] rearrangement and exclude any intermediate [4+2] cycloreversion. The cycloreversion (≈10%) observed during the rearrangement **27** → **29** has to be considered as a competing side reaction starting from **27**H$^+$. After **29**H$^+$ has been formed cycloreversion is no longer observed. Monitoring (VPC) the first minutes of the addition of $\mathbf{1}_{tr}$ to isoprene reveals even more information of general importance. Under the given acidic conditions cycloaddition between **1**H$^+$ and isoprene (**8**) has already proceeded to 38% after 34 s and has approached 96% after 13 min. Except for the first measurement, the ratio of **24**:**25**:**26** stays constant (Scheme 11). Only a very minor rearrangement **24** → **26** might



Scheme 11. Acid-catalyzed transformation of **24** and **27** into **26** and **29** by the Cope rearrangement.

have occurred. This means that all three cycloadducts are formed in competing reactions from the very beginning. The same conclusion can be drawn for systems **34**/*endo*-**35**, **38**/**40**, and **42**/**43**, since these pairs of isomers cannot be interconverted.

We therefore feel encouranged to describe all isomerizations of Scheme 6 as Cope rearrangements, although basic questions about mechanistic details[19] and proton-catalyzed aza-Cope rearrangements[20] are still under active discussion. Despite the obvious similarity of the systems depicted in Scheme 6, there are enormous differences in their accomodation of the transition state for the [3,3] rearrangement. The azo-bridged cycloadducts are isomerized by excess acid according to **10**, **12** > **14**, **16** ≫ **24**, **27** > **20**, **22**, partly decelerated and partly accelerated by the bridgehead methyl groups. Since the basicity of the developing pyrazolines should be rather similar, the strongly differing rates of isomerization must originate in the specific geometry of the molecular structures. Enlarging the cyclopentene moiety in **10** and **12** to a cyclohexene unit (**14** and **16**) definitely retards the rearrangement. But a flexible olefinic substituent, as in **24**/**27** and **20**/**22**, obviously needs much more energy to adapt a conformation suitable for [3,3] rearrangement (entropic factor?), although the thermodynamic driving force ($\Delta H^{\ddagger} = -16$ to -18 kcal mol^{-1}) for the olefins is by far the largest of all systems.

Isomerizations from pyrazolines to azo-bridged compounds by thermal reaction are only found with the examples *endo*-**11** and *endo*-**13**. With the exception of **10** ⇌ *endo*-**11** and **12** ⇌ *endo*-**13**, azo compounds **20**, **22**, **24**, and **27** as well as the hydropyridazine *endo*-**33** are thermodynamically strongly disfavored. Therefore they cannot result from any equilibration but rather owe their existence to *kinetic reaction control*. In other words, the above-mentioned azo-bridged compounds *must arise from a [4$^+$+2] cycloaddition in which* **1**H$^+$ *or* **2**H$^+$ *acts as the diene for a Diels–Alder reaction with inverse electron demand.*

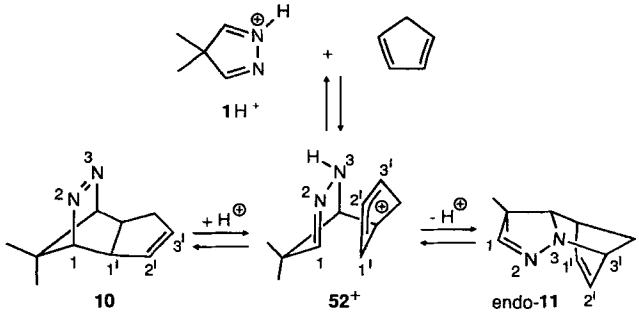
By contrast, hydropyridazine *endo*-**33** results from a fast [4+2$^+$] cycloaddition in which **3**H$^+$ acts as the electron-deficient dienophile for a normal Diels–Alder reaction. This is true even in the presence of excess acid, which does not prevent rearrangement of *endo*-**33** to the azo isomer **32** (Scheme 6). This [4+2$^+$] cycloaddition resembles similar reactions of dienes with (intermediate) protonated Schiff bases.[21]

Systems **10** ⇌ *endo*-**11** and **12** ⇌ *endo*-**13** represent unique examples in several respects.

a) The heat of formation for the isomers is very similar, with a slight preference for the azo bridged isomers.
b) Isomerization can be achieved quantitatively from both sides.
c) Both thermal and acid-catalyzed rearrangements proceed with low energy barriers.

Therefore, the experimental data allow no decision as to whether the azo isomers **10** and **12** are formed directly in a [4$^+$+2] cycloaddition of **1**H$^+$ or **2**H$^+$ with cyclopentadiene or by a fast [3,3] rearrangement of the primary [4+2$^+$] cycloadducts *endo*-**11** and *endo*-**13**.

The situation may be even more complicated for all cycloadditions discussed. Diels–Alder reactions and Cope rearrangements normally constitute typical examples for pericyclic reactions.[14] If, however, the differences in the π-MO energies become too great, the HOMO–LUMO interactions in the transition state may no longer be sufficient to compensate for the strongly negative entropies for concerted reactions.[22] Evidence for such a two-step Diels Alder reaction has even been provided for the dimerization of 1,3-butadiene[23] and very recently for substituted cycopentadienes.[24] Under these circumstances, as exemplified for **1**H$^+$ and cyclopentadiene, a cationic intermediate **52**$^+$ should be formed which connects not only the [4+2] and [4+2$^+$] cycloadditions but also the proton-catalyzed [3,2] rearrangements between the isomers (Scheme 12). Formation of the energetically disfavored cycloadduct is then caused by faster breakdown of the intermediates of type **52**$^+$. Although the assumption of a cationic intermediate of type **52**$^+$ is rather tempting, proof for its existence is still lacking. In some cycloadditions/reversions zwitterionic intermediates are very likely and have sometimes been trapped.[25] Our attempt to trap **52**$^+$ with methanol was unsuccessful.



Scheme 12. Formation and interconversion of [4+2] adduct **10** and [2+4] adduct *endo*-**11** through the common intermediate **52**$^+$.

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A ^{1}H NMR experiment in CH_3OD demonstrated that **10** is immediately rearranged to (protonated) *endo*-**11** by excess acid. Correspondingly, catalytic amounts of acid transform *endo*-**11** in CH_3OD quantitatively into **10**. These results do not disprove the existence of $\mathbf{52}^+$, since an intermediate allylic methyl ether may easily be reversibly cleaved.

The results presented in Scheme 11 can be interpreted in favor of an intermediate of type $\mathbf{52}^+$. Let us assume that the attack of $\mathbf{1}H^+$ at positions 1 or 4 in isoprene needs activation energies similar to those for the formation of the two isomeric allylic cations of type $\mathbf{52}^+$. Then ring closure of the 2 intermediate will yield **25** but the collapse of the 4 intermediate is expected to yield both **24** and **26**. Therefore the ratio of **25**:(**24** + **26**) should be close to 1:1, in accordance with the results in Scheme 3.

Radical intermediates formed by electron transfer from the two partners, for example, are probably less likely. Isomerization of *endo*-**13** to **12** was not affected by added phenazine.

Protonation versus methylation: The results of [3,3] rearrangements between the corresponding azo and pyrazoline isomers are partly governed by electrophilic catalysis by reversibly added protons. The effect of an irreversibly attached electrophile (Me^+ from Me_3OBF_4) has already been extensively studied[10] for some examples and can now be compared with those listed in Scheme 6. The azo-bridged isomers **10**, **14**, and **32** were smoothly methylated at the azo group to $\mathbf{10}Me^+$, $\mathbf{14}Me^+$ and $\mathbf{32}Me^+$, respectively.[10] Although excess acid triggers the rearrangements $\mathbf{10}H^+ \rightarrow$ *endo*-$\mathbf{11}H^+$ and $\mathbf{14}H^+ \rightarrow$ *endo*-$\mathbf{15}H^+$, such a rearrangement was not observed with $\mathbf{10}Me^+$ and $\mathbf{14}Me^+$. Rearrangement $\mathbf{32}Me^+ \rightarrow$ *endo*-$\mathbf{33}Me^+$ is not expected for energetic reasons. Methylation of the corresponding pyrazolines yielded some surprising results: instead of *endo*-$\mathbf{11}Me^+$ an irreversibly formed cage product derived from $\mathbf{10}Me^+$ is found. This consecutive reaction[26] probably shifts the equilibrium of this highly flexible system to the left side. By contrast, the expected methylated pyrazoline *endo*-$\mathbf{15}Me^+$ is obtained in high yield. Methylation of *endo*-**33** results in complete rearrangement to $\mathbf{32}Me^+$ as expected.

Conclusions

It has been demonstrated that in the acid-catalyzed [4+2] cycloaddition between cyclic azines and 1,3-dienes both partners may play the role of the diene or the dienophile, depending on particular structural features. The thermal or acid-catalyzed interconversion of isomeric [4+2] cycloadducts definitely occurs by a concerted [3,3] rearrangement and not by a [4+2] cycloreversion, which proceeds much more slowly. Although the components involved in these reactions differ greatly in their electronic properties, the systems follow the classic scheme of dicyclopentadiene rearrangements discovered by Woodward and Katz.[3] There is still some mechanistic ambiguity as to whether the [4+2] cycloadditions and [3,3] rearrangements pass through a concerted but asynchronous transition state[24] or through a cationic intermediate of type $\mathbf{52}^+$ as the crossing point for all observed reactions.

Experimental Section

Melting points were determined using a Kofler microscope and are corrected. IR: Perkin–Elmer 1420; UV: Perkin–Elmer 330; ^{1}H and ^{13}C NMR: Bruker AC200 200 MHz (^{1}H)/50 MHz (^{13}C) or Bruker WM400 400 MHz (^{1}H)/100 MHz (^{13}C); standard: TMS ($\delta = 0.00$), $CDCl_3$ (7.26/77.0), CD_3CN (1.95/1.2, 117.8) or [D_6]DMSO (2.50/39.7) (br = broad, c = centered); MS: Varian MAT CH7. Elemental analyses were performed by the analytical laboratory, Institute of Inorganic Chemistry, University of Würzburg.

Reactions in Scheme 3: General procedure: trifluoroacetic acid (μ equiv) was added to $\mathbf{1}_{tr}$,[8a] $\mathbf{2}_{tr}$,[27] or $\mathbf{3}_{tr}$[8b] (1.73 mmol) dissolved in $CHCl_3$ (3–4 mL). The mixture, which formed two phases, was cooled to $-5\,^\circ C$ before (an excess of) diene (**4**–**9**) was added and stirred. The reaction was performed either at $0\,^\circ C$ or at room temperature (at which the mixture became homogenous). If possible, the reaction was monitored by ^{1}H NMR or TLC. After the time given the mixture was slowly added to sat. K_2CO_3 solution (4 mL). The aqueous phase was extracted with $CHCl_3$ (2 × 2 mL). The organic phases were dried with K_2CO_3, the solvent evaporated, and the residue purified. The ratio of isomers was determined in the crude product either by ^{1}H NMR or medium-pressure liquid chromatography (MPLC).

Azo compound 10; pyrazolines *endo*-11 and *exo*-11:

a) Trimer $\mathbf{1}_{tr}$, TFA (0.15 mL, 2.0 mmol), Cp (**4**) (345 mg, 5.22 mmol), $0\,^\circ C$, 2 h. Kugelrohr distillation ($30\,^\circ C$, 0.01 Torr) yielded only **10**[8a] (642 mg, 76%), m.p. 30–31 °C.

b) Trimer $\mathbf{1}_{tr}$, TFA (1.20 mL, 15.6 mmol), Cp (**4**) (345 mg, 5.22 mmol), $0\,^\circ C$, 1 min. Kugelrohr distillation (30–35 °C, 0.01 Torr) yielded only *endo*-**11** (652 mg, 77%), m.p. 34–35 °C; IR (CCl_4): $\tilde{\nu} = 3140\ cm^{-1}$, 3080, 3040 (=C–H), 2980, 2960, 2920, 2880 (-C–H), 1600 (C=N, C=C), 1470, 1410, 1390, 1370 [$C(CH_3)_2$], 1330, 1270, 1260, 1220, 1200; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 0.85$ (s, 3H, 3′-CH_3), 0.99 (s, 3H, 3″-H), 1.41 (A, 1H, 9-H_A, $J_{AB} = 8.5$ Hz), 1.60 (B; 1H, 9-H_B), 2.80 (brs, 1H, 4-H), 3.39 (d, 1H, 3a-H, $J_{3a-4} = 1.5$ Hz), 4.34 (brs, 1H, 7-H), 5.69 (mc, 1H, 6-H), 6.02 (m, 1H, 5-H), 6.29 (s, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 20.37$ (q, CH_3), 29.12 (q, CH_3), 44.88 (s, C-3), 45.76 (d, C-4), 49.92 (t, C-9), 66.44 (d, C-3a), 75.72 (d, C-7), 131.54 (d, C-5), 133.78 (d, C-6), 155.90 (d, C-2); MS (70 eV): m/z (%) = 162 (7, M^+), 97 (100, $C_5H_9N_2$), 66 (44, cp); $C_{10}H_{14}N_2$ (162.3): calcd C 74.04, H 8.70, N 17.27; found C 73.42, H 8.89, N 16.96.

c) Trimer $\mathbf{1}_{tr}$, TFA (1.60 mL, 20.8 mmol), Cp (**4**) (345 mg, 5.22 mol), $0\,^\circ C$, 5 d, afforded only *exo*-**11** (97 mg, 47%), Kugelrohr distillation (30–35 °C, 0.01 Torr), colorless oil; IR (CCl_4): $\tilde{\nu} = 3060\ cm^{-1}$ (=C–H), 2980, 2950, 2920, 2860 (-C–H), 1600 (C=N, C=C), 1470, 1460, 1450, 1390, 1360 [$C(CH_3)_2$], 1325, 1300, 1255, 1200; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.06$ (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.49 (mc, 2H, 9-H), 2.75 (mc, 1H, 4-H), 2.93 (brs, 3a-H), 4.34 (mc, 1H, 7-H), 6.28 (m, 1H, 6-H), 6.43 (m, 1H, 5-H), 6.73 (s, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 19.28$ (q, CH_3), 28.68 (q, CH_3), 41.61 (t, C-9), 43.23 (d, C-4), 45.24 (s, C-3), 65.56 (d, C-3a), 73.00 (d, C-7), 135.08 (d, C-5), 142.82 (d, C-6), 159.15 (d, C-2); $C_{10}H_{14}N_2$ (162.3): calcd C 74.04, H 8.70, N 17.27; found C 73.42, H 8.89, N 16.96.

Pyrazoline *endo*-13: Trimer 2_{tr}, TFA (1.21 mL, 15.7 mmol), Cp (**4**) (345 mg, 5.22 mmol), $0\,^\circ C$, 10 min. Sublimation (25 °C/0.01 Torr) yielded *endo*-**13** (802 mg, 87%), colorless crystals, m.p. 53–43 °C; IR (CCl_4): $\tilde{\nu} = 3065\ cm^{-1}$ (=C–H), 2970, 2950, 2900, 2860 (-C–H), 1620 (C=C, C=N), 1470, 1460, 1440, 1390, 1380 [$C(CH_3)_2$], 1360, 1325, 1300, 1250, 1235, 1200; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 0.86$ (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.30 (A, 1H, 9-H_A, $J_{AB} = 8.4$ Hz), 1.57 (s, 3H, 2-CH_3), 1.58 (B, 1H, 9-H_B), 2.80 (brs, 1H, 4-H), 3.46 (brs, 1H, 3a-H), 4.32 (brs, 1H, 7-H), 5.72 (m, 1H, 5-H), 6.01 (m, 1H, 6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 11.72$ (q, CH_3), 20.08 (q, CH_3), 29.02 (q, CH_{3-2}), 45.91 (d, C-4), 46.00 (s, C-3), 49.55 (t, C-9), 66.66 (d, C-3a), 76.94 (C-7), 131.52 (d, C-5), 134.33 (d, C-6), 162.54 (s, C-2); MS (70 eV): m/z (%) = 176 (6, M^+), 111 (100, $C_6H_{10}N_2^+$), 105 (11), 66 (40, $C_5H_6^+$); $C_{11}H_{16}N_2$ (176.3): calcd C 74.96, H 9.15, N 15.89; found C 74.34, H 8.75, N 15.88.

Azo compound 14 and pyrazoline *endo*-15:

a) Trimer $\mathbf{1}_{tr}$, TFA (1.20 mL, 15.6 mol), 1,3-cyclohexadiene (**5**) (416 mg, 5.22 mmol), $0\,^\circ C$, 2 min. Kugelrohr distillation (30–35 °C/0.01 Torr) yielded

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731 mg (80%) of **14** and *endo*-**15** (12:88, ^{1}H NMR). By MPLC (PE/EE, 4:1 for fraction 1, EE for fraction 2) the pure isomers were obtained.

Azo compound 14: (80 mg, 9%) after sublimation (30 °C/0.01 Torr), colorless crystals, m.p. 45 °C; IR (CCl_4): $\tilde{\nu}$ = 3020 cm^{-1} (=C–H), 2980, 2960, 2930, 2880, 2840 (-C–H), 1660, 1640 (C=C), 1495, 1470, 1460, 1445 (N=N), 1395, 1380 [$C(CH_3)_2$], 1290, 1280, 1230; UV (hexane): λ_{max} (lg ε) = 357 nm (257), 346 (120), 342 (sh, 100), 324 (25); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.63 (s, 3H, 9-*exo*-CH_3), 1.01 (s, 3H, 9-*endo*-CH_3), 1.25 (mc, 1H), 1.64 (mc, 2H), 1.76 (m, 1H, 7,-8-H), 2.61 (m, 1H, 8a-H), 2.65 (m, 1H, 4a-H), 4.74 (d, 1H, $J_{1,8a}$ = 3 Hz), 4.76 (d, 1H, 4-H, $J_{4,4a}$ = 3 Hz), 5.70 (m, 2H, 5-,6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.83 (q, *exo*-CH_3-9), 19.40 (q, *endo*-CH_3-9), 21.10 (t, C-8), 22.91 (t, C-7), 34.99 (d, C-8a), 36.39 (s, C-4a), 53.22 (s, C-9), 87.97 (d, C-1), 89.52 (d, C-4), 125.83 (d, C-6), 129.05 (d, C-5); MS (70 eV): *m/z* (%) = 176 (3, M^+), 148 (5, $M^+ - N_2$), 133 (80, $M^+ - N_2, -CH_3$), 105 (100); $C_{11}H_{16}N_2$ (176.3): calcd C 74.96, H 9.15, N 15.89; found C 75.11, H 9.19, N 16.08.

Pyrazoline *endo*-15: (630 mg, 69%). After sublimation (30 °C/0.01 Torr) colorless crystals, m.p. 45–46 °C; IR (CCl_4): $\tilde{\nu}$ = 3040 cm^{-1} (=C–H), 2950, 2930, 2900, 2860 (-C–H), 1600 (C=N, C=C), 1470, 1460, 1440, 1390, 1380 [$C(CH_3)_2$], 1365, 1350, 1310, 1260, 1200; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.01 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.13 (m, 1H), 1.40 (mc, 1H), 1.49 (mc, 1H), 1.93 (mc, 1H, 9-,10-H), 2.45 (mc, 1H, 4-H), 3.15 (s, 1H, 3a-H), 4.29 (mc, 1H, 7-H), 5.90 (mc, 1H, 5-H), 6.21 (mc, 1H, 6-H), 6.37 (s, 1H; 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.61 (q, CH_3), 23.04 (t, C-9), 24.74 (t, C-10), 28.77 (q, CH_3), 32.38 (d, C-4), 48.82 (s, C-3), 53.64 (d, C-3a), 74.63 (d, C-7), 130.68 (d, C-5), 131.57 (d, C-6), 153.71 (d, C-2); MS (70 eV): *m/z* (%) = 176 (16, M^+), 97 (100, $C_5H_9N_2$), 80 (21, $C_6H_8^+$); $C_{11}H_{16}N_2$ (176.3): calcd C 74.96, H 9.15, N 15.89; found C 74.98, H 9.32, N 16.28.

b) Trimer $\mathbf{1}_{tr}$, TFA (1.60 mL, 20.8 mmol), **5** (416 mg, 5.22 mmol), 0 °C, 2 min. Kugelrohr distillation (30 °C/0.01 Torr) yielded *endo*-**15** (616 mg, 67%), m.p. 44–45 °C (^{1}H NMR).

Azo compound 16 and pyrazoline *endo*-17:

Trimer $\mathbf{2}_{tr}$, TFA (0.35 mL, 4.54 mmol), **5** (364 mg, 4.54 mmol), RT, 5 d. Sublimation (25 °C, 0.01 Torr) of the crude product afforded a mixture of **16** and *endo*-**17** (9:91, ^{1}H NMR). Separation by MPLC (PE/EE, 4:1).

Azo compound 16 (29 mg, 3%), colorless oil; IR (CCl_4): $\tilde{\nu}$ = 3030 cm^{-1} (=C–H), 2990, 2960, 2930, 2870, 2840 (-C–H), 1495, 1470, 1450 (N=N), 1395, 1380 [$C(CH_3)_2$], 1300, 1290, 1270; UV (*n*-hexane): λ_{max} (lg ε) = 358 nm (246), 344 (sh, 105), 336 (sh, 28); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.56 (s, 3H, 9-*exo*-CH_3), 0.92 (s, 3H, 9-*endo*-CH_3), 1.36 (m, 1H, 8-H), 1.67 (s, 3H, 4-CH_3), 1.69 (m, 2H), 1.82 (m, 1H, 7-,8-H), 2.37 (d, 1H, 8a-H), 2.64 (m, 1H, 4a-H), 4.83 (d, 1H, 1-H, $J_{1,8a}$ = 3.5 Hz), 5.80 (mc, 2H, 5-,6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.48 (q, CH_3-4), 17.79 (q, *exo*-CH_3-9), 18.16 (q, *endo*-CH_3-9), 21.41 (t, C-8), 39.62 (d, C-1), 54.83 (s, C-9), 89.29 (s, C-4), 91.10 (d, C-4a), 124.29 (d, C-6), 129.63 (d, C-5); MS (70 eV): *m/z* (%) = 190 (6, M^+), 162 (5, $M^+ - N_2$), 147 (41, $M^+ - N_2 - CH_3$), 111 (100); $C_{12}H_{18}N_2$ (190.3): calcd C 75.74, H 9.55, N 14.72; found C 75.84, H 9.63, N 14.94.

Pyrazoline *endo*-17: (346 mg, 30%), colorless crystals, m.p. 63–64 °C; IR (CCl_4): $\tilde{\nu}$ = 3020 cm^{-1} (=C–H), 2980, 2940, 2920, 2885, 2855 (-C–H), 1650, 1620 (C=C, C=N), 1465, 1455, 1430, 1385, 1380 [$C(CH_3)_2$], 1360, 1350, 1310, 1290, 1260, 1200; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.02 (m, 1H), 1.31 (m, 1H), 1.39 (m, 1H), 1.85 (m, 1H, 9-,10-H), 1.62 (s, 3H, 2-CH_3), 2.36 (mc, 1H, 4-H), 3.13 (s, 1H, 3a-H), 4.14 (s, 1H, 7-H), 5.82 (mc, 1H, 7-H), 4.14 (s, 1H, 7-H), 5.82 (mc, 1H, 5-H), 6.12 (mc, 1H, 6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.67 (q, CH_3), 20.94 (q, CH_3), 23.01 (t, C-9), 24.55 (t, C-10), 28.41 (q, CH_3-2), 32.36 (d, C-4), 49.49 (s, C-3), 53.49 (d, C-3a), 75.57 (d, C-7), 130.39 (d, C-5), 131.80 (d, C-6), 159.78 (s, C-2); MS (70 eV): *m/z* (%) = 190 (6, M^+), 111 (100, $C_6H_{10}N_2^+$), 79 (11, C_6H_8); $C_{12}H_{18}N_2$ (190.3): calcd C 75.74, H 9.53, N 14.72; found C 75.92, H 9.74, N 15.17.

Pyrazoline *endo*-18: Trimer $\mathbf{1}_{tr}$, TFA (1.20 mL, 15.6 mmol), cycloheptatriene (**6**) (920 mg, 10.0 mmol) RT, 5 d. Kugelrohr distillation (120 °C/0.01 Torr) afforded only *endo*-**18** (460 mg, 45%), colorless oil; IR (CCl_4): $\tilde{\nu}$ = 3040 cm^{-1}, 3020, 3000 (=C–H), 2940, 2890, 2860 (-C–H), 1590 (C=N), C=C), 1465, 1460, 1450, 1430, 1385, 1360 [$C(CH_3)_2$], 1300, 1265, 1200; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.21 (dt, 1H, 11′-H, $J_{11',11''}$ = 5.50 Hz, $J_{9,11}$ = $J_{10,11}$ = 3.5 Hz), 0.28 (dt, 1H, 11″-H, $J_{9,11''}$ = $J_{10,11''}$ = 7.5 Hz), 0.95 (ddtd, 1H, 9-H, $J_{9,10}$ = $J_{4,9}$ = 7.5 Hz), 1.03 (s, 3H, 3-CH_3), 1.12 (s, 3H, 3-CH_3), 1.15 (ddtd, 1H, 10-H), 2.80 (mc, 1H, 4-H), 3.33 (d, 1H, 3a-H), 4.58 (mc, 1H, 7-H), 5.58 (mc, 1H, 5-H), 5.73 (mc, 1H, 6-H), 6.42 (s, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 6.30 (t, C-11), 8.80 (d, C-9), 9.42 (d, C-10), 21.92 (q, CH_3), 29.05 (q, CH_3), 33.93 (d, C-4), 46.52 (s, C-3), 56.23 (d, C-3a), 75.18 (d, C-7), 124.47 (d, C-5), 127.99 (d, C-6), 154.50 (d, C-2); MS (70 eV): *m/z* (%) = 188 (4, M^+), 97 (37, $C_5H_9N_2$), 92 (51), 91 (100); $C_{12}H_{16}N_2$ (188.3): calcd C 76.56, H 8.57, N 14.88; found C 76.33, H 8.77, N 14.99.

Pyrazoline *endo*-19: Trimer $\mathbf{2}_{tr}$, TFA (1.20 mL, 15.7 mmol), **9** (962 mg, 10.4 mmol), RT, 6 d. The product was separated from a dark red impurity by flash chromatography (SiO_2, PE/EE, 2:1). Elution with methanol and sublimation of the product (80 °C/0.01 Torr) yielded *endo*-**19** (480 mg, 46%), colorless crystals, m.p. 84–85 °C; IR (CCl_4): $\tilde{\nu}$ = 3090 cm^{-1}, 3035, 3000 (=C–H), 2950, 2900, 2865 (-C–H), 1655, 1630 (C=C, C=N), 1470, 1460, 1435, 1390, 1380 [$C(CH_3)_2$], 1360, 1300, 1265, 1210; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.16 (dt, 1H, 11′-H, $J_{11',11''}$ = 5.50 Hz, $J_{9,11'}$ = 3.5 Hz), 0.23 (dt, 1H, 11″-H, $J_{9,11''}$ = $J_{10,11''}$ = 7.5 Hz), 0.89 (dddd, 1H, 9-H, $J_{9,10}$ = $J_{4,9}$ = 7.5 Hz), 1.01 (s, 3H, CH_3), 1.11 (s, 3H, 2-CH_3), 2.75 (mc, 1H, 4-H), 3.36 (brs, 1H, 3a-H), 4.49 (mc, 1H, 7-H), 5.55 (mc, 1H, 5-H), 5.70 (mc, 1H, 6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 5.93 (t, C-11), 8.60 (d, C-9), 9.44 (d, C-10), 11.05 (q, CH_3), 21.37 (q, CH_3), 28.87 (q, CH_3-2), 34.07 (d, C-4), 47.52 (s, C-3), 56.22 (d, C-3a), 76.27 (d, C-7), 124.32 (d, C-5), 128.41 (d, C-6), 161.38 (s, C-2); MS (70 eV): *m/z* (%) = 202 (6, M^+), 111 (100, $C_6H_{10}N_2^+$), 91 (46, $C_7H_8^+ - H$); $C_{13}H_{18}N_2$ (202.3): calcd C 77.18, H 8.97, N 13.85; found C 77.20, H 9.12, N 14.36.

Azo compound 20 and pyrazoline 21:

a) Trimer $\mathbf{1}_{tr}$, TFA (1.20 mL, 15.6 mmol), excess butadiene (**7**) bubbled into the solution, 0 °C, 20 min. Kugelrohr distillation of the crude product yielded a mixture of **20** and **21** (588 mg, 75%, ratio 66:34 by ^{1}H NMR). The mixture was separated by MPLC (PE/EE, 4:1 for the first fraction, EE for the second fraction).

Azo compound 20: Colorless oil (390 mg, 50%); IR (CCl_4): $\tilde{\nu}$ = 3080 cm^{-1} (=C–H), 2990, 2960, 2920, 2880 (-C–H), 1645 (C=C), 1495, 1480, 1460, 1430 (N=N), 1400, 1380 [$C(CH_3)_2$], 1320, 1295, 1275, 1250, 1210; UV (*n*-hexane): λ_{max} (lg ε) = 352 (148), 342 (89), 338 (sh, 72), 321 (sh, 21); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.63 (s, 3H, 7-*exo*-CH_3), 0.71 (dd, 1H, 5-H_A, J_{AB} = 13.5 Hz, J_{AX} = 4.5 Hz), 0.95 (s, 3H, 7-*endo*-CH_3), 1.98 (ddd, 1H, 5-H_B, $J_{5B,6}$ = 3 Hz, $J_{4,5A}$ = 8.75 Hz), 2.84 (mc, 1H, 4-H), 4.62 (d, 2H, 3-,6-H, $J_{3,4}$ = 3 Hz), 4.85 (ddd, 1H, 9-H_B, $J_{9A,9B}$ = 1 Hz, $J_{4,9B}$ = 2 Hz, $J_{8,9B}$ = 10 Hz), 4.96 (ddd, 1H, 9-H_A, $J_{4,9A}$ = 1.3 Hz, $J_{8,9A}$ = 17 Hz), 5.30 (ddd, 1H, 8-H, $J_{4,8}$ = 8.3 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.64 (q, *exo*-CH_3-7), 18.73 (t, C-5), 26.56 (q, *endo*-CH_3-7), 40.09 (d, C-4), 53.01 (s, C-7), 85.58 (d, C-6), 88.40 (d, C-3), 115.42 (t, C-9), 137.75 (d, C-8); MS (70 eV): *m/z* (%) = 135 (1, $M^+ - CH_3$), 120 (1, $M^+ - 2CH_3$), 107 (95, $M^+ - CH_3 - N_2$), 79 (100); $C_9H_{14}N_2$ (150.2): calcd C 71.96, H 9.39, H 18.65; found C 71.83 H 9.38, N 18.54.

Pyrazoline 21: Colorless oil (180 mg, 23%); IR (CCl_4): $\tilde{\nu}$ = 3040 cm^{-1} (=C–H), 2960, 2920, 2900, 2880, 2860, 2840, 2800 (-C–H), 1650 (C=C), 1560, 1540 (C=N), 1460, 1435, 1390, 1380 [$C(CH_3)_2$], 1365, 1350, 1335, 1300, 1280, 1260, 1220, 1210; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.90 (s, 3H, 3′-CH_3), 1.12 (s, 3H, 3″-CH_3), 2.00 (m, 1H, 4′-H, $J_{4',4''}$ = 16.5 Hz), 2.22 (mc, 1H, 4″-H), 2.40 (dd, 1H, 3a-H), 3.28 (dm, 1H, 7″-H, $J_{7'',7'}$ = 15.5 Hz), 4.00 (dm, 1H, 7′-H), 5.67 (m, 1H, 5-H), 6.59 (s, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.05 (q, CH_3), 23.65 (q, CH_3), 24.46 (t, C-4), 47.11 (s, C-3), 51.98 (t, C-7), 69.81 (d, C-3a), 124.86 (d, C-5), 125.11 (d, C-6), 152.90 (d, C-2); MS (70 eV): *m/z* (%) = 150 (100, M^+), 135 (87, $M^+ - CH_3$), 108 (13), 97 (19, $C_5H_9N_2^+$), 95 (51); $C_9H_{14}N_2$ (150.2): calcd C 71.96, H 9.39, N 18.65; found C 72.00, H 9.53, N 18.51.

b) Analogous to a) but with 4.00 mL (52.3 mmol) TFA, 15 min. Kugelrohr distillation afforded 517 mg (66%) of **20** + **21** (40:60). **20**: Colorless oil (190 mg, 24%). **21**: Colorless oil (290 mg, 37%).

Azo compound 22 and pyrazoline 23:

a) To a solution of $\mathbf{2}_{tr}$ (1.00 g, 3.03 mmol) and TFA (1.04 g, 9.09 mmol) in $CHCl_3$ (10 mL, 2 phases) for 10 h at RT. A mixture of **22** + **23** (2:1 by ^{1}H NMR) was obtained by Kugelrohr distillation (30 °C, 0.01 Torr). Flash chromatography (PE/EE, 9:1 for fraction 1, EE for fraction 2) yielded the two isomers after another Kugelrohr distillation.

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Azo compound 22: Colorless oil (100 mg, 7%); IR (CCl_4): $\tilde{\nu}$ = 3080 cm^{-1} (=C–H), 2980, 2960, 2920, 2870, 2830 (-C–H), 1640 (C=C), 1495, 1470, 1450, 1425 (N=N), 1390, 1380 [$C(CH_3)_2$], 1370, 1290, 1280, 1260; UV (*n*-hexane): λ_{max} (lg ε) = 353 (153), 344 (sh, 97), 338 (sh, 86); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.59 (sm 3H, 7-*exo*-CH_3), 0.86 (dd, 1H, 5-$H_{A'}$, J_{AB} = 14 Hz, J_{AX} = 4.5 Hz, 0.88 (s, 3H, 7-*endo*-CH_3), 1.55 (s, 3H, 3-CH_3), 2.06 (ddd, 1H, 5-H_B, $J_{5B,6}$ = 3.3 Hz, $J_{4,5B}$ = 8.8 Hz), 2.48 (mc, 1H, 4-H), 4.72 (d, 1H, 6-H), 4.86 (ddd, 1H, 9-H_B, $J_{9A,9B}$ = 1 Hz, $J_{4,9B}$ = 2 Hz, $J_{8,9B}$ = 10 Hz), 4.96 (ddd, 1H, 9-$H_{A'}$, $J_{4,9A}$ = 1.3 Hz, $J_{8,9A}$ = 17 Hz), 5.22 (dt, 1H, 8-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 9.85 (q, CH_3-3), 17.61 (q, *exo*-CH_3-7), 17.88 (q, *endo*-CH_3-7), 27.67 (t, C-5), 42.42 (s, C-3), 45.82 (d, C-4), 54.13 (s, C-7), 86.70 (d, C-6), 116.89 (t, C-9), 137.48 (d, C-8); MS (70 eV): *m/z* (%) = 164 (1, M^+), 149 (2, $M^+ - CH_3$), 136 (2, $M^+ - N_2$), 121 (71, $M^+ - N_2 - CH_3$), 93 (100); $C_{10}H_{16}N_2$ (164.3): calcd C 73.13, H 9.82, N 17.05; found C 72.61, H 9.66, N 17.37. The ^{1}H NMR spectra of **22** contain some additional signals (e.g., second signal for the bridgehead CH_3 group), which can be attributed to ca. 10% of an azo isomer containing the bridgehead methyl group and the vinyl group in a 1,3-position to each other.

Pyrazoline 23: Colorless oil (50 mg, 3%); IR (CCl_4): $\tilde{\nu}$ = 3020 cm^{-1} (=C–H), 2940, 2915, 2895, 2875, 2860, 2830 (-C–H), 1645, 1600 (C=N, C=C), 1460, 1450, 1430, 1375, 1360 [$C(CH_3)_2$], 1340, 1325, 1305, 1240, 1215; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.85 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.85 (s, 3H, 2-CH_3), 1.97 (A, 1H, 4′-H, $J_{4',4''}$ = 16.3 Hz), 2.20 (B, 1H, 4″-H), 2.36 (dd, 1H, 3a-H, $J_{3a,4''}$ = 10 Hz, $J_{3a,4'}$ = 3.5 Hz), 3.17 (A′, 1H, 7′-H, $J_{7',7''}$ = 16 Hz), 3.93 (B′, 1H, 7″-H), 5.72 (A″B″, 2H, 5-,6-H, $J_{5,6}$ = 9 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 11.72 (q, CH_3), 16.24 (q, CH_3), 22.92 (q, CH_3-2), 25.07 (t, C-4), 48.03 (s, C-3), 52.36 (t, C-7), 70.90 (d, C-3a), 125.01 (d, C-5), 125.09 (d, C-6), 160.31 (s, C-2); MS (70 eV): *m/z* (%) = 164 (92, M^+), 149 (100, $M^+ - CH_3$), 111 (17, $C_6H_{10}N_2^+$); $C_{10}H_{16}N_2$ (164.3): calcd C 73.13, H 9.82, N 17.05; found C 72.90, H 10.02, N 17.31.

b) Analogous to a) but with 3.12 g (27.2 mmol) of TFA and introduction of **7** as a gas for 3.5 h. Mixture of **22** + **23**. **22** (60 mg, 6%). **23** (960 mg, 62%).

Azo compound 24 and pyrazolines 25 and 26:

a) Trimer $\mathbf{1}_{tr}$, TFA (0.40 mL, 5.20 mmol), isoprene (**8**) (1.56 mL, 15.6 mmol), 0 °C to 20 °C, 27 d. Kugelrohr distillation of the crude product yielded a mixture of **24** and **25** [105 mg, 12%, ratio 89:11 by ^{1}H NMR (vide infra)].

b) Analogous to a) but with 1.20 mL (15.6 mmol) of TFA, 0 °C, 15 min. Mixture of **24** + **25** + **26** (36:58:6). The small amount of **26** could be identified by comparison with the ^{1}H NMR signals of pure **26** (vide infra). Flash chromatography (PE/EE, 4:1) afforded **24** and **25** after Kugelrohr distillation.

Azo compound 24: (143 mg, 17%), colorless oil; IR ($CDCl_3$): $\tilde{\nu}$ = 3095 cm^{-1} (=C–H), 3000, 2970, 2950, 2920, 2880 (C–H), 1650 (C=C), 1490, 1450, 1440 (N=N), 1305, 1275, 1245, 1210, 1150, 1125; UV (hexane): λ_{max} (lg ε) = 348 nm (2.23), 339 (2.01); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.71 (s, 3H, 7-*exo*-CH_3), 1.00–1.04 (dd, 1H, 5-H_A, $J_{5A,4}$ = 5.0 Hz), 1.04 (s, 3H, 7-*endo*-CH_3), 1.79 (brs, 3H, 1′-CH_3), 1.91–1.98 (ddd, 1H, 5-H_B, J_{AB} = 13.5 Hz, $J_{5B,4}$ = 3.0 Hz), 2.80–2.83 (mc, 1H, 4-H), 4.59 (brs, 1H, 3-H), 4.68 (d, 1H, 6-H), 4.69–4.71 (mc, 1H, 2′-H, $J_{2',4}$ = 2.75 Hz), 4.85–4.86 (dd, 1H, 2′-H, $J_{2',4}$ = 2.5 Hz, J_{AB} = 1.0 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.01 (q, *exo*-CH_3), 19.19 (q, 1′-CH_3), 22.92 (q, 7-*endo*-CH_3), 24.50 (t, C-5), 41.88 (d, C-4), 53.15 (s, C-7), 85.80 (d, C-6), 86.50 (d, C-3), 111.2 (t, C-2′), 142.7 (s, C-1′); MS (70 eV): *m/z* (%) = 164.1 (0.9, M^+), 149.1 (1.4, $M^+ - CH_3$), 136.1 (0.9, $M^+ - N_2$), 121.1 (100, $M^+ - N_2 - CH_3$), 105.1 (40.0), 93.1 (84.4), 80.2 (12.6, $M^+ - CH_3 - C_3H_5$), 79.1 (64.8), 67.1 (31.5), 53.1 (28.3), 41.1 (62.0), 27.1 (29.7); $C_{10}H_{16}N_2$ (164.3): calcd C 73.13, H 9.82, N 17.06; found C 73.13, H 9.72, N 17.19.

Pyrazoline 25 (257 mg, 30%) colorless oil; IR ($CDCl_3$): $\tilde{\nu}$ = 3045 cm^{-1} (=C–H), 2970, 2940, 2920, 2875, 2805 (C–H), 1575, 1565 (C=N), 1460, 1450, 1380 [$C(CH_3)_2$], 1365, 1300, 1280, 1215, 1110, 1060, 980, 840; UV (hexane): λ_{max} (lg ε) = 248 nm (3.64); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.92 (s, 3H, 3-CH_3), 1.13 (s, 3H, 3-CH_3), 1.72 (s, 3H, 5-CH_3), 1.82–1.87 (d, 1H, $J_{4'4''}$ = 16.3 Hz), 2.17–2.25 (t, 1H, 4-H), 2.39–2.43 (dd, 1H, 3a-H, $J_{3a,4'}$ = 11.3 Hz, $J_{3a,4''}$ = 3.8 Hz), 3.17–3.24 (dm, 1H, 7-H, $J_{7',7''}$ = 15.0 Hz), 3.92–3.96 (d, 1H, 7-H), 5.37–5.38 (brs, 1H, 6-H), 6.59 (s, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.00 (q, 3-CH_3), 23.11 (q, -CH_3), 23.64 (q, 3-CH_3), 29.10 (t, C-4), 47.06 (s, C-3), 51.49 (t, C-7), 69.98 (d, C-3a), 118.9 (d, C-6), 133.0 (s, C-5), 153.2 (d, C-2); MS (70 eV): *m/z* (%) = 164.2 (75.4, M^+), 149.1 (100, $M^+ - CH_3$), 122.1 (8.3), 97.1 (44.8, $C_5H_9N_2^+$), 82.1 (12.4, $C_5H_9N_2^+ - CH_3$), 68.1 (27, $C_5H_8^+$), 53.1 (18.2), 41.1 (33.3), 28.0 (17.2); $C_{10}H_{16}N_2$ (164.3): calcd C 73.13, H 9.82, N 17.06; found C 73.54, H 10.29, N 16.95.

c) Analogous to a) but with 2.40 mL (31.2 mmol) TFA, 0 °C, 105 min. Mixture of **24** and **25** (**26** not determined) 576 mg, 67%, ratio 17:83).

Azo compound 27 and pyrazolines 28 and 29:

a) Trimer $\mathbf{2}_{tr}$, TFA (516 mg, 4.53 mmol), **8** (926 mg, 13.6 mmol), RT, 7 d. Kugelrohr distillation of the crude product yielded a mixture of **27** + **28** + **29** (225 mg, 28%, ratio 28:34:38). Flash chromatography (PE/EE) 4:1 and Kugelrohr distillation of the two fractions afforded colorless oils.

Azo compound 27: (63 mg, 8%); IR ($CDCl_3$): $\tilde{\nu}$ = 3080 cm^{-1} (=C–H), 2995, 2970, 2935, 2880 (C–H), 1630 (C=C), 1490, 1470, 1450 (N=N), 1395, 1380, 1375 [C–H, def. symm., >$C(CH_3)_2$], 1295, 1280, 1265, 1220, 1120, 1040, 980; UV (CH_3CN): λ_{max} (lg ε) = 321 nm (sh, 1.42), 343 (sh, 2.00), 352 (2.11); ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.59 (s, 3H, 7_{ex}-CH_3), 0.91 (s, 3H, 7_{en}-CH_3), 1.02 (dd, $J_{5A,5B}$ = 14.0 Hz, 1H, 5_A-H), 1.49 (s, 3H, 1′-CH_3), 1.56 (s, 3H, 3-CH_3), 1.99 (ddd, 1H, 5_B-H), 2.62 (dd, $J_{4,5B}$ = 9.5 Hz, $J_{4,5A}$ = 5.5 Hz, 1H, 4-H), 4.70 (d, $J_{6,5B}$ = 3.3 Hz, 1H, 6-H), 4.74 and 4.80 (each m, each 1H, 2′-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 10.26 (q, 3-CH_3), 18.26 (q, 1′-CH_3), 17.77 and 21.95 (each q, 7-CH_3), 26.95 (t, C-5), 47.81 (d, C-4), 55.25 (s, C-7), 86.48 (d, C-6), 89.85 (s, C-3), 114.98 (t, C-2′), 143.00 (s, C-1′); MS (70 eV): *m/z* (%) = 178 (13, M^+), 163 (16, $M^+ - CH_3$), 150 (1, $M^+ - CH_3$), 150 (1, $M^+ - N_2$), 135 (39, $M^+ - N_2 - CH_3$), 109 (17, $M^+ - N_2 - C_3H_5$), 107 (60), 94 (9, $M^+ - N_2 - CH_3 - C_3H_5$), 93 (35), 67 (64), 53 (45), 41 (100); $C_{11}H_{18}N_2$ (178.3): calcd C 74.11, H 10.18, N 15.71; found C 74.47, H 10.41, N 16.12.

Pyrazolines 28 + 29 (162 mg, 20%); IR ($CDCl_3$): $\tilde{\nu}$ = 3040 cm^{-1} (=C–H), 2970, 2940, 2920, 2885, 2800, 2740 (-C–H), 1665, 1600 (C=C, C=N), 1465, 1455, 1435, 1380, 1360 [C–H, def. symm., >$C(CH_3)_2$), 1310, 1200, 1180, 1165, 1105, 1075, 1000, 975, 965; UV (CH_3CN): λ_{max} (lg ε) = 242 nm (3.67); MS (70 eV): *m/z* (%) = 178 (72, M^+), 163 (100, $M^+ - CH_3$), 148 (7, $M^+ - 2CH_3$), 133 (6, $M^+ - 3CH_3$), 111 (56, $C_6H_{11}N_2^+$), 94 (13), 67 (26, $C_5H_7^+$), 53 (12), 42 (41); $C_{11}H_{18}N_2$ (178.3): calcd C 74.11, H 10.18, N 15.71, found C 74.25; H 10.46, N 16.12. The NMR data of **28** were elucidated from the mixture of **28** + **29** by subtracting the data for **29** (vide infra); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.93 and 1.12 (each s, each 3H, 3-CH_3), 1.75 (s, 3H, 5-CH_3), 1.82 (brd, 1H, 4_A-H), 1.88 (s, 3H, 2-CH_3), 2.25 (mc, $J_{4B,4A}$ = 18.0 Hz, 1H, 4_B-H), 2.41 (dd, $J_{3a,4B}$ = 11.5 Hz, $J_{3a,4A}$ = 4.0 Hz, 1H, 3a-H), 3.14 (m, 1H, 7_A-H), 3.91 (brd, $J_{7B,7A}$ = 15.0 Hz, 1H, 7_B-H), 5.34 (brs, 1H, 6-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.92 and 16.37 (each q, 3-CH_3), 23.01 (q, 2-CH_3), 23.17 (q, 5-CH_3), 29.78 (t, C-4), 48.03 (s, C-3), 51.96 (t, C-7), 71.18 (d, C-3a), 119.15 (d, C-6), 133.05 (s, C-5), 160.78 (s, C-2).

b) Analogous to a) but with 1.55 g (13.6 mmol) of TFA, 130 min. Mixture of the isomers 412 mg (51%), ratio 3:42:55. FC yielded **27** (12 mg, 1%) and **28** + **29** (400 mg, 50%).

c) Analogous to a) but with 3.10 g (27.2 mmol) of TFA, 80 min. Mixture of **28** + **29** (206 mg, 26%), ratio 53:47.

Pyrazoline 30: Trimer $\mathbf{1}_{tr}$, TFA (1.20 mL, 15.6 mmol), 2,3-dimethylbutadiene-1,3 (**9**) (1.75 mL, 15.6 mmol), 0 °C, 9 min. Kugelrohr distillation and FC (PE/EE, 4:1) of the crude product yielded **30** as a colorless oil (459 mg, 50%); IR ($CDCl_3$): $\tilde{\nu}$ = 3050 cm^{-1} (=C–H), 2970, 2935, 2915, 2875, 2845, 2800 (C–H), 1570, 1460, 1385 [$C(CH_3)_2$], 1365, 1280, 1230, 1210, 1160, 1140, 1110, 1060, 840; UV (hexane): λ_{max} (lg ε) = 249 (3.68); ^{1}H NMR ($CDCl_3$): δ = 0.89 (s, 3H, 3-CH_3), 1.10 (s, 3H, 3-CH_3), 1.58 (s, 3H, 6-CH_3), 1.63 (s, 3H, 5-CH_3), 1.80–1.84 (d, 1H, 4-H, $J_{4',4''}$ = 16.0 Hz), 2.15–2.22 (mc, 1H, 4-H), 2.33–2.37 (dd, 1H, 3a-H, $J_{3a,4'}$ = 11.5 Hz, $J_{3a,4''}$ = 3.75 Hz), 3.12–3.17 (d, 1H, 7-H, $J_{7',7''}$ = 14.5 Hz), 3.76–3.80 (d, 1H, 7-H), 6.56 (s, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.51 (q, -CH_3), 16.95 (q, 3-CH_3), 18.67 (q, -CH_3), 23.59 (q, 3-CH_3), 29.99 (t, C-4), 47.19 (s, C-3), 56.35 (t, C-7), 70.17 (d, C-3a), 123.8 (s, C-6), 124.6 (s, C-5), 153.1 (d, C-2); MS (70 eV): *m/z* (%) = 178.2 (26.8, M^+), 163.2 (43.3, $M^+ - CH_3$), 110.2 (78.5), 107.1 (100), 97.1 (23.8, $C_5H_9N_2^+$), 92.1 (21.8), 82.2 (19.2, $C_5H_9N_2^+ - CH_3$, $C_6H_{10}^+$), 79.1 (42.5), 67.1 (33.5), 56.1 (36.9), 41.1 (54.6), 28.0 (52.5); $C_{11}H_{18}N_2$ (178.3): calcd C 74.11, H 10.18, N 15.71; found C 74.37, H 10.10, N 15.68.

Pyrazoline 31: Trimer $\mathbf{2}_{tr}$, TFA (1.55 g, 13.6 mmol), **9** (1.85 g, 22.5 mmol), 0 °C (2 h), 20 °C (70 min). Purification of the crude product according to **30** afforded **31** (620 mg, 71%) as a colorless oil; IR ($CDCl_3$): $\tilde{\nu}$ = 2970 cm^{-1},

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2920, 2870, 2800 (C–H), 1620, 1600 (C=N, C=C), 1460, 1455, 1435, 1380, 1360 [C–H def. symm., $>C(CH_3)_2$], 1310, 1240, 1205, 1180, 1145, 1120, 1100, 1070, 1025, 960; UV (CH_3CN): λ_{max} (lg ε) = 241 (3.63); ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.81 and 1.00 (each s, each 3H, 3-CH_3), 1.53 and 1.58 (each s, each 3H, 5-,6-CH_3), 1.74 (d, $J_{4A,4B}$ = 16.0 Hz, 1H, 4_A-H), 1.76 (s, 3H, 2-CH_3), 2.17 (m, 1H, 4_B-H), 2.28 (dd, $J_{3a,4A}$ = 3.0 Hz, $J_{3a,4B}$ = 11.0 Hz, 1H, 3a-H), 3.02 (brd, $J_{7A,7B}$ = 15.0 Hz, 1H, 7_A-H), 3.69 (brd, 1H, 7_B-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.73, 16.08, 16.53, 18.58 and 22.80 (each q, 2-,3-,5-,6-CH_3), 30.53 (t, C-4), 48.00 (s, C-3), 56.70 (t, C-7), 71.19 (d, C-3a), 123.75 and 124.49 (each s, C-5-,6), 160.74 (s, C-2); MS (70 eV): *m/z* (%) = 192 (49, M^+), 177 (100, $M^+ - CH_3$), 162 (9, $M^+ - 2CH_3$), 147 (9, $M^+ - 3CH_3$), 111 (62, $C_6H_{11}N_2^+$), 82 (15, $C_6H_{10}^+$), 67 (25, $C_6H_{10}^+ - CH_3$), 55 (11), 41 (34); $C_{12}H_{20}N_2$ (192.3): calcd C 74.95, H 10.48, N 14.75; found C 75.24, H 10.76, N 14.92.

Reactions in Scheme 4: The general procedure was the same as for Scheme 3.

Azo compound 32 and hydropyridazine *endo*-33: TFA (0.45 mL, 5.84 mmol) was added slowly to a solution of $\mathbf{3}_{tr}$ (500 mg, 2.03 mmol) and **4** (5 mL, 60 mmol) in $CHCl_3$ (2 mL) at −5 °C. Work-up after 1 h. Kugelrohr distillation (40 °C/0.05 Torr) yielded a mixture of **32** and *endo*-**33** (496 mg, 86%, ratio 81:19). Separation by FC [PE/EE, 2:3 + triethylamine (3%)].

Azo compound 32:[11b] After sublimation (40 °C, 0.5 Torr) colorless crystals, m.p. 46–47 °C (46–47 °C,[8b] 379 mg, 64%); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.11–1.24 (m, 2H, 8-,9-H), 1.46–1.56 (mc, 2H, 8-,9-H), 2.17–2.23 (m, 1H, 7-H), 2.39–2.52 (m, 2H, 7-,7a-H), 2.89–2.94 (m, 1H, 4a-H, $J_{4a,7a}$ = 13.0 Hz), 5.23–5.25 (m, 2H, 1-,4-H), 5.45 (s, 2H, 5-,6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.25 (t) and 20.46 (t, C-8,-9), 37.48 (d, C-7a), 37.75 (t, C-7), 49.45 (d, C-4a), 64.50 (d, C-1), 66.72 (d, C-4), 130.1 and 130.8 (d, C-5,-6). **Hydropyridazine *endo*-33**: Colorless oil (89 mg, 15%); IR ($CDCl_3$): $\tilde{\nu}$ = 3050 cm^{-1} (=C–H), 2970, 2930, 2880, 2820 (C–H), 1575 (C=N), 1430, 1415 (C–H), 1350, 1320, 1300, 1270, 1250, 1215, 1190, 1175, 1080, 1070, 1030, 1020, 1000, 960, 950, 830; UV (hexane): λ_{max} (lg ε) = 244 nm (3.75); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.52–0.62 (mc, 1H, 4_a-H, $J_{4n,4x}$ = 12.5 Hz, $J_{4n,4a}$ = 12.5 Hz, $J_{4n,3x}$ = 12.5 Hz, $J_{4n,3a}$ = 4.0 Hz), 1.45–1.48 (A, 1H, 10-H_A, J_{AB} = 8.75 Hz), 1.67–1.73 (m, 2H, 4_x-H and B, 10-H_a), 1.81–1.90 (m, 1H; 3_x-H), 1.98–2.05 (m, 1H, 3_n-H), 3.09 (brs, 1H, 5-H), 3.57–3.62 (ddd, 1H, 4a-H, $J_{4a,5}$ = 5.9 Hz, $J_{4a,10}$ = 2.5 Hz), 4.34 (brs, 1H, 8-H), 6.07–6.10 (m, 1H, 6-,7-H), 6.26–6.28 (mc, 1H, 6-,7-H), 6.64–6.66 (mc, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.00 (t, C-4), 22.58 (t, C-3), 45.70 (t, C-10) 47.37 (d, C-5), 59.60 (d, C-4a), 67.27 (d, C-8), 133.1 (d, C-6,-7), 136.1 (d, C-6,-7), 138.7 (d, C-2); MS (70 eV): *m/z* (%) = 148.3 (18.3, M^+), 105.2 (11.8), 91.1 (49.3), 83.3 (100, $C_4H_7N_2^+$), 79.3 (25.6), 66.1 (70.0, $C_5H_6^+$), 56.1 (12.8), 51.1 (10.1), 39.2 (30.8), 28.1 (17.9); $C_9H_{12}N_2$ (148.2): calcd C 72.94, H 8.16, N 18.90; found C 73.20, H 8.33, N 19.23.

Azo compound 34 and hydropyridazine *endo*-35: TFA (4.20 mL, 54.6 mmol) was slowly added to a solution of $\mathbf{3}_{tr}$ (1.50 g, 6.09 mmol) and **5** (4.20 mL, 54.6 mmol) in $CHCl_3$ (7 mL) at −5 °C. After being stirred for 2.3 h the reddish mixture remained biphasic. The crude product (2.76 mg of a brownish oil) was dissolved in EE and filtered through a pad of silica gel. After removal of the solvent and Kugelrohr distillation (40 °C, 0.05 Torr) a 1:1 mixture of **34** and *endo*-**35** (762 mg, 26%) was obtained. FC (EE) yielded two fractions.

Azo compound 34: After sublimation (40 °C/0.05 Torr) colorless crystals (355 mg, 12%), m.p. 66–68 °C; IR ($CDCl_3$): $\tilde{\nu}$ = 3020 cm^{-1}, (=C–H), 2955, 2930, 2900, 2865, 2840 (C–H), 1650 (C=C), 1460, 1450, 1440 (N=N, C–H), 1525, 1335, 1310, 1265, 1190, 1160, 1080; UV (hexane): λ_{max} (lg ε) = 382 nm (2.03), 372 (1.82), 345 (1.23); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.21–1.33 (m, 3H) and 1.57–1.79 (m, 5H, 7-,8-,9-,10-H), 2.19–2.26 (m, 1H, 8a-H), 2.39–2.42 (m, 1H, 4a-H, $J_{4a,8a}$ = 10.5 Hz), 5.13 (s, 1H, 1-H), 5.17 (s, 1H, 4-H), 5.60–5.63 (m, 1H, 5-H), 5.71–5.76 (m, 1H, 6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.11 (t) and 21.52 (t, C-9,-10), 22.62 (t, C-8), 25.44 (t, C-7), 36.39 (d, C-8a), 37.29 (d, C-4a), 66.50 (d, C-1), 68.49 (d, C-4), 127.9 (d) and 129.0 (d, C-5,-6); MS (70 eV): *m/z* (%) = 162.3 (5.9, M^+), 134.3 (7.8, $M^+ - N_2$), 119.3 (21.2), 105.1 (24.8), 91.2 (100), 79.3 (44.3, $M^+N_2 - C_4H_7$, $C_6H_7^+$), 65.2 (11.3), 53.1 (8.1), 41.1 (16.9), 39.1 (19.1), 28.1 (14.3); $C_{10}H_{14}N_2$ (162.2): calcd C 74.03, H 8.70, N 17.27; found C 73.97, H 8.75, N 17.09.

Hydropyridazine *endo*-35: After Kugelrohr distillation (40 °C, 0.05 Torr) colorless oil (352 mg, 12%); IR ($CDCl_3$): $\tilde{\nu}$ = 3050 cm^{-1} (=C–H), 2945, 2900, 2870, 2840 (C–H), 1600 (C=N), 1460, 1450, 1435 (C–H), 1370, 1325, 1270, 1180, 1130, 1100, 1070, 1050, 1000, 860, 835; UV (hexane): λ_{max} (lg ε) = 250 nm (3.79); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.79–0.90 (mc, 1H, 4_n-H, $J_{4n,4x}$ = 12.0 Hz, $J_{4n,3x}$ = 12.0 Hz, $J_{4n,4a}$ = 12.0 Hz, $J_{4n,3n}$ = 4.8 Hz), 1.17–1.33 (m, 2H, 10-,11-H), 1.40–1.46 (mc, 1H, 4_x-H), 1.51–1.58 (mc, 1H, 11-H), 1.81–1.96 (m, 2H, 3_x-,3_n-o,10-H), 1.99–2.06 (m, 1H, 3_n-o,10-H), 2.50–2.52 (m, 1H, 5-H), 3.31–3.35 (dd, 1H, 4a-H, $J_{4a,5}$ = 5.3 Hz), 3.93–3.96 (m, 1H, 8-H), 6.10–6.13 (mc, 6-,7-H), 6.27–6.30 (m, 1H, 6-,7-H), 6.42–6.43 (m, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.51 (t, C-4), 22.80 (t, C-3), 23.06 (t, C-10), 25.56 (t, C-11), 36.44 (d, C-5), 56.17 (d, C-4a), 60.92 (d, C-8), 130.8 (d, C-6,-7), 133.7 (d, C-6,-7), 134.8 (d, C-2); MS (70 eV): *m/z* (%) = 162.1 (23.4, M^+), 133.1 (66, $M^+ - C_2H_5$), 82.9 (100, $C_4H_7N_2^+$), 80.0 (19.6, $C_6H_5^+$), 55.9 (11.9), 38.9 (10.4), 27.9 (13.1); $C_{10}H_{14}N_2$ (162.2): calcd C 74.03, H 8.70, N 17.27; found C 73.78, H 8.57, N 17.43.

Azo compounds *endo/exo*-36: Compound **7** (4.57 g) was condensed into a solution of $\mathbf{3}_{tr}$ (1.50 g, 6.09 mmol) in $CHCl_3$ (7 mL) at −10 °C. After slow addition of TFA (4.23 mL, 54.9 mmol) the yellow mixture (two phases) was stirred for 2.5 h, after which more **7** was slowly bubbled into the reaction mixture. FC (PE/EE, 4:1) yielded *endo/exo*-**36** (3:1, 227 mg, 9%) as a colorless oil. Further fractions (247 mg) could not be identified. ***endo/exo*-36**: IR ($CDCl_3$): $\tilde{\nu}$ = 3160 cm^{-1}, 3090 (=C–H), 2975, 2880 (C–H), 1640, 1600, 1525, 1465, 1450 (N=N, C–H), 1420, 1385, 1380, 1325, 1215, 1170, 1095, 995; UV (hexane): λ_{max} (lg ε) = 377 nm (2.11), 367 (1.84), 3.42 (1.22); MS (70 eV): *m/z* (%) = 136.3 (9.2, M^+), 108.2 (1.3, $M^+ - N_2$), 93.1 (39.4), 79.2 (75.4), 67.1 (100), 54.1 (51.5), 41.1 (61.1), 28.0 (16.9); $C_8H_{12}N_2$ (136.2): calcd C 70.55, H 8.88, N 20.57; found C 70.73, H 9.03, N 20.96.

***endo*-36**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.08–1.17 (m, 1H, 7-H), 1.21–1.30 (m, 1H, 7-,8-H), 1.33–1.38 (dd, 1H, 5_n-H, $J_{5n,5x}$ = 13.75 Hz, $J_{5x,4}$ = 6.5 Hz), 1.46–1.57 (m, 2H, 7-,8-H), 1.71–1.79 (mc, 1H, 5_x-H), 2.01–2.07 (mc, 1H, 4-H), 4.95–4.97 (mc, 1H, 6-H), 5.10–5.15 (m, 3-H, 2′-$H_{A/B}$), 5.67–5.76 (ddd, 1H, 1′-H, $J_{1',2'A}$ = 17.0 Hz, $J_{1',2'B}$ = 10.5 Hz, $J_{1',4}$ = 7.0 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.34 (t, C-7), 21.50 (t, C-8), 26.01 (t, C-5), 34.69 (d, C-4), 61.02 (d, C-6), 65.60 (d, C-3), 116.2 (t, C-2′), 138.0 (d, C-1′).

***exo*-36**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.13–1.21 (m, 1H, 7-H), 1.31–1.34 (m, 2H, 7-,8-H), 1.60–1.67 (m, 2H, 5_n-,8-H), 1.88–1.94 (ddd, 1H, 5_x-H, $J_{5x,5n}$ = 13.75 Hz, $J_{5x,4}$ = 10.75 Hz, $J_{5x,6}$ = 1.75 Hz), 2.51–2.57 (mc, 1H, 4-H), 4.92–4.95 (dt, 1H, 2′-H_S), 4.98–5.03 (dt, 1H, 2′-H_A, J_{AB} = 1.0 Hz), 5.18–5.20 (m, 2H, 3-,6-H), 5.43–5.52 (ddd, 1H, 1′-H, $J_{1',2'A}$ = 17.0 Hz, $J_{1',2'B}$ = 10.25 Hz, $J_{1',4}$ = 8.0 Hz; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.78 (t, C-7), 21.35 (t, C-8), 28.25 (t, C-5), 39.72 (d, C-4), 61.33 (d, C-6), 65.76 (d, C-3), 114.1 (t, C-2′), 140.4 (d, C-1′).

Azo compounds 37–39 and hydropyridazine 40: Cooled TFA (4.23 mL, 54.9 mmol) was slowly added at −5 °C to a solution of $\mathbf{2}_{tr}$ (1.50 g, 6.09 mL) and isoprene (**8**, 4.23 mL, 54.9 mmol) in $CHCl_3$ (8 mL). After 3 h a red oil (2.79 g) was isolated, dissolved in ethyl acetate and filtered through a pad of silica gel (1.03 g). FC (EE) yielded two fractions. Fraction A: Kugelrohr distillation (30 °C, 0.05 Torr) yielded a colorless oil of **37**, **38**, and **39** (169 mg, 6%). After FC (PE/EE, 8:2 + 2% NEt_3), fraction A1: Kugelrohr distillation yielded **37**, fraction A2 a 4:1 mixture of **38** and **39**. Fraction B: Kugelrohr distillation (30 °C, 0.05 Torr) furnished **40** (568 mg, 21%); **37 + 38 + 39**: UV (hexane): λ_{max} (lg ε) = 380 nm (2.13), 370 (1.87), 343 (1.21); MS (70 eV): *m/z* (%) = 150.2 (5.2, M^+), 122.1 (3.6, $M^+ - N_2$), 107.1 (23.2, $M^+ - N_2 - CH_3$), 93.1 (36.0), 79.1 (100, $M^+ - N_2 - C_3H_5$), 68.1 (78.3), 53.2 (44.3), 41.1 (42.2), 27.1 (27.0); $C_9H_{14}N_2$ (150.2): calcd C 71.96, H 9.39, N 18.65; found C 72.07, H 9.24, N 19.36.

Azo compound 37: IR ($CDCl_3$): $\tilde{\nu}$ = 3090 cm^{-1} (=C–H), 2975, 2880 (C–H), 1635 (C=C), 1525, 1460, 1450, 1415 (N=N, C–H), 1375 (-CH_3), 1315, 1160, 1000; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.84 (s, 3H, -CH_3), 0.97–1.06 (mc, 1H, 7-H), 1.06–1.11 (ddd, 1H, 5_x-H, $J_{5x,5n}$ = 13.75 Hz), 1.14–1.23 (mc, 1H, 7-,8-H), 1.36–1.44 (mc, 1H, 7-,8-H), 1.70–1.79 (m, 2H, 5_n-, 8-H), 4.80–4.82 (dd, 1H, 3-H), 5.04–5.08 (d, 1H, 2′-H_B, J_{AB} = 0.75 Hz, $J_{2'B,1'}$ = 17.5 Hz), 5.04–5.07 (dd, 1H, 2′-H_A, $J_{2'A,1'}$ = 10.5 Hz), 5.13–5.16 (mc, 1H, 6-H), 5.72–5.79 (dd, 1H, 1′-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.31 (t, C-7), 19.61 (t, C-8), 27.74 (q, -CH_3), 33.17 (t, C-5), 38.20 (s, C-4), 62.68 (d, C-6), 70.48 (d, C-3), 112.6 (t, C-2′), 144.5 (d, C-1′).

Azo compound 38: IR ($CDCl_3$): $\tilde{\nu}$ = 3090 cm^{-1} (=C–H), 2970 (C–H), 1640 (C=C), 1525, 1470, 1445, 1415 (C–H, N=N), 1374 (-CH_3), 1315, 1160,

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1000; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.07–1.14 (m, 1H, 7-H), 1.14 (s, 3H, -CH_3), 1.25–1.34 (m, 2H, 5_n-, 7- or 8-H, $J_{5n,5x}$ = 13.5 Hz), 1.46–1.56 (m, 2H, 5_x-,7-or 8-H), 1.81–1.89 (m, 1H, 8-H); 8.45–4.88 (dd, 1H, 2′-H_A, J_{AB} = 0.75 Hz, $J_{2'A,1'}$ = 10.5 Hz), 4.92–4.93 (dd, 1H, 3-H), 4.90–4.95 (d, 1H, 2′-H_B, $J_{2'B,1'}$ = 17.5 Hz), 5.13–5.16 (mc, 1H, 6-H), 5.51–5.58 (dd, 1H, 1′-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.02 (t, C-7), 19.95 (t, C-8), 25.98 (q, -CH_3), 35.20 (t, C-5), 37.54 (s, C-4), 62.29 (d, C-6), 69.93 (d, C-3), 111.5 (t, C-2′), 145.6 (d, C-1′).

Azo compound 39: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.46–2.50 (dd, 1H, 4-H, $J_{4,5n}$ = 10.75 Hz, $J_{4,5x}$ = 7.0 Hz), 4.66–4.67 (m, 1H, 6-H), 4.75–4.76 (brs, 1H, 3-H), 5.18 (brs, 2H, 2′-H); the residual signals are obscured.

Hydropyridazine 40: UV (hexane): λ_{max} (lg ε) = 246 nm (3.63); IR ($CDCl_3$): $\tilde{\nu}$ = 3010 cm^{-1} (=C–H), 2960, 2920, 2860, 2820, 2800 (C–H), 1620 (C=N), 1450, 1430 (C–H), 1380 (-CH_3), 1355, 1340, 1225, 1210, 1175, 1110, 1070, 1025, 970; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.65 (s, 3H, -CH_3), 1.65–1.74 (m, 1H, 4_n-H), 1.88–2.25 (m, 5H, 4_x-, 3-, 5-H), 2.63–2.70 (mc, 1H, 4a-H), 3.22–3.29 (mc, 1H, 8-H), 3.80–3.85 (d, 1H, 8-H, $J_{8',8''}$ = 16.3), 5.37 (s, 1H, 7-H), 6.81–6.82 (m, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.53 (q, -CH_3), 23.11 (t, C-4), 25.92 (t, C-3), 37.17 (t, C-5), 51.76 (d, C-4a), 54.22 (t, C-8), 118.9 (d, C-7), 131.4 (s, C-6), 140.2 (d, C-2); MS (70 eV): *m/z* (%) = 150.2 (56.1, M^+), 135.2 (100, $M^+ - CH_3$), 94.0 (12.9), 83.0 (21.7, $C_4H_7N_2^+$), 68.1 (20.7, $C_5H_8^+$), 53.0 (11.8, $C_5H_8^+ - CH_3$), 40.9 (18.3), 28.0 (11.8); $C_9H_{14}N_2$ (150.2): calcd C 71.96, H 9.39, N 18.65; found C 71.61, H 9.30, N 18.38.

Azo compounds 41 and 42, hydropyridazine 43: As for **37**–**40**, $\mathbf{3}_{tr}$ (1.50 g, 6.09 mmol), **9** (3.75 mL, 31.8 mmol), and TFA (4.23 mL, 54.9 mmol) were allowed to react in $CHCl_3$ (7 mL) for 3 h at −5 °C. From the brown residue (3.60 g) a crude product was isolated (1.65 g). FC (EE) afforded four fractions which were purified by Kugelrohr distillation (30 °C, 0.05 Torr). Fraction 1: Polymeric material (residue). Fraction 2: colorless oil of **41** + **42** (76 mg). FC (PE/EE, 8:2 +2NEt$_3$) yielded, after sublimation (30 °C, 0.05 Torr), **41** (40 mg), m.p. 44–45 °C, and **42** (18 mg), m.p. 38–39 °C. Fraction 3: **41**/**42** + **43** (7:3, 14 mg). Fraction 4: colorless oil of **43** (902 mg, 29%).

Azo compounds 41 + 42: UV (hexane): λ_{max} (lg ε) = 380 nm (2.17), 370 (1.88), 342 (1.23); MS (70 eV): *m/z* (%) = 164.0 (4.8, M^+), 136.0 (2.9, $M^+ - N_2$), 121.0 (27.2, $M^+ - N_2 - CH_3$), 107.1 (27.1), 95.0 (43.1, $M^+ - N_2 - C_3H_5$), 92.9 (80.0), 79.1 (81.7), 67.0 (100), 55.1 (48.5), 41.0 (65.8), 28.0 (34.7); $C_{10}H_{16}N_2$ (164.3): calcd C 73.13, H 9.82, N 17.05; found C 73.03, H 9.55, N 17.55; **41**: IR ($CDCl_3$): $\tilde{\nu}$ = 3080 cm^{-1} (=C–H), 2960, 2940, 2870 (C–H), 1640 (C=C), 1530, 1455, 1450 (N=N, C–H), 1375 (-CH_3), 1215, 1170, 1140, 1105; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.89 (s, 3H, 4-CH_3), 1.01–1.21 (m, 3H, 5_x-,7-,8-H), 1.38–1.45 (mc, 1H, 7-,8-H), 1.62–1.70 (mc, 1H, 8-H), 1.79–1.80 (brs, 3H, 1′-CH_3), 1.99–2.03 (dd, 1H, 5_n-H, $J_{5n,5x}$ = 13.8 Hz), 4.86 (s, 1H, 2′-H), 4.89–4.90 (brs, 1H, 2′-H, J_{AB} = 0.75 Hz), 5.17–5.20 (m, 2H, 3-,6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.01 (t, C-7), 20.03 (t + q, C-8, 4-CH_3), 28.04 (q, 1′-CH_3), 32.62 (t, C-5), 41.46 (s, C-4), 63.08 (d, C-6), 68.29 (d, C-3), 110.9 (t, C-2′), 149.1 (s, C-1′); **42**: IR ($CDCl_3$): $\tilde{\nu}$ = 3100 cm^{-1} (=C–H), 2980, 2935, 2880 (C–H), 1635 (C=C), 1530, 1460, 1435 (N=N, C–H), 1380, 1375 (-CH_3), 1320, 1165, 1130; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.08–1.17 (m, 1H, 7-H), 117 (s, 3H, 4-CH_3), 1.29–1.36 (m, 2H, 5_n-,7- or 8-H, $J_{5n,5x}$ = 13.5), 1.50–1.60 (m, 2H, 5_x-,7- or 8-H), 1.70 (brs, 3H, 1′-CH_3), 1.83–1.90 (mc, 1H, 8-H), 4.72–4.73 (brs, 1H, 2′-H, J_{AB} = 0.75 Hz), 4.95 (s, 1H, 2′-H), 5.11–5.13 (mc, 1H, 6-H), 5.21–5.22 (dd, 1H, 3-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.19 (t, C-7), 19.98 (q, 4-CH_3), 20.11 (t, C-8), 26.87 (q, 1′-CH_3), 34.63 (t, C-5), 40.51 (s, C-4), 62.32 (d, C-6), 67.75 (d, C-3), 110.9 (t, C-2′), 149.5 (s, C-1′).

Hydropyridazine 43: UV (hexane): λ_{max} (lg ε) = 245 nm (3.63); IR ($CDCl_3$): $\tilde{\nu}$ = 3010 cm^{-1} (=C–H), 2980, 2910, 2870, 2850, 2820, 2790 (C–H), 1620 (C=N), 1450, 1430 (C–H), 1380 (-CH_3), 1340, 1330, 1240, 1220, 1210, 1145, 1110, 1070, 1025, 975; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.57 (s, 6H, -CH_3), 1.57–1.68 (mc, 1H, 4_n-H), 1.83–1.93 (m, 2H, 4_x-,5-H), 1.99–2.22 (m, 3H, 3-,5-H), 2.58–2.65 (mc, 1H, 4a-H), 3.15–3.20 (mc, 1H, 8-H), 3.62–3.66 (d, 1H, 8-H, $J_{8',8''}$ = 16.0 Hz), 6.77–6.79 (m, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.04 (q) and 17.80 (q, 6-,7-CH_3), 23.06 (t, C-4), 25.66 (t, C-3), 38.36 (t, C-5), 52.15 (d, C-4a), 58.98 (t, C-8), 123.2 (s) and 123.6 (s, C-6,-7), 140.1 (d, C-2); MS (70 eV): *m/z* (%) = 164.1 (45.1, M^+), 149.1 (100, $M^+ - CH_3$), 83.1 (19.3, $C_4H_7N_2^+$), 82.0 (9.0, $C_6H_{10}^+$), 67.1 (16.3, $C_6H_{10}^+ - CH_3$), 52.9 (7.3, $C_6H_{10}^+ - 2CH_3$), 40.9 (17.1), 28.0 (10.0); $C_{10}H_{16}N_2$ (164.3): calcd C 73.13, H 9.82, N 17.06; found C 72.82, H 9.74, N 16.91.

Dimeric 4*H*,5,6-dihydro-1,2-diazepine ($\mathbf{44}_{di}$): A solution of glutaric dialdehyde (**46**, 20.0 g, 25% in water) and water (20 mL) were cooled in an ice bath before hydrazine hydrate (100%, 2.51 g, 50.0 mmol) was slowly added. After 5 min a precipitate started to deposit, which was filtered off after 30 min. After sublimation (120 °C/0.05 Torr) of the crude product (5.11 g) $\mathbf{44}_{di}$ (980 mg, 20%) was obtained as a colorless, sparingly soluble powder with m.p. 119–122 °C; IR (KBr): $\tilde{\nu}$ = 3360 cm^{-1}, 3240 (N–H), 3150, 3060, 3040 (=C–H), 2990, 2950, 2910, 2890, 2850 (C–H), 1635 (C=N), 1395, 1365, 1340, 1325, 1290, 1270, 1230, 1200, 1180, 1080, 1050, 1010, 960, 940, 890, 870, 780, 760, 715, 620; ^{1}H NMR (250 MHz, [D_6]DMSO): δ = 1.20–2.20 (m, 10H), 3.80 (m, 1H), 4.45 (m, 1H) and 5.75–5.90 (m, 2H). The remaining signals are disguised by those of the solvent; MS (70 eV): *m/z* (%) = 192 (97, M^+), 135 (12), 122 (75), 95 (88, $C_5H_7N_2^+$), 82 (100), 68 (39), 54 (86), 41 (38); $C_{10}H_{16}N_4$ (192.3): calcd C 62.47, H 8.39, N 29.14; found C 62.64, H 8.58, N 29.55.

Adduct *endo-endo*-45: TFA (888 mg, 7.79 mmol) was added over 15 min to a suspension of $\mathbf{44}_{di}$ in $CHCl_3$ (3 mL) and Cp (**4**, 1.72 g, 26.1 mmol). The clear yellow mass was worked up over 10 min as described for Scheme 3. The crude product (541 mg) was dissolved in EE and filtered through a pad of silica gel. The product was eluted with methanol and sublimed (90 °C/0.01 Torr), affording *endo-endo*-**45** (128 mg, 22%) as colorless crystals, m.p. 103–105 °C. IR (KBr): $\tilde{\nu}$ = 3045 cm^{-1} (=C–H), 2920, 2890, 2870, 2840 (C–H), 1610 (C=C), 1440, 1370, 1355, 1300, 1265, 1225, 1130, 1120, 1100, 1055, 1045, 1020, 970, 860, 850, 830, 795, 780, 715, 695 (CH=CH, def.), 665, 640; ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.95–1.22 (m, 2H), 1.32–1.96 (m, 7H), 2.05–2.24 (m, 2H), 2.37 (m, 1H), 2.67 (ddd, J = 9.0 and 2.0 Hz, 1H), and 2.80 (br dd, J = 9.0 and 5.0 Hz, 1H, 7-,8-,9-,10-,11-,12-,13-,16-,17-H), 4.26 (br d, J = 9.0 Hz; 1H) and 4.50 (dm, J = 8.5 Hz, 1H, 1-,4-H), 5.37 (m, 2H), 5.50 (m, 1H) and 5.58 (m, 1H, 5-,6-,14-,15-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 20.66, 24.15, 27.31 (t, C-9,-10,-11), 33.40, 35.52 (t, C-16,-17), 41.52, 48.50 (d, C-7,-13), 64.48, 65.02 (d, C-1,-4), 71.24, 73.19 (d, C-8,-12), 128.66, 129.37, 132.68, 133.57 (d, C-5,-6,-14,-15); MS (70 eV): *m/z* (%) = 228 (14, M^+), 162 (100, $M^+ - C_5H_6$), 121 (99), 95 (10, $C_5H_7N_2^+$), 91 (14), 80 (16), 77 (17), 66 (19, $C_5H_6^+$), 55 (16), 41 (18), 39 (18), 32 (15); $C_{15}H_{20}N_2$ (228.3): calcd C 78.90, H 8.83, N 12.27; found C 78.46, H 8.87, N 12.49.

Rearrangements in Scheme 6: All physical data of the products agreed with those already described in this paper or in the literature.

a) Thermal rearrangements:

Reaction endo-11 → 10: *endo*-**11** (50 mg, 0.31 mmol) was heated for 3 h in the presence of some potassium carbonate (to prevent acid catalysis) to 70 °C (TLC monitoring). Kugelrohr distillation (30 °C/0.01 Torr) yielded **10** (45 mg, 90%). Distillation of **10** (90 °C/1 Torr) caused decomposition to $\mathbf{1}_{tr}$ and cyclopentadiene. *Exo*-**11** stayed unchanged under the same conditions.

Endo-13 → 12: In a closed vessel *endo*-**13** (100 mg, 0.57 mmol) was heated to 70 °C. After 15 h the educt was completely transformed into **12** (TLC monitoring). Sublimation (30 °C/0.01 Torr) yielded **12** (95 mg, 95%); IR (CCl_4): $\tilde{\nu}$ = 3050 cm^{-1}, 2980, 2955, 2900, 2860, 2840 (-C–H), 1620 (C=C), 1495, 1470, 1445 (N=N), 1395 [$C(CH_3)_2$], 1380, 1370, 1350, 1300, 1290, 1270; UV (*n*-hexane): λ_{max} (lg ε) = 360 nm (221), 350 (sh, 95), 345 (sh, 81), 327 (sh, 21); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.55 (s, 3H, 8-*exo*-CH_3), 0.90 (s, 3H, 8-*endo*-CH_3), 1.63 (s, 4-CH_3), 2.18 (m, 2H, 7-H), 2.89 (m, 1H, 7a-H), 3.10 (m, 1H, 4a-H), 4.86 (d, 1H, 1-H, $J_{1,7a}$ = 3.5 Hz), 5.42 (m, 1H, 6-H), 5.58 (m, 1H, 5-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 11.46 (q, CH_3-4), 17.67 (q, *exo*-CH_3-8), 17.95 (q, *endo*-CH_3-8), 31.87 (t, C-7), 38.91 (d, C-7a), 56.98 (s, C-8), 57.10 (d, C-1), 88.26 (s, C-4), 88.68 (d, C-4a), 126.92 (d, C-6), 133.00 (d, C-5); MS (70 eV): *m/z* (%) = 176 (6, M^+), 148 (4, $M^+ - N_2$), 133 (14, $M^+ - N_2$, -CH_3), 111 (100, $M^+ - Cp$); $C_{11}H_{16}N_2$ (176.3): calcd C 74.96, H 9.15, N 15.89, found C 74.34; H 8.75, N 15.88.

b) Acid-catalyzed rearrangements: In the following ^{1}H experiments 1,4-dibromobenzene was used as internal standard wherever possible.

Reaction endo-11 → 10: ^{1}H NMR monitoring of a solution of *endo*-**11** (150 mg, 0.92 mmol) in $CDCl_3$ (0.50 mL) and CF_3CO_2H (10 mg, 0.090 mmol) demonstrated clean conversion of *endo*-**11** to **10** that is quantitative after 20 min at ca. 20 °C.

Reaction 10 → endo-11: CF_3CO_2H (0.23 mL, 3.00 mmol) was added to a solution of **10** (162 mg, 1.00 mmol) in $CHCl_3$ (4.00 mL). An ^{1}H NMR spectrum taken immediately showed only the signals of *endo*-**11**H$^+$. The mixture was

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added to an ice-cold solution of K_2CO_3 (satd). The organic phase was separated off and the water phase extracted twice with $CHCl_3$. The $CHCl_3$ solution was dried (K_2CO_3), the solvent evaporated and the residue sublimed (30 °C/0.01 Torr). Colorless crystals of endo-**11** (480 mg, 96%), m.p. 33–34 °C.

Reaction ***14*** *→ endo-****15***: ^{1}H NMR monitoring of **14** (20 mg, 0.11 mmol) in $CDCl_3$ (0.30 mL) and CF_3CO_2H (0.04 mL, 0.55 mmol) revealed a smooth rearrangement to endo-**15**H^+, which was complete after 35 min.

Reaction ***16*** *→ endo-****17***: ^{1}H NMR monitoring of the reaction of **16** (22 mg, 0.12 mmol) in $CDCl_3$ (0.30 mL) and CF_3CO_2H (0.05 mL, 0.60 mmol) at ca. 20 °C indicated a smooth transformation of **16** into endo-**17**H^+, which was complete after 90 min.

Reaction ***20*** *→ 21*: ^{1}H NMR monitoring of **20** (30.0 mg, 0.333 mmol) in $CDCl_3$ (0.30ml) and CF_3CO_2H (0.12 mL, 1.66 mmol) indicated smooth transformation of **20** into **21**H^+ within 9 d.

Reaction ***22*** *→ 23*: $CDCl_3$ (0.50 mL) containing **22** (50.0 mg, 0.30 mmol) and CF_3CO_2H (173 mg, 1.52 mmol) were completely transformed into **23**H^+ after 6 d (^{1}H NMR). Work-up as for **10** → *endo*-**11** yielded **23** as a colorless oil (Kugelrohr distillation 50 °C/0.01 Torr, 44.0 mg, 88%).

Reaction ***24*** *→ 26*: ^{1}H monitoring of a solution of **24** (41 mg, 0.25 mmol) and CF_3CO_2H (0.10 mL, 1.30 mmol) in $CDCl_3$ (0.50 mL) revealed complete transformation into **26**H^+ within 4 d. Work-up as for **10** → *endo*-**11** afforded exclusively **26** (Kugelrohr distillation 30 °C/0.05 Torr, 37 mg, 90%); ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 0.90$ (s, 3H, 3-CH_3), 1.12 (s, 3H, 3-CH_3), 1.67 (s, 3H, 5-CH_3), 1.92–1.98 (br d, 1H, $J_{4',4''} = 15.5$ Hz), 2.13–2.21 (m, 1H, 4-H), 2.34–2.38 (dd, 1H, 3a-H, $J_{3a,4'} = 11.25$ Hz, $J_{3a,4''} = 3.75$ Hz), 3.16–3.22 (d m, 1H, 7-H), 3.82–3.85 (d, 1H, 7-H, $J_{7',7''} = 15.0$ Hz), 5.45–5.46 (br s, 1H, 5-H), 6.60 (s, 1H, 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 17.18$ (q, 3-CH_3), 20.71 (q, -CH_3), 23.74 (q, 3-CH_3), 23.92 (t, C-4), 47.03 (s, C-3), 55.92 (t, C-7), 69.87 (d, C-3a), 119.5 (d, C-5), 132.5 (s, C-6), 153.3 (d, C-2); $C_{16}H_{16}N_2$ (264.3): calcd C 73.13, H 9.82, N 17.06, found C 72.91, H 9.89, N 16.86.

Reaction ***27*** *→ 29*: A solution of **27** (54.0 mg, 0.303 mmol) in $CDCl_3$ (0.5 mL) was reacted with CF_3CO_2H (171 mg, 1.51 mmol). After 1 d (^{1}H NMR monitoring) **29**H^+ resulted exclusively. Work up according to **10** → *endo*-**11** yielded **29** (Kugelrohr distillation, 40 °C/0.05 Torr, 41.0 mg, 75%) as a colorless oil; ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 0.91$ and 1.11 (each s, each 3H, 3-CH_3), 1.71 (s, 3H, 6-CH_3), 1.88 (s, 3H, 2-CH_3), 1.97 (br d, 1H 4_A-H), 2.20 (m c, $J_{4B,4A} = 18.0$ Hz, 1H, 4_B-H), 2.34 (dd, $J_{3a,4B} = 11.5$ Hz, 1H, 3a-H), 3.14 (m c, 1H, 7_A-H), 3.81 (d, $J_{7B,7A} = 15.0$ Hz, 1H, 7_B-H), 5.48 (m, 1H, 5-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 11.92$ and 16.37 (each q, 3-CH_3), 20.80 (q, 6-CH_3), 23.01 (q, 2-CH_3), 24.50 (t, C-4), 47.94 (s, C-3), 56.28 (t, C-7), 70.94 (d, C-3a), 119.49 (d, C-5), 132.45 (s, C-6), 160.78 (s, C-2). Cf. **27** + **28** + **29**.

*Reaction endo-****33*** *→* ***32***:

a) ^{1}H monitoring of *endo*-**33** (50 mg, 0.338 mmol), $CDCl_3$ (0.40 mL) and CF_3CO_2H: $CDCl_3 = 1:50$ (0.13 mL, 0.034 mmol) revealed smooth transformation into **32** quantitatively in 6 d. b) CF_3CO_2H (0.30 mL, 3.89 mmol) was added to a solution of *endo*-**33** (33 mg, 0.22 mmol) in $CDCl_3$ (0.50 mL) at 0 °C. The ^{1}H NMR spectrum recorded immediately displayed only signals of **32**H^+. After treatment with K_2CO_3 the signals were identical with those of **32**.

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