Pergamon

Tetrahedron 54 (1998) 875–894

TETRAHEDRON

A NOVEL HETERO-DIELS-ALDER APPROACH TOWARDS PERHYDRO QUINOLINONES BEARING AN ANGULAR METHYL GROUP

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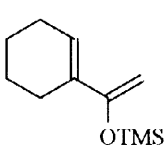
Received 6 October 1997; accepted 5 November 1997

Abstract: The title compounds **9-11** were synthesized by a hetero Diels-Alder reaction using the sterically demanding diene **2** as a new building block. The effect of commonly used Lewis acids and the substitution pattern of various imines **5** on both the mechanism and the diastereoselectivity of the reaction with the diene is discussed and compared with data obtained by *ab initio* calculations.

INTRODUCTION

The introduction of dienes and dienophiles containing hetero atoms proved to be a most powerful tool for the synthesis of various heterocyclic ringsystems. Especially cyclizations with highly activated silyloxy dienes showed tremendous synthetic utility.[1] A great variety of studies were carried out by condensations of such dienes with carbonyl compounds.[2] However, compared to their great importance as biologically active compounds, only few publications report reactions with imines leading to nitrogen heterocycles.[3]



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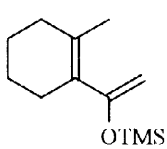

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A major research topic within our group is the construction of quinoline ringsystems bearing an angular methyl group as special feature and a hetero Diels-Alder approach towards these compounds seemed very promising. Recently a study of the reaction of trimethylsilyl enol ether **1** and various imines leading to bicyclic structures was published and influenced our own strategies significantly.[4] Though a methyl substituent at the activated diene causes additional sterical hinderance to some extent, the use of the silyl

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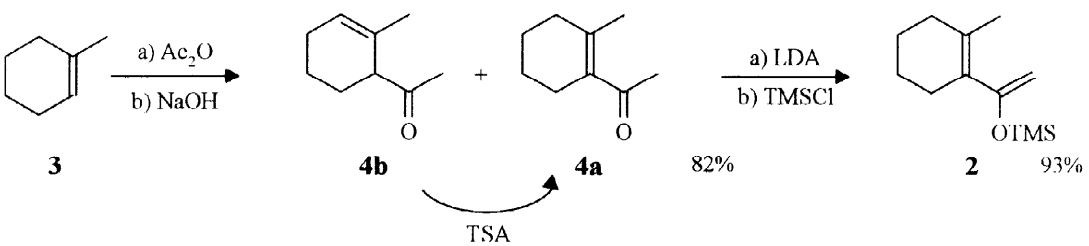
0040-4020/98/$19.00
PII: S0040-4020(97)10339-8

enol ether **2** for Diels-Alder reactions represents a new application of this compound as building block for the construction of fused heterocyclic ring systems. In the present paper we report the stereochemical and mechanistic aspects of the reaction with various imines **5a-f** under Lewis acid catalysis.

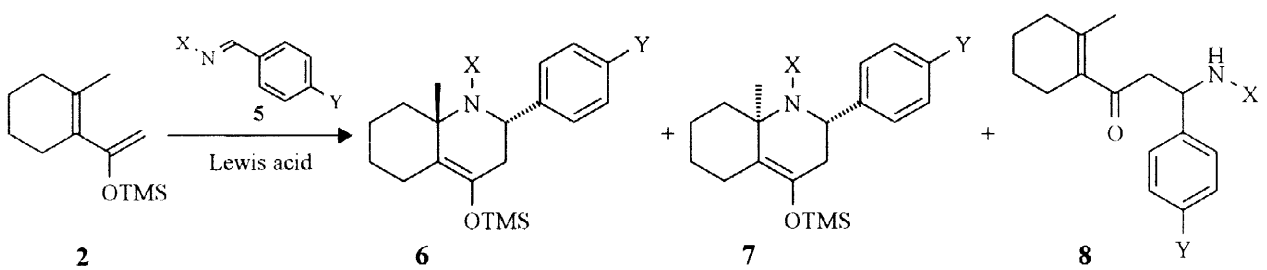
RESULTS

In the synthesis of diene **2** we were encountered with some problems. Starting from 1-methylcyclohexene **3** acylation under Lewis acid catalysis and subsequent elimination of AcOH gave a mixture of **4a** and **4b** (Scheme 1). Isomerization to the thermodynamically more stable conjugated product **4a** was achieved under both acidic or basic conditions. However, approximately 5% of **4b** remained in the resulting equilibrium mixture and no further conversion could be observed in contrast to the literature.[5] Formation of the diene was carried out following a slightly modified procedure by Rubottom *et al.* and gave **2** in good overall yield.[6]



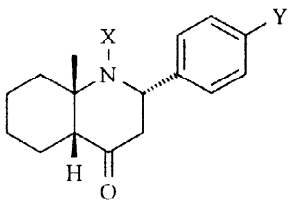
Scheme 1

As expected no reaction took place between diene **2** and various imines **5a-f** under thermal conditions. When the reaction was carried out under Lewis-acid catalysis, two different mechanisms seem to compete, depending on the type of the catalyst, the solvent and the distribution of the electron density in the imine. The desired Diels-Alder cyclization led to products of type **6** and **7** (Scheme 2), respectively, which could be converted to the coresponding ketones **9**, **10**, and **11**. However, as a side product the open-chain product of the general structure **8** was observed in some cases, obviously resulting from a nucleophilic addition of the silyl enol-ether **2** to the imine **5**.



Scheme 2

All silyl enol-ethers **6** and **7** proved to be rather sensitive to hydrolysis. In most cases the quinolines could only be isolated with great losses (**6/7b, c, e, f**) and we were not able to separate the two isomers **6d** and **7d**. Since the yields obtained proved not to be representative, the TMS group was subsequently cleaved by treatment of the crude compounds **6** and **7** with $MeOH/NEt_3$ immediately after cyclization and the resulting mixture of isomeric ketones **9** - **11** was analyzed (Table 1).



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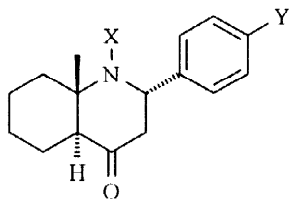

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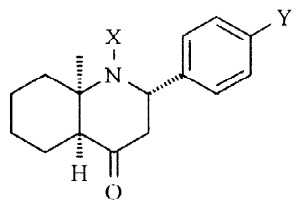

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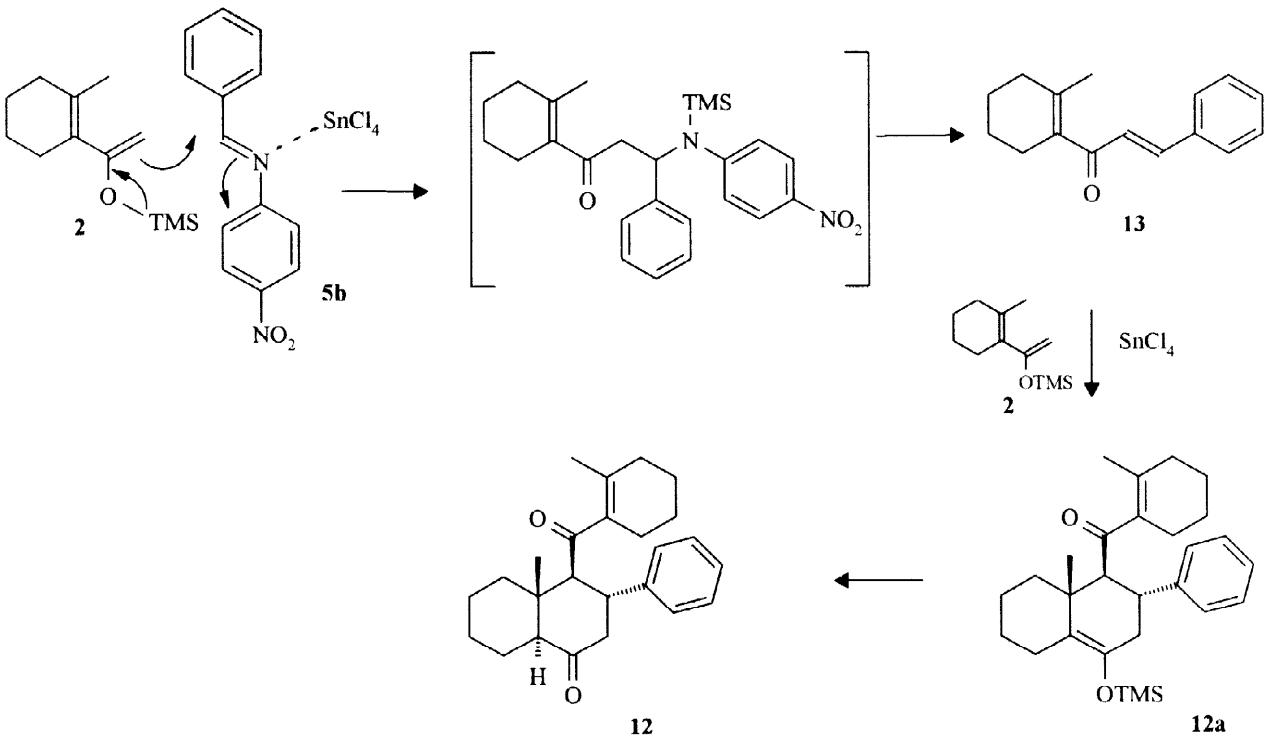
In the case of the imine **5a** (X=Ph, Y=H) the best results with respect to formation of bicyclic compounds were obtained using $TiCl_4$ as Lewis acid in CH_2Cl_2 (entry 1). Compound **6a** was isolated as the only product after basic (sat. $NaHCO_3$) workup, indicating complete *endo* selectivity for the cyclization. Cleavage of the TMS group led to a mixture of *cis*- and *trans*-isomers **9a** and **10a** in high over-all yield. Due to their similar polarity the two compounds could not be isolated on a preparative scale. $AlCl_3$ (entry 2) and $BF_3 \cdot Et_2O$ (entry 4) proved to be too aggressive catalysts leading to polymerization of the diene and the imine was recovered unchanged. Et_2AlCl (entry 3) and $SnCl_4$ (entries 5 and 6) showed somewhat weaker catalytic activity and longer reaction times had to be applied. However, the *endo* selectivity of the Diels-Alder cyclization was not influenced. ZnI_2 favored the competing addition reaction to **8a** (entries 7 and 8) which became the single product in a very slow reaction when the solvent was changed to the strong donor THF (entry 9).

Two facts indicate the existence of two independent mechanisms involved: First, we were not able to observe any bicyclic products formed from **8a** under standard cyclization conditions. Additionally, with increasing reaction time the ratio of both cyclic and acyclic products is increased (entries 7 and 8). Being an intermediate, **8a** should be consumed by the formation of heterocyclic compounds. Therefore we assume that the imine has to be activated to a certain degree in order to be able to undergo a fast Diels-Alder cyclization. If this point is not reached, a slower addition mechanism takes over and becomes predominant with decreasing activation by the Lewis acid.

As expected, an electron withdrawing *N*-substituent activated the imine **5b** (X=*p*-NO_2Ph, Y=H) by increasing the polarity but it also reversed the effect of the strong Lewis acid $TiCl_4$ and the weaker ZnI_2 (entries 10-12). Calculations of the Lewis acid / imine complexes on *ab initio* level indicated, that a large p_z-orbital coefficient at the imine carbon is essential for a successful Diels-Alder cyclization. Due to the weak interaction with $TiCl_4$ the increase is not sufficient, but polarization of the C=N bond seems still strong enough to allow a nucleophilic addition to form **8b**. The *endo* selectivity of the cyclized product **6a** was not influenced by the electron withdrawing substituent. After desilylation both isomers **9a** and **10a** were separated by preparative flash column chromatography and characterized by 2D NMR techniques.

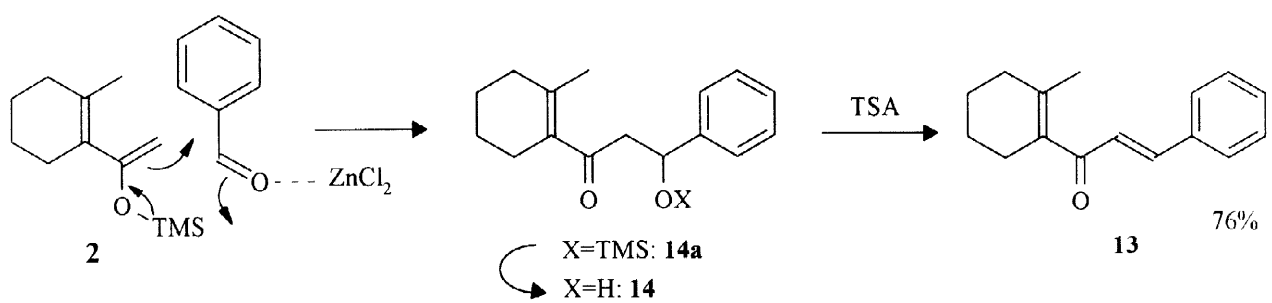
However, a rather unexpected product was formed when $SnCl_4$ was used as Lewis acid (entry 13). After a reaction time of 24 hours only the carbocyclic compound **12a** and subsequently the decalone **12** were isolated. Presumably the first step of the reaction is an addition of the diene to the imine, followed by a Lewis acid promoted elimination[7] to form the dienone **13**. Since diene **2** was always used in excess, a Lewis

acid catalyzed Diels-Alder cyclization can take place now leading to the silyl ether **12a** and finally to compound **12** (Scheme 3), similar to the reaction of diene **1** with activated carbon dienophiles reported.[8]



Scheme 3

In order to support this proposed mechanism we synthesized **13** by addition of **2** to benzaldehyde *via* the two intermediates **14a** and **14** (Scheme 4). Diene **2** could then be cyclized with **13** under similar reaction conditions to form product **12a**.



Scheme 4

Introduction of an electron donating *N*-substituent in the case of the imine **5c** (X=*p*-MeOPh, Y=H) led to a significant decrease of the *endo* selectivity of the hetero Diels-Alder reaction and the *exo*-product **7c** could be detected (entries 14-16). Subsequent cleavage of the TMS group led to the *cis*-fused compound **11c** as

the only possible isomer. $SnCl_4$ showed a slightly higher *endo* selectivity than $TiCl_4$. As expected, the general reactivity of the imine in the reaction with the diene was decreased leading to extended reaction times in order to achieve complete conversion.

A benzyl substituent on the imine nitrogen (**5d**, X=Bn, Y=H) seems to have a very similar effect on both the reactivity and the diastereoselectivity of the Diels-Alder cyclization (entries 17 and 18). The rate of the conversion was slowed down significantly and $SnCl_4$ had to be used as catalyst in order to avoid polymerization of the diene in the extended presence of the strong Lewis acid $TiCl_4$. Only a slight excess of *endo* quinolinones **9d** and **10d** was observed compared to the *exo* compound **11d**.

The influence of electron withdrawing (**5e**, X=Ph, Y=NO_2) as well as electron donating substituents (**5f**, X=Ph, Y=OMe) at the *C*-side of the imine was much weaker. Cyclization proceeded smoothly and only *endo* quinolinones **9d/e** and **10d/e** were isolated (entries 19 and 20). However, the yields dropped to 50% and imine **5f** reacted very sluggishly even when a fourfold excess of the diene was present and the reaction time was extended.

Table 1: Reaction of Diene 2 with Imines 5a-f under Various Conditions

entry	imine	X	Y	Lewis acid (altered cond.)	time [h]	**8**	product **9 + 10**	ratio[a] **11**	rec. **5**	yield[b] [%]
1	**5a**	Ph	H	$TiCl_4$	1	0	100	0	0	74
2	**5a**	Ph	H	$AlCl_3$	1	0	0	0	100	
3	**5a**	Ph	H	Et_2AlCl	20	0	71	0	29	
4	**5a**	Ph	H	$BF_3{\cdot}Et_2O$	1	0	0	0	100	
5	**5a**	Ph	H	$SnCl_4$	1	0	60	0	40	
6	**5a**	Ph	H	$SnCl_4$	20	0	100	0	0	65
7	**5a**	Ph	H	ZnI_2	2	6	80	0	12	
8	**5a**	Ph	H	ZnI_2	7	12	82	0	6	
9	**5a**	Ph	H	ZnI_2 (THF)	2	17	0	0	83	
10	**5b**	*p*-NO_2Ph	H	$TiCl_4$	1	traces	0	0	~100	
11	**5b**	*p*-NO_2Ph	H	$TiCl_4$ (-20°C)	2	100	0	0	0	41
12	**5b**	*p*-NO_2Ph	H	ZnI_2	22	30	70	0	0	91
13	**5b**	*p*-NO_2Ph	H	$SnCl_4$	24	exclusive formation of **12**				40
14	**5c**	*p*-MeOPh	H	$TiCl_4$	1	0	60	30	10	
15	**5c**	*p*-MeOPh	H	$TiCl_4$	2	0	65	35	0	75
16	**5c**	*p*-MeOPh	H	$SnCl_4$	20	0	84	8	8	
17	**5d**	Bn	H	$TiCl_4$	1	0	traces	traces	0	
18	**5d**	Bn	H	$SnCl_4$	24	0	53	47	0	55
19	**5e**	Ph	NO_2	$TiCl_4$	1	0	100	0	0	50
20	**5f**	Ph	MeO	$TiCl_4$	4	0	100	0	0	50

[a] standard reaction conditions: solvent CH_2Cl_2, 20°C; [b] represents the overall yield of reaction products

It turned out to be of great importance to cleave the TMS group under basic conditions ($MeOH/NEt_3$), since a *retro* Michael reaction could be observed when using 2*N* HCl/THF (Table 2). The ratio of **8a**:**9a**:**10a** changed from cyclized products only (entry 1) to a substantial amount of the open chain product (entry 2), which seems to be formed predominantly at cost of the *cis* isomer.

Table 2: Product Ratio Depending on TMS Cleavage Conditions

entry	conditions	**9a**	**10a**	**8a**	overall yield
1	basic (sat. $NaHCO_3$)	60	40	0	74%
2	acidic (2*N* HCl/THF)	60	5	35	65%

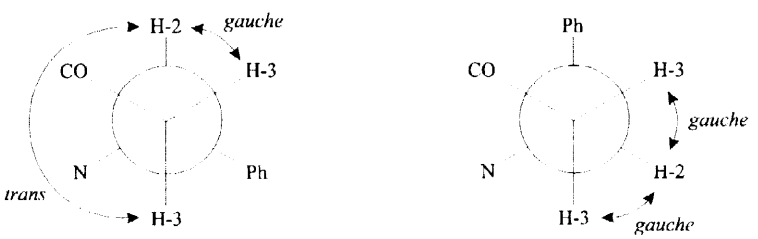
Separation of the *cis* and *trans* isomers of the *endo* quinolinones **9** and **10** was possible only in the case of **9/10b**. However, the obtained mixture of bicyclic products after cleavage of the TMS-group could be epimerized to the thermodynamically most stable *trans* form **10** using MeONa in excellent to quantitative yields.

Structural Assignment

Extended NMR studies were carried out with the quinolines **6** and **7** and the ketones **9** - **11**, and all signals essential for the structural analysis could be assigned. However, due to their instability towards hydrolysis, it was impossible to get stable single-crystals of the silyl enol ethers. Therefore, the structures determined by 2D-NMR studies for the isomers **9a**, **10a**, and **11c** were confirmed by X-ray diffraction.

The configuration at position 2 of the quinolinone system could be assigned by studying the coupling of protons H-2, H-3eq, and H-3ax. In all isolated compounds the variation of the coupling constants *J* observed is minimal.

The signal pattern of H-2 shows a doublet of doublets with a large *trans* coupling with H-3ax ($J_{trans}\approx 13Hz$) and a smaller *gauche* interaction with H-3eq ($J_{gauche}\approx 5Hz$) indicating the *axial* location of the hydrogen. Otherwise a *pseudo* tripplet would be expected for H-2 if it were in *equatorial* position .[9]



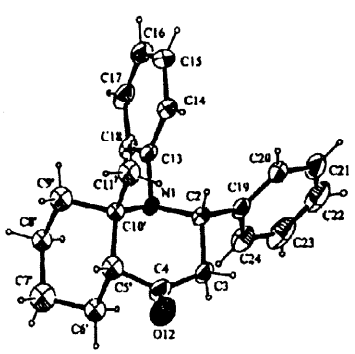
Since compounds **9** were converted to **10** by treatment with a base, this chemical behavior indicated a *cis/trans* relationship between the two isomers. However, structural assignment of the two products could be achieved with spectroscopic methods. The *cis* and *trans* fused isomers could be distinguished by a significant shift to lower field of one of the protons H-5 in all *cis* products. Furthermore the angular methyl group served as indicator for *cis* fused rings: the signal in the ^{13}C NMR was shifted at least 10ppm to higher field compared to the signal of the corresponding *trans* compound (Table 3). This result is in good

accordance with the decalin series, where a similar shift difference for an *equatorial* and an *axial* methyl group can be observed.[10] Therefore the structure of **11c** could be assigned correctly with spectroscopic methods prior to X-ray analysis.

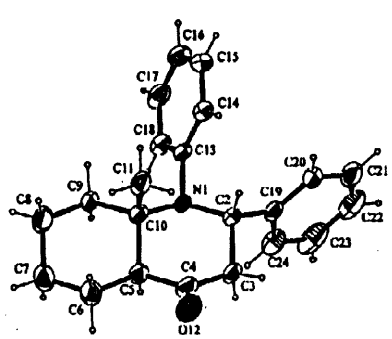
Table 3: ^{13}C NMR Parameters of the B-Ring of Quinolinones 9 - 11 ($CDCl_3$, 50MHz, δ in ppm)

compound	C-2	C-3	C-4	C-4a	C-8a	CH_3
9a	62.6	47.5	212.2	60.9	58.9	21.6
9b	62.5	47.4	211.0	60.5	60.0	21.9
9c	63.0	47.6	212.5	61.0	59.0	21.8
9d	65.1	47.2	212.2	61.0	59.6	19.7
9e	62.2	46.9	210.8	60.6	59.3	21.8
9f	62.0	47.8	212.6	61.0	59.0	21.9
10a	62.3	51.5	209.6	58.7	61.8	11.7
10b	61.9	50.1	208.2	58.0	62.2	13.4
10c	62.6	51.7	209.9	58.8	61.9	11.7
10d	65.4	50.3	209.7	58.1	63.0	10.8
10e	61.8	50.7	208.2	58.7	62.2	11.7
10f	61.7	51.8	209.9	58.8	61.8	11.7
11c	61.0	51.8	209.3	55.2	61.5	27.1
11d	62.8	49.4	209.4	54.7	62.4	26.2

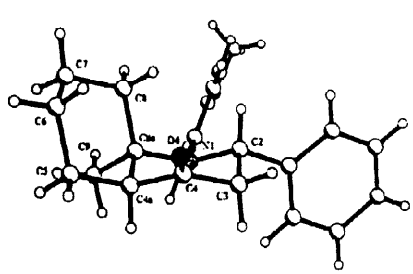
The single crystal X-ray structures obtained indicate that both the A and the B ring of all quinolinones exhibit a chair conformation. Both phenyl rings are almost orthogonal to the *pseudo*-plane of ring B, enabling π-interaction between the p_z-orbitals of the two aromatic systems. Table 4 contains selected torsion angles of compounds **9a**, **10a**, and **11c**.



9a



10a



11c

Table 4: Selected Torsion Angles of Compounds 9a, 10a, and 11c Determined by X-Ray Diffraction

angle	9a	10a	11c
CH_3-C8a-N1-C1'	63.1	69.8	59.1
CH_3-C8a-N1-C2	-56.7	-60.7	-170.3
CH_3-C8a-C4a-H4a	-43.0	175.0	50.3
CH_3-C8a-C4a-C4	89.1	60.0	166.5
H2-C2-C3-H3ax	163.1	163.1	-172.7
H2-C2-C3-H3eq	46.2	46.2	54.7
C1'-N1-C2-C1''	57.0	57.0	-53.2
C1'-N1-C2-C3	178.1	178.1	-173.1
C1''-C2-C3-C4	166.1	166.1	64.0
H4a-C4a-C5-H5α	52.5	-175.9	-48.7
H4a-C4a-C5-H5β	171.5	-57.9	68.7
N1-C2-C3-C4	44.1	44.1	-53.2
C2-C3-C4-C4a	-16.2	-50.7	54.9
C3-C4-C4a-C8a	10.7	58.7	-53.3
C4-C4a-C8a-N1	-32.8	-61.1	49.8
C4a-C8a-N1-C2	61.8	59.6	-53.3
C8a-N1-C2-C3	-63.3	-50.45	55.0
N1-C8a-C4a-C5	61.4	171.9	176.7
C8-C8a-C4a-C4	-162.1	-179.8	-73.5

Structural elucidation of the carbocyclic product **12** is based on the spin systems H-1, H-2, and H-3. The coupling constant $J_{H\text{-}1/H\text{-}2}$ = 11.6 Hz indicates a *trans* relationship between the two hydrogens, hence the two substituents occupy the *equatorial* positions. The configuration of the *trans* fused rings is unambiguous and both coupling constants at H-4a and the shift value of the angular methyl group are in good correlation to products **10**.

Discussion

The mechanism of hetero Diels-Alder reactions is a subject of intensive discussion in the literature and especially the distinction between the concerted cyclization and a sequential double Michael addition has given rise to much controversy.[1, 2, 4, 8, 11]

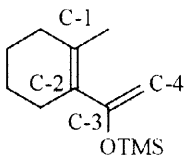
Two facts indicate the existance of two independent mechanisms involved in the reaction of the silyl enol ether **2** with various imines: First, we were not able to observe any bicyclic products formed from **8a** under standard cyclization conditions in contrast to reports in the literature with related diene systems.[12] Additionally, with increasing reaction time the ratio of both cyclic and acyclic products is increased (entries 7 and 8). Being an intermediate, **8a** should be consumed by the formation of heterocyclic compounds. Therefore we assume that the imine has to be activated to a certain degree in order to be able to undergo a fast Diels-Alder cyclization. If this point is not reached, a slower addition mechanism takes over and becomes predominant with decreasing activation by the Lewis acid.

This thesis is supported by calculations of orbital energies and coefficients of the complexes formed by imines **5** with various Lewis acids and the diene **2** on an *ab initio* level utilizing DFT procedures. Geometry optimization of the structures was performed using HF/LANL2MB. Subsequently the energy was derived as single point with B3LYP/LANL2DZ. All calculations were carried out using the program Gaussian94DFT.[13] The obtained data are summarized in Table 5 and 6:

Table 5: Calculated Electronic Properties of the HOMO of Diene 2

E_{HOMO} = 0.21eV	C-1	C-2	C-3	C-4
c^a	-0.41	-0.31	0.32	0.60
δ^b	+0.01	-0.02	+0.12	-0.12

[a] orbital coefficient; [b] charge



Due to the enhanced orbital coefficient at C-4 only quinolines are formed in the course of the Diels-Alder cyclization. However, a significant negative charge is placed at the same position, enabling the molecule to undergo a nucleophilic attack to form adducts of the type of compounds **8**.

Table 6: Calculated Electronic Properties of the LUMO of Selected Dienophiles 5

entry	imine_Lewis acid	c_C	c_N	δ_C	δ_N	E_{LUMO} [eV]
1	**2a**	0.43	-0.43	+0.12	-0.24	0.21
2	**2a**_$TiCl_4$	0.51	-0.49	+0.32	-0.29	0.09
3	**2a**_ZnI_2	0.43	-0.30	+0.26	-0.26	0.12
4	**2b**	0.44	-0.31	+0.13	-0.26	0.14
5	**2b**_$TiCl_4$	0.47	-0.24	+0.26	-0.29	0.05
6	**2b**_ZnI_2	0.66	-0.43	+0.30	-0.42	0.01
7	**2c**	0.43	-0.44	+0.11	-0.24	0.20
8	**2c**_$TiCl_4$	0.61	-0.56	+0.32	-0.29	0.11
9	**2c**_$SnCl_4$	0.74	-0.55	+0.32	-0.31	0.10
10	**2d**	0.38	-0.48	+0.10	-0.24	0.22
11	**2d**_$SnCl_4$	0.71	-0.54	+0.31	-0.30	0.11

Complexation of imine **2a** with $TiCl_4$ always leads to an enhancement of the orbital coefficient and the positive charge at the carbon of the dienophile. Activation of the system results in a significant decrease of the LUMO energy of the complex compared to the sole ligand enabling a Diels-Alder reaction (entries 1 and 2).

In the case of ZnI_2 as Lewis acid the effect at the imine carbon is much weaker, therefore the cyclization is not favored. However, the positive charge at the carbon atom seems sufficiently increased to undergo a nucleophilic attack by the silyl enol ether, leading to the open chain products of type **8** (entry 3). The calculation represent the trend observed in the experiments in Table 1.

The situation is reversed when imine **2b** is used as dienophile. Now $TiCl_4$ manages to increase c_C only to some extent resulting in exclusive addition completely consistent with the experiment. The effect of ZnI_2 is much stronger in this system, so that Diels-Alder cyclization is expected to proceed when this Lewis acid is applied (entries 4-6). Actually we observed both types of products in the reaction mixture.
The calculations indicate that the loss of *endo* selectivity for imines **2c** and **2d** could be attributed to a preferred formation of the kinetic reaction product (*exo*) due to an extended increase of the orbital coefficient at the imine carbon (entries 7-11). However, this hypothesis is subject to further investigations.

Experimental Section

General

All solvents were distilled prior to usage. Dry THF was prepared by distillation from sodium / benzophenone, dry CH_2Cl_2 by distillation from P_2O_5 and dry MeOH by distillation from Mg. TLC was performed on Merck precoated silica gel plates (5554) and flash column chromatography on silica gel 60 from E. Merck (40-63 μm, 9385). Basically conditioned silica gel was prepared by treatment of the commercial material with a 10% solution of NEt_3 in CH_2Cl_2. After filtration the silica gel was dried *in vacuo*. Melting points were determined using a Reichert micro hot stage apparatus and are uncorrected. Elemental analyses were performed in the Microanalytical Laboratory, University of Vienna. The NMR spectra were recorded of solutions in $CDCl_3$ or DMSO-d_6 with a Bruker AC 200 (200 MHz) spectrometer; chemical shifts are reported in ppm using Me_4Si as internal standard. Labeling of the signals was carried out according to the nomenclature, assigning the carbons of the phenyl rings at position 1 and 2 as C' and C'', respectively.
Imines **5a-f** were synthesized utilizing a procedure reported by DeKimpe:[14] A solution of the corresponding amine and aldehyde in dry CH_2Cl_2 were stirred at rt in the presence of Na_2SO_4 or $MgSO_4$ as drying agent. Evaporation of the volatiles gave the desired dienophiles in high purity and excellent to quantitative yields.

Trimethyl[1-(2-methyl-1-cyclohexen-1-yl)ethenyloxy]silane (2)

Diisopropylamine (38.5 g, 380 mmol) and dry THF were cooled to -25±5°C under a nitrogen atmosphere and this temperature was maintained for the whole reaction. *n*-BuLi (145 mL, 374 mmol, 2.58*M* in hexane) was added slowly and the solution was stirred for 20 min. After addition of **4a** the mixture was stirred for another 20 min. TMSCl (71.1 g, 657 mmol) was added quickly, the reaction was warmed to rt and stirred for 2 h. The resulting suspension was concentrated to remove all low boiling volatiles and treated repeatedly with dry light petroleum in order to dissolve the product and separate it from the inorganic percipitate. The extracts were combined and the solvent was distilled off. After Kugelrohr distillation of the crude product 67.1 g (93%) of **2** were isolated as colorless liquid. Bp.: 60-64°C / 2 mbar; ^{1}H NMR ($CDCl_3$): 0.20 (s, 9H, TMS), 1.50-1.72 (m, 4H, H-4 and H-5), 1.78 (m, 3H, CH_3), 1.85-2.20 (m, 4H, H-3 and H-6), 4.11 and 4.35 (2 s, 2 1H, $=CH_2$); ^{13}C NMR ($CDCl_3$): 0.1 (s, TMS), 21.3 (q, CH_3), 22.8 and 22.9 (2 t, C-4 and C-5), 27.9 (t, C-6), 31.9 (t, C-3), 93.8 (t, $=CH_2$), 129.9 and 131.3 (2 s, C-1 and C-2), 157.6 (s, C-OTMS).

(2-Methylcyclohexenyl)ethanone (4a)

1-Methylcyclohexene **3** (40.0 g, 416 mmol) and acetic anhydride (150 mL) were cooled to 0±2°C. After addition of a few crystals of ZnI_2 the mixture was stirred mechanically for 15 min. $ZnCl_2$ (58.3 g, 428 mmol) was added in small portions to avoid warming above 5°C. The resulting suspension was stirred for 4 h at 0±2°C, hydrolyzed with ice / 2*N* NaOH and further neutralized with 2*N* NaOH. After extraction

with diethyl ether the combined organic layers were alkalized with 2*N* NaOH, dried over Na_2SO_4 and freed from solvents. This mixture of isomers (**4a** and **4b** in almost quantitative yield) was heated under reflux with *p*-TSA (5.5 g, 32 mmol) in dry benzene (500 mL) for 16 h. The solution was washed with satd. $NaHCO_3$ solution, dried over Na_2SO_4, treated with charcoal, filtered, and evaporated. The crude product was distilled to give 47.4 g (82%) of **4b** as pale yellow liquid. Bp.: 84-88°C / 12 mbar. ^1H NMR ($CDCl_3$): 1.45-1.75 (m, 4H, H-4 and H-5), 1.82 (m, 3H, CH_3), 1.90-2.25 (m, 4H, H-3 and H-6), 2.20 (s, 3H, $COCH_3$); ^{13}C NMR ($CDCl_3$): 21.4 (q, CH_3), 22.0 and 22.1 (2 t, C-4 and C-5), 26.5 (t, C-6), 29.3 (q, $CO\underline{C}H_3$), 32.9 (t, C-3), 132.9 (s, C-1), 140.8 (s, C-2), 203.9 (s, CO).

General Procedure for the Diels-Alder Cyclization

The Lewis acid (1 equiv.) was added to a 5 % solution of the imine **5** (1 equiv.) in dry CH_2Cl_2 under nitrogen. After the mixture had been stired for 30 min a 20 % solution of diene **2** (2 equiv.) in dry CH_2Cl_2 was added and the stirring continued according to the period given at the specific quinolinone. The reaction mixture was hydrolyzed with satd. $NaHCO_3$ solution, extracted with CH_2Cl_2, and dried over Na_2SO_4. Evaporation of the volatiles gave the crude silyl enol ethers **6** and **7** which could be separated by column chromatography. Treatment of the crude products with a 1:1 mixture of dry NEt_3 and MeOH and removal of all volatiles gave the ketones **9** - **11**, which were finally separated by flash column chromatography (FCC).

trans-1,2,3,5,6,7,8,8a-Octahydro-8a-methyl-1,2-diphenyl-4-(trimethylsilyloxy)-quinoline (6a)

Imine **5a** (0.23 g, 1.28 mmol) gave 0.29 g (58%) of **6a** as an orange oil using $TiCl_4$ as Lewis acid for 1 h. Purification was performed *via* flash column chromatography (bas. cond. silicagel 30:1, light petroleum : ethyl acetate = 100:1). ^1H NMR ($CDCl_3$): 0.20 (s, 9H, TMS), 1.04-2.12 (m, 7H, H-5eq, H-6, H-7 and H-8), 1.20 (s, 3H, CH_3), 2.12-2.28 (m, **ABX**, J_{gem}=17Hz, 1H, H-3eq), 2.25-2.64 (m, **ABX**, J_{gem}=17Hz, J_{trans}=11Hz, 1H, H-3ax), 2.81-2.96 (m, J_{trans2}=15Hz, 1H, H-5ax), 4.60 (dd, **ABX**, J_{trans}=11Hz, J_{cis}=4Hz, 1H, H-2), 6.76-7.18 (m, 10H, arom. H). ^{13}C NMR ($CDCl_3$): 0.5 (q, TMS), 18.0 (q, CH_3), 22.8 (t, C-7*), 23.4 (t, C-5), 26.6 (t, C-6*), 41.6 (t, C-8*), 42.4 (t, C-3*), 58.4 (d, C-2), 58.6 (s, C-8a), 120.4 (s, C-4a), 124.1 (d, C-4'), 125.9 (d, C-4''), 126.6 (d, C-2'*), 127.5 (d, C-3'*), 128.4 (d, C-2''*), 131.9 (d, C-3''*), 139.3 (s, C-4), 144.1 (s, C-1''), 145.9 (s, C-1').

trans-1,2,3,5,6,7,8,8a-Octahydro-8a-methyl-1-(4-nitrophenyl)-2-phenyl-4-(trimethylsilyloxy)-quinoline (6b)

Imine **5b** (0.100 g, 0.442 mmol) gave 0.025 g (13%) of **6b** as an orange oil using ZnI_2 as catalyst for 22 h. Purification was performed *via* flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 100:1). ^1H NMR ($CDCl_3$): 0.21 (s, 9H, TMS), 1.19 (s, 3H, CH_3), 1.22-2.13 (m, 7H, H-5eq, H-6, H-7, H-8), 2.20-2.35 (m, **ABX**, J_{gem}=15Hz, 1H, H-3eq), 2.47-2.65 (m, **ABX**, J_{gem}=15Hz, J_{trans}=11Hz, 1H, H-3ax), 2.85-2.98 (m, J_{trans2}=15Hz, 1H, H-5ax), 4.62 (dd, **ABX**, J_{trans}=11Hz, J_{cis}=4Hz, 1H, H-2), 6.97-7.18 (m, 7H, H-2'' and 5 H'), 7.87 (d, J=10Hz, 2H, H-3''). ^{13}C NMR ($CDCl_3$): 0.6 (q, TMS), 18.6 (q, CH_3), 22.9 (t, C-7*), 23.5 (t, C-5), 26.4 (t, C-6*), 41.7 and 42.0 (2 t, C-3* and C-8*), 58.6 (d, C-2), 59.8 (s, C-8a), 119.9 (s, C-4a), 122.3 (d, C-2'), 126.7 (d, C-4''), 128.2 and 128.3 (2 d, C-3' and C-2''*), 131.7 (d, C-3''*), 139.5 (s, C-4), 143.1 (s, C-1''), 143.7 (s, C-4'), 153.8 (s, C-1').

trans-1,2,3,5,6,7,8,8a-Octahydro-1-(4-methoxyphenyl)-8a-methyl-2-phenyl-4-(trimethylsilyloxy)-quinoline (6c)

Imine **5c** (0.100 g, 0.473 mmol) gave 0.052 g (26%) of **6c** as a colorless oil using $SnCl_4$ as Lewis acid for 22 h. Purification was performed *via* flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 50:1). ^1H NMR ($CDCl_3$): 0.13 (s, 9H, TMS), 1.10 (s, 3H, CH_3), 1.14-2.05 (m, 7H, H-5eq, H-6, H-7, H-8), 2.05-2.20 (m, ABX, J_{gem}=16Hz, 1H, H-3eq), 2.38-2.56 (m, ABX, J_{gem}=16Hz, J_{trans}=11Hz, 1H, H-3ax), 2.74-2.89 (m, J_{trans2}=16Hz, 1H, H-5ax), 3.57 (s, 3H, OCH_3), 4.57 (dd, ABX, J_{trans}=11Hz, J_{cis}=4Hz, 1H, H-2), 6.44 (d, J=9Hz, 2H, H-3'), 6.80 (d, J=9Hz, 2H, H-2'), 6.87-7.20 (m, 5H, arom. H); ^{13}C NMR ($CDCl_3$): 0.7 (q, TMS), 18.1 (q, CH_3), 22.9 (t, C-7*), 23.5 (t, C-5), 26.6 (t, C-6*), 41.7 (t, C-8*), 42.5 (t, C-3*), 55.0 (q, OCH_3), 58.6 (s and d, C-2 and C-8a), 111.9 (d, C-3'), 120.5 (s, C-4a), 126.0 (d, C-4''), 127.6 (d, C-2'*), 128.5 (d, C-2''*), 132.6 (d, C-3''*), 138.8 (s, C-1'), 139.4 (s, C-4), 144.3 (s, C-1''), 156.0 (s, C-4').

trans-1,2,3,5,6,7,8,8a-Octahydro-8a-methyl-2-(4-nitrophenyl)-1-phenyl-4-(trimethylsilyloxy)-quinoline (6e)

Imine **5e** (0.100 g, 0.442 mmol) gave 0.017 g (9%) of **6e** as a yellow oil using ZnI_2 as catalyst for 19 h. Purification was performed *via* flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 100:1). ^1H NMR ($CDCl_3$): 0.20 (s, 9H, TMS), 1.20 (s, 3H, CH_3), 1.03-2.30 (m, 8H, H-3eq, H-5eq, H-6, H-7, H-8), 2.37-2.56 (m, ABX, J_{gem}=15Hz, J_{trans}=11Hz, 1H, H-3ax), 2.79-2.97 (m, J_{trans2}=15Hz, 1H, H-5ax), 4.75 (dd, ABX, J_{trans}=11Hz, J_{cis}=4Hz, 1H, H-2), 6.79-7.11 (m, 5H, arom. H), 7.33 (d, J=8Hz, 2H, H-2''), 7.91 (d, J=8Hz, 2H, H-3''). ^{13}C NMR ($CDCl_3$): 0.6 (q, TMS), 18.2 (q, CH_3), 22.8 (t, C-7*), 23.5 (t, C-5), 26.5 (t, C-6*), 41.6 and 42.2 (2 t, C-3 and C-8), 58.4 (d, C-2), 58.9 (s, C-8a), 120.7 (s, C-4a), 123.1 (d, C-3''), 124.8 (d, C-4'), 127.2, 129.0 and 131.6 (3 d, C-2', C-3' and C-2''), 138.7 (s, C-4), 145.6 and 146.2 (2 s, C-1' and C-4''), 152.1 (s, C-1'').

trans-1,2,3,5,6,7,8,8a-Octahydro-2-(4-methoxyphenyl)-8a-methyl-1-phenyl-4-(trimethylsilyloxy)-quinoline (6f)

Imine **5f** (0.100 g, 0.473 mmol) gave 0.053 g (27%) of **6f** as a colorless oil using $TiCl_4$ as Lewis acid for 2 h. Purification was performed *via* flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 100:1). ^1H NMR ($CDCl_3$): 0.20 (s, 9H, TMS), 1.17 (s, 3H, CH_3), 1.20-2.29 (m, 8H, H-3eq, H-5eq, H-6, H-7, H-8), 2.43-2.62 (m, ABX, J_{gem}=16Hz, J_{trans}=11Hz, 1H, H-3ax), 2.80-2.97 (m, J_{trans2}=16Hz, 1H, H-5ax), 3.66 (s, 3H, OCH_3), 4.55 (dd, ABX, J_{trans}=10Hz, J_{cis}=3Hz, 1H, H-2), 6.58 (d, J=9Hz, 2H, H-3''), 6.80-7.10 (m, 7H, arom. H). ^{13}C NMR ($CDCl_3$): 0.7 (q, TMS), 18.1 (q, CH_3), 22.9 (t, C-7*), 23.5 (t, C-5), 26.6 (t, C-6*), 41.8 (t, C-8*), 42.6 (t, C-3*), 55.0 (q, OCH_3), 57.7 (d, C-2), 58.7 (s, C-8a), 113.0 (d, C-3''), 120.5 (s, C-4a), 124.2 (d, C-4'), 126.7 (d, C-2'*), 129.4 (d, C-2''*), 132.1 (d, C-3'*), 136.5 (s, C-1''), 139.5 (s, C-4), 146.1 (s, C-1''), 157.6 (s, C-4').

cis-1,2,3,5,6,7,8,8a-Octahydro-1-(4-methoxyphenyl)-8a-methyl-2-phenyl-4-(trimethylsilyloxy)-quinoline (7c)

Imine **5c** (0.100 g, 0.473 mmol) gave 0.020 g (10%) of an unseparable mixture of isomers **6c**:**7c** = 4:1 as a colorless oil using $TiCl_4$ as Lewis acid for 1 h. Purification was performed *via* flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 50:1). Spectroscopic properties of the compound were obtained from this mixture. ^1H NMR ($CDCl_3$): 0.13 (s, 9H, TMS), 1.10-2.25 (m, 8H, aliphat. H), 1.37 (s, 3H, CH_3), 2.38-2.56 (m, 1H, H-3ax), 2.74-2.89 (m, 1H, H-5ax), 3.57 (s, 3H, OCH_3), 4.57 (dd, ABX, J_{trans}=11Hz, J_{cis}=4Hz, 1H, H-2), 6.44 (d, J=9Hz, 2H, H-3'), 6.80 (d, J=9Hz, 2H, H-2'), 6.87-7.20 (m, 5H, arom. H); ^{13}C NMR ($CDCl_3$): 0.5 (q, TMS), 23.7 (q, CH_3), 24.3, 26.3 and

27.3 (3 t, C-5, C-6 and C-7*), 35.2 (t, C-3), 43.1 (t, C-8), 55.0 (q, OCH_3), 59.4 (d, C-2), 59.6 (s, C-8a), 112.0 (d, C-3'), 121.6 (s, C-4a), 126.0 (d, C-4''), 127.6 (d, C-2'*), 128.5 (d, C-2''*), 132.5 (d, C-3''*), 139.1 (s, C-1'), 139.6 (s, C-4), 144.2 (s, C-1''), 155.9 (s, C-4').

1-(2-Methyl-1-cyclohexenyl)-3-phenyl-3-phenylamino-1-propanone (8a)

Imine **5a** (0.500 g, 0.276 mmol) gave 0.194 g (22%) of **8a** as a faint yellow oil according to the general procedure using $TiCl_4$ as Lewis acid and performing the cleavage of the TMS group under acidic conditions with 2*N* HCl/THF. Purification was carried out *via* flash column chromatography (bas. cond. silicagel 30:1, light petroleum : ethyl acetate = 30:1). ^1H NMR ($CDCl_3$): 1.46-1.68 (m, 4H, H-4 and H-5), 1.68-1.83 (m, 3H, CH_3), 1.91-2.20 (m, 4H, H-3 and H-6), 2.89-3.12 (m, 2H, $COCH_2$), ~4.5 (bs, 1H, NH), 4.83 (t, J=7Hz, 1H, NCH), 6.55 (d, J=8Hz, 2H, H-2'), 6.67 (t, J=8Hz, 1H, H-4'), 6.89-7.44 (m, 7H, arom. H); ^{13}C NMR ($CDCl_3$): 21.4 (q, CH_3), 22.0 and 22.1 (2 t, C-4 and C-5), 26.3 (t, C-6), 32.7 (t, C-3), 48.9 (t, CH_2), 54.7 (d, CH), 113.5 (d, C-2'), 117.4 (d, C-4'), 126.2 (d, C-2''*), 127.0 (d, C-4''), 128.5 and 128.9 (2 d, C-3' and C-3''*), 132.7 (s, C-1), 141.5 (s, C-2), 142.9 (s, C-1''), 146.9 (s, C-1'), 204.7 (s, CO). Anal.: Calc for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.31; H. 8.18; N, 4.24.

1-(2-Methyl-cyclohexenyl)-3-phenyl-3-(4-nitrophenyl)amino-1-propanone (8b)

Imine **5c** (0.300 g, 1.326 mmol) gave 0.200 g (41%) of **8c** as orange crystals according to the general procedure using $TiCl_4$ as Lewis acid at a temperature of -20°C and a reaction time of 2 h. Purification was carried out *via* flash column chromatography (bas. cond. silicagel 25:1, light petroleum : ethyl acetate = 7:1). Mp.: 155-159°C (FCC); ^1H NMR ($CDCl_3$): 1.50-1.67 (m, 4H, H-4 and H-5), 1.78 (s, 3H, CH_3), 2.00-2.16 (m, 4H, H-3 and H-6), 3.07 (d, J=6Hz, 2H, $COCH_2$), 4.94 (q, J=6Hz, 1H, NCH), 5.68 (bd, J=6Hz, 1H, NH), 6.50 (d, J=10Hz, 2H, H-2'), 7.20-7.38 (m, 5H, arom. H), 8.01 (d, J=10Hz, 2H, H-4'); ^{13}C NMR ($CDCl_3$): 21.6 (q, CH_3), 21.9 and 22.1 (2 t, C-4 and C-5), 26.3 (t, C-6), 33.1 (t, C-3), 47.9 (t, CH_2), 54.3 (d, CH), 112.0 (d, C-2'), 126.1 (2 d, C-3' and C-2''*), 127.7 (d, C-4''), 128.9 (d, C-3''*), 132.4 (s, C-1), 138.2 (s, C-4'), 141.1 (s, C-2), 143.4 (s, C-1''), 152.3 (s, C-1'), 203.9 (s, CO). Anal.: Calc for $C_{22}H_{24}N_2O_3$: C, 72.51; H, 6.64; N, 7.69. Found: C,. 72.34; H, 6.84; N, 7.60.

(2α, 4aβ, 8aβ)-2,3,4a,5,6,7,8,8a-Octahydro-8a-methyl-1,2-diphenyl-4(1*H*)-quinolinone (9a)

Imine **5a** (0.70 g, 3.86 mmol) gave 0.91 g (74%) of an unseparable mixture of isomers **9a**:**10a** in a ratio of 1:1.5 according to the general procedure using $TiCl_4$ as Lewis acid at rt and a reaction time of 1 h. Purification was performed *via* flash column chromatography (bas. cond. silicagel 30:1, light petroleum : ethyl acetate = 30:1). Spectroscopic data were obtained from the mixture with **10a**. ^1H NMR ($CDCl_3$): 0.94-2.50 (m, 10H, H-3, H-5, H-6, H-7, H-8), 1.23 (s, 3H, CH_3), 2.98 (dd, ABX, J_{gem}=14Hz, J_{trans}=11Hz, 1H, H-3ax), 4.70 (dd, ABX, J_{trans}=12.5Hz, J_{gauche}=3.5Hz, 1H, H-2), 6.82-7.32 (m, 10H, arom. H). ^{13}C NMR ($CDCl_3$): 21.6 (t, C-7*), 21.8 (q, CH_3), 25.6 (t, C-5*), 27.5 (t, C-6*), 37.2 (t, C-8), 47.5 (t, C-3), 58.9 (s, C-8a), 60.9 (d, C-4a), 62.6 (d, C-2), 125.3 (d, C-4'), 126.7 (d, C-4''), 127.6, 127.8 and 127.9 (3 d, C-2', C-3', C-2''*), 130.5 (d, C-3''*), 143.1 (s, C-1''), 146.3 (s, C-1'), 212.2 (s, CO). Anal. (mixture of **9a** and **10a**): Calc for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.5; H, 8.02; N, 4.31.

(2α, 4aβ, 8aβ)-2,3,4a,5,6,7,8,8a-Octahydro-8a-methyl-1-(4-nitrophenyl)-2-phenyl-4(1*H*)-quinolinone (9b)

Imine **5b** (0.300g, 1.326mmol) gave 62% of a mixture of isomers **9b** and **10b** and 29% of **8b** according to the general procedure using ZnI_2 as Lewis acid at rt and a reaction time of 22 h. Separation of the 3

products was carried out by flash column chromatography (silicagel 40:1, light petroleum : ethyl acetate = 10:1) and 0.074 g (15%) of pure **10a** could by isolated as yellow crystals. Mp.: 171-174°C (DIPE); ^{1}H NMR ($CDCl_3$): 1.06-2.15 (m, 8H, H-5, H-6, H-7, H-8), 1.22 (s, 3H, CH_3), 2.27-2.56 (m, 3H, H-3eq, H-4a and H-5), 3.00 (dd, **ABX**, J_{gem}=15Hz, J_{trans}=13Hz, 1H, H-3ax), 4.73 (dd, AB**X**, J_{trans}=13Hz, J_{gauche}=5Hz, 1H, H-2), 6.98-7.30 (m, 5H, arom. H), 7.34 (d, J=10Hz, 2H, H-2'), 7.96 (d, J=10Hz, 2H, H-3'). ^{13}C NMR ($CDCl_3$): 21.9 (q and t, CH_3 and C-7*), 25.4 (t, C-5*), 27.5 (t, C-6*), 37.4 (t, C-8), 47.4 (t, C-3), 60.0 (s, C-8a), 60.5 (d, C-4a), 62.5 (d, C-2), 123.3 (d, C-3'), 127.5 (d, C-4''), 127.8 and 128.5 (2 d, C-2'', C-3''), 130.7 (d, C-2'), 142.1 (s, C-1''), 145.0 (s, C-4'), 153.9 (s, C-1'), 211.0 (s, CO). Anal. (mixture of **9b** and **10b**): Calc for $C_{22}H_{24}N_2O_3$: C, 72.51; H, 6.64; N, 7.69. Found: C, 72.27; H, 6.59; N, 7.60.

(2α, 4aβ, 8aβ)-2,3,4a,5,6,7,8,8a-Octahydro-1-(4-methoxyphenyl)-8a-methyl-2-phenyl-4(1*H*)-quinolinone (9c)

Imine **5c** (0.300 g, 1.420 mmol) gave 0.242 g (49%) of an unseparable mixture of isomers **9c**:**10c** in a ratio of 1:2.5 according to the general procedure using $TiCl_4$ as Lewis acid at rt and a reaction time of 1 h. Purification was performed *via* flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 30:1). Spectroscopic data were obtained from the mixture with **10a**. ^{1}H NMR ($CDCl_3$): 0.90-2.52 (m, 10H, H-3, H-5, H-6, H-7, H-8), 1.13 (s, 3H, CH_3), 2.87 (dd, **ABX**, J_{gem}=15Hz, J_{trans}=12Hz, 1H, H-3ax), 3.65 (s, 3H, OCH_3), 4.56 (dd, AB**X**, J_{trans}=12.5Hz, J_{gauche}=5Hz, 1H, H-2, 6.50 (d, J=8Hz, 2H, H-3'), 6.84-7.22 (m, 7H, arom. H). ^{13}C NMR ($CDCl_3$): 21.6 (t, C-7*), 21.8 (q, CH_3), 25.7 (t, C-5*), 27.6 (t, C-6*), 37.3 (t, C-8), 47.6 (t, C-3), 55.0 (q, OCH_3), 59.0 (s, C-8a), 61.0 (d, C-4a), 63.0 (d, C-2), 112.9 (d, C-3'), 126.7 (d, C-4''), 127.9 and 128.0 (2 d, C-2'', C-3''), 131.2 (d, C-2'), 138.9 (s, C-1'), 143.5 (s, C-1''), 156.7 (s, C-4'), 212.5 (s, CO). Anal. (mixture of **9c** and **10c**): Calc for $C_{23}H_{27}NO_2$: C, 79.05; H, 7.79; N, 4.01. Found: C, 78.75; H, 8.04; N, 3.89.

(2α, 4aβ, 8aβ)-2,3,4a,5,6,7,8,8a-Octahydro-8a-methyl-1-(phenylmethyl)-2-phenyl-4(1*H*)-quinolinone (9d)

Imine **5c** (0.500 g, 2.560 mmol) gave 0.250 g (29%) of a mixture of isomers **9d** and **10d** as colorless oil and 26% of **11d** according to the general procedure using $SnCl_4$ as Lewis acid at rt and a reaction time of 16 h. Separation of *endo*- and *exo*- products was carried out by flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 30:1). The obtained *endo*-quinolinones in a ratio of *cis* : *trans* = 1:1.1 could not be separated and were spectroscopically characterized as mixture. ^{1}H NMR ($CDCl_3$): 0.98-2.53 (m, 10H, H-3eq, H-4a, H-5, H-6, H-7, H-8), 1.09 (s, 3H, CH_3), 2.95 (dd, **ABX**, J_{gem1}=15Hz, J_{trans}=13Hz, 1H, H-3ax), 3.52 (d, **AB**, J_{gem2}=17Hz, $PhCH_2$-a), 3.80 (d, **AB**, J_{gem2}=17Hz, $PhCH_2$-b), 4.10 (dd, AB**X**, J_{trans}=12Hz, J_{gauche}=5Hz, 1H, H-2), 6.99-7.49 (m, 10H, arom. H); ^{13}C NMR ($CDCl_3$): 19.7 (q, CH_3), 20.9 (t, C-7*), 25.4 (t, C-5*), 27.0 (t, C-6*), 37.8 (t, C-8), 47.2 (t, C-3*), 51.7 (t, $PhCH_2$*), 59.6 (s, C-8a), 61.0 (d, C-4a), 65.1 (d, C-2), 125.8 and 127.5 (2 d, C-4' and C-4''), 128.1, 128.2, 128.3 and 128.5 (4 d, C-2', C-3', C-2'' and C-3''), 141.7 and 143.4 (2 s, C-1' and C-1''), 212.2 (s, CO). Anal. (mixture of **9d** and **10d**): Calc for $C_{23}H_{27}NO$: C, 82.84; H, 8.16; N, 4.20. Found: C, 82.61; H, 8.31; N, 4.14.

(2α, 4aβ, 8aβ)-2,3,4a,5,6,7,8,8a-Octahydro-8a-methyl-2-(4-nitrophenyl)-1-phenyl-4(1*H*)-quinolinone (9e)

Imine **5e** (0.300g, 1.326mmol) gave 50% of an unseparable mixture of *cis*- and *trans*-isomers **9e** and **10e** according to the general procedure using $TiCl_4$ as Lewis acid at rt and a reaction time of 1 h. Purification was performed *via* flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 15:1). Spectroscopic data were obtained from the mixture with **10a**. ^{1}H NMR ($CDCl_3$): 0.92-2.98 (m,

12H, aliphat. H), 1.24 (s, 3H, CH_3), 4.85 (dd, **ABX**, J_{trans}=11Hz, J_{gauche}=5Hz, 1H, H-2), 6.77-7.25 (m, 5H, arom. H), 7.38 (d, J=9Hz, 2H, H-2''), 7.86 (d, J=9Hz, 2H, H-3''). ^{13}C NMR ($CDCl_3$): 21.6 (t, C-7*), 21.8 (q, CH_3), 25.5 (t, C-5*), 27.5 (t, C-6*), 37.1 (t, C-8), 46.9 (t, C-3), 59.3 (s, C-8a), 60.6 (d, C-4a), 62.2 (d, C-2), 123.5 (d, C-3''), 125.9 (d, C-4'), 127.8, 128.5 and 130.3 (3 d, C-2', C-3', C-2''), 145.7 (s, C-1'*), 146.6 (s, C-4''*), 150.7 (s, C-1''), 210.8 (s, CO). Anal. (mixture of **9e** and **10e**): Calc for $C_{22}H_{24}N_2O_3$: C, 72.51; H, 6.64; N, 7.69. Found: C, 72.28; H, 6.91; N, 7.61.

(2α, 4aβ, 8aβ)-2,3,4a,5,6,7,8,8a-Octahydro-2-(4-methoxyphenyl)-8a-methyl-1-phenyl-4(1*H*)-quinolinone (9f)

Imine **5f** (0.300g, 1.420mmol) gave 0.248 g (50%) of a 1:2 mixture of *cis*- and *trans*-isomers **9e** and **10e** as faint yellow oil according to the general procedure using $TiCl_4$ as Lewis acid at rt and a reaction time of 4 h. It proved to be necessary to use 4 equiv. of diene **2**, which were added in two portions at the beginning of the reaction and after 2 h. Purification was performed *via* flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 30:1). ^1H NMR ($CDCl_3$): 0.99-2.48 (m, 10H, H-3, H-5, H-6, H-7, H-8), 1.22 (s, 3H, CH_3), 2.94 (dd, **ABX**, J_{gem}=14Hz, J_{trans}=12Hz, 1H, H-3ax), 3.66 (s, 3H, OCH_3), 4.65 (dd, **ABX**, J_{trans}=13Hz, J_{gauche}=4Hz, 1H, H-2), 6.62 (d, J=8Hz, 2H, H-3''), 6.87-7.08 (m, 5H, arom. H), 7.17 (d, J=8Hz, 2H, H-2''); ^{13}C NMR ($CDCl_3$): 21.7 (t, C-7*), 21.9 (q, CH_3), 25.7 (t, C-5*), 27.6 (t, C-6*), 37.3 (t, C-8), 47.8 (t, C-3), 55.0 (q, OCH_3), 59.0 (s, C-8a), 61.0 (d, C-4a), 62.0 (d, C-2), 113.4 (d, C-3''), 125.4 (d, C-4'), 127.7, 128.9 and 130.6 (3 d, C-2', C-2'', C-3'), 135.4 (s, C-1''), 146.5 (s, C-1'), 158.0 (s, C-4''), 212.6 (s, CO). Anal. (mixture of **9f** and **10f**): Calc for $C_{23}H_{27}NO_2$: C, 79.05; H, 7.79; N, 4.01. Found: C, 78.92; H, 8.00; N, 3.90.

(2α, 4aα, 8aβ)-2,3,4a,5,6,7,8,8a-Octahydro-8a-methyl-1,2-diphenyl-4(1*H*)-quinolinone (10a)

Imine **5a** (0.70 g, 3.86 mmol) gave 74% of a mixture of *cis*- and *trans*-isomers **9a** and **10a** according to the general procedure using $TiCl_4$ as Lewis acid at rt and a reaction time of 1 h, which was treated with 1 equiv. of MeONa in dry MeOH for 4 days, freed from a major amount of the solvent, the residue poured onto water, extracted with CH_2Cl_2, dried over Na_2SO_4 and evaporated to dryness: 0.91 g (74%) of **10a** could by isolated as faint yellow crystals. Purification was performed *via* flash column chromatography (bas. cond. silicagel 30:1, light petroleum : ethyl acetate = 30:1). Mp.: 140-143°C (FCC); ^1H NMR ($CDCl_3$): 1.00-1.90 (m, 8H, H-5, H-6, H-7, H-8), 1.12 (s, 3H, CH_3), 2.57 (dd, **ABX**, J_{gem}=13Hz, $J_{gauche1}$=5Hz, 1H, H-3eq), 2.76 (t, **ABX**, J_{gem}=J_{trans1}=13Hz, H-3ax), 2.92 (dd, **ABM**, J_{trans2}=12.5Hz, $J_{gauche2}$=3.5Hz, 1H, H-4a), 4.86 (dd, **ABX**, J_{trans1}=13Hz, $J_{gauche1}$=5Hz, 1H, H-2), 6.84-7.31 (m, 10H, arom. H). ^{13}C NMR ($CDCl_3$): 11.7 (q, CH_3), 21.3 (t, C-7*), 22.1 (t, C-5*), 24.5 (t, C-6*), 40.6 (t, C-8), 51.5 (t, C-3), 58.7 (d, C-4a), 61.8 (s, C-8a), 62.3 (d, C-2), 125.1 (d, C-4'), 126.6 (d, C-4''), 127.4, 127.8 and 127.9 (3 d, C-2', C-3', C-2''*), 130.6 (d, C-3''*), 142.9 (s, C-1''), 145.5 (s, C-1'), 209.6 (s, CO). Anal. (mixture of **9a** and **10a**): Calc for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.5; H, 8.02; N, 4.31.

(2α, 4aα, 8aβ)-2,3,4a,5,6,7,8,8a-Octahydro-8a-methyl-1-(4-nitrophenyl)-2-phenyl-4(1*H*)-quinolinone (10b)

Imine **5b** (0.300 g, 1.326 mmol) gave 62% of a mixture of isomers **9b** and **10b** and 29% of **8b** according to the general procedure using ZnI_2 as Lewis acid at rt and a reaction time of 22 h. Separation of cyclic and acyclic products was carried out by flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 10:1). The obtained quinolinones (ratio approx. 1:1) were treated with 1 equiv. of MeONa in dry MeOH for 5 days, freed from a major amount of the solvent, the residue poured onto water, extracted with CH_2Cl_2, dried over Na_2SO_4 and evaporated to dryness. 0.298 g (62%) of **10b** could by isolated as yellow crystals. Mp.: 198-200°C (DIPE); ^1H NMR ($CDCl_3$): 1.16-1.95 (m, 8H, H-5, H-6, H-

7, H-8), 1.21 (s, 3H, CH_3), 2.70 (dd, **ABX**, J_{gem}=15Hz, J_{gauche}=6Hz, 1H, H-3eq), 2.79-2.95 (m, 2H, H-3ax and H-4a), 4.89 (dd, **ABX**, J_{trans}=10Hz, J_{gauche}=6Hz, 1H, H-2), 7.03-7.28 (m, 8H, arom. H), 7.89 (d, J=10Hz, H-3'). ^{13}C NMR ($CDCl_3$): 13.4 (q, CH_3), 21.3 (t, C-7*), 22.1 (t, C-5*), 24.3 (t, C-6*), 39.9 (t, C-8), 50.1 (t, C-3), 58.0 (d, C-4a), 61.9 (d, C-2), 62.2 (s, C-8a), 123.1 (d, C-4'), 127.2 (d, C-4''), 127.4, 128.5 and 128.6 (3 d, C-2', C-2'', C-3''), 141.8 (s, C-1''), 143.7 (s, C-4'), 152.9 (s, C-1'), 208.2 (s, CO). Anal. (mixture of **9b** and **10b**): Calc for $C_{22}H_{24}N_2O_3$: C, 72.51; H, 6.64; N, 7.69. Found: C, 72.27; H, 6.59; N, 7.60.

(2α, 4aα, 8aβ)-2,3,4a,5,6,7,8,8a-Octahydro-1-(4-methoxyphenyl)-8a-methyl-2-phenyl-4(1*H*)-quinolinone (10c)

Imine **5c** (0.300 g, 1.420 mmol) gave 49% of a mixture of isomers **9c** and **10c** and 26% of **11c** according to the general procedure using $TiCl_4$ as Lewis acid at rt and a reaction time of 1 h. Seperation of *endo*- and *exo*- products was carried out by flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 30:1). The obtained *endo*-quinolinones (ratio approx. 1:2.5) were treated with 1 equiv. of MeONa in dry MeOH for 5 days, freed from a major amount of the solvent, the residue poured onto water, extracted with CH_2Cl_2, dried over Na_2SO_4 and evaporated to dryness. 0.224 g (45%) of **10c** could by isolated as pale yellow crystalls. Mp.: 118-121°C (FCC); ^{1}H NMR ($CDCl_3$): 0.98-1.87 (m, 8H, H-5, H-6, H-7, H-8), 1.09 (s, 3H, CH_3), 2.54 (dd, **ABX**, J_{gem}=13Hz, $J_{gauche1}$=5Hz, 1H, H-3eq), 2.72 (t, **ABX**, J_{gem}=J_{trans1}=13Hz, H-3ax), 2.87 (dd, **ABM**, J_{trans2}=12.5Hz, $J_{gauche2}$=3Hz, 1H, H-4a), 3.65 (s, 3H, OCH_3), 4.75 (dd, **ABX**, J_{trans1}=13Hz, $J_{gauche1}$=5Hz, 1H, H-2), 6.57 (d, J=8Hz, 2H, H-3'), 6.97 (d, J=8Hz, 2H, H-2'), 7.01-7.29 (m, 5H, arom. H). ^{13}C NMR ($CDCl_3$): 11.7 (q, CH_3), 21.4 (t, C-7*), 22.2 (t, C-5*), 24.6 (t, C-6*), 40.7 (t, C-8), 51.7 (t, C-3), 55.1 (q, OCH_3), 58.8 (d, C-4a), 61.9 (s, C-8a), 62.6 (d, C-2), 112.6 (d, C-3'), 126.7 (d, C-4''), 127.9 and 128.1 (2 d, C-2'', C-3''), 131.3 (d, C-2'), 138.3 (s, C-1'), 143.2 (s, C-1''), 156.7 (s, C-4'), 209.9 (s, CO). Anal. (mixture of **9c** and **10c**): Calc for $C_{23}H_{27}NO_2$: C, 79.05; H, 7.79; N, 4.01. Found: C, 78.75; H, 8.04; N, 3.89.

(2α, 4aα, 8aβ)-2,3,4a,5,6,7,8,8a-Octahydro-8a-methyl-1-(phenylmethyl)-2-phenyl-4(1*H*)-quinolinone (10d)

Imine **5c** (0.500 g, 2.560 mmol) gave 0.250 g (29%) of a mixture of isomers **9d** and **10d** as colorless oil and 26% of **11d** according to the general procedure using $SnCl_4$ as Lewis acid at rt and a reaction time of 16 h. Separation of *endo*- and *exo*- products was carried out by flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 30:1). The obtained *endo*-quinolinones in a ratio of *cis* : *trans* = 1:1.1 could not be separated and were spectroscopically characterized as a mixture. ^{1}H NMR ($CDCl_3$): 0.98-1.90 (m, 8H, H-5, H-6, H-7, H-8), 1.06 (s, 3H, CH_3), 2.44 (dd, **ABX**, J_{gem1}=14Hz, J_{gauche}=5Hz, 1H, H-3eq), 2.69-2.87 (m, 2H, H-3ax and H-4a), 3.42 (d, **AB**, J_{gem2}=17Hz, $PhCH_2$-a), 3.82 (d, **AB**, J_{gem2}=17Hz, $PhCH_2$-b), 4.15 (dd, **ABX**, J_{trans}=13Hz, J_{gauche}=5Hz, 1H, H-2), 6.99-7.48 (m, 10H, arom. H); ^{13}C NMR ($CDCl_3$): 10.8 (q, CH_3), 21.1 (t, C-7*), 22.1 (t, C-5*), 24.4 (t, C-6*), 39.8 (t, C-8), 50.3 (t, C-3*), 51.0 (t, $PhCH_2$*), 58.1 (d, C-4a), 63.0 (s, C-8a), 65.4 (d, C-2), 125.5 and 127.43 (2 d, C-4' and C-4''), 126.9, 127.47, 128.10 and 128.12 (4 d, C-2', C-3', C-2'' and C-3''), 142.7 and 143.1 (2 s, C-1' and C-1''), 209.7 (s, CO). Anal. (mixture of **9d** and **10d**): Calc for $C_{23}H_{27}NO$: C, 82.84; H, 8.16; N, 4.20. Found: C, 82.61; H, 8.31; N, 4.14.

(2α, 4aα, 8aβ)-2,3,4a,5,6,7,8,8a-Octahydro-8a-methyl-2-(4-nitrophenyl)-1-phenyl-4(1*H*)-quinolinone (10e)

Imine **5e** (0.300g, 1.326mmol) gave 50% of a mixture of *cis*- and *trans*-isomers **9e** and **10e** according to the general procedure using $TiCl_4$ as Lewis acid at rt and a reaction time of 1 h, which was treated with 1 equiv. of MeONa in dry MeOH for 5 days, freed from a major amount of the solvent, the residue poured onto water, extracted with CH_2Cl_2, dried over Na_2SO_4 and evaporated to dryness. 0.225 g (47%) of **10e**

could by isolated as faint yellow crystals. Purification was performed *via* flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 15:1). Mp.: 130-134°C (DIPE); ^{1}H NMR ($CDCl_3$): 0.92-1.80 (m, 8H, H-5, H-6, H-7, H-8), 1.03 (s, 3H, CH_3), 2.37-2.67 (m, 2H, H-3), 2.83 (dd, ABM, J_{trans1}=13Hz, $J_{gauche1}$=4Hz, 1H, H-4a), 4.90 (dd, ABX, J_{trans2}=11Hz, $J_{gauche2}$=5Hz, 1H, H-2), 6.77-7.25 (m, 5H, arom. H), 7.38 (d, J=9Hz, 2H, H-2''), 7.86 (d, J=9Hz, 2H, H-3''). ^{13}C NMR ($CDCl_3$): 11.7 (q, CH_3), 21.2 (t, C-7*), 22.0 (t, C-5*), 24.4 (t, C-6*), 40.4 (t, C-8), 50.7 (t, C-3), 58.7 (d, C-4a), 61.8 (d, C-2), 62.2 (s, C-8a), 123.5 (d, C-3''), 125.7 (d, C-4'), 127.8, 128.5 and 130.3 (3 d, C-2', C-3', C-2''), 144.9 (s, C-1'*), 146.5 (s, C-4''*), 150.4 (s, C-1''), 208.2 (s, CO). Anal. (mixture of **9e** and **10e**): Calc for $C_{22}H_{24}N_2O_3$: C, 72.51; H, 6.64; N, 7.69. Found: C, 72.28; H, 6.91; N, 7.61.

(2α, 4aα, 8aβ)-2,3,4a,5,6,7,8,8a-Octahydro-2-(4-methoxyphenyl)-8a-methyl-1-phenyl-4(1*H*)-quinolinone (10f)

Imine **5f** (0.300g, 1.420mmol) gave 0.248 g (50%) of a mixture of *cis*- and *trans*-isomers **9e** and **10e** as faint yellow oil according to the general procedure using $TiCl_4$ as Lewis acid at rt and a reaction time of 4 h. It proved to be necessary to use 4 equiv. of diene **2**, which were added in two portions at the beginning of the reaction and after 2 h. Purification was performed *via* flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 30:1). ^{1}H NMR ($CDCl_3$): 0.99-1.87 (m, 8H, H-5, H-6, H-7, H-8), 1.10 (s, 3H, CH_3), 2.52 (dd, ABX, J_{gem}=13Hz, $J_{gauche1}$=4Hz, 1H, H-3eq), 2.71 (t, ABX, J_{gem}=J_{trans1}=13Hz, H-3ax), 2.89 (dd, ABM, J_{trans2}=13Hz, $J_{gauche2}$=3Hz, 1H, H-4a), 3.66 (s, 3H, OCH_3), 4.76 (dd, ABX, J_{trans1}=13Hz, $J_{gauche1}$=4Hz, 1H, H-2), 6.62 (d, J=8Hz, 2H, H-3''), 6.87-7.08 (m, 5H, arom. H), 7.17 (d, J=8Hz, 2H, H-2''); ^{13}C NMR ($CDCl_3$): 11.7 (q, CH_3), 21.4 (t, C-7*), 22.2 (t, C-5*), 24.6 (t, C-6*), 40.7 (t, C-8), 51.8 (t, C-3), 55.0 (q, OCH_3), 58.8 (d, C-4a), 61.7 (d, C-2), 61.8 (s, C-8a), 113.4 (d, C-3''), 125.1 (d, C-4'), 127.4, 128.8 and 130.6 (3 d, C-2', C-2'', C-3'), 135.2 (s, C-1''), 145.7 (s, C-1'), 158.0 (s, C-4''), 209.9 (s, CO). Anal. (mixture of **9f** and **10f**): Calc for $C_{23}H_{27}NO_2$: C, 79.05; H, 7.79; N, 4.01. Found: C, 78.92; H, 8.00; N, 3.90.

(2α, 4aα, 8aα)-2,3,4a,5,6,7,8,8a-Octahydro-1-(4-methoxyphenyl)-8a-methyl-2-phenyl-4(1*H*)-quinolinone (11c)

Imine **5c** (0.300 g, 1.420 mmol) gave 0.130 g (26%) of **11c** as colorless crystals according to the general procedure using $TiCl_4$ as Lewis acid at rt and a reaction time of 1 h. Separation of *endo*- and *exo*- products was carried out by flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 30:1). Mp.: 134-137°C (DIPE); ^{1}H NMR ($CDCl_3$): 1.17-2.38 (m, 8H, H-5, H-6, H-7, H-8), 1.25 (s, 3H, CH_3), 2.55 (dd, ABX, J_{gem}=14Hz, J_{gauche}=3Hz, 1H, H-3ax), 2.65-2.83 (m, 2H, H-3eq and H-4a), 3.65 (s, 3H, OCH_3), 4.77 (dd, ABX, J_{trans}=14Hz, J_{gauche}=3Hz, 1H, H-2), 6.57 (d, J=8Hz, 2H, H-3'), 7.01-7.29 (m, 7H, arom. H); ^{13}C NMR ($CDCl_3$): 21.5, 22.5 and 22.7 (3 t, C-5, C-6 and C-7), 27.1 (q, CH_3), 28.0 (t, C-8), 51.8 (t, C-3), 55.0 (q, OCH_3), 55.2 (d, C-4a), 61.0 (d, C-2), 61.5 (s, C-8a), 112.4 (d, C-3'), 126.6 (d, C-4''), 127.86 and 127.93 (2 d, C-2'' and C-3''), 132.1 (d, C-2'), 138.6 (s, C-1'), 143.2 (s, C-1''), 156.5 (s, C-4'), 209.3 (s, CO). Anal.: Calc for $C_{23}H_{27}NO_2$: C, 79.05; H, 7.79; N, 4.01. Found: C, 78.79; H, 8.00; N, 3.89.

(2α, 4aβ, 8aα)-2,3,4a,5,6,7,8,8a-Octahydro-8a-methyl-1-(phenylmethyl)-2-phenyl-4(1*H*)-quinolinone (11d)

Imine **5c** (0.500 g, 2.560 mmol) gave 0.220 g (26%) of **11d** as colorless crystals according to the general procedure using $SnCl_4$ as Lewis acid at rt and a reaction time of 16 h. Separation of the *endo*- and the *exo*-products was carried out by flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 30:1) or by fractional crystallization from DIPE. Mp.: 125-128°C (DIPE); ^{1}H NMR ($CDCl_3$): 1.05-2.35 (m, 8H, H-5, H-6, H-7, H-8), 1.38 (s, 3H, CH_3), 2.46 (dd, ABX, J_{gem1}=14Hz, J_{gauche}=4Hz,

1H, H-3eq), 2.63-2.90 (m, 2H, H-3ax and H-4a), 3.44 (d, AB, J_{gem2}=17Hz, $PhCH_2$-a), 3.98 (d, AB, J_{gem2}=17Hz, $PhCH_2$-b), 4.25 (dd, ABX, J_{trans}=12Hz, J_{gauche}=4Hz, 1H, H-2), 6.97-7.46 (m, 10H, arom. H); ^{13}C NMR ($CDCl_3$): 21.7, 22.2 and 22.7 (3 t, C-5, C-6 and C-7), 26.2 (q, CH_3), 27.5 (t, C-8), 49.4 (t, C-3), 51.2 (t, $PhCH_2$), 54.7 (d, C-4a), 62.4 (s, C-8a), 62.8 (d, C-2), 125.4 and 127.35 (2 d, C-4' and C-4''), 126.9, 127.45, 127.8 and 128.3 (4 d, C-2', C-3', C-2'' and C-3''), 142.0 and 143.2 (2 s, C-1' and C-1''), 209.4 (s, CO). Anal.: Calc for $C_{23}H_{27}NO$: C, 82.84; H, 8.16; N, 4.20. Found: C, 83.17; H, 8.46; N, 3.95.

(1α, 2β, 4aβ, 8aα)-2,3,4a,5,6,7,8,8a-Octahydro-8a-methyl-1-[(2-methyl-1-cyclohexenyl)carbonyl]-2-phenyl-4(1*H*)-naphthalinone (12)

Reaction of imine **5b** (0.200 g, 0.884 mmol) with diene **2b** in the presence of one equivalent of $SnCl_4$ according to the general procedure for cyclizations gave 0.129 g (40%) of **12** as colorless crystals after purification *via* flash column chromatography (bas. cond. silicagel 40:1, light petroleum : ethyl acetate = 30:1). Mp.: 150-151°C (DIPE); ^1H NMR ($CDCl_3$): 1.00 (s, 3H, CH_3), 1.12-2.40 (m, 16H, aliphat. H), 1.65 (bs, 3H, $=CCH_3$), 2.46 (dd, ABM, J_{trans}=11Hz, J_{gauche}=5Hz, 1H, H-4a), 2.54-2.73 (m, 2H, H-3), 3.56 (d, J=13Hz, 1H, H-1), 3.60-3.77 (m, 1H, H-2), 7.10-7.30 (m, 5H, arom. H); ^{13}C NMR ($CDCl_3$): 13.7 (q, CH_3), 20.4 and 21.1 (2 t, C-5 and C-7), 21.5 (q, $=CCH_3$), 21.9 and 22.4 (2 t, C-5' and C-7'), 24.9 (t, C-6), 26.7 (t, C-6'), 33.1 (t, C-3'), 38.6 (t, C-8), 43.0 (s, C-8a), 43.7 (d, C-2), 48.3 (t, C-3), 57.5 (d, C-4a), 61.1 (d, C-1), 126.8 (d, C-4''), 128.0 and 128.4 (2 d, C-2'' and C-3''), 134.6 (s, C-1'), 142.1 (2 s, C-1'' and C-2'), 205.9 (s, CO'), 210.1 (s, CO). MS: e/z = 364 (M^+), 123 (bp), 95, 67. Anal.: Calc for $C_{25}H_{32}O_2$: C, 82.37; H, 8.85. Found: C, 82.14; H. 8.75.

(1α, 2β, 8aα)-[1,2,3,5,6,7,8,8a-Octahydro-8a-methyl-4-(trimethylsilyloxy)naphthalin-1-yl]-(2-methyl-1-cyclohexenyl)-methanone (12a)

Compound **12a** could be isolated according to the procedure for the synthesis of **12** prior to treatment with $MeOH/NEt_3$. Imine **5b** (0.100 g, 0.442 mmol) gave 0.030 g (16%) of **12a** as yellow oil after purification *via* flash column chromatography (silicagel 40:1, light petroleum : ethyl acetate = 50:1). ^1H NMR ($CDCl_3$): 0.17 (s, 9H, TMS), 1.15 (s, 3H, CH_3), 1.65 (bs, 3H, $=CCH_3$), 1.35-2.86 (m, 18H, aliphat. H), 3.30-3.39 (m, 2H, H-1 and H-2), 7.05-7.30 (m, 5H, arom. H); ^{13}C NMR ($CDCl_3$): 0.6 (q, TMS), 20.7 and 21.3 (2 q, 2 CH_3), 22.1, 22.2, 22.51 and 22.52 (4 t, C-4', C-5, C-5' and C-7), 26.7 and 27.0 (2 t, C-6 and C-6'), 33.2 (t, C-3'), 39.36 and 40.8 (2 t, C-3 and C-8), 39.44 (d, C-2), 39.8 (s, C-8a), 59.2 (d, C-1), 121.0 (s, C-4a), 126.2 (d, C-4''), 128.2 (2 d, C-2'' and C-3''), 135.3 (s, C-1'), 140.4 (s, C-4*), 141.1 (s, C-1''*), 144.7 (s, C-2'), 207.4 (s, CO).

1-(2-Methyl-1-cyclohexenyl)-3-phenyl-propenone (13)

A mixture of benzaldehyde (0.300 g, 2.825 mmol), ZnI_2 (0.902 g, 2.825 mmol) and dry CH_2Cl_2 (6 mL) was stirred under nitrogen for 30 min at room temperature. Diene **2** (1.189 g, 5.649 mmol) in CH_2Cl_2 (4 mL) was added and the solution was stirred for 18 h. The crude mixture was hydrolyzed and washed with satd. $NaHCO_3$ solution, dried over Na_2SO_4 and the solvent was evaporated. The residue (**14a**) was dissolved in dry benzene (10 mL) and refluxed for 3 h in the presence of a few crystals of *p*-TSA. Diethyl ether was added to the cooled solution and the organic phase was washed with satd. $NaHCO_3$ solution, dried over Na_2SO_4 and treated with charcoal. After evaporation of the volatiles the crude product was distilled *via* Kugelrohr to give 0.483 g (76%) of a pale yellow oil. Bp.: 155-160°C / 0.03mbar; ^1H NMR ($CDCl_3$): 1.60-1.73 (m, 4H, H-4' and H-5'), 1.76 (s, 3H, CH_3), 2.03-2.35 (m, 4H, H-3' and H-6'), 6.83 (d, J_{trans}=16Hz, 1H, H-3), 7.22-7.65 (m, 6H, H-2 and arom. H); ^{13}C NMR ($CDCl_3$): 21.2 (q, CH_3), 22.2 and 22.4 (2 t, C-4' and C-5'), 26.8 (t, C-6'), 31.6 (t, C-3'), 126.5 (d, C-4''), 128.1 and 128.7 (2 d,

C-2'' and C-3''), 130.2 (d, C-3), 132.9, 134.7 and 136.6 (3 s, C-1', C-1'', C-2'), 144.1 (d, C-2), 199.4 (s, CO). Anal.: Calc. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 83.68; H, 8.10.

1-(2-Methyl-1-cyclohexenyl)-3-trimethylsilyloxy-3-phenyl-1-propanone (14a)

A mixture of benzaldehyde (0.100 g, 0.942 mmol), ZnI_2 (0.300 g, 0.942 mmol) and dry CH_2Cl_2 (2 mL) was stirred under nitrogen for 30 min at room temperature. Diene **2** (0.419 g, 1.884 mmol) in CH_2Cl_2 (1 mL) was added and the solution was stirred for 6 h. The crude mixture was hydrolized and washed with satd. $NaHCO_3$ solution, dried over Na_2SO_4 and the solvent was evaporated. The excess of diene was destroyed by treatment with dry methanol overnight. Evaporation of the volatiles and flash column chromatography (bas. cond. silica gel 70:1, light petroleum : ethyl acetate = 20:1) gave 0.140 g (47%) of **14a** as colorless oil. ^{1}H-NMR ($CDCl_3$): 0.00 (s, 9H, TMS), 1.51-1.62 (m, 4H, H-4' and H-5'), 1.75-1.80 (m, 3H, CH_3), 1.97-2.23 (m, 4H, H-3' and H-6'), 2.63 (dd, ABX, J_{gem}=16Hz, J_{vic}=4Hz, 1H, CH_2a), 3.10 (dd, ABX, J_{gem}=16Hz, J_{vic}=9Hz, 1H, CH_2b), 5.30 (dd, ABX, J_{vic}=9Hz, J_{vic}=4Hz, 1H, H-3), 7.17-7.29 (m, 5H, arom. H); ^{13}C-NMR ($CDCl_3$): 0.0 (q, TMS), 21.3 (q, CH_3), 22.2 (2 t, C-4' and C-5'), 26.2 (t, C-6'), 32.7 (t, C-3'), 52.4 (t, CH_2), 71.4 (d, CH), 125.8 (d, C-2''*), 127.2 (d, C-4''), 128.2 (d, C-3''*), 133.7 (s, C-1'), 139.6 (s, C-2'), 144.7 (s, C-1''), 204.7 (s, CO).

3-Hydroxy-1-(2-methyl-1-cyclohexenyl)-3-phenyl-1-propanone (14)

The reaction was carried out according to the synthesis of **14a**. Cleavage of the TMS group was carried out by treatment of the crude product with dry methanol (4 mL) and acetic acid (0.5 mL) for 1 h. After evaporation of the volatiles 0.229 g (99%) of **14** were isolated by flash column chromatography (silica gel 30:1, light petroleum : ethyl acetate = 25:1) as colorless oil. ^{1}H-NMR ($CDCl_3$): = 1.48-1.70 (m, 4H, H-4' and H-5'), 1.86-1.93 (m, 3H, CH_3), 2.02-2.27 (m, 4H, H-3' and H-6'), 2.90 (d, J=6Hz, 2H, CH_2), 4.3 (bs, J=6Hz, 1H, OH), 5.19 (t, 1H, CH), 7.19-7.44 (m, 5H, arom. H); ^{13}C-NMR ($CDCl_3$): 21.8 (q, CH_3), 22.0 and 22.1 (2 t, C-4' and C-5'), 26.3 (t, C-6'), 33.3 (t, C-3'), 49.7 (t, CH_2), 70.1 (d, CH), 125.6 (d, C-2''*), 127.4 (d, C-4''), 128.3 (d, C-3''*), 132.3 (s, C-1'), 143.0 and 143.4 (2 s, C-1'' and C-2'), 206.1 (s, CO). Anal.: Calc. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.51; H, 8.04.

ACKNOWLEDGEMENTS

We would like to express our gratitude to NOVARTIS - Crop Protection for financially supporting this project. Furthermore we would like to thank Prof. J. Fröhlich and Dr. C. Hametner, Institute of Organic Chemistry, Vienna University of Technology, for their assistance performing the 2D-NMR experiments.

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