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A Directed Stereoselective Aldol Reaction: Simple Synthesis of Enantiopure δ-Hydroxy-β-enamino Ketones by Condensation of Homochiral β-Enamino Ketones with Aldehydes and Ketones.

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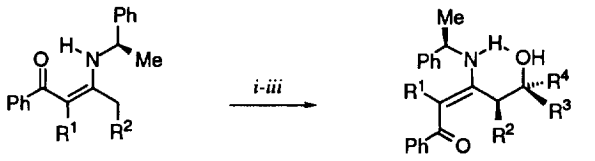
Abstract: A simple synthesis of enantiopure *anti*-δ-Hydroxy-β-enamino ketones **3** by condensation of homochiral lithium dianions derived from β-enamino ketones **1**" with aldehydes and ketones is reported. The mechanism for the directed enantioselective aldol reaction was investigated. The *anti* δ-hydroxyenaminone **3** is obtained as the major diastereomer through an open transition state. In acidic conditions the δ-hydroxyenaminones **3** are cyclized to 4-imino-2,3-dihydropyranones **4** which are instable and isomerize spontaneously to γ alkylidenenaminones **5**. Copyright © 1996 Elsevier Science Ltd

1,3 Diketones and related compounds constitute important structural subunits present in a variety of synthetic targets of natural origin[1] and in key intermediates for the construction of a large variety of heterocyclic compounds.[2] The introduction of an alkyl side chain containing an hydroxyl function of fixed configuration at the γ-position of 1,3-diketone represents an important synthetic goal since the added functionality would increase the synthetic scope of these intermediates

The reaction of enolate with a carbon electrophile represents the most classical approach to C-C bond formation α to a CO group of aldehydes and ketones.[3] The aldol reaction is one of the more powerful tools for the stereoselective construction of acyclic molecules.[3a] More recently metallated imines, have been used extensively as advantageous reactive enolate equivalents.[4] This has solved many of the problems associated with the classical carbonyl chemistry.[3] Among the most important advantages of the imine is the ability to introduce a "stereogenic center" via an enantiomerically pure amine, thus enabling diastereoselective control of the C-C bond forming process.[5]

We have recently reported on the highly efficient regioselective functionalization of β-enamino ketones.[6] This was achieved by the reaction of the regioselectively prepared α'- or γ-dianion of β-enamino ketones with electrophiles. Using an enantiomerically pure amine to form the enaminone we have developed the stereoselective synthesis of chiral 1,3-diketones, through the diastereoselective γ-alkylation of the intermediate chiral aza-dienolate.[7] Now we wish to report the enantioselective aldol condensation by reaction of lithium dianion of β-enamino ketones with aldehydes and ketones. affording the stereoselective synthesis of δ-hydroxy-β-enamino ketones **3** (see scheme of **Table 1**).

Table 1. Diastereoselective synthesis of δ-hydroxy enamino ketones **3aa-bf**.



1a-d **3aa-bf**

i: 3 MeLi/3 HMPA/THF, 0 to 30°C, 30'; *ii*: 2.5 R^3R^4C=O/THF, -100°C, 30'; *iii*: H_2O/THF, -50°C.

Entry	3	R^1	R^2	R^3	R^4	Yield of 3(%)[a]	*d.e.*[b,c]
1	(*R*)-**3aa**	H	H	H	Me	48	14
2	(4*S*,5*R*)-**3ba**	H	Me	H	Me	68	72[d]
3	(4*S*,5*R*)-**3ca**	H	Bn	H	Me	53	63[d]
4	(4*S*,5*R*)-**3da**	$(CH_2)_2$		H	Me	62	71
5	(3*S*,a"*R*)-**3db**	$(CH_2)_2$		H	$(CH_2)_2Ph$	51	52
6	(*S*)-**3ac**	H	H	H	Ph	60	35
7	(*S*,*S*)-**3bc**	H	Me	H	Ph	48	33[d]
8	(*S*)-**3ad**	H	H	H	Bu^t	87	84
9	(*S*,*S*)-**3bd**	H	Me	H	Bu^t	85	93
10	(*S*,*S*)-**3dd**	$(CH_2)_2$		H	Bu^t	88	96
11	(*S*)-**3be**	H	Me	Me	Me	82	94
12	(*S*)-**3ce**	H	Bn	Me	Me	78	92
13	(*S*)-**3de**	$(CH_2)_2$		Me	Me	80	88
14	(*S*,*S*)-**3bf**	H	Me	Me	Bu^t	81	94

[a] Yields of the pure isolated major diastereomer.[b] Determined by HPLC and ^1H NMR of purified but unchanged reaction mixtures of stereoisomers. [c] Relative to the C-4 or C-5 configuration of the major *anti* diastereomers. [d] The *anti*/*syn* ratio, refered to the relative configuration of the new stereogenic centers formed at C-4 and C-5 of the major diastereomers, for **3ba**, **3ca**, **3bc** is 5, 3, 3 respectively.

Lithium dianion was prepared by treatment of enaminone **1a-d** in THF with 3 eq of methyl lithium in the presence of 3 eq of HMPA from 0 to 30 °C for 30'. Then the cooled mixture (-100 °C) was treated with 2.5 eq. of aldehydes or ketones **2a-f** at the same temperature for 30'. After quenching (H_2O/THF, -50°C) usual work-up and chromatographic purification gave the enantiopure δ-hydroxy β-enamino ketones **3aa-bf**. As shown in **Table1**, high yields of the pure isolated major diastereoisomers (**3aa-bf**) have been obtained for the reaction of enaminones (**1a-d**) with a large variety of carbonyl compounds (**2a-f**). Using acetaldehyde with enaminone **1a** only, we have obtained a low *d.e.* because of the small size of the methyl group. The *d.e.* increases with increasing steric hindrance of the reacting carbonyl compounds and enaminones.

We preferred enantiopure α-methylbenzylamine as the chiral source because it is a very cheap and common amine, commercially available as both pure enantiomers; in our system it gives good *d.e.* as shown in the **Table 1**. An enhanced reactivity and the best *d.e.* was obtained using HMPA as solvent additive, precisely in equimolecular amounts to the MeLi, as also observed in the diastereoselective alkylation of enaminones.[7] To find the best conditions for the reaction we have investigated some synthesis of **3ce** with different ratios of methyl lithium referred to the starting enaminone**1c** in the presence of 3 eq of HMPA. Better yields of conversion and *d.e.* requires a molar ratio of methyl lithium above to 3 (see **Figure 1**).

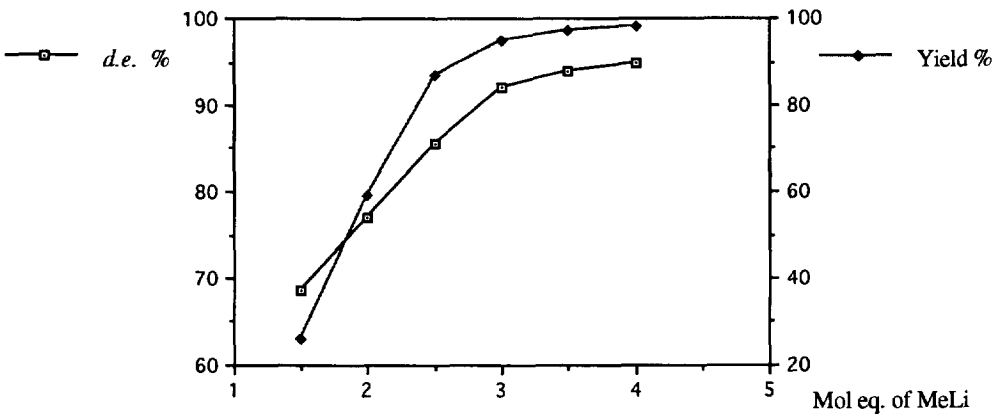


Figure 1. Yields of conversion and *d.e.* % obtained in the syntheses of **3ce** at different ratio of MeLi referred to the starting enaminone **1c**.

In the recent literature numerous examples of aldol reactions mediated by titanium, boron, tin and other metals are described with high stereochemical control. The intermediate metal enolates generally assume the (Z)-configuration and give *syn* aldols stereoselectivity.[8] In order to increase the stereoselectivity we have tentatively carried out the aldol reaction through titanium enolates of enaminones but a complex and incomprehensible reaction mixture have been obtained. Several attempts to extend the reaction to enaminones which can be metallated both in γ or in α'-position failed. We studied recently the conditions for a regiospecific metallation: using the MeLi/TMEDA couple in THF, we obtained the thermodynamically more stable dianion (γ), while using as metallating agent the LiTMP in THF we obtained mainly the kinetic dianion (α') that slowly changes in the thermodynamic one (γ).[6] Unfortunately the systems we have studied for a maximum of stereoselectivity gave a low regioselectivity because the steric factors are more important than the electronic ones. The γ-position in fact, is strongly hindered by the chiral group at the N atom, so that the alkylation take place preferentially on

the α' position and with low *d.e.* even if the metallation were performed under the optimum conditions to achieve γ alkylation.

All the new enantiopure isolated compounds are unknown in the literature neither as such nor as the usual derivatives. Therefore the absolute configuration of the new chiral isolated compounds was determined by X-ray diffraction of a single crystal for the compounds (α*R*,3*S*)-**3de** and (α*R*,4*S*,5*S*)-**3bd** (see **Figure 2**).[9] The absolute configuration of the other isolated compounds were determined by ^{1}H NMR correlations. Generally the *anti* adducts show an high J_{HH} (7.3-8.9 Hz) for the protons bond at the newly formed stereogenic centers. As it is possible to see on the X-ray crystal structure of the cyclic δ-hydroxy enaminones **3de** an hydrogen bond occur from the enaminic hydrogen and the carbonyl function, constraining the enaminonic conjugate system in the Z,*s-cis* geometry. Otherwise in the X-ray structure of acyclic **3bd** the hydrogen bond occur betwen N atom and hydroxyl group, and the benzoyl group is constrained *trans* with respect to the N atom. By ^{1}H NMR analysis it is possible to see that the NH proton in all the open enaminones **3** is deshielded (δ = 11.87-12.43 ppm) with respect to the cyclic ones (δ = 10.89-11.32 ppm, $\Delta\delta$ = 1.14 ppm). This findings show that the enaminones **3**, in chloroform solution assumed a structure similar to that in the crystals.

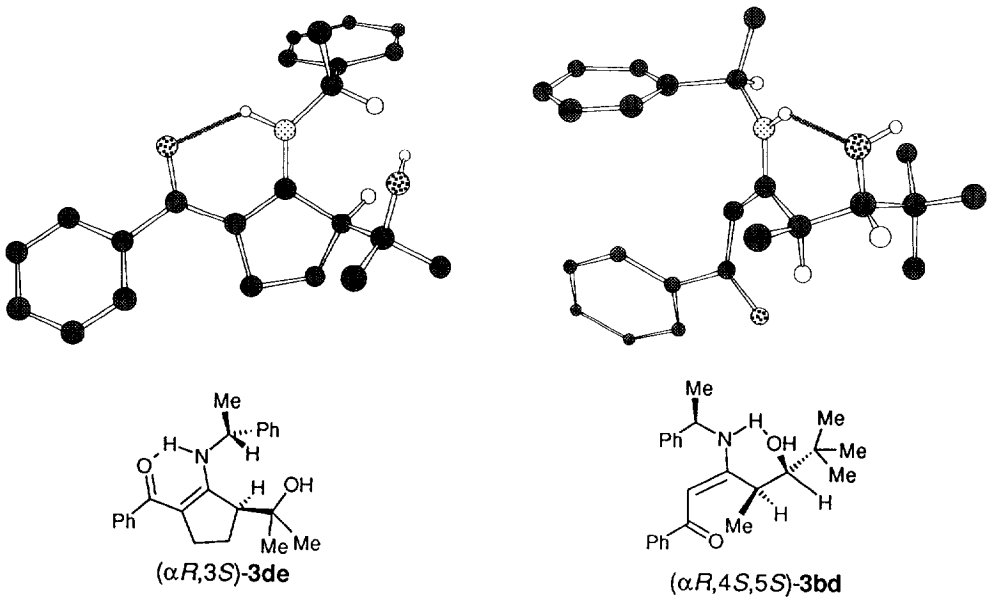
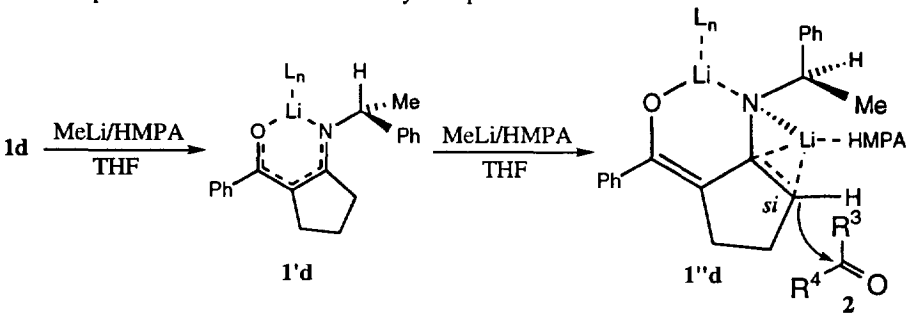


Figure 2. Ball and stick depiction of X-ray of the single crystal structures of cyclic (α*R*,3*S*)-**3de** and acyclic (α*R*,4*S*,5*S*)-**3bd** δ-hydroxy enaminones. Most of the hydrogen atoms have been omitted for clarity.

A possible explanation of the asymmetric induction can be proposed examining the steric aspect in the formation process of the chiral enaminone lithium dianion **1"d** (see **Scheme 1**). In this medium the lithium enaminones are present as reactive monomers, coordinated with HMPA and THF.[10] The first coordinated lithium ion in the monoanion **1'd** resides in the molecular plane, chelated between O and N, constraining the aza-allylic sistem in the *syn* configuration and providing the conformational rigidity necessary for an high asymmetric induction. The configuration of the chiral substituent at the N atom addresses the second metallation process to the less hindered side (back face of **1'd** in the case of the (*R*)-amine). In the dianion **1"d** the *re* face

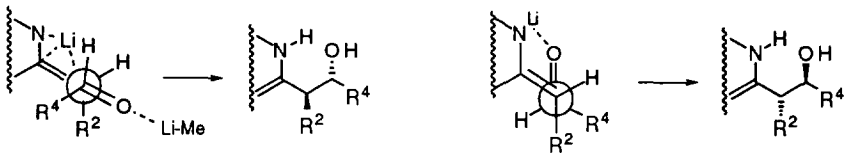
of the (*E*)-azaallylic system is highly hindered by the second lithium atom, strongly coordinated with the bulky and powerful ligand HMPA, preventing the attack of the electrophile on the same face. Thus the approach of the electrophilic carbonyl compoud takes place preferentially from the *si* face (the same stereoselective induction mechanism of γ-alkylation of enaminones[7]) affording the *anti*-aldol **3**.

Scheme 1. Formation process of the chiral enaminone lithium dianion **1"d** and nucleophilic attack of this to the carbonyl compounds **2**.



In our conditions the reaction proceeds through an open chain transition state **TS 1** in which the electrophilic carbonyl compounds, activated by the excess of methyl lithium, attack the nucleophilic (Z)-enaminone lithium dianion system affording the *anti*$_1$-**3** product (see **Scheme 2**).[11] The pericyclic transition state **TS 2**, usually associated with the aldol reactions (strong acyclic chelation stereocontrol), is less important in these conditions. The *anti*$_2$-**3** products expected from chelation control such as the *syn*-**3** products are obtained only with low yields.

Scheme 2 - The more probable transition state (**Ts 1**) and the chelation control transition state (**TS 2**) for the nucleophilic attack of lithium dianion **1"d** to the carbonyl compounds **2**.



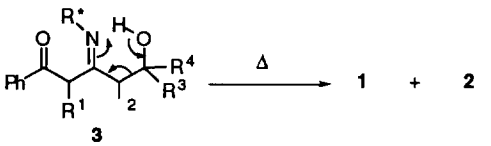
TS 1 *anti*$_1$-**3** **TS 2** *anti*$_2$-**3**

The δ-hydroxyenaminones **3** do not furnish the M^+ ion on GC-MS analysis but the spectra of alkenes **5** and mainly the spectra of the starting enaminones **1** (two peaks in the ratio of 1:1.5 respectively for **3bd**) in analogy with β-hydroxyketimines, wich at high temperature undergoes a thermolysis through a retro imino ene reaction as shown in the **Scheme 3**.[12]

In the attempt to hydrolize the δ-hydroxyenaminones **3** in acidic conditions (HCl 3 N / THF, 2 h at room temperature) we have found their cyclization to 4-imino-2,3-dihydro-4H-4-pyranones **4** with high yields.

Two diastereoisomers were obtained for the pyranones **4** where the (*Z*)-**4** are the major products. The *Z*/*E* structures of pyranones **4** was assigned as follows: generally in the major pyranones (*Z*)-**4** the phenyl of the N chiral group affords a shielding effect on the H-3 and R^4 of 0.2-0.4 ppm, while in the (*E*)-**4** the R^2 is shielded of 0.2-0.4 ppm is referred to (Z)-**4**. Those pyranones **4** in some cases show complex ^1H and ^{13}C NMR, as the sum of the spectra of two conformers derived from a restricted rotation of the N chiral group around the C-N bond.

Scheme 3. Gas chromatographic thermal retro imino ene decomposition of δ-hydroxyenaminones **3**.



Scheme 4

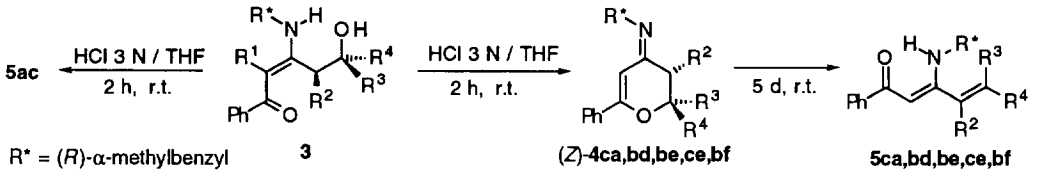


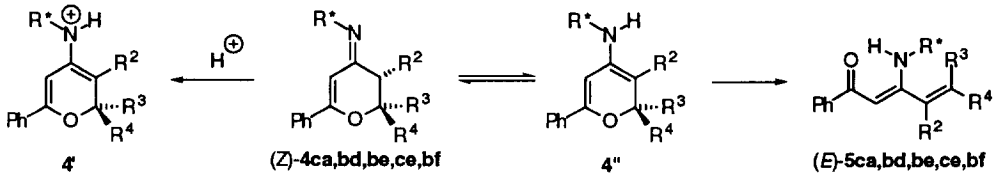
Table 2. Cyclization of δ-hydroxy enamino ketone **3** to 4-imino-2,3-dihydropyranones **4** and rearrangment of them to γ-alkyliden-β-enaminones **5**.

Entry	**3**	R^1	R^2	R^3	R^4	**4**	Yield of (*Z*)-**4** (%)[a]	**5**	Yield of **5** (%)[b]
1	(4*S*,5*R*)-**3ca**	H	Bn	H	Me	(2*R*,3*S*)-**4ca**	81 (12)	(*E*)**5ca**	87
2	(*S*)-**3ac**	H	H	H	Ph			(*E*)**5ac**	86
3	(*S*,*S*)-**3bd**	H	Me	H	Bu^t	(*S*,*S*)-**4bd**	78 (14)	(*E*)**5b** **d**	91
4	(*S*)-**3be**	H	Me	Me	Me	(*S*)-**4be**	82 (11)	**5be**	93 (1.3)
5	(*S*)-**3ce**	H	Bn	Me	Me	(*S*)-**4ce**	77	**5ce**	84 (1.4)
6	(*S*,*S*)-**3bf**	H	Me	Me	Bu^t	(*S*,*S*)-**4bf**	68 (18)	(*E*)**5bf**	90 (1.0)

[a] Yields of the pure isolated major (Z) **4**; in bracket yields of the minus (E)-**4**. [b] In brackets ^{1}H NMR ratio of atropisomers **5**.

The 4-imino-2,3-dihydropyranones **4** are generally stable in the same acidic conditions where it was formed (in this acidic medium probably the more stable protonated **4'** is present). In neutral conditions, the oily **4** undergoes spontaneously an electrocyclic rearrangement to γ-alkylidenenaminones **5** (see **Scheme 5**). The geometry of the C=C double bond obtained is *E* (the thermodinamically more stable diastereomer was formed). From the PM3 calculation of formation heat it is possible to see that the alkylidenenaminones **5** are generally more stable that the parent iminodihydropyranones **4** and the differences in stability are higher as more substituents are present in the positions 2 and 3 of the dihydropyranones. The ^{1}H and ^{13}C NMR spectra show that the γ-alkylidenenaminones **5** are a mixture of two atropisomeric structures, derived from a restricted rotation arround the C(3)-C(4) bond, if R^3 is different from hydrogen as in **5be, ce, bf**.

Scheme 5. Electrocyclic rearrangement of 4-imino-2,3-dihydropyranones to γ-alkylidenenaminones **5**.



In conclusion, the condensation of aldehydes and ketones with lithium dianion of chiral enaminone **1** takes place in HMPA/THF with good yields and *d.e.* The operational simplicity of this method has the advantage of providing a variety of *anti*-δ-hydroxylated enaminones **3** in quite high stereoisomeric purity after chromatographic separation, wherein the absolute configuration can be predicted with a high degree of confidence. Either antipode of the chiral products can be prepared choosing the α-methylbenzylamine of appropriate configuration. Some of the δ-hydroxyenaminones **3**, in acidic conditions cyclize to 4-imino-2,3-dihydropyranones **4** which are instable and isomerize spontaneously to the thermodinamically more stable (*E*)-γ-alkylidenenaminones **5**.

EXPERIMENTAL SECTION

^{1}H and ^{13}C-NMR spectra were recorded with a Varian VXR 300 instrument. Chemical shifts are given in ppm downfield from Me_4Si in $CDCl_3$ solution. Coupling constants are given in Hertz. IR spectra were recorded with a Perkin-Elmer 257 spectrometer. GC-MS analyses were performed with an HP 59970 workstation formed by an HP-5890 gas chromatograph equipped with a methyl silicone capillary column and by an HP-5970 mass detector. Optical rotations were measured with a Perkin-Elmer 241 polarimeter using 10 cm cells. THF was dried by refluxing over sodium wire until the blue colour of benzophenone ketyl persisted and then distilling into a dry receiver under nitrogen atmosphere. Commercial methyllithium and butyllithium solutions (Aldrich) were employed under dry atmosphere. Commercial HMPA, TMEDA and TMP (Aldrich) were dried and distilled before use. The (*R*)-(+)-1-phenylethylamine 98% $[\alpha]^{23}$ +38 (neat) were purchased from Aldrich and used without further purification.

Preparation of starting enaminones 1a-d.

The enaminone **1a** were prepared from benzoylacetone and (*R*)-1-phenylethylamine according to Singh and Tandon's procedure.[14] The enaminones **1b,c** were prepared by γ alkylation of enaminone **1a** according to our procedure previously reported.[6a] The enaminone **1d** were prepared by benzoylation of (*R*)-N-(α-methylbenzyl)-cyclopentaneimine according to our procedure previously reported.[15]

General procedure for the diastereoselective condensation of the enaminone 1ad with aldeides 2a-d and ketones 2e,f.

Lithium dianion was prepared according to the following typical procedure. A solution of methyllithium (12 mmol, 1.6 M in diethylether) was dropped into a stirred solution of the suitable enaminone **1a-d** (4 mmol) and HMPA (12 mmol) in THF (5 mL) at 0°C under nitrogen and the temperature was allowed slowly to rise to 30 °C for 30'. The ceased evolution of methane showed the complete formation of dianion. The mixture was cooled at -100 °C and then treated with aldehydes or ketones (10 mmol) in THF (5 mL) for 30'. The temperature was slowly allowed to rise to - 50 °C (1 h) followed by quenching with a solution of THF (1 mL)

and H_2O (0.5 mL). The reaction mixture was partitioned, at room temperature, between saturated aqueous ammonium chloride (15 ml) and dichloromethane (100 mL). The organic layer was dried (Na_2SO_4), evaporated under reduced pressure and the residue obtained was submitted to HPLC and ^1H NMR analysis for the determination of the yield of conversion and the ratio of diastereomers. Column chromatographic separation of crude material (n-hexane/ethyl acetate, 80:20) furnished the pure diastereomers.

(*R*,*R*)-1-Phenyl-3-(N-α-methylbenzyl)amino-5-hydroxy-2-hexen-1-one [(*R*,*R*)-3aa]: mp 154-156 °C (CH_2Cl_2-hexane); $[\alpha]^{20}_D$ -658.8 (c = 2.9, $CHCl_3$); IR (nujol) 3330, 1580, 1450, 1365 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (d, 3 H, *J* = 6.2 Hz), 1.61 (d, 3 H, *J* = 6.8 Hz), 2.10 (br s, 1 H), 2.29 (dd, 1 H, *J* = 13.9, 4.4 Hz), 2.45 (dd, 1 H, *J* = 13.9, 8.4 Hz), 3.91 (dqd, 1 H, *J* = 8.4, 6.2, 4.4 Hz), 4.93 (quint, 1 H, *J* = 7.3 Hz), 5.72 (br s, 1 H), 7.21-7.48 (m, 8 H), 7.84-7.94 (m, 2 H), 11.99 (br d, 1 H, *J* = 7.8 Hz). ^{13}C NMR ($CDCl_3$) δ 23.4, 24.9, 41.8, 53.2, 66.9, 92.2, 125.6, 126.9, 127.3, 128.2, 128.9, 130.7, 140.2, 144.3, 165.0, 188.3; Anal. Calcd. for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.85; H, 7.57; N, 4.69.

(α*R*, 5*S*)-3aa (minus diastereomer): ^1H NMR ($CDCl_3$) δ 1.26 (d, 3 H, *J* = 6.1 Hz), 1.60 (d, 3 H, *J* = 6.8 Hz), 2.10 (br s, 1 H), 2.29 (dd, 1 H, *J* = 13.9, 8.3 Hz), 2.47 (dd, 1 H, *J* = 13.9, 4.4 Hz), 4.06 (dqd, 1 H, *J* = 8.3, 6.1, 4.4 Hz), 4.83 (dq, 1 H, *J* = 8.2, 6.8 Hz), 5.70 (br s, 1 H), 7.21-7.48 (m, 8 H), 7.84-7.94 (m, 2 H), 11.90 (br d, 1 H, *J* = 8.2 Hz).

(α*R*, 4*S*, 5*R*)-1-Phenyl-3-(N-α-methylbenzyl)amino-4-methyl-5-hydroxy-2-hexen-1-one [(α*R*, 4*S*, 5*R*)-3ba]: mp 128-131 °C (CH_2Cl_2-hexane); $[\alpha]^{20}_D$ -678.0 (c = 1.4, $CHCl_3$); IR (nujol) 3320, 1570, 1440, 1365 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (d, 3 H, *J* = 6.9 Hz), 1.25 (d, 3 H, *J* = 6.1 Hz), 1.63 (d, 3 H, *J* = 6.8 Hz), 2.25 (br s, 1 H), 2.60 (dq, 1 H, *J* = 8.4, 6.9 Hz), 3.82 (dq, 1 H, *J* = 8.4, 6.1 Hz), 4.99 (quint, 1 H, *J* = 6.8 Hz), 5.76 (s, 1 H), 7.20-7.50 (m, 8 H), 7.84-7.94 (m, 2 H), 12.26 (br d, 1 H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$) δ 16.0, 20.7, 24.8, 43.0, 52.9, 71.7, 88.0, 125.6, 126.9, 127.2, 128.2, 128.9, 130.6, 140.5, 144.6, 171.5, 188.6. Anal. Calcd. for $C_{21}H_{25}NO_2$: C, 77.99; H, 7.79; N, 4.33. Found: C, 77.74; H, 7.88; N, 4.55.

(α*R*, 4*R*, 5*S*)-1-Phenyl-3-(N-α-methylbenzyl)amino-4-methyl-5-hydroxy-2-hexen-1-one [(α*R*, 4*R*, 5*S*)-3ba]:Yield 10 %; mp 142-144 °C (CH_2Cl_2-hexane); $[\alpha]^{20}_D$ -383.9 (c = 1.1, $CHCl_3$); IR (film) 3320, 1570, 1445, 1365 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (d, 3 H, *J* = 6.1 Hz), 1.22 (d, 3 H, *J* = 7.0 Hz), 1.57 (br s, 1 H), 1.63 (d, 3 H, *J* = 7.0 Hz), 2.66 (quint, 1 H, *J* = 7.4 Hz), 3.76 (quint, 1 H, *J* = 6.9 Hz), 4.87 (quint, 1 H, *J* = 7.1 Hz), 5.80 (s, 1 H), 7.20-7.47 (m, 8 H), 7.84-7.92 (m, 2 H), 12.28 (br d, 1 H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$) δ 17.6, 20.9, 25.4, 43.1, 53.2, 71.1, 88.4, 126.4, 127.4, 128.1, 128.7, 129.4, 131.1, 141.0, 144.3, 171.1, 189.2. Anal. Calcd. for $C_{21}H_{25}NO_2$: C, 77.99; H, 7.79; N, 4.33. Found: C, 78.18; H, 7.94; N, 4.57.

(α*R*, 4*S*, 5*R*)-1-Phenyl-3-(N-α-methylbenzyl)amino-4-benzyl-5-hydroxy-2-hexen-1-one [(α*R*, 4*S*, 5*R*)-3ca]: Oil; $[\alpha]^{20}_D$ -371.6 (c = 2.3, $CHCl_3$); IR (film) 3360, 1570, 1525, 1275 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (d, 3 H, *J* = 6.3 Hz), 1.62 (d, 3 H, *J* = 6.7 Hz), 2.22 (br s, 1 H), 2.57 (dd, 1 H, *J* = 12.0, 5.2 Hz), 2.80 (dt, 1 H, *J* = 7.8, 5.5 Hz), 2.91 (dd, 1 H, *J* = 12.0, 7.8 Hz), 3.86 (br quint, 1 H, *J* = 5.8 Hz), 4.77 (quint, 1 H, *J* = 6.9 Hz), 5.98 (s, 1H), 6.61-6.70 (m, 2 H), 7.03-7.49 (m, 11 H), 7.92-7.99 (m, 2 H), 12.29 (br d, 1 H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$) δ 21.6, 24.9, 36.55, 5.15, 5.14, 68.1, 90.0, 125.7, 126.2, 127.0, 127.3, 128.3, 128.3, 128.9, 129.0, 130.7, 138.7, 140.4, 144.5, 168.8, 188.1. Anal. Calcd. for $C_{27}H_{29}NO_2$: C, 81.17; H, 7.32; N, 3.51. Found: C, 81.23; H, 7.11; N, 3.34.

(αR, 4S, 5S)-1-Phenyl-3-(N-α-methylbenzyl)amino-4-benzyl-5-hydroxy-2-hexen-1-one [(αR, 4S, 5S)-3ca]: Yield 16 %; mp 120-122 °C (CH_2Cl_2-hexane); $[\alpha]^{20}_D$ -324.1 (c = 3.0, $CHCl_3$); IR (film) 3350, 1575, 1275, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (d, 3 H, J = 6.3 Hz), 1.58 (d, 3 H, J = 6.8 Hz), 1.83 (br s, 1 H), 2.66-3.06 (m, 3 H), 4.00 (quint, 1 H, J = 6.3 Hz), 4.80 (quint, 1 H, J = 6.8 Hz), 5.74 (s, 1 H), 6.68-7.50 (m, 13 H) 7.84-7.90 (m, 2 H), 12.20 (br d, 1 H, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$) δ 21.7, 25.5, 36.7, 49.5, 53.3, 70.7, 90.9, 126.2, 126.7, 127.4, 127.7, 128.7, 128.9, 129.3, 129.4, 131.1, 139.2, 141.0, 144.6, 168.9, 188.5. Anal. Calcd. for $C_{27}H_{29}NO_2$: C, 81.17; H, 7.32; N, 3.51. Found: C, 80.94; H, 7.16; N, 3.77.

(R, R, R)-1-Phenyl-3-(N-α-methylbenzyl)amino-4-benzyl-5-hydroxy-2-hexen-1-one [(R, R, R)-3ca]: Yield 8 %; Oil; $[\alpha]^{20}_D$ -465.4 (c = 1.3, $CHCl_3$); IR (film) 3360, 1570, 1520, 1275 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, 3 H, J = 6.2 Hz), 1.15 (d, 3 H, J = 6.8 Hz), 1.60 (br s, 1 H), 2.78 (ddd, 1 H, J = 9.7, 6.5, 4.1 Hz), 2.81-3.08 (m, 2 H), 3.86 (m, 1 H), 4.10 (quint, 1 H, J = 7.0 Hz), 6.08 (s, 1 H), 7.14-7.56 (m, 13 H), 7.91-7.99 (m, 2 H), 12.27 (br d, 1 H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$) δ 21.1, 24.3, 38.7, 50.5, 52.7, 69.3, 88.9, 125.9, 126.7, 126.9, 127.4, 128.2, 128.7, 128.8, 129.0, 130.6, 138.8, 140.5, 144.1, 168.8, 188.0. Anal. Calcd. for $C_{27}H_{29}NO_2$: C, 81.17; H, 7.32; N, 3.51. Found: C, 80.90; H, 7.06; N, 3.36.

(αR, 4R, 5S)-1-Phenyl-3-(N-α-methylbenzyl)amino-4-benzyl-5-hydroxy-2-hexen-1-one [(αR, 4R, 5S)-3ca]: Yield 11 %; Oil; $[\alpha]^{20}_D$ -431.6 (c = 1.1, $CHCl_3$); IR (film) 3360, 1570, 1520, 1275 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.69 (d, 3 H, J = 6.2 Hz), 1.07 (d, 3 H, J = 6.7 Hz), 2.17 (br s, 1 H), 2.50-3.00 (m, 3 H), 3.79 (dq, 1 H, J = 7.4, 6.2 Hz), 3.92 (quint, 1 H, J = 7.0 Hz), 5.78 (s, 1 H), 7.04-7.50 (m, 13 H), 7.86-7.98 (m, 2 H), 12.24 (br d, 1 H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$) δ 21.1, 24.3, 38.7, 50.5, 52.7, 69.3, 88.9, 125.9, 126.7, 126.9, 127.4, 128.2, 128.7, 128.8, 129.0, 130.6, 138.8, 140.5, 144.1, 168.8, 188.0. Anal. Calcd. for $C_{27}H_{29}NO_2$: C, 81.17; H, 7.32; N, 3.51. Found: C, 80.98; H, 7.14; N, 3.73.

(αR, 3S, α'R)-1-Benzoyl-2-(N-α-methylbenzyl)amino-3-(α'-hydroxy)-ethylcyclopentene [(αR, 3S, α'R)-3da]: Oil; $[\alpha]^{20}_D$ -493.1 (c = 4.4, $CHCl_3$); IR (film) 3360, 1515, 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (d, 3 H, J = 6.1 Hz), 1.59 (d, 3 H, J = 6.8 Hz), 2.30-2.87 (m, 6 H), 3.77 (dq, 1 H, J = 7.8, 6.1 Hz), 5.09 (dq, 1 H, J = 8.8, 6.8 Hz), 7.22-7.44 (m, 8 H), 7.63-7.71 (m, 2 H), 10.95 (br d, 1 H, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$) δ 15.8, 21.1, 26.1, 27.8, 28.7, 54.4, 54.8, 109.8, 125.4, 127.0, 127.8, 128.8, 129.4, 129.7, 140.5, 144.9, 173.2, 187.6. Anal. Calcd. for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.52; H, 7.67; N, 3.92.

(αR, α'R, 3S)-1-Benzoyl-2-(N-α-methylbenzyl)amino-3-(α'-hydroxy-γ'-phenyl)propylcyclopentene [(αR, α'R, 3S)-3db]: Oil ; $[\alpha]^{20}_D$ -494.1 (c = 2.1, $CHCl_3$); IR (film) 3350, 1590, 1445, 1315 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.61 (d, 3 H, J = 6.9 Hz), 1.45-4.05 (m, 10 H), 3.28 (td, 1 H, J =8.5, 2.0 Hz), 5.18 (dq, 1 H, J = 8.9, 6.9 Hz), 7.10-7.50 (m, 13 H), 7.65-7.85 (m, 2 H), 11.03 (br d, 1 H, J = 9.1 Hz). ^{13}C NMR ($CDCl_3$) δ 26.7, 28.4, 29.3, 32.4, 35.5, 50.6, 55.0, 71.7, 110.4, 125.9, 126.1, 128.4, 128.9, 128.9, 129.3, 130.0, 130.2, 131.6, 140.7, 142.4, 145.5, 163.4, 191.1. Anal. Calcd. for $C_{29}H_{31}NO_2$: C, 81.85; H, 7.34; N, 3.29. Found: C, 81.97; H, 7.58; N, 3.43.

(αR, 5S)-1,5-Diphenyl-3-(N-α-methylbenzyl)amino-5-hydroxy-2-penten-1-one [(αR, 5S)-3ac]: Oil; $[\alpha]^{20}_D$ -479.1 (c = 3.3, $CHCl_3$); IR (nujol) 3300, 1580, 1320, 1280 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59 (d, 3 H, J = 6.7 Hz), 2.20 (br s, 1 H), 2.54 (dd, 1 H, J = 13.9, 4.0 Hz), 2.73 (dd, 1 H, J = 13.9, 8.9 Hz), 4.75(dd, 1 H, J = 8.9, 4.0 Hz), 4.92 (quint, 1 H, J = 7.1 Hz), 5.81 (s, 1 H), 7.23-7.50 (m, 13 H),

7.86-7.96 (m, 2 H), 12.10 (br d, 1 H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$) δ 25.0, 42.0, 53.3, 73.1, 92.6, 125.6, 125.6, 127.0, 127.3, 128.0, 128.2, 128.6, 129.0, 130.7, 140.1, 143.2, 144.4, 164.4, 188.2. Anal. Calcd. for $C_{25}H_{25}NO_2$: C, 80.83; H, 6.78; N, 3.77. Found: C, 80.99; H, 6.59; N, 3.53. **(αR, 5R)-3ac** (minus diastereomer): ^{1}H NMR ($CDCl_3$) δ 1.48 (d, 3 H, J = 6.8 Hz), 2.46 (br s, 1 H), 2.60-2.70 (m, 2 H), 4.62(dd, 1 H, J = 7.5, 3.9 Hz), 4.89 (quint, 1 H, J = 6.8 Hz), 5.71 (s, 1 H), 7.23-7.50 (m, 13 H), 7.86-7.96 (m, 2 H), 11.87 (br d, 1 H, J = 7.5 Hz).

(αR, 4S, 5S)-1,5-Diphenyl-3-(N-α-methylbenzyl)amino-5-hydroxy-4-methyl-2-penten-1-one [(αR, 4S, 5S)-3bc]: m.p. 146-148 °C (CH_2Cl_2-hexane); $[\alpha]^{20}_D$ -436.2 (c = 1.1, $CHCl_3$); IR (nujol) 3350, 1590, 1445, 1320 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.63 (d, 3 H, J = 7.0 Hz), 1.59 (d, 3 H, J = 6.7 Hz), 2.58 (br s, 1 H), 2.91 (dq, 1 H, J = 8.8, 7.0 Hz), 4.60 (d, 1 H, J = 8.8 Hz), 4.96 (quint, 1 H, J = 6.7 Hz), 5.88 (s, 1 H), 7.13-7.50 (m, 13 H), 7.86-7.96 (m, 2 H), 12.10 (br d, 1 H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$) δ 16.9, 25.3, 43.2, 53.6, 79.5, 88.9, 126.1, 127.2, 127.5, 127.7, 128.7, 128.8, 129.1, 129.4, 131.1, 141.1, 142.5, 145.3, 171.8, 188.9. Anal. Calcd. for $C_{26}H_{27}NO_2$: C, 81.01; H, 7.06; N, 3.63. Found: C, 80.86; H, 6.87; N, 3.85. **(R, R, R)-3bc** (minus diastereomer): ^{1}H NMR ($CDCl_3$) δ 0.99 (d, 3 H, J = 7.0 Hz), 1.26 (d, 3 H, J = 6.7 Hz), 2.40 (br s, 1 H), 2.89 (quint, 1 H, J = 7.0 Hz), 4.37 (quint, 1 H, J = 6.7 Hz), 4.73 (d, 1 H, J = 7.3 Hz), 5.80 (s, 1 H), 7.08-7.46 (m, 13 H), 7.86-7.96 (m, 2 H), 11.94 (br d, 1 H, J = 7.1 Hz).

(αR, 5S)-1-Phenyl-3-(N-α-methylbenzyl)amino-5-hydroxy-6,6-dimethyl-2-epten-1-one [(αR, 5S)-3ad]: m.p. 153-155 °C (CH_2Cl_2-hexane); $[\alpha]^{20}_D$ - 627.1 (c = 2.3, $CHCl_3$); IR (nujol) 3450, 1570, 1450, 1315, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (s, 9 H), 1.61 (d, 3 H, J = 6.8 Hz), 2.19 (br s, 1 H), 2.20-2.42 (m, 2 H), 3.39 (dd, 1 H, J = 8.6, 4.3 Hz), 5.03 (quint, 1 H, J = 7.2 Hz), 5.74 (s, 1 H), 7.19-7.47 (m, 8 H), 7.84-7.96 (m, 2 H), 12.09 (br d, 1 H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$) δ 25.5, 26.0, 35.2, 35.7, 53.7, 79.2, 92.5, 126.1, 127.5, 127.7, 128.9, 129.4, 131.1, 140.8, 145.1, 167.5, 186.5. Anal. Calcd. for $C_{23}H_{29}NO_2$: C, 78.60; H, 8.32; N, 3.98. Found: C, 78.77; H, 8.53; N, 3.73.

(αR, 4S, 5S)-1-Phenyl-3-(N-α-methylbenzyl)amino-5-hydroxy-4,6,6-trimethyl-2-epten-1-one [(αR, 4S, 5S)-3bd]: m.p. 133-135 °C (CH_2Cl_2-hexane); $[\alpha]^{20}_D$ -438.7 (c = 2.2, $CHCl_3$); IR (nujol) 3220, 1590, 1520, 1320 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (d, 3 H, J = 6.8 Hz), 1.00 (s, 9 H), 1.64 (d, 3 H, J = 6.7 Hz), 2.11 (br s, 1 H), 2.83 (quint, 1 H, J = 7.2 Hz), 3.28 (br d, 1 H, J = 7.5 Hz), 4.93 (quint, 1 H, J = 6.7 Hz), 5.84 (s, 1 H), 7.20-7.48 (m, 8 H), 7.86-7.96 (m, 2 H), 12.28 (br d, 1 H, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$) δ 19.4, 25.3, 27.4, 36.4, 38.2, 53.8, 83.0, 89.3, 126.1, 127.4, 127.8, 128.7, 129.4, 131.0, 141.0, 145.4, 173.5, 188.8. Anal. Calcd. for $C_{24}H_{31}NO_2$: C, 78.87; H, 8.55; N, 3.83. Found: C, 78.96; H, 8.66; N, 3.96.

(αR, 4S, α'S)-1-Benzoyl-2-(N-α-methylbenzyl)amino-3-(α'-hydroxy)-neopenthylcyclopentene [(αR, 4S, α'S)-3dd]: m.p. 169-171 °C (CH_2Cl_2-hexane); $[\alpha]^{20}_D$ -707.1 (c = 1.6, $CHCl_3$); IR (nujol) 3300, 1590, 1450, 1325, 1075 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9 H), 1.40-1.65 (m, 2 H), 1.60 (d, 3 H, J = 6.70 Hz), 2.28-2.43 (m, 1 H), 2.61-2.82 (m, 2 H), 3.04 (d, 1 H, J = 8.8 Hz), 3.35 (br s, 1 H), 5.06 (dq, 1 H, J = 8.7, 6.7 Hz), 7.14-7.47 (m, 8 H), 7.71-7.81 (m, 2 H), 11.19 (br d, 1 H, J = 8.7 Hz). ^{13}C NMR ($CDCl_3$) δ 25.5, 27.0, 29.9, 31.0, 36.8, 46.2, 55.1, 77.3, 105.6, 125.9, 127.3, 128.3, 128.3, 129.2, 130.1, 142.2, 145.5, 173.3, 187.8. Anal. Calcd. for $C_{25}H_{31}NO_2$: C, 79.54; H, 8.28; N, 3.71. Found: C, 79.66; H, 8.37; N, 3.60.

(αR, 4S)-1-Phenyl-3-(N-α-methylbenzyl)amino-5-hydroxy-4,5-dimethyl-2-hexen-1-one [(αR, 4S)-3be]: oil; $[\alpha]^{20}_D$ - 604.6 (c = 5.4, $CHCl_3$); IR (film) 3360, 1575, 1515, 1275 cm^{-1}; ^{1}H NMR

($CDCl_3$) δ 0.89 (d, 3 H, J = 7.0 Hz), 1.29 (s, 3 H), 1.33 (s, 3 H), 1.62 (d, 3 H, J = 6.9 Hz), 1.93 (br s, 1 H), 2.67 (q, 1 H, J = 7.0 Hz), 4.99 (quint, 1 H, J = 6.9 Hz), 5.83 (s, 1 H), 7.19-7.47 (m, 8 H), 7.86-7.94 (m, 2 H), 12.28 (br d, 1 H, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$) δ 14.9, 25.1, 27.5, 29.4, 44.8, 53.7, 72.8, 90.8, 126.0, 127.4, 127.7, 128.7, 129.4, 131.1, 141.0, 145.5, 171.3, 188.5. Anal. Calcd. for $C_{22}H_{27}NO_2$: C, 78.30; H, 8.06; N, 4.15. Found: C, 78.54; H, 7.82; N, 4.36.

(αR, 4S)-1-Phenyl-3-(N-α-methylbenzyl)amino-4-benzyl-5-hydroxy-5-methyl-2-hexen-1-one [(αR, 4S)-3ce]: m.p. 168-170 °C (CH_2Cl_2-hexane); $[\alpha]^{20}_D$ - 300.1 (c = 1.0, $CHCl_3$); IR (nujol) 3415, 1580, 1445, 1365, 1125 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (s, 3 H), 1.41 (s, 3 H), 1.54 (d, 3 H, J = 6.9 Hz), 2.10 (br s, 1 H), 2.83 (dd, 1 H, J = 13.7, 9.7 Hz), 2.98 (dd, 1 H, J = 13.7, 4.8 Hz), 3.09 (dd, 1 H, J = 9.7, 4.8 Hz), 4.94 (quint, 1 H, J = 7.1 Hz), 5.99 (s, 1 H), 6.64-7.26 (m, 13 H), 7.90-8.00 (m, 2 H), 12.43 (br d, 1 H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$) δ 25.4, 28.1, 29.8, 36.3, 52.5, 53.4, 73.3, 91.2, 126.0, 126.5, 127.4, 127.5, 128.8, 128.8, 129.1, 129.3, 131.1, 139.5, 141.2, 144.6, 168.8, 188.0. Anal. Calcd. for $C_{28}H_{31}NO_2$: C, 81.32; H, 7.56; N, 3.39. Found: C, 81.19; H, 7.44; N, 3.25. **(R,R)-3ce** (minus diastereomer): ^1H NMR ($CDCl_3$) δ 0.94 (s, 3 H), 1.00 (d, 3 H, J = 6.8 Hz), 1.20 (s, 3 H), 1.64 (br s, 1 H), 2.81 (dd, 1 H, J = 11.6, 2.4 Hz), 2.96 (dd, 1 H, J = 12.4, 11.6 Hz), 3.22 (dd, 1 H, J = 12.4, 2.4 Hz), 3.96 (dq, 1 H, J = 7.4, 6.8 Hz), 6.21 (s, 1 H), 7.14-7.48 (m, 13 H), 7.90-8.00 (m, 2 H), 12.43 (br d, 1 H, J = 7.4 Hz).

(αR, 3S)-1-Benzoyl-2-(N-α-methylbenzyl)amino-3-(α-hydroxy-α-methyl)ethylcyclopentene [(αR, 3S)-3de]: m.p. 168-169 °C (CH_2Cl_2-hexane); $[\alpha]^{20}_D$ -662.3 (c = 2.8, $CHCl_3$); IR (nujol) 3250, 1590, 1515, 1325 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (s, 3 H), 1.36 (s, 3 H), 1.54 (d, 3 H, J = 6.9 Hz), 1.58-2.92 (m, 6 H), 5.27 (dq, 1 H, J = 9.9, 6.9 Hz), 7.15-7.45 (m, 8 H), 7.59-7.68 (m, 2 H), 10.89 (br d, 1 H, J = 9.9 Hz). ^{13}C NMR ($CDCl_3$) δ 23.1, 24.7, 29.8, 30.1, 32.2, 50.9, 53.6, 56.5, 111.6, 125.7, 126.8, 127.2, 127.8 128.8, 129.6, 142.1, 144.4, 166.8, 191.1. Anal. Calcd. for $C_{23}H_{27}NO_2$: C, 79.05; H, 7.79; N, 4.01. Found: C, 78.96; H, 7.89; N, 4.19. **(R,R)-3de** (minus diastereomer): ^1H NMR ($CDCl_3$) 1.23 (s, 3 H), 1.38 (s, 3 H), 1.53 (d, 3 H, J = 6.8 Hz), 1.58-2.90 (m, 5 H), 3.20 (d, 1 H, J = 9.0 Hz), 5.26 (dq, 1 H, J = 9.8, 6.8 Hz), 7.15-7.45 (m, 8 H), 7.59-7.68 (m, 2 H), 11.32 (br d, 1 H, J = 9.8 Hz).

(αR, 4S, 5S)-1-Phenyl-3-(N-α-methylbenzyl)amino-5-hydroxy-4,5,6,6-tetramethyl-2-epten-1-one [(αR, 4S, 5S)-3bf]: m.p. 164-165 °C (CH_2Cl_2-hexane); $[\alpha]^{20}_D$ -494.1 (c = 2.1, $CHCl_3$); IR (nujol) 3350, 1590, 1445, 1315 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (d, 3 H, J = 7.0 Hz), 1.02 (s, 9 H), 1.33 (s, 3 H), 1.61 (d, 3 H, J = 6.8 Hz), 1.64 (br s, 1 H), 3.08 (q, 1 H, J = 7.0 Hz), 5.14 (quint, 1 H, J = 6.9 Hz), 5.82 (s, 1 H), 7.23-7.50 (m, 8 H), 7.86-7.96 (m, 2 H), 12.40 (br d, 1 H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$) δ 17.3, 19.5, 24.8, 26.5, 26.8, 40.3, 53.0, 78.0, 91.1, 125.4, 126.9, 127.1, 128.2, 128.8, 130.5, 140.8, 145.3, 172.3, 187.5. Anal. Calcd. for $C_{25}H_{33}NO_2$: C, 79.11; H, 8.76; N, 3.69. Found: C, 79.18; H, 8.91; N, 3.54.

Cyclization of the δ-hydroxyenaminones 3ca,bd,be,ce,bf; synthesis of enantiomerically pure 4-imino-2,3-dihydro-4-pyranones 4ca,bd,be,ce,bf and isomerization to γ-alkyliden enaminones 5ca,bd,be,ce,bf. The enaminone (2 mmol) dissolved in THF (4 mL) was treated with aqueous 3 N HCl (4 mL) and stirred at room temperature for 2 h. The mixture was neutralized with Na_2CO_3 saturated aqueous solution and extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), evaporated under reduced pressure and the residue obtained, submitted to chromatographic purifiation (n-hexane/ethyl acetate, 80:20), furnished the optically pure (Z)-4-imino-2,3-dihydro-4-pyranones (yields 68-82 %). Sometimes a minus diastereoisomer (E)-4-imino-2,3-dihydro-4-pyranones where isolated. NMR experiment

showed that the (Z)- and (E)-4-imino-2,3-dihydro-4-pyranones in $CDCl_3$ solution appear as a mixture of two conformers. The 4-imino-2,3-dihydro-4-pyranones are instable and spontaneously isomerize in the time of 5 day to γ-alkylidenenaminones **5ca,bd,be,ce,bf**.

(α*R*, 2*R*, 3*S*, 4*Z*)-6-Phenyl-4-N(α-methylbenzyl)-imino-3-benzyl-2-methyl-2,3-dihydro-4H-pyran-4-one [(α*R*, 2*R*, 3*S*, 4*Z*)-4ca]: oil; IR (film) 1560, 1320, 1125, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (d, 3 H, J = 6.7 Hz), 1.54 (d, 3 H, J = 6.5 Hz), 2.56 (dd, 1 H, J = 13.6, 5.0 Hz), 2.69 (dd, 1 H, J = 13.6, 10.4 Hz), 2.97 (ddd, 1 H, J = 10.4, 5.0, 1.2 Hz), 4.59 (qd, 1 H, J = 6.7, 1.2 Hz), 4.83 (q, 1 H, J = 6.5 Hz), 6.20 (s, 1 H), 7.10-7.46 (m, 13 H), 7.70-7.82 (m, 2 H). MS m/z (%): 381 (M^+, 23), 366 (79), 290 (96), 186 (54), 105 (100). Anal. Calcd. for $C_{27}H_{27}NO$: C, 85.00; H, 7.13; N, 3.67. Found: C, 85.26; H, 7.31; N, 3.88 %.

(α*R*, 2*R*, 3*S*, 4*E*)-6-Phenyl-4-N(α-methylbenzyl)-imino-3-benzyl-2-methyl-2,3-dihydro-4H-pyran-4-one [(α*R*, 2*R*, 3*S*, 4*E*)-4ca]: oil; IR (film) 1570, 1320, 1120, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (d, 3 H, J = 6.8 Hz), 1.54 (d, 3 H, J = 6.6 Hz), 2.61 (dd, 1 H, J = 14.0, 8.1 Hz), 3.00 (dd, 1 H, J = 14.0, 5.7 Hz), 3.10-3.22 (m, 1 H), 4.28 (q, 1 H, J = 6.6 Hz), 4.49 (qd, 1 H, J = 6.8, 2.0 Hz),, 6.23 (s, 1 H), 6.98-7.46 (m, 13 H), 7.66-7.81 (m, 2 H). MS m/z (%): 381 (M^+, 20), 366 (66), 290 (89), 186 (47), 105 (100). Anal. Calcd. for $C_{27}H_{27}NO$: C, 85.00; H, 7.13; N, 3.67. Found: C, 85.14; H, 7.02; N, 3.83 %.

(α*R*, 2*S*, 3*S*, 4*Z*)-6-Phenyl-4-N(α-methylbenzyl)-imino-3-methyl-2-*terz*-butyl-2,3-dihydro-4H-pyran-4-one [(α*R*, 2*S*, 3*S*, 4*Z*)-4bd]: oil; IR (film) 1600, 1370, 1110, 755, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (s, 9 H), 1.37 (d, 3 H, J = 7.2 Hz), 1.59 (d, 3 H, J = 6.5 Hz), 2.86 (q, 1 H, J = 7.2 Hz), 4.02 (s, 1 H), 4.86 (q, 1 H, J = 6.5 Hz), 6.17 (s, 1 H), 7.13-7.48 (m, 8 H), 7.70-7.83 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 22.4, 24.8, 27.2, 30.9, 38.0, 58.1, 90.8, 91.3, 126.4, 126.8, 127.3, 128.7, 129.0, 130.5, 135.1, 146.4, 160.3, 163.2. MS m/z (%): 347 (M^+, 18), 290 (100), 186 (76), 105 (92). Anal. Calcd. for $C_{24}H_{29}NO$: C, 82.95; H, 8.41; N, 4.03. Found: C, 83.24; H, 8.33; N, 4.28 %.

(α*R*, 2*S*, 3*S*, 4*E*)-6-Phenyl-4-N(α-methylbenzyl)-imino-3-methyl-2-*terz*-butyl-2,3-dihydro-4H-pyran-4-one [(α*R*, 2*S*, 3*S*, 4*E*)-4bd]: oil; IR (film) 1600, 1370, 1110, 755, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 9 H), 1.07 (d, 3 H, J = 7.1 Hz), 1.57 (d, 3 H, J = 6.5 Hz), 3.29 (q, 1 H, J = 7.1 Hz), 3.99 (s, 1 H), 4.84 (q, 1 H, J = 6.5 Hz), 6.09 (s, 1 H), 7.18-7.52 (m, 8 H), 7.71-7.82 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 19.8, 25.2, 27.1, 28.3, 37.2, 58.1, 89.8, 101.2, 125.4, 126.7, 128.4, 128.4, 128.5, 129.5, 134.2, 146.1, 157.6, 163.9 MS m/z (%): 347 (M , 32), 332 (41), 290 (82), 186 (27), 105 (100). Anal. Calcd. for $C_{24}H_{29}NO$: C, 82.95; H, 8.41; N, 4.03. Found: C, 83.18; H, 8.19; N, 4.24 %.

(α*R*, 3*S*, 4*Z*)-6-Phenyl-4-N(α-methylbenzyl)-imino-2,2,3-trimethyl-2,3-dihydro-4H-pyran-4-one [(α*R*, 3*S*, 4*Z*)-4be]: oil; IR (film) 1600, 1560, 1360, 1070, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$) (two conformations in the ratio of 1:1) δ 1.19 and 1.23 (two d, 3 H, J = 7.1 Hz), 1.34, 1.44, 1.45 and 1.46 (four s, 6 H), 1.57 and 1.60 (two d, 3 H, J = 6.6 Hz), 2.45 (q, 1H, J = 7.1), 4.93 (q, 1 H, J = 6.6 Hz), 6.12 and 6.16 (two s, 1 H), 7.20-7.50 (m, 8 H), 7.65-7.78 (m, 2 H). MS m/z (%): 319 (M^+, 9), 304 (100), 200 (57), 105 (75). Anal. Calcd. for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.94; H, 7.65; N, 4.14 %.

(α*R*, 3*S*, 4*E*)-6-Phenyl-4-N(α-methylbenzyl)-imino-2,2,3-trimethyl-2,3-dihydro-4H-pyran-4-one [(α*R*, 3*S*, 4*E*)-4be]: oil; IR (film) 1605, 1555, 1360, 1060, 750, 695 cm^{-1}; ^1H NMR ($CDCl_3$) (two conformations in the ratio of 1:1) δ 0.94 and 1.17 (two d, 3 H, J = 7.0 Hz), 1.01, and 1.50 (two s, 3 H), 1.39 (s, 3 H), 1.52 and 1.63 (two d, 3 H, J = 6.5 Hz), 2.65 and 2.79 (two q, 1H, J = 7.0 Hz), 4.80 (q, 1 H, J = 6.5 Hz), 6.10 and 6.15 (two s, 1 H), 7.16-7.49 (m, 8 H), 7.63-7.77 (m, 2 H). MS m/z (%): 319 (M^+, 12),

304 (100), 200 (73), 105 (86). Anal. Calcd. for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.98; H, 7.61; N, 4.57 %.

(αR, 3S, 4Z)-6-Phenyl-4-N(α-methylbenzyl)-imino-3-benzyl-2,2-dimethyl-2,3-dihydro-4H-pyran-4-one [(αR, 3S, 4Z)-4ce]: oil; IR (film) 1610, 1360, 1055, 760, 690 cm^{-1}; ^1H NMR ($CDCl_3$) (two conformations in the ratio of 1:1) δ 1.22 and 1.55 (two d, 3 H, J = 6.6 Hz), 1.53, 1.56, 1.64 and 1.66 (four s, 6 H), 2.72-3.20 (m, 3 H), 4.78 and 4.89 (two q, 1 H, J = 6.6 Hz), 6.22 and 6.23 (two s, 1 H), 6.95-7.87 (m, 15 H). ^{13}C NMR ($CDCl_3$) (major conformers)δ 24.9, 25.6, 25.8, 34.9, 53.5, 57.9, 81.8, 91.0, 126.4, 126.5, 127.0, 128.5, 128.6, 128.8, 129.0, 130.0, 130.6, 135.4, 140.5, 147.0, 159.1, 162.0. MS m/z (%): 395 (M^+, 20), 380 (91), 304 (86), 276 (52), 200 (57), 105 (100). Anal. Calcd. for $C_{28}H_{29}NO$: C, 85.02; H, 7.39; N, 3.54. Found: C, 85.24; H, 7.53; N, 3.35 %.

(αR, 2S, 3S, 4Z)-6-Phenyl-4-N(α-methylbenzyl)-imino-2,3-dimethyl-2-*terz*-buthyl-2,3-dihydro-4H-pyran-4-one [(αR, 2S, 3S, 4Z)-4bf]: oil; IR (film) 1605, 1365, 1055, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$) (two conformations in the ratio of 2:1) δ 1.08 (s, 9 H), 1.21 (s, 3 H), 1.34 (d, 3 H, J = 7.2 Hz), 1.53 (d, 2 H, J = 6.6 Hz), 1.60 (d, 1 H, J = 6.6 Hz), 2.63 (q, 0.3 H, J = 6.6 Hz), 2.98 (q, 0.7 H, J = 6.6 Hz), 4.89 (q, 1 H, J = 7.2 Hz), 6.09 (s, 0.3 H), 6.18 (s, 0.7 H), 7.17-7.50 (m, 8 H), 7.65-7.75 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 16.7, 19.8, 25.3, 27.3, 40.4, 46.4, 58.4, 88.5, 90.9, 126.3, 126.3, 127.3, 128.7, 128.9, 130.3, 135.7, 147.0, 159.3, 166.6. MS m/z (%): 361 (M^+, 6), 346 (39), 304 (100), 242 (25), 200 (95), 105 (98). Anal. Calcd. for $C_{25}H_{31}NO$: C, 83.06; H, 8.64; N, 3.87. Found: C, 82.81; H, 8.77; N, 3.63 %. **(αR, 2S, 3S, 4E)-4bf** (minus diastereomer as two conformers in the ratio of 2:1) ^1H NMR ($CDCl_3$) (major conformer) δ 0.89 (d, 3 H, J = 7.0 Hz), 1.10 (s, 9 H), 1.58 (d, 3 H, J = 6.5 Hz), 3.27 (q, 1 H, J = 7.0 Hz), 4.89 (q, 1 H, J = 6.5 Hz), 6.10 (s, 1 H), 7.20-7.80 (m, 10 H).

(R)-1-Phenyl-3-(N-α-methylbenzyl)amino-4-benzyl-2,4-hexadien-1-one [(R)-5ca]: oil; IR (film) 3350, 1550, 1315, 1125, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39 (d, 3 H, J = 6.7 Hz), 1.84 (d, 3 H, J = 7.4 Hz), 3.42 (d, 1 H, J = 14.7 Hz), 3.73 (d, 1 H, J = 14.7 Hz), 4.56 (dq, 1 H, J = 9.2, 6.7 Hz), 5.55 (s, 1 H), 5.58 (q, 1 H, J = 7.4 Hz), 7.12-7.48 (m, 13 H), 7.76-7.87 (m, 2 H), 11.75 (br d, 1 H, J = 9.2 Hz). MS m/z (%): 381 (M^+, 10), 366 (60), 290 (100), 262 (24), 186 (31), 105 (91). Anal. Calcd. for $C_{27}H_{27}NO$: C, 85.00; H, 7.13; N, 3.67. Found: C, 84.76; H, 6.87; N, 3.45.

(R)-1,5-Diphenyl-3-(N-α-methylbenzyl)amino-2,4-pentadien-1-one [(R)-5ac]: oil; IR (film) 3350, 1550, 1320, 740, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67 (d, 3H, J = 6.9 Hz), 4.88 (quint, 1H, J = 7.0 Hz), 6.13 (s, 1 H), 6.76 (d, 1 H, J = 16.0 Hz), 7.22 (d, 1 H, J = 16.0 Hz), 7.28-7.52 (m, 13 H), 7.97-8.04 (m, 2 H), 11.86 (br d, 1 H, J = 7.1 Hz). MS m/z (%): 353 (M^+, 33), 262 (31), 248 (76), 144 (52), 105 (100). Anal. Calcd. for $C_{25}H_{23}NO$: C, 84.95; H, 6.56; N, 3.96. Found: C, 84.73; H, 6.69; N, 3.73.

(R)-1-Phenyl-3-(N-α-methylbenzyl)amino-4,6,6-trimethyl-2,4-heptadien-1-one [(R)-5bd]: oil; IR (film) 3350, 1550, 1310, 1015, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (s, 9 H), 1.59 (d, 3 H, J = 6.8 Hz), 1.85 (d, 3 H, J = 1.5 Hz), 4.73 (dq, 1 H, J = 9.1, 6.8 Hz), 5.37 (q, 1 H, J = 1.5 Hz), 5.63 (s, 1 H), 7.17-7.45 (m, 8 H), 7.88-7.94 (m, 2 H), 11.87 (br d, 1 H, J = 9.1 Hz). Anal. Calcd. for $C_{24}H_{29}NO$: C, 85.00; H, 7.13; N, 3.67. Found: C, 84.86; H, 7.27; N, 3.44.

(R)-1-Phenyl-3-(N-α-methylbenzyl)amino-4,5-dimethyl-2,4-hexadien-1-one [(R)-5be]: oil; IR (film) 3400, 1550, 1315, 1125, 750, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10-2.00 (m, 12 H), 4.55 and 4.60 (two dq, 1 H, J = 8.9, 6.9 Hz), 5.57 and 5.58 (two s, 1 H), 7.15-7.45 (m, 8 H), 7.81-7.96 (m, 2 H), 11.72-11.96 (m, 1 H). Anal. Calcd. for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.88; H, 7.96; N, 4.19 %.

(*R*)-1-Phenyl-3-(N-α-methylbenzyl)amino-4-benzyl-5-methyl-2,4-hexadien-1-one [(*R*)-5ce]: oil; IR (film) 3550, 1550, 1315, 1125, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13, 1.85, 1.89 and 1.96 (four s, 6 H), 1.26 and 1.61 (two d, 3 H, J = 6.8 Hz), 3.83-3.54 (m, 2 H), 4.38 and 4.67 (two dq, 1 H, J = 9.4, 6.8 Hz), 5.17 and 5.44 (two s, 1 H), 6.98-7.82 (m, 15 H), 11.98-11.80 (m, 1 H). Anal. Calcd. for $C_{28}H_{29}NO$: C, 85.02; H, 7.39; N, 3.54. Found: C, 85.24; H, 7.53; N, 3.37.

(*R*)-1-Phenyl-3-(N-α-methylbenzyl)amino-4,5,6,6-tetramethyl-2,4-heptadien-1-one [(*R*)-5bf]: oil; IR (film) 3550, 1550, 1315, 1125, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08-2.10 (m, 9 H), 1.16 and 1.23 (two s, 9 H), 4.59 and 4.61 (two dq, 1 H, J = 9.0, 6.7 Hz), 5.53 and 5.54 (two s, 1 H), 7.17-7.46 (m, 8 H), 7.84-7.96 (m, 2 H), 11.90 (br d, 1 H, J = 9.0 Hz). Anal. Calcd. for $C_{25}H_{31}NO$: C, 83.06; H, 8.64; N, 3.87. Found: C, 82.81; H, 8.82; N, 3.59.

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