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HIGHLY REGIO- AND syn-DIASTEREOSELECTIVE SYNTHESIS OF 4-HYDROXY-1,2-ALKADIENYLCARBAMATES FROM α-TITANATED 2-ALKYNYLCARBAMATES AND ALDEHYDES[1,2]

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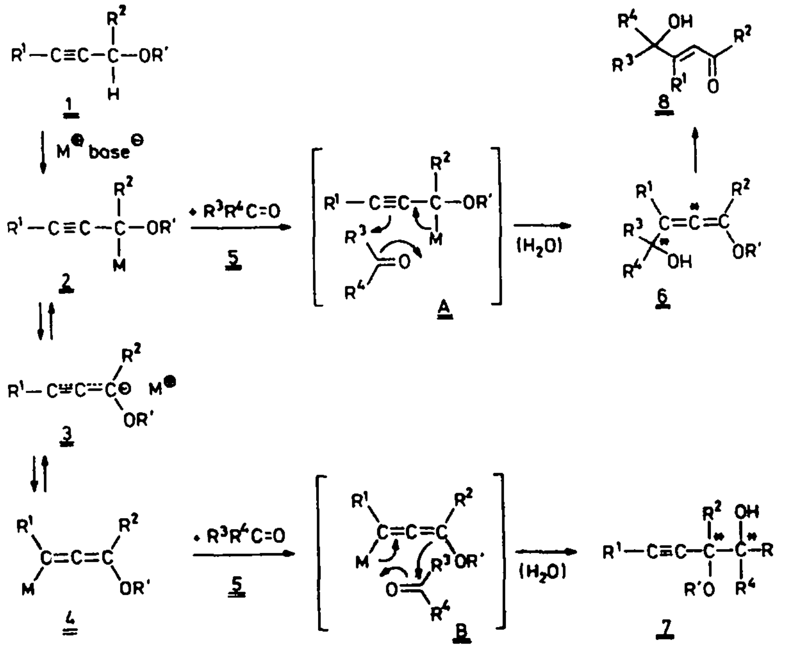
Abstract. N,N-Diisopropyl 2-alkynyl carbamates **9** are deprotonated by n-butyllithium to form lithium compounds **10**. After exchange of the cation, titanium reagents **13** add highly diastereoselective to aldehydes with formation of the title compounds **14**. In contrast to metallated 2-alkynyl ethers, the reagents **10** and **13** exhibit high γ-regioselectivity in carbonyl addition reactions, due to the chelating carbamoyl group. The syn-configuration of **14** was deduced from the crystal structure of the urethane derivative **21**.

Functionalized allenes demand growing interest in organic synthesis[3]. Among them, 1,4-bis-oxysubstituted 1,2-alkadienes of type **6** are of importance because they represent masked 4-hydroxy-2-alkenals[2a] (**8**, R^2 = H) or -alkenones (**8**, R^2 = alkyl, aryl) and also offer a versatile synthetic approach to furans, 2,5-dihydrofurans, and related compounds[3b]. For the synthesis of **6**, coupling of a 2-alkynylmetal **2** with a carbonyl compound **5** by formation of the C-3-C-4 bond is the most forwarding strategy.



R^1 - R^4 = H, alkyl or aryl; R' = alkyl, THP.

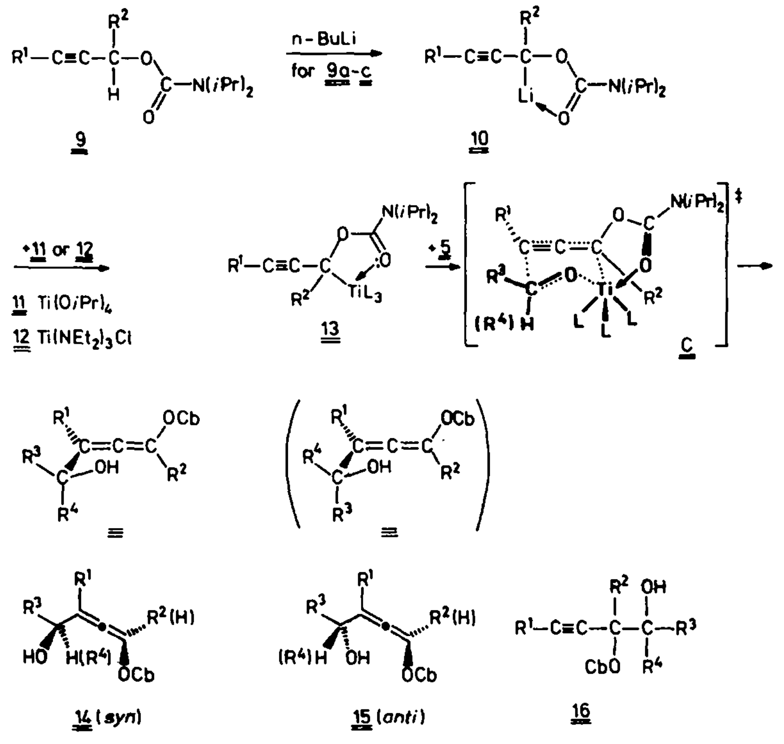
Despite many efforts[4], the main challenge remained unsolved, as there are: 1. γ-Regioselectivity[4]. Propargylmetals **2** and allenylmetals **4**, obtained by deprotonation of propargylic ethers[5,4] **1** are in rapid equilibrium (for M = K, Na or Li) via the mesomeric ion pair **3**, giving rise to isomeric mixtures of **6** and **7**. In principle, both tautomers **2** or **4** can be kinetically stabilized by introduction of more covalently bound "cations" M^+, e.g. R_2B[6], or X_3Ti[7], but now the problem of regioselectivity is shifted to the metal exchange step. Generally, and also true for M^+ = MgX or ZnX[4,7], enhanced α-selectivity is observed under these conditions yielding predominantly 3-alkynols **7** in kinetically controlled addition reactions. There is some evidence that allenylmetals **4** are favored[7]; they add carbonyl compounds in a six-membered pericyclic process[4,7] (transition state **B**), causing acetylene allene rearrangement, which is seen in product **7**. For the predominant formation of 2-alkynylmetals **2**, which are expected to form allenes **6** via transition state **A**, apparently, no reliable method was known.
2. Diastereoselectivity. Allenes of type **6** ($R^2 \neq R^3$) exist in two diastereomers; usually, selective formation of only one is desired. Although high non-induced diastereoselectivity[8] nowadays is common in allylmetal addition reactions[9,10], to our knowledge, no example was reported for 2-alkynylmetals which accomplishes the diastereoselective addition of a pro-axial- onto a pro-central-chiral unit[11].

We expected that propargylmetal tautomers **2**, needed for γ-regioselective formation of 4-hydroxy-1,2-alkadienes **6**, should be stabilized at the cost of **4** by a chelating ligand at the 1-oxygen atom. According to H. Yamamoto[7], the tetrahydropyranyl group (THP) does not suffice. In our recent work, the N,N-diisopropylcarbamoyloxy group and its powerful complexing ability towards cations had proven to be the key in the achievement of the first general method for homoaldol additions[10,12], exhibiting high regio- and stereoselectivities, when α-metallated 2-alkenyl carbamates are utilized for homoenolate reagents. Hence, we investigated the scope of metallated 2-alkynyl carbamates[1,2] **10** and **13**.

Addition of metallated 2-alkynyl carbamates to carbonyl compounds. The alkynyl carbamates **9a**[12], **d**, and **e** were prepared by acylation of the appropriate 2-alkynols with N,N-diisopropylcarbamoyl chloride[12,13]. **9b** and **c** were obtained by silylation or methylation of the propargyl carbamates **9d** or **9e** via the acetylenic anions (subsequent addition of n-butyllithium and chlorotrimethylsilane, 89%, or methyl iodide, 77%).

The deprotonation of **9a** or **b** proceeds smoothly within 30 min by adding a slight excess of n-butyllithium to the diethyl ether solution below -70 °C, affording the lithium derivatives **10a** or **10b**. For complete metallation of α-alkylated alkynyl carbamates, e.g. **9c**, activation by N,N,N',N'-tetramethyl ethylene diamine (TMEDA) and prolonged reaction times (1 h) are essential. On addition of acetaldehyde (**5a**), practically without any regio- and diastereoselectivity, a racemic mixture of the γ-adducts **14aa** (syn)[14,15] and **15aa** (anti)[14,15] together with two diastereomeric α-adducts **16aa** are formed (Table 1). Better γ-selectivity is observed if less reactive carbonyl compounds like 2-methylbutanal (**5b**), γ : α = 86 : 14, or acetone (**5g**; 95 : 5) are used. Both selectivities are dramatically enhanced to essentially complete formation[16] of **14** if lithium is exchanged by adding tetra(isopropoxy)titanium[17] (**11**) to the solution of **10**, forming tentative intermediate **13**, prior to aldehyde addition. In few cases where the γ-regioselectivity is still incomplete, the use of the stronger oxophilic chloro-tris(diethylamino)titanium[17] **12** results in further improvement. Reagents **10** or **13** also add to ketones (Table 1).

From the predominant formation of syn-adducts[16] **14**, we conclude that transition state **C** is passed. Evidently, both prochiral units approach in this particu-



9	R^1	R^2
a	CH_3	H
b	$SiMe_3$	H
c	CH_3	n-C_3H_7
d	H	H
e	H	nC_3H_7

5	R^3	R^4
a	CH_3	H
b	$(CH_3)_2CH$	H
c	$(CH_3)_3C$	H
d	C_6H_5	H
e	E-PhCH=CH_2	H
f	Ph(CH_3)CH	H
g	CH_3	CH_3
h	-$(CH_2)_4$-	

OCb = O-C(=O)N(iPr)$_2$

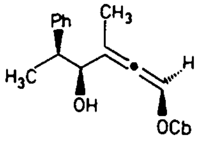
Table 1. Reaction of 2-alkynyl carbamates 9 with aldehydes and ketones 5

Compounds 9 and 5	Reagent (Procedure)	Products	Yield [%][a]	R^1	R^2	R^3	R^4	(14+15):16 γ:α[b]	14:15[b] syn:anti	Config. of 14
9a,5a	**10a**(A)[c]	**14,15,16aa**	90	CH_3	H	CH_3	H	65:35	50:50	aR*,4S*
	13a(B)[d]	**14aa**	89					>95:<5	>95:<5	
9a,5b	**10b**(A)	**14,15,16ab**	87	CH_3	H	$(CH_3)_2CH$	H	86:14	57:43	aR*,4S*
	13a(B)	**14ab**	87					>95:<5	>95:<5	
9a,5c	**13a**(B)	**14ac**	59	CH_3	H	$(CH_3)_3C$	H	>95:<5	>95:<5	aR*,4R*
9a,5d	**13a**(B)	**14,15,16ad**	86	CH_3	H	C_6H_5	H	71:29	80:20	aR*,4S*
	13a(C)[e]	**14,15ad**	97					>95:<5	85:15	
9a,5e	**13a**(C)	**14,15ae**	65	CH_3	H	E-PhCH=CH	H	>95:<5	80:20	aR*,4S*
9a,5f[f]	**13a**(B)	**14af**[g]	57	CH_3	H	Ph(CH_3)CH	H	97:3	>95:<5[g]	aR*,4S*
9a,5g	**10a**(A)	**14ag**	76	CH_3	H	CH_3	CH_3	>95:<5	-	
	13a(B)		76					>95:<5	-	
9a,5h	**13a**(B)	**14,16ah**	63	CH_3	H	-$(CH_2)_4$-		82:18	-	
	13a(C)	**14ah**	47					>95:<5	-	
9b,5a	**13b**(B)	**14ba**	89	$SiMe_3$	H	CH_3	H	>95:<5	>95:<5	aR*,4R*
9c,5a	**13c**(C)	**14,16ca**	83	CH_3	H	CH_3	n-C_3H_7	>95:5	82:18	aR*,4S*

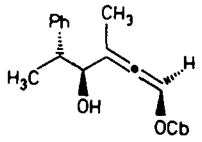
a) Combined yield after LC purification. b) Determined by ^1H NMR or ^{13}C NMR. c) Procedure A, counter ion Li. d) Procedure B, metal exchange with Ti(OiPr)$_4$ (**11**). e) Procedure C, metal exchange with ClTi(NEt$_2$)$_3$ (**12**). f) Racemic **5f** was used. g) Two syn-diastereomers, (5S*)- and (5R*)-**14af**, 82:18, were isolated.

lar arrangement, which minimizes repulsive interactions between the alkyl residue R^3 and the ligands at titanium.

From addition of the 2-butynyl titanium reagent **13a** to racemic 2-phenylpropanal (**5f**), two separable diastereomeric syn-adducts **14af** in a ratio 82 : 18 were isolated. We assume that these are a result of the attack of **13a** to both diastereotopic faces of the chiral aldehyde **5f**, forming the product of steric approach control (5S*)-**14af** in excess over (5R*)-**14af**. A very similar ratio of induced diastereoselectivity[8] is observed in the reaction of **5f** with titanated 2-(E)-butenyl carbamates[23,10], in which the relative configurations of adducts had been rigorously established by chemical transformation to known compounds.


(5S*)-14af

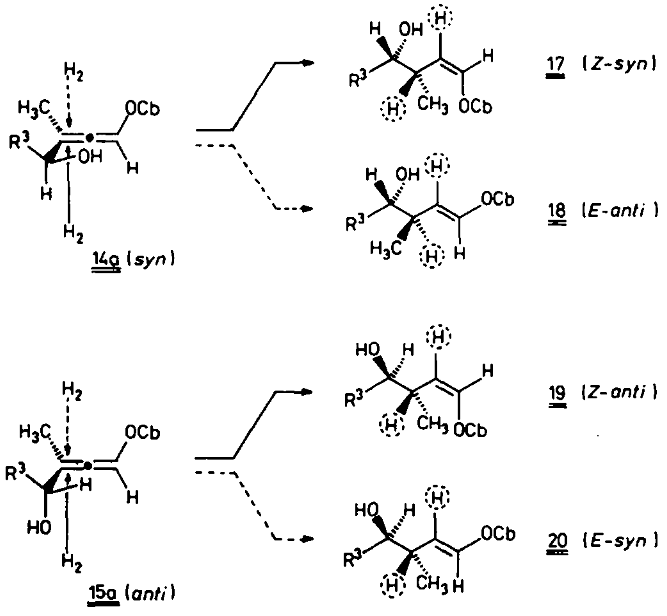
+


(5R*)-14af

Structure elucidation. Allenes **14** and **15** are recognized in their NMR spectra by the downfield absorption of C-2 (δ = 188-190 ppm), and (for R^2 = H) of H-1 (7.3-7.4 ppm) as well as by an IR band around 1975 cm^{-1}. The isomeric alkynes **16** show δ = 5.3-5.5 ppm for the propargylic proton and a triple bond absorption between 2200-2250 cm^{-1} in IR. In TLC analysis, alkyne **16** usually is the more polar isomer, which is also stained more slowly by iodine-vapour than allenes **14** and **15**.

We were not able to determine the relative configurations of γ-adducts **14** or **15** spectroscopically, because their ^1H NMR and ^{13}C NMR spectra are very similar without significant differences in chemical shifts or coupling constants.

Since catalytic hydrogenations of some allenes are reported to proceed cis-stereospecifically[18], partial hydrogenation of the central double bond of **14** (syn) is expected to deliver the 4-hydroxy-enol carbamates **17** (Z-syn) and **18** (E-anti), whereas from **15** (anti) the alkenes **19** (Z-anti) and **20** (E-syn) should derive; these four diastereomers are well known from our studies on homoaldol reactions[12,10].



14,15 aa $R^3 = CH_3$ 17-20 a $R^3 = CH_3$

ab $R^3 = CH(CH_3)_2$ b $R^3 = CH(CH_3)_2$

The acetaldehyde adduct **14aa**, obtained by the titanium-mediated procedure, yielded on treatment with H_2/P2 nickel/ethylene diamine[19] both the (Z)-alkenes **17a** and **19a** (46%) in a ratio 90 : 10 (GC); with H_2/ Lindlar catalyst the yield was 36% (81 : 19). **14ab** gave a similar result (P2 Ni, 41%, **17b** : **19b** = 73 : 27). Together with the reasonable assumption that the minor isomer **19** originates from a rapid[20] metal-catalyzed isomerization of the (E)-double bond in primarily formed **18** to give the more stable (Z)-enol carbamate **19**, these experiments can be taken as arguments for the syn-configuration of **14**. The anti-diastereomers **15** are expected to deliver **19** in excess by cis-addition of H_2 from the less shielded face.

Final evidence for the syn-configuration[21] was obtained from an X-ray crystal structure analysis[22,23] of the p-chlorophenyl urethane **21**, prepared from **14aa** and p-chlorophenyl isocyanate (Figure 1).

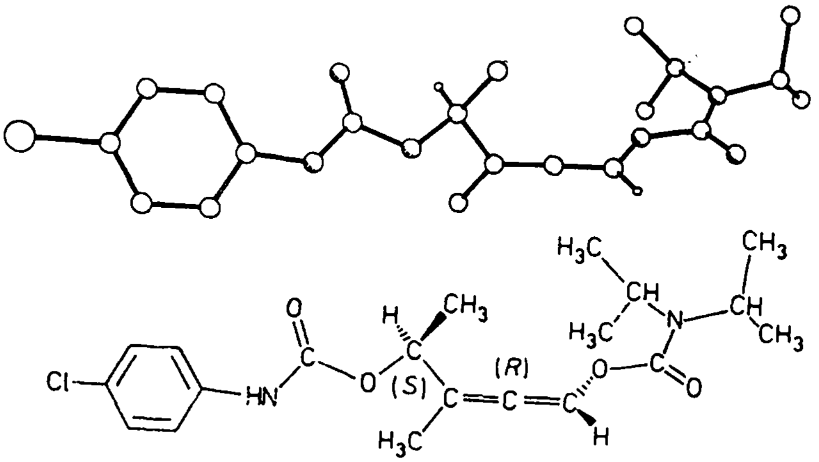
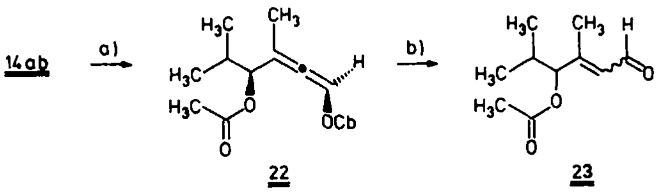


Figure 1. The conformation of **21** in the crystal[22]. H atoms (except for those at C-1 and C-4) are omitted.

Synthetic use of allenes **14**. The allenes **14** (or **15**), R^2 = H are masked 4-hydroxy-2-alkenals[3b]. For demonstration, **14ab** was acetylated to give the acetate **22**, which was treated with methanol and methanesulfonic acid to yield after hydrolysis the unstable enal **23** (54%, E : Z = 80 : 20).



a) Ac_2O, Et_3N, 4-(N,N-dimethylamino)pyridine, CH_2Cl_2; 72%. b) CH_3OH, CH_3SO_3H (1.0 equiv.), $Hg(OAc)_2$, -10 - 20 °C; H_2O; 54%.

In hydrolysis, the benefit of homogenous configuration in diastereomerically pure allenes **14** is wasted. Studies for its utilization in the synthesis of highly substituted 1,3-alkadienes by Claisen rearrangement, whose stereochemical course has been exploited[2b], are in progress.[24] Furthermore, stereospecific 1,4-eliminations lead to interesting, very reactive alk-3-en-1-ynyl carbamates[24].

EXPERIMENTAL

All organometallic reactions were performed under N_2 or Ar with exclusion of air and moisture. Diethyl ether and 1,2-dimethoxyethane were distilled over $LiAlH_4$, TMEDA and pyridine over CaH_2, prior to use. Tetra(isopropoxy)titanium was used after distillation under Ar. LC separations (>1 g) were carried out with "MN-Kieselgel 60", 0.05-0.2 mm, (Macherey-Nagel GmbH & Co KG, Düren), or (<1 g) at 1-3 bar on "Silica Woelm 32-63", 0.032-0.063 mm, (Woelm Pharma GmbH & Co, Eschwege).

N,N-Diisopropyl 2-alkynyl carbamates **9** from 2-alkynols; general procedure
The 2-alkynol (0.105 mmol) in dry pyridine (0.15 mmol, 12 g) and N,N-diisopropylcarbamoyl chloride[12,13] (0.100 mmol) were stirred at 90-100 °C for 12 h. The cool reaction mixture was poured to ice (50 g), 36% aq. HCl (20 mL), and diethyl ether (50 mL); the aq. soln. extracted twice with ether (each 30 mL). The etheral soln. was washed with sat. aq. $NaHCO_3$ (20 mL) and brine. After drying over $MgSO_4$, the solvent was evaporated in vacuum and the residue distilled or recrystallized.

N,N-Diisopropyl 2-butynyl carbamate (**9a**). cf. ref.[12]

N,N-Diisopropyl 2-propynyl carbamate (**9d**). Yield 16.4 g (89%), bp 118 °C/15 torr, mp 38-40 °C (from diethyl ether). - IR (KBr): 2130 (C≡C), 1695 cm^{-1} (C=O). - ^1H NMR ($CDCl_3$): δ = 1.24 (d) and 3.9 (m) (NiPr); 2.42 (t, $J_{3,1}$ = 2.5 Hz, 3-H); 4.67 ppm (d, 1-H). - $C_{10}H_{17}NO_2$ (183.25), calc. C 65.54 H 9.35, found C 65.50 H 9.24.

N,N-Diisopropyl 1-propyl-2-propynyl carbamate (**9e**). Yield 13.9 g (62%), bp 105 °C/8 torr. - IR (neat): 2110 (C≡C), 1685 cm^{-1} (C=O). - ^1H NMR ($CDCl_3$): δ = 0.95 (t) and 1.65 (m) (CH_2CH_3); 1.20 (d) and 3.35 (m) (NiPr); 2.37 (d, $J_{3,1}$ = 2 Hz, 3-H); 5.32 ppm (td, $J_{1,1'}$ = 6 Hz, 1-H).

N,N-Diisopropyl 3-(trimethylsilyl)-2-propynyl carbamate (**9b**). To a soln. of **9d** (3.7 g, 20 mmol) and TMEDA (2.3 g, 20 mmol) in diethyl ether (40 mL) at -10 °C n-butyllithium in hexane (13.8 mL 1.6N, 22 mmol) was dropped; the reaction mixture was cooled to -70 °C and trimethylchlorosilane (2.4 g, 22 mmol) was added. After warming to rt, usual aq. work-up, followed by distillation afforded 4.4 g (89%) **9b**, bp 107 °C/10 torr. - IR (neat): 2185 (C≡C), 1700 (C=O), 1250 and 845 cm^{-1} (Si-CH_3). - ^1H NMR ($CDCl_3$): δ = 0.2 (s, Si-CH_3); 1.25 (d) and 3.9 (m) (NiPr); 4.74 ppm (s, 1-H_2).

N,N-Diisopropyl 1-propyl-2-butynyl carbamate (**9c**). To a soln. of **9e** (19.6 g, 20.0 mmol) in 1,2-dimethoxyethane (40 mL) at -70 °C n-butyllithium in hexane (13.8 mL 1.6N, 22 mmol) was slowly added, the reaction mixture was stirred for 30 min and methyl iodide (5.7 g, 40 mmol) slowly added. After 30 min stirring between -70 to -78 °C, the reaction mixture was allowed to warm to rt, and aq. work-up was accomplished as usual. LC (diethyl ether/petroleum ether, 1 : 10) yielded 3.7 g (77%) **9c**, oil, R_F(1:1) = 0.55. - IR (neat): 2240 (C≡C), 1690 cm^{-1} (C=O). - ^1H NMR ($CDCl_3$): δ = 0.93 (t) and 1.5 (m) (CH_2CH_3); 1.23 (d) and 3.95 (m) (NiPr); 1.88 (d, $J_{1,4}$ = 2 Hz); 5.38 ppm (tq, $J_{1,1'}$ = 7 Hz, 1-H). - $C_{14}H_{25}NO_2$ (239.36), calc. C 70.25 H 10.53, found C 70.42 H 10.59.

4-Hydroxy-1,2-alkadienyl carbamates **14** and **15**; general procedure. To carbamate **9** (10.0 mmol) in diethyl ether (30 mL) at -78 to -70 °C n-butyllithium in hexane (6.9 mL 1.6N, 11 mmol) were introduced with a dry-ice cooled syringe and the yellow slurry of **10** was stirred at this temp. for 15 min.
Procedure A: Aldehyde or ketone **5** (11 - 20 mmol) was introduced slowly with a cooled syringe. Stirring at this temp. was continued for 1.5-15 h, and work-up was performed as described below.
Procedures B and C. Tetra(isopropoxy)titanium (**11**) (11 mmol; **B**) or chloro-tris-(diethylamino)titanium (**12**) in hexane (11 mmol; **C**) was added to the reaction mixture below -65 °C and stirring was continued for 15 min. **5** (11-20 mmol) was added and the mixture stirred for 1.5-15 h at -70 to -78 °C. For work-up, the reaction mixture was allowed to warm to 0 °C and poured to a mixture of ice (50 g), 2N aq. HCl (50 mL; 60 mL for **B**/TMEDA), and ether (100 mL). The aq. soln. was extracted twice with ether (each 50 mL), the combined etheral solns. were washed with water (50 mL), aq. sat. $NaHCO_3$ (50 mL), followed by aq. sat. KCl, and were dried over $MgSO_4$. After evaporation of the solvent in vacuum, the residue was purified by LC (silica gel; diethyl ether/petroleum ether).

(aR*,4S*)- and (aR*,4R*)-N,N-Diisopropyl 4-hydroxy-3-methyl-1,2-pentadienyl carbamate (**14aa** and **15aa**). **9a**, **11** and acetaldehyde (**5a**) (0.88 g, 20 mmol), **B**, 1.5 h, diethyl ether/petroleum ether (1:5), afforded 2.15 g (89%), **14aa**, R_F(1:1) = 0.24, mp 48 °C. - IR (neat): 3400 (br., OH), 1975 (C=C=C), 1690 cm^{-1} (C=O). - ^{1}H NMR (CDCl$_3$): δ = 1.25 (d) and 3.95 (sept)(NiPr); 1.36 (d, $J_{5,4}$ = 6 Hz, 5-H$_3$); 1.88 (d, $J_{3',1}$ = 2 Hz, 3-CH$_3$); 3.37 (m, OH); 4.26 (dq, $J_{4,1}$ = 2 Hz, 4-H); 7.34 ppm (dq, 1-H). - ^{13}C NMR (CDCl$_3$): δ = 16.57 (C-5); 20.87 and 46.30 (NiPr); 21.87 (3-CH$_3$); 68.73 (C-4); 112.50 (C-1); 118.98 (C-3); 153.10 (C=O); 188.43 ppm (C-2). $C_{13}H_{23}NO_3$ (241.33), calc. C 64.70 H 9.61, found C 64.91 H 9.54.

Procedure B, 1.5 h, afforded 2.16 (90%) of a mixture, consisting of **14aa** and **15aa** (65%), 50:50), R_F(1:1) = 0.24; and of N,N-diisopropyl 1-(1-hydroxyethyl)-2-butynyl carbamate (**16aa**), 2 diastereomers, R_F(1:1) = 0.22, 35% (^{1}H NMR).

15aa, from the mixture; ^{1}H NMR (CDCl$_3$): δ = 7.23 ppm (dq, $J_{1,4}$ = $J_{1,3'}$ = 2 Hz, 1-H); ^{13}C NMR (CDCl$_3$): δ = 16.25 (C-5); 21.68 (3-CH$_3$); 68.81 (C-4), 153.19 (C=O), 188.65 ppm (C-2).

16aa; IR (neat): 2220 cm^{-1} (C≡C); ^{1}H NMR (CDCl$_3$): δ = 3.49 (m, 1'-H); 5.33 ppm (m, 1-H).

(aR*,4S*)- and (aR*,4R*)-N,N-Diisopropyl 4-hydroxy-3,5-dimethyl-1,2-hexadienylcarbamate (**14ab** and **15ab**). **9a**, **11** (3.13 g) and 2-methylpropanal (**5b**) (0.95 g, 13 mmol), **B**, 7 h, diethyl ether/petroleum ether (1:5), afforded 2.34 g (87%) **14ab**, R_F(1:1) = 0.22, oil. - IR (neat): 3400 (br., OH), 1975 (C=C=C), 1690 cm^{-1} (C=O). - ^{1}H NMR (CDCl$_3$): δ = 0.92 and 1.02 (each d, $J_{5,6}$ = $J_{5,5'}$ = 7 Hz, 6-H$_3$ and 5-CH$_3$); 1.25 (d) and 3.6 - 4.2 (m) (NiPr and 5-H); 1.82 (d, $J_{3',1}$ = 2 Hz, 3-CH$_3$); 2.4 (m, OH); 3.84 (dd, $J_{4,5}$ = 6 Hz, $J_{4,1}$ = 2 Hz, 4-H); 7.36 ppm (dq, 1-H). - ^{13}C NMR (CDCl$_3$): δ = 16.30 and 16.72 (C-6 and 6-CH$_3$); 19.62 (C-5); 20.95 and 46.27 (NiPr); 31.34 (3-CH$_3$);77.73 (C-4); 111.82 (C-1); 117.09 (C-3); 153.23 (C=O); 189.33 ppm (C-2). - $C_{15}H_{27}NO_3$ (269.39), calc. C 66.88 H 10.10, found C 67.00 H 10.54.

A, 1 h, afforded 2.34 (87%) of a mixture, consisting of **14ab** and **15ab** (86%, 57:43), R_F(1:1) = 0.22, and of N,N-diisopropyl 1-(1-hydroxy-2-methylpropyl)-2-butynyl carbamate (**16ab**), 2 diastereomers, R_F(1:1) = 0.20, 14% (^{1}H NMR).

15ab, from the mixture; ^{1}H NMR (CDCl$_3$): δ = 7.22 ppm (dq, $J_{1,4}$ = $J_{1,3'}$ = 2 Hz, 1-H); ^{13}C NMR (CDCl$_3$): δ = 15.81 and 17.16 (C-6 and 5-CH$_3$); 19.53 (C-5); 31.04 (3-CH$_3$); 77.73 (C-4), 111.84 (C-1), 116.68 (C-3); 153.25 (C=O), 189.97 ppm (C-2).

16ab; IR (neat): 2220 cm^{-1} (C≡C); ^{1}H NMR (CDCl$_3$): δ = 5.48 ppm (m, 1-H).

(aR*,4R*)-N,N-Diisopropyl 4-hydroxy-3,5,5-trimethyl-1,2-hexadienyl carbamate (**14ac**). **9a**, **11** (3.13 g) and 2,2-dimethylpropanal (**5c**) (0.96 g, 11 mmol), **B**", 7 h, diethyl ether/petroleum ether (1:10), afforded 1.68 g (59%) **14ac**, R_F(1:1) = 0.39, mp 59 °C.- IR (KBr): 3400 (br., OH), 1973 (C=C=C), 1700 cm^{-1} (C=O). - ^{1}H NMR (CDCl$_3$): δ = 1.00 (s, 2x 6-H$_3$ and 5-CH$_3$); 1.26 (d) and 3.6 - 4.2 (m) (NiPr); 1.93 (d, $J_{3',1}$ = 2 Hz, 3-CH$_3$); 2.1 (m, OH); 3.73 (br. "s",4-H); 7.48 ppm (dq, $J_{1,4}$ = 2Hz, 1-H). - $C_{16}H_{29}NO_3$ (283.41), calc. C 67.81 H 10.31, found C 67.94 H 10.23.

(aR*,4S*)- and (aR*,4R*)-N,N-Diisopropyl 4-hydroxy-3-methyl-4-phenyl-1,2-pentadienyl carbamate (**14ad** and **15ad**). **9a** (0.592 g, 3.00 mmol), **12** (3.30 mmol), 27% in hexane, **C**) and benzaldehyde (**5d**) (0.318 g, 3.30 mmol), 3 h, diethyl ether/ petroleum ether (1:6), afforded 0.89 g (97%) of a mixture consisting of **14ad** and **15ad** (85 : 15, ^{1}H NMR), R_F(1:1) = 0.32, oil. - IR (neat): 3400 (br., OH), 1975 (C=C=C), 1680 cm^{-1} (C=O). - ^{1}H NMR (CDCl$_3$, from the mixture); **14ad**: δ = 1.23 (d) and 3.90 (sept) (NiPr); 1.65 (d, $J_{3',1}$ = 2 Hz, 3-CH$_3$); 3.15 (m, OH); 5.05 (m, 4-H); 7.38 ppm (m, 1-H and C$_6$H$_5$). - ^{13}C NMR (CDCl$_3$), **14ad**: δ = 16.21 (3-CH$_3$); 20.90 and 46.41 (NiPr); 75.37 (C-4); 113.18 (C-1); 117.82 (C-3); 126.7-128.5, 141.53 (phenyl-C); 153.14 (C=O); 189.41 ppm (C-2); **15ad**: 16.59 (3-CH$_3$); 113.85 (C-1); 141.67 (1 phenyl H); 188.91 ppm (C-2).

$C_{18}H_{25}NO_3$ (303.40), calc. C 71.26 H 8.31, found C 71.40 H 8.51.

B , 5 h, with **9a** (5.00 mmol) and **11** (5.50 mmol) afforded 1.28 g (86%) of a mixture, consisting of **14ad** and **15ad** (71%, 80 : 20; ^{13}C NMR), R_F(1:1) = 0.32; and of N,N-diisopropyl 1-(1-hydroxybenzyl)-2-butynyl carbamate (**16ad**),2 diastereomers (X:Y = 60 : 40), R_F(1:1) = 0.28, 29%. - IR (neat): 2240 cm^{-1} (C≡C). - ^{1}H NMR (CDCl$_3$): δ = 1.83 (X), 1.75 (Y) (d, $J_{4,1}$ = 2 Hz, 4-H$_3$); 4.95 (m, X-1'-H); 5.52 ppm (m, X-1-H). - ^{13}C NMR (CDCl$_3$): δ = 69.97 (X), 69.33 (Y) (C-3); 74.15 (X), 74.70 (Y) (C-2); 139.56 (X), 139.67 ppm (Y) (1 phenyl C).

(E)-(aR*,4S*)- and (E)-(aR*,4R*)-N,N-Diisopropyl 4-hydroxy-3-methyl-6-phenyl-1,2,5-hexatrienyl carbamate (**14ae** and **15ae**). **9a** (0.592 g, 3.00 mmol), **12** (3.3 mmol, 27% in hexane, **C**) and (E)-3-phenyl-2-propenal (**5e**) (0.35 g, 3.30 mmol), 15 h, diethyl ether/petroleum ether (1:6), afforded 0.65 g (65%) of a mixture consisting of **14ae** and **15ae** (80 : 20, ^{13}C NMR), R_F(1:1) = 0.30, oil. - IR (neat): 3400 (br., OH), 1975 (C=C=C), 1690 (C=O), 1595 and 1570 cm^{-1} (C=C). - ^{1}H NMR (CDCl$_3$, from the mixture); **14ae**: δ = 1.20 (d) and 3.90 (sept) (NiPr); 1.82 (d,

$J_{3',1}$ = 2 Hz, 3-CH$_3$); 2.50 (m, OH); 4.60 (d, $J_{4,5}$ = 8 Hz, 4-H); 6.13 (dd, $J_{5,6}$ = 16 Hz, 5-H); 6.62 (d, 6-H); 7.7 ppm (m, 1-H and C$_6$H$_5$). - ^{13}C NMR (CDCl$_3$), **14ad**: δ = 16.63 (3-CH$_3$); 20.89 and 46.35 (NiPr); 73.94 (C-4); 113.41 (C-1); 116.88 (C-3); 126.58 (C-5); 128.50 (C-6); 127.67, 129.71 and 131.46, 136.66 (phenyl-C); 152.98 (C=O); 189.20 ppm (C-2); **15ae**: 16.50 (3-CH$_3$); 113.17 (C-1); 189.39 ppm (C-2).

(aR*,4S*,5S*)- and (aR*,4S*,5R*)-N,N-Diisopropyl 4-hydroxy-3-methyl-5-phenyl-1,2-hexadienyl carbamate (5S*)-**14af** and (5R*)-**14af**). **9a** (0.99 g, 5.00 mmol), chlorotris(isopropoxy)titanium (**11b**) (5.50 mmol, 1N in hexane) and racemic 2-phenylpropanal rac-(**5f**) (0.74 g, 5.50 mmol), 15 h; diethyl ether/petroleum ether (1:10), afforded 0.95 g (57%) of a mixture of (5S*)- and 5R*)-**14af** (82 : 18), accompanied (^{1}H NMR) by 3% of N,N-diisopropyl 1-(1-hydroxy-2-phenylpropyl)-2-butynyl carbamate (**16af**). Repeated LC yielded (5S*)-**14af** together with **16af**, R_F(1:1) = 0.40, and pure (5R*)-**14af**, R_F(1:1) = 0.45. - IR (neat), mixture: 3400 (br., OH), 1970 (C=C=C), 1695 cm^{-1} (C=O).

(5S*)-**14af**; ^{1}H NMR (CDCl$_3$): δ = 1.25 (d) and 3.96 (m) (NiPr); 1.31 (d, $J_{6,5}$ = 7 Hz, 6-H$_3$); 1.78 (d, $J_{3',1}$ = 2 Hz, 3-CH$_3$); 2.17 (m, OH); 3.01 (dq, $J_{4,5}$= 5.5 Hz, $J_{5,6}$ = 7 Hz, 5-H); 4.10 (m, 4-H); 7.32 ppm (m, phenyl); 7.40 ppm (dq, $J_{1,3'}$ = $J_{1,4}$ = 2 Hz, 1-H); ^{13}C NMR (CDCl$_3$): δ = 15.18 (C-6); 17.22 (3-CH$_3$); 20.27-21.43 (br.) and 45.97-46.55 (br.) (NiPr); 43.56 (C-5); 77.20 (C-4); 113.21 (C-1); 116.89 (C-3); 126.34, 127.89, 128.21, 144.27 (phenyl); 152.99 (C=O); 189.59 ppm (C-2).

(5R*)-**14af**; ^{1}H NMR (CDCl$_3$): δ = 1.22 (d) and 3.90 (m) (NiPr); 1.30 (d, $J_{6,5}$ = 7 Hz, 6-H$_3$); 1.86 (d, $J_{3',1}$ = 2 Hz, 3-CH$_3$); 3.00 (dq, $J_{5,4}$ = $J_{5,6}$ = 7 Hz, 5-H); 4.19 (m, 4-H); 7.31 (m, phenyl); 7.47 ppm (m, 1-H).

16af, ^{1}H NMR (CDCl$_3$): 1.91 (d, $J_{4,1}$ = 2 Hz, 4-H$_3$), 5.08 ppm (m, 1-H).

$C_{20}H_{29}NO_3$ (331.46), calc. C 72.47 H 8.82, found C 72.57 H 8.88.

N,N-Diisopropyl 4-hydroxy-3,4-dimethyl-1,2-pentadienyl carbamate (**14ag**). **9a** (0.59 g, 3.00 mmol), **11** (3.30 mmol) and acetone (**5g**) (0.23 g, 4.0 mmol), **B**, 3 h, diethyl ether/petroleum ether (1:4), afforded 0.65 g (76%) **14ag**, R_F(1:1) = 0.20, viscous oil. - IR (neat): 3400 (br., OH), 1970 (C=C=C), 1690 cm^{-1} (C=O). - ^{1}H NMR (CDCl$_3$): δ = 1.20 (d) and 3.86 (sept) (NiPr); 1.35 (s, 6-H$_3$ and 5-H$_3$); 1.85 (d, $J_{3',1}$ = 2 Hz, 3-CH$_3$); 2.30 (m, OH); 7.20 ppm (q, 1-H).

$C_{14}H_{25}NO_3$ (255.36, calc .C 65.85 H 9.87, found 65.92 H 9.90.

A, 2 h, afforded 0.65 g (76%) **14ag**; α-adduct **16ag** was not recognized by ^{1}H NMR.

N,N-Diisopropyl 3-(1-hydroxycyclopentyl)-1,2-butadienyl carbamate (**14ah**). **9a** (0.59 g, 3.00 mmol), **12** (3.30 mmol, 27% in hexane) and cyclopentanone (**5h**) (0.34 g, 4.0 mmol), **C**, 15 h, diethyl ether/petroleum ether (1:5), afforded 0.27 g (47%) **14ah**, R_F(1:1) = 0.37, mp 51 $^{\circ}$C - IR (KBr): 3400 (br., OH), 1970 (C=C=C), 1690 cm^{-1} (C=O). - ^{1}H NMR (CDCl$_3$): δ = 1.20 (d) and 3.87 (sept) (NiPr); 1.75 (m, 4 CH$_2$); 1.82 (d, $J_{3',1}$= 2 Hz, 3-CH$_3$); 2.02 (m, OH); 7.23 ppm (q, $J_{4,1}$ = 2 Hz, 1-H).

$C_{16}H_{27}NO_3$ (281.40), calc. C 68.29 H 9.67, found C 68.12 H 9.64.

Procedure **B**, 2 h, afforded 0.53 g (63%) of a mixture containing **14ah** and N,N-diisopropyl 1-(1-hydroxycyclopentyl)-2-butynyl carbamate (**16ah**), R_F(1:1) = 0.35, 82 : 18, (^{1}H NMR). **16ah**, from the mixture, IR (neat): 2150 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$): δ = 5.10 ppm (q, $J_{1,4}$ = 3 Hz, 1-H).

(aR*4R*)-N,N-Diisopropyl 4-hydroxy-3-trimethylsilyl-1,2-pentadienyl carbamate (**14ba**). **9b** (1.28 g, 5.00 mmol) **11** (3.13 g, 5.50 mmol) and acetaldehyde (**5a**) (0.44 g, 10 mmol), **B**, 1 h, diethyl ether/petroleum ether (1:3), afforded 1.14 g (89%) **14ba**, R_F(1:1) = 0.31, viscous oil. The isomers **15ba** or **16ba** were not detected by ^{1}H NMR. - IR (neat): 3420 (br., OH), 1950 (C=C=C), 1685 cm^{-1} (C=O). - ^{1}H NMR (CDCl$_3$): δ = 0.19 (s, SiMe$_3$); 1.22 (d) and 3.5 - 4.2 (m) (NiPr); 1,35 (d, $J_{5,4}$ = 6.5 Hz, 5-H$_3$); 2.32 (m, OH); 4.43 (dq, $J_{4,1}$ = 2 Hz, 4-H); 7.47 ppm (dq, 1-H). - ^{13}C NMR (CDCl$_3$): δ = -1.01 (SiMe$_3$); 20.4 (br.) and 45.9 (br.) (NiPr); 24.15 (C-5); 67.47 (C-4); 113.21 (C-1); 122.08 (C-3); 153.26 (C=O); 195.78 ppm (C-2).

$C_{15}H_{29}NO_3Si$ (299.49), calc. C 60.16 H 9.76, found C 60.30 H 9.84.

(aR*,4S*)- and (aR*,4R*)-N,N-Diisopropyl 4-hydroxy-3-methyl-1-propyl-1,2-pentadienyl carbamate (**14ca** and **15ca**). **9c** (0.72 g, 3.00 mmol), TMEDA (0.35 g, 3.00 mmol), **12** (3.3 mmol, 27% in hexane), and acetaldehyde (**5a**) (0.44 g, 10 mmol), **C/TMEDA** , 3 h, diethyl ether/petroleum ether (1:6), afforded 0.71 g (83%) of a mixture of **14ca** and **15ca**, 82 : 18 (^{13}C NMR), R_F(1:1) = 0.23, viscous oil. **16ba** was not detected by ^{13}C NMR. - IR (neat): 3420 (br., OH), 1980 (C=C=C), 1690 cm^{-1} (C=O). - **14ca**, ^{1}H NMR (CDCl$_3$): δ = 0.93 (t, J = 7 Hz, 3'-H$_3$); 1.17 (d) and 3.5 - 4.3 (m) (NiPr and 4-H); 1.45 (m, 2'-H$_2$); 1.73 (s, 3-CH$_3$); 2.17 (t, J = 7 Hz, 1'-H$_2$). - ^{13}C NMR (CDCl$_3$): δ = 13.58 (C-3'); 16.42 (C-5); 19.78 (C-2'); 20.98 and 46.32 (NiPr); 22.85 (3-CH$_3$); 34.57 (C-1'); 68.85 (C-4); 24.15 (C-5); 116.73 (C-1);

126.60 (C-3); 154.29 (C=O); 189.43 ppm (C-2). **15ca**, no differences in 80 MHz ^{1}H NMR; ^{13}C NMR ($CDCl_3$): δ = 16.81 (C-5); 68.54 (C-4); 117.24 (C-1); 126,31 (C-3); 188.53 ppm (C-2).
$C_{16}H_{29}NO_3$ (283.14), calc. C. 67.81 H 10.31, found C 67.67 H 10.42.

*17 and 19; hydrogenation of the allenes **14aa** and **14ab**.* With the catalyst P2-Ni, prepared[19] in 5 mL ethanol from nickel diacetate (0.120 g, 0.60 mmol), ethanolic $NaBH_4$ (1M, 0.6 mL) and ethanolic ethylene diamine (1M, 0.2 mL), was saturated with H_2. **14aa** (0.964 g, 4.00 mmol) in ethanol (4 mL) was added with vigorous stirring. After 2.5 h stirring at 20 °C and 750 torr, the hydrogen consumption (112 mL, approx. 4 mmol) stopped. For work-up, the solvent was evaporated in vacuum, the residue stirred with dichloromethane (30 mL) and aq. 1M H_2SO_4 (30 mL), the organic phase washed with sat. aq. $NaHCO_3$, followed by brine, dried over $MgSO_4$ and evaporated. LC (silica gel, diethyl ether/petroleum ether, 1:4) afforded 0.39 g (46%) of a mixture of **17a** and **19a** (90 : 10, ^{1}H NMR, GC[12]). The identical ratio was found in samples, taken after 25 min (50% consumption) and after 24 h. In a second experiment, a ratio **17a** : **19a** = 80 : 20 was obtained. -
14ab (under identical conditions) yielded **17b** and **19b** (41%, 73 : 27).[12]
With Lindlar catalyst:[25] The catalyst (0.200 g) in THF (2 mL) was saturated with H_2, and **14aa** (0.241 g, 1.00 mmol) in THF (2 mL) was added. After 1.5 h at 20 °C and 750 torr, the hydrogen consumption (18 mL, approx. 0.7 mmol) stopped. Usual work-up and LC afforded 0.088 g (36%) **17a** and **19a**, 81 : 19.

Synthesis of alkenal 23; (aR,4S*)-N,N-diisopropyl 4-acetoxy-3,5-dimethyl-1,2-hexadienyl carbamate* (**22**). To a soln. of **14ab** (1.35 g, 5.00 mmol), triethylamine (15 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (0.5 mmol) in dichloromethane, acetanhydride (11 mmol) at -70 °C was added and the reaction mixture was allowed to warm to rt. After 2 h stirring at rt, usual work-up, followed by LC (diethyl ether/petroleum ether, 1:4), afforded 1.11 g (72%) **22**, R_F(1:1) = 0.45, oil, besides unreacted **14ab**. - IR (neat): 1980 (C=C=C), 1743 (C=O), 1710 cm^{-1} (NC=O). - ^{1}H NMR ($CDCl_3$): δ = 0.94 (d, 6-H_3 and 5-CH_3); 1.25 (d) and 3.9 (m) (N*i*Pr); 1.81 (d, $J_{3',1}$ = 2 Hz, 3-CH_3); 2.05 (s, CH_3C=O); 2.0 (m, 5-H); 4.94 (dd, $J_{4,5}$ = 7 Hz, $J_{4,1}$ = 2.5 Hz, 4-H); 7.43 ppm (m, 1-H).
$C_{17}H_{29}NO_4$ (311.42), calc. C 65.57 H 9.39, found C 65.52 H 9.44.
(E/Z)-4-Acetoxy-3,5-dimethyl-2-hexenal (**23**): To a soln. of **22** (0.622 g, 2.00 mmol) in methanol (10 mL) at -10 °C, methanesulfonic acid (2.00 mmol) and mercuric acetate (0.02 mmol) were added. After 1 h at -10 °C, stirring was continued at rt for 17 h. For work-up, the solvent was evaporated in vacuum, the residue dissolved in dichloromethane/water (20 + 20 mL), followed by rapid extraction of the organic layer with water (20 mL), aq. $NaHCO_3$ and brine. Evaporation of the solvent at rt and rapid LC on silica gel (60 g, diethyl ether/petroleum ether, 1:5) yielded 0.200 g (54%) instable **23**, *E* : *Z* = 80 : 20, R_F(1:1) = 0.24. - We were unable to obtain an analytically pure sample. - IR (neat): 1740 (OC=O); 1677 cm^{-1} (CH=O). - ^{1}H NMR ($CDCl_3$), (*E*)-**23**: δ = 0.90 (d, *J* = 7.Hz, 6-H_3 and 5-CH_3); 1.22 (m, 5-H); 2.08 (s, CH_3C=O); 2.14 (d, $J_{3',1}$ = 1 Hz, 3-CH_3); 4.90 (d, $J_{4,5}$ = 6 Hz, 4-H); 5.90 (d, $J_{2,1}$ = 8 Hz, 2-H); 10.5 (d, 1-H); (*Z*)-**23**: δ = 4.80 (d, 4-H); 5.80 ppm (d, 2-H). ^{13}C NMR ($CDCl_3$), (*E*)-**23**: δ = 14.58 and 17.25 (6-C and 5-CH_3); 19.22 (3-CH_3), 20.77 ($\underline{C}H_3C$=O); 30.18 (C-5); 81.49 (C-4); 127.04 (C-2); 159.00 (C-3); 170.19 (OC=O); 190.97 (C-1); (*Z*)-**23**: δ = 82.16 (C-4); 169.99 ppm (OC=O).

p-Chlorophenyl urethane 21. **14aa** (0.241 g, 1.00 mmol), pyridine (16mg, 0.2 mmol) and *p*-chlorophenyl isocyanate (0.20 g, 1.30 mmol) in toluene (5 mL) were allowed to stand at 20 °C for 60 h. Evaporation of the solvent in vacuum, followed by LC (silica gel, diethyl ether/petroleum ether, 1 : 20) afforded 0.233 g (59%) **21**. By applying the diffusion method (acetone/hexane) single crystals (mp 134 °C), suitable for X-ray analysis, were obtained. - IR (KBr): 3320 (NH), 1975 (C=C=C), 1730 and 1698 cm^{-1} (C=O). - ^{1}H NMR ($CDCl_3$): δ = 1.24 (d) and 3.97 (m) (N*i*Pr); 1.43 (d, $J_{5,4}$ = 6 Hz, 5-H_3); 1.88 (d, $J_{3',1}$ = 2 Hz, 3-CH_3), 5.35 (q, 4-H); 6.95 (br. s, NH); 7.3 (m, phenyl); 7.42 ppm (qd, $J_{1,4}$ = 2 Hz).
Crystal structure analysis of **21** ($C_{20}H_{27}ClN_2O_4$). Slightly yellow blocks from acetone/hexane, dimensions 0.6 x 0.6 x 0.5 mm^3, space group Pbca, *a* = 1172.5(1), *b* = 2434.5(2), *c* = 1570.1(1) pm, *V* = 4.482 nm^3, *Z* = 8, d_c = 1.17 g . cm^{-3}, μ = 0.19 mm^{-1} (Mo-Kα); 3931 unique intensities measured ($2\theta_{max}$ = 50°), 2535 with $|F| > 3\sigma(F)$ treated as observed, structure solution with direct methods (SHELXTL), non-hydrogen atoms refined anisotropically, H atoms at calculated positions, R = 0.097 (R_w = 0.110). The refinement of the central part of the molecule was supported by weak restraints. The final difference electron-density synthesis showed some peaks around the allene group; they also appeared in the crystal structure of the phenyl urethane of **14aa**, which could not be refined satisfactorily.

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