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ASYMMETRIC SYNTHESIS OF PRIMARY AMINES FROM ALKENES AND CHIRAL CHLORONITROSO SUGAR DERIVATIVES.

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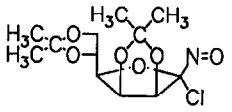
Abstract: A variety of alkenes **5 - 15, 38, 39** react with chloronitroso sugar derivatives **1 - 3** regioselectively at ambient temperature to give chiral hydroxylamines in 60 - 80% yield. In addition to these products of a formal ene reaction joined by a subsequent hydrolysis 2-substituted hydroxylamines **40 - 49** are also formed.The 2-substituted hydroxylamines **40, 41, 49** possess trans configurations exclusively. The product distribution is solvent dependent and susceptible to the addition of nucleophiles. The reactions employing the reagents **1** and **3** which are approximately mirror images in the vicinity of the chloronitroso function yield opposite enantiomers of the product. Their optical purity was determined by chemical reduction to the amine stage followed by the formation of diastereomeric camphorsulfonic- or Mosher acid amides and subsequent chromatographic or nmr spectrometric analysis. The optical purity for cyclic products was found in excess of 89% ee whereas acyclic alkenes yielded chiral amines in the range of 50 - 90% ee. Chemical degradation and comparison to authentic amino acids confirmed that in every case examined the reaction with the D-mannose derivative **1** yielded the *S*- configuration at the asymmetric carbon bearing the amino function. The formal ene reactions investigated thus provide another useful EPC synthesis of functionalized chiral amines in acceptable chemical yields and with a predictable stereochemical outcome.

Introduction

Among the many methods for the synthesis of biologically active amines procedures which furnish chiral members of this class by asymmetric induction (EPC synthesis) deserve special interest due to their inherent efficiency. A particularly attractive example[1] uses the ene reaction of chloronitroso sugar derivatives **1, 2, 3** with prochiral olefines (see scheme 1) to produce allylic nitrones or hydroxylamines which can easily be converted to the corresponding allylamino compounds. Compared to the alkyl chloronitroso analogues (e.g. **4**), which required days or weeks to react completely in ene reactions,[2] the readily accessible chiral chloronitroso enophiles **1 - 3** showed enhanced reactivity due to the inductive electron pull by the adjacent ether function.[3]

Though the excellent chemical yields reported so far are based on NMR determinations only, this transformation appears to make up a valuable access to chiral nitrogen compounds, since the optical yields may exceed 80% ee as was demonstrated in one case.[1] Moreover, in the course of the reaction the chiral reagent is degraded to a lactone, which in turn is easily recycled and thus contributes to the economy of the EPC synthesis.

Here we report on our results characterizing the conditions of this asymmetric ene reaction, its scope in terms of olefinic substrate structure, the product distribution and the assessment of the stereochemical outcome.



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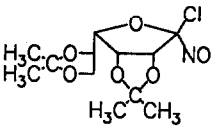

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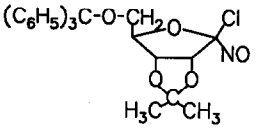

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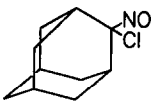

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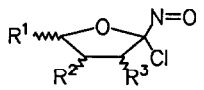
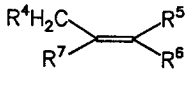


1, 2, 3,



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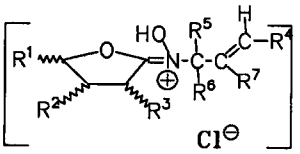
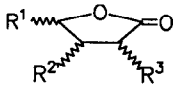
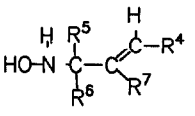


hydrolysis

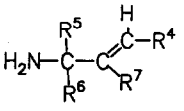


16, 17, 18,



19 – 29

reduction



30 – 37

alkene	hydroxylamine	amine	R^4	R^5	R^6	R^7
5	19	30	H	^{t}Bu	H	$-CH_3$
6	20	31	H	H	^{t}Bu	H
7	21	–	n-C_3H_7	H	$-CH_3$	H
8	22	–	n-C_5H_{11}	H	H	H
9	23	–	H	H	$-C_6H_5$	H
10	24	32	$-(CH_2)_2-$		H	H
11	25	33	$-(CH_2)_3-$		H	H
12	26	34	$-(CH_2)_3-$		H	$-CH_3$
13	27	35	$-(CH_2)_4-$		H	H
14	28	36	$-(CH_2)_5-$		H	H
15	29	37	$-CH_2CH=CH(CH_2)_2-$		H	H

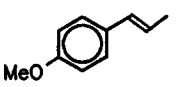
Scheme 1.

Results and Discussion

On mixing equal volumes of 0.2 M hexane solutions of the chloronitroso-D-mannose derivative **1** and the alkenes **5** – **15** the initially bright blue colour of the nitroso compound faded gradually. Finally, a colourless suspension resulted, which on concentration and redistribution between chloroform and dilute hydrochloric acid was hydrolyzed. From the aqueous phase the single product hydroxylamines **19** – **29** were isolated as the hydrochloride salts, whereas most of the bisisopropylidenemannonolactone **16** could be recovered from the organic layer. The isolated yields and duration of these ene reactions are given in table 1. The quality of the nitroso reagent, which is easy to purify by crystallization, exerted some influence on the product yield. However, a change of the solvent proved to be much more profound: Besides a rate acceleration with increasing solvent polarity a new product was observed and identified to be a vicinal chlorohydroxylamine. As a prototypical example cyclopentene **10** was treated with **1** in a variety of solvents giving the product distribution listed in table 2. The general result was the preferential formation of the chloro compound **40** relative to the allylic hydroxylamine **24**, if hexane was replaced by more polar solvents. Clear cut trends relating this behaviour to some solvent property were not discovered. The product ratio depended on structural elements of the olefin, too. Thus, though alkene **9** yielded a similiar product distribution pattern depending on solvent as **10**, the p-methoxy substituted alkene **38** exclusively gave the vicinal chloro hydroxylamine **46** even in hexane solution. The same observation applies to alkene **39**; the only product obtained in this case was the chloro compound **42**. As the chloronitroso sugars **1** – **3** deteriorate in solu-

Table 1. Isolated chemical yields and durations of the ene-reactions of 1, 2, 3, 4 with alkenes in hexane at room temperature.

alkene	hydroxylamine	α-chloronitroso compound	yield %	duration
5	19	1	88	7 d
		2	78	7 d
		3	78	12 d
		4	65	1.5 a
6	20	1	76	14 d
		3	77	7 d
		4	62	5 w
7	21	1	60	24 h
8	22	1	86	17 h
9	23	1	68	7 d
10	24	1	76	2 d
		2	68	3 d
		3	70	7 d
		4	60	2 d
13	27	1	79	2 d
		3	77	2 d
14	28	1	74	8 d
		3	64	10 d
15	29	1	63	7 d



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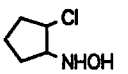

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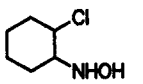

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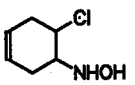

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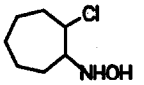

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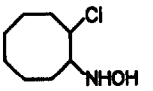

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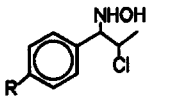
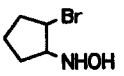


R = H 45
R = OCH_3 46



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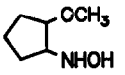

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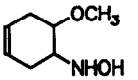

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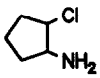

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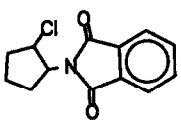

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Table 2 . Solvent dependence and duration of the reaction of 1 with 10 at room temperature under nitrogen.

solvent	duration	product distribution [a] 24 : 40	overall yield [b] %
hexane	2 d	24 only	60
ether	24 h	1 : 2	40
benzene	5 h	1 : 1	47
cyclopentene	5 h	1 : 1	40
acetonitrile	3 h	1 : 9	50
nitromethane	5 h	40 only	35
dimethylformamide	7 h	40 only	40
dimethyl sulfoxide	5 h	40 only	40
propylene carbonate	9 h	40 only	40
N-methylformamide	9 h	40 only	30
hexamethyl phosphoric acid triamide	9 h	40 only	30
1,2-Dihydroxypropane	9 h	40 only	20
1-methyl-2-pyrrolidone	9 h	40 only	20

[a] by GC
[b] yields by GC employing external standardization.

tion and this process may ultimately limit product yields, we investigated its dependence on the enophile/alkene molar ratio. The results listed in table 3 show clearly that the product distribution does not depend on the relative amounts of the reaction partners. However, product yields are definitely better, if the nitroso/alkene ratio increases, which supports the view that reagent degradation is a limiting factor of the overall process.

Though the mechanistic pathways of these ene reactions are still quite obscure and may well follow several distinct routes[4-7] the occurrence of vicinal chlorohydroxylamines is incompatible with a concerted electrocyclic process. Rather some intermediate must be formed[7] which may be attacked by external nucleophiles, since the addition of lithium halides shifted the product distribution ratio. As a corollary the bromo substituted compound **47** was formed, if lithium bromide was present in the ene reaction of **10** (table 4). In addition, on conducting the ene reactions of **10** or **39** in methanol the methoxy substitution products **48** and **49** were isolated in 15% or 8% yield, respectively.

The relative configurations of the chloro and hydroxylamino substituents in the cyclohexane derived products **49**, **41** and **42** were readily established based on the vicinal ^{1}H NMR coupling constants of the protons bonded to the asymmetric centres. The coupling constants were in excess of 10 Hz indicating the trans diequatorial relationship of the substituents. In the case of the cyclopentane derivative **40** the relative positions of the substituents could not be deduced from NMR coupling data.

Some support in favour of the trans arrangement of the functional groups was obtained from ^{1}H NOE difference spectra of **40**: If the proton signal arising from the H-C-Cl group was irradiated, the adjacent methylene ^{1}H signals experienced a stronger intensity enhancement than the ^{1}H signal of the constitutively equidistant H-C-N group. Thus at least one of the methylene protons must be located closer in space to the H-C-Cl proton than to the proton next to the hydroxyamino function. More reliable evidence for the trans diastereomeric substitution pattern emerged from chemical conversions: The hydride reduction (see below) of **40** gave the primary amino compound **50**, which on treatment with methanolic base furnished the aziridine **51**. This reaction is a well known intramolecular substitution and thereby proves the trans configuration of nucleophilic and leaving groups.

Table 3 . Dependence of product yield on educt stoichiometric ratio of 1 and 10 in isopropanol at room temperature.

1 [a]	10 [a]	24 : 40 [b]	yield % [c]
1	1	1 : 8	18
1	5	1 : 10	18
1	10	1 : 10	24
1	20	1 : 10	24
5	1	1 : 9	25
10	1	1 : 8	50
20	1	1 : 9	50

[a] mmol in 10 ml solvent.
[b] by GC.
[c] yields by GC employing external standardization.

The characterization of the optical purity and the absolute configurations of the products relied on their conversion to the amino compounds, since the stereochemical assignment in the latter class is highly developed. Most reduction methods of hydroxylamines are not likely to affect the configurational integrity of an adjacent stereochemical centre, so that quite a number of reductive conditions were tested (Zn/AcOH, $Al(Hg)_x$,[8] $LiBH_4/(CH_3)_3SiCl$,[9] $TiCl_3/HCl$,[10] $LiAlH_4$,[11]). Among these the reduction[11] with $LiAlH_4$ proved advantageous, furnishing the amino compounds in 60 - 85% yield while retaining the other functional groups.

Since none of the chiral compounds so obtained had been characterized by optical rotation data before, they were first converted to diastereomeric amides using the camphorsulfonic amide[12] or Mosher acid amide[13] routes. The open chain amines **30** and **31** formed diastereomeric camphorsulfonamide derivatives which were separable by capillary gas chromatography. The optical purities deduced from peak integration correlated with ^1H NMR spectroscopic diastereomer analysis to give the values listed in table 5. Distinctly higher ee values (table 6) were found with the cyclic primary amines **32 - 37, 50** which were determined by ^{19}F NMR peak integration of the diastereomeric Mosher acid amides, as the GC separation factors in general did not allow a precise analysis by this method.

These results confirm[1], that the ene reactions with nitroso sugar derivatives proceed with a very high degree of asymmetric induction. The mannose derived chiral reagent **1** seems to perform slightly better in this respect than the chloronitroso ribose derivative **3** probably due to the increased steric crowding at the reactive hemisphere of the former reagent.

Table 4 . Influence of external nucleophile on the reaction of 1 [0.1 M] and 10 [0.1 M] in isopropanol at room temperature.

	24 : 40 [a]
without added nucleophile	1 : 8
LiCl [0.1 M]	1 : 20
LiBr [0.1 M]	1 : 2 : 20 (47)

[a] by GC.

Table 5 . ee Values calculated from the integrals of ^1H NMR spectra and from the integrals of the GC signals of the (1S)-camphan-10-sulfonamides

amine	chloronitroso compounds	δ(^1H)[a] ppm	integral %	ee %	RI-values[b]	integral %	ee %
(+)30	1	3.45 3.35	8 : 92	84	2327	8 : 92	84
(−)30	3	2.96 2.90	76 : 24	52	2303	76 : 24	52
(+)31	1	3.48 3.45	5 : 95	90	2242	5 : 95	90
(−)31	3	2.95 2.92	91.5 : 8.5	83	2236	91.5 : 8.5	83

[a] observation of H-10.

[b] retention index related to alkane standards.

The assignment of the absolute configuration took advantage from well established oxidative degradations[14] of the alkenes **30** - **37** to amino acids : Ozonolysis of the N-acetylated allylic amines yielded N-acetylamino acids after oxidative workup, which were esterified and their optical rotations compared to authentic samples. This scheme could not be applied to the chloroamine **50**. Instead this compound was converted to the phthalimido compound **52** which underwent dehydrohalogenation to yield, after hydrazinolysis, the same enantiomeric cyclopentenylamine **32** that was obtained from the ene reaction of **10** and **1**. Thus, **50** and **32** possess identical configurations (*S*) at the N-substituted carbon atoms. Irrespective of the alkene structure all reactions using the mannose derivative **1** produced the same *S*-configuration in the product. Correspondingly we assign the *R*-configuration to all the products obtained in the reactions of **2** and **3** based on the inverse sense of rotation observed. These results impose unambiguous concrete restraints on the mechanistic options available for rationalization the reaction mode of alkenes and chloronitroso compounds.

Table 6 . ee-Values determined from ^{19}F-nmr integrals.

amine	chloronitroso compound	δ (^{19}F) ppm	integrals %	ee %
(-)32	1	12.43	3 : 97	94
(+)32	3	12.38	91 : 9	82
(-)33	1	-	-	96 [a]
(+)33	3	-	-	96 [a]
(-)34	1	-	-	96 [a]
(+)34	3	-	-	96 [a]
(-)35	1	11.09	2 : 98	96
(+)35	3	11.03	96 : 4	92
(+)36	1	11.10 11.00	2 : 98	96
(+)37	1	11.05 10.98	2 : 98	96
(-)50	1	6.96 6.91	5.5 : 94.5	89

[a] ee-values derived from the integrals of the GC-signals.

Conclusion

We have established that the reaction of cyclic and acyclic alkenes with readily available chiral chloronitroso sugars **1** - **3** is a preparatively simple and useful means to introduce one or two functionalized asymmetric centres with predictable configuration and regioselectivity into olefins.

EXPERIMENTAL

General procedure for the ene reaction

To a solution of 10 mmol chloronitroso compound in 100 ml of hexane the alkene (10 mmol) is added in the dark under nitrogen. The mixture is stirred at room temperature until the blue colour has disappeared. After the removal of the hexane in vacuo, the residue is dissolved in 50 ml of chloroform and stirred with 50 ml of 0.5 N hydrochloric acid at room temp. for 12 h. From the organic layer the sugar lactones can be obtained. The aqueous layer is neutralized with $KHCO_3$ and extracted with chloroform. The extract is dried with $MgSO_4$ and after removal of the solvent the hydroxylamines can be recrystallized from ether/pentane. The hydrochlorides are obtained by passing gaseous HCl into the ether/pentane solutions.

(+)-N-(2,4,4-Trimethylpent-1-en-3-yl)hydroxylamine hydrochloride (**19**) from **5** with **1** in ether as solvent. Yield 88%, colourless crystals. mp 210 °C (decomp.).$[\alpha]_D$ = + 6.63 ° (c=0.5; MeOH).
Anal. $C_8H_{18}ClNO$ (179.7) calcd. C 53.42 H 10.02 N 7.79; found C 53.35 H 9.98 N 7.63. ^{1}H NMR (CD_3OD): δ = 5.32 (s, 1H, H-1), 5.13 (s, 1H, H-1), 3.68 (s, 1H, H-3), 1.91 (s, 3H, CH_3), 1.11 (s, t-Bu). ^{13}C NMR (CD_3OD): δ = 138.8 (C-2), 120.4 (C-1), 77.6 (C-3), 34.4 (C-4), 27.8 (t-Bu-CH_3), 22.1 (CH_3). MS (EI) : m/z (%) = 143 (M^+-HCl, 0.5), 128 (1), 111 (2), 86 (100). IR (KBr) :ν= 3100, 2920, 2780, 1580, 1420, 920 cm^{-1}.

(-)-Isomer: $[\alpha]_D$ = - 6.6 ° (c=1.2; MeOH) when **2** is used instead of **1**. $[\alpha]_D$ = - 4.35 ° (c=0.7; MeOH) when **3** is used.

(3*S*)-(+)-N-(4,4-Dimethylpent-1-en-3-yl)hydroxylamine hydrochloride (**20**) from **6** with **1** in ether as solvent. Yield 76%, colourless crystals, mp. 172 °C (decomp.). $[\alpha]_D$ = + 10.65 ° (c=1.08; MeOH).
Anal. $C_7H_{16}ClNO$ (165.7) calcd. C 50.71 H 9.71 N 8.45; found C 50.70 H 9.50 N 8.44. ^{1}H NMR (CD_3OD): δ = 5.87 (m, 1H, H-2), 5.62 (dd, J=13 Hz, 1.5 Hz. 2H, H-1), 3,57 (d, J=13 Hz, 1H, H-3), 1.07 (s, t-Bu). ^{13}C NMR (CD_3OD): δ = 129.79 (C-2), 125.71 (C-1), 76.29 (C-3), 27.14 (C-5). MS (EI) : m/z (%) = 129 (M^+-HCl, 0.4), 97 (28), 72 (100), 56 (12), 36 (16). IR (KBr):ν= 3120, 3000, 2800, 1430, 1420, 1390, 1000, 960 cm^{-1}.

(3*R*)-(-)-Isomer: $[\alpha]_D$ = - 8,2 ° (c=2.4; MeOH) when **3** is used instead of **1**.

N-(Hept-3-en-2-yl)-hydroxylamine (**21**) from **7** and **1** in hexane. Yield 60%, colourless crystals, mp. 62 °C. $[\alpha]_D$ = + 19.7 ° (c=0.9; MeOH).
Anal. $C_7H_{15}NO$ (129.2) calcd. C 6.08 H 11.70 N 10.80; found C 65.43 H 11.80 N 10.72. ^{1}H NMR ($CDCl_3$): δ = 5.71 (br, NHOH), 5.65 (dd, J=10 Hz, 2 Hz, 1H, H-3), 5.37 (dt, J=6.0 Hz, 1.2 Hz, 1H, H-4), 3.53 (m, 1H, H-2), 2.02 (m, 2H, H-5), 1.33 (m, 2H, H-6), 1.17 (d, J=6.0 Hz, 3H, H-7), 0,89 (t, J=7.0 Hz, 3H, H-7). ^{13}C NMR ($CDCl_3$): δ = 133.36 (C-3), 130.47 (C-4), 59.52 (C-2), 34.43 (C-1), 22.25 (C-5), 18.04 (C-6), 13.56 (C-7). MS (EI) : m/z (%) = 129 (M^+, 1), 114 (3), 97 (28), 86 (13), 55 (100). IR (KBr) : ν = 3500 (br), 3150, 2600, 2300, 1500, 1200 cm^{-1}.

(+)-N-(Oct-2-en-1-yl)hydroxylamine (22) from 8 and 1 in hexane. Yield 86%, colourless crystals, mp. 54 °C. Anal. $C_8H_{17}NO$ (143.2), calcd. C 67.09 H 11.96 N 9.78; found C 66.89 H 11.72 N 9.82. ^{1}H NMR ($CDCl_3$): δ = 5.70 (dt, J=15 Hz, 7.5 Hz, 1H, H-2), 5.50 (dt, J=15 Hz, 7.5 Hz, 1H, H-3), 5.00 (br, NHOH), 3.49 (d. J=6 Hz, 1H, H-1), 2.03 (dt, J=7 Hz, 2H, H-4), 1.27 (m, 6H, H-5, H-6, H-7), 0.88 (t, J=7 Hz, 2H, H-8). ^{13}C NMR ($CDCl_3$): δ = 135.88 (C-2), 124.66 (C-3), 56.13 (C-1), 32.45 (C-4), 31.40 (C-5), 28.83 (C-6), 22.52 (C-7), 14.13 (C-8). MS (EI) : m/z (%) = 143 (M^+, 2), 126 (3), 110 (5), 96 (3), 86 (8), 82 (10), 72 (25), 69 (100), 55 (59), 41 (49). IR (KBr) : ν = 3240, 2920, 2840, 1440, 1170, 1030, 970, 870 cm^{-1}.

(+)-N-(1-Phenylprop-2-en-1-yl)hydroxylamine (23) from 9 and 1 in hexane. Yield 68%, colourless crystals, mp. 68 °C. $[\alpha]_D$ = + 21.2 ° (c=0.5; MeOH).
Anal. $C_9H_{11}NO$ (149.1) calcd. C 72.48 H 7.38 N 9.40; found C 72.63 H 7.39 N 9.43. ^{1}H NMR ($CDCl_3$) : δ = 7.31 (m, 5H, Ar-H), 6.00 (m, 1H, H-2), 5.50 (br, NHOH), 5.26 (dd, J=5 Hz, 3 Hz, 1H, H-3), 4.57 (d, J=3 Hz, 1H, H-1). ^{13}C NMR ($CDCl_3$): δ = 139.71 (Ar), 137.40 (C-2), 128.95 (Ar), 128.59 (Ar), 127.86 (Ar), 117.76 (C-3), 69.59 (C-1). MS (EI) : m/z (%) = 149 (M^+, 0.1), 132 (2), 122 (2), 118 (12), 117 (100), 115 (40), 104 (6), 91 (12), 77 (11). IR (KBr) : ν = 3260, 3190, 2880, 1770, 1500, 1460, 920, 760, 700 cm^{-1}.

(1*S*)-(-)-N-(Cyclopent-2-en-1-yl)hydroxylamine (24) from 10 and 1 in hexane. Yield 76%. colourless needles, mp. 66 °C. $[\alpha]_D$ = - 152.0 ° (c=0.5; MeOH).
Anal. C_5H_9NO (99.0) calcd. C 60.60 H 9.10 N 14.10; found, C 60.48 H 9.08 N 13.95. ^{1}H NMR ($CDCl_3$): δ = 6.11 (br, NHOH), 6.0 (m, 1H, H-2), 5.77 (m, 1H, H-3), 4.15 (m, 1H, H-1), 2.45 (m, 2H, H-4), 2.08 (m, 1H, H-5), 1.75 (m, 1H, H-5). ^{13}C NMR ($CDCl_3$): δ = 135.72 (C-2), 129.71 (C-3), 68.54 (C-1), 31.27 (C-4), 27.29 (C-5). MS (EI) : m/z (%) = 99 (M^+,4), 98 (1), 83 (6), 67 (100), 55 (2), 41 (18). IR (KBr): ν = 3260, 2930, 1620, 1440, 1370, 1070, 920 cm^{-1}.

(1*R*)-(+)-Isomer: $[\alpha]_D$ = + 150.0 ° (c=0.8; MeOH), when 2 is used. $[\alpha]_D$ = + 120.0 ° (c=0.4; MeOH), when 3 is used.

(1*S*)-(-)-N-(Cyclohex-2-en-1-yl)hydroxylamine (25) from 11 and 1 in ether. Yield 96%, colourless crystals, mp. 99 °C. $[\alpha]_D$ = -112.7 (c=1.0; $CHCl_3$).

Anal. $C_6H_{11}NO$ (113.2) calc. C 63.68 H 9.75 N 12.38; found C 63.55 H 9.53 N 12.25. ^{1}H NMR ($CDCl_3$) δ = 6.05 (br,NHOH), 5.95 (m, 1H, H-2), 5.70 (m, 1H, H-3), 3.53 (m, 1H, H-1), 2.00 (m, 2H, H-4), 1.69 (m, 4H, H-5 + H-6). ^{13}C NMR ($CDCl_3$) δ = 131.5 (C-2), 126.0 (C-3), 57.1 (C-1), 26.2, 25.3, 19.5, (C-4,C-5, C-6). MS (EI) m/z (%) = 113 (M^+,4), 81 (100), 80 (13), 79 (37), 77 (8), 70 (8), 67 (10), 53 (17), 41 (25(, 39 (14). IR ν = 3585,3265, 3000, 2940,2860, 2840, 1450, 1070, 1015, 1005, 960, 895, 870 cm^{-1}.

(1*R*)-(+)-Isomer: Yield 91%, $[\alpha]_D$ = +109.8 (c=1.2,$CHCl_3$), when 3 is used instead of 1.

(-)-N-(2-Methylcyclohex-2-en-1-yl)hydroxylamine (26) from 12 and 1 in ether. Yield 87%, colourless crystals, mp. 70 °C. $[\alpha]_D$ = - 142.1 ° (c=0.4; $CHCl_3$).
Anal. $C_7H_{13}NO$ (127.2) calcd. C 66.10 H 10.30 N 11.01; found C 65.98 H 10.68 N 10.79. ^{1}H NMR ($CDCl_3$): δ = 5.63 (m, 1H, H-3), 5.60 (m, NHOH), 3.34 (m, 1H, H-1), 2.00 (m, 3H, H-4, H-5, H-6), 1.76 (m, CH_3), 1.61 (m, 3H, H-4, H-5, H-6). ^{13}C NMR ($CDCl_3$) : δ = 131.2 (C-2), 127.7 (C-3), 60.4 (C-1), 25.7 (C-4), 25.4 (C-6), 21

(C-7), 18.0 (C-5). IR (KBr) :ν = 3580, 3270, 2995, 2935, 2860, 2835, 1445, 1375, 1285, 1240, 1200, 1150, 1110, 1085, 1030, 950, 900, 880 cm^{-1}.

(+)-Isomer: Yield 88% $[\alpha]_D$ = +134.8 (c=1.2,$CHCl_3$),when **3** is used.

(1*S*)-(-)-N-(Cyclohept-2-en-1-yl)hydroxylamine **(27)** from **13** and **1** in hexane. Yield 79%, colourless crystals, mp 107 °C. $[\alpha]_D$ = - 29,2 ° (c=1.06; $CHCl_3$). Anal. $C_7H_{13}NO$ (127.2), calcd. C 66.11 H 10.30 N 11.01; found C 66.05 H 9.97 N 11,05. ^{1}H NMR ($CDCl_3$): δ = 6.20 (br, NHOH), 5.84 (m, 1H, H-2), 5.69 (m, 1H, H-3), 3.66 (m, 1H, H-1), 2.2 - 1.2 (m, 8H, H-4, H-5, H-6, H-7). ^{13}C NMR ($CDCl_3$): δ = 133.20 (C-2), 131.95 (C-3), 62.80 (C-1), 30.86 (C-4), 28.65 (C-7), 28.38 (C-6), 26.65 (C-5). MS (EI) : m/z (%) = 127 (M^+, 4), 110 (9), 95 (100), 94 (29), 82 (27), 79 (23), 67 (67). IR (KBr) :ν = 3260, 3160, 2940, 2840, 1650, 1530, 1450, 1050, 910 cm^{-1}.

(1*R*)-(+)-Isomer: $[\alpha]_D$ = +28,4 ° (c=1.1; $CHCl_3$), when **3** is used.

(1*S*)-(+)-N-(Cyclooct-2-en-1-yl)hydroxylamine **(28)** from **14** and **1** in hexane. Yield 74%, colourless crystals, mp. 77 °C. $[\alpha]_D$ = + 68.97 ° (c=0.58; $CHCl_3$). Anal. $C_8H_{15}NO$ (141.2) calcd. C 68.05 H 10.71 N 9.92; found C 67.84 H 10.65 N 9.81. ^{1}H NMR ($CDCl_3$): δ = 6.0 - 5.0 (br, NHOH), 5.73 (m, 1H, H-3), 5.47 (dd, J=11 Hz, 8 Hz, 1H, H-2), 3.95 (m, 1H, H-1), 2.29 (m, 1H, H-4), 2.10 (m, 1H, H-4), 1.8-1.1 (m, 8H, H-5, H-6, H-7, H-8). ^{13}C NMR ($CDCl_3$): δ = 131.44 (C-2), 130.75 (C-3), 60.09 (C-1), 33.03 (C-8), 29.03 (C-7), 26.57 (C-5), 26.35 (C-6), 24.23 (C-4). MS (EI) : m/z (%) = 141 (M^+, 13), 124 (27), 109 (50), 108 (75), 98 (90), 81 (50), 67 (100). IR (KBr) :ν= 3200, 3000, 1450, 1050, 920, 760 cm^{-1}.

(1*R*)-(-)-Isomer: $[\alpha]_D$ = - 68.6 ° (c=0.3; $CHCl_3$) when **3** is used.

(1*S*)-(+)-N-(Cycloocta-2,5-dien-1-yl)hydroxylamine **(29)** from **15** in hexane. Yield 63%, colourless crystals, mp. 86 °C. $[\alpha]_D$ = + 120,1 ° (c=1.27; $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 6.32 (br, NHOH), 5.73 (m, 1H, H-3), 5.65 (m,1H, H-5), 5.48 (m, 1H, H-6), 5.34 (dd, J=12 Hz, 7.5 Hz, 1H, H-2), 4.21 (q, J=11 Hz, 7.5 Hz, 6 Hz, 1H, H-1), 2.85 (t, J=12 Hz, 4 Hz, 1H, H-4), 2,55 (m, 1H, H-7), 2.06 (m, 1H, H-7), 1.70 (tt, J=12 Hz, 4 Hz, 1H, H-4), 1,28 (tt, J=12 Hz, 4 Hz, 2H, H-8). MS (EI) : m/z (%) = 139 (M^+, 1), 122 (55), 111 (24), 106 (21), 94 (32), 91 (43), 85 (31), 79 (100), 77 (43), 67 (40). IR (KBr) : ν= 3260, 3150, 3010, 2880, 1650, 1540, 1460, 1340, 1260, 1090, 1040, 910, 810, 740, 660 cm^{-1}.

(+)-N-(2-Chloro-1-p-methoxyphenylpropyl)hydroxylamine **(46)** from **38** and **1** in hexane. Yield: 52%, colourless crystals, mp. 95 °C. $[\alpha]_D$ = + 21,0 ° (c=0.5; MeOH).

Anal. $C_{10}H_{14}ClNO_2$ (215.6), calcd. C 55.81 H 6.51 N 6.51; found C 55.52 H 6.48 N 6.55. ^{1}H NMR ($CDCl_3$): δ = 7.25 (d, J=3 Hz, 2H, Ar-H), 6.90 (d, J=3 Hz, 2H, Ar-H), 6.20 (br, NHOH), 4.58 (d, J=3 Hz, 1H, H-1), 3.81 (s. 3H, p-OCH_3), 3.10 (m, 1H, H-2), 0.95 (d, J=2 Hz, 3H, H-3). ^{13}C NMR ($CDCl_3$): δ = 159.35 (Ar), 133.97 (Ar), 128.04 (Ar), 113.90 (Ar), 75.80 (C-1), 62.46 (C-2), 55.28 (p-OCH_3), 14.36 (C-3). MS (EI) : m/z (%) = 179 (29), 148 (44), 138 (59), 137 (96), 135 (93), 109 (30), 77 (39), 60 (100). IR (KBr) :ν= 3380, 3260, 2980, 1610, 1590, 1510, 1310, 1250, 1180, 1060, 860 cm^{-1}.

(+)-N-(2-Chloro-1-phenylpropyl)hydroxylamine **(45)** from **9** and **1** in chloroform. Yield 56 %, colourless crystals, mp. 122 °C. $[\alpha]_D$ = + 91.7 ° (c=1.02; MeOH).
Anal. $C_9H_{12}ClNO$ (185.2), calcd. C 58.38 H 6.49 N 7.57; found C 58.10 H 6.32 N 7.76. ^{1}H NMR ($CDCl_3$) : δ = 7.36 (m, 5H, Ar-H), 5.80 (br, NHOH), 5.08 (d, J=8.7 Hz, 1H, H-1), 3.37 (dq, J=8.7 Hz, 7.7 Hz, 1H, H-2), 0.99 (d, J=7.6 Hz, 3H, H-3). ^{13}C NMR ($CDCl_3$): δ = 138.71 (Ar), 128.69 (Ar), 128.60 (Ar), 127.80 (Ar), 64.52 (C-1), 62.67 (C-2), 14.80 (C-3). MS (EI) : m/z (%) = 185 (M^+, 0.1), 169 (0.1) 125 (4), 117 (7), 105 (9), 91 (7), 60 (100). IR (KBr) : ν = 3200, 2990, 1450, 1400, 1260, 1160, 1020, 900, 740, 700 cm^{-1}.

(1*S*,2*S*)-(-)-N-(2-Chlorocyclopentyl)hydroxylamine **(40)** from **10** and **1** in isopropanol to which 10 mmol of LiCL was added. Yield 50%. colourles crystals, mp. 51 °C. $[\alpha]_D$ = - 92.8 ° (c=0.9; MeOH).
Anal. $C_5H_{10}ClNO$ (135.6), calcd. C 44.40 H 7.41 N 10.42; found C 44.59 H 7.68 N 10.67. ^{1}H NMR ($CDCl_3$): δ = 6.0 (br, NHOH), 4.3 (m, 1H, H-2), 3.5 (m, 1H, H-1), 2.1 (m, 2H, H-5), 1.8 (m, 3H, H-3, H-4), 1.45 (m, 1H, H-3). MS (EI) : m/z (%) = 135 (M^+, 11), 83 (3), 73 (16), 72 (100), 67 (40), 56 (9). IR (KBr) : ν = 3300, 2980, 1730, 1450, 1320, 1030, 910, 850 cm^{-1}.

N-(2-Bromocyclopentyl)hydroxylamine **(47)** from **10** and **1** in isopropanol to which 10 mmol of LiBr was added.
MS (EI) : m/z (%) = 181 (4), 179 (M^+, 4), 149 (4), 147 (4), 100 (9), 82 (6), 72 (100), 67 (31), 56 (24).

N-(2-Methoxycyclopentyl)hydroxylamine **(48)** from **10** and **1** in methanol.
^{1}H NMR ($CDCl_3$): δ = 6.06 (br, NHOH), 3.69 (dt, J=6.4 Hz, 4.0 Hz, 3.3 Hz, 1H, H-2), 3.38 (m, 1H, H-1), 3.42 (s, 2H, H-6), 2.2 - 1.4 (m, 6H, H-3, H-4, H-5) ^{13}C NMR ($CDCl_3$): δ = 94.44 (C-2), 68.00 (C-1), 56.82 (C-6), 30.53 (C-3), 27.97 (C-5), 22.07 (C-4). MS (EI) : m/z (%) = 131 (M^+, 2), 114 (10), 99 (9), 98 (6), 82 (28), 71 (100).

(1*R**, 2*R**)-(-)-N-(2-Chlorocyclohexyl)hydroxylamine **(41)** from **11** in chloroform. mp. 86 °C. $[\alpha]_D$ = -30.3 ° (c=0.6; CH_2Cl_2).
Anal. $C_6H_{12}ClNO$ (149.6) calcd. C 48.17 H 8.08 N 9.36; found C 47.82 H 7.91 N 9.78. ^{1}H NMR ($CDCl_3$): δ = 6.15 (br, NHOH), 4.02 (dt, J=10.4 Hz, 4.0 Hz, 1H, H-2), 2.72 (dt, 10.4 Hz, 4.0 Hz, 1H, H-1), 2.28 (m, 1H, H-3), 2.15 (m, 1H, H-6), 1.78 - .1.26 (m, 6H, H-3, H-4, H-5, H-6). ^{13}C NMR $CDCl_3$): δ = 66.3 (C-2), 61.0 (C-1), 36.3; 29.6; 25.9; 24.4 (C-3, C-4, C-5, C-6). MS (EI) : m/z (%) = 149 (M^+, 5), 151 (M^+, 2), 114 (9), 106 (3), 96 (3), 82 (3), 81 (16), 79 (5), 73 (4), 72 (100), 68 (14), 67 (5), 59 (23), 56 (11), 55 (6), 54 (6), 63 (7), 46 (10), 43 (9), 42 (5), 41 (22), 39 (13), 30 (4), 28 (7). MS (CI) : m/z (%) = 150 (M^++1, 42), 152 (M^++3, 14), 134 (100), 136

(31), 132 (16), 114 (10), 99 (8), 98 (100), 96 (12). **IR** (KBr) : ν = 3530, 3260, 2980, 2940, 2860, 1450, 1370, 1200, 1150, 1070, 1000, 950, 910, 850 cm^{-1}.

(1*R, 2*R**)-(-)-(2-Chlorocyclohex-4-en-1-yl)hydroxylamine (42)** from **39** and **1** in chloroform at -20 °C. $[\alpha]_D$ = -156 (c=1, $CHCl_3$).

Anal. $C_6H_{10}ClNO$ (147.6) calc. C 48.64 H 7.22 N 9.42; found C 48.82 H 6.83 N 9.49. ^{1}H NMR ($CDCL_3$): d = 5.62 (m, 2H, H-4, H-5), 4.45 (m, 1H, H-2), 3.70 (m, 1H, H-1), 2.3 - 2.8 (m, 4H, H-3, H-6). ^{13}C NMR ($CDCL_3$): d = 124.7, 123.4 (C-4, C-5), 60.3 (C-1), 53.5 (C-2), 33.9 (C-3), 25.4 (C-6). **MS** (EI) m/z (%) = 149/147 (M^+,4), 132/130 (4), 112 (10), 98 (28), 95 (34), 93 (100), 79 (36), 70 (40). **IR** (KBr)ν = 3300-3100 br, 3040, 3000, 2950-2900, 1655, 1550, 1500, 1450, 1120, 1010, 870 cm^{-1}.

N-(2-Methoxycyclohex-4-en-1-yl)-hydroxylamine (49) from **39** and **1** in methanol. Yield 20%.

^{1}H NMR ($CDCl_3$): δ = 5.43, 5.62 (m, 2H, H-4, H-5), 3.5 (m, 1H, H-2), 3.1 (m, 1H, H-1), 2.2 - 2.7 (m, 4H, H-3, H-6). ^{13}C NMR ($CDCl_3$): δ = 125.1, 123.6 (C-4, C-5), 76.1 (C-2), 60.7 (C-1), 56.5 (C-7), 36.2 (C-3), 29.9 (C-6).

N-(2-Chlorocycloheptyl)hydroxylamine (43) from **13** and **1** in isopropanol.

^{1}H NMR ($CDCl_3$): δ = 6.75 (br, NHOH), 4.08 (m, 1H, H-2), 2.90 (m, 1H, H-1), 2.0 - 1.0 (m,10H, H-3, H-4, H-5, H-6, H-7). ^{13}C NMR ($CDCl_3$): δ = 70.10 (C-1), 63.83 (C-2), 35.95 (C-7), 29.04 (C-3), 28.41 (C-6), 25.01 (C-4), 23.60 (C-5). **MS** (EI) : m/z (%) = 163 (M^+, 4), 146 (2), 128 (27), 112 (10), 95 (15), 72 (100), 56 (48).

N-(2-Chlorocyclooctyl)hydroxylamine (44) from **14** and **1** in isopropanol.

^{1}H NMR ($CDCl_3$): δ = 6.2 (br, NHOH), 4.26 (m, 1H, H-2), 3.10 (m, 1H, H-1), 2.2 - 1.2 (m, 12H, H-3, H-4, H-5, H-6, H-7, H-8). ^{13}C NMR ($CDCl_3$) : δ = 67.22 (C-1), 64.25 (C-2), 31.22 (C-8), 29.29 (C-3), 27.80 (C-7), 25.93 (C-4), 25.19 (C-6), 22.87 (C-5). **MS** (EI) : m/z (%) = 177 (M^+, 1), 175 (3), 158 (4), 147 (20), 140 (27), 113 (44), 112 (42), 81 (41), 67 (100), 55 (55), 41 (93).

Reduction of hydroxylamines with $LiAlH_4$ (method A)

10 mmol of hydroxylamine dissolved in 50 ml ether is added to 10 ml of 1 M $LiAlH_4$ in ether at -20 °C. The mixture is stirred at room temperature for 1 h and then 50 ml of aqueous 20% K-Na-tartrate solution is added. The aqueous layer is extracted with ether (3 x 20 ml) and the combined ether layers are dried with $MgSO_4$. The amine hydrochlorides are obtained on passing HCl gas into the ether solution.

Reduction of the hydroxylamines with $TiCl_3$ (method B)

5 mmol of hydroxylamine is dissolved in 20 ml of methanol. To this solution 8 ml of a 20% $TiCl_3$ solution in 15% hydrochloric acid are added at room temperature. The mixture is stirred for 15 minutes, then 40 ml of 20%

soda lye are added and the amine is extracted into methylene chloride. The amines are precipitated as hydrochlorides by passing HCl-gas through the solution.

Reduction of the hydroxylamines with $LiBH_4/Me_3SiCl$ (method C)

Hydroxylamine (5 mmol) dissolved in 5 ml of THF is added to 10 mmol of $LiBH_4$ suspended in 5 ml of THF, that contains 20 mmol of Me_3SiCl. The mixture is stirred at 60 °C for 24 h. After cooling, 10 ml of methanol are added and the solvents are distilled off. To the residue 20 ml of 20% KOH are added and the amine is extracted into methylene chloride. After drying with $MgSO_4$ the amine can be obtained as hydrochloride by passing HCl gas through the solution.

(+)-2,4,4-Trimethylpent-1-en-3-ylamine hydrochloride (30). Yield 86% (method A),, colourless crystals, mp. 270 °C (decomp.). $[\alpha]_D$ = + 21.6 ° (c=1.67; MeOH).
^{1}H NMR (CD_3OD): δ = 5.34 (s, 1H, H-1), 5.15 (s, 1H, H-1), 3.61 (s, 1H, H-3), 1.98 (s, 3H, H-6), 1.14 (s, 9H, t-Bu). ^{13}C NMR (CD_3OD): δ = 142.21 (C-2), 118.81 (C-1), 66.64 (C-3), 35.30 (C-4), 27.65 (C-5), 23.19 (C-6). MS (EI) : m/z (%) = 128 (M^+-HCl, 0.2), 112 (2), 71 (23), 70 (100), 43 (18), 36 (11). IR (KBr) : ν = 3050, 2950, 1650, 1600, 1520, 1370, 1260, 1100, 800 cm^{-1}.

(3*S*)-(+)-4,4-Dimethylpent-1-en-3-ylamine hydrochloride (31). Yield 63% (method A).. Colourless crystals, mp. 178 °C (decomp.). $[\alpha]_D$ = + 42.5 ° (c=0.4; MeOH).
^{1}H NMR (CD_3OD): δ = 5.91 (m, 1H, H-2), 5.46 (dd, J=10.6 Hz, 6.5 Hz, 1H, H-1), 3.49 (d, J=6.5 Hz, 1H, H-3), 1.02 (s, 9H, t-Bu). ^{13}C NMR (CD_3OD): δ = 132.78 (C-2), 122.45 (C-1), 64.67 (C-3), 34.01 (C-4), 26.27 (C-5). MS (EI) : m/z (%) = 149 (M^+, 0.05), 113 (0.2), 98 (4), 57 (11), 56 (100), 36 (13). IR (KBr) : ν = 3400, 2990, 1600, 1520, 1380, 1270, 1100, 940, 800 cm^{-1}.N-benzoylated amine, recrystallized from $CHCl_3$/hexan 1:4, mp. 115 °C.

(1*S*)-(-)-Cyclopent-2-en-1-ylamine hydrochloride (32). Yield, 77% (method A), 62% (method B). Colourless crystals, mp. 181 °C (decomp.). $[\alpha]_D$ = - 104.5 ° (c=0.9; MeOH).
Anal. $C_5H_{10}ClN$ (119.6), calcd. C 50.22 H 8.43 N 11.71; found C 50.00 H 8.45 N 11.74. ^{1}H NMR (CD_3OD): δ = 6.22 (m, 1H, H-2), 5.80 (m, 1H, H-3), 4.29 (m, 1H, H-1), 2.65 - 1,75 (m, 4H, H-4, H-5). ^{13}C NMR (CD_3OD) : δ = 140.15 (C-2), 128.08 (C-3), 58.33 (C-1), 32.32 (C-5), 29.19 (C-4). MS (EI) : m/z (%) = 119 (M^+, 0.02), 83 (21), 82 (100), 80 (8), 67 (13), 56 (23), 36 (46). IR (KBr) : ν = 3450, 3000, 2600, 2030, 1600, 1500, 1460, 1390 cm^{-1}.N-benzoylated amine: mp. 69 °C (ether/pentane 1 : 3).
N-phthaloylated amine: a) from **32** and phthalic anhydride: mp. 74 °C (ether/pentane 1 : 2),$[\alpha]_D$ = -27.0° (c=1; $CHCl_3$). b) from **52** and potassium tert.butoxide in acetonitrile: mp. 74 °C, $[\alpha]_D$ = -25.8° (c=0.3, $CHCl_3$).

Cyclohex-2-en-1-ylamine hydrochloride (33). Yield 67% (method A), 35% (method B). Colourless crystals. mp. 126 °C (decomp.).$[\alpha]_D$ = -65.2° (c=0.5; $CHCl_3$).
^{1}H NMR (CD_3OD): δ = 6.11 (m, 1H, H-2), 5.65 (m, 1H, H-3), 3.87, (m, 1H, H-1), 2.06 - 1.75 (m, 6H, H-4, H-5, H-6), ^{13}C NMR (CD_3OD): δ = 135.7 (C-2), 122.8 (C-3), 47.4 (C-1), 27.3 (C-4), 24.5 (C-6), 19.1 (C-5). IR (KBr) ν = 3600, 2500, 3050, 2980, 2940, 2860, 1500, 1450, 1440, 1370, 1250, 1190, 1170, 1070, 920, 850 cm^{-1}.
N-acetylated amine: mp. 80 °C (ether/pentane 1:3).

(-)-2-Methylcyclohex-2-en-1-ylamine hydrochloride (34). Yield 64% (method A). mp. 247 °C (decomp.). $[\alpha]_D$ = - 31.6 ° (c=2.5; MeOH).
^{1}H NMR (CD_3OD): δ = 5.81 (m, 1H, H-3), 3.66 (m, 1H, H-1), 2.03 - 1.71 (m, 6H, H-4, H-5, H-6), 1.79 (dd, J=1.5 Hz, 0.6 Hz, 3H, CH_3). ^{13}C NMR (CD_3OD): δ = 131,0 (C 3),.129.1 (C-2), 50.9 (C-1), 28.4 (C-4), 25.4 (C-6), 20.6 (C-7), 18.6 (C-5). IR (KBr) : ν = 3500, 3200, 3040, 2985, 2860, 1510, 1450, 1375, 1240, 1200 cm^{-1}.

(1*S*)-(-)-Cyclohept-2-en-1-ylamine hydrochloride (35). Yield 77% (method A). Colourless crystals. mp. 186 °C (decomp.). $[\alpha]_D$ = -14.5 ° (c=1.04; MeOH).
Anal. $C_7H_{14}ClN$ (147.7) calcd. C 56.94 H 9.56 N 9.49; found C 56.96 H 9.57 N 9.32. ^{1}H NMR (CD_3OD): δ = 6.0 (m, 1H, H-2), 5.68 (m, 1H, H-3), 4.00 (m, 1H, H-1), 2.30 - 1.30 (m, 8H, H-4, H-5, H-6, H-7). ^{13}C NMR (CD_3OD) : δ = 135.42 (C-2), 130.71 (C-3), 53.09 (C-1), 33.03 (C-7), 29.48 (C-4), 29.07 (C-6), 26.87 (C-5). MS (EI) : m/z (%) = 111 (M^+-HCl, 21), 94 (17), 83 (32), 82 (100), 56 (33), 36 (51). IR (KBr) : ν = 3500, 3000, 1600, 1540, 1450, 1410, 1000, 850, 675 cm^{-1}.
N-acetylated amine: mp. 91 °C (ether/pentane 1:1).

(1*S*)-(+)-Cyclooct-2-en-1-ylamine hydrochloride (36). Yield 72%. Colourless crystals. mp. 246 °C (decomp.). $[\alpha]_D$ = + 75.5 ° (c=0.62; MeOH).

Anal. $C_8H_{16}ClN$ (161,7), calcd. C 59.43 H 9.98 N 8.66; found C 59.19 H 9.86 N 8.52. ^{1}H NMR (CD_3OD) : δ = 5.90 (m, 1H, H-2), 5.49 (m. 1H, H-3), 4.20 (m, 1H, H-1), 2.3 - 1.4 (m, 10H, H-4, H-5, H-6, H-7, H-8). ^{13}C NMR (CD_3OD): δ = 133.07 (C-2), 126.17 (C-3), 48.89 (C-1), 33.95 (C-8), 28.26 (C-4), 25.69 (C-7), 25.30 (C-5), 23.39 (C-6). MS (EI) : m/z (%) = 125 (M^+-HCl, 15), 108 (7), 96 (5), 82 (100), 69 (12), 56 (28), 36 (29). IR (KBr) :ν= 3400, 2940, 2580, 1600, 1510, 1450, 1400 cm^{-1}.

N-acetylated amine: mp. 104 °C ($CHCl_3$/ hexane 1:4).

N-trifluoracetylated amine: mp. 130 °C (ether/pentane 1:2).

(1*S*)-(+)-Cycloocta-2,5-dien-1-ylamine hydrochloride 37. Yield 63%. Colourless crystals, mp. 216 °C (decomp.). $[\alpha]_D$ = + 108.11 ° (c=0.4; MeOH).
Anal. $C_8H_{14}ClN$ (159.7) calcd. C 60.18 H 8.84 N 8.77; found C 59.23 H 9.00 N 8.70. ^{1}H NMR (CD_3OD) : δ = 5.96 (m 1H, H-3), 5.75 (m, 1H, H-5), 5.52 (m, 1H, H-6), 5.27 (m, 1H, H-2), 4.45 (m, 1H, H-1), 2.94 (m, 2H, H-4), 2.62 (m, 1H, H-7), 2.15 (m, 1H, H-7), 1.89 (m, 1H, H-8), 1.53 (m, 1H, H-8). ^{13}C NMR (CD_3OD) : δ = 133.63 (C-2), 130.64 (C-3), 128.95 (C-6), 125.86 (C-5), 50.13 (C-1), 30.27 (C-8), 28.64 (C-4), 23.93 (C-7). MS (EI) : m/z (%) = 124 (M^+-HCl, 1), 122 (5), 108 (19), 95 (57), 80 (21), 69 (100), 56 (33), 43 (35), 36 (65). IR (KBr) : ν = 3440, 2900, 2000, 1490, 1420, 1130 cm^{-1}. N-acetylated amine: mp. 92 °C ($CHCl_3$/hexane 1:3).

Reduction of 40 by catalytical hydrogenation

5 mmol of **40** are dissolved in 5 ml of ethanol and 5 ml of 1 N hydrochloric acid. This solution is added to 50 mg of PtO_2 (prereduced) in 10 ml of 1 N hydrochloric acid and the mixture is stirred at room temperature for 24 h under hydrogen. The catalyst is filtered and the solvents are removed by destillation. The amine hydrochloride **50** is recrystallized from ethanol/ether 1:2.

(1*S*, 2*S*)-(-)-2-Chlorocyclopent-1-ylamine hydrochloride 50 Yield 82%. Colourless crystals, mp. 196 °C (decomp.). $[\alpha]_D$ = - 58.0 ° (c=0.5; MeOH).
Anal. $C_5H_{11}Cl_2N$ (156.0) calcd. C 38.48 H 7.10 N 8.98; found C 38.45 H 7.08 N 9.02. ^{1}H NMR (CD_3OD) : δ = 4.34 (m, 1H, H-2), 3.64 (m, 1H, H-1), 2.5 - 1.5 (m, 6H, H-3, H-4, H-5). ^{13}C NMR (CD_3OD) : δ = 61.43 (C-1), 61.24 (C-2), 35.46 (C-5), 30.68 (C-3), 21.88 (C-4). MS (EI) : m/z (%) = 121 (M^+-HCl, 2), 119 (M^+-HCl, 5), 92 (1), 90 (6), 85 (4), 67 (6), 56 (100), 36 (59). IR (KBr) : ν = 3400, 2980, 1600, 1500, 1400, 1140 cm^{-1}.
N-phthaloylated amine: mp. 124 °C (ether/pentane 1:1). $[\alpha]_D$ = +23.8° (c=0.2; MeOH).

Determination of optical yields (ee)

Method 1: (1*S*)-Camphor-10-sulfonyl chloride (1.1 mmol) is dissolved in 2 ml of CCl_4 and is added to a solution of 1 mmol amine hydrochloride and 50 mg of N,N-dimethylaminopyridine in 2 ml of pyridine at 60 °C. The mixture is stirred at 60 °C until all the educts had disappeared. After filtration the mixture is evaporated, the residue is taken up in 5 ml of CCl_4 and then is washed with 2 ml of 0.5 N hydrochloric acid, saturated solutions of $KHCO_3$ in water and 5% brine, dried ($MgSO_4$) and evaporated. The residue was dissolved in $CDCl_3$ and an aliquot was injected into GC or investigated by NMR.

Method 2: (2*S*)-2-Methoxy-2-phenyl-3,3,3-trifluoropropionic acid chloride (MTPA chloride) is prepared according to the literature[13a] and distilled. The reactions of MTPA-chloride with the amine hydrochlorides are carried out as described in the literature[13b].

Determination of the absolute configurations of the allylamines

The amine hydrochlorides are acylated by benzoyl chloride or acetic anhydride. These amides (10 mmol) are dissolved in 20 ml of dry methanol and cooled to -78 °C. Ozone is passed through this solution until there is no more amide detectable (tlc). After evaporation, 5 ml of formic acid and 4 ml of 30% H_2O_2 are added. The mixture is slowly heated and refluxed for 30 minutes. The mixture is evaporated to dryness. The residue is dissolved in 5 ml of dry methanol and an ethereal solution of diazomethane is added till a yellow colour persists. The excess of diazomethane is destroyed by hydrochloric acid, the mixture is evaporated and the amino acid derivatives are recrystallized. The absolute configurations are derived from the comparison of optical rotations so obtained with published values.

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