Enantioselective Preparation of (2*R*)- and (2*S*)-Azetidine-2-carboxylic Acids

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The enantiomerically pure amino ketones **13** and **31** were prepared starting from the commercially available amino diol **9** and D-serine (**21**), respectively. Irradiation afforded highly functionalized azetidinols **15** and **33** in a fully stereoselective manner and in high yields, whereas *N*-phenacylglycine **5** gave only the secondary products of a *Norrish-Type-II* cleavage. Compounds **15** and **33** were converted into (2*R*)- and (2*S*)-azetidine-2-carboxylic acids **20** and **37**, respectively, in several steps. The influence of H-bonds on efficiency, chemo-, and stereoselectivity of the photochemical cyclization of **5**, **13**, and **31** was discussed. It was shown that conformational analysis of corresponding triplet biradicals is often valuable in understanding the photochemistry of amino ketones.

Introduction. – The understanding of physiological effectivity of naturally occurring peptides and the synthesis of new peptide drugs are central problems of current chemistry. In this context, peptide conformation and the rules govering it are of crucial importance. One of the most common synthetic concepts involves the incorporation of unnatural amino acids into peptides in order to goal-directed change of peptide conformation. This approach has proved to be very successful as shown by several publications (*e.g.*, [1][2]). Therefore, there is indeed a large demand for new, highly stereoselective syntheses of unnatural amino acids.

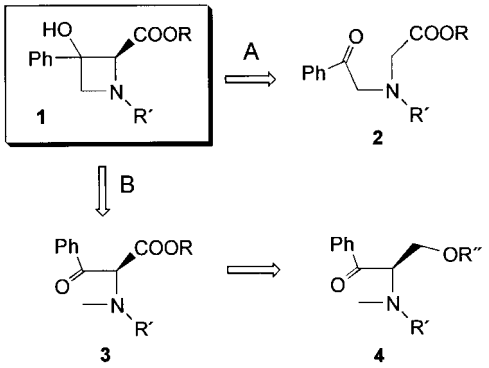
Recently, we have published photochemical synthesis of highly functionalized prolines following both the concepts of auxiliary control [3] and substrate control [4]. In the present paper, we report on two fully stereoselective synthetic routes leading to both (2*R*)- and (2*S*)-azetidine-2-carboxylic acids from commercially available chirons. The key step of our synthesis is a stereoselective photochemical ring closure of an amino ketone. Some recent works about thermal synthesis of azetidine-2-carboxylic acids confirm the great interest in this problem [5][6].

Results and Discussion. – *Retrosynthetic Approach*. In continuation of our previous work on stereoselective photocyclization of ketones, we were interested in a photochemical synthesis of azetidine-2-carboxylic acids. Although several photocyclizations of amino ketones giving azetidinols were published [7][8] nothing is known about an appropriate synthesis of azetidine-2-carboxylic acids. This fact is surprising in view of the cited successful azetidine ring-closure reactions. Below, we will discuss a probable reason.

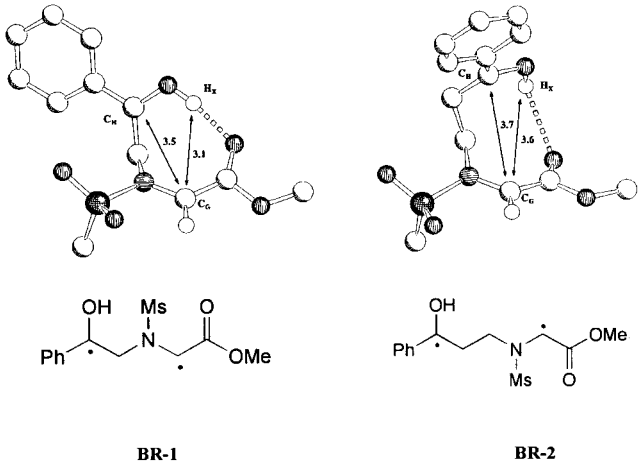
Firstly, we have defined protected azetidine-2-carboxylic acids **1** as target structure of ring closure. Two routes of ring closure are possible: *via Route A*, the C(2)–C(3) bond of the azetidine ring is formed, whereas *Route B* leads to the formation of the bond between C(3) and C(4) (*Scheme 1*). In analogy to our previous photochemical

proline synthesis [3][4], it was very likely to build up the four-membered ring according to *Route A*. This route involves an intramolecular photochemical alkylation of a *N*-phenacylglycine **2**.

Scheme 1. *Retrosynthetic Approach of Azetidine-2-carboxylic Acids*



Whereas the cyclization of the homologues *N*-(2-benzoylethyl)glycines was very successful [3][4], we have found that methyl *N*-phenacyl-*N*-tosylglycinate **5** (*cf. Scheme 2*) had a very low photoreactivity in aprotic solvents. Long irradiation times afforded only polymeric decomposition products. As well-known, low decay quantum yields of alkyl aryl ketones are due to predominant H back-transfer of the corresponding hydroxy biradicals [9]. We wondered, of course, why **5** undergoes H back-transfer exclusively in aprotic solvents. An answer could be obtained by looking at the low energy conformer of the triplet biradicals shown in *Fig. 1*.



BR-1 **BR-2**

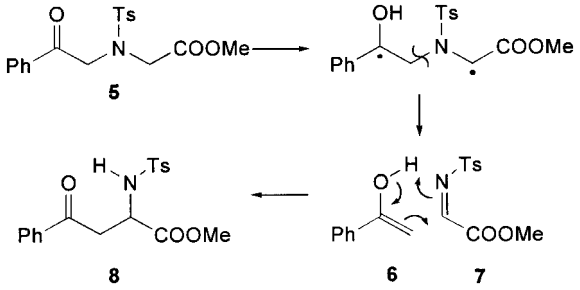
Fig. 1. *Low-energy conformers of triplet biradicals* **BR-1** *and* **BR-2**

To simplify quantum-chemical calculations, we replaced the Ts groups by Ms groups, respectively. **BR-1** represents an analogue of triplet biradical formed upon irradiation of **5**, whereas **BR-2** is derived by the homologue *N*-[2-(benzoyl)ethyl]gly-

cine. The geometries shown in *Fig. 1* were obtained by systematic conformational analysis at semiempirical UHF/PM3 level. All H-atoms except those being transferred upon irradiation (H_X) and those bonded on the glycine radical centres C_G are omitted in *Fig. 1*. It is seen that both **BR-1** and **BR-2** are stabilized by strong intramolecular H-bonds. However, the effects of these H-bonds are not identical for **BR-1** and **BR-2** due to the different distances between the radical centres. In **BR-1**, the distance between the H-atom H_X and the glycine radical centre C_G is remarkably smaller than the distance between the two radical centres C_G and C_H. On the other hand, the biradical **BR-2** is fixed in a conformation with nearly equal H_X-C_G and C_G-C_H distances. Considering the longer range of a p_Z orbital compared with an s orbital, it is understandable that **BR-1** should undergo H back-transfer exclusively, whereas **BR-2** should preferentially undergo cyclization.

The H back-transfer can be suppressed by irradiation in protic solvents. Indeed, the photoreactivity of **5** was highly increased in *t*-BuOH as solvent. Admittedly, the decay of the reactant stops after some time, indicating that products were formed which also absorb light at the irradiation wavelength. Upon chromatographic separation of the reaction mixture, we have obtained acetophenone and methyl 4-oxo-4-phenyl-2-(tosylamino)butanoate **8**. Compound **8** was identified unambiguously by an independent synthesis which we have described recently [4]. Formation of **8** can be explained by an aldol-like reaction of the primary products of *Norrish-Type-II* cleavage. We assume that enol **6** reacts with the highly reactive 2-(tosylimino)acetate **7** in the solvent cage to yield **8**. If either **6** or **7** escapes from the solvent cage or enol **6** is converted into the much more stable ketone, **7** should undergo less selective decomposition and acetophenone remains (*Scheme 2*). Enol **6** as primary product of *Norrish-Type-II* cleavage was already described [10].

Scheme 2

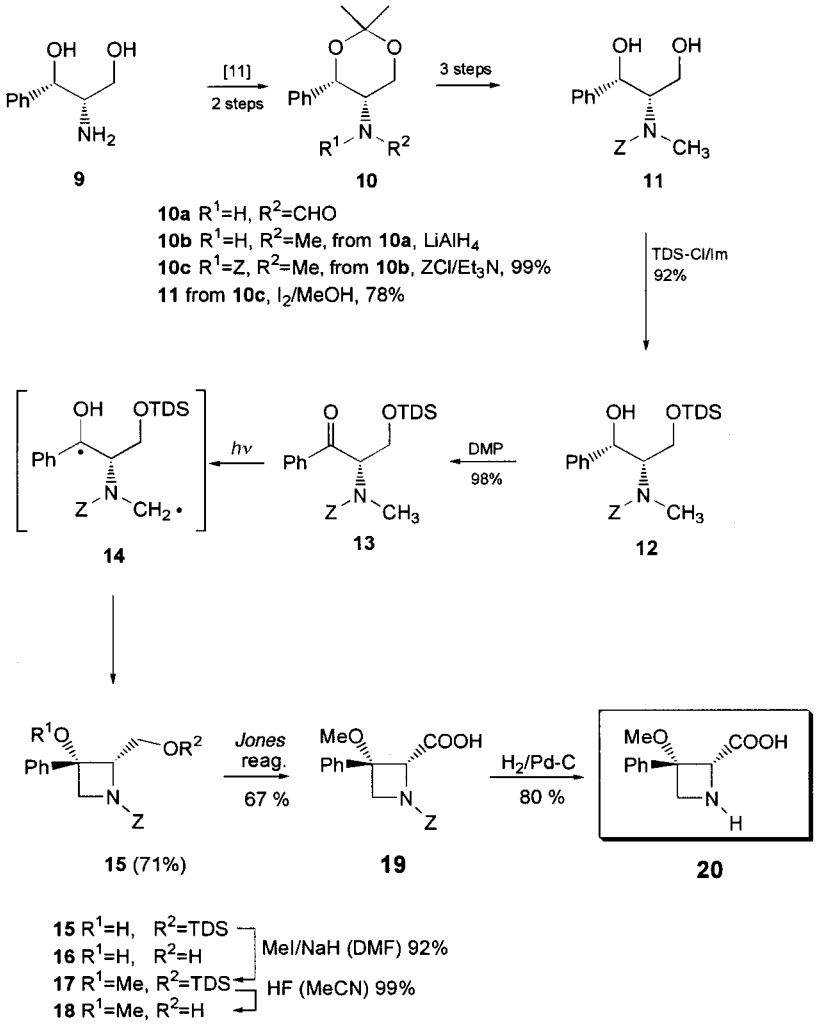


Obviously, *Norrish-Type-II* cleavage of the biradical formed from **5** is the only reaction taking place, if H back-transfer is suppressed. In our opinion, this is the main reason why nothing was reported on the preparation of azetidine-2-carboxylic acids *via Route A*.

Following *Route B* leads to *β*-keto ester **3** which should not be obtainable in enantiomerically pure form due to rapid enolization. Therefore, we chose a lower oxidation state in the form of 2-hydroxy-1-aminoethyl ketone **4**. We will now describe the syntheses of both (2*R*)- and (2*S*)-azetidine-2-carboxylic acids *via* **4** and its enantiomer.

(2R)-Azetidine-2-carboxylic Acids. Ketone **4** contains the framework of a commercially available and cheap chiral synthon, the amino diol **9** (*Scheme 3*). To prepare **4**, the following synthetic steps must be followed: *1*) *N*-methylation, *2*) selective protection of the primary OH group, and *3*) oxidation of the secondary OH group.

Scheme 3



Thus, **9** was converted into 5-(formylamino)-1,3-dioxane **10a** and then reduced with $LiAlH_4$, according to literature procedures, giving **10b** [11]. After introduction of the (benzyloxy)carbonyl group (Z) and opening of the ring, the diol **11** was obtained in good yields.

Selective protection of the primary OH group using (thexyl)(dimethyl)silyl chloride (TDS-Cl; thexyl = 1,1,2-trimethylpropyl) and subsequent oxidation with *Dess-Martin* periodinane (DMP) affords ketone **13**.

Upon irradiation of **13** in CH_2Cl_2, the excited C=O group abstracts a H-atom from the *N*-Me group leading to the biradical **14** which undergoes cyclization to the azetidinol **15** in excellent yield. Moreover, the ring closure occurs in a fully diastereoselective manner giving a *cis*-product with respect to the OH and $TDSOCH_2$ group. Another isomer could not be detected. Products of the *Norrish-Type-II* cleavage were neither detectable. Below, we will discuss the reasons for this surprising selectivity. The relative configuration of **15** was established by NOE experiments. To convert **15** into the target structure **1** we attempted to oxidize the primary OH group, after deprotection. Unfortunately, treatment of the *N*-protected amino diol **16** with various oxidation agents always provided several products. Obviously, oxidative ring cleavage occurs due to the unprotected tertiary alcohol. To avoid this, the tertiary OH group was methylated to **17**, followed by desilylation yielding the 2-(hydroxymethyl)azetidine **18** in nearly quantitative yields. Several oxidation methods were tested to convert the CH_2OH group into a COOH group. The best yield (67%) for carboxylic acid **19** was accomplished using *Jones* reagent (H_2SO_4/CrO_3) which has been applied in a similar system recently investigated by *Hanessian et al.* [5]. Our target compound, the *N*-deprotected amino acid **20**, was achieved by cleavage of the Z group upon catalytic hydrogenation (*Scheme 3*).

(2S)-Azetidine-2-carboxylic Acids. Successful synthesis of (2*R*,3*S*)-3-methoxy-3-phenylazetidine-2-carboxylic acid (**20**) encouraged us to develop a synthetic route to the corresponding (2*S*)-derivative which is an analogue of the naturally occurring (2*S*)-azetidinecarboxylic acid [12]. Unfortunately, the enantiomer of amino diol **9** is not commercially available[1]). Therefore, we had to find another chiral synthon. The unexpensive D-serine **21** contains a suitable pattern of substituents so that it was chosen as the starting reactant.

Firstly, we protected all three functional groups with orthogonal protecting groups. Thus, *N*,*C*-protected D-serine **22** was prepared according to a known procedure [14], and finally the OH group was silylated with TDS-Cl leading to **23** (*Scheme 4*).

Attempts to introduce the *N*-Me group at the stage of **23** failed. The action of strong bases upon **23**, required for deprotonation of the N-atom, afforded only decomposition products. Therefore, we prepared the *N*,*O*(3)-diprotected compound **26** in three steps. Reduction of **23** gave the optically active serinol **24** which was subsequently oxidized to the aldehyde **25**. Attempts to convert **23** into **25** directly using DIBAH were unsuccessful. It should be noted that **24** retained its optical activity. Indeed, this would be expected if 1,3 silyl migration takes place as described for other monoprotected diols [15].

The addition of PhMgBr to the aldehyde **25** proceeds with high stereoselectivity giving the *threo*-compound **26**, with the same relative configuration as the products derived from amino diol **9**, unambiguously established upon comparison of the NMR spectra and the optical rotations of **11** and **12** with the appropriate data of analogous products prepared from **26** (*vide infra*).

To prepare the enantiomer of **11**, the *N*-Me group must be introduced. Attempts using **26** failed due to the unprotected secondary OH group. Protection with the

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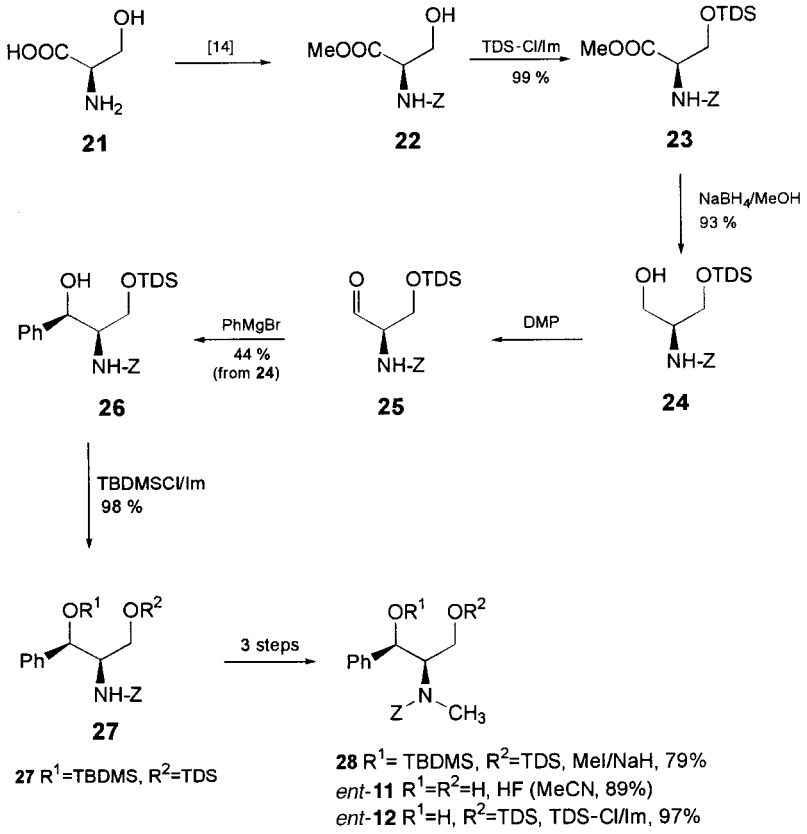
[1]) Amino diol **9** is a by-product of industrial synthesis of the antibiotic chloromycetine. The enantiomer of **9** is converted to a drug, whereas **9** remains [13].

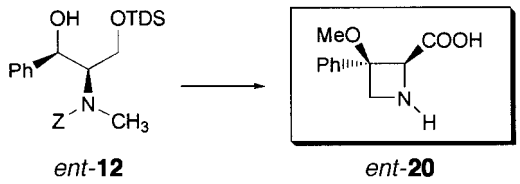
Scheme 4



TBDMS ((*t*-Bu)Me_2Si) group afforded **27**, which was *N*-methylated to give *ent*-**11** in good yields. Subsequent deprotection of both OH groups, followed by silylation of the primary OH group, finally gave compound *ent*-**12**. The following steps to the (2*S*,3*R*)-3-methoxy-3-phenylazetidine-2-carboxylic acid (*ent*-**20**) are analogous to those described for the corresponding (2*R*)-enantiomer (*Scheme 5*).

Mechanism and Stereoselectivity. The cyclization of the chiral ketones **13** and *ent*-**13** to the azetidinols **15** and *ent*-**15**, respectively, is remarkable in three different respects: *1*) The cyclization yield is high (71% isolated product), and no products of *Norrish*-

Scheme 5



Type-II cleavage could be isolated. *2*) The diastereoselectivity of the cyclization is very high (> 95%). *3*) The quantum yield of decay of **13** and *ent*-**13** amounts nearly unity within experimental inaccuracies.

These results were surprising with respect to the otherwise well-known behavior of alkyl aryl ketones. Normally, the irradiation of such ketones gives a considerable amount of *Norrish-Type-II* cleavage products, and often the cleavage dominates the cyclization [16]. On the other hand, it was observed that the introduction of a heteroatom into the side chain of the ketone increases the cyclization yield [8][17]. This effect can be explained by the conjugation of a heteroatom lone pair with the adjacent radical centre (see **B** in *Fig. 2*). The resulting conformation lacks an essential prerequisite for a *Norrish-Type-II* cleavage, the overlap of *both* radical p_z orbitals with the hybrid orbitals of the cleaving bond (see **A** in *Fig. 2*).

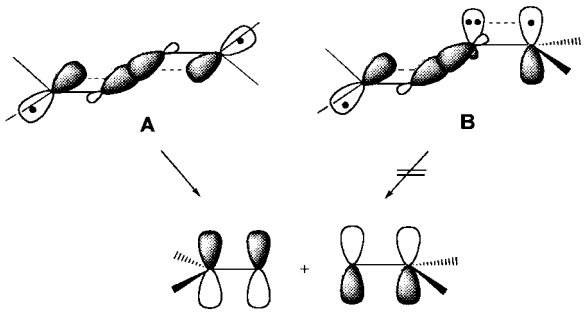


Fig. 2. *Stereoelectronic requirements of* Norrish-Type-II *cleavage* (**A**) *and circumstances in 1,4-biradicals containing a heteroatom* (**B**)

The very high quantum yield and diastereoselectivity have probably the same origin. We assume a strong H-bonding in the triplet biradicals **14** and *ent*-**14**. This bond holds the H-atom far away from the methylene-radical centre and thus prevents the back-transfer of the H-atom which would lead to the starting molecule. It is generally accepted that quantum yields of decay which are considerably smaller than unity result from an efficient H back-transfer of the triplet biradical. Furthermore, it is known that this process is prevented upon irradiation in highly polar solvents in which H-bonds of the OH radical with the solvent are formed. To support this hypothesis, we performed a conformational analysis of biradical **14** on a semiempirical level (UHF/PM3; for simplification of calculations, Z and TDS groups were replaced by CHO and Me, resp.). A low-energy conformer is reproduced in *Fig. 3*. One can see that the H-bonding is also the reason for the observed high diastereoselectivity. Only the diastereoisomer with *cis*-orientation of the OH and the $TDSOCH_2$ group was obtained.

Conclusion. – In this work, the synthesis of enantiomerically pure acetidine-2-carboxylic acids **20** and *ent*-**20** with (2*R*)- and (2*S*)-configuration, respectively, was described. We pursued two aims in our project. On one hand, we presented a complex synthetic route to highly functionalized molecules involving a photochemical key step. On the other hand, interesting discoveries concerning the photochemical behavior of alkyl aryl ketones were made. It was shown that H-bondings at the stage of triplet

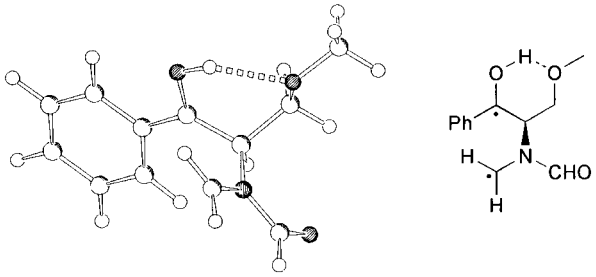


Fig. 3. *Low-energy conformer of triplet biradicals, analogous to* **14**

biradicals have an important influence on success or failure of a planned photocyclization. The results can be both drastically increasing (**13** and *ent*-**13**) and decreasing (**2**) quantum yields of decay. Furthermore, a very high diastereoselectivity of ring closure can be the consequence as we have described previously [3][4][18][19]. Finally, it should be noted that α-substituted *N*-acyl-*N*-methylamino ketones seem to be very suitable reactants for the synthesis of azetidines. Soon, we will report on further application of the concept.

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Experimental Part

General. TLC: alumina sheets with silica gel *60* F_{254} (*Merck*), detection by UV light. Flash chromatography (FC): silica gel, 40–63 μm (*Merck*). M.p.: *Boetius* micro melting-point apparatus (*Wagema*), uncorrected. Optical rotations: *DIP 370* (*Jasco*); *d* 10 cm. UV: *Uvikon 930* (*Kontron*). IR: *Perkin-Elmer-881*, solids as KBr pastills, oils on NaCl crystals as film. NMR: *Bruker DPX300* (^{1}H: 300 MHz, ^{13}C: 75.5 MHz), internal reference Me_4Si (= 0 ppm). EI-MS: *Hewlett-Packard 5995 A*, 70 eV at 293–593 K. *Photochemistry:* prep. irradiations with a 150-W high-pressure Hg-arc lamp (*Hanau*), anal. irradiations with a 500-W high-pressure Hg-arc lamp (*OSRAM HBO-500*), UV cuvet 1 × 1 cm, and filter *WG 295* (*Schott*).

Calculations. Semiempirical calculations were performed using the program MOPAC7 [20], the PM3 hamiltonian [21], and the spin-unrestricted *Hartree-Fock* method (UHF).

Methyl N-*Phenacyl*-N-*tosylglycinate* (**5**). Compound **5** was prepared in analogy to the procedure described by *Fuhrmann et al.* [8] from methyl tosylglycinate and phenacyl bromide. Yield 65%. M.p. 93–95°. TLC (CH_2Cl/MeOH 100:2): R_f 0.6. IR: 1752 (CO), 1705 (CO), 1345 (SO_2, sym.), 1155 (SO_2, asym.). ^{1}H-NMR ($CDCl_3$): 2.35 (*s*, 3 H); 3.56 (*s*, 3 H); 4.15 (*s*, 2 H); 4.91 (*s*, 2 H); 7.08–7.85 (*m*, 9 H). ^{13}C-NMR ($CDCl_3$): 21.5 (Me); 48.0 (CH_2); 52.1 (Me); 52.8 (CH_2); 127.3, 127.9, 128.8, 129.5, 133.9, 134.6, 136.6, 143.6 (arom. C); 169.4 (CO); 193.4 (CO). EI-MS: 302 (6, [*M* – COOMe]$^+$), 256 (56, [*M* – PhCO]$^+$), 228(11), 206(28), 155 (50, Ts$^+$), 105 (50, PhCO$^+$), 91(100), 77(67).

*Methyl (*RS*)-4-Oxo-4-phenyl-2-(tosylamino)butanoate* (**8**). Compound **5** (0.5 g, 1.4 mmol) was irradiated in *t*-BuOH until the reactant had disappeared. After removal of the solvent *in vacuo*, the residue was purified by FC (CH_2Cl_2/MeOH 100:2): 0.1 g (20%) of **8**. Colorless needles. TLC, IR, MS, and NMR data: identical to those reported in [4].

*(4*S*,5*S*)-5-[(Benzyloxycarbonyl)(methyl)amino]-2,2-dimethyl-4-phenyl-1,3-dioxan* (**10c**). Compound **10b** (9.86 g, 44.62 mmol) was dissolved in 150 ml of CH_2Cl_2 and 5.4 ml (1.2 equiv.) of Et_3N were added. After cooling to 0°, 7.9 ml of $PhCH_2OCOCl$ were added. After stirring at r.t. for 3 h, the mixture was washed successively with 50 ml of H_2O, 50 ml of dil. HCl, and 2 × 50 ml of H_2O. Drying ($MgSO_4$) and evaporation of the solvent *in vacuo* led to 16.7 g (99%) of **10c**. Pale-yellow oil. TLC (CH_2Cl_2/MeOH 100:1): R_f 0.4. IR: 2942, 1695 (C=O), 1451, 1381, 1204, 1153, 698. ^{1}H-NMR ($CDCl_3$): 1.53–1.67 (*m*, 6 H); 3.05; 3.17 (*s*, 3 H); 4.00 (*dd*, *J* = 12.5, 1.5, 1 H); 4.29–4.63 (*m*, 2 H); 4.86 (*d*, *J* = 12.5, 1 H); 4.97 (*d*, *J* = 12.5, 1 H); 5.14–5.31 (*m*, 1 H); 7.06–7.39 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$): 19.0, 19.1 (Me); 29.2 (Me); 32.5; 33.1 (Me); 50.4; 50.7 (CH); 63.7; 64.0 (CH_2); 66.7; 67.1 (CH_2); 99.4 (C_q); 125.0, 125.4, 125.7, 127.0, 127.5, 128.0, 128.4, 128.6, 136.6, 137.5, 138.2, 138.4 (arom. C); 156.0,

156.9 (CO). (Most of the signals appear twice due to hindered rotation around the N–CO bond.) EI-MS: 28(12), 43(16), 65(13), 91 (100, $PhCH_2^+$), 100(24), 146(14), 191(8).

(1S,2S)-2-[(Benzyloxycarbonyl)(methyl)amino]-1-phenylpropane-1,3-diol (**11**). Compound **10c** (23.73 g, 66.82 mmol) was dissolved in a soln. of I_2 in MeOH (1 g/100 ml) and stirred at 40° for 2 h. The reaction course is monitored by TLC (CH_2Cl_2/MeOH 100:1). After complete disappearance of **10c**, the soln. was evaporated *in vacuo* and the residue redissolved in CH_2Cl_2 (100 ml). The soln. was washed with an aq. soln. of $NaHCO_3$/$Na_2S_2O_3$ (25 g of $Na_2S_2O_3$ in 100 ml of sat. $NaHCO_3$ soln.), dried, and evaporated *in vacuo:* 16.62 g (79%) of **11**. White solid. M.p. 77–79°. TLC (CH_2Cl_2/MeOH 10:1): R_f 0.4. $[\alpha]_D = +91.64$ ($c = 1$, CH_2Cl_2, 20°). IR: 3423 (OH), 1669 (C=O), 1333, 1160, 698. ^{1}H-NMR (CD_3OD): 2.97; 3.01 (*s*, 3 H); 3.41–3.50 (*m*, 1 H); 3.60–3.72 (*m*, 1 H); 4.25–4.41 (*m*, 1 H); 4.72–4.83 (*m*, 1 H); 5.08 (*s*, 2 H); 7.26–7.37 (*m*, 10 H). ^{13}C-NMR (CD_3OD): 29.0 (br., Me); 60.4 (CH_2); 65.4 (br., CH); 68.1; 68.2 (CH_2); 73.2; 73.5 (CH); 127.7, 128.6, 128.8, 129.2, 129.4, 129.5, 138.1, 138.3, 143.8 (arom. C); 159.2, 159.3 (CO). (Some of the signals appear twice due to hindered rotation around the N–CO bond.) EI-MS: 42(15), 65(11), 74(41), 77 (20, Ph^+), 79(18), 91 (100, $PhCH_2^+$), 107(12).

(1S,2S)- and (1R,2R)-2-[(Benzyloxycarbonyl)(methyl)amino]-3-[(dimethyl)(1,1,2-trimethylpropyl)silyloxy]-1-phenylpropan-1-ol (**12** and *ent*-**12**, resp.). Compound **11** (*ent*-**11**) (2.29 g, 7.32 mmol), 0.98 g (2 equiv. of imidazole), and 1.44 (1.1 equiv.) of (dimethyl)(1,1,2-trimethylpropyl)silyl chloride (TDSCl) were dissolved in 5 ml of DMF, and the mixture was stirred for 3 h. Crushed ice (50 g) was added and the product extracted with 4×20 ml of Et_2O. The org. phase was separated, dried, and evaporated *in vacuo*. Traces of DMF were removed at < 1 torr. The product was purified by FC (CH_2Cl_2/MeOH 100:1): 3.24 g (97%) of **12** (*ent*-**12**). White solid. M.p. 53–56°. TLC (CH_2Cl_2/MeOH 100:1): R_f 0.5. $[\alpha]_D = +48.50$ ($c = 1$, CH_2Cl_2, 20°) (**12**), $[\alpha]_D = -41.35$ ($c = 1$, CH_2Cl_2, 23°) (*ent*-**12**). IR: 3406 (OH), 2958, 1700 (C=O); 1494, 1452, 1343, 1251, 1109, 832. ^{1}H-NMR ($CDCl_3$): −0.05–0.12 (*m*, 6 H); 0.75–0.90 (*m*, 12 H); 1.55–1.65 (*m*, 1 H); 2.76 (*s*, 3 H); 3.55–3.99 (*m*, 3 H); 4.90–5.21 (*m*, 3 H); 7.21–7.29 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$): −3.7 (Me); 18.5 (Me); 20.3 (Me); 25.0 (Me); 25.7 (C_q); 30.9, 34.1 (CH); 61.3 (CH_2); 67.2 (CH_2); 73.3 (CH); 125.9, 126.5, 126.6, 126.7, 126.8, 127.1, 127.4, 127.8, 127.9, 136.6, 142.0 (arom. C); 157.9 (CO). (Some of the signals appear twice due to hindered rotation around the N–CO bond). EI-MS: 59(7), 73(11), 75(11), 77 (8, Ph^+), 91 (100, $PhCH_2^+$), 130(7).

(2S)- and (2R)-2-[(Benzyloxycarbonyl)(methyl)amino]-3-[(dimethyl)(1,1,2-trimethylpropyl)silyloxy]-1-phenylpropan-1-on (**13** and *ent*-**13**, resp.). Compound **12** (*ent*-**12**) (3.00 g, 6.56 mmol) was dissolved in 50 ml of CH_2Cl_2, and 24.3 g (1 equiv.) of *Dess-Martin* periodinan [21] were added in portions. After stirring for 1 h, the mixture was diluted with 50 ml of Et_2O and washed with several portions of a soln. of $NaHCO_3$/$Na_2S_2O_3$ (25 g of $Na_2S_2O_3$ in 100 ml of sat. $NaHCO_3$ soln.), until a clear org. phase was obtained. After drying and evaporation, the residue was purified by FC (CH_2Cl_2): 1.75 g (60%) of **13** (*ent*-**13**). Stiffy oil. TLC (CH_2Cl_2): R_f 0.8. $[\alpha]_D = -68.48$ ($c = 1$, CH_2Cl_2, 23°) (**13**); $[\alpha]_D = +76.62$ ($c = 1$, CH_2Cl_2, 23°) (*ent*-**13**). IR: 2958, 1704–1689 (C=O), 1449, 1397, 1116, 697. ^{1}H-NMR ($CDCl_3$): −0.03–0.05 (*m*, 6 H); 0.71–0.83 (*m*, 12 H); 1.45–1.52 (*m*, 1 H); 2.77 (*s*, 3 H); 3.95 (*d*, $J = 6.8$, 1 H); 4.95–5.4 (*m*, 4 H); 7.17–7.35 (*m*, 8 H); 7.73 (*d*, 1 H); 7.91 (*d*, 1 H). ^{13}C-NMR ($CDCl_3$): −3.7 (Me); 18.4; 20.1 (Me); 25.0 (CH); 25.7 (C_q); 30.5; 31.0 (Me); 59.8 (CH_2); 60.9; 61.4 (CH); 67.4, 67.7 (CH_2); 127.4, 127.7, 127.9, 128.0, 128.2, 128.4, 128.6, 133.3, 135.7, 135.8, 136.6 (arom. CO); 155.8, 156.6, 198.1 (CO). (Some of the signals appear twice due to hindered rotation around the N–CO bond.) EI-MS: 41(4), 43(7), 59(5), 65(5), 73(11), 77 (10, Ph^+), 91 (100, $PhCH_2^+$), 130(5).

(2R,3S)- and (2S,3R)-1-(Benzyloxycarbonyl)-2-[(dimethyl)(1,1,2-trimethylpropyl)silyloxymethyl]-3-phenylazetidin-3-ol (**15** and *ent*-**15**, resp.). Compound **13** (*ent*-**13**) (1.45 g, 3.19 mmol) was dissolved in 300 ml of cyclohexane and irradiated for *ca.* 1 h, until the reactant is disappeared (TLC; CH_2Cl_2). The solvent was evaporated and the product purified by FC (CH_2Cl_2/MeOH 100:1): 1.16 g (80%) of **15** (*ent*-**15**). Pale-yellow oil. TLC (CH_2Cl_2/MeOH 100:1): R_f 0.7. $[\alpha]_D = +6.74$ ($c = 1$, CH_2Cl_2, 23°) (**15**); $[\alpha]_D = -5.46$ ($c = 1$, CH_2Cl_2, 23°) (*ent*-**15**). IR: 3456 (OH), 2958, 1709 (C=O), 1451, 1418, 1354, 1253, 1113, 699. ^{1}H-NMR ($CDCl_3$): −0.14–0.00 (*m*, 6 H); 0.66–0.78 (*m*, 12 H); 1.47–1.52 (*m*, 1 H); 3.87–4.19 (*m*, 4 H); 4.90–5.05 (*m*, 3 H); 7.12–7.27 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$): −3.8; −3.6 (Me); 18.5 (Me); 20.1 (Me); 25.0 (C_q); 25.7 (CH); 60.6 (CH_2); 66.7 (CH_2); 73.6 (CH); 124.2, 127.5, 127.9, 128.1, 128.3, 128.5, 137.2 (arom. C); 143.6 (CO). EI-MS: 55(16), 75(51), 77 (13, Ph^+), 91 (100, $PhCH_2^+$), 105(13), 117(7).

(2S,3S)-1-(Benzyloxycarbonyl)-2-(hydroxymethyl)-3-phenylazetidin-3-ol (**16**). Compound **15** (1.50 g, 3.30 mmol) was dissolved in 25 ml of MeCN and treated with 20 drops of aq. HF (40%). After stirring for 1 h at r.t., 0.5 g of $NaHCO_3$ were added, filtered, and the solvent was evaporated *in vacuo:* 1.03 g (99%) of **16**. White solid. M.p. 72–74°. TLC (CH_2Cl_2/MeOH 10:1): R_f 0.7. IR: 3420 (OH), 2855, 1697 (C=O), 1432, 1189, 1080, 700. ^{1}H-NMR ($CDCl_3$): 3.88 (*d*, $J = 11.7$, 1 H); 4.03 (*m*, 2 H); 4.24 (*m*, 2 H); 4.99 (*dd*, 2 H); 7.12–7.27 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$): 60.6 (CH_2); 64.9 (CH_2); 67.0 (CH_2); 73.5 (C_q); 73.7 (CH); 124.1, 124.4, 127.5,

127.7, 127.8, 128.1, 128.5, 136.1, 143.0 (arom. C); 156.4 (CO). EI-MS: 204 (4, $[M - PhCH_2 - H_2O]^+$), 150(10), 146(5), 132(6), 105 (26, $PhCO^+$), 91 (100, $PhCH_2^+$), 77 (15, Ph^+).

*(2*R*,3*S*)- and (2*S*,3*R*)-1-(Benzyloxycarbonyl)-2-[(dimethyl)(1,1,2-trimethylpropyl)silyloxymethyl]-3-methoxy-3-phenylazetidin-3-ol* (**17** and *ent*-**17**, resp.) NaH (80%, 0.14 g, 1 equiv.) was suspended in 10 ml of DMF, and a soln. of 2 g (4.40 mmol) of **15** (*ent*-**15**) in 2 ml of DMF was added at $-30°$ during 30 min. The mixture was stirred for 1 h, while the temp. was kept at $-30°$. MeI (0.41 ml, 1.5 equiv.) was added, the mixture was heated up to r.t. and stirred overnight. H_2O (30 ml) was added and the product extracted with petroleum ether. The extract was dried, evaporated *in vacuo* to give an oil (1.97 g, 96%), which was used without further purification. TLC (CH_2Cl_2/MeOH 100 : 1): R_f 0.7. $[\alpha]_D = +21.04$ ($c = 1$, CH_2Cl_2, 20°) (**17**); $[\alpha]_D = -18.22$ ($c = 1$, CH_2Cl_2, 23°) (*ent*-**17**). IR: 2957, 1711 (C=O), 1410, 1351, 1102, 1087. ^{1}H-NMR ($CDCl_3$): −0.03–0.02 (*m*, 6 H); 0.75–0.80 (*m*, 12 H); 1.49–1.56 (*m*, 1 H); 2.89 (*s*, 3 H); 3.89–4.31 (*m*, 5 H); 4.96 (*dd*, 2 H); 7.14–7.25 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$): −3.6 (Me); 18.5 (Me); 20.26 (Me); 25.1 (C_q); 34.1 (CH); 51.8 (CH); 57.1 (CH_2); 59.1 (CH_2); 66.8 (CH_2); 72.1 (CH); 78.2 (C_q); 124.2, 127.3, 127.5, 127.8, 128.0, 128.3, 128.4, 136.4, 139.9, 143.5 (arom. C); 156.9 (CO). EI-MS: 43(20), 59(8), 65(9), 73(10), 75(9), 77 (6, Ph^+), 91 (100, $PhCH_2^+$), 119(6), 133(10).

*(2*S*,3*S*)- and (2*R*,3*R*)-1-(Benzyloxycarbonyl)-2-(hydroxymethyl)-3-methoxy-3-phenylazetidin-3-ol* (**18** and *ent*-**18**). Compound **17** (*ent*-**17**) (1.97 g, 4.20 mmol) was dissolved in a mixture of 0.5 ml of aq. HF (40%) and 20 ml of MeCN and stirred for 30 min. Solid $NaHCO_3$ (2 g) was added, filtered, and the filtrate was dried and evaporated *in vacuo:* 1.37 g (99%) of **18** (*ent*-**18**); Colorless oil. TLC (CH_2Cl_2/MeOH 100 : 2): R_f 0.4. $[\alpha]_D = +55.2$ ($c = 1$, CH_2Cl_2, 21°) (**18**); $[\alpha]_D = -53.6$ ($c = 1$, CH_2Cl_2, 21°) (*ent*-**18**). IR: 3447–3423 (OH), 2946, 1705–1688 (C=O), 1448, 1424, 1353, 1110, 700. ^{1}H-NMR (DMSO): 2.96 (*s*, 3 H); 3.80–3.95 (*m*, 1 H); 4.00–4.10 (*m*, 2 H); 4.27–4.36 (*m*, 1 H); 4.66 (*t*, 1 H); 5.06 (*s*, 2 H); 7.33–7.49 (*m*, 10 H). ^{13}C-NMR (DMSO): 52.1 (Me); 57.2 (CH_2); 58.8 (CH_2); 66.8 (CH_2); 73.2 (CH); 79.0 (C_q); 126.3, 127.9, 128.4, 128.6, 128.7, 128.8, 129.2, 129.3, 137.6, 140.7 (arom. C); 157.2 (CO). EI-MS: 43(12), 65(21), 77 (25, Ph^+), 91 (100, $PhCH_2^+$), 105(24), 133(49), 134(38).

*(2*R*,3*S*)- and (2*S*,3*R*)-1-(Benzyloxycarbonyl)-3-methoxy-3-phenylazetidine-2-carboxylic Acid* (**19** and *ent*-**19**, resp.). Compound **18** (*ent*-**18**) (1.40 g, 4.28 mmol) was dissolved in 14 ml of acetone. Then, 1.52 ml of *Jones* reagent (2.6 mol/l, 1 equiv. [22]) were added slowly. After 30 min, the mixture was filtered over a plug of *Celite* and evaporated *in vacuo*. The residue was treated with 10 ml of H_2O and extracted with CH_2Cl_2. The org. phase was evaporated again, and the residue was dissolved in sat. aq. $NaHCO_3$ soln. The soln. was extracted with 3×20 ml of Et_2O, and the crude product was precipitated by addition of dil. HCl. Extraction with AcOEt, drying, and evaporation of the solvent afforded 0.6 g of a stiffy resin which was used in the next step without purification. TLC (AcOH/AcOEt/MeOH 0.5 : 50 : 2): R_f 0.7.

*(2*R*,3*S*)- and (2*S*,3*R*)-3-Methoxy-3-phenylazetidine-2-carboxylic Acid* (**20** and *ent*-**20**, resp.). Compound **19** (*ent*-**19**) (0.60 g, 1.76 mmol) was dissolved in 20 ml of MeOH, and 0.5 g of Pd/C (10%) were added, followed by addition of 0.37 ml (2.2 equiv.) of cyclohexa-1,4-diene. The mixture was refluxed for 30 min, cooled to r.t., and filtered over a plug of *Celite*. The plug was washed with hot H_2O, and the combined filtrates were evaporated *in vacuo*. For purification, the crude amino acid was dissolved in 15 ml of 1M H_3PO_4, and the soln. was washed with 3×10 ml of CH_2Cl_2. Then, the aq. soln. was applied to a column filled with 65 ml of cation exchanger *Dowex 50 WX8* (0.1–0.2 mm, H^+ form, capacity 110 mmol). The column was rinsed with 1 l of H_2O, followed by 500 ml of dil. aq. NH_3. The NH_3 soln. was evaporated *in vacuo* to give 0.26 g of white solid (29%, 2 steps). TLC (EtOH/conc. NH_3/H_2O 20 : 5 : 2): R_f 0.8. $[\alpha]_D = -80.88$ ($c = 1$, 10% HCl, 20°) (**20**); $[\alpha]_D = +95.62$ ($c = 1$, 10% HCl, 20°) (*ent*-**20**). M.p. 190–93°. IR: 3435–3415 (OH/NH), 3063, 1640 (C=O), 1386, 1317. ^{1}H-NMR (D_2O): 2.89 (*s*, 3 H); 4.12 (*d*, $J = 11.3$, 1 H); 4.51 (*d*, $J = 11.3$, 1 H); 4.85 (*s*, 1 H); 7.38–7.42 (*m*, 5 H). ^{13}C-NMR (D_2O): 51.2 (CH_2); 51.7 (Me); 69.4 (CH); 81.2 (C_q); 127.1, 129.3, 129.7, 136.5 (arom. C); 169.5 (CO). EI-MS: 29(57), 43(37), 51(49), 77 (71, Ph^+), 91 (51, $PhCH_2^+$), 104(53), 133(100).

*Methyl (*R*)-2-[(Benzyloxycarbonyl)amino]-3-[(dimethyl)(1,1,2-trimethylpropyl)silyl]propanoate* (**23**). Compound **22** (15.00 g, 59.25 mmol) was dissolved in 10 ml of DMF and treated with 7.26 g (1.8 equiv.) of imidazole and 17.7 ml (1.1 equiv.) TDS-Cl. After stirring for 3 h, crushed ice was added to the mixture, and the product was extracted with Et_2O (4×50 ml). The soln. was dried and the solvent evaporated *in vacuo:* 23 g (99%) of **23**. Colorless oil. TLC (CH_2Cl_2): R_f 0.6. $[\alpha]_D = -18.56$ ($c = 1$, CH_2Cl_2, 20°). IR: 2957, 1727 (C=O), 1502; 1253, 1206, 106, 831. ^{1}H-NMR ($CDCl_3$): −0.04–0.09 (*m*, 6 H); 0.77–0.88 (*m*, 12 H); 1.52 (*m*, 1 H); 3.69 (*s*, 3 H); 3.75–3.79 (*m*, 1 H); 3.96–3.99 (*m*, 1 H); 4.34–4.36 (*m*, 1 H); 5.08 (*s*, 2 H); 5.52 (*d*, NH); 7.21–7.33 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): −3.8 (Me); 18.4 (Me); 20.3 (Me); 25.1 (C_q); 34.1 (CH); 52.3 (Me); 56.0 (CH); 63.5 (CH_2); 66.9 (CH_2); 125.9, 128.0, 128.1, 128.5, 136.3 (arom. C); 155.9 (CO); 170.9 (CO). EI-MS: 41(23), 65(18), 77 (3, Ph^+), 84(18), 91 (100, $PhCH_2^+$), 135 (49, Z^+), 165(67).

(S)-2-[(Benzyloxycarbonyl)amino]-3-[(dimethyl)(1,1,2-trimethylpropyl)silyloxy]propan-1-ol (**24**). Compound **23** (20.75 g, 52.37 mmol) was dissolved in 200 ml of dry MeOH, and 8 g (4 equiv.) of $NaBH_4$ were added portionwise with stirring. After the reactant was completely disappeared (TLC), 400 ml of H_2O were added to the mixture, and the product was extracted with Et_2O (4 × 50 ml). Drying and evaporation of the solvent: 17.94 g (93%) of **24**. Colorless oil. TLC (CH_2Cl_2/MeOH 100 : 1): R_f 0.6. $[\alpha]_D = -13.7$ ($c = 1$, CH_2Cl_2, 20°). IR: 3441 – 3386 (OH/NH), 2957, 2870, 1708, 1512, 1252, 1031, 831. ^{1}H-NMR ($CDCl_3$): −0.10 – 0.05 (*m*, 6 H); 0.70 – 0.83 (*m*, 12 H); 1.45 – 1.60 (*m*, 1 H); 3.60 – 3.80 (*m*, 5 H); 5.01 (*s*, 2 H); 5.29 (*s*, NH). ^{13}C-NMR ($CDCl_3$): −3.7 (Me); 18.4 (Me); 20.4 (Me); 25.1 (C_q); 34.1 (CH); 53.1 (CH); 63.5 (Ch_2); 63.8 (CH_2); 66.8 (CH_2); 126.0, 126.8, 128.1, 136.4 (arom. C); 156.4 (CO). EI-MS: 41 (16), 75 (19), 91 (100, $PhCH_2^+$), 164 (9).

(R)-2-[(Benzyloxycarbonyl)amino]-3-[(dimethyl)(1,1,2-trimethylpropyl)silyloxy]propanal (**25**). To a soln. of 21.00 g (57.22 mmol) of **25** in 150 ml of dry CH_2Cl_2, 24.30 g (1 equiv.) *Dess-Martin* periodinan [23] were added in portions. After stirring for 1 h, the mixture was diluted with 100 ml of Et_2O and washed with several portions of a soln. of $NaHCO_3$/$Na_2S_2O_3$ (25 g of $Na_2S_2O_3$ in 100 ml of sat. $NaHCO_3$ soln.), until a clear org. phase was obtained. After drying and evaporation, the crude aldehyde **25** was used in the next step without further purification. TLC (CH_2Cl_2/MeOH 100 : 2): R_f 0.8. IR: 2958, 2968, 1722, 1506, 1253, 1111, 831. ^{1}H-NMR ($CDCl_3$): −0.01 – 0.06 (*m*, 6 H); 0.81 – 0.96 (*m*, 12 H); 1.51 – 1.68 (*m*, 1 H); 3.88 – 3.92 (*m*, 1 H); 4.20 – 4.25 (*m*, 1 H); 4.33 – 4.36 (*m*, 1 H); 5.17 (*s*, 2 H); 5.64 (*d*, NH); 7.34 – 7.40 (*m*, 5 H); 9.68 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): −3.76 (Me); 0.30 (Me); 18.5 (Me); 20.4 (Me); 25.1 (C_q); 34.2 (CH); 61.1 (CH_2); 61.9 (CH); 67.1 (CH_2); 128.2, 128.3, 128.6, 136.2 (arom. C); 156.1 (CO); 198.7 (CO). EI-MS: 39 (4), 41 (5), 73 (13), 77 (4, Ph^+), 91 (100, $PhCH_2^+$), 116 (5).

(1R,2R)-2-[(Benzyloxycarbonyl)amino]-3-[(dimethyl)(1,1,2-trimethylpropyl)silyloxy]-1-phenylpropan-1-ol (**26**). Crude aldehyde **25** (17.72 g, 48.55 mmol) was dissolved in 100 ml of dry THF and treated with 55 ml of PhMgBr (1.1 equiv., 0.98M in Et_2O) at −78°. The mixture was stirred for 15 min at −78° and warmed up to r.t. Stirring was continued for 5 h, and then 20 ml of sat. aq. NH_4Cl soln. were added. The org. phase was separated and the aq. soln. extracted with Et_2O (3 × 50 ml). The combined org. solns. were washed with brine, dried, and evaporated *in vacuo*. The residue was purified by FC (CH_2Cl_2/MeOH 100 : 1): 9.52 g (44%) of **26**. Colorless oil. TLC (CH_2Cl_2/MeOH 100 : 1): R_f 0.6. $[\alpha]_D = -35.25$ ($c = 1$, CH_2Cl_2, 20°). IR: 3440 – 3350 (OH/NH), 2957, 2868, 1705 (C=O), 1252, 831. ^{1}H-NMR ($CDCl_3$): 0.02 – 0.16 (*m*, 6 H); 0.83 – 0.93 (*m*, 12 H); 1.51 – 1.68 (*m*, 1 H); 3.58 – 3.91 (*m*, 3 H); 5.05 (*s*, 2 H); 5.13 – 5.16 (*m*, 1 H); 7.28 – 7.39 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): −3.8 (Me); 18.4 (Me); 20.1 (Me); 25.1 (C_q); 34.1 (CH); 53.4 (CH); 56.9 (CH); 64.6 (CH_2); 66.7 (CH_2); 125.7, 125.9, 127.5, 127.6, 127.9, 128.0, 128.2, 128.3, 136.5, 141.0 (arom. C); 156.6 (CO). EI-MS: 41 (5), 43 (9), 73 (14), 75 (15), 77 (6, Ph^+), 91 (100, $PhCH_2^+$), 116 (5).

*(1R,2R)-2-[(Benzyloxycarbonyl)amino]-1-[(*tert*-butyl)(dimethyl)silyloxy]-3-[(dimethyl)(1,1,2-trimethylpropyl)silyloxy]-1-phenylpropan* (**27**). Compound **26** (9.52 g, 21.49 mmol) was dissolved in 5 ml of DMF, and treated with 2.65 g (1.8 equiv.) of imidazole and 3.67 g (1.1 equiv.) of TBDMS-Cl. The mixture was stirred overnight at 40°, crushed ice was added, and the product was extracted with Et_2O (4 × 50 ml). The org. phase was dried with Na_2SO_4 and evaporated *in vacuo:* 10.86 g (98%) of **27**. Pale-yellow oil. TLC (CH_2Cl_2): R_f 0.9. $[\alpha]_D = -17.16$ ($c = 1$, CH_2Cl_2, 25°). IR: 2956, 2931, 1726 (C=O), 1499, 1252, 1100, 837. ^{1}H-NMR ($CDCl_3$): −0.10 – 0.20 (*m*, 12 H); 0.91 – 1.12 (*m*, 21 H); 1.77 – 1.81 (*m*, 1 H); 3.62 – 3.71 (*m*, 1 H); 3.95 – 4.02 (*m*, 1 H); 5.12 – 5.31 (*m*, 4 H); 7.36 – 7.51 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$): −5.2 (Me); −4.6 (Me); −3.5 (Me); 18.1 (Me); 20.4 (Me); 25.0 (C_q); 25.1 (CH); 25.8 (Me); 34.2 (Me); 59.1 (CH); 61.5 (CH_2); 66.5 (CH_2); 71.9 (CH_2); 126.2, 126.9, 127.3, 127.4, 127.8, 128.0, 128.1, 128.2, 128.4, 128.6, 142.3 (arom. C); 156.0 (CO). EI-MS: 43 (13), 72 (39), 91 (100, $PhCH_2^+$), 159 (19), 221 (21), 472 (11).

*(1R,2R)-2-[(Benzyloxycarbonyl)(methyl)amino]-1-[(*tert*-butyl)(dimethyl)silyloxy]-3-[(dimethyl)(1,1,2-trimethylpropyl)silyloxy]-1-phenylpropane* (**28**). Compound **27** (10.86 g, 19.49 mmol) was dissolved in 100 ml of dry THF containing 9.7 ml (8 equiv.) of MeI. NaH (1.76 g, 3 equiv.) was added portionwise. The mixture was stirred until the H_2 evolution was completed. Then, same amounts of MeI and NaH were added. After stirring overnight, the solvent was evaporated, the residue was triturated with H_2O and extracted with Et_2O (4 × 50 ml). After drying and evaporation *in vacuo*, the product was purified by FC (CH_2Cl_2): 8.75 g (79%) of **28**. Pale-yellow oil. TLC (CH_2Cl_2): R_f 0.7. $[\alpha]_D = -20.36$ ($c = 1$, CH_2Cl_2, 23°). IR: 2956, 1704 (C=O), 1251, 1091, 836. ^{1}H-NMR ($CDCl_3$): −0.01 – 0.03 (*m*, 12 H); 0.79 – 0.85 (*m*, 21 H); 1.51 – 1.62 (*m*, 1 H); 2.97 (*s*, 3 H); 3.61 – 4.20 (*m*, 3 H); 4.72 – 5.08 (*m*, 3 H); 7.19 – 7.32 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$): −5.4 (CH_3); −4.7 (Me); −3.7 (Me); 17.9 (Me); 20.2 (Me); 25.0 (C_q); 25.7 (CH); 34.2 (Me); 60.7 (CH_2); 66.9 (CH_2); 73.2 (CH); 74.1 (CH); 126.5, 126.6, 126.9, 127.4, 127.5, 127.6, 127.8, 127.9, 128.0, 128.2, 128.3, 136.9 (arom. C); 156.5 (CO). EI-MS: 18 (10), 43 (7), 57 (5), 73 (30), 91 (100, $PhCH_2^+$), 130 (7).

(1R,2R)-2-[(Benzyloxycarbonyl)(methyl)amino]-1-phenylpropane-1,3-diol (**29**). Compound **28** (5.78 g, 9.26 mmol) was dissolved in 50 ml of MeCN and treated with *ca.* 30 drops of HF (aq., 40%). After the reactant is

disappeared (TLC), 5 g of solid $NaHCO_3$ were added, filtered, and the dried soln. was evaporated *in vacuo:* 2.60 g (89%) of **29**. White solid. M.p. 77–79°. TLC (CH_2Cl_2/MeOH 10:): R_f 0.4. $[\alpha]_D = -109.66$ ($c = 1$, CH_2Cl_2, 20°). IR: 3423 (OH), 1669 (C=O), 1333, 1160, 698. ^{1}H-NMR (CD_3OD): 2.97; 3.01 (*s*, 3 H); 3.41–3.50 (*m*, 1 H); 3.60–3.72 (*m*, 1 H); 4.25–4.41 (*m*, 1 H); 4.72–4.83 (*m*, 1 H); 5.08 (*s*, 2 H); 7.26–7.37 (*m*, 10 H). ^{13}C-NMR (CD_3OD): 29.0 (br., Me); 60.4 (CH_2); 65.4 (br., CH); 68.1, 68.2 (CH_2); 73.2, 73.5 (CH); 127.7, 128.6, 128.8, 129.2, 129.4, 129.5, 138.1, 138.3, 143.8 (arom. C); 159.2, 159.3 (CO). (Some of the signals appear twice due to hindered rotation around the N–CO bond.) EI-MS: 42 (15), 65 (11), 74 (41), 77 (20, Ph^+), 79 (18), 91 (100, $PhCH_2^+$), 107 (12).

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