Diastereo- and Enantioselective Syntheses of C_2-Symmetric 1,*n*-Diamines by Nucleophilic Addition to Dialdehyde-SAMP-Hydrazones

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Dedicated to Professor Peter Welzel on the occasion of his 65th birthday.

Abstract: Different protected C_2-symmetric 1,*n*-diamines (*R*,*R*)- or (*S*,*S*)-**4** and **8** can be prepared in high diastereo- and enantiomeric purity by nucleophilic 1,2-addition of organocerium reagents to the CN double bond of *bis*-SAMP-hydrazones (*S*,*S*)-**2a**–**c**. The chiral starting materials are readily available by reaction of dialdehydes with the enantiopure hydrazine 1-amino-2-methoxymethylpyrrolidine (SAMP). Reductive NN bond cleavage of the hydrazines (*R*,*R*,*S*,*S*)- or (*S*,*S*,*S*,*S*)-**3** and **7** afforded the title compounds (de 72–98%, ee 96–98%). The novel entry for the asymmetric synthesis of *N*-protected C_2-symmetric diamines presented here is highly flexible, as both the distance of the amino functions and the introduced residues R can be varied.

Key words: amines, hydrazones, nucleophilic additions, asymmetric synthesis, cerium

Diastereo- and enantiomerically pure diamines play an important role in synthetic and medicinal chemistry.[1] Especially, 1,2-diamines are widely used in various applications[2] e.g. as chiral auxiliaries,[3] ligands[4,5] in asymmetric synthesis and as chiral reagents for the resolution of racemic mixtures[6] or the determination of enantiomeric ratios.[7] In addition, they are crucial structural features in a large number of natural products and synthetic compounds of pharmacological interest.

Especially, 1,*n*-diamines (*n* 3) are often seen in biologically active compounds. For example, certain peptide-based HIV-protease inhibitors[8] or antitumor agents[9] contain such 1,3-, 1,4- and 1,5-diamine structures which represent essential key units in the structural backbone of these pharmaceuticals.[10]

Due to their synthetic significance, quite a number of stereoselective syntheses of vicinal diamines have been developed in recent years.[2a] The most common starting materials for the synthesis of enantioenriched diamines are depicted in Scheme 1.

For instance, alkenes can be utilized in the direct vicinal diamination supported by certain metallic promotors (**A**).[11] Alternatively, transformations of CN-double bonds by nucleophilic 1,2-addition or reduction to obtain the desired diamines have been reported. α-Amino imines,[12a–c] -nitrones[12d] or -hydrazones[12e] (**B**),[12] bis-ketimines[13a–c] or -oxime ethers (**C**)[13d] as well as bis-aldimines,[14a–g] bis-nitrones[14h] or bis-hydrazones[14i] derived from dialdehydes (**H**) have been employed in these reactions with success. Most of the reported approaches are based on substitution reactions of vicinal diols,[15a–e] β-amino alcohols[15f–j] and related compounds by nitrogen nucleophiles (**D**).[15] Starting from other saturated precursors, ring opening of aziridines by nitrogen nucleophiles provides an additional route to diamines (**E**).[16] In addition, the reductive coupling of imines can be performed either under chemoreductive or photoreductive conditions (**F**).[17] Another efficient entry to 1,2-diamines is the 1,4-addition of ammonia equivalents to nitroalkenes followed by reduction of the nitro group (**G**).[18] Finally, various other methods have been described in the literature as for example based on imidazolidinones,[19a] ring closing metathesis,[19b] the nitro-Mannich reaction,[20] the Grignard-addition to bis(1,3-oxazolidinyl)alkanes,[21] the α-alkylation of *N*,*N*-dibenzylaminoacetaldehyde-SAMP-hydrazones,[22a] asymmetric lithiations of imidazolidines[22b] or the reaction of lithiated isocyanides with aziridines.[23]

We have recently disclosed in a communication[14i] a new asymmetric synthesis of protected 1,*n*-diamines by a double nucleophilic 1,2-addition to the CN double bond[24] of dialdehyde-bis-SAMP-hydrazones[25] according to the general route (**H**). We now wish to describe in detail this flexible, CC-connective and highly diastereo- and enantioselective methodology to protected C_2-symmetric 1,*n*-diamines.

The hydrazones (*S*,*S*)-**2a**–**c** were easily prepared by condensation with the chiral auxiliary 1-amino-2-methoxymethylpyrrolidine (SAMP),[25] starting from the commercially available dialdehydes **1a**–**c**, in 80–88% yield (Scheme 2). The subsequent nucleophilic 1,2-additions were carried out by treating the bis-SAMP-hydrazones with eight equivalents of the organocerium reagent[26] formed in situ from cerium chloride and the organo lithium or Grignard reagent in THF at low temperatures. In addition to unfunctionalized alkyl residues, functionalized groups like allyl, benzyl and the protected alcohol in the case of **3d** could be introduced.

The resulting metallohydrazides were trapped with methyl chloroformate (MocCl) or acetyl chloride (AcCl) in a one-pot reaction. The methoxycarbonyl protected hydrazines (*R*,*R*,*S*,*S*)- or (*S*,*S*,*S*,*S*)-**3a**–**h** were obtained in moderate to very good yields (55–93%) and in general with high diastereomeric excesses (69–91%). However, the

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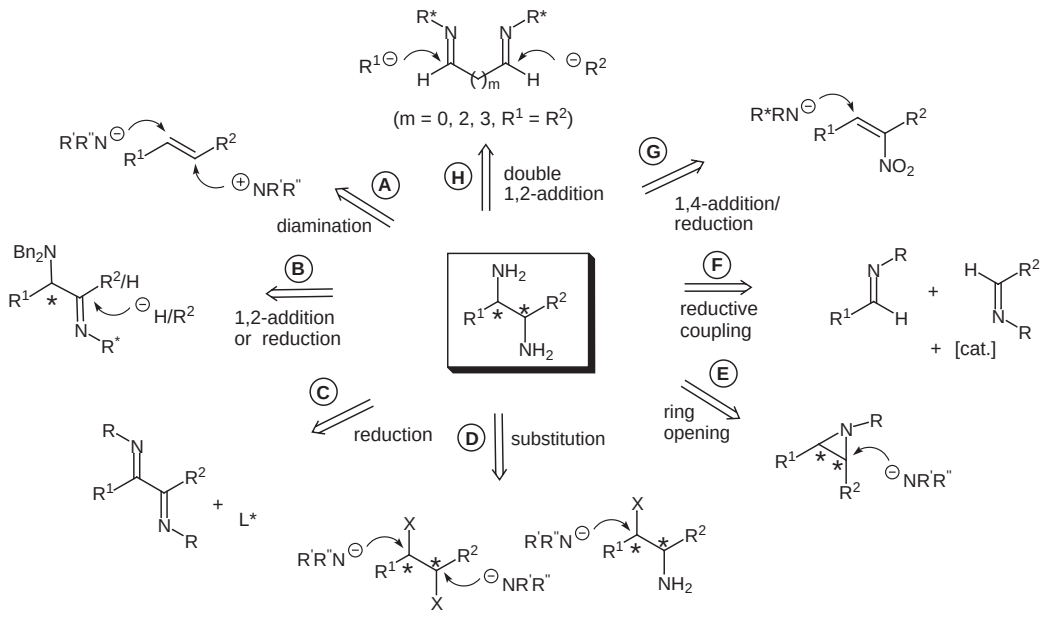
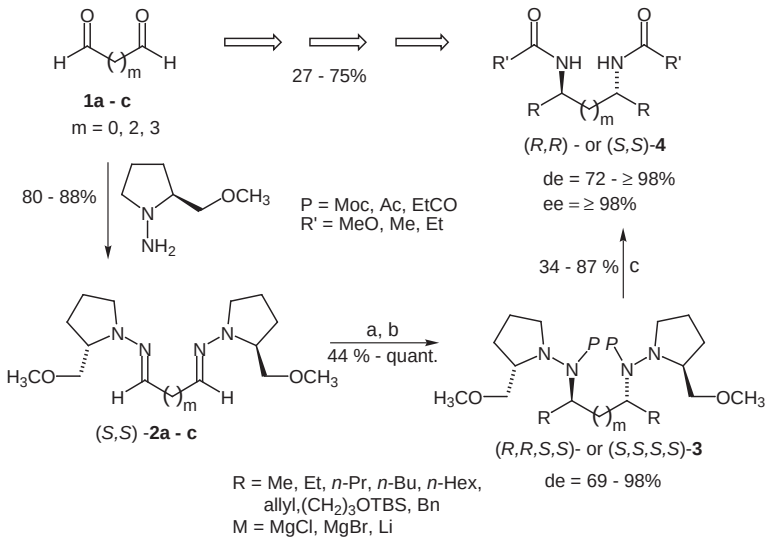


Scheme 1



Scheme 2 *Reagents and conditions*: (a) 8 equiv RM/$CeCl_3$, THF, –100 °C → r.t. (b) 24 equiv MocCl, 0 °C → r.t., 24 equiv AcCl, –78 °C → 0 °C or 24 equiv EtCOCl, –78 °C → 0 °C (c) Li/NH_3, THF, –33 °C.

yields achieved in the case of the *N*-acetyl hydrazines (*R*,*R*,*S*,*S*)- or (*S*,*S*,*S*,*S*)-**3i**–**l** were lower (44–78%), whereas the diastereomeric excesses were better (de 84–98%) (Table 1, Scheme 2).

In the case of the methyl cerium reagent addition products of the *N*-Moc-protected hydrazines (*R*,*R*,*S*,*S*)-**3a**,**e** and the *N*-acetyl hydrazine (*R*,*R*,*S*,*S*)-**3i** acceptable yields were obtained for the reductive cleavage of the auxiliary group. The cleavage of the activated NN bond with lithium in liquid ammonia[27] (56–62%) furnished the 1,*n*-diamines (*R*,*R*)-**4a**,**e**,**i** with excellent de and ee values (de 87–98%, ee 98%) (Table 2).

Since the total yields using methyl formate or acetyl as protecting and activating groups were not satisfactory for a general synthetic method, we were looking for a trapping reagent which would afford good chemical yields in both reactions. The reagent of choice turned out to be propionyl chloride (Scheme 2).

Nucleophilic 1,2-addition of various organocerium reagents to the hydrazones (*S*,*S*)-**2** and subsequent trapping with an excess of propionyl chloride led to *N*-propionyl hydrazines (*R*,*R*,*S*,*S*)- or (*S*,*S*,*S*,*S*)-**3m**–**u** in good to excellent yields (46%–quantitative) and with diastereomeric excesses (67–98%) comparable to the previous trapping experiments. The NN bond was then cleaved with lithium

Table 1 Diastereoselective Synthesis of Methoxycarbonyl or Acetyl Protected 1,*n*-*bis*-SAMP-hydrazines (*R*,*R*,*S*,*S*)- or (*S*,*S*,*S*,*S*)-**3**

3	P	R	*n*	Yield (%)	de[a] (%)	$[\alpha]_D^{r.t.}$ (*c*, $CHCl_3$)	Config.
a	CH_3CO	Me	4	68	86	–85.3 (0.93)	(*R*,*R*,*S*,*S*)
b	CH_3CO	Et	4	55	[b]	–78.2 (0.97)	(*R*,*R*,*S*,*S*)
c	CH_3CO	Bu	4	93	[b]	–65.3 (0.90)	(*R*,*R*,*S*,*S*)
d	CH_3CO	$TBSO(CH_2)_3$[c]	4	66	[b]	–45.8 (1.01)	(*S*,*S*,*S*,*S*)
e	CH_3CO	Me	5	85	91	–75.8 (0.92)	(*R*,*R*,*S*,*S*)
f	CH_3CO	Et	5	66	76	–77.5 (1.15)	(*R*,*R*,*S*,*S*)
g	CH_3CO	Bu	5	58	69	–70.5 (1.15)	(*R*,*R*,*S*,*S*)
h	CH_3CO	Allyl	5	85	82	–64.9 (0.91)	(*S*,*S*,*S*,*S*)
i	CH_3CO	Me	2	50	98	–99.5 (0.99)	(*R*,*R*,*S*,*S*)
j	CH_3CO	Me	4	47	84	–68.6 (1.08)	(*R*,*R*,*S*,*S*)
k	CH_3CO	Allyl	4	44	85	–43.6 (1.08)	(*S*,*S*,*S*,*S*)
l	CH_3CO	Allyl	5	78	84	–37.6 (0.98)	(*S*,*S*,*S*,*S*)

[a] Determined by gas chromatography.
[b] The de value could not be determined by either gas chromatography or by NMR spectroscopy.
[c] The organo lithium reagent was used for the addition.

Table 2 Diastereo- and Enantioselective Synthesis of Methoxycarbonyl or Acetyl Protected C_2-Symmetric 1,*n*-Diamines (*R*,*R*)- or (*S*,*S*)-**4**

4	*n*	R	P	de[a] **3** (%)	Yield **2** → **4**[b] (%)	$[\alpha]_D^{r.t.}$ **4** (*c*, $CHCl_3$)	de[a] **4** (%)	ee[c] **4** (%)	Config.
a	4	Me	CH_3OCO	86	38 (30)	+20.3 (1.02)	87	≥98	(*R*,*R*)
e	5	Me	CH_3OCO	91	52 (46)	–6.3 (1.06)	91	≥98	(*R*,*R*)
i	2	Me	CH_3CO	98	31 (27)	+44.9 (0.049)[d]	≥98	≥98	(*R*,*R*)[e]

[a] Determined by gas chromatography.
[b] In parentheses: overall yield **1** → **4**.
[c] According to GC-analysis employing a chiral stationary phase.
[d] Butanone was used as the solvent.
[e] Determined by correlation of optical rotation with literature data.[24]

in liquid ammonia without racemization to give the propionyl protected 1,*n*-diamines (*R*,*R*)- or (*S*,*S*)-**4m**–**u** in moderate to very high yields (26–87%) with acceptable to high diastereomeric excesses (de 65–98%) and excellent enantiomeric excesses (ee 98%). When necessary, the *meso* compound could be removed chromatographically to obtain a single diastereoisomer (Table 3).

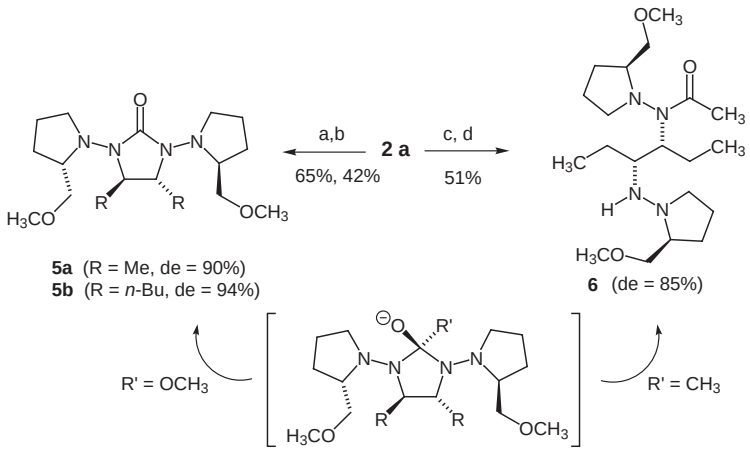
Whereas our method described up to this point represents a very good diastereo- and enantioselective access to protected 1,4- and 1,5-diamines, 1,3-diamines are not available in this manner, due to the easy deprotonation of the corresponding malonaldehyde-*bis*-SAMP-hydrazone preventing nucleophilic 1,2-additions. The important C_2-symmetric 1,2-diamines were obtained only in moderate yields in the case of the 2,3-diamino butane derivatives (**4i**,**m**) because of side-reactions depending on the nucleophile and the trapping agent employed. Addition of various organocerium reagents to the hydrazone (*S*,*S*)-**2a** led to the chiral cyclic urea derivatives (*R*,*R*,*S*,*S*)-**5a**,**b** in moderate yields (42–65%) and high diastereomeric excesses (de 90–94%) instead of the expected carbamates. When (*S*,*S*)-**2a** was treated with the organocerium reagent prepared from ethyl magnesium bromide and cerium trichloride, followed by trapping with acetyl chloride, the monoprotected hydrazine (*R*,*R*,*S*,*S*)-**6** was obtained in 51% yield and good diastereoselectivity (de 85%).

The formation of the side products **5** and **6** can be explained by assuming a common intermediate by cyclisation after the first hydrazide acylation (Scheme 3, Table 4).

Table 3 Diastereo- and Enantioselective Synthesis of Propionyl Protected C_2-Symmetric 1,*n*-Diamines (*R*,*R*)- or (*S*,*S*)-**4**

3, **4**	*n*	R	Yield **2** → **3** (%)	de[a] **3** (%)	Yield **2** → **4**[b] (%)	$[\alpha]_D^{r.t.}$ **4** (*c*, $CHCl_3$)	de[a,c] **4** (%)	ee[d] **4** (%)	Config.
m	2	Me	46	98	34 (30)	+65.5 (0.91)	98	≥98	(*R*,*R*)
n	4	Me	97	87	33 (26)	+32.4 (0.88)	86 (86)	≥98	(*R*,*R*)
o	4	Et	66	[e]	42 (33)	+56.3 (0.32)	98	96	(*R*,*R*)
p	4	Bu	98	83.5:16.0:0.5[f]	62 (49)	+35.1 (1.03)	91 (65)	≥98	(*R*,*R*)
q	4	Hex	91	84.0:15.3:0.7[f]	59 (47)	+25.5 (0.55)	≥98 (67)	≥96[g]	(*R*,*R*)
r	5	Me	98	94	85 (75)	–15.5 (1.06)	94	≥98	(*R*,*R*)
s	5	Bu	87	68	57 (50)	–17.3 (1.01)	72	≥98[h]	(*R*,*R*)
t	5	Allyl	90	83	53 (47)	–37.5 (0.12)	77	≥98	(*S*,*S*)
u	5	Bn	quant.	83	81 (71)	–30.9 (1.02)	86[i]	≥98[i]	(*S*,*S*)

[a] Determined by gas chromatography.
[b] In parentheses: overall yield **1** → **4**.
[c] After chromatography; in parentheses: the de value of the crude diamine.
[d] According to GC-analysis employing a chiral stationary phase.
[e] The de value could not be determined by either gas chromatography or by NMR spectroscopy.
[f] The diastereomeric ratio (dr) is given.
[g] The ee value was determined by NMR-shift experiments.
[h] The ee value could not be determined, it is given in analogy to **4p**,**r**,**t**,**u**.
[i] The de and ee values were determined by HPLC on a chiral stationary phase.



Scheme 3 *Reagents and conditions*: (a) 8 equiv RLi/$CeCl_3$, THF, –100 °C → r.t. (b) MocCl, 0 °C → r.t. (c) 10 equiv EtMgBr/$CeCl_3$, THF, –100 °C → r.t. (d) 12 equiv AcCl, –78 °C → 0 °C.

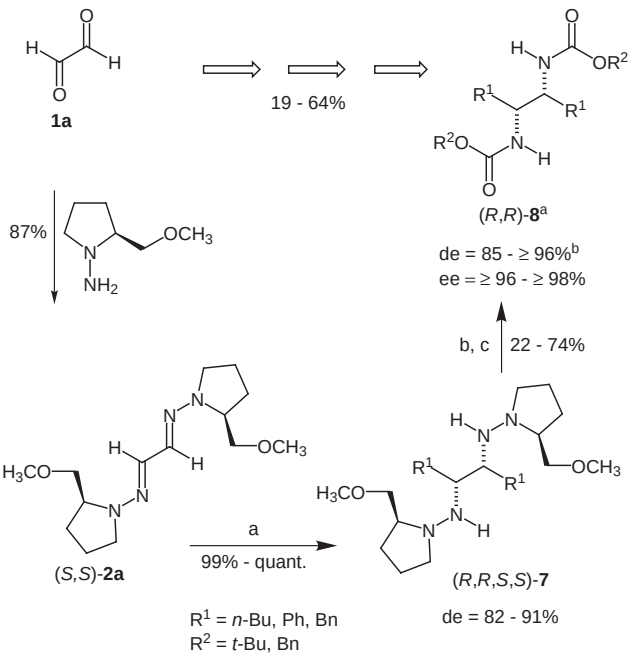
Table 4 Syntheses of the Cyclic Urea Derivatives **5** and the *mono*-Protected Hydrazine **6**

	R	RCOCl	Yield (%)	$[\alpha]_D^{r.t.}$ (*c*, $CHCl_3$)	de[a] (%)	Config.
5a	Me	CH_3OCOCl	65	–159.2 (0.91)	90	(*R*,*R*,*S*,*S*)
5b	Bu	CH_3OCOCl	42	–122.5 (0.72)	94	(*R*,*R*,*S*,*S*)
6	Et	CH_3COCl	51	–112.0 (0.52)	85	(*R*,*R*,*S*,*S*)

[a] Determined by GC or ^{13}C NMR spectroscopy.

In order to overcome the problems of side reactions caused by the necessary activation through N-acylation of the intermediate hydrazides before reductive auxiliary cleavage, we changed our protocol for the asymmetric synthesis of 1,2-diamines. The glyoxal *bis*-SAMP-hydrazone (*S*,*S*)-**2a** was treated with various organocerium compounds as described above, followed by hydrolysis of the 1,2-addition products giving rise to the unprotected hydrazines (*R*,*R*,*S*,*S*)-**7** in virtually quantitative yields and with good asymmetric inductions (de 82–91%). Attempts to purify the bis-hydrazines by chromatography led to significant loss of material and therefore the crude hydrazines were directly used in the subsequent auxiliary removal step. The NN-bond cleavage of the non-activated hydrazines by Raney-nickel/hydrogen[28] has two general disadvantages: very often epimerization occurs during the hydrogenation and the generated diamines may serve as chelating ligands for released Ni^{2+}-cations. Based on a literature procedure to reductively cleave the NN-bond of hydrazines by borane,[29] a procedure was developed to cleave the trisubstituted hydrazines derived from aldehyde-SAMP-hydrazones.[30] The crude hydrazines were dissolved in THF, treated at room temperature with a large excess of BH_3·THF, and heated under reflux for several days. The resulting crude diamines were directly converted into the corresponding carbamates (*R*,*R*)-**8**, which are easier to purify. Moderate to good yields (22–74%) and high stereoselectivities (de 85–98%, ee 96–98%) were obtained (Scheme 4, Table 5).

The advantage of the borane cleavage of the hydrazine NN bond is that aromatic rings present are not affected under the reaction conditions. The use of Raney-nickel could lead to reduced rings and with the lithium in liquid ammonia reductive cleavage the benzylic CN bond would be cleaved instead of the NN bond. Fortunately, the borane cleavage turned out not to be limited to the asymmetric synthesis of 1,2-diamines. As shown in Scheme 5, the protected 1,4-diamine (*S*,*S*)-**9**, related to some C_2-symmetric HIV-protease inhibitors, was obtained in the same manner (23%, de 64%, ee 98%). Additionally, the NMR analysis of the *bis*-MTPA amide proved the absolute configuration of the diamine as (*S*,*S*)-**9**.



a In the case of **8c**, the Boc-protected five membered cyclic urea was synthesized.
b After chromatography or recrystallization.

Scheme 4 *Reagents and conditions*: (a) 1. 8 equiv $R^1M/CeCl_3$, THF, –100 °C → r.t. 2. aq $NaHCO_3$ (b) 1.20 equiv BH_3·THF, THF, 65 °C. 2. HCl or MeOH (c) R^2OCOX (X = Cl, BocO).

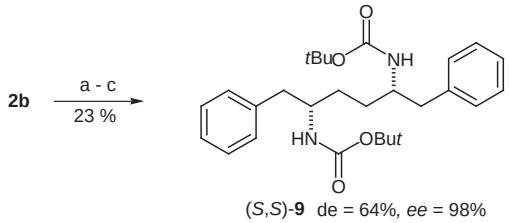
Whereas the diastereomeric and enantiomeric excesses of the diamines were determined by GC and HPLC using chiral stationary phases or ^{1}H NMR shift experiments, the absolute configurations are based on polarimetric data and comparison with known diamines and assuming a uniform reaction mechanism for all title compounds (see Ta-

Table 5 Diastereo- and Enantioselective Synthesis of Carbamate Protected C_2-Symmetric 1,2-Diamines (*R*,*R*)-**8**

7, 8	R	Yield **2** → **7** (%)	de[a] **7** (%)	Yield **2** → **8**[b] (%)	$[\alpha]_D^{r.t.}$ **8** (*c*, $CHCl_3$)	de[c] **8** (%)	ee[d] **8** (%)	Config.
a	Bu	quantitative	82	58 (50)	+43.2 (1.03)	85	≥98	(*R*,*R*)
b	Ph	99	91	22 (19)	–9.6 (0.53)	≥96	≥96	(*R*,*R*)[e]
c[f]	Bn	quantitative	[g]	74 (64)	–6.4 (0.5)	≥98	≥98[h]	(*R*,*R*)

[a] Determined by ^{13}C NMR spectroscopy.
[b] In parentheses: overall yield **1** → **8**.
[c] After chromatography or crystallisation; determined by GC (**8a**) or ^{1}H NMR spectroscopy (**8b**,**c**).
[d] According to GC-analysis employing a chiral stationary phase (**8a**) or NMR shift experiments (**10b**).
[e] By comparison of the optical rotation of (*R*,*R*)-**8b** with literature data and NMR shift experiments with original material.
[f] Instead of the *bis*-Boc-protected diamine the corresponding *bis*-Boc-protected urea was synthesised by variation of the reaction conditions (CH_3CN, Boc_2O, Et_3N, DMAP).
[g] The de value could not be determined by NMR spectroscopy.
[h] The ee value could not be determined, it is given in analogy to **8a**, **b**, **4i**, **6a**.

bles and experimental). These stereochemical results are in agreement with the relative topicity typical for all 1,2-additions to SAMP-hydrazones investigated so far.



Scheme 5 *Reagents and conditions*: (a) 1. 8 equiv $CeCl_3$/BnMgCl, THF, –100 °C → r.t. 2. aq $NaHCO_3$. (b) 1. 20 equiv BH_3·THF, THF, 65 °C. 2. aq HCl, then K_2CO_3 (c) $(Boc)_2O$, Et_3N, MeOH.

In summary, we have developed an efficient and flexible C-C-connective asymmetric synthesis of N-protected, C_2-symmetric 1,*n*-diamines. Starting from simple dialdehydes the key step of the procedure is the nucleophilic double 1,2-addition of nucleophiles to the CN double bond of the corresponding *bis*-SAMP-hydrazones and subsequent reductive removal of the auxiliary group. The title compounds are of enormous importance in synthetic and medicinal chemistry.

All moisture sensitive reactions were carried out using standard Schlenk techniques under argon. Solvents were dried and purified by conventional methods prior to use. THF was freshly distilled from potassium, Et_2O from sodium, MeOH from magnesium methoxide, and CH_2Cl_2 from CaH_2 under argon. Anhyd CH_3CN was purchased from Aldrich. Petroleum ether refers to the fraction with bp 40–80 °C. Reagents of commercial quality were used from freshly opened containers or purified by common methods. Methyl lithium [1.6 M (15%) in Et_2O] and BuLi [1.6 M (15%) in hexane] were purchased from Merck, Darmstadt. **1a** and **c** were used as their commercially available aq solutions. **1b** was liberated from 2,5-dimethoxytetrahydrofuran.[31] SAMP was synthesized according to literature procedures from (*S*)-proline;[32] SAMP and RAMP are commercially available. Analytical TLC: Merck glass-backed silica gel 60 F_{254} plates. Column chromatography: Merck silica gel 60, 0.040–0.063 or 0.063–0.100 mm (230–400 mesh). In some cases the silica gel was deactivated by the addition of 0.6 vol.% Et_3N to the eluent. Analytical GC: Siemens Sichromat 2 or 3 equipped with an OV-1-CB, OV-17-CB, and SE-54-CB (25 m × 0.25 mm), carrier gas nitrogen, FID. Optical rotations: Perkin–Elmer P 241 polarimeter; solvents of Merck Uvasol quality. IR spectra: Perkin–Elmer 1740 and Perkin–Elmer FT/IR 1750. ^{1}H NMR-spectra (300 or 500 MHz), ^{13}C NMR-spectra (75 or 125 MHz): Varian VXR 300, Varian Gemini 300, Varian Unity 500 (TMS as internal standard). Mass spectra: Varian MAT 212 (EI 70 eV), Finnigan SSQ 7000. Elemental analyses: Heraeus CHN-O-Rapid, elementar vario EL. HRMS: Finnigan MAT, MAT 95. Chemical nomenclature was verified by the programme Autonom (Version 1.1, Beilstein Informationssysteme GmbH, 1994).

Bis-Hydrazones (*S*,*S*)-2; General Procedure 1 (GP 1)

The dialdehydes **1** (15 mmol) were dissolved in CH_2Cl_2 (30 mL) at 0 °C. The SAMP hydrazine (30 mmol) was added and stirring was continued until reaction was complete (6–12 h). The organic phase was washed with H_2O, drying with $MgSO_4$, and purification by flash chromatography (deactivated SiO_2, Et_2O–petroleum ether) gave the pure hydrazones **2a**–**c** as colorless or pale yellow highly viscous oils.

Hydrazines (*R*,*R*,*S*,*S*)-/(*S*,*S*,*S*,*S*)-3, 7; General Procedure 2 (GP 2)

Cerium trichloride heptahydrate (8 mmol) was dried for 2 h at 140 °C and 0.1 Torr with cautious stirring. After cooling, the flask was flushed with argon and the solid suspended in THF (35 mL) at r.t. for 2 h, and ultrasound was applied for 1 h. The colorless suspension was cooled to –70 °C and then a soln of the organolithium reagent (8 mmol) was added slowly, or in the case of Grignard reagents, the procedure was carried out at 0 °C. Using organolithium reagents the suspension turned canary yellow, Grignard reagents normally led to a gray suspension (exceptions: AllylMgCl: orange, BnMgCl: light yellow), was stirred for further 2 h and then cooled to –100 °C. The resulting organocerium reagent was treated with a soln of *bis*-hydrazone (*S*,*S*)-**2** (1 mmol) in THF (6 mL), and then the reaction mixture was allowed to warm slowly to r.t. over 15 h. To obtain the unprotected hydrazines (*R*,*R*,*S*,*S*)-**7** the reaction was hydrolyzed at 0 °C with sat. $NaHCO_3$ soln (20 mL). The organic layer was separated and the residue extracted with Et_2O (4 × 25 mL). The combined organic layers were then dried over $MgSO_4$ and the solvent removed on a rotary evaporator.

The air- and temperature sensitive hydrazines were purified by chromatography, which led to losses in yields so the crude hydrazine was introduced into the next step without further purification. For the synthesis of *N*-Moc protected hydrazines, methyl chloroformate (24 mmol) was added at 0 °C and the soln stirred for 20 h at r.t. Alternatively, the soln was again cooled to –70 °C and acetyl or propionyl chloride (24 mmol) was added. The soln was stirred for 0.5 h at this temperature and for another h at 0 °C to yield the *N*-acylated hydrazines. The reaction was terminated by addition of a sat. $NaHCO_3$ soln (20 mL). The isolation procedure was similar to the one of the unprotected hydrazines. After purification of the yellow-brown crude products by chromatography (SiO_2, Et_2O–petroleum ether), colorless to light-yellow highly viscous oils were obtained.

***N*-Protected Diamines (*R*,*R*)-/(*S*,*S*)-4; General Procedure 3 (GP 3)**

Lithium (4.8 mmol) was dissolved in liquid ammonia (25 mL) at –70 °C. Then a soln of the hydrazides **3** (0.5 mmol) in THF (5 mL) was added. The cooling bath was removed and the soln allowed to warm up to reflux for 1–3 h. NH_4Cl (9.6 mmol) was then carefully added in order to terminate the reaction. After the ammonia had evaporated, the residue was extracted with CH_2Cl_2 (3 × 20 mL) and filtered. After removal of the solvent on a rotary evaporator and purification by flash chromatography (SiO_2, Et_2O, Et_2O–petroleum ether, Et_2O–MeOH) gave the acylated diamines as colorless solids.

Amines: General Procedure 4 (GP 4)

The hydrazines **7a**–**c** (0.3 mmol) were dissolved in THF (15 mL) and refluxed for 5 to 6 d with BH_3·THF (6 mL, 6 mmol, 1 M soln in THF). The reaction was terminated by addition of MeOH (2 mL) (path A) or 10% HCl (2 mL) (path B).

Path A

After the addition of the MeOH, the solvent was evaporated in vacuo, the residue was dissolved in MeOH (10 mL) and refluxed for 1 h. This soln was introduced into the next protecting step.

Path B

After the hydrolysis with HCl, the reaction mixture was stirred at r.t. for 2 h. The solvent was evaporated in vacuo and the remaining soln of the diamino hydrochloride was extracted with Et_2O (2 × 3 mL). To obtain the crude diamines the aq soln was saturated with solid K_2CO_3 and extracted with CH_2Cl_2 (3 × 15 mL). The combined ex-

tracts were carefully washed with brine (2 × 5 mL) and dried with Na_2SO_4. After the solvent was removed on a rotary evaporator the crude diamine was obtained, which was used directly in the next protecting step.

(2*S*,2′*S*)-(–)-2-{[2-(Methoxymethyl)pyrrolidine-1-yl]imino}-ethylidene-2-(methoxymethyl)pyrrolidine-1-ylamine [(*S*,*S*)-2a]
Glyoxal (**1a**, 40% aq soln, 2.2 g, 15 mmol) and SAMP (3.9 g, 30 mmol) were allowed to react according to GP 1. Flash chromatography (deactivated SiO_2, Et_2O–petroleum ether, 4:1) yielded **2a** (3.69 g, 87%) as a light yellow viscous oil which solidified in the freezer.

$[\alpha]_D^{23}$ –211 (*c* 1.07, $CHCl_3$), {lit. $[\alpha]_D^{20}$ – 246 (*c* 50–100 mg/mL, THF)}.

The spectroscopic data of **2a** corresponded with those reported.[33]

(2*S*,2′*S*)-(–)-4-{[2-(Methoxymethyl)pyrrolidine-1-yl]imino}-butylidene-2-(methoxymethyl)pyrrolidine-1-ylamine [(*S*,*S*)-2b]
Concd HCl (0.5 mL, 6 mmol) was added dropwise to 2,5-dimethoxytetrahydrofuran (1.32 g, 10 mmol) in H_2O (5 mL) and stirred 30 min at r.t. The acid soln was neutralized with solid $NaHCO_3$. This soln of the in situ prepared succinic aldehyde **1b** and SAMP (2.60 g, 20 mmol) were allowed to react according to GP 1. Flash chromatography (deactivated SiO_2, Et_2O–petroleum ether, 4:1) yielded **2b** (2.48 g, 80%) as a light yellow viscous oil.

$[\alpha]_D^{23}$ –162.4 (*c* 1.01, $CHCl_3$).

IR (film): 2952–2828, 1728, 1605 (w, C=N), 1461–1450, 1341, 1302, 1282, 1197, 1121, 1004, 973, 924–904, 733, 673–646, 556–525 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.75–2.00 (m, 8 H, $NCH_2CH_2CH_2$), 2.41 (m, 4 H, N=CHCH_2), 2.71 (m, 2 H, NC*H*H), 3.37 (s, 6 H, OCH_3), 3.32–3.45, (m, 6 H, NCH*H*, CH_2O), 3.56 (m, 2 H, C*H*CH_2O), 6.66 (t, *J* = 4.7 Hz, 2 H, HC=N).

^{13}C NMR ($CDCl_3$): δ = 22.12 (NCH_2CH_2), 26.55 ($NCH_2CH_2CH_2$), 31.24 (N=CHCH_2), 50.28 (NCH_2), 59.16 (OCH_3), 63.49 (*C*HCH_2), 74.76 (CH_2O), 137.63 (HC=N).

MS (70 eV): *m*/*z* (%) = 297 (12) [M^+ + 1], 296 (70) [M^+], 251 (54), 182 (86), 155 (15), 150 (12), 136 (57), 114 (77), 112 (19), 111 (12), 109 (17), 103 (36), 85 (14), 84 (28), 83 (15), 82 (57), 81 (10), 80 (15), 71 (55), 70 (77), 69 (40), 68 (33), 67 (14), 56 (13), 55 (41), 45 (100).

Anal. calcd for $C_{16}H_{30}N_4O_2$ (310.4): C, 61.90; H, 9.74; N, 18.05. Found: C, 61.90; H, 9.93; N, 18.29.

(2*S*,2′*S*)-(–)-5-{[2-(Methoxymethyl)pyrrolidine-1-yl]imino}-pentylidene-2-(methoxymethyl)pyrrolidine-1-ylamine [(*S*,*S*)-2c]
Glutaric aldehyde (**1c**, 50% aq soln, 6 g, 30 mmol) and SAMP (7.8 g, 60 mmol) were allowed to react according to GP 1. Flash chromatography (deactivated SiO_2, Et_2O–petroleum ether, 4:1) yielded **2c** (8.6 g, 88%) as a light yellow viscous oil.

$[\alpha]_D^{25}$ –168.2 (*c* 0.97, $CHCl_3$).

IR (film): 2922–2828, 2079, 1727, 1605 (m, C=N), 1460, 1368–1340, 1302–1282, 1197–1121, 1003, 973, 926, 904–868, 745, 684, 637 8w), 606, 528 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.66 (m, 2 H, $CH_2CH_2CH_2$), 1.75–2.00 (m, 8 H, $NCH_2CH_2CH_2$), 2.27 (m, 4 H, N=CHCH_2), 2.71 (m, 2 H, NC*H*H), 3.32–3.44 (m, 6 H, NCH*H*, CH_2O), 3.37 (s, 6 H, OCH_3), 3.56 (m, 2 H, C*H*CH_2O), 6.64 (t, *J* = 5.5 Hz, 2 H, HC=N).

^{13}C NMR ($CDCl_3$): δ = 22.13 (NCH_2CH_2), 26.00 (N=CHCH_2CH_2), 26.54 ($NCH_2CH_2CH_2$), 32.60 (N=CHCH_2), 50.30 (NCH_2), 59.14 (OCH_3), 63.41 (*C*HCH_2), 74.79 (CH_2O), 138.30 (HC=N).

MS (70 eV): *m*/*z* (%) = 324 (5) [M^+], 196 (13), 195 (100), 156 (11), 123 (20), 117 (25), 114 (33), 111 (34), 84 (15), 70 (35), 55 (11), 45 (12).

Anal. calcd for $C_{17}H_{32}N_4O_2$ (324.5): C, 62.93; H, 9.94; N, 17.27. Found: C, 62.92; H, 9.91; N, 17.53.

(1*R*,4*R*,2′*S*,2″*S*)-(–)-*N*-(2-Methoxymethylpyrrolidine-1-yl)-*N*-{4-[(2-methoxy-methylpyrrolidine-1-yl)-methoxycarbonylamino]1-methylpentyl}-methyl-carbamate [(*R*,*R*,*S*,*S*)-3a]
An organocerium reagent (13 mmol) prepared from $CeCl_3$ and MeMgBr (2.5 M soln in Et_2O) was treated according to GP 2 with hydrazone **2b** (0.31 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with methyl chloroformate (4.72 g, 50 mmol). Flash chromatography (SiO_2, Et_2O–petroleum ether, 2:1) yielded **3a** (0.31 g, 68%) as a colorless highly viscous oil.

De 86% (GC); $[\alpha]_D^{25}$ –85.8 (*c* 0.93, $CHCl_3$).

IR ($CHCl_3$): 2954–2826, 2744, 2317, 2073, 1701 (C=O), 1531, 1440, 1385, 1368, 1324, 1305, 1260, 1111, 1037, 973, 633, 601, 576, 535 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.14 (d, *J* = 6.7 Hz, 6 H, C*H*$_3$CH), 1.35–2.20 (m, 12 H, $NCH_2CH_2CH_2$, $CHCH_2CH_2CH$), 3.05–4.20 (m, 12 H, NCH_2, $CHCH_2O$, CH_3CH), 3.33 (s, 6 H, CH_2OCH_3), 3.69 (br s, 6 H, $OCOCH_3$).

^{13}C NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 19.11 (*C*H_3CH), 23.49 (NCH_2CH_2), 27.70 ($NCH_2CH_2CH_2$), 31.66 ($CHCH_2CH_2CH$), 52.10 (*C*H_3OCO), 54.60 (NCH_2), 54.60, 58.89, 61.31, 62.24 (CH_3CH, *C*HCH_2OCH_3), 75.47 (CH_2O). A carbonyl signal was not detected.

MS (70 eV): *m*/*z* (%) = 458 (7) [M^+], 414 (23), 413 (100) [M^+ – $CH_2OCH_3^+$], 184 (12), 156 (18), 143 (15), 114 (19), 112 (15), 111 (16), 70 (20), 68 (10), 55 (10), 45 (13) [$CH_2OCH_3^+$].

Anal. calcd for $C_{22}H_{42}N_4O_6$ (458.6): C, 57.62; H, 9.23; N, 12.22. Found: C, 57.67; H, 9.67; N, 12.40.

(1*R*,4*R*,2′*S*,2″*S*)-(–)-*N*-(2-Methoxymethylpyrrolidine-1-yl)-*N*-{4-[(2-methoxy-methylpyrrolidine-1-yl)-methoxycarbonylamino]-1-ethylhexyl}methyl-carbamate [(*R*,*R*,*S*,*S*)-3b]
An organocerium reagent (13 mmol) prepared from $CeCl_3$ and EtMgBr (1 M soln in THF) was treated according to GP 2 with hydrazone **2b** (0.31 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with methyl chloroformate (4.72 g, 50 mmol). Flash chromatography (SiO_2, Et_2O–petroleum ether, 2:1) yielded **3b** (0.27 g, 55%) as a colorless solid.

Mp 72 °C; $[\alpha]_D^{25}$ –78.2 (*c* 0.97, $CHCl_3$).

IR (film): 2964–2825 1702 (C=O), 1529, 1440, 1380, 1333, 1286, 1265, 1194, 1112, 1024, 993, 973, 922, 787, 765, 602, 543 cm^{-1}.

^1H NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 0.88 (t, *J* = 7.4 Hz, 6 H, C*H*$_3$CH$_2$), 1.36–2.20 (m, 16 H, $NCH_2CH_2CH_2$, $CHCH_2CH_2CH$, CH_3CH_2), 3.0–4.0 (m, 12 H, NCH_2, $CHCH_2O$, CH_3CH), 3.33 (s, 6 H, CH_2OCH_3), 3.68 (br s, 6 H, $OCOCH_3$).

^{13}C NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 11.31 (*C*H_3CH$_2$), 23.84 (NCH_2CH_2), 26.24, 27.50 (CH_3CH_2, $NCH_2CH_2CH_2$), 29.25 ($CHCH_2CH_2CH$), 52.06 (*C*H_3OCO), 54.19, 55.16 (rotamer) (NCH_2), 58.89, 60.21, 62.06, 63.22 (rotamer) (CH_3CH, *C*HCH_2OCH_3), 75.26 (CH_2O), 156.02 (C=O).

MS (70 eV): *m*/*z* (%) = 486 (9) [M^+], 442 (26), 441 (100) [M^+ – CH_2OCH_3], 198 (10), 184 (12), 157 (10), 143 (27), 114 (20), 112 (13), 111 (17), 71 (13), 70 (22), 69 (13), 68 810), 55 (12), 45 (13).

Anal. calcd for $C_{24}H_{46}N_4O_6$ (486.7): C, 59.23; H, 9.53; N, 11.51. Found: C, 59.21; H, 9.68; N, 11.39.

(1*R*,4*R*,2′*S*,2″*S*)-(–)-*N*-{1-Butyl-4-[(2-methoxymethylpyrrolidine-1-yl)-methoxy-carbonylamino]-octyl}-*N*-(2-methoxymethylpyrrolidine-1-yl)-methyl-carbamate [(*R*,*R*,*S*,*S*)-3c]
An organocerium reagent (20 mmol) prepared from $CeCl_3$ and BuLi (1.6 M soln in hexane) was treated according to GP 2 with hydrazone **2b** (0.62 g, 2 mmol). After the addition was complete (TLC) the reaction was trapped with methyl chloroformate (7.0 g, 74 mmol). Flash chromatography (SiO_2, Et_2O–petroleum ether, 1:1) yielded **3c** (1.01 g, 93%) as a colorless highly viscous oil.

$[\alpha]_D^{25}$ –65.3 (*c* 0.90, $CHCl_3$).

IR (film): 2955–2874, 2826, 1748, 1702 (C=O), 1529, 1440, 1384, 1334, 1286, 1253, 1230, 1193, 1112, 1076, 1029, 993, 973, 925, 765, 666, 602, 549 cm^{-1}.

^1H NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 0.88 (t, *J* = 7.0 Hz, 6 H, C*H*$_3$CH$_2$), 1.20–2.25 (m, 24 H, NCH$_2$C*H*$_2$C*H*$_2$, CHC*H*$_2$C*H*$_2$CH, CH$_3$C*H*$_2$C*H*$_2$C*H*$_2$), 3.00–4.10 (m, 12 H, NCH$_2$, C*H*CH$_2$O, CH$_3$C*H*), 3.33 (s, 6 H, CH$_2$OC*H*$_3$), 3.67 (br s, 6 H, OCOCH$_3$). ^{13}C NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 14.11 (*C*H$_3$CH$_2$), 22.79, 23.85 (CH$_3$*C*H$_2$, NCH$_2$*C*H$_2$), 27.51, 28.78 (CH$_3$CH$_2$*C*H$_2$, NCH$_2$CH$_2$*C*H$_2$), 29.64, 33.07 (*C*H$_2$CH*C*H$_2$*C*H$_2$CH), 52.07 (*C*H$_3$OCO), 54.15 (NCH$_2$), 58.29, 58.89, 62.09, 63.16 (rotamer) (CH$_3$*C*H, *C*HCH$_2$OCH$_3$), 75.20 (CH$_2$O). A carbonyl signal was not detected.

MS (70 eV): *m*/*z* (%) = 542 (7) [M^+], 498 (32), 497 (100) [M^+ – CH_2OCH_3], 384 (10), 226 (12), 143 (25), 114 (18), 112 (10), 111 (16), 71 (11), 70 (17), 69 (10), 55 (13), 45 (14) [$CH_2OCH_3^+$].

Anal. calcd for $C_{28}H_{54}N_4O_6$ (542.8): C, 61.96; H, 10.03; N, 10.32. Found: C, 61.46; H, 9.72; N, 11.35.

(1*S*,4*S*,2′*S*,2″*S*)-(–)-*N*-{7-*t*-Butyldimethylsilyloxy-1-(3-*t*-butyldimethylsilyloxy-propyl)-4-[(2-methoxymethylpyrrolidine-1-yl)-methoxycarbonylamino]-heptyl}-*N*-(2-methoxymethylpyrrolidine-1-yl)-methylcarbamate [(*S*,*S*,*S*,*S*)-3d]
To 3-*tert*-butyldimethysillyloxypropyliodide (0.84 g, 2.8 mmol) in Et_2O (3 mL) was added dropwise *t*-butyllithium (1.6 M soln in pentane) (4.2 mL, 6.7 mmol) at –78 °C. The reaction mixture was stirred for 0.5 h and then allowed to warm to 0 °C and stirred for an additional 2 h. The resulting yellow soln was added dropwise at –100 °C to the hydrazone **2b** (0.31 g, 1 mmol) in Et_2O (8 mL) and then the reaction mixture was allowed to warm up slowly to r.t. over 15 h. Methyl chloroformate (1.51 g, 16 mmol) was added at 0 °C and the soln stirred for 20 h at r.t. The reaction was terminated by addition of a sat. $NaHCO_3$ soln (20 mL). The organic layer was separated and the residue extracted with Et_2O (4 × 25 mL). The combined organic layers were then dried over $MgSO_4$ and the solvent removed on a rotary evaporator. Flash chromatography (SiO_2, Et_2O–petroleum ether, 1:1) yielded **3d** (0.51 g, 66%) as a colorless highly viscous oil.

De n.d.; $[\alpha]_D^{26}$ –45.8 (*c* 1.01, $CHCl_3$)

IR ($CHCl_3$): 2953, 2930, 2858, 2738, 1688 (C=O), 1561, 1509, 1472, 1461, 1441, 1386, 1361, 1333, 1288, 1255, 1217, 1193, 1106 (SiO), 1006, 972, 939, 837 (m, SiOC), 814, 757, 667, 521, 476, 465 cm^{-1}.

^1H NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 0.04 [s, 12 H, Si(C*H*$_3$)$_2$], 0.88 [s, 18 H, SiC(CH$_3$)$_3$], 1.20–2.25 (m, 18 H, NCH$_2$C*H*$_2$C*H*$_2$, C*H*$_2$CHC*H*$_2$C*H*H), 3.00–4.10 (m, 18 H, NCH$_2$, C*H*HC*H*$_2$OSi, CHCH$_2$O, C*H*CH$_2$CH$_2$C*H*), 3.33 (s, 6 H, CH$_2$OC*H*$_3$), 3.67 (br s, 6 H, CH$_3$OCO).

^{13}C NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = –5.30 [Si(CH$_3$)$_2$], 18.35 [SiC(*C*H$_3$)$_3$], 23.80 (NCH$_2$*C*H$_2$), 25.96 [Si*C*(CH$_3$)$_3$], 27.50 (NCH$_2$CH$_2$*C*H$_2$), 29.62, 29.97 (3 C) (*C*H$_2$CH*C*H$_2$C*H*$_2$), 52.13 (OCO*C*H$_3$), 54.20 (NCH$_2$), 58.46, 58.88, 62.07 (*C*HCH$_2$CH$_2$*C*H, *C*HCH$_2$OCH$_3$), 63.08 (CH$_2$OSi), 75.27 (CH$_2$OSi), 156 (C=O).

MS (70 eV): *m*/*z* (%) = 775 (0.73) [M^+], 732 (21), 731 (53), 730 (100) [M^+ – CH_2OCH_3], 718 (20), 643 (29), 641 (53), 143 (18), 114 (9).

Anal. calcd for $C_{38}H_{78}N_4O_8Si_2$ (775.2): C, 58.88; H, 10.14; N, 7.23. Found: C, 59.20; H, 9.89; N, 7.44.

(1*R*,5*R*,2′*S*,2″*S*)-(–)-*N*-(2-Methoxymethylpyrrolidine-1-yl)-*N*-{5-[(2-methoxy-methylpyrrolidine-1-yl)-methoxy-carbonyl-amino]-1-methylhexyl}-methyl-carbamate [(*R*,*R*,*S*,*S*)-3e]
An organocerium reagent (13 mmol) prepared from $CeCl_3$ and MeMgBr (2.5 M soln in Et_2O) was treated according to GP 2 with hydrazone **2c** (0.32 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with methyl chloroformate (4.72 g, 50 mmol). Flash chromatography (SiO_2, Et_2O–petroleum ether, 4:1) yielded **3e** (0.40 g, 85%) as a colorless highly viscous oil.

De 91% (GC); $[\alpha]_D^{25}$ –75.8 (*c* 0.92, $CHCl_3$).

IR ($CHCl_3$): 2952–2740, 2078, 1703 (C=O), 1615, 1531, 1441, 1385, 1369, 1320, 1240, 1195, 1110, 1056, 998, 973, 919, 906, 799, 767, 633 cm^{-1}.

^1H NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 1.13 (d, *J* = 6.8 Hz, 6 H, C*H*$_3$CH), 1.21–2.2 (m, 14 H, CHC*H*$_2$C*H*$_2$C*H*$_2$CH, NCH$_2$C*H*$_2$C*H*$_2$), 3.00–4.20 (m, 12 H, NCH$_2$, CHCH$_2$O, CH$_3$C*H*), 3.33 (br s, 6 H, CH$_2$OC*H*$_3$), 3.69 (br s, 6 H, OCOCH$_3$).

^{13}C NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 19.06 (*C*H$_3$CH), 23.48 (NCH$_2$*C*H$_2$), 24.12 (CH$_3$CHCH$_2$*C*H$_2$), 27.68 (NCH$_2$CH$_2$*C*H$_2$), 34.68 (CH$_3$CH*C*H$_2$), 52.07 (OCO*C*H$_3$), 54.30 (NCH$_2$), 55.20, 58.89, 61.36 (CH$_3$*C*H, *C*HCH$_2$OCH$_3$), 75.52 (CH$_2$O), 155.22 (C=O).

MS (70 eV): *m*/*z* (%) = 472 (3) [M^+], 428 (24), 427 (100) [M^+ – CH_2OCH_3], 191 (12),157 (10), 143 (20), 114 (23), 113 (10), 112 (20), 111 (16), 80 (10), 70 (17), 68 813), 55 (10), 45 (13).

Anal. calcd for $C_{23}H_{44}N_4O_6$ (472.6): C, 58.45; H, 9.38; N, 11.85. Found: C, 59.00; H, 9.71; N, 12.03.

(1*R*,5*R*,2′*S*,2″*S*)-(–)-*N*-(2-Methoxymethylpyrrolidine-1-yl)-*N*-{5-[(2-methoxy-methylpyrrolidine-1-yl)-methoxycarbonyl-amino]-1-ethylheptyl}-methyl-carbamate [(*R*,*R*,*S*,*S*)-3f]
An organocerium reagent (20 mmol) prepared from $CeCl_3$ and EtMgBr (1 M soln in THF) was treated according to GP 2 with hydrazone **2c** (0.64 g, 2 mmol). After the addition was complete (TLC) the reaction was trapped with methyl chloroformate (7.0 g, 74 mmol). Flash chromatography (SiO_2, Et_2O–petroleum ether, 2:1) yielded **3f** (0.66 g, 66%) as a colorless highly viscous oil.

De 76% (GC); $[\alpha]_D^{25}$ –77.5 (*c* 1.15, $CHCl_3$).

IR (film): 2965–2877, 2825, 1702 (C=O), 1530, 1459, 1441, 1385, 1337, 1299–1262, 1194, 1104, 1025, 994, 973, 923, 906, 757, 667 cm^{-1}.

^1H NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 0.87 (t, *J* = 7.0 Hz, 6 H, C*H*$_3$CH$_2$), 1.20–2.25 (m, 18 H, NCH$_2$C*H*$_2$C*H*$_2$, CHC*H*$_2$C*H*$_2$C*H*$_2$CH, CH$_3$C*H*$_2$), 3.00–3.95 (m, 12 H, NCH$_2$, C*H*CH$_2$O, CH$_3$C*H*), 3.33 (s, 6 H, CH$_2$OC*H*$_3$), 3.67 (br s, 6 H, OCOCH$_3$).

^{13}C NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 11.33 (*C*H$_3$CH$_2$), 23.82 (NCH$_2$*C*H$_2$), 24.13 (CHCH$_2$*C*H$_2$CH$_2$CH), 26.01, 27.52

(CH_3CH_2, $NCH_2CH_2CH_2$), 32.94 ($CH_3CH_2CHCH_2$), 52.09 (CH_3OCO), 54.05, 54.96 (rotamer) (NCH_2), 58.89, 61.26, 62.12, 63.27 (rotamer) (CH_3CH, $CHCH_2OCH_3$),75.38 (CH_2O). A carbonyl signal was not detected.

MS (70 eV): *m*/*z* (%) = 500 (5) [M^+], 456 (28), 455 (100) [$M^+ - CH_2OCH_3$], 143 (23), 114 (14), 112 (11), 111 (17), 70 (14), 45 (12).

Anal. calcd for $C_{25}H_{48}N_4O_6$ (500.7): C, 59.97; H, 9.97; N, 11.19. Found: C, 59.88; H, 9.79; N, 11.03.

(1*R*,5*R*,2′*S*,2″*S*)-(–)-*N*-{1-Butyl-5-[(2-methoxymethylpyrrolidine-1-yl)-methoxy-carbonylamino]-nonyl}-*N*-(2-methoxymethylpyrrolidine-1-yl)-methylcarbamate [(*R*,*R*,*S*,*S*)-3g]

An organocerium reagent (6 mmol) prepared from $CeCl_3$ and BuLi (1.6 M soln in hexane) was treated according to GP 2 with hydrazone **2c** (0.28 g, 0.86 mmol). After the addition was complete (TLC) the reaction was trapped with methyl chloroformate (1.7 g, 18 mmol). Flash chromatography (SiO_2, Et_2O–petroleum ether, 1:1) yielded **3g** (0.28 g, 58%) as a light yellow highly viscous oil.

De 69% (GC); $[\alpha]_D^{25}$ –70.5 (*c* 1.15, $CHCl_3$).

IR (film): 2956–2874, 2826, 2249, 1699 (C=O), 1531, 1441, 1385, 1337–1285, 1230, 1194, 1110, 1075, 1027, 994, 973, 922, 766, 737, 704 cm^{-1}.

^1H NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 0.88 (t, *J* = 7.0 Hz, 6 H, CH_3CH_2), 1.20–2.30 (m, 26 H, $NCH_2CH_2CH_2$, $CHCH_2CH_2CH_2CH$, $CH_3CH_2CH_2CH_2$), 3.00–4.05 (m, 12 H, NCH_2, $CHCH_2O$, CH_3CH), 3.33 (s, 6 H, CH_2OCH_3), 3.66 (br s, 6 H, $OCOCH_3$).

^{13}C NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 14.09 (CH_3CH_2), 22.79 (CH_3CH_2), 23.83 (NCH_2CH_2), 24.11 ($CHCH_2CH_2CH_2CH$), 27.55 ($NCH_2CH_2CH_2$), 28.81 ($CH_3CH_2CH_2$), 32.89, 33.22 ($CH_3CH_2CH_2CH_2CHCH_2$), 52.05 (CH_3OCO), 54.04, 54.96 (NCH_2), 58.86, 59.34, 62.11, 63.21 (CH_3CH, $CHCH_2OCH_3$), 75.34 (CH_2O), 155.89, 157.68 (C=O).

MS (70 eV): *m*/*z* (%) = 556 (6) [M^+], 512 (33), 511 (100) [$M^+ - CH_2OCH_3$], 233 (13), 143 (29), 114 (15), 111 (19), 70 (12), 55 (10), 45 (11).

Anal. calcd for $C_{29}H_{56}N_4O_6$ (556.8): C, 62.56; H, 10.14; N, 10.06. Found: C, 62.46; H, 10.37; N, 10.40.

(1*S*,5*S*,2′*S*,2″*S*)-(–)-*N*-{1-Allyl-5-[(2-methoxymethylpyrrolidine-1-yl)-methoxy-carbonylamino]-oct-7-enyl}-*N*-(2-methoxymethylpyrrolidine-1-yl)-methyl-carbamate [(*S*,*S*,*S*,*S*)-3h]

The organocerium reagent (20 mmol) prepared from $CeCl_3$ and allylMgCl (1 M soln in THF) was treated according to GP 2 with hydrazone **2c** (0.64 g, 2 mmol). After the addition was complete (TLC) the reaction was trapped with methyl chloroformate (7.0 g, 74 mmol). Flash chromatography (SiO_2, Et_2O–petroleum ether, 2:1) yielded **3h** (0.89 g, 85%) as a light yellow highly viscous oil.

De 82% (GC); $[\alpha]_D^{24}$ –64.9 (*c* 0.91, $CHCl_3$).

IR ($CHCl_3$): 3077, 3012, 2976, 2953, 2876, 2827, 2453, 1694 (C=O), 1642, 1441, 1385, 1335, 1299, 1272, 1237, 1217, 1195, 1110, 1025, 995, 972, 917, 757, 667, 648, 603, 538, 500 cm^{-1}.

^1H NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 1.20–2.50 (m, 16 H, $CHCH_2CH_2CH_2CH$, $NCHHCH_2CH_2$), 3.0−4.1 (m, 10 H, $NCHH$, $CHCH_2O$, $CH_2=CHCH_2CH$), 3.33 (s, 6 H, CH_2OCH_3), 3.68 (s, 6 H, $OCOCH_3$), 5.02 (m, 4 H, $CH=CH_2$), 5.75 (m, 2 H, $CH_2=CH$).

^{13}C NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 23.77, 24.06 ($CHCH_2CH_2CH_2CH$, NCH_2CH_2), 27.68 ($NCH_2CH_2CH_2$), 32.45 ($CHCH_2CH_2CH_2CH$), 37.86 ($CH_2=CHCH_2$), 52.17 ($OCOCH_3$), 54.32, 55.12 (NCH_2), 58.92, 59.45, 62.18, 63.16 ($CHCH_2OCH_3$, $CH_2=CHCH_2CH$), 75.43 (CH_2O), 116.56 ($CH=CH_2$), 136.05 ($CH_2=CH$), 155.67 (C=O).

MS (70 eV): *m*/*z* (%) = 525 (1.12) [$M^+ + 1$], 524 (3) [M^+], 480 (31), 479 (100), [$M^+ - C_3H_5O$], 217 (12), 143 (30), 114 (22), 112 (11), 111 (29), 71 (11), 70 (21), 69 (11), 68 (14), 45 (16).

Anal. calcd for $C_{27}H_{48}N_4O_6$ (524.7): C, 61.81; H, 9.22; N, 10.68. Found: C, 62.14; H, 9.52; N, 10.66.

(1*R*,2*R*,2′*S*,2″*S*)-(–)-*N*-{2-[Acetyl-(2-methoxymethylpyrrolidine-1-yl)-amino]-1-methylpropyl}-*N*-(2-methoxymethylpyrrolidine-1-yl)-acetamide [(*R*,*R*,*S*,*S*)-3i]

An organocerium reagent (13 mmol) prepared from $CeCl_3$ and MeLi (1.6 M soln in Et_2O) was treated according to GP 2 with hydrazone **2a** (0.28 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with AcCl (1.22 g, 15.6 mmol). Flash chromatography (SiO_2, Et_2O–petroleum ether, 4:1) yielded **3i** (0.20 g, 50%) as a light yellow solid.

Mp 50–51 °C; de 98% (GC); $[\alpha]_D^{25}$ –99.5 (*c* 0.99, $CHCl_3$).

IR ($CHCl_3$): 2979–2829, 1734, 1661 (C=O), 1447, 1416, 1380, 1360, 1317, 1259, 1197, 1110, 1076, 1038, 973, 914, 735, 702, 678, 617 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.35 (d, *J* = 6.3 Hz, 6 H, CH_3CH), 1.60–1.90 (m, 8 H, $NCH_2CH_2CH_2$), 2.02 (s, 6 H, CH_3CO), 2.80–3.30 (m, 10 H, CH_2NCHCH_2), 3.28 (s, 6 H, OCH_3), 4.11 (m, 2 H, CHCH).

^{13}C NMR ($CDCl_3$): δ = 17.08 (CH_3CH), 21.31 (CH_3CO), 21.97 (NCH_2CH_2), 25.84 ($NCH_2CH_2CH_2$), 50.53 (NCH_2), 54.48 (CHCH), 57.92, 58.10 ($CHCH_2OCH_3$), 73.66 (CH_2O), 175.71 (C=O).

MS (70 eV): *m*/*z* (%) = 398 (5) [M^+], 228 (15), 227 (100), 199 (10), 183 (21), 171 (10), 158 (11), 157 (83), 141 (14), 127 (11), 125 (17), 114 (71), 111 (18), 85 (10), 84 (29), 83 (12), 82 (13), 73 (16), 72 (12), 71 (21), 70 (40), 69 (10), 57 (15), 55 (13), 45 (25).

Anal. calcd for $C_{20}H_{38}N_4O_4$ (398.6): C, 60.27; H, 9.61; N, 14.06. Found: C, 59.90; H, 9.84; N, 13.65.

(1*R*,4*R*,2′*S*,2″*S*)-(–)-*N*-(2-Methoxymethylpyrrolidine-1-yl)-*N*-{4-[(2-methoxy-methylpyrrolidine-1-yl)-acetylamino]-1-methyl-pentyl}-acetamide [(*R*,*R*,*S*,*S*)-3j]

An organocerium reagent (16 mmol) prepared from $CeCl_3$ and MeLi (1.6 M soln in Et_2O) was treated according to GP 2 with hydrazone **2b** (0.62 g, 2 mmol). After the addition was complete (TLC) the reaction was trapped with acetyl chloride (3.77 g, 48 mmol, 3.41 mL). Flash chromatography (SiO_2, Et_2O) yielded **3j** (0.40 g, 47%) as a light yellow highly viscous oil.

De 84% (^{13}C NMR); $[\alpha]_D^{29}$ –68.6 (*c* 1.08, $CHCl_3$).

IR ($CHCl_3$): 2970, 2934, 2874, 2830, 2300, 1717, 1657 (C=O), 1442, 1363, 1326, 1256, 1197, 1123, 1036, 972, 940, 922, 897, 852, 754, 664, 611, 565, 511, 490 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.14 (d, *J* = 6.5 Hz, 6 H, CH_3CH), 1.50–2.15 (m, 12 H, $NCH_2CH_2CH_2$, CH_3CHCH_2), 2.07 (s, 6 H, CH_3CO), 2.80–3.40 (m, 12 H, NCH_2, $CHCH_2O$, CH_3CH), 3.34 (s, 6 H, OCH_3).

^{13}C NMR ($CDCl_3$): δ = 18.93 (CH_3CH), 21.28 (NCH_2CH_2), 22.53 (CH_3CO), 26.27 ($NCH_2CH_2CH_2$), 33.11 (CH_3CHCH_2), 51.15 (NCH_2), 51.73, 58.56, 59.12 ($CHCH_2OCH_3$, CH_3CH), 74.01 (CH_2O), 174.37 (C=O).

MS (70 eV): *m*/*z* (%) = 426 (0.24) [M^+], 381 (35) [$M^+ - C_2H_5O$], 255 (22), 173 (12), 142 (26), 141 (21), 140 (23), 127 (24), 114 (100) [$C_6H_{12}NO^+$], 98 (20), 97 86 (10), 85 (11), 84 (33), 83 (14), 82 (12), 71 (11), 70 (32), 68 (17), 45 (19), 44 (10), 43 (17).

Anal. calcd for $C_{22}H_{42}N_4O_4$ (426.60): C, 61.94; H, 9.92; N, 13.13. Found: C, 62.30; H, 9.68; N, 12.97.

(1*S*,4*S*,2′*S*,2″*S*)-(–)-*N*-{1-Allyl-4-[(2-methoxymethylpyrrolidine-1-yl)-acetyl-amino]-hept-6-enyl}-*N*-(2-methoxymethylpyrrolidine-1-yl)-acetamide [(*S*,*S*,*S*,*S*)-3k]
An organocerium reagent (16 mmol) prepared from $CeCl_3$ and allylMgCl (1.6 M soln in THF) was treated according to GP 2 with hydrazone **2b** (0.62 g, 2 mmol). After the addition was complete (TLC) the reaction was trapped with AcCl (3.77 g, 48 mmol, 3.41 mL). Flash chromatography (SiO_2, Et_2O–petroleum ether, 6:1) yielded **3k** (0.42 g, 44%) as a light yellow highly viscous oil.

De 85% (GC); $[\alpha]_D^{29}$ –43.6 (*c* 1.08, $CHCl_3$).

IR (film): 3074, 2975, 2925, 2874, 2830, 1721, 1658 (C=O), 1445, 1363, 1330, 1300, 1257, 1197, 1124, 1035, 999, 973, 916, 779, 683, 648, 611, 556, 453 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.60–2.10 (m, 12 H, $NCH_2CH_2CH_2$, $CHCH_2CH_2CH$), 2.07 (s, 6 H, CH_3CO), 2.50–3.40 (m, 16 H, $CHCH_2O$, CH_2=$CHCH_2CH$, NCH_2), 3.34 (s, 6 H, OCH_3), 5.05 (m, 4 H, CH=CH_2), 5.73 (m, 2 H, CH_2=C*H*).

^{13}C NMR ($CDCl_3$): δ = 21.24 (NCH_2CH_2), 22.23 (CH_3CO), 26.29 ($NCH_2CH_2CH_2$), 32.00 ($CHCH_2CH_2CH$), 37.45 (CH_2=$CHCH_2$), 51.88 (NCH_2), 56.42, 58.53, 59.02 ($CHCH_2OCH_3$, $CHCH_2CH_2CH$), 74.21 (CH_2O), 117.03 (CH=CH_2), 136.12 (CH_2=C*H*), 174.72 (C=O).

MS (70 eV): *m*/*z* (%) = 479 (1.23) [M^+ + 1], 478 (0.84) [M^+], 434 (25), 433 (100) [$M^+ - C_2H_5O$], 324 (36), 320 (14), 307 (18), 194 (21), 173 (13), 152 (11), 150 (10), 141 (17), 127 (49), 114 (98) [$C_6H_{12}NO^+$], 112 (12), 110 (18), 97 (12), 85 (16), 84 (10), 83 (14), 82 (16), 71 (19), 70 (40), 69 (11), 68 (22), 67 (1255 (14), 45 (14).

Anal. calcd for $C_{26}H_{46}N_4O_4$ (478.7): C, 65.24; H, 9.69; N, 11.70. Found: C, 65.29; H, 9.39; N, 11.28.

(1*S*,5*S*,2′*S*,2″*S*)-(–)-*N*-{1-Allyl-5-[(2-methoxymethylpyrrolidine-1-yl)-acetyl-amino]-oct-7-enyl}-*N*-(2-methoxymethylpyrrolidine-1-yl)-acetamide [(*S*,*S*,*S*,*S*)-3l]
An organocerium reagent (16 mmol) prepared from $CeCl_3$ and allylMgCl (1.6 M soln in THF) was treated according to GP 2 with hydrazone **2c** (0.64 g, 2 mmol). After the addition was complete (TLC) the reaction was trapped with acetyl chloride (3.77 g, 48 mmol, 3.41 mL). Flash chromatography (SiO_2, Et_2O–petroleum ether, 2:1) yielded **3l** (0.77 g, 78%) as a colorless solid.

Mp 131 °C; de 84% (GC); $[\alpha]_D^{26}$ –37.6 (*c* 0.98, $CHCl_3$).

IR (KBr): 3077, 2968, 2927, 2868, 2827, 2811, 2086, 1645 (C=O), 1561, 1543, 1509, 1447, 1421, 1365, 1328, 1302, 1288, 1247, 1197, 1134, 1112, 1033, 1000, 957, 911, 880, 773, 740, 688, 651, 609, 564, 510 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.32 (m, 2 H, $CHCH_2CH_2CH_2CH$), 1.60–2.20 (m, 12 H, $NCH_2CH_2CH_2$, CH_2=$CHCH_2CHCH_2$), 2.07 (s, 6 H, CH_3CO), 2.40–3.60 (m, 16 H, $CHCH_2O$, CH_2=$CHCH_2CH$, NCH_2), 3.32 (s, 6 H, OCH_3), 5.05 (m, 4 H, CH=CH_2), 5.73 (m, 2 H, CH_2=C*H*).

^{13}C NMR ($CDCl_3$): δ = 21.03 (NCH_2CH_2), 22.57 (CH_3CO), 25.40 ($CHCH_2CH_2CH_2CH$), 26.45 ($NCH_2CH_2CH_2$), 33.58 (CH_2=$CHCH_2CHCH_2$), 36.74 (CH_2=$CHCH_2$), 51.55 (NCH_2), 56.16, 58.49, 59.14 ($CHCH_2OCH_3$, CH_2=$CHCH_2CH$), 74.19 (CH_2O), 116.89 (CH=CH_2), 136.37 (CH_2=CH), 174.67 (C=O).

MS (70 eV): *m*/*z* (%) = 493 (0.34) [M^+ + 1], 492 (0.55) [M^+], 448 (20), 447 (70) [$M^+ - C_2H_5O$], 338 (18), 173 (13), 141 (29), 127 (43), 114 (100) [$C_6H_{12}NO^+$], 85 (11), 82 (12), 70 (29), 68 (12), 45 (15).

Anal. calcd for $C_{27}H_{48}N_4O_4$ (492.7): C, 65.82; H, 9.82; N, 11.37. Found: C, 65.30; H, 9.83; N, 11.19.

(1*R*,2*R*,2′*S*,2″*S*)-(–)-*N*-(2-Methoxymethylpyrrolidine-1-yl)-*N*-{2-[(2-methoxy-methylpyrrolidine-1-yl)-propionylamino]-1-methylpropyl}propionamide [(*R*,*R*,*S*,*S*)-3m]
An organocerium reagent (8 mmol) prepared from $CeCl_3$ and MeLi (1.6 M soln in Et_2O) was treated according to GP 2 with hydrazone **2a** (0.28 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with propionyl chloride (2.22 g, 24 mmol, 2.1 mL). Flash chromatography (SiO_2, Et_2O–petroleum ether, 4:1) yielded **3m** (0.20 g, 46%) as a light yellow highly viscous oil.

De 98% (GC); $[\alpha]_D^{23}$ –89.9 (*c* 0.82, $CHCl_3$).

IR (KBr): 2976, 2937, 2876, 2828, 2733, 2459, 2246, 2069, 1738, 1660 (C=O), 1551, 1462, 1447, 1423, 1378, 1346, 1290, 1271, 1240, 1196, 1112, 1074, 1019, 993, 973, 961, 916, 900, 852, 806, 788, 755, 700, 666, 646, 606, 580, 529, 465 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.02 (t, *J* = 7.4 Hz, 6 H, CH_3CH_2), 1.42 (d, *J* = 6 Hz, 6 H, CH_3CH), 1.60–2.00 (m, 8 H, $NCH_2CH_2CH_2$), 2.49 (m, 4 H, CH_3CH_2), 2.85–3.40, 4.20 (m, 12 H, CH_2NCHCH_2, CHNCO), 3.33 (s, 6 H, OCH_3).

^{13}C NMR ($CDCl_3$): δ = 8.93 (CH_3CH_2), 18.07 (CH_3CH), 22.33 (NCH_2CH_2), 26.70, 27.17 (CH_3CH_2, $NCH_2CH_2CH_2$), 51.61 (NCH_2), 55.44 ($NCHCH_3$), 58.89, 59.17 ($CHCH_2OCH_3$), 74.63 (CH_2O), 179.45 (C=O).

MS (70 eV): *m*/*z* (%): 426 (1.87) [M^+], 242 (15), 241 (100) [$M^+ - C_9H_{17}N_2O_2$], 213 (12), 183 (20), 157 (74), 155 (13), 141 (14), 114 (68) [$C_6H_{12}NO^+$], 111 (3284 (28), 71 (22), 70 (63), 57 (40), 55 (12), 45 (40), 44 (14), 43 (11), 42 (15), 41 (18).

HRMS (EI): *m*/*z* calcd for $C_{22}H_{42}N_4O_4$, 426.3206; found, 426.3204.

(1*R*,4*R*,2′*S*,2″*S*)-(–)-*N*-(2-Methoxymethylpyrrolidine-1-yl)-*N*-{4-[(2-methoxy-methylpyrrolidine-1-yl)-propionylamino]-1-methylpentyl}-propionamide [(*R*,*R*,*S*,*S*)-3n]
An organocerium reagent (8 mmol) prepared from $CeCl_3$ and MeLi (1.6 M soln in Et_2O) was treated according to GP 2 with hydrazone **2b** (0.31 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with propionyl chloride (2.22 g, 24 mmol, 2.1 mL). Flash chromatography (SiO_2, Et_2O–petroleum ether, 2:1) yielded **3n** (0.44 g, 97%) as a light yellow highly viscous oil.

De 87% (GC); $[\alpha]_D^{24}$ –84.2 (*c* 0.5, $CHCl_3$).

IR (Et_2O): 2973, 2937, 2875, 2830, 1656 (s, C=O), 1463, 1441, 1375, 1356, 1276, 1249, 1226, 1197, 1125, 1050, 952, 930, 886, 848, 805, 581, 540 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.03 (t, *J* = 7.4 Hz, 6 H, CH_3CH_2), 1.41 (d, *J* = 6.6 Hz, 6 H, CH_3CH), 1.60–2.40 (m, 16 H, $NCH_2CH_2CH_2$, $CHCH_2CH_2CH$, CH_2CH_3), 2.80–3.40 (m, 12 H, CH_3CH, CH_2NCHCH_2), 3.32 (s, 6 H, OCH_3).

^{13}C NMR ($CDCl_3$): δ = 9.04 (CH_3CH_2), 18.89 (CH_3CH), 21.21 (NCH_2CH_2), 26.16, 26.60 ($NCH_2CH_2CH_2$, CH_3CH_2), 33.50 ($CHCH_2CH_2CH$), 51.19 (NCH_2), 51.60 ($NCHCH_3$), 58.53, 58.98 ($CHCH_2OCH_3$), 73.90 (CH_2O), 177.23 (C=O).

MS (70 eV): *m*/*z* (%): 455 (0.2) [M^+ + 1], 454 (0.03) [M^+], 410 (26), 409 (100) [$M^+ - C_2H_5O$], 296 (15), 269 (17), 157 (12), 154 (21), 141 (25), 114 (95) [$C_6H_{12}NO^+$], 98 (16), 84 (15), 70 (24).

Anal. calcd for $C_{24}H_{46}N_4O_4$ (454.7): C, 63.40; H, 10.20; N, 12.32. Found: C, 63.48; H, 10.19; N, 12.20.

2-Methoxymethylpyrrolidine-1-yl)-*N*-{4-[(2-methoxy-methylpyrrolidine-1-yl)-propionylamino]-1-ethylhexyl}-propionamide [(*R*,*R*,*S*,*S*)-3o]
An organocerium reagent (8 mmol) prepared from $CeCl_3$ and EtMgBr (1 M soln in THF) was treated according to GP 2 with hydrazone **2b** (0.31 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with propionyl chloride (2.22 g, 24 mmol, 2.1

mL). Flash chromatography (SiO_2, Et_2O–petroleum ether, 2:1) yielded **3o** (0.32 g, 66%) as a light yellow highly viscous oil.

$[\alpha]_D^{30}$ –74.9 (*c* 0.72, $CHCl_3$).

IR (film): 2969, 2935, 2875, 2829, 1721, 1657 (C=O), 1461, 1429, 1375, 1357, 1254, 1198, 1124, 1017, 973, 923, 898, 876, 804, 582, 454 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 7.7 Hz, 6 H, C*H*$_3$CH$_2$CH), 1.04 (t, *J* = 7.4 Hz, 6 H, C*H*$_3$CH$_2$CO), 1.60–2.10 (m, 16 H, NCH$_2$C*H*$_2$C*H*$_2$, CHC*H*$_2$C*H*$_2$CH, CH$_3$C*H*$_2$CH), 2.20–2.55 (m, 4 H, CH$_3$C*H*$_2$CO), 2. 70–3.04 (m, 8 H, CHNCO, C*H*$_2$NC*H*CH$_2$), 3.22–3.36 (m, 4 H, CH_2O), 3.31 (s, 6 H, OCH_3).

^{13}C NMR ($CDCl_3$): δ = 9.19 (*C*H$_3$CH$_2$CO), 11.95 (*C*H$_3$CH$_2$CH), 21.12 (NCH$_2$*C*H$_2$), 25.62, 26.10, 26.53 (NCH$_2$CH$_2$*C*H$_2$, CH$_3$*C*H$_2$CH, CH$_3$*C*H$_2$CO), 32.96 (CH*C*H$_2$*C*H$_2$CH), 51.71 (NCH$_2$), 57.98, 58.47, 59.00 (*C*HCH$_2$CH$_3$, *C*HCH$_2$OCH$_3$), 73.99 (CH_2O), 177.39 (C=O).

MS (70 eV): *m*/*z* (%) = 482 (0.75) [M^+], 438 (11), 437 (41) [$M^+ - C_2H_5O$], 324 (12), 297 (20), 187 (14), 185 (10), 184 (19), 155 (16), 142 (12), 141 (38), 126 (24), 114 (100) [$C_6H_{12}NO^+$], 85 (11), 84 (22), 71 (10), 70 (24), 69 (14), 57 (11), 55 (14), 45 (13), 44 (10), 41 (12).

Anal. calcd for $C_{26}H_{50}N_4O_4$ (482.7): C, 64.69; H, 10.44; N, 11.61. Found: C, 64.56; H, 10.42; N, 11.95.

(1*R*,4*R*,2′*S*,2″*S*)-(–)-*N*-{1-Butyl-4-[(2-methoxymethylpyrrolidine-1-yl)-propionylamino]-octyl}-*N*-(2-methoxymethylpyrrolidine-1-yl)-propionamide [(*R*,*R*,*S*,*S*)-3p]

An organocerium reagent (8 mmol) prepared from $CeCl_3$ and BuLi (1.6 M soln in hexane) was treated according to GP 2 with hydrazone **2b** (0.31 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with propionyl chloride (2.22 g, 24 mmol, 2.1 mL). Flash chromatography (SiO_2, Et_2O–petroleum ether, 2:1) yielded **3p** (0.53 g, 98%) as a light yellow highly viscous oil.

Dr 83.5:16.0:0.5 (GC); $[\alpha]_D^{29}$ –52.2 (*c* 1.16, $CHCl_3$).

IR ($CHCl_3$): 2959, 2932, 2874, 1734, 1647 (C=O), 1462, 1377, 1357, 1274, 1244, 1216, 1197, 1124, 1077, 1014, 973, 923, 900, 804, 755, 665, 583 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 7.1 Hz, 6 H, C*H*$_3$CH$_2$CH$_2$), 1.03 (t, *J* = 7.4 Hz, 6 H, C*H*$_3$CH$_2$CO), 1.10–1.43, 1.60–2.10 (m, 24 H, NCH$_2$C*H*$_2$C*H*$_2$, CH$_3$C*H*$_2$C*H*$_2$C*H*$_2$, CHC*H*$_2$C*H*$_2$CH), 2.44 (m, 6 H, CH$_3$C*H*$_2$CO, NC*H*H), 2.76–3.40 (m, 10 H, NCH*H*, C*H*CH$_2$CH$_2$C*H*, $CHCH_2O$), 3.31 (s, 6 H, OCH_3).

^{13}C NMR ($CDCl_3$): δ = 9.22 (*C*H$_3$CH$_2$CO), 14.14 (*C*H$_3$CH$_2$CH$_2$), 21.20, 22.97 (CH$_3$*C*H$_2$CH$_2$, NCH$_2$*C*H$_2$), 26.11, 26.55 (NCH$_2$CH$_2$*C*H$_2$, CH$_3$CH$_2$CO), 29.92 (*C*H$_2$CH$_2$CH$_3$), 32.94, 32.98 (*C*H$_2$CHCH$_2$*C*H$_2$CHCH$_2$), 51.73 (NCH$_2$), 56.91, 58.43, 59.00 (*C*HCH$_2$CH$_2$*C*H, *C*HCH$_2$OCH$_3$), 73.95 (CH_2O), 177.59 (C=O).

MS (70 eV): *m*/*z* (%) = 539 (0.21) [M^+ + 1], 538 (0.44) [M^+], 494 (30), 493 (100) [$M^+ - C_2H_5O$], 380 (21), 353 (20), 224 (10), 187 (12), 182 (17), 142 (13), 141 (50), 114 (75) [$C_6H_{12}NO^+$], 86 (10), 85 (12), 83 (11), 71 (13), 70 (24), 57 (62), 55 (15).

Anal. calcd for $C_{30}H_{58}N_4O_4$ (538.8): C, 66.87; H, 10.85; N, 9.62. Found: C, 66.95; H, 10.85; N, 10.12.

(1*R*,4*R*,2′*S*,2″*S*)-(–)-*N*-{1-Hexyl-4-[(2-methoxymethylpyrrolidine-1-yl)-propionylamino]-decyl}-*N*-(2-methoxymethylpyrrolidine-1-yl)-propionamide [(*R*,*R*,*S*,*S*)-3q]

An organocerium reagent (8 mmol) prepared from $CeCl_3$ and *n*-hexyl lithium (2 M soln in hexane) was treated according to GP 2 with hydrazone **2b** (0.31 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with propionyl chloride (2.22 g, 24 mmol, 2.1 mL). Flash chromatography (SiO_2, Et_2O–petroleum ether, 1:1) yielded **3q** (0.54 g, 91%) as a light yellow highly viscous oil.

Dr 84.0:15.3:0.7 (GC); $[\alpha]_D^{23}$ –49.2 (*c* 1.09, $CHCl_3$).

IR ($CHCl_3$): 2957, 2929, 2873, 2858, 2464, 1733, 1648 (C=O), 1462, 1376, 1358, 1248, 1216, 1198, 1124, 1077, 1016, 973, 922, 804, 755, 665, 582 cm^{-1}.

^1H NMR ($CDCl_3$): Only the chemical shifts of the main diastereomer are given. δ = 0.87 (m, 6 H, C*H*$_3$CH$_2$CH$_2$), 1.03 (t, *J* = 7.4 Hz, 6 H, C*H*$_3$CH$_2$CO), 1.09–2.58 (m, 38 H, acyclic CH$_2$, NCH*H*CH$_2$C*H*$_2$, CH$_3$C*H*$_2$CO), 2.76–3.40 (m, 10 H, CHNCO, C*H*HNC*H*CH$_2$), 3.31 (s, 6 H, OCH_3).

^{13}C NMR ($CDCl_3$): Only the chemical shifts of the main diastereomer are given. δ = 9.23 (*C*H$_3$CH$_2$CO), 14.09 (*C*H$_3$CH$_2$CH$_2$), 21.22, 22.66 (CH$_3$*C*H$_2$CH$_2$, NCH$_2$*C*H$_2$), 26.11, 26.56, 27.67 (CH$_3$*C*H$_2$CO, NCH$_2$CH$_2$*C*H$_2$, CH$_3$CH$_2$*C*H$_2$), 29.55 (CH$_3$CH$_2$CH$_2$*C*H$_2$), 31.85, 33.01, 33.25 (*C*H$_2$*C*H$_2$CH*C*H$_2$), 51.73 (NCH$_2$), 56.93, 58.46, 59.00 (*C*HCH$_2$CH$_2$*C*H, *C*HCH$_2$OCH$_3$), 73.95 (CH_2O), 177.54 (C=O).

MS (70 eV): *m*/*z* (%) = 595 (1.67) [M^+ + 1], 551 (11), 550 (55), 549 (100) [$M^+ - C_2H_5O$], 537 (15), 437 (12), 436 (42), 409 (32), 392 (22), 377 (20), 296 (14), 294 (26), 252 (35), 246 (17), 238 (29), 236 (10), 227 (21), 187 (22), 185 (14), 181 (12), 155 (15), 154 (24), 142 (11), 140 (79), 129 (10), 115 (11), 114 (96) [$C_6H_{12}NO^+$], 112 (11), 97 (17), 85 (18), 84 (14), 83 (14), 82 (14), 71 (18), 70 (39), 69 (18), 68 (12), 57 (37), 55 (18), 45 (19).

Anal. calcd for $C_{34}H_{66}N_4O_4$ (594.9): C, 68.64; H, 11.18; N, 9.42. Found: C, 68.70; H, 11.18; N, 9.32.

(1*R*,5*R*,2′*S*,2″*S*)-(–)-*N*-(2-Methoxymethylpyrrolidine-1-yl)-*N*-{5-[(2-methoxy-methylpyrrolidine-1-yl)-propionylamino]-1-methylhexyl}-propionamide [(*R*,*R*,*S*,*S*)-3r]

An organocerium reagent (8 mmol) prepared from $CeCl_3$ and MeLi (1.6 M soln in Et_2O) was treated according to GP 2 with hydrazone **2c** (0.32 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with propionyl chloride (2.22 g, 24 mmol, 2.1 mL). Flash chromatography (SiO_2, Et_2O–petroleum ether, 4:1) yielded **3r** (0.46 g, 98%) as a light yellow highly viscous oil.

De 94% (GC); $[\alpha]_D^{24}$ –63.0 (*c* 0.96, $CHCl_3$).

IR ($CHCl_3$): 2976, 2936, 2876, 2458, 2401, 1730, 1646 (C=O), 1463, 1435, 1375, 1357, 1238, 1216, 1126, 972, 927, 891, 755, 667, 582 cm^{-1}.

^1H NMR ($CDCl_3$): Only the chemical shifts of the main diastereomer are given. δ = 1.04 (t, *J* = 7.5 Hz, 6 H, C*H*$_3$CH$_2$), 1.40 (d, *J* = 6.7 Hz, 6 H, C*H*$_3$CH), 1.60–2.60 (m, 14 H, NCH$_2$C*H*$_2$C*H*$_2$, CHC*H*$_2$C*H*$_2$C*H*$_2$CH), 2.47 (q, *J* = 7.5 Hz, 4 H, CH$_3$C*H*$_2$), 2.82–3.40 (m, 12 H, CHNCO, CH$_2$NCHCH$_2$), 3.32 (s, 6 H, OCH_3).

^{13}C NMR ($CDCl_3$): Only the chemical shifts of the main diastereomer are given. δ = 9.08 (*C*H$_3$CH$_2$), 18.45 (*C*H$_3$CH), 21.05 (NCH$_2$*C*H$_2$), 26.38, 26.77 (2C) (CH$_3$*C*H$_2$, NCH$_2$CH$_2$*C*H$_2$, CH$_3$CHCH$_2$*C*H$_2$), 34.64 (CH$_3$CH*C*H$_2$), 50.92 (NCH$_2$), 51.49 (N*C*HCH$_3$), 58.57, 59.10 (*C*HCH$_2$OCH$_3$), 74.07 (CH_2O), 177.45 (C=O).

MS (70 eV): *m*/*z* (%) = 424 (15), 423 (67) [$M^+ - C_2H_5O$], 149 (11), 141 (28), 115 (6), 114 (100) [$C_6H_{12}NO^+$], 112 (11), 85 (10), 84 (11), 83 (14), 71 (15), 70 (33), 69 (10), 58 (14), 57 (26), 55 (20), 45 (27), 44 (12), 43 (59), 41 (20).

Anal. calcd for $C_{25}H_{48}N_4O_4$ (468.7): C, 64.07; H, 10.32; N, 11.95. Found: C, 64.06; H, 10.34; N, 11.79.

(1*R*,5*R*,2′*S*,2″*S*)-(–)-*N*-{1-Butyl-5-[(2-methoxymethylpyrrolidine-1-yl)-propionylamino]-nonyl}-*N*-(2-methoxymethylpyrrolidine-1-yl)-propionamide [(*R*,*R*,*S*,*S*)-3s]

An organocerium reagent (8 mmol) prepared from $CeCl_3$ and BuLi (1.6 M soln in hexane) was treated according to GP 2 with hydrazone **2c** (0.32 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with propionyl chloride (2.22 g, 24 mmol, 2.1 mL). Flash chromatography (SiO_2, Et_2O–petroleum ether, 4:1) yielded **3s** (0.48 g, 87%) as a light yellow highly viscous oil.

De 68% (GC); $[\alpha]_D^{29}$ –48.6 (*c* 1.66, $CHCl_3$).

IR (film): 2956, 2932, 2872, 2735, 1733, 1658 (C=O), 1461, 1428, 1396, 1376, 1357, 1266, 1246, 1196, 1113, 1077, 1014, 973, 923, 901, 856, 805, 734, 580 cm^{-1}.

^1H NMR ($CDCl_3$): Only the chemical shifts of the main diastereomer are given. δ = 0.88 (t, *J* = 7.4 Hz, 6 H, C*H*$_3$CH$_2$CH$_2$), 1.04 (t, *J* = 7.4 Hz, 6 H, C*H*$_3$CH$_2$CO), 1.10–1.40 (m, 10 H, CH$_3$C*H*$_2$C*H*$_2$, CHCH$_2$C*H*$_2$CH$_2$CH), 1.60–2.55 (m, 20 H, NCH$_2$C*H*$_2$C*H*$_2$, CH$_2$C*H*$_2$CHC*H*$_2$CH$_2$, CH$_3$C*H*$_2$CO), 2.78–3.62 (m, 12 H, CHNCO, CH$_2$NCHCH$_2$), 3.32 (s, 6 H, OCH$_3$).

^{13}C NMR ($CDCl_3$): Only the chemical shifts of the main diastereomer are given. δ = 9.24 (*C*H$_3$CH$_2$CO), 14.15 (*C*H$_3$CH$_2$CH$_2$), 21.01, 22.99 (NCH$_2$*C*H$_2$, CH$_3$*C*H$_2$CH$_2$), 26.41, 26.77 (2C) (CH$_3$*C*H$_2$CO, CHCH$_2$*C*H$_2$CH$_2$CH, NCH$_2$CH$_2$*C*H$_2$), 30.00 (CH$_3$CH$_2$*C*H$_2$), 32.63, 33.99 (CH$_3$CH$_2$CH$_2$*C*H$_2$CH*C*H$_2$), 51.42 (NCH$_2$), 56.66, 58.34, 59.13 (*C*HNCO, *C*HCH$_2$OCH$_3$), 74.08 (CH$_2$O), 177.70 (C=O).

MS (70 eV): *m*/*z* (%) = 552 (0.15) [M^+], 507 (3.51) [$M^+ - C_2H_5O$], 196 (11), 187 (13), 155 (19), 142 (53), 114 (100) [$C_6H_{12}NO^+$], 85 (13), 84 (10), 82 (12), 74 (11), 70 (24), 69 (10), 57 (12), 55 (17), 45 (11).

Anal. calcd for $C_{31}H_{60}N_4O_4$ (552.8): C, 67.35; H, 10.94; N, 10.13. Found: C, 66.99; H, 10.82; N, 10.00.

(*1S*,*5S*,*2′S*,*2″S*)-(–)-*N*-{1-Allyl-5-[(2-methoxymethylpyrrolidine-1-yl)-propionylamino]-oct-7-enyl}-*N*-(2-methoxymethylpyrrolidine-1-yl)-propionamide [(*S*,*S*,*S*,*S*)-3t]

An organocerium reagent (8 mmol) prepared from $CeCl_3$ and allylMgCl (1 M soln in THF) was treated according to GP 2 with hydrazone **2c** (0.32 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with propionyl chloride (2.22 g, 24 mmol, 2.1 mL). Flash chromatography (SiO_2, Et_2O–petroleum ether, 2:1) yielded **3t** (0.47 g, 90%) as a colorless highly viscous oil which crystallized at 2 °C as needles.

De 83% (GC); $[\alpha]_D^{25}$ –28.2 (*c* 1.23, $CHCl_3$).

IR (film): 3075, 2975, 2935, 2875, 1735, 1657, 1462, 1447, 1395, 1375, 1358, 1278, 1240, 1196, 1125, 1112, 1076, 998, 973, 917, 877, 829, 806, 700, 648, 566 cm^{-1}.

^1H NMR ($CDCl_3$): Only the chemical shifts of the main diastereomer are given. δ = 1.04 (t, *J* = 7.5 Hz, 6 H, C*H*$_3$CH$_2$), 1.60–3.65 (m, 34 H, CH$_2$, CH except CH=CH$_2$), 3.32 (s, 6 H, OCH$_3$), 5.04 (m, 4 H, CH=C*H*$_2$), 5.72 (m, 2 H, C*H*=CH$_2$).

^{13}C NMR ($CDCl_3$): Only the chemical shifts of the main diastereomer are given. δ = 9.29 (*C*H$_3$CH$_2$), 20.97 (NCH$_2$*C*H$_2$), 26.42, 26.76 (2 C) (NCH$_2$CH$_2$*C*H$_2$, CH$_3$*C*H$_2$, CHCH$_2$*C*H$_2$CH$_2$CH), 33.75 (CH*C*H$_2$CH$_2$*C*H$_2$CH), 36.77 (*C*H$_2$CH=CH$_2$), 51.65 (NCH$_2$), 56.03, 58.50, 59.14 (*C*HNCO, *C*HCH$_2$OCH$_3$), 74.14 (CH$_2$O), 116.92 (*C*H$_2$=CH), 136.39 (*C*H=CH$_2$), 177.93 (C=O).

MS (70 eV): *m*/*z* (%) = 476 (17), 475 (52) [$M^+ - C_2H_5O$], 366 (21), 187 (10), 155 (15), 141 (43), 114 (100) [$C_6H_{12}NO^+$], 110 (10), 97 (11), 85 (15), 82 (12), 71 (15), 70 (28), 68 (12), 57 (28).

Anal. calcd for $C_{29}H_{52}N_4O_4$ (520.8): C, 66.89; H, 10.07; N, 10.76. Found: C, 66.73; H, 10.08; N, 10.70.

(1*S*,5*S*,2′*S*,2″*S*)-(+)-*N*-{1-Benzyl-5-[(2-methoxymethylpyrrolidine-1-yl)-propionylamino]-6-phenylhexyl}-*N*-(2-methoxymethylpyrrolidine-1-yl)-propionamide [(*S*,*S*,*S*,*S*)-3u]

An organocerium reagent (8 mmol) prepared from $CeCl_3$ and BnMgCl (1 M soln in THF) was treated according to GP 2 with hydrazone **2c** (0.32 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with propionyl chloride (2.22 g, 24 mmol, 2.1 mL). Flash chromatography (SiO_2, Et_2O–petroleum ether, 2:1) yielded **3u** (0.63 g, quant.) as a colorless highly viscous oil.

De 83% (^{13}C NMR); $[\alpha]_D^{26}$ +17.8 (*c* 0.99, $CHCl_3$).

IR (KBr): 3027, 2963, 2930, 2867, 2827, 1650 (C=O), 1495, 1458, 1427, 1375, 1355, 1279, 1258, 1194, 1114, 1081, 1016, 976, 920, 875, 842, 801, 750, 703, 586, 543, 500 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.08 (t, *J* = 7.4 Hz, 6 H, C*H*$_3$CH$_2$), 1.30–2.35 (m 18 H, NCH$_2$C*H*$_2$C*H*$_2$, C*H*$_2$C*H*$_2$CHC*H*$_2$Ph), 2.43 (q, *J* = 7.4 Hz, 4 H, CH$_3$C*H*$_2$), 2.80–3.50 (m, 12 H, CH$_2$NCHCH$_2$O, CHNCO), 3.28 (s, 6 H, OCH$_3$), 7.20 (m, 10 H, Ph).

^{13}C NMR ($CDCl_3$): δ = 9.33 (*C*H$_3$CH$_2$), 20.83 (NCH$_2$*C*H$_2$), 25.77 (PhCH$_2$CHCH$_2$*C*H$_2$), 26.28, 26.98 (CH$_3$*C*H$_2$, NCH$_2$CH$_2$*C*H$_2$), 33.91 (PhCH$_2$CH*C*H$_2$), 37.12 (PhCH$_2$), 50.03 (NCH$_2$), 58.31, 58.66, 59.13 (*C*HNCO, *C*HCH$_2$OCH$_3$), 74.12 (CH$_2$O), 126.29 (C_{para}), 128.22, 129.85 (C_{ortho}, C_{meta}), 140.24 (C_{ipso}), 178.09 (C=O).

MS (70 eV): *m*/*z* (%) = 620 (0.06) [M^+], 575 (19) [$M^+ - C_2H_5O$], 416 (21), 384 (12), 265 (19), 187 (17), 174 (12), 155 (20), 154 (10), 141 (62), 131 (11), 129 (10), 114 (100) [$C_6H_{12}NO^+$], 97 (11), 91 (73) [$C_7H_7^+$], 85 (13), 82 (10), 71 (10), 70 (21), 57 (23), 45 (11).

HRMS (EI): *m*/*z* calcd for $C_{35}H_{51}N_4O_3$ ($M^+ - C_2H_5O$), 575.3961; found, 575.3961.

(1*R*,4*R*)-(+)-*N*-(1-Methyl-4-methoxycarbonylaminopentyl)-methylcarbamate [(*R*,*R*)-4a]

Hydrazide **3a** (850 mg, 1.85 mmol) was allowed to react according to GP 3. After reductive cleavage (3 h) and work up flash column chromatography (SiO_2, Et_2O–petroleum ether, 4:1) yielded **4a** (240 mg, 56%) as a colorless solid.

De 87% (GC); ee 98% [GC_{CSP}: XE-60-S-Valin-S-X-Phenylethylamid, H_2 = 1.0 bar, T = 140–3–190 of (*R*,*R*)-**6a**]; $[\alpha]_D^{29}$ +20.3 (*c* 1.02, $CHCl_3$).

IR (KBr): 3319 (NH), 3070, 2969, 2950, 2908, 2860, 2848, 2797, 2373, 2345, 2199, 2053, 1688 (C=O), 1657, 1618, 1547, 1451, 1377, 1346, 1310, 1296, 1266, 1207, 1198, 1176, 1112, 1093, 1058, 1034, 1023, 963, 935, 868, 779, 708, 672, 519 cm^{-1}.

^1H NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 1.14 (d, *J* = 6.5 Hz, 6 H, C*H*$_3$CH), 1.46 (m, 4 H, CH$_2$), 3.65 (br s, 8 H, OCH$_3$, CH), 4.63 (br m, 2 H, NH).

^{13}C NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 21.44 (*C*H$_3$CH), 33.66 (CH$_2$), 47.02 (CH), 51.90 (OCH$_3$), 156.54 (C=O).

MS (70 eV): *m*/*z* (%) = 233 (1.09) [$M^+ + 1$], 232 (7) [M^+], 173 (17), 156 (10), 142 (14), 102 (100), 58 (9).

Anal. calcd for $C_{10}H_{20}N_2O_4$ (232.3): C, 51.71; H, 8.68; N, 12.06. Found: C, 51.71; H, 8.67; N, 12.00.

(1*R*,5*R*)-(–)-*N*-(1-Methyl-5-methoxycarbonylaminohexyl)-methylcarbamate [(*R*,*R*)-4e]

Hydrazide **3e** (790 mg, 1.67 mmol) was allowed to react according to GP 3. After reductive cleavage (2 h) and work up flash column chromatography (SiO_2, Et_2O–PE 4:1) yielded **4e** (250 mg, 61%) as a colorless solid.

Mp 105 °C; de 91% (GC); ee 98% (GC_{CSP}: 7-CD PERME 25 m, H_2 = 1 bar, T = 100–1–190); $[\alpha]_D^{28}$ –6.3 (*c* 1.06, $CHCl_3$).

IR (film): 3305 (NH), 3065, 2969–2947, 2864, 2850, 2850, 2798, 1717, 1693, 1544, 1452, 1374, 1357, 1341, 1296, 1260, 1235, 1193, 1161, 1097, 1064–1033, 1016, 977, 950, 920, 884, 847, 814, 783, 710, 669 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.13 (d, *J* = Hz, 6 H, CH_3CH), 1.39 (m, 6 H, CH_2), 3.66 (br s, 6 H, OCH_3), 4.5–4.8 (br, 4 H, NH, CH).

^{13}C NMR ($CDCl_3$): δ = 21.66 (*C*H_3CH), 22.20 (CH_2*C*$H_2$$CH_2$), 36.63 (CH*C*$H_2$), 46.55 (CH), 51.86 ($OCH_3$), 156.79 (C=O).

MS (70 eV): *m*/*z* (%) = 246 (2.07) [M^+], 171 (11), 156 (17), 102 (100), 58 (14), 44 (23).

Anal. calcd for $C_{11}H_{22}N_2O_4$ (232.3): C, 53.64; H, 9.00; N, 11.37. Found: C, 54.07; H, 9.08; N, 11.39.

(1*R*,2*R*)-(+)-*N*-(2-Acetylamino-1-methylpropyl)acetamide [(*R*,*R*)-4 i]

Hydrazide **3i** (60 mg, 0.15 mmol) was allowed to react according to GP 3. After reductive cleavage (2 h) and work up flash column chromatography (SiO_2, Et_2O–MeOH 8:1) yielded **4i** (16 mg, 62%) as a colorless solid.

Mp 191 °C; de 98% (GC); ee 98% (GC_{CSP}: 7-CD PERME 25 m, H_2 = 1 bar, T = 120–1–190); $[\alpha]_D^{28}$ +44.9 (*c* 0.049, butanone); {Lit.: $[\alpha]_D^{28}$ –54.9 (*c* 0.049, butanone for (*S*,*S*)-**4i**)}.

The spectroscopic data of **4i** corresponded with those reported in ref.[34]

(1*R*,2*R*)-(+)-*N*-(1-Methyl-2-propionylaminopropyl)propionamide [(*R*,*R*)-4m]

Hydrazide **3m** (104 mg, 0.24 mmol) was allowed to react according to GP 3. After reductive cleavage (3 h) and work up flash column chromatography (SiO_2, Et_2O–MeOH 20:1) yielded **4m** (35 mg, 73%) as a colorless solid.

Mp 162–165 °C; de 98% (GC); ee 98% (GC_{CSP}: XE-60-S-Valin-S-X-Phenylethylamide, H_2 = 1.4 bar, T = 110–3–190); $[\alpha]_D^{25}$ +65.5 (*c* 0.91, $CHCl_3$).

IR (KBr): 3288 (NH), 3083, 2970, 2929, 2877, 1641 (C=O), 1551, 1450, 1374, 1275, 1238, 1158, 1095, 1076, 1019, 980, 915, 699, 588, 518 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.12 (t, *J* = 7.7 Hz, 6 H, C$H_3$$CH_2$), 1.18 (d, *J* = 6.3 Hz, 6 H, CH_3CH), 2.16 (q, *J* = 7.7 Hz, 4 H, CH_2), 3.84 (m, 2 H, CH), 6.22 (br s, 2 H, NH).

^{13}C NMR ($CDCl_3$): δ = 9.94 (*C*$H_3$$CH_2$), 18.46 (*C*$H_3$CH), 29.83 ($CH_2$), 50.78 (CH), 174.47 (C=O).

MS (70 eV): *m*/*z* (%) = 201 (1.98) [M^+ + 1], 200 (0.28) [M^+], 127 (31) [$C_7H_{13}NO^+$], 101 (100) [$C_5H_{11}NO^+$], 100 (24) [$C_5H_{10}NO^+$], 86 (15), 72 (19), 57 (31).

HRMS (EI): *m*/*z* calcd for $C_{10}H_{20}N_2O_2$ (M^+ – H), 201.1603; found, 201.1596.

(1*R*,4*R*)-(+)-*N*-(1-Methyl-4-propionylaminopentyl)propionamide [(*R*,*R*)-4n]

Hydrazide **3n** (290 mg, 0.55 mmol) was allowed to react according to GP 3. After reductive cleavage (3 h) and work up flash column chromatography (SiO_2, Et_2O–MeOH, 20:1) yielded **4n** (43 mg, 34%) as a colorless solid.

Mp 183 °C; de 86% (GC); ee 98% (GC_{CSP}: XE-60-S-Valin-S-X-Phenylethylamide, H_2 = 1.0 bar, T = 140–3–190); $[\alpha]_D^{24}$ +32.4 (*c* 0.88, $CHCl_3$).

IR (KBr): 3855, 3839, 3287 (NH, s), 3078, 2961, 2925, 2855, 2372, 2345, 1641 (C=O), 1548, 1499, 1463, 1423, 1378, 1343, 1307, 1288, 1256, 1208, 1159, 1143, 1117, 1081, 1064, 1041, 1016, 954, 911, 875, 805, 765, 738, 701, 581, 532 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.13 (d, *J* = 6.0 Hz, 6 H, CH_3CH) 1.14 (t, *J* = 7.7 Hz, 6 H, C$H_3$$CH_2$), 1.45 (m, 4 H, CHC$H_2$), 2.18 (q, *J* = 7.7 Hz, 4 H, CH_3CH_2), 3.96 (m, 2 H, CH), 5.51 (br d, *J* = 8.0 Hz, 2 H, NH).

^{13}C NMR ($CDCl_3$): δ = 9.97 (*C*$H_3$$CH_2$), 21.02 (*C*$H_3$CH), 29.87 ($CH_3$*C*$H_2$), 33.58 (CH*C*$H_2$), 45.07 (CH), 173.25 (C=O).

MS (70 eV): *m*/*z* (%) = 228 (4.20) [M^+], 171 (45) [M^+ – C_3H_5O], 154 (38), 129 (23), 128 (16), 111 (11), 101 (31), 100 (77), 99 (12), 98 (67), 97 (17), 95 (10), 87 (14), 85 (19), 84 (31), 83 (20), 82 (10), 81 (12), 74 (22), 73 (20), 72 (10), 71 (29), 70 (13), 69 (19), 60 (18), 58 (13), 57 (50), 56 (13), 55 (31), 44 (100).

HRMS (EI): *m*/*z* calcd for $C_{12}H_{24}N_2O_2$ (M^+), 228.1838; found, 228.1837.

(1*R*,4*R*)-(+)-*N*-(1-Ethyl-4-propionylaminohexyl)-propionamide [(*R*,*R*)-4o]

Hydrazide **3o** (140 mg, 0.29 mmol) was allowed to react according to GP 3. After reductive cleavage (3 h) and work up flash column chromatography (SiO_2, Et_2O–MeOH, 20:1) yielded **3o** (47 mg, 63%) as a colorless solid.

Mp 179 °C; de 98% (GC); ee 96% (GC_{CSP}: Lipodex E 25 m, H_2 = 1.6 bar, T = 140–1–190); $[\alpha]_D^{25}$ +56.3 (*c* 0.32, $CHCl_3$).

IR (KBr): 3292 (NH), 3079, 2969, 2940, 2877, 2857, 2785, 2373, 2345, 1642 (C=O), 1548, 1462, 1376, 1286, 1269, 1249, 1237, 1196, 1149, 1115, 1082 ((m), 1039, 1011, 997, 974, 945, 924, 911, 880, 853, 783, 710, 582, 548 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.89 (t, *J* = 7.4 Hz, 6 H, C$H_3$$CH_2$CH), 1.15 (t, *J* = 7.4 Hz, 6 H, C$H_3$$CH_2$CO), 1.22–1.63 (m, 8 H, CH_2CHCH_2), 2.20 (q, *J* = 7.4 Hz, 4 H, CH_3CH_2CO), 3.81 (m, 2 H, CH), 5.31 (br d, *J* = 9.1 Hz, 2 H, NH).

^{13}C NMR ($CDCl_3$): δ = 10.12, 10.22 (CH_3), 27.93, 29.97, 31.42 (CH_2), 50.50 (CH), 173.63 (C=O).

MS (70 eV): *m*/*z* (%) = 257 (4.48) [M^+ + 1], 256 (1.57) [M^+], 199 (33) [M^+ – C_3H_5O], 182 (24), 154 (44), 142 (13), 126 (40), 115 (21), 114 (47), 100 (12), 98 (88), 74 (20), 58 (100), 57 (52), 56 (19), 55 (13).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{28}N_2O_2$ (M^+), 256.2151; found, 256.2153.

(1*R*,4*R*)-(+)-*N*-(1-Butyl-4-propionylaminooctyl)propionamide [(*R*,*R*)-4p]

Hydrazide **3p** (270 mg, 0.5 mmol) was allowed to react according to GP 3. After reductive cleavage (3 h) and work up flash column chromatography (SiO_2, Et_2O–MeOH, 20:1) yielded **4p** (98 mg, 63%) as a colorless solid.

Mp 190 °C; de 91% (after chromatography, crude: 65%, GC); ee 98% (GC_{CSP}: XE-60-S-Valin-S-X-Phenylethylamide, H_2 = 1.6 bar, T = 190-iso); $[\alpha]_D^{23}$ +35.1 (*c* 1.03, $CHCl_3$).

IR (KBr): 3292 (NH), 3077, 2938, 2857, 1642 (C=O), 1548, 1465, 1376, 1287, 1241, 1146, 1094, 906, 730 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 6 H, C$H_3$$CH_2$$CH_2$), 1.15 (t, *J* = 7.7 Hz, 6 H, C$H_3$$CH_2$CO), 1.20–1.60 (m, 16 H, CH_2 except $CH_3$$CH_2$CO), 2.19 (q, *J* = 7.7 Hz, 4 H, CH_3CH_2CO), 3.87 (m, 2 H, CH), 5.40 (d, *J* = 8.7 Hz, 2 H, NH).

^{13}C NMR ($CDCl_3$): δ = 10.13 (*C*$H_3$$CH_2$CO), 14.04 (*C*$H_3$$CH_2$$CH_2$), 22.63 ($CH_3$*C*$H_2$$CH_2$), 28.09, 29.94, 31.87 ($CH_3$$CH_2$*C*$H_2$*C*$H_2$, CH_3*C*H_2CO), 34.95 (CH*C*H_2*C*H_2CH), 49.12 (CH), 173.49 (C=O).

MS (70 eV): *m*/*z* (%) = 313 (1.39) [M^+ + 1], 255 (39) [M^+ – C_3H_5O], 239 (11), 238 (48), 183 (18), 182 (100), 170 (21) [M^+ – $C_8H_{16}NO$], 143 (12), 142 (52), 126 (86), 114 (19), 100 (12), 86 (71), 74 (20), 57 (45), 56 (15), 55 (14).

HRMS (EI): *m*/*z* calcd for $C_{18}H_{36}N_2O_2$ (M^+), 312.2777; found, 312.2772.

(1*R*,4*R*)-(+)-*N*-(1-Hexyl-4-propionylaminodecyl)-propionamide [(*R*,*R*)-4q]

Hydrazide **3q** (180 mg, 0.3 mmol) was allowed to react according to GP 3. After reductive cleavage (3 h) and work up flash column chromatography (SiO_2, Et_2O–MeOH, 20:1) yielded **4q** (72 mg, 65%) as a colorless solid.

Mp 162–165 °C; de 98% (GC, after chromatography,crude: 67%); ee 96% [^{1}H-Shift-NMR with (*R*)-1-Anthryl-2,2,2-trifluoroethanol]; $[\alpha]_D^{24}$ +25.5 (*c* 0.55, $CHCl_3$).

IR (KBr): 3292 (NH), 3078, 2928, 2855(m), 1642 (C=O), 1548, 1464, 1377, 1253, 1205, 1143, 945, 903, 724, 581 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 6.9, 6 H, C*H*$_3$CH$_2$CH$_2$), 1.15 (t, *J* = 7.7 Hz, 6 H C*H*$_3$CH$_2$CO), 1.20–1.70 (m, 24 H, CH_2 except CH_3CH_2CO), 2.19 (q, *J* = 7.7 Hz, 4 H, CH_3CH_2CO), 3.86 (m, 2 H, CH), 5.17 (d, *J* = 9.1, 2 H, NH).

^{13}C NMR ($CDCl_3$): δ = 10.12 (*C*H$_3$CH$_2$CO), 14.07 (*C*H$_3$CH$_2$CH$_2$), 22.60 (CH$_3$*C*H$_2$CH$_2$), 25.89, 29.25, 29.96 (CH$_3$*C*H$_2$CO, *C*H$_2$*C*H$_2$CH$_2$CH), 31.78 (CH$_2$CH$_2$*C*H$_2$CH), 35.25 (CH*C*H$_2$*C*H$_2$CH), 49.18 (CH), 173.47 (C=O).

MS (70 eV): *m*/*z* (%) = 368 (9.98) [M^+], 311 (41) [$M^+ - C_3H_5O$], 295 (11), 294 (24), 238 (34), 211 (12), 210 (90), 199 (10), 198 (21), 171 (18), 170 (62), 155 (10), 154 (91), 115 (16), 114 (100), 100 (11), 74 (48), 69 (21), 57 (55), 56 (22), 55 (26), 44 (32), 43 (31), 41 (17).

HRMS (EI): *m*/*z* calcd for $C_{22}H_{44}N_2O_2$ (M^+), 368.3403; found, 368.3402.

(1*R*,5*R*)-(–)-*N*-(1-Methyl-5-propionylaminohexyl)propionamide [(*R*,*R*)-4r]

Hydrazide **3r** (140 mg, 0.3 mmol) was allowed to react according to GP 3. After reductive cleavage (3.5 h) and work up flash column chromatography (SiO_2, Et_2O–MeOH, 20:1) yielded **4r** (63 mg, 87%) as a colorless solid.

Mp 150 °C; de 94% (GC); ee 9% (GC_{CSP}: XE-60-S-Valin-S-X-Phenylethylamid, H_2 = 1.0 bar, T = 120–1–190); $[\alpha]_D^{28}$ –15.5 (*c* 1.06, $CHCl_3$).

IR (KBr): 3292 (NH), 3077, 2970, 2941, 2876, 2857, 1640 (C=O), 1548, 1463, 1374, 1297, 1244, 1158, 1121, 1068, 1016, 911, 742, 586 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.13 (d, *J* = 6.4 Hz, 6 H, C*H*$_3$CH), 1.14 (t, *J* = 7.7 Hz, 6 H, C*H*$_3$CH$_2$), 1.24–1.55 (m, 6 H, CH$_2$CH$_2$), 2.19 (q, *J* = 7.7 Hz, 4 H, CH$_3$C*H*$_2$), 3.94 (m, 2 H, CH), 5.81 (d, *J* = 8.1 Hz, 2 H, NH).

^{13}C NMR ($CDCl_3$): δ = 10.10 (*C*H$_3$CH$_2$), 21.60 (*C*H$_3$CH), 22.34 (CH$_2$*C*H$_2$CH$_2$), 29.87, 36.42 (CH*C*H$_2$CH$_2$, CH$_3$*C*H$_2$), 44.48 (CH), 173.69 (C=O).

MS (70 eV): *m*/*z* (%) = 243 (1.38) [M^+ + 1], 242 (8.23) [M^+], 185 (22) [$M^+ - C_3H_5NO$], 142 (12), 114 (43), 112 (15), 101 (26), 100 (30), 98 (20), 74 (21), 58 (11), 57 (23), 55 (13), 44 (100).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{26}N_2O_2$ (M^+), 242.1994; found, 242.1995.

(1*R*,5*R*)-(–)-*N*-(1-Butyl-5-propionylaminononyl)propionamide [(*R*,*R*)-4s]

Hydrazide **3s** (170 mg, 0.3 mmol) was allowed to react according to GP 3. After reductive cleavage (3.5 h) and work up flash column chromatography (SiO_2, Et_2O–MeOH, 20:1) yielded **4s** (64 mg, 65%) as a colorless solid.

Mp 138 °C; de 72% (^{1}H NMR); ee 98% [according to (*R*,*R*)-**4p,r**, (*S*,*S*)-**4t,u**]; $[\alpha]_D^{27}$ –17.3 (*c* 1.01, $CHCl_3$).

IR (KBr): 3290 (NH), 3081, 2956, 2939, 2874, 2857, 2372, 2345, 1643(C=O), 1550, 1465, 1428, 1375, 1288, 1268, 1244, 1212, 1159, 1146, 1119, 1098, 1070, 1009, 945, 908, 732, 591, 467 cm^{-1}.

^{1}H NMR ($CDCl_3$): Isomers: major C_2-diastereomer: minor *meso*-diastereomer; δ = 0.88 (t, *J* = 6.9 Hz, 6 H, C*H*$_3$CH$_2$CH$_2$), 1.15:1.16 (t, *J* = 7.7 Hz, 6 H, C*H*$_3$CH$_2$CO), 1.20−1.60 (m, 18 H, CH_2 except CH_3CH_2CO), 2.20 (q, *J* = 7.7 Hz, 4 H, CH$_3$C*H*$_2$CO), 3.86 (m, 2 H, CH), 5.54−5.35 (d, *J* = 8.7 Hz, 2 H, NH).

^{13}C NMR ($CDCl_3$): δ = 10.18 (*C*H$_3$CH$_2$CO), 14.05 (*C*H$_3$CH$_2$CH$_2$), 21.90 (CHCH$_2$*C*H$_2$CH$_2$CH), 22.66 (CH$_3$*C*H$_2$CH$_2$), 28.11, 29.90, 34.52, 35.60 (CH$_3$CH$_2$*C*H$_2$*C*H$_2$CH*C*H$_2$, CH$_3$*C*H$_2$CO), 48.46 (CH), 173.85 (C=O).

MS (70 eV): *m*/*z* (%) = 327 (2.02) [M^+ + 1], 326 (5.57) [M^+], 269 (24) [$M^+ - C_3H_5O$], 197 (14), 196 (100), 156 (14), 142 (18), 140 (68), 128 (13), 86 (34), 74 (23), 69 (5), 57 (16), 56 (12).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{38}N_2O_2$ (M^+), 326.2933; found, 326.2931.

(1*S*,5*S*)-(–)-*N*-(1-Allyl-5-propionylaminooct-2-enyl)propionamide [(*S*,*S*)-4t]

Hydrazide **3t** (260 mg, 0.5 mmol) was allowed to react according to GP 3. After reductive cleavage (3 h) and work up flash column chromatography (SiO_2, Et_2O–MeOH, 20:1) yielded **4t** (87 mg, 59%) as a colorless solid.

Mp 112 °C; de 77% (GC); ee 98% (GC_{CSP}: Lipodex E 25 m, H_2 = 1.5 bar, T = 100–2–190); $[\alpha]_D^{27}$ –37.5 (*c* 0.12, $CHCl_3$).

IR (KBr): 3283 (NH), 3078, 2978, 2942, 2854, 2372, 1645(C=O), 1549, 1463, 1375, 1279, 1255, 1156, 1126, 990, 917, 741, 722, 525 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.14 (t, *J* = 7.4 Hz, 6 H, CH_3), 1.20–1.52 (m, 10 H, CH_2 except CH_3CH_2), 2.19 (q, *J* = 7.4 Hz, 4 H, CH$_3$C*H*$_2$), 3.94 (m, 2 H, CH), 5.07 (m, 4 H, C*H*$_2$=CH), 5.75 (m, 4 H, C*H*=CH$_2$, NH).

^{13}C NMR ($CDCl_3$): δ = 10.13 (CH_3), 21.95 (CH$_2$*C*H$_2$CH$_2$), 29.85, 33.70 (*C*H$_2$CH$_2$*C*H$_2$, CH$_3$*C*H$_2$), 39.95 (*C*H$_2$CH=CH$_2$), 47.78 (NCH), 117.61 (*C*H$_2$=CH), 134.55 (*C*H=CH$_2$), 173.98 (C=O).

MS (70 eV): *m*/*z* (%) = 295 (1.46) [M^+ + 1], 294 (0.87) [M^+], 181 (11), 180 (85) [$M^+ - C_3H_6NO–C_3H_6$], 125 (10), 124 (100), 82 (10), 70 (10), 57 (19), 56 (14).

HRMS (EI): *m*/*z* calcd for $C_{17}H_{30}N_2O_2$ (M^+), 294.2307; found, 294.2308.

(1*S*,5*S*)-(–)-*N*-(1-Benzyl-6-phenyl-5-propionylaminohexyl)propionamide [(*S*,*S*)-4u]

Hydrazide **3u** (310 mg, 0.5 mmol) was allowed to react according to GP 3. After reductive cleavage (3 h) and work up flash column chromatography (SiO_2, Et_2O–MeOH, 20:1) yielded **4u** (145 mg, 81%) as a colorless solid.

Mp 129 °C; de 86% (^{13}C NMR); ee 98% [$HPLC_{CSP}$: (*S*,*S*)-Whelk-O, eluent: cyclohexane−*i*-PrOH 9:1,R_t: 15.45 min]; $[\alpha]_D^{25}$ –30.9 (*c* 1.02, $CHCl_3$).

IR (KBr): 3303 (NH), 3064, 3028, 2976, 2943, 2856, 2375, 2164, 1644(C=O), 1545, 1497, 1456, 1374, 1240, 1196, 1125, 1075, 1032, 915, 750, 700, 509 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.07 (t, *J* = 7.7 Hz, 6 H, CH_3), 1.23–1.45 (m, 6 H, CHC*H*$_2$C*H*$_2$), 2.12 (q, *J* = 7.7 Hz, 4 H, CH$_3$C*H*$_2$), 2.74 (m, 4 H, C*H*$_2$Ph), 4.10 (m, 2 H, CH), 5.76 (d, *J* = 8.5 Hz, 2 H, NH), 7.12–7.32 (m, 10 H, Ph).

^{13}C NMR ($CDCl_3$): δ = 10.58 (CH_3), 22.57 (CHCH$_2$*C*H$_2$), 30.35, 33.86 (CH$_3$*C*H$_2$, CH*C*H$_2$CH$_2$), 42.29 (CH$_2$Ph), 50.06 (CH), 126.95 (C_{para}), 128.95, 129.93 (C_{ortho}, C_{meta}), 138.85 (C_{ipso}), 174.59 (C=O).

MS (70 eV): *m*/*z* (%) = 395 (0.45) [M^+ + 1], 303 (10) [$M^+ - C_7H_7$], 231 (11), 230 (66), 175 (14), 174 (100), 91 (42) [$C_7H_7^+$], 82 (14), 57 (33), 56 (23).

HRMS (EI): *m*/*z* calcd for $C_{18}H_{27}N_2O_2$ ($M^+ - C_7H_7$), 303.2073; found, 303.2072.

(4*R*,5*R*,2′*S*,2″*S*)-(–)-1,3-Bis-(2-methoxymethyl)pyrrolidine-1-yl-4,5-dimethyl-imidazolidin-2-one [(*R*,*R*,*S*,*S*)-5a]

An organocerium reagent (6.5 mmol mmol) prepared from $CeCl_3$ and MeLi (1.6 M soln in Et_2O) was treated according to GP 2 with hydrazone **2a** (0.14 g, 0.5 mmol). After the addition was complete (TLC) the reaction was trapped with methyl chloroformate (2.36 g, 25 mmol). Flash chromatography (SiO_2, Et_2O–petroleum ether, 2:1) yielded **5a** (0.11 g, 65%) as a colorless oil.

De 90% (GC); $[\alpha]_D^{25}$ –159.2 (*c* 0.91, $CHCl_3$).

IR (film): 2969–2826, 2739, 2083, 1711(C=O), 1460, 1377, 1335, 1286, 1230, 1200, 1117, 1080, 1012, 973, 919, 767, 707, 647, 596, 531 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.20 (d, 6 H, *J* = 6.7 Hz, C*H*$_3$CH), 1.60–2.10 (m, 8 H, NCH$_2$C*H*$_2$C*H*$_2$), 2.90 (m, 2 H, NC*H*H), 3.02 (m, 2 H, NCH*H*), 3.15–3.40 (m, 6 H, CHCH, C*HCH*HO), 3.34 (s, 6 H, OCH$_3$), 3.80 (m, 2 H, CH*H*O).

^{13}C NMR ($CDCl_3$): δ = 17.04 (*C*H$_3$CH), 22.81 (NCH$_2$*C*H$_2$), 26.88 (NCH$_2$CH$_2$*C*H$_2$), 47.72 (NCH$_2$), 57.80, 58.92, 61.24 (CHCH, *C*HCH$_2$OCH$_3$), 74.82 (CH$_2$O), 160.19 (C=O).

MS (70 eV): *m*/*z* (%) = 340 (38) [M^+], 308 (15), 296 (18), 295 (100) [$M^+ - C_2H_5O$], 263 (35), 227 (20), 226 (34), 206 (11), 195 (12), 183 (19), 182 (90), 180 (23), 163 (13), 157 (99), 155 (11), 142 (11), 139 (15), 125 (68), 115 (10), 114 (64), 113 (48), 82 (27), 71 (14), 70 (58), 69 (20), 68 (19), 67 (15), 57 (21), 56 (15), 55 (43), 45 (26), 44 (14), 43 (29).

Anal. calcd for $C_{17}H_{32}N_4O_3$ (340.5): C, 59.97; H, 9.47; N, 16.46. Found: C, 59.67; H, 9.08; N, 16.79.

(4*R*,5*R*,2′*S*,2″*S*)-(–)-1,3-Bis-(2-methoxymethyl)pyrrolidine-1-yl-4,5-dibutyl-imidazolidin-2-one [(*R*,*R*,*S*,*S*)-5b]

An organocerium reagent (8 mmol) prepared from $CeCl_3$ and BuLi (1.6 M soln in hexane) was treated according to GP 2 with hydrazone **2a** (0.28 g, 1 mmol). After the addition was complete (TLC) the reaction was trapped with methyl chloroformate (2.27 g, 24 mmol). Flash chromatography (SiO_2, Et_2O–petroleum ether, 1:1) yielded **5b** (0.18 g, 42%) as a colorless oil.

De 94% (GC); $[\alpha]_D^{30}$ –122.5 (*c* 0.72, $CHCl_3$).

IR ($CHCl_3$): 2958, 2930, 2873, 2828, 2738, 2458, 1700(C=O), 1457, 1385, 1345, 1285, 1254, 1237, 1216, 1199, 1113, 973, 951, 918, 756, 666, 603, 516, 504 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.93 (t, *J* = 6.5 Hz, 6 H, C*H*$_3$CH$_2$), 1.20–2.20 (m, 20 H, NCH$_2$C*H*$_2$C*H*$_2$, aliph. CH$_2$), 3.00–3.40, 3.90 (m, m, 12 H, NCH$_2$, CHCH, CHCH$_2$O), 3.33 (s, 6 H, OCH$_3$).

^{13}C NMR ($CDCl_3$): δ = 14.12 (*C*H$_3$CH$_2$), 22.76, 23.11 (NCH$_2$*C*H$_2$, CH$_3$*C*H$_2$), 26.84, 26.87 (NCH$_2$CH$_2$*C*H$_2$, CHCH$_2$*C*H$_2$), 32.39 (CHCH*C*H$_2$), 48.45 (NCH$_2$), 58.90, 58.92, 61.28 (CHCH, *C*HCH$_2$OCH$_3$), 74.78 (CH$_2$O), 159.84 (C=O).

MS (70 eV): *m*/*z* (%) = 425 (8.56) [M^+ + 1], 424 (32) [M^+], 380 (18), 379 (64) [$M^+ - C_2H_5O$], 347 (29), 279 (10), 267 (10), 266 (51), 264 (18), 200 (14), 199 (100) [$C_{11}H_{23}N_2O^+$], 197 (25), 168 (14), 167 (75), 153 (32), 142 (16), 114 (77) [$C_6H_{12}NO^+$], 111 (13), 84 (62), 83 (36), 82 (23), 71 (14), 70 (74), 69 (26), 57 (10), 55 (20), 45 (18), 43 (21), 41 (33).

Anal. calcd for $C_{23}H_{44}N_4O_3$ (424.6): C, 65.06; H, 10.44; N, 13.19. Found: C, 64.64; H, 10.24; N, 12.65.

(1*R*,2*R*,2′*S*,2″*S*)-(–)-*N*-[1-Ethyl-2-(2-methoxymethylpyrrolidine-1-ylamino)-butyl]-*N*-(2-methoxymethylpyrrolidine-1-yl)acetamide [(*R*,*R*,*S*,*S*)-6]

An organocerium reagent (20 mmol) prepared from $CeCl_3$ and EtMgBr (1 M soln in THF) was treated according to GP 2 with hydrazone **2a** (0.56 g, 2 mmol). After the addition was complete (TLC) the reaction was trapped with AcCl (1.88 g, 24 mmol). Flash chromatography (SiO_2, Et_2O–petroleum ether, 2:1) yielded **6** (0.39 g, 51%) as a yellowish oil.

De 85% (^{13}C NMR); $[\alpha]_D^{25}$ –112.0 (*c* 0.52, $CHCl_3$).

IR (Et_2O): 3259 (m, NH), 2966, 2933, 2875, 2829, 2058, 1729, 1660(C=O), 1459, 1377, 1365, 1323, 1297, 1244, 1197, 1110, 1048, 1016, 972, 941, 922, 881, 857, 803, 681, 646, 609, 559, 504, 484, 464 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.92 (t, *J* = 7.5 Hz, 3 H, C*H*$_3$CH$_2$), 1.06 (t, *J* = 7.5 Hz, 3 H, C*H*$_3$CH$_2$), 1.26–2.42 (m, 13 H, NCH$_2$C*H*$_2$C*H*$_2$, CH$_3$C*H*$_2$, NH), 2.17 (s, 3 H, CH$_3$C=O), 2.60 –3.80 (m, 11 H, NCH$_2$, CHCH$_2$O, CHCH, C*HCH*HO (Hydrazine), 3.10 (s, 3 H, OCH$_3$), 3.22 (s, 3 H, OCH$_3$), 3.83 (dd, *J* = 3.5, 8.5 Hz, 1 H, CH*H*O (Hydrazine).

^{13}C NMR ($CDCl_3$): δ = 8.82, 12.67 (*C*H$_3$CH$_2$), 21.44, 22.32, 22.84, 23.68 (NCH$_2$*C*H$_2$, CH$_3$*C*H$_2$), 22.58 (*C*H$_3$C=O), 27.11, 27.68 (NCH$_2$CH$_2$*C*H$_2$), 52.72, 56.53 (NCH$_2$), 58.60, 58.83, 60.11, 60.32, 66.04 (CHCH, *C*HCH$_2$OCH$_3$), 76.41, 76.69 (CH$_2$O), 174.14 (C=O).

MS (70 eV): *m*/*z* (%) = 384 (6) [M^+], 172 (10), 171 (100) [$C_9H_{19}N_2O^+$], 114 (14) [$C_6H_{12}NO^+$], 70 (23).

Anal. calcd for $C_{20}H_{40}N_4O_3$ (384.6): C, 62.47; H, 10.48; N, 14.57. Found: C, 62.09; H, 10.50; N, 14.57.

(5*R*,6*R*,2′*S*,2″*S*)-(–)-*N*,*N*-Di[2-(methoxymethyl)pyrrolidine-1-yl]-decane-5,6-diamine [(*R*,*R*,*S*,*S*)-7a]

An organocerium reagent (8 mmol) prepared from $CeCl_3$ and BuLi (1.6 M soln in hexane) was treated according to GP 2 with hydrazone **2a** (0.28 g, 1 mmol). After the addition was complete (TLC) the reaction was terminated by the addition of sat. $NaHCO_3$. Flash chromatography (deactivated SiO_2, Et_2O–petroleum ether, 4:1) yielded **7a** (crude: 0.44 g, quantitative; after chromatography: 0.11 g, 28%) with great losses in chemical yield as a brownish oil.

De 89% (^{13}C NMR, after chromatography, crude: 82%); $[\alpha]_D^{25}$ –100.1 (*c* 0.77, $CHCl_3$).

IR ($CHCl_3$): 2956, 2929, 2873, 2827, 1680, 1460, 1379, 1344, 1285, 1216, 1197, 1117, 969, 920, 756, 666, 529 cm^{-1}.

^1H NMR (C_6D_6): δ = 0.98 (t, *J* = 7 Hz, 6 H, C*H*$_3$CH$_2$), 1.36–1.92 (m, 20 H, NCH$_2$C*H*$_2$C*H*$_2$, CH$_3$C*H*$_2$C*H*$_2$C*H*$_2$), 2.10, 2.70 (q, *J* = 9 Hz, m, 6 H, NCH$_2$, NH), 3.01, 3.31 (m, m, 4 H, CHCH, C*H*CH$_2$O), 3.22 (s, 6 H, OCH$_3$), 3.40 (dd, *J* = 9.0, 7.0 Hz, 2 H, C*H*HO), 3.77 (dd, *J* = 9.0, 4.0 Hz, 2 H, CH*H*O).

^{13}C NMR (C_6D_6): δ = 14.47 (*C*H$_3$CH$_2$), 21.44, 23.71 (CH$_3$*C*H$_2$, NCH$_2$*C*H$_2$), 27.35, 29.16 (CH$_3$CH$_2$*C*H$_2$, NCH$_2$CH$_2$*C*H$_2$), 30.50 (*C*H$_2$CHCH), 57.23 (NCH$_2$), 58.82, 59.91, 66.10 (CHCH, *C*HCH$_2$OCH$_3$), 76.35 (CH$_2$O).

MS (70 eV): *m*/*z* (%) = 398 (7.72) [M^+], 200 (20), 199 (100) [$C_{11}H_{23}N_2O^+$], 154 (18), 153 (54), 114 (16) [$C_6H_{12}NO^+$], 70 (33), 45 (10).

HRMS (EI): *m*/*z* calcd for $C_{22}H_{46}N_4O_2$ (M^+), 398.3621; found, 398.3620.

(1*R*,2*R*)-(+)-*N*-(1-Butyl-2-*t*-butyloxycarbonylaminohexyl)-*t*-butylcarbamat [(*R*,*R*)-8a]

The crude hydrazine **7a** (120 mg, 0.3 mmol) was allowed to react according to GP 4. After reductive cleavage (5 d) and work up (path A), the soln containing the crude diamine was treated with Et_3N (1 mL) and di-*tert*-butyl dicarbonate (0.52 g, 2.4 mmol) at 0 °C and

stirred at r.t. until the reaction was complete (2 d). The solvent was removed in vacuo and the residue solved in Et_2O (15 mL). The organic layer was washed with a sat. soln of NH_4Cl (3 × 7 mL), brine (3 × 7 mL) and dried with $MgSO_4$. Evaporation of the solvent under reduced pressure and purification of the residue by flash column chromatography (SiO_2, Et_2O–petroleum ether, 1:4) yielded **8a** (65 mg, 58%) as a colorless solid.

Mp 120 ° C; de 85% (GC); ee 98% (GC_{CSP}: Chirasil-Dex CB, H_2 = 1.2 bar, T = 160–35iso–2–190); $[\alpha]_D^{29}$ +43.2 (*c* 1.03, $CHCl_3$).

IR (KBr): 3346 (m, NH), 2960, 2932, 2860, 1687(C=O), 1540, 1456, 1390, 1367, 1303, 1274, 1251, 1182, 1118, 1099, 1071, 1041, 1009, 871, 780, 756, 647 cm^{-1}.

^1H NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 0.89 (br t, *J* = 7.0 Hz, 6 H, C*H*$_3$CH$_2$), 1.20–1.60 (m, 12 H, CH_2), 1.44 [s, 18 H, C(C*H*$_3$)$_3$], 3.54 (m, 2 H, CH), 4.56 (m, 2 H, NH).

^{13}C NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 14.01 (*C*H$_3$CH$_2$), 22.60 (CH$_3$*C*H$_2$), 28.02 (*C*H$_2$CH$_2$CH), 28.44 [C(*C*H$_3$)$_3$], 32.75 (*C*H$_2$CH), 54.38 (CH), 79.05 (Cq), 156.52 (C=O).

MS (70 eV): *m*/*z* (%) = 372 (0.98) [M^+], 271 (18), 200 (14), 186 (17) [$C_{10}H_{20}NO_2^+$], 185 (13), 144 (15), 142 (10), 130 (70), 129 (11), 86 (71), 69 (13), 57 (100) [*t*-$C_4H_9^+$], 55 (13).

HRMS (EI): *m*/*z* calcd for $C_{20}H_{40}N_2O_4$ (M^+), 372.2988; found, 372.2986.

(1*R*,2*R*)-(–)-*N*-(1-Phenyl-2-benzyloxycarbonylamino-2-phenylethyl)benzyl-carbamate [(*R*,*R*)-8b]

An organocerium reagent (8 mmol) prepared from $CeCl_3$ and PhMgBr (1 M soln in THF) was treated according to GP 2 with hydrazone **2a** (0.24 g, 0.84 mmol). After the addition was complete (TLC) the reaction was terminated by the addition of sat. $NaHCO_3$. Work up yielded the crude hydrazine **7b** (0.405 g, 99%) as a yellow oil which was introduced into the reductive cleavage without further purification.

De 91% (^{13}C NMR).

^1H NMR (C_6D_6): δ = 1.35–1.83 (m, 8 H, NCH$_2$C*H*$_2$C*H*$_2$), 2.17 (q, *J* = 8 Hz, 2 H, NC*H*H), 2.77 (m, 2 H, NCH*H*), 3.06–3.32 (m, 4 H, NC*H*C*H*HO), 3.09 (s, 6 H, OCH$_3$), 3.53 (dd, *J* = 4.0, 5.0 Hz, 2 H, CH*H*O), 4.06 (br, 2 H, NH), 4.23 (s, 2 H, CHCH), 6.80 – 7.32, 7.46 (m, 10 H, Ph).

^{13}C NMR (C_6D_6): δ = 21.97 (NCH$_2$*C*H$_2$), 27.80 (NCH$_2$CH$_2$*C*H$_2$), 57.08 (NCH$_2$), 59.27, 66.47, 69.72 (CHCH, *C*HCH$_2$OCH$_3$), 76.52 (CH$_2$O), 127.46 (C_{para}), 128.40, 129.36 (C_{ortho}, C_{meta}), 143.51 (C_{ipso}).

The crude hydrazine **7b** (123 mg, 0.3 mmol) was allowed to react according to GP 4. After reductive cleavage (5.5 d) and work up (path B) the crude diamine was treated with benzyloxycarbonyl chloride (0.31 g, 1.8 mmol) and K_2CO_3 (90 mg) in CH_2Cl_2 (10 mL) at 0 °C and stirred for 2 h at r.t. The reaction mixture was hydrolyzed with a sat. $NaHCO_3$ (30 mL) and extracted with CH_2Cl_2 (3 × 50 mL), the combined extracts were dried with $MgSO_4$ and after removal of the solvent using a rotary evaporator and recrystallization from EtOH the protected diamine **8b** was obtained in colorless needles (34 mg, 22%).

Mp 187 °C (lit.[35] 188 °C); de 96% (^1H NMR); ee 96% (^1H Shift NMR with (*R*)-1-Anthryl-2,2,2-trifluoroethanol); $[\alpha]_D^{28}$ –9.6 (*c* 0.53, $CHCl_3$, after 6 h equilibration); {Lit.[35] $[\alpha]_D^{28}$ –10.2 (*c* 1.03, $CHCl_3$)}.

The spectroscopic data of **8b** corresponded with those reported in ref.[35]

(4*R*,5*R*)-(–)-Di(*t*-butyl)-4,5-dibenzyl-2-oxo-1,3-imidazolidin-dicarboxylate [(*R*,*R*)-8c]

An organocerium reagent (8 mmol) prepared from $CeCl_3$ and BnMgBr (1 M soln in THF) was treated according to GP 2 with hydrazone **2a** (0.18 g, 0.64 mmol). After the addition was complete (TLC) the reaction was terminated by the addition of a sat. $NaHCO_3$. Work up yielded the crude hydrazine **7c** (0.503 g, 60% purity) as a brownish oil which was introduced into the reductive cleavage without further purification.

^1H NMR (C_6D_6): δ = 1.22–1.86 (m, 8 H, NCH$_2$C*H*$_2$C*H*$_2$), 2.21–2.88 (m, 10 H, NCH$_2$, CH$_2$Ph, NH), 3.04–3.60 (m, 8 H, CHCH, CHCH$_2$O), 3.14 (s, 6 H, OCH$_3$), 6.97–7.41 (m, 10 H, Ph).

^{13}C NMR (C_6D_6): Only the peaks of the main product are given. δ = 21.57 (NCH$_2$*C*H$_2$), 27.46 (NCH$_2$CH$_2$*C*H$_2$), 36.57 (CH$_2$Ph), 57.56 (NCH$_2$), 58.73, 61.13, 66.36 (CHCH, *C*HCH$_2$OCH$_3$), 75.94 (CH$_2$O), 126.13–129.67 (C_{ortho}, C_{meta}, C_{para}), 141.25 (C_{ipso}).

The crude hydrazine **7c** (60% purity, 125 mg, 0.15 mmol) was allowed to react according to GP 4. After reductive cleavage (**6d**) and work up (path B) the crude diamine was treated with di-*tert*-butyl dicarbonate (0.33 g, 1.5 mmol), Et_3N (0.3 g, 3 mmol, 0.42 mL), catalytic amounts DMAP in CH_3CN (2 mL) at 0 °C and stirred at r.t. for 2 d. The solvent was removed in vacuo and the residue solved in Et_2O (10 mL). The organic layer was washed with a sat. NH_4Cl (3 × 4 mL), brine (3 × 4 mL) and dried with $MgSO_4$. Evaporation of the solvent under reduced pressure and purification of the residue by flash column chromatography (SiO_2, Et_2O–petroleum ether, 1:2) yielded **8c** (52 mg, 74%) as a colorless solid.

Mp 156–158 °C; de 98% (^1H NMR); ee 98% (according to **8a**,**b**; **4i,m**); $[\alpha]_D^{28}$ –6.4 (*c* 0.5, $CHCl_3$).

IR (KBr): 3061, 3026, 2974, 2928, 2855, 1797, 1713(C=O), 1604, 1496, 1455, 1387, 1369, 1320, 1285, 1252, 1222, 1160, 1079, 1041, 1004, 985, 921, 843, 777, 750, 737, 702, 635, 591, 500 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.52 [s, 18 H, C(CH$_3$)$_3$], 2.67 (dd, *J* = 9.0, 13.5 Hz, 2 H, C*H*HPh), 2.93 (dd, *J* = 3.5, 13.5 Hz, 2 H, CH*H*Ph), 4.03 (dd, *J* = 3.5, 8.5 Hz, 2 H, CH), 6.55 (m, 4 H, Ph), 7.17 (m, 6 H, Ph).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.09 [C(*C*H$_3$)$_3$], 38.81 (CH$_2$Ph), 56.27 (CH), 83.28 (C_q), 126.89 (C_{para}), 128.73, 129.15 (C_{ortho}, C_{meta}), 135.35 (C_{ipso}), 148.09 (NC=ON), 150.17 (NC=OO).

MS (70 eV): *m*/*z* (%) = 354 (3.38) [M^+ – 2·C_4H_8], 219 (44) [$C_{13}H_{17}NO_2^+$], 175 (32), 91 (49) [$C_7H_7^+$], 57 (100) [*t*-$C_4H_9^+$], 56 (25), 55 (15).

HRMS (EI): *m*/*z* calcd for: $C_{19}H_{18}N_2O_5$ (M^+ – C_8H_{16}), 354.1216; found, 354.1215.

(1*S*,4*S*)-(–)-*N*-(1-Benzyl-4-benzyloxycarbonylamino-5-phenylpentyl)-*t*-butyl-carbamate [(*S*,*S*)-9]

An organocerium reagent (8 mmol) prepared from $CeCl_3$ and BnMgBr (1 M soln in THF) was treated according to GP 2 with hydrazone **2b** (0.31 g, 1 mmol). After the addition was complete (TLC) the reaction was terminated by the addition of a sat. $NaHCO_3$. Work up yielded the crude hydrazine (0.680 g, 70% purity) as a brownish oil which was introduced into the reductive cleavage without further purification.

De 64% (^{13}C NMR).

^1H NMR (C_6D_6): δ = 1.38–1.90 (m, 12 H, NCH$_2$C*H*$_2$C*H*$_2$, CHC*H*$_2$C*H*$_2$CH), 2.42–2.70 (m, 6 H, NC*H*H, CH$_2$Ph), 2.90–3.32 (m, 8 H, NCH*H*, C*H*CH$_2$Ph, CHC*H*HO, NH), 3.16 (s, 6 H, OCH$_3$), 3.64 (dd, *J* = 4, 8.5 Hz, 2 H, CH*H*O), 7.08 (m, 10 H, Ph).

^{13}C NMR (C_6D_6): δ = 21.37 (NCH$_2$*C*H$_2$), 27.03, 28.17 (NCH$_2$CH$_2$*C*H$_2$, CH*C*H$_2$*C*H$_2$CH), 40.91 (CH$_2$Ph), 56.91 (NCH$_2$), 58.80, 60.53, 65.85 (*C*HCH$_2$Ph, *C*HCH$_2$OCH$_3$), 75.94 (CH$_2$O), 126.03 (C_{para}), 128.55–129.89 (C_{ortho}, C_{meta}), 141.91 (C_{ipso}).

The crude hydrazine (70% purity, 204 mg, 0.3 mmol) was allowed to react according to GP 4. After reductive cleavage (5 d) and work up (path B) the crude diamine was treated with Et_3N (1.2 g, 12 mmol, 1.7 mL) and di-*tert*-butyl dicarbonate (1.31 g, 6 mmol) in MeOH (10 mL) at 0 °C and stirred at r.t. until the reaction was complete (2 d). The solvent was removed in vacuo and the residue was dissolved in Et_2O (15 mL). The organic layer was washed with a sat. NH_4Cl (3 × 7 mL), brine (3 × 7 mL) and dried with $MgSO_4$. Evaporation of the solvent under reduced pressure and purification of the residue by flash column chromatography (SiO_2, Et_2O–petroleum ether, 1:2) yielded **9** (33 mg, 23%) as a colorless solid.

Mp 145 °C; de 64% (Determined by ^{1}H NMR analysis of the corresponding Mosher amide); ee 98% (Determined by ^{1}H NMR analysis of the corresponding Mosher amide); $[\alpha]_D^{27}$ –5.2 (*c* 0.82, $CHCl_3$).

IR (KBr): 3364 (NH), 3063, 3027, 2983, 2948, 2861, 2172, 1683(C=O), 1524, 1453, 1391, 1367, 1304, 1250, 1170, 1079, 1033, 997, 909, 878, 773, 753, 700, 632, 539, 493 cm^{-1}.

^{1}H NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 1.33–1.60 (m, 4 H, $CHCH_2CH_2$), 1.39 [s, 18 H, $C(CH_3)_3$], 2.72 (d, *J* = 6 Hz, 4 H, CH_2Ph), 3.77 (br s, 2 H, CH), 4.25 (m, 2 H, NH) 7.10–7.30 (m, 10 H, Ph).

^{13}C NMR ($CDCl_3$): Due to the limited rotation of the NN single bond only broad signals could be observed. δ = 28.38 [$C(CH_3)_3$], 30.91 ($CHCH_2CH_2$), 41.53 (CH_2Ph), 51.43 (CH), 79.09 [$C(CH_3)_3$], 126.33 (C_{para}), 128.34, 129.48 (C_{ortho}, C_{meta}), 138.01 (C_{ipso}), 155.46 (C=O).

MS (70 eV): *m*/*z* (%) = 469 (0.23) [M^+ + 1], 295 (9) [M^+ – *t*-C_4H_9O-*t*-$C_5H_9O_2$], 261 (10), 260 (50), 205 (15), 204 (100), 161 (12), 160 (96), 117 (10), 91 (19), 57 (73).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{23}N_2O$ (M^+ – $C_9H_{17}O_3$), 295.1810; found, 295.1812.

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