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Synthesis of Optically Active Heterocyclic Compounds by Preparation of 1,3-Dinitro Derivatives and Enzymatic Enantioselective Desymmetrization of Prochiral Diamines

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A general approach for the highly efficient chemical preparation of novel optically active 2-substituted propane-1,3-diamines is described. Diamines have been obtained from the corresponding commercially available aldehydes in a straightforward two-step synthesis via the corresponding 1,3-dinitro compounds, which were hydrogenated under mild reaction conditions by using platinum dioxide as the catalyst. Subsequent enzymatic enantioselective desymmetrization mediated by *Pseudomonas cepacia* lipase allowed the recovery of a family of monocarbamates in good to high enantiomeric excesses (70–90 % *ee*).

Introduction

The search for chiral materials has attracted considerable attention in recent years driven by the need of the industrial sector, in particular, to synthesize single enantiomeric compounds.[1] For instance, optically active amines are ubiquitous in a wide range of biologically active compounds, and they can also be used in a number of applications for the preparation of agrochemicals and pharmaceuticals.[2] These compounds have been extensively studied as organocatalysts and ligands in asymmetric synthesis and have shown strong potential in this field.[3] However, their main limitations reside in their difficult preparation because of their poor solubility in organic solvents, notorious instability towards moisture and cumbersome isolation protocols. Thus, the most popular asymmetric chemical syntheses are based on the reductive amination of ketones,[4] the catalytic hydrogenation of imines[5] or enamines,[6] the hydrosilylation of imines or oximes[7] and the alkylation of imines[8] or amino hydroxylation.[9]

In this synthetic context, biotransformations have presented themselves as practical tools for the production of chiral amines, with lipases,[10] amino oxidases[11] or transaminases[12] being the most efficient enzymes for this purpose.[13] Recently, we described a novel chemoenzymatic strategy for the production of optically active amines that involves the synthesis of 2-substituted propane-1,3-diamines for use in subsequent enantioselective enzymatic desymmetrization reactions, the corresponding amino carbamates being obtained with good to excellent enantiomeric excesses depending on the C-2 substituent present in the 1,3-diamine core.[14] This methodology allows the preparation of a wide range of optically active compounds through a multi-step pathway by using carboxylic acids, acyl chlorides, malonates or diols as commercially available starting materials. On the other hand, carbamates are a family of organic compounds with multiple applications in the textile industry, agriculture and especially in the design of new enzyme inhibitors and drugs, making attractive the development of novel compounds with this structural motif,[15] which is usually accessible only by the employment of harmful reagents such as phosgene or its derivatives.[16]

Results and Discussion

In the course of our ongoing research we attempted the synthesis of 2-(4-chlorophenyl)propane-1,3-diamine (**7a**) from the acyl chloride precursor **1** (Scheme 1). Thus, **1** was subjected to an esterification reaction with ethanol at room temperature leading to the corresponding ester **2** in 91% isolated yield. This ester was transformed into **3** by using lithium bis(trimethylsilyl)amide [$(Me_3Si)_2NLi$] and ethyl cyanoformate (EtOCOCN) prior to the reduction of the malonate with lithium aluminium hydride ($LiAlH_4$) to give diol **4**, which at this stage was protected with methanesulfonyl chloride (MsCl) and pyridine in nearly quantitative

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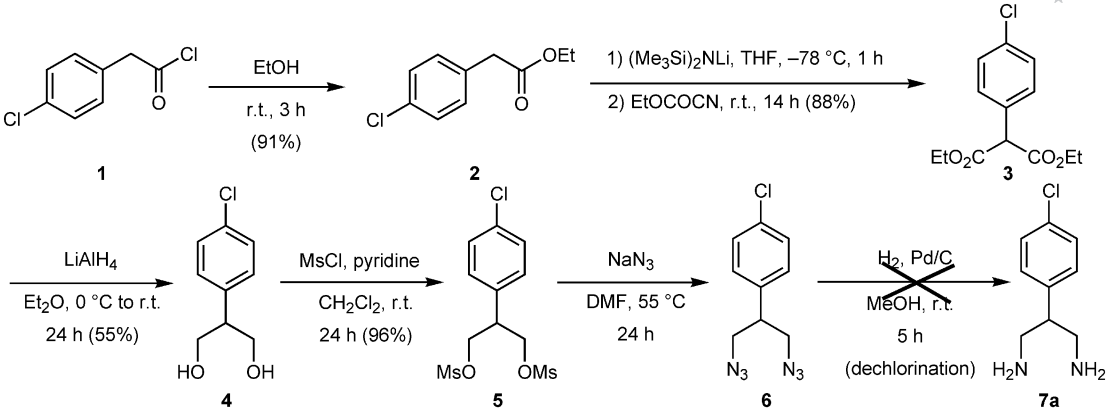


Scheme 1. Initial attempts at the synthesis of diamine **7a** with dechlorination occurring in the hydrogenolysis step.

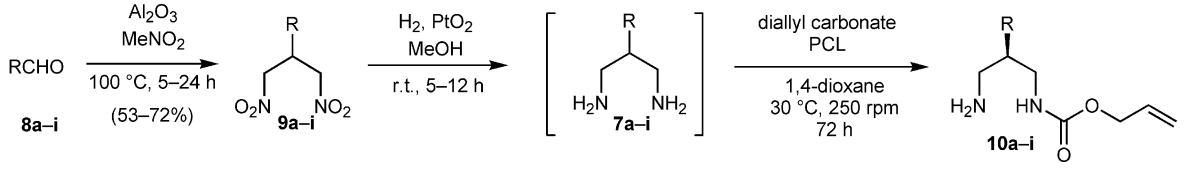
yield. Nucleophilic substitution of the resulting mesylated diol **5** with sodium azide at 55 °C in dry DMF allowed the recovery of diazide **6**, which was immediately hydrogenated in the presence of Pd/C in MeOH: unfortunately, we obtained a prochiral dehalogenated diamine as the unique final product instead of the desired chlorinated diamine **7a**. For this reason we decided to search for a more general synthetic route towards prochiral diamines, and we present in this paper the latest results of our research into the preparation of novel propane-1,3-diamine derivatives with high optical purity by chemoenzymatic processes.

We thus turned our attention to the potential of 1,3-dinitro compounds, building blocks of significant interest as they are ideal precursors for the production of 1,3-difunctionalized molecules.[17] During recent years the efficient preparation of 1,3-dinitro compounds has been reported by using inexpensive aldehydes as the starting materials in the presence of nitromethane ($MeNO_2$) and basic alumina (Al_2O_3).[18] This simple methodology presents the additional advantage that non-aqueous workup is possible, because the heterogeneous catalyst can be easily removed by filtration. Another interesting issue from a synthetic point of view is that many different functionalities can be preserved under these mild reaction conditions.

Thus, we explored this approach in the synthesis of novel dinitro derivatives, which can be used as precursors of the interesting and previously unreported heterocyclic and non-heterocyclic 1,3-diamines **7a**–**i** bearing a phenyl, pyridine, indole, thiophene, furan or pyrrole nucleus (Scheme 2). Thus, aldehydes **8a**–**i** were heated at 100 °C in the presence of basic alumina and nitromethane as solvent, recovering the dinitro compounds **9a**–**i** with an excellent level of purity and in moderate to good yields (53–72%). Then **9a**–**i** were subjected to a hydrogenation reaction at room temperature catalysed by platinum dioxide in MeOH. As occurred with basic alumina, the use of a heterogeneous catalyst facilitated the recovery of the diamines, avoiding extraction or chromatographic procedures that are incompatible with the physical properties of the diamine structures. Other advantages are that unsophisticated systems can be used and that the transformations are performed under safe and mild reaction conditions at room temperature.

The versatility of the "nitro route" has been compared with the synthetic approach that involves the use of commercially available acyl chlorides, carboxylic acids or malonates as starting materials.[14] This "old route" requires six steps depending on the starting material. For this reason, 2-(4-methoxyphenyl)propane-1,3-diamine, 2-(1-naphthyl)propane-1,3-diamine, 2-(2-naphthyl)propane-1,3-diamine and 2-(4-biphenyl-4-yl)propane-1,3-diamine were synthesized by using both methodologies, and their isolated yields are compared in Table 1 to illustrate the efficacy of the new synthetic strategy. As can be seen, fewer reaction steps are necessary for the preparation of the desired diamines when the 1,3-dinitro compounds serve as intermediates, and higher yields were obtained (21–37% compared with 49–57%).

The enzymatic enantioselective desymmetrization (EED)[19] reactions of these novel diamines **7a**–**i** were investigated under an inert gas by using diallyl carbonate as an alkoxycarbonylating agent and *Pseudomonas cepacia* lipase (also called *Burkholderia cepacia* lipase, PCL) as the biocatalyst (Scheme 2), a resolving agent and enzyme that have previously shown the best results in this type of stereoselective process with other 2-substituted propane-1,3-diamines.[14]



Scheme 2. Synthesis of diamines **7a**–**i** from aldehydes **8a**–**i** and their enantioselective enzymatic desymmetrization. R = 4-ClC_6H_4 (**a**), pyridin-3-yl (**b**), 1*H*-indol-2-yl (**c**), 1*H*-indol-3-yl (**d**), thien-2-yl (**e**), thien-3-yl (**f**), furan-2-yl (**g**), furan-3-yl (**h**), 1*H*-pyrrol-2-yl (**i**).

Table 1. Synthesis of propane-1,3-diamines by the "nitro" and "old" routes.

R	Starting material[a]	Old route [%][b]	Nitro route [%][c]
4-$MeOC_6H_4$	acyl chloride	37	56
2-Naphthyl	carboxylic acid	26	57
1-Naphthyl	carboxylic acid	32	49
4-PhC_6H_4	carboxylic acid	21	52

[a] Starting material used in the "old route". [b] Isolated yield of the diamine after six steps starting from the corresponding acyl chloride or carboxylic acid.[14] [c] Isolated yield of the diamine after two steps starting from the corresponding aldehyde.

Although enantioselective desymmetrizations can theoretically reach yields of 100%, optically active amino carbamates were obtained in moderate isolated yields in all cases after the hydrogenation of the dinitro compounds and the enzymatic desymmetrization of the diamines (45–58%). To account for this we reasoned that the biotransformations did not proceed to complete conversion, and also in some cases a small amount of the diamine could be lost in the purification process.

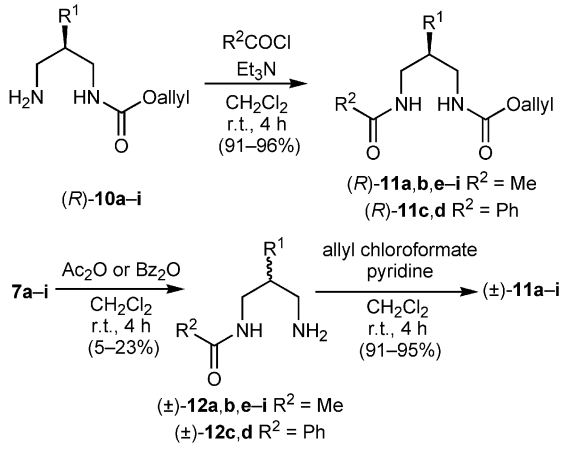
A detailed study of the experimental data revealed lower conversions when using benzo-fused rings (Table 2, Entries 3 and 4) or for compounds with a heteroatom located at the C-2 position of the ring (Entries 5 and 7). At the same time good to very high enantiomeric excesses were attained (70–91%), with lower values obtained for furan derivatives (Entries 7 and 8) and higher values for 4-chlorophenyl, pyridine and indole substitutions (Entries 1–4).

Table 2. Lipase-mediated desymmetrization of diamines **7a**–**i** by using PCL and diallyl carbonate at 30 °C and 250 rpm.

Entry	Product	R	Yield [%][a]	*ee* [%][b]
1	**10a**	4-ClC_6H_4	52	90
2	**10b**	pyridin-3-yl	58	89
3	**10c**	1*H*-indol-2-yl	47	88
4	**10d**	1*H*-indol-3-yl	45	87
5	**10e**	thien-2-yl	47	78
6	**10f**	thien-3-yl	55	79
7	**10g**	furan-2-yl	48	71
8	**10h**	furan-3-yl	54	70
9	**10i**	1*H*-pyrrol-2-yl	53	76

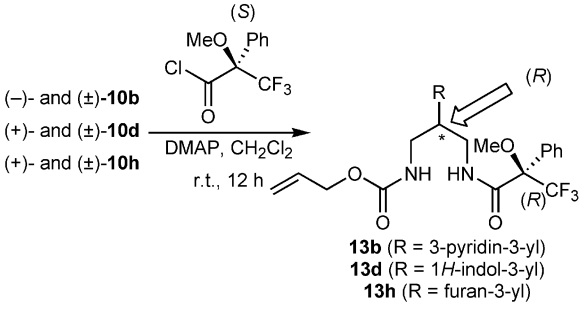
[a] Isolated yield of the monocarbamate after purification by flash chromatography. Two-step process: hydrogenation of the 1,3-dinitro compound and enzymatic desymmetrization of the diamine. [b] Determined by HPLC after suitable derivatization.

Racemic compounds **11a**–**i** were required for the measurement of the enantiomeric excesses by chiral HPLC analysis. They were prepared by a non-enzymatic monoacylation with acetic or benzoic anhydride followed by an alkoxycarbonylation with allyl chloroformate in the presence of pyridine (Scheme 3). In the monoacylation process, small portions of the corresponding anhydride were added at 10 min intervals to keep a low concentration of the acylating agent to minimize the amount of diacylated product. Nevertheless, both mono- and diamides were observed and separated by flash chromatography, obtaining racemic monoamides **12a**–**i** in low yields but with enough to carry out the chemical alkoxycarbonylation to finally afford the corresponding racemic amido carbamates **11a**–**i** in very high yields (91–95%). At this point appropriate chiral HPLC methods were developed and optimized, finding reliable conditions for the measurement of the enantiomeric excesses of the chiral monocarbamates obtained in the enzymatic desymmetrization processes (see the chromatograms in the Supporting Information). Thus, chemical acylation of the chiral amino carbamates **10a**–**i** obtained after lipase-catalysed desymmetrization was carried out by using acetyl or benzoyl chloride in the presence of Et_3N, which allowed the recovery of the amido carbamates **11a**–**i** after flash chromatography (91–96%).



Scheme 3. Preparation of the optically active and racemic amido carbamates **12a**–**i** for enantiomeric excess measurements. R = 4-ClC_6H_4 (**a**), pyridin-3-yl (**b**), 1*H*-indol-2-yl (**c**), 1*H*-indol-3-yl (**d**), thien-2-yl (**e**), thien-3-yl (**f**), furan-2-yl (**g**), furan-3-yl (**h**), 1*H*-pyrrol-2-yl (**i**).

To assign the absolute configurations of the amido carbamates obtained by PCL-mediated enantioselective desymmetrization, different attempts were made to obtain suitable crystals for X-ray diffraction analysis, but all of them were unsuccessful. Afterwards, ^1H NMR analysis was performed by treating a selection of monocarbamates **10b**,**d**,**h** in racemic and optically active form with (+)-(*S*)-α-methoxy-α-(trifluoromethyl)-α-phenylacetyl chloride (Scheme 4).[20]



Scheme 4. Preparation of racemic and optically active (*R*,*R*)-Mosher derivatives.

As previously occurred with other 2-arylpropane-1,3-diamines, for example, the 4-methylphenyl or 4-methoxyphenyl derivatives (see the Supporting Information),[14a]

the signals of the heterocyclic hydrogen atoms of the (*R*,*R*) isomer appear at lower fields than those of the (*R*,*S*) isomer. Thus, the (*R*) configuration was assigned to amino carbamates obtained through the lipase-catalysed desymmetrization processes.

Conclusions

We have reported a practical and straightforward synthesis of novel 2-substituted propane-1,3-diamines bearing phenyl, furan, indole, pyrrole, pyridine or thiophene moieties by the preparation and subsequent hydrogenation of 1,3-dinitro compounds using two heterogeneous catalysts, namely basic alumina and platinum dioxide, which have allowed the recovery of prochiral diamines through very simple and clean processes under mild reaction conditions. A significant advantage of this approach is the recovery of some known propane-1,3-diamines in better isolated yields and after fewer reaction steps compared with previously reported methods. We have also described the enantioselective enzymatic desymmetrizations of this novel class of 2-substituted propane-1,3-diamines mediated by *Pseudomonas cepacia* lipase, obtaining the monoamino carbamates in moderate yields and with good to high enantiomeric excesses through an environmentally friendly approach.

Experimental Section

General Methods: *Pseudomonas cepacia* lipase (PCL) immobilized on ceramics (PSL-C I, 1638 U/g), available from Sigma-Aldrich, was used for the desymmetrization procedure. Aluminium oxide (Al_2O_3; activated, basic, 50–200 micron, Brockmann activity I) was purchased from Acros Organics. All other reagents were purchased from different commercial sources and used without further purification. Solvents were distilled from an appropriate desiccant under nitrogen. Flash chromatography was performed on silica gel 60 (230–240 mesh). The full characterization of the new compounds is available in the Supporting Information. Melting points were measured on samples in open capillary tubes and are uncorrected. IR spectra were recorded by using NaCl plates or KBr pellets. ^{1}H, ^{13}C NMR and DEPT spectra were obtained by using a variety of spectrometers (^{1}H: 300.13 or 400.13 MHz; ^{13}C: 75.5 or 100.6 MHz). The chemical shifts are given in δ values and the coupling constants (*J*) in Hertz (Hz). The atomic numbering used for NMR assignment is presented in the Supporting Information. ESI$^+$, APCI$^+$ or APCI$^-$ experiments were carried out to record mass spectra (MS) by using a liquid chromatograph mass detector. High-resolution mass spectra (HRMS) were recorded in ESI$^+$ or ESI$^-$ mode. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. High-performance liquid chromatography (HPLC) analyses were carried out with a liquid chromatograph UV detector at 210 nm by using a CHIRALCEL OD, CHIRALPAK AS, CHIRALPAK IA or a CHIRALPAK IC column (25 cm × 4.6 mm i.d.); conditions and retention times are given in the Supporting Information.

General Procedure for the Synthesis of the 1,3-Dinitro Compounds 9a–i: Basic Al_2O_3 (4.66 g, 45.7 mmol) was added to a solution of the corresponding aldehyde **8a**–**i** (9.34 mmol) in nitromethane (9.31 mL, 172.8 mmol) under nitrogen, and the mixture was heated at reflux for 5–24 h. Then the reaction mixture was cooled to room temperature and filtered and the solid washed with EtOAc (5 × 10 mL). The solvent of the combined organic phases was evaporated under reduced pressure, and the resulting reaction crude was purified by flash chromatography on silica gel (mixtures of EtOAc/hexane), yielding the corresponding dinitro compounds **9a**–**i** (53–73%).

1-Chloro-4-[2-nitro-1-(nitromethyl)ethyl]benzene (9a): Yield: 57% (1.30 g). R_f (30% EtOAc/hexane) = 0.35. M.p. 79–81 °C. IR (KBr): $\tilde{\nu}$ = 3059, 2919, 1564, 1551, 1494, 1426, 1379, 1352, 1267, 1230, 1112, 1096 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 4.30 (m, 1 H, 1-H), 4.68–4.81 (m, 4 H, 2-H), 7.16 (A′B′ system, $^3J_{A'B'}$ = 8.3 Hz, 2 H, 4-H), 7.35 (A′B′ system, $J_{A'B'}$ = 8.3 Hz, 2 H, 5-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 41.0 (C-1), 76.4 (2 C-2), 128.7 (2 C-4), 129.7 (2 C-5), 132.5 (C-6), 135.1 (C-3) ppm. MS (APCI$^-$): *m*/*z* (%) = 243 (100) [M – H]$^-$, 198 (25) [M – NO_2]$^-$. HRMS (ESI$^-$): calcd. for $C_9H_9ClN_2O_4$ [M – H]$^-$ 243.0173; found 243.0152.

3-[2-Nitro-1-(nitromethyl)ethyl]pyridine (9b): Yield: 60% (1.18 g). R_f (70% EtOAc/hexane) = 0.33. M.p. 97–99 °C. IR (KBr): $\tilde{\nu}$ = 3018, 2917, 1559, 1482, 1425, 1379, 1305, 1209, 1103 cm^{-1}. ^{1}H NMR (MeOD, 300.13 MHz): δ = 4.49–4.71 (m, 1 H, 2-H), 5.04–5.25 (m, 4 H, 1-H), 7.63 (dd, $^3J_{HH}$ = 7.9, $^3J_{HH}$ = 4.8 Hz, 1 H, 5-H), 8.07 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 4-H), 8.69–8.76 (m, 2 H, 6-H + 7-H) ppm. ^{13}C NMR (MeOD, 75.5 MHz): δ = 41.1 (C-2), 77.4 (2 C-1), 125.9 (C-5), 134.2 (C-3), 137.8 (C-4), 150.5 (C-6 + C-7) ppm. MS (APCI$^+$): *m*/*z* (%) = 212 (100) [M + H]$^+$, 213 (10) [M + 2 H]$^+$. HRMS (ESI$^-$): calcd. for $C_8H_9N_3O_4$ [M – H]$^-$ 210.0515; found 210.0532.

2-[2-Nitro-1-(nitromethyl)ethyl]-1*H*-indole (9c): Yield: 72% (1.68 g). R_f (40% EtOAc/hexane) = 0.33. IR (NaCl): $\tilde{\nu}$ = 3405, 3059, 2923, 1556, 1455, 1428, 1377, 1342, 1313, 1290, 1266, 797, 737 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 4.26 (m, 1 H, 9-H), 4.63–4.51 (m, 4 H, 10-H), 6.28 (s, 1 H, 2-H), 7.12 (td, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.0 Hz, 1 H, 6-H), 7.19 (td, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.3 Hz, 1 H, 5-H), 7.29 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, 4-H), 7.54 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, 7-H), 8.40 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 35.2 (C-9), 75.4 (2 C-10), 100.7 (C-2), 111.1 (C-7), 120.3 (C-4), 120.5 (C-6), 122.7 (C-5), 127.5 (C-3), 131.5 (C-1), 135.9 (C-8) ppm. MS (APCI$^-$): *m*/*z* (%) = 248 (100) [M – H]$^-$. HRMS (ESI$^-$): calcd. for $C_{11}H_{11}N_3O_4$ [M – H]$^-$ 248.0672; found 248.0659.

3-[2-Nitro-1-(nitromethyl)ethyl]-1*H*-indole (9d): Yield: 55% (1.28 g). R_f (20% EtOAc/hexane) = 0.11. M.p. 95–97 °C. IR (NaCl): $\tilde{\nu}$ = 3427, 3132, 3045, 2915, 1551, 1456, 1420, 1378, 1337, 1230, 1104 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 300.13 MHz): δ = 4.70 (m, 1 H, 9-H), 5.09–5.26 (m, 4 H, 10-H), 7.15–7.26 (m, 2 H, 5-H + 6-H), 7.50–7.51 (m, 2 H, 1-H + 4-H), 7.80 (d, $^3J_{HH}$ = 7.4 Hz, 1 H, 7-H), 11.26 (s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO, 75.5 MHz): δ = 37.9 (C-9), 81.2 (2 C-10), 112.6 (C-2), 115.9 (C-7), 122.4 (C-4), 123.2 (C-6), 125.7 (C-5), 127.9 (C-1), 129.8 (C-3), 140.2 (C-8) ppm. MS (APCI$^-$): *m*/*z* (%) = 248 (100) [M – H]$^-$. HRMS (ESI$^-$): calcd. for $C_{11}H_{11}N_3O_4$ [M – H]$^+$ 248.0672; found 248.0690.

2-[2-Nitro-1-(nitromethyl)ethyl]thiophene (9e): Yield: 56% (1.13 g). R_f (20% EtOAc/hexane) = 0.18. M.p. 39–41 °C. IR (NaCl): $\tilde{\nu}$ = 3113, 3023, 2922, 1560, 1429, 1378, 1347, 1252, 1203, 1139 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 4.60 (m, 1 H, 5-H), 4.70–4.84 (m, 4 H, 6-H), 6.96 (s, 1 H, 2-H), 6.97 (s, 1 H, 3-H), 7.27 (t, $^3J_{HH}$ = 3.3 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 36.9 (C-5), 76.8 (2 C-6), 125.9 (C-4), 126.5 (C-2), 127.3 (C-3), 135.9 (C-1) ppm. MS (APCI$^-$): *m*/*z* (%) = 215 (100) [M – H]$^-$. HRMS (ESI$^-$): calcd. for $C_7H_8N_2O_4S$ [M – H]$^-$ 215.0127; found 215.0112.

3-[2-Nitro-1-(nitromethyl)ethyl]thiophene (9f): Yield: 55% (1.11 g). R_f (30% EtOAc/hexane) = 0.35. M.p. 81–83 °C. IR (NaCl): $\tilde{\nu}$ =

3056, 1561, 1421, 1376, 1337, 1266, 1190, 1088 cm^{-1}. ^1H NMR ($CDCl_3$, 300.13 MHz): δ = 4.45 (m, 1 H, 5-H), 4.69–4.82 (m, 4 H, 6-H), 6.97 (dd, $^3J_{HH}$ = 5.1, $^4J_{HH}$ = 1.4 Hz, 1 H, 3-H), 7.19–7.20 (m, 1 H, 1-H), 7.38 (dd, $^3J_{HH}$ = 5.1, $^4J_{HH}$ = 2.6 Hz, 1 H, 4-H) ppm. ^{13}C NMR (CDCl3, 75.5 MHz): δ = 37.2 (C-5), 76.5 (2 C-6), 123.5 (C-1), 125.6 (C-4), 127.7 (C-3), 134.3 (C-2) ppm. MS ($APCI^-$): *m*/*z* (%) = 215 (100) [M – H]$^-$. HRMS (ESI^-): calcd. for $C_7H_8N_2O_4S$ [M – H]$^-$ 215.0127; found 215.0134.

2-[2-Nitro-1-(nitromethyl)ethyl]furan (9g): Yield: 53% (988 mg). R_f (30% EtOAc/hexane) = 0.30. IR (NaCl): $\tilde{\nu}$ = 3056, 1562, 1508, 1422, 1375, 1266, 1149, 1018 cm^{-1}. ^1H NMR ($CDCl_3$, 300.13 MHz): δ = 4.42 (m, 1 H, 5-H), 4.75 (d, $^3J_{HH}$ = 6.6 Hz, 4 H, 6-H), 6.27 (d, $^3J_{HH}$ = 3.4 Hz, 1 H, 2-H), 6.33 (dd, $^3J_{HH}$ = 3.1, $^3J_{HH}$ = 1.7 Hz, 1 H, 3-H), 7.38 (dd, $^3J_{HH}$ = 2.0, $^4J_{HH}$ = 1.1 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 35.6 (C-5), 74.4 (2 C-6), 108.6 (C-2), 110.6 (C-3), 143.2 (C-4), 147.2 (C-1) ppm. MS ($APCI^-$): *m*/*z* (%) = 199 (100) [M – H]$^-$. HRMS (ESI^-): calcd. for $C_7H_8N_2O_5$ [M – H]$^-$ 199.0355; found 199.0362.

3-[2-Nitro-1-(nitromethyl)ethyl]furan (9h): Yield: 55% (1.02 g). R_f (30% EtOAc/hexane) = 0.30. M.p. 63–65 °C. IR (NaCl): $\tilde{\nu}$ = 3137, 3036, 1549, 1506, 1430, 1383, 1338, 1268, 1201, 1160, 1092, 1032 cm^{-1}. ^1H NMR ($CDCl_3$, 400.13 MHz): δ = 4.25 (m, 1 H, 5-H), 4.65–4.77 (m, 4 H, 6-H), 6.30 (s, 1 H, 3-H), 7.38 (s, 1 H, 1-H), 7.41 (s, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 33.1 (C-5), 76.2 (2 C-6), 108.3 (C-3), 118.7 (C-2), 140.3 (C-1), 144.3 (C-4) ppm. MS ($APCI^-$): *m*/*z* (%) = 199 (100) [M – H]$^-$. HRMS (ESI^-): calcd. for $C_7H_8N_2O_5$ [M – H]$^-$ 199.0355; found 199.0327.

2-[2-Nitro-1-(nitromethyl)ethyl]-1*H*-pyrrole (9i): Yield: 60% (1.12 g). R_f (30% EtOAc/hexane) = 0.25. M.p. 128–130 °C. IR (NaCl): $\tilde{\nu}$ = 3414, 3025, 1553, 1542, 1423, 1379, 1364, 1197, 1122, 1031 cm^{-1}. ^1H NMR ($CDCl_3$, 300.13 MHz): δ = 4.32 (m, 1 H, 5-H), 4.67 (d, $^3J_{HH}$ = 6.8 Hz, 4 H, 6-H), 6.05 (s, 1 H, 2-H), 6.13 (dd, $^3J_{HH}$ = 6.0, $^3J_{HH}$ = 3.9 Hz, 1 H, 3-H), 6.69 (dd, $^3J_{HH}$ = 4.0, $^4J_{HH}$ = 2.6 Hz, 1 H, 4-H), 8.52 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 34.9 (C-5), 76.0 (2 C-6), 106.3 (C-2), 108.8 (C-3), 118.8 (C-4), 124.2 (C-1) ppm. MS ($APCI^-$): *m*/*z* (%) = 198 (100) [M – H]$^-$. HRMS (ESI^-): calcd. for $C_7H_9N_3O_4$ [M – H]$^-$ 198.0515; found 198.0532.

General Procedure for the Synthesis of Diamines 7a–i: Deoxygenated MeOH (3.7 mL) was carefully added to a suspension containing the dinitro compound **9a**–**i** (1.00 mmol) and PtO_2 (45.4 mg, 0.20 mmol) in a 100 mL round-bottom flask to which a H_2 balloon was connected. The resulting suspension was stirred at room temperature for 6 h, and after this time the reaction was stopped and the mixture filtered through Celite® and washed with MeOH (5 × 10 mL). The solvent was evaporated under reduced pressure to afford the corresponding diamine **7a**–**i**, which was used in enzymatic desymmetrization without further purification.

2-(4-Chlorophenyl)propane-1,3-diamine (7a): R_f (3% NH_3/MeOH) = 0.08. ^1H NMR (MeOD, 400.13 MHz): δ = 2.90–2.98 (m, 3 H, 1-H + 2 2-H), 3.02–3.09 (m, 2 H, 2-H), 7.40 (A′B′ system, $J_{A'B'}$ = 8.1 Hz, 2 H, 4-H), 7.49 (A′B′ system, $J_{A'B'}$ = 8.1 Hz, 2 H, 5-H) ppm. ^{13}C NMR (MeOD, 100.6 MHz): δ = 46.2 (2 C-2), 52.6 (C-1), 130.2 (2 C-4), 131.1 (2 C-5), 133.9 (C-6), 141.7 (C-3) ppm.

2-(Pyridin-3-yl)propane-1,3-diamine (7b): R_f (3% NH_3/MeOH) = 0.12. ^1H NMR (MeOD, 300.13 MHz): δ = 3.04–3.08 (m, 5 H, 1-H + 4 2-H), 7.73 (dd, $^3J_{HH}$ = 7.9, $^3J_{HH}$ = 4.8 Hz, 1 H, 5-H), 8.06 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 4-H), 8.73–8.76 (m, 2 H, 6-H + 7-H) ppm. ^{13}C NMR (MeOD, 75.5 MHz): δ = 46.1 (2 C-1), 51.0 (C-2), 125.8 (C-5), 137.8 (C-4), 139.7 (C-3), 149.0 (C-6), 150.9 (C-7) ppm.

2-(1*H*-Indol-2-yl)propane-1,3-diamine (7c): R_f (3% NH_3/MeOH) = 0.18. ^1H NMR (MeOD, 300.13 MHz): δ = 2.92–3.11 (m, 5 H, 9-H + 4 10-H), 6.39 (s, 1 H, 2-H), 7.10–7.22 (m, 2 H, 5-H + 6-H), 7.47 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, 4-H), 7.62 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, 7-H) ppm. ^{13}C NMR (MeOD, 75.5 MHz): δ = 44.9 (2 C-10), 47.0 (C-9), 101.2 (C-2), 112.1 (C-7), 120.5 (C-4), 120.9 (C-6), 122.3 (C-5), 130.1 (C-3), 138.4 (C-1), 140.8 (C-8) ppm.

2-(1*H*-Indol-3-yl)propane-1,3-diamine (7d): R_f (3% NH_3/MeOH) = 0.06. ^1H NMR (MeOD, 400.13 MHz): δ = 3.03 (d, $^3J_{HH}$ = 6.6 Hz, 4 H, 10-H), 3.10–3.17 (m, 1 H, 9-H), 7.15 (t, $^3J_{HH}$ = 8.2 Hz, 1 H, 6-H), 7.22–7.26 (m, 2 H, 1-H + 5-H), 7.53 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, 4-H), 7.71 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, 7-H) ppm. ^{13}C NMR (MeOD, 100.6 MHz): δ = 43.2 (C-9), 43.9 (2 C-10), 111.4 (C-7), 113.5 (C-2), 118.4 (C-4), 118.6 (C-6), 121.4 (C-5), 122.6 (C-1), 126.8 (C-3), 137.3 (C-8) ppm.

2-(Thien-2-yl)propane-1,3-diamine (7e): R_f (3% NH_3/MeOH) = 0.18. ^1H NMR (MeOD, 400.13 MHz): δ = 2.93–2.98 (m, 2 H, 6-H), 3.08–3.13 (m, 2 H, 6-H), 3.20–3.30 (m, 1 H, 5-H), 7.11 (d, $^3J_{HH}$ = 2.0 Hz, 1 H, 2-H), 7.16 (d, $^3J_{HH}$ = 3.6 Hz, 1 H, 3-H), 7.46 (d, $^3J_{HH}$ = 3.6 Hz, 1 H, 4-H) ppm. ^{13}C NMR (MeOD, 100.6 MHz): δ = 47.0 (2 C-6), 48.5 (C-5), 125.5 (C-4), 126.8 (C-2), 128.4 (C-3), 145.8 (C-1) ppm.

2-(Thien-3-yl)propane-1,3-diamine (7f): R_f (3% NH_3/MeOH) = 0.12. ^1H NMR (MeOD, 400.13 MHz): δ = 2.91–3.07 (m, 5 H, 5-H + 4 6-H), 7.18 (d, $^3J_{HH}$ = 3.0 Hz, 1 H, 3-H), 7.34 (s, 1 H, 1-H), 7.58 (s, 1 H, 4-H) ppm. ^{13}C NMR (MeOD, 100.6 MHz): δ = 45.9 (2 C-6), 48.5 (C-5), 123.2 (C-1), 127.8 (C-4), 127.9 (C-3), 143.6 (C-2) ppm.

2-(2-Furyl)propane-1,3-diamine (7g): R_f (3% NH_3/MeOH) = 0.22. ^1H NMR (MeOD, 300.13 MHz): δ = 3.03 (br. s, 5 H, 5-H + 4 6-H), 6.38 (d, $^3J_{HH}$ = 3.2 Hz, 1 H, 2-H), 6.52–6.54 (m, 1 H, 3-H), 7.61 (d, $^3J_{HH}$ = 2.0 Hz, 1 H, 4-H) ppm. ^{13}C NMR (MeOD, 75.5 MHz): δ = 44.0 (2 C-6), 46.8 (C-5), 108.3 (C-2), 111.5 (C-3), 143.5 (C-4), 156.5 (C-1) ppm.

2-(3-Furyl)propane-1,3-diamine (7h): R_f (3% NH_3/MeOH) = 0.12. ^1H NMR (MeOD, 400.13 MHz): δ = 2.84–3.03 (m, 5 H, 5-H + 4 6-H), 6.55 (s, 1 H, 3-H), 7.60 (s, 1 H, 1-H), 7.67 (s, 1 H, 4-H) ppm. ^{13}C NMR (MeOD, 100.6 MHz): δ = 43.8 (C-5), 45.4 (2 C-6), 110.3 (C-3), 126.2 (C-2), 142.0 (C-1), 145.3 (C-4) ppm.

2-(1*H*-Pyrrol-2-yl)propane-1,3-diamine (7i): R_f (3% NH_3/MeOH) = 0.08. ^1H NMR (MeOD, 400.13 MHz): δ = 2.80–3.06 (m, 5 H, 5-H + 4 6-H), 6.10 (s, 1 H, 2-H), 6.23 (s, 1 H, 3-H), 6.86 (s, 1 H, 4-H) ppm. ^{13}C NMR (MeOD, 100.6 MHz): δ = 45.3 (2 C-6), 46.5 (C-5), 106.8 (C-2), 108.9 (C-3), 118.7 (C-4), 132.3 (C-1) ppm.

General Procedure for the Enzymatic Desymmetrization of Diamines 7a–i by Using Diallyl Carbonate: Diallyl carbonate (144 μL, 1.00 mmol) was added to a suspension of the corresponding diamine **7a**–**i** (1.00 mmol) and PCL (300 mg) in dry 1,4-dioxane (10.2 mL) under nitrogen and the mixture shaken at 30 °C and 250 rpm. The progress of the reaction was monitored by TLC analysis. The reaction was stopped after 72 h, the enzyme was filtered off and then washed with MeOH (3 × 5 mL). The solvent was evaporated under reduced pressure, and the resulting crude was purified by flash chromatography on silica gel (mixtures MeOH/EtOAc) to afford the corresponding amino carbamate (*R*)-**10a**–**i** (see Table 2).

Allyl (*R*)-[3-Amino-2-(4-chlorophenyl)propyl]carbamate (10a): Yield: 52% (139 mg). R_f (60% MeOH/EtOAc) = 0.12. IR (NaCl): $\tilde{\nu}$ = 3319, 2931, 1712, 1651, 1538, 1493, 1412, 1258, 1145, 1092, 1014, 993, 929, 825, 777 cm^{-1}. ^1H NMR ($CDCl_3$, 300.13 MHz): δ = 1.53 (br. s, 2 H, NH_2), 2.78–3.01 (m, 3 H, 2-H + 2 3-H), 3.29–3.38 (m, 1 H, 2-H), 3.49–3.57 (m, 1 H, 1-H), 4.52 (d, $^3J_{HH}$ = 5.5 Hz, 2 H,

9-H), 5.02 (br. s, 1 H, NH), 5.18 (d, $^3J_{cis}$ = 10.4 Hz, 1 H, 11-H), 5.23 (d, $^3J_{trans}$ = 17.2 Hz, 1 H, 11-H), 5.80–5.93 (m, 1 H, 10-H), 7.11 (A′B′ system, $J_{A'B'}$ = 8.4 Hz, 2 H, 5-H), 7.30 (A′B′ system, $J_{A'B'}$ = 8.4 Hz, 2 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 43.9 (C-3), 44.9 (C-2), 48.4 (C-1), 65.3 (C-9), 117.4 (C-11), 128.7 (2 C-5), 129.0 (2 C-6), 132.6 (C-7 + C-10), 139.0 (C-4), 156.0 (C-8) ppm. MS (ESI$^+$): *m*/*z* (%) = 269 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_{13}H_{17}ClN_2O_2$ [M + H]$^+$ 269.1057; found 269.1044. $[\alpha]_D^{20}$ = –5.6 (*c* = 0.5, EtOH) for 90% *ee*.

Allyl (*R*)-[3-Amino-2-(pyridin-3-yl)propyl]carbamate (10b): Yield: 58% (163 mg). R_f (50% MeOH/EtOAc) = 0.11. IR (NaCl): $\tilde{\nu}$ = 3288, 3045, 2933, 2863, 1706, 1646, 1550, 1477, 1429, 1325, 1259, 1147, 1026, 991, 930, 813, 773 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.40 (br. s, 2 H, NH_2), 2.77–2.96 (m, 3 H, 2 1-H + 3-H), 3.27–3.36 (m, 1 H, 3-H), 3.43–3.56 (m, 1 H, 2-H), 4.43 (d, $^3J_{HH}$ = 5.4 Hz, 2 H, 10-H), 4.92–5.28 (m, 2 H, 12-H), 5.53–5.91 (m, 2 H, 11-H + NH), 7.18 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 4.8 Hz, 1 H, 6-H), 7.45 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 5-H), 8.21–8.48 (m, 2 H, 7-H + 8-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 43.6 (C-1), 44.6 (C-3), 46.6 (C-2), 65.2 (C10), 117.3 (C-12), 123.4 (C-6), 132.6 (C-5), 135.0 (C-11), 136.3 (C-4), 148.1 (C-7), 149.5 (C-8), 156.2 (C-9) ppm. MS (ESI$^+$): *m*/*z* (%) = 236 (100) [M + H]$^+$, 258 (20) [M + Na]$^+$. HRMS (ESI$^+$): calcd. for $C_{12}H_{17}N_3O_2$ [M + H]$^+$ 236.1399; found 236.1378. $[\alpha]_D^{20}$ = –5.0 (*c* = 0.5, EtOH) for 89% *ee*.

Allyl (*R*)-[3-Amino-2-(1*H*-indol-2-yl)propyl]carbamate (10c): Yield: 47% (128 mg). R_f (60% MeOH/EtOAc) = 0.24. IR (NaCl): $\tilde{\nu}$ = 3320, 3059, 2932, 1704, 1651, 1548, 1532, 1488, 1456, 1291, 1265, 1152, 1075, 993, 929, 788, 737 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 2.50 (br. s, 2 H, NH_2), 3.01 (s, 3 H, 2 10-H + 11-H), 3.38–3.64 (m, 2 H, 9-H + 11-H), 4.54 (d, $^3J_{HH}$ = 5.7 Hz, 2 H, 13-H), 5.19 (d, $^3J_{cis}$ = 10.5 Hz, 1 H, 15-H), 5.27 (d, $^3J_{trans}$ = 17.1 Hz, 1 H, 15-H), 5.39 (br. s, 1 H, NH), 5.81–5.94 (m, 1 H, 14-H), 6.25 (s, 1 H, 2-H), 7.07–7.17 (m, 2 H, 5-H + 6-H), 7.32 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, 4-H), 7.54 (d, $^3J_{HH}$ = 7.4 Hz, 1 H, 7-H), 9.69 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 41.9 (C-9), 42.8 (C-10), 43.5 (C-11), 65.5 (C-13), 99.3 (C-2), 110.8 (C-7), 117.6 (C-15), 119.4 (C-4), 119.8 (C-6), 121.2 (C-5), 128.1 (C-3), 132.6 (C-14), 135.9 (C-1), 138.7 (C-8), 156.6 (C-12) ppm. MS (APCI$^+$): *m*/*z* = 274 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_{15}H_{19}N_3O_2$ [M + H]$^+$ 274.1555; found 274.1532. $[\alpha]_D^{20}$ = –1.8 (*c* = 0.5, EtOH) for 88% *ee*.

Allyl (*R*)-[3-Amino-2-(1*H*-indol-3-yl)propyl]carbamate (10d): Yield: 45% (123 mg). R_f (60% MeOH/EtOAc) = 0.09. IR (NaCl): $\tilde{\nu}$ = 3311, 3056, 2929, 2874, 1698, 1649, 1520, 1456, 1340, 1266, 1148, 1104, 1046, 1011, 993, 930 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.89 (br. s, 2 H, NH_2), 2.99–3.01 (m, 2 H, 10-H), 3.13–3.17 (m, 1 H, 11-H), 3.45–3.63 (m, 2 H, 9-H + 11-H), 4.54 (d, $^3J_{HH}$ = 5.1 Hz, 2 H, 13-H), 5.16–5.34 (m, 3 H, 2 15-H + NH), 5.82–5.95 (m, 1 H, 14-H), 6.93 (s, 1 H, 1-H), 7.09 (t, $^3J_{HH}$ = 7.7 Hz, 1 H, 6-H), 7.19 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, 5-H), 7.34 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 4-H), 7.58 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, 7-H), 9.09 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 40.4 (C-9), 43.3 (C-10), 43.9 (C-11), 65.3 (C-13), 111.4 (C-7), 114.0 (C-2), 117.5 (C-15), 118.7 (C-4), 119.2 (C-6), 121.9 (C-5 + C-1), 126.5 (C-3), 132.8 (C-14), 136.5 (C-8), 156.5 (C-12) ppm. MS (APCI$^+$): *m*/*z* = 274 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_{15}H_{19}N_3O_2$ [M + H]$^+$ 274.1555; found 274.1570. $[\alpha]_D^{20}$ = +6.8 (*c* = 0.5, EtOH) for 87% *ee*.

Allyl (*R*)-[3-Amino-2-(2-thienyl)propyl]carbamate (10e): Yield: 47% (113 mg). R_f (20% MeOH/EtOAc) = 0.08. IR (NaCl): $\tilde{\nu}$ = 3318, 3078, 2934, 2867, 1714, 1651, 1538, 1440, 1259, 1148, 1038, 993, 930 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 2.19 (br. s, 2 H, NH_2), 2.83–2.98 (m, 2 H, 6-H), 3.10–3.19 (m, 1 H, 7-H), 3.30–3.39 (m, 1 H, 7-H), 3.46–3.54 (m, 1 H, 5-H), 4.50 (d, $^3J_{HH}$ = 5.4 Hz, 2 H, 9-H), 5.15 (d, $^3J_{cis}$ = 10.2 Hz, 1 H, 11-H), 5.23 (d, $^3J_{trans}$ = 17.1 Hz, 1 H, 11-H), 5.43 (br. s, 1 H, NH), 5.79–5.91 (m, 1 H, 10-H), 6.84 (d, $^3J_{HH}$ = 3.6 Hz, 1 H, 2-H), 6.93 (dd, $^3J_{HH}$ = 5.1, $^3J_{HH}$ = 3.4 Hz, 1 H, 3-H), 7.16 (dd, $^3J_{HH}$ = 5.1, $^4J_{HH}$ = 1.1 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 44.3 (C-5 + C-6), 45.3 (C-7), 65.3 (C-9), 117.4 (C-11), 123.9 (C-4), 124.8 (C-2), 126.8 (C-3), 132.7 (C-10), 143.7 (C-1), 156.3 (C-8) ppm. MS (APCI$^+$): *m*/*z* = 241 (100) [M + H]$^+$, 242 (15) [M + 2 H]$^+$. HRMS (ESI$^+$): calcd. for $C_{11}H_{16}N_2O_2S$ [M + H]$^+$ 241.1010; found 241.1034. $[\alpha]_D^{20}$ = –5.5 (*c* = 0.5, EtOH) for 78% *ee*.

Allyl (*R*)-[3-Amino-2-(3-thienyl)propyl]carbamate (10f): Yield: 55% (136 mg). R_f (40% MeOH/EtOAc) = 0.14. IR (NaCl): $\tilde{\nu}$ = 3308, 3095, 1704, 1648, 1538, 1411, 1320, 1259, 1145, 993, 930, 858 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.91 (br. s, 2 H, NH_2), 2.80–3.01 (m, 3 H, 2 6-H + 7-H), 3.29–3.50 (m, 2 H, 5-H + 7-H), 4.48 (d, $^3J_{HH}$ = 5.4 Hz, 2 H, 9-H), 5.12–5.38 (m, 3 H, 2 11-H + NH), 5.78–5.91 (m, 1 H, 10-H), 6.92 (dd, $^3J_{HH}$ = 4.8, $^4J_{HH}$ = 1.1 Hz, 1 H, 3-H), 7.00 (dd, $^4J_{HH}$ = 2.8, $^4J_{HH}$ = 1.4 Hz, 1 H, 1-H), 7.27 (dd, $^3J_{HH}$ = 5.1, $^4J_{HH}$ = 3.0 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 43.5 (C-6), 44.2 (C-5), 44.5 (C-7), 65.2 (C-9), 117.4 (C-11), 121.3 (C-1), 126.1 (C-4), 126.4 (C-3), 132.7 (C-10), 141.3 (C-2), 156.2 (C-8) ppm. MS (ESI$^+$): *m*/*z* (%) = 241 (100) [M + H]$^+$, 263 (20) [M + Na]$^+$. HRMS (ESI$^+$): calcd. for $C_{11}H_{16}N_2O_2S$ [M + H]$^+$ 241.1010; found 241.1000. $[\alpha]_D^{20}$ = +5.1 (*c* = 0.5, EtOH) for 79% *ee*.

Allyl (*R*)-[3-Amino-2-(2-furyl)propyl]carbamate (10g): Yield: 48% (107 mg). R_f (20% MeOH/EtOAc) = 0.09. IR (NaCl): $\tilde{\nu}$ = 3321, 3117, 3082, 1704, 1538, 1441, 1417, 1328, 1259, 1149, 1012, 994, 926 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.78 (br. s, 2 H, NH_2), 2.87–3.00 (m, 3 H, 2 6-H + 7-H), 3.38–3.53 (m, 2 H, 5-H + 7-H), 4.50 (d, $^3J_{HH}$ = 5.4 Hz, 2 H, 9-H), 5.14–5.35 (m, 3 H, 2 11-H + NH), 5.80–5.93 (m, 1 H, 10-H), 6.09 (d, $^3J_{HH}$ = 3.1 Hz, 1 H, 2-H), 6.27 (dd, $^3J_{HH}$ = 3.1, $^3J_{HH}$ = 1.7 Hz, 1 H, 3-H), 7.31 (d, $^3J_{HH}$ = 1.7 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 41.5 (C-6), 42.4 (C-5), 42.6 (C-7), 65.3 (C-9), 106.2 (C-2), 110.0 (C-3), 117.4 (C-11), 132.7 (C-10), 141.6 (C-4), 154.3 (C-8), 156.3 (C-1) ppm. MS (APCI$^+$): *m*/*z* = 225 (100) [M + H]$^+$, 226 (10) [M + 2 H]$^+$. HRMS (ESI$^+$): calcd. for $C_{11}H_{16}N_2O_3$ [M + H]$^+$ 225.1239; found 225.1245. $[\alpha]_D^{20}$ = +3.7 (*c* = 0.5, EtOH) for 71% *ee*.

Allyl (*R*)-[3-Amino-2-(3-furyl)propyl]carbamate (10h): Yield: 54%. R_f (60% MeOH/EtOAc) = 0.14. IR (NaCl): $\tilde{\nu}$ = 3324, 3142, 3081, 1703, 1648, 1540, 1438, 1327, 1259, 1160, 1026, 993, 931 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.56 (br. s, 2 H, NH_2), 2.71–2.87 (m, 3 H, 2 6-H + 7-H), 3.26–3.45 (m, 2 H, 5-H + 7-H), 4.49 (d, $^3J_{HH}$ = 5.1 Hz, 2 H, 9-H), 5.13–5.33 (m, 3 H, 2 11-H + NH), 5.79–5.91 (m, 1 H, 10-H), 6.25 (s, 1 H, 3-H), 7.26 (s, 1 H, 1-H), 7.36 (s, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 39.5 (C-5), 43.1 (C-6), 44.1 (C-7), 65.3 (C-9), 108.9 (C-3), 117.4 (C-11), 124.0 (C-2), 132.7 (C-10), 139.6 (C-1), 143.3 (C-4), 156.2 (C-8) ppm. MS (APCI$^+$): *m*/*z* = 225 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_{11}H_{16}N_2O_3$ [M + H]$^+$ 225.1239; found 225.1229. $[\alpha]_D^{20}$ = +5.3 (*c* = 0.5, EtOH) for 70% *ee*.

Allyl (*R*)-[3-Amino-2-(1*H*-pyrrol-2-yl)propyl]carbamate (10i): Yield: 53% (121 mg). R_f (20% MeOH/EtOAc) = 0.08. IR (NaCl): $\tilde{\nu}$ = 3345, 3097, 2937, 2871, 1702, 1650, 1538, 1261, 1146, 1097, 1029, 993, 932 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 2.51 (br. s, 2 H, NH_2), 2.81–2.92 (m, 3 H, 2 6-H + 7-H), 3.29–3.45 (m, 2 H, 5-H + 7-H), 4.51 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, 9-H), 5.16–5.28 (m, 2 H, 11-H), 5.57 (br. s, 1 H, NH), 5.80–5.92 (m, 2 H, 2-H + 10-H), 6.11 (s, 1 H, 3-H), 6.66 (s, 1 H, 4-H), 9.78 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 41.1 (C-5), 43.0 (C-6), 43.6 (C-7),

65.4 (C-9), 104.7 (C-2), 107.8 (C-3), 117.0 (C-4), 117.4 (C-11), 130.9 (C-1), 132.6 (C-10), 156.6 (C-8) ppm. MS (APCI$^+$): *m/z* = 224 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_{11}H_{17}N_3O_2$ [M + H]$^+$ 224.1399; found 224.1379. $[\alpha]_D^{20}$ = +5.5 (*c* = 0.5, EtOH) for 76% *ee*.

General Procedure for the Synthesis of Chiral Amido Carbamates 11a–i: Et_3N (13 μL, 0.10 mmol) and acetyl or benzoyl chloride (0.10 mmol) were successively added to a solution of the corresponding compound (*R*)-**10a**–**i** (0.09 mmol) in dry CH_2Cl_2 (0.9 mL) under nitrogen. The mixture was stirred at room temperature for 4 h, and after this time the solvent was evaporated under reduced pressure to give a reaction crude that was purified by flash chromatography on silica gel (100% EtOAc) to afford the amido carbamate (*R*)-**11a**–**i** (91–96%).

Allyl [3-(Acetylamino)-2-(4-chlorophenyl)propyl]carbamate (11a): Yield: 93% (26 mg). R_f (70% EtOAc/hexane) = 0.10. IR (NaCl): ṽ = 3313, 3084, 2934, 1710, 1651, 1538, 1494, 1440, 1371, 1261, 1148, 1093, 1014, 993, 932, 825, 777, 737 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.93 (s, 3 H, 9-H), 2.94–3.02 (m, 1 H, 2-H), 3.28–3.57 (m, 4 H, 1-H + 2-H + 2 3-H), 4.51 (d, $^3J_{HH}$ = 5.4 Hz, 2 H, 11-H), 5.17–5.28 (m, 3 H, 2 13-H + NH), 5.80–5.93 (m, 1 H, 12-H), 6.10 (br. s, 1 H, NH), 7.08 (A′B′ system, $J_{A'B'}$ = 8.5 Hz, 2 H, 5-H), 7.27 (A′B′ system, $J_{A'B'}$ = 8.5 Hz, 2 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 23.1 (C-9), 41.1 (C-3), 42.9 (C-2), 44.6 (C-1), 65.6 (C-11), 117.6 (C-13), 128.8 (2 C-5), 128.9 (2 C-6), 132.6 (C-7), 132.9 (C-12), 138.6 (C-4), 156.7 (C-10), 170.5 (C-8) ppm. MS (ESI$^+$): *m/z* (%) = 311 (100) [M + H]$^+$, 333 (10) [M + Na]$^+$. HRMS (ESI$^+$): calcd. for $C_{15}H_{19}ClN_2O_3$ [M + Na]$^+$ 333.0982; found 333.0956. $[\alpha]_D^{20}$ = –5.1 (*c* = 0.5, EtOH) for 90% *ee*.

Allyl [3-(Acetylamino)-2-pyridin-3-ylpropyl]carbamate (11b): Yield: 91% (22.5 mg). R_f (100% EtOAc) = 0.09. IR (NaCl): ṽ = 3314, 3088, 2932, 1707, 1650, 1594, 1550, 1476, 1438, 1373, 1295, 1264, 1151, 991 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.94 (s, 3 H, 10-H), 3.01–3.05 (m, 1 H, 2-H), 3.31–3.63 (m, 4 H, 2 1-H + 2 3-H), 4.51 (d, $^3J_{HH}$ = 5.5 Hz, 1 H, 12-H), 5.18 (dd, $^3J_{cis}$ = 10.4, $^2J_{gem}$ = 1.3 Hz, 1 H, 14-H), 5.25 (d, $^3J_{trans}$ = 16.9 Hz, 1 H, 14-H), 5.62 (br. s, 1 H, NH), 5.80–5.93 (m, 1 H, 13-H), 6.51 (br. s, 1 H, NH), 7.23 (dd, $^3J_{HH}$ = 7.9, $^3J_{HH}$ = 5.0 Hz 1 H, 6-H), 7.50 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, 5-H), 8.37–8.40 (m, 2 H, 7-H + 8-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 23.0 (C-10), 40.8 (C-1), 42.6 (C-3), 43.1 (C-2), 65.6 (C-12), 117.6 (C-14), 123.6 (C-6), 132.6 (C-5), 135.2 (C-13), 135.9 (C-4), 148.4 (C-8), 149.2 (C-7), 156.8 (C-11), 170.8 (C-9) ppm. MS (ESI$^+$): *m/z* (%) = 278 (80) [M + H]$^+$, 300 (100) [M + Na]$^+$. HRMS (ESI$^+$): calcd. for $C_{14}H_{19}N_3O_3$ [M + Na]$^+$ 300.1324; found 300.1307. $[\alpha]_D^{20}$ = –6.1 (*c* = 0.5, EtOH) for 89% *ee*.

Allyl [3-(Benzoylamino)-2-(1*H*-indol-2-yl)propyl]carbamate (11c): Yield: 95% (32 mg). R_f (60% EtOAc/hexane) = 0.37. IR (NaCl): ṽ = 3305, 3057, 2933, 1704, 1524, 1457, 1425, 1343, 1265, 1149, 991, 788, 736 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 3.30–3.38 (m, 1 H, 16-H), 3.43–3.52 (m, 1 H, 10-H), 3.66–3.74 (m, 2 H, 10-H + 16-H), 3.89–3.97 (m, 1 H, 9-H), 4.57 (d, $^3J_{HH}$ = 5.5 Hz, 2 H, 18-H), 5.20 (d, $^3J_{cis}$ = 10.4 Hz, 1 H, 20-H), 5.28 (d, $^3J_{trans}$ = 17.2 Hz, 1 H, 20-H), 5.48 (br. s, 1 H, NH), 5.83–5.96 (m, 1 H, 19-H), 6.29 (s, 1 H, 2-H), 7.06–7.16 (m, 2 H, 5-H + 6-H), 7.30–7.55 (m, 6 H, 4-H + 7-H + 2 14-H + 15-H + NH), 7.79 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, 13-H), 9.32 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 39.7 (C-9), 40.1 (C-10), 41.9 (C-16), 65.8 (C-18), 95.5 (C-2), 111.0 (C-7), 117.8 (C-20), 119.7 (C-4), 119.8 (C-6), 121.6 (C-5), 126.9 (2 C-13), 128.3 (C-3), 128.6 (2 C-14), 131.6 (C-15), 132.5 (C-19), 133.8 (C-12), 135.9 (C-1), 137.3 (C-8), 157.3 (C-17), 168.2 (C-11) ppm. MS (APCI$^+$): *m/z* = 378 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_{22}H_{23}N_3O_3$ [M + Na]$^+$ 400.1637; found 400.1649. $[\alpha]_D^{20}$ = –1.1 (*c* = 0.5, EtOH) for 88% *ee*.

Allyl [3-(Benzoylamino)-2-(1*H*-indol-3-yl)propyl]carbamate (11d): Yield: 94% (32 mg). R_f (60% EtOAc/hexane) = 0.29. IR (NaCl): ṽ = 3320, 3058, 2932, 1704, 1651, 1538, 1488, 1457, 1435, 1264, 1149, 1105, 993, 929 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 3.36–3.60 (m, 3 H, 10-H + 2 16-H), 3.68–3.77 (m, 1 H, 10-H), 3.98–4.06 (m, 1 H, 9-H), 4.58 (d, $^3J_{HH}$ = 5.4 Hz, 2 H, 18-H), 5.19–5.33 (m, 3 H, 2 20-H + NH), 5.85–5.98 (m, 1 H, 19-H), 6.97 (s, 1 H, 1-H), 7.06–7.12 (m, 2 H, 5-H + NH), 7.19 (t, $^3J_{HH}$ = 7.7 Hz, 1 H, 6-H), 7.35–7.43 (m, 3 H, 2 14-H + 1 15-H), 7.46 (d, $^3J_{HH}$ = 7.1 Hz, 1 H, 4-H), 7.60 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, 7-H), 7.60 (d, $^3J_{HH}$ = 7.1 Hz, 2 H, 13-H), 8.61 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 37.1 (C-9), 40.7 (C-10), 42.2 (C-16), 65.6 (C-18), 111.4 (C-7), 114.3 (C-2), 117.6 (C-20), 118.8 (C-4), 119.6 (C-6), 121.4 (C-5), 122.3 (C-1), 126.4 (C-3), 126.9 (2 C-13), 128.5 (2 C-14), 131.4 (C-15), 132.7 (C-19), 134.2 (C-12), 136.4 (C-8), 157.1 (C-17), 167.8 (C-11) ppm. MS (APCI$^+$): *m/z* = 378 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_{22}H_{23}N_3O_3$ [M + Na]$^+$ 400.1637; found 400.1632. $[\alpha]_D^{20}$ = –2.2 (*c* = 0.5, EtOH) for 87% *ee*.

Allyl [3-(Acetylamino)-2-(2-thienyl)propyl]carbamate (11e): Yield: 92% (23 mg). R_f (70% EtOAc/hexane) = 0.26. IR (NaCl): ṽ = 3313, 3083, 2933, 1705, 1652, 1538, 1439, 1372, 1258, 1150, 1091, 1039, 993, 930, 849 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.98 (s, 3 H, 8-H), 3.24–3.37 (m, 3 H, 6-H + 2 9-H), 3.55–3.64 (m, 1 H, 6-H), 3.68–3.74 (m, 1 H, 5-H), 5.20 (dd, $^3J_{cis}$ = 10.2, $^2J_{gem}$ = 1.4 Hz, 1 H, 13-H), 5.28 (dd, $^3J_{trans}$ = 17.4, $^2J_{gem}$ = 1.4 Hz, 1 H, 13-H), 5.45 (br. s, 1 H, NH), 5.83–5.96 (m, 1 H, 12-H), 6.24 (br. s, 1 H, NH), 6.85 (d, $^3J_{HH}$ = 3.4 Hz, 1 H, 2-H), 6.97 (dd, $^3J_{HH}$ = 5.1, $^3J_{HH}$ = 3.4 Hz, 1 H, 3-H), 7.19 (d, $^3J_{HH}$ = 5.1 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 23.2 (C-8), 40.9 (C-5), 41.4 (C-6), 43.1 (C-9), 65.6 (C-11), 117.6 (C-13), 123.9 (C-4), 124.6 (C-2), 126.9 (C-3), 132.6 (C-12), 142.8 (C-1), 156.8 (C-10), 170.6 (C-7) ppm. MS (APCI$^+$): *m/z* = 283 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_{13}H_{18}N_2O_3S$ [M + Na]$^+$ 305.0940; found 305.0946. $[\alpha]_D^{20}$ = –5.1 (*c* = 0.5, EtOH) for 78% *ee*.

Allyl [3-(Acetylamino)-2-(3-thienyl)propyl]carbamate (11f): Yield: 93% (24 mg). R_f (70% EtOAc/hexane) = 0.29. IR (NaCl): ṽ = 3311, 3092, 1704, 1651, 1539, 1437, 1371, 1259, 1147, 1091, 993, 930, 857 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.97 (s, 3 H, 8-H), 3.11–3.17 (m, 1 H, 9-H), 3.25–3.36 (m, 2 H, 6-H + 9-H), 3.50–3.70 (m, 2 H, 5-H + 6-H), 4.54 (d, $^3J_{HH}$ = 5.7 Hz, 2 H, 11-H), 5.18–5.31 (m, 3 H, 2 13-H + NH), 5.83–5.96 (m, 1 H, 12-H), 6.14 (br. s, 1 H, NH), 6.95 (dd, $^3J_{HH}$ = 4.9, $^4J_{HH}$ = 1.1 Hz, 1 H, 3-H), 7.02 (d, $^4J_{HH}$ = 2.3 Hz, 1 H, 1-H), 7.31 (dd, $^3J_{HH}$ = 5.1, $^4J_{HH}$ = 3.1 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 23.2 (C-8), 40.7 (C-6), 40.8 (C-5), 42.5 (C-9), 65.6 (C-11), 117.6 (C-13), 121.1 (C-1), 126.3 (C-4), 126.7 (C-3), 132.7 (C-12), 140.7 (C-2), 156.8 (C-10), 170.6 (C-7) ppm. MS (ESI$^+$): *m/z* (%) = 283 (30) [M + H]$^+$, 305 (100) [M + Na]$^+$. HRMS (ESI$^+$): calcd. for $C_{13}H_{18}N_2O_3S$ [M + Na]$^+$ 305.0940; found 305.0919. $[\alpha]_D^{20}$ = –7.3 (*c* = 0.5, EtOH) for 79% *ee*.

Allyl [3-(Acetylamino)-2-(2-furyl)propyl]carbamate (11g): Yield: 96% (25 mg). R_f (100% EtOAc) = 0.25. IR (NaCl): ṽ = 3317, 3085, 2944, 1714, 1660, 1651, 1538, 1436, 1732, 1258, 1149, 1012, 995, 931 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.99 (s, 3 H, 8-H), 3.08–3.16 (m, 1 H, 9-H), 3.22–3.34 (m, 2 H, 6-H + 9-H), 3.60–3.69 (m, 1 H, 6-H), 3.75–3.84 (m, 1 H, 5-H), 4.52 (d, $^3J_{HH}$ = 5.5 Hz, 2 H, 11-H), 5.19–5.37 (m, 3 H, 2 13-H + NH), 5.84–5.97 (m, 1 H, 12-H), 6.11 (d, $^3J_{HH}$ = 3.1 Hz, 1 H, 2-H), 6.18 (br. s, 1 H, NH), 6.32 (dd, $^3J_{HH}$ = 3.2, $^3J_{HH}$ = 1.9 Hz, 1 H, 3-H), 7.34 (d, $^3J_{HH}$ = 1.7 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 23.2

(C-8), 38.8 (C-6), 39.2 (C-5), 40.5 (C-9), 65.6 (C-11), 106.4 (C-2), 110.3 (C-3), 117.6 (C-13), 132.7 (C-12), 141.7 (C-4), 153.9 (C-10), 156.9 (C-1), 170.6 (C-7) ppm. MS (APCI$^+$): *m*/*z* = 267 (100) [M + H]$^+$, 268 (10) [M + 2 H]$^+$. HRMS (ESI$^+$): calcd. for $C_{13}H_{18}N_2O_4$ [M + Na]$^+$ 289.1165; found 289.1130. $[\alpha]_D^{20}$ = –2.8 (*c* = 0.5, EtOH) for 71% *ee*.

Allyl [3-(Acetylamino)-2-(3-furyl)propyl]carbamate (11h): Yield: 93% (21.5 mg). R_f (60% EtOAc/hexane) = 0.16. IR (NaCl): $\tilde{\nu}$ = 3316, 3085, 1704, 1651, 1539, 1440, 1371, 1259, 1161, 1028, 993, 930, 874 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.97 (s, 3 H, 8-H), 2.88–2.97 (m, 1 H, 9-H), 3.16–3.26 (m, 2 H, 6-H + 9-H), 3.46–3.55 (m, 1 H, 6-H), 3.58–3.67 (m, 1 H, 5-H), 4.54 (d, $^3J_{HH}$ = 5.4 Hz, 2 H, 11-H), 5.18–5.33 (m, 3 H, 2 13-H + NH), 5.83–5.95 (m, 1 H, 12-H), 6.17 (br. s, 1 H, NH), 6.28 (s, 1 H, 3-H), 7.27 (s, 1 H, 1-H), 7.39 (s, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 23.2 (C-8), 36.5 (C-5), 40.2 (C-6), 41.9 (C-9), 65.6 (C-11), 109.4 (C-3), 117.6 (C-13), 123.7 (C-2), 132.7 (C-12), 139.2 (C-1), 143.4 (C-4), 156.8 (C-10), 170.6 (C-7) ppm. MS (APCI$^+$): *m*/*z* = 267 (100) [M + H]$^+$, 268 (15) [M + 2 H]$^+$. HRMS (ESI$^+$): calcd. for $C_{13}H_{18}N_2O_4$ [M + Na]$^+$ 289.1165; found 289.1150. $[\alpha]_D^{20}$ = –4.8 (*c* = 0.5, EtOH) for 70% *ee*.

Allyl [3-(Acetylamino)-2-(1*H*-pyrrol-2-yl)propyl]carbamate (11i): Yield: 94% (22 mg). R_f (100% EtOAc) = 0.22. IR (NaCl): $\tilde{\nu}$ = 3321, 3096, 2934, 1704, 1651, 1538, 1434, 1370, 1260, 1148, 1100, 1031, 992, 930 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.98 (s, 3 H, 8-H), 3.05–3.10 (m, 1 H, 9-H), 3.33–3.59 (m, 4 H, 5-H + 2 6-H + 9-H), 4.55 (d, $^3J_{HH}$ = 5.4 Hz, 2 H, 11-H), 5.19–5.32 (m, 2 H, 13-H), 5.47 (br. s, 1 H, NH), 5.84–5.94 (m, 2 H, 2-H + 12-H), 6.15 (s, 1 H, 3-H), 6.49 (br. s, 1 H, NH), 6.70 (s, 1 H, 4-H), 9.32 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 23.2 (C-8), 39.2 (C-5), 40.0 (C-6), 42.1 (C-9), 65.7 (C-11), 105.1 (C-2), 108.3 (C-3), 117.3 (C-4), 117.7 (C-13), 129.8 (C-1), 132.6 (C-12), 157.2 (C-10), 171.2 (C-7) ppm. MS (APCI$^+$): *m*/*z* = 266 (100) [M + H]$^+$, 267 (10) [M + 2 H]$^+$. HRMS (ESI$^+$): calcd. for $C_{13}H_{19}N_3O_3$ [M + Na]$^+$ 288.1324; found 288.1346. $[\alpha]_D^{20}$ = –4.5 (*c* = 0.5, EtOH) for 76% *ee*.

General Procedure for the Synthesis of Racemic Amido Amines 12a–i: Acetic or benzoic anhydride (1 mmol) was added in small portions at 10 min intervals to a solution of compound **7a**–**i** (1 mmol) in dry CH_2Cl_2 (2.0 mL) under nitrogen. The mixture was stirred at room temperature for 4 h, and after this time the solvent was evaporated under reduced pressure to give a reaction crude that was purified by flash chromatography on silica gel (100% MeOH to 1% NH_3/MeOH) to afford the corresponding racemic amino amide **12a**–**i** (5–23%).

***N*-[3-Amino-2-(4-chlorophenyl)propyl]acetamide (12a):** Yield: 21% (47 mg). R_f (100% MeOH) = 0.12. IR (NaCl): $\tilde{\nu}$ = 3406, 2934, 1643, 1564, 1493, 1377, 1306, 1093, 1014, 825 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ = 1.69–2.02 (s, 5 H, 3 9-H + NH_2), 2.77–2.95 (m, 3 H, 2-H + 2 3-H), 3.30–3.36 (m, 1 H, 2-H), 3.54–3.60 (m, 1 H, 1-H), 6.25 (br. s, 1 H, NH), 7.10 (A′B′ system, $J_{A'B'}$ = 8.3 Hz, 2 H, 5-H), 7.27 (A′B′ system, $J_{A'B'}$ = 8.3 Hz, 2 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 23.0 (C-9), 42.6 (C-2), 45.3 (C-3), 47.8 (C-1), 128.8 (2 C-5), 129.1 (2 C-6), 132.7 (C-7), 139.3 (C-4), 170.1 (C-8) ppm. MS (APCI$^+$): *m*/*z* (%) = 227 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_{11}H_{15}ClN_2O$ [M + H]$^+$ 227.0951; found 227.0949.

***N*-(3-Amino-2-pyridin-3-ylpropyl)acetamide (12b):** Yield: 23% (44.5 mg). R_f (3% NH_3/MeOH) = 0.36. IR (NaCl): $\tilde{\nu}$ = 3349, 2932, 2911, 2863, 1637, 1572, 1481, 1429, 1381, 1329, 1138, 1107 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.89 (s, 3 H, 10-H), 2.00 (br. s, 2 H, NH_2), 2.81–3.04 (m, 3 H, 2 1-H + 2-H), 3.41–3.50 (m, 1 H, 3-H), 3.57–3.66 (m, 1 H, 3-H), 6.41 (br. s, 1 H, NH), 7.20–7.27 (m, 1 H, 6-H), 7.51–7.55 (m, 1 H, 5-H), 8.38–8.51 (m, 2 H, 7-H + 8-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 23.0 (C-10), 42.5 (C-3), 45.1 (C-1), 46.0 (C-2), 123.7 (C-6), 135.1 (C-5), 136.5 (C-4), 148.4 (C-7), 149.6 (C-8), 170.3 (C-9) ppm. MS (ESI$^+$): *m*/*z* (%) = 194 (100) [M + H]$^+$, 216 (85) [M + Na]$^+$. HRMS (ESI$^+$): calcd. for $C_{10}H_{15}N_3O$ [M + H]$^+$ 194.1293; found 194.1271.

***N*-[3-Amino-2-(1*H*-indol-2-yl)propyl]benzamide (12c):** Yield: 5% (14.5 mg). R_f (100% MeOH) = 0.20. IR (NaCl): $\tilde{\nu}$ = 3291, 3062, 2929, 1643, 1577, 1535, 1488, 1457, 1290, 909, 790, 732 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.94 (br. s, 2 H, NH_2), 3.08–3.27 (m, 3 H, 2 10-H + 11-H), 3.67–3.75 (m, 1 H, 11-H), 3.88–3.97 (m, 1 H, 9-H), 6.31 (s, 1 H, 2-H), 7.03–7.16 (m, 2 H, 5-H + 6-H), 7.32–7.57 (m, 6 H, 4-H + 7-H + 2 15-H + 16-H + NH), 9.76 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 41.2 (C-9), 42.2 (C-10), 44.2 (C-11), 99.3 (C-2), 110.9 (C-7), 119.5 (C-4), 119.9 (C-6), 121.4 (C-5), 126.8 (2 C-14), 128.2 (C-3), 128.5 (2 C-15), 131.5 (C-16), 134.1 (C-13), 136.0 (C-1), 139.0 (C-8), 167.9 (C-12) ppm. MS (APCI$^+$): *m*/*z* (%) = 294 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_{18}H_{19}N_3O$ [M + H]$^+$ 294.1606; found 294.1623.

***N*-[3-Amino-2-(1*H*-indol-3-yl)propyl]benzamide (12d):** Yield: 8% (23 mg). R_f (3% NH_3/MeOH) = 0.34. IR (NaCl): $\tilde{\nu}$ = 3288, 3062, 2926, 1844, 1833, 1538, 1488, 1456, 1312, 1224, 1105, 1012, 929, 803 cm^{-1}. ^{1}H NMR (MeOD, 300.13 MHz): δ = 3.23–3.25 (m, 2 H, 10-H), 3.58–3.66 (m, 1 H, 11-H), 3.83–4.01 (m, 2 H, 9-H + 11-H), 7.20 (td, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.1 Hz, 1 H, 6-H), 7.30 (td, $^3J_{HH}$ = 7.1, $^4J_{HH}$ = 1.1 Hz, 1 H, 5-H), 7.36 (s, 1 H, 1-H), 7.58 (t, $^3J_{HH}$ = 7.7 Hz, 3 H, 2 15-H + 16-H), 7.66 (d, $^3J_{HH}$ = 7.3 Hz, 1 H, 4-H), 7.84 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, 7-H), 7.90 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, 14-H) ppm. ^{13}C NMR (MeOD, 75.5 MHz): δ = 41.2 (C-9), 44.0 (C-10), 44.8 (C-11), 112.8 (C-7), 115.1 (C-2), 119.9 (C-4), 120.2 (C-6), 122.9 (C-1), 123.6 (C-5), 128.5 (2 C-14 + C-3), 129.8 (2 C-15), 132.9 (C-16), 136.0 (C-13), 138.7 (C-8), 170.8 (C-12) ppm. MS (APCI$^+$): *m*/*z* (%) = 294 (100) [M + H]$^+$, 295 (20) [M + 2 H]$^+$. HRMS (ESI$^+$): calcd. for $C_{18}H_{19}N_3O$ [M + H]$^+$ 294.1606; found 294.1614.

***N*-[3-Amino-2-(2-thienyl)propyl]acetamide (12e):** Yield: 8% (16 mg). R_f (2% NH_3/MeOH) = 0.31. IR (NaCl): $\tilde{\nu}$ = 3292, 3073, 2931, 2873, 1654, 1561, 1438, 1373, 1268, 1107, 1039, 897, 837 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.53 (br. s, 1 H, NH_2), 1.91 (s, 3 H, 9-H), 2.86–2.99 (m, 2 H, 6-H), 3.09–3.18 (m, 1 H, 7-H), 3.36–3.44 (m, 1 H, 7-H), 3.59–3.68 (m, 1 H, 5-H), 6.13 (br. s, 1 H, NH), 6.86 (d, $^3J_{HH}$ = 3.3 Hz, 1 H, 2-H), 6.96 (dd, $^3J_{HH}$ = 5.0, $^3J_{HH}$ = 3.3 Hz, 1 H, 3-H) 7.18 (d, $^3J_{HH}$ = 5.0 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 23.1 (C-9), 43.1 (C-7), 44.2 (C-5), 45.9 (C-6), 123.9 (C-4), 124.7 (C-2), 126.9 (C-3), 144.1 (C-1), 170.2 (C-8) ppm. MS (APCI$^+$): *m*/*z* (%) = 199 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_9H_{14}N_2OS$ [M + H]$^+$ 199.0905; found 199.0927.

***N*-[3-Amino-2-(3-thienyl)propyl]acetamide (12f):** Yield: 17% (33 mg). R_f (3% NH_3/MeOH) = 0.40. IR (NaCl): $\tilde{\nu}$ = 3294, 3072, 2933, 2870, 1655, 1562, 1440, 1365, 1269, 1107, 1036 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ = 1.90 (s, 3 H, 9-H), 2.86–3.00 (m, 3 H, 2 6-H + 7-H), 3.38–3.45 (m, 1 H, 7-H), 3.57–3.63 (m, 1 H, 5-H), 6.08 (br. s, 1 H, NH), 6.95 (d, $^3J_{HH}$ = 3.2 Hz, 1 H, 3-H), 7.03 (s, 1 H, 1-H), 7.30–7.32 (m, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 23.1 (C-9), 42.4 (C-7), 43.9 (C-5), 45.2 (C-6), 121.3 (C-1), 126.3 (C-4), 126.5 (C-3), 141.6 (C-2), 170.1 (C-8) ppm. MS (APCI$^+$): *m*/*z* (%) = 199 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_9H_{14}N_2OS$ [M + H]$^+$ 199.0905; found 199.0918.

***N*-[3-Amino-2-(2-furyl)propyl]acetamide (12g):** Yield: 9% (16 mg). R_f (3% NH_3/MeOH) = 0.34. IR (NaCl): $\tilde{\nu}$ = 3291, 3112, 2936, 2876, 1650, 1563, 1506, 1440, 1376, 1301, 1149, 1108, 1074, 1012, 915, 808 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.63 (br. s, 2 H, NH_2), 1.91 (s, 3 H, 9-H), 2.89–2.99 (m, 3 H, 2 6-H + 7-H),

3.45–3.60 (m, 2 H, 5-H + 7-H), 6.09 (d, $^3J_{HH}$ = 3.1 Hz, 1 H, 2-H), 6.24–6.36 (m, 2 H, 3-H + NH), 7.32 (dd, $^3J_{HH}$ = 1.7, $^4J_{HH}$ = 0.8 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 23.1 (C-9), 40.2 (C-7), 42.1 (C-5), 43.0 (C-6), 106.4 (C-2), 110.1 (C-3), 141.6 (C-4), 154.6 (C-1), 170.3 (C-8) ppm. MS (APCI$^+$): *m*/*z* (%) = 183 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_9H_{14}N_2O_2$ [M + H]$^+$ 183.1133; found 183.1142.

***N*-[3-Amino-2-(3-furyl)propyl]acetamide (12h):** Yield: 10% (17.5 mg). R_f (3% NH_3/MeOH) = 0.33. IR (NaCl): $\tilde{\nu}$ = 3291, 3082, 2932, 2878, 1732, 1652, 1558, 1441, 1371, 1293, 1162, 1126, 1027, 913, 874 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.58 (br. s, 2 H, NH_2), 1.92 (s, 3 H, 9-H), 2.72–2.80 (m, 1 H, 6-H), 2.82–2.90 (m, 2 H, 6-H + 7-H), 3.33–3.42 (m, 1 H, 7-H), 3.49–3.57 (m, 1 H, 5-H), 6.11 (br. s, 1 H, NH), 6.28 (s, 1 H, 3-H), 7.29 (s, 1 H, 1-H) 7.40 (s, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 23.1 (C-9), 39.1 (C-5), 42.0 (C-7), 44.7 (C-6), 109.1 (C-3), 124.3 (C-2), 139.5 (C-1), 143.5 (C-4), 170.1 (C-8) ppm. MS (APCI$^+$): *m*/*z* (%) = 183 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_9H_{14}N_2O_2$ [M + H]$^+$ 183.1133; found 183.1122.

***N*-[3-Amino-2-(1*H*-pyrrol-2-yl)propyl]acetamide (12i):** Yield: 17% (31 mg). R_f (3% NH_3/MeOH) = 0.30. IR (NaCl): $\tilde{\nu}$ = 3288, 3097, 2933, 2871, 1651, 1563, 1439, 1374, 1269, 1098, 1031, 954, 909, 801 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.87–2.10 (m, 5 H, 3 9-H + NH_2), 2.86–3.10 (m, 3 H, 2 6-H + 7-H), 3.35–3.44 (m, 1 H, 7-H), 3.56–3.65 (m, 1 H, 5-H), 5.95 (s, 1 H, 2-H), 6.12–6.30 (m, 2 H, 3-H + NH), 6.70 (s, 1 H, 4-H), 9.74 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 23.2 (C-9), 40.8 (C-5), 41.7 (C-7), 44.3 (C-6), 104.9 (C-2), 107.9 (C-3), 117.1 (C-4), 131.5 (C-1), 170.6 (C-8) ppm. MS (APCI$^+$): *m*/*z* (%) = 182 (100) [M + H]$^+$. HRMS (ESI$^+$): calcd. for $C_9H_{15}N_3O$ [M + H]$^+$ 182.1293; found 182.1276.

General Procedure for the Synthesis of Racemic Amido Carbamates 11a–i: Pyridine (8 μL, 0.09 mmol) and allyl chloroformate (10 μL, 0.09 mmol) were successively added to a solution of the racemic amino amide **12a**–**i** (0.08 mmol) in dry CH_2Cl_2 (0.8 mL) under nitrogen. The mixture was stirred at room temperature for 4 h, and after this time the solvent was evaporated under reduced pressure to give a reaction crude that was purified by flash chromatography on silica gel (EtOAc/hexane mixtures) to afford the corresponding racemic amido carbamate **11a**–**i** (18.5–30.5 mg, 91–95%). Isolated yields for the racemic compounds **11a**–**i**: **11a**: 92%; **11b**: 92%; **11c**: 94%; **11d**: 91%; **11e**: 95%; **11f**: 91%; **11g**: 92%; **11h**: 91%; **11i**: 93%.

Supporting Information (see footnote on the first page of this article): Experimental procedures and characterization data for compounds **2**–**6**, examples of the atomic numbering used for NMR assignment, conditions for analytical separation by chiral HPLC of compounds **10a**–**i**, experimental protocols and characterization data for the Mosher derivatives and NMR spectra for the new compounds.

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