A Flexible Asymmetric Synthesis of *anti*-1,2-Sulfanyl Amines

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Dedicated to Professor Reinhard W. Hoffmann on the occasion of his 70th birthday

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An efficient and flexible asymmetric synthesis of various protected *anti*-1,2-sulfanyl amines bearing two adjacent stereogenic centres is described. Key steps are the diastereoselective α-alkylation of α-sulfanylated acetaldehyde-SAMP-hydrazones with various electrophiles and subsequent nucleophilic 1,2-addition of organocerium reagents to the hydrazone CN double bond. The resulting hydrazines were converted into the title compounds with excellent diastereomeric and enantiomeric excesses (*de* and *ee* values ≥ 96%) by reductive N,N bond cleavage to remove the chiral auxiliaries and protection of the amino functions. The relative and absolute configurations were determined by NOE experiments and X-ray structure analysis.

Introduction

Chiral 1,2-sulfanyl amines (β-amino sulfides, *vic*-thioether amines) and 1,2-amino thiols of high diastereomeric and enantiomeric purity are of great interest in synthetic organic chemistry. In recent years they have gained particular attention as N,S-ligands in asymmetric catalysis. N,N- and N,O-ligands have already been employed in numerous instances in catalytic asymmetric synthesis and have been used with great success.[1] *vic*-Sulfanyl amines offer additional possibilities over N,N- and N,O-ligands, since, for example, the sulfur atom becomes a stereocentre when coordinated to a metal.[2]

The lack of simple and flexible synthetic routes to suitable derivatives of the title compounds has been a major barrier in investigation of their use in asymmetric catalysis. Heterobidentate N,S-ligands have proved to be very effective in enantioselective palladium-catalysed allylic substitution reactions.[3] 1,2-Sulfanyl amines, 1,2-amino thiols, and their corresponding disulfides have also been shown to be particularly effective catalysts for the enantioselective addition of dialkylzinc reagents to prochiral carbonyl compounds.[4] Furthermore, they are also used in the enantioselective conjugate addition of organometallic reagents to α,β-unsaturated carbonyl compounds.[5]

Several methods for the synthesis of *vic*-sulfanyl amines have been described in the literature, but the choice of substituents is restricted. One possibility is to synthesise them from natural α-amino acids in an ex-chiral-pool synthesis.[6] Van Leeuwen et al., for example, synthesised two different ligands derived from cysteine and pseudo-ephedrine and used them in iridium(I)-catalysed asymmetric hydrogenation reactions.[7] Some diastereoselective syntheses[8] for this class of compounds have been reported, but to the best of our knowledge there is only one asymmetric synthesis.[9] One of the simplest routes is probably through treatment of thiols with aziridines in a regio- and stereoselective ring-opening reaction.[10] Kellogg et al., for example, have prepared these aziridines through a Mitsunobu reaction starting from ephedrine.[11] An alternative approach for the synthesis of *vic*-sulfanyl amines was developed by Ishibashi et al., who used a mixture of 2-oxazolidinone and thiols in the presence of alkoxides to afford the desired products.[12]

The 1,2-sulfanyl amine unit has also been found in a number of important biologically active compounds. It is a characteristic structural feature found in ecteinascidine family marine alkaloids that serve as an important class of anticancer agents.[13]

Our synthetic strategy, which employs the SAMP/RAMP-hydrazone methodology,[14] should provide an efficient and flexible route to the desired 1,2-sulfanyl amines and permit access to both *anti*-configured enantiomers. The concept of α-alkylation and 1,2-addition to SAMP/RAMP-hydrazones and subsequent N,N bond cleavage has already been demonstrated by our group in various applications.[15] We now wish to report an important extension of our previous procedure on the asymmetric synthesis of *anti*-1,2-*tert*-butylsulfanyl amines, as reported in our short com-

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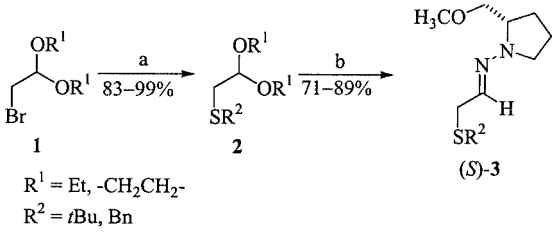
munication,[16] to *anti*-1,2-benzylsulfanyl amines and to describe this new technique in detail.

Results and Discussion

As shown in Scheme 1, acetaldehyde SAMP hydrazones (*S*)-**3** were obtained by a literature procedure[17] on a multigram scale from commercially available 2-(bromomethyl)-1,3-dioxolane (**1a**) or bromoacetaldehyde diethyl acetal (**1b**), which were treated with two different lithium thiolates. Nucleophilic displacement of bromide gave the acetals **2** in very good yields (83−99%, Table 1). Acidic hydrolysis of the acetal group afforded the α-sulfanylated acetaldehydes, which were directly converted in high yields (71−89%) into their corresponding SAMP hydrazones (*S*)-**3** by the standard procedure[18](Table 2).



Scheme 1. a) 1. R^2SH, *n*BuLi, THF, 0 °C; 2. **1**, THF, reflux, 4 h; b) 1. 6 N HCl, Et_2O, reflux, 7 h; 2. SAMP, $MgSO_4$, CH_2Cl_2, room temp.

Table 1. Synthesis of acetals **2**

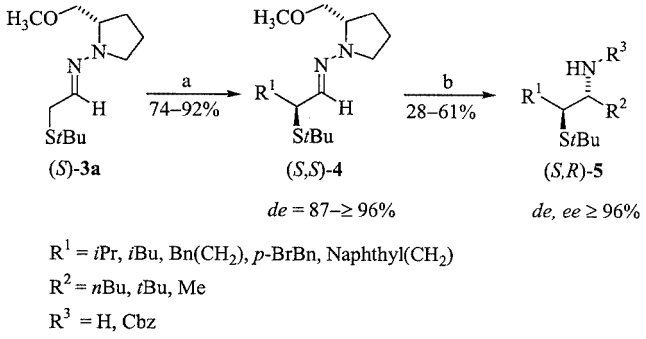
Product	R^1	R^2	Yield [%]
2a	$-CH_2CH_2-$	*t*Bu	83
2b	$-CH_2CH_2-$	Bn	96
2c	Et	Bn	99

Table 2. Synthesis of α-sulfanylated acetaldehyde-SAMP-hydrazones (*S*)-**3**

Starting material	Product	R^2	Yield [%]
2a	(*S*)-**3a**	*t*Bu	89
2b	(*S*)-**3b**	Bn	70
2c	(*S*)-**3b**	Bn	71

Synthesis of *anti*-1,2-*tert*-Butylsulfanyl Amines

As depicted in Scheme 2, the hydrazone (*S*)-**3a** was metallated with lithium diisopropylamide (LDA) in THF at 0 °C for 5 hours. For that purpose, the hydrazone was dissolved in THF and slowly added dropwise to the solution of LDA. The intermediate azaenolates were trapped with various alkyl halides at −100 °C to form the α-sulfanylated hydrazones (*S*,*S*)-**4**, which, after aqueous workup, were



Scheme 2. Synthesis of β-amino sulfides (*S*,*R*)-**5**: a) 1. LDA, THF, 0 °C, 5 h; 2. R^1X, −100 °C to room temp.; b) 1. $R^2Li/CeCl_3$, THF, −100 °C to room temp.; 2. BH_3·THF, THF, reflux, 4 h; (3. CbzCl, K_2CO_3, CH_2Cl_2/H_2O reflux)

purified by flash column chromatography to give the desired hydrazones in good yields (74−92%) and with high diastereomeric excesses (*de* = 87 to ≥ 96%). The results of the α-alkylation are summarised in Table 3. The configuration of the newly generated stereogenic centre has already been investigated[17,19] and was found to be in agreement with the proposed mechanism for the alkylation of metallated SAMP hydrazones.[14]

Table 3. Diastereoselective α-alkylation of hydrazone (*S*)-**3a** with various electrophiles

Product	R^1	Yield [%]	*de*[a] [%][a]
(*S*,*S*)-**4a**	*i*Pr	92	88
(*S*,*S*)-**4b**	*i*Bu	82	≥ 96
(*S*,*S*)-**4c**	$Bn(CH_2)$	85	87
(*S*,*S*)-**4d**	*p*-(BrBn)	74	87
(*S*,*S*)-**4e**	naphthyl(CH_2)	74	≥ 96

[a] Determined by ^1H and ^{13}C NMR spectroscopy.

For the subsequent nucleophilic 1,2-addition to the CN double bond, organocerium reagents were used. Initial attempts with the use of commercially available organolithium compounds turned out to present difficulties in obtaining the desired hydrazines. Because of their high basicity, elimination of the sulfur substituent was mainly observed. Thanks to the lower basicity and the higher nucleophilicity of Imamoto reagents, however, this problem could be circumvented simply and without any limitation in the choice of the electrophiles used in the previous step.[20] The cerium reagents were freshly prepared from the corresponding organolithium compound and dehydrated $CeCl_3$ in a lithium cerium transmetallation reaction. Because of the incomplete asymmetric induction in the α-alkylation step for (*S*,*S*)-**4a**, (*S*,*S*)-**4c**, and (*S*,*S*)-**4d**, the 1,2-addition products were expected to be mixtures of diastereomers. However, the NMR spectra of the crude hydrazines showed exclusively one set of signals (*de* ≥ 96%). Our conclusion was that the minor diastereomers did not react in the 1,2-addition step.

Many procedures to yield free amines from their corresponding hydrazines by cleavage of the N,N bond have been reported.[21] We decided to use the reductive cleavage with

Table 4. Synthesis of *anti*-1,2-*tert*-butylsulfanyl amines (*S*,*R*)-**5** by 1,2-addition, N,N bond cleavage and protection of the amino group

Product	R^1	R^2	R^3	Yield [%]	*de*[a] [%][a]	*ee*[b] [%]
(*S*,*R*)-**5a**	*i*Pr	Me	Cbz	28	≥ 96	≥ 96
(*S*,*R*)-**5b**	*i*Bu	*t*Bu	Cbz	61	≥ 96	≥ 96
(*S*,*R*)-**5c**	Bn(CH_2)	*t*Bu	Cbz	54	≥ 96	≥ 96
(*S*,*R*)-**5d**	*p*-(BrBn)	*n*Bu	H	41	≥ 96	≥ 96
(*S*,*R*)-**5e**	naphthyl(CH_2)	*n*Bu	H	32	≥ 96	≥ 96

[a] Determined by ^{1}H and ^{13}C NMR spectroscopy. [b] In correlation with the *de* value of the corresponding hydrazines determined by ^{1}H and ^{13}C NMR spectroscopy. The subsequent steps are racemisation-free

excess BH_3·THF complex as a very mild method not requiring activation of the N,N bond. The hydrazine was dissolved in THF and heated to reflux with a large excess of BH_3·THF complex, the corresponding amines being obtained after methanolysis. These were either purified by flash column chromatography to give (*S*,*R*)-**5d** or (*S*,*R*)-**5e**, or were directly protected as benzyl carbamates to yield (*S*,*R*)-**5a**–**c**. The results are summarised in Table 4.

The hydrazines were shown to be diastereomerically pure by ^{1}H and ^{13}C NMR spectroscopy. Because the reductive N,N bond cleavage and the protection of the amino group proceeded without epimerisation the synthesised β-amino sulfides (*S*,*R*)-**5** were not only diastereomerically but also enantiomerically pure within the limits of detection.

The relative configurations of the title compounds were determined to be *anti* by NOE measurements on (*S*,*R*)-**5a** (Figure 1). The known *S* configuration of the stereogenic centre generated by the α-alkylation[22] allowed the determination of the absolute configurations of the β-amino sulfides, which were assigned as (*S*,*R*).

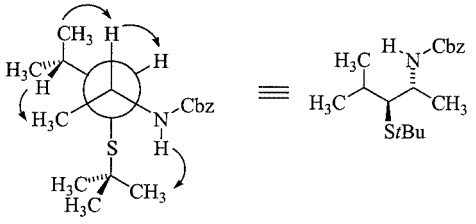
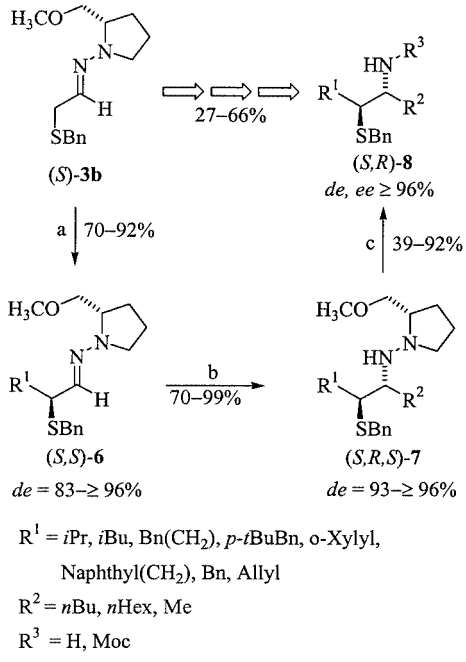


Figure 1. NOE measurements on (*S*,*R*)-**5a**

Synthesis of *anti*-1,2-Benzylsulfanyl Amines

The α-alkylation of the benzylsulfanyl hydrazones (*S*)-**3b** was initially carried out under the same conditions as used for the alkylation of the *tert*-butylsulfanyl hydrazones (*S*)-**3a**, but the desired products could not be obtained. Attempts to optimise the reaction conditions by variation of metallation time, temperature, and equivalents of LDA resulted either in the isolation of only small amounts of the desired products or in decomposition. It was assumed that a high concentration of base might not only produce the desired azaenolate but could also deprotonate the benzylic protons, finally resulting in the decomposition of the substrate, so a reversed addition of the LDA solution to the dissolved benzylsulfanyl hydrazone (*S*)-**3b** was carried out. This procedure allowed us to be sure that the concentration of the base was low at all times, so that it was possible to deprotonate only the α-position of the hydrazone moiety chemoselectively. The alkylated hydrazones (*S*,*S*)-**6** were obtained by this procedure in good yields (70–92%) and with very good diastereomeric excesses (*de* = 83 to ≥ 96%) (Scheme 3). The results of the α-alkylation are summarised in Table 5.



Scheme 3. Synthesis of 1,2-sulfanyl amines (*S*,*R*)-**8**: a) 1. LDA, THF, −20 °C, 2 h, 2. R^1X, −100 °C to room temp.; b) 1. R^2Li/$CeCl_3$, THF, −100 °C to room temp.; c) 1. BH_3·THF, THF, reflux, 4 h; 2. MocCl, K_2CO_3, CH_2Cl_2, reflux, 3 d

Table 5. Diastereoselective α-alkylation of hydrazone (*S*)-**3b** with various electrophiles to afford the α-thiolated hydrazones (*S*,*S*)-**6**

Product	R^1	Yield [%]	*de*[a] D [%][a]
(*S*,*S*)-**6a**	*i*Pr	92	83
(*S*,*S*)-**6b**	*i*Bu	70	≥ 96
(*S*,*S*)-**6c**	*o*-xylyl	73	94
(*S*,*S*)-**6d**	naphthyl(CH_2)	92	≥ 96
(*S*,*S*)-**6e**	Bn	90	≥ 96
(*S*,*S*)-**6f**	$BnCH_2$	81	≥ 96
(*S*,*S*)-**6g**	allyl	83	≥ 96
(*S*,*S*)-**6h**	*p*-(*t*BuBn)	74	≥ 96

[a] Determined by ^{1}H and ^{13}C NMR spectroscopy.

The nucleophilic 1,2-addition to the CN double bond was carried out under the same conditions as described above. Unlike the *tert*-butylsulfanyl hydrazines, which were used directly for the N–N bond cleavage, the benzylsul-

fanyl hydrazines (*S*,*R*,*S*)-**7** were isolated and fully characterised. The results of the 1,2-addition to the hydrazones (*S*,*S*)-**6** are summarised in Table 6.

Table 6. 1,2-Addition of organocerium reagents to the α-sulfanylated aldehyde SAMP-hydrazones (*S*,*S*)-**6** to afford the hydrazines (*S*,*R*,*S*)-**7**

Product	R^1	R^2	Yield [%]	*de*[a] [%][a]
(*S*,*R*,*S*)-**7a**	*i*Pr	*n*Bu	85	93
(*S*,*R*,*S*)-**7b**	*i*Bu	*n*Bu	98	≥ 96
(*S*,*R*,*S*)-**7c**	*o*-xylyl	*n*Bu	99	≥ 96
(*S*,*R*,*S*)-**7d**	naphthyl(CH_2)	*n*Bu	81	≥ 96
(*S*,*R*,*S*)-**7e**	Bn	*n*Bu	80	≥ 96
(*S*,*R*,*S*)-**7f**	Bn(CH_2)	*n*Bu	87	≥ 96
(*S*,*R*,*S*)-**7g**	Bn	*n*Hex	79	≥ 96
(*S*,*R*,*S*)-**7h**	Bn	Me	65	≥ 96
(*S*,*R*,*S*)-**7i**	*p*-(*t*BuBn)	*n*Bu	70	≥ 96

[a] Determined by ^{1}H and ^{13}C NMR spectroscopy.

The corresponding amines were obtained by reductive cleavage of the N,N bond with an excess of BH_3·THF. It was observed that the use of 1 N HCl instead of methanol, combined with washing with saturated aqueous $NaHCO_3$ solutions, gave significant improvements in the yields. The crude amines obtained were either purified by flash column chromatography or protected directly. The results of the reductive cleavage and the protection are summarised in Table 7.

Table 7. Synthesis of the 1,2-benzylsulfanyl amines (*S*,*R*)-**8** by reductive cleavage of the N,N bond and protection of the amino group

Product	R^1	R^2	R^3	Yield [%]	*de*[a]	[%][a]	*ee*[b] [%]
(*S*,*R*)-**8a**	*i*Pr	*n*Bu	H	80	≥ 96		≥ 96
(*S*,*R*)-**8b**	*i*Bu	*n*Bu	H	39	≥ 96		≥ 96
(*S*,*R*)-**8c**	*o*-xylyl	*n*Bu	H	81	≥ 96		≥ 96
(*S*,*R*)-**8d**	naphthyl(CH_2)	*n*Bu	Moc	55	≥ 96		≥ 96
(*S*,*R*)-**8e**	Bn	*n*Bu	Moc	92	≥ 96		≥ 96
(*S*,*R*)-**8f**	Bn(CH_2)	*n*Bu	Moc	68	≥ 96		≥ 96
(*S*,*R*)-**8g**	Bn	*n*Hex	Moc	57	≥ 96		≥ 96
(*S*,*R*)-**8h**	Bn	Me	Moc	71	≥ 96		≥ 96

[a] Determined by ^{1}H and ^{13}C NMR spectroscopy. [b] In correlation with the *de* value of the corresponding hydrazines (*S*,*R*,*S*)-**7** determined by ^{1}H and ^{13}C NMR spectroscopy. The subsequent steps are racemisation-free.

The relative and absolute configurations of the 1,2-benzylsulfanyl amine (*S*,*R*)-**8e** were determined by X-ray crystallography as depicted in Figure 2.

The obtained relative and absolute configurations of the *anti*-1,2-sulfanyl amines (*S*,*R*)-**5** and (*S*,*R*)-**8** are in full agreement with our previous results on nucleophilic 1,2-additions of organolithium, Grignard and organocerium reagents to aldehyde-SAMP-hydrazones.[23] To explain the fact that at least two equivalents of the nucleophile are necessary in order for 1,2-addition to be observed, we assume a precoordination of the first equivalent of the organocerium reagent. As shown in Figure 3, the hydrazone substrates can act as bidentate (pyrrolidino nitrogen and

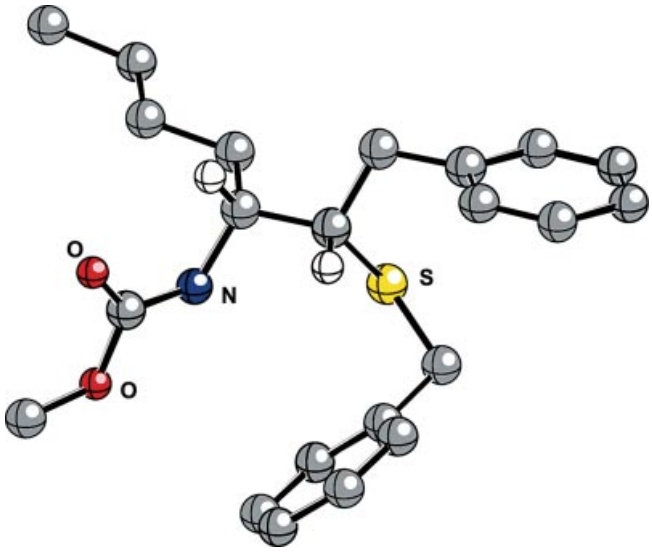


Figure 2. Crystal structure of the 1,2-benzylsulfanyl amine (*S*,*R*)-**8e**

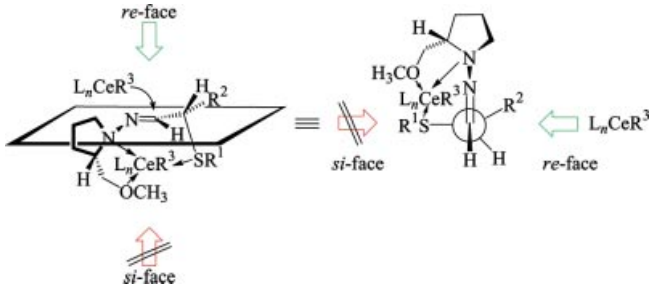


Figure 3. Proposed transition state for the asymmetric 1,2-addition

methoxy group) and even tridentate (plus thioether group) ligands, resulting in the steric hindrance of the *si*-face. The second organocerium equivalent would then attack the *re*-face of the CN double bond. The observed relative topicity is also in agreement with the Felkin−Anh model.

Conclusion

In summary, we have developed an efficient method for the α-alkylation of α-sulfanylated acetaldehyde SAMP-hydrazones and subsequent nucleophilic 1,2 addition to the CN double bond to afford α-sulfanylated hydrazines, which were easily converted into the title N-protected *anti*-1,2-sulfanyl amines with high diastereomeric and enantiomeric excesses (*de* and *ee* ≥ 96%). Deprotection of the 1,2-benzylsulfanyl amines to afford their corresponding 1,2-amino thiols should open a facile route to novel N,S-ligands for asymmetric catalysis and to useful precursors of oligopeptidosulfonamides.[24]

Experimental Section

General Remarks: All reagents were purchased from common commercial suppliers and used from freshly opened containers. Solvents for chromatography and for workup were dried and purified by

conventional methods prior to use. Tetrahydrofuran was freshly distilled from sodium/lead and benzophenone under argon. *n*BuLi (1.6 N in hexane) was purchased from Merck, Darmstadt. Diisopropylamine was distilled from CaH_2 and stored over molecular sieves. Preparative flash column chromatography was carried out with Merck silica gel 60, particle size 0.040−0.063 mm. Optical rotation values were measured with a Perkin−Elmer P 241 polarimeter, solvents used were of Merck UVASOL quality. IR spectra: Perkin−Elmer FT/IR 1750 and Perkin−Elmer FT/IR 1720 X. NMR spectra: Varian VXR 300, Varian Gemini 300 and Varian Inova 400, TMS as internal standard. MS: Varian MAT 212 (EI, 70 eV, 1 mA) and Finnigan MAT SSQ 7000 (CI, 100 eV). Microanalyses were obtained with a Heraeus, CHN-O-Rapid instrument. High-resolution MS: Finningan MAT, MAT 95. Merck TLC plates silica gel 60 F_{254} were used for TLC analyses and the products were viewed by UV detection or by use of phosphormolybdic acid (5 wt.-% in EtOH). The diastereomeric excesses were determined by NMR spectroscopy. The chiral auxiliary SAMP [(*S*)-1-amino-2-(methoxymethyl)pyrrolidine] was prepared from (*S*)-proline by literature procedures.[25]

General Procedure for the Synthesis of the Acetals 2 (GP 1): The thiol (1.0 equiv.) was dissolved in dry THF (1 mL/mmol) under argon atmosphere and cooled to 0 °C. *n*BuLi (1.0 equiv.) was slowly added dropwise, and the solution was stirred at this temperature for 1 h. The reaction mixture was allowed to warm up to room temperature, and acetal **1** (1.1−1.2 equiv.) was then slowly added. The solution was heated at reflux for 4 h and after cooling to room temperature it was quenched with pH 7 buffer solution and extracted three times with Et_2O. The combined organic phases were dried with $MgSO_4$ and concentrated in vacuo. The crude product was distilled under reduced pressure.

2-(*tert*-Butylsulfanylmethyl)-1,3-dioxolane (2a): *tert*-Butyl thioalcohol (5.6 mL, 50.0 mmol) was treated with 2-(bromomethyl)-1,3-dioxane (**1a**, 6.2 mL, 60.0 mmol) as described in GP 1, and **2a** was obtained as a colourless oil after reduced pressure distillation. Yield: 7.30 g (83%). R_t = 6. 37 min (OV-17, 60−10−260). R_f = 0.42 (pentane/Et_2O, 10:1). b.p. 81 °C (7 mbar). IR (film): $\tilde{\nu}$ = 3521 (w), 2962 (s), 2928 (s), 2888 (s), 2746 (w), 2649 (w), 2603 (w), 2384 (w), 2177 (w), 1999 (w), 1473 (m), 1469 (s), 1424 (m), 1390 (m), 1365 (s), 1212 (m), 1133 (s), 1040 (s), 971 (s), 945 (s), 617 (m), 772 (w), 709 (w), 657 (w), 592 (w), 469 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.34 [s, 9 H, $C(CH_3)_3$], 2.78 (d, *J* = 4.7 Hz, 2 H, SCH_2), 3.90 (m, 2 H, OCH_2), 4.02 (m, 2 H, OCH_2), 5.04 (t, *J* = 4.7 Hz, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.9 (CH_3), 32.3 (SCH_2), 42.1 [$C(CH_3)_3$], 65.2 (OCH_2CH_2O), 103.6 (CH) ppm. MS (EI, 70 eV): *m*/*z* (%) = 176 (12) [M^+], 73 (100), 57 (9). $C_8H_{16}O_2S$ (176.09): calcd. C 54.51, H 9.15; found C 54.01, H 9.17.

2-(Benzylsulfanylmethyl)-1,3-dioxolane (2b): Benzyl thioalcohol (7.7 mL, 65.0 mmol) was treated with 2-(bromomethyl)-1,3-dioxane (**1a**, 8.0 mL, 78.0 mmol) as described in GP 1, and **2b** was obtained as a colourless oil after reduced pressure distillation. Yield: 13.15 g (96%). R_t = 11.58 min (CP-Sil-8, 80−10−300). R_f = 0.31 (pentane/Et_2O, 10:1). b.p. 125 °C (1 mbar). IR (film): $\tilde{\nu}$ = 3390 (w), 3084 (m), 3061 (m), 3028 (m), 2958 (m), 2919 (m), 2885 (s), 2747 (w), 2701 (w), 1602 (w), 1494 (m), 1474 (m), 1454 (s), 1407 (m), 1387 (m), 1322 (w), 1231 (m), 1133 (s), 1072 (m), 1038 (s), 978 (s), 945 (s), 918 (m), 875 (w), 806 (w), 752 (m), 703 (s), 565 (m), 472 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.61 (d, *J* = 4.4 Hz, 2 H, SCH_2), 3.82 (s, 2 H, CH_2Ph), 3.88 (m, 2 H, OCH_2), 4.00 (m, 2 H, OCH_2), 5.04 (t, *J* = 4.4 Hz, 1 H, CH), 7.24 (m, 1 H, $CH_{arom.}$), 7.32 (m, 4 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.1 (SCH_2), 36.6 (CH_3), 65.2 (OCH_2CH_2O), 104.4 (CH), 127.0, 128.5, 129.1 (Ar-*C*), 138.2 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 210 (6) [M^+], 148 (16), 91 (26), 73 (100), 45 (23). $C_{11}H_{14}O_2S$ (210.29): calcd. C 62.83, H 6.71; found C 62.41, H 6.80.

[(2,2-Diethoxyethyl)sulfanylmethyl]benzene (2c): Benzylthiol (6.2 mL, 50.0 mmol) was treated with bromoacetaldehyde diethyl acetal (**1b**, 7.7 mL, 51.0 mmol) as described in GP 1 to yield **2c** as a colourless oil after reduced pressure distillation (113 °C, 3 mbar). Yield: 11.90 g (99%). R_t = 9.63 min (CP-Sil-8, 100−10−300). The spectroscopic data were in accordance with those reported in the literature.[17]

General Procedure for the Synthesis of the α-Sulfonylated Acetaldehyde SAMP-Hydrazones (GP 2): HCl (6 N, 3.0 mL/mmol) was added to a solution of acetal **2** in Et_2O (7.0 mL/mmol). The mixture was heated at reflux for 7 h. After the mixture had cooled to room temperature, a pH 7 buffer solution was added and the aqueous layer was extracted three times with Et_2O. The combined organic phases were washed with brine, dried with $MgSO_4$ and concentrated in vacuo. The crude 2-sulfanylated acetaldehyde was dissolved in CH_2Cl_2 and treated with (*S*)-1-amino-2-(methoxymethyl)pyrrolidine (SAMP) in the presence of $MgSO_4$ to afford the corresponding crude SAMP hydrazones (*S*)-**3**, which were purified by flash column chromatography.

(2*S*)-(−)-[2-(*tert*-Butylsulfanyl)ethylidene][2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*)-3a]: Dioxolane **2a** (3.0 g, 17.1 mmol) and SAMP (2.34 g, 18.0 mmol) were converted as described in GP 2 into the SAMP hydrazone (*S*)-**3a**, which could be obtained as a colourless oil after flash column chromatography (SiO_2, pentane/Et_2O, 15:1, 1% NEt_3). Yield: 3.72 g (89%). R_t = 8.52 min (OV-17, 100−10−260). R_f = 0.55 (pentane/Et_2O, 3:1). $[\alpha]_D^{25}$ = −278.9 (*c* = 1.13, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.34 [s, 9 H, $C(CH_3)_3$], 1.80 (m, 1 H, NCH_2CH_2CH), 1.93 (m, 3 H, NCH_2CH_2, NCH_2CH_2CH), 2.79 (m, 1 H, NCH), 3.36 (m, 2 H, CHO, NCH), 3.37 (s, 3 H, OCH_3), 3.46 (m, 1 H, OCH_2CH), 3.54 (dd, *J* = 8.5, 3.6 Hz 1 H, CHHO), 6.51 (t, *J* = 6.0 Hz, 1 H, N=CH), ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2 (NCH_2CH_2), 26.7 ($NCH_2CH_2CH_2$), 31.5 (CH_3), 31.9 (SCH_2), 42.8 [$C(CH_3)$], 49.8 (NCH_2), 59.2 (OCH_3), 63.1 (NCH), 74.7 (CH_2OCH_3), 133.2 (C=N) ppm. The spectroscopic data were in accordance with those reported in the literature.[26]

(2*S*)-(−)-[2-(Benzylsulfanyl)ethylidene][2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*)-3b]: Acetal **2c** (4.80 g, 20.0 mmol) and SAMP (2.60 g, 20.0 mmol) were converted as described in GP 2 into the SAMP hydrazone (*S*)-**3b**, which could be obtained as a colourless oil after flash column chromatography (SiO_2, pentane/Et_2O, 6:1, 1% NEt_3). Yield: 3.95 g (71%). R_t = 16.85 min (CP-Sil-8, 80−10−300). R_f = 0.11 (pentane/Et_2O, 6:1). $[\alpha]_D^{25}$ = −158.1 (*c* = 1.8, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3393 (w), 3083 (w), 3060 (m), 3027 (m), 2974 (s), 2919 (s), 2877 (s), 2825 (s), 1590 (m), 1494 (s), 1453 (s), 1414 (m), 1382 (m), 1342 (s), 1323 (m), 1304 (m), 1284 (m), 1197 (s), 1120 (s), 1073 (s), 1029 (m), 1002 (m), 973 (m), 923 (m), 907 (m), 865 (m), 771 (m), 701 (s), 565 (m), 474 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.73−2.02 (m, 4 H, $NCH_2CH_2CH_2$), 2.74 (m, 1 H, NCHH), 3.21 (d, *J* = 6.0 Hz, 2 H, CH_2C=N), 3.28−3.63 (m, 4 H, $NCHCH_2OCH_3$, NCHH), 3.38 (s, 3 H, OCH_3), 3.68 (s, 2 H, SCH_2Ph), 6.44 (t, *J* = 6.0 Hz, 1 H, N=CH), 7.18−7.36 (m, 5 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.1 (NCH_2CH_2), 26.6 ($NCH_2CH_2CH_2$), 33.6 (SCH_2), 34.9 ($ArCH_2$), 49.6 (NCH_2), 59.2 (OCH_3), 63.2 (NCH), 74.5 CH_2OCH_3), 126.6, 128.2, 128.9 (Ar-*C*), 131.9 (C=N), 138.5 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 278 (15) [M^+], 235 (6), 234 (17), 233 (100), 187

(16), 156 (12), 155 (28), 109 (8), 91 (62), 82 (6), 71 (12), 70 (7), 68 (5), 55 (10), 45 (17). $C_{15}H_{22}N_2OS$ (278.41): calcd. C 64.71, H 7.97, N 10.06; found C 64.57, H 8.19, N 10.16.

General Procedure for the α-Alkylation of α-Sulfanylated Acetaldehyde-SAMP-Hydrazone (*S*)-3a (GP 3): Compound (*S*)-**3a** (1 equiv.) was added dropwise at 0 °C to a solution of LDA (1.05 equiv.), freshly prepared from *n*BuLi and diisopropylamine, in dry THF (2.0 mL/mmol). After the mixture had been stirred at this temperature for 5 h, alkyl halide (1.1 equiv.) was added at −100 °C. This solution was allowed to warm up to room temperature over 15 h. The reaction mixture was quenched with brine and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed in a rotary evaporator and the crude product was purified by flash column chromatography (SiO_2, pentane/Et_2O, 15:1, 1% NEt_3).

(2*S*,2*S*)-(+)-[2-(*tert*-Butylsulfanyl)-3-methylbutylidene][2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*S*)-4a]: Hydrazone (*S*)-**3a** (1.43 g, 5.9 mmol) was alkylated with 2-iodopropane (0.9 mL, 6.5 mmol) as described in GP 3. Compound (*S*,*S*)-**4a** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 15:1, 1% NEt_3). Yield: 1.55 g (92%); *de* = 88%. R_t = 7.04 min (OV-17, 120−10−260). R_f = 0.35 (pentane/Et_2O, 5:1). $[\alpha]_D^{25}$ = +105.0 (*c* = 1.0, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2959 (s), 2925 (s), 2873 (s), 2825 (m), 1592 (m), 1460 (s), 1384 (m), 1365 (s), 1341 (m), 1303 (m), 1282 (w), 1249 (w), 1197 (m), 1162 (s), 1122 (s), 1074 (m), 1026 (w), 997 (w), 973 (m), 927 (w), 893 (m) cm^{-1}. ^1H NMR (400 MHz, C_6D_6), (*Z* isomer): δ = 1.02 (d, *J* = 6.7 Hz, 3 H, SCHCH_3), 1.13 (d, *J* = 6.7 Hz, 3 H, SCHCH_3), 1.32 [s, 6 H, C(CH_3)$_3$], 1.55−1.75 (m, 3 H, NCHCH*H*, NCH$_2$CH_2), 1.91 (m, 1 H, NCHC*H*H), 2.19 [m, 1 H, (CH$_3$)$_2$C*H*], 2.89 (m, 1 H, NCH*H*), 3.14 (s, 3 H, OCH_3), 3.16 (m, 1 H, NC*H*H), 3.25 (dd, *J* = 8.8, 6.6 Hz, CHH_2), 3.44 (m, 1 H, NC*H*), 3.50 (dd, *J* = 8.8, 4.9 Hz, 1 H, C*H*HO), 4.19 (dd, *J* = 8.2, 4.1 Hz, 1 H, SC*H*), 7.26 (d, *J* = 8.2 Hz, 1 H, N=C*H*) ppm. ^{13}C NMR (100 MHz, C_6D_6), (*Z* isomer): δ = 19.0, 20.4 [CH(*C*H$_3$)$_2$], 23.2 (NCH$_2$*C*H$_2$), 27.2 (NCH$_2$CH$_2$*C*H$_2$), 31.1 [*C*H(CH$_3$)$_2$], 31.7 [C(*C*H$_3$)$_3$], 42.9 [*C*(CH$_3$)$_3$], 47.1 (S*C*H), 55.1 (N*C*H$_2$), 58.7 (O*C*H$_3$), 67.7 (N*C*H), 75.6 (*C*H$_2$OCH$_3$), 159.0 (*C*=N) ppm. MS (EI, 70 eV): *m*/*z* (%) = 286 (5) [M^+], 241 (9), 198 (13), 197 (100), 185 (7), 116 (11), 114 (13), 82 (6), 70 (18), 57 (10). $C_{15}H_{30}N_2OS$ (286.48): calcd. C 62.89, H 10.56, N 9.78; found C 62.59, H 10.64, N 10.16.

(2*S*,2*S*)-(−)-[2-(*tert*-Butylsulfanyl)-4-methylpentylidene][2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*S*)-4b)]: Hydrazone (*S*)-**3a** (1.43 g, 5.9 mmol) was alkylated with *sec*-butyl iodide (0.8 mL, 6.5 mmol) as described in GP 3. Compound (*S*,*S*)-**4b** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 15:1, 1% NEt_3). Yield: 1.43 g (81%); *de* ≥ 96%. R_t = 7.55 min (OV-17, 120−10−260). R_f = 0.50 (pentane/Et_2O, 5:1). $[\alpha]_D^{25}$ = −146.7 (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3373 (w), 3190 (w), 2956 (s), 2925 (s), 2898 (s), 2870 (s), 2826 (s), 2718 (w), 1722 (w), 1595 (m), 1460 (s), 1384 (m), 1364 (s), 1341 (m), 1303 (m), 1282 (m), 1197 (s), 1163 (s), 1122 (s), 1072 (m), 1024 (m), 1003 (m), 973 (m), 899 (m), 856 (m), 758 (m), 651 (w), 596 (w) cm^{-1}. ^1H NMR (400 MHz, C_6D_6), (*E* isomer): δ = 0.92 (d, *J* = 6.6 Hz, 6 H, CH(CH_3)$_2$] 1.42 [s, 9 H, SC(CH_3)$_3$], 1.50 (m, 1 H, NCH$_2$CH*H*), 1.58−1.77 (m, 5 H, NCH$_2$C*H*H, NCH$_2$CH$_2$CH_2, SCHCH_2), 1.92 [m, 1 H, C*H*(CH$_3$)$_3$], 2.52 (m, 1 H, NCH*H*), 3.08 (m, 1 H, NC*H*H), 3.16 (s, 3 H, OCH_3), 3.39 (dd, *J* = 7.4, 9.1 Hz, 1 H, CH*H*O), 3.53 (m, 1 H, OCH$_2$C*H*), 3.66 (dd, *J* = 3.6, 9.1 Hz, 1 H, C*H*HO), 3.91 (dt, *J* = 8.0, 15.8 Hz, 1 H, SC*H*), 6.35 (d, *J* = 8.0 Hz, 1 H, N=C*H*) ppm. ^{13}C NMR (100 MHz, C_6D_6), (*E* isomer): δ = 22.2 (NCH$_2$*C*H$_2$), 22.3, 22.9 [CH(*C*H$_3$)$_2$], 25.8 [*C*H(CH$_3$)$_2$], 27.1 (NCH$_2$CH$_2$*C*H$_2$), 32.0 [C(*C*H$_3$)$_3$], 43.4 [*C*(CH$_3$)$_3$], 43.6 (CH*C*H$_2$), 44.7 (S*C*H), 49.4 (N*C*H$_2$), 58.8 (O*C*H$_3$), 63.4 (N*C*H), 75.5 (*C*H$_2$OCH$_3$), 139.1 (*C*=N) ppm. MS (EI, 70 eV): *m*/*z* (%) = 300 (3) [M^+], 255 (7), 212 (15), 211 (100), 199 (6), 114 (9), 112 (6), 71 (7), 70 (11), 57 (10), 55 (6), 45 (7). $C_{16}H_{32}N_2OS$ (300.50): calcd. C 63.95, H 10.73, N 9.32; found C 63.94, H 10.65, N 9.55.

(2*S*,2*S*)-(+)-[2-(*tert*-Butylsulfanyl)-4-phenylbutylidene][2-(methoxymethyl)pyrrolidin-1-yl]amine (*S*,*S*)-4c: Hydrazone (*S*)-**3a** (1.22 g, 5.0 mmol) was alkylated with (2-iodoethyl)benzene (0.9 mL, 6.5 mmol) as described in GP 3. Compound (*S*,*S*)-**4c** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 15:1, 1% NEt_3). Yield: 1.51 g (85%); *de* = 87%. R_t = 11.33, 11.49 min (OV-17, 140−10−260). R_f = 0.30 (pentane/Et_2O, 5:1). $[\alpha]_D^{25}$ = +44.0 (*c* = 1.2, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3083 (m), 3062 (m), 3026 (s), 2958 (s), 2923 (s), 2896 (s), 2825 (s), 2742 (w), 1944 (w), 1872 (w), 1804 (w), 1719 (w), 1602 (m), 1496 (m), 1473 (m), 1456 (s), 1389 (m), 1364 (s), 1342 (m), 1324 (m), 1302 (m), 1282 (m), 1197 (s), 1162 (s),1122 (s), 1076 (m), 1030 (m), 1002 (m), 973 (m), 934 (m), 903 (m), 882 (m), 843 (w), 813 (w), 749 (m), 700 (s), 671 (w), 597 (w), 554 (w), 504 (w) cm^{-1}. ^1H NMR (400 MHz, C_6D_6), (*Z* isomer): δ = 1.28 [s, 9 H, C(CH_3)$_3$], 1.60 (m, 1 H, NCHCH*H*), 1.75 (m, 2 H, NCH$_2$CH_2), 1.87 (m, 2 H, SCHCH*H*, NCHC*H*H), 2.04 (m, 1 H, SCHCH*H*), 2.69 (m, 1 H, NCH*H*), 2.82 (m, 2 H, PhCH_2), 2.94 (m, 1 H, NCH*H*), 3.16 (s, 3 H, OCH_3), 3.25 (m, 1 H, C*H*HO), 3.40 (m, 1 H, OCH$_2$C*H*), 3.47 (m, 1 H, CH*H*O), 4.09 (m, 1 H, SC*H*), 6.36 (m, 1 H, N=C*H*), 7.06−7.22 (m, 5 H, C$H_{arom.}$) ppm. ^{13}C NMR (100 MHz, C_6D_6), (*Z* isomer): δ = 23.1 (NCH$_2$*C*H$_2$), 27.1 (NCH$_2$CH$_2$*C*H$_2$), 31.7 [C(*C*H$_3$)$_3$], 32.4 (Ar*C*H$_2$), 33.7 (ArCH$_2$*C*H$_2$), 40.5 (S*C*H), 43.5 [*C*(CH$_3$)$_3$], 49.2 (N*C*H$_2$), 58.7 (O*C*H$_3$), 67.3 (N*C*H), 75.3 (*C*H$_2$OCH$_3$), 126.0, 128.3, 128.8 (Ar-*C*), 141.5 (Ar-C_q), 158.5 (*C*=N) ppm. MS (EI, 70 eV): *m*/*z* (%) = 348 (3) [M^+], 303 (12), 260 (15), 259 (100), 161 (5), 144 (5), 129 (12), 123 (10), 117 (19), 114 (12), 112 (6), 91 (15), 82 (7), 71 (7), 70 (15), 57 (15), 55 (6), 45 (9). $C_{20}H_{32}N_2OS$ (348.55): calcd. C 68.92, H 9.25, N 8.04; found C 68.76, H 9.62, N 8.47.

(2*S*,2*S*)-(−)-[3-(4-Bromophenyl)-2-(*tert*-butylsulfanyl)propylidene][2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*S*)-4d]: Hydrazone (*S*)-**3a** (1.22 g, 5.0 mmol) was alkylated with 4-bromobenzyl bromide (1.38 g, 5.5 mmol) as described in GP 3. Compound (*S*,*S*)-**4d** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 15:1, 1% NEt_3). Yield: 1.62 g (74%); *de* = 87%. R_t = 16.24 min (CP-Sil-8, 120−10−300). R_f = 0.54 (pentane/Et_2O, 5:1). $[\alpha]_D^{25}$ = −62.1 (*c* = 0.9, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2960 (s), 2923 (s), 2894 (s), 2826 (s), 1592 (m), 1488 (s), 1473 (s), 1459 (s), 1403 (m), 1390 (m), 1364 (s), 1342 (m), 1324 (m), 1303 (m), 1283 (m), 1197 (s), 1161 (s), 1122 (s), 1073 (s), 1012 (s), 972 (m), 929 (m), 902 (m), 872 (m), 839 (m), 801 (s), 757 (s), 713 (w), 666 (w), 641 (w), 592 (w), 525 (m) cm^{-1}. ^1H NMR (400 MHz, C_6D_6), (*E* isomer): δ = 1.30 [s, 9 H, SC(CH_3)$_3$], 1.44 (m, 1 H, NCH$_2$CH$_2$CH*H*), 1.67 (m, 3 H, NCH$_2$CH_2, NCH$_2$CH$_2$C*H*H), 2.44 (m, 1 H, NCH*H*), 2.82 (dd, *J* = 7.2, 13.8 Hz, 1 H, ArCH*H*), 2.92 (dd, *J* = 7.7, 13.8 Hz, 1 H, ArC*H*H), 3.00 (m, 1 H, NC*H*H), 3.13 (s, 3 H, OCH_3), 3.35 (dd, *J* = 6.9, 9.1 Hz, 1 H, CH*H*O), 3.43 (m, 1 H, C*H*CH$_2$O), 3.57 (dd, *J* = 3.6, 9.1 Hz, 1 H, C*H*HO), 3.86 (dt, *J* = 7.4, 14.8 Hz, 1 H, SC*H*), 6.32 (d, *J* = 7.4 Hz, 1 H, N=C*H*), 6.83 (m, 2 H, C$H_{arom.}$), 7.22 (m, 2 H, C$H_{arom.}$) ppm. ^{13}C NMR (100 MHz, C_6D_6), (*E* isomer): δ = 22.3 (NCH$_2$*C*H$_2$), 27.1 (NCH$_2$CH$_2$*C*H$_2$), 31.7 [C(*C*H$_3$)$_3$], 40.4 (Ar*C*H$_2$), 43.7 [*C*(CH$_3$)$_3$], 47.5 (S*C*H), 49.3 (N*C*H$_2$), 58.8 (O*C*H$_3$), 63.2 (N*C*H), 75.4 (*C*H$_2$OCH$_3$), 120.3 (Ar-C_q), 131.2, 131.6 (Ar-*C*),

137.0 (*C*=N), 138.2 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 413 (6) [M^+], 412 (7), 369 (24), 367 (24), 326 (16), 325 (98), 324 (21), 323 (100), 313 (9), 279 (14), 277 (16), 244 (24), 243 (43), 199 (35), 187 (32), 169 (5), 155 (31), 143 (27), 141 (13), 131 (6), 130 (8), 129 (6), 115 (6), 114 (19), 112 (13), 109 (17), 102 (6), 82 (14), 71 (27), 70 (42), 69 (6), 68 (12), 57 (55), 56 (8), 55 (15), 45 (40). $C_{19}H_{29}BrN_2OS$ (413.42): calcd. C 55.20, H 7.07, N 6.78; found C 54.98, H 7.18, N 6.94.

(2*S*,2*S*)-(−)-[2-(*tert*-Butylsulfanyl)-3-(naphthalen-2-yl)propylidene]-[2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*S*)-4e]: Hydrazone (*S*)-**3a** (1.22 g, 5.0 mmol) was alkylated with 2-(bromomethyl)naphthalene (1.22 g, 5.5 mmol) as described in GP 3. Compound (*S*,*S*)-**4e** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 15:1, 1% NEt_3). Yield: 1.42 g (74%); *de* ≥ 96%. R_t = 14.05, 14.21 min (CP-Sil-8, 160−10−300). R_f = 0.29 (pentane/Et_2O, 5:1). $[\alpha]_D^{25}$ = −44.2 (*c* = 1.3, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3578 (w), 3052 (m), 2960 (vs), 2923 (s), 2893 (s), 2873 (s), 2827 (s), 2727 (w), 1914 (w), 1719 (m), 1631 (m), 1600 (m), 1509 (m), 1471 (m), 1459 (s), 1388 (m), 1364 (s), 1342 (m), 1303 (m), 1271 (m), 1197 (s), 1161 (w), 1123 (s), 1019 (m), 969 (m), 899 (m), 854 (m), 818 (s), 785 (m), 747 (s), 639 (w), 622 (w), 594 (w), 547 (w), 477 (m) cm^{-1}. ^1H NMR (400 MHz, C_6D_6), (*Z* isomer): δ = 1.33 [s, 9 H, C(C*H*$_3$)$_3$] 1.40 (m, 1 H, NCH$_2$CH$_2$CH*H*), 1.62 (m, 3 H, NCH$_2$C*H*$_2$, NCH$_2$CH$_2$C*H*H), 2.46 (m, 1 H, NCH*H*), 3.02 (m, 1 H, NC*H*H), 3.12 (s, 3 H, OC*H*$_3$), 3.16−3.39 (m, 4 H, CH*H*O, OCH$_2$C*H*, SCHC*H*$_2$), 3.57 (m, 1 H, C*H*HO), 4.12 (m, 1 H, SC*H*), 6.45 (d, *J* = 7.7 Hz, 1 H, N=C*H*) 7.16−7.69 (m, 7 H, C*H*$_{arom.}$) ppm. ^{13}C NMR (100 MHz, C_6D_6), (*Z* isomer): δ = 22.2 (NCH$_2$*C*H$_2$), 27.0 (NCH$_2$CH$_2$*C*H$_2$), 31.7 [C(*C*H$_3$)$_3$], 40.4 (Ar*C*H$_2$), 43.7 [*C*(CH$_3$)$_3$], 47.7 (S*C*H), 49.3 (N*C*H$_2$), 55.3 (O*C*H$_3$), 63.2 (N*C*H), 75.3 (*C*H$_2$OCH$_3$), 128.3, 128.3, 127.7, 127.7, 125.8, 125.3 (Ar-*C*), 136.7, 133.8, 132.6 (Ar-C_q), 137.7 (*C*=N) ppm. MS (EI, 70 eV): *m*/*z* (%) = 384 (5) [M^+], 339 (16), 396 (21), 295 (100), 244 (6), 243 (37), 187 (22), 182 (10), 180 (14), 154 (5), 153 (7), 141 (16), 115 (5), 114 (8), 70 (11), 57 (11), 45 (8). $C_{23}H_{32}N_2OS$ (384.224): calcd. C 71.83, H 8.39, N 7.28; found C 71.79, H 8.70, N 7.60.

General Procedure for 1,2-Addition, N,N Cleavage and the Protection of the Amino Groups of *tert*-Butylsulfanyl Hydrazones (*S*,*S*)-4 (GP 4): $CeCl_3 \cdot 7H_2O$ (3.0 equiv.) was dehydrated for 2 h at 130 °C in vacuo (0.1 Torr) and then suspended in dry THF (3.0 mL/mmol) with sonification. The suspension was stirred overnight at room temperature. After the mixture had been cooled to −78 °C, organolithium reagent (3.0 equiv.) was added, and the mixture was stirred for 2 h at this temperature. Hydrazone (*S*,*S*)-**4** (1.0 equiv.), dissolved in dry THF (4.0 mL/mmol), was added to the resulting yellow suspension at −100 °C. The solution was allowed to warm up to room temperature over 15 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and the aqueous portion was extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4 and concentrated in vacuo. The crude hydrazines were used directly in the N,N cleavage. For that purpose, the crude hydrazines (1.0 equiv.) were dissolved in dry THF (10 mL/mmol), $BH_3 \cdot$THF (12 equiv.) was then added, and the solution was heated at reflux for 4 h. The reaction mixture was hydrolysed with methanol and concentrated in vacuo. The residue was dissolved in methanol (10.0 mL/mmol) and heated at reflux for another 2 h. The mixture was concentrated in vacuo and the crude amine was either purified by flash column chromatography on silica gel or subsequently converted into the benzylcarbamate. For that purpose the crude amine was dissolved in CH_2Cl_2 (10.0 mL/mmol), K_2CO_3 (2.7 equiv.), and CbzCl (2.5 equiv.) were added, and the system was heated at reflux for 3 days. The aqueous layer was extracted three times with CH_2Cl_2, and the combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (SiO_2, pentane/Et_2O).

Benzyl (2*S*,1*R*)-[2-(*tert*-Butylsulfanyl)-1,3-dimethylbutyl]carbamate [(*S*,*R*)-5a]: Compound (*S*,*S*)-**4a** (0.20 g, 1.4 mmol) and $CeCl_3$/MeLi (3.0 equiv.) were treated as described in GP 4 to afford the corresponding hydrazine, which was directly used in the next step. N,N bond cleavage with $BH_3 \cdot$THF (12.0 equiv.) afforded the crude amine, which was dissolved in CH_2Cl_2 and treated with K_2CO_3 (3.8 mmol, 0.52 g) and CbzCl (3.5 mmol, 0.58 g). The carbamic ester was obtained as a colourless solid after flash column chromatography (SiO_2, pentane/Et_2O, 15:1). Yield: 0.06 g (28% over three steps). *de*, *ee* ≥ 96%. R_t = 9.90 min (OV-17, 140−10−260). R_f = 0.60 (pentane/Et_2O, 3:1). $[\alpha]_D^{25}$ = −1.2 (*c* = 1.0, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3854 (w), 3842 (w), 3676 (w), 3650 (w), 3630 (w), 3334 (s), 3033 (m), 2957 (s), 2865 (m), 2175 (w), 1682 (s), 1529 (s), 1457 (s), 1383 (m), 1365 (s), 1344 (m), 1324 (m), 1249 (s), 1161 (s), 1095 (s), 1028 (s), 970 (m), 930 (m), 912 (m), 863 (w), 848 (w), 784 (m), 756 (m), 732 (m), 698 (s), 629 (m), 596 (w), 583 (w), 539 (w), 508 (w), 486 (w) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ = 0.90 [d, *J* = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$], 0.94 (d, *J* = 6.7 Hz, 3 H, NCHC*H*$_3$), 1.07 [d, *J* = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.13 [s, 9 H, C(C*H*$_3$)$_3$], 1.55 [m, 1 H, C*H*(CH$_3$)$_2$], 2.45 (dd, *J* = 4.0, 8.9 Hz, 1 H, SC*H*), 4.27 (m, 1H C*H*NH), 5.03 (d, *J* = 9.0 Hz, 1 H, N*H*), 5.12 (d, *J* = 12.5 Hz, PhC*H*$_2$), 7.07 (m, 1 H, CH$_{arom.}$), 7.13 (m, 2 H, CH$_{arom.}$), 7.35 (m, 2 H, CH$_{arom.}$) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 20.7 (*C*H$_3$), 22.1, 16.4 [CH(*C*H$_3$)$_2$], 32.2 [*C*(CH$_3$)$_3$], 32.4 [*C*H(CH$_3$)$_2$], 42.7 [C(*C*H$_3$)$_3$], 47.5 (S*C*H), 56.0 (*C*HNH), 66.4 (Ar*C*H$_2$), 127.9, 128.2, 128.4, (Ar-*C*), 137.4 (Ar-C_q), 155.1 (*C*=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 323 (4) [M^+], 178 (13), 172 (14), 146 (21), 145 (13), 144 (17), 134 (24), 92 (9), 91 (100), 89 (39), 57 (23). $C_{18}H_{29}NO_2S$ (323.500): calcd. C 66.83, H 9.04, N 4.33; found C 66.44, H 9.38, N 4.13.

Benzyl (3*S*,2*R*)-(−)-[3-(*tert*-Butylsulfanyl)-1,1,5-trimethylhex-2-yl]-carbamate [(*S*,*R*)-5b]: Compound (*S*,*S*)-**4b** (0.30 g, 1.0 mmol) and $CeCl_3$/*t*BuLi (3.0 equiv.) were treated as described in GP 4 to afford the corresponding hydrazine, which was directly used in the next step. N,N bond cleavage with $BH_3 \cdot$THF (12.0 equiv.) afforded the crude amine, which was dissolved in CH_2Cl_2 and treated with K_2CO_3 (2.7 mmol, 0.37 g) and CbzCl (2.5 mmol, 0.43 g). The carbamic ester was obtained as a colourless oil after flash column chromatography (SiO_2, pentane/Et_2O, 15:1). Yield: 0.23 g (61% over 3 steps); *de*, *ee* ≥ 96%. R_t = 12.37 min (CP-Sil-8, 140−10−300). R_f = 0.70 (pentane/Et_2O, 3:1). $[\alpha]_D^{25}$ = −47.8 (*c* = 1.3, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3458 (w), 3277 (m), 3149 (w), 3090 (w), 3065 (w), 3033 (w), 2956 (s), 2899 (m), 2867 (s), 2716 (w), 1949 (w), 1707 (s), 1608 (w), 1598 (w), 1508 (s), 1469 (w), 1458 (w), 1405 (m), 1365 (s), 1341 (s), 1218 (s), 1163 (m), 1114 (m), 1054 (s), 1029 (m), 1009 (m), 917 (w), 895 (w), 875 (w), 753 (m), 697 (m), 666 (w), 607 (w), 571 (w), 527 (w), 491 (w) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ = 0.87 [d, *J* = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$], 0.92 [s, 9 H, CHC(C*H*$_3$)$_3$], 1.14 (m, 2 H, SCHC*H*$_2$), 1.32 [s, 9 H, SC(C*H*$_3$)$_3$], 2.10 [m, 1 H, C*H*(CH$_3$)$_2$], 3.05 (m, 1 H, SC*H*), 4.31 (dd, *J* = 10.7, 1.8 Hz, 1 H, C*H*NH), 4.75 (m, d, *J* = 10.7 Hz, 1 H, N*H*), 5.17 (d, *J* = 12.4 Hz, 2 H, C*H*$_2$Ar), 7.10 (m, 3 H, CH$_{arom.}$), 7.28 (m, 2 H, CH$_{arom.}$) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 23.0 [*C*H(CH$_3$)$_2$], 24.8, 20.8 [CH(*C*H$_3$)$_2$], 27.4 [C(*C*H$_3$)$_3$], 30.9 [SC(*C*H$_3$)$_3$], 35.8 [*C*(CH$_3$)$_3$], 39.4 (*C*H$_2$CH(CH$_3$)$_2$], 41.8 (S*C*H), 42.0 [*C*(CH$_3$)$_3$], 63.7 (*C*HNH), 65.8 (Ar*C*H$_2$), 127.6, 127.5, 127.0 (Ar-*C*), 136.7 (Ar-C_q), 156.1 (*C*=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 379 (2) [M^+], 221 (7), 220 (53), 177 (10), 176 (71), 158 (10), 103 (8), 92 (8), 91 (100), 57 (17). HRMS: $C_{22}H_{37}NO_2S$: calcd. 379.2545; found 379.2546.

Benzyl (3*S*,2*R*)-(−)-[3-(*tert*-Butylsulfanyl)-1,1-dimethyl-5-phenylpent-2-yl]carbamate [(*S*,*R*)-5c]: Compound (*S*,*S*)-**4c** (0.20 g, 0.56 mmol) and $CeCl_3$/*t*BuLi (1.68 mmol, 3.0 equiv.) were treated as described in GP 4 to afford the corresponding hydrazine, which was directly used in the next step. N,N bond cleavage with BH_3·THF (6.70 mmol, 12.0 equiv.) afforded the crude amine, which was dissolved in CH_2Cl_2 and treated with K_2CO_3 (1.5 mmol, 0.21 g) and CbzCl (1.40 mmol, 0.24 g). The carbamic ester was obtained as a colourless oil after flash column chromatography (SiO_2, pentane/Et_2O, 15:1). Yield: 0.13 g (54% over 3 steps); *de*, *ee* ≥ 96%. R_t = 16.80 min (CP-Sil-8, 140−10−300). R_f = 0.60 (pentane/Et_2O, 3:1) $[\alpha]_D^{25}$ = −12.9 (*c* = 0.8, $CHCl_3$). IR ($CHCl_3$): ṽ = 3425 (m), 3278 (m), 3149 (m), 3086 (m), 3063 (m), 3028 (m), 2960 (s), 2865 (m), 1949 (w), 1873 (w), 1807 (w), 1705 (s), 1604 (m), 1586 (w), 1510 (s), 1472 (s), 1455 (s), 1405 (m), 1365 (s), 1342 (s), 1218 (s), 1163 (m), 1130 (m), 1083 (m), 1058 (s), 1030 (m), 1016 (m), 930 (w), 909 (w), 754 (s), 699 (s), 667 (m), 609 (m), 566 (m), 526 (w), 494 (m) cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ = 0.82 [s, 9 H, $SC(CH_3)_3$], 1.32 [s, 9 H, $NCHC(CH_3)_3$], 1.38 (m, 1 H, $PhCH_2CHH$), 1.68 (m, 1 H, $PhCH_2CHH$), 2.58 (m, 1 H, $PhCHH$), 2.90 (m, 1 H, SCH), 3.05 (m, 1 H, $PhCHH$), 4.29 (dd, *J* = 1.6, 11.0 Hz, 1 H, $CHNH$), 4.66 (d, *J* = 11.0 Hz, 1 H, NH), 5.15 (d, *J* = 12.4 Hz, 2 H, OCH_2Ph), 7.12 (m, 10 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 27.2 [$SC(CH_3)_3$], 30.9 [$C(CH_3)_3$], 33.0 ($ArCH_2CH_2$), 33.5 ($ArCH_2$), 35.7 [$SC(CH_3)_3$], 42.2 [$C(CH_3)_3$], 43.4 (SCH), 63.6 ($HNCH$), 65.8 ($ArCH_2O$), 127.7, 127.6, 127.5, 125.3 (Ar-*C*), 141.2, 136.7 (Ar-C_q), 156.1 (*C*=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 428 (1) [M^+], 221 (7), 220 (50), 208 (19), 177 (10), 176 (73), 117 (13), 92 (8), 91 (100), 57 (16). HRMS: $C_{26}H_{37}NO_2S$: calcd. 427.2545; found 427.2546.

(2*S*,1*R*)-(+)-1-[2-(4-Bromophenyl)-1-(*tert*-butylsulfanyl)ethyl]-pentylamine [(*S*,*R*)-5d]: Compound (*S*,*S*)-**4d** (0.20 g, 0.48 mmol) and $CeCl_3$/MeLi (1.44 mmol 3.0 equiv.) were treated as described in GP 4 to afford the corresponding hydrazine, which was directly used in the next step. N,N bond cleavage with BH_3·THF (5.8 mmol, 12.0 equiv.) afforded the crude amine, which was obtained as a colourless oil after flash column chromatography (SiO_2, pentane/Et_2O, 1:1). Yield: 0.03 g (41% over 2 steps); *de*, *ee* ≥ 96%. R_t = 7.52 min (CP.Sil-8, 180−10−300). R_f = 0.29 (pentane/Et_2O, 1:1). $[\alpha]_D^{25}$ = +33.4 (*c* = 0.8, $CHCl_3$). IR ($CHCl_3$): ṽ = 3257 (m), 3136 (w), 3023 (w), 2958 (s), 2930 (s), 2862 (s), 2368 (s), 2323 (s), 2276 (m), 1579 (s), 1489 (s), 1460 (s), 1404 (m), 1393 (m), 1382 (m), 1365 (s), 1303 (m), 1274 (m), 1166 (s), 1137 (m), 1106 (m), 1073 (s), 1045 (m), 1012 (s), 957 (m), 928 (w), 895 (w), 834 (m), 798 (m), 757 (m), 733 (m), 628 (w), 596 (w), 527 (w), 473 (w) cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ = 0.91 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.02 [s, 9 H, $C(CH_3)_3$], 1.17−1.33 (m, 4 H, $CH_3CH_2CH_2$), 1.41 [m, 2 H, $CH(N)CH_2$], 2.61 (m, 2 H, $ArCHH$, SCH), 2.69 (dd, *J* = 3.3, 10.4 Hz, 1 H, $ArCHH$), 2.80 (m, 1 H, CHN), 6.85 (m, 2 H, $CH_{arom.}$), 7.29 (m, 2 H, $CH_{arom.}$), ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 14.4 (CH_2CH_3), 23.2 (CH_2CH_3), 29.5 ($CH_2CH_2CH_3$), 31.5 [$C(CH_3)_3$], 34.0 ($CH_2CH_2CH_2CH_3$), 38.4 ($ArCH_2$), 42.8 [$C(CH_3)_3$], 53.2 (SCH), 55.5 (H_2NCH), 120.3 (*C*Br), 131.4, 131.8 (Ar-*C*), 139.9 (Ar-C_q), ppm. MS (CI, isobutane): *m*/*z* (%) = 417 (3) [M^+ +59], 415 (3) [M^+ +57], 398 (5) [M^+ +40], 396 (5) [M^+ +38], 361 (20) [M^+ +3], 360 (100) [M^+ +2], 359 (20) [M^+ +1], 358 (95) [M^+], 280 (14), 86 (36). $C_{17}H_{28}BrNS$ (358.386): calcd. C 56.97, H 7.88, N 3.91; found C 57.07, H 8.25, N 4.19.

(2*S*,1*R*)-1-[1-(*tert*-Butylsulfanyl)-2-naphthalen-2-ylethyl]pentylamine [(*S*,*R*)-5e]: Compound (*S*,*S*)-**4e** (0.35 g, 0.91 mmol) and $CeCl_3$/*n*BuLi (2.73 mmol, 3.0 equiv.) were treated as described in GP 4 to afford the corresponding hydrazine, which was directly used in the next step. N,N bond cleavage with BH_3·THF (10.9 mmol, 12.0 equiv.) afforded the crude amine, which was obtained as a colourless oil after flash column chromatography (SiO_2, pentane/Et_2O, 1:1). Yield: 0.10 g (32% over 2 steps); *de*, *ee* ≥ 96%. R_t = 9.59 min (CP.Sil-8, 180−10−300) R_f = 0.28 (pentane/EtOA*c* = 3:1). $[\alpha]_D^{25}$ = +19.7 (*c* = 1.2, $CHCl_3$). IR ($CHCl_3$): ṽ = 3259 (m), 3224 (m), 3137 (w), 3053 (m), 3007 (m), 2958 (s), 2931 (s), 2862 (s), 2369 (s), 2323 (s), 2277 (m), 1765 (w), 1705 (s), 1632 (w), 1601 (m), 1578 (s), 1509 (m), 1460 (s), 1393 (m), 1366 (s), 1302 (m), 1271 (m), 1215 (m), 1171 (s), 1137 (m), 1083 (w), 1046 (m), 1018 (m), 983 (w), 961 (m), 932 (w), 896 (m), 855 (m), 817 (s), 757 (s), 667 (m), 642 (w), 623 (w), 598 (w), 477 (m) cm^{-1}.^1H NMR (400 MHz, C_6D_6): δ = 0.91 (t, *J* = 7.4 Hz, 3 H, CH_2CH_3), 1.05 [s, 9 H, $C(CH_3)_3$], 1.28 (m, 6 H, $CH_3CH_2CH_2CH_2$), 2.93 (m, 2 H, $CHNH_2$, SCH), 3.03 (m, 2 H, $ArCH_2$), 7.26 (m, 2 H, $CH_{arom.}$), 7.36 (m, 1 H, $CH_{arom.}$), 7.67 (m, 4 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 14.4 (CH_2CH_3), 23.2 (CH_2CH_3), 29.5 ($CH_2CH_2CH_3$), 31.6 [$SC(CH_3)_3$], 33.9 ($CH_2CH_2CH_2CH_3$), 39.9 ($ArCH_2$), 43.0 [$SC(CH_3)_3$], 53.7 (SCH), 55.3 (H_2NCH), 125.7 126.2, 127.3, 127.7, 127.8, 127.9, 128.5 (Ar-*C*), 132.8, 133.8, 135.8 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 330 (5) [M^+], 244 (16), 141 (14), 87 (5), 86 (100), 57 (8). HRMS: $C_{21}H_{31}NS$: calcd. 329.2177; found 329.2178.

General Procedure for the α-Alkylation of α-Sulfanylated Acetaldehyde-SAMP-Hydrazone (*S*)-3b (GP 5): Compound (*S*)-**3b** (1 equiv.) was dissolved in dry THF (2.0 mL/mmol) and the system was cooled to −20 °C under argon. LDA (1.0 equiv.), freshly prepared from *n*BuLi (1.0 equiv.) and diisopropylamine (1.05 equiv.), was added to this solution. After the system had been stirred at this temperature for 2 to 3 h, alkyl halide (1.2 equiv.) was added at −100 °C. This solution was allowed to warm up to room temperature over 15 h. The reaction mixture was quenched with brine and the aqueous portion was extracted three times with Et_2O. The combined organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed in a rotary evaporator and the crude product was purified by flash column chromatography (SiO_2, pentane/Et_2O, 1% NEt_3).

(2*S*,2*S*)-(−)-(2-Benzylsulfanyl-3-methylbutylidene)[2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*S*)-6a]: Hydrazone (*S*)-**3b** (0.64 g, 2.3 mmol) was alkylated with 2-iodopropane (0.47 g, 2.8 mmol) as described in GP 5. Compound (*S*,*S*)-**6a** was obtained as a yellow oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 6:1, 1% NEt_3). Yield: 0.68 g (92%); *de* = 83%. R_f = 0.22 (pentane/Et_2O, 6:1). $[\alpha]_D^{25}$ = −248.9 (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): ṽ = 3083 (w), 3060 (m), 3027 (m), 2960 (vs), 2924 (vs), 2874 (vs), 2825 (s), 1587 (m), 1493 (m), 1455 (s), 1418 (w), 1384 (m), 1367 (m), 1342 (m), 1304 (w), 1240 (m), 1197 (s), 1121 (vs), 1071 (s), 1029 (m), 972 (m), 887 (m), 768 (m), 702 (vs), 565 (w), 470 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$), (*E* isomer): δ = 0.97 [d, *J* = 6.9 Hz, 3 H, $CH(CH_3)_2$], 0.98 [d, *J* = 6.9 Hz, 3 H, $CH(CH_3)_2$], 1.79−2.02 [m, 5 H, $NCH_2CH_2CH_2$, $CH(CH_3)_2$], 2.79 (dt, *J* = 8.2, 8.2 Hz, 1 H, $NCHH$), 3.15 (dd, *J* = 6.9, 8.5 Hz, 2 H, SCH), 3.35−3.71 (m, 6 H, $NCHCH_2OCH_3$, $NCHH$, SCH_2Ph), 3.38 (s, 3 H, OCH_3), 6.45 (d, *J* = 8.2 Hz, N=C*H*), 7.19−7.37 (m, 5 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), (*E* isomer): δ = 20.3, 20.6 (CH_3), 22.1 (NCH_2CH_2), 26.6 ($NCH_2CH_2CH_2$), 31.2 [$CH(CH_3)_2$], 34.6 (SCH_2), 50.1 (NCH_2), 54.2 (SCH), 59.2 (OCH_3), 63.1 (NCH), 74.6 (CH_2OCH_3), 126.4, 128.1, 128.9 (Ar-*C*), 136.5 (Ar-C_q), 139.0 (*C*=N) ppm. MS (EI, 70 eV): *m*/*z* (%) = 320 (6) [M^+], 275 (18) [M^+ − CH_2OCH_3], 198 (17), 197 (100) [M^+ − SC_7H_7], 114 (6), 91 (22) [C_7H_7], 70 (12), 45 (10) [CH_2OCH_3]. $C_{18}H_{28}N_2OS$ (320.49): calcd. C 67.46, H 8.81, N 8.74; found C 67.17, H 9.12, N 8.41.

(2*S*,2*S*)-(−)-(2-Benzylsulfanyl-4-methylpentylidene)[2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*S*)-6b]: Hydrazone (*S*)-**3b** (1.40 g, 5.0 mmol) was alkylated with isobutyl iodide (1.10 g, 6.0 mmol) as described in GP 5. Compound (*S*,*S*)-**6b** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 6:1, 1% NEt_3). Yield: 1.17 g (87%); *de* ≥ 96%. R_f = 0.38 (pentane/Et_2O, 6:1). $[\alpha]_D^{25}$ = −232.5 (*c* = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3084 (w), 3061 (m), 3028 (m), 2955 (vs), 2725 (w), 1713 (m), 1588 (m), 1494 (m), 1454 (s), 1419 (w), 1384 (m), 1367 (m), 1341 (m), 1304 (w), 1236 (m), 1197 (s), 1120 (vs), 1072 (m), 1028 (w), 973 (s), 899 (m), 768 (m), 702 (s), 566 (m), 475 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$), (*E* isomer): δ = 0.81 [d, *J* = 6.6 Hz, 3 H, $CH(CH_3)_2$], 0.84 [d, *J* = 6.6 Hz, 3 H, $CH(CH_3)_2$], 1.50 [m, 2 H, $CH_2CH(CH_3)_2$], 1.72 [m, 1 H, $CH(CH_3)_2$], 1.79−2.02 (m, 4 H, $NCH_2CH_2CH_2$), 2.76 (dt, *J* = 8.2/8.2 Hz, 1 H, NCHH), 3.34−3.52 (m, 7 H, $NCHCH_2OCH_3$, SCH, NCHH), 3.34 (s, 3 H, OCH_3), 3.63 (d, *J* = 13.5 Hz, 1 H, SCHHPh), 3.71 (d, *J* = 13.5 Hz, 1 H, SCHHPh), 6.45 (d, *J* = 8.5 Hz, N=CH), 7.19−7.37 (m, 5 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), (*E* isomer): δ = 22.1 (NCH_2CH_2), 22.3, 22.5 (CH_3), 25.8 [$CH(CH_3)_2$], 26.5 ($NCH_2CH_2CH_2$), 34.5 (SCH_2), 41.5 [$CH_2CH(CH_3)_2$], 45.3 (SCH), 49.8 (NCH_2), 59.2 (OCH_3), 63.1 (NCH), 74.5 (CH_2OCH_3), 126.4, 128.1, 128.9 (Ar-*C*), 137.6 (*C*=N), 139.1 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 334 (4) [M^+], 289 (12) [$M^+ - CH_2OCH_3$], 212 (16), 211 (100) [$M^+ - SC_7H_7$], 123 (6) [SC_7H_7], 91 (15) [C_7H_7], 70 (6), 45 (7) [CH_2OCH_3]. $C_{19}H_{30}N_2OS$ (334.52): calcd. C 68.22, H 9.04, N 8.37; found C 68.31, H 8.98, N 8.41.

(2*S*,2*S*)-(−)-(2-Benzylsulfanyl-3-*o*-tolylpropylidene)[2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*S*)-6c]: Hydrazone (*S*)-**3b** (0.56 g, 2.0 mmol) was alkylated with 1-bromomethyl-2-methylbenzene (0.48 g, 2.6 mmol) as described in GP 5. Compound (*S*,*S*)-**6c** was obtained as a yellow oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 6:1, 1% NEt_3). Yield: 0.56 g (73%); *de* = 94%. R_f = 0.18 (pentane/Et_2O, 6:1). R_t = 14.34 min (CP-Sil-8, 160−10−300). $[\alpha]_D^{25}$ = −180.2 (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3374 (w), 3060 (m), 3025 (s), 2921 (vs), 2876 (vs), 2825 (vs), 2733 (w), 1711 (w), 1587 (s), 1493 (vs), 1453 (vs), 1342 (m), 1303 (m), 1284 (w), 1197 (vs), 1156 (s), 1119 (vs), 1072 (s), 1029 (m), 973 (m), 901 (m), 868 (m), 769 (m), 746 (vs), 703 (vs), 597 (w), 565 (w), 465 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$), (*E* isomer): δ = 1.74−1.98 (m, 4 H, $NCH_2CH_2CH_2$), 2.22 (s, 3 H, $ArCH_3$), 2.66 (dt, *J* = 8.2, 8.0 Hz, 1 H, NCHH), 2.94 (m, 2 H, $ArCH_2$) 3.27−3.62 (m, 5 H, SCH, $CHCH_2OCH_3$, NCHH), 3.35 (s, 3 H, OCH_3), 3.63 (d, *J* = 13.5 Hz, 1 H, SCHHPh), 3.71 (d, *J* = 13.5 Hz, 1 H, SCHHPh), 6.40 (d, *J* = 7.4 Hz, N=CH), 7.05−7.32 (m, 9 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), (*E* isomer): δ = 19.6 (CH_3), 22.0 (NCH_2CH_2), 26.5 ($NCH_2CH_2CH_2$), 34.9 ($ArCH_2$), 36.4 (SCH_2), 46.9 (SCH), 49.6 (NCH_2), 59.1 (OCH_3), 62.9 (NCH), 74.4 (CH_2OCH_3), 125.4, 126.2, 126.5, 128.1, 128.9, 129.7, 130.0 (Ar-*C*), 136.2 (*C*=N), 136.1, 136.7, 138.7 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 382 (7) [M^+], 338 (6), 337 (24) [$M^+ - CH_2OCH_3$], 278 (7), 277 (39) [$M^+ - C_8H_9$], 260 (21), 259 (100) [$M^+ - SC_7H_7$], 141 (6), 105 (7) [C_8H_9], 91 (27) [C_7H_7], 70 (8), 45 (11) [CH_2OCH_3]. $C_{23}H_{30}N_2OS$ (382.56): calcd. C 72.21, H 7.90, N 7.32; found C 71.74, H 8.26, N 7.67.

(2*S*,2*S*)-(−)-[2-Benzylsulfanyl-3-(naphthalen-2-yl)propylidine][2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*S*)-6d]: Hydrazone (*S*)-**3b** (0.56 g, 2.0 mmol) was alkylated with 2-(bromomethyl)naphthalene (0.58 g, 2.6 mmol) as described in GP 5. Compound (*S*,*S*)-**6d** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 6:1, 1% NEt_3). Yield: 0.76 g (90%); *de* ≥ 96%. R_f = 0.14 (pentane/Et_2O, 6:1). $[\alpha]_D^{25}$ = −144.62 (*c* = 1.00, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3399 (w), 3056 (s), 3026 (s), 2921 (vs), 1947 (w), 1712 (m), 1631 (m), 1599 (s), 1509 (m), 1495 (m), 1453 (s), 1383 (m), 1365 (m), 1343 (m), 1304 (w), 1272 (m), 1240 (m), 1198 (s), 1121 (vs), 1072 (s), 1021 (w), 970 (m), 902 (m), 855 (s), 818 (s), 745 (s), 703 (vs), 621 (w), 565 (w), 477 (vs) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$), (*E* isomer): δ = 1.74−1.96 (m, 4 H, $NCH_2CH_2CH_2$), 2.67 (dt, *J* = 8.2, 7.7 Hz, 1 H, NCHH), 3.08 (dd, *J* = 14.3, 6.9 Hz, 1 H, ArCHH), 3.17 (dd, *J* = 14.0, 8.0 Hz, 1 H, ArCHH), 3.23−3.78 (m, 7 H, $NCHCH_2OCH_3$, SCH, NCHH, SCH_2Ph), 3.34 (s, 3 H, OCH_3), 6.41 (d, *J* = 7.7 Hz, 1 H, N=CH), 7.20−7.81 (m, 12 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), (*E* isomer): δ = 22.0 (NCH_2CH_2), 26.5 ($NCH_2CH_2CH_2$), 34.9 (SCH_2), 39.3 ($Ar\text{-}CH_2$), 47.9 (SCH), 49.6 (NCH_2), 59.1 (OCH_3), 62.9 (NCH), 74.4 (CH_2OCH_3), 125.1, 125.6, 126.5, 127.4, 127.5, 127.5, 127.6, 128.2, 128.9 (Ar-*C*), 132.0, 133.2 (Ar-C_q), 135.8 (C=N), 135.9, 138.7 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 306 (7), 278 (10), 251 (10), 249 (11), 235 (5), 234 (16), 233 (100), 199 (9), 187 (11), 184 (8), 180 (7), 156 (8), 155 (26), 142 (6), 141 (42), 111 (5), 109 (6), 92 (5), 91 (62, C_7H_7), 71 (8), 70 (9), 45 (6) [CH_2OCH_3]. $C_{26}H_{30}N_2OS$ (418.60): calcd. C 74.60, H 7.22, N 6.69; found C 74.24, H 7.03, N 6.77.

(2*S*,2*S*)-(−)-(2-Benzylsulfanyl-3-phenylpropylidene)[2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*S*)-6e]: Hydrazone (*S*)-**3b** (0.42 g, 1.5 mmol) was alkylated with benzyl bromide (0.31 g, 1.8 mmol) as described in GP 5. Compound (*S*,*S*)-**6e** was obtained as a yellow oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 6:1, 1% NEt_3). Yield: 0.50 g (90%); *de* ≥ 96%. R_f = 0.23 (pentane/Et_2O, 6:1). R_t = 15.86 min (CP-Sil-8, 140−10−300). $[\alpha]_D^{25}$ = −184.8 (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3083 (m), 3061 (m), 3027 (s), 2972 (vs), 2921 (vs), 2876 (vs), 2826 (m), 1586 (m), 1495 (s), 1453 (s), 1341 (m), 1303 (m), 1283 (w), 1197 (s), 1120 (vs), 1072 (s), 1030 (m), 973 (m), 899 (w), 752 (s), 700 (vs), 568 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$), (*E* isomer): δ = 1.74−1.98 (m, 4 H, $NCH_2CH_2CH_2$), 2.67 (dt, *J* = 8.5, 7.7 Hz, 1 H, NCHH), 2.92 (dd, *J* = 14.0, 7.1 Hz, 1 H, ArCHH), 3.01 (dd, *J* = 14.0, 8.0 Hz, 1 H, ArCHH), 3.28−3.63 (m, 5 H, $NCHCH_2OCH_3$, SCH, NCHH), 3.35 (s, 3 H, OCH_3), 3.63 (d, *J* = 14.0 Hz, 1 H, SCHHPh), 3.70 (d, *J* = 13.5 Hz, 1 H, SCHHPh), 6.37 (d, *J* = 7.4 Hz, 1 H, N=CH), 7.12−7.32 (m, 10 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), (*E* isomer): δ = 22.0 (NCH_2CH_2), 26.5 ($NCH_2CH_2CH_2$), 34.8 (SCH_2), 39.1 ($ArCH_2$), 48.0 (SCH), 49.6 (NCH_2), 59.1 (OCH_3), 62.9 (NCH), 74.4 (CH_2OCH_3), 126.1, 126.5, 127.9, 128.2, 128.8, 129.1 (Ar-*C*), 136.0 (*C*=N), 138.3, 138.7 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 368 (9) [M^+], 324 (6), 323 (29) [$M^+ - CH_2OCH_3$], 277 (20) [$M^+ - C_7H_7$], 246 (19), 245 (100) [$M^+ - SC_7H_7$], 199 (11), 91 (29) [C_7H_7], 70 (8), 45 (11) [CH_2OCH_3]. $C_{22}H_{28}N_2OS$ (368.54): calcd. C 71.70, H 7.66, N 7.60; found C 71.84, H 7.99, N 7.88.

(2-Benzylsulfanyl-4-phenylbutylidene)[2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*S*)-6f]: Hydrazone (*S*)-**3b** (0.84 g, 3.0 mmol) was alkylated with benzyl bromide (0.91 g, 3.9 mmol) as described in GP 5. Compound (*S*,*S*)-**6f** was obtained as a yellow oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 6:1, 1% NEt_3). Yield: 0.93 g (81%); *de* ≥ 96%. R_f = 0.25 (pentane/Et_2O, 6:1) (R_t = 8.80 min (CP-Sil-8, 160−10−300). $[\alpha]_D^{25}$ = −232.2 (*c* = 0.9, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3084 (m), 3060 (m), 3026 (s), 2973 (vs), 2922 (vs), 2876 (vs), 2825 (s), 1601 (m), 1586 (m), 1495 (s), 1454 (s), 1418 (w), 1341 (m), 1303 (w), 1283 (w), 1197 (s), 1120 (vs), 1072 (m), 1030 (m), 973 (m), 902 (w), 879 (m), 752 (s), 769 (m), 751 (m), 700 (vs), 564 (m), 504 (w), 474 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$), (*E* isomer): δ = 1.76−2.04 (m, 6 H, $NCH_2CH_2CH_2$, $PhCH_2CH_2$), 2.67 (m, 3 H, NCHH, $PhCH_2CH_2$),

3.29−3.60 (m, 5 H, NC*H*C*H*$_2$OCH$_3$, SC*H*, NCH*H*), 3.37 (s, 3 H, OC*H*$_3$), 3.64 (d, *J* = 13.6 Hz, 1 H, SCH*H*Ph), 3.71 (d, *J* = 13.6 Hz, 1 H, SC*H*HPh), 6.34 (d, *J* = 7.7 Hz, 1 H, N=C*H*), 7.04−7.37 (m, 10 H, C*H*$_{arom.}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$), (*E* isomer): δ = 22.5 (NCH$_2$*C*H$_2$), 27.0 (NCH$_2$CH$_2$*C*H$_2$), 33.9, 35.0, 35.0 (S*C*H$_2$, Ar*C*H$_2$, Ar*C*H$_2$CH$_2$), 47.0 (S*C*H), 50.1 (N*C*H$_2$), 59.7 (O*C*H$_3$), 63.5 (N*C*H), 75.0 (*C*H$_2$OCH$_3$), 126.1, 126.9, 128.6, 128.6, 128.7, 129.3 (Ar-*C*), 137.1 (*C*=N), 139.4, 141.8 (Ar-C$_q$) ppm. MS (EI, 70 eV): *m*/*z* (%) = 382 (4) [M$^+$], 338 (5), 337 (20) [M$^+$ − CH$_2$OCH$_3$], 260 (20), 259 (100) [M$^+$ − SC$_7$H$_7$], 213 (17), 144 (7), 129 (7), 123 (10), 117 (11), 114 (7), 91 (34) [C$_7$H$_7$], 70 (7), 45 (5) [CH$_2$OCH$_3$]. C$_{23}$H$_{30}$N$_2$OS (382.56) calcd. C 72.21, H 7.90, N 7.32; found C 72.03, H 7.93, N 7.66.

(2*S*,2*S*)-(−)-[2-(Benzylsulfanyl)pent-4-enylidene][2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*S*)-6g]: Hydrazone (*S*)-**3b** (0.70 g, 2.5 mmol) was alkylated with allyl bromide (0.55 g, 3.3 mmol) as described in GP 5. Compound (*S*,*S*)-**6g** was obtained as a yellow oil after purification by flash column chromatography (SiO$_2$, pentane/Et$_2$O, 6:1, 1% NEt$_3$). Yield: 0.66 g (83%); *de* ≥ 96%. R_f = 0.40 (pentane/Et$_2$O, 6:1). R_t = 11.87 min (*E* isomer), 11.75 (*Z* isomer) (CP-Sil-8, 160−10−300). $[\alpha]_D^{25}$ = −269.2 (*c* = 1.1, $CHCl_3$). IR (film): ṽ = 3062 (m), 3027 (m), 2975 (vs), 2922 (vs), 2877 (vs), 2826 (vs), 1714 (w), 1640 (m), 1587 (s), 1495 (s), 1453 (vs), 1417 (m), 1342 (m), 1304 (m), 1283 (w), 1197 (vs), 1120 (vs), 1072 (s), 1029 (m), 992 (m), 973 (m), 915 (vs), 867 (m), 770 (m), 703 (vs), 618 (w), 565 (m), 472 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$), (*E* isomer): δ = 1.80−2.03 (m, 4 H, NCH$_2$C*H*$_2$C*H*$_2$), 2.42 (m, 2 H, CH$_2$=CHC*H*$_2$), 2.76 (dt, *J* = 8.5, 8.2 Hz, 1 H, NC*H*H), 3.33−3.80 (m, 7 H, C*H*$_2$OCH$_3$, SC*H*, SC*H*$_2$Ph, C*H*CH$_2$OCH$_3$, NCH*H*), 3.38 (s, 3 H, OC*H*$_3$), 5.06 (m, 2 H, *H*$_2$C=CH), 5.77 (m, 1 H, H$_2$C=C*H*), 6.35 (d, *J* = 8.0 Hz, 1 H, N=C*H*), 7.21−7.37 (m, 5 H, C*H*$_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), (*E* isomer): δ = 22.1 (NCH$_2$*C*H$_2$), 26.5 (NCH$_2$CH$_2$*C*H$_2$), 34.6 (S*C*H$_2$), 37.3 (*C*H$_2$CH), 46.4 (S*C*H), 49.7 (N*C*H$_2$), 59.2 (O*C*H$_3$), 63.0 (N*C*H), 74.4 (*C*H$_2$OCH$_3$), 116.9 (H$_2$*C*=CH), 126.5, 128.2, 128.9 (Ar-*C*), 134.8 (H$_2$C=*C*H), 136.3 (*C*=N), 138.9 (Ar-C$_q$) ppm. MS (EI, 70 eV): *m*/*z* (%) = 318 (2) [M$^+$], 273 (19) [M$^+$ − CH$_2$OCH$_3$], 196 (11), 195 (67) [M$^+$ − SC$_7$H$_7$], 177 (7), 173 (12), 149 (13), 141 (6), 124 (5), 123 (31) [SC$_7$H$_7$], 115 (9), 114 (7), 99 (6), 92 (8), 91 (100) [C$_7$H$_7$], 89 (5), 88 (5), 87 (5), 85 (5), 82 (5), 73 (40), 71 (9), 70 (16), 65 (8), 55 (9), 45 (54) [CH$_2$OCH$_3$]. C$_{18}$H$_{26}$N$_2$OS (318.48): calcd. C 67.88, H 8.23, N 8.80; found C 67.72, H 8.34 N 9.22.

(2*S*,2*S*)-(−)-[2-Benzylsulfanyl-3-(4-*tert*-butylphenyl)propylidene][2-(methoxymethyl)pyrrolidin-1-yl]amine (*S*,*S*)-6h: Hydrazone (*S*)-**3b** (0.64 g, 2.3 mmol) was alkylated with 4-*tert*-butylbenzyl bromide (0.63 g, 2.8 mmol) as described in GP 5. Compound (*S*,*S*)-**6h** was obtained as a yellow oil after purification by flash column chromatography (SiO$_2$, pentane/Et$_2$O, 6:1, 1% NEt$_3$). Yield: 0.72 g (74%); *de* ≥ 96%. R_f = 0.20 (pentane/Et$_2$O, 6:1). $[\alpha]_D^{25}$ = −147.7 (*c* = 0.9, $CHCl_3$). IR ($CHCl_3$): ṽ = 3084 (w), 3059 (m), 3026 (m), 2962 (vs), 2873 (vs), 2826 (s), 1712 (w), 1587 (m), 1515 (m), 1495 (m), 1455 (s), 1413 (w), 1364 (m), 1342 (m), 1269 (m), 1217 (m), 1198 (m), 1118 (s), 1072 (m), 1023 (m), 973 (w), 901 (w), 836 (m), 812 (m), 757 (vs), 702 (s), 666 (m), 565 (m), 472 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$), (*E* isomer): δ = 1.29 [s, 9 H, C(C*H*$_3$)$_2$], 1.76−1.99 (m, 4 H, NCH$_2$C*H*$_2$C*H*$_2$), 2.68 (dt, *J* = 8.8/8.0 Hz, 1 H, NC*H*H), 2.89 (dd, *J* = 14.0, 6.9 Hz, 1 H, ArCH*H*), 2.99 (dd, *J* = 14.0, 8.0 Hz, 1 H, ArC*H*H), 3.28−3.64 (m, 5 H, NC*H*CH$_2$, SC*H*, NCH*H*), 3.35 (s, 3 H, OC*H*$_3$), 3.63 (d, *J* = 13.5 Hz, 1 H, SCH*H*Ph), 3.70 (d, *J* = 13.5 Hz, 1 H, SC*H*HPh), 6.39 (d, *J* = 7.4 Hz, 1 H, N=C*H*), 7.05−7.32 (m, 9 H, C*H*$_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), (*E* isomer): δ = 22.1 (NCH$_2$*C*H$_2$), 26.5 (NCH$_2$CH$_2$*C*H$_2$), 31.3 (*C*H$_3$), 34.3 [*C*(CH$_3$)$_2$], 34.8 (S*C*H$_2$), 38.6 (Ar*C*H$_2$), 48.0 (S*C*H), 49.7 (N*C*H$_2$), 59.2 (O*C*H$_3$), 63.0 (N*C*H), 74.4 (*C*H$_2$OCH$_3$), 124.9, 126.5, 128.1, 128.8, 128.9 (Ar-*C*), 136.3 (*C*=N), 135.2, 138.8 (Ar-C$_q$), 148.8 (Ar-C$_q$) ppm. MS (EI, 70 eV): *m*/*z* (%) = 424 (3) [M$^+$], 380 (5), 379 (20) [M$^+$ − CH$_2$OCH$_3$], 333 (3) [M$^+$ − C$_7$H$_7$], 302 (24), 301 (100) [M$^+$ − SC$_7$H$_7$], 278 (8), 277 (46), 141 (6), 132 (6), 91 (15) [C$_7$H$_7$], 70 (5), 45 (5) [CH$_2$OCH$_3$]. C$_{26}$H$_{36}$N$_2$OS (424.64): calcd. C 73.54, H 8.54, N 6.60; found C 73.43, H 8.84, N 6.89.

General Procedure for the 1,2-Addition to α-Sulfanylated SAMP-Hydrazones (*S*,*S*)-6 (GP 6): $CeCl_3 \cdot 7H_2O$ (3.0 equiv.) was dehydrated in vacuo (0.1 Torr) for 2 h at 130 °C and then suspended in dry THF (3.0 mL/mmol) with sonification. The suspension was stirred overnight at room temperature. After the system had been cooled to −78 °C, lithiumorganyl (3.0 equiv.) was added and the mixture was stirred at this temperature for 2 h. Hydrazone (*S*,*S*)-**6** (1.0 equiv.), dissolved in dry THF (4.0 mL/mmol), was then added at −100 °C to the resulting canary yellow suspension. The solution was allowed to warm up to room temperature over 15 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and the aqueous portion was extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4 and concentrated in vacuo. The crude hydrazines were purified by flash column chromatography (SiO$_2$, pentane/Et$_2$O).

(2*S*,1*R*,2*S*)-(−)-[1-(1-Benzylsulfanyl-2-methylpropyl)pentyl][2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*R*,*S*)-7a]: This compound was prepared as described in GP 6, by 1,2-addition of $CeCl_3$/*n*BuLi (1.5 mmol) to hydrazone (*S*,*S*)-**6a** (0.16 g, 0.5 mmol). Compound (*S*,*R*,*S*)-**7a** was obtained as a colourless oil after purification by flash column chromatography (SiO$_2$, pentane/Et$_2$O, 6:1). Yield: 0.16 g (85%); *de* = 93%. R_f = 0.50 (pentane/Et$_2$O, 6:1). R_t = 13.18 min (CP-Sil-8, 140−10−300). $[\alpha]_D^{25}$ = −108.7 (*c* = 2.3, $CHCl_3$). IR (film): ṽ = 3062 (w), 3027 (m), 2956 (vs), 2871 (vs), 1726 (w), 1602 (w), 1493 (m), 1456 (s), 1382 (m), 1364 (m), 1196 (m), 1126 (s), 1070 (m), 1027 (w), 918 (m), 766 (w), 701 (s), 564 (w), 471 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.4 Hz, 3 H, CH$_2$C*H*$_3$), 0.95 [d, *J* = 6.6 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.03 [d, *J* = 6.6 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.13−1.50 [m, 6 H, CH(NH)C*H*$_2$C*H*$_2$C*H*$_2$), 1.60 (m, 1 H, NCH$_2$CH$_2$CH*H*), 1.70 (m, 2 H, NCH$_2$C*H*$_2$), 1.87 (m, 1 H, NCH$_2$CH$_2$C*H*H), 1.99 [m, 1 H, C*H*(CH$_3$)$_2$], 2.11 (m, 1 H, NCH*H*), 2.57 (m, 1 H, NC*H*CH$_2$OCH$_3$), 2.68 (dd, *J* = 3.6, 5.5 Hz, 1 H, SC*H*), 2.90 (m, 1 H, C*H*NH), 3.19 (m, 1 H, NC*H*H), 3.32 (m, 1 H, C*H*HOCH$_3$), 3.35 (s, 3 H, OC*H*$_3$), 3.53 (dd, *J* = 3.9, 9.3 Hz, 1 H, CH*H*OCH$_3$), 3.70 (d, *J* = 12.9 Hz, 1 H, SC*H*HPh), 3.74 (d, *J* = 12.6 Hz, 1 H, SCH*H*Ph), 7.19−7.33 (m, 5 H, C*H*$_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (CH$_2$*C*H$_3$), 20.8, 22.0 (*C*H$_3$), 21.1 (NCH$_2$*C*H$_2$), 23.0 (*C*H$_2$CH$_3$), 26.0 (NCH$_2$CH$_2$*C*H$_2$), 28.8 (*C*H$_2$CH$_2$CH$_3$), 29.6 [*C*H(CH$_3$)$_2$], 30.5 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 37.23 (S*C*H$_2$), 56.3 (S*C*H), 57.0 (N*C*H$_2$), 59.0 (O*C*H$_3$), 60.8 (*C*HNH), 66.5 (N*C*H), 74.8 (*C*H$_2$OCH$_3$), 126.8, 128.2, 128.9 (Ar-*C*), 138.5 (Ar-C$_q$) ppm. MS (EI, 70 eV): *m*/*z* (%) = 378 (13) [M$^+$], 200 (13), 199 (100), 129 (5), 114 (9), 91 (14) [C$_7$H$_7$], 70 (13), 45 (6) [CH$_2$OCH$_3$]. HRMS: calcd. 378.2705; found 378.2705.

(2*S*,1*R*,2*S*)-(−)-(2-Benzylsulfanyl-1-butyl-4-methylpentyl)[2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*R*,*S*)-7b]: This compound was prepared as described in GP 6, by 1,2-addition of $CeCl_3$/*n*BuLi (3.0 mmol) to hydrazone (*S*,*S*)-**6b** (0.33 g, 1.0 mmol). Compound (*S*,*R*,*S*)-**7b** was obtained as a colourless oil after purification by flash column chromatography (SiO$_2$, pentane/Et$_2$O, 6:1). Yield: 0.48 g (98%); *de* ≥ 96%. R_f = 0.60 (pentane/Et$_2$O, 5:1). R_t = 11.38 min (CP-Sil-8, 160−10−300). $[\alpha]_D^{25}$ = −176.3 (*c* = 0.7,

$CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3084 (w), 3063 (w), 3028 (m), 2955 (vs), 2929 (vs), 2870 (vs), 2730 (w), 1725 (w), 1601 (w), 1494 (m), 1466 (m), 1454 (m), 1384 (m), 1368 (m), 1343 (w), 1236 (w), 1217 (m), 1199 (m), 1113 (m), 1071 (m), 1029 (w), 918 (m), 897 (w), 757 (vs), 701 (s), 667 (m), 565 (w), 471 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.68 [d, *J* = 6.6 Hz, 3 H, $CH(CH_3)_2$], 0.86 [d, *J* = 6.6 Hz, 3 H, $CH(CH_3)_2$], 0.87 (t, *J* = 6.9 Hz, 3 H, CH_2CH_3), 1.03−1.78 [m, 12 H, $CH(NH)CH_2CH_2CH_2$, $CH_2CH(CH_3)_2$, $NCH_2CH_2CH_2$], 1.89 [m, 1 H, $CH(CH_3)_2$], 2.18 (m, 1 H, NCH*H*), 2.57 (m, 2 H, SC*H*, NC*H*CH_2OCH_3), 2.82 (m, 1 H, C*H*NH), 3.24 (m, 1 H, NC*H*H), 3.32 (m, 1 H, CH*H*OCH_3), 3.35 (s, 3 H, OCH_3), 3.52 (dd, *J* = 3.6, 9.1 Hz, 1 H, C*H*$HOCH_3$), 3.67 (d, *J* = 13.5 Hz, 1 H, SC*H*HPh), 3.72 (d, *J* = 13.5 Hz, 1 H, SCH*H*Ph), 7.20−7.33 (m, 5 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_2CH_3), 21.0 (NCH_2CH_2), 21.5, 23.3 (CH_3), 23.0 (CH_2CH_3), 25.6 [$CH(CH_3)_2$], 26.1 ($NCH_2CH_2CH_2$), 28.6 ($CH_2CH_2CH_3$), 30.2 ($CH_2CH_2CH_2CH_3$), 35.7 (SCH_2), 38.1 [$CH_2CH(CH_3)_2$], 45.1 (SCH), 56.6 (NCH_2), 59.0 (CH_2OCH_3), 60.0 (CHNH), 66.0 (NCH), 74.7 (CH_2OCH_3), 126.8, 128.2, 128.9 (Ar-*C*), 138.4 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 392 (3) [M^+], 213 (5), 200 (8), 199 (60), 195 (7), 194 (8), 193 (11), 183 (5), 156 (7), 137 (18), 123 (87), 114 (7), 113 (5), 103 (11), 102 (6), 92 (11), 91 (100, C_7H_7), 73 (13), 70 (12), 69 (15), 65 (6), 60 (10), 57 (10), 55 (10). $C_{23}H_{40}N_2OS$ (392.64): calcd. C 70.36 H 10.27 N 7.13; found C 70.60 H 10.60, N 7.17.

(2*S*,1*R*,2*S*)-(−)-{1-[1-Benzylsulfanyl-2-(*o*-tolyl)ethyl]pentyl}-[2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*R*,*S*)-7c]: This compound was prepared as described in GP 6, by 1,2-addition of $CeCl_3$/*n*BuLi (2.7 mmol) to hydrazone (*S*,*S*)-**6d** (0.21 g, 0.9 mmol). Compound (*S*,*R*,*S*)-**7d** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 6:1). Yield: 0.44 g (99%); *de* ≥ 96%. R_f = 0.19 (pentane/Et_2O, 6:1). R_t = 15.47 min (CP-Sil-8, 160−10−300). $[\alpha]_D^{25}$ = −37.2 (*c* = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3061 (m), 3025 (m), 2928 (vs), 2871 (vs), 1602 (w), 1492 (s), 1455 (vs), 1378 (m), 1346 (w), 1238 (w), 1192 (m), 1126 (vs), 1071 (m), 1030 (w), 917 (m), 764 (m), 744 (s), 702 (s), 564 (w), 518 (w), 460 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$,): δ = 0.87 (t, *J* = 6.9 Hz, 3 H, CH_2CH_3), 1.15 (m, 2 H, $CH_2CH_2CH_3$), 1.28 (m, 2 H, CH_2CH_3), 1.43 [m, 2 H, $CH(NH)CH_2$], 1.55 (m, 1 H, NCH_2CH_2CHH), 1.64 (m, 2 H, NCH_2CH_2), 1.86 (m, 1 H, NCH_2CH_2CHH), 2.11 (dt, *J* = 8.8, 8.5 Hz, 1 H, NC*H*H), 2.28 (s, 3 H, $ArCH_3$), 2.55 (m, 1 H, NC*H*CH_2OCH_3), 2.79 (dd, *J* = 14.3, 9.7 Hz, 1 H, ArCHH), 2.82 (m, 1 H, C*H*NH), 2.95 (dd, *J* = 14.3, 5.5 Hz, 1 H, ArCH*H*), 3.02 (m, 1 H, NCH*H*), 3.20 (m, 1 H, SC*H*), 3.27 (s, 3 H, OCH_3), 3.32−3.47 (m, 4 H, CH_2OCH_3, SCH_2Ph), 7.09−7.25 (m, 9 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_2CH_3), 19.7 (CH_3), 21.1 (NCH_2CH_2), 23.0 (CH_2CH_3), 26.2 ($NCH_2CH_2CH_2$), 29.0 ($CH_2CH_2CH_3$), 29.9 ($CH_2CH_2CH_2CH_3$), 35.4 ($ArCH_2$), 36.3 (SCH_2), 48.5 (SCH), 57.1 (NCH), 58.9 (OCH_3), 61.8 (CHNH), 66.4 (NCH), 75.0 (CH_2OCH_3), 125.5, 126.1, 126.7, 128.1, 128.9, 130.0, 130.1 (Ar-*C*), 136.2, 138.2 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 440 (16) [M^+], 200 (13), 199 (100), 129 (5), 114 (7), 105 (5), 91 (14, C_7H_7), 70 (11), 45 (5) [CH_2OCH_3]. $C_{27}H_{40}N_2OS$ (440.69): calcd. C 73.59, H 9.15, N 6.36; found C 73.30, H 9.30, N 6.84.

(2*S*,1*R*,2*S*)-(−)-{1-[1-Benzylsulfanyl-2-(naphthalen-2-yl)ethyl]-pentyl}[2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*R*,*S*)-7d]: This compound was prepared as described in GP 6, by 1,2-addition of $CeCl_3$/*n*BuLi (7.5 mmol) to hydrazone (*S*,*S*)-**6e** (0.88 g, 2.1 mmol). Compound (*S*,*R*,*S*)-**7e** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 6:1). Yield: 0.81 g (81%); *de* ≥ 96%. R_f = 0.23 (pentane/Et_2O, 6:1). R_t = 19.66 min (CP-Sil-8, 180−10−300). $[\alpha]_D^{25}$ = −15.1 (*c* = 1.4, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3056 (m), 3026 (m), 2928 (vs), 2871 (vs), 1725 (w), 1701 (w), 1632 (w), 1601 (w), 1508 (m), 1494 (m), 1454 (s), 1377 (m), 1238 (w), 1197 (m), 1125 (s), 1100 (s), 1071 (m), 1028 (w), 950 (m), 918 (m), 892 (m), 854 (m), 817 (s), 752 (s), 701 (s), 477 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 3 H, CH_2CH_3), 1.29 (m, 4 H, $CH_2CH_2CH_3$), 1.50 [m, 3 H, NCH_2CH_2CHH, $CH(NH)CH_2$], 1.65 (m, 2 H, NCH_2CH_2), 1.85 (m, 1 H, NCH_2CH_2CHH), 2.15 (m, 1 H, NCHH), 2.54 (m, 1 H, NC*H*CH_2OCH_3), 2.88 (m, 2 H, ArCH*H*, C*H*NH), 3.05−3.20 (m, 2 H, NCH*H*, ArC*H*H), 3.18 (s, 3 H, OCH_3), 3.23−3.42 (m, 5 H, SC*H*, CH_2OCH_3), 3.46 (m, 2 H, SCH_2Ph), 7.10 (m, 2 H, $CH_{arom.}$), 7.17 (m, 2 H, $CH_{arom.}$), 7.30 (m, 2 H, $CH_{arom.}$), 7.44 (m, 2 H, $CH_{arom.}$), 7.60 (m, 2 H, $CH_{arom.}$), 7.78 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 21.1 (NCH_2CH_2), 23.0 (CH_2CH_3), 26.2 ($NCH_2CH_2CH_2$), 28.9 ($CH_2CH_2CH_3$), 29.9 ($CH_2CH_2CH_2CH_3$), 36.3 (SCH_2), 37.8 ($ArCH_2$), 49.5 (SCH), 57.1 (NCH_2), 58.8 (OCH_3), 61.1 (CHNH), 66.5 (NCH), 74.8 (CH_2OCH_3), 125.1, 125.7, 126.7, 127.35, 127.38, 127.41, 127.6, 128.1, 128.3, 128.8 (Ar-*C*), 131.9, 133.3, 137.5, 138.0 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 476 (12) [M^+], 353 (6) [M^+ − SBn], 200 (12), 199 (100), 167 (6), 153 (5), 141 (10), 129 (6), 114 (10), 91 (13) [C_7H_7], 70 (13).HRMS: calcd. 476.2861; found 476.2864.

(2*S*,1*R*,2*S*)-(−)-[1-(1-Benzylsulfanyl-2-phenylethyl)pentyl][2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*R*,*S*)-7e]: This compound was prepared as described in GP 6, by 1,2-addition of $CeCl_3$/*n*BuLi (0.9 mmol) to hydrazone (*S*,*S*)-**6e** (0.10 g, 0.3 mmol). Compound (*S*,*R*,*S*)-**7e** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 4:1). Yield: 0.10 g (87%); *de* ≥ 96%. R_f = 0.29 (pentane/Et_2O, 3:1). R_t = 14.78 min (CP-Sil-8, 160−10−300). $[\alpha]_D^{25}$ = −12.1 (*c* = 2.2, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3084 (m), 3062 (m), 3027 (s), 2929 (vs), 2872 (vs), 1946 (w), 1695 (m), 1602 (m), 1536 (w), 1495 (m), 1453 (s), 1378 (m), 1345 (w), 1239 (w), 1197 (m), 1123 (s), 1073 (m), 1030 (m), 967 (w), 918 (m), 753 (m), 701 (vs), 564 (w), 508 (w), 474 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 1.19 (m, 2 H, $CH_2CH_2CH_3$), 1.29 (m, 2 H, CH_2CH_3), 1.43 [m, 2 H, $CH(NH)CH_2$], 1.55 (m, 1 H, NCH_2CH_2CHH), 1.64 (m, 2 H, NCH_2CH_2), 1.85 (m, 1 H, NCH_2CH_2CHH), 2.11 (dt, *J* = 8.5, 8.8 Hz, 1 H, NCHH), 2.58 (m, 1 H, NC*H*CH_2OCH_3), 2.71 (dd, *J* = 14.3, 5.0 Hz, 1 H, ArCH*H*), 2.84 (m, 1 H, C*H*NH), 2.96 (dd, *J* = 14.3, 5.5 Hz, 1 H, ArCH*H*), 3.04 (m, 1 H, NCH*H*), 3.12−3.46 (m, 5 H, SC*H*, CH_2OCH_3, SCH_2Ph), 3.27 (s, 3 H, OCH_3), 7.12−7.31 (m, 10 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 21.1 (NCH_2CH_2), 22.9 (CH_2CH_3), 26.1 ($NCH_2CH_2CH_2$), 28.9 ($CH_2CH_2CH_3$), 29.8 ($CH_2CH_2CH_2CH_3$), 36.2 (SCH_2), 37.9 ($ArCH_2$), 49.9 (SCH), 57.1 (NCH_2), 58.9 (OCH_3), 61.2 (CHNH), 66.5 (NCH), 74.8 (CH_2OCH_3), 126.0, 126.7, 128.0, 128.8, 128.9, 129.1 (Ar-*C*), 138.1, 140.1 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 426 (14) [M^+], 213 (6), 200 (13), 199 (100), 183 (8), 129 (6), 114 (6), 91 (25, C_7H_7), 70 (11), 45 (5) [CH_2OCH_3]. $C_{26}H_{38}N_2OS$ (426.66): calcd. C 73.19, H 8.98, N 6.57; found C 73.54, H 8.97, N 6.43.

(2*S*,1*R*,2*S*)-(−)-[1-Benzylsulfanyl-3-(phenylpropyl)pentyl][2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*R*,*S*)-7f]: This compound was prepared as described in GP 6, by 1,2-addition of $CeCl_3$/*n*BuLi (0.9 mmol) to hydrazone (*S*,*S*)-**6f** (0.12 g, 0.3 mmol). Compound (*S*,*R*,*S*)-**7f** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 6:1). Yield: 115 mg (87%); *de* ≥ 96%. R_f = 0.20 (pentane/Et_2O, 6:1). R_t = 13.69 min (CP-Sil-8, 180−10−300). $[\alpha]_D^{25}$ = −149.43, (*c* = 0.87,

$CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3084 (m), 3061 (m), 3027 (s), 2929 (vs), 2871 (vs), 1602 (m), 1495 (m), 1454 (vs), 1378 (m), 1340 (w), 1284 (w), 1238 (w), 1188 (m), 1127 (vs), 1100 (s), 1071 (m), 1029 (m), 917 (m), 752 (vs), 701 (vs), 667 (w), 567 (w), 473 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 0.90 (m, 1 H, $CHHCH_2CH_3$), 1.20 (m, 4 H, $CHHCH_2CH_3$, $ArCH_2CHH$), 1.40−1.80 (m, 5 H, NCH_2CH_2, $CH_2CH_2CH_2CH_3$, $ArCH_2CHH$) 1.85 (m, 2 H, $NCH_2CH_2CH_2$), 2.16 (dt, *J* = 8.4, 8.7 Hz, 1 H, NC*H*H), 2.54 (m, 2 H, $NCHCH_2OCH_3$, ArCH*H*), 2.74−2.88 (m, 3 H, SC*H*, ArC*H*H, C*H*NH), 3.13 (m, 1 H, NCH*H*), 3.30 (m, 1H $CHHOCH_3$), 3.34 (s, 3 H, OCH_3), 3.51 (dd, *J.* = 9.2, 3.5 Hz, 1H $CHHOCH_3$), 3.64 (d, *J* = 13.4 Hz, 1 H, SC*H*HPh) 3.72 (d, *J* = 13.4 Hz, 1 H, SC*H*HPh), 7.05−7.31 (m, 10 H, $CH_{arom.}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (CH_2CH_3), 20.9 (NCH_2CH_2), 23.0 (CH_2CH_3), 26.0 ($NCH_2CH_2CH_2$), 28.5 (CH_2 CH_2CH_3), 30.1, 31.5, ($CH_2CH_2CH_2CH_2CH_3$, $ArCH_2CH_2$), 33.6 ($ArCH_2$), 35.7 (SCH_2), 46.2 (SCH), 56.6 (NCH_2), 58.9 (OCH_3), 60.4 (CHNH), 66.1 (NCH), 74.5 (CH_2OCH_3), 125.5, 126.7, 128.0, 128.2, 128.4, 128.8 (Ar-*C*), 138.4, 141.7 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 440, (14) [M^+], 200 (13), 199 (100), 126 (6), 117 (9), 114 (8), 91 (25) [C_7H_7], 70 (11), 45 (5) [CH_2OCH_3]. $C_{27}H_{40}N_2OS$ (440.70): calcd. C 73.59, H 9.15, N 6.36; found C 73.42, H 9.42, N 6.22.

(2*S*,1*R*,2*S*)-(−)-[1-(1-Benzylsulfanyl-2-phenylethyl)heptyl][2-(methoxymethyl)pyrrolidin-1-yl]amine (*S*,*R*,*S*)-7g: This compound was prepared as described in GP 6, by 1,2-addition of $CeCl_3$/*n*-HexLi (0.9 mmol) to hydrazone (*S*,*S*)-**6e** (0.10 g, 0.3 mmol). Compound (*S*,*R*,*S*)-**7g** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 9:1). Yield: 115 mg (84%); *de* ≥ 96%. R_f = 0.27 (pentane/Et_2O, 6:1). $[\alpha]_D^{25}$ = −37.2, (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3061 (m), 3027 (s), 2926 (vs), 2856 (vs), 1602 (m), 1494 (w), 1454 (s), 1376 (w), 1239 (w), 1191 (m), 1124 (s), 1030 (w), 917 (m), 751 (m), 701 (vs), 625 (w), 565 (w), 514 (w), 472 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 1.22−1.33 (m, 4 H, $CH_2CH_2CH_3$), 1.43 [m, 2 H, $CH(NH)CH_2$], 1.55 (m, 1 H, NCH_2CH_2CHH), 1.64 (m, 2 H, NCH_2CH_2), 1.85 (m, 1 H, NCH_2CH_2CHH), 2.11 (m, 1 H, NC*H*H), 2.55 (m, 1 H, $NCHCH_2OCH_3$), 2.71 (dd, *J* = 14.3, 9.4 Hz, 1 H, ArCH*H*), 2.84 (m, 1 H, C*H*NH), 2.96 (dd, *J* = 14.3, 5.5 Hz, 1 H, ArC*H*H), 3.04 (m, 1 H, NCH*H*), 3.12−3.46 (m, 5 H, SC*H*, CH_2OCH_3, SCH_2Ph), 3.27 (s, 3 H, OCH_3), 7.12−7.31 (m, 10 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_2CH_3), 21.0 (NCH_2CH_2), 22.6 (CH_2CH_3), 26.1 ($NCH_2CH_2CH_2$), 26.6, 29.5, 30.1, 31.8 ($CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 36.3 ($SCH_2$), 37.9 ($ArCH_2$), 49.9 (SCH), 57.1 ($NCH_2$), 58.9 ($OCH_3$), 61.2 (CHNH), 66.4 (NCH), 74.8 (CH_2OCH_3), 126.0, 126.7, 128.0, 128.1, 128.9, 129.1 (Ar-*C*), 138.1, 140.1 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 454 (2) [M^+], 247 (11), 228 (12), 227 (100), 223 (7), 211 (5), 181 (5), 149 (6), 131 (7), 129 (11), 117 (6), 114 (20), 113 (5), 105 (5), 97 (6), 91 (40) [C_7H_7], 85 (7), 84 (6), 83 (5), 82 (5), 71 (8), 70 (18), 69 (9), 59 (5), 57 (8), 55 (8), 51 (8), 45 (8) [CH_2OCH_3]. $C_{28}H_{42}N_2OS$ (454.71) calcd. C 73.96, H 9.31, N 6.16, found C 73.52, H 9.42, N 6.22.

(2*S*,1*R*,2*S*)-(−)-[2-Benzylsulfanyl-1-methyl-3-phenylpropyl][2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*R*,*S*)-7h]: This compound was prepared as described in GP 6, by 1,2-addition of $CeCl_3$/MeLi (3.0 mmol) to hydrazone (*S*,*S*)-**6e** (0.37 g, 1.0 mmol). Compound (*S*,*R*,*S*)-**7h** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 6:1). Yield: 0.25 g (65%); *de* ≥ 96% R_f = 0.20 (pentane/Et_2O, 6:1). $[\alpha]_D^{25}$ = −40.8, (*c* = 1.1, $CHCl_3$), IR (film): $\tilde{\nu}$ = 3382 (w), 3084 (m), 3061 (m), 3027 (s), 2970 (vs), 2925 (vs), 2826 (s), 1721 (m), 1692 (m), 1692 (m), 1602 (m), 1495 (s), 1453 (vs), 1373 (m), 1328 (w), 1238 (m), 1197 (m), 1117 (vs), 1030 (m), 918 (m), 804 (w), 755 (vs), 701 (vs), 511 (w), 475 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.04 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.52 (m, 1 H, NCH_2CH_2CHH), 1.65 (m, 2 H, NCH_2CH_2), 1.85 (m, 1 H, NCH_2CH_2CHH), 2.15 (dt, *J* = 8.5, 8.8 Hz, 1 H, NC*H*H), 2.55 (m, 1 H, $NCHCH_2OCH_3$), 2.74 (dd, *J* = 14.3, 5.5 Hz, 1 H, ArCH*H*), 2.93 (dd, *J* = 14.3, 6.04 Hz, 2 H, ArC*H*H) 3.05 (m, 3 H, SC*H*, C*H*NH, NCH*H*), 3.23 (dd, *J* = 9.1, 6.0 Hz, 1H $CHHOCH_3$) 3.27 (s, 3 H, OCH_3), 3.34 (dd, *J* = 9.1, 4.4 Hz, 1H $CHHOCH_3$), 3.48 (d, *J* = 12.6 Hz, 1 H, SCH*H*Ph), 3.54 (d, *J* = 12.9 Hz, 1 H, SC*H*HPh), 7.15−7.30 (m, 10 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.0 (CH_3), 21.0 (NCH_2CH_2), 26.1 ($NCH_2CH_2CH_2$), 36.2 (SCH_2), 38.4 ($ArCH_2$), 51.2 (SCH), 56.0 (CHNH), 57.0 (NCH_2), 58.9 (OCH_3), 66.2 (NCH), 75.1 (CH_2OCH_3), 126.0, 126.7, 128.1, 128.2, 128.8, 129.0 (Ar-*C*), 138.2, 139.9 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 384 (3) [M^+], 261 (6), 259 (12), 193 (5), 158 (6), 157 (100), 153 (6), 147 (5), 131 (6), 129 (9), 125 (8), 114 (9), 92 (5), 91 (60, C_7H_7), 70 (15), 65 (6), 55 (6), 51 (5), 45 (15, CH_2OCH_3). HRMS: ($C_{23}H_{32}N_2OS$) calcd. 384.2235; found 384.2236.

(2*S*,1*R*,2*S*)-(−)-{1-[1-Benzylsulfanyl-2-(4-*tert*-butylphenyl)ethyl]-pentyl}[2-(methoxymethyl)pyrrolidin-1-yl]amine [(*S*,*R*,*S*)-7i]: This compound was prepared as described in GP 6, by 1,2-addition of $CeCl_3$/*n*BuLi (1.5 mmol) to hydrazone (*S*,*S*)-**6h** (0.21 g, 0.5 mmol). Compound (*S*,*R*,*S*)-**7i** was obtained as a colourless oil after purification by flash column chromatography (SiO_2, pentane/Et_2O, 6:1). Yield: 0.17 g (70%); *de* ≥ 96%. R_f = 0.43 (pentane/Et_2O, 5:1). $[\alpha]_D^{25}$ = −22.7 (*c* = 0.8, $CHCl_3$). IR spectrum ($CHCl_3$): $\tilde{\nu}$ = 3058 (w), 3024 (m), 2958 (vs), 2870 (vs), 1702 (s), 1602 (s), 1513 (m), 1494 (m), 1456 (m), 1393 (w), 1364 (m), 1268 (m), 1238 (w), 1217 (m), 1200 (m), 1110 (s), 1022 (w), 918 (m), 834 (m), 815 (w), 757 (vs), 701 (m), 666 (w), 565 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 1.15−1.36 (m, 4 H, $CH_2CH_2CH_3$), 1.32 [s. 9 H, $C(CH_3)_3$] 1.42 [m, 2 H, $CH(NH)CH_2$], 1.55 (m, 1 H, NCH_2CH_2CHH), 1.64 (m, 2 H, NCH_2CH_2), 1.85 (m, 1 H, NCH_2CH_2CHH), 2.11 (dt, *J* = 8.8, 8.5 Hz, 1 H, NC*H*H), 2.53 (m, 1 H, $NCHCH_2OCH_3$), 2.69 (dd, *J* = 14.3, 9.1 Hz, 1 H, ArCH*H*), 2.84 (m, 1 H, C*H*NH), 2.93 (dd, *J* = 14.3, 5.8 Hz, 1 H, ArC*H*H), 3.03 (m, 1 H, NCH*H*), 3.13−3.46 (m, 5 H, SC*H*, CH_2OCH_3, SCH_2Ph), 3.27 (s, 3 H, OCH_3), 7.09−7.32 (m, 9 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_2CH_3), 21.0 (NCH_2CH_2), 23.0 (CH_2CH_3), 26.1 ($NCH_2CH_2CH_2$), 28.9 ($CH_2CH_2CH_3$), 29.8 ($CH_2CH_2CH_2CH_3$), 31.4 [$C(CH_3)_3$], 34.4 [$C(CH_3)_3$], 36.3 (SCH_2), 37.4 ($ArCH_2$), 50.0 (SCH), 57.2 (NCH_2), 58.9 (OCH_3), 61.3 (CHNH), 66.5 (NCH), 74.8 (CH_2OCH_3), 124.9 126.7, 128.1, 128.7, 128.9 (Ar-*C*), 137.0, 138.2, 148.8 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 483 (6) [M^+], 482 (19), 359 (6), 200 (13), 199 (100), 195 (8), 183 (6), 129 (7), 114 (6), 91 (18), 70 (11), 57 (8), 45 (7). $C_{30}H_{46}N_2OS$ (482.77): calcd. C 74.64, H 9.60, N 5.80; found C 74.36, H 9.53, N 6.26.

General Procedure for the N,N Bond Cleavage and Protection of the Amino Groups of the Hydrazines (*S*,*R*,*S*)-7 (GP 7): The hydrazines (*S*,*R*,*S*)-**7** (1.0 equiv.) were dissolved in dry THF (10.0 mL/mmol), BH_3·THF (12 equiv.) was then added, and the solution was heated at reflux for 4 h. The reaction mixture was cooled to 0 °C and hydrolysed with 1 N HCl. The solvent was removed under reduced pressure and the residue was dissolved in saturated aqueous $NaHCO_3$ solution. The crude amine was extracted with CH_2Cl_2 and either purified by flash column chromatography or directly used in the next step. For that purpose, the solution of the crude amine, dissolved in CH_2Cl_2, was treated with K_2CO_3 (5.0 equiv.) and MocCl (5.0 equiv.) and heated at reflux for 2 days. After that,

the reaction mixture was quenched with water and the aqueous portion was extracted three times with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4 and the solvent was removed in a rotary evaporator. The residue was purified by flash column chromatography (SiO_2, pentane/Et_2O).

(2*S*,1*R*)-(+)-1-(1-Benzylsulfanyl-2-methylpropyl)pentylamine [(*S*,*R*)-8a]: This compound was prepared as described in GP 7; NN bond cleavage of hydrazine (*S*,*R*,*S*)-**7a** (70 mg, 0.18 mmol) with BH_3·THF (2.2 mL, 12.0 equiv.) afforded amine (*S*,*R*)-**8a** as a colourless oil after flash column chromatography (SiO_2, pentane/Et_2O, 1:1). Yield: 0.04 g (80%); *de*, *ee* ≥ 96%. R_f = 0.11 (pentane/Et_2O, 1:1). R_t = 10.34 min (CP-Sil-8, 120−10−300). $[\alpha]_D^{25}$ = +12.3 (*c* = 0.6, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3375 (w), 3083 (w), 3061 (m), 3027 (m), 2956 (vs), 2927 (vs), 2868 (s), 1602 (w), 1494 (m), 1456 (s), 1381 (m), 1364 (m), 1323 (w), 1237 (w), 1070 (w), 1028 (w), 827 (m), 767 (w), 700 (s), 564 (w), 474 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.1 Hz, 3 H, $CH_2CH_2CH_3$), 0.92 [d, *J* = 6.6 Hz, 3 H, $CH(CH_3)_2$], 1.03 [d, *J* = 6.6 Hz, 3 H, $CH(CH_3)_2$], 1.09−1.40 (m, 6 H, $CH_2CH_2CH_2CH_3$), 1.95 [m, 1 H, $CH(CH_3)_2$], 2.23 (dd, *J* = 5.2, 6.9 Hz, 1 H, SC*H*), 2.84 (m, 1 H, H_2NCH), 3.70 (d, *J* = 12.9 Hz, 1 H, SC*H*HPh), 3.76 (d, *J* = 12.9 Hz, 1 H, SCH*H*Ph), 7.20−7.31 (m, 5 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_2CH_3), 20.3, 21.4 (CH_3), 22.8 (CH_2CH_3), 28.9 ($CH_2CH_2CH_3$), 30.5 [$CH(CH_3)_2$], 33.0 ($CH_2CH_2CH_2CH_3$), 38.7 (SCH_2), 53.0 (H_2NCH), 61.7 (S*C*H), 126.8, 128.3, 129.0 (Ar-*C*), 138.7 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 265 (2) [M^+], 208 (1) [$M^+ - C_4H_9$], 180 (2), 112 (2), 91 (15) [C_7H_7], 86 (100) [$H_2NCH(CH_2)_3CH_3$], 85 (3), 69 (3), 65 (2), 56 (2), 55 (2). HRMS: calcd. 265.1864; found 265.1865.

(2*S*,1*R*)-(−)-(2-Benzylsulfanyl-1-butyl-4-methylpentyl)amine [(*S*,*R*)-8b]: This compound was prepared as described in GP 7; NN bond cleavage of hydrazine (*S*,*R*,*S*)-**7b** (0.43 g, 1.09 mmol) with BH_3·THF (13.0 mL, 12.0 equiv.) afforded amine (*S*,*R*)-**8b** as a colourless oil after flash column chromatography (SiO_2, pentane/Et_2O, 1:4). Yield: 0.12 g (39%); *de*, *ee* ≥ 96%. R_f = 0.10 (pentane/Et_2O, 1:4). R_t = 8.81 min (CP-Sil-8, 140−10−300). $[\alpha]_D^{25}$ = −86.9 (*c* = 0.9, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3372 (w), 3084 (w), 3062 (m), 3028 (m), 2955 (vs), 2928 (vs), 2867 (vs), 1729 (w), 1602 (m), 1494 (m), 1455 (s), 1382 (m), 1368 (m), 1267 (w), 1238 (w), 1168 (w), 1125 (w), 1071 (m), 1030 (w), 915 (w), 838 (m), 815 (m), 767 (m), 702 (s), 622 (w), 566 (w), 472 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.68 [d, *J* = 6.6 Hz, 3 H, $CH(CH_3)_2$], 0.86 [d, *J* = 6.6 Hz, 3 H, $CH(CH_3)_2$], 0.89 (t, *J* = 7.1 Hz, 3 H, $CH_2CH_2CH_3$), 1.18−1.40 [m, 8 H, $(CH_3)_2CHCH_2$, $CH_2CH_2CH_2CH_3$], 1.75 [m, 1 H, $CH(CH_3)_2$], 2.56 (dt, *J* = 2.8, 10.2 Hz, 1 H, SC*H*), 2.86 (dt, *J* = 2.8, 6.3 Hz, 1 H, H_2NCH), 3.68 (d, *J* = 13.5 Hz, 1 H, SC*H*HPh), 3.73 (d, *J* = 13.5 Hz, 1 H, SCH*H*Ph), 7.20−7.33 (m, 5 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_2CH_3), 21.4, 23.5 (CH_3), 22.7 (CH_2CH_3), 25.3 [$CH(CH_3)_2$], 29.0 ($CH_2CH_2CH_3$), 33.5 ($CH_2CH_2CH_2CH_3$), 35.9 (SCH_2), 38.1 [$CH_2CH(CH_3)$], 49.7 (S*C*H), 53.3 (H_2NCH), 126.8, 128.2, 128.8, 138.5 (Ar-*C*) ppm. MS (EI, 70 eV): *m*/*z* (%) = 128 (4), 114 (3), 91 (14, C_7H_7), 87 (6), 86 (100), 85 (3), 69 (4), 65 (2), 57 (2), 56 (4), 55 (2). $C_{17}H_{29}NS$ (279.48): calcd. C = 73.06, H 10.46, N 5.01; found C 72.60, H 10.37, N 5.36.

(2*S*,1*R*)-(+)-{1-[1-Benzylsulfanyl-2-(*o*-tolyl)ethyl]pentyl}amine [(*S*,*R*)-8c]: This compound was prepared as described in GP 7; NN bond cleavage of hydrazine (*S*,*R*,*S*)-**7c** (0.12 g, 0.27 mmol) with BH_3·THF (3.3 mL, 12.0 equiv.) afforded amine (*S*,*R*)-**8c** as a colourless oil after flash column chromatography (SiO_2, pentane/Et_2O, 1:4). Yield: 0.07 g (81%); *de*, *ee* ≥ 96%. R_f = 0.10 (pentane/Et_2O, 1:4). R_t = 13.48 min (CP-Sil-8, 140−10−300). $[\alpha]_D^{25}$ = +43.2 (*c* = 0.7, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3369 (w), 3061 (m), 3025 (m), 2955 (vs), 2927 (vs), 2857 (vs), 1946 (w), 1804 (w), 1729 (w), 1602 (m), 1493 (s), 1454 (s), 1380 (m), 1290 (w), 1262 (w), 1238 (m), 1197 (w), 1159 (w), 1125 (m), 1071 (m), 1052 (m),1029 (m), 945 (w), 916 (w), 851 (w), 821 (w), 765 (m), 744 (vs), 703 (vs), 620 (w), 565 (w), 465 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.1 Hz, 3 H, $CH_2CH_2CH_3$), 1.17−1.55 (m, 6 H, $CH_2CH_2CH_2CH_3$), 2.25 (s, 3 H, CH_3), 2.76 (m, 1 H, SC*H*), 2.82−2.96 (m, 2 H, $ArCH_2$, H_2NCH), 3.27 (d, *J* = 13.5 Hz, 1 H, SC*H*HPh), 3.45 (d, *J* = 13.5 Hz, 1 H, SCH*H*Ph), 7.05−7.26 (m, 9 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_2CH_3), 19.6 (CH_3), 22.7 (CH_2CH_3), 29.0 ($C\text{-}CH_2CH_2CH_3$), 33.2 ($CH_2CH_2CH_2CH_3$), 35.1 ($ArCH_2$), 36.5 (SCH_2), 53.3 (S*C*H), 54.2 (H_2NCH), 125.5, 126.2, 126.7, 128.1, 128.7, 130.1, 130.2 (Ar-*C*), 136.1, 137.6, 138.1 (Ar-C_q) ppm. MS (EI, 70 eV): *m*/*z* (%) = 245 (5), 236 (5) [$M^+ - C_7H_7$], 127 (5), 126 (23), 105 (12), 91 (25) [C_7H_7], 86 (100) [$H_2NCH(CH_2)_3CH_3$], 70 (5). HRMS: calcd. 327.2021; found 327.2019.

Methyl (2*S*,1*R*)-(+)-{1-[1-Benzylsulfanyl-2-(naphthalen-2-yl)ethyl]-pentyl}carbamate [(*S*,*R*)-8d]: This compound was prepared as described in GP 7; NN bond cleavage of hydrazine (*S*,*R*,*S*)-**7d** (0.47 g, 1.0 mmol) with BH_3·THF (12.0 mL, 12.0 equiv.) afforded the crude amine, which was directly converted into the carbamic acid methyl ester (*S*,*R*)-8d by treatment with K_2CO_3 (0.69 g, 5.0 mmol) and MocCl (0.38 mL, 5.0 mmol). The product was obtained as a colourless oil after flash column chromatography (SiO_2, pentane/Et_2O, 9:1). Yield: 0.23 g (55% over 2 steps); *de*, *ee* ≥ 96%. R_f = 0.34 (pentane/Et_2O, 3:1) R_t = 13.49 min (CP-Sil-8, 180−10−300). $[\alpha]_D^{25}$ = +135.4 (*c* = 0.7, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3406 (m), 3336 (m), 3056 (m), 3025 (m), 2954 (s), 2858 (m), 1721 (vs), 1632 (w), 1601 (m), 1508 (vs), 1454 (s), 1354 (m), 1292 (w), 1239 (s), 1193 (m), 1117 (m), 1075 (m), 1016 (m), 939 (w), 916 (w), 890 (w), 855 (m), 818 (m), 754 (s), 703 (s), 563 (w), 477 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3 H, $CH_2CH_2CH_3$), 1.18−1.60 (m, 6 H, $CH_2CH_2CH_2CH_3$), 2.90−3.00 (m, 3 H, $ArCH_2$, SC*H*), 3.08 (m, 1 H, SC*H*HPh), 3.34 (d, *J* = 13.2 Hz, 1 H, SCH*H*Ph), 3.57 (s, 3 H, OCH_3), 3.80 (m, 1 H, C*H*N), 4.84 (d, *J* = 9.6 Hz, 1 H, N*H*), 7.00−7.80 (m, 12 H, $CH_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3 (CH_3), 22.8 (CH_2CH_3), 28.6 ($CH_2CH_2CH_3$), 30.1 ($CH_2CH_2CH_2CH_3$), 37.4 (SCH_2), 41.2 ($ArCH_2$), 52.3 (OCH_3), 53.3 (S*C*H), 54.3 (H_2NCH), 125.8, 126.3, 127.2, 127.9, 128.0, 128.3, 128.7, 128.9, 129.2 (Ar-*C*), 132.6, 133.8, 136.8, 138.3 (Ar-C_q), 156.9 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 421 (1) [M^+], 298 (15), 297 (75), 280 (6), 278 (13), 255 (10), 240 (20), 186 (5), 185 (10), 165 (5), 145 (8), 144 (100), 141 (23), 91 (28) [C_7H_7], 88 (17). HRMS: calcd. 421.2076; found 421.2075.

Methyl (2*S*,1*R*)-(+)-[1-(1-Benzylsulfanyl-2-phenylethyl)pentyl]carbamate [(*S*,*R*)-8e]: This compound was prepared as described in GP 7; NN bond cleavage of hydrazine (*S*,*R*,*S*)-**7e** (2.13 g, 5.0 mmol) with 60.0 mL (12.0 equiv.) BH_3·THF afforded the crude amine, which was directly converted into the carbamic acid methyl ester (*S*,*R*)-**8e** by treatment with K_2CO_3 (3.46 g, 25.0 mmol) and MocCl (1.93 mL, 25.0 mmol). The product was obtained as a colourless solid after flash column chromatography (SiO_2, pentane/Et_2O, 6:1); m.p. 47.5 °C. Yield: 1.71 g (92% over 2 steps); *de*, *ee* ≥ 96%. R_f = 0.13 (pentane/Et_2O, 9:1). $[\alpha]_D^{25}$ = +108.9 (*c* = 1.0, $CHCl_3$) IR ($CHCl_3$): $\tilde{\nu}$ = 3405 (m), 3336 (m), 3084 (w), 3061 (m), 3027 (m), 2954 (vs), 2859 (m), 1723 (vs), 1602 (w), 1507 (vs), 1454 (s), 1352 (m), 1291 (m), 1241 (s), 1194 (m), 1156 (w), 1115 (w), 1074 (m), 1031 (m), 938 (w), 916 (w), 756 (m), 701 (vs), 506 (w), 470 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.9 Hz, 3 H, $CH_2CH_2CH_3$), 1.18−1.60 (m, 6 H, $CH_2CH_2CH_2CH_3$), 2.75−2.98 (m, 3 H, $ArCH_2$, SC*H*), 3.10 (d, *J* = 13.2 Hz, 1 H, SC*H*HPh), 3.38

(d, J = 12.9 Hz, 1 H, SCH*H*Ph), 3.56 (s, 3 H, OCH_3), 3.74 (m, 1 H, C*H*N), 4.83 (d, J = 9.6 Hz, 1 H, N*H*), 7.04−7.33 (m, 10 H, C$H_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (*C*H_3), 22.5 (*C*H_2CH$_3$), 28.3 (*C*H_2CH$_2$CH$_3$), 29.7 (*C*H_2CH$_2$CH$_2$CH$_3$), 36.9 (S*C*H$_2$), 40.8 (Ar*C*H$_2$), 51.9 (O*C*H$_3$), 53.1 (S*C*H), 53.7 (*C*HNH), 126.6, 126.9, 128.4, 128.9, 129.0 129.4 (Ar-*C*), 138.1, 139.0 (Ar-C_q), 156.5 (*C*=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 371 (1) [M^+], 296 (10), 280 (7), 248 (5), 247 (27), 228 (11), 205 (8), 145 (8), 144 (100), 143 (5), 91 (10), 88 (17). $C_{22}H_{29}NO_2S$ (371.55): calcd. C 71.12, H 7.87, N 3.77; found C 70.71, H 7.86, N 4.14. After column flash chromatography the compound was recrystallised from *n*-heptane in order to provide crystals for X-ray structure analysis.

Methyl (2*S*,1*R*)-(+)-[1-(1-Benzylsulfanyl-3-phenylpropyl)pentyl]carbamate [(*S*,*R*)-8f]: This compound was prepared as described in GP 7; NN bond cleavage of hydrazine (*S*,*R*,*S*)-**7f** (0.47 g, 1.1 mmol) with BH_3·THF (14.0 mL, 12.0 equiv.) afforded the crude amine, which was directly converted into the carbamic acid methyl ester (*S*,*R*)-**8f** by treatment with K_2CO_3 (0.74 g, 5.4 mmol) and MocCl (0.41 mL, 5.4 mmol). The product was obtained after flash column chromatography (SiO_2, pentane/Et_2O, 9:1) as a colourless solid; m.p. 48.5 °C. Yield: 0.28 g (68% over 2 steps); *de*, *ee* ≥ 96%. R_f = 0.18 (pentane/Et_2O, 9:1). $[\alpha]_D^{25}$ = +22.9 (*c* = 1.0, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3363 (s), 3085 (w), 3059 (m), 3029 (m), 2940 (s), 2855 (m), 1699 (vs), 1602 (w), 1525 (vs), 1496 (m), 1454 (m), 1351 (m), 1287 (m), 1243 (s), 1187 (m), 1120 (m), 1088 (m), 1074 (m), 1004 (m), 923 (w), 779 (w), 766 (w), 740 (m), 699 (s), 639 (w), 565 (w), 494 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, J = 6.9 Hz, 3 H, $CH_2CH_2CH_3$), 1.15−1.92 (m, 8 H, $CH_2CH_2CH_2CH_3$, PhCH_2), 2.52 (m, 1 H, PhCH_2C*H*H), 2.65 (m, 1 H, SC*H*), 2.80 (m, 1 H, PhCH_2CH*H*), 3.63 (s, 3 H, OCH_3), 3.66 (d, J = 12.91 Hz, 1 H, SCH*H*Ph), 3.74 (d, J = 13.5 Hz, 1 H, SCH*H*Ph), 3.81 (m, 1 H, C*H*NH), 4.77 (d, J = 9.89 Hz, 1 H, N*H*), 7.10−7.32 (m, 10 H, C$H_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (*C*H_3), 22.5 (*C*H_2CH$_3$), 28.3 (*C*H_2CH$_2$CH$_3$), 30.1, 33.5, 35.1 (Ar*C*H_2*C*H_2, *C*H_2CH$_2$CH$_2$CH$_3$), 37.1 (S*C*H$_2$), 50.8 (S*C*H), 52.0 (O*C*H$_3$), 53.7 (*C*HNH), 126.0, 127.1, 128.4, 128.5, 128.6, 129.0 (Ar-*C*), 138.5, 141.6 (Ar-C_q), 156.7 (*C*=O). ppm. MS (EI, 70 eV): *m*/*z* (%) = 385 (6) [M^+], 310 (11), 294 (10), 243 (5), 242 (29), 145 (8), 144 (100), 117 (16), 91 (26) [C_7H_7], 88 (16). $C_{23}H_{31}NO_2S$ (385.57): calcd. C 71.65, H 8.10, N 3.63; found C 71.49, H 8.34, N 3.51.

Methyl (2*S*,1*R*)-(+)-[1-(1-Benzylsulfanyl-2-phenylethyl)heptyl]carbamate [(*S*,*R*)-8g]: This compound was prepared as described in GP 7; NN bond cleavage of hydrazine (*S*,*R*,*S*)-**7g** (0.72 g, 1.6 mmol) with BH_3·THF (19.0 mL, 12.0 equiv.) afforded the crude amine, which was directly converted into the carbamic acid methyl ester (*S*,*R*)-**8g** by treatment with K_2CO_3 (1.10 g, 8.0 mmol) and MocCl (0.61 mL, 8.0 mmol). The product was obtained as a colourless oil after flash column chromatography (SiO_2, pentane/Et_2O, 9:1). Yield: 0.36 g (57% over 2 steps); *de*, *ee* ≥ 96%. R_f = 0.20 (pentane/Et_2O, 9:1). $[\alpha]_D^{25}$ = +104.2 (*c* = 1.6, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3334 (m), 3083 (w), 3061 (m), 3027 (s), 2927 (vs), 2856 (s), 1722 (vs), 1602 (m), 1507 (m), 1454 (vs), 1355 (m), 1240 (s), 1193 (m), 1118 (m), 1073 (m), 1031 (m), 937 (w), 916 (w), 756 (m), 701 (vs), 505 (w), 470 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 6.4 Hz, 3 H, CH_3), 1.17−1.62 [m, 10 H, (CH_2)$_5$CH$_3$], 2.75−2.98 (m, 3 H, CH_2Ph, SC*H*), 3.10 (d, J = 13.1 Hz, 1 H, SC*H*HPh), 3.38 (d, J = 13.1 Hz, 1 H, SCH*H*Ph), 3.56 (s, 3 H, OCH_3), 3.74 (m, 1 H, C*H*NH), 4.81 (d, J = 9.7 Hz, 1 H, N*H*), 7.05−7.35 (m, 10 H, C$H_{arom.}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (*C*H_3), 22.6 (*C*H_2CH$_3$), 26.1 [*C*H_2(CH$_2$)$_3$CH$_3$], 29.1 [*C*H_2(CH$_2$)$_2$CH$_3$], 30.0 (*C*H_2CH$_2$CH$_3$), 31.7 [*C*H_2(CH$_2$)$_4$CH$_3$], 37.0 (S*C*H$_2$), 40.8 (Ar*C*H$_2$), 51.9 (O*C*H$_3$), 53.1 (S*C*H), 53.7 (*C*HNH), 126.6, 126.9, 128.4, 128.7, 128.9, 129.4 (Ar-*C*), 138.1, 139.0 (Ar-C_q), 156.5 (*C*=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 324 (10), 308 (8), 276 (7), 275 (30), 233 (9), 228 (11), 226 (5), 173 (12), 172 (100), 135 (8), 92 (5), 91 (58), 88 (34), 76 (5), 59 (7), 55 (12), 45 (7). $C_{24}H_{33}NO_2S$ (399.60): calcd. C 72.14, H 8.32, N 3.51; found C 72.15, H 8.34, N 3.99.

Methyl (2*S*,1*R*)-(+)-(2-Benzylsulfanyl-1-methyl-3-phenylpropyl)carbamate [(*S*,*R*)-8h]: This compound was prepared as described in GP 7; NN bond cleavage of hydrazine (*S*,*R*,*S*)-**7h** (0.48 g, 1.2 mmol) with BH_3·THF (15.0 mL, 12.0 equiv.) afforded the crude amine, which was directly converted into the carbamic acid methyl ester (*S*,*R*)-**8h** by treatment with K_2CO_3 (0.86 g, 6.2 mmol) and MocCl (0.48 mL, 6.2 mmol). The product was obtained as a colourless oil after flash column chromatography (SiO_2, pentane/Et_2O, 6:1). Yield: 0.29 g (71% over 2 steps); *de*, *ee* ≥ 96%. R_f = 0.12 (pentane/Et_2O, 6:1). $[\alpha]_D^{25}$ = +113.4 (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3408 (m), 3336 (m), 3083 (m), 3061 (m), 3026 (m), 2973 (m), 2948 (m), 2845 (s), 1804 (w), 1720 (vs), 1602 (m), 1505 (vs), 1453 (vs), 1380 (m), 1351 (m), 1240 (s), 1194 (m), 1115 (m), 1070 (s), 1031 (m), 966 (w), 936 (w), 843 (w), 804 (w), 757 (vs), 702 (vs), 668 (w) 505 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (d, J = 6.6 Hz, 3 H, CH_3), 2.78 (m, 1 H, CH*H*Ph), 2.89 (m, 2 H, C*H*HPh, SC*H*), 3.16 (d, J = 13.2 Hz, 1 H, SC*H*HPh), 3.41 (d, J = 13.2 Hz, 1 H, SCH*H*Ph), 3.56 (s, 3 H, OCH_3), 3.87 (m, 1 H, C*H*NH), 4.97 (d, J = 8.5 Hz, 1 H, N*H*), 7.06−7.33 (m, 10 H, C$H_{arom.}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.8 (*C*H_3), 36.8 (S*C*H$_2$), 41.0 (Ar*C*H$_2$), 48.9 (*C*HNH), 51.8 (O*C*H$_3$), 52.9 (S*C*H), 126.4, 126.8, 128.25, 128.28, 128.7, 129.1 (Ar-*C*), 137.9, 138.7 (Ar-C_q), 155.7 (*C*=O) ppm, MS (EI, 70 eV): *m*/*z* (%) = 254 (7), 228 (5), 227 (6), 205 (22), 193 (10), 163 (8), 149 (12), 135 (11), 130 (6), 104 (5), 103 (5), 102 (59), 92 (9), 91 (100) [C_7H_7], 70 (5), 65 (12), 59 (7), 58 (11), 57 (9), 56 (5), 55 (6), 45 (17). HRMS: calcd. 297.1187 (M^+ − CH_4O); found 297.1187.

X-ray Crystallographic Study: X-ray Crystallographic Study of (*S*,*R*)-**8e**. Suitable crystals were obtained by crystallisation from *n*-heptane. The compound ($C_{22}H_{29}NO_2S$; M_r = 371.55) crystallises in orthorhombic space group $P2_12_12$ (no.18) with cell dimensions a = 17.715(3), b = 21.850(1), and c = 5.3278(4) Å. With Z = 4 the cell volume V = 2062.2(4) Å^3 results in a calculated density of $d_{calcd.}$ = 1.197 g·cm^{-3}. 4797 reflections were collected at T = 150 K on an ENRAF-NONIUS CAD4 diffractometer by use of graphite-monochromated Cu-K_α-radiation (λ = 1.54179 Å) in the ω)/2Θ mode. Data collection covered the range $-6 \le h \le 6$, $-21 \le k \le 21$, and $-25 \le l \le 27$ up to Θ_{max} = 72.7°. Lorentz and polarisation correction were applied to the diffraction data but no absorption correction (μ = 1.503 mm^{-1}) was made. The structure was solved by direct methods as implemented in the Xtal3.7 suite of crystallographic routines[27] by employment of GENSIN to generate the structure-invariant relationships and GENTAN for the general tangent phasing procedure. 4015 observed reflections [$I > 2\sigma(I)$] were included in the final full-matrix, least-squares refinement on F involving 347 parameters and converging at $R(R_w)$ = 0.061(0.065, w = l/[20σ(F)$^{-2}$]), a final shift/error <0.0002, S = 1.075, and a residual electron density of −1.68/1.00 e·Å^{-3}. X_{abs}= −0.014(45)[28] for the structure shown in Figure 2. All hydrogen positions except H^6 could be located in a difference Fourier map and were refined isotropically. CCDC 207541 contains the supplementary crystallographic data for structure (*S*,*R*)-**8e**. These data can be obtained free of charge at www.ccdc.cam.ac.uk./conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1 EZ, UK; fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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