Enantioselective Synthesis of Hydroxy-Substituted DBN-Type Amidines as Potential Chiral Catalysts

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The synthesis and X-ray crystal structures of three enantiopure hydroxy-substituted amidines of the DBN-type are described. The key starting material, a 5-(phenylsulfonyl)pyrrolidin-2-one, was obtained by an oxazaborolidine-catalysed reductive desymmetrization of a *meso*-imide and was functionalized through *N*-acyliminium ion chemistry. The hydroxy groups were introduced by ozonolysis or reduction. Preliminary results on the use of the hydroxyamidines as chiral, bifunctional catalysts in selected Michael reactions are described.

Introduction

Catalytic asymmetric synthesis is one of the most challenging topics in contemporary organic chemistry.[1] A great deal of research in this area has focused on the utilization of transition-metal-containing catalysts. The application of purely organic compounds as homogeneous catalysts, however, has remained a relatively unexplored field. The potential advantages of such a catalytic system include low costs, a low level of toxicity, and high stability under the reaction conditions. Notable examples are an (*S*)-proline-catalysed aldol cyclization,[2] enantioselective reactions catalysed by cinchonidine **1** and other members of the cinchona alkaloids,[3] and the addition of HCN to benzaldehyde, catalysed by the dipeptide **2**.[4] More recently, Corey and co-workers modified the structure of cinchonidine to give the phase-transfer catalyst **3**, which was applied in the enantioselective alkylation of imino esters.[5] A very recent example was reported by the same group; in this case the C_2-symmetric guanidine **4** was employed in catalytic asymmetric Strecker reactions.[6] Alternatively, in the group of Jacobsen, a combinatorial-chemistry approach was used to develop the amino-acid-derived catalyst **5**, which was also applied in asymmetric Strecker reactions.[7] In addition, the topic of asymmetric conjugate addition reactions has been covered in a recent review article.[8]

The excellent catalytic properties of bases **1** and **2** was ascribed to their bifunctionality. In a base-catalysed process, the basic moiety in the catalyst is believed to activate the nucleophile, while, at the same time, the hydrogen-donating group can activate the electrophile through hydrogen bonding. In this way both the reaction partners are activated and held closely together to allow a successful and enantioselective reaction. Amino alcohols such as **1** are, however, limited in their applicability as catalysts due to the relatively low basicity of the nitrogen atom. A more basic functionality in the chiral catalyst might extend the scope of organic base catalysis. The amidine function is an example of such a stronger base.[9] The combination of an amidine with an alcohol could, therefore, possibly lead to a catalytic system possessing enantioselectivity-inducing properties. Previous research from our group resulted in the synthesis of hydroxy amidine **6**, which was prepared in eleven steps from (*S*)-pyroglutamic acid.[10]

Because hydroxy amidine **6** displayed only limited enantioselectivity in base-catalysed reactions, we decided to design new types of hydroxy amidines (viz. **7**–**9**). These enantiopure bases feature an additional six-membered ring, which to some extent could block the top face of the basic molecule. Furthermore, the six-membered ring renders the system more hydrophobic than **6**, so that better solubility in apolar solvents is achieved. These features might positively influence the asymmetry-inducing properties. This article describes the synthesis of amidine **7**, which contains an ethyl side chain with a primary hydroxy group, and of the diastereomeric amidines **8** and **9**, which contain a phenylethyl side chain with a secondary hydroxy group. Both dia-

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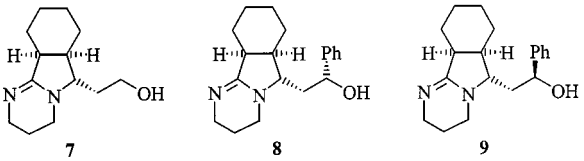
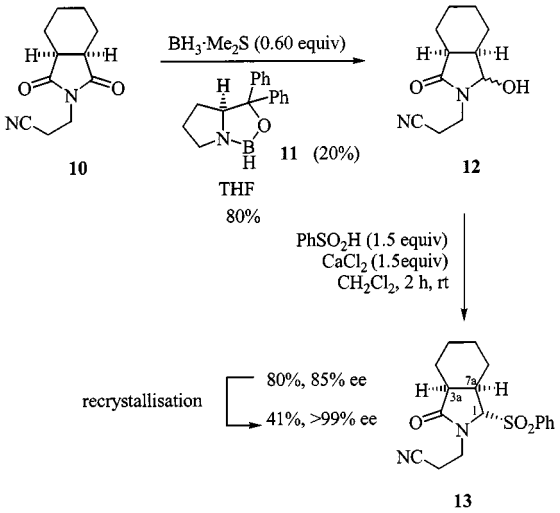
stereomers were synthesized in order to investigate a possible matched/mismatched selectivity.



Results and Discussion

A suitable intermediate to arrive at the targeted hydroxyamidines **7**−**9** was deemed to be sulfonyllactam **13** (Scheme 1). Lactam **13** was obtained from an oxazaborolidine-catalysed reductive desymmetrization[11] of the corresponding *meso*-imide **10** according to a recently published procedure developed by our group.[12] Compared to this published procedure, we have greatly improved the enantioselective synthesis of lactam **12** by using neat $BH_3{\cdot}Me_2S$ instead of $BH_3{\cdot}THF$.[12a] In this way, more reproducible results were obtained without affecting yields and ee's. Thus, when imide **10** was treated with a mixture of $BH_3{\cdot}Me_2S$ (0.60 equiv.) and oxazaborolidine **11** (20 mol-%), the hydroxylactams **12** were obtained in 80% yield (Scheme 1). Rather than converting the mixture of hydroxylactams into the ethoxylactam,[12a] we treated it directly with benzenesulfinic acid and $CaCl_2$, to afford the sulfone **13** in 80% yield and 85% ee. After a single recrystallization, enantiopure material was obtained (> 99% ee, 32% overall yield from **10**) as crystals (m.p. 95−96.5°C) which were suitable for X-ray analysis (Figure 1). The crystal structure clearly showed the *trans* stereochemistry at C1 and C7a, and confirmed the (1*S*,3a-*S*,7a*R*) absolute configuration that was determined previously by chemical correlation.[10]



Scheme 1. Synthesis of sulfonyllactam **13**

The synthesis of our first target molecule, hydroxyamidine **7**, is detailed in Scheme 2. Treatment of sulfone **13** with allyltrimethylsilane in the presence of $BF_3{\cdot}OEt_2$ provided

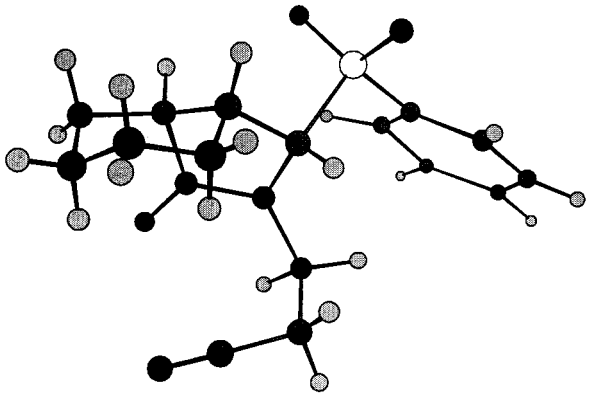
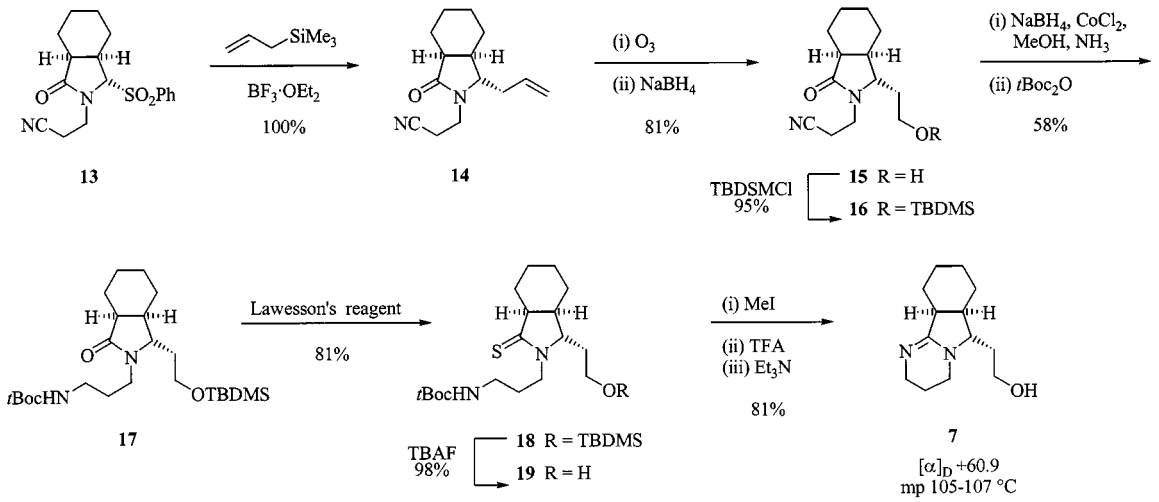


Figure 1. Crystal structure of **13**

the allylated lactam **14** in quantitative yield. This reaction, which presumably proceeds via an *N*-acyliminium ion,[13] took place in > 98% de, as shown by ^1H- and ^{13}C NMR data. The alcohol group was introduced by ozonolysis of the double bond and subsequent in situ reduction with $NaBH_4$ to afford **15** in 81% yield. The primary alcohol was protected with a *tert*-butyldimethylsilyl group to give **16** in 95% yield, after which the amidine moiety could be introduced with chemistry developed previously in our group.[10] This involved a series of reactions, the first of which is reduction of the nitrile function. Treatment of **16** with $CoCl_2$ (2 equiv.) and an excess of $NaBH_4$ in $MeOH/NH_3$ (to prevent the formation of dimers)[14] resulted in the formation of the amine which was not purified, but immediately protected with a *t*Boc group to afford **17** in 58% yield after purification by column chromatography. Direct cyclization to the lactam proved not possible at this stage. Therefore, a mild cyclization route was followed.[10] Treatment of **16** with Lawesson's reagent[15] afforded thiolactam **18** in 81% yield. After the alcohol group was deprotected with TBAF, **19** was treated with neat MeI to give the methylthioiminium salt. The *t*Boc group was then removed with trifluoroacetic acid; cyclization of the resulting amine onto the activated lactam was promoted by an excess of Et_3N, with the hydroxyamidine **7** forming in 81% yield. The product was purified by recrystallization from benzene to afford crystals suitable for X-ray analysis (Figure 2). The crystal structure clearly showed the *trans* relationship between the *cis*-fused six-membered ring and the two-carbon side chain. The C=N bond length was found to be 1.28 Å and the C−N bond length 1.36 Å.

Next, the syntheses of amidines **8** and **9** were investigated. It was envisioned that both compounds might be derived from ketone **21** (Equation 1). Extensive experimentation eventually showed that the most efficient route to **21** involved treatment of sulfone **13** with the enol acetate of acetophenone[16] in the presence of $AlCl_3$; this reaction afforded **21** in 89% yield (for example reaction with the commercially available trimethylsilyl enol ether of acetophenone and $BF_3{\cdot}OEt_2$ afforded **21** in only 21%). As expected, this *N*-acyliminium ion mediated reaction occurred with complete diastereoselectivity.



Scheme 2. Synthesis of hydroxyamidine **7**

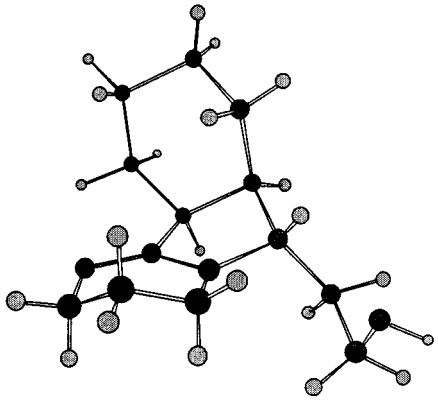
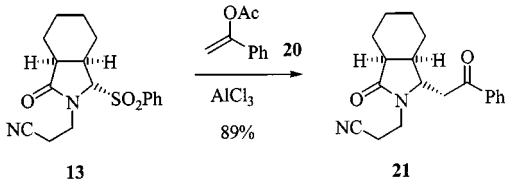
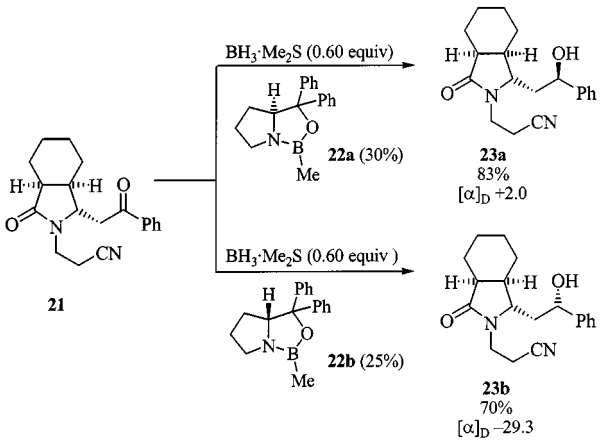


Figure 2. Crystal structure of **7**



Reduction of ketone **21** with $NaBH_4$ afforded a 4:3 mixture of diastereomers **23a** and **23b**, which could not be separated by flash column chromatography or recrystallization. Therefore, the application of a chiral reducing reagent in this reaction was investigated. It was found that the combination of borane and an oxazaborolidine was the best choice to obtain the desired products as single diastereomers. Whereas the *B*-H oxazaborolidine **11** was the reagent of choice for the enantioselective reduction of *meso*-imides (Scheme 1), we preferred to use the corresponding *B*-Me catalysts **22a** and **22b** in this case (Scheme 3), because they are significantly more stable and display equal selectivity.[11] The *B*-Me catalysts are nowadays commercially available, but can also be synthesized from the appropriate diphenylprolinol enantiomer and trimethylboroxine.[17] Treatment of **21** with $BH_3{\cdot}Me_2S$ and oxazaborolidine **22a** (30%) afforded alcohol **23a** in > 98% de according to ^1H- and ^{13}C NMR spectroscopy. The supposed (*R*) configuration at the benzylic position could not be confirmed by NMR data, but was proven later by the X-ray crystal structure of the corresponding hydroxyamidine (see Figure 3). On the other hand, when ketone **21** was treated with $BH_3{\cdot}Me_2S$ and oxazaborolidine **22b** [derived from (*R*)-diphenylprolinol], the (*S*)-alcohol **22b** was formed as a single diastereomer, thus confirming the complete reagent control of the oxazaborolidines.



Scheme 3. Reduction of ketone **21**

Both alcohols **23a** and **23b** underwent the previously described chemical reactions that lead to amidines (Scheme 4). The hydroxy groups were protected as *tert*-butyldimethylsilyl ethers with TBDSMOTf; followed by an identical series of events to afford the hydroxyamidines **8** and **9** in comparable yields. Amidine **8** was obtained as a solid which, upon recrystallization, gave crystals that were analysed by an X-ray crystal structure determination (m.p. 104−107°C). From this crystal structure (Figure 3) it became clear that in the solid state, two molecules of **8** were linked to one molecule of H_2O through four hydrogen bonds. Amidine **9** was obtained as a foam and, in our hands, could not be crystallized.

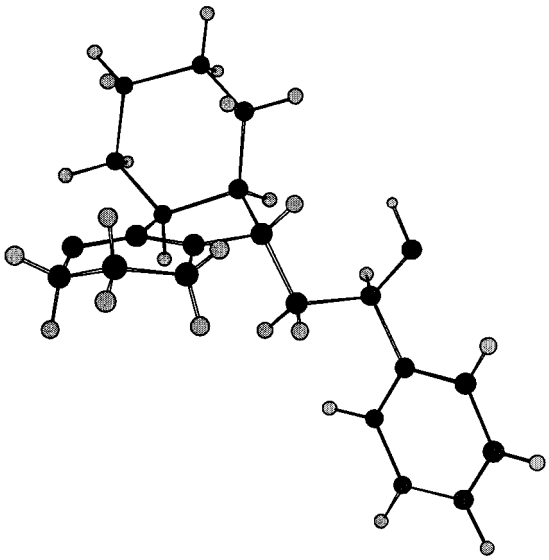
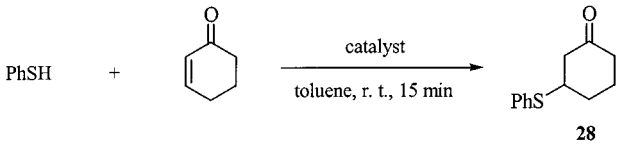


Figure 3. Crystal structure of **8**

The hydroxy amidines **7**−**9** were tested for their catalytic activity and enantioselectivity. A well-studied Michael-type addition, the addition of thiophenol to cyclohexenone, was chosen as an asymmetric test reaction.[3a] The results are summarized in Table 1. The reaction proceeded well in the presence of 1−5 mol-% of catalyst to give thioether **28** in good yields (72−100%). The highest optical purity (23%) was obtained with hydroxyamidine **7** that contains the primary alcohol group. Catalysts **8** and **9** gave the product in 15% and 14% o.p., respectively. Remarkably, the sign of optical rotation of product **28** was independent of the stereochemistry in the side chain.

Carbon nucleophiles such as nitromethane, 2,4-pentanedione, and dimethyl malonate also reacted with cyclohexenone in the presence of catalyst **7**. In all cases, the products were obtained in good yields (56−70%). An optically active product was obtained only with dimethyl malonate (Equation 2). When 25% of **7** was used, product **29** was obtained in 56% yield and 35% o.p.[18]

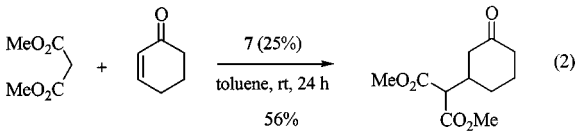
Table 1. Conjugate addition results



28

Entry	Catalyst	Amount (%)	Yield (%)	$[\alpha]_{578}$	o.p. (%)[a]
1	**7**	5	72	+22.4	23
2	**8**	5	100	+14.0	15
3	**9**	1	86	+13.8	14

[a] Determined from the known specific rotation.[3a]



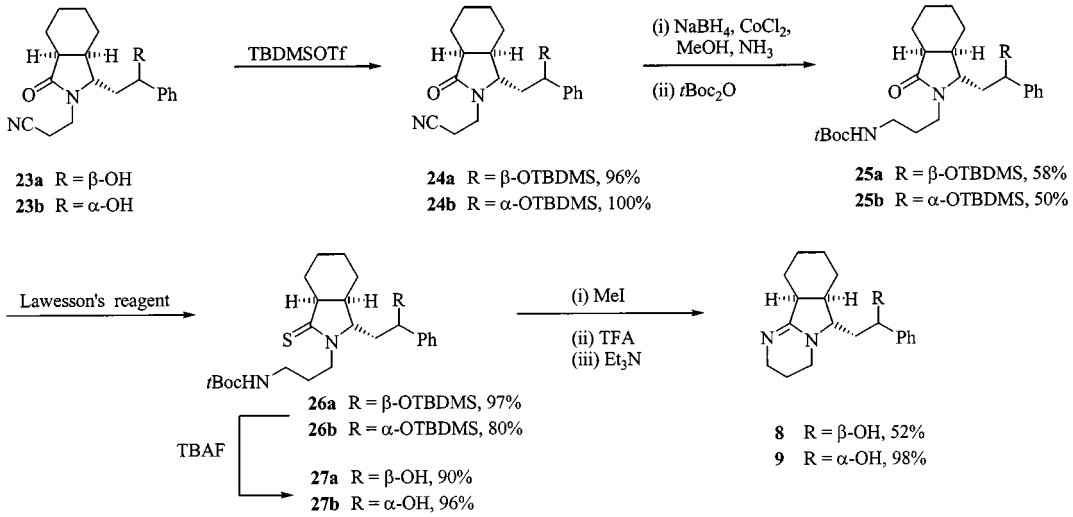
(2)

29

$[\alpha]_D$ +1.4, o.p[18] 35%

Conclusion

In conclusion, three enantiopure hydroxyamidines were synthesized from the readily available sulfonyllactam **13** as the starting material. These compounds belong to a structural class of amidines which is virtually unknown in the literature. The structures of **7** and **8** were proven by X-ray crystal structure determinations. The most simple catalyst **7**, containing a primary alcohol, effected slightly better enantioselectivity than **8** and **9**: The introduction of an extra, phenyl-substituted secondary stereocentre did not lead to higher selectivities. Moreover, both diastereomers of cata-



Scheme 4. Synthesis of hydroxyamidines **8** and **9**

lysts **8** and **9** gave the same enantiomer of the Michael-type product **28**; this implies that this stereocentre does not play an essential role in the enantioselective catalysis. Despite the fact that these amidines showed satisfactory catalytic activity, it is evident that the enantioselectivity-inducing properties are inferior compared to previously obtained ee′s.[3]

Further studies towards new hydroxyamidines will focus on the relative orientation of the amidine and the hydroxy functions in order to search for better enantioselectivity in base-catalysed processes

Experimental Section

General: All reactions were carried out under dry nitrogen, unless described otherwise. Standard syringe techniques were applied for transfer of dry solvents and air- or moisture-sensitive reagents. − IR: Bruker IFS 28 (absorptions are reported in cm^{-1}). − NMR: Bruker AC 200, Bruker WM 250, Bruker ARX 400 (200, 250 or 400 MHz for ^1H; 50, 63, or 100 MHz for ^{13}C). NMR spectra were obtained from $CDCl_3$ solutions. Chemical shifts are reported in δ relative to an internal standard of residual chloroform (δ = 7.27 for ^1H NMR and δ = 77.0 for ^{13}C NMR). − HRMS: JEOL JMS SX/SX102A, coupled to a JEOL MS-MP7000. − Elemental analyses: Vario EL. − Optical rotations: Perkin−Elmer 241 (in the indicated solvent at ambient temerature). − Melting points and boiling points are uncorrected. − Ethyl acetate (EtOAc) and petroleum ether 60−80 (PE) were distilled before use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled from sodium benzophenone ketyl prior to use. CH_2Cl_2, toluene, CH_3CN, EtOH, and MeOH were dried and distilled from CaH_2 or $LiAlH_4$ and stored over 4 Å (MeOH over 3 Å) molecular sieves under nitrogen. Et_3N and pyridine were dried and distilled from KOH pellets and stored over KOH pellets under nitrogen. − Compounds **10−14** were described previously.[12a]

Crystallographic Data for 13: Orthorhombic crystals, $P2_12_12_1$, a = 8.4904(5), b = 11.0928(5), c = 17.4835(11) Å, V = 1646.6(2) $Å^3$, Z = 4, D_X = 1.34 g cm^{-3}, λ (Cu-K_α) = 1.5418 Å, μ (Cu-K_α) = 18.9 cm^{-1}, F(000) = 704, −25°C. Final R = 0.057 for 1870 observed reflections.[19]

3-[(1*R*,3a*S*,7a*R*)-1-(2-Hydroxyethyl)-3-oxooctahydroisoindol-2-yl)]-propionitrile (15): Ozone was bubbled through a solution of **13** (28.8 mg, 0.12 mmol) in MeOH (2 mL) at −78°C. After 2 min, the solution turned blue. The ozone was replaced with nitrogen and after 5 min, $NaBH_4$ (47 mg, 1.2 mmol) was added in portions. Stirring was continued for 15 min at −78°C and 1 h at room temp. The reaction mixture was quenched with 5% aqueous HCl. The water layer was extracted (CH_2Cl_2, 5 ×) and the combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. After flash chromatography (EtOAc) **15** (23 mg, 0.10 mmol, 81%) was obtained as a colourless oil. − IR (film): $\tilde{\nu}$ = 3410 cm^{-1}, 2249, 1667. − ^1H NMR (400 MHz): δ = 3.85−3.79 (dt, 1 H, J = 13.9, 6.5 Hz, NC*H*H), 3.69−3.62 (m, 2 H, CH_2OH), 3.33−3.30 (dd, 1 H, J = 8.7, 4.2 Hz NC*H*), 3.25−3.18 (dt, 1 H, J = 13.9, 6.7 Hz, NCH*H*), 2.73−2.65 (m, 1 H, NCH_2CHH), 2.62−2.54 (m, 2 H, C*H*C(O) and NCH_2CHH), 2.17−2.11 (dt, 1 H, J = 10.5, 5.9 Hz, NCHC*H*), 2.06−2.02 (br. d, 1 H, J = 14.8 Hz, C(O)CHC*H*H), 1.80−1.73 (m, 2 H), 1.70−1.63 (m, 1 H), 1.57−1.40 (m, 3 H), 1.22−1.06 (m, 3 H). − ^{13}C NMR (100 MHz): δ = 176.2 [s, *C*(O)], 118.1 (s, *C*N), 60.8 (d, N*C*H), 59.0 (t, *C*H_2OH), 39.0 [d, C(O)*C*H], 37.4 (d, NCH*C*H), 37.3 (t, N*C*H_2), 33.2 (t, *C*H_2CH_2OH), 28.8, 23.7, 22.9, 21.7, [t, −(*C*H_2)$_4$−], 16.1 (t, *C*H_2CN). − HRMS (FAB+) calcd. for $C_{13}H_{21}N_2O_2$ (M + H) 237.1603, found 237.1598. − $[\alpha]_D$ = −31.1 (c = 1.0; $CHCl_3$).

3-{(1*R*,3a*S*,7a*R*)-1-[2-(*tert*-Butyldimethylsilyloxy)ethyl]-3-oxo-octahydroisoindol-2-yl}propionitrile (16): To a solution of **15** (6.60 g, 28.0 mmol) in CH_2Cl_2 (40 mL) was added TBDMSCl (4.40 g, 29.4 mmol), imidazole (4.80 g, 70.0 mmol), and DMAP (324 mg, 2.8 mmol). After being stirred at room temperature for 3 h, the reaction mixture was quenched with 5% aqueous HCl. After the water layer was extracted (CH_2Cl_2, 4 ×), the combined organic layers were dried (Na_2SO_4), and in vacuo concentration took place, the product was obtained, after flash chromatography (EtOAc/PE, 1:1), as a white solid (9.3 g, 26.6 mmol, 95%), m.p. 44−45°C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2250 cm^{-1}, 1681. − ^1H NMR (400 MHz): δ = 3.84−3.77 (dt, 1 H, J = 13.9, 6.4 Hz, NC*H*H), 3.65−3.62 (t, 2 H, J = 5.5 Hz, CH_2OSi), 3.29−3.25 (dd, 1 H, J = 8.8, 4.1 Hz NC*H*), 3.19−3.13 (quint, 1 H, J = 6.9 Hz, NCH*H*), 2.72−2.64 (m, 1 H, NCH_2CHH), 2.57−2.50 [m, 2 H, C*H*C(O) and NCH_2CHH], 2.17−2.14 (dt, 1 H, J = 10.8, 5.7 Hz, NCHC*H*), 2.09−2.05 [br. d, 1 H, J = 14.2 Hz, C(O)CHC*H*H], 1.76−1.41 (m, 6 H), 1.19−1.06 (m, 3 H), 0.84 [s, 9 H, SiC(CH_3)$_3$], 0.00 [s, 6 H, Si(CH_3)$_2$]. − ^{13}C NMR (100 MHz): δ = 175.8 [s, *C*(O)], 117.9 (s, *C*N), 61.0 (d, N*C*H), 59.7 (t, *C*H_2OSi), 38.9 [d, C(O)*C*H], 37.4 (d, NCH*C*H), 37.3 (t, N*C*H_2), 33.3 (t, *C*H_2CH_2OH), 25.7 (q, SiC(*C*H_3)$_3$), 28.9, 23.7, 22.9, 22.8 [t, −(*C*H_2)$_4$−], 18.0 [s, Si*C*(CH$_3$)$_3$], 16.1 (t, *C*H_2CN), −5.60, −5.62 [q, Si(*C*H_3)$_2$]. $-C_{19}H_{34}N_2O_2Si$ (350.6): calcd. C 65.09, H 9.78, N 7.99; found C 64.78, H 9.55, N, 8.11. − $[\alpha]_D$ = −26.2 (c = 1.0; $CHCl_3$).

{3-[(1*R*,3a*S*,7a*R*)-1-[2-(*tert*-Butyldimethylsilyloxy)ethyl]-3-oxo-octahydroisoindol-2-yl]propyl}carbamic Acid *tert*-Butyl Ester (17): To a vigorously stirred, purple solution of $CoCl_2 \cdot H_2O$ (6.2 g, 26.2 mmol) in MeOH (20 mL) was added, at 0°C, $NaBH_4$ (124 mg, 3.3 mmol). The deep-black solution was stirred for 15 min at room temperature and cooled again. Then a solution of **16** (4.6 g, 13.1 mmol) in 2% NH_3 in MeOH (40 mL) was added dropwise. $NaBH_4$ pellets (5.0 g, 131 mmol) were added in portions over 1.5 h; hydrogen gas evolved. After being stirred another 1.5 h at 0°C, the reaction mixture was quenched with H_2O and filtered through Celite. The Celite was washed three times with MeOH/H_2O, 9:1. The solution was concentrated in vacuo and the residue was taken up in 5% aqueous NH_3. After extraction of the water layer (EtOAc, 5 ×), drying of the combined organic layers (Na_2SO_4) and concentration in vacuo, the crude product was obtained as a purple oil (4.1 g, 11.7 mmol, 89%). To a solution of this amine in CH_2Cl_2 (40 mL) was added Boc_2O (4.9 g, 22.6 mmol) and a catalytic amount of DMAP. After being stirred for 3 h at room temperature, the reaction mixture was concentrated in vacuo and purified by flash chromatography (EtOAc/PE, 1:1); the product was obtained as a yellow oil (3.5 g, 7.6 mmol, 58% from **15**). − IR (film): $\tilde{\nu}$ = 3400 cm^{-1}, 1684. − ^1H NMR (400 MHz): δ = 5.55 (br. t, 1 H, N*H*Boc), 3.63 (m, 3 H, NC*H*H, CH_2OSi), 3.24 (m, 1 H, C*H*HNHBoc), 3.09 (dd, 1 H, J = 9.3, 3.2 Hz, NC*H*), 2.90 (m, 2 H, NCH*H*CH_2, CH*H*NHBoc), 2.56 [br. t, 1 H, J = 5.6 Hz, C(O)C*H*], 2.14 [dt, 1 H, J = 10.8, 6.4 Hz, C(O)CHC*H*H], 2.07 (br. d, 1 H, J = 13.3 Hz, NCHC*H*), 1.7−1.4 (m, 8 H), 1.38 [s, 9 H, CO_2C(CH_3)$_3$], 1.1−0.9 (m, 3 H), 0.84 [s, 9 H, SiC(CH_3)$_3$], 0.00 [s, 6 H, Si(CH_3)$_2$]. − ^{13}C NMR (100 MHz): δ = 175.9 [s, NC(O)], 156.0 [s, NH*C*(O)], 78.6 [s, $CO_2C(CH_3)_3$], 60.3 (d, N*C*H), 59.8 (t, *C*H_2OSi), 39.0 [d, C(O)*C*H], 37.4 (t, N*C*H_2 and t, *C*H_2NHBoc), 37.1 (d, NCH*C*H), 32.8 and 27.3 (t, *C*H_2CH_2OH and t, $NCH_2CH_2CH_2$), 28.3 [q, $CO_2C(CH_3)_3$], 25.7 [q, SiC(*C*H_3)$_3$], 29.2, 23.8, 23.1, 22.9 [t, −(*C*H_2)$_4$−], 18.0 [s, Si*C*(CH$_3$)$_3$], −5.58, −5.63

[t, Si(CH_3)$_2$]. − HRMS (FAB+) calcd. for $C_{24}H_{47}N_2O_4Si$ (M + H) 455.3305, found 455.3280. − $[\alpha]_D$ = +30.0 (c = 1.0; $CHCl_3$).

{3-[(1*R*,3a*S*,7a*R*)-1-[2-(*tert*-Butyldimethylsilyloxy)ethyl]-3-thioxooctahydroisoindol-2-yl]propyl}carbamic Acid *tert*-Butyl Ester (18): To a solution of **17** (3.5 g, 7.7 mmol) in toluene (20 mL) was added Lawesson's reagent (1.7 g, 4.2 mmol). After being stirred at 80°C for 30 min, the reaction mixture was concentrated in vacuo. After purification by flash chromatography (EtOAc/PE, 1:4), the product was isolated as a yellow oil (2.9 g, 6.2 mmol, 81%). − IR (film): $\tilde{\nu}$ = 3400 cm^{-1}, 1609. − ^{1}H NMR (400 MHz): δ = 5.39 (br. s, 1 H, N*H*Boc), 4.42−4.35 (dt, 1 H, J = 13.5, 8.4 Hz, NC*H*H), 3.72−3.61 (m, 2 H, CH_2OSi), 3.47−3.44 (dd, 1 H, J = 9.6, 2.8 Hz, NC*H*), 3.29−3.27 (m, 1 H, C*H*HNHBoc), 3.21−3.15 (dt, 1 H, J = 13.6, 5.7 Hz, NCH*H*), 2.96−2.91 (m, 1 H, CH*H*NHBoc), 2.83 [br. t, 1 H, C(S)C*H*], 2.49−2.45 (br. d, 1 H, J = 13.6 Hz, NCHC*H*), 2.29−2.23 [quint, 1 H, J = 6.0 Hz, C(S)CHC*H*H], 1.83−1.47 (m, 8 H), 1.41 [s, 9 H, $CO_2C(CH_3)_3$], 1.25−1.02 (m, 3 H), 0.87 [s, 9 H, SiC(CH_3)$_3$], 0.00 [s, 6 H, Si(CH_3)$_2$]. − ^{13}C NMR (100 MHz): δ = 203.9 [s, N*C*(S)], 155.9 [s, NH*C*(O)], 78.8 [s, $CO_2C(CH_3)_3$], 67.3 (d, N*C*H), 59.8 (t, *C*H$_2$OSi), 49.0 [d, C(S)*C*H], 42.9 (t, N*C*H$_2$ and t, *C*H$_2$NHBoc), 38.8 (d, NCH*C*H), 31.8 and 26.7 (t, *C*H$_2$CH$_2$OSi and t, NCH$_2$*C*H$_2$CH$_2$), 28.4 [q, $CO_2C(CH_3)_3$], 25.7 [q, SiC(CH_3)$_3$], 28.6, 26.1, 23.9 22.1 [t, −(*C*H$_2$)$_4$−], 18.1 [s, Si*C*(CH$_3$)$_3$], −5.50, −5.56 [q, Si(CH_3)$_2$]. − HRMS (FAB+) calcd. for $C_{24}H_{47}N_2O_3SSi$ (M + H) 471.3077, found 471.3115. − $[\alpha]_D$ = −31.4 (c = 1.0; $CHCl_3$).

{3-[(1*R*,3a*S*,7a*R*)-1-(2-Hydroxyethyl)-3-thioxooctahydroisoindol-2-yl]propyl}carbamic Acid *tert*-Butyl Ester (19): To a solution of **18** (300 mg, 0.64 mmol) in THF (5 mL) was added TBAF (0.70 mL, 0.76 mmol, 1.1 M in THF). After being stirred at room temperature for 90 min, the reaction mixture was quenched with water. After extraction of the water layer (CH_2Cl_2, 4 ×), drying of the combined organic layers (Na_2SO_4) and concentration in vacuo, the product was obtained, after flash chromatography (EtOAc/PE, 3:1), as a white solid (224 mg, 0.63 mmol, 98%). An analytical sample was recrystallized from a 1:2:2 mixture of MeOH/EtOAc/pentane, m.p. 157−158°C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3353 cm^{-1}, 1684. − ^{1}H NMR (250 MHz): δ = 5.29 (br. s, 1 H, N*H*Boc), 4.44−4.32 (dt, 1 H, J = 13.6, 7.5 Hz, NC*H*H), 3.82−3.64 (m, 2 H, CH_2OH), 3.57−3.46 (dd, 1 H, J = 6.2, 2.9 Hz, NC*H*), 3.28−3.18 (m, 2 H, NCH*H*, C*H*HNHBoc), 2.99 (m, 1 H, CH*H*NHBoc), 2.85 [br. t, 1 H, C(S)C*H*], 2.49−2.44 (br. d, 1 H, J = 13.9 Hz, NCHC*H*), 2.29−2.19 [quint, 1 H, J = 6.1 Hz, C(S)CHC*H*H], 1.88−1.36 (m, 8 H), 1.42 [s, 9 H, $CO_2C(CH_3)_3$], 1.25−1.02 (m, 3 H). − ^{13}C NMR (50 MHz): δ = 203.7 [s, N*C*(S)], 156.0 [s, NH*C*(O)], 78.7 [s, $CO_2C(CH_3)_3$], 67.0 (d, N*C*H), 59.3 (t, *C*H$_2$OH), 49.4 [d, C(S)*C*H], 42.9 (t, N*C*H$_2$ and t, *C*H$_2$NHBoc), 38.9 (d, NCH*C*H), 31.8, (t, *C*H$_2$CH$_2$OH), 28.3 (t, NCHCH*C*H$_2$), 28.2 [q, $CO_2C(CH_3)_3$], 26.6, 25.9, 23.7, 21.9 [t, −(*C*H$_2$)$_4$−]. − $C_{18}H_{32}N_2O_3S$ (356.5): calcd. C 60.64, H 9.05, N 7.86; found C 60.88, H 8.99, N 7.71. − $[\alpha]_D$ = −52.3 (c = 1.2; $CHCl_3$).

2-[(4b*S*,8a*R*,9*R*)-1,2,3,4b,5,6,7,8,8a,9-Decahydro-4,9a-diazafluoren-9-yl]ethanol (7): A solution of **19** (1.9 g, 5.6 mmol) in MeI (15 mL) was stirred for 17 h at room temperature in the dark. After concentration in vacuo, a pale yellow foam was obtained. This methylated compound was dissolved in CH_2Cl_2 (20 mL), then TFA (3 mL) was added at 0°C and the yellow solution was stirred for 2 h. At the same temperature, Et_3N (9.2 mL) was slowly added. The mixture decolorized; stirring was continued for 2 h. The reaction mixture was extracted with 5% aqueous HCl (3 ×), and solid NaOH was added at 0°C until the water layer was basic. The basic aqueous solution was extracted (CH_2Cl_2, 5 ×). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The amidine was obtained as a colourless oil (1.0 g, 4.5 mmol, 81%) which was crystallized from benzene, m.p. 105−107°C. − ^{1}H NMR (400 MHz, C_6D_6): δ = 3.80−3.77 (t, 2 H, J = 6.2 Hz, CH_2OH), 3.53−3.48 (m, 1 H, C=NC*H*H), 3.36−3.30 (m, 1 H, C=NCH*H*), 3.13−3.03 (m, 2 H, C−NC*H*H, NC*H*), 2.86−2.81 (m, 1 H, C−NCH*H*), 2.71−2.70 (m, 1 H, N=CC*H*), 2.38−2.35 (m, 1 H, N=CCHC*H*H), 1.94−1.91 (m, 1 H, C−NCHC*H*), 1.84−1.75 (m, 1 H, C−NCHC*H*H), 1.67−1.47 (m, 8 H), 1.24−1.17 (m, 2 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 160.7 (*C*=N), 64.4 (C−N*C*H), 58.5 (CH$_2$*C*H$_2$OH), 43.6 (C=N*C*H$_2$), 42.2 (C−N*C*H$_2$), 39.6 (N=C*C*H), 39.2 (N−CH*C*H), 34.7 (*C*H$_2$CH$_2$OH), 28.4 (N−CHCH*C*H$_2$), 24.2 [N=CCH*C*H$_2$), 24.1, 22.9 (N=CCHCH$_2$−(*C*H$_2$)$_2$−], 21.0 (C=NCH$_2$*C*H$_2$). − $[\alpha]_D$ = +60.9 (c = 1.0; $CHCl_3$). − Crystallographic data for **7**: orthorhombic, $P2_12_12_1$, a = 7.1184(5), b = 8.4949(4), c = 21.1830(8) Å, V = 1280.9(1) Å^3, Z = 4, D_X = 1.15 g cm^{-3}, λ (Cu-K_α) = 1.5418 Å, μ (Cu-K_α) = 5.7 cm^{-1}, F(000) = 488, room temperature. Final R = 0.057 for 1211 observed reflections.[19]

α-Acetoxystyrene (20): A mixture of isopropenyl acetate (10 mL, 90.8 mmol, 2 equiv), acetophenone (5.3 mL, 45.4 mmol) and H_2SO_4 (cat) was heated at 90°C. Acetone was distilled from the reaction mixture for 7 h. The product was isolated together with acetophenone, as a 3:1 mixture, after distillation (b.p. 90−110°C, 20 Torr). This mixture could not be separated by distillation or column chromatography. − ^{1}H NMR (200 MHz): δ = 7.6−7.2 (m, 5 H, *Ph*), 5.5 (d, 1 H, C*H*H=C), 5.0 (d, 1 H, CH*H*=C), 2.6 (s, 3 H, CH_3).

3-[(1*R*,3a*S*,7a*R*)-1-Oxo-3-(2-oxo-2-phenylethyl)octahydroisoindol-2-yl]propionitrile (21): To a solution of sulfonyllactam **13** (7.51 g, 22.6 mmol), in CH_2Cl_2 (50 mL), were slowly added, at −78°C, aluminium trichloride (4.81 g, 36.1 mmol, 1.6 equiv) and α-acetoxystyrene (6.04 mL, 45.2 mmol, 2.0 equiv). After the reaction mixture was stirred for 15 min at −78°C, the temperature was allowed to rise slowly to −20°C in 2 h. The reaction mixture was poured in ice-cold aqueous saturated NaCl. After extraction of the water layer (CH_2Cl_2, 5 ×), the combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The residue was chromatographed (EtOAc/PE, 1:1) to give the product (6.21 g, 20.0 mmol, 89%) as a white solid, which was recrystallized from EtOAc/pentane as colourless crystals, m.p. 136−138°C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2252 cm^{-1}, 1697, 1674. − ^{1}H NMR (400 MHz): δ = 7.93−7.90 (m, 2 H, *o*-phenyl), 7.60−7.55 (m, 1 H, *p*-phenyl), 7.48−7.44 (m, 2 H, *m*-phenyl), 3.86−3.79 (m, 2 H, NC*H*, NCH*H*), 3.31−3.14 [m, 3 H, PhC(O)CH_2, NC*H*H], 2.71−2.58 [m, 3 H, CH_2CN, C(O)C*H*], 2.13−2.06 [m, 2 H, NCHC*H*, C(O)CHC*H*H], 1.95−1.91 (m, 1 H, NCHCHC*H*H), 1.60−1.44 (m, 3 H, NCHCHC*H*C*H*CH*H*), 1.25−1.11 [m, 3 H, NC(O)CHC*H*C*H*C*H*]. − ^{13}C NMR (100 MHz): δ = 197.8 [s, Ph*C*(O)], 176.0 [s, N*C*(O)], 136.2 (s, Ph-C_q), 133.7 (d, *p*-phenyl), 128.7 (d, *m*-phenyl), 127.9 (d, *o*-phenyl), 118.0 (s, *C*N), 58.9 (d, N*C*H), 40.1 [t, PhC(O)*C*H$_2$], 39.1 [d, NC(O)*C*H], 38.7 (d, NCH*C*H), 37.7 (t, N*C*H$_2$), 28.4, 23.5, 22.9, 22.7 [t, −(*C*H$_2$)$_4$−], 16.1 (t, *C*H$_2$CN). − $C_{19}H_{22}N_2O_2$ (310.4): calcd. C 73.52, H 7.14, N 9.03; found C 73.65, H 7.04, N 9.10. − $[\alpha]_D$ = −13.7 (c = 1.0; $CHCl_3$).

3-{(1*R*,3a*S*,7a*R*)-1-[2-(*R*)-Hydroxy-2-phenylethyl]-3-oxooctahydroisoindol-2-yl}propionitrile (23a): To a solution of ketone **21** (3.79 g, 12.2 mmol) in toluene (60 mL), and the (*S*)-oxazaborolidine catalyst **22a** (7.4 mL, 3.7 mmol, 0.5 M solution in toluene, 0.3 equiv), was slowly added BH_3·Me_2S (0.73 mL, 7.3 mmol). After being stirred for 45 min, the reaction mixture was poured into 5% aqueous HCl. After the water layer (CH_2Cl_2, 5 ×) was extracted, the combined organic layers were dried (Na_2SO_4) and concentrated

in vacuo. The residue was chromatographed (EtOAc/PE, 1:1) to give the product (3.14 g, 10.0 mmol, 82%) as a colourless oil and a single diastereomer. − IR ($CHCl_3$): $\tilde{\nu}$ = 3400 cm^{-1}, 2250, 1685. − ^1H NMR (200 MHz): δ = 7.40−7.23 (m, 5 H, *Ph*), 4.78−4.72 (dd, 1 H, *J* = 14.3, 7.1 Hz, PhC*H*OH), 3.87−3.73 (dt, 1 H, *J* = 13.9, 6.5 Hz, NCH*H*), 3.50−3.44 (dd, 1 H, *J* = 9.6, 2.6 Hz, NC*H*), 3.24−3.11 (dt, 1 H, *J* = 13.8, 6.8 Hz, NC*H*H), 2.75−2.45 (m, 4 H), 2.25−1.07 (m, 11 H). δ = ^{13}C NMR (50 MHz): δ = 175.7 [s, N*C*(O)], 144.2 (s, *Ph*), 128.4, 127.6, 125.2 (d, *Ph*), 117.9 (s, *C*N), 71.2 (d, *C*HOH), 60.6 (d, N*C*H), 39.5 [t, PhC(O)*C*H$_2$], 38.7, 37.4 [d, C(O)C*H*C*H*], 36.8 (t, N*C*H$_2$), 28.8, 23.5, 22.8, 22.6 [t, −(*C*H$_2$)$_4$−], 15.9 (t, *C*H$_2$CN). − HRMS (EI+) calcd. for $C_{19}H_{24}N_2O_2$ 312.1838, found 312.1826. − $[\alpha]_D$ = +2.0 (*c* = 1.0; $CHCl_3$).

3-{(1*R*,3a*S*,7a*R*)-1-[2-(*S*)-Hydroxy-2-phenylethyl]-3-oxooctahydroisoindol-2-yl}propionitrile (23b): According to the procedure described for **23a**, 2.50 g (8.1 mmol) of ketone **21** was reduced with (*R*)-catalyst **22b** (4.0 mL, 2.0 mmol, 0.5 M solution in toluene, 0.25 equiv.) to give the product (1.76 g, 10.0 mmol, 70%, colourless oil). − IR ($CHCl_3$): $\tilde{\nu}$ = 3400 cm^{-1}, 2250, 1685. − ^1H NMR (200 MHz): δ = 7.41−7.12 (m, 5 H, *Ph*), 4.79−4.72 (dd, 1 H, *J* = 5.4, 2.3 Hz, PhC*H*OH), 3.91−3.78 (dt, 1 H, *J* = 13.8, 6.5 Hz, NCH*H*), 3.27−3.13 [m, 3 H, NC*H*, NCH*H* and NC(O)C*H*] 2.88−2.41 (m, 3 H), 2.12−1.08 (m, 11 H). − ^{13}C NMR (50 MHz): δ = 178.1 [s, N*C*(O)], 143.9 (s, *Ph*), 128.4, 127.7, 125.4 (d, *Ph*), 117.9 (s, *C*N), 71.6 (d, *C*HOH), 60.5 (d, N*C*H), 40.1 [t, PhC(OH)*C*H$_2$], 38.8, 38.3 [d, C(O)C*H*C*H*], 37.5 (t, N*C*H$_2$), 28.5, 23.6, 22.7, 22.6 [t, −(*C*H$_2$)$_4$−], 15.8 (t, *C*H$_2$CN). − HRMS (EI+) calcd. for $C_{19}H_{24}N_2O_2$ 312.1838 found, 312.1838. − $[\alpha]_D$ = −29.3 (*c* = 1.0; $CHCl_3$).

3-{(1*R*,3a*S*,7a*R*)-1-[2-(*R*)-(*tert*-Butyldimethylsilanyloxy)-2-phenylethyl]-3-oxooctahydroisoindol-2-yl}propionitrile (24a): To a solution of alcohol **23a** (3.0 g, 9.6 mmol) in CH_2Cl_2 (30 mL) was added, at 0°C, TBDMSOTf (6.6 mL, 28.8 mmol, 3 equiv) and 2,6-lutidine (4.4 mL, 38.5 mmol, 4 equiv.). After being stirred for 10 min at 0°C, and for 4 h at room temperature, the reaction mixture was poured into 5% aqueous HCl. After the water layer (CH_2Cl_2, 5 ×) was extracted, the combined organic fractions were dried (Na_2SO_4) and concentrated in vacuo. The residue was chromatographed (EtOAc/PE, 1:3) to give the product (3.93 g, 9.2 mmol, 96%) as a colourless oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 2220 cm^{-1}, 1681. − ^1H NMR (400 MHz): δ = 7.35−7.24 (m, 5 H, *Ph*), 4.76−4.74 (dd, 1 H, *J* = 8.3, 3.0 Hz, PhC*H*OSi), 3.79−3.72 (dt, 1 H, *J* = 13.5, 6.5 Hz, NCH*H*), 3.33−3.30 (dd, 1 H, *J* = 10.2, 2.1 Hz, NC*H*), 3.05−2.98 (dt, 1 H, *J* = 13.8, 6.9 Hz, NCH*H*), 2.66−2.56 [m, 2 H, C*H*HCN, C(O)C*H*], 2.49−2.42 (dt, 1 H, *J* = 16.8, 6.4 Hz, CH*H*CN), 2.27−2.23 [m, 1 H, C(O)CHC*H*H], 2.19−2.15 (m, 1 H, NCHC*H*), 1.86−1.10 (m, 9 H), 0.91 [s, 9 H, SiC(C*H*$_3$)$_3$], 0.06, −0.20, [2 × s, 6 H, Si(C*H*$_3$)$_2$]. − ^{13}C NMR (100 MHz): δ = 176.0 [s, N*C*(O)], 144.2 (s, *Ph*), 128.3, 127.4, 125.2 (d, *Ph*), 117.9 (s, *C*N), 72.2 (d, Ph*C*HOSi), 60.3 (d, N*C*H), 40.9 [t, PhC(OSi)*C*H$_2$], 38.8, 37.7 [d, C(O)C*H*C*H*], 37.0 (t, N*C*H$_2$), 25.7 [q, SiC(*C*H$_3$)$_3$], 29.0, 24.0, 22.9, 22.8 [t, −(*C*H$_2$)$_4$−], 18.0 [s, Si*C*(CH$_3$)$_3$], 16.0 (t, *C*H$_2$CN), −4.7, −5.0 [q, Si(*C*H$_3$)]. − HRMS (FAB+) calcd. for $C_{25}H_{39}N_2O_2Si$ (M + H) 427.2781, found 427.2781. − $[\alpha]_D$ = +1.2 (*c* = 0.64; $CHCl_3$).

3-{(1*R*,3a*S*,7a*R*)-1-[2-(*S*)-(*tert*-Butyldimethylsilanyloxy)-2-phenylethyl]-3-oxooctahydroisoindol-2-yl}propionitrile (24b): According to the procedure described for **24a**, 1.76 g (5.6 mmol) of alcohol **23b** was transformed into 2.39 g (5.6 mmol, 100%, colourless oil) of **24b**. − IR ($CHCl_3$): $\tilde{\nu}$ = 2225 cm^{-1}, 1681. − ^1H NMR (400 MHz): δ = 7.35−7.24 (m, 5 H, *Ph*), 4.81−4.78 (t, 1 H, *J* = 5.8 Hz, PhC*H*OSi), 3.83−3.76 (dt, 1 H, *J* = 13.4, 6.4 Hz, NCH*H*), 3.13−3.10 (dd, 1 H, *J* = 9.5, 2.4 Hz, NC*H*), 3.08−3.01 (dt, 1 H, *J* = 13.9, 7.0 Hz, NCH*H*), 2.66−2.58 (dt, 1 H, *J* = 16.8, 7.1 Hz, C*H*HCN), 2.55−2.52 [br. t, 1 H, *J* = 6.0 Hz, C(O)C*H*], 2.50−2.43 (dt, 1 H, *J* = 16.8, 6.2 Hz, CH*H*CN), 2.12−2.09 (m, 1 H, NCHC*H*) 1.99−1.91 [m, 2 H, C(O)CHC*H*H, C*H*HC(OSi)], 1.80−1.75 [m, 1 H, CH*H*C(OSi)], 1.63−1.01 (m, 8 H), 0.89 [s, 9 H, SiC(C*H*$_3$)$_3$], 0.04, −0.19, [2 × s, 6 H, Si(C*H*$_3$)$_2$]. − ^{13}C NMR (100 MHz): δ = 175.6 [s, N*C*(O)], 143.9 (s, *Ph*), 128.3, 127.5, 125.6 (d, *Ph*), 117.8 (s, *C*N), 73.0 (d, Ph*C*HOSi), 60.6 (d, N*C*H), 40.8 [t, PhC(OSi)*C*H$_2$], 38.8, 38.2 [d, C(O)C*H*C*H*], 37.0 (t, N*C*H$_2$), 25.7 [q, SiC(*C*H$_3$)$_3$], 28.6, 23.7 22.8, 22.8 [t, −(*C*H$_2$)$_4$−], 18.0 [s, Si*C*(CH$_3$)$_3$], 16.0 (t, *C*H$_2$CN) −4.7, −5.0 [q, Si(*C*H$_3$)$_2$]. − HRMS (EI+) calcd. for $C_{25}H_{38}N_2O_2Si$ 426.2703, found 426.2703. − $[\alpha]_D$ = −4.7 (*c* = 1.0; $CHCl_3$).

(3-{(1*R*,3a*S*,7a*R*)-1-[2-(*R*)-(*tert*-Butyldimethylsilanyloxy)-2-phenylethyl]-3-oxooctahydroisoindol-2-yl}propyl)carbamic Acid *tert*-Butyl Ester (25a): According to the procedure described for **16**, 3.93 g (9.2 mmol) of **24a** was transformed into the corresponding amine (3.45 g, 8.0 mmol, 87%), which was transformed into 2.85 g of **25a** (5.4 mmol, 58% from **24a**, colourless oil). − IR ($CHCl_3$): $\tilde{\nu}$ = 3400 cm^{-1}, 1669. − ^1H NMR (200 MHz): δ = 7.33−7.24 (m, 5 H, *Ph*), 5.50 (br. s, 1 H, N*H*Boc), 4.75−4.70 (dd, 1 H, *J* = 8.5, 2.9 Hz, PhC*H*OSi), 3.70−3.55 (m, 1 H, NCH*H*), 3.35−3.20 (m, 1 H, C*H*HNHBoc), 3.18−3.12 (dd, 1 H, *J* = 10.2, 2.0 Hz, NC*H*), 2.95−2.73 (m, 2 H, NC*H*H, CH*H*NHBoc), 2.62−2.52 [m, 1 H, C(O)C*H*], 2.29−2.07 [m, 2 H, NCHC*H*, C(O)CHC*H*H], 1.9−1.5 (m, 8 H), 1.43 [s, 9 H, CO$_2$C(C*H*$_3$)$_3$], 1.2−0.9 (m, 3 H), 0.90 [s, 9 H, SiC(C*H*$_3$)$_3$], 0.04, −0.22, [2 × s, 6 H, Si(C*H*$_3$)$_2$]. − ^{13}C NMR (100 MHz): δ = 176.0 [s, N*C*(O)], 156.0 [s, NH*C*(O)], 144.3 (s, *Ph*), 128.2, 127.3, 125.5 (d, *Ph*), 79.3 [s, CO$_2$*C*(CH$_3$)$_3$], 72.4 (d, Ph*C*HOSi), 59.5 (d, N*C*H), 40.5 [t, PhC(OSi)*C*H$_2$], 38.9, 37.5 [d, NC(O)C*H*C*H*], 37.1 (t, N*C*H$_2$), not observed (t, *C*H$_2$NHBoc), 28.3 [q, CO$_2$C(*C*H$_3$)$_3$], 27.3 (t, *C*H$_2$CH$_2$NHBoc), 25.6 [q, SiC(*C*H$_3$)$_3$], 29.3, 24.0, 23.0, 22.9 [t, −(*C*H$_2$)$_4$−], 17.9 [s, Si*C*(CH$_3$)$_3$], −4.7, −5.2 [q, Si(*C*H$_3$)$_2$]. − HRMS (FAB+) calcd. for $C_{30}H_{51}N_2O_4Si$ (M + H) 531.3618, found 531.3618. − $[\alpha]_D$ = +65.4 (*c* = 1.1; $CHCl_3$).

(3-{(1*R*,3a*S*,7a*R*)-1-[2-(*S*)-(*tert*-Butyldimethylsilanyloxy)-2-phenylethyl]-3-oxooctahydroisoindol-2-yl}propyl)carbamic Acid *tert*-Butyl Ester (25b): According to the procedure described for **16**, 2.40 g (5.6 mmol) of **24b** was transformed into the corresponding amine (1.9 g, 4.4 mmol, 79%), which was transformed into 1.1 g of **25b** (2.1 mmol, 50% from **24b**, colourless oil). − IR ($CHCl_3$): $\tilde{\nu}$ = 3400 cm^{-1}, 1668. − ^1H NMR (250 MHz): δ = 7.34−7.24 (m, 5 H, *Ph*), 5.54 (br. s, 1 H, N*H*Boc), 4.79−4.74 (t, 1 H, *J* = 5.7 Hz, PhC*H*OSi), 3.66−3.54 (m, 1 H, NCH*H*), 3.26−3.21 (m, 1 H, C*H*HNHBoc), 2.93−2.78 (m, 3 H, NC*H*, NC*H*H, CH*H*NHBoc), 2.54−2.52 [m, 1 H, C(O)C*H*], 1.9−1.4 (m, 8 H), 1.41 [s, 9 H, CO$_2$C(C*H*$_3$)$_3$], 1.2−0.9 (m, 3 H), 0.87 [s, 9 H, SiC(C*H*$_3$)$_3$], 0.03, −0.12, [2 × s, 6 H, Si(C*H*$_3$)$_2$]. − ^{13}C NMR (100 MHz): δ = 175.7 [s, N*C*(O)], 156.0 [s, NH*C*(O)], 144.0 (s, *Ph*), 128.3, 127.4, 125.6 (d, *Ph*), 78.7 [s, CO$_2$*C*(CH$_3$)$_3$], 73.1 (d, Ph*C*HOSi), 59.7 (d, N*C*H), 40.4 [t, PhC(OSi)*C*H$_2$], 38.9, 37.5 [d, NC(O)C*H*C*H*], 37.1 (t, N*C*H$_2$), not observed (t, *C*H$_2$NHBoc), 28.3 [q, CO$_2$C(*C*H$_3$)$_3$], 28.0 (t, *C*H$_2$CH$_2$NHBoc), 25.7 [q, SiC(*C*H$_3$)$_3$], 29.3, 23.8, 22.9, 22.9 [t, −(*C*H$_2$)$_4$−], 18.0 [s, Si*C*(CH$_3$)$_3$], −4.7, −5.0 [q, Si(*C*H$_3$)$_2$]. − HRMS (FAB+) calcd. for $C_{30}H_{51}N_2O_4Si$ (M + H) 531.3618, found 531.3629. − $[\alpha]_D$ = −4.7 (*c* = 1.0; $CHCl_3$).

(3-{(1*R*,3a*S*,7a*R*)-1-[2-(*R*)-(*tert*-Butyldimethylsilanyloxy)-2-phenylethyl]-3-thioxooctahydroisoindol-2-yl}propyl)carbamic Acid *tert*-Butyl Ester (26a): According to the procedure described for **17**, 2.75 g of **25a** (5.2 mmol) was transformed into 2.76 g of the product (5.1 mmol, 97%, colourless oil). − IR ($CHCl_3$): $\tilde{\nu}$ = 2275 cm^{-1},

1699, 1683. − ^{1}H NMR (200 MHz): δ = 7.38−7.25 (m, 5 H, *Ph*), 5.37 (br. s, 1 H, N*H*Boc), 4.79−4.73 (dd, 1 H, *J* = 7.8, 3.6 Hz, PhC*H*OSi), 4.38−4.31 (m, 1 H, NCH*H*), 3.50−3.44 (dd, 1 H, *J* = 9.4, 2.7 Hz, NC*H*), 3.31−3.21 (m, 1 H, C*H*HNHBoc), 3.06−2.81 [m, 3 H, NC*H*, CH*H*NHBoc, C(S)C*H*], 2.61−2.54 (m, 1 H, NCHC*H*), 2.39−2.27 [m, 1 H, C(S)CHC*H*H], 1.9−1.4 (m, 8 H), 1.45 [s, 9 H, $CO_2C(CH_3)_3$], 1.3−1.1 (m, 3 H), 0.91 [s, 9 H, $SiC(CH_3)_3$], 0.05, −0.20, [2 × s, 6 H, $Si(CH_3)_2$]. − ^{13}C NMR (100 MHz): δ = not observed [s, N*C*(S), $CH_2NHCO_2C(CH_3)_3$], 143.8 (s, *Ph*), 128.3, 127.5, 125.4 (d, *Ph*), 72.4 (d, Ph*C*HOSi), 66.4 (d, N*C*H), 49.2 [d, C(S)*C*H], 42.6 (d, N*C*H$_2$), 39.4 (d, NCH*C*H), 39.4 [t, C(OSi)*C*H$_2$], 28.3 [q, $CO_2C(CH_3)_3$], 26.6 (t, *C*H$_2$CH$_2$NHBoc), 25.7 [q, $SiC(CH_3)_3$], 28.6, 24.0, 22.0, 22.0 [t, −(*C*H$_2$)$_4$−], 17.9 [s, Si*C*(CH$_3$)$_3$] −4.8, −5.0 [q, Si(*C*H$_3$)$_2$]. − HRMS (FAB+) calcd. for $C_{30}H_{50}N_2O_4Si$ (M + H) 547.3390, found 547.3390. − $[\alpha]_D$ = −0.2 (*c* = 0.4; $CHCl_3$).

(3-{(1*R*,3a*S*,7a*R*)-1-[2-(*S*)-(*tert*-Butyldimethylsilanyloxy)-2-phenylethyl]-3-thioxooctahydroisoindol-2-yl}propyl)carbamic Acid *tert*-Butyl Ester (26b): According to the procedure described for **17**, 1.71 g (3.2 mmol) of lactam **25b** was transformed into 1.36 g of the product (2.5 mmol, 80%, colourless oil). − IR ($CHCl_3$): ṽ = 2275 cm^{-1}, 1692, 1681. − ^{1}H NMR (400 MHz): δ = 7.35−7.25 (m, 5 H, *Ph*), 5.30 (br. s, 1 H, N*H*Boc), 4.84−4.81 (t, 1 H, *J* = 5.6 Hz, PhC*H*OSi), 4.38−4.34 (m, 1 H, NCH*H*), 3.28−3.26 (m, 2 H, NC*H*, NC*H*H), 3.09−3.06 (m, 1 H, C*H*HNHBoc), 2.89−2.78 [m, 2 H, CH*H*NHBoc, C(S)C*H*], 2.50−2.47 [m, 1 H, C(S)CHC*H*H], 1.98−1.40 (m, 9 H), 1.43 [s, 9 H, $CO_2C(CH_3)_3$], 1.25−1.10 (m, 3 H), 0.90 [s, 9 H, $SiC(CH_3)_3$], 0.05, −0.16, [2 × s, 6 H, $Si(CH_3)_2$]. − ^{13}C NMR (100 MHz): δ = 203.7 [s, N*C*(S)], not observed [*C*H$_2$N*C*O$_2$*C*(CH$_3$)$_3$], 143.6 (s, *Ph*), 128.3, 127.6, 125.5 (d, *Ph*), 72.8 (d, Ph*C*HOSi), 66.5 (d, N*C*H), 49.2 [d, C(S)*C*H], 42.6 (t, N*C*H$_2$), 39.9 (d, NCH*C*H), 39.3 [t, C(OSi)*C*H$_2$], 28.2 [q, $CO_2C(CH_3)_3$], 26.6 (t, *C*H$_2$CH$_2$NHBoc), 25.7 [q, $SiC(CH_3)_3$], 28.3, 25.9, 23.8, 22.0 [t, −(*C*H$_2$)$_4$−], 18.0 [s, Si*C*(CH$_3$)$_3$], −4.8, −5.0 [q, Si(*C*H$_3$)$_2$]. − HRMS (FAB+) calcd. for $C_{30}H_{50}N_2O_4Si$ (M + H) 547.3390, found 547.3390. − $[\alpha]_D$ = −5.2 (*c* = 0.5; $CHCl_3$).

(3-{(1*R*,3a*S*,7a*R*)-1-[2-(*R*)-Hydroxy-2-phenylethyl]-3-thioxooctahydroisoindol-2-yl}propyl)carbamic Acid *tert*-Butyl Ester (27a): According to the procedure described for **18**, 2.35 g of **26a** (4.3 mmol) was transformed into 1.66 g of **27a** (3.8 mmol, 90%, colourless oil). − IR ($CHCl_3$): ṽ = 3452 cm^{-1}, 2360, 1703. − ^{1}H NMR (200 MHz): δ = 7.35−7.26 (m, 5 H, *Ph*), 4.81−4.75 (dd, 1 H, *J* = 9.6, 2.9 Hz, PhC*H*OH), 4.45−4.31 (dt, 1 H, *J* = 13.4, 8.2 Hz, NCH*H*), 3.72−3.68 (dd, 1 H, *J* = 9.7, 2.7 Hz, NC*H*), 3.37−3.14 (m, 2 H, C*H*$_2$NHBoc), 3.03−2.87 [m, 2 H, C(S)C*H*C*H*H], 2.57−2.50 (m, 1 H, NCHC*H*), 2.35−2.25 (m, 1 H), 2.0−1.5 (m, 8 H), 1.44 [s, 9 H, $CO_2C(CH_3)_3$], 1.2−1.0 (m, 3 H). − ^{13}C NMR (50 MHz): δ = 203.5 [s, N*C*(S)], 155.9 [s, NH*C*(O)], 143.7 (s, *Ph*), 128.5, 127.8, 125.2 (d, *Ph*), 79.0 [s, $CO_2C(CH_3)_3$], 71.5 (d, Ph*C*HOH), 66.9 (d, N*C*H), 49.2 [t, C(S)*C*H], 42.6 (t, N*C*H$_2$), 38.9 (d, NCH*C*H), 38.0 [t, PhC(OH)*C*H$_2$], 37.3 (t, *C*H$_2$NHBoc), 28.2 [q, $CO_2C(CH_3)_3$], 26.7 (t, *C*H$_2$CH$_2$NHBoc), 28.6, 25.8, 23.8, 21.9 [t, −(*C*H$_2$)$_4$−]. − HRMS (FAB+) calcd. for $C_{24}H_{36}N_2O_3S$ (M + H) 433.2525, found 433.2525. − $[\alpha]_D$ = −33.8 (*c* = 1.0; $CHCl_3$).

(3-{(1*R*,3a*S*,7a*R*)-1-[2-(*S*)-Hydroxy-2-phenylethyl]-3-thioxooctahydroisoindol-2-yl}propyl)carbamic Acid *tert*-Butyl Ester (27b): According to the procedure described for **18**, 1.36 g of **26b** (2.50 mmol) was transformed into 1.05 g of **27b** (2.40 mmol, 96%, colourless oil). − IR ($CHCl_3$): ṽ = 3500 cm^{-1}, 3300, 1699. − ^{1}H NMR (400 MHz): δ = 7.40−7.26 (m, 5 H, *Ph*), 5.28 (br. s, 1 H, N*H*Boc) 4.83−4.80 (t, 1 H, *J* = 6.2 Hz, PhC*H*OH), 4.44−4.36 (dt, 1 H, *J* = 14.8, 7.8 Hz, NCH*H*), 3.37−3.34 (dd, 1 H, *J* = 8.4, 3.9 Hz, NC*H*), 3.27−3.16 (m, 2 H, NC*H*H and C*H*HNHBoc), 2.97−2.86 [m, 2 H, CH*H*NHBoc, C(S)C*H*], 2.51−2.47 [m, 1 H, C(S)CHC*H*H], 2.35−2.17 (m, 2 H), 2.06−1.88 (m, 2 H), 1.80−1.50 (m, 5 H), 1.44 [s, 9 H, $CO_2C(CH_3)_3$], 1.20−1.10 (m, 2 H), 0.99−0.80 (m, 2 H). − ^{13}C NMR (100 MHz): δ = 203.7 [s, N*C*(S)], not observed [$CO_2C(CH_3)_3$], 143.5 (s, *Ph*), 128.8, 128.2, 125.5 (d, *Ph*), 79.0 [s, $CO_2C(CH_3)_3$], 72.3 (d, Ph*C*HOH), 67.0 (d, N*C*H), 49.4 [d, C(S)*C*H], 43.2 (t, N*C*H$_2$), 40.0 (d, NCH*C*H), 38.0 [t, *C*H$_2$C(OH)], 37.3 (t, *C*H$_2$NHBoc) 28.3 [q, $CO_2C(CH_3)_3$], 26.4 (t, *C*H$_2$CH$_2$NHBoc), 28.3, 25.9 23.8, 22.0, [t, −(*C*H$_2$)$_4$−]. − HRMS (FAB+) calcd. for $C_{24}H_{36}N_2O_3S$ (M + H) 433.2525 found 433.2525. − $[\alpha]_D$ = −5.4 (*c* = 0.32; $CHCl_3$).

(1*R*)-2-[(4b*S*,8a*R*,9*R*)-1,2,3,4b,5,6,7,8,8a,9-Decahydro-4,9a-diazafluoren-9-yl]-1-phenylethanol (8): A solution of **25a** (1.40 g, 3.3 mmol) in MeI (10 mL) was stirred for 17 h at room temperature and in the dark. After concentration in vacuo, the iodine salt was obtained as a pale yellow foam (1.89 g, 3.3 mmol, 100%). This iodine salt (250 mg, 0.44 mmol) was dissolved in CH_2Cl_2 (3 mL). TFA (1 mL) was added at 0°C and the resulting yellow solution was stirred for 2 h at room temp., after which the reaction mixture was concentrated in vacuo. This concentrated reaction mixture was redissolved in CH_2Cl_2 (4 mL), and at 0°C, Et_3N (122 mL, 0.87 mmol, 2 equiv.) was added. The mixture decolorized; stirring was continued for 2 h. The reaction mixture was extracted with 5% aqueous HCl (3 ×), and solid NaOH was added at 0°C until the water layer was basic. The basic aqueous solution was extracted (CH_2Cl_2, 5 ×). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The amidine was obtained as a white foam (106 mg, 0.36 mmol, 82%). After purification by crystallization from benzene/2-propanol, the product was obtained as a colourless crystalline compound (65.7 mg, 52%), m.p. 104−107°C. − IR ($CHCl_3$): ṽ = 3400 cm^{-1}, 1652. − ^{1}H NMR (400 MHz): δ = 7.35−7.24 (m, 5 H, *Ph*), 4.74−4.72 (dd, 1 H, *J* = 9.4, 3.5 Hz, PhC*H*OH), 3.38−3.06 (m, 5 H), 2.71 (m, 1 H), 2.10−1.95 (m, 3 H), 1.76−1.64 (m, 4 H), 1.53−1.44 (m, 3 H), 1.27−1.16 (m, 4 H). − ^{13}C NMR (100 MHz): δ = 161.5 (s, *C*=N), 144.6 (s, *Ph*), 128.5, 127.7, 125.5, (d, *Ph*), 71.5 (d, C*H*OH), 64.5 (d, NC*H*), 41.7, 39.9, (t, C=N*C*H$_2$ and N*C*H$_2$), 39.4, 38.9, (d, N=C*C*H and NCH*C*H), 28.4, 23.9, 23.9, 22.6, 22.6, 20.5. − $[\alpha]_D$ = +66.9 (*c* = 0.13; $CHCl_3$). − Crystallographic data for **8**: *P*2$_1$, *a* = 10.070(1), *b* = 17.244(5), *c* = 10.508(1) Å, β = 106.720(6)°, *V* = 1747.7(5) Å^3, *Z* = 2, D_X = 1.17 g cm^{-3}, λ (Cu-K_α) = 1.5418 Å, μ (Cu-K_α) = 5.47 cm^{-1}, *F*(000) = 668, −25°C. Final *R* = 0.059 for 2326 observed reflections. There is one H_2O molecule between two molecules which are connected by four hydrogen bonds. N1a−O1s 2.708(8), N1b−O1s 2.723(7), O1b−O1s 2.725(7), O1a−O1s 2.752(7) Å.[19]

2-(*S*)-[(4b*S*,8a*R*,9*R*)-1,2,3,4b,5,6,7,8,8a,9-Decahydro-4,9a-diazafluoren-9-yl]-1-phenylethanol (9): A solution of **25b** (1.05 g, 2.4 mmol) in MeI (10 mL) was stirred for 17 h at room temperature in the dark. After concentration in vacuo, the iodine salt was obtained as a pale yellow foam (1.42 g, 2.4 mmol, 100%). This iodine salt (250 mg, 0.44 mmol) was dissolved in CH_2Cl_2 (3 mL). TFA (1 mL) was added at 0°C and the yellow solution was stirred for 2 h at room temp., after which the reaction mixture was concentrated in vacuo. This concentrated reaction mixture was redissolved in CH_2Cl_2 (4 mL) and, at 0°C, Et_3N (122 mL, 0.87 mmol, 2 equiv.) was added. The mixture decolorized; stirring was continued for 2 h. The reaction mixture was extracted with 5% aqueous HCl (3 ×), and solid NaOH was added at 0°C until the water layer was basic. The basic aqueous solution was extracted (CH_2Cl_2, 5 ×). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The amidine was obtained as a white foam (126 mg, 0.43 mmol, 98% crude). The product could not be purified by crys-

tallization and was washed with benzene. – IR ($CHCl_3$): $\tilde{\nu}$ = 3400 cm^{-1}, 1651. – ^1H NMR (400 MHz): δ = 7.32–7.22 (m, 5 H, *Ph*), 4.74–4.71 (dd, 1 H, *J* = 7.9, 5.2 Hz, C*H*OH), 3.37–2.98 (m, 5 H), 2.68 (m, 1 H), 2.01–1.05 (m, 14 H). – ^{13}C NMR (100 MHz): δ = 161.3 (s, *C*=N), 145.5 (s, *Ph*), 128.2, 127.2, 125.7, (d, *Ph*), 71.4 (d, C*H*OH), 64.5 (d, NC*H*), 42.7, 41.1, (d, N=C*C*H and NCH*C*H), 39.7, 39.3, (t, C=N*C*H_2 and N*C*H_2), 28.1, 24.0, 23.8, 22.9, 22.6, 20.7. – HRMS (FAB+) calcd. for $C_{19}H_{27}N_2O$ (M + H) 299.2123, found 299.2125. – $[\alpha]_D$ = +21.1 (*c* = 0.9; $CHCl_3$).

Thiophenol Addition Product 28: A mixture of thiophenol (51.0 mL, 0.29 mmol) and amidine **6** (5.0 mg, 0.015 mmol) was dissolved in toluene (1 mL). Cyclohexenone (43.7 mL, 0.29 mmol) was added and after being stirred for 20 min at room temperature, the reaction mixture was diluted with toluene and washed (5% aqueous HCl, 2 ×). The organic layer was dried ($MgSO_4$) and concentrated in vacuo, yielding the product (66.6 mg, 0.32 mmol, 72%) as a colourless oil. Spectral data was as reported previously.[3a] – $[\alpha]_D$ = +21.3 (*c* = 0.70; CCl_4). $[\alpha]_{578}$ = +22.4. – O.p. 23%.[3a]

Malonate Addition Product 29: A mixture of dimethyl malonate (20.0 mL, 0.18 mmol) and amidine **7** (9.6 mg, 0.043 mmol) was dissolved in toluene (1 mL). Cyclohexenone (16.7 mL, 0.17 mmol) was added and after being stirred for 24 h at room temp., the reaction mixture was diluted with toluene and washed (5% aqueous HCl, 2 ×). The organic layer was dried ($MgSO_4$) and concentrated in vacuo, yielding the product (27 mg, 0.12 mmol, 70%) as a colourless oil. Spectral data was as reported previously.[18] – $[\alpha]_D$ = +1.4 (*c* = 0.5; $CHCl_3$). – O.p.[18] 35%.

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