Enantioselective Hydrosilylation and Hydrogenation of Alkaloid Precursors[1)]

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Enantioselective hydrosilylations of the 3,4-dihydropyrrole derivatives **1a–c** and **5** with in-situ catalysts consisting of $[Rh(cod)Cl]_2$ and optically active phosphines yield the *N*-silyl compounds **2a–c** and **6** in up to 66.1 % ee. The *N*-silyl derivatives were treated with acetic formic anhydride or trifluoroacetic anhydride to give the *N*-formyl and *N*-trifluoroacetyl compounds **3a–c, 4a–c, 7,** and **8**. The alkaloids nicotine and macrostomine were synthesized with 63.3 and 33 % ee by reduction of the *N*-formyl compounds **8** and **12**. Enantioselective hydrogenations of the *N*-formyl and *N*-trifluoroacetyl-2-phenylpyrrolines **14** and **15** with the same in-situ catalysts produce the cyclic amides **3a** and **4a** in up to 36.1 % ee.

Enantioselektive Hydrosilylierung und Hydrierung von Alkaloidvorläufern[1)]

Die enantioselektive Hydrosilylierung der 3,4-Dihydropyrrol-Derivate **1a–c, 5** mit in-situ-Katalysatoren bestehend aus $[Rh(cod)Cl]_2$ und optisch aktiven Phosphinen ergab die N-Silylverbindungen **2a–c, 6** in bis zu 66.1 % ee. Die N-Silyl-Derivate wurden mit Acetylformylanhydrid bzw. Trifluoracetanhydrid versetzt, wobei die N-Formyl- und N-Trifluoracetyl-Verbindungen **3a–c, 4a–c, 7** und **8** gebildet wurden. Die Alkaloide Nicotin und Macrostomin wurden mit 63.3 und 33 % ee durch Reduktion der N-Formyl-Verbindungen **8** und **12** synthetisiert. Die enantioselektive Hydrierung der N-Formyl- und N-Trifluoracetyl-2-phenylpyrroline **14** und **15** mit denselben in-situ-Katalysatoren ergab die cyclischen Amide **3a, 4a** mit bis zu 36.1 % ee.

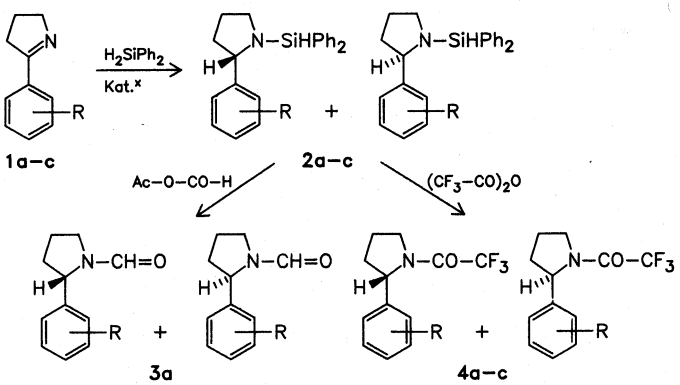
In the enantioselective catalytic synthesis of optically active alkaloids starting from prochiral precursors, the methods hydrosilylation and hydrogenation have been used successfully[2–4)]. For the enantioselective hydrosilylation of prochiral 3,4-dihydro-2H-pyrrole derivatives we have obtained chemical yields of more than 80 % with optical inductions of up to 64 % ee[3)].

In a continuation of our efforts we describe the hydrosilylation of other 3,4-dihydro-2H-pyrrole derivatives and the hydrogenation of N-acyl-2-phenylpyrrolines with the aim to develop enantioselective syntheses of the pyrrolidine alkaloids nicotine and macrostomine[5, 6)]. We approached this goal by using a new work-up of the N-silyl compounds with acetic formic anhydride which allows the introduction of a N-formyl group and its reduction to the N-methyl group typical for nicotine and macrostomine. By this reaction sequence, cyclic five-membered imines can be converted into the alkaloids nicotine and macrostomine.

The catalytic hydrosilylation of the cyclic imines **1a–1c** with diphenylsilane, which gave the silylamines **2a–c**, is shown in Scheme 1. Generally the N-Si-derivatives were not isolated but processed directly.

After derivatization with trifluoroacetic anhydride the optical purity of **4a–4c** was measured by GC on a 50 m Chirasil-L-Val column. The configuration was assigned on the basis of the assumption that the R-enantiomer is eluted prior to the S-enantiomer[7)].

The imine **1a** was hydrosilylated with in-situ catalysts derived from $[Rh(cod)Cl]_2$, cod = 1,5-cyclooctadiene, and different chiral phosphine ligands. In the hydrosilylation of **1a** with $[Rh(cod)Cl]_2$/(–)-Diop in toluene **4a** was obtained in



a: R = H, b: R = m-CH_3, c: R = p-CH_3

64 % ee (R)[3)]. In CH_2Cl_2 and $CHCl_3$ the optical induction decreased to about 40 % ee with chemical yields close to 90 % (Table 1). The catalysts containing (R)-(+)-Prophos, (S) (R)-(+)-BPPFA and (R,R)-(–)-Norphos gave lower optical inductions than the catalysts containing (R,R)-(–)-Diop. The in-situ catalyst $[Rh(cod)Cl]_2$/(–)-Diop converted the substrates **1b** and **1c** into the products **4b** and **4c** with optical purities of 37.2 % ee (R) and 49.6 % ee (R), respectively (Table 1).

In addition to trifluoroacetic anhydride, acetic formic anhydride was introduced for work-up. In this derivatization, N-formyl compounds are obtained. For **3a** it was shown that this change does not influence the chemical and the optical yield. An advantage of the use of acetic formic anhydride for work-up is the fact that N-formyl groups can be easily reduced to methyl groups[8)]. Therefore, the alkaloids nicotine and macrostomine are accessible from **8** and **12**. As the formyl

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Table 1. Hydrosilylation of 2 mmol of imines **1a–c, 5, 10** in 2 ml toluene with 5 mmol (0.9 ml) of diphenylsilane and the in-situ catalysts $[Rh(cod)Cl]_2$/optically active phosphine L; Rh: substrate ratio = 1:50; reaction temperature 0 → 20 °C[11, 12]; work-up method A

substrate imine	phosphine L	Rh/L	t (h)	number of runs	isolated product	chemical yield (%)	optical induction ee (%)
1a	(+)-Diop	1:1.8	48	1	**3a**[3]	90	64.5 (S)
1a	(−)-Diop	1:1.8	48	4	**4a**	90	62.5–65.1 (R)
1a[1]	(−)-Diop	1:1.8	48	1	**4a**	87	39.4 (R)
1a[2]	(−)-Diop	1:1.8	48	2	**4a**	88	39.1–40.9 (R)
1a	(+)-Prophos	1:1.2	40	3	**4a**	88	27.4–28.2 (S)
1a	(+)-BPPFA	1:1.2	40	3	**4a**	92	11.6–12.7 (S)
1a	(−)-Norphos	1:1.3	40	2	**4a**	90	21.9–22.9 (R)
1b	(−)-Diop	1:1.8	48	3	**4b**	92	36.8–37.9 (R)
1c	(−)-Diop	1:1.8	48	3	**4c**	91	49.1–50.5 (R)
5	(+)-Diop	1:1.8	48	6	**7**	28	61.5–66.1 (S)
5	(+)-Diop	1:1.8	48	1	**8**[3]	32	63.3 (S)
10[4]	(+)-Diop	1:1.3	48	1	**12**[3]	90	33.0 (S)

1) Solvent 2 ml CH_2Cl_2.
2) Solvent 2 ml $CHCl_3$.
3) Work-up method B.
4) 0.4 mmol **10**, 1 mmol H_2SiPh_2; Rh: substrate ratio = 1:10.

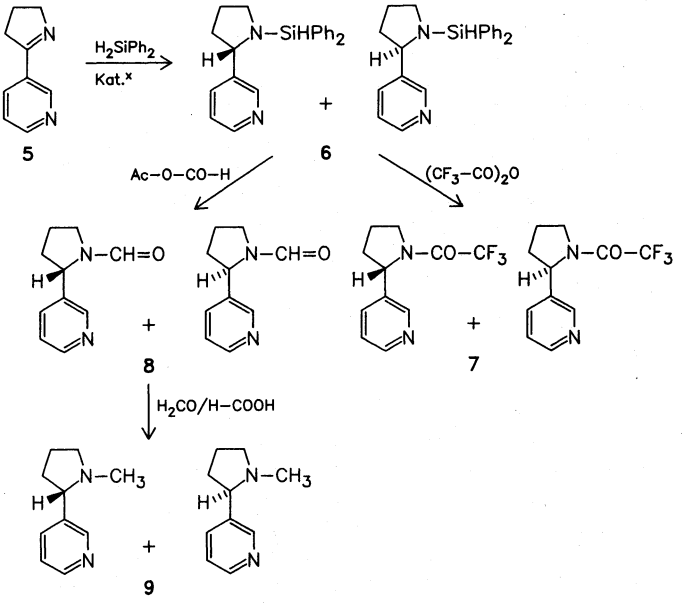
group can also be removed from the N-atom, nornicotine can be synthesized from the corresponding N-formyl derivative[6].

The tobacco alkaloid nicotine **9** was prepared by hydrosilylation of the natural product myosmine **5**[6] to give **6**, work-up with acetic formic anhydride and reduction of **8** with HCHO/HCOOH (Scheme 2).

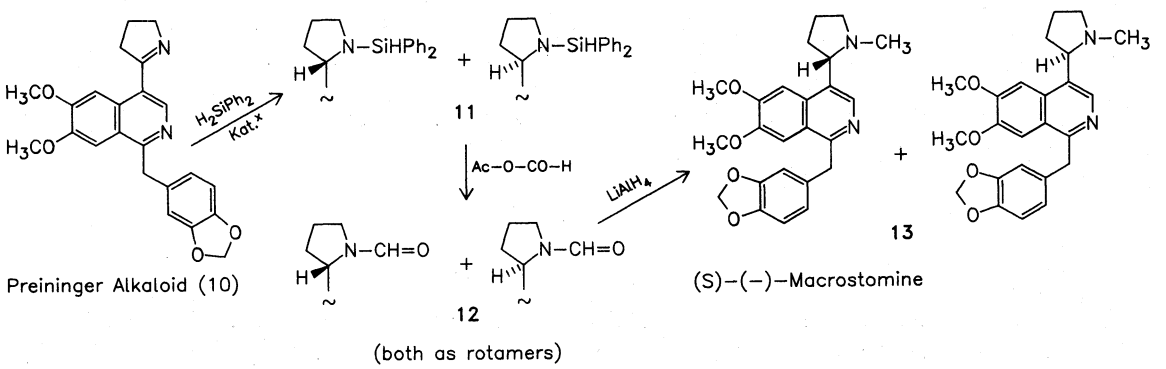
After hydrosilylation of **5** with $[Rh(cod)Cl]_2$/(+)-Diop, the N-silylamine **6** was treated with trifluoroacetic anhydride to give **7** als well as with acetic formic anhydride to give **8**. **7** was shown to have an enantiomeric excess of 63.3 % (S). As **8** could not be measured by GC, it was reduced with HCHO/HCOOH to nicotine **9**, which according to polarimetric measurements in 1 % aqueous KOH[9] had an optical purity of 63.3 % (S).

The hydrosilylation of the *Preininger* Alkaloid **10**, which is insoluble in toluene, was carried out in methylene chloride with the catalyst $[Rh(cod)Cl]_2$/(+)-Diop. After 72 h the hydrosilylation was complete. Treatment of **11** with acetic formic anhydride gave **12** which was reduced to **13**. The enantiomeric excess, determined by optical rotation, was 33 % (S)[10].

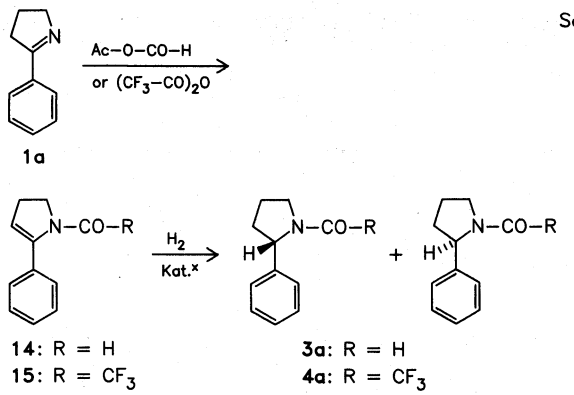
The enamides **14** and **15** were prepared in yields > 90 % by treating the cyclic imine **1a** with acetic formic anhydride or trifluoroacetic anhydride, respectively (Scheme 4).



The hydrogenations of **14** and **15** were carried out in a 100 ml autoclave (Table 2). The chiral phosphine ligands (+)-Prophos, (−)-Norphos, (+)-BPPFA and (−)-Diop in the rhodium catalyzed hydrogenation of **15** gave optical inductions decreasing from 36.1 % ee (Table 2). The preferred configuration is (R) except for (−)-Diop which gives predominantly (S)-products.



Scheme 4



14: R = H
15: R = CF_3

3a: R = H
4a: R = CF_3

In an attempt to prepare the alkaloid macrostomine **13** by enantioselective hydrogenation of the enamine, derived from **10** by formally replacing the 3,4-dihydropyrrole system by the N-methyl-4,5-dihydropyrrole moiety[6], with the catalyst $[Rh(cod)Cl]_2$/(–)-Norphos, there was no reaction even at H_2-pressures of up to 65 bar.

Experimental Part

General remarks

IR-spectra: Beckman Acculab 3. – ^{1}H-NMR spectra: Varian EM 390 (90 MHz), Bruker WM 250 (250 MHz) und Varian EM 360 L (60 MHz); 35 °C, i-TMS in $CDCl_3$. – MS: Varian MAT CH 5. – Optical rotation: Perkin-Elmer polarimeter 241. – GC: Varian Aerograph 1800, T(injector) 250 °C, 50 m-Chirasil-L-Val column, FID; integrator: Spectra Physics SP 4100.

Hydrosilylation and hydrogenation reactions were carried out in dry solvents with exclusion of air.

Hydrosilylation

Method A: The procatalyst $[Rh(cod)Cl]_2$ (10 mg, 0.040 mmol Rh), the optically active cocatalyst (0.048 mmol), and the imine (2 mmol) were dissolved in toluene (2 ml). The solution was stirred for 10 min at room temp. and then cooled to 0 °C. After 10 min diphenylsilane (0.92 ml, 5 mmol) was added. Then, the reaction mixture was slowly warmed up to room temp. and stirred for the reaction time indicated in Table 1. For work-up, the solution was cooled to 0 °C, THF (2 ml) and an excess of trifluoroacetic anhydride (0.8 ml) was added. The mixture was stirred for 10 min at room temp. and cooled to 0 °C. Addition of a saturated $NaHCO_3$ solution (8 ml) brought the pH to 8–9. The mixture was extracted three times with 15 ml of ether. The ether layers were dried over $MgSO_4$.

After filtration the solvent was removed and the product was purified by Kugelrohr distillation.

For the determination of the enantiomeric excess, about 30 mg of the trifluoroacetamide were dissolved in 1 ml of CH_2Cl_2. This solution was used for the GC analysis the conditions of which are given for each individual compound.

Method B: Acetic formic anhydride[15] was used for work-up instead of trifluoroacetic anhydride. The resulting formamide was analyzed in the same way as the trifluoroacetamide.

Hydrogenation

The procatalyst $[Rh(cod)Cl]_2$ (10 mg, 0.040 mmol Rh), the cocatalyst (0.073 mmol), and the enamine (1.0 mmol) were dissolved in MeOH (5 ml). The solution was stirred in a 100 ml autoclave at 20 bar H_2 pressure. After the reaction time indicated in Table 2 the solvent was removed and the product was purified by Kugelrohr distillation.

About 20 mg of the pure product were dissolved in 1 ml of CH_2Cl_2 for measuring the enantiomeric excess by GC as described for each compound.

(S)-(–)-N-Formyl-2-phenylpyrrolidine **(3a)**

Obtained by hydrosilylation of **1a**[3] (method B). B. p. 120 °C/0.05 mm Hg, colourless oil. Yield 95 %. – IR (film): NCO 1671 cm^{-1}. – ^{1}H-NMR (mixture of rotamers): δ (ppm) = 1.68–2.58 (m, 4H), 3.50–3.85 (m, 2H), 4.74–4.95 (m, 0.75H), 4.95–5.22 (m, 0.25H), 7.30–7.53 (m, 5H), 8.10 (s, 0.75H), 8.30 (s, 0.25H). – GC-determination of ee (Table 1): T(column) (T_c) 115 °C, retention time (r. t.) 91.5 and 93.0 min.

(R)-(+)-N-Trifluoroacetyl-2-(3-methylphenyl)pyrrolidine **(4b)**

By hydrosilylation of **1b**[16] (method A). B. p. 120 °C/0.05 mm Hg, colourless oil. Yield > 90 %. – IR (film): NCO 1695 cm^{-1}. – 60 MHz-^{1}H-NMR: δ (ppm) = 1.70–2.33 (m, 4H), 2.37 (s, 3H), 3.67–4.03 (m, 2H), 5.05–5.38 (m, 1H), 6.80–7.60 (m, 4H). – GC-determination of ee (Table 1): T_c 135 °C, r. t. 34.0 and 35.0 min.

(R)-(+)-N-Trifluoroacetyl-2-(4-methylphenyl)pyrrolidine **(4c)**

By hydrosilylation of **1c**[16] (method A). B. p. 120 °C/0.05 mm Hg, colourless oil. Yield > 90 %. – IR (film): NCO 1694 cm^{-1}. – ^{1}H-NMR: δ (ppm) = 1.67–2.47 (m, 4H), 2.33 (s, 3H), 3.63–4.03 (m, 2H), 5.03–5.42 (m, 1H), 6.85–7.80 (m, 4H). – GC-determination of ee (Table 1): T_c 135 °C, r. t. 34.2 and 35.2 min.

(S)-(–)-N-Trifluoroacetyl-2-(3-pyridinyl)pyrrolidine **(7)**

By hydrosilylation of **5**[17] (method A). After drying ($MgSO_4$) the residue was purified by column chromatography (cc) (SiO_2, Merck; ethyl aceta-

Table 2. Hydrogenation of 1 mmol of enamine **14, 15** in 5 ml MeOH with the in-situ catalysts $[Rh(cod)Cl]_2$/optically active phosphine L at 20 °C and 20 bar H_2-pressure[13, 14].
Rh/substrate = 1:25; Rh/L = 1:1.8.

substrate enamine	phosphine L	t (h)	number of runs	isolated product	chemical yield (%)	optical induction ee (%)
14[1]	(–)-Norphos	120	1	**3a**	45	10.7 (R)
15	(+)-Prophos	72	3	**4a**	93	33.5–36.1 (R)
15	(–)-Norphos	72	2	**4a**	91	27.5–28.0 (R)
15	(+)-BPPFA	90	3	**4a**	54	17.4–19.6 (R)
15	(–)-Diop	72	3	**4a**	94	9.4–10.5 (S)
15[2]	(–)-Diop	72	2	**4a**	90	6.9– 7.3 (S)
15[3]	(–)-Diop	72	2	**4a**	92	4.0– 4.8 (S)

1) Rh/substrate = 1:10. 2) Solvent 5 ml toluene. 3) Solvent 5 ml THF.

te), followed by Kugelrohr distillation (100–110 °C, 0.1 mm Hg). Colourless oil. Yield 28 %. – IR (film): NCO 1700 cm^{-1}. – ^{1}H-NMR: δ (ppm) = 1.77–2.65 (m, 4H), 3.65–4.12 (m, 2H), 5.10–5.45 (m, 1H), 7.15–7.60 (m, 2H), 8.40–8.68 (m, 2H). – MS (70 eV): m/z = 244 ($M^{+\cdot}$, 23 %), 175 (60), 166 (41), 147 (100). – GC-determination of ee (Table 1): T_c 140 °C, r. t. 24.0 and 25.1 min.

(S)-(–)-N-Formyl-2-(3-pyridinyl)pyrrolidine, [(S)-(–)-N-Formylnornicotine] **(8)**

By hydrosilylation of **5**[17] (method B). Work-up included cc-purification as described for **7**. Colourless oil. Yield 32 %. IR (film): NCO 1670 cm^{-1}. – ^{1}H-NMR[6] (mixture of rotamers): δ (ppm) = 1.75–2.15 (m, 3H), 2.25–2.60 (m, 1H), 3.47–3.97 (m, 2H), 4.85–5.20 (m, 1H), 7.27–7.54 (m, 2H), 8.39 (s, 0.35H), 8.15 (s, 0.65H), 8.67–8.40 (m, 2H).

(S)-(–)-Nicotine **(9)**

26.4 mg **8** were heated to 100 °C in an autoclave with 1 ml HCHO (37 %) and 1 ml HCOOH (98 %). After 18 h the autoclave was cooled to 0 °C. The excess of HCOOH and HCHO was removed, the residue was treated with 2 N NaOH and extracted with CH_2Cl_2 after saturation with NaCl. After drying (Na_2SO_4) the solvent was removed and the crude product was purified by careful Kugelrohr distillation with efficient cooling (dry ice) at 35–40 °C/0.1 mm Hg. Colourless oil. Yield 90 %. – IR (film): NCH_3 2793 cm^{-1}. – ^{1}H-NMR: δ (ppm) = 1.50–2.52 (m, 5H), 2.11 (s, 3H), 2.92–3.44 (m, 2H), 7.12–7.37 (m, 1H), 7.59–7.80 (m, 1H), 8.38–8.63 (m, 2H). – $[\alpha]_D^{24} = -49.23°$ (c 0.9; 1 % KOH[9]), corresponding to 63.3 % ee (S).

(S)-(–)-6,7-Dimethoxy-1-(3,4-methylenedioxybenzyl)-4-(N-formylpyrrolidinyl-2-)isoquinoline, [N-Formylnormacrostomine] **(12)**

By hydrosilylation of **10**[10] (method B) with Rh:substrate ratio 1:10 and CH_2Cl_2 as solvent. Work-up: 2 ml of acetic formic anhydride were added to the solution at 0 °C. After 20 min the excess of anhydride was destroyed with a saturated $NaHCO_3$-solution (8 ml) and the mixture was extracted immediately with CH_2Cl_2. After drying (Na_2SO_4) and cc (neutral alumina, activity grade 2, Woelm; $CHCl_3$) a pale oil was obtained. Yield 81 %. – ^{1}H-NMR (crude; mixture of rotamers): δ (ppm) = 1.81–2.26 (m, 4H), 3.63–4.22 (m, 2H), 3.91 (s, 3H), 4.01 (s, 3H), 4.49 (s, 2H), 5.34–5.57 (m, 0.8H), 5.69–5.81 (m, 0.2H), 5.87 (s, 2H), 6.73 (s, 3H), 6.99–7.47 (m, 2H), 8.03–8.30 (m, 1.6H), 8.46 (s, 0.4H). – IR- and mass spectra were measured using the white amorphous powder obtained on trituration of 5 mg of crude **12** with a few drops of butyl methyl ether. – IR (KBr): NCO 1673 cm^{-1}. – MS (70 eV): m/z = 420 ($M^{+\cdot}$, 94 %), 419 (100), 405 (58), 391 (17), 389 (23), 377 (11), 310 (19).

Reduction of **12** *to (S)-(–)-Macrostomine* **(13)**

To a suspension of $LiAlH_4$ (31 mg) in 4 ml of absol. THF was added **12** (22 mg) in 3 ml of absol. THF dropwise at 0 °C under N_2 protection. After stirring 15 min at 0 °C and 15 min at room temp. the suspension was refluxed for 40 min. Curiously the reduction is accompanied by formation of a deep red color as already stated in ref.[18]. After cooling to 0 °C the excess of $LiAlH_4$ was destroyed by a few drops of water, the precipitate was stirred subsequently 3x with 10 ml of ether and 1x with 10 ml of CH_2Cl_2. After drying the combined filtrate and extracts (Na_2SO_4), the solvent was evaporated, giving 26 mg of crude **13** (macrostomine). Cc (4 cm, 1.5 cm ∅, neutral alumina, act. grade 2, Woelm; CH_2Cl_2/CH_3CN 9:1) afforded 19.3 mg (90 %) of amorphous **13**; $[\alpha]_D^{25}$ –17.4° (c 0.89, $CHCl_3$), corresponding to 33 % ee (S)[10]. – 250 MHz – ^{1}H-NMR: δ (ppm) = 1.81–2.15 (m, 3H), 2.25 (s, 3H), 2.18–2.46 (m, 2H), 3.26–3.38 (m, 1H), 3.48–3.62 (m, 1H), 3.89 (s, 3H), 4.02 (s, 3H), 4.48 (s, 2H), 5.87 (s, 2H), 6.68–6.82 (m, 3H), 7.32 (s, 1H), 7.80 (s, 1H), 8.40 (s, 1H). – IR-, UV-, ^{1}H-NMR – (90 MHz) and mass spectra as well as tlc in 16 solvents were identical with those of an authentic sample of macrostomine racemate[19].

N-Formyl-4,5-dihydro-2-phenylpyrrole **(14)**

580.08 mg (4 mmol) of **1a**[3], dissolved in 5 ml of acetic formic anhydride, were stirred 15 min at 0 °C, then 1 h at room temp. The excess of anhydride was distilled off i. vac. at 30 °C. Kugelrohr distillation (100–105 °C/0.05 mm Hg) of the residue gave a colourless oil. Yield 669 mg (95 %). **14** is stable under N_2 at –20 °C for at least 3 weeks. – IR (film): NCO 1670 cm^{-1}. – ^{1}H-NMR: δ (ppm) = 2.54–2.86 (m, 2H), 3.86–4.20 (m, 2H), 5.19–5.35 (m, 1H), 7.18–7.58 (m, 5H), 8.40 (s, 1H).
Enantioselective hydrogenation of **14** gave **3a** (see above) (Table 2).

N-Trifluoroacetyl-4,5-dihydro-2-phenylpyrrole **(15)**

To 2.904 g (0.02 mol) of **1a**[3] in 10 ml of absol. THF were added drop by drop 3.5 ml of $(F_3C-CO)_2O$ in 5 ml of absol. THF ab 0 °C. This solution was stirred for 30 min at 0 °C, then 30 min at room temp. The excess of THF and of the anhydride was removed i. vac. at 10 °C/0.05 mm Hg, the residue was distilled by Kugelrohr distillation (70 °C/0.05 mm Hg): colourless oil, which gave white crystals on standing. Yield 4.34 g (90 %). Recrystallization from hexane, m.p. 46–47 °C. **15** is stable under N_2 at –20 °C at least for 1 month. $C_{12}H_{10}F_3NO$ (241.2) Calc. C 59.8 H 4.18 N 5.8 Found C 59.8 H 4.19 N 5.7. – IR (KBr): NCO 1700 cm^{-1}. – ^{1}H-NMR: δ (ppm) = 2.53–2.85 (m, 2H), 4.15–4.30 (m, 2H), 5.70–5.80 (m, 1H), 7.13–7.40 (m, 5H).
Enantioselective hydrogenation of **15** gave **4a** (see above) (Table 2).

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[Ph 357]