Asymmetric Catalysis, 154 [1]. New 1,1'-Binaphthyl Ligands for Enantioselective Catalysis

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Z. Naturforsch. **58b,** 821 – 826 (2003); received June 10, 2003

Chiral binaphthyl compounds, especially those with different substituents in 2- and 2'-position of the binaphthyl system, have gained interest as constituents of successful ligands in various catalytic reactions. Here, we present the synthesis and characterization of new binaphthyl ligands containing oxazoline, cyano and amide substituents in 2'-position in addition to methoxy, hydroxy or amino groups in 2-position. Starting from these compounds new ligands for enantioselective catalysis will be accessible.

Key words: Binaphthyl Derivatives, Chirality, X-Ray Structure

Introduction

1,1'-Binaphthyls substituted in 2- and 2'-position are interesting ligands for enantioselective catalysis. Normally, the same substituents have been used, *e.g.* in BINOL, BINAM or BINAP and their derivatives. However, 1,1'-binaphthyl systems with different substituents in 2- and 2'-position are also easily accessible, *e.g.* those originating from 2-amino-2'-hydroxy-1,1'-binapthyl. In a previous publication we had introduced a new methodology for the synthesis of (*S*)-2-amino-2'-hydroxy-1,1'-binaphthyl ((*S*)-NOBIN) **4** by cleavage of the methylether bond in (*S*)-2-amino-2'-methoxy-1,1'-binaphthyl ((*S*)-NOMBIN) **3** with BBr_3 (Scheme 1) [2]. Thus, **3** and **4** could be prepared enantiomerically pure in large quantities and used as precursors for the synthesis of more sophisticated compounds [2 – 5]. In this paper we describe new 1,1'-binaphthyl derivatives with different substituents in 2- and 2'-position including characterization by X-ray diffraction and conformational analysis [6].

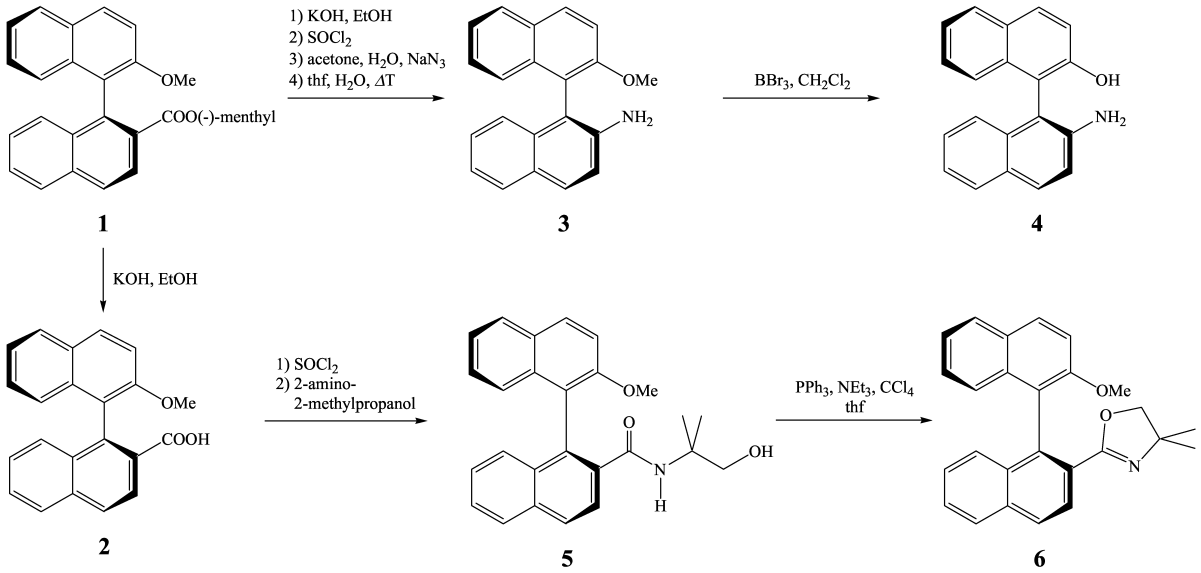
Results and Discussion

Our attempts to optimize the catalytic transfer hydrogenation of acetophenone with 2-propanol focused on binaphthyl systems with different substituents in 2- and 2'-position. Indeed, the Schiff base derived from NOBIN **4** and 2-pyridinealdehyde in combination with $Ru(PPh_3)_3Cl_2$ gave enantioselectivities up to 97.8% ee [2]. In this study we describe the synthesis of the compounds **5**, **6** and **8 – 12** which occurred without racemization.

The synthesis of NOMBIN **3** according to Miyano involved compound **1** (Scheme 1) obtained from the Grignard compound of 1-bromo-2-methoxynaphthalene and (-)-menthyl 1-(-)-menthoxy-2-naphthalenecarboxylate [7]. According to a COSY study we assigned the high field NMR signal at -0.22 ppm of **1** in $CDCl_3$ solution to H^6-axial of the menthyl group. It is a doublet of doublets with $^3J = 11.1$ and 11.9 Hz indicating two axial-axial couplings, the couplings to H^1 (4.49 ppm) and H^5 (1.35 ppm) of the menthyl system. The coupling of H^6-axial to H^6-equatorial results in a small cross peak at 1.22 ppm and a line broadening of 3 Hz. The high-field shift of the H^6-axial signal can be explained with the ring current of the neighboring aromatic system [6, 8]. H^1, H^2, H^5, and H^6 are the hydrogens attached to C1, C2, C5, and C6 (see Fig. 1). From compound **1** crystals suitable for X-ray structure analysis were obtained by slow evaporation of an ethanolic solution (Fig. 1).

A crystal structure analysis of compound **1** had been published in which the crystals had been obtained from hexane [8]. In this orthorhombic form two conformations were found differing in the torsion angle of the naphthalene rings (89.0° and 97.8°) and in the torsion angle of the menthyl substituent at the binaphthyl backbone (C13-C12-C11-O1 1.1° and 10.5°). By the crystallisation from ethanol we obtained a different

* X-ray structure analysis.



Scheme 1.

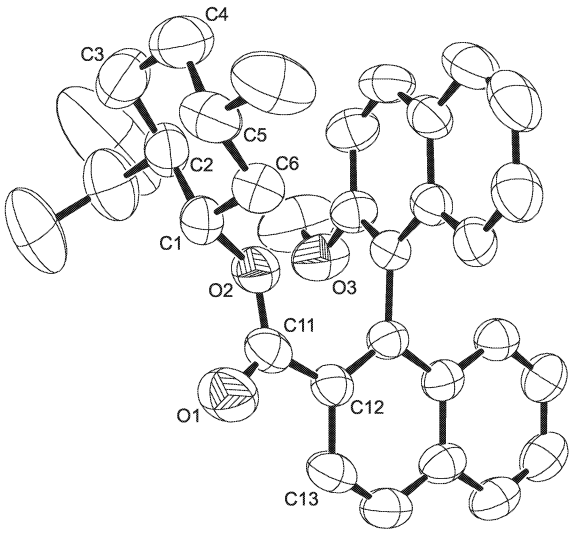


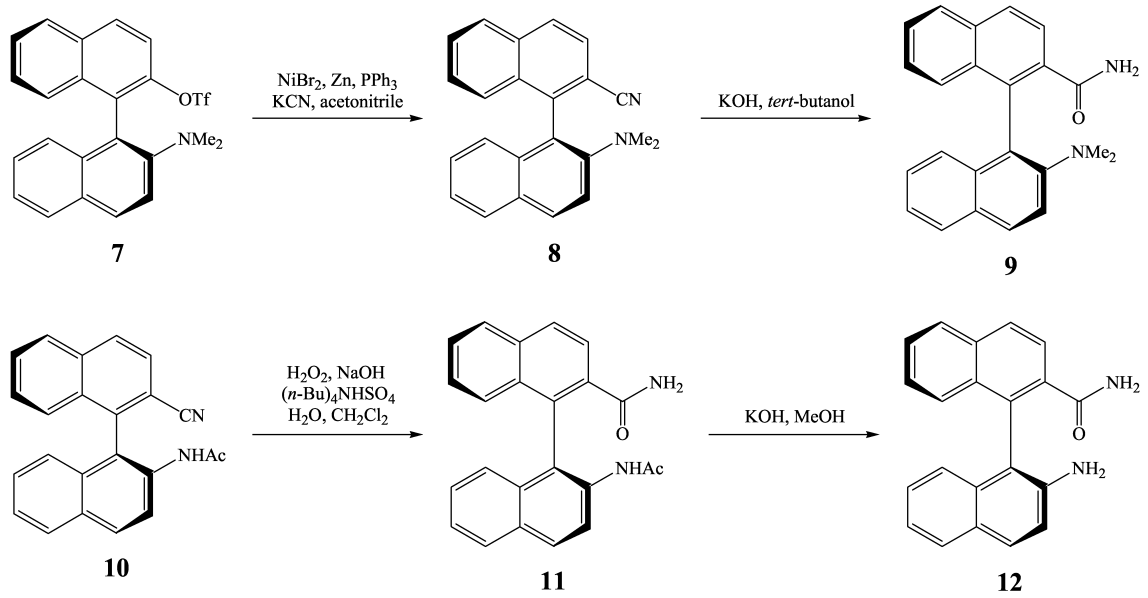
Fig. 1 Molecular structure of **1** in the crystal and atom numbering scheme.

modification with torsion angles of 98.1° for the naphthalene rings and 14.4° for the menthyl substituent (C13-C12-C11-O1) which explains the NMR results. The two protons H^2 and H^6-axial are close to the binaphthyl system. The proton H^6-axial is only 2.7 Å away from the center of the closest aromatic ring. For H^2 the analogous distance is 3.2 Å. Therefore, both protons experience the aromatic ring current leading to the observed high-field shift.

Alkaline hydrolysis of the menthyl ester **1** afforded the carboxylic acid **2** which was transformed to its acid chloride by refluxing in $SOCl_2$. Reaction with 2-amino-2-methylpropanol resulted in formation of amide **5**. The subsequent Mitsunobu reaction closed the ring to give the oxazoline derivative **6** (Scheme 1).

The transformation of NOBIN **4** to triflate **7** was carried out according to literature procedures [9, 10] including methylation of the primary amine with formaldehyde and $NaBH_4$ and subsequent reaction with triflic acid anhydride. Following protocols for triflate substitution reactions [11 – 13] in a one pot synthesis the triflate group was substituted for the cyano group to afford nitrile **8**, which was hydrolysed to carboxamide **9** (Scheme 2). In the ^{1}H NMR spectrum of **9**, the amide protons turned out to be non-equivalent due to restricted rotation in the carboxamide moiety.

In addition to the series of the dimethylamino compounds **7 – 9** the triflate→cyano→carboxamide reaction sequence was also applied to the series of the acetyl-protected compounds **10** and **11**. The synthesis of nitrile **10** from the corresponding triflate was carried out analogously to the reaction **7**→**8**. The hydrolysis of cyanide **10** to carboxymide **11** is more difficult than that of **8**, as it should leave the *N*-acetyl functionality untouched. Phase transfer conditions with H_2O_2 according to ref. 14 selectively led to the formation of **11**. The acetyl group in **11** could be removed by alkaline hydrolysis resulting in the primary amine **12**. As



Scheme 2.

in **9** the amide protons of **11** and **12** showed different chemical shifts.

Experimental Section

IR: Bio-Rad FT-IR-Spektrometer FTS 155; NMR: Bruker AC-250 (^{1}H: 250.1 MHz, ^{13}C: 62.9 MHz, T = 24 °C), Bruker Avance 300 (^{1}H: 300.1 MHz, T = 22 °C), Bruker ARX 400 (^{1}H: 400.1, ^{13}C: 100.6 MHz, ^{31}P: 162.0 MHz, T = 21 °C) und Bruker Avance 400 (^{1}H: 400.1, ^{13}C: 100.6 MHz, ^{31}P: 162.0 MHz, T = 24 °C); TMS (^{1}H and ^{13}C) or H_3PO_4 (^{31}P) were used as standard; MS: Finnigan MAT 95 (FAB (Xe), LSI (Cs^+), PI-DCI (NH_3)), Varian MAT 311A (EI), and Thermo Quest Finnigan TSQ 7000 (ESI); M.p.: Büchi SMP 20; melting points not corrected; optical rotations: Perkin Elmer 241 polarimeter (1 dm cells at r.t.); elemental analysis: Elementar Vario EL III.

(*S*)-2-Amino-2'-methoxy-1,1'-binaphthyl ((*S*)-NOMBIN) [15], (*S*)-2-amino-2'-hydroxy-1,1'-binaphthyl ((*S*)-NOBIN) [2], (*S*)-2-dimethylamino-2'-hydroxy-1,1'-binaphthyl [16], (*S*)-2-acetamino-2'-trifluoromethansulfonyloxy-1,1'-binaphthyl [16] and (*S*)-2-dimethylamino-2'-trifluoromethansulfonyloxy-1,1'-binaphthyl [10] were prepared according to literature methods. All reactions were performed under nitrogen protection in dry solvents.

(S)-(-)-2-Menthoxycarbonyl-2'-methoxy-1,1'-binaphthyl (**1**)

Synthesis according to ref. [7].

^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.19 - 8.10$ (m, 1H, Ar-*H*), 8.04 – 7.90 (m, 3H, Ar-*H*), 7.89 – 7.80 (m, 1H, Ar-*H*), 7.58 – 7.48 (m, 1H, Ar-*H*), 7.46 – 7.23 (m, 4H, Ar-*H*), 7.22 – 7.12 (m, 1H, Ar-*H*), 7.01 – 6.92 (m, 1H, Ar-*H*), 4.49 (dt, ^3J(H,H) = 10.7 Hz, ^3J(H,H) = 4.4 Hz, 1H, OC*H*-Menthyl), 3.75 (s, 3H, OCH_3), 1.61 – 1.10 (m, 6H, C*H*-Menthyl), 0.93 – 0.43 (m, 11H, C*H*-Menthyl), −0.22 (dd, ^3J(H,H) = 11.9 Hz, ^3J(H,H) = 11.1 Hz, 1H, C^6*H*-Menthyl, axial).

(S)-(-)-2-(2-Hydroxy-1,1-dimethylethyl)aminocarbonyl-2'-methoxy-1,1'-binaphthyl (**5**)

Heating a mixture of (*S*)-2-carboxy-2'-methoxy-1,1'-binaphthyl **2** [7] (1.5 g, 4.57 mmol) and thionylchloride (20 ml) for 3 h to reflux results in formation of the carboxy chloride. After evaporation of the volatile liquids the residue was dissolved in thf (10 ml) and dropped to a solution of 2-amino-2-methylpropanol (1.25 g, 14.0 mmol) and triethylamine (2 ml) in thf (15 ml) at 0 °C. After stirring at r.t. for 1 h 2/3 of the solvent was evaporated and the resulting suspension poured in ethyl acetate (200 ml). This mixture was washed with 2n hydrochloric acid (100 ml) and saturated $NaHCO_3$ solution (100 ml). The organic phase was dried over Na_2SO_4 and the solvent was removed in vacuum. The product was isolated by chromatography on silica with ethyl acetate and subsequent recrystallization from toluene (1.61 g, 4.03 mmol, 88%, beige powder). M.p. 198 °C. – $[\alpha]_\lambda^{20}$ (c = 1.0, CH_2Cl_2): −24 (589), −25 (578), −30 (546), −82 (436 nm); IR (KBr): ν = 3353m br (OH), 3060w, 2967w, 2933w, 2900w, 2841w, 1641s (CONHR), 1518s, 1464s, 1336m, 1266s, 1080m, 1061s, 807m, 761m cm^{-1}. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.11 - 7.86$ (m, 5H, Ar-*H*), 7.56 – 7.45 (m, 2H, Ar-*H*), 7.41 – 7.18 (m, 4H, Ar-*H*),

7.01 (d, ^3J(H,H) = 7.1 Hz, 1H, Ar-*H*), 5.87 (sb, 1H, N*H*), 3.80 (s, 3H, OCH_3), 3.28, 3.16 (AB, ^2J(H,H) = 11.9 Hz, 2H, CH^AH^B), 0.72 (s, 3H, CH_3), 0.50 (s, 3H, CH_3). – ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$): δ = 170.0 (C^qO), 154.4 (C^q), 134.7 (C^q), 134.4 (C^q), 133.9 (C^q), 132.5 (C^q), 131.5 (C^q), 130.5 (*C*H), 129.2 (C^q), 128.6 (*C*H), 128.2 (*C*H), 128.1 (*C*H), 127.8 (*C*H), 127.1 (*C*H), 126.8 (2 *C*H), 125.5 (*C*H), 124.6 (*C*H), 124.4 (*C*H), 120.6 (C^q), 113.3 (*C*H), 70.5 (CH_2), 56.6 (OCH_3), 56.0 ($C^q(CH_3)_2$), 24.0 (CH_3), 23.4 (CH_3). – MS (FD, CH_2Cl_2): *m/z* (%) = 399.3 (M^+, 100). – $C_{26}H_{25}NO_3$ (399.5): calcd. C 78.17, H 6.31, N 3.51; found C 78.12, H 6.37, N 3.37.

(S)-(-)-2-(4,4-Dimethyloxazol-2-yl-2'-methoxy)-1,1'-binaphthyl (**6**)

5 (1.0 g, 2.50 mmol) was added to a solution of triphenylphosphane (1.7 g, 6.48 mmol), triethylamine (1.3 ml, 0.94 g, 9.33 mmol) and CCl_4 (1.7 ml) in thf (30 ml) and heated to reflux for 4 h. Then nearly all the solvent was evaporated and the residue dissolved in ethyl acetate (200 ml). The mixture was washed with saturated $NaHCO_3$ solution (100 ml) and saturated NaCl solution (100 ml). After drying the organic phase over Na_2SO_4 the solvent was evaporated and the product isolated by chromatography on silica with ethyl acetate/triethylamine 100:1. The oily product was dissolved in hexane (400 ml) and most of the solvent removed to leave 25 ml. After 24 h at −25 °C the product separated as a light brown solid and could be isolated by filtration (0.90 g, 2.36 mmol, 94%, beige solid). M.p. 65 – 70 °C. – $[\alpha]_\lambda^{20}$ (c = 1.0, THF): −119 (589), −125 (578), −147 (546), −322 (436 nm). – IR (KBr): ν = 3060w, 2966w, 2931w, 2892w, 2840w, 1649m, 1626m, 1594m, 1509m, 1464m, 1357m, 1334m, 1264s, 1254s, 1101m, 1078s, 973m, 809s, 752s cm^{-1}. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.01 – 7.81 (m, 5H, Ar-*H*), 7.55 – 7.37 (m, 3H, Ar-*H*), 7.35 – 7.16 (m, 3H, Ar-*H*), 7.10 – 7.04 (m, 1H, Ar-*H*), 3.77 (s, 3H, OCH_3), 3.54, 3.24 (d, ^2J(H,H) = 7.9 Hz, 2H, CH^AH^B), 1.04 (s, 3H, CH_3), 0.90 (s, 3H, CH_3). – ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$): δ = 163.7 (C^qON), 154.7 (C^q), 135.0 (C^q), 134.5 (C^q), 133.8 (C^q), 132.8 (C^q), 129.4 (*C*H), 128.9 (C^q), 128.1 (*C*H), 127.9 (*C*H), 127.6 (*C*H), 127.3 (C^q), 127.1 (*C*H), 126.9 (*C*H), 126.5 (*C*H), 126.4 (*C*H), 126.3 (*C*H), 125.3 (*C*H), 123.4 (*C*H), 121.9 (C^q), 113.6 (*C*H), 79.2 (CH_2), 66.9 ($C^q(CH_3)_2$), 56.8 (OCH_3), 27.9 (CH_3), 27.8 (CH_3). – MS (EI, 70 eV): *m/z* (%) = 381.2 (M^+, 7), 350.2 (M^+-CH_3O, 100), 294.2 (M^+-$C_5H_{11}O$, 20). – $C_{26}H_{23}NO_2$ (381.5): calcd. C 81.86, H 6.08, N 3.67; found C 81.48, H 6.34, N 3.47.

(S)-(+)-2-Cyano-2'-dimethylamino-1,1'-binaphthyl (**8**)

7 (3.1 g, 6.97 mmol), KCN (4.5 g, 69.7 mmol), $NiBr_2$ (0.67 g, 3.10 mmol), PPh_3 (3.66 g, 14.0 mmol) and activated Zn powder (0.63 g, 9.63 mmol) were suspended in acetonitrile (100 ml). After 6 h heating to reflux the cooled suspension was diluted with ethyl acetate (200 ml) and washed two times with saturated aqueous NaCl solution. The organic phase was dried over $MgSO_4$ and the solvent was removed. The product was isolated by chromatography on silica (CH_2Cl_2/petroleum ether 40/60 1:1) and crystallized from methanol (2.10 g, 6.51 mmol, 94%, yellow needles). M.p. 161 °C. – $[\alpha]_\lambda^{20}$ (c = 1.0, CH_2Cl_2): +87 (589), +91 (578), +108 (546 nm). – IR (KBr): ν = 3064w, 2944w, 2841w, 2796w (NCH_3), 2227m (CN), 1619m, 1595m, 1504s, 1426m, 1334s, 1133s, 992s, 822s, 753s cm^{-1}. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.05 – 7.94 (m, 3H, Ar-*H*), 7.97 (d, ^3J(H,H) = 7.9 Hz, 1H, Ar-*H*), 7.80 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-*H*), 7.65 – 7.55 (m, 2H, Ar-*H*), 7.49 – 7.14 (m, 4H, Ar-*H*), 6.88 (d, ^3J(H,H) = 7.5 Hz, 1H, Ar-*H*), 2.55 (s, 6H, N(CH_3)$_2$). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 150.7 (C^q), 144.2 (C^q), 134.9 (C^q), 133.3 (C^q), 132.7 (C^q), 130.6 (*C*H), 130.0 (C^q), 128.6 (*C*H), 128.5 (*C*H), 128.3 (*C*H), 128.1 (*C*H), 127.6 (*C*H), 127.5 (*C*H), 127.4 (*C*H), 126.7 (*C*H), 124.7 (*C*H), 124.4 (C^q), 124.1 (*C*H), 120.0 (*C*H), 119.0 (*C*N), 112.1 (C^q), 43.9 (2 CH_3). – MS (EI, 70 eV): *m/z* (%) = 322.2 (MH^+, 100), 278.2 (M^+-C_2H_6N, 27). – $C_{23}H_{18}N_2$ (322.4): calcd. C 85.68, H 5.63, N 8.69; found C 85.49, H 5.67, N 8.60.

(S)-(+)-2-Carbamoyl-2'-dimethylamino-1,1'-binaphthyl (**9**)

To a solution of KOH (1.4 g, 25.0 mmol) in *tert*-butanol (25 ml) was added **8** (1.0 g, 3.10 mmol) and heated to reflux for 20 h. The cooled reaction mixture was diluted with dichloromethane (200 ml) and washed several times with water (50 ml). The organic phase was dried over Na_2SO_4 and the solvent was removed. By chromatography on silica (ethyl acetate/petroleum ether 40/60 1:1) the product was separated from the by-products. The solid obtained was dissolved in ethyl acetate (5 ml) and poured into vigorously stirred hexane (200 ml). After 15 h stirring the solid product was separated by filtration (0.75 g, 2.20 mmol, 71%, colorless solid). – M.p. 130 – 131 °C. – $[\alpha]_\lambda^{20}$ (c = 1.0, CH_2Cl_2): +27 (589), +29 (578), +36 (546 nm). – IR (KBr): ν = 3381m br, 3062w, 2838w, 1681s, 1635s ($CONH_2$), 1504m, 1463m, 1381m, 1132m, 980m, 821s, 765s, 652m cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (s, 2H, Ar-*H*), 7.97 – 7.91 (m, 2H, Ar-*H*), 7.82 (d, ^3J(H,H) = 8.2 Hz, 1H, Ar-*H*), 7.52 – 7.45 (m, 2H, Ar-*H*), 7.33 – 7.24 (m, 2H, Ar-*H*), 7.20 (d, ^3J(H,H) = 8.6 Hz, 1H, Ar-*H*), 7.16 – 7.11 (m, 1H, Ar-*H*), 6.84 (s, 1H, NH^{trans}), 6.83 (d, ^3J(H,H) = 8.8 Hz, 1H, Ar-*H*), 5.42 (s, 1H, NH^{cis}), 2.51 (s, 6H, N(CH_3)$_2$). –^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.2 (*C*O), 149.2 (C^q), 134.4 (C^q), 133.9 (C^q), 133.8 (C^q), 133.6 (C^q), 133.2 (C^q), 129.8 (*C*H), 129.6 (C^q), 128.4 (*C*H), 128.2 (*C*H), 127.8 (*C*H), 127.6 (*C*H), 127.0 (*C*H), 126.9 (*C*H), 126.8 (*C*H), 126.3 (*C*H), 125.2 (*C*H), 125.1 (C^q), 124.2 (*C*H), 119.1 (*C*H), 43.3 (2 CH_3). –

MS (EI, 70 eV): 340.2 (M^+, 97), 294.2 (M^+-C_2H_8N, 100). – $C_{23}H_{20}N_2O$ (340.4): calcd. C 81.15, H 5.92, N 8.23; found C 80.91, H 6.00, N 8.27.

(S)-(-)-2-Acetamino-2'-cyano-1,1'-binaphthyl (**10**)

9 (3.40 g, 7.41 mmol), KCN (4.80 g, 74.0 mmol), $NiBr_2$ (0.72 g, 3.30 mmol), PPh_3 (3.90 g, 14.8 mmol) and activated Zn powder (0.66 g, 10.1 mmol) were suspended in acetonitrile. After 5 h heating the cooled mixture was diluted with ethyl acetate (200 ml) and washed two times with concentrated aqueous NaCl solution (100 ml). The organic phase was dried over $MgSO_4$ and the solvent was removed. The residue was chromatographed on silica (toluene/ethyl acetate 4:1) and crystallized from methanol (2.05 g, 6.02 mmol, 82%, colorless crystals). M.p. 207 – 208 °C. – $[\alpha]_\lambda^{20}$ (c = 1.0, CH_2Cl_2): −62 (589), −65 (578), −78 (546), −191 (436 nm). – IR (KBr): ν = 3262m br, 3061w, 2226m (CN), 1665s, 1595m, 1502s, 1429m, 1280s, 819s, 749s cm^{-1}. – ^{1}H NMR (250 MHz, DMSO-d_6): δ = 9.11 (s, 1H, N*H*), 8.25 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-*H*), 8.19 – 7.91 (m, 5H, Ar-*H*), 7.74 – 7.64 (m, 1H, Ar-*H*), 7.52 – 7.25 (m, 3H, Ar-*H*), 7.13 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-*H*), 6.82 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-*H*), 1.69 (s, 3H, COC*H*$_3$). – ^{13}C NMR (63 MHz, DMSO-d_6): δ = 168.6 (*C*O), 140.2 (C^q), 135.2 (C^q), 134.6 (C^q), 132.2 (C^q), 131.5 (C^q), 130.8 (C^q), 129.5 (*C*H), 129.1 (*C*H), 128.9 (*C*H), 128.6 (*C*H), 128.2 (*C*H), 127.8 (*C*H), 127.1 (*C*H), 127.0 (*C*H), 126.1 (*C*H), 125.4 (*C*H), 124.8 (*C*H), 124.7 (C^q), 124.4 (*C*H), 118.4 (*C*N), 111.9 (C^q), 22.9 (*C*H$_3$). – MS (EI, 70 eV): *m/z* (%) = 336.2 (M^+, 53), 294.2 (M^+-C_2H_2O, 100). – $C_{23}H_{16}N_2O$ (340.4): calcd. C 82.12, H 4.79, N 8.33; found C 82.25, H 4.76, N 8.20.

(S)-(+)-2-Acetamino-2'-carbamoyl-1,1'-binaphthyl (**11**)

To a solution of **10** (1.0 g, 2.98 mmol) in CH_2Cl_2 (10 ml) were added an aqueous H_2O_2 solution (30%, 1.5 ml), an aqueous NaOH solution (20%, 1.1 ml), and (n-Bu)$_4$NHSO$_4$ (205 mg, 0.60 mmol). After stirring for 24 h at r.t. the mixture was diluted with CH_2Cl_2 (100 ml) and extracted several times with water (100 ml). After drying the organic phase over Na_2SO_4 and evaporating the solvent, the residue was chromatographed on silica with ethyl acetate. First the starting material was eluted (0.450 mg, 45%) and then the product. The solid obtained from the second fraction was dissolved in CH_2Cl_2 (5 ml) and poured into vigorously stirred hexane (250 ml). After 15 h stirring the product was isolated by filtration (0.50 g, 1.41 mmol, 48%, light yellow solid). M.p. 238 – 239 °C. – $[\alpha]_\lambda^{20}$ (c = 0.5, CH_2Cl_2): +39 (589), +35 (578), +42 (546), +96 (436), +101 (365 nm). – IR (KBr): ν = 3441m (NH), 3275m br (NH), 3136m br, 3062m, 1655s, 1599s, 1500s, 1426s, 1401s, 1296m, 822s, 753s cm^{-1}. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.16 – 7.86 (m, 6H, Ar-*H* und N*H*Ac), 7.60 – 7.51 (m, 1H, Ar-*H*), 7.47 – 7.39 (m, 1H, Ar-*H*), 7.36 – 7.12 (m, 4H, Ar-*H*), 7.02 (d, ^3J(H,H) = 7.9 Hz, 1H, Ar-*H*), 6.00 (s, 1H, NH^{trans}), 5.37 (s, 1H, NH^{cis}), 1.77 (s, 3H, C*H*$_3$). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 171.0 (*C*O), 169.4 (*C*O), 134.4 (C^q), 134.3 (C^q), 134.2 (C^q), 132.9 (C^q), 132.0 (C^q), 131.6 (C^q), 131.0 (C^q), 129.6 (*C*H), 129.4 (*C*H), 128.4 (*C*H), 128.3 (*C*H), 127.7 (*C*H), 127.6 (*C*H), 127.2 (*C*H), 126.5 (*C*H), 125.8 (*C*H), 125.3 (*C*H), 125.2 (*C*H), 125.0 (C^q), 123.5 (*C*H), 23.9 (*C*H$_3$). – MS (EI, 70 eV): *m/z* (%) = 354.1 (M^+, 61), 312.1 (M^+-C_2H_2O, 20), 295.1 (M^+-C_2H_5NO, 100). – $C_{23}H_{18}N_2O_2$ (354.4): calcd. C 77.95, H 5.12, N 7.90; found C 78.28, H 5.43, N 7.39.

(S)-(+)-2-Amino-2'-carbamoyl-1,1'-binaphthyl (**12**)

11 (200 mg, 0.56 mmol) was dissolved in methanol (40 ml) and KOH (400 mg, 7.13 mmol) was added. The solution was heated to reflux for 48 h, after cooling diluted with dichloromethane and washed several times with water (50 ml). The organic phase was dried over $MgSO_4$ and the solvent was evaporated. In the chromatography of the remaining oil on silica with ethyl acetate, the product was eluted first and thus separated from the starting material which eluted as a second fraction (67 mg, 33%). The yellow oil was dissolved in dichloromethane (5 ml) and poured into vigorously stirred hexane (300 ml). After 5 h the solid product was separated (90 mg, 0.29 mmol, 51%, light yellow solid). M.p. 104 – 106 °C. – $[\alpha]_\lambda^{20}$ (c = 0.5, CH_2Cl_2): +4 (589 nm), +1 (578 nm), +6 (546 nm), +94 (436 nm). – IR (KBr): ν = 3460m br (NH), 3345m br (NH), 3209m, 3058m, 1662s, 1621s, 1512m, 1470m, 1388m, 822s, 751s cm^{-1}. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.14 – 8.02 (m, 2H, Ar-*H*), 7.97 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-*H*), 7.88 – 7.76 (m, 2H, Ar-*H*), 7.60 – 7.51 (m, 1H, Ar-*H*), 7.37 – 7.15 (m, 4H, Ar-*H*), 7.11 (d, ^3J(H,H) = 8.7 Hz, 1H, Ar-*H*), 6.87 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-*H*), 6.17 (sb, 1H, NH^{trans}), 5.32 (sb, 1H, NH^{cis}), 3.67 (sb, 2H, N*H*$_2$). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 170.5 (*C*O), 141.9 (C^q), 135.1 (C^q), 134.0 (C^q), 133.8 (C^q), 132.1 (C^q), 131.9 (C^q), 130.2 (*C*H), 129.0 (*C*H), 128.3 (*C*H), 128.2 (*C*H), 128.1 (C^q), 127.6 (*C*H), 127.5 (*C*H), 127.3 (*C*H), 126.7 (*C*H), 126.5 (*C*H), 123.7 (*C*H), 123.0 (*C*H), 118.1 (*C*H), 114.8 (C^q); MS (PI-DCI (NH_3)): *m/z* (%) = 313.3 (MH^+, 100). – $C_{21}H_{16}N_2O$ (312.4): calcd. C 80.75, H 5.16, N 8.97; found C 79.57, H 5.32, N 8.53.

X-ray structure analysis of **1**

The structure was solved by direct methods (SIR-97 and SHELXS-97) and refined by full-matrix least-squares (SHELXL 97) on F^2 with anisotropic displacement parameters for all non-H atoms. The absolute configuration of **1** was given by that of the menthyl substituent. The H atoms were calculated geometrically and a riding model was applied during the refinement process. An absorption correction was not applied [17 – 19].

$C_{32}H_{34}O_3$, MW = 466.59; colorless needles, size [mm]: $0.44 \times 0.16 \times 0.08$; space group P_1; monoclinic; $Z = 2$; $a/b/c$ [Å] = 12.1914(15)/8.5075(5)/13.8950(17); β [°] = 115.978(9); $V = 1295.6(3)$ Å^3; $\rho_{\text{calcd.}} = 1.196$ g·cm^{-3}; $F(000) = 500$; $\mu = 0.588$ mm^{-1}; T = 297 K; ω-scans: $3.54 < 2\theta < 64.83$ °; 4708 reflections collected, 2356 independent, 1965 observed ($I > 2\sigma_1$); $R_{\text{int}} = 0.0382$; diffractometer Enraf-Nonius CAD 4 (Cu-K$_\alpha$, graphite monochromator); R ($I > 2\sigma_1$): $R1 = 0.0485$; $wR2 = 0.1358$; R (all data): $R1 = 0.0582$; $wR2 = 0.1449$; Goof = 1.024. CCDC 208122.

Acknowledgement

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 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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