Monatshefte für Chemie 129, 1319–1327 (1998)

Monatshefte für Chemie
Chemical Monthly

2,2′-Dimethoxy-1,1′-binaphthyl-3,3′-diboronic Acid, a Versatile Intermediate in the Synthesis of 3,3′-Diaryl Substituted Binaphthyl Derivatives

Petra Kratky, Ulrike Haslinger, and **Michael Widhalm***

Institut für Organische Chemie, Universität Wien, A-1090 Wien, Austria

Summary. 2,2′-Dimethoxy-1,1′-binaphthyl-3,3′-diboronic acid was prepared in 48% yield from 2,2′-dimethoxy-1,1′-binaphthyl and used as a key intermediate in *Suzuki* cross-coupling reactions to yield various 2,2′,3,3′-symmetrically substituted binaphthyl derivatives in 22–72% yield.

Keywords. Cross-coupling reaction; *ortho*-Lithiation.

2,2′-Dimethoxy-1,1′-binaphthyl-3,3′-diborsäure, ein vielseitiges Zwischenprodukt in der Synthese 3,3′-diarylsubstituierter Binaphthylderivate

Zusammenfassung. 2,2′-Dimethoxy-1,1′-binaphthyl-3,3′-diborsäure wurde in 48% Ausbeute aus 2,2′-Dimethoxy-1,1′-binaphthyl hergestellt und als Schlüsselverbindung in *Suzuki*-Cross-Kupplungsreaktionen eingesetzt, um zahlreiche 2,2′,3,3′ symmetrisch tetrasubstituierte Binaphthylderivate darzustellen.

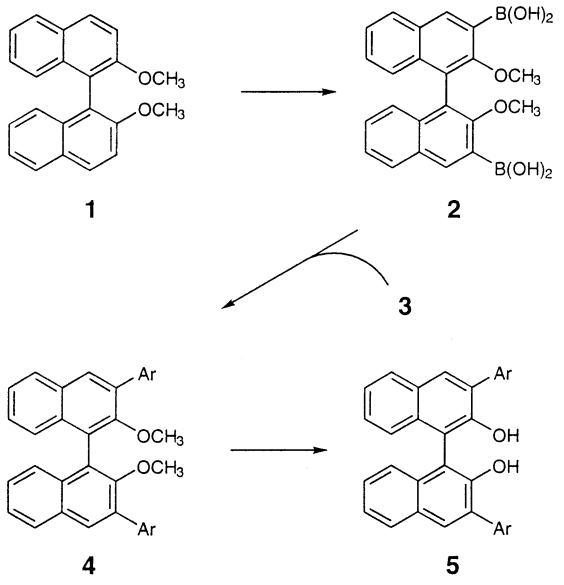
Introduction

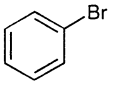
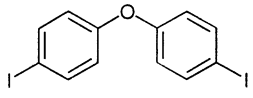
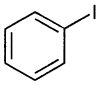
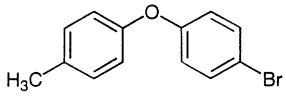
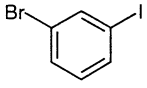
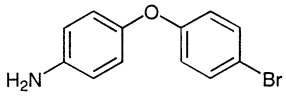
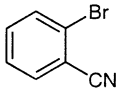
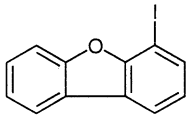
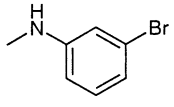
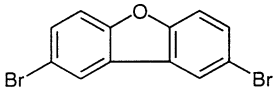
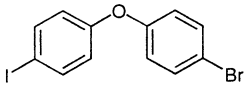
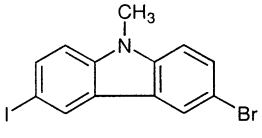
3,3′-Disubstituted 2,2′-binaphthol derivatives have attracted much attention as chiral modifiers in Lewis acid catalyzed reactions [1]. Whereas the *ortho* lithiation/electrophilic substitution protocol permits the introduction of various substituents like halogens, -CHO, -COOH, -CR_2OH, alkyls, or trialkylsilyl groups in a simple one-step procedure [2], the tethering of aromatic moieties often requires a two-step sequence. It has recently been demonstrated that 3,3′-dibromo- and 3,3′-diiodo-2,2-dimethoxy-1,1′-binaphthyl are suitable precursors in the *Suzuki* cross-coupling reaction with aromatic boronic acids [3]. An alternative approach in this methodology is the object of the present report.

Results and Discussion

We recently discovered an alternative approach to a group of 3,3′-diarylsubstituted binaphthyls **4a-l** when exchanging -$B(OH)_2$ and halogen functionalities in the

* Corresponding author



	Ar-Hal (**3**)	Yield of **4**		Ar-Hal (**3**)	Yield of **4**
a		57%	**g**		34%
b		72%	**h**		50%
c		70%	**i**		59%
d		39%[a]	**j**		58%
e		61%	**k**		22%
f		56%	**l**		28%

[a] considerable amount of amide was formed

Scheme 1

reactants of a *Suzuki* coupling (Scheme 1) which offers two advantages. The key intermediate, the 3,3′-diboronic acid **2** of 2,2′-dimethoxy-1,1′-binaphthyl (**1**) was obtained by two-fold *ortho*-lithiation using a standard procedure [4] which was followed by reaction with $B(OCH_3)_3$. After extractive work-up only a single recrystallization step was necessary to obtain a pure product, thus avoiding a chromatographic purification step. Moreover, various aromatic compounds bearing halogen rather than boronic acid substituents are either commercially available or easy to prepare. The convenient access of functionalized haloaromates (*e.g. via* selective monolithiation of symmetrical dihalogenated species) and the mild reaction conditions applied in the *Suzuki* coupling reaction result in the tolerance for many functional groups and opens the access to more complicated structures incorporating a C_2-symmetrical binaphthyl fragment. We found this method to proceed with acceptible yields in the majority of cases, producing binaphthyl derivativatives **4a–l**, in part with extended functionalized side arms. The final cleavage of the methoxy group proceeds smoothly under standard conditions (BBr_3/CH_2Cl_2, 0°C) to afford the bisphenol in good yield as demonstrated for **5c**, **5f**, and **5j**. The application of the new ligands in asymmetric *Diels-Alder* reactions will be the subject of further investigations.

Experimental

Melting points: Kofler melting point apparatus, uncorrected. NMR: Bruker AM 400 spectrometer at 400.13 MHz (^1H) and 100.61 MHz (^{13}C) in $CDCl_3$ if not otherwise noted; chemical shifts are reported in ppm relative to $CHCl_3$ (7.24 or 77.00 ppm). Coupling patterns are designated as s(ingulett), d(oublett), t(riplett), p(seudo), and b(road). $^{13}C\{^1H\}$ NMR spectra are recorded in a *J*-modulated mode (APT). MS: MAT 900 spectrometer (70 eV electron impact or field desorption).

Petroleum ether (*PE*) and CH_2Cl_2 were distilled, N,N,N′,N′-tetramethylethylenediamine (*TMEDA*) was distilled from CaH_2, diethyl ether from $LiA1H_4$, *n*-BuLi was used as a 1.6 molar solution in hexane (Aldrich). Column chromatography was performed on silica gel Si 60, 25–40 µm (Merck). All other chemicals were of analytical grade and used without further purification. Compounds **3a-d** were commercially available and used as purchased, 2,2′-dimethoxy-1,1′-binaphthyl (**1**) was prepared according to Ref. [4]. Elemental analyses of the new compounds agreed satisfactorily with the calculated values.

2,2′-Dimethoxy-1,1′-binaphthyl-3,3′-diboronic acid (**2**, $C_{22}H_{20}B_2O_6$)

To a solution of 5 ml of *TMEDA* (33.3 mmol) in 180 ml of dry diethyl ether, 22.5 ml of *n*-BuLi (36.0 mmol) were added. After stirring for 10 min at room temp. 5.00 g of 2,2′-dimethoxy-1,1′-binaphthyl (**1**, 15.9 mmol) was added and the suspension was stirred for 3 h. The mixture was cooled to −78°C, and 10.8 ml of $B(OCH_3)_3$ (95.1 mmol) were added slowly. After reaching room temp. the reaction mixture was worked up extractively using 2 N HCl and CH_2Cl_2. The organic phase was dried (Na_2SO_4) and evaporated. The solid residue was crystallized from ethyl acetate. The crystallization process starts slowly and takes several days.

Yield: 3.09 g (48%); m.p.: >240°C (dec.); ^1H NMR (*DMSO*-d_6): $\delta = 3.42$ (6H, s), 6.97 (2H, d, $J = 8.5$ Hz), 7.25 (2H, pt, $J = 7.6$ Hz), 7.38 (2H, pt, $J = 7.4$ Hz), 7.97 (2H, d, $J = 8.1$ Hz), 8.17–8.23 (4H, s, D_2O-exchange), 8.20 (2H, s) ppm; ^{13}C NMR (*DMSO*–d_6) $\delta = 60.58$ (CH_3), 122.73 (C), 124.30 (CH), 125.04 (CH), 126.53 (CH), 128.19 (CH), 129.69 (C), 134.31 (C), 135.43 (CH), 158.70 (C), 170.35 (C) ppm; MS (240°C): $m/z = 402$ (2%, M^+).

3-Bromo-N-methylaniline (**3e**)

Prepared from 3-bromoaniline in three steps following reported procedures [5].

^{1}H NMR: $\delta = 2.80$ (3H, s), 3.75 (1H, s), 6.51 (1H, ddd, $J = 8.2$, 2.3, 0.8 Hz), 6.73 (1H, pt, $J = 2.1$ Hz), 6.84 (1H, ddd, $J = 7.8$, 1.8, 0.8 Hz), 7.04 (1H, pt, $J = 8.0$ Hz) ppm; ^{13}C NMR: $\delta = 30.45$ (CH_3), 111.19 (CH), 114.75 (CH), 119.85 (CH), 123.25 (C), 130.36 (CH), 150.52 (C) ppm; MS (30°C): $m/z = 185/187$ (100/100%, M^+).

4-Bromo-4′-iododiphenylether (**3f**)

A solution of 10.00 g of *bis*(4-bromophenyl)ether (30.5 mmol) in 150 ml of diethylether was degassed and cooled to −78°C. 4.5 ml of *TMEDA* (30.0 mmol) were added followed by 20 ml of *n*-BuLi (32.0 mmol). After stirring for 3 h, 11.4 g of I_2 (44.9 mmol) were added, and the reaction was allowed to reach room temp. Excess of I_2 was destroyed by addition of a sat. Na_2SO_3 solution. The organic layer was separated, and the aqueous layer was repeatedly extracted with ether. The combined extracts were washed with brine and dried (Na_2SO_4). The solvent was evaporated, and the crude product was recrystallized from 200 ml of CH_3OH.

Yield: 7.59 g (66%); m.p.: 90–95°C [6]; ^{1}H NMR: $\delta = 6.76$ (2H, d, $J = 8.7$ Hz), 6.88 (2H, d, $J = 9.0$ Hz), 7.45 (2H, d, $J = 8.8$ Hz), 7.63 (2H, d, $J = 9.0$ Hz) ppm; ^{13}C NMR: $\delta = 86.50$ (C), 116.24 (C), 120.65 (CH), 120.92 (CH), 132.81 (CH), 138.78 (CH), 155.81 (C), 156.86 (C) ppm; MS (50°C): $m/z = 374/376$ (100/100%, M^+).

Bis(4-iodophenyl)ether (**3g**)

A similar procedure as reported for the preparation of diiododibenzofuran was applied [7]. 34.00 g of diphenylether (0.20 mol), 48 g of I_2 (0.19 mol), and 60 ml of conc. HNO_3 in 150 ml of $CHCl_3$ were refluxed for 3 h. The precipitated product was separated, washed with water and *PE* and dried over KOH. Crystallization from *PE*/ethyl acetate (4:1) afforded 56.52 g (67%) of **3g**.

M.p.: 139°C [6]; ^{1}H NMR: $\delta = 6.77$ (4H, d, $J = 8.9$ Hz), 7.63 (4H, d, $J = 8.9$ Hz) ppm; ^{13}C NMR: $\delta = 86.62$ (C), 121.04 (CH), 138.80 (CH), 156.70 (C) ppm; MS (30°C): $m/z = 422$ (100%, M^+).

4-Bromo-4′-methyldiphenylether (**3h**)

A solution of 10.00 of *bis*(4-bromophenyl)ether (30.5 mmol) in 180 ml of dry ether was degassed and cooled to −78°C. 5 ml of TMEDA (33.5 mmol) and 21 ml of *n*-BuLi (33.5 mmol) were added dropwise. After 3 h, 20 ml of CH_3I (320 mmol) were introduced by a syringe and the reaction was slowly warmed up to room temp. Water was added, and the mixture was extracted with ether. The organic phase was dried and the solvent was removed under vacuum. The crude product was filtered over a short pad of silica gel. The obtained product was sufficiently pure for the next step.

Yield: 7.47g (93%) [8]; ^{1}H NMR: $\delta = 2.34$, (3H, s), 6.85 (2H, d, $J = 8.8$ Hz), 6.90 (2H, d, $J = 8.5$ Hz), 7.15 (2H, d, $J = 8.5$ Hz), 7.40 (2H, d, $J = 8.7$ Hz) ppm; ^{13}C NMR: $\delta = 21.14$ (CH_3), 115.57 (C), 119.67 (CH), 120.33 (CH), 130.81 (CH), 132.99 (CH), 133.86 (C), 154.67 (C), 157.58 (C) ppm; MS (30°C): $m/z = 262/264$ (100/100%, M^+).

4-Bromo-4′-aminodiphenylether (**3i**)

Prepared according to a reported procedure [9].

^{1}H NMR: $\delta = 3.46$ (1H, bs), 6.66 (2H, m), 6.78 (2H, m), 6.83 (2H, m), 7.34 (2H, m) ppm; ^{13}C NMR: $\delta = 114.25$ (C), 116.18 (CH), 118.81 (CH), 121.08 (CH), 132.33 (CH), 143.02 (C), 148.02 (C) 158.12 (C) ppm; MS (30°C): $m/z = 263/265$ (100/100%, M^+).

1-Iododibenzofuran (**3j**)

Prepared according to a reported procedure [10].

^{1}H NMR: $\delta = 7.10$ (1H, pt, $J = 7.7$ Hz), 7.36 (1H, pt, $J = 7.5$ Hz), 7.49 (1H, pt, $J = 7.8$ Hz), 7.66 (1H, d, $J = 8.3$ Hz), 7.81 (1H, d, $J = 7.7$ Hz), 7.90 (1H, d, $J = 7.7$ Hz), 7.92 (1H, d, $J = 7.7$ Hz) ppm; ^{13}C NMR: $\delta = 75.86$ (C), 112.48 (CH), 120.93 (CH), 121.55 (CH), 123.57 (CH), 124.80 (CH), 124.93 (C), 124.98 (C), 128.14 (CH), 136.33 (CH), 156.09 (C), 156.83 (C) ppm; MS (40°C): $m/z = 294$ (100%, M^+).

3,6-Dibromodibenzofuran (**3k**)

Prepared from dibenzofuran [11].

^{1}H NMR: $\delta = 7.42$ (2H, d $J = 8.8$ Hz), 7.55 (2H, dd, $J = 8.7$, 2.0 Hz), 8.00 (2H, d, $J = 1.8$ Hz) ppm; ^{13}C NMR: $\delta = 113.37$ (CH), 115.94 (C), 123.69 (CH), 125.14 (C), 130.73 (CH), 155.34 (C) ppm; MS (50°C): $m/z = 326$ (100%, M^+).

3-Bromo-6-trimethylsilyl-N-methylcarbazol, (**6**, $C_{16}H_{18}BrNSi$)

The preparation followed a standard procedure [12]. In a typical run, 4.00 g of 3,6-dibromo-N-methylcarbazol (11.8 mmol) were converted to 6.45 g (82%) of **6**.

M.p.: >54°C (dec, CH_2Cl_2/*PE*); ^{1}H NMR: $\delta = 0.35$ (9H, s), 3.79 (3H, s), 7.23 (1H, d, $J = 8.7$ Hz), 7.38 (1H, d, $J = 8.0$ Hz), 7.53 (1H, dd, $J = 8.7$, 1.8 Hz), 7.63 (1H, dd, $J = 8.2$, 1.1 Hz), 8.19 (1H, d, $J = 1.0$ Hz), 8.23 (1H, d, $J = 1.8$ Hz) ppm; ^{13}C NMR: $\delta = -0.65$ (CH_3), 29.10 (CH_3), 108.32 (CH), 109.81 (CH), 111.83 (C), 121.62 (C), 122.97 (CH), 124.43 (C), 125.64 (CH), 128.23 (CH), 129.66 (C), 131.24 (CH), 139.56 (C), 141.83 (C) ppm; MS (50°C): $m/z = 331/333$ (4/5%, M^+), 316/318 (8/8%, M-CH_3), 259/261(100/90%, M-Si(CH_3)$_3$); HRMS: calc. for $C_{16}H_{18}BrNSi$: 331.039, found: 331.041.

3-Iodo-6-bromo-N-methylcarbazole (**3l**, $C_{13}H_9BrIN$)

The preparation followed a standard procedure [12]. In a typical run, 6.35 g of **5** (16.4 mmol) afforded 5.57 g (75%) of **3l**.

M.p.: >230°C (dec); ^{1}H MMR: $\delta = 3.70$ (3H, s), 7.09 (1H, d, $J = 8.4$ Hz), 7.16 (1H, d, $J = 8.4$ Hz), 7.51 (1H, dd, $J = 8.9$, 2.0 Hz), 7.67 (1H, dd, $J = 8.9$, 1.8 Hz), 8.02 (1H, d, $J = 1.5$ Hz), 8.22 (1H, d, $J = 2.0$ Hz) ppm; ^{13}C NMR: $\delta = 29.17$ (CH_3), 81.63 (C), 109.97 (CH), 110.63 (CH), 112.07 (C), 122.98 (C), 123.05 (CH), 124.01 (C), 128.94 (CH), 129.17 (CH), 134.48 (CH), 139.40 (C), 140.20 (C) ppm; MS: (30°C): $mz = 385/387$ (5/5%, M^+), 259/261 (100/100%, M-I); HRMS: calc. for $C_{13}H_9BrIN$: 384.896, found: 384.894.

Suzuki cross-coupling (typical procedure): 3,3′-Bis (4-(4-bromophenoxy)phenyl)-2,2′-dimethoxy-1, 1′-binaphthyl (**4f**)

To a degassed solution of 4.198 g of 4-bromo-4′-iododiphenylether (**3f**, 11.2 mmol) and 150 mg of $Pd(PPh_3)_4$ (0.13 mmol) in 150 ml of toluene, 7.46 ml of a 2 *M* Na_2CO_3 solution (14.9 mmol) and a solution of 1.500 g of 2,2′-dimethoxy-1,1′-binaphthyl-3,3′-diboronic acid (**2**, 3.7 mmol) in 9 ml of dry ethanol were added sequentially. The reaction mixture was refluxed in the dark for 20 h. After cooling, the bulk of solvent was removed under vacuum, and saturated NaCl solution was added. The mixture was extracted exhaustively with CH_2Cl_2, and the combined extracts were washed with brine and dried (Na_2SO_4). The solvent was removed, and the crude product was purified by column chromatography (*PE*/CH_2Cl_2, 6:4) and recrystallyzed (*PE*/CH_2Cl_2) to give 1.696 g (56%) of **4f**.

3,3′-Diphenyl-2,2′-dimethoxy-1,1′-binaphthyl (**4a** = **4b**) [3, 4]

^{1}NMR: $\delta = 3.19$ (6H, s), 7.22–7.27 (4H, m), 7.35–7.43 (4H, m), 7.44–7.49 (4H, m), 7.78 (4H, m), 7.91 (2H, bd, $J = 8.4$ Hz), 7.98 (2H, s) ppm; ^{13}C NMR: $\delta = 60.52$ (CH_3), 124.98 (CH), 125.77 (CH), 125.89 (C), 126.25 (CH), 127.26 (CH), 128.04 (CH), 128.30 (CH), 129.31 (CH), 130.50 (CH), 130.79 (C), 133.61 (C), 135.01 (C), 138.91 (C), 154.07 (C) ppm; MS (200°C): $m/z = 466$ (100%, M^+).

3,3′-Bis(3-bromophenyl)-2,2′-dimethoxy-1,1′-binaphthyl (**4c**, $C_{34}H_{24}Br_2O_2$)

M.p.: 92–97°C; ^{1}H NMR: $\delta = 3.18$ (6H, s), 7.20 (2H, bd, $J = 7.9$ Hz), 7.28 (2H, ddd, $J = 7.9$, 6.5, 1.0 Hz), 7.32 (2H, t, $J = 7.9$ Hz), 7.41 (2H, ddd, $J = 7.9$, 6.6, 1.0 Hz), 7.51 (2H, ddd, $J = 8.4$, 2.0, 1.0 Hz), 7.70 (2H, m), 7.91 (2H, bd, $J = 9.8$ Hz), 7.92 (2H, d, $J = 3.5$ Hz), 7.96 (2H, s) ppm; ^{13}C NMR: $\delta = 60.70$ (CH_3), 122.36 (C), 125.24 (CH), 125.69 (CH), 125.87 (C), 126.67 (CH), 128.04 (CH), 128.17 (CH), 129.83 (CH), 130.32 (CH), 130.65 (CH), 130.69 (C), 132.10 (CH), 133.50 (C), 133.79 (C), 140.88 (C), 153.74 (C) ppm; MS (300°C): $m/z = 624$ (100%, M^+).

3,3′-Bis(2-cyanophenyl)-2,2′-dimethoxy-1,1′-binaphthyl (**4d**, $C_{36}H_{24}N_2O_2$)

After work-up, the crude product was dissolved in CH_2Cl_2 and filtered over silica gel. Preparative TLC (ethyl acetate/*PE* 30:70) gave a crystalline product.

M.p.: >245°C (dec); ^{1}H NMR: $\delta = 3.16$ (6H, s), 7.35 (4H, m), 7.43 (2H, dd, $J = 8.5$, 3.9 Hz), 7.47 (2H, ptd, $J = 7.5$, 1.3 Hz), 7.64 (2H, dd, $J = 8.1$, 1.6 Hz), 7.69 (2H, ptd, $J = 8.1$, 1.3 Hz), 7.79 (2H, dd, $J = 7.8$, 1.0 Hz), 7.92 (2H, d, $J = 8.8$ Hz), 7.98 (2H, s) ppm; ^{13}C NMR: $\delta = 60.98$ (CH_3), 113.19 (C), 118.46 (C), 125.09 (C), 125.42 (CH), 125.94 (CH), 127.26 (CH), 127.76 (CH), 128.24 (CH), 130.26 (C), 131.14 (CH), 131.32 (CH), 131.80 (C), 132.29 (CH), 133.00 (CH), 134.43 (C), 142.62 (C), 153.59 (C) ppm; MS (280°C): $m/z = 516$ (100%, M^+).

3,3′-Bis(3-N-methylaminophenyl)-2,2′=dimethoxy-1,1′-binaphthyl (**4e**, $C_{36}H_{32}N_2O_2$)

^{1}H NMR: $\delta = 3.15$ (6H, s), 7.01 (2H, d, $J = 8.9$ Hz), 7.21 (4H, m), 7.30 (2H, bd, $J = 8.4$ Hz), 7.36 (4H, m), 7.75 (2H, bd, $J = 8.4$ Hz), 7.88 (2H, bd, $J = 7.9$ Hz), 8.02 (2H, s), 8.07 (2H, s), 8.08 (2H, s), 8.34 (2H, s) ppm; ^{13}C NMR: $\delta = 60.44$ (CH_3), 110.64 (CH), 112.12 (CH), 112.16 (C), 120.98 (CH), 122.37 (C), 123.03 (CH), 125.04 (C), 125.06 (CH), 125.80 (CH), 126.00 (C), 126.13 (CH), 128.00 (CH), 128.12 (CH), 128.43 (CH), 130.39 (C), 130.70 (CH), 130.96 (C), 133.39 (C), 135.47 (C), 138.31 (C), 139.14 (C), 154.17 (C) ppm; MS (200°C): $m/z = 524$ (100%, M^+).

3,3′-Bis(4-(4-bromophenoxy)phenyl)-2,2′-dimethoxy-1,1′-binaphthyl (**4f**, $C_{46}H_{32}Br_2O_4$)

M.p.: 125–130°C; ^{1}H NMR: $\delta = 3.20$ (6H, s), 6.97 (4H, d, $J = 8.7$ Hz), 7.10 (4H, d, $J = 8.5$ Hz), 7.24 (4H, m), 7.42 (2H, t, $J = 8.1$ Hz), 7.47 (4H, d, $J = 8.7$ Hz), 7.76 (4H, d, $J = 8.5$ Hz), 7.92 (2H, d, $J = 8.1$ Hz), 7.98 (2H, s) ppm; ^{13}C NMR[a]: $\delta = 60.48$ (CH_3), 115.78 (C), 118.67 (CH), 120.59 (CH), 125.07 (CH), 125.72 (CH), 125.89 (C), 126.29 (CH), 127.99 (CH), 130.29 (CH), 130.79 (CH), 132.71 (CH), 133.54 (C), 134.14 (C), 134.24 (C), 153.97 (C), 156.17 (C), 156.35 (C) ppm; MS (140°C): $m/z = 809$ (10%, M^+).

3,3′-Bis(4-(4-iodophenoxy)phenyl)-2,2′-dimethoxy-1,1′-binaphthyl (**4g**, $C_{46}H_{32}I_2O_4$)

M.p.: 133–135°C; ^{1}H NMR: $\delta = 3.21$ (6H, s), 6.85 (4H, d, $J = 8.9$ Hz), 7.10 (4H, d, $J = 8.7$ Hz), 7.25 (4H, m), 7.41 (2H, pt, $J = 8.0$ Hz), 7.64 (4H, d, $J = 8.9$ Hz), 7.76 (4H, d, $J = 8.6$ Hz), 7.92 (2H, d,

[a] One C_{quart} was not observed

$J = 8.2$ Hz), 7.98 (2H, s) ppm; ^{13}C NMR[a]: $\delta = 60.48$ (CH_3), 86.08 (C), 118.80 (CH), 121.00 (CH), 125.08 (CH), 125.74 (CH), 125.91 (C), 126.31 (CH), 128.01 (CH), 130.30 (CH), 130.81 (CH), 133.58 (C), 134.16 (C), 134.35 (C), 138.70 (CH), 154.00 (C), 156.03 (C), 157.27 (C) ppm; MS (250°C): $m/z = 902$ (10%, M^+), 776 (15%, M-I), 684 (100%, M-OC_6H_4I).

3,3′-Bis(4-(4-methylphenoxy)phenyl)-2,2′-dimethoxy-1,1′-binaphthyl (**4h**, $C_{48}H_{38}O_4$)

M.p.: 133–140°C; ^{1}H NMR: $\delta = 2.34$ (6H, s), 3.20 (6H, s), 6.99 (4H, d, $J = 8.5$ Hz), 7.07 (4H, d, $J = 8.6$ Hz), 7.16 (4H, d, $J = 8.4$ Hz), 7.23 (4H, m), 7.39 (2H, m), 7.72 (4H, d, $J = 8.6$ Hz), 7.90 (2H, d, $J = 8.2$ Hz), 7.96 (2H, s) ppm; ^{13}C NMR: $\delta = 20.70$ (CH_3), 60.43 (CH_3), 118.00 (CH), 119.27 (CH), 124.98 (CH), 125.76 (CH), 125.92 (C), 126.17 (CH), 127.97 (CH), 130.21 (CH), 130.27 (CH), 130.58 (CH), 130.81 (C), 133.36 (C), 133.51 (C), 134.33 (C), 154.08 (C), 154.56 (C), 157.32 (C) ppm; MS (270°C): $m/z = 678$ (100%, M^+).

3,3′-Bis(4-(4-aminophenoxy)phenyl)-2,2′-dimethoxy-1,1′-binaphthyl (**4i**, $C_{46}H_{36}N_2O_4$)

M.p.: 125–129°C; ^{1}H NMR: $\delta = 3.19$ (6H, s), 3.57 (4H, bs) 6.67 (4H, m), 6.92 (4H, m), 7.01 (4H, m), 7.22 (4H, m), 7.37 (2H, ddd, $J = 8.0$, 5.6, 2.3 Hz), 7.68 (4H, m), 7.88 (2H, bd, $J = 8.2$ Hz), 7.94 (2H, s) ppm; ^{13}C NMR: $\delta = 60.39$ (CH_3), 116.20 (CH), 116.89 (CH), 121.19 (CH), 124.92 (CH), 125.72 (CH), 125.86 (C), 126.08 (CH), 127.91 (CH), 130.11 (CH), 130.43 (CH), 130.77 (C), 132.58 (C), 133.42 (C), 134.42 (C), 142.79 (C), 148.36 (C), 154.05 (C), 158.36 (C) ppm; MS (280°C): $m/z = 681$ (50%, M^+).

3,3′-Bis(1-dibenzofuranyl)-2,2′-dimethoxy-1,1′-binaphthyl (**4j**, $C_{46}H_{30}O_4$)

M.p.: 205–209°C; ^{1}H NMR: $\delta = 3.25$ (6H, s), 7.30–7.52 (14H, m), 7.78 (2H, d, $J = 7.6$ Hz), 7.96 (6H, m), 8.25 (2H, s) ppm; ^{13}C NMR: $\delta = 60.87$ (CH_3), 111.81 (CH), 119.85 (CH), 120.64 (CH), 122.67 (CH), 122.75 (CH), 123.41 (C), 124.39 (C), 124.48 (C), 124.99 (CH), 125.53 (C), 125.95 (CH), 126.56 (CH), 127.08 (CH), 128.23 (CH), 128.79 (CH), 129.85 (C), 130.57 (C), 131.61 (CH), 134.11 (C), 153.96 (C), 154.68 (C), 156.21 (C) ppm; MS (240°C): $m/z = 646$ (100%, M^+).

3,3′-Bis(6-bromo-dibenzofuran-3-yl)-2,2′-dimethoxy-1,1′-binaphthyl (**4k**, $C_{46}H_{28}Br_2O_4$)

M.p.: 135–139°C; ^{1}H NMR: $\delta = 3.20$ (6H, s), 7.30 (4H, m), 7.44 (2H, m), 7.45 (2H, d, $J = 6.8$ Hz), 7.55 (2H, dd, $J = 8.1$, 1.5 Hz), 7.65 (2H, d, $J = 8.1$ Hz), 7.92 (2H, dd, $J = 8.9$, 1.9 Hz), 7.95 (2H, d, $J = 8.1$ Hz), 8.06 (2H, s), 8.12 (2H, d, $J = 1.7$ Hz), 8.33 (2H, d, $J = 1.4$ Hz) ppm; ^{13}C NMR: $\delta = 60.58$ (CH_3), 111.63 (CH), 113.24 (CH), 115.67 (C), 121.56 (CH), 123.38 (C), 123.70 (CH), 125.20 (CH), 125.80 (CH), 126.05 (C), 126.36 (C), 126.43 (CH), 128.08 (CH), 129.57 (CH), 129.98 (CH), 130.78 (CH), 130.87 (C), 133.66 (C), 134.06 (C), 134.63 (C), 154.01 (C), 155.32 (C), 156.10 (C) ppm; MS (280°C): $m/z = 802$ (5%, M^+), 636 (22%), 560 (78%).

3,3′-Bis(6-Bromo-N-methylcarbazo-3-yl)-2,2′-dimethoxy-1,1′-binaphthyl (**4l**, $C_{48}H_{34}Br_2N_2O_2$)

M.p.: 320–325°C (dec); ^{1}H NMR : $\delta = 3.23$ (6H, s), 3.88 (6H, s), 7.25–7.34 (6H, m), 7.44 (2H, m), 7.49 (2H, d, $J = 8.9$ Hz), 7.67 (2H, bd, $J = 8.4$ Hz), 7.97 (4H, m), 8.10 (2H, s), 8.28 (2H, bs), 8.48 (2H, s) ppm; ^{13}C NMR: $\delta = 29.31$ (CH_3), 60.43 (CH_3), 108.48 (CH), 109.99 (CH), 111.83 (C), 121.18 (CH), 121.92 (C), 123.19 (CH), 124.67 (C), 124.98 (CH), 125.86 (CH), 126.05 (CH), 126.10

[a] One C_{quart} was not observed

(C), 127.96 (CH), 128.21 (CH), 128.38 (CH), 130.22 (C), 130.56 (CH), 130.99 (C), 133.46 (C), 135.43 (C), 139.95 (C), 140.67 (C), 154.28 (C) ppm; MS (290°C): $m/z = 830$ (100%, M^+).

3,3′-Bis(3-bromophenyl)-2,2′-dihydroxy-1,1′-binaphthyl (**5c**, $C_{32}H_{20}Br_2O_2$) (*typical procedure*)

A solution of 300 mg of **4c** (0.48 mmol) in 8 ml of CH_2Cl_2 was cooled to −78°C and, 0.15 ml of BBr_3 (excess) were added. The solution was stirred first at −78°C (0.5 h) and then at room temp. (5 h). Water was added to the ice cold solution, and the aqueous layer was extracted twice with CH_2Cl_2 (2×10 ml). The organic extracts were washed with brine and dried (Na_2SO_4). Evaporation left a white powder which was dried *in vacuo* at 80°C overnight;

Yield: 286 mg (100%); m.p.: 106–109°C; ^{1}H NMR: $\delta = 5.30$ (2H, s), 7.19 (2h, bd, $J = 8.5$ Hz), 7.33 (4H, m), 7.40 (2H, m), 7.52 (2H, m), 7.66 (2H, m), 7.89 (2H, pt, $J = 1.8$ Hz), 7.92 (2H, bd, $J = 7.5$ Hz), 8.01 (2H, s) ppm; ^{13}C NMR: $\delta = 112.06$ (C), 122.41 (C), 124.12 (CH), 124.64 (CH), 127.84 (CH), 128.24 (CH), 128.61 (CH), 129.20 (C), 129.41 (C), 129.84 (CH), 130.68 (CH), 131.73 (CH), 132.59 (CH), 133.03 (C), 139.53 (C), 150.01 (C) ppm; MS (FD, 190°C): $m/z = 596.2$ (100%, M^+); HRMS: calc. for $C_{32}H_{20}Br_2O_2$: 593.9830, found: 593.9841.

3,3′-Bis(4-(4-bromophenoxy)phenyl)-2,2′-dihydroxy-1,1′-binaphthyl (**5f** $C_{44}H_{28}Br_2O_4$)

Yield: 93%; m.p.: 176–179°C; ^{1}H NMR: $\delta = 5.33$ (2H, s), 6.95 (4H, bd, $J = 8.8$ Hz), 7.09 (4H, bd, $J = 8.8$ Hz), 7.20 (2H, bd, $J = 8.3$ Hz), 7.31 (2H, bpt, J≈7.3 Hz), 7.38 (2H, bpt, J≈7.2 Hz), 7.44 (4H, bd, $J = 8.8$ Hz), 7.70 (4H, bd, $J = 8.8$ Hz), 7.91 (2H, bd, $J = 7.8$ Hz), 8.01 (2H, s) ppm; ^{13}C NMR[a] $\delta = 112.18$ (C), 115.94 (C), 118.70 (CH), 120.76 (CH), 124.19 (CH), 124.47 (CH), 127.45 (CH), 128.44 (CH), 129.50 (C), 129.86 (C), 131.16 (CH), 131.35 (CH), 132.76 (CH), 132.81 (C), 150.18 (C), 156.27 (C), 156.58 (C) ppm; MS (255°C): $m/z = 780$ (100%, M^+), 610/608 (95/80%); HRMS: calc. for $C_{44}H_{28}Br_2O_4$: 788.0354, found: 778.0392.

3,3′-Bis(1-dibenzofuranyl)-2,2′-dihydroxy-1,1′-binaphthyl (**5j**, $C_{44}H_{26}O_4$)

Chromatography on SiO_2 (CH_2Cl_2/*PE*, 1:1) afforded at white foam. Yield: 69%; ^{1}H NMR: $\delta = 5.54$ (2H, s), 7.35 (2H, ddd, $J = 8.0$, 7.5, 0.9 Hz), 7.39–7.49 (10H, m), 7.52 (2H, bd, $J = 8.2$ Hz), 7.74–7.76 (2H, m), 7.96–8.02 (6H, m), 8.28 (2H, s) ppm; ^{13}C NMR: $\delta = 111.86$ (CH), 112.79 (C), 120.32 (CH), 120.70 (CH), 122.07 (C), 122.78 (CH), 122.85 (CH), 124.29 (C), 124.33 (CH), 124.55 (CH), 124.67 (C), 127.22 (CH), 127.55 (CH), 128.63 (CH), 128.84 (CH), 129.06 (C), 129.31 (C), 132.56 (CH), 133.37 (C), 150.58 (C), 153.95 (C), 156.13 (C) ppm; MS (150°C): $m/z = 618.9$ (100%, M^+); HRMS: calc. for $C_{44}H_{26}O_4$: 618.183, found: 618.186.

References

[1] See: (a) Narasaka K (1991) Synthesis 1; (b) Altenbach HJ (1992) In: Organic Synthetic Highlights 1991. VCH, p 66; (c) Maruoka K, Yamamoto H (1993) In: Ojima I (ed) Asymmetric Synthesis. VCH, p 413
[2] Snieckus V (1990) Chem Rev **90**: 879
[3] Cox P J, Wang W, Snieckus V (1992) Tetrahedron Lett **33**: 2253
[4] Lingenfelter DS, Helgeson RC, Cram DJ (1981) J Org Chem **46**: 393
[5] Gorvin JH (1955) J Chem Soc 83
[6] Scarborough HA (1929) J Chem Soc London 2361

[a] One C_{quart} was not observed

[7] Gilman H, Brown GE, Bywater WG, Kirkpatrick WH (1934) J Am Chem Soc **56**: 2473
[8] Brewster RQ, Slocombe R (1945) J Am Chem Soc **67**: 562
[9] Suter CM (1929) J Am Chem Soc **51**: 258
[10] Gilman H, Avakian S (1945) J Am Chem Soc **67**: 349
[11] (a) Hoffmeister W (1871) Ann Chem Pharm **159**: 191; (b) Cullinane NM, Davey HG, Padfield HJH (1934) J Chem Soc 716
[12] Paek K, Kim K, Kim Y (1993) Bull Korean Chem Soc **14**: 732

Received August 3, 1998. Accepted August 24, 1998