Palladium-Catalyzed Reactions, 2[◇]

Suzuki Coupling of Chiral 1,1′-Binaphthyl Systems − New Synthetic Routes to Functionalize the 2- and 2,2′-Positions

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1,1′-Binaphthyl derivatives **1**-**5**, substituted in the 2- or 2,2′-positions are used in palladium-catalyzed Suzuki coupling reactions. The *mono*- and *bis*-borylated coupling components **2**, **4** and **5** can easily be prepared and purified, are air-stable and are therefore interesting starting materials for Suzuki coupling reactions with several aryl halides. Thus a variety of new axially-chiral 2- and 2,2′-arylated 1,1′-binaphthyls can be synthesized. Selective monoarylation of **3**, **4** and **5** can be performed. Subsequent and stepwise arylation offers general access to unsymmetrically substituted binaphthyls. Moreover, interesting atropisomeric complex molecules, such as 4,4′-bis[2-(1,1′-binaphthyl)]-1,1′-biphenyl (**18a**), are accessible. Compounds of type **18**, which can be obtained by twofold Pd-catalyzed coupling reactions, are of high potential value as ligands or promoters in catalytic, asymmetric processes or as chiral precursor molecules for host-guest interactions.

Axially-chiral compounds are of great synthetic value in organic chemistry. The binaphthyl-based atropisomers, especially, have proved to be extremely important as chiral inductors for asymmetric synthesis, with a high degree of enantioselectivity in various stoichiometric and catalytic asymmetric transformations[2]. Our investigations of the syntheses and applications of chiral organoboranes[3] have led to the development of bidentate Lewis acids offering the possibility of cooperative binding effects in asymmetric catalysis. We have thus recently reported on the first synthesis of 2- and 2,2′-boryl-substituted 1,1′-binaphthyls[4]. Meanwhile, the synthesis of **2** could be optimized by borylation of **1** and subsequent esterification with pinacol to yield 58% of the pinacol ester **2**.

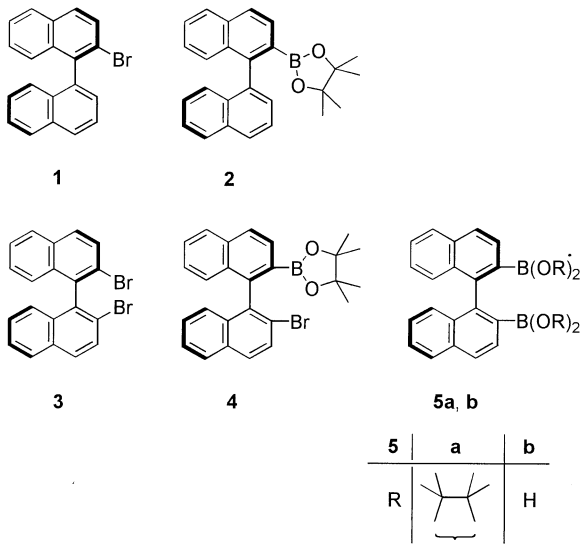
These new axially-chiral mono- and bis-borylated 1,1′-binaphthyls offer new synthetic routes towards functionalized binaphthyl systems and are interesting starting materials for Pd-catalyzed C−C coupling reactions such as the Suzuki coupling. Cross-coupling reactions of aryl boron derivatives with aryl halides to synthesize biaryls have been extensively studied[5].

This type of Suzuki coupling reaction can be used for the synthesis of natural products, containing polyfused aromatic rings, such as azafluoranthene alkaloids[6] or (−)-steganone[7] (antileukaemic bisbenzocyclooctadiene lignan lactone).

In recent years, Suzuki couplings have been used to obtain aromatic rigid-rod polymers, such as polyphenylenes[8], which play an important role in a number of diverse technologies, including high-performance engineering materials, conducting polymers and nonlinear optical materials. Moreover, by repetitive Suzuki coupling, interesting nanostructures can be achieved[9].

Diederich et al.[10] described the synthesis of potential chiral receptors based on binaphthyl units, which can be obtained by Stille coupling. But there are only a few ex-

Scheme 1. Potential starting materials for Suzuki coupling reactions



[◇] Part 1: See ref.[1].

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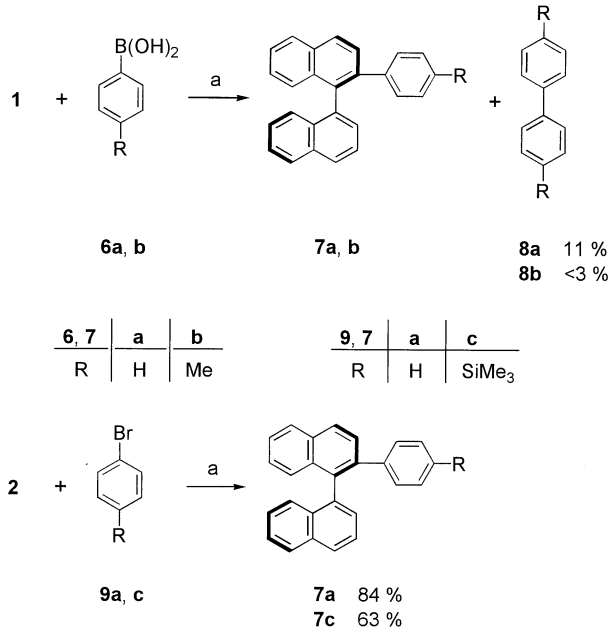
amples of Suzuki coupling of binaphthyls, such as the bisarylation in the 3,3′-positions[11]. Pu et al. investigated Suzuki coupling reactions in the 6,6′-binaphthyl positions to synthesize conjugated polymers with main-chain chirality[12]. This paper is the first to report on Suzuki coupling of chiral binaphthyls in the 2- and 2,2′-positions, which offers easy and general access to a number of new atropisomeric 1,1′-binaphthyl derivatives.

Results and Discussion

As the arylboronic acid components **2**, **4** and **5** are *o*-substituted, the Suzuki coupling reactions were expected to be sensitive to steric hindrance[13][5b]. We decided to use nonaqueous reaction conditions[14]. The couplings were performed either in a mixture of toluene and ethanol or in DMF, using freshly synthesized tetrakis(triphenylphosphane)palladium(0) as catalyst. Solid sodium carbonate was used as base, and the reaction was heated at 100°C for 12−24 h. Investigating the following reactions all axially-chiral substances shown were used as racemates.

Scheme 2. Synthesis of monoarylated binaphthyl systems

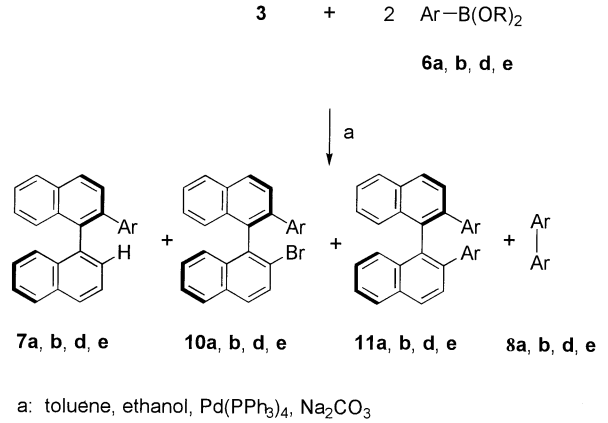


a: toluene, ethanol, $Pd(PPh_3)_4$, Na_2CO_3

2-Bromo-1,1′-binaphthyl (**1**) was reacted with the boronic acids **6a** and **6b**, to give 2-monoarylated binaphthyls **7a** and **7b** in good to excellent yields (81−95%, see Scheme 2). Some homocoupling[15] of the boronic acid components was observed (11% of biphenyl **8a** and < 3% of 4,4′-dimethylbiphenyl **8b**). When 1,1′-binaphthyl-2-boronic acid pinacol ester (**2**) was treated with the aryl halides **9a** and **9c**, no homocoupling of the boronic acid component was detected. The products **7a** and **7c** were isolated in good yields (63−84%). 2-(4-Trimethylsilylphenyl)-1,1′-binaphthyl (**7c**) is a very interesting coupling product, since the trimethylsilyl group can easily be further substituted (for example, by halides or by boronic acid functionalities by means of silicon-boron exchange) to offer new possibilities for subsequent Suzuki coupling reactions.

Further investigations were carried out with 2,2′-disubstituted 1,1′-binaphthyls **3**−**5**.

Scheme 3. Suzuki coupling of 2,2′-dibromo-1,1′-binaphthyl (**3**)



a: toluene, ethanol, $Pd(PPh_3)_4$, Na_2CO_3

As shown in Scheme 3, 2,2′-dibromo-1,1′-binaphthyl (**3**) could be selectively monoarylated by means of coupling reactions with phenyl boronic acids and esters **6a**, **6b** and **6d** or with 1-naphthyl boronic acid (**6e**). The resulting 2-bromo-2′-aryl-1,1′-binaphthyls **10** (assignment of the structure on the basis of MS data) were reduced to yield the 2-aryl-1,1′-binaphthyls **7** as main products (34−67%, Table 1). The bisarylated species could only be detected in trace amounts (< 3%) by mass spectrometry. As before, 2−9% of the homocoupled products **8** of the boronic acid components were obtained. Therefore, the Suzuki coupling reaction allows the synthesis of a variety of new chiral monoarylated binaphthyl compounds **7a**−**7f** (see Schemes 2−4).

Suzuki coupling of 1,1′-binaphthyl-2,2′-diboronic acid (**5b**) with several aryl halides **9b**, **12a**, **12d** and **12f** in DMF led to the formation of 2-monoarylated 1,1′-binaphthyls **7** in modest yields (23−34%, see Scheme 4, Table 2). The by-product **7a** (10−30%) could be separated (except for entry 2) and results from the partial incorporation of phenyl groups from the triphenylphosphane ligands of the catalyst[16]. For entry 4, 11% of the homocoupled product of 4-nitroiodobenzene (**12f**) (4,4′-dinitro-1,1′-biphenyl) could be isolated. This coupling type has already been reported by Dziuba et al.[17]. When purifying the crude reaction mixture by flash chromatography, the primary products 2-aryl-1,1′-binaphthyl-2′-boronic acids were probably cleaved by the silica gel to the corresponding 2-aryl-1,1′-binaphthyls **7**. To confirm this, the crude product mixture of a coupling reaction of the diboronic acid **5b** with **9a** was reacted with pinacol. In this case, 30% of the stable 2-phenyl-1,1′-binaphthyl-2′-boronic acid pinacol ester (**13**) could be isolated. Better yields were obtained when the diboronic acid bispinacol ester **5a** was coupled directly with **9a** to give 41% of **13**. In the synthesis of **13**, the by-product 2-phenyl-1,1′-binaphthyl (**7a**, by deborylation of **13**) and the autoxidation product 2-hydroxy-2′-phenyl-1,1′-binaphthyl (**14**) were observed. The autoxidation of organoboron compounds is described in

Table 1. Suzuki coupling of 2,2′-dibromo-1,1′-binaphthyl (**3**)

Entry	$ArB(OR)_2$	Yields of the products			
1	**6a** $H-C_6H_4-B(OH)_2$	67% of **7a**	<3% of **10a**[a]	<3% of **11a**[a]	2% of **8a**[a]
2	**6b** p-$CH_3-C_6H_4-B(OH)_2$	50% of **7b**	16% of **10b**[a]	<3% of **11b**[a]	3% of **8b**[a]
3	**6d** p-$CH_3O-C_6H_4-B(O_2C_6H_{12})$	34% of **7d**	14% of **10d**[a]	<3% of **11d**[a]	9% of **8d**
4	**6e** 1-$C_{10}H_7-B(OH)_2$	62% of **7e**	≈4% of **10e**[a]	<3% of **11e**[a]	8% of **8e**

[a] Detection and assignment by mass spectrometry.

Scheme 4. Suzuki coupling of borylated binaphthyl systems

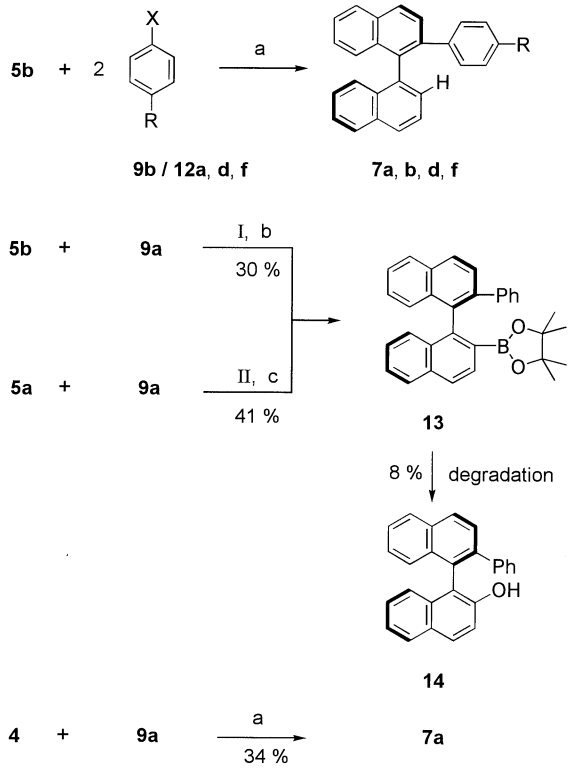


Table 2. Suzuki coupling of bisborylated binaphthyl (**5b**)

Entry	no.	R	X	Products	By-product
1	**12a**	H	I	34% of **7a**	–
2	**9b**	Me	Br	24% of **7b**	10% of **7a**
3	**12d**	OMe	I	23% of **7d**	30% of **7a**
4	**12f**	NO_2	I	26% of **7f**	22% of **7a**

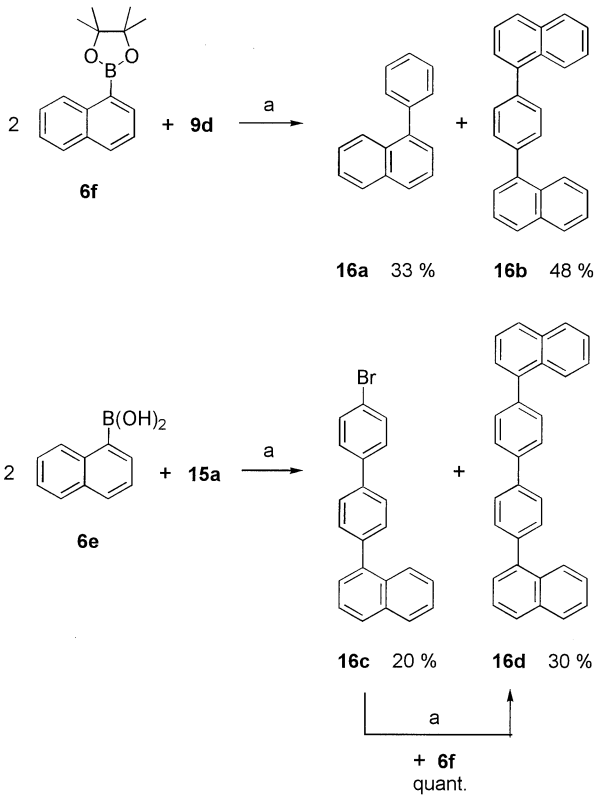
[a] Products **7a** and **7b** could not be separated.

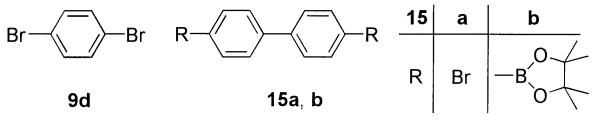
the literature, even under anhydrous conditions[18]. Route I for the synthesis of **13** yielded 9% of **7a** and 8% of **14**, whereas route II yielded 2% of **7a** and 23% of **14**. Monoarylated, monoboronic acid pinacol esters of type **13** can be obtained in fair yields. A subsequent Suzuki reaction should open up new routes to chiral 2,2′-bisarylated binaphthyl systems.

2-Bromo-1,1′-binaphthyl-2′-boronic acid pinacol ester (**4**) is a valuable starting material for Suzuki coupling reactions. Compound **4** was coupled with **9a** to obtain 34% of **7a** (see Scheme 4). As shown before (see Scheme 3), the bromo-functionality of the primary coupling product was reduced.

A great challenge in our work was the twofold palladium-catalyzed Suzuki reactions using the starting materials shown in Scheme 1. To optimize the reaction conditions, coupling reactions with the naphthyl system were performed first (see Scheme 5).

Scheme 5. Twofold Pd-catalyzed Suzuki coupling



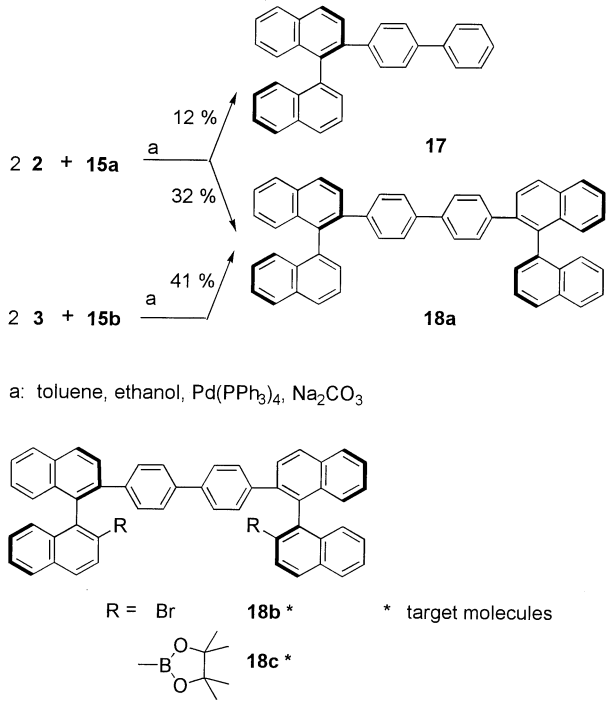


1,4-Bis(1-naphthyl)benzene (**16b**) could easily be obtained (48%) by coupling of **6f** with 1,4-dibromobenzene

[**9d**, by-product: 33% of 1-phenylnaphthalene (**16a**), monoarylation product with subsequent reduction of the bromo-functionality]. Similarly, 4,4′-bis(1-naphthyl)-1,1′-biphenyl (**16d**) can be synthesized in one step (30%) by coupling of **6e** with 4,4′-dibromo-1,1′-biphenyl (**15a**) or by isolating 20% of the monoarylated 1-[4-(4′-bromo-1,1′-biphenyl)]naphthalene (**16c**, no reduction of the bromo-functionality) and subsequent coupling with a second equivalent of **6f** to obtain **16d** quantitatively.

Therefore, the Suzuki coupling offers access to polyfused aromatics, such as **16b** (Hart synthesized **16b** by a Grignard reaction in 21% yield[19]; Suzuki reaction shown in this paper: 48% yield) and **16d** which are interesting substances because of their fluorescence properties[20].

Scheme 6. Synthesis of complex molecules



As shown in Scheme 6, the hitherto unknown complex molecule 4,4′-bis[2-(1,1′-binaphthyl)]-1,1′-biphenyl (**18a**) could be obtained in 32% yield by the coupling of monoborylated **2** with **15a** {by-product: 12% of 2-[4-(1,1′-biphenyl)]-1,1′-binaphthyl (**17**), monoarylation product with subsequent reduction of the bromo-functionality}. **18a** could either be obtained as racemate or as the corresponding *meso* compound. In the NMR spectra no diastereoisomeric signals could be observed. The reaction of 2,2′-dibromo-1,1′-binaphthyl (**3**) with 1,1′-biphenyl-4,4′-diboronic acid bispinacol ester (**15b**), which can be synthesized in 67% yield from 4,4′-dibromo-1,1′-biphenyl (**15a**), also gave **18a** (41%). No bromo-substituted monoarylation product could be detected, as it was obviously immediately reduced to **18a**. Future target molecules are the dibrominated and the bisborylated substances **18b** and **18c**, respectively (see Scheme 6). These compounds could be accessible by Suzuki reaction of **3**, **4** and **5** with the appropriate halide and boronic acid components. Atropisomeric target molecules of type **13** or **18** are of high potential value for chiral recognition reactions (especially as enantioselective bioorganic sensor molecules to differentiate carbohydrates and other biomolecules[21]) or as ligands or promoters in catalytic, asymmetric processes.

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Experimental Section

All experiments were carried out under dry purified nitrogen or under argon in flame-dried reaction flasks. All solvents were dried by standard methods. − IR: Bruker Vector 22 FT-IR. − NMR: Bruker AMX 400 or AC 250 P (400 MHz or 200 MHz and 100 MHz or 50 MHz, for ^{1}H, ^{13}C and ^{11}B, respectively) with TMS (internal) and $^{11}BF_3 \cdot OEt_2$ (external) as reference. − MS (70 eV, EI; CI): Hewlett-Packard 5989B; MS (high-resolution): Finnigan MAT 95; Institut für Organische Chemie (Göttingen). − Melting points (uncorrected): Büchi apparatus. − Elemental analyses: Institut für Pharmazeutische Chemie (Braunschweig). − Chromatography: Flash silica gel 60 (230−400 mesh, ASTM, Merck). − Starting material: 2-bromo-1,1′-binaphthyl[22] (**1**) and 2,2′-dibromo-1,1′-binaphthyl[23] (**3**) were prepared according to published procedures, 1,1′-binaphthyl-2-boronic acid pinacol ester (**2**), 2-bromo-1,1′-binaphthyl-2′-boronic acid pinacol ester (**4**), 1,1′-binaphthyl-2,2′-diboronic acid bispinacol ester (**5a**) and 1,1′-binaphthyl-2,2′-diboronic acid (**5b**) were prepared as described in the preceeding paper[4]. An optimized synthetic route to the *mono* boronic acid pinacol ester (**2**) is presented in this paper. All axially-chiral substances were used as racemates.

2-Bromo-1,1′-binaphthyl (**1**): To a solution of 2,2′-dibromo-1,1′-binaphthyl (**3**, 2.000 g, 4.85 mmol) in 30 ml of THF a 1.6 M solution of *n*-butyllithium (3.03 ml, 4.85 mmol) was added at −40°C. After 1 h of stirring the mixture was cooled to −78°C and 5 equiv. of 1 N hydrochloric acid (0.45 ml, 25.00 mmol) were added. The reaction mixture was allowed to warm to room temperature overnight. The solvents were evaporated under reduced pressure. The solid residue was dissolved in 50 ml of diethyl ether and was then hydrolyzed with 1 N hydrochloric acid. The product was extracted with 500 ml of diethyl ether, which was washed successively with a saturated aqueous sodium hydrogen carbonate solution, water and a saturated sodium chloride solution. The crude product was dried with sodium sulfate. The solvents were evaporated under reduced pressure and purified by flash column chromatography (hexane). The product **1** (1.422 g, 72%) was isolated as a yellow solid, m.p. 107−108°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3055 (w, ArH), 1581 (m), 1503 (s), 1373 (m), 1114 (m), 803 (s), 778 (s). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.15−7.35 (m, 4 H, arom. CH), 7.37−7.54 (m, 3 H, arom. CH), 7.62 (dd, *J* = 8.4, *J* = 7.2 Hz, 1 H, arom. CH), 7.78 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.83 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.90 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.96 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.97 (d, *J* = 8.4 Hz, 1 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 122.67 (arom. quat. C−Br, 1 C), 125.48, 125.71, 126.00, 126.09, 126.34, 126.76, 126.92, 127.91 and 127.94 (arom. CH, 9 C), 128.33 (arom. CH, 2 C), 129.27 and 129.94 (arom. CH, 2 C), 131.98, 132.27, 133.61, 134.36, 137.28 and 138.04 (arom. quat. C, 6 C). − MS (70 eV, EI); *m/z* (%): 335 (6) and 333 (6, $M^+ + 1$), 334 (24) and 332 (23, M^+), 253 (100), 252 (66), 127 (31), 126 (56), 125 (34). − $C_{20}H_{13}Br$ (333.2): calcd. C 72.09, H 3.93, Br 23.98; found C 72.31, H 4.00, Br 23.64.

Monoborylation of 2-Bromo-1,1′-binaphthyl (**1**) *and Subsequent Esterification with Pinacol Giving 1,1′-Binaphthyl-2-boronic Acid Pinacol Ester* (**2**): To a solution of 2-bromo-1,1′-binaphthyl (**1**, 161 mg, 0.48 mmol) in 20 ml of THF a 1.7 M solution of *n*-butyllithium (0.28 ml, 0.48 mmol) was added at −40°C. After stirring for 1 h, the mixture was cooled to −78°C and added to a solution of 2.5 equiv. of trimethyl borate (0.13 ml, 1.210 mmol) in 20 ml of THF. The reaction mixture was allowed to warm to room temperature overnight. The solvents were evaporated under reduced pressure. The solid residue was dissolved in 50 ml of diethyl ether and was then hydrolyzed with 1 N hydrochloric acid. The product was extracted with 250 ml of diethyl ether, which was washed with a saturated aqueous sodium hydrogen carbonate solution and water. The crude product was dried with sodium sulfate. The solvents were evaporated under reduced pressure and the solid residue was dissolved in 10 ml of toluene. Pinacol (118 mg, 1.210 mmol, 2.5 equiv.) was added and the solution was heated under reflux for 12 h. The solvents were evaporated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ethyl acetate, 25:1). The product **2** (107 mg, 58%) was isolated as a white solid and was identified by comparison to authentic material[4].

Suzuki Coupling; General Procedure: To a solution of the arylboronic acid or the arylboronic acid pinacol ester in ethanol, was added the aryl halide dissolved in toluene, and 1−10 mol% of the catalyst tetrakis(triphenylphosphane)palladium(0). In some cases, which are especially mentioned, DMF was used as solvent. In all cases, sodium carbonate was used as a base and the reaction mixture was heated at 100°C. The solution was then hydrolyzed with 1 N hydrochloric acid and extracted with diethyl ether. The combined organic phases were washed three times with a saturated sodium hydrogen carbonate solution, twice with water and twice with a saturated sodium chloride solution. They were then dried with anhydrous sodium sulfate and finally the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel.

Coupling of 2-Bromo-1,1′-binaphthyl (**1**) *with 1-Phenylboronic Acid* (**6a**) *Giving 2-Phenyl-1,1′-binaphthyl* (**7a**): Compound **1** (134 mg, 0.403 mmol) in 20 ml of toluene, 1 equiv. of **6a** (49 mg, 0.403 mmol) in 20 ml of ethanol and $Pd(PPh_3)_4$ (47 mg, 0.040 mmol, 10 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane). The by-products, biphenyl (**8a**, 7 mg, 11%) and 1,1′-binaphthyl (**8e**, 15 mg , 14%) could be isolated and identified. The main product **7a** was isolated as a white solid (107 mg, 81%), m.p. 133°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3055 (m, ArH), 2953 (m), 2926 (m), 1593 (w), 1495 (m), 1445 (w), 1368 (w), 1029 (w), 824 (m), 783 (m), 762 (s). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.96−7.11 (m, 5 H, arom. CH), 7.20−7.30 (m, 4 H, arom. CH), 7.33−7.50 (m, 4 H, arom. CH), 7.66 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.79 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.85 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.95 (d, *J* = 8.4 Hz, 1 H, arom. CH), 8.01 (d, *J* = 8.4 Hz, 1 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 125.23, 125.53, 125.69 and 125.97 (arom. CH, 4 C), 126.27 (arom. CH, 2 C), 126.58 and 127.14 (arom. CH, 2 C), 127.43 (arom. CH, 2 C), 127.50, 127.83, 127.95, 128.17 and 128.33 (arom. CH, 5 C), 129.17 (arom. CH, 3 C), 132.59, 133.19, 133.26, 133.53, 135.68, 136.90, 139.46 and 141.91 (arom. quat. C, 8 C). − MS (70 eV, EI); *m/z* (%): 331 (27, M^+ + 1), 330 (100, M^+), 329 (40), 313 (19), 300 (6), 289 (4), 276 (3), 253 (17), 252 (20), 163 (7), 157 (7), 77 (1). − $C_{26}H_{18}$ (330.4): calcd. C 94.51, H 5.49; found C 94.36, H 5.58.

Coupling of 2-Bromo-1,1′-binaphthyl (**1**) *with 4-Methylphenyl-1-boronic Acid* (**6b**) *Giving 2-(4-Methylphenyl)-1,1′-binaphthyl* (**7b**): Compound **1** (150 mg, 0.450 mmol) in 20 ml of toluene, 1 equiv. of **6b** (61 mg, 0.450 mmol) in 20 ml of ethanol and $Pd(PPh_3)_4$ (52 mg, 0.045 mmol, 10 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane). The by-products (< 3%), 4,4′-dimethyl-1,1′-biphenyl (**8b**) and 1,1′-binaphthyl (**8e**) were characterized on the basis of GC-MS data. The main product **7b** was isolated as a white solid (147 mg, 95%), m.p. 123°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3045 (m, ArH), 2964 (w), 1590 (w), 1364 (w), 1260 (m), 1022 m, 801 (s), 780 (s), 771 (s), 750 (s). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.09 (s, 3 H, CH_3), 6.77 (d, *J* = 8.4 Hz, 2 H, arom. CH), 6.90 (d, *J* = 8.4 Hz, 2 H, arom. CH), 7.12−7.42 (m, 8 H, arom. CH), 7.57 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.74 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.79 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.86 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.92 (d, *J* = 8.4 Hz, 1 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.97 (CH_3, 1 C), 125.29, 125.52, 125.55, 125.96, 126.19, 126.62, 127.09, 127.41, 127.80, 127.89 and 128.16 (arom. CH, 11 C), 128.22 (arom. CH, 2 C), 128.52 (arom. CH, 1 C), 129.03 (arom. CH, 2 C), 129.07 (arom. CH, 1 C), 132.49, 133.19, 133.31, 133.58, 135.51, 135.82, 137.09, 138.95 and 139.36 (arom. quat. C, 9 C). − MS (70 eV, EI); *m/z* (%): 345 (28, M^+ + 1), 344 (100, M^+), 343 (24), 329 (26), 313 (14), 300 (5), 289 (3), 276 (3), 253 (11), 252 (14), 163 (15), 157 (15), 77 (1), 65 (1). − $C_{27}H_{20}$ (344.5): calcd. C 94.15, H 5.85; found C 93.99, H 5.92; HR MS: calcd. 344.1565; found 344.1565.

Coupling of 1,1′-Binaphthyl-2-boronic Acid Pinacol Ester (**2**) *with Bromobenzene* (**9a**) *Giving 2-Phenyl-1,1′-binaphthyl* (**7a**): Compound **2** (50 mg, 0.132 mmol) in 20 ml of ethanol, 1 equiv. of **9a** (0.01 ml, 0.132 mmol) in 20 ml of toluene and $Pd(PPh_3)_4$ (15 mg, 0.013 mmol, 10 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane). The product **7a** was isolated as a white solid (37 mg, 84%), spectroscopic data for **7a** see above.

Coupling of 1,1′-Binaphthyl-2-boronic Acid Pinacol Ester (**2**) *with 1-Bromo-4-trimethylsilylbenzene* (**9c**) *Giving 2-(4-Trimethylsilylphenyl)-1,1′-binaphthyl* (**7c**): Compound **2** (36 mg, 0.094 mmol) in 20 ml of ethanol, 1 equiv. of **9c** (22 mg, 0.094 mmol) in 20 ml of toluene and $Pd(PPh_3)_4$ (11 mg, 0.009 mmol, 10 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane). The product **7c** was isolated as a white solid (24 mg, 63%), m.p. 66°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3056 (s, ArH), 2954 (s), 1593 (m), 1505 (m), 1366 (w), 1248 (s), 1115 (m), 842 (s), 812 (m), 781 (w). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.14 [s, 9 H, $Si(CH_3)_3$], 7.07 (d, *J* = 8.4 Hz, 2 H, arom. CH), 7.15−7.30 (m, 6 H, arom. CH), 7.33−7.48 (m, 4 H, arom. CH), 7.66 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.81 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.88 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.94 (d, *J* = 8.4 Hz, 1 H, arom. CH), 8.00 (d, *J* = 8.4 Hz, 1 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = −1.19 [$Si(CH_3)_3$, 3 C], 125.38, 125.53, 125.67, 126.03, 126.24, 126.65 and 127.17 (arom. CH, 7 C), 127.44 (arom. quat. C, 1 C), 127.49, 127.81, 127.98 and 128.18 (arom. CH, 4 C), 128.47 (arom. CH, 2 C), 129.09 (arom. CH, 1 C), 132.53 (arom. CH, 3 C), 133.18, 133.32, 133.71, 135.61, 136.96, 137.96, 139.27 and 142.21 (arom. quat. C, 8 C). − MS (70 eV, EI); *m/z* (%): 403 (34, M^+ + 1), 402 (88, M^+), 388 (36), 387 (100), 339 (4), 329 (9), 326 (13), 313 (5), 253 (3), 252 (7), 194 (13), 73 (21), 59 (20). − $C_{29}H_{26}Si$ (402.61): HR MS: calcd. 402.1804; found 402.1804.

Coupling of 2,2′-Dibromo-1,1′-binaphthyl (**3**) *with 1-Phenylboronic Acid* (**6a**): Compound **3** (250 mg, 0.607 mmol) in 20 ml of toluene, 2 equiv. of **6a** (148 mg, 1.213 mmol) in 20 ml of ethanol and $Pd(PPh_3)_4$ (70 mg, 0.061 mmol, 10 mol%) were allowed to

react for 24 h. The crude product was purified by flash column chromatography (hexane). The by-products **10a** (< 3%), **11a** (< 3%) and biphenyl (**8a**, 2%) could be assigned on the basis of MS data. The by-product 1,1′-binaphthyl (**8e**, 7 mg, 4%) and the main product 2-phenyl-1,1′-binaphthyl (**7a**, 135 mg, 67%) were isolated as white solids, spectroscopic data for **7a** see above.

2-Bromo-2′-phenyl-1,1′-binaphthyl (**10a**): MS (70 eV, EI); *m/z* (%): 411 (10) and 409 (9, $M^+ + 1$), 410 (31) and 408 (32, M^+), 329 (100), 327 (61), 326 (66), 313 (29), 300 (12), 252 (16), 163 (26), 157 (28), 156 (24), 77 (7), 51 (9).

2,2′-Diphenyl-1,1′-binaphthyl (**11a**): MS (70 eV, EI); *m/z* (%): 407 (2, $M^+ + 1$), 406 (6, M^+), 330 (38), 329 (20), 313 (8), 264 (3), 252 (11), 239 (5), 163 (15), 157 (17), 129 (24), 77 (4).

Coupling of 2,2′-Dibromo-1,1′-binaphthyl (**3**) *with 4-Methylphenyl-1-boronic Acid* (**6b**): Compound **3** (205 mg, 0.497 mmol) in 15 ml of toluene, 2.4 equiv. of **6b** (150 mg, 1.105 mmol) in 15 ml of ethanol and $Pd(PPh_3)_4$ (25 mg, 0.022 mmol, 4 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane). The by-products **10b** (≈ 16%), **11b** (< 3%) and 2,2′-dimethyl-1,1′-biphenyl (**8b**, 3%) could be assigned on the basis of MS data. The main product 2-(4-methylphenyl)-1,1′-binaphthyl (**7b**) was isolated as a white solid (86 mg, 50%), spectroscopic data for **7b** see above.

2-Bromo-2′-(4-methylphenyl)-1,1′-binaphthyl (**10b**): MS (70 eV, EI); *m/z* (%): 425 (12) and 423 (13, $M^+ + 1$), 424 (41) and 422 (41, M^+), 344 (32), 343 (100), 328 (59), 327 (55), 326 (59), 313 (15), 252 (5), 163 (42), 157 (26), 150 (13), 77 (1).

2,2′-Bis(4-methylphenyl)-1,1′-binaphthyl (**11b**): MS (70 eV, EI); *m/z* (%): 435 (36, $M^+ + 1$), 434 (100, M^+), 420 (71), 419 (17), 404 (8), 389 (6), 344 (54), 343 (32), 328 (27), 326 (39), 313 (18), 300 (7), 252 (10), 239 (4), 200 (9), 163 (13), 91 (11).

Coupling of 2,2′-Dibromo-1,1′-binaphthyl (**3**) *with 4-Methoxyphenyl-1-boronic Acid Pinacol Ester* (**6d**): Compound **3** (400 mg, 0.971 mmol) in 30 ml of toluene, 2 equiv. of **6d** (454 mg, 1.941 mmol) in 30 ml of ethanol and $Pd(PPh_3)_4$ (112 mg, 0.097 mmol, 10 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane/ethyl acetate, 10:1). The by-products **10d** (14%) and **11d** (< 3%) could be assigned on the basis of MS data. The by-product 4,4′-dimethoxy-1,1′-biphenyl (**8d**, 19 mg, 9%) was obtained as a white solid. The main product 2-(4-methoxyphenyl)-1,1′-binaphthyl (**7d**) was isolated as a white solid (119 mg, 34%).

2-(4-Methoxyphenyl)-1,1′-binaphthyl (**7d**): M.p. 148°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3053 (m, ArH), 2928 (m), 2835 (w), 1608 (m), 1578 (w), 1511 (m), 1243 (s) and 1032 (s, C−O), 818 (w), 780 (w), 752 (w). − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.62 (s, 3 H, OCH_3), 6.54 (d, *J* = 8.4 Hz, 2 H, arom. CH), 6.99 (d, *J* = 8.4 Hz, 2 H, arom. CH), 7.18−7.27 (m, 4 H, arom. CH), 7.32−7.45 (m, 4 H, arom. CH), 7.64 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.80 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.85 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.92 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.98 (d, *J* = 8.4 Hz, 1 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 54.95 (OCH_3, 1 C), 112.92 (arom. CH, 2 C), 125.32, 125.50, 125.53, 125.98, 126.19, 126.54, 127.02, 127.44, 127.79, 127.90, 128.19, 128.51 and 129.08 (arom. CH, 13 C), 130. 24 (arom. CH, 2 C), 132.40, 133.22, 133.31, 133.50, 134.29, 135.43, 137.10 and 138.98 (arom. quat. C, 8 C), 157.95 (arom. quat. C−O, 1 C). − MS (70 eV, EI); *m/z* (%): 361 (29, $M^+ + 1$), 360 (100, M^+), 345 (9), 329 (23), 327 (21), 315 (23), 302 (12), 289 (6), 252 (4), 239 (12), 157 (17). − $C_{27}H_{20}O$ (360.46): HR MS: calcd. 360.1514; found 360.1514.

2-Bromo-2′-(4-methoxyphenyl)-1,1′-binaphthyl (**10d**): MS (70 eV, EI); *m/z* (%): 441 (17) and 439 (22, $M^+ + 1$), 440 (65) and 438 (66, M^+), 359 (100), 344 (23), 328 (35), 326 (33), 313 (59), 250 (4), 163 (32), 157 (44).

2,2′-Bis(4-methoxyphenyl)-1,1′-binaphthyl (**11d**): MS (70 eV, EI); *m/z* (%): 467 (9, $M^+ + 1$), 466 (22, M^+), 436 (48), 435 (5), 405 (4), 404 (3), 360 (75), 359 (21), 344 (10), 328 (22), 313 (27), 289 (11), 262 (42), 252 (32), 239 (13), 183 (44), 156 (28), 108 (29), 69 (48).

Coupling of 2,2′-Dibromo-1,1′-binaphthyl (**3**) *with 1-Naphthylboronic Acid* (**6e**): Compound **3** (300 mg, 0.728 mmol) in 20 ml of toluene, 2.2 equiv. of **6e** (278 mg, 1.618 mmol) in 15 ml of ethanol and $Pd(PPh_3)_4$ (24 mg, 0.021 mmol, 3 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane). The by-products **10e** (≈ 4%) and **11e** (< 3%) could be assigned on the basis of MS data. The by-product 1,1′-binaphthyl (**8e**, 14 mg, 8%) and the main product **7e** (172 mg, 62%) were isolated as white solids.

2-(1-Naphthyl)-1,1′-binaphthyl (**7e**): M.p. 175°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3040 (m, ArH), 1618 (w), 1590 (w), 1502 (m), 1394 (w), 1365 (w), 1255 (w), 1013 (w), 827 (m), 799 (m), 779 (s), 748 (m). − ^1H NMR (400 MHz, $CDCl_3$): δ = 6.80−7.07 (m, 3 H, arom. CH), 7.08−7.71 (m, 13 H, arom. CH), 7.72−7.87 (m, 2 H, arom. CH), 7.96−8.14 (m, 2 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 124.67, 125.17, 125.37, 125.42, 125.67, 125.83, 125.87, 126.24, 126.29, 126.39, 126.76 and 127.02 (arom. CH, 12 C), 127.20 (arom. CH, 2 C), 127.24, 127.35, 127.95, 128.05, 128.12 and 129.17 (arom. CH, 6 C), 132.40, 132.70, 132.96, 133.23, 133.39, 133.43, 136.80, 137.26, 138.08 and 139.23 (arom. quat. C, 10 C). − MS (70 eV, EI); *m/z* (%): 381 (32, $M^+ + 1$), 380 (100), 363 (14), 350 (7), 301 (5), 265 (4), 253 (16), 252 (23), 239 (2), 187 (9), 182 (10), 176 (4), 128 (4), 127 (3). − $C_{30}H_{20}$ (380.49): HR MS: calcd. 380.1565; found 380.1565.

2-Bromo-2′-(1-naphthyl)-1,1′-binaphthyl (**10e**): MS (70 eV, EI); *m/z* (%): 461 (9) and 459 (11, $M^+ + 1$), 460 (27) and 458 (30, M^+), 380 (31), 379 (100), 377 (44), 376 (39), 374 (20), 363 (26), 350 (11), 252 (5), 189 (15), 182 (25), 175 (13), 125 (4).

2,2′-Bis(1-naphthyl)-1,1′-binaphthyl (**11e**): MS (70 eV, EI); *m/z* (%): 507 (43, $M^+ + 1$), 506 (100), 490 (4), 456 (26), 380 (34), 379 (24), 378 (14), 363 (13), 252 (20), 239 (5), 188 (10), 127 (3), 69 (4).

Coupling of 1,1′-Binaphthyl-2,2′-diboronic Acid (**5b**) *with Iodobenzene* (**12a**): Compound **5b** (80 mg, 0.234 mmol, 1.1 equiv.), 2 equiv. of **12a** (0.05 ml, 0.425 mmol) in 30 ml of DMF and $Pd(PPh_3)_4$ (24 mg, 0.026 mmol, 6 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane). The by-product 1,1′-binaphthyl (**8e**, 12 mg, 23%) and the main product 2-phenyl-1,1′-binaphthyl (**7a**, 24 mg, 34%) were isolated as white solids, spectroscopic data for **7a** see above.

Coupling of 1,1′-Binaphthyl-2,2′-diboronic Acid (**5b**) *with 1-Bromo-4-methylbenzene* (**9b**): Compound **5b** (100 mg, 0.292 mmol, 1.1 equiv.), 2 equiv. of **9b** (91 mg, 0.532 mmol) in 20 ml of DMF and $Pd(PPh_3)_4$ (19 mg, 0.016 mmol, 3 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane). A white solid (31 mg) could be obtained consisting of a 1:2.6 mixture of the by-product 2-phenyl-1,1′-binaphthyl (**7a**, 10%) and the main product 2-(4-methylphenyl)-1,1′-binaphthyl (**7b**, 24%), spectroscopic data for **7a** and **7b** see above.

Coupling of 1,1′-Binaphthyl-2,2′-diboronic Acid (**5b**) *with 1-Iodo-4-methoxybenzene* (**12d**): Compound **5b** (80 mg, 0.234 mmol, 1.1 equiv.), 2 equiv. of **12d** (100 mg, 0.425 mmol) in 30 ml of DMF and $Pd(PPh_3)_4$ (50 mg, 0.043 mmol, 10 mol%) were allowed to

react for 24 h. The crude product was purified by flash column chromatography (hexane and hexane/ethyl acetate, 5:1). The undesired product 2-phenyl-1,1′-binaphthyl (**7a**, 21 mg, 30%) and the main product 2-(4-methoxyphenyl)-1,1′-binaphthyl (**7d**, 18 mg, 23%) were isolated as white solids, spectroscopic data for **7a** and **7d** see above.

Coupling of 1,1′-Binaphthyl-2,2′-diboronic Acid (**5b**) *with 1-Bromo-4-nitrobenzene* (**12f**) *Giving 2-(4-Nitrophenyl)-1,1′-binaphthyl* (**7f**): Compound **5b** (80 mg, 0.234 mmol, 1.1 equiv), 2 equiv. of **12f** (100 mg, 0.425 mmol) in 30 ml of DMF and $Pd(PPh_3)_4$ (25 mg, 0.021 mmol, 5 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane and hexane/ethyl acetate, 8:1). The by-product 2-phenyl-1,1′-binaphthyl (**7a**, 15 mg, 22%, spectroscopic data see above) and the yellow solid 4,4′-dinitro-1,1′-biphenyl[24] (12 mg, 11%) were isolated and identified. The main product **7f** was isolated as a yellow solid (21 mg , 26%), m.p. 209°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3047 (w, ArH), 1598 (m), 1518 (s) and 1345 (s, NO), 1108 (w), 1015 (w), 829 (w), 801 (w), 781 (w). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21−7.26 (m, 3 H, arom. CH), 7.27−7.35 (m, 4 H, arom. CH), 7.38−7.47 (m, 2 H, arom. CH), 7.53 (ddd, *J* = 8.4, *J* = 5.6 and *J* = 0.5 Hz, 1 H, arom. CH), 7.62 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.82−7.90 (m, 4 H, arom. CH), 7.99 (d, *J* = 8.4 Hz, 1 H, arom. CH), 8.07 (d, *J* = 8.4 Hz, 1 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 122.75 (arom. CH, 2 C), 125.23, 125.89, 126.06, 126.40, 126.49, 126.77, 127.20, 127.24, 127.94, 128.14, 128.44, 128.47 and 129.17 (arom. CH, 13 C), 129.96 (arom. CH, 2 C), 133.07 and 133.11 (arom. quat. C, 2 C), 133.22 (arom. quat. C, 2 C), 135.90, 136.32, 137.09 and 146.24 (arom. quat. C, 4 C), 148.87 (arom. quat. C−N, 1 C). − MS (70 eV, EI); *m/z* (%): 376 (28, $M^+ + 1$), 375 (100, M^+), 374 (21), 360 (7), 327 (28), 326 (33), 313 (19), 300 (12), 289 (9), 276 (6), 253 (29), 252 (20), 163 (16), 156 (17), 150 (13). − $C_{26}H_{17}NO_2$ (375.43): HR MS: calcd. 375.1259; found 375.1259.

Coupling of 1,1′-Binaphthyl-2,2′-diboronic Acid (**5b**) *and Bromobenzene* (**9a**), *Subsequent Esterification with Pinacol*: Compound **5b** (200 mg, 0.585 mmol) in 20 ml of ethanol, 2 equiv. of **9a** (0.123 ml, 1.170 mmol) in 20 ml of toluene and $Pd(PPh_3)_4$ (68 mg, 5 mol%) were allowed to react for 24 h. The reaction mixture was worked up by hydrolysis with 5 ml of 1 N hydrochloric acid. The combined organic phases were washed with 10 ml of a saturated sodium hydrogen carbonate solution. After drying the organic layer with anhydrous sodium sulfate, the solvents were removed under reduced pressure. The solid residue, containing the corresponding diboronic acid was dissolved in 30 ml of toluene. After addition of pinacol (173 mg, 1.462 mmol) the reaction mixture was heated under reflux for 12 h. The solvent was then removed under reduced pressure. The crude product was purified by flash column chromatography (hexane/ethyl acetate, 25:1 and hexane/ethyl acetate, 6:1). The by-product 2-phenyl-1,1′-binaphthyl (**7a**, 17 mg, 9%, spectroscopic data see above) and the by-product 2-hydroxy-2′-phenyl-1,1′-binaphthyl (**14**, 16 mg, 8%) were isolated as white solids. The main product 2-phenyl-1,1′-binaphthyl-2′-boronic acid pinacol ester (**13**) was obtained as a white solid (81 mg, 30%).

2-Phenyl-1,1′-binaphthyl-2′-boronic Acid Pinacol Ester (**13**): M.p. 70−71°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3055 (m, ArH), 2976 (m), 2927 (m), 1595 (m), 1559 (w), 1494 (w), 1471 (s), 1377 (s) and 1303 (s, B−O), 1146 (s) and 1114 (s, C−O), 821 (m), 762 (m), 749 (m), 700 (m). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.76 and 0.96 [2 s, 12 H, $OC(CH_3)_2$], 6.95−7.00 (m, 3 H, arom. CH), 7.14−7.24 (m, 5 H, arom. CH), 7.35−7.44 (m, 3 H, arom. CH), 7.60 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.77−7.83 (m, 3 H, arom. CH), 7.92 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.99 (d, *J* = 8.4 Hz, 1 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.00 and 24.55 [$OC(CH_3)_2$, 4 C], 83.01 [$OC(CH_3)_2$, 2 C], 125.15, 125.61, 125.77, 126.03, 126.31, 126.48 and 126.92 (arom. CH, 7 C), 127.05 (arom. CH, 2 C), 127.23, 127.33, 127.41, 127.82 and 128.02 (arom. CH, 5 C), 129.28 (arom. CH, 2 C), 130.07 (arom. CH, 1 C), 132.56, 132.82, 134.11, 134.40, 136.32, 139.21, 142.34 and 144.13 (arom. quat. C, 8 C). − ^{11}B NMR (400 MHz, $CDCl_3$): δ = 30.37 (s). − MS (70 eV, EI); *m/z* (%): 457 (23, $M^+ + 1$), 456 (69, M^+), 356 (36), 355 (33), 341 (15), 340 (23), 337 (34), 329 (44), 328 (100), 327 (59), 313 (19), 279 (6), 263 (2), 252 (9), 84 (22), 77 (4). − $C_{32}H_{29}BO_2$ (456.2): calcd. C 84.22, H 6.40; found C 83.29, H 6.39; HR MS: calcd. 456.2261; found 456.2260.

2-Hydroxy-2′-phenyl-1,1′-binaphthyl (**14**): M.p. 165°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3482 (s, O−H, free), 3418 (br.s, O−H), 3056 (w, ArH), 1619 (m), 1597 (m), 1517 (w), 1379 (w), 1263 (m), 1205 (m), 1103 (m) and 1027 (m, C−O), 816 (m), 761 (m), 749 (m), 698 (m). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.83 (d, *J* = 1.2 Hz, 1 H, OH), 7.02−7.16 (m, 7 H, arom. CH), 7.18−7.35 (m, 4 H, arom. CH), 7.48−7.54 (m, 1 H, arom. CH), 7.71 (dd, *J* = 8.4 and 1.2 Hz, 1 H, arom. CH), 7.77 (d, *J* = 8.4 Hz, 2 H, arom. CH), 7.98 (d, *J* = 8.4 Hz, 1 H, arom. CH), 8.09 (dd, *J* = 8.4 and 1.2 Hz, 1 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 117.12 (arom. CH, 1 C), 117.66 (arom. quat. C, 1 C), 123.18, 125.00, 126.32, 126.39, 126.57, 126.95 and 127.16 (arom. CH, 7 C), 127.65 (arom. CH, 2 C), 128.04 and 128.17 (arom. CH, 2 C), 128.58 (arom. CH, 3 C), 128.67 (arom. quat. C, 1 C), 129.43 and 129.83 (arom. CH, 2 C), 133.11, 133.20, 134.13, 140.77, 141.54 and 141.60 (arom. quat. C, 6 C), 150.91 (arom. quat. C−O, 1 C). − MS (70 eV, EI); *m/z* (%): 347 (27, $M^+ + 1$), 346 (100, M^+), 329 (12), 315 (11), 302 (12), 269 (5), 252 (3), 239 (13), 77 (9). − $C_{26}H_{18}O$ (346.4): HR-MS: calcd. 346.1358; found 346.1358.

Coupling of 1,1′-Binaphthyl-2,2′-diboronic Acid Bispinacol Ester (**5a**) *with Bromobenzene* (**9a**): Compound **5a** (42 mg, 0.0832 mmol) in 5 ml of ethanol, 2 equiv. of **9a** (0.018 ml, 0.1664 mmol) in 5 ml of toluene and $Pd(PPh_3)_4$ (19 mg, 0.017 mmol, 10 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane/ethyl acetate, 20:1 and hexane/ethyl acetate, 6:1). 25% of the starting material **5a** could be recovered. The by-product 2-phenyl-1,1′-binaphthyl (**7a**, 2%) could be assigned on the basis of GC-MS data, the by-product 2-hydroxy-2′-phenyl-1,1′-binaphthyl (**14**) was obtained as a white solid (7 mg, 23%). The main product 2-phenyl-1,1′-binaphthyl-2′-boronic acid pinacol ester (**13**) was isolated as a white solid (16 mg, 41%), spectroscopic data for **13** and **14** see above.

Coupling of 2-Bromo-1,1′-binaphthyl-2,2′-boronic Acid Pinacol Ester (**4**) *with Bromobenzene* (**9a**): Compound **4** (30 mg, 0.065 mmol) in 10 ml of ethanol, 1 equiv. of **9a** (0.01 ml, 0.065 mmol) in 10 ml of toluene, and $Pd(PPh_3)_4$ (8 mg, 0.007 mmol, 10 mol%) were allowed to react for 24 h. The yields were determined by gas chromatographic (GC-MS) analysis and by comparison to authentic material, spectroscopic data of **7a** see above. 62% of the starting material **4** could be recovered. The by-product 1,1′-binaphthyl (**8e**, 4%) and the main product 2-phenyl-1,1′-binaphthyl (**7a**, 34%) were characterized.

Coupling of 1-Naphthylboronic Acid Pinacol Ester (**6f**) *with 1,4-Dibromobenzene* (**9d**) *Giving 1,4-Bis(1-naphthyl)benzene* (**16b**): Compound **6f** (200 mg, 0.787 mmol, 2 equiv.) in 20 ml of ethanol, **9d** (93 mg, 0.394 mmol) in 20 ml of toluene and $Pd(PPh_3)_4$ (46 mg, 0.039 mmol, 5 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane). 1-Phenylnaphthalene (**16a**) was obtained as a by-product (27 mg, 33%). The main product **16b** was isolated as a white solid (62 mg

, 48%), m.p. 201−202°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3028 (w, ArH), 1590 (w), 1504 (w), 1393 (m), 1016 (w), 798 (s), 790 (s), 777 (s). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48−7.61 (m, 8 H, arom. CH), 7.64−7.65 (m, 4 H, arom. CH), 7.91 (d, *J* = 8.0 Hz, 2 H, arom. CH), 7.95 (d, *J* = 8.4 Hz, 2 H, arom. CH), 8.09 (d, *J* = 8.4 Hz, 2 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 125.44, 125.82, 126.07, 126.10, 127.05, 127.73 and 128.33 (arom. CH, 14 C), 129.96 (arom. CH, 4 C), 131.63, 133.86, 139.66 and 139.95 (arom. quat. C, 8 C). − MS (70 eV, EI); *m/z* (%): 331 (26, M^+ + 1), 330 (100, M^+), 329 (17), 313 (10), 203 (11), 202 (25), 178 (6), 165 (10), 163 (17), 151 (6), 128 (12), 127 (6). − $C_{26}H_{18}$ (330.4): calcd. C 94.51, H 5.49; found C 94.27 H 5.31.

Coupling of 1-Naphthylboronic Acid (**6e**) *with 4,4′-Dibromo-1,1′-biphenyl* (**15a**): Compound **6e** (150 mg, 0.872 mmol, 2 equiv.) in 20 ml of ethanol, **15a** (136 mg, 0.436 mmol) in 40 ml of toluene and $Pd(PPh_3)_4$ (50 mg, 0.044 mmol, 5 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane). The by-product 1,1′-binaphthyl (**8e**) was obtained as a white solid (21 mg, 9%). The products **16c** (32 mg, 20%) and **16d** (53 mg, 30%) were isolated as white solids.

1-[4-(4′-Bromo-1,1′-biphenyl)]naphthalene (**16c**): M.p. 165°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3026 (w, ArH), 1504 (w), 1483 (m), 1394 (m), 1070 (m), 1001 (m), 803 (m), 783 (s), 739 (s). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42−7.63 (m, 10 H, arom. CH), 7.68 (d, *J* = 8.4 Hz, 2 H, arom. CH), 7.88 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.92 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.95 (d, *J* = 8.4 Hz, 1 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 121.63 (arom. quat. C−Br, 1 C), 125.40, 125.84, 125.90 and 126.12 (arom. CH, 4 C), 126.78 (arom. CH, 2 C), 126.92, 127.81 and 128.33 (arom. CH, 3 C), 128.69 and 130.62 (arom. CH, 4 C), 131.52 (arom. quat. C, 1 C), 131.96 (arom. CH, 2 C), 133.82, 138.85, 139.62, 139.73 and 140.18 (arom. quat. C, 5 C). − MS (70 eV, EI); *m/z* (%): 361 (20) and 359 (30, M^+ + 1), 360 (100) and 358 (91, M^+), 278 (54), 276 (42), 203 (21), 202 (24), 126 (16), 77 (8), 51 (8). − $C_{22}H_{15}Br$ (359.3): calcd. C 73.55, H 4.21, Br 22.24; found C 73.56, H 4.19, Br 21.18.

4,4′-Bis(1-naphthyl)-1,1′-biphenyl (**16d**): M.p. 170°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3043 and 3026 (w, ArH), 1591 (w), 1494 (w), 1394 (m), 1003 (w), 823 (m), 800 (s), 774 (s), 569 (m). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45−7.58 (m, 8 H, arom. CH), 7.63 (d, *J* = 8.4 Hz, 4 H, arom. CH), 7.82 (d, *J* = 8.4 Hz, 4 H, arom. CH), 7.89 (d, *J* = 8.4 Hz, 2 H, arom. CH), 7.93 (d, *J* = 8.4 Hz, 2 H, arom. CH), 8.02 (d, *J* = 8.4 Hz, 2 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 125.43, 125.82, 126.02 and 126.10 (arom. CH, 8 C), 126.97 (arom. CH, 6 C), 127.74 and 128.33 (arom. CH, 4 C), 130.59 (arom. CH, 4 C), 131.61, 133.86, 139.71, 139.84 and 139.86 (arom. quat. C, 10 C). − MS (70 eV, EI); *m/z* (%): 407 (37, M^+ + 1), 406 (100, M^+), 405 (6), 389 (6), 276 (4), 263 (1), 252 (1), 203 (19), 202 (21), 201 (8), 200 (8), 165 (2), 126 (1), 77 (1), 63 (1). − $C_{32}H_{22}$ (406.5): calcd. C 94.55, H 5.45; found C 93.49, H 5.40: HR MS: calcd: 406.1722; found 406.1721.

Coupling of 1-[4-(4′-Bromo-1,1′-biphenyl)]naphthalene (**16c**) *with 1-Naphthylboronic Acid Pinacol Ester* (**6f**): Compound **16c** (10 mg, 0.028 mmol) in 4 ml of toluene, 1 equiv. of **6f** (7 mg, 0.028 mmol) in 4 ml of ethanol and $Pd(PPh_3)_4$ (3 mg, 0.0028 mmol, 10 mol%) were allowed to react for 24 h. The reaction was monitored by gas chromatography. The starting material was quantitatively transformed into the product 4,4′-bis(1-naphthyl)-1,1′-biphenyl (**16d**), spectroscopic data for **16d** see above.

Coupling of 1,1′-Binaphthyl-2-boronic Acid Pinacol Ester (**2**) *with 4,4′-Dibromo-1,1′-biphenyl* (**15a**): Compound **2** (148 mg, 0.388 mmol, 2 equiv) in 20 ml of ethanol, **15a** (61 mg, 0.194 mmol) in 20 ml of toluene and $Pd(PPh_3)_4$ (45 mg, 0.049 mmol, 10 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane and hexane/ethyl acetate, 20:1). The by-product **17** (10 mg, 12%) and the main product **18a** (41 mg, 32%) were isolated as white solids.

2-[4-(1,1′-Biphenyl)]-1,1′-binaphthyl (**17**): M.p. 210°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3042 and 3027 (w, ArH), 1619 (w), 1596 (w), 1502 (w), 1486 (m), 1365 (w), 819 (s), 802 (m), 783 (m), 766 (s), 752 (m), 730 (m). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, *J* = 8.4 Hz, 2 H, arom. CH), 7.22−7.30 (m, 7 H, arom. CH), 7.31−7.37 (m, 2 H, arom. CH), 7.38−7.43 (m, 3 H, arom. CH), 7.44−7.49 (m, 3 H, arom. CH), 7.71 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.81 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.87 (d, *J* = 8.4 Hz, 1 H, arom. CH), 7.96 (d, *J* = 8.4 Hz, 1 H, arom. CH), 8.01 (d, *J* = 8.4 Hz, 1 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 125.36, 125.59, 125.73 and 126.06 (arom. CH, 4 C), 126.12 (arom. CH, 2 C), 126.30 and 126.57 (arom. CH, 2 C), 126.84 (arom. CH, 2 C), 127.09, 127.16, 127.57, 127.84, 128.04, 128.24 and 128.33 (arom. CH, 7 C), 128.61 (arom. CH, 2 C), 129.16 (arom. CH, 1 C), 129.60 (arom. CH, 2 C), 132.61, 133.23, 133.32, 133.59, 135.72, 136.91, 138.80, 138.96, 140.55 and 140.93 (arom. quat. C, 10 C). − MS (70 eV, EI); *m/z* (%): 407 (34, M^+ + 1), 406 (100, M^+), 405 (15), 389 (7), 326 (8), 313 (8), 276 (4), 253 (8), 252 (12), 239 (2), 203 (5), 129 (3), 77 (6). − $C_{32}H_{22}$ (406.5): HR MS: calcd. 406.1722; found 406.1721.

4,4′-Bis[2-(1,1′-binaphthyl)]-1,1′-biphenyl (**18a**): M.p. 181°C. − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3050 (m, ArH), 1619 (w), 1592 (w), 1496 (m), 1366 (w), 813 (s), 802 (s), 781 (s), 750 (m). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.00−7.04 (m, 8 H, arom. CH), 7.17−7.26 (m, 8 H, arom. CH), 7.31−7.46 (m, 8 H, arom. CH), 7.63 (d, *J* = 8.4 Hz, 2 H, arom. CH), 7.76 (d, *J* = 8.4 Hz, 2 H, arom. CH), 7.82 (d, *J* = 8.4 Hz, 2 H, arom. CH), 7.93 (d, *J* = 8.4 Hz, 2 H, arom. CH), 7.99 (d, *J* = 8.4 Hz, 2 H, arom. CH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 125.34, 125.58 and 125.69 (arom. CH, 6 C), 125.81 (arom. CH, 4 C), 126.03, 126.27, 126.52, 127.12, 127.54, 127.81, 127.98, 128.23, 128.31 and 129.07 (arom. CH, 20 C), 129.43 (arom. CH, 4 C), 132.56, 133.18, 133.29, 133.54, 135.63, 136.88, 138.11, 138.94 and 140.72 (arom. quat. C, 18 C). − MS (70 eV, EI); *m/z* (%): 658 [M^+], 644 (2), 574 (1), 513 (1), 458 (1), 402 (1), 329 (9, $M^+/2$), 328 (6), 313 (2), 253 (4), 252 (3), 239 (1). − $C_{52}H_{34}$ (658.8): HR MS: calcd. 658.2661; found 658.2661.

Coupling of 2,2′-Dibromo-1,1′-binaphthyl (**3**) *with 1,1′-Biphenyl-4,4′-diboronic Acid Bispinacol Ester* (**15b**): Compound **3** (412 mg, 1.000 mmol, 2 equiv.) in 20 ml of toluene, **15b** (203 mg, 0.500 mmol) in 10 ml of ethanol and $Pd(PPh_3)_4$ (116 mg, 0.100 mmol, 10 mol%) were allowed to react for 24 h. The crude product was purified by flash column chromatography (hexane and hexane/ethyl acetate, 20:1). The by-product 1,1′-binaphthyl (**8e**) was obtained as a white solid (24 mg, 9%). The main product 4,4′-bis[2-(1,1′-binaphtyl)]-1,1′-biphenyl (**18a**, 134 mg, 41%) was isolated as a white solid, spectroscopic data for **18a** see above.

1,1′-Biphenyl-4,4′-diboronic Acid Bispinacol Ester (**15b**): To a solution of 4,4′-dibromo-1,1′-biphenyl (**15a**, 3.000 g, 9.62 mmol) in 30 ml THF, was added a 1.6 M solution of *n*-butyllithium (13.22 ml, 21.15 mmol) at −40°C. After stirring for 1 h, the mixture was cooled to −78°C and added to a solution of 5 equiv. of trimethyl borate (5.36 ml, 48.07 mmol) in 80 ml of THF. The reaction mixture was allowed to warm to room temperature overnight. The solvents were evaporated under reduced pressure. The solid residue was dissolved in 50 ml of diethyl ether and was then hydrolyzed with 1 N hydrochloric acid. The product was extracted with 250 ml of diethyl ether, which was washed with a saturated aqueous sodium hydrogen carbonate solution and water. The crude product

was dried with sodium sulfate. The solvents were evaporated under reduced pressure and the solid residue was dissolved in 50 ml of toluene. Pinacol (5.681 g, 48.07 mmol, 5 equiv.) was added and the solution was heated under reflux for 12 h. The solvents were evaporated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ethyl acetate, 25:1). The product **15b** (1.499 g, 67%) was isolated as a white solid, m.p. 221°C. – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3029 (w, ArH), 2982 (s), 1607 (m), 1502 (w), 1393 and 1357 (s, B–O), 1145 and 1093 (s, C–O), 860 (m), 820 (m), 657 (m). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (s, 24 H, $OCCH_3$), 7.63 (d, *J* = 8.4 Hz, 4 H, arom. CH), 7.88 (d, *J* = 8.4 Hz, 4 H, arom. CH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.85 ($OCCH_3$, 8 C), 83.82 ($OCCH_3$, 4 C), 126.49 and 135.23 (arom. CH, 8 C), 143.61 (arom. quat. C, 2 C). – MS (70 eV, EI); *m/z* (%): 407 (26, $M^+ + 1$), 406 (100, M^+), 405 (49), 391 (19), 320 (63), 307 (41), 291 (13), 290 (8), 220 (18), 207 (41), 206 (26), 188 (7), 85 (21). – $C_{24}H_{32}B_2O_4$ (406.1): calcd. C 70.98, H 7.94; found C 71.40, H 8.05.

[1] J. C. Namyslo, D. E. Kaufmann, *Chem. Ber.* **1997**, *130*, 1327–1331.

[2] [2a] C. Rosini, L. Franzini, A. Raffaelli, P. Salvadori, *Synthesis* **1992**, 503–517. – [2b] O. Reiser, *Nachr. Chem. Tech. Lab.* **1996**, *44*, 380–388.

[3] G. Bir, Chr. Ernst, U.-M. Gross, C. Rehwinkel, B. Schilling, S. Thormeier, V. Kaiser, D. E. Kaufmann in *Advances in Boron Chemistry*, The Royal Society of Chemistry, Cambridge **1997**, 193–200.

[4] B. Schilling, V. Kaiser, D. E. Kaufmann, *Chem. Ber.* **1997**, *130*, 923–932.

[5] [5a] N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.* **1981**, *11*, 513–519. – [5b] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483. – [6] J.-M. Fu, B.-P. Zhao, M. J. Sharp, V. Snieckus, *Can. J. Chem.* **1994**, *72*, 227–236.

[7] M. Uemura, A. Daimon, Y. Hayashi, *J. Chem. Soc., Chem. Commun.* **1995**, 1943–1944.

[8] [8a] T. I. Wallow, B. M. Novak, *J. Am. Chem. Soc.* **1991**, *113*, 7411–7412. – [8b] T. M. Miller, T. X. Neenan, R. Zayas, H. E. Bair, *J. Am. Chem. Soc.* **1992**, *114*, 1018–1025. – [8c] M. B. Goldfinger, T. M. Swager, *J. Am. Chem. Soc*. **1994**, *116*, 7895–7896.

[9] [9a] P. Liess, V. Hensel, A.-D. Schlüter, *Liebigs Ann.* **1996**, 1037–1040. – [9b] A.-D. Schlüter, G. Wegner, *Acta Polym*. **1993**, *59*, 44.

[10] S. Anderson, U. Neidlein, V. Gramlich, F. Diederich, *Angew. Chem.* **1995**, *107*, 1722–1725; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1596–1599.

[11] P. J. Cox, W. Wang, V. Snieckus, *Tetrahedron Lett.* **1992**, *33*, 2253–2256.

[12] [12a] Q.-S. Hu, D. Vitharana, G.-Y. Liu, V. Jain, M. W. Wagaman, L. Zhang, T. R. Lee, L. Pu, *Macromolecules* **1996**, *29*, 1082–1084. – [12b] Q.–S. Hu, D. Vitharana, G. Liu, V. Jain, L. Pu, *Macromolecules* **1996**, *29*, 5075–5082. – [12c] L. Ma, Q.-S. Hu, K. Y. Musick, D. Vitharana, C. Wu, C. M. S. Kwan, L. Pu, *Macromolecules* **1996**, *29*, 5083–5090. – [12d] L. Ma, Q.-S. Hu, D. Vitharana, C. Wu, C. M. S. Kwan, L. Pu, *Macromolecules* **1997**, *30*, 204–218.

[13] W. J. Thompson, J. Gaudino, *J. Org. Chem.* **1984**, *49*, 5237–5243.

[14] E. M. Campi, W. R. Jackson, S. M. Marcuccio, C. G. M. Naesland, *J. Chem. Soc., Chem. Commun.* **1994**, 2395.

[15] [15a] N. Miyaura, A. Suzuki, *Main Group Met. Chem.* **1987**, 295–300. – [15b] Z. Z. Song, H. C. Wong, *J. Org. Chem.* **1994**, *59*, 33–41.

[16] [16a] K.-C. Kong, C.-H. Cheng, *J. Am. Chem. Soc.* **1991**, *113*, 6313–6315. – [16b] D. F. O′Keefe, M.C. Dannock, S.M. Marcuccio, *Tetrahedron Lett.* **1992**, *33*, 6679–6680.

[17] K. Dziuba, M. Kuznikowski, K. M. Pietrusiewicz, poster 184, OMCOS 9, **1997**, Göttingen, Germany.

[18] H. R. Snyder, J. A. Kuck, J. R. Johnson, *J. Am. Chem. Soc.* **1938**, *60*, 105–111.

[19] H. Hart, K. Harada, C.-J. F. Du, *J. Org. Chem.* **1985**, *50*, 3104–3110.

[20] [20a] Y. B. Sheck, N. P. Kovalenko, M. V. Alfimov, *J. Luminescence* **1977**, *15*, 157–168.– [20b] A. Bahl, W. Grahn, S. Stadler, F. Feiner, G. Bourhill, C. Bräuchle, A. Reisner, P. G. Jones, *Angew. Chem.* **1995**, *107*, 1587–1590; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1485–1488.

[21] [21a] T. D. James, K. R. A. Samankumara, S. Shinkai, *Angew. Chem.* **1996**, *108*, 2038–2050; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1910–1922. – [21b] H. Suenaga, H. Yamamoto, S. Shinkai, *Pure Appl. Chem.* **1996**, *68*, 2179–2186.

[22] D. Hansen, *Dissertation* Heidelberg, Germany, **1995**.

[23] H. Takaya, S. Akutagawa, R. Noyori, *Org. Synth*. **1988**, *67*, 20–32.

[24] H. C. Gull, E. E. Turner, *J. Chem. Soc.* **1929**, 491–500.

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