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Microwave-promoted Suzuki–Miyaura coupling of arylboronic acids with 1-bromo-2-naphthol, *o*-bromophenol, and *o*-chlorophenol

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Abstract—In this letter we report a simple and efficient way for the direct Suzuki–Miyaura cross-coupling of unprotected 2-hydroxyaryl bromides and of 2-chlorophenol with arylboronic acids using suitable phosphine/$Pd(OAc)_2$ catalysts systems with moist K_3PO_4/toluene or moist CsF/dioxane and microwave heating (20 min 105 °C to 3 h 100–120 °C) with an internal temperature control providing 2-hydroxybiaryls in yields up to 98%.

The Suzuki–Miyaura cross-coupling of aryl halides and arylboronic acids has emerged as an extremely powerful and environmentally friendly tool and is today certainly the most widely used method in the synthesis of biaryls,[1–3] which are a key element in a growing number of pharmaceuticals and natural products[4] and highly efficient asymmetric catalysts with axial chiral ligands.[5] The particular advantages of the Suzuki–Miyaura coupling are the wide tolerance of functional groups, the stability to water and oxygen and the nontoxic properties of organoboronic acids. Recent research revealed that in situ Pd-catalysts with highly basic and bulky phosphine or *N*-heterocyclic carbene ligands[3,6] or bulky palladacycles[7] in combination with suitable salts like K_3PO_4, Cs_2CO_3, KF, CsF or nBu$_4$NBr allow the coupling of arylboronic acids even with bulky and deactivated aryl halides including chlorides under mild conditions. Since the reactivity of aryl halides is substantially lowered by hydroxylate donor groups formed in the presence of basic salts like phosphates or carbonates, usually protected phenol derivatives are employed to synthesize hydroxyl-biaryls. However, the direct use of hydroxyaryl halides would be desirable to simplify the synthesis not only of biaryl-based natural products but also simple hydroxybiaryls. 4-Iodophenol is known to be sufficiently reactive to couple with various arylboronic acids even in the presence of Pd/C catalysts in aqueous K_2CO_3 in high yields, 2-iodophenol in a lower yield.[8] 4-Bromophenol is much less suitable under these conditions, but catalysis with the highly efficient $Pd_2(dba)_3$/P(t-Bu)$_3$/KF catalyst system introduced by Fu et al. furnished 4-hydroxybiphenyl in an excellent yield.[9] Coupling of the more bulky 2-bromophenol with phenylboronic acid in the presence of $Pd(OAc)_2$/(m-$C_6H_4SO_3Na)_3$P/iPr$_2$NH (CH_3CN/H_2O 3:1) required extended heating (72 h) and a high catalyst load to afford 60% of 2-hydroxybiphenyl.[10] Electron-releasing groups like 3-CHO or COOMe in the 2-bromophenol and use of $Pd(PPh_3)_4/K_2CO_3$ or K_3PO_4/DMF or DME–water reduced the reaction time with arylboronic acids or their pinacol esters to 16–49 h at 90–120 °C.[11] Two to four bromine or iodine atoms in the phenol allow rapid coupling with phenyl boronic acid in the microwave-assisted coupling, catalyzed by $Pd(OAc)_2$/KF–Al_2O_3.[12] The reaction of 1-bromo-2-naphthol with 4-methoxyphenylboronic acid in the presence of $Pd(PPh_3)_4/Na_2CO_3$/DME–EtOH–water is somewhat faster, as shown by the consumption of all reactants after 4 h reflux, but the yield of the coupling product was only 56%.[13]

Hydroxyfunctional aryl chlorides have been used to the best of our knowledge so far only in very few recent examples to obtain hydroxybiphenyls: (1) coupling of 2-chloro-6-methylphenol with phenyl- and 3-furylboronic

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acid, respectively, catalyzed by a not commercially available very bulky and basic phosphine stabilized palladacycle in the presence of KF/dioxane (110 °C overnight, yield 60% and 41%, respectively),[14] (2) low yield (26%) coupling of a 2,3-dichlorophenol derivative with phenylboronic acid in the presence of $Pd_2(dba)_2$/*c*Hex_3P/Cs_2CO_3 in toluene (1 h 80 °C),[15] and (3) the coupling of the electron-deficient 5-chloro-3-hydroxypyridine with 3-pyridylboronic acid which gives much better yield (87%) even with the 'classical' $Pd_2(dba)_3/PCy_3/K_3PO_4$ (dioxane–water, 18 h, 100 °C).[16]

Continuing earlier investigations on 2-hydroxy-2′-phosphinobiaryl ligands[17] with a changed synthesis strategy, we studied the Suzuki–Miyaura coupling of 1-bromo-2-naphthol and *o*-bromophenol with excessive phenyl- and 1-naphthylboronic acid choosing at first a 'classical' catalyst system $Pd(OAc)_2/R_3P/K_3PO_4$ (toluene) with R = Ph, *o*-Tol, Mes, *t*-Bu. Microwave heating was applied in most of the experiments, since this technique is reported to shorten the reaction times of Suzuki–Miyaura couplings, in particular in water or aqueous organic media.[2] The coupling experiments were usually carried out at 105 °C with heating for 20 min.[18] Screening of the coupling of phenylboronic acid with 1-bromo-2-naphthol to **1** with various phosphine ligands, usually in a Pd/R_3P 1:2 molar ratio, showed an increased yield in the presence of the basic and bulky ligands *t*-Bu_3P and *o*-Tol_3P as compared to the use of neat $Pd(OAc)_2/K_3PO_4$ while Ph_3P lowered the yield, and, surprisingly, the more bulky Mes_3P in a 1:2 ratio deactivated the catalyst (Table 1, entries 1–5). To improve the efficiency of microwave heating, small amounts of water (0.5 mL) were added. Indeed, the yields of **1** increased in all experiments using stabilising phosphine additives by about 10% (except the deactivating trimesitylphosphine) while the yield decreased when neat $Pd(OAc)_2/K_3PO_4$ was used (Table 1, entries 7–11).

Surprisingly, the conversion was further improved by adding smaller amounts of water. Water was found unsuitable as solvent while moist K_3PO_4 with ca. 50 mg water/g K_3PO_4 (ca. 0.6 H_2O) proved to give excellent yields of **1** (87–92%) with 2.5 mol % $Pd(OAc)_2$/5 mol % *t*-Bu_3P or *o*-Tol_3P and yet 73% **1** with 0.25 mol % $Pd(OAc)_2$/0.5 mol % *o*-Tol_3P within 20 min at 105 °C. A strong excess of *o*-Tol_3P (5 mol %/0.25 mol % Pd) dropped the yield to about 50% (Table 1, entries 12–16). Heating in the classical way in a silicon oil bath required much longer time or higher temperature to reach a comparable yield using the same catalyst systems (entries 6 and 17). The separation of **1** from unconverted components and homocoupling products was performed by column chromatography on silica gel by an elution with *n*-hexane/methylene chloride (2:1).

The high yield of **1** in the above Suzuki–Miyaura cross-coupling with moist K_3PO_4 encouraged us to extend this protocol to the cross-coupling of both 1-bromo-2-naphthol with 1-naphthylboronic acid and of 2-bromophenol with phenyl- and 1-naphthylboronic acid. Tris-(*o*-tolyl)phosphine was chosen as the ligand because of similar yields to *t*-Bu_3P in the above screenings but much higher air stability. Naphthylnaphthol **2** and naphthylphenol **4** were obtained in nearly quantitative yields while the cross-coupling to 2-hydroxydiphenyl **3** was less favourable under equal conditions (Scheme 1, Table 2, entries 1–4). The yield increases in the order $\mathbf{3} < \mathbf{4} \approx \mathbf{1} < \mathbf{2}$. This effect is possibly due to the more extended π-delocalization of the negative charge in naphtholate compared to phenolate. By the usually strong response to steric hindrance of the Suzuki–Miyaura coupling it seems less likely that the naphthyl group favours the reductive elimination sterically. Tests with the biaryl ligand 2-dicyclohexylphosphino-1-(2-trimethylsilylphenyl)-pyrrole (**5**),[19] a representative of a ligand

Table 1. Suzuki–Miyaura cross-coupling of 1-bromo-2-naphthol with phenylboronic acid using various Pd catalysts and different amounts of moisture[a]

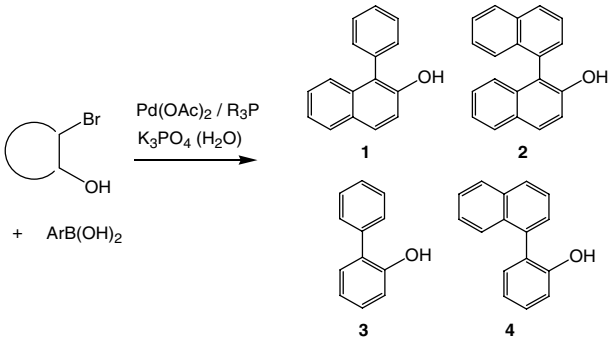
Entry	$Pd(OAc)_2$ (mol %)	R_3P (mol %)	Yield of **1** (%)
Dry K_3PO_4			
1	2.5	*t*-Bu_3P/5	65
2	2.5	*o*-Tol_3P/5	60
3	2.5	Ph_3P/5	19
4	2.5	Mes_3P/5	0
5	5.0	None	56
6[b]	2.5	*o*-Tol_3P/5	61[b]
Dry K_3PO_4 and 0.5 mL of water			
7	2.5	*t*-Bu_3P/5	75
8	2.5	*o*-Tol_3P/5	72
9	2.5	Ph_3P/5	29
10	2.5	Mes_3P/5	0
11	5	None	45
Moist K_3PO_4[c]			
12	5	*t*-Bu_3P/10	87
13	2.5	*t*-Bu_3P/5	92
14	2.5	*o*-Tol_3P/5	90
15	0.25	*o*-Tol_3P/0.5	73
16	0.25	*o*-Tol_3P/5	50
17[d]	2.5	*o*-Tol_3P/5	64[d]

[a] Reaction conditions: 1 equiv of hydroxyaryl bromide, 2 equiv of organoboronic acid, 2.5 mol % of $Pd(OAc)_2$, 5 mol % R_3P, 2 equiv of K_3PO_4, toluene (15 mL), microwave heating at 105 °C for 20 min, yield after separation by column chromatography on silica gel (average of each two experiments).

[b] Heating in a silicon oil bath at 120 °C for 12 h, other conditions as in footnote a.

[c] Water content 50 mg/g K_3PO_4.

[d] Heating in a silicon oil bath at 140 °C for 30 min, other conditions as in footnote a.



Scheme 1. Suzuki–Miyaura couplings with 2-hydroxyaryl bromides.

Table 2. Cross-coupling of 1-bromo-2-naphthol or 2-bromophenol with phenyl- or 1-naphthylboronic acid using $Pd(OAc)_2/R_3P$/moist K_3PO_4

Entry	R_3P	2-Hydroxyaryl-bromide	Boronic acid	Product, yield (%)
1[a]	*o*-Tol_3P	1-$BrC_{10}H_6$-2-OH	$PhB(OH)_2$	**1**, 90
2[a]	*o*-Tol_3P	1-$BrC_{10}H_6$-2-OH	1-$NaphB(OH)_2$	**2**, 97
3[a]	*o*-Tol_3P	2-BrC_6H_4OH	$PhB(OH)_2$	**3**, 48
4[a]	*o*-Tol_3P	2-BrC_6H_4OH	1-$NaphB(OH)_2$	**4**, 88
5[b]	**5**	2-BrC_6H_4OH	1-$NaphB(OH)_2$	**4**, 75
5[a]	**6**	1-$BrC_{10}H_6$-2-OH	$PhB(OH)_2$	**1**, 66
6[a]	**7**	1-$BrC_{10}H_6$-2-OH	$PhB(OH)_2$	**1**, 74
7[c]	**7**	1-$BrC_{10}H_6$-2-OH	$PhB(OH)_2$	**1**, 98

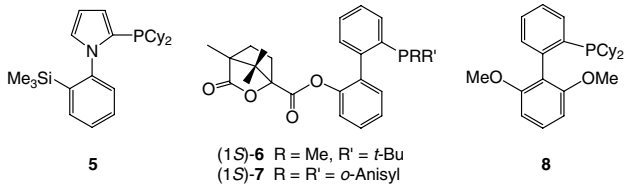
[a] Reaction conditions: 1 equiv of hydroxyaryl bromide, 2 equiv of organoboronic acid, 2.5 mol % of $Pd(OAc)_2$, 5 mol % R_3P, 2 equiv of moist K_3PO_4, toluene (15 mL for $PhB(OH)_2$, 25 mL for 1-Naph-$B(OH)_2$), microwave heating at 105–110 °C for 20 min, yield after separation by column chromatography.
[b] Microwave heating at 70–80 °C, else as footnote a.
[c] 5 mol % of $Pd(OAc)_2$, 10 mol % of **7**, microwave heating at 95 °C, other conditions as in footnote a.

family optimized for Pd-catalyzed cross-coupling reactions,[20] gave good yields of **4** under milder conditions (Fig. 1).

Two of the 2-O-substituted 2′-phosphinobiphenyls synthesized from **3**, *tert*-butylmethyl-(2-camphanoyloxy-biphenyl)phoshine **6** and di-*o*-anisyl-(2-camphanoyloxy-biphenyl)phoshine **7**,[17b] proved to be somewhat less efficient than *o*-Tol_3P as the ligand (Table 2, entries 5–8). Only the double catalyst load caused almost quantitative formation of **1** while at 70 °C low catalyst concentration (0.25 mol % Pd/0.5 mol % **6**) did not provide **1**.

Attempts to couple 2-chlorophenol or 1-chloro-2-naphthol with phenylboronic acid with the Pd/*o*-Tol_3P/K_3PO_4 catalyst system under the same conditions or by heating in dioxane at 100 °C failed completely. Attempts with in situ catalysts composed of $Pd(OAc)_2$ and the biarylphosphine ligands **5**–**7** as well as with 2′-dicyclohexylphosphino-2-(*N*,*N*-dimethylamino)-biphenyl (DavePhos)[21] also failed to couple 2-chlorophenol with 1-naphthylboronic acid, at least in substantial amounts. At 120–140 °C/4–6 h in dioxane in the presence of moist or dry CsF, only naphthalene was provided along with unconverted 2-chlorophenol (Table 3).

However, using 2′-dicyclohexylphosphino-2,6-dimethoxy-biphenyl (**8**)[22] as the ligand, allowed cross-coupling with hydroxyaryl chlorides. Tests with 1-chloro-2-naphthol gave so far only low yields of **2**, but the coupling with 2-chlorophenol provided **4** in a



5 (1*S*)-**6** R = Me, R' = *t*-Bu (1*S*)-**7** R = R' = *o*-Anisyl 8

Figure 1. Biaryl phosphines tested as ligands.

Table 3. Cross-coupling of 1-chloro-2-naphthol or 2-chlorophenol with 1-naphthylboronic acid using $Pd(OAc)_2$/**8**/moist CsF

Entry	R_3P	2-Hydroxyaryl-bromide	Boronic acid	Product, yield (%)
1[a]	**8**	1-$ClC_{10}H_6$-2-OH	1-$NaphB(OH)_2$	**2**, 10
2[b]	**8**	2-ClC_6H_4OH	1-$NaphB(OH)_2$	**4**, 80
3[c]	**8**	2-ClC_6H_4OH	1-$NaphB(OH)_2$	**4**, 50

[a] Reaction conditions: 1-$ClC_{10}H_6$-2-OH (178.5 mg, 1.0 mmol) or 2-ClC_6H_4OH (128.5 mg, 1.0 mmol), 1-$NaphB(OH)_2$ (344 mg, 2 mmol), 2.5 mol % of $Pd(OAc)_2$, 2.5 mol % **8**, CsF (304 mg, 2.1 mmol), 30 μL H_2O, 1,4-dioxane (10 mL), microwave heating at 120 °C for 1 h, yield after separation by column chromatography.
[b] Microwave heating at 100 °C for 1 h, then at 120 °C for 2 h, else as footnote a.
[c] Microwave heating at 140 °C for 5 h, else as footnote a.

high yield at 100–120 °C (3 h).[23] A higher temperature led to lower amounts of **4**, possibly due to catalyst decomposition.

In summary, a simple and efficient way for the direct Suzuki–Miyaura cross-coupling of unprotected 2-hydroxyaryl bromides and 2-chlorophenol with arylboronic acids was developed. In combination with moist K_3PO_4 as an efficient base in toluene and *o*-Tol_3P or with **8** and CsF in dioxane, this Pd-catalyzed C–C coupling gives good to excellent yields of 2-hydroxybiaryls under relative mild conditions (20 min at 105 °C or 3 h at 100–120 °C). The high yields in particular of the 1-aryl-2-naphthols suggest that this approach may be widely applicable also for other and more heavily substituted aryl-2-naphthols.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.10.055.

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23. Typical procedure: A microwave pressure vessel (50 mL) was charged with 1-chloro-2-naphthol (178.5 mg, 1.0 mmol) or 2-chlorophenol (128.5 mg, 1.0 mmol), 1-naphthylboronic acid (344 mg, 2.0 mmol), and CsF (304 mg, 2.1 mmol). The corresponding phosphine ligand (0.025 mmol, for **8** 10.3 mg) was dissolved in dioxane (10 mL), then $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) was added. The mixture was stirred until all solutes were dissolved and then added to the reaction vessel (before it was evacuated and filled with argon). Water (30 μL) was then added and the mixture heated with shaking and rotation (inside temperature regulation, temperature and time see Table 3). After cooling to room temperature, the mixture was worked up as described above.[18]