Palladium-Catalyzed Borylation of Ortho-Substituted Phenyl Halides and Application to the One-Pot Synthesis of 2,2′-Disubstituted Biphenyls

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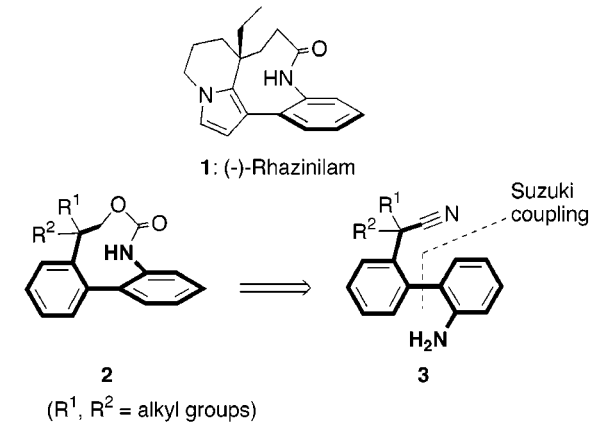
Ortho-disubstituted biaryls are key structural elements of numerous pharmacologically active natural or synthetic products, for instance, the antibiotic vancomycin,[1] the antimitotics colchicine and steganacin,[2] the CDK inhibitors paullones,[3] and the antihypertensive losartan.[4] The Suzuki−Miyaura coupling is a well-established and powerful tool for the construction of the biaryl bond of such molecules due to both its efficiency and the innocuous character of the boron derivatives produced.[5] Nevertheless improvements of the existing methods are still necessary especially when sterically hindered or electronically deactivated coupling partners are involved.

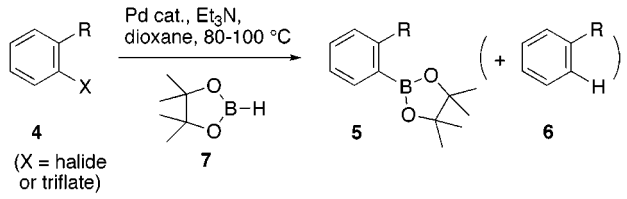
In the course of our research program directed toward the total synthesis of the antimitotic (−)-rhazinilam **1**[6,7] and biaryl analogues such as **2**[8] (Scheme 1), we envisioned to build the ortho-disubstituted biaryl framework (precursor **3**) via a Suzuki coupling. We expected that the reaction conditions used in this key step would be versatile enough to allow a rapid and efficient construction of a library of analogues for biological screening purposes.

The ortho-substituted arylboronic acid or arylboronate component of the coupling can be synthesized by two principal methods, namely: (1) the transmetalation between an arylmetal and a boron halide or alkoxide,[9] (2)

Scheme 1



Scheme 2



the more recently developed $PdCl_2$(dppf)-catalyzed borylation of aryl halides or triflates **4** with a tetra(alkoxy)diboron[10] or with a dialkoxyborane such as pinacolborane **7** (Scheme 2).[11] We turned our attention toward the last method due to the better availability of pinacolborane and its apparent greater reactivity compared to the diboron species.[11]

The pinacolboronates **5** formed in this process are attractive synthons since they are air-, moisture-, temperature-, and generally chromatography-stable. However there are rather few examples of the Pd-catalyzed borylation of ortho-substituted aryl halides, especially of bromides that are yet more readily available, compared to their para and meta counterparts.[10,11] To synthesize ortho-substituted phenylboronates **5**, leading potentially to rhazinilam analogues **2**, we began with the study of the borylation of 2-bromoaniline **4a** (Table 1).

Under catalysis with $PdCl_2$(dppf), we were able to obtain the corresponding boronate **5a** in 48% yield (entry 1) after 4 h at 100 °C. With other ortho-substituted phenyl bromides, the boronate was obtained in very low to moderate yields (vide infra). We ascribed these results mostly to the steric hindrance created by the ortho substituent. We then turned our attention toward the very interesting results obtained by the Buchwald and the Fu groups concerning the Suzuki couplings of sterically hindered substrates under mild conditions, using sterically hindered phosphine ligands, respectively, 2-(dialkylphosphino)biphenyls such as **8** (Table 1)[12] and

(1) (a) Williams, D. H.; Bardsley, B. *Angew. Chem., Int. Ed.* **1999**, *38*, 1172. (b) Nicolaou, K. C.; Boddy, C. N. C.; Bräse, S.; Winssinger, N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2096.

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(5) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263. (c) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.

(6) David, B.; Sévenet, T.; Morgat, M.; Guénard, D.; Moisand, A.; Tollon, Y.; Thoison, O.; Wright, M. *Cell Motil. Cytoskeleton* **1994**, *28*, 317.

(7) For total syntheses, see: (a) Ratcliffe, A. H.; Smith, G. F.; Smith, G. N. *Tetrahedron Lett.* **1973**, *52*, 5179. (b) Johnson, J. A.; Sames, D. *J. Am. Chem. Soc.* **2000**, *122*, 6321.

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(9) (a) Vaultier, M.; Carboni, B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 11, p 191. (b) Miyaura, N.; Maruoka, K. In *Synthesis of Organometallic Compounds*; Komiya, S., Ed.; Wiley: New York, 1997.

(10) (a) Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508. (b) Ishiyama, T.; Itoh, Y.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1997**, *38*, 3447.

(11) (a) Murata, M.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **1997**, *62*, 6458. (b) Murata, M.; Oyama, T.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **2000**, *65*, 164.

(12) (a) Wolfe, J. P.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 2413. (b) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550.

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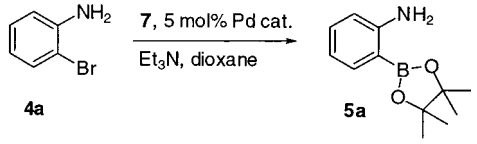
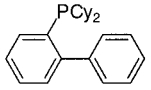
Table 1. Borylation of 2-Bromoaniline 4a[a]



4a **5a**

entry	Pd catalyst	time (h)	temp (°C)	**5a** (%)[b]
1	5% $PdCl_2$(dppf)	4	100	48
2	5% $Pd(OAc)_2$/10% **8**	1	80	49
3	5% $Pd(OAc)_2$/20% **8**	1	80	81
4	5% $Pd(OAc)_2$/20% P(*t*-Bu)$_3$	1	80	0
5	2.5% Pd_2dba_3/6% P(*t*-Bu)$_3$	2	80	0
6	5% $Pd(PPh_3)_4$	14	100	0
7	5% $PdBnCl(PPh_3)_2$	14	100	0
8	2.5% Pd_2dba_3	14	100	0

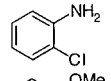
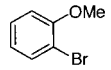
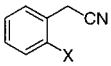
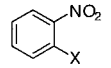
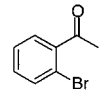
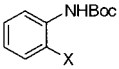
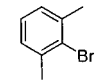
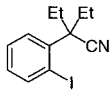
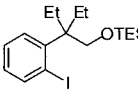
[a] Conditions: Et_3N (4.0 equiv), **7** (3.0 equiv), dioxane. [b]Isolated yields after flash chromatography (aniline was the only isolated byproduct).

8 =  (Cy=cyclohexyl)

trialkylphosphines such as P(*t*-Bu)$_3$.[13] By analogy, we thought these ligands might improve the borylation of ortho-substituted aryl halides. As shown in Table 1, the use of biphenylphosphine ligand **8** improved significantly the borylation process (entries 2, 3). With a ratio of four ligands to the catalyst (entry 3), a high isolated yield of 81% was obtained, with reduced time and temperature compared to the original conditions (entry 1).[14] With P(*t*-Bu)$_3$ in different ratios to the palladium catalyst (entries 4, 5), no boronate was observed, the major isolated compound being the dehalogenated product, i.e., aniline. The use of other Pd catalysts (entries 6−8) failed to give the borylation product, variable mixtures of starting material and aniline being recovered after a prolonged period of heating.

To investigate the scope of this method, other ortho-subsituted phenyl halides were subjected to the same reaction conditions (Table 2). Whereas the borylation of 2-chloroaniline was inefficient (entry 1), reasonable yields could be obtained from 2-bromoanisole (entry 2) and 2-bromophenylacetonitrile (entry 3) using $Pd(OAc)_2$/**8**. In the latter example, employing $PdCl_2$(dppf) gave, like in the 2-bromoaniline case (Table 1), a much lower yield despite harsher conditions (entry 4). With bromides bearing electron-withdrawing groups, such as 2-bromonitrobenzene (entry 7) and 2′-bromoacetophenone (entry 9), little or no pinacolboronate was obtained, in accordance with the literature observations.[11] The borylation of sterically hindered bromides using $Pd(OAc)_2$/**8** (entries 10, 13) furnished the pinacolboronate in moderate yields. Yet the borylation using this catalytic system was again much more efficient and milder than with $PdCl_2$(dppf) (entry 14). It should be noted that changing the solvent from dioxane to toluene or DME in the borylation of Boc-protected 2-bromoaniline (entry 10) gave similar or lower yields of pinacolboronate[15] (43% **5** + 43% **6** for toluene, 31% **5** + 57% **6** for DME), as reported for $PdCl_2$(dppf)-mediated borylations.[10,11] Similarly, among the bases tested which do not promote undesired Suzuki coupling

Table 2. Synthesis of Ortho-Substituted Phenylboronates 5 from Halides 4 (according to Scheme 2)[a]

entry	halide 4		catalyst[b]	time (h)	temp (°C)	**5** (%)[c]	**6** (%)[c]
1			A	2	100	7	-
2			A	1	80	59[d]	15
3		X = Br	A	1	80	59	20
4		Br	B	4	100	23	13
5		X = I	A	0.5	80	90	10
6		I	B	3	100	76	-
7		X = Br	A	3	100	20[d]	-
8		X = I	A	1	80	44	-
9			A	1	80	-[e]	-
10		X = Br	A	1	80	40[f]	55
11		X = I	A	1	80	57	14
12		I	B	2	100	46	8
13			A	0.5	80	51	-
14			B	6	100	< 5	-
15			A	1	80	87	-
16			B	24	100	22	-
17			A	0.5	80	85	13

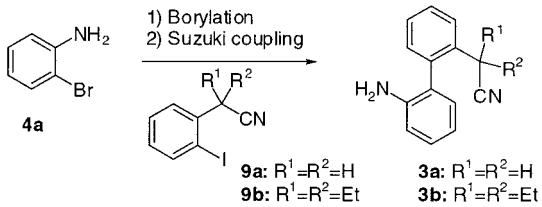
[a] Conditions: see note *a* in Table 1. [b]A = 5 mol % $Pd(OAc)_2$/20 mol % **8**, B = 5 mol % $PdCl_2$(dppf). [c]Isolated yields after flash chromatography. [d]Compound described in ref 10b. [e]Complex mixtures were obtained. [f]Compound described in ref 15. Boc = *tert*-butyloxycarbonyl, TES = triethylsilyl.

of the produced boronate **5** with the starting halide **4** during the borylation process (KOAc and tertiary amines),[10,11] Et_3N seemed the best candidate. Compared to bromides, the borylation of iodides with $Pd(OAc)_2$/**8** was higher yielding (entries 5, 8, 11), with identically mild reaction conditions. The difference in the borylation of these iodides using $Pd(OAc)_2$/**8** (entries 5, 11) or $PdCl_2$-(dppf) (entries 6, 12) seemed smaller than in the case of bromides, yet better yields under milder conditions were again obtained with the former catalyst. The negative effect of strong electron-withdrawing substituents on the borylation was again observed with 2-iodonitrobenzene (entry 8), as expected from earlier works.[11] In the case of sterically hindered 2-iodobenzenes (entries 15−17, both compounds being advanced intermediates in the synthesis of rhazinilam analogues),[8a−b] the borylation with Pd-$(OAc)_2$/**8** was very high-yielding whereas $PdCl_2$(dppf) was rather inefficient (entry 16). Thus, increasing the steric hindrance in the ortho position to the halogen atom (entries 5 → 15 → 17) did not substantially affect the efficiency of the borylation with $Pd(OAc)_2$/**8**, similarly to what was observed in the case of Suzuki couplings mediated by this catalyst.[12] In conclusion, the use of ligand **8** in the borylation of ortho-substituted phenyl bromides and sterically hindered phenyl iodides afforded higher yields of pinacolboronate in milder conditions than with $PdCl_2$(dppf).

With these results in hand, we thought that this methodology could be extended to the synthesis of 2,2′-disubstituted biphenyls via a one-pot Suzuki cross-coupling reaction. This was indeed achieved by adding,

(13) (a) Littke, A. F.; Fu, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 3387. (b) Littke, A. F.; Dai, C.; Fu, G. *J. Am. Chem. Soc.* **2000**, *122*, 4020.
(14) Using excess **7** (3 equiv) was necessary, the reagent being partly consumed by the deprotonation of the amino group.
(15) This compound was previously described: Lamba, J. J. S.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11723.

Table 3. One-Pot Synthesis of Biphenyls 3[a]



9a: $R^1=R^2=H$ **3a:** $R^1=R^2=H$
9b: $R^1=R^2=Et$ **3b:** $R^1=R^2=H$

entry	iodide	base	time (h)	product	yield (%)
1	**9a**	K_3PO_4	12	**3a**	65
2	**9a**	$Ba(OH)_2$	1	**3a**	73
3	**9b**	K_3PO_4	12	**3b**	40
4	**9b**	$Ba(OH)_2$	1	**3b**	66

[a] Conditions: (1) **4a**, Et_3N (4.0 equiv), **7** (3.0 equiv), $Pd(OAc)_2$ (5 mol %), **8** (20 mol %), dioxane, 80 °C, 1 h; (2) iodide **9** (1.0 equiv), base (3.0 equiv), H_2O, 100 °C.

after completion of the borylation step, the needed ingredients in the same reaction vessel, i.e., a second aryl halide and a suitable base (Table 3).

Thus, the borylation of 2-bromoaniline **4a** in the above conditions (80 °C, 1 h) was followed by addition of H_2O (which both hydrolyzes excess **7** and favors the coupling), *1 equiv* of 2-iodophenylacetonitrile **9a**, excess K_3PO_4 (3 equiv), and heating overnight to 100 °C (entry 1). Under these conditions, the cross-coupling product **3a** could be obtained in 65% isolated yield (together with dehalogenated products). Adding fresh catalyst for the coupling step did not improve the yield of the reaction, on the contrary to previously reported examples.[16] With diethyl-substituted phenylacetonitrile **9b** (entry 3), the coupling product **3b** was obtained in 40% yield under the same conditions, showing the negative effect of the steric hindrance on the Suzuki coupling step. Significant improvements were accomplished by using the stronger base $Ba(OH)_2$ instead of K_3PO_4, the former being known to favor the cross-coupling of sterically hindered substrates.[5] Thus, **3a** and **3b** were, respectively, obtained in 73% and 66% yields from **4a** after a very short heating time of 1 h (entries 2, 4).[17] Reversing the order of reagents, i.e., starting with the borylation of **9b** (Table 2, entry 15) and performing the Suzuki coupling with **4a** failed to give any coupled material **3b**, **4a** and borylated **9b** being recovered after 24 h at 100 °C.[18] Next, **3a** and **3b** can be further elaborated to give rhazinilam biphenyl analogues **2** (Scheme 1).[8]

In conclusion, we reported the borylation of ortho-substituted phenyl halides, in particular bromides and sterically hindered iodides, using the previously reported phosphine ligand **8**. These findings were extended to one-pot Suzuki−Miyaura reactions with ortho-substituted phenyl iodides, yielding sterically hindered 2,2′-biphenyls in an unprecedented simple, rapid, and efficient manner. Further developments of the methodology will include the solution and solid-phase synthesis of analogues of the antimitotic rhazinilam **1**, as well as other biologically active compounds having ortho-disubstituted biaryl frameworks.

(16) One pot syntheses of biaryls having meta and para substituents were reported in the case of diboron-mediated borylations: see ref 10b and Giroux, A.; Han, Y.; Prasit, P. *Tetrahedron Lett.* **1997**, *38*, 3841.

(17) Changing the solvent to toluene lead to decreased yields of coupled materials **3a**,**b** (data not shown).

(18) Further experiments are underway to propose a rationale accounting for this behavior.

Experimental Section

All compounds were commercially available or synthesized according to the literature procedures.[8b,15] Dioxane was distilled from Na/benzophenone and triethylamine from KOH prior to use.

General Procedure for the Synthesis of Phenylboronates 5 (Tables 1, 2). To a solution of phenyl halide (0.41 mmol) in 1 mL of dioxane were added, under argon, triethylamine (229 μL, 1.65 mmol), palladium(II) acetate (4.6 mg, 0.021 mmol), 2-(dicyclohexylphosphino)biphenyl **8** (28.8 mg, 0.08 mmol), and pinacolborane (179 μL, 1.23 mmol) dropwise. The reaction mixture was heated at 80 °C for 30 min. After cooling to room temperature, the reaction was quenched by adding a sat. solution of NH_4Cl, and the aqueous phase was extracted with ether. After drying over $MgSO_4$, the solution was filtered and evaporated under vacuum. The resulting oil was purified by flash chromatography (SiO_2 deactivated with 5% Et_3N).

Pinacol (2-aminophenyl)boronate: ^{1}H NMR (250 MHz, $CDCl_3$) $\delta = 7.63$ (dd, $J = 7.5$, 1.6 Hz, 1H), 7.23 (td, $J = 8.0$, 1.8 Hz, 1H), 6.69 (td, $J = 7.3$, 1.5 Hz, 1H), 6.61 (d, $J = 8.2$ Hz, 1H), 4.75 (br s, 2H), 1.36 (s, 12H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) $\delta = 153.6$, 136.8, 132.7, 129.2, 116.8, 114.8, 83.5, 24.9 ppm; FTIR (film) $\nu = 3487$, 3384, 2977, 1606, 1354 cm^{-1} ; HRMS (IE) calcd for $C_{12}H_{18}BNO_2$ [$M^{+\bullet}$]: 219.1431; found: 219.1437.

Pinacol (2-methoxyphenyl)boronate: ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.68$ (dd, $J = 7.8$, 1.8 Hz, H), 7.39 (td, $J = 8.0$, 1.8 Hz, 1H), 6.93 (td, $J = 7.4$, 1.4 Hz, 1H), 6.85 (d, $J = 8.7$ Hz, 1H), 3.82 (s, 3H), 1.35 (s, 12H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) $\delta =$ 164.1, 136.6, 132.4, 120.1, 110.4, 83.3, 55.7, 24.7 ppm; FTIR (film) $\nu = 2977$, 1600, 1354 cm^{-1} ; HRMS (IE) calcd for $C_{13}H_{19}BO_3$ [$M^{+\bullet}$]: 234.1427; found: 234.1439.

Pinacol (2-cyanomethylphenyl)boronate: ^{1}H NMR (250 MHz, $CDCl_3$) $\delta = 7.88$ (d, $J = 6.8$ Hz, 1H), 7.46 (m, 2H), 7.33 (m, 1H), 4.11 (s, 2H), 1.37 (s, 12H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) $\delta = 136.8$, 136.6, 131.8, 128.5, 127.2, 118.9, 84.1, 24.9, 23.5 ppm; FTIR (film) $\nu = 2980$, 2248, 1602, 1350 cm^{-1} ; HRMS (IE) calcd for $C_{14}H_{18}BNO_2$ [$M^{+\bullet}$]: 243.1431; found: 243.1445.

Pinacol (2-nitrophenyl)boronate: ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 8.16$ (d, $J = 8.1$ Hz, 1H), 7.66 (t, $J = 8.4$ Hz, 1H), 7.55 (m, 2H), 1.43 (s, 12H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) $\delta =$ 133.7, 132.8, 130.0, 122.9, 84.6, 24.7 ppm; FTIR (film) $\nu = 2979$, 1526, 1352 cm^{-1} ; HRMS (FAB) calcd for $C_{12}H_{16}BNO_4$ [$(M + H)^+$]: 250.1251; found: 250.1258.

Pinacol [*N*-(*tert*-butoxycarbonyl)-2-aminophenyl]boronate: identical spectroscopic data to those previously described.[15]

Pinacol (2,6-dimethylphenyl)boronate: ^{1}H NMR (250 MHz, $CDCl_3$) $\delta = 7.13$ (t, $J = 7.6$ Hz, 1H), 6.95 (d, $J = 7.5$ Hz, 2H), 2.40 (s, 6H), 1.39 (s, 12H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 141.7$, 129.1, 126.4, 83.6, 24.9, 22.2 ppm; FTIR (film) $\nu =$ 2978, 1597, 1333 cm^{-1} ; HRMS (IE) calcd for $C_{14}H_{21}BO_2$ [$M^{+\bullet}$]: 232.1635; found: 232.1648.

Pinacol [2-(1-cyano-1-ethylprop-1-yl)phenyl]boronate: ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.65$ (dd, $J = 7.5$, 1.5 Hz, 1H), 7.60 (d, $J = 7.5$ Hz, 1H), 7.39 (td, $J = 7.7$, 1.5 Hz, 1H), 7.27 (td, $J = 7.5$, 1.2 Hz, 1H), 2.31 (dq, $J = 14.7$, 7.5 Hz, 2H), 2.06 (dq, $J = 14.7$, 7.8 Hz, 2H), 1.37 (s, 12H), 0.92 (t, $J = 7.8$ Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 141.9$, 135.8, 129.8, 128.3, 126.5, 123.5, 84.2, 51.6, 32.5, 24.8, 9.7 ppm; FTIR (film) $\nu = 2976$, 2231, 1596, 1342 cm^{-1} ; HRMS (IE) calcd for $C_{18}H_{26}BNO_2$ [$M^{+\bullet}$]: 299.2057; found: 299.2084.

Pinacol [2-(1-triethylsilanyloxymethyl-1-ethylprop-1-yl)phenyl]boronate: ^{1}H NMR (250 MHz, $CDCl_3$) $\delta = 7.43$ (d, $J = 6.8$ Hz, 1H), 7.26 (m, 1H), 7.13 (m; 2H), 3.86 (s, 2H), 1.84 (dq, $J = 7.0$, 2.8 Hz, 4H), 1.37 (s, 12H), 0.93 (t, $J = 7.9$ Hz, 9H), 0.65 (t, $J = 6.8$ Hz, 6H), 0.55 (q, $J = 7.8$ Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 148.8$, 133.7, 128.5, 127.3, 124.5, 83.7, 64.9, 47.3, 28.1, 24.7, 8.3, 6.8, 4.4 ppm; FTIR (film) $\nu = 2959$, 1594, 1339 cm^{-1} ; HRMS (FAB) calcd for $C_{24}H_{42}BO_3Si$ [$(M - H)^+$] (nonclassical fragmentation): 417.2996; found: 417.2974; calcd for $C_{22}H_{38}BO_3Si$ [$(M - Et)^+$]: 389.2683; found: 389.2680.

General Procedure for the Synthesis of Biphenyls 3 (Table 3). To a solution of 2-bromoaniline **4a** (80 mg, 0.47 mmol) in dioxane (1 mL) were added, under argon, triethylamine (259 μL, 1.86 mmol), palladium(II) acetate (5.2 mg, 0.023 mmol), 2-(dicyclohexylphosphino)biphenyl (33 mg, 0.093 mmol), and

pinacolborane (202 μL, 1.40 mmol) dropwise. The mixture was stirred at 80 °C for 1 h and then cooled to room temperature, and water (200 μL), barium hydroxide octahydrate (440 mg, 1.40 mmol), and iodide **9a** or **9b** (0.47 mmol) dissolved in 0.1 mL of dioxane were successively added. The mixture was heated to 100 °C under stirring for 1 h and then cooled to room temperature and filtered through Celite. Brine was added, and the aqueous phase was extracted with CH_2Cl_2. After drying over $MgSO_4$, the solvents were removed under vacuum, and the residue was purified by flash chromatography (SiO_2).

2′-Aminobiphen-2-ylacetonitrile (3a): ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.59 (m, 1H), 7.41 (m, 2H), 7.27 (m, 1H), 7.19 (td, 7.8, 1.5 Hz, 1H), 6.99 (d, J = 7.8, 1.5 Hz), 6.79 (m, 2H), 3.72 (d, J = 19.0 Hz, 1H), 3.52 (d, J = 18.8 Hz, 1H), 3.45 (br s, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 143.4, 138.2, 130.6, 129.9, 129.4, 129.2, 128.5, 124.8, 118.6, 118.2, 115.3, 21.3 ppm; FTIR (film) ν = 3460, 3368, 2248, 1616, 1482 cm^{-1}; HRMS (FAB) calcd for $C_{13}H_{10}N_2$ [$(M + H)^+$]: 209.1079; found: 209.1066.

2-(2′-Aminobiphen-2-yl)-2-ethylbutyronitrile (3b): identical spectroscopic data to those previously described.[8b]

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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