Synthesis of 1,2-Diarylnaphthalenes by Chemoselective Suzuki–Miyaura Reactions of 2-Bromo-1-(trifluoromethanesulfonyloxy)naphthalene

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Abstract: Suzuki–Miyaura reactions of 2-bromo-1-(trifluoromethanesulfonyloxy)naphthalene, readily available from 1-tetralone in two steps, afforded a variety of 1,2-diarylnaphthalenes. The reactions proceed with excellent chemoselectivity in favor of the bromide position, while the triflate remained unattacked.

Key words: catalysis, palladium, Suzuki–Miyaura reaction, naphthalene, chemoselectivity

Various naturally occurring naphthalenes possess a biaryl linkage. The biaryl axis governs the biological activity of these natural products and is responsible to introduce atropisomerism into some of these compounds due to restricted rotation along the biaryl axis. For example, naphthylisoquinolines, such as the michellamines [e.g., michellamine A (**1**), Figure 1] isolated from *Ancistrocladus korupensis*, have attracted the scientific community primarily because of their antimalaria and anti-HIV activity.[1–3] Resveratrol (**2**) is a naturally occurring potent anticancer drug, which, however, suffers from chemical and metabolic instability.[4,5] To overcome these limitations a series of arylated naphthalenes were synthesized in which the stilbene double bond was substituted by a naphthalene ring. Among these compounds, which are stable and structurally more rigid, derivative **3** was found to be most active against human breast cancer cell line B. Konzik et al. have shown that the phenyl substituents of naphthalenes have a strong influence on their fungistatic activity.[6]

In the literature, several synthetic approaches to 1,2-diphenylnaphthalenes have been described. However, classic approaches have limitations with regard to low yields, need of several synthetic steps, availability of the starting materials, and low regioselectivity.[7] For example, Bergmann et al. prepared 1,2-diphenylnaphthalene from α-phenyltetralone and phenyl magnesium bromide in three steps in 46% overall yield.[7b]

In recent years, regioselective palladium-catalyzed reactions of polyhalogenated arenes or heteroarenes and of bis(triflates) have been widely studied.[8,9] In general, the first attack occurs at the sterically less hindered and electronically most deficient position. Another strategy for the selective functionalization of arenes or heteroarenes relies

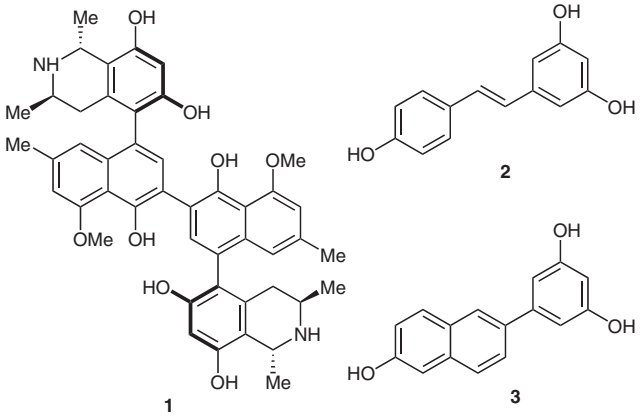

Figure 1 Pharmacologically important naphthalene derivatives

on the chemoselectivity of substrates containing different leaving groups (e.g., triflate and bromide). Recent reports show that several parameters influence the chemoselectivity of Suzuki–Miyaura reactions of arenes containing a bromide and a triflate group.[10] While various palladium-catalyzed cross-coupling reactions of naphthalene derivatives have been reported,[3] regio- and chemoselective transformations of naphthalenes containing two or more reactive sites, such as bromide or triflate groups, have only scarcely been studied so far. Recently, we have reported regioselective palladium-catalyzed Suzuki cross-coupling reactions of the bis(triflate) of phenyl 1,4-dihydroxy-2-naphthoate.[11] Herein, we wish to report what are, to the best of our knowledge, the first Suzuki–Miyaura reactions of 2-bromo-1-(trifluoromethanesulfonyloxy)naphthalene. These reactions proceed with excellent chemoselectivity and provide a convenient approach to various arylated naphthalene derivatives which are not readily available by other methods.

The bromination of naphth-1-ol is known to result in the formation of mixtures of 2- and 4-brominated naphthalenes. In 2005, Bekaert et al. reported[12] the selective synthesis of 2-bromonaphth-1-ol (**5**) by reaction of 1-tetralone (**4**) with *N*-methylpyrrolidin-2-one hydrotribromide {MPHT, $[NMP]_2HBr_3$}. We have developed an alternative approach to **5** which relies on the bromination[13] of **4** using NBS (2.2 equiv) and $(PhCOO)_2$ (5 mol%, Scheme 1).[14] The advantage of this method is that the product is formed in very good yield (84%) and that inexpensive reagents are used. It is noteworthy that, although

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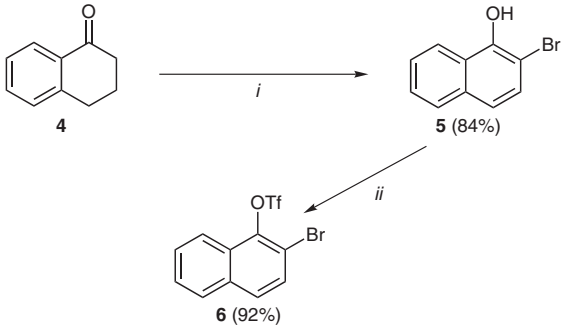
free-radical conditions were applied, bromination at position 4 was not observed. 2-Bromonaphth-1-ol (**5**) was transformed to its triflate **6** in very good yield.[15]



Scheme 1 Synthesis of **5** and **6**. *Reagents and conditions*: *i*, **4** (1.0 equiv), NBS (2.2 equiv), $(PhCOO)_2$ (5 mol%), benzene, reflux, 5 h; *ii*, **5** (1.0 equiv), Tf_2O (1.2 equiv), pyridine (2.0 equiv), CH_2Cl_2, 20 °C, 12 h.

The structure of product **5** was elucidated by 2D NMR spectroscopy (NOESY, COSY, HMBC, HMQC). A NOESY correlation between hydrogen atoms H-4 (δ = 7.44 ppm, d, *J* = 8.8 Hz) and H-5 (δ = 7.72 ppm, m) was observed (Figure 2).

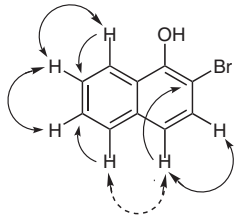
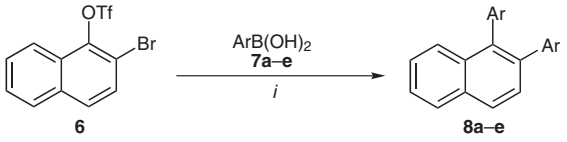


Figure 2 Important HMBC (single head arrows), NOESY (dashed arrows), and COSY (double head arrows) correlations of **5**

The Suzuki–Miyaura reaction of **6** with arylboronic acids **7a–e** (2.2 equiv) afforded the 1,2-diarylnaphthalenes **8a–e** in 62–94% yield (Scheme 2, Table 1).[16] Both electron-poor and electron-rich arylboronic acids could be successfully employed. Arylboronic acids bearing electron-withdrawing groups provided better yields than those containing electron-donating groups. The best yields were obtained using $Pd(PPh_3)_4$ (5 mol%) as the catalyst and K_3PO_4 (3.0 equiv) as the base. The reactions were carried out in 1,4-dioxane at 110 °C.

The Suzuki–Miyaura reaction of **6** with arylboronic acids **7a**,**c–f** (1.0 equiv) afforded the 2-arylnaphth-1-yl trifluoromethanesulfonates **9a–e** in 60–88% yields (Scheme 3,



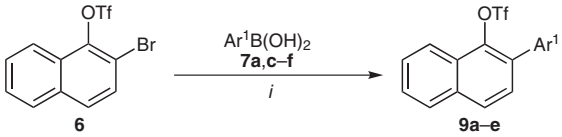
Scheme 2 Synthesis of **8a–e**. *Reagents and conditions*: *i*, **6** (1.0 equiv), $ArB(OH)_2$ (2.2 equiv), $Pd(PPh_3)_4$ (5 mol%), K_3PO_4 (3.0 equiv), dioxane, 110 °C, 4 h.

Table 1 Synthesis of 1,2-Diarylnaphthalenes **8a–e**

7,8	Ar	Yield of **8** (%)[a]
a	2-$MeOC_6H_4$	62
b	4-*t*-BuC_6H_4	71
c	4-MeC_6H_4	79
d	4-ClC_6H_4	94
e	4-FC_6H_4	86

[a] Yields of isolated compounds.

Table 2).[16,17] The reactions proceeded with very good chemoselectivity in favor of the bromide position, while the triflate remained unattacked. During the optimization, it proved to be important to use exactly 1.0 equivalent of the arylboronic acid and $Pd(PPh_3)_4$ (5 mol%) as the catalyst. The temperature played an important role as well. A good selectivity was achieved only when the reaction was carried out at 90 °C (instead of 110 °C) because the reaction of the triflate was slow at this temperature. The reactions were successful for both electron-rich and electron-poor arylboronic acids, but again electron-poor boronic acids provided better yields. The structures of the products could be easily established based on the fact that the triflate group is still present in the molecule (^{13}C NMR, ^{19}F NMR).



Scheme 3 Synthesis of **9a–e**. *Reagents and conditions*: *i*, **6** (1.0 equiv), $Ar^1B(OH)_2$ (1.0 equiv), $Pd(PPh_3)_4$ (5 mol%), K_3PO_4 (1.5 equiv), dioxane, 90 °C, 4 h.

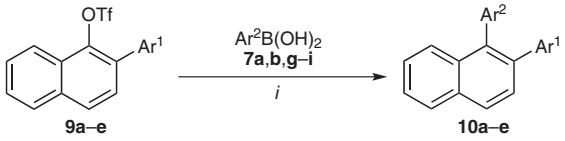
Table 2 Synthesis of **9a–e**

7	9	Ar^1	Yield of **9** (%)[a]
a	**a**	2-$MeOC_6H_4$	60
c	**b**	4-MeC_6H_4	73
f	**c**	Ph	77
d	**d**	4-ClC_6H_4	88
e	**e**	4-FC_6H_4	85

[a] Yields of isolated compounds.

The Suzuki–Miyaura reaction of **9a–e** with arylboronic acids **7a**,**b**,**g–i** (1.1 equiv) afforded the 1,2-diarylnaphthalenes **10a–e** containing two different aryl groups (Scheme 4, Table 3).[16,18] The reactions were carried out at 110 °C. The application of a one-pot synthesis of products **10** by sequential addition of two different arylboronic acids to **6** resulted in a decrease of the yield (with respect to

the stepwise protocol). Therefore, this approach was not further investigated.



Scheme 4 Synthesis of **10a–e**. *Reagents and conditions*: *i*, **9a–e** (1.0 equiv), $Ar^2B(OH)_2$ (1.1 equiv), $Pd(PPh_3)_4$ (5 mol%), K_3PO_4 (1.5 equiv), dioxane, 110 °C, 4 h.

Table 3 Synthesis of **10a–e**

10	7	9	Ar^1	Ar^2	Yield of **10** (%)[a]
a	**b**	**a**	2-$MeOC_6H_4$	4-*t*-BuC_6H_4	80
b	**g**	**b**	4-MeC_6H_4	2,5-$(MeO)_2C_6H_3$	65
c	**a**	**c**	Ph	2-$MeOC_6H_4$	69
d	**h**	**d**	4-ClC_6H_4	3,5-$Me_2C_6H_3$	72
e	**i**	**e**	4-FC_6H_4	3-MeC_6H_4	77

[a] Yields of isolated compounds.

Aryl bromides usually undergo Suzuki–Miyaura reactions more rapidly than aryl triflates.[10] This reactivity order is different for other palladium-catalyzed cross-coupling reactions. One of the explanations for that is based on the high borane–halide affinity. However, other parameters influence the selectivity as well.[10e]

In conclusion, we have reported chemoselective Suzuki–Miyaura reactions of 2-bromo-1-(trifluoromethanesulfonyloxy)naphthalene which is readily available from 1-tetralone in two steps. The strategy outlined herein provides a convenient approach to 1,2-diarylnaphthalenes which are not readily available by other methods.

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(14) **Synthesis of 2-Bromonaphth-1-ol (5)**
A benzene suspension (30 mL) of 1-tetralone (**4**, 1.8 mL, 13.7 mmol), NBS (5.4 g, 30.2 mmol), and $(PhCOO)_2$ (0.17 g, 5mol%) was refluxed under Argon atmosphere for 4 h and then cooled to 20 °C. To the reaction mixture was added Et_3N (1 mL), and the solvent was removed in vacuo. The reaction mixture was diluted with H_2O and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in

vacuo. The residue was purified by flash chromatography (silica gel, heptane–EtOAc) to give **5** as a colorless solid (2.57 g, 84%). R_f = 0.54 (heptane–EtOAC = 4:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.89 (s, 1 H, OH), 7.24 (d, 1 H, *J* = 8.8 Hz), 7.38–7.41 (d, 1 H, *J* = 8.8 Hz), 7.43–7.46 (m, 2 H), 7.66–7.75 (m, 1 H), 8.12–8.19 (m, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 104.0 (C), 121.3, 122.2, 124.1 (CH), 124.4 (C), 124.8, 127.5, 128.3 (CH), 133.7, 148.1 (C). IR (KBr): ν = 3400 (s), 3051, 1958, 1931, 1883, 1877, 1624 (w), 1586, 1574 (m), 1504 (w), 1453, 1396, 1384, 1347, 1240, 1212, 1202, 1140, 1126, 1054, 1021, 876, 856 (m), 829, 792, 768, 736 (s), 716, 641, 600, 561 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 222 (98) [M]$^+$, 115 (92). HRMS (EI, 70 eV): *m/z* calcd for $C_{10}H_7BrO$ [M]$^+$: 221.96803; found: 221.96799.

(15) **Synthesis of 2-Bromonaphth-1-yl Trifluoromethanesulfonate (6)**

To a solution of **5** (2.4 g, 10.8 mmol) in CH_2Cl_2 (25 mL) was added pyridine (1.8 mL, 21.6 mmol) at 20 °C under an argon atmosphere. After stirring for 10 min at 0 °C, Tf_2O (2.7 mL, 16.4 mmol) was added. The mixture was allowed to warm to 20 °C and stirred for further 6 h. The reaction mixture was filtered, and the filtrate was concentrated in vacuo. The residue was directly purified by chromatography without aqueous workup (flash silica gel, heptane–EtOAc) to give **6** as a light yellow oil (3.53 g, 92%). R_f = 0.71 (heptane–EtOAc, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.69 (m, 4 H), 7.83 (d, 1 H, *J* = 7.8 Hz), 8.13 (d, 1 H, *J* = 8.1 Hz). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –73.0. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 114.1 (C), 118.5 (q, $J_{F,C}$ = 321.0 Hz, CF_3), 121.2, 127.5 (CH), 127.9 (C), 128.1, 128.5, 129.4, 129.9 (CH), 133.7, 142.6 (C). IR (KBr): ν = 1589, 1501, 1457 (m), 1408 (s), 1370, 1365 (m), 1203, 1181 (s), 1124 (s), 1032, (m)1018, 890, 801, 761 (s), 743, 703, 665, 616, 587, (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 354 (100) [M]$^+$, 223 (52). HRMS (EI, 70 eV): *m/z* calcd for $C_{11}H_6BrF_3O_3S$: 353.91731 [M]$^+$; found: 353.91711.

(16) **General Procedure for Suzuki–Miyaura Reactions**

A 1,4-dioxane (5 mL per 1 mmol) solution of **6** or **9a–e** (1.0 equiv), K_3PO_4 (1.5 equiv per cross-coupling step), $Pd(PPh_3)_4$ (5 mol%), and arylboronic acid **3** (1.0–1.1 equiv per cross-coupling step) was stirred at 90–110 °C for 4 h. After cooling to 20 °C, H_2O was added. The organic and the aqueous layers were separated, and the latter was extracted with CH_2Cl_2 (15 × 3 mL). The combined organic layer was dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography.

(17) **Synthesis of 2-(4-Fluorophenyl)naphth-1-yl Trifluoromethanesulfonate (9e)**

Starting with **6** (200 mg, 0.73 mmol), 4-fluorophenylboronic acid **7e** (102 mg, 0.73 mmol), $Pd(PPh_3)_4$ (42 mg, 5 mol%), K_3PO_4 (232 mg, 1.5 mmol), and 1,4-dioxane (5 mL), **9e** was isolated as a highly viscous oil (229 mg, 85%). R_f = 0.51 (heptane–EtOAc, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05–7.15 (m, 2 H), 7.38–7.45 (m, 3 H), 7.49–7.62 (m, 2 H), 7.80–7.59 (m, 2 H), 8.09 (d, 1 H, *J* = 8.4 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –113.2, –74.0. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 115.6 (d, $J_{F,C}$ = 21.4 Hz, 2 CH), 117.1 (q, $J_{F,C}$ = 316.2 Hz, CF_3), 119.7 (C), 121.7, 127.3, 128.0 (CH), 128.2 (d, $J_{F,C}$ = 2.6 Hz, 2 CH), 128.6, 131.4, 131.6 (CH), 132.3, 132.4, 134.1, 141.9 (C), 161.9 (d, $J_{F,C}$ = 248.5 Hz, CF). IR (KBr): ν = 2961, 1606 (w), 1513, 1498 (m), 1405 (s), 1341 (w), 1201 (s), 1159 (m), 1132 (s), 1088, 1018, 1007 (m), 894 (s), 867 (m), 816, 804 (s), 764 (m), 749 (s), 703, 683, 622, 598, 556, (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 370 (19) [M$^+$], 237 (100), 209 (51), 183 (12). HRMS (EI, 70 eV): *m/z* calcd for $C_{17}H_{10}F_4O_3S$ [M]$^+$: 370.02813; found: 370.02763.

(18) **Synthesis of 2-(4-Fluorophenyl)-1-(*m*-tolyl)naphthalene (10e)**

Starting with **9e** (100 mg, 0.27 mmol), 3-tolylboronic acid (40 mg, 0.29 mmol), $Pd(PPh_3)_4$ (16 mg, 5 mol%), K_3PO_4 (86 mg, 0.41 mmol), and 1,4-dioxane (5 mL), **10e** was isolated as a highly viscous oil (65 mg, 77%). R_f = 0.44 (heptane–EtOAc, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.2 (s, 3 H, CH_3), 6.75–6.91 (m, 4 H), 7.00–7.05 (m, 3 H), 7.10 (t, 1 H, *J* = 7.4 Hz), 7.28–7.40 (m, 2 H), 7.43 (d, 1 H, *J* = 8.6 Hz), 7.58 (br d, 1 H, *J* = 8.5 Hz), 7.81 (d, 2 H, *J* = 8.2 Hz). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –116.6. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 114.5 (d, $J_{F,C}$ = 21.3 Hz, 2 CH), 125.8, 126.3, 126.9, 127.6, 127.8, 127.9, 128.1, 128.5, 131.5, 131.6, 132.1 (CH), 132.7, 132.8, 137.2, 137.4, 137.9, 138.1 (d, $J_{F,C}$ = 3.3 Hz, C), 138.7 (C), 161.5 (d, $J_{F,C}$ = 245.6 Hz, CF). IR (KBr): ν = 3050, 2920 (m), 2852 (w), 1601 (m), 1499 (s), 1457 (m), 1234 (w), 1218 (s), 1155, 1092, 1023 (m), 962 (w), 863, 841 (m), 817, 803, 778, 743, 713, 693 (s), 653, 544 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 312 (100) [M$^+$], 222 (55), 204 (7). HRMS (EI, 70 eV): *m/z* calcd for $C_{23}H_{17}F$ [M]$^+$: 312.13143; found: 312.13133.