SUPPORTING INFORMATION

Palladium-Catalyzed Suzuki-Miyaura Cross-Couplings of Sulfonyl Chlorides and Boronic Acids

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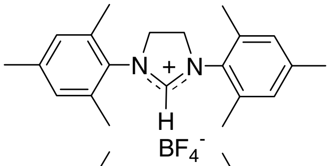
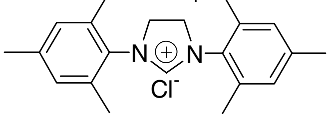
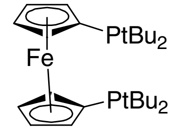
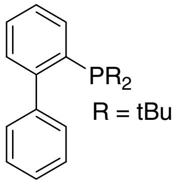
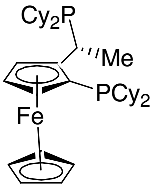
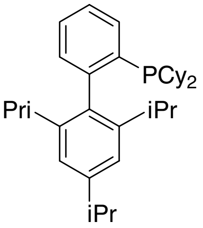
Methods: Unless stated otherwise, reactions were conducted in flame-dried glassware under a vacuum. THF was distilled before to use from sodium and benzophenone. Solvents after reactions and extraction were evaporated in a rotatory evaporator under vacuum (solvents were removed cooling at –20 °C, in the case of low boiling point or low molecular mass compounds). TLC for reaction monitoring was performed on 60 F_{254} (Merck) with detection by UV light and charring with $KMnO_4$ or Pancaldi reagent. M.p.: uncorrected by using Tottoli (Büchi SMP-20) apparatus. ^{1}H and ^{13}C NMR spectra were recorded by using Bruker-DPX-400, or Bruker-ARX-400 spectrometer at 400 MHz and 100.6 MHz respectively and are reported relative to Me_4Si (δ 0.0) or to the solvents residual ^{1}H-signal ($CH\text{-}Cl_3$, δ(H) 7.27). Data for ^{1}H NMR spectra are reported as follows: Chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{13}C NMR spectra reported in terms of chemical shift. IR spectra were recorded on a Perkin-Elmer-1420 spectrometer and are reported in frequency of absorption (cm^{-1}). High Resolution MALDI-TOF mass spectra were obtained from the Institute of Molecular and Biology Chemistry, Swiss Institute of Technology Mass Spectral Facility.

Materials: All ligands and palladium sources were purchased from Strem Chemicals.

Here we are giving that palladium and ligands catalog numbers from Strem Chemicals.

Compound	**Catalog No.**	**Compound**	**Catalog No.**
$Pd(OAc)_2$	46-1780		07-0302
$PdCl_2(PhCN)_2$	46-0400		
$PdCl_2(CH_3CN)_2$	46-0370		07-0299
$Pd(PPh_3)_4$	46-2150		
$Pd_2(dba)_3$	46-3000		
P(*t*-Bu)$_3$, (10 wt% in hexane)	15-5812		26-0275
	15-1045		26-1000
	15-1149	$NiCl_2(dppf)$	28-0500

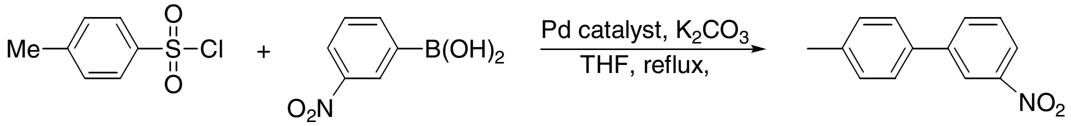
K_2CO_3, Na_2CO_3, Li_2CO_3, Et_3N were dried before reaction.

Typical Experimental Procedure for Catalyst B (Table 3) in text: In a round bottom flask dried under *vacuum* were placed under nitrogen atmosphere, the corresponding sulfonyl chloride (1.00 mmol), Pd_2dba_3 (0.015 mmol), ligand **7** (0.06 mmol), Na_2CO_3 (3 mmol) and the boronic acid (2 mmol) (were weighed in a glove box). Then, the flask was connected to a *vacuum* line and filled with argon (3 times), and THF (5 mL) was added under argon. The reaction mixture was stirred at reflux for 15-35 h. After cooling to room temperature, the mixture was diluted with ether and washed with water. The aqueous layer was extracted again with ether (3 times). The combined organic phases were dried (Na_2SO_4), filtered and concentrated under reduced pressure (solvents were removed under reflux on cooling to –20 ^{o}C). The residue was purified by flash chromatography.

Typical Experimental Procedure for Catalyst A (Table 3) in text. In a round bottom flask dried under *vacuum* were placed under nitrogen atmosphere, the corresponding sulfonyl chloride (1.00 mmol), $Pd(PPh_3)_4$ (0.08 mmol) K_2CO_3 (3 mmol) and the boronic acid (2 mmol) (were weighed in a glove box). Then, flask connected to a *vacuum* line and filled with argon (3 times), and THF (5 mL) was added under argon. The reaction mixture was stirred at reflux for 15-35

h. After cooling to room temperature, the mixture was diluted with ether and washed with water. The aqueous layer was extracted again with ether (3 times). The combined organic phases were dried (Na_2SO_4), filtered and concentrated under reduced pressure (solvents were removed under reflux on cooling to -20 °C). The residue was purified by flash chromatography (Na_2SO_4), filtered and concentrated under pressure, and purified by flash chromatography

Table 2. Effect of palladium-catalyst in Suzuki cross-coupling of aryl sulfonyl chloride.[a]

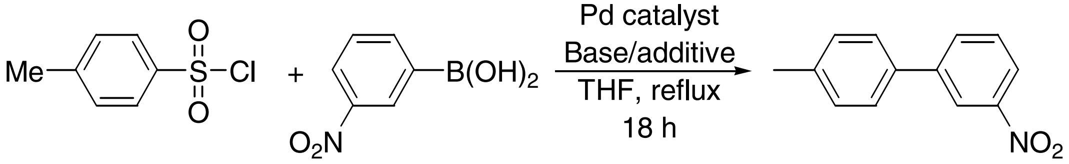


Entry	Palladium catalyst (equiv.)	Yield [%][b]
1	-	0
2	$Pd(PPh_3)_4$ (8%)	55
3	$PdCl_2(PhCN)_2$(13%)	40
4	$Pd_2(dba)_3$ (1.5%)/P(tBu)$_3$ (3.6%)	12[d]
5	$Pd_2(dba)_3$ (5%)/ L (15%)	38[e]
6	$Pd_2(dba)_3$ (5%)/ L (15%)	14[f]

[a] palladium and ligands were purched from Aldrich and Acros company **Reaction conditions**: 1.0 equiv of *p*-

toluenesulfonyl chloride, Pd catalyst (see Table 1), 1.5 equiv of 3-nitrobenezeneboronic acid, 2.0-3.0 equiv. of K_2CO_3 and THF (5 mL per 1mmol of sulfonyl chloride), reflux for 15 h. [b] Determined after flash chromatography. [c] Dioxane as solvent, reflux for 48 h. [d] L = 2-(di-t-butyl phosphino) biphenyl and dioxane as solvent, reflux for 48 h. [e] L = 2-(di cyclohexyl phosphino) biphenyl and dioxane as solvent, reflux for 48 h.

Table 3. Effect of base (additive) on the palladium-catalyzed Suzuki cross-coupling of aryl sulfonyl chloride.[a]



Entry	Palladium catalyst (equiv.)	Base/Additive	Yield [%][b]
1	$Pd(PPh_3)_4$ (8%)	-	0
2	$PdCl_2(PhCN)_2$(13%)	-	0
3	$Pd(PPh_3)_4$ (8%)	K_2CO_3	50
4	$Pd(PPh_3)_4$ (8%)	NEt_3	10
5	$Pd(PPh_3)_4$ (8%)	K_3PO_4	15
6	$Pd(PPh_3)_4$ (8%)	Cs_2CO_3	0
7	$Pd(PPh_3)_4$ (8%)	CuCl	40
8	$Pd(PPh_3)_4$ (8%)	$CuBr{\cdot}Me_2S$	7
9	$Pd(PPh_3)_4$ (8%)	CuI	0

10	$Pd_2(dba)_3$ (1.5%)/P(tBu)$_3$ (3.6%)	Cs_2CO_3	0[c]
11	$Pd_2(dba)_3$ (5%)/L (15%)	K_2CO_3	15d]
12	$Pd_2(dba)_3$ (5%)/L (15%)	K_3PO_4	12[d]

[a] palladium and ligands were purched from Aldrich and Acros company **Reaction conditions**: 1.0 equiv of *p*-toluenesulfonyl nitrobenezeneboronic acid, 2.0-3.0 equiv. of K_2CO_3, THF (5 mL per 1mmol of sulfonyl chloride), reflux for 15 h. [b] Determined after flash chromatography. [c] Dioxane as solvent, reflux for 48 h. [d] L = 2-(di-t-butyl phosphino)biphenyl and dioxane as solvent, reflux for 48 h.

4-methylbiphenyl (Table 3, entry 1): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (55% yield) as a white solid.[1]

4,4′-dimethyl-biphenyl (Table 3, entry 2): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (70% yield) as a white solid.[2]

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[1] a) Mowery, E. M; DeShong, P. *J. Org. Chem*, **1999**, *64*, 3266-3270; b) Rao, M.S.C.; Rao, G.S.K. *Synthesis* **1987**, 231-233; c) Srogl, J.; Allred, G.D.; Liebeskind, L.S. *J. Am. Chem. Soc.* **1997**, *119*, 12376-12377; d) Bergbreiter, D.E.; Osburn, P.L.; Wilson, A.; Sink, E.M. *J. Am. Chem. Soc.* **2000**, *122*, 9058-9064.

[2] Koza, D.J.; Carita, E. *Synthesis* **2002**, 2183-2186.

Using the Typical Experimental Procedure for **catalyst B,** the product is obtained(92% yield) as a white solid.

3-nitro-4′-methyl-biphenyl (Table 3, entry 3): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (60% yield) as a yellow solid.[3]

4′-methylbiphenyl-3-carboxadehyde (Table 3, entry 4): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (55% yield) as a colourless oil.[4]

4-methoxy-4′-methyl-biphenyl (Table 3, entry 5): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (50% yield) as a white solid.[5]

Using the Typical Experimental Procedure for **catalyst B,** the product is obtained (65% yield) as a white solid.

4′-methyl-2-phenylfuran (Table 3, entry 6): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (40% yield) as a colourless oil.[6]

1-methyl-4-[(E)-2-phenyl-1-ethenyl]benzene (Table 3, entry 7): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (39% yield) as a white solid.[7]

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[3] Hassan, J.; Hathroubi, C.; Gozzi, C.; Lemaire, M. *Tetrahedron* **2001**, *57*, 7845-7855.

[4] Rao, M.S.C.; Rao, G.S.K. *Indian J. Chem.*, Sect.B: **1988**, *27B*, 213-216.

[5] Ueda, M.; Saitoh, A.; Oh-tani, S.; Miyaura, N. *Tetrahedron* **1998**, *54*, 13079-13086.

[6] Pelter, A.; Rowlands, M.; Clements, G. *Synthesis* **1987**, 51-53.

Using the Typical Experimental Procedure for **catalyst B,** the product is obtained (48% yield) as a white solid.

4-chloro-4′-methyl-biphenyl (Table 3, entry 8): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (60% yield) as a white solid.[8]

Using the Typical Experimental Procedure for **catalyst B,** the product is obtained (78% yield) as a white solid.

1-(4-methylphenyl)-naphthalene (Table 3, entry 9): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (60% yield) as a colourless solid.[9]

Using the Typical Experimental Procedure for **catalyst B,** the product is obtained (76% yield) as a colourless solid.

3-nitro-4′-chloro-biphenyl (Table 3, entry 10): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (65% yield) as a light yellow solid.[10]

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[7] a) Katritzky, A.R.; Cheng, D.; Henderson, S.A.; Li. J. *J. Org. Chem*, **1998**, *63*, 6704-6709; b) Katritzky, A.R.; Cheng, D.; Henderson, S.A.; Li. J. *J. Org. Chem*, **1998**, *63*, 3438-3444.

[8] Xia, M.; Chen, Z-C. *Synth. Commun*. **1999**, *29*, 2457-2466.

[9] Nishimura, M.; Ueda, M.; Miyaura, N. *Tetrahedron* **2002**, *58*, 5779-5787.

[10] Podgornova, N.N.; Lipina, E.S.; Perekalin, V.V. *Zhurnal Organicheskoi Khimii*, **1974**, *10*, 1985-6; *J. Org. Chem*, USSR (Engl. Trans.) **1974**, *10*, 1993-1994.

4-chloro-4′-methyl-biphenyl (Table 3, entry 11): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (62% yield) as a white solid.[11]

Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (80% yield) as a white solid.

Biphenyl: Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (68% yield) as a colourless solid.[12]

1-(3-formylphenyl)-naphthalene (Table 3, entry 12): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (55% yield) as a colourless oil.[13]

Using the Typical Experimental Procedure for **catalyst B,** the product is obtained (72% yield) as a colourless solid.

1-(3-nitrophenyl)-naphthalene (Table 3, entry 13): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (61% yield) as a yellow solid.[14]

1-(4-methylphenyl)-naphthalene (Table 1, entry 14): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (55% yield) as a colourless solid.[15]

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[11] Xia, M.; Chen, Z-C. *Synth. Commun.* **1999**, *29*, 2457-2466.

[12] Nishimura, M.; Ueda, M.; Miyaura, N. *Tetrahedron* **2002**, *58*, 5779-5787.

[13] Manning, C.; Leznoff, C.C. ; *Can. J. Chem.*; **1975**, 805-808..

[14] Hassan, J.; Hathroubi, C.; Gozzi, C.; Lemaire, M. *Tetrahedron* **2001**, *57*, 7845-7855.

Using the Typical Experimental Procedure for **catalyst B,** the product is obtained (82% yield) as a colourless solid.

3,3′-dinitro-biphenyl (Table 3, entry 18): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (78% yield) as colourless needles.[16]

3-nitro-4′-methyl-biphenyl (Table 3, entry 19): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (70% yield) as a yellow solid.[17]

4-nitro-4′-methyl-biphenyl (Table 3, entry 20): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (64% yield) as a yellow solid.[18]

4-methyldiphenylmethane (Table 3, entry 21): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (30% yield) as a colourless liquid.[19]

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[15] Nishimura, M.; Ueda, M.; Miyaura, N. *Tetrahedron* **2002**, *58*, 5779-5787.

[16] Bushby, R.J.; McGill, D.R.; Ng, K.M.; Taylor, N. *J. Chem. Soc, Perkin Trans.2*, **1997**, 7, 1405-1414.

[17] Hassan, J.; Hathroubi, C.; Gozzi, C.; Lemaire, M. *Tetrahedron* **2001**, *57*, 7845-7855.

[18] a) Carsten, G.;Markus, K.; Heimo, S.; Lother, E.; Gernot, B. *Mutat. Res*, **2002**, *515*, 15-38; b) Noriyoshi, A.; Koichi, N. *Bull. Chem. Soc. Japan*, **1995**, *68*, 1707-1714.

[19] a) Darbeau, R.W.; White, E.H.; Song, F.; Darbeau, N.R.; Chou, J. *J. Org. Chem*, **1999**, *64*, 5966-5978; b) Kabalka, G.W.; Maddox, J.T.; Bogas, E.; Kelley, S.W. *J. Org. Chem*, **1997**, *62*, 3688-3695.

Using the Typical Experimental Procedure for **catalyst B,** the product is obtained (52% yield) as a colourless liquid

3-nitrodiphenylmethane (Table 3, entry 22): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (35% yield) as a pale yellow oil.[20]

Using the Typical Experimental Procedure for **catalyst B,** the product is obtained (50% yield) as a pale yellow oil.

1-(2-methylprop-2-enyl)-3′-nitrobenzene (Table 3, entry 23): Using the Typical Experimental Procedure for **catalyst A,** the product is obtained (35% yield) as a yellow oil. R_F 0.22 (8.5:1.5 pentane and CH_2Cl_2 eluent); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (t, *J* = 1.9 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.61 (dt, *J* = 8.0, 1.3 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 4.93 (s, 1H), 4.90 (br s, 1H), 3.62 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 149.0, 143.8, 141.0, 135.0, 129.5, 123.6, 120.9, 115.2, 41.3, 21.2; IR (film): ν = 2900, 2923, 1529, 1347, 1262, 1093, 800 cm^{-1}**;** HRMS(MALDI-TOF): cald. ($C_{10}H_{11}NO_2$+Na) 200.0687; found 200.0645.

4′′-methyl-3-nitro-1,1′:4,1′′-terphenyl (Scheme 2, Compound No 17): In a round bottom flask dried under *vacuum* were placed under nitrogen atmosphere, the corresponding Bromo benzenesulfonyl chloride (1.00 mmol), $Pd(PPh_3)_4$ (0.08

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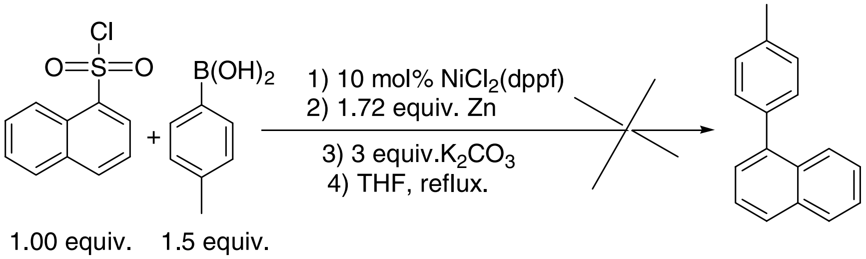
[20] Robison, G.E.; Thomas, C.B.; Vernon, J.M. *J. Chem. Soc*, B; **1971**, 1273-1282.

mmol), K_2CO_3 (3 mmol) and the 4-methylbenzene boronic acid (1 mmol) were weighed in a glove box. Then, flask connected to a *vacuum* line and filled with an argon (3 times), and THF (5 mL) was added under argon. The reaction mixture was stirred at reflux for 20 h. Then addition of 3-nitrobenzene boronic acid (2 mmol) and $Pd(PPh_3)_4$ (0.08 mmol) and K_2CO_3(3 mmol) were added under nitrogen. The reaction mixture was stirred at reflux for 20 h. After cooling to room temperature, the mixture was diluted with ether and washed with water. The aqueous layer was extracted again with ether (3 times). The combined organic phases were dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by flash chromatography.

The product is obtained (57% yield) as a light yellow solid. M.p: 164.5-165.5; R_F 0.26 (7.5:2.5 pentane and CH_2Cl_2 eluent); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (t, *J* = 1.9 Hz, 1H), 8.22 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.97 (dt, *J* = 8.0, 1.3 Hz, 1H), 7.72 (br s, 4H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 149.1, 142.7, 141.6, 137.8, 137.5, 137.3, 133.0, 129.9, 129.8, 127.8, 127.6, 127.1, 122.2, 121.9, 21.3; IR (KBr): ν = 1527, 1450, 1350, 805 cm^{-1}; HRMS(MALDI-TOF): cald. ($C_{19}H_{15}NO_2$+Na) 312.1000; found 312.1012.

Without success of Nickel-Catalyzed Suzuki-Miyaura Cross-coupling:



In a round bottom flask dried under *vacuum* were placed under nitrogen atmosphere, the corresponding sulfonyl chloride (1.00 mmol), $NiCl_2$(dppf) (0.10 mmol), K_2CO_3 (3 mmol) and the boronic acid (1.5 mmol) were weighed in a glove box. Then, flask connected to a *vacuum* line and filled with an argon (3 times), and THF (5 mL) was added under an argon. The reaction mixture was stirred at reflux for 30 h. After cooling to room temperature, the mixture was diluted with ether and washed with water. The aqueous layer was extracted again with ether (3 times). The combined organic phases were dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by flash chromatography. The formation of cross-coupling product was not observed, but where as homo-coupling product of boronic acid was isolted in 12% yield.