***Supporting Information for :***

# Metal-Catalyzed Release of Solid Supported Arylboronic Acids for C-C Bond Formation

**Christelle Pourbaix, François Carreaux,* Bertrand Carboni***

*Université Rennes 1, Synthèse et Electrosynthèse organiques, UMR 6510 associée au CNRS, Campus de Beaulieu, 35042 Rennes Cedex, France*

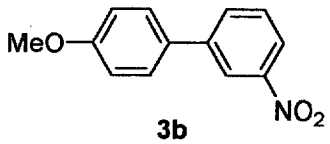
## Experimental Section

**General Procedures**. Reactions were performed in oven-dried glassware under an argon atmosphere. Tetrahydrofuran (THF) was distilled from deep blue solutions of sodium/benzophenone ketyl prior to use. All boronic acids were purchased (Lancaster Synthesis Ltd) except 1-hexenylboronic acid.[1] Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ on a 200- or 300-MHz spectrometer operating in the Fourier transform mode. $^{13}$C-NMR spectra were obtained with broadband proton decoupling. Chemical shifts were recorded relative to the internal TMS (tetramethylsilane) reference signal. HRMS were performed by Centre Régional de Mesures Physiques de l'Ouest. Microanalysis were done at the Central Laboratory for Analysis, CNRS, Lyon, (France). Silica gel 60F254 was used for column chromatography.

### General procedure for the Suzuki coupling

The supported arylboronic acid (0.4 mmol) was suspended in DMF (8 mL). Aryl halide (2 mmol), $PdCl_2$(dppf) (0.02 mmol) and a solution of $K_3PO_4$ (2M, 1.2 mmol) were added. The mixture is degassed and then heated at 60°C under argon for 24h. After cooling to rt, the resin was filtered, washed with DMF (2×5 mL), $CH_2Cl_2$ (3×5 mL) and THF (3×5 mL). The filtrate was partially concentrated, diluted with EtOAc (10 mL) and washed with water (10 mL). The aqueous layer was extracted with EtOAc (3×10 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatography on silica (EtOAc/Heptane) then afforded the desired product.

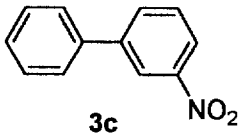
### 4'-Methoxy-3-nitrobiphenyl (3b)




**3b**

**3b** was isolated as a yellow solid (60%); mp = 79-81°C; $^1$H NMR ($CDCl_3$, 200 MHz) δ 8.39 (1H, dd, $J$ = 2.3, 2.0 Hz), 8.13 (1H, ddd, $J$ = 8.1, 2,3, 1.0 Hz), 7.86 (1H, ddd, $J$ = 7.8, 2,0, 1.0 Hz), 7.61-7.51 (3H, m), 7.00 (2H, m), 3.86 (3H, s); $^{13}$C RMN ($CDCl_3$, 50 MHz) δ 160.1, 148.7, 142.4, 132.5, 131.0, 129.6, 128.3, 121.3, 114.6, 55.4; HRMS (EI) for $C_{13}H_{11}O_3N$ ($M^+$) calcd. 229.0739, found 229.0729.

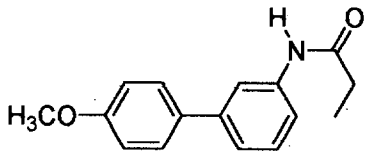
**3-Nitrobiphenyl (3c)**




**3c**

**3c** was isolated as a yellow solid (75%); mp = 60-61°C [lit.[2] mp = 58.5-59.5]; $^1$H NMR ($CDCl_3$, 200 MHz) δ 8.42 (1H, d, $J$ = 2.3, 2.0 Hz), 8.17 (1H, ddd, $J$ = 8.1, 2.3, 1.0 Hz), 7.88 (1H, ddd, $J$ = 7.8, 1.8, 1.0 Hz), 7,68-7.55 (6H, m); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 148.8, 142.9, 138.6, 133.0, 129,7, 129.2, 128.5, 127.1, 122.0, 121.9.

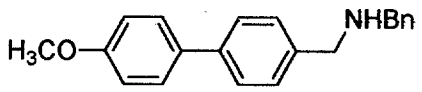
***N*-(4'-methoxybiphenyl-3-yl)-propionamide (3d)**




**3d**

**3d** was isolated as a beige solid (75%); mp = 123-126°C; $^1$H NMR ($CDCl_3$, 200 MHz) δ 7.83-7.75 (2H, m), 7.56-7.22 (5H, m), 6.92 (2H, d, $J$ = 8.8Hz), 3.81 (3H, s), 2.39 (2H, q, $J$ = 7.6Hz), 1.23 (3H, t, $J$ = 7.6Hz); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 172.4, 159.2, 141.6, 138.5, 133.2, 129.3, 128.7, 127.1, 122.5, 118.2, 114.1, 55.3, 30.7, 9.7; HRMS (EI) for $C_{16}H_{17}O_2N$ ($M^+$) calcd. 255.1259, found 255.1253.

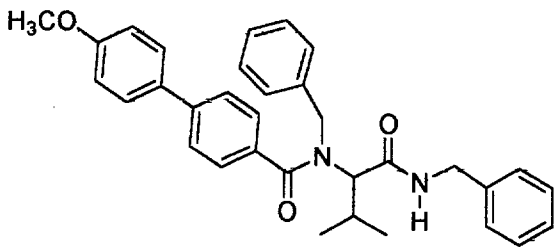
***N*-(4'-methoxybiphenyl-4-yl-methyl)-benzylamine (3e)**




**3e**

**3e** was isolated as a beige solid (53%); mp = 57°C; $^1$H NMR ($CDCl_3$, 200 MHz) δ 7.60-7.24 (11H, m), 6.97 (2H, d, $J$ = 8.8Hz), 3.84-3.81 (7H, s), 1.99 (1H, brs); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 159.1, 140.2, 139.5, 138.6, 133.5, 128.6, 128.4, 128.2, 128.0, 127.0, 126.7, 114.2, 55.3, 53.1, 52.8; HRMS (EI) for $C_{21}H_{21}ON$ ($M^+$) calcd. 303.1623, found 303.1620.

***N*-(1-benzylcarbamoyl-2-methyl-propyl)-*N*-benzyl-(4'-methoxybiphenyl-4-yl)carboxamide (3f)**




**3f**

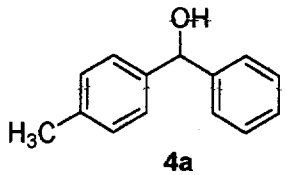
**3f** was isolated as a yellow oil (45%); $^1$H NMR ($CDCl_3$, 200 MHz) δ 7.76 (1H, brs), 7.51 (4H, m), 7.37-7.27 (7H, m), 7.11-7.21 (3H, m), 7.00-6.95 (4H, m), 4.64-4.55 (2H, m), 4.42-4.15 (3H, m), 3.86 (3H, s), 2.87-2.77 (1H, m), 1.07-1.04 (6H, m); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 174.2, 170.4, 159.7, 142.4, 138.5, 132.6, 128.7, 127.4, 126.7, 114.4, 68.5, 55.4, 53.0, 43.3, 27.1, 20.1, 19.5; HRMS (EI) for $C_{33}H_{34}O_3N_2$ ($M^+$) calcd. 506.2569, found 506.2572.

**General Procedure for the Rhodium-Catalyzed Addition of supported boronic acids to Aldehydes**

A suspension of the aldehyde (0.3 mmol), supported boronic acid (0.3 mmol), [Rh(acac)$(CO)_2$] (0.009 mmol) and dppf (0.009 mmol) in a 5 :1 mixture of DME/$H_2O$ (6 mL) was heated at 80°C for 24h. The resin was filtered off and washed with 5 mL each of $CH_2Cl_2$ (3 x), THF (3 x). The layers were separated and the aqueous layer extracted with EtOAc (3 x 5 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated. To the

resulting solid was added toluene (6 mL), PTSA (0.01 eq.) and resin **1** (0.3 mmol). The mixture was heated at reflux for 24h. The reaction mixture was cooled and subjected to filtration (fritted glass funnel). The resin was successively washed with toluene (10 mL), $CH_2Cl_2$ (10 mL), THF (10 mL). The combined liquid phases were concentrated and the resulting solid was extracted with $CH_2Cl_2$. After filtration through silica and concentration, the corresponding benzyl alcohol was obtained which was shown to be >95% pure by GC.

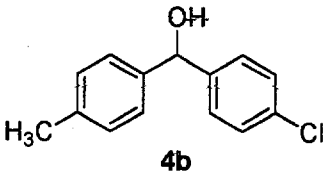
**(4-Methylphenyl)phenylmethanol (4a)**




**4a**

**4a** was isolated as a colourless solid (62%); mp = 52°C [lit.[3] mp = 52-53°C]; $^1$H NMR ($CDCl_3$, 200MHz) δ 7.37-7.10 (9H, m), 5,76 (1H, s), 2.31 (3H, s); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 144.0, 141.0, 137.3, 129.2, 128.5, 127.5, 126.6, 126.5, 76.1, 21.2; HRMS (EI) for $C_{14}H_{14}O$ ($M^+$) calcd. 198.1045, found 198.1043.

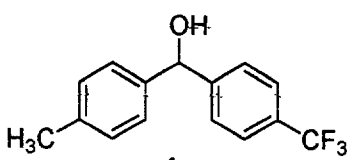
**(4-Chlorophenyl)(4-methylphenyl)methanol (4b)**




**4b**

**4b** was isolated as a colourless solid (43%); mp = 73-74°C [lit.[4] mp = 74-74.2°C]; $^1$H NMR ($CDCl_3$, 200MHz) δ 7.30-7.14 (8H, m), 5,78 (1H, s), 2.33 (3H, s), 2.23 (1H, brs); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 142.4, 140.7, 137.7, 129.4, 128.6, 127.9, 126.6, 75.5, 21.2; HRMS (EI) for $C_{14}H_{13}OCl$ ($M^+$) calcd. 232.0655, found 232.0643.

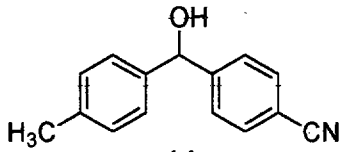
**(4-Methylphenyl)(4-trifluoromethyl)methanol (4c)**




**4c**

**4c** was isolated as a colourless solid (63%); mp = 85-86°C [lit.[5] mp = 88-90]; $^1$H NMR ($CDCl_3$, 200MHz) δ 7.60-7.30 (4H, m), 7.20-7.00 (4H, m), 5,83 (1H, s), 2.87 (1H, brs), 2.33 (3H, s) ; $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 147.8, 140.4, 138.0, 129.5, 129.3, 126.7, 126.6, 125.4, 125.3, 121.5, 75.6, 21.2; HRMS (EI) for $C_{15}H_{13}OF_3$ ($M^+$) calcd. 266.0918, found 266.0927.

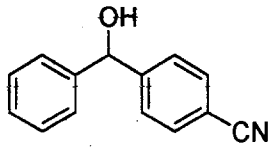
**(4-Cyanophenyl)(4-methylphenyl)methanol (4d)**




**4d**

**4d** was isolated as a clear, colourless oil (81%); $^1$H NMR ($CDCl_3$, 200MHz) δ 7.60 (2H, d, $J$ = 8.3 Hz), 7.50 (2H, d, $J$ = 7.8 Hz), 7.21-7.11 (4H, m), 5,82 (1H, s), 2.46 (1H, brs), 2.33 (3H, s); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 142.4, 140.7, 137.7, 132.3, 129.6, 127.0, 126.7, 118.9, 111.1, 75.5, 21.2; HRMS (EI) for $C_{15}H_{13}NO$ ($M^+$) calcd. 223.0997, found 223.0994.

**(4-Cyanophenyl)phenylmethanol (4e)**




**4e**

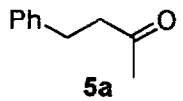
**4e**[6] was isolated as a clear, colourless oil (56%); $^1$H NMR ($CDCl_3$, 200MHz) δ 7.58 (2H, d, $J$ = 8.3 Hz), 7.51 (2H, d, $J$ = 8.1Hz), 7.38-7.31 (5H, m), 5,86 (1H, s), 2.64 (1H, brs); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 148.9, 142.9, 132.3, 128.9, 128.3, 127.1, 126.7, 118.9, 111.2, 75.7; HRMS (EI) for $C_{14}H_{11}NO$ ($M^+$) calcd. 209.0841, found 209.0854.

**General procedure for the rhodium-catalyzed addition of supported boronic acids to enones**

A suspension of the supported boronic acid (0.3 mmol), $Rh(CO)_2(acac)$ (0.01 mmol), and $P(Ph)_3$ (0.02 mmol) in 7:6:1 mixture of THF/MeOH/$H_2O$ (14 mL) was shaken for 15 min at rt. Methyl vinyl ketone (1.5 mmol) was then added and the reaction mixture heated at 50°C for 24h. After cooling to rt, the resin was filtered, washed with THF (3×5 mL) and $CH_2Cl_2$

(3×5 mL). The layers were separated and the aqueous layer extracted with $CH_2Cl_2$ (3 x 5 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The NMR of the crude product indicates the presence of triphenylphosphine oxide (10-30%). Silica gel chromatography (EtOAc/Heptane) then afforded the desired product.

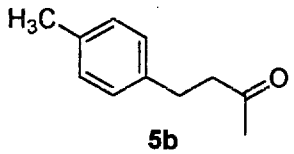
**4-phenylbutan-2-one (5a)**




**5a**

**5a**[6] was isolated as a clear, colourless oil (60%); $^1$H NMR ($CDCl_3$, 200MHz) δ 7.32-7.16 (5H, m), 2.90 (2H, m), 2.76 (2H, m), 2.14 (3H, s); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 207.7, 141.5, 128.6, 128.4, 126.2, 45.3, 30.2, 29.8.

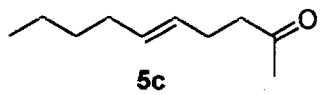
**4-(4-Methylphenyl)butan-2-one (5b)**




**5b**

**5b** was isolated as a clear, colourless oil (47%); $^1$H NMR ($CDCl_3$, 200MHz) δ 7.12-7.07 (4H, m), 2.88 (2H, m), 2.70 (2H, m), 2.31 (3H, s), 2.13 (3H, s); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 207.1, 137.9, 135.7, 129.3, 128.2, 45.4, 30.1, 29.4, 21.1; HRMS (EI) for $C_{11}H_{14}O$ ($M^+$) calcd. 162.1045, found 162.1049.

**(E)-Dec-5-en-2-one (5c)**




**5c**

**5c**[6] was isolated as a clear, colourless oil (55%); $^1$H NMR ($CDCl_3$, 200MHz) δ 5.45-5.25 (2H, m), 2.40 (2H, m), 2.19 (2H, q, $J$ = 7.0 Hz), 2.07 (3H, s), 1.97-1.84 (2H, m), 1.30-1.18 (4H, m), 0.82 (3H, t, $J$ = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 208.2, 131.4, 128.0, 43.4, 32.0, 31.5, 29.7, 26.7, 22.0, 13.7.

(1) Brown, H. C.; Campbell, J. B. *J. Org. Chem.* **1980**, *45*, 389-395.

(2) Kaslow, C. E.; Summers, R. M. *Org. Synth. Coll.*, vol. 6, 718-721 (1963).

(3) Tietz, R. F.; Mc Even, W. E. *J. Am. Chem. Soc.* **1955**, *77*, 4007-4011.

(4) Nishida, S. *J. Org. Chem.* **1967**, 2695-2697.

(5) Kelly, D. P.; Jenkins, M. J. *J. Org. Chem.* **1984**, *49*, 409-413.

(6) Batey, R. A. ; Thadani, A. N. ; Smil, D. V. *Org. Lett.* **1999**, *1*, 1683-1686.