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Electronic Supplementary Information

~ Experimental Procedures and Spectral/Analytical Data ~

Use of Dimethyl Carbonate as a Solvent Greatly Enhances the Biaryl Coupling of Aryl Iodides and Organoboron Reagents without Adding Any Transition Metal Catalysts

Kiyofumi Inamoto,* Chisa Hasegawa, Kou Hiroya, Yoshinori Kondo, Takao Osako, Yasuhiro Uozumi and Takayuki Doi*

Graduate School of Pharmaceutical Sciences, Tohoku University
6-3, Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan

inamoto@mail.pharm.tohoku.ac.jp, doi_taka@mail.pharm.tohoku.ac.jp

General Comments

All reactions were carried out under an Ar atmosphere unless otherwise noted. Anhydrous dimethyl carbonate (DMC) was purchased from Aldrich (catalogue # : 517217) and used as received. Inorganic bases including K_3PO_4 (Junsei Chemical, catalogue # : 84080-1201) was dried *in vacuo* while heating prior to use. All other commercially available materials, including aryl iodides (4-iodobenzonitrile; purchased from TCI, catalogue # : I0661) and boronic acids (phenylboronic acid; purchased from TCI, catalogue # : B0857), were used as received. All glassware employed for the reactions was thoroughly cleaned with aqua regia prior to use.

Melting points were measured with a Yazawa micro melting point apparatus and uncorrected. IR spectra were recorded on a SHIMADZU FTIR-8400. ^{1}H-NMR spectra were recorded on a JEOL JNM-AL400 (400 MHz) spectrometer. Chemical shifts (δ) are given from TMS (0 ppm) in $CDCl_3$ and coupling constants are expressed in herts (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, sext = sextet, m = multiplet. ^{13}C-NMR spectra were recorded on a JEOL JNM-AL400 (100 MHz) spectrometer and chemical shifts (δ) are given from $^{13}CDCl_3$ (77.0 ppm). Mass spectra and high resolution mass spectra were measured on a JEOL JMS-DX303, JMS-700 or JMS-T 100GC instrument. Inductively coupled plasma-mass spectrometry (ICP-MS) was performed with a Agilent HP-4500 instrument at Technical Division of School of Engineering, Tohoku University.

Typical Procedure for Coupling Reaction of Aryl Iodides (1) with Boronic Acids (2) (Table 1, Entry 1)

A mixture of 4-iodobenzonitrile **1a** (60.0 mg, 0.26 mmol), $PhB(OH)_2$ **2a** (38.3 mg, 0.31 mmol) and K_3PO_4 (66.7 mg, 0.31 mmol) in DMC (2.6 mL, 0.1 M) was heated in a sealed tube at 135 °C for 12 h. The solvent was evaporated and the residue was purified by silica gel column chromatography using hexane-AcOEt (9 : 1) as an eluent to give the coupling product **3aa** as a colorless solid.

4-Cyanobiphenyl (3aa)

Mp 85–86 ºC (lit.1) mp 85–86 ºC); IR ν (film, cm^{-1}) 2226, 1606, 1484, 769; ^1H-NMR (400 MHz, $CDCl_3$) δ 7.42 (1H, t, *J* = 7.1 Hz), 7.48 (2H, t, *J* = 7.1 Hz), 7.58 (2H, d, *J* = 7.1 Hz), 7.67 (2H, d, *J* = 8.4 Hz), 7.71 (2H, d, *J* = 8.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 110.8, 118.9, 127.2, 127.7, 128.6, 129.1, 132.5, 139.1, 145.6; MS *m/z* (relative intensity) 179 (M^+, 100); HRMS calcd for $C_{13}H_9N$ 179.0735, found 179.0722.

4,4’-Dicyanobiphenyl (3ab)

Mp 242–243 ºC (colorless prisms from hexane-AcOEt, lit.2) mp 226–228 ºC); IR ν (film, cm^{-1}) 2227, 817; ^1H-NMR (400 MHz, $CDCl_3$) δ 7.71 (4H, d, *J* = 8.2 Hz), 7.79 (4H, d, *J* = 8.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 111.2, 118.4, 127.9, 132.8, 143.4; MS *m/z* (relative intensity) 204 (M^+, 100); HRMS calcd for $C_{14}H_8N_2$ 204.0688, found 204.0690.

4-Cyano-4’-methoxybiphenyl (3ac)

Mp 101–102 ºC (colorless prisms from hexane-AcOEt, lit.1) mp 101–102 ºC); IR ν (film, cm^{-1}) 2224, 1495, 882; ^1H-NMR (400 MHz, $CDCl_3$) δ 3.86 (3H, s), 7.00 (2H, d, *J* = 8.8 Hz), 7.53 (2H, d, *J* = 8.8 Hz), 7.63 (2H, d, *J* = 8.8 Hz), 7.68 (2H, d, *J* = 8.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.3, 109.9, 114.4, 119.0, 127.0 128.2, 131.3, 132.4, 145.1, 160.1; MS *m/z* (relative intensity) 209 (M^+, 100); HRMS calcd for $C_{14}H_{11}NO$ 209.0841, found 209.0834.

4-Cyano-3’-methylbiphenyl (3ad)

Colorless oil; IR ν (film, cm^{-1}) 2226, 1606, 784; ^1H-NMR (400 MHz, $CDCl_3$) δ 2.43 (3H, s), 7.23 (1H, s), 7.34–7.40 (3H, m), 7.66 (2H, d, *J* = 8.4 Hz), 7.70 (2H, d, *J* = 8.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.4, 110.6, 118.9, 124.2, 127.6, 127.8, 128.9, 129.3, 132.4, 138.7, 139.0, 145.7; MS *m/z* (relative intensity) 193 (M^+, 100); HRMS calcd for $C_{14}H_{11}N$ 193.0892, found 193.0879.

4-Cyano-2’-methoxybiphenyl (3ae)

Pale yellow oil; IR ν (film, cm^{-1}) 2226, 1486, 754; ^1H-NMR (400 MHz, $CDCl_3$) δ 3.82 (3H, s), 7.00 (1H, d, *J* = 7.8 Hz), 7.05 (1H, t, *J* = 7.8 Hz), 7.29 (1H, d, *J* = 7.8 Hz), 7.38 (1H, t, *J* = 7.8 Hz), 7.63 (2H, d, *J* = 8.0 Hz), 7.67 (2H, d, *J* = 8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.4, 110.3, 111.3, 119.0, 120.9, 128.5, 129.8, 130.1, 130.5, 131.6, 143.3, 156.2; MS *m/z* (relative intensity) 209 (M^+, 100); HRMS calcd for $C_{14}H_{11}NO$ 209.0841, found 209.0834.

4-Cyano-2'-methylbiphenyl (3af)

Mp 54–56 ºC (colorless prisms from hexane-AcOEt, lit.[1)] mp 54–56 ºC); IR ν (film, cm^{-1}) 2226, 1609; ^{1}H-NMR (400 MHz, $CDCl_3$) 2.25 (3H, s), 7.18 (1H, d, *J* = 7.2 Hz), 7.25–7.33 (3H, m), 7.43 (2H, d, *J* = 7.6 Hz), 7.70 (2H, d, *J* = 7.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 20.4, 110.7, 118.9, 126.0, 128.2, 129.3, 129.9, 130.6, 131.9, 134.9, 139.9, 146.7; MS *m/z* (relative intensity) 193 (M^+, 100); HRMS calcd for $C_{14}H_{11}N$ 193.0892, found: 193.0904.

4-[(*E*)-Pent-1-enyl]benzonitrile (3ag)

Colorless oil; IR ν (film, cm^{-1}) 2960, 2225, 1604, 967; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.96 (3H, t, *J* = 7.3 Hz), 1.51 (2H, sext, *J* = 7.3 Hz), 2.21–2.23 (2H, m), 6.36–6.39 (2H, m), 7.40 (2H, d, *J* = 8.2 Hz), 7.56 (2H, d, *J* = 8.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.6, 22.1, 35.0, 109.8, 119.0, 126.3, 128.5, 132.2, 135.2, 142.3; MS *m/z* (relative intensity) 171 (M^+, 58), 129 (100); HRMS calcd for $C_{12}H_{13}N$ 171.1048, found 171.1033.

4-Nitrobiphenyl (3ba)

Mp 110–111 ºC (pale orange prisms from hexane-AcOEt, lit.[3)] mp 113–115 ºC); IR ν (film, cm^{-1}) 1512, 1339; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.44 (1H, t, *J* = 7.1 Hz), 7.49 (2H, t, *J* = 7.1 Hz), 7.62 (2H, d, *J* = 7.1 Hz), 7.72 (2H, d, *J* = 9.0 Hz), 8.28 (2H, d, *J* = 9.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 124.0, 127.3, 127.7, 128.9, 129.1, 138.6, 147.0, 147.5; MS *m/z* (relative intensity) 199 (M^+, 100); HRMS calcd for $C_{12}H_9NO_2$ 199.0633, found 199.0621.

4-Acetylbiphenyl (3ca)

Mp 119–120.5 ºC (pale yellow prisms from hexane-AcOEt, lit.[1)] mp 121–122 ºC); IR ν (film, cm^{-1}) 1682, 765; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.63 (3H, s), 7.39 (1H, t, *J* = 7.4 Hz), 7.47 (2H, t, *J* = 7.4 Hz), 7.62 (2H, d, *J* = 7.4 Hz), 7.68 (2H, d, *J* = 8.2 Hz), 8.03 (2H, d, *J* = 8.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.6, 127.16, 127.21, 128.2, 128.86, 128.90, 135.8, 139.8, 145.7, 197.7; MS *m/z* (relative intensity) 196 (M^+, 46), 181 (100); HRMS calcd for $C_{14}H_{12}O$ 196.0888, found 196.0880.

4-Methoxycarbonylbiphenyl (3da)

Mp 117–119 ºC (colorless prisms from hexane-AcOEt, lit.[3)] mp 115–117 ºC); IR ν (film, cm^{-1}) 1720, 1290, 1115, 749; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.93 (3H, s), 7.38 (1H, t, *J* = 7.2 Hz), 7.45 (2H, t, *J* = 7.2 Hz), 7.61 (2H, d, *J* = 7.2 Hz), 7.64 (2H, d, *J* = 8.6 Hz), 8.10 (2H, d, *J* = 8.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 52.0, 127.0, 127.2, 128.1, 128.9 (two carbons), 130.1, 139.9, 145.6, 166.9; MS *m/z* (relative intensity) 212 (M^+, 93) 181 (100); HRMS calcd for $C_{14}H_{12}O_2$ 212.0837, found 212.0832.

4-Methoxybiphenyl (3ea)

Mp 86–87 ºC (colorless prisms from hexane-AcOEt, lit.1) mp 86–87 ºC); IR ν (film, cm^{-1}) 1036, 834, 761, 689; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.82 (3H, s), 6.96 (2H, d, *J* = 8.4 Hz), 7.28 (1H, t, *J* = 7.5 Hz), 7.40 (2H, t, *J* = 7.5 Hz), 7.50–7.55 (4H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.3, 114.2, 126.6, 126.7, 128.1, 128.7, 133.7, 140.8, 159.1; MS *m/z* (relative intensity) 184 (M^+, 100); HRMS calcd for $C_{13}H_{12}O$ 184.0888, found 184.0891.

4-Methylbiphenyl (3fa)

Pale yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.37 (3H, s), 7.22 (2H, d, *J* = 8.0 Hz), 7.29 (1H, t, *J* = 7.5 Hz), 7.40 (2H, t, *J* = 7.5 Hz), 7.47 (2H, d, *J* = 8.0 Hz), 7.56 (2H, d, *J* = 7.5 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.1, 126.92, 126.92, 126.95, 128.7, 129.4, 136.9, 138.3, 141.1; MS *m/z* (relative intensity) 168 (M^+, 100); HRMS calcd for $C_{13}H_{12}$ 168.0939, found 168.0921.

Biphenyl (3ga)

Colorless solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.34 (2H, t, *J* = 7.3 Hz), δ 7.43 (4H, t, *J* = 7.3 Hz), δ 7.59 (4H, d, *J* = 7.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 127.1, 127.2, 128.7, 141.2; MS *m/z* (relative intensity) 154 (M^+, 100); HRMS calcd for $C_{12}H_{10}$ 154.0783, found 154.0771.

2-Methoxybiphenyl (3ha)

Colorless oil; IR ν (film, cm^{-1}) 1483, 1430, 1259, 1236, 753, 693; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.79, (3H, s), 6.98 (1H, d, *J* = 8.1 Hz), 7.02 (1H, t, *J* = 8.1 Hz), 7.29–7.33 (3H, m), 7.40 (2H, t, *J* = 8.0 Hz), 7.53 (2H, d, *J* = 8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.5, 111.2, 120.8, 126.9, 127.9, 128.6, 129.5, 130.7, 130.9, 138.5, 156.4; MS *m/z* (relative intensity) 184 (M^+, 100); HRMS calcd for $C_{13}H_{12}O$ 184.0888, found 184.0870.

2-Methylbiphenyl (3ia)

Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.27 (3H, s), 7.21–7.26 (4H, m), 7.30–7.35 (3H, m), 7.38–7.42 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 20.5, 125.7, 126.7, 127.2, 128.0, 129.2, 129.8, 130.3, 135.3, 141.92, 141.94; MS *m/z* (relative intensity) 168 (M^+, 100); HRMS calcd for $C_{13}H_{12}$ 168.0939, found 168.0927.

References

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2) Q. Wu and L. Wang, *Synthesis*, 2008, 2007.

3) S.-D. Cho, H.-K., Kim, H.-S., Yim, M.-R., Kim, J.-K., Lee, J.-J., Kim and Y.-J., Yoon, *Tetrahedron*, 2007, **47**, 1345.

Results of ICP-MS

Quantitative elemental analyses of commercially available reagents (4-iodobenzonitrile, phenylboronic acid, tripotassium phosphate, and DMC), as well as the reaction mixture after the reaction is finished, were carried out for the detection of transition metals such as Fe, Ni, Cu, Ru, Rh, Pd, and Pt. The results are shown in the table below. All values are expressed in ppb (ng / g).

Preparation of samples

$NC–C_6H_4–I$: 6.26 mg of $NC–C_6H_4–I$ was heated at 125–145 ºC in nitric acid (2 mL) for 2 days and diluted with ultra pure water (total amount = 25 mL).

$NC–C_6H_4–I$ (for analysis of Fe): 32.69 mg of $NC–C_6H_4–I$ in nitric acid (1 mL), hydrochloric acid (3 mL), and hydrofluoric acid (1 mL) was irradiated with microwave and the residue was filtered. The filtrate was diluted with ultra pure water (total amount = 25 mL).

$PhB(OH)_2$, K_3PO_4: 6.41 mg of $PhB(OH)_2$, 6.02 mg of K_3PO_4, or 30.30 mg of K_3PO_4 (for analysis of Fe) was heated at 115 ºC in nitric acid (1 mL) for 3 hours and diluted with ultra pure water (total amount = 25 mL).

DMC: 1.08 g of DMC was heated at 80–90 ºC to be exsiccated. The residue was diluted with nitric acid (1 mL) and ultra pure water (total amount = 25 mL).

Reaction Mixture: After the completion of the reaction, DMC was evaporated. 47.87 mg of the residue in nitric acid (15 mL) and hydrogen peroxide solution (3 mL) was irradiated with microwave and then filtered. The filtrate was diluted with ultra pure water (total amount = 50 mL).

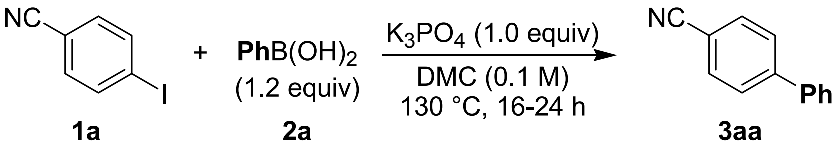
Element	$NC–C_6H_4–I$	$PhB(OH)_2$	K_3PO_4	DMC	Reaction Mixture
Fe	84.63	17.14	ND	ND	88.45
Ni	0.54	0.21	1.14	ND	3.51
Cu	0.62	2.24	1.34	1.24	2.77
Ru	0.55	0.34	0.13	0.09	0.08
Rh	ND	ND	ND	ND	0.04[a]
Pd	0.06[a]	ND	ND	0.44	0.42
Pt	ND	ND	ND	ND	0.03[a]

unit : ppb

detection limit (ppb) : Fe; 10.24, Ni; 0.06, Cu; 0.25, Ru; 0.05, Rh; 0.05, Pd; 0.10, Pt; 0.06

[a] A value below the detection limit.

Reactions Using Reagents from Various Suppliers



Entry	(4-I)C_6H_4CN	$PhB(OH)_2$	K_3PO_4	Yield (%)
1	TCI	TCI	Junsei	88
2	Aldrich	TCI	Junsei	80
3	TCI	Aldrich	Junsei	93
4	TCI	Wako	Junsei	90
5	TCI	TCI	Wako	76