

Electronic Supplementary Information

Suzuki-Miyaura Cross Coupling Reaction from a Low-Leaching and Highly Recyclable Gold-Supported Palladium Material and Two Types of Microwave Equipment

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General

¹H-NMR spectra were recorded in CDCl₃ at 25 °C unless otherwise noted, at 400 or 500 MHz, with TMS as an internal standard. ¹³C-NMR spectra were recorded in CDCl₃ at 25 °C unless otherwise noted, at 100 or 125 MHz. Mass spectra were obtained using a JEOL JMS-700TZ. ICP-mass spectra were obtained on an AGILRNT ICP-MS 7500CS. HPLC was carried out using a Mighysil RP-18 (Kanto Chemical Co. Inc) and HPLC spectra were detected by a Shimadzu SPD-10AV (254 nm) and recorded by a Shimadzu CR-8A. Column chromatography were performed with silica gel 60N (spherical, neutral, 63-210 mm, Kanto Chemical Co., Inc.) unless otherwise stated. Microwave instrument were performed with EYELA MWO-1000S and EYELA NWS-1000 for single-mode and multi-mode, respectively.

Preparation of Sulfur-modified Au-supported Pd material SAPd

To a stirring ice cooled 98% H₂SO₄ (4.7 g) was added Na₂S₂O₈ (4.0 g) in a small portions and then the crushed ice (13.0 g) and water (4.0 g) were added to the above solution while the temperature was kept below 15 °C. When all the salt dissolved to a homogeneous solution, the Au (100 mesh-14 × 12 mm², 100.7 mg) was placed in the above solution (3.0 mL) for 5 min and then washed first by H₂O (3.0 mL × 10) and then with EtOH (3.0 mL × 6). The resulted Au-mesh was placed in a round bottom flask and dried for 10 min under reduced pressure (*ca.* 6 mm Hg). The resulting sulfur-modified Au was placed in a solution of Pd(OAc)₂ (5.3 mg, 0.023 mmol) in xylene (3.0 mL) and stirred at 100 °C for 12 h under the Ar atmosphere. Then it was rinsed with xylene (3.0 mL × 50) and, after vacuum drying, it was placed in xylene (3.0 mL) and heated at 135 °C for 12 h. Finally, it was rinsed with xylene (3.0 mL × 50) and dried under vacuum for 10 min to give sulfur-modified Au-supported Pd material SAPd (100.8 mg, immobilized Pd: 57 ± 16 μg) and only this SAPd was used throughout this research.

Typical experimental procedure of microwave assisted flowing for Suzuki-Miyaura coupling using iodobenzene **1a** catalyzed by SAPd;

To a reaction tube (suitable for microwave), iodobenzene (**1a**, 102.0 mg, 0.50 mmol), SAPd and EtOH (2.0 mL) were added and then the tube was fixed in the single-mode microwave chamber. The tube was irradiated in a single-mode microwave conditions, MW (S): temp: 80 °C, time: 60 min, power: 200 W and after completing the irradiation, the SAPd was removed from the tube, washed with xylene (6 × 3.0 mL) and kept for next cycle. The irradiated solution was transferred to reaction vessel, which was previously charged with 4-chlorophenylboronic acid (**2a**, 117.3 mg, 0.75 mmol) and K₂CO₃ (138.2 mg, 1.0 mmol). The SAPd containing tube was washed with EtOH (2 × 1 mL) and the washing solvents were also poured into the above reaction vessel. The resulting reaction vessel was then irradiated in

a multi-mode microwave conditions, MW (M): temp: 82 °C, time: 60 min, power: 500 W. The reaction mixture was then cooled to room temperature and was poured into water (10.0 mL) and the organic layer was extracted with AcOEt (3×20 mL). The combined organic extracts were washed with brine (3×25 mL) and dried over Na₂SO₄. Concentration at reduced pressure gave yellowish oil, which was chromatographed on silicagel with hexane–AcOEt (98:2 v/v) as eluent to give the 4-chlorobiphenyl (**3a**, 93.6 mg, 99%) as a white solid. The above reaction condition was maintained as for 2nd cycle and this procedure was repeated for a total 10 cycles.

Typical experimental procedure of microwave assisted flowing for Suzuki-Miyaura coupling using bromobenzene 1b catalyzed by SAPd;

To a reaction tube (suitable for microwave), bromobenzene (**1b**, 78.5 mg, 0.50 mmol), SAPd and DMF (2.0 mL) were added and then the tube was fixed in the single-mode microwave chamber. The tube was irradiated in a single-mode microwave conditions, MW (S): temp: 90 °C, time: 50 min, power: 300 W and after completing the irradiation, the SAPd was removed from the tube, washed with xylene (6 × 3.0 mL) and kept for next cycle. The irradiated solution was transferred to reaction vessel, which was previously charged with 4-chlorophenylboronic acid (**2a**, 117.3 mg, 0.75 mmol) and K₂CO₃ (138.2 mg, 1.0 mmol). The SAPd containing tube was washed with toluene (2 × 1 mL) and the washing solvents along with H₂O (1.0 mL) were poured into the above reaction vessel. The resulting reaction vessel was then irradiated in a multi-mode microwave conditions, MW (M): temp: 104 °C, time: 60 min, power: 500 W. The reaction mixture was then cooled to room temperature and was poured into water (10.0 mL) and the organic layer was extracted with AcOEt (3 × 20.0 mL). The combined organic extracts were washed with brine (3 × 25.0 mL) and dried over Na₂SO₄. Concentration at reduced pressure gave yellowish oil, which was chromatographed on silicagel with hexane–AcOEt (98:2 v/v) as eluent to give the 4-chlorobiphenyl (**3a**, 93.8 mg, 99%) as a white solid. The above reaction condition was maintained as for 2nd cycle and this procedure was repeated for a total 10 cycles.

Table S1. Amount of Pd in the reaction mixtures of **1a** with **2a**^a, **1b** with **2a**^b and on SAPd itself

Reactions	Amount of leached-Pd (ng) in the reaction mixtures ^{c, d, e}										Pd on SAPd (µg)	
	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th	8 th	9 th	10 th	Before use	After use
1a + 2a	170 ±	144 ±	107 ±	120 ±	103 ±	65 ±	86 ±	58 ±	56 ±	62 ±	81	93
	181	143	84	113	53	23	62	22	24	26	± 27	± 30
	(0.05)	(0.04)	(0.03)	(0.03)	(0.03)	(0.02)	(0.02)	(0.02)	(0.02)	(0.02)		
1b + 2a	487 ±	1016 ±	1321 ±	667 ±	862 ±	1010 ±	723 ±	711 ±	533 ±	360 ±	81	49
	153	821	970	274	445	709	496	602	367	204	± 23	± 13
	(0.11)	(0.22)	(0.29)	(0.15)	(0.19)	(0.22)	(0.16)	(0.16)	(0.12)	(0.08)		

^a Reaction conditions: **1a** (0.50 mmol), **2a** (0.75 mmol), K₂CO₃ (1.00 mmol), single-mode microwave settings, MW (S): solvent: EtOH (2.0 mL), temp: 80 °C, time: 60 min, power: 200 W; multi-mode microwave settings, MW (M): solvent: EtOH (2.0 mL), temp: 82 °C, time: 60 min, power: 500 W. ^b **1b** (0.50 mmol), **2a** (0.75 mmol), K₂CO₃ (1.00 mmol), single-mode microwave settings, MW (S): solvent: DMF (2.0 mL), temp: 90 °C, time: 50 min, power: 300 W; multi-mode microwave settings, MW (M): solvent: toluene/H₂O (3:1, 2.0 mL), temp: 104 °C, time: 60 min, power: 500 W. ^c The entire reaction mixture was acidified and subjected directly to ICP-MS measurement. ^d The standard deviation was calculated from 4 sets of samples. ^e Numbers in parentheses indicate the amount of leached Pd in ppm.

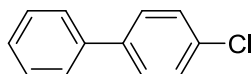
Table S2. Suzuki-Miyaura cross-coupling reactions of various substrates using SAPd^a

Ar—X		Solution		(HO) ₂ B—Ar'										Ar—Ar'
1c-1j		MW (S)		K ₂ CO ₃ , solvent (2 mL) + MW (S) solvent										3b-3h
				MW (M)										
Entry	Ar-X	Ar'-B(OH) ₂		Yields of 3 (%) ^b										Average yields (%)
		Ar'	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th	8 th	9 th	10 th		
1	4-MeOC ₆ H ₄ Br (1c)	4-ClC ₆ H ₄ (2a)	98	99	98	99	98	97	98	98	97	98	98	
2	4-MeC ₆ H ₄ Br (1d)	4-ClC ₆ H ₄ (2a)	95	93	95	94	93	95	95	95	93	94	94	
3	4-NO ₂ C ₆ H ₄ Br (1e)	4-ClC ₆ H ₄ (2a)	98	99	99	>99	98	98	99	99	99	98	99	
4	4-CNC ₆ H ₄ Br (1f)	4-ClC ₆ H ₄ (2a)	99	>99	98	99	97	98	99	99	98	99	99	
5	C ₆ H ₅ Br (1b)	C ₆ H ₅ (2b)	97	98	97	97	96	97	93	95	94	95	96	
6	C ₆ H ₅ Br (1b)	4-MeC ₆ H ₄ (2c)	99	98	96	98	94	98	96	99	98	97	98	
7	4-MeOC ₆ H ₄ I (1g)	4-ClC ₆ H ₄ (2a)	97	98	98	97	96	96	97	97	98	97	97	
8	2-MeC ₆ H ₄ I (1h)	4-ClC ₆ H ₄ (2a)	96	95	95	97	95	96	95	95	95	95	95	
9	4-AcC ₆ H ₄ I (1i)	4-ClC ₆ H ₄ (2a)	>99	>99	98	99	99	98	99	97	98	99	99	
10	4-NO ₂ C ₆ H ₄ I (1j)	4-ClC ₆ H ₄ (2a)	99	>99	99	95	98	98	99	99	98	99	99	
11	C ₆ H ₅ I (1a)	C ₆ H ₅ (2b)	95	95	96	96	96	95	96	96	95	95	96	
12	C ₆ H ₅ I (1a)	4-MeC ₆ H ₄ (2c)	96	97	96	96	96	95	96	94	95	96	96	

^a Reaction conditions for arylbromides: arylbromides (0.50 mmol), boronic acids (0.75 mmol), K₂CO₃ (1 mmol), single-mode microwave settings, MW (S): solvent: DMF (2.0 mL), temp: 90 °C, time: 50 min, power: 300 W, multi-mode microwave settings, MW (M): solvent: toluene/H₂O (3:1, 2 mL), temp: 102 °C, time: 60 min, power: 500 W; Reaction conditions for aryl iodides: aryl iodides (0.50 mmol), boronic acids (0.75 mmol), K₂CO₃ (1 mmol),

single-mode microwave settings, MW (S): solvent: EtOH (2.0 mL), temp: 80 °C, time: 60 min, power: 200 W, multi-mode microwave settings, MW (M): solvent: EtOH (2.0 mL), temp: 82 °C, time: 60 min, power: 500 W. ^b The isolated yields.

4-Chlorobiphenyl (**3a**)^{1,2}

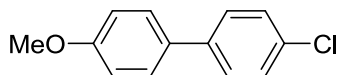


From arylbromide method: average yield: 99%.

From aryl iodide method: average yield: 99%.

White solid; mp 78-78.5 °C (MeOH) (lit.² 78.5 °C, benzene). ¹H-NMR (500 MHz, CDCl₃): δ 7.54 (2H, d, *J* = 7.5 Hz), 7.51 (2H, d, *J* = 7.5 Hz), 7.45–7.39 (4H, m), 7.37–7.34 (1H, m); ¹³C-NMR (125 MHz, CDCl₃): δ 139.94, 139.62, 133.33, 128.88, 128.86, 128.36, 127.56, 126.95; LRMS (EI) *m/z* 188 (100%, M⁺).

4-Chloro-4'-methoxybiphenyl (**3b**)^{1,2}

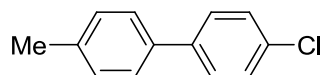


From arylbromide method: By following the same procedure described for **3a**, biaryl **3b** was prepared from 4-bromoanisole (**1c**) and 4-chlorophenylboronic acid (**2a**): average yield: 98%.

From aryl iodide method: By following the same procedure described for **3a**, biaryl **3b** was prepared from 4-iodoanisole (**1g**) and 4-chlorophenylboronic acid (**2a**): average yield: 97%.

White solid; mp 115-115.5 °C (lit.² 116 °C, EtOH). ¹H-NMR (500 MHz, CDCl₃): δ 7.46 (4H, t, *J* = 8.5 Hz), 6.96 (2H, d, *J* = 8.5 Hz), 3.83 (3H, s); ¹³C-NMR (100 MHz, CDCl₃): δ 159.32, 139.22, 132.62, 132.43, 128.80, 127.97, 127.90, 114.27, 55.32; LRMS (EI) *m/z* 218 (100%, M⁺).

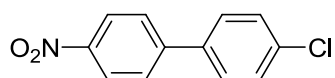
4-Chloro-4'-methylbiphenyl (**3c**)^{3,4}



By following the same procedure described for **3a**, biaryl **3c** was prepared from 4-bromotoluene (**1d**) and 4-chlorophenylboronic acid (**2a**): average yield: 94%.

White solid. mp 122-122.5 °C (lit.⁴ 122 °C). ¹H-NMR (500 MHz, CDCl₃): δ 7.49 (2H, d, *J* = 8.2 Hz), 7.44 (2H, d, *J* = 8.2 Hz), 7.38 (2H, d, *J* = 8.4 Hz), 7.24 (2H, d, *J* = 8.0 Hz), 2.39 (3H, s); ¹³C-NMR (125 MHz, CDCl₃): δ 139.55, 137.42, 137.07, 132.99, 129.58, 129.02, 128.82, 128.20, 126.79, 21.10; LRMS (EI) *m/z* 202 (90%, M⁺).

4-Chloro-4'-nitrobiphenyl (**3d**)^{2,5}

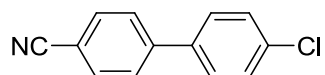


From arylbromide method: By following the same procedure described for **3a**, biaryl **3d** was prepared from 4-bromonitrobenzene (**1e**) and 4-chlorophenylboronic acid (**2a**): average yield: 99%.

From aryl iodide method: By following the same procedure described for **3a**, biaryl **3d** was prepared from 4-iodonitrobenzene (**1j**) and 4-chlorophenylboronic acid (**2a**): average yield: 99%.

Pale yellow solid. mp 145.5-146 °C (lit.² 146 °C, EtOH). ¹H-NMR (400 MHz, CDCl₃): δ 8.29 (2H, d, *J* = 8.4 Hz), 7.70 (2H, d, *J* = 8.4 Hz), 7.56 (2H, d, *J* = 8.4 Hz), 7.46 (2H, t, *J* = 8.4 Hz); ¹³C-NMR (100 MHz, CDCl₃): δ 147.14, 146.22, 137.10, 135.17, 129.31, 128.57, 127.60, 124.15; LRMS (EI) *m/z* 233 (100%, M⁺).

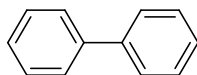
4'-Chlorobiphenyl-4-carbonitrile (**3e**)^{6,7}



By following the same procedure described for **3a**, biaryl **3e** was prepared from 4-bromobenzonitrile (**1f**) and 4-chlorophenylboronic acid (**2a**): average yield: 99%.

White solid. mp 125-126 °C (lit.⁷ 124-126 °C). ¹H-NMR (400 MHz, CDCl₃): δ 7.72 (2H, d, *J* = 8.0 Hz), 7.64 (2H, d, *J* = 7.6 Hz), 7.52 (2H, d, *J* = 8.4 Hz), 7.44 (2H, d, *J* = 8.4 Hz); ¹³C-NMR (100 MHz, CDCl₃): δ 144.24, 137.46, 134.84, 132.60, 129.22, 128.39, 127.47, 118.69, 111.14; LRMS (EI) *m/z* 213 (100%, M⁺).

Biphenyl (**3f**)^{1,8}

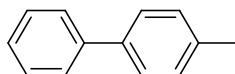


From arylbromide method: By following the same procedure described for **3a**, biaryl **3f** was prepared from bromobenzene (**1b**) and phenylboronic acid (**2b**): average yield: 96%.

From aryl iodide method: By following the same procedure described for **3a**, biaryl **3f** was prepared from iodobenzene (**1a**) and phenylboronic acid (**2b**): average yield: 96%.

White solid. mp 70.0-70.5 °C (lit.⁸ 70-71 °C, MeOH). ¹H-NMR (400 MHz, CDCl₃): δ 7.59 (4H, d, *J* = 7.6 Hz), 7.43 (4H, t, *J* = 7.6 Hz), 7.35-7.31(2H, m); ¹³C-NMR (100 MHz, CDCl₃): δ 141.20, 128.73, 127.22, 127.14; LRMS (EI) *m/z* 154 (100%, M⁺).

4-Methylbiphenyl (**3g**)^{1,9}

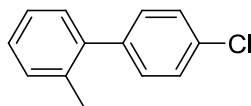


From arylbromide method: By following the same procedure described for **3a**, biaryl **3g** was prepared from bromobenzene (**1b**) and 4-methylphenylboronic acid (**2c**): average yield: 98%.

From aryl iodide method: By following the same procedure described for **3a**, biaryl **3g** was prepared from iodobenzene (**1a**) and 4-methylphenylboronic acid (**2c**): average yield: 96%.

White solid. mp 48.5-49 °C (lit.⁹ 49-50 °C, EtOH). ¹H-NMR (500 MHz, CDCl₃): δ 7.58 (2H, d, *J* = 8.6 Hz), 7.49 (2H, d, *J* = 8.0 Hz), 7.44–7.41 (2H, m), 7.33–7.31 (1H, m), 7.26–7.24 (2H, m), 2.39 (1H, s); ¹³C-NMR (125 MHz, CDCl₃): δ 141.14, 138.33, 137.01, 129.46, 128.70, 126.98, 126.96, 21.10; LRMS (EI) *m/z* 168 (100%, M⁺).

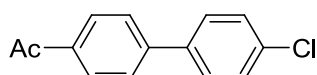
4'-chloro-2-methylbiphenyl (**3h**)¹⁰



By following the same procedure described for **3a**, biaryl **3h** was prepared from *o*-iodotoluene (**1h**) and 4-chlorophenylboronic acid (**2a**): average yield: 95%.

Light yellow oil. ¹H-NMR (500 MHz, CDCl₃): δ 7.36 (2H, d, *J* = 8.5 Hz), 7.25–7.20 (5H, m), 7.17 (1H, d, *J* = 7.0 Hz), 2.24 (3H, s); ¹³C-NMR (125 MHz, CDCl₃): δ 140.61, 140.30, 135.21, 132.78, 130.48, 130.40, 129.62, 128.23, 127.55, 125.86, 20.37; LRMS (EI) *m/z* 202 (100%, M⁺).

1-(4'-Chlorobiphenyl-4-yl)ethanone (**3i**)^{3, 11}



By following the same procedure described for **3a**, biaryl **3i** was prepared from 4-acetyliodobenzene (**1i**) and 4-chlorophenylboronic acid (**2a**): average yield: 99%.

White solid. mp 104-104.5 °C (lit 103-104 °C, MeOH). ¹H-NMR (400 MHz, CDCl₃): δ 8.01 (2H, d, *J* = 8.4 Hz), 7.62 (2H, d, *J* = 8.0 Hz), 7.53 (2H, d, *J* = 8.8 Hz), 7.42 (2H, d, *J* = 8.4 Hz), 2.62 (3H, s); ¹³C-NMR (100 MHz, CDCl₃): δ 197.54, 14.31, 138.16, 135.97, 134.35, 129.06, 128.93, 128.42, 126.96, 26.61; LRMS (EI) *m/z* 230 (50%, M⁺).

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