

## Electronic Supplementary Information

### Ligand-free Hiyama Cross-Coupling Reaction Catalyzed by Palladium on Carbon

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**General experimental.** Dry-type 10% Pd/C (K-type) or dry-type 5% Pd/C (K-type) was supplied by the N.E. Chemicat Corporation (Tokyo, Japan). All reagents and solvents were purchased from commercial sources and used without further purification. Flash column chromatography was performed using Silica Gel 60 N (Kanto Chemical Co., Inc., 63–210  $\mu\text{m}$  spherical, neutral).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL AL 400 spectrometer (400 MHz for  $^1\text{H}$  NMR spectroscopy and 100 MHz for  $^{13}\text{C}$  NMR spectroscopy) or JEOL ECA 500 spectrometer (500 MHz for  $^1\text{H}$  NMR spectroscopy and 125 MHz for  $^{13}\text{C}$  NMR spectroscopy). Chemical shifts ( $\delta$ ) are expressed in ppm and are internally referenced (0.00 ppm for TMS for  $\text{CDCl}_3$  for  $^1\text{H}$  NMR spectroscopy and 77.0 ppm for  $\text{CDCl}_3$  for  $^{13}\text{C}$  NMR spectroscopy). Mass spectra were taken on JEOL JMS-SX102A or a JEOL T100TD instrument. GC-MS analysis for the side reaction was conducted by JEOL Jms Q1000GC Mk2.

**Screening of solvents and fluoride sources for the Pd/C-catalyzed Hiyama coupling reaction (Table 1).** A mixture of 4-bromonitrobenzene (101 mg, 500  $\mu\text{mol}$ ), phenyltriethoxysilane (182  $\mu\text{L}$ , 750  $\mu\text{mol}$ ), dry-type 10% Pd/C (26.6 mg, 25.0  $\mu\text{mol}$ , 5.00 mol % of 4-bromonitrobenzene), the solvent (1 mL) and the fluoride source (1.00 mmol) in a 15-mL test tube was stirred under Ar at 120  $^\circ\text{C}$  using the Chemist Plaza Chemi Chemi-100 (Shibata, Tokyo) or ChemiStation personal organic synthesizer PPS (EYELA, Tokyo) for the given time and then passed through a Celite pad (3.0 cm) to remove the catalyst. To the filtrate were added EtOAc (50 mL) and  $\text{H}_2\text{O}$  (50 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (10 mL) and the combined organic layers were dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. The residue was dissolved in  $\text{CDCl}_3$  and the yield was

determined by  $^1\text{H}$  NMR spectroscopy using 1,4-dioxane (8.5  $\mu\text{L}$ , 100  $\mu\text{mol}$ ) as an internal standard.

**Effect of proton sources on the Pd/C-catalyzed Hiyama coupling reaction (Table 2).** A mixture of 4-bromonitrobenzene (101 mg, 500  $\mu\text{mol}$ ), phenyltriethoxysilane (182  $\mu\text{L}$ , 750  $\mu\text{mol}$ ), Pd/C (5.00 mol% of 4-bromonitrobenzene: 10% Pd/C, 26.6 mg; 5% Pd/C, 53.2 mg), tetrabutylammonium fluoride (316 mg, 1.00 mmol) and toluene (1 mL), and the additive given in Table 2 in a 15-mL test tube were stirred under Ar at 120  $^{\circ}\text{C}$  using the Chemist Plaza Chemi Chemi-100 (Shibata, Tokyo) or ChemiStation personal organic synthesizer PPS (EYELA, Tokyo) for the given time and then passed through a Celite pad (3.0 cm) to remove the catalyst. To the filtrate were added EtOAc (50 mL) and  $\text{H}_2\text{O}$  (50 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (10 mL) and the combined organic layers were dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. The residue was dissolved in  $\text{CDCl}_3$  and the yield was determined by  $^1\text{H}$  NMR spectroscopy using 1,4-dioxane (8.5  $\mu\text{L}$ , 100  $\mu\text{mol}$ ) as an internal standard.

**Effect of the dose of 5% Pd/C on the Hiyama cross-coupling reaction (Table 3).** A mixture of 4-bromonitrobenzene (101 mg, 500  $\mu\text{mol}$ ), phenyltriethoxysilane (182  $\mu\text{L}$ , 750  $\mu\text{mol}$ ), dry-type 5% Pd/C (the amounts are given in Table 3), tetrabutylammonium fluoride (316 mg, 1.00 mmol), AcOH (43.0  $\mu\text{L}$ , 750  $\mu\text{mol}$ ) and toluene (1 mL) in a 15-mL test tube was stirred under Ar at 120  $^{\circ}\text{C}$  or 80  $^{\circ}\text{C}$  using the Chemist Plaza Chemi Chemi-100 (Shibata, Tokyo) or ChemiStation personal organic synthesizer PPS (EYELA, Tokyo) for the given time and then passed through a Celite pad (3.0 cm) to remove the catalyst. To the filtrate were added EtOAc (50 mL) and

H<sub>2</sub>O (50 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (10 mL) and the combined organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was dissolved in CDCl<sub>3</sub> and the yield was determined by <sup>1</sup>H NMR spectroscopy using 1,4-dioxane (8.5 μL, 100 μmol) as an internal standard.

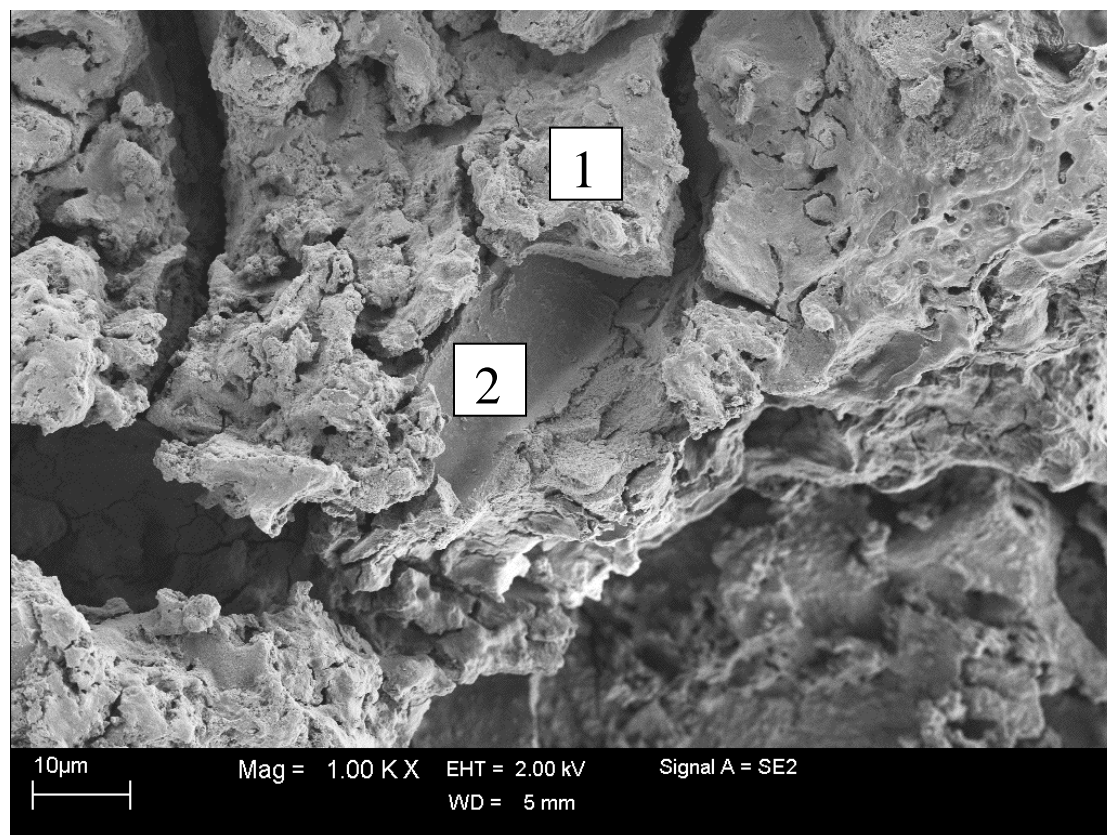
**General procedure for the Hiyama cross-coupling of various aryl halides and aryltriethoxysilanes (Table 4).** A mixture of TBAF·3H<sub>2</sub>O (316 mg, 1.00 mmol), 5% Pd/C (5.4 mg, 5.00 μmol), aryl halides (500 μmol), aryltriethoxysilane (750 μmol), AcOH (43.0 μL), and toluene (1 mL) in a 15 mL test tube was stirred under Ar at 120 °C using the Chemist Plaza Chemi Chemi-100 (Shibata, Tokyo) or ChemiStation personal organic synthesizer PPS (EYELA, Tokyo) for the given time and then passed through a Celite pad (3.0 cm) to remove the catalyst. To the filtrate were added EtOAc (50 mL) and saturated aqueous NH<sub>4</sub>Cl (50 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (10 mL) and the combined organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as an eluent to give the corresponding biphenyl.

**Reuse test of 5% Pd/C (Table 5).** A mixture of 4-bromonitrobenzene (101 mg, 500 μmol), phenyltriethoxysilane (182 μL, 750 μmol), dry-type 5% Pd/C (5.4 mg, 5.00 μmol), tetrabutylammonium fluoride (316 mg, 1.00 mmol), AcOH (43.0 μL, 750 μmol) and toluene (1 mL) in each five 15 mL-test tube was stirred under Ar at 120 °C using the Chemist Plaza Chemi Chemi-100 (Shibata, Tokyo) for 24 h. Each reaction mixture was passed through a filter paper [Kiriya, No.5 C (1 μm), diameter = 60

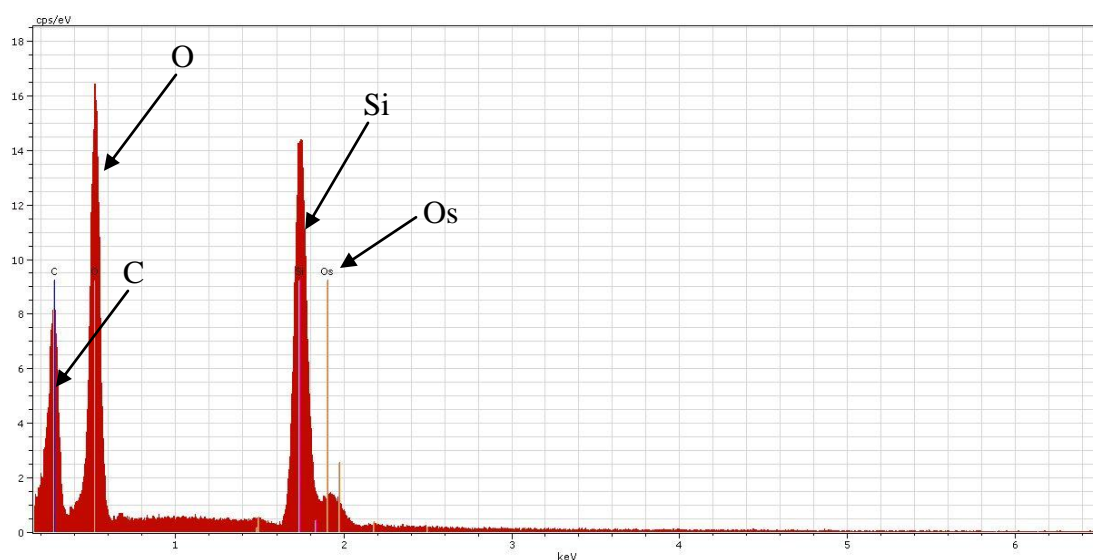
mm] and the catalyst on the filter paper was washed with H<sub>2</sub>O (100 mL) and EtOAc (100 mL). To the filtrate were added EtOAc (50 mL) and H<sub>2</sub>O (50 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (10 mL) and the organic layers obtained from five test tubes were combined, dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was dissolved in CDCl<sub>3</sub> and the yield was determined by <sup>1</sup>H NMR spectroscopy using 1,4-dioxane (8.5 μL, 100 μmol) as the internal standard.

The recovered Pd/C (133 mg, Figure) was dried in a desiccator under vacuum for more than 12 h, divided equally into five portions (26.6 mg), and used for the 2nd run. The reuse test was carried out using recovered 5% Pd/C (26.6 mg), 4-bromonitrobenzene (101 mg, 500 μmol), phenyltriethoxysilane (182 μL, 750 μmol), tetrabutylammonium fluoride (316 mg, 1.00 mmol), AcOH (43.0 μL, 750 μmol) and toluene (1 mL) in each five 15 mL-test tube under Ar at 120 °C using the Chemist Plaza Chemi Chemi-100 (Shibata, Tokyo) for 24 h. The reaction mixtures were treated in a similar manner to the 1st run. The residue obtained from five reactions was dissolved in CDCl<sub>3</sub>, and the yield was determined by <sup>1</sup>H NMR spectroscopy using 1,4-dioxane (8.5 μL, 100 μmol) as the internal standard. The recovered 5% Pd/C (225 mg) was divided equally into five portions and used for the 3rd run, which was carried out in a similar manner to 2nd run. The recovered 5% Pd/C obtained after 3<sup>rd</sup> run was contained with significant amounts of inseparable colorless silicon residue. The existence of approximately 20 weight % of silicon element in the residue was confirmed by scanning electron microscopy-energy dispersion X-ray spectrometry (Figure, Roentec QuanTax with XFlash 3001, Roentec).

Figure: Data of scanning electron microscopy-energy dispersion X-ray spectrometry  
(SEM-EDS of the recovered 5% Pd/C).

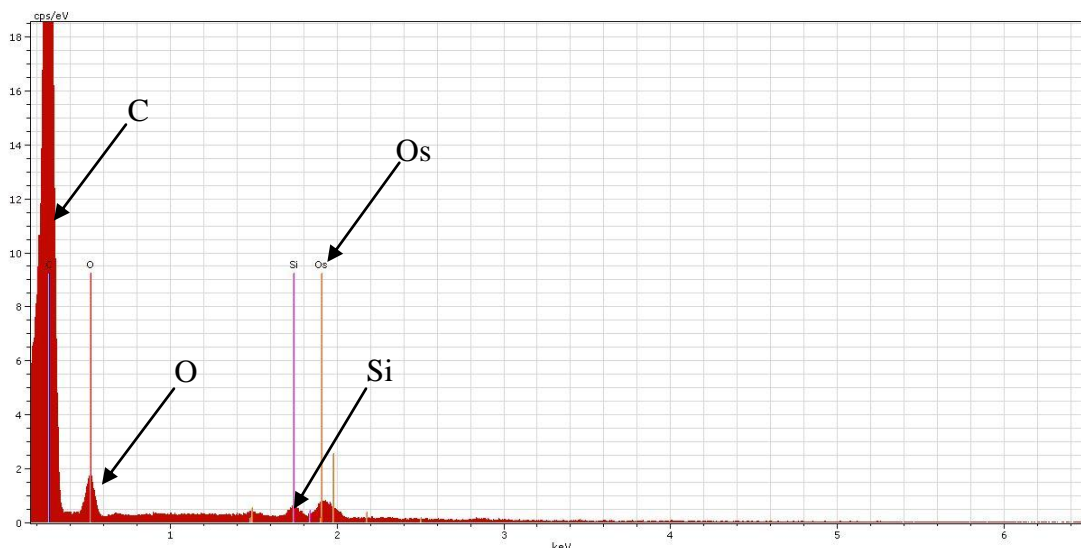


#### Data at the position of No. 1



OsO<sub>4</sub> was added for the enhancement of the conductivity of the sample.

#### Data at the position of No. 2



OsO<sub>4</sub> was added for the enhancement of the conductivity of the sample.

### Effect of leached palladium species on the present Hiyama cross-coupling reaction (Table 6).

#### Entry 1

A mixture of 5% Pd/C (5.4 mg, 5.00  $\mu$ mol), AcOH (43.0  $\mu$ L), and toluene (1 mL) in a 15 mL test tube was stirred under Ar at 120 °C using the Chemist Plaza Chemi Chemi-100 (Shibata, Tokyo) for 24 h and then passed through a membrane filter (Millipore, Millex-LH, 0.45  $\mu$ m). The filtrate was transferred to another 15 mL-test tube, and 4-bromonitrobenzene (101 mg 500  $\mu$ mol), phenyltriethoxysilane (182  $\mu$ L, 750  $\mu$ mol) and TBAF·3H<sub>2</sub>O (315 mg, 1.00 mmol) were added. The mixture was stirred under Ar at 120 °C using the Chemist Plaza Chemi Chemi-100 (Shibata, Tokyo) for 24 h. The mixture was diluted with EtOAc (50 mL) and saturated aqueous NH<sub>4</sub>Cl (50 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (10 mL) and the combined organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was dissolved in CDCl<sub>3</sub> and no formation of 4-nitrobiphenyl was observed by <sup>1</sup>H NMR analysis.

#### Entry 2



A mixture of 5% Pd/C (5.4 mg, 5.00  $\mu\text{mol}$ ), TBAF $\cdot$ 3H<sub>2</sub>O (315 mg, 1.00 mmol), AcOH (43.0  $\mu\text{L}$ ), and toluene (1 mL) in a 15 mL-test tube was stirred under Ar at 120 °C using the Chemist Plaza Chemi Chemi-100 (Shibata, Tokyo) for 24 h and then passed through a membrane filter (Millipore, Millex-LH, 0.45  $\mu\text{m}$ ). The filtrate was transferred to another 15 mL-test tube, and 4-bromonitrobenzene (101 mg 500  $\mu\text{mol}$ ) and phenyltriethoxysilane (182  $\mu\text{L}$ , 750  $\mu\text{mol}$ ) were added. The mixture was stirred under Ar at 120 °C using the Chemist Plaza Chemi Chemi-100 (Shibata, Tokyo) for 24 h. The mixture was diluted with EtOAc (50 mL) and saturated aqueous NH<sub>4</sub>Cl (50 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (10 mL) and the combined organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was dissolved in CDCl<sub>3</sub> and no formation of 4-nitrobiphenyl was observed by <sup>1</sup>H NMR analysis.

#### Entry 3

A mixture of 4-bromonitrobenzene (101 mg 500  $\mu\text{mol}$ ), phenyltriethoxysilane (182  $\mu\text{L}$ , 750  $\mu\text{mol}$ ), and TBAF $\cdot$ 3H<sub>2</sub>O (315 mg, 1.00 mmol) and Filtrate 2 in a 15 mL-test tube was stirred under Ar at 120 °C using the Chemist Plaza Chemi Chemi-100 (Shibata, Tokyo) for 24 h. The mixture was diluted with EtOAc (50 mL) and saturated aqueous NH<sub>4</sub>Cl (50 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (10 mL) and the combined organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was dissolved in CDCl<sub>3</sub> and no formation of 4-nitrobiphenyl was observed by <sup>1</sup>H NMR analysis.

#### **Time-course study on filtrates after the removal of the Pd/C (Figure 1).<sup>1</sup>**

A mixture of 5% Pd/C (5.4 mg, 5.00  $\mu\text{mol}$ ), TBAF $\cdot$ 3H<sub>2</sub>O (315 mg, 1.00 mmol), AcOH (43.0  $\mu\text{L}$ ), and toluene (1 mL) in a 15 mL-test tube was stirred under Ar at



120 °C using the Chemist Plaza Chemi Chemi-100 (Shibata, Tokyo) for 30 min and then passed through a glass fiber filter (Toyo Roshi Kaisha, GS-25, <1.00 μm) without cooling. The filtrate was transferred to another 15 mL-test tube and heated at reflux for the additional given time. The mixture was diluted with EtOAc (50 mL) and water (50 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (10 mL) and the combined organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was dissolved in CDCl<sub>3</sub> and the yield of 4-nitrobiphenyl was determined by <sup>1</sup>H NMR spectroscopy using 1,4-dioxane (8.5 μL, 100 μmol) as an internal standard (48%). Another reaction was carried out under the same conditions (30 min). After cooling to rt (24 h), 5% Pd/C was removed from the mixture through a membrane filter (Millipore, Millex-LH, 0.20 μm). The filtrate was transferred to another 15 mL-test tube and heated at reflux for the additional given time. The mixture was diluted with EtOAc (50 mL) and water (50 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (10 mL) and the combined organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The yield of 4-nitrobiphenyl was determined by <sup>1</sup>H NMR spectroscopy (52%) in the same manner as above mentioned.

#### **4-Acethylbiphenyl (Table 4, Entries 1 and 2)**<sup>2, 3, 4</sup>

A mixed solvent (hexane/EtOAc, 20 : 1) was used as an eluent for the purification using silica gel column chromatography. <sup>1</sup>H NMR δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.50–7.39 (m, 3 H), 2.65 (s, 3 H); <sup>13</sup>C NMR δ 197.7, 145.6, 139.7, 135.7, 128.9, 128.2, 128.1, 127.2, 127.1, 26.6; MS (EI) *m/z* 196 (M<sup>+</sup>, 56%), 181 (100), 152 (38).

**4-Acethyl-4'-chlorobiphenyl (Table 4, Entry 3)** <sup>5</sup>

A mixed solvent (hexane/EtOAc, 20 : 1) was used as an eluent for the purification using silica gel column chromatography. <sup>1</sup>H NMR δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 2.62 (s, 3H); <sup>13</sup>C NMR δ 197.5, 144.3, 138.2, 136.0, 134.3, 129.1, 128.9, 128.4, 127.0, 26.6; MS (EI) *m/z* 230 (*M*<sup>+</sup>, 47%), 215 (100), 152 (67), 76 (11).

**4-Acethyl-4'-methylbiphenyl (Table 4, Entry 4)** <sup>5</sup>

A mixed solvent (hexane/EtOAc, 20 : 1) was used as an eluent for the purification using silica gel column chromatography. <sup>1</sup>H NMR δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 3.05 (s, 3H), 2.39 (s, 3H); <sup>13</sup>C NMR δ 197.6, 145.5, 138.1, 136.8, 135.4, 129.7, 129.6, 128.8, 127.0, 26.5, 21.1; MS (EI) *m/z* 210 (*M*<sup>+</sup>, 51%), 195 (100), 165 (19), 152 (26).

**4-Acethyl-4'-methoxybiphenyl (Table 4, Entry 5)** <sup>4, 6</sup>

A mixed solvent (hexane/EtOAc, 20 : 1) was used as an eluent for the purification using silica gel column chromatography. <sup>1</sup>H NMR δ 7.99 (2 H, d, *J* = 6.6 Hz), 7.63 (2 H, d, *J* = 6.6 Hz), 7.57 (2 H, d, *J* = 6.9 Hz), 6.99 (2 H, d, *J* = 6.9 Hz), 3.85 (3 H, s), 2.61 (3 H, s); <sup>13</sup>C NMR δ 197.6, 159.8, 145.2, 135.2, 132.1, 128.9, 128.3, 126.5, 114.3, 55.3, 26.6; MS (EI) *m/z* 226 (*M*<sup>+</sup>, 63%), 211 (100), 183 (11), 168 (18), 152 (10), 139 (20).

**4-Nitobiphenyl (Table 4, Entries 6)** <sup>3, 4, 6, 7</sup>

A mixed solvent (hexane/EtOAc, 50 : 1) was used as an eluent for the purification using silica gel column chromatography. <sup>1</sup>H NMR δ 8.25 (d, *J* = 8.9 Hz, 2H), 7.69 (d,

$J = 8.9$  Hz, 2H), 7.60 (d,  $J = 7.4$  Hz, 2H), 7.49–7.41 (m, 3H);  $^{13}\text{C}$  NMR  $\delta$  147.4, 146.9, 138.6, 129.0, 128.8, 127.6, 127.2, 123.9; MS (EI)  $m/z$  199 ( $\text{M}^+$ , 100%), 169 (28), 152 (65), 141 (22).

**4-Cyanobiphenyl (Table 4, Entry 7)**<sup>2, 4, 6</sup>

A mixed solvent (hexane/EtOAc, 20 : 1) was used as an eluent for the purification using silica gel column chromatography.  $^1\text{H}$  NMR  $\delta$  7.71 (d,  $J = 8.3$  Hz, 2H), 7.67 (d,  $J = 8.3$  Hz, 2H), 7.58 (d,  $J = 7.5$  Hz, 2H), 7.49–7.40 (m, 3H);  $^{13}\text{C}$  NMR  $\delta$  145.5, 139.0, 132.4, 129.0, 128.5, 127.6, 127.0, 118.8, 110.7; MS (EI)  $m/z$  179 ( $\text{M}^+$ , 100%), 151 (6).

**4-Phenylbenzaldehyde (Table 4, Entry 8)**<sup>2, 6</sup>

A mixed solvent (hexane/EtOAc, 50 : 1) was used as an eluent for the purification using silica gel column chromatography.  $^1\text{H}$  NMR  $\delta$  10.00 (s, 1H), 7.94 (d,  $J = 8.0$  Hz, 2H), 7.74 (d,  $J = 8.0$  Hz, 2H), 7.63 (d,  $J = 8.0$ , 2H), 7.49–7.39 (m, 3H);  $^{13}\text{C}$  NMR  $\delta$  191.9, 147.1, 139.6, 135.1, 130.2, 129.0, 128.4, 127.6, 127.3; MS (EI)  $m/z$  181 ( $\text{M}^+$ , 100%), 152 (63), 127 (6), 76 (12), 44 (8).

**2-Phenylbenzaldehyde (Table 4, Entry 9)**<sup>8</sup>

A mixed solvent (hexane/EtOAc, 50 : 1) was used as an eluent for the purification using silica gel column chromatography.  $^1\text{H}$  NMR  $\delta$  9.99 (1H, s), 8.03 (d,  $J = 7.8$  Hz, 1H), 7.64 (ddd,  $J = 1.5, 7.8, 15$  Hz, 1H), 7.39–7.37 (m, 7H);  $^{13}\text{C}$  NMR  $\delta$  191.7, 147.0, 139.5, 135.1, 130.1, 128.9, 128.3, 127.5, 127.2; MS (EI)  $m/z$  181 ( $\text{M}^+$ , 100%), 152 (41), 76 (22).

**Biphenyl-4-carboxylic acid (Table 4, Entry 10)**<sup>6</sup>

A mixed solvent (hexane/EtOAc, 3 : 1) was used as an eluent for the purification using silica gel column chromatography.  $^1\text{H}$  NMR  $\delta$  8.19 (d,  $J$  = 8.6 Hz, 2H), 7.71 (d,  $J$  = 8.6 Hz, 2H), 7.65 (d,  $J$  = 7.4 Hz, 2H), 7.49 (t,  $J$  = 7.7 Hz, 2H), 7.41 (t,  $J$  = 7.2 Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  171.3, 146.5, 139.9, 130.7, 129.0, 128.3, 127.3, 127.2; MS (EI)  $m/z$  181 ( $\text{M}^+$ , 100%), 152 (63), 127 (6), 76 (12), 44 (8).

#### **4-Fluorobiphenyl (Table 4, Entry 11) <sup>6</sup>**

A mixed solvent (hexane/EtOAc, 50 : 1) was used as an eluent for the purification using silica gel column chromatography.  $^1\text{H}$  NMR  $\delta$  7.53–7.52 (m, 4H), 7.42 (t,  $J$  = 7.2 Hz, 2H), 7.33 (d,  $J$  = 7.2 Hz, 1H), 7.11 (d,  $J$  = 8.6 Hz, 2H);  $^{13}\text{C}$  NMR  $\delta$  162.6 (d,  $J$  = 244.4 Hz), 140.4, 137.5 (d,  $J$  = 2.4 Hz), 129.0, 128.8 (d,  $J$  = 8.3 Hz), 127.4, 127.2, 115.8 (d,  $J$  = 21.5 Hz); MS (EI)  $m/z$  198 ( $\text{M}^+$ , 100%), 181 (44), 152 (37).

#### **4-phenyltoluene (Table 4, Entry 12) <sup>9</sup>**

A solvent (hexane) was used as an eluent for the purification using silica gel column chromatography.  $^1\text{H}$  NMR  $\delta$  7.56 (d,  $J$  = 8.1 Hz, 2H), 7.49 (d,  $J$  = 6.3 Hz, 2H), 7.42 (t,  $J$  = 7.8 Hz, 2H), 7.32 (t,  $J$  = 7.7, 1H), 7.25 (m, 2H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  141.1, 138.3, 137.0, 129.5, 128.7, 127.0, 21.1; MS (EI)  $m/z$  168 ( $\text{M}^+$ , 100%), 152 (29), 82 (14).

#### **3-Methoxybiphenyl (Table 4, Entry 13) <sup>2</sup>**

A mixed solvent (hexane/EtOAc, 20 : 1) was used as an eluent for the purification using silica gel column chromatography.  $^1\text{H}$  NMR  $\delta$  7.59 (d,  $J$  = 7.7 Hz, 2H), 7.44 (t,  $J$  = 7.7 Hz, 2H), 7.33–7.38 (m, 2H), 7.18 (d,  $J$  = 8.0 Hz, 1H), 7.13 (m, 1H), 6.89 (dd,

$J = 7.6, 2.8$  Hz, 1H), 3.87 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  159.5, 142.3, 140.7, 129.3, 128.3, 126.7, 119.2, 112.5, 112.2, 54.8; MS (EI)  $m/z$  184 ( $\text{M}^+$ , 100%), 141 (24).

#### 4-Methoxybiphenyl (Table 4, Entry 14)<sup>2, 3, 4, 6, 7</sup>

A mixed solvent (hexane/EtOAc, 50 : 1) was used as an eluent for the purification using silica gel column chromatography.  $^1\text{H}$  NMR  $\delta$  7.56–7.52 (m, 4H), 7.41 (t,  $J = 7.2$  Hz, 2H), 7.30 (t,  $J = 6.9$  Hz, 1H), 6.97 (d,  $J = 7.3$  Hz, 2H), 3.89 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3; MS (EI)  $m/z$  184 ( $\text{M}^+$ , 100%), 169 (36), 141 (36), 115 (24).

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