Supporting Information

Direct C–H Arylation of (Hetero)arenes with Aryl Iodides via Rhodium Catalysis

Shuichi Yanagisawa,[†] Tomoko Sudo,[†] Ryoji Noyori,[†] and Kenichiro Itami^{*,†,‡}

[†] *Department of Chemistry and Research Center for Materials Science, Nagoya University, Nagoya 464-8602, Japan*

[‡] *PRESTO, Japan Science and Technology Agency (JST)*

E-mail: itami@chem.nagoya-u.ac.jp

Table of Contents

1.	General	S2
2.	Synthesis of Rhodium Complex 1	S3
3.	X-Ray Crystal Structure Analysis of Rhodium Complex 1	S3–S4
4.	Typical Procedure for Mono-Arylation of Heteroarenes (Conventional Heating Protocol)	S5
5.	Typical Procedure for Mono-Arylation of Heteroarenes (Microwave Heating Protocol)	S5
6.	Typical Procedure for Double-Arylation of Heteroarenes (Microwave Heating Protocol)	S6
7.	Compound Data for Other C–H Arylation Products	S6–S9
8.	Direct Arylation of Anisole	S9–S10
9.	Direct Arylation of 1,3-Dimethoxybenzene	S10
10.	¹ H and ¹³ C NMR Spectra of Arylation Products	S11–S42

1. General

Unless otherwise noted, all materials including dry solvents (toluene and *m*-xylene) were obtained from commercial suppliers and used without further purification. The ligand P[OCH(CF₃)₂]₃ was prepared according to procedures reported in the literature.¹ Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of argon in flame-dried glassware with standard vacuum-line techniques. All arylation reactions using conventional heating were carried out in glass vessels equipped with J. Young® O-ring tap, heated in a 8-well reaction block (heater + magnetic stirrer). All microwave reactions were performed in a regularly calibrated CEM Focused MicrowaveTM Synthesis System (Discover) with IR temperature monitor and non-invasive pressure transducer using 10 mL vials with septa. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F₂₅₄ precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm) and ethanolic phosphomolybdic acid. Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh). Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-9204 instrument equipped with JAIGEL-1H/JAIGEL-2H columns using chloroform as an eluent. Gas chromatography (GC) analysis was conducted on a Hewlett-Packard 6890 instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard). GC/MS analysis was conducted on a Hewlett Packard 6890/5973N instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard). High-resolution mass spectra (HRMS) were obtained from a Waters Micromass LCT Premier (electrospray ionization time-of-flight mass spectrometry, ESI-TOFMS) or a JEOL JMS-700 (fast atom bombardment mass spectrometry, FABMS). Infrared spectra were recorded on a JASCO FTIR-6100 spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-600 (¹H 600 MHz, ¹³C 150 MHz, ³¹P 243 MHz) spectrometer. Chemical shifts for ¹H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.0 ppm). Chemical shifts for ¹³C NMR are expressed in parts ppm relative to CDCl₃ (δ 77.0 ppm). Chemical shifts for ³¹P{¹H} NMR are reported downfield in ppm relative to external 85% H₃PO₄ (δ 0.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration. The structures of arylation products were determined based on 2D NMR experiments.

(1) van Leeuwen, P. W. N. M.; Roobeek, C. F. *Tetrahedron* **1981**, *37*, 1973.

2. Synthesis of Rhodium Complex 1

A solution of $[\text{RhCl}(\text{CO})_2]_2$ (200.4 mg, 0.51 mmol) and $\text{P}[\text{OCH}(\text{CF}_3)_2]_3$ (1.09 g, 2.06 mmol) in dry toluene (2.0 mL) was stirred at 50 °C for 2 h under argon. After cooling the reaction mixture to room temperature, solvent was removed under reduced pressure. Reprecipitation from hexane/ CH_2Cl_2 followed by filtration and vacuum drying afforded *trans*- $\text{RhCl}(\text{CO})\{\text{P}[\text{OCH}(\text{CF}_3)_2]_3\}_2$ (**1**: 1.25 g, quant) as yellow solid. ^1H NMR (600 MHz, CDCl_3) δ 5.64 (br, 6H). ^{31}P $\{^1\text{H}\}$ NMR (243 MHz, $\text{THF}-d_8$) δ 123.3 (d, $J_{\text{Rh-P}} = 224$ Hz). IR (KBr) 2070, 1371, 1302, 1250, 1207, 1113, 1088 cm^{-1} .

3. X-Ray Crystal Structure Analysis of Rhodium Complex 1

Single crystals suitable for X-ray analysis were obtained by slow diffusion of toluene into an acetonitrile solution of **1**. Intensity data were collected at 173 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with graphite-monochromated Mo- $\text{K}\alpha$ radiation. A total of 30758 reflections were corrected, of which 8832 were independent reflections ($R_{\text{int}} = 0.0312$). The structure was solved by direct methods (SHELXS-97²) and refined by the full-matrix least-squares on F^2 (SHELXL-97²). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The crystal data are as follows: $\text{C}_{19}\text{H}_6\text{ClF}_{36}\text{O}_7\text{P}_2\text{Rh}$, $FW = 1230.54$, crystal size $0.20 \times 0.20 \times 0.20 \text{ mm}^3$, monoclinic, space group $C 2/c$ (No. 15). $a = 33.050(5) \text{ \AA}$, $b = 17.903(2) \text{ \AA}$, $c = 13.525(2) \text{ \AA}$, $\alpha = 90.0000(5)^\circ$, $\beta = 105.3324(7)^\circ$, $\gamma = 90.0000(5)^\circ$, $V = 7717.8(19) \text{ \AA}^3$, $Z = 4$, $D_c = 1.059 \text{ g/cm}^3$. The refinement converged to $R_1 = 0.0419$, $wR_2 = 0.1010$ ($I > 2\sigma(I)$), $\text{GOF} = 1.105$.

(2) Sheldrick, G. M. *SHELX-97, Program for the Refinement of Crystal Structures*; University of Gottingen: Gottingen, Germany, 1997.

Figure S1. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selective bond length (Å): Rh(1)–Cl(1) = 2.3561(8), Rh(1)–P(1) = 2.2597(8), Rh(1)–P(2) = 2.2550(7), Rh(1)–C(19) = 1.853(3), C(19)–O(7) = 1.127(4). Selected angles (deg): P(1)–Rh(1)–Cl(1) = 90.90(3), Cl(1)–Rh(1)–P(2) = 89.87(3), P(2)–Rh(1)–C(19) = 89.74(9), C(19)–Rh(1)–P(1) = 89.50(9), P(1)–Rh(1)–P(2) = 177.93(3), Cl(1)–Rh(1)–C(19) = 179.58(10), Rh(1)–C(19)–O(7) = 179.5(3).

Figure S2. Space-filling model of **1**.

4. Typical Procedure for Mono-Arylation of Heteroarenes (Conventional Heating Protocol)

A 20-mL glass vessel equipped with J. Young® O-ring tap, containing a magnetic stirring bar, was flame-dried under vacuum and filled with argon after cooling to room temperature. To this vessel were added Rh complex **1** (14.9 mg, 12 μmol), Ag_2CO_3 (111.9 mg, 0.41 mmol), 1,2-dimethoxyethane (36.0 mg, 0.40 mmol), 3-methoxythiophene (**2a**: 68.5 mg, 0.60 mmol), iodobenzene (**3a**: 81.6 mg, 0.40 mmol), and dry *m*-xylene (2.0 mL) under a stream of argon. The vessel was sealed with O-ring tap, and then heated at 150 °C for 12 h in a 8-well reaction block with stirring. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad ($\text{EtOAc}/\text{CHCl}_3$). The filtrate was evaporated and the residue was subjected to gel permeation chromatography (CHCl_3) to afford 3-methoxy-2-phenylthiophene (**4aa**: 57.1 mg, 75%) as pale yellow oil. The double-arylation product **5aaa** was isolated in 8% yield.

3-Methoxy-2-phenylthiophene (4aa): ^1H NMR (600 MHz, CDCl_3) δ 3.91 (s, 3H), 6.92 (d, J = 5.5 Hz, 1H), 7.14 (d, J = 5.5 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.73 (d, J = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 58.7, 117.5, 120.2, 122.1, 126.4, 126.9, 128.5, 133.4, 153.7. HRMS (ESI-TOF) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{OS}$ $[\text{MH}]^+$: 191.0531, found 191.0540.

5. Typical Procedure for Mono-Arylation of Heteroarenes (Microwave Heating Protocol)

A 10-mL flame-dried microwave vial containing a magnetic stirring bar was fitted with a septum and cooled under a stream of argon. To this vial were added Rh complex **1** (18.8 mg, 15 μmol), Ag_2CO_3 (138.7 mg, 0.50 mmol), 1,2-dimethoxyethane (45.1 mg, 0.50 mmol), 3-methoxythiophene (**2a**: 86.6 mg, 0.75 mmol), iodobenzene (**3a**: 102.0 mg, 0.50 mmol), and dry *m*-xylene (2.5 mL). The vial was sealed and heated with stirring at 200 °C for 30 min in a CEM Discover microwave apparatus. After the reaction vial was cooled down to room temperature, the mixture was passed through a short silica gel pad ($\text{EtOAc}/\text{CHCl}_3$). The filtrate was evaporated and the residue was subjected to gel permeation chromatography (CHCl_3) to afford **4aa** (69.7 mg, 73%) as pale yellow oil. The double-arylation product **5aaa** was isolated in 9% yield.

6. Typical Procedure for Double-Arylation of Heteroarenes (Microwave Heating Protocol)

A 10-mL flame-dried microwave vial containing a magnetic stirring bar was fitted with a septum and cooled under a stream of argon. To this vial were added Rh complex 1 (29.5 mg, 24 μmol), Ag₂CO₃ (220.6 mg, 0.80 mmol), 3-methoxythiophene (2a: 45.7 mg, 0.40 mmol), iodobenzene (3a: 179.5 mg, 0.88 mmol), and dry *m*-xylene (2.0 mL). The vial was sealed and heated with stirring at 200 $^\circ\text{C}$ for 30 min in a CEM Discover microwave apparatus. After the reaction vial was cooled down to room temperature, the mixture was passed through a short silica gel pad (EtOAc/CHCl₃). The filtrate was evaporated and the residue was subjected to gel permeation chromatography (CHCl₃) to afford 3-methoxy-2,5-diphenylthiophene (5aaa: 84.1 mg, 79%) as pale yellow solid.

3-Methoxy-2,5-diphenylthiophene (5aaa): ¹H NMR (600 MHz, CDCl₃) δ 3.93 (s, 3H), 7.13 (s, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 58.8, 113.4, 120.0, 125.1, 126.4, 126.7, 127.7, 128.5, 128.9, 133.4, 134.2, 139.8, 154.0. HRMS (ESI-TOF) *m/z* calcd for C₁₇H₁₅OS [MH]⁺: 267.0844, found 267.0834.

7. Compound Data for Other C–H Arylation Products

All biaryl compounds (4) described in this section were prepared using a microwave heating protocol (150–200 $^\circ\text{C}$, 30 min) following the typical procedure given in Section 5 (page S5). Compounds were purified by either flash silica gel column chromatography (EtOAc/hexane) or gel permeation chromatography (CHCl₃).

2-(*p*-Acetylphenyl)-3-methoxythiophene (4ab): 94% isolated yield (99% NMR yield) from 3-methoxythiophene (2a) and 4-iodoacetophenone (3b) (microwave heating, 200 $^\circ\text{C}$, 30 min). ¹H NMR (600 MHz, CDCl₃) δ 2.59 (s, 3H), 3.95 (s, 3H), 6.94 (d, *J* = 5.5 Hz, 1H), 7.24 (d, *J* = 5.5 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 2H), 7.94 (d, *J* = 8.9 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 26.5, 58.7, 117.3, 118.7, 124.0, 126.2, 128.7, 134.4, 138.3, 155.3, 197.4. HRMS (ESI-TOF) *m/z* calcd for C₁₃H₁₃O₂S [MH]⁺: 233.0636, found 233.0635.

3-Methoxy-2,3'-bithiophene (4ac): 52% isolated yield (58% NMR yield) from 3-methoxythiophene (**2a**) and 3-iodothiophene (**3c**) (microwave heating, 200 °C, 30 min). ¹H NMR (600 MHz, CDCl₃) δ 3.92 (s, 3H), 6.88 (d, *J* = 5.5 Hz, 1H), 7.06 (d, *J* = 5.5 Hz, 1H), 7.29 (dd, *J* = 4.8, 2.8 Hz, 1H), 7.38 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.57 (dd, *J* = 2.8, 1.4 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 58.6, 116.0, 116.9, 119.5, 121.1, 125.2, 126.5, 133.3, 153.4. HRMS (ESI-TOF) *m/z* calcd for C₉H₆OS₂ [MH]⁺: 197.0095, found 197.0094.

2-Ethyl-5-phenylthiophene (4ba): 76% isolated yield (99% NMR yield) from 2-ethylthiophene (**2b**) and iodobenzene (**3a**) (microwave heating, 200 °C, 30 min). ¹H NMR (600 MHz, CDCl₃) δ 1.34 (t, *J* = 7.6 Hz, 3H), 2.86 (q, *J* = 7.6 Hz, 2H), 6.75 (d, *J* = 3.4 Hz, 1H), 7.12 (d, *J* = 3.4 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 15.9, 23.6, 122.7, 124.3, 125.5, 127.0, 128.8, 134.8, 141.6, 147.2. HRMS (FAB) *m/z* calcd for C₁₂H₁₂S [M]⁺: 188.0660, found 188.0661.

2-(*p*-Acetylphenyl)-5-ethylthiophene (4bb): 79% isolated yield (87% NMR yield) from 2-ethylthiophene (**2b**) and 4-iodoacetophenone (**3b**) (microwave heating, 200 °C, 30 min). ¹H NMR (600 MHz, CDCl₃) δ 1.34 (t, *J* = 7.6 Hz, 3H), 2.58 (s, 3H), 2.87 (q, *J* = 7.6 Hz, 2H), 6.78 (d, *J* = 3.4 Hz, 1H), 7.23 (d, *J* = 3.4 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 15.7, 23.6, 26.5, 124.4, 124.8, 125.0, 129.0, 135.2, 139.1, 140.0, 149.2, 197.2. HRMS (ESI-TOF) *m/z* calcd for C₁₄H₁₅OS [MH]⁺: 231.0844, found 231.0843.

2-Ethyl-5-*p*-tolylthiophene (4bd): 50% isolated yield (64% NMR yield) from 2-ethylthiophene

(**2b**) and 4-iodotoluene (**3d**) (microwave heating, 180 °C, 30 min). ^1H NMR (600 MHz, CDCl_3) δ 1.33 (t, $J = 7.6$ Hz, 3H), 2.34 (s, 3H), 2.85 (q, $J = 7.6$ Hz, 2H), 6.73 (d, $J = 3.4$ Hz, 1H), 7.07 (d, $J = 3.4$ Hz, 1H), 7.15 (d, $J = 7.6$ Hz, 2H), 7.44 (d, $J = 7.6$ Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 15.9, 21.1, 23.6, 122.1, 124.2, 125.4, 129.4, 132.0, 136.8, 141.7, 146.6. HRMS (FAB) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{S}$ $[\text{M}]^+$: 202.0816, found 202.0819.

5-(p-Acetylphenyl)-2,2'-bithiophene (4cb): 64% isolated yield from 2,2'-bithiophene (**2c**) and 4-iodoacetophenone (**3b**) (microwave heating, 200 °C, 30 min). ^1H NMR (600 MHz, CDCl_3) δ 2.61 (s, 3H), 7.04 (dd, $J = 5.5, 4.1$ Hz, 1H), 7.17 (d, $J = 3.4$ Hz, 1H), 7.23 (d, $J = 3.4$ Hz, 1H), 7.25 (d, $J = 5.5$ Hz, 1H), 7.34 (d, $J = 4.1$ Hz, 1H), 7.67 (d, $J = 8.3$ Hz, 2H), 7.96 (d, $J = 8.3$ Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 26.5, 124.1, 124.8, 124.9, 125.27, 125.33, 128.0, 129.1, 135.7, 137.0, 138.4, 138.5, 141.4, 197.2. HRMS (ESI-TOF) m/z calcd for $\text{C}_{16}\text{H}_{13}\text{OS}_2$ $[\text{MH}]^+$: 285.0408, found 285.0416.

2-(p-Acetylphenyl)-4,5-dimethylfuran (4db): 64% isolated yield from 2,3-dimethylfuran (**2d**) and 4-iodoacetophenone (**3b**) (microwave heating, 200 °C, 30 min). ^1H NMR (600 MHz, CDCl_3) δ 1.99 (s, 3H), 2.29 (s, 3H), 2.58 (s, 3H), 6.59 (s, 1H), 7.64 (d, $J = 8.2$ Hz, 2H), 7.93 (d, $J = 8.2$ Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 9.9, 11.6, 26.4, 111.1, 116.8, 122.7, 128.9, 134.8, 135.2, 149.1, 149.7, 197.3. HRMS (ESI-TOF) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2$ $[\text{MH}]^+$: 215.1072, found 215.1073.

2-(p-Cyanophenyl)-4,5-dimethylfuran (4de): 66% isolated yield from 2,3-dimethylfuran (**2d**) and 4-iodobenzonitrile (**3e**) (microwave heating, 150 °C, 30 min). ^1H NMR (600 MHz, CDCl_3) δ 1.99 (s, 3H), 2.29 (s, 3H), 6.59 (s, 1H), 7.59 (d, $J = 8.3$ Hz, 2H), 7.63 (d, $J = 8.3$ Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 9.8, 11.6, 109.1, 111.7, 117.0, 119.2, 123.1, 132.4, 134.9, 148.9, 149.5. HRMS (ESI-TOF) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{NO}$ $[\text{MH}]^+$: 198.0919, found 198.0918.

3-(p-Acetylphenyl)-1-phenylpyrrole (4eb): 58% isolated yield (86% NMR yield) from N-phenylpyrrole (**2e**) and 4-iodoacetophenone (**3b**) (microwave heating, 200 °C, 30 min). ¹H NMR (600 MHz, CDCl₃) δ 2.56 (s, 3H), 6.66–6.67 (m, 1H), 7.09–7.11 (m, 1H), 7.24–7.27 (m, 1H), 7.40–7.44 (m, 5H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 26.4, 108.8, 117.0, 120.5, 120.9, 124.7, 125.6, 126.1, 129.0, 129.7, 134.4, 140.19, 140.22, 197.5. HRMS (FAB) *m/z* calcd for C₁₈H₁₅NO [M]⁺: 261.1154, found 261.1153.

3-(p-Acetylphenyl)-1-methylindole (4fb): 57% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 2.62 (s, 3H), 3.84 (s, 3H), 7.23 (dd, *J* = 8.3, 6.8 Hz, 1H), 7.31 (dd, *J* = 8.3, 6.8 Hz, 1H), 7.34 (s, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 26.5, 33.0, 109.8, 115.5, 119.8, 120.5, 122.3, 125.8, 126.6, 127.6, 129.0, 134.2, 137.7, 140.8, 197.6. HRMS (ESI-TOF) *m/z* calcd for C₁₇H₁₆NO [MH]⁺: 250.1232, found 250.1234.

2-(p-Acetylphenyl)-1-methylindole (4fb'):³ 23% isolated yield. ¹H NMR (600 MHz, CDCl₃) δ 2.66 (s, 3H), 3.79 (s, 3H), 6.66 (s, 1H), 7.16 (dd, *J* = 8.2, 6.8 Hz, 1H), 7.29 (dd, *J* = 8.2, 6.8 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 26.7, 31.4, 103.0, 109.8, 120.2, 120.8, 122.4, 127.9, 128.6, 129.2, 136.1, 137.4, 138.9, 140.2, 197.6. HRMS (ESI-TOF) *m/z* calcd for C₁₇H₁₆NO [MH]⁺: 250.1232, found 250.1224.

8. Direct Arylation of Anisole

A 10-mL flame-dried microwave vial containing a magnetic stirring bar was fitted with a septum and cooled under a stream of argon. To this vial were added Rh complex **1** (32.3 mg, 26

(3) Lane, B. S.; Sames, D. *Org. Lett.* **2004**, *6*, 2897.

μmol), Ag_2CO_3 (139.9 mg, 0.51 mmol), anisole (**6**: 1.49 g, 13.8 mmol), and 1-iodo-4-nitrobenzene (**3f**: 128.5 mg, 0.52 mmol). The vial was sealed and heated with stirring at 200 °C for 30 min in a CEM Discover microwave apparatus. After the reaction vial was cooled down to room temperature, the mixture was passed through a short silica gel pad (EtOAc). The filtrate was evaporated and the residue was subjected to gel permeation chromatography (CHCl_3) to afford biaryls (58.1 mg, 51%) as a mixture of *para*-isomer (**7**) and *ortho*-isomer (**8**). The ratio of **7**/**8** was determined to be 71/29 by ^1H -NMR analysis. These isomers could be separated by HPLC (silica gel).

4-Methoxy-4'-nitrobiphenyl (7):⁴ ^1H NMR (600 MHz, CDCl_3) δ 3.87 (s, 3H), 7.01 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.9 Hz, 2H), 7.67 (d, J = 8.9 Hz, 2H), 8.25 (d, J = 8.9 Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 55.4, 114.6, 124.1, 127.0, 128.5, 131.0, 146.5, 147.1, 160.4. HRMS (FAB) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_3$ $[\text{M}]^+$: 229.0739, found 229.0739.

4-Methoxy-2-nitrobiphenyl (8):⁵ ^1H NMR (600 MHz, CDCl_3) δ 3.80 (s, 3H), 6.98 (d, J = 8.3 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.36 (dd, J = 8.3, 7.6 Hz, 1H), 7.65 (d, J = 8.9 Hz, 2H), 8.21 (d, J = 8.9 Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 55.6, 111.4, 121.1, 123.2, 128.2, 130.1, 130.3, 130.6, 145.4, 146.6, 156.4. HRMS (FAB) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_3$ $[\text{M}]^+$: 229.0739, found 229.0739.

9. Direct Arylation of 1,3-Dimethoxybenzene

A 10-mL flame-dried microwave vial containing a magnetic stirring bar was fitted with a septum and cooled under a stream of argon. To this vial were added Rh complex **1** (31.5 mg, 26 μmol), Ag_2CO_3 (139.7 mg, 0.51 mmol), 1,3-dimethoxybenzene (**9**: 1.90 g, 13.7 mmol), and 1-iodo-4-nitrobenzene (**3f**: 127.5 mg, 0.50 mmol). The vial was sealed and heated with stirring at 200 °C for 30 min in a CEM Discover microwave apparatus. After the reaction vial was cooled down to room temperature, the mixture was passed through a short silica gel pad (EtOAc). The filtrate was evaporated and the residue was subjected to gel permeation chromatography (CHCl_3) to afford **10** (98.5 mg, 76%) as pale yellow solid.

2,4-Dimethoxy-4'-nitrobiphenyl (10):⁴ ^1H NMR (600 MHz, CDCl_3) δ 3.82 (s, 3H), 3.86 (s, 3H), 6.58 (d, J = 2.1 Hz, 1H), 6.59 (dd, J = 8.4, 2.1 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.9 Hz, 2H), 8.21 (d, J = 8.9 Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 55.4, 55.5, 99.0, 105.1, 121.0, 123.2, 129.9, 131.3, 145.3, 146.1, 157.5, 161.5. HRMS (FAB) m/z calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_4$ $[\text{M}]^+$: 259.0845, found 259.0847.

(4) Mee, S. P. H.; Lee, V.; Baldwin, J. E. *Chem. Eur. J.* **2005**, *11*, 3294.

(5) Dai, M.; Liang, B.; Wang, C.; Chen, J.; Yang, Z. *Org. Lett.* **2004**, *6*, 221.

10. ^1H and ^{13}C NMR Spectra of Arylation Products

^1H -NMR (600 MHz, CDCl_3) of 4aa

^{13}C -NMR (150 MHz, CDCl_3) of 4aa

^1H -NMR (600 MHz, CDCl_3) of 5aaa

^{13}C -NMR (150 MHz, CDCl_3) of 5aaa

^1H -NMR (600 MHz, CDCl_3) of 4ab

^{13}C -NMR (150 MHz, CDCl_3) of 4ab

^1H -NMR (600 MHz, CDCl_3) of 4ac

^{13}C -NMR (150 MHz, CDCl_3) of 4ac

^1H -NMR (600 MHz, CDCl_3) of 4ba

^{13}C -NMR (150 MHz, CDCl_3) of 4ba

^1H -NMR (600 MHz, CDCl_3) of 4bb

^{13}C -NMR (150 MHz, CDCl_3) of 4bb

^1H -NMR (600 MHz, CDCl_3) of 4bd

^{13}C -NMR (150 MHz, CDCl_3) of **4bd**

^1H -NMR (600 MHz, CDCl_3) of 4cb

^{13}C -NMR (150 MHz, CDCl_3) of 4cb

^1H -NMR (600 MHz, CDCl_3) of 4db

^{13}C -NMR (150 MHz, CDCl_3) of 4db

^1H -NMR (600 MHz, CDCl_3) of 4de

^{13}C -NMR (150 MHz, CDCl_3) of 4de

^1H -NMR (600 MHz, CDCl_3) of 4eb

^{13}C -NMR (150 MHz, CDCl_3) of 4eb

^1H -NMR (600 MHz, CDCl_3) of 4fb

^{13}C -NMR (150 MHz, CDCl_3) of 4fb

^1H -NMR (600 MHz, CDCl_3) of 4fb'

^{13}C -NMR (150 MHz, CDCl_3) of 4fb'

^1H -NMR (600 MHz, CDCl_3) of 7

^{13}C -NMR (150 MHz, CDCl_3) of 7

^1H -NMR (600 MHz, CDCl_3) of **8**

^{13}C -NMR (150 MHz, CDCl_3) of 8

^1H -NMR (600 MHz, CDCl_3) of 10

^{13}C -NMR (150 MHz, CDCl_3) of 10