Supporting Information for
Iron-catalyzed oxidative coupling of arylboronic acids with benzene derivatives through homolytic aromatic substitution mechanism
Nanase Uchiyama, Eiji Shirakawa,* Ryo Nishikawa, and Tamio Hayashi*

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**General Remarks.** All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a nitrogen atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL JNM LA500 spectrometer (1H, 500 MHz) or a JEOL JNM LA600 spectrometer (13C, 150 MHz) using tetramethylsilane (1H and 13C) as an internal standard. GC spectra were taken on Shimazu GC-18A. GC-MS spectra were taken on Shimazu GCMS-QP5050A. High-resolution mass spectra were obtained with a Bruker Daltonics microTOF-Q spectrometer (ESI). Di-tert-butyli hyponitrite was prepared according to a literature procedure. Unless otherwise noted, reagents were commercially available and used without further purification. 1H NMR analysis using p-dimethoxybenzene as an internal standard showed that arylboronic acids used are free from the corresponding boroxines in DMSO-d6 and the molar amounts of the arylboron moieties are within a margin of error of plus or minus 5% compared with those calculated on the assumption that the arylboronic acids are pure.

**Preparation of 4,7-Bis[4-(trifluoromethyl)phenyl]-1,10-phenanthroline (L3).** The title compound was prepared according to a literature method for the coupling of 4,7-dibromo-1,10-phenanthroline with 4-methoxy-3,5-dimethylphenylzinc chloride with a slight modification. To a solution of 1-bromo-4-(trifluoromethyl)benzene (339 mg, 1.50 mmol) in THF (10 mL) at −78 °C was added n-BuLi (0.94 mL, 1.6 M solution in hexane, 1.5 mmol). To this mixture was added at −78 °C a solution of ZnCl2 (204 mg, 1.50 mmol) in THF (5 mL), cooled by ice bath, via cannula. It was allowed to warm to room temperature and a suspension of 4,7-dichloro-1,10-phenanthroline (125 mg, 0.500 mmol) and Pd(PPh3)4 (28.9 mg, 0.0250 mmol) in THF (10 mL) was added to the organozinc intermediate using a large gauge cannula. The mixture was heated at reflux for 12 h, cooled to room temperature, quenched with sat. NH4Cl aq. (15 mL), and neutralized with sat. NaHCO3 aq. (30 mL). After extraction with EtOAc (30 mL x 3) and washing with brine, the organic layer was dried over MgSO4 and concentrated. The residue was subjected to SiO2 column chromatography (EtOAc then CH2Cl2/MeOH/NH3 aq. = 93/5/2) to give 4,7-bis[4-(trifluoromethyl)phenyl]-1,10-phenanthroline (L3: 161 mg, 59% yield).

**4,7-Bis[4-(trifluoromethyl)phenyl]-1,10-phenanthroline (L3).**

A white solid. 1H NMR (500 MHz, CDCl3) δ 7.61 (d, J = 4.4 Hz, 2 H), 7.66 (d, J = 8.3 Hz, 4 H), 7.78 (s, 2 H), 7.82 (d, J = 8.3 Hz, 4 H), 9.30 (d, J = 4.4 Hz, 2 H). 13C NMR (150 MHz, CDCl3) δ123.6, 124.03, 124.04 (q, J = 274 Hz), 125.8 (q, J = 2.9 Hz), 126.2, 130.1, 130.9 (q, J = 32 Hz), 141.5, 146.9, 147.0, 150.1. HRMS (ESI) Calcd for C26H14F6N2+: [M+Na]+, 491.0959.

**Iron-Catalyzed Oxidative Coupling of 4-Bromophenylboronic Acid with Benzene (Table 1): General Procedure.** To a partial suspension of an iron complex (0.0120 mmol) and 4-bromophenylboronic acid (1a: 24.1 mg, 0.120 mmol) in benzene (2a: 1.07 mL, 12.0 mmol) in a 20 mL Schlenk tube was added a ligand (0.012 mmol) and t-BuOOt-Bu (3: 44.0 µL, 0.240 mmol). After stirring at 80 °C for the time specified in Table 1, nonane as an internal standard was added. An aliquot of the solution was subjected to GC analysis. The rest of the solution was poured into brine (20 mL) and extracted with Et2O (25 mL x 3). The organic layer was dried over MgSO4, filtered, and concentrated. The residue was subjected to 1H NMR
analysis using MeNO₂ as an internal standard.

**4-Bromobiphenyl (4ao).** A white solid. 

\[ \text{Fe(OTf)}_3 (10.1 \text{ mg}, 0.0200 \text{ mmol}) + 4,7-
\text{bis[4-(trifluoromethyl)phenyl]-1,10-phenanthroline (L3: 9.4 \text{ mg},}
0.0200 \text{ mmol)} + 4 \text{mmol arylboronic acid in an arene (2:}
20.0 \text{ mmol) in a 20 mL Schlenk tube was added t-BuOOt-Bu (3: 73.0}
\mu \text{L}, 0.400 \text{ mmol). After stirring at 80 °C for the time specified}
in Table 2 or Scheme 1, the resulting solution was poured into brine
(20 mL) and extracted with Et₂O (25 mL x 3). The organic layer was
dried over MgSO₄, filtered, and concentrated. The residue was subjected
to SiO₂ chromatography (PTLC) to give the corresponding coupling
product (4).

\[ \text{Biphenyl (4bo).} \]

\[ \text{4-Methylbiphenyl (4co).} \]

\[ \text{4-Chlorobiphenyl (4do).} \]

\[ \text{3-Bromobiphenyl (4eo).} \]

\[ \text{2-Chlorobiphenyl (4fo).} \]

\[ \text{4-(Trifluoromethyl)biphenyl (4go).} \]

\[ \text{4-Cyanobiphenyl (4ho).} \]
A mixture of three isomers of (4-fluorophenyl)chlorobenzene (o/m/p = 64/20/16) (4np). A colorless oil. The ratio of o/m/p was determined as follows. $^1$H NMR showed that the peaks of the ortho isomer are the largest and those of the para isomer are the smallest, determined mainly from the integral the triplets (2 H, ortho to F) that appear at 7.1209 ppm (the ortho isomer), 7.13 (meta) and 7.1265 (para). However, the determination of the exact isomer ratio was difficult because of overlap of the peaks. The ratio of o/m/p was estimated by the integral on GC to be 64/20/16.

4-Ethoxycarboxylibiphenyl (4io). A white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.42 (t, $J = 7.1$ Hz, 3 H), 4.41 (q, $J = 7.1$ Hz, 2 H), 7.39 (t, $J = 7.4$ Hz, 1 H), 7.47 (t, $J = 7.6$ Hz, 2 H), 7.63 (d, $J = 7.2$ Hz, 2 H), 7.66 (d, $J = 8.2$ Hz, 2 H), 8.12 (d, $J = 8.2$ Hz, 2 H).

4-Methoxybiphenyl (4jo). A white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.86 (s, 3 H), 6.98 (d, $J = 8.4$ Hz, 2 H), 7.30 (t, $J = 7.4$ Hz, 1 H), 7.42 (t, $J = 7.6$ Hz, 2 H), 7.53 (d, $J = 8.4$ Hz, 2 H), 7.55 (d, $J = 7.2$ Hz, 2 H).

3-Methoxybiphenyl (4ko). A colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.87 (s, 3 H), 6.91 (dd, $J = 8.2$, 2.6 Hz, 1 H), 7.14 (t, $J = 2.0$ Hz, 1 H), 7.19 (d, $J = 7.6$ Hz, 1 H), 7.33–7.38 (m, 2 H), 7.44 (t, $J = 7.8$ Hz, 2 H), 7.59 (d, $J = 7.2$ Hz, 2 H).

3-Chloro-4-methoxybiphenyl (4lo). A white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.95 (s, 3 H), 7.00 (d, $J = 8.6$ Hz, 1 H), 7.33 (t, $J = 7.4$ Hz, 1 H), 7.42 (t, $J = 7.8$ Hz, 2 H), 7.45 (dd, $J = 8.6$, 2.3 Hz, 1 H), 7.53 (d, $J = 7.1$ Hz, 2 H), 7.62 (d, $J = 2.3$ Hz, 1 H).

3-Phenylthiophene (4mo). A white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.30 (t, $J = 7.4$ Hz, 1 H), 7.38–7.43 (m, 4 H), 7.46 (dd, $J = 2.6$, 1.8 Hz, 1 H), 7.61 (d, $J = 8.2$ Hz, 2 H).

2-Chloro-4’-fluorobiphenyl. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.12 (t, $J = 8.7$ Hz, 2 H), 7.25–7.33 (m, 3 H), 7.38–7.43 (m, 2 H), 7.44–7.48 (m, 1 H).

3-Chloro-4’-fluorobiphenyl. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.13 (t, $J = 8.7$ Hz, 2 H), 7.31 (m, 1 H), 7.36 (t, $J = 7.8$ Hz, 1 H), 7.39–7.43 (m, 1 H), 7.45–7.54 (m, 3 H).

4-Chloro-4’-fluorobiphenyl. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.13 (t, $J = 8.8$ Hz, 2 H), 7.39–7.43 (m, 2 H), 7.45–7.48 (m, 2 H), 7.49–7.54 (m, 2 H).
4′-(Ethoxycarbonyl)-2,5-difluorobiphenyl (4iq). A white solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.42 (t, \(J = 7.2\) Hz, 3 H), 4.41 (q, \(J = 7.2\) Hz, 2 H), 7.02–7.07 (m, 1 H), 7.11–7.19 (m, 2 H), 7.61 (d, \(J = 8.7\) Hz, 2 H), 8.13 (d, \(J = 8.7\) Hz, 2 H).

4′-(Ethoxycarbonyl)-2,4,6-trifluorobiphenyl (4ir). A white solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.41 (t, \(J = 7.1\) Hz, 3 H), 4.41 (q, \(J = 7.1\) Hz, 2 H), 6.78 (t, \(J = 8.2\) Hz, 2 H), 7.50 (d, \(J = 8.2\) Hz, 2 H), 8.13 (d, \(J = 8.2\) Hz, 2 H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 14.4, 61.2, 100.8 (td, \(J = 24, 7.2\) Hz), 114.2 (t, \(J = 22\) Hz), 129.6, 130.36, 130.43, 133.0, 160.3 (ddd, \(J = 250, 15, 10\) Hz), 162.3 (dt, \(J = 250, 16\) Hz), 166.3. Anal. Calcd for C\(_{13}\)H\(_{10}\)F\(_3\)O\(_2\): C, 64.29; H, 3.96. Found: C, 64.33; H, 3.79.

A mixture of two isomers of (4-bromophenyl)thiophene (2-/3- = 84/16) (4as). A pale yellow solid. The isomer ratio was determined by GC and confirmed by \(^1\)H NMR.

\[ \text{2-(4-Bromophenyl)thiophene.} \]
\[ \text{3-(4-Bromophenyl)thiophene.} \]

A mixture of two isomers of (3-methoxyphenyl)-3-bromothiophene (2-/5- = 75/25) (4kt). A colorless oil. The isomer ratio was determined by GC and confirmed by \(^1\)H NMR.

\[ \text{3-Bromo-2-(3-methoxyphenyl)thiophene.} \]
\[ \text{4-Bromo-2-(3-methoxyphenyl)thiophene.} \]

ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) of Fe(OTf)\(_3\) (Footnote 15). A sample was prepared by diluting Fe(OTf)\(_3\) with 1-methyl-2-pyrrolidone in 10,000-fold. Analysis was conducted on Agilent 7500cs using XSTC-7, 13B (SPEX) as a standard solution for calibration curve. The contents are shown in Table S1.

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**Reaction of 4-Bromophenylboronic Acid with Di-tert-butyl Hyponitrite and CDCl₃ (Scheme 2).** A solution of 4-bromophenylboronic acid (1a: 24.1 mg, 0.120 mmol) and di-tert-butyl hyponitrite (25.1 mg, 0.144 mmol) in CDCl₃ (1.0 mL) was stirred at 60 °C for 12 h. After adding MeNO₂ as an internal standard, the resulting solution was subjected to ¹H NMR analysis to determine the yield of 1-bromo-4-deuteriobenzene (6) and its deuteriation ratio.

**Reaction of Iron Complexes with Di-tert-butyl Peroxide in the Presence of 4-Bromophenylboronic Acid and CDCl₃ (Scheme 3): General Procedure.** To a partial suspension of Fe(OTf)₃, (30.2 mg, 0.0600 mmol), a ligand (0.060 mmol), and 4-bromophenylboronic acid (1a: 12.0 mg, 0.0600 mmol) in 0.60 mL of CDCl₃ in a 20 mL Schlenk tube was added tert-BuOOH (3a: 11 µL, 0.059 mmol). After stirring at 60 °C for the time specified in Scheme 3, nonane as an internal standard was added to the resulting solution. An aliquot of the solution was subjected to GC analysis to determine the yield of 1-bromo-4-deuteriobenzene (6) and the conversion of 3. After concentration, the residue was subjected to SiO₂ chromatography (PTLC) to obtain 6 for determination of its deuteriation ratio by ¹H NMR.

**References**

$^1$H and $^{13}$C NMR Spectra of a Ligand and the Coupling Products
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