Electronic Supplementary Information for

Rhodium-Catalyzed Oxidative Coupling of Aromatic Imines with Internal Alkynes via Regioselective C–H Bond Cleavage

Tatsuya Fukutani, Nobuyoshi Umeda, Koji Hirano, Tetsuya Satoh,* and Masahiro Miura*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

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General: S2 Experimental Procedures: S2 Characterization Data of Products: S3 – S6 Figure S1: S7 Figure S2: S7 References: S7 ¹H and ¹³C NMR Spectra of Products: S8 – S25 **General.** ¹H and ¹³C NMR spectra were recorded at 400 and 100 MHz, respectively, for CDCl₃ solutions. MS data were obtained by EI, unless noted. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm x 25 m). GC-MS analysis was carried out using a CBP-1 capillary column (i. d. 0.25 mm x 25 m) on a Shimadzu QP-5050. The structures of all products listed below were unambiguously determined by ¹H and ¹³C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

Imines $\mathbf{1b}$ - \mathbf{g}^{14} and $\mathbf{6}^{15}$ and diarylacetylenes $\mathbf{2b}$ - \mathbf{d}^{16} were prepared according to published procedures. Other starting materials were commercially available.

Experimental Procedures. The following experimental procedures may be regarded as typical in methodology and scale.

Procedure for the reaction of *N*-benzylideneaniline (1a) with diphenylacetylene (2a) (entry 6 in Table 1): To a 20 mL two-necked flask were added *N*-benzylideneaniline (1a) (1 mmol, 181 mg), diphenylacetylene (2a) (0.5 mmol, 89 mg), $[(Cp*RhCl_2)_2]$ (0.01 mmol, 6 mg), $Cu(OAc)_2 \cdot H_2O$ (1 mmol, 199 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMF (3 mL) were added. The resulting mixture was stirred under N₂ at 80 °C for 6 h. GC and GC-MS analyses of the mixtures confirmed formation of **3a**. Then, the reaction mixture was cooled to room temperature and extracted with EtOAc (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times), and dried over Na₂SO₄. Product **3a** (136 mg, 76%) was isolated by column chromatography on silica gel using hexane-ethyl acetate (99:1, v/v) as eluant.

Procedure for the reaction of benzophenone imine (4) with diphenylacetylene (2a) (entry 1 in Table 3): To a 20 mL two-necked flask were added benzophenone imine (4) (0.5 mmol, 91 mg), diphenylacetylene (2a) (0.5 mmol, 89 mg), $[(Cp*RhCl_2)_2]$ (0.005 mmol, 3 mg), $Cu(OAc)_2 \cdot H_2O$ (1 mmol, 199 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMF (3 mL) were added. The resulting mixture was stirred under N₂ at 80 °C for 2 h. GC and GC-MS analyses of the mixtures confirmed formation of **5**. Then, the reaction mixture was cooled to room temperature and extracted with Et_2O (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times), and dried over Na₂SO₄. Product **5** (160 mg, 90%) was isolated by column chromatography on silica gel using hexane-ethyl acetate (99:1, v/v) as eluant.

Characterization Data of Products.

N-(**2**,**3**-Diphenyl-1*H*-inden-1-ylidene)benzenamine (**3**a): Mp 173-174 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.47 (d, *J* = 7.3 Hz, 1H), 6.89 (dt, *J* = 7.7, 1.8 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 7.15-7.28 (m, 6H), 7.32-7.40 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 117.87, 120.77, 123.83, 125.91, 127.10, 127.27, 127.70, 128.25, 128.27, 128.52,129.08 (overlapped), 130.75, 131.12, 132.70, 133.67, 136.64, 145.43, 148.61, 152.15, 166.11; HRMS m/z (M+) calcd for C₂₇H₁₉N: 357.1517, found: 357.1514. Anal. calcd for C₂₇H₁₉N: C, 90.72; H, 5.36; N, 3.89, found: C, 90.43; H, 5.41; N, 3.89.

N-(5-Chloro-2,3-diphenyl-1*H*-inden-1-ylidene)benzenamine (3b): Mp 212-213 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.37 (d, J = 8.1 Hz, 1H), 6.86 (d, J = 7.4 Hz, 1H), 6.94 (d, J = 8.5 Hz, 2H), 7.14-7.41 (m, 14H); ¹³C NMR (100 MHz, CDCl₃) δ 117.83, 121.22, 124.12, 126.34, 126.69, 126.71, 127.56, 127.77, 128.56, 128.72, 128.97, 129.13, 131.09, 132.26, 133.11, 136.96, 137.95, 147.45, 147.53, 151.82, 164.96; HRMS m/z (M+) calcd for C₂₇H₁₈ClN: 391.1128, found: 391.1124. Anal. calcd for C₂₇H₁₈ClN: C, 82.75; H, 4.63; N, 3.57, found: C, 82.46; H, 4.67; N, 3.56.

N-(**5**-Methyl-2,3-diphenyl-1*H*-inden-1-ylidene)benzenamine (**3**c): Mp 170-171 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.26 (s, 3H), 6.34 (d, *J* = 7.7 Hz, 1H), 6.69 (d, *J* = 7.7 Hz, 1H), 6.94-6.98 (m, 3H), 7.14-7.27 (m, 3H), 7.31-7.40 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 21.73, 117.98, 121.79, 123.72, 125.76, 125.82, 127.20, 127.37, 127.67, 128.18, 128.52, 129.03, 129.10, 131.11, 132.77, 133.81, 136.95, 141.31, 145.76, 148.45, 152.32, 166.03; HRMS m/z (M+) calcd for C₂₈H₂₁N: 371.1674, found: 371.1672.

4-Chloro-*N***-(2,3-diphenyl-1***H***-inden-1-ylidene)benzenamine (3d): Mp 215-216 °C; ¹H NMR (400 MHz, CDCl₃) \delta 6.56 (d,** *J* **= 7.7 Hz, 1H), 7.18-7.28 (m, 3H), 7.18-7.28 (m, 5H), 7.30-7.39 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) \delta 119.43, 120.97, 125.86, 127.20, 127.38, 127.74 128.12, 128.39, 128.54, 129.03, 129.17, 129.20, 131.04 (overlapped), 132.52, 133.47, 136.54, 145.46, 148.99, 150.52, 166.71; HRMS m/z (M+) calcd for C₂₇H₁₈CIN: 391.1128, found: 391.1124. Anal. calcd for C₂₇H₁₈CIN: C, 82.75; H, 4.63; N, 3.57, found: C, 82.73; H, 4.70; N, 3.58.**

4-Methoxy-*N***-(2,3-diphenyl-1***H***-inden-1-ylidene)benzenamine** (**3e**): Mp 169-170 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.86 (s, 3H), 6.64 (d, *J* = 7.7 Hz, 1H), 6.90-6.95 (m, 5H),

7.18-7.27 (m, 5H), 7.32- 7.39 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 55.54, 114.37, 119.40, 120.69, 125.74, 127.10, 127.20, 127.68, 128.15, 128.21, 128.49, 129.10, 130.64, 131.15, 132.82, 133.75, 136.87, 145.42 (overlapped), 148.36, 156.64, 166.54; HRMS m/z (M+) calcd for C₂₈H₂₁NO: 387.1623, found: 387.1619.

4-Chloro-*N***-(5-chloro-2,3-diphenyl-1***H***-inden-1-ylidene)benzenamine** (**3f**): Mp 215-217 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.47 (d, *J* = 8.1 Hz, 1H), 6.87-6.93 (m, 3H), 7.15 (s, 1H), 7.23-7.40 (m. 12H); ¹³C NMR (100 MHz, CDCl₃) δ 119.39, 121.44, 126.19, 126.60, 126.80, 127.67, 127.80, 128.67, 128.74, 128.92, 129.27, 129.48, 131.01, 132.06, 132.89, 137.28, 137.84, 147.45, 147.89, 150.13, 165.52; HRMS m/z (M+) calcd for C₂₇H₁₇Cl₂N: 425.0738, found: 425.0735.

N-(**2,3-Diphenyl-1***H*-benz[*f*]inden-1-ylidene)benzenamine (**3**g) : Mp 225-226 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.86 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.21-7.32 (m, 5H), 7.38-7.45 (m, 11H), 7.47 (s, 1H), 7.65 (d, *J* = 7.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 118.08, 119.44, 123.71, 126.08, 127.12, 127.32, 127.46, 127.73, 127.81, 128.34, 128.38, 128.60, 129.19, 129.24, 130.04, 131.06, 132.67, 132.70, 133.78, 134.44, 139.80, 141.55, 149.37, 152.66, 165.20; HRMS m/z (M+) calcd for C₃₁H₂₁N: 407.1674, found: 407.1662.

N-[2,3-Bis(4-chlorophenyl)-1*H*-inden-1-ylidene]benzenamine (3h): Mp 202-203 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.49 (d, *J* = 7.7 Hz, 1H), 6.90-6.95 (m, 3H), 7.13-7.29 (m, 9H), 7.36-7.41 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 117.78, 120.65, 124.12, 126.08, 127.51, 128.02, 128.18, 129.06, 129.17, 130.40, 130.84, 130.95, 131.80, 132.35, 133.58, 134.48, 135.79, 144.77, 147.68, 151.80, 165.65; HRMS m/z (M+) calcd for C₂₇H₁₇Cl₂N: 425.0738, found: 425.0735

N-[2,3-Bis(4-methylphenyl)-1*H*-inden-1-ylidene]benzenamine (3i): Mp 192-193 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.30 (s, 3H), 2.38 (s, 3H), 6.44 (d, *J* = 7.7 Hz, 1H), 6.85-6.89 (m, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 7.14-7.19 (m, 5H), 7.25 (m, 4H), 7.36 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.31, 21.41, 117.92, 120.66, 123.70, 125.81, 126.86, 128.37, 128.51, 129.00 (overlapped), 129.22, 129.85, 130.64, 130.78, 130.95, 136.28, 136.90, 138.07, 145.67, 148.06, 152.29, 166.31; HRMS m/z (M+) calcd for C₂₉H₂₃N: 385.1830, found: 385.1833.

N-[2,3-Bis(4-methoxyphenyl)-1*H*-inden-1-ylidene]benzenamine (3j): Mp 183-184 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.78 (s, 3H), 3.83 (s, 3H), 6.43 (d, *J* = 7.4 Hz, 1H), 6.81-6.96 (m, 7H), 7.14-7.20 (m, 3H), 7.28-7.39 (m, 6H); ¹³C NMR (100 MHz,

CDCl₃) δ 55.14, 55.25, 113.36, 114.01, 117.93, 120.50, 123.70, 125.26, 125.77, 126.06, 126.78, 128.41, 129.02, 130.49, 130.63, 132.31, 135.52, 145.72, 147.27, 152.28, 158.76, 159.48, 166.37; HRMS m/z (M+) calcd for C₂₉H₂₃NO₂: 417.1729, found: 417.1733.

N-(2,3-Dipropyl-1*H*-inden-1-ylidene)benzenamine (3k): Oil; ¹H NMR (400 MHz, CDCl₃) δ 0.98-1.07 (m, 6H), 1.60-1.68 (m, 4H), 2.47-2.56 (m, 4H), 6.28 (d, *J* = 7.3 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.4 Hz, 2H), 7.05 (d, *J* = 7.4 Hz, 1H), 7.12-7.17 (m, 2H), 7.35 (m, 2H); ¹³C NMR (100MHz, CDCl₃) δ 14.34, 14.48, 21.66, 23.43, 26.04, 27.96, 118.18, 118.63, 123.58, 125.06, 125.83, 128.73, 128.98, 130.51, 137.75, 146.32, 148.55, 152.17, 166.78; HRMS m/z (M+) calcd for C₂₁H₂₃N: 289.1830, found: 289.1832.

1,3,4-Triphenylisoquinoline (**5a**):¹⁷ Mp 130-132 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.15-7.20 (m, 3H), 7.28-7.31 (m, 2H), 7.35-7.44 (m, 5H), 7.49-7.60 (m, 5H), 7.72 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 6.6 Hz, 2H), 8.18 (d, J = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 125.44, 126.02, 126.54, 126.97, 127.27, 127.49, 127.52, 128.28, 128.30, 128.50, 129.75, 129.91, 130.23, 130.45, 131.36, 137.00, 137.58, 139.85, 140.92, 149.67, 159.79; HRMS m/z (M+) calcd for C₂₇H₁₉N: 357.1517, found: 357.1503. Anal. calcd for C₂₇H₁₉N: C, 90.72; H, 5.36; N, 3.92, found: C, 90.48; H, 5.40; N, 3.94.

3,4-Bis(4-chlorophenyl)-1-phenylisoquinoline (**5b**): Mp 193-194 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.18 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H) 7.35 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.49-7.57 (m, 4H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.66 (t, *J* = 9.1 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 8.18 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 125.54, 125.64, 126.94, 127.69, 127.96, 128.37, 128.56, 128.72, 128.85, 130.14, 130.31, 131.74, 132.60, 133.34, 133.65, 135.79, 136.77, 139.10, 139.51, 148.47, 160.32; HRMS m/z (M+) calcd for C₂₇H₁₇Cl₂N: 425.0738, found: 425.0729. Anal. calcd for C₂₇H₁₇ClN: C, 76.06; H, 4.02; N, 3.29, found: C, 75.93; H, 4.00; N, 3.31.

3,4-Bis(4-methylphenyl)-1-phenylisoquinoline (**5**c): Mp 173-174 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.27 (s, 3H), 2.41 (s, 3H), 6.99 (d, J = 7.6 Hz, 2H), 7.17-7.22 (m, 4H), 7.34 (d, J = 7.9 Hz, 2H), 7.46-7.58 (m, 5H), 7.71 (d, J = 7.9 Hz, 1H), 7.80-7.83 (m, 2H), 8.16 (d, J = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.16, 21.32, 125.31, 126.07, 126.31, 127.42, 128.23, 128.29, 128.42, 129.08, 129.44, 129.71, 130.26,

130.35, 131.16, 134.67, 136.55, 136.81, 137.25, 138.16, 139.98, 149.59, 159.48; HRMS m/z (M+) calcd for $C_{29}H_{23}N$: 385.1830, found: 385.1825.

3,4-Bis(4-methoxyphenyl)-1-phenylisoquinoline (**5d**): Mp 162-163 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.75 (s, 3H), 3.86 (s, 3H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H) 7.46-7.59 (m, 5H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 8.15 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 55.18, 55.28, 113.09, 113.95, 125.25, 125.94, 126.23, 127.45, 128.23, 128.42, 128.83, 129.73, 129.94, 130.23, 131.71, 132.38, 133.63, 137.41, 139.98, 149.37, 158.63, 158.78, 159.44; HRMS m/z (M+) calcd for C₂₉H₂₃NO₂: 417.1729, found: 417.1716.

1-Phenyl-3,4-dipropylisoquinoline (**5e**):¹⁸ Oil; ¹H NMR (400 MHz, CDCl₃) δ 1.05 (t, J = 7.4 Hz, 3H), 1.13 (t, J = 7.4 Hz, 3H), 1.71-1.88 (m, 4H), 2.99-3.08 (m, 4H), 7.38-7.52 (m, 4H), 7.62 (m, 3H), 8.00-8.03 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.36, 14.68, 23.63, 24.14, 29.98, 37.41, 123.30, 125.25, 125.28, 127.11, 128.06, 128.13, 128.23, 129.41, 130.04, 136.13, 140.20, 152.26, 158.07; HRMS m/z (M+) calcd for C₂₁H₂₃N: 289.1830, found: 289.1833.

4-Methyl-1,3-diphenylisoquinoline (**5f**): Mp 77-78 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.68 (s, 3H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.42-7.53 (m, 6H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.71 (m, 3H), 8.11 (t, *J* = 9.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 15.65, 123.03, 123.87, 125.38, 126.26, 127.42, 127.98, 128.02, 128.17, 128.24, 129.83, 130.08, 130.18, 137.06, 139.92, 141.54, 151.08, 158.20; HRMS m/z (M+) calcd for C₂₂H₁₇N: 295.1361, found: 295.1346.

N-{[2-(1,2-Diphenylethenyl)phenyl]phenylmethylene}benzenamine (7): Mp 97-98 $^{\circ}$ C; ¹H NMR (400 MHz, CDCl₃) δ 6.95-7.04 (m, 6H), 7.25-7.36 (m, 7H), 7.46-7.49 (m, 4H), 7.71-7.86 (m, 7H), 7.97 (t, J = 7.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 126.99, 127.28, 128.11, 128.13, 128.14, 128.26, 128.28, 128.53, 128.82, 129.22, 130.08, 130.45, 130.60 (overlapped), 130.91, 131.15, 131.68, 132.33, 133.97, 136.39, 138.75, 139.17, 140.72, 145.59, 160.13; HRMS m/z (M+) calcd for C₃₃H₂₅N: 435.1987, found: 435.1993.



Figure S1. ORTEP drawing of compound **3a**. Crystal data: C27H19N, Mw = 357.45, monoclinic, space group P 1 21 1, T = 296 K, a = 9.8978(8), b = 9.7275(10), c = 10.0052(9), β = 95.038(7), V = 959.59(15), Z = 2, 2951 reflections measured, R = 0.0423, Rw = 0.1001.



Figure S2. NOE enhancement in ¹H NMR of 3a.

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160

140

120



100 δ/ppm