Supporting Information

Ruthenium-Catalyzed Intermolecular Coupling Reactions of Arylamines with Ethylene and 1,3-Dienes: A Mechanistic Insight on Hydroamination vs *ortho*-C-H Bond Activation

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General Information. All operations were carried out in an inert-atmosphere glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. Tetrahydrofuran, benzene, hexanes and Et₂O were distilled from purple solutions of sodium and benzophenone immediately prior to use. The NMR solvents were dried from activated molecular sieves (4 Å). All amine and alkene substrates were received from commercial sources and used without further purification. The ¹H, ¹³C and ³¹P NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer. Mass spectra were recorded from a Hewlett-Packard HP 5970 GC/MS spectrometer. High resolution FAB mass spectra were obtained at the Center of Mass Spectrometry, Washington University, St. Louis, MO. Elemental analyses were performed at the Midwest Microlab, Indianapolis, IN.

General Procedure of the Kinetic Measurement of the Catalytic Reaction. In a glove box, an equal amount of **1** (5 – 15 mol%) and aniline (0.1 – 0.7 mmol) was placed into 5-8 separate 25 mL Schlenk tubes (thick-walled), and each tube was charged with benzene (2 mL). The reaction tubes were brought out of the glove box, and cooled in a liquid nitrogen bath. Excess ethylene (3 – 14 mmol) was condensed into each tube via a vacuum line transfer. The reaction tubes were warmed to room temperature and were immersed in an oil bath (preset at 80 °C) at the same time. The tube was removed periodically from oil bath and small aliquot was injected to GC to determine the conversion. The k_{obs} was estimated from a first-order plot of –
 $\ln([\text{aniline}]_t/[\text{aniline}]_0)$ vs time.

Figure S1. Pseudo first-order plots of $-\ln([\text{aniline}]_t/[\text{aniline}]_0)$ vs time using 10 mol % of the catalyst **1**. The $k_{\text{obs}} = 2.9 \times 10^{-2} \text{ h}^{-1}$ for aniline and $k_{\text{obs}} = 1.3 \times 10^{-2} \text{ h}^{-1}$ for aniline- d_7 .

Figure S2. The product yield of **3a** and **3a-d** vs reaction time for the coupling reaction of aniline and aniline- d_7 using 10 mol % of the catalyst **1**.

Figure S3. Plot of k_{obs} vs [ethylene] using **1** (10 mol%) as the catalyst.

Figure S4. Plot of k_{obs} vs [**1**] for the hydroamination of ethylene with aniline. The line represents a least-square fit to the data points.

Figure S5. Plot of k_{obs} vs [aniline] using **1** as the catalyst. The line represents a least-square fit to the data points.

Figure S6. Hammett plot of k_x/k_H vs σ_p^+ for the hydroamination of p -X-C₆H₄NH₂ (X = OMe, CH₃, H, CF₃) using **1** (5 mol%) as the catalyst.

Typical Procedure of the Catalytic Reaction. In a glove box, complex **1** (5-10 mol %) and an amine (0.65 mmol) were dissolved in 2 mL benzene solution in a thick-walled 25 mL Schlenk tube equipped with a magnetic stirring bar. The tube was brought out of the box, and cooled in a liquid nitrogen bath. Excess ethylene (8 mmol) was condensed into the tube via a vacuum line. The reaction tube was gradually warmed to room temperature and stirred in an oil bath at 80-100 °C for 36-48 h. The tube was opened to air at room temperature, and the crude product mixture was analyzed by GC. The solvent was removed under a rotary aspirator, and the organic product was isolated by a column chromatography on silica gel (hexane/CH₂Cl₂).

General Comments on the Characterization and Purity of Organic Products. Since most organic products are already known compounds, the structure of organic products was established by comparing with the reported spectroscopic data. The purity of isolated products was determined by ¹H NMR. The compounds **2a-2d**, **3a**, **3b** and **4d** are commercially available. The specific references for other products:

For **3c**: Hamada, Y.; Takeuchi, I. *J. Org. Chem.* **1977**, *42*, 4209.

For **5e** and **6e**: Ozawa, F.; Okamoto, H.; Kawagishi, S.; Yamamoto, S.; Minami, T.; Yoshifuji, M. *J. Am. Chem. Soc.* **2002**, *124*, 10968.

For **5f**: Minami, T.; Okamoto, H.; Ikeda, S.; Tanaka, R.; Ozawa, F.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4501.

For **5g**: Loeber, O.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 4366.

For **5h**: Takeuchi, H.; Koyama, K.; Mitani, M.; Ihara, R.; Uno, T.; Okazaki, Y.; Kai, Y.; Kasai, N. *J. Chem. Soc., Perkin Trans. 1* **1985**, 677.

For **5i**: Krowicki, K.; Paillous, N.; Riviere, M.; Lattes, A. *J. Heterocyclic Chem.* **1976**, *13*, 555.

For **6i**: Izumi, T.; Kasahara, A. *J. Heterocyclic Chem.* **1990**, *27*, 1173

Selected Spectroscopic Data of Organic Products:

For **2a**: ¹H NMR (CDCl₃, 300 MHz) δ 7.14 (m, 2H, Ar), 6.67 (tt, *J* = 7.2, 0.9 Hz, 1H, Ar), 6.56 (m, 2H, Ar), 3.45 (br s, NH), 3.09 (q, *J* = 7.2 Hz, CH₂), 1.18 (t, *J* = 6.9 Hz, CH₃); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 148.5 (Ar), 129.3 (Ar), 117.2 (Ar), 112.8 (Ar), 38.5 (CH₂), 14.9 (CH₃); GC-MS (*M*⁺ = 121).

For **2b**: ¹H NMR (C₆D₆, 300 MHz) δ 7.12 (d, *J* = 8.4 Hz, 2H, Ar), 6.11 (d, *J* = 8.4 Hz, 2H, Ar), 2.79 (br s, NH), 2.56 (q, *J* = 6.9 Hz, CH₂), 0.79 (t, *J* = 6.9 Hz, CH₃); ¹³C{¹H} NMR (C₆D₆, 75 MHz) δ 147.6 (Ar), 129.6

(Ar), 122.1 (Ar), 114.3 (Ar), 38.7 (CH₂), 15.0 (CH₃); GC-MS (M⁺ = 155).

For **2c**: ¹H NMR (CDCl₃, 300 MHz) δ 7.76 (m, 1H, Ar), 7.43 – 7.20 (m, 5H, Ar), 6.59 (dd, *J* = 7.2, 0.6 Hz, 1H, Ar), 4.19 (br s, NH), 3.25 (q, *J* = 6.9 Hz, CH₂), 1.36 (t, *J* = 7.5 Hz, CH₃); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 143.7 (Ar), 134.4 (Ar), 128.8 (Ar), 126.9 (Ar), 125.8 (Ar), 124.8 (Ar), 123.4 (Ar), 120.0 (Ar), 117.3 (Ar), 104.4 (Ar), 38.8 (CH₂), 14.9 (CH₃); GC-MS (M⁺ = 171).

For **3a**: ¹H NMR (CDCl₃, 300 MHz) δ 8.04 (d, *J* = 8.4 Hz, 1H, Ar), 7.96 (d, *J* = 8.4 Hz, 1H, Ar), 7.71 – 7.62 (m, 2H, Ar), 7.43 (t, *J* = 8.1 Hz, 1H, Ar), 7.20 (d, *J* = 8.1 Hz, 1H, Ar), 2.71 (s, CH₃); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 158.9 (C=N), 147.8 (Ar), 136.1 (Ar), 129.4 (Ar), 128.6 (Ar), 127.5 (Ar), 126.4 (Ar), 125.6 (Ar), 121.9 (Ar), 25.4 (CH₃); GC-MS (M⁺ = 143).

For **3b**: ¹H NMR (CDCl₃, 300 MHz) δ 7.92 (dd, *J* = 9.0, 6.9 Hz, 2H, Ar), 7.71 (d, *J* = 2.1 Hz, 1H, Ar), 7.60 (dd, *J* = 9.3, 2.4 Hz, 1H, Ar), 7.28 (d, *J* = 8.7 Hz, 1H, Ar), 2.72 (s, CH₃); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 159.5 (C=N), 146.3 (Ar), 135.3 (Ar), 131.3 (Ar), 130.4 (Ar), 130.3 (Ar), 127.1 (Ar), 126.3 (Ar), 123.0 (Ar), 25.5 (CH₃); GC-MS (M⁺ = 177).

For **3c**: ¹H NMR (CDCl₃, 300 MHz) δ 9.31 (d, *J* = 7.8 Hz, 1H, Ar), 8.04 (d, *J* = 7.8 Hz, 1H, Ar), 7.86 – 7.61 (m, 5H, Ar), 7.38 (d, *J* = 7.8 Hz, 1H, Ar), 2.83 (s, CH₃); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 158.0 (C=N), 146.2 (Ar), 136.2 (Ar), 134.0 (Ar), 131.6 (Ar), 128.2 (Ar), 128.0 (Ar), 127.0 (Ar), 126.9 (Ar), 125.5 (Ar), 124.6 (Ar), 124.4 (Ar), 122.4 (Ar), 25.7 (CH₃); GC-MS (M⁺ = 193).

For **5e**: ¹H NMR (CDCl₃, 300 MHz) δ 7.17 (m, 2H, Ar), 6.67 (tt, *J* = 7.2, 0.9 Hz, 1H, Ar), 6.60 (m, 2H, Ar), 5.82 (ddd, *J* = 17.4, 10.2, 5.4 Hz, CHCH=CH₂), 5.19 (dt, *J* = 17.4, 1.2 Hz, CHCH=CHH), 5.07 (dt, *J* = 10.2, 1.2 Hz, CHCH=CHH), 3.98 (m, NCH), 3.64 (br s, NH), 1.31 (d, *J* = 6.9 Hz, CH₃); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 147.6 (Ar), 141.4 (CH=CH₂), 129.3 (Ar), 117.5 (Ar), 113.5 (CH=CH₂), 113.1 (Ar), 51.1 (NCH), 18.0 (CH₃); GC-MS (M⁺ = 147).

For **5f**: ¹H NMR (C₆D₆, 300 MHz) δ 7.49 – 7.13 (m, 7H, Ar), 6.77 – 6.69 (m, 3H, Ar), 6.63 (d, *J* = 15.9 Hz, PhCH=CH), 6.24 (ddd, *J* = 15.9, 5.9, 1.5 Hz, PhCH=CH), 4.14 (m, CHN), 3.71 (br s, NH), 1.45 (dd, *J* = 6.9, 1.8 Hz, CH₃); ¹³C{¹H} NMR (C₆D₆, 75 MHz) δ 146.3 (Ar), 135.8 (Ar), 132.1 (PhCH=CH), 128.1 (Ar), 128.0 (PhCH=CH), 127.4 (Ar), 126.1 (Ar), 125.2 (Ar), 116.2 (Ar), 112.2 (Ar), 49.7 (CHNPh), 21.0 (CH₃); GC-MS (M⁺ = 223).

For **5g**: ¹H NMR (C₆D₆, 300 MHz) δ 6.87 (t, *J* = 8.1 Hz, 2H, Ar), 6.45 (t, *J* = 7.2 Hz, 1H, Ar), 6.21 (d, *J*

= 7.5 Hz, 2H, Ar), 4.63 (d, J = 1.2 Hz, C=CHH), 4.48 (d, J = 1.2 Hz, C=CHH), 3.36 (q, J = 6.6 Hz, NCH), 2.93 (br s, NH), 1.20 (s, CHCH₃), 0.67 (d, J = 6.6 Hz, CH₃C=CH₂); ¹³C{¹H} NMR (C₆D₆, 75 MHz) δ 148.3, 148.0, 129.7, 117.9, 113.9, 111.2, 55.0 (NCH), 21.6 (CH₃), 18.6 (CH₃); GC-MS (M^+ = 161).

For **5h**: ¹H NMR (C₆D₆, 300 MHz) δ 7.45 (t, J = 7.8 Hz, 2H, Ar), 6.65 (t, J = 7.2 Hz, 1H, Ar), 6.20 (d, J = 7.5 Hz, 2H, Ar), 5.21 (d, J = 9.8 Hz, CH=C), 4.10 (m, CH), 3.50 (br s, NH), 1.84 (s, 2CH₃), 0.97 (d, J = 6.6 Hz, CH₃); ¹³C{¹H} NMR (C₆D₆, 75 MHz) δ 143.5, 129.5, 128.9, 116.9, 113.0, 111.9, 47.1 (CH₃CH), 24.8 and 21.5 ((CH₃)₂C=C), 17.4 (CH₃CH); GC-MS (M^+ = 175).

For **5i**: ¹H NMR (CDCl₃, 300 MHz) δ 7.11 – 7.06 (m, 2H, Ar), 6.66 (t, J = 8.1 Hz, 1H, Ar), 6.53 (d, J = 7.5 Hz, 1H, Ar), 5.96 (ddd, J = 17.4, 10.5, 5.4 Hz, CH=CH₂), 5.27 – 5.19 (m, CH=CH₂), 4.24 (m, CH), 3.39 (m, NCH₂), 2.97 (t, J = 8.4 Hz, NCH₂CH₂), 1.35 (d, J = 6.6 Hz, CH₃); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 151.2, 138.5, 130.4, 127.3, 124.6, 117.3, 115.8, 107.7, 52.6(CH), 47.2 (NCH₂), 28.3 (NCH₂CH₂), 15.5 (CH₃); GC-MS (M^+ = 173).

For **6e**: ¹H NMR (CDCl₃, 300 MHz) δ 7.17 (m, 2H, Ar), 6.67 (tt, J = 7.2, 0.9 Hz, 1H, Ar), 6.60 (m, 2H, Ar), 5.67 (dq, J = 15.6, 6.3, 1.2 Hz, CH₂CH=CHCH₃), 5.59 (dtq, J = 15.6, 5.7, 1.2 Hz, CH₂CH=CHCH₃), 3.67 (dd, J = 5.7, 1.2 Hz, NCH₂), 3.64 (br s, NH), 1.70 (dd, J = 6.3, 1.2 Hz, CH₃); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 148.4 (Ar), 129.4 (Ar), 128.2 (CH=CH), 128.1 (CH=CH), 117.5 (Ar), 114.3 (Ar), 46.2 (NCH₂), 21.8 (CH₃); GC-MS (M^+ = 147).

For **6i**: ¹H NMR (CDCl₃, 300 MHz) δ 7.11 – 7.05 (m, 2H, Ar), 6.66 (t, J = 8.1 Hz, 1H, Ar), 6.53 (d, J = 7.5 Hz, 1H, Ar), 5.71 (dq, J = 15.2, 6.3, 1.2 Hz, CH=CHCH₃), 5.57 (dtq, J = 15.2, 6.5, 1.2 Hz CH=CHCH₃), 3.67 (m, CH₂CH=CH₃), 3.33 (t, J = 8.1 Hz, NCH₂CH₂), 2.96 (t, J = 8.1 Hz, NCH₂CH₂), 1.74 (dd, J = 6.3, 1.2 Hz, CH₃); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 152.4, 130.5, 128.8, 127.4, 126.8, 124.6, 117.7, 107.6, 53.2 (NCH₂CH₂), 51.4 (NCH₂CH=), 28.7 (NCH₂CH₂), 17.9 (CH₃); GC-MS (M^+ = 173).

¹H and ¹³C NMR Spectra of Selected Compounds

3a