Supplementary Material (ESI) for Chemical Communications

Anti-Markovnikov Hydroamination and Hydrothiolation of Electron-Deficient Vinylarenes Catalyzed by Well-Defined Monomeric Copper(I) Amido and Thiolate Complexes

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Supporting Information

Table of Contents

General Methods. All procedures were performed under an inert atmosphere of dinitrogen in a nitrogen-filled glovebox or using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer (O_2 < 15 ppm for all reactions). Benzene, toluene and tetrahydrofuran were purified by distillation over sodium/benzophenone. Pentane was distilled over sodium prior to use. Hexanes were purified by passage through a column of activated alumina. Benzene-d_6 and chloroform-d_1 were degassed via three freeze-pump-thaw cycles and stored under a dinitrogen atmosphere over 4Å molecular sieves. ^{1}H and ^{13}C NMR spectra were acquired using a Varian Mercury spectrometer operating at 300 or 400 MHz and 75 or 100 MHz, respectively, and referenced to TMS using residual proton signals or the ^{13}C resonances of the deuterated solvent. ^{19}F NMR spectra were acquired using a Varian Mercury spectrometer operating at 282 MHz with C_6F_6 (-163.0 ppm) as the external standard. Elemental analyses were performed by Atlantic Microlabs, Inc. (IPr)Cu(NHPh) (**1**), (IPr)Cu(SPh) (**3**), (IPr)Cu(SCH$_2$Ph) (**4**), and (IPr)CuCl were prepared according to published procedures.[1-3] All other reagents were used as purchased from commercial sources.

Potential Generation (^{1}H NMR) of (IPr)Cu(NHCH$_2$Ph) (2). The complex (IPr)Cu(NHPh) (**1**) (0.014 g, 0.026 mmol) and C_6D_6 were combined in an NMR tube to give a homogeneous solution. After addition of benzylamine (29 μL, 0.27 mmol), the tube was sealed with a rubber septum, and a ^{1}H NMR spectrum was acquired. Upon heating to 100 ºC for 32 hours, disappearance of the anilido resonances and growth of peaks due to free aniline were observed by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6, δ): 6.35 (s, 2H, IPr NC*H*), 2.60 (br sept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.10 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). Specific resonances due to the phenyl group of the putative NHCH$_2$Ph ligand

were not identified presumably due to overlap with aryl resonances from free benzyl amine, aniline and the IPr ligand. The NH and methylene resonances of the benzyl amido were not observed likely due to a dynamic process with free benzyl amine, which is similar to behavior observed for the combination of (IPr)Cu(NHPh) (**1**) and free aniline. Multiple attempts to isolate the putative complex (IPr)Cu($NHCH_2Ph$) (**2**) resulted in decomposition.

Reaction of Aniline and *p*-Nitrostyrene (1:1 molar ratio) with Catalytic (IPr)Cu(NHPh) (1). *p*-Nitrostyrene (61.5 mg, 0.412 mmol) and **1** (0.011 g, 0.021 mmol) were combined with C_6D_6 (0.5 mL) in a small vial, and the resulting solution was transferred to an NMR tube. Aniline (38.0 μL, 0.417 mmol) and hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard) were added, and the tube was sealed with a rubber septum. The reaction was heated to 80 ºC and monitored periodically by ^1H NMR spectroscopy. After 42 hours, 63% conversion to *N*-phenyl-*p*-nitrophenethylamine was observed.

Reaction of Aniline and *p*-Nitrostyrene (5:1 molar ratio) with Catalytic (IPr)Cu(NHPh) (1). The previous procedure was followed using 0.012 g (0.022 mmol) **1**, 65.4 mg (0.438 mmol) *p*-nitrostyrene, 0.20 mL (2.2 mmol) aniline, 2.0 μL (0.0094 mmol) hexamethyldisiloxane, and 0.5 mL C_6D_6. After 19 hours at 80 ºC, *N*-phenyl-*p*-nitrophenethylamine was observed in 77% yield. The volume of the reaction mixture was reduced *in vacuo*, and the resulting residue was taken up in diethyl ether (3 mL). Upon addition of 5% aqueous HCl solution (3 mL), a white precipitate was observed. The precipitate was collected by filtration and washed with ether (3 x 5 mL). The solid was combined with methylene chloride (10 mL) and saturated [Na][HCO_3] solution in a separatory funnel. The organic layer was collected (3 x 10 mL), washed with water (5 x 10 mL), and dried with $MgSO_4$. The original aqueous layer (from initial addition of acid) was neutralized with [Na][HCO_3], and

the organic materials were extracted into diethyl ether (3 x 15 mL). This organic layer was washed with water (5 x 10 mL), dried with $MgSO_4$, and combined with the methylene chloride solution. The product was isolated by removing solvent *in vacuo* to give an orange oil (0.061 g, 64% yield). ^{1}H NMR ($CDCl_3$ δ): 8.19 (d, $^3J_{HH}$ = 9 Hz, 2H, *o*-NO_2-aryl), 7.39 (d, $^3J_{HH}$ = 9 Hz, 2H, *m*-NO_2-aryl), 7.21 (t, $^3J_{HH}$ = 7 Hz, 2H, anilido *m*-phenyl), 6.75 (t, $^3J_{HH}$ = 7 Hz, 1H, anilido *p*-phenyl), 6.63 (d, $^3J_{HH}$ = 7 Hz, 2H, anilido *o*-phenyl), 3.67 (br s, 1H, N*H*), 3.48 (t, $^3J_{HH}$ = 7 Hz, 2H, -NHC*H*$_2$), 3.05 (t, $^3J_{HH}$ = 7 Hz, 2H, -NHCH$_2$C*H*$_2$-). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 147.5, 147.3, 129.8, 129.5, 124.0, 118.0, 113.1 (each a s, phenyl- and aryl-, one resonance absent likely due to coincidental overlap); 44.8 (s, -*C*H$_2$NH), 35.8 (s, -*C*H$_2$CH$_2$NH). Anal. Calcd. $C_{14}H_{14}N_2O_2$: C, 69.39; H, 5.83; N, 11.57; Found: C, 69.78; H, 6.00; N, 11.15.

Control Reaction: Aniline and *p*-Nitrostyrene. An NMR tube was charged with a solution of *p*-nitrostyrene (65.3 mg, 0.437 mmol) and C_6D_6 (0.5 mL). After addition of aniline (39.5 μL, 0.433 mmol) and hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard), the NMR tube was sealed with a rubber septum. The reaction was monitored by ^{1}H NMR spectroscopy. After 5 days at 80 ºC, no reaction was observed.

Reaction of Aniline and *m*-Nitrostyrene with Catalytic (IPr)Cu(NHPh) (1). An NMR tube was charged with **1** (0.011 g, 0.020 mmol), aniline (40 μL, 0.44 mmol), hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard) and C_6D_6 (0.5 mL), and the NMR tube was sealed with a rubber septum. *m*-Nitrostyrene (50 μL, 0.36 mmol) was added via microsyringe, and a ^{1}H NMR spectrum was acquired. The reaction was heated to 100 ºC and monitored periodically by NMR spectroscopy. After 27 hours, no reaction was observed.

Reaction of Aniline and *p*-Cyanostyrene (1:1 molar ratio) with Catalytic (IPr)Cu(NHPh) (1). A screw-cap NMR tube was charged with **1** (0.012 g, 0.021 mmol), aniline

(39.0 μL, 0.428 mmol), hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard) and C_6D_6 (0.5 mL), and the NMR tube was sealed. *p*-Cyanostyrene (35.5 μL, 0.425 mmol) was added via microsyringe, and a ^{1}H NMR spectrum was acquired. The reaction was heated to 120 ºC and monitored periodically by ^{1}H NMR spectroscopy. After 7 days at 120 ºC, *N*-phenyl-*p*-cyanophenethylamine was observed in 25% yield.

Reaction of Aniline and *p*-Cyanostyrene (5:1 molar ratio) with Catalytic (IPr)Cu(NHPh) (1). The previous procedure was followed using 0.011 g (0.021 mmol) **1**, 0.20 mL (2.2 mmol) aniline, 34.0 μL (0.415 mmol) *p*-cyanostyrene, 2.0 μL (0.0094 mmol) hexamethyldisiloxane, and 0.5 mL C_6D_6. After 75 hours at 120 ºC, 85% conversion to *N*-phenyl-*p*-cyanophenethylamine was observed. The volume of the reaction mixture was reduced *in vacuo*, and the resulting residue was taken up in diethyl ether (3 mL). Upon addition of 5% aqueous HCl solution (3 mL), a white precipitate was observed. The precipitate was collected by filtration and washed with ether (3 x 5 mL). The solid was combined with methylene chloride (10 mL) and saturated [Na][HCO_3] solution in a separatory funnel. The organic layer was collected (3 x 10 mL), washed with water (5 x 10 mL), and dried with $MgSO_4$. The original aqueous layer (from initial addition of acid) was neutralized with [Na][HCO_3], and the organic materials were extracted into diethyl ether (3 x 15 mL). This organic layer was washed with water (5 x 10 mL), dried with $MgSO_4$, and combined with the methylene chloride solution. The product was isolated by removing solvent *in vacuo* to give an orange oil (0.039 g, 42% yield). ^{1}H NMR ($CDCl_3$, δ): 7.62 (d, $^3J_{HH}$ = 8 Hz, 2H, *o*-CN-aryl), 7.35 (d, $^3J_{HH}$ = 8 Hz, 2H, *m*-CN-aryl), 7.20 (t, $^3J_{HH}$ = 8 Hz, 2H, *m*-NH-phenyl), 6.75 (t, $^3J_{HH}$ = 7 Hz, 1H, *p*-NH-phenyl), 6.62 (d, $^3J_{HH}$ = 8 Hz, 2H, *o*-NH-phenyl), 3.65 (br s, 1H, N*H*), 3.45 (t, $^3J_{HH}$ = 7 Hz, 2H, -NH-CH_2), 2.99 (t, $^3J_{HH}$ = 7 Hz, 2H, -NHCH$_2$CH_2-). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 147.7, 145.3, 132.5, 129.8, 128.5,

119.1, 118.0, 113.1, 110.5 (each an s, phenyl-, aryl- and –CN); 44.7 (s, -NH*C*$H_2$$CH_2$), 35.8 (-NHC$H_2$*C*$H_2$). Anal. Calcd. $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60; Found: C, 80.92; H, 6.41; N, 12.39.

Control Reaction: Aniline and *p*-Cyanostyrene. An NMR tube was charged with aniline (38.0 μL, 0.421 mmol), hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard) and C_6D_6 (0.5 mL). After sealing with a rubber septum, *p*-cyanostyrene (34.5 μL, 0.421 mmol) was added via microsyringe. The reaction was monitored by ^{1}H NMR spectroscopy. After 5 days at 120 ºC, no reaction was observed.

Reaction of Aniline and *p*-X-styrene (5:1 molar ratio) with Catalytic (IPr)Cu(NHPh) (1) (X = CF_3, Br, Cl, H). Catalytic experiments were conducted with **1** (5 mol % versus vinylarene), aniline and *p*-CF_3-, *p*-Br-, *p*-Cl or *p*-H-styrene (5:1 ratio of amine to vinylarene). After prolonged heating to 120 ºC, no reaction was observed for any of the vinylarenes. A sample NMR experiment is described; all reaction times can be found in Table S1. A screw-cap NMR tube was charged with **1** (0.011 g, 0.020 mmol), aniline (0.20 mL, 2.2 mmol), hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard) and C_6D_6 (0.5 mL), and the NMR tube was sealed with a rubber septum. *p*-(Trifluoromethyl)styrene (61.8 μL, 0.418 mmol) was added via microsyringe, and a ^{1}H NMR spectrum was acquired. The reaction was heated to 120 ºC and monitored periodically by ^{1}H NMR spectroscopy. No reaction was observed after 7 days. Attempts to catalyze this reaction with 10 mol % of complex **1** were also unsuccessful.

Reaction of Benzylamine and *p*-Nitrostyrene (1:1 molar ratio) with Catalytic (IPr)Cu(NHPh) (1). A stock solution of complex **1** (0.022 g, 0.040 mmol) and C_6D_6 (1.0 mL) was prepared, and 0.5 mL of this solution was delivered to a vial containing *p*-nitrostyrene (60.1 mg, 0.403 mmol). The resulting solution was transferred to an NMR tube followed by addition

of benzylamine (44.0 μL, 0.403 mmol) and hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard). The NMR tube was sealed with a rubber septum, and the reaction was periodically monitored by ^{1}H NMR spectroscopy. After 17 hours at 60 ºC, conversion to *N*-benzyl-*p*-nitrophenethylamine was observed in 35% yield. Note that this reaction is complicated by the formation of a precipitate in situ.

Reaction of Benzylamine and *p*-Nitrostyrene (5:1 molar ratio) with Catalytic (IPr)Cu(NHPh) (1). The previous procedure was followed using 0.021 mmol **1**, 0.23 mL (2.1 mmol) benzylamine, 0.64 g mg (0.43 mmol) *p*-nitrostyrene, 2.0 μL (0.0094 mmol) hexamethyldisiloxane, and 0.6 mL C_6D_6. After 22 hours at 60 ºC, *N*-benzyl-*p*-nitrophenethylamine was observed in 66% yield. The product was isolated as dark orange oil using the acidic work-up described on page S5 (0.049 g, 46%). ^{1}H NMR ($CDCl_3$, δ): 8.16 (d, $^3J_{HH}$ = 9 Hz, 2H, *o*-NO_2-aryl), 7.38-7.27 (m, 7H, aryl and phenyl), 3.83 (br s, 2H, -NHC*H*$_2$Ph), 2.95 (br s, 4H, overlap of NCH_2CH_2- and -NHC*H*$_2$$CH_2$), 1.58 (br s, 1H, N*H*). Coupling between methylene protons was observed only in C_6D_6. ^{1}H NMR (C_6D_6, δ): 3.49 (s, 2H, -NHC*H*$_2$Ph), 2.41 (t, $^3J_{HH}$ = 7 Hz, -NHC*H*$_2$$CH_2$), 2.27 (t, $^3J_{HH}$ = 7 Hz, -NHC*H*$_2$$CH_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 129.8, 128.7, 128.4, 127.4, 123.9, 113.2 (each an s, phenyl and aryl, two resonances are missing likely due to coincidental overlap); 53.9 (s, -NH*C*H_2-), 49.9 (s, -NH*C*H_2CH_2-), 36.4 (s, -$NHCH_2$*C*H_2-). Anal. Calcd. $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93; Found: C, 69.97; H, 6.02; N, 10.43.

Control Reaction: Benzylamine and *p*-Nitrostyrene. An NMR tube was charged with a solution of *p*-nitrostyrene (0.061 g, 0.41 mmol) and C_6D_6 (0.5 mL). After addition of benzylamine (44.0 μL, 0.403 mmol) and hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard) the NMR tube was sealed with a rubber septum. The reaction was monitored

by ^{1}H NMR spectroscopy. After 3 days at 60 ºC, hydroamination product was observed in only trace quantities.

Reaction of Benzylamine and *p*-Cyanostyrene (1:1 molar ratio) with Catalytic (IPr)Cu(NHPh) (1). A stock solution was prepared with **1** (0.023 g, 0.042 mmol) and C_6D_6 (1.2 mL). An aliquot (0.6 mL, 0.021 mmol **1**) of this solution was transferred to an NMR tube, followed by addition of benzylamine (46.0 μL, 0.421 mmol) and hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard). The tube was sealed with a rubber septum, and *p*-cyanostyrene (34 μL, 0.42 mmol) was added via microsyringe. The reaction was heated to 80 ºC and monitored periodically by ^{1}H NMR spectroscopy. After 25 hours, *N*-benzyl-*p*-cyanophenethylamine was observed in 57% yield.

Reaction of Benzylamine and *p*-Cyanostyrene (5:1 molar ratio) with Catalytic (IPr)Cu(NHPh) (1). The previous procedure was followed using 0.021 mmol **1**, 0.23 mL (2.1 mmol) benzylamine, 34.9 μL (0.415 mmol) *p*-cyanostyrene, 2.0 μL (0.0094 mmol) hexamethyldisiloxane, and 0.6 mL C_6D_6. After 6 hours at 80 ºC, quantitative conversion to *N*-benzyl-*p*-cyanophenethylamine was observed. The product was isolated using the acidic work-up described above as pale yellow oil (0.049 g, 51%). ^{1}H NMR ($CDCl_3$, δ): 7.59 (d, $^3J_{HH}$ = 7.8 Hz, 2H, *o*-CN-aryl), 7.33- 7.27 (m, 7H, aryl and phenyl), 3.82 (s, 2H, -NHCH_2Ph), 2.91 (br s, 4H, overlap of -NHCH$_2$CH_2- and -NHCH_2CH$_2$-). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 146.0, 132.4, 129.7, 128.7, 128.3, 127.3, 119.2, 110.3 (s, phenyl- and aryl-); 140.0 (s, -C≡N), 54.0 (s, -NH*C*H$_2$Ph), 49.9 (s, -NH*C*H$_2$CH$_2$), 36.7 (-NHCH$_2$*C*H$_2$). Anal. Calcd. $C_{16}H_{16}N_2$: C, 81.31; H, 6.83; N, 11.86; Found: C, 81.06; H, 6.92; N, 11.62.

Control Reaction: Benzylamine and *p*-Cyanostyrene. An NMR tube was charged with benzylamine (0.040 mL, 0.37 mmol) and C_6D_6 (0.5 mL). After sealing the NMR tube with a

rubber septum, *p*-cyanostyrene (30.0 μL, 0.367 mmol) was added via microsyringe. The reaction was monitored by ^{1}H NMR spectroscopy. After seven days at 80 ºC, no reaction was observed.

Reaction of Benzylamine and *p*-(Trifluoromethyl)styrene (1:1 molar ratio) with Catalytic (IPr)Cu(NHPh) (1). A stock solution was prepared with **1** (0.022 g, 0.040 mmol) and C_6D_6 (1.2 ml). An aliquot (0.6 mL, 0.020 mmol **1**) of this solution was transferred to an NMR tube, followed by addition of benzylamine (44 μL, 0.40 mmol) and hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard). The NMR tube was then sealed with a rubber septum, and *p*-(trifluoromethyl)styrene (60 μL, 0.41 mmol) was added via microsyringe. The reaction was heated to 120 ºC and monitored periodically by ^{1}H NMR spectroscopy. After 52 hours, *N*-benzyl-*p*-(trifluoromethyl)phenethylamine was observed in 6% yield.

Reaction of Benzylamine and *p*-(Trifluoromethyl)styrene (5:1 molar ratio) with Catalytic (IPr)Cu(NHPh) (1). The previous procedure was followed using 0.0208 mmol **1**, 0.230 mL (2.11 mmol) benzylamine, 61.0 μL (0.413 mmol) *p*-(trifluoromethyl)styrene, 2.0 μL (0.0094 mmol) hexamethyldisiloxane, and 0.5 mL C_6D_6. After 86 hours at 120 ºC, *N*-benzyl-*p*-(trifluoromethyl)phenethylamine was observed in > 95% yield. The product was isolated using the acidic work-up described above as pale yellow oil (102 mg, 79%). ^{1}H NMR ($CDCl_3$, δ): 7.55 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, *o*-CF_3-aryl), 7.32- 7.24 (m, 7H, aryl and phenyl), 3.80 (s, 2H, -NHCH_2Ph), 2.89 (br s, 4H, overlap of -NHCH$_2$CH_2- and -NHCH_2CH$_2$-), 1.54 (br s, 1H, N*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 144.4, 140.2, 129.2, 128.59, 128.2, 127.2 (s, phenyl- and aryl-); 128.63 (q, $^{2}J_{CF}$ = 32 Hz, *ipso*-CF_3-aryl), 125.5 (q, $^{3}J_{CF}$ = 4 Hz, *ortho* to -CF_3), 124.5 (q, $^{1}J_{CF}$ = 270 Hz, -*C*F_3), 54.0 (s, -NH*C*H$_2$Ph), 50.2 (s, -NH*C*H$_2$CH$_2$-), 36.4 (s, -NHCH$_2$*C*H$_2$). ^{19}F{^{1}H} NMR ($CDCl_3$, δ): -58.8 (-C*F*$_3$). Anal. Calcd. $C_{16}H_{16}NF_3$: C, 68.79; H, 5.78; N, 5.02; Found: C, 69.26; H, 6.14; N, 5.00.

Control Reaction: Benzylamine and *p*-(Trifluoromethyl)styrene. An NMR tube was charged with benzylamine (0.040 mL, 0.37 mmol) and C_6D_6 (0.5 mL). After sealing with a rubber septum, *p*-(trifluoromethyl)styrene (54 μL, 0.37 mmol) was added via microsyringe and a ^{1}H NMR spectrum acquired. The reaction was monitored periodically by ^{1}H NMR spectroscopy. After six days at 120 ºC, no reaction was observed.

Reaction of Benzylamine and *p*-X-styrene (5:1 molar ratio) with Catalytic (IPr)Cu(NHPh) (1) (X = Br, Cl, H).

Catalytic experiments were conducted with **1** (5 mol % versus vinylarene), benzylamine and *p*-Br-, *p*-Cl or *p*-H-styrene (5:1 ratio of amine to vinylarene). After prolonged heating to 120 ºC, no reaction was observed for any of the vinylarenes. A sample NMR experiment is described; all reaction times can be found in Table S1. A screw-cap NMR tube was charged with **1** (0.013 g, 0.024 mmol), benzylamine (0.265 mL, 2.43 mmol), hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard) and C_6D_6 (0.5 mL). The tube was sealed, *p*-bromostyrene (63 μL, 0.48 mmol) was added via microsyringe, and a ^{1}H NMR spectrum was acquired. The reaction was heated to 120 ºC and monitored periodically by ^{1}H NMR spectroscopy. No reaction was observed after 5 days.

Reaction of *N*-Benzylmethylamine and *p*-Nitrostyrene (5:1 molar ratio) with Catalytic (IPr)Cu(NHPh) (1). A stock solution was prepared with **1** (0.022 g, 0.040 mmol) and C_6D_6 (1.2 mL). An aliquot (0.6 mL, 0.020 mmol **1**) of this solution was combined with *p*-nitrostyrene (60.4 mg, 0.405 mmol) and transferred to an NMR tube. After addition of *N*-benzylmethylamine (0.26 mL, 2.3 mmol) and hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard), the tube was sealed with a rubber septum. The reaction was heated to 60 ºC and monitored periodically by ^{1}H NMR spectroscopy. After 72 hours, 70% conversion to *N*-

benzyl-*N*-methyl-*p*-nitrophenethylamine was observed. The product was isolated using the acidic work-up described above as pale orange oil (0.053 g, 48%). ^{1}H NMR ($CDCl_3$, δ): 8.14 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, *o*-NO_2-aryl), 7.35- 7.25 (m, 7H, aryl and phenyl), 3.59 (s, 2H, NC*H*$_2$Ph), 2.95 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, NC*H*$_2$CH$_2$-), 2.57 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H, NCH$_2$C*H*$_2$Ar), 2.32 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 129.8, 129.2, 128.5, 127.5, 123.8 (s, phenyl- and aryl-, three missing resonance due to coincidental overlap); 62.4 (s, -N*C*H$_3$), 58.0 (s, -N*C*H$_2$Ph-), 42.3 (s, -N*C*H$_2$CH$_2$), 33.8 (s, -NCH$_2$*C*H$_2$-). Anal. Calcd. $C_{16}H_{18}N_2O_2$: C, 71.08; H, 6.72; N, 10.37; Found: C, 71.36; H, 6.74; N, 10.24.

Reaction of Benzene Thiol and *p*-Nitrostyrene (1:1 molar ratio) with Catalytic (IPr)Cu(SPh) (3). *p*-Nitrostyrene (0.061 g, 0.41 mmol) and **3** (0.011 g, 0.020 mmol) were combined with C_6D_6 (0.5 mL) in a vial, and the resulting solution was transferred to an NMR tube. Hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard) was added, and the tube was sealed with a rubber septum. After addition of benzene thiol (40 μL, 0.39 mmol) via syringe, a ^{1}H NMR spectrum was acquired. The reaction was heated to 60 ºC and monitored periodically by ^{1}H NMR spectroscopy. After 9 hours, quantitative conversion to 1-nitro-4-[2-(phenylthio)ethyl]-benzene was observed. The reaction mixture was transferred into a round bottom flask, the NMR tube was rinsed with diethyl ether (2 mL) and the added to the reaction solution, and the solvent volume was reduced *in vacuo* to 0.5 mL. Hexanes were added to precipitate the catalyst and the solid was removed by vacuum filtration. The volatiles were removed under reduced pressure to give a white solid (0.072 g, 71% yield). ^{1}H NMR ($CDCl_3$, δ): 8.15 (d, $^{3}J_{HH}$ = 9 Hz, 2H, *o*-NO_2-aryl), 7.37-7.19 (m, 7H, overlapping phenyl and aryl), 3.20 (t, $^{3}J_{HH}$ = 8 Hz, 2H, SC*H*$_2$CH$_2$-), 3.02 (t, $^{3}J_{HH}$ = 7 Hz, 2H, SCH$_2$C*H*$_2$-). ^{13}C {^{1}H} NMR ($CDCl_3$, δ): 147.8, 146.8, 135.6, 129.8, 129.6, 129.2, 126.6, 123.8 (s, phenyl- and aryl-), 35.4 (s, -

S*C*H_2CH_2-), 34.7 (s, -SCH_2*C*H_2-). Anal. Calcd. $C_{13}H_{14}NO_2S$: C, 64.84; H, 5.05; N, 5.40; Found: C, 64.58; H, 5.04; N, 5.40.

Control Reaction: Benzene Thiol and *p*-Nitrostyrene. An NMR tube was charged with a solution of *p*-nitrostyrene (0.047 g, 0.32 mmol) and C_6D_6 (0.5 mL). After addition of hexamethyldisiloxane as internal standard, the NMR tube was sealed with a rubber septum. Benzene thiol (33 μL, 0.32 mmol) was added via syringe, and a ^{1}H NMR spectrum was acquired. The reaction was monitored by ^{1}H NMR spectroscopy. After 9 hours, no reaction was observed.

Reaction of Benzyl Mercaptan and *p*-Nitrostyrene (1:1 molar ratio) with Catalytic (IPr)Cu(SCH$_2$Ph) (4). A solution of **4** (0.011 g, 0.020 mmol) in 0.50 mL C_6D_6 was prepared. This solution was combined with *p*-nitrostyrene (0.059 g, 0.39 mmol) in a vial, and the resulting solution was transferred to an NMR tube and this was sealed with a rubber septum. Benzyl mercaptan (50 μL, 0.43 mmol) was added via syringe, and the reaction was monitored periodically by ^{1}H NMR spectroscopy at room temperature. After 2 hours, quantitative conversion to 1-nitro-4-[2-(benzylthio)ethyl]-benzene was observed. The product was isolated by precipitating the catalyst out of the solution as described above (0.064 g, 60% yield). ^{1}H NMR ($CDCl_3$, δ): 8.08 (d, $^3J_{HH}$ = 9 Hz, 2H, *o*-NO_2-aryl), 7.20-7.17 (m, 7H, overlapping phenyl and aryl), 3.67 (s, 2H, PhCH_2S-), 2.87 (t, $^3J_{HH}$ = 8 Hz, 2H, SCH_2CH$_2$-), 2.65 (t, $^3J_{HH}$ = 8 Hz, 2H, SCH$_2$CH_2-). ^{13}C {^{1}H} NMR ($CDCl_3$, δ): 148.3, 146.9, 138.3, 129.6, 129.1, 128.9, 127.4, 123.9 (each an s, -aryl and –phenyl), 36.8 (s, -S*C*H$_2$Ph), 35.8 (s, -S*C*H$_2$CH$_2$-), 32.3 (s, -SCH$_2$*C*H$_2$-). Anal. Calcd. $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12; Found: C, 66.03; H, 5.53; N, 5.01.

Control Reaction: Benzyl Mercaptan and *p*-Nitrostyrene. An NMR tube was charged with a solution of *p*-nitrostyrene (0.066 g, 0.44 mmol) and C_6D_6 (0.5 mL). After addition of hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard), the NMR tube was sealed

with a rubber septum. Benzyl mercaptan (0.5 mL, 0.4 mmol) was added via syringe. The reaction was monitored periodically by ^{1}H NMR spectroscopy. After 69 hours, the hydrothiolation product was observed only in trace quantities.

Reaction of Aniline and *p*-Nitrostyrene (5:1 molar ratio) with Catalytic [Li][NHPh]. A stock solution was prepared with [Li][NHPh] (0.008 g, 0.08 mmol) and tetrahydrofuran (0.40 mL). An aliquot (0.10 mL, 0.02 mmol [Li][NHPh]) of this solution was transferred to an NMR tube, and the solvent was removed under vacuum. A solution of *p*-nitrostyrene (0.061 g, 0.41 mmol) and C_6D_6 (0.5 mL) was added to the NMR tube, followed by addition of aniline (0.181 mL, 1.99 mmol) and hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard). The tube was then sealed with a rubber septum. The reaction was heated to 80 ºC and monitored by ^{1}H NMR spectroscopy. After 19 hours, no reaction was observed.

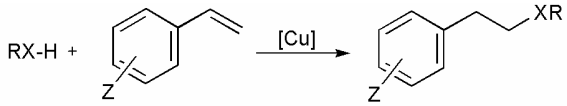
Reaction of Aniline and *p*-Cyanostyrene (5:1 molar ratio) with Catalytic [Li][NHPh]. A stock solution was prepared with [Li][NHPh] (0.008 g, 0.08 mmol) and tetrahydrofuran (0.40 mL). An aliquot (0.10 mL, 0.02 mmol [Li][NHPh]) of this solution was transferred to a screw-cap NMR tube, and the solvent was removed under vacuum. The tube was then charged with C_6D_6 (0.5 mL), aniline (0.181 mL, 1.99 mmol) and hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard). The tube was sealed and *p*-cyanostyrene (33 μL, 0.39 mmol) was added via microsyringe. The reaction was heated to 120 ºC and monitored periodically by ^{1}H NMR spectroscopy. After 75 hours, no reaction was observed.

Reaction of Benzylamine and *p*-Cyanostyrene (5:1 molar ratio) with Catalytic Pyridine. An NMR tube was charged with C_6D_6 (0.5 mL), benzylamine (0.22 mL, 2.0 mmol), pyridine (1.6 μL, 0.020 mmol) and hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard). The tube was sealed and *p*-cyanostyrene (33 μL, 0.39 mmol) was added via

microsyringe. The reaction was heated to 80 ºC and monitored periodically by ^{1}H NMR spectroscopy. After 6 hours, no reaction was observed.

Reaction of Aniline and *p*-Nitrostyrene (5:1 molar ratio) with Catalytic Pyridine. A solution of *p*-nitrostyrene (0.062 g, 0.41 mmol) and C_6D_6 (0.5 mL) was added to an NMR tube, followed by addition of aniline (0.18 mL, 2.0 mmol), pyridine (1.6 μL, 0.020 mmol) and hexamethyldisiloxane (2.0 μL, 0.0094 mmol, as internal standard). The tube was then sealed with a rubber septum. The reaction was heated to 80 ºC and monitored by ^{1}H NMR spectroscopy. After 19 hours, no reaction was observed.

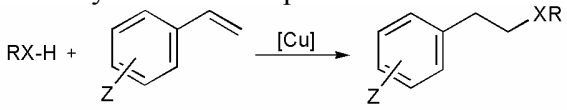
Table S1. Hydroamination of electron-deficient styrenes catalyzed by (IPr)Cu(NHPh) (**1**) and uncatalyzed control experiments.



Nucleophile	Z	Ratio[a]	Cat.	Temp. (ºC)	Time (hr)	NMR yield (%)	Isolated yield (%)
$PhNH_2$	*p*-NO_2	1:1	none	80	5 d[b]	0	--
$PhNH_2$	*p*-NO_2	1:1	**1**	80	42	63	--
$PhNH_2$	*p*-NO_2	5:1	**1**	80	19	77	64
$PhNH_2$	*m*-NO_2	1:1	**1**	100	27	0	--
$PhNH_2$	*p*-CN	1:1	none	120	5 d	0	--
$PhNH_2$	*p*-CN	1:1	**1**	120	7 d	25	--
$PhNH_2$	*p*-CN	5:1	**1**	120	75	85	42
$PhNH_2$	*p*-CF_3	1:1	**1**	120	5 d	0	--
$PhNH_2$	*p*-CF_3	5:1	**1**	120	7 d	0	--
$PhNH_2$	*p*-Br	5:1	**1**	120	90	0	--
$PhNH_2$	*p*-Cl	5:1	**1**	120	90	0	--
$PhNH_2$	*p*-H	5:1	**1**	120	90	0	--
$PhCH_2NH_2$	*p*-NO_2	1:1	none	60	3 d	1	--
$PhCH_2NH_2$	*p*-NO_2	1:1	**1**	60	17	35	--
$PhCH_2NH_2$	*p*-NO_2	5:1	**1**	60	22	66	46
$PhCH_2N(H)Me$	*p*-NO_2	1:1	none	60	20	2	--
$PhCH_2N(H)Me$	*p*-NO_2	1:1	**1**	60	19	50	--
$PhCH_2N(H)Me$	*p*-NO_2	5:1	**1**	60	72	70	48
$PhCH_2NH_2$	*p*-CN	1:1	none	80	7 d	0	--
$PhCH_2NH_2$	*p*-CN	1:1	**1**	80	25	57	--
$PhCH_2NH_2$	*p*-CN	5:1	**1**	80	6	>95	51
$PhCH_2NH_2$	*p*-CF_3	1:1	none	120	6 d	0	--
$PhCH_2NH_2$	*p*-CF_3	1:1	**1**	120	52	6	--
$PhCH_2NH_2$	*p*-CF_3	5:1	**1**	120	86	>95	79
$PhCH_2NH_2$	*p*-Br	5:1	**1**	120	5 d	0	--
$PhCH_2NH_2$	*p*-Cl	5:1	**1**	120	88	0	--
$PhCH_2NH_2$	*p*-H	1:1	**1**	120	91	0	--

[a]Molar ratio of amine:vinylarene (catalyst present in 5 mol% based on vinylarene). [b]d = days.

Table S2. Hydrothiolation of electron-deficient styrenes catalyzed by (IPr)Cu(SPh) (**3**) and (IPr)Cu(SCH_2Ph) (**4**), and uncatalyzed control experiments.



Nucleophile	Z	Ratio[1]	Cat.	Temp. (ºC)	Time (hr)	NMR yield (%)	Isolated yield (%)
PhSH	*p*-NO_2	1:1	none	RT	9	0	--
PhSH	*p*-NO_2	1:1	**3**	RT	9	>95	71
$PhCH_2SH$	*p*-NO_2	1:1	none	RT	2	0	--
$PhCH_2SH$	*p*-NO_2	1:1	**4**	RT	2	>95	60

[a]Molar ratio of thiol:vinylarene (catalyst present in 5 mol% based on vinylarene).

References

(1) Goj, L. A.; Blue, E. D.; Munro-Leighton, C.; Gunnoe, T. B.; Petersen, J. L. *Inorg. Chem.* **2005**, *44*, 8647-8649.

(2) Mankad, N. P.; Gray, T. G.; Laitar, D. S.; Sadighi, J. P. *Organometallics* **2004**, *23*, 1191-1193.

(3) Delp, S. A.; Munro-Leighton, C.; Goj, L. A.; Ramirez, M. A.; Gunnoe, T. B.; Petersen, J. L.; Boyle, P. D. *Inorg. Chem.* **2007**, *46*, 2365-2367.