

Rhodium-Catalyzed Anti-Markovnikov Hydroamination of Vinylarenes

Supporting Information

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General comments. All reactions were performed under a nitrogen atmosphere using standard Schlenk and drybox techniques. Toluene, diethyl ether, and pentane were distilled from sodium and benzophenone under nitrogen. Vinylarenes, amines, 2-(2-dimethylaminoethyl)pyridine and ligands in Table 1, except for DBFphos were purchased from commercial sources and were used without further purification. DBFphos was synthesized by literature procedures.¹ Dimethylamine was purchased from Aldrich as a 2.0 M solution in tetrahydrofuran. NMR spectra were recorded on Bruker DPX 400 and 500 MHz instruments. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ.

[Rh(cod)(DPEphos)]BF₄. In a drybox, [Rh(cod)Cl]₂ (192 mg, 0.389 mmol) and AgBF₄ (160 mg, 0.822 mmol) were mixed in CH₂Cl₂ (4.0 mL) in a screw-capped vial. DPEphos (432 mg, 0.802 mmol) was added to the resulting suspension. The suspension was stirred at room temperature for 2 h. It was then filtered through Celite to remove AgBF₄, and the filtrate was added to 100 mL of pentane. The precipitate was collected by filtration and washed with three times with 10.0 mL of pentane. [Rh(cod)(DPEphos)]BF₄ was obtained as an orange powder (280 mg, 86%): ¹H NMR (400 MHz, CD₂Cl₂, TMS) δ 2.02-2.16 (m, 4H), 2.22-2.36 (m, 4H), 4.40-4.48 (br, 4H), 6.90-7.06 (m, 8H), 7.34-7.52 (m, 20H); ³¹P{¹H} NMR (202.44 MHz, CD₂Cl₂) δ 13.6 (d, *J*_{Rh-P} = 121.5 Hz); Anal. Calcd for C₄₄H₄₀BF₄OP₂Rh•CH₂Cl₂: C, 58.66; H, 4.59. Found: C, 58.43; H, 4.38.

General Procedure for the Hydroamination of Vinylarenes with Secondary Amines (Table 2). In a drybox, vinylarene (4.00 mmol) and amine (1.00 mmol) were added to a suspension of [Rh(cod)(DPEphos)]BF₄ (41.8 mg, 50.0 μmol) in toluene (1.00 mL) in a screw-capped vial. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. The reaction mixture was then stirred at 70 °C for 48 h. After the reaction, the ratio of amine:enamine was determined by GC analysis. The reaction mixture was adsorbed onto silica gel and purified by flash column chromatography.

***N*-(2-Phenethyl)morpholine (Table 2, Entry 1).**² The general procedure was followed with styrene (458 μ l, 4.00 mmol) and morpholine (87.4 mg, 1.00 mmol). The reaction mixture was purified by flash column chromatography (20% EtOAc in hexane) to give 136 mg (71%) of the hydroamination product: ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.44 (t, *J* = 4.6 Hz, 4H), 2.61 (m, 2H), 2.81 (m, 2H), 3.74 (t, *J* = 4.6 Hz, 4H), 7.20 (m, 3H), 7.29 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 33.3, 53.6, 60.8, 66.9, 126.0, 128.3, 128.6, 140.0; MS, *m/z*: 191 [M⁺], 100 [CH₂N(CH₂CH₂)₂O⁺], 91 [C₆H₅CH₂⁺], 77 [C₆H₅].

***N*-[2-(4-Methylphenyl)ethyl]morpholine (Table 2, Entry 2).**² The general procedure was followed with 4-methylstyrene (527 μ l, 4.00 mmol) and morpholine (86.9 mg, 1.00 mmol). The reaction mixture was purified by flash column chromatography (10% EtOAc in hexane) to give 148 mg (72%) of the hydroamination product. ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.31 (s, 3H), 2.52 (t, *J* = 4.5 Hz, 4H), 2.57 (m, 2H), 2.76 (m, 2H), 3.74 (t, *J* = 4.5 Hz, 4H), 7.09 (s, 4H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 20.9, 32.7, 53.6, 60.9, 66.8, 128.4, 129.0, 135.4, 136.9; MS, *m/z*: 205 [M⁺], 100 [CH₂N(CH₂CH₂)₂O⁺].

***N*-[2-(4-Methoxyphenyl)ethyl]morpholine (Table 2, Entry 3).**² The general procedure was followed with 4-methoxystyrene (532 μ l, 4.00 mmol) and morpholine (86.8 mg, 1.00 mmol). The reaction mixture was purified by flash column chromatography (20% EtOAc in hexane) to give 158 mg (71%) of the hydroamination product. ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.51 (t, *J* = 4.4 Hz, 4H), 2.56 (m, 2H), 2.74 (m, 2H), 3.74 (t, *J* = 4.4 Hz, 4H) 3.78 (s, 3H), 6.83 (d, *J* = 6.6 Hz, 2H), 7.12 (d, *J* = 6.6 Hz, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 32.4, 53.7, 55.2, 61.2, 67.0, 113.8, 129.6, 132.1, 158.0; MS, *m/z*: 221 [M⁺], 135 [CH₃OC₆H₄CH₂CH₂⁺], 121 [CH₃OC₆H₄CH₂⁺], 100 [CH₂N(CH₂CH₂)₂O⁺].

***N*-[2-(3, 4-Dimethoxyphenyl)ethyl]morpholine (Table 2, Entry 4).**² The general procedure was followed with 4-methoxystyrene (592 μ l, 4.00 mmol) and morpholine (86.8 mg, 1.00 mmol). The reaction mixture was purified by flash column chromatography (20% EtOAc in

hexane, then 100% EtOAc) to give 176 mg (70%) of the hydroamination product as an oil. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.52 (t, J = 4.4 Hz, 4H), 2.52-2.62 (m, 2H), 2.72-2.79 (m, 2H), 3.75 (t, J = 4.4 Hz, 4H), 3.86 (s, 3H), 3.87 (s, 3H), 6.72-6.77 (m, 2H), 6.77-6.82 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 32.8, 53.6, 55.7, 55.8, 60.9, 66.9, 111.0, 111.8, 120.4, 132.6, 147.2, 148.6; MS, m/z : 251 [M^+], 100 [$\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}^+$].

***N*-[2-(4-Chlorophenyl)ethyl]morpholine (Table 2, Entry 5).**² The general procedure was followed with 10 mol% of $[\text{Rh}(\text{cod})(\text{DPEphos})]\text{BF}_4$ (83.6 mg, 100 μmol), 4-Chlorostyrene (480 μl , 4.00 mmol) and morpholine (86.7 mg, 1.00 mmol). The suspension was heated at 70 $^\circ\text{C}$ for 72 h. The reaction mixture was purified by flash column chromatography (20% EtOAc in hexane) to give 109 mg (48%) of the hydroamination product. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.50 (t, J = 4.5 Hz, 4H), 2.52-2.60 (m, 2H), 2.72-2.80 (m, 2H), 3.73 (t, J = 4.5 Hz, 4H), 7.13 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 32.6, 53.6, 60.5, 66.9, 128.4, 130.0, 131.8, 138.6; m/z : 224 [$\text{M}^+ - \text{H}$], 125 [$\text{ClC}_6\text{H}_4\text{CH}_2^+$], 100 [$\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}^+$].

***N*-[2-(3-Trifluoromethylphenyl)ethyl]morpholine (Table 2, Entry 6).**² The general procedure was followed with 10 mol% of $[\text{Rh}(\text{cod})(\text{DPEphos})]\text{BF}_4$ (83.6 mg, 100 μmol), 2.0 eq. of 3-trifluoromethylstyrene (297 μl , 2.00 mmol) and morpholine (87.5 mg, 1.00 mmol). The suspension was heated at 70 $^\circ\text{C}$ for 72 h. The reaction mixture was purified by flash column chromatography (20% EtOAc in hexane) to give 105 mg (40%) of the hydroamination product. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.45-2.55 (m, 4H), 2.58-2.65 (m, 2H), 2.84-2.92 (m, 2H), 3.76 (t, J = 4.6 Hz, 4H), 7.39-7.44 (m, 2H), 7.46-7.52 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 33.0, 53.6, 60.3, 66.9, 123.0 (q, J = 3.8 Hz), 124.2 (q, J = 272.2 Hz), 125.4 (q, J = 3.8 Hz), 128.8, 130.5 (q, J = 32.2 Hz), 130.9, 132.1, 141.0; m/z : 258 [$\text{M}^+ - \text{H}$], 100 [$\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}^+$].

***N*-(2-Phenethyl)piperidine (Table 2, Entry 7).**³ The general procedure was followed with styrene (458 μl , 4.00 mmol) and piperidine (85.1 mg, 1.00 mmol). The suspension was

heated at 75 °C for 72 h. The reaction mixture was purified by flash column chromatography (10% EtOAc in hexane) to give 108 mg (57%) of the hydroamination product. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.40-1.49 (m, 2H), 1.57-1.66 (m, 4H), 2.34-2.56 (m, 4H), 2.51-2.55 (m, 2H), 2.77-2.83 (m, 2H), 7.14-7.22 (m, 3H), 7.24-7.31 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 24.4, 25.9, 33.5, 54.5, 61.4, 125.9, 128.3, 128.7, 140.6; MS, m/z : 188 [$\text{M}^+ - \text{H}$], 105 [$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2^+$], 98 [$\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{CH}_2^+$], 91 [$\text{C}_6\text{H}_5\text{CH}_2^+$].

***N*-[2-(3, 4-Dimethoxyphenyl)ethyl]piperidine (Table 2, Entry 8).**⁴ The general procedure was followed with 3, 4-dimethoxystyrene (592 μL , 4.00 mmol) and piperidine (87.3 mg, 1.02 mmol). The reaction mixture was purified by flash column chromatography on silica gel (20% EtOAc in hexane) to give 169 mg (66%) of the hydroamination product as an oil. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.41-1.51 (m, 2H), 1.58-1.67 (m, 4H), 2.40-2.57 (m, 4H), 2.50-2.59 (m, 2H), 2.72-2.80 (m, 2H), 3.85 (s, 3H), 3.87 (s, 3H), 6.72-6.81 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 24.2, 25.8, 33.0, 54.4, 55.6, 55.7, 61.4, 111.0, 111.8, 120.3, 132.9, 147.1, 148.6; MS, m/z : 249 [M^+], 165 [$(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2^+$], 151 [$(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{CH}_2^+$], 98 [$\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{CH}_2^+$].

1-Phenyl-4-(2-phenylethyl)piperazine (Table 2, Entry 9). The general procedure was followed with styrene (458 μL , 4.00 mmol) and 4-phenylpiperazine (162 mg, 1.00 mmol). The suspension was heated at 75 °C for 72 h. The reaction mixture was purified by flash column chromatography (10% EtOAc in hexane) to give 154 mg (58%) of the hydroamination product. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.61-2.68 (m, 2H), 2.69 (t, $J = 5.0$ Hz, 4H), 2.81-2.88 (m, 2H), 3.23 (t, $J = 5.0$ Hz, 4H), 6.86 (t, $J = 7.3$ Hz, 1H), 6.94 (d, $J = 8.1$ Hz, 2H), 7.17-7.33 (m, 7H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 33.6, 49.1, 53.2, 60.5, 116.0, 119.6, 126.0, 128.4, 128.7, 129.1, 140.2, 151.2; MS, m/z : 266 [M^+], 175 [$\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}_6\text{H}_5^+$], 91 [$\text{C}_6\text{H}_5\text{CH}_2^+$], 77 [C_6H_5^+]; Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2$: C, 81.16; H, 8.32; N, 10.52. Found: C, 81.00; H, 8.11; N, 10.25.

***N*-(2-Phenylethyl)-4-*tert*-butyl piperazinecarboxylate (Table 2, Entry 10).**⁵ The general procedure was followed with styrene (458 μ L, 4.00 mmol) and *tert*-Butyl 1-piperazinecarboxylate (186 mg, 1.00 mmol) in 0.50 mL of toluene. The suspension was heated at 70 °C for 72 h. The reaction mixture was purified by flash column chromatography (20% EtOAc in hexane) to give 153 mg (53%) of the hydroamination product. ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.45 (s, 9H), 2.46 (t, *J* = 4.5 Hz, 4H), 2.56-2.64 (m, 2H), 2.77-2.84 (m, 2H), 3.46 (t, *J* = 5.0 Hz, 4H), 7.17-7.23 (m, 3H), 7.25-7.32 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 28.4, 33.4, 43.2 (broad), 43.9 (broad), 52.9, 60.4, 79.5, 126.0, 128.3, 128.6, 140.0, 154.7; MS, *m/z*: 290 [M⁺], 217 [C₆H₅CH₂CH₂N(CH₂CH₂)₂NCO⁺], 199 [CH₂N(CH₂CH₂)₂NCO₂⁺Bu⁺], 105 [C₆H₅CH₂CH₂⁺], 91 [C₆H₅CH₂⁺].

***N*-(2-Phenylethyl)-2,5-dimethylmorpholine (Table 2, Entry 11).** The general procedure was followed with styrene (458 μ L, 4.00 mmol) and 2,5-dimethylmorpholine (115 mg, 1.00 mmol) in 0.50 mL of toluene. The suspension was heated at 75 °C for 72 h. The reaction mixture was purified by flash column chromatography (20% EtOAc in hexane) to give 111 mg (51%) of the hydroamination product. ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.18 (d, *J* = 6.3 Hz, 6H), 1.79 (t, *J* = 10.7 Hz, 2H), 2.52-2.62 (m, 2H), 2.76-2.86 (m, 4H), 3.66-3.76 (m, 2H), 7.17-7.23 (m, 3H), 7.24-7.32 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 19.2, 33.3, 59.5, 60.5, 71.7, 126.1, 128.4, 128.7, 140.2; MS, *m/z*: 218 [M⁺ - H], 128 [CH₂N(CH(CH₃)CH₂)₂O⁺], 105 [(C₆H₅CH₂CH₂)⁺], 91 [C₆H₅CH₂⁺]; Anal. Calcd for C₁₄H₂₁NO: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.43; H, 9.44; N, 6.24.

***N*-[2-(4-Methoxyphenyl)ethyl]perhydroisoquinoline (Table 2, Entry 12).** The general procedure was followed with 4-methoxystyrene (532 μ L, 4.00 mmol) and a diastereomeric mixture of perhydroisoquinoline (140 mg, 1.00 mmol). The reaction mixture was purified by flash column chromatography (10% EtOAc in hexane) to give 170 mg (62%) of the two diastereomeric hydroamination products. A second column was run to obtain the pure major

isomer for the purpose of obtaining spectral data. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 0.82-1.06 (m, 2H), 1.18-1.45 (m, 4H), 1.51-1.80 (7H), 1.93-2.03 (m, 1H), 2.46-2.56 (m, 2H), 2.70-2.80 (m, 2H), 2.81-2.89 (m, 1H), 2.97-3.05 (m, 1H), 3.78 (s, 3H), 6.79-6.86 (m, 2H), 7.08-7.15 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 26.1, 26.5, 30.7, 32.7, 32.9, 32.9, 41.7, 41.9, 54.4, 55.2, 60.4, 61.2, 113.8, 129.6, 132.5, 157.9; MS, m/z : 272 [$\text{M}^+ - \text{H}$], 152 [$\text{CH}_2\text{NC}_9\text{H}_{16}^+$], 135 [$\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}_2^+$], 121 [$\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2^+$]; Anal. Calcd for $\text{C}_{18}\text{H}_{27}\text{NO}$: C, 79.07; H, 9.95; N, 5.12. Found: C, 78.99; H, 10.09; N, 5.24.

***N*-[2-(4-Methylphenyl)ethyl]dimethylamine (Table 2, Entry 13).**⁶ In a dry box, 4-methylstyrene (527 μl , 4.00 mmol) and dodecane (GC internal standard) was added to a suspension of $[\text{Rh}(\text{cod})(\text{DPEphos})]\text{BF}_4$ (41.8 mg, 50.0 μmol) in toluene (0.50 mL) in a screw-capped vial. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. Then a 2.0 M solution of dimethylamine in THF (447 mg, 526 μL , 1.05 mmol) was added to the vial, and the reaction mixture was heated at 70 $^\circ\text{C}$ for 72 h. The yield of hydroamination products (50%) and amine : enamine selectivity were determined by GC analysis. An authentic sample for GC analysis was obtained by flush column chromatography (100% EtOAc). ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.31 (s, 6H), 2.31 (s, 3H), 2.49-2.58 (m, 2H), 2.70-2.79 (m, 2H), 7.09 (s, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 21.0, 33.7, 45.3, 61.6, 128.6, 129.1, 135.5, 137.0; MS, m/z : 163 [$\text{M}^+ - \text{H}$], 119 [$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2^+$], 105 [$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2^+$], 58 [$\text{CH}_2\text{N}(\text{CH}_3)_2^+$].

***N*-[2-(3, 4-Dimethoxyphenyl)ethyl]dimethylamine (Table 2, Entry 14).**⁷ In a dry box, 3,4-dimethoxystyrene (592 μl , 4.00 mmol) was added to $[\text{Rh}(\text{cod})(\text{DPEphos})]\text{BF}_4$ (41.8 mg, 50.0 μmol) in a screw-capped vial. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. A 2.0 M solution of dimethylamine in THF solution (427 mg, 503 μl , 1.01 mmol) was then added to the vial, and the reaction mixture was heated at 70 $^\circ\text{C}$ for 72 h. The reaction mixture was purified by flash column chromatography (100% EtOAc) to give 156

mg (74%) of the hydroamination product. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.30 (s, 6H), 2.48-2.56 (m, 2H), 2.70-2.76 (m, 2H), 3.85 (s, 3H), 3.88 (s, 3H), 6.74 (d, $J = 7.7$ Hz, 2H), 6.80 (d, $J = 7.7$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 33.8, 45.3, 55.7, 55.8, 61.6, 111.1, 111.8, 120.3, 132.7, 147.2, 148.7; MS, m/z : 210 [M^+], 165 [$(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2^+$], 151 [$(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{CH}_2^+$], 58 [$\text{CH}_2\text{N}(\text{CH}_3)_2^+$].

2-(2-Dimethylaminoethyl)pyridine (Table 2, Entry 15).⁸ In a dry box, 2-vinylpyridine (431 μl , 4.00 mmol) and dodecane (GC internal standard) were added to a suspension of $[\text{Rh}(\text{cod})(\text{DPEphos})]\text{BF}_4$ (41.8 mg, 50.0 μmol) in toluene (0.50 mL) in a screw-capped vial. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. Dimethylamine was then added as a 2.0 M solution in THF (440 mg, 517 μL , 1.03 mmol), and the reaction mixture was heated at 70 $^\circ\text{C}$ for 48 h. The yield of hydroamination product (79%) and amine : enamine selectivity were determined by GC analysis. MS, m/z : 150 [$\text{M}^+ - \text{H}$], 106 [$\text{C}_5\text{H}_4\text{NCH}_2\text{CH}_2^+$], 79 [$\text{C}_5\text{H}_5\text{N}^+$], 58 [$\text{CH}_2\text{N}(\text{CH}_3)_2^+$].

Identification of the enamine side products. All the enamines formed as side product have been published previously and were identified by GC/MS analysis of crude reaction mixtures.

(*E*)-*N*-(2-Phenylethenyl)morpholine (Table 2, Entry 1).² MS, m/z : 189 [M^+], 104 [$(\text{C}_6\text{H}_5\text{CHCH}_2^+]$, 91 [$\text{C}_6\text{H}_5\text{CH}_2^+$], 77 [C_6H_5^+].

(*E*)-*N*-[2-(4-Methylphenyl)ethenyl]morpholine (Table 2, Entry 2).² MS, m/z : 203 [M^+], 188 [$\text{M}^+ - \text{H}$], 119 [$\text{CH}_3\text{C}_6\text{H}_4\text{CHCH}_2^+$], 105 [$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2^+$], 91 [$\text{C}_6\text{H}_5\text{CH}_2^+$].

(*E*)-*N*-[2-(4-Methoxyphenyl)ethenyl]morpholine (Table 2, Entry 3).² MS, m/z : 219 [M^+], 204 [$\text{M}^+ - \text{CH}_3$], 134 [$\text{CH}_3\text{OC}_6\text{H}_4\text{CHCH}_2^+$].

(*E*)-*N*-[2-(3, 4-Dimethoxyphenyl)ethenyl]morpholine (Table 2, Entry 4).² MS, m/z : 249 [M^+], 234 [$\text{M}^+ - \text{CH}_3$].

(E)-N-[2-(4-Chlorophenyl)ethenyl]morpholine (Table 2, Entry 5).² MS, m/z: 223 [M⁺], 138 [ClC₆H₄CHCH₂⁺], 100 [CH₂N(CH₂CH₂)₂O⁺].

(E)-N-[2-(3-Trifluoromethylphenyl)ethenyl]morpholine (Table 2, Entry 6).² MS, m/z: 257 [M⁺].

(E)-N-(2-Phenylethenyl)piperidine (Table 2, Entry 7).⁹ MS, m/z: 187 [M⁺], 130 [C₆H₅CHCHNCH₂⁺], 104 [C₆H₅CHCH₂⁺], 91 [C₆H₅CH₂⁺].

(E)-N-[2-(3, 4-Dimethoxyphenyl)ethenyl]piperidine (Table 2, Entry 8).⁴ MS, m/z: 247 [M⁺], 165 [(CH₃O)₂C₆H₃CHCH₂⁺], 151 [(CH₃O)₂C₆H₃CH₂⁺].

(E)-1-Phenyl-4-(2-phenylethenyl)piperazine (Table 2, Entry 9). MS, m/z: 264 [M⁺], 104 [C₆H₅CHCH₂⁺], 91 [C₆H₅CH₂⁺].

(E)-N-(2-Phenylethenyl)-4-tert-butyl piperazinecarboxylate (Table 2, Entry 10). MS, m/z: 288 [M⁺], 215 [M⁺ - OC₄H₉], 104 [C₆H₅CHCH₂⁺], 91 [C₆H₅CH₂⁺], 77 [C₆H₅⁺].

(E)-N-(2-Phenylethenyl)-2,5-dimethylmorpholine (Table 2, Entry 11). MS, m/z: 217 [M⁺], 128 [CH₂N(CH(CH₃)CH₂)₂O⁺], 91 [C₆H₅CH₂⁺].

(E)-N-[2-(4-Methoxyphenyl)ethenyl]perhydroisoquinoline (Table 2, Entry 12). MS, m/z: 271 [M⁺], 256 [M⁺ - CH₃], 134 [CH₃OC₆H₄CHCH₂⁺].

(E)-N-[2-(4-Methylphenyl)ethenyl]dimethylamine (Table 2, Entry 13). MS, m/z: 161 [M⁺ - H], 58 [CH₂N(CH₃)₂⁺].

(E)-N-[2-(3, 4-Dimethoxyphenyl)ethenyl]dimethylamine (Table 2, Entry 14). MS, m/z: 207 [M⁺ - H], 163 [(CH₃O)₂C₆H₃CHCH⁺], 58 [CH₂N(CH₃)₂⁺].

(E)-2-(2-Dimethylaminoethenyl)pyridine (Table 2, Entry 15).¹⁰ MS, m/z: 149 [M⁺], 105 [C₅H₄NCH₂CH₂⁺], 79 [C₅H₅N], 58 [CH₂N(CH₃)₂⁺].

Reactions of *p*-Methyl Styrene with Morpholine in the Presence of (E)-N-(2-Phenylethenyl)morpholine (Scheme 1). In a drybox, morpholine (17 μ l, 0.20 mmol), *p*-methyl styrene (106 μ l, 0.800 mmol) and (E)-N-(2-phenylethenyl)morpholine (38 mg, 0.20 mmol) were

added to a screw-capped vial containing a suspension of $[\text{Rh}(\text{cod})(\text{DPEphos})]\text{BF}_4$ (8.4 mg, 20 μmol) in 0.20 mL of toluene. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. The reaction mixture was stirred at 70 °C. After 48 h, the yields were determined by GC analysis.

Reactions Conducted with a Combination of Styrene and *m*-Trifluoromethylstyrene (Scheme 2). In a drybox, morpholine (17 μl , 0.20 mmol), styrene (46 μl , 0.40 mmol) and *m*-trifluoromethylstyrene (60 μl , 0.40 mmol) were added to a screw-capped vial containing a suspension of $[\text{Rh}(\text{cod})(\text{DPEphos})]\text{BF}_4$ (8.4 mg, 20 μmol) in 0.20 mL of toluene. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. The reaction mixture was stirred at 70 °C. After 48 h, the ratios of amines to enamines were determined by GC analysis.

Analysis of the Ratio of Amine : Enamine versus Time. In a drybox, 950 μl of styrene were mixed with toluene to create 1.00 mL of total volume. To a screw-capped vial containing morpholine (17 μl , 0.20 mmol) and $[\text{Rh}(\text{cod})(\text{DPEphos})]\text{BF}_4$ (8.4 mg, 20 μmol) was added 0.20 mL of the stock solution. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. The reaction mixture was stirred at 70 °C. The yield of amine and enamine and the ratio of amine:enamine was determined by GC analysis, correcting for the different response factors of the two materials.

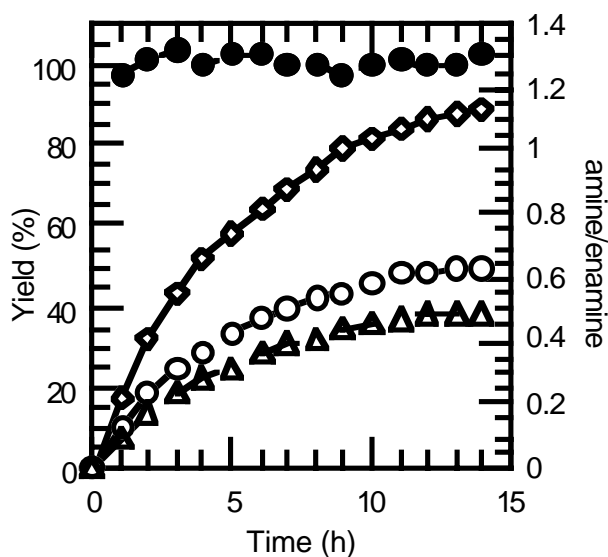


Figure S1. Appearance of hydroamination and enamine products. : \diamond = total yield of amine and enamine; O = amine yield; Δ = enamine yield; \bullet = amine : enamine ratio.

Synthesis of (*E*)-*N*-(2-Phenylethenyl)morpholine.⁴ Phenylacetaldehyde (1.60 g, 13.3 mmol) and morpholine (4.00 g, 46.0 mmol) were stirred at room temperature for 3 h with 5.0 g of 4A Molecular Sieves. The reaction mixture was concentrated under vacuum, and the product was isolated by distillation. (1.76 g, 71%): ^1H NMR (400 MHz, CDCl_3 , TMS) δ 3.03 (t, $J = 4.8$ Hz, 4H), 3.76 (t, $J = 4.8$ Hz, 4H), 5.38 (d, $J = 14.0$ Hz, 1H), 6.62 (d, $J = 14.0$ Hz, 1H), 7.05 (m, 1H), 7.23 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 48.9, 66.4, 101.4, 124.2, 124.4, 128.5, 138.6, 139.6; MS: m/z : 189, 158, 130, 104, 91, 77.

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