Platinum-Catalyzed Intermolecular Hydroamination of Unactivated Olefins with Carboxamides

Xiang Wang and Ross A. Widenhoefer*

P. M. Gross Chemical Laboratory

Duke University

Durham, NC 27708-0346

email: rwidenho@chem.duke.edu

Supporting Information

Experimental procedures and spectroscopic data for alkylated carboxamides and 3-ethyl-2-oxazolidinone (4 pages).

Experimental

General Methods. Pressurized reactions were performed behind a 3/8 inch plexiglass blast shield in a thick-walled glass tube equipped with a pressure gauge and a valve that allowed the pressure of the tube to be controlled throughout the transformation. NMR spectra were obtained on a Varian spectrometer operating at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR in CDCl_3 unless otherwise noted. Gas chromatography was performed on a Hewlett-Parkard 5890 gas chromatography equipped with a 25 m polydimethylsiloxane capillary column. Flash column chromatography was performed employing 200-400 mesh silica gel (EM). Thin layer chromatography (TLC) was performed on silica gel 60 F₂₅₄ eluting with a 5:1 mixture of hexanes and ethyl acetate unless otherwise noted. 1,4-Dioxane (Acros, anhydrous), $[\text{PtCl}_2(\text{H}_2\text{C}=\text{CH}_2)]_2$ (**1**) (Strem), phosphines, carboxamides, and 2-oxazolidone (Aldrich) were used as received.

***N*-Ethylbenzamide (Table 1, entry 9).** A solution of benzamide (121 mg, 1.0 mmol), **1** (15 mg, 2.5×10^{-3} mmol), PPh_3 (13 mg, 0.05 mmol) in dioxane (0.5 mL) in a thick-walled tube was evacuated, pressurized with ethylene (50 psi), and heated to 120 °C while maintaining constant pressure. The reaction mixture was heated at 120 °C for 24 h, cooled to room temperature, and chromatographed (SiO_2 , hexanes–EtOAc = 2:1) to give *N*-ethylbenzamide (144 mg, 97 %) as a pale yellow solid. mp 71-72 °C. ^1H NMR δ 7.74-7.77 (m, 2 H), 7.44-7.48 (m, 1 H), 7.37-7.41 (m, 2 H), 6.41 (br s, 1 H), 3.46 (dq, J = 5.6, 7.2 Hz, 2 H), 1.22 (t, J = 7.2 Hz, 3 H). ^{13}C { ^1H } NMR: δ 167.7, 135.0, 131.5, 128.7, 127.1, 35.1, 15.1.

***N*-Ethyl-4-methoxybenzamide (Table 2, entry 1).** mp 76-77 °C. ^1H NMR: δ 7.73 (d, J = 8.8 Hz, 2 H), 6.81 (d, J = 8.8 Hz, 2 H), 3.75 (s, 3 H), 3.39 (dq, J = 6.0, 7.2 Hz, 2 H), 1.15 (t, J = 7.2 Hz, 3 H). ^{13}C { ^1H } NMR: δ 167.4, 162.1, 129.0, 127.2, 113.7, 55.5, 35.0, 15.1.

***N*-Ethyl-4-bromobenzamide (Table 2, entry 2).** mp 110-111 °C. ^1H NMR: δ 7.61 (d, J = 8.8 Hz, 2 H), 7.28 (d, J = 8.4 Hz, 2 H), 6.78 (br s, 1 H), 3.42 (dq, J = 5.6, 7.2 Hz, 2 H), 1.19 (t, J = 7.2 Hz, 3 H). ^{13}C { ^1H } NMR: δ 166.8, 133.8, 131.8, 128.8, 35.2, 15.0.

***N*-Ethyl-4-nitrobenzamide (Table 2, entry 3).** mp 140-142 °C. ¹H NMR: δ 8.22 (d, *J* = 8.4 Hz, 2 H), 7.92 (d, *J* = 8.4 Hz, 2 H), 6.70 (s, 1 H), 3.45-3.51 (m, 2 H), 1.24 (t, *J* = 7.2 Hz, 3 H). ¹³C {¹H} NMR: δ 165.7, 149.6, 140.6, 128.3, 123.9, 35.5, 14.9.

***N*-Ethyl-4-toluamide (Table 2, entry 4).** ¹H NMR: δ 7.67 (d, *J* = 8.4 Hz, 2 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 6.94 (s, 1 H), 3.39 (dq, *J* = 6.0, 7.2 Hz, 2 H), 2.31 (s, 3 H), 1.15 (t, *J* = 7.2 Hz, 3 H). ¹³C {¹H} NMR: δ 167.8, 141.6, 132.1, 129.2, 127.2, 35.0, 21.6, 15.0.

***N*-Ethyl-2-toluamide (Table 2, entry 5).** mp 48-49 °C. ¹H NMR: δ 7.20-7.24 (m, 2 H), 7.07-7.13 (m, 2 H), 6.20 (m, 1 H), 3.33 (dq, *J* = 6.0, 7.2 Hz, 2 H), 2.34 (s, 3 H), 1.14 (t, *J* = 7.2 Hz, 3 H). ¹³C {¹H} NMR: δ 170.3, 136.9, 135.9, 131.0, 129.7, 126.8, 125.8, 34.8, 19.8, 15.0.

***N*-Ethyl-2-naphthylcarboxamide (Table 2, entry 6).** mp 125-126 °C. ¹H NMR: δ 8.27 (s, 1 H), 7.79-7.84 (m, 4 H), 7.74-7.53 (m, 2 H), 6.74 (br s, 1 H), 3.52 (dq, *J* = 5.6, 7.2 Hz, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H). ¹³C {¹H} NMR: δ 167.8, 134.8, 132.8, 132.2, 129.1, 128.5, 127.9, 12.7, 127.6, 126.8, 123.9, 35.3, 15.1.

***N*-Ethyl-1-naphthylcarboxamide (Table 2, entry 7).** mp 101-102 °C. ¹H NMR: δ 8.21- 8.23 (m, 1 H), 7.79-7.83 (m, 2 H), 7.44-7.50 (m, 3 H), 7.32 (dd, *J* = 7.2, 8.4 Hz, 1 H), 6.33 (br s, 1 H), 3.43 (dq, *J* = 6.0, 7.2 Hz, 2 H), 1.18 (t, *J* = 7.2 Hz, 2 H). ¹³C {¹H} NMR: δ 169.7, 134.9, 133.8, 130.5, 130.3, 128.4, 127.1, 126.5, 125.6, 125.6, 125.0, 124.9, 35.0, 15.0.

***N*-Ethylvaleramide (Table 2, entry 8).** ¹H NMR: δ 6.28 (br s, 1 H), 3.18 (dq, *J* = 5.6, 7.2 Hz, 2 H), 2.08 (t, *J* = 7.6 Hz, 2 H), 1.48-1.55 (m, 2 H), 1.25 (sept, *J* = 7.6 Hz, 2 H), 1.04 (t, *J* = 7.2 Hz, 3 H), 0.82 (t, *J* = 7.2 Hz, 3 H). ¹³C {¹H} NMR: δ 173.5, 36.6, 34.3, 28.1, 22.5, 14.9, 13.9.

***N*-Ethylcyclohexanecarboxamide (Table 2, entry 9).** mp 92-93 °C. ¹H NMR; δ 5.63 (br s, 1 H), 3.24 (dq, *J* = 5.6, 7.2 Hz, 2 H), 2.02 (tt, *J* = 7.2, 15.0 Hz, 2 H), 1.73-1.83 (m, 4 H), 1.62-1.66 (m, 1 H), 1.36-1.47 (m, 2 H), 1.14-1.28 (m, 3 H), 1.09 (t, *J* = 7.2 Hz, 3 H). ¹³C {¹H} NMR: δ 176.2, 45.7, 34.3, 29.9, 25.9, 15.1.

***N*-Ethylpivalamide (Table 2, entry 10).** mp 44-45 °C. ¹H NMR: δ 5.75 (br s, 1 H), 3.20 (dq, *J* = 5.6, 7.2 Hz, 2 H), 1.13 (s, 9 H), 1.06 (t, *J* = 7.2 Hz, 3 H). ¹³C {¹H} NMR: δ 178.5, 38.7, 34.5, 27.7, 15.0.

***N*-Ethyl-2-piperidinone (Table 2, entry 11).** ¹H NMR: δ 3.25 (q, *J* = 7.2 Hz, 2 H), 3.11-3.14 (m, 2 H), 2.19 (t, *J* = 6.4 Hz, 2 H), 1.61-1.67 (m, 2 H), 0.96 (t, *J* = 7.2 Hz, 3 H). ¹³C {¹H} NMR: δ 169.3, 47.2, 41.8, 32.4, 23.3, 21.5, 12.2.

3-Ethyl-2-oxazolidinone (Table 2, entry 12). ¹H NMR: δ 4.29-4.33 (m, 2 H), 3.52-3.57 (m, 2 H), 3.32 (q, *J* = 7.2 Hz, 2 H), 1.16 (q, *J* = 7.2 Hz, 3 H). ¹³C {¹H} NMR: δ 158.4, 61.9, 44.0, 39.0, 12.6.

***N*-Isopropylvaleramide (eq 2).** A thick-walled tube containing valeramide (101 mg, 1.0 mmol), **1** (30 mg, 0.05 mmol), PPh₃ (26 mg, 0.10 mmol) and dioxane (0.5 mL) was evacuated, pressurized with propylene (100 psi), and heated to 120 °C while maintaining constant pressure. The reaction mixture was heated at 120 °C for 80 h, cooled to room temperature and chromatographed (SiO₂, hexanes–EtOAc = 2:1) to give *N*-isopropylvaleramide (105 mg, 73%) as a pale yellow oil. ¹H NMR δ 5.44 (br s, 1 H), 4.05 (d sept, *J* = 5.2, 10.8 Hz, 1 H), 2.10 (t, *J* = 7.6 Hz, 2 H), 1.53-1.61 (m, 2 H), 1.31 (sextet, *J* = 7.2 Hz, 2 H), 1.11 (d, *J* = 6.4 Hz, 6 H), 0.88 (t, *J* = 7.2 Hz, 3 H). ¹³C {¹H} NMR: δ 172.5, 41.4, 36.9, 28.1, 23.0, 25.6, 14.0.