Supporting information for *Angew. Chem. Int. Ed.*

A Rh-Catalyzed C–H Insertion Reaction for the Oxidative Conversion of Carbamates to Oxazolidinones

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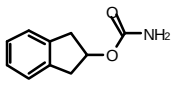
General. All reagents were commercially obtained unless otherwise noted. Reactions were performed using oven-dried glassware under an atmosphere of dry nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated under reduced pressure (ca. 10 mm Hg) by rotary evaporation. Dichloromethane and chlorobenzene were freshly distilled from CaH_2 prior to use. Reagent grade methanol was used without purification. Light magnesium oxide was flame-dried twice under reduced pressure (1 mm Hg) immediately prior to use. Chromatographic purification of products was accomplished using forced-flow chromatography on EM Science Geduran silica gel 60 (35–75 μm). All compounds purified by chromatography on silica gel with hexanes/EtOAc as eluant were applied to the adsorbent bed in a minimum amount of dichloromethane. Thin layer chromatography was performed on EM Science silica gel 60 F_{254} plates (250 μm). Visualization of the developed chromatogram was accomplished by fluorescence quenching and by staining with either ethanolic anisaldehyde or aqueous potassium permanganate solution.

NMR spectra were acquired on a Varian XL–400 operating at 400 and 100 MHz for ^{1}H and ^{13}C, respectively, and are referenced internally according to residual protio solvent signals. Data for ^{1}H are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet), integration, coupling constant (Hz). Data for ^{13}C are reported in terms of chemical shift (δ, ppm). IR spectra were recorded on a Perkin-Elmer Paragon 500 FTIR spectrometer using NaCl salt plates and are reported in frequency of absorption. Gas chromatograms were acquired on a Hewlett-Packard HP6890 Series GC using a J&W Scientific CYCLOSILB cyclodextrin column. High-resolution mass spectra were obtained from the Mass Spectrometry Facility, University of California at San Francisco, supported by the NIH Division of Research and Resources.

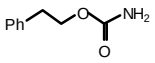
[$Rh_2(TPA)_4$] preparation: Rhodium triphenylacetate dimer, [$Rh_2(TPA)_4$], was prepared following a slight modification of the method described by Ikegami.[1] To a suspension of triphenylacetic acid (1.57 g, 5.43 mmol, 8.0 equiv) in 75 mL of chlorobenzene was added [$Rh_2(OAc)_4$] (300 mg, 0.68 mmol). The reaction flask was equipped with a short-path distillation apparatus and a receiving bulb, and the contents heated to ~135 °C. At this temperature, solvent distilled at a rate of ca. 5 mL/hr. After 7 hrs, the reaction was cooled to 25 °C and diluted with 40 mL of CH_2Cl_2. The solution was washed with 3 x 75 mL of saturated aqueous $NaHCO_3$, 1 x 100 mL of saturated aqueous NaCl, and dried over $MgSO_4$. Evaporation of the organic extract

under reduced pressure yielded a yellow-green solid. The unpurified material was dissolved in 10 mL of CH_2Cl_2 and filtered through a short pad of silica gel using 3:1 CH_2Cl_2/EtOAc as eluant. The product was isolated as a deep green solid and dried *in vacuo* at 80 °C for 8 hr (875 mg, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.08 (t, 12H, *J* = 7.3 Hz), 6.88 (t, 24H, *J* = 7.7 Hz), 6.62 (d, 24H, *J* = 7.6 Hz) ppm.

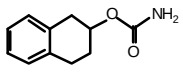
Carbamate preparation[2]**:** Trichloroacetyl isocyanate (7.9 g, 42 mmol, 1.2 equiv) was added slowly to a solution of alcohol (32 mmol) in 90 mL of CH_2Cl_2 at 0 °C. The reaction was warmed to 25 °C and stirred for 2–6 hrs. Following completion of the reaction as indicated by TLC analysis, the contents were evaporated under reduced pressure. The unpurified material was dissolved in 70 mL of MeOH to which solid K_2CO_3 (485 mg, 0.35 mmol, 0.1 equiv) was added. The solution was stirred for 2–8 hrs, then partitioned between 50 mL of CH_2Cl_2 and 70 mL of saturated aqueous NH_4Cl. The organic phase was collected, and the aqueous layer was extracted with 2 x 30 mL of CH_2Cl_2. The combined organic extracts were washed with 1 x 100 mL of saturated aqueous NaCl, dried with $MgSO_4$, and evaporated under reduced pressure to afford the product as an oily residue. This material was suspended in 15 mL of toluene and concentrated under reduced pressure to dryness. Repeating this process a second time furnished the unpurified carbamate as a tractable white solid. Purification was accomplished by recrystallization or by chromatography on silica gel (as indicated).



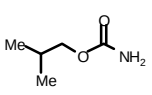
Recrystallized from MeOH/Et_2O; white needles (85%): TLC R_f = 0.42 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28–7.17 (m, 4H), 5.50–5.44 (m, 1H), 4.66 (br s, 2H), 3.30 (dd, 2H, *J* = 17.0, 6.2 Hz), 3.05 (dd, 2H, *J* = 17.0, 2.5 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.7, 140.5, 126.7, 124.6, 76.1, 39.7 ppm; IR (thin film) ν 3417, 3322, 3019, 2950, 1682, 1611, 1414, 1341, 1062 cm^{-1}.



Recrystallized from Et_2O; white leaflets (88%): TLC R_f = 0.20 (2:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28–7.20 (m, 5H), 4.88 (br s, 2H), 4.29 (t, 2H, *J* = 7.0 Hz), 2.94 (t, 2H, *J* = 7.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 400 MHz) δ 157.0, 137.9, 128.9, 128.5, 126.5, 65.5, 35.4 ppm; IR (thin film) ν 3420, 3333, 3024, 2965, 1683, 1606, 1409, 1339, 1079 cm^{-1}.

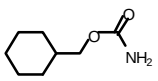


Purification by chromatography on silica gel (5:2 hexanes/EtOAc); white microcrystalline solid (70%): TLC R_f = 0.44 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$) δ 7.20–7.05 (m, 4H), 5.13 (m, 1H), 4.57 (br s, 2H), 3.13 (dd, 1H, *J* = 16.6, 5.0 Hz), 2.99–2.80 (m, 3H), 2.10–1.94 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.7, 135.6, 133.7, 129.4, 128.6, 126.0, 125.9, 70.2, 34.7, 27.8, 26.1; IR (thin film) ν 3418, 3320, 2959, 1682, 1614, 1434, 1414, 1334, 1058 cm^{-1}.

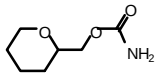


Recrystallized from hexanes; white leaflets (76%): TLC R_f = 0.45 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.04 (br s, 2H), 3.81 (d, 2H, *J* = 6.7 Hz), 1.89 (sept, 1H, *J* = 6.7 Hz), 0.90 (d, 6H, *J* = 6.7 Hz) ppm; ^{13}C NMR

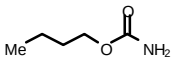
($CDCl_3$, 100 MHz) δ 157.8, 71.1, 27.8, 18.9 ppm; IR (thin film) ν 3426, 3339, 2961, 1698, 1603, 1414, 1335, 1069 cm^{-1}.



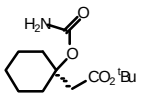
Recrystallized from hexanes/MeOH; white leaflets (78%): TLC R_f = 0.42 (1:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$; 400 MHz) δ 4.69 (br s, 2H), 3.87 (d, 2H, *J* = 6.6 Hz), 1.78–1.56 (m, 6H), 1.32–1.10 (m, 3H), 1.04–0.86 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.4, 70.3, 37.3, 29.5, 26.3, 25.6 ppm; IR (thin film) ν 3435, 3322, 3259, 2855, 2929, 1686, 1616, 1460, 1419, 1355, 1066 cm^{-1}.



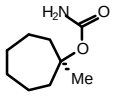
Purification by chromatography on silica gel (1:1 hexanes/EtOAc), white solid (71%): TLC R_f = 0.33 (1:2 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 400 MHz) δ 4.72 (br s, 2H), 4.13 (dd, 1H, *J* = 11.6, 3.0 Hz), 4.06–3.99 (m, 1H), 3.97 (dd, 1H, *J* = 11.6, 7.1 Hz), 3.58–3.52 (m, 1H), 3.45 (dt, 1H, *J* = 11.4, 2.5 Hz), 1.92–1.84 (m, 1H), 1.66–1.44 (m, 4H), 1.38–1.26 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.1, 75.7, 68.3, 68.0, 27.5, 25.6, 22.9 ppm; IR (thin film) ν 3429, 3330, 3294, 3192, 2935, 2854, 1723, 1706, 1617, 1414, 1326, 1068 cm^{-1}.



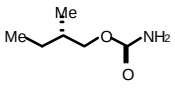
Recrystallized from hexanes; white leaflets (60%): TLC R_f = 0.26 (2:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 400 MHz) δ 4.87 (br s, 2H), 4.04 (t, 2H, *J* = 6.6 Hz), 1.62–1.55 (m, 2H), 1.41–1.32 (m, 2H), 0.91 (t, 3H, *J* = 7.5 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.8, 64.8, 30.9, 18.9, 13.6 ppm; IR (thin film) ν 3493, 3411, 3330, 2962, 2874, 1704, 1604, 1413, 1339, 1077 cm^{-1}.



Recrystallized from hexanes; white solid (68%): TLC R_f = 0.32 (2:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 400 MHz) δ 4.74 (s, 2H), 2.85 (s, 2H), 2.26–2.14 (m, 2H), 1.62–1.44 (m, 7H), 1.42 (s, 9H), 1.30–1.18 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.8, 156.0, 80.3, 43.7, 34.8, 28.0, 25.2, 21.6 ppm; IR (thin film) ν 3453, 3371, 3272, 2977, 2935, 2864, 1715, 1601, 1450, 1369, 1256, 1155, 1127, 1042 cm^{-1}.



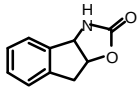
Recrystallized from hexanes/MeOH; white crystalline solid (62%): TLC R_f = 0.38 (2:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 400 MHz) δ 4.75 (br s, 2H), 2.08 (dd, 2H, *J* = 14.5, 8.2 Hz), 1.71 (dd, 2H, *J* = 14.6, 10.0 Hz), 1.65–1.50 (m, 6H), 1.48 (s, 3H), 1.44–1.37 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.7, 85.3, 40.3, 29.5, 27.0, 22.6 ppm; IR (thin film) ν 3452, 3328, 3326, 3209, 2924, 2856, 1681, 1607, 1391, 1129, 1053 cm^{-1}.



Recrystallized from hexanes; white leaflets (73%): TLC R_f = 0.42 (1:1 hexanes/EtOAc), ^1H NMR ($CDCl_3$, 400 MHz) δ 4.71 (br s, 2H), 3.94 (dd, 1H, *J* = 10.5, 6.2 Hz), 3.85 (dd, 1H, *J* = 10.5, 6.8 Hz), 1.78–1.64 (m, 1H), 1.49–1.37 (m, 1H), 1.24-1.10 (m, 1H), 0.93–0.88 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.5, 69.8, 34.3, 25.9, 16.2, 11.1 ppm; IR (thin film) ν 3410, 3330, 3271, 2963, 1685, 1604, 1411, 1335, 1076 cm^{-1}.

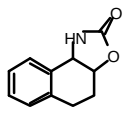
2–Oxazolidinone preparation: To a solution of carbamate (1.26 mmol) in 8 mL of CH_2Cl_2 were added successively MgO (117 mg, 2.89 mmol, 2.3 equiv), $PhI(OAc)_2$ (486 mg, 1.51 mmol, 1.4 equiv) and Rh^{II} catalyst (63 μmol, 0.05 equiv). The mixture was stirred vigorously and heated at

40 °C for 12 hrs. After cooling to 25 °C, the reaction was diluted with 10 mL of CH_2Cl_2 and filtered through a pad of Celite (30 x 20 mm). The filter cake was rinsed with 2 x 10 mL of CH_2Cl_2. The combined filtrates were evaporated under reduced pressure and the isolated residue purified by chromatography on silica gel.

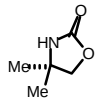


Catalyst = **[$Rh_2(OAc)_4$]**, 86% yield; purification by chromatography on silica gel (3:1 CH_2Cl_2/EtOAc): TLC R_f = 0.26 (3:1 CH_2Cl_2/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34–7.25 (m, 4H), 6.58 (br s, 1H), 5.42 (ddd, 1H, *J* = 7.2, 6.1, 2.1 Hz), 5.17 (d, 1H, *J* = 7.3 Hz); 3.36–3.32 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.9, 140.3, 139.7, 129.3, 127.9, 125.5, 124.8, 80.6, 61.2, 38.8 ppm; IR (thin film) ν 3250, 3131, 1753, 1705, 1484, 1385, 1232, 1180, 1102 cm^{-1}; HRMS (EI) calcd for $C_{10}H_9NO_2$ 175.0633 found 175.0630 (M^+).

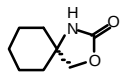
Catalyst = **[$Rh_2(TPA)_4$]**, 74% yield; purification by chromatography on silica gel (5:1 CH_2Cl_2/EtOAc): TLC R_f = 0.28 (5:1 CH_2Cl_2/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60–7.22 (m, 5H), 6.72 (br s, 1H), 4.94 (t, 1H, *J* = 7.0 Hz), 4.70 (t, 1H, *J* = 8.7 Hz), 4.14 (dd, 1H, *J* = 8.6, 7.0 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.9, 139.5, 129.6, 128.8, 126.0, 72.5, 56.3 ppm; IR (thin film) ν 3262, 1744, 1723, 1456, 1402, 1238, 1037 cm^{-1}; HRMS (EI) calcd for $C_9H_9NO_2$ 163.0633 found 163.0639 (M^+).



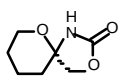
Catalyst = **[$Rh_2(TPA)_4$]**, 77% yield; purification by chromatography on silica gel (3:1 CH_2Cl_2/EtOAc): TLC R_f = 0.28 (3:1 CH_2Cl_2/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.12 (m, 4H), 6.99 (br s, 1H), 5.14–5.08 (m, 1H), 4.91 (d, 1H, *J* = 8.3 Hz), 2.90 (ddd, 1H, *J* = 15.8, 8.2, 3.7 Hz), 2.61 (dt, 1H, *J* = 15.9, 4.3 Hz), 2.30–2.21 (m, 1H), 1.86–1.76 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.8, 137.4, 133.5, 128.9, 128.7, 128.0, 127.2, 75.6, 53.4, 27.3, 23.9 ppm; IR (thin film) ν 3267, 3031, 2944, 1744, 1495, 1387, 1233, 1070 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{11}NO_2$ 189.0790 found 189.0778 (M^+).



Catalyst = **[$Rh_2(OAc)_4$]**, 83% yield; purification by chromatography on silica gel (3:1 CH_2Cl_2/EtOAc): TLC R_f = 0.18 (3:1 CH_2Cl_2/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.72 (br s, 1H), 4.08 (s, 2H), 1.36 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.5, 76.9, 55.2, 27.5 ppm; IR (thin film) ν 3286, 2974, 1749, 1482, 1395, 1296, 1214, 1039 cm^{-1}; HRMS (EI) calcd for $C_5H_9NO_2$ 115.0633 found 116.0705 (MH^+).

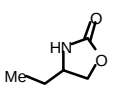


Catalyst = **[$Rh_2(OAc)_4$]**, 77% yield; Catalyst = **[$Rh_2(TPA)_4$]**, 79%; purification by chromatography on silica gel (2:1 hexanes/EtOAc): TLC R_f = 0.23 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.48 (br s, 1H), 4.09 (s, 2H), 1.72–1.34 (m, 10H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.9, 75.7, 57.8, 36.9, 24.7, 22.5 ppm; IR (thin film) ν 3227, 3122, 2931, 2850, 1747, 1479, 1339, 1250 cm^{-1}; HRMS (EI) calcd for $C_8H_{13}NO_2$ 155.0946 found 155.0950 (M^+).

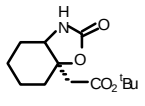


Catalyst = **[$Rh_2(OAc)_4$]**, 82% yield; Catalyst = **[$Rh_2(TPA)_4$]**, 84% yield; purification by chromatography on silica gel (1:2 hexanes/EtOAc): TLC R_f = 0.30 (1:2 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (br s, 1H), 4.32 (d, 1H, *J* = 9.3

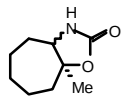
Hz), 4.11 (d, 1H, *J* = 9.3 Hz), 3.82–3.69 (m, 2H), 1.87–1.68 (m, 4H), 1.64–1.54 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.9, 87.2, 76.3, 62.9, 33.5, 24.5, 19.8 ppm; IR (thin film) ν 3213, 3134, 2963, 2860, 1753, 1445, 1398, 1304, 1046 cm^{-1}; HRMS (EI) calcd for $C_7H_{11}NO_3$ 157.0739 found 157.0740 (M^+).



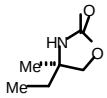
Catalyst = **[Rh_2(TPA)$_4$]**, 44% yield; purification by chromatography on silica gel (1:1 hexanes/EtOAc): TLC R_f = 0.13 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.67 (br s, 1H), 4.47 (t, 1H, *J* = 8.5 Hz), 4.01 (dd, 1H, *J* = 8.4, 6.1 Hz), 3.85–3.76 (m, 1H), 1.64–1.53 (m, 2H), 0.93 (t, 3H, *J* = 7.4 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.3, 70.0, 53.8, 28.2, 9.3 ppm; IR (thin film) ν 3280, 2968, 1745, 1408, 1237, 1052 cm^{-1}; HRMS (EI) calcd for $C_5H_9NO_2$ 115.0633 found 116.0702 (MH^+).



Catalyst = **[Rh_2(OAc)$_4$]**, 82% yield; purification by chromatography on silica gel (2:1 hexanes/EtOAc): TLC R_f = 0.28 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.45 (br s, 1H), 3.95 (dd, 1H, *J* = 4.6, 4.0 Hz), 2.67 (d, 1H, *J* = 14.8 Hz), 2.52 (d, 1H, *J* = 14.8 Hz), 1.88–1.67 (m, 3H), 1.64–1.51 (m, 3H), 1.50–1.32 (m, 11H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.6, 159.5, 81.8, 81.5, 54.5, 44.3, 30.4, 27.9, 26.7, 18.0, 16.9 ppm; IR (thin film) ν 3287, 2939, 2873, 1753, 1728, 1456, 1369, 1257, 1155, 1047 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{21}NO_4$ 255.1470 found 198.0771 (M^+–^{t}Bu).



Catalyst = **[Rh_2(OAc)$_4$]**, 83% yield (8:1 cis/trans mixture by ^{1}H NMR; stereochemistry of major product assigned by X–ray crystallography); purification by chromatography on silica gel (1:1 hexanes/EtOAc): TLC R_f = 0.19 (1:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) δ 5.40 (br s, 1H), 3.51 (dd, 1H, *J* = 8.2, 3.0 Hz), 1.96–1.42 (m, 9H), 1.40–1.28 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.0, 86.2, 62.6, 37.3, 32.1, 30.7, 28.4, 24.9, 23.7 ppm; IR (thin film) ν 3283, 2930, 2860, 1744, 1446, 1380 cm^{-1}; HRMS (EI) calcd for $C_9H_{15}NO_2$ 169.1103 found 170.1188 (MH^+).



Catalyst = **[Rh_2(TPA)$_4$]**, 72% yield; purification by chromatography on silica gel (3:1 CH_2Cl_2/EtOAc): TLC R_f = 0.28 (3:1 CH_2Cl_2/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.35 (br s, 1H), 4.13 (d, 1H, *J* = 8.4 Hz), 4.03 (d, 1H, *J* = 8.4 Hz), 1.60 (q, 2H, *J* = 7.5 Hz), 1.31 (s, 3H), 0.94 (t, 3H, *J* = 7.5 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) 159.7, 75.4, 58.1, 33.1, 25.3, 8.0 ppm; IR (thin film) ν 3278, 2972, 2934, 1748, 1462, 1397, 1273, 1197, 1039 cm^{-1}; HRMS (EI) calcd for $C_6H_{11}NO_2$ 129.0790 found 130.0873 (MH^+).

(1) Hashimoto, S.-i.; Watanabe, N.; Ikegami, S. *Tetrahedron Lett.* **1992**, *33*, 2709-2712.

(2) Kocovsky, P. *Tetrahedron Lett.* **1986**, *27*, 5521-5524.