Supporting Information

Direct Intermolecular Hydroacylation of *N,N*-Dialkylacrylamides with Aldehydes Catalyzed by Cationic Rhodium(I)/dppb Complex

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I. General

Anhydrous CH_2Cl_2 (No. 27,099-7), $(\text{CH}_2\text{Cl})_2$ (No. 28,450-5), and toluene (No. 24,451-1) were obtained from Aldrich and used as received. Solvents for the synthesis of substrate **4** were dried over Molecular Sieves 4A (Wako) prior to use. All reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried glassware with magnetic stirring.

II. Synthesis of Substrate

4-(3-Oxopropyl)benzaldehyde (**4**).¹

A solution of $\text{Pd}(\text{OAc})_2$ (1.6 mg, 0.0071 mmol) in NMP (10 mL) was added to a stirred suspension of NaOAc (1.35 g, 16.5 mmol), bromobenzaldehyde (2.78 g, 15.0 mmol), and NMP (20 mL). After heating to 120 °C, *n*-butyl acrylate (1.79 g, 21 mmol) was added to the resulting mixture. The mixture was stirred at 135 °C for 2 h. The mixture was cooled to room temperature, poured into water, and extracted with Et_2O . The organic layer was washed with water and brine, dried over Na_2SO_4 , and concentrated, which afforded crude 3-(4-formylphenyl)acrylic acid *n*-butyl ester (4.21 g) as a brown oil.

A solution of crude 3-(4-formylphenyl)acrylic acid *n*-butyl ester (4.21 g) in THF (25 mL) was added to a suspension of LiAlH_4 (1.57 g, 41 mmol) in THF (25 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 h and quenched with water at 0 °C. The mixture was added to aqueous HCl and extracted with ether.

The organic layer was washed with water, dried over Na₂SO₄, and concentrated. The residue was purified by silica gel chromatography (EtOAc), which afforded 89:11 mixture of 3-(4-hydroxymethylphenyl)-1-propanol and 3-(4-hydroxymethylphenyl)prop-2-en-1-ol (0.78 g) as a colorless oil.

An EtOH (10 mL) solution of this crude product (0.78 g) was added to 3 wt% Pt/C (69 mg) and stirred at room temperature under H₂ (1 atm) for 3 h. Filtration followed by concentration to dryness afforded 3-(4-hydroxymethylphenyl)-1-propanol (0.73 g, 4.4 mmol, 29% yield from bromobenzaldehyde, unoptimized) as a colorless oil.

A solution of DMSO (2.13 g, 27.2 mmol) in CH₂Cl₂ (20 mL) was added to a stirred solution of (COCl)₂ (2.29 g, 18.0 mmol) in CH₂Cl₂ (5 mL) at -78 °C. The resulting mixture was stirred for 5 min, and a solution of 3-(4-hydroxymethylphenyl)-1-propanol (0.73 g, 4.4 mmol) in CH₂Cl₂ (10 mL) was added at -78 °C. After stirring at -78 °C for 40 min, Et₃N (6.1 mL, 43.9 mmol) was added dropwise. The resulting mixture was allowed to warm to 0 °C and stirred at 0 °C for 1 h. The reaction was quenched with water and extracted with CH₂Cl₂. The organic layer was washed with water and brine, dried over Na₂SO₄, and concentrated. The residue was purified by silica gel chromatography (hexane/EtOAc = 5:1–2:1), which afforded **4** (0.48 g, 2.9 mmol, 66% yield, unoptimized) as a pale yellow oil.

IR (neat) 2820, 1690, 1605, 1165 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 9.98 (s, 1H), 9.84 (t, *J* = 1.1 Hz, 1H), 7.82 (dt, *J* = 8.1, 1.8 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H), 2.84 (t, *J* = 7.2 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 200.5, 191.8, 147.7, 134.8, 130.0, 129.0, 44.6, 28.1; HRMS (EI) calcd for C₁₀H₁₀O₂ [M]⁺ 162.0681, found 162.0672.

III. Intermolecular Hydroacylation of Alkenes with Aldehydes

Representative procedure (Table 1, entry 2): Under an argon atmosphere, dppb (10.7 mg, 0.025 mmol) and [Rh(cod)₂][BF₄] (10.2 mg, 0.025 mmol) were dissolved in CH₂Cl₂ (2.0 mL) and the mixture was stirred at room temperature for 5 min. H₂ was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 0.5 h, the resulting mixture was concentrated to dryness. To the residue was added a solution of **1a** (67.1 mg, 0.500 mmol) and **2b** (76.6 mg, 0.550 mmol) in (CH₂Cl)₂ (0.2 mL) at room temperature and washed the remaining substrates away by using (CH₂Cl)₂ (0.8 mL). The mixture was stirred at 80 °C for 2 h. The resulting solution was concentrated and purified by silica gel column chromatography (hexane/EtOAc = 2:1–0:1), which furnished **6ab** (130.5 mg, 0.477 mmol, 95% yield) as a pale brown oil.

3-Methyl-6-phenyl-1-pyrrolidin-1-ylhexane-1,4-dione (**3ab**).

IR (neat) 2860, 1700, 1620, 1430, 695 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.32–7.23 (m, 2H), 7.23–7.13 (m, 3H), 3.53–3.30 (m, 4H), 3.23–3.08 (m, 1H), 3.03–2.84 (m, 4H), 2.78 (dd, *J* = 16.2, 9.3 Hz, 1H), 2.20 (dd, *J* = 16.2, 4.5 Hz, 1H), 2.02–1.89 (m, 2H),

1.89–1.77 (m, 2H), 1.06 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 213.2, 169.7, 141.5, 128.3, 128.2, 125.8, 46.5, 45.5, 43.2, 41.7, 38.0, 29.6, 26.0, 24.3, 16.8; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_2$ $[\text{M}]^+$ 273.1729, found 273.1660.

4-Oxo-6-phenylhexanoic acid dimethylamide (3aa).

Pale yellow oil; IR (neat) 2880, 1700, 1620, 1390, 695 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.32–7.22 (m, 2H), 7.22–7.14 (m, 3H), 3.03 (s, 3H), 2.97–2.88 (m, 2H), 2.93 (s, 3H), 2.88–2.79 (m, 2H), 2.73 (t, $J = 6.0$ Hz, 2H), 2.60 (t, $J = 6.0$ Hz, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 209.0, 171.4, 141.0, 128.3, 128.2, 125.9, 44.3, 37.2, 36.9, 35.3, 29.6, 27.0; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$ $[\text{M}]^+$ 233.1416, found 233.1446.

2-Methyl-4-oxo-6-phenylhexanoic acid dimethylamide (3ac).

Pale yellow oil; IR (neat) 2900, 1700, 1625, 1400, 700 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.31–7.23 (m, 2H), 7.22–7.13 (m, 3H), 3.32–3.16 (m, 1H), 3.12 (s, 3H), 3.08 (dd, $J = 17.7, 9.3$ Hz, 1H), 2.95–2.82 (m, 2H), 2.94 (s, 3H), 2.82–2.68 (m, 2H), 2.34 (dd, $J = 17.7, 4.2$ Hz, 1H), 1.08 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 209.1, 175.6, 141.0, 128.4, 128.3, 126.0, 46.9, 44.4, 37.2, 35.7, 31.1, 29.5, 17.2; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_2$ $[\text{M}]^+$ 247.1572, found 247.1544.

2-Methyl-4-oxoundecanoic acid dimethylamide (3bc).

Pale yellow oil; IR (neat) 2900, 1700, 1630, 1400, 1110 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 3.31–3.17 (m, 1H), 3.12 (s, 3H), 3.08 (dd, $J = 17.4, 9.0$ Hz, 1H), 2.93 (s, 3H), 2.43 (t, $J = 7.2$ Hz, 2H), 2.37 (dd, $J = 17.4, 4.2$ Hz, 1H), 1.63–1.44 (m, 2H), 1.41–1.14 (m, 8H), 1.09 (d, $J = 6.9$ Hz, 3H), 0.87 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 210.1, 175.6, 46.6, 42.8, 37.0, 35.5, 31.5, 30.8, 29.0, 28.9, 23.5, 22.4, 17.1, 13.8; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{27}\text{NO}_2$ $[\text{M}]^+$ 241.2042, found 241.2024.

4-Cyclohexyl-2,N,N-trimethyl-4-oxobutyramide (3cc).

Pale yellow oil; IR (neat) 2900, 1695, 1630, 1395, 1110 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 3.30–3.16 (m, 1H), 3.20 (s, 3H), 3.08 (dd, $J = 17.7, 8.7$ Hz, 1H), 2.93 (s, 3H), 2.41 (dd, $J = 17.7, 4.2$ Hz, 1H), 2.41–2.26 (m, 1H), 1.96–1.58 (m, 5H), 1.83–1.12 (m, 5H), 1.08 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 212.9, 175.6, 50.5, 44.6, 37.0, 35.5, 30.7, 28.2, 28.0, 25.7, 25.5, 25.3, 17.1; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{23}\text{NO}_2$ $[\text{M}-\text{Cy}]^+$ 142.0868, found 142.0899.

***N,N*-Dimethyl-4-oxo-4-phenylbutyramide (3da).²**

Pale yellow oil; ¹H NMR (CDCl₃, 300 MHz) δ 8.04–7.98 (m, 2H), 7.60–7.51 (m, 1H), 7.51–7.41 (m, 2H), 3.36 (t, *J* = 6.6 Hz, 2H), 3.10 (s, 3H), 2.97 (s, 3H), 2.79 (t, *J* = 6.6 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 199.3, 171.6, 136.8, 133.0, 128.5, 128.1, 37.1, 35.5, 33.6, 27.2.

3-Methyl-4-phenyl-1-pyrrolidin-1-ylbutane-1,4-dione (3db).

Pale yellow oil; IR (neat) 2870, 1620, 1420, 1230, 700 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 8.07–8.00 (m, 2H), 7.58–7.50 (m, 1H), 7.50–7.41 (m, 2H), 4.19–4.04 (m, 1H), 3.58–3.36 (m, 4H), 2.96 (dd, *J* = 16.2, 8.7 Hz, 1H), 2.37 (dd, *J* = 16.2, 4.8 Hz, 1H), 2.01–1.89 (m, 2H), 1.89–1.76 (m, 2H), 1.22 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 204.0, 169.7, 136.1, 132.7, 128.5, 46.4, 45.5, 38.3, 37.0, 25.9, 24.3, 17.9; HRMS (EI) calcd for C₁₅H₁₉NO₂ [M]⁺ 245.1416, found 245.1429.

2,*N,N*-Trimethyl-4-oxo-4-phenylbutyramide (3dc).³

Pale yellow solid; Mp 79.8–81.3 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.02–7.94 (m, 2H), 7.59–7.50 (m, 1H), 7.50–7.40 (m, 2H), 3.67 (dd, *J* = 18.0, 8.7 Hz, 1H), 3.51–3.37 (m, 1H), 3.20 (s, 3H), 2.97 (s, 3H), 2.93 (dd, *J* = 18.0, 4.5 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 199.4, 175.7, 136.7, 132.9, 128.4, 128.0, 42.9, 37.1, 35.6, 31.2, 17.4.

2,*N,N*-Trimethyl-4-oxo-4-*o*-tolylbutyramide (3ec).

Pale yellow solid; Mp 54.5–55.5 °C; IR (neat) 2900, 1675, 1630, 1400, 1110 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.75 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.35 (dt, *J* = 7.2, 1.5 Hz, 1H), 7.29–7.18 (m, 2H), 3.59 (dd, *J* = 17.7, 9.0 Hz, 1H), 3.50–3.35 (m, 1H), 3.18 (s, 3H), 2.96 (s, 3H), 2.80 (dd, *J* = 17.7, 4.5 Hz, 1H), 2.46 (s, 3H), 1.19 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 203.1, 175.5, 137.8, 137.6, 131.5, 131.0, 128.5, 125.5, 45.7, 37.1, 35.6, 31.4, 21.0, 17.2; HRMS (EI) calcd for C₁₄H₁₉NO₂ [M]⁺ 233.1416, found 233.1446.

4-(4-Methoxyphenyl)-2,*N,N*-trimethyl-4-oxobutyramide (3fc).

Colorless solid; Mp 102.0–103.0 °C; IR (neat) 2900, 1630, 1600, 1160 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.00–7.92 (m, 2H), 6.96–6.88 (m, 2H), 3.86 (s, 3H), 3.59 (dd, J = 17.7, 8.4 Hz, 1H), 3.50–3.36 (m, 1H), 3.19 (s, 3H), 2.96 (s, 3H), 2.89 (dd, J = 17.7, 4.8 Hz, 1H), 1.19 (d, J = 6.9 Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 197.3, 175.7, 163.2, 130.1, 129.7, 113.4, 55.2, 42.4, 37.0, 35.5, 31.1, 17.3; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3$ $[\text{M}]^+$ 249.1365, found 249.1329.

2, N,N-Dimethyl-4-(4-(trifluoromethyl)phenyl)-4-oxobut-2-enamide (3gc).

Pale yellow solid; Mp 66.8–68.0 °C; IR (neat) 2900, 1680, 1630, 1325, 1130 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.68 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 3.72 (dd, J = 18.0, 9.0 Hz, 1H), 3.52–3.37 (m, 1H), 3.20 (s, 3H), 2.96 (s, 3H), 2.90 (dd, J = 18.0, 4.2 Hz, 1H), 1.22 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 198.3, 175.5, 139.5, 134.1, 128.4, 125.6 (q), 121.8, 43.2, 37.2, 35.7, 31.4, 17.4; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{NO}_2$ $[\text{M}]^+$ 287.1133, found 287.1079.

4-Oxo-4-phenylbutyric acid methyl ester (3ae).⁴

Colorless oil; ^1H NMR (CDCl_3 , 300 Mz, **6ae**) δ 7.33–7.23 (m, 2H), 7.23–7.13 (m, 3H), 3.66 (s, 3H), 2.97–2.86 (m, 2H), 2.84–2.74 (m, 2H), 2.70 (t, J = 6.0 Hz, 2H), 2.58 (t, J = 6.0 Hz, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 207.8, 173.1, 140.9, 128.4, 128.2, 126.1, 51.7, 44.2, 37.1, 29.6, 27.6.

6-(4-Formylphenyl)-2-methyl-4-oxohexanoic acid dimethylamide (5).

Pale yellow oil; IR (neat) 2870, 1680, 1630, 1610, 1395 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 9.96 (s, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 3.32–3.18 (m, 1H), 3.11 (dd, J = 17.4, 6.6 Hz, 1H), 3.12 (s, 3H), 3.02–2.87 (m, 2H), 2.94 (s, 3H), 2.87–2.68 (m, 2H), 2.24 (dd, J = 17.4, 4.2 Hz, 1H), 1.09 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 208.4, 191.8, 175.4, 148.5, 134.5, 129.9, 128.9, 46.7, 43.5, 37.1, 35.6, 31.2, 29.5, 17.1; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_3$ $[\text{M}]^+$ 275.1521, found 275.1499.

IV. References

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4-(3-Oxopropyl)benzaldehyde (**4**)

4-Oxo-6-phenylhexanoic acid dimethylamide (**3aa**)

3-Methyl-6-phenyl-1-pyrrolidin-1-ylhexane-1,4-dione (**3ab**)

2-Methyl-4-oxo-6-phenylhexanoic acid dimethylamide (**3ac**)

2-Methyl-4-oxoundecanoic acid dimethylamide (**3bc**)

4-Cyclohexyl-2,*N,N*-trimethyl-4-oxobutamide (**3cc**)

N,N-Dimethyl-4-oxo-4-phenylbutyramide (**3da**)

3-Methyl-4-phenyl-1-pyrrolidin-1-ylbutane-1,4-dione (**3db**)

2,*N,N*-Trimethyl-4-oxo-4-phenylbutyramide (**3dc**)

2,*N,N*-Trimethyl-4-oxo-4-*o*-tolylbutyramide (**3ec**)

4-(4-Methoxyphenyl)-2,*N,N*-trimethyl-4-oxobutamide (**3fc**)

2,*N,N*-Trimethyl-4-oxo-4-(4-trifluoromethylphenyl)butyramide (**3gc**)

4-Oxo-6-phenylhexanoic acid methyl ester (**3ae**)

6-(4-Formylphenyl)-2-methyl-4-oxohexanoic acid dimethylamide (**5**)