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6/03

**A Deacylative Oxidation Strategy for the Preparation
of α -Functionalized Carbonyls**

Supplementary Material
(8 pages)

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General. All reagents were obtained commercially unless otherwise noted. Reactions were performed using oven-dried glassware under an atmosphere of dry nitrogen. Air- and moisture-sensitive solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated under reduced pressure (ca. 15 mm Hg) by rotary evaporation. Molecular sieves (3 Å) were flame-dried under vacuum (ca. 1 mm Hg) and stored in a dessicator. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. Dichloromethane (CH₂Cl₂) was distilled from CaH₂ and allowed to stand over activated 3 Å molecular sieves for at least 24 hours prior to use. *N,N*-Dimethylformamide (DMF) was dried over activated 3 Å molecular sieves. Methanol (MeOH) was distilled from Mg/I₂ immediately prior to use. Diisopropylamine was distilled from CaH₂ immediately prior to use. Benzyl alcohol, allyl alcohol, and cyclopentyl alcohol were purified by distillation and stored over activated 3 Å molecular sieves. Solid lithium bis(trimethylsilyl)amide (LiN(SiMe₃)₂, 97%) was purchased from Aldrich and transferred in an inert atmosphere N₂ glovebox. Chromatographic purification of products was accomplished using forced-flow chromatography on EM Science Geduran silica gel 60 (35-75 µm). Thin layer chromatography was performed on EM Science silica gel 60 F₂₅₄ plates (250 µm). Visualization of the developed chromatogram was accomplished by fluorescence quenching and by staining with ethanolic anisaldehyde, aqueous potassium permanganate, or aqueous ceric ammonium molybdate (CAM) solution.

Nuclear Magnetic Resonance (NMR) spectra were acquired on a Varian Mercury 400 operating at 400 and 100 MHz for ¹H and ¹³C, respectively, and are referenced internally according to residual solvent signals. Data for ¹H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; br, broad), integration, and coupling constant (Hz). Data for ¹³C are reported in terms of chemical shift (δ, ppm). Infrared (IR) spectra were recorded as thin films on a Thermo-Nicolet 300 FT-IR spectrometer using NaCl plates and are reported in frequency of absorption. High resolution mass spectra were obtained from the Vincent Coates Foundation Mass Spectrometry Laboratory at Stanford University.

o-Nitrobenzenesulfonyl Azide (*o*-NBSA)¹

(CAUTION: Although we have not experienced any problems with either the preparation or use of *o*-NBSA, we note that sulfonyl azides in general are heat- and shock-sensitive and should be handled with due care. We recommend storing *o*-NBSA in a freezer at -20 °C protected from light.)

To a vigorously stirred solution of NaN₃ (3.2 g, 49.6 mmol, 1.1 equiv) in 14 mL of H₂O and 22 mL of acetone was added a solution of *o*-nitrobenzenesulfonyl chloride (10.0 g, 45.1 mmol) in 24 mL of acetone. The resulting biphasic mixture was stirred at 23 °C for 2 h then concentrated under reduced pressure (rotary evaporator bath ≤ 23 °C) to remove most of the acetone solvent. The aqueous mixture was transferred to a separatory funnel and extracted with 2 x 50 mL of CH₂Cl₂. The combined organic layers were washed successively with 1 x 25 mL of H₂O and 1 x 25 mL of saturated aqueous NaCl, dried over MgSO₄, and concentrated under reduced pressure to afford the product as a pale yellow solid (10.1 g, 98%). This material was used in subsequent reactions without further purification. TLC R_f = 0.60 (3:1 CH₂Cl₂/hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 8.19 (ddd, 1H, *J* = 7.8, 1.4, 0.5 Hz), 7.93-7.81 (m, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 147.7, 135.7, 133.1, 132.5, 131.7, 125.4 ppm; IR (thin film) ν 3101, 2352, 2149, 1592, 1546, 1443, 1378, 1309, 1177, 1125, 854, 755 cm⁻¹.

Experimental procedure and characterization data for products appearing in Table 1

Procedure A: A solution of $\text{LiN}(\text{SiMe}_3)_2$ (201 mg, 1.2 mmol, 1.2 equiv) in 2.0 mL of THF was cooled to -78°C . To the reaction flask was cannulated dropwise a solution of the substrate (1.0 mmol) in 3.0 mL of THF. The resulting mixture was stirred for 20 min at -78°C . Neat trifluoroethyl trifluoroacetate (200 μL , 1.5 mmol, 1.5 equiv) was then added via syringe. After stirring for an additional 15 min at -78°C , the contents were poured rapidly into a separatory funnel containing 5 mL of 5% (v/v) aqueous HCl and 5 mL of Et_2O . The organic layer was collected and the aqueous layer was extracted with 2 x 5 mL of Et_2O . The combined organic extracts were washed with 1 x 5 mL of saturated aqueous NaCl, dried over Na_2SO_4 , and concentrated under reduced pressure to afford the trifluoroacetylated product. This material was employed in the subsequent reaction without additional purification.

The unpurified trifluoroketone was dissolved in 10.0 mL of CH_2Cl_2 and the solution was cooled to 0°C . Powdered 3 Å molecular sieves (500 mg), RXH (4.0 mmol, 4.0 equiv), $\text{Rh}_2(\text{oct})_4$ (15.6 mg, 20 μmol , 0.02 equiv) and *o*-NBSA (228 mg, 1.0 mmol) were added successively to the reaction flask. The resulting green suspension was mixed vigorously while anhydrous Cs_2CO_3 (326 mg, 1.0 mmol) was added in a single portion. The reaction mixture was warmed to 23°C over the course of ~ 4 h and stirred for an additional 10 h. Following this time, the brown suspension was diluted with 15 mL of Et_2O and filtered through a small pad of Celite. The filter cake was washed with copious amounts (~ 40 mL) of Et_2O and the combined filtrates were concentrated under reduced pressure. Purification by chromatography on silica gel (conditions given below) furnished the desired product.

Procedure B: *n*-Butyllithium (2.5 M in hexanes, 480 μL , 1.2 mmol, 1.2 equiv) was added dropwise to a 0°C solution of $^i\text{Pr}_2\text{NH}$ (170 μL , 1.2 mmol, 1.2 equiv) in 2.0 mL of THF. After 10 min, the LDA mixture was cooled to -78°C and to the reaction flask was transferred by cannula a solution of the substrate (1.0 mmol) in 3.0 mL of THF. The reaction contents were stirred for 15 min at -78°C . Neat trifluoroethyl trifluoroacetate (200 μL , 1.5 mmol, 1.5 equiv) was then added via syringe. After 20 min, the cold solution was poured rapidly into a separatory funnel containing 5 mL of 5% (v/v) aqueous HCl and 5 mL of Et_2O . The organic layer was collected and the aqueous layer was extracted with 2 x 5 mL of Et_2O . The combined organic extracts were washed with 1 x 5 mL of saturated aqueous NaCl, dried over Na_2SO_4 , and concentrated under reduced pressure to afford the trifluoroacetylated product. This material was employed in the subsequent reaction without additional purification.

The unpurified product was dissolved in 10.0 mL of CH_2Cl_2 and the solution was cooled to 0°C . Powdered 3 Å molecular sieves (500 mg), RXH (4.0 mmol, 4.0 equiv), $\text{Rh}_2(\text{oct})_4$ (15.6 mg, 20 μmol , 0.02 equiv) and *o*-NBSA (228 mg, 1.0 mmol) were added successively to the reaction flask. The resulting green suspension was mixed vigorously while anhydrous Cs_2CO_3 (326 mg, 1.0 mmol) was added in a single portion. The reaction mixture was warmed to 23°C over the course of ~ 4 h and stirred for an additional 8 h. Following this time, the brown suspension was diluted with 15 mL of Et_2O and filtered through a small pad of Celite. The filter cake was washed with copious amounts (~ 40 mL) of Et_2O and the combined filtrates were concentrated under reduced pressure. Purification by chromatography on silica gel (conditions given below) furnished the desired product.

Prepared according to procedure A and purified by chromatography on silica gel using 10% EtOAc/hexanes as eluent (68%, 3.5:1 diastereoselectivity); **major diastereomer**: pale yellow oil; TLC R_f = 0.35 (20% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.40-7.29 (m, 5H), 4.98 (d, 1H, J = 11.9 Hz), 4.75 (d, 1H, J = 11.9 Hz), 4.29-4.21 (m, 2H), 2.55 (ddd, 1H, J = 12.7, 8.2, 5.5 Hz), 1.92-1.60 (m, 3H), 0.99 (t, 3H, J = 7.5 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 175.1, 137.0, 128.5, 128.1(2), 78.1, 73.6, 72.2, 35.2, 28.5, 9.2 ppm; IR (thin film) ν

2970, 2938, 2880, 1781, 1455, 1340, 1197, 1138, 1027, 950 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3$ 220.1099 found 243.1009 (MNa^+); **minor diastereomer**: pale yellow solid; TLC R_f = 0.39 (20% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.39-7.28 (m, 5H), 4.90 (d, 1H, J = 11.7 Hz), 4.67 (d, 1H, J = 11.7 Hz), 4.60 (quint, 1H, J = 6.7 Hz), 4.14 (dd, 1H, J = 7.2, 4.4 Hz), 2.35 (ddd, 1H, J = 13.7, 6.6, 4.1 Hz), 2.08-2.01 (m, 1H), 1.77-1.56 (m, 2H), 0.99 (t, 3H, J = 7.5 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 174.5, 137.0, 128.5, 128.1, 128.0, 80.4, 73.5, 71.9, 35.3, 28.5, 9.4 ppm; IR (thin film) ν 2968, 2922, 2880, 1777, 1455, 1339, 1189, 1116, 1027, 952 cm^{-1} .

Prepared according to procedure A and purified by chromatography on silica gel using 10% EtOAc/hexanes as eluent (74%, 3:1 diastereoselectivity); **major diastereomer**: colorless oil; TLC R_f = 0.34 (20% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 5.93-5.83 (m, 1H), 5.29 (dq, 1H, J = 17.2, 1.6 Hz), 5.19 (dq, 1H, J = 10.4, 1.4 Hz), 4.35 (ddt, 1H, J = 12.7, 5.5, 1.4 Hz), 4.28-4.22 (m, 1H), 4.23 (dd, 1H, J = 10.4, 8.2 Hz), 4.16 (ddt, 1H, J = 12.7, 6.0, 1.3 Hz), 2.59 (ddd, 1H, J = 12.7, 8.2, 5.5 Hz), 1.86-1.59 (m, 3H), 0.95 (t, 3H, J = 7.4 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 174.9, 133.6, 118.0, 77.9, 73.7, 71.3, 35.0, 28.3, 9.0 ppm; IR (thin film) ν 2972, 2940, 2882, 1783, 1462, 1338, 1197, 1140, 1002, 949 cm^{-1} ; HRMS (EI) calcd for $\text{C}_9\text{H}_{14}\text{O}_3$ 170.0943 found 193.0869 (MNa^+); **minor diastereomer**: colorless oil; TLC R_f = 0.47 (20% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 5.94-5.84 (m, 1H), 5.32 (dq, 1H, J = 17.2, 1.6 Hz), 5.22 (dq, 1H, J = 10.4, 1.4 Hz), 4.58 (quint, 1H, J = 6.6 Hz), 4.34 (ddt, 1H, J = 12.7, 5.3, 1.4 Hz), 4.15 (ddt, 1H, J = 12.7, 6.1, 1.3 Hz), 4.11 (dd, 1H, J = 7.3, 4.3 Hz), 2.32 (ddd, 1H, J = 13.6, 6.4, 4.4 Hz), 2.10-2.03 (m, 1H), 1.77-1.56 (m, 2H), 0.98 (t, 3H, J = 7.5 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 174.4, 133.5, 118.1, 80.3, 73.5, 71.0, 35.2, 28.5, 9.4 ppm; IR (thin film) ν 2971, 2940, 2881, 1779, 1463, 1337, 1189, 1117, 996, 951 cm^{-1} .

Prepared according to procedure A and purified by chromatography on silica gel using 5% EtOAc/ CH_2Cl_2 as eluent (colorless oil, 79%): TLC R_f = 0.37 (5% EtOAc/ CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ 3.95 (t, 1H, J = 7.8 Hz), 3.90 (dq, 1H, J = 9.2, 7.1 Hz), 3.72 (ddd, 1H, J = 10.9, 8.4, 4.0 Hz), 3.55 (dq, 1H, J = 9.2, 6.9 Hz), 3.47 (ddd, 1H, J = 10.9, 7.8, 7.3 Hz), 2.23 (dtd, 1H, J = 13.0, 7.3, 4.0 Hz), 1.91-1.82 (m, 1H), 1.44 (s, 9H), 1.15 (t, 3H, J = 7.0 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.9, 150.0, 82.8, 76.9, 65.9, 42.4, 27.8, 25.5, 15.0 ppm; IR (thin film) ν 2979, 2933, 1787, 1756, 1717, 1368, 1315, 1257, 1154, 958, 850, 779 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{19}\text{NO}_4$ 229.1314 found 252.1244 (MNa^+).

Prepared according to procedure A and purified by chromatography on silica gel using 5% EtOAc/ CH_2Cl_2 as eluent (white solid, 66%): TLC R_f = 0.38 (5% EtOAc/ CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ 3.89 (t, 1H, J = 7.8 Hz), 3.76 (ddd, 1H, J = 11.0, 8.5, 4.0 Hz), 3.53 (s, 3H), 3.54-3.48 (m, 1H), 2.27 (dtd, 1H, J = 8.0, 7.2, 4.0 Hz), 1.94-1.85 (m, 1H), 1.48 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.7, 150.0, 83.1, 78.5, 58.2, 42.5, 27.9, 25.2 ppm; IR (thin film) ν 2981, 2935, 2832, 1786, 1758, 1717, 1370, 1316, 1257, 1155, 1096, 1015, 937, 850 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{17}\text{NO}_4$ 215.1158 found 238.1071 (MNa^+).

Prepared according to procedure **A** and purified by chromatography on silica gel using 10% EtOAc/hexanes as eluent (74%, 2:1 diastereoselectivity); **major diastereomer**: clear oil; TLC R_f = 0.48 (20% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 4.42-4.35 (m, 1H), 4.35-4.29 (m, 1H), 4.23 (dd, 1H, J = 10.0, 8.4 Hz), 3.81-3.72 (m, 2H), 2.49 (ddd, 1H, J = 12.7, 8.3, 6.0 Hz), 2.11-2.03 (m, 1H), 1.83-1.47 (m, 8H), 0.89 (s, 9H), 0.07 (s, 6H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 175.1, 81.9, 72.9, 64.3, 32.6, 32.2, 31.7, 25.8, 23.39, 23.35, 18.3, -5.4 ppm; IR (thin film) ν 2955, 2858, 1786, 1472, 1334, 1255, 1194, 1133, 1006, 838, 779 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{30}\text{O}_4\text{Si}$ 314.1913 found 337.1809 (MNa^+); **minor diastereomer**: white solid; TLC R_f = 0.64 (20% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 4.62-4.57 (m, 1H), 4.37-4.32 (m, 2H), 3.86 (dd, 1H, J = 11.6, 2.4 Hz), 3.63 (dd, 1H, J = 11.6, 2.4 Hz), 2.45 (ddd, 1H, J = 13.0, 8.4, 3.1 Hz), 2.26-2.18 (m, 1H), 1.82-1.49 (m, 8H), 0.89 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 175.9, 81.7, 77.4, 72.2, 64.7, 32.6, 32.3, 32.1, 25.8, 23.4(2), 18.2, -5.5, -5.6 ppm; IR (thin film) ν 2955, 2859, 1785, 1471, 1329, 1255, 1190, 1123, 1024, 838, 779 cm^{-1} .

Prepared according to procedure **A** and purified by chromatography on silica gel using 10% EtOAc/hexanes as eluent (75%, 2:1 diastereoselectivity); **major diastereomer**: colorless oil; TLC R_f = 0.32 (20% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 5.98-5.89 (m, 1H), 5.36-5.30 (m, 1H), 5.26-5.22 (m, 1H), 4.44-4.37 (m, 2H), 4.27 (dd, 1H, J = 9.6, 8.4 Hz), 4.21 (ddt, 1H, J = 12.7, 6.1, 1.3 Hz), 3.83 (dd, 1H, J = 11.4, 4.1 Hz), 3.75 (dd, 1H, J = 11.4, 4.6 Hz), 2.50 (ddd, 1H, J = 12.8, 8.4, 6.0 Hz), 2.15 (dt, 1H, J = 12.8, 9.6 Hz), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 174.7, 133.7, 118.2, 76.8, 73.5, 71.3, 64.0, 30.9, 25.8, 18.3, -5.4 ppm; IR (thin film) ν 2930, 2858, 1786, 1463, 1362, 1334, 1256, 1132, 1006, 837, 779 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{26}\text{O}_4\text{Si}$ 286.1600 found 309.1512 (MNa^+); **minor diastereomer**: colorless oil; TLC R_f = 0.49 (20% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 5.96-5.86 (m, 1H), 5.35-5.29 (m, 1H), 5.25-5.21 (m, 1H), 4.64-4.60 (m, 1H), 4.40-4.35 (m, 2H), 4.20 (ddt, 1H, J = 12.7, 6.1, 1.3 Hz), 3.86 (dd, 1H, J = 11.2, 2.4 Hz), 3.63 (dd, 1H, J = 11.2, 2.0 Hz), 2.47 (ddd, 1H, J = 13.0, 8.5, 2.9 Hz), 2.31-2.23 (m, 1H), 0.88 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 175.5, 133.8, 118.2, 77.5, 72.9, 71.3, 64.7, 31.8, 25.8, 18.2, -5.6, -5.7 ppm; IR (thin film) ν 2955, 2931, 2859, 1785, 1463.2, 1362, 1255, 1191, 1119, 1028, 838, 780 cm^{-1} .

Prepared according to procedure **B** and purified by chromatography on silica gel using 10% EtOAc/hexanes as eluent (78%, 1.5:1 diastereoselectivity); **major diastereomer**: colorless oil; TLC R_f = 0.35 (20% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.40-7.27 (m, 5H), 4.96 (d, 1H, J = 12.0 Hz), 4.62 (d, 1H, J = 12.0 Hz), 4.27-4.20 (m, 1H), 4.06 (t, 1H, J = 8.5 Hz), 2.27-2.17 (m, 1H), 1.95-1.84 (m, 2H), 1.82-1.61 (m, 3H), 1.57-1.42 (m, 2H), 1.38-1.23 (m, 4H), 0.88 (t, 3H, J = 6.9 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.2, 137.5, 128.4, 127.89, 127.86, 78.1, 72.2, 71.3, 35.3, 31.5, 25.9, 24.9, 24.7, 22.4, 13.9 ppm; IR (thin film) ν 2932, 2861, 1753, 1455, 1250, 1195, 1128, 954, 736 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{24}\text{O}_3$ 276.1725 found 299.1620 (MNa^+); **minor diastereomer**: white solid; TLC R_f = 0.49 (20% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.39-7.27 (m, 5H), 4.91 (d, 1H, J = 11.7 Hz), 4.67 (d, 1H, J = 11.7 Hz), 4.52-4.45 (m, 1H), 3.95 (dd, 1H, J = 8.0, 6.0 Hz), 2.18-2.10 (m, 1H), 2.04-1.92 (m, 2H), 1.72-1.23 (m, 9H), 0.89 (t, 3H, J = 6.8 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.1, 137.4, 128.4, 128.0, 127.9,

80.2, 73.9, 72.6, 35.6, 31.5, 27.1, 26.5, 24.5, 22.4, 13.9 ppm; IR (thin film) ν 2933, 2861, 1743, 1455, 1235, 1183, 1119, 946, 737 cm^{-1} .

Prepared according to procedure **B** and purified by chromatography on silica gel using 5% EtOAc/ CH_2Cl_2 as eluent (76%, 1.5:1 diastereoselectivity); **major diastereomer**: white solid; TLC R_f = 0.31 (5% EtOAc/ CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ 5.45 (br s, 1H), 4.41-4.34 (m, 1H), 4.14-4.08 (m, 1H), 3.69 (s, 3H), 2.49-2.42 (m, 1H), 2.04-1.98 (m, 1H), 1.86-1.67 (m, 3H), 1.64-1.55 (m, 2H), 1.53-1.41 (m, 1H), 1.40-1.23 (m, 4H), 0.89 (t, 3H, J = 6.9 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 170.8, 156.7, 82.9, 52.4, 51.8, 36.0, 31.5, 28.5, 27.5, 24.5, 22.5, 14.0 ppm; IR (thin film) ν 3338, 2955, 2861, 1723, 1529, 1462, 1329, 1240, 1192, 1068, 945, 735 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{21}\text{NO}_4$ 243.1471 found 266.1375 (MNa^+).

Prepared according to procedure **A** and purified by chromatography on silica gel using 4% EtOAc/ CH_2Cl_2 as eluent (colorless oil, 72%); TLC R_f = 0.59 (5% EtOAc/ CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ 4.23-4.18 (m, 1H), 3.86 (dd, 1H, J = 7.2, 5.6 Hz), 3.73-3.66 (m, 1H), 3.60-3.53 (m, 1H), 2.03-1.46 (m, 12H), 1.47 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.5, 152.6, 82.7, 81.4, 75.4, 44.7, 32.8, 31.9, 27.9, 27.8, 23.29, 23.26, 19.7 ppm; IR (thin film) ν 2957, 1772, 1718, 1455, 1367, 1325, 1293, 1251, 1150, 989, 852, 779 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{25}\text{NO}_4$ 283.1784 found 306.1671 (MNa^+).

Prepared according to procedure **A** and purified by chromatography on silica gel using 5% EtOAc/ CH_2Cl_2 as eluent (white solid, 64%); TLC R_f = 0.57 (5% EtOAc/ CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ 4.03 (dd, 1H, J = 7.6, 5.6 Hz), 3.77-3.71 (m, 1H), 3.66-3.59 (m, 1H), 2.01-1.90 (m, 2H), 1.88-1.75 (m, 2H), 1.50 (s, 9H), 1.23 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.4, 152.7, 82.6, 75.4, 70.5, 44.8, 29.5, 28.0, 27.9, 19.8 ppm; IR (thin film) ν 2976, 1773, 1717, 1476, 1368, 1294, 1254, 1150, 1086, 972, 853, 779 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{25}\text{NO}_4$ 271.1784 found 294.1668 (MNa^+).

Prepared according to procedure **A** and purified by chromatography on silica gel using 10% EtOAc/hexanes as eluent (73%, 1.5:1 diastereoselectivity); **major diastereomer**: colorless oil; TLC R_f = 0.42 (20% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.38-7.26 (m, 5H), 4.94 (d, 1H, J = 11.9 Hz), 4.71 (d, 1H, J = 12.0 Hz), 4.06-4.01 (m, 2H), 3.86 (dd, 1H, J = 9.6, 3.6 Hz), 3.79 (dd, 1H, J = 9.5, 7.5 Hz), 2.26-2.12 (m, 2H), 1.54 (s, 9H), 0.88 (s, 9H), 0.04 (s, 6H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.2, 150.1, 137.6, 128.3, 127.9, 127.7, 83.3, 75.7, 71.9, 63.5, 56.6, 28.0, 27.5, 25.8, 18.2, -5.4 ppm; IR (thin film) ν 2955, 2930, 2858, 1788, 1753, 1719, 1472, 1368, 1308, 1255, 1156, 1124, 1007, 839, 778 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{37}\text{NO}_5\text{Si}$ 435.2441 found 458.2318 (MNa^+); **minor diastereomer**: white solid; TLC R_f = 0.23 (10% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.39-7.25 (m, 5H), 5.02 (d, 1H, J = 12.0 Hz), 4.78 (d, 1H, J = 11.9 Hz), 4.41 (dd, 1H, J = 9.8, 8.7 Hz), 4.15 (br d, 1H, J = 9.3 Hz), 3.92 (dd, 1H, J = 10.5, 2.7 Hz), 3.57 (dd, 1H, J = 10.6, 1.8 Hz), 2.28 (dd, 1H, J = 12.6, 8.7 Hz), 2.08 (dt, 1H, J = 12.7, 9.6 Hz), 1.53 (s, 9H), 0.80 (s, 9H), -0.04 (s, 6H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 173.2, 150.1, 137.7, 128.4, 128.0,

127.8, 83.1, 75.2, 72.3, 63.9, 55.6, 30.4, 28.0, 25.8, 18.1, -5.7 ppm; IR (thin film) ν 2955, 2931, 2858, 1790, 1756, 1715, 1471, 1368, 1309, 1256, 1156, 1115, 1025, 837, 778 cm^{-1} .

Prepared according to a modification of procedure **B** with 2.0 equiv of $\text{LiN}(\text{cHx})\text{tPr}$ in place of 1.2 equiv of LiN^iPr_2 . Purified by chromatography on silica gel using 10% EtOAc/hexanes as eluent (colorless oil, 65%); TLC R_f = 0.52 (20% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.33–7.24 (m, 8H), 7.20–7.17 (m, 2H), 4.69 (d, 1H, J = 11.9 Hz), 4.40 (d, 1H, J = 11.9 Hz), 4.22–4.17 (m, 2H), 4.14 (dd, 1H, J = 8.1, 5.2 Hz), 3.13–3.03 (m, 2H), 1.25 (t, 3H, J = 7.2 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.1, 137.3, 137.0, 129.4, 128.2 (2), 127.8, 127.6, 126.6, 79.2, 72.3, 60.8, 39.3, 14.1 ppm; IR (thin film) ν 3030, 2982, 2932, 1747, 1496, 1455, 1273, 1187, 1113, 1029, 741, 699 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{20}\text{O}_3$ 284.1412 found 307.1317 (MNa^+).

$\text{Rh}_2(\text{HNCOCF}_3)_4$. A 25 mL recovery flask was charged with $\text{Rh}_2(\text{OAc})_4$ (140 mg, 0.32 mmol) and 18.5 mL of $\text{C}_6\text{H}_5\text{Cl}$, and to this suspension was added CF_3CONH_2 (512 mg, 4.5 mmol, 14 equiv). The reaction flask was equipped with a short-path distillation head fitted with a 25 mL receiving bulb. The apparatus was placed in an oil bath preheated to 155 $^\circ\text{C}$. At this temperature, solvent distilled at a rate of ~ 1 mL/h for 36 h. Throughout the initial 24 h, a thin rod was used to return to the refluxing solution the solid CF_3CONH_2 that had sublimed into the path of the distillation head. This process was conducted at 2 h intervals and found to be essential. Approximately every 6–8 h, an appropriate amount of $\text{C}_6\text{H}_5\text{Cl}$ was added in order to restore the solvent volume of the reaction to ~ 18 mL. The solution color slowly changed to a deep green and a white crystalline precipitate (CF_3CONH_2) collected in the receiving flask. After 36 h, additional CF_3CONH_2 (512 mg, 4.5 mmol, 14 equiv) was added to this reaction mixture and heating at 155 $^\circ\text{C}$ was continued. Within 48 h, a dark blue-green solid had formed on the sides of the reaction vessel. Following this time, the reaction was cooled to 25 $^\circ\text{C}$ and the mixture was filtered. The blue-green solid was washed thoroughly with CH_2Cl_2 , and the filtrate discarded. To ensure quantitative recovery of the desired product, acetone was used to dissolve the powder. The purple filtrate was concentrated under reduced pressure and the isolated material was dried by heating at 50 $^\circ\text{C}$ *in vacuo* (1 mm Hg) for 1 h. For all applications, the $\text{Rh}_2(\text{tfacam})_4$ complex was used without further purification. Purification of this material by chromatography on silica gel (3:1 $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ using ~ 1 mL of acetone to dissolve the product) is possible and affords the product as a blue-green solid (82%); TLC R_f = 0.34 (3:1 $\text{CH}_2\text{Cl}_2/\text{EtOAc}$); ^{19}F NMR (282 MHz, CD_3CN , $\text{C}_6\text{H}_5\text{CF}_3$ standard at -63.7 ppm) δ -74.4 ppm; IR (KBr pellet) ν 3401, 1655, 1433, 1270, 1202, 1152, 854, 732 cm^{-1} ; HRMS calcd for $\text{C}_8\text{H}_4\text{F}_{12}\text{N}_4\text{O}_4\text{Rh}_2$ 653.8151 found 653.8122 (M^+).

Experimental procedure and characterization data for products in Figure 3

A flask containing substrate (0.25 mmol) was charged with 5.0 mL of a 60 mM solution of TsN_3 (0.30 mmol, 1.2 equiv) in CH_2Cl_2 . Neat RXH (1.25 mmol, 5.0 equiv), $\text{Rh}_2(\text{HNCOCF}_3)_4$ (12.5 μmol , 0.05 equiv), and Cs_2CO_3 (0.30 mmol, 1.2 equiv) were added successively. The reaction vessel was fitted with a reflux condenser and placed in an oil bath pre-heated to 45 $^\circ\text{C}$. The green slurry was stirred at a gentle reflux until TLC analysis indicated that the starting dicarbonyl reagent had been consumed (ca. 11–16 h). After cooling the reaction to 23 $^\circ\text{C}$, 5 mL of Et_2O was added. The mixture was filtered through a small pad of Celite and the filter cake was washed with copious amounts of Et_2O (~ 40 mL). Concentration of the combined filtrates under reduced pressure afforded an oily residue that was purified by chromatography on silica gel (conditions given below).

Purified by chromatography on silica gel using 10% EtOAc/hexanes as eluent (colorless oil, 60%); TLC R_f = 0.41 (10% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.38-7.27 (m, 5H), 4.70 (d, 1H, J = 11.6 Hz), 4.45 (d, 1H, J = 11.6 Hz), 4.28-4.16 (m, 2H), 4.05 (q, 1H, J = 6.9 Hz), 1.44 (d, 3H, J = 6.9 Hz), 1.30 (t, 3H, J = 7.2 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 173.3, 137.6, 128.4, 128.0, 127.8, 74.0, 72.0, 60.8, 18.7, 14.2 ppm; IR (thin film) ν 2985, 2938, 2874, 1747, 1454, 1372, 1271, 1200, 1143, 1065, 1026, 739, 698 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$ 208.1099 found 231.0986 (MNa^+).

Purified by chromatography on silica gel using 60% CH_2Cl_2 /hexanes as eluent (colorless oil, 58%); TLC R_f = 0.37 (75% CH_2Cl_2 /hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.48-7.44 (m, 2H), 7.38-7.30 (m, 3H), 4.86 (s, 1H), 4.24-4.10 (m, 2H), 3.64-3.48 (m, 2H), 1.28 (t, 3H, J = 7.0 Hz), 1.21 (t, 3H, J = 7.1 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.0, 136.8, 128.5(2), 127.1, 80.9, 65.2, 61.1, 15.1, 14.1 ppm; IR (thin film) ν 2980, 2934, 2898, 1749, 1454, 1369, 1258, 1206, 1178, 1113, 1031 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$ 208.1099 found 231.0992 (MNa^+).

Purified by chromatography on silica gel using CH_2Cl_2 as eluent gel (white solid, 51%); TLC R_f = 0.29 (CH_2Cl_2); ^1H NMR (C_6D_6 , 400 MHz) δ 7.24-6.94 (m, 10H), 5.70 (br d, 1H, J = 6.4 Hz), 5.52 (d, 1H, J = 7.2 Hz), 5.03 (d, 1H, J = 12.0 Hz), 4.98 (d, 1H, J = 12.0 Hz), 3.84-3.65 (m, 2H), 0.71 (t, 3H, J = 7.1 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 170.7, 155.3, 136.7, 136.1, 128.9, 128.5(2), 128.2, 128.1, 127.1, 67.0, 61.9, 57.9, 13.9 ppm; IR (thin film) ν 3353, 2982, 1722, 1499, 1455, 1370, 1324, 1211, 1182, 1050, 1028, 775, 698 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_4$ 313.1314 found 336.1210 (MNa^+).

The general experimental protocol was followed with the exception that addition of RXH was omitted. Purified by chromatography on silica gel using 25% EtOAc/hexanes as eluent (colorless oil, 69%). TLC R_f = 0.20 (20% EtOAc/hexanes); ^1H NMR (CDCl_3 , 400 MHz, 1:1 mixture of rotamers) δ 7.37-7.25 (m, 10H), 5.17 (d, 1H, J = 12.4 Hz), 5.15 (d, 1H, J = 12.4 Hz), 5.11 (d, 1H, J = 12.4 Hz), 5.06 (d, 1H, J = 12.4 Hz), 4.37 (dd, 1H, J = 8.6, 3.4 Hz), 4.32 (dd, 1H, J = 8.6, 3.7 Hz), 4.19 (q, 2H, J = 7.1 Hz), 4.11-3.98 (m, 2H), 3.66-3.57 (m, 2H), 3.56-3.44 (m, 2H), 2.28-2.14 (m, 2H), 2.04-1.83 (m, 6H), 1.26 (t, 3H, J = 7.2 Hz), 1.13 (t, 3H, J = 7.2 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz, 1:1 mixture of rotamers) δ 172.8, 172.6, 154.8, 154.3, 136.7, 136.5, 128.4, 128.3, 127.9, 127.83, 127.80, 127.7, 66.90, 66.88, 61.04, 60.96, 59.2, 58.9, 46.9, 46.4, 30.9, 29.9, 24.2, 23.5, 14.1, 14.0 ppm; IR (thin film) ν 2980, 2882, 1745, 1709, 1448, 1416, 1352, 1279, 1197, 1119, 1089, 1026 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_4$ 277.1314 found 300.1197 (MNa^+).

(1) The procedure is adapted from: Curphey, T. J. *Org. Prep. Proced. Int.* **1981**, 13, 112-115.