A Mild C-O Bond Formation Catalyzed by a Rhenium-Oxo Complex

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Supporting Information

General Information. Unless otherwise noted all commercial materials were used without further purification. Reactions were carried out in two dram vials fitted with threaded caps. ACS grade acetonitrile and methanol were obtained from EM science. 2-propanol was obtained from Fisher Scientific. 3-chloro-1-propanol, sec-phenethyl alcohol, 2-methoxyethanol, and isopropanol were obtained from Aldrich Chemical Company. 3-buten-1-ol was obtained from Fluka Chemika. *mer*-[ReOCl₃(dppm)] was prepared according to literature procedures.¹ Optically pure 1-phenyl-2-heptyn-1-ol was obtained according to the procedure of Midland et. al,² and enantiomeric purity was determined by chiral HPLC analysis, Chiralcel OD column, 95:5 hexanes:2-propanol, 1 mL/min; retention times 9.09 and 13.58 min. TLC analysis of reaction mixtures was performed on Merck silica gel 60 F₂₅₄ TLC plates. Chromatography was carried out on ICN SiliTech 32-63 D 60 Å silica gel. ¹H and ¹³C NMR spectra were recorded with Bruker AMX-300 and AMX-400 spectrometers and referenced to CDCl₃ unless otherwise noted. Mass spectral and CHN data were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

General procedure for propargylic etherification reactions catalyzed by *mer*-[ReOCl₃(dppm)]: A 100 mg sample of propargyl alcohol was dissolved in 0.5 mL of MeCN in a two dram vial. Three equivalents of alcohol nucleophile and 1 mol % catalyst were added. The vial was capped and placed in a 65° oil bath. Reactions were maintained at the temperature indicated until complete - as judged by TLC analysis of the reaction mixture. Crude reaction mixtures were loaded onto a silica gel column and purified by chromatography.

Determination of Chirality Transfer for Rhenium catalyzed propargylation: The substitution reaction was carried out in the manner described above using 1-phenyl-2-heptyn-1-ol of 86% optical purity. The enantiomeric excess of the product was determined by chiral HPLC analysis, Chiralcel OD column, 98:2 hexanes:2-propanol, 0.5 mL/min; retention times 11.18 and 13.54 min.

Purified by chromatography on silica gel (9:1 hexanes/Et₂O); colorless oil (78%): ¹H NMR (CDCl₃, 300 MHz) δ 7.52-7.48 (m, 2H), 7.39-7.29 (m, 3H), 5.16 (t, 1H, J = 2.0

Hz), 3.82 – 3.77 (m, 1H), 3.67-3.57 (m, 3H), 2.29 (td, 2H, $J = 7.0, 2.1$ Hz), 2.06 (quintet, 2H, $J = 6.3$ Hz), 1.59-1.49 (m, 2H), 1.47-1.39 (m, 2H), 0.92 (t, 3H, $J = 7.2$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\square$ 139.2, 128.4, 128.2, 127.3, 88.6, 77.7, 72.0, 64.5, 42.1, 32.8, 30.7, 22.0, 18.5, 13.6 ppm.

Purified by chromatography on silica gel (24:1 hexanes/ Et_2O , 1% TEA); yellow oil (76%): ^1H NMR (C_6D_6 , 300 MHz) $\square$ 7.60 (app d, 2H, $J = 7.2$ Hz), 7.34-7.31 (m, 2H), 7.16-7.04 (m, 3H), 6.88-6.85 (m, 3H), 5.83-5.69 (m, 1H), 5.28 (s, 1H), 5.01-4.91 (m, 2H), 3.78-3.70 (m, 1H), 3.48-3.41 (m, 1H), 2.31-2.24 (m, 2H) ppm; ^{13}C NMR (C_6D_6 , 100 MHz) $\square$ 139.3, 135.2, 132.5, 128.4, 128.3, 128.2 (2), 122.8, 116.1, 87.8, 87.4, 72.1, 67.7, 34.2 ppm; CHN and HRMS data were not obtained due to product instability.

Purified by chromatography on silica gel (10:1 hexanes/ Et_2O); colorless oil (74 %). ^1H NMR (CDCl_3 , 300 MHz) $\square$ 7.53 (m, 2H), 7.38 (m, 3H), 5.20 (s, 1H), 3.81 (m, 1H), 3.66 (m, 3H), 2.08 (app. pentet, 2H, $J = 6.3$ Hz), 0.24 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\square$ 138.9, 128.2, 127.4, 102.8, 92.7, 72.3, 64.4, 42.1, 32.5, 0.3 ppm; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{21}\text{ClOSi}$: 280.1050, found: 280.1049; Anal calcd: C, 64.14; H, 7.54. Found: C, 64.96; H, 8.20.

Purified by chromatography on silica gel (10:1 hexanes/ Et_2O); colorless oil (88 %). ^1H NMR (CDCl_3 , 300 MHz) $\square$ 7.53 (m, 2H), 7.36 (m, 3H), 5.87 (m, 1H), 5.22 (s, 1H), 5.17-5.08 (m, 2H), 3.66 (m, 2H), 2.42 (m, 2H), 0.24 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) $\square$ 138.4, 135.1, 128.4, 128.3, 127.5, 116.4, 103.2, 92.5, 71.9, 67.4, 34.1, 29.8, 0.22 ppm; Anal calcd for $\text{C}_{16}\text{H}_{22}\text{OSi}$: C, 74.36; H, 8.58. Found: C, 74.53, H, 8.89.

A 1:1 mixture of diastereomers was obtained. The diastereomeric mixture, inseparable by column chromatography, was purified on silica gel (3:1 hexanes/Et₂O); colorless oil (60%). ¹H NMR (CDCl₃, 300 MHz) The following was observed for the mixture of diastereomers: δ 7.53 (m, 2H), 7.37-7.27 (m, 3H), 5.55 (s, 1H), 5.53 (s, 1H), 5.34 (s, 1H), 5.28 (s, 1H), 4.59 (s, 1H), 4.30 (m, 2H), 4.03 (m, 1H), 3.77, (m, 2H), 2.28 (m, 2H), 1.59-1.26 (m, 4H), 1.55 (s, 3H), 1.44, (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H), 0.92 (t, 3H, *J* = 7.2 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 139.2 (2), 128.3, 128.1 (2), 127.5, 109.2, 109.1, 108.5, 96.3, 88.8, 88.6, 77.7, 77.5, 72.0, 71.8, 71.2, 71.0, 70.7(2), 70.6, 67.5, 66.4, 66.2, 66.1, 30.7, 26.1 (2), 26.0, 25.0 (2), 24.5 (2), 22.0, 18.6 (2), 13.6 ppm; HRMS (EI) calcd for C₂₅H₃₄O₆: 430.2355, found: 430.2356.

Purified by chromatography on silica gel (1:1 Et₂O/hexanes); colorless oil (53%); ¹H NMR (CDCl₃, 400 MHz) δ 7.49 (app d, 2H, *J* = 8.0 Hz), 7.39-7.29 (m, 3H), 5.06 (t, 1H, *J* = 2.0 Hz), 3.67 (t, 2H, *J* = 6.2 Hz), 3.40 (s, 3H), 2.34 (td, 2H, *J* = 6.8, 2.0 Hz), 1.73-1.60 (m, 4H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 139.0, 128.4, 128.3, 127.4, 88.2, 781, 73.2, 62.4, 55.7, 31.9, 24.9, 18.7 ppm.

A 1.6:1 mixture of diastereomers was obtained. The diastereomeric mixture, inseparable by column chromatography, was purified on silica gel (10:1 hexanes/Et₂O); light yellow oil (79 %). ¹H NMR (CDCl₃, 300 MHz) Major diastereomer: δ 7.74 (s, 1H), 5.14 (s, 1H), 5.06 (q, 1H, *J* = 6.6 Hz), 2.33 (td, 2H, *J* = 6.9, 2.1 Hz), 1.67 (s, 9H), 1.56 (d, 3H, *J* = 6.6 Hz), 0.97 (t, 3H, *J* = 6.9 Hz) ppm; Minor diastereomer: δ 7.87 (d, 1H, *J* = 7.8 Hz), 7.59 (s, 1H), 5.30 (s, 1H), 4.63, (q, 1H, *J* = 6.6 Hz), 2.22 (td, 2H, *J* = 6.9, 2.1 Hz), 1.69 (s, 9H), 1.48 (d, 3H, *J* = 6.6 Hz), 0.88 (t, 3H, *J* = 6.9 Hz) ppm; The following were observed for both diastereomers: δ 8.13 (m, 1H), 7.53-7.19 (m, 6H), 1.84-1.30 (m, 4H) ppm; ¹³C NMR (CDCl₃, 100 MHz) The following were observed for the mixture of diastereomers: δ 149.7, 143.5, 142.9, 135.9, 128.6, 128.5, 128.4, 127.9, 127.5, 127.0, 126.5, 124.6, 124.5,

122.6, 122.5, 120.6, 120.0, 119.9, 119.4, 115.2, 87.3, 86.7, 83.8, 83.6, 78.1, 77.3, 75.2, 74.8, 71.4, 62.6, 61.9, 30.8, 30.6, 28.2 (2), 24.0, 23.8, 22.0 (2), 18.6 (2), 13.7, 13.6 ppm; Anal calcd for $C_{28}H_{33}NO_3$: C, 77.93; H, 7.71; N, 3.25. Found: C, 78.17; H, 7.98; N, 3.08.

A 1:1 mixture of diastereomers was obtained. The inseparable diastereomeric mixture was purified on silica gel (5:1 hexanes/ Et_2O); light yellow oil (85 %). 1H NMR ($CDCl_3$, 300 MHz) δ 8.11 (m, 1H), 7.96 (m, 2H), 7.34-7.21 (m, 2H), 5.44 (m, 1H), 3.74, (m, 1H), 3.66-3.55 (m, 1H), 3.62 (s, 3H), 2.77 (m, 1H), 1.92 (m, 3H), 1.67 (s, 9H), 1.17 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.4, 175.1, 149.7, 135.9, 128.6, 128.5, 124.8, 124.6, 122.7, 120.2, 119.1 (2), 115.2 (2), 83.8, 83.0, 75.9 (2), 71.3, 69.2, 68.8, 65.3, 65.1, 51.7, 40.1, 40.0, 28.3, 28.2, 14.2, 3.7 ppm; HRMS (EI) calcd for $C_{22}H_{27}NO_5$: 385.1889, found: 385.1892.

Purified by chromatography on silica gel (1:1 hexanes/ Et_2O); colorless oil (86%): 1H NMR ($CDCl_3$, 300 MHz) δ 7.43 (d, 1H, J = 8.7 Hz), 6.82 (d, 1H, J = 8.4 Hz), 6.05-5.92 (m, 1H), 5.29 (q, 1H, J = 2.1 Hz), 5.02-4.89 (m, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 3.76-3.71 (m, 1H), 3.65-3.60 (m, 1H), 3.58-3.54 (m, 4H), 3.36 (s, 3H), 1.89 (d, 3H, J = 2.1 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.7, 147.3, 137.2, 132.1, 130.3, 123.8, 115.0, 110.4, 83.6, 71.8, 69.1, 67.1, 60.7, 58.9, 55.6, 9.9, 20.3, 3.8 ppm; HRMS (EI) calcd for $C_{18}H_{24}O_4$: 304.1675 found 304.1678; Anal calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 71.46; H, 7.93.

Purified by chromatography on silica gel (3:1 hexanes/ Et_2O); colorless oil (69%): 1H NMR ($CDCl_3$, 300 MHz) δ 7.41 (d, 1H, J = 8.7 Hz), 6.83 (d, 1H, J = 8.7 Hz), 6.05-5.92 (m, 1H), 5.26 (q, 1H, J = 2.1 Hz), 5.04-4.91 (m, 2H), 3.91-3.85 (m, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.57-3.55 (m, 2H), 1.87 (d, 3H, J = 2.1 Hz), 1.19 (app. t, 6H, J = 6.3 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.5, 147.2, 137.2, 131.6, 131.5, 123.5, 115.0, 110.4, 82.5, 78.2, 68.9, 65.7, 60.7, 55.6, 29.8, 22.8, 21.6, 3.8 ppm; HRMS (EI) calcd for

$C_{18}H_{24}O_3$ 288.1725 found 288.1722; Anal calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 75.26; H, 8.60.

Purified by chromatography on silica gel (4:1 hexanes/EtOAc); colorless oil (69%): 1H NMR ($CDCl_3$, 300 MHz) δ 7.40 (app. d, 2H, J = 6.6 Hz), 6.91 (app. d, 2H, J = 6.6 Hz), 5.21 (s, 1H), 4.25 (q, 2H, J = 7.1 Hz), 3.81-3.78 (m, 4H), 3.66-3.62 (m, 3H), 2.06 (pentet, 2H, J = 6.4 Hz), 1.32 (t, 3H, J = 7.2 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.1, 153.3, 128.8, 114.1, 84.6, 78.8, 71.2, 65.2, 62.2, 55.3, 41.7, 32.6, 14.0 ppm; Anal calcd for $C_{16}H_{19}ClO_4$: C, 61.84; H, 6.16. Found: C, 61.47; H, 6.27.

Purified by chromatography on silica gel (9:1 hexanes/ Et_2O); colorless oil (82%): 1H NMR ($CDCl_3$, 300 MHz) δ 7.42 (app d, 2H, J = 8.7 Hz), 6.89 (app d, 2H, J = 9.0 Hz), 4.98 (q, 1H, J = 2.1 Hz), 3.81 (s, 3H), 3.37 (s, 3H), 1.92 (d, 3H, J = 2.4 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.6, 131.6, 131.3, 128.8, 113.6, 83.7, 72.8, 55.5, 55.3, 3.7 ppm.

Purified by chromatography on silica gel (24:1 hexanes/ Et_2O); colorless oil (79%): 1H NMR ($CDCl_3$, 300 MHz) δ 6.83 (s, 2H), 5.87-5.74 (m, 1H), 5.45 (q, 1H, J = 2.4 Hz), 5.10-4.99 (m, 2H), 3.64-3.57 (m, 1H), 3.38-3.31 (m, 1H), 2.44 (s, 6H), 2.25 (s, 3H), 1.83 (d, 3H, J = 2.1 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.4, 136.8, 135.3, 132.6, 129.8, 116.3, 82.3, 77.2, 67.7, 67.5, 34.3, 20.9, 20.3, 3.9 ppm; Anal. calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 83.96; H, 9.44.

Purified by chromatography on silica gel (9:1 hexanes/ Et_2O); colorless oil (85%): 1H NMR ($CDCl_3$, 300 MHz) δ 7.01 (d, 1H, J = 1.5 Hz), 6.96-6.93 (m, 1H), 6.77 (d, 1H, J = 7.8 Hz), 5.95 (s, 2H), 5.87 (m, 1H), 5.13-5.01 (m, 3H), 3.66-3.59 (m, 1H), 3.52-3.44 (m, 1H), 2.37 (m, 2H), 1.91 (d, 3H, J = 2.1 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.8, 147.5, 135.2, 133.4, 121.0, 116.4, 107.9, 101.1, 83.6, 77.4, 71.5, 67.2, 63.9, 34.1, 3.8

ppm; HRMS (EI) calcd for $C_{15}H_{16}O_3$ 244.1096 found 244.1099 (M^+); Anal calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.63; H, 6.56.

Purified by chromatography on silica gel (1:1 hexanes/ Et_2O); colorless oil (78%): 1H NMR ($CDCl_3$, 300 MHz) δ 7.25 (dd, 1H, J = 7.6, 1.2 Hz), 7.08 (t, 1H, J = 7.9 Hz), 6.87 (dd, 1H, J = 8.1, 1.5 Hz), 5.55 (q, 1H, J = 2.4 Hz), 3.91-3.76 (m, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.65-3.55 (m, 2H), 3.35 (s, 3H), 1.87 (d, 3H, J = 2.4 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.5, 146.6, 133.3, 124.1, 120.5, 112.3, 82.9, 71.7, 67.5, 66.22, 61.1, 58.9, 55.8, 3.8 ppm; Anal calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.27; H, 7.79.

Purified by chromatography on silica gel (5:1 hexanes/ Et_2O); colorless oil (60%): 1H NMR ($CDCl_3$, 300 MHz) δ 7.47 (m, 2H), 7.37 (m, 2H), 5.82 (m, 1H), 5.13-5.01 (m, 2H), 5.07 (m, 1H), 3.66 (m, 1H), 3.49 (m, 1H), 2.37 (m, 2H), 2.85 (d, 3H, J = 2.4 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.5, 135.1, 131.5, 129.0, 122.1, 116.5, 84.2, 71.2, 71.0, 67.5, 34.1, 3.8 ppm.

Purified by chromatography on silica gel (24:1 hexanes/ Et_2O); colorless oil (69%): 1H NMR ($CDCl_3$, 300 MHz) δ 7.46-7.39 (m, 2H), 7.33-7.27 (m, 3H), 3.77 (t, 2H, J = 5.8 Hz), 3.68 (t, 2H, J = 6.3 Hz), 2.05 (pentet, 2H, J = 6.1 Hz), 1.54 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.7, 128.3, 128.2, 122.9, 91.4, 84.1, 706, 60.5, 42.2, 33.2, 28.4 ppm; HRMS (EI) calcd for $C_{14}H_{17}OCl$ 236.0968 found 236.0968 (M^+); Anal calcd for $C_{14}H_{17}OCl$: C, 71.03; H, 7.24. Found: C, 70.90; H, 7.41.

Purified by chromatography on silica gel (3:1 hexanes/ Et_2O); yellow oil (58%): 1H NMR ($CDCl_3$, 300 MHz) δ 7.52 (app d, 2H, J = 6.6 Hz), 7.34-7.27 (m, 3H), 5.27 (t, 1H, J = 1.8 Hz), 3.78-3.63 (m, 2H), 3.60-3.57 (m, 2H), 3.38 (s, 3H), 2.28 (td, 2H, J = 7.1, 2.0 Hz), 1.57-1.49 (m, 2H), 1.47-1.38 (m, 2H), 0.91 (t, 3H, J = 7.2 Hz) ppm; ^{13}C NMR ($CDCl_3$,

100 MHz) δ 139.1, 128.3, 128.1, 127.5, 88.7, 77.6, 72.0, 71.8, 66.7, 59.0, 30.7, 22.0, 18.6, 13.6 ppm.

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