Supporting Information 1

Allylic Etherification Via Ir(I)/Zn(II) Bimetallic Catalysis

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General. Unless otherwise noted, all reactions were conducted in flame-dried glassware under an argon atmosphere using anhydrous solvents (passed through an activated alumina column). Commercially available reagents were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz or a Varian Inova 400 MHz spectrometer. Infrared (IR) spectra were recorded on a Nicolet 730 or a Perkin-Elmer Paragon 500 FT-IR spectrometer. High resolution mass spectra (HRMS) were obtained from the UCR Mass Spectrometry Facility, the Princeton University Mass Spectrometry Facility or the Scripps Research Institute Mass Spectrometry Facility.

Procedure for allylic etherification using stoichiometric Et_2Zn (Method A).

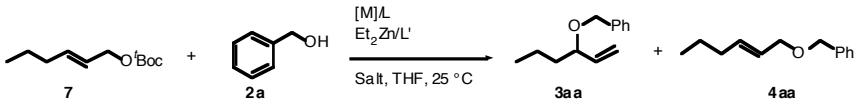
To a solution of carbonate **1a** (100 mg, 0.50 mmol) and benzyl alcohol (**2a**, 60 mg, 0.55 mmol) in THF (0.25 mL) was added dropwise Et_2Zn (0.28 mL, 0.28 mmol, 1.0 M in hexane) via a syringe at 25 °C. The resulting mixture was stirred for 15 min during which time it turned a cloudy white and became viscous. To this suspension was added NH_4I (73 mg, 0.50 mmol). After stirring for 15 min, the solution became more heterogeneous. In a separate test tube was prepared a solution of $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol) and pyridine (2.3 μL, 0.025 mmol) in THF (0.25 mL). This solution was then added via syringe to the flask containing substrates. After stirring for 5 min, the reaction was diluted with diethyl ether (20 mL) and washed with saturated NH_4Cl aqueous solution (5 mL). The aqueous layer was extracted with additional diethyl ether (10 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated and purified by flash column chromatography eluting with a mixture of hexanes and diethyl ether (40:1) to give benzyl ether **3aa** (91 mg, 96%) as a colorless oil.

Procedure for allylic etherification using catalytic Et_2Zn (Method B).

To a solution of L-tryptophan (4.1 mg, 0.020 mmol) and NH_4I (2.9 mg, 0.020 mmol) in THF (0.05 mL) was added dropwise Et_2Zn (20 μL, 0.020 mmol, 1.0 M in hexane) via a syringe at 25 °C. The resulting mixture was stirred for 15 min during which time it turned cloudy white. To this suspension were added carbonate **1a** (40 mg, 0.20 mmol) and benzyl alcohol (**2a**, 32 mg, 0.30 mmol) in THF (0.1 mL) via a syringe at 25 °C. This mixture was allowed to stir for 5 min at which time a solution of $[Ir(COD)Cl]_2$ (3.4 mg, 0.0051 mmol) and pyridine (0.9 μL, 0.01 mmol) in THF (0.05 mL) was added via syringe 25 °C. After stirring for 15 min, the reaction was diluted with diethyl ether (20 mL) and washed with saturated NH_4Cl aqueous solution (5 mL). The aqueous layer was extracted with an additional diethyl ether (10 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated, and purified by flash column

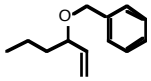
chromatography eluting with a mixture of hexanes and diethyl ether (40:1) to give benzyl ether **3aa** (34 mg, 89%) as a colorless oil.

Allylic etherification of the linear substrate 7 (Scheme 1).

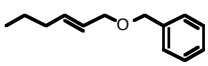


7 2a 3aa 4aa

Following method A, carbonate **7** (100 mg, 0.50 mmol), benzyl alcohol (**2a**, 60 mg, 0.55 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.3 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 0.28 mL, 0.28 mmol) and NH_4I (72 mg, 0.50 mmol) were reacted in THF (0.5 mL, 1.0 M) to afford a 1:9 mixture of inseparable ethers **3aa** and **4aa** (66 mg, 0.35 mmol, 70%) as a clear, colorless oil after column chromatography (hexanes:diethyl ether = 40:1). Following the literature procedure,[1] carbonate **7** (100 mg, 0.50 mmol), benzyl alcohol (**2a**, 60 mg, 0.55 mmol) and Et_2Zn (1.0 M in hexanes, 0.28 mL, 0.028 mmol) were reacted in THF (0.50 mL, 1.0 M) in the presence of $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) to afford **4aa**[2] (36 mg, 0.19 mmol, 38%) exclusively as a clear, colorless oil.



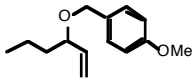
3-Benzyloxy-1-hexene (**3aa**). Following method A, **1a** (100 mg, 0.50 mmol), **2a** (60 mg, 0.55 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.3 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 0.28 mL, 0.28 mmol) and NH_4I (72 mg, 0.50 mmol) were reacted in THF (0.5 mL, 1.0 M) to afford **3aa** (91 mg, 0.48 mmol, 96%) as a clear, colorless oil after column chromatography (hexanes:diethyl ether = 40:1). Following method B, **1a** (40 mg, 0.20 mmol), **2a** (32 mg, 0.30 mmol), $[Ir(COD)Cl]_2$ (3.4 mg, 0.0051 mmol), pyridine (0.90 μL, 0.010 mmol), Et_2Zn (1.0 M in hexanes, 20 μL, 0.020 mmol), L-tryptophan (4.1 mg, 0.020 mmol) and NH_4I (2.9 mg, 0.020 mmol) were reacted in THF (0.20 mL, 1.0 M) to afford **3aa** (34 mg, 0.18 mmol, 89%). IR (film) 2959, 2933, 2871, 1096, 1070, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20-7.40 (m, 5H), 5.75 (ddd, J = 8.8, 6.7, 1.8 Hz, 1H), 5.25 (d, J = 1.8 Hz, 1H), 5.24 (d, J = 8.8 Hz, 1H), 4.62 (d, J = 12.1 Hz, 1H), 4.37 (d, J = 12.1 Hz, 1H), 3.75 (q, J = 6.7 Hz, 1H), 1.20-1.80 (m, 4H), 0.91 (t, J = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.5, 139.1, 128.5, 128.0, 117.2, 80.6, 70.3, 37.9, 18.9, 14.3; HRMS (EI-MS) Calcd for $C_{13}H_{18}O$ [M+] 190.1358, Found 190.1358.



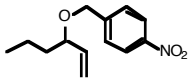
(*E*)-1-Benzyloxy-2-hexene (4aa). ^1H NMR (300 MHz, $CDCl_3$) δ 7.26-7.43 (m, 5H), 5.56-5.77 (m, 2H), 4.51 (s, 2H), 3.98 (dd, J = 6.7, 0.7 Hz, 2H), 2.04 (q, J = 7.2 Hz, 2H), 1.20–1.75 (m, 2H), 0.91 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 134.8, 128.3, 127.7, 127.4, 126.2, 71.7, 70.9, 34.3, 22.2, 13.6.

[1] Kim, H.; Lee, C. *Org. Lett.* **2002**, *4*, 4369.

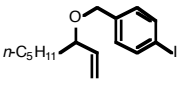
[2] Crich, D.; Beckwith, A. L. J.; Chen, C.; Yao, Q.; Davison, I. G. E.; Longmore, R. W.; Anaya de Parrodi, C.; Quinter-Cortes, L.; Sandoval-Ramirez, J. *J. Am. Chem. Soc.* **1995**, *117*, 8757.



3-(4-Methoxybenzyloxy)-1-hexene (**3ab**). Following method A, **1a** (100 mg, 0.50 mmol), **2b** (76 mg, 0.55 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 0.28 mL, 0.28 mmol) and NH_4I (72 mg, 0.50 mmol) were reacted in THF (0.5 mL, 1.0 M) to afford **3ab** (85 mg, 0.38 mmol, 77%) as a clear, light yellow oil after column chromatography (hexanes:diethyl ether = 30:1). Following method B, **1a** (100 mg, 0.50 mmol), **2b** (104 mg, 0.75 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 50 μL, 0.50 mmol), L-tryptophan (10 mg, 0.50 mmol) and NH_4I (7.2 mg, 0.050 mmol) were reacted in THF (0.50 mL, 1.0 M) to afford **3ab** (72 mg, 0.33 mmol, 66%). IR (film) 2958, 2934, 2871, 1514, 1248, 1038 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 8.3 Hz, 2H), 6.88 (d, J = 8.3 Hz, 2H), 5.74 (ddd, J = 18.4, 10.0, 6.8 Hz, 1H), 5.21 (d, J = 10.0 Hz, 1H), 5.20 (d, J = 18.4 Hz, 1H), 4.53 (d, J = 11.5 Hz, 3.80 (s, 3H), 3.72 (q, J = 6.8 Hz, 1H), 1.20-1.75 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 139.6, 131.2, 129.6, 117.1, 113.9, 80.3, 69.9, 55.5, 37.9, 18.9, 14.2; HRMS (EI-MS) Calcd for $C_{14}H_{20}O_2$ [M+] 220.1463, Found 220.1463.

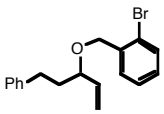


3-(4-Nitrobenzyloxy)-1-hexene (**3ac**). Following method A, **1a** (100 mg, 0.50 mmol), **2c** (84 mg, 0.55 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 0.28 mL, 0.28 mmol) and NH_4I (72 mg, 0.50 mmol) were reacted in THF (0.50 mL, 1.0 M) to afford **3ac** (73 mg, 0.31 mmol, 62%) as a clear, yellow oil after column chromatography (hexanes:diethyl ether = 30:1). Following method B, **1a** (100 mg, 0.50 mmol), **2c** (110 mg, 0.75 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 50 μL, 0.050 mmol), L-tryptophan (10 mg, 0.050 mmol) and NH_4I (7.3 mg, 0.050 mmol) were reacted in THF (0.50 mL, 1.0 M) to afford **3ac** (84 mg, 0.36 mmol, 71%). IR (film) 3080, 2960, 2934, 2872, 1735, 1606, 1521, 1459, 1422, 1347, 1319, 1097, 993, 930, 843, 738 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 5.71 (ddd, J = 17.7, 10.5, 7.9 Hz, 1H), 5.24 (d, J = 10.4 hz, 1H), 5.19 (d, J = 17.0 Hz, 1H), 4.66 (d, J = 13.4 Hz, 1H), 4.43 (d, J = 13.4 Hz, 1H), 3.74 (q, J = 6.8 Hz, 1H), 1.31-1.73 (m, 4H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4, 147.0, 138.8, 127.9, 123.7, 117.8, 81.6, 69.0, 37.8, 18.8, 14.2; HRMS (FAB-MS) Calcd for $C_{13}H_{17}O_3N$ [MH+] 236.1287, Found 236.1280.

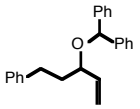


3-(4-Iodobenzyloxy)-1-octene (**3bd**). Following method A, **1b** (230 mg, 1.0 mmol), **2d** (260 mg, 1.1 mmol), $[Ir(COD)Cl]_2$ (17 mg, 0.25 mmol), pyridine (4.7 μL, 0.050 mmol), Et_2Zn (1.0 M in hexanes, 0.55 mL, 0.55 mmol) and NH_4I (140 mg, 1.0 mmol) were reacted in THF (1.0 mL, 1.0 M) to afford **3bd** (330 mg, 0.97 mmol, 97%) as a clear, yellow oil after column chromatography (hexanes:diethyl ether = 40:1). Following method B, **1b** (57 mg, 0.25 mmol), **2d** (88 mg, 0.38 mmol), $[Ir(COD)Cl]_2$ (4.2 mg, 0.0062 mmol), pyridine (1.0 μL, 0.012 mmol), Et_2Zn (1.0 M in hexanes, 25 μL, 0.025 mmol), L-tryptophan (5.1 mg, 0.025 mmol) and NH_4I (3.6 mg, 0.025 mmol) were reacted in THF (0.25 mL, 1.0 M) to afford **3bd** (70 mg, 0.20 mmol,

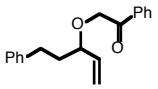
81%). $[\alpha]_D^{23}$ -0.288(*c* 1.08, CH_2Cl_2); IR (film) 2957, 2931, 2859, 1484, 1466, 1369, 1276, 1255, 1162, 1084, 1008, 926, 798 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 5.69 (ddd, J = 18.2, 10.3, 7.8 Hz, 1H), 5.20 (d, J = 10.2 Hz, 1H), 5.16 (d, J = 17.2 Hz, 1H), 4.50 (d, J = 12.2 Hz, 1H), 4.26 (d, J = 12.2 Hz, 1H), 3.66 (q, J = 6.7 Hz, 1H), 1.55-1.69 (m, 2H), 1.15-1.50 (m, 6H), 0.86 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 138.8, 137.6, 129.8, 117.4, 92.9, 81.0, 69.5, 35.6, 32.0, 31.0, 28.0, 25.2, 22.8, 14.3 ; HRMS (EI-MS) Calcd for $C_{15}H_{21}OI$ [M+] 344.0637, Found 344.0621.



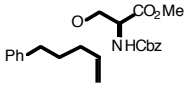
3-(2-Bromobenzyloxy)-5-phenyl-1-pentene (**3ce**). Following method A, **1c** (130 mg, 0.50 mmol), **2e** (100 mg, 0.55 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 0.28 mL, 0.28 mmol) and NH_4I (72 mg, 0.50 mmol) were reacted in THF (0.50 mL, 1.0 M) to afford **3ce** (130mg, 0.39 mmol, 78%) as a clear, yellow oil after column chromatography (hexanes:diethyl ether = 40:1). Following method B, **1c** (130 mg, 0.50 mmol), **2e** (140 mg, 0.75 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 50 μL, 0.050 mmol), L-tryptophan (10 mg, 0.050 mmol) and NH_4I (7.3 mg, 0.050 mmol) were reacted in THF (0.50 mL, 1.0 M) to afford **3ce** (120 mg, 0.38 mmol, 75%). IR (film) 3063, 3026, 2925, 2861, 1744, 1454, 1094, 1027, 749, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51-7.60 (m, 2H), 7,14-7.35 (m, 7H), 5.76-5.89 (m, 1H), 5.24-5.32 (m, 2H), 4.65 (d, J = 13.0 Hz, 1H), 4.44 (d, J = 12.9 Hz, 1H), 3.83 (q, J 5.7 Hz, 1H), 2.67-2.86 (m, 2H), 1.99-2.11 (m, 1H), 1.82-1.94 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 138.8, 138.4, 132.7, 129.5, 129.0, 128.7, 128.6, 127.6, 126.0, 123.0, 117.8, 80.6, 69.8, 37.4, 31.9; HRMS (FAB-MS) Calcd for $C_{18}H_{19}OBr$ [MH+] 331.0698, Found 331.0691.



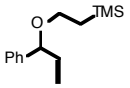
3-Diphenylmethoxy-5-phenyl-1-pentene (**3cf**). Following method A, **1c** (130 mg, 0.50 mmol), **2f** (100 mg, 0.55 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 0.28mL, 0.28 mmol) and NH_4I (72mg, 0.50 mmol) were reacted in THF (0.50 mL, 1.0 M) to afford **3cf** (65 mg, 0.20 mmol, 40%) as a clear, light yellow oil after column chromatography (hexanes:diethyl ether = 40:1). Following method B, **1c** (130 mg, 0.50 mmol), **2f** (140 mg, 0.75 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 50 μL, 0.050 mmol), L-tryptophan (10 mg, 0.050 mmol) and NH_4I (7.3 mg, 0.050 mmol) were reacted in THF (0.5 mL, 1.0 M) to afford **3cf** (100 mg, 0.31 mmol, 61%). IR (film) 3063, 3027, 2980, 2931, 2863, 1743, 1495, 1454, 1278, 1255, 1157, 1052, 926, 742, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7,14-7,42 (m, 15H), 5.83 (ddd, J = 17.3, 10.3, 7.1 Hz, 1H), 5.54 (s, 1H), 5.28 (d, J = 10.3 Hz, 1H), 5.20 (d, J = 17.2 Hz, 1H), 3.84 (q, J = 7.0 Hz, 1H), 2.60-2.85 (m, 2H), 2.04-2.12 (m, 1H), 1.83-1.92 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 142.5, 142.4, 140.4, 139.0, 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 127.8, 127.5, 127.3, 127.2, 127.0, 125.9, 118.0, 80.1, 78.1, 37.6, 31.9; HRMS (FAB-MS) Calcd for $C_{24}H_{24}O$ [MNa+] 351.1725, Found 351.1711.



3-(1-phenyl-1-oxo-2-ethyl)-1-pentene (**3cg**). Following method A, **1c** (130 mg, 0.50 mmol), **2g** (75 mg, 0.55 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 0.28 mL, 0.28 mmol) and NH_4I (72mg, 0.50 mmol) were reacted in THF (0.50 mL, 1.0 M) to afford **3cg** (42 mg, 0.15 mmol, 30%) as a clear, yellow oil after column chromatography (hexanes:diethyl ether = 20:1). Following method B, **1c** (130 mg, 0,50 mmol), **2g** (100 mg, 0.75 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 50 μL, 0.050 mmol), L-tryptophan (10 mg, 0.050 mmol) and NH_4I (7.3 mg, 0.050 mmol) were reacted in THF (0.50 mL, 1.0 M) to afford **3cg** (64 mg, 0.23 mmol, 46%). IR (film) 3062, 3026, 2926, 2860, 1703, 1598, 1496, 1450, 1284, 1226, 1130, 978, 932, 754, 691 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8 Hz, 2H), 7.58 (t, J = 6.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.15-7.32 (M, 5H), 5.76 (ddd, J 17.1, 10.3, 7.0 hz, 1H), 5.28 (d, J = 10.3 Hz, 1H), 5.24 (d, J = 17.1 Hz, 1H), 4.83 (d, J = 16.7 Hz, 1H), 4.64 (d, J = 16.6 Hz, 1H), 3.83 (q, J = 7.0 Hz, 1H), 2.66-2.85 (m, 2H), 2.04-2.18 (m, 1H), 1.82-1.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 142.2, 138.2, 135.4, 133.6, 128.9, 128.7, 128.6, 128.2, 126.0, 118.8, 81.8, 71.3, 37.1, 31.7; HRMS (FAB-MS) Calcd for $C_{19}H_{20}O_2$ [MH+] 281.1542, Found 281.1549.

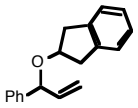


Methyl (*S*)-2-benzyloxycarbonylamino-3-[(*R*S**)-5-phenyl-1-penten-3-oxy]-propionate** (**3ch**). Following method A, (±)-**1c** (52 mg, 0.20 mmol), (*S*)-**2h** (56 mg, 0.22 mmol), $[Ir(COD)Cl]_2$ (3.4 mg, 0.0051 mmol), pyridine (0.90 μL, 0.010 mmol), Et_2Zn (1.0 M in hexanes, 0.11 mL, 0.11 mmol) and NH_4I (29 mg, 0.20 mmol) were reacted in THF (0.20 mL, 1.0 M) to afford **3ch** (58 mg, 0.14 mmol, 73%) as a clear, light yellow oil after column chromatography (hexanes:ethyl acetate = 8:1). Following method B, **1c** (52 mg, 0.20 mmol), **2h** (76 mg, 0.30 mmol), $[Ir(COD)Cl]_2$ (3.4 mg, 0.0051 mmol), pyridine (0.90 μL, 0.010 mmol), Et_2Zn (1.0 M in hexanes, 20 μL, 0.020 mmol), L-tryptophan (4.1 mg, 0.0020 mmol) and NH_4I (2.9 mg, 0.0020 mmol) were reacted in THF (0.20 mL, 1.0 M) to afford **3ch** (55 mg, 0.14 mmol, 69%). IR (film) 3334, 3028, 2951, 1727, 1499, 1342, 1208, 1108, 1065, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.17-7.37 (m, 10H), 5.54-5.71 (m, 2H), 5.09-5.25 (M, 4H), 4.50 (d, J = 7.4 Hz, 1H), 3.92 (dd, J = 9.4, 2.8 Hz, 0.5H), 3.67-3.82 (m, 4H), 3.53-3.66 (m, 1H), 3.52 (dd, J = 9.5, 2.4 Hz, 0.5H), 2.56-2.68 (m, 2H), 1.72-1.88 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 171.1, 156.3, 142.0, 141.9, 138, 2, 136.5, 128.8, 128.6, 128.4, 128.3, 126.1, 117.9, 117.8, 81.3, 81.1, 68.6, 68.2, 67.3, 54.7, 52.7, 37.2, 36.9, 31.6; HRMS (EI-MS) Calcd for $C_{23}H_{27}O_5N$ [(M-Bn)+] 306.1341, Found 306.1334.

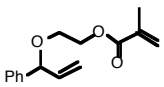


1-(2-Trimethylsilylethanoxy)-1-phenyl-2-propene (**3di**). Following method A, **1d** (120 mg, 0.50 mmol), **2i** (65 mg, 0.55 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 0.28 mL, 0.28 mmol) and NH_4I (72 mg, 0.50 mmol) were reacted in THF (0.50 mL, 1.0 M) to afford **3di** (40 mg, 0.17 mmol, 34%) as a clear, colorless oil after column chromatography (hexanes:diethyl ether = 40:1). Following method B, **1d** (120 mg, 0.50 mmol), **2i** (89 mg, 0.75 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025

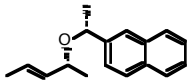
mmol), Et_2Zn (1.0 M in hexanes, 50 μL, 0.50 mmol), L-tryptophan (10 mg, 0.050 mmol) and NH_4I (7.3 mg, 0.050 mmol) were reacted in THF (0.50 mL, 1.0 M) to afford **3di** (85 mg, 0.36 mmol, 73%). IR (film) 3029, 2953, 2892, 1249, 1067, 860, 838, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.95 (ddd, J = 17.1, 10.2, 6.7 Hz, 1H), 5.28 (dt, J = 17.2, 1.4 Hz, 1H), 5.19 (dt, J = 10.3, 1.4 Hz, 1H), 4.75 (d, J = 6.7 Hz, 1H), 3.45-3.63 (m, 2H), 1.01 (t, J = 8.3 Hz, 2H), 0.02 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7, 139.6, 128.6, 127.7, 127.0, 116.0, 82.9, 66.0, 18.5, -1.0; HRMS (EI-MS) Calcd for $C_{14}H_{22}OSi$ [(M-H)+] 233.1362, Found 233.1369.



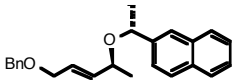
1-(2-Indanoxy)-1-phenyl-2-propene (**3dj**). Following method A, **1d** (120 mg, 0.50 mmol), **2j** (74 mg, 0.55 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 0.28 mL, 0.28 mmol) and NH_4I (72 mg, 0.50 mmol) were reacted in THF (0.5 mL, 1.0 M) to afford **3dj** (78 mg, 0.31 mmol, 62%) as a clear, colorless oil after column chromatography (hexanes:diethyl ether = 40:1). Following method B, **1d** (120 mg, 0.50mmol), **2j** (100 mg, 0.75 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 50 μL, 0.050 mmol), L-tryptophan (10 mg, 0.050 mmol) and NH_4I (7.3 mg, 0.050 mmol) were reacted in THF (0.50 mL, 1.0 M) to afford **3dj** (100 mg, 0.40 mmol, 80%). IR (film) 3066, 3025, 2941, 2906, 2845, 1739, 1483, 1305, 1088, 1058, 926, 743, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.16-7.43 (m, 9H), 6.02 (ddd, J = 17.0, 10.3, 6.6 Hz, 1H), 5.32 (dt, J = 17.1, 1.4 Hz, 1H), 5.24 (dt, J = 10.2, 1.3 Hz, 1H), 4.96 (d, J = 6.6 Hz, 1H), 4.50 (quint, J = 5.6 Hz, 1H), 2.97-3.29 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.6, 141.2, 139.6, 128.7, 127.9, 127.2, 126.7, 124.9, 116.4, 81.6, 78.2, 39.8, 39.7; HRMS (FAB-MS) Calcd for $C_{18}H_{18}O$ [MNa+] 273.1255, Found 273.1245.



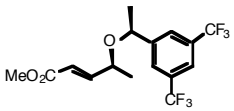
2-(1-Phenyl-2-propenoxy)-ethyl 2-methylpropenoate (**3dk**). Following method A, **1d** (120 mg, 0.50 mmol), **2k** (72mg, 0.55 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 0.28 mL, 0.28 mmol) and NH_4I (72 mg, 0.50 mmol) were reacted in THF (0.50 mL, 1.0 M) to afford **3dk** (71 mg, 0.29 mmol, 58%) as a clear, colorless oil after column chromatography (hexanes:diethyl ether = 25:1). Following method B, **1d** (120 mg, 0.50 mmol), **2k** (98 mg, 0.75 mmol), $[Ir(COD)Cl]_2$ (8.4 mg, 0.012 mmol), pyridine (2.6 μL, 0.025 mmol), Et_2Zn (1.0 M in hexanes, 50 μL, 0.050 mmol), L-tryptophan (10 mg, 0.050 mmol) and NH_4I (7.3 mg, 0.050 mmol) were reacted in THF (0.50 mL, 1.0 M) to afford **3dk** (90 mg, 0.36 mmol, 73%). IR (film) 2926, 1720, 1452, 1296, 1169, 1101, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26-7.36 (m, 5H), 6.15 (s, 1H), 5.95 (ddd, J = 17.2, 10.3, 6.5 Hz, 1H), 5.58 (s, 1H), 5.29 (d, J = 17.2 Hz, 1H), 5.21 (d, J = 10.3 Hz, 1H), 4.81 (d, J = 6.5 Hz, 1H), 4.33 (t, J = 4.7 Hz, 2H), 3.62-3.77 (m, 2H), 1.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 140.9, 138.9, 136.5, 128.7, 128.0, 127.0, 125.9, 116.7, 83.4, 66.5, 64.2, 18.6; HRMS (FAB-MS) Calcd for $C_{15}H_{18}O_3$ [MNa+] 269.1154, Found 269.1166.



(2*R*,1'*R*)-2-[1'-(2"-naphthyl)ethoxy]-3-pentene (**3el**). Following method A, (*S*)-**1e**[3] (37 mg, 0.20 mmol), (*R*)-**2l** (38 mg, 0.22 mmol), $[Ir(COD)Cl]_2$ (3.4 mg, 0.0051 mmol), pyridine (0.90 μL, 0.010 mmol), Et_2Zn (1.0 M in hexanes, 0.11 mL, 0.11 mmol) and NH_4I (29 mg, 0.20 mmol) were reacted in THF (0.20 mL, 1.0 M) to afford **3el** (45 mg, 0.19 mmol, 94%) as a clear, colorless oil after column chromatography (hexanes:diethyl ether = 30:1). No reaction was observed using method B. Carbonate **1e** was recovered quantitatively. $[\alpha]_D^{23}$ +0.319 (*c* 0.55, $CHCl_3$); IR (film) 3056, 2973, 2928, 2867, 1449, 1367, 1308, 1087, 966, 856, 818, 747 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.27 (d, J=6.3 Hz, 3H), 1.51 (d, J=6.4 Hz, 3H), 1.63 (d, J=6.4 Hz, 3H), 3.92 (qu, J=6.3 Hz, 1H), 4.73 (q, J=6.4 Hz, 1H), 5.42 (ddqu, J=15.4, 6.4, 1.0 Hz, 1H), 5.55 (ddqu, J=15.4, 6.3, 0.8 Hz, 1H), 7.42-7.76 (m, 4H), 7.81-7.86 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.9, 20.7, 23.9, 73.5, 124.8, 125.1, 125.8, 126.2, 126.6, 127.9, 128.1, 128.3, 133.1, 133.5, 134.0, 142.4; HRMS (DEI-MS) Calcd for $C_{17}H_{20}O$ [M+] 240.1512, Found 240.1514.



(4*S*,1'*R*)-1-Benzyloxy-4-[1'-(2"-naphthyl0-ethoxy]-2-pentene (**3fl**). Following method A, (*S*)-**1f**[4] (120 mg, 0.40 mmol), (*R*)-**2l** (76 mg, 0.44 mmol), $[Ir(COD)Cl]_2$ (6.7 mg, 0.010 mmol), pyridine (1.9 μL, 0.020 mmol), Et_2Zn (1.0 M in hexanes, 0.22 mL, 0.22 mmol) and NH_4I (58 mg, 0.40 mmol) were reacted in THF (0.40 mL, 1.0 M) to afford **3fl** (73 mg, 0.21 mmol, 52%) as a clear, yellow oil after column chromatography (hexanes:diethyl ether = 20:1). No reaction was observed using method B. Carbonate **1f** was recovered quantitatively. $[\alpha]_D^{23}$ +0.260 (*c* 1.025, $CHCl_3$); IR (film) 3542, 2981, 2957, 2935, 2874, 1732, 1662, 1438, 1372, 1282, 1176, 1136, 1097, 899, 709 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (d, J=6.3 Hz, 3H), 1.54 (d, J=6.4 Hz, 3H), 3.97 (d, J=4.7 Hz, 2H), 4.04 (qu, j+4.2 Hz, 1H), 4.44 (s, 2H), 4.77 (q, J=6.4 Hz, 1H), 5.65-5.74 (m, 2H), 7.29-7.39 (m, 5H), 7.46-7.53 (m, 3H), 7.78-7.85 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8, 24.1, 70.5, 72.2, 73.2, 75.1, 124.7, 125.1, 125.9, 126.3, 127.3, 127.8, 127.9, 128.0, 128.1, 128.4, 128.6, 133.2, 133.5, 136.0, 138.56, 142.2; HRMS (DEI-MS) Calcd for $C_{24}H_{26}O_2$ [M+] 346.1929, Found 346.1933.



(4*S*,1'*S*)-4-[1'-(3",5"-Bis-trifluoromethylphenyl)-ethoxy]-pent-2-enoic acid methyl ester (**3gm**). Following method A, (*S*)-**1g**[5] (46 mg, 0.20 mmol), (*S*)-**2m**[6] (57 mg, 0.22 mmol), $[Ir(COD)Cl]_2$ (3.4 mg, 0.0051 mmol), pyridine (0.90 μL, 0.010 mmol), Et_2Zn (1.0 M in hexanes, 0.11 mL, 0.11 mmol) and NH_4I (29 mg, 0.20 mmol) were reacted in THF (0.2mL, 1.0 M) to afford **3gm** (73 mg, 0.10 mmol, 50%) as a clear, light yellow oil after column chromatography (hexanes:ethyl acetate = 16:1). No reaction was observed using method B. Carbonate **1g** was recovered quantitatively. $[\alpha]_D^{23}$ -0.816 (*c* 0.91, $CHCl_3$); IR (film) 3058, 3030, 2973, 2928, 2859,

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[4] Mulzer, J.; Salimi, N.; Hartl, H. *Tetrahedron: Asymmetry* **1993**, *4*, 457.
[5] Pickard, S. T.; Smith, H. E. *J. Am. Chem. Soc.* **1990**, *112*, 5741.
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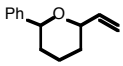
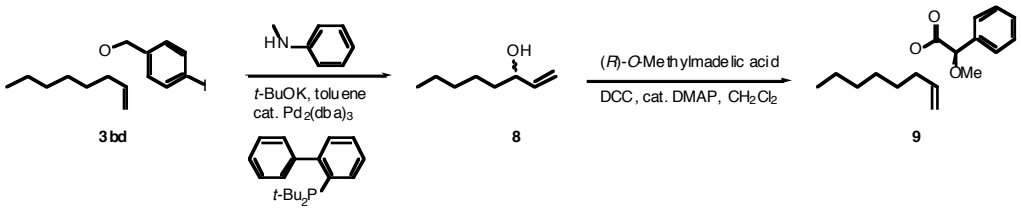
1739, 1453, 1367, 1309, 1089, 970, 820, 747, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.25 (d, J=6.5 Hz, 3H), 1.44 (d, J=6.5 Hz, 3H), 3.77 (s, 3H), 3.85 (dqu, J=6.3, 0.8 Hz, 1H), 4.56 (q, J=6.5 Hz, 1H), 5.95 (dd, J=15.8, 1.1 Hz, 1H), 6.86 (dd, J=15.8, 6.2 Hz, 1H), 7.75 (s, 2H), 7.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 24.8, 28.7, 51.9, 73.0, 75.1, 121.3, 121.8, 126.4, 132.0, 132.4, 147.0, 149.2, 166.8; HRMS (DEI-MS) Calcd for $C_{16}H_{16}F_6O_3$ [MH+] 371.1071, Found 371.1082.



(*R*,S)-2-Phenyl-6-vinyl-tetrahydro-pyran** (**6**). Following method A, hydroxycarbonate **5**[7] (61 mg, 0.20 mmol), $[Ir(COD)Cl]_2$ (3.4 mg, 0.0051 mmol), pyridine (0.90 μL, 0.010 mmol), Et_2Zn (1.0 M in hexanes, 0.11 mL, 0.11 mmol) and NH_4I (29 mg, 0.20 mmol) were reacted in THF (0.20 mL, 1.0 M) to afford the known tetrahydropyran **6**[5,8] (36 mg, 0.19 mmol, 96%) as a clear, colorless oil after column chromatography (hexanes:diethyl ether = 40:1). Following method B, **5** (61.3 mg, 0.200 mmol), $[Ir(COD)Cl]_2$ (3.4 mg, 0.0051 mmol), pyridine (0.9 μL, 0.01 mmol), Et_2Zn (1.0 M in hexanes, 20 μL, 0.020 mmol), L-tryptophan (4.1 mg, 0.020 mmol) and NH_4I (2.9 mg, 0.20 mmol) were reacted in THF (0.2 mL, 1.0 M) to afford **6** (19.0 mg, 0.101 mmol, 50%). Obtained as a 1:1 mixture of diastereomers. ^1H NMR (300 MHz, $CDCl_3$) δ 7.20-7.46 (m, 5H), 5.9-6.1 (m, 1H), 5.34 (dt, J = 7.2, 1.7 Hz, 0.5H), 5.23-5.31 (m, 1H), 5.12 (dt, J = 10.6, 1.7 Hz, 0.5H), 4.82 (dd, J = 7.0, 3.8 Hz, 0.5H), 4.41-4.46 (m, 1H), 4.0-4.09 (m, 0.5H), 1.39-2.04 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 142.9, 139.7, 138.8, 128.6, 128.4, 127.4, 127.3, 126.5, 126.1, 116.4, 114.6, 80.0, 78.9, 73.1, 73.0, 33.9, 31.9, 31.5, 28.9, 24.2, 19.4.

Procedure for sterochemical analysis of 3bd from the reaction of (*S*)-1b with 2d.[9,10]



To a solution of *p*-iodobenzylether **3bd** (69 mg, 0.20 mmol), $Pd_2(dba)_3$ (9.2 mg, 0.010 mmol) and biphenyl-di-*tert*-butylphosphine (12 mg, 0.040 mmol) in toluene (0.40 mL, 0.5 M) at room temperature was added *N*-methylaniline (26 μL, 0.24 mmol). The resulting mixture was allowed to stir for 5 min at which time potassium *tert*-butoxide was added. After stirring for 30 min, trifluoroacetic acid (50 μL) was added, the reaction mixture was diluted with diethyl ether (20 mL) and washed with a saturated, aqueous $NaHCO_3$ solution (5 mL). The aqueous layer was extracted with additional diethyl ether (10 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated to afford crude 1-octen-3-ol (**7**, 16 mg, 0.13 mmol, 65%), which was carried on to the next reaction without further purification.

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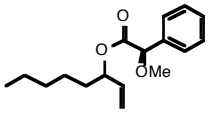
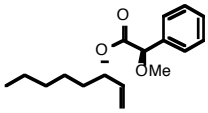
To a solution of 1-octen-3-ol (**8**, 16 mg, 0.13 mmol) from the previous deprotection, (*R*)-*O*-methylmandelic acid (32 mg, 0.19 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (1.6 mg, 0.013 mmol) in CH_2Cl_2 at 0 °C was added dicyclohexylcarbodiimide (1 M in CH_2Cl_2, 0.19 mL, 0.19 mmol). The resulting mixture was allowed to stir for 1 h, diluted with CH_2Cl_2 (20 mL) and washed with water (10 mL). The aqueous layers were extracted with additional CH_2Cl_2 (10 mL). The combined organic layers were washed with saturated, aqueous $NaHCO_3$ solution (10 mL), dried with $MgSO_4$, filtered, concentrated and purified by flash chromatography eluting with a mixture of hexanes and diethyl ether (10:1) to give the *O*-methylmandelate ester **9** as a 3.7:1 mixture of diastereomers (35 mg, 100%), as determined by comparison of its ^1H NMR spectrum with those of the (*R*)-*O*-methylmandelate esters prepared from racemic and enantiomerically pure (*S*)-configured forms of 1-octen-3-ol (**8**), respectively.



(±)-1-Octen-3-yl (*R*)-*O*-methylmandelate (a 1:1 mixture of diastereomers) (*RS*,*R*-9). IR (film) 2932, 2860, 2828, 1750, 1734, 1456, 1252, 1199, 1176, 1116, 999, 928, 733, 697 cm^{-1}; ^1H NMR (300 MHz, C6D6) δ 7.59-7.20 (m, 4H), 7.09-7.20 (m, 6H), 5.54-5.75 (m, 2H), 5.43 (qu, J = 6.4 Hz, 2H), 5.18 (dt, J = 17.3, 1.4 Hz, 1H), 5.04 (dt, J = 17.3, 1.4 Hz, 1H), 5.00 (dt, J = 10.5, 1.2 Hz, 1H), 4.91 (dt, J = 10.5, 1.2 Hz, 1H), 4.78 (s, 1H), 4.74 (s, 1H), 3.25 (s, 6H), 0.80-1.60 (m, 22H); ^{13}C NMR (75 MHz, C_6D_6) δ 169.8, 137.5, 136.8, 136.5, 116.4, 116.4, 83.4, 83.2, 75.1, 57.1, 34.4, 34.3, 31.7, 31.6, 24.9, 24.7, 22.7, 14.1; HRMS (ESI-TOF-MS) Calcd for $C_{17}H_{24}O_3$ [MNa+] 299.1618, Found 299.1618.



(*S*)-1-Octen-3-yl (*R*)-*O*-methylmandelate (*S*,*R*-9). $[\alpha]_D^{23}$ -0.282 (*c* 0.91, CH_2Cl_2); IR (film) 2932, 2858, 2119, 1750, 1455, 1359, 1255, 1199, 1175, 1117, 1001, 928, 734, 697 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 7.60-7.64 (m, 2H), 7.06-7.20 (m, 3H), 5.59 (ddd, J = 17.0, 10.5, 6.1 Hz, 1H), 5.43 (qt, J = 5.9, 1.3 Hz, 1H), 5.04 (dt, J = 17.2, 1.3 Hz, 1H), 4.87 (dt, J = 10.5, 1.2 Hz, 1H), 4.78 (s, 1H), 3.25 (s, 3H), 1.55-1.69 (m, 2H), 1.15-1.50 (m, 6H), 0.85 (t, J = 6.5 H, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 169.8, 137.5, 136.5, 116.3, 83.4, 75.1, 57.0, 55.7, 35.3, 34.4, 31.7, 25.7, 24.9, 24.8, 22.8, 14.1; HRMS (ESI-TOF-MS) Calcd for $C_{17}H_{24}O_3$ [MNa+] 299.1618, Found 299.1616.