Supporting Information

A Mild and Efficient Method for the Stereoselective Formation of C–O bonds : Palladium–Catalyzed Allylic Etherification Using Zinc(II) Alkoxides

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Procedure for primary allylic acetates using Pd(PPh₃)₄ (Condition A).

To a solution of MeOH (32.0 mg, 1.0 mmol) in THF (0.5 mL) was added dropwise Et₂Zn (0.5 mL, 1.0 M in hexane) via a syringe at 25 °C. The resulting mixture was stirred for 30 min during which time it turned cloudy white. To this suspension were added cinnamyl acetate (**1**, 176.2 mg, 1.0 mmol) and Pd(PPh₃)₄ (58 mg, 0.05 mmol). After stirring for 2 h, the reaction mixture was loaded directly onto a silica gel column and eluted with a mixture of hexanes and EtOAc (25:1) to give methyl ether **3b** (123 mg, 83%) as a colorless oil.

Procedure for secondary allylic acetates using Pd(OAc)₂/7 (Condition B).

To a solution of BnOH (20.6 mg, 0.20 mmol) in THF (0.1 mL) was added dropwise Et₂Zn (0.1 mL, 1.0 M in hexane) via a syringe at 25 °C. After 30 min the mixture turned cloudy white. To this suspension were added in one portion methyl ester **4** (38 mg, 0.2 mmol), Pd(OAc)₂ (2.24 mg, 0.01 mmol), ligand **7** (4.50 mg, 0.015 mmol), and NH₄OAc (1.54 mg / 0.02 mmol) in THF (0.2 mL). After 6 h, the reaction mixture was moved directly onto a silica gel column. Purification by flash chromatography (hexanes:EtOAc = 10:1) gave benzyl ether **5a** (33 mg, 70%) and diene **6** (2.8 mg, 10%) both as colorless oils.

(1E)-3-Benzyloxy-1-phenylpropene (3a)

IR (film) 3026, 2849, 1360, 1116, 966, 733 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.44-7.23 (m, 10H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.35 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.59 (s, 2H), 4.22 (dd, *J* = 6.0, 1.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 138.2, 136.7, 132.5, 128.5, 128.4, 127.8, 127.64, 127.62, 126.4, 126.0, 72.1, 70.7; HRMS Calcd for C₁₆H₁₆O [M⁺] 224.1201, Found 224.1204.

(1E)-3-Methoxy-1-phenylpropene (3b)

IR (film) 2925, 2820, 1448, 1121, 966, 692 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.24 (m, 5H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.09 (dd, *J* = 6.0, 1.4 Hz, 2H), 3.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 136.6, 132.4, 128.5, 127.6, 126.4, 125.9, 73.3, 57.9; HRMS Calcd for C₁₀H₁₂O [M⁺] 148.0888, Found 148.0896.

(1E)-3-Isopropoxy-1-phenylpropene (3c)

IR (film) 2971, 2851, 1124, 1058, 966, 665 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.21 (m, 5H), 6.59 (d, $J = 16.0$ Hz, 1H), 6.29 (dt, $J = 15.9, 5.9$ Hz, 1H), 4.13 (dd, $J = 6.0, 1.5$ Hz, 2H), 3.68 (sept, $J = 6.1$ Hz, 1H), 1.20 (d, $J = 6.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.8, 131.7, 128.5, 127.5, 126.8, 126.4, 70.9, 68.7, 22.1; HRMS Calcd for $\text{C}_{12}\text{H}_{16}\text{O}$ [M^+] 176.1201, Found 176.1205.

(1*R,5*R**)-5-Benzzyloxy-cyclohex-3-enecarboxylic acid methyl ester(5a)**

IR (film) 3030, 2950, 2846, 1735, 1094, 1063 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.23 (m, 5H), 5.80 (dd, $J = 3.0, 0.5$ Hz, 2H), 4.64 (d, $J = 11.8$ Hz, 1H), 4.56 (d, $J = 11.8$ Hz, 1H), 4.14 (m, 1H), 3.70 (s, 3H), 2.65 (m, 1H), 2.42 (m, 1H), 2.29 (m, 2H), 1.75 (dt, $J = 12.4, 9.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.0, 138.5, 128.7, 128.3, 127.7, 127.6, 127.5, 73.3, 70.0, 51.8, 38.2, 31.1, 27.6; HRMS Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$ [M^+] 246.1256, Found 246.1256.

(1*E*)-3-(2-Bromoethoxy)-1-phenylpropene (11a)

IR (film) 3395, 3028, 2861, 1736, 1115, 968 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.21 (m, 5H), 6.61 (d, $J = 16.0$ Hz, 1H), 6.27 (dt, $J = 16.0, 6.1$ Hz, 1H), 4.20 (dd, $J = 6.1, 1.4$ Hz, 2H), 3.79 (t, $J = 6.2$ Hz, 2H), 3.49 (t, $J = 6.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.4, 133.0, 128.6, 127.8, 126.5, 125.4, 71.7, 69.9, 30.5; HRMS Calcd for $\text{C}_{11}\text{H}_{13}\text{BrO}$ [M^+] 240.0150, Found 240.0150.

(1*E*)-3-(2-Trimethylsilylethoxy)-1-phenylpropene (11b)

IR (Film,) 2952, 2849, 1248, 1077, 835, 691 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.21 (m, 5H), 6.61 (d, $J = 16.0$ Hz, 1H), 6.30 (dt, $J = 16.0, 5.9$ Hz, 1H), 4.12 (dd, $J = 5.9, 1.5$ Hz, 2H), 3.57 (m, 2H), 1.00 (m, 2H), 0.03 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 136.8, 131.9, 128.5, 127.5, 126.5, 126.4, 70.9, 67.6, 18.3, -1.4; HRMS Calcd for $\text{C}_{14}\text{H}_{22}\text{OSi}$ [M^+] 234.1440, Found 234.1422.

(1*E*)-3-(2 -Bromobenzyloxy)-1-phenylpropene (11c)

IR (film) 3334, 3026, 2852, 1106, 966, 749 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.56-7.13 (m, 9H), 6.68 (d, $J = 15.9$ Hz, 1H), 6.36 (dt, $J = 15.9, 6.0$ Hz, 1H), 4.64 (s, 2H), 4.28 (dd, $J = 6.0, 1.3$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.5, 136.6, 132.6, 132.5, 129.1, 128.9, 128.5, 127.7, 127.4, 126.5, 125.8, 122.7, 71.418, 71.3; HRMS Calcd for $\text{C}_{16}\text{H}_{15}\text{BrO}$ [M^+] 302.0306, Found 302.0283.

(1E)-3-(Prop-3-ynyloxy)-1-phenylpropene (11d)

IR (film) 2981, 2843, 1730, 1177, 1010, 736 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.22 (m, 5H), 6.63 (d, $J = 15.9$ Hz, 1H), 6.26 (dt, $J = 15.9, 6.2$ Hz, 1H), 4.23 (dd, $J = 6.2, 1.4$ Hz, 2H), 4.19 (d, $J = 2.4$ Hz, 2H), 2.45 (t, $J = 2.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.5, 133.4, 128.5, 127.8, 126.5, 125.0, 79.7, 74.5, 70.2, 57.0; HRMS Calcd for $\text{C}_{12}\text{H}_{12}\text{O}$ [M^+] 172.0888, Found 170.0886.

(1R*,5R*)-5-Allyloxy-cyclohex-3-enecarboxylic acid methyl ester (11e)

IR (film) 2952, 2847, 1736, 1170, 1089, 665 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.92 (ddt, $J = 17.2, 10.3, 5.5$ Hz, 1H), 5.82-5.73 (m, 2H), 5.29 (ddd, $J = 17.2, 3.3, 1.6$ Hz, 1H), 5.17 (ddd, $J = 10.3, 2.6, 1.3$ Hz, 1H), 4.12-3.99 (m, 3H), 3.70 (s, 3H), 2.68-2.60 (m, 1H), 2.39-2.34 (m, 1H), 2.30-2.26 (m, 2H), 1.67 (dt, $J = 12.4, 9.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.0, 135.0, 128.7, 127.7, 116.8, 73.4, 69.1, 51.8, 38.2, 31.1, 27.5; HRMS Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_3$ [M^+] 196.1099, Found 196.1118.

(1R*,5R*)-5-(2-Indanyloxy)cyclohex-3-ene carboxylic acid methyl ester (11f)

IR (film) 2948, 2846, 1735, 1095, 743, 665 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.13 (m, 4H), 5.82-5.72 (m, 2H), 4.54 (sept, $J = 6.7, 5.0, 1.2$ Hz, 1H), 4.21-4.17 (m, 1H), 3.71 (s, 3H), 2.97 (dd, $J = 15.8, 5.4$ Hz, 2H), 2.72-2.64 (m, 1H), 2.44-2.39 (m of d, 1H), 2.31-2.27 (m, 2H), 1.70 (dt, $J = 12.0, 9.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.0, 140.8, 140.7, 129.2, 127.6, 126.5, 124.6, 78.2, 72.7, 51.8, 40.2, 39.8, 38.3, 31.9, 27.5; HRMS Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3$ [M^+] 272.1412, Found 272.1394.

(4*RS*,1*S*)-4-[1-(2-Naphthyl)ethoxy]-but-2-ene (11g)

IR (film) 3056, 2972, 2927, 1088, 1052, 965 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.89-7.79 (m, 3H), 7.73 (s, 0.5H), 7.68(s, 0.5H), 7.49-7.41 (m, 3H), 5.56-5.34 (m, 2H), 4.73-4.64 (m, 1H), 3.90 (m, 0.5H), 3.64 (q, $J = 7.5$ Hz, 0.5H), 1.72 (dd, $J = 6.6, 1.3$ Hz, 1.5H), 1.60 (ddd, $J = 6.3, 2.1, 1.4$ Hz, 1.5H), 1.48 (d, $J = 6.5$ Hz, 1.5H), 1.45 (d, $J = 6.5$ Hz, 1.5H), 1.25 (d, $J = 6.3$ Hz, 1.5H), 1.17 (d, $J = 6.6$ Hz, 1.5H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 142.1, 142.0, 133.7, 133.2, 132.9, 132.8, 128.3, 128.0, 127.8, 127.8, 127.5, 126.4, 126.0, 125.9, 125.6, 125.5, 125.0, 124.8, 124.6, 124.4, 74.2, 73.9, 73.3, 73.2, 24.6, 23.6, 22.2, 20.4, 17.8; HRMS Calcd for $\text{C}_{17}\text{H}_{20}\text{O}$ [M^+] 240.1514, Found 240.1516.

Methyl (4*R*,1*RS*)-(cyclohex-2-enyloxy)-pent-2-enoate (11h)

IR (film) 2935, 2865, 1726, 1435, 1272, 1168 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.93-6.85 (m, 1H), 6.03-5.98 (m, 1H), 5.88-5.82 (m, 1H), 5.75-5.67 (m, 1H), 4.23-4.16 (m, 1H), 3.91-3.84 (m, 1H), 3.74 (s, 1.5H), 3.74 (s, 1.5H), 2.09-2.00 (m, 1H), 1.96-1.89 (m, 1H), 1.80-1.71 (m, 2H), 1.69-1.61 (m, 1H), 1.59-1.51 (m, 1H), 1.28 (d, $J = 6.6$ Hz, 1.5H), 1.28 (d, $J = 6.6$ Hz, 1.5H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 166.8, 150.630, 150.5, 131.2, 131.0, 127.8, 127.5, 120.2, 120.0, 72.2, 71.8, 71.4, 70.7, 51.6, 29.4, 28.2, 25.1, 21.4, 21.2, 19.3, 18.9; HRMS Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_3$ [M^+] 284.1412, Found 284.1416.

Methyl (4*R*,1*S*)-4-(1-(2-naphthyl)ethoxy)-pent-2-enoate (12)

$[\alpha]_{\text{D}}^{25\text{ }^\circ\text{C}}$ -254.4 (c 0.59, CHCl_3); IR (film) 3056, 2976, 2870, 1725, 1272, 1093 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.88-7.83 (m, 3H), 7.71 (s, 1H), 7.51-7.47 (m, 3H), 6.91 (dd, $J = 15.8, 6.4$ Hz, 1H), 5.98 (dd, $J = 15.8, 1.2$ Hz, 1H), 4.62 (q, $J = 12.2, 6.4$ Hz, 1H), 3.94 (dq, $J = 6.4, 1.2$ Hz, 1H), 3.8 (s, 3H), 1.53 (d, $J = 6.5$ Hz, 3H), 1.25 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 149.9, 140.9, 133.2, 128.5, 127.8, 127.7, 126.2, 125.8, 125.2, 124.0, 120.7, 75.8, 71.6, 51.6, 24.4, 21.3; HRMS Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_3$ [M^+] 284.1412, Found 284.1416.

Methyl (4*R*,1*R*)-4-(1-(2-naphthyl)ethoxy)-pent-2-enoate (13)

$[\alpha]_D^{25}$ BC -48.8 (c 0.01, $CHCl_3$); IR (film) 3056, 2975, 2870, 1724, 1273, 1091 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) 7.84-7.81 (m, 3H), 7.72 (s, 1H), 7.50-7.45 (m, 3H), 6.82 (dd, J = 15.7, 5.0 Hz, 1H), 6.019 (dd, J = 15.7, 1.6 Hz, 1H), 4.74 (q, J = 6.4 Hz, 1H), 4.08 (m, 1H), 3.69 (s, 3H), 1.53 (d, J = 6.4 Hz, 3H), 1.32 (d, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 150.0, 141.0, 133.2, 133.0, 128.4, 127.8, 127.6, 126.1, 125.8, 125.0, 124.1, 119.7, 75.3, 71.1, 51.5, 23.9, 19.4; HRMS Calcd for $C_{18}H_{20}O_3$ [M^+] 284.1412, Found 284.1416.

(2*RS*,5*RS*)-2-Phenyl-5-vinyltetrahydrofuran (14)

Characterized as a 1:1 diastereomeric mixture (ref. Macs ri, I.; Szabo, K. J. *Chem. Eur. J* **2001**, 7, 4097). IR (film) 3029, 2971, 1723, 1450, 1050, 923, 699 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) 7.40-7.25 (m, 5H), 6.08-5.89 (m, 1H), 5.35 (dt, J = 17.2, 1.2 Hz, 0.5H), 5.32 (dt, J = 17.1, 1.3 Hz, 0.5H), 5.16 (dt, J = 10.4, 1.2 Hz, 0.5H), 5.14 (dt, J = 10.4, 1.3 Hz, 0.5H), 5.08 (t, J = 7.7 Hz, 0.5H), 4.96 (t, J = 7.0 Hz, 0.5H), 4.68 (q, J = 6.1 Hz, 0.5H), 4.49 (qt, J = 6.6, 1.1 Hz, 0.5H), 2.42-2.35 (m, 1H), 2.34-2.26 (m, 1H), 1.96-1.70 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 143.5, 143.1, 139.3, 139.0, 128.3, 128.2, 127.2, 127.1, 125.8, 125.6, 115.6, 115.1, 81.1, 80.7, 80.64, 80.60, 35.1, 34.3, 32.7, 31.9

(2*RS*,6*RS*)-2-Phenyl-6-vinyltetrahydropyran (15)

Characterized as a 1:1 diastereomeric mixture (ref. Brown, D. S.; Bruno, M.; Davenport, R. J.; Ley, S. V. *Tetrahedron* **1989**, 45, 4293). IR (film) 3063, 2936, 1451, 1088, 1042, 919, 751, 699 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) 7.43-7.25 (m, 5H), 6.05-5.91 (m, 1H), 5.33-5.23 (m, 1.5H), 5.10 (dt, J = 10.6, 1.4 Hz, 0.5H), 4.80 (dd, J = 7.6, 3.7 Hz, 0.5H), 4.50-4.42 (m, 0.5H), 4.43 (dd, J = 11.4, 2.2 Hz, 0.5H), 4.05-4.00 (m, 0.5H), 2.05-1.90 (m, 0.5H), 1.90-1.65 (m, 5.5H); ^{13}C NMR (100MHz, $CDCl_3$) δ 143.3, 142.6, 139.4, 138.5, 128.3, 128.2, 127.14, 127.07, 126.2, 125.8, 116.1, 114.4, 79.7, 78.6, 72.85, 72.77, 33.6, 31.6, 31.2, 28.6, 23.9, 19.2.