Supporting Information

Copper-Catalyzed Regioselective Allylic Substitution Reactions with Indium Organometallics

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General considerations. NMR spectra were recorded in CDCl₃ at 200 MHz for ¹H and at 50 MHz for ¹³C. DEPT was used to assign carbon types. The electron-impact mass spectra were measured at 70 eV. Gas chromatography was performed on a HP-1 capillary column (30 m × 0.32 mm × 0.25 μm) using N₂ as carrier gas (2 mL/min) and equipped with a FID detector (300 °C)

Cinnamyl diethyl phosphate (1e).¹ ¹H NMR (CDCl₃) δ 1.35 (t, *J* = 6.8 Hz, 6 H), 4.11 (q, *J* = 6.8 Hz, 2 H), 4.17 (q, *J* = 6.8 Hz, 2 H), 4.69 (br d, *J* = 6.3 Hz, 1 H), 4.73 (br d, *J* = 6.3 Hz, 1 H), 6.31 (dt, *J* = 15.7, 7.8 Hz, 1 H), 6.69 (d, *J* = 15.7, Hz, 1 H), 7.30–7.42 (m, 5 H); ¹³C NMR (CDCl₃) δ 16.1 (d, *J* = 7.1 Hz, 2 × CH₃), 63.8 (d, *J* = 6.4 Hz, 2 × CH₂), 67.9 (d, *J* = 5.7 Hz, CH₂), 123.6 (d, *J* = 6.4 Hz, CH), 126.7 (2 × CH), 128.1 (CH), 128.6 (2 × CH), 133.9 (CH), 136.0 (C); MS (EI) *m/z* 270 (M⁺, 6), 115 (100).

3-Phenyl-1-heptene (2, R = *n*-Bu).² ¹H NMR (CDCl₃) δ 0.88 (t, *J* = 6.8 Hz, 3 H), 1.22–1.38 (m, 4 H), 1.70 (q, *J* = 6.8 Hz, 2 H), 3.24 (q, *J* = 7.8 Hz, 1 H), 4.97–5.08 (m, 2 H), 5.87–6.05 (m, 1 H), 7.15–7.35 (m, 5 H); ¹³C NMR (CDCl₃) δ 14.0 (CH₃), 22.6 (CH₂), 29.7 (CH₂), 35.1 (CH₂), 49.9 (CH), 113.8 (CH₂), 126.0 (CH), 127.6 (2 × CH), 128.4 (2 × CH), 142.6 (CH), 144.7 (C); MS (FAB) *m/z* 174 (M⁺, 9), 173 (M⁺ – 1, 32), 147 (100); GC [oven temperature: 100 °C (5 min) to 200 °C at 10 °C/min] *t*_R (**2**) = 9.6 min, *t*_R (**3**) = 13.5 min.

3-Phenyl-1-butene (2, R = Me).³ ¹H NMR (CDCl₃) δ 1.38 (d, *J* = 6.8 Hz, 3 H), 3.41–3.55 (m, 1 H), 5.05 (br d, *J* = 10.0 Hz, 1 H), 5.07 (br d, *J* = 16.8 Hz, 1 H), 6.03 (ddd, *J* = 17.1, 10.2, 6.4 Hz, 1 H), 7.17–7.37 (m, 5 H); ¹³C NMR (CDCl₃) δ 20.7 (CH₃), 43.2 (CH), 113.1 (CH₂), 125.9 (CH), 126.1 (2 × CH), 128.4 (2 × CH), 143.2 (CH), 145.5 (C); MS (EI) *m/z* 132 (M⁺, 17), 117 (M⁺ – CH₃, 63), 84 (100); GC (oven temperature: 100 °C) *t*_R (**2**) = 4.1 min, *t*_R (**3**) = 6.1 min.

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(2) Yanagisawa, A.; Nomura, N.; Yamamoto, H. *Tetrahedron* **1994**, *50*, 6017–6028.

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3,3-Diphenyl-1-propene (2. R = Ph).⁴ ¹H NMR (CDCl₃) δ 4.75 (d, J = 7.3 Hz, 1 H), 5.01 (d, J = 17.1 Hz, 1 H), 5.24 (d, J = 9.8 Hz, 1 H), 6.32 (ddd, J = 17.1, 10.2, 7.3 Hz, 1 H), 7.17–7.37 (m, 10 H); ¹³C NMR (CDCl₃) δ 55.0 (CH), 116.3 (CH₂), 126.3 (2 $\times$ CH), 128.4 (4 $\times$ CH), 128.6 (4 $\times$ CH), 140.6 (2 $\times$ CH), 143.3 (2 $\times$ C); MS (FAB) m/z 194 (M⁺, 20), 147 (100); GC [oven temperature: 100 °C (5 min) to 200 °C at 10 °C/min] t_R (2) = 13.9 min, t_R (3) = 16.4 min.

1-Trimethylsilyl-2-phenyl-3-butene (2 R = CH₂SiMe₃).⁵ ¹H NMR (CDCl₃) δ -0.10 (s, 9 H), 1.07 (d, J = 7.8 Hz, 2 H), 3.43 (q, J = 7.3 Hz, 1 H), 4.94 (d, J = 10.2 Hz, 1 H), 5.01 (d, J = 17.6 Hz, 1 H), 5.99 (ddd, J = 17.6, 10.2, 7.8 Hz, 1 H), 7.17–7.33 (m, 5H); ¹³C NMR (CDCl₃) δ -1.0 (3 $\times$ CH₃), 23.7 (CH₂), 45.9 (CH), 112.3 (CH₂), 126.0 (CH), 127.4 (2 $\times$ CH), 128.4 (2 $\times$ CH), 144.9 (CH), 146.2 (C); MS (FAB) m/z 204 (M⁺, 8), 133 (100); GC [oven temperature: 80 °C (2 min) to 200 °C at 10 °C/min] t_R (2) = 12.5 min, t_R (3) = 15.3 min.

Geranyl diethyl phosphate (4c).¹ ¹H NMR (CDCl₃) δ 1.34 (t, J = 6.8 Hz, 6 H), 1.61 (s, 3 H), 1.69 (s, 3 H), 1.71 (s, 3 H), 2.02–2.12 (m, 4 H), 4.09 (q, J = 6.8 Hz, 2 H), 4.13 (q, J = 6.8 Hz, 1 H), 4.55 (d, J = 7.3 Hz, 1 H), 4.59 (d, J = 7.3 Hz, 1 H), 5.04–5.12 (m, 1 H), 5.41 (br t, J = 7.3 Hz, 1 H); ¹³C NMR (CDCl₃) δ 16.0 (d, J = 6.4 Hz, CH₃), 16.1 (d, J = 6.4 Hz, CH₃), 16.4 (CH₃), 17.6 (CH₃), 25.6 (CH₃), 26.2 (CH₂), 39.5 (CH₂), 63.6 (d, J = 5.7 Hz, 2 $\times$ CH₂), 64.1 (d, J = 5.7 Hz, CH₂), 118.9 (d, J = 7.1 Hz, CH), 123.6 (CH), 131.9 (C), 142.5 (C).

2,6-Dimethyl-6-vinyl-2-decene (5, R = *n*-Bu).⁶ ¹H NMR (CDCl₃) δ 0.89 (t, J = 7.3 Hz, 3 H), 0.96 (s, 3 H), 1.20–1.33 (m, 8 H), 1.60 (s, 3 H), 1.69 (s, 3 H), 1.81–1.93 (m, 2 H), 4.89 (dd, J = 17.6, 1.5 Hz, 1 H), 4.98 (dd, J = 10.7, 1.5 Hz, 1 H), 5.05–5.14 (m, 1 H), 5.71 (dd, J = 17.6, 10.7 Hz, 1 H); ¹³C NMR (CDCl₃) δ 14.1 (CH₃), 17.5 (CH₃), 22.6 (CH₃), 22.8 (CH₂), 23.5 (CH₂), 25.6 (CH₃), 26.2 (CH₂), 39.4 (C), 40.5 (CH₂), 40.7 (CH₂), 111.2 (CH₂), 125.1 (CH), 130.9 (C), 147.5 (CH); MS (FAB) m/z 194 (M⁺, 5), 179 (M⁺ – CH₃, 11), 133 (100); GC [oven temperature: 100 °C (5 min) to 200 °C at 10 °C/min] t_R (5) = 10.2 min, t_R (6) = 8.9 min.

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3,3,7-Trimethyl-1,6-octadiene (5, R = Me).³ ¹H NMR (CDCl₃) δ 1.00 (s, 6 H), 1.25–1.33 (m, 2 H), 1.60 (s, 3 H), 1.68 (s, 3 H), 1.83–1.91 (m, 2 H), 4.91 (dd, J = 18.1, 1.5 Hz, 1 H), 4.92 (dd, J = 10.3, 1.5 Hz, 2 H), 5.05–5.14 (m, 1 H), 5.79 (dd, J = 18.1, 10.3 Hz, 1 H); ¹³C NMR (CDCl₃) δ 17.5 (CH₃), 23.3 (CH₂), 25.6 (CH₃), 26.6 (2 $\times$ CH₃), 36.5 (C), 42.7 (CH₂), 110.2 (CH₂), 125.0 (CH), 131.0 (C), 148.4 (CH); MS (FAB) m/z 152 (M⁺, 5), 131 (100); GC [oven temperature: 100 °C (5 min) to 200 °C at 10 °C/min] t_R (5) = 4.3 min, t_R (6) = 5.3 min.

3,7-Dimethyl-3-phenyl-1,6-octadiene (5, R = Ph).⁷ ¹H NMR (CDCl₃) δ 1.40 (s, 3 H), 1.53 (s, 3 H), 1.67 (s, 3 H), 1.77–1.81 (m, 4 H), 5.06 (dd, J = 17.6, 1.5 Hz, 1 H), 5.08 (m, 1 H), 5.12 (dd, J = 10.7, 1.5 Hz, 1 H), 6.06 (dd, J = 17.6, 10.7 Hz, 1 H), 7.17–7.35 (m, 5 H); ¹³C NMR (CDCl₃) δ 17.5 (CH₃), 23.3 (CH₂), 24.9 (CH₃), 25.6 (CH₃), 41.1 (CH₂), 44.3 (C), 111.7 (CH₂), 124.7 (CH), 125.7 (CH), 126.6 (2 $\times$ CH), 128.0 (2 $\times$ CH), 131.3 (C), 146.9 (CH), 147.4 (C); MS (EI) m/z 214 (M⁺, 5), 199 (M⁺ – CH₃, 6), 131 (100); GC [oven temperature: 100 °C (5 min) to 200 °C at 10 °C/min] t_R (5) = 13.7 min, t_R (6) = 14.9 min.

3,7-Dimethyl-3-(trimethylsilyl)methyl-1,6-octadiene (5, R = CH₂SiMe₃). ¹H NMR (CDCl₃) δ 0.00 (s, 9 H), 0.77 (s, 2 H), 1.06 (s, 3 H), 1.28–1.37 (m, 2 H), 1.59 (s, 3 H), 1.68 (s, 3 H), 1.98–2.05 (m, 4 H), 4.89 (dd, J = 17.1, 1.5 Hz, 1 H), 4.92 (dd, J = 11.2, 1.5 Hz, 1 H), 5.04–5.16 (m, 1 H), 5.77 (dd, J = 17.1, 11.2 Hz, 1 H); ¹³C NMR (CDCl₃) δ 0.9 (3 $\times$ CH₃), 17.6 (CH₃), 23.3 (CH₂), 25.3 (CH₃), 25.6 (CH₃), 30.6 (CH₂), 39.3 (C), 44.4 (CH₂), 110.1 (CH₂), 125.0 (CH), 130.9 (C), 149.2 (CH); MS (FAB) m/z 224 (M⁺, 8), 209 (M⁺ – CH₃, 9), 147 (100); HRMS (EI) calcd for C₁₄H₂₈Si 224,1960 (M⁺), found 224,1948; GC [oven temperature: 80 °C (2 min) to 200 °C at 10 °C/min] t_R (5) = 13.4 min, t_R (6) = 14.2 min.

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