Platinum-Catalyzed Intramolecular Hydroalkoxylation of γ - and δ -Hydroxy Olefins to Form Cyclic Ethers

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Supporting Information

Experimental procedures, analytical and spectroscopic data, and copies of NMR spectra for hydroxy olefins and cyclic ethers (42 pages).

Experimental

General Methods. Catalytic reactions were performed in sealed glass tubes under an atmosphere of dry nitrogen. NMR spectra were obtained on a Varian spectrometer operating at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR in CDCl_3 unless noted otherwise. IR spectra were obtained on a Bomen MB-100 FT IR spectrometer. Gas chromatography was performed on a Hewlett-Parkard 5890 gas chromatograph equipped with a 25 m polydimethylsiloxane capillary column. Flash column chromatography was performed employing 200-400 mesh silica gel (EM). Thin layer chromatography (TLC) was performed on silica gel 60 F₂₅₄ eluting with hexanes/ethyl acetate (5:1) unless noted otherwise. Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ).

$[\text{PtCl}_2(\text{H}_2\text{C}=\text{CH}_2)]_2$ and tertiary phosphines were purchased from Strem and used as received. 1,4-Dioxane (anhydrous, Aldrich or Acros) and CCl_4 (anhydrous, Aldrich) were used as received. THF was freshly distilled over sodium benzoquinone ketyl under nitrogen. 1,2-Dichloroethane (DCE) and 1,1,2,2-tetrachloroethane were freshly distilled over CaH_2 under nitrogen. 3-(*N*-Phthalimido)propionaldehyde was synthesized employing a literature procedure.¹

Hydroxy Olefins

2,2-Diphenyl-4-penten-1-ol (2). A solution of methyl diphenylacetate (5.0 g, 22.1 mmol) in THF (10 mL) was added slowly to a solution of LDA [generated from diisopropylamine (3.7 g, 26.2 mmol) and *n*-BuLi (9.0 mL, 2.5 M in hexanes, 22.5 mmol) in THF (20 mL) at $-78\text{ }^\circ\text{C}$] over 30 min and the resulting solution was stirred for additional 15 min. Allyl bromide (2.4 mL, 26.5 mmol) was added over 10 min and the resulting mixture was warmed to room temperature, stirred overnight, quenched with HCl (3 N, 15 mL), and extracted with ether ($4 \times 50\text{ mL}$). The combined ether extracts were washed with water (50 mL), dried (MgSO_4), and concentrated under vacuum. Column chromatography of the

residue (SiO₂; hexanes–ether = 5:1) gave methyl 2,2-diphenyl-4-pentenoate (4.8 g, 81%) as a viscous colorless oil.

A solution of methyl 2,2-diphenyl-4-pentenoate (4.8 g, 17.6 mmol) in THF (20 mL) was added slowly to a suspension of LiAlH₄ (0.95 g, 24.5 mmol) in THF (25 mL) at 0 °C. The resulting mixture was stirred at room temperature overnight, quenched by sequential addition of water (5 mL) and aqueous NaOH (15%, 5 mL) at 0 °C. The resulting suspension was filtered through Celite and eluted with ether. The ether eluant was dried (MgSO₄) and concentrated under vacuum. Chromatography of the residue (SiO₂; hexanes–ether = 5:1) gave 2,2-diphenyl-4-penten-1-ol (**2**) (3.6 g, 86%) as a white solid.

For methyl 2,2-diphenyl-4-pentenoate:² ¹H NMR: δ 7.31-7.21 (m, 10 H), 5.64-5.54 (m, 1 H), 4.96-4.93 (m, 1 H), 4.92-4.90 (m, 1 H), 3.68 (s, 3 H), 3.17 (td, *J* = 1.2, 6.8 Hz, 2 H). ¹³C{¹H} NMR: δ 174.8, 142.8, 134.6, 129.3, 128.2, 127.2, 118.5, 60.6, 52.6, 43.1.

For 2: mp 46-47 °C. TLC (hexanes–ether = 5:1): *R_f* = 0.20. ¹H NMR: δ 7.34-7.18 (m, 10 H), 5.45 (tdd, *J* = 7.2, 10.0, 17.2 Hz, 1 H), 5.11 (tdd, *J* = 1.2, 2.0, 17.2 Hz, 1 H), 5.00 (tdd, *J* = 1.2, 2.0, 10.0 Hz, 1 H), 4.16 (s, 2 H), 2.98 (td, *J* = 1.2, 6.8 Hz, 2 H), 1.26 (s, 1 H). ¹³C{¹H} NMR: δ 145.6, 134.9, 128.6, 128.5, 126.7, 118.5, 68.2, 51.9, 41.3. IR (neat, cm⁻¹): 3548, 3441, 3058, 3026, 2975, 2932, 2882, 1638, 1598, 1495, 1445, 1055, 1037, 916, 757, 696. Anal. Calcd. (found) for C₁₇H₁₈O: C, 85.67 (85.65); H, 7.61(7.51).

3-Phenyl-4-penten-1-ol (Table 2, entry 1). 3-Phenyl-4-penten-1-ol was synthesized according to a published procedure.³ ¹H NMR: δ 7.34-7.30 (m, 2 H), 7.24-7.20 (m, 3 H), 5.99 (ddd, *J* = 7.6, 10.0, 17.2 Hz, 1 H), 5.12-5.05 (m, 2 H), 3.67-3.57 (m, 2 H), 3.48 (q, *J* = 7.2 Hz, 1 H), 2.07-1.92 (m, 2 H), 1.51 (br s, 1 H). ¹³C{¹H} NMR: δ 144.0, 142.1, 128.9, 127.9, 126.7, 114.7, 61.2, 46.6, 38.3.

5-Methyl-1-phenyl-5-hexen-2-ol (Table 2, entry 2). A solution of 4-bromo-2-methyl-1-butene (2.07 g, 13.9 mmol) in THF (10 mL) was added slowly to a suspension of

Mg (0.45 g, 18.5 mmol) and iodine (~10 mg) in THF (20 mL) at room temperature. The mixture was refluxed for 1 h and cooled to room temperature. A solution of phenylacetaldehyde (1.11 g, 9.26 mmol) in THF (20 mL) was added and the resulting mixture was stirred at room temperature for 3 h and quenched with saturated aqueous NH_4Cl . The resulting mixture was extracted with ether, washed with brine, dried (MgSO_4), and concentrated under vacuum. Chromatography of the residue (hexanes–ether = 25:1 $\rightarrow$ 10:1) gave 5-methyl-1-phenyl-5-hexen-2-ol (0.64 g, 36%) as a pale yellow oil. TLC: R_f = 0.32. ^1H NMR: δ 7.32–7.27 (m, 2 H), 7.23–7.19 (m, 3 H), 4.71–4.69 (m, 2 H), 3.83–3.77 (m, 1 H), 2.82 (dd, J = 4.0, 13.8 Hz, 1 H), 2.65 (dd, J = 8.4, 13.2 Hz, 1 H), 2.24–2.17 (m, 1 H), 2.14–2.06 (m, 1 H), 1.71 (s, 3 H), 1.68–1.59 (m, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 146.0, 138.9, 129.7, 128.9, 126.8, 110.5, 72.8, 44.4, 34.9, 34.4, 22.7. IR (neat, cm^{-1}): 3400, 3064, 2934, 1648, 1494, 1453, 1083, 1030, 866, 743, 699. Anal. Calcd. (found) for $\text{C}_{13}\text{H}_{18}\text{O}_2$: C, 82.06 (82.17); H, 9.53 (9.72).

6-Methyl-6-hepten-1,3-diol (Table 2, entry 3). A solution of methyl 6-methyl-3-oxo-6-heptenoate (1.70 g, 10 mmol) in THF (10 mL) was added slowly to a suspension of LiAlH_4 (0.70 g, 18.4 mmol) in THF (10 mL) at 0 °C. The resulting mixture was stirred at room temperature overnight and quenched by sequential addition of water and 10% aqueous NaOH solution. The resulting suspension was filtered through Celite and eluted with ether. The eluant was dried (MgSO_4) and concentrated under vacuum. Chromatography of the residue (SiO_2 ; hexanes–ether = 2:1 $\rightarrow$ ether) gave 6-methyl-6-hepten-1,3-diol (0.69 g, 48%) as a colorless oil. TLC (ether): R_f = 0.50. ^1H NMR: δ 4.73–4.72 (m, 2 H), 3.92–3.80 (m, 3 H), 2.60 (br s, 1 H), 2.55 (br s, 1 H), 2.20–2.04 (m, 2 H), 1.76–1.57 (m, 7 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 146.1, 110.6, 72.5, 62.2, 38.6, 35.8, 34.3, 22.7. IR (neat, cm^{-1}): 3348, 2934, 1650 ($\nu_{\text{C}=\text{C}}$), 1445, 1373, 1095, 1056, 881, 667. Anal. Calcd. (found) for $\text{C}_8\text{H}_{16}\text{O}_2$: C, 66.63 (66.43); H, 11.18 (11.43).

1-Benzyloxy-7-methyl-7-octen-4-ol (Table 2, entry 4). DIBAL-H (10.8 mL, 60 mmol) was added slowly to a solution of ethyl 4-methyl-4-pentenoate (4.80 mL, 30 mmol) in CH₂Cl₂ (120 mL) at -78 °C. The resulting mixture was stirred for 2.5 h and quenched by sequential addition of methanol (10 mL) and water (20 mL). The resulting biphasic mixture was warmed to room temperature and poured into aqueous HCl (1 N, 150 mL). The layers were separated and aqueous layer was extracted with CH₂Cl₂. The combined organic extracts were washed with brine, dried (MgSO₄), filtered through a pad of silica gel, and concentrated under vacuum to give 4-methyl-4-pentenal (2.81 g, 95%) as a colorless oil.

A solution of benzyl 3-bromopropyl ether (3.0 g, 13.1 mmol) in THF (15 mL) was added drop wise to a vigorously stirred suspension of Mg powder (0.33 g, 13.8 mmol) and iodine (~10 mg) in THF (5 mL) at room temperature and the resulting mixture was stirred for 30 min. 4-Methyl-4-pentenal (0.90 g, 9.2 mmol) was added drop wise to the resulting mixture and the resulting mixture was stirred for 3 h at room temperature, quenched with saturated aqueous NH₄Cl, and extracted with ether. The combined ether extracts were washed with brine, dried (MgSO₄), and concentrated under vacuum. Chromatography of the residue (SiO₂; hexanes-ether = 5:1 → 2:1) gave 1-benzyloxy-7-methyl-7-octen-4-ol (1.50 g, 66%) as a colorless oil.

For 4-methyl-4-pentenal:⁴ ¹H NMR: δ 9.76 (t, *J* = 2.0 Hz, 1 H), 4.76-4.74 (m, 1 H), 4.68-4.66 (m, 1 H), 2.58-2.54 (m, 2 H), 2.33 (br t, *J* = 7.6 Hz, 2 H), 1.74-1.73 (m, 3 H). ¹³C{¹H} NMR: δ 202.5, 144.0, 111.0, 42.1, 30.1, 22.9.

For 1-benzyloxy-7-methyl-7-octen-4-ol: TLC (hexanes-ether = 2:1): *R_f* = 0.18. ¹H NMR: δ 7.38-7.27 (m, 5 H), 4.73-4.69 (m, 2 H), 4.52 (s, 2 H), 3.65-3.57 (m, 1 H), 3.52 (t, *J* = 6.0 Hz, 2 H), 2.44 (d, *J* = 4.0 Hz, 1 H), 2.21-2.14 (m, 1 H), 2.11-2.03 (m, 1 H), 1.90-1.44 (m, 9 H, including a singlet at δ 1.74). ¹³C{¹H} NMR: δ 146.2, 138.5, 128.7, 128.0, 127.9, 110.2, 73.3, 71.6, 70.8, 35.6, 35.0, 34.4, 26.5, 22.8. IR (neat, cm⁻¹): 3416, 3070, 3032, 2930, 2856, 2798, 1650 (ν_{C=C}), 1494, 1450, 1358, 1090, 1022, 881, 735, 691. Anal. Calcd. (found) for C₁₆H₂₄O₂: C, 77.38 (77.23); H, 9.74 (9.87).

6-Methyl-1-(*N*-phthalimido)-6-hepten-3-ol (Table 2, entry 5). 4-Bromo-2-methyl-1-butene (1.0 g, 6.7 mmol) was added drop wise to a well-stirred suspension of Mg powder (0.18 g, 7.5 mmol) and iodine (~10 mg) in THF (5 mL) at room temperature and the resulting mixture was stirred for 30 min and cooled to $-78\text{ }^{\circ}\text{C}$. A solution of 3-(*N*-phthalimido)propionaldehyde (1.0 g, 4.9 mmol) in THF (10 mL) was added rapidly to the reaction mixture, which was stirred for 1 h, quenched with saturated aqueous NH_4Cl , warmed to room temperature, and extracted with ether. The combined ether extracts were washed with brine, dried (MgSO_4), and concentrated under vacuum. Chromatography of the residue (SiO_2 ; hexanes–ethyl acetate = 5:1) gave 6-methyl-1-(*N*-phthalimido)-6-hepten-3-ol (283 mg, 21%) as a colorless oil.

For 3-(*N*-phthalimido)propionaldehyde:⁵ ^1H NMR: δ 9.82 (t, $J = 1.6\text{ Hz}$, 1 H), 7.86–7.83 (m, 2 H), 7.74–7.71 (m, 2 H), 4.04 (t, $J = 6.8\text{ Hz}$, 2 H), 2.88 (dt, $J = 1.2, 7.2\text{ Hz}$, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 199.7, 168.4, 134.5, 132.3, 123.7, 42.7, 32.0.

For 6-methyl-1-(*N*-phthalimido)-6-hepten-3-ol: TLC (hexanes–ethyl acetate = 2:1): $R_f = 0.31$. ^1H NMR (Figure S1): δ 7.86–7.82 (m, 2 H), 7.74–7.70 (m, 2 H), 4.65 (m, 2 H), 3.92–3.82 (m, 2 H), 3.56–3.49 (m, 1 H), 2.79 (d, $J = 4.8\text{ Hz}$, 1 H), 2.21–2.14 (m, 1 H), 2.06–1.98 (m, 1 H), 1.87–1.78 (m, 1 H), 1.74–1.51 (m, 6 H, including a singlet at δ 1.69). $^{13}\text{C}\{^1\text{H}\}$ NMR (Figure S2): δ 169.2, 146.0, 134.4, 132.4, 123.7, 110.3, 68.6, 36.6, 35.4, 35.0, 34.4, 22.8. IR (neat, cm^{-1}): 3470, 3075, 2934, 2866, 1771, 1703, 1397, 1368, 1124, 1090, 959, 891, 716. HRMS Calcd. (found) for $\text{C}_{16}\text{H}_{20}\text{NO}_3$ (MH^+): 274.1444 (274.1437).

2,2-Dimethyl-propionic acid 2-allyl-2-hydroxymethyl-pent-4-enyl ester (Table 2, entry 6). Triethylamine (1.20 mL, 8.54 mmol) and pivaloyl chloride (0.77 mL, 6.26 mmol) were added to a solution of 2,2-diallyl-propane-1,3-diol (0.89 g, 5.69 mmol) in CH_2Cl_2 (30 mL). The resulting mixture was stirred at room temperature overnight and quenched with brine. The layers were separated and the organic layer was dried (MgSO_4) and concentrated under vacuum. Column chromatography of the residue (SiO_2 ; hexanes–ether = 10:1) gave 2,2-dimethyl-propionic acid 2-allyl-2-hydroxymethyl-pent-4-

enyl ester (0.86 g, 63%) as a colorless oil. TLC: R_f = 0.26. ^1H NMR: δ 5.86-5.76 (m, 2 H), 5.11-5.07 (m, 4 H), 3.95 (s, 2 H), 3.34 (s, 2 H), 2.43 (br s, 1 H), 2.10-1.98 (m, 4 H), 1.21 (s, 9 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 179.4, 133.5, 118.9, 66.2, 65.1, 42.6, 39.3, 36.0, 27.6. IR (neat, cm^{-1}): 3505, 3075, 2975, 2932, 1729, 1712, 1480, 1286, 1166, 1035, 915. Anal. Calcd. (found) for $\text{C}_{14}\text{H}_{24}\text{O}_3$: C, 69.96 (69.87); H, 10.07 (10.29).

Acetic acid 2-hydroxymethyl-4-methyl-2-(2-methylallyl)-4-pentenyl ester (Table 2, entry 7). A solution of acetyl chloride (0.44 mL, 6.1 mmol) in CH_2Cl_2 (10 mL) was added slowly to a solution of 2,2-bis-(2-methyl-2-propenyl)-propane-1,3-diol (1.02 g, 5.5 mmol) and triethylamine (1.17 mL, 8.3 mmol) in CH_2Cl_2 (20 mL) at 0 °C over 2 h. The reaction mixture was stirred at room temperature overnight, quenched with water, and extracted with CH_2Cl_2 (3×40 mL). The combined organic extracts were washed with brine, dried (MgSO_4) and concentrated under vacuum. Chromatography of the residue (SiO_2 : hexanes-ether = 5:1 $\rightarrow$ 2:1) gave acetic acid 2-hydroxymethyl-4-methyl-2-(2-methylallyl)-4-pentenyl ester (0.69 g, 55%) as a colorless oil. TLC (hexanes-ether = 1:1): R_f = 0.34. ^1H NMR: δ 4.91-4.90 (m, 2 H), 4.76-4.75 (m, 2 H), 4.00 (s, 2 H), 3.50 (d, J = 6.4 Hz, 2 H), 2.15, 2.13 (AB q, J = 13.2 Hz, 4 H), 2.07 (s, 3 H), 2.04 (t, J = 6.4 Hz, 1 H), 1.79 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 171.6, 142.7, 115.8, 67.2, 65.8, 43.0, 41.1, 25.6, 21.2. IR (neat, cm^{-1}): 3494, 3080, 2944, 1732, 1640, 1463, 1377, 1241, 1032, 978, 896. Anal. Calcd. (found) for $\text{C}_{13}\text{H}_{22}\text{O}_3$: C, 68.99 (68.84); H, 9.80 (10.03).

2-(*tert*-Butyldimethylsiloxymethyl)-4-methyl-2-(2-methylallyl)-4-penten-1-ol (Table 2, entry 8). *t*-Butyldimethylchlorosilane (0.69 mL, 4.61 mmol) was added slowly to a solution of 2,2-bis-(2-methyl-2-propenyl)-propane-1,3-diol (0.85 g, 4.61 mmol) and imidazole (0.63 g, 9.22 mmol) in DMF (15 mL) at room temperature. The resulting mixture was stirred overnight, quenched with brine, and extracted with ether (50 mL). The combined organic extracts were dried (MgSO_4) and concentrated under vacuum. The resulting residue was chromatographed (hexanes-ether = 25:1) to give 2-(*tert*-

butyldimethylsiloxymethyl)-4-methyl-2-(2-methylallyl)-4-penten-1-ol (0.78 g, 57 %) as a colorless oil. TLC: R_f = 0.54. ^1H NMR: δ 4.89 (m, 2 H), 4.75 (m, 2 H), 3.60 (m, 4 H), 2.65 (t, J = 6.0 Hz, 1 H), 2.17, 2.10 (ABq, J = 13.6 Hz, 4 H), 1.80 (s, 6 H), 0.91 (s, 9 H), 0.07 (s, 6 H). ^{13}C $\{^1\text{H}\}$ NMR: δ 143.3, 115.3, 69.3, 68.9, 43.5, 41.0, 26.2, 25.7, 18.5, -5.3. IR (neat, cm^{-1}): 3447, 2952, 2856, 1638, 1255, 1089, 892, 836. Anal. Calcd. (found) for $\text{C}_{17}\text{H}_{34}\text{O}_2\text{Si}$: C, 68.39 (68.39); H, 11.48 (11.38).

2-(*tert*-Butyldiphenylsiloxymethyl)-4-methyl-2-(2-methylallyl)-4-penten-1-ol (Table 2, entry 9). 2-(*tert*-Butyldiphenylsiloxymethyl)-4-methyl-2-(2-methylallyl)-4-penten-1-ol was isolated in 72% yield as a colorless oil employing a procedure analogous to that used to synthesize 2-(*tert*-butyldimethylsiloxymethyl)-4-methyl-2-(2-methylallyl)-4-penten-1-ol. TLC: R_f = 0.53. ^1H NMR: δ 7.68-7.66 (m, 4 H), 7.47-7.38 (m, 6 H), 4.85 (s, 2 H), 4.71 (s, 2 H), 3.64 (s, 2 H), 3.63 (s, 2 H), 2.34 (br s, 1 H), 2.20, 2.14 (ABq, J = 13.6 Hz, 4 H), 1.74 (s, 6 H), 1.11 (s, 9 H). ^{13}C $\{^1\text{H}\}$ NMR: δ 143.2, 136.1, 133.3, 130.2, 128.1, 115.4, 69.7, 68.2, 44.0, 40.8, 27.4, 25.7, 19.6. IR (neat, cm^{-1}): 3466, 3071, 2931, 2857, 1426, 1112, 1083, 894, 822, 701. Anal. Calcd. (found) for $\text{C}_{27}\text{H}_{38}\text{O}_2\text{Si}$: C, 76.72 (76.44); H, 9.06 (9.31).

5-Methyl-2,2-diphenyl-4-hexen-1-ol (Table 2, entry 10). Methyl 5-methyl-2,2-diphenyl-4-hexenoate was isolated in 92% yield as a pale yellow oil from reaction of methyl diphenylacetate and 1-bromo-3-methyl-2-butene employing a procedure analogous to that used to synthesize methyl 2,2-diphenyl-4-pentenoate. 5-Methyl-2,2-diphenyl-4-hexen-1-ol was isolated in 62% yield as a white solid from methyl 5-methyl-2,2-diphenyl-4-hexenoate employing a procedure analogous to that used to synthesize **2**.

For methyl 5-methyl-2,2-diphenyl-4-hexenoate:² ^1H NMR: δ 7.29-7.19 (m, 10 H), 5.14-4.98 (m, 1 H), 3.67 (s, 3 H), 3.06 (d, J = 6.8 Hz, 2 H), 1.55 (s, 3 H), 1.24 (s, 3 H). ^{13}C $\{^1\text{H}\}$ NMR: δ 175.2, 143.0, 135.2, 129.4, 128.0, 127.0, 119.8, 61.0, 52.7, 37.2, 26.2, 17.8.

For 5-methyl-2,2-diphenyl-4-hexen-1-ol: mp 50-51 °C. TLC (hexanes–ether = 5:1): R_f = 0.30. ^1H NMR: δ 7.30-7.16 (m, 10 H), 4.85-4.81 (m, 1 H), 4.10 (d, J = 6.4 Hz, 2 H), 2.87 (d, J = 7.2 Hz, 2 H), 1.58 (s, 3 H), 1.53 (s, 3 H), 1.20 (t, J = 6.0 Hz, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 145.9, 134.9, 128.6, 128.4, 126.6, 120.1, 68.6, 52.6, 35.3, 26.3, 18.2. IR (neat, cm^{-1}): 3553, 3440, 3056, 3027, 2973, 2915, 2886, 1596, 1494, 1441, 1373, 1061, 1031, 1017, 756, 696, 634. Anal. Calcd. (found) for $\text{C}_{19}\text{H}_{22}\text{O}$: C, 85.67 (85.92); H, 8.32 (8.47).

(Z)-2,2-Diphenyl-4-hepten-1-ol (Table 2, entry 11). (Z)-Methyl 2,2-diphenyl-4-heptenoate was isolated in 23% yield as a yellow oil from reaction of methyl diphenylacetate and (Z)-1-bromo-2-pentene employing a procedure analogous to that used to synthesize methyl 2,2-diphenyl-4-pentenoate. (Z)-2,2-Diphenyl-4-hepten-1-ol was isolated in 79% yield as a colorless oil from (Z)-methyl 2,2-diphenyl-4-heptenoate employing a procedure analogous to that used to synthesize **2**.

For methyl (Z)-2,2-diphenyl-4-heptenoate: TLC: R_f = 0.76. ^1H NMR: δ 7.31-7.19 (m, 10 H), 5.34-5.27 (m, 1 H), 5.23-5.15 (m, 1 H), 3.68 (s, 3 H), 3.14 (br d, J = 6.8 Hz, 2 H), 1.83-1.76 (m, 2 H), 0.76 (t, J = 7.6 Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 175.1, 142.9, 134.8, 129.3, 128.1, 127.1, 124.3, 60.6, 52.7, 36.3, 20.9, 14.1. IR (neat, cm^{-1}): 3058, 2960, 1731, 1495, 1446, 1222. Anal. Calcd. (found) for $\text{C}_{20}\text{H}_{22}\text{O}_2$: C, 81.60 (81.50); H, 7.53 (7.44).

For (Z)-2,2-diphenyl-4-hepten-1-ol: TLC: R_f = 0.57. ^1H NMR: δ 7.36-7.14 (m, 10 H), 5.45-5.34 (m, 1 H), 5.08-4.99 (m, 1 H), 4.11 (s, 2 H), 2.94 (d, J = 7.2 Hz, 2 H), 2.03-1.86 (m, 2 H), 1.22 (br s, 1 H), 0.88 (t, J = 7.2 Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 145.7, 134.9, 128.6, 128.5, 126.6, 124.5, 68.4, 52.3, 34.3, 21.0, 14.4. IR (neat, cm^{-1}): 3426, 3020, 2962, 2873, 1494, 1444, 1063, 1038, 757, 699. Anal. Calcd. (found) for $\text{C}_{19}\text{H}_{22}\text{O}$: C, 85.67 (85.99); H, 8.32 (8.44).

(*E*)-2,2-Diphenyl-4-hexen-1-ol (Table 2, entry 12). Methyl 2,2-diphenyl-4-hexenoate was isolated in 85% yield as a 6:1 mixture of *E*:*Z* isomers as a colorless oil from reaction of methyl diphenylacetate and crotyl chloride employing a procedure analogous to that used to synthesize methyl 2,2-diphenyl-4-pentenoate. 2,2-Diphenyl-4-hexen-1-ol was isolated in 89% yield as a white solid from methyl 2,2-diphenyl-4-hexenoate employing a procedure analogous to that used to synthesize **2**.

For methyl (*E*)-2,2-diphenyl-4-hexenoate:² *E*:*Z* = 6:1. ¹H NMR (*E* isomer): δ 7.30-7.19 (m, 10 H), 5.31-5.16 (m, 2 H), 3.67 (s, 3 H), 3.07 (br d, *J* = 6.4 Hz, 2 H), 1.50 (br d, *J* = 6.0 Hz, 3 H). ¹³C{¹H} NMR (*E* isomer): δ 175.0, 143.0, 129.3, 128.9, 128.1, 127.0, 126.6, 61.0, 52.6, 41.9, 18.4.

For (*E*)-2,2-diphenyl-4-hexen-1-ol: mp 54-55 °C. TLC (hexanes–ether = 5:1): *R_f* = 0.19. *E*:*Z* = 6:1. ¹H NMR (*E* isomer): δ 7.30-7.14 (m, 10 H), 5.53-5.43 (m, 1 H), 5.11-5.00 (m, 1 H), 4.11 (d, *J* = 6.8 Hz, 2 H), 2.87 (td, *J* = 1.2, 6.8 Hz, 2 H), 1.54 (qd, *J* = 1.2, 6.4 Hz, 3 H), 1.18 (t, *J* = 6.4 Hz, 1 H). ¹³C{¹H} NMR (*E* isomer): δ 145.8, 129.1, 128.54, 128.49, 127.0, 126.6, 68.4, 52.1, 40.1, 18.4. IR (neat, cm⁻¹): 3557, 3435, 3061, 3022, 2934, 2915, 2886, 2856, 1596, 1494, 1445, 1377, 1051, 1032, 969, 750, 698. Anal. Calcd. (found) for C₁₈H₂₀O: C, 85.67 (85.63); H, 7.99 (8.14).

2-(2-Cyclohexenyl)-2,2-diphenylethanol (Table 2, entry 13). Methyl (2-cyclohexenyl)diphenylacetate was isolated in 96% yield as a white solid from reaction of methyl diphenylacetate and 3-chloro-1-cyclohexene employing a procedure analogous to that used to synthesize methyl 2,2-diphenyl-4-pentenoate. 2-(2-Cyclohexenyl)-2,2-diphenylethanol was isolated in 57% yield as a white solid from methyl (2-cyclohexenyl)diphenylacetate employing a procedure analogous to that used to synthesize **2**.

For methyl (2-cyclohexenyl)diphenylacetate: mp 79-80.5 °C. TLC (hexanes–ether = 5:1): *R_f* = 0.60. ¹H NMR (Figure S3): δ 7.30-7.20 (m, 10 H), 5.65-

5.57 (m, 2 H), 3.82-3.76 (m, 1 H), 3.61 (s, 3 H), 1.90-1.81 (m, 2 H), 1.72-1.62 (m, 1 H), 1.60-1.49 (m, 1 H), 1.42-1.38 (m, 1 H), 1.05-0.96 (m, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (Figure S4): δ 174.8, 141.3, 140.5, 130.5, 130.4, 129.7, 128.6, 127.9, 127.6, 127.1, 127.0, 64.9, 52.6, 40.4, 26.0, 25.4, 22.3. IR (neat, cm^{-1}): 3061, 3032, 2944, 2836, 1728, 1601, 1494, 1445, 1431, 1221, 1173, 1008, 721, 696. HRMS (EI) Calcd. (found) for $\text{C}_{21}\text{H}_{22}\text{O}_2$ (M^+): 306.1620 (306.1609).

For 2-(2-cyclohexenyl)-2,2-diphenylethanol: mp 111-112 °C. TLC (hexanes–ether = 5:1): R_f = 0.24. ^1H NMR (500 MHz): δ 7.33-7.23 (m, 10 H), 5.83 (br d, J = 10.0 Hz, 1 H), 5.69 (dtd, J = 2.0, 4.5, 10.0 Hz, 1 H), 4.22 (dd, J = 11.5 Hz, 2 H), 3.34 (m, 1 H), 1.93-1.72 (m, 3 H), 1.66- 1.53 (m, 2 H), 1.31 (s, 1 H), 1.12-1.03 (m, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz): δ 144.1, 142.4, 129.41, 129.38, 129.1, 129.0, 128.1, 127.5, 126.4, 126.2, 68.2, 56.1, 39.2, 25.00, 24.99, 22.4. IR (neat, cm^{-1}): 3552, 3426, 3022, 2930, 2881, 2837, 1596, 1494, 1445, 1139, 1042, 759, 696, 662, 638. Anal. Calcd. (found) for $\text{C}_{20}\text{H}_{22}\text{O}$: C, 86.29 (86.34); H, 7.97 (8.07).

3-(1-Cyclohexenyl)-2,2-diphenylpropanol (Table 2, entry 14). Methyl 3-(1-cyclohexenyl)-2,2-diphenylpropionate was isolated in 76% yield as a white solid from reaction of methyl diphenylacetate and 1-bromomethylcyclohexene employing a procedure analogous to that used to synthesize methyl 2,2-diphenyl-4-pentenoate. 3-(1-Cyclohexenyl)-2,2-diphenylpropanol was isolated in 87% yield as a white solid from methyl 3-(1-cyclohexenyl)-2,2-diphenylpropionate employing a procedure analogous to that used to synthesize **2**.

For methyl 3-(1-cyclohexenyl)-2,2-diphenylpropionate: mp 64-65 °C. TLC: R_f = 0.61. ^1H NMR: δ 7.29-7.17 (m, 10 H), 5.13 (br s, 1 H), 3.65 (s, 3 H), 3.05 (s, 2 H), 1.79 (br s, 2 H), 1.42-1.32 (m, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 174.9, 143.7, 134.2, 129.3, 127.9, 126.9, 60.9, 52.4, 46.7, 30.3, 25.8, 23.4, 22.3. IR (neat, cm^{-1}): 3056, 2925, 1731, 1495,

1444, 1201, 1021, 727. Anal. Calcd. (found) for $C_{22}H_{24}O_2$: C, 82.46 (82.56); H, 7.55 (7.66).

For 3-(1-cyclohexenyl)-2,2-diphenylpropanol: mp 69-70 °C. TLC: R_f = 0.32. 1H NMR: δ 7.27-7.23 (m, 4 H), 7.20-7.14 (m, 6 H), 5.38 (br s, 1 H), 4.19 (s, 2 H), 2.81 (m, 2 H), 1.93-1.90 (m, 2 H), 1.40-1.34 (m, 2 H), 1.31-1.25 (m, 2 H), 1.14 (br s, 1 H), 1.11-1.02 (m, 2 H). $^{13}C\{^1H\}$ NMR: δ 146.4, 134.9, 128.7, 128.4, 127.0, 126.6, 67.7, 52.1, 44.7, 30.6, 25.9, 23.5, 22.4. IR (neat, cm^{-1}): 3436, 2922, 2853, 1492, 1442, 1013, 754. Anal. Calcd. (found) for $C_{21}H_{24}O_2$: C, 86.26 (86.37); H, 8.27 (8.49).

2,2-Bis(2-methylallyl)propane-1,3-diol (Table 2, entry 15). 2,2-Bis(2-methylallyl)propane-1,3-diol was isolated in 91% yield as a colorless oil from dimethyl bis(2-methylallyl)malonate employing a procedure analogous to that used to synthesize 2,2-diphenyl-4-penten-1-ol (**2**).

For 2,2-bis(2-methylallyl)propane-1,3-diol: TLC: R_f = 0.05. 1H NMR: δ 4.91 (br s, 2 H), 4.78 (br s, 2 H), 3.65 (s, 4 H), 2.54 (br s, 2 H), 2.14 (s, 4 H), 1.82 (s, 6 H). $^{13}C\{^1H\}$ NMR: δ 143.5, 115.5, 68.5, 43.8, 41.5, 25.7. IR (neat, cm^{-1}): 3422, 3073, 2968, 2934, 1640, 1450, 1368, 1039, 891. Anal. Calcd. (found) for $C_{11}H_{20}O_2$: C, 71.70 (71.49); H, 10.94 (11.07).

2,2-Diphenyl-5-hexen-1-ol (Table 2, entry 17). Methyl 2,2-diphenyl-5-hexenoate was isolated in 59% yield as a viscous colorless oil from reaction of methyl diphenylacetate and 4-bromo-1-butene employing a procedure analogous to that used to synthesize methyl 2,2-diphenyl-4-pentenoate. 2,2-diphenyl-5-hexen-1-ol was isolated in 84% yield as a viscous colorless oil from methyl 2,2-diphenyl-5-hexenoate employing a procedure analogous to that used to synthesize **2**.

For methyl 2,2-diphenyl-5-hexenoate: TLC (hexanes-ether = 5:1): R_f = 0.62. 1H NMR (Figure S5): δ 7.30-7.21 (m, 10 H), 5.75 (tdd, J = 6.4, 10.4, 16.8 Hz, 1 H), 4.97-4.88 (m, 2 H), 3.66 (s, 3 H), 2.47-2.42 (m, 2 H), 1.82-1.76 (m, 2 H). $^{13}C\{^1H\}$ NMR

(Figure S6): δ 175.0, 143.1, 138.7, 129.2, 128.2, 127.1, 114.9, 60.5, 52.7, 37.7, 30.0. IR (neat, cm^{-1}): 3061, 3027, 2954, 2861, 1728, 1640, 1596, 1494, 1441, 1222, 1115, 1061, 910, 755, 725, 696. HRMS (EI) Calcd. (found) for $\text{C}_{19}\text{H}_{20}\text{O}_2$ (M^+): 280.1463 (280.1470).

For 2,2-diphenyl-5-hexen-1-ol: TLC (hexanes–ether = 5:1): R_f = 0.24. ^1H NMR: δ 7.34-7.20 (m, 10 H), 5.80 (tdd, J = 6.4, 10.4, 16.8 Hz, 1 H), 5.01-4.92 (m, 2 H), 4.17 (s, 2 H), 2.29-2.25 (m, 2 H), 1.85-1.80 (m, 2 H), 1.22 (s, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 145.7, 139.1, 128.55, 128.54, 126.7, 114.7, 68.4, 52.2, 35.8, 29.0. IR (neat, cm^{-1}): 3557, 3431, 3061, 3027, 2934, 2886, 1640, 1596, 1494, 1441, 1037, 910, 750, 696, 626. Anal. Calcd. (found) for $\text{C}_{20}\text{H}_{22}\text{O}$: C, 85.67 (85.53); H, 7.99 (7.73).

2,2-Diphenyl-5-methyl-5-hexen-1-ol (Table 2, entry 18). Methyl 2,2-diphenyl-5-methyl-5-hexenoate was isolated in 17% yield as a yellow oil from reaction of methyl diphenylacetate and toluene-4-sulfonic acid 3-methyl-but-3-enyl ester employing a procedure analogous to that used to synthesize methyl 2,2-diphenyl-4-pentenoate. 2,2-Diphenyl-5-methyl-5-hexen-1-ol was isolated in 87% yield as a colorless oil from methyl 2,2-diphenyl-5-hexenoate employing a procedure analogous to that used to synthesize **2**.

For methyl 2,2-diphenyl-5-methyl-5-hexenoate: TLC: R_f = 0.56. ^1H NMR (Figure S7): δ 7.31-7.21 (m, 10 H), 4.67 (br s, 1 H), 4.66 (br s, 1 H), 3.67 (s, 3 H), 2.53-2.48 (m, 2 H), 1.75 (m, 2 H), 1.67 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (Figure S8): δ 175.1, 146.1, 143.1, 129.2, 128.2, 127.1, 110.1, 60.5, 52.6, 36.8, 33.7, 23.0. IR (neat, cm^{-1}): 3068, 2950, 1731, 1495, 1445, 1218, 887. HRMS Calcd. (found) for $\text{C}_{20}\text{H}_{23}\text{O}_2$ (MH^+): 295.1698 (295.1696).

For 2,2-diphenyl-5-methyl-5-hexen-1-ol. TLC: R_f = 0.57. ^1H NMR (Figure S9): δ 7.31-7.27 (m, 4 H), 7.23-7.17 (m, 6 H), 4.67 (br s, 1 H), 4.66 (br s, 1 H), 4.14 (s, 2 H), 2.32-2.27 (m, 2 H), 1.76-1.72 (m, 2 H), 1.66 (s, 3 H), 1.23 (s, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (Figure S10): δ 146.4, 145.8, 128.6, 126.7, 109.9, 68.5, 52.2, 34.8, 32.7, 23.0. IR (neat,

cm⁻¹): 3431, 3056, 3024, 2933, 1646, 1597, 1493, 1443, 1040, 885, 755. HRMS Calcd. (found) for C₉H₂₃O (MH⁺): 267.1749 (267.1757).

1-Phenyl-6-hepten-2-ol (Table 2, entry 19). 1-Phenyl-6-hepten-2-ol was isolated in 22% yield as a colorless oil from reaction of phenylacetaldehyde and 5-bromo-1-pentene employing a procedure similar to that used to synthesize 5-methyl-1-phenyl-5-hexen-2-ol. TLC: R_f = 0.27. ¹H NMR: δ 7.34-7.27 (m, 2 H), 7.23-7.18 (m, 3 H), 5.85-5.74 (m, 1 H), 4.97-4.92 (m, 2 H), 3.82-3.76 (m, 1 H), 2.81 (dd, *J* = 4.0, 13.6 Hz, 1 H), 2.62 (dd, *J* = 8.4, 13.4 Hz, 1 H), 2.10-2.05 (m, 2 H), 1.61-1.41 (m, 5 H). ¹³C{¹H} NMR: δ 139.0, 138.9, 129.7, 128.9, 126.8, 115.0, 72.9, 44.4, 36.4, 34.6, 25.4. IR (neat, cm⁻¹): 3390, 3027, 2933, 2859, 1640, 1495, 1454, 1082, 1031, 996, 910, 745. Anal. Calcd. (found) for C₁₃H₁₈O: C, 82.06 (81.85); H, 9.53 (9.36).

Cyclic Ethers

2-Methyl-4,4-diphenyltetrahydrofuran (3). A solution of [PtCl₂(H₂C=CH₂)]₂ (**1**) (6 mg, 0.010 mmol), P(4-C₆H₄CF₃)₃ (9 mg, 0.020 mmol) and 2,2-diphenyl-4-penten-1-ol (**2**) (240 mg, 1.0 mmol) in 1,1,2,2-tetrachloroethane (0.5 mL) was stirred at 70 °C for 24 h. Column chromatography of the reaction mixture (SiO₂; hexanes → hexanes-ether = 10:1) gave 2-methyl-4,4-diphenyltetrahydrofuran (**3**) (188 mg, 78%) as an off-white solid. mp 42-44 °C. TLC (hexanes-ether = 5:1): R_f = 0.45. ¹H NMR: δ 7.33-7.17 (m, 10 H), 4.60 (dd, *J* = 0.8, 8.4 Hz, 1 H), 4.23-4.14 (m, 2 H), 2.65 (ddd, *J* = 0.8, 6.0, 12.0 Hz, 1 H), 2.28 (dd, *J* = 9.6, 12.0 Hz, 1 H), 1.31 (d, *J* = 6.0 Hz, 3 H). ¹³C{¹H} NMR: δ 146.7, 146.6, 128.7, 128.6, 127.5, 126.7, 126.5, 77.2, 56.7, 46.9, 21.7. IR (neat, cm⁻¹): 3058, 3025, 2968, 2925, 2864, 1598, 1494, 1446, 1378, 1084, 1033, 756, 699. Anal. Calcd. (found) for C₁₇H₁₈O: C, 85.67 (85.58); H, 7.61 (7.53).

All remaining cyclic ethers synthesized employing a procedure analogous to that used for the synthesis of **3** unless noted otherwise.

2-Methyl-3-phenyltetrahydrofuran (Table 2, entry 1).⁶ ¹H NMR (*trans:cis* = 8:1): δ 7.33-7.15 (m, 5 H), [4.18-4.13 (m), 4.06-3.98 (m), 1:8, 2 H], 3.89-3.82 (m, 1 H), [3.21 (td, J = 6.0, 8.0 Hz), 2.79 (q, J = 8.8 Hz), 1:8, 1 H], 2.42-2.33 (m, 1 H), 2.21-2.06 (m, 1 H), [1.22 (d, J = 6.0 Hz), 0.84 (d, J = 6.4 Hz), 8:1, 3 H]. ¹³C{¹H} NMR (*trans*): δ [142.1, 141.8 (1:8)], [128.9, 128.6 (8:1)], [128.4, 127.9 (1:8)], [126.9, 126.6 (8:1)], [82.5, 78.5 (8:1)], [67.6, 67.2 (8:1)], [53.3, 48.6 (8:1)], [35.7, 33.0 (8:1)], [19.2, 17.1 (8:1)].

2-Benzyl-5,5-dimethyltetrahydrofuran (Table 2, entry 2). Pale yellow oil, 91%. TLC: R_f = 0.56. ¹H NMR: δ 7.29-7.16 (m, 5 H), 4.22-4.15 (m, 1 H), 2.99 (dd, J = 5.2, 13.4 Hz, 1 H), 2.68 (dd, J = 4.0, 13.4 Hz, 1 H), 1.95-1.83 (m, 1 H), 1.71-1.61 (m, 3 H), 1.25 (s, 3 H), 1.23 (s, 3 H). ¹³C{¹H} NMR: δ 139.0, 129.7, 128.5, 126.4, 81.0, 79.6, 43.0, 38.6, 31.5, 29.5, 28.5. IR (neat, cm^{-1}): 3026, 2967, 2930, 2867, 1496, 1453, 1364, 1141, 1047, 888, 746, 699. Anal. Calcd. (found) for C₁₃H₁₈O₂: C, 82.06 (81.97); H, 9.53 (9.49).

2-(5,5-Dimethyltetrahydrofuran-2-yl)ethanol (Table 2, entry 3).⁷ ¹H NMR: δ 4.18-4.11 (m, 1 H), 3.78-3.74 (m, 2 H), 3.15 (br s, 1 H), 2.08-2.00 (m, 1 H), 1.81-1.62 (m, 5 H), 1.24 (s, 3 H), 1.21 (s, 3 H). ¹³C{¹H} NMR: δ 81.8, 79.2, 62.0, 38.5, 38.2, 32.4, 29.6, 28.4.

5-(3-Benzyloxypropyl)-2,2-dimethyltetrahydrofuran (Table 2, entry 4). Colorless oil, 79%. TLC (hexanes-ether = 2:1): R_f = 0.53. ¹H NMR: δ 7.34-7.25 (m, 5 H), 4.50 (s, 2 H), 3.99-3.93 (m, 1 H), 3.54-3.44 (m, 2 H), 2.04-1.96 (m, 1 H), 1.78-1.50 (m, 7 H), 1.24 (s, 3 H), 1.22 (s, 3 H). ¹³C{¹H} NMR: δ 139.0, 128.6, 127.9, 127.8, 80.6, 78.6, 73.1, 70.8, 38.8, 33.3, 32.1, 29.6, 28.5, 26.6. IR (neat, cm^{-1}): 3061, 3032, 2968, 2934, 2861, 1450, 1372, 1363, 1095, 1027, 735, 691. Anal. Calcd. (found) for C₁₆H₂₄O₂: C, 77.38 (77.15); H, 9.74 (9.90).

2,2-Dimethyl-5-[2-(*N*-phthalimido)ethyl]tetrahydrofuran (Table 2, entry 5). Colorless oil, 73%. TLC (hexanes–EtOAc = 2:1): R_f = 0.52. ^1H NMR (Figure S11): δ 7.82 (m, 2 H), 7.62 (m, 2 H), 3.99 (quintet, J = 6.0 Hz, 1 H), 3.87–3.79 (m, 1 H), 3.72 (ddd, J = 5.4, 8.0, 13.6 Hz, 1 H), 2.11–2.03 (m, 1 H), 2.00–1.91 (m, 1 H), 1.84–1.75 (m, 1 H), 1.74–1.57 (m, 1 H), 1.16 (s, 3 H), 1.14 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (Figure S12): δ 168.8, 134.1, 132.7, 123.4, 81.0, 76.7, 38.6, 36.0, 35.4, 32.3, 29.5, 28.3. IR (neat, cm^{-1}): 3061, 2968, 2871, 1771, 1713, 1611, 1465, 1436, 1397, 1363, 1134, 1090, 1051, 886, 716. HRMS Calcd. (found) for $\text{C}_{16}\text{H}_{20}\text{NO}_3$ (MH^+): 274.1444 (274.1449).

2,2-Dimethylpropionic acid 3-allyl-5-methyltetrahydrofuran-3-ylmethyl ester (Table 2, entry 6). Colorless oil, 71%. TLC: R_f = 0.39. ^1H NMR (isomeric ratio = 1.7:1): δ 5.76–5.67 (m, 1 H), 5.06–5.01 (m, 2 H), 4.04–3.86 (m, 3 H), [3.75 (d, J = 9.2 Hz), 3.66 (d, J = 8.8 Hz) 1:1.7, 1 H], [3.55 (d, J = 9.2 Hz), 3.43 (d, J = 9.2 Hz), 1.7:1, 1 H], 2.30–2.16 (m, 2 H), [1.89 (dd, J = 6.4, 12.8 Hz), 1.86 (dd, J = 6.4, 12.8 Hz), 1:1.7, 1 H], [1.33 (dd, J = 9.2, 12.8 Hz) (the pattern corresponding to the second diastereomer is obscured by the large *tert*-butyl resonance at δ 1.18), 1 H], [1.23 (d, J = 6.0 Hz), 1.22 (d, J = 6.4 Hz), 1.7:1, 3 H], 1.18 (s, 9 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ [178.6, 178.5 (1.7:1)], [134.3, 134.2 (1.7:1)], 118.7, [75.6, 75.4 (1.7:1)], [74.9, 74.8 (1:1.7)], [68.2, 67.5 (1:1.7)], [47.4, 47.3 (1.7:1)], [42.5, 42.0 (1.7:1)], 41.1, [39.6, 39.2 (1.7:1)], 27.5, [21.4, 21.3 (1:1.7)]. IR (neat, cm^{-1}): 2972, 2933, 2871, 1731, 1480, 1397, 1283, 1158, 1035, 916. Anal. Calcd. (found) for $\text{C}_{14}\text{H}_{24}\text{O}_3$: C, 69.96 (69.78); H, 10.07 (10.23).

Acetic acid 5,5-dimethyl-3-(2-methylallyl)tetrahydrofuran-3-yl-methyl ester (Table 2, entry 7). Colorless oil, 92%. TLC (hexanes–ether = 1:1): R_f = 0.63. ^1H NMR: δ 4.83 (m, 1 H), 4.67 (m, 1 H), 3.96, 3.94 (ABq, J = 11.2 Hz, 2 H), 3.77 (d, J = 9.6 Hz, 1 H), 3.58 (d, J = 9.6 Hz, 1 H), 2.28 (d, J = 13.6 Hz, 1 H), 2.17 (d, J = 13.6 Hz, 1 H), 2.05 (s, 3 H), [1.72 (s), 1.68 (apparent q, J = 13.2 Hz), 5 H], 1.27 (s, 3 H), 1.25 (s, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 171.3, 142.4, 115.2, 81.0, 73.9, 67.6, 47.8, 47.7, 43.7, 29.6, 28.9, 24.5, 21.2. IR

(neat, cm^{-1}): 3075, 2973, 2939, 2871, 1743 ($\nu_{\text{C=O}}$), 1644 ($\nu_{\text{C=C}}$), 1453, 1381, 1365, 1238, 1038, 894, 776. Anal. Calcd. (found) for $\text{C}_{13}\text{H}_{22}\text{O}_3$: C, 68.99 (68.72); H, 9.80 (9.93).

***tert*-Butyl-[5,5-dimethyl-3-(2-methylallyl)-tetrahydrofuran-3-ylmethoxy]-dimethylsilane (Table 2, entry 8).** Colorless oil, 75%. TLC: $R_f = 0.73$. ^1H NMR: δ 4.83-4.81 (m, 1 H), 4.70, (m, 1 H), 3.73 (d, $J = 8.8$ Hz, 1 H), 3.52 (d, $J = 9.2$ Hz, 1 H), 3.47 (d, $J = 9.2$ Hz, 1 H), 3.40 (d, $J = 9.2$ Hz, 1 H), 2.24, 2.16 (ABq, $J = 13.2$ Hz, 2 H), 1.73-1.72 (m, 3 H), 1.63, 1.59 (ABq, $J = 13.2$ Hz, 2 H), 1.25 (s, 3 H), 1.24 (s, 3 H), 0.89 (s, 9 H), 0.031 (s, 3 H), 0.026 (s, 3 H). ^{13}C $\{^1\text{H}\}$ NMR: δ 143.4, 114.5, 80.9, 73.9, 65.9, 50.2, 46.8, 43.0, 29.8, 29.1, 26.2, 24.8, 18.6, -5.20, -5.21. IR (neat, cm^{-1}): 2956, 2856, 1642, 1471, 1364, 1094, 850. Anal. Calcd. (found) for $\text{C}_{17}\text{H}_{34}\text{O}_2\text{Si}$: C, 68.39 (68.22); H, 11.48 (11.53).

***tert*-Butyl-[5,5-dimethyl-3-(2-methylallyl)-tetrahydrofuran-3-ylmethoxy]-diphenylsilane (Table 2, entry 9).** Colorless oil, 84%. TLC: $R_f = 0.65$. ^1H NMR (Figure S13): δ 7.68-7.64 (m, 4 H), 7.44-7.35 (m, 6 H), 4.83 (s, 1 H), 4.73 (s, 1 H), 3.82 (d, $J = 9.2$ Hz, 1 H), 3.59 (d, $J = 9.6$ Hz, 1 H), 3.57 (d, $J = 8.8$ Hz, 1 H), 3.47 (d, $J = 9.6$ Hz, 1 H), 2.36, 2.29 (ABq, $J = 13.6$ Hz, 2 H), 1.71 (s, 3 H), 1.61 (s, 2 H), 1.23 (s, 3 H), 1.08 (s, 12 H). ^{13}C $\{^1\text{H}\}$ NMR (Figure S14): δ 143.3, 136.13, 136.12, 134.0, 133.8, 129.97, 129.96, 128.0, 127.9, 114.7, 80.9, 73.7, 66.9, 50.5, 46.7, 43.2, 29.4, 29.1, 27.3, 24.9, 19.7. IR (neat, cm^{-1}): 3070, 2964, 2930, 2856, 1427, 1111, 1089, 824, 822, 739. HRMS Calcd. (found) for $\text{C}_{27}\text{H}_{39}\text{O}_2\text{Si}$ (MH^+): 423.2719 (423.2714).

2,2-Dimethyl-5,5-diphenyltetrahydropyran (Table 2, entry 10 and 18). Off-white solid, 98%. mp 85-86 $^{\circ}\text{C}$. TLC (hexanes-ether = 5:1): $R_f = 0.62$. ^1H NMR: δ 7.30-7.12 (m, 10 H), 4.03 (s, 2 H), 2.42-2.39 (m, 2 H), 1.39-1.36 (m, 2 H), 1.20 (s, 6 H). ^{13}C $\{^1\text{H}\}$ NMR: δ 146.8, 128.4, 128.2, 126.3, 71.5, 69.3, 46.2, 32.9, 31.1, 26.7. IR (neat, cm^{-1}): 3057, 3024, 2971, 2941, 2863, 1598, 1494, 1446, 1380, 1365, 1085, 765, 753, 699. Anal. Calcd. (found) for $\text{C}_{19}\text{H}_{22}\text{O}$: C, 85.67 (85.81); H, 8.32 (8.41).

4,4-Diphenyl-2-propyltetrahydrofuran (Table 2, entry 11). Pale-yellow oil, 47%. TLC: R_f = 0.67. ^1H NMR (Figure S15): δ 7.34-7.27 (m, 6 H), 7.25-7.18 (m, 4 H), 4.63 (dd, J = 1.2, 8.8 Hz, 1 H), 4.14 (d, J = 8.4 Hz, 1 H), 4.08-4.02 (m, 1 H), 2.64 (ddd, J = 1.2, 6.4, 12.4 Hz, 1 H), 2.30 (dd, J = 6.4, 12.0 Hz, 1 H), 1.72-1.62 (m, 1 H), 1.57-1.29 (m, 3 H), 0.94 (t, J = 7.2 Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (Figure S16): δ 146.8, 146.5, 128.7, 128.6, 127.5, 126.7, 126.5, 79.0, 77.0, 56.3, 45.3, 38.7, 19.8, 14.5. IR (neat, cm^{-1}): 3057, 2956, 2927, 2867, 1492, 1446, 1087, 1040, 756. HRMS Calcd. (found) for $\text{C}_{19}\text{H}_{22}\text{O}$ (M^+): 266.1671 (266.1671).

Cyclization of (*E*)-2,2-diphenyl-4-hexen-1-ol (Table 2, entry 12). A solution of **1** (12 mg, 0.020 mmol), $\text{P}(\text{4-C}_6\text{H}_4\text{CF}_3)_3$ (18 mg, 0.040 mmol) and (*E*)-2,2-diphenyl-4-hexen-1-ol (250 mg, 1.0 mmol) in 1,1,2,2-tetrachloroethane (0.5 mL) was stirred at 80 °C for 48 h. Column chromatography of the reaction mixture (SiO_2 ; hexanes→hexanes-ether = 10:1) gave a 3.6:1 mixture of 2-ethyl-4,4-diphenyltetrahydrofuran and 5,5-diphenyltetrahydropyran in 63% combined yield. Pure 5,5-diphenyltetrahydropyran was isolated from platinum-catalyzed cyclization of 2,2-diphenyl-5-hexen-1-ol (Table 2, entry 11, see below). The IR, TLC, and combustion analysis data described below were obtained on the 3.6:1 mixture of 2-ethyl-4,4-diphenyltetrahydrofuran and 5,5-diphenyltetrahydropyran. The NMR data refers to the resonances corresponding to 2-ethyl-4,4-diphenyltetrahydrofuran. TLC (hexanes-ether = 5:1): R_f = 0.55. ^1H NMR: δ 7.46-7.15 (m, 10 H), 4.63 (d, J = 8.8 Hz, 1 H), 4.14 (d, J = 8.8 Hz, 1 H), 4.01-3.94 (m, 1 H), 2.62 (dd, J = 6.0, 12.0 Hz, 1 H), 2.30 (dd, J = 9.6, 12.0 Hz, 1 H), 1.76-1.65 (m, 1 H), 1.62-1.52 (m, 1 H), 0.95 (t, J = 7.6 Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 146.7, 146.4, 128.7, 128.6, 127.5, 127.4, 126.7, 126.5, 80.5, 77.0, 56.3, 44.8, 29.2, 10.6. IR (neat, cm^{-1}): 3057, 3028, 2964, 2930, 2867, 1602, 1493, 1446, 1381, 1092, 1079, 1048, 772, 699. Anal. Calcd. (found) for $\text{C}_{20}\text{H}_{22}\text{O}$: C, 85.67 (85.47); H, 7.99 (7.90).

***cis*-3,3-Diphenyloctahydrobenzofuran (Table 2, entry 13).** White solid, 87%. mp 81-83 °C. TLC: R_f = 0.52. ^1H NMR (500 MHz, Figure S17): δ 7.46 (d, J = 3.6 Hz, 2 H), 7.30-7.25 (m, 4 H), 7.18-7.14 (m, 4 H), 4.79 (d, J = 8.5 Hz, 1 H), 4.67 (d, J = 8.5 Hz, 1 H), 4.21 (br dd, J = 3.0, 6.0 Hz, 1 H), 2.80 (ddd, J = 4.0, 6.0, 12.0 Hz, 1 H), 1.98 (br d, J = 13.0 Hz, 1 H), 1.74-1.65 (m, 2 H), 1.55-1.38 (m, 3 H), 1.20 (tq, J = 3.5, 12.0 Hz, 1 H), 0.96 (dq, J = 3.5, 13.0 Hz, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, Figure S18): δ 146.4, 143.5, 128.4, 128.2, 126.8, 126.0, 126.0, 125.9, 76.3, 74.5, 59.5, 44.4, 28.9, 25.7, 24.5, 20.1. IR (neat, cm^{-1}): 2929, 2876, 1490, 1450, 1055, 1031, 744, 702. Anal. Calcd. (found) for $\text{C}_{20}\text{H}_{22}\text{O}$: C, 86.29 (86.05); H, 7.97 (8.15).

Stereochemistry of *cis*-3,3-Diphenyloctahydrobenzofuran. The stereochemistry of *cis*-3,3-diphenyloctahydrobenzofuran was determined by NOE (Figures S19 and S20). In particular, irradiation of the H_5 resonance at δ 4.21 led to enhancement of the H_4 resonance at δ 2.80 (Figure S19) and irradiation of the H_4 resonance at δ 2.80 led to enhancement of the H_5 resonance at δ 4.21 (Figure S20).

3,3-Diphenyl-1-oxaspiro[4.5]decane (Table 2, entry 14). Colorless oil, 98%. TLC: R_f = 0.62. ^1H NMR: δ 7.32-7.26 (m, 8 H), 7.20-7.16 (m, 2 H), 4.45 (s, 2 H), 2.57 (s, 2 H), 1.70-1.60 (m, 2 H), 1.54-1.32 (m, 8 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 147.4, 128.6, 127.5, 126.3, 83.7, 75.2, 56.4, 50.0, 38.3, 25.7, 24.0. IR (neat, cm^{-1}): 3023, 2929, 2853, 1492, 1445, 1066, 749, 699. Anal. Calcd. (found) for $\text{C}_{21}\text{H}_{24}\text{O}$: C, 86.26 (86.12); H, 8.27 (8.22).

3,3,8,8-Tetramethyl-2,7-dioxaspiro[4.4]nonane (Table 2, entry 15). Yellow oil, 69%. TLC: R_f = 0.24. ^1H NMR (C_6D_6): δ 3.73 (d, J = 8.4 Hz, 2 H), 3.46 (d, J = 8.4 Hz, 2 H), 1.45 (d, J = 12.4 Hz, 2 H), 1.41 (d, J = 12.8 Hz, 2 H), 1.09 (s, 6 H), 1.06 (s, 6 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 79.7, 76.6, 52.9, 49.6, 28.9, 28.5. IR (neat, cm^{-1}): 2968, 2928, 2834, 1449, 1365, 1262, 1168, 1050, 869, 775. Anal. Calcd. (found) for $\text{C}_{11}\text{H}_{20}\text{O}_2$: C, 71.70 (71.52); H, 10.94 (10.99).

2-Methyl-5,5-diphenyltetrahydropyran (Table 2, entry 17). Off-white solid, 90%. mp 49.5-50 °C. TLC (hexanes–ether = 5:1): R_f = 0.74. ^1H NMR: δ 7.44-7.14 (m, 10 H), 4.64 (dd, J = 2.8, 12.0 Hz, 1 H), 3.60-3.53 (m, 2 H), 2.50-2.37 (m, 2 H), 1.58-1.52 (m, 1 H), 1.28-1.16 (m, 1 H), 1.17 (d, J = 6.0 Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 147.1, 146.2, 129.3, 128.6, 128.3, 127.3, 126.6, 125.9, 75.4, 74.3, 46.1, 35.1, 30.1, 22.0. IR (neat, cm^{-1}): 3087, 3061, 3022, 2971, 2941, 2846, 1597, 1494, 1442, 1378, 1249, 1146, 1090, 1065, 924, 876, 750. Anal. Calcd. (found) for $\text{C}_{20}\text{H}_{22}\text{O}$: C, 85.67 (85.39); H, 7.99 (7.85).

***cis*-2-Benzyl-6-methyltetrahydropyran (Table 2, entry 19).**⁸ ^1H NMR (C_6D_6): δ 7.20-7.07 (m, 4 H), 7.03-6.98 (m, 1 H), 3.37-3.31 (m, 1 H), 3.20-3.11 (m, 1 H), 2.90 (dd, J = 6.4, 13.6 Hz, 1 H), 2.54 (dd, J = 6.4, 13.6 Hz, 1 H), 1.49-1.44 (m, 1 H), 1.28-1.14 (m, 2 H), 1.12-0.93 (m, 3 H), 1.07 (d, J = 6.4 Hz, 3 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 139.4, 129.7, 128.2, 126.1, 78.6, 73.7, 43.5, 33.4, 30.9, 23.8, 22.3.

Control Experiments

Three control experiments were performed to ascertain the contribution of an acid-catalyzed pathway in the Pt-catalyzed hydroalkoxylation of γ - and δ -hydroxy olefins. For an acid-catalyzed pathway to contribute to hydroalkoxylation, two conditions must be met. Firstly, the hydroxy olefin must cyclize at an appreciable rate in the presence of trace amounts of HCl (≤ 0.04 M) and secondly, HCl must be generated under the reaction conditions. Control experiments ruled out both of these possibilities and for this reasons, we conclude that an acid-catalyzed pathway does not contribute significantly to the platinum-catalyzed hydroalkoxylation of hydroxy olefins. In one experiment, a solution of HCl (0.02 mmol, 0.04 M), 2-(2-cyclohexenyl)-2,2-diphenylethanol (1.0 mmol) and methoxybenzene as internal standard in $\text{Cl}_2\text{CHCHCl}_2$ (0.5 mL) was stirred at 70 °C and monitored periodically by ^1H NMR analysis. After 20 h, no detectable (<5%) amounts of *cis*-3,3-diphenyloctahydrobenzofuran had formed. In a second experiment, a solution of

HCl (0.05 mmol, 0.10 M), 2,2-diphenyl-5-hexen-1-ol (250 mg, 1.0 mmol) and *n*-hexadecane internal standard in Cl₂CHCHCl₂ (0.5 mL) was stirred at 70 °C and monitored periodically by GC analysis. After 15 h, no detectable amounts (< 5%) of 2-methyl-5,5-diphenyltetrahydropyran had formed. A third experiment was predicated on two assumptions. The first assumption was that if HCl were generated under reaction conditions, it would be formed via metathesis of the Pt–Cl bond of **1** with the OH bond of the hydroxy olefin to form a platinum alkoxide complex and HCl (eq S1). The second assumption was that if this process were operative, it would be driven to completion through addition of a base to the reaction mixture. When a solution of **1** (30 mg, 0.050 mmol), P(4-C₆H₄CF₃)₃ (48 mg, 0.10 mmol), Et₃N (70 μL, 0.50 mmol), and methanol (20 μL, 0.50 mmol) in Cl₂CHCHCl₂ (0.5 mL) was stirred at 70 °C for 24 h, ¹H NMR analysis of the resulting reaction mixture revealed no detectable formation of a platinum methoxide complex. On the basis of this experiment, we conclude that HCl is not generated during the platinum-catalyzed hydroalkoxylation of hydroxy olefins.

Figure S1. ^1H NMR spectrum of 6-methyl-1-(*N*-phthalimido)-6-hepten-3-ol.

Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 6-methyl-1-(*N*-phthalimido)-6-hepten-3-ol.

Figure S3. ^1H NMR spectrum of methyl (2-cyclohexenyl)diphenylacetate.

Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of methyl (2-cyclohexenyl)diphenylacetate.

Figure S5. ^1H NMR spectrum of methyl 2,2-diphenyl-5-hexenoate.

Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of methyl (2-cyclohexenyl)diphenylacetate.

Figure S7. ^1H NMR spectrum of methyl 2,2-diphenyl-5-methyl-5-hexenoate.

Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of methyl 2,2-diphenyl-5-methyl-5-hexenoate.

Figure S9. ^1H NMR spectrum of 2,2-diphenyl-5-methyl-5-hexen-1-ol.

Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2,2-diphenyl-5-methyl-5-hexen-1-ol.

Figure S11. ^1H NMR spectrum of 2,2-dimethyl-5-[2-(*N*-phthalimido)ethyl]tetrahydrofuran.

Figure S12. $^{13}\text{C}\{^1\text{H}\}$ spectrum of 2,2-dimethyl-5-[2-(*N*-phthalimido)ethyl]tetrahydrofuran.

Figure S13. ^1H NMR spectrum of 2-(*tert*-butyldiphenylsiloxymethyl)-4-methyl-2-(2-methylallyl)-4-penten-1-ol.

Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-(*tert*-butyldiphenylsiloxymethyl)-4-methyl-2-(2-methylallyl)-4-penten-1-ol.

Figure S15. ^1H NMR spectrum of 4,4-diphenyl-2-propyltetrahydrofuran.

Figure S16. $^{13}\text{C}\{^1\text{H}\}$ spectrum of 4,4-diphenyl-2-propyltetrahydrofuran.

Figure S17. ^1H NMR spectrum of *cis*-3,3-diphenyloctahydrobenzofuran.

Figure S18. $^{13}\text{C}\{^1\text{H}\}$ spectrum of *cis*-3,3-diphenyloctahydrobenzofuran.

Figure S19. NOE spectrum of *cis*-3,3-diphenyloctahydrobenzofuran with irradiation of the resonance at δ 4.21.

Figure S20. NOE spectrum of *cis*-3,3-diphenyloctahydrobenzofuran with irradiation of the resonance at δ 2.80.

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