Palladium–Catalyzed Synthesis of Tetrahydrofurans from γ–Hydroxy Terminal Alkenes: Scope, Limitations, and Stereoselectivity.

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Supporting Information

Experimental procedures and characterization data for new compounds in Tables 2–9 and complete descriptions of stereochemical assignments (37 pages).

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General. All reactions were carried out under an argon or nitrogen atmosphere in oven- or flame-dried glassware. All catalysts and reagents were obtained from commercial sources and were used without further purification with the exception of 2-(4-bromophenyl)-[1,3]dioxolane,[1] (*E*)-1-bromodec-1-ene,[2] and 4-bromobenzoic acid *tert*-butyl ester,[3] hex-5-en-2-ol (**11a**),[4] hept-6-en-3-ol (**11b**),[5] 1-(4-methoxyphenyl)pent-4-en-1-ol (**15c**),[4] 2-hydroxyhex-5-enoic acid ethyl ester (**11d**),[6] 1-phenyl-4-penten-1-ol (**11e**),[7] *tert*-butyldimethyloxiranylmethoxysilane,[8] 2-phenylpent-4-en-1-ol (**22c**),[7] 3-phenylpent-4-en-1-ol (**20c**),[7] (±)-(1*S*,2*R*)-2-allylcyclohexanol (**24b**),[9] (±)-(1*R*,2*R*)-2-

allylcyclopentanol (**25a**),[10] 4-methylpent-4-en-1-ol (**2**),[11] 2,5-dimethylhex-5-en-2-ol (**5**),[12] and 1-but-3-enylcyclopentanol (**4**),[13] which were made according to literature procedures. Compounds **6a**, **6c**, **8a**, **8b**, **8c**, **12c**, **12d**, **21d**, and **23c** have been described in a preliminary communication of these studies.[7] Data for these compounds can be found in the supporting information accompanying the preliminary communication.[7] Toluene and THF were purified using a GlassContour solvent purification system. Yields refer to isolated yields of compounds estimated to be ≥95% pure as determined by ^{1}H NMR and either capillary GC (known compounds) or combustion analysis (new compounds). The yields reported in the supporting information describe the result of a single experiment, whereas the yields reported in Tables 2–9 are average yields of two or more experiments. Thus, the yields reported in the supporting information may differ from those shown in Tables 2–9.

Preparation and Characterization of Alcohol Substrates

General Procedure 1: Reduction of Esters with $LiAlH_4$. An oven or flame dried flask was purged with argon or nitrogen and charged with $LiAlH_4$ (2 equiv, 1.0 M in THF). Additional THF was added to provide a 0.5 M solution of $LiAlH_4$, which was then cooled to 0 °C. The appropriate ester was added dropwise via syringe and the resulting solution was warmed to rt and stirred for 2-4 h until the starting material was found to be completely consumed as judged by TLC analysis. The reaction was diluted twofold with THF and quenched according to the Fieser[14] procedure by successively adding water (0.4 mL/mmol $LiAlH_4$), NaOH (0.4 mL/mmol $LiAlH_4$, 10 M), and water (1.2 mL/mmol $LiAlH_4$) in a dropwise manner. The resulting suspension was decanted and the organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude primary alcohol product was purified by chromatography on silica gel.

General Procedure 2: Addition of MeMgBr to Esters. An oven or flame dried flask was purged with argon or nitrogen and charged with MeMgBr (3 equiv, 3.0 M in diethyl ether). Additional ether was added to provide a 1.0 M solution of MeMgBr, which was then cooled to 0 °C. The appropriate ester was added dropwise via syringe and the resulting mixture was warmed to rt and stirred for 2–4 h until the starting material was found to be completely consumed as judged by TLC analysis. A saturated solution of aqueous NH_4Cl (1:1 by volume with reaction mixture) was added dropwise and the resulting mixture was then diluted with ethyl acetate (100 mL). The layers were separated and aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude tertiary alcohol product was then purified by flash chromatography on silica gel.

General Procedure 3: Johnson Orthoester Claisen Rearrangements.[15] A round bottom flask equipped with a short path distillation head and a recovery flask was charged with the appropriate allylic alcohol, triethyl orthoacetate (10 equiv), and pivalic acid (0.06 equiv). The mixture was heated to 100 °C with stirring for 2 h then heated to 140 °C for 12 h until the starting material had been completely consumed as judged by GC analysis. The reaction mixture was cooled to room temperature and diluted with ethyl acetate (1:1 by volume). A solution of 1 M HCl (1:1 by volume) was slowly added and the resulting biphasic mixture was stirred for 1 h at rt. The layers were separated and the organic layer was washed with water (2 x 50 mL), and saturated $NaHCO_3$ (1 x 50 mL). The organic layer was then dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude ester product was used without further purification.

4-Methylpent-4-en-1-ol (**2**).[16] Reaction of 2-methylbut-2-en-1-ol (1.82 g, 25 mmol) with triethylorthoacetate according to general procedure 3 afforded 2.13 g (60 %) of crude 4-

methylpent-4-enoic acid ethyl ester as a yellow oil that was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.74 (s, 1 H), 4.68 (s, 1 H), 4.12 (q, *J* = 7.0 Hz, 2 H), 2.44 (t, *J* = 8.0 Hz, 2 H), 2.32 (t, *J* = 8.0 Hz, 2 H), 1.73 (s, 3 H), 1.24 (t, *J* = 6.0 Hz, 3 H).

The reduction of 4-methylpent-4-enoic acid ethyl ester with $LiAlH_4$ was carried out using general procedure 1 to afford 327 mg (51 %) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73–4.72 (m, 2 H), 3.68–3.65 (m, 2 H), 2.12–2.08 (m, 2 H), 1.74–1.70 (m, 5 H), 1.39 (s, 1 H).

2,5-Dimethylhex-5-en-2-ol (**5**).[12] 4-Methylpent-4-enoic acid ethyl ester (1.22 g, 8.62 mmol) was treated with MeMgBr (7.7 mL, 23.1 mmol, 3.0 M solution in THF) according to general procedure 2 to afford 0.70 g (70 %) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (m, 2 H), 2.11–2.07 (m, 2 H), 1.75 (s, 3 H), 1.64–1.61 (m, 2 H), 1.45 (s, 1 H), 1.25 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 109.6, 70.8, 41.5, 32.4, 29.1, 22.5; IR (film) 3369, 1131 cm^{-1}. MS (EI) *m/z* 100.0888 (100.0884 calcd for $C_8H_{16}O$).

2,2-Dimethylhept-6-en-3-ol (**11c**). A flame-dried flask was cooled under a stream of argon, charged with Mg turnings (3.4 g, 144 mmol) and purged with argon. Diethyl ether (24 mL) was added and the suspension was cooled to 0 °C. Neat 4-bromo-1-butene (10.80 g, 80 mmol) was added dropwise to the suspension and the resulting mixture was warmed to rt and stirred for 1h. The resulting solution was transferred to a dry, argon-filled flask via cannula, and additional Et_2O (20 mL) was added via syringe. A solution of pivaldehyde (3.4 g, 40 mmol) in Et_2O (4 mL) was added, the resulting mixture was stirred at rt for 8 h, and then a saturated aqueous solution of NH_4Cl (50 mL) was added dropwise. The layers were separated and the aqueous layer was extracted with Et_2O (2 x 20 mL). The combined organic layers were then dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel to afford 3.61 g (64 %) of the title compound as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90–5.80 (m, 1 H), 5.08–4.95 (m, 2 H), 3.21 (dd, *J* = 2.0, 10.6 Hz,

1 H), 2.35–2.29 (m, 1 H), 2.14–2.08 (m, 1 H), 1.65–1.57 (m, 1 H), 1.44 (s, 1 H), 1.40–1.31 (m, 1 H), 0.87 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 114.6, 79.2, 34.8, 31.2, 30.6, 25.6; IR (film) 3390, 1076 cm^{-1}. MS (CI) *m/z* 160.1705 (160.1701 calcd for $C_9H_{18}O$, M + NH_4^+).

1-Methoxyhex-5-en-2-ol (**13a**). A flame dried flask was cooled under a stream of argon and charged with allylmagnesium bromide (48 mL, 48 mmol, 1 M solution in THF) and cooled to 0 °C. Neat 2-methoxymethyloxirane (2.64 g, 30 mmol) was slowly added and the resulting mixture was warmed to rt and stirred for 4 h. A saturated aqueous solution of NH_4Cl (40 mL) was slowly added to the reaction mixture, the layers were separated, and the aqueous layer was extracted with diethyl ether (3 x 20 mL). The combined organic layers were then dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by distillation (78 °C, 35 torr) to afford 3.55 g (91 %) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87–5.77 (m, 1 H), 5.07–4.95 (m, 2 H), 3.82–3.76 (m, 1 H), 3.43-3.38 (m, 4 H), 3.26–3.20 (m, 1 H), 2.27–2.12 (m, 3 H), 1.60–1.25 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 114.5, 76.9, 69.3, 58.7, 32.0, 29.5; IR (film) 3435, 1120 cm^{-1}. Anal calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.28; H, 11.03.

1-(*tert*-Butyldimethylsilyloxy)hex-5-en-2-ol (**13b**).[17] A flame dried flask was purged with argon and charged with allylmagnesium bromide (30 mL, 30 mmol, 1M in diethyl ether). The flask was cooled to –20 °C, *tert*-Butyldimethyloxiranylmethoxysilane[8] (5.78 g, 30 mmol) was added dropwise, and the mixture was warmed to rt and stirred for 2 h. Saturated NH_4Cl (aq) (30 mL) was slowly added, the mixture was stirred for 10 minutes, and then the aqueous layer was separated and extracted with diethyl ether (3 x 30 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel to afford 5.86 g (82 %) of the title compound as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88–5.78 (m, 1 H), 5.06–4.95 (m, 2 H), 3.68–3.61 (m, 2 H), 3.43–3.38 (m, 1 H), 2.37 (s, 1 H), 2.26–2.10 (m, 2 H), 1.57–1.45 (m, 2 H), 1.51 (s, 9 H), 0.08 (s,

6 H).

1-(2,6-Di-*tert*-butyl-4-methylphenoxy)hex-5-en-2-ol (**13c**). A flame dried flask was purged with argon and charged with *p*-toluenesulfonyl chloride (6.73 g, 38.12 mmol), triethylamine (6.3 g, 62.38 mmol), and methylene chloride (34 mL). The solution was cooled to 0 °C and glycidol (2.56 g, 34.66 mmol) was added dropwise. The reaction was warmed to rt and stirred for 4h, then water (30 mL) was added to the reaction mixture and the layers were separated. The organic layer was washed with water (2 x 30 mL) and brine (1 x 30 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel to afford 3.33 g (42 %) of toluene-4-sulfonic acid oxiranylmethyl ester[18] as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 4.25 (dd, *J* = 3.6, 11.2 Hz, 1 H), 3.95 (dd, *J* = 6.4, 11.4 Hz, 1 H), 3.43–3.50 (m, 1 H), 3.20–3.17 (m, 1 H), 2.60–2.58 (m, 1 H), 2.45 (s, 3 H).

A flame dried flask was purged with argon and charged with sodium hydride (0.64 g, 16.06 mmol, 60% suspension in mineral oil) and DMF (15 mL). The suspension was cooled to 0 °C and a solution of 2,6-di-*tert*-butyl-4-methylphenol (3.53 g, 16.06 mmol) in DMF (7 mL) was added dropwise. The resulting mixture was stirred for 30 min at 0 °C, and then toluene-4-sulfonic acid oxiranylmethyl ester (3.33 g, 14.6 mmol) was added dropwise. The reaction mixture was warmed to rt and stirred for 8 h, then water (40 mL) was added and the resulting mixture was stirred for an additional 10 min. The layers were separated and the aqueous layer extracted with ethyl acetate (3 x 30 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel to afford 1.72 g (43 %) of 2-(2,6-di-*tert*-butyl-4-methylphenoxymethyl)oxirane as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 2 H), 4.16 (dd, *J* = 2.8, 11.0 Hz, 1 H), 3.88 (dd, *J* = 5.6, 11.0 Hz, 1 H), 3.48–3.46 (m, 1 H), 2.98–2.95 (m, 1 H), 2.89–2.87 (m, 1 H), 2.41 (s, 3 H), 1.57 (s, 18 H).

A flame dried flask was purged with argon and charged with allylmagnesiumbromide (10.6 mL,

10.6 mmol, 1 M in diethyl ether). The solution was cooled to 0 °C and a solution of 2-(2,6-di-*tert*-butyl-4-methylphenoxymethyl)oxirane (1.72 g, 6.2 mmol) in diethyl ether (10 mL) was added dropwise. The reaction mixture was warmed to rt and stirred for 8 h, then a saturated aqueous solution of NH_4Cl (20 mL) was added dropwise. The layers were separated, the aqueous layer was extracted with diethyl ether (3 x 20 mL), and the combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel to afford 1.49 g (76 %) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 2 H), 5.87–5.78 (m, 1 H), 5.08–4.97 (m, 2 H), 4.23–4.21 (m, 1 H), 3.84–3.79 (m, 1 H), 3.67–3.63 (m, 1 H), 2.41 (s, 1 H), 2.28 (s, 3 H), 2.26–2.16 (m, 2 H), 1.62–1.53 (m, 2 H), 1.42 (s, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.1, 143.1, 138.0, 131.9, 127.5, 115.0, 79.9, 70.1, 35.6, 32.2, 32.0, 29.6, 21.2; IR (film) 3436, 1204 cm^{-1}. Anal calcd for $C_{21}H_{34}O_2$: C, 79.19; H, 10.76. Found: C, 79.30; H, 10.81.

4-(1-Hydroxypent-4-enyl)benzonitrile (**15a**). The title compound was prepared from 4-formyl benzonitrile (0.70 g, 5.3 mmol) and 4-bromo-1-butene (1.43 g, 10.6 mmol) using a procedure analogous to that employed for the synthesis of **11c**. This procedure afforded 0.34 g (34 %) of 4-(hydroxypent-4-enyl)benzonitrile as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 6.0 Hz, 2 H), 7.47 (d, *J* = 8.5 Hz, 2 H), 5.86–5.79 (m, 1 H), 5.08–5.00 (m, 2 H), 4.80–4.79 (m, 1 H), 2.19–2.13 (m, 2 H), 2.03 (s, 1 H), 1.88–1.77 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 137.6, 132.2, 126.4, 118.8, 115.5, 73.1, 38.1, 29.7; IR (film) 3429, 2229, 1066 cm^{-1}. Anal calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.71; H, 7.18; N, 7.34.

1-(4-Trifluoromethylphenyl)pent-4-en-1-ol (**15b**). The title compound was prepared from 4-trifluormethyl benzaldehyde (0.75 g, 4.3 mmol) and 4-bromo-1-butene (1.16 g, 8.6 mmol) using a procedure analogous to that employed for the synthesis of **11c**. This procedure afforded 0.38 g (38 %) of 1-(4-trifluoromethylphenyl)pent-4-en-1-ol as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 5.89–5.78 (m, 1 H), 5.08–4.99 (m,

2 H), 4.79–4.76 (m, 1 H), 2.21–2.10 (m, 2 H), 1.98 (s, 1 H), 1.89–1.75 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 137.7, 126.1, 125.4, 125.3, 122.2, 115.3, 73.3, 38.1, 29.8; IR (film) 3350, 1127 cm^{-1}. Anal calcd for $C_{12}H_{13}F_3O$: C, 62.60; H, 5.69. Found: C, 62.59; H, 5.72.

1-(4-Dimethylaminophenyl)pent-4-en-1-ol (**15d**). The title compound was prepared from 4-*N,N*-dimethylamino benzaldehyde (0.71 g, 4.8 mmol) and 4-bromo-1-butene (1.29 g, 9.6 mmol) using a procedure analogous to that employed for the synthesis of **11c**. This procedure afforded 0.77 g (78 %) of 1-(4-dimethylaminophenyl)pent-4-en-1-ol as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.21 (m, 2 H), 6.75–6.72 (m, 2 H), 5.91–5.81 (m, 1 H), 5.07–4.97 (m, 2 H), 4.59–4.56 (m, 1 H), 2.95 (s, 6 H), 2.18 (s, 1 H), 2.16–2.03 (m, 2 H), 1.96–1.87 (m, 1 H), 1.82–1.74 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 138.7, 132.8, 127.1, 114.8, 112.8, 73.9, 40.9, 37.9, 20.4; IR (film) 3384 cm^{-1}. Anal calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 75.81; H, 9.41; N, 6.83.

3-Methylhept-6-en-3-ol (**18a**). A flame dried flask was purged with argon and charged with ethylmagnesium bromide (16 mL, 5.33 mmol, 3.0 M in diethyl ether) and additional diethyl ether (32 mL). The solution was cooled to 0 °C and a solution of hex-5-en-2-one (3.92 g, 40 mmol) in diethyl ether (6 mL) was added dropwise. The resulting mixture was warmed to rt and stirred for 3 h, then saturated aqueous NH_4Cl (50 mL) was added and the mixture was stirred for 10 min. The layers were separated and the aqueous layer was extracted with diethyl ether (2 x 30 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel to afford 1.94 g (38 %) of the title compound as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89–5.79 (m, 1 H), 5.06–4.92 (m, 2 H), 2.14–2.03 (m, 2 H), 1.55–1.46 (m, 4 H), 1.30 (s, 1 H), 1.14 (s, 3 H), 0.89 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 114.2, 72.7, 40.1, 34.2, 28.2, 26.1, 8.1; IR (film) 3380, 1145 cm^{-1}. MS (CI) *m/z* 146.1549 (146.1545 calcd for $C_8H_{16}O$, M + NH_4^+).

2-Phenylhex-5-en-2-ol (**18b**).[12] The title compound was prepared from hex-5-en-2-one (3.92 g, 40 mmol) and phenylmagnesium chloride (24 mL, 48 mmol, 2.0 M in THF) using a procedure analogous to that employed in the synthesis of **18a.** This procedure afforded 6.33 g (90 %) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 2 H), 7.37–7.33 (m, 2 H), 7.26–7.23 (m, 1 H), 5.83–5.76 (m, 1 H), 4.99–4.91 (m, 2 H), 2.17–2.04 (m, 1 H), 1.96–1.87 (m, 3 H), 1.79 (s, 1 H), 1.57 (s, 3 H).

3-Methylpent-4-en-1-ol (**20a**).[19] But-2-en-1-ol (5.88 mL, 70 mmol) was treated with triethyl orthoacetate (22.6 mL, 124 mmol) using general procedure 3 to afford 6.4 g (65 %) of 3-methylpent-4-enoic acid ethyl ester as a yellow oil. This material was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84–5.72 (m, 1 H), 5.06–4.94 (m, 2 H), 4.14 (q, J = 7.2 Hz, 2 H), 2.69 (sp, J = 7.2 Hz, 1 H), 2.39–2.22 (m, 2 H), 1.25 (t, J = 7.2 Hz, 3 H), 1.06 (d, J = 6.9 Hz, 3 H).

3-Methylpent-4-enoic acid ethyl ester (1.0 g, 7 mmol) was treated with $LiAlH_4$ (17.6 mL, 17.6 mmol, 1M solution in THF) using general procedure 1 to afford 420 mg (60 %) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79–5.67 (m, 1 H), 5.05–4.94 (m, 2 H), 3.67 (t, J = 8.4 Hz, 2 H), 2.31 (sp, J = 10 Hz, 1 H), 1.62–1.55 (m, 2 H), 1.32 (s, 1 H), 1.03 (d, J = 9.2 Hz, 3 H).

3-Ethylpent-4-en-1-ol (**20b**).[20] Pent-2-en-1-ol (5.90 mL, 58 mmol) was treated with triethyl orthoacetate (22.6 mL, 124 mmol) using general procedure 3 to afford 5.40 g (60 %) of 3-ethylpent-4-enoic acid ethyl ester as a yellow liquid. This material was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.99–5.57 (m, 1 H), 5.07–4.99 (m, 2 H), 4.11 (q, J = 7.2 Hz, 2 H), 2.48–2.24 (m, 3 H), 1.50–1.31 (m, 2 H), 1.24 (t, J = 7.2 Hz, 3 H), 0.88 (t, J = 7.5 Hz, 3 H).

3-Ethylpent-4-enoic acid ethyl ester (2.0 g, 13 mmol) was treated with $LiAlH_4$ (32 mL, 32 mmol, 1 M solution in THF) using general procedure 1 to afford 890 mg (60 %) of the title compound

as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59–5.52 (m, 1 H), 5.02–4.99 (m, 2 H), 3.70–3.59 (m, 2 H), 2.05–1.99 (m, 1 H), 1.70–1.64 (m, 1 H), 1.52–1.47 (m, 1 H), 1.46–1.39 (m, 2 H), 1.32–1.23 (m, 1 H), 0.85 (t, *J* = 6.0 Hz, 3 H).

2-(*tert*-Butyl)pent-4-en-1-ol (20d).[21] A flame dried 3-neck flask equipped with a reflux condenser was charged with pivaldehyde (4.0 g, 46 mmol), carboethoxymethylene triphenyl phosphorane (24.0 g, 69 mmol), and THF (46 mL). The resulting suspension was heated to reflux under argon for 3 hours, then was cooled to rt and concentrated *in vacuo*. The resulting material was triturated with pentane (150 mL) and filtered. The pentane solution was concentrated *in vacuo* to afford 4.87 g (68 %) of (*E*)-4,4-dimethylpent-2-enoic acid ethyl ester as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (d, *J* = 15.0 Hz, 1 H), 5.72 (d, *J* = 16.0 Hz, 1 H), 4.18 (q, *J* = 8.0 Hz, 2 H), 1.28 (t, *J* = 7.0 Hz, 3 H), 1.07 (s, 9 H).

(*E*)-4,4-Dimethylpent-2-enoic acid ethyl ester (3.5 g, 22.4 mmol) was treated with DIBAL (49 mL, 49 mmol, 1 M solution in hexane) according to the procedure of Pericas[22] to afford 1.80 g (70 %) of (*E*)-4,4-dimethylpent-2-en-1-ol as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72–5.68 (d, *J* = 14.0 Hz, 1 H), 5.57–5.50 (m, 1 H), 4.09 (t, *J* = 6.0 Hz, 2 H), 1.32 (s, 1 H), 1.01 (s, 9 H).

(*E*)-4,4-Dimethylpent-2-en-1-ol (1.80 g, 15.7 mmol) was treated with triethyl orthoacetate (28 mL, 157 mmol) using general procedure 3 to afford 2.20 g (76 %) of 3-*tert*-butylpent-4-enoic acid ethyl ester as a yellow oil that was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70–5.62 (m, 1 H), 5.03–4.98 (m, 2 H), 4.08 (q, *J* = 8 Hz, 2 H), 2.50 (dd, *J* = 3.5, 13.7 Hz, 1 H), 2.33–2.28 (m, 1 H), 2.17 (dd, *J* = 11.0, 14.0 Hz, 1 H), 1.24 (t, *J* = 7.0 Hz, 3 H), 0.86 (s, 9 H).

3-*tert*-Butylpent-4-enoic acid ethyl ester (2.20 g, 11.9 mmol) was treated with $LiAlH_4$ (47.6 mL, 47.6 mmol, 1.0 M solution in THF) using general procedure 1 to afford 1.22 g (72 %) of the title compound as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67–5.60 (m, 1 H), 5.06 (dd, *J* = 2.0, 14.8 Hz, 1 H), 4.99 (dd, *J* = 2.5, 17.0 Hz, 1 H), 3.69–3.65 (m, 1 H), 3.58–3.53 (m, 1 H),

2.05–1.78 (m, 2 H), 1.43–1.36 (m, 2 H), 0.86 (s, 9 H).

2,4-Dimethylhex-5-en-2-ol (20e).[23] 3-Methylpent-4-enoic acid ethyl ester (1.50 g, 10.6 mmol) was treated with methylmagnesium bromide (10 mL, 30 mmol, 3 M solution in diethyl ether) using general procedure 2 to afford 746 mg (55 %) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83–5.76 (m, 1 H), 5.07 (dd, *J* = 1.0, 17.5 Hz, 1 H), 4.95 (dd, *J* = 1.5, 10.0 Hz, 1 H), 2.47–2.41 (m, 1 H), 1.73 (s, 1 H), 1.58 (dd, *J* = 9.5, 14.0 Hz, 1 H), 1.49 (dd, *J* = 3.5, 14.5 Hz, 1 H), 1.24 (s, 3 H), 1.19 (s, 3 H), 1.02 (d, *J* = 7.0 Hz, 3 H).

2-Methylpent-4-en-1-ol (22a).[24] A flame-dried flask was purged with argon and charged with diisopropylamine (15 mL, 105.6 mmol), and THF (30 mL). The solution was cooled to 0 °C and a solution of *n*-butyllithium (40.2 mL, 100.5 mmol, 2.5 M in hexanes) was added dropwise. The resulting mixture was stirred for 10 min at 0 °C and then a solution of ethyl propionate (7.2 g, 70.4 mmol) in THF (2 mL) was added dropwise. The mixture was stirred at 0 °C for 30 min, then was cooled to –78 °C and DMPU (7.3 mL, 60.4 mmol) and allyl bromide (9.6 mL, 110.6 mmol) were added. The reaction mixture was stirred for 2 h at –78 °C, then warmed to rt and stirred for an additional 10 h. Saturated NH_4Cl (aq.) (50 mL) and pentane (100 mL) were added, the layers were separated, and the aqueous layer was extracted with pentane (2 x 100 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was fractionally distilled (150 °C, 760 torr) to afford 2.2 g (22 %) of 2-methylpent-4-enoic acid ethyl ester[25] as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79–5.58 (m, 1 H), 5.03–4.98 (m, 2 H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.54–2.07 (m, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.15 (d, *J* = 7.2 Hz, 3 H).

2-Methylpent-4-enoic acid ethyl ester (2.2 g, 15.4 mmol) was treated with $LiAlH_4$ using general procedure 1 to afford 1.04 g (67 %) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86–5.76 (m, 1 H), 5.07–4.99 (m, 2 H), 3.54–3.44 (m, 2 H), 2.21–2.14 (m, 1 H), 1.98–1.91 (m, 1 H), 1.78–1.70 (m, 1 H), 1.22 (s, 1 H), 0.92 (d, *J* = 7.2 Hz, 3 H).

2-Ethylpent-4-en-1-ol (**22b**).[26] Ethyl butyrate (8.2 g, 70.4 mmol) was alkylated with allyl bromide (13.4 g, 110.6 mmol) using a procedure analogous to that described above for the synthesis of 2-methylpent-4-enoic acid ethyl ester to afford 1.07 g (10 %) of 2-ethylpent-4-enoic acid ethyl ester as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79–5.69 (m, 1 H), 5.07–4.98 (m, 2 H), 4.11 (q, *J* = 7.2 Hz, 2 H), 2.39–2.31 (m, 2 H), 2.29–2.20 (m, 1 H), 1.68–1.48 (m, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 0.94 (t, *J* = 7.2 Hz, 3 H)

2-Ethylpent-4-enoic acid ethyl ester (1.07 g, 7.0 mmol) was treated with $LiAlH_4$ using general procedure 1 to afford 0.28 g (36 %) of the title compound as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86–5.78 (m, 1 H), 5.08–5.00 (m, 2 H), 3.59–3.53 (m, 2 H), 2.13–2.10 (m, 2 H), 1.56–1.50 (m, 1 H), 1.42–1.31 (m, 3 H), 0.91 (t, *J* = 7.5 Hz, 3 H).

2-*tert*-Butylpent-4-en-1-ol (**22d**).[27] A flame dried flask was purged with argon and charged with ethanol (5.06 g, 110 mmol), triethylamine (11.1 g, 110 mmol), and diethyl ether (100 mL). The solution was cooled to 0 °C and 3,3-dimethylbutyryl chloride (13.45 g, 100 mmol) was added dropwise with stirring. The resulting mixture was then warmed to rt and stirred for 1 h, then water (50 mL) was added and the mixture was stirred for an additional 5 min. The layers were separated and the aqueous layer was extracted with diethyl ether (2 x 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was distilled (145 °C, 760 torr) to afford 7.81 g (54 %) of 3,3-dimethylbutyric acid ethyl ester[28] as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.85 (q, *J* = 7.0 Hz, 2 H), 1.92 (s, 2 H), 0.99 (t, *J* = 7.0 Hz, 3 H), 0.76 (s, 9 H).

3,3-Dimethylbutyric acid ethyl ester (7.81 g, 55.5 mmol) was alkylated with allyl bromide (7.6 mL, 87.23 mmol) using a procedure analogous to that described above for the synthesis of 2-methylpent-4-enoic acid ethyl ester to afford 5.58 g (38 %) of 2-*tert*-butylpent-4-enoic acid ethyl ester[20] as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.75–5.67 (m, 1 H), 5.07–4.95 (m, 2 H), 4.11 (q, *J* = 7.0 Hz, 2 H), 2.40–2.33 (m, 2 H), 2.25–2.20 (m, 1 H), 1.24 (t, *J* = 7.0 H, 3 H),

0.98 (s, 9 H).

2-*tert*-Butylpent-4-enoic acid ethyl ester (4.0 g, 21.8 mmol) was treated with $LiAlH_4$ using general procedure 1 to afford 1.02 g (25 %) of the title compound as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97–5.88 (m, 1 H), 5.13–5.01 (m, 2 H), 3.77 (dd, *J* = 4.0, 11.5 Hz, 1 H), 3.62 (dd, *J* = 5.5, 11.3 Hz, 1 H), 2.37–2.32 (m, 1 H), 2.05–1.98 (m, 1 H), 1.35–1.32 (m, 2 H), 0.94 (s, 9 H).

2,4-Dimethylpent-4-en-1-ol (**22e**).[29] 2-Methylprop-2-en-1-ol (3.02 g, 42 mmol) was treated with triethyl orthopropionate following the general procedure 3 to provide 3.93 g (60 %) of 2,4-dimethylpent-4-enoic acid ethyl ester as a yellow oil, which was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.72 (d, *J* = 18.0 Hz, 2 H), 4.11 (q, *J* = 7.0 Hz, 2 H), 2.65–2.56 (m, 1 H), 2.43–2.27 (m, 2 H), 1.70 (s, 3 H), 1.24 (t, *J* = 7.0 Hz, 3 H), 1.13 (d, *J* = 7.0 Hz, 3 H).

2,4-Dimethylpent-4-enoic acid ethyl ester (4.00 g, 25.6 mmol) was treated with $LiAlH_4$ using general procedure 1 to afford 0.83 g (31 %) of the title compound as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (d, *J* = 20.8 Hz, 2 H), 3.53–3.42 (m, 2 H), 2.17–2.10 (m, 1 H), 1.91–1.82 (m, 2 H), 1.72 (s, 3 H), 1.41 (s, 1 H), 0.90 (d, *J* = 4.8 Hz, 3 H).

(±)-(1*R*,2*R*)-2-Allylcyclohexanol (**24a**).[30] 2-Allylcyclohexanone[31] (1.70 g, 12.3 mmol) in THF (40 mL) was treated with L-selectride (14 mL, 14 mmol, 1.0 M solution in THF) using the procedure developed Marvell and Rusay for the reduction of 2-substituted cyclohexanones.[32] This procedure afforded 740 mg (43 %) of the title compound as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86–5.78 (m, 1 H), 5.08–5.00 (m, 2 H), 3.90 (s, 1 H), 2.20–2.14 (m, 1 H), 2.06–2.00 (m, 1 H), 1.81–1.77 (m, 1 H), 1.69–1.65 (m, 1 H), 1.60–1.34 (m, 6 H), 1.29–1.21 (m, 2 H).

(±)-(1*S*,2*R*)-2-Allylcyclopentanol (**25b**).[33] (±)-(1*S*,2*R*)-2-Allylcyclopentanol was prepared

from 2-allylcyclopentanone (4.12 g, 33 mmol) and L-selectride (34 mL, 34 mmol, 1 M solution in THF) using a procedure analogous to that employed in the synthesis of (±)-(1*R*,2*R*)-2-allylcyclohexanol to afford 1.25 g (30 %) of (±)-(1*S*,2*R*)-2-allylcyclopentanol. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87–5.79 (m, 1 H), 5.05–4.93 (m, 2 H), 4.13–4.11 (m, 1 H), 2.26–2.21 (m, 1 H), 2.13–2.08 (m, 1 H), 1.83–1.66 (m, 5 H), 1.65–1.59 (m, 1 H), 1.61–1.47 (m, 1 H), 1.41–1.37 (m, 1 H).

Characterization data for tetrahydrofuran products.

2-(4-methylbenzyl)tetrahydrofuran (**6b**).[34] Reaction of 4-penten-1-ol (43 mg, 0.5 mmol) with 4-bromotoluene (123 μL, 1.0 mmol) following the general procedure afforded 57 mg (65%) of the title compound as a colorless oil. NMR data were consistent with previously published data[34] and the compound was judged to be ≥ 95% pure by ^{1}H NMR and GC analysis.

4-(Tetrahydrofuran-2-ylmethyl)benzonitrile (**6d**). Reaction of 4-penten-1-ol (25 mg, 0.25 mmol) with 4-bromobenzonitrile (91 mg, 0.5 mmol) following the general procedure afforded 18 mg (40 %) of the title compound as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58–7.56 (m, 2 H), 7.35–7.33 (m, 2 H), 4.08–4.03 (m, 1 H), 3.89–3.84 (m, 1 H), 3.75–3.70 (m, 1 H), 2.91–2.82 (m, 2 H), 2.00–1.94 (m, 2 H), 1.89–1.83 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 132.0, 130.1, 119.0, 110.0, 79.1, 68.0, 41.9, 31.1, 25.5; IR (film) 2200, 1060 cm^{-1}. Anal calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found C, 76.09; H, 6.83; N, 7.64.

The major side product formed in this transformation was 4-pent-4-enyloxybenzonitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.55 (m, 2 H), 6.94–6.91 (m, 2 H), 5.88–5.78 (m, 2 H), 5.08–4.99 (m, 1 H), 4.01 (t, J = 6.8 Hz, 2 H), 2.26–2.21 (m, 2 H), 1.89 (pentet, J = 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 137.3, 133.9, 119.2, 115.5, 115.1, 103.7, 67.4, 29.8, 28.0; IR (film) 2225 cm^{-1}; MS (EI) *m/z* 187.0993 (187.0997 calcd for $C_{12}H_{13}NO$).

4-(Tetrahydrofuran-2-ylmethyl)benzoic acid *tert*-butyl ester (6e). Reaction of 4-penten-1-ol (25 mg, 0.25 mmol) with 4-bromobenzoic acid *tert*-butyl ester (128 mg, 0.5 mmol) following the general procedure afforded 24 mg (37 %) of the title compound as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93–7.91 (m, 2 H), 7.29–7.27 (m, 2 H), 4.09–4.06 (m, 1 H), 3.91–3.87 (m, 1 H), 3.76–3.72 (m, 1 H), 2.94 (dd, *J* = 6.5, 13.5 Hz, 1 H), 2.82 (dd, *J* = 6.0, 13.5 Hz, 1 H), 1.93–1.84 (m, 2 H), 1.61 (s, 9 H), 1.57–1.52 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 143.8, 129.9, 129.4, 129.0, 80.7, 79.5, 67.9, 41.8, 30.9, 28.1, 25.5; IR (film) 1760, 1292 cm^{-1}. Anal calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found C, 73.07; H, 8.43.

The main side product formed in this reaction was 4-pent-4-enyloxybenzoic acid *tert*-butylester, which was characterized by examination of the ^{1}H NMR spectrum of the crude reaction mixture and correlation of the extraneous peaks with the closely related known compound 4-butoxybenzoic acid *tert*-butyl ester.[35] Data for the side product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93–7.91 (m, 2 H), 6.89–6.86 (m, 2 H), 5.87–5.81 (m, 1 H), 5.07–4.99 (m, 2 H), 4.00 (t, *J* = 6.5 Hz, 2 H), 2.38–2.25 (m, 2 H), 2.02–1.97 (m, 2 H), 1.58 (s, 9 H).

2-(*E*)-(β-Styryl)-tetrahydrofuran[36] **(6f)**. Reaction of 4-penten-1-ol (25 mg, 0.25 mmol) with β-bromostyrene (91 mg, 0.5 mmol) following the general procedure afforded 13 mg (30 %) of the title compound as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.34 (m, 2 H), 7.30–7.27 (m, 2 H), 7.21–7.17 (m, 1 H), 6.45 (d, *J* = 15.6 Hz, 1 H), 6.24 (dt, *J* = 7.2, 15.6 Hz, 1 H), 3.99–3.88 (m, 2 H), 3.78–3.72 (m, 1 H), 2.54–2.46 (m, 1 H), 2.44–2.37 (m, 1 H), 2.04–1.99 (m, 1 H), 1.99–1.85 (m, 2 H), 1.61–1.54 (m, 1H).

The main side product formed in this reaction was 2-pent4-enyloxyvinylbenzene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.22 (m, 5 H), 7.03 (d, *J* = 16.4 Hz, 1 H), 6.35 (d, *J* = 16.0 Hz, 1 H), 5.85–5.78 (m, 1 H), 5.08–4.97 (m, 2 H), 3.82 (t, *J* = 6.8 Hz, 2 H), 2.20–2.14 (m, 2 H), 1.78

(pentet, J = 6.8 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 141.2, 131.4, 128.1, 123.3, 115.2, 108.0, 105.8, 69.1, 29.9, 28.4; IR(film) 2360 cm^{-1}; MS (EI) *m/z* 188.1208 (188.1201 calcd for $C_{12}H_{16}O$).

2-Methyl-2-(4-methylbenzyl)tetrahydrofuran (7) Reaction of 4-methylpent-4-en-1-ol (25 mg, 0.25 mmol) with 4-bromotoluene (85.5 mg, 0.5 mmol) following the general procedure afforded 10 mg (20 %) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.21 (m, 4 H), 4.02–3.96 (m, 1 H), 3.94–3.89 (m, 1 H), 2.89 (s, 2 H), 2.46 (s, 3 H), 2.06–1.83 (m, 3 H), 1.78–1.70 (m, 1 H), 1.31 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.49, 135.44, 130.2, 128.5, 82.8, 67.3, 46.4, 36.1, 26.3, 26.0, 21.0; IR (film) 1046 cm^{-1}. Anal calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.05; H, 9.49.

2-(4-*tert*-Butylbenzyl)-1-oxaspiro[4.4]nonane (**9**). Reaction of 1-but-3-enylcyclopentanol[16] (**4**) (35 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106 mg, 0.50 mmol) following the general procedure afforded 48 mg (71 %) of the title compound as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.26 (m, 2 H), 7.17–7.12 (m, 2 H), 4.19–4.10 (m, 1 H), 2.97 (dd, J = 6.0, 12.0 Hz, 1 H), 2.64 (dd, J = 6.0, 12.0 Hz, 1 H), 1.96–1.48 (m, 12 H), 1.29 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 135.8, 129.0, 125.1, 91.3, 79.2, 42.3, 39.2, 38.4, 36.4, 34.3, 31.4, 24.0, 23.9; IR (film) 1092 cm^{-1}. Anal calcd for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.57; H, 10.36.

2-(2-Methylbenzyl)-1-oxaspiro[4.4]nonane (**10**). Reaction of 1-but-3-enylcyclopentanol[16] (35 mg, 0.25 mmol) with 2-bromotoluene (85.5 mg, 0.50 mmol) following the general procedure afforded 35 mg (61 %) of the title compound as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26–7.15 (m, 4 H), 4.20–4.15 (m, 1 H), 3.03 (dd, J = 6.0, 15.0 Hz, 1 H), 2.69 (dd, J = 6.0, 13.5 Hz, 1 H), 2.35 (s, 3 H), 1.93–1.54 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2, 136.5, 130.1, 130.0, 126.1, 125.7, 91.2, 78.1, 39.8, 39.3, 38.5, 36.5, 31.4, 24.0, 23.9, 19.7; IR (film)

1165 cm^{-1}. Anal calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.31; H, 9.74.

(±)-(2*R*,5*S*)-2-(4-*tert*-Butylbenzyl)-5-methyltetrahydrofuran (**12a**). Reaction of hex-4-en-2-ol (25 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106.5 mg, 0.5 mmol) was conducted following the general procedure. After the starting material had been completely consumed, the reaction mixture was cooled to rt, a solution of $LiAlH_4$ (0.1 mL, 0.1 mmol, 1.0 M in THF) was added, and the resulting mixture was stirred for 1 h at rt. Water (0.1 mL), NaOH (0.1 mL, 10 M), and additional water (0.3 mL) were added slowly in succession, then ethyl acetate (10 mL) was added and the layers were separated. The aqueous layer was extracted with ethyl acetate (2 x 10 mL) and the combined organic layers were dried over anhydrous (Na_2SO_4), filtered, and concentrated *in vacuo*. This alternate workup was employed to facilitate chromatographic separation of an undesired ketone side product. The crude material was purified by flash chromatography on silica gel to afford 24 mg (41 %) of the title compound as a colorless oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 4.27–4.24 (m, 1 H), 4.18–4.14 (m, 1 H), 2.96 (dd, *J* = 5.5, 13.5 Hz, 1 H), 2.67 (dd, *J* = 7.5, 13.5 Hz, 1 H), 2.07–1.96 (m, 2 H), 1.67–1.61 (m, 1 H), 1.56–1.46 (m, 1 H), 1.45 (s, 9 H), 1.23 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 135.7, 128.9, 125.1, 79.5, 74.7, 41.8, 34.3, 33.8, 31.8, 31.4, 21.4; IR (film) 1088 cm^{-1}. Anal calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.69; H, 10.45.

(±)-(2*R*,5*S*)-2-(4-*tert*-Butylbenzyl)-5-ethyltetrahydrofuran (**12b**). Reaction of hept-4-en-2-ol (28 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106.5 mg, 0.5 mmol) was conducted following the general procedure. After the starting material had been completely consumed, the reaction mixture was cooled to rt, a solution of $LiAlH_4$ (0.1 mL, 0.1 mmol, 1.0 M in THF) was added, and the resulting mixture was stirred for 1 h at rt. Water (0.1 mL), NaOH (0.1 mL, 10 M), and additional water (0.3 mL) were added slowly in succession, then ethyl acetate (10 mL) was added and the layers were separated. The aqueous layer was extracted with ethyl acetate (2 x 10

mL) and the combined organic layers were dried over anhydrous (Na_2SO_4), filtered, and concentrated *in vacuo*. This alternate workup was employed to facilitate chromatographic separation of an undesired ketone side product. The crude material was purified by flash chromatography on silica gel to afford 21 mg (34 %) of the title compound as a colorless oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 4.24–4.18 (m, 1 H), 3.98–3.93 (m, 1 H), 2.98 (dd, *J* = 5.5, 13.5 Hz, 1 H), 2.67 (dd, *J* = 8.0, 13.2 Hz, 1 H), 2.05–1.93 (m, 2 H), 1.69–1.57 (m, 2 H), 1.49–1.42 (m, 2 H), 1.35 (s, 9 H), 0.96 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 135.7, 128.9, 125.1, 80.3, 79.5, 41.7, 34.3, 31.6, 31.4, 31.3, 31.3, 28.8, 10.3; IR (film) 1086 cm^{-1}. Anal calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.99; H, 10.53.

6-(4-*tert*-Butylphenyl)-2-hydroxyhex-4-enoic acid ethyl ester (Product from Reaction of 11d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2 H), 7.10 (d, *J* = 8 Hz, 2 H), 5.72–5.67 (m, 1 H), 5.54–5.44 (m, 1 H), 4.26–4.21 (m, 1 H), 4.18 (q, *J* = 7.0 Hz, 2 H), 3.31 (d, *J* = 6.5 Hz, 2 H), 2.80 (d, *J* = 6 Hz, 1 H), 2.56–2.52 (m, 1 H), 2.45–2.39 (m, 1 H), 1.30 (s, 9 H), 1.21–1.22 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.5, 148.8, 137.2, 133.7, 128.0, 125.2, 124.8, 70.2, 61.6, 38.5, 37.4, 34.3, 31.3, 14.1; IR (film) 3468, 1734 cm^{-1}; MS (ESI) *m/z* 313.1780 (313.7180 calcd for $C_{18}H_{26}O_3Na$, $M + Na^+$).

(±)-(2*R*,5*S*)-2-[4-(5-Phenyltetrahydrofuran-2-ylmethyl)phenyl]-[1,3]dioxolane (12e). Reaction of 1-phenyl-4-penten-1-ol (40.5 mg, 0.25 mmol) with 2-(4-bromophenyl)-1,3-dioxolane (114.5 mg, 0.50 mmol) following the general procedure afforded 47 mg (61 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44–7.22 (m, 9 H), 5.81 (s, 1 H), 5.04–4.99 (m, 1 H), 4.48–4.44 (m, 1 H), 4.15–4.01 (m, 4 H), 3.07 (dd, *J* = 6.0, 12.0 Hz, 1 H), 2.85 (dd, *J* = 6.0, 12.0 Hz, 1 H), 2.34–2.28 (m, 1 H), 2.05–2.01 (m, 1 H), 1.86–1.70 (m, 2 H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 143.7, 139.7, 135.7, 129.5, 128.3, 127.0, 126.4, 125.5, 103.7, 80.5, 80.4, 77.3, 77.0, 76.7, 65.3, 41.9, 35.2, 31.6; IR (film) 1219 cm^{-1}. Anal calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.35; H, 7.11.

(±)-(2*R*,5*R*)-2-Phenyl-5-[(*E*)-3-phenylallyl]tetrahydrofuran (**12f**). Reaction of 1-phenyl-4-penten-1-ol (40.5 mg, 0.25 mmol) with β-bromostyrene (91.5 mg, 0.50 mmol) following the general procedure afforded 25 mg (38 %) of the title compound as a pale yellow oil.[37] This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.19 (m, 10 H), 6.50 (d, *J* = 15.0 Hz, 1 H), 6.36–6.26 (m, 1 H), 5.06 (t, *J* = 6.0 Hz, 1 H), 4.39–4.35 (m, 1 H), 2.66–2.59 (m, 1 H), 2.55–2.48 (m, 1 H), 2.41–2.36 (m, 1 H), 2.18–2.13 (m, 1 H), 1.93–1.78 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 137.8, 132.4, 128.7, 128.5, 127.3, 126.8, 126.3, 125.8, 94.6, 80.8, 79.7, 39.8, 35.5, 31.9; IR (film) 1055 cm^{-1}. Anal calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.11; H, 7.47.

(±)-(2*R*,5*R*)-2-Phenyl-5-[(*E*)-undec-2-enyl]tetrahydrofuran (**12g**). Reaction of 1-phenyl-4-penten-1-ol (40.5 mg, 0.25 mmol) with (*E*)-1-bromo-1-undecene (109.5 mg, 0.50 mmol) following the general procedure afforded 22 mg (29 %) of the title compound as a pale yellow oil.[37] This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.30 (m, 4 H), 7.26–7.22 (m, 1 H), 5.55–5.53 (m, 2 H), 5.01 (dd, *J* = 6.0, 6.6 Hz, 1 H), 4.25–4.22 (m, 1 H), 2.43–2.32 (m, 2 H), 2.28–2.23 (m, 1 H), 2.11–2.06 (m, 1 H), 1.90–1.80 (m, 1 H), 1.75–1.67 (m, 1 H), 1.44–1.27 (m, 14 H), 0.88 (t, *J* = 6.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 133.2, 133.0, 130.7, 129.4, 128.4, 128.0, 127.0, 125.8, 80.4, 79.8, 42.6, 39.2, 35.1, 32.7, 31.9, 29.3, 22.7, 14.1; IR (film) 1057 cm^{-1}. Anal calcd for $C_{21}H_{32}O$: C, 83.94; H, 10.73. Found: C, 83.98; H, 10.94.

(±)-(2*R*,5*R*)-2-(4-*tert*-Butylbenzyl)-5-methoxymethyltetrahydrofuran (**14a**). Reaction of 1-methoxyhex-5-en-2-ol (33 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106.5 mg, 0.5

mmol) following the general procedure afforded 50 mg (75 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 4.23–4.19 (m, 2 H), 3.39–3.35 (m, 5 H), 3.01 (dd, *J* = 5.0, 10.8 Hz, 1 H), 2.66 (dd, *J* = 8.0, 13.5 Hz, 1 H), 1.99–1.91 (m, 2 H), 1.68–1.54 (m, 2 H), 1.30 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 135.5, 128.9, 125.1, 80.2, 77.5, 75.6, 59.2, 41.3, 34.3, 31.3, 31.1, 28.3; IR (film) 1086 cm^{-1}. Anal calcd for $C_{17}H_{26}O$: C, 77.82; H, 9.99. Found: C, 77.82; H, 9.94.

(±)-*tert*-Butyl-[(2*R*,5*R*)-5-(4-*tert*-butylbenzyl)tetrahydrofuran-2-ylmethoxy]dimethylsilane (**14b**). Reaction of 1-(*tert*-butyldimethylsilyloxy)hex-5-en-2-ol (58 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106.5 mg, 0.5 mmol) following the general procedure afforded 62 mg (68 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 4.20–4.17 (m, 1 H), 4.15–4.07 (m, 1 H), 3.63 (dd, *J* = 4.8, 10.8 Hz, 1 H), 3.55 (dd, *J* = 5.2, 10.2 Hz, 1 H), 2.93 (dd, *J* = 6.0, 13.4 Hz, 1 H), 2.66 (dd, *J* = 7.6, 13.6 Hz, 1 H), 1.95 (m, 2 H), 1.70–1.62 (m, 1 H), 1.61–1.56 (m, 1 H), 1.35 (s, 9 H), 0.85 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 135.8, 128.9, 125.1, 80.2, 79.2, 65.9, 41.5, 34.3, 31.4, 31.3, 27.9, 25.9, 18.4, –5.3; IR (film) 1084 cm^{-1}. Anal calcd for $C_{22}H_{38}SiO$: C, 72.87; H, 10.56. Found: C, 72.94; H, 10.55.

(±)-(2*R*,5*R*)-2-(4-*tert*-Butylbenzyl)-5-(2,6-di-*tert*-butyl-4-methylphenoxymethyl)tetrahydrofuran (**14c**). Reaction of 1-(2,6-di-*tert*-butyl-4-methylphenoxy)hex-5-en-2-ol (80 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106.5 mg, 0.5 mmol) following the general procedure afforded 91 mg (81 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.45 (m, 1 H), 7.45–7.35 (m, 2 H), 7.32–7.30 (m, 2 H), 7.10–7.05 (m, 1 H), 4.61–4.57 (m, 1 H), 4.24–4.19 (m, 1 H), 3.86–3.74 (m, 1 H), 3.45–3.42 (m, 1 H), 3.01 (dd,

J = 6.0, 12.5 Hz, 1 H), 2.83 (dd, *J* = 7.5, 13.5 Hz, 1 H), 2.35 (s, 3 H), 2.18–2.01 (m, 1 H), 2.04–2.01 (m, 1 H), 1.78–1.70 (m, 2 H), 1.40 (s, 18 H), 1.28 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.6, 148.8, 143.3, 135.8, 131.5, 131.0, 129.1, 128.9, 127.4, 127.2, 125.1, 125.0, 79.9, 78.3, 77.6, 41.3, 35.6, 34.3, 32.2, 32.1, 31.5, 31.4, 31.4, 31.2, 30.3, 28.4, 21.3; IR (film) 1096 cm^{-1}. Anal calcd for $C_{31}H_{46}O$: C, 82.61; H, 10.29. Found: C, 82.31; H, 10.16.

(±)-*tert*-Butyl-[(2*R*,5*R*)-5-(4-[1,3-dioxolan-2-yl]benzyl)tetrahydrofuran-2-ylmethoxy]dimethylsilane (**14d**). Reaction of 1-(*tert*-butyldimethylsilyloxy)hex-5-en-2-ol (57.5 mg, 0.25 mmol) with 2-(4-bromophenyl)-1,3-dioxolane (114.5 mg, 0.50 mmol) following the general procedure afforded 37 mg (39 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.34 (m, 2 H), 7.26–7.22 (m, 2 H), 7.79 (s, 1 H), 4.19–4.01 (m, 6 H), 3.61 (dd, *J* = 3.0, 9.0 Hz, 1 H), 3.55 (dd, *J* = 3.0, 9.0 Hz, 1 H), 2.95 (dd, *J* = 6.0, 12.0 Hz, 1 H), 2.71 (dd, *J* = 6.0, 12.0 Hz, 1 H), 1.94–1.87 (m, 2 H), 1.72–1.67 (m, 1 H), 1.58–1.53 (m, 1 H), 0.88 (s, 9 H), 0.04 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 131.7, 129.5, 128.4, 126.6, 103.9, 80.3, 79.5, 66.2, 65.5, 41.9, 31.4, 28.1, 26.1, –5.1; IR (film) 1252 cm^{-1}. Anal calcd for $C_{21}H_{34}O_4Si$: C, 66.62; H, 9.05; Found: C, 66.60; H, 9.15.

(±)-*tert*-Butyldimethyl-[(2*R*,5*R*)-5-[(*E*)-3-phenylallyl]tetrahydrofuran-2-ylmethoxy]silane (**14e**). Reaction of 1-(*tert*-butyldimethylsilyloxy)hex-5-en-2-ol (58 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene(106.5 mg, 0.5 mmol) following the general procedure afforded 30 mg (36 %) of the title compound as a pale yellow oil.[37] This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 10.0 Hz, 2 H), 7.30 (d, *J* = 5.0 Hz, 2 H), 7.21 (m, 1 H), 6.44 (d, *J* = 16.0 Hz, 1 H), 6.26–6.20 (m, 1 H), 4.13–4.06 (m, 2 H), 3.64 (dd, *J* = 5.0, 9.7 Hz, 1 H), 3.57 (dd, *J* = 5.0, 10.5 Hz, 1 H), 2.53–2.47, (m, 1 H), 2.41–2.35 (m, 1 H), 2.03–1.97 (m, 2 H), 1.80–1.74 (m, 1 H), 1.64–1.58 (m, 1 H), 0.92 (s, 9 H), 0.08 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 131.8, 128.4, 126.9, 126.8, 126.0, 79.4,

78.9, 65.9, 39.3, 31.2, 28.0, 25.9, 19.3, 18.4, –5.3; IR (film) 1252 cm^{-1}. Anal calcd for $C_{20}H_{32}SiO$: C, 72.23; H, 9.70. Found: C, 72.05; H, 9.64.

(±)-4-[(2*R*,5*R*)-5-(4-*tert*-Butylbenzyl)tetrahydrofuran-2-yl]benzonitrile (**16a**). Reaction of 4-(1-hydroxypent-4-enyl)benzonitrile (47 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106.5 mg, 0.5 mmol) following the general procedure afforded 67 mg (84 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2 H), 7.45–7.42 (m, 2 H), 7.35–7.32 (m, 2 H), 7.21–7.19 (m, 2 H), 5.08 (t, *J* = 14.4 Hz, 1 H), 4.48–4.43 (m, 1 H), 3.03 (dd, *J* = 6.4, 13.8 Hz, 1 H), 2.80 (dd, *J* = 6.8, 13.6 Hz, 1 H), 2.42–2.36 (m, 1 H), 2.10–2.04 (m, 1 H), 1.83–1.71 (m, 2 H), 1.32 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 149.0, 135.2, 132.1, 128.8, 126.0, 125.2, 118.8, 110.6, 81.0, 79.6, 41.5, 35.1, 34.3, 31.7, 31.4; IR (film) 1059 cm^{-1}. Anal calcd for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.34; H, 7.84; N, 4.17.

(±)-(2*R*,5*R*)-2-(4-*tert*-Butylbenzyl)-5-(4-trifluoromethylphenyl)tetrahydrofuran (**16b**). Reaction of 1-(4-trifluoromethylphenyl)pent-4-en-1-ol (58 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106.5 mg, 0.5 mmol) following the general procedure afforded 50 mg (57 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56(d, *J* = 8.8 Hz, 2 H), 7.46–7.39 (m, 2 H), 7.32–7.19 (m, 4 H), 5.10–4.48 (m, 1 H), 4.48–4.45 (m, 1 H), 3.03 (dd, *J* = 6.0, 13.6 Hz, 1 H), 2.79 (dd, *J* = 6.8, 13.6 Hz, 1 H), 2.39–2.33 (m, 1 H), 2.06–2.01 (m, 1 H), 1.82–1.73 (m, 2 H), 1.32 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 148.1, 135.3, 128.9, 125.6, 125.2, 125.2, 125.1, 80.9, 79.8, 41.5, 35.1, 34.3, 31.6, 31.3; IR (film) 1067 cm^{-1}. MS (EI) *m/z* 362.1858 (362.1857 calcd for $C_{22}H_{25}F_3O$).

(±)-(2*S*,5*S*)-2-(4-*tert*-Butylbenzyl)-5-phenyltetrahydrofuran (**16c**). Reaction of 1-phenylpent-4-en-1-ol (40 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106.5 mg, 0.5 mmol) following

the general procedure afforded 47 mg (64 %) of the title compound as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.31 (m, 5 H), 7.24–7.21 (m, 4 H), 5.09–5.02 (m, 1 H), 4.50–4.54 (m, 1 H), 3.07 (dd, *J* = 5.5, 16.7 Hz, 1 H), 2.79 (dd, *J* = 7.5, 13.5 Hz, 1 H), 2.38–2.32 (m, 1 H), 2.09–2.04 (m, 1 H), 1.88–1.72 (m, 2 H), 1.33 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 143.8, 135.5, 128.9, 128.2, 127.0, 125.5, 125.1, 80.6, 80.4, 41.7, 35.1, 34.3, 31.7, 31.3; IR (film) 1054 cm^{-1}. Anal calcd for $C_{21}H_{26}O$: C, 85.67; H, 8.90. Found: C, 85.38; H, 8.86.

(±)-(2*R*,5*R*)-2-(4-*tert*-Butylbenzyl)-5-(4-methoxyphenyl)tetrahydrofuran (**16d**) Reaction of 1-(4-methoxyphenyl)pent-4-en-1-ol (48 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106.5 mg, 0.5 mmol) following the general procedure afforded 51 mg (63 %) of an inseparable 5:1 mixture of the title compound and 1-(4-methoxyphenyl)pent-4-en-1-one[38] as judged by ^{1}H NMR analysis. Characterization data are for the title compound, which was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.08 (m, 8 H), 5.01–4.96 (m, 1 H), 4.50–4.43 (m, 1 H), 3.80 (s, 3 H), 2.99 (dd, *J* = 8.0, 21.0 Hz, 1 H), 2.77 (dd, *J* = 7.5, 21.0 Hz, 1 H), 2.34–2.27 (m, 1 H), 2.09–2.03 (m, 1 H), 1.88–1.71 (m, 2 H), 1.28 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 148.8, 135.7, 135.5, 128.9, 126.8, 125.1, 113.6, 80.4, 80.1, 41.7, 35.0, 34.3, 31.8, 31.3, 31.2; IR (film) 1053 cm^{-1}. MS (ESI) *m/z* 347.1993 (347.1987 calcd for $C_{22}H_{28}O_2Na$, M + Na^+).

Data for 1-(4-methoxyphenyl)pent-4-en-1-one:[38] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 2 H), 6.93 (d, *J* = 7.0 Hz, 2 H); 5.93–5.87 (m, 1 H), 5.10–4.99 (m, 2 H), 3.87 (s, 3 H), 3.02 (t, *J* = 7.5 Hz, 2 H), 2.51–2.46 (m, 2 H).

(±)-{4-[(2*R*,5*R*)-5-(4-*tert*-Butylbenzyl)tetrahydrofuran-2-yl]phenyl}dimethylamine (**16e**). Reaction of 1-(4-dimethylamino)pent-4-en-1-ol (51 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106.5 mg, 0.5 mmol) following the general procedure afforded 26 mg (31 %) of an inseparable 3:1 mixture of the title compound and 1-(4-dimethylaminophenyl)pent-4-en-1-one as

judged by ^{1}H NMR analysis. Characterization data are for the title compound, which was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.19 (m, 8 H), 4.98–4.95 (m, 1 H), 4.47–4.40 (m, 1 H), 3.07 (dd, *J* = 8.0, 13.6 Hz, 1 H), 2.93 (s, 6 H), 2.76 (dd, *J* = 8.0, 13.5 Hz, 1 H), 2.30–2.23 (m, 1 H), 2.20–2.03 (m, 1 H), 1.91–1.82 (m, 1 H), 1.78–1.71 (m, 1 H), 1.27 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 148.8, 135.6, 130.9, 128.9, 126.7, 125.1, 112.6, 80.4, 80.2, 41.7, 40.7, 34.8, 31.9, 31.3; IR (film) 1053 cm^{-1}. MS (ESI) 338.2482 (338.2484 calcd for $C_{23}H_{32}NO$, M + H^+).

Data for 1-(4-dimethylaminophenyl)pent-4-en-1-one: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 11.5 Hz, 2 H), 6.65 (d, *J* = 11.5 Hz, 2 H), 5.92–5.88 (m, 1 H), 5.10–4.97 (m, 2 H), 3.05 (s, 6 H), 2.97 (t, *J* = 9 Hz, 2 H), 2.50–2.45 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.4, 153.2, 137.7, 130.0, 124.7, 114.7, 110.4, 39.8, 36.8, 28.6; IR (film) 1639 cm^{-1}; MS (ESI) *m/z* 226.1208 (226.1208 calcd for $C_{13}H_{17}NONa$, M + Na^+).

(±)-(2*S*,5*R*)-5-(4-*tert*-Butylbenzyl)-2-ethyl-2-methyltetrahydrofuran (**19a**). Reaction of 2-methylhept-6-en-2-ol (32 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106.5 mg, 0.5 mmol) following the general procedure afforded 37 mg (57 %) of the title compound as a pale yellow oil. This material was obtained as a ca 3:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major diastereomer**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.31 (m, 2 H), 7.20–7.15 (m, 2 H), 4.20–4.08 (m, 1 H), 3.03–2.94 (m, 1 H), 2.66–2.59 (m, 1 H), 1.94–1.80 (m, 2 H), 1.77–1.56 (m, 4 H), 1.34 (s, 9 H), 1.22 (s, 1.25) 1.17 (s, 1.75 H), 0.93–0.87 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 135.8, 135.7, 128.9, 128.9, 127.9, 125.08, 125.06, 83.4, 83.3, 79.8, 79.1, 42.3, 42.1, 36.2, 35.9, 34.6, 34.3, 33.9, 31.42, 31.37, 26.5, 25.7, 9.05, 9.01; IR (film) 1109 cm^{-1}. Anal calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 80.28; H, 10.46.

(±)-(2*R*,5*R*)-5-(4-*tert*-Butylbenzyl)-2-methyl-2-phenyltetrahydrofuran (**19b**). Reaction of 2-phenylhex-5-en-2-ol (44 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106.5 mg, 0.5

mmol) following the general procedure afforded 61 mg (78 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 1 H), 7.34–7.31 (m, 4 H), 7.26–7.21 (m, 4 H), 4.30–4.24 (m, 1 H), 3.09 (dd, *J* = 5.5, 13.2 Hz, 1 H), 2.78 (dd, *J* = 8.0, 13.7 Hz, 1 H), 2.20–2.15 (m, 1 H), 2.03–1.98 (m, 1 H), 1.84–1.72 (m, 2 H), 1.54 (s, 3 H), 1.33 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 148.8, 129.3, 128.3, 126.5, 125.4, 124.9, 84.9, 79.9, 42.4, 39.4, 34.6, 31.6, 31.1, 31.0; IR (film) 1109 cm^{-1}. Anal calcd for $C_{22}H_{28}O$: C, 85.66; H, 9.15. Found: C, 85.31; H, 9.27.

(±)-2-{4-[(2*R*,5*R*)-5-Methyl-5-phenyltetrahydrofuran-2-ylmethyl]phenyl}-1,3-dioxolane (**19c**). A reaction of 2-phenyl-5-hexen-2-ol (44 mg, 0.25 mmol) with (4-bromophenyl)-1,3-dioxolane (114.5 mg, 0.50 mmol) following the general procedure afforded 69 mg (85 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.19 (m, 9 H), 5.80 (s, 1 H), 4.28–4.17 (m, 1 H), 4.15–4.01 (m, 4 H), 3.08 (dd, *J* = 6.0, 12.0 Hz, 1 H), 2.84 (dd, *J* = 6.0, 12.0 Hz, 1 H), 2.18–2.12 (m, 1 H), 2.02–1.93 (m, 1 H), 1.80–1.67 (m, 2 H), 1.53 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 139.8, 135.6, 131.4, 129.5, 128.1, 128.0, 126.3, 124.7, 103.7, 84.7, 79.3, 65.2, 42.3, 39.0, 30.6; IR (film) 1273 cm^{-1}. Anal calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.88; H, 7.49.

(±)-4-[(2*R*,5*R*)-5-Methyl-5-phenyltetrahydrofuran-2-ylmethyl]benzoic acid *tert*-butyl ester (**19d**). Reaction of 2-phenyl-5-hexen-2-ol (44 mg, 0.25 mmol) with 4-bromobenzoic acid *tert*-butyl ester (128.5 mg, 0.50 mmol) following the general procedure afforded 56 mg (64 %) of the title compound as a pale yellow oil. This material was obtained as a ca. 4:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95–7.87 (m, 2 H), 7.39–7.18 (m, 7 H), 4.29–4.25 (m, 1 H), 3.07 (dd, *J* = 6.0, 15.0 Hz, 1 H), 2.89 (dd, *J* = 6.0, 13.5 Hz, 1 H), 2.21–2.12 (m, 1 H), 1.99–1.91 (m, 1 H),

1.84–1.80 (m, 2 H), 1.60 (s, 9 H), 1.52 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 148.3, 143.6, 130.0, 129.4, 129.3, 128.1, 126.3, 124.5, 84.8, 80.7, 79.0, 42.4, 39.0, 30.8, 30.6, 28.2; IR (film) 1291 cm^{-1}. Anal calcd for $C_{23}H_{28}O_3$: C, 78.38; H, 8.01. Found: C, 78.27; H, 8.06.

(±)-(2*R*,5*R*)-2-Methyl-2-phenyl-5-[(*E*)-3-phenylallyl]tetrahydrofuran (**19e**). A reaction of 2-phenyl-5-hexen-2-ol (44 mg, 0.25 mmol) with β-bromostyrene (91.5 mg, 0.50 mmol) following the general procedure afforded 40 mg (58 %) of the title compound as a pale yellow oil.[37] This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44–7.20 (m, 10 H), 6.50 (d, *J* = 15.0 Hz, 1 H), 6.36–6.28 (m, 1 H), 4.19–4.15 (m, 1 H), 2.63–2.59 (m, 1 H), 2.55–2.48 (m, 1 H), 2.26–2.20 (m, 1 H), 2.12–2.03 (m, 1 H), 1.94–1.87 (m, 1 H), 1.79–1.74 (m, 1 H), 1.57 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 137.6, 132.1, 128.5, 128.1, 127.0, 126.6, 126.3, 126.0, 124.6, 84.7, 78.3, 39.7, 39.2, 30.8, 30.7; IR (film) 1264 cm^{-1}. Anal calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.19; H, 7.91.

(±)-(2*R*,3*S*)-2-Biphenyl-4-yl-3-methyltetrahydrofuran (**21a**). Reaction of 3-methyl-4-penten-1-ol (50 mg, 0.5 mmol) with 4-bromobiphenyl (232 mg, 1.0 mmol) following the general procedure afforded 95 mg (76 %) of the title compound as a pale yellow oil. The product was isolated as a ca. 3:1 mixture of diastereomers as determined by ^{1}H NMR. Data is for the major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.61 (m, 2 H), 7.58–7.55 (m, 2 H), 7.50–7.44 (m, 2 H), 7.38–7.34 (m, 3 H), 3.90–3.86 (m, 2 H), 3.68–3.63 (m, 1 H), 2.95 (dd, *J* = 4.4, 14.0 Hz, 1 H), 2.88–2.84 (m, 1 H), 2.14–2.10 (m, 1 H), 1.97–1.94 (m, 1 H), 1.61–1.56 (m, 1 H), 1.06 (t, *J* = 8.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 138.5, 129.9, 129.6, 128.9, 127.3, 127.24, 127.21, 86.6, 67.1, 40.4, 38.9, 34.8, 17.5; IR (film) 1076 cm^{-1}. Anal calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.71; H, 8.05.

(±)-(2*R*,3*S*)-3-Ethyl-2-(4-methylbenzyl)tetrahydrofuran (**21b**). Reaction of 3-ethyl-4-propen-1-ol (57 mg, 0.5 mmol) with 4-bromotoluene (171 mg, 1.0 mmol) following the general procedure

afforded 67 mg (66 %) of the title compound as a pale yellow oil. The product was isolated as a ca. 6:1 mixture of diastereomers as determined by ^{1}H NMR. Data is for the major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–7.09 (m, 4 H), 3.85–3.73 (m, 2 H), 3.70–3.65 (m, 1 H), 2.84 (dd, *J* = 4.4, 13.8 Hz, 1 H), 2.76 (dd, *J* = 7.2, 13.8 Hz, 1 H), 2.33 (s, 3 H), 2.09–2.02 (m, 1 H), 1.78–1.73 (m, 1 H), 1.58–1.52 (m, 1 H), 1.50–1.44 (m, 1 H), 1.27–1.19 (m, 1 H), 0.97 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.3, 135.7, 129.4, 129.2, 85.2, 67.2, 46.1, 40.9, 32.5, 26.1, 21.3, 12.9; IR (film) 1074 cm^{-1}. Anal calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.36; H, 9.94.

(±)-(2*R*,3*S*)-3-Ethyl-2-(2-methoxybenzyl)tetrahydrofuran (**21c**). Reaction of 3-ethyl-4-penten-1-ol (28.5 mg, 0.25 mmol) with 2-bromoanisole (93.5 mg, 0.50 mmol) following the general procedure afforded 31 mg (56 %) of the title compound as a pale yellow oil. The product was isolated as a ca. 8:1 mixture of diastereomers as determined by ^{1}H NMR. Data is for the major diastereomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26–7.16 (m, 2 H), 6.92–6.83 (m, 2 H), 3.90–3.70 (m, 6 H), 2.90 (dd, *J* = 6.0, 15.0 Hz, 1 H), 2.77 (dd, *J* = 6.0, 15.0 Hz, 1 H), 2.13–2.03 (m, 1 H), 1.80–1.72 (m, 1 H), 1.61–1.35 (m, 2 H), 1.26–1.16 (m, 1 H), 0.88 (t, *J* = 6.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 133.5, 131.1, 127.7, 120.5, 110.3, 83.6, 67.1, 55.3, 46.2, 35.6, 32.5, 26.2, 12.7; IR (film) 1241 cm^{-1}. Anal calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.27; H, 8.93.

(±)-(2*R*,3*S*)-3-*tert*-Butyl-2-(4-methylbenzyl)tetrahydrofuran (**21e**). Reaction of 3-*tert*-butyl-4-penten-1-ol (71 mg, 0.5 mmol) with 4-bromotoluene (171 mg, 1.0 mmol) following the general procedure afforded 63 mg (54 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.11 (m, 4 H), 4.04–3.99 (m, 1 H), 3.82–3.71 (m, 2 H), 2.81 (dd, *J* = 4.0, 14.2 Hz, 1 H), 2.71 (dd, *J* = 8.0, 14.4 Hz, 1 H), 2.34 (s, 3 H), 1.91–1.72 (m, 3 H), 0.91 (s, 9 H); ^{13}C NMR (125

MHz, $CDCl_3$) δ 136.8, 135.7, 129.4, 129.1, 81.4, 67.5, 54.4, 42.6, 32.4, 28.9, 28.1, 21.2; IR (film) 1076 cm^{-1}. Anal calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.80; H, 10.41.

(±)-(2*R*,3*S*)-5-Biphenyl-4-ylmethyl-2,2,4-trimethyltetrahydrofuran (21f). Reaction of 1,1,3-trimethyl-4-penten-1-ol (64 mg, 0.5 mmol) with 4-bromobiphenyl (232 mg, 1.0 mmol) following the general procedure afforded 109 mg (78 %) of the title compound as a pale yellow oil. The product was isolated as a ca. 8:1 mixture of diastereomers as determined by ^1H NMR. Data is for the major diastereomer. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2 H), 7.55–7.53 (m, 2 H), 7.44–7.42 (m, 2 H), 7.36–7.34 (m, 3 H), 3.82–3.77 (m, 1 H), 2.93–2.91 (m, 2 H), 2.08–1.92 (m, 2 H), 1.48–1.42 (m, 2 H), 1.30 (s, 3 H), 1.17 (s, 3 H), 0.91 (d, J = 6.4 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 139.1, 138.2, 130.2, 128.9, 127.2, 127.0, 85.4, 79.6, 48.3, 40.4, 38.9, 29.8, 29.6, 16.9; IR (film) 1066 cm^{-1}. Anal calcd for $C_{20}H_{26}O$: C, 85.67; H, 8.63. Found: C, 85.39; H, 8.81.

(±)-(2*S*,4*S*)-2-Biphenyl-4-ylmethyl-4-methyltetrahydrofuran (23a). Reaction of 2-methylpent-4-en-1-ol (25 mg, 0.25 mmol) with 4-bromobiphenyl (116.5 mg, 0.5 mmol) following the general procedure afforded 44 mg (70 %) of the title compound as a pale yellow oil. This material was isolated as a ca. 1.5:1 mixture of diastereomers as judged by ^1H NMR analysis. Data are for the mixture. ^1H NMR (500 MHz, $CDCl_3$) δ 7.60–7.59 (m, 2 H), 7.54–7.53 (m, 2 H), 7.45–7.42 (m, 2 H), 7.35–7.31 (m, 3 H), 4.28–4.23 (m, 0.4 H), 4.19–4.14 (m, 0.6 H), 4.05 (dd, J = 7.0, 8.2 Hz, 0.4 H), 3.93 (t, J = 8.0 Hz, 0.6 H), 3.42 (t, J = 8.0 Hz, 0.6 H), 3.31 (t, J = 8.0 Hz, 0.4 H), 3.00 (dd, J = 6.5, 15.0 Hz, 0.6 H), 2.94 (dd, J = 7.0, 13.7 Hz, 0.4 H), 2.84 (dd, J = 7.0, 13.7 Hz, 0.6 H), 2.79 (dd, J = 6.0, 13.5 Hz, 0.4 H), 2.38–2.30 (m, 1 H), 2.17–2.12 (m, 0.6 H), 1.86–1.81 (m, 0.4 H), 1.63–1.58 (m, 0.4 H), 1.28–1.21 (m, 0.6 H), 1.07–1.02 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 139.1, 138.1, 138.1, 129.6, 129.5, 128.6, 127.0, 126.9, 126.9, 80.7, 79.4, 75.1, 74.6, 41.9, 41.9, 40.6, 39.1, 34.3, 33.1, 17.9, 17.4; IR (film) 1040 cm^{-1}. Anal calcd for $C_{18}H_{20}O$: C, 82.70; H, 10.41. Found: C, 82.47; H, 10.39.

(±)-(2*S*,4*S*)-2-Biphenyl-4-ylmethyl-4-ethyltetrahydrofuran (**23b**). Reaction of 2-ethylpent-4-en-1-ol (28 mg, 0.25 mmol) with 4-bromobiphenyl (116.5 mg, 0.5 mmol) following the general procedure afforded 54 mg (81 %) of the title compound as a pale yellow oil. This material was obtained as a ca. 1.5:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59–7.56 (m, 2 H), 7.53–7.51 (m, 2 H), 7.44–7.40 (m, 2 H), 7.34–7.29 (m, 3 H), 4.21–4.09 (m, 1 H), 4.07–4.03 (m, 0.6 H), 3.91 (t, *J* = 7.6 Hz, 0.4 H), 3.48 (t, *J* = 7.6 Hz, 0.6 H), 3.34 (t, *J* = 7.6 Hz, 0.4 H), 3.00–2.90 (m, 1 H), 2.84–2.74 (m, 1 H), 2.20–2.09 (m, 1.4 H), 1.83–1.76 (m, 0.4 H), 1.66–1.60 (m, 0.4 H), 1.45–1.34 (m, 2 H), 1.26–1.17 (m, 0.8 H), 0.92–0.87 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 139.1, 138.1, 129.6, 129.5, 128.6, 127.0, 126.9, 80.6, 79.4, 73.4, 73.8, 41.9, 41.8, 41.6, 40.6, 38.5, 37.0, 26.5, 26.3, 12.8, 12.7; IR (film) 1075 cm^{-1}. Anal calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.68; H, 8.31.

(±)-(2*S*,4*R*)-2-Biphenyl-4-ylmethyl-4-*tert*-butyltetrahydrofuran (**23d**). Reaction of 2-*tert*-butylpent-4-en-1-ol (35 mg, 0.25 mmol) with 4-bromobiphenyl (116.5 mg, 0.5 mmol) following the general procedure afforded 54 mg (88 %) of the title compound as a pale yellow oil. The material was obtained as a ca. 2:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.56 (m, 2 H), 7.53–7.51 (m, 2 H), 7.44–7.40 (m, 2 H), 7.34–7.28 (m, 3 H), 4.14–4.06 (m, 1 H), 3.96 (t, *J* = 8.4 Hz, 0.34 H), 3.79 (t, *J* = 8.4 Hz, 0.66 H), 3.72 (t, *J* = 8.4 Hz, 0.66 H), 3.49 (t, *J* = 8.8 Hz, 0.34 H), 3.01–2.90 (m, 1 H), 2.84–2.73 (m, 1 H), 2.18–2.10 (m, 1 H), 1.92–1.85 (m, 0.66 H), 1.79–1.74 (m, 0.34 H), 1.67–1.62 (m, 0.34 H), 1.40–1.27 (m, 0.66 H), 0.87 (s, 9 H); ^{13}C NMR (100 MHz, CDCl3) δ 141.1, 139.1, 138.1, 129.5, 129.4, 128.7, 127.0, 127.0, 126.9, 126.8, 80.8, 80.3, 69.5, 69.0, 50.5, 49.2, 41.9, 41.5, 33.8, 32.5, 31.3, 31.2, 27.6, 27.5; IR (film) 1120 cm^{-1}. Anal calcd for $C_{21}H_{26}O$: C, 85.67; H, 8.90. Found: C, 85.59; H, 8.72.

(±)-{4-[(2*S*,4*R*)-4-*tert*-Butyltetrahydrofuran-2-ylmethyl]phenyl}dimethylamine (**23e**). Reaction of 2-*tert*-butyl-4-penten-1-ol (35.5 mg, 0.25 mmol) with *p*-bromo-1,1-dimethylaniline (100 mg, 0.50 mmol) following the general procedure afforded 50 mg (77 %) of the title compound as a pale green oil. The material was obtained as a ca. 2:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the mixture. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12–7.09 (m, 2 H), 6.73–6.70 (m, 2 H), 4.04–3.92 (m, 1.33 H), 3.81–3.75 (m, 0.66 H), 3.69–3.63 (m, 0.66 H), 4.01–3.92 (m, 0.34 H), 2.94–2.81 (m, 7 H), 2.69–2.60 (m, 1 H), 2.15–2.09 (m, 1 H), 1.88–1.80 (m, 1 H), 1.37–1.26 (m, 1 H), 0.87 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 129.7, 112.9, 81.4, 80.8, 69.4, 68.9, 50.5, 49.2, 41.3, 40.9, 33.8, 32.3, 31.3, 31.2, 27.6, 27.5; IR (film) 1059 cm^{-1}. Anal calcd for $C_{17}H_{27}NO$: C, 78.11; H, 10.41; N, 5.36. Found: C, 77.87; H, 10.38; N, 5.24.

(±)-(2*R*,4*R*)-4-*tert*-Butyl-2-[(*E*)-3-phenylallyl]tetrahydrofuran (**23f**). Reaction of 2-*tert*-butyl-4-penten-1-ol (35.5 mg, 0.25 mmol) with β-bromostyrene (91.5 mg, 0.50 mmol) following the general procedure afforded 41 mg (64 %) of the title compound as a pale yellow oil. The material was obtained as a ca. 2:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the mixture. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.14 (m, 5 H), 6.47–6.45 (m, 1 H), 6.16–6.16 (m, 1 H), 3.97–3.88 (m, 1.34 H), 3.80–3.74 (m, 0.66 H), 3.67–3.62 (m, 0.66 H), 3.50–3.41 (m, 0.34 H), 2.54–2.34 (m, 2 H), 2.17–2.08 (m, 1 H), 1.94–1.86 (m, 0.66 H), 1.82–1.72 (m, 0.34 H), 1.64–1.52 (m, 0.34 H), 1.36–1.25 (m, 0.66 H), 0.86 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 132.1, 128.6, 127.2, 126.9, 126.3, 79.9, 79.3, 69.7, 69.2, 50.8, 49.5, 39.8, 32.6, 31.5, 27.8, 27.7; IR (film) 1067 cm^{-1}. Anal calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.67; H, 9.94.

(±)-(2*S*,4*S*)-2-Biphenyl-4-ylmethyl-2,4-dimethyltetrahydrofuran (**23g**). Reaction of 2,4-dimethylpent-4-en-1-ol (28 mg, 0.25 mmol) with 4-bromobiphenyl (116.5 mg, 0.5 mmol) following the general procedure afforded 50 mg (75 %) of the title compound as a pale yellow oil. The material was obtained as a ca. 1:1 mixture of diastereomers as judged by ^{1}H NMR analysis.

Data are for the mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60–7.58 (m, 2 H), 7.53–7.50 (m, 2 H), 7.44–7.40 (m, 2 H), 7.34–7.28 (m, 3 H), 4.0–3.95 (m, 1 H), 3.38–3.34 (m, 0.5 H), 3.26–3.21 (m, 0.5 H), 2.90–2.83 (m, 1 H), 2.81–2.74 (m, 1 H), 2.46–2.36 (m, 1 H), 2.17–2.10 (m, 1 H), 1.87–1.82 (dd, *J* = 8, 12.2 Hz, 0.5 H), 1.54–1.46 (dd, *J* = 12.4, 16.0, Hz, 0.5 H), 1.26 (s, 1.5 H), 1.21 (s, 1.5 H), 1.00–0.96 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 141.0, 138.9, 138.9, 137.7, 137.6, 130.8, 130.7, 128.7, 126.9, 126.9, 126.6, 126.5, 83.5, 83.4, 74.4, 74.2, 47.4, 46.8, 45.4, 45.3, 34.2, 33.9, 27.4, 26.8, 17.3, 16.8; IR (film) 1042 cm^{-1}. Anal calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.80; H, 8.35.

(±)-(2*R*,3*aR*,7*aR*)-2-Biphenyl-4-ylmethyloctahydrobenzofuran (**26a**). Reaction of (±)-(1*R*,2*R*)-2-allylcyclohexanol (70 mg, 0.5 mmol) with 4-bromobiphenyl (232 mg, 1.0 mmol) following the general procedure afforded 87.6 mg (60 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.60 (m, 4 H), 7.57–7.44 (m, 2 H), 7.38–7.27 (m, 3 H), 4.49–4.46 (m, 1 H), 4.04–4.01 (m, 1 H), 3.05 (dd, *J* = 5.6, 13.4 Hz, 1 H), 2.81 (dd, *J* = 6.8, 13.4 Hz, 1 H), 2.07–2.04 (m, 1 H), 1.97–1.93 (m, 1 H), 1.79–1.76 (m, 1 H), 1.64–1.20 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 139.2, 138.1, 130.1, 130.0, 128.9, 127.2, 127.1, 78.1, 76.9, 42.9, 38.5, 38.3, 28.6, 27.8, 24.3, 20.9; IR (film) 1016 cm^{-1}. Anal calcd for $C_{21}H_{24}O$: C, 86.29; H, 8.27. Found: C, 86.29; H, 8.26.

(±)-(2*R*,3*aR*,7*aS*)-2-Biphenyl-4-ylmethyloctahydrobenzofuran (**26b**) Reaction of (±)-(1*S*,2*R*)-2-allylcyclohexanol (70 mg, 0.5 mmol) with 4-bromobiphenyl (232 mg, 1.0 mmol) following the general procedure afforded 102 mg (70 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.59 (m, 2 H), 7.55–7.53 (m, 2 H), 7.46–7.43 (m, 2 H), 7.37–7.32 (m, 3 H), 4.38–4.33 (m, 1 H), 3.23–3.18 (m, 1 H), 3.06 (dd, *J* = 5.2, 10.8 Hz, 1 H), 2.83 (dd, *J* = 5.6, 10.6 Hz, 1 H), 2.16–2.12 (m, 1 H), 2.10–2.05 (m, 1 H), 1.94–1.90 (m, 1 H), 1.85–1.83 (m, 1 H),

1.78–1.70 (m, 1 H), 1.50–1.44 (m, 1 H), 1.39–1.13 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 139.3, 138.3, 130.0, 129.0, 127.3, 127.2, 82.7, 79.4, 77.6, 46.5, 42.9, 38.1, 31.8, 29.3, 26.0, 24.6; IR (film) 1068 cm^{-1}. Anal calcd for $C_{21}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.48; H, 8.62.

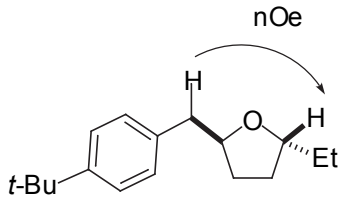
(±)-(2R,3aR,7aS)-2-Undec-2-enyloctahydrobenzofuran (**27**). Reaction of (35 mg, 0.25 mmol) of (±)-(1*S*,2*R*)-2-allylcyclohexanol with (*E*)-1-bromoundec-1-ene (109.5 mg, 0.50 mmol) following the general procedure afforded 29.5 mg (42 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.48–5.40 (m, 2 H), 4.07–4.02 (m, 1 H), 3.11–3.09 (m, 1 H), 2.35–2.29 (m, 1 H), 2.20–2.16 (m, 1 H), 2.09–1.70 (m, 11 H), 1.28–1.05 (m, 14 H), 0.87 (t, *J* = 6.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.1, 126.0, 82.4, 78.3, 46.3, 39.9, 37.4, 32.7, 31.9, 31.5, 29.5, 29.3, 29.2, 29.0, 25.7, 24.4, 22.7, 14.1; IR (film) 1061 cm^{-1}. Anal calcd for $C_{19}H_{34}O$: C, 81.95; H, 12.31. Found: C, 81.70; H, 12.17.

(±)-(2*R*,3*aR*,6*aR*)-2-(4-*tert*-Butylbenzyl)-hexahydrocyclopenta[*b*]furan (**28**). Reaction of (±)-(1*S*,2*S*)-2-allylcyclopentanol (31.5 mg, 0.25 mmol) with 1-bromo-4-*tert*-butylbenzene (106 mg, 0.50 mmol) following the general procedure afforded 32.5 mg (51 %) of the title compound as a pale yellow oil. This material was obtained with dr > 20:1 as judged by ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.30 (d, *J* = 6.0 Hz, 2 H), 7.16–7.13 (d, *J* = 9.0 Hz, 2 H), 4.60–4.57 (m, 1 H), 4.21–4.16 (m, 1 H), 2.90 (dd, *J* = 6.0, 15.0 Hz, 1 H), 2.67–2.59 (m, 2 H), 1.86–1.63 (m, 8 H), 1.38 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 135.9, 131.0, 128.8, 125.2, 84.5, 80.1, 42.6, 41.0, 39.3, 34.8, 32.9, 31.4, 24.9; IR (film) 1042 cm^{-1}. Anal calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.45; H, 10.21.

Assignment of Stereochemistry

2,5-Disubstituted Tetrahydrofurans (Table 3 and Table 5)

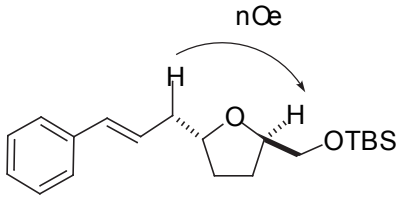
The trans stereochemistry of (±)-(2*R*,5*S*)-2-(4-*tert*-butylbenzyl)-5-ethyltetrahydrofuran (**12b**) was assigned on the basis of nOe signals between the hydrogen on C2 and one of the benzylic hydrogens on C1' as shown below.



The *trans*-stereochemistry of the remaining 2,5-disubstituted tetrahydrofuran products shown in Tables 3 and 5 was assigned based on analogy to the above molecule.

2,5- Disubstituted Alkoxymethyl Tetrahydrofurans (Table 4)

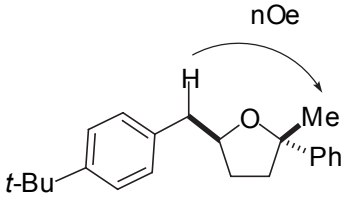
The trans stereochemistry of (±)- *tert*-butyldimethyl-{(2*R*,5*R*)-5-[(*E*)-3-phenylallyl]tetrahydrofuran-2-ylmethoxy}silane (**14e**) was assigned on the basis of nOe signals between the hydrogen on C2 and one of the benzylic hydrogens on C1' as shown below.



The *trans*-stereochemistry of the remaining 2,5-disubstituted tetrahydrofuran products shown in Table 4 were assigned based on analogy to the above molecule.

2,5,5-Trisubstituted Tetrahydrofurans (Table 6)

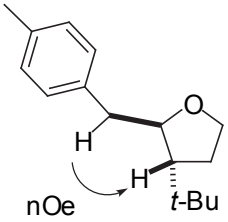
The trans stereochemistry of (±)-(2*R*,5*R*)-5-(4-*tert*-butylbenzyl)-2-methyl-2-phenyltetrahydrofuran (**19b**) was assigned on the basis of nOe signals between the methyl group attached to C2 and one of the benzylic hydrogens on C1' as shown below.



The *trans*-stereochemistry of the remaining 2,5,5-trisubstituted tetrahydrofuran products shown in Table 6 were assigned based on analogy to the above molecule.

2,3-Disubstituted Tetrahydrofurans (Table 7)

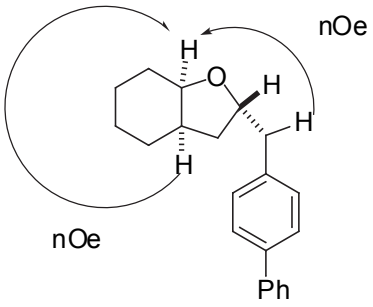
The trans stereochemistry of the 2,3-disubstituted tetrahydrofuran product (±)-(2*R*,3*S*)-3-*tert*-butyl-2-(4-methylbenzyl)tetrahydrofuran (**21e**) was assigned on the basis of nOe signals between the hydrogen attached to C3 and one of the benzylic hydrogens on C1' as shown below.



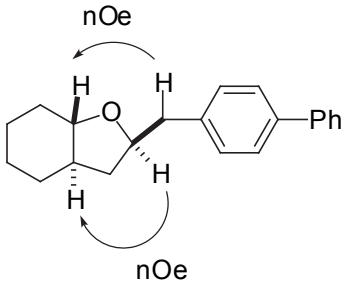
The *trans*-stereochemistry of the remaining 2,3-disubstituted tetrahydrofurans products shown in Table 7 were assigned based on analogy to the above molecule.

Octahydrobenzofurans (Table 9)

The relative stereochemistry of the octahydrobenzofuran product (±)-(2*R*,3*aR*,7*aR*)-2-biphenyl-4-ylmethyloctahydrobenzofuran (**26a**) was determined on the basis of nOe signals shown below.



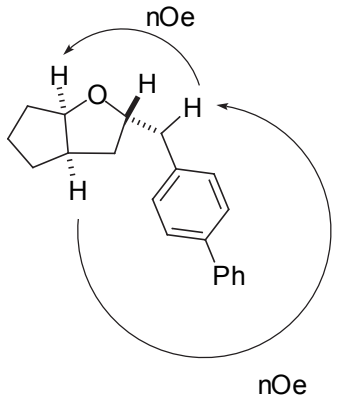
The relative stereochemistry at the C2, C3a, and C6a carbons of the octahydrobenzofuran product (±)-(2*R*,3*aR*,7*aS*)-2-biphenyl-4-ylmethyloctahydrobenzofuran (**26b**) was determined on the basis of nOe signals as shown below.



The relative stereochemistry of (±)-(2*R*,3*aR*,7*aS*)-2-undec-2-enyloctahydrobenzofuran (**27**) was assigned based on analogy to the above molecule.

Cyclopenta[*b*]furans (Table 9)

The relative stereochemistry of the cyclopenta[*b*]furan product (±)-(2*R*,3*aR*,6*aR*)-2-(4-*tert*-butylbenzyl)hexahydrocyclopenta[*b*]furan (**28**) was determined on the basis of nOe signals as shown below.



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