Supporting Information

A Copper Catalyzed Method for the Facially Selective Addition of Grignard Reagents to Cyclopropenes

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• Stereochemical assignments for **13** and **3** (Scheme 1)

The HWE protocol of Ogura¹ provided **28:29** as a 2.9:1 mixture that was separated by column chromatography using a gradient of EtOAc in hexane (the initial eluent was 4% EtOAc/hexane; **28** eluted first). The assignments of stereochemistry were based on the chemical shifts of the allylic hydrogens—those positioned *cis* to the ester resonate at relatively low field.^{1,2} Reduction of **28** with DIBAL (2.2 equiv, toluene, 0 °C→rt, 76% yield) and methylenation [CH_2I_2 (2.0 equiv), Zn (2.6 equiv), CuCl (2.6 equiv), Et_2O , reflux, 69% yield] gave **13**. Reaction of **13** with MOMCl (1.2 equiv) and $i\text{Pr}_2\text{NEt}$ (1.2 equiv) gave **3**. Similarly, a mixture of **28** and **29** was transformed into syn/anti mixtures

Scheme 1

of **13** and **3**.

• Stereochemical assignments for **14**, **16** and **18** (Schemes 2 and 3)

HWE reaction of 3-nonanone and trimethylphosphonoacetate gave **30** and **31** in nearly equal amounts (86% yield). Separation by column chromatography (the eluent was toluene) gave a 9:1 mixture of **31:30**. Again, assignments of stereochemistry were based on ^1H NMR chemical shifts of the allylic hydrogens. Subsequent reduction with DIBAL (2.3 equiv, pentane, rt) and Simmons-Smith reaction [CH_2I_2 (3.0 equiv), Zn (2.6 equiv), CuCl (2.6 equiv), Et_2O , reflux] gave a 9:1 mixture of **14:32** in 35% yield after removal of **Scheme 2**

unreacted **30** and **31** by ozonolysis (-78°C , CH_2Cl_2).

The assignments of **5**, **16** and **18** were proven by correlation with **14**. Reduction of **16** (prepared from vinylMgBr and **11**) with H₂/RaNi (EtOH, rt, 2h) gave **14:32** in a >99:1 ratio and in >65% yield as determined by GC and ¹H NMR. Reaction of **16** with MOMCl gave **5**. Removal of the TMS group of **18** with TBAF (1.3 equiv) in THF gave **33** in 76% yield. Reduction of **33** with H₂/RaNi gave a 6:4 mixture of **16** and **14**. Analysis of the ¹H NMR of the crude material indicated that these two materials composed >60% of the mixture; **32** was not detected, and **16** was the only vinyl product that was detected.

• The assignment of **4** was based on NOESY and COSY experiments. The assignments of **8**, **17**, **26** and **27** were established by selective 1-D NOE experiments using a double pulsed field gradient spin echo sequence.³ The spectra are displayed in the Supporting **Scheme 3**

Information.

Experimental Section

General Considerations All reactions were carried out in glassware that was flame-dried under vacuum and cooled under nitrogen. GC analyses were performed using either an HP5 or HP1 column and a FID detector. Pentane, toluene, THF, ether and CH_2Cl_2 were dried with columns packed with activated neutral alumina.⁴ Alternatively, pentane was distilled from Na/benzophenone. Cyclopropenes **1**, **11** and **12** were stored as 0.1 M solutions in pentane at -20°C . Copper(I)iodide (98%) and copper(I)chloride (99%) were purchased from Acros. Copper iodide was stored in the air. Copper chloride was stored in the glove box—small portions were removed and weighed in the air immediately before use. Methyl and ethyl Grignard reagents were purchased from Aldrich Chemical Co., others were prepared in a straightforward manner unless described otherwise.⁵ DIBAL was purchased from Aldrich either as a neat material (pentane solutions were prepared in the glove box), or as a 1.0 M solution in heptane. Tributyltin chloride (96%) was purchased from Aldrich Chemical Co. Methyl iodide was purchased from Acros Chemical Co., and prior to use was distilled from CaCl_2 . Yields in Tables 1 and 2 refer to isolated yields (average of 2 runs). Chromatography was performed on silica gel (ICN SiliTech 32-62D, 60Å). For ^1H NMR, the abbreviation 'app' stands for apparent (e.g. 'app d' = apparent doublet). For ^{13}C NMR, multiplicities were distinguished using an APT pulse sequence: typical methylene and quaternary carbons appear 'up' (u); methine and methyl carbons 'down' (dn). Exceptions are methine carbons of alkynes and cyclopropenes, which either have the same phase as 'normal' methylenes and quaternary carbons⁶ or, as in the case of **12**, do not appear at all in the APT experiment.

1-Hexyl-3-hydroxymethylcyclopropene (11). To a dry 100 mL round bottomed flask was added ethyl 1-hexylcyclopropen-3-ylcarboxylic ester⁷ (1.96 g, 10 mmol) and 25 mL pentane. The solution was cooled in a bath of dry ice/acetone, swept with nitrogen and stirred. A solution of DIBAL (2.98 g, 21.0 mmol) in 20 mL pentane was added dropwise via syringe, and the mixture was allowed to stir at -78°C for 1 h, and then at rt for 1 h. The mixture was quenched by 10% HCl (aq) and extracted with ether (3×20 mL). The organic phase was washed with water, dried (Na_2SO_4), filtered, and concentrated. Chromatography (20% ether in pentane) gave 1.43 g (93%) of the title compound, a colorless oil. ^1H NMR (CDCl_3 , 400 MHz, δ): 6.62 (m, 1H); 3.58 (dd, $J=10.6$, 4.1 Hz, 1H), 3.45 (ddd, $J=10.7$, 4.8 Hz, 1H), 2.47 (dt, $J=7.3$, 1.2 Hz, 2H), 1.68 (app dt, $J=4.4$, 1.6 Hz, 1H), 1.56 (m, 2H), 1.42–1.22 (m, 7H), 0.88 (t, $J=7.0$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 126.1 (u), 102.1 (u), 69.2 (u), 32.0 (u), 29.3 (u), 27.6 (u), 26.7 (u), 23.0 (u), 20.8 (dn), 14.5 (dn); IR (neat, cm^{-1}): 3334, 3133, 2955, 2921, 2857, 1770, 1460, 1426, 1378, 1014, 701; HRMS–CI (NH_3) m/z : [M–H] calcd for $\text{C}_{10}\text{H}_{17}\text{O}$, 153.1279; found, 153.1277.

1-Hexyl-3-hydroxymethyl-3-phenylcyclopropene (12). DIBAL (5.6 mmol; 5.6 mL of a 1.0 M solution in heptane) was added dropwise to a solution of methyl 1-butyl-3-phenylcyclopropen-3-ylcarboxylate⁷ (645 mg, 2.80 mmol) in pentane (50 mL) that had been cooled in a bath of dry ice/acetone. After stirring for 15 min at -78°C , the bath was removed, and stirring continued while the solution warmed to rt. The reaction was quenched by adding ca. 1 mL of EtOH, and the mixture was directly loaded onto a column of silica gel (2"×12"). Chromatography with 20% Et₂O/pentane gave 554 mg (98%) of the title compound as a clear oil. ¹H NMR (CDCl₃, 360 MHz, δ): 7.32–7.12 (m, 5H), 6.89 (m, 1H), 4.13 (d, $J=10.8$ Hz, 1H), 4.01 (d, $J=11.1$ Hz, 1H), 2.50 (m, 2H), 1.56 (m, 2H), 1.38 (m, 2H), 1.20 (bs, 1H), 0.88 (t, $J=6.8$ Hz, 3H); ¹³C NMR (CDCl₃, 90 MHz, δ): 146.0 (u), 128.4 (dn), 126.4 (dn), 126.3 (u), 125.6 (dn); 101.6 (not observed by APT); 67.9 (u), 31.7 (u), 29.6 (u), 24.8 (u), 22.6 (u), 13.9 (dn); IR (neat, cm^{-1}): 3366, 3082, 3056, 3021, 2956, 2929, 2871, 1773, 1599, 1493, 1465, 1445, 1424, 1378, 1064, 1008, 976, 771, 698; HRMS–CI (NH₃) m/z : [M⁺] calcd for C₁₄H₁₈O, 202.1358; found, 202.1348.

1-Hexyl-3-methoxymethoxymethyl cyclopropene (1). To a dry 100 mL round bottomed flask was added 1-hexyl-3-hydroxymethylcyclopropene (**11**) (770 mg, 5.00 mmol), N,N-di-isopropylethylamine (770 mg, 5.97 mmol) and 30 ml dichloromethane. The flask was swept with nitrogen and cooled in an ice bath. Methyl chloromethylether (480 mg, 6.00 mmol) was added via syringe, and the ice bath was removed. The mixture was allowed to stir for 2 h while warming to rt, at which point it was washed twice with 10 mL portions of water, dried (Na₂SO₄), filtered, and concentrated. Chromatography (10% ether in pentane) gave 910 mg (92%) of the title compound, a colorless oil. ¹H NMR (CDCl₃, 400 MHz, δ): 6.64 (m, 1H), 4.65 (s, 2H), 3.45 (dd, $J=10.0, 4.9$ Hz, 1H), 3.37 (dd, $J=10.0, 5.4$ Hz, 1H), 3.37 (s, 3H), 2.48 (app t, $J=7.2$ Hz, 2H), 1.68 (app dt, $J=5.3, 1.5$ Hz, 1H), 1.57 (m, 2H), 1.36–1.28 (m, 6H), 0.89 (t, 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 125.5 (u), 102.2 (u), 96.0 (u), 75.5 (u), 55.0 (dn), 31.6 (u), 28.9 (u), 27.1 (u), 26.3 (u), 22.6 (u), 17.6 (dn), 14.1 (dn); IR (neat, cm^{-1}): 3125, 2941, 2857, 1773, 1466, 1378, 1341, 1212, 1147, 1114, 1065, 1032, 918, 700; Anal. calcd for C₁₂H₂₂O₂: C, 72.7; H, 11.2. Found: C, 72.5; H, 11.5.

1 α -Hexyl-1 β -methyl-2 β -methoxymethoxymethyl cyclopropane (3). A dry 25 mL round bottomed flask was charged with a stirbar and CuCl (5.0 mg, 0.05 mmol) and fitted with a gas inlet with a septum adapter. The apparatus was evacuated, briefly (for ca. 2 sec) dried with an open flame, and filled with nitrogen after it had cooled to rt. 1-Hexyl-3-methoxymethoxymethyl cyclopropene (**1**) (0.50 mmol; 5.0 mL of 0.10 M solution in

pentane) and 5.0 mL dry pentane were added and the mixture was cooled in a bath of dry ice and ethylene glycol/ethanol⁸ (4:1; –20°C) and stirred vigorously. MeMgCl (1.20 mmol; 0.40 mL of a 3.0 M solution in THF) was added via syringe, and vigorous stirring was maintained for 1 h at –20°C. The reaction was quenched at –20 °C with 1% HCl (aq) and extracted with ether (3×5 mL). The organic layers were combined, washed with water, dried (Na₂SO₄), filtered, and concentrated. Analysis of the crude material by GC indicated that the ratio of the title compound to its 1β-hexyl–1α-methyl diastereomer was 95:5. Chromatography (10% ether in hexane) gave 91 mg (85%) of the title compound as a clear oil. The purity was determined to be 96% by GC and ¹H NMR analysis—contaminants were ca. 2.5% of the 1β-hexyl–1α-methyl-2β-methoxymethoxymethyl cyclopropane and ca. 1.5% of an uncharacterized impurity. A similar experiment gave 93 mg (87%) of the title compound. ¹H NMR (CDCl₃, 400 MHz, δ): 4.66 (d, *J*=6.4 Hz, 1H), 4.64 (d, *J*=6.4 Hz, 1H), 3.59 (dd, *J*=10.6, 6.8 Hz, 1H), 3.46 (dd, *J*=10.6, 8.2 Hz, 1H), 3.38 (s, 3H), 1.4–1.1 (m, 10H), 1.06 (s, 3H), 0.88 (t, *J*=6.8 Hz, 3H); 0.86 (m, 1H), 0.51 (dd, *J*= 4.5, 8.6 Hz, 1H), 0.10 (app t, *J*=4.8 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz, δ): 96.5 (u), 69.1 (u), 55.5 (dn), 41.5 (u), 32.4 (u), 29.9 (u), 27.0 (u), 23.4 (dn), 23.1 (u), 20.4 (u), 18.0 (u), 17.7 (dn), 14.6 (dn); IR (neat, cm^{–1}): 3059, 2991, 2954, 2856, 1461, 1213, 1148, 1106; HRMS–CI (NH₃) *m/z*: [M+NH₄] calcd for C₁₃H₃₀O₂N, 232.2277; found, 232.2266.

1β-Formyl-2α-hexyl-2β-methyl-3β-methoxymethoxymethyl cyclopropane (4). A dry 25 mL round bottomed flask was charged with a stirbar and CuCl (5 mg, 0.05 mmol) and fitted with a gas inlet with a septum adapter. The apparatus was evacuated, briefly (for ca. 2 sec) dried with an open flame, and filled with nitrogen after it had cooled to rt. 1-Hexyl-3-methoxymethoxymethyl cyclopropene (**1**) (0.50 mmol; 5.0 mL of 0.10 M solution in pentane) and 5.0 mL dry pentane were added and the mixture was cooled in a bath of dry ice and ethylene glycol/ethanol (4:1; –20°C) and stirred vigorously. MeMgBr (1.20 mmol; 0.40 mL of a 3.0 M solution in Et₂O) was added via syringe, and vigorous stirring was maintained for 1 h at –20°C. DMF (0.36 mL, 5.0 mmol) was added via syringe, the cold bath was removed, and the mixture allowed to stir for 1 h while warming to rt. The reaction was quenched with 1% HCl (aq) and extracted with ether (3×5 mL). The organic phase was washed with water, dried (Na₂SO₄), filtered, and concentrated. Analysis by GC indicated that the ratio of the title compound to an isomeric aldelyde (presumably 1α-formyl-2β-hexyl-2α-methyl-3β-methoxymethoxymethyl cyclopropane) was 95:5. Chromatography (10% ether in hexane) gave 79 mg (65%) of the title compound— a clear oil that was free of the isomeric impurity. The purity was measured by ¹H NMR and GC to be ≥99%. A similar experiment gave 82 mg (68%) of the title compound. ¹H NMR (CDCl₃, 400 MHz, δ):

9.58 (d, $J=5.2$ Hz, 1H), 4.64 (d, $J=6.7$ Hz, 1H), 4.62 (d, $J=6.6$ Hz, 1H), 3.97 (dd, $J=10.9, 7.4$ Hz, 1H), 3.84 (dd, $J=10.9, 7.6$ Hz, 1H), 3.35 (s, 3H), 1.76 (dd, $J=8.6, 5.2$ Hz, 1H), 1.68 (app dt, $J=8.6, 7.4$ Hz, 1H), 1.4–1.2 (m, 10H), 1.32 (s, 3H), 0.88 (t, $J=6.7$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 201.2 (dn), 96.7 (u), 63.3 (u), 55.7 (dn), 43.0 (u), 38.2 (dn), 35.8 (dn), 34.2 (u), 32.2 (u), 29.6 (u), 26.6 (u), 23.0 (u), 14.5 (dn), 12.8 (dn); IR (neat, cm^{-1}): 2961, 2928, 2857, 2773, 1725, 1687, 1468, 1442; HRMS–CI (NH_3) m/z : [M–H] calcd for $\text{C}_{14}\text{H}_{25}\text{O}_3$, 241.1804; found, 241.1793.

1 α -Hexyl-2 β -methoxymethoxymethyl-1 β -vinylcyclopropane (5). The procedure was identical to that used to prepare **3**, except that vinylmagnesium bromide (1.0 mmol; 2.5 mL of a 0.40 M solution in THF) and 30 mg (0.15 mmol) of CuI were used. Chromatography (10% ether in hexane) gave 90 mg (80%) of the title compound as a colorless oil. The purity was measured to be $\geq 95\%$ by ^1H NMR and GC. A similar experiment gave 92 mg (81%) of the title compound. ^1H NMR (CDCl_3 , 400 MHz, δ): 5.81 (dd, $J=17.2, 10.5$ Hz, 1H), 5.09 (dd, $J=10.5, 1.7$ Hz, 1H), 4.99 (dd, $J=17.2, 1.7$ Hz, 1H), 4.62 (d, $J=6.5$ Hz, 1H), 4.59 (d, $J=6.6$ Hz, 1H), 3.51 (dd, $J=10.6, 6.3$ Hz, 1H), 3.37 (m, 1H), 3.35 (s, 3H), 1.62 (m, 1H), 1.40–1.05 (m, 10H), 0.88 (t, $J=6.7$ Hz, 3H), 0.67 (dd, $J=8.4, 4.9$ Hz, 1H), 0.62 (app t, $J=5.2$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 139.2 (dn), 115.3 (u), 96.5 (u), 68.2 (u), 55.5 (dn), 38.8 (u), 32.3 (u), 29.9 (u), 29.3 (u), 27.2 (u), 25.4 (dn), 23.1 (u), 15.6 (u), 14.5 (dn); IR (neat, cm^{-1}): 3065, 2997, 2927, 2856, 1461, 1148, 1107, 1048, 917; HRMS–CI (NH_3) m/z : [M+] calcd for $\text{C}_{14}\text{H}_{26}\text{O}_2$, 226.1933; found, 226.1922.

1 α -Hexyl-2 β -methoxymethoxymethyl-3 β -methyl-1 β -vinylcyclopropane (6). A dry 25 mL round bottomed flask was charged with a stirbar and CuI (30 mg, 0.15 mmol) and fitted with a gas inlet with a septum adapter. The apparatus was evacuated, briefly (for ca. 2 sec) dried with an open flame, and filled with nitrogen after it had cooled to rt. 1-Hexyl-3-methoxymethoxymethyl cyclopropene (**1**) (0.50 mmol; 5.0 mL of 0.10 M solution in pentane) and 5.0 mL dry pentane were added and the mixture was cooled in a bath of dry ice and ethylene glycol/ethanol (4:1; -20°C) and stirred vigorously. Vinylmagnesium bromide (1.0 mmol; 2.5 mL of a 0.40 M solution in THF) was added via syringe, and vigorous stirring was maintained for 1 h at -20°C . MeI (710 mg, 5.0 mmol) was added via syringe, and the cold bath removed while stirring continued for 1 h as the mixture warmed to rt. The reaction was quenched with 1% HCl (aq) and extracted with ether (3 $\times$ 5 mL). The combined organics were washed with water, dried (Na_2SO_4), filtered, and concentrated. Analysis by GC indicated that the ratio of the title compound to an isomeric compound (presumably 1 β -hexyl-2 β -methoxymethoxymethyl-3 α -methyl-1 α -vinylcyclopropane) was 96:4. Chromatography (10% ether in hexane) gave

102 mg (85%) of the title compound. The purity of the compound was determined to be 95% by GC and ^1H NMR analysis—the most significant contaminant (presumably 1 β -hexyl-2 β -methoxymethoxymethyl-3 α -methyl-1 α -vinylcyclopropane) represented <3% of the chromatogram. A similar experiment gave 96 mg (80%) of the title compound. ^1H NMR (CDCl_3 , 400 MHz, δ): 5.61 (dd, J = 10.9, 17.5 Hz, 1H), 5.17 (dd, J = 10.9, 1.8 Hz, 1H), 5.09 (dd, J = 17.5, 1.8 Hz, 1H), 4.61 (m, 2H), 3.59 (dd, J = 10.5, 6.5 Hz, 1H), 3.49 (dd, J =10.7, 8.4 Hz, 1H), 3.34 (s, 3H), 1.45–1.17 (m, 10H), 1.07–0.92 (m, 5H), 0.85 (t, J =7.1 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 136.2 (dn), 117.1 (u), 96.6 (u), 65.1 (u), 55.6 (dn), 40.0 (u), 32.3 (u), 29.9 (u), 29.5 (u), 28.1 (dn), 26.8 (u), 23.1 (u), 23.0 (dn), 14.5 (dn), 9.6 (dn); IR (neat, cm^{-1}): 3084, 2993, 2927, 1630, 1466, 1260, 1146, 1106, 1047, 921, 804; HRMS–CI (NH_3) m/z : $[\text{M}–\text{OMe}]$ calcd for $\text{C}_{14}\text{H}_{25}\text{O}$, 209.1905; found, 209.1899.

1 α -Hexyl-2 β -methoxymethoxymethyl-3 β -tributylstannyl-1 β -vinylcyclopropane (7).

A dry 25 mL round bottomed flask was charged with a stirbar and CuI (30 mg, 0.15 mmol) and fitted with a gas inlet with a septum adapter. The apparatus was evacuated, briefly (for ca. 2 sec) dried with an open flame, and filled with nitrogen after it had cooled to rt. 1-Hexyl-3-methoxymethoxymethyl cyclopropene (**1**) (0.50 mmol; 5.0 mL of 0.10 M solution in pentane) and 5.0 mL dry pentane were added and the mixture was cooled in a bath of dry ice and ethylene glycol/ethanol (4:1; -20°C) and stirred vigorously. Vinylmagnesium bromide (1.0 mmol; 2.5 mL of a 0.40 M solution in THF) was added via syringe, and vigorous stirring was maintained for 1 h at -20°C . Tributyltin chloride (1.0 g, 3.0 mmol) was added via syringe, and stirring continued at rt for 1 h. The reaction was quenched by 1% HCl (aq) and extracted with ether (3 $\times$ 5 mL). The combined organics were washed with water, dried (Na_2SO_4), filtered, and concentrated.

Chromatography (3% ether in hexane) gave 186 mg (72%) of the title compound. Analysis by ^1H NMR indicated that the purity was $\geq 95\%$. The compound was not suitable for analysis by GC. A similar experiment gave 209 mg (81%) of the title compound. ^1H NMR (CDCl_3 , 400 MHz, δ): 5.54 (m, 1H), 5.15–5.05 (m, 2H), 4.64 (m, 2H), 3.54 (dd, J = 10.5, 6.2 Hz, 1H), 3.42 (dd, J = 8.7, 10.5 Hz, 1H), 3.36 (s, 3H), 1.64 (m, 1H), 1.50–1.20 (m, 22H), 0.90–0.80 (m, 18H), 0.31 (d, J =9.7 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 141.2 (dn; $J_{\text{C-Sn}}$ =27 Hz), 114.7 (u), 96.5 (u), 69.4 (u; $J_{\text{C-Sn}}$ =29 Hz), 55.6 (dn), 40.3 (u), 32.3 (u), 30.8 (u), 30.5 (dn), 30.1 (u; $J_{\text{C-Sn}}$ =19 Hz), 29.5 (u, $J_{\text{C-Sn}}$ =20 Hz), 27.4 (u, $J_{\text{C-Sn}}$ =57 Hz), 26.8 (u), 22.6 (u), 17.2 (dn, $J_{\text{C-Sn}}$ = 370, 352 Hz), 14.1 (dn), 13.7 (dn), 10.7 (u, $J_{\text{C-Sn}}$ =333, 319 Hz); IR (neat, cm^{-1}): 2957, 2927, 1607, 1516, 1464, 1457, 1150, 1106, 1042; HRMS–CI (NH_3) m/z : $[\text{M}–\text{C}_4\text{H}_9]$ calcd for $\text{C}_{22}\text{H}_{43}\text{O}_2\text{Sn}$, 459.2285; found, 459.2291.

1 β -(cis-propen-1-yl)-1 β -hexyl-2 β -methoxymethoxymethyl cyclopropane (8). The

procedure was identical to that used to prepare **3**, except that cis-propen-1-yl magnesium bromide (1.0 mmol; 2.5 mL of a 0.40 M solution in THF) and 30 mg (0.15 mmol) of CuI were used, and that the reaction was conducted at $-40\text{ }^{\circ}\text{C}$. cis-Propen-1-yl magnesium bromide was prepared from cis-1-bromopropene (3.02 g, 25.0 mmol) and Mg turnings (720 mg, 29.6 mmol) in THF (40 mL). The turnings were activated by sequential washings with 1% HCl (aq) (3×15 mL), water (3×20 mL), acetone (3×20 mL) and ether (4×15 mL). The Mg was then dried under vacuum and stored under nitrogen. Before addition of the bromoalkene to the Mg/THF, the turnings were further activated by addition of dibromoethane (0.1 mL). To maintain the temperature below $25\text{ }^{\circ}\text{C}$ (which is necessary to minimize isomerization to trans-1-propenylmagnesium bromide)⁵, the bromoalkene (as a solution in 10 mL THF) was added dropwise over the course of an hour, and the reaction was cooled by a water bath that was maintained below $25\text{ }^{\circ}\text{C}$. The ratio of cis/trans-propen-1-ylmagnesium bromide was determined to be 9:1 by adding a sample of the reagent to benzaldehyde and analyzing the mixture by GC and ^1H NMR. The reagent was stored in a freezer to prevent further isomerization⁵, and the cis/trans ratio was assayed immediately before use. From the addition of the Grignard reagent with **1**, two adducts were detected by GC in a ratio of 7:1— the title compound and an adduct from trans-propen-1-yl magnesium bromide, respectively. Chromatography (10% ether in hexane) gave 97 mg (81%) of the title compound, a colorless oil. Analysis by GC indicated that the purity of the compound was $\geq 98\%$, and analysis of the ^1H NMR spectrum indicated that the purity was $\geq 95\%$. A similar experiment gave 96 mg (80%) of the title compound. ^1H NMR (CDCl_3 , 400 MHz, δ): 5.59 (dq, $J = 10.8, 6.8\text{ Hz}$, 1H), 5.51 (m, 1H), 4.65 (d, $J = 6.5\text{ Hz}$, 1H), 4.63 (d, $J = 6.5\text{ Hz}$, 1H), 3.41 (m, 2H), 3.37 (s, 3H), 1.70 (dd, $J = 6.6, 1.5\text{ Hz}$, 3H), 1.40–1.20 (m, 10H), 0.97 (m, 1H), 0.88 (t, $J = 6.7\text{ Hz}$, 3H), 0.80 (dd, $J = 8.3, 4.5\text{ Hz}$, 1H), 0.45 (app t, $J = 4.8\text{ Hz}$, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 130.4 (dn), 129.6 (dn), 96.6 (u), 69.8 (u), 55.5 (dn), 40.7 (u), 32.4 (u), 29.9 (u), 27.5 (u), 24.4 (u), 23.1 (u), 23.1 (dn), 18.5 (u), 14.8 (dn), 14.6 (dn); IR (neat, cm^{-1}): 3062, 2994, 2955, 2927, 2857, 1461, 1261, 1147, 1049; HRMS–CI (NH_3) m/z : [$\text{M}-\text{OCH}_3$] calcd for $\text{C}_{14}\text{H}_{25}\text{O}$, 209.1905; found, 209.1904.

1 α -Hexyl-2 β -hydroxymethyl-1 β -methylcyclopropane (13). A dry 25 mL round bottomed flask was charged with a stirbar and CuI (10 mg, 0.05 mmol) and fitted with a gas inlet with a septum adapter. The apparatus was evacuated, briefly (for ca. 2 sec) dried with an open flame, and filled with nitrogen after it had cooled to rt. 1-Hexyl-3-hydroxymethylcyclopropene (**11**) (0.50 mmol; 5.0 mL of 0.10 M solution in pentane) and 5.0 mL dry pentane were added and the mixture was stirred vigorously (so that a vortex formed). MeMgBr (1.8 mmol, 0.60 mL of a 3.0 M solution in Et_2O) was added via syringe and a vortex maintained for 1 h. [Note: for this particular reaction, we observed

several times that the reaction did not proceed if stirring was not vigorous. In those cases, the reagent solidified to form an unreactive cake at the bottom of the flask. However, the addition reaction was reproduced more than 10 times by 3 different workers when the reactions were stirred to vortex]. The reaction was quenched with 1% HCl (aq) and extracted with ether (3×5 mL). The combined organics were washed with water, dried (Na₂SO₄), filtered, and concentrated. Chromatography (20% ether in hexane) gave 70 mg (82%) of the title compound, a clear oil that was ≥95% pure as determined by ¹H NMR. The major impurity by ¹H NMR was 1β-hexyl-1α-methyl-2β-hydroxymethylcyclopropane, which was estimated by ¹H NMR to compose 3% of the product. The purity by GC was measured to be ≥99%. A similar experiment gave 71 mg (83%) of the title compound. ¹H NMR (CDCl₃, 400 MHz, δ): 3.73 (dd, *J*= 11.4, 6.7 Hz, 1H), 3.52 (dd, *J*= 11.4, 8.5 Hz, 1H), 1.40–1.10 (m, 11H), 1.08 (s, 3H), 0.89 (m, 1H), 0.88 (t, *J*=7.0 Hz, 3H), 0.50 (dd, *J*= 8.6, 4.4 Hz, 1H), 0.13 (app t, *J*= 4.8 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz, δ): 64.5 (u), 41.6 (u), 32.3 (u), 29.9 (u), 27.2 (u), 26.4 (dn), 23.1 (u), 20.6 (u), 18.1 (u), 17.6 (dn), 14.6 (dn); IR (neat, cm⁻¹): 3344, 3057, 2989, 2923, 1466, 1382, 1262, 1081, 1014; HRMS–CI (NH₃) *m/z*: [M–OH] calcd for C₁₁H₂₁, 153.1643; found, 153.1645.

1β-Ethyl-1α-Hexyl-2β-hydroxymethylcyclopropane (14). The procedure was identical to that used to prepare **13**, except that 30 mg (0.15 mmol) of CuI and ethylmagnesium bromide (1.7 mmol; 0.85 mL of a 2.0 M solution in ether) were used. Chromatography (15% ether in hexane) gave 72 mg (78%) of a clear oil. GC analysis indicated that three compounds were formed in ratio of 79:12:9. The first of these was identified as the title compound, and the second as 1α-ethyl-1β-hexyl-2β-hydroxymethylcyclopropane. Spectral data for the mixture are displayed.

1β-Benzyl-1α-hexyl-2β-hydroxymethylcyclopropane (15). A dry 25 mL round bottomed flask was charged with a stirbar and CuI (30 mg, 0.15 mmol) and fitted with a gas inlet with a septum adapter. The apparatus was evacuated, briefly (for ca. 2 sec) dried with an open flame, and filled with nitrogen after it had cooled to rt. 1-Hexyl-3-hydroxymethylcyclopropene (**11**) (0.50 mmol; 5.0 mL of 0.10 M solution in pentane) and 5.0 mL dry pentane were added and the mixture was cooled in a bath of ethylene glycol/ethanol (4:1, –20 °C) and stirred vigorously. Benzylmagnesium chloride (3.5 mmol, 7.0 mL of a 0.5 M solution in THF) was then added dropwise via syringe over 10 min, and the mixture stirred vigorously at –20 °C for 1h. The reaction was quenched with 1% HCl (aq) and extracted with ether (3×5 mL). The combined organics were washed with water, dried (Na₂SO₄), filtered, and concentrated. Chromatography (15% ether in hexane) gave 97 mg (79%) of the title compound, a clear oil. The material was

judged to be 95% pure by ^1H NMR, and $\geq 96\%$ pure by GC. Similar experiments gave 94 mg (76%) and 96 mg (78%) of the title compound. ^1H NMR (CDCl_3 , 400 MHz, δ): 7.34–7.25 (m, 5H), 3.81 (dd, $J = 11.5, 6.9$ Hz, 1H), 3.72 (dd, $J = 11.4, 8.2$ Hz, 1H), 2.86 (d, $J = 14.9$ Hz, 1H), 2.61 (dd, $J = 14.9$ Hz, 1H), 1.45–1.15 (m, 10H), 1.05 (m, 1H), 0.89 (m, 1H), 0.88 (t, $J = 7.1$ Hz, 3H), 0.65 (dd, $J = 9.4, 4.7$ Hz, 1H), 0.49 (app t, $J = 5.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 140.7 (u), 129.4 (dn), 128.7 (dn), 126.4 (dn), 64.1 (u), 37.4 (u), 36.6 (u), 32.2 (u), 29.8 (u), 26.9 (u), 26.3 (dn), 25.7 (u), 23.0 (u), 17.7 (u), 14.5 (dn); IR (neat, cm^{-1}): 3343, 2954, 2925, 2855, 1601, 1495, 1454, 1029, 698; HRMS–CI (NH_3) m/z : $[\text{M} - \text{OH}]$ calcd for $\text{C}_{17}\text{H}_{25}$, 229.1956; found, 229.1946.

1 α -Hexyl-2 β -hydroxymethyl-1 β -vinylcyclopropane (16). The procedure was identical to that used to prepare **13**, except that 30 mg (0.15 mmol) of CuI and vinylmagnesium bromide (1.5 mmol; 3.8 mL of a 0.4 M solution in THF) were used. Chromatography (20% ether in hexane) gave 73 mg (80%) of the title compound, a clear oil. The material was judged to be $\geq 95\%$ pure by NMR, and $\geq 99\%$ pure by GC. A similar experiment gave 75 mg (82%) of the title compound. ^1H NMR (CDCl_3 , 400 MHz, δ): 5.81 (dd, $J = 17.2, 10.6$ Hz, 1H), 5.13 (dd, $J = 10.6, 1.5$ Hz, 1H), 5.04 (dd, $J = 17.3, 1.6$ Hz, 1H), 3.70 (dd, $J = 11.6, 6.2$ Hz, 1H), 3.41 (dd, $J = 11.6, 9.0$ Hz, 1H), 1.6 (m, 1H), 1.4–1.1 (m, 11H), 0.88 (t, $J = 6.8$ Hz, 3H), 0.71–0.63 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 139.1 (dn), 115.6 (u), 63.6 (u), 38.6 (u), 32.3 (u), 29.9 (u), 28.7 (dn), 28.3 (u), 27.3 (u), 23.1 (u), 16.5 (u), 14.5 (dn); IR (neat, cm^{-1}): 3370, 3064, 2955, 2856, 1631, 1461, 1036, 910; HRMS–CI (NH_3) m/z : $[\text{M} +]$ calcd for $\text{C}_{12}\text{H}_{22}\text{O}$, 182.1671; found, 182.1664.

1 α -Hexyl-2 β -hydroxymethyl-1 β -(2-propenyl)cyclopropane (17). The procedure was identical to that used to prepare **13** except that 30 mg (0.15 mmol) of CuI and 2-propenylmagnesium bromide (1.5 mmol; 3.8 mL of a 0.4 M solution in THF) were used. Chromatography (20% ether in hexane) gave 79 mg (81%) of the title compound, a clear oil. The material was judged to be $\geq 94\%$ pure by ^1H NMR. The GC trace of the purified material indicated that three compounds were present in a ratio of 95:4:1. A similar experiment gave 80 mg (82%) of the title compound. ^1H NMR (CDCl_3 , 400 MHz, δ): 4.91 (m, 1H), 4.75 (m, 1H), 3.54 (dd, $J = 11.1, 7.4$ Hz, 1H), 3.42 (dd, $J = 11.1, 6.9$ Hz, 1H), 1.95 (m, 1H), 1.76 (s, 3H), 1.33–1.16 (m, 10H), 1.08–1.00 (m, 1H), 0.87 (t, $J = 6.7$ Hz, 3H), 0.75 (m, 1H), 0.63–0.55 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 144.8 (u), 114.3 (u), 63.7 (u), 38.1 (u), 33.0 (u), 32.5 (u), 29.7 (u), 27.1 (u), 26.9 (dn), 23.1 (u), 22.0 (dn), 15.2 (u), 14.5 (dn); IR (neat, cm^{-1}): 3319, 2078, 2997, 2957, 2856, 1645, 1456, 1362, 1041, 1026, 896; HRMS–CI (NH_3) m/z : $[\text{M} +]$ calcd for $\text{C}_{13}\text{H}_{24}\text{O}$, 196.1827; found, 196.1831

1 α -Hexyl-2 β -hydroxymethyl-1 β -(trimethylsilylethynyl)cyclopropane (18). The procedure was identical to that used to prepare **13** except that 30 mg (0.15 mmol) of CuI and trimethylsilylethynylmagnesium bromide (prepared as described below; 1.6 mmol; 4.1 mL of a 0.40 M solution in THF) were used. Chromatography (20% ether in hexane) gave 96 mg (76%) of the title compound. Only one peak was detected in the GC trace. The purity by NMR was measured to be $\geq 98\%$. A similar experiment gave 98 mg (78%) of the title compound.

Trimethylsilylethynylmagnesium bromide was prepared as follows: a 100 ml round bottomed flask was fitted with a gas inlet with septum adapter, evacuated and filled with nitrogen. Trimethylsilylacetylene (2.80 g, 30.0 mmol) and THF (40 mL) were sequentially added via syringe, and the flask was cooled in bath of dry ice and ethylene glycol/ethanol (1:1; $-50\text{ }^{\circ}\text{C}$). MeLi (32 mmol; 20 mL of a 1.6 M solution in ether) was added dropwise over the course of 45-60 min. The bath was then removed and stirring continued for 1 h while the mixture warmed to rt. The nitrogen pressure was increased, the septum removed, and $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$ (7.7 g; 30 mmol) added as a solid in a single portion. The septum was replaced, additional THF (10 mL) was used to rinse the sides of the flask, and the mixture allowed to stir for 1 h.

Spectral data for **18**: ^1H NMR (CDCl_3 , 400 MHz, δ): 3.91 (m, 1H), 3.52 (m, 1H), 1.87 (m, 1H), 1.52–1.15 (m, 11H), 0.89 (t, $J=7.1$ Hz, 3H), 0.82–0.77 (m, 2H), 0.14 (s, 9H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 109.6 (u), 83.7 (u), 65.1 (u), 38.5 (u), 32.2 (u), 29.4 (u), 28.8 (dn), 27.9 (u), 23.0 (u), 20.7 (u), 18.1 (u), 14.5 (dn), 0.6 (dn); IR(neat, cm^{-1}): 3341, 2957, 2928, 2857, 2147, 1454, 1249, 1044, 842, 759; HRMS–CI (NH_3) m/z : $[\text{M}-\text{H}]$ calcd for $\text{C}_{15}\text{H}_{27}\text{OSi}$, 251.1831; found, 251.1824.

1 α -Hexyl-2 β -hydroxymethyl-1 β -(phenylethynyl)cyclopropane (19). The procedure was identical to that used to prepare **13** except that 30 mg (0.15 mmol) of CuI and phenylethynylmagnesium bromide (prepared as described below; 1.6 mmol; 4.1 mL of a 0.40 M solution in THF) were used. Chromatography (25% ether in hexane) gave 94 mg (73%) of the title compound. The purity was measured to be $>99\%$ by GC and $>95\%$ by ^1H NMR. A similar experiment gave 97 mg (76%) of the title compound.

Phenylethynylmagnesium bromide was prepared as follows: a dry 100 ml round bottomed three-neck flask was fitted with a gas inlet, reflux condenser and a dropping funnel. The apparatus was evacuated, filled with nitrogen. Phenylacetylene (3.10 g, 30.0 mmol) and THF (60 mL) were sequentially added via syringe. MeMgBr (30 mmol; 10 mL of a 3.0 M solution in ether) was added dropwise over the course of 1 h, and the mixture was heated and stirred at reflux temperature for 1 h and subsequently cooled to rt.

Spectral data for **19**: ^1H NMR (CDCl_3 , 400 MHz, δ): 7.38–7.26 (m, 5H), 3.94 (m, 1H), 3.65 (m, 1H), 1.77 (dd, J = 10.0, 4.8 Hz, 1H); 1.64–1.25 (m, 11H), 0.92–0.85 (m, 5H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 132.0 (dn), 128.7 (dn), 128.1 (dn), 123.9 (u), 92.2 (u), 79.6 (u), 65.3 (u), 38.9 (u), 32.3 (u), 29.5 (u), 28.9 (dn), 28.2 (u), 23.1 (u), 20.6 (u), 18.1 (u), 14.5 (dn); HRMS–CI (NH_3) m/z : $[\text{M}^+]$ calcd for $\text{C}_{18}\text{H}_{24}\text{O}$, 256.1827; found, 256.1827.

Lactone 20. The procedure was identical to that used to prepare **13**, except that the reaction was quenched with an excess of freshly crushed dry ice. The reaction was allowed to stir for 1h at rt while the dry ice dissipated. After acidification with 1% HCl (aq) and extraction with CHCl_3 (3 $\times$ 10 mL), the organics were combined, washed with water, dried (Na_2SO_4), filtered, and concentrated. Chromatography (7% ether in hexane) gave 56 mg (57%) of lactone **20**, a clear oil. The purity by GC was measured to be $\geq 97\%$, and the purity by ^1H NMR measured to be $\geq 96\%$. A similar experiment gave 67 mg (68%) of **20**. ^1H NMR (CDCl_3 , 400 MHz, δ): 4.38 (dd, J = 9.9, 5.5 Hz, 1H); 4.15 (app dt, J = 9.9, 0.9 Hz, 1H), 2.04 (m, 1H), 1.95 (dd, J = 6.4, 0.9 Hz, 1H), 1.43–1.21 (m, 10H), 1.14 (s, 3H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 175.5 (u), 66.9 (u), 39.6 (u), 32.1 (u), 30.3 (dn), 29.8 (dn), 29.7 (u), 27.3 (u), 26.8 (u), 23.0 (u), 14.5 (dn), 12.2 (dn); IR(neat, cm^{-1}): 2960, 2930, 2858, 1777, 1260, 1173, 1097, 1043; HRMS–CI (NH_3) m/z : $[\text{M}+\text{H}]$ calcd for $\text{C}_{12}\text{H}_{21}\text{O}_2$, 197.1542; found, 197.1539.

Lactone 21. A dry 25 mL round bottomed flask was charged with a stirbar and CuI (30 mg, 0.15 mmol) and fitted with a gas inlet with a septum adapter. The apparatus was evacuated, briefly (for ca. 2 sec) dried with an open flame, and filled with nitrogen after it had cooled to rt. 1-Hexyl-3-hydroxymethylcyclopropene (**11**) (0.50 mmol; 5.0 mL of 0.10 M solution in pentane) and 5.0 mL dry pentane were added and the mixture was stirred vigorously (so that a vortex formed). Vinylmagnesium bromide (1.5 mmol, 3.8 mL of a 0.40 M solution in THF) was added via syringe and a vortex maintained for 1 h. The reaction was quenched with an excess of freshly crushed dry ice, and then allowed to stir for 1h at rt while the dry ice dissipated. After acidification with 1% HCl (aq) and extraction with CHCl_3 (3 $\times$ 10 mL), the organics were combined, washed with water, dried (Na_2SO_4), filtered, and concentrated. Chromatography (7% ether in hexane) gave 68 mg (65%) of lactone **21**, a clear oil. The purity by GC was measured to be 99%, and the purity by ^1H NMR measured to be 96%. A similar experiment gave 59 mg (57%) of **21**. ^1H NMR (CDCl_3 , 400 MHz, δ): 5.72 (dd, J =17.2, 10.8 Hz, 1H), 5.41–5.35 (m, 2H), 4.36 (dd, J = 9.9, 5.4 Hz, 1H), 4.17 (m, 1H), 2.21–2.14 (m, 2H), 1.56–1.22 (m, 10H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 175.2 (u), 131.8 (dn), 121.3 (u), 66.8 (u), 37.6 (u), 33.9 (u), 32.1 (u), 30.98 (dn), 30.96 (dn), 29.6 (u), 26.7 (u), 22.9 (u), 14.5 (dn); IR(neat, cm^{-1}): 2958, 2930, 2858, 1771, 1652, 1635, 1446, 1175, 1043; HRMS–CI

(NH₃) *m/z*: [M+H] calcd for C₁₃H₂₁O₂, 209.1542; found, 209.1542.

1 α -Hexyl-2 β -hydroxymethyl-3 β -iodo-1 β -vinylcyclopropane (22). A dry 25 mL round bottomed flask was charged with a stirbar and CuI (30 mg, 0.15 mmol) and fitted with a gas inlet with a septum adapter. The apparatus was evacuated, briefly (for ca. 2 sec) dried with an open flame, and filled with nitrogen after it had cooled to rt. 1-Hexyl-3-hydroxymethylcyclopropene (**11**) (0.50 mmol; 5.0 mL of 0.10 M solution in pentane) and 5.0 mL dry pentane were added and the mixture was stirred vigorously (so that a vortex formed). Vinylmagnesium bromide (1.5 mmol, 3.8 mL of a 0.4 M solution in THF) was added via syringe and a vortex maintained for 1 h. Crystals of I₂ (760 mg, 3.0 mmol) were added directly to the mixture, and stirring continued for another hour. The reaction was quenched with 1% HCl (aq) and then saturated Na₂SO₃ (aq) was added to reduce unreacted I₂. The mixture was extracted with ether (3 $\times$ 10 mL), dried (Na₂SO₄), filtered, concentrated and chromatographed (15% ether in hexane) to give 131 mg (85%) of the title compound as a pale yellow oil. The purity of the material was measured to be 95% by ¹H NMR analysis. The compound was not suitable for analysis by GC. A similar experiment gave 125 mg (81%) of the title compound. ¹H NMR (CDCl₃, 400 MHz, δ): 5.63 (dd, *J*= 17.5, 10.9 Hz, 1H), 5.33 (dd, *J*= 10.9, 1.3 Hz, 1H), 5.21 (dd, *J*=17.5, 1.3 Hz, 1H), 3.74 (dd, *J*=11.9, 6.4 Hz, 1H), 3.60 (dd, *J*=11.9, 8.3 Hz, 1H), 2.86 (d, *J*= 7.8 Hz, 1H), 1.72 (m, 1H), 1.4–1.2 (m, 10H), 1.14 (app dt, *J*=8.0, 6.4 Hz, 1H), 0.88 (t, *J*=9.0 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz, δ): 138.7 (dn), 118.7 (dn), 65.4 (u), 38.7 (u), 32.2 (u), 30.4 (dn), 29.8 (u), 29.4 (u), 26.4 (u), 23.0 (u), 14.5 (dn), 8.1 (dn); IR(neat, cm⁻¹): 3335, 3085, 2954, 2926, 2856, 1232, 1177, 1027, 908; HRMS–CI (NH₃) *m/z*: [M–H] calcd for C₁₂H₂₀OI, 307.0559; found, 307.0545.

1 α -Hexyl-2 β -hydroxymethyl-3 β -iodo-1 β -methylcyclopropane (23). The procedure was identical to that used to prepare **22**, except that MeMgBr (1.8 mmol, 0.60 mL of a 3.0 M solution) and 10 mg of CuI (0.05 mmol) were used. Chromatography gave 123 mg (83%) of the title compound, a pale yellow oil. The material was judged to be $\geq$ 98% pure by analysis of the ¹H NMR spectrum and GC trace. A similar experiment gave 115 mg (78%) of the title compound. ¹H NMR (CDCl₃, 400 MHz, δ): 3.74 (m, 1H), 3.60 (m, 1H), 2.69 (d, *J*=7.9 Hz, 1H), 1.46 (m, 1H), 1.40–1.22 (m, 10H), 1.11 (s, 3H), 0.90–0.84 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz, δ): 65.1 (u), 41.4 (u), 32.3 (u), 29.7 (u), 27.9 (dn), 26.8 (u), 23.9 (u), 23.0 (u), 18.9 (dn), 14.5 (dn), 9.1 (dn); IR(neat, cm⁻¹): 3343, 2954, 928, 2855, 1461, 1383, 1023; HRMS–CI (NH₃) *m/z*: [M+NH₄] calcd for C₁₁H₂₅NOI, 314.0980; found, 314.0968.

1 α -Hexyl-2 β -hydroxymethyl-3 β -tributylstannyl-1 β -vinylcyclopropane (24). A dry 25 mL round bottomed flask was charged with a stirbar and CuI (30 mg, 0.15 mmol) and fitted with a gas inlet with a septum adapter. The apparatus was evacuated, briefly (for ca. 2 sec) dried with an open flame, and filled with nitrogen after it had cooled to rt. 1-Hexyl-3-hydroxymethylcyclopropene (**11**) (0.50 mmol; 5.0 mL of 0.10 M solution in pentane) and 5.0 mL dry pentane were added and the mixture was stirred vigorously (so that a vortex formed). Vinylmagnesium bromide (1.5 mmol, 3.8 mL of a 0.4 M solution in THF) was added via syringe and a vortex maintained for 1 h. Tributyltin chloride (1.0 g, 5.0 mmol) was added via syringe, and stirring continued for 1 h. The reaction was quenched with 1% HCl (aq) and extracted with ether (3 $\times$ 5 mL). The combined organics were washed with water, dried (Na₂SO₄), filtered, and concentrated. Chromatography (10% ether in hexane) gave 160 mg (68%) of the title compound, a clear oil. Analysis of the ¹H NMR spectrum indicated that the material was $\geq$ 98% pure. The material was not suitable for analysis by GC. A similar experiment gave 172 mg (73%) of the title compound. ¹H NMR (CDCl₃, 400 MHz, δ): 5.56 (m, 1H), 5.18–5.12 (m, 2H), 3.74 (m, 1H), 3.41 (m, 1H), 1.55–0.82 (m, 41H), 0.34 (d, J = 9.5 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz, δ): 141.2 (dn), 115.1 (u), 65.1 (u, J_{C-Sn} =29.0 Hz), 39.9 (u), 33.8 (dn, J_{C-Sn} =19.1 Hz), 32.3 (u), 30.6 (u), 30.1 (u), 29.6 (u, J_{C-Sn} =19.9 Hz), 27.8 (u), 27.4 (u), 23.1 (u), 18.6 (dn, J_{C-Sn} =362 Hz), 14.5 (dn), 14.1 (dn), 11.1 (u, J_{C-Sn} =334, 318 Hz); IR(neat, cm⁻¹): 3336, 2854, 1627, 1456, 1375, 1021. Further support for the assigned structure was provided by treating **24** with MOMCl and diisopropylethyl amine in THF, which gave **7** in 57% yield.

1 α -Butyl-2 β -hydroxymethyl-2 α -phenyl-1 β -vinylcyclopropane (25). A dry 25 mL round bottomed flask was charged with a stirbar and CuI (30 mg, 0.15 mmol) and fitted with a gas inlet with a septum adapter. The apparatus was evacuated, briefly (for ca. 2 sec) dried with an open flame, and filled with nitrogen after it had cooled to rt. 1-Butyl-3-hydroxymethyl-3-phenylcyclopropene (**12**) (0.30 mmol; 3.0 mL of 0.10 M solution in pentane) and 5.0 mL dry pentane were added and the mixture was stirred vigorously (so that a vortex formed). Vinylmagnesium bromide (1.0 mmol, 2.5 mL of a 0.4 M solution in THF) was added via syringe and a vortex maintained for 1 h. The reaction was quenched with 1% HCl (aq) and extracted with ether (3 $\times$ 5 mL). The combined organics were washed with water, dried (Na₂SO₄), filtered, and concentrated. Chromatography (25% ether in hexane) gave 59 mg (85%) of the title compound, a clear oil. The purity by NMR was $\geq$ 98%, and only one peak was detected in the GC trace of the purified material. A similar experiment gave 58 mg (84%) of the title compound. ¹H NMR (CDCl₃, 400 MHz, δ): 7.37–7.22 (m, 5H), 6.02 (dd, J = 17.2, 10.5, 1H), 5.25 (dd, J =10.3, 1.5 Hz, 1H),

5.14 (dd, $J=17.2, 1.6$ Hz, 1H), 3.78 (dd, $J=11.6, 4.2$ Hz, 1H), 3.61 (dd, $J=11.5, 7.2$ Hz, 1H), 1.55 (m, 1H), 1.40–1.25 (m, 2H), 1.23 (dd, $J=5.1, 1.5$ Hz, 1H), 1.20–1.04 (m, 3H), 1.00 (d, $J=5.1$ Hz, 1H), 0.76 (t, $J=7.2$ Hz, 3H), 0.47 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 141.0 (u), 139.7 (dn), 130.6 (dn), 128.8 (dn), 127.1 (dn), 116.8 (u), 68.9 (u), 39.6 (u), 35.5 (u), 34.0 (u), 29.8 (u), 23.1 (u), 20.5 (u), 14.5 (dn); IR (neat, cm^{-1}): 3396, 3059, 2871, 1634, 1602, 1494, 1446, 1378, 1029, 913; HRMS–CI (NH_3) m/z : $[\text{M}+\text{H}]$ calcd for $\text{C}_{16}\text{H}_{23}\text{O}$, 231.1749; found, 231.1739.

1 α -Butyl-2 β -hydroxymethyl-1 β -methyl-2 α -phenylcyclopropane (26). A dry 25 mL round bottomed flask was charged with a stirbar and CuI (30 mg, 0.15 mmol) and fitted with a gas inlet with a septum adapter. The apparatus was evacuated, briefly (for ca. 2 sec) dried with an open flame, and filled with nitrogen after it had cooled to rt. 1-Butyl-3-hydroxymethyl-3-phenylcyclopropene (**12**) (0.50 mmol; 5.0 mL of 0.10 M solution in pentane) and 5.0 mL dry pentane were added and the mixture was stirred vigorously (so that a vortex formed). MeMgBr (2.0 mmol, 0.7 mL of a 3.0 M solution in ether) was added via syringe and a vortex maintained for 1 h. The reaction was quenched with 1% HCl (aq) and extracted with ether (3 $\times$ 5 mL). The combined organics were washed with water, dried (Na_2SO_4), filtered, and concentrated. Chromatography (20% ether in hexane) gave 90 mg (83%) of the title compound, a clear oil. Only one peak was detected in the GC trace, and the purity by ^1H NMR was measured to be $\geq 99\%$. A similar experiment gave 90 mg (83%) of the title compound. ^1H NMR (CDCl_3 , 400 MHz, δ): 7.33–7.22 (m, 5H), 3.92 (dd, $J=11.5, 5.4$ Hz, 1H), 3.71 (dd, $J=11.5, 7.3$ Hz, 1H), 1.46–1.00 (m, 6H), 1.28 (s, 3H), 0.92 (d, $J=4.8$ Hz, 1H), 0.75 (t, $J=7.3$ Hz, 3H), 0.70 (d, $J=4.8$ Hz, 1H), 0.61 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 141.8 (u), 130.7 (dn), 128.7 (dn), 126.9 (dn), 69.3 (u), 38.4 (u), 37.8 (u), 29.3 (u), 26.0 (u), 23.4 (u), 23.3 (u), 18.7 (dn), 14.5 (dn); IR (neat, cm^{-1}): 3410, 3057, 2872, 1601, 1495, 1446, 1377, 1037, 1018; HRMS–CI (NH_3) m/z : $[\text{M}-\text{OH}]$ calcd for $\text{C}_{15}\text{H}_{21}$, 201.1643; found, 201.1639.

1 α -Butyl-2 β -hydroxymethyl-3 β -iodo-1 β -methyl-2 α -phenylcyclopropane (27). The procedure was identical to that used to prepare **26**, except that the reaction was quenched by adding crystals of I_2 (760 mg, 3.0 mmol) directly to the mixture. After stirring for 1 h, 1% HCl (aq) was added. Saturated Na_2SO_3 (aq) was then added to reduce unreacted I_2 . The mixture was extracted with ether (3 $\times$ 5 mL), dried (Na_2SO_4), filtered, concentrated and chromatographed (15% ether in hexane) to give 137 mg (80%) of the title compound, a pale yellow oil. The purity was measured to be $\geq 98\%$ by analysis of the ^1H NMR spectrum. The material was not suitable for analysis by GC. A similar experiment gave 139 mg (81%) of the title compound. ^1H NMR (CDCl_3 , 360 MHz, δ): 7.35–7.30 (m, 2H), 7.29–7.24 (m, 3H), 4.00 (dd, $J=11.8, 5.4$ Hz, 1H), 3.82 (dd, $J=11.8, 4.5$ Hz, 1H), 3.10

(s, 1H), 1.5–1.0 (m, 6H), 1.29 (s, 3H), 0.77 (t, $J=7.2$ Hz, 3H), 0.65 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, δ): 140.1 (u), 130.5, (dn), 129.3 (dn), 127.9 (dn), 70.0 (u), 39.2 (u), 37.5 (u), 29.0 (u), 28.4 (u), 22.9 (u), 19.2 (dn), 14.1 (dn), 13.3 (dn); IR(neat, cm^{-1}): 3436, 3056, 2957, 2931, 2858, 1601, 1500, 1484, 1445, 1378, 1263, 1072, 1025, 811; HRMS–CI (NH_3) m/z : $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{15}\text{H}_{25}\text{NOI}$, 362.0981; found, 362.0976.

References and Notes

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