JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
J. Am. Chem. Soc., 1997, 119(38), 8817-8825, DOI:10.1021/ja971538g

Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at http://pubs.acs.org/page/copyright/permissions.html

ACS Publications
MOST TRUSTED. MOST CITED. MOST READ.

Copyright © 1997 American Chemical Society

©1997 American Chemical Society J. Am. Chem. Soc. V119 Page8817 Molander Supplemental Page 1

SYNTHESIS OF SUBSTRATES FOR CATALYZED CYCLIZATION/SILYLATION

5-((*tert*-Butyldimethylsilyl)oxy)-1-cyclohexyl-1-pentyne (1a). General Procedure for the Preparation of Cyclohexyl Substituted Alkynes from Terminal Alkynes. The hydroxyl group of 4-pentyn-1-ol was protected in 87% yield to afford 5-((*tert*-butyldimethylsilyl)oxy)-1-pentyne. 5-((*tert*-Butyldimethylsilyl)oxy)-1-pentyne (3.0 g, 15.1 mmol) in 21 mL of THF was treated at 0 °C with 9.0 mL (15 mmol) of 1.67 M *n*-BuLi in hexanes. After stirring for 0.5 h the lithium acetylide solution was added via cannula to a previously prepared solution of 15 mmol of tricyclohexylborane in 15 mL of THF maintained at 0 °C. The reaction was stirred for 2 h at 0 °C and then cooled to -78 °C followed by the dropwise addition of a solution of 3.8 g of I_2 in 30 mL of THF. The reaction was stirred for 1 h at -78 °C, then warmed to rt. The resulting dark brown reaction mixture was transferred to a separatory funnel and washed two times with 3 N NaOH containing 2% $NaHSO_3$. The resulting layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were treated with 8 mL of 3 N NaOH and 2 mL of a 30% solution of H_2O_2, then stirred for 0.5 h. The aqueous layer was saturated with K_2CO_3 and the organic extracts were decanted, dried with K_2CO_3, and concentrated. Flash chromatography using 3% Et_2O in hexanes afforded 88% (3.7 g, 13.2 mmol) of **1a**: R_f 0.33 (3% Et_2O in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 0.03 (s, 6H), 0.87 (s, 9H), 1.93-1.37 (m, 5H), 1.42-1.52 (m, 1H), 1.66 (dq appearing as a five line pattern, *J*= 6.7, 6.5 Hz, 4H), 1.73-1.77 (m, 2H), 2.21 (dt, *J*= 7.0, 2.2 Hz, 2H), 2.25-2.32 (m, 1H), 3.67 (t, *J*= 6.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.3, 15.11, 18.37, 24.97, 25.96, 29.16, 32.19, 33.15, 61.76, 79.44, 84.81; HRMS calc'd for $C_{17}H_{31}OSi$: $(M-H)^+$ 279.2144, found 279.2166; LRMS (EI) *m/z* (relative intensity): 279 (2), 223 (57), 141 (35), 75 (100).

6-((*tert*-Butyldimethylsilyl)oxy)-1-cyclohexyl-1-hexyne (1b). The hydroxyl group of 5-hexyn-1-ol was protected in 84% yield to afford 6-((*tert*-butyldimethylsilyl)oxy)-1-hexyne. Compound **1b** was prepared from 6-((*tert*-butyldimethylsilyl)oxy)-1-hexyne according to the general procedure outlined for the preparation of **1a**. Flash chromatography using 4% EtOAc in hexanes afforded **1b** in

©1997 American Chemical Society J. Am. Chem. Soc. V119 Page8817 Molander Supplemental Page 2

87% yield: R_f 0.72 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.02 (s, 6H), 0.86 (s, 9H), 1.21-1.40 (m, 5H), 1.46-1.52 (m, 3H), 1.53-1.75 (m, 6H), 2.15 (dt, *J*= 6.8, 2.1 Hz, 2H), 2.28 (br s, 1H), 3.61 (t, *J*= 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.30, 18.33, 18.53, 24.93, 25.58, 25.94, 29.12, 31.95, 33.14, 62.80, 79.77, 84.80.

5-Cyclohexyl-4-pentynol (2a). General Procedure for the Deprotection of *tert*-Butyldimethylsilyl Ethers. A solution of 3.64 g (13.0 mmol) of **1a** in 100 mL of THF was treated with 20 mL of 1M TBAF in THF at 0 °C and allowed to warm to rt. After stirring for 3 h at rt the reaction was diluted with Et_2O, washed with H_2O and brine, and the aqueous layers were extracted with Et_2O. The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. Purification by column chromatography using 3% Et_2O in hexanes afforded 90% (1.94 g 11.7 mmol) of **2a**: R_f 0.32 (30% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17-1.35 (m, 5H), 1.41-1.49 (m, 1H), 1.58-1.74 (m, 6H), 2.21-2.28 (m, 4H), 3.68 (d, *J*= 6.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.35, 24.85, 25.81, 29.03, 31.57, 32.98, 61.86, 79.10, 85.38; IR (neat) 3340 cm^{-1} (br).

6-Cyclohexyl-5-hexyn-1-ol (2b). Deprotection of **1b** following the general procedure outlined for the preparation of **2a** afforded alcohol **2b** in 96% yield: R_f 0.34 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19-1.38 (m, 5H), 1.43-1.56 (m, 3H), 1.60-1.74 (m, 7H), 2.17 (dt, *J*= 6.8, 2.1 Hz, 2H), 2.27 (br s, 1H), 3.62 (t, *J*= 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.46, 24.91, 25.37, 25.87, 29.09, 31.79, 33.09, 62.40, 79.46, 85.06.

5-Cyclohexyl-4-pentynal (3a). General Procedure for the Oxidation of Alcohols to Aldehydes. Alcohol **2a** (1.83 g, 11.0 mmol) in 70 mL of CH_2Cl_2 was treated with 4.45 g (44 mmol) of Et_3N, cooled to 0 °C, treated with a solution of 4.55 g (28.6 mmol) of sulfur trioxide pyridinium complex in 33 mL of DMSO, and stirred for 4 h at 0 °C. The reaction mixture was partitioned between 2:1 hexanes/Et_2O and saturated aqueous $NaHCO_3$. The aqueous layer was extracted with 2:1 hexanes/Et_2O, and the combined organic layers were washed with 1 M NaH_2PO_4 solution, brine, dried with Na_2SO_4 and concentrated in vacuo. Purification by column chromatography using 10% Et_2O in hexanes afforded 88% (1.59 g, 9.7 mmol) of the desired aldehyde **3a**: R_f 0.44 (20% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13-1.32 (m, 5H), 1.40-1.48 (m, 1H), 1.60-1.77 (m, 4H), 2.25-2.32 (m, 1H), 2.43 (t, *J*=

©1997 American Chemical Society J. Am. Chem. Soc. V119 Page8817 Molander Supplemental Page 3

6.9 Hz, 2H), 2.56 (t, *J*= 7.0 Hz, 2H), 9.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.21, 24.77, 25.80, 28.94, 32.83, 42.98, 77.58, 85.80, 201.03; IR (neat) 1731.7 cm^{-1}.

6-Cyclohexyl-5-hexyn-1-al (3b). Oxidation of **2b** following the general procedure outlined for the preparation of **3a** afforded aldehyde **3b** in 89% yield: *Rf* 0.43 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21-1.32 (m, 5H), 1.41-1.48 (m, 1H), 1.57-1.79 (m, 6H), 2.17-2.24 (m, 3H), 2.50-2.53 (m, 2H), 9.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.11, 21.51, 24.83, 25.79, 28.99, 32.94, 42.71, 78.42, 85.86, 202.08.

7-Cyclohexyl-1-hepten-6-yn-3-ol (4a). General Procedure for the Grignard Addition to Aldehydes. Aldehyde **3a** (1.12 g, 6.8 mmol) in 10 mL of THF was added dropwise via cannula to 11.7 mL of a 0.86 M solution of vinylmagnesium bromide in THF at -78 °C. The solution was stirred for 2 h at -78 °C and then allowed to warm slowly to rt. The reaction was cooled to 0 °C and quenched with 1 mL of saturated aqueous NH_4Cl, washed with H_2O, brine, and the aqueous layer was extracted with EtOAc. Concentration in vacuo, column chromatography using 5% EtOAc in hexanes followed by Kugelrohr distillation afforded 1.152 g (6.0 mmol) of **4a** in 88% yield: GC purity >98%; ot 70-80 °C/0.45 mm Hg; *Rf* 0.38 (20% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20-1.38 (m, 5H), 1.44-1.51 (m, 1H), 1.62-1.76 (m, 6H), 2.11 (br s, 1H), 2.19-2.33 (m, 3H), 4.24 (q, *J*= 6.0 Hz, 1H), 5.09 (d, *J*= 10.4 Hz, 1H), 5.23 (d, *J*= 17.2 Hz, 1H), 5.83 (ddd, *J*= 17.1, 10.4, 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.04, 24.88, 25.86, 29.06, 33.00, 35.87, 72.20, 79.13, 85.60, 114.71, 140.48; HRMS calc'd for $C_{13}H_{19}O$: $(M-H)^+$ 191.14363, found 191.1425; LRMS (EI) *m/z* (relative intensity): 191 (3),109 (100), 93 (78), 79 (89).

8-Cyclohexyl-1-octen-7-yn-3-ol (4b). Prepared from **3b** according to the general procedure outlined for **4a**. Flash chromatography using 15% EtOAc in hexanes afforded 86% of **4b**: *Rf* 0.27 (15% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20-1.38 (m, 5H), 1.43-1.78 (m, 10H), 2.15 (dt, *J*= 6.7, 2.2 Hz, 2H), 2.27 (br s, 1H), 4.06-4.11 (m, 1H), 5.06 (dt, *J*= 10.4, 1.3 Hz, 1H), 5.18 (dt, *J*= 17.2, 1.4 Hz, 1H), 5.83 (ddd, *J*= 17.1, 10.4, 6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.56, 24.89, 25.87, 29.08, 33.08, 35.98, 72.71, 79.49, 85.09, 114.62, 141.07; HRMS calc'd for

©1997 American Chemical Society J. Am. Chem. Soc. V119 Page8817 Molander Supplemental Page 4

$C_{14}H_{21}O$: $(M-H)^+$ 205.1592, found 205.1601; LRMS (EI) *m/z* (relative intensity): 206 (8), 189 (93), 145 (67), 107 (100); IR (neat) 3356.4 cm^{-1} (br).

***N,N*-Dimethylhydrazone of 6-Cyclohexyl-5-hexyn-1-al (5).** Aldehyde **3b** (1.81 g, 10.2 mmol) was cooled to 0 °C and treated with 2 mg of *p*-toluenesulfonic acid and 0.67 g (11.2 mmol) of *N,N*-dimethylhydrazine. The reaction was warmed to 50 °C and stirred for 14 h, cooled to rt, diluted with pentane, dried with Na_2SO_4, decanted, and concentrated in vacuo. Kugelrohr distillation afforded **5** in 98% yield (2.08 g, 10.0 mmol): R_f 0.42 (25% EtOAc in hexanes); ot 95-110 °C/11 mm Hg; ^1H NMR (400 MHz, $CDCl_3$): δ 1.16-1.19 (m, 3H), 1.20-1.32 (m, 2H), 1.38-1.43 (m, 1H), 1.55-1.62 (m, 4H), 1.66-1.69 (m, 2H), 2.13 (dt, *J*= 7.1, 2.2 Hz, 2H), 2.21-2.26 (m, 3H), 2.64 (s, 6H), 6.56 (t, *J*= 5.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.22, 24.79, 25.78, 27.22, 28.98, 32.05, 32.97, 43.13, 79.22, 84.91, 138.06.

7-Cyclohexyl-3-methyl-1-hepten-6-yne (6). General Procedure for the Alkylation of Hydrazone 5 Followed by a Wittig Reaction. Diisopropylamine (1.01 g, 10.0 mmol) in 4 mL of THF was treated with 6.25 mL (10 mmol) of a 1.6 M solution of *n*-BuLi in hexanes at 0 °C. After stirring for 0.5 h, a solution of 2.0 g (9.6 mmol) of hydrazone **5** in 4 mL of THF was added at 0 °C. The reaction was warmed to rt, stirred for 16 h, cooled to -78 °C, and treated with 2.13 g (15 mmol) of methyl iodide. The reaction was stirred for 0.5 h at -78 °C, quenched with saturated aqueous NH_4Cl, diluted with Et_2O, washed with H_2O, extracted with Et_2O, and concentrated in vacuo. Acetone was added to the wet product until the two layers were miscible and then wet Amberlyst was added. The mixture was stirred for 16 h, followed by removal of acetone by rotary evaporation, dilution with Et_2O, filtration to remove the Amberlyst, drying with Na_2SO_4, and concentration in vacuo. Flash chromatography using 10% Et_2O in hexanes afforded 61% (1.14 g, 5.9 mmol) of 6-cyclohexyl-2-methylhex-5-ynal: R_f 0.56 (20% Et_2O in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, *J*= 7.1 Hz, 3H), 1.19-1.38 (m, 5H), 1.45-1.55 (m, 2H), 1.62-1.76 (m, 4H), 1.87-1.96 (m, 1H), 2.17-2.29 (m, 3H), 2.51 (sextet, *J*= 6.9 Hz, 1H), 9.66 (t, *J*= 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.92, 16.36, 24.93, 25.86, 29.09, 29.70, 32.98, 45.29, 78.49, 85.99, 204.73; IR (neat) 1707.1 cm^{-1}.

©1997 American Chemical Society J. Am. Chem. Soc. V119 Page8817 Molander Supplemental Page 5

6-Cyclohexyl-2-methylhex-5-ynal was reacted according to the general procedure for the Wittig reaction of aldehydes outlined for the preparation of **16**. Purification by flash chromatography using hexanes followed by Kugelrohr distillation afforded 83% (0.48 g, 2.5 mmol) of **6**: GC purity >99%; ot 95-110 °C/11 mm Hg; R_f 0.36 (in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (d, *J*= 6.8 Hz, 3H), 1.21-1.51 (m, 8H), 1.63-1.76 (m, 4H), 2.05-2.20 (m, 2H), 2.22-2.31 (m, 2H), 4.92 (d, *J*= 10.2 Hz, 1H), 4.97 (d, *J*= 17.2 Hz, 1H), 5.64 (ddd, *J*= 17.6, 10.3, 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.64, 19.88, 24.94, 25.94, 29.14, 33.16, 35.88, 36.88, 79.80, 84.75, 113.13, 143.83; HRMS calc'd for $C_{14}H_{22}$: 190.1722, found 190.1738; LRMS (EI) *m/z* (relative intensity): 190 (2), 107 (100), 93 (83), 79 (80).

7-Cyclohexyl-3-ethyl-1-hepten-6-yne (7). The alkylation of hydrazone **5** with iodoethane followed by a Wittig reaction according to the general procedure outlined for **6** afforded **7** in 53% overall yield: GC purity >99%; ot 100-110 °C/10 mm Hg; R_f 0.30 (in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (t, *J*= 7.4 Hz, 3H), 1.18-1.29 (m, 4H), 1.32-1.43 (m, 4H), 1.44-1.61 (m, 2H), 1.63-1.75 (m, 4H), 1.93-2.10 (m, 3H), 2.26-2.33 (m, 1H), 4.97 (d, *J*= 18.1 Hz, 1H), 4.98 (d, *J*= 8.9 Hz, 1H), 5.46 (ddd, *J*= 16.6, 10.7, 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.61, 16.64, 24.94, 25.96, 27.47, 29.15, 33.18, 33.99, 44.94, 80.00, 84.66, 115.02, 142.16; HRMS calc'd for $C_{15}H_{24}$: 204.1878, found 204.1863; LRMS (EI) *m/z* (relative intensity): 204 (2), 175 (85), 107 (53), 93 (100).

6-Cyclohexyl-3-(methoxymethyl)-1-hepten-6-yne (8). The alkylation of hydrazone **5** with bromomethyl methyl ether followed by a Wittig reaction according to the general procedure outlined for **6** afforded **8** in 40% overall yield: GC purity >99%; ot 45-55 °C/0.01 mm Hg; R_f 0.41 (10% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20-1.49 (m, 7H), 1.60-1.77 (m, 5H), 2.05-2.23 (m, 2H), 2.28 (br s, 1H), 2.80-2.94 (m, 1H), 3.29 (s, 1H), 3.30 (s, 4H), 5.07 (d, *J*= 10.2 Hz, 1H), 5.08 (d, *J*= 17.7 Hz, 1H), 5.59 (ddd, *J*= 18.8, 10.3, 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.36, 24.93, 25.92, 29.12, 30.53, 33.13, 43.03, 58.77, 76.08, 79.49, 84.95, 116.30, 139.25; HRMS calc'd for $C_{15}H_{24}O$: 220.1827, found 220.1834; LRMS (EI) *m/z* (relative intensity): 175 (26), 105 (17), 93 (32), 45 (100).

©1997 American Chemical Society J. Am. Chem. Soc. V119 Page8817 Molander Supplemental Page 6

6-Cyclohexyl-2-vinyl-5-hexyn-1-ol (9). A solution of 0.45 g (2.0 mmol) of **8** in 15 mL of chloroform was prepared in a Teflon valved Schlenk tube containing a magnetic stirbar. The solution was freeze/pump/thaw degassed and backfilled with Ar. Iodotrimethylsilane (0.44 g, 2.2 mmol) was added via syringe. The tube was sealed, heated to 90 °C, and stirred for 18h. The reaction was allowed to cool, then pipetted into 3 mL of methanol containing 1 drop of concentrated HCl. The volatiles were removed by rotary evaporation and the product was diluted with Et_2O, washed with saturated aqueous $NaHCO_3$, dried with $MgSO_4$, and concentrated in vacuo. Flash chromatography using 25% Et_2O in hexanes followed by Kugelrohr distilllation afforded 95% (0.39 g, 1.9 mmol) of alcohol **9**: GC purity >99%; ot 50-65 °C/0.02 mm Hg; R_f 0.24 (25% Et_2O in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 1.18-1.48 (m, 7H), 1.55-1.74 (m, 6H), 2.05-2.39 (m, 4H), 3.40-3.46 (m, 1H), 3.53-3.59 (m, 1H), 5.14 (d, *J*= 16.7 Hz, 1H), 5.15 (d, *J*= 9.9 Hz, 1H), 5.50-5.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.37, 24.90, 25.86, 29.08, 30.02, 33.07, 45.94, 65.31, 79.33, 85.10, 117.90, 138.93; HRMS calc'd for $C_{14}H_{22}$: 206.1671, found 206.1660; LRMS (EI) *m/z* (relative intensity): 206 (1), 175 (76), 107 (46), 93 (100).

3-(((*tert*-Butyldimethylsilyl)oxy)methyl)-7-cyclohexyl-1-hepten-6-yne (10). Prepared from **9** according to the general procedure outlined for **20**. Flash chromatography using 10% CH_2Cl_2 in hexanes followed by Kugelrohr distillation afforded 71% of **10**: GC purity >97%; ot 75-85 °C/0.02 mm Hg; R_f 0.25 (10% CH_2Cl_2 in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 0.01 (s, 6H), 0.87 (s, 9H), 1.23-1.47 (m, 7H), 1.57-1.74 (m, 5H), 2.04-2.34 (m, 4H), 3.49 (B of ABX, *J*= 9.8, 6.7 Hz, 1H), 3.52 (A of ABX, *J*= 9.8, 6.0 Hz, 1H), 5.03 (d, *J*= 10.4 Hz, 1H), 5.04 (d, *J*= 17.9 Hz, 1H), 5.58 (ddd, *J*= 17.3, 10.1, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.37, -5.33, 16.46, 18.32, 24.92, 25.91, 25.97, 29.14, 30.35, 33.16, 45.64, 66.41, 79.82, 84.76, 116.08, 139.41; HRMS calc'd for $C_{20}H_{36}OSi$: 320.2535, found 320.2532; LRMS (EI) *m/z* (relative intensity): 263 (65), 187 (69), 89 (53), 75 (100).

1-((*tert*-Butyldimethylsilyl)oxy)-4-penten-3-ol (12). Prepared according to the general procedure for the preparation of **4a.** 3-((*tert*-Butyldimethylsilyl)oxy)propanal (**11**) was treated with vinylmagnesium bromide to provide 90% of **12**: R_f 0.34 (25% Et_2O in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 0.02 (s, 6H), 0.85 (s, 9H), 1.62-1.76 (m, 2H), 3.42 (d, *J*= 3.6 Hz, 1H), 3.72-3.77 (m, 1H),

©1997 American Chemical Society J. Am. Chem. Soc. V119 Page8817 Molander Supplemental Page 7

3.80-3.86 (m, 1H), 4.27-4.32 (m, 1H), 5.04 (dt, *J*= 10.5, 1.2 Hz, 1H), 5.22 (dt, *J*= 17.2, 1.6 Hz, 1H), 5.82 (ddd, *J*= 17.1, 10.5, 5.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.37, -5.31, 18.09, 25.81, 38.19, 61.88, 72.40, 114.09, 140.58.

3-(Triphenylmethoxy)-5-((*tert*-butyldimethylsilyl)oxy)-1-pentene (13). Alcohol **12** was protected as outlined in the general procedure for **20** to provide 69% of **13**: *Rf* 0.33 (30% CH_2Cl_2 in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ –0.03 (s, 3H), -0.02 (s, 3H), 0.83 (s, 9H), 1.44-1.53 (m, 1H), 1.62-1.70 (m, 1H), 3.48-3.59 (m, 2H), 4.06 (dt, *J*= 7.6, 4.0 Hz, 1H), 4.68 (d, *J*= 18.0 Hz, 1H), 4.70 (d, *J*= 10.5 Hz, 1H), 5.58 (ddd, *J*= 17.5, 10.6, 7.2 Hz, 1H), 7.18-7.31 (m, 9H), 7.49-7.51 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.37, -5.31, 18.18, 25.89, 39.05, 59.32, 73.16, 87.16, 113.47, 126.83, 127.51, 129.11, 139.63, 145.19.

3-(Triphenylmethoxy)-1-penten-5-ol (14). Deprotection of the *tert*-butyldimethylsilyl-protected primary alcohol according to the general procedure outlined for the preparation of **2a** afforded alcohol **14** in 97% yield: *Rf* 0.32 (30% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35–1.40 (m, 2H), 1.75 (dd, *J*= 7.1, 4.3 Hz, 1H), 3.44-3.51 (m, 1H), 3.62-3.69 (m, 1H), 4.14 (q, *J*= 5.7 Hz, 1H), 4.83 (d, *J*= 10.7 Hz, 1H), 4.86 (d, *J*= 17.5 Hz, 1H), 5.70 (ddd, *J*= 17.3, 10.5, 6.7 Hz, 1H), 7.17-7.26 (m, 9H), 7.45-7.47 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.76, 59.44, 74.07, 87.76, 114.26, 127.10, 127.70, 129.00, 139.38, 144.69; IR (neat) 3389.5 cm^{-1} (br).

5-Bromo-3-(triphenylmethoxy)-1-pentene (15). Alcohol **14** (0.93 g, 2.7 mmol) in 8 mL of pyridine was added to a stirred solution of 1.26 g (3.0 mmol) of Ph_3PBr_2 in 2 mL of pyridine at 0 °C. The reaction was stirred for 4 h, then poured into 30 mL of cold saturated aqueous $NaHCO_3$, extracted with hexanes, washed with H_2O and brine, dried with $MgSO_4$, and concentrated in vacuo. Flash chromatography using 5% Et_2O in hexanes afforded 77% (0.85 g, 2.1 mmol) of bromide **15**: *Rf* 0.52 (5% Et_2O in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.56–1.63 (m, 1H), 1.67-1.75 (m, 1H), 3.16-3.32 (m, 2H), 4.08 (dt, *J*= 7.2, 4.0 Hz, 1H), 4.89 (d, *J*= 10.4 Hz, 1H), 4.90 (d, *J*= 17.2 Hz, 1H), 5.58-5.68 (m, 1H), 7.20-7.30 (m, 9H), 7.47-7.52 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.95, 38.48, 73.98, 87.44, 114.90, 127.00, 127.65, 128.92, 138.40, 144.77; HRMS calc'd for $C_{24}H_{23}OBr$:

©1997 American Chemical Society J. Am. Chem. Soc. V119 Page8817 Molander Supplemental Page 8

406.0932, found 406.0929; LRMS (EI) *m/z* (relative intensity): 408 (2), 406 (2), 331 (4), 329 (5), 243 (100), 183 (69), 165 (76), 105 (85).

7-Cyclohexyl-1-hepten-6-yne (16). General Procedure for the Wittig Reaction of Aldehydes. To a suspension of 0.45 g (4.0 mmol) of potassium *tert*-butoxide in 10 mL of Et_2O at 0 °C was added 1.43 g (4.0 mmol) of methyltriphenylphosphonium bromide. The reaction was warmed to rt and stirred for 1.5 h, and 0.50 g (2.8 mmol) of 6-cyclohexyl-5-hexyn-1-al (**3b**) was added. The reaction was stirred for 4 h at rt, cooled to 0 °C, and quenched with H_2O. The reaction mixture was concentrated in vacuo and the solids were extracted with pentane, dried over $MgSO_4$, and concentrated in vacuo. Purification by column chromatography using 5% CH_2Cl_2 in hexanes followed by Kugelrohr distillation afforded 86% of **16**: ot 85-100 °C/12 mm Hg; R_f 0.33 (5% CH_2Cl_2 in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22-1.41 (m, 5H), 1.45-1.50 (m, 1H), 1.55 (quintet, *J*= 7.5 Hz, 2H), 1.63-1.78 (m, 4H), 2.10-2.17 (m, 4H), 2.27-2.33 (m, 1H), 4.94 (dd, *J*= 10.2, 0.5 Hz, 1H), 5.00 (dd, *J*= 17.1, 1.3 Hz, 1H), 5.73-5.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.14, 24.94, 25.94, 28.37, 29.14, 32.78, 33.15, 79.58, 84.98, 114.89, 138.16; HRMS calc'd for $C_{13}H_{20}$: 176.1565 found 176.1572; LRMS (EI) *m/z* (relative intensity): 161 (20), 93 (69), 79 (100).

8-Methyl-1-decen-6-yne (18). General Procedure for the Alkylation of Terminal Alkynes with Alkyl Halides. 3-Methyl-1-pentyne was alkylated with 5-bromo-1-pentene by the following procedure. A solution of 1.009 g (12.3 mmol) of the alkyne in 15 mL of THF was treated with 8.0 mL of a 1.38 M solution of *n*-BuLi in hexanes at -78 °C. After stirring for 0.5 h a solution of 1.508 g (10.1 mmol) of 5-bromo-1-pentene in 2.5 mL of HMPA and 5 mL of THF was added and the reaction mixture was allowed to warm to rt and stirred for 16 h. The reaction was cooled to 0 °C and quenched with 1 mL of saturated aqueous NH_4Cl, diluted with hexanes, washed with H_2O and brine, extracted with hexanes, and concentrated in vacuo. Flash chromatography of the crude reaction mixture using hexanes yielded 75% (1.144 g, 7.6 mmol) of **18**: GC purity >98%; R_f 0.31 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, *J*= 7.4 Hz, 3H), 1.10 (d, *J*= 7.0 Hz, 3H), 1.31-1.46 (m, 2H), 1.51-1.60 (m, 2H), 2.09-2.17 (m, 4H), 2.25-2.34 (m, 1H), 4.94 (br d, *J*= 10.2 Hz, 1H), 5.01 (br d, *J*= 17.1 Hz, 1H), 5.73-5.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.76, 18.13, 21.10, 27.56, 28.40, 30.22, 32.78,

©1997 American Chemical Society J. Am. Chem. Soc. V119 Page8817 Molander Supplemental Page 9

79.91, 85.06, 114.88, 138.16; HRMS calc'd for $C_{11}H_{17}$: $(M-H)^+$ 149.1330, found 149.1348; LRMS (EI) *m/z* (relative intensity): 135 (18), 121 (49), 93 (100), 81 (94).

3-((*tert*-Butyldimethylsilyl)oxy)-7-cyclohexyl-1-hepten-6-yne (20). General Procedure for the Preparation of *tert*-Butyldimethylsilyl Ethers. Alcohol **4a** (0.29 g, 1.5 mmol) in 15 mL of DMF was treated with 0.12 g (1.8 mmol) of imidazole and 0.28 g (1.8 mmol) of *tert*-butyldimethylsilyl chloride at 0 °C. The reaction was warmed to rt and stirred for 14 h. After dilution with Et_2O, washing with saturated aqueous $NaHCO_3$, H_2O, and brine, and extraction of the aqueous layers with Et_2O, the organics were combined, dried over $MgSO_4$, and concentrated in vacuo. Flash chromatography using 2% Et_2O in hexanes followed by Kugelrohr distillation afforded 0.43 g (0.52 mmol) of the desired silyl ether **20** in 93% yield: GC purity >97%; ot 70-80 °C/0.01 mm Hg; R_f 0.52 (2% Et_2O in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 0.02 (s, 3H), 0.04 (s, 3H), 0.87 (s, 9H), 1.23-1.38 (m, 5H), 1.44-1.52 (m, 1H), 1.56-1.73 (m, 4H), 1.75-1.79 (m, 2H), 2.12-2.24 (m, 2H), 2.29 (br s, 1H), 4.22 (dt, *J*= 6.5, 6.1 Hz, 1H), 5.01 (dt, *J*= 10.4, 1.4 Hz, 1H), 5.15 (dt, *J*= 17.2, 1.4 Hz, 1H), 5.77 (ddd, *J*= 16.6, 10.5, 6.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -4.88, -4.38, 14.81, 18.27, 24.97, 25.89, 25.95, 29.16, 33.16, 37.37, 72.47, 79.55, 84.96, 113.94, 141.33; HRMS calc'd for $C_{19}H_{34}OSi$: 306.2379, found 306.2379; LRMS (EI) *m/z* (relative intensity): 291 (2), 249 (55), 135 (40), 115 (15), 75 (100).

7-Cyclohexyl-3-((triisopropylsilyl)oxy)-1-hepten-6-yne (22). Alcohol **4a** (0.31 g, 1.6 mmol) in 4 mL of DMF was treated with 0.13 g (1.9 mmol) of imidazole and 0.38 g (2.0 mmol) of triisopropylsilyl chloride at 0 °C. The reaction was warmed to rt and stirred for 14 h. After dilution with Et_2O, washing with saturated aqueous $NaHCO_3$, H_2O, and brine, and extraction of the aqueous layers with Et_2O, the organics were combined, dried over $MgSO_4$, and concentrated in vacuo. Flash chromatography using a gradient of 0-5% Et_2O in hexanes followed by Kugelrohr distillation afforded 0.31 g (0.95 mmol) of the desired silyl ether **22** in 59% yield: GC purity >99%; ot 65-80 °C/0.01 mm Hg; R_f 0.20 (in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 1.00-1.10 (m appears as a broad singlet at 1.04, 21H), 1.20-1.40 (m, 5H), 1.45-1.51 (m, 1H), 1.55-1.80 (m, 6H), 2.07-2.15 (m, 1H), 2.19-2.31 (m, 2H), 4.33 (dt, *J*= 6.8, 5.7 Hz, 1H), 5.04 (dt, *J*= 10.4, 1.8 Hz, 1H), 5.14 (dt, *J*= 17.3, 1.8 Hz, 1H),

©1997 American Chemical Society J. Am. Chem. Soc. V119 Page8817 Molander Supplemental Page 10

5.77 (ddd, *J*= 17.2, 10.4, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.39, 14.38, 18.09, 18.12, 24.97, 25.97, 29.17, 33.13, 37.47, 73.02, 79.60, 84.84, 114.37, 141.17; HRMS calc'd for $C_{22}H_{39}OSi$: $(M-H)^+$ 347.2777, found 347.2777; LRMS (EI) *m/z* (relative intensity): 305 (31), 131 (100), 103 (53).

7-Cyclohexyl-3-(triphenylmethoxy)-1-hepten-6-yne (24). General Procedure for the Installation of the Trityl Protecting Group. Alcohol **4a** (0.10 g, 0.52 mmol) in 3 mL of CH_2Cl_2 was treated with 0.16 g (1.1 mmol) of DBU and 0.17 g (0.62 mmol) of trityl chloride at 0 °C. The reaction was warmed to rt and stirred for 16 h. After dilution with Et_2O, washing with saturated aqueous $NaHCO_3$, H_2O, and brine, and extraction of the aqueous layers with Et_2O, the organics were combined, dried over $MgSO_4$, and concentrated in vacuo. Flash chromatography using 5% Et_2O in hexanes followed by removal of solvents at 50 °C/0.01 mm Hg for 2 h afforded 0.18 g (0.41 mmol) of the desired trityl ether **24** in 79% yield: GC purity >99%; *Rf* 0.34 (5% Et_2O in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27-1.42 (m, 6H), 1.43-1.58 (m, 2H), 1.62-1.72 (m, 4H), 1.99-2.18 (m, 2H), 2.26 (br s, 1H), 4.04 (dt, *J*= 4.0, 7.6 Hz, 1H), 4.73 (d, *J*= 17.7 Hz, 1H), 4.74 (d, *J*= 11.0 Hz, 1H), 5.49-5.58 (m, 1H), 7.20-7.30 (m, 9H), 7.47-7.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.08, 24.82, 25.92, 29.00, 32.98, 34.94, 74.45, 79.56, 84.58, 87.15, 113.95, 126.84, 127.00, 127.29, 127.54, 127.65, 127.89, 129.04, 138.95, 145.13; HRMS calc'd for $C_{32}H_{34}O$: 434.2610 found 434.2592; LRMS (EI) *m/z* (relative intensity): 434 (0.3), 243 (100), 165 (39), 105 (40).

7-Cyclohexyl-3,*N*'-isoindolinyl-1-hepten-6-yne (26). A solution of 1.07 g (5.6 mmol) of alcohol **4a** in 8 mL of THF was added to a solution of 2.19 g (8.4 mmol) of PPh_3 and 0.98 g (6.7 mmol) of phthalimide in 15 mL of THF. The combined solutions were treated dropwise with a solution of 1.45 g (8.3 mmol) of DEAD in 7 mL of THF at 0 °C, warmed to rt, and stirred for 14 h. The volatiles were removed by rotary evaporation and the residue was diluted with 2:1 Et_2O/hexanes and stored at 0 °C to allow the solids to precipitate out of solution. After 24 h the organics were decanted off, the solids were extracted with Et_2O, and the organics were concentrated in vacuo. Flash chromatography using 20% Et_2O in hexanes afforded 7-cyclohexyl-3,*N*'-phthalimidyl-1-hepten-6-yne in 63% yield (1.13 g, 3.5 mmol): *Rf* 0.50 (20% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14-1.28 (m, 5H), 1.36-1.46 (m, 1H), 1.56-1.61 (m, 4H), 2.00-2.28 (m, 5H), 4.84-4.90 (m, 1H), 5.14 (dt, *J*= 10.3, 1.1 Hz, 1H), 5.22 (dt, *J*=

©1997 American Chemical Society J. Am. Chem. Soc. V119 Page8817 Molander Supplemental Page 11

17.2, 1.2 Hz, 1H), 6.14 (ddd, *J*= 17.7, 10.2, 7.6 Hz, 1H), 7.63-7.80 (AA'BB', 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.10, 24.87, 25.77, 28.97, 30.89, 32.82, 53.15, 77.97, 85.67, 117.63, 123.08, 131.92, 133.76, 135.08, 167.94. To a suspension of 0.19 g (5.0 mmol) of LAH in 15 mL of THF was added a solution of 0.50 g (1.54 mmol) of 7-cyclohexyl-3,*N*'-phthalimidyl-1-hepten-6-yne at 0 °C. The reaction was warmed to reflux for 2 h, then cooled to 0 °C and quenched with H_2O. The reaction was washed with 3N NaOH, the aqueous layer was extracted with Et_2O, and the organics were concentrated in vacuo. Flash chromatography using 20% Et_2O in hexanes followed by Kugelrohr distillation afforded 0.36 g (1.23 mmol) of **26** in 80% yield: GC purity >99%; ot 135-150 °C/0.01 mm Hg; R_f 0.23 (20% Et_2O in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24-1.28 (m, 3H), 1.35-1.42 (m, 2H), 1.46-1.51 (m, 1H), 1.61-1.76 (m, 5H), 1.93-2.01 (m, 1H), 2.10-2.18 (m, 1H), 2.24-2.31 (m, 2H), 3.15 (dt, *J*= 9.1, 4.2 Hz, 1H), 3.91-3.98 (m, 4H), 5.19 (dd, *J*= 10.2, 1.9 Hz, 1H), 5.24 (dd, *J*= 17.2, 1.9 Hz, 1H), 5.73 (ddd, *J*= 17.2, 10.1, 8.9 Hz, 1H), 7.14-7.19 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.38, 24.92, 25.92, 29.12, 33.06, 33.12, 56.66, 66.86, 79.60, 84.97, 117.46, 122.27, 126.59, 138.64, 139.84; HRMS calc'd for $C_{21}H_{27}N$: 293.2144, found 293.2127; LRMS (EI) *m/z* (relative intensity): 293 (14), 210 (27), 158 (100), 118 (49).

8-((*tert*-Butyldimethylsilyl)oxy)-3-(triphenylmethoxy)-1-nonen-6-yne (32). Prepared by the alkylation of 3-((*tert*-butyldimethylsilyl)oxy)-1-butyne with bromide **15** according to the general procedure outlined for the preparation of **18**, followed by deprotection of the propargyl alcohol with TBAF. Deprotection allowed the separation of the alkylation product from bromide **15** by column chromatography using 40% Et_2O in hexanes. 7-(Triphenylmethoxy)-8-nonen-3-yn-2-ol was obtained in 48% over 2 steps: R_f 0.28 (40% Et_2O in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33-1.42 (m, 1H, with 2 overlapping doublets, 1.34, *J*= 6.7 Hz and 1.35, *J*= 6.4 Hz, 3H), 1.49-1.58 (m, 1H), 1.73-1.77 (m, 1H), 2.03-2.12 (m, 1H), 2.15-2.23 (m, 1H), 4.02-4.07 (m, 1H), 4.39-4.42 (m, 1H), 4.79 (d, *J*= 11.8 Hz, 1H), 4.80 (d, *J*= 16.1 Hz, 1H), 5.53-5.63 (m, 1H), 7.20-7.30 (m, 9H), 7.50-7.53 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.84, 24.54, 24.59, 34.49, 58.38, 58.39, 74.16, 82.15, 84.25, 84.27, 87.21, 114.24, 126.90, 127.55, 129.01, 138.90, 145.01. 7-(Triphenylmethoxy)-8-nonen-3-yn-2-ol was reprotected as the silyl ether using the general procedure outlined for the preparation of **20**.

©1997 American Chemical Society J. Am. Chem. Soc. V119 Page8817 Molander Supplemental Page 12

Flash chromatography using 5% Et_2O in hexanes followed by removal of the solvents at 70 °C/0.01 mm Hg afforded 87% (0.52 g, 1.04 mmol) of **32**: GC purity >99%; R_f 0.55 (10% Et_2O in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 0.03-0.05 (m, 6H), 0.85-0.86 (m, 9H), 1.24-1.33 (m with 2 overlapping d, *J*= 6.4 Hz, 4H), 1.37-1.48 (m, 1H), 1.97-2.16 (m, 2H), 3.99 (dt, *J*= 3.8, 7.2 Hz, 1H), 4.36-4.43 (m, 1H), 4.74-4.81 (m, 2H), 5.51-5.60 (m, 1H), 7.17-7.27 (m, 9H), 7.46-7.49 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -4.90, -4.52, -4.48, 13.91, 18.24, 25.70, 25.86, 34.53, 59.13, 74.28, 82.60, 83.29, 87.24, 114.25, 126.92, 127.60, 129.04, 138.98, 145.09; HRMS calc'd for $C_{34}H_{42}O_2Si$: 510.2954, found 510.2951; LRMS (EI) *m/z* (relative intensity): 453 (9), 271 (65), 243 (100), 165 (77), 105 (68).

7,5'-(2',2'-Dimethyl-1',3'-dioxanyl)-3-(triphenylmethoxy)-1-hepten-6-yne (34). 2,2-Dimethyl-5-ethynyl-1,3-dioxane was alkylated with bromide **15** according to the general procedure outlined for the preparation of **18**. A solution of 0.57 g (4.1 mmol) of the alkyne in 7 mL of THF was treated with 2.5 mL of a 1.6 M solution of *n*-BuLi in hexanes at -78 °C. After stirring for 0.5 h a solution of 1.22 g (3.0 mmol) of **15** in 0.7 mL of HMPA and 6 mL of THF was added and the reaction mixture was allowed to warm to rt and stirred for 16 h. The incomplete reaction was cooled to 0 °C and quenched with 1 mL of saturated aqueous NH_4Cl, diluted with Et_2O, washed with H_2O and brine, extracted with Et_2O, and concentrated in vacuo. Flash chromatography using 10% Et_2O in hexanes of the crude reaction mixture yielded starting materials and the desired product. Recrystallization of the product from Et_2O afforded 30% (0.33 g, 0.70 mmol) of **34** based on recovered starting materials: GC purity >99%; mp 122 °C; R_f 0.24 (10% Et_2O in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 1.25-1.51 (m, 2H with 2 overlapping singlets at 1.36, 3H and 1.42, 3H), 1.94-2.13 (m, 2H), 2.65-2.71 (m, 1H), 3.64 (dt, *J*= 11.2, 1.8 Hz, 2H), 3.75-3.81 (m, 2H), 3.98 (dt, *J*= 13.7, 7.4 Hz, 1H), 4.74 (d, *J*= 17.6 Hz, 1H), 4.75 (d, *J*= 11.1 Hz, 1H), 5.49-5.57 (m, 1H), 7.18-7.27 (m, 9H), 7.46-7.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.86, 18.72, 27.80, 28.85, 34.59, 63.93, 63.94, 74.18, 75.84, 83.53, 87.19, 97.66, 114.20, 126.93, 127.58, 127.90, 129.00, 138.85, 145.03; HRMS calc'd for $C_{32}H_{34}O_3$: 466.2508, found 466.2493; LRMS (EI) *m/z* (relative intensity): 451 (9), 243 (100), 165 (85), 105 (85).

3-((*tert*-Butyldimethylsilyl)oxy)-8-cyclohexyl-1-octen-6-yne (37). Prepared from **4b** according to the general procedure outlined for **20**. Flash chromatography using 3% Et_2O in hexanes

©1997 American Chemical Society J. Am. Chem. Soc. V119 Page8817 Molander Supplemental Page 13

followed by Kugelrohr distillation afforded 82% of **37**: GC purity >99%; ot 90-110 °C/0.01 mm Hg; R_f 0.57 (3% Et_2O in hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 0.01 (s, 3H), 0.03 (s, 3H), 0.87 (s, 9H), 1.23-1.27 (m, 3H), 1.32-1.38 (m, 2H), 1.42-1.51 (m, 3H), 1.52-1.62 (m, 2H), 1.63-1.69 (m, 2H), 1.72-1.77 (m, 2H), 2.14 (dt, *J*= 6.8, 2.2 Hz, 2H), 2.29 (br s, 1H), 4.09 (q, *J*= 5.9 Hz, 1H), 5.00 (dt, *J*= 10.4, 1.5 Hz, 1H), 5.12 (dt, *J*= 17.2, 1.6 Hz, 1H), 5.77 (ddd, *J*= 17.1, 10.4, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -4.85, -4.42, 18.26, 18.70, 24.77, 24.93, 25.88, 25.95, 29.14, 33.15, 37.05, 73.42, 79.77, 84.88, 113.61, 141.61; HRMS calc'd for $C_{20}H_{36}OSi$: 320.2535, found 320.2509; LRMS (EI) *m/z* (relative intensity): 263 (63), 171 (44), 135 (25), 75 (100).

Table 1s. Crystal data for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclopentanol, 36.**

Identification code	bc111
Empirical formula	$C_{13}H_{22}O_2$
Formula mass	210.31
Crystal size, mm	0.60 × 0.40 × 0.35
Crystal color, habit	colorless plate
Crystal system	Monoclinic
Space group	$P2_1$
a, Å	5.2723(6)
b, Å	38.903(5)
c, Å	6.3631(7)
α, °	90
β, °	111.102(5)
γ, °	90
Volume, Å^3	1217.6(2)
Z, formula units/cell	4
Density (calculated), Mg·m^{-3}	1.147
Absorption coefficient, mm^{-1}	0.075
F(000)	464
Absorption correction	None
Range Transmission Coefficients	0.98 and 0.97

Table 2s. Data collection parameters for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclopentanol, 36.**

Diffractometer	Siemens SMART
Temperature, K	163(2)
Radiation source	sealed tube
Wavelength, Å	0.71073 MoKα
Monochromator	graphite
Cell measurement	
Reflections used	1870
θ range	$1.05 < \theta < 25.99$
θ range, data collection	$1.05 < \theta < 25.99$
Scan type	ω scans
Index ranges	$-7 \le h \le 6$,
	$-48 \le k \le 51$,
	$-8 \le l \le 7$
Reflections collected	7139
Independent reflections	4351 (R(int) = 0.0855)
Standard reflections	50 frames re-measured
Stability of standards	no decay observed

Table 3s. Structure Solution and Refinement for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclopentanol, 36.**

System used[1,2]	Siemens SHELXTL
Structure solution	direct
Data/ restraints/ parameters	4350 / 1/ 271
Hydrogen atoms	riding, with riding isotropic U
weighting scheme	calc $w^{-1}=[\sigma^2(F_o^2)+(0.1521P)^2]$ where $P=(F_o^2+2F_c^2)\div 3$
Final R indices[3] [I>2σ(I)]	R1 = 0.1071, wR2 = 0.2432
Reflections observed	2399
R indices (all data)	R1 = 0.1766, wR2 = 0.2936
Goodness-of-fit[4] on F^2	1.039
Absolute structure parameter[5]	-2.56(367)
Largest diff. peak and hole	0.451 and -0.555

1) G. M. Sheldrick, SHELXTL, *A Program for Crystal Structure Determination.* Version 5.03, 1995, Siemens Analytical X-ray Instruments, Madison, Wisconsin.

2) Scattering factors (neutral atoms) are from "International Tables for Crystallography" Vol. C, D. Reidel Publishing Co. Boston, 1991.

3) $R1=\frac{\sum\|F_o|-|F_c\|}{\sum|F_o|}$; $wR2=\sqrt{\frac{\sum[w(F_o^2-F_c^2)^2]}{\sum[w(F_o^2)^2]}}$;

4) $GooF=S=\sqrt{\frac{\sum[w(F_o^2-F_c^2)^2]}{(M-N)}}$ where M is the number of reflections and N is the number of parameters refined.

5) H. D. Flack, *Acta Cryst.* **1983**, *A39*, 876-881

Table 4s. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclopentanol, 36.**

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	Ueq
O(1)	7897(10)	2551(1)	7469(8)	29(1)
O(2)	665(10)	2433(1)	2120(9)	31(1)
C(1)	3436(14)	1798(2)	4543(11)	19(2)
C(2)	4181(13)	2170(2)	5162(11)	21(2)
C(3)	3499(15)	2354(2)	2885(12)	22(2)
C(4)	4050(16)	2079(2)	1388(12)	31(2)
C(5)	3026(17)	1750(2)	2081(12)	32(2)
C(6)	3204(15)	1561(2)	5964(13)	28(2)
C(7)	2548(15)	1188(2)	5409(13)	26(2)
C(8)	-519(15)	1130(2)	4354(15)	34(2)
C(9)	-1249(18)	752(2)	3856(17)	41(2)
C(10)	-23(18)	530(2)	5933(16)	41(2)
C(11)	3036(18)	586(2)	6992(16)	41(2)
C(12)	3731(17)	955(2)	7491(14)	34(2)
C(13)	7179(15)	2207(2)	6642(13)	24(2)
O(3)	-5921(10)	-2041(1)	9882(8)	30(1)
O(4)	1354(10)	-1971(1)	15326(8)	26(1)
C(14)	-1232(15)	-1317(2)	12952(12)	22(2)
C(15)	-2082(14)	-1689(2)	12276(11)	21(2)
C(16)	-1464(15)	-1876(2)	14540(12)	22(2)
C(17)	-1949(16)	-1600(2)	16050(12)	28(2)
C(18)	-842(17)	-1274(2)	15420(12)	29(2)
C(19)	-960(15)	-1079(2)	11582(12)	27(2)
C(20)	-189(16)	-710(2)	12150(13)	27(2)
C(21)	2886(17)	-655(2)	13194(15)	36(2)
C(22)	3623(17)	-279(2)	13774(17)	42(2)
C(23)	2396(19)	-52(2)	11700(17)	41(2)
C(24)	-650(19)	-95(2)	10648(16)	40(2)
C(25)	-1395(18)	-476(2)	10125(14)	37(2)
C(26)	-5128(16)	-1700(2)	10794(13)	27(2)

Table 5s. Bond lengths (Å) for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclopentanol, 36.**

O(1)-C(13)	1.437(9)	O(2)-C(3)	1.428(9)
C(1)-C(6)	1.328(10)	C(1)-C(2)	1.514(9)
C(1)-C(5)	1.514(9)	C(2)-C(13)	1.528(10)
C(2)-C(3)	1.538(9)	C(3)-C(4)	1.531(10)
C(4)-C(5)	1.516(11)	C(6)-C(7)	1.504(10)
C(7)-C(8)	1.528(10)	C(7)-C(12)	1.540(10)
C(8)-C(9)	1.524(11)	C(9)-C(10)	1.516(12)
C(10)-C(11)	1.523(12)	C(11)-C(12)	1.488(11)
O(3)-C(26)	1.445(9)	O(4)-C(16)	1.435(9)
C(14)-C(19)	1.313(10)	C(14)-C(18)	1.518(10)
C(14)-C(15)	1.531(10)	C(15)-C(16)	1.540(9)
C(15)-C(26)	1.542(10)	C(16)-C(17)	1.521(10)
C(17)-C(18)	1.510(11)	C(19)-C(20)	1.500(10)
C(20)-C(25)	1.519(11)	C(20)-C(21)	1.530(11)
C(21)-C(22)	1.523(11)	C(22)-C(23)	1.525(13)
C(23)-C(24)	1.510(12)	C(24)-C(25)	1.538(11)

Table 6s. Bond angles (°) for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclopentanol, 36.**

C(6)-C(1)-C(2)	124.5(6)	C(6)-C(1)-C(5)	127.1(7)
C(2)-C(1)-C(5)	108.4(6)	C(1)-C(2)-C(13)	111.3(6)
C(1)-C(2)-C(3)	104.5(6)	C(13)-C(2)-C(3)	112.1(6)
O(2)-C(3)-C(4)	110.3(6)	O(2)-C(3)-C(2)	106.4(6)
C(4)-C(3)-C(2)	103.1(6)	C(5)-C(4)-C(3)	104.1(6)
C(1)-C(5)-C(4)	105.2(6)	C(1)-C(6)-C(7)	125.5(7)
C(6)-C(7)-C(8)	111.2(6)	C(6)-C(7)-C(12)	112.2(6)
C(8)-C(7)-C(12)	109.2(6)	C(9)-C(8)-C(7)	112.4(6)
C(10)-C(9)-C(8)	111.9(8)	C(9)-C(10)-C(11)	110.9(7)
C(12)-C(11)-C(10)	111.8(7)	C(11)-C(12)-C(7)	113.1(7)
O(1)-C(13)-C(2)	113.0(6)	C(19)-C(14)-C(18)	127.2(7)
C(19)-C(14)-C(15)	124.7(7)	C(18)-C(14)-C(15)	108.1(6)
C(14)-C(15)-C(16)	104.0(6)	C(14)-C(15)-C(26)	109.5(6)
C(16)-C(15)-C(26)	112.4(6)	O(4)-C(16)-C(17)	110.4(6)
O(4)-C(16)-C(15)	106.9(6)	C(17)-C(16)-C(15)	103.3(6)
C(18)-C(17)-C(16)	104.8(6)	C(17)-C(18)-C(14)	105.2(6)
C(14)-C(19)-C(20)	126.8(7)	C(19)-C(20)-C(25)	112.1(7)
C(19)-C(20)-C(21)	113.1(6)	C(25)-C(20)-C(21)	109.8(6)
C(22)-C(21)-C(20)	112.2(7)	C(21)-C(22)-C(23)	110.8(8)
C(24)-C(23)-C(22)	111.8(7)	C(23)-C(24)-C(25)	110.5(7)
C(20)-C(25)-C(24)	113.5(7)	O(3)-C(26)-C(15)	111.1(6)

Table 7s. Anisotropic displacement parameters ($Å^2 \times 10^3$) for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclopentanol, 36.**

The anisotropic displacement factor exponent takes the form:

$-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	32(3)	38(3)	10(3)	2(2)	-1(2)	-6(3)
O(2)	27(3)	35(3)	22(3)	-4(2)	-1(2)	11(2)
C(1)	16(4)	29(4)	11(4)	-4(3)	3(3)	-1(3)
C(2)	17(4)	37(5)	9(3)	3(3)	4(3)	5(3)
C(3)	27(4)	28(5)	9(4)	5(3)	4(3)	-3(3)
C(4)	27(5)	50(5)	11(4)	3(3)	2(4)	9(4)
C(5)	46(5)	38(5)	7(4)	-10(3)	4(3)	-10(4)
C(6)	34(5)	30(4)	20(4)	-2(3)	10(4)	0(4)
C(7)	27(4)	31(4)	21(4)	-1(3)	9(3)	0(3)
C(8)	25(5)	46(5)	33(5)	7(4)	13(4)	8(4)
C(9)	32(5)	42(6)	48(6)	5(4)	15(4)	-7(4)
C(10)	54(6)	25(5)	52(6)	1(4)	29(5)	-2(4)
C(11)	48(6)	33(5)	40(5)	12(4)	13(4)	-2(4)
C(12)	34(5)	34(5)	26(5)	13(4)	2(4)	-2(4)
C(13)	28(4)	28(4)	14(4)	3(3)	4(3)	2(3)
O(3)	35(3)	40(4)	7(3)	-3(2)	-2(2)	-12(2)
O(4)	28(3)	31(3)	12(3)	2(2)	0(2)	5(2)
C(14)	24(4)	28(4)	9(4)	-4(3)	2(3)	-1(3)
C(15)	25(4)	28(4)	4(3)	2(3)	1(3)	-2(3)
C(16)	27(4)	29(4)	7(4)	-4(3)	3(3)	-8(3)
C(17)	26(4)	44(5)	8(4)	-6(3)	-2(3)	-1(3)
C(18)	42(5)	29(4)	11(4)	-3(3)	4(3)	12(4)
C(19)	35(5)	33(5)	11(4)	-2(3)	8(4)	-2(4)
C(20)	32(5)	33(5)	19(4)	3(3)	12(4)	-2(4)
C(21)	42(5)	30(5)	33(5)	-4(4)	9(4)	-7(4)
C(22)	32(5)	37(5)	52(6)	-9(4)	10(5)	-6(4)
C(23)	45(6)	32(5)	50(6)	2(4)	22(5)	-13(4)
C(24)	55(7)	32(5)	36(5)	8(4)	22(5)	5(4)
C(25)	40(5)	44(6)	26(5)	3(4)	10(4)	0(4)
C(26)	28(4)	28(4)	16(4)	-5(3)	-1(4)	-4(4)

Table 8s. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclopentanol, 36.**

	x	y	z	Ueq
H(1)	8727(10)	2647(1)	6726(8)	35
H(2)	457(10)	2646(1)	2214(9)	37
H(2A)	3023(13)	2264(2)	5972(11)	25
H(3A)	4638(15)	2564(2)	3007(12)	26
H(4A)	3053(16)	2129(2)	-225(12)	37
H(4B)	6017(16)	2063(2)	1658(12)	37
H(5A)	1079(17)	1713(2)	1173(12)	38
H(5B)	4074(17)	1549(2)	1880(12)	38
H(6A)	3475(15)	1633(2)	7456(13)	34
H(7A)	3371(15)	1118(2)	4283(13)	32
H(8A)	-1388(15)	1218(2)	5393(15)	41
H(8B)	-1251(15)	1263(2)	2936(15)	41
H(9A)	-3251(18)	727(2)	3278(17)	49
H(9B)	-586(18)	673(2)	2668(17)	49
H(10A)	-400(18)	285(2)	5514(16)	49
H(10B)	-876(18)	587(2)	7043(16)	49
H(11A)	3764(18)	451(2)	8406(16)	49
H(11B)	3910(18)	500(2)	5953(16)	49
H(12A)	5734(17)	980(2)	8104(14)	41
H(12B)	3036(17)	1032(2)	8665(14)	41
H(13A)	7595(15)	2048(2)	7939(13)	29
H(13B)	8308(15)	2138(2)	5762(13)	29
H(3)	-6362(10)	-2159(1)	10802(8)	36
H(4)	1501(10)	-2184(1)	15548(8)	31
H(15A)	-967(14)	-1788(2)	11444(11)	25
H(16A)	-2671(15)	-2080(2)	14390(12)	27
H(17A)	-3913(16)	-1577(2)	15772(12)	34
H(17B)	-978(16)	-1657(2)	17658(12)	34
H(18A)	1108(17)	-1246(2)	16347(12)	35
H(18B)	-1852(17)	-1071(2)	15640(12)	35
H(19A)	-1286(15)	-1148(2)	10075(12)	32
H(20A)	-972(16)	-638(2)	13298(13)	33
H(21A)	3631(17)	-795(2)	14580(15)	44
H(21B)	3736(17)	-735(2)	12125(15)	44
H(22A)	5626(17)	-254(2)	14368(17)	50
H(22B)	2940(17)	-205(2)	14961(17)	50
H(23A)	2827(19)	191(2)	12135(17)	49
H(23B)	3225(19)	-111(2)	10577(17)	49
H(24A)	-1353(19)	41(2)	9239(16)	48

H(24B)	-1509(19)	-7(2)	11692(16)	48
H(25A)	-3400(18)	-499(2)	9552(14)	44
H(25B)	-754(18)	-552(2)	8917(14)	44
H(26A)	-6223(16)	-1633(2)	11705(13)	32
H(26B)	-5497(16)	-1533(2)	9544(13)	32

Notes on the structure determination of (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclopentanol, 36.**

Crystals were examined under Exxon Paratone N oil. The datum crystal was mounted using silicone grease to the end of a thin glass fiber attached to a copper mounting-pin. Data collection was performed at 163 K using a Siemens SMART CCD diffractometer equipped with a locally modified LT-2A low-temperature apparatus.

Cell parameters were determined after indexing reflections harvested from 3 orthogonal sets of 20 0.3° ω scans. A hemisphere of data was collected to about 32° θ. Cell refinement utilized 1870 strong reflections, $I > 10\sigma(I)$, chosen from the data set. All data were corrected for Lorentz and polarization effects.

Structure solution via direct methods in the centrosymmetric space group $P2_1$ revealed the non-hydrogen structure. The asymmetric unit is comprised of two crystallographically independent molecules. While the two molecules are related by inversion, a crystallographic inversion center could not be located. A search for higher symmetry using LePage's MISSYM routine in the analytical package PLATON (Spek, A.L. (1990). Acta Cryst. A46, C34) indicated no additional symmetry or pseudo-symmetry. Attempts to move the system to a centrosymmetric space group by applying an origin shift also proved unsuccessful.

Anisotropic parameters for thermal motion were used for all non-hydrogen atoms. Hydrogens were placed at calculated positions with isotropic thermal parameters set to 1.2 times the equivalent isotropic U of the parent atom. Hydroxy hydrogens were located by Fourier map and refined at idealized geometry. Data above 26° θ were discarded during refinement because of poor agreement between observed and calculated values.

Table 9s. Crystal data for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclohexanol, 41.**

Identification code	bc141m
Empirical formula	$(C_{14}H_{24}O_2)_2$
Formula mass	448.66
Crystal size, mm	0.04 × 0.08 × 0.24
Crystal color, habit	colorless plate
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	18.8975(15)
b, Å	8.2950(6)
c, Å	18.8975(15)
α, °	90
β, °	116.7520(10)
γ, °	90
Volume, Å^3	2645.2(4)
Z, formula units/cell	4
Density (calculated), Mg·m^{-3}	1.127
Absorption coefficient, mm^{-1}	0.073
F(000)	992
Absorption correction	None
Range Transmission Coefficients	0.995 to 0.997

Table 10s. Data collection parameters for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclohexanol, 41.**

Diffractometer	Siemens SMART CCD
Temperature, K	172(2)
Radiation source	sealed tube
Wavelength, Å	0.71073, MoKα
Monochromator	graphite
Cell measurement	
Reflections used	2698
θ range, °	$2.16 < \theta < 24.80$
θ range, data collection	$2.16 < \theta < 24.80$
Scan type	ω scans
Index ranges	$-22 \le h \le 14$,
	$-9 \le k \le 9$,
	$-21 \le l \le 22$
Reflections collected	13061
Independent reflections	4523 (R(int) = 0.1396)
Standard reflections	50 frames re-measured
Stability of standards	no decay observed

Table 11s. Structure Solution and Refinement for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclohexanol, 41.**

System used[1,2]	Siemens SHELXTL
Structure solution	direct
Data/ restraints/ parameters	4393 / 0/ 290
Hydrogen atoms	riding, with riding isotropic U
weighting scheme	calc $w^{-1}=[\sigma^2(F_o^2)+(0.0000P)^2+5.6309P]$ where $P=(F_o^2+2F_c^2)\div 3$
Final R indices[3] [I>2σ(I)]	R1 = 0.0985, wR2 = 0.1522
Reflections observed	2565
R indices (all data)	R1 = 0.1821, wR2 = 0.1957
Goodness-of-fit[4] on F^2	1.174
Extinction coefficient	0.0011(3)
Largest diff. peak and hole	0.384 and -0.357

6) G. M. Sheldrick, SHELXTL, *A Program for Crystal Structure Determination.* Version 5.03, 1995, Siemens Analytical X-ray Instruments, Madison, Wisconsin.

7) Scattering factors (neutral atoms) are from "International Tables for Crystallography" Vol. C, D. Reidel Publishing Co. Boston, 1991.

8) $R1=\frac{\sum\|F_o|-|F_c\|}{\sum|F_o|}$; $wR2=\sqrt{\frac{\sum[w(F_o^2-F_c^2)^2]}{\sum[w(F_o^2)^2]}}$;

9) $GooF=S=\sqrt{\frac{\sum[w(F_o^2-F_c^2)^2]}{(M-N)}}$ where M is the number of reflections and N is the number of parameters refined.

Table 12s. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclohexanol, 41.**

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	Ueq
O(1)	4542(2)	8783(4)	3459(2)	40(1)
O(2)	4085(2)	8255(4)	1058(2)	33(1)
C(1)	3624(2)	8931(5)	2036(2)	22(1)
C(2)	4061(3)	7723(5)	1769(3)	25(1)
C(3)	3660(3)	6074(5)	1583(3)	30(1)
C(4)	2787(3)	6193(6)	1001(3)	33(1)
C(5)	2345(3)	7370(5)	1286(3)	30(1)
C(6)	2748(3)	8988(6)	1473(2)	24(1)
C(7)	2403(3)	10405(6)	1189(3)	27(1)
C(8)	1547(3)	10774(6)	650(3)	27(1)
C(9)	1462(3)	11380(6)	-157(3)	33(1)
C(10)	605(3)	11852(6)	-713(3)	40(1)
C(11)	304(3)	13112(6)	-333(3)	40(1)
C(12)	376(3)	12505(6)	454(3)	38(1)
C(13)	1219(3)	12025(6)	1010(3)	36(1)
C(14)	3744(3)	8559(6)	2876(3)	34(1)
O(3)	4342(2)	13538(4)	5969(2)	34(1)
O(4)	4758(2)	11702(4)	4135(2)	34(1)
C(15)	3905(2)	11858(5)	4755(2)	23(1)
C(16)	4413(3)	12832(5)	4466(3)	27(1)
C(17)	3934(3)	14103(6)	3852(3)	34(1)
C(18)	3223(3)	13355(6)	3161(3)	37(1)
C(19)	2687(3)	12451(6)	3442(3)	32(1)
C(20)	3146(3)	11242(5)	4078(2)	23(1)
C(21)	2902(3)	9747(6)	4094(2)	23(1)
C(22)	2127(3)	9007(5)	3514(3)	25(1)
C(23)	1448(3)	9651(6)	3661(3)	31(1)
C(24)	658(3)	8913(6)	3111(3)	35(1)
C(25)	687(3)	7092(6)	3167(3)	42(1)
C(26)	1344(3)	6432(6)	3004(3)	43(1)
C(27)	2140(3)	7168(6)	3551(3)	31(1)
C(28)	3681(3)	12843(6)	5313(3)	28(1)

Table 13s. Bond lengths (Å) for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclohexanol, 41.**

O(1)-C(14)	1.424(5)	O(2)-C(2)	1.435(5)
C(1)-C(6)	1.513(6)	C(1)-C(2)	1.521(6)
C(1)-C(14)	1.529(6)	C(2)-C(3)	1.526(6)
C(3)-C(4)	1.519(6)	C(4)-C(5)	1.532(6)
C(5)-C(6)	1.504(6)	C(6)-C(7)	1.334(6)
C(7)-C(8)	1.505(6)	C(8)-C(13)	1.517(6)
C(8)-C(9)	1.543(6)	C(9)-C(10)	1.532(6)
C(10)-C(11)	1.516(7)	C(11)-C(12)	1.516(7)
C(12)-C(13)	1.515(6)	O(3)-C(28)	1.427(5)
O(4)-C(16)	1.436(5)	C(15)-C(20)	1.517(6)
C(15)-C(16)	1.533(6)	C(15)-C(28)	1.536(6)
C(16)-C(17)	1.527(6)	C(17)-C(18)	1.522(6)
C(18)-C(19)	1.535(6)	C(19)-C(20)	1.505(6)
C(20)-C(21)	1.328(6)	C(21)-C(22)	1.508(6)
C(22)-C(23)	1.526(6)	C(22)-C(27)	1.527(6)
C(23)-C(24)	1.513(6)	C(24)-C(25)	1.514(6)
C(25)-C(26)	1.509(7)	C(26)-C(27)	1.519(6)

Table 14s. Bond angles (°) for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclohexanol, 41.**

C(6)-C(1)-C(2)	111.9(4)	C(6)-C(1)-C(14)	109.9(4)
C(2)-C(1)-C(14)	111.2(4)	O(2)-C(2)-C(1)	111.1(3)
O(2)-C(2)-C(3)	106.4(3)	C(1)-C(2)-C(3)	112.3(4)
C(4)-C(3)-C(2)	111.9(4)	C(3)-C(4)-C(5)	111.9(4)
C(6)-C(5)-C(4)	110.6(4)	C(7)-C(6)-C(5)	125.9(4)
C(7)-C(6)-C(1)	119.5(4)	C(5)-C(6)-C(1)	114.5(4)
C(6)-C(7)-C(8)	129.3(4)	C(7)-C(8)-C(13)	111.6(4)
C(7)-C(8)-C(9)	109.6(4)	C(13)-C(8)-C(9)	109.7(4)
C(10)-C(9)-C(8)	111.6(4)	C(11)-C(10)-C(9)	110.9(4)
C(12)-C(11)-C(10)	110.4(4)	C(13)-C(12)-C(11)	111.7(4)
C(12)-C(13)-C(8)	112.5(4)	O(1)-C(14)-C(1)	112.8(4)
C(20)-C(15)-C(16)	112.5(4)	C(20)-C(15)-C(28)	108.1(4)
C(16)-C(15)-C(28)	112.0(4)	O(4)-C(16)-C(17)	110.5(4)
O(4)-C(16)-C(15)	106.9(4)	C(17)-C(16)-C(15)	112.5(4)
C(18)-C(17)-C(16)	111.3(4)	C(17)-C(18)-C(19)	111.5(4)
C(20)-C(19)-C(18)	111.7(4)	C(21)-C(20)-C(19)	123.9(4)
C(21)-C(20)-C(15)	120.1(4)	C(19)-C(20)-C(15)	115.9(4)
C(20)-C(21)-C(22)	126.7(4)	C(21)-C(22)-C(23)	110.2(3)
C(21)-C(22)-C(27)	112.5(4)	C(23)-C(22)-C(27)	109.8(4)
C(24)-C(23)-C(22)	112.6(4)	C(23)-C(24)-C(25)	111.2(4)
C(26)-C(25)-C(24)	110.8(4)	C(25)-C(26)-C(27)	111.6(4)
C(26)-C(27)-C(22)	112.3(4)	O(3)-C(28)-C(15)	114.0(4)

Table 15s. Anisotropic displacement parameters ($Å^2 \times 10^3$) for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclohexanol, 41.**

The anisotropic displacement factor exponent takes the form:

$-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	32(2)	47(2)	29(2)	-2(2)	4(2)	10(2)
O(2)	45(2)	29(2)	36(2)	3(2)	29(2)	4(2)
C(1)	20(2)	21(2)	25(2)	-2(2)	10(2)	3(2)
C(2)	25(3)	27(3)	25(3)	4(2)	14(2)	4(2)
C(3)	44(3)	20(3)	34(3)	1(2)	25(3)	5(2)
C(4)	39(3)	28(3)	31(3)	-4(2)	16(2)	-6(2)
C(5)	28(3)	29(3)	29(3)	4(2)	10(2)	-4(2)
C(6)	26(3)	28(3)	20(2)	0(2)	13(2)	3(2)
C(7)	26(3)	29(3)	27(3)	-1(2)	13(2)	-2(2)
C(8)	25(3)	21(3)	31(3)	2(2)	8(2)	-2(2)
C(9)	36(3)	31(3)	28(3)	2(2)	11(2)	3(2)
C(10)	30(3)	41(3)	39(3)	11(3)	8(3)	-3(3)
C(11)	31(3)	31(3)	51(3)	14(3)	13(3)	6(3)
C(12)	28(3)	39(3)	49(3)	5(3)	19(3)	8(2)
C(13)	34(3)	39(3)	33(3)	0(2)	12(2)	3(3)
C(14)	31(3)	39(3)	24(3)	-2(2)	7(2)	0(2)
O(3)	27(2)	36(2)	32(2)	-13(2)	6(2)	2(2)
O(4)	44(2)	27(2)	44(2)	-4(2)	31(2)	-4(2)
C(15)	22(2)	22(2)	22(2)	-1(2)	7(2)	3(2)
C(16)	29(3)	22(3)	31(3)	-6(2)	14(2)	-1(2)
C(17)	37(3)	26(3)	38(3)	3(2)	17(3)	-3(2)
C(18)	45(3)	29(3)	30(3)	10(2)	11(2)	-3(3)
C(19)	34(3)	25(3)	29(3)	1(2)	9(2)	-3(2)
C(20)	26(3)	21(3)	24(2)	-2(2)	13(2)	-2(2)
C(21)	26(3)	29(3)	19(2)	-1(2)	14(2)	2(2)
C(22)	27(3)	21(3)	23(2)	-2(2)	10(2)	-1(2)
C(23)	30(3)	27(3)	35(3)	-4(2)	15(2)	1(2)
C(24)	31(3)	29(3)	40(3)	3(2)	12(2)	2(2)
C(25)	35(3)	29(3)	51(3)	4(3)	9(3)	-2(3)
C(26)	43(3)	23(3)	51(3)	-7(3)	12(3)	-2(3)
C(27)	32(3)	28(3)	33(3)	-6(2)	15(2)	1(2)
C(28)	29(3)	29(3)	27(3)	-5(2)	13(2)	2(2)

Table 16s. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for (1*R, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclohexanol, 41.**

	x	y	z	Ueq
H(1)	4806(2)	9199(4)	3247(2)	48
H(2)	3997(2)	9251(4)	1001(2)	39
H(1A)	3851(2)	10023(5)	2043(2)	26
H(2A)	4615(3)	7601(5)	2197(3)	30
H(3A)	3931(3)	5370(5)	1358(3)	36
H(3B)	3714(3)	5573(5)	2081(3)	36
H(4A)	2542(3)	5113(6)	929(3)	39
H(4B)	2735(3)	6556(6)	481(3)	39
H(5A)	1793(3)	7496(5)	870(3)	36
H(5B)	2330(3)	6932(5)	1766(3)	36
H(7A)	2747(3)	11311(6)	1349(3)	32
H(8A)	1232(3)	9759(6)	561(3)	32
H(9A)	1812(3)	12325(6)	-70(3)	40
H(9B)	1636(3)	10521(6)	-408(3)	40
H(10A)	578(3)	12284(6)	-1213(3)	47
H(10B)	263(3)	10885(6)	-842(3)	47
H(11A)	616(3)	14116(6)	-247(3)	48
H(11B)	-257(3)	13362(6)	-691(3)	48
H(12A)	201(3)	13360(6)	705(3)	45
H(12B)	23(3)	11563(6)	359(3)	45
H(13A)	1235(3)	11589(6)	1504(3)	44
H(13B)	1561(3)	12995(6)	1149(3)	44
H(14A)	3394(3)	9266(6)	3002(3)	40
H(14B)	3587(3)	7428(6)	2897(3)	40
H(3)	4762(2)	13110(4)	6013(2)	41
H(4)	5028(2)	12201(4)	3954(2)	41
H(15A)	4221(2)	10904(5)	5056(2)	28
H(16A)	4847(3)	13380(5)	4930(3)	32
H(17A)	3748(3)	14935(6)	4106(3)	40
H(17B)	4277(3)	14637(6)	3653(3)	40
H(18A)	3411(3)	12598(6)	2877(3)	44
H(18B)	2913(3)	14214(6)	2785(3)	44
H(19A)	2432(3)	13236(6)	3649(3)	38
H(19B)	2264(3)	11887(6)	2986(3)	38
H(21A)	3250(3)	9076(6)	4513(2)	28
H(22A)	2028(3)	9333(5)	2968(3)	30
H(23A)	1562(3)	9422(6)	4216(3)	37
H(23B)	1416(3)	10835(6)	3589(3)	37
H(24A)	513(3)	9241(6)	2559(3)	42

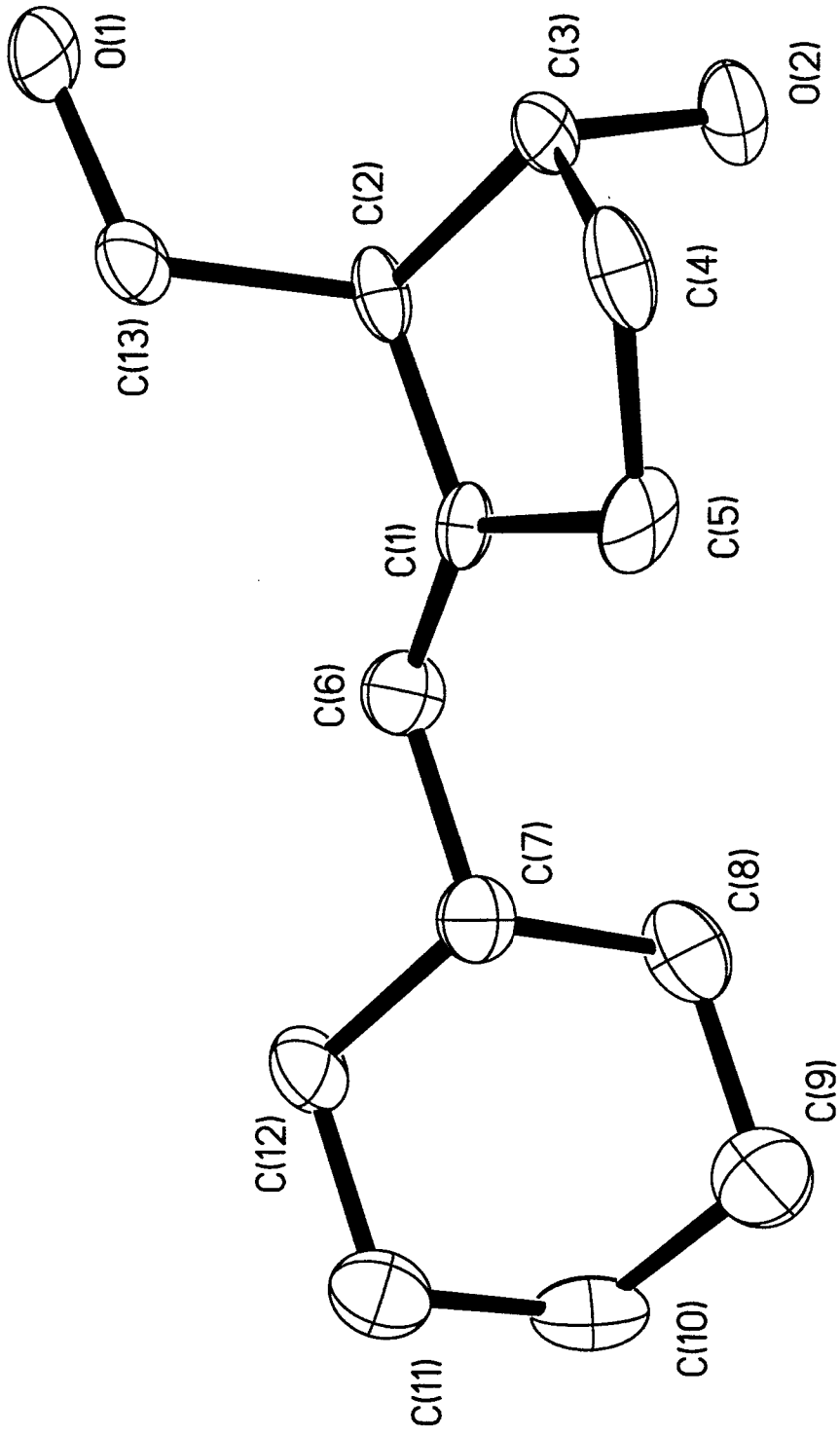
H(24B)	245(3)	9322(6)	3250(3)	42
H(25A)	776(3)	6760(6)	3704(3)	51
H(25B)	174(3)	6640(6)	2779(3)	51
H(26A)	1223(3)	6662(6)	2447(3)	51
H(26B)	1372(3)	5248(6)	3075(3)	51
H(27A)	2548(3)	6759(6)	3403(3)	37
H(27B)	2291(3)	6824(6)	4102(3)	37
H(28A)	3315(3)	13718(6)	5005(3)	34
H(28B)	3392(3)	12135(6)	5517(3)	34

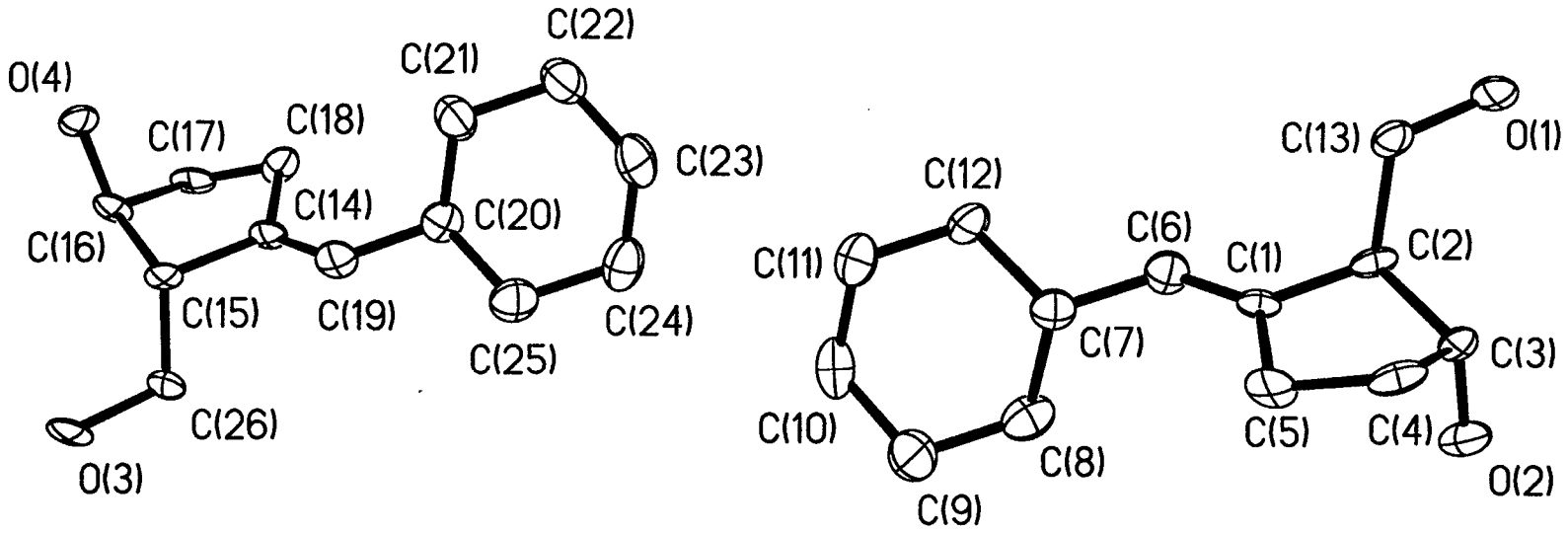
Notes on the structure determination of (1*R**, 2*R**, 3*E*)-3-(Cyclohexylmethylene)-2-hydroxymethyl-1-cyclohexanol, 41.

Crystals were examined under Exxon Paratone N oil. The datum crystal was mounted using silicone grease to the end of a thin glass fiber attached to a copper mounting-pin. Data collection was performed at 172 K using a Siemens SMART CCD diffractometer equipped with a locally modified LT-2A low-temperature apparatus.

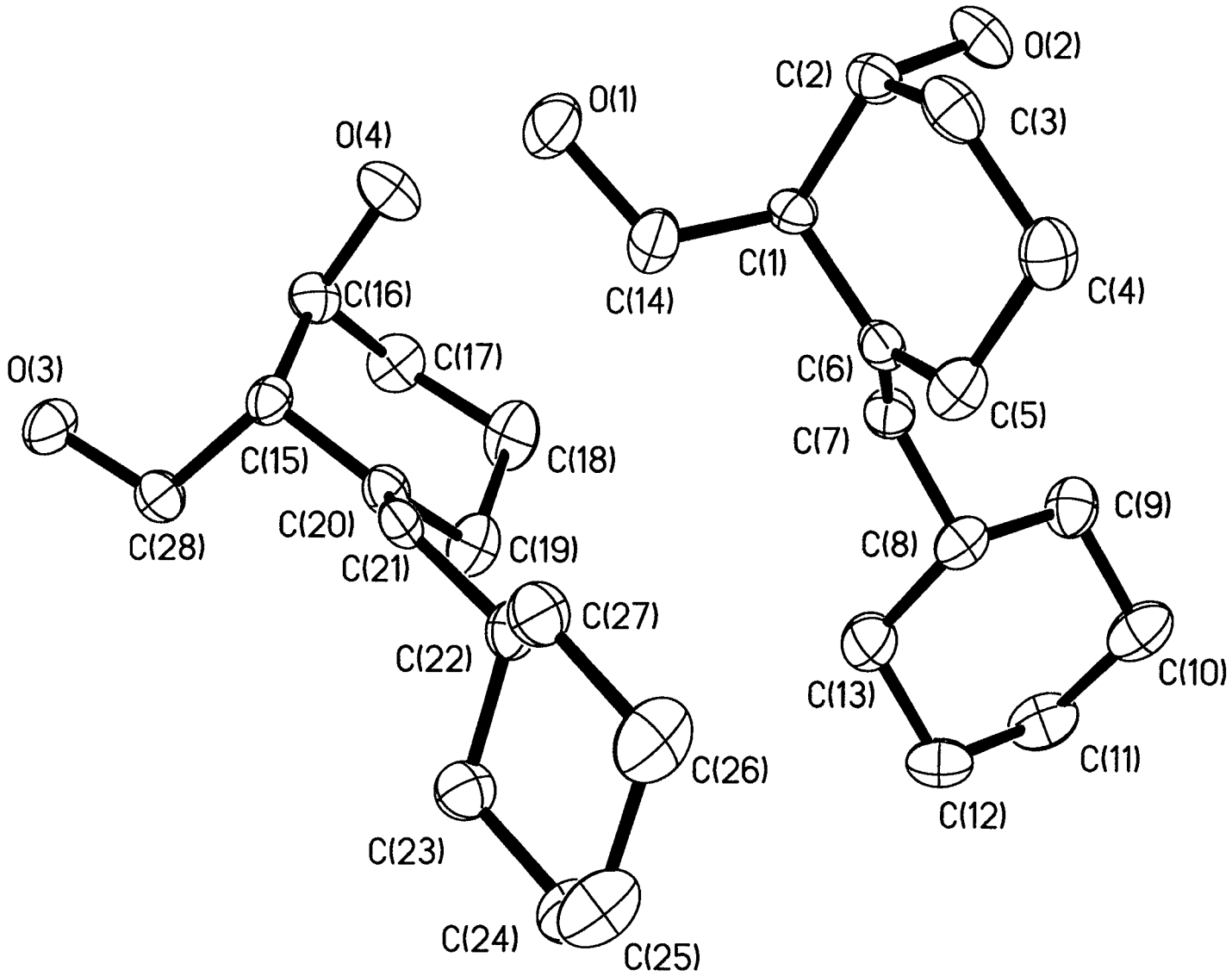
Cell parameters were determined after indexing reflections harvested from 3 orthogonal sets of 20 0.3° ω scans. A hemisphere of data was collected to about 32° θ. Cell refinement utilized 2698 strong reflections, $I > 10\sigma(I)$, chosen from the data set. All data were corrected for Lorentz and polarization effects.

Structure solution via direct methods in the centrosymmetric space group $P2_1/c$ revealed the non-hydrogen structure. The asymmetric unit is comprised of two crystallographically independent molecules. Anisotropic parameters for thermal motion were used for all non-hydrogen atoms. Hydrogens were placed at calculated positions with isotropic thermal parameters set to 1.2 times the equivalent isotropic U of the parent atom. Data above 25° θ were discarded during refinement because of poor agreement between observed and calculated values. Nineteen inconsistent equivalents with $\sigma(\langle F_o^2 \rangle) > 20$ were edited to remove the largest outlier of each set.

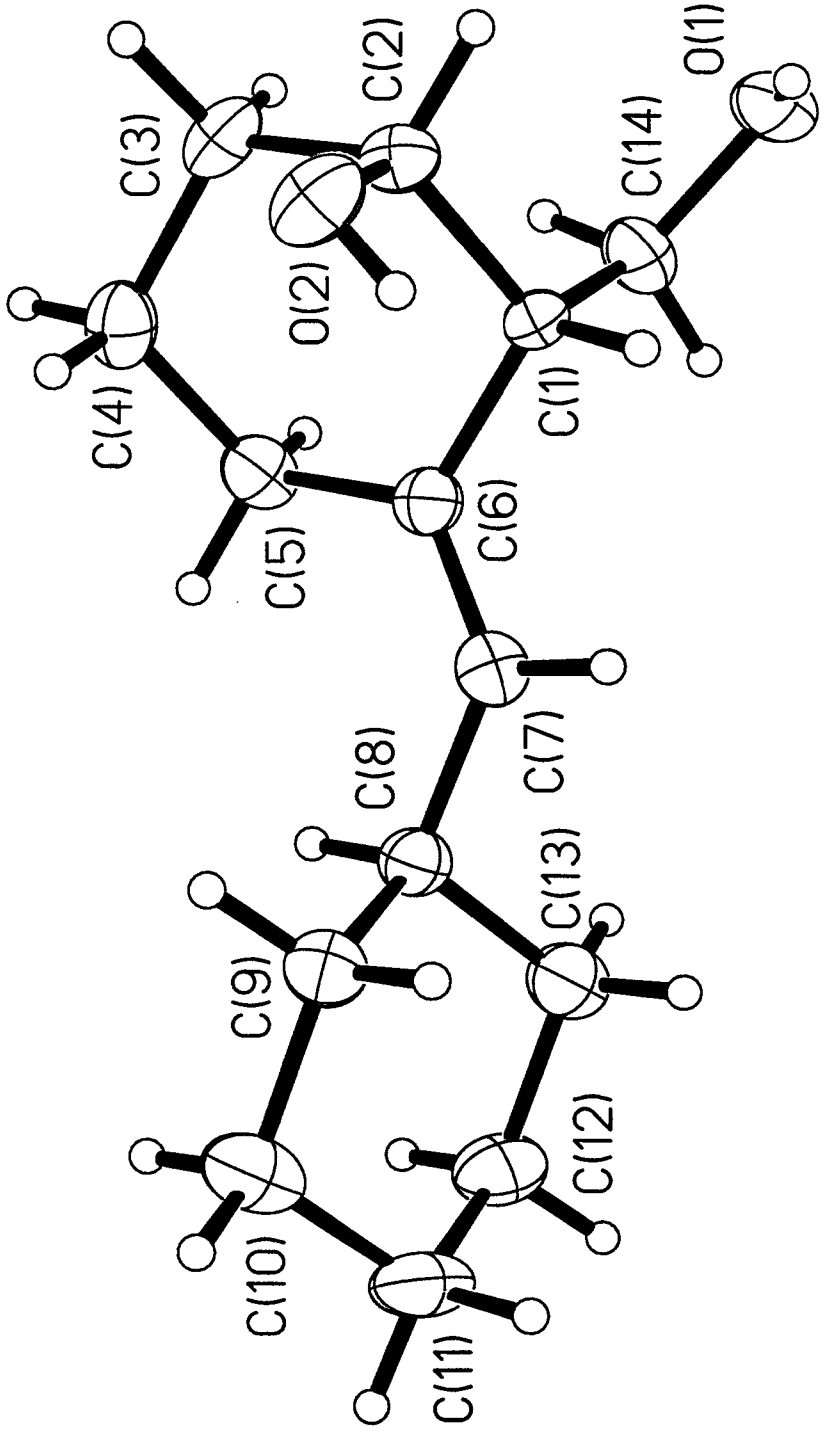

O(1)
C(3)
O(2)
C(2)
C(4)
C(13)
C(1)
C(5)
C(6)
C(7)
C(8)
C(12)
C(9)
C(11)
C(10)

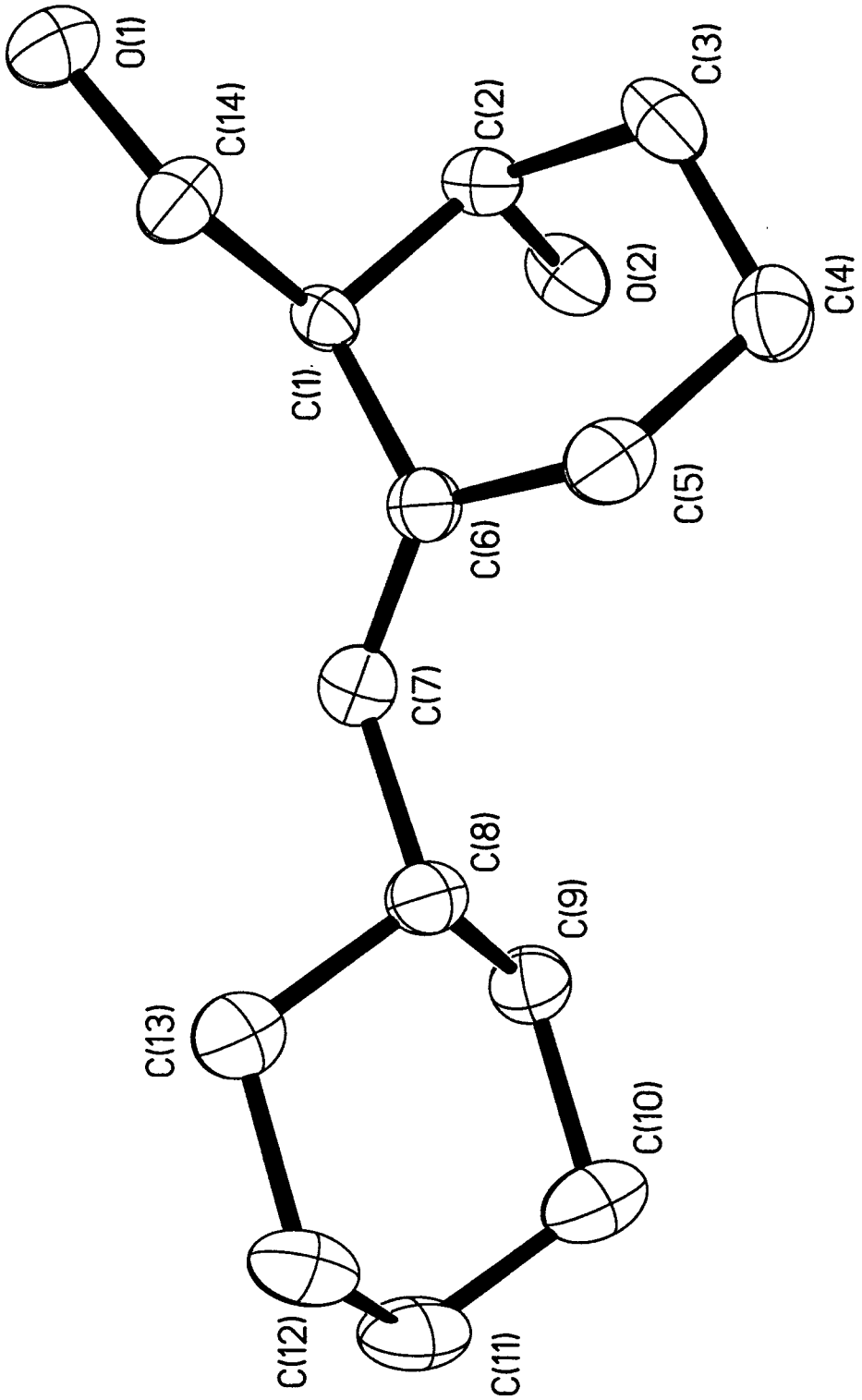


©1997 American Chemical Society



©1997 American Chemical Society


O(1)
C(14)
C(2)
C(3)
O(2)
C(4)
C(1)
C(5)
C(6)
C(7)
C(8)
C(13)
C(9)
C(12)
C(10)
C(11)


O(1)
C(14)
C(2)
C(3)
O(2)
C(4)
C(1)
C(5)
C(6)
C(7)
C(8)
C(9)
C(13)
C(10)
C(12)
C(11)