rhodium acetate and 15 mL of 2,3-dimethyl-2-butene while the temperature was maintained at -70 °C. The mixture was allowed to warm to room temperature with stirring which was continued for 4 days. The residue obtained after removal of the solvent was subjected to preparative TLC (alumina, benzene) to afford 32 mg (0.10 mmol, 30% yield) of **47** as a white solid. Further purification was achieved by repeated crystallization from methanol to provide **47** as white crystals, mp 194.6-196.8 °C. Crystals appropriate to allow an X-ray determination were grown by slow evaporation of a methanol solution of **47**: IR (CCl_4) 1755 (C=O) cm^{-1}; UV (ethanol) λ_{max} 207 nm (43 400), 290 (3060), 336 (92); ^1H NMR ($CDCl_3$) δ 1.17 (s, 6 H), 1.58 (s, 6 H), 2.10 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 2.8 (q), 4.3 (q), 4.5 (q), 12.3 (q), 15.3 (q), 23.2, 40.0, 48.9, 111.8, 114.2, 127.6, 144.0, 207.0 (C=O); mass spectrum, m/e 312 (M^+). Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.55; H, 7.70.

Reaction of 1 with *o*-Dihydroxybenzene. Synthesis of 49 and 51. To a solution containing 1.32 mmol of **1** in 10 mL of CH_2Cl_2 was added dropwise a solution of 290 mg (2.64 mmol) of *o*-dihydroxybenzene in 20 mL of CH_2Cl_2 while the temperature was maintained at -80 °C. The mixture was allowed to warm to room temperature overnight. The solvent was removed in vacuo to leave a brown residue. Upon the addition of ether, 157 mg (0.60 mmol, 45% overall yield) of a brown-white precipitate was obtained, consisting of a mixture of **49** and **51** (ratio 5:2, respectively). Crystallization of this precipitate from CH_2Cl_2/hexane and methanol gave 30 mg of **49** as white crystals, mp 127.1-127.4 °C. The combined mother liquors were subjected to high-pressure LC (silica gel, 9/1 CH_2Cl_2/CH_3CN) to furnish 83 mg of **49** (total yield of **49** was 113 mg, 0.40 mmol, 30%) and 43 mg (0.17 mmol, 13%) of **51** as white crystals, mp 121.5-122.1 °C. Crystals of **49** appropriate to allow an X-ray determination were grown from a slowly evaporating methanol solution. Spectroscopic data for **49**: IR ($CHCl_3$) 3540 (OH), 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.31 (s, 3 H), 1.49 (s, 3 H), 1.58 (s, 3 H), 2.52 (s, 1 H), 5.62 (br s, 1 H), 6.87 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 4.3 (q), 4.7 (q), 7.9 (q), 16.6 (q), 34.6, 43.9, 50.6 (d, J_{CH} = 180 Hz), 71.5, 87.1, 115.5 (d, J_{CH} = 156 Hz), 119.8 (d, J_{CH} = 156 Hz), 121.9 (d, J_{CH} = 162 Hz), 124.7 (d, J_{CH} = 162 Hz), 141.3, 149.0, 187.0 (C=O); mass spectrum, found m/e 258.130, calcd m/e 258.126 (M^+). Spectroscopic data for **51**: IR ($CHCl_3$) 3520 (OH), 1710 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (s, 3 H), 1.32 (s, 3 H), 1.50 (s, 3 H), 1.56 (s, 3 H), 3.11 (s, 1 H), 5.63 (br s, 1 H), 6.86 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 3.8 (q), 4.0 (q), 5.7 (q), 18.3 (q), 33.8, 47.0, 57.1, 67.1 (d, J_{CH} = 168 Hz), 85.1, 115.5 (d, J_{CH} = 162 Hz), 120.1 (d, J_{CH} = 162 Hz), 120.2 (d, J_{CH} = 162 Hz), 124.2 (d, J_{CH} = 162 Hz), 141.7, 148.5, 184.7 (C=O); mass spectrum, found m/e 258.128, calcd m/e 258.126 (M^+).

Registry No. **1**, 68255-25-4; **2**, 56745-78-9; **3**, 74744-17-5; **4**, 70993-60-1; **5**, 68255-26-5; **6**, 68255-27-6; **7**, 74725-13-6; **8**, 56745-77-8; **9**, 74744-18-6; **11**, 67024-12-8; **14A/14B**, 68255-28-7; **16**, 74725-14-7; **17**, 74744-19-7; **23**, 74725-15-8; **24**, 74725-16-9; **25**, 74725-17-0; **34**, 74725-18-1; **35**, 74725-19-2; **36**, 74725-20-5; **47**, 74725-21-6; **49**, 74725-22-7; **51**, 74725-23-8; acrylonitrile, 107-13-1; dimethyl acetylenedicarboxylate, 762-42-5; tetrachloro-*o*-quinone, 2435-53-2; vinyl acetate, 108-05-4; 2,3-dimethyl-2-butene, 563-79-1; 2-methylpropene, 115-11-7; *o*-dihydroxybenzene, 120-80-9; $AgClO_4$, 7783-93-9; $Cu(Acac)_2$, 13395-16-9; $Rh_2(OAc)_4$, 11071-42-4.

Synthesis of 1,2,3-Decanetriol Stereoisomers

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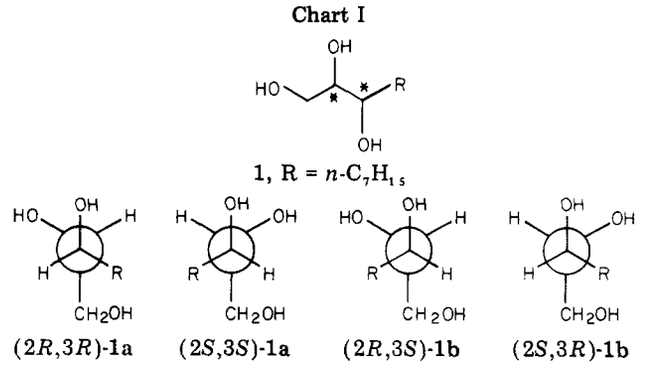
The synthesis and ^{13}C NMR spectra of 1,2,3-decanetriol stereoisomers are described. High enantiomeric purity triols are obtained by chromatographic resolution of diastereomeric carbamates derived from 1-decyn-3-ol and (*R*)-1-(1-napthyl)ethylamine. The triol is obtained by conversion of the acetylene to an olefin, stereoselective epoxidation with *tert*-butyl hydroperoxide and a transition-metal catalyst, and stereospecific ring opening of the epoxide with KOH.

In connection with ^{13}C NMR relaxation studies of highly associated molecules, interesting results have been obtained from the study of 1,2-decanediol.[2] To continue these studies and to further clarify the mechanism of this novel relaxation behavior, we found it desirable to prepare and study the relaxation properties of 1,2,3-alkanetriols. To eliminate spectral complication and to examine possible differences in NMR chemical shift and relaxation properties of the diastereomers and enantiomers in racemic and enantiomerically pure form, we prepared the four stereoisomers of 1,2,3-decanetriol (Chart I, **1**).

Problems attending the synthesis of optically active materials include the determinations of absolute configuration and enantiomeric composition of the final product. We report a relatively simple synthesis of 1,2,3-alkanetriols applied to **1** which allows direct assignment of the absolute configuration and enantiomeric purity as a consequence of the reaction sequence, NMR spectral properties, and chemical properties of key intermediates in the synthesis.

Chart I



Results and Discussion

The synthesis of 1,2,3-decanetriol (**1**) is described in Scheme I. The preparation of optically active **1** hinges upon the chromatographic separation of the enantiomers of propargyl alcohol (**2**) via their diastereomeric carbamate

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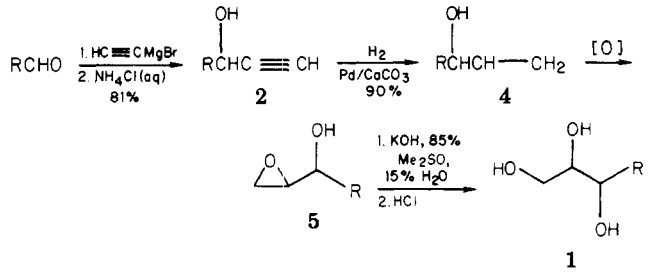
(2) Levy, G. C.; Cordes, M. P.; Lewis, J. S.; Axelson, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 5492.

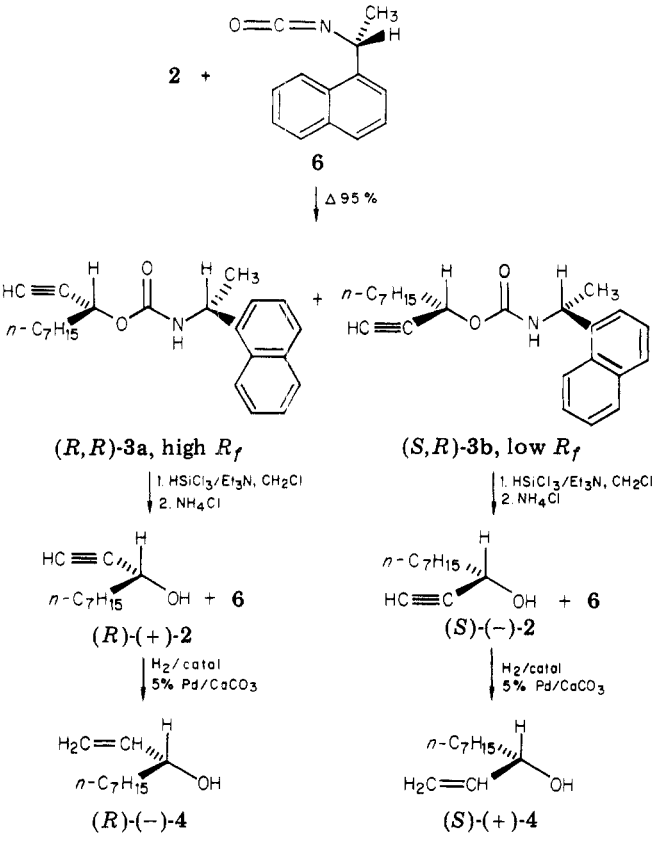
0022-3263/80/1945-4348$01.00/0

Scheme I[a]



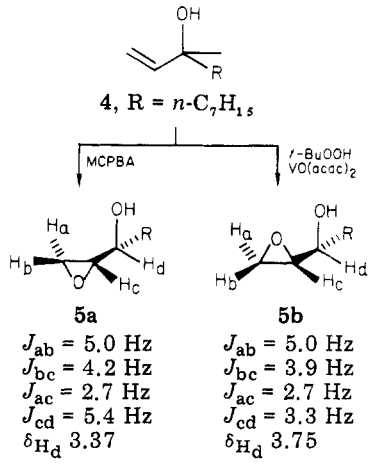
[a] R = n-C_7H_{15}.

Scheme II



derivatives (**3a** and **3b**, Scheme II).[3] Pirkle and Hauske[4] have shown that the relative elution orders of a wide variety of carbamates, similar in structure to **3**, can be explained by a predominance of the conformers depicted by **3** in Scheme II. Interaction with a polar stationary phase such as silica gel occurs primarily at the polar carbonyl substituent, so that the relative elution orders are dependent upon the accessibility of the carbonyls to the stationary phase. This in turn is dependent upon the relative repulsive ability of the substituents on the carbinol and amine moieties of **3** toward the stationary phase. In the case of propargylic carbamates, the acetylenic group is more repulsive than the alkyl chain, and the aryl substituent is more repulsive than the methyl group. In **3a** the two more repulsive groups are on opposite faces of the carbonyl, preventing approach from both faces. In **3b**, both of the more repulsive groups are on the same face of the carbonyl, so that one face is more accessible in **3b** relative to **3a**. On the basis of the chromatographic elution orders of diastereomers **3a** and **3b** [CH_2Cl_2–hexane (1:4), silica gel] and the known configuration of the starting amine, the absolute configurations can be assigned.[3,4]

Scheme III



Additional support for the configurational assignments made is provided by the proton NMR chemical shifts of the $NCCH_3$ resonances of **3a** and **3b**. It has been shown[5] that exchange between various conformers of **3** is slow on the NMR time scale and that the major conformers populated are depicted by **3a** and **3b** (Scheme II).[4,5] This has implications with regard to the relative proton chemical shifts of **3a** and **3b**. The NMR shielding anisotropy of the triple bond causes the syn facial CH_3 resonance of **3a** (δ 1.65) to be downfield of the antara facial CH_3 resonance of **3b** (δ 1.46).[4] Thus by the relative shielding of the methyl groups in the two diastereomers, the absolute configurations can be assigned. By measurement of the integrated intensities of the two sets of resonances, an estimate of the diastereomeric purity of the two carbamates can be obtained. In this case since only one isomer could be detected by ^1H NMR, a lower limit of ~95% diastereomeric purity was estimated for **3a** and **3b**.

Silanolysis using trichlorosilane/triethylamine[6] converts **3a** and **3b** to (*R*)-(+)- and (*S*)-(−)-**2**, respectively, in 75–85% yield. Reduction of (*R*)-(+)- and (*S*)-(−)-**2** with Lindlar catalyst and hydrogen yields allylic alcohols (*R*)-(−)- and (*S*)-(+)-**4**, respectively.

Recently, the use of transition-metal catalysts for the stereoselective epoxidation of cyclic allylic alcohols has been demonstrated.[7,8] Acyclic allylic alcohols have also been oxidized with varying degrees of stereoselectivity.[9] This appears to be an excellent method to use the chiral center in **4** to fix the stereochemistry of the remaining chiral carbinol center of the desired triol. When *t*-BuOOH with $Mo(CO)_6$ as a catalyst was used, very little reaction took place even in refluxing benzene. The other two oxidation reagents, *m*-chloroperoxybenzoic acid (MCPBA) and *t*-BuOOH/$VO(acac)_2$, gave quantitative yields of epoxy alcohols **5a** and **5b**.

Oxidation of numerous terminal allylic alcohols with $VO(acac)_2$ has been shown to yield predominantly the erythro epoxy alcohols while MCPBA preferentially forms threo epoxy alcohols.[10,11] As an aid to the assignment of

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Table I. ^{13}C NMR Chemical Shifts of 5 and 1[a,b]

carbon	chemical shift[c] 5a	5b	1a	1b
1	45.19	43.56	67.7	69.8
2	55.58	54.71	*d*	78.24
3	71.59	68.61	72.18	73.72
4	34.36	33.57	32.72	33.17
5	25.37	25.37	25.78	25.48
6	29.56	29.66	29.70	29.70
7	29.30	29.30	29.28	29.28
8	31.84	31.84	31.89	31.89
9	22.67	22.67	22.66	22.66
10	14.08	14.08	14.00	14.00

[a] Obtained at 67.9 MHz: 6000-Hz spectral window, 8K data points, 2-Hz line broadening, 10% solution in $CDCl_3$, δ relative to Me_4Si. [b] 5a and 1a are *RR/SS*; 5b and 1b are *RS/SR*. [c] In parts per million from Me_4Si (δ); 10% solution in $CDCl_3$. Assignments were made by comparison with calculated chemical shifts, with the aid of single-frequency off-resonance decoupling and T_1 experiments. [d] Obscured by solvent resonance.

Table II. Oxidation of 4 under Various Conditions

reagent/solvent	temp, °C	5a[a]	5b
MCPBA/$CHCl_3$	0	54	46
	−15	61	39
t-BuO_2H, $VO(acac)_2/C_6H_6$	80	42	58
	25	27	73
$C_6H_5CH_3$	0	20	80
	−50	15	85
	−75 to rt[b]	15	85

[a] Determined by ^{13}C NMR signal intensities for C-1, C-2, C-3, and C-4, under conditions such that quantitative results could be obtained from integrated signal intensities. 5a is *RR/SS*; 5b is *RS/SR*. [b] Room temperature.

the erythro and threo isomers, Mihelich[10] has found that the erythro diastereomers consistently have couplings J_{cd} = 3.25 Hz, while the threo diastereomer have $J_{cd} \geq 5.0$ Hz. This is consistent with our results (Scheme III). Also consistent is the fact that δ_{H_d} of the erythro is downfield relative to δ_{H_d} of the threo diastereomer.[10]

Previous workers have chosen to use GLC to assay for the relative amounts of erythro and threo epoxy alcohols. Alternatively, we have found ^{13}C NMR to be useful. Although the proton NMR spectra are relatively complex even at high field, the ^{13}C NMR spectra of the two diastereomers are simple (Table I). It is therefore trivial to determine the diastereomeric ratio of the epoxidation products under various conditions (Table II). Oxidation with MCPBA produces a slight excess of the threo diastereomer **5a**. Below −15 °C the reaction does not proceed to a measurable extent. With *tert*-butyl hydroperoxide in the presence of $VO(acac)_2$ the erythro diastereomer is produced in excellent yield, with high stereoselectivity despite the nonrigidity of the acyclic allylic alcohol.

Previously, the erythro and threo isomers of α,β-epoxy alcohols were found to be separable by liquid chromatography.[10] Although this was also true for **5a** and **5b**, it was more convenient to convert **5** to triol **1** and to recrystallize the mixture of diastereomers once from chloroform to provide the pure stereoisomers.

The final step in the sequence involved highly stereoselective epoxide ring opening of **5** to yield the desired stereoisomers of **1**. This is accomplished by using the method of Berti et al.[12] Ring opening of several epoxides was found to be stereospecific with KOH in Me_2SO/H_2O. As with **5** the diastereomeric ratio of **1a** to **1b** can easily be determined by ^{13}C NMR (Table II). Although intramolecular rearrangement of α-hydroxy epoxides is known,[13] in the case of **5** the reaction is highly stereoselective (the ratio of erythro to threo diastereomers remained constant in the conversion of **5** to **1**). The yield is low for this reaction, probably as a result of polymerization processes which are likely to occur. The epoxide ring opening was performed on an 80:20 mixture of erythro–threo diastereomers. Although previous workers have found the erythro and threo epoxy alcohols to be separable by medium-pressure liquid chromatography, the epoxides were converted to triols, which could be recrystallized from chloroform to yield >95% pure (2*R*,3*S*)- and (2*S*,3*R*)-1,2,3-decanetriol.

The reaction sequence described demonstrates the applicability of the resolution technique of Pirkle et al.[3-5] for synthesis of high enantiomeric purity alkanetriols. We have only prepared the 2*R*,3*S* and 2*S*,3*R* stereoisomers of **1**. However, highly stereoselective epoxide ring opening of *threo*-**5** enantiomers would yield (2*R*,3*R*)- and (2*S*,3*S*)-**1**.

This reaction sequence is currently being applied to the synthesis of higher homologues in the series, including 1,2,3-hexadecanetriol.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 137 spectrometer. Proton NMR spectra were obtained by using Varian A-60 and Bruker HX-270 spectrometers, and ^{13}C spectra were recorded by using a Bruker HX-270 spectrometer, with chemical shifts reported relative to internal Me_4Si. Mass spectra were obtained with an AEI MS902 instrument, and optical rotations were measured with a Bellingham-Stanley visual polarimeter with a 1-dm cell. Melting points were obtained on a Büchi apparatus and are uncorrected.

(*R*,*S*)-1-Decyn-3-ol (2). This compound was prepared from ethynylmagnesium bromide and octanal by a procedure identical with that used for the preparation of 1-phenyl-1-penten-4-yn-3-ol.[14] Workup and distillation afforded a clear colorless liquid in 81% yield: bp 67–69 °C (0.2 mm); NMR ($CDCl_3$) 4.33 (dt, 1 H, J = 2 Hz, J' = 5.5 Hz, OCH), 2.83 (br s, 1 H, OH), 2.42 (d, J = 2 Hz, 1 H, C≡CH), 1.0–1.9 (m, 12 H, CH_2's), 0.88 (t, 3 H, CH_3); IR (neat) 3200–3600, 2960, 2860, 2100, 1470, 1380, 1220–1350, 1120, 950–1100, 750 cm^{-1}; mass spectrum, *m/e* (relative intensity) 153 (1.1), 121 (9), 107 (23), 97 (21), 92 (28), 83 (30), 79 (47), 70 (64), 57 (100), 55 (74), 43 (68), 41 (91).

(*R*,*S*)-1-Decen-3-ol (4). Lindlar catalyst (1.0 g) was added to a solution of **2** (30.0 g, 0.20 mol) in 250 mL of hexane. The flask, attached to an inverted buret in a beaker of water, was flushed with hydrogen and then vigorously stirred with a magnetic stirrer. When the theoretical amount of hydrogen was absorbed, the mixture was filtered, the solvent removed, and the residue distilled to yield 27 g (90%) of a clear colorless liquid: bp 110–114 °C (15 mm); NMR ($CDCl_3$) δ 5.0–6.3 (AMX, 3 H, CH=CH_2), 4.10 (m, 1 H, CHOH), 3.08 (br s, 1 H, OH), 1.1–1.8 (m, 12 H, CH_2's), 0.89 (t, 3 H, CH_3); IR (neat) 3200–3600, 2960, 2880, 1625, 1450, 1400, 1380, 1200–1300, 1000–1100, 980, 910, 715 cm^{-1}; mass spectrum, *m/e* (relative intensity) 156 (0.17), 140 (1.3), 138 (1.3) 127 (12.5), 72 (34), 69 (18), 56 (100), 43 (28), 41 (42), 28 (100).

(±)-1,2-Epoxy-3-decanols (5a,b). These compounds could be obtained as a mixture of diastereomers by either of two methods.

Method A. A solution of 85% *m*-chloroperoxybenzoic acid (14.3 g, 0.07 mol, in 100 mL of CH_2Cl_2) was added dropwise to a stirred solution of **4** (10.0 g, 0.064 mol) in 100 mL of CH_2Cl_2 at 0 °C. The reaction mixture was stirred and allowed to warm

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overnight to room temperature. The solution was filtered, extracted twice with saturated Na_2CO_3 solution, and dried over K_2CO_3. Distillation afforded 14.8 g (94%) of a clear colorless liquid, which was found to be a 3:2 mixture of diastereomers **5a** and **5b**: bp 65–68 °C (0.15 mm); NMR ($CDCl_3$) for **5a** δ 3.37 (m, 1 H, CHOH), 2.95 (m, 1 H, CH_2CHO), 2.79 and 2.68 (m, 2 H, CH_2CHO), 2.84 (br s, 1 H, OH), 1.5 (m, 2 H, CH_2CHOH), 1.27 (m, 10 H, CH_2's), 0.88 (t, 3 H, CH_3); for **5b** δ 3.75 (m, 1 H, CHOH), 2.96 (m, 1 H, $CHCH_2O$), 2.79 and 2.70 (m, 2 H, CH_2CHO), 2.41 (br s, 1 H, OH), 1.5 (m, 2 H, CH_2CHOH), 1.27 (m, 10 H, CH_2's), 0.88 (t, 3 H, CH_3); IR (neat) 3200–3600, 2900, 2850, 1450, 1380, 1150, 1000–1100, 950, 900, 850 cm^{-1}; mass spectrum, *m/e* (relative intensity) 172 (0.2), 130 (8.0), 111 (21.4), 83 (13), 73 (26.8), 69 (100), 57 (28.5), 55 (50), 43 (35.7), 41 (44.6).

Method B. A solution of *tert*-butylhydroperoxide (6.0 mL) in 10 mL of toluene was added dropwise to a stirred solution of **4** (1.7 g, 0.011 mol) and $VO(acac)_2$ (0.1 g) in 25 mL of toluene at −78 °C. The mixture was allowed to warm overnight to room temperature with continuous stirring. Solvent removal and distillation afforded 1.55 g (82%) of a clear colorless liquid which was found by NMR to be an 85:15 mixture of **5b** and **5a**: bp 72–74 °C (0.3 mm); IR and mass spectra corresponded to those of the **5a/5b** mixture obtained by method A.

1,2,3-Decanetriols (1a,b). These diastereomers were prepared by a method similar to that reported in the literature.[9] An 85:15 mixture of **5a** and **5b** (5.0 g, 32 mmol) was added to 400 mL of 0.3 N KOH in 85% Me_2SO/15% H_2O. The mixture was heated for 24 h at 80 °C. After cooling, the resultant solution was acidified with 10% HCl and extracted with dichloromethane (4 × 250 mL). The organic solution was extracted with saturated $NaHCO_3$ and dried with Na_2SO_4. Solvent removal afforded a yellow liquid, which when distilled yielded 3.5 g (61%) of a clear colorless liquid which solidified on cooling: bp 145–150 °C (0.2 mm): mp 75–78 °C; NMR ($CDCl_3$) δ 3.4–3.8 (m, 4 H, $HOCH_2CH(OH)CH(OH)$), 2.57 (br s, 3 H, OH's), 1.44 (m, 2 H, $CH(OH)CH_2$), 1.22 (br s, 10 H, $CH_2(CH_2)_5CH_3$), 0.83 (t, 3 H, CH_3); IR (KBr) 3200, 2900, 1500, 1470, 1330, 1060, 1040, 1020, 940, 880 cm^{-1}; mass spectrum, *m/e* (relative intensity) 191 (0.04), 159 (3.6), 129 (32), 111 (42), 110 (9.2), 83 (11), 81 (11), 69 (100), 61 (14), 57 (23), 55 (74), 43 (48), 41 (48), 31 (11), 29 (22).

Anal. Calcd for $C_{10}H_{22}O_3$: C, 63.12; H, 11.66. Found: C, 63.15; H, 11.70.

1-Ethynyloctyl *N*-[1-(1-Naphthyl)ethyl]carbamates (3a,b). These compounds were prepared by heating 15.4 g (0.10 mol) of **2** with 19.7 g (0.10 mol) of isocyanate **6** [derived from (*R*)-(−)-1-(1-naphthyl)ethylamine in 50 mL of toluene with 1 drop of *N,N*-dimethylethanolamine, as previously described.[4] Solvent removal afforded 33 g of a white solid (94% yield) which was a 1:1 mixture of **3a** and **3b**. These compounds were separated by chromatography on a silica gel column (10 × 122 cm) by using a 1:5 mixture of dichloromethane and hexane.

The high R_f carbamate **3a** was the *R,R* diastereomer: mp 77.5–78 °C; NMR ($CDCl_3$) δ 7.2–8.1 (m, 7 H, aryl), 5.61 (quintet, 1 H, NCH), 5.29 (t, 1 H, OCH), 5.03 (d, 1 H, NH), 2.44 (S, 1 H, C≡CH), 1.65 (d, 3 H, $CHCH_3$), 1.24 (m, 12 H, CH_2's), 0.87 (t, 3 H, CH_2CH_3); IR (Nujol) 3230, 1670, 1520, 1280, 1230, 1060, 1020, 800, 720 cm^{-1}; mass spectrum, *m/e* (relative intensity) 351 (23), 214 (100), 170 (58), 155 (91), 129 (63), 57 (40), 55 (53), 43 (70), 42 (77), 41 (65).

The low R_f carbamate **3b** was the *S,R* diastereomer: mp 90–91 °C; NMR ($CDCl_3$) δ 7.2–8.1 (m, 7 H, aryl), 5.59 (m, 1 H, NCH), 5.25 (m, 1 H, OCH), 5.01 (d, 1 H, NH), 2.39 (s, 1 H, C≡CH), 1.61 (d, 3 H, $CHCH_3$), 1.24 (m, 12 H, CH_2's), 0.87 (t, 3 H, CH_2CH_3); IR (Nujol) 3230, 1670, 1520, 1280, 1230, 1060, 1020, 800, 720 cm^{-1}; mass spectrum, *m/e* (relative intensity) 351 (18), 214 (100), 170 (48), 155 (93), 129 (53), 57 (34), 55 (38), 43 (43), 42 (38), 41 (45).

(*R*)-(+)-2. This compound was prepared by cleavage of **3a** (7.0 g, 0.02 mol) with trichlorosilane (2.2 mL, 0.022 mol) and triethylamine (3.2 mL, 0.022 mol) in refluxing CH_2Cl_2 as described in the literature.[6] After workup with aqueous NH_4Cl, the organic layer was distilled, first at atmospheric pressure to remove solvent and then at reduced pressure, to yield 2.3 g (75%) of a clear colorless liquid: bp 60–61 °C (0.05 mm); d = 0.861 g/mL; $[\alpha]^{25}_D$ + 10.6° (neat); NMR and IR identical with those of racemic **2**.

(*S*)-(−)-2. This compound was obtained by treatment of **3b** in a manner similar to that used for the preparation of (*R*)-(+)-**2**. A clear colorless liquid was obtained in a similar yield: bp 67–69 °C (0.2 mm); $[\alpha]^{25}_D$ −11.2 ± 1.0° (*c* 10, $CHCl_3$); NMR and IR identical with those of racemic **2**.

(*R*)-(−)-4. This compound was obtained by catalytic hydrogenation of 5.1 g of (*R*)-(+)-**2** as described above for the racemate: 5.0 g (97%); clear colorless liquid; bp 70–75 °C (4 mm); $[\alpha]^{25}_D$ −14.9 ● 0.5° (neat); d = 0.828 g/mL; NMR and IR spectra identical with those of racemic **4**.

(*S*)-(+)-4. This compound was obtained by catalytic hydrogenation of 1.2 g of (*S*)-(−)-**2** as described above for the racemate: 1.15 g (96%); clear colorless liquid; bp 70–75 °C (4 mm); $[\alpha]^{25}_D$ +13.0 ± 0.5° (neat); NMR and IR identical with those of racemic **4**.

(2*S*,3*R*)-5b. This compound was obtained by epoxidation of (*R*)-(−)-**4** using method B described above and was found by ^{13}C NMR to consist of an 80–20 mixture of (2*S*,3*R*)-**5b** and (2*R*,3*R*)-**5a**: $[\alpha]^{25}_D$ −2.4 ± 0.5° (neat); d = 0.92 g/mL; NMR and IR identical with those of the racemic **5b/5a** mixture.

(2*R*,3*S*)-5b. This compound was obtained by epoxidation of (*S*)-(+)-**4** using method B described above and was found by ^{13}C NMR to consist of an 80:20 mixture of (2*R*,3*S*)-**5b** and (2*S*,3*S*)-**5a**: $[\alpha]^{25}_D$ +2.6 ± 0.5° (neat); NMR and IR identical with those of the racemic **5b/5a** mixture.

(2*S*,3*R*)-1b. This compound was prepared from (2*S*,3*R*)-**5b** as described for the preparation of racemic **1**. The product consisted of an 80:20 mixture of (2*S*,3*R*)-**1b** and (2*R*,3*R*)-**1a** (as shown by ^{13}C NMR), which was recrystallized once from $CHCl_3$ to yield a white solid, in which only one isomer could be detected by ^{13}C NMR: >95% pure; mp 97–98 °C; $[\alpha]^{25}_D$ +11.3 ± 0.5° (*c* 5, *n*-propanol); NMR and IR similar to those of racemic **1**.

(2*R*,3*S*)-1b. This compound was prepared from (2*S*,3*R*)-**5b** as described above for the preparation of racemic **1**. The product consisted of an 80:20 mixture of (2*R*,3*S*)-**1b** and (2*S*,3*S*)-**1a** (as shown by ^{13}C NMR), which was recrystallized once from $CHCl_3$ to yield a white solid, in which only one isomer could be detected by ^{13}C NMR: >95% pure; mp 98–99 °C; $[\alpha]^{25}_D$ −11.7 ± 0.5° (*c* 5, *n*-propanol); NMR and IR similar to those of racemic **1**.

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Registry No. (*R,R*)-(±)-**1a**, 74824-51-4; (2*R*,3*R*)-**1a**, 74867-37-1; (2*S*,3*S*)-**1a**, 74867-38-2; (*R,S*)-(±)-**1b**, 74824-52-5; (2*R*,3*S*)-**1b**, 74867-39-3; (2*S*,3*R*)-**1b**, 74867-40-6; (*R,S*)-**2**, 74824-53-6; (*R*)-(+)-**2**, 74867-41-7; (*S*)-(−)-**2**, 74867-42-8; (*R,R*)-**3a**, 74824-54-7; (*R,S*)-**3b**, 74824-55-8; (*R,S*)-**4**, 74824-56-9; (*R*)-(−)-**4**, 74867-43-9; (*S*)-(+)-**4**, 74867-44-0; (*R,R*)-(±)-**5a**, 74824-57-0; (2*R*,3*R*)-**5a**, 74867-45-1; (2*S*,3*S*)-**5a**, 74867-46-2; (*R,S*)-(±)-**5b**, 74835-29-3; (2*R*,3*S*)-**5b**, 74867-47-3; (2*S*,3*R*)-**5b**, 74867-48-4; (*R*)-(−)-**6**, 42340-98-7; ethynyl bromide, 593-61-3; octanal, 124-13-0.