9.93 (d, 1 H, J = 8.30 Hz, aromatic, (*R*)-(+))($\Delta\Delta\delta$ 0.18 ppm); HPLC (Daicel Chiralcel OB) retention volumes of 86.9 ((*S*)-(−)) and 125.5 ((*R*)-(+)) mL, respectively.

(*R*)-(+)-Methyl 2-Naphthyl Sulfoxide. Oxidation of methyl 2-naphthyl sulfide in β-CD with peracetic acid at 0 °C for 65 h under N_2 gave methyl 2-naphthyl sulfoxide: yield 186 mg (98%); mp 105–107 °C (lit.[32] mp 103–108 °C); IR (KBr) 1040 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 2.79 (s, 3 H, CH_3), 7.56–7.62 (m, 3 H, aromatic), 7.89–8.00 (m, 3 H, aromatic) 8.22 (s, 1 H, aromatic); $[\alpha]^{25}_D$ +69.1° (*c* 1.0, $CHCl_3$), 49% ee (*R* predominates) based on $[\alpha]^{25}_D$ +127° (*c* 2, $CHCl_3$), 90% ee,[7] (*R*)-(+).[32]

(+)-Methyl 9-Phenanthryl Sulfoxide. Oxidation of methyl 9-phenanthryl sulfide in γ-CD with peracetic acid at 0 °C for 20 h under N_2 gave methyl 9-naphthyl sulfoxide: yield 209 mg (87%); mp 113–115 °C; IR (KBr) 1060 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 2.89 (s, 3 H, CH_3), 7.62–7.78 (m, 4 H, aromatic), 7.89–8.06 (m, 2 H, aromatic), 8.46 (s, 1 H, aromatic), 8.66–8.78 (m, 2 H, aromatic); $[\alpha]^{25}_D$ +99.4° (*c* 0.5, $CHCl_3$), 37% ee, as confirmed by HPLC analysis on a Daicel Chiralcel OC column or by ^1H NMR method as mentioned previously; ^1H NMR ($CDCl_3$, 270 MHz, [Eu(hfc)$_3$]/[(+)-sulfoxide] = 0.4) δ 6.09 (s, 3 H, CH_3 (−)-sulfoxide), 6.16 (s, 3 H, CH_3, (+)-sulfoxide), 9.61 (m, 1 H, aromatic, (−)-sulfoxide), 9.87 (m, 1 H, aromatic, (+)-sulfoxide); HPLC (Daicel Chiralcel OC) retention volumes of 179.0 ((+)-sulfoxide) and 213.4 ((−)-sulfoxide) mL, respectively. No optical separation of the sulfoxide, however, was observed by HPLC analysis using a Daicel Chiralcel OB column.

Supplementary Material Available: X-ray diffraction diagrams and TG-DSC data for β-CD complexes of methyl 1- and 2-naphthyl sulfides (3 pages). Ordering information is given on any current masthead page.

1-Chloroalkyl *p*-Tolyl Sulfoxides as Useful Agents for Homologation of Carbonyl Compounds: Conversion of Carbonyl Compounds to α-Hydroxy Acids, Esters, and Amides and α,α′-Dihydroxy Ketones

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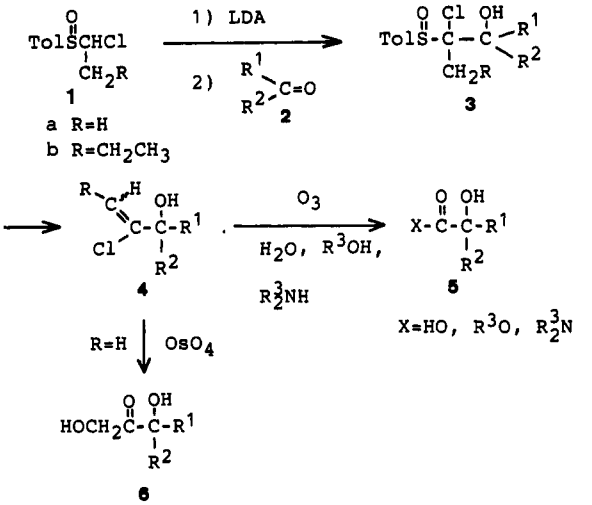
One-carbon homologation of carbonyl compounds to α-hydroxy acids, esters, and amides by the use of 1-chloroalkyl *p*-tolyl sulfoxide as a hydroxycarbonyl anion equivalent is reported. Oxidation of the vinyl chlorides, the intermediates of the above-mentioned method, with osmium tetraoxide gives α,α′-dihydroxy ketones which are found in biologically active natural products such as cortisone and adriamycin.

One-carbon homologation of carbonyl compounds is an important and extensively used method in organic synthesis.[1] Various kinds of homologating agents have been reported;[1] however, in view of the usefulness of the method, new homologating agents are eagerly sought.

We recently reported some novel synthetic methodologies using 1-chloroalkyl aryl sulfoxides via α,β-epoxy sulfoxides.[2] In continuation of our studies on the use of 1-chloroalkyl *p*-tolyl sulfoxides **1**, including optically active ones, in organic synthesis, we describe herein a novel method for homologation of carbonyl compounds **2** into α-hydroxy acids (**5**, X = OH), esters (**5**, X = R^3O), and amides (**5**, X = R^3_2N) and α,α′-dihydroxy ketones **6** (Scheme I).

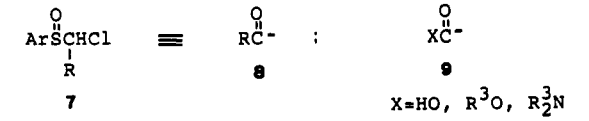
Scheme I



Results and Discussion

Homologation of Carbonyl Compounds to α-Hydroxy Acids, Esters, and Amides with 1-Chloroethyl *p*-Tolyl Sulfoxide as One-Carbon Homologating Agent. Innumerable methods for the synthesis of aldehydes and ketones from lower carbonyl compounds by homologation have been reported;[1] however, relatively few methods for the synthesis of carboxylic acids, esters, or amides by one-carbon homologation have appeared.

Scheme II



Classically, α-hydroxy acid derivatives are synthesized from carbonyl compounds with hydrogen cyanide via cyanohydrins.[3] This reaction requires a toxic reagent, and

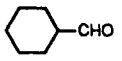
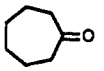
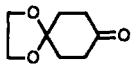
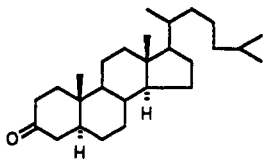
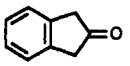
(1) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. Lever, O. W., Jr. *Tetrahedron* **1976**, *32*, 1943. Grobel, B.-T.; Seebach, D. *Synthesis* **1977**, 357. Martin, S. F. *Synthesis* **1979**, 633. Stowell, J. C. *Chem. Rev.* **1984**, *84*, 409. Hase, T. A. *Umpoled Synthons*; John Wiley and Sons: New York, 1987.

(2) (a) Satoh, T.; Yamakawa, K. *Yuki Gosei Kagaku Kyokaishi* **1989**, *47*, 734. (b) Satoh, T.; Oohara, T.; Ueda, Y.; Yamakawa, K. *J. Org. Chem.* **1989**, *54*, 3130. (c) Satoh, T.; Sato, T.; Oohara, T.; Yamakawa, K. *J. Org. Chem.* **1989**, *54*, 3973. (d) Satoh, T.; Sugimoto, A.; Itoh, M.; Yamakawa, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2942. (e) Satoh, T.; Kawase, Y.; Yamakawa, K. *J. Org. Chem.* **1990**, *55*, 3962. (f) Satoh, T.; Kawase, Y.; Yamakawa, K. *Tetrahedron Lett.* **1990**, *31*, 3609.

0022-3263/91/1956-4129$02.50/0

Table I. Synthesis of α-Hydroxy Acids and Esters from 1-Chloroethyl *p*-Tolyl Sulfoxide (1a) and Aldehydes or Ketones by One-Carbon Homologation

$$\mathrm{TolS(O)CMeHCl} \xrightarrow{\mathrm{R^1COR^2}} \mathrm{TolS(O)CMeClCR^1R^2OH} \rightarrow \mathrm{CH_2{=}CClCR^1R^2OH} \xrightarrow[\mathrm{ROH}]{\mathrm{O_3}} \mathrm{ROC(O)CR^1R^2OH}$$

entry	aldehyde or ketone	chloro alcohol (yield, %)[a]	vinyl chloride (yield, %)[a]	ROH	α-hydroxy acid or ester (yield, %)[a]
1	$CH_3(CH_2)_8CHO$	**10** (95)	**11** (96)	H_2O	**12b** (99)[b]
2				CH_3OH	**12a** (93)
3				CH_3CH_2OH	**25** (90)
4				$CH_3(CH_2)_4OH$	**26** (80)
5				$(CH_3)_2CHOH$	**27** (50)
6	$PhCH_2CH_2CHO$	(79)	**19** (89)	H_2O	**28** (89)[b]
7				CH_3OH	**29** (82)
8				CH_3CH_2OH	**30** (93)
9				$CH_3(CH_2)_4OH$	**31** (89)
10				$PhCH_2OH$	**32** (60)
11				$(CH_3)_2CHOH$	**33** (27)
12		(89)	**20** (91)	H_2O	**34** (99)[b]
13				CH_3OH	**35** (93)
14				CH_3CH_2OH	**36** (90)
15		**15** (94)	**21** (96)	H_2O	**37** (81)[b]
16				CH_3CH_2OH	**38** (86)
17				$CH_3(CH_2)_4OH$	**39** (65)
18		**16** (94)	**22** (98)	CH_3CH_2OH	**40** (83)
19		**17** (81)	**23** (97)	CH_3OH	**41** (93)[c]
20		**18** (93)	**24** (97)	H_2O	**42** (93)[b]
21				CH_3CH_2OH	**43** (93)

[a] Isolated purified yield after silica gel column chromatography. [b] Purified by recrystallization. [c] 3α-Hydroxy 3β-carboxylic acid methyl ester; for the stereochemistry of the steroid derivatives, see ref 10.

the acidic hydrolysis of the cyanohydrins does not always give good yields. Recent methods using tris[(phenylthio)methyl]lithium[4] and tris[(methylthio)methyl]lithium[5] as hydroxycarbonyl anion equivalents are preferable, but they still need acidic hydrolysis with a mercury salt to obtain the α-hydroxy esters. Other reductive nucleophilic carboxylations giving carboxylic acids or esters from carbonyl compounds by one-carbon homologation have also been reported.[6]

1-Chloroalkyl aryl sulfoxides **7** (Scheme II) are quite easily prepared in racemic form from arenethiols and alkyl halides in two steps[7] and are obtained in optically active form from optically active alkyl aryl sulfoxides.[2b] In previous papers we have reported several synthetic methods using **7** as an acyl anion equivalent **8**.[2] However, the use of **7** as a hydroxycarbonyl, alkoxycarbonyl, and formamide anion equivalent **9** remains to be investigated.

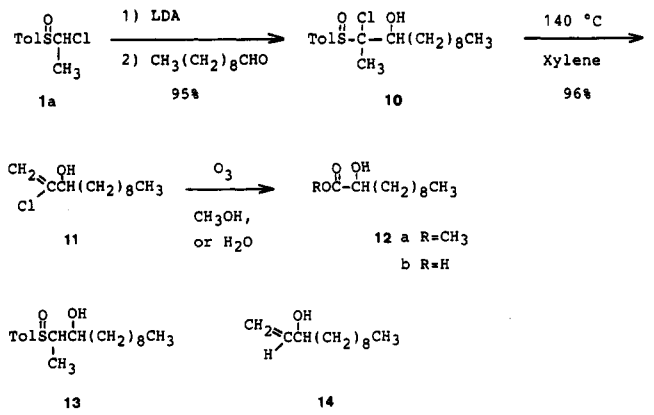
The oxidation state of the carbon atom (of **7**) bearing the sulfinyl group and the chlorine atom is equal to that of ketones and aldehydes. When this carbon is used as a hydroxycarbonyl anion equivalent, one higher level of oxidation state is required. To this end, we studied the three-step conversion of **1** to α-hydroxy acid derivatives **5** via vinyl chlorides **4** as shown in Scheme I.

The synthesis of methyl 2-hydroxyundecanoate (**12a**) from decanal and 1-chloroethyl *p*-tolyl sulfoxide (**1a**) as alkoxycarbonyl anion equivalent is reported as a representative example (Scheme III). Sulfoxide **1a**, easily prepared from ethyl *p*-tolyl sulfide, was treated with LDA in THF at −60 °C followed by decanal to give the adduct **10** in 95% yield as a mixture of two inseparable diastereomers. Heating the mixture in refluxing xylene for 20 min gave cleanly the desired vinyl chloride **11** in quantitative yield. In this thermal elimination of the sulfinyl group, it was anticipated that hydrogens at either carbon attached to the carbon bearing the sulfinyl group (H at CH_3, or H at the carbon bearing the hydroxyl group) might be eliminated; however, we obtained only vinyl chloride **11**. This result is quite similar to the thermal elimination of selenoxides from β-hydroxy selenides with hydrogen peroxide giving allylic alcohols as reported by Sharpless.[8] Further, the reaction rate of the thermal elimination of chloride **10** was found to be much faster than that of **13**. The thermal elimination of the sulfinyl group of **13** required over 2 h in refluxing xylene to complete the reaction giving the corresponding allylic alcohol (**14**; 79% yield).

Ozonolysis of **11** in methanol at −60 °C followed by reductive workup (adding excess dimethyl sulfide) gave

(3) Mowry, D. T. *Chem. Rev.* **1948**, *42*, 189.
(4) Woessner, W. D. *Chem. Lett.* **1976**, 43.
(5) Damon, R. E.; Luo, T.; Schlessinger, R. H. *Tetrahedron Lett.* **1976**, 2749.
(6) Gross, H.; Costisella, B. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 391. Schollkopf, U.; Schroder, R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 311. Seebach, D.; Grobel, B.-T.; Beck, A. K.; Braun, M.; Geiss, K.-H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 443. Dinizo, S. E.; Freerksen, R. W.; Pabst, W. E.; Watt, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 182. Schubert, U. *Synthesis* **1978**, 364. Takahashi, K.; Shibasaki, K.; Ogura, K.; Iida, H. *J. Org. Chem.* **1983**, *48*, 3566. Kowalski, C. J.; Haque, M. S.; Fields, K. W. *J. Am. Chem. Soc.* **1985**, *107*, 1429.
(7) Satoh, T.; Kaneko, Y.; Izawa, T.; Sakata, K.; Yamakawa, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1983.
(8) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697.

Scheme III



12a in 93% yield. As previously mentioned, this reaction is expected to take place via the acid chloride. Therefore, if this reaction were carried out in the presence of water, α-hydroxy acid would be formed. This expectation was realized by treatment of 11 with ozone in acetone followed by dimethyl sulfide and water. After the usual workup for isolation of the carboxylic acids, 2-hydroxyundecanoic acid (12b) was obtained in 99% yield.

Representative examples of the preparation of α-hydroxy acids and esters from aldehydes and ketones by one-carbon homologation using 1-chloroethyl *p*-tolyl sulfoxide (1a) as the agent for the homologation are summarized in Table I. The characteristics of this method are as follows. (1) The overall yields are uniformly good. (2) In the ozonolysis, various primary alcohols can be used to give the corresponding esters in good yields. (3) Secondary alcohol gave esters, although the yields were moderate (entry 5, 11). (4) Because the conditions of the thermal elimination and the ozonolysis are relatively mild and completely neutral, this method is compatible with acid-sensitive functional groups in the molecule (entry 18).

Next, we investigated the synthesis of α-hydroxy amides by this method. The best conditions were found to be as follows. The vinyl chloride was ozonized in dry CH_2Cl_2 at −60 °C. After the starting material disappeared (monitored on TLC), excess dry dimethyl sulfide was added followed by an excess of the desired amine. The mixture was stirred for several hours at room temperature to afford α-hydroxy amide in good yields (see Table II).

It was found that, in this reaction, purity of the solvent was important. As commercial CH_2Cl_2 contains a very small amount of methanol as a stabilizer, the ozonolysis and amine treatment of the vinyl chlorides in dried (CaH_2) and distilled CH_2Cl_2 gave significant amounts of α-hydroxy acid methyl ester as a byproduct. To avoid this problem, commercial CH_2Cl_2 was washed carefully with sulfuric acid (see Experimental Section).

As shown in Table II, this method gave the desired α-hydroxy amides in quite good yields. Ammonia (29% in water) and primary and secondary amines reacted similarly; however, secondary amines were found to give slightly lower yields compared with primary amines.

This method was extended to the asymmetric synthesis of both enantiomers of α-hydroxy acids and their derivatives using optically acitve (−)-1-chlorobutyl *p*-tolyl sulfoxides (1b) as chiral starting material.[9] Detailed experimental procedures for the synthesis and characterization data are available as supplementary material.

(9) Preliminary communication of this study: Satoh, T.; Onda, K.; Yamakawa, K. *Tetrahedron Lett.* **1990**, *31*, 3567.

(10) Satoh, T.; Kaneko, Y.; Yamakawa, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2463.

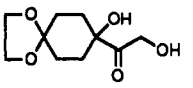
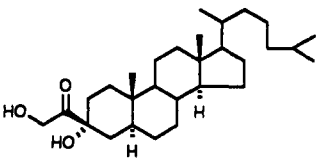
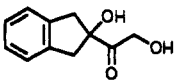
Table II. Synthesis of α-Hydroxy Amides from Aldehydes and Ketones by One-Carbon Homologation through the Vinyl Chlorides

$$CH_2{=}CClCR^1R^2OH \xrightarrow[R_2NH]{O_3} R_2NC(O)CR^1R^2OH$$

entry	vinyl chloride	R_2NH	α-hydroxy amide (yield, %)[a]
1	11	NH_3[b]	44 (99)
2		$PhCH_2NH_2$	45 (97)
3		piperidine	46 (62)
4	19	NH_3[b]	47 (95)
5		$CH_3(CH_2)_5NH_2$	48 (84)
6		$PhCH_2NH_2$	49 (93)
7		Et_2NH	50 (66)
8		piperidine	51 (68)
9	20	NH_3[b]	52 (82)
10		$PhCH_2NH_2$	53 (99)
11	21	$PhCH_2NH_2$	54 (83)
12	22	$CH_3(CH_2)_5NH_2$	55 (91)
13		piperidine	56 (82)
14	23	$PhCH_2NH_2$	57 (91)
15	24	NH_3[b]	58 (90)
16		$CH_3(CH_2)_5NH_2$	59 (74)
17		piperidine	60 (75)

[a] Isolated yield. [b] Ammonia in water, 29%.

Table III. Synthesis of α,α′-Dihydroxy Ketones by Oxidation of the Vinyl Chlorides with Osmium Tetraoxide

vinyl chloride	α,α′-dihydroxy ketone (yield, %)[a]
22	 61 (67; 88[b])
23	 62 (68; 89[b])
24	 63 (79; 85[b])

[a] Isolated purified yield after silica gel column chromatography. [b] Conversion yield.

Synthesis of α,α′-Dihydroxy Ketones from Ketones by Oxidation of Vinyl Chlorides with OsO_4. The dihydroxyacetone component found in biologically active substances, such as cortisone and adriamycin, is essential for their biological activity, and many methods have already been reported for the synthesis of α,α′-dihydroxy ketones from ketones by two-carbon homologation.[11]

In continuation of our work with the vinyl chlorides, we found that oxidation with OsO_4[12] gave the desired α,α′-dihydroxy ketones in good yields. For example, vinyl chloride 22 in acetone was treated with a solution of 4-methylmorpholine *N*-oxide (NMO) (1.5 equiv) and OsO_4 (0.25 equiv) in aqueous acetone at room temperature. The reaction took place cleanly, though sluggishly, to afford

(11) Some recent papers: Kita, Y.; Yakura, T.; Terashi, H.; Haruta, J.; Tamura, Y. *Chem. Pharm. Bull.* **1989**, *37*, 891. Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1989**, *30*, 3323; *J. Am. Chem. Soc.* **1989**, *111*, 6257. Reid, J. G.; Debiak-Krook, T. *Tetrahedron Lett.* **1990**, *31*, 3669.

(12) Schroder, M. *Chem. Rev.* **1980**, *80*, 187. McCormick, J. P.; Tomasik, W.; Johnson, M. W. *Tetrahedron Lett.* **1981**, *22*, 607.

61 (see Table III) in 67% yield along with the starting material 22 (24%). Two other examples are shown in Table III.

In conclusion, because of its simplicity and high overall yields, we believe that the method presented will prove valuable in the synthesis of α-hydroxy acids, esters, and amides in racemic and optically active form. Also, the method is useful for the synthesis of biologically active natural products having a dihydroxyacetone moiety in the molecule.

Experimental Section

All melting points are uncorrected. Unless otherwise noted, ^{1}H NMR spectra were measured in a $CDCl_3$ solution at 100 MHz. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel BW-127 ZH (Fuji-Devison) containing 2% fluorescence reagent 254 and a quartz column were used for column chromatography, and the products having a suitable chromophore were detected by UV fluorescence. In experiments requiring dry solvent, THF and ether were distilled from benzophenone ketyl; toluene and xylene were dried over CaH_2 and distilled. Special precautions were taken in the purification of CH_2Cl_2. To remove methanol, 3 L of commercial CH_2Cl_2 was washed successively with concentrated sulfuric acid (50 mL × 2), water (50 mL × 2), saturated aqueous $NaHCO_3$ (50 mL × 2), and finally saturated brine (50 mL × 3). The washed CH_2Cl_2 was dried over $CaCl_2$ overnight and then distilled in the presence of CaH_2.

2-Chloro-1-dodecen-3-ol (11). To a stirred solution of LDA (7.47 mmol) in 10 mL of THF at −60 °C under N_2 was added dropwise a solution of **1a**[2b] (1.26 g, 6.22 mmol) in 2 mL of THF. The mixture was stirred at −60 °C for 10 min. The mixture turned yellow in color. Decanal (1.69 mL, 8.96 mmol) was added to the reaction mixture dropwise through a syringe, and after 5 min, the reaction was quenched with saturated aqueous NH_4Cl. The whole was extracted with ether–benzene, and the organic layer was washed once with saturated aqueous NH_4Cl and then dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by silica gel column chromatography (hexane:AcOEt = 10:1) to afford **10** (2.12 g, 95%) as colorless crystals: IR (KBr) 3300, 1030 cm^{-1}.

A solution of **10** (1.48 g, 4.12 mmol) in 60 mL of xylene was refluxed under N_2 for 20 min. The solvent was evaporated under vacuum, and the residue was chromatographed on silica gel (benzene:AcOEt = 20:1) to give vinyl chloride **11** (856 mg, 96%) as a colorless oil: IR (neat) 3380, 1640 cm^{-1}; ^{1}H NMR δ 0.88 (3 H, t, J = 7 Hz), 1.1–1.8 (16 H, m), 4.16 (1 H, t, J = 7 Hz), 5.24, 5.40 (each 1 H, m); MS, m/z (relative intensity) 218 (M$^+$, trace), 200 (trace), 183 (10), 155 (8); found m/z 218.1474, calcd for $C_{12}H_{23}OCl$ M 218.1436.

Methyl 2-Hydroxyundecanoate (12a). A solution of **11** (110 mg, 0.5 mmol) in 10 mL of MeOH at −60 °C was treated with ozone. After the starting material disappeared, excess dimethyl sulfide (2 mL) was added to the reaction mixture and the solution was stirred at room temperature for 1 h. The solvent was evaporated, and the residue was purified by silica gel column chromatography (hexane:AcOEt = 20:1) to afford **12a** (100 mg, 93%) as a colorless oil: IR (neat) 3500, 1745 cm^{-1}; ^{1}H NMR δ 0.88 (3 H, t, J = 7 Hz), 1.1–1.9 (16 H, m), 3.77 (3 H, s), 4.18 (1 H, dd, J = 7, 5 Hz); MS, m/z (relative intensity) 216 (M$^+$, 4), 157 (75), 127 (6), 83 (100); found m/z 216.1743, calcd for $C_{12}H_{24}O_3$ M 216.1724.

2-Hydroxyundecanoic Acid (12b). A solution of **11** (66 mg, 0.3 mmol) in 7 mL of acetone at −60 °C was treated with ozone. After the starting material disappeared, 0.5 mL of dimethyl sulfide and water (1 mL) were added to the reaction mixture. The reaction mixture was stirred at room temperature for 1 h, and then the solvent was evaporated. The residue was extracted with ether, and then the organic layer was extracted twice, each time with 10 mL of 5% NaOH. The combined alkaline extract was acidified with 10% HCl, and then the solution was extracted with ether. The ether layer was dried ($MgSO_4$) and evaporated to afford **12b** (60 mg, 99%) as colorless crystals: mp 104–105 °C (AcOEt–hexane); IR (KBr) 3580, 1690 cm^{-1}; ^{1}H NMR δ 0.88 (3 H, t, J = 7 Hz), 1.0–2.0 (16 H, m), 4.27 (1 H, t, J = 6 Hz); MS, m/z (relative intensity) 202 (M$^+$, 10), 157 (64), 113 (33), 97 (44), 83 (100). Anal. Calcd for $C_{11}H_{22}O_3$: C, 65.31; H, 10.96. Found: C, 65.18; H, 11.07.

Chloro Alcohols 15–18. These chloro alcohols were synthesized from 1-chloroethyl p-tolyl sulfoxide (**1a**) and ketones in a way similar to that described for the synthesis of **10** as single products (yield, see Table I). **15**: colorless crystals; mp 117–119 °C (AcOEt–hexane); IR (KBr) 3310, 1040 cm^{-1}; ^{1}H NMR δ 1.46 (3 H, s), 1.2–2.4 (12 H, m), 2.43 (3 H, s), 7.2–7.6 (4 H, m). Anal. Calcd for $C_{16}H_{23}ClO_2S$: C, 61.03; H, 7.36; Cl, 11.26; S, 10.18. Found: C, 61.42; H, 7.48; Cl, 11.34; S, 10.30. **16**: colorless crystals; mp 152–153 °C (AcOEt–hexane); IR (KBr) 3350, 1000 cm^{-1}; ^{1}H NMR δ 1.47 (3 H, s), 1.4–2.4 (8 H, m), 2.43 (3 H, s), 3.95 (4 H, s), 7.2–7.7 (4 H, m). Anal. Calcd for $C_{17}H_{23}ClO_4S$: C, 56.89; H, 6.46; Cl, 9.88; S, 8.93. Found: C, 56.93; H, 6.60; Cl, 10.44; S, 8.86. **17**: colorless crystals; mp 183–184 °C ($CHCl_3$–AcOEt); IR (KBr) 3450, 1050 cm^{-1}; ^{1}H NMR δ 0.65 (3 H, s), 0.86 (6 H, d, J = 7 Hz), 0.90 (3 H, d, J = 7 Hz), 0.98 (3 H, s), 1.46 (3 H, s), 2.43 (3 H, s), 7.2–7.7 (4 H, m). **18**: colorless crystals; mp 164–167 °C ($CHCl_3$–hexane); IR (KBr) 3350, 1040 cm^{-1}; ^{1}H NMR δ 1.52 (3 H, s), 2.43 (3 H, s), 3.20 (2 H, dd, J = 17, 6 Hz), 3.68 (2 H, dd, J = 17, 2 Hz), 7.17 (4 H, s), 7.2–7.7 (4 H, m). Anal. Calcd for $C_{18}H_{19}ClO_2S$: C, 64.56; H, 5.72; Cl, 10.59; S, 9.57. Found: C, 64.67; H, 5.62; Cl, 10.94; S, 10.10.

Vinyl Chlorides 19–24. These vinyl chlorides were synthesized from the chloro alcohols in a way similar to that described for the synthesis of **11** as single products (yield; see Table I).

2-Chloro-5-phenyl-1-penten-3-ol (19): colorless oil; IR (neat) 3400, 1635 cm^{-1}; ^{1}H NMR δ 1.8–2.2 (2 H, m), 2.69 (2 H, t, J = 7 Hz), 4.16 (1 H, t, J = 6 Hz), 5.30 (1 H, m), 5.40 (1 H, m), 7.0–7.4 (5 H, m); MS, m/z (relative intensity) 196 (M$^+$, 23), 178 (7), 161 (4), 143 (53); found m/z 196.0652, calcd for $C_{11}H_{13}ClO$ M 196.0653.

2-Chloro-1-cyclohexyl-2-propen-1-ol (20): colorless oil; IR (neat) 3400, 1640 cm^{-1}; ^{1}H NMR δ 0.7–2.1 (11 H, m), 3.85 (1 H, d, J = 7 Hz), 5.30 (1 H, m), 5.35 (1 H, m); MS, m/z (relative intensity) 174 (M$^+$, 2), 139 (5), 92 (57), 83 (100); found m/z 174.0810, calcd for $C_9H_{15}ClO$ M 174.0810.

1-(1-Chloroethenyl)cycloheptanol (21): colorless oil; IR (neat) 3420, 1630 cm^{-1}; ^{1}H NMR δ 1.1–2.2 (12 H, m), 5.21 (1 H, d, J = 2 Hz), 5.44 (1 H, d, J = 2 Hz); MS, m/z (relative intensity) 174 (M$^+$, 3), 139 (35), 117 (64), 104 (100); found m/z 174.0825, calcd for $C_9H_{15}ClO$ M 174.0810.

1-(1-Chloroethenyl)-4,4-(ethylenedioxy)cyclohexanol (22): colorless crystals; mp 78–79 °C (AcOEt–hexane); IR (KBr) 3430, 1630, 1100 cm^{-1}; ^{1}H NMR δ 1.4–2.3 (8 H, m), 3.94 (4 H, s), 5.28 (1 H, d, J = 2 Hz), 5.46 (1 H, d, J = 2 Hz); MS, m/z (relative intensity) 218 (M$^+$, trace), 190 (1.5), 157 (2.5), 99 (100). Anal. Calcd for $C_{10}H_{15}ClO_3$: C, 54.92; H, 6.91; Cl, 16.21. Found: C, 54.84; H, 6.66; Cl, 16.19.

Steroidal vinyl chloride (3α-OH) 23: colorless crystals; mp 68–71 °C (AcOEt–MeOH); IR (KBr) 3380, 1635 cm^{-1}; ^{1}H NMR δ 0.65 (3 H, s), 0.86 (6 H, d, J = 7 Hz), 0.90 (3 H, d, J = 7 Hz), 0.98 (3 H, s), 5.24 (1 H, d, J = 2 Hz), 5.46 (1 H, d, J = 2 Hz); MS, m/z (relative intensity) 448 (M$^+$, 65), 415 (21), 391 (6), 293 (31), 275 (60); found m/z 448.3471, calcd for $C_{29}H_{49}ClO$ M 448.3470.

2-(1-Chloroethenyl)-2-indanol (24): colorless oil; IR (neat) 3420, 1640 cm^{-1}; ^{1}H NMR δ 2.98 (2 H, d, J = 17 Hz), 3.54 (2 H, d, J = 17 Hz), 5.35 (1 H, d, J = 2 Hz), 5.62 (1 H, d, J = 2 Hz), 7.18 (4 H, s); MS, m/z (relative intensity) 194 (M$^+$, 42), 159 (16), 131 (8), 105 (100); found m/z 194.0495, calcd for $C_{11}H_{11}ClO$ M 194.0497.

α-Hydroxy Acids and Esters 25–43. These α-hydroxy acids and esters were synthesized from the vinyl chlorides in a way similar to that described for the synthesis of **12a** and **12b**.

Ethyl 2-hydroxyundecanoate (25): colorless oil; IR (neat) 3470, 1740 cm^{-1}; ^{1}H NMR δ 0.87 (3 H, t, J = 7 Hz), 1.0–1.9 (19 H, m), 4.14 (1 H, m), 4.22 (2 H, q, J = 7 Hz); MS, m/z (relative intensity) 230 (M$^+$, 2), 157 (55), 83 (10); found m/z 230.1879, calcd for $C_{13}H_{26}O_3$ M 230.1880.

Pentyl 2-hydroxyundecanoate (26): colorless oil; IR (neat) 3500, 1730 cm^{-1}; ^{1}H NMR δ 0.90 (6 H, m), 1.1–2.0 (22 H, m), 4.16 (1 H, m), 4.16 (2 H, t, J = 7 Hz); MS, m/z (relative intensity) 272 (M$^+$, 1.5), 202 (5.5), 157 (52); found m/z 272.2349, calcd for $C_{16}H_{32}O_3$ M 272.2349.

Isopropyl 2-hydroxyundecanoate (27): colorless oil; IR (neat) 3500, 1735 cm^{-1}; ^{1}H NMR δ 0.88 (3 H, t, J = 7 Hz), 1.0–2.0

(22 H, m), 4.10 (1 H, t, J = 7 Hz), 5.08 (1 H, septet, J = 7 Hz); MS, m/z (relative intensity) 244 (M^+, 0.6), 202 (7), 157 (62); found m/z 244.2033, calcd for $C_{14}H_{28}O_3$ M 244.2036.

2-Hydroxy-3-phenylbutanoic acid (28): colorless crystals; mp 99–100 °C (benzene–hexane); IR (KBr) 3480, 1720 cm^{-1}; ^{1}H NMR (CD_3OD–$CDCl_3$) δ 1.7–2.3 (2 H, m), 2.77 (2 H, t, J = 7 Hz), 4.16 (1 H, dd, J = 7, 6 Hz), 7.22 (5 H, m); MS, m/z (relative intensity) 180 (M^+, 15), 162 (3), 117 (13), 91 (100). Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.30; H, 6.51.

Methyl 2-hydroxy-4-phenylbutyrate (29): colorless oil; IR (neat) 3500, 1750 cm^{-1}; ^{1}H NMR δ 1.7–2.3 (2 H, m), 2.75 (2 H, t, J = 8 Hz), 3.72 (3 H, s), 4.17 (1 H, dd, J = 7, 6 Hz), 7.20 (5 H, m); MS, m/z (relative intensity) 194 (M^+, 25), 117 (13), 105 (17), 90 (100); found m/z 194.0939, calcd for $C_{11}H_{14}O_3$ M 194.0941.

Ethyl 2-hydroxy-4-phenylbutyrate (30): colorless oil; IR (neat) 3500, 1740 cm^{-1}; ^{1}H NMR δ 1.28 (3 H, t, J = 7 Hz), 1.7–2.3 (2 H, m), 2.76 (2 H, t, J = 8 Hz), 4.16 (1 H, m), 4.19 (2 H, q, J = 7 Hz), 7.20 (5 H, m); MS, m/z (relative intensity) 208 (M^+, 18), 117 (20), 104 (100); found m/z 208.1098, calcd for $C_{12}H_{16}O_3$ M 208.1098.

Pentyl 2-hydroxy-4-phenylbutyrate (31): colorless oil; IR (neat) 3500, 1740 cm^{-1}; ^{1}H NMR δ 0.90 (3 H, t, J = 7 Hz), 1.1–1.8 (6 H, m), 1.8–2.3 (2 H, m), 2.76 (2 H, t, J = 8 Hz), 4.13 (2 H, t, J = 7 Hz), 4.16 (1 H, m), 7.20 (5 H, m); MS, m/z (relative intensity) 250 (M^+, 15), 146 (54), 117 (15), 105 (25); found m/z 250.1568, calcd for $C_{15}H_{22}O_3$ M 250.1567.

Benzyl 2-hydroxy-4-phenylbutyrate (32): colorless oil; IR (neat) 3400, 1740 cm^{-1}; ^{1}H NMR δ 1.8–2.3 (2 H, m), 1.45 (2 H, m), 4.20 (1 H, dd, J = 7, 6 Hz), 5.14 (2 H, s), 7.18 (5 H, m), 7.32 (5 H, s); MS, m/z (relative intensity) 270 (M^+, 1), 179 (20), 161 (17), 133 (22), 90 (100); found m/z 270.1260, calcd for $C_{17}H_{18}O_3$ M 270.1255.

Isopropyl 2-hydroxy-4-phenylbutyrate (33): colorless oil; IR (neat) 3400, 1735 cm^{-1}; ^{1}H NMR δ 1.25 (6 H, d, J = 7 Hz), 1.7–2.3 (2 H, m), 2.75 (2 H, t, J = 8 Hz), 4.13 (1 H, dd, J = 7, 6 Hz), 5.07 (1 H, septet, J = 7 Hz), 7.22 (5 H, m); MS, m/z (relative intensity) 222 (M^+, 13), 180 (8), 162 (7), 118 (28), 105 (41), 91 (100); found m/z 222.1261, calcd for $C_{13}H_{18}O_3$ M 222.1255.

Hexahydromandelic acid (34): colorless crystals; mp 129–130 °C (AcOEt–hexane); ref 13.

Methyl 2-hydroxy-2-cyclohexylacetate (35): colorless oil; IR (neat) 3510, 1745 cm^{-1}; ^{1}H NMR δ 1.0–1.9 (11 H, m), 3.78 (3 H, s), 4.00 (1 H, d, J = 3 Hz); MS, m/z (relative intensity) 172 (M^+, trace), 143 (1), 90 (100); found m/z 172.1095, calcd for $C_9H_{16}O_3$ M 172.1098.

Ethyl 2-hydroxy-2-cyclohexylacetate (36): colorless oil; IR (neat) 3530, 1730 cm^{-1}; ^{1}H NMR δ 1.0–1.9 (11 H, m), 1.30 (3 H, t, J = 7 Hz), 3.98 (1 H, m), 4.24 (2 H, q, J = 7 Hz); MS, m/z (relative intensity) 186 (M^+, trace), 156 (1), 143 (0.8), 113 (50), 104 (80), 95 (100); found m/z 186.1250, calcd for $C_{10}H_{18}O_3$ M 186.1254.

1-Hydroxycycloheptanecarboxylic acid (37): colorless crystals; mp 71–73 °C (AcOEt–hexane); IR (KBr) 3350, 1730 cm^{-1}; ^{1}H NMR (CD_3OD) 1.5–2.3 (m); MS, m/z (relative intensity) 159 (M + 1, 0.7), 158 (M^+, trace), 141 (5), 103 (100). Anal. Calcd for $C_8H_{14}O_3$: C, 60.72; H, 8.92. Found: C, 60.91; H, 8.72.

Ethyl 1-hydroxycycloheptanecarboxylate (38): colorless oil; IR (neat) 3540, 1735 cm^{-1}; ^{1}H NMR δ 1.29 (3 H, t, J = 7 Hz), 1.4–2.1 (12 H, m), 4.21 (2 H, q, J = 7 Hz); MS, m/z (relative intensity) 186 (M^+, trace), 169 (0.1), 139 (0.3), 113 (100); found m/z 186.1236, calcd for $C_{10}H_{18}O_3$ M 186.1254.

Pentyl 1-hydroxycycloheptanecarboxylate (39): colorless oil; IR (neat) 3550, 1735 cm^{-1}; ^{1}H NMR δ 0.90 (3 H, t, J = 7 Hz), 1.1–2.1 (18 H, m), 4.14 (2 H, t, J = 7 Hz); MS, m/z (relative intensity) 228 (M^+, trace), 158 (0.3), 141 (0.4), 113 (100); found m/z 228.1712, calcd for $C_{13}H_{24}O_3$ M 228.1723.

Ethyl 1-hydroxy-4,4-(ethylenedioxy)cyclohexanecarboxylate (40): colorless crystals; mp 64–65 °C (AcOEt–hexane); IR (KBr) 3530, 1735, 1260, 1110 cm^{-1}; ^{1}H NMR δ 1.29 (3 H, t, J = 7 Hz), 1.5–2.3 (8 H, m), 3.96 (4 H, s), 4.22 (2 H, q, J = 7 Hz); MS, m/z (relative intensity) 230 (M^+, trace), 202 (1.3), 182 (1), 157 (20), 99 (100). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.17; H, 7.75.

Methyl ester 41: colorless crystals; mp 123–125 °C (EtOH); IR (KBr) 3580, 1740 cm^{-1}; ^{1}H NMR δ 0.65 (3 H, s), 0.85 (6 H, d, J = 7 Hz), 0.90 (3 H, d, J = 7 Hz), 0.97 (3 H, s), 3.77 (3 H, s); MS, m/z (relative intensity) 446 (M^+, 7), 428 (7), 413 (6), 387 (100). Anal. Calcd for $C_{29}H_{50}O_3$: C, 77.97; H, 11.28. Found: C, 78.03; H, 11.39.

2-Hydroxy-2-indancarboxylic acid (42): colorless crystals; mp 180–181.5 °C (AcOEt–hexane); IR (KBr) 3430, 1720 cm^{-1}; ^{1}H NMR (CD_3OD) δ 3.08 (2 H, d, J = 16 Hz), 3.54 (2 H, d, J = 16 Hz), 7.15 (4 H, m). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 66.92; H, 5.57.

Ethyl 2-hydroxy-2-indancarboxylate (43): colorless crystals; mp 89–90 °C (AcOEt–hexane); IR (KBr) 3500, 1725 cm^{-1}; ^{1}H NMR δ 1.28 (3 H, t, J = 7 Hz), 3.11 (2 H, d, J = 17 Hz), 3.52 (1 H, d, J = 17 Hz), 4.25 (2 H, q, J = 7 Hz), 7.17 (4 H, s). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.92; H, 6.80.

2-Hydroxyundecanamide (44). Vinyl chloride 11 (75 mg) in 14 mL of dry CH_2Cl_2 in a dry flask was treated with dry ozone at −60 °C till all the starting material disappeared. To this reaction mixture was added Me_2S (0.5 mL) followed by ammonia in water (29%; 0.5 mL). The temperature of the reaction mixture was allowed to warm to room temperature. The solvent was evaporated, and the residue was extracted with benzene. The benzene solution was washed once with water. The product was purified by silica gel column chromatography to afford 44 (68.5 mg, 99%) as colorless crystals: mp 143–144 °C (AcOEt–hexane); IR (KBr) 3420, 3310, 1650 cm^{-1}; ^{1}H NMR (CD_3OD–$CDCl_3$) δ 0.88 (3 H, t, J = 7 Hz), 1.1–2.0 (16 H, m), 4.01 (1 H, m); MS, m/z (relative intensity) 201 (M^+, 3), 157 (23), 130 (3), 97 (30), 75 (100). Anal. Calcd for $C_{11}H_{23}NO_2$: C, 65.63; H, 11.52; N, 6.96. Found: C, 65.44; H, 12.08; N, 6.72.

***N*-Benzyl-2-hydroxyundecanamide (45)**: colorless crystals; mp 99–100 °C (AcOEt–hexane); IR (KBr) 3360, 3290, 1645, 1635 cm^{-1}; ^{1}H NMR δ 0.88 (3 H, t, J = 7 Hz), 1.1–1.9 (16 H, m), 4.12 (1 H, m), 4.43 (2 H, d, J = 6 Hz), 6.85 (1 H, br s), 7.26 (5 H, m); MS, m/z (relative intensity) 291 (M^+, 31), 165 (62), 135 (30), 91 (100); found m/z 291.2206, calcd for $C_{18}H_{29}NO_2$ M 291.2197.

***N*-(2-Hydroxyundecanoyl)piperidine (46)**: colorless oil; IR (neat) 3430, 1645 cm^{-1}; ^{1}H NMR δ 0.87 (3 H, t, J = 7 Hz), 1.0–1.8 (22 H, m), 3.1–3.7 (4 H, m), 4.31 (1 H, m); MS, m/z (relative intensity) 269 (M^+, 5), 143 (67), 113 (100); found m/z 269.2359, calcd for $C_{16}H_{31}NO_2$ M 269.2353.

2-Hydroxy-4-phenylbutanamide (47): colorless crystals; mp 132–133 °C (AcOEt–hexane); IR (KBr) 3410, 3350, 1645 cm^{-1}; ^{1}H NMR (CD_3OD–$CDCl_3$) δ 1.6–2.3 (2 H, m), 2.75 (2 H, t, J = 8 Hz), 4.02 (1 H, m), 7.19 (5 H, m); MS, m/z (relative intensity) 179 (M^+, 1.2), 149 (1), 117 (3), 91 (50), 75 (100). Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.81. Found: C, 66.80; H, 7.19; N, 7.68.

***N*-Hexyl-2-hydroxy-4-phenylbutanamide (48)**: colorless crystals; mp 70.5–71.5 °C (benzene–ether–hexane); IR (KBr) 3300, 1625 cm^{-1}; ^{1}H NMR δ 0.87 (3 H, t, J = 7 Hz), 1.1–1.6 (8 H, m), 1.7–2.3 (2 H, m), 2.74 (2 H, t, J = 8 Hz), 3.21 (1 H, m), 4.06 (1 H, m), 6.65 (1 H, m), 7.19 (5 H, m); MS, m/z (relative intensity) 263 (M^+, 3), 159 (100). Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.97; H, 9.57; N, 5.32. Found: C, 73.15; H, 9.48; N, 5.13.

***N*-Benzyl-2-hydroxy-4-phenylbutanamide (49)**: colorless crystals; mp 85.5–86 °C (AcOEt–hexane); IR (KBr) 3270, 1625 cm^{-1}; ^{1}H NMR δ 1.7–2.3 (2 H, m), 2.73 (2 H, t, J = 8 Hz), 4.10 (1 H, m), 4.38 (2 H, d, J = 6 Hz), 6.96 (1 H, m), 7.0–7.4 (10 H, m); MS, m/z (relative intensity) 269 (M^+, 3), 165 (76), 91 (100). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.65; H, 7.15; N, 5.19.

***N*,*N*-Diethyl-2-hydroxy-4-phenylbutanamide (50)**: colorless oil; IR (neat) 3440, 1650 cm^{-1}; ^{1}H NMR δ 1.08, 1.11 (each 3 H, t, J = 7 Hz), 1.7–2.0 (2 H, m), 2.80 (2 H, t, J = 8 Hz), 2.9–3.7 (4 H, m), 4.23 (1 H, m), 7.21 (5 H, m); MS, m/z (relative intensity) 235 (M^+, 1.4), 187 (1), 131 (100); found m/z 235.1578, calcd for $C_{14}H_{21}NO_2$ M 235.1571.

***N*-(2-Hydroxy-4-phenylbutanoyl)piperidine (51)**: colorless oil; IR (neat) 3450, 1640 cm^{-1}; ^{1}H NMR δ 1.3–2.0 (8 H, m), 2.80 (2 H, t, J = 8 Hz), 3.10 (2 H, m), 3.52 (2 H, m), 4.28 (1 H, m), 7.20 (5 H, m); MS, m/z (relative intensity) 247 (M^+, 1.4), 199 (1.4), 143 (100); found m/z 247.1599, calcd for $C_{15}H_{21}NO_2$ M 247.1571.

2-Cyclohexyl-2-hydroxyethanamide (52): colorless crystals; mp 139–142 °C (AcOEt–hexane); IR (KBr) 3460, 3320, 1640 cm^{-1};

(13) Goodman, M.; Steinfeld, A.; Tonelli, A.; Lepore, U.; Palumbo, M.; Donzel, B. *Bioorg. Chem.* **1974**, *3*, 184.

^{1}H NMR (CD_3OD–$CDCl_3$) δ 0.9–2.1 (11 H, m), 3.86 (1 H, d, J = 4 Hz); MS, m/z (relative intensity) 158 (M + 1, 3.6), 157 (M^+, trace), 95 (93), 75 (100). Anal. Calcd for $C_6H_{15}NO_2$: C, 60.74; H, 9.56; N, 8.85. Found: C, 60.87; H, 9.81; N, 8.72.

***N*-Benzyl-2-cyclohexyl-2-hydroxyethanamide (53)**: colorless crystals; mp 99–100 °C (AcOEt–hexane); IR (KBr) 3360, 3240, 1640 cm^{-1}; ^{1}H NMR δ 0.9–2.0 (11 H, m), 3.94 (1 H, d, J = 3 Hz), 4.42 (2 H, d, J = 6 Hz), 6.90 (1 H, m), 7.25 (5 H, m); MS, m/z (relative intensity) 247 (M^+, 30), 229 (7), 201 (3), 165 (96). Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.69; H, 8.73; N, 5.67.

***N*-Benzyl-1-hydroxycycloheptanecarboxamide (54)**: colorless crystals; mp 105–106 °C (AcOEt–hexane); IR (KBr) 3410, 1650 cm^{-1}; ^{1}H NMR δ 1.4–2.4 (12 H, m), 4.40 (2 H, d, J = 6 Hz), 7.00 (1 H, m), 7.26 (5 H, m). Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.99; H, 8.59; N, 5.54.

Amide 55: colorless crystals; mp 81–82.5 °C (AcOEt–hexane); IR (KBr) 3330, 1650 cm^{-1}; ^{1}H NMR δ 0.88 (3 H, t, J = 7 Hz), 1.1–2.4 (16 H, m), 3.23 (2 H, m), 3.95 (4 H, s), 6.64 (1 H, m). Anal. Calcd for $C_{15}H_{27}NO_4$: C, 63.13; H, 9.54; N, 4.91. Found: C, 63.17; H, 9.35; N, 4.66.

Amide 56: colorless crystals; mp 133–134 °C (AcOEt–hexane); IR (KBr) 3410, 1610 cm^{-1}; ^{1}H NMR δ 1.4–2.3 (14 H, m), 3.62 (4 H, m), 3.95 (4 H, m). Anal. Calcd for $C_{14}H_{23}NO_4$: C, 62.43; H, 8.61; N, 5.20. Found: C, 62.56; H, 8.73; N, 5.06.

Amide 57: colorless crystals; mp 148–151 °C (AcOEt–hexane); IR (KBr) 3425, 1665 cm^{-1}; ^{1}H NMR δ 0.64 (3 H, s), 0.87 (6 H, d, J = 7 Hz), 0.90 (3 H, d, J = 7 Hz), 0.98 (3 H, s), 4.40 (2 H, d, J = 6 Hz), 7.26 (5 H, m); MS, m/z (relative intensity) 521 (M^+, 8), 503 (3), 387 (32), 369 (30), 107 (100). Anal. Calcd for $C_{35}H_{55}NO_2$: C, 80.56; H, 10.62; N, 2.68. Found: C, 80.65; H, 10.82; N, 2.54.

Amide 58: colorless crystals; mp 193–194 °C (AcOEt); IR (KBr) 3375, 3300, 1695, 1655 cm^{-1}; ^{1}H NMR (CD_3OD) δ 3.00 (2 H, d, J = 16 Hz), 3.54 (2 H, d, J = 16 Hz), 7.14 (4 H, m). Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.68; H, 6.23; N, 7.79.

Amide 59: colorless crystals; mp 123–124 °C (AcOEt–hexane); IR (KBr) 3360, 3325, 1645 cm^{-1}; ^{1}H NMR δ 0.88 (3 H, t, J = 7 Hz), 1.1–1.8 (8 H, m), 2.92 (2 H, d, J = 16 Hz), 3.23 (2 H, q, J = 7 Hz), 3.56 (2 H, d, J = 16 Hz), 6.76 (1 H, m), 7.17 (4 H, s). Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.59; H, 9.01; N, 5.32.

Amide 60: colorless crystals; mp 105–107 °C (AcOEt–hexane); IR (KBr) 3410, 1615 cm^{-1}; ^{1}H NMR δ 1.6 (6 H, m), 3.24 (2 H, d, J = 18 Hz), 3.44 (2 H, d, J = 18 Hz), 3.0–3.7 (4 H, m), 7.21 (4 H, m). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.36; H, 7.83; N, 5.66.

α,α′-Dihydroxy Ketone 61. A solution of *N*-methylmorpholine *N*-oxide (61.5 mg, 0.53 mmol) in a mixture of water (0.5 mL) and acetone (1 mL) was added to a solution of OsO_4 (0.04 M in *t*-BuOH; 1.5 mL) in *t*-BuOH. To this solution was added a solution of **22** (76.5 mg, 0.35 mmol) in 1 mL of acetone. The reaction mixture was stirred at room temperature for 65 h; then $Na_2S_2O_4$ (100 mg) was added, and the reaction mixture was stirred for 10 min, diluted with AcOEt, and dried over $MgSO_4$. The dried solution was passed through a short pad of Florisil. The solvent was evaporated to give crystals, which were purified by silica gel column chromatography to give 51 mg (67%) of **61** and 18 mg (23.5%) of the starting material **22**. **61**: colorless crystals; mp 122–124 °C (AcOEt–hexane); IR (KBr) 3470, 1720 cm^{-1}; ^{1}H NMR δ 1.5–2.1 (8 H, m), 3.96 (4 H, s), 4.52 (2 H, s); MS, m/z (relative intensity) 217 (M + 1, 2), 198 (3), 188 (14), 157 (95), 99 (100). Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 55.67; H, 7.59.

α,α′-Dihydroxy ketone 62: colorless crystals; mp 163–165 °C (MeOH); IR (KBr) 3420, 1725 cm^{-1}; ^{1}H NMR δ 0.65 (3 H, s), 0.87 (6 H, d, J = 7 Hz), 0.91 (3 H, d, J = 7 Hz), 0.99 (3 H, s), 4.55 (2 H, s). Anal. Calcd for $C_{29}H_{50}O_3 \cdot {}^1/_2H_2O$: C, 76.43; H, 11.28. Found: C, 76.71; H, 11.65.

α,α′-Dihydroxy ketone 63: colorless crystals; mp 106–108 °C (AcOEt–hexane); IR (KBr) 3390, 1725 cm^{-1}; ^{1}H NMR δ 3.12 (2 H, d, J = 17 Hz), 3.40 (2 H, d, J = 17 Hz), 4.46 (2 H, s). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.97; H, 6.18.

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Supplementary Material Available: ^{1}H NMR spectra of compounds **11**, **12a**, **17**, **19–21**, **23–27**, **29–33**, **35**, **36**, **38**, **39**, **45**, **46**, **50**, and **51** and detailed experimental procedures and characterization data for the asymmetric synthesis of α-hydroxy acids and their derivatives from (–)-1-chlorobutyl *p*-tolyl sulfoxide (32 pages). Ordering information is given on any current masthead page.