New Chiral C_3-Symmetric Triols as Ligands for Vanadium and Titanium Complexes†

Henning Lütjens, Günter Wahl, Frank Möller, Paul Knochel,* and Jörg Sundermeyer*

Fachbereich Chemie der Philipps-Universität Marburg, D-35032 Marburg, Germany

Received June 23, 1997⊗

Several new chiral triols **1a**−**c** with C_3 symmetry have been prepared in enantiopure form via a route involving the iterative catalytic asymmetric alkylation of aldehydes by organozinc reagents followed by diastereoselective hydroboration. Reactions of these chiral triols with titanates $Ti(OR)_4$ and vanadates $V(O)(OR)_3$ are reported. The structure of the binuclear vanadium triolato(3−) complex $[V(O)\{(OCH\text{-}Et)_3CH\}]_2$ (**12a**) has been determined by X-ray analysis. A series of model reactions was conducted to assess the catalytic properties of the chirally modified titanium and vanadium secondary alkoxides. The reactions chosen were the addition of diethylzinc and of trimethylsilyl cyanide to benzaldehyde and the oxidation of geraniol and of ethyl phenyl sulfide with *tert*-butyl hydroperoxide. Only a moderate asymmetric induction was found in some model reactions catalyzed by titanium complexes **11a**,**b**. On the other hand, a very efficient chemoselective oxidation of sulfides to sulfoxides with *tert*-butyl hydroperoxide was possible in the presence of vanadium complex **12a**.

Introduction

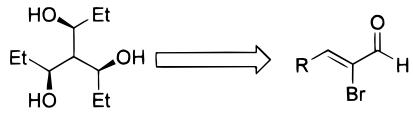
Many asymmetric reactions are catalyzed by transition-metal complexes having chiral C_2-symmetric diols, such as tartrate esters or binaphthol, as ligands.[1] The use of a C_3-symmetric triol, on the other hand, should be advantageous in several respects. First, the resulting complex will be more stable under the reaction conditions due to stronger chelation effects. Second, the presence of three rather than two stereocenters in the ligand furnishes a higher density of stereochemical information around the metal, possibly leading to better asymmetric induction. Third, in reactions proceeding *via* an octahedral intermediate, facial coordination of a tridentate ligand possessing C_3 symmetry will render the remaining coordination sites equivalent, as opposed to the case of a bidentate ligand with C_2 symmetry. Nevertheless, chiral tripod ligands have been used far less in organic synthesis.[2]

Recently, we have reported the synthesis of the chiral C_3-symmetric triol **1a** in optically pure form using the catalytic asymmetric addition of dialkylzincs to aldehydes in the presence of the chiral disulfonamide **2**,[3] allowing the generation of two of the three stereocenters of **1a** (Scheme 1).[4] Herein, we wish to communicate the extension of this methodology to the preparation of other triols bearing different alkyl side chains and investigations concerning the use of these triols as ligands in transition-metal catalysts.

Results and Discussion

Synthesis of the Chiral Triols. The commercially available aldehydes **3a**−**c** were converted to their

Scheme 1



α-bromo derivatives by a bromination−elimination sequence.[5] The thermally sensitive bromo aldehydes **4a**−**c** were obtained in good yield (72−93%). Alkylation with the appropriate dialkylzinc (1.6 equiv) in the presence of titanium tetraisopropoxide and the chiral disulfonamide **2** (8 mol %) furnished the chiral allyl

† Dedicated to Professor Waldemar Adam, Würzburg, Germany, on occasion of his 60th birthday.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1997.

(1) (a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994. (b) Ojima, I., Ed. *Catalytic Asymmetric Synthesis*; VCH: Weinheim, Germany, 1993. (c) Morrison, J. D., Ed. *Asymmetric Synthesis; Chiral Catalysis;* Academic Press: New York, 1985; Vol. 5. (d) Whitesell, J. K *Chem. Rev.* **1989**, *89*, 1581. (e) Noyori, R.; Kitamura, M. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: Berlin, Heidelberg, 1989.

(2) Chiral C_3-symmetrical ligands: (a) di Furia, F.; Licini, G.; Modena, G.; Motterle, R.; Nugent, W. A. *J. Org. Chem.* **1996**, *61*, 5175. (b) Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1994**, *116*, 6142. (c) Nugent, W. A. *J. Am. Chem. Soc.* **1992**, *114*, 2768. (d) Baker, M. J.; Pringle, P. G. *J. Chem. Soc., Chem. Commun.* **1993**, 314. (e) Tokar, C. J.; Kettler, P. B.; Tolman, W. B. *Organometallics* **1992**, *11*, 2737. (f) Adolfson, H, Wärnmark, K.; Moberg, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1054. (g) Burk, M. J.; Feaster, J. E.; Harlow, R. L. *Tetrahedron: Asymmetry* **1991**, *2*, 569. (h) Burk, M. J.; Harlow, R. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *102*, 1511. Related tridentate ligands: Mann, S.; Huttner, G.; Zsolnai, L.; Heinze, K. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 2808. (i) Severin, K.; Beck, W.; Trojand, G.; Polborn, K.; Steglich, W. *Angew. Chem.* **1995**, *105*, 1570. (j) Friedrich, S.; Memmler, H.; Gade, L. H.; Li, W.-S.; McPartlin, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 676. (k) Tse, B.; Kishi, Y. *J. Org. Chem.* **1994**, *59*, 7807. Hahn, F. E.; Tamm, M. *Organometallics* **1994**, *13*, 3002. (l) Seitz, T.; Asam, A.; Huttner, G.; Walter, O.; Zsolnai, L. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 1287. (m) Seitz, T.; Muth, A.; Huttner, G. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 1045. (n) Seitz, T.; Muth, A.; Huttner, G.; Klein, T.; Walter, O.; Fritz, M.; Zsolnai, L. *J. Organomet. Chem.* **1994**, *469*, 155. (o) Power, J. M.; Evertz, K.; Henling, L.; Marsh, R.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1990**, *29*, 5058.

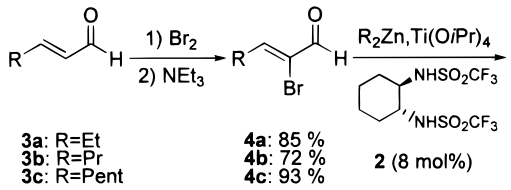
(3) (a) Yoshioka, M.; Kawakita, T.; Ohno, M. *Tetrahedron Lett.* **1989**, *30*, 1657. (b) Takahashi, H.; Kawakita, T.; Yoshioka, M.; Kobayashi, S.; Ohno, M. *Tetrahedron Lett.* **1989**, *30*, 7095. (c) Takahashi, H.; Kawakita, T.; Ohno, M.; Yoshioka M.; Kobayashi, S. *Tetrahedron* **1992**, *48*, 5691.

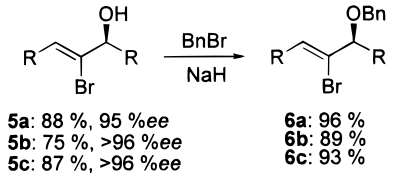
(4) Lütjens, H.; Knochel, P. *Tetrahedron: Asymmetry* **1994**, *5*, 1161.

(5) Kowalski, C. J.; Weber, A. E.; Fields, K. W. *J. Org. Chem.* **1982**, *47*, 5088.

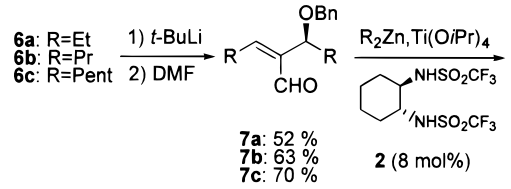
S0276-7333(97)00523-2 CCC: $14.00

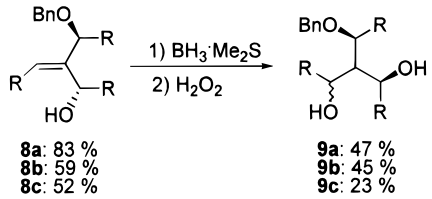
Scheme 2





Scheme 3



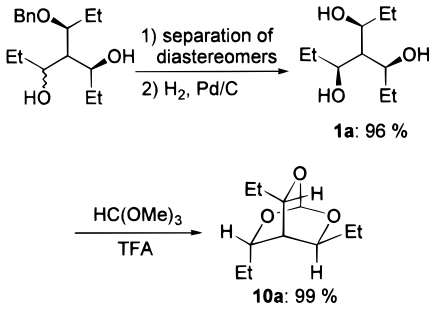


alcohols **5a**−**c** in excellent yields (75−88%) and enantioselectivities (95−96% ee),[6] as determined by ^{1}H NMR using the method of Parker.[7] The presence of a bromine atom in an α-position has been shown previously to increase the selectivity of this asymmetric alkylation.[8] Benzylation to protect the alcohol function was achieved using benzyl bromide (1.1 equiv) and an excess of sodium hydride in THF (Scheme 2). It should be noted that the use of DMF as solvent results in elimination, thus leading to chiral propargyl alcohols.[9]

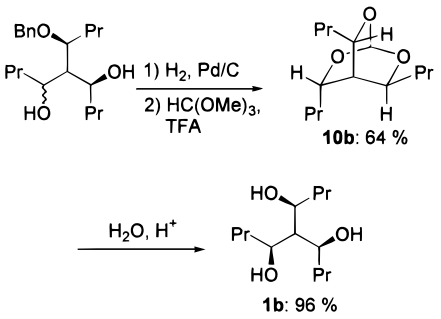
Bromine−lithium exchange at −105 °C followed by quenching with excess DMF gave the α,β-unsaturated aldehydes **7a**−**c** in good yields (52−70%). However, in the case of R = Pr, surprisingly, a substantial loss of double-bond geometry was observed. After this, a second alkylation with dialkylzinc in the presence of **2** and titanium tetraisopropoxide afforded the desired monoprotected diols **8a**−**c** in good yields (52−89%) and excellent diastereoselectivities.

The third stereocenter was introduced *via* diastereoselective hydroboration. Thus, the reaction of the allyl alcohols **8a**−**c** with borane (3 equiv) in ether followed by oxidative workup gave predominantly the desired isomers of the monobenzylated triols **9a**−**c**, albeit in low yield (23−47%; Scheme 3). The observed selectivity is in accordance with the results of Still in related cases.[10]

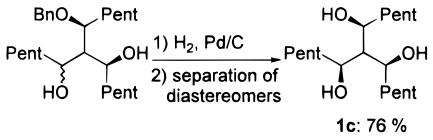
Scheme 4



Scheme 5



Scheme 6



Benzyl alcohol was found as a byproduct, indicating degradation as a side reaction, which accounts for the low yield.

In the case of R = Et, the desired isomer **9a** could be separated by flash chromatography and debenzylated in quantitative yield to give the optically pure triol **1a**. C_3 symmetry was confirmed by the single set of signals observed in both ^{1}H and ^{13}C NMR. The cyclic ortho ester **10a** was formed in quantitative yield with methyl orthoformate in the presence of an acid (Scheme 4).

With R = Pr, it was impossible to separate the isomers of **9b**. After debenzylation, a similarly inseparable mixture of triols was obtained. However, it was found that only the C_3-symmetric isomer forms the cyclic ortho ester **10b** and thus could be separated from its epimer. Hydrolysis of **10b** then gave optically pure **1b** (Scheme 5).

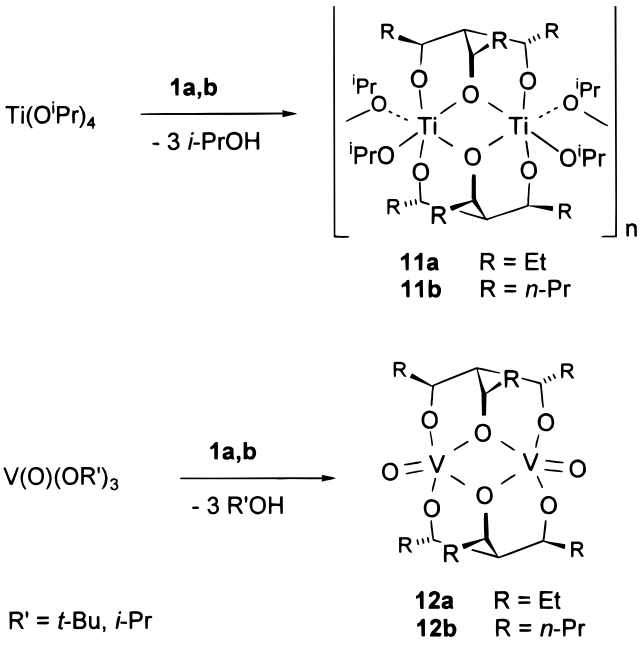
Finally, when R = Pent, it was found that after debenzylation the epimeric triols could be separated by flash chromatography, giving optically pure **1c** and its epimer (Scheme 6).

Unfortunately, a further extension of this method to the synthesis of cyclohexyl- and phenyl-substituted triols turned out to be impossible. While dicyclohexylzinc did not add to the corresponding aldehyde at all, the addition reaction of diphenylzinc to α-bromocinnamaldehyde proceeded without any enantioselectivity under our conditions.

Preparation of the Metal Complexes. Organic triols have attracted much attention as chelating or bridging ligands in the coordination chemistry of the

(6) Rozema, M. J.; Achyutha Rao, S.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 1956.
(7) Parker, D. *J. Chem. Soc., Perkin Trans. 2* **1983**, 83.
(8) Rozema, M. J.; Eisenberg, C.; Lütjens, H.; Ostwald, R.; Belyk, K.; Knochel, P. *Tetrahedron Lett.* **1993**, *34*, 3115.
(9) Lütjens, H.; Nowotny, S.; Knochel, P. *Tetrahedron: Asymmetry* **1995**, *6*, 2675.
(10) (a) Still, W. C.; Barrish, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 2487. (b) Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307.

Scheme 7



early transition metals, especially in recent titanium[11] and vanadium[12] alkoxide chemistry. The most commonly studied triols have been those which are commercially available and typically contain three primary alcohol functions such as those found in tris(hydroxymethyl)alkyl ligands ($(HOCH_2)_3CR$) and in the tris(hydroxyethyl)amine ligand ($(HOCH_2CH_2)_3N$). With our approach using a secondary triol ligand, we hoped not only to introduce three centers of chirality into the ligand regime but also to increase the steric constraints of such a ligand onto the metal center. This again should have an effect in reducing the trend of metal alkoxides to form oligomeric or polymeric species via bridging alkoxide moieties. It was hoped that by increasing the steric hindrance dynamic processes of ligand exchange *via* ligand-bridged intermediates might be frozen out. This again would be an essential condition for the use of chiral ligands of the triol type in order to create chiral Lewis acids or Lewis acidic metal centers in an disymmetric ligand environment of C_3 symmetry.

However, it was found that the reaction product of triol **1a** with titanium tetraisopropoxide showed complex NMR spectra with broad signals, indicating species that even at low temperatures are rapidly equilibrating *via* bridging alkoxide intermediates. Integration of signals of the ligand methyl groups *versus* signals of protons adjacent to oxygen of the isopropoxide and triol as well as combustion analyses confirmed the 1:1 ratio of triol to isopropoxide ligands. On the basis of their good solubility in hydrocarbon solvents, complexes **11a,b** are regarded as oligomers with at least six-coordinate titanium centers, as suggested in Scheme 7.

Whereas both titanates $[Ti(OiPr)\{(OCHR)_3CH\}]_n$ (**11a,b**) were fluxional on the NMR time scale, two nondynamic vanadates of the composition $[V(O)\{(OCHR)_3CH\}]_2$ (**12a,b**) could be isolated in good yields from transesterification reactions of either $[VO(OiPr)_3]$ or $[VO(OtBu)_3]$ with triols **1a** and **1b**. The well-resolved ^{1}H and ^{13}C NMR spectra revealed the presence of three magnetically nonequivalent triol arms, thus ruling out a tripodal ligand arrangement of C_3 symmetry on one tetrahedral metal center, but rather anticipating one bridging and two different terminal alkoxide ligands.

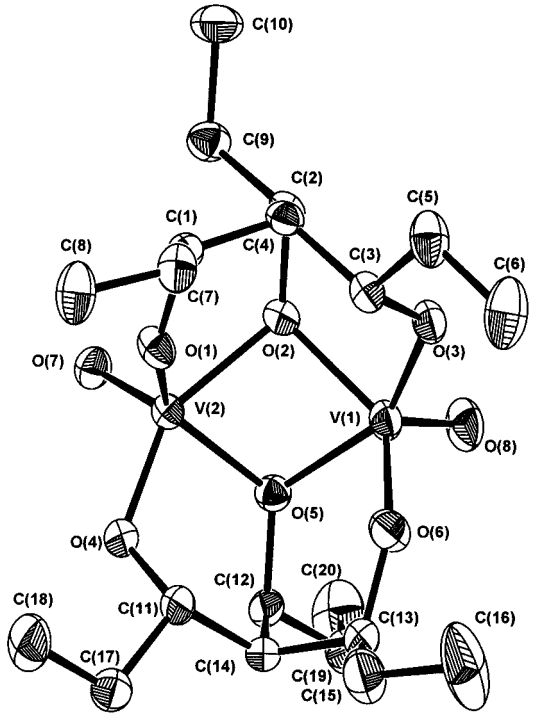


Figure 1. Molecular structure of vanadyl complex **12a** (ORTEP plot). Hydrogen atoms are omitted for clarity.

Structure of Vanadyl Complex 12a. In order to confirm the bonding mode of the triolato ligand in **12a**, an X-ray analysis was performed. Yellow crystals were obtained from a hexane solution at −30 °C. The molecular structure is presented in Figure 1. The ligand induced the formation of a binuclear vanadium complex. The two triolato ligands bridge the centers V(1) and V(2) by donating to each vanadium center one terminal alkoxy group and to both vanadium centers one bridging alkoxy group. Both vanadium centers are pentacoordinated in a distorted-tetragonal-pyramidal fashion. Both polyhedra have one terminal oxo group in the axial position and two bridging alkoxy groups in an edge-sharing fashion. The four-membered ring incorporating V(1), V(2), O(2), and O(5) is folded with dihedral angles of V(1)−O(2)−O(5)−V(2) = 43.4° and O(2)−V(1)−V(2)−O(5) = 56.1°. The bridging oxygen atoms are far from planar with sum of angles at O(3) Σ° = 341.3 and O5 Σ° = 340.6. Both terminal oxo groups are in a distorted *syn* orientation with respect to each other (torsion angle O7−V2−V1−O8 = 26.5°). A similar μ-κ^3 coordination mode of an achiral triolato(2−) ligand was found in $[V(O)Cl\{(OCH_2)_2CMe(CH_2OH)\}]_2$[13] with a *trans* orientation of the two oxo groups in edge-sharing octahedra as well as in pentacoordinate $[V(O)(\mu\text{-}C_5Me_5O_3\text{-}\kappa^3)]_2$,[14] an interesting product from the air oxidation of $[(C_5Me_5)_2V]$. The metal to oxygen bond distances and the decreasing bond order in the series terminal oxo groups (average V−O distance 1.585 Å in **12a**) > terminal alkoxy groups

(11) Representative examples: (a) Boche, G.; Möbus, K.; Harms, K.; Marsh, M. *J. Am. Chem. Soc.* **1996**, *118*, 2770. (b) Bonchio, M.; Licini, G.; Modena, G.; Moro, S.; Bortolini, O.; Traldi, P.; Nugent, W. A. *J. Chem. Soc., Chem. Commun.* **1997**, 869.

(12) Representative example: Khan, M. I.; Chen, Q.; Goshorn, D. P.; Hope, H.; Parkin, S.; Zubieta, J. *J. Am. Chem. Soc.* **1992**, *114*, 3341.

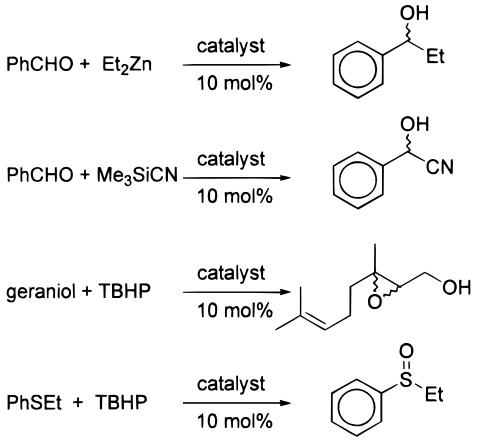
(13) Chang, Y.; Chen, Q.; Khan, M. I.; Salta, J.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1993**, 1872.

(14) Bottomley, F.; Magill, C. P.; White, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 3070.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 12a

V(1)−O(8)	1.584(4)	V(1)−O(6)	1.774(4)
V(1)−O(3)	1.778(4)	V(1)−O(2)	1.968(4)
V(1)−O(5)	2.009(4)	V(2)−O(7)	1.585(4)
V(2)−O(4)	1.778(4)	V(2)−O(1)	1.785(4)
V(2)−O(5)	1.969(3)	V(2)−O(2)	1.995(3)
V(1)−V(2)	3.0330(14)		
O(8)−V(1)−O(6)	113.6(2)	O(8)−V(1)−O(3)	104.0(2)
O(6)−V(1)−O(3)	97.3(2)	O(8)−V(1)−O(2)	113.8(2)
O(6)−V(1)−O(2)	130.2(2)	O(3)−V(1)−O(2)	85.2(2)
O(8)−V(1)−O(5)	102.6(2)	O(6)−V(1)−O(5)	86.5(2)
O(3)−V(1)−O(5)	148.9(2)	O(2)−V(1)−O(5)	69.31(14)
O(8)−V(1)−V(2)	133.3(2)	O(6)−V(1)−V(2)	94.01(14)
O(3)−V(1)−V(2)	109.04(12)	O(2)−V(1)−V(2)	40.39(10)
O(5)−V(1)−V(2)	39.84(10)	O(7)−V(2)−O(4)	103.7(2)
O(7)−V(2)−O(1)	112.5(2)	O(4)−V(2)−O(1)	98.0(2)
O(7)−V(2)−O(5)	113.2(2)	O(4)−V(2)−O(5)	85.0(2)
O(1)−V(2)−O(5)	132.1(2)	O(7)−V(2)−O(2)	102.6(2)
O(4)−V(2)−O(2)	148.9(2)	O(1)−V(2)−O(2)	86.9(2)
O(5)−V(2)−O(2)	69.6(2)	O(7)−V(2)−V(1)	133.1(2)
O(4)−V(2)−V(1)	109.18(13)	O(1)−V(2)−V(1)	95.26(13)
O(5)−V(2)−V(1)	40.80(11)	O(2)−V(2)−V(1)	39.73(11)
C(2)−O(2)−V(1)	119.7(3)	C(3)−O(3)−V(1)	117.0(3)
C(2)−O(2)−V(2)	121.7(3)	C(13)−O(6)−V(1)	139.4(4)
V(1)−O(2)−V(2)	99.9(2)	C(11)−O(4)−V(2)	118.4(3)
C(12)−O(5)−V(2)	119.6(3)	C(13)−O(6)−V(1)	139.4(4)
C(12)−O(5)−V(1)	121.6(3)	V(2)−O(5)−V(1)	99.4(2)

Scheme 8



(average V−O distance 1.779 Å) > bridging alkoxy groups (average V−O distance 1.985 Å) follow the typical trend in vanadium chemistry.[15] Selected data are listed in Table 1.

Catalytic Properties. A series of model reactions was conducted to assess the catalytic properties of the titanium and vanadium complexes **11a,b** and **12a,b** (Scheme 8). The reactions chosen were the addition of diethylzinc[16] and of trimethylsilyl cyanide[17] to benzaldehyde and the oxidation of geraniol[18] and of ethyl phenyl sulfide[19] with *tert*-butyl hydroperoxide (TBHP).

Titanium Complexes. The results for the reactions using *in situ* prepared titanium complexes **11a**,**b** are summarized in Table 2. The titanium alkoxide **11a**, having **1a** as a ligand, was able to catalyze the ethylation of benzaldehyde, affording (*R*)-1-phenylpropanol in 20% ee. The addition of trimethylsilyl cyanide to benzaldehyde in the presence of **11a** gave, after acidic workup, (+)-mandelonitrile in 26% ee. The use of 100 mol % of the titanium complex increased the enantioselectivity to 44%. No improvement could be observed by lowering the temperature. Also, **11a** was able to catalyze the epoxidation of geraniol; however, the product turned out to be racemic. Surprisingly, no acceleration of the TBHP oxidation of ethyl phenyl sulfide occurred in the presence of **11a**.

Table 2. Reactions Catalyzed by Titanium Complexes 11a and 11b

reacn	cat.	temp (°C)	yield (%)	ee (%)
PhCHO + Et_2Zn	**11a**	−35	96	20[a,b]
	11b	−15	91	20[b]
PhCHO + Me_3SiCN	**11a**	0	93	26[a,b]
	11a[c]	0	95	44[a]
	11b	room temp	96	7[b]
geraniol + TBHP	**11a**	−20	90	*rac*[a,b]
	11b	−20	88	*rac*[b]
PhSEt + TBHP	**11a**	room temp	n.c.	
	11b	room temp	n.c.	

[a] Determined by ^{1}H NMR of mandelate. [b] Determined by chiral GC. [c] 100 mol %.

In comparison, complex **11b**, formed from titanium tetraisopropoxide and **1b**, in general gave much slower reactions. Both addition reactions with benzaldehyde required higher temperatures and longer reaction times to run to completion. In the ethylation reaction, which had to be conducted at a slightly higher temperature, 20% ee in the product alcohol was likewise obtained. The reaction with trimethylsilyl cyanide, on the other hand, was finished after 16 h at room temperature, and the product was formed in only 7% ee. A slower conversion was also observed in the epoxidation of geraniol, racemic epoxide being formed. As was the case with **11a**, no catalysis of the oxidation of ethyl phenyl sulfide was found.

Since the length of the side chain apparently had no beneficial effect on the ee values of the products, no experiments were conducted using **11c**.

Vanadyl Complexes. The complex **12a**, formed from **1a** and vanadyl isopropoxide, could be obtained in crystalline form. When tested for catalytic activity, it showed no effect in either ethylation or cyanation of benzaldehyde, i.e. as a Lewis acid catalyst. However, it was found that **12a** was a very efficient catalyst for oxidations using TBHP as oxygen source.[20] Geraniol was completely converted to its epoxide in the presence of as little as 0.1 mol % of **12a** within 2 h in 96% yield. A control experiment run under identical conditions but employing vanadyl isopropoxide as catalyst required 5 h for completion. Despite this apparent ligand acceleration, the epoxide obtained in the presence of **12a** was again racemic. The improvements in the reaction rate are probably due to the lower aggregation of the vanadyl species compared to that of vanadyl isopropoxide.

(15) Clark, R. J. H. *The Chemistry of Titanium and Vanadium*; Elsevier: Amsterdam, 1968.

(16) Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992**, *92*, 807 and references cited therein.

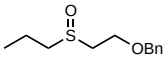
(17) Jackson, W. R.; Jacobs, H. A.; Jayatilake, G.; Matthews, B. R.; Watson, K. G. *Aust. J. Chem.* **1990**, *43*, 2045, North, M. *Synlett* **1993**, 807.

(18) (a) Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922. (b) Sharpless, K. B.; Verhoeven, T. R. *Aldrichim. Acta* **1979**, *12*, 63. (c) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136. (d) Itoh, T.; Jitsukawa, K.; Kaneda, K.; Teranishi, S. *J. Am. Chem. Soc.* **1979**, *101*, 159. (e) Mihelich, E. D.; Daniels, K.; Eickhoff, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 7690. (f) Butler, A.; Clague, M. J.; Meister, G. E. *Chem. Rev.* **1994**, *94*, 625.

(19) (a) Pitchen, P.; Duñach, E.; Deshmukh, M. N.; Kagan, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 8188. (b) di Furia, F.; Licini, G.; Modena, G.; Motterle, R.; Nugent, W. A. *J. Org. Chem.* **1996**, *61*, 5175. (c) Bolm, C.; Bienewald, F., *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2640. (d) Adam, W.; Golsch, D.; Sundermeyer, J.; Wahl, G. *Chem. Ber.* **1996**, *129*, 1177.

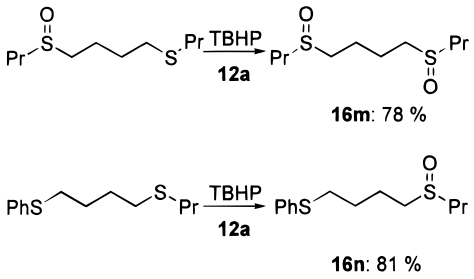
(20) (a) Di Furia, F.; Modena, G.; Curci, R.; Edwards, J. O. *Gazz. Chim. Ital.* **1979**, *109*, 571. (b) Curci, R.; Di Furia, F.; Edwards, J. O.; Modena, G. *Chim. Ind. (Milan)* **1978**, *60*, 595.

Table 3. Oxidation of Sulfides to Sulfoxides with TBHP Catalyzed by 12a

entry no.	product	R^1	R^2	yield (%)
1	**16a**	Et	Ph	84
2	**16b**	Me	Ph	83
3	**16c**	*i*Pr	Ph	84
4	**16d**	*t*Bu	Ph	81
5	**16e**	Bu	Ph	83
6	**16f**	Oct	Ph	89
7	**16g**	*c*Hex	Ph	88
8	**16h**	Bu	Ph	95
9	**16i**	Ph	Ph	91
10	**16j**	Bu	Bu	87
11	**16k**		Ph	90
12	**16l**			78
13	**17**	$PhSO_2Et$		88[a]

[a] 2.5 equiv of TBHP used.

Scheme 9



A similarly high catalytic activity was found in the vanadium-catalyzed oxidation of sulfides to sulfoxides by TBHP, which was studied in more detail. The presence of 0.1 mol % of **12a** was sufficient to give complete reaction of ethyl phenyl sulfide within 4 h, this again being superior to uncomplexed vanadyl isopropoxide. In the presence of 0.01 mol % of **12a** the reaction time increased to 8 h. Furthermore, when only 1 equiv of oxidant was employed, only the sulfoxide **16a** was formed. This is especially noticeable, since upon use of 2.5 equiv of TBHP complete conversion to the corresponding sulfone **17** took place.

A series of sulfides were oxidized to the corresponding sulfoxides **16a**−**n** in almost quantitative yield (Table 3, Scheme 9). Unfortunately, the catalyst failed to induce any chirality, as determined by chiral HPLC. No improvement of the *ee* could be observed by lowering the temperature or by raising the amount of catalyst.

The last two entries highlight the chemoselectivity of the catalyst, as both reactions give just one product, making it possible to oxidize a sulfide in the presence of a sulfoxide and an dialkyl sulfide in the presence of an alkyl aryl sulfide (Scheme 9).

Similar effects were observed when **12b** was employed as catalyst. Longer reaction times were needed in both reactions, but yields and chemoselectivity were comparable to those of **12a**.

Conclusion

The preparation and use of several new chiral C_3-symmetric triols as ligands have been reported. While no synthetically useful asymmetric inductions could be obtained using catalysts derived from **1a** or **1b**, the dinuclear vanadium complex **12a**, whose structure was determined by X-ray diffraction, allowed a chemoselective oxidation of sulfides to sulfoxides with TBHP when used in amounts as small as 0.1 mol %. The length of the alkyl chains in **1a** and **1b** appears to have an influence only on the reaction time.

Experimental Section

General Remarks. All manipulations involving air- or moisture-sensitive compounds were conducted under an atmosphere of argon using standard techniques. Dry oxygen-free solvents were used where appropriate.

Warning! All operations involving pyrophoric diethylzinc should be performed wearing leather gloves and a face shield for additional protection.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker ARX-200 and AC-300 spectrometers and were indirectly referenced to TMS using residual solvent signals. δ values are given in ppm and J values in hertz. IR spectra were recorded on a Perkin-Elmer 281 spectrophotometer; all values are given in cm^{-1}. Mass spectra were obtained on a Varian MAT CH7A, with all values given in m/z (relative intensities in parentheses). Elemental analyses were performed at our institute. Optical rotations were measured on a Perkin-Elmer 141 polarimeter at room temperature. Chiral GC experiments were conducted on a Chrompack Chirasil-Dex CB column. Chiral HPLC examinations were done with a Daicel Chiracel OD column. Flash chromatography was conducted according to the procedure of Still,[21] using mixtures of petroleum ether (PE) and methyl *tert*-butyl ether (MTBE) as eluant. A water-free solution of TBHP in toluene was prepared according to the procedure of Sharpless.[22]

Preparation of (*Z*)-2-Bromo-2-pentenal (4a). To a stirred solution of (*E*)-2-pentenal (**3a**; 8.40 g, 100 mmol) in CH_2Cl_2 (100 mL) was added dropwise a solution of bromine (16.0 g, 100 mmol) in CH_2Cl_2 at 0 °C followed by triethylamine (20 mL). The reaction mixture was warmed to room temperature and was washed with dilute HCl, dried, and evaporated. Filtration over silica gel afforded **4a** as a pale yellow liquid (13.85 g, 85 mmol, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz): 9.21 (s, 1H), 7.10 (t, 1H, J = 7.1), 2.45 (m, 2H), 1.11 (t, 3H, J = 7.5). ^{13}C NMR ($CDCl_3$, 75 MHz): 186.09, 156.83, 128.19, 25.48, 11.82. IR (film): 2980 (s), 2930 (s), 2875 (s), 2740 (w), 1690 (s), 1635 (s), 1450 (m), 1170 (m), 1090 (m), 860 (w). MS (EI): 164 (60), 162 (62), 83 (69), 55 (78), 43 (24), 39 (100), 27 (88). Anal. Calcd for C_5H_7BrO: C, 36.84, H, 4.33. Found: C, 36.79; H, 4.40.

Preparation of (*Z*)-2-Bromo-2-hexenal (4b). To a stirred solution of (*E*)-2-hexenal (**3b**; 9.81 g, 100 mmol) in CH_2Cl_2 (100 mL) was added dropwise a solution of bromine (16.0 g, 100 mmol) in CH_2Cl_2 at 0 °C followed by triethylamine (20 mL). The reaction mixture was warmed to room temperature and was washed with dilute HCl, dried, and evaporated. Filtration over silica gel afforded **4b** as a pale yellow liquid (12.67 g, 72 mmol, 72%). ^{1}H NMR ($CDCl_3$, 300 MHz): 9.13 (s, 1H), 7.09 (t, 1H, J = 7.2), 2.43 (q, 2H, J = 7.3), 1.52 (sex, 2H, J = 7.5), 0.93 (t, 3H, J = 7.4). ^{13}C NMR ($CDCl_3$, 75 MHz): 185.99, 155.48, 128.78, 33.83, 20.83, 13.68. IR (film): 2960 (s), 2820 (m), 1690 (s), 1615 (w), 1460 (m), 1170 (m). MS (EI): 178 (10), 176 (10), 135 (24), 97 (35), 42 (100), 39 (59). Anal. Calcd for C_6H_9BrO: C, 40.71; H, 5.12. Found: C, 40.68; H, 5.10.

Preparation of (*Z*)-2-Bromo-2-octenal (4c). To a stirred solution of (*E*)-2-octenal (**3c**; 6.06 g, 48 mmol) in CH_2Cl_2 (100 mL) was added dropwise a solution of bromine (7.82 g, 49 mmol) in CH_2Cl_2 at 0 °C followed by triethylamine (15 mL). The reaction mixture was warmed to room temperature and was washed with dilute HCl, dried, and evaporated. Filtration over silica gel afforded **4c** as a pale yellow liquid (9.19 g, 44 mmol, 93%). ^{1}H NMR ($CDCl_3$, 300 MHz): 9.20 (s, 1H), 7.14 (t, 1H, J = 7.2), 2.45 (q, 2H, J = 7.4), 1.53−1.45 (m, 2H), 1.31−1.23 (m, 4H), 0.83 (t, 3H, J = 7.1). ^{13}C NMR ($CDCl_3$, 75

(21) Still, C. W.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(22) Hill, J. G.; Rossiter, B. E.; Sharpless, K. B. *J. Org. Chem.* **1983**, *48*, 3607.

MHz): 185.89, 155.78, 128.55, 31.84, 31.23, 27.00, 22.17, 13.70. IR (film): 2940 (s), 2830 (m), 1705 (s), 1620 (m), 1465 (w), 1090 (w). MS (EI): 150 (36), 148 (39), 95 (39), 69 (100), 55 (96), 42 (96). Anal. Calcd for $C_8H_{13}BrO$: C, 46.85; H, 6.39. Found: C, 46.58; H: 6.40.

Preparation of (3*S*)-(*Z*)-4-Bromohept-4-en-3-ol (5a). To a solution of **2** (1.003 g, 2.65 mmol) and Ti(O*i*Pr)$_4$ (25 mL, 83 mmol) in toluene (25 mL) was added at −60 °C diethylzinc (8.0 mL, 80 mmol) followed by **4a** (8.08 g, 49.5 mmol) and the reaction mixture stirred at −50 °C for 2 h. The mixture was poured into dilute aqueous HCl and extracted with ether, and the extract was washed with dilute aqueous NaOH to remove **2**. The organic phase was dried, the ether evaporated, and the crude product distilled under reduced pressure. **5a** was obtained as a clear liquid (bp 88−89 °C/10 mmHg, 8.41 g, 43.5 mmol, 88%, 95% ee). ^{1}H NMR ($CDCl_3$, 300 MHz): 5.94 (t, 1H, J = 6.9), 3.98−3.92 (m, 1H), 2.20 (m, 2H), 1.91 (s, 1H), 1.72−1.57 (m, 2H), 1.03 (t, 3H, J = 7.5), 0.86 (t, 3H, J = 7.4). ^{13}C NMR ($CDCl_3$, 75 MHz): 131.97, 130.55, 78.04, 28.61, 24.15, 12.75, 9.67. IR (film): 3355 (br, s), 2970 (s), 2875 (s), 1650 (w), 1455 (m), 1380 (m), 1015 (m), 845. MS (EI): 194 (3), 192 (2), 165 (30), 55 (100), 43 (11), 29 (24). Anal. Calcd for C_7H_{13}-BrO: C, 43.54; H, 6.79. Found: C, 43.30; H, 6.58. $[\alpha]_D$: −5.20 (c = 1.68, benzene).

Preparation of (4*S*)-(*Z*)-5-Bromonon-5-en-4-ol (5b). To a solution of **2** (775 mg, 2.05 mmol) and Ti(O*i*Pr)$_4$ (18.5 mL, 62 mmol) in ether (25 mL) was added at −60 °C dipropylzinc (11.0 mL, 80 mmol) followed by **4b** (7.22 g, 41 mmol) and the reaction mixture stirred at −20 °C for 4 h. The mixture was poured into dilute aqueous HCl and extracted with ether, and the extract was washed with dilute aqueous NaOH to remove **2**. The organic phase was dried, the ether evaporated, and the crude product distilled under reduced pressure. **5b** was obtained as a clear liquid (bp 59 °C/0.2 mmHg, 6.74 g, 30.0 mmol, 75%, >96% ee). ^{1}H NMR ($CDCl_3$, 300 MHz): 5.88 (t, 1H, J = 6.9), 4.01−3.96 (m, 1H), 2.14, 2.06 (m, 3H), 1.60−1.51 (m, 2H), 1.41−1.22 (m, 4H), 0.88 (t, 6H, J = 7.5). ^{13}C NMR ($CDCl_3$, 75 MHz): 131.66, 129.92, 76.37, 37.73, 32.62, 21.51, 18.56, 13.73, 13.60. IR (film): 3350 (br, s), 2930 (s), 1650 (w), 1455 (m), 1025 (m). MS (EI): 222 (6), 220 (6), 179 (68), 177 (83), 137 (96), 135 (100), 69 (27), 55 (30). Anal. Calcd for $C_9H_{17}BrO$: C, 48.88; H, 7.75. Found: C, 48.54; H, 7.75. $[\alpha]_D$: −1.15 (c = 3.47, benzene).

Preparation of (6*S*)-(*Z*)-7-bromotridec-7-en-6-ol (5c). To a solution of **2** (416 mg, 1.1 mmol) and Ti(O*i*Pr)$_4$ (11.2 mL, 37.4 mmol) in ether (25 mL) was added at −30 °C dipentylzinc (10.38 mL, 50 mmol) followed by **4c** (4.53 g, 22 mmol), and the reaction mixture was stirred at −20 °C for 5 h. The mixture was poured into dilute aqueous HCl and extracted with ether, and the extract was washed with dilute aqueous NaOH to remove **2**. The organic phase was dried, the ether evaporated, and the crude product purified by flash chromatography (eluant PE−MTBE (20:1)). **5c** was obtained as a clear liquid (5.28 g, 19 mmol, 87%, >96% ee). ^{1}H NMR ($CDCl_3$, 300 MHz): 5.88 (t, 1H, J = 6.9), 3.96 (t, 1H, J = 6.7), 2.16−2.08 (m, 2H), 1.96 (br s, 1H), 1.59−1.54 (m, 2H), 1.36−1.19 (m, 12H), 0.84−0.78 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): 131.39, 130.21, 76.58, 35.47, 31.38, 31.20, 30.50, 27.81, 24.90, 22.39, 22.29, 13.80 (2 C). IR (film): 3340 (br, m), 2930 (s), 1650 (w), 1460 (m), 1030 (m). MS (EI): 207 (73), 205 (72), 153 (48), 125 (41), 67 (45), 55 (100), 43 (51). Anal. Calcd for $C_{13}H_{25}BrO$: C, 56.32; H, 9.09. Found: C, 56.35; H, 9.27. $[\alpha]_D$: +6.09 (c = 2.13, benzene).

Preparation of (3*S*)-(*Z*)-3-(Benzyloxy)-4-bromohept-4-ene (6a). To a stirred solution of **5a** (9.23 g, 47.8 mmol) and benzyl bromide (8.55 g, 50 mmol) in THF (50 mL) was added at 0 °C NaH (as an 80% suspension in white oil, 1.50 g, 50 mmol) in several portions. The ice bath was removed, and the reaction mixture was stirred at room temperature overnight. After the usual workup, the crude product was purified by flash chromatography (eluant PE−MTBE (20:1)). **6a** was obtained as a clear oil (12.99 g, 45.9 mmol, 96%).^{1}H NMR ($CDCl_3$, 300 MHz): 7.37−7.27 (m, 5H), 5.94 (t, 1H, J = 6.9), 4.44 (m, 2H), 3.65 (t, 1H, J = 6.8), 2.33−2.23 (m, 2H), 1.77−1.67 (m, 2H), 1.05 (t, 3H, J = 7.6), 0.84 (t, 3H, J = 7.5). ^{13}C NMR ($CDCl_3$, 75 MHz): 138.25, 134.03, 128.32, 128.23, 127.91, 127.54, 84.42, 69.85, 27.15, 24.22, 12.96, 9.78. IR (film): 3030 (m), 2965 (s), 2880 (s), 1650 (m), 1445 (s), 1070 (s), 740 (s), 700 (s). MS (EI): 255 (2), 253 (2), 178 (2), 176 (2), 107 (8), 91 (100), 55 (5). Anal. Calcd for $C_{14}H_{19}BrO$: C, 59.37; H, 6.76. Found: C; 59.16; H, 6.52. $[\alpha]_D$: −45.03 (c = 1.71, benzene).

Preparation of (4*S*)-(*Z*)-4-(Benzyloxy)-5-bromonon-5-ene (6b). To a stirred solution of **5b** (6.75 g, 30 mmol) and benzyl bromide (6.25 g, 37 mmol) in THF (50 mL) was added at 0 °C NaH (as 80% suspension in white oil, 1.35 g, 45 mmol) in several portions. The ice bath was removed, and the reaction mixture was stirred at room temperature overnight. After the usual workup, the crude product was purified by flash chromatography (eluant PE−MTBE (20:1)). **6b** was obtained as a clear oil (8.30 g, 26.7 mmol, 89%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.26−7.13 (m, 5H), 5.85 (t, 1H, J = 7.0), 4.47−4.14 (m, 2H), 3.65 (1H, J = 6.8), 2.18−2.14 (m, 2H), 1.57−1.20 (m, 6H), 0.87 (t, 3H, J = 7.2), 0.80 (t, 3H, J = 7.4). ^{13}C NMR ($CDCl_3$, 50 MHz): 136.03, 129.96, 127.15, 126.13, 125.27, 125,36, 80.59, 67.61, 34.20, 30.50, 19.52, 16.44, 11.68, 11.54. IR (film): 3040 (w), 2920 (s), 1645 (w), 1450 (s), 1080 (m), 735 (s), 695 (s). MS (EI): 269 (3), 267 (3), 206 (4), 204 (4), 91 (100), 65 (5). Anal. Calcd for $C_{16}H_{23}BrO$: C, 60.74; H, 7.45. Found: C, 60.79; H, 7.59. $[\alpha]_D$: −43.5 (c = 2.25, $CHCl_3$).

Preparation of (6*S*)-(*Z*)-6-(Benzyloxy)-7-bromotridec-7-ene (6c). To a stirred solution of **5c** (4.14 g, 15 mmol) and benzyl bromide (5.13 g, 30 mmol) in THF (30 mL) was added at 0 °C NaH (as 80% suspension in white oil, 900 mg, 30 mmol) in several portions. The ice bath was removed, and the reaction mixture was stirred at room temperature overnight. After the usual workup, the crude product was purified by flash chromatography (eluant PE−MTBE (40:1)). **6c** was obtained as a clear oil (5.10 g, 13.9 mmol, 93%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.26−7.15 (m, 5H), 5.84 (t, 1H, J = 6.9), 4.54−4.13 (m, 2H), 3.63 (t, 1H, J = 6.6), 2.20−2.16 (m, 2H), 1.61−1.55 (m, 2H), 1.27−1.18 (m, 12H), 0.82−0.78 (m, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz): 138.49, 132.80, 129.42, 128.60, 128.24, 127.83, 83.26, 70.05, 34.40, 31.84, 31.66, 30.93, 28.35, 25.28, 22.84, 22.75, 14.32, 14.30. IR (film): 3030 (w), 2940 (s), 1650 (w), 1455 (m), 1080 (s); 735 (s), 700 (s). MS (EI): 297 (2), 295 (2), 262 (1), 260 (1), 91 (100). Anal. Calcd for $C_{20}H_{31}$-BrO: C, 65.40; H, 8.45. Found: C, 65.63; H, 8.73. $[\alpha]_D$: −48.09 (c = 4.28, $CHCl_3$).

Preparation of (*Z*)-2-((1*S*)-1-(Benzyloxy)propyl)-2-pentenal (7a). To a solution of **6a** (11.3 g, 39.9 mmol) in ether (200 mL) was added dropwise at −105 °C a solution of *t*BuLi (86.4 mmol) in pentane (58 mL). After the mixture was stirred for one h at −105 °C, DMF (15 mL) was added dropwise. After the usual workup, the crude product was purified by flash chromatography (eluant PE−MTBE (20:1)). **7a** was obtained as a light yellow oil (4.75 g, 20.4 mmol, 52%). ^{1}H NMR ($CDCl_3$, 300 MHz): 10.13 (s, 1H), 7.32−7.23 (m, 5H), 6.74 (t, 1H, J = 8.2), 4.34 (m, 2H, J = 11.7), 4.27−4.23 (m, 1H), 2.65−2.54 (m, 2H), 1.64−1.48 (m, 2H), 1.11 (t, 3H, J = 7.5), 0.89 (t, 3H, J = 7.3). ^{13}C NMR ($CDCl_3$, 75 MHz): 190.47, 151.06, 139.05, 138.55, 128.32, 127.70, 127.53, 76.76, 71.03, 29.06, 20.22, 14.28, 9.87. IR (film): 3035 (w), 2940 (m), 2870 (m), 1675 (s), 1495 (w), 1455 (m), 1375 (m), 1205 (m), 1075 (s), 735 (s), 695 (s). MS (EI): 203 (1), 141 (3), 126 (13), 107 (16), 91 (100), 79 (13), 67 (11), 55 (13), 41 (15), 28 (80). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.32; H, 8.98. $[\alpha]_D$: −23.7 (c = 4.30, benzene).

Preparation of (*Z*)-2-((1*S*)-1-(Benzyloxy)butyl)-2-heptenal (7b). To a solution of **6b** (8.05 g, 26 mmol) in ether (150 mL) was added dropwise at −105 °C a solution of *t*BuLi (60 mmol) in pentane (40 mL). After the mixture was stirred for 1 h at −105 °C, DMF (15 mL) was added dropwise. After the usual workup, the crude product was purified by flash chromatography (eluant PE−MTBE (20:1)). **7b** was obtained as a light yellow oil (4.27 g, 16.4 mmol, 63%) as a 2:1 mixture of isomers. ^{1}H NMR ($CDCl_3$, 300 MHz): 10.13 (s, 0.66H), 9.40

(s, 0.33H), 7.31−7.24 (m, 5H), 6.76 (t, 0.66 H, J = 8.3), 6.54 (t, 0.33H, J = 7.6), 4.61−4.23 (m, 3H), 2.65−2.54 (m, 2H), 1.63−1.47 (m, 6H), 0.97 (t, 3H, J = 7.4), 0.89 (t, 3H, J = 7.5). ^{13}C NMR ($CDCl_3$, 75 MHz): major isomer, 190.74, 149.24, 140.33, 138.50, 128.30, 127.70, 127.51, 75.54, 71.00, 38.68, 28.54, 22.74, 18.91, 18.91, 13.87 (2C); minor isomer, 194.26, 157.94, 142.43, 138.46, 128.24, 127.66, 127.46, 73.82, 70.45, 37.22, 31.01, 22.15, 19.22, 13.57 (2C). IR (film): 2960 (s), 2870 (m), 1670 (s), 1455 (m), 1370 (m), 1090 (m), 735 (s), 700 (s). MS (EI): 260 (1), 217 (2), 184 (18), 91 (100), 65 (6). Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H: 9.29. Found: C, 78.73; H, 9.62. $[\alpha]_D$: −22.5, (c = 4.30, benzene).

Preparation of (*Z*)-2-((1*S*)-1-(Benzyloxy)hexyl)-2-octenal (7c). To a solution of **6c** (2.57 g, 7 mmol) in ether (50 mL) was added dropwise at −105 °C a solution of *t*BuLi (20 mmol) in pentane (30 mL). After the mixture was stirred for 1 h at −105 °C, DMF (10 mL) was added dropwise. After the usual workup, the crude product was purified by flash chromatography (eluant PE−MTBE (20:1)). **7c** was obtained as a clear oil (1.55 g, 4.9 mmol, 70%). ^{1}H NMR ($CDCl_3$, 200 MHz): 10.07 (s, 1H), 7.31−7.20 (m, 5H), 6.69 (t, 1H, J = 7.8), 4.56−4.16 (m, 3H), 2.52 (q, 2H, J = 7.8), 1.43−1.17 (m, 12H), 0.81 (t, 3H, J = 7.9), 0.77 (t, 3H, J = 7.9). ^{13}C NMR ($CDCl_3$, 50 MHz): 190.82, 150.05, 140.30, 138.72, 128.59, 128.00, 127.81, 75.76, 71.27, 36.70, 31.88, 31.56, 29.46, 26.88, 25.56, 22.85, 22.67, 14.30, 14.22. IR (film): 3030 (w), 2930 (s), 1675 (s), 1640 (s), 1090 (m), 735 (m), 700 (m). MS (EI): 316 (1), 245 (3), 210 (17), 107 (10), 91 (100), 43 (12). Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19. Found: C, 75.63; H, 9.71. $[\alpha]_D$: −41.84 (c = 1.65, $CHCl_3$).

Preparation of (3*S*)-4-((1*S*)-1-(Benzyloxy)propyl)hept-4-en-3-ol (8a). To a solution of **2** (385 mg, 1.02 mmol) and Ti(O*i*Pr)$_4$ (10.2 mL, 34 mmol) in ether (20 mL) was added at −50 °C diethylzinc (4.0 mL, 40 mmol) followed by **7a** (4.75 g, 20.4 mmol). After 2 h of stirring at −20 °C, the reaction was worked up as described above and the crude product purified by flash chromatography (eluant PE−MTBE (10:1)). **8a** (4.51 g, 17 mmol, 83%) was obtained as a yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.34−7.21 (m, 5H), 5.48 (t, 1H, J = 7.5), 4.47 (m, 2H), 4.37−4.32 (m, 1H), 3.79 (t, 1H, J = 7.0), 2.22−2.11 (m, 3H), 1.73−1.48 (m, 4H), 1.10−0.87 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): 139.42, 138.79, 131.73, 128.19, 127.68, 127.30, 82.39, 71.48, 69.97, 29.88, 28.01, 20.94, 14.37, 10.78, 10.60. IR (film): 3450 (br, s), 3035 (w), 2930 (s), 2870 (s), 1495 (w), 1455 (m), 1060 (m), 735 (s), 695 (s). MS (EI): 233 (3), 125 (26), 91 (100), 77 (6), 55 (14), 41 (11), 28 (92). Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.73; H, 10.03. $[\alpha]_D$: −46.5 (c = 1.70, benzene).

Preparation of (4*S*)-5-((1*S*)-1-(Benzyloxy)butyl)non-5-en-4-ol (8b). To a solution of **2** (310 mg, 0.82 mmol) and Ti(O*i*Pr)$_4$ (8.2 mL, 27 mmol) in ether (20 mL) was added at −30 °C dipropylzinc (7 mL, 50 mmol) followed by **7b** (4.27 g, 16.4 mmol). After 5 h of stirring at −20 °C, the reaction was worked up as described above and the crude product purified by flash chromatography (eluant PE−MTBE (10:1)). **8b** (2.13 g, 7 mmol, 59%) was obtained as a clear oil as a mixture of two isomers. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.34−7.23 (m, 5H), 5.68 (t, 0.67H, J = 7.4), 5.49 (t, 0.33H, J = 7.51), 4.59−4.22 (m, 3.67H), 3.91−3.87 (m, 0.33H), 2.58 (br s, 1H), 2.16−2.05 (m, 2H), 1.54−1.33 (m, 10H), 0.96−0.87 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): major isomer, 140.44, 138.57, 129.60, 128.27, 127.68, 127.47, 76.99, 70.62, 70.40, 38.29, 36.57, 29.32, 22.98, 19.37, 19.28, 14.03, 13.92, 13.81; resolved signals of minor isomer, 140.97, 138.86, 128.23, 127.76, 127.35, 80.64, 69.98, 69.67, 39.20, 37.87, 29.60, 19.49, 19.45. IR (film): 3440 (br, m), 2930 (s), 1450 (m), 1060 (m), 735 (m), 700 (m). MS (EI): 261 (3), 189 (17), 153 (24), 91 (100), 71 (11), 43 (15). Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 78.71, H, 10.84. $[\alpha]_D$: −55.5 (c = 1.42, benzene).

Preparation of (6*S*)-(*Z*)-7-((1*S*)-1-(Benzyloxy)hexyl)-tridec-7-en-6-ol (8c). To a solution of **2** (142 mg, 0.37 mmol) and Ti(O*i*Pr)$_4$ (3.8 mL, 12.7 mmol) in ether (20 mL) was added at −30 °C dipentylzinc (4.15 g, 20 mmol) followed by **7c** (2.37 g, 7.5 mmol). After 6 h of stirring at −20 °C, the reaction was worked up as described above and the crude product purified by flash chromatography (eluant PE−MTBE (10:1)). **8c** (1.50 g, 3.9 mmol, 52%) was obtained as a clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.31−7.21 (m, 5H), 5.48 (t, 1H, J = 7.4), 4.58−4.30 (m, 3H), 3.87 (dd, 1H, J = 7.6, J = 5.1), 2.18−2.11 (m, 2H), 2.06 (br s, 1H), 1.69−1.17 (br, m, 22H), 0.90−0.84 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): 140.53, 138.75, 129.89, 128.16, 127.69, 127.28, 80.80, 69.95, 69.88, 36.90, 35.34, 31.62, 31.59, 31.45, 29.46, 27.48, 25.92, 25.81, 22.50 (2C), 22.42, 13.88 (3C). IR (film): 3450 (br, m), 2930 (s), 1460 (m), 1070 (m), 740 (m), 700 (m). MS (EI): 317 (11), 209 (78), 91 (100), 69 (10), 43 (21). Anal. Calcd for $C_{26}H_{44}O_2$: C, 80.36; H, 11.41. Found: C, 80.24, H, 11.50. $[\alpha]_D$: −40.46 (c = 2.64, $CHCl_3$).

Preparation of (3*S*)-3-((1*S*)-1-(Benzyloxy)propyl)hept-4-en-3-ol (9a). Borane−methyl sulfide (2.0 mL, 20 mmol) was added to a solution of **8a** (1.59 g, 6 mmol) in ether (15 mL) and the resulting solution stirred at room temperature overnight. The volatiles were removed and H_2O_2 (30%, 5 mL) and NaOH (2 M, 5 mL) added. After this mixture was stirred at 60 °C for 2 h, the usual workup followed by flash chromatography (eluant PE−MTBE (2:1)) afforded pure **9a** (791 mg, 2.8 mmol, 47%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.31−7.22 (m, 5H), 4.71 (s, 2H), 4.12−4.04 (m, 2H), 3.89−3.84 (m, 1H), 3.79 (s, 1H), 3.46 (s, 1H), 1.81−1.36 (m, 7H), 097−0.82 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): 138.14, 128.50, 127.94, 127.79, 80.63, 73.22, 72.27, 71.75, 46.04, 27.98, 25.89, 10.88, 10.75, 10.17. IR (film): 3460 (br, s), 3040 (w), 2970 (s), 2940 (s), 2880 (s), 1500 (w), 1460 (m), 1060 (m), 735 (s), 700 (s). MS (EI): 175 (M − 105, 5), 149 (3), 127 (6), 107 (7), 91 (100), 85 (18), 59 (12), 57 (24), 41 (7). Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H: 10.06. Found: C, 72.62; H, 10.01. $[\alpha]_D$: +18.4 (c = 1.25, benzene).

Preparation of (3*S*)-4-((1*S*)-1-(Benzyloxy)propyl)non-5-en-4-ol (9b). Borane−methyl sulfide (1.5 mL, 15 mmol) was added to a solution of **8b** (1.52 g, 5 mmol) in ether (10 mL) and the resulting solution stirred at room temperature overnight. The volatiles were removed and H_2O_2 (30%, 5 mL) and NaOH (2 M, 5 mL) added. After this mixture was stirred at 60 °C for 2 h, the usual workup followed by flash chromatography (eluant PE−MTBE (2:1)) afforded an inseparable mixture (730 mg, 2.23 mmol, 45%) of **9b** and its epimer. ^{1}H NMR ($CDCl_3$, 200 MHz): 7.35−7.28 (m, 5H), 4.68−4.57 (m, 2H), 4.26−4.24 (m, 2H), 4.00 (t, 1H, J = 6.5), 3.83 (br s, 1H), 3.49 (br s, 1H), 1.82−1.31 (m, 13H), 1.03−0.92 (m, 9H). ^{13}C NMR ($CDCl_3$, 50 MHz): major isomer, 138.51, 128.95, 128.43, 128.25, 79.61, 72.69, 71.88, 70.41, 47.96, 37.94, 37.25, 36.09, 20.05, 19.85, 19.54, 14.56 (3C). IR (film): 3450 (br, s), 3035 (w), 2960 (s), 1500 (m), 1455 (m), 1070 (m), 735 (m), 700 (m). MS (EI): 175 (5), 149 (3), 107 (7), 91 (100), 85 (18), 57 (24). Anal. Calcd for $C_{20}H_{34}O_3$: C, 74.49; H, 10.63. Found: C, 74.39; H, 10.62. $[\alpha]_D$: −56.43 (c = 3.47, $CHCl_3$).

Preparation of (6*S*)-7-((1*S*)-1-(Benzyloxy)hexyl)tridecane-6,8-diol (9c). Borane−methyl sulfide (1.2 mL, 12 mmol) was added to a solution of **8c** (1.50 g, 3.9 mmol) in ether (10 mL) and the resulting solution stirred at room temperature overnight. The volatiles were removed and H_2O_2 (30%, 5 mL) and NaOH (2 M, 5 mL) added. After this mixture was stirred at 60 °C for 2 h, the usual workup followed by flash chromatography (eluant PE−MTBE (2:1)) afforded an inseparable mixture (370 mg, 0.9 mmol, 23%) of **9c** and its epimer. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.30−7.18 (m, 5H), 4.52 (s, 2H), 3.84−3.81 (m, 0.7H), 3.69−3.50 (m, 2.3H), 3.20 (br s, 1H), 2.92 (br s, 1H), 1.51−1.13 (br m, 35H), 0.85 (t, 9H, J = 6.8). ^{13}C NMR ($CDCl_3$, 75 MHz): major isomer, 141.15, 128.50, 127.50, 126.98, 75.15, 73.70, 72.04, 65.09, 45.67, 36.02, 35.78, 34.13, 31.99, 31.97, 31.90, 29.94, 29.68, 29.45, 22.74, 22.69 (2C), 14.10, 14.07. IR (film): 3350 (br, s), 2930 (s), 1460 (m), 1025 (m), 730 (m), 700 (m). MS (EI): 285 (26), 211 (18), 182 (55), 108 (48), 83 (66), 55 (100), 43 (86). Anal. Calcd for $C_{26}H_{46}O_3$: C, 76.83; H, 11.41. Found: C, 76.54; H, 11.43.

Preparation of (*S*,*S*,*S*)-4-(1-Hydroxypropyl)heptane-3,5-diol (1a). Pd/C (10%, 100 mg) was added to a solution of

9a (706 mg, 2.5 mmol) in ethyl acetate (5 mL) and the mixture stirred under a hydrogen atmosphere for 4 h. Filtration and evaporation of the solvent afforded pure **1a** (456 mg, 2.4 mmol, 96%) as a viscous oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 4.08 (t, 3H, J = 6.4), 3.49 (br s, 3H), 1.98−1.63 (m, 3H), 1.48−1.35 (m, 3H), 1.18 (q, 1H, J = 1.8), 0.89 (t, 3H, J = 7.4). ^{13}C NMR ($CDCl_3$, 75 MHz): 73.55, 45.42, 28.13, 10.72. IR (film): 3420 (br, s), 2960 (w), 2940 (w), 1640 (br, m), 1455 (w), 910 (m), 730 (w). MS (EI): 161 (1), 143 (3), 125 (1), 141 (7), 85 (100), 57 (19), 43 (16). Anal. Calcd for $C_{10}H_{22}O_3$: C, 63.12; H, 11.65. Found: C, 63.31; H, 12.00. $[\alpha]_D$: −17.98 (c = 0.98, benzene).

Preparation of (4*S*,6*S*)-5-(1-Hydroxybutyl)nonane-4,6-diol (1b) and Its Epimer. Pd/C (10%, 200 mg) was added to a solution of **9b** (730 mg, 2.23 mmol) in ethyl acetate (6 mL) and the mixture stirred under a hydrogen atmosphere for 4 h. Filtration and evaporation of the solvent afforded **1b** together with its epimer (513 mg, 2.2 mmol, 99%) as an inseparable mixture. ^{1}H NMR ($CDCl_3$, 200 MHz): 4.32−4.18 (m, 2H), 4.08−4.04 (m, 0.35H), 3.89−3.86 (m, 0.33H), 3.78−3.74 (m, 0.33H), 3.37 (br s, 3H), 1.52−1.28 (br m, 13H), 0.88 (t, 9H, J = 7.1). ^{13}C NMR ($CDCl_3$, 50 MHz): major isomer, 72.00, 50.09, 37.6, 19.58, 14.23; resolved signals of minor isomer, 75.81, 75.69, 71.85, 46.96, 40.25, 39.68, 38.10, 20.06, 19.88, 19.70, 14.29.

Preparation of (*S*,*S*,*S*)-7-(1-Hydroxyhexyl)undecane-6,8-diol (1c). Pd/C (10%, 50 mg) was added to a solution of **9c** (180 mg, 0.44 mmol) in ethyl acetate (5 mL) and the mixture stirred under a hydrogen atmosphere overnight. Filtration and evaporation of the solvent followed by flash chromatography (eluant PE−MTBE (2:1)) afforded pure **1c** (106 mg, 0.33 mmol, 76%) along with its epimer (26 mg, 0.08 mmol, 19%). ^{1}H NMR ($CDCl_3$, 300 MHz): 4.18−4.10 (m, 3H), 3.96 (br s, 3H), 1.71−1.63 (m, 3H), 1.44−1.21 (m, 21H), 1.13−1.10 (m, 1H), 0.84 (t, 9H, J = 6.6). ^{13}C NMR ($CDCl_3$, 75 MHz): 72.05, 46.52, 35.13, 31.70, 25.86, 22.49, 13.89. IR (film): 3360 (br, s), 2930 (s), 2870 (s), 1470 (m), 725 (w). MS (EI): 229 (11), 211 (25), 182 (100), 111 (24), 83 (67), 55 (71). Anal. Calcd for $C_{19}H_{40}O_3$: C, 72.10; H, 12.74. Found: C, 72.13; H: 12.37. $[\alpha]_D$: −6.03 (c = 1.99, $CHCl_3$).

Preparation of (3*S*,5*S*,8*S*)-3,5,7-triethyl-2,6,8-trioxabicyclo[2.2.2]octane (10a). To a solution of **1a** (130 mg, 0.68 mmol) in methyl orthoformate (2 mL) was added a drop of trifluoroacetic acid, and stirring was continued for 2 h. The volatiles were removed *in vacuo*. Purification by flash chromatography (eluant PE−MTBE (20:1)) afforded **10a** (136 mg, 0.68 mmol, 99%) as an oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 5.44 (s, 1H), 4.06 (t, 3H, J = 7.1), 1.87−1.72 (m, 3H), 1.61−1.42 (m, 3H), 0.88 (t, 9H (J = 7.5). ^{13}C NMR ($CDCl_3$, 75 MHz): 103.82, 71.78, 35.94, 24.22, 9.59. IR (film): 2940 (s), 1720 (m), 1460 (m), 1170 (s), 990 (s), 870 (m). MS (EI): 171 (52), 125 (52), 143 (36), 85 (71), 69 (52), 55 (100), 43 (49). Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.06. Found: C, 65.81; H, 10.09. $[\alpha]_D$: −53.8 (c = 0.43, $CHCl_3$).

Preparation of (3*S*,5*S*,8*S*)-3,5,7-Tripropyl-2,6,8-trioxabicyclo[2.2.2]octane (10b). A mixture of **1b** and its epimer (440 mg, 1.9 mmol) were stirred with methyl orthoformate (2 mL) and a drop of trifluoroacetic acid. After 2 h all volatiles were removed *in vacuo*. Purification by flash chromatography (eluant PE−MTBE (20:1)) afforded **10b** (295 mg, 1.22 mmol, 64%) as an oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 5.43 (s, 1H), 4.16 (dd, 3H, J = 7.7, J = 5.1), 1.82−1.68 (m, 3H), 1.46−1.22 (m, 10H), 0.90 (t, 9H, J = 7.2). ^{13}C NMR ($CDCl_3$, 75 MHz): 103.95, 70.35, 37.64, 33.63, 18.77, 14.02. IR (film): 2930 (s), 1460 (s), 1070 (s), 980 (s), 815 (m). MS (EI): 199 (62), 153 (88), 126 (38), 99 (45), 69 (72), 57 (100), 43 (57). Anal. Calcd for $C_{14}H_{26}O_3$: C, 69.38; H, 10.81. Found: C, 69.20; H, 10.61: $[\alpha]_D$: −52.6 (c = 3.06, $CHCl_3$).

Preparation of (*S*,*S*,*S*)-5-(1-Hydroxybutyl)-nonane-4,6-diol (1b). A solution of **10b** (250 mg, 1.03 mmol) in wet THF (4 mL) was stirred with a drop of trifluoroacetic acid for 5 h. Removal of all volatiles *in vacuo* afforded **1b** as an oil (229 mg, 0.99 mmol, 96%). ^{1}H NMR ($CDCl_3$, 300 MHz): 4.13−4.08 (m, 3H), 3.81 (br s, 3H), 1.61−1.54 (m, 6H), 1.38−1.21 (m, 12H), 1.18 (br s, 1H), 0.83 (t, 9H, J = 7.0). ^{13}C NMR ($CDCl_3$, 75 MHz): 71.31, 47.14, 37.59, 19.40, 13.96. IR (film): 3400 (br, s), 2955 (s), 1715 (w), 1465 (s), 1125 (m), 1070 (m). MS (EI): 189 (1), 171 (2), 142 (5), 99 (100), 57 (41), 43 (17). Anal. Calcd for $C_{13}H_{28}O_3$: C, 67.19; H, 12.14. Found: C, 66.84; H, 11.70. $[\alpha]_D$: −14.8 (c = 2.84, $CHCl_3$).

Preparation of Titanium Complex 11a. To a solution of $Ti(OiPr)_4$ (142 mg, 0.5 mmol) in CH_2Cl_2 (1 mL) was added **1a** (95 mg, 0.5 mmol) in CH_2Cl_2 (0.5 mL) and the yellow solution stirred for 2 h. Upon evaporation of the solvent **11a** (145 mg, 0.49 mmol) was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): 4.72−3.95 (br m, 4H), 1.94−0.92 (br m, 13H), 0.90−0.46 (br m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): 87.07, 79.18 (br), 64.34, 44.78 (br), 27.38−25.30 (m), 10.75−9.93 (m). IR ($CDCl_3$): 2965 (m), 2875 (m), 1460 (m), 1275 (m), 910 (s), 735 (s). MS (EI): 922 (6), 865 (11), 806 (32), 756 (55), 269 (100), 45 (77). Anal. Calcd for $C_{13}H_{26}O_4Ti$: C, 53.07; H, 8.91. Found: C, 52.82; H, 8.93.

Preparation of Titanium Complex 11b. To a solution of $Ti(OiPr)_4$ (165 mg, 0.58 mmol) in CH_2Cl_2 (1 mL) was added **1b** (136 mg, 0.58 mmol) in CH_2Cl_2 (0.5 mL) and the yellow solution stirred for 2 h. Upon evaporation of the solvent **11b** (195 mg, 0.58 mmol) was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): 4.75−4.05 (br m, 4H), 2.06−1.01 (br m, 19H), 0.99−0.83 (br m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): 78.88−77.17 (m), 45.51 (br), 38.71−34.92 (m), 26.26−24.47 (m), 19.53−18.81 (m), 14.27−13.95 (m). IR ($CDCl_3$): 2960 (s), 2930 (m), 1465 (m), 910 (s), 740 (s). MS (EI): 1190 (2), 1134 (4), 987 (10), 915 (19), 848 (41), 259 (43), 44 (100), 28 (89). Anal. Calcd for $C_{16}H_{32}O_4Ti$: C, 57.14; H, 9.59. Found: C, 57.38; H, 9.42.

Preparation of Vanadyl Complex 12a. To a solution of vanadyl isopropoxide (113 mg, 0.463 mmol) in $CHCl_3$ (1 mL) was added a solution of **1a** (88 mg, 0.463 mmol) in $CHCl_3$ (1 mL) and the yellow solution stirred at 40 °C for 12 h. Evaporation of solvent gave **12a** (114 mg, 97%) as a pale yellow solid. From a solution of **12a** (114 mg) in hexane (1 mL) yellow crystals (mp 121 °C, 80 mg, 68%) formed at −30 °C within 3 days. ^{1}H NMR (200 MHz, $CDCl_3$): 5.04−4.97 (m, 2H), 4.74−4.66 (m, 2H), 4.42−4.33 (m, 2H), 2.32−2.14 (m, 2H), 1.90−1.72 (m, 2H), 1.63−1.46 (m, 2H), 1.54−1.37 (m, 2H), 1.67−1.52 (m, 2H), 1.51−1.34 (m, 2H), 1.05 (t, 6H, J = 7.00), 0.93 (t, 6H, J = 6.75), 0.88 (t, 6H, J = 6.75). ^{13}C NMR (50 MHz, $CDCl_3$): 84.83, 82.84, 82.62, 48.53, 32.03, 25.33, 25.16, 10.81, 10.57, 10.18. IR (Nujol): 1252 (m), 1223 (w), 1119 (m), 1103 (s), 1044 (m), 988 (s), 961 (s), 894 (m), 843 (s), 810 (m) , 601 (m), 593 (s), 526 (s), 551 (w). MS (EI): 508 (1), 450 (10), 392 (23), 334 (3), 254 (3), 196 (100), 138 (5), 58 (1), 57 (4). Anal. Calcd for $C_{20}H_{38}O_8V_2$: C, 47.25; H, 7.53. Found C, 47.38; H, 7.39.

Preparation of Vanadyl Complex 12b. To a solution of vanadyl *tert*-butoxide (132 mg, 0.461 mmol) in CH_2Cl_2 (10 mL) was added a solution of **1b** (107 mg, 0.460 mmol) in CH_2Cl_2 (5 mL), and the yellow solution was stirred for 20 h. Evaporation of solvent gave **12b** (mp 47 °C, 130 mg, 95%) as a pale yellow waxy solid. ^{1}H NMR (200 MHz, $CDCl_3$): 5.13 (m , 2H), 4.84−4.80 (m, 2H), 4.50 (br, 2H), 2.32−2.10 (m, 2H), 1.76−1.24 (m, 24H), 0.96 (t, 6H, J = 7.24), 0.91 (t, 6H, J = 6.95), 0.86 (t, 6H, J = 6.24). ^{13}C NMR (50 MHz, $CDCl_3$): 83.28, 81.09, 80.32, 49.44, 41.25, 36.47, 34.06, 19.69, 19.50, 18.92, 14.03, 13.96, 13.48. IR (Nujol): 1248 (m), 1214 (w), 1119 (m), 1110 (s), 1007 (s), 949 (s), 872 (m), 756 (m), 695 (s), 627 (m), 557 (m), 526 (s), 451 (w). MS (EI): 520 (6), 296 (2), 225 (9), 224 (100), 152 (20), 71 (1), 55 (14), 43 (11), 41 (15), 29 (5), 28 (20). Anal. Calcd for $C_{26}H_{50}O_8V_2$: C, 52.70; H, 8.50. Found: C, 52.55; H, 8.44.

Addition of Diethylzinc to Benzaldehyde Catalyzed by 11a. To a solution of **11a** (550 mg, 0.52 mmol, 10 mol %) in toluene (5 mL) was added at −35 °C benzaldehyde (5.2 mmol) followed by diethylzinc (1.0 mL, 10 mmol). After the reaction mixture was stirred overnight at −35 °C, it was worked up as usual. Flash chromatography (eluant PE−MTBE (2:1)) gave (+)-(*R*)-1-phenylpropanol (**13**; 700 mg, 96%) in 20% ee. ^{1}H NMR ($CDCl_3$, 200 MHz): 7.26−7.18 (m, 5H),

4.46 (t, 1H, J = 6.6), 2.63 (br s, 1H), 1.76−1.58 (m, 2H), 0.80 (t, 3H, J = 7.4). ^{13}C NMR ($CDCl_3$, 50 MHz): 145.23, 129.03, 128.12, 126.66, 76.65, 32.51, 10.81. $[\alpha]_D$: +8.8 (c = 6.25, $CHCl_3$).

Addition of Trimethylsilyl Cyanide to Benzaldehyde Catalyzed by 11a. To a solution of **11a** (0.66 mmol, 100 mol%) in CH_2Cl_2 (5 mL) was added molecular sieves (200 mg), benzaldehyde (70 mg, 0.66 mmol), and trimethylsilyl cyanide (80 mg, 0.8 mmol), and the solution was stirred at 0 °C for 3 h. After acidic workup, flash chromatography (eluant PE−MTBE (4:1)) afforded (+)-(*R*)-mandelonitrile (**14**; 83 mg, 0.62 mmol, 95%) in 44% ee. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.49−7.41 (m, 5H), 5.46 (s, 1H), 4.10 (br s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 135.00, 129.66, 129.05, 126.56, 118.89, 63.26. IR (film): 3400 (br, s), 2980 (s), 1495 (m), 1195 (m), 1045 (m), 740 (s), 695 (s). $[\alpha]_D$: +28.07 (c = 0.44, ether).

Epoxidation of Geraniol Catalyzed by 11a. To a solution of **11a** (1 mmol, 10 mol %) in CH_2Cl_2 (10 mL) was added molecular sieves (300 mg) and a solution of TBHP (15 mmol) in toluene (5 mL). After 30 min of stirring at −20 °C, geraniol (1.54 g, 10 mmol) was added and the yellow solution stirred for 8 h. Following workup, flash chromatography (eluant PE−MTBE (2:1)) gave racemic 2,3-epoxygeraniol (**15**; 1.53 g, 9.0 mmol, 90%). ^{1}H NMR ($CDCl_3$, 300 MHz): 5.04−4.98 (m, 1H), 3.77−3.71 (m, 1H), 3.62−3.56 (m, 1H), 3.07 (br s, 1H), 2.91 (dd, 1H, J = 6.8, J = 4.1), 1.67−1.54 (m, 9H), 1.45−1.38 (m, 1H), 1.22 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): 131.92, 123.23, 63.14, 61.19, 61.08, 38.38, 25.51, 23.53, 17.48, 16.58. IR (film): 3380 (br, s), 2915 (s), 1665 (w), 1445 (m), 1380 (m), 1025 (m). MS (EI): 170 (1), 139 (3), 109 (30), 82 (51), 69 (81), 41 (100). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.34; H, 10.75. $[\alpha]_D$: 0 (c = 2.25, $CHCl_3$).

Oxidation of Ethyl Phenyl Sulfide in the Presence of 11a. To a solution of **11a** (0.05 mmol, 10 mol %) in CH_2Cl_2 (2 mL) was added ethyl phenyl sulfide (mg, 0.5 mmol) and a solution of TBHP (0.5 mmol) in toluene (0.54 mL). After the mixture was stirred for 6 h at 0 °C, no conversion was observed. Raising the temperature to room temperature and stirring overnight did not lead to any appreciable reaction.

Addition of Diethylzinc to Benzaldehyde Catalyzed by 11b. To a solution of **11b** (0.05 mmol, 10 mol %) in CH_2Cl_2 (1 mL) and toluene (5 mL) was added at −35 °C benzaldehyde (53 mg, 0.5 mmol) followed by diethylzinc (0.1 mL, 1.0 mmol). After the reaction mixture was stirred overnight at −25 °C, it was worked up as usual. Flash chromatography (eluant PE−MTBE (2:1)) gave (+)-(*R*)-1-phenylpropanol (**13**; 62 mg, 0.46 mmol, 91%) in 20% ee. ^{1}H NMR ($CDCl_3$, 200 MHz): 7.26−7.18 (m, 5H), 4.46 (t, 1H, J = 6.6), 2.63 (br s, 1H), 1.76−1.58 (m, 2H), 0.80 (t, 3H, J = 7.4). ^{13}C NMR ($CDCl_3$, 50 MHz): 145.23, 129.03, 128.12, 126.66, 76.65, 32.51, 10.81.

Addition of Trimethylsilyl Cyanide to Benzaldehyde Catalyzed by 11b. To a solution of **11b** (0.05 mmol, 10 mol %) in CH_2Cl_2 (6 mL) was added molecular sieves (200 mg), benzaldehyde (53 mg, 0.5 mmol), and trimethylsilyl cyanide (80 mg, 0.8 mmol), and the solution was stirred at 0 °C overnight. After acidic workup, flash chromatography (eluant PE−MTBE (4:1)) afforded (+)-(*R*)-mandelonitrile **14** (84 mg, 0.63 mmol, 96%) in 7% ee. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.49−7.41 (m, 5H), 5.46 (s, 1H), 4.10 (br s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 135.00, 129.66, 129.05, 126.56, 118.89, 63.26. IR (film): 3400 (br, s), 2980 (s), 1495 (m), 1195 (m), 1045 (m), 740 (s), 695 (s).

Epoxidation of Geraniol Catalyzed by 11b. To a solution of **11b** (0.05 mmol, 10 mol %) in CH_2Cl_2 (1 mL) was added molecular sieves (300 mg) and a solution of TBHP (0.68 mmol) in toluene (0.34 mL). After 30 min of stirring at −20 °C, geraniol (77 mg, 0.5 mmol) was added and the yellow solution stirred overnight. Following workup, flash chromatography (eluant PE−MTBE (2:1)) gave racemic 2,3-epoxygeraniol (**15**; 75 mg, 0.44 mol, 88%).

Oxidation of Ethyl Phenyl Sulfide in the Presence of 11b. To a solution of **11b** (0.05 mmol, 10 mol %) in CH_2Cl_2 (3 mL) was added ethyl phenyl sulfide (69 mg, 0.5 mmol) and a solution of TBHP (0.5 mmol) in toluene (0.54 mL). After the mixture was stirred for 6 h at 0 °C, no conversion was observed. Raising the temperature to room temperature and stirring overnight did not lead to any appreciable reaction.

Epoxidation of Geraniol Catalyzed by 12a. To a solution of geraniol (77 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) was added **12a** (0.0005 mmol, 0.1 mol %) in CH_2Cl_2 (1.5 mL) and TBHP (0.68 mmol, 1.36 equiv) in toluene (0.34 mL). After the mixture was stirred at room temperature for 2 h, it was concentrated. Flash chromatography (eluant PE−MTBE (2:1)) gave racemic **15** (82 mg, 0.48 mmol, 96%).

Typical Procedure for the Oxidation of Sulfides to Sulfoxides Using 12a. To a solution containing **12a** (0.0005 mmol, 0.1 mol %) in CH_2Cl_2 (1.5 mL) was added the sulfide (0.5 mmol) and a solution of TBHP (0.5 mmol) in toluene (0.25 mL). The reaction mixture was stirred at room temperature until the reaction was complete (about 4 h for aryl alkyl sulfides) and then concentrated. Flash chromatography (eluant MTBE or ethyl acetate) afforded the sulfoxide.

Preparation of Ethyl Phenyl Sulfoxide (16a). According to the typical procedure, from ethyl phenyl sulfide (69 mg, 0.5 mmol) was obtained **16a** (65 mg, 0.42 mmol, 84%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.52−7.36 (m, 5H), 2.85−2.58 (m, 2H), 1.06 (t, 3H, J = 7.6). ^{13}C NMR ($CDCl_3$, 50 MHz): 143.49, 131.07, 129.30, 124.29, 50.36, 6.05.

Preparation of Methyl Phenyl Sulfoxide (16b). According to the typical procedure, from methyl phenyl sulfide (62 mg, 0.5 mmol) was obtained **16b** (58 mg, 0.42 mmol, 83%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.57−7.52 (m, 2H), 7.44−7.33 (m, 3H), 2.60 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz):145.68, 130.94, 129.27, 123.39, 43.88.

Preparation of Isopropyl Phenyl Sulfoxide (16c). According to the typical procedure, from isopropyl phenyl sulfide (76 mg, 0.5 mmol) was obtained **16c** (70 mg, 0.42 mmol, 84%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.48−7.36 (m, 5H), 2.72 (sept, 1H, J = 6.7), 1.12 (d, 3H, J = 6.7), 1.01 (d, 3H, J = 6.7). ^{13}C NMR ($CDCl_3$, 50 MHz): 141.99, 131.11, 129.04, 125.07, 54.61, 16.09, 13.93.

Preparation of *tert*-Butyl Phenyl Sulfoxide (16d). According to the typical procedure, from *tert*-butyl phenyl sulfide (83 mg, 0.5 mmol) was obtained **16d** (74 mg, 0.4 mmol, 81%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.50−7.45 (m, 2H), 7.38−7.35 (m, 3H), 1.05 (s, 9H). ^{13}C NMR ($CDCl_3$, 50 MHz): 140.20, 131.40, 129.04, 126.45, 55.93, 22.97.

Preparation of *n*-Butyl Phenyl Sulfoxide (16e). According to the typical procedure, from *n*-butyl phenyl sulfide (83 mg, 0.5 mmol) was obtained **16e** (83 mg, 0.56 mmol, 83%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.50−7.45 (m, 2H), 7.38−7.35 (m, 3H), 1.05 (s, 9H). ^{13}C NMR ($CDCl_3$, 50 MHz): 137.92, 133.15, 129.07, 128.87, 46.17, 31.41.

Preparation of Octyl Phenyl Sulfoxide (16f). According to the typical procedure, from octyl phenyl sulfide (119 mg, 0.5 mmol) was obtained **16f** (106 mg, 0.44 mmol, 89%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.56−7.39 (m, 5H), 2.69 (t, 2H, J = 7.6), 1.60−1.09 (m, 12H), 0.74 (t, 3H, J = 6.8). ^{13}C NMR ($CDCl_3$, 50 MHz): 143.96, 130.69, 128.99, 123.81, 57.17, 31.53, 28.95, 28.81, 28.49, 22.41, 21.96, 13.90.

Preparation of Cycohexyl Phenyl Sulfoxide (16g). According to the typical procedure, from cyclohexyl phenyl sulfide (96 mg, 0.5 mmol) was obtained **16g** (91 mg, 0.44 mmol, 88%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.50−7.38 (m, 5H), 2.53−2.41 (m, 1H), 1.72−1.12 (br m, 11H). ^{13}C NMR ($CDCl_3$, 50 MHz): 142.19, 131.23, 129.22, 125.27, 63.39, 26.62, 25.77, 24.22.

Preparation of Benzyl Phenyl Sulfoxide (16h). According to the typical procedure, from benzyl phenyl sulfide (100 mg, 0.5 mmol) was obtained **16h** (mp 125 °C, 102 mg, 0.47 mmol, 95%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.38−6.94 (m, 10H), 4.07−3.90 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): 143.17, 131.56, 130.76, 129.55, 129.25, 128.83, 128.63, 124.82, 63.93.

Preparation of Diphenyl Sulfoxide (16i). According to the typical procedure, from diphenyl sulfide (93 mg, 0.5 mmol) was obtained **16i** (92 mg, 0.45 mmol, 91%). ^{1}H NMR ($CDCl_3$,

200 MHz): 7.59−7.54 (m, 4H), 7.37−7.35 (m, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz): 145.94, 131.49, 129.75, 125.16.

Preparation of Dibutyl Sulfoxide (16j). According to the typical procedure, from dibutyl sulfide (73 mg, 0.5 mmol) was obtained **16j** (71 mg, 0.44 mmol, 87%). ^{1}H NMR ($CDCl_3$, 200 MHz): 2.43 (t, 4H, J = 7.0), 1.54−1.31 (m, 8H), 0.84 (t, 3H, J = 7.2). ^{13}C NMR ($CDCl_3$, 50 MHz): 32.17 (2C), 22.40, 14.04.

Preparation of Allyl Phenyl Sulfoxide (16k). According to the typical procedure, from allyl phenyl sulfide (75 mg, 0.5 mmol) was obtained **16k** (75 mg, 0.45 mmol, 90%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.52−7.40 (m, 5H), 5.58−5.50 (m, 1H), 5.27−5.06 (m, 2H), 3.52−3.42 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): 143.25, 131.48, 129.42, 125.60, 124.69, 124.26, 61.18.

Preparation of 2-(Benzyloxy)ethyl Ethyl Sulfoxide (16l). According to the typical procedure, from 2-(benzyloxy)-ethyl ethyl sulfide (69 mg, 0.5 mmol) was obtained **16l** (65 mg, 0.42 mmol, 84%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.52−7.36 (m, 5H), 2.85−2.58 (m, 2H), 1.06 (t, 3H, J = 7.6). ^{13}C NMR ($CDCl_3$, 50 MHz): 143.49, 131.07, 129.30, 124.29, 50.36, 6.05.

Preparation of 1,4-Bis(propylsulfinyl)butane (16m). According to the typical procedure, from 4-(sulfinylpropyl)butyl propyl sulfide (111 mg, 0.5 mmol) was obtained, after recrystallization from THF, **16m** (mp 127 °C, 93 mg, 0.39 mmol, 78%). ^{1}H NMR ($CDCl_3$, 300 MHz): 2.70−2.49 (m, 8H), 1.94−1.90 (m, 4H), 1.81−1.69 (m, 4H), 1.02 (t, 6H, J = 7.3). ^{13}C NMR ($CDCl_3$, 75 MHz): 54.52, 51.64, 21.90, 16.29, 13.38. MS (EI): 195 (62), 147 (28), 10 (58), 63 (57), 55 (100), 43 (51). Anal. Calcd for $C_{10}H_{22}O_2S_2$: C, 50.38; H, 9.30. Found: C, 49.88; H, 8.83.

Preparation of 4-(Thiopropyl)butyl Phenyl Sulfoxide (16n). According to the typical procedure, from 4-(thiopropyl)-butyl phenyl sulfide (121 mg, 0.5 mmol) was obtained **16n** (103 mg, 0.405 mmol, 81%). ^{1}H NMR ($CDCl_3$, 200 MHz):7.28−7.14 (m, 5H), 2.88 (t, 2H, J = 6.6), 2.63−2.52 (m, 4H), 1.82−1.71 (m, 6H), 1.00 (t, 3H, J = 7.4). ^{13}C NMR ($CDCl_3$, 50 MHz): 136.47, 129.76, 129.36, 126.52, 54.78, 52.19, 33.61, 28.71, 22.14, 16.69, 13.83. IR (film): 2920 (s), 1440 (m), 1010 (m), 905 (s), 720 (s). MS (EI): 256 (2), 239 (19), 165 (100), 123 (61), 55 (50), 45 (32). Anal. Calcd for $C_{13}H_{20}OS_2$: C, 60.89; H, 7.86. Found: C, 60.61; H, 8.20.

Preparation of Ethyl Phenyl Sulfone (17). To a solution containing **12a** (0.0005 mmol, 0.1 mol %) in dichloromethane (1.5 mL) was added ethyl phenyl sulfide (69 mg, 0.5 mmol) and a solution of TBHP (1.25 mmol) in toluene (0.63 mL). The reaction mixture was stirred at room temperature for 5 h and then concentrated. Flash chromatography (eluant PE−MTBE (2:1)) gave pure ethyl phenyl sulfone (**17**; 75 mg, 0.44 mmol, 88%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.85−7.80 (m, 2H), 7.59−7.49 (m, 3H), 3.05 (q, 2H, J = 7.4), 1.17 (t, 3H, J = 7.4). ^{13}C NMR ($CDCl_3$, 50 MHz): 138.35, 133.72, 129.27, 128.33, 50.55, 7.39.

Epoxidation of Geraniol Catalyzed by 12b. To a solution of geraniol (77 mg, 0.5 mmol) in dichloromethane (5 mL) were added **12b** (0.0005 mmol, 0.1 mol %) in dichloromethane (0.2 mL) and TBHP (0.68 mmol, 1.36 equiv) in toluene (0.34 mL). After it was stirred at room temperature for 4 h, the reaction mixture was concentrated. Flash chromatography (eluant PE−MTBE (2:1)) gave racemic **15** (82 mg, 0.48 mmol, 96%).

Oxidation of Ethyl Phenyl Sulfide in the Presence of 12b. To a solution containing **12b** (0.0005 mmol, 0.1 mol %) in dichloromethane (0.2 mL) was added ethyl phenyl sulfide (69 mg, 0.5 mmol) and a solution of TBHP (0.5 mmol) in toluene (0.25 mL). The reaction mixture was stirred at room temperature for 8 h and then concentrated. Flash chromatography (eluant MTBE) gave pure ethyl phenyl sulfoxide (**16a**; 66 mg, 0.43 mmol, 85%) as the only product.

Crystal Data and Structure Refinement for 12a. Details are given in Table 4.

Table 4. Crystal Data and Structure Refinement for 12a

empirical formula	$C_{20}H_{38}O_8V_2$
fw	508.38
temp	293(2) K
wavelength	0.709 30 Å
cryst syst	orthorhombic
space group	$P2_12_12_1$
unit cell dimens	
a	12.970(4) Å
b	13.503(2) Å
c	14.567(5) Å
α	90°
β	90°
γ	90°
V	2551.2(12) Å^3
Z	4
density (calcd)	1.324 Mg/m^3
abs coeff	0.770 mm^{-1}
F(000)	1072
cryst size	0.50 × 0.30 × 0.20 mm
θ range for data collection	2.05−27.41°
index ranges	$0 \le h \le 16$, $0 \le k \le 17$, $0 \le l \le 18$
no. of rflns collected	3279
no. of indep rflns	3276 [R(int) = 0.0000]
no. of refinement method	full-matrix least squares on F^2
no. of data/restraints/params	3275/0/271
goodness of fit on F^2	1.155
final R indices ($I > 2\ \sigma(I)$)	R1 = 0.0448, wR2 = 0.0862
R indices (all data)	R1 = 0.0948, wR2 = 0.1129
absolute structure param	-0.07(4)
largest diff peak and hole	+0.295 and −0.300 e Å^{-3}

Data Collection and Reduction. The yellow prismatic crystal (0.5 × 0.3 × 0.2 mm^{-3}) was mounted under argon in a Lindemann capillary. Data were collected with an Enraf-Nonius CAD4 diffractometer and Mo Kα (λ = 71.069 pm) radiation using the ω/θ-scan. Unit-cell parameters were determined by least-squares analysis of automatically centered reflections in the range $10 < \theta > 16°$. Data were collected in the range $2\theta = 3-54.8°$.

Structure Solution and Refinement. Following Lorentz, polarization, and empirical absorption correction (ψ-scan method, minimum transmission 98.24%), and without linear decay correction (intensity decay 3.7%), 3276 independent reflections were measured. Structure solution and refinement were carried out with the programs SHELXS-86[23] and SHELXL-93.[24] The coordinates of the vanadium atoms were obtained by the Patterson method and the remaining non-hydrogen atoms located from difference Fourier synthesis. The positions of the hydrogen atoms were calculated according to an ideal geometry and refined isotropically. The heavy atoms were refined with anisotropic thermal parameters by full-matrix least squares.

Acknowledgment. We thank the Fonds der Chemischen Industrie and the DFG (SPP "Peroxidchemie" and SFB 260) for generous support of this research, and BASF AG and Witco (Bergkamen) for generous gifts of chemicals.

Supporting Information Available: Text giving details of the crystal structure study and tables of positional and thermal parameters, anisotropic thermal parameters, and intramolecular distances and bond angles for compound **12a** (8 pages). Ordering information is given on any current masthead page.

OM970523O

(23) Sheldrick, G. M. SHELXS-86 Program for Crystal Structure Determination; Göttingen, Germany, 1986.
(24) .Sheldrick, G. M. SHELXL-93 Program for the Refinement of Crystal Structures; Göttingen, Germany, 1993.