WITHDRAWAL

On the Beneficial Effect of *ortho*-Methoxy Groups in the Asymmetric Ring Opening of *meso* Epoxides with Silicon Tetrachloride Catalyzed by Chiral *ortho*-Methoxyphenyldiazaphosphonamide Lewis Bases**

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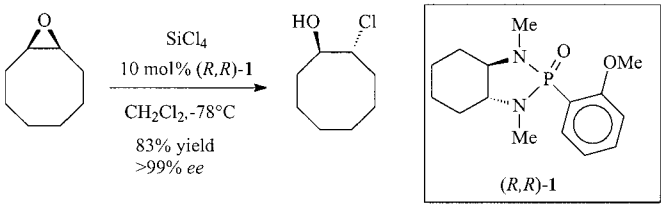
We published in this journal a communication on the enantioselective opening of *meso* epoxides with silicon tetrachloride in the presence of a catalytic amount of chiral phosphonamides.[1] In that paper we reported the asymmetric ring opening of cyclooctene oxide with $SiCl_4$ in the presence of 10 mol% of chiral phophonamide base (*R*,*R*)-**1** as a catalyst (Scheme 1).



Scheme 1.

For this reaction, we described up to 83% yield and enantiomeric excess higher than 99%. This spectacular result attracted the attention of Professor Scott E. Denmark, who pioneered this research field,[2] because it was found that cyclooctene oxide is one of the slowest acting epoxides in this catalytic system and produced the racemic chlorohydrin. However, Denmark et al. did not succeed in reproducing the results we disclosed and submitted a rebuttal to our paper.[3] We were then contacted by the Editor and Prof. Denmark and prompted to elucidate the origin of such a striking discrepancy. At this stage, I asked my co-workers[4] to check the experimental procedures and analytical conditions and to try to reproduce the described results. I was provided with experimental data and material that fully confirmed our original claims. On the basis of these results we sent a first answer to the rebuttal published in *Angewandte Chemie*, an answer that could not explain why our observation differed from Prof. Denmark's. One month later, we received a letter from the Editor who required further complementary analytical data and information. When I had these new data from my co-workers in hand, I noticed several inconsistencies with the analytical material they had previously provided. Therefore, I decided to reproduce *personally* and *independently* the whole experimental procedures from the very beginning. I was unable to observe the opening of cyclooctene oxide under the described conditions and to reproduce the analytical data (for example, NMR, retention times in chiral GPC and HPLC analyses) provided by my co-workers. Instead, I obtained results similar to those reported by Denmark et al. in their rebuttal.[3] A cross-check undertaken by several colleagues led to identical results. To date, my co-workers[4] have been unable to provide an appropriate scientific rationale for the non-reproducibility of the former results and analyses. Under these circumstances, although our communication presented several other *meso* epoxide openings with fair to high enantioselectivities, which require experimental verification, I wish to withdraw that communication.[1] Other pieces of work based on related experimental results that were published elsewhere will also be withdrawn.[5, 6]

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[**] A Response to the correspondence by Professor Scott E. Denmark et al.[3]

[1] J. M. Brunel, O. Legrand, S. Reymond, G. Buono, *Angew. Chem.* **2000**, *112*, 2654; *Angew. Chem. Int. Ed.* **2000**, *39*, 2554.
[2] S. E. Denmark, P. A. Barsanti, K.-T. Wong, R. A. Stavenger, *J. Org. Chem.* **1998**, *63*, 2428.
[3] S. E. Denmark, T. Wynn, B. G. Jellerichs, *Angew. Chem.* **2001**, *113*, 2315; *Angew. Chem. Int. Ed.* **2001**, *40*, 2255.
[4] Except O.L. who left my group in July 1999.
[5] S. Reymond, J. M. Brunel, G. Buono, *Tetrahedron: Asymmetry* **2000**, *11*, 4441.
[6] S. Reymond, O. Legrand, J. M. Brunel, G. Buono, *Eur. J. Org. Chem.* **2001**, 2819.

APOLOGY

In the Communication "A Lewis Acid Catalyst Anchored on Silica Grafted with Quaternary Alkylammonium Chloride Moieties" by **M. V. Landau et al**. the authors made no reference to their thematically related communication "A comparative study of an MCM-41 anchored quaternary ammonium chloride/$SnCl_4$ catalyst and its silica gel analogue" (T. M. Jyothi, M. L. Kaliya, M. Herskowitz, M. V. Landau, *Chem. Commun.* **2001**, 992–993) and vice versa, even though both manuscripts were submitted to their respective journals at the same time. The authors apologize for this oversight.

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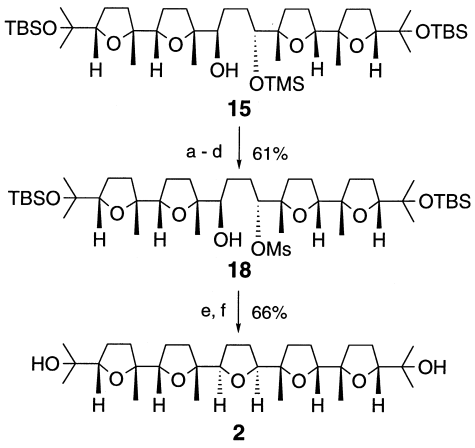
Table 1. Comparison of ^{1}H and ^{13}C NMR chemical shifts of natural and synthetic compounds.[a]

Compound	NMR nucleus	Chemical shift[b] at positions: 1, 30	2, 23	3, 22	4, 21	5, 20	6, 19	7, 18	8, 17	9, 16	10, 15	11, 14	12, 13	24, 25	26, 29	27, 28
natural glabrescol	^{1}H	1.05		3.79	1.80 2.08	1.39 2.23		3.97	1.48 1.72	1.53 1.96		**3.83**	1.60 1.92	1.27	1.09	1.11
	^{13}C	25.38	71.57	85.74	26.62	31.14	85.60	84.17	29.01	34.75	**85.27**	**85.01**	**28.23**	28.28	25.16	22.11
1	^{1}H	1.05		3.78	1.80 2.06	1.37 2.22		3.97	1.46 1.69	1.51 2.02		**3.70**	1.54 1.80	1.28	1.09	1.10
	^{13}C	25.26	71.57	85.59	26.48	30.88	85.49	84.20	28.98	34.52	**84.48**	**83.93**	**27.01**	28.11	24.98	22.48
2	^{1}H	1.04		3.79	1.80 2.05	1.38 2.17		3.96	1.42 1.73	1.49 2.01		3.63	1.61 1.79	1.27	1.10	1.20
	^{13}C	25.29	71.50	85.62	26.51	31.02	85.24	83.52	29.11	33.72	83.54	84.22	26.13	28.04	25.06	24.34

[a] NMR spectra were measured in $CDCl_3$:C_6D_6 (7:3). [b] Chemical shifts quoted in ppm.



Scheme 5. Synthesis of **2**. a) Ac_2O, Et_3N; b) HCl; c) MsCl, Et_3N; d) DIBAH; e) NaH; f) *n*-Bu_4NF.

[1] W. W. Harding, P. A. Lewis, H. Jacobs, S. McLean, W. F. Reynolds, L.-L. Tay, J.-P. Yang, *Tetrahedron Lett*. **1995**, *36*, 9137.

[2] For the synthetic studies of glabrescol, see: Y. Morimoto, T. Iwai, T. Yoshimura, T. Kinoshita, *Bioorg. Med. Chem. Lett*. **1998**, *8*, 2005.

[3] For the stereoselective synthesis of *trans-threo*-penta(tetrahydrofuran), see: a) U. Koert, M. Stein, K. Harms, *Angew. Chem.* **1994**, *106*, 1238; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1180; b) U. Koert, M. Stein, H. Wagner, *Chem. Eur. J.* **1997**, *3*, 1170.

[4] For our examples of natural product synthesis using baker's yeast reduction, see: a) M. Kodama, S. Yoshio, T. Tabata, Y. Deguchi, Y. Sekiya, Y. Fukuyama, *Tetrahedron Lett*. **1997**, *38*, 4627; b) H. Hioki, H. Ooi, Y. Mimura, S. Yoshio, M. Kodama, *Synlett* **1998**, 729.

[5] M. Kodama, H. Minami, Y. Mima, Y. Fukuyama, *Tetrahedron Lett*. **1990**, *31*, 4025. The optical purity was determined to be 98% *ee* by liquid chromatographic analysis using a chiral column.

[6] The stereochemistry of **4** and **5** was determined by a modified Mosher's method. See Ref. [4a].

[7] Z.-X. Wang, Y. Tu, M. Frohn, J.-R. Zhang, Y. Shi, *J. Am. Chem. Soc*. **1997**, *119*, 11 224.

[8] The stereochemistry of the Sharpless asymmetric epoxidation has been unambiguously established. See: a) M. G. Finn, K. B. Sharpless, *Asymmetric Synthesis* (Ed.: J. D. Morrison), Academic Press, New York, **1985**, Chap. 8, p. 247; b) T. Katsuki, V. S. Martin, *Org. React*. **1996**, *48*, 1.

[9] Compound **9**: $[\alpha]_D^{19}$ +7.69 ($c = 1.09$, $CHCl_3$); ^{1}H NMR: $\delta = 0.07$ (3H, s), 0.08 (3H, s), 0.85 (9H, s), 1.16 (3H, s), 1.18 (3H, s), 1.18 (3H, s), 1.19 (3H, s), 1.53–1.66 (2H, m), 1.79–1.97 (6H, m), 2.69–2.74 (2H, m), 3.03 (1H, dd, $J = 3.9$, 3.0 Hz), 3.71 (1H, dd, $J = 7.2$, 7.2 Hz), 3.92 (1H, dd, $J = 7.0$, 7.0 Hz).

[10] I. Nagawa, T. Hata, *Tetrahedron Lett*. **1975**, 1409.

[11] Compound **12**: $[\alpha]_D^{25.5}$ −4.19 ($c = 1.8$, $CHCl_3$); ^{1}H NMR: $\delta = 0.08$ (6H, s), 0.86 (9H, s), 1.12 (3H, s), 1.14 (3H, s), 1.22(3H, s), 1.57 (3H, br.s), 1.20–2.40 (8H, m), 3.21 (1H, dd, $J = 8.8$, 2.5 Hz), 3.54 (2H, d, $J = 7.4$ Hz), 3.74 (1H, t, $J = 7.0$ Hz), 3.80 (3H, s), 4.47 (1H, d, $J = 11.0$ Hz), 4.59 (1H, d, $J = 11.0$ Hz), 5.31 (1H, br.t, $J = 7.7$ Hz), 6.86 (2H, d, $J = 8.8$ Hz), 7.16–7.36 (7H, m).

[12] The stereochemistry of diol **14** was based on the empirical rule. See: a) K. B. Sharpless, W. Amberg, Y. L. Bennani, G. A. Crispino, J. Hartung, K.-S. Jeong, H.-L. Kwong, K. Morikawa, Z.-M. Wang, D. Xu, X.-L. Zhang, *J. Org. Chem*. **1992**, *57*, 2768; b) H. Becker, S. B. King, M. Taniguchi, K. P. M. Vanhessche, K. B. Sharpless, *J. Org. Chem*. **1995**, *60*, 3940.

[13] The AD-mix-α oxidation afforded **14** and its diastereomer in the ratio of 5.2:1.

[14] No difference was observed in ^{1}H and ^{13}C NMR spectra of **1** when they were recorded at the lower concentration.

Beneficial Effect of *ortho*-Methoxy Groups in the Asymmetric Ring Opening of *meso* Epoxides with Silicon Tetrachloride Catalyzed by Chiral *ortho*-Methoxyphenyldiazaphosphonamide Lewis Bases**

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The asymmetrization of suitable *meso* compounds is an attractive approach to the synthesis of complex molecules and often greatly simplifies their preparation.[1] Numerous procedures to effect asymmetrization have been developed, including the deprotonation,[2] protonation,[3] esterification,[4] hydrolysis,[5] and ring cleavage of *meso* carboxylic anhydrides.[6]

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

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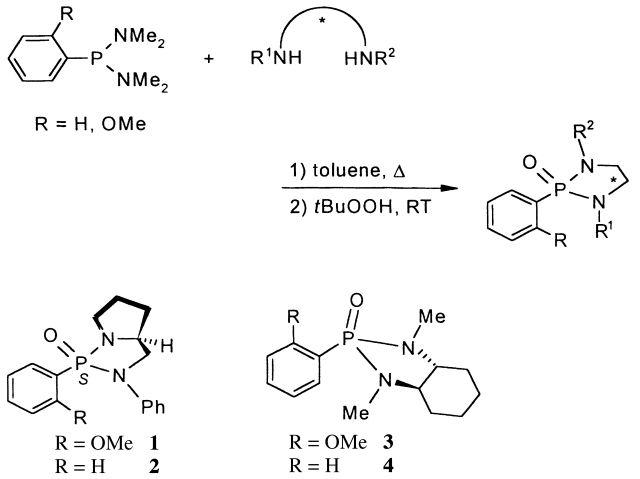
Epoxides are valuable intermediates for the stereocontrolled preparation of organic compounds.[7] Thus, the desymmetrization of *meso* epoxides by enantioselective addition of nucleophiles appears to be an efficient strategy for asymmetric synthesis since it establishes two contiguous stereogenic centers.[8] In this area, halide ions have been extensively applied in the ring opening of epoxides.[9] Nevertheless, no highly efficient, catalytic methods affording enantiomerically enriched chlorohydrins have been reported. Only chiral organophosphorus Lewis bases coordinated to and thereby activating silylated nucleophiles have been introduced by Denmark et al. as catalysts in this field; these led to the formation of optically active chlorohydrins in moderate enantiomeric excess (*ee*).[10]

Recently, we have described the synthesis of new chiral *ortho*-hydroxyaryl phosphine oxides[11] and their application as chiral Lewis bases[12] in various asymmetric catalytic systems. In the context of our studies on nonorganometallic phosphorus reagents in enantioselective catalysis,[13] we report in this paper the highly efficient use of *ortho*-methoxyphenyldiazaphosphonamides in the catalytic asymmetric ring opening of *meso* epoxides with silicon tetrachloride.

Diastereomerically pure aryl phosphonic amides **1**–**4** were easily prepared in 84, 80, 91, and 80% yield, respectively, by an exchange reaction between bis(dimethylamino)aryl phosphine and the corresponding (*R*,*R*)-*N*,*N*′-dimethylcyclohexane-1,2-diamine or (*S*)-2-anilinomethyl pyrrolidine, followed by oxidation of the crude phosphines with *tert*-butyl hydroperoxide (Scheme 1). The crystalline compounds **1**–**4** were



Scheme 1. Synthesis of chiral aryl phosphonic amides **1**–**4**.

characterized by standard methods, including ^{31}P NMR spectroscopy ($\delta = 24.4$, 32.2, 32.5, and 26.5 in $CDCl_3$). The structure of **1** was unambiguously determined by a single X-ray diffraction study probing the phosphorus atom, which was shown to possess *S* absolute configuration (Figure 1).[14]

These compounds have been successfully employed as chiral Lewis bases in a catalytic asymmetric ring opening by $SiCl_4$ with cyclooctene oxide as the test substrate (Table 1). It is clear that the experimental conditions have a dramatic impact on the outcome of the reaction. In all cases, the expected chlorohydrin was obtained in good chemical yield

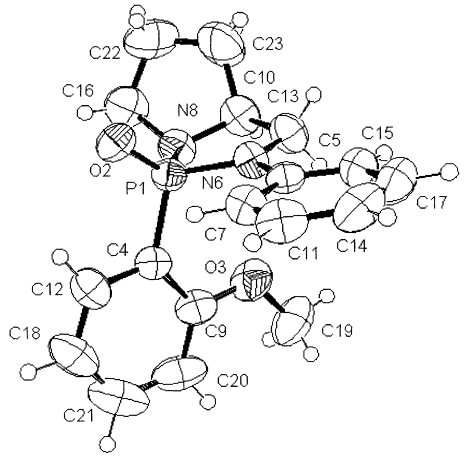
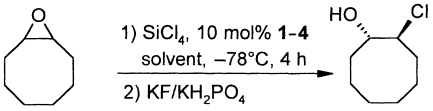


Figure 1. Structure of **1** with atom labeling. Selected bond lengths [Å] and angles [°]: P1-O2 1.466(1), P1-N6 1.669(1), P1-N8 1.648(2), P1-C4 1.788(2), N6-C5 1.414(2), C9-O3 1.372(2), O3-C19 1.410(2); O2-P1-C4 108.4(1), O2-P1-N6 116.4(1), O2-P1-N8 117.7(1), C4-P1-N6 110.3(1), C4-P1-N8 108.4(1), N6-P1-N8 94.9(1), C9-O3-C19 117.5(2), P1-C4-C9 124.3(1), P1-N8-C16 118.5(1), P1-N8-C10 113.3(1), C10-N8-C16 106.3(1).

Table 1. Catalytic asymmetric ring opening of cyclooctene oxide with $SiCl_4$.[a]



Entry	Lewis base	Solvent	Yield [%][b]	*ee* [%][c]
1	**1**	THF	68	30
2	**1**	toluene	61	98
3	**1**	DMF	–[d]	–
4	**1**	CH_2Cl_2	60	34
5	**1**	CH_2Cl_2	77	>99
6	**1**[e]	CH_2Cl_2	75	75
7	**2**	CH_2Cl_2	78	30
8	**3**	CH_2Cl_2	83	>99
9	**4**	CH_2Cl_2	78	50

[a] Reactions were all performed on 1.2 mmol scale at −78 °C for 4 h with freshly distilled $SiCl_4$, except for the reaction in entry 4 which was performed using commercial $SiCl_4$ without any purification. [b] Yield after flash chromatography. [c] *ee* values were determined by chiral GC analysis with a Lipodex E column. [d] In this case, a low conversion (<15%) was encountered, even at room temperature. [e] Reaction was performed using 5 mol% of **1**.

(varying from 60 to 83%). Nevertheless, toluene and CH_2Cl_2 appeared to be the best solvents in terms of enantioselectivity (entries 2 and 5, 98 and >99% *ee*, respectively), whilst a polar solvent such as THF led to a poor *ee* value (entry 1, 30% *ee*). Furthermore, the use of freshly distilled $SiCl_4$ significantly enhanced the enantiomeric excess from 34 to >99% *ee* (entries 4 and 5).[15] The influence of decreasing the amount of catalyst **1** from 10 to 5 mol% was also investigated and a substantial decrease in enantioselectivity was observed (entry 6, 75% *ee*). Replacement of a methoxy group on the aromatic ring with a hydrogen atom has a detrimental effect on the enantioselectivity (entries 7 and 9, 30% and 50% *ee*, respectively).[16]

In order to explain the differences in enantioselectivity observed with the chiral base catalysts **1** and **3** relative to **2** and

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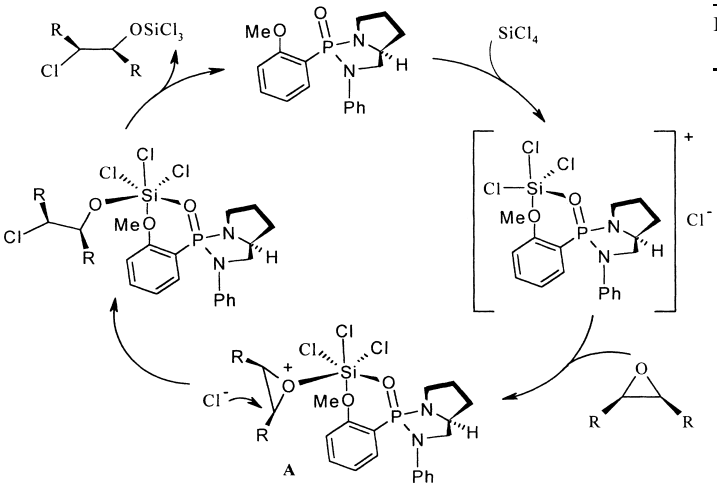
4, we believe that, for **1** and **3**, the reaction with the epoxide proceeds through a hexacoordinate structure, with chelatation to the catalyst organized around a cationic silicon intermediate **A** (Scheme 2). On the other hand, for **2** and **4**, we can



Scheme 2. Proposed mechanistic rationale for the enantioselective ring opening of *meso* epoxides.

postulate a pentacoordinate intermediate in equilibrium with a hexacoordinate structure; these structures would involve one or two phosphonamide molecules, respectively, coordinated by only the oxygen of the P=O moiety.[17]

Under the best experimental conditions previously described (those in entry 5, Table 1), this study has been extended to a series of *meso* epoxides. The results are summarized in Table 2. In all cases, the chlorohydrins were obtained in good yields varying from 41 to 91%. However, the enantioselectivity of the reaction was highly substrate dependent. In the case of cyclic substrates, there is a dramatic effect with different ring sizes. Thus, using catalyst **1**, cyclopentene oxide afforded the expected product in low *ee* (entry 1, 23% *ee*) whereas cyclohexene, cycloheptene, and cyclooctene oxides led to the formation of the corresponding chlorohydrins in, respectively, 82, 98, and up to 99% *ee* (entries 5, 6, and 8). The acyclic substrates also gave good to excellent results in terms of enantioselectivity (entries 9–14, 60–94% *ee*).[19, 20]

In conclusion, a new and efficient type of chiral Lewis bases has been developed, and its utility has been demonstrated in a catalytic enantioselective ring opening of *meso* epoxides. Further studies dealing with mechanistic features of this reaction are currently under investigation.

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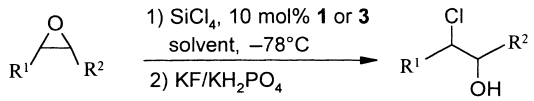
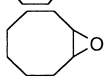
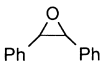
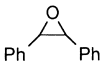
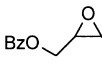
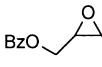
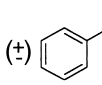
Table 2. Catalytic asymmetric ring opening of various *meso* epoxides.[a]



Entry	Lewis base	Substrate	Solvent	t [h][b]	Yield [%][c]	*ee* [%] (config.)[d]
1	**1**		THF[e]	0.3	68	23 (1*R*,2*R*)[f]
2	**1**		CH_2Cl_2	3	41	48[f]
3	**3**		CH_2Cl_2	3	44	37[f]
4	**1**		CH_2Cl_2	0.3	85	62 (1*R*,2*R*)[g]
5	**3**		CH_2Cl_2	0.3	84	82 (1*R*,2*R*)[g]
6	**1**		CH_2Cl_2	3	79	98 (1*R*,2*R*)[g]
7	**3**		CH_2Cl_2	3	75	73 (1*R*,2*R*)[g]
8	**1**		CH_2Cl_2	4	77	>99 (1*R*,2*R*)[g]
9	**1**		THF[e]	3.5	68	92 (1*S*,2*S*)[h]
10	**3**		CH_2Cl_2	3.5	71	60 (1*S*,2*S*)[h]
11	**1**		CH_2Cl_2	3.5	78	94 (2*S*,3*S*)[h]
12	**3**		CH_2Cl_2	3.5	95	90 (2*S*,3*S*)[h]
13	**1**		THF	3.5	53[i]	12[j]

[a] Reactions were all performed on 1.2 mmol scale at −78 °C using freshly distilled $SiCl_4$. [b] t = reaction time. [c] Yield after flash chromatography. [d] Configuration of the product where determined. [e] A low enantiomeric excess (<20% *ee*) was encountered performing the reaction in CH_2Cl_2. [f] *ee* values were determined by chiral GC analysis with a Lipodex E column. [g] *ee* values were determined by ^{13}C NMR analysis with lactic acid derivatives as chiral shift reagents.[18] [h] *ee* values were determined by HPLC analysis on a Daicel Chiralcel OD-H column. [i] Reaction was performed using 0.5 equivalents of $SiCl_4$ and quenched after 56% conversion of the substrate. [j] *ee* values were determined by HPLC analysis on a Daicel Chiralcel OJ column.

[1] a) M. C. Wills, *J. Chem. Soc. Perkin Trans. 1* **1999**, 1765; b) E. N. Jacobsen, M. H. Wu, *Comprehensive Asymmetric Catalysis, Vol. III* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamumoto), Springer, **1999**, Chap. 35, pp. 1309–1326; c) A. S. Rao, S. K. Paknikar, J. G. Kirtane, *Tetrahedron* **1983**, *39*, 2323.
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[3] K. Fuji, M. Node, S. Terada, M. Murata, H. Nagasawa, *J. Am. Chem. Soc.* **1985**, *107*, 6404.
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[14] Single crystal X-ray analysis of **1**: $C_{18}H_{21}N_2O_2P$, $M_r = 328.35$, white plate (recrystallized in ethylacetate), $0.5 \times 0.5 \times 0.4\ mm^3$. All the measurements were made on a Rigaku diffractometer with $Cu_{K\alpha}$ radiation. Cell constants and the orientation matrix for data collection were obtained from a least square refinement using setting angles of 30 reflections in the range $1 < \theta < 25.45^\circ$; orthorhombic, $P2_12_12_1$, $a = 9.1502(2)$, $b = 10.9705(4)$, $c = 16.8227(6)$ Å, $Z = 4$, $\rho_{calcd} = 1.25\ g\,cm^{-3}$. A total of 1925 reflections were measured at $T = 298$ K. The standards were measured after every 25 reflections. Among the first 20 pairs of reflections, the signs of the corresponding calculated differences established that the molecule is described with the correct *S* absolute configuration. Moreover, the sum of the bond angles around the nitrogen atom of the pyrrolidine ring is 338.1°, showing a nonplanar configuration. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140554. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[19] A careful analysis of the chlorohydrin issued from cyclohexene oxide is necessary. Indeed, a racemization occurred in CH_2Cl_2 solution, with the $[\alpha]_D^{25}$ varying from -30 to -20 after 4 hours ($c = 1.0$, $CHCl_3$). Moreover, the chlorohydrin generated in entry 11 is not very stable and a decomposition of the product has been noticed after few hours.

[20] Numerous racemic epoxides have been submitted in an attempt at an asymmetric ring opening resolution with $SiCl_4$ catalyzed by the chiral *ortho*-methoxyphenyldiazaphosphonamide Lewis bases. Whatever the experimental conditions, low enantiomeric excess values of chlorohydrins (<10% *ee*) and poor regioselectivity have been encountered, except when opening racemic phenyloxirane, where a total regioselectivity has been observed but with only 12% ee. The residual epoxide was isolated in 35% yield and 20% *ee*.

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