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Oxiranyl Anion-Mediated Synthesis of Highly Enantiomerically Enriched Styrene Oxide Derivatives

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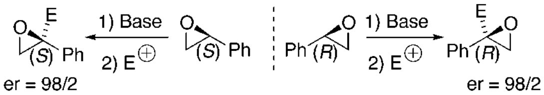
ABSTRACT



The stereospecific α-lithiation of optically active styrene oxides and the trapping reaction of the corresponding highly reactive intermediates with electrophiles to produce optically active styrene oxide derivatives are described. This methodology has been applied to the synthesis of an optically active oral antifungal agent of industrial interest.

The utility of optically active styrene oxide derivatives as chiral building blocks for the synthesis of natural products and biologically active compounds is well documented.[1] Accordingly, efforts have been made for the development of catalytic, stereoselective epoxidation methodologies of terminal olefins.[2] The hydrolytic kinetic resolution of terminal epoxides using chiral (salen)−Cr and (salen)−Co(III) complexes[3] and of epoxide hydrolases[4] has also been developed. Indirect routes are based mainly on asymmetric dihydroxylation chemistry[5] followed by stereospecific cyclodehydration.[6] The successful use of the Mitsunobu reaction[7] and of the asymmetric reduction of substituted 2-sulfonyloxyacetophenone derivatives[8] for the stereoselective synthesis of styrene oxides have been also recently described.

To our knowledge, the oxiranyl anion-based methodology[9] directed to the preparation of enantiomerically enriched styrene oxide derivatives has not been investigated yet, although some evidences reported by Eisch[10] on racemic *cis*-disubstituted *β*-phenylepoxysilanes and *cis*- and *trans*-diphenyloxiranes and by our group[11] on *β*-aryl-substituted oxazolinyloxiranes have proved the configurational stability

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[1] For recent examples, see: (a) Hattori, K.; Nagano, M.; Kato, T.; Nakanishi, I.; Imai, K.; Kinoshita, T.; Sakane, K. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 2821−2824. (b) Di Fabio, R.; Pietra, C.; Thomas, R. J.; Ziviani, L. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 551−554. (c) Sher, P. M.; Mathur, A.; Fisher, L. G.; Wu, G.; Skwish, S.; Michel, I. M.; Seiler, S. M.; Dickinson, K. E. J. *Bioorg. Med. Chem. Lett.* **1997**, *7*, 1583−1588.

[2] (a) Collman, J. P.; Wang, Z.; Straumanis, A.; Quelquejeu, M.; Rose, E. *J. Am. Chem. Soc.* **1999**, *121*, 460. (b) Palucki, M.; Popisil, P. J.; Zhang, W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1994**, *116*, 9333. (c) For a review, see: Jacobsen, E. N.; Wu, M. H. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; Vol. II, Chapter 18.2. (d) Warren, J. D.; Shi, Y. *J. Org. Chem.* **1999**, *64*, 7675−7677. (e) Tian, H.; She, X.; Xu, J.; Shi, Y. *Org. Lett.* **2001**, *3*, 1929.

[3] (a) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936−938. (b) Brandes, B. D.; Jacobsen, E. N. *Tetrahedron: Asymmetry* **1997**, *8*, 3927. (c) Keith, J. M.; Larrow, J. F.; Jacobsen, E. N. *Adv. Synth. Catal.* **2001**, *343*, 5−26. (d) Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 1307−1315.

[4] For an application, see: Pedragosa-Moreau, S.; Morriseau, C.; Zylber, J.; Archelas, A.; Baratti, J.; Furstoss, R. *J. Org. Chem.* **1996**, *61*, 7402.

[5] For a review, see: Kolb, H. C.; Sharpless, K. B. *Transition Met. Org. Synth.* **1998**, *2*, 219.

[6] (a) Jang, D. O.; Joo, Y. H.; Cho, D. H. *Synth. Commun.* **2000**, 4489. (b) For a review, see: Kolb, H. C.; Van Nieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483. (c) Adiyaman, M.; Khanapure, S. P.; Hwang, S. W.; Rokack, J. *Tetrahedron Lett.* **1995**, 7367. (d) O'Donnell, C. J.; Burke, S. D. *J. Org. Chem.* **1998**, *63*, 8614.

[7] Weissman, S. A.; Rossen, K.; Reider, P. J. *Org. Lett.* **2001**, *3*, 2513.

[8] Cho, B. T.; Choi, O. K. *Bull. Korean Chem. Soc.* **2001**, *22*, 443−444 and references therein.

[9] (a) Satoh, T. *Chem. Rev.* **1996**, *96*, 3303−3325. (b) Mori, Y. *Rev. Heteroatom Chem.* **1997**, *17*, 183-211. (c) Hodgson, D. M.; Norsikian, S. L. M. *Org. Lett.* **2001**, *3*, 461−463. (d) Yamauchi, Y.; Katagiri, T.; Uneyama, K. *Org. Lett.* **2002**, *4*, 173−176.

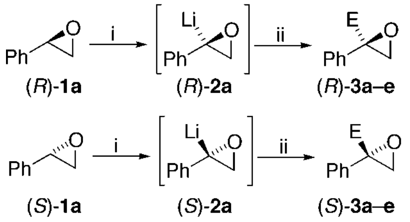
[10] (a) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1988**, *341*, 293−313. (b) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1990**, *55*, 4835−4840.

[11] Capriati, V.; Degennaro, L.; Favia, R.; Florio, S.; Luisi, R. *Org. Lett.* **2002**, *4* (*9*), 1551−1554.

10.1021/ol026212d CCC: $22.00

of aryl-substituted lithiated oxiranes. Therefore, we felt encouraged to study the lithiation of optically active (*R*)- and (*S*)-styrene oxides and subsequent trapping reaction with electrophiles. We considered that the use of such stereochemically stable terminal oxiranyllithiums could open a useful route to optically active more functionalized styrene oxide derivatives that would be key building blocks, from a synthetic standpoint, for asymmetric synthesis of "target" molecules. Herein, we describe the successful use of this oxiranyl anion methodology for the stereoselective synthesis of styrene oxide derivatives. The typical procedure for the generation of oxiranyllithiums starting from either (*S*)- or (*R*)-styrene oxide and reactions with electrophiles is illustrated in Scheme 1.

Scheme 1[a]



3a = D; **3b** = CH_3; **3c** = CH_3CH_2,
3d = $CH_2{=}C(CH_3)CH_2$, **3e** = $PhCH_2$

[a] Key: (i) *s*-BuLi/TMEDA, THF, −98 °C, 10 min; (ii) electrophile.

Treatment of a precooled mixture (−98 °C) of styrene oxide (*R*)-**1a** (1 equiv) and TMEDA (3 equiv) with *s*-BuLi (1.2 equiv) in THF for 10 min led to regioselective generation of oxiranyllithium (*R*)-**2a**, which was subsequently allowed to react with a series of electrophiles to give stereospecifically the corresponding α,α-disubstituted epoxides (*R*)-**3a**−**e** in good to excellent yields and very high enantiomeric ratios (er 98/2 in all cases) (Table 1).

The optical activity of **3a**−**e** was measured; **3a** showed the same optical rotation of the starting material,[12] while that of **3b**,**c** matched quite well the values of the literature.[2d,12] This fact proves that the reactions proceed without epimerization at the stereogenic center. The *R* configuration to compounds **3d**,**e** was presumed and assigned by analogy.

Table 1. Reaction of Lithiated (*R*)- and (*S*)-**1a** with Electrophiles

1a	electrophile	product (% yield)	er	$[\alpha]^{26}_D$[a]
R	CH_3OD	(*R*)-**3a** (>95)[b]	98/2[c]	−24[d]
S	CH_3OD	(*S*)-**3a** (>95)[b]	98/2[c]	+27[d]
R	CH_3I	(*R*)-**3b** (>95)[b]	98/2[c]	−20[e]
S	CH_3I	(*S*)-**3b** (>95)[b,f]	98/2[c]	+17
R	CH_3CH_2I	(*R*)-**3c** (>95) [b]	98/2[c]	−30[g]
S	CH_3CH_2I	(*S*)-**3c** (>95)[b,f]	98/2[c]	+29
R	$CH_2{=}C(CH_3)CH_2Cl$	(*R*)-**3d** (65)[f,h]	98/2[i]	−42
S	$CH_2{=}C(CH_3)CH_2Cl$	(*S*)-**3d** (65)[f,h]	98/2[i]	+42
R	$PhCH_2Br$	(*R*)-**3e** (45)[f,h,j]	98/2[k]	−22
S	$PhCH_2Br$	(*S*)-**3e** (40)[f,h,j]	98/2[k]	+20

[a] *c* 0.5−1.4, $CHCl_3$ (see the Supporting Information for details). [b] Yield calculated by weighing the crude reaction product and ^1H NMR analysis; no starting material or other byproducts could be observed. [c] Enantiomeric ratio by GC analysis on a chiraldex B-DM capillary column. [d] See ref 12. [e] Lit. −20.1 (*c* 1.02, $CHCl_3$), see ref 12. [f] Presumed configuration. [g] Lit. −25.2 (*c* 0.64, $CHCl_3$), see ref 2d. [h] Isolated yields. [i] Enantiomeric ratio by HPLC employing a Daicel Chiralcel OD-H column. [j] Diphenylethane also formed as byproduct. [k] Enantiomeric ratio by ^1H NMR analysis in the presence of a chiral solvating agent (see the Supporting Information for details).

The combination of base, ligand, and solvent was examined to optimize the yield of **3a**−**e**. The use of *s*-BuLi (*n*-BuLi and LDA were ineffective) as the base (1.2 equiv) and a donor solvent such as THF and of TMEDA (3 equiv)[13] as the ligand gave the best results, affording the product almost quantitatively.

The presence of TMEDA was unavoidable, as lithiation of racemic styrene oxide in the absence of this ligand produced a mixture of products that originated from the *s*-BuLi-promoted degradation reaction of lithiated styrene oxide: 3-methyl-2-phenyl-pent-1-ene **4**,[14] *trans*-3-methyl-1-phenyl-pent-1-ene **5**,[14] and diastereomeric 2,3-diphenyl-2-buten-1,4-diols **6**[15] which were isolated and characterized (Figure 1). It is also worth pointing out that under these optimized conditions the anion proved to be stable, at −98 °C, for only 30 min.[16]

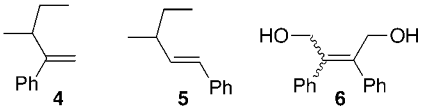


Figure 1.

Lithiated styrene oxide (*R*)-**2a** also reacted smoothly with ketones (acetone and cyclopentanone) to give products **3f**,**g** in good yields (Scheme 2 and Table 2). The reaction of (*R*)-**2a** with aldehydes (benzaldehyde and *p*-chlorobenzaldehyde) led to good yields of products **3h**−**k**, although with poor diastereoselection at the newly created stereogenic center (anti/syn ratio = 66/34).[17,18] Diastereomers could be nicely

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(12) It is interesting to observe that while the $[\alpha]^{20}_D$ reported for the commercial samples (Aldrich) of (*R*)- and (*S*)-styrene oxides, measured neat, are +33 and −33, respectively, those measured by us in $CHCl_3$ solution are opposite as signs for both. (*R*)-styrene oxide: $[\alpha]^{26}_D = -23$ (*c* 0.8, $CHCl_3$); (*S*)-styrene oxide: $[\alpha]^{28}_D = +23$ (*c* 0.7, $CHCl_3$). A solvent-dependent optical rotation sign has been also recently ascertained in the case of α-methylstyrene oxide (see: Archelas, A.; Furstoss, R. *J. Org. Chem.* **1999**, *64*, 6112−6114) and of other styrene oxide derivatives (see: Imanishi, H.; Katsuki, T. *Tetrahedron Lett.* **1997**, *38*, 251−254).

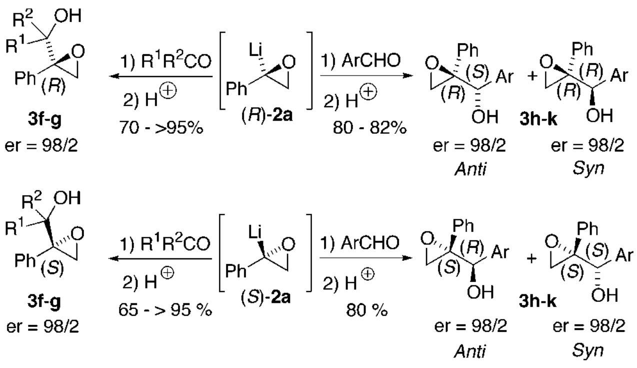
(13) Quantity of TMEDA less than 1 equiv led to the recovery of starting material and to minor yields of products.

(14) Doris, E.; Dechoux, L.; Mioskowski, C. *Tetrahedron Lett.* **1994**, *35*, 7943.

(15) Spectral data matched very well those reported in the literature: Toda, F.; Takeira, Y.; Kataoka, Y.; Mori, K.; Sato, T.; Segawa, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1234−1235.

(16) A computational and NMR investigation on the lithiated styrene oxide is underway and will be reported in due course.

Scheme 2



separated by preparative HPLC (see the Supporting Information) and analyzed via chiral GC or chiral HPLC (er = 98/2, see the Supporting Information) (Scheme 2 and Table 2).

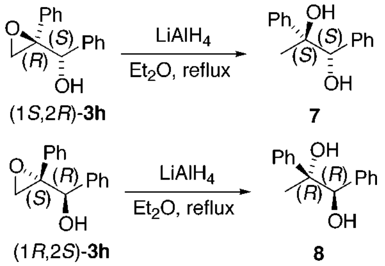
Table 2. Reaction of Lithiated (*R*)- and (*S*)-**1a** with Ketones and Aldehydes

1a	electrophile	product (% yield)		er	[α]$^{26}_{D}$[a]
R	(CH$_3$)$_2$CO	(*R*)-**3f** (>95)[b,c]		98/2[d]	−49
S	(CH$_3$)$_2$CO	(*S*)-**3f** (>95)[b,c]		98/2[d]	+50
R	cyclopentanone	(*R*)-**3g** (70)[c,e]		98/2[d]	−56
S	cyclopentanone	(*S*)-**3g** (65)[c,e]		98/2[d]	+52
R	PhCHO	(1*S*,2*R*)-**3h**	(80%)[e−g]	98/2[d]	−44
		(1*R*,2*R*)-**3i**		98/2[d]	−45
S	PhCHO	(1*R*,2*S*)-**3h**	(80%)[e,f,h]	98/2[d]	+41
		(1*S*,2*S*)-**3i**		98/2[d]	+45
R	*p*-ClC$_6$H$_4$CHO	(1*S*,2*R*)-**3j**	(82%)[e−g]	98/2[i]	−80
		(1*R*,2*R*)-**3k**		98/2[i]	−39
S	*p*-ClC$_6$H$_4$CHO	(1*R*,2*S*)-**3j**	(80%)[e,f,h]	98/2[i]	+87
		(1*S*,2*S*)-**3k**		98/2[i]	+42

[a] *c* 0.6−1.0, CHCl$_3$ (see the Supporting Information for details). [b] Yield calculated by weighing the crude reaction product and ^{1}H NMR analysis; no starting material or other byproducts could be observed. [c] Presumed configuration. [d] Enantiomeric ratio by GC analysis on a chiraldex B-DM or Supelco *β*-DEX 120 capillary column. [e] Isolated yields. [f] Overall yields in both diastereoisomers; dr 1*S*,2*R*/1*R*,2*R* (or 1*R*,2*S*/1*S*,2*S*) = 66/34, separated by preparative HPLC. [g] Relative and absolute configuration ascertained as described. [h] Relative and absolute configuration assigned by analogy and ascertained in the case of (1*R*,2*S*)-**3h**. [i] Enantiomeric ratio by HPLC employing a Daicel Chiralcel OD-H column.

Preliminary indications about the diastereomers' relative configurations (syn or anti, see Scheme 2) came from a careful inspection of their ^{1}H NMR spectra. Use was made of the observation[19] that for such diastereomeric epoxy alcohols the carbinol proton of the syn isomer absorbs at lower field than the corresponding proton of the anti isomer (δ 5.05 vs 5.02 for **3i** and **3h**; 5.04 vs 4.99 for **3k** and **3j**, respectively). The relative configuration of **3i** was also confirmed by crystallographic X-ray analysis.[20] In the case of (1*S*,2*R*)-**3h**, its relative and absolute configuration was unambiguously ascertained by LiAlH$_4$ reduction[19] and comparison of the optical activity ([α]$^{26}_{D}$ = −27, *c* 0.82 THF) and spectroscopic data (^{1}H NMR) of the resulting diol **7** (Scheme 3) with the literature data of its enantiomer (*R*,*R*)-**8** ([α]$^{26}_{D}$ = +34, *c* 1.01, THF).[21] Therefore, we presume that **7** should have the *S*,*S* configuration.[22] The absolute configuration to diastereomeric epoxy alcohols **3i** and **3j**,**k** was assigned by analogy.

Scheme 3



In a similar way, lithiation of (*S*)-**1a** (Scheme 1) and reactions of the resulting α-lithiated styrene oxide (*S*)-**2a** with the same electrophiles stereospecifically furnished good yields of products (*S*)-**3a**−**e** (Table 1) and **3f**−**k** (Scheme 2 and Table 2), *S* configured at the α-carbon.

The ring opening of **3h**, presumed to be (1*R*,2*S*), by LiAlH$_4$ gave the (*R*,*R*)-diol **8** (Scheme 3), whose optical activity ([α]$^{26}_{D}$ = +32, *c* 0.80, THF) matched very well the literature value reported above. A short, highly efficient synthesis of an industrial relevant triazole antifungal agent such as **13**[23] (Scheme 4) illustrates the value of our methodology starting from optically active (*S*)-4-chlorostyrene oxide **10** (Scheme 4).

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(17) The convention employed for describing syn and anti diastereomers is as follows: if the main chain is written in an extended (zigzag) conformation, the diastereomer that has the oxiranyl ring and the hydroxy group both projecting either forward (bold bonds) or away from the viewer (dashed bonds) is called syn.

(18) The anti stereoselection observed conforms to the empirical steric model for the prediction of the stereochemical outcome of reactions of chiral anions with aldehydes in the absence of chelation control, proposed by Bassindale and Taylor (Bassindale, A. R.; Ellis, R. J.; Lau, J. C.-Y.; Taylor, P. G. *J. Chem. Soc.*, *Chem. Commun.* **1986**, 98−100) and that has been also applied by Molander to explain the relative stereochemistry of the major diastereoisomer formed by oxiranyl anions addition to carbonyl compounds (Molander, G. A.; Mautner, K. *J. Org. Chem.* **1989**, *54*, 4042−4050). Probably, small energy differences between the two diastereomeric transition states could explain, also in our case, the low diastereoselectivity observed in the case of epoxy alcohols **3h**−**k**.

(19) Adam, W.; Braun, M.; Griesbeck, A.; Lucchini, V.; Staab, E.; Will, B. *J. Am. Chem. Soc.* **1989**, *111*, 203-212.

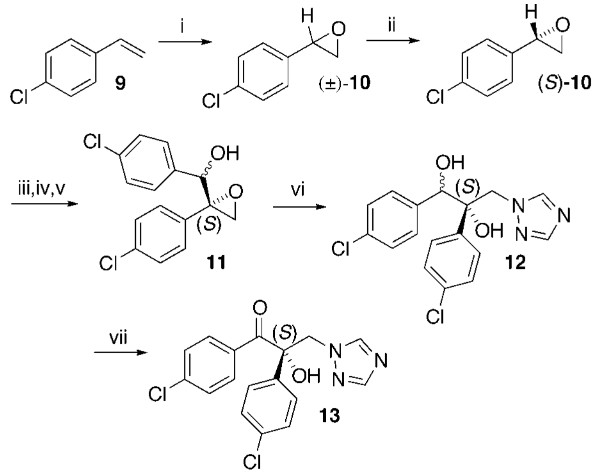
(20) Crystallographic data for compound (1*R*,2*R*)-**3i** have been deposited at the Cambridge Crystallographic Data Centre (deposition no. CCDC-186824). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax: (int.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk]. ORTEP view and CIF file for compound (1*R*, 2*R*)-**3i** have been also reported as Supporting Information.

(21) Rosini, C.; Scamuzzi, S.; Focati, M. P.; Salvadori, P. *J. Org. Chem.* **1995**, *60*, 8289−8293. Spectroscopic data of racemic (1*R**,2*S**)-1,2-diphenylpropane-1,2-diol were reported (Bach, T.; Kather, K. *J. Org. Chem.* **1996**, *61*, 3900−3901) and were also compared with those obtained by the ring opening of a sample of racemic (1*R**,2*R**)-**3i**, which gave the (1*R**,2*S**)-diol.

(22) The configuration at the tertiary benzylic carbon becomes *S* as the priority of the groups around this stereogenic centre is inverted in the opened product.

(23) (a) Takahashi, K.; Ogata, M. *J. Org. Chem.* **1987**, *52*, 1877−1880. (b) Ogata, M.; Matsumoto, H.; Tawara, K.; Ishiguro, T.; Hatta, T. (Shionogi and Co., Ltd., Japan) *Eur. Pat. Appl.* EP 117578 A2 19840905, 1984.

Scheme 4[a]



[a] Key: (i) CF_3COCH_3/H_2O_2, quantitative yield; (ii) (*S*,*S*)-(salen)Co^{III}·OAc, H_2O (0.55 equiv), 0 °C, 38% yield, er 99/1; (iii) *s*-BuLi/TMEDA, THF, −98 °C, 10 min; (iv) *p*-ClC_6H_4CHO; 80% yield, anti/syn 2/1; (v) H^+; (vi) NaH/1,2,4-triazole, DMF, 70 °C, 3 h, 78% yield; (vii) Swern oxidation (quantitative).

(*S*)-**10** was easily synthesized (er 99/1, by chiral GC)[24] by epoxidation of the corresponding commercially available olefin **9** using H_2O_2 as oxidant and CF_3COCH_3 as the catalyst (quantitative yield)[25] followed by a hydrolytic kinetic resolution[3d] (HKR) catalyzed by the chiral (*S*,*S*)-(salen)Co^{III} complex·OAc (38% isolated yield). Subsequent lithiation with *s*-BuLi/TMEDA in THF in the usual way and reaction with *p*-chlorobenzaldehyde afforded a mixture of diastereomeric epoxy alcohols **11** (80% isolated yield; anti/syn 2/1)[26] that was afterward reacted with 1,2,4-triazole/NaH in DMF at 70 °C for 3 h leading to diol **12** (78% isolated yield). Swern oxidation[27] of **12** furnished quantitatively the target hydroxy ketone (*S*)-**13**,[28] which is a known antifungal agent. Further synthetic applications are now in progress.

In conclusion, we proved in this paper that optically pure styrene oxides can be successfully deprotonated and trapped stereospecifically (retention of configuration) to produce enantiomerically enriched substituted styrene oxide derivatives. This methodology, coupled with Jacobsen's HKR of terminal aryl epoxides, has been advantageously applied to the synthesis of a known oral antifungal agent.

Acknowledgment. This work was carried out under the framework of the National Project "Stereoselezione in Sintesi Organica, Metodologie ed Applicazioni" supported by the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR, Rome) and by the University of Bari and CNR (Rome). We are also grateful to Prof. Marcel Pierrot of the Centre Scientifique Saint-Jerome, Marseille, France, for performing X-ray analysis on compound (1*R*,2*R*)-**3i**.

Supporting Information Available: Full experimental details and characterization data (^{1}H and ^{13}C NMR, physical data) for compounds **3a**−**k**, for syn and anti epoxy alcohols **11**. ORTEP view (Figure S1) and CIF file for compound (1*R*,2*R*)-**3i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) $[\alpha]^{26}_D = +27$ (*c* 1, $CHCl_3$) (lit.[4] $[\alpha]^{20}_D = +19.3$ (*c* 1.16, $CHCl_3$, ee > 98%)). It is worth pointing out that Jacobsen (ref 3d) has reported an optical activity ($[\alpha]^{24}_D = -23.8$, *c* 3.41 $CHCl_3$, ee > 99%) of the enantiomer (*R*)-**10**.

(25) Shu, L.; Shi, Y. *J. Org. Chem.* **2000**, *65*, 8807−8810.

(26) Syn and anti diastereomeric epoxy alcohols **11** could be separated by preparative HPLC and spectroscopically characterized. Both resulted to be optically pure (er 99/1, by chiral HPLC) so testifying once more the configurational stability (*S*) of the corresponding α-lithiated *p*-chloro-substituted oxiranyllithium. The configuration to the carbinol carbon was assigned by analogy to the other epoxy alcohols.

(27) Lindstrom, U. M.; Somfai, P. *Synthesis* **1998**, 109−117.

(28) Mp: 118−120 °C (Et_2O) (lit.[23a] mp 161−163 °C (Et_2O), lit. (±)-**13** (Ogata, M.; Matsumoto, H.; Takahashi, K.; Shimizu, S.; Kida, S.; Murabayashi, A.; Shiro, M.; Tawara, K. *J. Med. Chem.* **1987**, *30*, 1064−1068) mp 102−104 °C (AcOEt/*i*Pr_2O)). $[\alpha]^{26}_D = +113.5$ (*c* 1.6, $CHCl_3$) (lit.[23a] $[\alpha]^{23}_D = +117.3$ (*c* 1.0, $CHCl_3$)). The synthesis of (*S*)-(+)-3-(4-chlorophenyl)-2-phenyl-3-oxo-1-(1*H*-1,2,4-triazol-1-yl)propan-2-ol starting from (*S*)-styrene oxide gave a product (overall yield 62%) with ee 98/2 by chiral HPLC (OB-H, hexane/*i*PrOH 95/5, flow rate 0.7 mL/min, $t_{Rminor} = 28.44$ min, $t_{Rmajor} = 45.8$ min), $[\alpha]^{26}_D = +203$ (*c* 0.65, $CHCl_3$).