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A mild access to chiral *syn* 1,2-diaryl glycols by stereoselective ring opening of *ortho* substituted *trans* 2,3-diaryl-oxiranes using Amberlyst 15 in H_2O/THF system

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ABSTRACT

Amberlyst 15 was an efficient and green catalyst for the reaction of 2,3-diaryloxiranes with H_2O in organic co-solvent to prepare glycols in high yield. *Ortho* substituted *trans* 2,3-diaryloxiranes afforded the corresponding *syn* glycols stereo- and enantiospecifically. Stereoselectivity appeared related to the coordination ability of the substituents, irrespective of their electronic properties. Indeed *o*-OCH_3 and *o*-OBn substituted *syn* glycols were obtained in high stereochemical ratios (6/1 and 10/1, respectively), and *o*-OTIPS and *o*-NO_2 substituted ones were obtained as exclusive products, with the same *ee* of the parent epoxides.

1. Introduction

Epoxides are among the most intriguing and challenging moieties in organic synthesis because they are not only significant synthetic endpoints, but also highly useful synthetic intermediates.[1]

Utility and convenience of their use can be enhanced by the modulation of their reactivity with the help of Lewis acids coordinating to the oxygen atom. Thus, ring-openings of epoxides have been applied on an industrial scale for the synthesis of bulk chemicals, and in the synthesis of natural products and pharmaceuticals.

A wide range of nucleophiles are described to react efficiently with epoxides and the regioselectivity of the opening is usually predicted by the different electrophilicity of the two oxiranyl carbons and/or the formation of chelates in the presence of other coordinating moieties in the molecule. The stereochemistry in the opening reaction is mostly assured by the S_N2 pathway and there is usually low, if any, epimerization at the electrophilic oxiranyl carbon.

2,3-Diaryloxiranes can be considered non-conventional epoxides in terms of their synthesis and, above all, their reactivity. If compared to alkyl ones, they usually show lower reactivity towards nucleophiles and they need some activation by Lewis acids. Due to the characteristic chemical behaviour of benzyl type carbons in neutral or acidic medium they appear challenging substrates due to the small reactivity differences of the two oxiranyl carbons and the possible side reactions such as eliminations or rearrangements.[2] The so-called 'Meinwald rearrangement' of epoxides to carbonyl compounds represents a key topic of a rich literature and a number of inorganic and organometallic Lewis acids have been employed, ranging from the classical lithium salts or $BF_3 \cdot Et_2O$[3] to the more recent copper tetrafluoroborate[4] or mixed-valent iron trifluoroacetate.[5] Concerning the Brønsted acid-catalysed rearrangement, acidic zeolite HZSM-5,[6] Nafion-H[7] and nanoporous alumino- and borosilicates[8] are efficient for isomerization of styrene oxide and stilbene oxide.

Epoxide ring-opening reactions by hydrolysis and alcoholysis are in general practical and widely employed strategies in synthesis[9] although, in most cases, they deal with the handling of toxic and/or expensive reagents, intolerance to highly sensitive groups and the formation of unwanted byproducts. In this respect, new 'green' methods under solvent free conditions have been recently developed.[10]

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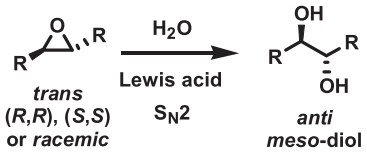
Epoxide hydrolysis usually occurs through a general S_N2 mechanism, with inversion of configuration at the oxiranyl carbon approached by the water molecule. Thus, simple *trans*-symmetrical 2,3-disubstituted oxiranes lead invariably to *meso*-diols as the main reaction product (Scheme 1).



Scheme 1. Hydrolysis of *trans* symmetrical epoxides through S_N2 mechanism.

In the case of certain tertiary mono-aryl substituted oxiranes consistent amounts of *syn* adducts in the acid hydrolysis were justified by means of an ion-dipole pair mechanism.[11]

Herein we report the direct conversion of different 2,3-diaryloxiranes into the corresponding 1,2-diols (or *vic*-diols) by water in the presence of the acid resin Amberlyst 15.

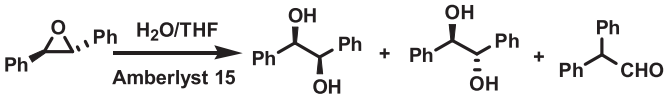
In the last twenty years the chemistry of Amberlyst 15 has experienced a rapid development. Such growing interest is mainly due to its mild and highly selective properties, combined with its environmentally benign character and commercial availability at low cost and it is testified by a recent review, which only partially covered all its wide applicability.[12]

During our studies on oxiranyl ring opening reactions on diaryl epoxides we noted a general stereoretention at the reacting carbon using different nucleophiles, in the presence of Amberlyst 15 as acidic promoter. Thus *ortho*-methoxy and *ortho*-nitro *trans* 2,3-diaryloxiranes were stereoselectively converted to the *syn*-bromohydrins by LiBr/Amb. 15 system,[13] while *trans* 4,5-diaryl-2,2-dimethyl-1,3-dioxolanes were obtained stereospecifically by acetone/Amb. 15 system.[14] This last reaction was successfully applied to a calix[4]arene bis-epoxide[15] and to the synthesis of Combretastatine derivatives.[16]

These results prompted us to investigate water as the nucleophile in the presence of Amberlyst 15 with a variety of 2,3-diaryloxiranes.

2. Results and discussion

We first tested the chemoselectivity of the method, with respect to competitive rearrangement reactions. Thus, we studied the behaviour of the model *trans* stilbene oxide at different reaction temperatures and solvents. The use of an organic water-miscible solvent was required to dissolve the substrate, so H_2O/THF 1:9 mixture was used (Scheme 2).



Scheme 2. Hydrolysis of *trans* stilbene oxide by Amberlyst 15.

The reaction ran slowly at room temperature and, after 24 h, afforded an equimolar mixture of *syn* and *anti* diols, diphenylacetaldehyde and unreacted epoxide. On the other hand, the substrate was completely converted within 2 h 30 min when the reaction was performed at 65 °C, affording the *syn* diol as the main reaction product. These results were then compared to those obtained with *p*-TsOH, which can be considered the homogenous counterpart of Amberlyst 15.

Using *p*-TsOH (20% mol) as acidic catalyst, at room temperature, the conversion was<5% after 48 h while at 65 °C the reaction was complete within 12 h. Encouraged by the higher reaction rates using Amberlyst 15 and the positive effect of the temperature on the efficiency and the stereochemical outcome of the reaction, we extended our procedure to substituted *trans* 2,3-diaryloxiranes. In this way, we could evaluate the effect of different substituents and their position, to achieve diols bearing an extra coordinating group.

Chiral diols are frequently used ligands in asymmetric transformations.[17] They have been successfully employed as enantioselective hydrogen-bonding organocatalysts in hetero-Diels–Alder reactions,[18] in various asymmetric cycloaddition reactions,[19,20] in asymmetric *N*-nitroso aldol reactions of enamines[21] and in enantioselective, vinylogous Mukaiyama aldol reactions,[22] as well as additives in direct aldol reaction catalysed by Proline.[23] Also the substitution pattern of the chiral diol unit may have a great influence on the enantioselectivity of the reaction. [17a]

The catalytic asymmetric dihydroxylation of olefins is by far the most used method for their synthesis.[24] Despite its widespread application, the high cost, hazardous toxicity, volatility and contamination of products with osmium are the main drawbacks, notably in the field of green chemistry. This is highly pointed out by the literature on immobilization of the catalyst on suitable inorganic or organic supports as polymers,[25] dendrimers,[26] ion-exchange resins,[27] silica gels,[28] hydroxyapatites,[29] fullerenes,[30] mesoporous and microporous solids.[31] In particular, substituted stilbene derivatives are rarely encountered.[32]

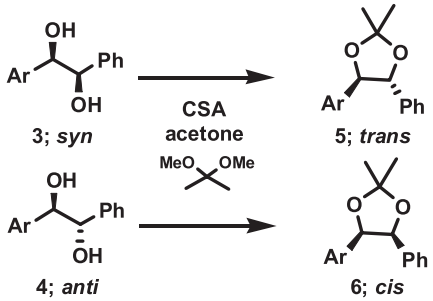
Thus a series of new enantioenriched 2-aryl-3-phenyloxiranes was prepared by asymmetric sulfur ylide mediated epoxidation of aldehydes,[33] using Isothiocineole as chiral precursor, which is readily available in both enantiomeric forms and has been recently shown to be highly efficient in epoxidation and aziridination reactions, with high levels of enantioselectivity.[34]

Reactions of the corresponding benzyl sulfonium salt[35] with aromatic aldehydes in presence of KOH as a base, in either H_2O/CH_3CN or *t*-BuOH/CH_3CN solvent mixtures, worked smoothly well in all cases, furnishing good yields and very high levels of diastereo- and enantioselectivity (Table 1).

The method confirmed its wide applicability with aromatic aldehydes. Isothiocineole was always recovered at the end of the purification in 75–85% yield, thus underlining the practical value of this stoichiometric enantioselective epoxidation.

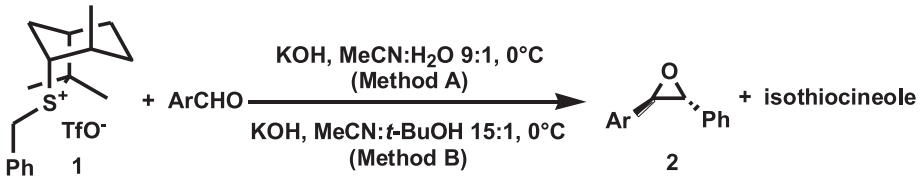
Epoxides were then tested in different hydrolytic conditions in the presence of Amberlyst 15 and the results are collected in Table 2.

The relative stereochemistry (*syn* vs *anti*) of diols was determined by stereospecific formation of the corresponding 2,2-dimethyl-1,3-dioxolanes (Scheme 3) and determination of the *trans*/*cis* ratio of the products.[36]



Scheme 3. Formation of 2,2-dimethyl-1,3-dioxolanes from the parent diols.

Table 1
Preparation of enantioenriched *trans* 2-aryl-3-phenyloxiranes



Entry	Ar	Method	Prod., yield (%)[a]	*d.r.*[b] *(trans/cis)*	*e.r.(trans)*[c]
1	*o*-Br-C_6H_4	B	**2a**, 60[d]	95/5	97/3
2	*o*-Cl-C_6H_4	B	**2b**, 60[d]	95/5	96/4
3	*o*-NO_2-C_6H_4	A	**2c**, 80	only *trans*	>99/1
4	*o*-CH_3O–C_6H_4	B	**2d**, 88	only *trans*	>99/1
5	*o*-TsO-C_6H_4	B	**2e**, 68	only *trans*	95/5
6	*o*-TIPSO-C_6H_4	B	**2f**, 65[d]	only *trans*	>99/1
7	*o*-BnO-C_6H_4	B	**2g**, 80	only *trans*	>99/1
8	3′,5′-di-CH_3O-C_6H_3	A	**2h**, 78	only *trans*	95/5
9	*p*-NO_2-C_6H_4	A	**2i**, 70	only *trans*	95/5

[a] Isolated Yield.
[b] *trans/cis*.
[c] Determined by chiral HPLC; see Experimental Section for details.
[d] The main product was isolated by preparative TLC.

Table 2
Hydrolysis of 2-aryl-3-phenyloxiranes by Amberlyst 15

Entry	Ar	Method[a]	Time (h)	Yield (%)[b]	*syn/anti* (**3**/**4**)
1	*o*-Br-C_6H_4 (**2a**)	A	20	63	(**3a**/**4a**) 3/1
2	*o*-Br-C_6H_4 (**2a**)	B	2	55	(**3a**/**4a**) 3/1
3	*o*-Cl-C_6H_4 (**2b**)	A	20	65	(**3b**/**4b**) 3/1
4	*o*-Cl-C_6H_4 (**2b**)	B	2	57	(**3b**/**4b**) 3/1
5	*o*-NO_2-C_6H_4 (**2c**)	A	11	75	only *syn* (**3c**)
6	*o*-CH_3O–C_6H_4 (**2d**)	A	2	70	(**3d**/**4d**) 6/1
7	*o*-TsO-C_6H_4 (**2e**)	A	24	60	(**3e**/**4e**) 3/1
8	*o*-TsO-C_6H_4 (**2e**)	B	3	55	(**3e**/**4e**) 3/1
9	*o*-TIPSO-C_6H_4 (**2f**)	A	2	70	only *syn* (**3f**)
10	*o*-BnO-C_6H_4 (**2g**)	A	2	65	(**3g**/**4g**) 10/1
11	3′,5′-di-CH_3O-C_6H_3 (**2h**)	A	4	80	(**3h**/**4h**) 3/2
12	*p*-NO_2-C_6H_4 (**2i**)	A	24	80	(**3i**/**4i**) 1/1

[a] All the reactions were performed with 660 mg Amb. 15 per mmol of the substrate in 0.1 M H_2O/org. solv. 1:9 solution.
[b] Isolated yield.

As it can be noted in Table 2, the diols were obtained in good yield within acceptable reaction time. In certain cases (entries 2, 4 and 8) the use of the higher boiling dioxane allowed the reaction time to be considerably reduced. Comparing the results of *ortho*- versus *para*-substituted substrates the stereoselectivity of the reaction was deeply affected by the position of the substituent. In the presence of an *ortho*-substituent the *syn* isomer was always the main product, the stereoisomeric ratio ranging between 3/1 for *o*-Br, *o*-Cl and *o*-OTs derivatives, to 10/1 in the case of *o*-OBn ones and complete stereoselectivity in the case of *o*-NO_2 and *o*-OTIPS diols. If no *ortho*-substituent is present, as in the case of 3′,5′-dimethoxy and *p*-NO_2 derivatives, *syn*/*anti* ratio dropped to 3/2 and 1/1, respectively.

From a deeper analysis of the results obtained for *ortho*-substituted epoxides, the type of substituent played a decisive role in boosting the stereoselectivity from moderate ratios (*o*-Br, *o*-Cl, *o*-OTs derivatives) to synthetically useful ones (*o*-NO_2, *o*-OCH_3, *o*-OBn, *o*-OTIPS[37]), which afforded *syn* diols in >60% chemical yield. While electronic properties of the substituents seem to have no effect on the stereoselectivity (*o*-NO_2, and *o*-OTIPS epoxides **2c** and **2f** gave the same results), the coordination ability of the heteroatoms in the substituent can be invoked to explain the observed stereochemical outcome. Cationic chelates of type **A** and **B** can be proposed, in which the substituent hinders the *anti* position to the approaching nucleophile (Fig. 1). Five-membered chelates **A**, in which the positive charge is partially released to the X group, are more favoured in the case of highly coordinating OCH_3, OTIPS and OBn substituents (entries 6, 9 and 10) than in the case of Br, Cl and OTs (entries 1–4, 7–8). In the case of *o*-NO_2 derivative the six member chelate **B** or a neighbouring group inversion can explain the complete stereoselectivity toward the *syn* diol.

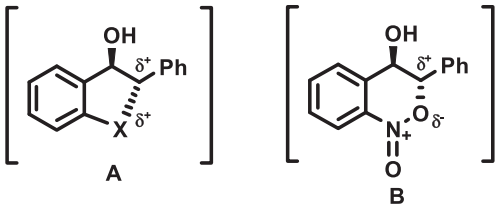


Fig. 1. Proposed cationic intermediates.

Apart from mechanistic considerations, the synthetic value of the procedure is unquestionable, considering, at least, the synthetic versatility of *o*-NO_2- and *o*-OTIPS substituted *syn* diols **3c** and **3f** and their optical purity, which remained the same of the parent epoxides.

3. Conclusions

In conclusion, Amberlyst 15, THF/H_2O system proved to be efficient for the stereoselective conversion of enantioenriched *ortho* substituted *trans* 2-aryl-3-phenyl-oxiranes to corresponding chiral 1,2-diols, which are useful intermediates to polydentate organocatalysts and ligands.

4. Experimental section

4.1. General

All solvents or reagents were purified according to literature procedures. IR data were collected on a Perkin–Elmer Model 2000 FTIR spectrometer. ^{1}H NMR spectra were recorded on a high field NMR spectrometer (at 500 or 400 MHz) and are reported relative to $CDCl_3$ signal. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and b, broad. ^{13}C NMR spectra were recorded on a high field NMR spectrometer (at 125 or 100 MHz). Data for ^{13}C NMR spectra are reported in terms of chemical shift and are reported in parts per million (ppm, δ). Thin-layer chromatography (TLC) was carried out using pre-coated silica gel sheets (Merck 60 F254). Visual detection was performed using UV light at 254 nm and phosphomolybdic acid. Column chromatography was carried out on Merck silica gel (0.063–0.200 mm particle size) by progressive elution with suitable solvent mixtures.

MS spectra were recorded on a gas-chromatograph equipped with an MS capillary column (30 m×0.25 mm i.d.×0.25 μm film thickness; injection temperature: 250 °C, column temperature program: 100 °C for 3 min, then 10 °C min^{-1} until 250 °C) and a mass selective detector (mass range: 15–800 amu; scan rate: 1.9 scans s^{-1}; EM voltage: 1435). Enantiomeric excess was determined by HPLC analysis performed on a JASCO PU-1580 pump with a Varian 2550 UV detector and Daicel CHIRALCEL® columns (internal diameter 4.6 mm, column length 250 mm, particle size 10 μm). The optical rotation was evaluated by using a JASCO Mod Dip-370 polarimeter.

(*1R*,*4R*,*5R*,*6R*)-6-Benzyl-4,7,7-trimethyl-6-thioniabicyclo[3.2.1] octane trifluoromethanesulfonate was prepared according to literature procedure.[18]

4.2. General epoxidation

4.2.1. Method A. Sulfonium salt (820 mg, 2.0 mmol, 1 equiv) was dissolved in a 9:1 mixture of acetonitrile and water (10 mL). Then the aldehyde (1.1 equiv) was added. The solution was then placed in a 0 °C bath and freshly ground KOH (123 mg, 1.1 equiv) was added. The solution was stirred at 0 °C overnight. Acetonitrile was then evaporated under reduced pressure and dichloromethane (20 mL) and water (20 mL) were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (2×20 mL). The organic phases were then combined, dried with MgSO4 and the solvent evaporated under reduced pressure. Products were purified by chromatography on silica gel at atmospheric pressure (unless stated otherwise).

4.2.2. Method B. Sulfonium salt (410 mg, 1 mmol, 1 equiv) was dissolved in a 15:1 mixture of acetonitrile and *tert*-butanol (6 mL). Then the aldehyde (2 equiv) was added. The solution was then placed in a 0 °C bath and freshly ground KOH (62 mg, 1.1 equiv) was added. The solution was stirred at 0 °C overnight. Acetonitrile and *tert*-butanol were then evaporated under reduced pressure and dichloromethane (15 mL) and water (15 mL) was added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (2×15 mL). The organic phases were then combined, dried with $MgSO_4$ and the solvent evaporated under reduced pressure. Products were purified by chromatography on silica gel at atmospheric pressure (unless stated otherwise).

In each case the chiral-phase HPLC *Rt* given is for the major enantiomer obtained using salts derived from **(*R*)-1**.

*4.2.3. trans (2R,3R)-2-(2-Bromo-phenyl)-3-phenyl-oxirane **2a**.* *trans* (2*R*,3*R*)-2-(2-Bromo-phenyl)-3-phenyl-oxirane **2a** was obtained (165 mg, 60%) as a pale yellow oil after chromatografic purification on preparative thin layer silica gel plate (2% Et_2O/PE). [Found: C, 60.85; H, 4.10. $C_{14}H_{11}BrO$ requires C, 61.11; H, 4.03%]; R_f (2% Et_2O/PE) 0.60; $[\alpha]_D^{25}$ +48 (*c*=1.2, CH_2Cl_2); *ee* 94%. HPLC conditions: Chiralcel OD column, 5% *i*PrOH/*n*-hexane, 1 mL/min t_R=7.87 min; IR (neat), ν_{max} 2962, 2924, 1472, 1456, 1260, 1091, 1024, 798, 696, 612 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.68 (*d*, 1H, *J*=1.6 Hz), 4.10 (*d*, 1H, *J*=1.6 Hz), 7.30–7.34 (*m*, 8H), 7.49 (*d*, 1H, *J*=8.4 Hz); δ_C (100 MHz, $CDCl_3$); 62.1, 62.2, 122.5, 125.7, 126.2, 127.6, 128.4, 128.6, 129.3, 132.3, 136.6, 136.8. MS (*m*/*z*, %): 274 (28) $[M]^+$, 276 (28) $[M+2]^+$, 245 (38), 247 (37), 183 (26), 185 (25), 89 (100).

(2*S*,3*S*)-enantiomer was prepared from sulfonium salt derived from (+)-isothiocineole. t_R=4.97 min *ee* 94%. $[\alpha]_D$[25] −49 (*c*=0.5, CH_2Cl_2).

*4.2.4. trans (2R,3R)-2-(2-Chloro-phenyl)-3-phenyl-oxirane **2b**.* *trans* (2*R*,3*R*)-2-(2-Chloro-phenyl)-3-phenyl-oxirane **2b** was obtained (138 mg, 60%) as a pale yellow oil after chromatografic purification on preparative thin layer silica gel plate (R_f 0.45, 2% Et_2O/PE): [Found: C, 72.75; H, 4.90. $C_{14}H_{11}ClO$ requires C, 72.89; H, 4.81%]; R_f (2% Et_2O/PE) 0.45; $[\alpha]_D^{25}$ +56 (*c*=0.6, $CHCl_3$); *ee* 92%. HPLC conditions: Chiralcel OD column, 5% *i*PrOH/*n*-hexane, 0.5 ml/min; t_R=17.29 min; IR (neat), ν_{max} 3064, 2925, 1456, 1051, 885, 700, 612 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 4.25 (*d*, 1H, *J*=2.0 Hz), 3.78 (*d*, 1H, *J*=2.0 Hz), 7.20–7.40 (*m*, 9H); δ_C (125 MHz, $CDCl_3$) 59.9, 62.2, 125.7, 125.8, 127.1, 128.4, 128.6, 129.0, 129.1, 133.2, 135.1, 137.6. MS (*m*/*z*, %): 230 (43) $[M]^+$, 232 (14) $[M+2]^+$, 201 (78) $[M-29]^+$, 203 (26) $[M-27]^+$, 139 (41) $[M-91]^+$, 141 (13) $[M-89]^+$, 89 (100).

(2*S*,3*S*)-enantiomer was prepared from sulfonium salt derived from (+)-isothiocineole *ee* 92%. t_R=10.32 min $[\alpha]_D^{25}$ −60 (*c*=0.8, $CHCl_3$).

*4.2.5. trans (2R,3R)-4-Methyl-benzenesulfinic acid 2-(3-phenyl-oxiranyl)-phenyl ester **2e**.* *trans* (2*R*,3*R*)-4-Methyl-benzenesulfinic acid 2-(3-phenyl-oxiranyl)-phenyl ester **2e** was obtained (249 mg, 68%) as colourless oil after purification by column chromatography at atmospheric pressure (30% Et_2O/EP); [Found: C, 72.1; H, 5.0; S, 9.1. $C_{21}H_{18}O_3S$ requires C, 71.98; H, 5.18; S, 9.15%]; R_f (30% Et_2O/EP) 0.6; $[\alpha]_D^{25}$ +59 (*c* 0.8, $CHCl_3$); *ee* 90%. HPLC Chiralcel OD, *n*-hexane/2-propanol 90/10, 1.0 mL/min; t_R=8.97 min; IR (neat), ν_{max} 3033, 2925, 1494, 1455, 1361, 1291, 1178, 850, 800, 650 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 2.35 (*s*, 3H), 3.98 (br s, 1H), 3.72 (br s, 1H), 7.08 (*d*, *J*=8.5 Hz, 2H), 7.19–7.41 (*m*, 9H), 7.54 (*d*, *J*=8.5 Hz, 2H); δ_C (125 MHz, $CDCl_3$) 21.7, 57.6, 62.5, 122.7, 125.9, 125.9, 127.6, 128.2, 128.5, 128.6, 129.1, 129.9, 131.1, 132.3, 136.6, 145.6, 147.9. MS (*m*/*z*, %): 366 (1) $[M^+]$, 337 (20) $[M-29]^+$, 275 (35) $[M-91]^+$, 207 (18), 183 (100).

(2*S*,3*S*)-enantiomer was prepared from sulfonium salt derived from (+)-isothiocineole. *ee* 90%. t_R=11.98 min $[\alpha]_D^{25}$ −60 (*c*=0.8, $CHCl_3$).

4.2.6. trans (2R,3R)-3-phenyl-2-(2-triisopropylsilyloxy-phenyl)-oxirane ***2f****. trans* (2*R*,3*R*)-3-Phenyl-2-(2-triisopropylsilyloxy-phenyl)-oxirane **2f** was obtained (239 mg, 65%) as pale yellow oil after chromatografic purification on preparative thin layer plate (2% Et_2O/PE); [Found: C, 74.8; H, 8.9; Si, 7.5. $C_{23}H_{32}O_2Si$ requires C, 74.95; H, 8.75; Si, 7.62%]; R_f (2% Et_2O/EP) 0.5; $[\alpha]_D^{25}$ +32 (*c* 1.2, $CHCl_3$); *ee* 99%. HPLC Chiralcel OD, *n*-hexane/2-propanol 99/1, 0.5 mL/min; IR (neat), ν_{max} 3050, 2965, 1465, 1405, 752, 696, 614 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.54 (*d*, *J*=8.6 Hz, 9H), 0.76 (*d*, *J*=8.6 Hz, 9H), 3.74 (br s, 1H), 4.28 (br s, 1H), 6.83 (*d*, *J*=8.8 Hz, 1H), 6.99 (dd, J_1=J_2=8.8 Hz, 1H), 7.18 (dd, J_1=J_2=8.8 Hz, 1H), 7.22–7.40 (*m*, 6H). δ_C (100 MHz, $CDCl_3$) 17.8, 29.7, 59.4, 62.4, 118.2, 121.1, 124.9, 125.4, 127.7, 128.1, 128.3, 128.6, 137.3, 154.6. MS (*m*/*z*, %): 368 (6) [M^+], 327 (7), 325 (100), 237 (8), 165 (9).

(2*S*,3*S*)-enantiomer was prepared from sulfonium salt derived from (+)-isothiocineole.

ee 99%. $[\alpha]_D^{25}$ −31 (*c*=1.2, $CHCl_3$).

4.2.7. trans (2R,3R)-2-(2-Benzyloxy-phenyl)-3-phenyl-oxirane ***2g****. trans* (2*R*,3*R*)-2-(2-Benzyloxy-phenyl)-3-phenyl-oxirane **2g** was obtained (242 mg, 80%) as colourless oil after purification by column chromatography at atmospheric pressure (20% Et_2O/EP); [Found: C, 83.3; H, 6.1. $C_{21}H_{18}O_2$ requires C, 83.42; H, 6.00%]; R_f (20% Et_2O/EP) 0.4; $[\alpha]_D^{25}$ +34 (*c* 1.05, $CHCl_3$); *ee* 99%. HPLC Chiralcel OD, *n*-hexane/2-propanol 98/2, 0.5 mL/min; t_R=12.87 min; IR (neat), ν_{max} 3013, 3005, 1497, 1452, 1253, 1216, 859, 761, 696 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 3.81 (*d*, *J*=1.5 Hz, 1H), 4.30 (*d*, *J*=1.5 Hz, 1H), 5.08 (br s, 2H), 6.92 (*d*, *J*=8.2 Hz, 1H), 6.99 (dd, J_1=J_2=7.2 Hz, 1H), 7.24–7.35 (*m*, 12H); δ_C (125 MHz, $CDCl_3$) 58.4, 62.1, 70.0, 111.8, 121.1, 125.2, 125.7, 126.3, 126.8, 127.7, 128.1, 128.4, 128.4, 128.8, 136.8, 137.3, 157.1; MS (*m*/*z*, %): 302 [M^+] (1), 273 (10), 212 (10), 211 (67), 183 (29), 181 (19), 167 (14), 91 (100).

(2*S*,3*S*)-enantiomer was prepared from sulfonium salt derived from (+)-isothiocineole. t_R=10.64 min $[\alpha]_D^{25}$ −34 (*c* 0.75, $CHCl_3$).

4.2.8. trans (2R,3R)-2-(3,5-Dimethoxy-phenyl)-3-phenyl-oxirane ***2h****. trans* (2*R*,3*R*)-2-(3,5-Dimethoxy-phenyl)-3-phenyl-oxirane **2h** was obtained (200 mg, 78%) as colourless oil after purification by column chromatography at atmospheric pressure (15% Et_2O/EP); [Found: C, 74.8; H, 6.4. $C_{16}H_{16}O_3$ requires C, 74.98; H, 6.29%]; R_f (15% Et_2O/EP) 0.5; $[\alpha]_D^{25}$ +38 (*c* 1.2, CH_2Cl_2); *ee* 90%, HPLC Chiralcel OD, *n*-hexane/2-propanol 98/2, 0.5 mL/min t_R=10.23 min; IR (neat), ν_{max} 3014, 2939, 1607, 1463, 1353, 1215, 1156, 1065, 837, 754, 700 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.82 (*s*, 3H), 3.85 (br s, 2H), 6.45 (dd, J_1=J_2=2.3 Hz, 1H), 6.54 (*d*, *J*=2.4 Hz, 2H), 7.35–7.42 (*m*, 5H). δ_C (100 MHz, $CDCl_3$) 55.4, 62.6, 62.8, 100.5, 103.1, 125.5, 128.3, 128.5, 136.9, 139.6, 161.1; MS (*m*/*z*, %): 256 (45) [M^+], 228 (60), 227 (100), 212 (37), 197 (22), 196 (35).

(2*S*,3*S*)-enantiomer was prepared from sulfonium salt derived from (+)-isothiocineole. t_R=9.61 min $[\alpha]_D^{25}$ −192 (*c* 1.1, $CHCl_3$).

4.2.9. General hydrolysis method. Amberlyst 15 (660 mg) was added in one portion to a solution of diaryl oxirane (1 mmol) in the appropriate solvent mixture (THF/H_2O 9:1, **Method A**, 1,4-dioxane/H_2O 9:1, **Method B**) (10 mL) and the mixture was kept stirring at reflux temperature till completion of the reaction (by TLC and GC analysis). The mixture was cooled to rt, the Amberlyst was filtered off and $NaHCO_3$ s.s (10 mL) was poured into the solution. The organic solvent was then evaporated and the aqueous layer was extracted with Et_2O (3×10 mL). The combined organic layers were dried with Na_2SO_4 and the solvent was removed. The crude product was purified by silica gel chromatography to give the mixture of diols, which was analysed by ^1H NMR and used as substrate for the formation of the corresponding acetals.

4.2.9.1. syn (1R,2R)-1-(2-Nitro-phenyl)-2-phenyl-ethane-1,2-diol ***3c****. syn* (1*R*,2*R*)-1-(2-Nitro-phenyl)-2-phenyl-ethane-1,2-diol **3c** was obtained (194 mg, 75%, method A) as pale yellow oil after chromatographic purification (50% E_2O/EP); [Found: C, 64.7; H, 5.1. $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05]; R_f (50% E_2O/EP) 0.4; $[\alpha]_D^{25}$ −16 (*c* 1.0, $CHCl_3$) *ee* 99%;[38] IR (neat), ν_{max} 3600–3200 (br s), 2950, 1524, 1345, 758, 700 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 2.67–3.05 (br s, 2H), 4.94 (*d*, *J*=4.0 Hz, 1H), 5.51 (*d*, *J*=4.0 Hz, 1H), 7.29–7.36 (m, 5H), 7.44 (dd, J_1=J_2=7.8 Hz, 1H), 7.64 (dd, J_1=J_2=7.8 Hz, 1H), 7.80 (*d*, *J*=7.8 Hz, 1H), 7.89 (*d*, *J*=7.8 Hz, 1H); δ_C (125 MHz, $CDCl_3$) 73.1, 76.4, 124.5, 126.2, 128.0, 128.5, 128.5, 129.3, 133.1, 136.2, 140.1, 147.9.

(*S*,*S*)-*syn* diol was prepared from the parent (*S*,*S*)-epoxide.

ee 99%[21] $[\alpha]_D^{25}$ +15 (*c* 1.0, $CHCl_3$).

4.2.9.2. (R,R)-syn 2-phenyl-1-(2-Triisopropylsilyloxy-phenyl)-ethane-1,2-diol ***3f****.* (*R*,*R*)-*syn* 2-phenyl-1-(2-Triisopropylsilyloxy-phenyl)-ethane-1,2-diol **3f** was obtained (270 mg, 70% by method A) as colourless oil after chromatographic purification (5% Et_2O/$CHCl_3$). [Found: C, 71.5; H, 8.7. $C_{23}H_{34}O_3Si$ requires C, 71.46; H, 8.86]; $[\alpha]_D^{25}$ +37 (*c* 1.3, $CHCl_3$); *ee* 99%;[21] IR (neat), ν_{max} 3500–3200 (br s), 3030, 2980, 1450, 1405, 750, 700 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.12 (*d*, *J*=7.6 Hz, 18H), 1.30–1.40 (*m*, 3H), 3.15 (br s, 1H, OH), 3.29 (*d*, *J*=6.5 Hz, 1H, OH), 4.90 (*d*, *J*=6.8 Hz, 1H), 4.93 (dd, J_1=6.8 Hz, J_2=6.5 Hz, 1H), 6.77 (d, *J*=8.1 Hz, 1H), 6.84 (dd, J_1=J_2=8.1 Hz, 1H), 7.01 (dd, J_1=8.0 Hz, J_2=1.6 Hz, 1H), 7.11 (ddd, J_1=J_2=8.1 Hz, J_3=1.6 Hz, 1H), 7.19–7.39 (*m*, 5H). δ_C (125 MHz, $CDCl_3$) 13.1, 18.1, 76.1, 76.7, 117.8, 120.8, 126.8, 127.3, 127.6, 128.0, 128.6, 129.2, 140.2, 153.3.

(*S*,*S*)-*syn* diol was prepared from the corresponding (*S*,*S*)-epoxide.

ee 99%.[21] $[\alpha]_D^{25}$ −35 (*c* 1.0, $CHCl_3$).

4.2.9.3. syn and anti 1-(2-Benzyloxy-phenyl)-2-phenyl-ethane-1,2-diols ***3g*** *and* ***4g****. syn* and *anti* 1-(2-Benzyloxy-phenyl)-2-phenyl-ethane-1,2-diols **3g** and **4g** were obtained (208 mg, 65%) as *syn*/*anti* 10:1 mixture after chromatographic purification (5% CH_3OH/CH_2Cl_2); δ_H (500 MHz, $CDCl_3$) 2.70 (br s, 1H, OH, *anti*), 2.92 (br s, 1H, OH, *anti*), 3.10 (br s, 1H, OH, *syn*), 3.19 (br s, 1H, OH, *syn*), 4.86 (*m*, 1H, C*H*OH, *syn* and *anti*), 4.89 (*d*, *J*=11.2 Hz, 1H, C*H*OH, *syn* and *anti*), 4.95 (*m*, 1H, C*H*OH, *syn* and *anti*), 5.00 (*d*, *J*=11.2 Hz, 1H, C*H*OH, *syn* and *anti*), 6.88 (*m*, 2H, *syn* and *anti*), 7.08–7.22 (*m*, 7H), 7.33–7.39 (*m*, 5H).

4.2.10. Conversion of the diols to acetals: general procedure. A solution of diols (1 mmol), 2,2-dimethoxypropane (0.2 mL), camphorsulfonic acid (CSA, 20 mg) in acetone (20 mL) was kept stirring at room temperature till completion of the reaction (ca. 1–2 h). The mixture was cooled to 0 °C and $NaHCO_3$ s.s (20 mL) was poured into the solution. The organic solvent was then evaporated and the aqueous layer was extracted with Et_2O (3×10 mL). The combined organic layers were dried with Na_2SO_4 and the solvent was removed. The crude product was purified by silica gel chromatography to give the corresponding acetals, which were analysed by ^1H NMR.

4.2.10.1. trans (R,R) 4-(2-Bromo-phenyl)-2,2-dimethyl-5-phenyl-[1,3]dioxolane ***5a****. trans* (*R*,*R*) 4-(2-Bromo-phenyl)-2,2-dimethyl-5-phenyl-[1,3]dioxolane **5a** was obtained (232 mg, 70%) from the parent *syn*/*anti* mixture of diols after chromatographic purification (5% Et_2O/EP). [Found: C, 61.4; H, 5.1. $C_{17}H_{17}BrO_2$ requires C, 61.28; H, 5.14]; $[\alpha]_D^{25}$ +9 (*c* 1.0 CH_2Cl_2); *ee* 94%. HPLC Chiralcel OD, *n*-hexane/2-propanol 95/5, 0.5 mL/min t_R=11.78 min; IR (neat), ν_{max} 2955,

2910, 1490, 1450, 1260, 1030, 800, 705, 630 cm^{-1};δ_H (400 MHz, $CDCl_3$) 1.71 (*s*, 3H), 1.72 (*s*, 3H), 4.74 (*d*, *J*=8.8 Hz, 1H), 5.27 (*d*, *J*=8.8 Hz, 1H), 7.17 (*ddd*, J_1=J_2=7.8 Hz, J_3=1.8 Hz, 1H), 7.24–7.40 (*m*, 6H), 7.43 (dd, J_1=J_2=7.8 Hz, 1H), 7.70 (dd, J_1=7.8 Hz, J_2=1.8 Hz, 1H); δ_C (100 MHz, $CDCl_3$) 27.2, 27.2, 83.3, 85.8, 109.5, 126.7, 127.1, 127.7, 128.3, 128.4, 128.6, 129.6, 132.9, 135.8, 136.1; MS (*m*/*z*, %): 334 $[M+2]^+$ (0.2), 332 $[M^+]$ (0.2), 277 (7), 275 (7), 259 (6), 257 (6), 228 (80), 226 (80), 147 (100).

(*S*,*S*)-*trans* dioxolane was prepared from the corresponding (*S*,*S*)-diol. *ee* 94%. t_R=10.73 min $[\alpha]_D^{25}$ −9 (*c* 1.0 CH_2Cl_2).

4.2.10.2. cis 4-(2-Bromo-phenyl)-2,2-dimethyl-5-phenyl-[1,3]dioxolane ***6a****. cis* 4-(2-Bromo-phenyl)-2,2-dimethyl-5-phenyl-[1,3]dioxolane **6a** was obtained (93 mg, 28%) after chromatographic purification (5% Et_2O/EP); [Found: C, 61.2; H, 5.2. $C_{17}H_{17}BrO_2$ requires C, 61.28; H, 5.14; IR (neat), ν_{max} 2962, 2924, 1472, 1460, 1260, 1100, 1025, 797, 690, 620 cm^{-1};δ_H (400 MHz, $CDCl_3$) characteristic signals 1.65 (*s*, 3H), 1.86 (*s*, 3H), 5.67 (*d*, *J*=7.2 Hz, 1H), 5.89 (*d*, *J*=7.2 Hz, 1H), 6.89–7.63 (aromatics); MS (*m*/*z*, %): 334 $[M+2]^+$ (0.2), 332 $[M^+]$ (0.2), 277 (6), 275 (6), 259 (5), 257 (5), 228 (83), 226 (83), 185 (13), 183 (13), 171 (28), 169 (28), 148 (83), 147 (100).

4.2.10.3. trans (R,R)-4-(2-Chloro-phenyl)-2,2-dimethyl-5-phenyl-[1,3]dioxolane ***5b****. trans* (*R*,*R*)-4-(2-Chloro-phenyl)-2,2-dimethyl-5-phenyl-[1,3]dioxolane **5b** was obtained (202 mg, 70%) from the parent *syn*/*anti* 3:1 mixture of diols after chromatographic purification (5% Et_2O/EP). [Found: C, 70.8; H, 5.9. $C_{17}H_{17}ClO_2$ C, 70.71; H, 5.93]. $[\alpha]_D^{25}$ +8 (*c* 0.5 CH_2Cl_2); *ee* 92% HPLC Chiralcel OD, *n*-hexane/2-propanol 95/5, 0.5 mL/min t_R=11.02 min; IR (neat), ν_{max} 3060, 2940, 1450, 1035, 880, 705, 602 cm^{-1};δ_H (500 MHz, $CDCl_3$) 1.69 (*s*, 6H) 4.75 (*d*, *J*=8.5 Hz, 1H), 5.30 (*d*, *J*=8.5 Hz, 1H), 6.90–7.36 (*m*, 8H), 7.70 (*d*, *J*=7.5 Hz, 1H); δ_C (100 MHz, $CDCl_3$) 27.2, 27.2, 81.1, 85.6, 103.6, 126.6, 127.1, 128.3, 128.4, 128.6, 129.1, 129.2, 129.6, 130.0, 136.2, 145.2; MS (*m*/*z*, %): 286 $[M^+]$, 288 $[M+2]^+$, 213 (8), 215 (3), 125 (43), 127 (15), 182 (100).

(*S*,*S*)-*trans* dioxolane was prepared from the corresponding (*S*,*S*)-diol. *ee* 92%. t_R=7.41 min $[\alpha]_D^{25}$ −8 (*c* 1.0 CH_2Cl_2).

4.2.10.4. cis 4-(2-Chloro-phenyl)-2,2-dimethyl-5-phenyl-[1,3]dioxolane ***6b****. cis* 4-(2-Chloro-phenyl)-2,2-dimethyl-5-phenyl-[1,3]dioxolane **6b** was obtained (81 mg, 27%) after chromatographic purification (5% Et_2O/EP). [Found: C, 70.6; H, 6.0. $C_{17}H_{17}ClO_2$ requires C, 70.71; H, 5.93]. IR (neat), ν_{max} 3064, 2925, 1456, 1060, 880, 700, 610 cm^{-1};δ_H (500 MHz, $CDCl_3$) 1.62 (*s*, 3H), 1.83 (*s*, 3H), 5.61 (*d*, *J*=7.0 Hz, 1H), 5.90 (*d*, *J*=7.0 Hz, 1H), 7.03–6.89 (*m*, 8H), 7.26 (*d*, *J*=9.5 Hz, 1H); δ_C (125 MHz, $CDCl_3$) 24.2, 26.6, 78.0, 80.4, 108.7, 126.1, 127.1, 127.3, 127.3, 128.0, 128.2, 128.4, 128.4, 131.6, 135.6, 137.8; MS (*m*/*z*, %): 286 $[M]^+$, 288 $[M+2]^+$, 213 (7), 215 (2), 182 (94), 184 (31), 125 (45), 127 (14), 147 (100).

4.2.10.5. trans (R,R) [2-(2,2-Dimethyl-5-phenyl-[1,3]dioxolan-4-yl)-phenoxy]-triisopropyl-silane ***5f****. trans* (*R*,*R*) [2-(2,2-Dimethyl-5-phenyl-[1,3]dioxolan-4-yl)-phenoxy]-triisopropyl-silane **5f** was obtained (405 mg, 95%) as colourless oil after chromatographic purification (20% Et_2O/EP). [Found C, 73.2; H, 9.0. $C_{26}H_{38}O_3Si$ requires C, 73.19; H, 8.98]. $[\alpha]_D^{25}$=+23 (*c* 1.1, $CHCl_3$); *ee* 99%. HPLC Chiralcel OD, *n*-hexane/2-propanol 98/2, 0.5 mL/min t_R=4.45 min; IR (neat), ν_{max} 3030, 2980, 1452, 1412, 758, 691, 605 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 0.90 (*d*, *J*=7.3 Hz, 18H), 1.05–1.07 (*m*, 3H), 1.64 (*s*, 3H), 1.68 (*s*, 3H), 4.86 (*d*, *J*=8.7 Hz, 1H), 5.40 (*d*, *J*=8.7 Hz, 1H), 6.72 (*d*, *J*=8.2 Hz, 1H), 7.03 (dd, J_1=J_2=8.2 Hz, 1H), 7.15 (dd, J_1=J_2=8.2 Hz, 1H), 7.24–7.60 (*m*, 5H), 7.61 (*d*, *J*=8.2 Hz, 1H); δ_C (125 MHz, $CDCl_3$) 12.8, 17.9, 27.0, 27.5, 77.7, 84.9, 108.7, 118.2, 121.1, 126.1, 126.9, 127.7, 128.2, 128.4, 129.0, 137.2, 154.4.

(*S*,*S*)-*trans* dioxolane was prepared from the corresponding (*S*,*S*)-diol. *ee* 99%. t_R=3.18 min $[\alpha]_D^{25}$=+21 (*c* 0.7, $CHCl_3$)

4.2.10.6. trans and cis 2,2-Dimethyl-4-(4-nitro-phenyl)-5-phenyl-[1,3]dioxolanes ***5i*** *and* ***6i****. trans* and *cis* 2,2-Dimethyl-4-(4-nitro-phenyl)-5-phenyl-[1,3]dioxolanes **5i** and **6i** were obtained (284 mg, 95%) as *trans*/*cis*=45:55 mixture after chromatographic purification (50% Et_2O/EP). δ_H (400 MHz, $CDCl_3$) 1.64 (*s*, 3H, *cis*), 1.70 (*s*, 3H, *trans*), 1.72 (*s*, 3H, *trans*), 1.85 (*s*, 3H, *cis*), 4.66 (*d*, *J*=8.3 Hz, 1H, *trans*), 4.86 (*d*, *J*=8.3 Hz, 1H, *trans*), 5.58 (A of AB system, J_{AB}=7.8 Hz, 1H, *cis*), 5.61 (A of AB system, J_{AB}=7.8 Hz, 1H, *cis*), 6.99–7.37 (*m*, 5H), 7.92 (*d*, *J*=8.7 Hz, 2H, *cis*+*trans*), 8.18 (*d*, *J*=8.7 Hz, 2H, *cis*+*trans*).

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Supplementary data

Supplementary data (Characterizations of epoxides **2c**, **2d**, **2i**, diols **3a**, **4a**, **3b**, **4b**, **3d**, **4d**, **3e**, **4e**, **3h**, **4h**, **3i**, **4i**, dioxolanes **5c**, **5d**, **6d**, **5e**, **6e**, **5g**, **6g**, **5h**, **6h**) related to this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.06.039.

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35. This was prepared in high yield by alkylation of the sulfide with BnBr and required 24 h at 20 °C.
36. The stereochemistry of the dioxolanes was easily determined by characteristic ^{1}H NMR signal pattern of the two *gem* methyl groups: in the *trans* isomers, possessing a *pseudo-C2* symmetry, the two singlets' shifts differed less than 0. 05 ppm, while in the *cis* isomers they split up more than 0.2 ppm.
37. Given the steric encumbrance of OTIPS group, also an influence of such effect can not be excluded.
38. Calculated by *ee* of the corresponding 2,2-dimethyl-1,3-dioxolane