- 1 Separation of enantiomers of chiral sulfoxides in high-performance liquid
- 2 chromatography with cellulose-based chiral selectors using methanol and methanol-
- 3 water mixtures as mobile phases
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Abstract

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The interplay between structural details of chiral analytes and selectors in the separation of 14 chiral sulfoxides was systematically studied on 18 different polysaccharide-based chiral columns. Retention and enantioselectivity of a set of chiral sulfoxides were of primary interest. Several of chiral columns studied exhibited quite powerful chiral recognition ability in pure methanol. With addition of water to the mobile phase retention increased in the most cases and the separation factor improved. However, several exceptions were also noted. Of monosubstituted phenylcarbamates of cellulose as chiral selectors, chlorosubstituted ones did not show better enantiomer resolving ability compared to unsubstituted cellulose tris(phenylcarbamate). Out of disubstituted phenylcarbamates of cellulose the ones with methylsubstituents showed higher enantiomer resolving ability compared to chlorosubstituted ones and substitution in positions 3 and 5 of the phenyl moiety was clearly advantageous. From disubstituted derivatives those possessing a combination of methyl- and chloro-substituents were advantageous compared to the ones having dimethyl- or dichlorosubstituents. Interesting examples of reversal in enantiomer elution order (EEO) were observed on cellulose tris(4-chloro-3-methylphenylcarbamate)- and cellulose tris(3-chloro-4methylphenylcarbamate)-based chiral stationary phases (CSPs) function of the water content in the mobile phase.

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- **Keywords:** Chiral sulfoxides / Separation of enantiomers / Enantiomer elution
- 38 order/Polysaccharide-based chiral selectors

1 Introduction

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Polysaccharide derivatives belong to the most successful chiral selectors for the separation of enantiomers in liquid phase separation techniques, such as high-performance liquid chromatography (HPLC) [1-3], capillary or nano-liquid chromatography (nano-LC) [4-6] and capillary electrochromatography (CEC) [7-9]. In HPLC polysaccharide derivatives can be used in combination with hydrocarbon-alcohol [1, 2, 10-12], pure polar organic [2, 13-15] and aqueous-organic [2, 16-18] mobile phases. The first of these 3 modes was historically called normal-phase mode and the last reversed-phase mode. Polysaccharide-based chiral stationary phases although follow typical normal-phase LC behavior in hydrocarbon-alcohol mobile phase, several examples of deviation from this behavior have been recently reported [19, 20]. In aqueous-organic mobile phases polysaccharide derivative-based CSPs are known to follow atypical reversed-phase behavior in some cases even up to 30% water (v/v) content [18, 21-23] especially with aprotic organic modifiers such as acetonitrile. The effect of structural variations of polysaccharide-based chiral selectors on their chiral recognition ability towards diverse group of chiral analytes was recognized fairly early [10, 24-26]. A wide variety of chiral analytes were used for evaluating the success rates of various chiral selectors. Thus, in most published work on enantioseparations in HPLC either single or more rarely several columns are evaluated for chiral recognition toward a large set of analytes. However, from a mechanistic viewpoint it is important to study the effect of variations in the structure of chiral selectors in combination with minor variations in the structure of chiral analytes (part of a family of compounds) on enantiomer resolution. In line with this strategy, the present study included various phenylcarbamates of cellulose having electron-withdrawing chloro- and/or electron-donating methyl substituents, or two chloro-, or two methyl- substituents in various positions of the phenyl moieties. The enantiomer resolving ability of such specifically synthetized CSPs along with some

commercially available cellulose-based chiral columns with structurally similar chiral selectors was studied towards 14 chiral sulfoxides with certain structural variability.

2 Materials and Methods

2.1 Chemicals

14 chiral sulfoxides, 2-(benzylsulfinyl)-benzamide (1), 3-(benzylsulfinyl)-benzamide (2), 2-(benzylsulfinyl)-N-methylbenzamide (3), 3-(benzylsulfinyl)-N-methylbenzamide (4), 4-(benzylsulfinyl)-N-methyl-benzamide (6), 2-(benzylsulfinyl)methylbenzoate (11), 3- (benzylsulfinyl)-methylbenzoate (12), 4-(benzylsulfinyl)-methylbenzoate (13), 2-(propylsulfinyl)-N-methylbenzamide (8), 2-(4-nitro-benzylsulfinyl)-N-methylbenzamide (9), 2-(methylsulfinyl)-N-methylbenzamide (7), 2-(benzylsulfinyl)-N,N-dimethylbenzamide (14), 2-(4-trifluoromethyl-benzylsulfinyl)-N-methylbenzamide (10), 2-(benzylsulfinyl)-(dihydronaphthalene)-ethylbenzamide (5), used in this study, were synthesized as described earlier [27, 28]. The structures of these compounds are shown in Fig. 1. HPLC quality solvents such as methanol and water were acquired from Carl Roth (Karlsruhe, Germany).

2.2 Chiral columns

Cellulose derivatives, such as cellulose tris(phenylcarbamate), cellulose tris(2-chlorophenylcarbamate), cellulose tris(3-chlorophenylcarbamate), cellulose tris(4-chlorophenylcarbamate), cellulose tris(2,3-dichlorophenylcarbamate), cellulose tris(2,4-dichlorophenylcarbamate), cellulose tris(2,5-dichlorophenylcarbamate), cellulose tris(2,6-dichlorophenylcarbamate), cellulose tris(3,4-dichlorophenylcarbamate), cellulose tris(3,5-dichlorophenylcarbamate), cellulose tris(2-methylphenylcarbamate), cellulose tris(3-methylphenylcarbamate), cellulose tris(4-methylphenylcarbamate) and cellulose tris(3,4-dimethylphenylcarbamate) were synthesized as described earlier [10, 26]. Cellulose

derivatives were dissolved in appropriate solvents and coated on aminopropylsilanized silica of 5 micrometer nominal particle size and 100 nm nominal pore size (Daiso, Osaka, Japan). The coated materials (chiral stationary phase, CSP) were packed in 4.6 x 250 mm column hardware from Isolation Technologies (Hopedale, MA, USA). Commercially available chiral columns Lux Cellulose-1 [Cellulose tris(3,5-dimethylpnenylcarbamate)], Lux Cellulose-2 [Cellulose tris(3-chloro-4-methylpnenylcarbamate)], Lux Cellulose-3 [Cellulose tris(4-methylbenzoate)] and Lux Cellulose-4 [Cellulose tris(4-chloro-3-methylpnenylcarbamate)], were kindly provided by Phenomenex (Torrance, CA, USA). All commercial columns also had the dimensions 250 mm x 4.6 mm and were packed with 5 µm particles. A few other chiral selectors proved impractical because they were found to be soluble in common mobile phases used in HPLC and therefore could not be evaluated. The schematic structures of the chiral selectors in the studied chiral columns are shown in Fig. 2.

2.3 High-performance Liquid Chromatography

All HPLC experiments were performed with an Agilent 1200 HPLC instrument (Agilent Technologies, Waldbronn, Germany) equipped with a G1367C HiP ALS-SL autosampler, a G1316B TCC-SL temperature controller, a G1311A quaternary pump and a G1314D VWD variable wavelength detector. The Chemstation software (version B.03.02-SR2) was used for instrument control, data acquisition and data handling. Samples were dissolved in the mobile phase used for the respective separation at a concentration of 1.0 mg/ml. HPLC separations were performed at 20°C with 1.0 ml/min mobile phase flow rate and detection was performed at 254 nm.

Results and Discussion

3.1 Effect of structure of chiral analyte on retention and enantioseparation of chiral sulfoxides

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The results of enantioseparations of 14 chiral sulfoxides on 18 different cellulose-based chiral columns in pure methanol and in aqueous methanol mobile phase are summarized in Tables 1-4. These results enable making some conclusions regarding the effect of analyte- and chiral-selector structure on retention and enantioseparation.

The most striking effect is that shifting of the benzylsulfinyl substituent from position 2 to position 3 from the amide moiety (compound 1 and compound 2) leads to a drastic decrease (actually, in most cases to total loss) of enantioseparation on all columns and in all studied mobile phases (see results for compound 1 and compound 2 in all 4 tables). The excessive retention of one enantiomer of 2-(benzylsulfinyl)-benzamide (1) on most cellulose phenylcarbamate derivatives in contrast to minimal retention of the other enantiomer of the same compound remains puzzling, especially in the light of a totaly different result for the closely related compound 3-(benzylsulfinyl)-benzamide (2). In addition, it seems worth noting that the first enantiomer of 2-(benzylsulfinyl)-benzamide (1) retains shorter on most columns compared to the enantiomers of 3-(benzylsulfinyl)-benzamide (2) (Tables 1-4). One explanation for these unexpected behaviors may be based on the combination of intra- and inter-molecular hydrogen bonding effects. Such explanation needs further experimental and theoretical confirmation. Significantly higher chiral recognition ability of the cellulose tris(3,5-dichlorophenylcarbamate)-based chiral column towards the enantiomers of compound 1 compared to cellulose tris(3,5-dimethylphenylcarbamate)-based chiral column supports the involvement of hydrogen bonding-type interactions in the chiral recognition of this analyte. As reported in earlier studies, the former chiral selector contains a higher number of free carbamate moieties (able to participate in selector-selectand hydrogen bond formation) than the latter [2,10,21,24-26]. Increase in retention of the first eluting enantiomer and decrease in enantioselectivity due to N-methylation (compound 3) and N,N-dimethylation (compound 14) of the amino moiety is additional support for the critical importance of hydrogen-bonding type interactions in enantioselective recognition of studied chiral sulfoxides with cellulose-based chiral selectors (Tables 1-4).

It seems quite interesting to compare the retention and separation characteristics of compounds 3, 7, 8, 9 and 10. The difference between the structures of these compounds is that the sulfinyl group is linked with methyl, n-propyl, benzyl, 4-nitrbenzyl and 4-trifluoromethylbenzyl moieties, respectively. It is interesting to note that although less retained on most of the columns in all mobile phases, alkylsulfinyl derivatives were better enantioseparated on some chiral columns compared to benzylsulfinyl derivatives (Tables 1-4). Significantly less retention of 4-trifluoromethylbenzyl-substituted sulfoxide (compound 10) among all aromatic ones under this study also deserves attention. Less retention did not lead to lower selectivity of enantioseparation for this compound (Table 1-4).

Comparison of separation results for compounds **3** and **5** indicate that replacement of methyl substituent with a bulky (aromatic) substituent resulted as expected in increased retention and also improved separation of enantiomers, especially in aqueous methanol but not markedly (Tables 1-4).

The 2-, 3-and 4-benzylsulfinyl methylbenzoate derivatives (compounds 11, 12 and 13) were quite well retained but not enantioseparated by most columns studied. The most successful chiral columns to separate the enantiomers of the sulfoxides 11, 12 and 13 proved to be Lux Cellulose-2, Lux Cellulose-4 and the column having cellulose tris(3,5-dichlorophenylcarbamate as the chiral selector, all based on carbamate derivatives of cellulose along with 4-methylbenzoate derivative of cellulose (Lux Cellulose-3), the only non-carbamate derivative of cellulose (Tables 1-4).

In summary, it must be noted that the location of the benzylsulfinyl substituent in position 2 (*ortho*) in relation to the amide moiety is of key importance for highly successful enantiodiscrimination associated with high separation factors in HPLC. Free N-H moiety

instead of its alkyl- or aryl-substituted analogues favors enantiomer differentiation by most chiral selectors. These results are in good agreement with our previous observations on a smaller set of similar compounds studied in chiral HPLC under different mobile phase conditions [28] and with other techniques, such as nano-LC, CEC [29] and SFC [30].

3.2 Effect of structure and composition of chiral selectors on retention and selectivity of enantioseparation of chiral sulfoxides

Retention of the first enantiomer of most studied chiral sulfoxides in methanol as mobile phase was higher on unsubstituted cellulose tris(phenylcarbamate) compared to 2-Cl-, 3-Cl- and 4-Cl-substituted derivatives of cellulose. The selectivity of separation was lower on cellulose tris(2-chlorophenylcarbamate) compared to unsubstituted cellulose tris(phenylcarbamate). In methanol, none of mono-substituted chlorophenylcarbamates of cellulose showed higher success rate compared to unsubstituted cellulose tris(phenylcarbamate) (Table 1, Fig. 3). The monosubstituted tris(methylphenylcarbamates) of cellulose with substituents in position 3 and 4 performed slightly better compared to unsubstituted cellulose tris(phenylcarbamate) (Table 3, Fig. 3).

A different trend was observed in aqueous methanol (30/70, v/v) as mobile phase, both in terms of retention and degree of separation of enantiomers. In particular, for most compounds longer retention for the first enantiomer was observed on cellulose tris(3-chlorophenylcarbamate) (Table 2). For few analytes the selectivity of enantioseparation was also rather high (compounds 1 and 5) on this column, while the success rate in the same aqueous methanol was similar or slightly worse for mono-chloro-substituted phenylcarbamates compared to unsubstituted one (Table 2 and Fig. 3b).

Introduction of an additional chloro-substituent in positions 3, 4 or 5 of already 2-chloro-substituted cellulose derivative did not improve the enantiomer resolving ability significantly while the introduction of the second chloro-substituent in position 6 diminished

retention and caused a complete loss in enantioselectivity for all studied compounds in both studied mobile phases (Tables 1 and 2 and Fig. 3a and b). These observations underline the important role played by carbamate moieties in enantiorecognition with polysaccharide phenylcarbamates; these moieties apparently become inaccessible for analytes when phenyl moieties get substituted with bulky chloro-substituents simultaneously in the positions 2 and 6.

Introducing of a second chloro-substituent at position 4 in addition to one at position 3 did not improve the enantiomer resolving ability significantly in methanol, however some improvement was observed in aqueous methanol as mobile phase. Thus, compounds **2**, **4**, **6**, **11** and **13** which were not enantioseparated on the cellulose tris(3-chlorophenylcarbamate)-based column in methanol/water (70/30, v/v), were either partially or baseline resolved on a cellulose tris(3,4-dichlorophenylcarbamate)-based column in the same mobile phase (Table 2).

A different effect was observed when an additional chloro-substituent was introduced at position 5 to already 3-chloro-substituted cellulose derivative: a cellulose tris(3,5-dichlorophenylcarbamate)-based chiral column separated some compounds that could not be separated by either unsubstituted- or 3-chloro-substituted cellulose-based columns (compound 6) or only by one of them (compound 12) and in methanol as a mobile phase (Table 1). This effect was favored in methanol/water (70/30, v/v) as a mobile phase. In this mobile phase high separation factors were observed on cellulose tris(3,5-dichlorophenylcarbamate)-based chiral column for the enantiomers of several analytes (for instance compounds 1, 3 and 5) (Table 2).

The behavior of 2-, 3-, and 4-methylsubstituted cellulose tris(phenylcarbamate)-based columns was quite similar to that of chloro-substituted cellulose tris(phenylcarbamate)-based chiral columns, i.e. no drastic improvement in chiral recognition ability was achieved due to mono-methylation in any position and the 2-substituted derivative was even a less effective

chiral selector than unsubstituted cellulose tris(phenylcarbamate) (Fig. 3 and Table 3). Some of the dimethylsubstituted tris(phenylcarbamates) of cellulose were soluble in the applied mobile phases and could not be evaluated in HPLC. However, cellulose tris(3,4-dimethylphenylcarbamate) and cellulose tris(3,5-dimethylphenylcarbamate) are stable in all studied solvents and were compared with mono-substituted methylated derivatives, as well as with each other. Thus, the introduction to the second methyl group to the already 3-methylsubstituted phenylcarbamate of cellulose at positions 4 or 5 improved the enantiomer resolving ability of such chiral selectors, this effect being more pronounced for cellulose tris(3,5-dimethylphenylcarbamate) (Table 3 and 4, and Fig. 3).

Interesting results were obtained when a second methyl-substituent was introduced at position 4 to an already 3-chloro-substituted phenylcarbamate derivative of cellulose. A marked improvement in enantiomer resolving ability was achieved and all the analytes previously not enantioseparated by a cellulose tris(3-chlorophenylcarbamate)-based column were at least partially enantioseparated by a cellulose tris(3-chloro-4-methylphenylcarbamate)-based column (Table 3). A similar effect was observed by the introduction of chloro-substituent to position 4 to already 3-methyl substituted phenylcarbamate derivative of cellulose. In some cases enantiomers that were not resolved at all on cellulose tris(3-methylphenylcarbamate)-based chiral column were baseline-resolved on cellulose tris(3-methyl-4-chlorophenylcarbamate)-based column (Fig. 4). The superiority of chloro-methyl trisphenylcarbamates of cellulose over corresponding chloro-, methyl-, dichloro- or dimethyl- trisphenylcarbamates as chiral selectors are especially evident in aqueous-methanol as mobile phase (Table 4). Again, remarkable enantioselectivity was observed with cellulose tris(3-methyl-4-chlorophenylcarbamate)-based column toward several chiral sulfoxides (Fig. 5).

These observations are in good agreement with earlier theoretical and practical considerations (observed with a different set of chiral compounds and different mobile

phases) which led to the development and commercialization of a new family of polysaccharide-based chiral selectors for liquid phase separation of enantiomers [24-26, 31].

Since the chiral analytes studied here possess in their structure both, hydrogen bond donor, as well as hydrogen bond acceptor moieties, the separation of their enantiomers seems also possible with cellulose tris(4-methylbenzoate)-based chiral column (a hydrogen-bond acceptor). This column resolved the enantiomers of 8 analytes in methanol and of 12 analytes in aqueous methanol (Tables 3 and 4, respectively). It seems that together with hydrogen bonding, hydrophobic type interactions are also important for chiral recognition with this material especially in aqueous-organic mobile phase. This becomes evident with the lack of separation of racemates 7 and 8 which do not possess an aromatic moiety linked to the sulfinyl moiety and therefore are not capable of strongly interacting with the CSP based on hydrophobicity (or via π - π attraction). In contrast, compound 5 having a bulky naphthyl moiety attached to the amide moiety (Table 4) is well separated. It seems also worth mentioning that chiral sulfinyl derivatives having methylbenzoate substituents (compounds 11, 12 and 13) instead of benzamide derivatives are rather difficult to be enantioseparated on cellulose phenylcarbamate-based columns. In contrast, these compounds were well enantioseparated on cellulose tris(4-methylbenzoate)-based column. In addition, the recognition, contrary to benzamide derivatives, was improved when benzylsulfinily moiety was shifted from position 2 to position 3 (Tables 3 and 4). Thus, cellulose tris(4methylbenzoate)-based chiral column proved to be complementary to cellulose tris(phenylcarbamate)-based columns.

Although this work does not specifically deal with the elution order of enantiomers few remarkable cases of enantiomer elution order reversal based on the type of chiral selector were observed and one of them is shown in Fig. 6.

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3.3. The effect of water content (in methanol) on retention and enantioselectivity for chiral sulfoxides

Methanol, as protic solvent, should interfere with any strong hydrogen-bonding between chiral compounds and the chiral selector. However, in our understanding hydrogen-bonding seems to take place between polysaccharide-phenylcarbamate derivatives and some analytes studied here even in the pure methanol as mobile phase. This effect certainly depends on the nature of both analyte and chiral selector and is expressed to different extent.

The most common observation was the increase in retention and improvement or appearance of enantioselectivity (not observed in pure methanol) as the water content was increased in methanol mobile phase (Fig. 7). However, for some analytes, especially on the columns based on cellulose tris(3,5-dichlorophenylcarbamate) or cellulose tris(4-chloro-3-methylphenylcarbamatae), their retention did not increase significantly with addition of up to 10% water (v/v) and sometimes even adequate enantioselectivity observed in pure methanol was lost (Fig. 8). These observations suggest that some hydrogen bonding type interactions are present between the chiral selector and chiral analytes even in pure methanol and that such interactions favor enantio-discrimination. With addition of water, the hydrogen bonds become increasingly disrupted and concomitantly hydrophobic type interactions intensify. Perhaps these two opposite effects on analyte retention compensate each other up to a certain percentage of water in the mobile phase and therefore, retention does not change significantly with increasing water content in the mobile phase. Apparently, for such particular analyte-selector combinations hydrogen bonding plays a major role in enantioseparation, which is lost as the water content in the mobile phase is gradually increased.

For some compounds chiral recognition pattern based on polar interactions (for instance, hydrogen bonding) and chiral recognition pattern, based on hydrophobic type interactions may be opposite to each other. In such cases the enantiomer elution order will revert based on the content of water in the mobile phase [18]. Good examples for such cases

were observed for 2-(methylsulfinyl)-N-methylbenzamide (7) on cellulose tris(3-chloro-4-methylpnenylcarbamate) and cellulose tris(4-chloro-3-methylpnenylcarbamate)-based chiral columns (Fig. 9).

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Conclusions

As the results of this study indicate, structural details of chiral compounds such as the location of benzylsulfinyl substituent in position 2 relative to the amide moiety are critical for enantioseparation by cellulose phenylcarbamate-based chiral selectors but not critical for enantiorecognition by cellulose benzoate-based column. In confirmation to earlier results [1,2,10,24,25] obtained with hydrocarbon-alcohol (so called normal-phase) eluents, cellulose phenylcarbamate derivatives having substituents (especially bulky halogens) in position 2 show limited chiral recognition ability also in aqueous-organic mobile phases and when the substituents are in both positions 2 and 6, the carbamates simply do not exhibit enantiomer resolving ability. The presence of a chloro- or methyl-substituent it the structure of polysaccharide phenylcarbamate derivatives in addition to one of the same kind located at position 3 does improve their chiral recognition ability towards studied analytes in methanol or aqueous methanol mobile phases. However, a combination of different substituents on the phenyl moiety (such as chloro- and methyl-substituents), especially in positions 3 and 4 (although not reported here [26], but the same applies to substituents in positions 3 and 5) can significantly improve the enantioseparating power of cellulose phenylcarbamates towards individual sulfoxides (higher α), as well as significantly improve the success rate especially in aqueous methanol as mobile phase. These findings are in agreement with earlier results reported in references [2, 24-26, 31] for a similar set of cellulose and amylose phenylcarbamates but observed in hydrocarbon-alcohol-type (so called normal-phase) eluents. As this study indirectly indicates hydrogen bonding type interactions may be involved in

chiral recognition with cellulose phenylcarbamates also in pure methanol and even in aqueous methanol with lower (5-10%, v/v) content of water.

Acknowledgement

This project was supported financially in part by the RNSF-CNR joint grants 04/02, 2014-2015 and 04/02, 2016-2017.

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| 441 | | |

Figure legends:

- 443 **Fig. 1** Structure of chiral sulfoxides included in this study.
- 444 Fig. 2 Schematic representation of structure of chiral selectors in chiral columns used in this
- study.

- 446 Fig. 3 Number of enantioseparated chiral compounds on cellulose -based chiral columns.
- 447 **Fig. 4** Separation of 3-(benzylsulfinyl)-N-methylbenzamide (4) enantiomers of cellulose
- tris(3-methylphenylcarbamate)- (a and c) and cellulose tris(4-chloro-3-
- methylphenylcarbamate)-based (b and d) chiral columns in methanol (a and b) and
- 450 methanol-water (70/30, v/v) (c and d) mobile phases.
- 451 **Fig. 5** Separation of enantiomers of 2-(benzylsulfinyl)-benzamide (1, a), 2-(benzylsulfinyl)-
- N-methylbenzamide (3, b) and 2-(benzylsulfinyl)-N,N-dimethylbenzamide (14, c) on
- cellulose tris(4-chloro-3-methylphenylcarbamate)-based column in methanol-water
- 454 (70/30, v/v) as a mobile phase.
- 455 **Fig. 6** Separation of enantiomers of 3-(benzylsulfinyl)-N-methylbenzamide (4)on cellulose
- 456 tris(4-methylbenzoate)-(a), cellulose tris(3,5-dimethylphenylcarbamate)-(b), cellulose
- 457 tris(3-chloro-4-methylphenylcarbamate)- (c) and cellulose tris(4-chloro-3-
- methylphenylcarbamate)-based column in methanol-water (70/30, v/v) as a mobile
- 459 phase.
- 460 Fig. 7 Effect of water content in the mobile phase on separation of enantiomers of 2-(4-
- nitrobenzylsulfinyl)-N-methylbenzamide (9) on cellulose tris(4-chloro-3-
- methylphenylcarbamate)-based column in pure methanol (a) and water-methanol
- mobile phases with 10 (b) and 30% (c) (v/v) water content in mobile phase.
- 464 Fig. 8 Effect of water content in the mobile phase on separation of enantiomers of 2-
- 465 (methylsulfinyl)-N-methylbenzamide (7) on cellulose tris(4-chloro-3-

| 466 | | methylphenylcarbamate)-based column in pure methanol (a) and water-methanol |
|-----|--------|--|
| 467 | | mobile phases with 10 (b) and 30% (c) (v/v) water content in mobile phase. |
| 468 | Fig. 9 | Effect of water content in the mobile phase on separation of enantiomers of 2- |
| 469 | | (methylsulfinyl)-N-methylbenzamide (3) on cellulose tris(3-chloro-4- |
| 470 | | methylphenylcarbamate)- (a, b and c) and cellulose tris(4-chloro-3- |
| 471 | | methylphenylcarbamate)-based column (d, e and f) in pure methanol (a and d) and |
| 472 | | water-methanol mobile phases with 30 (b and e) and 60% (c and f) (v/v) water content |
| 473 | | in mobile phase. |
| 474 | | |
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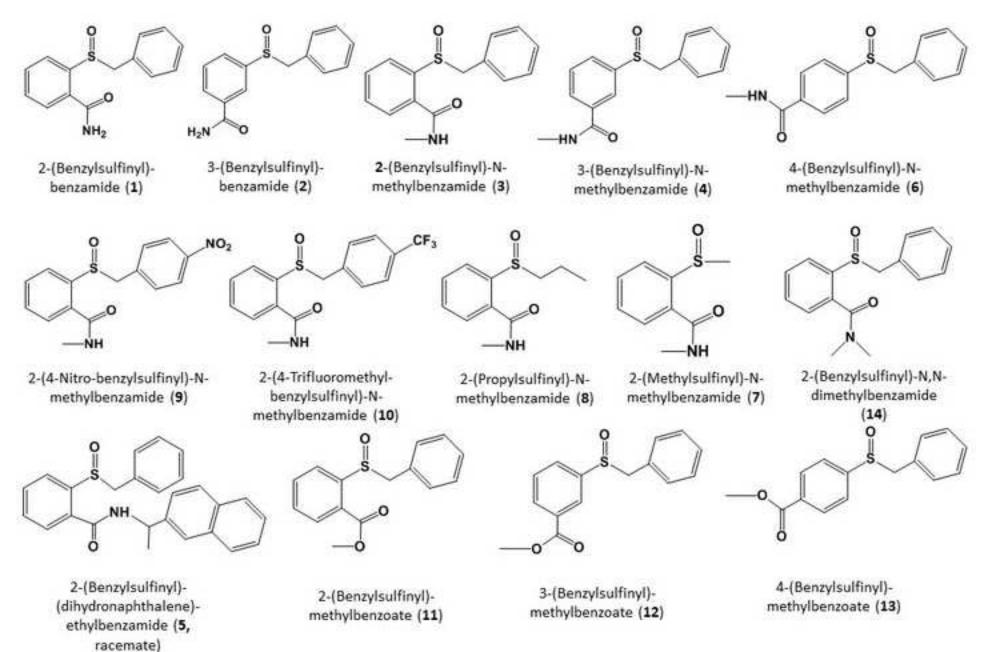
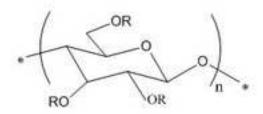


Fig. 1

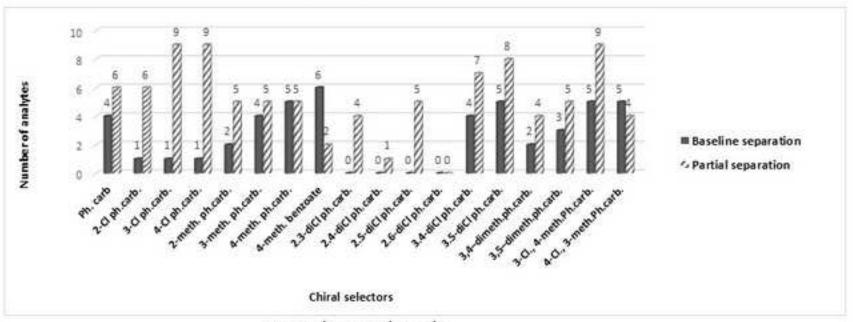


| Chiral selector | R | Chiral selector | R | Chiral selector | R |
|---|------|--|------|--|-------|
| Cellulose tris (phenylcarbamate) | 4-0 | Cellulose tris (2,5-dichloro- phenylcarbamate) | 4°Q | Cellulose tris (4-methyl- phenylcarbamate) | √1-O- |
| Cellulose tris (2-chlorophenylcarbamate) | 4 | Cellulose tris (2,6-dichloro- phenylcarbamate) | | Cellulose tris (3,4-dimethyl- phenylcarbamate) | 40 |
| Cellulose tris (3-chlorophenykarbamate) | 40 | Cellulose tris (3,4-dichloro- phenylcarbamate) | 4-0 | Cellulose-1 Cellulose tris (3,5-dimethyl- phenylcarbamate) | 40 |
| Cellulose tris (4-chlorophenylcarbamate) | ₹O-° | Cellulose tris (3,5-dichloro- phenylcarbamate) | 44 | Cellulose-2 [Cellulosetris (3-chloro-4-methyl- phenylcarbamate)] | 40 |
| Cellulose tris (2,3-dichlorophenylcarbamate) | 7 | Cellulose tris (2-methyl- phenylcarbamate) | 4:40 | Cellulose-3 Cellulose tris [(4 - methylbenzoate)] | ~> |
| Cellulose tris (2,4-dichlorophenylcarbamate) | 45 | Cellulose tris (3-methyl- phenylcarbamate) | 4 | Cellulose-4 [Cellulose tris (4-chloro-3-methyl- phenylcarbamate)] | |

Fig. 2

Figure 3
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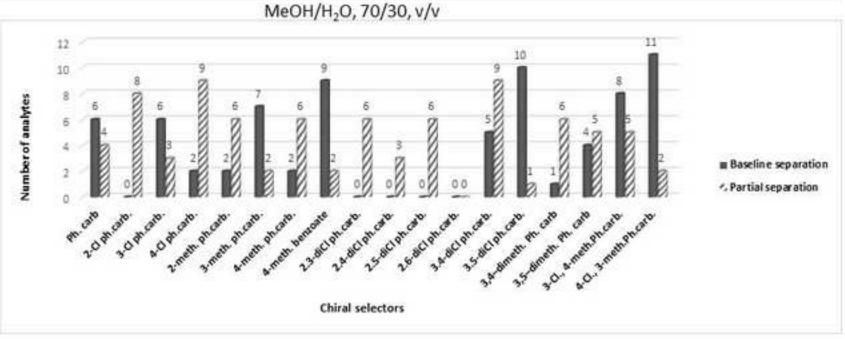


Figure 4
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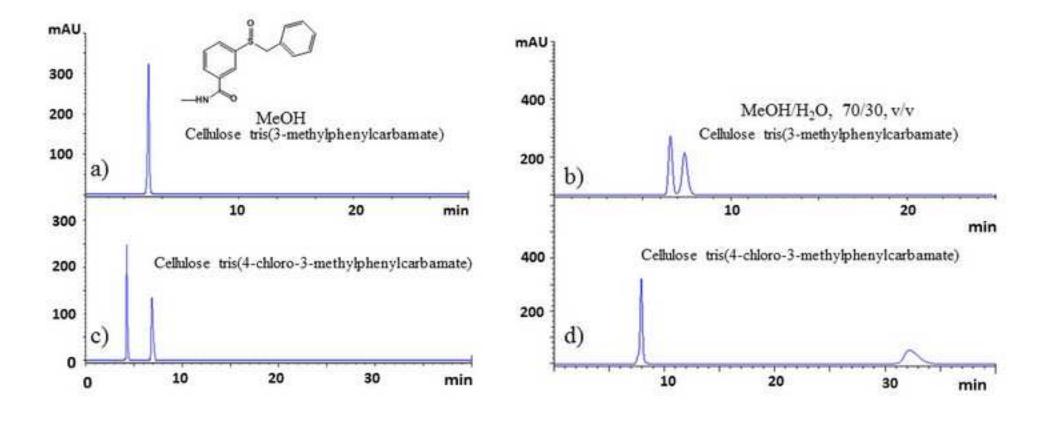


Fig. 4

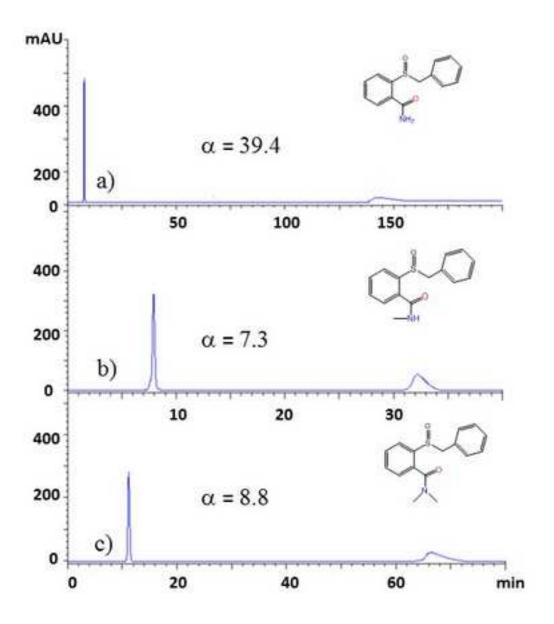
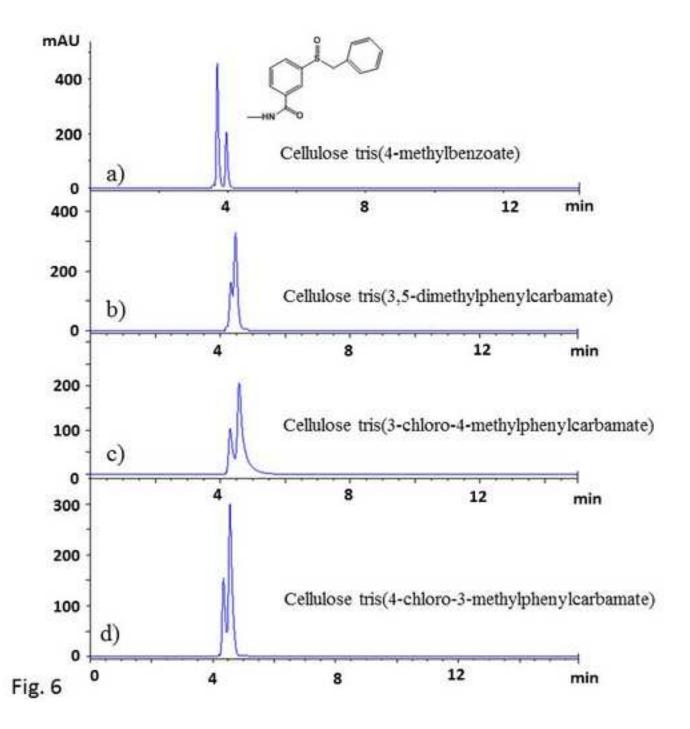


Fig. 5



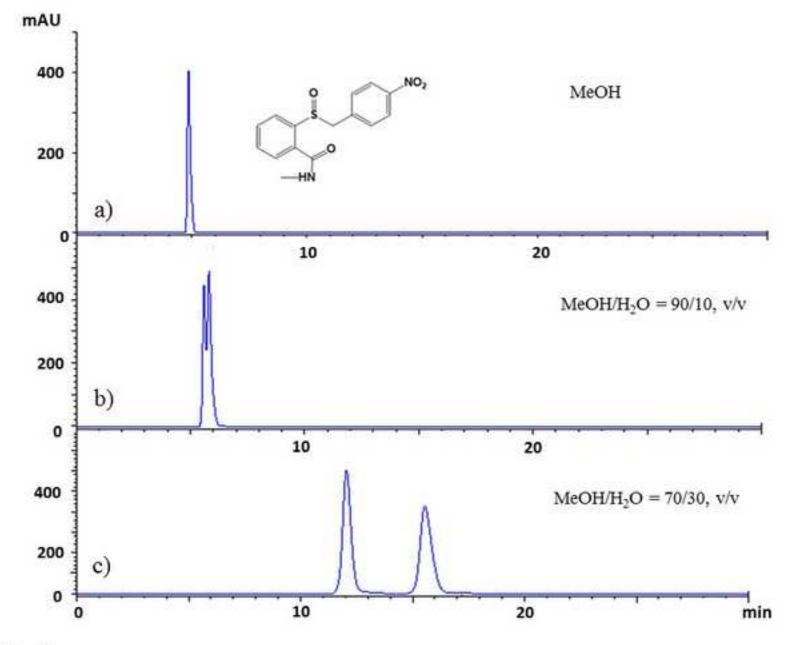


Fig. 7

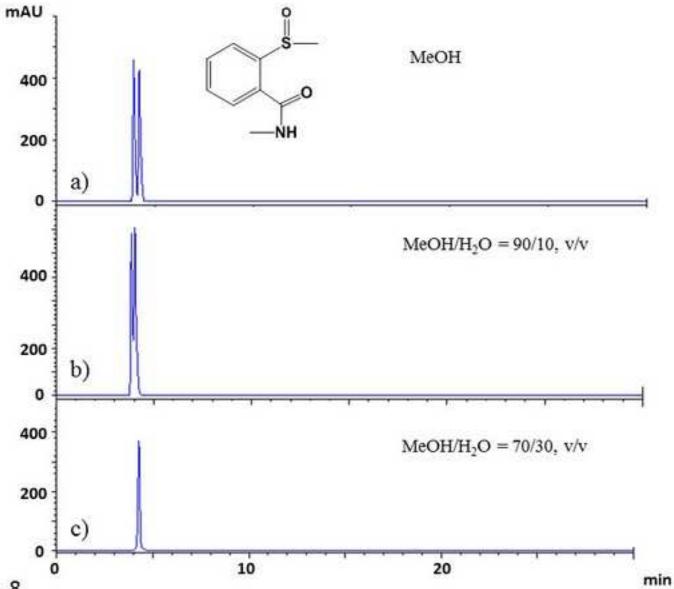


Fig. 8

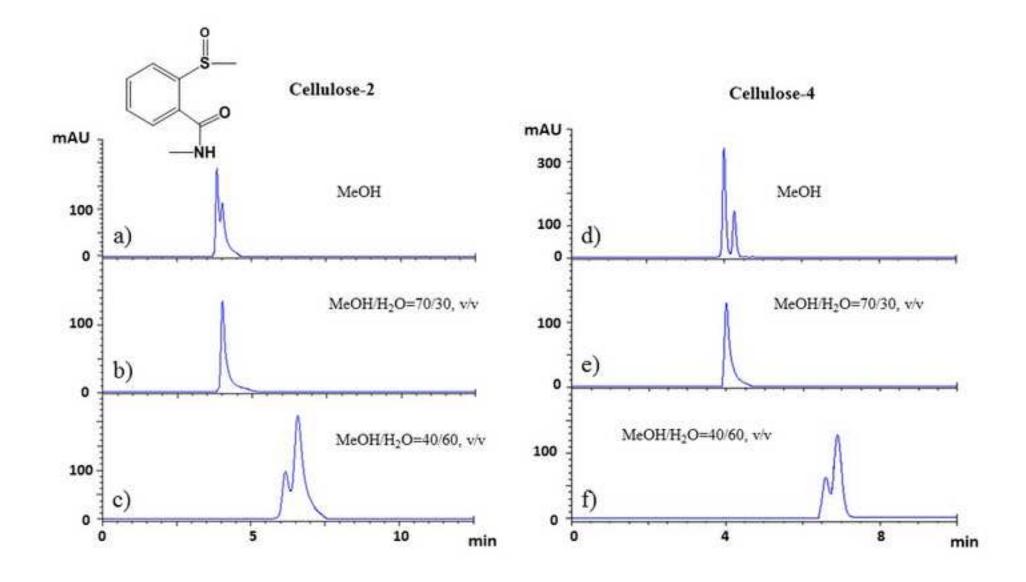


Fig. 9

Table 1 Retention factor for the first enantiomer and separation factor of 14 chiral sulfoxides in methanol as a mobile phase on chiral columns made of 9 chlorosubstituted cellulose derivatives.

| No | Chiral | | | | | | | | | | | Chiral S | elector | | | | | | | | |
|----|--|-------|------|------------------|------|------------------|------|------------------|------|-------|------|------------------|---------|-------|------|-------|------|------------------|------|-------|-------|
| | Analyte | I-Z | | O CI | | H-N-N | CI | H-Z | CI | CI CI | C | CI, | CI | | CI | CI CI | | T-z- | CI | I-2 0 | CI |
| | | k_1 | α | k ₁ ′ | α | k ₁ ′ | α | k ₁ ′ | α | k_1 | α | \mathbf{k}_{1} | α | k_1 | α | k_1 | α | k ₁ ′ | α | k_1 | α |
| 1 | S NH ₂ | 0.38 | 2.36 | 0.18 | 1.72 | 0.26 | 5.97 | 0.35 | 4.37 | 0.30 | 1.79 | 0.25 | 1.32 | 0.23 | 2.13 | 0.21 | 1.00 | 0.33 | 5.40 | 0.35 | 10.27 |
| 2 | i s | 0.61 | 1.00 | 0.28 | 1.00 | 0.43 | 1.00 | 0.49 | 1.09 | 0.40 | 1.00 | 0.27 | 1.00 | 0.33 | 1.00 | 0.38 | 1.00 | 0.43 | 1.00 | 0.52 | 1.00 |
| 3 | S NH | 0.44 | 1.31 | 0.23 | 1.31 | 0.37 | 1.64 | 0.39 | 1.18 | 0.37 | 1.17 | 0.30 | 1.00 | 0.31 | 1.49 | 0.26 | 1.00 | 0.43 | 1.57 | 0.53 | 2.67 |
| 4 | S. S | 0.66 | 1.07 | 0.33 | 1.00 | 0.59 | 1.00 | 0.54 | 1.08 | 0.48 | 1.00 | 0.35 | 1.00 | 0.41 | 1.00 | 0.35 | 1.00 | 0.43 | 1.08 | 0.78 | 1.14 |
| 5 | | 0.54 | 1.61 | 0.41 | 1.43 | 0.36 | 2.86 | 0.62 | 1.00 | 0.77 | 1.35 | 0.66 | 1.59 | 0.67 | 1.72 | 0.22 | 1.00 | 0.41 | 1.20 | 0.62 | 4.36 |
| 6 | -HN S | 0.72 | 1.00 | 0.42 | 1.00 | 0.60 | 1.00 | 0.54 | 1.00 | 0.63 | 1.00 | 0.47 | 1.00 | 0.51 | 1.17 | 0.45 | 1.00 | 0.50 | 1.00 | 0.75 | 1.13 |
| 7 | S N | 0.27 | 1.71 | 0.17 | 1.41 | 0.28 | 1.71 | 0.30 | 1.21 | 0.25 | 1.00 | 0.28 | 1.00 | 0.21 | 1.00 | 0.29 | 1.00 | 0.14 | 2.55 | 0.49 | 1.19 |
| 8 | -HN | 0.21 | 1.52 | 0.12 | 1.39 | 0.24 | 1.39 | 0.24 | 1.13 | 0.2 | 1.00 | 0.18 | 1.00 | 0.21 | 1.00 | 0.15 | 1.00 | 0.09 | 2.31 | 0.41 | 1.11 |

| 9 | NO ₂ | 0.70 | 1.35 | 0.68 | 1.00 | 0.59 | 1.68 | 0.55 | 1.07 | 0.90 | 1.00 | 0.67 | 1.00 | 0.81 | 1.00 | 0.63 | 1.00 | 0.45 | 1.85 | 1.25 | 1.04 |
|----|-----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|-------|
| 10 | DE CE-3 | 0.15 | 1.29 | 0.08 | 1.00 | 0.13 | 1.43 | 0.18 | 1.00 | 0.16 | 1.00 | 0.14 | 1.00 | 0.13 | 1.00 | 0.05 | 1.00 | 0.07 | 2.41 | 0.30 | 1.08 |
| 11 | °° | 0.75 | 1.08 | 0.51 | 1.11 | 0.74 | 1.31 | 0.66 | 1.00 | 1.08 | 1.18 | 0.81 | 1.00 | 0.84 | 1.34 | 0.26 | 1.00 | 0.61 | 1.11 | 1.14 | 1.54 |
| 12 | | 1.04 | 1.00 | 0.61 | 1.00 | 1.12 | 1.19 | 0.72 | 1.09 | 1.04 | 1.00 | 0.69 | 1.00 | 0.83 | 1.00 | 0.49 | 1.00 | 0.84 | 1.00 | 1.63 | 11.75 |
| 13 | | 1.13 | 1.00 | 0.73 | 1.00 | 1.15 | 1.00 | 0.84 | 1.04 | 1.44 | 1.00 | 1.00 | 1.00 | 1.14 | 1.00 | 0.59 | 1.00 | 0.96 | 1.00 | 1.56 | 1.10 |
| 14 | | 0.70 | 1.20 | 0.40 | 1.13 | 0.70 | 1.58 | 0.60 | 1.37 | 0.59 | 1.00 | 0.59 | 1.00 | 0.82 | 1.00 | 0.30 | 1.00 | 0.48 | 1.19 | 0.92 | 2.23 |

Table 2. Retention factor for the first enantiomer and separation factor of 14 chiral sulfoxides in methanol/water (70/30, v/v) as a mobile phase on chiral columns made of 9 chlorosubstituted cellulose derivatives.

| No | Chiral | | | | | | | | | | | Chiral S | elector | | | | | | | | |
|----|---------------------------------------|------------------|------|----------|------|------------------|------|------------------|------|-------|------|----------|---------|---------|------|-------|------|-------|------|-------|-------|
| | Analyte | I-Z | | T-Z O | | 1-Z | CI | H-Z | CI | CI CI | CI | CI | CI | C 1-2 0 | CI | CI CI | | I-Z | CI | T-Z-M | CI |
| | | k ₁ ′ | α | k_1 | α | \mathbf{k}_{1} | α | k ₁ ′ | α | k_1 | α | k_1 | α | k_1 | α | k_1 | α | k_1 | α | k_1 | α |
| 1 | S NH ₂ | 0.54 | 2.59 | 0.38 | 1.47 | 1.20 | 9.28 | 0.60 | 5.48 | 0.60 | 1.53 | 1.31 | 1.23 | 1.42 | 1.67 | 0.25 | 1.00 | 0.47 | 7.13 | 1.41 | 15.73 |
| 2 | H _b N | 0.79 | 1.00 | 0.48 | 1.00 | 1.64 | 1.00 | 0.71 | 1.08 | 0.66 | 1.00 | 1.37 | 1.00 | 1.70 | 1.00 | 0.43 | 1.00 | 0.63 | 1.08 | 1.66 | 1.00 |
| 3 | S | 0.64 | 1.46 | 0.48 | 1.22 | 1.93 | 2.52 | 0.71 | 1.29 | 0.73 | 1.15 | 1.79 | 1.00 | 2.28 | 1.41 | 0.28 | 1.00 | 0.60 | 2.23 | 2.27 | 5.58 |
| 4 | -HN- | 0.92 | 1.07 | 0.58 | 1.00 | 2.58 | 1.00 | 0.86 | 1.00 | 0.81 | 1.00 | 1.83 | 1.00 | 2.43 | 1.00 | 0.39 | 1.00 | 0.85 | 1.18 | 2.68 | 1.18 |
| 5 | | 1.98 | 1.76 | 2.39 | 1.33 | 2.37 | 5.29 | 1.70 | 1.39 | 5.30 | 1.31 | 4.52 | 1.00 | 1.67 | 1.66 | 0.40 | 1.00 | 1.22 | 2.31 | 20.36 | 6.82 |
| 6 | HN S | 0.98 | 1.00 | 0.66 | 1.17 | 2.56 | 1.00 | 0.87 | 1.08 | 0.91 | 1.16 | 2.23 | 1.00 | 2.77 | 1.32 | 0.48 | 1.00 | 0.85 | 1.12 | 2.48 | 1.22 |
| 7 | o o o o o o o o o o o o o o o o o o o | 0.22 | 1.77 | 0.15 | 1.35 | 0.40 | 1.80 | 0.28 | 1.20 | 0.21 | 1.00 | 0.30 | 1.00 | 0.40 | 1.00 | 0.24 | 1.00 | 0.33 | 1.44 | 0.59 | 1.12 |
| 8 | S S O HN | 0.25 | 1.45 | 0.18 | 1.29 | 0.73 | 1.26 | 0.33 | 1.17 | 0.31 | 1.00 | 0.58 | 1.00 | 0.85 | 1.00 | 0.15 | 1.00 | 0.35 | 1.24 | 1.11 | 1.00 |

| 9 | NO ₂ | 1.22 | 1.32 | 1.43 | 1.00 | 4.35 | 1.92 | 1.13 | 1.04 | 1.89 | 1.00 | 4.64 | 1.00 | 6.05 | 1.13 | 0.77 | 1.00 | 1.31 | 1.27 | 7.78 | 1.00 |
|----|-----------------|------|------|------|------|-------|------|------|------|------|------|-------|------|-------|------|------|------|------|------|-------|------|
| 10 | CF ₃ | 0.39 | 1.11 | 0.38 | 1.00 | 2.12 | 1.07 | 0.46 | 1.00 | 0.65 | 1.00 | 2.32 | 1.00 | 2.88 | 1.00 | 0.09 | 1.00 | 0.35 | 1.07 | 1.08 | 1.40 |
| 11 | | 1.61 | 1.15 | 1.46 | 1.17 | 10.83 | 1.00 | 1.86 | 1.06 | 3.42 | 1.12 | 11.22 | 1.00 | 12.18 | 1.22 | 0.39 | 1.00 | 1.78 | 1.44 | 10.67 | 2.16 |
| 12 | | 2.04 | 1.00 | 1.49 | 1.00 | 4.31 | 1.00 | 1.78 | 1.11 | 2.79 | 1.00 | 7.67 | 1.00 | 9.30 | 1.00 | 0.68 | 1.00 | 2.40 | 1.00 | 1.150 | 1.25 |
| 13 | | 2.28 | 1.00 | 1.81 | 1.00 | 10.93 | 1.00 | 2.23 | 1.00 | 3.81 | 1.11 | 3.08 | 1.04 | 12.23 | 1.20 | 0.78 | 1.00 | 2.39 | 1.06 | 12.74 | 1.14 |
| 14 | 0=0 | 0.96 | 1.29 | 0.66 | 1.09 | 3.32 | 2.16 | 1.26 | 1.52 | 1.61 | 1.00 | 2.87 | 1.16 | 4.21 | 1.13 | 0.32 | 1.00 | 1.28 | 2.32 | 4.75 | 3.04 |

Table 3. Retention factor for the first enantiomer and separation factor of 14 chiral sulfoxides in methanol as a mobile phase on chiral columns made of methyl and chlorosubstituted cellulose derivatives.

| No | Chiral Analyte | H-K-W | | T-z | | T N | | o N-Z-T | | H-N-(| <u></u> | H-Z | | H-N-M | CI | H-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N | CI | | |
|----|---------------------------------------|------------------|------|------------------|------|------------------|------|------------------|------|------------------|---------|-------|------|-------|-------|---|-------|------------------|------|
| | | k ₁ ′ | α | k_1 | α | k_1 | α | k ₁ ′ | α | k ₁ ′ | α |
| 1 | S S NH ₂ | 0.38 | 2.36 | 0.23 | 1.65 | 0.28 | 3.02 | 0.37 | 2.67 | 0.27 | 2.65 | 0.34 | 1.62 | 0.37 | 15.97 | 0.25 | 19.82 | 0.21 | 1.39 |
| 2 | H ₂ N | 0.61 | 1.00 | 0.31 | 1.00 | 0.45 | 1.00 | 0.44 | 1.00 | 0.39 | 1.00 | 0.35 | 1.00 | 0.36 | 1.12 | 0.27 | 1.00 | 0.25 | 1.20 |
| 3 | S NH | 0.44 | 1.31 | 0.26 | 1.31 | 0.37 | 1.00 | 0.43 | 1.25 | 0.30 | 1.00 | 0.36 | 1.00 | 0.41 | 3.25 | 0.31 | 3.58 | 0.20 | 1.00 |
| 4 | -HN | 0.66 | 1.07 | 0.32 | 1.00 | 0.44 | 1.08 | 0.61 | 1.10 | 0.43 | 1.00 | 0.40 | 1.08 | 0.45 | 1.19 | 0.32 | 1.20 | 0.22 | 1.33 |
| 5 | | 0.54 | 1.61 | 0.27 | 1.59 | 0.42 | 1.20 | 0.54 | 1.66 | 0.46 | 1.00 | - | - | 0.46 | 2.17 | 0.37 | 1.61 | 0.33 | 2.39 |
| 6 | -HN S | 0.72 | 1.00 | 0.39 | 1.00 | 0.51 | 1.00 | 0.74 | 1.00 | 0.51 | 1.00 | 0.77 | 1.21 | 0.57 | 1.05 | 0.41 | 1.00 | 0.24 | 1.62 |
| 7 | o o o o o o o o o o o o o o o o o o o | 0.27 | 1.71 | 0.19 | 1.28 | 0.15 | 2.44 | 0.27 | 1.81 | 0.13 | 1.95 | 0.14 | 1.30 | 0.28 | 1.23 | 0.21 | 1.41 | 0.14 | 1.00 |
| 8 | S S O | 0.21 | 1.52 | 0.13 | 1.42 | 0.10 | 2.18 | 0.21 | 1.59 | 0.11 | 1.62 | 0.15 | 1.18 | 0.22 | 1.20 | 0.15 | 1.18 | 0.12 | 1.00 |
| 9 | NO ₂ | 0.70 | 1.35 | 0.53 | 1.21 | 0.43 | 1.97 | 071 | 1.43 | 0.56 | 1.26 | 0.38 | 1.25 | 0.71 | 1.07 | 0.50 | 1.00 | 0.23 | 1.00 |

| 10 | CF ₃ | 0.15 | 1.29 | 0.10 | 1.34 | 0.08 | 2.23 | 0.14 | 1.34 | 0.14 | 1.50 | 0.25 | 1.00 | 0.22 | 1.14 | 0.15 | 1.00 | 0.13 | 1.00 |
|----|-----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 11 | s s | 0.75 | 1.08 | 0.39 | 1.00 | 0.63 | 1.11 | 0.85 | 1.07 | 0.71 | 1.00 | 0.70 | 1.18 | 0.81 | 1.33 | 0.60 | 1.35 | 0.51 | 1.29 |
| 12 | | 1.04 | 1.00 | 0.43 | 1.03 | 0.86 | 1.00 | 1.10 | 1.00 | 0.85 | 1.00 | 0.73 | 1.00 | 0.85 | 1.04 | 0.59 | 1.16 | 0.46 | 1.34 |
| 13 | | 1.13 | 1.00 | 0.50 | 1.00 | 0.98 | 1.00 | 1.18 | 1.00 | 1.07 | 1.00 | 0.94 | 1.00 | 1.04 | 1.07 | 0.75 | 1.00 | 0.62 | 1.56 |
| 14 | | 0.70 | 1.20 | 0.35 | 1.15 | 0.49 | 1.19 | 0.72 | 1.22 | 0.41 | 1.22 | 0.45 | 1.15 | 0.65 | 4.14 | 0.52 | 4.47 | 0.23 | 1.00 |

Table 4. Retention factor for the first enantiomer and separation factor of 14 chiral sulfoxides in methanol/water (70/30, v/v) as a mobile phase on chiral columns made of methyl and chlorosubstituted cellulose derivatives.

| No | Chiral Analyte | Z-I | | | | , e | | 0 H-N-V | | | | T N | | H-N-M | CI | O Z-1 | CI | | |
|----|---------------------------------------|------------------|------|------------------|------|------------------|------|------------------|------|------------------|------|-------|------|------------------|-------|------------------|-------|------------------|------|
| | | k ₁ ′ | α | k_1 | α | k ₁ ′ | α | k ₁ ′ | α | k ₁ ′ | α |
| 1 | S NH ₂ | 0.54 | 2.59 | 0.80 | 1.67 | 0.85 | 3.48 | 0.53 | 2.42 | 0.56 | 1.54 | 1.31 | 1.55 | 0.86 | 21.88 | 0.87 | 39.40 | 0.82 | 1.56 |
| 2 | H ₂ NVO | 0.79 | 1.00 | 0.82 | 1.00 | 1.17 | 1.00 | 0.60 | 1.00 | 0.51 | 1.00 | 0.89 | 1.07 | 0.72 | 1.11 | 0.63 | 1.06 | 0.62 | 1.53 |
| 3 | o o o o o o o o o o o o o o o o o o o | 0.64 | 1.46 | 0.97 | 1.30 | 1.20 | 1.22 | 0.68 | 1.33 | 0.57 | 1.00 | 1.39 | 1.00 | 0.93 | 4.72 | 0.95 | 7.27 | 0.66 | 1.22 |
| 4 | -HN | 0.92 | 1.07 | 0.99 | 1.00 | 1.36 | 1.05 | 0.75 | 1.11 | 0.60 | 1.00 | 1.14 | 1.11 | 0.89 | 1.21 | 0.80 | 1.20 | 0.60 | 1.78 |
| 5 | | 1.98 | 1.76 | 5.77 | 1.59 | 0.13 | 1.31 | 3.46 | 1.42 | 3.14 | 1.00 | - | - | 3.74 | 3.26 | 7.69 | 2.28 | 7.44 | 4.99 |
| 6 | -HN S | 0.98 | 1.00 | 1.09 | 1.00 | 1.35 | 1.04 | 0.81 | 1.00 | 0.64 | 1.00 | 10.71 | 1.21 | 1.03 | 1.16 | 1.04 | 1.05 | 0.69 | 2.18 |
| 7 | S S | 0.22 | 1.77 | 0.23 | 1.22 | 0.16 | 2.43 | 0.17 | 1.38 | 0.12 | 1.39 | 0.18 | 1.42 | 0.29 | 1.00 | 0.05 | 1.00 | 0.14 | 1.00 |
| 8 |) S | 0.25 | 1.45 | 0.35 | 1.23 | 0.29 | 1.68 | 0.26 | 1.22 | 0.19 | 1.17 | 0.39 | 1.25 | 0.36 | 1.47 | 0.17 | 2.07 | 0.17 | 1.00 |
| 9 | NO ₂ | 1.22 | 1.32 | 2.32 | 1.19 | 1.80 | 1.78 | 1.55 | 1.00 | 1.07 | 1.14 | 1.96 | 1.40 | 1.84 | 1.31 | 1.96 | 1.44 | 0.83 | 1.11 |

| 10 | O CF3 | 0.39 | 1.11 | 1.09 | 1.17 | 1.06 | 1.26 | 0.82 | 1.00 | 0.63 | 1.15 | 4.73 | 1.00 | 0.95 | 1.64 | 1.08 | 2.00 | 0.59 | 1.34 |
|----|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 11 | 0 | 1.61 | 1.15 | 2.74 | 1.00 | 3.64 | 1.28 | 1.99 | 1.11 | 1.61 | 1.05 | 5.00 | 1.27 | 3.38 | 1.69 | 5.06 | 2.47 | 4.90 | 1.48 |
| 12 | | 2.04 | 1.00 | 2.36 | 1.00 | 4.31 | 1.00 | 1.93 | 1.00 | 1.60 | 1.00 | 3.94 | 1.00 | 2.96 | 1.07 | 3.91 | 1.15 | 2.89 | 1.58 |
| 13 | | 2.28 | 1.00 | 2.80 | 1.00 | 4.79 | 1.09 | 2.31 | 1.00 | 2.05 | 1.00 | 5.04 | 1.00 | 3.81 | 1.16 | 4.73 | 1.12 | 4.32 | 2.18 |
| 14 | | 0.96 | 1.29 | 1.08 | 1.18 | 1.36 | 1.34 | 0.87 | 1.51 | 0.63 | 1.19 | 1.53 | 1.09 | 1.42 | 5.68 | 1.75 | 8.77 | 0.68 | 1.04 |

Table 1 Retention factor for the first enantiomer and separation factor of 14 chiral sulfoxides in methanol as a mobile phase on chiral columns made of 9 chlorosubstituted cellulose derivatives.

| No | Chiral | | | | | | | | | | | Chiral S | elector | | | | | | | | |
|----|--|------------------|------|------------------|------|---|------|---|------|-------|------|------------------|---------|----------|------|-------|------|--------|------|------------------|-------|
| | Analyte | I-Z | | CI | | H-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N | CI | H-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N | CI | CI CI | CI | CI, | CI | I-Z O | CI | CI CI | | H-Z | CI | H-Z | CI |
| | | \mathbf{k}_{1} | α | k ₁ ′ | α | \mathbf{k}_{1} | α | k_1 | α | k_1 | α | \mathbf{k}_{1} | α | k_1 | α | k_1 | α | k_1' | α | k ₁ ′ | α |
| 1 | S NH ₂ | 0.38 | 2.36 | 0.18 | 1.72 | 0.26 | 5.97 | 0.35 | 4.37 | 0.30 | 1.79 | 0.25 | 1.32 | 0.23 | 2.13 | 0.21 | 1.00 | 0.33 | 5.40 | 0.35 | 10.27 |
| 2 | l _N N o | 0.61 | 1.00 | 0.28 | 1.00 | 0.43 | 1.00 | 0.49 | 1.09 | 0.40 | 1.00 | 0.27 | 1.00 | 0.33 | 1.00 | 0.38 | 1.00 | 0.43 | 1.00 | 0.52 | 1.00 |
| 3 | O NH | 0.44 | 1.31 | 0.23 | 1.31 | 0.37 | 1.64 | 0.39 | 1.18 | 0.37 | 1.17 | 0.30 | 1.00 | 0.31 | 1.49 | 0.26 | 1.00 | 0.43 | 1.57 | 0.53 | 2.67 |
| 4 | S. S | 0.66 | 1.07 | 0.33 | 1.00 | 0.59 | 1.00 | 0.54 | 1.08 | 0.48 | 1.00 | 0.35 | 1.00 | 0.41 | 1.00 | 0.35 | 1.00 | 0.43 | 1.08 | 0.78 | 1.14 |
| 5 | | 0.54 | 1.61 | 0.41 | 1.43 | 0.36 | 2.86 | 0.62 | 1.00 | 0.77 | 1.35 | 0.66 | 1.59 | 0.67 | 1.72 | 0.22 | 1.00 | 0.41 | 1.20 | 0.62 | 4.36 |
| 6 | -HN S | 0.72 | 1.00 | 0.42 | 1.00 | 0.60 | 1.00 | 0.54 | 1.00 | 0.63 | 1.00 | 0.47 | 1.00 | 0.51 | 1.17 | 0.45 | 1.00 | 0.50 | 1.00 | 0.75 | 1.13 |
| 7 | S | 0.27 | 1.71 | 0.17 | 1.41 | 0.28 | 1.71 | 0.30 | 1.21 | 0.25 | 1.00 | 0.28 | 1.00 | 0.21 | 1.00 | 0.29 | 1.00 | 0.14 | 2.55 | 0.49 | 1.19 |
| 8 |) S O HN | 0.21 | 1.52 | 0.12 | 1.39 | 0.24 | 1.39 | 0.24 | 1.13 | 0.2 | 1.00 | 0.18 | 1.00 | 0.21 | 1.00 | 0.15 | 1.00 | 0.09 | 2.31 | 0.41 | 1.11 |

| 9 | NO ₂ | 0.70 | 1.35 | 0.68 | 1.00 | 0.59 | 1.68 | 0.55 | 1.07 | 0.90 | 1.00 | 0.67 | 1.00 | 0.81 | 1.00 | 0.63 | 1.00 | 0.45 | 1.85 | 1.25 | 1.04 |
|----|-----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|-------|
| 10 | O CF3 | 0.15 | 1.29 | 0.08 | 1.00 | 0.13 | 1.43 | 0.18 | 1.00 | 0.16 | 1.00 | 0.14 | 1.00 | 0.13 | 1.00 | 0.05 | 1.00 | 0.07 | 2.41 | 0.30 | 1.08 |
| 11 | ° | 0.75 | 1.08 | 0.51 | 1.11 | 0.74 | 1.31 | 0.66 | 1.00 | 1.08 | 1.18 | 0.81 | 1.00 | 0.84 | 1.34 | 0.26 | 1.00 | 0.61 | 1.11 | 1.14 | 1.54 |
| 12 | | 1.04 | 1.00 | 0.61 | 1.00 | 1.12 | 1.19 | 0.72 | 1.09 | 1.04 | 1.00 | 0.69 | 1.00 | 0.83 | 1.00 | 0.49 | 1.00 | 0.84 | 1.00 | 1.63 | 11.75 |
| 13 | | 1.13 | 1.00 | 0.73 | 1.00 | 1.15 | 1.00 | 0.84 | 1.04 | 1.44 | 1.00 | 1.00 | 1.00 | 1.14 | 1.00 | 0.59 | 1.00 | 0.96 | 1.00 | 1.56 | 1.10 |
| 14 | | 0.70 | 1.20 | 0.40 | 1.13 | 0.70 | 1.58 | 0.60 | 1.37 | 0.59 | 1.00 | 0.59 | 1.00 | 0.82 | 1.00 | 0.30 | 1.00 | 0.48 | 1.19 | 0.92 | 2.23 |

Table 2. Retention factor for the first enantiomer and separation factor of 14 chiral sulfoxides in methanol/water (70/30, v/v) as a mobile phase on chiral columns made of 9 chlorosubstituted cellulose derivatives.

| No | Chiral | | | | | | | | | | | Chiral S | Selector | | | | | | | | |
|----|---------------------------------|------------------|------|-------|------|------------------|------|-------|------|-------|------|------------------|----------|-------|------|-------|------|-------|------|-------|-------|
| | Analyte | I-Z- | | CI, | | I - Z - I | CI | T-Z-T | CI | CI | CI | CI | CI | I-N | CI | O CI | | L-Z- | CI | L-z- | CI |
| | | k ₁ ′ | α | k_1 | α | \mathbf{k}_{1} | α | k_1 | α | k_1 | α | k ₁ ′ | α | k_1 | α | k_1 | α | k_1 | α | k_1 | α |
| 1 | S S NH ₂ | 0.54 | 2.59 | 0.38 | 1.47 | 1.20 | 9.28 | 0.60 | 5.48 | 0.60 | 1.53 | 1.31 | 1.23 | 1.42 | 1.67 | 0.25 | 1.00 | 0.47 | 7.13 | 1.41 | 15.73 |
| 2 | H ₃ N ⁻ O | 0.79 | 1.00 | 0.48 | 1.00 | 1.64 | 1.00 | 0.71 | 1.08 | 0.66 | 1.00 | 1.37 | 1.00 | 1.70 | 1.00 | 0.43 | 1.00 | 0.63 | 1.08 | 1.66 | 1.00 |
| 3 |) NH | 0.64 | 1.46 | 0.48 | 1.22 | 1.93 | 2.52 | 0.71 | 1.29 | 0.73 | 1.15 | 1.79 | 1.00 | 2.28 | 1.41 | 0.28 | 1.00 | 0.60 | 2.23 | 2.27 | 5.58 |
| 4 | - HN | 0.92 | 1.07 | 0.58 | 1.00 | 2.58 | 1.00 | 0.86 | 1.00 | 0.81 | 1.00 | 1.83 | 1.00 | 2.43 | 1.00 | 0.39 | 1.00 | 0.85 | 1.18 | 2.68 | 1.18 |
| 5 | | 1.98 | 1.76 | 2.39 | 1.33 | 2.37 | 5.29 | 1.70 | 1.39 | 5.30 | 1.31 | 4.52 | 1.00 | 1.67 | 1.66 | 0.40 | 1.00 | 1.22 | 2.31 | 20.36 | 6.82 |
| 6 | -HN S | 0.98 | 1.00 | 0.66 | 1.17 | 2.56 | 1.00 | 0.87 | 1.08 | 0.91 | 1.16 | 2.23 | 1.00 | 2.77 | 1.32 | 0.48 | 1.00 | 0.85 | 1.12 | 2.48 | 1.22 |
| 7 | o=o o HX | 0.22 | 1.77 | 0.15 | 1.35 | 0.40 | 1.80 | 0.28 | 1.20 | 0.21 | 1.00 | 0.30 | 1.00 | 0.40 | 1.00 | 0.24 | 1.00 | 0.33 | 1.44 | 0.59 | 1.12 |
| 8 | S S HN | 0.25 | 1.45 | 0.18 | 1.29 | 0.73 | 1.26 | 0.33 | 1.17 | 0.31 | 1.00 | 0.58 | 1.00 | 0.85 | 1.00 | 0.15 | 1.00 | 0.35 | 1.24 | 1.11 | 1.00 |

| 9 | NO ₂ | 1.22 | 1.32 | 1.43 | 1.00 | 4.35 | 1.92 | 1.13 | 1.04 | 1.89 | 1.00 | 4.64 | 1.00 | 6.05 | 1.13 | 0.77 | 1.00 | 1.31 | 1.27 | 7.78 | 1.00 |
|----|-----------------|------|------|------|------|-------|------|------|------|------|------|-------|------|-------|------|------|------|------|------|-------|------|
| 10 | CF ₃ | 0.39 | 1.11 | 0.38 | 1.00 | 2.12 | 1.07 | 0.46 | 1.00 | 0.65 | 1.00 | 2.32 | 1.00 | 2.88 | 1.00 | 0.09 | 1.00 | 0.35 | 1.07 | 1.08 | 1.40 |
| 11 | | 1.61 | 1.15 | 1.46 | 1.17 | 10.83 | 1.00 | 1.86 | 1.06 | 3.42 | 1.12 | 11.22 | 1.00 | 12.18 | 1.22 | 0.39 | 1.00 | 1.78 | 1.44 | 10.67 | 2.16 |
| 12 | | 2.04 | 1.00 | 1.49 | 1.00 | 4.31 | 1.00 | 1.78 | 1.11 | 2.79 | 1.00 | 7.67 | 1.00 | 9.30 | 1.00 | 0.68 | 1.00 | 2.40 | 1.00 | 1.150 | 1.25 |
| 13 | | 2.28 | 1.00 | 1.81 | 1.00 | 10.93 | 1.00 | 2.23 | 1.00 | 3.81 | 1.11 | 3.08 | 1.04 | 12.23 | 1.20 | 0.78 | 1.00 | 2.39 | 1.06 | 12.74 | 1.14 |
| 14 | | 0.96 | 1.29 | 0.66 | 1.09 | 3.32 | 2.16 | 1.26 | 1.52 | 1.61 | 1.00 | 2.87 | 1.16 | 4.21 | 1.13 | 0.32 | 1.00 | 1.28 | 2.32 | 4.75 | 3.04 |

Table 3. Retention factor for the first enantiomer and separation factor of 14 chiral sulfoxides in methanol as a mobile phase on chiral columns made of methyl and chlorosubstituted cellulose derivatives.

| No | Chiral Analyte | h / o | | T-z- | | The state of the s | | o New York | | H-N-(| — | H-2 | | H-N- | CI | H-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N | CI | | |
|----|-------------------------------|------------------|------|------------------|------|--|------|---------------|------|-------|----------|------------------|------|------------------|-------|---|-------|-------|------|
| | | k ₁ ′ | α | k ₁ ′ | α | k ₁ ′ | α | k_1 | α | k_1 | α | k ₁ ′ | α | k ₁ ′ | α | k ₁ ′ | α | k_1 | α |
| 1 | S NH ₂ | 0.38 | 2.36 | 0.23 | 1.65 | 0.28 | 3.02 | 0.37 | 2.67 | 0.27 | 2.65 | 0.34 | 1.62 | 0.37 | 15.97 | 0.25 | 19.82 | 0.21 | 1.39 |
| 2 | H ₂ N ² | 0.61 | 1.00 | 0.31 | 1.00 | 0.45 | 1.00 | 0.44 | 1.00 | 0.39 | 1.00 | 0.35 | 1.00 | 0.36 | 1.12 | 0.27 | 1.00 | 0.25 | 1.20 |
| 3 | o NH | 0.44 | 1.31 | 0.26 | 1.31 | 0.37 | 1.00 | 0.43 | 1.25 | 0.30 | 1.00 | 0.36 | 1.00 | 0.41 | 3.25 | 0.31 | 3.58 | 0.20 | 1.00 |
| 4 | -HN | 0.66 | 1.07 | 0.32 | 1.00 | 0.44 | 1.08 | 0.61 | 1.10 | 0.43 | 1.00 | 0.40 | 1.08 | 0.45 | 1.19 | 0.32 | 1.20 | 0.22 | 1.33 |
| 5 | | 0.54 | 1.61 | 0.27 | 1.59 | 0.42 | 1.20 | 0.54 | 1.66 | 0.46 | 1.00 | - | - | 0.46 | 2.17 | 0.37 | 1.61 | 0.33 | 2.39 |
| 6 | HN S | 0.72 | 1.00 | 0.39 | 1.00 | 0.51 | 1.00 | 0.74 | 1.00 | 0.51 | 1.00 | 0.77 | 1.21 | 0.57 | 1.05 | 0.41 | 1.00 | 0.24 | 1.62 |
| 7 | o n | 0.27 | 1.71 | 0.19 | 1.28 | 0.15 | 2.44 | 0.27 | 1.81 | 0.13 | 1.95 | 0.14 | 1.30 | 0.28 | 1.23 | 0.21 | 1.41 | 0.14 | 1.00 |
| 8 | O HN | 0.21 | 1.52 | 0.13 | 1.42 | 0.10 | 2.18 | 0.21 | 1.59 | 0.11 | 1.62 | 0.15 | 1.18 | 0.22 | 1.20 | 0.15 | 1.18 | 0.12 | 1.00 |
| 9 | NO ₂ | 0.70 | 1.35 | 0.53 | 1.21 | 0.43 | 1.97 | 071 | 1.43 | 0.56 | 1.26 | 0.38 | 1.25 | 0.71 | 1.07 | 0.50 | 1.00 | 0.23 | 1.00 |

| 10 | CF ₃ | 0.15 | 1.29 | 0.10 | 1.34 | 80.0 | 2.23 | 0.14 | 1.34 | 0.14 | 1.50 | 0.25 | 1.00 | 0.22 | 1.14 | 0.15 | 1.00 | 0.13 | 1.00 |
|----|-----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 11 | s s | 0.75 | 1.08 | 0.39 | 1.00 | 0.63 | 1.11 | 0.85 | 1.07 | 0.71 | 1.00 | 0.70 | 1.18 | 0.81 | 1.33 | 0.60 | 1.35 | 0.51 | 1.29 |
| 12 | | 1.04 | 1.00 | 0.43 | 1.03 | 0.86 | 1.00 | 1.10 | 1.00 | 0.85 | 1.00 | 0.73 | 1.00 | 0.85 | 1.04 | 0.59 | 1.16 | 0.46 | 1.34 |
| 13 | | 1.13 | 1.00 | 0.50 | 1.00 | 0.98 | 1.00 | 1.18 | 1.00 | 1.07 | 1.00 | 0.94 | 1.00 | 1.04 | 1.07 | 0.75 | 1.00 | 0.62 | 1.56 |
| 14 | | 0.70 | 1.20 | 0.35 | 1.15 | 0.49 | 1.19 | 0.72 | 1.22 | 0.41 | 1.22 | 0.45 | 1.15 | 0.65 | 4.14 | 0.52 | 4.47 | 0.23 | 1.00 |

Table 4. Retention factor for the first enantiomer and separation factor of 14 chiral sulfoxides in methanol/water (70/30, v/v) as a mobile phase on chiral columns made of methyl and chlorosubstituted cellulose derivatives.

| No | Chiral Analyte | | H-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N | | | O H-N | | O H - N - N - N - N - N - N - N - N - N - | | | | H-N- | | | CI | 0 Z-z-1 | CI | | |
|----|--|------------------|---|------------------|------|-------|------|---|------|------|------|-------|------|------------------|-------|------------|-------|-----------------|------|
| | | k ₁ ′ | α | k ₁ ′ | α | k_1 | α | k ₁ ′ | α | | | | | k ₁ ′ | α | k_1 | α | $\mathbf{k_1}'$ | α |
| 1 | S S NH ₂ | 0.54 | 2.59 | 0.80 | 1.67 | 0.85 | 3.48 | 0.53 | 2.42 | 0.56 | 1.54 | 1.31 | 1.55 | 0.86 | 21.88 | 0.87 | 39.40 | 0.82 | 1.56 |
| 2 | H ₂ N | 0.79 | 1.00 | 0.82 | 1.00 | 1.17 | 1.00 | 0.60 | 1.00 | 0.51 | 1.00 | 0.89 | 1.07 | 0.72 | 1.11 | 0.63 | 1.06 | 0.62 | 1.53 |
| 3 | S NH | 0.64 | 1.46 | 0.97 | 1.30 | 1.20 | 1.22 | 0.68 | 1.33 | 0.57 | 1.00 | 1.39 | 1.00 | 0.93 | 4.72 | 0.95 | 7.27 | 0.66 | 1.22 |
| 4 | S | 0.92 | 1.07 | 0.99 | 1.00 | 1.36 | 1.05 | 0.75 | 1.11 | 0.60 | 1.00 | 1.14 | 1.11 | 0.89 | 1.21 | 0.80 | 1.20 | 0.60 | 1.78 |
| 5 | | 1.98 | 1.76 | 5.77 | 1.59 | 0.13 | 1.31 | 3.46 | 1.42 | 3.14 | 1.00 | - | - | 3.74 | 3.26 | 7.69 | 2.28 | 7.44 | 4.99 |
| 6 | -HN O | 0.98 | 1.00 | 1.09 | 1.00 | 1.35 | 1.04 | 0.81 | 1.00 | 0.64 | 1.00 | 10.71 | 1.21 | 1.03 | 1.16 | 1.04 | 1.05 | 0.69 | 2.18 |
| 7 | 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 | 0.22 | 1.77 | 0.23 | 1.22 | 0.16 | 2.43 | 0.17 | 1.38 | 0.12 | 1.39 | 0.18 | 1.42 | 0.29 | 1.00 | 0.05 | 1.00 | 0.14 | 1.00 |
| 8 | on one of the other of the othe | 0.25 | 1.45 | 0.35 | 1.23 | 0.29 | 1.68 | 0.26 | 1.22 | 0.19 | 1.17 | 0.39 | 1.25 | 0.36 | 1.47 | 0.17 | 2.07 | 0.17 | 1.00 |
| 9 | NO ₂ | 1.22 | 1.32 | 2.32 | 1.19 | 1.80 | 1.78 | 1.55 | 1.00 | 1.07 | 1.14 | 1.96 | 1.40 | 1.840 | 1.31 | 1.96 | 1.44 | 0.83 | 1.11 |

| 10 | 0-0-0-CF3 | 0.39 | 1.11 | 1.09 | 1.17 | 1.06 | 1.26 | 0.82 | 1.00 | 0.63 | 1.15 | 4.73 | 1.00 | 0.95 | 1.64 | 1.08 | 2.00 | 0.59 | 1.34 |
|----|-----------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 11 | 0 | 1.61 | 1.15 | 2.74 | 1.00 | 3.64 | 1.28 | 1.99 | 1.11 | 1.61 | 1.05 | 5.00 | 1.27 | 3.38 | 1.69 | 5.06 | 2.47 | 4.90 | 1.48 |
| 12 | | 2.04 | 1.00 | 2.36 | 1.00 | 4.31 | 1.00 | 1.93 | 1.00 | 1.60 | 1.00 | 3.94 | 1.00 | 2.96 | 1.07 | 3.91 | 1.15 | 2.89 | 1.58 |
| 13 | | 2.28 | 1.00 | 2.80 | 1.00 | 4.79 | 1.09 | 2.31 | 1.00 | 2.05 | 1.00 | 5.04 | 1.00 | 3.81 | 1.16 | 4.73 | 1.12 | 4.32 | 2.18 |
| 14 | | 0.96 | 1.29 | 1.08 | 1.18 | 1.36 | 1.34 | 0.87 | 1.51 | 0.63 | 1.19 | 1.53 | 1.09 | 1.42 | 5.68 | 1.75 | 8.77 | 0.68 | 1.04 |