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TETRAHEDRON: *ASYMMETRY*

Synthesis, crystal structure and oxidation of (*R*)-(+)-8,9-dimethoxy-6,10b-dihydro-5*H*-thiazolo-[2,3-*a*]isoquinolin-3-one

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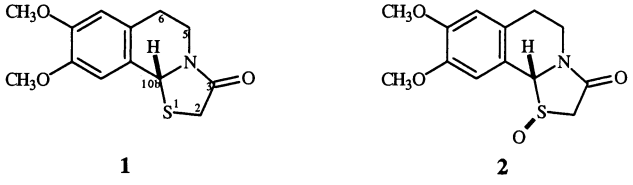
Abstract—(*R*)-(+)-8,9-Dimethoxy-6,10b-dihydro-5*H*-thiazolo[2,3-*a*]isoquinolin-3-one **1** has been synthesized from 6,7-dimethoxy-3,4-dihydroisoquinoline and menthyl thioglycolate. Compound **1** was obtained in the enantiomerically pure form (mp 150–153°C, $[\alpha]_D$ +436) by a single crystallization of the crude reaction product (68% e.e.) from 96% ethanol. The absolute 10b*R* configuration was established by X-ray diffraction. Oxone oxidation of **1** resulted in a configurationally unstable dextrorotatory *syn*-sulfoxide **2** (mp 173–175°C, $[\alpha]_D$ +62.8).

1. Introduction

In connection with our study on sulfur-mediated syntheses of isoquinoline alkaloids we have used the dihydrothiazolo[2,3-*a*]isoquinolinone derivatives **1** and **2** (Fig. 1) in racemic form as intermediates in the synthesis of (±)-salsolidine.[1] Recently, we have undertaken the synthesis of **1** and **2** in non-racemic form with a view to developing routes for the asymmetric synthesis of isoquinoline alkaloids.

Several synthetic methods for the construction of the partially-hydrogenated, racemic thiazolo[2,3-*a*]isoquinoline heterocyclic system, of the type **1**, have been developed. Most usually, they involve cyclocondensation reactions between 3,4-dihydroisoquinoline derivatives and α-mercaptoacids,[2–5] their esters[2] or β-mercaptoacid halides,[2–6] or ethylene sulfide.[7,8] The reactions of 3,4-dihydroisothiocarbostyril with α-haloacids,[9] and of *N*-thioacylated β-phenylethylamine with α-haloacid halides[10,11] have also been successfully applied.



1 **2**

Figure 1.

As far as we know, none of the above synthetic strategies has been adapted for asymmetric synthesis of thiazolo[2,3-*a*]isoquinoline derivatives, neither has any compound of this type been obtained in enantiomerically pure form. Herein, we describe our investigations into the asymmetric synthesis of compounds **1** and **2** from 6,7-dimethoxy-3,4-dihydroisoquinoline and (−)-menthyl thioglycolate **3**, resulting in enantiomerically pure (*R*)-(+)-8,9-dimethoxy-6,10b-dihydro-5*H*-thiazolo[2,3-*a*]isoquinolin-3-one **1**. The absolute configuration of **1** was also established by X-ray crystallography.

Enantiomerically pure or enriched sulfoxides can be conveniently prepared by a variety of procedures involving asymmetric oxidation of the corresponding sulfide.[12] In our case, the chiral sulfide **1** was used as a substrate to give (+)-8,9-dimethoxy-6,10b-dihydro-5*H*-thiazolo[2,3-*a*]isoquinolin-3-one *S*-oxide **2** on oxidation with oxone.

2. Results and discussion

For asymmetric synthesis of **1**, cyclocondensation of 3,4-dihydroisoquinoline with thioglycolic acid deriva-

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tives seemed to us to be the method of choice (Scheme 1).

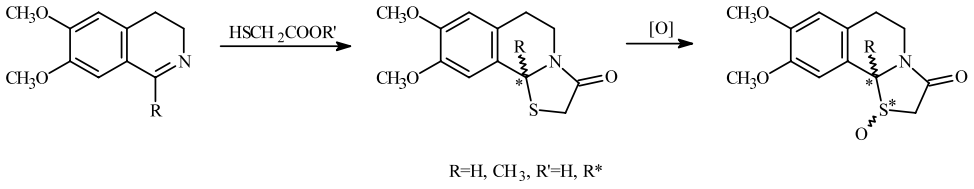
This synthetic pathway offers the possibility of carrying out both diastereoselective and enantioselective syntheses. We assumed that the synthesis of **1** could be realized by using chiral thioglycolic acid derivatives, e.g. esters or amides, prepared with chiral alcohols or amines. On the other hand, the use of external chiral controllers might also effect the enantioselective synthesis. The corresponding *S*-oxides, of the type **2**, could be prepared either from racemic **1** by asymmetric oxidation,[12] or from chiral nonracemic **1** by achiral oxidants.

In the initial step of the diastereoselective synthesis, enantiomerically pure esters **3** and **4** and amide **5** were first synthesized (Fig. 2). Esters **3** (oil, $[\alpha]_D$ −76) and **4** (mp 43–47°C, $[\alpha]_D$ +21) were obtained in high yield (96 and 89%, respectively) by condensing thioglycolic acid with (−)-menthol and (−)-8-phenylmenthol, respectively, in refluxing toluene under Dean–Stark conditions, followed by chromatographic separation. In an analogous reaction between thioglycolic acid and (+)-α-phenylethylamine, amide **5** (65%, mp 70–75°C, $[\alpha]_D$ +72), accompanied by the corresponding dimeric disulfide (19%, mp 136–139°C, $[\alpha]_D$ +156), were formed.

The ^{1}H NMR spectra of esters **3** and **4**, revealed the characteristic bands assigned to the two methylene group protons of the methylthio substituent and the methine -C*H*OCO- proton. In the spectrum of ester **3** the –CH_2-S- group protons appeared as two singlets at 3.22 and 3.25 ppm, whereas in the spectrum of **4**, they gave rise to a doublet of AB quartet with $^2J=15$ Hz and $^3J=8$ Hz, at 2.55 ppm. The -C*H*OCO- methine proton multiplet was shifted downfield, to 4.71 (in **3**) and to 4.82 ppm (in **4**), relative to its absorption observed in the spectra of the parent alcohols, e.g. 3.40 ppm (menthol) and 3.48 ppm (phenylmenthol). In the ^{1}H NMR spectrum of amide **5**, the CH_3C*H*N group protons appeared as a doublet and multiplet at 1.52 and 5.12 ppm, respectively, with $J=6.9$ Hz, along with a characteristic absorption of protons within the –CH_2-S*H* substituent in the form a triplet at 1.87 ppm and a doublet at 3.24 ppm with $J=9.3$ Hz. The carbonyl group absorption was found at 1728 and 1730 cm^{-1} in the IR spectra of esters **3**, **4**, and of the amide **5** at 1640 cm^{-1}. The molecular formula of the three compounds was confirmed by high resolution mass spectrometry.

The Lewis acid-catalyzed cyclocondensation of 6,7-dimethoxy-3,4-dihydroisoquinoline with the three chiral derivatives of thioglycolic acid, **3**, **4** and **5** was then investigated. To optimize the reaction conditions, several parameters, including the solvent, the temperature and nature of the Lewis acid, were varied. The best results, as to the yield (77%) and enantioselectivity (68% e.e.), were achieved, when menthyl thioglycolate **3** was used and the reaction was carried out in isopropyl ether, at rt, in the presence of titanium(IV) isopropoxide, under an argon atmosphere. To our surprise, the use of ester **4**, derived from 8-phenylmenthol, recommended as a more powerful inductor of chirality,[13] resulted in the formation of a racemic product in only 27% yield. The possible reasons for this failure could be steric hindrance which could also account for the lack of reactivity of 1-methyl-3,4-dihydroisoquinoline with menthyl thioglycolate **3**. Amide **5**, also turned out to be unreactive in the addition at rt, whereas at elevated temperature it decomposed spontaneously.

Enantiomerically pure **1** (mp 150–153°C, $[\alpha]_D$ +436), was obtained by a single crystallization of the crude reaction product from 96% ethanol. It was identical, both spectroscopically and chromatographically, with a sample of racemic **1**,[9] and its configurational integrity was confirmed by ^{1}H NMR spectra measured in the presence of DNBA[14] and TADDOL[15] as well as by HPLC analysis, applying Chiracel OD-H column. The



Scheme 1.

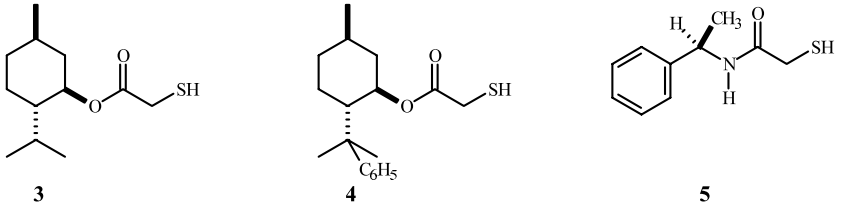


Figure 2.

absolute *R* configuration was then established by single-crystal X-ray analysis; the ORTEP presentation of (+)-**1** is shown in Fig. 3.

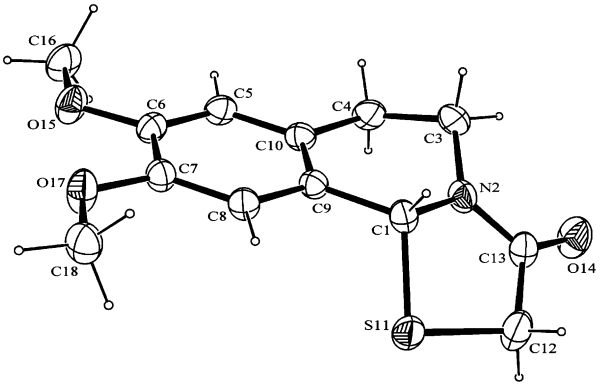


Figure 3.

The hydrogen atom at the stereogenic C10b centre exhibits a β-orientation and occupies a pseudo-axial position with respect to the partially saturated pyridine ring and the five-membered ring. In the solid state, the five-membered thiazolinone ring has an envelope conformation {Cremer and Pople[16] puckering parameters: $Q=0.344(2)$ Å, $\varphi=354.8(4)°$}, whereas the partially hydrogenated pyridine moiety has a conformation intermediate between a half-chair and envelope, but nearer to the envelope one {Cremer and Pople[16] puckering parameters: $Q=0.445(2)$ Å, $\theta=52.1(3)°$, $\varphi=48.0(4)°$}. The dihedral angles between the best-fit planes of the central ring of the tricyclic skeleton and the outer six- and five-membered rings are 7.66(10) and 38.17(7)°. The angle between the outer rings is 40.19(7)°. Both methoxy groups on the fused aromatic ring are inclined at 2.3(3)° (C8–OCH_3) and 2.2(3)° (C9–OCH_3) out of the plane of the ring. The majority of the bond lengths and angles in the structure of (+)-**1** are comparable with those observed in the corresponding *S*-oxides.[17] In the five-membered thiazolinone ring, the C3–N4 bond distance, 1.353(3) Å, is typical of a tertiary amide C–N bond length, 1.346(5) Å.[18] Along the *b* axis, the screw-related molecules are linked by C–H···O intermolecular three-centre hydrogen bonds {C2···O2^{i}, 3.378(4) Å, C2···O3^{i}, 3.249(3) Å; (i): $1-x$, $1/2+y$, $2-z$} to form an infinite one-dimensional chain.

In the attempted enantioselective synthesis of compound **1**, we used chiral oxazolines **6**, **7**, TADDOL **8** and BINOL as external inductors of chirality (Fig. 4).

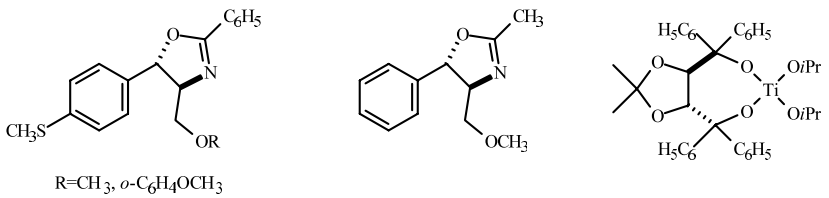
Oxazolines have already been reported to be efficient chiral ligands in additions of organometallic reagents to imines,[19,20] whereas TADDOL–titanate proved very useful in additions to carbonyl compounds.[21]

In our experiments, however, these compounds exhibited poor catalytic activity (yields 5–28%) and asymmetric induction properties. Only in one experiment, in which 6,7-dimethoxy-3,4-dihydroisoquinoline reacted with thioglycolic acid in the presence of TADDOL–titanate, *ent*-**1** was formed in 38% yield and 8% e.e. (by ^{1}H NMR).

As a direct route for the synthesis of sulfoxide **2** asymmetric oxidation of racemic thiazoloisoquinoline **1** was preferred. Several methods based on the Sharpless epoxidation procedures adapted for oxidation of sulfides to chiral sulfoxides, including the protocols presented by Kagan,[22,23] Modena[24] and Uemura,[25] were applied and were unsuccessful. The C-1-methyl derivative was resistant to oxidation, while **1** was converted into optically inactive sulfoxide **2** in yields ranging between 9 and 46%. In several reactions, the unreacted starting material was isolated and its enantiomeric composition was investigated by specific rotation and NMR spectra measurements, in the hope that a kinetic resolution process was taking place. Unfortunately, only optically inactive **1** was found, indicating a lack of selectivity in the oxidation of the heterocyclic system.

Since we had enantiopure **1** in hand, we decided to carry out oxidation with an achiral oxidizing agent. Thus, enantiomerically enriched (91% e.e.) thiazoloisoquinoline **1** was oxidized with Oxone, resulting in the formation of two diastereomeric sulfoxides (TLC). The initially formed less polar diastereomer was isolated in 68% yield from the reaction mixture by extraction with carbon tetrachloride. It was characterized by mp (173–175°C), the specific rotation value ($[\alpha]_D$ +62.8) and ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum was identical with that of racemic *syn*-sulfoxide **2**, but differed from that of the *anti*- diastereomer, (whose configuration was established by X-ray analysis).[17] We were unable to determine the enantiomeric purity of the sulfoxide, because the spectral (^{1}H NMR with shift reagents) and chromatographic (HPLC with chiral Chiralcel OD-H column) methods failed.

The *syn*-diastereomer isomerized easily to the *anti* one on attempted crystallization, or in the NMR tube in $CHCl_3$, to give a mixture of *syn*/*anti* isomers at a



6 **7** **8**

Figure 4.

constant ratio 1:3.3. This process was accompanied by loss of configuration at the stereogenic centres, which also took place in the solid state, after a few weeks, even at 0°C, the *anti* isomer so formed was optically inactive. We have observed a similar *syn*/*anti* isomerization in the case of racemic **1**.

3. Conclusion

In conclusion, we have reported a facile and stereoselective approach to chiral, non-racemic dihydro-5*H*-thiazolo[2,3-*a*]isoquinolinone derivatives from readily available 3,4-dihydroisoquinolines and the menthyl ester of a thioglycolic acid, and its oxidation to an optically active sulfoxide. The configurational instability of the sulfoxide may discourage the use of such compounds as intermediates in asymmetric synthesis. It should be added that this study represents the first reported preparation and characterization of chiral non-racemic derivatives containing the thiazolo[2,3-*a*]isoquinoline heterocyclic ring system.

4. Experimental

4.1. General

Melting points were determined on a Koffler block and are not corrected. IR spectra were recorded on Perkin–Elmer 180, in KBr pellets. NMR spectra were taken in $CDCl_3$ and in DMSO-d_6 on Varian Gemini 300 with TMS as internal standard. Mass spectra (EI) and FAB techniques were obtained by using Joel D-100 75 eV. For FAB-mass spectra, 3-nitrobenzyl alcohol was used as a matrix. Merck silica gel 60 (70–230 mesh) was used for column chromatography and Merck DC-alufolien silica gel 60_{254} for TLC. High performance liquid chromatographic data (HPLC) were obtained using a Waters HPLC system with Mallinkrodt–Baker Chiracel OD-H column.

4.2. (−)-Menthyl thioglycolate, 3

A mixture of thioglycolic acid (0.45 g, 8.64 mmol), (−)-menthol (1.3 g, 8.3 mmol) and *p*-toluenesulfonic acid (0.2 g) in toluene (80 ml) was heated under reflux with azeotropic removal of water for 10 h. After cooling to rt, the reaction mixture was washed with 1% aqueous sodium hydroxide and water, and then dried. The solvent was then removed and the residue was purified by column chromatography (silica gel 1:10) with hexane/ethyl acetate (100:1) as eluent, to give **3** as colorless oil. Yield: 96%; $[\alpha]_D$ −75.5 (*c* 0.5, $CHCl_3$); IR (KBr) cm^{-1}: 1730; ^1H NMR ($CDCl_3$) δ: 0.76 (d, $J=6.9$ Hz, 3H, CH_3), 0.99 (d, $J=3.4$ Hz, 3H, CH_3), 0.92 (d, $J=3.4$ Hz, 3H, CH_3), 0.92–1.09 (m, 3H), 1.36–1.48 (m, 2H), 1.61–1.72 (m, 2H), 1.88–2.03 (m, 3H), 3.22 and 3.25 (2s, 2H, CH_2S), 4.71 (dt, $J=10.9$, 10.9, 4.4 Hz, 1H, CHOCO). EI MS *m*/*z* (%): 230 (M^+, 0.14), 139 (56), 95 (26), 83 (100), 69 (41), 55 (58), 47 (31), 41 (42). HR MS calcd for $C_{12}H_{22}O_2S$ (M^+): 388.15826; found: 388.16087.

4.3. (+)-8-Phenylmenthyl thioglycolate, 4

Compound **4** was prepared in the same way as ester **3**. Yield: 89%; mp 43–47°C; $[\alpha]_D$ +21 (*c* 1, $CHCl_3$); IR (KBr) cm^{-1}: 1728; ^1H NMR ($CDCl_3$) δ: 0.79–1.27 (m, 3H), 0.88 (d, $J=6.6$ Hz, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.38–1.54 (m, 1H), 1.62–1.73 (m, 2H), 1.80–1.88 (m, 2H), 2.02–2.11 (m, 1H), 2.50 (dABq, $^2J=15.4$, $J=8.4$ Hz, 2H, CH_2S), 4.82 (dt, $J=10.7$, 10.7, 4,4 Hz, 1H, CHOCO), 7.11–7.21 (m, 1H), 7.22–7.37 (m, 4H). EI MS *m*/*z* (%): 306 (M^+, 1), 215 (21), 119 (100), 91 (21). HR MS calcd for $C_{18}H_{26}O_2S$ (M^+): 306.16534, found: 306.16343.

4.4. (+)-Thioglycolic acid *N*-[(*R*)-α-methylbenzyl] amide, 5

Compound **5** was prepared in the same way as ester **3**. Yield: 65%; mp 70–75°C (ethyl ether); $[\alpha]_D$ +72 (*c* 0.21, $CHCl_3$); IR (KBr) cm^{-1}: 1640, 2560, 3277; ^1H NMR ($CDCl_3$) δ: 1.52 (d, $J=6.9$ Hz, 3H, CH_3), 1.87 (t, $J=9.3$ Hz, 1H, SH), 3.24 (d, $J=9.3$ Hz, 2H, CH_2), 5.12 (m, 1H, ArCHC), 6.92 (s, 1H, NH), 7.26–7.39 (m, 5H, ArH). EI MS *m*/*z* (%): 195 (M^+, 6), 162 (74), 120 (19), 105 (100), 91 (11), 79 (20), 77 (28). HR MS calcd for $C_{10}H_{13}NOS$ (M^+): 195.07179, found: 195.07065.

4.5. (+)-Thioglycolic acid *N*-[(*R*)-α-methylbenzyl] amide dimmer

Yield: 19%; mp 136–139°C; $[\alpha]_D$ +155.7 (*c* 0.53, $CHCl_3$); IR (KBr) cm^{-1}:1646, 3275. ^1H NMR ($CDCl_3$) δ: 1.52 (d, $J=6.9$ Hz, 3H, CH_3), 3.30 (s, 2H, CH_2), 5.12 (m, 1H, ArCHC), 6.96 (d, $J=7.1$ Hz, 1H, NH), 7.24–7.35 (m, 5H, ArH). EI MS *m*/*z*: 388 (M^+, 1), 162 (86), 120 (22), 105 (100), 77 (19). HR MS calcd for $C_{20}H_{24}N_2O_2S_2$ (M^+): 388.14358, found: 388.14362.

4.6. (*R*)-(+)-8,9-Dimethoxy-6,10b-dihydro-5*H*-thiazolo[2,3-*a*]isoquinolin-3-one, 1

(−)-Menthyl thioglycolate (0.506 g, 2.2 mmol) and titanium isopropoxide (0.66 ml, 2.2 mmol) in dry isopropyl ether (20 ml) was stirred at rt for 0.5 h under the argon atmosphere. A solution of 6,7-dimethoxy-3,4-dihydroisoquinoline[26] (0.382 g, 2 mmol) in isopropyl ether (15 ml) was then added and the mixture stirred for 48 h at rt, after that time the precipitated product **1** was filtered off (0.408 g, 77%, 68% e.e.) and recrystallized from ethanol to deposit racemic **1** (0.192 g, 47%), while enantiomerically pure (*R*)-(+)-**1** (0.2 g, 49%) was obtained from the mother liquors. Mp 150–153°C, $[\alpha]_D$ +436 (*c* 1, $CHCl_3$). IR (KBr) cm^{-1}: 1670. ^1H NMR ($CDCl_3$) δ: 2.68–2.73 (m, 1H, H-$6_{\psi e}$), 2.96 (ddd, $^2J=13.7$ Hz, $^3J=12$,2 and 5.6 Hz, 1H, H-$6_{\psi a}$), 3.11 (dt, $^2J=12.2$ Hz, $^3J=12.2$ and 3.8 Hz, 1H, H-5_a), 3.61 (d, $J=15.4$ Hz, 1H, H-2α), 3.83 (d, $J=15.4$ Hz, 1H, H-2β), 3.87 and 3.88 (2×s, 6H, 2×OCH_3), 4.45 (ddd, $^2J=12.2$ Hz, $^3J=5.6$ and 1.8 Hz, 1H, H-5_e), 6.01 (s, 1H, H-10b), 6.61 (s, 2H, ArH). EI MS *m*/*z* (%): 265 (M^+, 100), 232 (14), 190 (76), 176 (16). HR MS (M^+) calcd for: $C_{13}H_{15}NO_3S$ (M^+): 265.07727; found: 265.07770.

4.7. (+)-(2*R*,10b*R*)-8,9-Dimethoxy-6,10b-dihydro-5*H*-thiazolo[2,3-*a*]isoquinolin-3-one *S*-oxide, 2

To a solution of (+)-(*R*)-**1** (91% e.e., 0.10 g, 0.38 mmol) in a mixture (2:1) of chloroform/methanol (30 ml) Oxone (0.123 g, 0.4 mmol) in water (3 ml) was added at 0°C. After 0.5 h, water (30 ml) was added and the reaction mixture was extracted with carbon tetrachloride. Sulfoxide **2** was obtained after work-up in yield 68%, mp 173–175°C $[\alpha]_D$ +62.8 (*c* 0.35, $CHCl_3$). IR (KBr) cm^{-1}: 1711; ^1H NMR (DMSO-d_6) δ: 2.68–2.72 (m, 2H, H-6), 2.97 (dt, $^2J=12.3$ Hz, $^3J=12.3$ and 3.9 Hz, 1H, H-5_a), 3.75 and 3.77 (2×s, 6H, 2×OCH_3), 3.98 (d, $J=14.5$ Hz, 1H, H-2β), 4.15 (d, $J=14.5$ Hz, 1H, H-2α), 4.26 (ddd, $^2J=12.3$ Hz, $^3J=4.6$ and 2.1 Hz, 1H, H-5_e), 5.61 (s, 1H, H-10b), 6.87 and 6.95 (2×s, 2H, ArH). EI MS *m*/*z* (%): 281 (M^+, 45), 233 (22), 191 (100), 176 (47), 133 (9). HR MS (M^+) calcd for $C_{13}H_{15}NO_4S$ (M^+): 281.07309; found: 281.07219.

4.8. X-Ray crystallography

4.8.1. General. Intensity data were collected using Kuma Diffraction KM-4 diffractometer with graphite monochromated Cu-Kα radiation ($\lambda=1.54178$ Å). The data were measured using $\tilde{\omega}2\theta$ scan method. The psi-scan absorption correction was applied.[27] The absolute configuration of (+)-**1** was established by the structure refinement using Bijvoet-pair reflections.[28] The programs used were KM-4 Software,[29] SHELXS-97,[30] SHELXL-97,[30] PLATON,[31] and ORTEP-3 for Windows.[32]

4.8.2. Crystal data for (+)-(*R*)-1. $C_{13}H_{15}NO_3S$, $M=265.33$, monoclinic, space group $P2_1$, $a=4.3530(10)$, $b=19.534(4)$, $c=7.516(2)$ Å, $\beta=95.30(3)°$; $V=636.4(3)$ $Å^3$, $T=293(2)$ K, $Z=2$, μ(Cu-Kα)=2.27 mm^{-1}, 2498 data measured of which 2313 were unique, $R_{int}=0.037$, $\theta_{max}=70.1°$, all unique data used in refinement against F^2 values to give final $wR=0.1085$ (on F^2 for all data), $R=0.0374$ {for 2276 data with $F^2>4\sigma(F^2)$}, $S=1.075$ (on F^2 for all data), minimum and maximum transmission: $T_{min}=0.055$, $T_{max}=0.204$, absolute structure parameter $x=-0.005(19)$, H-atom parameters constrained.

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