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Synthesis of new optically active sulfoxides with chelating properties

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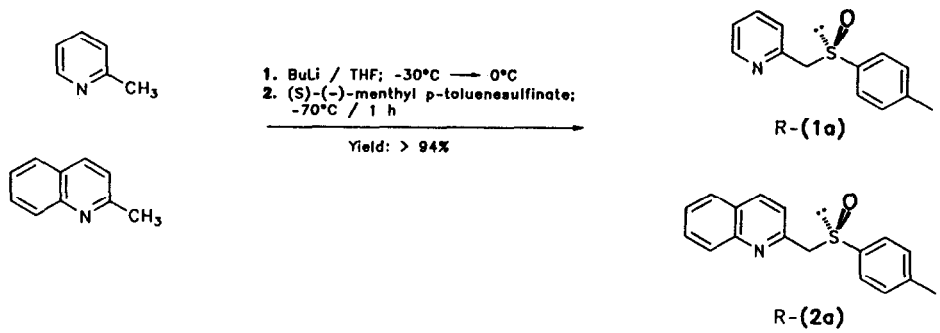
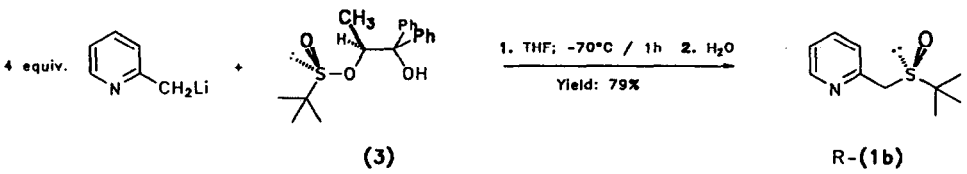
Abstract: Access to enantiomerically pure 2-pyridinylmethyl sulfoxides and β-imino sulfoxides was sought. The latter were obtained in tautomeric mixtures with their enamines by condensation of optically active β-keto sulfoxides with primary amines. 2-Pyridinylmethyl sulfoxides were synthesized by sulfinate substitution. Titanium catalysed oxidation gave good results for the synthesis of (+)-8-(methylsulfinyl)quinoline from the corresponding sulfide.

Transition metal promoted asymmetric synthesis has taken a role of outstanding importance in organic chemistry[1]. The field has clearly been dominated by catalysts carrying chiral bidentate phosphorus ligands (P-P type)[1g,2]. Ligands which utilize two nitrogen donor-atoms (N-N type)[3], nitrogen and oxygen (N-O)[4], nitrogen and phosphorus (P-N)[5] and - last but not least - two oxygen donor-atoms (O-O)[6], have also gained widespread interest and have led to useful results. Very much less attention has been paid to sulfoxide ligands[7]. James tried (+)-methyl p-tolyl sulfoxide as a ligand in Ru and Rh catalysed hydrogenation of olefins with disappointing results[8]. Better results were achieved with mono- and bidentate sulfoxide ligands which carried chirality in their backbones. More recently some promising asymmetric inductions were found in Rh catalysed transfer-hydrogenation of ketones using the chelating N-acetyl-(S)-methionine (R,S)-sulfoxide[9]. Up to 75% ee were reached although this ligand had to be used as a diastereomeric mixture (racemic at sulfur), due to the non-stereoselective sulfide oxidation during its preparation procedure. We feel encouraged to develop methods which lead to enantiomerically pure sulfoxide chelates, i.e. N-S(O)-chelates like the family of the 2-pyridinylmethyl sulfoxides (PMSO), their quinoline analogs and β-imino sulfoxides (IMSO). Thus, the advantageous σ-donor-π-acceptor properties of the C=N-ligand part can be combined with the chiral sulfur-donor. For deeper insight into the ligating properties of the sulfoxide group, e.g. π-acceptance, we project the coordination of these compounds to transition metals in low oxidation states[10]. This goes hand in hand with the search for new chiral ligands for the Fe(0)-catalysed dimerization of mono-olefines and dienes[3a,11]. Furthermore, PMSO related compounds are currently under intense investigation as anti-inflammatory agents[12], and methods to gain access to these substances as enantiomerically pure compounds (EPC) will also be a useful contribution to pharmaceutical chemistry.

R-(+)-2-(p-tolylsulfinylmethyl)pyridine (**1a**) and (R)-(+)-2-(p-tolylsulfinylmethyl)quinoline (**2a**) were readily obtained by Andersen's method[13, 29] (Scheme 1). Adding (S)-(-)-menthyl-p-toluenesulfinate at -70°C to ca. 3 equivalents of lithiated 2-methylpyridine or 2-methylquinoline in THF gave (**1a**) and (**2a**), respectively. R-(+)-2-(*t*-butylsulfinylmethyl)pyridine (**1b**) was synthesized by the analogous substitution on the *t*-butyl sulfinate (3) according to a new method that we have developed recently[14] (Scheme 2).



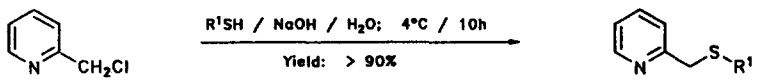
Scheme 1



Scheme 2

These reactions are very clean and products can be obtained in almost quantitative yields after chromatography. There is no evidence for racemization. Since sulfinate ester substitutions are known to proceed under inversion at the sulfur atom[15], we assign (R)-configuration to the obtained PMSO. The scope of this method is limited by the small number of easily accessible enantiomerically pure sulfinates.

We then investigated an additional route to sulfoxides by asymmetric oxidation. Pyridinylmethyl sulfides (4) can be prepared by nucleophilic thiolate attack on 2-(chloromethyl)pyridine (Scheme 3). Unfortunately, the asymmetric sulfide oxidation with the water-modified Sharpless reagent[6b] turned out to proceed without satisfactory enantiomeric excess (Table 1).



(4)

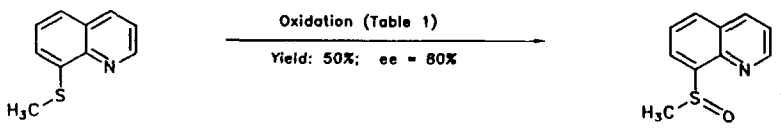
Scheme 3

Table 1. Ti catalysed oxidation of the sulfides (4a,c,d) and (5) to the sulfoxides (1a,c,d) and (2b).

Sulfide	R^1	Oxidising system[a]	Reaction-temp. and time	Product and yield[b]	$[\alpha]_D$ in acetone	ee[d]
(4a)	4-MePh	1.0 Ti/ 2.0 DET/ 1.0 H_2O/ 0.9 TBHP	-20°C/ 18 h	(1a) 50%	-	12 (±3)%
(4c)	Me	1.0 Ti/ 2.0 DET/ 1.0 H_2O/ 1.1 TBHP	-19°C/ 20 h	(1c) 60%	-23 (±2) (c=7)	26 (±3)%
(4c)	Me	1.0 Ti/ 2.0 DET/ 1.0 H_2O/ 1.1 TBHP	4°C / 16 h	(1c) 75%[c,e]	-17 (±2) (c=2)	-
(4c)	Me	0.8 Ti/ 1.6 DET/ 0.8 H_2O/ 0.9 CHP	-28°C/ 15 h	(1c) 45%	-25 (±2) (c=4)	25 (±2)%
(4c)	Me	0.8 Ti/ 1.6 DMT/ 0.8 H_2O/ 0.8 TBHP	-20°C/ 16 h	(1c) 70%	-	12 (±2)%
(4c)	Me	1.0 Ti/ 0.5 DET/ - / 1.0 TBHP	-21°C/ 62 h	(1c) 80%[c]	-	0 (±2)%
(4c)	Me	0.6 Ti/ 0.7 DET/ - / 0.6 TBHP	-21°C/ 60 h	(1c) 60%[c]	-	0 (±2)%[f]
(4d)	2-Naph	0.8 Ti/ 1.6 DMT/ 0.8 H_2O/ 0.9 TBHP	-20°C/ 16 h	(1d) 60%	-8 (±3) (c=10)	5 (±2)%
(4d)	2-Naph	1.0 Ti/ 2.0 DET/ 1.0 H_2O/ 1.0 TBHP	-19°C/ 20 h	(1d) 50%	-	4 (±2)%
(5)		1.0 Ti/ 2.0 DET/ 1.0 H_2O/ 1.0 TBHP	-20°C/ 16 h	(2b) 50%	-	80 (±5)%[f]

a) Solvent: CH_2Cl_2; given are molar equivalents of pre-catalysts: Ti as titanium isopropanolate, DET = (+)-diethyl tartrate, DMT = (+)-dimethyl tartrate, TBHP = tert.-butyl hydroperoxide, CHP = cumene hydroperoxide. *b*) Isolated yield (referred to sulfide) after chromatography unless otherwise stated; yields are for small scale oxidations and not optimised. *c*) Yield estimated from ^1H NMR of crude product. *d*) Determined by ^1H NMR with chiral shift reagent Eu(hfc)$_3$. *e*) Approx. 20% of sulfone was formed. *f*) Determined by ^1H NMR in presence of a chiral amide (ref. 17).

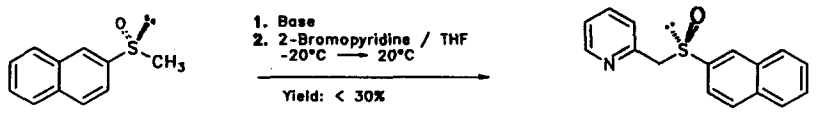
Only 8-(methylthio)quinoline (5) could be oxidized with good ee (ca. 80%). The (+)-8-(methylsulfinyl)-quinoline (2b) was obtained as EPC after a single crystallization of the crude product (Scheme 4).



(5) (2b)

Scheme 4

As a third approach to various PMSO we tried to condense the anion of a chiral sulfoxide directly on the pyridine ring in a nucleophilic aromatic substitution reaction with 2-bromopyridine. We performed a series of experiments with racemic and (+)-(R)-2-(methylsulfinyl)naphthalene (6) as model sulfoxide (Scheme 5).



R-(6) R-(1d)

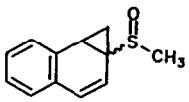
Scheme 5

Table 2. NMR data of compounds (1), (2), (4) and (5) in $CDCl_3$ at 20°C.

compd.	^{1}H NMR δ (J in Hz)	^{13}C NMR δ (multiplicity[a])
(1a)	2.403[3H; s], 4.144[1H; d(12.5)], 4.226[1H; d(12.5)], 7.17-7.30[4H[b]], 7.42[2H; m], 7.64[1H; t(7.7)d(1.8)], 8.56[1H; m]	21.4(p), 65.8(s), 122.8(t), 124.1(t; 2C), 125.3(t), 129.7(t; 2C), 136.5(t), 139.9(q), 141.6(q), 149.8(t), 150.8(q)
(1b)	1.343[9H; s], 3.787[1H; d(12.5)], 4.048[1H; d(12.5)], 7.25 [1H; m], 7.42[1H; d(7.8)], 7.69[1H; t(7.7)d(1.8)], 8.61[1H; m]	22.9(p), 53.8(q), 54.9(s), 122.7(t), 125.2(t), 136.7(t), 149.8(t), 152.5(q)
(1c)	2.579[3H; s], 4.121[1H; d(12.7)], 4.196[1H; d(12.7)], 7.28 [1H; m], 7.38[1H; m], 7.73[1H; t(7.7)d(1.8)], 8.62[1H; m]	37.8(p), 61.4(s), 123.0(t), 125.2(t), 136.7(t), 149.8(t), 150.5(q)
(1d)	4.28[2H, AB[b]], 7.23[2H; m], 7.51-7.68[4H[b]], 7.82-8.00[3H[b]], 8.05[1H; m], 8.52[1H; m]	65.5, 119.9, 122.9, 124.7, 125.3, 127.1, 127.7, 127.9 128.4, 129.1, 132.7[c], 134.4[c], 136.5, 140.2[c], 149.8, 150.7[c]
(2a)	2.390[3H; s], 4.330[1H; d(12.3)], 4.439[1H; d(12.3)], , 7.22-7.33[3H[b]], 7.43-7.48[2H[b]], 7.54[1H; m], 7.74[1H, m], 7.82[1H; d(8.1)], 8.02[1H; d(8.5)], 8.11[1H; d(8.4)]	21.4(p), 66.5(s), 122.7(t), 124.2(t; 2C), 126.7(t), 127.3(q), 127.6(t), 129.1(t), 129.7(t; 2C), 129.8(t), 136.6(t), 140.1(q), 141.7(q), 148.1(q), 151.5(q)
(2b)	3.033[3H; s], 7.525[1H; d(4.3)d(8.4)], 7.775[1H; d(7.2) d(8.2)], 7.970[1H; d(1.5)d(8.2)], 8.270[1H; d(1.7)d(8.4)], 8.319[1H; d(1.5)d(7.2)], 8.920[1H; d(1.7)d(4.3)]	42.4, 122.0, 125.8, 126.8, 128.2, 130.2, 136.4, 143.6, 143.9, 150.1
(4a)	2.280[3H; s], 4.209[2H; s], 7.0-7.3[6H[b]], 7.56[1H; td], 8.52[1H; m]	21.0(p), 41.3(s), 121.9(t), 123.0(t), 129.6(t; 2C), 130.5 (t; 2C), 131.9(q), 136.4(t), 136.5(q), 149.3(t), 157.9(q)
(4c)	2.065[3H; s], 3.808[2H; s], 7.18[1H; m], 7.26[1H; d(8.0)], 7.67[1H; td], 8.56[1H; m]	14.9(p), 39.8(s), 121.6(t), 122.7(t), 136.3(t), 149.0(t), 158.3(q)
(4d)	4.379[2H; s], 7.1-7.8[10H[b]], 8.56[1H; m]	40.3, 122.1, 122.9, 125.7, 126.4, 127.1, 127.4(2C), 127.6 128.3, 131.8[c], 133.3[c], 133.7[c], 136.6, 149.4, 157.6[c]
(5)	2.580[3H; s], 7.37-7.59[4H[b]], 8.13[1H; d(1.7)d(8.3)], 8.94[1H; d(1.7)d(4.2)]	14.3, 121.7, 122.8, 123.5, 126.7, 128.1[c], 136.4, 139.9[c], 145.3[c], 149.1

a) Multipl. (*prim.*, *sec.*, *tert.*, *quar.*) from attached proton test. *b*) not resolved. *c*) quarternary, as supposed from low signal intensity.

On the one hand the formation of the sulfoxide anion demands a strong base, as bases weaker than LDA do not give satisfactory results. Even sodium bis(trimethylsilyl)amide and sodium hydride are inappropriate and give very low conversion. On the other hand an excess of lithium base has to be avoided to suppress lithiation of the pyridine. In any case, the reaction is rather sluggish giving large quantities of side products, presumably from pyridine ring opening and polymerization. Some of these can hardly be separated from the product (**1d**) by chromatography and inhibit proper crystallization. We could not find any considerable acceleration of the substitution in the presence of 2 mol-% dibromo-[1,3-bis(diphenylphosphino)propan]nickel(II) or dichloro-bis(triphenylphosphin)palladium(II)[16].

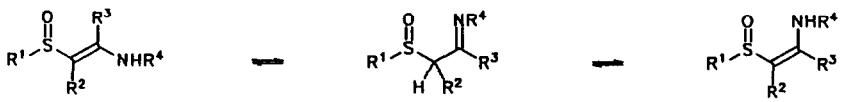


(7a,b)

Scheme 6

The two diastereomeric cyclopropyl compounds (**7a,b**) (Scheme 6) were found as important side products when the reaction mixture (anion of (**6**), pre-formed with 1 equiv. of LDA; 1 equiv. of 2-bromopyridine in THF; no metal complex additive) was allowed to react at room temperature for 15 h. The diastereomers could not be separated by gas-chromatography. Neither could they be completely separated from (**6**) by a preparative scale chromatography. However, NMR and GC-MS allowed unambiguous characterization. Further experiments should be carried out to establish the absolute configuration of each diastereomer. Both diastereomers were found to be partially racemized at sulfur during the reaction or purification procedure (ee ≈ 80% compared to 94% of the starting material (+)-(**6**), determined with the chiral NMR reagent (S)-(+)-N-(3,5-dinitrobenzoyl)-1-phenylethylamine[17]); no further racemization of the isolated material was observed in $CDCl_3$ solution at 20°C. The proportion of (**7a**) and (**7b**) among all sulfoxides (i.e. (**1d**), (**6**), (**7a,b**)) in the crude product was determined by ^1H NMR to be approximately 18% and 13%. Evidently, carbene-addition to (**6**) has occurred - a known feature of intermediately formed sulfoxonium methylide species[18].

β-Imino sulfoxides (IMSO) (**8**) have been subject to previous studies[19]. Most of these compounds exist preferentially in the tautomeric enamine forms E-(**9**) and Z-(**9**) (Scheme 7). Optically active material with determined configuration at sulfur was obtained in several cases by Andersen's method[19c,h], by addition of a enantiomerically pure sulfoxide anion to benzonitrile[19a], or separation of diastereomers after the imine formation of racemic β-keto sulfoxides with chiral amines[19g,i].

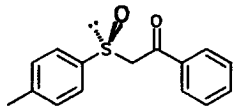


E-(**9**) (**8**) Z-(**9**)

Substituents R used in this work: R^1 = 4-MePh ; R^2 = H ; R^3 = Ph ;

R^4 =		
	2,6-Me_2Ph	(**a**)
	i-Pr.	(**b**)
	H	(**c**)

Scheme 7



(10)

Scheme 8

Since a variety of enantiomerically pure β-keto sulfoxides are accessible[20], a general method for their imine formation would be highly desirable. The convenient method introduced by Kozerski appears to be limited to the use of aliphatic amines[19d]. We tried to condense (**10**) with an aromatic amine (2,6-dimethylaniline) by the use of titanium tetrachloride[21] (Scheme 8). The imine (**8a**) was actually formed thus, but the yield was very poor, due to side-reactions during the condensation and a tedious, anhydrous work-up. (**8a**) did not crystallize and was not obtained sufficiently pure for microanalysis. ^{1}H NMR spectra in $CDCl_3$ and C_6D_6 show that an imine form predominates in both solvents. The two methyl groups on the aromatic N-substituent are diastereotopic and magnetically inequivalent due to hindered rotation of the N-C single bond. Condensation of (**10**) with iso-propylamine gave (**8b**)/(**9b**). The product could be purified by crystallization from ether. In C_6D_6 solution (and similarly in $CDCl_3$) the compound exists clearly in four tautomeric forms: two enamines (Z- and E-(**9b**)) and two imines, very probably E-(**8b**) and Z-(**8b**). The distribution is roughly 8.2 : 1.0 : 2.9 : 1.3 (= enamine I : enamine II : imine I : imine II)[22] at 20°C and 3.2 : 1.0 : 2.5 : 1.4 at 70°C in benzene as estimated from appropriate ^{1}H NMR signals. An equilibrium between the four tautomers is evident; but the proton exchange is too slow to be traced in NMR spin saturation transfer and NOESY experiments at 20°C. Kozerski et al. report on similar β-sulfinyl enamines which have E-configuration in the solid phase and appear as an equilibrium mixture of the Z-enamine and the imine tautomers in aprotic solvents[19d-g].

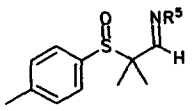
^{1}H NMR data of the tautomeric forms of (8b)/(9b) (R^4 = *i*-Pr).

compound		^{1}H NMR δ (C_6D_6, 20°C)[a]
(**8b**)	imine I	4.03[d(12.5Hz); S(O)CH_2], 3.80[d(12.5Hz); S(O)CH_2], 3.70[sept(6.2Hz); $CH(CH_3)_2$], 1.89[s; $PhCH_3$], 1.19[d(6.2Hz); $CH(CH_3)_2$], 1.02[d(6.2Hz); $CH(CH_3)_2$].
	imine II	3.87[d(13.3Hz); S(O)CH_2], 3.64[d(13.3Hz); S(O)CH_2], 3.59[sept(ca. 6.5Hz); $CH(CH_3)_2$], 1.94[s; $PhCH_3$], 1.13[d(ca. 6.4Hz); $CH(CH_3)_2$], 1.10[d(ca. 6.4Hz); $CH(CH_3)_2$].
(**9b**)	enamine I	5.396[d(^{5}J=0.6Hz); S(O)CH=C], 3.34[br.; d(ca. 6.5Hz); NH], 2.94[m; $CH(CH_3)_2$], 1.993[s; $PhCH_3$], 0.650[d(ca. 6.3Hz); $CH(CH_3)_2$], 0.625[d(ca. 6.3Hz); $CH(CH_3)_2$].
	enamine II	6.44[br.; d(ca. 6.5Hz); NH], 5.092[s; S(O)CH=C], 3.19[m; $CH(CH_3)_2$], 1.99[s; $PhCH_3$], 0.877[d(6.3Hz); $CH(CH_3)_2$], 0.63[d(ca. 6.4Hz); $CH(CH_3)_2$].

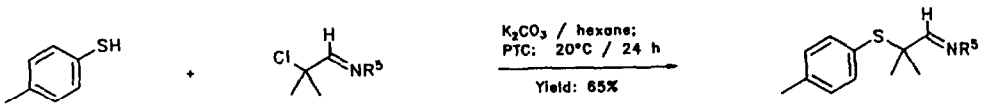
a) The signals of the aromatic protons (range 6.7 - 7.8 ppm) are not assigned.

An attempt to synthesize (**8b**) by addition of methyl p-tolyl sulfoxide anion to benzonitrile and subsequent N-alkylation with 2-iodopropane failed: after chromatography an oil of two isomers of (**9c**) was obtained from which one isomer crystallized slowly in the form of colourless needles.

α,α-Dimethylated IMSO-systems like **(11)** are apt to appear as E-imines as the only isomeric form. We synthesized the sulfide precursors by nucleophilic substitution of commercially available N-(2-chloro-2-methylpropylidene)-alkylamine **(13)** under phase-transfer conditions (Scheme 9).



(11a,b)



(13) **(14)**

Scheme 9

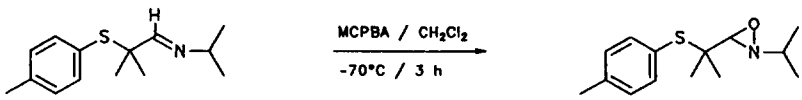
Table 3. Ti catalysed oxidation of the sulfides **(14)** and **(15)** to **(11)** and **(12)**.

Sulfide	R^5	Oxidising system[a]	Reaction-temp. and time	Product and yield[b]	$[\alpha]_D$ in $CDCl_3$	ee[d]
(14a)	*i*-Pr	1.0 Ti/ 2.0 DET/ 1.0 H_2O/ 0.9 CHP	-23°C/ 5 d	(11a) 25%	0	0 (±3)%
(14b)	*t*-Bu	0.8 Ti/ 1.5 DET/ - / 0.8 CHP	-23°C/ 3 d	(11b) 60%	0.0 (c=1.4)	-
(15)	-	1.0 Ti/ 1.2 DET/ - / 1.0 CHP	-23°C / 44 h	(12) 20%[c,e]	-	48 (±2)%
(15)	-	0.8 Ti/ 1.6 DET/ 0.7 H_2O/ 1.0 CHP	-23°C/ 15 h	(12) 10%[c,f]	-	0 (±3)%

a) Solvent: CH_2Cl_2; given are molar equivalents of pre-catalysts: Ti as titanium isopropanolate, DET = (+)-diethyl tartrate, CHP = cumene hydroperoxide. *b*) Isolated yield (referred to sulfide) after chromatography unless otherwise stated; yields are for small scale oxidations and not optimised. *c*) Yield estimated from ^{1}H-NMR of crude product. *d*) Determined by ^{1}H-NMR with chiral shift reagent Eu(hfc)$_3$. *e*) Approx. 40% of sulfone was formed. *f*) Approx. 35% of sulfone was formed.

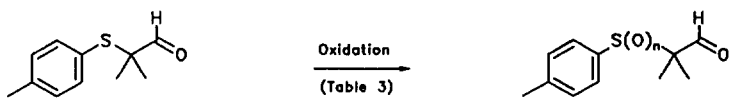
Ti catalysed oxidation was found to be slow and gave significant amounts of sulfone, leaving equivalent amounts of sulfide unchanged (Table 3). The product was always racemic. To prevent hydrolysis the work-up had to be anhydrous. The crude product could be separated fairly well from the titanium complexes by extraction with cold hexane and subsequent chromatography over dehydrated silica gel.

It is worth mentioning that oxidation with MCPBA at -70°C did not lead to racemic IMSO but to exclusive oxidation of the C=N double bond under formation of one diastereomer of the oxaziridine (**16**) (Scheme 10).



(**14a**) (**16**)

Scheme 10



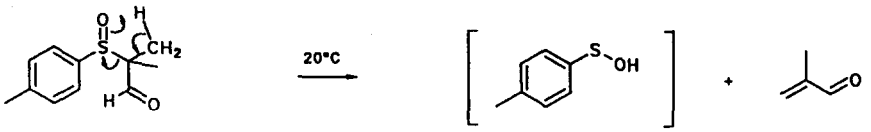
(**15**)

(**12**): n = 1
(**17**): n = 2

Scheme 11

The imino sulfide (**14**) was easily hydrolysed by flash-chromatography over silica gel to give the aldehyde (**15**). Unfortunately, oxidation of (**15**) did not give satisfying results either (Scheme 11 / Table 3). The sulfinyl aldehyde (**12**) was obtained as a racemate by oxidation with the water-modified Sharpless reagent. A titanium catalyst that resembled more the original Sharpless reagent (1.0 equiv. Ti(O*i*Pr)$_4$ / 1.2 equiv. (+)-DET / 1.0 equiv. CHP in CH_2Cl_2; 44h at -23°C) gave sulfinyl aldehyde (**12**) with 48% ee, but in poor yield (approx. 20% of the initial sulfide). At the same time significantly more sulfonyl aldehyde (**17**) was formed (ca. 40%). The enantio-discriminating reaction may be the first oxidation step (sulfide to sulfoxide) or the second (sulfoxide to sulfone), giving rise to a kinetic resolution of the enantiomeric sulfoxides.

Regardless, the sulfinyl aldehydes (**12**) are thermally unstable and can hardly be re-condensed to the desired imines (**11**). In chloroform solution at 20°C (**12**) decomposes completely in the course of a few days. Sulfenic acid is eliminated to give methacrolein (Scheme 12)[23]. Sulfenic acids are unstable themselves and only their recombination-products (i.e. ditolyl thiosulfinate and ditolyl disulfide) are detected. The imines (**11**) are slightly more stable but they also decompose rapidly on warming giving the corresponding imines of methacrolein. In contact with dilute aqueous NaOH, (**11**) hydrolyses and the formed (**12**) is quickly decarbonylated to give iso-propyl tolyl sulfoxide.



(12)

Scheme 12

In conclusion it is to be said that some PMSO are now readily accessible as EPC and wait for their application in coordination chemistry. It is still desirable to find better conditions for the aromatic substitution illustrated in Scheme 5 and to find new tools for the asymmetric oxidation of 2-pyridinylmethyl sulfides[24]. While enantiomerically pure imino sulfoxides (**8**) are also accessible by several approaches, inherent lability of α,α-dialkylated compounds like (**11**) and (**12**) will limit their application. Also, the very direct approach to (**11**) via oxidation of (**14**) cannot be achieved with the modified Sharpless reagent - presumably due to the sterically very demanding substituents on sulfur. However, Andersen's sulfinate substitution may give access to optically active (**12**)[25] which is an interesting building-block for asymmetric synthesis.

Experimental:

Melting points were determined on a heat-block equipped Reichert microscope and are not corrected. NMR spectra were recorded on a Bruker AM 250 (250 MHz) and a Bruker AM 200 (200 MHz for ^{1}H, 50 MHz for ^{13}C) using degassed deuterated solvents with internal standards. Appropriate pulse angles, sweep widths, aquisition and relaxation times were chosen. IR spectra were taken on a Perkin-Elmer Spectrophotometer 883, neat if liquid, in KBr pills if crystalline. Mass spectra were recorded with a Riber-Mag R 10-10 (70 eV electron impact ionization) using a direct inlet system or via GC-MS coupling. Optical rotation at the Na-D line were measured in a 1.0000 dm cell (1 mL) at 22°C (± 2°C) using a Perkin-Elmer Polarimeter 241. Deviations were estimated from the uncertainties of weighing and volumetric measurement as well as from sample purities. Microanalyses were performed by the Service de Microanalyse du CNRS, Gif sur Yvette. Unless otherwise stated, silica gel 60 (230 - 400 mesh) was used as purchased from Merck. Dehydrated silica gel was obtained by keeping it for several hours at 0.5 mbar and 100°C. Chromatographies were performed under 200 mbar pressure using cyclohexane / ethyl acetate mixtures of increasing polarity. Solvents were distilled before use and, if necessary, dried following literature methods and kept under an inert atmosphere. All reactions were carried out under argon.

(R)-(+)-2-[(4-Methylphenyl)sulfinylmethyl]pyridine (**1a**) by Andersen's method: 2-methylpyridine (4.0 g / 43 mmol; distilled from calcium hydride) are dissolved in 120 mL of THF and 15 mL of 1.6 M butyllithium in hexane (24 mmol / Aldrich) are added at -30°C. After having kept the clear, red solution at 0°C for 30 min it is cooled to -70°C. (S)-(-)-[(1R)-menthyl]-p-toluenesulfinate (3.07 g / 10.4 mmol / Fluka, dried in vacuo) in 25 mL of THF are added slowly. After 1 h at -70°C it is quenched with sat. ammonium chloride solution, diluted with 100 mL of hexane, washed with brine, dried over sodium sulfate and then the solvent is removed. Chromatography of the residue gives as the last component 2.4 g of product (quant. yield, traces of 2-methylpyridine left, $[\alpha]_D$= +271 (c= 1, acetone)). Crystallization from acetone/hexane gives 2.21 g of colourless crystals of pure (**1a**), $[\alpha]_D$= +274 (±3) (c=1, acetone), mp 105°C. Found: C 67.72%; H 5.77%; N 5.95%; O 7.04%; S 14.02%. $C_{13}H_{13}NOS$ requires: C 67.50%; H 5.67%; N 6.06%; O 6.92%; S 13.86%. Mass spectrum, *m/z* (relative intensity): 231(5.7 M^+); 183(36.3); 182(28.7); 92(100); 65(48.7). IR: ν(S=O) = 1046 cm^{-1}.

Analogously: *(R)-(+)-2-[(4-Methylphenyl)sulfinylmethyl]quinoline* (**2a**) from 2-methylquinoline; 94% yield of colourless fine needles, $[\alpha]_D$= +149° (±3°) (c=1.3, acetone), mp 119-120°C. Found: C 72.43%; H 5.42%; N 4.82%. $C_{17}H_{15}NOS$ requires: C 72.57%; H 5.37%; N 4.98%. Mass spectrum, *m/z* (relative intensity): 281(7.9 M^+); 233(39.5); 142(100); 116(27.9); 115(46.1). IR: ν(S=O) = 1036 cm^{-1}.

(R)-(+)-2-[(1,1-Dimethylethyl)sulfinylmethyl]pyridine (**1b**): (-)-*t*-butylsulfinate (**3**)[12] (159 mg / 0.48 mmol) in THF (8 mL) is slowly added to 12 mL of a 0.3 M solution of 2-methylpyridine anion (3.6 mmol, prepared as above), maintaining the temperature at ca. -72°C for 1 h. Quenching and work-up as above gives 75 mg of product after chromatography (0.38mmol, 79%), $[\alpha]_D$= +304° (±5°). The product crystallized after several days at 4°C from acetone/ether/hexane; mp 57 - 59°C. Found: C 60.27%; H 7.52%; N 6.90%. $C_{10}H_{15}NOS$ requires: C 60.87%; H 7.66%; N 7.10%. Mass spectrum, *m/z* (relative intensity): 141(27.6); 93(100); 65(25.6); 57(55.7); 41(28.8). IR: ν(S=O) = 1037 cm^{-1}.

(R)-(+)-2-(2-Naphthylsulfinylmethyl)pyridine (**1d**) from nucleophilic aromatic substitution, and the diastereomeric *cyclopropanes* (**7a,b**): LDA (10 mmol) is prepared from diisopropylamine and n-butyllithium in 5 mL of THF at -30°C. (R)-(+)-2-(methylsulfinyl)naphthalene (**6**) (0.28 g / 1.5 mmol / ca. 94% ee[15]) in 4 mL of THF is added at -50°C and slowly warmed to 0°C. After 2 h the mixture is cooled again to -20°C and 1.3 mL of a 0.6 M solution of 2-bromopyridine in THF are added. In the course of 2 h the solution warms up to room temperature, where it is left for another 13 h. After quenching and dilution with hexane and ether, the phases are separated, the organic phase is washed with brine and dried over sodium sulfate. A ^1H NMR is taken for analysis of the crude product. Chromatography with cyclohexane gives ditolyl disulfide (60 mg), then with slowly increasing polarity of the eluent 2-bromopyridine and a fraction that contains the cyclopropyl derivatives (**7a**):(**7b**) = 4:3 and less than 10% of (**6**). Immediately afterwards the rest of (**6**) is eluted, followed by (**1d**). The later fractions are brownish red from pyridine decomposition products. Several crystallizations from acetone/hexane and ether give finally a few almost colourless crystals of (**1d**); mp 102 - 104°C, $[\alpha]_D$= +241° (c= 0.7 in acetone), ee ≈ 93% determined by ^1H NMR with Eu(hfc)$_3$. Found: C 71.28%; H 4.78%; N 5.19%. $C_{16}H_{13}NOS$ requires: C 71.88%; H 4.90%; N 5.24%. Mass spectrum, *m/z* (rel. intensity): 267(13.3 M^+); 219(75.5); 218(100); 92(84.5); 65(73.0). IR: ν(S=O) = 1043 cm^{-1}.

(**7a**) ^1H NMR ($CDCl_3$) δ 0.267 [1H; d(4.3Hz) d(5.9Hz)], 2.016 [1H; d(4.3Hz) d(10.4Hz)], 2.474 [3H; s], 3.091 [1H; d(ca. 6.0Hz) d(ca. 10.5Hz)], 6.107 [1H; d(0.9Hz) d(9.8Hz)], 6.548 [1H; d(9.8Hz)], 7.1 - 7.5 [4H; m]. ^{13}C NMR ($CDCl_3$) δ 10.2; 20.5; 37.4; 42.8; 120.6; 132.9; and 6 signals in the range of 126.8 to 130.0.

(**7b**) ^1H NMR ($CDCl_3$) δ 0.481 [1H; d(4.7Hz) d(5.8Hz)], 2.107 [1H; d(4.7Hz) d(10.2Hz)], 2.594 [3H, s], 2.715 [1H; d(ca. 5.6Hz) d(ca. 10.4Hz)], 6.439 [1H; d(ca. 1.0Hz) d(9.8Hz)], 6.601 [1H, d(9.9Hz)]. ^{13}C NMR ($CDCl_3$) δ 11.7; 23.4; 36.9; 41.9; 118.9; 132.1; and 6 signals in the range of 126.8 to 130.0

Mass spectrum of (**7a**) + (**7b**), *m/z* (relative intensity): 204(2.2 M^+); 142(11.8); 141(100); 139(14.5); 115(39.4) 63(11.5).

2-[(4-Methylphenyl)thiomethyl]-pyridine (**4a**): p-thiocresol (5.28 g / 42 mmol / Janssen) is stirred at 0°C with 50 mL of 3 M aqueous sodium hydroxide to give a white suspension. 2-(chloromethyl)pyridine hydrochloride (6.90 g / 42 mmol / Aldrich) is added 30 min. later. After 10 h at 4°C a brownish solid has separated. The product is extracted with ether, the organic phase washed with 2 M NaOH and brine, dried over sodium sulfate and the solvent removed, leaving 9.4 g of a brown oil. Purification is performed by flash chromatography, giving 8.2 g of a slightly yellow oil (90% yield). Found: C 72.77%; H 6.00%; N 6.35%; S 15.01%. $C_{13}H_{13}NS$ requires: C 72.52%; H 6.09%; N 6.51%; S 14.89%. Mass spectrum, *m/z* (relative intensity): 215(100 M^+); 200(38.7); 182(78.3); 167(38.7); 92(56.6); 65(63.3).

Analogously: *2-(2-naphthylthiomethyl)pyridine* (**4d**), purification by crystallization from hexane, mp 40°C, quant. yield. Found: C 76.26%; H 5.21%; N 5.35%; S 12.91%. $C_{16}H_{13}NS$ requires: C 76.45%; H 5.21%; N 5.57%; S 12.76%. Mass spectrum, *m/z* (relative intensity): 251(55.4 M^+); 236(21.3); 218(100); 217(32.8); 115(46.4); 65(23.6).

2-(Methylthiomethyl)pyridine (**4c**) (liquid; mass spec., *m/z* (rel. int.): 139(2.6 M^+); 94(7.4); 93(100); 92(8.5); 65(15.9); 39(15.4)) and *8-(methylthio)quinoline* (**5**) (mp 82 - 84°C; mass spectrum, *m/z* (relative intensity): 175(100 M^+); 174(29.8); 142(66.2); 130(22.5); 129(43.6)) are similarly synthesized from 2-pyridinylmethylthiol (Lancaster) and 8-mercaptoquinoline hydrochloride (Fluka), respectively, and an excess of iodomethane as the electrophile. Reaction time: 2 h at 0°C. The products can be purified from N-alkylation side products by flash chromatography, giving 80 - 90% yield.

N-[2-(4-Methylphenylthio)-2-methylpropylidene]-2-propylamine (**14a**): p-thiocresol (2.7 g / 22 mmol / Janssen) are stirred in 50 mL of hexane and N-(2-chloro-2-methylpropyliden)-2-propylamine (**13**) (4.0 g / 27 mmol / Merck), anhydrous potassium carbonate (6 g), and Aliquat 336 (0.1 mL / Aldrich) are added[26]. After 24 h the mixture is filtered, the solvent removed and the residue distilled (kugelrohr, 140°C / 0.3 mbar). Yield: 3.4 g (14.4 mol / 65%) of a slightly yellow oil. Found: C 71.16%; H 9.06%; N 5.65%. $C_{14}H_{21}NS$ requires: C 71.43%; H 8.99%; N 5.95%. Mass spectrum, *m/z* (relative intensity): 235(27.2 M^+); 202(51.1); 133(55.0); 124(100); 70(71.6); 43(61.6). IR: ν(C=N) = 1659 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.051 [6H; d(6.3Hz)], 1.363 [6H; s], 2.317 [3H; s], 3.306 [1H; sept(6.3Hz)], 7.06 [2H; m], 7.29 [2H; m], 7.597 [1H; d(<1Hz)]. Analogously: *N-[2-(4-Methylphenylthio)-2-methylpropylidene]-2-methyl-2-propylamine* (**14b**), colourless oil (bp. ca. 160°C / 1 mbar). Found: C 72.31%; H 9.21%. $C_{15}H_{23}NS$ requires: C 72.23%; H 9.30%. Mass spectrum, *m/z* (relative intensity): 249(20.4 M^+); 166(54.2); 165(73.8); 124(50.0); 70(100.0); 57(100.0); 41(44.9). IR: ν(C=N) = 1651 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.064 [9H; s], 1.347 [6H; s], 2.315 [3H, s], 7.07 [2H; m], 7.30 [2H; m], 7.524 [1H; s]. ^{13}C NMR ($CDCl_3$) δ 21.2; 25.3; 29.6; 51.1; 56.5; 128.1; 129.2 [2C]; 136.6 [2C]; 138.6; and 160.3.

2-(4-Methylphenylthio)-2-methylpropanal (**15**) is obtained by the same reaction followed by chromatography of the crude product over fresh silica gel. Found: C 67.81%; H 7.08%. $C_{11}H_{14}OS$ requires: C 67.99%; H 7.26%. Mass spectrum, *m/z* (relative intensity): 194(26.1 M^+); 165(100); 123(14.9); 91(28.6); 77(14.6); 73(45.3). IR: ν(C=O) = 1714 cm^{-1}.

General procedure for Ti catalysed oxidation of sulfides[27]: Distilled titanium isopropanolate (0.5 mL / 1.7 mmol / Aldrich) is stirred with the calculated quantity of the tartrate in 20 mL of dry CH_2Cl_2. After 30 min water is added (for the modified Sharpless reagent, only). The water has to be added very slowly via syringe (it can advantageously be diluted with a fivefold excess of acetone), maintaining vigourous stirring. The sulfide is added 2 h later, the flask cooled to ca. -35°C and the hydroperoxide (CHP, 80% in cumene, Fluka; or TBHP, 3 M in octane, Aldrich) added. The flask is kept at the given temperature (see Tables 1 and 3).

Normal work-up: Some mL of water are added to the cold reaction mixture. It is warmed to 20°C during 1 h and filtered through celite. The filtrate is stirred with an excess of aqueous NaOH (concentrated with NaCl) for two hours. The phases are separated, the aqueous phase extracted several times with CH_2Cl_2, the organic phases washed with brine, dried over sodium sulfate and the solvent evaporated. Chromatography gives the sulfoxide as the last fraction. Some PMSO require acetone as final eluent. Yield of isolated PMSO: 50-80%. *2-(Methylsulfinylmethyl)pyridine* (**1c**), colourless liquid: Found: C 54.00%; H 5.90%; N 8.88%. C_7H_9NOS requires: C 54.16%; H 5.84%; N 9.02%. IR: ν(S=O) = 1049 cm^{-1}. *8-(Methylsulfinyl)quinoline* (**2b**), colourless crystals from hexane/ether (mp 105-107°C), $[\alpha]_D$= +526 (±10) (c= 0.6, acetone). Found: C 62.70%; H 4.33%; N 6.82%. $C_{10}H_9NOS$ requires: C 62.80%; H 4.74%; N 7.32%. Mass spectrum, *m/z* (relative intensity): 191(4.2 M^+); 176(20.7); 143(100); 129(61.5); 101(18.2); 75(20.7). IR: ν(S=O) = 1037 cm^{-1}.

2-(4-Methylphenylsulfinyl)-2-methylpropanal (**12**) (^1H NMR ($CDCl_3$) δ 1.319 [3H; s], 1.447 [3H; s], 2.422 [3H; s], 7.32 [2H; m], 7.46 [2H; m], 9.540 [1H; s].) can be isolated following the same procedure, but must not be treated with NaOH. *2-(4-Methylphenylsulfonyl)-2-methylpropanal* (**17**) is obtained as colourless, liquid by-product. Mass spectrum, *m/z* (relative intensity): 226(9.1 M^+); 198(17.3); 155(32.2); 92(34.5); 91(100); 71(17.8); 65(31.7). ^1H NMR ($CDCl_3$) δ 1.462 [6H; s], 2.458 [3H; s], 7.36 [2H; m], 7.66 [2H; m], 9.798 [1H; s].

Anhydrous work-up (for the imines (**11**)): The solvent is directly evaporated from the reaction mixture, keeping the temperature below -20°C. The viscous residue is stirred several times with 10 mL portions of ice-cold hexane, the extract each time decanted. The combined hexane extracts are left to stand for 40 h at -23°C to precipitate more titanium complex and decanted. The hexane is removed, the residue diluted with cyclohexane and subjected to flash-chromatography using dehydrated silica gel. Yield of (**11**): 25-70% (always contaminated with small amounts of the aldehyde (**12**) and racemic as measured by optical rotation and ^{1}H NMR with Eu(hfc)$_3$). The corresponding sulfone is eluted earlier.

N-[2-(4-Methylphenylsulfinyl)-2-methylpropylidene]-2-propylamine (**11a**): ^{1}H NMR ($CDCl_3$) δ 1.056 [3H; d(6.3Hz); $CH(CH_3)$], 1.100 [3H; d(6.3Hz); $CH(CH_3)$], 1.342 [3H; s; $C(CH_3)_2$], 1.358 [3H; s; $C(CH_3)_2$], 2.398 [3H; s; $PhCH_3$], 3.323 [1H; sept(6.4Hz); $CH(CH_3)_2$], 7.27 [2H; m], 7.42 [2H; m], 7.583 [1H; s; CH=N]. ^{13}C NMR ($CDCl_3$) δ 18.6; 19.2; 21.4; 23.6; 23.9; 61.6; 62.0; 126.1; 129.1; 136.4; 141.9; 160.4.

N-[2-(4-Methylphenylsulfinyl)-2-methylpropylidene]-2-methyl-2-propylamine (**11b**): ^{1}H NMR ($CDCl_3$) δ 1.089 [9H; s; $C(CH_3)_3$], 1.352 [6H; s(!); $C(CH_3)_2$], 2.397 [3H; s; $PhCH_3$], 7.26 [2H; m], 7.42 [2H; m], 7.472 [1H; s; CH=N].

N-[2-(4-Methylphenylsulfonyl)-2-methylpropylidene]-2-methyl-2-propylamine: ^{1}H NMR ($CDCl_3$) δ 1.083 [9H; s; $C(CH_3)_3$], 1.457 [6H; s; $C(CH_3)_2$], 2.428 [3H; s; $PhCH_3$], 7.29 [2H; m], 7.62 [2H; m], 7.717 [1H; s; CH=N].

Oxidation of (**14a**) with 3-chloro-peroxobenzoic acid (MCPBA): commercial 50-60% MCPBA (4 g / Fluka) is dissolved in 75 mL of CH_2Cl_2, the water separated and the solution dried over molecular sieves (4Å) for 2 h at 4°C. This solution is added dropwise to 2.3 g of (**14a**) (10 mmol) in CH_2Cl_2 (50 mL), vigourously stirred at -70°C. White precipitate forms soon. After 2 h at -70°C the mixture is transferred to -23°C filtered after 12 h and the solvent removed. Chromatography gives as main product *N-(2-propyl)-3-[1-methyl-1-(4-methylphenylthio)ethyl]-oxaziridine* (**16**): ^{1}H NMR ($CDCl_3$) δ 1.103 [3H; s], 1.108 [3H; d(6.6Hz)], 1.216 [3H; d(6.2Hz)], 1.248 [3H; s], 2.166 [1H; sept(6.4Hz)], 2.358 [3H; s], 3.823 [1H; d(≤0.5Hz)], 7.14 [2H; m], 7.45 [2H; m].

Formation of (**8a**) from (**10**)[28]: (**10**) (1.46 g / 5.6 mmol) and 2,6-dimethylaniline (2.1 mL / 17 mmol / dist. from CaH_2) are dissolved in 25 mL of dry CH_2Cl_2. A 1.0 M solution of titanium tetrachloride in CH_2Cl_2 (2.8 mmol / Aldrich) is slowly added at 20°C. The mixture turns immediately violett, later black, and a precipitate is formed. One filters through celite (12 h later) and removes the solvent. Ether is added, leaving a white solid (aniline hydrochloride) undissolved. The solution is separated and the ether removed. Chromatography over dehydrated silica gel gives firstly a variety of side-products, considerable amounts of starting material and finally the desired product (**8a**) as a yellow oil, still contaminated with (**10**) and the aniline. ^{1}H NMR ($CDCl_3$) δ 1.994 [3H; s], 2.024 [3H; s], 2.350 [3H; s], 3.732 [1H; d(13.0Hz)], 4.072 [1H; d(13.0Hz)], 6.9 - 8.2 (arom. H). ^{1}H NMR (C_6D_6) δ 1.863 [3H; s], 1.966 [3H; s], 2.040 [3H; s], 3.614 [1H; d(12.8Hz)], 3.930 [1H; d(12.9Hz)], 6.6 - 8.4 (arom. H).

Tautomeric mixture (**8b**)/(**9b**): *i*-propylamine (1g / 17 mmol) and (**11**) (0.75 g / 2.9 mmol) are dissolved in 10 mL of dry CH_2Cl_2. Titanium tetrachloride in CH_2Cl_2 (1.65 mmol) is slowly added, giving a red-brown colour. After 4 h at 20°C the colour has disappeared. Work-up as above. Chromatography gives 0.25 g of yellowish oil (yield: 29% / $[\alpha]_D$= -119 (c=1, acetone). Faintly yellow crystals of pure product are obtained from heptane/benzene or ether (mp 124 - 126°C). Found: C 72.68%; H 6.98%; N 4.55%. $C_{18}H_{21}NOS$ requires: C 72.20%; H 7.07%; N 4.68%.

2-(4-Methylphenylsulfinyl)-1-phenyl-ethenylamine (**9c**): LDA (4 mmol in 15 mL of THF) was prepared from diisopropylamine and n-butyllithium at -30°C. A solution of 0.60 g of (R)-(+)-methyl p-tolyl sulfoxide[27] (3.9 mmol) in THF is added at -30°C. After 2 h it is cooled to -70°C to add 0.42 g of benzonitrile (4.1 mmol / dried over molecular sieves) in 15 mL of THF. In the course of 3 h the mixture warms up to ambient temperature. When 2-iodopropane (5 mmol) is

added to this solution at -20°C, no alkylation occurs. It is hydrolysed with 0.1 mL of water, the solvent removed and the residue subjected to chromatography. A yellow oil (0.5 g) is obtained, from which colourless needles cristallize slowly on treatment with ether (mp 112 - 115°C). Found: C 70.16%; H 5.63%; N 5.22%; O 6.24%; S 12.19%. $C_{15}H_{15}NOS$ requires: C 70.00%; H 5.88%; N 5.44%; O 6.22%; S 12.46%. IR: ν(S=O) = 1011 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.390 [3H; s], 5.26 [ca.2H; s, broad], 5.265 [ca.1H; s], 7.1 - 7.7 [arom. H]. ^1H NMR (C_6D_6) δ 1.977 [3H; s], 5.10 [3H; broad], 6.85 - 7.10 [7H; m], 7.69 [2H; m]. ^{13}C NMR ($CDCl_3$) δ 21.3; 96.9; 124.6; 126.3; 128.7; 129.6; 130.2; 137.2; 140.4; 142.5; 155.0.

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