Copper(I) and silver(I) complexes of 1,5-methylene- and diethylmethylene-bridged bis(oxazoline) ligands. In situ Cu(II)-catalyzed oxidation of methylene bridge

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Abstract — Silver(I) and copper(I) complexes of C 2 -symmetric bis(oxazoline) ligands were studied by UV, NMR, IR, EPR and ES-MS spectroscopies. The stability constants of the Ag–1a and Ag–1b complexes with 1:1 and 1:2 stoichiometries in acetonitrile were determined by NMR spectrometric titrations. The evidence of tetrahedral coordination for complex (Ag(1a) 2 ) 3 + was obtained from the complexation induced shifts (CIS) and NOEs. Mass spectra revealed the Cu(II) mediated oxidation of methylene bridge in copper complexes of 1a and 1b, which was in accordance with the UV, NMR, IR and EPR findings. The efficiency of Cu(I) complexes of methylene-bridged 1,5-bis(oxazoline)s as chiral catalysts in stereoselective cyclopropanation of styrene with ethyl diazoacetate, was compared to that of the dialkylmethylene-bridged 1,5-bis(oxazoline)s 2.

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1. Introduction

Over the last years a wide variety of chiral, C 2 -symmetric bis(oxazoline) ligands has been synthesized and their metallic complexes used as stereoselective catalysts in different reactions, including cyclopropanations and aziridinations of olefins and imines, Diels–Alder and hetero Diels–Alder reactions, 1,2-1,3-dipolar cycloadditions, allylic displacement, addition of dialkylzinc to aldehydes, organolithium addition to imines, hydroisylative reduction, allylic oxidation of olefins, hydroisylation of ketones, Friedel–Crafts reaction, diene cyclization/hydroisylation, glyoxylate–ene reaction, Canizzaro reaction etc. The Lewis basicity of the nitrogen donor atoms and the conformational rigidity of chelates formed represent important structural features of C 2 -symmetric bis(oxazoline) ligands. Among 1,5-bis(oxazoline) ligands, the most frequently used ones in catalytic transformations can be divided into two groups: the bis(oxazolines) with methylene spacer (I) and the bis(oxazolines) with the dialkylmethylene spacer (II) (Scheme 1).

Keywords: Bis(oxazoline); Metal complex; Chiral catalysts.

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Scheme 1.

Both types of the ligands are capable to form six-membered metal chelates, which fixes their conformation in nearly planar geometry. Recently, we have prepared a series of macrocyclic 28 and acyclic 29 1,5-bis(oxazoline) derivatives, the latter possessing elongated aromatic arms of variable length and flexibility attached on chiral centres. We have also performed a detailed study of the structure, stoichiometry and conformation of Cu(I) and Ag(I) complexes with type II bis(oxazoline) ligands in solution. 30 In the type II of the 1,5-bis(oxazoline) ligands, the presence of dialkylmethylene spacer fixes two oxazoline double bonds in an isolated position. However, if the type I ligands are...
considered, the presence of the methylene bridge allows formation of two tautomeric forms, \( \text{Ia} \) and \( \text{Ib} \), the latter possessing a 4\( \pi \) conjugated system (Scheme 1). It should be noted that removal of the NH proton in \( \text{Ib} \) may give an anionic ligand which should exhibit different affinity toward metal cations and as the consequence the properties of such catalytic complex may also be altered. PE and NMR spectra of bis(oxazolines) \( \text{1f} \) and \( \text{1h} \) (Chart 1) revealed that the \( \text{Ia} \) tautomeric form presents the dominant species in the gas phase as well as in the solution. On the other hand, a UV spectroscopic investigation of ligand \( \text{1h} \), indicated the presence of a small amount of the enamine \( \text{Ib} \) in solution.\(^{31} \)

To investigate possible differences between methylene- (\( \text{1a}, \text{1b} \)) and the previously studied diethylmethylene (\( \text{2a}, \text{2b} \))\(^{30} \) bridged 1,5-bis(oxazoline) ligands (Chart 1) we undertook a detailed spectroscopic study of \( \text{1a} \), \( \text{1b} \)–Ag(I) and Cu(I) complexes and the comparative study of the catalytic properties of type \( \text{I} \) and type \( \text{II} \) (Chart 2) Cu(I) complexes in the cyclopropanation of styrene with ethyl diazoacetate.

For comparison, the cyclopropanations were also performed by using the Cu(I) catalytic complexes of alkoxyphenyl substituted ligands \( \text{1c}, \text{1d}, \text{1e} \) \(^{29} \) and commercially available ligands \( \text{1f}, \text{1g}, \text{1h} \) and \( \text{2c}, \text{2d}, \text{2e} \) lacking long substituents on chiral centres. All of the 1,5-bis(oxazoline) ligands studied are based on \( \text{S}-\)tyrosine and \( \text{R} \)–4-hydroxyphenylglycine. The aromatic arms of variable length and flexibility attached onto stereogenic centers of the ligands may influence both their complexation and catalytic properties and may result by different stereochemical outcome.

2. Results and discussion

2.1. Spectroscopic studies of 1a and 1b silver(I) and copper(I) complexes in solution

2.1.1. Silver(I) complexes. The UV spectral changes in the titrations of \( \text{1a} \) and \( \text{1b} \) with Ag(I) in MeCN were insufficient

![Figure 1. Complexation-induced shifts (CIS) for 1a–Ag⁺ complexes.](image-url)
to enable accurate analysis, and changes remained only very slight over longer period of time. Therefore, the formation of Ag⁺ complexes of 1a and 1b in MeCN-$d_3$ was studied by $^1$H NMR. The spectra of the free ligands were found concentration-independent in the concentration range of $2 \times 10^{-3}$ to $2 \times 10^{-2}$ mol dm$^{-3}$ showing lack of ligand self-association.

Addition of Ag⁺ produced significant shifts in all of the ligand resonances, without significant line broadening, indicating fast equilibrium kinetics on the NMR time scale. The observed complexation induced shifts (CIS; $\Delta \delta = \delta H_{lig} - \delta H_{compl}$, ppm), were plotted against the $c(Ag^+)/c(1a,1b)$ ratio (Fig. 1). In the case of ligand 1a, additions of Ag⁺ induced upfield shifts of C(2)–CH$_2$ (methylene bridge), C(4)–H and C(2')–H (aromatic) signals, until the ratio of 0.5 was reached followed by downfield shifts of all resonances at higher ratios. The upfield shifts observed up to the molar ratio of 0.5 suggests formation of the (Ag(1a)$_2$)$_2$ (1+ complex, whereas downfield shifts of all of the ligand resonances in the $c(Ag^+)/c(1a)$ range of 0.5–2.0 shows transformation of the first complex into (Ag(1a))$^{2+}$ one. Strong deshielding effects were observed for C(4)–H, C(5)–H and C(2')–H (aromatic) signals, (see Figure 2 for numera-
tion) on going from 1:2 to 1:1 complex (Fig. 1). Also the methylene bridge protons experienced the strongest deshielding effect on going from the (Ag(1a)$_2$)$_2$ towards the (Ag(1a))$^{2+}$ complex. This suggests that the same protons

are strongly shielded in (Ag(1a)$_2$)$_2$ (1+ complex. In the 1:1 complex the protons close to the metal centre [C(4)–H, C(5)–H and C(2')–H] should be strongly deshielded upon Ag⁺ coordination by the through bond effects; in the 1:2 Ag⁺–ligand complex, such effects are less pronounced being distributed between two bis(oxazoline) units. Exactly the same trend of induced shifts was observed for (Ag(2a)$_2$)$_2$ and (Ag(2a)$_2$) complexes and explained by formation of the pseudotetrahedral Ag⁺ complex of 1:2 stoichiometry, with the cation bound to four nitrogen atoms of two orthogonally oriented bis(oxazoline) units. In such a complex, each bis(oxazoline) unit is located between two C(4)–phenyl groups of the second ligand molecule, which results through shielding of C(4)–H and C(2')–H. The bridging methylene protons are shielded by two distant phenyls of the C(4')–O-benzyl arms in the 1:2 complex. Additional support for the structure of the 1:2 complex comes from the analysis of the NOESY spectrum taken at the $c(Ag^+)/c(1a)$ ratio of 0.5.

Examination of the CPK model of 1a shows that the majority of the observed NOE crosspeaks could be explained by the favourable distances between respective hydrogen atoms in a single 1a molecule. However, a clear crosspeak corresponding to NOE interaction between C(4')–OCH$_3$ and C(4)–H is observed. The closest possible distance between these protons in the model of 1a is over 6 Å, well exceeding the limiting value of 2.2–5 Å, necessary for observation of the NOE effect. Thus, this crosspeak could be explained only by mutual interaction of two 1a ligands in the pseudotetrahedral [Ag(1a)$_2$]$^{2+}$ complex (Fig. 2).

The additions of Ag⁺ to ligand 1b also induced upfield shifts of C(4)–H, C(4')–CH$_2$, C(2')–H (aromatic), and C(4')–OCH$_3$ signals until the ratio of 0.5 was reached; further additions of the cation produced downfield shifts of all resonances (Fig. 3). A clear maximum at the $c(Ag^+)/c(1b)$ ratio of 0.5 suggests initial formation of the Ag⁺–1b complex of a 1:2 stoichiometry (Fig. 4) which at higher ratios transforms to the 1:1 complex. The strongest

![Figure 2. Schematic presentation of (Ag(1a)$_2$)$_2$ (1+ pseudotetrahedral complex and intermolecular NOE interaction between C(4)H and OCH$_2$–Ph observed in the NOESY spectrum of [Ag(1a)$_2$]$^{2+}$.](image)

![Figure 3. Complexation induced shifts for 1b–Ag⁺ complexes.](image)
MeCN determined by 1H NMR titrations corresponding to the singly charged species [Ag(1b)]+

Among several chemically reasonable speciations used in the fitting of the spectrometric data, two (set by assuming the presence of [AgL]+ and [AgL2]+ or [AgL2]+ and [AgL2]+; L standing for either 1a or 1b) gave satisfactory results. As the electrospray mass spectrometry (ES-MS) of 1a and 1b Ag+ complexes unambiguously indicated the formation of [AgL]+ and [AgL2]+, and no evidence of the presence of [AgL2]2+ species, we could exclude the formation of [AgL2]2+ (see Figures 1 and 2 in the Supplementary Material). The electrospray mass spectra of Ag+(1a) and Ag+(1b) solutions in MeCN showed peaks at m/z = 625 for [Ag(1a)]2+ and 1145 for [Ag(1a)]2+ and 653 for [Ag(1b)]2+ and 1201 for [Ag(1b)]2+ (Figs. 1 and 2, Supplementary Material). The isotopic abundances of the peaks at m/z = 625 and 653 showed peak separation of 1 Da, corresponding to the singly charged species [Ag(1a)]+ and [Ag(1b)]+, respectively. The stability constants of the Ag+ complexes calculated from the 1H NMR titration data are collected in Table 1. Both, 1a and 1b form quite stable 1:1 (KAgL1 ≈ 10^5 M⁻¹) and 1:2 (KAgL2 ≈ 10^5–10^6 M⁻¹)

Table 1. Stability constants of Ag+ complexes with 1a, 1b, 2a and 2b in MeCN determined by 1H NMR titrations

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<td>Ag(1b)1</td>
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<td>Ag(2b)</td>
<td>3.9b</td>
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<td>3.1b</td>
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</table>

Table 1. Stability constants of Ag+ complexes with 1a, 1b, 2a and 2b in MeCN determined by 1H NMR titrations

a K = [AgL+n]/[AgL+n−1][L], L standing for 1a, 1b, 2a or 2b; n = 1,2. 
b See Ref. 30.

complexes with Ag+ in MeCN; generally, their stability constants are for more than one order of magnitude higher than those of the corresponding diethylmethylene bridged derivatives 2a and 2b (except that of Ag(1b)2 being somewhat lower than that of Ag(2b)2). See Ref. 30.

2.1.2. Copper(I) complexes. 1H NMR spectroscopic titrations of 1a and the corresponding diethylmethylene bridged 2a with (Cu(MeCN)4)PF6 showed significant differences. The methylene bridged bis(oxazoline) 1a gave at least two sets of signals upon addition of Cu(I) salt indicating formation of mixture of complexes (Fig. 5). In contrast, ligand 2a showed a single set of signals with significant downfield shifts of the oxazoline protons in accord with fast complex formation and simultaneous coordination of the cation with both nitrogens (Fig. 6). In addition, Cu(I) salt induced severe broadening of 1a lines (as shown in Figure 5) and besides the signals of the free ligand, new resonances shifted downfield for 0.3 ppm could be observed. In the spectrum at c(Cu+) / c(1a) molar ratio of 0.1 only new resonances with integrals approximately 20% of those of the free ligand indicated the initial formation of (Cu(1a))2(+) complex. However, further additions of Cu+, (Fig. 5; c(Cu+)/c(1a)=0.3) resulted in...
severe line broadening and diminished intensity of oxazo-
line proton resonances, being characteristic for the presence
of a paramagnetic species; presumably air oxidation of Cu+ to paramagnetic Cu2+ occurred. The process can be also
observed visually through appearance of violet-blue colour.
The corresponding diethylmethylene bridged ligand 2a could be titrated with Cu+ up to the c(Cu+)/c(2a) molar
ratio of 1.0 lacking any line broadening (Fig. 6) or colour
change.

In order to shed more light on the transformations of copper
complexes of 1a and 1b the IR- and MS-investigations were
performed. The IR spectra of freshly prepared and aged
(four weeks) Cu–1a complexes showed changes
(broadening of the band) in the region of carbon–heteroatom
double bonds (about 1670 cm⁻¹) indicating an oxidative
process on methylene bridge of 1a to carbonyl group by air-
oxygen, thus generating the new chromophore with three
conjugated double bonds. All other bands remained
unaffected. Opposite to this, IR spectra of Ag+ complexes
do not show any change during 4 weeks of standing.

The FTIR spectra of the 1a–Ag+ complex did not show any
change during 4 weeks, showing that the presence of copper
ions was necessary for oxidation. The mass spectra of the
freshly prepared acetonitrile solutions of (Cu(MeCN))2PF6
and 1a and 1b, respectively, show the simultaneous
presence of the free ligand and 1:1 and 1:2 complexes
(Fig. 7a here and Fig. 3a in Supplementary Material). However, the same solutions after standing for 24 h at room
temperature gave different mass spectra; the peaks of free
ligands and 1:1 and 1:2 complexes disappeared and new
peaks corresponding to 1:1- and 1:2-complexes increased
for 14 and 28 mass units, respectively, were observed
(Fig. 7b, here and Fig. 3b, Supplementary Material). In
contrast, the mass spectra of AgBF4 and 1a and 1b
acetonitrile solutions did not show any changes after 24 h
at room temperature (see Figures 1 and 2 in Supplementary
Material).

The increase of masses of the complexes for 14 and 28 mass
units clearly show that oxidation of methylene bridge into
carbonyl group took place accompanied presumably by the
reduction of Cu(II) back to Cu(I), as outlined in Scheme 2.
The presence of Cu(II) was additionally confirmed by EPR
spectrum which showed the formation of a para-magnetic
Cu(II) immediately after mixing the solutions of Cu(I) salt
and ligand 1a. These results are in agreement with those of
NMR and FTIR experiments. Similar oxidation of methyl-
ene bridge in Cu(II)–benzimidazole complex was recently
reported.33

All our attempts to avoid oxidation by working under argon
atmosphere failed, since even the very small amount of
residual oxygen was sufficient to initiate the deleterious
oxidative processes.

The UV spectral changes observed upon mixing of equimolar amounts of 1a and [Cu(MeCN)]nPF6 (c = 1 × 10⁻⁴ mol dm⁻³) in acetonitrile at 25 °C can be grouped
into two types.

As can be seen in Figure 8, the addition of Cu⁺ to 1a
solution caused a rather significant hyperchromic effect on
the ligand UV spectrum, accompanied by the occurrence of
a shoulder at ≈ 300 nm. According to ES-MS results
(Fig. 7) and the previously reported spectrophotometric

![Figure 7. ES-MS spectra of Cu–1a complex in acetonitrile, freshly
prepared (a) and after 24 h standing at room temperature (b).]

![Scheme 2.]
Titration of 2a and 2b with Cu\textsuperscript{2+},\textsuperscript{30} these spectral changes can be attributed to the formation of \([\text{Cu(1a)}]^{+}\) and \([\text{Cu(1a)}_{2}]^{+}\) complexes. The initial increase in the spectrum intensity (up to approx. 5 min from mixing) was followed by a drop in absorbance at spectral maximum (at about 280 nm) of several hours, by a hypsochromic shift of the spectrum and its broadening, and by disappearance of a shoulder at z300 nm (Fig. 8).

This indicated that another process took place in the solution. We believe that it was the Cu\textsuperscript{2+} mediated oxidation of the methylene bridge in the \([\text{Cu(1a)}]^{+}\) and \([\text{Cu(1a)}_{2}]^{+}\) complexes, which is in accordance with the EPR results and the observed time-dependent changes of the corresponding ES-MS spectra. The Cu\textsuperscript{2+} + 1b system showed a similar behaviour. The UV spectra recorded for this system can be found in the Supplementary Material (Fig. 4). As already mentioned, upon mixing of 1a and [Cu(MeCN)\textsubscript{4}]PF\textsubscript{6} at higher concentrations, the resulting acetonitrile solution appeared pronouncedly violet-blue. The colour changed with time to yellow-green, and finally became dark brown. The starting blue colour was assumed to be due to the presence of Cu\textsuperscript{2+} in the solution. For this reason, an experiment was performed in which a solution containing 5.5 \times 10^{-3} mol dm\textsuperscript{-3} of both Cu\textsuperscript{2+} and 1a was prepared, and its spectrum dependence on time was followed simultaneously in the UV and visible regions. Since the absorption coefficients in the UV region were about 100 times higher than in the visible one, the measuring cells of 0.01 and 1 cm path lengths were used, respectively. The spectra collected during three hours are displayed in Figure 9. The changes of the UV spectrum were faster, but basically similar to those described above for the case of the lower reactant concentrations. The visible absorption band recorded \(\approx 1\) min after mixing was centred at app. 620 nm. The spectrum then started to broaden, the

**Figure 8.** Time dependence of the UV spectra of acetonitrile solution containing 1a \((c=1 \times 10^{-4} \text{ mol dm}^{-3})\) and [Cu(MeCN)\textsubscript{4}]PF\textsubscript{6} \((c=1 \times 10^{-4} \text{ mol dm}^{-3})\). Spectra are labelled with the approximate times after mixing of 1a and Cu\textsuperscript{2+}, \(l=1\ \text{cm}, \ t=(25.0 \pm 0.1)\ ^\circ\text{C}\). (a) Spectrum of the free ligand solution and its changes during the first 10 min after the addition of Cu\textsuperscript{2+}. (b) Spectra corresponding to the ‘second process’, recorded in the period of several hours.

**Figure 9.** Time dependence of the absorption spectra of an equimolar acetonitrile solution of 1a and [Cu(MeCN)\textsubscript{4}]PF\textsubscript{6} \((c=5.5 \times 10^{-3} \text{ mol dm}^{-3})\). Spectra are labelled with the approximate times after mixing of 1a and Cu\textsuperscript{2+}, \(l=(25.0 \pm 0.1)\ ^\circ\text{C}\). (a) Spectra recorded in the UV region; \(l=0.01\ \text{cm}\). (b) Spectra recorded in the visible region; \(l=0.01\ \text{cm}\).
absorbances at higher wavelengths decreased, whereas at lower wavelengths the spectrum intensity increased for a quite long period of time (Fig. 9). According to the NMR, EPR and ES-MS findings, these observations can be tentatively explained by the initial oxidation of coordinated Cu(I) to Cu(II), followed by the reversible reaction, i.e. reduction of copper and the oxidation of the ligand bridge from the methylene to the carbonyl one. Obviously, oxygen plays an important role in these reactions. The main final reaction products are Cu(I) complexes with oxidized 1a (stoichiometries 1:1 and 1:2), in agreement with the species observed by ES-MS (Fig. 7).

2.2. Catalytic cyclopropanation

The results of cyclopropanation of styrene with diazoacetate catalyzed by Cu(I) complexes of the ligands 1a–h and 2a–e are collected in Table 2. The results show that the catalytic activities obtained by ligands and 4% for trans to ligand complexes revealed the significant increase of ee.

Table 2. Enantioselectivity in cyclopropanation of styrene catalyzed by Cu(I) complexes of 1a–h and 2a–e

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</tbody>
</table>

\[ r = \frac{[\text{ligand}]}{[\text{Cu}^+]}. \]

Enantiomeric excesses were determined by gas chromatography using GLC chiral CP-Chirasil-Dex CB capillary column.

Combined spectroscopic studies of silver(I) and copper(I) complexes of 1,5-dinitrogen ligands with C2-symmetric 1a and 1b have shown that they form stable 1:2 metal/ligand complexes with a pseudotetrahedral arrangement of coordinating N atoms around the central metal ion, which transform on ulterior addition of metal ions to 1:1 complexes. The stability constants (Table 1) were determined for [Ag–1a]\(^{+}\) and [Ag–1b]\(^{+}\) complexes of 1:2 and 1:1 stoichiometries. All spectroscopic investigations of copper complexes of 1a and 1b revealed the oxidative transformation of methylene bridge concomitant with oxidation of Cu(I) to Cu(II). C2-Symmetric bis(oxazolines) with methylene bridge (1) and dialkylmethylene bridge (2) in the form of Cu(I) catalytic complexes were tested in enantioselective cyclopropanations of styrene with ethyl diazoacetate. Most of the ligands exhibited modest

3. Conclusion
enantioselectivity with the highest enantioselectivity of 62% ee for cis- and 56% ee for trans-isomer obtained by the Cu(I) complex of 2b (Table 2). The observed oxidative transformation of the Cu(I) complexes of methylene bridged ligands may account for the lower enantioselectivities obtained in the cyclopropanations with this type of catalytic complexes.

4. Experimental

Preparation of compounds 1a–e and 2a,b was reported previously,29 and compounds 1f–h and 2c–e were obtained from Aldrich. Reagents were purchased from Aldrich and Fluka and were used without further purification. All solvents were purified and dried according to standard procedures. IR spectra were taken in KBr pellets on a Perkin Elmer 297 spectrometer. NMR spectra were recorded on the Bruker spectrometer, at 300 or 600 MHz. Mass spectra were recorded by means of Finnigan LCQ Deca instrument. EPR spectra were recorded at Varian E-9 spectrometer.

4.1. Spectrometry

The UV/Vis absorption spectra were recorded at (25.0 ± 0.1) by means of a Varian Cary 5 spectrophotometer equipped with a thermostating device. Quartz cells of 0.01 and 1 cm path lengths were used. Absorbances were sampled at 1 nm intervals.

1H NMR titrations of 1a, 1b and 2a were carried out at ambient temperature in CD3CN (data taken in Δδ/ppm according to the signal of solvent used as internal standard) with Bruker 300 and 600 MHz. c(1a,1b,2a)=2×10−3 mol dm−3, V0=0.5 mL, c(AgBF4)=0–4×10−2 mol dm−3, c(Cu(MeCN)4)2PF6=0–2×10−2 mol dm−3. Aliquots of the metal ion solution were added into the solution of the ligand in a NMR probe with Hamilton syringe. The obtained spectrometric data were processed using the SPECFIT program.34

4.2. Catalytic cyclopropanation

To an excess of styrene (0.52 g, 0.57 ml, 5.0 mmol) the precatalytic Cu(I) trifluoromethanesulphonate benzene complex (15 μmol, available from Fluka) and the corresponding quantity of chiral oxazoline ligand were added. Then ethyl diazoacetate (1.0 mmol, 1.0 ml of 1 mol dm−3 solution in 1,2-dichloroethane) was added dropwise by a syringe pump over a period of 4.5 h. The reaction mixture was stirred under inert argon atmosphere overnight at room temperature. Diastereomeric mixture of cis/trans ethyl 2-phenylcyclopropan-1-carboxylates was isolated by chromatography on a silica gel column (1×15 cm) with ethylacetate–light petroleum (gradient 0–10%) as eluent.

Diastereomeric composition and chemical yield were determined by gas chromatography on the HP-1 capillary column with biphenyl as an internal standard. Enantiomeric excesses were determined by gas chromatography using GLC chiral CP-Chirasil-Dex CB capillary column. Cyclopropanation products were characterized by independent synthesis as described.5,35

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2004.06.117

References and notes