Zinc(II)-catalysed transformation of epoxides to aziridines

Dorte Kühnau, Ib Thomsen and Karl Anker Jørgensen *

Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

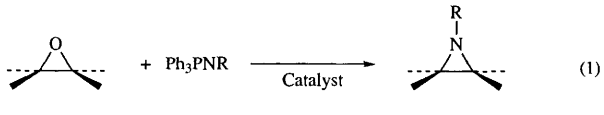
The Lewis acid-catalysed transformation of epoxides to aziridines with iminophosphoranes as the nitrogen-fragment donor has been investigated. Of the Lewis acids tested, zinc(II) complexes had the best catalytic properties. The method works best for terminal and cyclic epoxides, internal epoxides being less reactive. Of the various iminophosphoranes employed *N*-(triphenylphosphoranylidene)-aniline and -isopropylamine were the most successful. The zinc(II)-catalysed reaction has been studied for chiral styrene oxides for which the enantiomeric excess of the aziridine produced is dependent on the reaction time. The reaction of achiral and chiral styrene oxides and *N*-(triphenylphosphoranylidene)aniline in the presence of a zinc(II) complex having a chiral ligand has been investigated as has the reaction for *cis*-deuteriostyrene oxide in order to obtain information about the stereochemical outcome of the reaction. A mechanism for the title reaction is discussed on the basis of the experimental results.

Introduction

Since epoxides serve as fundamental building blocks in organic chemistry their ring-opening reactions are of fundamental interest. Various procedures are available to induce such reactions, some of which allow selective attack at one or other carbon atom in the epoxide with steric and, to a certain extent, electronic effects being taken into account.[1]

Aziridines, in many respects closely related to epoxides and also of fundamental interest in organic chemistry,[2] can be synthesised from a variety of precursors such as amino acids, carbohydrates, hydroxy acids and from alkenes *via* 1,2-diols or epoxides.[2,3] The preparation of aziridines from epoxides can be achieved by first ring-opening with azide followed by ring-closure,[3] a procedure which is useful for both achiral and chiral epoxides. For chiral epoxides, the epoxide to aziridine transformation involves, in general, an overall inversion of the configuration.[2] Attempts to prepare aziridines from epoxides using iminophosphoranes ($R^1{}_3P = NR^2$)[4] or the sodium salt of an *N*-substituted amidophosphoric ester ($[R^1N\text{-}P(=O)\text{-}(OR^2)]^-$) as the nitrogen-fragment donor,[5] have also been attempted, but these reactions required very high temperatures (up to 200 °C) to proceed and the yields are generally low.[4,5] By the reaction of $Ph_3P{=}NCH_2R$, formed *in situ* from 1-(triphenylphosphoranylideneaminoethyl)benzotriazole and methylmagnesium iodide, with styrene oxide at room temperature the corresponding aziridine was formed in moderate yield after 48 h.[6]

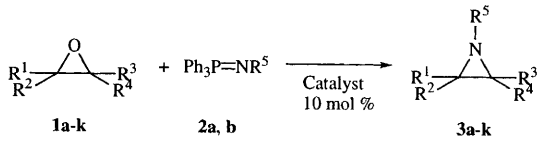
This paper presents a new metal-catalysed epoxide **1** to aziridine **3** transformation under mild reaction conditions, by which terminal and cyclic epoxides, in particular, are transformed into the corresponding aziridines using iminophosphoranes **2** as the nitrogen-fragment donor [reaction (1)]:



The epoxide to aziridine transformation has been investigated for a series of different achiral and chiral epoxides. The synthetic aspects of the reaction will be presented, and in an attempt to obtain information about the reaction mechanism both chiral and deuterium labelling experiments have been performed.

Results and Discussion

The reaction of styrene oxide **1a** and *N*-(triphenylphosphoranylidene)aniline **2a** to give the aziridine **3a** has been investigated in the presence of the following Lewis and Brønsted acids to study their catalytic properties [reaction (2)]:



1a R^1 = Ph, $R^2 = R^3 = R^4$ = H
1b R^1 = Et, $R^2 = R^3 = R^4$ = H
1c $R^1 = C_6H_{13}$, $R^2 = R^3 = R^4$ = H
1d R^1 = Ph, R^2 = Me, $R^3 = R^4$ = H
1e R^1 = Ph, R^3 = Me, $R^2 = R^4$ = H
1f $R^1 = p\text{-}NO_2C_6H_4$, $R^2 = R^3 = R^4$ = H
1g $R^1 = p\text{-}MeC_6H_4$, $R^2 = R^3 = R^4$ = H
1h $R^1 = p\text{-}NO_2C_6H_4C(H){=}CH_2$, $R^2 = R^3 = R^4$ = H
1i $R^1 = PhOCH_2$, $R^2 = R^3 = R^4$ = H
1j $R^1 = R^2 = (CH_2)_4$, $R^3 = R^4$ = H
1k $R^1 = R^2 = (CH_2)_3$, $R^3 = R^4$ = H

2a R^5 = Ph
2b $R^5 = Pr^i$

3a R^1 = Ph, $R^2 = R^3 = R^4$ = H, R^5 = Ph
3aa R^1 = Ph, $R^2 = R^3 = R^4$ = H, $R^5 = Pr^i$
3b R^1 = Et, $R^2 = R^3 = R^4$ = H, R^5 = Ph
3c $R^1 = C_6H_{13}$, $R^2 = R^3 = R^4$ = H, R^5 = Ph
3d R^1 = Ph, R^2 = Me, $R^3 = R^4$ = H, R^5 = Ph
3e R^1 = Ph, R^3 = Me, $R^2 = R^4$ = H, R^5 = Ph
3f $R^1 = p\text{-}NO_2C_6H_4$, $R^2 = R^3 = R^4$ = H, R^5 = Ph
3g $R^1 = p\text{-}MeC_6H_4$, $R^2 = R^3 = R^4$ = H, R^5 = Ph
3h $R^1 = p\text{-}NO_2C_6H_4C(H){=}CH_2$, $R^2 = R^3 = R^4$ = H, R^5 = Ph
3i $R^1 = PhOCH_2$, $R^2 = R^3 = R^4$ = H, R^5 = Ph
3ii $R^1 = PhOCH_2$, $R^2 = R^3 = R^4$ = H, $R^5 = Pr^i$
3j $R^1 = R^2 = (CH_2)_4$, $R^3 = R^4$ = H, R^5 = Ph
3k $R^1 = R^2 = (CH_2)_3$, $R^3 = R^4$ = H, R^5 = Ph

CH_3CO_2H, CF_3CO_2H, $AlCl_3$, $BF_3{\cdot}OEt_2$, $TiCl_4$, $CuCl_2$, $CuCl_2$–phenanthroline and ZnX_2 (X = Cl, I, OTf).

Of the Lewis acids tested as catalysts for the reaction the zinc(II) complexes ZnX_2 (X = Cl, I, OTf) were the most effective giving a >70% product yield. In contrast, CH_3CO_2H failed to catalyse the reaction, CF_3CO_2H catalysed only the formation of the halohydrins PhCH(OH)-

Table 1 Transformations of the epoxides **1a–k** to the aziridines **3a–k** using *N*-(triphenylphosphoranilidene)aniline **2a** or *N*-(triphenylphosphoranylidene)isopropylimine **2b** in the presence of zinc(II) complexes

Entry	Epoxide	Catalyst	Yield of aziridine (%)
1	**1a**	ZnX_2 (X = Cl, I)	**3a** (72)
2	**1a**	ZnI_2	**3aa** (65)
3	**1b**	ZnX_2 (X = Cl, I)	**3b** (34)
4	**1c**	ZnI_2	**3c** (42)
5	**1d**	ZnI_2	**3d** (< 5)
6	**1e**	ZnI_2	**3e** (10)
7	**1f**	$ZnCl_2$	**3f** (84)
8	**1g**	$ZnCl_2$	**3g** (60)
9	**1h**	ZnX_2 (X = Cl, I, OTf)	**3h** (< 5)
10	**1i**	ZnI_2	**3i** (65)
11	**1i**	ZnI_2	**3ii** 72)
12	**1j**	ZnX_2 (X = Cl, I)	**3j** (78)
13	**1k**	ZnI_2	**3k** (26)

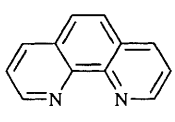
$CH_2OC(O)CF_3$ and $PhCH[OC(O)CF_3]CH_2OH$, while $BF_3{\cdot}OEt_2$ decomposed the substrate. $AlCl_3$, $CuCl_2$ and $CuCl_2$–phenanthroline as catalysts gave **3a** in only low yield, while $TiCl_4$ gave the halohydrins $PhCH(OH)CH_2Cl$ and $PhCH(Cl)CH_2OH$ at room temperature and a 5% yield of **3a** at 0 °C.

The reaction has also been investigated for iminophosphoranes other than compound **2a**. Thus, **1a** reacted with *N*-(triphenylphosphoranylidene)isopropylamine **2b** in the presence of $ZnCl_2$ to give the corresponding aziridine **3aa** (65%). Since the iminophosphoranes **2** (R^5 = Me, Et and Bu^t) were less promising in the reaction than **2a,b**, the latter were used in our work.

The synthetic potential of the epoxide to aziridine transformation with zinc(II) complexes, mainly $Zn^{II}I_2$, as the catalyst have been examined for reactions of compounds **2a,b** with the epoxides **1a–k**, the results for which are presented in Table 1 (see Experimental section).

The results show that the zinc(II)-catalysed epoxide to aziridine transformation is especially suitable for terminal and cyclic epoxides since these compounds can be converted into the corresponding *N*-phenyl- and *N*-isopropyl-aziridines in reasonable yield under mild reaction conditions. Styrene oxide **1a** is converted into the corresponding *N*-phenylaziridine **3a** (72%) and *N*-isopropylaziridine **3aa** (65%) (entries 1, 2). The method can also be applied to terminal aliphatic epoxides such as but-1-ene oxide **1b** and oct-1-ene oxide **1c** which are converted into the aziridines **3b** (34%) and **3c** (42%) yield, respectively (entries 3, 4). Internal epoxides such as *cis*-β-methylstyrene oxide **1d** and *cis*- and *trans*-stilbene oxide (not presented in Table 1) are less reactive under the reaction conditions used, **3d** being formed in only low yield (entry 5). α-Methylstyrene oxide **1e** can also be converted into the corresponding *N*-phenylaziridine **3e**, although the yield in this reaction is moderate (10%; entry 6). A styrene oxide having an electron-withdrawing *para*-substituent, **1f**, gave the aziridine **3f** in 84% yield (entry 7). In contrast, an electron-donating substituent in the *para* position, **1g**, gives the aziridine **3g** (entry 8), but in lower yield. Vinyl epoxides, such as **1i**, are not suitable substrates for the described reaction since they mainly polymerise (entry 9). Phenyloxymethyl epoxide **1i** reacts with **2a,b** to give **3i** (65%; entry 10), **3ii** (73%; entry 11), respectively. The cyclic epoxides as **1j,k** also give the corresponding *N*-phenylaziridines **3j,k**, respectively. Cyclohexene oxide **1j** gives **3j** in good yield (entry 12), while cyclopentene oxide gives only a low yield of **3k** (entry 13). The $ZnCl_2$-catalysed reaction of **1j** with **2a** gave 1-phenylamino-2-chlorocyclohexane as a minor by-product.

The zinc(II)-catalysed reaction of the epoxide **1a** with **2a** to give the aziridine **3a** has also been attempted in the presence of different nitrogen ligands in the hope of improving the catalytic properties, as well as inducing an enantiomeric excess in the nitrogen-transfer step. Thus, phenanthroline **4** was introduced for the purpose of improving the catalytic properties of the catalytic system, and the chiral bisoxazoline **5** to bring about an enantiomeric excess (ee) in the epoxide to aziridine transformation. The zinc(II) complex **6** containing an alkyl-substituted nitrogen ligand is commercially available.



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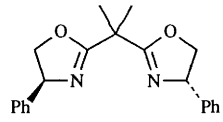

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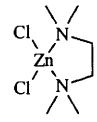

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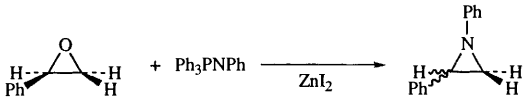
The presence of compounds **4** and **5**, had no significant influence on the yield of **3a** formed from **1a** and **2a** in the presence of ZnI_2. Similarly, compound **5** failed to give an enantiopurified aziridine as no ee for the aziridine **3a** could be detected by ^1H NMR spectroscopy using $Eu(hfc)_3$ as the chiral shift reagent. The zinc(II) complex **6** was found to have no significant catalytic effect on the **1a** to **3a** transformation.

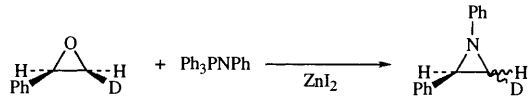
The epoxide to aziridine transformation has also been investigated for enantiopure epoxides. Reaction of (*R*)-(+)-styrene oxide (*R*)-**1a** with compound **2a** with ZnI_2 as the catalyst [reaction (3)] under the standard reaction conditions



(*R*)-**1a** **2a** **3a** (3)

gave a 58% conversion after 0.5 h with a 71% ee of **3a** (absolute configuration not assigned). A longer reaction time gave a lower diastereoisomeric excess and after 1.5–2 h a nearly racemic mixture of **3a** was formed. Reaction of (*S*)-(−)-styrene oxide (*S*)-**1a** with **2a** in the presence of ZnI_2 under similar reaction conditions gave the other enantioisomer and with a prolonged reaction time giving rise to a nearly racemic product. All attempts to improve the ee of the aziridine formed from the reactions of (*S*)-**1a** and (*R*)-**1a** with **2a** in the presence of ZnI_2 and the bisoxazoline **5** were unsuccessful.

In order to understand the mechanism for the epoxide to aziridine transformation we allowed *cis*-deuteriostyrene oxide **1ab** to react with **2a** in the presence of ZnI_2 under a variety of reaction conditions and for different reaction times [reaction (4)].

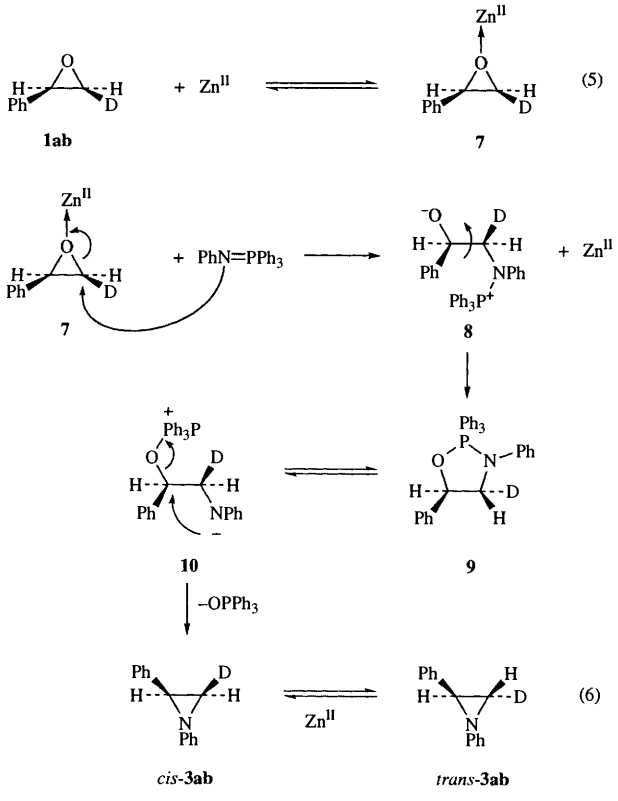


1ab **3ab** (4)

Results for the reaction illustrated in equation (4) show that the reaction time influenced the stereochemical outcome; thus, after 0.5 h the *cis*:*trans* ratio of **3ab** was 2.3:1, while after 1 h it was 1.4:1. There was no indication of significant isomerisation of the epoxide during the reaction.

From the results for the reactivity of different epoxides and the labelling experiments the mechanism in illustrated Scheme 1 is proposed. The mechanism for the reaction of **1ab** with **2a** in the presence of zinc(II) accounts for the *cis* to *trans* isomerisation which is especially notable after a prolonged reaction time. Initially, zinc(II) coordinates to **1ab** to give **7** [see Eqn. (5)]. This activates the carbon–oxygen bond of the epoxide for a nucleophilic attack by the nitrogen atom of the iminophosphorane to give the intermediate **8**. Two reasons, steric and electronic, account for iminophosphorane attack at the terminal carbon atom of **7**. The terminal carbon atom is the most reactive

towards a nucleophile in an S_N2 reaction[7] and, furthermore, coordination of zinc(II) to the oxygen atom of **1ab** leads to a change in the epoxide's electronic structure. We have tried to account for the change by calculation of the electronic structure of styrene oxide and **7** using AM1 calculations[8] (only the results for **7** will be discussed in the following). The LUMO and second LUMO of **7** located at −0.99 and −0.05 eV, respectively, have the following amplitudes at the terminal and internal carbon atoms, −0.20 and 0.19 for the LUMO, and 0.19 and −0.29 for the second LUMO. These amplitudes indicate that the terminal carbon atom of **7** would be expected to be the most reactive towards a nucleophile. The calculated atomic charge at the terminal and internal carbon atom also supports a nucleophile attack at the terminal carbon atom, as the charges are 0.03 and −0.25, for the terminal and internal carbon atom, respectively.



Scheme 1

The formation of **8** leads to a zwitterion in which rotation around the carbon–carbon bond is possible and the formation of a 1,3,2-oxazaphospholane **9**, where the configuration at the carbon–carbon bond is now *trans*. Breaking of the nitrogen–phosphorus bond leads to a new zwitterionic system **10** which, after a new rotation around the carbon–carbon bond, has the possibility of forming the *cis*-aziridine *cis*-**3ab** by a nucleophilic attack of the negatively charged nitrogen atom at the carbon atom with triphenylphosphine oxide as the leaving group. The reduction of the *cis*:*trans* ratio for prolonged reaction times can be accounted for by a zinc(II)-induced *cis* to *trans* rearrangement as proposed in reaction (6) in Scheme 1. The zinc(II)-induced *cis* to *trans* rearrangement also accounts for the change in enantiomeric excess observed when chiral epoxides are used as substrates. There are some precedents for the reaction mechanism outlined in Scheme 1. Thus, formation of **9** has been observed in a related, uncatalysed, reaction[4] and related heterocyclic compounds have been postulated, for the preparation of aziridines by reaction of amino alcohols with diethoxy(triphenyl)phosphorane[9a] or diphenylphosphinic acid dichloride;[9b] or by the reaction of azido alcohols with phosphines.[3e,9c,10] Furthermore, it is noteworthy, that zinc(II)-catalysed aziridine isomerization as postulated in reaction (6) has been observed for other aziridines in the presence of Lewis acids.[11]

Experimental

The ^1H NMR and ^{13}C NMR spectra were obtained in a Varian Gemini at 300 MHz and 75 MHz respectively. Chemical shifts for ^1H NMR and ^{13}C NMR are recorded in $CDCl_3$ and reported in ppm downfield from tetramethylsilane (TMS). *J* Values are given in Hz. Mass spectra were recorded on a Micromass 7070F mass spectrometer and GC–MS on a Trio-2 spectrometer.

Materials

The solvents were purified according to standard methods before use. The epoxides **1a**,**b**,**j**,**k**, (*R*)-**1a** and (*S*)-**1a** are commercially available, while **1c–g**,**i** were prepared by oxidation of the corresponding alkene by *m*-chloroperbenzoic acid. The allylic epoxide **1h** was prepared by selective oxidation of the terminal alkene of the corresponding diene by NaOCl using a manganese(III) (salen) complex as the catalyst.[12] The epoxide **1ab** was prepared from the corresponding *cis*-deuterium styrene[13] by reaction with *m*-chloroperbenzoic acid. The zinc(II) complexes ZnX_2 (X = Cl, I, OTf) and **6** are commercially available and were dried and stored under N_2. The ligands **4** and **5** and $Eu(hfc)_3$ are also commercially available. The iminophosphoranes **2** (R = Me, Et, Pr^i, Bu^t and Ph) were prepared according to the literature.[4,14]

General procedure for the transformation of epoxides to aziridines catalysed by zinc(II) complexes

The epoxide (5 mmol) was dissolved in $ClCH_2CH_2Cl$ (200–400 mm^3) to which the iminophosphorane (6 mmol) and the zinc(II) complex (0.5 mmol) were added. The reaction mixture was stirred for 1 h at 80 °C (unless otherwise stated in the text) after which it was chromotographed on an Al_2O_3 plate using 5–10% Et_2O–light petroleum as the eluent. The products were subjected to ^1H and ^{13}C NMR spectroscopy and MS. The spectral data are given below for those aziridines isolated in > 10% yield.

The reactions in the presence of phenanthroline **4** and bisoxazoline ligands **5**, were performed as above with the addition of the ligand (0.75 mmol) to the reaction mixture.

The reactions using chiral and labelled epoxides were performed as above.

Spectroscopic data (all NMR spectra in $CDCl_3$): 3a. δ_H 2.42 (dd, *J* 1.1, 3.3, 1 H), 2.48 (dd, *J* 1.1, 6.3, 1 H), 3.12 (dd, *J* 3.3, 6.6, 1 H) and 7.15–7.41 (m, 10 H); *m*/*z* 195 (M^+).

3aa. δ_H 1.18 (d, *J* 7.5, 1 H), 1.63 (m, 1 H), 1.77 (d, *J* 2.5, 1 H), 1.92 (d, *J* 1.2, 1 H), 2.35 (m, 1 H) and 7.3 (m, 5 H); δ_C 21.7, 22.3, 36.5, 40.7, 61.8, 126.3, 126.6, 128.1 and 140.4; *m*/*z* 160 ($M^+ - 1$).

3b. δ_H 1.16 (t, *J* 7.5, 3 H), 1.55 (m, 2 H), 2.1 (m, 3 H), 6.98 (m, 3 H) and 7.24 (m, 2 H); *m*/*z* 147 (M^+).

3c. δ_H 0.8–1.6 (m, 13 H), 2.07 (d, *J* 5.5, 2 H), 6.84 (m, 3 H) and 7.18 (m, 2 H); δ_C 14.7, 23.2, 28.2, 29.8, 32.5, 33.8, 34.6, 40.7, 121.3, 122.6 and 129.6; *m*/*z* 203 (M^+).

3e. δ_H 1.10 (d, *J* 5.6, 3 H), 3.17 (d, *J* 6.4, 1 H), 2.43 (q, *J* 6.0) and 6.7–7.5 (m, 10 H); *m*/*z* 195 (M^+).

3f. δ_H 2.41 (d, *J* 3.3, 1 H), 2.6 (d, *J* 6.3; 1 H), 3.3 (d, *J* 3.3; 1 H) and 6.8–7.4 (m, 9 H); *m*/*z* 239 (M^+).

3g. δ_H 2.28 (d, *J* 3.3, 1 H), 2.25 (s, 3 H), 2.45 (d, *J* 6.3, 1 H), 3.21 (d, *J* 3.3, 1 H) and 6.8–7.25 (m, 9 H); *m*/*z* 209 (M^+).

3i. δ_H 2.24 (d, *J* 6.6, 1 H), 2.34 (d, *J* 3.8, 1 H), 2.6 (m, 1 H), 4.05 (dd, *J* 7.2, 9.9, 1 H), 4.26 (dd, *J* 5.9, 10.4, 1 H), 6.95 (m, 6 H) and 7.15 (m, 4 H); δ_C 32.0, 39.0, 70.6, 115.2, 115.3, 121.3, 121.6, 123.2, 129.6, 130.1, 130.2, 154.4 and 159.3; *m*/*z* 225 (M^+).

3ii. δ_H 1.16 (dd, *J* 6.6, 9.2, 6 H), 1.41 (d, *J* 6.6, 1 H), 1.49 (m, 1 H), 1.74 (d, 2.7, 1 H), 1.81 (m, 1 H), 3.91 (m, 2 H), 6.87 (m, 3 H) and 7.23 (m, 2 H); δ_C 21.7, 22.0, 31.1, 37.0, 60.7, 70.1, 114.4, 120.6, 129.2 and 158.6; *m*/*z* 191 (M^+).

3j. δ_H 1.2 (m, 2 H), 1.4 (m, 2 H), 1.8 (m, 2 H), 2.0 (m, 2 H) 2.2 (m, 2 H), 6.84 (m, 3 H) and 7.2 (m, 2 H); δ_C 20.9, 25.2, 39.2, 120.9, 122.3, 129.4 and 156.2; *m/z* 173 (M^+).

3k. δ_H 1.6 (m, 2 H), 2.9 (m, 2 H), 2.72 (s, 2 H), 6.9 (m, 3 H) and 7.1 (m, 2 H); *m/z* 159 (M^+).

References

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