Pergamon

Tetrahedron: Asymmetry, Vol. 8, No. 17, pp. 2989–2995, 1997
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Printed in Great Britain
PII: S0957-4166(97)00345-5
0957-4166/97 $17.00 + 0.00

First hetero-Diels–Alder reaction of an enantiopure 2-sulfinylbuta-1, 3-diene: mild and effective stereocontrolled synthesis of pyranoid derivatives

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Abstract: $LiClO_4$ catalyzed cycloaddition of (R_S,E)-3-[(1S)-isoborneol-10-sulfinyl]-1-methoxybuta-1,3-diene **1** with ethyl glyoxalate occurred with good *endo* and facial diastereoselectivities to give (2R,6S,R_S)-6-ethoxycarbonyl-4-[(1S)-isoborneol-10-sulfinyl]-2-methoxy-5,6-dihydro-2H-pyran **2** as the main product, easily isolated as crystalline material in high yield. © 1997 Elsevier Science Ltd

Lewis acid catalyzed homo Diels–Alder (DA) reaction of (R_S,E)-3-[(1S)-isoborneol-10-sulfinyl]-1-methoxybuta-1,3-diene **1**[1] with methyl acrylate occurred with complete regioselectivity and high *endo* and facial diastereoselectivities, showing the efficiency of the isoborneolsulfinyl group as a chiral auxiliary when it is linked to the diene moiety.[2] In the aim of extending the use of this enantiopure diene to asymmetric syntheses of natural compounds, hetero-DA reactions of **1** with commercially available aromatic aldehydes were attempted under mild conditions and in the presence of Lewis acids. The results obtained,[3] disappointing in many ways, prompted us to move our attention towards an electron deficient aldehyde such as ethyl glyoxalate, which would represent a more reactive dienophile, also more convenient for application of the corresponding pyranoid cycloadducts to the synthesis of enantiopure carbohydrates and carbohydrate-like products.[4]

Glyoxalates have been previously used in [4+2] cycloadditions with electron-rich dienes.[4a,5] In particular, alkoxydienes have proven to be excellent partners for these cycloadditions. Usually the alkoxydihydropyran adducts have been isolated in good yields as mixtures of *endo* and *exo* products whose ratio was reported to be dependent on the reaction conditions. For instance, cycloadditions of Danishefsky's diene with several glyoxalate esters occurred both in atmospheric and high pressure (6–10 kbar) conditions.[5] The latter procedure normally enhanced the *endo/exo* ratio of cycloadducts even if the use of $Eu(fod)_3$ as catalyst allowed the completion of these hetero-DA reactions under mild conditions with good *endo/exo* diastereoisomeric ratios and yields. In an extensive series of papers[4b,5b,6] Jurczak and coworkers examined asymmetric induction in the DA reactions of a number of dienes with several enantiopure esters of glyoxylic acid or N-glyoxaloyl derivatives. The mildest conditions and best stereoselection results were achieved just recently by the use of N-glyoxyloyl-(2R)-bornane-10,2-sultam as dienophile. Total synthesis of natural compounds,[4b,c] such as compactin and mevinolin, would represent an interesting application of these cycloadditions.

In this paper we describe hetero-DA reactions of ethyl glyoxalate with a 1-alkoxybuta-1,3-diene bearing a chiral sulfinyl group on C-3, and report about the influence of Lewis acid catalysis on the stereochemical outcome of these cycloadditions.

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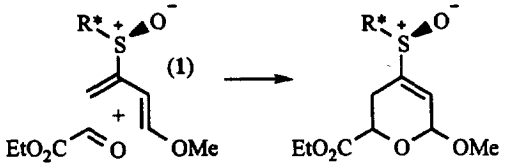
Table 1. Asymmetric [4+2] cycloadditions of diene **1** to ethyl glyoxalate, in CH_2Cl_2 as solvent

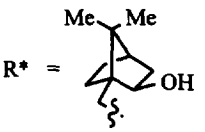
Entry	Temp.	Time	Catalyst	Total	Content of diastereoisomers, %[a]				*endo/exo*	facial sel.
	°C	h		yield, %	**2**	**3**	**4**	**5**	(2+3):(4+5)	(2+4):(3+5)
1	25	24	none	80	45	28	18	9	73 : 27	63 : 37
2	25	10	$LiClO_4$	82	59	21	14	6	80 : 20	73 : 27
3	25	48	$Eu(fod)_3$	52	9	5	61	25	14 : 86	70 : 30
4	0		$TiCl_4$[b]							
5	25	2	$ZnCl_2$	40	9	9	39	43	18 : 82	48 : 52

[a] Measured by integrating ^1H NMR resonances of H_2-10'. [b] Extensive decomposition of reactants was observed.

Results and discussion

Ethyl glyoxalate was freshly prepared according to Hook procedure,[7] and reacted with enantiopure sulfinyldiene **1**[1] in CH_2Cl_2 at room temperature, affording in 24 hours and in good yield (80%) a 3:1 mixture of *endo* (**2** and **3**) and *exo* (**4** and **5**) cycloadducts.





(2) 2R,6S *endo*
(3) 2S,6R *endo*
(4) 2R,6R *exo*
(5) 2S,6S *exo*

Facial diastereoselection was moderate (63% attack of the dienophile onto the preferred diene face, entry 1 in Table 1). When the same cycloaddition was performed in the presence of a suspension of $LiClO_4$ in CH_2Cl_2 (entry 2), significant decrease of reaction time (10 hours) and enhancement of diastereofacial selectivity (73%) were observed, giving (2R,6S,R_S)-6-ethoxycarbonyl-4-[(1S)-isoborneol-10-sulfinyl]-2-methoxy-5,6-dihydro-2H-pyran (**2**) as the main product of the reaction (48% yield of the isolated cycloadduct). All four pyranoid diastereoisomers **2–5** were easily obtained as single enantiopure compounds. *Endo*-adducts (**2+3**) were isolated as a solid by crystallization of the crude cycloadduct mixture from ethyl acetate. Concentration of the mother liquors gave the *exo*-mixture (**4+5**) as a pale yellow oil. Finally the separation of the facial diastereomers was accomplished by column chromatography.

X-ray crystallographic analysis of the major adduct **2** allowed the assignment of the configuration (2R,6S) to the two new-formed stereogenic centres (Figure 1), and the envelope conformation of the pyranoid ring was verified.[8] An analogous conformational preference can be suggested for **2** in $CDCl_3$ solution mainly on the basis of the same vicinal spin–spin coupling constant (5.4 Hz) shown by H-6 with both H_2-5. Similarly H-6 resonates as a triplet ($J_{5,6}$ 5.0 Hz) in the adduct **3**, facial diastereomer of **2**, while the ^1H NMR spectra of the two *exo*-adducts **4** and **5** are characterized by the H-6 resonance appearing as a doublet of doublets, with two different vicinal coupling constants typical of an axial/axial and an axial/equatorial proton interaction. Both C-5 methylene protons show significant allylic ^4J and homoallylic ^5J couplings with H-3 and H-2 respectively.[9]

The facial selectivity improvement, observed in the presence of $LiClO_4$, was moderate, but a tentative rationalization of this result can be suggested taking into account the relative stabilities of the transition states resulting from the *endo*-approach of the dienophile to different conformations of the diene around the C-3-S bond. In the absence of lithium cation, the preferred approach occurs to the *Re* face of the diene, which is also its more nucleophilic side, in the conformation depicted in Figure 2A,

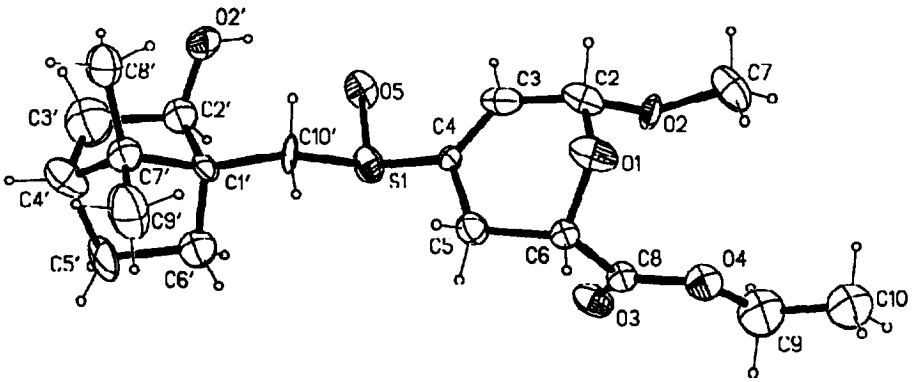


Figure 1. X-ray structure of **2**.

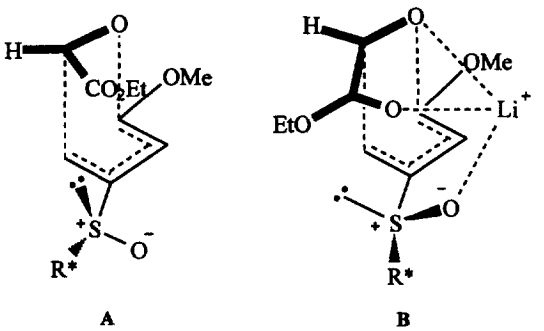


Figure 2. Favoured approach of ethyl glyoxalate in uncatalyzed (A) and $LiClO_4$ catalyzed (B) hetero-DA reaction of (R_S,E)-3-[(1S)-isoborneol-10-sulfinyl]-1-methoxybuta-1,3-diene **1**.

where the SO bond adopts the favoured *s-trans* relationship with respect to C-3–C-4 double bond. The Li^+ ability to co-ordinate not only both dienophile carbonyl oxygens but also diene sulfinyl oxygen in the transition state shown in Figure 2B may account for the improvement of diastereoselectivity and increased reaction rate observed in this cycloaddition.

Further experiments (entries 3–5 in Table 1) were performed in the presence of different Lewis acids in CH_2Cl_2 solution, using a 1:6:0.8 molar ratio of diene/dienophile/catalyst in all cases. The obtained results deserve some comments. When a very strong Lewis acid such as $TiCl_4$ was used, an extensive decomposition of the reactants was observed, even at low temperature.[10] $ZnCl_2$ or $Eu(fod)_3$ catalysis led to a reversal of the *endo/exo*-diastereoselectivity in favour of the *exo*-approach (compare entry 2 with entries 3 and 5 in Table 1). This result can be attributed to catalyst sizes. Because of Lewis acid co-ordination forces the dienophile in its *s-cis* conformation, the highly sterically demanding $ZnCl_2$ or $Eu(fod)_3$ can favour the less sterically congested *exo*-transition state. A moderate enhancement of facial diastereoselection was observed in the $Eu(fod)_3$ catalyzed cycloaddition (see entries 1 and 3 in Table 1) but the yield of the reaction was low.

In conclusion, this article reports the first hetero-DA cycloaddition of (R_S,E)-3-[(1S)-isoborneol-10-sulfinyl]-1-methoxybuta-1,3-diene **1** with ethyl glyoxalate. The efficiency of the chiral diene **1** in promoting stereoselectivity was corroborated. Moreover, $LiClO_4$ comfirms its effectiveness as catalyst in enhancing facial diastereoselectivity[11] even if Lewis acid catalysis appears in general less efficient than for homo-DA cycloadditions of diene **1** with methyl acrylate.[2a,c]

Experimental

IR spectra were taken with a Perkin Elmer 1600 FT spectrophotometer in $CHCl_3$ solutions. Mass spectra were measured by Fast Atom Bombardment (FAB, *m*-nitrobenzyl alcohol as matrix) with a Finnigan MAT 90 instrument. Mps were measured on a microscopic apparatus and are uncorrected. Optical rotations were measured on a Perkin Elmer 241 MC polarimeter equipped with a 1 ml quartz cell; the solvent was $CHCl_3$ and the reported concentrations are expressed in g/100 ml. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer at 300 and 75 MHz respectively in $CDCl_3$ solutions with $SiMe_4$ as internal standard; J values are given in Hz; the attributions are supported by Attached Proton Test (APT) and decoupling experiments. X-ray diffraction analysis was performed on a Siemens automated four-circle single-crystal diffractometer R3m/V. Ethyl glyoxalate was prepared according to the literature procedure[7] and (R_S,E)-3-[(1S)-isoborneol-10-sulfinyl]-1-methoxybuta-1,3-diene **1** was obtained following our own methodology.[1,2c] Solvents were purified according to standard procedures. All reactions were monitored by TLC on commercially available precoated plates (Aldrich silica gel 60 F 254). Silica gel used for column chromatography was Aldrich 60. Reaction times and yields are shown in Table 1.

DA cycloaddition of diene 1 with ethyl glyoxalate without catalyst

A solution of (R_S,E)-3-[(1S)-isoborneol-10-sulfinyl]-1-methoxybuta-1,3-diene **1** (100 mg, 0.35 mmol) in 1.5 ml of anhydrous dichloromethane was added to 214 mg (2.1 mmol) of ethyl glyoxalate dissolved in 0.5 ml of anhydrous dichloromethane. The reaction mixture was stirred at room temperature, under nitrogen, until the diene totally disappeared, as verified by TLC monitoring (chloroform/ethyl acetate 90:10). The solvent was removed under vacuum and the crude mixture was column chromatographed eluting firstly with chloroform and then with chloroform/ethyl acetate (99:1) to give 109 mg (80%) of the pure mixture of cycloadducts **2–5** [ν_{max} 3452 (OH), 3027, 3006, 2956, 1745 (CO), 1074 cm^{-1}; m/z (%) 387 (M+1, 41), 203 (59), 135 (100)]. Crystallization of this cycloadduct mixture from ethyl acetate gave *endo*-adducts **2** and **3** as solid matter, while *exo*-adducts **4** and **5** were obtained as a pale yellow oil by concentrating the mother liquors. Further column chromatography was performed on the mixture of compounds **2** and **3** using a 60:1 ratio of silica gel/adduct mixture, and eluting with light petroleum/ethyl acetate (90:10). First eluted was adduct **3**, followed by **2**. Also the oily mixture of compounds **4** and **5** was separated by column chromatography using a 60:1 ratio of silica gel/adduct mixture, but eluting with chloroform/ethyl acetate (99:1). First eluted was adduct **5**, followed by **4**.

(2S,6R,R_S)-6-Ethoxycarbonyl-4-[(1S)-isoborneol-10-sulfinyl]-2-methoxy-5,6-dihydro-2H-pyran 3

Mp 98–100°C; $[\alpha]_D^{20}$+51.0 (c 1.93) (Found: C, 59.29; H, 7.45. $C_{19}H_{28}O_6S$ requires C, 59.35; H, 7.34%); δ_H 6.46 (ddd, $J_{2,3}$ 1.8, $J_{3,5A}$=$J_{3,5B}$ 1.7, H-3), 5.20 (ddd, $J_{2,5A}$=$J_{2,5B}$ 1.7, H-2), 4.54 (t, $J_{5,6}$ 5.0, H-6), 4.28 and 4.22 (split AB system, J_{gem} 11.0, J_{vic} 7.1, OCH_2), 4.10 (dd, $J_{2',3'}$ 8.2 and 3.6, H-2′), 3.55 (s, OMe), 3.21 and 2.66 (AB system, $J_{10'A,10'B}$ 13.4, H_2-10′), 2.56 and 2.51 (split AB system, $J_{5A,5B}$ 17.0, H_2-5), 1.9–1.1 (m, H_2-3′,5′,6′, H-4′), 1.33 (t, CH_2*Me*), 1.09 (s, H_3-8′), 0.86 (s, H_3-9′); δ_C 169.8 (CO), 144.1 (C-4), 125.5 (C-3), 96.8 (C-2), 77.2 (C-2′), 69.2 (C-6), 61.6 (OCH_2), 56.3 (OMe), 54.7 (C-10′), 51.5 (C-1′), 48.4 (C-7′), 45.1 (C-4′), 38.4 (C-3′), 31.0 and 27.2 (C-5′,6′), 24.1 (C-5), 20.5 (C-8′), 19.9 (C-9′), 14.1 (CH_2*Me*).

(2R,6S,R_S)-6-Ethoxycarbonyl-4-[(1S)-isoborneol-10-sulfinyl]-2-methoxy-5,6-dihydro-2H-pyran 2

Mp 113–114°C; $[\alpha]_D^{20}$+6.1 (c 1.40) (Found: C, 59.42; H, 7.40%); δ_H 6.31 (ddd, $J_{2,3}$=$J_{3,5A}$=$J_{3,5B}$ 1.9, H-3), 5.17 (ddd, $J_{2,5A}$=$J_{2,5B}$ 1.9, H-2), 4.51 (t, $J_{5,6}$ 5.4, H-6), 4.27 and 4.22 (split AB system, J_{gem} 10.9, J_{vic} 7.1, OCH_2), 4.08 (dd, $J_{2',3'}$ 8.8 and 4.3, H-2′), 3.55 (s, OMe), 3.43 and 2.37 (AB system, $J_{10'A,10'B}$ 13.1, H_2-10′), 2.71 (m, H_2-5), 1.9–1.1 (m, H_2-3′,5′,6′, H-4′), 1.33 (t, CH_2*Me*), 1.10 (s, H_3-8′), 0.83 (s, H_3-9′); δ_C 169.7 (CO), 144.1 (C-4), 127.8 (C-3), 96.7 (C-2), 77.2 (C-2′), 69.3 (C-6),

61.6 (OCH_2), 56.6 (OMe), 53.3 (C-10′), 51.4 (C-1′), 48.4 (C-7′), 45.0 (C-4′), 38.5 (C-3′), 29.7 and 27.1 (C-5′,6′), 21.9 (C-5), 20.5 (C-8′), 19.9 (C-9′), 14.1 (CH_2*Me*).

(2S,6S,R$_S$)-6-Ethoxycarbonyl-4-[(1S)-isoborneol-10-sulfinyl]-2-methoxy-5,6-dihydro-2H-pyran **5**

Oil; $[\alpha]_D^{20}$ −9.9 (c 1.87) (Found: C, 59.41; H, 7.27%); δ_H 6.42 (ddd, $J_{2,3}$=$J_{3,5B}$ 2.7, $J_{3,5A}$ 0.9, H-3), 5.16 (m, $J_{2,5B}$ 1.5, H-2), 4.57 (dd, $J_{5A,6}$ 3.5, $J_{5B,6}$ 11.2, H-6), 4.31 (q, J_{vic} 7.0, OCH_2), 4.08 (dd, $J_{2',3'}$ 8.2 and 3.8, H-2′), 3.52 (s, OMe), 3.40 and 2.29 (AB system, $J_{10'A,10'B}$ 13.0, H_2-10′), 2.77 and 2.52 (split AB system, $J_{5A,5B}$ 17.3, H_2-5), 1.9–1.1 (m, H_2-3′,5′,6′, H-4′), 1.35 (t, CH_2*Me*), 1.09 (s, H_3-8′), 0.83 (s, H_3-9′); δ_C 170.0 (CO), 144.6 (C-4), 127.3 (C-3), 95.3 (C-2), 77.3 (C-2′), 66.1 (C-6), 61.8 (OCH_2), 56.3 (OMe), 53.8 (C-10′), 51.5 (C-1′), 48.4 (C-7′), 45.0 (C-4′), 38.4 (C-3′), 30.8 and 27.1 (C-5′,6′), 23.1 (C-5), 20.5 (C-8′), 19.9 (C-9′), 14.2 (CH_2*Me*).

(2R,6R,R$_S$)-6-Ethoxycarbonyl-4-[(1S)-isoborneol-10-sulfinyl]-2-methoxy-5,6-dihydro-2H-pyran **4**

Oil; $[\alpha]_D^{20}$+27.0 (c 1.40) (Found: C, 59.39; H, 7.30%); δ_H 6.45 (m, $J_{2,3}$ 3.0, H-3), 5.22 (br d, H-2), 4.57 (dd, $J_{5,6}$ 5.7 and 9.1, H-6), 4.32 and 4.30 (split AB system, J_{gem} 10.2, J_{vic} 7.2, OCH_2), 4.10 (dd, $J_{2',3'}$ 8.3 and 4.1, H-2′), 3.52 (s, OMe), 3.18 and 2.44 (AB system, $J_{10'A,10'B}$ 13.0, H_2-10′), 2.47 (m, H_2-5), 1.9–1.1 (m, H_2-3′,5′,6′, H-4′), 1.35 (t, CH_2*Me*), 1.08 (s, H_3-8′), 0.84 (s, H_3-9′); δ_C 170.0 (CO), 144.0 (C-4), 125.9 (C-3), 95.9 (C-2), 76.9 (C-2′), 65.7 (C-6), 61.8 (OCH_2), 56.2 (OMe), 53.7 (C-10′), 51.4 (C-1′), 48.4 (C-7′), 45.0 (C-4′), 38.4 (C-3′), 30.8 and 27.1 (C-5′,6′), 25.4 (C-5), 20.5 (C-8′), 19.8 (C-9′), 14.1 (CH_2*Me*).

DA cycloadditions of diene **1** *with ethyl glyoxalate in the presence of Lewis acids [Eu(fod)$_3$, LiClO$_4$, ZnCl$_2$]*

The Lewis acid (0.42 mmol) was added to a solution of diene **1** (150 mg, 0.53 mmol) and ethyl glyoxalate (325 mg, 3.18 mmol) in dichloromethane (3 ml) under nitrogen at room temperature. The reaction mixture was stirred until the diene was totally disappeared, as verified by TLC monitoring. Isolation and purification of cycloadducts **2–5** were performed as previously described.

DA cycloaddition of diene **1** *with ethyl glyoxalate in the presence of TiCl$_4$*

The Lewis acid (0.42 mmol from a 0.5 M solution in dichloromethane) was added dropwise to a solution of diene **1** (150 mg, 0.53 mmol) and ethyl glyoxalate (325 mg, 3.18 mmol) in dichloromethane (3 ml) under nitrogen at −78°C. The reaction mixture was allowed to reach 0°C slowly, and maintained at this temperature under stirring until the diene was totally disappeared, as verified by TLC monitoring. Then 10% $NaHCO_3$ solution (5 ml) was added. The organic layer was separated and the aqueous layer extracted with dichloromethane. Finally the combined organic layers were dried (Na_2SO_4), evaporated under vacuum, and column chromatographed.

X-ray structure determination of (2R,6S,R$_S$)-6-ethoxycarbonyl-4-[(1S)-isoborneol-10-sulfinyl]-2-methoxy-5,6-dihydro-2H-pyran **2**

Crystal data and measurement conditions are given in Table 2. Reflection intensities were evaluated by profile fitting of a 96-steps peak scan among 2θ shells procedure[12] and then corrected for Lorentz polarization effects. Standard deviations σ(I) were estimated from counting statistics. The structure was solved by direct methods subsequently completed by a combination of least squares technique and Fourier syntheses (SHELXTL-PLUS[13]) and refined by the full-matrix least squares technique (SHELXL-93[14]) based on F^2. Hydrogens have been located on idealized positions, with an unique common fixed isotropic displacement parameter (0.080 Å^2). Data reduction, structure solution and drawings were performed with SHELXTL-PLUS[12,13] package, and the geometrical calculations were obtained from PARST[15] programme, respectively. All calculations were performed on a μ-VAX 3400 and an AXP DecStation 3000/400.

Acknowledgements

Financial support by MURST 40% is gratefully acknowledged.

Table 2. Crystal data and measurements conditions for the adduct **2**

Formula	$C_{19}H_{28}O_6S$
Crystal System	Monoclinic
Space Group	$P2_1$
a/Å	7.1010(1)
b/Å	20.629(4)
c/Å	14.257(3)
β/°	92.700(3)
Volume/Å^3	2086.1(7)
Z	4
M	384.47
D_x/mg/m^3	1.224
μ/mm^{-1}	0.185
F(000)	824
Radiation	MoKα (λ = 0.71073 Å)
Temperature	293 K
θ_{min}, θ_{max} /°	3.5, 52.0
Index ranges	-4/8 , -24/24 , -16/16
Collected reflections	7528
Independent reflections	4286 (R_{int} = 0.0472%)
Number of refined parameters	414
R(F)[I>2σ(I)]	0.0380
ωR^2 (all data)	0.0349

References

1. Aversa, M. C.; Bonaccorsi, P.; Giannetto, P.; Jafari, S. M. A.; Jones, D. N. *Tetrahedron: Asymmetry* **1992**, *3*, 701–704.
2. (a) Adams, H.; Jones, D. N.; Aversa, M. C.; Bonaccorsi, P.; Giannetto, P. *Tetrahedron Lett.* **1993**, *34*, 6481–6484; (b) Adams, H.; Bailey, N. A.; Jones, D. N.; Aversa, M. C.; Bonaccorsi, P.; Giannetto, P. *Acta Crystallogr., Sect. C* **1995**, *51*, 1357–1359; (c) Aversa, M. C.; Barattucci, A.; Bonaccorsi, P.; Giannetto, P.; Jones, D. N. *J. Org. Chem.* **1997**, *62*, 4376–4384.
3. Aversa, M. C.; Barattucci, A.; Bonaccorsi, P.; Bruno, G.; Giannetto, P.; Nicolò, F. *J. Chem. Soc., Perkin Trans. 2* **1997**, 273–277.
4. (a) Terada, M.; Mikami, K.; Nakai, T. *Tetrahedron Lett.* **1991**, *32*, 935–938; (b) Bauer, T.; Chapuis, C.; Jezewski, A.; Kozak, J.; Jurczak, J. *Tetrahedron: Asymmetry* **1996**, *7*, 1391–1404, and references quoted therein; (c) Bauer, T.; Jezewski, A.; Jurczak, J. *ibid.* **1996**, *7*, 1405–1412.
5. (a) Jung, M.E.; Shishido, K.; Light, L.; Davis, L. *Tetrahedron Lett.* **1981**, *22*, 4607–4610; (b) Jurczak, J.; Tkacz, M. *J. Org. Chem.* **1979**, *44*, 3347–3352; (c) Weinreb, S. M.; Staib, R. R. *Tetrahedron*, **1982**, *38*, 3087–3128 and references quoted therein.
6. (a) Jurczak, J.; Zamojski, A. *Tetrahedron* **1972**, *28*, 1505–1516; (b) Konowal, A.; Jurczak, J.; Zamojski, A. *ibid.* **1976**, *32*, 2957–2959; (c) Jurczak, J.; Jezewski, A. *Tetrahedron: Asymmetry* **1996**, *7*, 1413–1418.
7. Hook, J. M. *Synth. Commun.* **1984**, *14*, 83–87.
8. Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354–1358.
9. Günther, H. *NMR Spectroscopy*, John Wiley & Sons, Chichester **1994**, pp. 124–128.
10. Lattmann, E.; Coombs, J.; Hoffmann, H. M. R. *Synthesis*, **1996**, 171–177.

11. Aversa, M. C.; Barattucci, A.; Bonaccorsi, P.; Giannetto, P. *Tetrahedron: Asymmetry* **1997**, *8*, 1339–1367.
12. Diamond, R. *Acta Crystallogr., Sect. A* **1969**, *25*, 43–55.
13. *SHELXTL-PLUS* **1991**, V.4.2, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin.
14. Sheldrick, G. M. **1994**, *SHELXL-93, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany.
15. Nardelli, M. *Comput. Chem.* **1983**, *7*, 95–98 (locally modified version).

(Received in UK 28 July 1997)