Pergamon

Tetrahedron: *Asymmetry* 12 (2001) 765–769

TETRAHEDRON: *ASYMMETRY*

Easy access to optically active Hagemann's esters

Mohammed Nour,* Kimny Tan, Raphael Jankowski and Christian Cavé

Unité de Molécules d'Intérêt Biologique JE 2244, UFR de Pharmacie, BP 87900, 21079 Dijon cedex, France

Received 14 February 2001; accepted 1 March 2001

Abstract—The synthesis of optically active Hagemann's esters was investigated. The starting materials in this approach were enamino esters (*R*,*Z*)-**8**, prepared through the condensation of keto ester **6** with (*R*)-1-phenylethylamine **7**. Michael addition reaction of the enamino esters (*R*,*Z*)-**8** with methyl vinyl ketone gave the expected adducts **10** with good e.e.s of 93–96%. Subsequent annulation of the adducts furnished optically active Hagemann's esters.

1. Introduction

Commercially available Hagemann's ester **1** and its analogues have been extensively used in the synthesis of a variety of complex molecules, including terpenes, alkaloids, taxane core, steroids and flavones.[1] As a part of our program directed toward synthesising new chiral building blocks, the enantiopure four-substituted Hagemann's esters **2** have recently attracted our attention (Scheme 1).

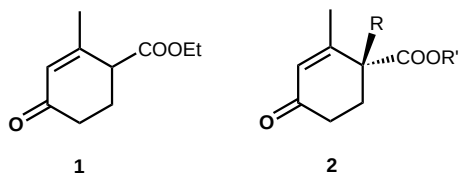
Although several racemic Hagemann's esters **2** have been previously prepared,[2] to our knowledge only one stereoselective approach to such a compound, (*S*)-**2** ($R = CH_3$; $R' = C_2H_5$), based on the microbial reduction of a β-keto ester,[3] has been disclosed so far.

We planned to elaborate such molecules through an efficient enantioselective methodology we have developed based on the asymmetric Michael addition reaction using chiral β-enamino esters. Thus, condensation of chiral enamino-esters **3** (derived from cyclic or acyclic β-keto esters and enantiopure 1-phenylethylamine) to electron-deficient alkenes **4** under neutral conditions furnished, after hydrolytic work-up, β-keto esters **5**, in moderate yields and excellent enantiomeric excesses (e.e.s) (Scheme 2).[4]

Herein, we report a short, efficient enantioselective approach to various Hagemann's esters of type **2** by applying this methodology. These compounds were obtained in good yields, and with excellent e.e.s of 93–96%.

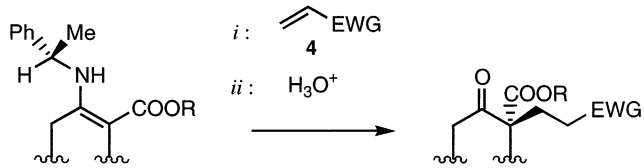
2. Results and discussion

The enamino esters **8** were first prepared from reaction between the 2-substituted acetoacetate **6** and enantiomerically pure (*R*)-1-phenylethylamine **7** over 12 hours in toluene at reflux in the presence of catalytic *p*-TsOH. The (*R*)-esters were isolated in 72–86% purified yield. The (*Z*)-geometry in these compounds is secured by intramolecular hydrogen bonding.



1 2

Scheme 1.

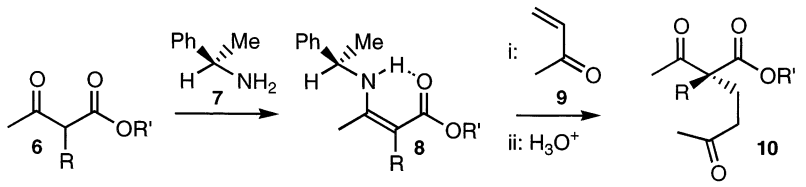


3 5

Scheme 2.

* Corresponding author. E-mail: mohammed.nour@u-bourgogne.fr

0957-4166/01/$ - see front matter
PII: S0957-4166(01)00105-7



a : R = Me, R' = Et
b : R = Et, R' = Et
c : R = Allyl, R' = Me
d : R = Bn, R' = Me

Scheme 3.

Addition of enamino ester (*R*)-**8** to methyl vinyl ketone **9** required the presence of 1 equiv. of zinc chloride. This condensation, which was carried out in THF for 1 hour at 0°C and quenched with 20% aqueous AcOH, furnished α,α-disubstituted β-keto esters **10** in 67–75% yield (Scheme 3).

The e.e.s of **10** (93–96%) were determined by ^{1}H NMR spectroscopy in the presence of the chiral shift reagent Eu(hfc)$_3$. The sense of induction of this Michael addition was deduced from mechanistic considerations (vide infra) and was unequivocally determined through the correlation of Hagemann's ester **2a** to the known derivative (*S*)-**2a**.[3]

As previously reported,[2] catalytic piperidinium acetate effects cyclisation of **10** furnishing mainly Hagemann's esters **2** in 65–79% yields (Scheme 4).

It is of interest to note that the stereochemical outcome observed in the previous Michael reactions using acyclic enamino esters **8** follows the general mechanism established in this series.[5] In accordance with this mechanism, the reaction proceeds through the 'aza-ene'-like transition state **11**, in which the N–H proton of the enamino ester is transferred to the α-carbon atom of the electrophilic alkene concertedly with the creation of the C–C bond. This requires a *synclinal* arrangement of the two reactants, as shown in the corresponding compact approach **12**. According to such a model, alkylation takes place predominantly *anti* to the bulky phenyl ring of the chiral amine moiety portrayed in its energetically preferred conformation, minimising A^{1,3}-type strain, with the C–H bond more or less eclipsing the enamine ring. This accounts for the absolute configuration in adducts **10** (Scheme 5).

Studies directed at the utilisation of Hagemann's esters **2c** and **2d** as chiral building blocks are currently under investigation in our laboratory.

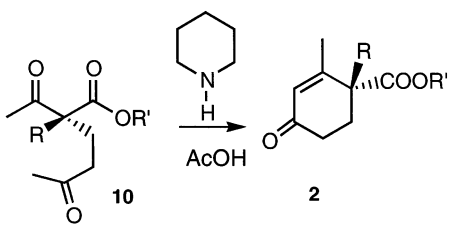
3. Experimental

3.1. General

Melting points were recorded on a Kofler bench. Infrared (IR) spectra were obtained on a Perkin–Elmer 881 as neat films between NaCl plates or KBr pellets. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 P (200 and 50 MHz, for ^{1}H and ^{13}C, respectively) in $CDCl_3$. Recognition of methyl, methylene, methine and quaternary carbon nuclei in ^{13}C NMR spectra rests on the *J*-modulated spin echo sequence. Optical rotations were measured at 20°C on a Polax L polarimeter in a 1 dm cell at 589 nm. Analytical thin-layer chromatography was performed on Merck silica gel 60F$_{254}$ pre-coated plates. All solvents were purified before use. Tetrahydrofuran (THF) was distilled from sodium–benzophenone ketyl. Methanol was dried over magnesium and distilled. Toluene was distilled from calcium hydride. All reactions involving air- or water-sensitive compounds were routinely conducted in flame-dried glassware under positive pressure of nitrogen. Organic extracts were dried over anhydrous $MgSO_4$. Compounds obtained from commercial suppliers were used without further purification. All elemental analyses were performed by the Service de Microanalyse, Centre d'Etudes Pharmaceutiques, Châtenay-Malabry, France, with a Perkin–Elmer 2400 analyser.

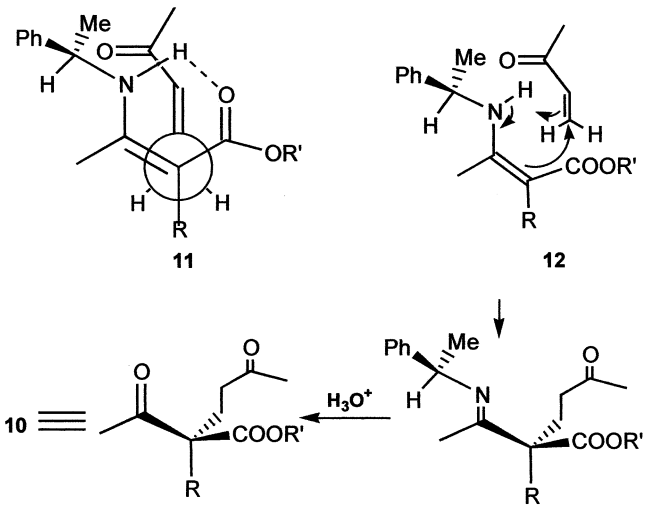
3.2. General procedure for the preparation of enamino esters

To a solution of keto ester **6** (0.05 mol) and *p*-toluenesulfonic acid (catalytic) in anhydrous toluene (100 mL) was added *R*-(+)-1-phenylethylamine (0.0055 mol). The mixture was stirred under reflux for 14 h with azeotropic removal of water using a Dean–Stark trap. The solution was cooled to 20°C, concentrated in vacuo and the residue purified by distillation.



a : R = Me, R' = Et
b : R = Et, R' = Et
c : R = Allyl, R' = Me
d : R = Bn, R' = Me

Scheme 4.



Scheme 5.

3.2.1. (*R*)-2-Methyl-3-(1-phenylethylamino)-but-2-enoic acid ethyl ester 8a. Oil; yield 86%; bp (0.1 mmHg): 135°C; $[\alpha]_D=-298$ ($c=5.5$, $CHCl_3$); IR (neat, cm^{-1}): 3244, 1646, 1603, 1592, 1450; ^1H NMR (200 MHz, $CDCl_3$) δ 1.3 (t, $J=7.0$ Hz, 3H), 1.5 (d, $J=7.0$ Hz, 3H), 1.75 (s, 3H), 4.19 (q, $J=7.0$ Hz, 2H), 4.6 (quint, $J=7.0$ Hz, 1H), 7.2–7.4 (m, 5H), 9.6 (d, $J=7.0$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.0 (C), 159.0 (C), 142.5 (C), 128.9 (2 CH), 127.2 (CH), 125.5 (2 CH), 87.5 (C), 58.6 (CH_2), 53.0 (CH), 25.1 (CH_3), 15.6 (CH_3), 14.5 (CH_3), 12.4 (CH_3).

3.2.2. (*R*)-2-Ethyl-3-(1-phenylethylamino)-but-2-enoic acid ethyl ester 8b. Syrup; yield 72%; bp (0.1 mmHg): 140°C; $[\alpha]_D=-315.2$ ($c=2.85$, $CHCl_3$); IR (neat, cm^{-1}): 3250, 2980, 1650, 1600; ^1H NMR (200 MHz, $CDCl_3$) δ 0.9 (t, $J=6.0$ Hz, 3H), 1.38 (t, $J=7.0$ Hz, 3H), 1.40 (d, $J=7$ Hz, 3H), 1.78 (s, 3H), 2.20 (q, $J=6$ Hz, 2H), 4.10 (q, $J=7$ Hz, 2H), 4.60 (quint, $J=7.0$ Hz, 1H), 7.10–7.30 (m, 5H), 9.65 (d, $J=7$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 176.0 (C), 159.5 (C), 142.5 (C), 128.2 (2 CH), 126.8 (CH), 124.9 (2 CH), 95.0 (C), 59.4 (CH_2), 52.4 (CH), 24.8 (CH_3), 22.5 (CH_2), 17.5 (CH_3), 16.8 (CH_3), 16.6 (CH_3).

3.2.3. (*R*)-2-Allyl-3-(1-phenylethylamino)-but-2-enoic acid methyl ester 8c. Syrup; yield 75%; bp (0.1 mmHg): 140°C; $[\alpha]_D=-387$ ($c=12.3$, $CHCl_3$); IR (neat, cm^{-1}): 3230, 2900, 1648, 1600; ^1H NMR (200 MHz, $CDCl_3$) δ 1.25 (d, $J=6.0$ Hz, 3H), 1.78 (s, 3H), 2.85–3.0 (m, 2H), 3.69 (s, 3H), 4.60 (quint, $J=6.0$ Hz, 1H), 4.80–4.90 (m, 2H), 5.60–5.90 (m, 1H), 7.10–7.29 (m, 5H), 9.80 (d, $J=6.0$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 176.0 (C), 160.6 (C), 145.5 (C), 138.3 (CH), 128.8 (2 CH), 127.0 (CH), 125.5 (2 CH), 113.0 (CH_2), 90.1 (C), 53.2 (CH_3), 50.5 (CH), 31.1 (CH_2), 25.2 (CH_3), 15.3 (CH_3).

3.2.4. (*R*)-2-Benzyl-3-(1-phenylethylamino)-but-2-enoic acid methyl ester 8d. Syrup; yield 84%; bp (0.1 mmHg): 150°C; $[\alpha]_D=-310$ ($c=1.4$, $CHCl_3$); IR (neat, cm^{-1}): 3190, 1717, 1648; ^1H NMR (200 MHz, $CDCl_3$) δ 1.25 (d, 3H, $J=7.0$ Hz), 1.70 (s, 3H), 3.48 (d, $J=14$ Hz, 1H), 3.70 (d, $J=14$ Hz, 1H), 3.80 (s, 3H), 4.60 (quint, $J=7$ Hz, 1H), 7.00–7.40 (m, 5H), 9.90 (d, $J=7.0$ Hz 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.13 (C), 158.8 (C), 142.2 (C), 137.5 (C), 90.1 (C), 129.2 (2 CH), 128.4 (2 CH), 128.1 (2 CH), 127.3 (2 CH), 126.7 (CH), 125.5 (CH), 52.7 (CH), 50.8 (CH_3), 30.7 (CH_2), 24.9 (CH_3), 18.6 (CH_3).

3.3. General procedure for the addition of methyl vinyl ketone

Methyl vinyl ketone (0.055 mol) was added to a solution of $ZnCl_2$ (catalytic) in anhydrous toluene (40 mL). The mixture was stirred for 1 h at 0°C. A solution of enamino ester **8** (0.05 mol) in anhydrous toluene (5 mL) was added and the mixture was stirred at 0°C for 2 h. A 10% aqueous acetic acid solution was then added (30 mL) and the resulting mixture was stirred for 2 h. The aqueous phase was saturated with NaCl and extracted with ethyl acetate (3×50 mL). The collected organic layers were dried over sodium sulfate and concentrated. The crude oil was purified by flash chromatography [silica gel, ethyl acetate:hexane (2:8)].

3.3.1. (*R*)-2-Acetyl-2-methyl-5-oxo-hexanoic acid ethyl ester 10a. Oil; yield 72%; $[\alpha]_D=+8.5$ ($c=4.8$, $CHCl_3$); IR (film, cm^{-1}): 1717 1682 1357, 1250; ^1H NMR (200 MHz, $CDCl_3$) δ 1.20 (t, $J=6.0$ Hz, 3H), 1.25 (s, 3H), 1.80–2.10 (m, 2H), 2.05 (s, 3H), 2.09 (s, 3H), 2.20–2.45 (m, 2H), 4.1 (q, $J=6.0$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 207.1 (C), 205.1 (C), 172.4 (C), 61.2 (CH_2), 58.4 (C), 38.3 (CH_2), 29.7 (CH_3), 28.3 (CH_2), 25.9 (CH_3), 19.0 (CH_3), 13.9 (CH_3). Anal. calcd for $C_{11}H_{18}O_4$: C, 61.66, H 8.47. Found: C, 61.79; H, 8.52%.

3.3.2. (*R*)-2-Acetyl-2-ethyl-5-oxo-hexanoic acid ethyl ester 10b. Oil; yield 67%; $[\alpha]_D=+8.7$ ($c=1.6$, $CHCl_3$); IR (film, cm^{-1}): 2975, 1717 1361, 1235; ^1H NMR (200 MHz, $CDCl_3$) δ 0.7 (t, $J=6.0$ Hz, 3H), 1.25 (t, $J=6.0$ Hz, 3H), 1.89 (m, 2H), 2.00 (s, 3H), 2.05 (s, 3H), 2.10–2.20 (m, 2H), 2.25–2.40 (m, 2H), 4.2 (q, $J=6.0$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 209.1 (C), 207.2 (C), 176.0 (C), 60.7 (C), 59.8 (CH_2), 38.3 (CH_2), 28.1 (CH_2), 25.9 (CH_2), 24.7 (CH_3), 19.6 (CH_3), 14.1 (CH_3), 8.5 (CH_3). Anal. calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.34; H, 8.72%.

3.3.3. (*S*)-2-Acetyl-2-(3-oxobutyl)-pent-4-enoic acid methyl ester 10c. Oil; yield 73%; $[\alpha]_D=+18.6$ ($c=9.9$, $CHCl_3$); IR (film, cm^{-1}): 1730, 1714; ^1H NMR (200 MHz, $CDCl_3$) δ 2.05 (s, 3H), 2.07 (s, 3H), 2.05–2.19 (m, 2H), 2.29–2.39 (m, 2H), 2.45–2.65 (m, 2H), 3.65 (s, 3H), 4.90–5.10 (m, 2H), 5.49–5.62 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 207.0 (C), 201.9 (C), 176.8 (C), 131.9 (CH), 119.2 (CH_2), 62.4 (C), 52.4 (CH_3), 38.1 (CH_2), 36.8 (CH_2), 29.9 (CH_3), 26.9 (CH_3), 25.4 (CH_2). Anal. calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.76; H, 7.79%.

3.3.4. (*S*)-2-Acetyl-2-benzyl-5-oxo-hexanoic acid methyl ester 10d. White powder; mp 77–79°C; yield 75%; $[\alpha]_D=-26.9$ ($c=4.5$, $CHCl_3$); IR (film, cm^{-1}): 1735, 1668; ^1H NMR (200 MHz, $CDCl_3$) δ 2.05 (s, 3H), 2.07 (s, 3H), 2.01–2.10 (m, 2H), 2.15–2.45 (m, 2H), 3.10 (s,

2H), 3.71 (s, 3H), 6.95–7.05 (m, 2H), 7.14–7.20 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 204.9 (C), 201.3 (C), 171.1 (C), 139.4 (C), 130.7 (2 CH), 128.1 (2 CH), 125.7 (CH), 60.9 (C), 52.3 (CH_3), 39.7 (CH_2), 36.1 (CH_2), 29.4 (CH_2), 26.4 (CH_3), 23.1 (CH_3). Anal. calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.68; H, 7.17%.

3.4. General procedure for synthesis of Hagemann's ester cyclisation

To the adduct (0.010 mol) was added piperidine (0.008 mol) and acetic acid (0.0095 mol). The mixture was stirred at 80°C for 1.5 h, dissolved in diethyl ether (20 mL), and the organic phase washed with water (3×15 mL). The aqueous layer was extracted with diethyl ether (2×30 mL). The combined organic extracts were dried over sodium sulfate and concentrated in vacuo and the evaporation residue was purified by flash chromatography [silica gel, ethyl acetate:hexane (2:8)].

3.4.1. (*R*)-1,2-Dimethyl-4-oxo-cyclohex-2-enecarboxylic acid ethyl ester 2a. Oil; yield 78%; $[\alpha]_D = +108.3$ ($c = 4.1$, $CHCl_3$); IR (film, cm^{-1}): 1734, 1678, 1627; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25 (t, $J = 7$ Hz, 3H), 1.40 (s, 3H), 1.95 (d, $J = 1$ Hz, 3H), 2.00–2.30 (m, 2H), 2.40–2.60 (m, 2H), 4.20 (q, $J = 7$ Hz, 2H), 5.90 (q, $J = 1$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.8 (C), 173.5 (C), 161.1 (C), 127.7 (CH), 60.9 (CH_2), 46.9 (C), 33.9 (CH_2), 33.9 (CH_2), 21.9 (CH_3), 19.8 (CH_3), 13.7 (CH_3). Anal. calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.20; H, 8.35%.

3.4.2. (*R*)-1-Ethyl-2-methyl-4-oxo-cyclohex-2-enecarboxylic acid ethyl ester 2b. Oil; yield 68%; $[\alpha]_D = +109.7$ ($c = 6.2$, $CHCl_3$); IR (film, cm^{-1}): 1714, 1675, 1652; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (t, $J = 7$ Hz, 3H), 1.26 (t, $J = 7$ Hz, 3H), 1.65–1.74 (m, 2H) 1.98 (d, $J = 1$ Hz, 3H), 1.98–2.10 (m, 2H), 2.30–2.60 (m, 2H), 4.18 (q, $J = 7$ Hz, 2H), 5.95 (q, $J = 1$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.0 (C), 170.5 (C), 162.1 (C), 126.7 (CH), 60.8 (CH_2), 55.1 (C), 29.5 (CH_2), 28.0 (CH_2), 22.9 (CH_2), 24.8 (CH_3), 13.9 (CH_3), 9.8 (CH_3). Anal. calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.42; H, 8.27%.

3.4.3. (*S*)-1-Allyl-2-methyl-4-oxo-cyclohex-2-enecarboxylic acid methyl ester 2c. Syrup; yield 79%; $[\alpha]_D = +88.4$ ($c = 12.8$, $CHCl_3$); IR (film, cm^{-1}): 1731, 1678; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.96 (d, $J = 1$ Hz, 3H), 2.00–2.07 (m, 1H), 2.25–2.45 (m, 3H), 2.50–2.70 (m, 2H), 3.69 (s, 3H), 5.09–5.15 (m, 2H), 5.60–5.75 (m, 1H), 5.90 (q, $J = 1$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.1 (C), 173.0 (C), 159.9 (C), 132.8 (CH), 129.4 (CH), 119.4 (CH_2), 55.7 (C), 50.4 (CH_3), 39.9 (CH_2), 34.1 (CH_2), 30.4 (CH_2), 21.3 (CH_3). Anal. calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.18; H, 7.77%.

3.4.4. (*S*)-1-Benzyl-2-methyl-4-oxo-cyclohex-2-enecarboxylic acid methyl ester 2d. White powder; mp 40–43°C; yield 65%; $[\alpha]_D = -62.5$ ($c = 3.2$, CCl_4); IR (film, cm^{-1}): 3100, 1740, 1680; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.78–1.95 (m, 1H), 2.0 (d, $J = 1$ Hz, 3H), 2.10–2.50 (m, 3H), 2.80 (d, $J = 14$ Hz, 1H), 3.45 (d, $J = 14$ Hz, 1H), 3.70 (s, 3H), 5.9 (d, $J = 1$ Hz, 1H), 7.0–7.1 (m, 2H), 7.15–7.25 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 194.6 (C), 171.4 (C), 162.2 (C), 136.5 (C), 130.7 (2 CH), 128.1 (2 CH), 126.7 (CH), 126.0 (CH), 56.9 (C), 52.4 (CH_3), 39.8 (CH_2), 29.5 (CH_2), 28.8 (CH_2), 24.1 (CH_3). Anal. calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.52; H, 7.29%.

Acknowledgements

The authors are grateful to the Ballu company for the generous gift of optically active 1-phenylethylamine and Nadia Pelligrini for her technical assistance.

References

1. (a) Cardwell, H. M. E. *J. Chem. Soc.* **1949**, 715–719; (b) Johnson, W. S.; Jensen, N. P.; Hooz, J.; Leopold, E. J. *J. Am. Chem. Soc.* **1968**, *90*, 5872–5881; (c) Sakan, K.; Craven, B. M. *J. Am. Chem. Soc.* **1983**, *105*, 3732–3734; (d) Jones, J. B.; Dodds, D. R. *Can. J. Chem.* **1987**, *65*, 2397–2404; (e) Ackland, D. J.; Pinhey, J. T. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2689–2694; (f) Hormann, R. E. *Eur. Pat. Appl.* 773216 A1, 14 May 1997; *Chem. Abstr.* **1997**, *127*, P 34126 b; (g) Cavé, C.; Valancogne, I.; Casas, R.; d'Angelo, J. *Tetrahedron Lett.* **1998**, *39*, 5872–5881.
2. (a) Begbie, A. L.; Golding, B. T. *J. Chem. Soc., Perkin Trans. 1* **1972**, 602–605; (b) Nasipuri, D.; Mitra, K.; Venkataraman, S. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1836–1838.
3. Frater, G.; Müller, U.; Günter, W. *Tetrahedron* **1984**, *40*, 1269–1277.
4. For recent developments: Cavé, C.; Desmaële, D.; d'Angelo, J.; Riche, C. *J. Org. Chem.* **1996**, *61*, 4361–4368; Hervouet, K.; Guingant, A. *Tetrahedron: Asymmetry* **1996**, *7*, 421–424; Jabin, I.; Revial, G.; Melloul, K.; Pfau, M. *Tetrahedron: Asymmetry* **1997**, *8*, 1101–1109; Witschel, M. C.; Bestmann, H. J. *Synthesis* **1997**, 107–112; Cavé, C.; Gassama, A.; Mahuteau, J.; d'Angelo, J.; Riche, C. *Tetrahedron Lett.* **1997**, *38*, 4773–4776; d'Angelo, J.; Cavé, C.; Desmaële, D. *Isr. J. Chem.* **1997**, *37*, 81–85; Cavé, C.; Le Porhiel-Castellon, Y.; Daley, D.; Riche, C.; Chiaroni, A.; d'Angelo, J. *Tetrahedron Lett.* **1997**, *38*, 8703–8706; Da Silva Goes, A. J.; Cavé, C.; d'Angelo, J. *Tetrahedron Lett.* **1998**, *39*, 1339–1340; d'Angelo, J.; Cavé, C.; Desmaële, D.; Gassama, A.; Thominiaux, C.; Riche, C. *Heterocycles* **1998**, *47*, 725–746; Thominiaux, C.; Roussé, S.; Desmaële, D.; d'Angelo, J.; Riche, C. *Tetrahedron: Asymmetry* **1999**, *10*, 2015–2021; Lim, S.; Jabin, I.; Revial, G. *Tetrahedron Lett.* **1999**, *40*, 4177–4180; Daley, V.; d'Angelo, J.; Cavé, C.; Mahuteau, J.; Chiaroni, A.; Riche, C. *Tetrahedron Lett.* **1999**, *40*, 1657–1660; Gassama, A.; d'Angelo, J.; Cavé, C.; Mahuteau, J.; Riche, C. *Eur. J. Org. Chem.* **2000**, 3165–3169; Nour, M.; Tan, K.; Cavé, C.; Villeneuve, D.; Desmaelle, D.; d'Angelo, J.; Riche, C. *Tetrahedron: Asymmetry* **2000**, *11*, 995–1002; Revial, G.; Lim, S.; Viossat, B.; Lemoine, P.; Tomas, A.; Duprat, A. F.; Pfau, M.

J. Org. Chem. **2000**, *65*, 4593–4600; Muri, E.; Kanazawa, A.; Barreiro, E.; Greene, A. E. *J. Chem. Soc., Perkin Trans. 1* **2000**, 731–735.

5. (a) Sevin, A.; Tortajada, J.; Pfau, M. *J. Org. Chem.* **1986**, *51*, 2671–2675; (b) Sevin, A.; Masure, D.; Giessner-Prettre, C.; Pfau, M. *Helv. Chim. Acta* **1990**, *73*, 552–573; (c) Tran Huu Dau, M. E.; Riche, C.; Dumas, F.; d'Angelo, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1059–1064.