A NEW STEREOCONTROLLED APPROACH TO A KEY INTERMEDIATE IN THE SYNTHESIS OF (2*S*,3*R*)-CAPREOMYCIDINE

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Dedicated to Professor Antonín Holý on the occasion of his 70th birthday.

A new stereocontrolled approach to the synthesis of advanced intermediate in the synthesis of nonproteinogenic amino acid (2*S*,3*R*)-capreomycidine via the novel domino reaction has been developed.

Keywords: Capreomycidine; Capreomycins; Stereoselectivity; Nonproteinogenic amino acids; [3,3]-Sigmatropic rearrangements; Total synthesis.

The synthesis of enantiopure nonproteinogenic α-amino acids is of great importance due to their role as pharmaceuticals, chiral ligands and building blocks in the synthesis of natural products[1]. Among recent developments in the preparation of such compounds, the functionalization of readily available proteinogenic α-amino acids and their derivatives has become an atractive method.

In this paper we demonstrate that D-methionine can be converted very efficiently into pure (2*S*,3*R*)-2,3-diacetamido-5-acetoxypentanoic acid (**17**) as the important intermediate in the stereocontrolled synthesis of (2*S*,3*R*)-capreomycidine, which is a constituent of the tuberculostatic cyclic peptide antibiotics capreomycins and related tuberactinomycins[2].

Several syntheses of this nonproteinogenic amino acid in both racemic and also optically pure form have been reported[3]. Recently we published[4] preliminary communication concerning a new stereocontolled approach to a key precursor for the synthesis of the cyclic guanidino amino acid L-capreomycidine via the novel domino reaction of the [3,3]-sigmatropic rearrangement of chiral thiocyanates easily prepared by chain lengthening

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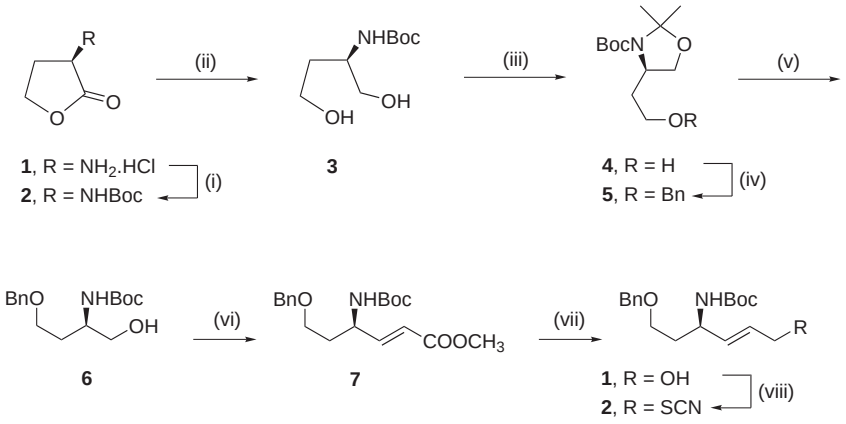
starting from the corresponding α-amino acids followed by stereoselective cyclization[5].

We now describe a sequence of the reaction steps for the preparation of the protected chiral amino acid **17**. As the staring material we have chosen D-methionine which was converted into (*R*)-2-aminobutano-4-lactone hydrochloride[6] (**1**). Furthermore, *tert*-butoxycarbonylation of **1** with di-*tert*-butyl dicarbonate in triethylamine, using CH_2Cl_2 as the solvent, gave protected lactone **2** (92%; Scheme 1), which was then ring-opened using $NaBH_4$ to form *N*-Boc-D-homoserinol (**3**) in 92% yield. Our subsequent strategy consisted in a specific protection of the primary alcoholic group in position 4. We assumed that due to bulky *tert*-butoxycarbonyl group the two primary alcohol functions of **3** could be differentiated easily. But treatment of **3** with TBDMSCl/pyridine gave a mixture of three products (two monosilylated regioisomers and one double-protected derivative). A similar situation has been observed employing *tert*-butyldiphenylsilyl chloride[7].

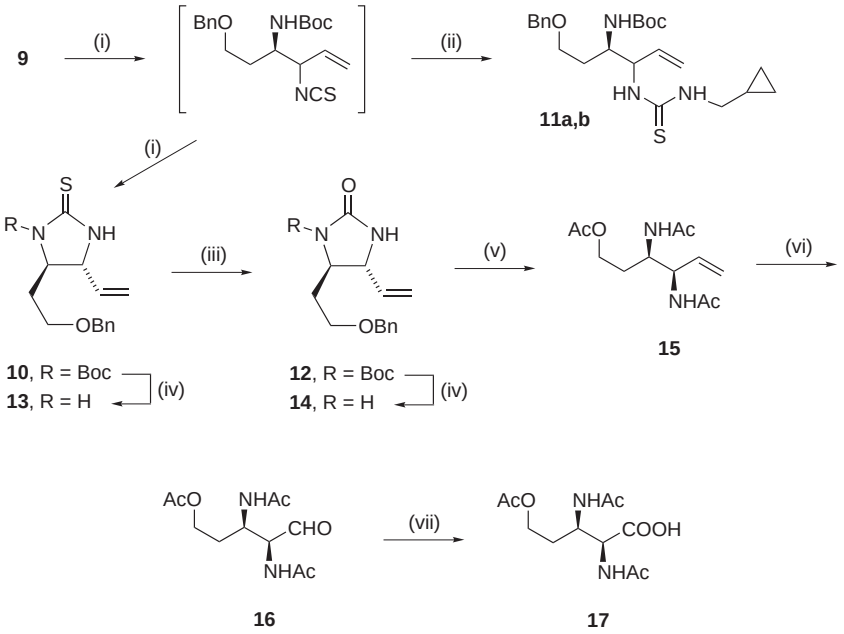


(i) Boc_2O, NEt_3; (ii) $NaBH_4$, THF; (iii) acetone, DMP; (iv) BnBr, NaH; (v) Amberlite, CH_3OH/H_2O; (vi) IBX, DMSO/$Ph_3PCH{=}COOCH_3$; (vii) DIBAH, CH_2Cl_2; (viii) MsCl, NEt_3/KSCN, MeCN

SCHEME 1

Therefore we decided for the formation of the oxazolidine ring which was achieved under mild conditions with 2,2-dimethoxypropane (DMP) in acetone at room temperature with $BF_3{\cdot}OEt_2$ as a catalyst, yielding acetonide **4** in 83% yield. The benzylation of **4** was carried out with BnBr and NaH in THF to afford 4-*O*-benzyl derivative **5** (87%; Scheme 1). Hydrolysis of the acetonide using Amberlite IR120 H^+ in CH_3OH/H_2O gave suitably protected alcohol **6** (89%) which was subsequently oxidized with

o-iodoxybenzoic acid[8] (IBX) in DMSO to yield corresponding aldehyde. The aldehyde was used directly in the olefination under Wittig conditions (Ph_3P=$CHCOOCH_3$) giving (*E*)-ester **7** in 80% overall yield, the ester was subjected to reduction with diisobutylaluminium hydride to yield allylic alcohol **8** (80%). The required thiocyanate **9** was easily prepared by the two-step process of mesylation of alcohol **8** followed by displacement using KSCN in CH_3CN in 64% overall yield. Thermal rearangement of thiocyanate **9** (Scheme 1) proceeded upon heating at 80 °C in dry xylene in the presence of catalytic amount of 2-hydroxypyridine to afford (4*R*,5*R*)-**10** as the only isolatable product in 85% yield. The observed stereochemistry of cyclic thiourea **10** is in agreement with previous work[5]. The *trans* product **10** is formed by intramolecular amino addition to *syn*-isothiocyanate (Scheme 2) which was in the reaction mixture together with *anti* derivative without selelectivity (*syn*/*anti* ≈ 50:50) as shown by NMR analysis of the crude reactiom mixture after heating at 80 °C for 35 min when the rearrangement was complete. These diastereoisomers, however, could not be



(i) xylene, 80 °C, 2-hydroxypyridine; (ii) (aminomethyl)cyclopropane, Et_2O; (iii) MNO, CH_3CN; (iv) CF_3COOH/H_2O 95:5; (v) 6M HCl, N_2, heating, then pyridine, Ac_2O; (vi) $NaIO_4$, $RuCl_3$, $CCl_4/CH_3CN/H_2O$ 1:1:1; (vii) $NaClO_2$, CH_3CN/*t*-BuOH/2-methylbut-2-ene 4:4:1

SCHEME 2

easily separated by chromatography, therefore they were converted into the thioureas **11a** and **11b** easily differentiable by the reaction with (aminomethyl)cyclopropane (Scheme 2). Our approach to the build-up of chiral amino acid **17** was based on hydrolysis of cyclic thiourea **10**. Treatment of **10** with 6 M HCl resulted in no reaction. Unprotected cyclic thiourea **13** was isolated from the reaction mixture as a major product. Removal of the *tert*-butoxycarbonyl protecting group from **10** with TFA/H_2O provided the same thiourea **13** (80%). We therefore proceeded with cyclic urea **12**, which was prepared from **10** by the use of mesitylnitrile oxide[9] (MNO) in acetonitrile in 86% yield and fully characterized in the form of the unprotected cyclic urea **14** (87%; Scheme 2). The cyclic urea **12** was converted into the pure suitably protected diamino acid **17** in two reaction steps. First, **12** was subjected to reaction with 6 M HCl and then the acetylation of dihydrochloride with acetic anhydride in pyridine gave fully protected acetate **15** in 76% overall yield. Surprisingly, during the hydrolysis (6 M HCl, reflux) the benzyl protecting group was removed. The oxidation of **15** was accomplished with a catalytic amount of ruthenium(III) chloride and $NaIO_4$ in $CCl_4/CH_3CN/H_2O$ (1:1:1) to give aldehyde **16** instead of corresponding acid[10]. Without purification (this product was used immediately in the next step due to instability of α-amino aldehydes), the crude **16** was selectively oxidized to protected diamino acid **17** by treatment with sodium chlorite/2-methylbut-2-ene in 73% yield after flash chromatography (Scheme 2).

A stereocontrolled synthesis of chiral non-racemic advanced intermediate **17** in the synthesis of nonproteinogenic amino acid (2*S*,3*R*)-capreomycidine has been reported employing D-methionine as a reactant. It was found that the novel domino reaction[4,5] is a useful strategy for the preparation of diastereomerically pure (4*R*,5*R*)-4-vinyltetrahydroimidazole-2-thione **10**.

EXPERIMENTAL

The melting points were determined on the Kofler block and are uncorrected. Optical rotations were measured with a P3002 Krüss polarimeter in chloroform and H_2O and reported as follows: $[\alpha]_D^{25}$ (*c* in g/100 ml solvent). NMR spectra were recorded at room temperature on a FT NMR spectrometer Varian Mercury Plus 400 (^1H at 400.13 MHz and ^{13}C at 100.6 MHz), on a FT NMR spectrometer Bruker AMX 360 (^1H at 360.13 MHz and ^{13}C at 90.55), on a FT NMR spectrometer Bruker Avance 500 (^1H at 500.13 MHz and ^{13}C at 125.7 MHz) and on a FT NMR spectrometer Varian Unity-500 (^1H at 499.8 MHz and ^{13}C at 125.7 MHz). Chemical shifts (δ, ppm) are referenced either to tetramethylsilane as internal standard for ^1H or to the solvent signal (^{13}C NMR, δ($CDCl_3$) 77.0). ^{13}C NMR multiplicities were determined using a DEPT pulse sequence. Coupling constants (*J*) are given in Hz. IR spectra (wavenumbers in

cm^{-1}) were recorded on a Perkin–Elmer 599 IR spectrometer in $CHCl_3$. The reaction course was routinely monitored by TLC (Merck 60 F_{254}) and the products were visualized by UV light absorption at 254 nm or by spraying with Mo reagent or $KMnO_4$ reagent. All reactions were performed under an atmosphere of nitrogen when anhydrous solvents were used. Column chromatography was carried out in glass columns using silica gel Kieselgel (0.035–0.070 mm).

(*R*)-2-Aminobutano-4-lactone Hydrochloride (**1**)

^{13}C NMR (90 MHz, D_2O): 31.0 (C-3′); 52.7 (C-2′); 71.6 (C-4′); 178.7 (C=O). The procedure, m.p. and $[\alpha]_D$ were consistent with those reported[6]. ^{13}C NMR spectroscopic data have not previously been reported[6].

(*R*)-2-[(*tert*-Butoxycarbonyl)amino]butano-4-lactone (**2**)

To a suspension of (*R*)-2-aminobutano-4-lactone hydrochloride (**1**; 4.60 g, 33.5 mmol) in dry CH_2Cl_2 (42 ml) were added Et_3N (4.60 ml, 33.5 mmol) and $(Boc)_2O$ (7.30 g, 33.5 mmol). After stirring at room temperature for 12 h, the reaction mixture was washed with 1 M aqueous $KHSO_4$ (40 ml), 1 M aqueous $NaHCO_3$ (40 ml), brine (20 ml) and dried (Na_2SO_4). Evaporation of the solvent at reduced pressure and chromatography of the residue (dichloromethane–methanol, 95:5) afforded 6.20 g (92%) of compound **2** as a white solid, m.p. 115–118 °C (dichloromethane–methanol), $[\alpha]_D^{25}$ –13.6 (*c* 0.23, $CHCl_3$). (Ref.[11] gives $[\alpha]_D^{21}$ –9.9 (*c* 1.3, $CHCl_3$) but ^{13}C NMR data were not correct in this literature; in ref.[12] ^1H and ^{13}C NMR data are published but without $[\alpha]_D$). For $C_9H_{15}NO_4$ (201.2) calculated: 53.72% C, 7.51% H, 6.96% N; found: 53.51% C, 7.30% H, 6.72% N. ^1H NMR (400 MHz, $CDCl_3$): 1.46 s, 9 H (3 × CH_3); 2.20 m, 1 H (H-3′); 2.76 m, 1 H (H-3′); 4.25 ddd, 1 H, *J*(4′,4′) = 9.3, *J*(4′,3′) = 5.9, *J*(4′,3′) = 2.1 (H-4′); 4.36 m, 1 H (H-2′); 4.45 m, 1 H (H-4); 5.09 s, 1 H (NH). ^{13}C NMR (100 MHz, $CDCl_3$): 28.1 (3 × CH_3); 31.0 (C-3′); 49.9 (C-2′); 65.5 (C-4′); 80.3 ($(CH_3)_3C$); 155.3 (C=O); 175.2 (C-1′).

(*R*)-2-[(*tert*-Butoxycarbonyl)amino]butane-1,4-diol (**3**)

To a solution of lactone **2** (6.10 g, 30.3 mmol) in dry THF (74 ml) was added $NaBH_4$ (2.47 g, 60.6 mmol). The reaction mixture was refluxed for 1 h, cooled and quenched with methanol (3 ml). The mixture was poured into saturated aqueous $NaHCO_3$ (40 ml), the product was extracted with ethyl acetate (3 × 40 ml). The combined organic layers were dried (Na_2SO_4) and concentrated at reduced pressure. The residue was chromatographed on silica gel (cyclohexane–ethyl acetate, 1:2) and afforded 5.75 g (92%) of diol **3** as a white solid, m.p. 64–68 °C, $[\alpha]_D^{25}$ +9.9 (*c* 0.95, $CHCl_3$). (Ref.[13] gives $[\alpha]_D^{25}$ +30.8 (*c* 0.4, MeOH), Aldrich handbook for (*S*)-isomer $[\alpha]_D^{20}$ –8 (*c* 1, $CHCl_3$); refs[12,14] do not report $[\alpha]_D$). For $C_9H_{19}NO_4$ (205.3) calculated: 52.67% C, 9.33% H, 6.82% N; found: 52.81% C, 9.29% H, 6.65% N. ^1H NMR (400 MHz, $CDCl_3$, D_2O): 1.45 s, 9 H (3 × CH_3); 1.61 m, 1 H (H-3′); 1.81 m, 1 H (H-3′); 3.59–3.72 m, 4 H (H-1′, H-4′); 3.80 m, 1 H (H-2′). ^{13}C NMR (100 MHz, $CDCl_3$): 28.4 (3 × CH_3); 34.8 (C-3′); 49.5 (C-2′); 58.7 (C-4′); 65.1 (C-1′); 80.0 ($(CH_3)_3C$); 157.1 (C=O).

tert-Butyl (4*R*)-4-(2-Hydroxyethyl)-2,2-dimethyl-1,3-oxazolidine-3-carboxylate (**4**)

Diol **3** (5.70 g, 27.80 mmol) was dissolved in a mixture of acetone (100 ml) and 2,2-dimethoxypropane (30 ml) to which $BF_3 \cdot OEt_2$ (0.20 ml) was added. The resulting solution was stirred at room temperature for 1 h (TLC showed no starting **3**). The solvent was removed under reduced pressure, residual oil taken up in CH_2Cl_2 (100 ml) and the resulting solution was washed with a mixture of saturated aqueous $NaHCO_3$ and H_2O (60 ml, 1:1), then brine (60 ml), dried (Na_2SO_4) and the solvent was evaporated. Chromatography of the residue (cyclohexane–ethyl acetate, 2:1) gave 5.63 g (83%) of compound **4** as a white solid, m.p. 74–76 °C, $[\alpha]_D^{25}$ +13.4 (*c* 1.8, $CHCl_3$). For $C_{12}H_{23}NO_4$ (245.3) calculated: 58.75% C, 9.45% H, 5.71% N; found: 58.83% C, 9.34% H, 5.82% N. ^{1}H NMR (500 MHz, $CDCl_3$): 1.49 s, 12 H (4 × CH_3); 1.53 s, 3 H (CH_3); 1.71 m, 1 H (H-3′); 1.82 m, 1 H (H-3′); 3.53 m, 1 H (H-4′); 3.62 m, 1 H (H-2′); 3.68 d, 1 H, *J* = 8.7 (OH); 3.99 m 2 H (H-1′); 4.21 m, 1 H (H-4′). ^{13}C NMR (100 MHz, $CDCl_3$, 50 °C): 24.4 (CH_3); 27.8 (CH_3); 28.4 (3 × CH_3); 37.7 (C-3′); 54.1 (C-2′); 58.7 (C-4′); 68.3 (C-1′); 80.9 ((CH_3)$_3$C); 93.7 (OCN); 153.8 (C=O). ^{1}H NMR spectroscopic data were consistent with those reported in refs[14b,15]. ^{13}C NMR data have not previously been reported in refs[14b,15].

tert-Butyl (4*R*)-4-[2-(Benzyloxy)ethyl]-2,2-dimethyl-1,3-oxazolidine-3-carboxylate (**5**)

To a solution of alcohol **4** (4.20 g, 17.12 mmol) in dry THF (34 ml) at 0 °C was added NaH (1.37 g, 34.32 mmol, 60% dispersion in mineral oil, freed of oil with anhydrous THF). The reaction was stirred at 0 °C for 20 min and then BnBr (3.10 ml, 25.68 mmol) was added at the same temperature. The mixture was allowed to warm to room temperature and stirred for 12 h and then partitioned between CH_2Cl_2 (50 ml) and ice water (50 ml). The aqueous phase was extracted with another portion of CH_2Cl_2 (50 ml). The combined organic phases were dried (Na_2SO_4) and the solvent evaporated under reduced pressure. The chromatography of residue on silica gel (cyclohexane–ethyl acetate, 9:1) afforded 5.00 g (87%) of compound **5** as a colorless oil, $[\alpha]_D^{25}$ +16 (*c* 0.24 $CHCl_3$). For $C_{19}H_{29}NO_4$ (335.5) calculated: 68.03% C, 8.71% H, 4.18% N; found: 68.14% C, 8.61% H, 4.27% N. ^{1}H NMR (400 MHz, $CDCl_3$): 1.47 s, 12 H (4 × CH_3); 1.57 s, 3 H (CH_3); 1.85 m, 1 H (H-3′); 2.06 m, 1 H (H-3′); 3.53 s, 2 H (H-4′); 3.93 m, 3 H (H-1′, H-2′); 4.47 d, 1 H, *J* = 12.4 (CH_2Ph); 4.51 d, 1 H, *J* = 12.4 (CH_2Ph); 7.26–7.34 m, 5 H (Ph). ^{13}C NMR (100 MHz, $CDCl_3$): 24.6 (CH_3); 27.6 (CH_3); 28.5 (3 × CH_3); 33.8 (C-3′); 56.3 (C-2′); 67.4 (C-1′); 68.0 (C-4′); 72.9 (CH_2Ph); 80.0 ((CH_3)$_3$C); 93.5 (OCN); 127.5 (3 × C-arom.); 128.3 (2 × C-arom.); 138.4 (C-arom.); 152.2 (C=O).

tert-Butyl *N*-[(1*R*)-3-(Benzyloxy)-1-(hydroxymethyl)propyl]carbamate (**6**)

To a solution of **5** (4.90 g, 14.61 mmol) in methanol–H_2O (9:1, 62 ml) was added Amberlite IR-120 H^+ (18.57 g). The mixture was stirred at room temperature overnight, filtered and the solid was washed with methanol. Evaporation of the solvent from the combined filtrates gave an oil which was purified by chromatography on silica gel (cyclohexane–ethyl acetate, 3:1) to afford 3.85 g (89%) of the alcohol **6** as a colorless oil, $[\alpha]_D^{25}$ +15 (*c* 0.23, $CHCl_3$). For $C_{16}H_{25}NO_4$ (295.4) calculated: 65.06% C, 8.53% H, 4.74% N; found: 64.83% C, 8.59% H, 4.62% N. ^{1}H NMR (400 MHz, $CDCl_3$): 1.44 s, 9 H (3 × CH_3); 1.77–1.94 m, 2 H (H-3′); 3.25 bs, 1 H (OH); 3.57–3.62 m, 4 H (H-1′, H-4′); 3.76 m, 1 H (H-2′); 4.46 d, 1 H, *J* = 12.3 (CH_2Ph); 4.49 d, 1 H, *J* = 12.3 (CH_2Ph); 5.23 bs, 1 H (NH); 7.24–7.37 m, 5 H (Ph). ^{13}C NMR (100 MHz, $CDCl_3$): 28.5 (3 × CH_3); 31.5 (C-3′); 51.3 (C-2′); 65.7 (C-4′ or C-1′); 67.3 (C-4′ or

C-1′); 73.4 (CH_2Ph); 79.5 (($CH_3)_3C$); 127.9 (3 × C-arom.); 128.6 (2 × C-arom.); 137.8 (C-arom.); 156.4 (C=O).

Methyl (2*E*,4*R*)-6-(Benzyloxy)-4-[(*tert*-butoxycarbonyl)amino]hex-2-enoate (**7**)

To a solution of **6** (3.80 g, 12.86 mmol) in DMSO (29 ml) was added IBX (4.00 g, 14.15 mmol). The reaction mixture was stirred at room temperature for 5 h. Ice water (90 ml) was added and the precipitate was filtered off. The filtrate was extracted with CH_2Cl_2 (2 × 90 ml). The combined organic phases were dried (Na_2SO_4) and the solvent was removed under reduced pressure. To the aldehyde dissolved in CH_2Cl_2 (34 ml), [(methoxycarbonyl)methylidene]triphenylphosphorane (5.16 g, 15.43 mmol) was added. The reaction mixture was stirred at room temperature overnight. The solvent was removed at reduced pressure and the residue was chromatographed on silica gel (cyclohexane–ethyl acetate, 5:1) to give 3.60 g (80%) of ester **7** as a colorless oil, $[\alpha]_D^{25}$ +53 (*c* 0.09, $CHCl_3$). For $C_{19}H_{27}NO_5$ (349.4) calculated: 65.31% C, 7.79% H, 4.01% N; found: 65.14% C, 7.63% H, 4.14% N. ^{1}H NMR (400 MHz, $CDCl_3$): 1.44 s, 9 H (3 × CH_3); 1.79 m, 1 H (H-5′); 1.99 m, 1 H (H-5′); 3.55 m, 2 H (H-6′); 3.72 s, 3 H (CH_3O); 4.48 m, 2 H (CH_2Ph); 4.49 m, 1 H (H-4′); 5.37 d, 1 H, *J* = 6.6 (NH); 5.93 dd, 1 H, *J*(3′,2′) = 15.7, *J*(4′,2′) = 1.7 (H-2′); 6.87 dd, 1 H, *J*(3′,2′) = 15.7, *J*(4′,3′) = 4.9 (H-3′); 7.27–7.37 m, 5 H (Ph). ^{13}C NMR (100 MHz, $CDCl_3$): 28.4 (3 × CH_3); 33.6 (C-5′); 50.2 (C-4′); 51.6 (CH_3O); 67.0 (C-6′); 73.3 (CH_2Ph); 79.5 (($CH_3)_3C$); 120.6 (C-2′); 127.7 (2 × C-arom.); 127.8 (C-arom.); 128.5 (2 × C-arom.); 137.8 (C-arom.); 148.5 (C-3′); 155.2 (C=O); 166.7 (C=O).

tert-Butyl *N*-{(1*R*,2*E*)-1-[2-(Benzyloxy)ethyl]-4-hydroxybut-2-en-1-yl}carbamate (**8**)

To a solution of ester **7** (3.50 g, 10.02 mmol) in dry CH_2Cl_2 (47 ml) was added $BF_3{\cdot}OEt_2$ (0.19 ml) at –10 °C. Then diisobutylaluminium hydride (30.15 ml, 1.2 M toluene solution) was dropped into cooled solution, the resulting mixture was stirred at –10 °C for 1 h and then quenched with methanol (7.5 ml). The mixture was allowed to warm to room temperature and poured into 30% aqueous KNa tartarate (157 ml). After stirring for 30 min, the product was extracted with CH_2Cl_2 (3 × 70 ml). The combined organic layers were dried (Na_2SO_4) and the solvent evaporated under reduced pressure. Chromatography of the residue (cyclohexane–ethyl acetate, 1:1) afforded 2.58 g (80%) of allylic alcohol **8** as a colorless oil, $[\alpha]_D^{25}$ +61 (*c* 0.18, $CHCl_3$). For $C_{18}H_{27}NO_4$ (321.4) calculated: 67.26% C, 8.47% H, 4.36% N; found: 67.01% C, 8.22% H, 4.48% N. ^{1}H NMR (400 MHz, $CDCl_3$): 1.44 s, 9 H (3 × CH_3); 1.74 m, 1 H (H-5′); 1.91 m, 1 H (H-5′); 3.50–3.61 m, 3 H (H-6′, OH); 4.07 dd, 1 H, *J*(1′,1′) = 12.0, *J*(2′,1′) = 5.3 (H-1′); 4.09 dd, 1 H, *J*(1′,1′) = 12.0, *J*(2′,1′) = 5.0 (H-1′); 4.28 m, 1 H (H-4′); 4.48 s, 2 H (CH_2Ph); 5.20 bs, 1 H (NH); 5.61 dd, 1 H, *J*(3′,2′) = 15.4, *J*(4′,3′) = 5.1 (H-3′); 5.74 ddd, 1 H, *J*(3′,2′) = 15.4, *J*(2′,1′) = 5.3, *J*(2′,1′) = 5.0 (H-2′); 7.28–7.37 m, 5 H (Ph). ^{13}C NMR (100 MHz, $CDCl_3$): 28.4 (3 × CH_3); 34.6 (C-5′); 50.3 (C-4′); 62.9 (C-1′); 67.2 (C-6′); 73.2 (CH_2Ph); 79.2 (($CH_3)_3C$); 127.7 (3 × C-arom.); 128.4 (2 × C-arom.); 129.6 (C-2′); 131.8 (C-3′); 138.1 (C-arom.); 155.5 (C=O).

tert-Butyl *N*-{(1*R*,2*E*)-1-[2-(Benzyloxy)ethyl]-4-thiocyanatobut-2-en-1-yl}carbamate (**9**)

To a solution of alcohol **8** (2.00 g, 6.22 mmol) in dry CH_2Cl_2 (21.70 ml) were added Et_3N (1.30 ml, 9.33 mmol) and CH_3SO_2Cl (0.58 ml, 7.46 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and then at room temperature for 2 h. The solvent was evaporated

under reduced pressure. The residue was diluted with diethyl ether (40 ml) and the solid was removed by filtration. The solvent was evaporated to afford the crude mesylate which was used in the subsequent reaction directly without further purification.

The crude mesylate was dissolved in CH_3CN (22 ml) KSCN (0.90 g, 9.33 mmol) was added. After stirring at room temperature for 1 h, the solvent was evaporated. The residue was diluted with diethyl ether (45 ml) and the solid was removed by filtration. Evaporation of the solvent at reduced pressure and chromatography of the residue (cyclohexane–ethyl acetate, 5:1) afforded 1.44 g (64%) of thiocyanate **9** as a colorless oil, $[\alpha]_D^{25}$ +208 (*c* 0.15, $CHCl_3$). For $C_{19}H_{26}N_2O_3S$ (362.5) calculated: 62.96% C, 7.23% H, 7.73% N, 8.85% S; found: 63.06% C, 7.38% H, 7.89% N, 8.59% S. ^{1}H NMR (400 MHz, $CDCl_3$): 1.44 s, 9 H (3 × CH_3); 1.79 m, 1 H (H-5′); 1.95 m, 1 H (H-5′); 3.47–3.67 m, 4 H (H-1′, H-6′); 4.35 m, 1 H (H-4′); 4.47 d, 1 H, *J* = 11.8 (CH_2Ph); 4.51 d, 1 H, *J* = 11.8 (CH_2Ph); 5.35 bs, 1 H (NH); 5.64–5.76 m, 2 H (H-2′, H-3′); 7.26–7.34 m, 5 H (Ph). ^{13}C NMR (100 MHz, $CDCl_3$): 28.3 (3 × CH_3); 34.0 (C-5′); 35.7 (C-1′); 50.2 (C-4′); 66.9 (C-6′); 73.1 (CH_2Ph); 79.2 ((CH_3)$_3$C); 111.8 (SCN); 122.7 (C-2′); 127.6 (2 × C-arom.); 127.7 (C-arom.); 128.3 (2 × C-arom.); 138.0 (C-3′); 138.1 (C-arom.); 155.2 (C=O).

tert-Butyl (4*R*,5*R*)-4-[2-(Benzyloxy)ethyl]-2-thioxo-5-vinylimidazolidine-1-carboxylate (**10**)

To a solution of thiocyanate **9** (1.35 g, 3.72 mmol) in dry xylene (32 ml) was added 2-hydroxypyridine (35.4 mg, 0.372 mmol). The reaction mixture was heated at 80 °C for 5 h under nitrogen atmosphere. The solvent was evaporated at reduced pressure, the chromatography of residue on silica gel (cyclohexane–ethyl acetate, 5:1) gave 1.15 g (85%) of imidazolidine **10** as a colorless oil, $[\alpha]_D^{25}$ +52 (*c* 0.26, $CHCl_3$). For $C_{19}H_{26}N_2O_3S$ (362.5) calculated: 62.96% C, 7.23% H, 7.73% N, 8.85% S; found: 63.06% C, H, 7.38% H, 7.89% N, 8.59% S. IR ($CHCl_3$): 1470 (C=S); 1740 (C=O); 3450 (NH). ^{1}H NMR (400 MHz, $CDCl_3$): 1.52 s, 9 H (3 × CH_3); 1.98–2.07 m, 1 H (H-8′); 2.09–2.16 m, 1 H (H-8′); 3.55 ddd, 1 H, *J*(9′,9′) = 10.6, *J*(9′,8′) = 6.0, *J*(9′,8′) = 4.6 (H-9′); 3.60 ddd, 1 H, *J*(9′,9′) = 10.6, *J*(9′,8′) = 5.6, *J*(9′,8′) = 4.1 (H-9′); 4.10 dd, 1 H, *J*(6′,5′) = 6.6, *J*(5′,4′) = 5.4 (H-5′); 4.25 ddd, 1 H, *J*(8′,4′) = 9.0, *J*(5′,4′) = 5.4, *J*(8′,4′) = 2.7 (H-4′); 4.46 d, 1 H, *J* = 11.8 (CH_2Ph); 4.50 d, 1 H, *J* = 11.8 (CH_2Ph); 5.17 dd, 1 H, *J*(7′*cis*,6′) = 10.2, *J*(7′*cis*,7′*trans*) = 0.7 (H-7′*cis*); 5.21 dd, 1 H, *J*(7′*trans*,6′) = 17.0, *J*(7′*cis*,7′*trans*) = 0.7 (H-7′*trans*); 5.77 ddd, 1 H, *J*(7′*trans*,6′) = 17.0, *J*(7′*cis*,6′) = 10.2, *J*(6′,5′) = 6.6 (H-6′); 7.27–7.36 m, 5 H (Ph); 7.56 s, 1 H (NH). ^{13}C NMR (100 MHz, $CDCl_3$): 28.1 (3 × CH_3); 33.2 (C-8′); 60.5 (C-5′); 64.5 (C-4′); 66.5 (C-9′); 73.4 (CH_2Ph); 83.6 ((CH_3)$_3$C); 117.6 (C-7′); 127.8 (3 × C-arom.); 128.5 (2 × C-arom.); 135.6 (C-6′); 137.9 (C-arom.); 150.0 (C=O); 180.2 (C=S).

rel tert-Butyl {(3*R*,4*S*)-1-(Benzyloxy)-4-[3-(cyclopropylmethyl)thioureido]hex-5-en-3-yl}-carbamate (**11a**) and *tert*-Butyl {(3*R*,4*R*)-1-(Benzyloxy)-4-[3-(cyclopropylmethyl)-thioureido]hex-5-en-3-yl}carbamate (**11b**)

A solution of thiocyanate **9** (0.25 g, 0.69 mmol) in dry xylene (6 ml) was heated at 80 °C for 35 min under nitrogen atmosphere. The solvent was evaporated, the crude residue was dissolved in diethyl ether (5 ml) and (aminomethyl)cyclopropane (0.07 ml, 0.76 mmol) was added. The reaction mixture was stirred at room temperature for 1.5 h, then concentrated under reduced pressure. Purification of the residue by flash chromatography (cyclohexane–ethyl acetate, 7:1) afforded thioureas **11a** (0.10 g, 33.4%) and **11b** (0.15 g, 50.1%).

11b: Colorless oil, $[\alpha]_D^{25}$ +197 (*c* 0.13, $CHCl_3$). For $C_{23}H_{35}N_3O_3S$ (433.6) calculated: 63.71% C, 8.14% H, 9.69% N, 7.39% S; found: 63.52% C, 8.21% H, 9.48% N, 7.54% S. ^{1}H NMR (500 MHz, $CDCl_3$): 0.25 m, 2 H ($CH_{2cycloprop}$); 0.54 m, 2 H ($CH_{2cycloprop}$); 1.06 m, 1 H ($CH_{cycloprop}$); 1.44 s, 9 H (3 × CH_3); 1.70 1 H, m (H-2′); 1.98 m, 1 H (H-2′); 3.30 m, 2 H (CH_2N); 3.57 m, 1 H (H-1′); 3.60 m, 1 H (H-4′); 3.62 m, 1 H (H-1′); 3.76 m, 1 H (H-3′); 4.49 d, 1 H, *J* = 11.7 ($PhCH_2O$); 4.52 d, 1 H, *J* = 11.7 ($PhCH_2O$); 5.27 bd, 1 H *J*(6′*cis*,5′) = 10.6 (H-6′*cis*); 5.30 bd, 1 H, *J*(6′*trans*,5′) = 17.0 (H-6′*trans*); 5.74 ddd, 1 H, *J*(6′*trans*,5′) = 17.0, *J*(6′*cis*,5′) = 10.6, *J*(5′,4′) = 6.3 (H-5′). ^{13}C NMR (125.7 MHz, $CDCl_3$): 3.6 (2 × $CH_{2cycloprop}$); 10.0 ($CH_{cycloprop}$); 28.3 (3 × CH_3); 29.7 (C-2′); 31.8 (CH_2NH); 52.9 (C-3′); 67.7 (C-1′); 73.4 ($PhCH_2$); 80.1 (($CH_3)_3$**C**); 118.0 (C-6′); 127.7 (3 × C-arom.); 128.4 (2 × C-arom); 128.5 (C-5′); 137.8 (C-arom.); 157.3 (C=O); 180.9 (C=S).

11a: Colorless oil, $[\alpha]_D^{25}$ +28 (*c* 0.18, $CHCl_3$). For $C_{23}H_{35}N_3O_3S$ (433.6) calculated: 63.71% C, 8.14% H, 9.69% N, 7.39% S; found: 63.56% C, 8.23% H, 9.52% N, 7.44% S. ^{1}H NMR (500 MHz, $CDCl_3$): 0.22 m, 2 H ($CH_{2cycloprop}$); 0.54 m, 2 H ($CH_{2cycloprop}$); 1.02 m, 1 H ($CH_{cycloprop}$); 1.44 s, 9 H (3 × CH_3); 1.78 m, 1 H (H-2′); 1.92 m, 1 H (H-2′); 3.18 m, 2 H (CH_2N); 3.57 m, 1 H (H-1′); 3.62 m, 1 H (H-1′); 3.74 m, 1 H (H-4′); 3.93 m, 1 H (H-3′); 4.48 d, 1 H, *J* = 11.6 ($PhCH_2O$); 4.51 d, 1 H, *J* = 11.6 ($PhCH_2O$); 5.28 bd, 1 H, *J*(6′*trans*,5′) = 16.8 (H6′*trans*); 5.31 bd, 1 H, *J*(6′*cis*,5′) = 10.5 (H6′*cis*); 5.75 ddd, 1 H, *J*(6′*trans*,5′) = 16.8, *J*(6′*cis*,5′) = 10.5, *J*(5′,4′) = 5.9 (H-5′). ^{13}C NMR (125.7 MHz, $CDCl_3$): 3.6 (2 × $CH_{2cycloprop}$); 10.0 ($CH_{cycloprop}$); 28.3 (3 × CH_3); 29.7 (C-2′); 32.0 (CH_2NH); 53.8 (C-3′); 67.5 (C-1′); 73.4 (CH_2Ph); 80.1 (($CH_3)_3$**C**); 118.0 (C-6′); 127.8 (3 × C-arom); 128.5 (2 × C-arom.); 133.4 (C-5′); 137.8 (C-arom.); 157.1 (C=O); 180.9 (C=S).

tert-Butyl (4*R*,5*R*)-4-[2-(Benzyloxy)ethyl]-2-oxo-5-vinylimidazolidine-1-carboxylate (**12**)

To a solution of **10** (0.67 g, 1.85 mmol) in CH_3CN (19 ml) was added mesitylnitrile oxide (MNO) (0.158 g, 0.98 mmol). The reaction mixture was stirred at room temperature for 15 min, CH_3CN was evaporated under reduced pressure. The chromatography of residue on silica gel (cyclohexane–ethyl acetate, 3:1) gave 0.55 g (86%) of **12** as a colorless oil, $[\alpha]_D^{25}$ +105 (*c* 0.16, $CHCl_3$). For $C_{19}H_{26}N_2O_4$ (346.4) calculated: 65.87% C, 7.57% H, 8.09% N; found: 65.98% C, 7.36% H, 7.94% N. ^{13}C NMR (90 MHz, $CDCl_3$): 28.0 (3 × CH_3); 33.3 (C-8′); 55.9 (C-5′); 59.6 (C-4′); 66.4 (C-9′); 73.1 (CH_2Ph); 82.4 (($CH_3)_3$**C**); 116.3 (C-7′); 127.5 (2 × C-arom.); 127.6 (C-arom.); 128.3 (2 × C-arom.); 137.0 (C-6′); 137.9 (C-arom.); 150.1 (C=O); 155.6 (C=O).

(4*R*,5*R*)-4-[2-(Benzyloxy)ethyl]-5-vinylimidazolidine-2-thione (**13**)

Imidazolidine **10** (0.15 g, 0.414 mmol) was dissolved in a mixture of CF_3COOH and H_2O (95:5, 5 ml). The reaction mixture was stirred at room temperature for 30 min and then concentrated under reduced pressure. The residue was diluted with diethyl ether (10 ml) and washed with saturated aqueous $NaHCO_3$ (5 ml). The organic phase was dried (Na_2SO_4), the solvent was evaporated and the resulting crude product was purified by flash chromatography on silica gel (cyclohexane–ethyl acetate, 1:1) to provide 0.087 g (80%) of **13** as a white solid, m.p. 69–70 °C, $[\alpha]_D^{25}$ +51 (*c* 0.86, $CHCl_3$). For $C_{14}H_{18}N_2OS$ (262.4) calculated: 64.09% C, 6.92% H, 10.68% N, 12.22% S; found: 64.28% C, 6.76% H, 10.74% N, 12.01% S. ^{1}H NMR (400 MHz, $CDCl_3$): 1.81 m, 1 H (H-8′); 1.95 m, 1 H (H-8′); 3.52 m, 1 H (H-9′); 3.58 m, 1 H (H-9′); 3.78 ddd 1 H, *J*(5′,4′) = 8.1, *J*(8′,4′) = 5.1, *J*(8′,4′) = 3.6 (H-4′); 4.08 dd,

1 H, *J*(5′,4′) = 8.1, *J*(6′,5′) = 7.7 (H-5′); 4.49 d, 1 H, *J* = 12.2 (CH_2Ph); 4.52 d, 1 H, *J* = 12.2 (CH_2Ph); 5.23 d, 1 H, *J*(7′*cis*,6′) = 10.1 (H-7′*cis*); 5.28 d, 1 H, *J*(7′*trans*,6′) = 17.5 (H-7′*trans*); 5.81 ddd, 1 H, *J*(7′*trans*,6′) = 17.5, *J*(7′*cis*,6′) = 10.1, *J*(6′,5′) = 7.7 (H-6′); 6.01 bs, 1 H (NH); 6.50 bs, 1 H (NH); 7.29–7.39 m, 5 H (Ph). ^{13}C NMR (100 MHz, $CDCl_3$): 33.7 (C-8′); 62.9 (C-5′); 66.4 (C-4′); 67.5 (C-9′); 73.4 (CH_2Ph); 119.1 (C-7′); 127.8 (2 × C-arom.); 128.0 (C-arom.); 128.6 (2 × C-arom.); 135.2, 137.6 (C-arom.); 183.2 (C=S).

(4*R*,5*R*)-4-[2-(Benzyloxy)ethyl]-5-vinylimidazolidin-2-one (**14**)

Compound **12** (0.10 g, 0.289 mmol) was dissolved in a mixture of CF_3COOH and H_2O (95:5, 3.50 ml). The reaction mixture was stirred at room temperature for 20 min and then concentrated under reduced pressure. The residue was diluted with diethyl ether (7 ml) and washed with saturated aqueous $NaHCO_3$ (3.50 ml). The organic phase was dried (Na_2SO_4), the solvent was evaporated and the resulting crude product purified by flash chromatography on silica gel (cyclohexane–ethyl acetate, 1:2) to provide 0.062 g (87%) of **13** as a white solid, m.p. 76–78 °C, $[\alpha]_D^{25}$ +29.4 (*c* 0.15, $CHCl_3$). For $C_{14}H_{18}N_2O_2$ (246.3) calculated: 68.27% C, 7.37% H, 11.37% N; found: 68.43% C, 7.56% H, 11.14% N. ^{1}H NMR (400 MHz, $CDCl_3$): 1.85 m, 2 H (H-8′); 3.56 m, 3 H (H-4′, H-9′); 3.85 dd, 1 H, *J*(5′,4′) = 7.3, *J*(6′,5′) = 7.3 (H-5′); 4.47 d, 1 H, *J* = 12.7 (CH_2Ph); 4.50 d, 1 H, *J* = 12.7 (CH_2Ph); 5.09 bs, 1 H (NH); 5.16 dd, 1 H, *J*(7′*cis*,6′) = 10.1, *J*(7′*cis*,7′*trans*) = 0.9 (H-7′*cis*); 5.24 dd, 1 H, *J*(7′*trans*,6′) = 17.1, *J*(7′*cis*,7′*trans*) = 0.9 (H-7′*trans*); 5.25 bs, 1 H (NH); 5.82 ddd, 1 H, *J*(7′*trans*,6′) = 17.1, *J*(7′*cis*,6′) = 10.1, *J*(6′,5′) = 7.3 (H-6′); 7.24–7.36 m, 5 H (Ph). ^{13}C NMR (100 MHz, $CDCl_3$): 34.3 (C-8′); 57.9 (C-5′); 62.1 (C-4′); 67.8 (C-9′); 73.3 (CH_2Ph); 117.6 (C-7′); 127.7 (2 × C-arom.); 127.8 (C-arom.); 128.5 (2 × C-arom.); 137.0 (C-6′); 137.9 (C-arom.); 162.6 (C=O).

(3*R*,4*R*)-3,4-Diacetamidohex-5-en-1-yl Acetate (**15**)

Compound **12** (0.41 g, 1.183 mmol) was dissolved in 6 M HCl (20 ml) and the solution was heated under reflux for 6 h in nitrogen atmosphere. The solvent was removed under reduced pressure, the resulting solid was diluted with pyridine (2 ml) and Ac_2O (0.9 ml, 9.54 mmol) was added. The reaction mixture was stirred at room temperature overnight, the solvent was evaporated and the residue chromatographed on silica gel (dichloromethane–methanol, 95:5) to give 0.23 g (76%) of **15** as a white solid, m.p. 101–102 °C, $[\alpha]_D^{25}$ +30.3 (*c* 0.165, $CHCl_3$). For $C_{12}H_{20}N_2O_4$ (256.3) calculated: 56.24% C, 7.87% H, 10.93% N; found: 56.40% C, 7.56% H, 11.04% N. ^{1}H NMR (400 MHz, $CDCl_3$): 1.98 s, 3 H (CH_3); 1.99 s, 3 H (CH_3); 2.05 s, 3 H (CH_3); 1.74 m, 1 H (H-2′); 2.02 m, 1 H (H-2′); 4.03 m, 1 H (H-3′); 4.13 m, 2 H (H-1′); 4.41 ddd, 1 H, *J*(4′,NH) = 8.4, *J*(4′,3′) = 7.6, *J*(5′,4′) = 7.0 (H-4′); 5.24 dd, 1 H, *J*(6′*cis*,5′) = 10.1, *J*(6′*cis*,6′*trans*) = 0.5 (H-6′*cis*); 5.29 dd, 1 H, *J*(6′*trans*,5′) = 17.1, *J*(6′*cis*,6′*trans*) = 0.5 (H-6′*trans*); 5.76 ddd, 1 H, *J*(6′*trans*,5′) = 17.1, *J*(6′*cis*,5′) = 10.1, *J*(5′,4′) = 7.0 (H-5′); 6.77 d, 1 H, *J*(3′,NH) = 8.9 (NH); 6.93 d, 1 H, *J*(4′,NH) = 8.4 (NH). ^{13}C NMR (100 MHz, $CDCl_3$): 20.9 (CH_3); 23.0 (CH_3); 23.1 (CH_3); 30.5 (C-2′); 50.2 (C-3′); 56.4 (C-4′); 61.2 (C-1′); 118.1 (C-6′); 134.9 (C-5′); 170.4 (C=O); 171.0 (C=O); 171.5 (C=O).

(2*S*,3*R*)-2,3-Diacetamido-5-acetoxypentanoic Acid (**17**)

To a suspension of **15** (0.10 g, 0.39 mmol) in CCl_4–MeCN–H_2O (1:1:1, 15 ml) were added $NaIO_4$ (0.42 g, 2.10 mmol) and $RuCl_3 \cdot H_2O$ (1 mg). The reaction mixture was stirred at room temperature for 3 h, and the solid was removed by filtration. After evaporation of the sol-

vent under reduce pressure, the crude aldehyde **16** (9.59 ppm for HCO, 197.8 ppm for C=O) was used in the subsequent reaction without purification.

A solution of $NaClO_2$ (162 mg, 1.79 mmol, 80 wt.%) and $NaH_2PO_4 \cdot 2H_2O$ (205 mg, 1.31 mmol) in 1 ml of water was added dropwise to a solution of aldehyde **16** (50 mg, 0.194 mmol) in acetonitrile–*tert*-butyl alcohol–2-methylbut-2-ene (4:4:1, 4 ml) at 0 °C over 5 min and the resulting solution was stirred at the same temperature for 1 h. Then the reaction mixture was poured into brine (1 ml) and extracted with ethyl acetate (2 × 10 ml). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was chromatographed on silica gel (dichloromethane–methanol, 3:1) affording 39 mg (73%) of acid **17** as a colorless oil, $[\alpha]_D^{25}$ +36 (*c* 0.21, H_2O). For $C_{11}H_{18}N_2O_6$ (274.3) calculated: 48.17% C, 6.62% H, 10.21% N; found: 48.32% C, 6.34% H, 10.38% N. ^{1}H NMR (400 MHz, D_2O): 1.71–1.80 m, 2 H (H-4′); 1.98 s, 3 H (CH_3); 2.04 s, 3 H (CH_3); 2.07 s, 3 H (CH_3); 4.10 m, 2 H (H-5′); 4.27 m, 1 H (H-2′); 4.34 m, 1 H (H-3′). ^{13}C NMR (400 MHz, D_2O): 23.1 (CH_3); 24.7 (2 × CH_3); 32.6 (C-4′); 51.3 (C-3′); 57.1 (C-2′); 60.9 (C-5′); 169.3 (C=O); 170.9 (C=O; 171.6 (2 × C=O).

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