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Domino conversions of allyl tetronates and 4-allyloxycoumarins to all-*trans* 1,3,4,5-tetrasubstituted γ-butyrolactams

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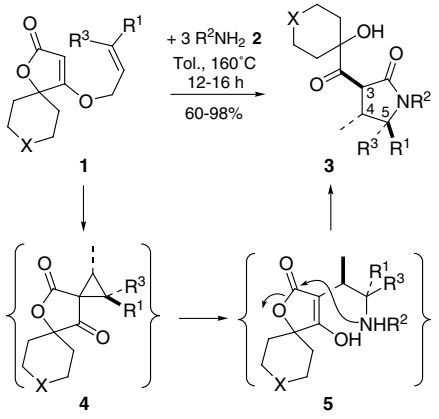
Abstract—All-*trans* 1,3,4,5-tetrasubstituted γ-butyrolactams **3** and **7** are readily available in one-pot from allyl tetronates or 4-allyloxycoumarins and amines via a four-step domino Claisen–Conia ring-opening transamidation reaction.

We have recently[1] found a thermal four-step domino conversion of an allyl tetronate **1a**[2] in the presence of allylamine into a 1,3,4,5-tetrasubstituted γ-butyrolactam **3a**. This sequence seems to be rather general for 5,5-disubstituted tetronates, which furnish in good to excellent yields predominantly, if not exclusively, the all-trans isomers. In accordance with earlier findings[1,3] for the mechanism of [2,3]-sigmatropic rearrangements of **1**, it comprises consecutive Claisen and Conia rearrangements, the opening of the intermediate spirocyclopropanes **4** by the amine to give 3-(β-amino)alkyltetronic acids **5** and a final lactone → lactam transamidation[4] to **3** (Scheme 1, Table 1). This contrasts with the reaction of similar 2-acylcyclopropane-carboxylates with amines as reported by Lhommet and co-workers where the amine group in the intermediates analogous to **5** reacts with the keto/enol rather than the ester carbonyl moiety yielding 3-alkoxycarbonyldihydropyrrols.[5] Ring-opening of **4** takes place selectively at the carbon atom bearing residues R^1 larger than C_2H_5 (e.g., **4e**). Only for $R^1 = C_2H_5$ were mixtures of tetrasubstituted lactams found, which result from attack of the amine on both tertiary carbon atoms of the 3-ring. This and the formation of the 4,5-*trans* configured lactams **3** suggest that the amine attacks **4** at a relatively advanced stage of ring-opening with a good deal of carbenium ion character of the carbon atom bearing R^1. Reacting stable derivatives of **4** with amines at room temperature normally furnishes the syn diastereomers of **5**.[1]



Scheme 1. Four-step domino synthesis of all-*trans*-γ-lactams **3** from allyl tetronates **1** and amines **2**.

Bohlmann et al.[7] reported that 4-allyloxycoumarins like **6** when heated in *N*,*N*-diethylaniline also undergo [2,3]-rearrangements via spirocyclopropanes followed by ring-closure to give furocoumarins at sufficiently high temperatures. Hence, reaction of **6** with amines should produce 3-(*o*-hydroxy)phenacyllactams **7** in analogy to the synthesis of **3** from **1**. While the reaction of **6** with butyl- and benzylamine in toluene at 160 °C actually led to the formation of the expected lactams **7**,[8] *exo*-benzylidenelactam **10a**[9] was found upon reaction of **6a** ($R^1 = R^3 = Me$) with an excess of allylamine. This can be rationalized by assuming a cascade extended by three steps: formation of an *N*-allylimine **8**, tautomerization of the latter to give **9** and an eventual β-elimination of a vinylimine to leave *E*-configured product **10** (Scheme 2, Table 2).

Keywords: Domino reactions; Lactams; Rearrangements; Tetronates; Coumarins; Microwaves.
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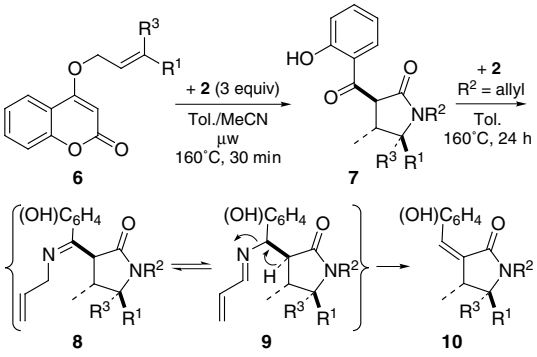
Table 1. γ-Lactams **3**[6] from allyl tetronates **1** and amines **2**

	R^1	R^2	R^3	X	Yield (%)
3a	Ph	$CH_2CH{=}CH_2$	H	CH_2	94
3b	Ph	*i*-Bu	H	CH_2	72[a]
3c	Ph	Bu	H	CH_2	84
3d	Ph	$CH_2CH{=}CH_2$	H	O	71
3e	Pr	Bu	H	CH_2	65[a]
3f	CH_3	$CH_2(CH_2)_2OC_2H_5$	CH_3	CH_2	89

[a] Containing 10% of the 3,4-*cis* isomer as to NMR.



Scheme 2. γ-Lactams **7/10** from 4-allyloxycoumarins **6** and amines **2**.

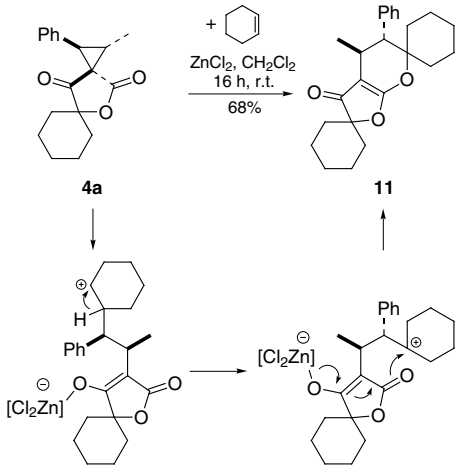
Table 2. γ-Lactams **7/10** from 4-allyloxycoumarins **6** and amines **2**

	R^1	R^2	R^3	Yield (%)
7a	Me	CH_2 $CH{=}CH_2$	Me	58[a]
7b	Ph	$CH_2CH{=}CH_2$	H	53[a]
7c	Me	Bn	Me	51[a]
7d	Me	Bu	Me	62[a]
7e	Ph	Bu	H	60[a]
10a	Me	$CH_2CH{=}CH_2$	Me	40[b]

[a] PhMe/MeCN (9:1), microwave, 160 °C, 30 min.
[b] PhMe, 160 °C, 24 h.

Better stabilization of positive partial charges next to the phenyl ring in **7/9** when compared to the saturated six-membered ring in **3** explains the different outcome in the tetronate and coumarin series. However, lactams **7** were obtained in every case, including derivatives with R^2 = allyl, when the reaction was carried out in toluene/acetonitrile under microwave irradiation at 160 °C for 30 min. These conditions strongly favour the initial pericyclic steps over imine formation and elimination.[10]

Only amines seem capable of attacking both the 3-ring and the lactone ring of intermediates **4** and **5** in a nucleophilic manner. In contrast, reaction of diastereopure 3-spirocyclopropyl-dihydrofurane-2,4-dione **4a**[3] with the soft nucleophile cyclohexene under $ZnCl_2$ catalysis furnished the furo[2,3-*b*]-pyran-3-one **11** as the sole product of a formal [5+1] cycloaddition in 68% yield.[11] Mechanistically, we assume an initial 'electrophilically assisted' ring-opening of **4a** by the alkene attacking the phenyl-bearing cationoid carbon atom. The resulting secondary cation rearranges to a tertiary one, which gets eventually trapped by the ester enolate oxygen atom producing **11** with the trans configuration of residues Me and Ph preserved ($^3J_{HH}$ = 11.2 Hz). Interestingly, tertiary alcohols as conceivable products of a Prins-type reaction of cyclohexene with the keto carbonyl group of **4a** were not observed (Scheme 3).



Scheme 3. Furo[2,3-*b*]pyran-3-one **11** from tandem ring-opening/recyclization of **4a** with cyclohexene.

In summation, a regio- and stereoselective one-pot synthesis of densely substituted γ-butyrolactams from 5, 5-disubstituted allyl tetronates or from 4-allyloxycoumarins has been developed.

Acknowledgement

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6. Lactams **3**[12] and **10a**—general procedure: A mixture of **1** or **6a** (1.0 mmol), amine **2**(3–5 mmol) and dry toluene (5 mL) in a sealed glass tube was heated in an oil bath at 160 °C (12–16 h for **3**, 24 h for **10a**). After cooling all volatiles were removed on a rotary evaporator and the residue was purified by column chromatography (silica gel 60; diethyl ether/hexane, 1:1, v/v). 1-Isobutyl-3-[(1′-hydroxy-cyclohexyl)carbonyl]-4-methyl-5-phenylpyrrolidin-2-one (**3b**): colourless oil; ν_{max} (neat)/cm^{-1} 3324, 2930, 1715, 1661; ^{1}H NMR ($CDCl_3$): δ 0.70 and 0.76 (each 3H, d, J = 6.7 Hz), 0.97 (3H, d, J = 6.7 Hz, 4-Me), 1.15–1.84 (11H, m), 2.35 (1H, dd, J = 13.6, 5.6 Hz, NC*H*H), 2.82 (1H, ddq, J = 10.0, 8.5, 6.7 Hz, 4-H), 3.29 (1H, dd, J = 13.6, 9.6 Hz, NCH*H*), 4.08 (1H, d, J = 8.5 Hz, 5-H), 4.26 (1H, d, J = 10.0 Hz, 3-H), 5.78 (1H, d, J = 2.0 Hz, OH), 7.18–7.35 (5H, m, Ph); ^{13}C NMR ($CDCl_3$): δ 16.5, 19.8, 20.3, 20.8, 20.9, 25.4, 26.1, 33.7, 34.0, 38.3, 48.5, 58.4, 69.1, 79.0, 127.5, 128.4, 128.9, 138.2, 172.3, 210.5; *m*/*z* (EI) 357 (M$^+$, 0.1%), 339 (4%), 314 (2%), 296 (3%), 231 (100%). Compound **3c**: colourless oil; ν_{max} (neat)/cm^{-1} 3324, 2932, 1714, 1664; ^{1}H NMR ($CDCl_3$): δ 0.84 (3H, t, J = 7.2 Hz), 1.02 (3H, d, J = 6.7 Hz, 4-Me), 1.14–1.87 (14H, m), 2.56 (1H, dt, J = 13.7, 6.8 Hz, NC*H*H), 2.78–2.91 (1H, m, 4-H), 3.56 (1H, dt, J = 13.7, 7.9 Hz, NCH*H*), 4.11 (1H, d, J = 8.4 Hz, 5-H), 4.26 (1H, d, J = 10.1 Hz, 3-H), 5.81 (1H, d, J = 1.9 Hz, OH), 7.25–8.00 (5H, m, Ph); ^{13}C NMR ($CDCl_3$): δ 13.6, 16.3, 19.9, 20.7, 20.8, 25.3, 28.7, 33.9, 34.0, 38.1, 41.0, 58.5, 68.7, 79.1, 127.7, 128.6, 128.8, 128.9, 138.2, 172.0, 210.5; *m*/*z* (EI) 358 (1%), 357 (0.2%), 231 (100%). Compound **3d**: white solid, mp 85 °C; ν_{max} (KBr)/cm^{-1} 3402, 2961, 1717, 1661; ^{1}H NMR ($CDCl_3$): δ 1.00 (3H, d, J = 6.7 Hz, 4-Me), 1.45–1.59 and 2.12–2.24 (4H, m), 2.86 (1H, ddq, J = 10.1, 8.4, 6.7 Hz, 4-H), 3.05 (1H, dd, J = 15.0, 7.6 Hz, NCH*H*), 3.76–3.92 (4H, m), 4.11 (1H, d, J = 8.4 Hz, 5-H), 4.18 (1H, ddt, J = 15.0, 4.9, 1.5 Hz, NC*H*H), 4.21 (1H, d, J = 10.1 Hz, 3-H), 4.89 (1H, d, J = 17.1 Hz, =CHH_{trans}), 5.10 (1H, d, J = 10.1 Hz, =CHH_{cis}), 5.51–5.64 (1H, m, C*H*=CH$_2$), 6.00 (1H, d, J = 2.3 Hz, OH), 7.18–7.38 (5H, m, Ph); ^{13}C NMR ($CDCl_3$): δ 16.2, 34.0, 34.3, 37.8, 43.9, 58.6, 62.5, 62.9, 68.3, 76.5, 119.1, 127.5, 127.8, 128.0, 130.7, 137.7, 171.7, 208.5; *m*/*z* (EI) 344 (4%), 343 (M$^+$, 1%), 315 (4%), 242 (6%), 216 (24%), 215 (100%). Compound **3e**: clear oil; ν_{max} (KBr)/cm^{-1} 3317, 2931, 1713, 1659; ^{1} H NMR ($CDCl_3$): δ 0.78–0.85 (6H, m, 2 Me), 1.00 (3H, d, J = 6.9 Hz, 4-Me), 1.05–1.80 (18H, m), 2.62 (1H, ddq, J = 8.4, 8.2, 6.9 Hz, 4-H), 2.80–2.85 (1H, m, NC*H*H), 3.07–3.12 (1H, m, 5-H), 3.41–3.50 (1H, m, NCH*H*), 4.21 (1H, d, J = 8.2 Hz, 3-H), 5.95 (1H, s, OH); ^{13}C NMR ($CDCl_3$): δ 13.6, 14.0, 19.1, 20.0, 20.5, 20.7, 20.8, 25.3, 33.9, 34.25, 34.3, 36.1, 39.7, 40.3, 58.3, 59.4, 63.6, 79.1, 79.2, 170.9, 210.8; *m*/*z* (EI) 324 (1%), 323 (M$^+$, 1%), 197 (74%), 155 (17%), 154 (100%). Compound **3f**: colourless oil; ν_{max} (KBr)/cm^{-1} 3307, 2932, 2859, 1714; ^{1} H NMR ($CDCl_3$): δ 0.88 (3H, d, J = 6.9 Hz, 4-Me), 1.02 (3H, s, 5-Me), 1.14 (3H, t, J = 7.0 Hz, OCMe), 1.26 (3H, s, 5-Me), 1.36–1.82 (10H, m), 2.56 (1H, dq, J = 11.4, 6.9 Hz, 4-H), 3.01–3.11 (1H, m, NC*H*H), 3.24–3.34 (1H, m, NCH*H*), 3.35–3.44 (4H, m, OCH$_2$), 4.04 (1H, d, J = 11.4 Hz, 3-H), 5.80 (1H, d, J = 2.1 Hz, OH); ^{13}C NMR ($CDCl_3$): δ 12.7, 15.3, 20.9, 21.0, 21.1, 25.6, 26.2, 29.7, 34.0, 34.1, 38.3, 39.5, 56.9, 63.0, 66.4, 68.2, 79.2, 171.5, 211.2; *m*/*z* (EI) 340 (3%), 339 (M$^+$, 0.1%), 294 (5%), 214 (32%), 213 (100%).

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8. Lactams **7**[12]—general procedure: A sealed glass vial containing coumarin **6** (1.0 mmol), amine **2** (3–5 mmol), dry toluene (5 mL) and acetonitrile (0.5 mL) was irradiated in a CEM Discover™ single-mode microwave synthesizer at 160 °C for 30 min. Work-up as described above for lactams **3**. Compound **7a**: yellow oil; ν_{max} (KBr)/cm^{-1} 3335, 2970, 1682, 1630; ^{1} H NMR ($CDCl_3$): δ 1.05 (3H, d, J = 6.9 Hz, 4-Me), 1.10 and 1.30 (6H, s each, 5-Me), 2.80 (1H, dq, J = 11.2, 6.9 Hz, 4-H), 3.70 (1H, ddt, J = 15.7, 5.7, 1.4 Hz, NCH), 3.95 (1H, ddt, J = 15.7, 6.2, 1.4 Hz, NCH), 4.10 (1H, d, J = 11.2 Hz, H-3), 5.10 (1H, dq, J = 10.2, 1.4 Hz, =CHH_{cis}), 5.20 (1H, dq, J = 17.1, 1.4 Hz, =CHH_{trans}), 5.8 (1H, m, =CH), 6.9–7.9 (4H, m, H-ar), 12.2 (1H, s, OH); ^{13}C NMR ($CDCl_3$): δ 12.7, 21.0, 22.1, 42.5, 42.6, 55.4, 61.7, 116.8, 118.1, 118.9, 120.4, 131.9, 134.0, 136.7, 162.8, 168.8, 201.5; *m*/*z* (EI) 288 (18%), 287 (94%), 272 (53%), 121 (100%). Compound **7b**: yellow oil; ν_{max} (KBr)/cm^{-1} 3338, 1689, 1631; ^{1}H NMR ($CDCl_3$): δ 1.10 (3H, d, J = 6.7 Hz, 4-Me), 3.0–3.1 (1H, m, 4-H), 3.10–3.15 (1H, m, NC*H*H), 4.20 (1H, d, J = 8.0 Hz, 5-H), 4.30 (1H, d, J = 9.5 Hz, 3-H), 4.30–4.35 (1H, m, NCH*H*), 4.90 (1H, dq, J = 17.1, 1.4 Hz, =CHH_{trans}), 5.15 (1H, dq, J = 10.2, 1.4 Hz, =CHH_{cis}), 5.6–5.7 (1H, m, =CH), 7.0–7.9 (9H, m, H-ar), 12.25 (1H, s, OH); ^{13}C NMR ($CDCl_3$): δ 12.6, 40.4, 43.9, 57.4, 67.8, 118.3, 118.8, 119.0, 120.1, 127.8, 128.6, 128.9, 131.2, 131.9, 136.9, 138.2, 163.0, 169.8, 201.2; *m*/*z* (EI) 336 (22%), 335 (94%), 214 (100%). Compound **7c**: yellow oil; ν_{max} (KBr)/cm^{-1} 3353, 1682, 1631; ^{1}H NMR ($CDCl_3$): δ 1.00 (3H, d, J = 6.9 Hz, 4-Me), 1.05 (3H, s, 5-Me), 1.20 (3H, s, 5-Me), 2.80–2.85 (1H, m, 4-H), 4.20 (1H, d, J = 11.3 Hz, 3-H), 4.30 (1H, d, J = 15.4 Hz, NCH), 4.60 (1H, d, J = 15.4 Hz, NCH), 7.0–7.9 (9H, m, H-ar), 12.20 (1H, s, OH); ^{13}C NMR ($CDCl_3$): δ 12.9, 21.1, 26.3, 42.3, 43.8, 55.8, 62.3, 118.3, 119.0, 120.4, 127.3, 127.4, 128.5, 131.9, 136.8, 138.3, 163.2, 169.8, 201.8; *m*/*z* (EI) 338 (20%), 337 (86%), 322 (40%), 91 (100%). Compound **7d**: yellow oil; ν_{max}(KBr)/cm^{-1} 1681, 1631; ^{1}H NMR ($CDCl_3$): δ 0.90 (3H, t, J = 7.3 Hz, Me), 1.05 (3H, d, J = 6.9 Hz, 4-Me), 1.10 (3H, s, 5-Me), 1.20–1.40 (2H, m), 1.30 (3H, s, 5-Me), 1.40–1.60 (2H, m), 2.80 (1H, dq, J = 11.2, 6.9 Hz, 4-H), 2.95 (1H, ddd, J = 13.7, 9.9, 5.6 Hz, NCH), 3.30 (1H, ddd, J = 13.7, 9.9, 5.9 Hz, NCH), 4.10 (1H, d, J = 11.2 Hz, 3-H), 6.9–7.9 (4H, m, H-ar), 12.20 (1H, s, OH); ^{13}C NMR ($CDCl_3$): δ 12.8, 13.7, 20.4, 20.8, 26.1, 31.7, 40.3, 41.4, 55.7, 61.6, 118.1, 118.9, 120.4, 132.0, 136.7, 162.8, 169.0, 201.5; *m*/*z* (EI) 304 (6%), 303 (21%), 182 (47%), 212 (100%). Compound **7e**: yellow oil; ν_{max} (KBr)/cm^{-1} 3304, 2960, 1689, 1631; ^{1}H NMR ($CDCl_3$): δ 0.80 (3H, t, J = 7.3 Hz, Me), 1.10 (3H, d, J = 10.1 Hz, 4-Me), 1.10–1.20 (2H, m), 1.30–1.50 (2H, m), 2.65 (1H, mc, NCH*H*), 2.90–2.95 (1H, m, 4-H), 3.70 (1H, m, NC*H*H), 4.10 (1H, d, J = 8.0 Hz, 5-H), 4.20 (1H, d, J = 9.6 Hz, 3-H), 6.90–7.90 (9H, m, H-ar), 12.10 (1H, s, OH); ^{13}C NMR ($CDCl_3$): δ 13.6, 16.8, 20.0, 28.8, 40.5, 41.0, 57.5, 68.2, 118.3, 119.0, 120.2, 127.7, 131.9, 136.9, 138.5, 162.9, 169.8, 201.3; *m*/*z* (EI) 352 (68%), 351 (98%), 336 (97%), 230 (100%).

9. *exo*-Assignment by NOE experiments. Compound **10a**: yellow oil; ν_{max} (KBr)/cm^{-1} 3265, 2970, 1770, 1643; ^{1}H NMR ($CDCl_3$): δ 1.00 and 1.30 (6H, s each, 5-Me), 1.20 (3H, d, J = 6.9 Hz, 4-Me), 2.80 (1H, dq, J = 2.7, 6.9 Hz, 4-H), 3.90 (1H, ddt, J = 1.5, 5.8, 15.6 Hz, NCH), 4.05 (1H, ddt, J = 1.5, 6.1, 15.6 Hz, NCH′), 5.15 (1H, dq, J = 1.5, 10.2 Hz, =CHH_{cis}), 5.20 (1H, dq, J = 1.5, 17.2 Hz, =CHH_{trans}), 5.8–5.9 (1H, m, H$_2$C=C*H*), 6.55 (1H, d, J = 2.7 Hz, =CH), 6.8–7.2 (5H, m, H-ar, OH); ^{13}C NMR ($CDCl_3$): δ 12.7, 21.3, 26.0, 42.5, 46.9, 62.4, 117.3, 120.1, 121.5, 125.2, 129.5, 130.3, 132.9, 133.6, 133.7, 155.7, 169.4; MS (70 eV), *m*/*z* (EI) 272 (16%), 271 (77%), 257 (17%), 256 (100%).

10. Schobert, R.; Gordon, G. J.; Mullen, G.; Stehle, R. *Tetrahedron Lett.* **2004**, *45*, 1121.
11. Compound **11**: A solution of **4a**[3] (200 mg, 0.70 mmol) in dry CH_2Cl_2 (15 mL) was chilled to 0 °C and treated via syringe first with a 45% solution of $ZnCl_2$ in diethyl ether (163 μL, 0.70 mmol) and finally with cyclohexene (72 μL, 58 mg, 0.70 mmol). After stirring the mixture for 16 h at room temperature, all volatiles were removed in vacuo and the remainder was purified by column chromatography (silica gel 60; diethyl ether/cyclohexane, 1:2, v/v; R_f 0.37). Yield: 162 mg (58%) of colourless crystalline **11**, mp 170 °C. (Found: C, 78.84; H, 8.36. $C_{24}H_{30}O_3$ requires C, 78.65; H, 8.25.) ν_{max} (KBr)/cm^{-1} 2934, 2858, 1694, 1593, 1442; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (3H, d, ^3J = 6.6 Hz), 1.40–1.82 (20H, m), 2.48 (1H, d, ^3J = 11.3 Hz), 2.97 (1H, dq, ^3J = 11.3, 6.6 Hz), 7.14–7.29 (5H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 16.3 (Me), 20.9, 21.0, 21.7, 21.8, 24.4, 24.9, 26.7 (Me–*C*), 27.7, 31.5, 31.9, 35.6, 58.4 (Ph–*C*), 88.4, 89.9, 91.6, 127.4, 128.3, 128.4, 130.0, 138.1, 178.8, 199.1; *m*/*z* (EI) 367 (M$^+$, 2%), 196 (11), 177 (25), 172 (100).
12. All new compounds gave satisfactory microanalyses to an accuracy of C ± 0.15%, H ± 0.10% and N ± 0.05%. The stereochemistry was determined from coupling constants and correlation of these with earlier X-ray structure analytical data.[1]