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Regioselective Photochemical Rearrangement of *N*-Mesyloxylactams

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N-Mesyloxylactams can undergo ring contraction either by C-3 (usually observed) or C-5 migration. C-5 migration can occur when the C-3 migration product possesses ring strain, but it does not usually compete with C-3 migration. The greater preference for C-3 migration is due to the carbonyl oxygen atom, which greatly stabilizes the intermediate.

Introduction

The Lossen rearrangement is a well-known reaction that permits the formation of a C–N bond by the stereospecific migration of a C–C bond.[1] There are a number of known rearrangements of this type, which include the Schmidt,[2] Hofmann[3] and Curtius[4] rearrangements (Figure 1).[5] Many use basic or acidic reaction conditions to convert a carboxylic acid derivative into an isocyanate, which then reacts with a nucleophile to give an amide derivative.

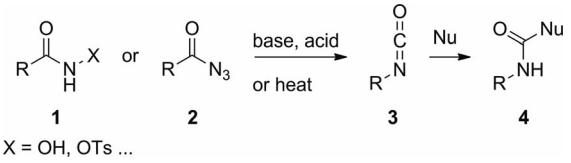


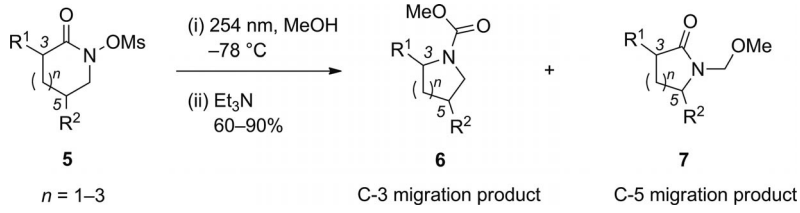
Figure 1. Lossen, Schmidt, Hofmann and Curtius rearrangements.

We recently published the photochemical ring contraction of five–eight-membered *N*-mesyloxylactams,[6,7c] the only rearrangement of this type that works on secondary amide derivatives (Scheme 1).[8] Rigid bicyclic lactam derivatives also underwent this ring contraction efficiently. The very mild reaction conditions (254 nm light, MeOH, –78 °C) and the conservation of stereochemistry at the migrating carbon atom make this unique rearrangement a valuable tool for chemists in the field of C–N bond formation in cyclic substrates.

N-Mesyloxylactams possess two C–C bonds normally aligned with the leaving group that permit two different migration pathways that potentially lead to the C-3 migration product **6** and/or the C-5 migration product **7** (cf. Scheme 1). Edwards and co-workers observed a fair amount of C-5 migration product **10** when they irradiated steroid derivatives **8a**,**b** (Scheme 2).[6] Yet, the formation of products that arise from C-5 migration was not encountered in the course of our study of the photochemical rearrangement of *N*-mesyloxylactams[7c] or *N*-chlorolactams[7a,7b] (cf. Scheme 1). This inconsistency compelled us to investigate factors that control the regiochemistry of migration in order to better predict when such products are likely to arise.

Results and Discussion

We started by irradiating smaller bicyclic *N*-mesyloxylactams that resembled Edwards' steroidal compounds (Table 1, Entries 1–4). We found that octahydroquinoline derivatives **13a** and **13b** gave a substantial amount of C-5 migration products **15** along with the "normal" C-3 migration products **14a** and **14b**, respectively, in good combined yields (Entries 1 and 2). Similarly, the irradiation of octahydroquinoline derivatives **16a** or **16b** gave mixtures of bicyclic products **17a** and **18** or **17b** and **18**, respectively (Entries 3 and 4). Products **15** and **18** have the same stereochemistry at the aminal carbon atom regardless of their



Scheme 1. Photochemical ring contraction of *N*-mesyloxylactams **5**.

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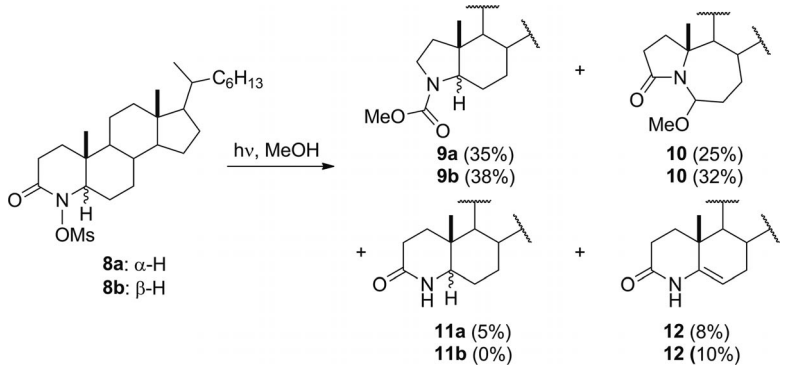
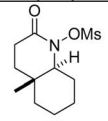
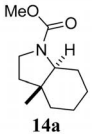
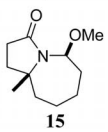
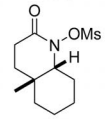
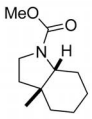
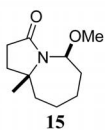
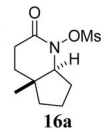
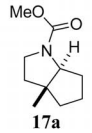
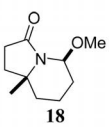
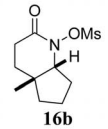
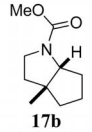
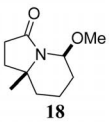
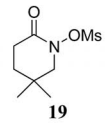
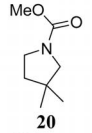
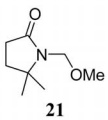
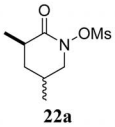
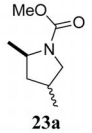
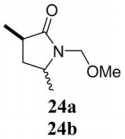
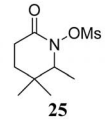
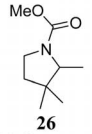
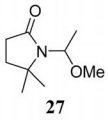
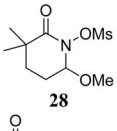
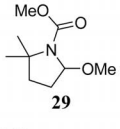
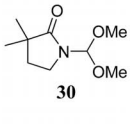
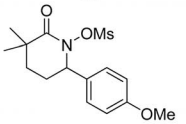
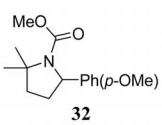
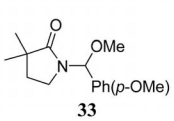


Scheme 2. Examples of the C-5 migration in steroid derivatives.

Table 1. Photochemical ring contractions of *N*-mesyloxylactams.[a]

Entry	*N*-Mesyloxylcatam	C-3 product	C-5 product	C-3/C-5 ratio	Yield[b]
1	 **13a**	 **14a**	 **15**	1:1	74%
2	 **13b**	 **14b**	 **15**	3:1	68%
3	 **16a**	 **17a**	 **18**	1:3	73%
4	 **16b**	 **17b**	 **18**	3:1	67%
5	 **19**	 **20**	 **21**	100:0	50%
6	 **22a** **22b**	 **23a** **23b**	 **24a** **24b**	α: 100:0 β: 100:0	67% 52%
7	 **25**	 **26**	 **27**	4:1	61%
8	 **28**	 **29**	 **30**	–	39–46%[c]
9	 **31**	 **32**	 **33**	4:1	60%[d]

[a] Reaction conditions: (i) MeOH, 254 nm, –78 °C; (ii) Et_3N. [b] Combined isolated yields of C-3 and C-5 migration products. [c] Isolated yields of C-3 migration products from three trials. [d] Isolated yield of **32** and **33**. Compound **36** was isolated as a mixture with **33** and, from the analysis of the NMR spectrum of the isolated products, we determined that the yield of **33** was 13% and that of **36** was 30%.

provenance. Presumably, it is derived from a stereoselective attack of methanol on the corresponding *N*-acyliminium ion.

We observed a clear decrease in the C-3/C-5 product ratio when the *trans*-fused *N*-mesyloxylactams **13a** and **16a** were irradiated as opposed to the analogous *cis*-fused *N*-mesyloxylactams **13b** and **16b** (compare Entry 1 with 2 and Entry 3 with 4). This decrease can be explained by the strain in the final products. The *trans*-fused 5,6-bicyclic compound **14a** and 5,5-bicyclic compound **17a** are more strained than their *cis*-fused counterparts **14b** and **17b**, respectively. With the C-5 migration product **15** or **18**, which are the same whether one starts with *cis*- or *trans*-fused *N*-mesyloxylactams, it is expected that the more strained products **14a** and **17a** will be formed in lower amounts than **14b** and **17b**, respectively. Nonetheless, the formation of **17a** in 19% isolated yield is noteworthy as *trans*-fused bicyclo[3.3.0] systems are very strained[9] and normally very difficult to prepare.[10]

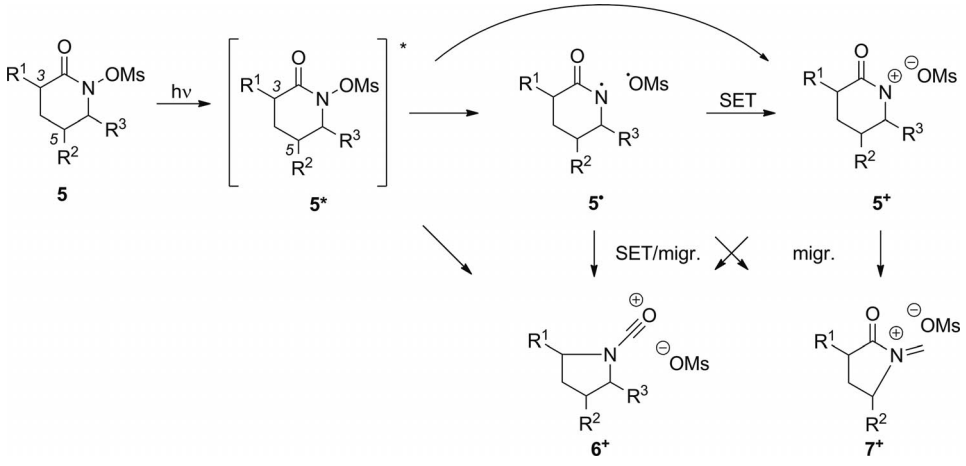
The fact that *N*-mesyloxylactams **13a**–**b** and **16a**–**b** bear no substituents α to the carbonyl group is no accident. We have previously shown that the yield of the C-3-rearranged product **6** increased with increasing substitution at C-3 (cf. Scheme 1). Substrates with no α-substituents typically gave 35–50% yield of rearranged products, whereas substrates with one or two substituents α to the carbonyl group gave 70–90% yield of products.[7b] In all of the examples in our previous studies, the C-5 position was occupied by a methylene group, and no trace of the corresponding C-5 migration product was ever observed.

We know from previous experiments that the rearrangement is not radical in nature.[7b] Although the radical species **5**$^{\cdot}$ is possibly formed from the activated complex **5***,[11] the stereospecificity of the migration precludes radical intermediates during migration. However, it is not certain that a true *N*-acylnitrenium ion **5**$^{+}$ is formed from **5*** or **5**$^{\cdot}$, as these species are known to be high-energy cations (Scheme 3).[12] An alternative is that migration occurs either directly from **5*** by heterolytic cleavage of the N–O bond or via **5**$^{\cdot}$ by a concomitant single electron transfer from N to O. This difficult assessment is compounded by the fact that we do not know if all or any of these species (except **5***) is in a photochemically or vibrationally excited state. Very little is known about the photochemistry of *N*-chlorolactams, and nothing is known of that of their *N*-mesyloxy analogs; however, it is beyond the scope of this article to address photochemical issues.[13]

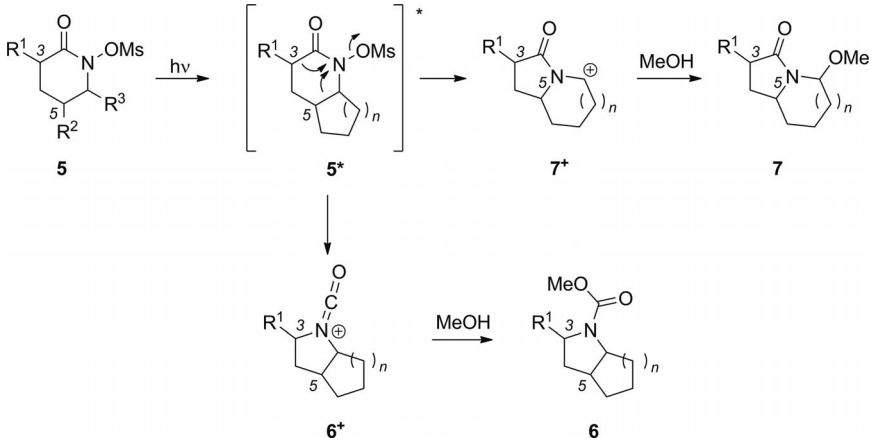
Experimental results unequivocally show that the migration of C-3 is greatly favoured when there is no built-in bias for the C-5 migration to occur (Table 1, Entries 5 and 6 and many examples in ref.[7b]). Thus, the C-5 position in bicyclic *N*-mesyloxylactams **13** and **16** and in Edwards' steroidal substrates must have benefited somewhat from a higher substitution at the migrating carbon atom. In the case of *trans*-fused **13a** and **16a**, this was combined with the developing strain in the C-3 migration products **14a** and **17a** to increase substantially the amount of C-5 migration product formed (**6**$^{+}$ vs. **7**$^{+}$ in Scheme 4).

Entries 5 and 6 of Table 1 lend some support to these affirmations. Substitution alone is not enough to explain the observed C-3/C-5 product ratio as indicated by the absence of products **21** and **24a**,**b**. Yet, if C-6 is substituted such that a secondary carbocation is formed at that position upon C-5 migration, then the formation of product **27** is increased (Entry 7). In accordance with our above assertion on the development of strain in bicyclic products, *N*-mesyloxylactam **25**, which is not constrained by the presence of a second ring, produced less of the C-5 migration product **27** upon irradiation than its bicyclic homologues **13** and **16**.

If the stability of the developing carbocation were the controlling element in C-3 vs. C-5 migration, we ought to be able to substitute the C-6 position with a heteroatom to favour the migration of C-5. *N*-Mesyloxyimides do not undergo the photolytic ring contraction, presumably because of the inherently high energy associated with a developing biacylnitrenium ion. We therefore prepared *N*-mesyloxylactam **28** substituted with a methoxy group at C-6 (Entry 8). Despite the fact that **29** was difficult to isolate (it was partly converted during the reaction to **34** and **35**), we were able to determine that 39–46% of the products iso-



Scheme 3. Mechanistic pathways of the photochemical rearrangement.



Scheme 4. C-3 and C-5 migration pathways.

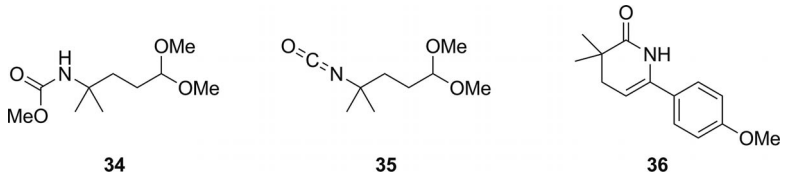


Figure 2. Side products formed during the photolysis of *N*-mesyloxylactams **28** and **31**.

lated had undergone a C-3 migration (cf. **34** and **35** in Figure 2). We did not observe **30** in the crude mixture, but it is possible that it was too unstable to survive under the reaction conditions. Thus, **31** was constructed in the hope that its migration products would be more stable (Entry 9). This was indeed the case and, to our surprise, we were able to determine a 4:1 ratio of products, still in favour of the C-3-migration product **32** over the C-5-migration product **33**. Compound **36**, which resulted from the loss (or migration?) of a proton, was also formed in 30% yield (Figure 2).

There can be little doubt that *N*-acylimminium ions[14] **7b**$^+$ and **7c**$^+$ are more stable than azaacylium ion[15] **6a**$^+$ due to the neighbouring methoxy or *p*-methoxyphenyl groups (Figure 3). Yet, even in these cases, C-3 migration was favoured over C-5 migration (Entries 8 and 9, Table 1). We must therefore conclude that the stability of the developing carbocation plays a minor role in the outcome of the migration reaction. To be true, this implies that the cation character of the transition state (TS) must be weak. It becomes possible to argue that the carbonyl electron pair in **TS-6***, which is fixed and perfectly aligned with σ* of the migrating bond, assists the departure of the migrating C-3 carbon atom (Figure 3). There is no delocalization in **TS-7*** (R = H or Me), and the delocalization from the methoxy lone pair (R = OMe) or *p*-methoxyphenyl group (R = *p*-MeOPh) is less favourable from an entropy point of view, because the oxygen electron pairs are not fixed in the proper alignment. The energy difference between **TS-6*** and **TS-7*** will depend on other factors, such as the developing strain in the product and the electronics of the migrating carbon atom (i.e. its migration ability).

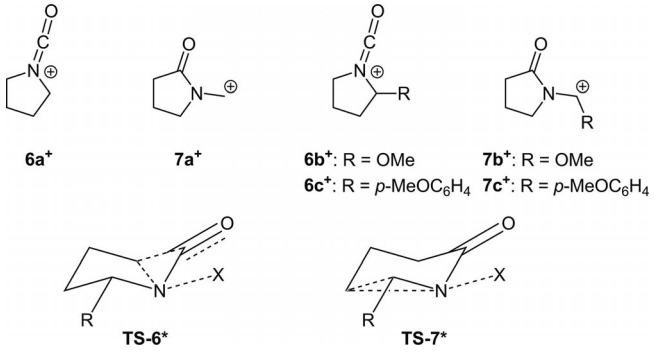
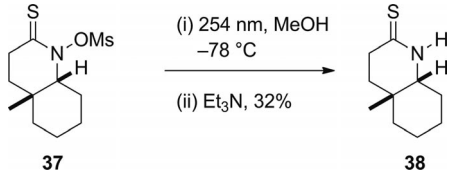


Figure 3. Carbocations and possible transition states involved in the photochemical rearrangement of *N*-mesyloxylactams.

The results discussed so far show how effective the amide carbonyl oxygen lone pair of electrons is in the promotion of the rearrangement, which provides a bias for C-3 migration. It follows that replacing the carbonyl oxygen atom or otherwise impeding its donation should remove this bias or even reverse it. Complexation of the carbonyl oxygen atom with a Lewis acid seemed like a good way to cancel its electron-donating ability. Several Lewis acids were tested in stoichiometric amounts, which included $BF_3{\cdot}Et_2O$, $Yb(OTf)_3$ and $Ti(iPrO)_4$, but, surprisingly, in no case was a significant change in ratio observed. We verified that complexation occurred by ^1H NMR spectroscopy of the starting material. This observation, coupled to the fact that all the reactions carried out in the presence of a Lewis acid were slower than usual, seemed to indicate that the rearrangement took place only on the uncomplexed substrate.

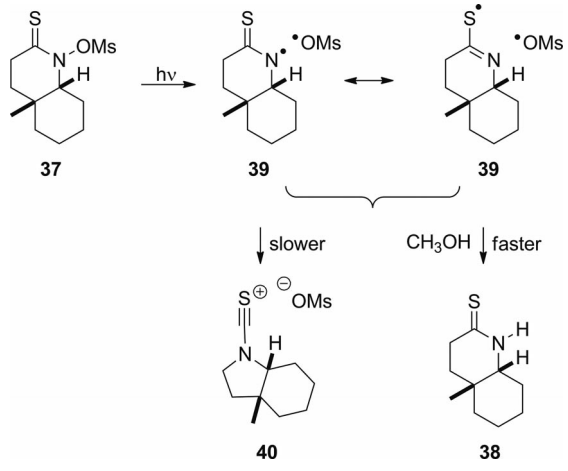
The slower reaction rate could come from a lower concentration of free carbonyl group upon the addition of a Lewis acid. The absorption band of the *N*-mesyloxyamide **13b** is blueshifted when complexed to $BF_3{\cdot}Et_2O$, which slowed the reaction.[16] However, the latter argument does not explain why the C-3 migration was still favoured.

Our next approach was to replace the carbonyl oxygen atom by a sulfur atom, for which the stabilization of a positive charge is less than that of oxygen[17] (Scheme 5). We believed that *N*-mesyloxythiolactam **37** would be able to absorb light and undergo the rearrangement. After its irradiation at 254 nm in MeOH at –78 °C, we isolated only the demesyloxythiolactam **38** in 32% yield.



Scheme 5. Irradiation of *N*-mesyloxythiolactam **37**.

Nonetheless, this surprising result gave us new insights into the reaction mechanism. Lactam **38** would be formed by hydrogen abstraction from methanol by an intermediate radical **39** if the synchronous rearrangement/SET (**39** → **40**) is not fast enough (Scheme 6). The larger energy gap between the thioamidyl radical **39** and the *N*-thioacyl ion **40** could explain this difference in the reaction rate.



Scheme 6. Proposed mechanism for the irradiation of *N*-mesyloxythiolactam **37**.

Conclusions

We have shown that C-5 migration in the photochemical ring contraction of *N*-mesyloxylactams is exceptional and does not usually compete with C-3 migration. We have shown that the carbonyl oxygen atom of the lactam is the responsible factor behind this effect. C-5 migration will occur when the C-3 migration product possesses ring strain, yet even the very strained *trans*-5–5-fused ring system was not enough to shut out C-3 migration completely. Our attempts to interfere with the carbonyl oxygen atom have not been successful so far. However, we are currently developing a series of useful substrates where proper alignment of the leaving mesyloxy group with the C-2–C-3 bond is not possible. C-5 migration in such systems should prevail, and those results will be reported in due course.

Experimental Section

General: All reactions were performed under argon in flame-dried glassware. Solvents were distilled from potassium/benzophenone ketyl (Et_2O, tetrahydrofuran), from calcium hydride (CH_2Cl_2, toluene, benzene, triethylamine) or from 4 Å molecular sieves (MeOH, DMF) prior to use. ^1H NMR spectra were recorded with a 300 or 400 MHz spectrometer. NMR samples were dissolved in $CDCl_3$ (unless specified otherwise), and chemical shifts are reported in ppm relative to the residual protic solvent. ^{13}C NMR spectra were recorded with a 75.5 or 100.7 MHz spectrometer. NMR samples were dissolved in $CDCl_3$ (unless specified otherwise), and chemical shifts are reported in ppm relative to the solvent. MS analyses were performed with a GC system spectrometer (30 m length, 25 μ OD, DB-5ms column) coupled with a mass spectrometer or with a ZAB-1F micromass spectrometer. HRMS was performed with a ZAB-1F micromass spectrometer. Reactions were monitored by TLC on 0.25 mm silica gel coated glass plates UV 254. Silica gel (230–400 mesh) was used for flash chromatography.

General Procedure for Rearrangements: Mesylated hydroxamic acid (1.00 equiv.) was dissolved in methanol (35 mL). The solution was transferred to a quartz cell, cooled to –78 °C and irradiated with 254 nm light. After irradiation at –78 °C, the reaction mixture was transferred to a round-bottomed flask, and triethylamine (1.10 equiv.) was added. After stirring at room temperature for 15 min, the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and water, the phases were separated, and the aqueous layer was extracted with dichloromethane (twice). The organic extracts were combined, dried with anhydrous magnesium sulfate, filtered and concentrated. The crude product was purified by flash chromatography on silica gel.

Methyl *trans*-3a-Methyloctahydro-1*H*-indole-1-carboxylate (14a): Carbamate **14a** was synthesized according to the general procedure. The reaction was carried out on a 1.15 mmol scale, the reaction time was 2 h, the solution was stirred at room temperature for 18 h, the eluent for the flash chromatography was a mixture of ethyl acetate and hexanes (20:80 and 50:50), and the product was obtained in 39% yield as a colourless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 3 H), 3.36 (dd, J = 10.4, 3.8 Hz, 2 H), 2.83 (dd, J = 11.8, 3.0 Hz, 1 H), 2.55 (br. s, 1 H), 1.77–1.12 (m, 9 H), 0.82 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 156.8 (s), 66.1 (d), 51.7 (q), 45.3 (t), 40.9 (s), 37.7 (t), 36.2 (t), 25.0 (t), 24.7 (t), 20.6 (t), 16.8 (q) ppm. IR (neat): $\tilde{\nu}$ = 2940, 2927, 2856, 1708, 1456, 1125, 772 cm^{-1}. MS: m/z (%) = 196 (100) $[M - H]^+$, 182 (85) $[M - Me]^+$. HRMS: calcd. for $C_{11}H_{18}NO_2$ $[M - H]^+$ 196.1337; found 196.1342.

***cis*-5-Methoxy-9a-methylhexahydro-1*H*-pyrrolo[1,2-*a*]azepin-3(2*H*)-one (15):** Lactam **15** was synthesized according to the general procedure. The reaction was carried out on a 1.15 mmol scale, the reaction time was 2 h, the solution was stirred at room temperature for 18 h, the eluent for the flash chromatography was a mixture of ethyl acetate and hexanes (25:75 and 50:50), and the product was obtained in 16% yield as a colourless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.37 (dd, J = 8.2, 6.0 Hz, 1 H), 3.21 (s, 3 H), 2.40 (dd,

J = 8.8, 7.2 Hz, 2 H), 2.06–1.92 (m, 1 H), 1.85–1.49 (m, 8 H), 1.34 (s, 3 H), 1.27–1.12 (m, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 176.1 (s), 83.0 (d), 63.9 (s), 55.8 (q), 39.5 (t), 34.9 (t), 33.7 (t), 29.8 (t), 25.8 (q), 25.0 (t), 22.7 (t) ppm. IR (neat): $\tilde{\nu}$ = 2936, 2861, 1695, 1461, 1403, 1337, 1081 cm^{-1}. MS: *m*/*z* (%) = 197 (1) $[M]^+$, 182 (50) $[M - Me]^+$, 166 (40), 98 (100). HRMS: calcd. for $C_{11}H_{19}NO_2$ $[M]^+$ 197.1416; found 197.1412. M.p. 40–44 °C.

Methyl *cis*-3a-Methyloctahydro-1*H*-indole-1-carboxylate (14b): Carbamate **14b** was synthesized according to the general procedure. The reaction was carried out on a 0.72 mmol scale, the reaction time was 2 h, the solution was stirred at room temperature for 18 h, the eluent for the flash chromatography was a mixture of ethyl acetate and hexanes (25:75 and 50:50), and the product was obtained in 46% yield as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (s, 3 H), 3.60–3.23 (m, 3 H), 2.27–1.84 (m, 2 H), 1.65–1.03 (m, 8 H), 0.98 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): Rotamer A: δ = 155.9 (s), 62.6 (d), 52.0 (q), 43.7 (t), 40.3 (s), 34.7 (t), 33.1 (t), 28.9 (t), 27.8 (q), 23.7 (t), 21.7 (t) ppm; Rotamer B: δ = 155.5 (s), 62.6 (d), 52.0 (q), 43.5 (t), 39.5 (s), 34.5 (t), 31.6 (t), 28.1 (t), 27.6 (q), 23.3 (t), 21.7 (t) ppm. IR (neat): $\tilde{\nu}$ = 2958, 2936, 2861, 1704, 1452, 1386, 1107 cm^{-1}. MS: *m*/*z* (%) = 197 (30) $[M]^+$, 182 (100) $[M - Me]^{+\cdot}$, 140 (80), 122 (30). HRMS: calcd. for $C_{11}H_{19}NO_2$ $[M]^+$ 197.1416; found 196.1418.

Methyl *trans*-3a-Methylhexahydrocyclopenta[*b*]pyrrole-1(2*H*)-carboxylate (17a): Carbamate **17a** was synthesized according to the general procedure. The reaction was carried out on a 0.81 mmol scale, the reaction time was 3 h, the solution was stirred at room temperature for 18 h, the eluent for the flash chromatography was a mixture of ethyl acetate and hexanes (20:80 and 75:25), and the product was obtained in 16% yield as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.95–3.62 (m, 2 H), 3.63 (s, 3 H), 3.33–3.22 (m, 1 H), 2.15–1.85 (m, 2 H), 1.64–1.23 (m, 6 H), 0.87 (s, 3 H) ppm. ^{13}C NMR(75.5 MHz, $CDCl_3$): Rotamer A: δ = 156.9 (s), 70.9 (d), 52.7 (t), 52.0 (q), 50.9 (s), 33.5 (t), 30.0 (t), 26.3 (t), 23.3 (t), 18.3 (q) ppm; Rotamer B: δ = 156.9 (s), 70.9 (d), 52.7 (t), 52.0 (q), 50.2 (s), 33.5 (t), 30.0 (t), 26.3 (t), 22.7 (t), 18.3 (q) ppm. IR (neat): $\tilde{\nu}$ = 2960, 2935, 2897, 2875, 1689, 1460, 1368, 1132 cm^{-1}. MS: *m*/*z* (%) = 183 (15) $[M]^+$, 182 (20), 168 (65) $[M - CH_3]^+$, 140 (100), 81 (20). HRMS: calcd. for $C_{10}H_{17}NO_2$ $[M]^+$ 183.1259; found 183.1254.

***cis*-5-Methoxy-8a-methylhexahydroindolizin-3(5*H*)-one (18):** Lactam **18** was synthesized according to the general procedure. The reaction was carried out on a 0.86 mmol scale, the reaction time was 3.5 h, the solution was stirred at room temperature for 18 h, the eluent for the flash chromatography was a mixture of ethyl acetate and hexanes (25:75 and 75:25), and the product was obtained in 16% yield as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.28 (d, *J* = 3.8 Hz, 1 H), 3.27 (s, 3 H), 2.63–2.50 (m, 1 H), 2.32 (*J* = 17.2, 9.8, 2.1 Hz, ddd. 1 H), 2.05–1.33 (m, 8 H), 1.37 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 175.0 (s), 78.6 (d), 59.1 (s), 55.3 (q), 39.0 (t), 35.9 (t), 29.9 (t), 29.3 (t), 24.4 (q), 15.7 (t) ppm. IR (neat): $\tilde{\nu}$ = 2942, 2874, 2849, 2842, 1701, 1690, 1672, 1393, 1079 cm^{-1}. MS: *m*/*z* (%) = 183 (5) $[M]^+$, 168 (100), 152 (100), 140 (30), 98 (50). HRMS: calcd. for $C_{10}H_{17}NO_2$ $[M]^+$ 183.1259; found 183.1254.

Methyl *trans*-3a-Methylhexahydrocyclopenta[*b*]pyrrole-1(2*H*)-carboxylate (17b): Carbamate **17b** was synthesized according to the general procedure. The reaction was carried out on a 0.86 mmol scale, the reaction time was 3.5 h, the solution was stirred at room temperature for 18 h, the eluent for the flash chromatography was a mixture of ethyl acetate and hexanes (25:75 and 75:25), and the product was obtained in 37% yield as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (s, 3 H), 3.65–3.36 (m, 3 H), 1.94–1.40 (m, 8 H), 1.15 (s, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): Rotamer A: δ = 155.4 (s), 69.6 (d), 52.1 (q), 50.3 (s), 46.5 (t), 39.1 (t), 38.1 (t), 33.8 (t), 26.3 (q), 24.9 (t) ppm; Rotamer B: δ = 155.4 (s), 69.0 (d), 52.1 (q), 49.4 (s), 46.1 (t), 39.1 (t), 37.5 (t), 32.9 (t), 26.3 (q), 24.9 (t) ppm. IR (neat): $\tilde{\nu}$ = 2946, 2867, 1723, 1712, 1690, 1447, 1350, 1243, 1189, 1122, 1086 cm^{-1}. MS: *m*/*z* (%) = 183 (15) $[M]^+$, 168 (60), 140 (100), 81 (30). HRMS: calcd. for $C_{10}H_{17}NO_2$ $[M]^+$ 183.1259; found 183.1254.

Methyl 3,3-Dimethylpyrrolidine-1-carboxylate (20): Carbamate **20** was synthesized according to the general procedure. The reaction was carried out on a 0.39 mmol scale, the reaction time was 45 min, the solution was stirred at room temperature for 15 min, the eluent for the flash chromatography was a mixture of ethyl acetate and hexanes (10:90 and 50:50), and the product was obtained in 37% yield as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): Rotamer A: δ = 3.67 (s, 3 H), 3.45 (t, *J* = 7.0 Hz, 2 H), 3.12 (s, 2 H), 1.62 (q, *J* = 7.0 Hz, 2 H), 1.05 (s, 6 H) ppm; Rotamer B: δ = 3.66 (s, 3 H), 3.38 (t, *J* = 7.0 Hz, 2 H), 3.05 (s, 2 H), 1.62 (q, *J* = 7.0 Hz, 2 H), 1.05 (s, 6 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): Rotamer A: δ = 155.7 (s), 58.8 (t), 52.2 (q), 45.3 (t), 39.2 (t), 37.4 (s), 26.0 (q) ppm; Rotamer B: δ = 155.6 (s), 58.5 (t), 52.2 (q), 44.9 (t), 38.4 (t), 29.6 (s), 26.0 (q) ppm. IR (neat): $\tilde{\nu}$ = 3013, 2964, 2876, 1685, 1460, 1396, 1195, 1118 cm^{-1}. MS: *m*/*z* (%) = 157 (30) $[M]^+$, 142 (50) $[M - CH_3]^+$, 101 (100). HRMS: calcd. for $C_8H_{15}NO_2$ $[M]^+$ 157.1103; found 157.1108.

Methyl *trans*-2,4-Dimethylpyrrolidine-1-carboxylate (23a): Carbamate **23a** was synthesized according to the general procedure. The reaction was carried out on a 0.50 mmol scale, the reaction time was 1 h, the solution was stirred at room temperature for 15 min, the eluent for the flash chromatography was a mixture of dichloromethane and hexanes (75:25) followed by a mixture of dichloromethane and methanol (10:90). The product was obtained in 67% yield as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): Mixture of rotamers: δ = 4.07–3.80 (m, 2 H), 3.65 (s, 6 H), 3.60–3.42 (m, 2 H), 2.97–2.75 (m, 2 H), 2.43–2.24 (m, 2 H), 1.71–1.51 (m, 4 H), 1.17 (d, *J* = 6.3 Hz, 3 H), 1.12 (d, *J* = 6.3 Hz, 3 H), 1.00 (d, *J* = 6.4 Hz, 6 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): Rotamer A: δ = 155.8 (s), 76.6 (q), 53.6 (t), 53.0 (d), 40.5 (t), 31.2 (d), 20.3 (q), 17.6 (q) ppm; Rotamer B: δ = 155.2 (s), 76.6 (q), 53.3 (t), 51.9 (d), 41.2 (t), 30.3 (d), 20.9 (q), 17.6 (q) ppm. IR (neat): $\tilde{\nu}$ = 2964, 2937, 2817, 1701, 1450, 1379, 1188 cm^{-1}. MS: *m*/*z* (%) = 157 (5) $[M]^+$, 142 (100) $[M - Me]^+$. HRMS: calcd. for $C_8H_{15}NO_2$ $[M]^+$ 157.1103; found 157.1107.

Methyl *cis*-2,4-Dimethylpyrrolidine-1-carboxylate (23b): Carbamate **23b** was synthesized according to the general procedure. The reaction was carried out on a 0.42 mmol scale, the reaction time was 30 min, the solution was stirred at room temperature for 15 min, the eluent for the flash chromatography was a mixture of ethyl acetate and hexanes (15:85 and 50:50), and the product was obtained in 52% yield as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): Mixture of rotamers: δ = 3.90–3.76 (m, 2 H), 3.65 (s, 3 H), 2.85–2.68 (dd, *J* = 10.2, 10.2 Hz, 1 H), 2.28–2.14 (m, 1 H), 2.13–1.94 (m, 1 H), 1.33–1.15 (m, 3 H), 1.14–1.03 (m, 1 H), 0.99 (d, *J* = 6.5 Hz, 3 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): Rotamer A: δ = 155.8 (s), 54.2 (q), 53.6 (t), 51.9 (d), 42.6 (t), 32.5 (d), 20.6 (q), 17.1 (q) ppm; Rotamer B: δ = 155.3 (s), 54.2 (q), 53.8 (t), 51.9 (d), 43.3 (t), 32.3 (d), 21.6 (q), 17.1 (q) ppm. IR (neat): $\tilde{\nu}$ = 2960, 2930, 2874, 1705, 1450, 1383, 1203, 1106, 769 cm^{-1}. MS: *m*/*z* (%) = 157 (10) $[M]^+$, 142 (100) $[M - Me]^+$. HRMS: calcd. for $C_8H_{15}NO_2$ $[M]^+$ 157.1103; found 157.1099.

Methyl 2,3,3-Trimethylpyrrolidine-1-carboxylate (26): Carbamate **26** was synthesized according to the general procedure. The reac-

tion was carried out on a 1.27 mmol scale, the reaction time was 4.25 h, the solution was stirred at room temperature for 15 min, the eluent for the flash chromatography was a mixture of ethyl acetate and hexanes (10:90 and 40:60), and the product was obtained in 56% yield as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.64 (s, 3 H), 3.51–3.44 (m, 1 H), 3.42–3.24 (m, 2 H), 1.70 (ddd, J = 10.9, 10.9, 10.9 Hz, 1 H), 1.50 (dt, J = 10.9, 5.5 Hz, 1 H), 1.09–088 (m, 3 H), 0.96 (s, 3 H), 0.94 (s, 3 H) ppm. ^{13}C NMR (100.7 MHz, $CDCl_3$): Rotamer A: δ = 156.1 (s), 62.7 (d), 52.3 (q), 44.6 (t), 40.9 (s), 36.9 (t), 27.7 (q), 23.2 (q), 16.8 (q) ppm; Rotamer B: δ = 155.8 (s), 62.3 (d), 52.2 (q), 44.3 (t), 40.1 (s), 35.9 (t), 27.5 (q), 23.0 (q), 16.0 (q) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2960, 2875, 1689, 1456, 1382, 1340, 1294, 1122, 1051 cm^{-1}. MS: m/z (%) = 171 (15) $[M]^+$, 156 (100), 115 (80), 97 (15). HRMS: calcd. for $C_9H_{17}NO_2$ $[M]^+$ 171.1259; found 171.1264.

1-(1-Methoxyethyl)-5,5-dimethylpyrrolidin-2-one (27): Lactam **27** was synthesized according to the general procedure. The reaction was carried out on a 1.27 mmol scale, the reaction time was 4.25 h, the solution was stirred at room temperature for 15 min, the eluent for the flash chromatography was a mixture of ethyl acetate and hexanes (10:90 and 40:60), and the product was obtained in 10% yield as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.33 (q, J = 6.4 Hz, 1 H), 3.25 (s, 3 H), 2.42 (t, J = 8.8 Hz, 1 H), 2.41 (t, J = 6.8 Hz, 1 H), 1.82 (t, J = 8.2 Hz, 2 H), 1.50 (d, J = 6.4 Hz, 3 H), 1.40 (s, 3 H), 1.37 (s, 3 H) ppm. ^{13}C NMR (100.7 MHz, $CDCl_3$): δ = 175.9 (s), 81.1 (d), 61.7 (s), 55.8 (q), 36.3 (t), 30.2 (t), 28.5 (q), 28.2 (q), 20.8 (q) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2992, 2942, 2826, 1664, 1449, 1403, 1354, 1245, 1189, 1139, 1093, 1051, 910, 847 cm^{-1}. MS: m/z (%) = 171 (10) $[M]^+$, 156 (100), 115 (60), 98 (35), 84 (20). HRMS: calcd. for $C_9H_{17}NO_2$ $[M]^+$ 171.1259; found 171.1264.

Methyl 5-Methoxy-2,2-dimethylpyrrolidine-1-carboxylate (29) and Methyl 5,5-Dimethoxy-2-methylpent-2-ylcarbamate (34): Carbamates **29** and **34** were synthesized according to the general procedure. The reaction was carried out on a 0.31 mmol scale, the reaction time was 1 h, the solution was stirred at room temperature for 15 min, the solvent was removed under reduced pressure and the crude mixture was directly purified by flash chromatography. The eluent was a mixture of ethyl acetate and hexanes (15:85), and the products were obtained in 17% yield for **29** (not characterized because of instability) and in 29% yield for **34** as colourless oils. Carbamate **34**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.65 (br. s, 1 H), 4.34 (t, J = 5.5 Hz, 1 H), 3.59 (br. s, 3 H), 3.31 (s, 6 H), 1.75–1.64 (m, 2 H), 1.63–1.53 (m, 2 H), 1.27 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5 (s), 104.9 (d), 53.0 (q), 52.5 (s), 51.7 (q), 35.3 (t), 29.9 (t), 27.6 (t), 27.3 (q) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3411–3137 (br.), 3017, 2960, 2837, 1720, 1509, 1269, 1206, 1121, 1058 cm^{-1}. MS: m/z (%) = 204 (2) $[M - CH_3]^+$, 188 (10) $[M - OMe]^+$, 172 (25), 156 (40), 116 (100), 97 (15). HRMS: calcd. for $C_9H_{18}NO_4$ $[M - CH_3]^+$ 204.1236; found 204.1239.

4-Isocyanato-1,1-dimethoxy-4-methylpentane (35): Isocyanate **35** was synthesized according to the general procedure. The reaction was carried out on a 0.58 mmol scale, the reaction time was 30 min, the solution was stirred at room temperature for 18 h, the solvent was removed under reduced pressure, the crude product was directly purified by flash chromatography, the eluent was a mixture of ethyl acetate and hexanes (15:85), and the product was obtained in 17% yield as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.36 (t, J = 5.4 Hz, 2 H), 3.32 (s, 6 H), 1.76–1.60 (m, 2 H), 1.59–1.51 (m, 2 H), 1.34 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.6 (s), 104.5 (d), 58.1 (s), 53.1 (q), 38.6 (t), 30.4 (q), 28.0 (t) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3013, 2982, 2939, 2837, 2259, 1463, 1445, 1386, 1364, 1125, 1072 cm^{-1}. MS: m/z (%) = 186 (3) $[M - H]^+$, 172 (3) $[M - CH_3]^+$, 156 (20) $[M - OMe]^+$, 124 (15), 113 (60), 74 (100). HRMS: calcd. for $C_9H_{16}NO_3$ $[M - H]^+$ 186.1130; found 186.1133.

Methyl 5-(4-Methoxyphenyl)-2,2-dimethylpyrrolidine-1-carboxylate (32): Carbamate **32** was synthesized according to the general procedure. The reaction was carried out on a 0.92 mmol scale, the reaction time was 30 min, the solution was stirred at room temperature for 15 min, the eluent for the flash chromatography was a mixture of ethyl acetate and hexanes (10:90 and 20:80), and the product was obtained in 47% yield as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): Rotamer A: δ = 7.20–7.03 (m, 2 H), 6.84 (d, J = 8.7 Hz, 2 H), 5.06–4.91 (m, 1 H), 3.79 (s, 3 H), 3.48 (s, 3 H), 2.40–2.20 (m, 2 H), 2.02–1.53 (m, 2 H), 1.67 (s, 3 H), 1.43 (s, 3 H) ppm; Rotamer B: δ = 7.20–7.03 (m, 2 H), 6.84 (d, J = 8.7 Hz, 2 H), 5.06–4.91 (m, 1 H), 3.69 (s, 3 H), 3.48 (s, 3 H), 2.40–2.20 (m, 2 H), 2.02–1.53 (m, 2 H), 1.58 (s, 3 H), 1.37 (s, 3 H) ppm. ^{13}C NMR (100.7 MHz, $CDCl_3$): Rotamer A: δ = 158.3 (s), 155.1 (s), 136.8 (s), 126.6 (d), 113.7 (d), 63.5 (s), 62.5 (d), 55.5 (q), 51.9 (q), 38.9 (t), 32.3 (t), 27.3 (q), 25.2 (q) ppm; Rotamer B: δ = 158.3 (s), 156.1 (s), 136.4 (s), 126.8 (d), 113.8 (d), 63.5 (s), 62.1 (d), 55.5 (q), 52.1 (q), 40.2 (t), 31.7 (t), 28.2 (q), 26.5 (q) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3051, 2995, 2935, 1689, 1615, 1587, 1446, 1372, 1298, 1174, 1086 cm^{-1}. MS: m/z (%) = 263 (60) $[M]^+$, 248 (90) $[M - Me]^+$, 207 (100), 173 (75). HRMS: calcd. for $C_{15}H_{21}NO_3$ $[M]^+$ 263.1521; found 263.1523.

6-(4-Methoxyphenyl)-3,3-dimethyl-3,4-dihydropyridin-2(1*H*)-one (36) and 1-[Methoxy(4-methoxyphenyl)methyl]-3,3-dimethylpyrrolidin-2-one (33): Lactams **36** and **33** were synthesized according to the general procedure. The reaction was carried out on a 0.92 mmol scale, the reaction time was 30 min, the solution was stirred at room temperature for 15 min, the eluent for the flash chromatography was a mixture of ethyl acetate and hexanes (10:90 and 20:80), and a mixture of the products (2:1) was obtained in 43% yield as a beige solid. Lactam **36**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (d, J = 8.6 Hz, 2 H), 7.11 (s, 1 H), 6.89 (d, J = 8.6 Hz, 2 H), 5.27 (td, J = 4.7, 1.6 Hz, 1 H), 3.81 (s, 3 H), 2.30 (d, J = 4.7 Hz, 2 H), 1.21 (s, 6 H) ppm. ^{13}C NMR (100.7 MHz, $CDCl_3$): δ = 177.4 (s), 160.1 (s), 136.1 (s), 127.8 (s), 127.4 (d), 114.4 (d), 100.4 (d), 55.6 (q), 37.1 (s), 36.1 (t), 24.7 (q) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3544–3023 (br.), 2995, 2967, 2939, 2872, 2844, 1689, 1657, 1611, 1460, 1446, 1287, 1178, 1079 cm^{-1}. MS: m/z (%) = 231 (90) $[M]^+$, 216 (100), 203 (35), 188 (65), 162 (35), 146 (40), 134 (50). HRMS: calcd. for $C_{14}H_{17}NO$ $[M]^+$ 231.1259; found 231.1263. Lactam **33**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (d, J = 8.2 Hz, 2 H), 6.86 (d, J = 8.2 Hz, 2 H), 6.19 (s, 1 H), 3.79 (s, 3 H), 3.40 (s, 3 H), 3.23–3.11 (m, 1 H), 2.87–2.74 (m, 1 H), 1.91–1.66 (m, 2 H), 1.23 (s, 3 H), 1.14 (s, 3 H) ppm. ^{13}C NMR (100.7 MHz, $CDCl_3$): δ = 181.1 (s), 159.5 (s), 129.9 (s), 126.2 (d), 113.9 (d), 82.6 (d), 55.9 (q), 55.5 (q), 41.7 (s), 38.0 (t), 34.2 (t), 24.9 (q), 24.5 (q) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3544–3023 (br.), 2995, 2967, 2939, 2872, 2844, 1689, 1657, 1611, 1460, 1446, 1287, 1178, 1079 cm^{-1}. MS: m/z (%) = 263 (5) $[M]^+$, 248 (50) $[M - Me]^+$, 232 (20), 135 (100). HRMS: calcd. for $C_{15}H_{21}NO_3$ $[M]^+$ 263.1521; found 263.1526.

***cis*-4a-Methyloctahydroquinoline-2(1*H*)-thione (38):** Thiolactam **38** was synthesized according to the general procedure. The reaction was carried out on a 0.49 mmol scale, the reaction time was 30 min, the solution was stirred at room temperature for 15 min, the solvent was removed under reduced pressure, the crude mixture was directly purified by flash chromatography, the eluent was a mixture of ethyl acetate and hexanes (5:95), and the product was obtained in 30% yield as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (br. s, 1 H), 3.16–3.08 (m, 1 H), 2.93 (t, J = 6.6 Hz, 2 H), 1.90–1.79 (m, 1 H), 1.72 (dt, J = 13.6, 6.6 Hz, 1 H), 1.62–1.32 (m,

6 H), 1.31–1.14 (m, 2 H), 1.03 (s, 3 H) ppm. ^{13}C NMR (100.7 MHz, $CDCl_3$): δ = 202.3 (s), 60.7 (d), 36.4 (t), 33.1 (t), 31.4 (t), 30.7 (s), 29.3 (t), 25.7 (q), 21.8 (t), 21.0 (t) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3354, 3280–3111 (br.), 3059, 2942, 2865, 1565, 1530, 1449, 1301, 1093 cm^{-1}. MS: *m*/*z* (%) = 199 (1) $[M]^+$, 183 (100) $[M - Me]^+$, 150 (50) $[M - (Me + SH)]^+$, 88 (50). HRMS: calcd. for $C_{10}H_{17}NOS$ $[M]^+$ 199.1031; found 199.1027.

CCDC-840317 (for **15**) and -840318 (for **49a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Experimental procedures and characterization for all new compounds in the synthesis of *N*-mesyloxylactams **13a**, **13b**, **16a**, **16b**, **19**, **22a**, **22b**, **25**, **28** and **31**.

Acknowledgments

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