Pergamon

Tetrahedron 57 (2001) 5123–5130

TETRAHEDRON

N-Acyliminium ion chemistry and palladium catalysis: a useful combination to obtain bicyclic heterocycles

Willem F. J. Karstens,[†] Dirk Klomp, Floris P. J. T. Rutjes[‡] and Henk Hiemstra[*]

Institute of Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, Netherlands

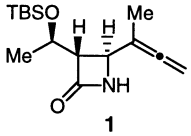
Dedicated to Professor Barry M. Trost on the occasion of his 60th birthday

Received 3 February 2001; revised 28 February 2001; accepted 1 March 2001

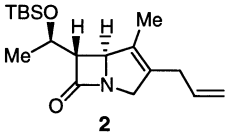
Abstract—By using *N*-acyliminium ion chemistry, several ω-propadienyllactams and a propadienyloxazolidine were prepared from *N*-acyliminium ion precursors and propargylsilanes. Treatment of these allene containing lactams and oxazolidinone with allyl halides or an allyl carbonate using Pd(II)-salts as the catalyst gave rise to a coupling–cyclization reaction, yielding bicyclic systems in which the allyl moiety is incorporated. With this methodology several substituted pyrrolizinones, an oxazolone and indolizinone were prepared.

1. Introduction

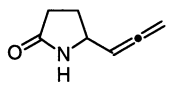
The construction of nitrogen heterocycles is an important goal in organic synthesis because of their abundance in natural and pharmaceutical products.[1] Among the well established methods for the preparation of such compounds are heteroannulation processes involving unsaturated functionality and Pd-catalysis.[2,3] Despite their interesting chemical properties due to the cumulated double bonds,[4] allenes have received relatively little attention in this area. However, interest in the preparation of heterocyclic molecules via cyclization of heteroatoms onto tethered allenes has increased considerably over the last few years.[5–7]



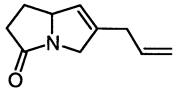
1



2



3

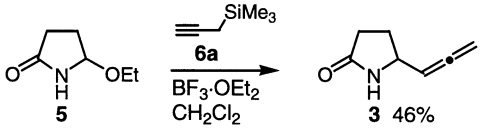


4

In one of the earlier examples, Prasad and Liebeskind described a remarkable reaction in which β-lactam **1** was reacted with an excess of allyl bromide and catalytic palladium acetate to give carbapenem skeleton **2**.[8] We were particularly intrigued by this reaction, because some time ago we reported an efficient synthesis of the allene substituted lactam **3**.[9] This allene was prepared utilizing *N*-acyliminium ion chemistry, which we have also used in our laboratory to prepare a variety of interesting compounds, natural products and natural product analogs.[10] It seemed promising to combine our efficient *N*-acyliminium ion technology with palladium catalysis to obtain an easy entry into the class of pyrrolizine alkaloid analogues, e.g. pyrrolizidinones **4**. Furthermore, this investigation is an extension of other recent work from our group on palladium catalyzed cyclization reactions of acetylene[11] and allene[12] containing lactams and amino acids.[13]

2. Results

Some years ago, we developed syntheses of allenyllactams by means of *N*-acyliminium ion chemistry. The reaction can be carried out with an acyliminium ion precursor (viz. **5**) in the presence of a Lewis acid and a propargylsilane, both in intra-[14] and intermolecular[9] fashion. In order to obtain the first starting material, ethoxylactam **5** was reacted with commercially available propargyltrimethylsilane **6a**[15] in the presence of a Lewis acid to give allenyllactam **3**.[9]



(1)

Keywords: palladium catalysis; pyrrolizines; allenes; propargylsilanes; indolizines.

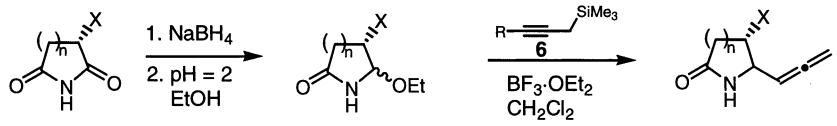
* Corresponding author. Tel.: +31-20-5255941; fax: +31-20-5255670; e-mail: henkh@org.chem.uva.nl

† Current address: Department of Medicinal Chemistry, N.V. Organon, Oss, Netherlands.

‡ Current address: Department of Organic Chemistry, University of Nijmegen, Netherlands.

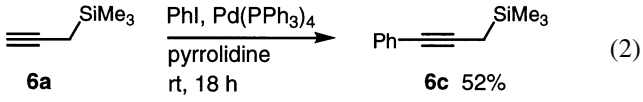
0040–4020/01/$ - see front matter
PII: S0040-4020(01)00364-7

Table 1.



entry	imide	ethoxylactam	propargylsilane	allenyllactam
1	succinimide (**7a**)	**5** 81%	**6a** R = H	**3** 55%
2		**5**	**6b** R = Me	**8** 64%
3		**5**	**6c** R = Ph	**9** 18%
4	glutarimide (**7b**)	**10** 88%	**6b**	**11** 68%
5	**12** n = 1, X = OAc	**13** 49% *cis/trans 20 : 80*	**6b**	**14** 37% $[\alpha]_D$ +24.3

Then, we set out to prepare substituted 5-propadienyl-2-pyrrolidinones. In order to introduce substituents on the allenic moiety of the pyrrolidinones, two other π-nucleophiles for the *N*-acyliminium ion reactions were prepared. 2-Butynyltrimethylsilane (**6b**) was conveniently prepared following a literature procedure,[16] while the corresponding Ph-substituted propargylsilane **6c** was synthesized via a new route using a modification of the Sonogashira reaction[17] in 52% yield (Eq. 2):

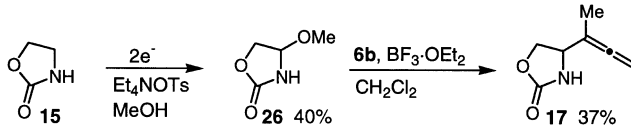


6a **6c** 52% (2)

The required *N*-acyliminium ion precursors were readily available by partial reduction of cyclic imides using $NaBH_4$ in ethanol, followed by ethanolysis at pH 2 of the intermediate *N*,*O*-hemiacetals.[18] For example, reduction of succinimide afforded ethoxylactam **5** in 81% yield. Lewis acid mediated coupling ($BF_3{\cdot}OEt_2$, 2–3.5 equiv.) of this *N*-acyliminium ion precursor with propargyltrimethylsilane **6a** (2 equiv.) afforded allenyllactam **3** in 55% yield (entry 1, Table 1). Similarly, the methyl-substituted allenyllactam **8** was obtained in 64% yield when 2-butynyltrimethylsilane **6b** was reacted with **5** (entry 2). Unfortunately, the phenyl-substituted allene was obtained in a much lower yield (18%).

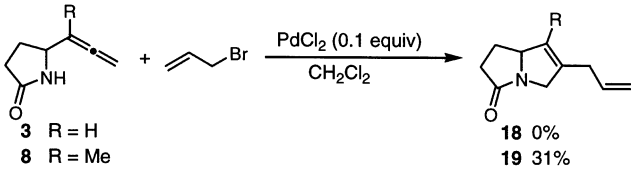
The methylallene-substituted piperidinone **11** was prepared via reduction[18] of glutarimide to **10**, followed by reaction with propargylsilane **6b** (entry 4). Moreover, an enantiopure allenyllactam was prepared using similar methodology. Thus, reduction of the (*S*)-malic acid derived imide **12**[19c] gave a *cis/trans* mixture of ethoxylactams **13**,[19] which after $BF_3{\cdot}OEt_2$ mediated reaction with **6b** gave the enantiopure allenyllactam **14** (entry 5). A small amount (ca. 2%) of the *cis*-isomer of **14** was also formed in this reaction, but this diastereoisomer could be separated from **14** by means of column chromatography.

In addition to these lactams, an oxazolidinone analogue was prepared in two steps, starting from oxazolidin-2-one **15**. Methoxylation of **15** by means of electrochemical oxidation afforded *N*,*O*-acetal **16** (40%),[20] which after reaction with **6b** (2 equiv.) gave **17** in a yield of 37% (Eq. 3):



15 **26** 40% **17** 37% (3)

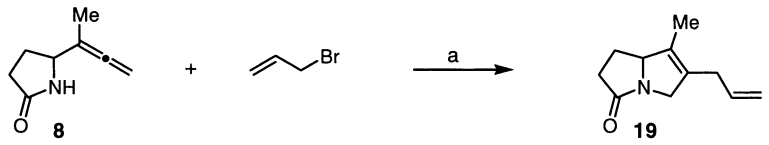
With the different allenes in hand, the stage was set to study the palladium catalyzed cyclization reactions. Unsubstituted allenyllactam **3** was treated under Liebeskind's conditions with allyl bromide (5 equiv.) and $PdCl_2$ (0.1 equiv.) in CH_2Cl_2. Unfortunately, a complex mixture of reaction products was obtained in which the desired product **18** could not be detected by ^1H NMR (Eq. 4):



3 R = H
8 R = Me
18 0%
19 31% (4)

The successful example presented by Liebeskind involved

Table 2. Reagents and conditions: (a) **8** (0.5 mmol), allyl bromide (5 equiv.), PdX_2 (0.1 equiv.), base (0–2 equiv.), indicated solvent (0.1 M)

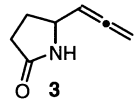
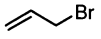
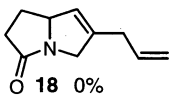
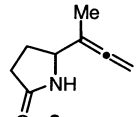
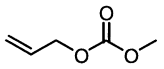
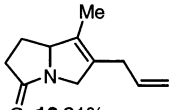
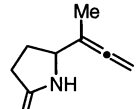
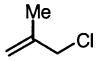
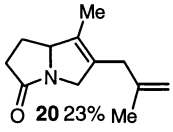
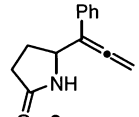
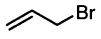
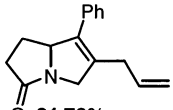
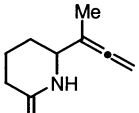
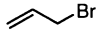
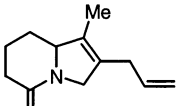
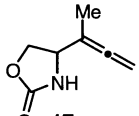
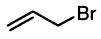
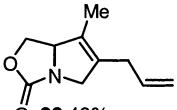


Entry	Solvent	Catalyst	Base	T (°C)	Time (h)	Yield (%)
1	CH_2Cl_2	$Pd(OAc)_2$	–	Rt	18	<5
2	CH_2Cl_2	$Pd_2(MeCN)_2$	–	Rt	18	42
3	MeCN	$Pd_2(MeCN)_2$	–	Rt	18	41
4	MeCN	$Pd(OAc)_2$	–	Rt	18	<5
5	MeCN	$PdCl_2(MeCN)_2$	Et_3N	Rt	18	<5
6	MeCN	$PdCl_2(MeCN)_2$	K_2CO_3	Rt	18	50
7	MeCN	$PdCl_2(PPh_3)_2$	K_2CO_3	Rt	18	<5
8	MeCN	$PdCl_2(MeCN)_2$	K_2CO_3	0	18	45
9	MeCN	$PdCl_2(MeCN)_2$	K_2CO_3	75	1	56

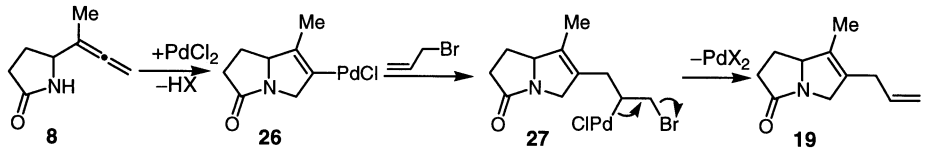
allenic β-lactam **1** which contained a methyl substituent on the internal allenic carbon. When we applied the aforementioned cyclization conditions to methyl-substituted allene **8**, a successful reaction occurred, giving pyrrolizidinone **19** in 31% yield (Eq. 4).

Encouraged by the formation of the desired bicyclic product, we tried to increase the yield of the reaction (Table 2). First, $Pd(OAc)_2$ was used, which was reported by Liebeskind to be an equally effective catalyst for this type of conversion. In our case, however, this catalyst was not active at all and the starting material could be recovered after stirring for 18 h at room temperature (entry 1, Table 2). When the more soluble bisacetonitrile complex of $PdCl_2$ was used in the reaction, the yield increased substantially to 42% (entry 2). Use of the same catalyst in acetonitrile

Table 3.

entry	allene	allylating agent	product, yield[a]
1	 **3**		 **18** 0%
2	 **8**		 **19** 21%
3	**8**	" "	**19** 48%[b]
4	 **8**		 **20** 23% Me
5	 **9**		 **21** 72%
6	 **11**		 **22** 66%
7	 **17**		 **23** 49%

[a] Allenyllactam (1 equiv), allylating agent (5 equiv), $PdCl_2(MeCN)_2$ (0.1 equiv), K_2CO_3 (2 equiv), MeCN (0.1 M).
[b] The reaction was run without K_2CO_3.



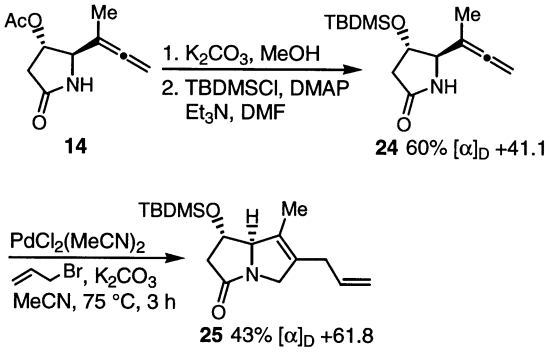
Scheme 1.

gave a similar yield of the product (entry 3), whereas $Pd(OAc)_2$ was equally ineffective in this solvent as in CH_2Cl_2 (entry 4).

One equivalent of hydrogen bromide is formed in the reaction. This strong acid might influence the reaction, or prevent the use of acid-sensitive groups in the starting material. Therefore, a base was added to the reaction mixture. In the case of triethylamine the bicyclic product could not be isolated, whereas the use of K_2CO_3 increased the yield to 50% (entries 5 and 6). No conversion of starting material was observed when the bistriphenylphosphine analogue of the catalyst was used (entry 7). Lowering the temperature of the reaction mixture slightly decreased the yield, but when the reaction was performed at 75°C, the yield increased to 56% and the reaction time was lowered considerably (entries 8 and 9). It was decided to use the latter set of reaction conditions to convert the other allenyllactams to the corresponding bicyclic products with different allylating agents (Table 3).

Unfortunately, allenyllactam **3** still did not afford the desired bicyclic product using the improved reaction conditions (entry 1). When methyl-substituted allene **8** was subjected to an allylic carbonate rather than an allylic halide, the yield dropped to 21%. The use of base, however, is not necessary in this case, because no acid is produced in the reaction. When the reaction was run without base, **19** was produced in 48% yield (entries 2 and 3). Methallyl chloride could also be used, leading to the expected product **20** in a moderate yield of 23% (entry 4). Although the synthesis of phenylallene **9** was not very efficient, the cyclization reaction with allyl bromide afforded **21** in a good yield of 72% (entry 5).

The glutarimide derived methylallene **11** could also be effectively cyclized to the corresponding allylated indolizidinone **22** (66%, entry 6). Finally, allenic oxazolidinone **17** behaved in a similar fashion as the allenic lactams, giving 49% of the desired cyclization product **23** (entry 7).



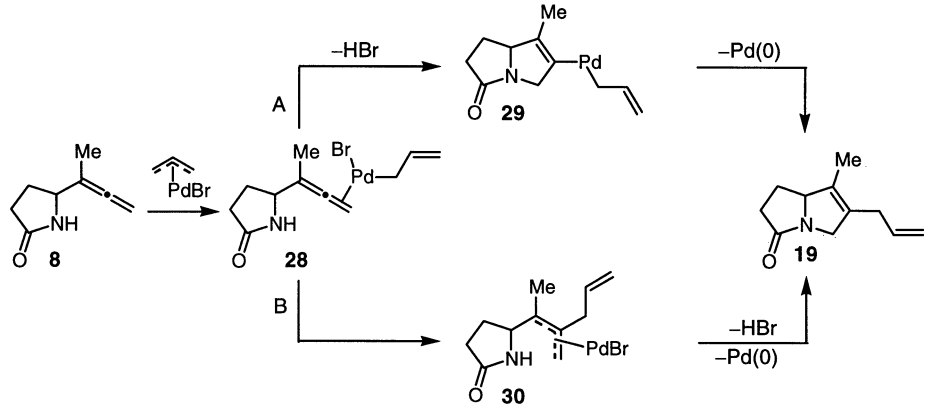
(5)

The enantiopure precursor **14** was first transprotected in order to prevent deprotection of the acetate under the cyclization conditions. First it was deprotected with K_2CO_3 in MeOH and then reprotected with the more stable *tert*-butyldimethylsilyl group to give allene **24** (60%). Subjection to the optimal cyclization conditions afforded the enantiopure pyrrolizidinone **25** in 43% yield (Eq. 5).

3. Mechanism

Both Liebeskind and Kimura have suggested a mechanism for this type of reaction. Liebeskind's proposal involves attack of the lactam nucleophile onto the π-complex of the palladium(II) salt and the allene, giving rise to the σ-vinylpalladium complex **26**. An insertion of allyl bromide gives σ-palladium complex **27**, which after β-elimination affords the product **19** regenerating a palladium(II) salt that can enter the next catalytic cycle (Scheme 1).[8]

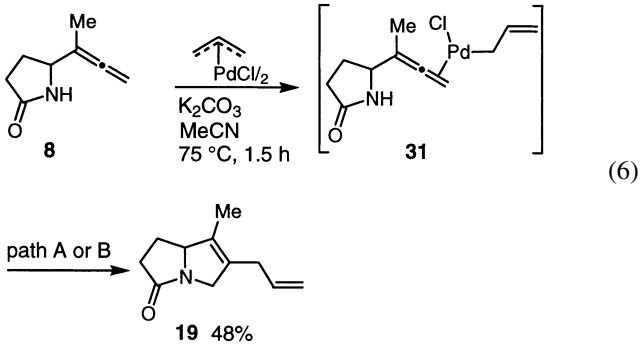
Although this might be the mechanism in operation, another possibility was suggested by Kimura for related reactions of



Scheme 2.

allenic tosylcarbamates.[7n,o] This mechanism starts with in situ reduction of Pd(II) to Pd(0), which thus reacts with allyl bromide to give π-allylpalladium bromide. This organopalladium(II) species can coordinate to the allene resulting in the formation of π-complex **28**. This π-complex has two possible modes of reaction. Pathway A consists of a nucleophilic attack of the lactam nitrogen onto the allene which is activated by the coordination of the electrophilic organopalladium(II) species. A reductive elimination of Pd(0) would convert vinyl(allyl)palladium(II) intermediate **29** into **19** (Scheme 2). On the other hand, an insertion reaction of the allene into the palladium–allyl bond converts **28** into π-allylpalladium complex **30**.[21] Intramolecular nucleophilic attack of the lactam nitrogen would also afford the observed product (pathway B, Scheme 2).

Apart from the fact that we cannot exclude that other mechanisms are also possible, an experiment was performed to test the possible involvement of the two mechanistic proposals shown in Scheme 2. Thus, a reaction was performed employing a stoichiometric amount of π-allylpalladium chloride dimer as the allylating agent (Eq. 6). As it turned out, this reaction was successful affording **19** in 48% yield. In this case, the reaction cannot occur via the mechanism illustrated in Scheme 1, but has to involve π-complex **31**, similar to **28**. Unfortunately, we are not able to discern between path A or B. Pathway B involves a geometrically unfavorable 5-*endo-trig* cyclization,[22] whereas in palladium complex **28** the allene double bond might not be sufficiently activated to allow cyclization toward **29**.



4. Experimental

4.1. General information

All reactions were carried out under an inert atmosphere of dry nitrogen, unless stated otherwise. Standard syringe techniques were applied for transfer of Lewis acids and dry solvents. Infrared (IR) spectra were obtained from $CHCl_3$ solutions or neat, using a Perkin–Elmer 298 spectrophotometer or a Bruker IFS 28 FT-spectrophotometer and wavelengths (ν) are reported in cm^{-1}. Proton nuclear magnetic resonance (^1H NMR) spectra were determined in $CDCl_3$ (unless stated otherwise) using a Bruker AC 200 (200 MHz), a Bruker ARX 400 (400 MHz) or a Varian Inova (500 MHz) spectrometer. The latter machines were also used for ^{13}C NMR (APT) spectra (100 MHz and 125 MHz, respectively) in $CDCl_3$ (unless stated otherwise). Chemical shifts (δ) are given in ppm downfield from tetramethylsilane. Mass spectra and accurate mass measurements were carried out using a JEOL JMS-SX/SX 102 A Tandem Mass Spectrometer, a Varian NIAT 711 or a VG Micromass ZAB-HFQQ instrument. Elemental analyses were performed by Dornis u. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Optical rotations were measured with a Perkin–Elmer 241 polarimeter in a 1 dm cell in the indicated solvent. R_f values were obtained by using thin layer chromatography (TLC) on silica gel-coated plastic sheets (Merck silica gel 60 F_{254}) with the indicated solvent (mixture). Dry THF and Et_2O were distilled from sodium benzophenone ketyl prior to use. Dry DMF, CH_2Cl_2, and MeCN were distilled from CaH_2 and stored over 4 Å MS under a dry nitrogen atmosphere. $BF_3{\cdot}OEt_2$ was distilled and stored under a dry nitrogen atmosphere. Triethylamine and pyridine were dried and distilled from KOH pellets. All commercially available reagents were used as received, unless indicated otherwise.

4.1.1. 5-Propa-1,2-dienylpyrrolidin-2-one (3). Ethoxylactam **5** (500 mg, 3.87 mmol)[18] was dissolved in CH_2Cl_2 (7.5 mL) and to this solution propargyltrimethylsilane **6a** (1.30 g, 11.6 mmol)[15] was added. The solution was cooled to −20°C and $BF_3{\cdot}OEt_2$ (1.47 mL, 11.6 mmol) was added dropwise. The solution was allowed to warm to rt and was stirred for an additional 30 min and poured into brine (10 mL). Extraction with CH_2Cl_2 (3×15 mL), followed by drying of the combined organic layers ($NaSO_4$), gave after concentration and flash chromatography (EtOAc/acetone 3:1) **3**[9] (260 mg, 2.11 mmol, 55%) as a light yellow oil; R_f 0.4 (EtOAc/acetone 1:1); IR (neat) 3249, 1958, 1684; ^1H NMR (400 MHz, $CDCl_3$) δ 6.12 (br s, 1H), 5.15 (q, J= 6.6 Hz, 1H), 4.87 (dd, J=6.6, 2.1 Hz, 2H), 4.20–4.17 (m, 1H), 2.43–2.26 (m, 3H), 1.98–1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.8, 178.0, 92.5, 77.4, 53.1, 29.7, 27.6; HRMS (EI) calcd for C_7H_9NO 123.0684, found 123.0693.

4.1.2. (3-Phenyl-2-propynyl)trimethylsilane (6c). Pyrrolidine (2.5 mL) was degassed with nitrogen. Iodobenzene (1.0 mL, 8.91 mmol) was added and the temperature was lowered to 0°C. $Pd(PPh_3)_4$ (52 mg, 0.05 mmol) and propargyltrimethylsilane **6a** (0.50 g, 4.45 mmol) were added and the reaction mixture was stirred overnight at rt. The solution was poured into water (15 mL) and extracted with hexanes (4×15 mL). The organic layers were washed with brine (15 mL), dried ($NaSO_4$) and concentrated. Purification by means of flash chromatography (pentane) gave **6c**[23] (431 mg, 2.24 mmol, 52%) as a reddish liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.35 (m, 2H), 7.29–7.22 (m, 3H), 1.70 (s, 2H), 0.17 (s, 9H).

4.1.3. 5-(1-Methylpropa-1,2-dienyl)pyrrolidin-2-one (8). The reaction was performed as described for allene **3**, with ethoxylactam **5** (1.50 g, 11.6 mmol), 2-butynyltrimethylsilane **6b** (2.91 g, 23.2 mmol)[16] and $BF_3{\cdot}OEt_2$ (2.9 mL, 23.2 mmol) in CH_2Cl_2 (30 mL). Stirring for 2 h at rt, followed by work-up and chromatography and an additional bulb-to-bulb distillation (0.05 mbar), gave **8** (1.02 g, 5.4 mmol, 64%) as a colorless oil; IR (neat) 3245, 1959, 1684; ^1H NMR (400 MHz, $CDCl_3$) δ 6.78 (br s, 1H), 4.75–4.72 (m, 2H), 4.09–4.05 (m, 1H), 2.37–2.22 (m,

3H), 2.00–1.91 (m, 1H), 1.66 (t, J=3.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 178.3, 99.8, 77.1, 56.0, 29.9, 26.2, 14.5; HRMS (EI) calcd for $C_8H_{11}NO$ 137.0841, found 137.0842.

4.1.4. 5-(1-Phenylpropa-1,2-dienyl)pyrrolidin-2-one (9). The reaction was performed as described for allene **3**, with ethoxylactam **5** (1.90 g, 14.7 mmol), (3-phenyl-prop-2-ynyl)trimethylsilane **8c** (5.53 g, 29.4 mmol)[17,22] and $BF_3{\cdot}OEt_2$ (5.58 mL, 44.05 mmol) in CH_2Cl_2 (50 mL). Stirring for 18 h at rt, followed by work-up and chromatography, gave **9** (2.26 g, 2.20 mmol, 18%) as a light orange solid; mp 33–35°C; R_f 0.3 (EtOAc); IR (neat) 3214, 1940. 1695; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.32 (m, 3H), 7.27–7.22 (m, 2H), 5.65 (br s, 1H), 5.30–5.22 (m, 2H), 4.72–4.67 (m, 1H), 2.52–2.42 (m, 1H), 2.40–2.29 (m, 2H), 2.13–2.06 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.3, 178.2, 133.7, 128.6, 127.2, 126.2, 108.0, 81.7, 52.6, 29.4, 27.4; HRMS (EI) calcd for $C_{13}H_{13}NO$ 199.0997, found 199.1004.

4.1.5. 6-(1-Methylpropa-1,2-dienyl)piperidin-2-one (11). The reaction was performed as described for allene **3**, with 6-ethoxypiperidin-2-one **10** (1.00 g, 6.98 mmol),[18] 2-butynyltrimethylsilane **6b** (1.76 g, 14.0 mmol) and $BF_3{\cdot}OEt_2$ (1.77 mL, 13.97 mmol) in CH_2Cl_2 (15 mL). Stirring for 4 h at rt, followed by work-up and chromatography, gave **11** (0.71 g, 4.72 mmol, 68%) as a colorless oil; R_f 0.2 (EtOAc); IR (neat) 3215, 2949, 1959, 1656; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (br s, 1H), 4.85–4.77 (m, 2H), 3.84–3.82 (m, 1H), 2.42–2.25 (m, 2H), 2.01–1.87 (m, 2H), 1.73–1.64 (m, 1H), 1.69 (t, J=3.1 Hz, 3H), 1.61–1.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 172.1, 100.4, 77.9, 54.8, 31.2, 26.8, 19.2, 14.9; HRMS (EI) calcd for $C_9H_{13}NO$ 151.0997, found 151.0990.

4.1.6. (4*S*,5*R*)-4-Acetoxy-5-ethoxy-pyrrolidin-2-one (13). To a solution of imide **12**[19c] (3.97 g, 25.3 mmol) in ethanol (215 mL) $NaBH_4$ (870 mg, 23.0 mmol) was added at −15°C. After 20 min, the temperature was lowered to −30°C and the mixture was acidified with a 2 M H_2SO_4 solution in ethanol to pH=2. The solution was warmed to rt and stirred for 2.5 h. The mixture was neutralized using a 5% NaOH solution in EtOH. The solvent was evaporated and the residue was dissolved in $CHCl_3$, filtered over Celite® and the filtrate was washed with brine. After drying (Na_2SO_4) and evaporation, the product was purified using chromatography (EtOAc/hexanes 3:2) to give **13** (2.3 g, 12.4 mmol, 49%) as a yellow oil (4:1 mixture of *trans*:*cis* isomers). Data of the *trans* isomer: R_f 0.25 (EtOAc/hexanes 3:2); IR (neat): 3440, 3000, 2970, 2930, 1710, 1240. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (br s, 1H), 5.07 (d, J=6.2 Hz, 1H), 4.77 (s, 1H), 3.60–3.47 (m, 2H), 2.82 (dd, J=6.3, 18.0 Hz, 1H), 2.19 (d, J=18.0 Hz, 1H), 2.03 (s, 3H), 1.16 (t, J=7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 170.1, 89.2, 73.4, 63.4, 35.4, 20.8, 14.9. HRMS (EI) calcd for $C_8H_{13}NO_4$ 187.0845, found 187.0875.

4.1.7. (4*S*,5*R*)-4-Acetoxy-5-(1-methylpropa-1,2-dienyl)-pyrrolidin-2-one (14). The reaction was performed as described for allene **3**, with ethoxylactam **13** (76 mg, 0.41 mmol), 2-butynyltrimethylsilane **6b** (103 mg, 0.81 mmol) and $BF_3{\cdot}OEt_2$ (0.36 mL, 2.80 mmol) in CH_2Cl_2 (5 mL). Stirring for 5 days at rt, followed by work-up and chromatography, gave **14** (31 mg, 0.16 mmol, 37%) as a light yellow oil. A small amount (ca. 2 mg, 0.01 mmol, 2%) of the *cis*-isomer was also isolated. *Trans*-**14**: R_f 0.30 (EtOAc); $[\alpha]_D$+24.3 (*c* 0.3, $CHCl_3$); IR (neat) 3229, 2918, 1960, 1741, 1711; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (br s, 1H), 5.19 (d, J=6.5 Hz, 1H), 4.87–4.79 (m, 2H), 3.94 (s, 1H), 2.71 (dd, J=6.6, 17.8 Hz, 1H), 2.28 (dd, J=1.4, 17.8 Hz, 1H), 2.07 (s, 3H), 1.77 (t, J=3.1, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 170.2, 98.0, 78.4, 72.8, 62.1, 35.9, 20.9, 15.2 (C-10). *cis*-**14**: R_f 0.25 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (br s, 1H), 5.54 (m, J=3.7, 5.6, 6.2 Hz, 1H), 4.85–4.82 (m, 2H), 4.29 (m, 1H), 2.72 (dd, J=6.8, 17.4 Hz, 1H), 2.44 (dd, J=3.7, 17.4 Hz, 1H), 2.07 (s, 3H), 1.69 (t, J=3.1 Hz, 3H).

4.1.8. 4-(1-Methylpropa-1,2-dienyl)oxazolidin-2-one (17). The reaction was performed as described for allene **3**, with methoxy-oxazolidinone **26** (710 mg, 6.07 mmol),[20] 2-butynyltrimethylsilane **6b** (1.53 g, 12.1 mmol) and $BF_3{\cdot}OEt_2$ (15.4 mL, 12.1 mmol) in CH_2Cl_2 (15 mL). Stirring for 2 h at rt, followed by work-up and chromatography, gave **17** (312 mg, 2.21 mmol, 37%) as a colorless oil; R_f 0.4 (EtOAc); IR (neat) 3264, 1960, 1749; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (br s, 1H), 4.87–4.80 (m, 2H), 4.51 (t, J=8.4 Hz, 1H), 4.35–4.31 (m, 1H), 4.27–4.24 (m, 1H), 1.72 (t, J=3.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.3, 160.0, 97.6, 77.5, 68.8, 54.4, 13.7; HRMS (EI) calcd for $C_7H_9NO_2$ 139.0633, found 139.0628.

4.1.9. 6-Allyl-7-methyl-1,2,5,7a-tetrahydropyrrolizin-3-one (19). Allyl bromide (0.22 mL, 2.50 mmol), K_2CO_3 (138 mg, 1.00 mmol) and $PdCl_2(MeCN)_2$ (20 mg, 0.08 mmol) were added to a solution of allene **8** (69 mg, 0.50 mmol) in MeCN (5 mL). After stirring for 2 h at 75°C, the mixture was poured into brine (10 mL) and extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were washed with brine (10 mL), dried (Na_2SO_4) and concentrated in vacuo. Flash chromatography gave **19** (50 mg, 0.28 mmol, 56%) as a colorless oil; R_f 0.3 (EtOAc/PE 4:1); IR (neat) 2975, 2859, 1707; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72–5.62 (m, J=2×6.7, 10.0, 16.9 Hz, 1H), 5.02–5.97 (m, 2H), 4.48 (br m, 1H), 4.22 (d, J=14.9 Hz, 1H), 3.57 (d, J=14.9 Hz, 1H), 2.84–2.74 (m, 2H), 2.64 (ddd, J=8.3, 12.7, 16.1 Hz, 1H), 2.33–2.23 (m, 2H), 1.77–1.66 (m, 1H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 134.3, 131.9, 130.9, 116.2, 70.5, 51.6, 33.5, 30.9, 28.7, 9.5; HRMS (EI) calcd for $C_{11}H_{15}NO$ 177.1154, found 177.1148.

The reaction was also performed using allyl methyl carbonate: allene **8** (69 mg, 0.50 mmol) was dissolved in acetonitrile (5 mL). To this solution allyl methyl carbonate (0.29 ml, 2.50 mmol) and $PdCl_2(MeCN)_2$ (20 mg, 0.08 mmol) were added. The reaction mixture was stirred overnight at ambient temperature and was worked up in the same way as in the procedure mentioned above, giving **19** (33 mg, 0.24 mmol, 48%) as a colorless oil.

The reaction was also performed using a stoichiometric amount of allylpalladium chloride dimer: allene **8** (13 mg, 0.09 mmol) was dissolved in acetonitrile (2.5 mL). To this solution K_2CO_3 (28 mg, 0.20 mmol) and allylpalladium chloride dimer (17.7 mg, 0.05 mmol) were added. This

mixture was heated up to 75°C and stirred for 1.5 h. The work-up was performed as mentioned above, giving **19** (5.9 mg, 0.04 mmol, 48%) as a colorless oil.

4.1.10. 7-Methyl-6-(2-methylallyl)-1,2,5,7a-tetrahydropyrrolizin-3-one (20). The reaction was performed as described for pyrrolizinone **19** with allene **8** (69 mg, 0.5 mmol), 3-chloro-2-methylpropene (0.25 mL, 2.50 mmol), K_2CO_3 (138 mg, 1.00 mmol) and $PdCl_2(MeCN)_2$ (20 mg, 0.08 mmol) in MeCN (5 mL) at 75°C. Stirring for 2 h, followed by work-up and chromatography, gave **20** (22 mg, 0.12 mmol, 23%) as a colorless oil. Continued elution with EtOAc afforded starting material **8** (16 mg, 0.12 mmol, 23%). **19**: R_f 0.3 (EtOAc/PE 4:1); IR (neat) 2969, 2913, 2854, 1710; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (s, 1H), 4.66 (s, 1H), 4.53–4.50 (br m, 1H), 4.21 (d, *J*=14.9 Hz, 1H), 3.56 (d, *J*=14.9 Hz, 1H), 2.75 (br s, 2H), 2.66 (ddd, *J*=8.3, 12.7, 16.1 Hz, 1H), 2.36–2.26 (m, 2H), 1.78–1.68 (m, 1H), 1.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 142.0, 132.6, 130.9, 111.8, 70.6, 51.7, 35.0, 33.5, 28.9, 22.0, 9.6; HRMS (EI) calcd for $C_{12}H_{17}NO$ 191.1310, found 191.1308.

4.1.11. 6-Allyl-7-phenyl-1,2,5,7a-tetrahydropyrrolizin-3-one (21). The reaction was performed as described for pyrrolizinone **19** with allene **9** (200 mg, 1.00 mmol), allyl bromide (0.43 mL, 5.00 mmol), K_2CO_3 (278 mg, 2.01 mmol) and $PdCl_2(MeCN)_2$ (39 mg, 0.15 mmol) in MeCN (10 mL) at 75°C for 1 h. Work-up and flash chromatography gave **21** (173 mg, 0.72 mmol, 72%) as an oil; R_f 0.5 (EtOAc); IR (neat) 2975, 2853, 1703, 1386; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.33 (m, 2H), 7.29–7.25 (m, 1H), 7.23–7.19 (m, 2H), 5.84–5.74 (m, 1H), 5.12–5.06 (m, 3H), 4.49 (dd, *J*=3.6, 15.6 Hz, 1H), 3.72 (dd, *J*=3.7, 15.6 Hz, 1H), 3.04 (dd, *J*=6.1, 15.5 Hz, 1H), 2.89 (dd, *J*=6.1, 15.5 Hz, 1H), 2.67 (ddd, *J*=8.5, 12.6, 16.2 Hz, 1H), 2.35–2.26 (m, 2H), 1.81–1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 136.7, 134.2, 133.3, 134.0, 128.4, 127.4, 127.3, 116.7, 69.3, 52.2, 33.2, 31.8, 29.0; HRMS (EI) calcd for $C_{16}H_{17}NO$ 239.1310, found 239.1305.

4.1.12. 2-Allyl-1-methyl-6,7,8,8a-tetrahydroindolizin-5-one (22). The reaction was performed as described for pyrrolizinone **19** with allene **11** (76 mg, 0.50 mmol), allyl bromide (0.22 mL, 2.50 mmol), K_2CO_3 (138 mg, 1.00 mmol) and $Pd(MeCN)_2Cl_2$ (20 mg, 0.08 mmol) in MeCN (5 mL) at 75°C for 1 h. Work-up and flash chromatography gave **22** (63 mg, 0.33 mmol, 66%) as a colorless oil; R_f 0.3 (EtOAc); IR (neat) 2945, 2856, 1640; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76–5.66 (m, 1H, H-11), 5.07–5.00 (m, 2H), 4.40 (d, *J*=15.4 Hz, 1H), 4.14 (br d, *J*=10.5 Hz, 1H), 3.92 (d, *J*=15.4 Hz, 1H), 2.90–2.80 (m, 2H), 2.4 (ddd, *J*=2.6, 7.8, 17.8 Hz, 1H), 2.33 (ddd, *J*=8.0, 9.7, 17.8 Hz, 1H), 2.16–2.04 (m, 1H), 2.00–1.92 (m, 1H), 1.83–1.70 (m, 1H), 1.63 (s, 3H), 1.26–1.16 (dq, *J*=4.4, 12.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 134.3, 130.6, 128.8, 116.2, 67.5, 54.2, 30.6, 30.4, 27.4, 20.4, 10.2; HRMS calcd for $C_{12}H_{17}NO$ 191.1310, found 191.1306.

4.1.13. 6-Allyl-7-methyl-5,7a-dihydropyrrolo[1,2-*c*]oxazol-3-one (23). The reaction was performed as described for pyrrolizinone **19** with allene **17** (117 mg, 1.00 mmol), allyl bromide (0.43 mL, 5.00 mmol), K_2CO_3 (276 mg, 2.00 mmol) and $PdCl_2(MeCN)_2$ (26 mg, 0.10 mmol) in MeCN (10 mL) at 75°C for 2 h. Work-up and flash chromatography gave **23** (89 mg, 0.49 mmol, 49%) as a colorless oil; IR (neat) 2974, 2911, 2854, 1753; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74–5.64 (m, 1H), 5.05–5.01 (m, 2H), 4.56 (br m, 1H), 4.50 (t, *J*=8.5 Hz, 1H), 4.22 (d, *J*=14.8 Hz, 1H), 4.21 (dd, *J*=4.7, 8.3 Hz, 1H), 3.75 (d, *J*=14.8, 1H), 2.89–2.78 (m, 2H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 133.8, 133.5, 133.0, 116.4, 67.7, 67.4, 56.7, 30.5, 9.4; HRMS (EI) calcd for $C_{10}H_{13}NO_2$ 179.0946, found 179.0951.

4.1.14. (4*S*,5*R*)-5-(1-Methylpropa-1,2-dienyl)-4-(*tert*-butyldimethylsilyloxy)-pyrrolidin-2-one (24). To a solution of allene **14** (30 mg, 0.15 mmol) in methanol (1.5 mL) K_2CO_3 (3 mg) was added and the reaction was stirred at rt for 1 h. Et_2O (15 mL) was added and the mixture was filtered over Celite. The filter was washed with Et_2O (45 mL) and CH_2Cl_2 (45 mL), followed by concentration of the filtrates in vacuo. The residue was dissolved in DMF (1mL), and imidazole (21.0 mg, 0.31 mmol), TBDMSCl (25.5 mg, 0.17 mmol) and DMAP (4 mg) were added. After stirring for 4 h, extra imidazole (10.5 mg, 0.15 mmol) and TBDMSCl (12.8 mg, 0.08 mmol) were added and the solution was stirred for an additional 18 h. DMF was evaporated in vacuo and the product was purified using flash chromatography giving **24** (24.5 mg, 0.09 mmol, 60%) as white crystals; mp 76–79°C; R_f 0.3 (EtOAc/PE 1:1); $[\alpha]_D$+41.1 (*c* 1.2, $CHCl_3$); IR (neat) 3214, 2930, 1960, 1710; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (br s, 1H), 4.76 (t, *J*=2.7 Hz, 2H), 4.31–4.28 (m, 1H), 3.90–3.81 (m, 1H), 2.59 (dd, *J*=6.7, 16.9 Hz, 1H), 2.22 (dd, *J*=3.9, 16.9 Hz, 1H), 1.70 (t, *J*=3.1 Hz, 3H), 0.87 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.1, 175.5, 97.8, 77.2, 72.2, 65.3, 40.0, 25.5, 17.8, 15.0, −4.8, −5.0; HRMS (FAB) calcd. for $C_{14}H_{26}NO_2Si$ (MH^+) 268.1733, found 268.1725.

4.1.15. (1*S*,7a*R*)-6-Allyl-1-(*tert*-Butyldimethylsilyloxy)-7-methyl-1,2,5,7a-tetrahydropyrrolizin-3-one (25). The reaction was performed as described for pyrrolizinone **19** with allene **24** (24.5 mg, 0.09 mmol), allyl bromide (0.04 mL, 0.46 mmol), K_2CO_3 (25 mg, 0.18 mmol) and $PdCl_2(MeCN)_2$ (3 mg, 0.01 mmol) in MeCN (1 mL) at 75°C for 3 h. Work-up and flash chromatography gave **24** (12 mg, 0.04 mmol, 43%) as a white solid; mp 33–35°C; $[\alpha]_D$=+61.8 (*c* 0.60, $CHCl_3$); IR (neat) 2955, 2929, 2857, 1714; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74–5.64 (m, 1H), 5.05–5.01 (m, 2H), 4.28–4.16 (m, 3H), 3.58 (d, *J*=14.6 Hz, 1H), 2.88–2.77 (m, 2H), 2.58 (dd, *J*=9.8, 15.3 Hz, 1H), 2.53 (dd, *J*=7.5, 15.3 Hz, 1H), 1.71 (s, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174, 134.2, 131.6, 130.7, 116.4, 77.8, 75.1, 51.6, 43.4, 30.9, 25.6, 17.7, 10.1, −4.2, −5.1; HRMS (EI) calcd for $C_{17}H_{29}NO_2Si$ 307.1968, found 307.1970.

5. Conclusion

In conclusion, the preparation of allenyl substituted lactams was described by means of *N*-acyliminium ion reactions between imide derived *N*,*O*-acetals and several propargylsilanes. These allenes could be efficiently cyclized to densely functionalized pyrrolizidinones and indolizidinones,

using $PdCl_2(MeCN)_2$ and allyl halides or carbonates, provided that they a contained a substituent on the internal carbon atom of the allene.

Acknowledgements

This research was financially supported (in part) by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW–NWO).

References

1. For example, see: Gribble, G. W., Gilchrist, T. L., Eds.; *Progress in Heterocyclic Chemistry*; Pergamon: Oxford, 2000; Vol. 12.
2. For recent reviews on palladium in organic synthesis, see: (a) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley & Sons: New York, 1995. (b) Bäckvall, J. E. In *Metal-catalyzed Cross Coupling Reactions*; Stang, P., Diederich, F., Eds.; VCH: Weinheim, 1998; pp. 339–382.
3. For general reviews on metal-catalyzed amination, see: (a) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675. (b) Johanssen, M.; Jorgensen, K. A. *Chem. Rev.* **1998**, *98*, 1639.
4. For reviews on allene chemistry, see: (a) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley-Interscience: New York, 1984. (b) Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805. (c) Smadja, W. *Chem. Rev.* **1983**, *83*, 263. (d) Munson, J. W. In *The Chemistry of Ketenes, Allenes and Related Compounds, Part 1*; Patai, S., Ed.; Wiley-Interscience: New York, 1980; p. 165.
5. For a review on palladium–allene chemistry, see: Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067.
6. For oxygen nucleophiles, see for example: (a) Kang, S. K.; Yamaguchi, T.; Pyung, S. J.; Lee, Y. T.; Baik, T. G. *Tetrahedron Lett.* **1998**, *39*, 2127. (b) Ma, S.; Shi, Z. *J. Org. Chem.* **1998**, *63*, 6387. (c) Jonasson, C.; Bäckvall, J. E. *Tetrahedron Lett.* **1998**, *39*, 3601. (d) Walkup, R. D.; Guan, L.; Kim, L. S.; Kim, S. W. *Tetrahedron Lett.* **1995**, *36*, 3805. (e) Walkup, R. D.; Guan, L.; Kim, S. W.; Kim, Y. S. *Synlett* **1993**, 88. (f) Besson, L.; Bazin, J.; Goré, J.; Cazes, B. *Tetrahedron Lett.* **1994**, *35*, 2881.
7. For nitrogen nucleophiles, see: (a) Trost, B. M.; Pinkerton, A. B.; Kremzow, D. *J. Am. Chem. Soc.* **2000**, *122*, 12007. (b) Chang, H. M.; Cheng, C. H. *J. Chem. Soc. Perkin Trans. 1* **2000**, 3799. (c) Jonasson, C.; Horvath, A.; Bäckvall, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 9600. (d) Kang, S. K.; Baik, T. G.; Hur, Y. *Tetrahedron* **1999**, *55*, 6863. (e) Kang, S. K.; Baik, T. G.; Kulak, A. N. *Synlett* **1999**, 324. (f) Ohno, H.; Toda, A.; Miwa, Y.; Taga, T.; Osawa, E.; Yamaoka, Y.; Fujii, N.; Ibuka, T. *J. Org. Chem.* **1999**, *64*, 2992. (g) Anzai, M.; Toda, A.; Ohno, H.; Takemoto, Y.; Fujii, N.; Ibuka, T. *Tetrahedron Lett.* **1999**, *40*, 7393. (h) Zenner, J. M.; Larock, R. C. *J. Org. Chem.* **1999**, *64*, 7312. (i) Larock, R. C.; He, Y.; Leong, W. W.; Han, X.; Refvik, M. D.; Zenner, J. M. *J. Org. Chem.* **1998**, *63*, 2154. (j) Diederen, J. H.; Sinkeldam, R. W.; Frühauf, H. W.; Hiemstra, H.; Vrieze, K. *Tetrahedron Lett.* **1998**, *39*, 5421. (k) Meguro, M.; Yamamoto, Y. *Tetrahedron Lett.* **1998**, *39*, 5421. (l) Desarbre, E.; Mérour, J. Y. *Tetrahedron Lett.* **1996**, *37*, 43. (m) Davies, I. W.; Scopes, D. I. C.; Gallagher, T. *Synlett* **1993**, 85. (n) Tamaru, Y.; Kimura, M. *Synlett* **1997**, 749. (o) Kimura, M.; Tanaka, S.; Tamaru, Y. *J. Org. Chem.* **1995**, *60*, 3764.
8. Prasad, J. S.; Liebeskind, L. S. *Tetrahedron Lett.* **1988**, *29*, 4257.
9. Hiemstra, H.; Fortgens, H. P.; Speckamp, W. N. *Tetrahedron Lett.* **1984**, *25*, 3115.
10. For reviews, see: (a) Speckamp, W. N.; Moolenaar, M. J. *Tetrahedron* **2000**, *56*, 3817. (b) De Koning, H.; Moolenaar, M. J.; Hiemstra, H.; Speckamp, W. N. In *Studies in Natural Products Chemistry*; Atta-ur-Rahman, W. N., Ed.; Elsevier: Amsterdam, 1993; Vol. 13, p. 473. (c) Hiemstra, H.; Speckamp, W. N. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 2, p. 1047.
11. For acetylenic lactams, see: Karstens, W. F. J.; Stol, M.; Rutjes, F. P. J. T.; Kooijman, H.; Spek, A. L.; Hiemstra, H. *J. Organomet. Chem.* **2001**, *624*, 245.
12. For allene containing lactams, see: (a) Karstens, W. F. J.; Rutjes, F. P. J. T.; Hiemstra, H. *Tetrahedron Lett.* **1997**, *38*, 6275. (b) Karstens, W. F. J.; Stol, M.; Rutjes, F. P. J. T.; Hiemstra, H. *Synlett* **1998**, 1126. (c) Jonasson, C.; Karstens, W. F. J.; Hiemstra, H.; Bäckvall, J. E. *Tetrahedron Lett.* **2000**, *41*, 1619.
13. (a) Rutjes, F. P. J. T.; Tjen, K. C. M. F.; Wolf, L. B.; Karstens, W. F. J.; Schoemaker, H. E.; Hiemstra, H. *Org. Lett.* **1999**, *1*, 717. (b) Wolf, L. B.; Tjen, K. C. M. F.; Rutjes, F. P. J. T.; Hiemstra, H.; Schoemaker, H. E. *Tetrahedron Lett.* **1998**, *39*, 5081.
14. For example, see: Klaver, W. J.; Moolenaar, M. J.; Hiemstra, H.; Speckamp, W. N. *Tetrahedron* **1988**, *44*, 3805.
15. Brandsma, L.; Verkruijsse, H. D. In *Allenes and Cumulenes: a Laboratory Manual*; Elsevier: Amsterdam, 1981; p. 16.
16. Iyer, S.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1987**, *109*, 2759.
17. Alami, M.; Ferri, F.; Linstrumelle, G. *Tetrahedron Lett.* **1993**, *34*, 6403.
18. (a) Hubert, J. C.; Steege, W.; Speckamp, W. N.; Huisman, H. O. *Synth. Commun.* **1971**, *1*, 103. (b) Hubert, J. C.; Wijnberg, J. B. P. A.; Speckamp, W. N. *Tetrahedron* **1975**, *31*, 1437.
19. (a) Koot, W. J. *Synthesis and Applications of (R)-1-Acetyl-5-isopropoxy-3-pyrrolin-2-one*. Ph.D. Thesis, University of Amsterdam: The Netherlands, 1993. (b) Louwrier, S. *Studies towards the Synthesis of Ptilomycalin A*. Ph.D. Thesis, University of Amsterdam: The Netherlands, 1996. (c) Chamberlin, A. R.; Chung, J. Y. L. *J. Am. Chem. Soc.* **1983**, *105*, 3653.
20. Shono, T.; Matsumura, Y.; Uchida, K.; Kobayashi, H. *J. Org. Chem.* **1985**, *50*, 3243.
21. For a stoichiometric example, see: Medema, D.; van Helden, R. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 304.
22. Although unfavorable, 5-*endo-trig* cyclizations are well known. For examples, see e.g.: Trost, B. M. *Angew. Chem. Int. Ed.* **1986**, *25*, 1.
23. Pornet, J.; Kolani, N.; Mesnard, D.; Miginiac, L.; Jaworski, K. *J. Organomet. Chem.* **1982**, *236*, 177.