The Intramolecular Heck Reaction and the Synthesis of Indolizidinone, Quinolizidinone and Benzoazepinone Derivatives

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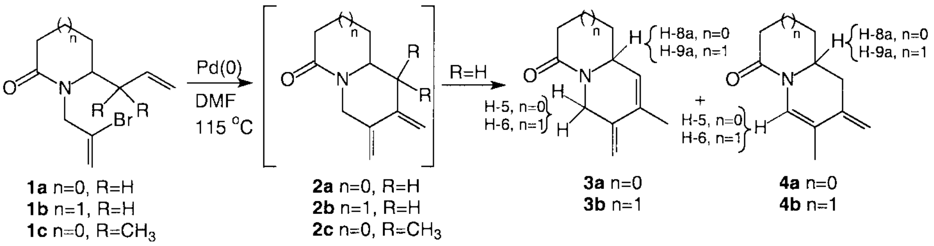
Abstract: The intramolecular Heck cyclization of *N*-allyl-, -aryl- or -benzyl-5-allyl-2-pyrrolidinones and *N*-allyl-, -aryl- or -benzyl-6-allyl-2-piperidinones (**1a**–**f**), prepared through allyltrimethylsilane addition to the corresponding cyclic *N*-acyliminium ions, afforded indolizidinones (**3a**, **5a**, **5b**), quinolizidinones (**3b**, **4b)** and benzoazepinones (**7a**, **8a**, **7b**, **8b)** in moderate to good yields (56–90%). Exclusive *exo*-trig over *endo*-trig mode of cyclization was observed in all examples investigated, and it was accompanied by double bond migration, which precluded our attempts of a one-pot tandem Diels–Alder cycloaddition with dienophiles such as maleic anhydride, methyl vinyl ketone and diethyl azodicarboxylate. Catalytic hydrogenation of a 2:1 mixture of regioisomeric indolizidinones **5a**–**5b** afforded the stereoisomerically enriched *cis* indolizidinone **6a** (20:1 mixture) in quantitative yield. A similar behavior was observed in the catalytic hydrogenation of regioisomeric benzoazepinones **7b**–**8b**.

Key words: Heck reaction, intramolecular cylization, hydrogenation

Over the last decade palladium-catalyzed reactions have emerged as extremely versatile methods for the synthesis of highly complex carbo- and heterocyclic systems.[1] The coupling of vinyl or aryl halides, triflates or similar intermediates with alkenes under palladium(0) catalysis is known as the Heck reaction and both its inter- and intramolecular versions are powerful tools in organic synthesis due to their chemo- and regioselectivity, mild reaction conditions and efficiency.[2] In particular, the Heck reaction has proved its synthetic value when incorporated in a tandem process, which allows the regio- and stereocontrolled formation of several bonds and/or ring systems in a single synthetic operation.[3] An interesting sequence for the construction of bicyclic systems containing at least one six membered ring arises when an intramolecular Heck reaction or palladium-catalyzed enyne cycloisomerization, which gives a vicinal *exo*-bismethylene cycloalkane is immediately followed by a Diels–Alder reaction.[4]

The intramolecular Heck coupling of bromodialkenyl amines, lactams and ethers has been reported[5] and recently de Meijere[6] and coworkers described the formation of substituted tetrahydroisoindolines, tetrahydroisoindolin-1-ones and hexahydrobenzo[*c*]furans through the intramolecular 5-*exo* cyclization of 2-bromo-4-aza- and 2-bromo-4-oxa-1,6-dienes, followed by in situ [4+2] cycloaddition.

As part of our current interest in the synthesis of pyrrolizidine and indolizidine alkaloids,[7] we were attracted to study the regiochemistry of the intramolecular Heck reaction when applied to 2-allyl lactams derived from 2-pyrrolidinone and 2-piperidinone. These compounds feature a 2-bromo-4-aza-1,7-diene moiety amenable to undergo either a 6-*exo*-trig or a 7-*endo*-trig cyclization. Additionally, the intramolecular 7-*exo*-trig vs. 8-*endo*-trig Heck reaction of *N*-(*o*-halobenzyl)-2-allyllactams was envisioned as a short approach to benzoazepine derivatives. Lactams **1a**–**f** were prepared in good yields from the corresponding imides according to literature procedure[8] after $LiBEt_3H$ reduction to the corresponding ethoxylactams, followed by $BF_3·OEt_2$ promoted addition of allyltrimethylsilane. Our first choice of reaction conditions for the intramolecular Heck reaction with **1a** included the use of 5 mol% palladium acetate as catalyst, (which is assumed to be reduced in situ to palladium(0) species by the solvent, amine or the added ligand)[9] degassed DMF as solvent,



Scheme 1

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triphenylphosphine (10 mol%) and potassium carbonate (10 equiv) or triethylamine (1.2 equiv) as base. Under these conditions, a smooth reaction ensued upon heating at 115 ºC under an inert atmosphere and indolizidinone **3a** was isolated in 56% yield after column chromatography. The same results were observed when tri-*o*-tolylphosphine[10] or DIPHOS were employed whereas attempts to carry out the cyclization in acetonitrile were unsuccessful (Table).

The reaction product was characterized by the absence of the stretching of the C_{sp2}−Br at 920 cm^{-1} in the IR spectrum and by significant changes in the δ 3.50−5.70 region of its ^1H NMR spectrum as compared to the same region for **1a**: H−8a appeared at δ 4.26 as a broad triplet (^3J = 6.0 Hz), the olefinic protons of the exocyclic methylene as doublets (^2J = 1.5 Hz) at δ 4.99 and 5.09 and the endocyclic hydrogen H−8 as a singlet at δ 5.63. The presence of a methyl group at δ 1.86 as a singlet and of the two methylenic hydrogens at C−5 as doublets (^2J = 15.4 Hz) at δ 3.57 and 4.70 were diagnostic for the assignment of structure **3a** to the isolated indolizidinone (HRMS *m/z*: [M^+] calcd for $C_{10}H_{13}NO$, 163.0997; found, 163.0994). The downfield shift observed for one of the hydrogens at C-5 (Δδ 1.13) was assigned to the anisotropic shift of the carbonyl group as inspection of molecular models and geometry optimization by ab initio method (HF/6-31g(d)) revealed the coplanar orientation of one of the hydrogens at C-5 and the carbonyl group.[11]

The isolation of **3a** as the sole product was rationalized as involving the initial formation of the *exo*-bismethylene **2a** followed by prototropic shift promoted either thermally or through a sequence of β-hydride elimination, re-addition of a hydridopalladium species and elimination as observed in the arylation of allylic alcohols.[12]

In our case, changing the base from triethylamine to potassium carbonate[13] did not avoid prototropic shift. Attempts to carry out the reaction at lower temperatures using the conditions described by Jeffery[14] (tetrabutyl ammonium chloride as phase-transfer catalyst and potassium carbonate as base) were unsuccessful and the intramolecular coupling with this catalytic system was only observed above 100 ºC with exclusive formation of **3a** in 52% yield.

A final attempt to preclude double bond migration during cyclization of **1a** involved the use of silver carbonate as a halide scavenger[6,15] but no reaction was observed in the presence of either triphenylphosphine or DIPHOS even after 7 d at 115 ºC. The lack of reactivity with these catalytic systems contrasts with the results by de Meijere and coworkers[6] for the 5-*exo*-trig cyclization of 2-bromo-4-aza-1,6-dienes and was rationalized through the intervention of a stable cationic palladium intermediate (Figure)

An analogous reactivity pattern emerged for 2-allyllactam **1b**. No cyclization was observed when silver carbonate was employed but a 5:1−6.4:1 diastereomeric mixture of quinolizidinones **3b**–**4b** was formed when potassium carbonate or triethylamine was used as the base (Table). This mixture is readily separable by silica gel column chromatography. The ^1H NMR spectrum of the major regioisomer **3b** closely resembled that of **3a** with the major differences being the downfield shift of H-6 (δ 5.22 and 3.28) and an upfield shift of H-9a (δ 4.04) that appeared as a broad doublet (^3J = 5.0 Hz). The structural assignment of **4b** emerged from its ^1H NMR spectrum, which

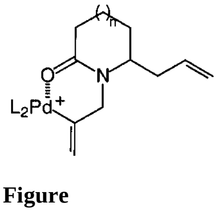
Table Intramolecular Heck Reaction of **1a** and **1b** (Scheme 1)

Entry	Substrate	Method[a]	Ratio (**3**:**4**)	Yield (%)[c]
1	**1a**	A, B, E	1:0	55
2	**1a**	C[b], I[b], L[b]	–	–
3	**1a**	D	1:0	56
4	**1a**	F, J	1:0	52
5	**1a**	G, K	1:0	50
6	**1a**	H	1:0	53
7	**1a**	I	–	–
8	**1b**	A	5.2:1	74
9	**1b**	B	6:1	70
10	**1b**	C[b], I[b], L[b]	–	–
11	**1b**	D	5:1	60
12	**1b**	E	6.4:1	52
13	**1b**	F	6.4:1	67
14	**1b**	G	5.8:1	68
15	**1b**	H, J, K	5:1	48

[a] Reaction temperature: 115 ºC; reaction time: 12 h.

[b] Quantitative substrate recovery.

[c] Isolated yield after column chromatography; Conditions: (**A**): 0.02 equiv $Pd(OAc)_2$, 0.04 equiv PPh_3, 10 equiv K_2CO_3, DMF (**B**): 0.02 equiv $Pd(OAc)_2$, 0.04 equiv. PPh_3, 1.2 equiv Et_3N, DMF (**C**): 0.02 equiv $Pd(OAc)_2$, 0.04 equiv PPh_3, 2.0 equiv Ag_2CO_3, DMF (**D**): 0.02 equiv $Pd(OAc)_2$, 0.04 equiv P(*o*-tol)$_3$, 10 equiv K_2CO_3, DMF (**E**): 0.02 equiv $Pd(OAc)_2$, 0.04 equiv P(*o*-tol)$_3$, 1.2 equiv Et_3N, DMF (**F**): 0.02 equiv $Pd(OAc)_2$, 0.04 equiv PPh_3, 10 equiv K_2CO_3, 1.2 equiv Bu_4NCl, DMF (**G**): 0.02 equiv $Pd(OAc)_2$, 0.04 equiv PPh_3, 1.2 equiv Et_3N, 1.2 equiv Bu_4NCl, DMF (**H**): 0.02 equiv $Pd(OAc)_2$, 0.04 equiv DIPHOS, 10 equiv K_2CO_3, DMF (**I**): 0.02 equiv $Pd(OAc)_2$, 0.04 equiv DIPHOS, 2.0 equiv Ag_2CO_3, DMF (**J**): 0.02 equiv $Pd(Ph_3)_4$, 0.04 equiv PPh_3, 10 equiv K_2CO_3, DMF (**K**): 0.02 equiv $Pd(Ph_3)_4$, 0.04 equiv PPh_3, 1.2 equiv Et_3N, DMF (**L**): 0.02 equiv $Pd(Ph_3)_4$, 0.04 equiv PPh_3, 2.0 equiv Ag_2CO_3, DMF.



Figure

featured the strongly deshielded H−6 as a singlet at δ 7.21 and H-9a as a multiplet at δ 3.54. The formation of regioisomers **3b** and **4b** was not thermally promoted as no interconversion was observed even under extended heating (Condition A, Table: 5 d at 115 ºC).

Despite the elusive nature of the *exo* bismethylene intermediates **2a** and **2b**, we attempted their in situ [4+2] cycloaddition with several dienophiles, such as maleic anhydride, methyl vinyl ketone and diethyl azodicarboxylate under conditions A and B, described in Table. In each case, only indolizidinone **3a** (from **2a**) and quinolizidinones **3b** and **4b** (from **2b**) were formed.

When double bond isomerization to the C7-C8 position was blocked, intramolecular cyclization of **1c** (condition A, Table) afforded *exo* bismethylenic indolizidinone **2c** in 65% yield characterized by the presence of four terminal olefinic hydrogens (δ 5.06, 4.90 and 4.84) in ^{1}H NMR spectrum and two CH_2 in the olefinic region (δ 112.3 and 108.5) in ^{13}C NMR spectrum. Interestingly, double bond migration to the C5-C6 position was not observed but attempts to trap **2c** in situ with maleic anhydride failed.

An additional example for the preference of 6-*exo*-trig vs. 7-*endo*-trig with double bond migration emerged from the intramolecular cyclization of lactam **1d**, readily prepared from succinic anhydride after 3 steps. Under condition A, depicted in the Table, a 2:1 molar ratio of indolizidinones **5a** and **5b** (74% combined yield) were isolated, however they were inseparable by flash chromatography (Scheme 2).

Fortunately, hydrogenation of a 2:1 mixture of regioisomers **5a** and **5b** in methanol and palladium over carbon as catalyst afforded a 20:1 mixture of stereoisomeric indolizidinones **6a** and **6b** in quantitative yield (Scheme 2). The *cis* relationship of the hydrogens at C-5 and C-6a in the major isomer **6a** was corroborated by NOE increments observed at H-6a (2.3%) upon irradiation at H-5 and at H-5 (3.4%) upon irradiation at H-6a. No increment in the intensity of the methyl absorption was observed upon irradiation of H-6a. The reason for the high diastereoisomeric ratio, which accompanied hydrogenation of the mixture of regioisomers **5a**–**5b** has not being fully explored but it may be associated with double bond migration from exocyclic to the endocyclic position before reduction.

The study on regioselectivity of the intramolecular Heck reactions was next extended to lactams **1e** and **1f**, which could conceivably undergo a 7-*exo*-trig or a 8-*endo*-trig cyclization. In fact, only products arising from 7-*exo*-trig cyclization were isolated from **1e** (6.5:1 mixture of benzoazepines **7a** and **8a**, in 80% combined yield) and from **1f** (2:1 mixture of **7b** and **8b**, in 90% combined yield) when condition A was employed (Table, Scheme 3).

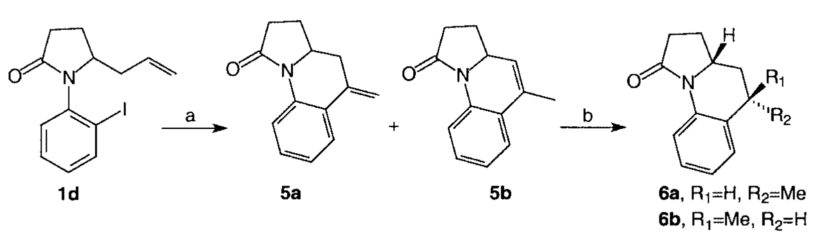
The structure of the major isomer formed from **1e** was unambiguously established by NMR spectroscopy: the presence of two olefinic hydrogens as doublets (^2J = 1.5 Hz) at δ 5.25 and δ 5.20 together with the absence of a methyl signal in the ^{1}H NMR spectrum and an olefinic methylene at δ 117.1 in the corresponding ^{13}C NMR spectrum fully agree with **7a** as the major benzoazepine.

As before, the mixtures of regioisomers obtained from **1e** and **1f** were inseparable by flash chromatography on silica gel and benzoazepines **7a**–**8a** and **7b**–**8b** were hydrogenated under the conditions described previously for **5a**–**5b**. In both cases, the *cis* isomer was obtained preferentially with some erosion of diastereoselectivity observed for **7a**–**8a** (4.5:1 molar ratio of **9a**–**10a**, in 94% yield) while a significant increment in the *cis*–*trans* ratio was observed in the hydrogenation of an equimolar mixture of **7b**–**8b** (6.5:1 mixture of **9b**–**10b**, in 98% yield).

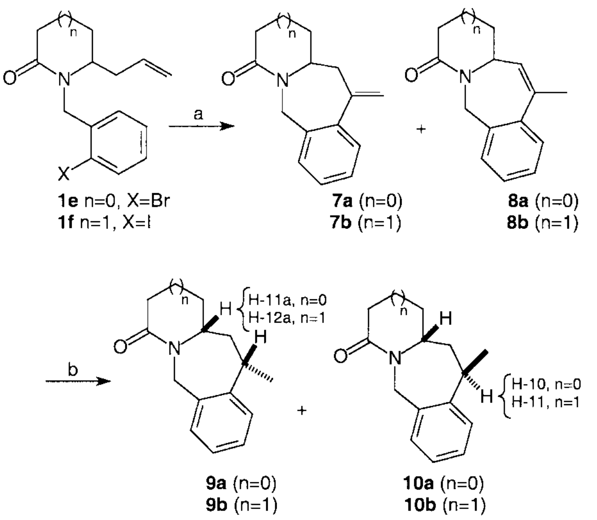
The *cis* configuration of **9a** was assigned after NOE experiments with an analytically pure sample obtained after flash chromatography on silica gel: a 3.2% increment in the H-11a signal was observed upon irradiation of H-10 while a 2.6% enhancement in the H-10 signal was observed upon irradiation of H-11a. Only 0.8% increment was observed in the methyl doublet signal when H-11a was irradiated. Even stronger increments were observed when **9b** was submitted to NOE studies: irradiation of H-11 led to a 8.4% enhancement of H−12a signal while 4.7% increment of H-11 signal was observed upon irradiation of H-12a.

Allyltrimethylsilane addition to *N*-acyliminium ions derived from succinimide and glutarimide provided an expeditious access to 5-allyl lactams **1a**−**f** in moderate to good yields. The intramolecular Heck cyclization of lactam **1a** was extensively investigated and indolizidinone **3a** was formed exclusively in moderate yields (50−56%) through a 6-*exo*-trig pathway. Lactam **1a** was recovered when Ag_2CO_3 was employed as base.

An analogous reactivity pattern was observed in the cyclization of **1b** and mixtures (5:1, 6.4:1) of indolizidinones **3b** and **4b** were isolated in moderate to good yields (48−74%). An additional example of the preference for a



Scheme 2 a) 0.02 equiv Pd $(OAc)_2$, 0.04 equiv PPh_3, 10 equiv K_2CO_3, DMF, 115 °C (**5a**:**5b**, 2:1, 74%); b) H_2, Pd/C, MeOH, r.t. (100%).



Scheme 3 a) 0.02 equiv Pd (OAc)$_2$, 0.04 equiv PPh$_3$, 10 equiv K$_2$CO$_3$, DMF, 115 °C (**7a**:**8a**, 6.5:1, 80%; **7b**:**9b**, 2:1, 90%); b) H$_2$, Pd/C, MeOH, r.t. (**9a**:**10a**, 4.5:1, 94%; **9b**:**10b**, 6.5:1, 98%).

6-*exo*-trig vs. 7-*endo*-trig process came from the intramolecular cyclization of lactam **1d**, which provided a 2:1 mixture of indolizidinones **5a** and **5b** (74% yield). Surprisingly, catalytic hydrogenation stereoselectively converted the above mixture to *cis*-**6a** (20:1 ratio) in quantitative yield.

Despite the propensity for double bond migration of the putative *exo* bismethylene intermediates **2a** and **2b**, attempts to carry out a one−pot tandem [4+2] cycloadditon with maleic anhydride, methylvinylketone and diethyl azodicarboxylate were unsuccessful. When double bond migration was precluded in lactam **1c**, the corresponding *exo*−bismethylene intermediate was isolated in 65% yield. Finally, exclusive 7-*exo*-trig cyclization was observed for lactams **1e** and **1f** and benzoazepines **7a**–**8a** (4.5:1 ratio) and **7b**–**8b** (6.5:1 ratio) were formed in good yields. The results described here provide an attractive route to indolizidinones, quinolizidinones and benzodiazepinones and the utilization of this approach in the total synthesis of alkaloids will be investigated.

^{1}H and ^{13}C NMR spectra were recorded at 300.1 MHz and 75.4 MHz, respectively, on a Varian Gemini 2000 instrument using CDCl$_3$ as solvent and tetramethylsilane as the internal standard, unless otherwise noted. Chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. Signal multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), double dublet (dd), double triplet (dt), q (quartet), dq (double quartet), m (multiplet), quint (quintet). Infrared spectra were recorded as film on KBr cells on a Nicolet Impact 410 FT-IR instrument and the wavenumbers are expressed in cm^{-1}. Melting points were measured with an Eletrothermal AZ9003 MK3 apparatus and are uncorrected. GC analyses were recorded on Hewlett-Packard 5890 instrument, and GC-MS analyses were recorded on Hewlett-Packard 5890 coupled to HP-5988. HRMS analyses were recorded on Micromass VGAutoSpec instrument.Column chromatography was preformed with silica gel (70−230 Mesh).

N-2-Bromopropenyl-5-allylpyrrolidin-2-one (1a)

To a solution of *N*-2-bromopropenyl-5-ethoxy-2-pyrrolidin-2-one[16] (0.412 g, 1.14 mmol) in CH$_2$Cl$_2$ (5.70 mL) at 0 °C was added allyltrimethylsilane (0.262 g, 2.29 mmol). To the resulting solution was added BF$_3$·OEt$_2$ (0.486 g, 0.421 mL, 3.42 mmol). The mixture was stirred at 0 °C for 12 h and quenched by the addition of 1% NaHCO$_3$ solution (5.7 mL). The layers were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 5.7 mL). The combined organic layers was dried (MgSO$_4$), filtered and concentrated under reduced pressure, the residue was purified by column chromatography (hexane−EtOAc, 1:1) to afford **1a** in 59% yield as a colorless oil.

IR (KBr): 3073, 2979, 2915, 1700, 1646, 1631, 1443, 1428 and 922 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 1.76−1.85 (m, 1 H, C*H*$_2$CH$_2$), 2.10−2.33 (m, 2 H, C*H*$_2$CH$_2$ and C*H*$_2$CH=), 2.35−2.46 (m, 3 H, C*H*$_2$CO and C*H*$_2$CH=), 3.74 (d, *J* =15.7, 1 H, C*H*$_2$N), 3.70−3.76 (m, 1 H, C*H*N), 4.65 (d, *J* = 15.7, 1 H, C*H*$_2$N), 5.16 (d, 1 H, *J* =16.1, C*H*$_2$=CH), 5.17 (d, 1 H, *J* =17.6, C*H*$_2$=CH), 5.62−5.80 (m, 3 H, C*H*$_2$=CBr and C*H*=CH$_2$).

^{13}C NMR (CDCl$_3$): δ 23.6 (*C*H$_2$CH$_2$), 30.0 (*C*H$_2$CO), 37.6 (*C*H$_2$CH=), 48.5 (*C*H$_2$N), 56.7 (*C*HN), 119.5 (*C*H$_2$=CH), 119.7 (*C*H$_2$=CBr), 128.9 (*C*Br), 133.2 (*C*H=CH$_2$) and 176.0 (*C*O).

HRMS (EI): *m/z* calcd for C$_{10}$H$_{14}$NOBr, 245.0239. Found: 245.0242.

N-2-Bromopropenyl-6-allylpiperidin-2-one (1b)

The same procedure as described above for **1a** was employed starting from *N*-2-bromopropenyl-5-ethoxypiperidin-2-one.[16] After evaporation under reduced pressure, the residue was purified by column chromatography (hexane−EtOAc, 1:1) to afford **1b** in 55% yield as a grey oil.

IR (KBr): 3082, 2959, 1650, 1445, 1426 and 922 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 1.76−1.80 (m, 1 H, C*H*$_2$CH$_2$CO), 1.80−1.96 (m, 3 H, C*H*$_2$CH$_2$CO and C*H*$_2$CH$_2$CH$_2$), 2.21−2.39 (m, 1 H, C*H*$_2$CH=), 2.40−2.49 (m, 3 H, C*H*$_2$CH= and C*H*$_2$CO), 3.46−3.55 (m, 1 H, C*H*N), 3.67 (d, *J* = 15.0, 1 H, C*H*$_2$N), 5.00 (d, *J* = 15.0, 1 H, C*H*$_2$N), 5.10−5.20 (m, 2 H, C*H*$_2$=CHCH$_2$), 5.60−5.78 (m, 3 H, C*H*$_2$=CBr and C*H*=CH$_2$).

^{13}C NMR (CDCl$_3$): δ 17.3 (*C*H$_2$CH$_2$CH$_2$), 26.5 (*C*H$_2$CH$_2$CO), 32.1 (*C*H$_2$CO), 37.3 (*C*H$_2$N), 51.9 (*C*H$_2$CH=), 55.8 (*C*HN), 118.7 (*C*H$_2$=CBr), 119.0 (*C*H$_2$=CHCH$_2$), 129.4 (*C*Br), 134.4 (*C*H=CH$_2$), 171.2 (*C*O).

GC-MS (70 eV): *m/z* (%) = 218 (98), 216 (100), 178 (39), 98 (14).

HRMS (CI: *iso*-butane): *m/z* calcd for C$_{11}$H$_{16}$NOBr: 257.0415. Found: 259.0395, 257.0420 and 259.0400.

N-2-Bromopropenyl-5-(1,1-dimethylallylpyrrolidin-2-one (1c)

The same procedure as described above for **1a** was employed except (3,3−dimethylallyl)tributylstannane (2.0 equiv) was used instead of allyltrimethylsilane. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (hexane−EtOAc, 1:1) to afford **1c** in 40% yield as a grey oil.

IR (KBr): 3084, 2964, 2929, 2875, 1697, 1633, 1415 and 914 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$): δ 1.01 (s, 3 H, C*H*$_3$), 1.02 (s, 3 H, C*H*$_3$), 1.94 (m, 1 H, C*H*$_2$CH$_2$CO), 2.03−2.10 (m, 1 H, C*H*$_2$CH$_2$CO), 2.33−2.43 (m, 2 H, C*H*$_2$CO), 3.50 (dd, *J* = 9.0 and 2.7, 1 H, C*H*N), 3.90 (d, *J* = 15.9, 1 H, C*H*$_2$N), 4.78 (d, *J* = 15.9, 1 H, C*H*$_2$N), 5.06 (dd, *J* = 17.6 and 1.0, 1 H, C*H*$_2$=CH), 5.07 (dd, *J* = 10.5, 1.0, 1 H, C*H*$_2$=CH), 5.63 (dd, *J* = 3.5, 2.0, 1 H, C*H*$_2$=CBr), 5.73 (dd, *J* = 3.5, 2.0, 1 H, C*H*$_2$=CBr), 5.83 (dd, *J* = 17.6, 10.5, 1 H, C*H*=CH$_2$).

^{13}C NMR (125 MHz, CDCl$_3$): δ 21.8 (*C*H$_3$), 22.0 (*C*H$_2$CH$_2$CO), 25.9 (*C*H$_3$), 30.9 (*C*H$_2$CO), 42.7 (*C*CH$_3$), 51.2 (*C*H$_2$N), 65.5 (*C*HN), 113.5 (*C*H$_2$=CH), 120.1 (*C*H$_2$=CBr), 129.6 (*C*Br), 146.5 (*C*H=CH$_2$), 177.6 (*C*O).

HRMS (CI- *iso*-butane): *m/z* calcd for $C_{12}H_{18}NOBr$: 271.0572 and 273. 0552. Found: 271.0570 and 273.0550.

N-2-Iodophenyl-5-allylpyrrolidin-2-one (1d)

The same procedure as described above for **1a** was employed starting from *N*-(2-iodophenyl)-5-ethoxypyrrolidin-2-one.[17] After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (hexane−EtOAc, 1:1) to afford **1d** in 65% yield as a colorless oil.

IR (KBr): 3069, 2974, 2925, 1698, 1577, 1016, 920 and 758 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 1.92−2.02 (m, 1 H, C*H*$_2$CH$_2$CO), 2.13−2.51 (m, 3 H, C*H*$_2$CH$_2$CO and C*H*$_2$CO), 2.54−2.61 (m, 2 H, C*H*$_2$CH$_2$), 4.16 (s, br, 1 H, C*H*N), 5.10 (d, br, *J* = 15.7, 2 H, C*H*$_2$=CH), 5.64−5.73 (m, 1 H, C*H*=CH$_2$), 7.09 (dt, *J* = 6.0, 1.5, 1 H, C*H*$_{Ar}$), 7.19 (dd, *J* = 6.0, 1.5, 1 H, C*H*$_{Ar}$), 7.40 (dt, *J* = 7.0, 1.5, 1 H, C*H*$_{Ar}$), 7.92 (dd, *J* = 7.0, 1.5, 1 H, C*H*$_{Ar}$).

^{13}C NMR (CDCl$_3$): δ 24.3 (br, *C*H$_2$CH$_2$CO), 29.7 (*C*H$_2$CO), 38.3 (*C*H$_2$N), 59.1 (br, *C*HN), 98.0 (br, *C*I), 118.8 (*C*H$_2$=CH), 129.4 (CH$_{Ar}$), 130.0 (*C*H$_{Ar}$), 131.8 (br,*C*$_{Ar}$), 133.1 (2 *C*H$_{Ar}$), 140.3 (*C*H=CH$_2$), 175.1 (*C*O).

HRMS (EI): *m/z* calcd for $C_{13}H_{14}NOI$: 327.0123. Found: 327.0120.

N-2-Bromobenzyl-5-allylpyrrolidin-2-one (1e)

The same procedure as described above for **1a** was employed starting from *N*-(2-bromobenzyl)-5-ethoxypyrrolidin-2-one.[16] After evaporation under reduced pressure, the residue was purified by column chromatography (hexane−EtOAc, 1:1) to afford **1e** in 95% yield as a colorless oil.

IR (KBr): 3068, 2972, 2925, 1691, 1570, 1441, 754 and 661 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 1.78−1.88 (m, 1 H, C*H*$_2$CH$_2$CO), 2.05−2.25 (m, 2 H, C*H*$_2$CH$_2$CO and C*H*$_2$CO), 2.37−2.57 (m, 3 H, C*H*$_2$CO, C*H*$_2$CH=), 3.52−3.60 (m, 1 H, C*H*N), 4.32 (d, *J* = 16.1, 1 H, C*H*$_2$N), 4.94 (d, *J* = 16.1, 1 H, C*H*$_2$N), 5.11 (d, *J* = 11.3, 1 H, C*H*$_2$=CH), 5.12 (d, *J* = 14.3, 1 H, C*H*$_2$=CH), 5.60−5.74 (m, 1 H, C*H*=CH$_2$), 7.12−7.17 (m, 1 H, C*H*$_{Ar}$), 7.24−7.32 (m, 2 H, C*H*$_{Ar}$), 7.55 (d, *J* = 7.7, 1 H, C*H*$_{Ar}$).

^{13}C NMR (CDCl$_3$): δ 23.0 (*C*H$_2$CH$_2$CO), 29.6 (*C*H$_2$CO), 37.2 (*C*H$_2$CH=), 44.0 (*C*H$_2$N), 57.0 (*C*HN), 119.0 (*C*H$_2$=CH), 123.5 (*C*Br), 127.9 (*C*H$_{Ar}$), 129.2 (*C*H$_{Ar}$), 129.7 (*C*H$_{Ar}$), 132.8 (*C*H$_{Ar}$), 133.1 (*C*H=CH$_{2r}$), 136.0 (*C*$_{Ar}$), 175.8 (C, *C*O).

HRMS (EI): *m/z* calcd for $C_{14}H_{16}NOBr$: 293.0415 and 295.0396. Found: 251.9360 and 253.9343 (M^+ - C_3H_5).

N-2-Iodobenzyl-6-allylpiperidin-2-one (1f)

The same procedure as described above for **1a** was employed starting from *N*-(-2-iodobenzyl)-5-ethoxy-2-piperidinone.[16] After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane−EtOAc, 1:1) to afford **1f** in 95% yield as a yellow oil: mp 27−28 °C.

IR (KBr): 3064, 2947, 2873, 1643, 1564, 1463, 1344, 1279, 1012, 918, 748 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 1.74−1.82 (m, 3 H, C*H*$_2$CH$_2$CH$_2$ and C*H*$_2$CH$_2$CO), 1.83−1.96 (m, 1 H, C*H*$_2$CH$_2$CH$_2$), 2.23−2.29 (m, 1 H, C*H*$_2$CH=), 2.49−2.52 (m, 3 H, C*H*$_2$CO and C*H*$_2$CH=), 3.30−3.34 (m, 1 H, C*H*N), 4.21 (d, *J* = 16.0, 1 H, C*H*$_2$N), 5.07−5.13 (m, 2 H, C*H*$_2$=CH), 5.21 (d, *J* = 16.0, 1 H, C*H*$_2$N), 5.62−5.70 (m, 1 H, C*H*=CH$_2$), 6.95 (dt, *J* = 8.1, 1.5, 1 H, C*H*$_{Ar}$), 7.26 (dd, *J* = 8.1, 1.5, 1 H, C*H*$_{Ar}$), 7.72 (dt, *J* = 3.0, 1.5, 1 H, C*H*$_{Ar}$), 7.82 (dd, *J* = 8.1, 1.5, 1 H, C*H*$_{Ar}$).

^{13}C NMR (CDCl$_3$): δ 17.0 (*C*H$_2$CH$_2$CH$_2$), 26.0 (*C*H$_2$CH$_2$CO), 31.9 (*C*H$_2$CO), 37.0 (*C*H$_2$CH=), 52.5 (*C*H$_2$N), 55.5 (*C*HN), 98.7 (*C*I), 118.2 (*C*H$_2$=CH), 128.0 (*C*H$_{Ar}$), 128.4 (*C*H$_{Ar}$), 128.8 (*C*H$_{Ar}$), 133.9 (*C*H=CH$_2$), 139.2 (*C*H$_{Ar}$), 139.4 (*C*$_{Ar}$), 170.5 (*C*O).

HRMS (EI): *m/z* calcd for $C_{15}H_{18}NOI$: 355.0429. Found: 355.0454.

7-Methyl-6-methylene-1,2,3,5,6,8a-hexahydroindolizin-3-one (3a)

In a Pyrex flask was added a solution of **1a** (0.412 g, 1,14 mmol) in DMF (16.0 mL), followed by Pd(OAc)$_2$ (0.0040 g, 0.018 mmol), PPh$_3$ (0.011 g, 0.040 mmol) and K_2CO_3 (0.538 g, 3.90 mmol) under an Ar atmosphere. The mixture was kept at 110 °C for 12 h. Upon completion of the reaction, DMF was carefully evaporated under reduced pressure (0.2 mmHg, 40−50 °C), the residue was dissolved in EtOAc and filtered through a column of celite. Purification by column chromatography (hexane−EtOAc, 1:1) afforded **3a** (36.0 mg, 0.220 mmol) in 56% yield as a pale yellow oil.

IR (KBr): 2925, 2857, 1694, 1606, 1445 and 1423 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 1.61−1.72 (m, 1 H, C*H*$_2$CH$_2$CO), 1.86 (s, 3 H, C*H*$_3$), 2.26−2.28 (m, 1 H, C*H*$_2$CH$_2$CO), 2.39−2.49 (m, 2 H, C*H*$_2$CO), 3.57 (d, *J* = 15.4, 1 H, C*H*$_2$N), 4.26 (t, br, *J* = 6.0, 1 H, C*H*N), 4.70 (d, *J* = 15.4, 1 H, C*H*$_2$N), 4.99 (d, *J* = 1.5, 1 H, C*H*$_2$=C), 5.09 (d, *J* = 1.5, 1 H, C*H*$_2$=C), 5.63 (s, 1 H, C*H*=H).

^{13}C NMR (CDCl$_3$): δ 19.3 (*C*H$_3$), 26.3 (*C*H$_2$CH$_2$CO), 31.4 (*C*H$_2$CO), 43.1 (*C*H$_2$N), 55.6 (*C*HN), 111.5 (*C*H$_2$=C), 128.0 (*C*H=C), 132.1 (*C*CH$_3$), 139.2 (*C*=CH$_2$), 173.6 (*C*O). HRMS (EI): *m/z* calcd for $C_{10}H_{13}NO$: 163.0994. Found: 163.0997.

8-Methyl-7-methylene-1,3,4,6,7,9a-hexahydro-2*H*-quinolizin-4-one (3b) and 7-Methyl-8-methylene-1,3,4,8,9,9a-hexahydro-2*H*-quinolizin-4-one (4b)

The same procedure as described above for **3a** was employed starting from **1b**. Quinolizidinone **3b** was obtained in 62% yield as a brown oil and **4b** was obtained in 12% yield as a red oil after column chromatography (hexane−EtOAc, 1:1).

3b: IR (KBr): 2945, 2864, 1641, 1442 and 1412 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 1.44−1.50 (m, 1 H, C*H*$_2$CH$_2$CO), 1.53−1.74 (m, 2 H, C*H*$_2$CH$_2$CH$_2$), 1.83 (s, 3 H, C*H*$_3$), 1.97−2.08 (m, 1 H, C*H*$_2$CH$_2$CO), 2.22−2.37 (m, 1 H, C*H*$_2$CO), 2.39−2.48 (m, 1 H, C*H*$_2$CO), 3.28 (d, *J* = 15.0, 1 H, C*H*$_2$N), 4.04 (d, br, *J* = 5.0, 1 H, C*H*N), 4.99 (s, br, 2 H, C*H*$_2$=C), 5.22 (d, *J* = 15.0, 1 H, C*H*$_2$N), 5.42 (s, br, 1 H, C*H*=CCH$_3$).

^{13}C NMR (CDCl$_3$,): δ 18.1 (*C*H$_3$), 19.4 (*C*H$_2$CH$_2$CH$_2$), 29.9 (*C*H$_2$CH$_2$CO), 32.1 (*C*H$_2$CO), 44.5 (*C*H$_2$N), 55.5 (*C*HN), 110.1 (*C*H$_2$=C), 128.2 (*C*H=CCH$_3$), 132.2 (=*C*CH$_3$), 139.8 (*C*=CH$_2$), 169.2 (*C*O).

GC-MS: *m/z* (%) = 177 (40), 162 (100), 107 (24).

HRMS (EI): *m/z* calcd for $C_{11}H_{15}NO$: 177.1153. Found: 177.1154.

4b: IR (KBr): 3082, 2935, 2876, 1641, 1450 and 1406 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 1.50−1.59 (m, 1 H, C*H*$_2$CH$_2$CO), 1.64−1.97 (m, 2 H, C*H*$_2$CH$_2$CH$_2$), 1.84 (s, 3 H, C*H*$_3$), 2.03−2.10 (m, 1 H, C*H*$_2$CH$_2$CO), 2.29−2.61 (m, 4 H, C*H*$_2$CO, C*H*$_2$C=), 3.54 (m, 1 H, C*H*N), 4.82 (d, *J* = 1.1, 1 H, C*H*$_2$=C), 4.90 (d, *J* = 1.1, 1 H, C*H*$_2$=C), 7.21 (s, 1 H, =C*H*N).

^{13}C NMR (CDCl$_3$): δ 16.1 (*C*H$_3$), 19.5 (*C*H$_2$CH$_2$CH$_2$), 29.6 (*C*H$_2$CH$_2$CO), 32.2 (*C*H$_2$CO), 38.6 (*C*H$_2$C=), 55.9 (*C*HN), 108.0 (*C*H$_2$=C), 117.5 (=*C*CH$_3$), 122.9 (=*C*HN), 139.8 (*C*=CH$_2$), 167.6 (*C*O).

GC-MS: *m/z* (%) = 177 (100), 148 (18), 134 (20), 120 (36), 108 (85) and 93 (20).

HRMS (EI): *m/z* calcd for $C_{11}H_{15}NO$: 177.1157. Found: 177.1154.

8,8-Dimethyl-6,7-dimethyleneperhydro-indolizin-3-one (2c)

The same procedure as described above for **3a** was employed starting from **1c**. Indolizidinone **2c** was obtained in 67% yield as a yellow oil.

IR (KBr): 2968, 2875, 1689, 1458, 1421, 1284, 1255 and 1182 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 0.84 (s, 3 H, CH_3), 1.11 (s, 3 H, CH_3), 1.81−1.86 (m, 1 H, CH_2CH_2CO), 2.01−2.08 (m, 1 H, CH_2CH_2CO), 2.38 (t, *J* = 7.7, 2 H, CH_2CO), 3.36 (dd, *J* = 8.4, 5.5, 1 H, CHN), 3.46 (d, br, *J* = 14.6, 1 H, CH_2N), 4.60 (d, *J* = 14.6, 1 H, CH_2N), 4.84 (s, br, 1 H, $CH_2{=}CCH_2$), 4.90 (s, br, 1 H, $CH_2{=}CCH_2$), 5.06 (s, br, 2 H, $CH_2{=}CCCH_3$).

^{13}C NMR($CDCl_3$): δ 18.7 (CH_2CH_2CO), 20.0 (CH_3), 22.1 (CH_3), 30.3 (CH_2CO), 40.1 ($C(CH_3)_2$), 45.7 (CH_2N), 64.4 (CHN), 108.5 ($CH_2{=}C$), 112.3 ($CH_2{=}C$), 141.8 ($C{=}CH_2$), 155.0 ($C{=}CH_2$), 174.0 (CO).

HRMS (EI): *m/z* calcd for $C_{12}H_{17}NO$: 191.1310. Found: 191.1392.

5-Methyl-5,6,6a,7,8,9-hexahydroazolo[1,2-*a*]quinolin-9-one (6a)

The same procedure as described above for **3a** was employed starting from **1d**. An inseparable 2:1 mixture of **5a**–**5b** was obtained in 74% yield (HRMS [EI]: *m/z* calcd for $C_{13}H_{13}NO$: 199.0997; found: 199.0994) and dissolved in MeOH (2.0 mL). After addition of 10% Pd/C (0.002 g),the resulting mixture was purged with H_2 and stirred for 8 h under H_2 atmosphere (2 bar) at r.t.. Upon completion of the reaction, the residue was filtered through a column of celite. Evaporation of the solvent under reduced pressure afforded **6a** (0.024 g, 0.12 mmol, 20:1 mixture with **6b**) in quantitative yield as a hygroscopic white solid.

IR (KBr): 2962, 1687, 1485, 1092, 1024, 800 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37 (d, *J* = 6.8, 3 H, CH_3), 1.50 (q, *J* = 12.0, 1 H, CH_2CHCH_3), 1.70−1.75 (m, 1 H, CH_2CH_2CO), 2.20 (ddd, *J* = 12.0, 5.6, 2.4, 1 H, CH_2CHCH_3), 2.27−2.30 (m, 1 H, CH_2CH_2CO), 2.47−2.57 (m, 1 H, CH_2CO), 2.59−2.65 (m, 1 H, CH_2CO), 3.04−3.06 (m, 1 H, $CHCH_3$), 3.95−3.97 (m, 1 H, CHN), 7.07 (dt, *J* = 7.8, 3.2, 1 H, CH_{Ar}), 7.21 (dt, *J* = 7.8, 1.0, 1 H, CH_{Ar}), 7.29−7.31 (m, 1 H, CH_{Ar}), 8.67 (dd, *J* = 8.5, 1.2, 1 H, CH_{Ar}).

^{13}C NMR (125 MHz, $CDCl_3$): δ 20.8 (CH_3), 25.2 (CH_2CH_2CO), 31.4 ($CHCH_3$), 32.0 (CH_2CO), 39.3 (CH_2CHCH_3), 57.5 (CHN), 119.0 (C_{Ar}), 123.7 (CH_{Ar}), 126.8 (CH_{Ar}), 127.0 (CH_{Ar}), 130.7 (CH_{Ar}), 136.2 (C_{Ar}), 173.4 (CO).

HRMS (EI): *m/z* calcd for $C_{13}H_{15}NO$: 201.1154. Found: 201.1153.

10-Methylene-2,3,5,10,11,11a-hexahydro-1*H*-azolo[1,2-*a*]benzo[*e*]azepin-3-one (7a) and 10-Methyl-2,3,5,11a-tetrahydro-1*H*-azolo[1,2-*a*]benzo[*e*]azepin-3-one (8a)

The same procedure as described above for **3a** was employed starting from **1e**. After evaporation under reduced pressure, the residue was purified by column chromatography (hexane-EtOAc, 1:1) to afford a 6.5:1 mixture of **7a**–**8a** in 80% yield as a colorless oil.

7a (data from an analytically pure sample):

IR (KBr): 3068, 2929, 1682 and 784 cm^{-1}.

^{1}H NMR($CDCl_3$): δ 1.77−1.81 (m, 1 H, CH_2CH_2CO), 2.20−2.36 (m, 1 H, CH_2CH_2CO), 2.38−2.46 (m, 3 H, $CH_2C{=}$ and CH_2CO), 2.80 (dd, *J* = 13.2, 3.7, 1 H, $CH_2C{=}$), 3.91 (m, 1 H, CHN), 4.10 (d, *J* = 15.0, 1 H, CH_2N), 4.95 (d, *J* = 15.0, 1 H, CH_2N), 5.20 (d, *J* = 1.5, 1 H, $CH_2{=}C$), 5.25 (d, *J* = 1.5, 1 H, $CH_2{=}C$), 7.22−7.32 (m, 4 H, CH_{Ar}).

^{13}C NMR ($CDCl_3$): δ 23.7 (CH_2CH_2CO), 29.8 (CH_2CO), 43.0 ($CH_2{=}C$), 45.9 (CH_2N), 60.7 (CHN), 117.1 ($CH_2{=}C$), 127.8 (CH_{Ar}, × 2), 128.6 (CH_{Ar}), 128.7 (CH_{Ar}), 134.6 (C_{Ar}), 142.4 (C_{Ar}), 146.4 ($C{=}CH_2$), 174.2 (CO).

GC-MS: *m/z* (%) = 213 (78), 198 (5), 184 (5), 170 (8), 156 (4), 130 (100), 115 (54), 102 (4), 91 (7), 84 (28) and 77 (8).

HRMS (EI): *m/z* calcd for $C_{14}H_{15}NO$: 213.1154. Found: 213.1153.

8a (data from an enriched fraction of the mixture **7a**–**8a**):

^{1}H NMR ($CDCl_3$) δ = 1.77−1.84 (m, 1 H, CH_2CH_2CO), 2.18 (s, 3 H, CH_3), 2.20−2.34 (m, 1 H, CH_2CH_2CO), 2.35−2.43 (m, 2 H, CH_2CO), 3.81−3.87 (m, 1 H, CHN), 3.90 (d, *J* = 13.5, 1 H, CH_2N), 4.69 (d, *J* = 13.5, 1 H, CH_2N), 5.74 (d, *J* = 1.1, 1 H, $CH{=}CCH_3$), 7.20−7.26(m, 1 H, C*H-Ar*), 7.32−7.37 (m, 3 H, CH_{Ar}).

GC-MS: *m/z* (%) = 213 (23), 198 (100), 184 (4), 170 (6), 156 (9), 142 (6), 128 (12), 115 (14), 91 (6), 84 (3) and 77 (6).

10-Methyl-2,3,5,10,11,11a-hexahydro-1*H*-azolo[1,2-*a*]benzo[*e*]azepin-3-one (9a)

A 6.5:1 mixture of **7a**–**8a** was dissolved in MeOH (5 mL) and stirred for 10 h under H_2 atmosphere (4 bar) at r.t. After evaporation under reduced pressure and column chromatography (hexane−EtOAc, 1:1), a 4.5:1 mixture of **9a**–**10a** was obtained in 94% yield.

Data for the major isomer: white solid, mp 89–90 °C.

IR (KBr): 2962, 2922, 2875, 2852, 1682, 1489 and 760 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 1.44 (d, *J* = 7.1, 3 H, CH_3), 1.43−1.58(m, 1 H, CH_2CHCH_3), 1.74 (m, 1 H, CH_2CHCH_3), 1.88 (dd, *J* = 14.5, 3.3, 1 H, CH_2CH_2CO), 2.19−2.37 (m, 3 H, CH_2CH_2CO and CH_2CO), 3.20−3.29 (m, 1 H, CHN), 3.87−3.93 (m, 1 H, $CHCH_3$), 4.09 (d, *J* = 14.3, 1 H, CH_2N), 4.97 (d, *J* = 14.3, 1 H, CH_2N), 7.16−7.32 (m, 3 H, CH_{Ar}), 7.36 (m, 1 H, CH_{Ar}).

^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6 (CH_3), 24.9 (CH_2CH_2CO), 29.7 (CH_2CO), 34.3 ($CHCH_3$), 44.4 (CH_2CHCH_3), 46.0 (CH_2N), 62.1 (CHN), 124.7 (CH_{Ar}), 126.5 (CH_{Ar}), 128.1 (CH_{Ar}), 129.9 (CH_{Ar}), 136.6 (C_{Ar}), 145.4 (C_{Ar}), 174.1(CO).

HRMS (EI): *m/z* calcd for $C_{14}H_{17}NO$: 215.1310. Found: 215.1310.

11-Methyl-1,2,3,4,6,11,12,12a-octahydrobenzo[*e*]pyrido[1,2-*a*]azepin-4-one (9b, 10b)

The same procedure as described above for **3a** was employed starting from **1f**. After evaporation under reduced pressure, the residue was purified by column chromatography (hexane−EtOAc, 5:3→1:1) to afford an inseparable 2:1 mixture of **7b**–**8b** in 90% yield as a colorless oil.

GC-MS: **7b** *m/z* (%) = 227 (76), 212 (5), 198 (3), 184 (5), 170 (10), 156 (6), 144 (7), 130 (100), 115 (5), 98 (5). **8b** *m/z* (%) = 227 (31), 212 (100), 198 (23), 184 (13), 170 (13), 157 (21), 143 (8), 130 (21), 115 (22), 98 (21).

The above mixture was dissolved in MeOH (5.0 mL) and stirred for 10 h under H_2 atmosphere (4 bar). After evaporation under reduced pressure, a 6.5:1 mixture of **9b**–**10b** was obtained in 98% yield. Column chromatography (hexane−EtOAc, 1:1) afforded the major isomer **9b** as a white solid: mp 114−115 °C.

IR (KBr): 3060, 3030, 2939, 2873, 1635, 1464, 1417, 1365, 1259, 1184 and 760 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (d, *J* = 5.0, 3 H, CH_3), 1.56−1.76 (m, 5 H, $CH_2CH_2CH_2$, CH_2CHCH_3 and CH_2CH_2CO), 1.91−2.12 (m, 1 H, CH_2CH_2CO), 2.19−2.25(m, 1 H, CH_2CO), 2.29−2.39 (m, 1 H, CH_2CO), 3.26−3.33 (m, 1 H, CHN), 3.83−3.89 (m, 1 H, $CHCH_3$), 3.87 (d, *J* = 13.9, 1 H, CH_2N), 5.30 (d, *J* = 13.9, 1 H, CH_2N), 7.16−7.26 (m, 3 H, CH_{Ar}), 7.45 (dd, *J* = 7.4, 1.5, 1 H, CH_{Ar}).

^{13}C NMR (125 MHz, $CDCl_3$): δ 18.3 (CH_3), 20.9 ($CH_2CH_2CH_2$), 30.5 (CH_2CH_2CO), 32.8 (CH_2CO), 35.4 ($CHCH_3$), 44.6 (CH_2CHCH_3), 49.9 (CH_2N), 61.4 (CHN), 124.7 (CH_{Ar}), 126.4 (CH_{Ar}), 127.7 (CH_{Ar}), 130.4 (CH_{Ar}), 137.7 (C_{Ar}), 145.0 (C_{Ar}), 169.3 (*C*).

HRMS (EI): *m/z* calcd for $C_{15}H_{19}NO$: 229.1466.Found: 229.1467.

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