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A Novel Approach to 2-Amino-1,3-Dienes by Coupling of α-Chloro Enamines and Alkenyl Lithium Compounds

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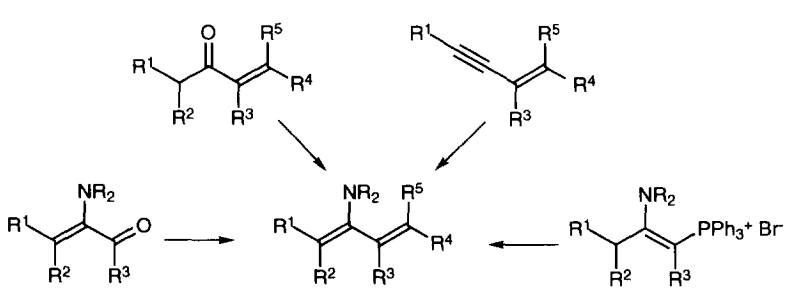
Abstract: Coupling of α-chloro enamines as key building blocks with alkenyl lithium compounds lead to the formation of 2-amino-1,3-dienes **6**. These cross conjugated enamines constitute important diene components for stereoselective Diels-Alder reactions and were prepared in 32-75% overall yield starting from the corresponding amides.

INTRODUCTION

Stereoselective Diels-Alder reactions[1] employing 2-amino-1,3-butadienes as electron rich dienes have recently become a topic of growing interest.[2,3] Since it has been demonstrated that chiral amines such as (*S*)-2-(methoxymethyl)pyrrolidine[2b] can strikingly control the relative and absolute stereochemistry during [4+2]-cycloadditions, an increasing research activity in this field has been observed.[2-4] In spite of the fact that different methods for the preparation of 2-amino-1,3-butadienes have been established (Scheme 1), the methodologies for their syntheses are of limited generality.

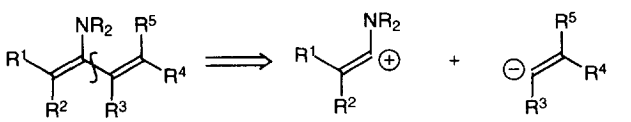
Studies of this laboratory have shown that chiral 2-amino-1,3-butadienes can be conveniently prepared by Wittig olefination of α-oxo-enamines[2b] or by reaction of β-aminopropenylphosphonium salts with aldehydes.[5a,2a] Alternatively, Barluenga *et al.*[5b-e] added secondary amines under $Hg(OAc)_2$ catalysis to enynes to form cross conjugated enamines. The condensation of α,β-unsaturated ketones and amines in the presence of titanium(IV) chloride also leads to the formation of 2-amino-1,3-butadienes as was shown by Pitacco and Valentin.[6]



Scheme 1. Selected examples for the preparation of 2-amino-1,3-dienes

Other even more restricted methods for the preparation of 2-amino-1,3-butadienes include the conjugate addition of organo copper or zinc reagents to (2-propynylidene)morpholinium triflates[7] or the dehydrohalogenation of chloro enamines.[8] Mixtures of 2-amino- and 1-amino-1,3-butadienes have also been obtained by Hickmott *et al.* by selfcondensation of alkylmethylketones and secondary amines.[9]

However, no method based on the most obvious synthetic approach, namely coupling of an a^1-enamine and a d^1-alkenyl synthetic equivalent,[10] has been developed so far (Scheme 2). In this paper, we describe an efficient methodology for a stereoselective synthesis of a variety of 2-amino-1,3-dienes starting from carboxylic acid amides and alkenyl halides based on an a^1-enamine/ d^1-alkenyl equivalent cross coupling.



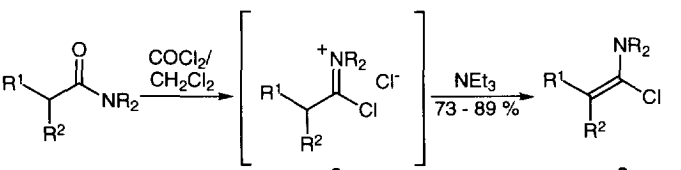
a^1-enamine-synthon d^1-alkenyl-synthon

Scheme 2. New retrosynthetic approach for the synthesis of 2-amino-1,3-dienes

RESULTS

a^1-Enamine equivalents are commonly used in organic synthesis[11] and from the variety of reagents, α-chloro enamines[12] are the most important. They exist in an equilibrium between the α-chloro enamine and the ketene iminium structure that can be shifted from the dominant covalent form to the ketene iminium form.[11,13] Moreover, α-chloro enamines are useful organic reagents. They react with electrophiles at C-2 and, importantly for our synthetic approach, with nucleophiles giving substitution of the chlorine atom at C-1.[11,12] 1-Acyloxy enamines[14] or Vilsmeier-Haack adducts[15] were also used as enamine equivalents as well as ketene iminium salt[13] precursors. Nevertheless, due to the accessibility from the corresponding amides and phosgene, we directed our attention to α-chloro enamines as precursors for the synthesis of the 2-amino-1,3-dienes.

The preparation of the α-chloro enamines **3** was readily achieved by a well known two step procedure.[12] First, amides **1**[16] were treated with phosgene at -50 °C to form the corresponding amide chlorides **2**, which were not isolated. Treatment of **2** with 1.5 eq. of triethyl amine at 50 °C accomplished the dehydrochlorination and the formation of the α-chloro enamines **3** (Scheme 3).



1 **2** **3**

Scheme 3. Synthesis of α-chloro enamines **3**

After purification, the α-chloro enamines were isolated as colourless, sensitive liquids in good chemical yields (73-89%; Table 1). All new compounds (**3d,f**) were characterised by NMR (^{1}H, ^{13}C), IR, MS as well as microanalysis. **3a-c,e**[11,12,13] were known before, however, these compounds were characterised to confirm

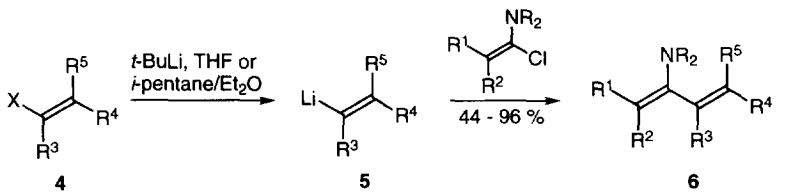
their structure.[20] In order to prove the applicability of our new method, different amines, an acyclic amine (diethyl amine; **3a,b**), a six-membered cyclic amine (piperidine; **3c,d**) and two five-membered cyclic amines [(*S*)-2-(methoxymethyl)pyrrolidine (SMP)[18], (*S*)-2-(1-methoxy-1-methylethyl)pyrrolidine (SDP); **3e,f**], were converted to the corresponding α-chloro enamines **3**.

Table 1. α-Chloro Enamines **3**.

Compound	NR_2	R^1	R^2	Yield [%]	α_D^{20} (neat)
3a	$N(C_2H_5)_2$	CH_3	CH_3	73	-
3b	$N(C_2H_5)_2$	$-(CH_2)_5-$		89	-
3c	piperidine	CH_3	CH_3	73	-
3d	piperidine	$-(CH_2)_5-$		82	-
3e	SMP	CH_3	CH_3	78	–54.90
3f	SDP	CH_3	CH_3	84	–5.40

Essential for the next reaction step was the availabilty of a d^1-alkenyl synthetic equivalent. For this purpose, alkenyl lithium compounds[21] have been previously used. Easily accessible from *t*-butyl lithium and alkenyl halides by metal halogen exchange, these organometallic compounds appeared to be the perfect precursors for the intended coupling reactions.

Thus, the synthesis leading to the formation of the 2-amino-1,3-butadienes **6** was accomplished by a two step *one pot* procedure (Scheme 4). First, by treatment of the alkenyl halides **4**[22] with two equivalents of *t*-butyl lithium, the alkenyl lithium compounds **5** were generated *in situ*. In the case of cyclic alkenyl halides, for example 1-iodocyclohexene, the metal halogen exchange was carried out at -78 °C in THF under standard conditions.[21a] When acyclic alkenyl halides were used, it proved necessary to carry out the metalation in a diethyl ether : *i*-pentane mixture (1:1) at -120 to -130 °C to diminish typical side reactions,[23b] especially the formation of alkynyl lithium compounds. Under both reaction conditions, metalation was complete within 2-3 h, and the reaction sequence completed by addition of the appropriate α-chloro enamine **3**. The reaction mixtures were warmed up to room temperature, the solvents were removed, and the 2-amino-1,3-butadienes **6** were isolated after Kugelrohr distillation as sensitive, colourless liquids in moderate to very good yields (44-96%, Table 2).



4 **5** **6**

Scheme 4. Coupling of lithium compounds **5** with α-chloro enamines **3**

The previously unknown 2-amino-1,3-butadienes **6** were characterised by NMR (^1H, ^{13}C), IR, MS as well as microanalysis.[25] Besides, compounds **6** exhibited the typical spectroscopic features of cross conjugated

enamines; for example, the two IR absorptions for the two different C=C vibrations ($\nu_{C=C}$ and $\nu_{NC=C}$) and the ^{13}C NMR resonance of the enamine N-C-carbon atom at approximately 140 ppm. For further details on the spectroscopic data see the experimental section.

Table 2. Synthesis of 2-Amino-1,3-Dienes **6**.

Compound	NR_2	R^1	R^2	R^3	R^4	Yield [%]	$[\alpha]_D^{20}$ (c, $CHCl_3$)
6a	$N(C_2H_5)_2$	CH_3	CH_3	H	H	54	-
6b	$N(C_2H_5)_2$	CH_3	CH_3	H	*n*-C_4H_9	62	-
6c	$N(C_2H_5)_2$	CH_3	CH_3	H	C_6H_5	44	-
6d	$N(C_2H_5)_2$	CH_3	CH_3	-$(CH_2)_4$-		48	-
6e	$N(C_2H_5)_2$	-$(CH_2)_5$-		H	H	46	-
6f	$N(C_2H_5)_2$	-$(CH_2)_5$-		H	*n*-C_4H_9	64	-
6g	$N(C_2H_5)_2$	-$(CH_2)_5$-		H	C_6H_5	56	-
6h	$N(C_2H_5)_2$	-$(CH_2)_5$-		-$(CH_2)_4$-		50	-
6i	piperidine	CH_3	CH_3	H	H	49	-
6j	piperidine	CH_3	CH_3	H	*n*-C_4H_9	72	-
6k	piperidine	CH_3	CH_3	H	C_6H_5	83	-
6l	piperidine	CH_3	CH_3	-$(CH_2)_4$-		50	-
6m	piperidine	-$(CH_2)_5$-		H	H	49	-
6n	piperidine	-$(CH_2)_5$-		H	*n*-C_4H_9	61	-
6o	piperidine	-$(CH_2)_5$-		H	C_6H_5	64	-
6p	piperidine	-$(CH_2)_5$-		-$(CH_2)_4$-		50	-
(*S*)-**6q**	SMP	CH_3	CH_3	H	H	70	+186.38 (1.40)
(*S*)-**6r**	SMP	CH_3	CH_3	H	*n*-C_4H_9	60	+159.30 (neat)
(*S*)-**6s**	SMP	CH_3	CH_3	H	C_6H_5	96	+129.50 (1.05)
(*S*)-**6t**	SMP	CH_3	CH_3	-$(CH_2)_4$-		58	+306.30 (neat)
(*S*)-**6u**	SDP	CH_3	CH_3	H	H	62	+194.70 (1.06)
(*S*)-**6v**	SDP	CH_3	CH_3	H	*n*-C_4H_9	54	+261.52 (neat)
(*S*)-**6w**	SDP	CH_3	CH_3	H	C_6H_5	77	+209.25 (neat)
(*S*)-**6x**	SDP	CH_3	CH_3	-$(CH_2)_4$-		51	+365.10 (0.96)

The whole assortment of prepared α-chloro enamines **3** was converted to the cross conjugated enamines **6**. The reaction prooceded well with all combinations of α-chloro enamines and alkenyl lithium compounds. This proves that the new methodology has a general appliciability for the synthesis of cross conjugated enamines. Furthermore, as exhibited by the coupling patterns in the ^1H NMR spectra, the coupling reactions proceeded stereoselective under retention of the configuration at the double bond.

CONCLUSION

In summary, by this novel methodology, we have provided a new efficient entry into the class of 2-amino-1,3-butadienes with hitherto unknown substitution pattern. The starting materials are readily available by standard laboratory procedures, and the coupling of the α-chloro enamines and alkenyl lithium compounds to cross conjugated enamines proceeded in good overall yields. Complete retention of the double bond geometry was observed and further extensions of this novel method to synthesise (*Z*)-substituted 2-amino-1,3-butadienes via the use of (*Z*)-halo alkenes is obviously possible and will widen the scope of this methodology.

We also consider the employment of monosubstituted α-chloro enamines,[24] which have been previously used by Ghosez *et al.*[24b] and Heimgartner *et al.*[24c] to synthesise azirines, to prepare 2-amino-1,3-butadienes with different substitution patterns. Furthermore, stereoselective [4+2]-cycloadditions with these new 2-amino-1,3-butadienes are currently investigated in our laboratories.

EXPERIMENTAL SECTION

General. All reactions were carried out using standard Schlenk techniques. Solvents were dried and purified by conventional methods prior to use. Tetrahydrofuran and diethyl ether were freshly distilled from sodium, *i*-pentane and dichloromethane from CaH_2 under argon. Reagents were purchased from common commercial suppliers and were used from freshly opened containers unless otherwise stated.

Apparatus. Optical rotations: Perkin-Elmer P 241 polarimeter; solvents of Merck UVASOL quality unless otherwise stated. - IR spectra: Perkin-Elmer 1420. - ^1H NMR spectra (300 MHz), ^{13}C NMR spectra (75 MHz): Varian VXR 300 (δ in ppm, solvent: $CDCl_3$, TMS as internal standard). - Mass spectra: Varian MAT 212 (EI 70 eV) (relative intensities in parentheses). - Microanalyses: Heraeus CHN-O-Rapid.[25]

Procedure for the preparation of α-chloro enamines 3:

Enamines **3a-f** were obtained according to a standard procedure.[12] A flame dried Schlenk flask was cooled to -50 °C. Phosgene gas (500 mmol) was condensed in the flask and CH_2Cl_2 (50 mL) was added. Amide **1** (100 mmol), dissolved in CH_2Cl_2 (50 mL), was gradually added from a dropping funnel. The mixture was allowed to slowly warm to room temperature. After stirring overnight, the solvent was removed and the residue redissolved in CH_2Cl_2 (30 mL). Triethylamine (150 mmol), dissolved in CH_2Cl_2 (30 mL), was added and the mixture heated to 50 °C for 2 h. After cooling to room temperature, light petroleum (50 mL) was added. After stirring for one additional h, the precipitate was filtered off and the solvent removed under reduced pressure. The moisture sensitive compounds were purified by Kugelrohr distillation under reduced pressure.

General procedure for the preparation of 2-amino-1,3-butadienes 6:

A flame dried Schlenk flask was charged with the alkenyl halide (5 mmol) and THF (50 mL) and was cooled to -78 °C. *t*-Butyl lithium (10 mmol) was added by syringe. After stirring the reaction mixture for 3 h, the α-chloro enamine (5 mmol), dissolved in THF (5 mL), was added dropwise to the lithium compound. After slowly warming the reaction mixture up to room temperature overnight, the solvent was removed under oil pump vacuum and the 2-amino-1,3-butadiene was purified by Kugelrohr distillation. When employing acyclic alkenyl halides, a diethyl ether : *i*-pentane mixture (1:1) was used as solvent, and the reaction was carried out at -120 to -130 °C accordingly.

(1-Chloro-2-methylpropenyl)diethylamine (**3a**): 73% Yield from amide after distillation (48 °C /9 mmHg). - IR (film): $\tilde{\nu}$ = 2970, 2930, 2840 (s, CH), 1740 (w), 1645 (s, C=C), 1445, 1375 (s), 1340, 1300, 1252 (m), 1225 (s), 1150, 1130, 1090, 1070 (m), 985, 810 (s) cm^{-1}. - ^1H NMR: δ = 0.97 (t, *J* = 7.0 Hz, 6H, CH_2CH_3), 1.81 (s, 6H, $(H_3C)_2C$=), 2.63 (q, *J* = 7.0 Hz, 4H, CH_2CH_3). - ^{13}C NMR: δ = 12.7 (CH_2CH_3), 20.8 ($(H_3C)_2C$=), 47.8 (NCH_2), 128.1 (C=C(Cl)-N), 136.6 (C=C(Cl)-N). - MS (70 eV), *m/z* (%): 164 (3) $[M^+ +1]$, 163 (27) $[M^+]$, 162 (8) $[M^+ +1]$, 161 (84) $[M^+]$, 148 (5) $[M^+ - CH_3]$, 146 (16) $[M^+ - CH_3]$, 132 (9) $[M^+ - C_2H_5]$, 126 (100) $[M^+ - Cl]$, 98 (32), 97 (27), 70 (84) $[C_4H_8N]$, 69 (45), 68 (22), 56 (33), 54 (12).

(1-Chloro-cyclohexylidenemethyl)diethylamine (**3b**): 89% Yield from amide after distillation (50 °C /0.05 mmHg). - IR (film): $\tilde{\nu}$ = 2975, 2930, 2855 (s, CH), 2680 (w), 1800 (w), 1745 (m), 1645 (s, C=C), 1450, 1380 (s), 1345 (m), 1300, 1260, 1245, 1230, 1215 (s), 1175, 1160, 1145, 1120, 1095, 1075, 1007 (m), 980, 815, 785 (s) cm^{-1}. - ^1H NMR: δ = 0.98 (t, *J* = 7.0 Hz, 6H, CH_2CH_3), 1.52 (m, 6H, CH_2), 2.37 (m, 4H, H_2CC=), 2.60 (q, *J* = 7.0 Hz, 4H, CH_2CH_3). - ^{13}C NMR: δ = 12.9 (CH_2CH_3), 26.7, 27.5, 31.3 (CH_2), 47.6 (NCH_2), 134.1, 135.3 (C=C(Cl)N, C=C(Cl)N). - MS (70 eV), *m/z* (%): 203 (11) $[M^+]$, 201 (32) $[M^+]$, 188 (3) $[M^+ - CH_3]$, 186 (7) $[M^+ - CH_3]$, 174 (7) $[M^+ - C_2H_5]$, 172 (20) $[M^+ - C_2H_5]$, 167 (13), 166 (100) $[M^+ - Cl]$, 138 (18), 136 (11), 110 (18), 109 (12), 108 (11), 81 (16), 67 (12), 56 (37), 53 (11).

1-(1-Chloro-2-methylpropenyl)piperidine (**3c**): 73% Yield from amide after distillation (58 °C /3 mmHg). - IR (film): $\tilde{\nu}$ = 3005 (m), 2945, 2865, 2835 (s, CH), 1745 (w), 1650 (s, br., C=C), 1453, 1445, 1380, 1323 (s), 1272 (m), 1225, 1193, 1065, 1048, 990, 860, 842, 803 (s), 645 (m) cm^{-1}. - ^1H NMR: δ = 1.46-1.52 (m, 2H, $NCH_2CH_2CH_2$), 1.61 (quint, *J* = 5.5 Hz, 4H, NCH_2CH_2), 1.78 (s, 6H, $(H_3C)_2C$=), 2.62 (t, *J* = 5.5 Hz, 4H, NCH_2). - ^{13}C NMR: δ = 20.2 ($(H_3C)_2C$=), 23.8, 25.7 (CH_2), 51.2 (NCH_2), 123.6 (C=C(Cl)N), 139.8 (C=C(Cl)N). - MS (70 eV), *m/z* (%): 176 (2) $[M^+ +1]$, 175 (16) $[M^+]$, 174 (7) $[M^+ +1]$, 173 (55) $[M^+]$, 160 (15) $[M^+ - CH_3]$, 158 (48) $[M^+ - CH_3]$, 144 (16), 139 (10), 138 (100) $[M^+ - Cl]$, 95 (16), 70 (21), 69 (20), 68 (10), 67 (12), 55 (22).

1-(1-Chloro-cyclohexylidenemethyl)piperidine (**3d**): 82% Yield from amide after distillation (55 °C /0.001 mmHg). - IR (film): $\tilde{\nu}$ = 2925, 2855 (s, CH), 1740 (s), 1650 (s, C=C), 1450 (s), 1380, 1335, 1320, 1270, 1255, 1239, 1225, 1212 (m), 1175, 1130, 1100 (s), 1040, 1010, 980, 848 (m), 800, 793 (s) cm^{-1}. - ^1H NMR: δ = 1.35-1.55 (m, 8H, $NCH_2CH_2CH_2$, H_2CH_2CC=), 1.60 (quint, *J* = 5.6 Hz, 4H, NCH_2CH_2), 2.33 (t, *J* = 5.6 Hz, 4H, H_2CC=), 2.63 (t, *J* = 5.6 Hz, 4H, NCH_2). - ^{13}C NMR: δ = 23.8 ($NCH_2CH_2CH_2$), 25.6 (NCH_2CH_2), 26.8 , 27.5 (CH_2), 30.8 (H_2CC=), 51.8 (NCH_2), 130.7 (C=C(Cl)N), 137.7 (C=C(Cl)N). - MS (70 eV), *m/z* (%): 215 (8) $[M^+]$, 213 (24) $[M^+]$, 179 (13), 178 (100) $[M^+ - Cl]$, 156 (13), 67 (11). - $C_{12}H_{20}ClN$ (213.76): Calcd. C 67.43, H 9.43, N 6.55; found C 67.01, H 9.37, N 6.69.

(S)-(-)-1-(1-Chloro-2-methylpropenyl)-2-(methoxymethyl)pyrrolidine (**3e**): 78% Yield from amide after distillation (45 °C /0.001 mmHg). - α_D^{20} = –54.90 (neat). - IR (film): $\tilde{\nu}$ = 2970, 2925, 2875, 2830 (s, CH), 1745 (m), 1650 (s, C=C), 1460, 1453, 1420 (s), 1365, 1345 (m), 1250, 1235, 1120, 1050 (s), 1010, 975, 910 (m), 850 (s) cm^{-1}. - ^1H NMR: δ = 1.61-1.88 (m, 4H, CH_2CH_2), 1.71 (s, 6H, $(H_3C)_2C$=), 2.85 (m, 2H, CH_2N), 3.10 (dd, *J* = 8.0, 6.0 Hz, 1H, CH_2OCH_3), 3.13-3.23 (m, 2H, NCH, CH_2OCH_3), 3.24 (s, 3H, OCH_3). - ^{13}C NMR: δ = 20.3 ($(H_3C)_2C$=), 23.6, 28.5 (CH_2), 51.4 (NCH_2), 58.7, 59.8 (NCH, OCH_3), 74.6 (CH_2OCH_3), 126.8 (C=C(Cl)N),

136.1 (C=***C***(Cl)N). - MS (70 eV), *m/z* (%): 205 (2) [M^+], 203 (4) [M^+], 168 (36) [M^+–Cl], 160 (33) [M^+–C_2H_5O], 158 (199) [M^+–C_2H_5O], 68 (10), 55 (10).

(S)-(-)-1-(1-Chloro-2-methylpropenyl)-2-(1-methoxy-1-methylethyl)pyrrolidine (**3f**): 84% Yield from amide after distillation (50 °C /0.001 mmHg). - α_D^{20} = –5.40 (neat). - IR (film): $\tilde{\nu}$ = 2980, 2940, 2890, 2835 (s, CH), 1795 (w), 1745 (m), 1655 (s, C=C), 1472, 1465 (s), 1425 (m), 1385, 1370, 1272, 1255, 1190, 1165, 1125, 1093, 1040 (s), 905 (m), 855, 720 (s) cm^{-1}. - ^1H NMR: δ = 1.11 (s, 6H, NCHC(CH_3)$_2$), 1.70-1.88 (m, 10H, CH_2CH_2, (H_3C)$_2$C=), 2.90 (m, 1H, CH_2N), 3.04 (m, 1H, CH_2N), 3.42 (dd, *J* = 7.5, 5.5 Hz, 1H, NCH). - ^{13}C NMR: δ = 20.7 ((H_3C)$_2$C=), 21.2, 22.3 (NCHC(CH_3)$_2$), 25.0, 27.4 (CH_2), 49.2 (NCH), 54.5 (NCH_2), 65.4 (OCH_3), 77.7 (NCHC(CH_3)$_2$), 124.3 (***C***=C(Cl)N), 139.0 (C=***C***(Cl)N). - MS (70 eV), *m/z* (%): 233 (1) [M^+], 231 (4) [M^+], 202 (1) [M^+–OCH_3], 200 (2) [M^+–OCH_3], 196 (8) [M^+–Cl], 160 (32) [M^+–C_4H_9O], 158 (100) [M^+–C_4H_9O]. - $C_{12}H_{22}ClNO$ (231.77): Calcd. C 62.19, H 9.57, N 6.04; found C 61.29, H 9.51, N 6.30.

Diethyl(1-isopropylideneallyl)amine (**6a**): 54% Yield from **3a** and bromoethene after distillation (60 °C /9 mmHg). - IR (film): $\tilde{\nu}$ = 3100 (m, C=CH), 2910, 2860, 2820 (s, CH), 2730 (m), 1630, 1600 (m, C=C), 1465, 1450, 1380 (s), 1345, 1310, 1270 (m), 1215 (s), 1150 (m), 1100 (s), 1070, 1060 (m), 1000, 925, 910 (s), 850, 800 (w) cm^{-1}. - ^1H NMR: δ = 0.96 (t, *J* = 7.0 Hz, 6H, CH_2CH_3), 1.77 (s, 3H, (H_3C)$_2$C=), 1.81 (s, 3H, (H_3C)$_2$C=), 2.84 (q, *J* = 7.0 Hz, 4H, CH_2CH_3), 5.05 (dd, *J* = 11.0, 2.5 Hz, 1H, CH=CH_2), 5.17 (dd, *J* = 17.5, 2.5 Hz, 1H, CH=CH_2), 6.36 (dd, *J* = 17.5, 11.0 Hz, 1H, C*H*=CH_2). - ^{13}C NMR: δ = 14.4 (CH_2CH_3), 20.1, 21.0 ((H_3C)$_2$C=), 47.3 (NCH_2), 114.5 (=CH_2), 131.3 (***C***=C(Cl)N), 131.9 (CH=), 139.3 (C=***C***(Cl)N). - MS (70 eV), *m/z* (%): 154 (8) [M^++1], 153 (70) [M^+], 139 (10), 138 (100) [M^+–CH_3], 124 (10) [M^+–C_2H_5], 110 (17), 97 (15), 96 (64), 82 (34), 79 (21), 70 (16), 69 (17), 68 (16), 56 (17), 55 (52), 54 (28). - $C_{10}H_{19}N$ (153.27): Calcd. C 78.37, H 12.46, N 9.14; found C 77.81, H 12.72, N 8.76.

Diethyl(1-isopropylidenehept-2-enyl)amine (**6b**): 62% Yield from **3a** and (*E*)-1-iodohex-1-ene after distillation (100 °C /0.001 mmHg). - IR (film): $\tilde{\nu}$ = 3040 (w, C=CH), 2970, 2930, 2870, 2860, 2820 (s, CH), 1640, 1615 (w, C=C), 1470, 1463, 1450, 1380 (s), 1340, 1310, 1270 (m), 1215 (s), 1150 (m), 1095 (s), 1070 (m), 975 (s) cm^{-1}. - ^1H NMR: δ = 0.87-0.93 (m, 3H, $(CH_2)_3CH_3$), 0.94 (t, *J* = 7.0 Hz, 6H, NCH_2CH_3), 1.25-1.45 (m, 4H, $CH_2(CH_2)_2CH_3$), 1.75 (s, 3H, (H_3C)$_2$C=), 1.78 (s, 3H, (H_3C)$_2$C=), 2.10 (tdd, *J* = 6.5, 7.5, 1.0 Hz, 2H, CH=CHCH_2), 2.78 (q, *J* = 7.0 Hz, 4H, NCH_2), 5.61 (dt, *J* = 15.5, 7.0 Hz, 1H, CH=C*H*CH_2), 5.94 (d, *J* = 15.5 Hz, 1H, C*H*=$CHCH_2$). - ^{13}C NMR: δ = 14.0 ($(CH_2)_3CH_3$), 14.2 (NCH_2CH_3), 20.3, 20.7 ((H_3C)$_2$C=), 22.4 ($(CH_2)_2CH_2CH_3$), 32.1, 32.9 (=CH(CH_2)$_2$), 47.5 (NCH_2), 124.6 (***C***H=$CHCH_2$), 128.5 (CH=***C***HCH_2), 132.3 (***C***=C(Cl)N), 138.8 (C=***C***(Cl)N). - MS (70 eV), *m/z* (%): 209 (3) [M^+], 194 (2) [M^+–CH_3], 180 (7) [M^+–C_2H_5], 166 (3) [M^+–C_3H_7], 152 (50) [M^+–C_4H_9], 110 (100) [$C_7H_{12}N$], 98 (13), 95 (13), 83 (13), 82 (16), 81 (20), 70 (20), 69 (40), 55 (35). - $C_{14}H_{27}N$ (209.38): Calcd. C 80.31, H 13.00, N 6.69; found C 79.95, H 12.88, N 6.51.

Diethyl(1-isopropylidene-3-phenylallyl)amine (**6c**): 44% Yield from **3a** and (*E*)-(2-bromovinyl)benzene after distillation (100 °C /0.001 mmHg). - IR (film): $\tilde{\nu}$ = 3080, 3060, 3020 (m), 2970, 2930, 2865, 2850, 2820 (s, CH), 1620, 1595 (m, C=C), 1490 (m), 1445, 1375 (s), 1305, 1270, 1220, 1145, 1100, 1080, 1035 (m), 970, 760, 700 (s) cm^{-1}. - ^1H NMR: δ = 1.01 (t, *J* = 7.0 Hz, 6H, CH_2CH_3), 1.85 (s, 3H, (H_3C)$_2$C=), 1.87 (s, 3H,

$(H_3C)_2C$=), 2.93 (q, J = 7.0 Hz, 4H, CH_2CH$_3$), 6.61 (d, J = 16.0 Hz, 1H, C*H*=CH), 6.89 (d, J = 16.0 Hz, 1H, CH=C*H*), 7.14-7.39 (m, 5H, C_6H_5). - ^{13}C NMR: δ = 14.5 (CH_2*C*H$_3$), 20.5, 21.4 ((H_3*C*)$_2$C=), 47.4 (NCH_2), 125.1 (CH=*C*HPh), 126.2 (*o*-Ph), 126.8 (*p*-Ph), 128.5 (*m*-Ph), 128.8 (*C*H=CHPh), 132.0 (*C*=C(Cl)N), 138.7 (*i*-Ph), 139.4 (C=*C*(Cl)N). - MS (70 eV), *m/z* (%): 230 (37) [M^++1], 229 (100) [M^+], 215 (33), 214 (94) [M^+–CH_3], 200 (25) [M^+–C_2H_5], 186 (65) [M^+–C_3H_7], 172 (81) [M^+–C_4H_9], 158 (32), 157 (38) [M^+–$C_4H_{10}N$], 152 (76) [M^+–C_6H_5], 143 (40), 142 (74), 141 (61), 128 (45), 117 (66), 110 (64), 105 (33), 98 (82), 91 (63), 77 (26) [C_6H_5], 70 (65). - $C_{16}H_{23}N$ (229.37): Calcd. C 83.79, H 10.11, N 6.11; found C 83.82, H 10.11, N 6.16.

(1-Cyclohex-1-enyl-2-methylpropenyl)diethylamine (**6d**): 48% Yield from **3a** and 1-iodocyclohexene after distillation (50 °C /0.005 mmHg). - IR (film): $\tilde{\nu}$ = 3040 (m, C=CH), 2980, 2950, 2870, 2850 (s, CH), 1635 (m, C=C), 1445, 1375 (s), 1370, 1360, 1300, 1270, 1255 (m), 1215, 1195 (s), 1175 (m), 1140, 1110 (s), 1080 (m), 1035, 1000 (w), 925 (m), 870 (w), 820, 805 (m) cm^{-1}. - ^{1}H NMR: δ = 0.95 (t, J = 7.0 Hz, 6H, CH_2C*H*$_3$), 1.60 (m, 4H, CH_2CH_2), 1.63 (s, 3H, $(H_3C)_2$C=), 1.72 (s, 3H, $(H_3C)_2$C=), 1.90, 2.07 (2m, 4H, =CHC*H*$_2$, *H*$_2$CC=CH), 2.66 (q, J = 7.0 Hz, 4H, C*H*$_2$CH$_3$), 5.37 (m, 1H, =C*H*CH$_2$). - ^{13}C NMR: δ = 14.8 (CH_2*C*H$_3$), 19.7, 20.9 ((H_3*C*)$_2$C=), 22.5, 23.1 (CH_2CH_2), 25.4, 29.7 (=*C*HCH$_2$, H_2C*C*=CH), 47.2 (NCH_2), 122.5 (*C*=CH), 127.2 (C=*C*H), 135.0 (*C*=C(Cl)N), 144.3 (C=*C*(Cl)N). - MS (70 eV), *m/z* (%): 208 (13) [M^++1], 207 (77) [M^+], 206 (24), 193 (15), 192 (100) [M^+–CH_3], 178 (18) [M^+–C_2H_5], 165 (10), 164 (59) [M^+–C_3H_7], 136 (26) [M^+–C_5H_{11}], 108 (15), 93 (17), 91 (15), 81 (22), 79 (17), 72 (10) [$C_4H_{10}N$], 67 (18), 55 (12). - $C_{14}H_{25}N$ (207.36): Calcd. C 81.09, H 12.15, N 6.75; found C 80.88, H 12.13, N 6.93.

(1-Cyclohexylideneallyl)diethylamine (**6e**): 46% Yield from **3b** and bromoethene after distillation (45 °C /0.001 mmHg). - IR (film): $\tilde{\nu}$ = 2970, 2910, 2850 (s, CH), 1640 (s, C=C), 1610 (m, C=C), 1445, 1370 (s), 1340, 1305, 1290 (m), 1255, 1230, 1205 (s), 1155 (m), 1115, 1090, 1070 (s), 1010, 990, 920, 900 (m), 855, 810, 790 (w) cm^{-1}. - ^{1}H NMR: δ = 0.95 (t, J = 7.0 Hz, 6H, CH_2C*H*$_3$), 1.54 (m, 6H, $CH_2CH_2CH_2$), 2.28 (m, 2H, H_2CC=), 2.39 (m, 2H, H_2CC=), 2.81 (q, J = 7.0 Hz, 4H, C*H*$_2$CH$_3$), 5.07 (dd, J = 11.0, 2.5 Hz, 1H, CH=C*H*$_2$), 5.17 (dd, J = 17.5, 2.5 Hz, 1H, CH=C*H*$_2$), 6.35 (dd, J = 17.5, 11.5 Hz, 1H, C*H*=CH_2). - ^{13}C NMR: δ = 14.4 (CH_2*C*H$_3$), 27.1, 28.0, 28.4 (CH_2), 30.4, 30.8 (H_2*C*C=), 47.5 (NCH_2), 115.0 (=CH_2), 131.2 (CH=), 136.5 (*C*=C(Cl)N), 139.5 (C=*C*(Cl)N). - MS (70 eV), *m/z* (%): 194 (2) [M^++1], 193 (16) [M^+], 178 (22) [M^+–CH_3], 164 (27) [M^+–C_2H_5], 152 (10), 150 (11) [M^+–C_3H_7], 139 (11), 138 (100) [M^+–C_4H_7], 136 (14), 125 (23), 122 (10), 110 (22), 96 (35), 91 (13), 82 (18), 81 (16), 79 (22), 67 (19), 54 (21).

(1-Cyclohexylidenehept-2-enyl)diethylamine (**6f**): 64% Yield from **3b** and (*E*)-1-iodohex-1-ene after distillation (90 °C /0.005 mmHg). - IR (film): $\tilde{\nu}$ = 3040 (w, C=CH), 2970, 2930, 2855, 2835 (s, CH), 1640, 1600 (w, C=C), 1460, 1450, 1375 (s), 1340, 1270, 1260 (m), 1235, 1210 (s), 1105, 1095, 1070 (m), 970 (s), 855 (w) cm^{-1}. - ^{1}H NMR: δ = 0.90 (t, J = 6.5 Hz, 3H, $(CH_2)_3$C*H*$_3$), 0.93 (t, J = 7.0 Hz, 6H, NCH_2C*H*$_3$), 1.25-1.60 (m, 10H, C*H*$_2$C*H*$_2$C*H*$_2$, CH_2(C*H*$_2$)$_2$CH$_3$), 2.10 (m, 2H, CH=CHC*H*$_2$), 2.26 (m, 2H, H_2CC=), 2.37 (m, 2H, H_2CC=), 2.74 (q, J = 7.0 Hz, 4H, NCH_2), 5.60 (dt, J = 15.5, 7.0 Hz, 1H, CH=C*H*CH_2), 5.92 (d, J = 15.5 Hz, 1H, C*H*=$CHCH_2$). - ^{13}C NMR: δ = 14.0 ((CH_2)$_3$*C*H$_3$), 14.2 (NCH_2*C*H$_3$), 22.4, 27.2, 28.1, 28.5 (CH_2), 30.2, 30.9 (H_2*C*C=), 32.1, 32.9 (=CH(*C*H$_2$)$_2$), 47.6 (NCH_2), 123.8 (*C*H=$CHCH_2$), 132.8 (CH=*C*HCH_2), 135.9 (*C*=C(Cl)N), 137.0 (C=*C*(Cl)N). - MS (70 eV), *m/z* (%): 250 (4) [M^++1], 249 (23) [M^+], 234 (5) [M^+–CH_3],

220 (32) [M^+–C_2H_5], 206 (5) [M^+–C_3H_7], 193 (14), 192 (100) [M^+–C_4H_9], 110 (65), 67 (10), 55 (14). - $C_{17}H_{31}N$ (249.44): Calcd. C 81.86, H 12.53, N 5.62; found C 81.85, H 12.44, N 5.54.

(1-Cyclohexylidene-3-phenylallyl)diethylamine (**6g**): 56% Yield from **3b** and (*E*)-(2-bromovinyl)benzene after distillation (120 °C /0.005 mmHg). - IR (film): $\tilde{\nu}$ = 3090, 3070, 3040 (m, C=CH), 2980, 2930, 2860, 2840 (s, CH), 1620, 1600 (m, C=C), 1500, 1450, 1380 (s), 1340, 1325 (m), 1275, 1235, 1210 (s), 1130, 1110, 1095, 1075, 1035 (m), 970 (s), 860 (w), 760, 700 (s) cm^{-1}. - ^1H NMR: δ = 1.00 (t, *J* = 7.0 Hz, 6H, CH_2CH_3), 1.57 (m, 6H, $CH_2CH_2CH_2$), 2.39 (m, 4H, H_2CC=), 2.91 (q, *J* = 7.0 Hz, 4H, NCH_2), 6.61 (d, *J* = 16.0 Hz, 1H, C*H*=CH), 6.91 (d, *J* = 16.0 Hz, 1H, CH=C*H*), 7.16-7.40 (m, 5H, C_6H_5). - ^{13}C NMR: δ = 14.5 (CH_2CH_3), 27.0, 28.0, 28.4 (CH_2), 30.8, 31.1 (H_2CC=), 47.6 (NCH_2), 124.5 (CH=CHPh), 126.2 (*o*-Ph), 126.7 (*p*-Ph), 128.5 (*m*-Ph), 129.3 (CH=CHPh), 136.7 (C=C(Cl)N), 138.4 (*i*-Ph), 140.5 (C=C(Cl)N). - MS (70 eV), *m/z* (%): 270 (15) [M^++1], 269 (72) [M^+], 268 (19), 254 (44) [M^+–CH_3], 240 (27) [M^+–C_2H_5], 228 (13), 215 (18), 214 (100) [M^+–C_4H_7], 201 (18), 192 (20) [M^+–C_6H_5], 186 (219), 172 (43), 138 (27), 115 (22), 110 (28), 91 (30), 83 (11), 77 (9) [C_6H_5]. - $C_{19}H_{27}N$ (269.43): Calcd. C 84.70, H 10.10, N 5.20; found C 85.02, H 10.09, N 5.24.

(1-Cyclohex-1-enylcyclohexylidenemethyl)diethylamine (**6h**): 50% Yield from **3b** and 1-iodocyclohexene after distillation (160 °C /0.001 mmHg). - IR (film): $\tilde{\nu}$ = 3010 (w, C=CH), 2960, 2920, 2850 (s, CH), 1655, 1640 (m, C=C), 1460 (m), 1450, 1375 (s), 1340, 1305, 1270 (m), 1255, 1235 (s), 1210, 1135 (m), 1110 (s), 1065, 1040, 1025 (m), 920, 855, 800 (w) cm^{-1}. - ^1H NMR: δ = 0.95 (t, *J* = 7.0 Hz, 6H, CH_2CH_3), 1.40-1.68 (m, 10H, $CH_2CH_2CH_2$, CH_2CH_2), 1.91, 2.07 (2m, 4H, =CHCH_2, H_2CC=CH), 2.11 (t, *J* = 6.5 Hz, 2H, H_2CC=), 2.30 (t, *J* = 6.5 Hz, 2H, H_2CC=), 2.65 (q, *J* = 7.0 Hz, 4H, NCH_2), 5.36 (m, 1H, C=CH). - ^{13}C NMR: δ = 14.6 (CH_2CH_3), 22.5, 23.1 (CH_2CH_2), 25.4, 27.4, 28.0, 29.1, 29.7 (CH_2), 30.3, 31.6 (H_2CC=), 47.4 (NCH_2), 126.4 (C=CH), 131.6 (C=CH), 134.5 (C=C(Cl)N), 141.4 (C=C(Cl)N). - MS (70 eV), *m/z* (%): 248 (5) [M^++1], 247 (29) [M^+], 246 (11), 232 (40) [M^+–CH_3], 218 (27) [M^+–C_2H_5], 204 (38) [M^+–C_3H_7], 192 (30) [M^+–C_4H_7], 190 (30) [M^+–C_4H_9], 164 (92), 150 (100), 136 (50), 122 (22), 108 (29), 95 (33), 93 (30), 91 (49), 81 (51), 79 (47), 67 (49).

1-(1-Isopropylideneallyl)piperidine (**6i**): 49% Yield from **3c** and bromoethene after distillation (25 °C /0.01 mmHg). - IR (film): $\tilde{\nu}$ = 3100, 3060, 3020 (w, C=CH), 3000, 2930, 2860, 2810 (s, CH), 2740 (m), 1625, 1600 (w, C=C), 1455, 1445, 1380 (s), 1340, 1270, 1240, 1225 (m), 1200 (s), 1180 (m), 1130 (s), 1115, 1070, 1040, 990, 915, 860, 800 (m) cm^{-1}. - ^1H NMR: δ = 1.40–1.65 (m, 6H, $NCH_2CH_2CH_2$), 1.73 (s, 3H, $(H_3C)_2C$=), 1.78 (s, 3H, $(H_3C)_2C$=), 2.77 (t, *J* = 5.0 Hz, 4H, NCH_2), 5.08 (dd, *J* = 11.0, 2.5 Hz, 1H, CH=CH_2), 5.27 (dd, *J* = 17.5, 2.5 Hz, 1H, CH=CH_2), 6.33 (dd, *J* = 17.5, 11.0 Hz, 1H, CH=CH_2). - ^{13}C NMR: δ = 20.2, 20.4 ($(H_3C)_2C$=), 24.8 ($NCH_2CH_2CH_2$), 27.7 (NCH_2CH_2), 51.7 (NCH_2), 114.7 (=CH_2), 126.3 (C=C(Cl)N), 132.4 (CH=), 142.9 (C=C(Cl)N). - MS (70 eV), *m/z* (%): 166 (11) [M^++1], 165 (92) [M^+], 164 (69), 150 (79) [M^+–CH_3], 136 (17) [M^+–C_2H_5], 122 (100) [M^+–C_3H_7], 108 (27) [M^+–C_4H_9], 94 (22), 84 (30), 81 (12), 80 (15), 79 (13), 67 (23), 55 (16), 54 (24).

1-(1-Isopropylidenehept-2-enyl)piperidine (**6j**): 72% Yield from **3c** and (*E*)-1-iodohex-1-ene after distillation (110 °C /0.001 mmHg). - IR (film): $\tilde{\nu}$ = 2960, 2920, 2860, 2800 (s, CH), 2740, 2700, 2670 (m), 1720 (w), 1640 (m, C=C), 1465, 1452, 1442, 1380 (s), 1365, 1340, 1270, 1235, 1225 (m), 1200 (s), 1180, 1150 (m), 1130,

1115 (s), 1040 (m), 975 (s), 860 (m) cm^{-1}. - ^1H NMR: δ = 0.91 (t, *J* = 7.0 Hz, 3H, $(CH_2)_3CH_3$), 1.20–1.66 (m, 10H, $NCH_2CH_2CH_2$, $CH_2(CH_2)_2CH_3$), 1.70 (s, 3H, $(H_3C)_2C=$), 1.76 (s, 3H, $(H_3C)_2C=$), 2.11 (m, 2H, $CH=CHCH_2$), 2.73 (t, *J* = 5.2 Hz, 4H, NCH_2), 5.69 (dt, *J* = 15.5, 6.8 Hz, 1H, $CH=CHCH_2$), 5.89 (d, *J* = 15.5 Hz, 1H, $CH=CHCH_2$). - ^{13}C NMR: δ = 14.0 ($(CH_2)_3CH_3$), 19.9, 20.5 ($(H_3C)_2C=$), 22.4 ($(CH_2)_2CH_2CH_3$), 24.9 ($NCH_2CH_2CH_2$), 27.2 (NCH_2CH_2), 32.0, 32.8 ($=CH(CH_2)_2$), 52.0 (NCH_2), 123.3 ($C=C(Cl)N$), 125.2 ($CH=CHCH_2$), 132.7 ($CH=CHCH_2$), 142.6 ($C=C(Cl)N$). - MS (70 eV), *m/z* (%): 222 (4) $[M^++1]$, 221 (92) $[M^+]$, 206 (8) $[M^+–CH_3]$, 192 (25) $[M^+–C_2H_5]$, 178 (10) $[M^+–C_3H_7]$, 165 (14), 164 (100) $[M^+–C_4H_9]$, 122 (66), 84 (19), 67 (11), 55 (13). - $C_{15}H_{27}N$ (221.39): Calcd. C 81.38, H 12.29, N 6.33; found C 81.04, H 12.22, N 6.44.

1-(1-Isopropylidene-3-phenylallyl)piperidine (**6k**): 83% Yield from **3c** and (*E*)-(2-bromovinyl)benzene after distillation (120 °C /0.001 mmHg). - IR (film): $\tilde{\nu}$ = 3090, 3070, 3035 (m, C=CH), 2940, 2860, 2810 (s, CH), 1650 (s, C=C), 1600 (m, C=C), 1500, 1455, 1450, 1385 (s), 1370, 1345 (m), 1280 (s), 1245, 1230 (m), 1200, 1185 (s), 1160 (m), 1130 (s), 1080 (m), 1035, 970 (s), 915, 865 (w), 760, 700 (s) cm^{-1}. - ^1H NMR: δ = 1.46–1.63 (m, 6H, $NCH_2CH_2CH_2$), 1.82 (s, 3H, $(H_3C)_2C=$), 1.83 (s, 3H, $(H_3C)_2C=$), 2.86 (t, *J* = 5.0 Hz, 4H, NCH_2), 6.69 (d, *J* = 16.0 Hz, 1H, $CH=CH$), 6.82 (d, *J* = 16.0 Hz, 1H, $CH=CH$), 7.15-7.39 (m, 5H, C_6H_5). - ^{13}C NMR: δ = 20.7, 20.8 ($(H_3C)_2C=$), 24.8 ($NCH_2CH_2CH_2$), 27.2 (NCH_2CH_2), 51.7 (NCH_2), 125.3 ($CH=CHPh$), 126.2 (*o*-Ph), 126.8 (*p*-Ph), 127.3 ($C=C(Cl)N$), 128.5 (*m*-Ph), 129.2 ($CH=CHPh$), 138.3 (*i*-Ph), 142.8 ($C=C(Cl)N$). - MS (70 eV), *m/z* (%): 242 (11) $[M^++1]$, 241 (58) $[M^+]$, 240 (38), 226 (20) $[M^+–CH_3]$, 212 (3) $[M^+–C_2H_5]$, 199 (16), 198 (100) $[M^+–C_3H_7]$, 184 (8) $[M^+–C_4H_9]$, 170 (10), 164 (47), 142 (12), 141 (14), 130 (15), 128 (20), 122 (24), 115 (13), 91 (11), 84 (16). - $C_{17}H_{23}N$ (241.38): Calcd. C 84.59, H 9.60, N 5.80; found C 84.21, H 9.75, N 6.19.

1-(1-Cyclohex-1-enyl-2-methylpropenyl)piperidine (**6l**): 50% Yield from **3c** and 1-iodocyclohexene after distillation (110 °C /0.001 mmHg). - IR (film): $\tilde{\nu}$ = 3030 (m, C=CH), 2990, 2930, 2855, 2800 (s, CH), 2740, 2700, 2670 (m), 1645 (m, C=C), 1455, 1445, 1383 (s), 1325 (m), 1280 (s), 1265 (m), 1235, 1200, 1170 (s), 1142 (m), 1125 (s), 1085, 1075, 1065 (m), 1040 (s), 1005, 970 (w), 930 (s), 890 (m), 810 (w) cm^{-1}. - ^1H NMR: δ = 1.39 (m, 2H, $NCH_2CH_2CH_2$), 1.50–1.65 (m, 8H, $NCH_2CH_2CH_2$, CH_2CH_2), 1.74 (s, 3H, $(H_3C)_2C=$), 1.88 (s, 3H, $(H_3C)_2C=$), 2.01 (m, 4H, $=CHCH_2$, $H_2CC=CH$), 2.72 (t, *J* = 5.0 Hz, 4H, NCH_2), 5.46 (m, 1H, $=CHCH_2$). - ^{13}C NMR: δ = 19.1, 20.8 ($(H_3C)_2C=$), 22.7, 23.2 (CH_2CH_2), 25.2 ($NCH_2CH_2CH_2$), 25.6, 30.3 ($=CHCH_2$, $H_2CC=CH$), 27.2 (NCH_2CH_2), 52.7 (NCH_2), 119.0 ($C=CH$), 126.9 ($C=CH$), 136.3 ($C=C(Cl)N$), 147.5 ($C=C(Cl)N$). - MS (70 eV), *m/z* (%): 219 (89) $[M^+]$, 218 (47), 204 (73) $[M^+–CH_3]$, 190 (26) $[M^+–C_2H_5]$, 177 (17), 176 (100) $[M^+–C_3H_7]$, 162 (50) $[M^+–C_4H_9]$, 148 (22) $[M^+–C_5H_{11}]$, 134 (11), 108 (12), 93 (13), 92 (14), 84 (30), 79 (15), 77 (11), 55 (14). - $C_{15}H_{25}N$ (219.37): Calcd. C 82.13, H 11.49, N 6.39; found C 82.04, H 11.53, N 6.59.

1-(1-Cyclohexylideneallyl)piperidine (**6m**): 49% Yield from **3d** and bromoethene after distillation (90 °C /0.001 mmHg). - IR (film): $\tilde{\nu}$ = 2910, 2850, 2800 (s, CH), 1620 (m, C=C), 1450, 1440 (s), 1410 (m), 1380 (s), 1355, 1340 (m), 1270, 1250, 1235 (s), 1200, 1180 (m), 1125 (s), 1075, 1040, 1010 (m), 1000 (s), 940 (m), 920, 910 (s), 855 (m) cm^{-1}. - ^1H NMR: δ = 1.40–1.60 (m, 12H, $NCH_2CH_2CH_2$, $CH_2CH_2CH_2$), 2.22 (m, 2H, $H_2CC=$), 2.33 (m, 2H, $H_2CC=$), 2.76 (t, *J* = 5.5 Hz, 4H, NCH_2), 5.07 (dd, *J* = 11.0, 2.5 Hz, 1H, $CH=CH_2$), 5.27 (dd, *J* =

17.5, 2.5 Hz, 1H, CH=CH_2), 6.34 (dd, J = 17.5, 11.0 Hz, 1H, CH=CH_2). - ^{13}C NMR: δ = 24.8 (NCH_2CH_2-CH_2), 27.0, 28.1, 28.3 (CH_2), 27.2 (NCH_2CH_2), 29.9, 30.8 (H_2CC=), 52.2 (NCH_2), 115.0 (=CH_2), 133.0 (CH=), 134.6 (*C*=C(Cl)N), 140.7 (C=*C*(Cl)N). - MS (70 eV), *m/z* (%): 206 (6) [M^++1], 205 (42) [M^+], 204 (18), 190 (8) [M^+–CH_3], 176 (16) [M^+–C_2H_5], 164 (14), 162 (21) [M^+–C_3H_7], 151 (15), 150 (100) [M^+–C_4H_7], 137 (27), 136 (11), 122 (15), 84 (15).

1-(1-Cyclohexylidenehept-2-enyl)piperidine (**6n**): 61% Yield from **3d** and (*E*)-1-iodohex-1-ene after distillation (110 °C /0.002 mmHg). - IR (film): $\tilde{\nu}$ = 3040 (w, C=CH), 2940, 2860, 2800 (s, CH), 2765 (m), 2705, 2675 (w), 1640, 1605 (w, C=C), 1450, 1445, 1380 (s), 1345, 1330, 1310 (m), 1270 (s), 1255 (m), 1235, 1200 (s), 1180, 1155 (m), 1125, 1115 (s), 1040 (m), 1010, 975, 860 (s) cm^{-1}. - ^{1}H NMR: δ = 0.91 (t, J = 7.0 Hz, 3H, $(CH_2)_3CH_3$), 1.30–1.60 (m, 16H, $NCH_2CH_2CH_2$, $CH_2CH_2CH_2$, $CH_2(CH_2)_2CH_3$), 2.10 (m, 2H, CH=CHCH_2), 2.20 (m, 2H, H_2CC=), 2.32 (m, 2H, H_2CC=), 2.71 (t, J = 5.5 Hz, 4H, NCH_2), 5.67 (dt, J = 15.5, 7.0 Hz, 1H, CH=C$H$$CH_2$), 5.92 (d, J = 15.5 Hz, 1H, CH=$CHCH_2$). - ^{13}C NMR: δ = 14.0 ($(CH_2)_3CH_3$), 22.4 ($(CH_2)_2CH_2CH_3$), 24.8 ($NCH_2CH_2CH_2$), 27.1, 28.2, 28.3 (CH_2), 27.2 (NCH_2CH_2), 29.6, 30.9 (H_2CC=), 32.0, 32.7 (=$CH(CH_2)_2$), 52.5 (NCH_2), 124.8 (*C*H=$CHCH_2$), 131.6 (*C*=C(Cl)N), 132.8 (CH=*C*HCH_2), 140.5 (C=*C*(Cl)N). - MS (70 eV), *m/z* (%): 262 (5) [M^++1], 261 (26) [M^+], 233 (16), 232 (69) [M^+–C_2H_5], 218 (9) [M^+–C_3H_7], 205 (15), 204 (100) [M^+–C_4H_9], 178 (14), 150 (11), 136 (10), 123 (12), 122 (90), 105 (10), 93 (14), 91 (18), 84 (31), 79 (24), 77 (20), 67 (27), 55 (34). - $C_{18}H_{31}N$ (261.45): Calcd. C 82.69, H 11.95, N 5.36; found C 82.48, H 11.99, N 5.76.

1-(1-Cyclohexylidene-3-phenylallyl)piperidine (**6o**): 64% Yield from **3d** and (*E*)-(2-bromovinyl)benzene after distillation (150 °C /0.002 mmHg). - IR (film): $\tilde{\nu}$ = 2980, 2940, 2860 (s, CH), 1640 (w, C=C), 1465, 1445 (s), 1385, 1370, 1310, 1275, 1240 (m), 1185 (s), 1135, 1115 (m), 1075 (s), 1045, 1010 (m), 920 (s) cm^{-1}. - ^{1}H NMR: δ = 1.40–1.67 (m, 12H, $NCH_2CH_2CH_2$, $CH_2CH_2CH_2$), 2.31 (m, 2H, H_2CC=), 2.36 (m, 2H, H_2CC=), 2.85 (t, J = 5.5 Hz, 4H, NCH_2), 6.71 (d, J = 16.0 Hz, 1H, CH=CH), 6.84 (d, J = 16.0 Hz, 1H, CH=CH), 7.17-7.40 (m, 5H, C_6H_5). - ^{13}C NMR: δ = 24.7 ($NCH_2CH_2CH_2$), 27.0, 28.2, 28.4 (CH_2), 27.2 (NCH_2CH_2), 30.3, 31.2 (H_2CC=), 52.2 (NCH_2), 125.0 (CH=*C*HPh), 126.3 (*o*-Ph), 126.8 (*p*-Ph), 128.5 (*m*-Ph), 129.4 (*C*H=CH-Ph), 135.9 (*C*=C(Cl)N), 138.3 (*i*-Ph), 140.5 (C=*C*(Cl)N). - MS (70 eV), *m/z* (%): 282 (11) [M^++1], 281 (55) [M^+], 280 (29), 252 (11) [M^+–C_2H_5], 240 (16), 238 (16) [M^+–C_3H_7], 227 (20), 226 (100) [M^+–C_4H_7], 224 (17), 213 (35), 204 (24), 198 (74), 190 (19), 141 (14), 122 (29), 115 (24), 91 (27), 84 (26). - $C_{20}H_{27}N$ (281.44): Calcd. C 85.35, H 9.67, N 4.98; found C 84.65, H 9.66, N 4.81.

1-(1-Cyclohex-1-enylcyclohexylidenemethyl)piperidine (**6p**): 50% Yield from **3d** and 1-iodocyclohexene after distillation (180 °C /0.002 mmHg). - IR (film): $\tilde{\nu}$ = 3020 (w, C=CH), 2930, 2850, 2800 (s, CH), 2840, 2770 (w), 1650, 1640 (s, C=C), 1450, 1380, 1275, 1260, 1200, 1120 (s), 1085, 1040, 1010, 930, 860 (m) cm^{-1}. - ^{1}H NMR: δ = 1.36–1.85 (m, 16H, $NCH_2CH_2CH_2$, $CH_2CH_2CH_2$, CH_2CH_2), 1.91, 2.05 (2m, 4H, =CHCH_2, H_2CC=CH), 2.15 (m, 2H, H_2CC=), 2.26 (m, 2H, H_2CC=), 2.64 (t, J = 5.5 Hz, 4H, NCH_2), 5.33 (m, 1H, C=CH). - ^{13}C NMR: δ = 22.4, 22.8 (CH_2CH_2), 24.8 ($NCH_2CH_2CH_2$), 25.4, 26.9, 27.3, 27.9, 28.8, 28.9 (CH_2, NCH_2CH_2), 30.5, 31.3 (H_2CC=), 55.0 (NCH_2), 125.9 (*C*=CH), 126.6 (C=*C*H), 135.6 (*C*=C(Cl)N), 145.0 (C=*C*(Cl)N). - MS (70 eV), *m/z* (%): 260 (17) [M^++1], 259 (97) [M^+], 258 (54), 244 (8) [M^+–CH_3], 230 (33)

$[M^+–C_2H_5]$, 217 (23), 216 (86) $[M^+–C_3H_7]$, 204 (45) $[M^+–C_4H_7]$, 202 (56) $[M^+–C_4H_9]$, 176 (100), 148 (26), 91 (21), 84 (21), 79 (17).

(S)-(+)-2-(Methoxymethyl)-1-(1-isopropylideneallyl)pyrrolidine (**6q**): 70% Yield from (*S*)-**3e** and bromoethene after distillation (50 °C /0.01 mmHg). - $[\alpha]_D^{20}$ = +186.38 (*c* = 1.40, $CHCl_3$). - IR (film): $\tilde{\nu}$ = 3090, 3055, 3020 (m, C=CH), 2970, 2925, 2870, 2825 (s, CH), 1715, 1675 (w), 1625, 1595 (m, C=C), 1460, 1450 (s), 1385, 1350, 1310, 1295, 1250, 1220 (m), 1200, 1180, 1160, 1115 (s), 1075, 990, 975 (m), 900 (s) cm^{-1}. - ^1H NMR: δ = 1.77 (s, 3H, $(H_3C)_2C$=), 1.78 (s, 3H, $(H_3C)_2C$=), 1.70-2.10 (m, 4 H, CH_2CH_2), 2.94 (dt, *J* = 7.0, 8.0 Hz, 1H, CH_2N), 3.04 (t, *J* = 8.5 Hz, 1H, C***H***$_2OCH_3$), 3.08 (m, 1H, CH_2N), 3.16 (dd, *J* = 8.5, 3.5 Hz, 1H, C***H***$_2OCH_3$), 3.28 (s, 3H, OCH_3), 3.49 (tt, *J* = 8.5, 3.5 Hz, 1H, NCH), 5.03 (dd, *J* = 11.0, 2.5 Hz, 1H, CH=C***H***$_2$), 5.07 (dd, *J* = 17.5, 2.5 Hz, 1H, CH=C***H***$_2$), 6.39 (dd, *J* = 17.5, 11.0 Hz, 1H, C***H***=CH_2). - ^{13}C NMR: δ = 20.0, 20.5 ($(H_3C)_2C$=), 24.6, 29.8 (CH_2CH_2), 51.5 (CH_2N), 58.8, 58.9 (NCH, OCH_3), 76.7 (***C***H_2OCH_3), 113.3 (=CH_2), 130.5 (CH=), 132.0 (***C***=C(Cl)N), 137.4 (C=***C***(Cl)N). - MS (70 eV), *m/z* (%): 195 (10) $[M^+]$, 164 (2) $[M^+–CH_3]$, 151 (11), 150 (100) $[M^+–CH_2OCH_3]$, 79 (12), 70 (22). - $C_{12}H_{21}NO$ (195.31): Calcd. C 73.80, H 10.84, N 7.17; found C 73.74, H 11.18, N 6.87.

(S)-(+)-2-(Methoxymethyl)-1-(1-isopropylidenehept-2-enyl)pyrrolidine (**6r**): 60% Yield from (*S*)-**3e** and (*E*)-1-iodohex-1-ene after distillation (100 °C /0.001 mmHg). - α_D^{20}= +159.30 (neat). - IR (film): $\tilde{\nu}$ = 2940, 2890, 2860 (s, CH), 1655, 1610 (w, C=C), 1460, 1450 (s), 1380, 1350, 1310, 1250, 1220 (m), 1200 (s), 1180, 1160 (m), 1135, 1120, 975 (s), 930, 910 (w) cm^{-1}. - ^1H NMR: δ = 0.90 (t, *J* = 7.0 Hz, 3H, $(CH_2)_3CH_3$), 1.25-1.42 (m, 4H, $CH_2(CH_2)_2CH_3$), 1.74 (s, 3H, $(H_3C)_2C$=), 1.75 (s, 3H, $(H_3C)_2C$=), 1.76-2.06 (m, 4 H, CH_2CH_2), 2.11 (m, 2H, CH=C***H***CH_2), 2.89 (dt, *J* = 7.0, 8.0 Hz, 1H, CH_2N), 3.02 (t, *J* = 9.0 Hz, 1H, C***H***$_2OCH_3$), 3.16 (dd, *J* = 9.0, 4.0 Hz, 1H, C***H***$_2OCH_3$), 3.28 (s, 3H, OCH_3), 3.40-3.51 (m, 2H, CH_2N, NCH), 5.54 (dt, *J* = 15.5, 7.0 Hz, 1H, CH=C***H***CH_2), 6.00 (d, *J* = 15.5 Hz, 1H, C***H***=$CHCH_2$). - ^{13}C NMR: δ = 13.9 ($(CH_2)_3$***C***H_3), 20.0, 20.2 ($(H_3C)_2C$=), 22.3 ($(CH_2)_2$***C***H_2CH_3), 24.5, 29.8 (CH_2CH_2), 32.0, 32.7 (=CH(***C***$H_2)_2$), 51.6 (CH_2N), 58.8, 58.9 (NCH, OCH_3), 76.7 (***C***H_2OCH_3), 123.6 (***C***H=$CHCH_2$), 128.7 (CH=***C***HCH_2), 131.0 (***C***=C(Cl)N), 136.9 (C=***C***(Cl)N). - MS (70 eV), *m/z* (%): 252 (3) $[M^+$+1], 251 (17) $[M^+]$, 236 (2) $[M^+–CH_3]$, 222 (7) $[M^+–C_2H_5]$, 220 (9) $[M^+–OCH_3]$, 208 (4) $[M^+–C_3H_7]$, 206 (100) $[M^+–CH_2OCH_3]$, 162 (12), 138 (10), 95 (12), 81 (15), 71 (11), 70 (23), 67 (14).

(S)-(+)-2-(Methoxymethyl)-1-(1-isopropylidene-3-phenylallyl)pyrrolidine (**6s**): 96% Yield from (*S*)-**3e** and (*E*)-(2-bromovinyl)benzene after distillation (130 °C /0.001 mmHg). - $[\alpha]_D^{20}$= +129.50 (*c* = 1.05, $CHCl_3$). - IR (film): $\tilde{\nu}$ = 3090, 3070, 3035 (m, C=CH), 2975, 2930, 2880, 2830 (s, CH), 1655, 1600 (s, C=C), 1500, 1470, 1460 (s), 1390, 1370, 1355, 1315, 1300 (m), 1200, 1125, 1080 (s), 1040 (m), 975, 920, 765, 700 (s) cm^{-1}. - ^1H NMR: δ = 1.83 (s, 3H, $(H_3C)_2C$=), 1.88 (s, 3H, $(H_3C)_2C$=), 1.75-2.15 (m, 4H, CH_2CH_2), 3.01 (m, 1H, CH_2N), 3.08 (t, *J* = 8.0 Hz, 1H, C***H***$_2OCH_3$), 3.17 (m, 1H, CH_2N), 3.20 (dd, *J* = 8.0, 3.5 Hz, 1H, C***H***$_2OCH_3$), 3.27 (s, 3H, OCH_3), 3.56 (tt, *J* = 8.0, 3.5 Hz, 1H, NCH), 6.49 (d, *J* = 16.0 Hz, 1H, C***H***=CH), 6.90 (d, *J* = 16.0 Hz, 1H, CH=C***H***), 7.16-7.39 (m, 5H, C_6H_5). - ^{13}C NMR: δ = 20.3, 20.8 ($(H_3C)_2C$=), 24.7, 29.9 (CH_2CH_2), 51.6 (CH_2N), 58.9, 59.2 (NCH, OCH_3), 76.6 (***C***H_2OCH_3), 123.9 (CH=***C***HPh), 126.2 (*o*-Ph), 126.8 (*p*-Ph), 127.9 (***C***H=CHPh), 128.5 (*m*-Ph), 133.0 (***C***=C(Cl)N), 137.3 (C=***C***(Cl)N), 138.2 (*i*-Ph). - MS (70 eV), *m/z* (%): 272 (4) $[M^+$+1], 271 (21) $[M^+]$, 256 (2) $[M^+–CH_3]$, 240 (6) $[M^+–OCH_3]$, 227 (17), 226 (100) $[M^+–$

CH_2OCH_3], 157 (56), 142 (59), 141 (17). - $C_{18}H_{25}NO$ (271.41): Calcd. C 79.66, H 9.28, N 5.16; found C 79.42, H 9.46, N 5.73.

(S)-(+)-1-(1-Cyclohex-1-enyl-2-methylpropenyl)-2-(methoxymethyl)pyrrolidine (**6t**): 58% Yield from (*S*)-**3e** and 1-iodocyclohexene after distillation (90 °C /0.001 mmHg). - α_D^{20}= +306.30 (neat). - IR (film): $\tilde{\nu}$ = 2910, 2850 (s, CH), 1640 (m, C=C), 1460, 1450 (s), 1345 (m), 1310, 1300 (s), 1275, 1260 (m), 1220, 1195, 1135, 1115, 1095 (s), 1075, 1055, 1035, 975, 965 (m), 925 (s), 910 (m), 875, 830, 805 (w) cm^{-1}. - ^1H NMR: δ = 1.63 (s, 3H, $(H_3C)_2C$=), 1.66 (s, 3H, $(H_3C)_2C$=), 1.50-2.15 (m, 12H, $NCH_2CH_2CH_2$, =$CHCH_2CH_2CH_2$, H_2CC=CH), 2.75 (dt, *J* = 8.5, 6.8 Hz, 1H, CH_2N), 2.96 (t, *J* = 8.5 Hz, 1H, CH_2OCH_3), 3.19-3.28 (m, 3H, CH_2N, CH_2OCH_3, NCH), 3.29 (s, 3H, OCH_3), 5.45 (m, 1H, =$CHCH_2$). - ^{13}C NMR: δ = 19.7, 20.7 ($(H_3C)_2C$=), 22.5, 22.8 (=$CHCH_2CH_2CH_2$), 24.5, 25.4, 28.8, 29.7 ($NCH_2CH_2CH_2$, =$CHCH_2$, H_2CC=CH), 53.5 (CH_2N), 58.9, 59.1 (NCH, OCH_3), 77.3 (CH_2OCH_3), 119.1 (C=CH), 127.5 (C=CH), 135.5 (C=C(Cl)N), 142.5 (C=C(Cl)N). - MS (70 eV), *m/z* (%): 250 (3) [M^++1], 249 (18) [M^+], 234 (2) [M^+-CH_3], 218 (6) [M^+-OCH_3], 205 (15), 204 (100) [$M^+-CH_2OCH_3$], 107 (15), 93 (12), 70 (27). - $C_{16}H_{27}NO$ (249.40): Calcd. C 77.06, H 10.91, N 5.62; found C 76.93, H 10.93, N 5.96.

(S)-(+)-2-(Methoxy-1-methylethyl)-1-(1-isopropylideneallyl)pyrrolidine (**6u**): 62% Yield from (*S*)-**3f** and bromoethene after distillation (60 °C /0.001 mmHg). - $[\alpha]_D^{20}$= +194.70 (*c* = 1.06, $CHCl_3$). - IR (film): $\tilde{\nu}$ = 2970, 2940, 2830 (s, CH), 1655 (s, C=C), 1595 (m, C=C), 1470, 1460 (s), 1410 (m), 1380, 1365 (s), 1305, 1270, 1250, 1230, 1210, 1180 (m), 1155, 1085 (s), 1000, 920, 905 (m), 870, 840 (w) cm^{-1}. - ^1H NMR: δ = 0.97 (s, 3H, $NCHC(CH_3)_2$), 1.07 (s, 3H, $NCHC(CH_3)_2$), 1.76 (s, 3H, $(H_3C)_2C$=), 1.82 (s, 3H, $(H_3C)_2C$=), 1.70-2.00 (m, 4H, $NCHCH_2CH_2$), 2.85 (m, 1H, CH_2N), 3.16 (s, 3H, OCH_3), 3.20 (m, 1H, CH_2N), 3.47 (dd, *J* = 8.0, 3.5 Hz, 1H, NCH), 5.04 (dd, *J* = 17.5, 2.0 Hz, 1H, CH=CH_2), 5.13 (dd, *J* = 11.0, 2.0 Hz, 1H, CH=CH_2), 6.26 (dd, *J* = 17.5, 11.0 Hz, 1H, CH=CH_2). - ^{13}C NMR: δ = 20.18, 20.21, 20.7, 22.3 ($(H_3C)_2C$=, $NCHC(CH_3)_2$), 25.6, 27.3 (CH_2CH_2), 49.1 (OCH_3), 54.4 (CH_2N), 64.9 (NCH), 79.2 ($NCHC(CH_3)_2$), 114.5 (=CH_2), 128.4 (C=C(Cl)N), 130.9 (CH=), 140.6 (C=C(Cl)N). - MS (70 eV), *m/z* (%): 223 (3) [M^+], 192 (1) [M^+-OCH_3], 151 (11), 150 (100) [$M^+-C_4H_9O$], 70 (15).

(S)-(+)-2-(Methoxy-1-methylethyl)-1-(1-isopropylidenehept-2-enyl)pyrrolidine (**6v**): 54% Yield from (*S*)-**3f** and (*E*)-1-iodohex-1-ene after distillation (110 °C /0.001 mmHg). - α_D^{20} = +261.52 (neat). - IR (film): $\tilde{\nu}$ = 2970, 2910, 2860, 2820 (s, CH), 1650 (w, C=C), 1470, 1460, 1380 (s), 1365, 1305, 1295, 1210, 1200, 1180 (m), 1155, 1145, 1080 (s), 975 (m) cm^{-1}. - ^1H NMR: δ = 0.90 (t, *J* = 7.0 Hz, 3H, $(CH_2)_3CH_3$), 0.97 (s, 3H, $NCHC(CH_3)_2$), 1.07 (s, 3H, $NCHC(CH_3)_2$), 1.30-1.45 (m, 4H, $CH_2(CH_2)_2CH_3$), 1.73 (s, 3H, $(H_3C)_2C$=), 1.78 (s, 3H, $(H_3C)_2C$=), 1.60-2.05 (m, 4H, $NCHCH_2CH_2$), 2.13 (m, 2H, CH=$CHCH_2$), 2.83 (dt, *J* = 8.5, 3.5 Hz, 1H, CH_2N), 3.16 (s, 3H, OCH_3), 3.19 (m, 1H, CH_2N), 3.46 (dd, *J* = 3.5, 8.5 Hz, 1H, NCH), 5.50 (dt, *J* = 16.0, 7.0 Hz, 1H, CH=$CHCH_2$), 5.85 (d, *J* = 15.5 Hz, 1H, CH=$CHCH_2$). - ^{13}C NMR: δ = 13.9 ($(CH_2)_3CH_3$), 20.2, 20.3, 20.4, 22.38, 22.40 ($(H_3C)_2C$=, $NCHC(CH_3)_2$, $(CH_2)_2CH_2CH_3$), 25.7, 27.3 ($NCHCH_2CH_2$), 32.0, 32.9 (=$CH(CH_2)_2$), 49.1 (OCH_3), 54.6 (CH_2N), 64.9 (NCH), 79.3 ($NCHC(CH_3)_2$), 124.2 (CH=$CHCH_2$), 125.1 (C=C(Cl)N), 132.5 (CH=$CHCH_2$), 140.4 (C=C(Cl)N). - MS (70 eV), *m/z* (%): 279 (5) [M^+], 248 (1) [M^+-OCH_3], 207 (15), 206 (100) [$M^+-C_4H_9O$], 70 (10).

(S)-(+)-2-(Methoxy-1-methylethyl)-1-(1-isopropylidene-3-phenylallyl)pyrrolidine (**6w**): 77% Yield from (*S*)-**3f** and (*E*)-(2-bromovinyl)benzene after distillation (150 °C /0.001 mmHg). - α_D^{20} = +209.25 (neat). - IR (film): $\tilde{\nu}$ = 3080, 3060, 3020 (m, C=CH), 2960, 2930, 2900, 2850, 2820 (s, CH), 1635 (s, C=C), 1600 (m, C=C), 1495, 1465, 1460, 1445, 1380, 1360 (s), 1340, 1325, 1300, 1280 (m), 1180, 1155, 1145, 1070, 965 (s), 920 (w), 752, 690 (s) cm^{-1}. - ^{1}H NMR: δ = 1.00 (s, 3H, NCHC(C***H***$_3$)$_2$), 1.10 (s, 3H, NCHC(C***H***$_3$)$_2$), 1.85 (s, 3H, (H$_3$C)$_2$C=), 1.87 (s, 3H, (H$_3$C)$_2$C=), 1.80-2.10 (m, 4H, C***H***$_2$C***H***$_2$), 2.95 (m, 1H, CH$_2$N), 3.13 (s, 3H, OCH$_3$), 3.27 (m, 1H, CH$_2$N), 3.52 (dd, *J* = 8.0, 4.0 Hz, 1H, NCH), 6.44 (d, *J* = 15.5 Hz, 1H, C***H***=CH), 6.77 (d, *J* = 15.5 Hz, 1H, CH=C***H***), 7.16-7.39 (m, 5H, C$_6$H$_5$). - ^{13}C NMR: δ = 20.2, 20.5, 21.0, 22.4 ((H$_3$***C***)$_2$C=, NCHC(***C***H$_3$)$_2$), 25.7, 27.5 (NCH***C***H$_2$***C***H$_2$), 49.2 (OCH$_3$), 54.4 (CH$_2$N), 65.5 (NCH), 79.3 (NCH***C***(CH$_3$)$_2$), 123.9 (CH=***C***HPh), 126.2 (*o*-Ph), 126.9 (*p*-Ph), 128.5 (*m*-Ph), 128.8 (***C***H=CHPh), 129.5 (***C***=C(Cl)N), 138.12 (*i*-Ph), 140.5 (C=***C***(Cl)N). - MS (70 eV), *m/z* (%): 300 (1) [M$^+$+1], 299 (6) [M$^+$], 268 (1) [M$^+$–OCH$_3$], 227 (18), 226 (100) [M$^+$–C$_4$H$_9$O], 157 (40). - C$_{20}$H$_{29}$NO (299.46): Calcd. C 80.22, H 9.76, N 4.67; found C 80.28, H 9.78, N 4.89.

(S)-(+)-1-(1-Cyclohex-1-enyl-2-methylpropenyl)-2-(methoxy-1-methylethyl)pyrrolidine (**6x**): 51% Yield from (*S*)-**3f** and 1-iodocyclohexene after distillation (110 °C /0.001 mmHg). - $[\alpha]_D^{20}$ = +365.1 (*c* = 0.96, CHCl$_3$). - IR (film): $\tilde{\nu}$ = 3060 (m, C=CH), 2970, 2825 (s, CH), 1640 (s, C=C), 1470, 1375, 1360, 1305, 1295, 1275, 1260, 1215, 1200, 1185, 1155, 1145, 1075 (s), 1030, 970, 960 (m), 930 (s), 890, 880, 845, 815 (m), 735, 720, 630, 620 (w) cm^{-1}. - ^{1}H NMR: δ = 0.99 (s, 3H, NCHC(C***H***$_3$)$_2$), 1.05 (s, 3H, NCHC(C***H***$_3$)$_2$), 1.50-2.15 (m, 12H, NCHC***H***$_2$C***H***$_2$, =CHC***H***$_2$C***H***$_2$C***H***$_2$, ***H***$_2$CC=CH), 1.65 (s, 3H, (H$_3$C)$_2$C=), 1.71 (s, 3H, (H$_3$C)$_2$C=), 2.81 (m, 1H, CH$_2$N), 3.18 (s, 3H, OCH$_3$), 3.21 (m, 1H, CH$_2$N), 3.36 (m, 1H, NCH), 5.44 (m, 1H, =C***H***CH$_2$). - ^{13}C NMR: δ = 20.06, 20.11, 21.0, 22.7 ((H$_3$***C***)$_2$C=, NCHC(***C***H$_3$)$_2$), 22.5, 22.8 (=CHCH$_2$***C***H$_2$***C***H$_2$), 25.39, 25.42, 27.0, 28.4 (NCH$_2$***C***H$_2$***C***H$_2$, =CH***C***H$_2$, H$_2$***C***C=CH), 49.3 (OCH$_3$), 55.8 (CH$_2$N), 64.9 (NCH), 79.7 (NCH***C***(CH$_3$)$_2$), 117.8 (***C***=CH), 129.1 (C=***C***H), 135.2 (***C***=C(Cl)N), 145.6 (C=***C***(Cl)N). - MS (70 eV), *m/z* (%): 277 (4) [M$^+$], 246 (1) [M$^+$–OCH$_3$], 205 (16), 204 (100) [M$^+$–C$_4$H$_9$O], 107 (14), 93 (11), 70 (27). - C$_{18}$H$_{31}$NO (277.45): Calcd. C 77.92, H 11.26, N 5.05; found C 77.92, H 11.24, N 5.66.

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16. Aminolysis of *c*-hexyl and *i*-butyric acid chlorides with diethyl amine and piperidine gave the amides **1a-d** following standard procedures.[17] Alternatively, for the synthesis of the corresponding (*S*)-2-

(methoxymethyl)pyrrolidine (SMP)[18] and (*S*)-2-(1-methoxy-1-methylethyl)pyrrolidine (SDP)[18] amides, the secondary amines were deprotonated by addition of *n*-butyl lithium[19]. Subsequent addition of the carboxylic acid chlorides leads to the formation of **1e,f**.

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25. Due to their instability, no satisfactory microanalyses were obtained for the following compounds: **6e,h,i,m,p,r,u,v**.

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