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C. R. Chimie 7 (2004) 855–864
COMPTES RENDUS CHIMIE

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# Intramolecular carbolithiation of *N*-allyl-*N*-2-lithioallylamines: effect of the allyl moiety

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Received 17 November 2003; accepted 3 February 2004

Available online 30 July 2004

**Abstract**

The preparation of new *N*-2-bromoallyl-*N*-(3-functionalized)allylamines and the intramolecular carbolithiation reactions of the corresponding organolithiums generated by bromine–lithium exchange are reported. The effect of the substituent at the terminal position of the allyl moiety is studied. This methodology allows the efficient synthesis of a variety of interesting functionalized pyrrolidine and hexahydroindole derivatives from simple starting materials. ***To cite this article: J. Barluenga et al., C. R. Chimie 7 (2004)***.


**Résumé**

La préparation de nouvelles *N*-2-bromoallyl-*N*-(3-functionalized)allylamines ainsi que la carbolithiation intramoléculaire des organolithiens correspondants générés par échange bromine–lithium est présentée. L'effet du substituant en position terminale du fragment allyle est étudié. Cette méthodologie permet la synthèse efficace d'une variété intéressante de pyrrolidine fonctionnalisées et d'hexahydroindoles provenant de produits de départ simples. ***Pour citer cet article : J. Barluenga et al., C. R. Chimie 7 (2004)***.


*Keywords:* Organolithium compounds; Carbolithiation; Pyrrolidines; Hexahydroindoles

*Mots-clés :* Composés organolithiens ; Carbolithiation ; Pyrrolidines ; Hexahydroindoles

## 1. Introduction

Although simple alkenes are not generally thought of as sites of nucleophilic attack, the formation of ring systems by the anionic cyclisation of olefinic alkyl, aryl and vinyllithiums is an interesting synthetic transformation and provides a regiospecific and highly stereoselective route to five-membered carbocycles [1,2] and heterocycles [3]. Most importantly, it should be possible to functionalize the initially formed cyclisation product by reaction with electrophiles, a reaction

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doi:10.1016/j.crci.2004.02.015

that is not generally possible in the case of radical cyclisations. A major drawback of this kind of carbocyclisations is that they are limited to terminal double bonds; however, it has been possible to obtain cyclised products for 1,2-disubstituted olefins in which the initially formed alkyllithium product is substituted with a moderately activating group [4] or with a leaving group in a β-position [5]. Although the development of this methodology for the preparation of heterocyclic systems has received less attention, several oxygen and nitrogen heterocycles, such as tetrahydrofurans [5,6], pyrrolidines [7], indolines [8,9] or indoles [10], have been synthesized via intramolecular carbolithiation reactions. Moreover, the fact that the ring closure of achiral olefinic organolithiums could proceed enantioselectively in the presence of (–)-sparteine dramatically increases the potential of this kind of processes [11,12]. In this area, we have studied in the last years the behaviour of 2-lithioallyl and 2-lithioaryl amines [13,14], as well as of 2-lithioaryl ethers [15], in their anionic cyclisations onto unactivated double bonds. Here we report our studies about the effect of different substituents at the terminal position of the allyl moiety in the intramolecular carbolithiation reaction of *N*-allyl-*N*-2-lithioallylamine derivatives.

## 2. Results and discussion

Sometime ago, we reported that *N*-allyl-*N*-(2-lithioallyl)amines **2**, generated by bromine-lithium exchange from the corresponding *N*-allyl-*N*-(2-bromoallyl)amines **1**, undergo a 5-*exo* intramolecular carbolithiation in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) to afford 3-lithiomethyl-4-methylenepyrrolidines **3** when the starting amine is aliphatic (R = alkyl) [13]. However, if the 2-bromoallylamine **1** is aromatic (R = aryl), the secondary amide **4** is generated (Fig. 1). In this case, we initially proposed a 6-*endo* cyclisation followed by an irreversible β-elimination (for an alternative mechanism involving an *exo* cyclisation of organolithium **3**, γ-elimination, and a rapid and irreversible fragmentation of the corresponding cyclopropyl intermediate, see [3]). Aside from the mechanistic pathways, these cyclisations provide an efficient method for the preparation of methylenepyrrolidine derivatives.

In order to investigate the effect of the substituents of the allyl moiety of the starting amine in the outcome of the intramolecular cyclisation, we decided to prepare several allyl amines substituted at the terminal position. The syntheses of these compounds **6** were carried out according to Fig. 2. The commercially available *N*-allyl-*N*-cyclohexylamine or *N*-allylaniline was selectively functionalized by successive treatment with *n*-BuLi and *t*-BuLi and further reaction with electrophiles (chlorotrimethylsilane, diphenyldisulfide or tributyltin chloride), affording secondary amines **5a-d** as the *Z*-isomers [16]. On the other hand, the aromatic amines **5e–f** were easily obtained by alkylation of aniline with cinnamyl and crotyl bromide, respectively. Finally, tertiary amines **6** were prepared by alkylation of the corresponding amine **5** with 2,3-dibromopropene using potassium carbonate as base (Table 1).

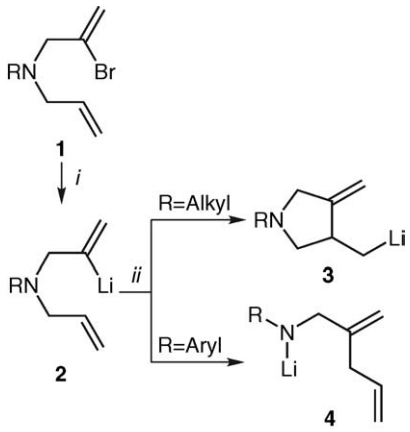


Fig. 1. Intramolecular carbolithiation of *N*-allyl-*N*-(2-lithioallyl) amines **2**.

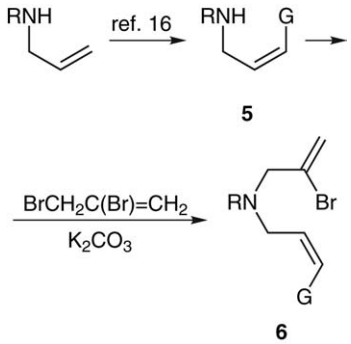


Fig. 2. Synthesis of *N*-(3-substituted-2-propenyl)-*N*-(2-bromoallyl) amines **6**.

Table 1
Preparation of tertiary *N*-(2-bromoallyl)amines **6**

| Starting amine | R | G | Product | Yield (%)[a] |
|---|---|---|---|---|
| **5a** | *c*-$C_6H_{11}$ | (*Z*)-SPh | **6a** | 72 |
| **5b** | *c*-$C_6H_{11}$ | (*Z*)-$SiMe_3$ | **6b** | 71 |
| **5c** | *c*-$C_6H_{11}$ | (*Z*)-$SnBu_3$ | **6c** | 79 |
| **5d** | Ph | (*Z*)-$SiMe_3$ | **6d** | 83 |
| **5e** | Ph | (*E*)-Ph | **6e** | 81 |
| **5f** | Ph | Me[b] | **6f** | 75 |

[a] Isolated yields based on starting amines **5**.
[b] Mixture of *E:Z*-diastereoisomers (6:1).

Treatment of *N*-(2-bromoallyl) amines **6** with 2 equiv. of *t*-BuLi at –78 °C in diethyl ether afforded the vinyllithium derivatives **7**. Addition of TMEDA (2.2 equiv) at low temperature, warming up of the mixture until 0 °C and further reaction with different electrophiles allowed the isolation, after hydrolysis and purification by column chromatography, of 3-substituted-4-methylenepyrrolidines **8** in good yields (Fig. 3 and Table 2). The formation of these pyrrolidine derivatives can be understood by assuming a 5-*exo* intramolecular carbolithiation process that would give rise to the organolithium intermediates **9**, which are finally functionalized by treatment with electrophiles.

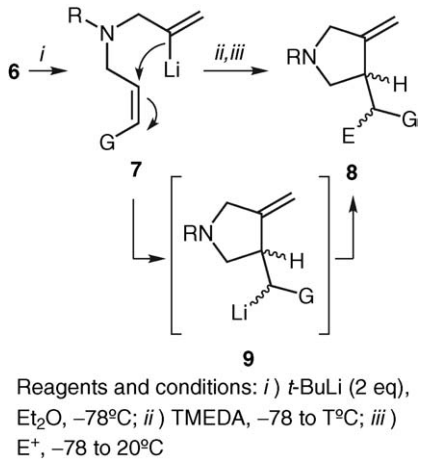


Fig. 3. Intramolecular carbolithiation of *N*-(2-lithioallyl)amines **7**.

In those cases in which the E and G groups are different, pyrrolidine derivatives **8** were obtained as an approximately 2:1 mixture of diastereoisomers. This fact seems to indicate that if we assume that carbolithiation reactions are stereospecific *syn*-addition processes, organolithiums **9** must be configurationally labile at the temperature required to achieve the cyclisation [17,18].

The lack of formation of pyrrolidine derivatives starting from amine **6f**, with a methyl group at the

Table 2
Synthesis of 3-functionalized-4-methylenepyrrolidines **8**

| Starting amine | Organolithium compound | R | G | E | Product | Yield (%)[a] |
|---|---|---|---|---|---|---|
| **6a** | **7a** | *c*-$C_6H_{11}$ | SPh | D | **8a** | 92 |
| **6a** | **7a** | *c*-$C_6H_{11}$ | SPh | SPh | **8b** | 90 |
| **6a** | **7a** | *c*-$C_6H_{11}$ | SPh | $SnBu_3$ | **8c** | 83[b] |
| **6a** | **7a** | *c*-$C_6H_{11}$ | SPh | $C(OH)Ph_2$ | **8d** | 84[b] |
| **6b** | **7b** | *c*-$C_6H_{11}$ | $SiMe_3$ | D | **8e** | 90 |
| **6b** | **7b** | *c*-$C_6H_{11}$ | $SiMe_3$ | $SiMe_3$ | **8f** | 80 |
| **6b** | **7b** | *c*-$C_6H_{11}$ | $SiMe_3$ | SPh | **8g** | 85[b] |
| **6b** | **7b** | *c*-$C_6H_{11}$ | $SiMe_3$ | $SnBu_3$ | **8h** | 73[b] |
| **6c** | **7c** | *c*-$C_6H_{11}$ | $SnBu_3$ | D | **8i** | 94 |
| **6d** | **7d** | Ph | $SiMe_3$ | D | **8j** | 53[c] |
| **6d** | **7d** | Ph | $SiMe_3$ | SPh | **8k** | 50[b,c] |
| **6d** | **7d** | Ph | $SiMe_3$ | $SnBu_3$ | **8l** | 55[b,c] |
| **6e** | **7e** | Ph | Ph | D | **8m** | 61 |

[a] Isolated yields based on starting amines **6**.
[b] Yields referred to the mixture of diastereoisomers.
[c] Low yields obtained due to a partial decomposition of the product on the purification by silica gel chromatography.

terminal position of the double bond, could be attributed to the fact that in the carbolithiation step a non-stabilized secondary carbanion would be generated.

It is interesting to note the effect that the trimethylsilyl and phenyl groups at the terminal position of the allyl moiety exert on the regioselectivity of the process when the starting amine is aromatic (R = Ph). Organolithium compounds **7d** and **7e** undergo regioselectively 5-*exo* cyclisations giving rise to pyrrolidine derivatives **8j-m**. These results contrast with our previous report where aromatic *N*-allyl-*N*-(2-lithioallyl)amines undergo a 6-*endo* cyclisation processes [13] (see Fig. 1). So, the presence of the trimethylsilyl or phenyl groups at the terminal position of the double bond not only favours the carbolithiation of 1,2-disubstituted alkenes but also directs it to a 5-*exo* closure. So, the observed regioselectivity of the cyclisation of aromatic amines is inverted when the double bond is substituted at the terminal position with a moderately activating group such as phenyl or trimethylsilyl.

Moreover, although carbolithiation reactions of phenyl, trimethylsilyl or phenylthio-substituted double bonds are known [4,19], in this paper we present the first example of this kind of carbocyclisations in which the alkene moiety to be carbolithiated is functionalized with a tributyltin group (see organolithium **7c**). Surprisingly, this reaction takes place almost quantitatively though it is well known the easy tin-lithium transmetalation reaction.

In order to know the temperature at which the carbolithiation processes take place for each of the *N*-2-(lithioallyl)amines **7**, the cyclisations were monitored by GC–MS analysis of aliquots quenched with MeOD at different temperature intervals. After this study, we can conclude that in all the cases the temperature at which the cyclisation reaction takes place is lower than the temperature at which the unsubstituted parent *N*-allyl-*N*-(2-lithioallyl)amines **2** cyclises (see Fig. 1). In addition, some interesting differences were found depending on the G group and on the nitrogen electron density. So, organolithium compound **7a**, with a phenylthio substituent at the allyl moiety, cyclises at –78 °C, whereas **7b**, substituted with a trimethylsilyl group, cyclises at –20 °C. On the other hand, the exact temperature at which the cyclisation of tributyltin-substituted **7c** occurs could not be determined with accuracy. However, we could estimate that, in this, case the cyclisation step proceeds at temperature lower

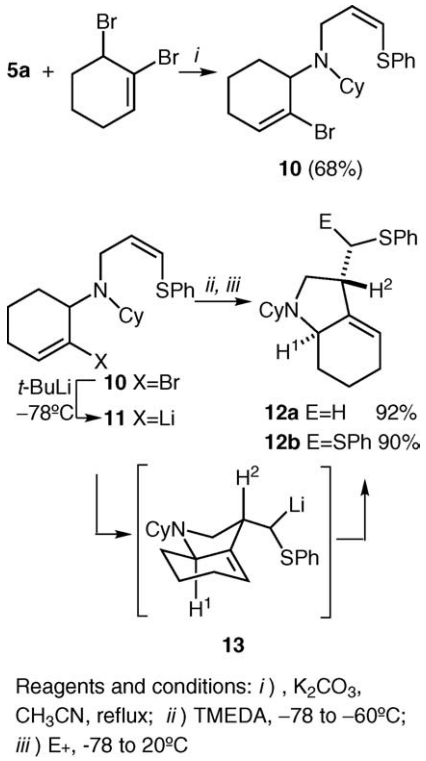


Fig. 4. Diastereoselective intramolecular carbolithiation of organolithium compound **11**.

than –50 °C. In the case of the organolithium compound **7d**, derived from an aromatic amine and activated with a trimethylsilyl group, the cyclisation takes place at –50 °C and so, by comparing with **7b**, we can conclude that the carbolithiation reactions are faster with aromatic amines than with aliphatic ones. This result could be interpreted taking into account that aliphatic amines could coordinate better with the lithium atom in the organolithium compounds **7**, decreasing the reactivity of these intermediates.

Taking into account the activation effect of a phenylthio group on the double bond and with the aim of extending this reactivity to other starting amines, *N*-(2-bromo-2-cyclohexenyl)-*N*-[(*Z*)-3-phenylthio-2-propenyl]cyclohexylamine **10** was synthesized by alkylation of secondary amine **5a** with 1,6-dibromocyclohexene [20] in the usual way (Fig. 4). Treatment of **10** with *t*-BuLi at –78 ºC rendered organolithium derivative **11** by a bromine-lithium exchange. Addition of TMEDA (2.2 equiv) at the same temperature and warming to –60 °C followed by reaction with MeOH or $Ph_2S_2$ from –78 to 20 °C afforded hexahydroindole deriva-

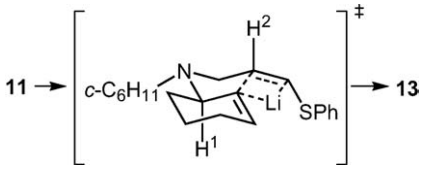


Fig. 5. Proposed transition state for the cyclisation of organolithium **11**.

tives **12a,b** in excellent yields and as single diastereoisomers. The structure of compounds **12** and the *anti* relationship of $H^1$ and $H^2$ were unequivocally ascertained by 2D-NMR experiments (COSY, HMQC, HMBC, and NOESY). Again, the formation of the bicyclic compounds **12** can be explained by assuming a 5-*exo* intramolecular carbolithiation process that gives rise to the organolithium intermediate **13**. Further reaction with the corresponding electrophile produces the final products **12** (Fig. 4).

The observed diastereoselectivity of this cyclisation is consistent with a four-centre transition state similar to the one proposed by Chamberlin for the synthesis of related methylenecyclopentane derivatives [21]. A preferred coplanar approach of the C–Li bond to the double bond would give the observed product (Fig. 5).

In conclusion, we have described the intramolecular carbolithiation of *N*-allyl-*N*-2-lithioallylamines that present a moderately activating group at the terminal position of the double bond. These groups favour the cyclisation and the 5-*exo* regioselectivity. The first example of this kind of reactions with a tributyltin-substituted olefin has also been presented. Following this strategy, interesting functionalized pyrrolidine and hexahydroindole derivatives have been synthesized.

## 3. Experimental part

### 3.1. General remarks

Experiments involving organometallics were carried out in dried glassware under an atmosphere of dry nitrogen using standard Schlenk techniques. Liquid nitrogen was used as a cryoscopic fluid. All common reagents and solvents were obtained from commercial suppliers and used without further purification, unless otherwise indicated. *n*-BuLi was used as a 2.5-M solution in hexane. *t*-BuLi was used as a 1.5-M solution in pentane. THF and $Et_2O$ were freshly distilled from sodium-benzophenone ketyl prior to use. TLC was performed on Al-backed plates coated with silica gel 60 with $F_{254}$ indicator (Merck). Flash column chromatography was carried out over Merck silica gel 60. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian Inova 400 (400 and 100.6 MHz, respectively), Varian Gemini VXR-200 (200 and 50.3 MHz, respectively) and Bruker AC-300 (300 and 75.5 MHz, respectively). Chemical shifts are reported in $\delta$ relative to an internal standard of residual chloroform ($\delta = 7.27$ for $^1$H NMR and $\delta = 76.95$ for $^{13}$C NMR). Low-resolution electron impact mass spectra (EI–LRMS) were obtained at 70 eV on a HP 5971 A instrument, and the intensity of the molecular peak is reported as a percentage relative to the base peak after the corresponding *m/z* value. Elemental analyses were performed with a LECO CHNS-932.

### 3.2. General preparation of compounds *6* and *10*

The corresponding secondary amine **5** (10 mmol), $K_2CO_3$ (10 mmol), 2,3-dibromopropene or 1,6-dibromocyclohexene (10 mmol), and acetonitrile (20 ml) were placed in a flask. The mixture was heated at reflux overnight. The solvent was removed (15 mm Hg), the residue was extracted with $Et_2O$ (3 × 10 ml), dried over $Na_2SO_4$ and the residue purified by column chromatography to afford amines **6** and **10**.

#### 3.2.1. N-*(2-Bromoallyl)*-N-*[(Z)-3-phenylthioallyl]cyclohexylamine* ***6a***

From amine **5a** (2.64 g, 72%). $R_f$ = 0.28 (hexane/AcOEt, 30:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.36–7.18 (m, 5H, ArH), 6.31–6.26 (m, 1H, CH=C*H*S), 6.01–5.99 (m, 1H, C(Br)=C*H*H), 5.97–5.85 (m, 1H, C*H*=CHS), 5.54–5.52 (m, 1H, C(Br)=CH*H*), 3.36 (dd, $J$ = 6.4 and 1.2 Hz, 2H, NC$H_2$CH=), 3.30 (s, 2H, NC$H_2$C(Br)=), 2.60–2.49 (m, 1H, NC*H*), 1.90–1.10 (m, 10H, 5 × C$H_2$ cyclohexyl). $^{13}$C NMR (50.3 MHz, $CDCl_3$): $\delta$ 134.1, 131.4, 129.0, 128.9, 126.3, 124.6, 123.5, 116.7, 59.8, 58.6, 48.5, 29.2, 26.2, 26.1. EI-LRMS, *m/z* (%): 367 (5) [$M^+$+2], 365 (5) [$M^+$], 149 (100). Elemental analysis calcd (%) for $C_{18}H_{24}BrNS$ (366.4): C 59.01, H 6.60, N 3.82; found C 59.08, H 6.53, N 3.92.

#### 3.2.2. N-*(2-Bromoallyl)*-N-*[(Z)-3-trimethylsilylallyl]cyclohexylamine* ***6b***

From amine **5b** (2.34 g, 71%). $R_f$ = 0.3 (hexane). $^1$H NMR (400 MHz, $CDCl_3$): δ 6.32 (dt, $J$ = 14.4 and

6.8 Hz, 1H, C*H*=CHSi), 5.98–5.96 (m, 1H, C(Br)=C*H*H), 5.58 (dt, *J* = 14.4 and 1.6 Hz, 1H, CH=C*H*Si), 5.51–5.49 (m, 1H, C(Br)=CH*H*), 3.25 (s, 2H, NC$H_2$C(Br)=), 3.22 (dd, *J* = 6.8 and 1.6 Hz, 2H, NC$H_2$CH=), 2.54–2.44 (m, 1H, NC*H*), 1.81–1.73 (m, 4H, cyclohexyl), 1.64–1.57 (m, 1H, cyclohexyl), 1.28–0.98 (m, 5H, cyclohexyl), 0.11 (s, 9H, 3 × C$H_3$ $SiMe_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ 148.0, 134.2, 130.4, 116.4, 59.4, 58.1, 52.3, 29.3, 26.2, 26.0, 0.20. EI-LRMS, *m/z* (%): 331 (8) [$M^+$+2], 329 (8) [$M^+$], 250 (100), 73 (98). Elemental analysis calcd (%) for $C_{15}H_{28}BrNSi$ (330.4): C 54.53, H 8.54, N 4.24; found C 54.65, H 8.48, N 4.31.

*3.2.3.* N-*(2-Bromoallyl)*-N-*[(Z)-3-tributyltinallyl]cyclohexylamine* ***6c***

From amine **5c** (4.32 g, 79%). $R_f$ = 0.4 (hexane). $^1$H NMR (400 MHz, $CDCl_3$): *δ* 6.51 (dt, *J* = 12.4 and 6.4 Hz, 1H, C*H*=CHSn), 5.99–5.97 (m, 1H, C(Br)=C*H*H), 5.95 (dt, *J* = 12.4 and 1.6 Hz, 1H, CH=C*H*Sn), 5.51–5.49 (m, 1H, C(Br)=CH*H*), 3.25 (s, 2H, NC$H_2$C(Br)=), 3.15 (dd, *J* = 6.4 and 1.6 Hz, 2H, NC$H_2$CH=), 2.53–2.48 (m, 1H, NC*H*), 1.78–0.80 (m, 37H, 5 × C$H_2$ cyclohexyl and 3 × (C$H_2$)$_3$C$H_3$ $SnBu_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): *δ* 148.1, 134.3, 129.8, 116.3, 59.4, 58.0, 56.0, 29.2, 29.1, 27.3, 26.3, 26.1, 13.7, 10.3. EI-LRMS, *m/z* (%): 490 (7) [$M^+$-$C_4H_9$], 313 (29), 256 (30), 176 (100). Elemental analysis calcd (%) for $C_{24}H_{46}BrNSn$ (547.2): C 52.67, H 8.47, N 2.56; found C 52.81, H 8.60, N 2.51.

*3.2.4.* N-*(2-Bromoallyl)*-N-*[(Z)-3-trimethylsilylallyl]aniline* ***6d***

From amine **5d** (2.69 g, 83%). $R_f$ = 0.38 (hexane). $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.40–7.30 (m, 2H, ArH), 6.91–6.81 (m, 3H, ArH), 6.49 (dt, *J* = 14.6 and 6.2 Hz, 1H, C*H*=CHSi), 5.97–5.87 (m, 2H, CH=C*H*Si and C(Br)=C*H*H), 5.69–5.67 (m, 1H, C(Br)=C*H*H), 4.22–4.13 (m, 4H, 2 × NC$H_2$), 0.34 (s, 9H, 3 × C$H_3$ $SiMe_3$). $^{13}$C NMR (50.3 MHz, $CDCl_3$): *δ* 147.6, 144.6, 132.5, 129.6, 129.2, 117.3, 115.8, 112.2, 58.5, 52.0, 0.1. EI-LRMS, *m/z* (%): 325 (40) [$M^+$+2], 323 (40) [$M^+$], 244 (52), 224 (64), 73 (100). Elemental analysis calcd (%) for $C_{15}H_{22}BrNSi$ (324.3): C 55.55, H 6.84, N 4.32; found C 55.48, H 6.75, N 4.39.

*3.2.5.* N-*(2-Bromoallyl)*-N-*[(*E*)-cinnamyl]aniline* ***6e***

From amine **5e** (2.66 g, 81%). $R_f$ = 0.33 (hexane:AcOEt, 40:1). $^1$H NMR (300 MHz, $CDCl_3$): *δ* 7.40–6.80 (m, 10H, ArH), 6.60 (d, *J* = 15.9 Hz, 1H, PhC*H*=), 6.35–6.25 (m, 1H, $CH_2$C*H*=), 5.80 (t, *J* = 1.7 Hz, 1H, C(Br)=C*H*H), 5.60 (t, *J* = 1.7 Hz, 1H, C(Br)=CH*H*), 4.20–4.15 (m, 4H, 2 × NC$H_2$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): *δ* 147.5, 136.5, 131.4, 129.4, 129.2, 128.4, 127.4, 126.2, 124.8, 117.2, 115.8, 112.1, 58.3, 52.2. Elemental analysis calcd (%) for $C_{18}H_{18}BrN$ (328.2): C 65.86, H 5.53, N 4.27; found C 65.58, H 5.71, N 4.29.

*3.2.6.* N-*(2-Bromoallyl)*-N-*(2-butenyl)aniline* ***6f***

From amine **5f** (1.99 g, 75%, mixture of *Z,E*-diastereoisomers). $R_f$ = 0.43 (hexane:AcOEt, 25:1). Data from the (*E*) diastereoisomer: $^1$H NMR (300 MHz, $CDCl_3$): *δ* 7.30–6.70 (m, 5H, ArH), 5.80–5.50 (m, 4H, C*H*=C*H* and C(Br)=C$H_2$), 4.10 (s, 2H, NC$H_2$C(Br)), 3.90 (d, *J* = 5.2 Hz, 2H, NC$H_2$CH=), 1.70 (d, *J* = 6.0 Hz, 3H, C$H_3$). $^{13}$C NMR (50.3 MHz, $CDCl_3$): δ 147.6, 129.6, 129.0, 127.7, 125.8, 116.9, 115.6, 112.0, 58.2, 47.1, 17.6. EI-LRMS, *m/z* (%): 267 (43) [$M^+$+2], 265 (46) [$M^+$], 186 (100). Elemental analysis calcd (%) for $C_{13}H_{16}BrN$ (266.2): C 58.66, H 6.06, N 5.26; found C 58.50, H 6.01, N 5.09.

*3.2.7.* N-*(2-Bromo-2-cyclohexenyl)*-N-*[(Z)-3-phenylthioallyl]aniline* ***10***

From amine **5a** (2.76 g, 68%). $R_f$ = 0.26 (hexane). $^1$H NMR (400 MHz, $CDCl_3$): *δ* 7.36–6.95 (m, 5H, ArH), 6.30–6.26 (m, 1H, C(Br)=C*H*), 6.21 (dt, *J* = 9.2 and 1.6 Hz, 1H, CH=C*H*S), 6.02–5.95 (m, 1H, C*H*=CHS), 3.59–3.49 (m, 2H, NC$H_2$CH=), 3.31 (ddd, *J* = 15.6, 4.8 and 2.0 Hz, 1H, NC*H*C(Br)=), 2.63–2.54 (m, 1H, NC*H*), 2.14–1.00 (m, 16H, 5 x C$H_2$ cyclohexyl and 3 × C$H_2$ cyclohexenyl). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ 136.4, 134.7, 133.2, 129.1, 128.9, 128.6, 126.1, 122.5, 59.5, 58.4, 44.2, 32.6, 31.7, 28.8, 27.6, 26.4, 26.3, 26.2, 20.9. EI-LRMS, *m/z* (%): 407 (2.3) [$M^+$+2], 405 (1.3) [$M^+$], 149 (100). Elemental analysis calcd (%) for $C_{21}H_{28}BrNS$ (406.4): C 62.06, H 6.94, N 3.45; found C 61.95, H 6.98, N 3.37.

*3.3. General preparation of compounds* ***8*** *and* ***12***

A solution of the corresponding 2-bromoallylamine **6** or **10** (2 mmol) in $Et_2O$ (15 ml) was treated with 2 equiv of *t*-BuLi (4 mmol, 2.67 ml of a 1.5 M solution in pentane) at –78 ºC. The mixture was stirred for 20 min at this temperature, and then TMEDA

(4.4 mmol, 0.66 ml) was added. The resulting mixture was stirred for 2 h at –78 ºC in the case of amine **6a**, for 2 h at –20 °C in the case of amine **6b**, for 30 min at 0 °C in the case of amine **6c** and for 1 h at –50 ºC in the case of aromatic amine **6d**. In all the cases, the ethereal solution of the cyclised anions **9** and **13** was cooled to –78 °C and 1.1 equiv (2.2 mmol) of the corresponding electrophile (deuterium oxide, chlorotrimethylsilane, tributyltin chloride, diphenyl disulfide, benzophenone) was added. Then, the mixture was allowed to reach room temperature, and the reaction was further stirred for 3 h. The mixture was hydrolysed with water and extracted with $Et_2O$ (3 × 10 ml). The combined organic layers were dried over anhydrous $Na_2SO_4$ and the resulting residue was purified by column chromatography yielding compounds **8** and **12**.

*3.3.1. 1-Cyclohexyl-3-(1-deuterio-1-phenylthiomethyl)-4-methylenepyrrolidine **8a***

From amine **6a** (0.53 g, 92%). $R_f$ = 0.28 (hexane/AcOEt, 1:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.35–7.31 (m, 2H, ArH), 7.28–7.22 (m, 2H, ArH), 7.17–7.12 (m, 1H, ArH), 4.97–4.95 (m, 1H, =C*H*H), 4.93–4.90 (m, 1H, =CH*H*), 3.38 (d, *J* = 13.6 Hz, 1H, NC*H*HC=), 3.19 (d, *J* = 4.8 Hz, 1H, CHC*H*DS), 3.14 (ddd, *J* = 13.6, 4.4 and 2.0 Hz, 1H, NCH*H*C=), 3.04 (dd, *J* = 9.2 and 7.2 Hz, 1H, NC*H*HCH), 2.88–2.80 (m, 1H, C*H*CHDS), 2.43 (dd, *J* = 9.2 and 6.8 Hz, 1H, NCH*H*CH), 2.00–1.50 (m, 6H, cyclohexyl and NC*H*), 1.29–1.11 (m, 5H, cyclohexyl). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 150.9, 136.3, 129.0, 128.7, 125.8, 105.5, 63.3, 57.5, 57.1, 41.6, 37.5 (t, *J* = 21.3 Hz), 31.4, 25.9, 24.8. EI-LRMS, *m/z* (%): 288 (1) [$M^+$], 165 (100). Elemental analysis calcd (%) for $C_{18}H_{24}DNS$ (288.5): C 74.94, H/D 9.08, N 4.86; found C 74.88, H/D 9.01, N 4.93.

*3.3.2. 3-[1,1Bis(phenylthio)methyl]-1-cyclohexyl-4-methylenepyrrolidine **8b***

From amine **6a** (0.71 g, 90%). $R_f$ = 0.2 (hexane/AcOEt, 2:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.47–7.42 (m, 2H, ArH), 7.42–7.37 (m, 2H, ArH), 7.31–7.20 (m, 6H, ArH), 5.10–5.07 (m, 1H, =C*H*H), 5.07–5.04 (m, 1H, =CH*H*), 4.59 (d, *J* = 3.6 Hz, 1H, C*H*$S_2$), 3.58 (d, *J* = 12.8 Hz, 1H, NC*H*HC=), 3.34–3.22 (m, 2H, NC*H*HC*H*), 3.10 (dd, *J* = 12.8 and 2.4 Hz, 1H, NCH*H*C=), 2.58 (t, *J* = 8.0 Hz, 1H, NCH*H*CH), 2.12–2.05 (m, 1H, NC*H*), 2.00–1.55 (m, 5H, cyclohexyl), 1.32–1.14 (m, 5H, cyclohexyl). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 148.3, 134.8, 134.6, 132.3, 132.2, 128.8, 128.7, 127.5, 127.4, 106.5, 63.0, 62.4, 58.1, 54.2, 46.2, 31.2, 31.1, 25.8, 24.6, 24.5. EI-LRMS, *m/z* (%): 395 (0.05) [$M^+$], 164 (100). Elemental analysis calcd (%) for $C_{24}H_{29}NS_2$ (395.6): C 72.86, H 7.39, N 3.54; found C 72.78, H 7.31, N 3.64.

*3.3.3. 1-Cyclohexyl-3-(1-phenylthio-1-tributyltinmethyl)-4-methylenepyrrolidine **8c***

From amine **6a** (0.96 g, 83%). $R_f$ = 0.2 (hexane/AcOEt, 10:1). Data from major diastereoisomer: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.36–7.32 (m, 2H, ArH), 7.29–7.23 (m, 2H, ArH), 7.16–7.10 (m, 1H, ArH), 4.94–4.91 (m, 1H, =C*H*H), 4.88–4.84 (m, 1H, =CH*H*), 3.31–3.08 (m, 4H, NC*HH*C=, C*H*C*H*SSn), 2.92 (dd, *J* = 8.8 and 7.2 Hz, 1H, NC*H*HCH), 2.55 (dd, *J* = 8.8 and 5.6 Hz, 1H, NCH*H*CH), 2.00–1.42 (m, 12H, NC*H*, $SnBu_3$ and cyclohexyl), 1.39–1.28 (m, 6H, $SnBu_3$), 1.28–1.10 (m, 5H, cyclohexyl), 1.09–0.85 (m, 15H, $SnBu_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 152.3, 138.2, 128.8, 128.4, 125.5, 104.9, 63.7, 58.2, 57.6, 44.8, 33.6, 31.7, 31.2, 29.2, 27.5, 26.1, 25.2, 25.1, 13.7, 11.0. EI-LRMS, *m/z* (%): 520 (0.2) [$M^+$–$C_4H_9$], 518 (0.19), 176 (100), 164 (82). Elemental analysis calcd (%) for $C_{30}H_{51}NSSn$ (576.5): C 62.50, H 8.92, N 2.43; found C 62.56, H 8.86, N 2.48.

*3.3.4. 1-Cyclohexyl-3-(2,2-diphenyl-1-phenylthio-2-hydroxyethyl)-4-methylenepyrrolidine **8d***

From amine **6a** (0.79 g, 84%). Mp = 151–153 °C. Data from major diastereoisomer: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.45 (s broad, 1H, O*H*), 7.67 (d, *J* = 7.2 Hz, 4H, ArH), 7.40–7.06 (m, 11H, ArH), 4.81–4.77 (m, 1H, =C*H*H), 4.72 (d, *J* = 4.8 Hz, 1H, CHC*H*S), 4.55–4.51 (m, 1H, =CH*H*), 3.83 (d, *J* = 9.2 Hz, 1H, NC*H*-HCH), 3.24–3.17 (m, 1H, C*H*CHS), 2.82 (d, *J* = 14.0 Hz, 1H, NC*H*HC=), 2.63 (d, *J* = 14.0 Hz, 1H, NCH*H*C=), 2.30 (dd, *J* = 9.2 and 7.2 Hz, 1H, NCH-*H*CH), 2.16–1.22 (m, 11H, C*H*N and 5 × C$H_2$ cyclohexyl). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 147.8, 147.7, 146.5, 136.4, 131.6, 128.8, 127.6, 127.0, 126.7, 126.6, 126.2, 125.8, 125.2, 108.6, 79.5, 62.6, 62.2, 56.7, 53.6, 47.6, 31.2, 31.0, 25.7, 24.9, 24.8. EI–LRMS, *m/z* (%): 359 (9) [$M^+$–PhSH], 163 (100). Elemental analysis calcd (%) for $C_{31}H_{35}NOS$ (469.7): C 79.27, H 7.51, N 2.98; found C 79.21, H 7.43, N 2.90.

*3.3.5. 1-Cyclohexyl-3-(1-deuterio-1-trimethylsilyl-methyl)-4-methylenepyrrolidine **8e***

From amine **6b** (0.45 g, 90%). $R_f$ = 0.19 (hexane/AcOEt, 5:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.87–4.84 (m, 1H, =C*H*H), 4.80–4.77 (m, 1H, =CH*H*), 3.64 (d, $J$ = 14.0 Hz, 1H, NCH*H*C=), 3.21 (t, $J$ = 8.0 Hz, 1H, NC*H*HCH), 2.90 (ddd, $J$ = 14.0, 4.8 and 2.4, 1H, NCH*H*C=), 2.68–2.57 (m, 1H, C*H*CHD), 1.97–1.83 (m, 4H, NCH*H*CH, NC*H* and cyclohexyl), 1.77–1.54 (m, 3H, cyclohexyl), 1.28–1.05 (m, 5H, cyclohexyl), 0.96–0.92 (m, 1H, C*H*D), –0.01 (s, 9H, 3 × C$H_3$ $SiMe_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 155.2, 103.1, 63.8, 59.6, 57.1, 38.9, 31.7, 31.6, 26.0, 25.0, 24.9, 19.7 (t, $J$ = 18.4 Hz), –0.9. EI–LRMS, *m/z* (%): 252 (14) [$M^+$], 209 (100), 73 (57). Elemental analysis calcd (%) for $C_{15}H_{28}DNSi$ (252.5): C 71.35, H/D 11.98, N 5.55; found C 71.27, H/D 12.05, N 5.63.

*3.3.6. 3-[1,1Bis(trimethylsilyl)methyl]-1-cyclohexyl-4-methylenepyrrolidine **8f***

From amine **6b** (0.52 g, 80%). $R_f$ = 0.33 (hexane/AcOEt, 4:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.86–4.82 (m, 1H, =C*H*H), 4.76–4.72 (m, 1H, =CH*H*), 3.67 (d, $J$ = 14.8 Hz, 1H, NCH*H*C=), 3.16 (t, $J$ = 8.0 Hz, 1H, NC*H*HCH), 2.99–2.90 (m, 2H, NCH*H*C= and C*H*CH$Si_2$), 2.15 (dd, $J$ = 10.4 and 8.0 Hz, 1H, NCH*H*CH), 2.02–1.53 (m, 6H, NC*H* and cyclohexyl), 1.30–1.05 (m, 5H, cyclohexyl), 0.39 (d, $J$ = 1.2 Hz, 1H, C*H*$Si_2$), 0.01 (s, 9H, 3 × C$H_3$ $SiMe_3$), 0.00 (s, 9H, 3 × C$H_3$ $SiMe_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 154.3, 103.2, 63.7, 57.6, 57.2, 41.4, 31.6, 31.5, 26.0, 25.1, 25.0, 16.6, 2.5, 0.7. EI–LRMS, *m/z* (%): 323 (5) [$M^+$], 322 (8), 151 (100), 73 (90). Elemental analysis calcd (%) for $C_{18}H_{37}NSi_2$ (323.7): C 66.80, H 11.52, N 4.33; found C 66.71, H 11.47, N 4.39.

*3.3.7. 1-Cyclohexyl-3-(1-phenylthio-1-trimethylsilyl-methyl)-4-methylenepyrrolidine **8g***

From amine **6b** (0.61 g, 85%). Data from minor diastereoisomer: $R_f$ = 0.5 (hexane/AcOEt, 4:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.37–7.32 (m, 2H, ArH), 7.28–7.23 (m, 2H, ArH), 7.16–7.11 (m, 1H, ArH), 4.94–4.91 (m, 1H, =C*H*H), 4.86–4.83 (m, 1H, =CH*H*), 3.32 (d, $J$ = 13.6 Hz, 1H, NC*H*HC=), 3.27–3.20 (m, 1H, NCH*H*C=), 3.11–3.03 (m, 1H, C*H*CHSSi), 2.95 (dd, $J$ = 8.8 and 7.2 Hz, 1H, NC*H*HCH), 2.80 (d, $J$ = 3.6 Hz, 1H, CHC*H*SSi), 2.62 (dd, $J$ = 8.8 and 6.4 Hz, 1H, NCH*H*CH), 2.02–1.85 (m, 3H, NC*H* and cyclohexyl), 1.77–1.55 (m, 3H, cyclohexyl), 1.30–1.10 (m, 5H, cyclohexyl), 0.19 (s, 9H, 3 × C$H_3$ $SiMe_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 151.5, 137.3, 129.0, 128.9, 125.8, 105.0, 63.6, 58.3, 55.6, 45.2, 37.8, 31.6, 31.4, 26.0, 25.0, 24.9, –0.2. EI-LRMS, *m/z* (%): 359 (0.16) [$M^+$], 164 (100). Elemental analysis calcd (%) for $C_{21}H_{33}NSSi$ (359.6): C 70.13, H 9.25, N 3.89; found C 70.19, H 9.18, N 3.98. Data from major diastereoisomer: $R_f$ = 0.35 (hexane/AcOEt, 1:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.38–7.34 (m, 2H, ArH), 7.20–7.14 (m, 2H, ArH), 7.12–7.07 (m, 1H, ArH), 4.82–4.79 (m, 1H, =C*H*H), 4.66–4.63 (m, 1H, =CH*H*), 3.62 (d, $J$ = 13.2 Hz, 1H, NC*H*HC=), 3.23–3.10 (m, 2H, NC*H*HCH and C*H*CHSSi), 2.88 (ddd, $J$ = 13.2, 4.8 and 2.8 Hz, 1H, NCH*H*C=), 2.82 (d, $J$ = 2.8 Hz, 1H, CHC*H*SSi), 2.37 (dd, $J$ = 9.2 and 8.4 Hz, 1H, NCH*H*CH), 2.10–2.00 (m, 1H, NC*H*), 1.98–1.55 (m, 5H, cyclohexyl), 1.32–1.07 (m, 5H, cyclohexyl), 0.12 (s, 9H, 3 × C$H_3$ $SiMe_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ 150.3, 139.0, 130.3, 128.4, 125.8, 105.4, 63.6, 58.3, 55.3, 43.9, 37.9, 31.6, 31.5, 26.0, 25.0, 24.9, -1.7. EI-LRMS, *m/z* (%): 359 (0.16) [$M^+$], 164 (100). Elemental analysis calcd (%) for $C_{21}H_{33}NSSi$ (359.6): C 70.13, H 9.25, N 3.89; found C 70.18, H 9.35, N 3.80.

*3.3.8. 1-Cyclohexyl-3-methylene-4-(1-tributyltin-1-trimethylsilylmethyl)pyrrolidine **8h***

From amine **6b** (0.79 g, 73%). Data from minor diastereoisomer: $R_f$ = 0.22 (hexane/AcOEt, 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.91–4.87 (m, 1H, =C*H*H), 4.81–4.78 (m, 1H, =CH*H*), 3.70 (d, $J$ = 13.2 Hz, 1H, NC*H*HC=), 3.21–2.95 (m, 3H, NCH*H*C=, C*H*CHSiSn and NC*H*HCH), 2.20–0.68 (m, 40H, CHC*H*SiSn, NC*H*, NCH*H*CH, 5 × $CH_2$ cyclohexyl and 3 × $(CH_2)_3CH_3$ $SnBu_3$), 0.02 (s, 9H, 3 × C$H_3$ $SiMe_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 155.0, 104.5, 63.9, 59.5, 57.8, 43.0, 31.6, 31.5, 29.2, 27.6, 26.0, 25.1, 25.0, 13.8, 13.7, 10.9, 2.1. EI–LRMS, *m/z* (%): 485 (1), 483 [$M^+$–$C_4H_9$] (0.6), 250 (100). Elemental analysis calcd (%) for $C_{27}H_{55}NSiSn$ (540.5): C 59.99, H 10.26, N 2.59; found C 60.10, H 10.31, N 2.51. Data from major diastereoisomer: $R_f$ = 0.21 (hexane/AcOEt, 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.90–4.85 (m, 1H, =C*H*H), 4.80–4.76 (m, 1H, =CH*H*), 3.72 (d, $J$ = 14.4 Hz, 1H, NC*H*HC=), 3.27 (t, $J$ = 8.0 Hz, 1H, NC*H*HCH), 3.20–3.10 (m, 1H, C*H*CH-SiSn), 3.00–2.93 (m, 1H, NCH*H*C=), 2.00–0.68 (m,

40H, CHC*H*SiSn, NC*H*, NCH*H*CH, 5 × C$H_2$ cyclohexyl and 3 × (C$H_2$)$_3$C$H_3$ SnBu$_3$), 0.03 (s, 9H, 3 × C$H_3$ SiMe$_3$). $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ 155.1, 103.5, 63.8, 60.3, 57.0, 42.5, 31.6, 31.5, 29.2, 27.6, 26.0, 25.1, 25.0, 15.3, 13.6, 11.6, 0.5. EI-LRMS, *m/z* (%): 483 (5) [M$^+$–C$_4$H$_9$], 248 (100). Elemental analysis calcd (%) for C$_{27}$H$_{55}$NSiSn (540.5): C 59.99, H 10.26, N 2.59; found C 60.12, H 10.33, N 2.50.

*3.3.9. 1-Cyclohexyl-3-(1-deuterio-1-tributyltinmethyl)-4-methylenepyrrolidine* ***8i***

From amine **6c** (0.88 g, 94%). $R_f$ = 0.32 (hexane/AcOEt, 5:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.89–4.87 (m, 1H, =C*H*H), 4.82–4.80 (m, 1H, =CH*H*), 3.62 (d, *J* = 14.0 Hz, 1H, NC*H*HC=), 3.14 (t, *J* = 8.0 Hz, 1H, NC*H*HCH), 2.98 (ddd, *J* = 14.0, 4.8 and 2.0 Hz, 1H, NCH*H*C=), 2.86–2.77 (m, 1H, C*H*CHDSn), 1.97–1.83 (m, 40H, 5 × C$H_2$ cyclohexyl, NC*H*, 3 × (C$H_2$)$_3$C$H_3$ SnBu$_3$, NCH*H*CH and CHC*H*DSn). $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ 155.6, 103.5, 63.8, 60.9, 57.6, 40.9, 31.7, 31.6, 29.2, 27.4, 26.0, 25.0, 24.9, 13.7, 12.0 (t, *J* = 19.8 Hz), 9.4. Elemental analysis calcd (%) for C$_{24}$H$_{46}$DNSn (469.4): C 61.42, H/D 10.31, N 2.98; found C 61.91, H/D 10.39, N 2.91.

*3.3.10. 3-(1-Deuterio-1-trimethylsilylmethyl)-4-methylene-1-phenylpyrrolidine* ***8j***

From amine **6d** (0.26 g, 53%). Mp = 43–45 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33 (dd, *J* = 8.4 and 7.6 Hz, 2H, ArH), 6.80 (t, *J* = 7.6 Hz, 1H, ArH), 6.66 (d, *J* = 8.4, 2H, ArH), 5.06–5.03 (m, 1H, =C*H*H), 5.02–4.99 (m, 1H, =CH*H*), 4.15 (d, *J* = 13.6 Hz, 1H, NC*H*HC=), 3.92 (dd, *J* = 13.6 and 1.6 Hz, 1H, NCH*H*C=), 3.75 (t, *J* = 6.8 Hz, 1H, NC*H*HCH), 3.00–2.88 (m, 2H, NCH*H*CH and C*H*CHDSi), 1.07 (s, 1H, C*H*D), 0.72 (d, *J* = 10.4 Hz, 1H, CD*H*), 0.18 (s, 9H, 3 × C$H_3$ SiMe$_3$). $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ 152.7, 147.7, 129.1, 116.1, 111.8, 104.3, 55.1, 52.8, 39.0, 18.6 (t, *J* = 18.7 Hz), –0.9. EI–LRMS, *m/z* (%): 246 (75) [M$^+$], 173 (56), 158 (100), 73 (84). Elemental analysis calcd (%) for C$_{15}$H$_{22}$DNSi (246.4): C 73.10, H/D 9.82, N 5.68; found C 73.15, H/D 9.75, N 5.74.

*3.3.11. 3-Methylene-1-phenyl-4-(1-phenylthio-1-trimethylsilylmethyl)pyrrolidine* ***8k***

From amine **6d** (0.35 g, 50%). Data from minor diastereoisomer: $R_f$ = 0.16 (hexane/AcOEt, 25:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.45–7.41 (m, 2H, ArH), 7.36–7.19 (m, 5H, ArH), 6.79 (t, *J* = 7.4 Hz, 1H, ArH), 6.67 (d, *J* = 8.8 Hz, 2H, ArH), 5.15–5.12 (m, 1H, =C*H*H), 5.07–5.03 (m, 1H, =CH*H*), 4.07 (dd, *J* = 14.0 and 2.0 Hz, 1H, NC*H*HC=), 3.87 (d, *J* = 14.0 Hz, 1H, NCH*H*C=), 3.55–3.47 (m, 2H, NC*HH*CH), 3.31 (m, 1H, C*H*CHSSi), 2.91 (d, *J* = 4.0 Hz, 1H, CHC*H*-SSi), 0.20 (s, 9H, 3 × C$H_3$ SiMe$_3$). $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ 149.0, 147.7, 138.5, 130.2, 129.1, 128.5, 126.0, 116.5, 112.3, 107.0, 53.6, 51.8, 44.2, 38.2, -1.5. EI–LRMS, *m/z* (%): 353 (0.15) [M$^+$], 158 (100). Elemental analysis calcd (%) for C$_{21}$H$_{27}$NSSi (353.6): C 71.33, H 7.70, N 3.96; found C 71.25, H 7.80, N 3.85. Data from major diastereoisomer: $R_f$ = 0.13 (hexane/AcOEt, 25:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.42–7.38 (m, 2H, ArH), 7.33–7.15 (m, 5H, ArH), 6.78 (t, *J* = 7.4 Hz, 1H, ArH), 6.63 (d, *J* = 8.8 Hz, 2H, ArH), 5.00–4.97 (m, 1H, =C*H*H), 4.93–4.90 (m, 1H, =CH*H*), 4.02 (d, *J* = 14.0 Hz, 1H, NC*H*HC=), 3.85 (dd, *J* = 14.0 and 2.0 Hz, 1H, NCH*H*C=), 3.70–3.60 (m, 1H, NC*H*HCH), 3.46–3.36 (m, 2H, NCH*H*CH and C*H*CHSSi), 2.94 (d, *J* = 2.8 Hz, 1H, CHC*H*SSi), 0.25 (s, 9H, 3 × C$H_3$ SiMe$_3$). $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ 149.0, 147.7, 138.5, 130.2, 129.1, 128.5, 126.0, 116.5, 112.3, 107.0, 53.6, 51.8, 44.2, 38.2, –1.5. EI–LRMS, *m/z* (%): 353 (0.15) [M$^+$], 158 (100). Elemental analysis calcd (%) for C$_{21}$H$_{27}$NSSi (353.6): C 71.33, H 7.70, N 3.96; found C 71.24, H 7.82, N 3.90.

*3.3.12. 3-Methylene-1-phenyl-4-(1-tributyltin-1-trimethylsilylmethyl)pyrrolidine* ***8l***

From amine **6d** (0.59 g, 55%). Mixture of diastereoisomers: $R_f$ = 0.24 (hexane). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.37–7.31 (m, 2H, ArH), 6.85–6.79 (m, 1H, ArH), 6.70–6.65 (m, 2H, ArH), 5.20–5.15 (m, 1H, =C*H*H), 5.08–5.04 (m, 1H, =CH*H*), 4.26–4.16 (m, 2H, NC*HH*C=, major diast.), 4.05–3.93 (m, 2H, NC*HH*C=, minor diast.), 3.87 (t, *J* = 8.8 Hz, 1H, NC*H*HCH, major diast.), 3.71 (t, *J* = 8.8 Hz, 1H, NC*H*HCH, minor diast.), 3.56–3.47 (m, 1H, C*H*CH-SiSn, major diast.), 4.47–3.38 (m, 1H, C*H*CHSiSn, minor diast.), 3.13 (t, *J* = 8.8 Hz, 1H, NCH*H*CH, minor diast.), 2.86 (t, *J* = 8.8 Hz, 1H, NCH*H*CH, major diast.), 1.70–1.30 (m, 13H, CHC*H*SiSn and SnBu$_3$), 1.12–0.80 (m, 15H, SnBu$_3$), 0.22 (s, 9H, 3 × C$H_3$ SiMe$_3$, major diast.), 0.15 (s, 9H, 3 × C$H_3$ SiMe$_3$, minor diast.). $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$ 153.4,

153.2, 147.7, 147.4, 129.1, 116.4, 116.3, 112.1, 111.9, 105.5, 104.4, 56.4, 55.7, 53.6, 52.9, 43.0, 41.9, 29.3, 29.2, 27.6, 27.5, 15.7, 14.4, 13.7, 13.6, 11.4, 11.0, 2.0, 0.4. EI–LRMS, *m/z* (%): major diast.: 477 (5) [$M^+$-$C_4H_9$], 242 (100); minor diast.: 477 (1.8) [$M^+$-$C_4H_9$], 242 (100). Elemental analysis calcd (%) for $C_{27}H_{49}NSiSn$ (534.5): C 60.67, H 9.24, N 2.62; found C 60.78, H 9.29, N 2.57.

*3.3.13. 3-(1-Deuterio-1-phenylmethyl)-4-methylene-1-phenylpyrrolidine* ***8m***

From amine **6e** (0.31 g, 61%). $R_f$ = 0.38 (hexane/AcOEt, 10:1). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 7.53–6.73 (m, 10H, ArH), 5.24 and 5.13 (2s, 2H, =C*H*H and =CH*H*), 4.15 (s, 2H, NC$H_2$C=), 3.55 (dd, *J* = 7.0 and 6.7 Hz, 1H, NC*H*HCH), 3.32–3.08 (m, 3H, NCH*H*CH, C*H* and C*H*D). $^{13}$C NMR (50.5 MHz, $CDCl_3$): $\delta$ 149.5, 147.7, 139.9, 129.0, 128.7, 128.3, 126.1, 116.3, 112.0, 105.8, 53.1, 52.9, 44.2, 38.8 (t, *J* = 20.3 Hz). EI-LRMS, *m/z* (%): 250 (20) [$M^+$], 249 (18), 158 (100), 156 (37).

*3.3.14. (2*R**,7a*R**)-1-Cyclohexyl-3-phenylthio-2,3,5,6,7,7a-hexahydro-1*H*-indole* ***12a***

From amine **10** (0.60 g, 92%). $R_f$ = 0.32 (hexane/AcOEt, 5:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.35–7.30 (m, 2H, ArH), 7.28–7.22 (m, 2H, ArH), 7.18–7.12 (m, 1H, ArH), 5.54–5.50 (m, 1H, =C*H*), 3.22 (dd, *J* = 8.8 and 7.2 Hz, 1H, NC*H*HCH), 3.16–3.11 (m, 1H, CHC*H*HS), 3.08–3.00 (m, 1H, NC*H*C=), 2.89–2.77 (m, 2H, C*H*CH*H*S), 2.71–2.61 (m, 1H, NC*H*), 2.32 (dd, *J* = 8.8 and 8.0 Hz, 1H, NCH*H*CH), 1.85–0.99 (m, 16H, 5 × C$H_2$ cyclohexyl and =CHC$H_2$C$H_2$C$H_2$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 143.2, 136.4, 129.1, 128.7, 125.8, 119.9, 58.3, 56.6, 51.9, 39.2, 39.1, 32.1, 28.1, 26.4, 25.7, 25.1, 24.1, 20.3. EI–LRMS, *m/z* (%): 327 (3) [$M^+$], 204 (100), 176 (78). Elemental analysis calcd (%) for $C_{21}H_{29}NS$ (327.5): C 77.01, H 8.92, N 4.28; found C 77.10, H 9.04, N 4.21.

*3.3.15. (2*R**,7a*R**)-3-[1,1-Bis(phenylthio)methyl]-1-cyclohexyl-2,3,5,6,7,7a-hexahydro-1*H*-indole* ***12b***

From amine **10** (0.78 g, 90%). $R_f$ = 0.32 (hexane/AcOEt, 5:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.44–7.36 (m, 4H, ArH), 7.29–7.18 (m, 6H, ArH), 5.63–5.59 (m, 1H, =C*H*), 4.55 (d, *J* = 4.0 Hz, 1H, CHC*H*$S_2$), 3.31–3.20 (m, 2H, NCHHC*H*, NC*H*C=), 3.18 (t, *J* = 8.4 Hz, 1H, NC*H*HCH), 2.77 (dd, *J* = 8.4 and 7.6 Hz, 1H, NCH*H*CH), 2.73–2.67 (m, 1H, NC*H*), 2.15–0.81 (m, 16H, 5 × C$H_2$ cyclohexyl and =CHC$H_2$C$H_2$C$H_2$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 141.2, 135.1, 134.7, 132.6, 132.3, 128.9, 128.8, 127.6, 127.4, 121.4, 63.8, 59.3, 56.8, 48.6, 44.4, 32.0, 28.3, 26.4, 25.8, 25.2, 24.3, 20.2. Elemental analysis calcd (%) for $C_{27}H_{33}NS_2$ (435.7): C 74.43, H 7.63, N 3.21; found C 74.48, H 7.55, N 3.25.

## Acknowledgements

Financial support from the Ministerio de Ciencia y Tecnología (MCYT, BQU2001–1079) and Junta de Castilla y León (BU24/02) is gratefully acknowledged. Y.F. thanks Junta de Castilla y León for a fellowship.

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