Trianions by Regio- and Stereo-selective Lithiation of Diallylamines and Structurally Related Compounds: Synthetic Applications

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The successive treatment of diallylamines **1** and related systems **8** and benzylallylamines **12** or **17** with alkyllithium reagents leads to several trianionic intermediates **4**, **10** and **15**, respectively; in the case of *N,N'*-diallylethylenediamine **18** tetranionic species are obtained under the same reaction conditions. These trianions and tetranions are characterized by reaction with deuterium oxide to yield the corresponding deuteriated compounds **5**, **11**, **16** and **21**. Likewise, another trianion **3a** is obtained in an indirect way from diallylamine **1a** *via* stereoselective removal of a vinylic hydrogen and further transmetallation of the vinyltin reagent **22**. Models are proposed to explain the lithiation and addition steps, which take place to give the trianions. Finally, all the lithiated intermediates react with different electrophiles (diethyl carbonate, carbon dioxide, dichlorodimethylsilane and dichlorodiethylgermanium) to give the corresponding products **27**, **29**, **30** and **35–44**.

Reactions that involve specific removal of a proton from a carbon atom and subsequent reaction of the resulting carbanion with electrophiles are important processes in organic synthesis.[1] We have described reactions in which secondary allylic amines undergo regio- and stereo-selective deprotonations to give the corresponding dilithiated dianions and their reaction with different electrophiles.[2] In the present article we present the behaviour of diallylamines and related compounds towards several alkyllithium reagents and the reaction of the resulting intermediates with different electrophiles.

Results and Discussion

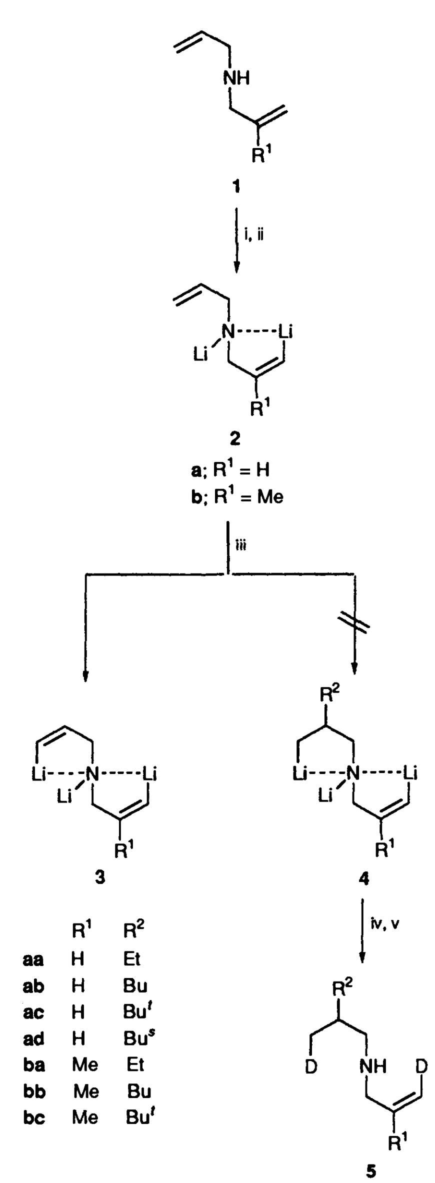
Lithiation of Diallylamines.—Successive treatment of diallylamines **1** with butyllithium and *tert*-butyllithium at temperatures in the range −50 to 20 °C led to the vinylic lithiated dianion **2**.[2] In this context, it is interesting to note the high chemoselectivity shown by compound **1b**, which affords exclusively dianion **2b**. The reaction of the intermediates **2** with Bu^tLi at temperatures in the range −20 to 20 °C did not give rise to deprotonation of the vinylic hydrogen of the other allyl moiety to afford the trilithiated diallylamines **3**, but instead quantitative addition of Bu^tLi to the double bond led to formation of the corresponding trianion **4**.† When Bu^sLi was added instead of Bu^tLi the corresponding addition product was again formed. The addition of a primary alkyllithium (EtLi and BuLi) occurs in a similar manner, but the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was necessary in order to favour the addition reaction. These trianions were characterized by treatment with deuterium oxide to yield the deuteriated compound **5**[4] (Scheme 1 and Table 1).

The above results can be understood as follows. The lithiation of the first allyl group can occur if we assume that the nitrogen atom of the lithium amide, formed in the first step, can coordinate to the lithium atom of Bu^tLi, increasing its reactivity and inducing a proximity effect.[5] The other lithium atom interacts with the double bond thereby fixing the s-*cis* geometry and allowing the vinylic hydrogen atom placed at the *cis* position relative to the nitrogen substituent to be removed (see model **6** of Fig. 1). In agreement with this is the fact that no reaction was observed when the amine lacks *cis* hydrogen atoms. On the other hand, model **7** (Fig. 1) accounts well for the addition step. So, the interaction of the lithium atom of the amide with the alkyl group of the organolithium reagent together with the simultaneous proximity effect allows the coordination of the double bond to the lithium atom and consequently the addition reaction.

Lithiation of Structurally Related Systems.—In order to verify the above proposed models to explain the results obtained for the lithiation of diallylamines, we attempted the lithiation of compounds structurally related to diallylamines. Treatment of *N*-allyl-1-naphthylamine **8** with BuLi and Bu^tLi at temperatures in the range −50 to 20 °C afforded the dianion **9** by removal of the *peri* hydrogen. Treatment of this intermediate with an equimolecular amount of Bu^tLi or a primary alkyllithium (EtLi, BuLi) in the presence of TMEDA led to the expected trianion **10** by quantitative addition of the corresponding alkyllithium to the carbon–carbon double bond of the allyl group. These trianions were characterized by reaction with D_2O to yield, after hydrolysis, the deuteriated products **11** (Scheme 2 and Table 1). When the same reaction was carried out with *N*-allylbenzylamine **12** a nearly equimolecular mixture of dianion **13**, obtained by deprotonation of the vinylic hydrogen, and trianions **15**, obtained by removal of the *ortho* hydrogen[6] and subsequent addition of the alkyllithium to the double bond of the allyl moiety, was obtained. Further reaction with D_2O afforded the deuteriated products **14** and **16**. In order to avoid the competition between the *ortho* and vinylic deprotonation in the metallation step we started from *N*-allyl-2-bromobenzylamine **17**, which, when treated under the same reaction conditions, led exclusively to dideuterio product **16** (Scheme 2 and Table 1).

Finally, the successive reaction of *N,N'*-diallylethylenediamine **18** with BuLi and Bu^tLi or BuLi–TMEDA at temperatures in the range −50 to 20 °C did not lead to the abstraction of the vinylic hydrogens, but instead gave quantitative

† The addition of an alkyllithium reagent to the unactivated carbon–carbon double bond is very unusual.[3]



Scheme 1 *Reagents and conditions:* i, BuLi, −50 to −30 °C; ii, Bu^{t}Li, −30 to 20 °C; iii, R^2Li (R^2 = Bu^t, Bu^s), −20 to 20 °C or R^2Li (R^2 = Et, Bu)/TMEDA, 20 °C; iv, D_2O, 20 °C; v, water

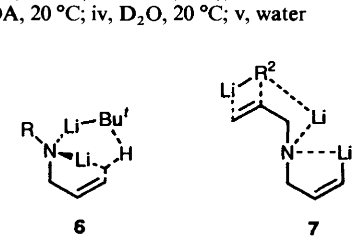
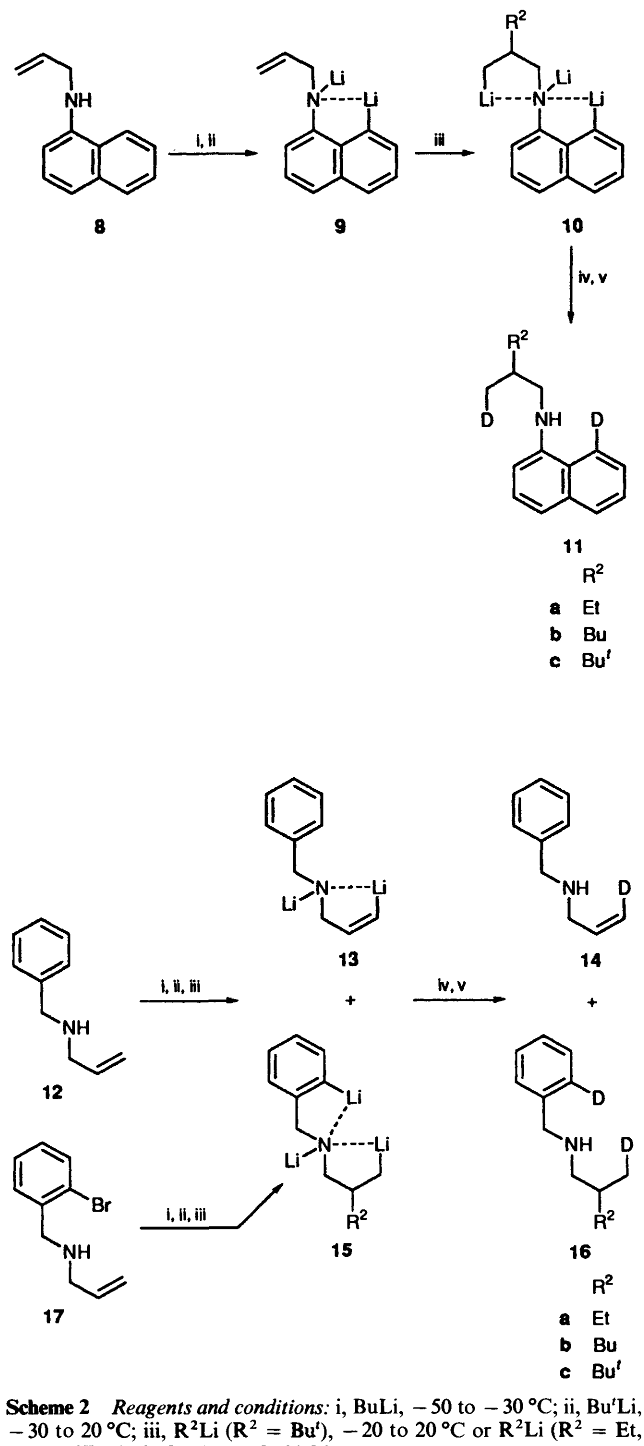


Fig. 1

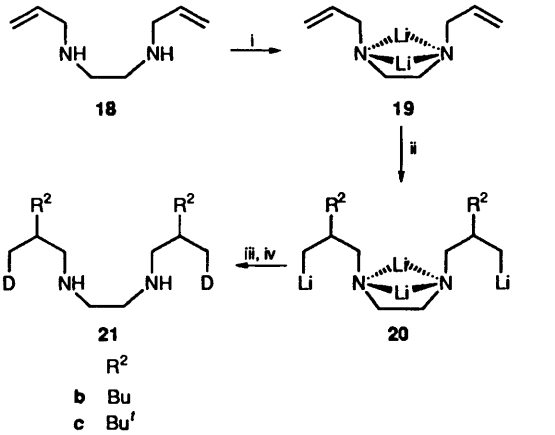


Scheme 2 *Reagents and conditions:* i, BuLi, −50 to −30 °C; ii, Bu^{t}Li, −30 to 20 °C; iii, R^2Li (R^2 = Bu^t), −20 to 20 °C or R^2Li (R^2 = Et, Bu)/TMEDA, 20 °C; iv, D_2O, 20 °C; v, water

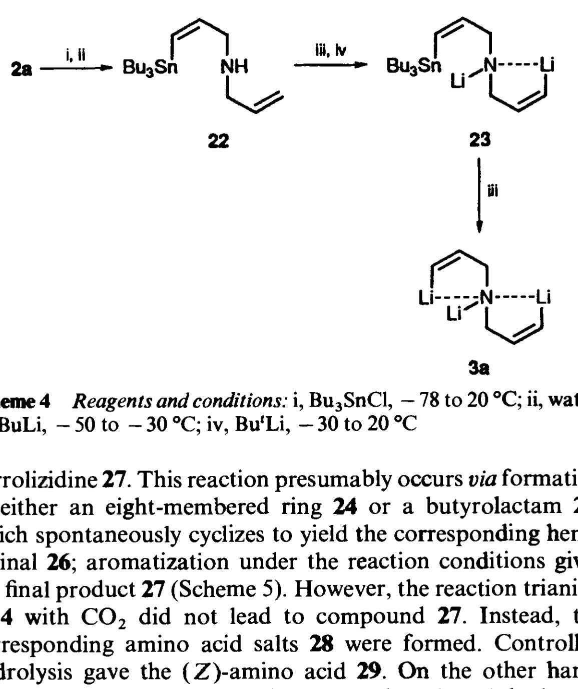
addition of alkyllithium to the double bonds, which led to the formation of the corresponding tetraanion **20**, which reacted with D_2O to yield the products **21** (Scheme 3 and Table 1). The fact that the vinylic hydrogens are not removed can be explained by assuming that the two nitrogen atoms of the amide **19** can coordinate with both lithium atoms thus avoiding the coordination with the lithium atom of the alkyllithium reagent and consequently the induction for the lithiation.

Synthesis of Compound **3a**.—The intermediate **3a** cannot be prepared by direct lithiation of compound **1a**, but can be indirectly obtained from the stannane **22**, formed by reaction of dianion **2a** with tributylchlorotin. Successive reaction of compound **22** with BuLi and Bu^{t}Li afforded the dianionic species **23**, which *in situ* reacts with BuLi at temperatures in the range −30 to 20 °C to give trianion **3a** (Scheme 4). It is worth noting that the preparation of trianion **3a** can be carried out in a one-pot process starting from compound **1a**.[7]

Reaction with Electrophiles.—The synthetic utility of the lithiated intermediates was studied with respect to different electrophiles. The reaction of trianion **4** with diethyl carbonate at −78 to 20 °C afforded, after hydrolysis, the corresponding



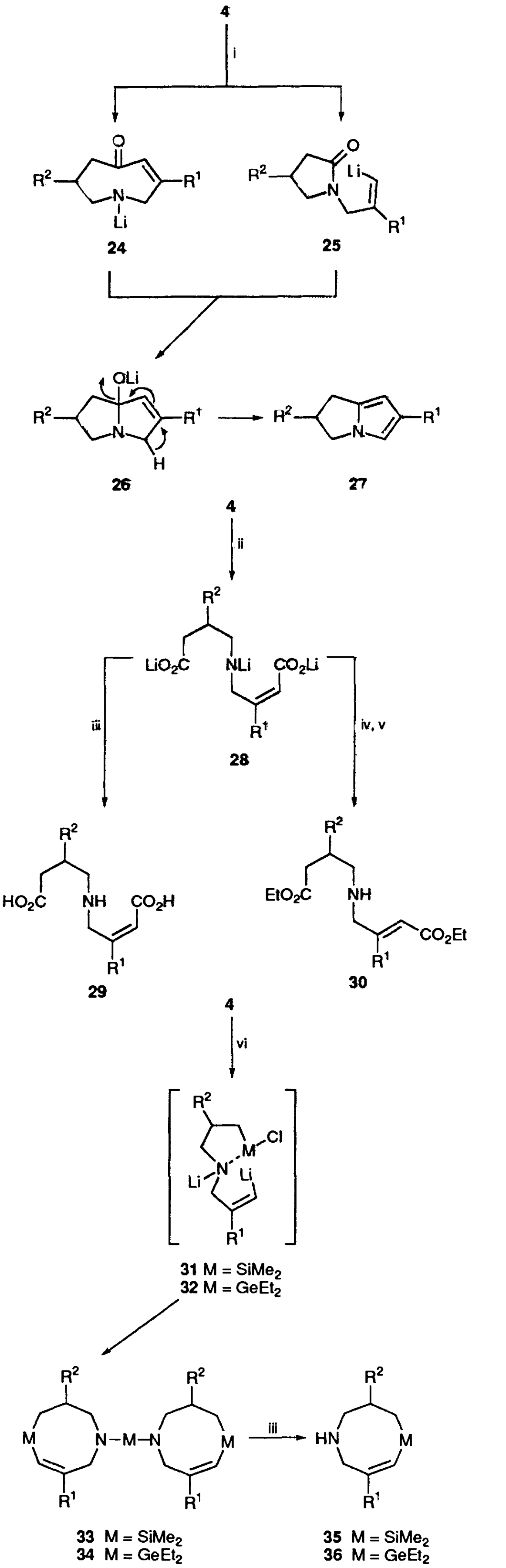
Scheme 3 *Reagents and conditions:* i, BuLi, −50 to −30 °C; ii, R^2Li (R^2 = Bu^t), −30 to 20 °C or R^2Li (R^2 = Bu)/TMEDA, 20 °C; iii, D_2O, 20 °C; iv, water



Scheme 4 *Reagents and conditions:* i, Bu_3SnCl, −78 to 20 °C; ii, water; iii, BuLi, −50 to −30 °C; iv, Bu^tLi, −30 to 20 °C

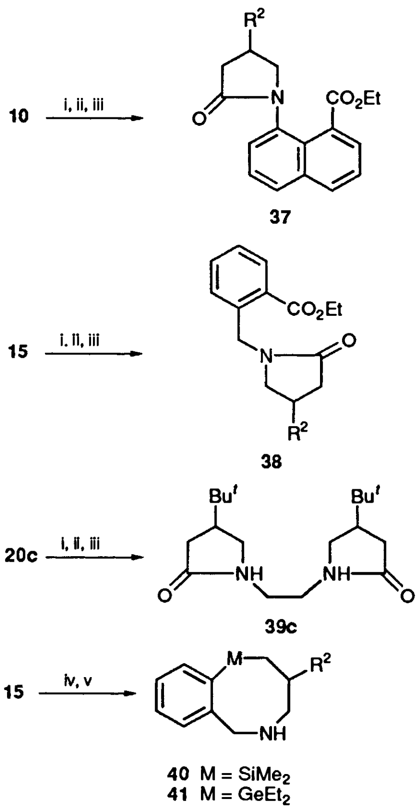
pyrrolizidine **27**. This reaction presumably occurs *via* formation of either an eight-membered ring **24** or a butyrolactam **25**, which spontaneously cyclizes to yield the corresponding hemiaminal **26**; aromatization under the reaction conditions gives the final product **27** (Scheme 5). However, the reaction trianion of **4** with CO_2 did not lead to compound **27**. Instead, the corresponding amino acid salts **28** were formed. Controlled hydrolysis gave the (*Z*)-amino acid **29**. On the other hand, esterification of **28** with anhydrous ethanol and hydrogen chloride in order to facilitate the isolation of the product took place with isomerization of the double bond to afford the corresponding (*E*)-amino ester **30**[8] (Scheme 5 and Table 1). Moreover, the reaction of trianion **4** with dichlorodimethylsilane or dichlorodiethylgermanium in the range −78 to 20 °C yielded, after hydrolysis, the corresponding azasilocine or azagermocine derivatives **35** and **36** (Scheme 5 and Table 1). We have observed that an excess of dichlorometalloid is necessary, because when 1 mol equiv. is used the yields are lower, and after deuteriolysis, along with the products **35** and **36**, the deuteriated derivatives **5**, which arise from the unchanged intermediates **4**, were observed. According to these observations, the reaction can be explained by assuming the formation of the species **31** or **32**, which favour cyclization to the eight-membered-ring compounds. These intermediates **31** and **32** yield the metallo bridged compounds **33** and **34**, which, after hydrolysis, afford final products **35** and **36**, respectively (Scheme 5). The proposed mechanism is supported by the ^{29}Si NMR data. Compound **33ab** shows two signals at δ_{Si} 11.8 and −16.5 for the silicon atoms, whereas the product **35ab** presents one signal at δ_{Si} −26.9 in the spectrum (both referred to hexamethyldisiloxane).[9]

On the other hand, the reactivity of intermediates **10**, **15** and



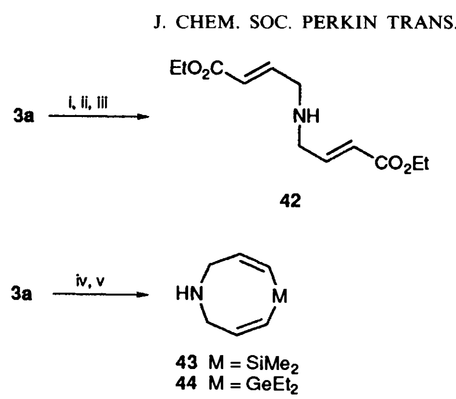
Scheme 5 *Reagents and conditions:* i, $(EtO)_2CO$, −78 to 20 °C; ii, CO_2, −78 to 20 °C; iii, water, 20 °C; iv, EtOH/HCl, reflux; v, Na_2CO_3; vi, MCl_2 (M = $SiMe_2$, $GeEt_2$), −78 to 20 °C

20c has been tested towards CO_2 and dichlorodimethylsilane and dichlorodiethylgermanium. The carbonation of these intermediates and further esterification with ethanol and hydrogen chloride led to the lactams **37**, **38** and **39c**, respectively. On the other hand, the reaction of intermediate **15** with the corresponding dichlorometalloid led to the benzazasilocine and benzazagermocine derivatives **40** and **41**, respectively (Scheme 6 and Table 1).



Scheme 6 *Reagents and conditions:* i, CO_2, −78 to 20 °C, ii, EtOH/HCl, reflux; iii, Na_2CO_3; iv, MCl_2 (M = $SiMe_2$, $GeEt_2$), −78 to 20 °C; v, water

Finally, we have studied the reaction of intermediate **3a** with three electrophiles (carbon dioxide, dichlorodimethylsilane, and dichlorodiethylgermanium). The reaction with CO_2 and further esterification with EtOH–HCl led to the diester **42** with isomerization in both double bonds. The reaction with Me_2SiCl_2 and Et_2GeCl_2 afforded, after hydrolysis, the corresponding azasilocine and azagermocine derivatives **43** and **44** (Scheme 7 and Table 1).



Scheme 7 *Reagents and conditions:* i, CO_2, −78 to 20 °C; ii, EtOH/HCl, reflux; iii, Na_2CO_3; iv, MCl_2 (M = $SiMe_2$, $GeEt_2$), −78 to 20 °C; v, water

Experimental

All reactions involving organometallic reagents were executed under nitrogen in glassware that had been flame dried, and then cooled under nitrogen. M.p.s were measured on a Büchi-Tottoli capillary melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 and AC-300 spectrometers. Tetramethylsilane was used as the internal standard with $CDCl_3$ as the solvent for the ^1H NMR spectra and the central line of $CDCl_3$ (δ_C 76.95) was referenced in ^{13}C NMR spectra. *J* Values are given in Hz. Mass spectra (EI) were determined at 70 eV with a Hewlett-Packard 5987A spectrometer; only selected ions are reported here. HRMS were measured with an AutoSpecEQ/VG spectrometer. Elemental analysis was carried out with a Perkin-Elmer 240 Elemental Analyzer. All solvents and reagents were obtained from commercial sources and were used without further purification. Diethyl ether was distilled from sodium/benzophenone under nitrogen before use. TMEDA was distilled from BuLi and stored under nitrogen.

General Procedure for the Lithiation of Compounds **1**, **8**, **12**, **17** *and* **18** *and the Reaction with Electrophiles.*—A solution of BuLi (5 mmol) in hexane was added to a solution of the corresponding amine (5 mmol) in diethyl ether (20 cm^3) at −50 °C under nitrogen and the mixture was stirred for 20 min at temperatures in the range −50 to −30 °C. A solution of Bu^{t}Li (5 mmol) in pentane was added to the resulting mixture at −30 °C with further stirring for 2 h while the temperature was allowed to rise to 20 °C. The mixture was cooled to −20 °C, a solution of alkyllithium (5 mmol) was added [when primary alkyllithium was used, TMEDA (5 mmol) was added at 20 °C] and the mixture was stirred for 2 h in the range −20 to 20 °C. After being cooled to −78 °C, the mixture was treated with an excess of the corresponding electrophile, and was stirred while the temperature was allowed to rise to 20 °C. The resulting mixture was then hydrolysed with water and extracted with diethyl ether. The combined ether layers were dried over Na_2SO_4, filtered, concentrated under reduced pressure, and the resulting crude was purified by distillation, recrystallization or flash column chromatography.

(Z)-3-*Deuterio*-N-[2-(*deuteriomethyl*)*butyl*]*allylamine* **5aa**. B.p. 22–24 °C/0.1 mmHg; δ_H 0.8 (5 H, d and t, *J* 7.0, Me and CH_2D), 1.0–1.5 (3 H, m, CH_2Me and $CHCH_2D$), 1.6 (1 H, s, NH), 2.2 (1 H, dd, *J* 11.5 and 5.5, NCH_2CHC), 2.4 (1 H, dd, *J* 11.5 and 6.0, NCH_2CHC), 3.1 (2 H, d, *J* 6.0, NCH_2CH=C), 4.9 (1 H, d, *J* 10.0, CHD=CH) and 5.8 (1 H, m, CH=CHD); δ_C 10.9 (Me), 17.0 (t, J_{CD} 19.0, CH_2D), 27.1 (CH_2C), 34.5 ($CHCH_2D$), 52.3 and 55.2 (2 × CH_2N), 115.0 (t, J_{CD} 23.5, CD=CH) and 136.7 (CH=CD); *m/z* 129 (M^+, 2%), 71 (100) and 42 (20) (Found: C, 74.1; H/D, 14.3; N, 11.0. $C_8H_{15}D_2N$ requires C, 74.3; H/D, 14.8; N, 10.8%).

(Z)-3-*Deuterio*-N-[2-(*deuteriomethyl*)*hexyl*]*allylamine* **5ab**. B.p. 42–44 °C/0.1 mmHg; δ_H 0.9–1.0 (5 H, d and t, *J* 7.0, CH_2D and Me), 1.1–1.4 (7 H, m, 3 × CH_2C and NH), 1.5–1.6 (1 H, m, $CHCH_2D$), 2.5 (1 H, dd, *J* 11.5 and 7.5, NCH_2CHCH_2D), 2.6 (1 H, dd, *J* 11.5 and 6.0, NCH_2CHCH_2D), 3.2 (2 H, d, *J* 5.5, NCH_2CH=CD), 5.1 (1 H, d, *J* 10.0, CHD=CH) and 5.9–6.0 (1 H, m, CH=CHD); δ_C 13.6 (Me), 17.4 (t, J_{CD} 19.0, CH_2D), 22.6, 28.9 and 34.3 (3 × CH_2C), 32.8 ($CHCH_2D$), 52.3 and 55.6 (2 × CH_2N), 114.8 (t, J_{CD} 23.5, CD=C) and 136.6 (C=CD); *m/z* 157 (M^+, 4%), 71 (100) and 42 (19) (Found C, 76.6; H/D, 14.5; N, 8.7. $C_{10}H_{19}D_2N$ requires C, 76.35; H/D, 14.7; N, 8.9%).

(Z)-3-*Deuterio*-N-(2-*deuteriomethyl*-3,3-*dimethylbutyl*)*allylamine* **5ac**. B.p. 38–40 °C/0.1 mmHg; δ_H 0.9–1.0 (11 H, s and d, *J* 7.0, 3 × Me and CH_2D), 1.2–1.3 (1 H, s, NH), 1.3–1.4 (1 H, m, $CHCMe_3$), 2.2 (1 H, t, *J* 11.0, NCH_2CHCH_2D), 2.8 (1 H, dd, *J* 11.0 and 3.0, NCH_2CHCH_2D), 3.2 and 3.3 (2 H, 2 dd, *J* 14.0 and

Table 1 Preparation of intermediates **3**, **4**, **10**, **15** and **20** from amines **1**, **8**, **17**, **18** and **22**, and reaction with electrophiles to give products **5**, **11**, **16**, **21**, **27**, **29**, **30** and **35–44**

Starting amine	Intermediate	R^1	R^2	Electrophile	Product	% Yield[a]
1a	**4aa**	H	Et	D_2O	**5aa**[b]	86
1a	**4ab**	H	Bu	D_2O	**5ab**[b]	87
1a	**4ac**	H	Bu^t	D_2O	**5ac**[b]	93
1a	**4ad**	H	Bu^s	D_2O	**5ad**[b,c]	91
1b	**4bb**	Me	Bu	D_2O	**5bb**[b]	85
1b	**4bc**	Me	Bu^t	D_2O	**5bc**[b]	86
8	**10a**		Et	D_2O	**11a**[b]	86
8	**10b**		Bu	D_2O	**11b**[b]	87
8	**10c**		Bu^t	D_2O	**11c**[b]	90
17	**15a**		Et	D_2O	**16a**[b]	87
17	**15b**		Bu	D_2O	**16b**[b]	89
17	**15c**		Bu^t	D_2O	**16c**[b]	90
18	**20b**		Bu	D_2O	**21b**[b,d]	81
18	**20c**		Bu^t	D_2O	**21c**[b,d]	85
1a	**4ab**	H	Bu	$(EtO)_2CO$	**27ab**	85
1a	**4ac**	H	Bu^t	$(EtO)_2CO$	**27ac**	79
1b	**4bb**	Me	Bu	$(EtO)_2CO$	**27bb**	76
1b	**4bc**	Me	Bu^t	$(EtO)_2CO$	**27bc**	74
1a	**4ab**	H	Bu	CO_2	**29ab**	42
1a	**4ab**	H	Bu	CO_2[e]	**30ab**	82
1a	**4ac**	H	Bu^t	CO_2[e]	**30ac**	78
1a	**4ab**	H	Bu	Me_2SiCl_2	**33ab**	71
1a	**4aa**	H	Et	Me_2SiCl_2	**35aa**	69
1a	**4ab**	H	Bu	Me_2SiCl_2	**35ab**	72
1b	**4ba**	Me	Et	Me_2SiCl_2	**35ba**	62
1b	**4bb**	Me	Bu	Me_2SiCl_2	**35bb**	67
1a	**4aa**	H	Et	Et_2GeCl_2	**36aa**	63
1a	**4ab**	H	Bu	Et_2GeCl_2	**36ab**	71
1b	**4ba**	Me	Et	Et_2GeCl_2	**36ba**	64
1b	**4bb**	Me	Bu	Et_2GeCl_2	**36bb**	68
8	**10a**		Et	CO_2[e]	**37a**	72
8	**10b**		Bu	CO_2[e]	**37b**	63
8	**10c**		Bu^t	CO_2[e]	**37c**	60
17	**15a**		Et	CO_2[e]	**38a**	65
17	**15b**		Bu	CO_2[e]	**38b**	64
17	**15c**		Bu^t	CO_2[e]	**38c**	67
18	**20c**		Bu^t	CO_2[e]	**39c**[d]	69
17	**15a**		Et	Me_2SiCl_2	**40a**	67
17	**15b**		Bu	Me_2SiCl_2	**40b**	74
17	**15a**		Et	Et_2GeCl_2	**41a**	64
17	**15b**		Bu	Et_2GeCl_2	**41b**	71
22	**3a**	H		CO_2[e]	**42**	58
22	**3a**	H		Me_2SiCl_2	**43**	48
22	**3a**	H		Et_2GeCl_2	**44**	54(52)[f]

[a] Isolated yield based on starting amine. [b] Over 95% deuterium by mass spectrometry. [c] Equimolecular mixture of diastereoisomers. [d] Only one diastereoisomer. [e] Further esterification with EtOH–HCl. [f] From diallylamine **1a** in one-pot process.

6.0, $NCH_2CH{=}C$), 5.1 (1 H, d, *J* 10.0, *CH*D=CH) and 5.9 (1 H, m, *CH*=CHD); δ_C 12.8 (t, J_{CD} 19.0, CH_2D), 27.1 (3 × Me), 32.1 (*C*Me$_3$), 42.4 (*C*HCMe$_3$), 50.9 and 52.0 (2 × CH_2N), 115.8 (t, J_{CD} 23.5, *C*D=C) and 135.9 (*C*=CD); *m/z* 157 (M^+, 4%), 71 (100) and 42 (10) (Found: C, 76.5; H/D, 14.3; N, 8.7%).

(Z)-3-*Deuterio*-N-(2-*deuteriomethyl*-3-*methylpentyl*)*allylamine* **5ad**. B.p. 41–43 °C/0.1 mmHg; δ_H 0.8–1.0 (8 H, t and 2 d, *J* 7.0, 2 × Me and CH_2D), 1.1–1.8 (5 H, m, CH_2C, 2 × CHC and NH), 2.4 (1 H, m, NCH_2CHCH_2D), 2.6 (1 H, m, NCH_2CHCH_2D), 3.2 (2 H, d, *J* 6.0 $NCH_2CH{=}CD$), 5.0 (1 H, d, *J* 10.0, *CH*D=CH) and 5.8–5.9 (1 H, m, CH=CHD); δ_C 11.8, 13.6 and 15.9 (2 × Me), 12.2 and 14.6 (t, J_{CD} 19.0, CH_2D), 25.1 and 27.3 (*C*H$_2$Me), 36.2, 36.3 and 37.5 (2 × *C*HC), 52.4, 52.5 and 53.8 (2 × CH_2N), 115.0 (t, J_{CD} 23.0, *C*D=C) and 136.8 (*C*=CD); *m/z* 157 (M^+, 4%), 71 (100) and 42 (20) (Found: C, 76.6; H/D, 14.5; N, 8.75%).

(Z)-3-*Deuterio*-N-[2-(*deuteriomethyl*)*hexyl*]-2-*methylallylamine* **5bb**. B.p. 53–55 °C/0.1 mmHg; δ_H 0.8–0.9 (5 H, d and t, *J* 7.0, *Me*CH$_2$ and CH_2D), 1.1–1.4 (7 H, m, 3 × CH_2C and NH), 1.5–1.6 (1 H, m, *CH*CH$_2$D), 1.8 (3 H, s, MeC=CD), 2.3 (1 H, dd, *J* 11.5 and 7.5, NCH_2CH), 2.5 (1 H, dd, *J* 11.5 and 6.0, NCH_2CH), 3.1 (2 H, s, NCH_2C and 4.8 (1 H, s, CHD=C); δ_C 13.8 (*Me*CH$_2$), 17.5 (t, J_{CD} 19.0, CH_2D), 20.3 (*Me*C=CD), 22.8, 29.0 and 34.4 (3 × *C*H$_2$C), 32.9 (*C*HCH$_2$D), 55.5 and 55.6 (2 × CH_2N), 109.8 (t, J_{CD} 23.5, *C*D=C) and 143.8 (*C*=CD); *m/z* 171 (M^+, 4%), 85 (100) and 56 (12) (Found: C, 77.25; H/D, 14.5; N, 8.1. $C_{11}H_{21}D_2N$ requires C, 77.1; H/D, 14.7; N, 8.2%).

(Z)-3-*Deuterio*-N-(2-*deuteriomethyl*-3,3-*dimethylbutyl*)-2-*methylallylamine* **5bc**. B.p. 50–52 °C/0.1 mmHg; δ_H 0.9 (11 H, s and d, *J* 7.0, 3 × MeC and CH_2D), 1.3–1.5 (2 H, m, *CH*CMe$_3$ and NH), 1.7 (3 H, s, MeC=CD), 2.2 (1 H, dd, *J* 11.5 and 10.0, NCH_2CH), 2.7 (1 H, dd, *J* 11.5 and 3.0, NCH_2CH), 3.1 and 3.2 (2 H, 2 d, *J* 14.5, NCH_2C) and 4.8 (1 H, s, CHD); δ_C 13.0 (t, J_{CD} 19.0, CH_2D), 20.5 (*Me*CH=CD), 27.2 (3 × *Me*C), 32.1 (*C*Me$_3$), 42.9 (*C*HCMe$_3$), 51.2 and 55.7 (2 × CH_2N), 109.9 (t, J_{CD} 23.5, *C*D=C) and 143.8 (*C*=CD); *m/z* 171 (M^+, 1%). 85 (100), 57 (14), 56 (30), 42 (16) and 41 (14) (Found: C, 77.4; H/D, 14.3; N, 8.3%).

8-*Deuterio*-N-[2-(*deuteriomethyl*)*butyl*]-1-*naphthylamine* **11a**. R_f 0.20 (hexane); δ_H 0.8 (5 H, m, Me and CH_2D), 1.0–1.6 (3 H, m, *CH*CH$_2$ and *CH*$_2$Me), 2.9 (1 H, dd, *J* 11.9 and 7.0, CH_2N), 3.0 (1 H, dd, *J* 11.9 and 6.0, CH_2N), 4.2 (1 H, s, NH) and 6.4–7.6 (6 H, m, ArH); δ_C 11.2 (Me), 17.3 (t, J_{CD} 19.4,

CH_2D), 27.4 (CH_2C), 34.1 (CH), 49.9 (CH_2N), 119.3 (t, J_{CD} 23.6, CD) and 103.8, 116.7, 123.1, 124.2, 125.4, 126.5, 128.5, 134.2 and 143.5 (ArC); *m/z* 215 (M^+, 23%), 158 (13), 157 (100), 130 (22) and 129 (13) (Found: C, 83.8; H/D, 9.6; N, 6.3. $C_{15}H_{17}D_2N$ requires C, 83.65; H/D, 9.85; N, 6.5%).

*8-Deuterio-*N*-[2-(deuteriomethyl)hexyl]-1-naphthylamine* **11b**. R_f 0.21 (hexane); δ_H 0.9 (3 H, t, *J* 7.0, Me), 1.1 (2 H, d, 7.0, CH_2D), 1.2–1.6 (7 H, m, 3 × CH_2C and NH), 1.9 (1 H, m, $CHCH_2D$), 3.0 (1 H, dd, *J* 11.5 and 7.5, CH_2N), 3.2 (1 H, dd, *J* 11.5 and 6.0, CH_2N) and 6.6–7.8 (6 H, m, ArH); δ_C 13.8 (Me), 17.6 (t, J_{CD} 19.0, CH_2D), 22.6, 28.9 and 34.3 (3 × CH_2C), 32.3 ($CHCH_2D$), 50.1 (CH_2N), 119.0 (t, J_{CD} 22.0, CD) and 103.7, 116.5, 122.9, 124.0, 125.2, 126.3, 128.3, 133.9 and 143.3 (ArC); *m/z* 243 (M^+, 29%), 158 (12), 157 (100) and 130 (16) (Found: C, 83.7; H/D, 10.1; N, 5.5. $C_{17}H_{21}D_2N$ requires C, 83.9; H/D, 10.35; N, 5.75%).

*8-Deuterio-*N*-(2-deuteriomethyl-3,3-dimethylbutyl)-1-naphthylamine* **11c**. R_f 0.22 (hexane); δ_H 1.1 (11 H, s, and d, *J* 7.0, 3 × Me and CH_2D), 1.4 (1 H, s, NH), 1.8 (1 H, m, $CHCH_2D$), 3.0 (1 H, dd, *J* 12.0 and 10.0, CH_2N), 3.6 (1 H, dd, *J* 12.0 and 3.0, CH_2N) and 6.7–7.9 (6 H, m, ArH); δ_C 13.5 (t, J_{CD} 19.0, CH_2D), 27.5 (3 × Me), 32.5 (CMe_3), 42.5 ($CHCH_2D$), 46.5 (CH_2N), 119.3 (t, J_{CD} 23.0, CD) and 104.0, 116.8, 123.2, 124.3, 125.5, 126.6, 128.6, 134.3 and 143.6 (ArC); *m/z* 243 (M^+, 17%), 158 (12), 157 (100), 130 (29), 129 (14) and 116 (12) (Found: C, 84.2; H/D, 10.1; N, 5.8%).

*2-Deuterio-*N*-[2-(deuteriomethyl)butyl]benzylamine* **16a**. R_f 0.22 (hexane–ethyl acetate 1 : 1); δ_H 0.8 (5 H, m, Me and CH_2D), 1.0–1.5 (4 H, m, CH_2C, CH and NH), 2.3 (1 H, dd, *J* 11.5 and 7.0, NCH_2CH), 2.4 (1 H, dd, *J* 11.5 and 6.0, NCH_2CH), 3.7 (2 H, s, NCH_2C) and 7.1–7.2 (4 H, m, ArH); δ_C 11.2 (Me), 17.2 (t, J_{CD} 19.1, CH_2D), 27.4 (CH_2C), 34.6 (CH), 54.0 and 55.5 (2 × CH_2N) and 126.7, 128.0, 128.2 and 140.5 (ArC); *m/z* 179 (M^+, 2%), 121 (57) and 92 (100) (Found: C, 80.7; H/D, 11.5; N, 7.7. $C_{12}H_{17}D_2N$ requires C, 80.4; H/D, 11.8; N, 7.8%).

*2-Deuterio-*N*-[2-(deuteriomethyl)hexyl]benzylamine* **16b**. R_f 0.29 (hexane–ethyl acetate 1:1); δ_H 0.8–1.5 (13 H, m, $Me[CH_2]_3CHCH_2D$ and NH), 2.3 (1 H, dd, *J* 11.5 and 7.2, NCH_2CH), 2.5 (1 H, dd, *J* 11.5 and 5.9, NCH_2CH), 3.7 (2 H, s, CH_2NC) and 7.2–7.3 (4 H, m, ArH); δ_C 14.1 (Me), 17.7 (t, J_{CD} 19.1, CH_2D), 22.9, 29.12 and 34.5 (3 × CH_2C), 33.0 (CH), 54.0 and 55.8 (2 × CH_2N) and 126.7, 128.0, 128.2 and 140.5 (ArC); *m/z* 207 (M^+, 2%), 121 (94) and 92 (100) (Found: C, 81.25; H/D, 11.9; N, 6.8. $C_{14}H_{21}D_2N$ requires C, 81.1; H/D, 12.15; N, 6.75%).

*2-Deuterio-*N*-[2-(deuteriomethyl)-3,3-dimethylbutyl]benzylamine* **16c**. R_f 0.26 (hexane–ethyl acetate 1 : 1); δ_H 0.8 (9 H, s, 3 × Me), 0.9 (2 H, m, CH_2D), 1.3 (1 H, m, CH), 1.5 (1 H, s, NH), 2.2 (1 H, dd, *J* 11.4 and 10.2, NCH_2CH), 2.8 (1 H, dd, *J* 11.4 and 3.0, NCH_2CH), 3.7 and 3.9 (2 H, 2 d, *J* 13.2, CH_2NC) and 7.2–7.3 (4 H, m, ArH); δ_C 13.0 (t, J_{CD} 19.4, CH_2D), 27.3 (3 × Me), 32.2 (CMe), 42.8 (CH), 51.5 and 53.9 (2 × CH_2N) and 126.6, 127.8, 128.1 and 140.3 (ArC); *m/z* 207 (M^+, 4%), 121 (70) and 92 (100); (Found: C, 81.3; H/D, 12.05; N, 6.6%).

N,N'-Bis-[2-(deuteriomethyl)hexyl]ethylenediamine **21b**. B.p. 106–108 °C/0.1 mmHg; δ_H 0.8–1.5 (26 H, m, 2 × Me $[CH_2]_3$-CH, 2 × CH_2D and 2 × NH), 2.3 (2 H, dd, *J* 11.6 and 7.3, 2 × NCH_2CH), 2.4 (2 H, dd, *J* 11.6 and 6.2, 2 × NCH_2CH) and 2.6 (4 H, s, 2 × CH_2N); δ_C 13.9 (2 × Me), 17.6 (t, J_{CD} 18.8, 2 × CH_2D), 22.8, 29.0 and 34.5 (6 × CH_2C), 32.9 (2 × CH) and 49.3 and 56.3 (4 × CH_2N); *m/z* 257 (M^+ – 1, 1%), 130 (12), 129 (100), 58 (12) and 44 (47) (Found: C, 74.5; H/D, 14.5; N, 10.9. $C_{16}H_{34}D_2N_2$ requires C, 74.35; H/D, 14.8; N, 10.85%).

N,N'-Bis-[2-(deuteriomethyl)-3,3-dimethylbutyl]ethylenediamine **21c**. B.p. 97–99 °C/0.1 mmHg; δ_H 0.8 (22 H, m, 6 × Me and 2 × CH_2D), 1.1–1.4 (4 H, m, 2 × CH and 2 × NH), 2.1 (2 H, dd, *J* 11.2 and 10.0, 2 × NCH_2CH) and 2.5–2.8 (6 H, m, 2 × NCH_2CH and 2 × CH_2N); δ_C 12.9 (t, J_{CD} 19.1, 2 × CH_2D), 27.2 (6 × Me), 32.0 (2 × C), 42.8 (2 × CH) and 49.3 and 51.8 (4 × CH_2N); *m/z* 243 (M^+ – 15, 4%), 172 (21), 130 (12), 129 (100) and 57 (16) (Found: C, 74.5; H/D, 14.6; N, 10.9%).

*2-Butyl-2,3-dihydro-1*H*-pyrrolizine* **27ab**. B.p. 52–54 °C/0.1 mmHg; δ_H 0.9 (3 H, t, *J* 7.0, Me), 1.3–1.5 (6 H, m, 3 × CH_2C), 2.5 (1 H, dd, *J* 14.5 and 7.5, CH_2CN), 2.9 (1 H, m, $CHCH_2$), 3.0 (1 H, dd, *J* 14.5 and 8.0, CH_2CN), 3.6 and 4.1 (2 H, 2 dd, *J* 10.0 and 7.5, CH_2N), 5.8 (1 H, dd, *J* 3.0 and 1.0, CH=CN), 6.2 (1 H, t, *J* 3.0, C*H*=CHN) and 6.6 (1 H, dd, *J* 3.0 and 1.0, NC*H*=CH); δ_C 13.9 (Me), 22.6, 30.2, 30.8 and 34.1 (4 × CH_2C), 42.8 ($CHCH_2$), 51.9 (CH_2N), 98.8 (CH=CN), 111.5 (CHN), 113.4 (CH=CHN) and 136.5 (CN); *m/z* 163 (M^+, 24%), 106 (100), 80 (20) and 41 (10) (Found: C, 81.0; H, 10.4; N, 8.55. $C_{11}H_{17}N$ requires C, 80.9; H, 10.5; N, 8.6%).

*2-tert-Butyl-2,3-dihydro-1*H*-pyrrolizine* **27ac**. B.p. 50–52 °C/0.1 mmHg; δ_H 0.9 (9 H, s, 3 × Me), 2.6–2.9 (3 H, m, $CHCH_2$ and CH_2C), 3.8 (1 H, dd, *J* 10.0 and 9.5, CH_2N), 4.0 (1 H, dd, *J* 10.0 and 8.0, CH_2N), 5.8 (1 H, dd, *J* 3.0 and 1.0, CH=CN), 6.2 (1 H, t, *J* 3.0, C*H*=CHN) and 6.6 (1 H, dd, *J* 3.0 and 1.0, NC*H*=CH); δ_C 25.8 (H_2CN), 27.2 (3 × Me), 31.7 (CMe_3), 47.5 (CH_2N), 53.3 ($CHCH_2$), 98.6 (CH=CN), 111.5 (CHN), 113.2 (CH=CHN) and 136.5 (CN); *m/z* 163 (M^+, 55%), 148 (17), 106 (100), 80 (37) and 41 (18) (Found: C, 80.8; H, 10.5; N, 8.5%).

*2-Butyl-6-methyl-2,3-dihydro-1*H*-pyrrolizine* **27bb**. B.p. 67–69 °C/0.1 mmHg; δ_H 0.8 (3 H, t, *J* 7.0, $MeCH_2$), 1.0–1.5 (6 H, m, 3 × CH_2C), 2.0 (3 H, s, MeC), 2.4 (1 H, dd, *J* 14.5 and 7.5, CH_2CN), 2.7 (1 H, m, $CHCH_2$), 2.8 (1 H, dd, *J* 14.5 and 8.0, CH_2CN), 3.4 and 3.9 (2 H, 2 dd, *J* 10.0 and 7.5, CHN), 5.5 (1 H, d, *J* 1.0, CH=CN) and 6.2 (1 H, d, *J* 1.0, NC*H*=CMe); δ_C 12.3 and 13.8 (2 × Me), 22.5, 30.1, 30.9 and 34.1 (4 × CH_2C), 42.3 ($CHCH_2$), 51.8 (CH_2N), 100.2 (CH=CN), 111.2 (NCH=CMe), 122.5 (CMe=CHN) and 136.2 (CN=CH); *m/z* 193 (M^+ + 16, 12%), 136 (100), 80 (15), 69 (60) and 41 (20) (Found: C, 81.1; H, 11.0; N, 7.6. $C_{12}H_{19}N$ requires C, 81.3; H, 10.8; N, 7.9%.

*2-tert-Butyl-6-methyl-2,3-dihydro-1*H*-pyrrolizine* **27bc**. B.p. 64–66 °C/0.1 mmHg; δ_H 1.0 (9 H, s, 3 × *Me*CCH), 2.1 (3 H, s, *Me*C=CH), 2.5–2.8 (3 H, m, CH_2CN and $CHCH_2$), 3.7 (1 H, dd, *J* 10.0 and 9.5, CH_2N), 3.9 (1 H, dd, *J* 10.0 and 8.0, CH_2N), 5.6 (1 H, d, *J* 1.0, CH=CN) and 6.4 (1 H, d, *J* 1.0, NC*H*=CMe); δ_C 12.3 (*Me*C=CH), 25.9 (CH_2CN), 27.1 (3 × *Me*CCH), 31.6 (CMe_3), 47.4 (CH_2N), 52.9 ($CHCH_2$), 99.9 (CH=CN), 111.1 (NCH=CMe), 122.5 (CMe=CHN) and 136.4 (CN=CH); *m/z* 193 (M^+ + 16, 6%), 136 (100), 80 (15), 69 (89) and 41 (21) (Found: C, 81.4; H, 10.6; N, 7.9%).

(Z)-7-Butyl-5-azanon-2-enedioic acid **29ab**. Oil; δ_H 0.9 (3 H, t, *J* 7.0, Me), 1.1–1.5 (7 H, m, 3 × CH_2C and NH), 2.1 (1 H, dd, *J* 16.5 and 7.5, CH_2CO_2), 2.3 (1 H, m, $CHCH_2CO_2$), 2.6 (1 H, dd, *J* 16.5 and 8.5, CH_2CO_2), 3.0 (1 H, dd, *J* 9.5 and 7.0, NCH_2-CHC), 3.5 (1 H, dd, *J* 9.5 and 8.5, NCH_2CHC), 4.4 (2 H, d, *J* 6.0, NCH_2CH=C), 5.9 (1 H, d, *J* 11.5, C=$CHCO_2$), 6.1 (1 H, dt, *J* 11.5 and 6.0, C*H*=$CHCO_2$) and 9.0 (2 H, s, 2 × OH); δ_C 13.6 (Me), 22.3, 29.2 and 34.0 (3 × CH_2C), 31.5 ($CHCH_2$), 37.1 (CH_2CO), 40.8 and 53.2 (2 × CH_2N), 122.7 ($CHCO_2$), 143.8 (CH=$CHCO_2$) and 168.7 and 175.1 (2 × CO); *m/z* 225 (M^+ – 18, 34%), 181 (18), 180 (76), 179 (32), 166 (14), 152 (50), 142 (14), 140 (19), 124 (14), 123 (11), 122 (54), 114 (23), 113 (38), 98 (10), 97 (24), 96 (40), 95 (35), 94 (27), 85 (19), 84 (42), 83 (35), 82 (20), 81 (11), 80 (12), 70 (21), 69 (31), 68 (77), 67 (41), 57 (29), 56 (30), 55 (98), 54 (16), 53 (19), 45 (14), 43 (25), 42 (26), 41 (100), 40 (13) and 39 (48).

(E)-Diethyl 7-butyl-5-azanon-2-enedioate **30ab**. B.p. 123–125 °C/0.1 mmHg; δ_H 0.9 (9 H, t, *J* 7.0, 2 × $MeCH_2O$ and $MeCH_2C$), 1.1–1.6 (7 H, m, 3 × CH_2C and NH), 2.1 (1 H, dd, *J* 16.5 and 8.5, CH_2CO_2), 2.3 (1 H, m, $CHCH_2CO_2$), 2.5 (1 H, dd, *J* 16.5 and 7.5, CH_2CO_2), 3.0 (1 H, dd, *J* 9.5 and 7.0, NCH_2CHC), 3.4 (1 H, dd, *J* 9.5 and 8.0, NCH_2CHC), 4.0 and

4.1 (2 H, 2 dd, *J* 15.5 and 5.5, NCH_2CH=C), 4.2 (4 H, q, *J* 7.0, 2 × CH_2O), 5.9 (1 H, d, *J* 16.0, C=CHCO_2) and 6.8 (1 H, dt, *J* 16.0 and 5.5, C*H*=CHCO_2); δ_C 13.6 and 13.8 (3 × Me), 22.2, 29.2 and 34.0 (3 × CH_2C), 31.5 (*C*HCH_2), 37.0 (CH_2CO_2), 42.9 and 52.6 (2 × CH_2N), 60.1 (2 × CH_2O), 122.6 (*C*HCO), 141.7 (*C*H=CHCO_2) and 165.3 and 174.2 (2 × CO); *m/z* 270 (M^+ − 29, 5%), 253 (20), 224 (42), 208 (37), 207 (40), 196 (30), 181 (13), 180 (100), 179 (68), 178 (19), 154 (11), 142 (18), 122 (34), 112 (13), 96 (22), 95 (14), 85 (16), 84 (18), 83 (15), 69 (13), 68 (45), 67 (16), 57 (13), 56 (16), 55 (90), 43 (14), 42 (17), 41 (58) and 39 (20) (Found: C, 64.5; H, 9.4; N, 4.5. $C_{16}H_{29}NO_4$ requires C, 64.2; H, 9.75; N, 4.7%).

(E)-*Diethyl* 7-tert-*butyl*-5-*azanon*-2-*enedioate* **30ac**. B.p. 117–119 °C/0.1 mmHg; δ_H 0.8 (9 H, s, 3 × MeC), 1.2 (6 H, t, *J* 7.0, 2 × *Me*CH_2O), 2.1–2.4 (4 H, m, CH_2CO_2, C*H*CH_2 and NH), 3.0 (1 H, dd, *J* 9.5 and 7.0, NCH_2CHC), 3.2 (1 H, dd, *J* 9.5 and 8.5, NCH_2CHC), 3.8 and 4.0 (2 H, 2 dd, *J* 15.5 and 5.5, NCH_2CH=C), 4.1 (4 H, q, *J* 7.0, 2 × CH_2O), 5.8 (1 H, d, *J* 16.0, C=CHCO_2) and 6.7 (1 H, dt, *J* 16.0 and 5.5, C*H*=CHCO_2); δ_C 13.9 (2 × *Me*CH_2), 26.5 (3 × MeC), 31.3 (*C*Me_3), 32.4 (CH_2CO), 41.9 (CHCMe_3), 43.0 and 48.4 (2 × CH_2N), 60.3 (2 × CH_2O), 122.8 (*C*HCO_2), 141.7 (*C*H=CHCO_2) and 165.5 and 174.3 (2 × CO); *m/z* 253 (M^+ − 46, 14%), 224 (24), 208 (22), 207 (32), 196 (15), 180 (58), 179 (31), 150 (20), 142 (24), 124 (17), 123 (15), 122 (100), 96 (15), 94 (18), 85 (17), 84 (28), 83 (14), 82 (13), 69 (27), 68 (32), 67 (15), 57 (49), 55 (44), 43 (10), 42 (11), 41 (60) and 39 (18) (Found: C, 64.5; H, 9.6; N, 4.9%).

Bis-(3-*Butyl*-5,5-*dimethyl*-1,2,3,4,5,8-*hexahydro*-1,5-*azasilocin*-1-*yl*)*dimethylsilane* **33ab**. B.p. 75 °C/10^{-3} mmHg; δ_H 0.0, 0.1, 0.4 and 0.5 (18 H, 4 s, 6 × MeSi), 0.3 (2 H, dd, *J* 14.0 and 13.0, 2 × CH_2Si), 0.7 (2 H, d, *J* 14.0, 2 × CH_2Si), 0.9 (6 H, t, *J* 6.5, 2 × *Me*CH_2), 1.0–1.7 (14 H, m, 6 × CH_2C and 2 × C*H*-CH_2Si), 2.3 (2 H, t, *J* 13.1, 2 × NCH_2CHCH_2), 2.8 (2 H, dd, *J* 13.1 and 2.3, 2 × NCH_2CHCH_2), 3.2 and 3.7 (4 H, 2 ddd, *J* 19.5, 3.1 and 2.3, 2 × NCH_2CH=CH), 5.4 (2 H, dt, *J* 14.3 and 2.1, 2 × CH=C*H*Si) and 6.4 (2 H, dt, *J* 14.3 and 3.1, 2 × C*H*=CHSi); δ_C 1.9, 2.0 and 2.1 (6 × MeSi), 14.0 (2 × *Me*-CH_2), 21.2, 22.9, 29.3 and 36.1 (6 × CH_2C and 2 × CH_2Si), 37.0 (2 × *C*HCH_2Si), 53.4 and 58.8 (4 × CH_2N), 126.4 (2 × CH=*C*HSi) and 147.6 (2 × *C*H=CHSi); $\delta(^{29}Si)$ −16.5 and 11.8.

3-*Ethyl*-5,5-*dimethyl*-1,2,3,4,5,8-*hexahydro*-1,5-*azasilocine* **35aa**. R_f 0.23 (hexane–diethyl ether 9:1); δ_H 0.0 and 0.1 (6 H, 2 s, 2 × MeSi), 0.3 (1 H, dd, *J* 14.5 and 10.8, CH_2Si), 0.8 (1 H, ddd, *J* 14.5, 4.3 and 1.7, CH_2Si), 0.9 (3 H, t, *J* 7.0, *Me*CH_2), 1.0–1.4 (4 H, m, CH_2Me, C*H*CH_2Si and NH), 2.0 (1 H, t, *J* 11.5, NCH_2CHCH_2), 2.8 (1 H, dd, *J* 11.5 and 1.7, NCH_2CHCH_2), 3.3 (2 H, t, *J* 2.5, NCH_2CH=CH), 5.6 (1 H, dt, *J* 12.8 and 2.5, CH=C*H*Si) and 6.3 (1 H, dt, *J* 12.8 and 2.5, C*H*=CHSi); δ_C 2.5 and 4.1 (2 × MeSi), 11.7 (*Me*CH_2), 22.3 (CH_2Si), 28.9 (*C*H_2Me), 38.7 (*C*HCH_2Si), 51.1 and 55.7 (2 × CH_2N), 129.3 (CH=*C*HSi) and 145.3 (*C*H=CHSi); *m/z* 168 (M^+ − 15, 100%), 126 (48), 113 (19), 112 (78), 110 (12), 99 (13), 98 (99), 83 (23) and 59 (17) (Found: C, 65.3; H, 11.7; N, 7.35. $C_{10}H_{21}NSi$ requires C, 65.5; H, 11.5; N, 7.65%).

3-*Butyl*-5,5-*dimethyl*-1,2,3,4,5,8-*hexahydro*-1,5-*azasilocine* **35ab**. R_f 0.27 (hexane–diethyl ether 9:1); δ_H 0.0 and 0.1 (6 H, 2 s, 2 × MeSi), 0.2 (1 H, dd, *J* 14.5 and 10.9, CH_2Si), 0.8 (1 H, ddd, *J* 14.5, 4.5 and 1.7, CH_2Si), 0.9 (3 H, t, *J* 6.5, *Me*CH_2), 1.0–1.5 (8 H, m, 3 × CH_2C, C*H*CH_2Si and NH), 2.0 (1 H, t, *J* 10.8, NCH_2CHCH_2), 2.8 (1 H, dd, *J* 10.8 and 1.7, NCH_2CHCH_2), 3.3 (2 H, t, *J* 2.5, NCH_2CH=CH), 5.5 (1 H, dt, *J* 12.7 and 2.5, CH=C*H*Si) and 6.3 (1 H, dt, *J* 12.7 and 2.5, C*H*=CHSi); δ_C 2.5 and 4.2 (2 × MeSi), 14.1 (*Me*CH_2), 22.8, 23.0, 29.5 and 36.0 (3 × CH_2C and CH_2Si), 36.9 (*C*HCH_2Si), 51.1 and 56.1 (2CH_2N), 129.3 (CH=*C*HSi) and 145.2 (*C*H=CHSi); $\delta(^{29}Si)$ −26.9; *m/z* 196 (M^+ − 15, 100%), 126 (64), 114 (21), 113 (72), 112 (19), 98 (77), 83 (16) and 59 (11) (Found: C, 67.9; H, 12.2; N, 6.4. $C_{12}H_{25}NSi$ requires C, 68.15; H, 11.9; N, 6.6%).

3-*Ethyl*-5,5,7-*trimethyl*-1,2,3,4,5,8-*hexahydro*-1,5-*azasilocine* **35ba**. R_f 0.37 (hexane–diethyl ether 9:1); δ_H 0.0, 0.1 (6 H, 2 s, 2 × MeSi), 0.3 (1 H, dd, *J* 14.5 and 10.8, CH_2Si), 0.8 (1 H, ddd, *J* 14.5, 4.5 and 1.7, CH_2Si), 1.0 (3 H, t, *J* 7.4, *Me*CH_2), 1.1–1.5 (4 H, m, CH_2Me, C*H*CH_2Si and NH), 1.8 (3 H, s, *Me*C=CH), 2.1 (1 H, t, *J* 11.2, NCH_2CHCH_2), 2.9 (1 H, dd, *J* 11.2 and 1.7, NCH_2CHCH_2), 3.2 (2 H, s, NCH_2C=CH) and 5.3 (1 H, s, CH=C); δ_C 2.9 and 4.7 (2 × MeSi), 11.7 (*Me*CH_2), 22.5 (CH_2Si), 23.2 (*Me*C=CH), 28.8 (*C*H_2Me), 38.6 (*C*HCH_2Si), 54.3 and 55.8 (2 × CH_2N), 124.2 (*C*H=C) and 152.0 (*C*=CH); *m/z* 182 (M^+ − 15, 64%), 140 (41), 127 (13), 126 (79), 124 (14), 113 (13), 112 (100), 97 (37), 59 (22) and 43 (12) (Found: C, 66.6; H, 11.9; N, 6.8. $C_{11}H_{23}NSi$ requires C, 66.9; H, 11.75; N, 7.1%).

3-*Butyl*-5,5,7-*trimethyl*-1,2,3,4,5,8-*hexahydro*-1,5-*azasilocine* **35bb**. R_f 0.44 (hexane–diethyl ether 9:1); δ_H 0.0, 0.1 (6 H, 2 s, 2 × MeSi), 0.2 (1 H, dd, *J* 14.5 and 10.9, CH_2Si), 0.7 (1 H, ddd, *J* 14.5, 4.7 and 1.7, CH_2Si), 0.9 (3 H, t, *J* 7.0, *Me*CH_2), 1.0–1.5 (8 H, m, 3 × CH_2C, C*H*CH_2Si and NH), 1.7 (3 H, s, *Me*C=CH), 1.9 (1 H, t, *J* 11.3, NCH_2CHCH_2), 2.8 (1 H, dd, *J* 11.3 and 1.7, NCH_2CHCH_2), 3.1 (2 H, s, NCH_2C=CH and 5.2 (1 H, s, CH=C); δ_C 2.9 and 4.7 (2 × MeSi), 14.1 (*Me*CH_2), 23.2 (*Me*C=CH), 23.0, 23.1, 29.5 and 35.9 (3 × CH_2C and CH_2Si), 36.9 (*C*HCH_2Si), 54.3 and 56.1 (2 × CH_2N), 124.3 (*C*H=C) and 152.5 (*C*=CH); *m/z* 210 (M^+ − 15, 100%), 168 (34), 140 (35), 127 (11), 126 (68), 124 (11), 112 (67), 97 (24), 59 (13), 41 (11) and 32 (27) (Found: C, 69.4; H, 12.0; N, 6.0. $C_{13}H_{27}NSi$ requires C, 69.25; H, 12.1; N, 6.2%).

3,5,5-*Triethyl*-1,2,3,4,5,8-*hexahydro*-1,5-*azagermocine* **36aa**. R_f 0.25 (hexane–diethyl ether 4:1); δ_H 0.4 (1 H, dd, *J* 13.4 and 11.2, CHCH_2Ge), 0.7–1.4 (18 H, m, 2 × EtGe, MeCH_2CH, CHCH_2Ge and NH), 2.0 (1 H, t, *J* 11.7, NCH_2CHCH_2), 2.7 (1 H, d, *J* 11.7, NCH_2CHCH_2), 3.2 and 3.4 (2 H, 2 dt, *J* 18.4 and 2.5, NCH_2CH=CH), 5.6 (1 H, dt, *J* 12.5 and 2.5, CH=C*H*Ge) and 6.3 (1 H, dt, *J* 12.5 and 2.5, C*H*=CHGe); δ_C 9.1 and 9.2 (2 × MeCH_2Ge), 9.4 and 9.9 (2 × Me*C*H_2Ge), 11.6 (2 × *Me*CH_2C), 18.1 (CH*C*H_2Ge), 29.3 (Me*C*H_2CH), 38.5 (*C*HCH_2Ge), 51.7 and 56.5 (2 × CH_2N), 126.4 (CH=*C*HGe) and 144.0 (*C*H=CHGe); *m/z* 228 (M^+ − 29, 100%), 227 (30), 226 (69), 224 (54), 130 (11), 128 (15) and 126 (12) (Found: C, 56.5; H, 10.1; N, 5.25. $C_{12}H_{25}NGe$ requires C, 56.3; H, 9.85; N, 5.45%).

3-*Butyl*-5,5-*diethyl*-1,2,3,4,5,8-*hexahydro*-1,5-*azagermocine* **36ab**. R_f 0.28 (hexane–diethyl ether 4:1); δ_H 0.4 (1 H, dd, *J* 13.3 and 11.3, CHCH_2Ge), 0.7–1.5 (22 H, m, 2 × EtGe, Me$[CH_2]_3$CH, CHCH_2Ge and NH), 2.1 (1 H, t, *J* 11.7, NCH_2CHCH_2), 2.8 (1 H, d, *J* 11.7, NCH_2CHCH_2), 3.3 and 3.5 (2 H, 2 dt, *J* 18.3 and 2.7, NCH_2CH=CH), 5.7 (1 H, dt, *J* 12.5 and 2.7, CH=C*H*Ge), 6.4 (1 H, dt, *J* 12.5 and 2.7, C*H*=CHGe); δ_C 9.1 and 9.2 (2 × *Me*CH_2Ge), 9.4 and 9.8 (2 × Me*C*H_2Ge), 14.1 (*Me*CH_2C), 18.6 (CH*C*H_2Ge), 23.0, 29.5 and 36.4 (3 × CH_2C), 36.8 (*C*HCH_2Ge), 51.6 and 56.8 (2 × CH_2N), 126.5 (CH=*C*HGe) and 143.9 (*C*H=CHGe); *m/z* 256 (M^+ − 29, 100%), 255 (27), 254 (69), 252 (53), 158 (11), 156 (10), 142 (10), 130 (15), 128 (15), 126 (18), 115 (10), 113 (10), 103 (17), 101 (17), 99 (13), 75 (11), 68 (16), 55 (22), 43 (26), 42 (15), 41 (58) and 39 (20) (Found: C, 58.95; H, 10.6; N, 5.1. $C_{14}H_{29}NGe$ requires C, 59.2; H, 10.3; N, 4.9%).

3,5,5-*Triethyl*-7-*methyl*-1,2,3,4,5,8-*hexahydro*-1,5-*azagermocine* **36ba**. R_f 0.33 (hexane–diethyl ether 4:1); δ_H 0.3 (1 H, dd, *J* 13.2 and 11.2, CHCH_2Ge), 0.6–1.4 (18 H, m, 2 × EtGe, MeCH_2CH, CHCH_2Ge and NH), 1.7 (3 H, s, *Me*C=CH), 2.0 (1 H, t, *J* 10.9, NCH_2CHCH_2), 2.8 (1 H, d, *J* 10.9, NCH_2CHCH_2), 3.1 and 3.2 (2 H, 2 d, *J* 17.8, NCH_2C=CH and 5.3 (1 H, s, CH=C); δ_C 9.3 (2 × *Me*CH_2Ge), 9.4 and 10.1 (2 × Me*C*H_2Ge), 11.7 (*Me*CH_2C), 18.1 (CH*C*H_2Ge), 23.9 (*Me*C=CH), 29.2 (Me*C*H_2CH), 38.5 (*C*HCH_2Ge), 54.9 and 56.5 (2 × CH_2N), 121.0 (*C*H=C) and 150.7 (*C*=CH); *m/z* 242 (M^+ − 29, 71%), 241 (22), 240 (54), 238 (39), 156 (10), 144 (11), 142 (23) 140 (16), 138

(12) 128 (10), 113 (15), 111 (11), 103 (27), 102 (13), 101 (26), 99 (20), 89 (13), 87 (10), 82 (22), 75 (19), 74 (11), 73 (14), 68 (22), 56 (17), 55 (42), 53 (18), 43 (38), 42 (29), 41 (100) and 39 (40) (Found: $M^+ - 1$, 270.1285. $C_{13}H_{26}NGe$ requires *m/z*, 270.1277).

3-*Butyl*-5,5-*diethyl*-7-*methyl*-1,2,3,4,5,8-*hexahydro*-1,5-*azagermocine* **36bb**. R_f 0.38 (hexane–diethyl ether 4:1); δ_H 0.3 (1 H, dd, *J* 13.2 and 11.3, $CHCH_2Ge$), 0.6–1.5 (22 H, m, 2 × EtGe, $Me[CH_2]_3CH$, $CHCH_2Ge$ and NH), 1.7 (3 H, s, *Me*C=CH), 2.0 (1 H, t, *J* 11.7, NCH_2CHCH_2), 2.7 (1 H, d, *J* 11.7, NCH_2CHCH_2), 3.1 and 3.2 (2 H, 2 d, *J* 17.8, NCH_2C=CH) and 5.3 (1 H, s, CH=C); δ_C 9.3 and 9.4 (2 × $MeCH_2Ge$), 9.5 and 10.0 (2 × $MeCH_2Ge$), 14.1 ($MeCH_2C$), 18.7 ($CHCH_2Ge$), 23.9 (*Me*C=CH), 23.0, 29.5 and 36.4 (3 × CH_2C), 36.7 ($CHCH_2Ge$), 54.8 and 56.7 (2 × CH_2N), 121.3 (*C*H=C) and 150.5 (*C*=CH); *m/z* 270 ($M^+ - 29$, 100%), 269 (29), 268 (72), 266 (55), 142 (13), 140 (12), 103 (10), 55 (15), 43 (12) and 41 (26) (Found: C, 60.5; H, 10.7; N, 4.5. $C_{15}H_{31}NGe$ requires C, 60.45; H, 10.5; N, 4.7%).

Ethyl 8-(4-*ethyl*-2-*oxopyrrolidino*)-1-*naphthoate* **37a**. R_f 0.36 (hexane–ethyl acetate 4:1); δ_H 0.9 (3 H, t, *J* 7.4, $MeCH_2C$), 1.2 (3 H, t, *J* 7.1, $MeCH_2O$), 1.2–1.5 (2 H, m, CH_2Me), 2.4 (3 H, m, CH and CH_2CO), 3.8 (1 H, dd, *J* 14.0 and 6.3, CH_2N), 3.9 (1 H, dd, *J* 14.0 and 7.1, CH_2N), 4.0 (2 H, q, *J* 7.1, CH_2O) and 7.0–8.0 (6 H, m, ArH); δ_C 10.7 and 13.9 (2 × Me), 24.4 and 35.9 (2 × CH_2C), 35.9 (CH), 43.4 (CH_2N), 60.1 (CH_2O), 105.3, 119.9, 123.9, 124.8, 126.1, 128.3, 128.3, 128.7, 130.5 and 139.2 (ArC), 168.1 and 172.6 (2 × CO); *m/z* 311 (M^+, 16%), 183 (26), 182 (100), 169 (18), 127 (24) and 44 (23) (Found: C, 77.5; H, 7.0; N, 4.3. $C_{19}H_{21}NO_3$ requires C, 73.3; H, 6.8; N, 4.5%).

Ethyl 8-(4-*butyl*-2-*oxopyrrolidino*)-1-*naphthoate* **37b**. R_f 0.38 (hexane–ethyl acetate 4:1); δ_H 0.7 (3 H, t, *J* 7.0, $MeCH_2C$), 1.1 (3 H, t, *J* 7.1, $MeCH_2O$), 1.1–1.4 (6 H, m, 3 × CH_2C), 2.2–2.4 (3 H, m, CH and CH_2CO), 3.8 (2 H, m, CH_2N), 3.9 (2 H, q, *J* 7.1, CH_2O) and 6.9–7.9 (6 H, m, ArH); δ_C 13.9 and 14.0 (2 × Me), 22.7, 28.7, 31.6 and 36.6 (4 × CH_2C), 34.7 (CH), 43.9 (CH_2N), 60.2 (CH_2O), 105.4, 120.1, 124.1, 124.9, 126.3, 128.4, 128.5, 128.9, 130.7 and 139.4 (ArC) and 168.2 and 172.7 (2 × CO); *m/z* 339 (M^+, 19%), 183 (27), 182 (100), 169 (25), 154 (11) and 127 (24) (Found: C, 74.05; H, 7.2; N, 4.3. $C_{21}H_{25}NO_3$ requires C, 74.3; H, 7.4; N, 4.1%).

Ethyl 8-(4-tert-*butyl*-2-*oxopyrrolidino*)-1-*naphthoate* **37c**. R_f 0.35 (hexane–ethyl acetate 4:1); δ_H 0.8 (3 H, t, *J* 7.1, $MeCH_2$), 1.1 (9 H, s, 3 × Me), 2.3 (1 H, dd, *J* 16.2 and 6.9, CH_2CO), 2.4 (1 H, dd, *J* 16.2 and 4.7, CH_2CO), 2.5 (1 H, m, $CHCH_2$), 3.4 and 3.5 (2 H, 2 dq, *J* 10.8 and 7.1, CH_2Me), 3.9 (1 H, dd, *J* 14.0 and 4.4, CH_2N), 4.0 (1 H, dd, *J* 14.0 and 10.8, CH_2N) and 7.0–8.0 (6 H, m, ArH); δ_C 13.4 ($MeCH_2$), 27.2 (3 × *Me*C), 32.7 (*C*Me), 33.7 (CH_2CO), 41.3 (CH_2N), 43.6 ($CHCH_2$), 59.8 (CH_2O), 105.3, 119.9, 123.8, 124.9, 126.2, 128.2, 128.3, 128.7, 130.5 and 139.2 (ArC) and 168.2 and 173.0 (2 × CO); *m/z* 339 (M^+, 13%), 208 (15), 183 (17), 182 (100), 169 (21), 154 (15), 127 (31) and 57 (11) (Found: C, 74.5; H, 7.1; N, 3.9%).

Ethyl 2-[(4-*ethyl*-2-*oxopyrrolidino*)*methyl*]*benzoate* **38a**. R_f 0.31 (hexane–ethyl acetate 2:1); δ_H 0.9 (3 H, t, *J* 7.3, $MeCH_2C$), 1.1 (3 H, t, *J* 7.6, $MeCH_2O$), 1.4 (2 H, m, CH_2Me), 2.3 (3 H, m, $CHCH_2$ and CH_2CO), 3.5 (1 H, dd, *J* 13.8 and 6.0, NCH_2CH), 3.6 (1 H, dd, *J* 13.8 and 8.2, NCH_2CH), 3.9 and 4.0 (2 H, 2 dq, *J* 10.8 and 7.2, CH_2O), 4.3 and 4.5 (2 H, 2 d, *J* 16.9, CH_2NC) and 7.3–7.8 (4 H, m, ArH); δ_C 10.7 and 13.8 (2 × Me), 24.7 (CH_2C), 35.8 ($CHCH_2$), 36.3 (CH_2CO), 45.9 and 50.2 (2 × CH_2N), 60.1 (CH_2O), 122.5, 123.4, 127.7, 131.1, 132.3 and 141.1 (ArC) and 168.7 and 172.8 (2 × CO); *m/z* 275 (M^+, 10%), 230 (13), 201 (12), 188 (11), 146 (100) and 91 (22) (Found: C, 70.15; H, 7.5; N, 5.3. $C_{16}H_{21}NO_3$ requires C, 69.8; H, 7.7; N, 5.1%).

Ethyl 2-[(4-*butyl*-2-*oxopyrrolidino*)*methyl*]*benzoate* **38b**. R_f 0.36 (hexane–ethyl acetate 2:1); δ_H 0.8 (3 H, t, *J* 7.0, $MeCH_2C$), 1.0 (3 H, t, *J* 7.3, $MeCH_2O$), 1.2–1.3 (6 H, m, 3 × CH_2C), 2.2 (3 H, m, $CHCH_2$ and CH_2CO), 3.4 (1 H, dd, *J* 13.8 and 6.0, NCH_2CH), 3.5 (1 H, dd, *J* 13.8 and 8.2, NCH_2CH), 3.8 and 3.9 (2 H, 2 dq, *J* 10.7 and 7.3, CH_2O), 4.2 and 4.4 (2 H, 2 d, *J* 17.0, NCH_2C and 7.3–7.7 (4 H, m, ArH); δ_C 13.8 and 13.9 (2 × Me), 22.7, 28.6 and 31.9 (3 × CH_2C) 34.5 ($CHCH_2$), 36.9 (CH_2CO), 46.4 and 50.3 (2 × CH_2N), 60.2 (CH_2O), 122.6, 123.5, 127.8, 131.1, 132.4 and 141.1 (ArC) and 168.8 and 172.9 (2 × CO); *m/z* 303 (M^+, 6%), 147 (18), 146 (100), 91 (17) and 44 (13) (Found: M^+, 303.1847. $C_{18}H_{25}NO_3$ requires M, 303.1834).

Ethyl 2-[(4-tert-*butyl*-2-*oxopyrrolidino*)*methyl*]*benzoate* **38c**. R_f 0.27 (hexane–ethyl acetate 2:1); δ_H 0.7 (9 H, s, 3 × MeC), 1.3 (3 H, t, *J* 7.0, $MeCH_2$), 2.1–2.3 (3 H, m, $CHCH_2$ and CH_2CO), 3.0 (1 H, dd, *J* 9.8 and 8.6, NCH_2CH), 3.1 (1 H, dd, *J* 9.8 and 8.0, NCH_2CH), 4.2 (2 H, q, *J* 7.0, CH_2O), 4.6 and 4.8 (2 H, 2 d, *J* 15.9, NCH_2C) and 7.2–7.8 (4 H, m, ArH); δ_C 14.0 ($MeCH_2$), 26.1 (3 × *Me*C), 30.9 (*C*Me), 32.2 (CH_2CO), 41.4 ($CHCH_2$), 43.5 and 48.1 (2 × CH_2N), 60.8 (CH_2O), 126.5, 127.8, 128.9, 130.0, 131.7 and 137.1 (ArC) and 167.0 and 174.4 (2 × CO); *m/z* 303 (M^+, 13%), 258 (16), 257 (23), 246 (87), 228 (14), 218 (22), 200 (23), 172 (100), 146 (29), 145 (69), 144 (14), 135 (50), 134 (21), 133 (69), 132 (25), 130 (10), 118 (16), 117 (18), 105 (15), 104 (12), 91 (35), 90 (27), 89 (25), 84 (18), 79 (18), 77 (40), 69 (19), 68 (10), 57 (42), 55 (34), 41 (57) and 39 (11) (Found: C, 71.0; H, 8.5; N, 4.8. $C_{18}H_{25}NO_3$ requires C, 71.25; H, 8.3; N, 4.6%).

4,4′-*Di*-tert-*butyl*-1,1′-*ethylenedi*(*pyrrolidin*-2-*one*) **39c**. M.p. 102–104 °C (from hexane–$CHCl_3$); δ_H 0.8 (18 H, s, 6 × Me), 2.0–2.2 (6 H, m, 2 × CH and 2 × CH_2CO), 3.2–3.3 (4 H, m, 2 × NCH_2CH) and 3.4 (4 H, s, 2 × CH_2N); δ_C 26.7 (6 × Me), 31.4 (2 × *C*Me), 32.8 (2 × CH_2CO), 39.1 and 48.2 (4 × CH_2N), 42.1 (2 × CH) and 174.9 (2 × CO); *m/z* 308 (M^+, 3%), 251 (17), 168 (31), 167 (100), 154 (33), 110 (16), 70 (12), 57 (12), 55 (22) and 41 (15) (Found: C, 70.15; H, 10.3; N, 9.1. $C_{18}H_{32}N_2O_2$ requires C, 70.1; H, 10.4; N, 9.1%).

3-*Ethyl*-1,1-*dimethyl*-1,2,3,4,5,6-*hexahydro*-5,1-*benzazasilocine* **40a**. R_f 0.28 (hexane–ethyl acetate 95:5); δ_H 0.1 (6 H, 2 s, 2 × MeSi), 0.2 (1 H, dd, *J* 15.1 and 10.6, CH_2Si), 0.8 (3 H, t, *J* 7.3, MeC), 0.8 (1 H, ddd, *J* 15.1, 5.6 and 1.7, CH_2Si), 0.9–1.2 (2 H, m, CH_2C), 1.3 (1 H, m, $CHCH_2$), 1.5 (1 H, s, NH), 1.9 (1 H, t, *J* 11.2, NCH_2CH), 2.7 (1 H, ddd, *J* 11.2, 3.7 and 1.7, NCH_2CH), 3.8 and 4.0 (2 H, 2 d, *J* 16.1, NCH_2C) and 7.0–7.6 (4 H, m, ArH); δ_C 2.4 and 4.2 (2 × MeSi), 11.7 (*Me*C), 23.0 and 28.6 (2 × CH_2C), 38.7 ($CHCH_2$), 51.7 and 52.7 (2 × CH_2N) and 125.8, 125.9, 128.6, 136.1, 138.0 and 146.0 (ArC); *m/z* 218 ($M^+ - 15$, 100%), 176 (49), 163 (12), 162 (75), 160 (19), 149 (16), 148 (56), 133 (25), 132 (13), 131 (11) and 105 (12) (Found: C, 71.9; H, 10.1; N, 6.3. $C_{14}H_{23}NSi$ requires C, 72.05; H, 9.95; N, 6.0%).

3-*Butyl*-1,1-*dimethyl*-1,2,3,4,5,6-*hexahydro*-5,1-*benzazasilocine* **40b**. R_f 0.33 (hexane–ethyl acetate 95:5); δ_H 0.1 (6 H, 2 s, 2 × MeSi), 0.2 (1 H, dd, *J* 14.6 and 10.4, CH_2Si), 0.8 (3 H, t, *J* 6.0, MeC), 0.9 (1 H, ddd, *J* 14.6, 5.5 and 1.7, CH_2Si), 1.1–1.5 (8 H, m, $CH[CH_2]_3$ and NH), 1.9 (1 H, t, *J* 11.6, NCH_2CH), 2.7 (1 H, ddd, *J* 11.6, 3.4 and 1.7, NCH_2CH), 3.8 and 4.1 (2 H, 2 d, *J* 16.0, NCH_2C) and 7.0–7.6 (4 H, m, ArH); δ_C 2.5 and 4.2 (2 × MeSi), 14.1 (*Me*C), 22.9, 23.5, 29.5 and 35.7 (4 × CH_2C), 37.0 ($CHCH_2$), 51.7 and 53.0 (2 × CH_2N), 125.9, 126.0, 128.7, 136.2, 138.1 and 146.0 (ArC); *m/z* 246 ($M^+ - 15$, 100%), 177 (13), 176 (74), 163 (14), 162 (88), 160 (19), 149 (17), 148 (66), 133 (28), 132 (13), 131 (11), 105 (12), 91 (10), 86 (10) and 59 (11) (Found: C, 73.3; H, 10.6; N, 5.0. $C_{16}H_{27}NSi$ requires C, 73.5; H, 10.4; N, 5.35%).

1,1,3-*Triethyl*-1,2,3,4,5,6-*hexahydro*-5,1-*benzazagermocine* **41a**. R_f 0.23 (hexane–ethyl acetate 9:1); δ_H 0.4 (1 H, dd, *J* 13.3 and 11.2, $GeCH_2CH$), 0.7–1.4 (18 H, m, 2 × EtGe, $EtCHCH_2Ge$ and NH), 2.0 (1 H, t, *J* 12.0, NCH_2CH), 2.7 (1 H, ddd, *J* 12.0, 3.4 and 1.7, NCH_2CH), 3.9 (2 H, s, NCH_2C) and

7.0–7.5 (4 H, m, ArH); δ_C 8.6 (2 × Ge*C*H$_2$Me), 9.3 (2 × MeCH$_2$Ge), 11.5 (*Me*CH$_2$C), 18.7 and 29.0 (2 × *C*H$_2$C), 38.5 (*C*HCH$_2$), 53.1 and 53.6 (2 × CH$_2$N) and 125.6, 126.6, 127.7, 134.9, 137.9 and 145.6 (ArC); *m/z* 278 (M$^+$ − 29, 100%), 277 (34), 276 (79), 274 (59), 208 (16), 206 (13), 178 (17), 176 (14), 174 (12), 165 (11), 163 (13), 91 (29) and 44 (10) (Found: M$^+$ − 1, 306.1277. $C_{16}H_{26}NGe$ requires *M*, 306.1277.

3-*Butyl*-1,1-*diethyl*-1,2,3,4,5,6-*hexahydro*-5,1-*benzazagermocine* **41b**. R_f 0.28 (hexane–ethyl acetate 9:1); δ_H 0.4 (1 H, dd, *J* 13.7 and 11.2, GeC*H$_2$*CH), 0.7–1.4 (22 H, m, 2 × EtGe, *Me*[C*H$_2$*]$_3$C*H*C*H$_2$*Ge and NH), 1.9 (1 H, t, *J* 12.0, NC*H$_2$*CH), 2.7 (1 H, ddd, *J* 12.0, 3.1 and 1.4, NC*H$_2$*CH), 3.9 (2 H, s, NC*H$_2$*C) and 7.0–7.5 (4 H, m, ArH); δ_C 8.8 (2 × Ge*C*H$_2$Me), 9.5 (2 × *Me*CH$_2$Ge), 14.1 (*Me*CH$_2$C), 19.4, 23.0, 29.5 and 36.3 (4 × *C*H$_2$C), 37.1 (*C*HCH$_2$), 53.2 and 54.0 (2 × CH$_2$N) and 125.8, 126.8, 127.9, 135.1, 138.2 and 145.8 (ArC); *m/z* 306 (M$^+$ − 29, 100%), 305 (32), 304 (67), 302 (53), 208 (16), 206 (14), 178 (17), 176 (14), 165 (11), 163 (12), 91 (32) and 44 (12) (Found: C, 64.45; H, 9.5; N, 4.0. $C_{18}H_{31}NGe$ requires C, 64.7; H, 9.35; N, 4.2%).

Preparation of (Z)-N-*Allyl*-3-(*tributylstannyl*)*allylamine* **22**.—A solution of BuLi (5 mmol) in hexane was added to a solution of diallylamine **1a** (5 mmol) in diethyl ether (20 cm^3) at −50 °C under nitrogen and the mixture was stirred for 20 min at temperatures in the range −50 to −30 °C. A solution of Bu^{t}Li (5 mmol) in pentane was added to the resulting mixture at −30 °C which was then stirred for 2 h while the temperature was allowed to rise to 20 °C. The mixture was cooled at −78 °C, and tributylchlorotin (5 mmol) was added, and the mixture was stirred while the temperature was allowed to rise to 20 °C. The resulting mixture was then hydrolysed with water and extracted with diethyl ether. The organic layer was dried over Na_2SO_4, the solvents were removed (15 mmHg), and the residue was purified by flash column chromatography (silica gel; hexane–diethyl ether 1:1) to obtain amine **22** (1.78 g 92%); R_f (hexane–diethyl ether 1:1); δ_H 0.8–1.6 (28 H, m, 3 × BuSn and NH), 3.2 (2 H, d, *J* 6.3, NC*H$_2$*CH=CHSn), 3.3 (2 H, d, *J* 5.6, NC*H$_2$*CH=CH$_2$), 5.1 (1 H, d, *J* 10.2, C*H$_2$*=CH), 5.2 (1 H, d, *J* 17.2, C*H$_2$*=CH), 5.9 (1 H, m, C*H*=CH$_2$), 6.0 (1 H, d, *J* 12.6, CHSn) and 6.6 (1 H, dt, *J* 12.6 and 6.3, C*H*=CHSn); δ_C 10.3 (3 × CH$_2$Sn), 13.6 (3 × Me), 27.2 and 29.1 (6 × *C*H$_2$C), 52.1 and 54.5 (2 × CH$_2$N), 115.8 (*C*H$_2$=C) and 130.9, 136.6 and 146.5 (3 × *C*H=C); *m/z* 330 (M$^+$ − 57, 100%), 329 (34), 328 (78), 327 (31), 326 (47), 177 (13), 175 (12), 174 (12), 121 (26), 120 (16), 119 (22), 118 (12), 117 (13), 96 (36), 94 (14), 41 (41) and 39 (11) (Found: C, 55.9; H, 9.5; H, 9.5; N, 3.65. $C_{18}H_{37}NSn$ requires C, 55.8; H, 9.6; N, 3.6%).

General Procedure for the Preparation of Intermediate **3a** *and its Reaction with Electrophiles*.—A solution of BuLi (5 mmol) in hexane was added to a solution of the amine **22** (5 mmol) in diethyl ether (20 cm^3) at −50 °C under nitrogen and the mixture was stirred for 20 min at temperatures in the range −50 to −30 °C. A solution of Bu^{t}Li (5 mmol) in pentane was added to the resulting mixture at −30 °C, and the mixture was stirred for 4 h while the temperature was allowed to rise to 20 °C. The mixture was cooled to −30 °C, a solution of BuLi (5 mmol) in hexane was added, and the mixture was stirred for 4 h at between −20 and 20 °C. After cooling of the mixture to −78 °C, an excess of the corresponding electrophile was added, and the mixture was stirred while the temperature was allowed to rise to 20 °C. The resulting mixture was then hydrolysed with water and extracted with diethyl ether. The combined ether layers were dried over Na_2SO_4, filtered, concentrated under reduced pressure, and the resulting crude was purified by flash column chromatography.

(E,E)-*Diethyl* 5-*azanona*-2,7-*dienedioate* **42**. R_f 0.38 (Et_2O); δ_H 1.3 (6 H, t, *J* 7.1, 2 × Me), 1.5 (1 H, s, NH), 3.4 (4 H, dd, *J* 5.3 and 1.8, 2 × CH$_2$N), 4.2 (4 H, q, *J* 7.1, 2 × C*H$_2$*Me), 6.0 (2 H, dt, *J* 15.7 and 1.8, 2 × CHCO) and 6.9 (2 H, dt, *J* 15.7 and 5.3, 2 × C*H*CH$_2$N); δ_C 13.9 (2 × Me), 49.3 (2 × CH$_2$N), 60.1 (2 × CH$_2$O), 121.5 (2 × *C*HCO), 145.9 (2 × *C*HCH$_2$N) and 166.0 (2 × CO); *m/z* 212 (M$^+$ − 29, 7%), 128 (100), 114 (11), 94 (19), 86 (12), 85 (60), 84 (13), 82 (30), 68 (37), 57 (16), 55 (11) and 39 (13) (Found: C, 59.5; H, 7.7; N, 5.5. $C_{12}H_{19}NO_4$ requires C, 59.7; H, 7.9; N, 5.8%).

5,5-*Dimethyl*-1,2,5,8-*tetrahydro*-1,5-*azasilocine* **43**. R_f 0.33 (hexane–diethyl ether 2:1); δ_H 0.1 (6 H, s, 2 × Me), 1.6 (1 H, s, NH), 3.4 (4 H, t, *J* 2.5, 2 × CH$_2$N), 5.6 (2 H, dt, *J* 12.3 and 2.5, 2 × CHSi), 6.4 (2 H, dt, *J* 12.3 and 2.5, 2 × C*H*CH$_2$); δ_C 3.7 (2 × Me), 52.2 (2 × CH$_2$N), 129.9 (2 × CHSi) and 145.7 (2 × *C*HCH$_2$); *m/z* 138 (M$^+$ − 15, 100%), 112 (25), 110 (21) and 109 (27) (Found: C, 62.5; H, 10.1; N, 8.9 $C_8H_{15}NSi$ requires C, 62.7; H, 9.85; N, 9.1%).

5,5-*Diethyl*-1,2,5,8-*tetrahydro*-1,5-*azagermocine* **44**. R_f 0.34 (hexane–diethyl ether 1:2); δ_H 0.8 (4 H, q, *J* 7.7, 2 × CH$_2$Ge), 1.0 (6 H, t, *J* 7.7, 2 × Me), 1.3 (1 H, s, NH), 3.4 (4 H, dd, *J* 4.1 and 1.6, 2 × CH$_2$N), 5.9 (2 H, dt, *J* 12.1 and 1.6, 2 × CHGe) and 6.4 (2 H, dt, *J* 12.1 and 4.1, 2 × C*H*CH$_2$N); δ_C 9.1 (2 × CH$_2$Ge and 2 × Me), 50.2 (2 × CH$_2$N), 129.2 (2 × CHGe) and 142.9 (2 × *C*HCH$_2$N); *m/z* 198 (M$^+$ − 29, 100%), 197 (30), 196 (78), 194 (55), 128 (22), 126 (17), 113 (12), 101 (14), 99 (14) and 94 (15) (Found: 53.45; H, 8.3; N, 6.0. $C_{10}H_{19}NGe$ requires C, 53.2; H, 8.5; N, 6.2%).

Acknowledgements

Financial support from the Dirección General de Investigación Científica y Técnica (DGICYT, PB89-0538) is gratefully acknowledged. R. G. thanks the Ministerio de Educación y Ciencia for a fellowship. J. B. acknowledges Dr. X. Huguet for the measurement of the HRMS spectra.

References

1 G. P. Lutz, A. P. Wallin, S. T. Kerrick and P. Beak, *J. Org. Chem.*, 1991, **56**, 4938 and references cited therein.
2 J. Barluenga, F. J. Fañanás, F. Foubelo and M. Yus, *J. Chem. Soc., Chem. Commun.*, 1988, 1135; *Tetrahedron Lett.*, 1988, **29**, 4859; J. Barluenga, F. Foubelo, F. J. Fañanás and M. Yus, *J. Chem. Res.*, 1989, (*S*) 200; (*M*) 1524.
3 See, for example: J. K. Crandall and A. C. Clark, *J. Org. Chem.*, 1972, **37**, 4236; J. K. Crandall and A. C. Rojas, *Org. Synth.*, 1976, **55**, 1.
4 J. Barluenga, F. Foubelo, R. González, F. J. Fañanás and M. Yus, *J. Chem. Soc., Chem. Commun.*, 1990, 587.
5 P. Beak and A. I. Meyers, *Acc. Chem. Res.*, 1986, **19**, 356.
6 R. E. Ludt and C. R. Hauser, *J. Org. Chem.*, 1971, **36**, 1607; N. J. R. van Eikema Hommes and P. von Ragué Schleyer, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 755.
7 J. Barluenga, R. González and F. J. Fañanás, *Tetrahedron Lett.*, 1992, **33**, 831.
8 J. Barluenga, F. Foubelo, R. González, F. J. Fañanás and M. Yus, *J. Chem. Soc., Chem. Commun.*, 1990, 1521.
9 J. Barluenga, F. Foubelo, R. González, F. J. Fañanás and M. Yus, *J. Chem. Soc., Chem. Commun.*, 1991, 1001.

Paper 3/06244I
Received 19th *October* 1993
Accepted 26th *November* 1993