Pergamon

Tetrahedron Vol. 51, No. 29, pp. 7959-7980, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00412-2

Radical Cyclisations of Imines and Hydrazones

W. Russell Bowman,*[a] Peter T. Stephenson,[b] Nicholas K. Terrett,[b] and Adrian R. Young[a]

[a] Department of Chemistry, University of Technology, Loughborough, Leics. LE11 3TU, Great Britain

[b] Department of Discovery Chemistry, Pfizer Central Research, Sandwich, Kent CT13 9NJ, Great Britain

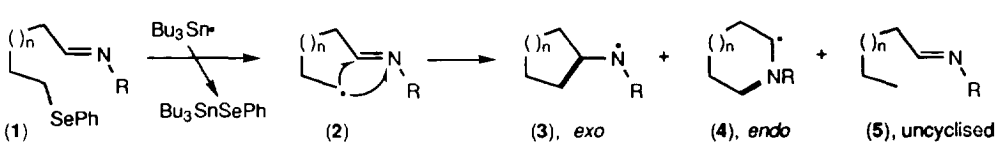
Abstract: Radical cyclisation of sp^3 carbon-centred radicals onto imines and hydrazones provides a new method for the synthesis of 5- and 6-membered ring nitrogen heterocycles. Cyclisation onto the electrophilic carbon of the C=N group and 5-*exo* stereoelectronic selectivity are the dominating mechanistic parameters. The C-centred radical intermediates were generated from benzeneselenyl precursors using Bu_3SnH.

Radical cyclisation has become one of the major methods of synthesis in organic chemistry over the last decade.[1] The vast majority of these studies have been concerned with cyclisation onto alkenes, and to a lesser extent, onto alkynes. Studies of the addition of radicals to multiple bonds containing heteroatoms have developed more slowly.[2] The addition of radicals onto thiocarbonyl bonds in the development of synthetic methods has been well exploited by several groups, notably by Barton and co-workers.[3] Similarly, studies of the addition of radicals to aldehydes and ketones have led to a number of novel synthetic methods.[4] In the last few years there has also been an increasing number of reports of radical addition to *N*-containing multiple bonds, *e.g.* azides,[5] diazirines,[6] diazenes (N=N),[7] nitriles,[8] and nitronates ($R_2C{=}NO_2^-$).[9] The formation of nitroxyls by radical addition to nitrones and nitroso compounds in spin-trapping is well studied. Cyclisation of radicals onto C=N bonds has been most widely studied on oxime-ethers ($R_2C{=}NOR$).[10]

The first major study of the addition of radicals onto imines reported that aryl radical additions proceeded predominantly by 6-*endo* cyclisation.[11,12] Tandem reactions via 3-*exo* cyclization onto the carbon,[13] and onto the nitrogen,[14,15] of an imine, 5-*endo* cyclisation onto the nitrogen of an imine,[16] and bimolecular addition onto the carbon of aldimines[17] have also been reported. Recent reports have shown hydrazones undergo radical cyclisation onto the carbon of the C=N moiety, *e.g.* *N*-aziridinyl imines,[18] mesitylsulfonylhydrazones,[19] β-allenic hydrazones,[20] and SmI_2 driven cyclisation of ω-halogeno- and keto-hydrazones.[21] To our knowledge, there are no reports of radical addition to iminium salts but the addition to pyridinium and related aza-heteroarene salts is well known.[22,23]

The aim of our study was to investigate the cyclisation of sp^3-C centred radicals onto imines (Scheme 1), *e.g.* the effect of ring size, polarisation of the imine, intermediate radical stability, and steric hindrance, and to develop a new methodology which can be applied to the synthesis of nitrogen-heterocycles. Our initial results have been published in preliminary form[24] and the full studies are detailed in this paper.

Scheme 1



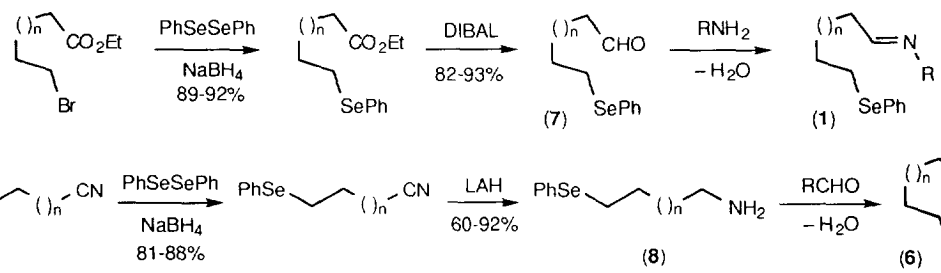
The addition of radicals to the carbon of imines as shown in Scheme 1 provides a further method for the generation of aminyl radicals.[25] Recently, we have developed the use of sulfenamides[26] for the generation of aminyl radicals and Newcomb *et al* have used *N*-hydroxypyridine-2-thione carbamates.[27] In further studies, the intermediate aminyl radicals (**3**) will be used in tandem cyclisations.

Synthesis of radical precursors

Synthetic building blocks, which could be used in a range of radical syntheses, including the required imine precursors (**1**) and (**6**) as shown in Scheme 2, were prepared in good yields. The formation of imines was carried out as the last step prior to radical cyclisation because of their sensitivity to hydrolysis and oxidation. Imines were formed in quantitative yields and once characterised were used without isolation. ω-Benzeneselenyl groups were chosen to avoid unwanted reactions with amines or imines in the syntheses which could be predicted if halogens were used.[18] Benzeneselenyl groups are abstracted by $Bu_3Sn^{\bullet}$ radicals at rates comparable with bromine, *e.g.* $PhSeCH_2CO_2Et$ and $BrCH_2CO_2Et$ react at rates of 1.0 and 0.7 x 10^5 M^{-1} s^{-1} respectively at 50 °C.[28] *p*-Toluidine and phenylethylamine were used as the amine portion. Benzylamine was avoided initially because of the fear of migration of the unsaturated bond into conjugation with the phenyl ring. However, later studies showed this concern to be unfounded. The phenylethyl and benzyl groups are protective groups which can be removed later in syntheses by standard methods. Although of lesser interest, the 'reverse' imines (**6**) were also synthesised using similar methods (Scheme 2). The introduction of the benzeneselenyl group was best facilitated by the use of diphenyl diselenide and $NaBH_4$.[29]

Scheme 2

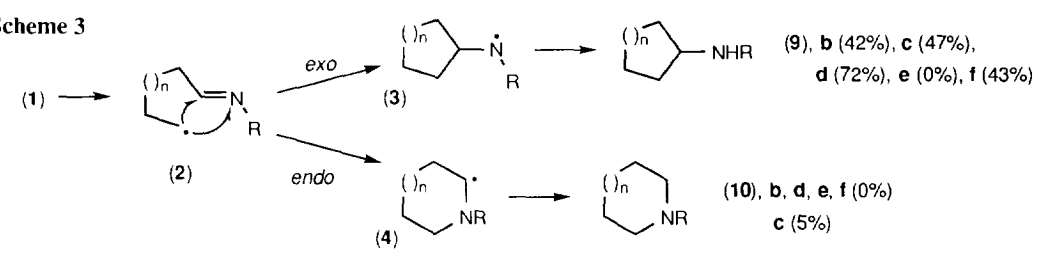
a, n = 0, R = *p*-tolyl **b**, n = 1, R = *p*-tolyl **c**, n = 1, R = CH_2CH_2Ph **d**, n = 1, R = CH_2Ph **e**, n = 2, R = *p*-tolyl **f**, n = 2, R = CH_2CH_2Ph



Cyclisation of *N*-(ω-benzeneselenylalk-1-ylidene)amines (1a-f)

Imines (**1a**)-(**1f**) were reacted with Bu_3SnH using syringe pump addition over 5 h to encourage cyclisation (Scheme 3). The anilyl imines (**1a**), (**1b**), and (**1e**) were purified prior to reaction with Bu_3SnH and the aliphatic imines (**1c**), (**1d**), and (**1f**) were formed and reacted *in situ*. In the latter case yields are based on starting ω-benzeneselenylaldehydes (**7**). The crude product mixture was normally reduced with $NaBH_4$ to convert any uncyclised imine to the respective amine to avoid hydrolysis of imine products during work-up. Amines were separated form tributyltin products by extraction into hydrochloric acid. Secondary amines were

Scheme 3

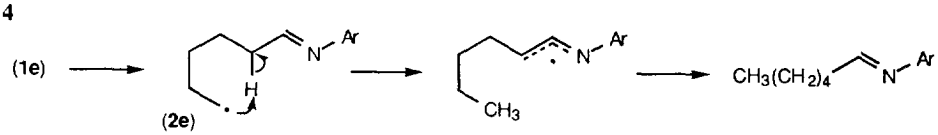


separated from tertiary amines by conversion to their *N*-acetyl amides and products were identified by comparison to authentic materials. Yields were determined from crude amine product mixtures using GLC and ^{1}H NMR spectroscopy with an internal standard by comparison with independently synthesised compounds.

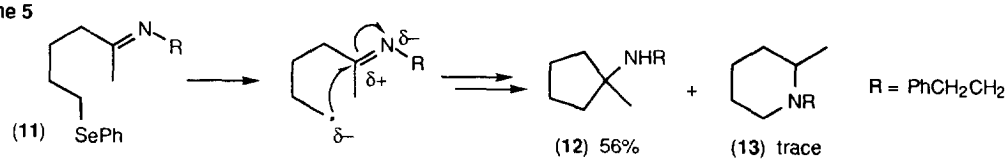
As predicted, imines (**1b**), (**1c**), and (**1d**) gave 5-*exo* cyclisation to yield the corresponding cycloalkylamines, (**9b**, 42%), (**9c**, 47%), and (**9d**, 72%). The *N*-benzyl imine gave the highest yield but was only used towards the end of the study and may yet prove to be the best substituent in future studies. The 5-*exo* stereoelectronic effect and attack of the nucleophilic alkyl radical on the electrophilic centre of the imine are clearly the determining factors in the cyclisations. Surprisingly, (**1c**) also yielded some of the 6-*endo* product (**10c**, 5%) indicating that formation of stable α-aminoalkyl radical[30] intermediates (**4**) may be a minor determining factor. The selective 5-*exo* cyclisation of (**1b**) is possibly influenced by the stability of the intermediate anilyl radical (**3b**). Anilyl radicals are known to be strongly stabilised by overlap of the unpaired electron on the nitrogen with the π-cloud of the benzene ring.[31] Cyclisation by 4-*exo* and 5-*endo* routes was not expected and the reaction of imine (**1a**) did not yield any cyclised products and red polymeric material was obtained. However, a 5-*endo* cyclisation onto an imine, yielding a particularly stable radical, has been reported.[16] 4-*exo* Cyclisation would yield a cyclobutylaminyl radical which has a fast rate of ring-opening.[25]

Imine (**1f**) gave selective 6-*exo* cyclisation (43%) over 7-*endo* cyclisation as expected, but the imine (**1e**) gave only uncyclised material. We explain this apparently contradictory result by a competition between 1,5-hydrogen abstraction and 6-*exo* cyclisation for the intermediate (**2e**) (Scheme 4). The extra conjugation by the aryl ring facilitates faster 1,5-hydrogen abstraction than cyclisation. A similar dichotomy has been observed and proven for the cyclisation onto alkenes; 6-*exo* takes place with isolated alkenes, but selective 1,5-hydrogen abstraction with styryl alkenes.[24,25]

Scheme 4



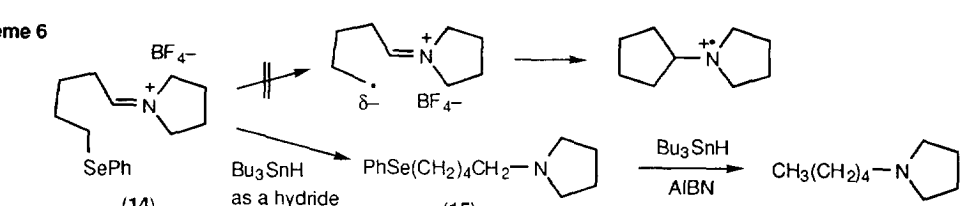
Scheme 5



Cyclisations onto alkenes are hindered by the presence of *endo*-substituents on the alkene, *e.g.* a 5-substituent on hex-5-en-1-yl radicals.[1] The analogous imine cyclisation would be cyclisation onto ketimines, an important reaction if this methodology is to be of synthetic application. Cyclisation of the ω-benzeneselenylketimine (**11**) gave a good yield of 5-*exo* cyclisation (**12**, 56%) with only traces of the 6-*endo* product (**13**), indicating that radical cyclisation onto imines does not suffer from steric hindrance as observed for cyclisation onto alkenes. The cyclisation is facilitated by favourable philicity, *i.e.* a nucleophilic radical attacking the electrophilic carbon-centre of the imine.

The cyclisation onto iminium salts was investigated with the prediction of rapid and selective 5-*exo* cyclisation (Scheme 6). The intermediate aminium cation radicals[25] would cyclise rapidly with alkenes for use

Scheme 6

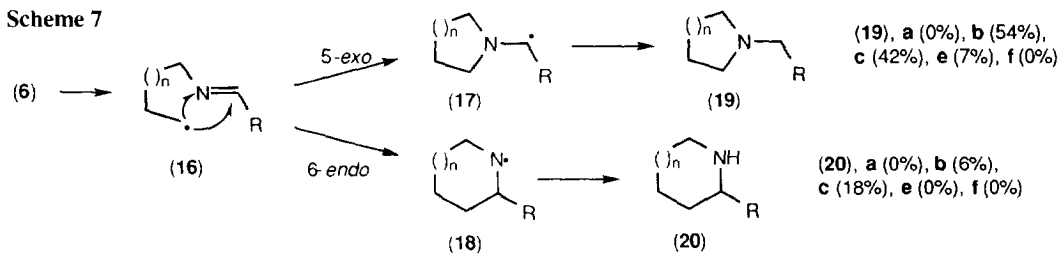


in synthetic tandem reactions. Reaction between Bu_3SnH and the iminium salt (**14**) gave the uncyclised *N*-pentylpyrrolidine (75%) indicating that hydride addition to the imine is faster than radical abstraction of the benzeneselenyl moiety. A repeat reaction using tris(trimethylsilyl)silane which is a much weaker hydride donor also gave only the uncyclised *N*-pentylpyrrolidine (68%). Reaction between (**14**) and Bu_3SnH under non radical conditions gave only the benzeneselenylamine (**15**, 27%). The ability of Bu_3SnH to act as a hydride has been observed in reactions with pyridinium salts.[22] The use of iminium salts was not further investigated.

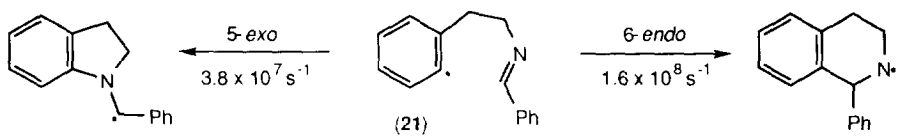
Cyclisation of *N*-alkylidene-ω-(benzeneselenyl)amines (6)

6-*endo* Cyclisation of sp^3 C-centred radical intermediates (**16**), generated from *N*-alkylidene-ω-(benzeneselenyl)amines (**6**), also yield aminyl radicals (**18**) which are of interest for synthetic applications. The reactions of intermediate radicals (**16**) provides a competition between the stereoelectronically favoured 5-*exo* cyclisation onto the imine N-atom (**17**) and the preference for the nucleophilic C-centred radical to attack at the electrophilic imine C-atom via 6-*endo* cyclisation (**18**) (Scheme 7). Our results show dominance of the stereoelectronic control over philicity effects, whereas the the opposite has been reported in the cyclisation of the analogous aryl radicals (**21**) onto imines (Scheme 8).[11,12] The aryl radical cyclisation results are explained by a faster rate of 6-*endo* cyclisation ($>10^8$ s^{-1} at 50 °C), and a slower rate of 5-*exo* cyclisation, than the equivalent rates for cyclisation onto C=C; an example is shown in Scheme 8.[11]

Scheme 7

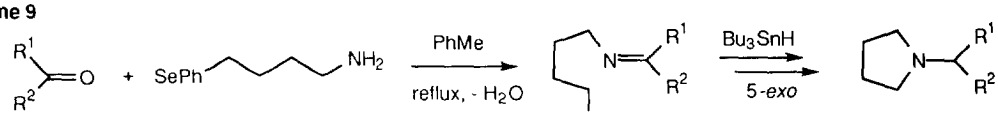


Scheme 8



The aromatic imine (**6b**) mainly underwent 5-*exo* cyclisation (**19b**, 54%) with no uncyclised product and a small amount of 6-*endo* (**20b**, 6%) detected, whereas the aliphatic imine (**6c**) gave both 5-*exo* (**19c**, 42%) and 6-*endo* (**20c**, 18%) cyclisation. The cyclisations of (**6a**), 4-*exo* onto the imine *N*-atom or 5-*endo* onto imine *C*-atom, were expected to be unlikely, and uncyclised product, 4-methyl-*N*-propylbenzylamine, was isolated (63%) after $NaBH_4$ reduction. The imines (**6e**) and (**6f**) gave poor results with largely uncyclised products indicating that neither 6-*exo* nor 7-*endo* cyclisation is favourable [(**6e**): *exo* (**19e**, 7%), *endo* (**20e**, 0%), 4-methyl-*N*-pentylbenzylamine (40%); (**6f**): *exo*/*endo* (0%), *N*-pentyl-3-phenylpropylamine (39%)]. The stability of the intermediate α-amino benzylic radical (**17b**) may explain why little 6-*endo* cyclisation to (**20b**) was observed. Our results, in contrast to those of the aryl radical analogues,[11] show a balance between stereoelectronic and imine polarisation effects.

Scheme 9



(**22**) **a**, R^1R^2CO = 2-phenylcyclohexanone ; **b** = 2-tetralone

Cyclisation of aryl radicals onto ketimines (as illustrated in Scheme 8 for aldimines) is affected by steric hindrance and biased towards 5-*exo* cyclisation away from the favoured 6-*endo* cyclisation observed for aldimines.[12] Our studies on two sample ketimines (**23a**,**b**), derived from 2-phenylcyclohexanone and 2-tetralone, gave only 5-*exo* cyclisation; (**24a**) (55%), and (**24b**) (19%) and 2-butylamino-1,2,3,4-tetrahydronaphthalene (20%) respectively (Scheme 9).

Cyclisation onto hydrazones

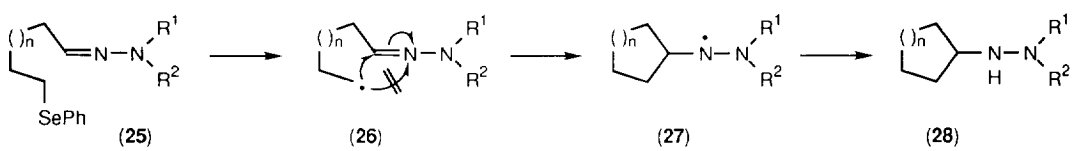
There are now several reports of the cyclisation of radicals onto hydrazones.[18-21] Since our preliminary communication[24] was published, a report [21] shows that the rates of cyclisation of secondary alkyl radicals onto the *C*-atom of *N,N*-diphenylhydrazones are faster than the analogous carbon radicals onto alkenes:

Rates of *exo*-cyclisation at 80 °C [$MeCH(\bullet)(CH_2)_nCH{=}NNPh_2$]

5-*exo* (n = 3): *cis* = 1.1 x 10^8 s^{-1}, *trans* = 4.6 x 10^7 s^{-1}; 6-*exo* (n = 4): *cis* and *trans* = 9.4 x 10^5 s^{-1}

A range of hydrazones were synthesised from the respective hydrazines and the aldehydes (**7**, n = 1, 2) and reacted with Bu_3SnH under standard conditions using a syringe pump (Scheme 10). The reactions of the hydrazones (**25, a-d**) gave selective 5-*exo* cyclisation onto the C-atom of the hydrazone and no 6-*endo* cyclisation was observed [(**28**), **a** (18%), **b** (50%), **c** (60%), **d** (32%)]. The cyclisations are stereoelectronically favoured, have a nucleophilic radical attacking an electrophilic carbon, and yield stable intermediate hydrazyl radicals (**27**). Some of the yields were disappointing and optimization failed. The low yield of (**28a**) from the phenyl hydrazone (**25a**) may be due to the NH present in the hydrazine which could allow disproportionation to the respective hydrazine and diazene. The hydrazones (**28b**) and (**28c**), which contain electron-withdrawing groups gave higher yields. The enhanced electrophilicity on the α C-atom of the hydrazones is likely to increase the rate of cyclisation and thereby disfavour side-reactions. Attempted 6-*exo* cyclisations with hydrazones (**25e**) and (**25f**) were unsuccessful and only low amounts of uncyclised products, the respective hydrazones of hexanal, were isolated. These reactions were not further pursued although 6-*exo* cyclisations have been reported from ω-bromoalkylidine hydrazones.[21]

Scheme 10



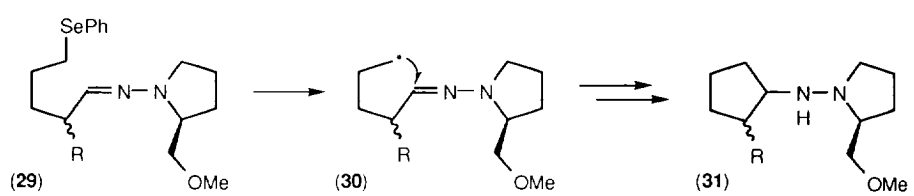
n = 1; **a**, R^1 = H, R^2 = Ph; **b**, R^1 = H, R^2 = COPh; **c**, R^1 = H, R^2 = $CONHNH_2$; **d**, R^1 = R^2 = Ph

n = 2; **e**, R^1 = H, R^2 = COPh; **f**, R^1 = R^2 = Ph

The success of the cyclisation onto hydrazones prompted us to study the possibility of diastereoselective cyclisation using the homochiral hydrazones derived from SAMP and RAMP, which have been extensively applied to diastereoselective alkylation.[32] The exploitation of stereoselectivity in radical reactions has become of importance in recent years.[33] Diastereoisomeric selectivity has also been observed in the 6-*exo* cyclisation of aryl radicals onto imines (see Scheme 8).[11a] Therefore, the hydrazone, 1-[(5-benzeneselenylpentylidene)-amino]-2*S*-(methoxymethyl)pyrrolidine (**29a**), was synthesised to initially test the feasibility of the cyclisation (Scheme 11). Reaction between (**29a**) and Bu_3SnH gave the the 5-*exo* product, 1-cyclo-pentylamino-2*S*-(methoxymethyl)pyrrolidine (**31a**) (42%) indicating the feasibility of using this cyclisation.

Scheme 11

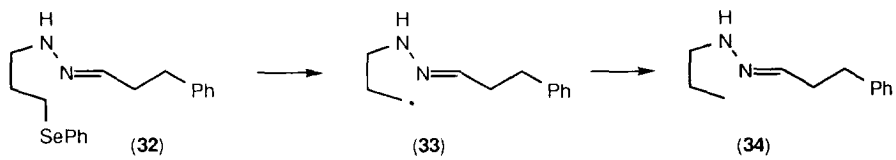
a = H
b = Me



The hydrazone (**29b**) with an extra chiral centre was synthesised from SAMP and racemic 5-benzeneselenyl-2-methylpentanal. An equivalent hydrazone, 1-[(5-benzeneselenyl-2-methylpentylidene)-amino]-2*R*-(methoxymethyl)pyrrolidine (**29c**) was synthesised using RAMP. Reaction between the *S*-hydrazone (**29b**), a 1:1 mixture of diastereoisomers, and Bu_3SnH yielded the 5-*exo* product, (**31b**) (40%), as a 50:50 mixture of diastereoisomers (by ^1H NMR spectroscopy). Although the stereochemistry of the two diastereoisomers have not been elucidated, the most probable explanation is selective *trans* cyclisation but with no stereoselective influence of the SAMP group. The *R*-hydrazone (**29c**) also gave a 50:50 mixture of diastereoisomers (39%). At the end of our study, an example of 50% de in the 5-*exo* cyclisation of a SAMP hydrazone was published.[20]

The radical reaction of the 'reverse' hydrazone (**32**) was also investigated (Scheme 12). The intermediate radical (**33**) could cyclise via 5-*exo* cyclisation onto the imine *N*-atom and/or 6-*endo* cyclisation onto the imine *C*-atom, of the hydrazone. Unfortunately, the uncyclised hydrazone (**34**) (26%) was the only isolable product.

Scheme 12



Conclusions

Our results and those in related studies[11,12,17-19] indicate that cyclisation onto imines and hydrazones is as facile as onto alkenes and provides a useful extension of radical cyclisation. In particular, the methodology will allow the development of novel routes to nitrogen heterocycles. Our initial studies of the synthesis of nitrogen heterocycles using tandem cyclisations via cyclisation onto imines will be reported in the near future.

Acknowledgements

We gratefully thank Pfizer Central Research, Sandwich, and Loughborough University of Technology for a Postgraduate Research Studentship (A.R.Y) and the EPSRC MS Service at University College, Swansea.

EXPERIMENTAL

General Procedures

IR spectra were run as neat samples using a Nicolet 205 FT-IR spectrometer. Elemental analyses were carried using a Perkin Elmer 2400 CHN Elemental Analyser. Mass spectra were run on a Kratos MS80 spectrometer and also carried out by the EPSRC Mass Spectrometry Service at University College, Swansea. All mass spectra are electron impact (E.I.) spectra unless otherwise stated. ^1H NMR spectra were run at 250 MHz and ^{13}C NMR spectra were 62.9 MHz using a Bruker AC 250 spectrometer unless otherwise stated. $CDCl_3$ was used as the NMR solvent with TMS as internal standard. *p*-Dimethoxybenzene was used as an internal standard for the calculation of yields using ^1H NMR spectroscopy. GLC analyses were undertaken using a Pye series 104 Chromatograph on a column of 15% diethylene glycol succinate (DEGS) on alumina at 150 °C and *N*-methylcyclohexylamine was the internal standard for aliphatic amines and *N*-methylaniline for aromatic amines. Solvents were purified by standard procedures. Light petroleum refers to the b.p. 40-60 °C fraction. TLC was performed on aluminium plates coated with Merck silica gel 60F254 or neutral alumina, and compounds were visualised by UV light, iodine vapour, or Dragendorff's reagent. Flash chromatography was carried using silica gel as absorbent and light petroleum and ethyl acetate mixtures as eluant.

ω-Benzeneselenyl esters

(a) Ethyl 4-benzeneselenylbutyrate.[35] *General procedure for the synthesis of ω-benzeneselenyl compounds.* Diphenyl diselenide (476 mg, 1.5 mmol) was stirred in absolute ethanol (25 cm^3) at r.t. under nitrogen and $NaBH_4$ (152 mg, 4.5 mmol) was added. After 30 min, ethyl 4-bromobutyrate (632 mg, 3.3 mmol) dissolved in abs. ethanol (5 cm^3) was added and the mixture was stirred for 16 h. The reaction was quenched

with 2 M hydrochloric acid (10 cm^3) and the solution extracted with diethyl ether. The ether extracts were washed with sat. sodium hydrogen carbonate and brine, dried, and evaporated to dryness. The residue was purified by dry flash chromatography to yield ethyl 4-benzeneselenylbutyrate as a yellow oil (782 mg, 89%); the IR, ^1H- and ^{13}C-NMR, and mass spectra were the same as those reported in the literature.[34]

The following ω-benzeneselenyl esters were synthesised using the general procedure.

(b) Ethyl 5-benzeneselenylpentanoate. Orange-yellow oil (824 mg, 90%); ν_{max} /cm^{-1} 3057, 2935, 1736, 1576, 1477, 1437, and 739; δ_H 7.47 (2 H, m, Ph *o*-H), 7.24 (3 H, m, phenyl H), 4.10 (2 H, q, *J* 7.1 Hz, MeCH_2), 2.90 (2 H, t, *J* 7.0 Hz, 5-H), 2.29 (2 H, t, *J* 7.1 Hz, 2-H), 1.70-1.76 (4 H, m, 3,4-H), and 1.23 (3 H, t, *J* 7.1 Hz, Me); δ_C 173.15 (C=O), 132.46 (Ar-CH), 130.20 (Ar-C), 128.97 and 126.68 (Ar-CH), 60.19 (MeCH_2), 33.65 (2-C), 29.52, 27.21 and 25.03 (3,4,5-C), and 14.22 (Me); *m/z* 286.0460 [M^+ (9.4%), $C_{13}H_{18}O_2Se$ requires 286.0472], 157 (15), 129 (75), 101 (92), 83 (48), 77 (27), and 55 (70).

(c) Ethyl 6-benzeneselenylhexanoate. Orange-yellow oil (876 mg, 92%); ν_{max} /cm^{-1} 3055, 2937, 1733, 1577, 1480, 1437, and 739; δ_H 7.47 (2 H, m, Ph *o*-H), 7.24 (3 H, m, Ph-H), 4.11 (2 H, q, *J* 7.1 Hz, MeCH_2), 2.90 (2 H, t, *J* 7.4 Hz, 6-H), 2.27 (2 H, t, *J* 7.4 Hz, 2-H), 1.45-1.65 (6 H, m, 3,4,5-H), and 1.24 (3 H, t, *J* 7.1 Hz, CH_3); δ_C 173.24 (C=O), 132.37 (Ar-CH), 130.25 (Ar-C), 128.95 and 126.61 (Ar-CH), 60.16 (MeCH_2), 34.07 (2-C), 29.71 (6-C), 29.18, 27.49, 24.35 (3,4,5-C), and 14.23 (Me); *m/z* 300.0620 [M^+ (12%), $C_{14}H_{20}O_2Se$ requires 300.0628], 158 (12), 143 (28), 115 (23), 97 (63), 69 (100), 55 (25), and 41 (49).

ω-Benzeneselenyl aldehydes

ω-Benzeneselenyl aldehydes were synthesised by DIBAL reduction of the respective ω-benzeneselenyl esters using the literature procedure for 4-benzeneselenylbutanal.[35]

(a) 4-Benzeneselenylbutanal (**7**, n = 0).[35] Yellow oil (92%), with data identical to reported data.[35]

(b) 5-Benzeneselenylpentanal (**7**, n = 1).[36] Yellow oil (727 mg, 93%); ν_{max} /cm^{-1} 3055, 2937, 1720, 1577, 1479, and 1439; δ_H 9.72 (1 H, s, 1-H), 7.48 (2.H, m, Ph *o*-H), 7.25 (3 H, m, Ph-H), 2.89 (2 H, t, *J* 7.6 Hz, 5-H), 2.42 (2 H, t, *J* 6.9 Hz, 2-H), and 1.72 (4 H, m, 3,4-H); δ_C 202.03 (C=O), 132.58 (Ar-CH), 130.20 (Ar-C), 129.02 and 126.78 (Ar-CH), 43.15 (2-C), 29.46, 27.28, and 22.05 (3,4,5-C); *m/z* 242.0224 [M^+ (19%), $C_{11}H_{13}OSe$ requires 242.0210], 158 (61), 108 (77), 91 (46), 85 (38), 79 (83), 69 (100), and 57 (46).

(c) *6-Benzeneselenylhexanal* (**7**, n = 2).[37] Yellow oil (656 mg, 82%), with data identical to reported data.[36]

ω-Benzeneselenyl nitriles

The following ω-benzeneselenyl nitriles were synthesised from the respective ω-bromonitriles using the general procedure for ω-benzeneselenyl compounds. *(a) 3-Benzeneselenylpropanonitrile*.[38] Orange oil (88%); ν_{max}/cm^{-1} 3057, 2944, 2247, 1576, 1477, 1437, and 739; δ_H 7.54 (2.H, m, Ph *o*-H), 7.27 (3 H, m, Ph-H), 3.02 (2 H, t, *J* 7.6 Hz, 3-H), and 2.66 (2 H, t, *J* 7.6 Hz, 2-H); δ_C 133.96 (Ar-CH), 129.39 (Ar-C), 128.04 and 127.58 (Ar-CH), 118.64 (CN), 21.70 (3-C), and 18.88 (2-C); *m/z* 210.9910 [M^+ (100%), C_9H_9NSe requires 210.9900] 171 (83), 157, 115 (7), 91 (61), 77 (44), and 39 (8).

(b) 4-Benzeneselenylbutanonitrile.[39] Yellow oil (81%); with data identical to reported data.[39]

(c) 5-Benzeneselenylpentanonitrile. Yellow oil (88%); ν_{max} /cm^{-1} 3057, 2938, 2247, 1576, 1477, 1437, and 739; δ_H 7.46 (2 H, m, Ph *o*-H), 7.25 (3 H, m, Ph-H), 2.89 (2 H, t, *J* 7.0 Hz, 5-H), 2.29 (2 H, t, *J* 7.0 Hz, 2-H), and 1.72-1.82 (4 H, m, 3,4-H); δ_C 132.70 (Ar-CH), 129.75 (Ar-C), 129.15 and 127.0 (Ar-CH), 119.47 (CN), 28.88 (5-C), 26.59 (2-C), 25.19, and 16.64 (3,4-C); *m/z* 239.0206 [M^+ (93%), $C_{11}H_{13}NSe$ requires 239.0213] 158 (100), 91 (24), 82 (54), 78 (91), 55 (60), and 41 (35).

ω-Benzeneselenyl amines

(a) 3-Benzeneselenyl-1-propylamine (**8**, n = 0).[40] *General procedure for the $LiAlH_4$ reduction of ω-benzeneselenyl amines*. Dry diethyl ether (40 cm^3) was added to lithium aluminium hydride (140 mg, 4.8 mmol, 0.75 equiv.) and the reaction mixture was cooled to 0 °C. A solution of 3-benzeneselenylpropanonitrile in dry diethyl ether (10 cm^3) was added dropwise and the mixture was stirred for 2 h. Sodium hydroxide solution (0.1 M, 20 cm^3) was added dropwise and the amine extracted with diethyl ether. The amine was extracted into 2 M hydrochloric acid, the extracts washed with diethyl ether, the aqueous solution neutralised with solid sodium

carbonate and made strongly basic with sodium hydroxide, and extracted with ethyl acetate. The extracts were dried and evaporated to dryness to yield 3-benzeneselenyl-1-propylamine as an orange-red oil (708 mg, 60%); ν_{max} /cm^{-1} 3367, 3293, 3056, 2933, 1635, 1574, 1479, and 1439; δ_H 7.48 (2 H, m, Ph *o*-H), 7.24 (3 H, m, Ph-H), 2.94 (2 H, t, *J* 7.4 Hz, 3-H), 2.73 (2 H, t, *J* 5.8 Hz, 1-H), 1.85 (2 H, m, 2-H), and 1.73 (2 H, brs, NH); δ_C 132.40 (Ar-CH), 130.16 (Ar-C), 129.20 and 126.76 (Ar-CH), 41.61 (1-C), 29.66 (3-C), and 24.95 (2-C); *m/z* 215 (M^+, 18%), 157 (15), 117 (3.5), 106 (14), 91 (4.7), 77 (16), and 30 (100).

(b) 4-Benzeneselenyl-1-butylamine (**8**, n = 1).[40] Yellow oil (91%); ν_{max}/cm^{-1} 3390, 3293, 3057, 2931, 1660, 1576, 1477, and 1437; δ_H 7.47 (2.H, m, Ph *o*-H), 7.25 (3 H, m, Ph-H), 2.91 (2 H, t, *J* 7.0 Hz, 4-H), 2.69 (2 H, t, *J* 7.0 Hz, 1-H), 1.52-1.58 (4 H, m, 2,3-H), and 1.40 (2 H, brs, NH); δ_C 132.38 (Ar-CH), 130.75 (Ar-C), 128.94 and 126.61 (Ar-CH), 50.66 (1-C), 41.35 (4-C), 28.11 (2-C), and 27.52 (3-C); *m/z* 229 (M^+, 4%), 157 (15), 117 (4), 106 (14), 91 (5), 77 (16), 57 (26), and 30 (100).

(c) 5-Benzeneselenyl-1-pentylamine (**8**, n = 2). Yellow oil (820 mg, 92%); ν_{max} /cm^{-1} 3363, 3293, 3057, 2931, 1650, 1576, 1477, and 1437; δ_H 7.46 (2 H, m, Ph *o*-H), 7.25 (3 H, m, Ph-H), 2.89 (2 H, t, *J* 7.0 Hz, 5-H), 2.63 (2 H, t, *J* 7.0 Hz, 1-H), 1.67 (2 H, m, *J* 7.0 Hz, 2-H), 1.56 (2 H, brs, NH), and 1.38-1.48 (4 H, m, 3,4-H); δ_C 132.40 (Ar-CH), 131.01 (Ar-C), 128.96 and 126.61 (Ar-CH), 41.93 (1-C), 33.09 (5-C), 29.88 (2-C), 27.78, and 27.00 (3,4-C); *m/z* 243 (M^+, 1.5%), 158 (13), 112 (6), 91 (8), 77 (5), 69 (23), and 30 (100).

Synthesis of imines (1) and (6)

(a) N-(4-Benzeneselenylbut-1-ylidene)-4-methylaniline (**1a**). *General procedure for the synthesis of imines using molecular sieves (method A).* A solution of *p*-toluidine (127 mg 1.18 mmol) in dry toluene (20 cm^3) was added a solution of 4-benzeneselenylbutanal (268 mg, 1.18 mmol) in dry toluene (20 cm^3) followed by type 4 Å molecular sieves (*ca.* 5 g). The mixture was stirred at room temperature for 24 h after which the sieves were removed by filtration and washed with dry toluene. The solution was evaporated to dryness and the crude imine purified by flash sinter chromatography to give *N*-(4-benzeneselenylbut-1-ylidene)-4-methylaniline as an orange-red oil (300 mg, 80%); ν_{max} /cm^{-1} 3051, 2921, 2853, 1660, 1617, 1577, 1476, and 1437; δ_H 7.44 (2 H, m, PhSe *o*-H), 7.20-7.28 (3 H, m), 6.98 (1 H, m, 1-H), 6.90 (2 H, m) 6.52 (2 H, m), 2.80-2.96 (2 H, m, 4-H), 2.28 (3 H, s, Me), and 1.46-1.77 (4 H, m, 2,3-H); δ_C 144.27 (Ar-C), 132.60 and 132.31 (Ar-CH), 130.03 (Ar-C), 129.07 and 126.61 (Ar-CH), 120.67 (C=N), 113.86 (Ar-CH), 112.66 (Ar-C), 54.19 (2-C), 32.56, 27.68 (3,4-C), and 20.53 (Me); *m/z* 317.0383 [M^+ (1.7%), $C_{17}H_{19}NSe$ requires 317.0682], 314 (37), 235 (18), 157 (80), 77 (100), and 55 (86).

The following imines were synthesised using the general procedure (method A). *(b) N-(5-Benzeneselenylpent-1-ylidene)-4-methylaniline* (**1b**). Orange-red oil (84%); ν_{max} /cm^{-1} 3024, 2931, 2858, 1663, 1616, 1576, 1477, 1437, and 739; δ_H 7.47 (2 H, m, PhSe *o*-H), 7.20-7.28 (m, Ph-H), 6.98 (1 H, m, 1-H), 6.90 (2 H, m), 6.52 (2 H, m), 2.85 (2 H, m, 5-H), 2.25 (3 H, s, Me), and 1.61-1.72 (6 H, m, CH_2); δ_C 145.42 (Ar-C), 132.65 (Ar-CH), 130.00 (Ar-C), 129.13, 126.73 and 125.42 (Ar-CH), 120.40 (C=N), 113.57 (Ar-CH), 112.65 (Ar-C), 54.21 (2-C), 30.26, 28.21, 28.05 (3,4,5-C), and 20.55 (Me); *m/z* 331.0359 [M^+ (0.3%), $C_{18}H_{21}NSe$ requires 331.0839], 314 (51), 234 (23), 157 (100), 106 (82), 77 (82), and 69 (49).

(c) N-(6-Benzeneselenylhex-1-ylidene)-4-methylaniline (**1e**). Orange-red oil (90%); ν_{max} /cm^{-1} 3024, 2931, 2858, 1663, 1616, 1576, 1483, 1437, and 733; δ_H 7.45 (2 H, m, PhSe *o*-H), 7.12-7.27 (m, Ph-H), 6.99 (1 H, m, 1-H), 6.89 (2 H, m), 6.57 (2 H, m), 2.85 (2 H, t, *J* 7.5 Hz, 6-H), 2.32 (3 H, s, Me), 2.22 (2 H, dd, *J* 3.2 Hz, 10 Hz, 2-H), and 1.36-1.65 (6 H, m, CH_2); δ_C 145.38 (Ar-C), 132.52 (Ar-CH), 130.62, (Ar-C) 129.08, 128.21 and 126.46 (Ar-CH), 120.35 (C=N), 113.60 (Ar-CH), 112.71 (Ar-C), 54.10 (2-C), 29.71 (6-C), 27.67, 27.53, 25.51 (3,4,5-C), and 21.42 (Me); *m/z* 345.0980 [M^+ (8%), $C_{19}H_{23}NSe$ requires 345.0995], 424 (3), 190 (23), 158 (19), 120 (100), 106 (40), 91 (22), 78 (36), and 55 (28).

(d) 3-Benzeneselenyl-N-(4-methylbenzylidene)-1-propylamine (**6a**). Orange oil (75%); ν_{max} /cm^{-1} 3057, 2931, 2858, 1649, 1603, 1576, 1477, 1437, and 739; δ_H 8.21 (1 H, s, CH=N), 7.60 (3 H, m), 7.45 (2 H, m, PhSe *o*-H), 7.18-7.25 (4 H, m), 3.68 (2 H, t, *J* 6.5 Hz, 1-H), 2.98 (2 H, t, *J* 7.0 Hz, 3-H), 2.37 (3 H, s, Me), and 2.04-2.17 (2 H, m, 2-H); δ_C 161.50 (C=N), 140.85 (Ar-C), 133.53 and 132.43 (Ar-CH), 131.46 (Ar-C), 129.29 (Ar-CH), 128.20 (Ar-C), 126.69 and 126.15 (Ar-CH), 60.70 (1-C), 31.17 (3-C), 25.40 (2-C), and

21.48 (Me); *m/z* 317.0432 [M^+, (7%), $C_{17}H_{19}NSe$ requires 317.0682], 240 (5), 159 (30), 157 (31), 133 (100), 117 (65), 105 (42), 91 (24), and 77 (50).

General procedure for the synthesis of imines using Na_2SO_4 (method B). (a) 4-Benzeneselenyl-N-(4-methylbenzylidene)-1-butylamine (**6b**). 4-Benzeneselenyl-1-butylamine (206 mg, 0.9 mmol) and *p*-tolualdehyde (108 mg, 0.9 mmol) were dissolved in dry dichloromethane and anhydrous sodium sulphate (*ca.* 3 g) was added. The reaction mixture was stirred for 3 days, the solution filtered, and the filtrate evaporated to dryness to yield 4-benzeneselenyl-*N*-(4-methylbenzylidene)-1-butylamine as an orange oil (310 mg, 90%); ν_{max} /cm^{-1} 3059, 3026, 2933, 2840, 1645, 1607, 1579, 1476, and 1438; δ_H 8.17 (1 H, s, CH=N), 7.58 (2 H, m), 7.47 (2 H, m, PhSe *o*-H), 7.16-7.22 (5 H, m), 3.58 (2 H, t, *J* 6.8 Hz, 1-H), 2.92 (2 H, t, *J* 7.0 Hz, 4-H), 2.34 (3 H, s, Me), and 1.76-1.83 (4 H, m, 2,3-H); δ_C 160.93 (C=N), 140.74 (Ar-C), 133.61 and 132.44 (Ar-CH), 129.68 (Ar-C), 129.28 (Ar-CH), 128.02 (Ar-C), 126.62 and 125.29 (Ar-CH), 60.91 (1-C), 31.01(4-C), 27.92 (2-C), 27.63 (3-C), and 21.47 (Me); *m/z* 331.0384 [M^+, (1%), $C_{18}H_{21}NSe$ requires 331.0839], 314 (48), 234 (20), 174 (23), 157 (100), 132 (5), 119 (27), 91 (32), and 77 (85).

(b) 5-Benzeneselenyl-N-(4-methylbenzylidene)-1-pentylamine (**6e**). Orange oil (91%); ν_{max} /cm^{-1} 3057, 2918, 2851, 1649, 1609, 1576, 1477, 1437, and 733; δ_H 8.20 (1 H, s, CH=N), 7.58 (2 H, d, *J* 7.6 Hz), 7.43 (2 H, d, *J* 7.6 Hz), 7.14-7.23 (m, Ar-H), 3.52 (2 H, t, *J* 6.8 Hz, 1-H), 2.85 (2 H, t, *J* 7.5 Hz, 5-H), 2.25 (3 H, s, Me), and 1.45-1.64 (6 H, m, 2,3,4-H); δ_C 160.85 (C=N), 140.62 (Ar-C), 133.45 and 132.28 (Ar-CH), 129.21 (Ar-C), 128.89 and 127.96 (Ar-CH), 127.23 (Ar-C), 61.29 (1-C), 30.28 (5-C), 29.66 (2-C), 27.59 and 27.44 (3,4-C), and 21.41 (Me); *m/z* 345.0975 [M^+, (6%), $C_{19}H_{23}NSe$ requires 345.0995], 314 (3), 188 (100), 157 (20), 146 (25), 119 (45), 105 (51), 91 (75), 77 (44), 51 (32), and 41 (44).

Cyclisation of *N*-(ω-benzeneselenylalk-1-ylidene)amines.

General procedure for radical cyclisations of N-(ω-benzeneselenylalk-1-ylidene)-4-methylanilines.

(a) Attempted cyclisation of N-(4-benzeneselenylbut-1-ylidene)-4-methylaniline (**1a**). The imine (**1a**) (240 mg, 0.76 mmol) was dissolved in dry toluene (100 cm^3) and nitrogen was bubbled through the solution for 30 min and the brought to a steady reflux. Bu_3SnH (0.35 cm^3, 1.3 mmol, 1.7 equiv.) and AIBN (42 mg, 0.26 mmol, 0.34 equiv.) were dissolved in dry toluene (25 cm^3) and nitrogen was bubbled through for 30 min. The solution of Bu_3SnH and AIBN was transferred under nitrogen to a 50 cm^3 syringe and was added to the refluxing imine solution at a rate of 5.0 cm^3/h using a syringe pump. After the addition of the tin hydride was completed, the reaction mixture was refluxed for a further 30 min before cooling to r.t. An excess of sodium borohydride dissolved in methanol (5 cm^3) was added and the mixture stirred for 18 h. The mixture was extracted with 2 M hydrochloric acid and the extracts washed with light petroleum. Solid sodium carbonate was added to neutralise the acid and once all effervescing had ceased the solution was made strongly basic with sodium hydroxide solution and the products extracted into diethyl ether. The ether extracts were dried and evaporated to dryness to yield a red oil (65 mg) which was analysed using GLC against authentic standards. The crude product was dissolved in diethyl ether, acetic anhydride (0.2 cm^3) and triethylamine (0.2 cm^3) added, and the mixture was stirred at r.t. for 24 h. The tertiary amines were extracted into hydrochloric acid, basified, and re-extracted into diethyl ether. The extracts were dried and evaporated to dryness to yield the tertiary amine product. The residual ether solution was dried, evaporated to dryness to yield the acetylated secondary amines were further purified by TLC on alumina plates or by flash sinter chromatography. In this particular reaction no identifiable products were isolated.

(b) Cyclisation of N-(5-benzeneselenylpent-1-ylidene)-4-methylaniline (**1b**). The imine (390 mg) gave a crude oil (97 mg). GLC and ^{1}H NMR spectral analysis showed *N*-cyclopentyl-4-methylaniline (**9c**) as the only significant product (39%). Purification gave (**9c**) identical with an authentic sample. Repeat cyclisations gave yields of 35-42%.

(c) Cyclisation of N-(6-benzeneselenylhex-1-ylidene)-4-methylaniline (**1e**). The imine (**1e**) (247 mg) gave a crude oil (80 mg) of recovered material (59%). GLC and ^{1}H NMR spectral analysis and comparison to authentic material showed that the acyclic amine *N*-hexyl-4-methylaniline as the only major product. Repeat reactions gave yields in the range 40-42%.

General procedure for N-(ω-benzeneselenylalk-1-ylidene)-2-phenylethylamines. (a) Formation and cyclisation of N-(5-benzeneselenyl-1-pentylidene)-2-phenylethylamine (**1c**). 5-Benzeneselenylpentanal (**7**, n = 1) (1.68 mmol) and 2-phenylethylamine (1.68 mmol) were dissolved in toluene (120 cm^3) and refluxed for 3 h using a Dean-Stark water separator. The imine was not isolated and reacted with Bu_3SnH using the general procedure. GLC and ^1H NMR spectral analysis showed *N*-cyclopentyl-4-methyl-aniline (**9c**) (47%) and *N*-(2-phenylethyl)piperidine (**10c**)[41] (5%). (**10c**)[41] and *N*-acetyl-(**9c**) were identical to authentic samples.

(b) Formation and cyclisation of N-(5-benzeneselenyl-1-pentylidene)benzylamine (**1d**). 5-Benzeneselenylpentanal (**7**, n = 1) (1.51 mmol) and benzylamine (1.51 mmol) were reacted to yield an oil which on purification gave the 5-*exo* (**9d**)[42] as the only reaction product (72%), identical to an authentic sample.

(c) Formation and cyclisation of N-(6-benzeneselenyl-1-hexylidene)-2-phenylethylamine (**1f**). 6-Benzeneselenylhexanal (**7**, n = 2) (0.71 mmol) and 2-phenylethylamine (0.71 mmol) which on purification gave the 5-*exo* (**9f**) as the only product (43%), identical to an authentic sample.

Independent synthesis of products from *N*-(ω-benzeneselenylalk-1-ylidene)amine reactions.

For convenience, all the characterisation of products is presented with the independent syntheses.

(a) N-Cyclobutyl-4-methylaniline (**9a**). *General procedure for amine synthesis (method A).* Cyclobutanone (487 mg, 6.95 mmol) and *p*-toluidine (744 mg, 6.95 mmol) were dissolved in dry diethyl ether (10 cm^3), 4 Å molecular sieves (*ca.* 2 g) added, and the mixture was stirred at room temperature for 2 days. The solution was filtered, the molecular sieves washed with diethyl ether, and the filtrate evaporated to dryness to yield the crude imine as a red oil. The formation of the imine was confirmed by IR spectroscopy. The imine was reduced using sodium borohydride in dry diethyl ether to yield the amine which was purified by dry flash chromatography to give *N*-cyclobutyl-4-methylaniline as a light red oil (866 mg, 77%); ν_{max} /cm^{-1} (imine) 2945, 2866, 1708, 1617, 1545, 1452, and 814; (amine) 3355, 3019, 2931, 2863, 1668, 1619, 1518, 1455, 1303, and 813; δ_H 6.95 (2 H, d, *J* 8.0 Hz), 6.56 (2 H, d, *J* 8.0 Hz, Ar-H), 3.58 (1 H, m, NH), 2.78 (1 H, m, CH-N), 2.22 (3 H, s, Me), and 1.40-1.80 (6 H, m, CH_2); δ_C 143.49 (Ar-C), 129.34 and 115.56 (Ar-CH), 113.21 (Ar-C), 49.85 (1-C), 33.73, 28.94 [2(4),3-C], and 20.39 (Me).

(b) N-Cyclopentyl-4-methylaniline (**9b**). Orange oil from cyclopentanone and *p*-toluidine (65%); (Found: C, 67.25; H, 8.86; N, 6.73. $C_{12}H_{17}N.HCl$ requires C, 68.09; H, 8.51; N, 6.62%); ν_{max} /cm^{-1} 3355, 2921, 2866, 1671, 1621, 1548, 1274, and 814; δ_H 7.10 (2.H, d, *J* 8.0 Hz), 6.64 (2 H, d, *J* 8.0 Hz), 3.87 (1 H, m, CH-N), 3.52 (1 H, m, NH), 2.15 (3 H, s, Me), and 1.56 -2.10 (8 H, m, cyclopentyl); δ_C 145.92 (Ar-C), 129.69 and 115.24 (Ar-CH), 113.41 (Ar-C), 54.91 (1-C), 33.52 (2,5-C), 23.18 (3,4-C), and 20.35 (Me); *m/z* 175.1348 [M^+ (62%), $C_{12}H_{17}N$ requires 175.1361], 146 (100), 133 (37), 118 (15), 106 (17), and 91 (19).

(c) N-Cyclohexyl-4-methylaniline (**9e**).[43] Orange oil from cyclohexanone and *p*-toluidine (66%); ν_{max} /cm^{-1} 3374, 3015, 2928, 1671, 1620, 1528, 1450, and 809; δ_H 6.96 (2 H, d, *J* 8.6 Hz), 6.50 (2 H, d, J 8.6 Hz), 3.83 (1 H, m, NH), 3.20 (1 H, m, CH-N), 2.22 (3 H, s, Me), 1.73 -2.04 (4 H, m, 2,6-H), and 1.13-1.38 (6 H, m, 3,4,5-H); δ_C 144.33 (Ar-C), 129.74, 126.2 and 115.27 (Ar-CH), 113.6 (Ar-C), 52.66, (1-C) 33.28 (2,6-C), 25.95 (3,5-C), 25.06 (4-C), and 20.43 (Me); *m/z* 189.1513 [M^+ (46%), $C_{13}H_{19}N$ requires 189.1517], 146 (100), 134 (30), 120 (10), 106 (17), and 91 (15).

(d) N-Hexyl-4-methylaniline. Red oil from hexanal and *p*-toluidine (11%); ν_{max} /cm^{-1} 3355, 3048, 2927, 1672, 1621, 1515, and 813; δ_H 6.96 (2 H, d, *J* 8.0 Hz), 6.54 (2 H, d, *J* 8.0 Hz), 3.51 (1 H, s, NH), 2.22 (3 H, s, Me), 2.18 (2 H, t, *J* 7.5 Hz, 1-H), 1.32-1.48 (8 H, m, 2,3,4,5-H), and 0.90 (3 H, t, *J* 7.6 Hz, 6-H); δ_C 145.62 (Ar-C), 129.72 and 115.25 (Ar-CH), 112.74 (Ar-C), 50.00 (1-C), 39.01 (2-C), 36.38 (3-C), 26.13 (4-C), 25.72 (5-C), 20.44 (Me), and 14.09 (6-C); *m/z* 191.1673 [M^+ (26%), $C_{13}H_{21}N$ requires 191.1674], 149 (12), 134 (26), 120 (70), 106 (100), 91 (99), and 77 (14).

(e) N-Hexyl-2-phenylethylamine.[44] Yellow oil from hexanal and 2-phenylethylamine (20%); ν_{max} /cm^{-1} 3363, 3028, 2956, 2871, 1664, 1604, 1497, 1455, 1378, and 748; δ_H 7.16-7.32 (5 H, m), 3.63 (1 H, m, NH), 2.78-2.91 (4 H, m, Et 1,2-H), 2.62 (2 H, t, *J* 7.5 Hz, hexyl 1-H), 1.89 (2 H, m, 2-H), 1.47 (2 H, m, 3-H), 1.23-1.28 (4 H, m, 4,5-H), and 0.87 (3 H, t, *J* 6.9 Hz, 6-H); δ_C 139.96 (Ar-C), 128.77, 128.39 and 126.08 (Ar-CH), 51.06 and 49.76 (CH_2N), 36.13 (2-C), 31.66 (3-C), 29.77 and 22.52 (4,5-C), and 13.96 (6-C).

General procedure for amine synthesis (method B). (a) 4-Methyl-N-pentylaniline. 1-Bromopentane (1.511 g, 10 mmol), dissolved in toluene, was added to *p*-toluidine (3.02 g, 28 mmol) and the mixture was refluxed for 24 h, the solution evaporated to dryness, and the products separated by flash chromatography to yield 4-methyl-*N*-pentylaniline as an orange-red oil (105 mg, 6%); ν_{max} /cm^{-1} 3410 , 3054, 2927, 2839, 1654, 1617, 1521, 1457, and 807; δ_H 6.96 (2 H, d, *J* 8.0 Hz), 6.52 (2 H, d, *J* 8.0 Hz), 3.07 (2 H, m, 1-H), 2.23 (3 H, s, Me), 2.15 (1 H, s, NH), 1.59 (2 H, m, 2-H), 1.36 (4 H, m, 3,4-H), and 0.95 (3 H, t, 7.5 Hz, 5-H); δ_C 130.17 (Ar-C), 129.76 and 124.43 (Ar-CH), 113.89 (Ar-C), 45.19 (1-C), 29.72, 28.95 and 22.5 (2,3,4-C), 20.43 (Me), and 14.02 (5-C).

(b) N-(2-Phenylethyl)piperidine (**10c**).[41] Colourless oil (36%) from piperidine and 1-bromo-2-phenylethane; ν_{max} /cm^{-1} 2934, 2855, 1603, 1497, 1470, 1468, 1453, 1374, 1352, 1115, 746, and 699; δ_H 7.18-7.30 (5 H, m, Ph), 2.81 (2H, t, *J* 8.5 Hz, ethyl 1-H), 2.56 (2 H, t, *J* 8.5 Hz, ethyl 2-H), 2.46 (4 H, m, piperidine 2,6-H), 1.60-1.66 (4 H, m, 3,5-H), and 1.45 (2 H, m, 4-H); δ_C 140.81 (Ar-C), 128.72, 128.36 and 125.95 (Ar-CH), 61.43 and 54.56 (CH_2N), 33.64 (2,6-C), 25.97 (3,5-C), and 24.43 (4-C); *m/z* 189.1505 [M^+ (0.7%), $C_{13}H_{19}N$ requires 189.1517], 105 (7), 98 (100), 91 (9.7), 77 (6.4), 69 (56), and 42 (22).

(c) N-Benzylcyclopentylamine (**9d**).[42] Yellow oil (30%) from cyclopentylamine and benzyl chloride; (Found: C, 68.04; H, 8.57; N, 6.30. $C_{12}H_{17}N.HCl$ requires C, 68.10; H, 8.57; N, 6.62%); ν_{max} /cm^{-1} 3296, 3027, 2953, 2866, 1678, 1604, 1496, 1454, 750, and 700; δ_H 7.23-7.32 (5.H, m, Ph), 3.77 (2 H, s, PhCH_2), 3.59 (1 H, m, NH), 3.11 (1 H, s, cyclopentyl 1-H), 1.64-1.86 (4 H, m), and 1.24-1.38 (4 H, m, cyclopentyl); δ_C 140.63 (Ar-CH), 128.25 (Ar-C), 128.06 and 126.70 (Ar-CH), 59.04 (CHN), 52.64 (CH_2N), 33.06 (2,5-C), and 23.99 (3,4-C).

General procedure for amine synthesis (method C). The procedure was the same as method A except that the imine was prepared using refluxing toluene with a Dean-Stark water separator.

(a) N-Cyclopentyl-2-phenylethylamine (**9c**). (48%); (Found: C, 69.04; H, 9.29; N, 6.12. $C_{13}H_{19}N.HCl$ requires C, 69.20; H, 8.93; N, 6.20%); ν_{max} /cm^{-1} 3296, 3027, 2953, 2866, 1678, 1604, 1496, 1454, 750, and 700; δ_H 7.17-7.34 (5 H, m, Ph), 3.45 (1 H, m, cyclopentyl 1-H), 3.06 (1 H, s NH), 2.77-2.88 (4 H, m, propyl 2,3-H), and 1.64-1.81 (8 H, m, cyclopentyl); δ_C 140.18 (Ar-CH), 128.69 (Ar-C), 128.28 and 126.11 (Ar-CH), 59.78 (CHN), 49.99 (CH_2N), 36.39 (CH_2Ar), 33.12, and 23.23 (cyclopentyl-C); *m/z* 189.1516 [M^+, (1.5%), $C_{13}H_{19}N$ requires 189.1517], 190 (7), 105 (14), 98 (100), 91 (30), 69 (15) 41 (16), and 30 (47).

(b) N-Cyclohexyl-2-phenylethylamine (**9f**). Yellow oil from cyclohexanone and 2-phenylethylamine (46%); (Found: C, 67.90; H, 8.70; N, 5.80. $C_{14}H_{21}N.HCl.5H_2O$ requires C, 67.60; H, 8.91; N, 5.63%); ν_{max} /cm^{-1} 3288, 3027, 2928, 2857, 1660, 1604, 1584, 1496, 1453, and 1346; δ_H 7.17-7.32 (5 H, m, Ph), 3.59 (1 H, m, NH), 2.81-2.87 (4 H, m, ethyl 1,2-H), 2.42 (1 H, m, cyclohexyl 1-H), 1.71-1.88 (4 H, m, 2,6-H), and 1.18-1.28 (6 H, m, 3,4,5-H); δ_C 140.05 (Ar-C), 128.76, 128.33 and 126.03 (Ar-CH), 56.63 (CHN), 48.07 (CH_2N), 35.51(CH_2Ar), 26.05 (2,6-C), 24.98 (3,5-C), and 24.10 (4-C); *m/z* 203.1664 [M^+, (0.7%), $C_{14}H_{21}N$ requires 203.1674], 190 (6), 112 (99), 105 (17), 91 (25), 82 (12),72 (89) 41 (21), and 30 (100).

General procedure for amine synthesis (method D). (a) N-p-Tolylpyrrolidine (**10a**). *p*-Toluidine (3.45 g, 32 mmol) was dissolved in light petroleum (100 cm^3) and 1,4-diiodobutane (2.00 g, 6.5 mmol) dissolved in light petroleum (10 cm^3) was added. The mixture was stirred at r.t. for 3 days and the resulting dark red solution treated with acetic anhydride and triethylamine (both 5 equiv. relative to *p*-toluidine) and stirred for a further 24 h. The precipitate of *N*-acetyl-*p*-toluidine was filtered off and the solution extracted with 2 M hydrochloric acid. The combined extracts were washed with light petroleum, neutralised with Na_2CO_3 carbonate, extracted into diethyl ether, washed with water, and dried. The solution was evaporated to dryness to yield *N*-(*p*-tolyl)pyrrolidine as a red oily solid (550 mg, 53%); ν_{max} /cm^{-1} 3047, 2974, 2837, 1678, 1624, 1525, 1442, 1188, and 1158; δ_H 7.05 (2 H, d, *J* 8.5 Hz), 6.58 (2 H, d, *J* 8.5 Hz), 3.27 (4 H, t, *J* 6.8 Hz, 2,5-H), 2.25 (3 H, s, Me), and 2.00 (4 H, t, *J* 6.8 Hz, 3,4-H); δ_C 146.25 (Ar-C), 129.62 and 113.01 (Ar-CH), 111.79 (Ar-C), 47.84 (2,5-C), 25.39 (3,4-C), and 20.27 (Me).

(b) N-p-Tolylpiperidine (**10b**). Method D was repeated using 1,5-dibromopentane. Oily red-black solid (31%); ν_{max} /cm^{-1} 3054, 2985, 2939, 1678, 1608, 1514, 1453, and 815; δ_H 7.04 (2.H, d, *J* 8.5 Hz), 6.84 (2 H, d, *J* 8.5 Hz), 3.06 (4 H, t, *J* 5.5 Hz, 2,6-H), 2.24 (3 H, s, Me), 1.69 (4 H, m, 3,5-H), and 1.52 (2 H, m,

4-H); δ_C 135.61 (Ar-C), 129.55 and 120.19 (Ar-CH) 117.04 (Ar-C), 51.43 (2,6-C), 25.86 (3,5-C), 24.23 (4-C), and 20.41 (Me).

Acetylation of amines. Amines were acetylated using acetic anhydride and triethylamine at r.t. for 24 h.

(a) N-Acetyl-N-cyclopentyl-4-methylaniline. Yellow oil (197 mg, 53%); ν_{max} /cm^{-1} 3032, 2959, 2928, 2873, 1655, 1608, 1513, 1453,1398, 1311, 1261, 910, and 738; δ_H 7.20 (2 H, d, *J* 8.0 Hz), 6.98 (2 H, d, *J* 8.0 Hz), 4.93 (1 H, m, 1-H), 2.39 (3 H, s, Me), 1.83-1.88 (2 H, m), 1.74 (3 H, s, Ac), and 1.47-1.54 (6 H, m); δ_C 171.15 (C=O), 138.35 and 137.78 (Ar-C), 129.93 and 129.88 (Ar-CH), 56.32 (1-C), 29.52 (2,5-C), 23.59 (MeCO), 22.67 (3,4-C), and 20.35 (Me); *m/z* 217.1467 [*M*$^+$ (16%), $C_{14}H_{19}NO$ requires 217.1472], 174 (11), 149 (75), 107 (100), 91 (56), and 65 (24).

(b) N-Acetyl-N-hexyl-4-methylaniline. (50%); ν_{max} /cm^{-1} 3057, 2931, 2857, 1652, 1609, 1558, 1540, 1515, 1457, 1118, 733, and 666; δ_H 7.09 (2 H, m), 6.98 (2 H, m), 2.35 (2 H, m, 1-H), 2.24 (3 H, s, MeAr), 2.16 (3 H, s, Ac), 1.20-1.45 (8 H, m, 2,3,4,5-H), and 0.90 (3 H, t, *J* 6.5 Hz, 6-H); δ_C 166.58 (C=O), 135.30 (Ar-C), 129.87 and 129.36 (Ar-CH), 128.32 (Ar-C), 37.34 (2-C), 31.58 (3-C), 29.00 (4-C), 24.47 (MeCO) 22.50 (5-C), 20.99 (MeAr), and 14.04 (6-C); *m/z* 233.1775 [*M*$^+$ (1.7%), $C_{15}H_{23}NO$ requires 233.1780], 176 (15), 149 (42), 134 (15), 120 (26), 107 (100), 91 (49), 77 (23), and 43 (95).

(c) N-Acetyl-N-cyclopentyl-2-phenylethylamine. Yellow oil (55%); ν_{max} /cm^{-1} 3027, 2954, 2870, 1655, 1605, 1585, 1454, 1421, 1368, 1229, 748, and 701 cm^{-1}; δ_H (2 stereoisomers) 7.13-7.35 (5 H, m, Ph), 4.64 and 4.07 (1H, 2 m, cyclopentyl 1-H), 3.32-3.40 (2 H, t, *J* 8.0 Hz, ethyl 1-H), 2.81-2.91 (2 H, t, *J* 8.0 Hz, ethyl 2-H), 2.15 and 2.08 (3 H, 2 s, Ac), and 1.50-1.81 (8 H, m, cyclopentyl); δ_C (2 stereoisomers) 171.22 and 170.75 (C=O), 128.82 (Ar-CH), 128.44 (Ar-C), 126.76 and 126.22 (Ar-CH), 59.70 and 56.30 (cyclopentyl 1-C), 47.30 and 43.95 (ethyl 1-C), 37.37 and 35.49 (ethyl 2-C), 29.77 and 29.22 (2,5-C), 23.47 (3,4-C), and 22.27 (MeCO); *m/z* 231.1629 [*M*$^+$ (5%), $C_{15}H_{21}NO$ requires 231.1623] 146 (6), 140 (37), 98 (100), 91 (25), 72 (11), and 43 (34).

Synthesis and cyclisation of *N*-(6-benzeneselenylhex-2-ylidene)-2-phenylethylamine (11).

Synthesis. (a) 1-Benzeneselenyl-3-chloropropane. Using the general procedure for the introduction of the benzeneselenyl group, 1-chloro-3-iodopropane (2.62 g, 12.8 mmol) gave 1-benzeneselenyl-3-chloropropane as a yellow-orange oil (2.94 g, 98%); ν_{max} /cm^{-1} 3072, 2956, 2940, 1579, 1478, 1438, 1304, 1233, 1072, and 739; δ_H 7.44-7.49 (2 H, m, Ph *o*-H), 7.25-7.30 (3 H, m, Ph-H), 3.62 (2 H, t, *J* 6.3 Hz, 3-H), 3.03 (2 H, t, *J* 7.0 Hz, 1-H), and 2.10-2.15 (2 H, m, 2-H); δ_C 132.82 and 132.68 (Ar-CH), 129.23 (Ar-C), 127.25 (Ar-CH), 44.20 (3-C), 32.46, and 25.05; *m/z* 233.9710 [*M*$^+$ (100%), $C_9H_{11}ClSe$ requires 233.9714], 171 (15), 158 (75), 117 (11), 91 (31), 78 (81), 51 (30), and 41 (56).

(b) Ethyl 2-acetyl-5-benzeneselenylpentanoate. Sodium hydride (160 mg of 60% suspension in mineral oil) was placed in a dried flask and was washed using dry light petroleum, under nitrogen. Freshly dried and distilled THF (20 cm^3) was added and to the suspension was added solution of ethyl acetoacetate (403 mg, 3.1 mmol) in THF (10 cm^3). After stirring at room temperature for 30 min, the solution was cooled to 0 °C and 1-benzeneselenyl-3-chloropropane (724 mg, 3.1 mmol) in THF (10 cm^3) was added dropwise over 10 min. The mixture was stirred at r.t. for 2 h. The solvent was removed, water (10 cm^3) was added, and the organic products extracted into diethyl ether. The extracts were dried, evaporated to dryness, and the crude product purified by dry flash chromatography to give ethyl 2-acetyl-5-benzeneselenylpentanoate as a yellow oil (878 mg, 86%); ν_{max} /cm^{-1} 3072, 2957, 2939, 1741, 1718 , 1579, 1478, 1438, 1304, 1234, 1023, 735, and 691; δ_H 7.44-7.48 (2 H, m, Ph *o*-H), 7.21-7.23 (3 H, m), 4.15 (2 H, q, *J* 7.2 Hz, MeC*H*$_2$), 3.39 (1 H, t, *J* 7.3 Hz, 2-H), 2.88 (2 H, t, *J* 7.3 Hz, 5-H), 2.18 (3 H, s, Ac), 1.91-1.99 (2 H, m), 1.60-1.67 (2 H, m), and 1.25 (3 H, t, *J* 7.3 Hz, C*H*$_2$CH$_3$); δ_C 202.63 (ketone-C), 169.49 (ester-C), 132.62 (Ar-CH), 129.99 (Ar-C), 129.05 and 126.86 (Ar-CH), 61.35 (Me*C*H$_2$), 59.17 (2-C), 28.72 (*C*H$_3$CO), 28.02, 27.62, 26.63 and 14.06 (CH$_2$*C*H$_3$); *m/z* 328.0543 [*M*$^+$ (3.5%), $C_{15}H_{20}O_3Se$ requires 328.0577], 253 (8), 234 (66), 169 (30), 158 (PhSeH$^+$, 62), 105 (23), 91 (51), 78 (86), and 41 (100).

(c) 6-Benzeneselenyl-2-hexanone. Ethyl 2-acetyl-5-benzeneselenylpentanoate (362 mg, 1.1 mmol) dissolved in freshly dried and distilled DMF (2 cm^3) was added to a solution of lithium chloride (46 mg, 1.1 mmol) in DMF (10 cm^3) containing water (40 mg, 2.2 mmol). The mixture was heated at 170 °C for 18 h, cooled to r.t.,

and water (10 cm^3) was added followed by dilute hydrochloric acid (2 cm^3). The product was extracted into diethyl ether, washed with water, dried, and evaporated to dryness. The product was purified using dry flash chromatography to give 6-benzeneselenyl-2-hexanone as a yellow oil (213 mg, 75%); ν_{max} /cm^{-1} 3056, 2933, 2862, 1719, 1579, 1478, 1438, 1369, 1232, 1073, 1023 and 737; δ_H 7.44-7.48 (2 H, m, Ph *o*-H), 7.20-7.25 (3 H, m), 2.87 (2 H, t, *J* 8.0 Hz, 6-H), 2.39 (2 H, t, *J* 7.8 Hz, 3-H), 2.09 (3 H, s, Me), and 1.64-1.69 (4 H, m, 4,5-H); δ_C 208.72 (C=O), 132.42 (Ar-CH), 131.40 (Ar-C), 128.97 and 126.69 (Ar-CH), 42.90 (CH_2), 29.77 (Me), 29.51, 27.36, and 23.76; *m/z* 256.0370 [M^+ (4%), $C_{12}H_{16}OSe$ requires 256.0366], 157 (9), 141 (3), 113 (3), 99 (28), 78 (12), and 43 (100).

Formation and cyclisation of N-(6-benzeneselenylhex-2-ylidene)-2-phenylethylamine. 6-Benzeneselenyl-2-hexanone (197 mg, 0.77 mmol) and 2-phenylethylamine (93 mg, 0.77 mmol) were dissolved in toluene (120 cm^3) and refluxed for 3 h using a Dean-Stark water separator. The imine was not isolated and reacted with Bu_3SnH using the general procedure. The ^1H NMR spectrum of the crude product indicates (**12**) as the major product with traces of (**13**). The crude product was purified using flash chromatography using alumina as absorbent to give a yellow oil of *N*-(1-methylcyclopent-1-yl)-2-phenylethylamine (**12**) as the only product (56%); ν_{max} /cm^{-1} 3027, 2956, 1668, 1603, 1496, 1454, 1082, and 749; δ_H 7.20-7.34 (5 H, m, Ph-H), 2.71-2.84 (4 H, m, CH_2CH_2Ph), 2.12-2.21 (2 H, m), 1.47-1.58 (4 H, m), 1.29-1.36 (2 H, m), and 1.21 (3 H, s, Me); δ_C 127.50 (Ar-C) 128.63, 128.00 and 126.10 (Ar-CH), 62.02 (cyclopentyl 1-C) 44.89, 39.00, 37.04, 25.57 (Me), and 23.85; *m/z* 203.1658 [M^+ (1.2%), $C_{14}H_{21}N$ requires 203.1674], 158 (34), 112 (69), 104 (8), 91 (37), 83 (20), 78 (44), 41 (48), and 30 (100).

N-(5-Benzeneselenylpent-1-ylidene)pyrrolidinium tetrafluoroborate (14).

(a) 5-(Benzeneselenyl)pentanal (**7**, n = 1) (781 mg, 3.24 mmol), pyrrolidine (250 mg, 3.52 mmol) and tetrafluoroboric acid (500 mg of 54 % solution in Et_2O, 3.20 mmol) were dissolved in toluene (120 cm^3) and refluxed for 3 h using a Dean-Stark water separator. The solution was evaporated to dryness to yield the iminium salt (**14**) as an orange solid (1.22 g, 98%) which did not require further purification; ν_{max} /cm^{-1} 2932, 2861, 1733, 1579, 1478, 1457, 1438, 1374, 1196, 1018, 736, and 691; δ_H 7.56-7.58 (2 H, m, Ph *o*-H), 7.20-7.26 (3 H, m), 7.16 (1 H, t, *J* 6.5 Hz, 1-H), 3.35-33.49 (4 H, m, pyrrolidine 2,5-H), 2.92 (2 H, t, *J* 7.3 H, 5-H), 1.98-2.12 (6 H, m), and 1.70-1.79 (4 H, m); δ_C 132.30 (ArCH), 130.15 (ArC), 128.95, 126.71 and 125.20 (ArC and 1-C), 46.62 (pyrrolidine 2,5-C), 29.73, 29.12, 27.45, 24.31, and 23.79 (CH_2).

(b) Attempted cyclisation of (**14**) *using Bu_3SnH.* The iminium salt (**14**) was reacted with Bu_3SnH using the general procedure. The product, *N*-pentylpyrrolidine[45] was isolated as the hydrochloride salt as colourless crystals (75%); m.p. 145-146 °C (EtOAc/EtOH), (Found: C, 60.91; H, 11.08; N, 7.72. $C_9H_{19}N.HCl$ requires C, 60.80; H, 11.30; N, 7.88 %); ν_{max} /cm^{-1} 3443, 2959, 2873, 2689, 2346, 1459, 1275, 11047, 733, and 699; δ_H 9.50 (1 H, broad s, NH^+), 7.62 and 7.45 (1 H, 2 x m), 4.15 (1 H, m, pentyl 1-H), 3.23-3.27 (4 H, m, pyrrolidine 2,5-H), 1.92-1.96 (4 H, m, pyrrolidine 3,4-H), 1.20-1.30, (6 H, m, pentyl, 2,3,4-H) and 0.86 (3 H, t, *J* 7.3 Hz, pentyl 5-H); δ_C 130.77 and 128.63 (pentyl 1-C), 67.98 (pyrrolidine 2,5-C), 39.54, 30.18, 28.75, 23.56, 22.82 (CH_2), and 13.91 (Me). The salt was identical to an authentic sample synthesised from 1-bromopentane and pyrrolidine using amine synthesis method A.

(c) N-(5-Benzeneselenylpent-1-yl)pyrrolidine. A mixture of the iminium salt (**14**) (391 mg, 1.02 mmol) and Bu_3SnH (0.6 cm^3, 2.23 mmol) in toluene (50 cm^3) was stirred under nitrogen at 100 °C for 3 h. The white precipitate (Bu_3SnF) was filtered and the filtrate extracted with 2 M hydrochloric acid, neutralised (NaOH), and the amine extracted into ethyl acetate. The extracts were dried, evaporated to dryness, and the residue purified by flash chromatography using alumina as absorbent and CH_2Cl_2 as eluent to yield the amine as a yellow oil (82 mg, 27%); ν_{max} /cm^{-1} 2955, 2859, 1578, 1477, 1453, 1438, 1376, 1290, 1073, 1023, 733, and 691; δ_H 7.46-7.50 (2 H, m, Ph *o*-H), 7.23-7.27 (3 H, Ph), 2.88-2.94 (2 H, t, *J* 7.5 Hz, 5-H), 2.54-2.58 (2 H, m, 1-H), 2.12-2.20 (4 H, m, pyrrolidine 2,5-H), 1.70-1.80 (4 H, m) and 1.44-1.60 (6 H, m); δ_C 132.38 (ArCH), 130.55 (ArC), 128.94, 126.62 (ArCH), 54.39, 53.59 (CH_2N), 30.38, 29.66, 27.99, 27.52, 23.70, and 23.54 (CH_2).

(d) Attempted cyclisation of (**14**) *using tris(trimethylsilyl)silane.* The iminium salt (531 mg, 1.39 mmol) was reacted with $(Me_3Si)_3SiH$ (460 mg, 1.85 mmol) and AIBN (78 mg, 0.4 mmol) in toluene using the general procedure for radical reactions to give (**15**) (167 mg), isolated as the hydrochloride salt (68%).

Cyclisation studies of ω-benzeneselenyl-*N*-(alkylidene)amines (6).

Radical reactions of ω-benzeneselenyl-N-(4-methylbenzylidene)amines. (a) 3-Benzeneselenyl-N-(4-methylbenzylidene)-1-propylamine (**6a**). The imine (**6a**) (263 mg, 0.84 mmol) was reacted with Bu_3SnH using the general procedure for radical cyclisations. Purification yielded the uncyclised amine, 4-methyl-*N*-propylbenzylamine (63%) identical to authentic material;[26] ν_{max} /cm^{-1} 3308, 3025, 2960, 2829, 1645, 1614, 1515, 1457, 1379, 806, and 753; δ_H 7.22 (2 H, d, *J* 8.0 Hz), 7.10 (2 H, d, *J* 8.0 Hz), 3.74 (2 H, s, $ArCH_2N$), 2.58 (2 H, t, *J* 7.3 Hz, RCH_2N), 2.36 (1 H, s, NH), 2.31 (3 H, s, Me), 1.56 (2 H, m, *J* 7.3 Hz, 2-H), and 0.93 (3 H, t, *J* 7.3 Hz, 3-H); δ_C 136.46 (Ar-C), 129.18, 128.14 and 126.87 (Ar-CH), 53.62 and 51.18 (CH_2N), 24.10 (2-C), 21.06 (3-C), and 11.76 (Me). A repeat reaction gave slightly lower yields.

(b) Cyclisation of 4-benzeneselenyl-N-(4-methylbenzylidene)-1-butylamine (**6b**). The imine (300 mg, 0.91 mmol) gave an oil (123 mg); GLC and ^{1}H NMR spectral analysis showed the 5-*exo* (**19b**)[46] (54%) the *endo* (**20b**)[47] (6%). The crude product was acetylated, (**19b**)[46] separated by extraction into hydrochloric acid, and (**20b**)[47] purified by preparative TLC on alumina. Both products were identical to authentic samples. A repeat reaction gave slightly lower yields.

(c) Cyclisation of 5-benzeneselenyl-N-(4-methylbenzylidene)-1-pentylamine (**6e**). The imine (342 mg, 1.00 mmol) gave an oil (100 mg). GLC and ^{1}H NMR spectral analysis showed the 6-*exo* (**19e**)[48] (7%) and the uncyclised 4-methyl-*N*-pentylbenzylamine (40%). The crude product was acetylated, (**19e**)[48] separated by extraction into hydrochloric acid, and *N*-acetyl-4-methyl-*N*-pentylbenzylamine purified by preparative TLC on alumina. Both products were identical to authentic samples. Two repeat cyclisations gave lower yields.

Formation and cyclisation of ω-benzeneselenyl-N-(3-phenylpropylidene)amines. (a) 4-Benzeneselenyl-N-(3-phenylpropylidene)-1-butylamine (**6c**). 4-Benzeneselenylbutylamine (**8**, n = 1) (285 mg, 1.25 mmol) and 3-phenylpropionaldehyde (167 mg, 1.25 mmol) were reacted using the general procedure for the formation and cyclisation of *N*-(ω-benzeneselenylalk-1-ylidene)-2-phenylethylamines to yield an oil (172 mg). GLC analysis showed the *exo* (**19c**)[49] (42%) and *endo* (**20c**)[50] (18%) products. The crude oil was acetylated, (**19c**) separated by extraction into hydrochloric acid, and (**20c**) purified as the acetate, *N*-acetyl-2-(2-phenylethyl)piperidine. Both products were identical to authentic samples and no *N*-pentyl-3-phenylpropylamine or *N*-acetyl-*N*-pentyl-3-phenylpropylamine were detected.

(b) 5-Benzeneselenyl-N-(3-phenylpropylidene)-1-pentylamine (**6f**). 5-Benzeneselenylpentylamine (**8**, n = 2) (202 mg, 0.83 mmol) and 3-phenylpropionaldehyde (112 mg, 0.83 mmol) an oil (94 mg). GLC and ^{1}H NMR spectral analysis showed the uncyclised *N*-pentyl-3-phenylpropylamine, identical to an authentic sample. No cyclised products, (**19f**) or (**20f**), were detected.

Independent synthesis of products from reactions of *N*-(ω-benzeneselenylalkyl)imines.

The following were prepared using the general procedure for amine synthesis (method B):

(a) N-(4-Methylbenzyl)pyrrolidine (**19b**).[46] Colourless oil (40%) from 4-methylbenzyl bromide and pyrrolidine; b.p. 207 °C at 10 mmHg; (Found: C, 68.04; H, 8.79; N, 6.69. $C_{12}H_{17}N.HCl$ requires C, 68.09; H, 8.51; N, 6.62%); ν_{max} /cm^{-1} 3025, 2925, 2780, 1616, 1515, 1459, 1445, 1374, 881, and 807; δ_H 7.19 (2 H, d, *J* 8.0 Hz), 7.09 (2 H, d, *J* 8.0 Hz), 3.55 (2 H, s, $ArCH_2N$), 2.47 (4 H, t, *J* 6.8 Hz, RCH_2N), 2.31 (3 H, s, Me), and 1.73 (4 H, m, pyrrolidine-3,4-H); δ_C 136.26 and 136.22 (Ar-C), 128.83 and 128.80 (Ar-CH), 60.39 and 54.06 (CH_2N), 23.37 (pyrrolidine-3,4-C), and 21.07 (Me); *m/z* 175.1349 [M^+, (16%), $C_{12}H_{17}N$ requires 175.1361], 174 (28), 146 (48), 136 (26), 119 (38), 105 (100), and 91 (54).

(b) 4-Methyl-N-pentylbenzylamine. Colourless oil (43%) from 4-methylbenzyl bromide and *n*-pentylamine; ν_{max} /cm^{-1} 3308, 2926, 2859, 1665, 1604, 1547, 1515, 1377, 1114, 805, and 731; δ_H 7.21 (2 H, d, *J* 7.0 Hz), 7.12 (2 H, d, *J* 7.0 Hz), 3.75 (2H, s, $ArCH_2N$), 2.80 (1 H, s, NH), 2.61 (2 H, t, *J* 7.0 Hz, RCH_2N), 2.31 (3 H, s, ArMe), 1.48-1.54 (2 H, m, 2-H), 1.22-1.32 (4 H, m, 3,4-H), and 0.88 (3 H, t, *J* 7.0 Hz, 5-H); δ_C 136.99 (Ar-C), 136.08 (Ar-CH), 128.77 (Ar-CH) 128.20 (Ar-CH), 57.80 and 49.26 (CH_2N), 32.35 (2-C), 26.69, (3-C) 22.63 (4-C), 21.10 (Me), and 14.16 (5-C); *m/z* 191.1674 [M^+ (4%), $C_{13}H_{21}N$ requires 191.1674] 146 (7), 134 (30), 105 (100), 91 (25), 72 (11), and 30 (72).

(c) N-(4-methylbenzyl)piperidine (**19e**).[48] Colourless oil (43%) from 4-methylbenzyl bromide and piperidine; (Found: C, 69.05; H, 9.15; N, 6.32. $C_{13}H_{19}N.HCl$ requires C, 69.18; H, 8.87; N, 6.21%); ν_{max}

/cm^{-1} 3024, 2924, 2858, 1616, 1516, 1470, 1443, 1370, 1352, 806, and 779; δ_H 7.19 (2 H, d, *J* 8.0 Hz), 7.09 (2 H, d, *J* 8.0 Hz), 3.38 (2 H, s, $ArCH_2N$), 2.34 (4 H, t, *J* 7.4 Hz, RCH_2N), 2.31 (3 H, s, Me), 1.55 (4 H, m, piperidine-3,5-H), and 1.41 (2 H, m, piperidine-4-H); δ_C 136.32 and 135.47 (Ar-C), 129.17 and 128.75 (Ar-CH), 63.61 and 54.42 (CH_2N), 25.99 (3,5-C), 24.43 (4-C), and 21.07 (Me); *m/z* 189.1513 [M^+, (56%), $C_{13}H_{19}N$ requires 189.1517], 188 (54), 146 (5), 105 (100), 98 (69), and 77 (14).

(d) N-(3-Phenylpropyl)pyrrolidine (**19c**).[47] Colourless oil (56%) from 1-bromo-3-phenylpropane and pyrrolidine; (Found: C, 67.22; H, 9.07; N, 5.89. $C_{13}H_{19}N.HCl.H_2O$ requires C, 66.50; H, 9.01; N, 5.97%); ν_{max} /cm^{-1} 3026, 2938, 2875, 1603, 1497, 1454, 1351, 1146, 1123, 745, and 699; δ_H 7.15-7.32 (5 H, m), 2.65 (2 H, t, *J* 7.0 Hz, propyl 1-H), 2.48 (6 H, m, pyrrolidine-2,5-H and propyl 3-H), and 1.74-1.87 (6 H, m, propyl 2-H and pyrrolidine-3,4-H); δ_C 142.20 (Ar-C), 128.30, 128.21 and 125.63 (Ar-CH), 56.02 and 54.11 (CH_2N), 33.87 (propyl 3-C), 30.63 (propyl 2-C), and 23.35 (pyrrolidine-3,4-C); *m/z* 189.1519 [M^+ (6%), $C_{13}H_{19}N$ requires 189.1517], 91 (9), 84 (100), and 42 (9).

(e) N-(3-Phenylpropyl)piperidine (**19f**). Colourless oil (46%) from 1-bromo-3-phenylpropane and piperidine; (Found: C, 70.16; H, 9.63; N, 5.70. $C_{14}H_{21}N.HCl$ requires C, 70.10; H, 9.25; N, 5.84%); ν_{max} /cm^{-1} 3026, 2935, 2854, 1605, 1496, 1445, 1351, 1267, 1123, 747, and 700; δ_H 7.12-7.27 (5 H, m), 2.60 (2 H, t, J 7.7 Hz, propyl 1-H), 2.35 (4 H, m, piperidine-2,6-H), 1.83 (2 H, m, propyl 3-H), 1.52-1.62 (6 H, m, piperidine-3,5-H and propyl 2-H), and 1.42 (2 H, m, piperidine-4-H); δ_C 142.20 (Ar-C), 128.27, 128.15 and 125.57 (Ar-CH), 58.79 and 54.49 (CH_2N), 33.81 (propyl 3-C), 28.51 (propyl 2-C), 25.89 (3,5-C), and 24.40 (4-C); *m/z* 203.1692 [M^+ (4%), $C_{14}H_{21}N$ requires 203.1674], 127 (14), 98 (100), 91 (10), and 84 (28).

(f) N-Pentyl-3-phenylpropylamine. Colourless oil (47%) from 1-bromo-3-phenylpropane and pentylamine; ν_{max}/cm^{-1} 3312, 2955, 2858, 1665, 1604, 1496, 1465, 1454, 1372, 1242, 1128, 746, and 699; δ_H 7.12-7.28 (5 H, m), 2.62 (2 H, t, *J* 7.0 Hz, propyl 1-H), 2.57 (2 H, t, *J* 7.3 Hz, pentyl 1-H), 1.78-1.84 (2 H, m, propyl 3-H), 1.44-1.47 (2 H, m, propyl 2-H), 1.20-1.30 (6 H, m, 2,3,4-H), and 0.89 (3 H, t, *J* 6.8 Hz, 5-H); δ_C 142.15 (Ar-C), 128.35, 125.78 and 125.68 (Ar-CH), 49.99 and 49.52 (CH_2N), 33.76 (propyl 3-C), 31.68 (propyl 2-C), 29.75 (2-C), 29.62 (3-C), 22.72 (4-C), and 14.09 (5-C); *m/z* 205.1832 [M^+ (10%), $C_{14}H_{23}N$ requires 205.1830], 148 (22), 118 (4), 100 (48), 91 (32), and 44 (100).

General procedure for amine synthesis (method E). (a) *2-(p-Tolyl)piperidine* (**20b**).[47] Freshly distilled *p*-bromotoluene (1.17 g, 8.5 mmol) and magnesium (1.43 g, 60 mmol, 7 equiv.) were stirred in dry diethyl ether (25 cm^3) at 34 °C for 2 h until the Grignard reagent formed. The solution was cooled down to 0 °C and a solution of 5-chloropentanonitrile (1.00 g, 8.5 mmol) in diethyl ether (5 cm^3) were added dropwise, and the solution stirred overnight at r.t. An excess of lithium aluminium hydride (289 mg, 8.5 mmol) was added and the reaction mixture stirred for a further 3 h. The reaction was quenched by the dropwise addition of 1 M aqueous sodium hydroxide solution, the ether layer separated, filtered, and extracted with dilute hydrochloric acid. The acid solution was neutralised with sodium carbonate and extracted into dichloromethane. The organic extracts were dried and evaporated to dryness to yield 2-*p*-tolylpiperidine as an orange oil (680 mg, 46%); ν_{max} /cm^{-1} 3329, 3027, 2936, 2860, 1670, 1604, 1496, 1458, 1446, 1380, 1117, 730, and 695; δ_H 7.23 (2 H, d, *J* 7.8 Hz), 7.15 (2 H, d, *J* 7.8 Hz), 3.54 (1 H, m, 2-H), 3.50 (1 H, s, NH), 2.90 and 3.12 (2 H, 2 x m, 6-H), 2.33 (3 H, s, ArMe), and 1.40-1.81 (6 H, m, 3,4,5-H); δ_C 137.81 (Ar-C), 129.02 (Ar-CH), 128.21 (Ar-C), 125.29 (Ar-CH), 65.60 (2-C), 45.02 (6-C), 31.96 (5-C), 27.38 (3-C), 24.03 (4-C), and 21.44 (Me); *m/z* 175.1365 [M^+ (0.75%), $C_{12}H_{17}N$ requires 175.1361] 105 (6), 98 (100), 91 (6.0), 83 (7.4), 77 (4.2), 55 (13), and 41 (15).

(b) 2-(2-Phenylethyl)piperidine (**20c**).[50] Red oil (19%) from 1-bromo-2-phenylethane and 5-chloropentanonitrile; ν_{max} /cm^{-1} 2937, 2864, 1655 1604, 1497, 1454, 1311, 1117, 911, 731, and 701; δ_H 7.18-7.27 (5 H, m), 4.98 (1 H, s, NH), 3.48-3.54 (3 H, m, 2,6-H), 2.89 (2 H, m, ethyl 2-H), 2.73 (2 H, m, ethyl 1-H), and 1.71-1.96 (6 H, m, 3,4,5-H); δ_C 140.29 (Ar-C), 128.32, 128.26 and 126.25 (Ar-CH), 56.72 (CHN), 44.62 (6-C), 41.99 (ethyl 1-C), 34.78 (ethyl 2-C), 31.28, 22.44, and 22.15 (piperidine-3,4,5-C).

Acetylation of amines. (a) N-Acetyl-2-(p-tolyl)piperidine. Orange oil (24%); ν_{max} /cm^{-1} 2937, 2864, 1640, 1609, 1450, 1428, 1312, 1222, 1119, and 649; δ_H 7.21-7.24 (4 H, m), 3.59 (1 H, t, *J* 6.1 Hz, 2-H), 2.87 (2 H, t, *J* 7.8 Hz, 6-H), 2.34 (3 H, s, MeAr), 2.24 (3 H, s, MeCO), 2.15-2.19 (2 H, m, 3-H), and 1.44-1.74 (4

H, m, 4,5-H); *m/z* 217.1458 [M^+ (1.6%), $C_{14}H_{19}NO$ requires 217.1467], 146 (6), 98 (11), 91 (17), 72 (20), 55 (18), and 30 (100).

(b) N-Acetyl-4-methyl-N-pentylbenzylamine. Yellow oil (45%); ν_{max} /cm^{-1} 2958, 2858, 1650, 1604, 1516, 1456, 1377, 924, and 731; δ_H (2 stereoisomers) 7.26 (2 H, d, *J* 7.1 Hz), 7.14 (2 H, d, *J* 7.1 Hz), 4.56 and 4.49 (2 H, 2 x s, $ArCH_2N$), 3.34 and 3.17 (2 H, 2 x t, *J* 7.5 Hz, 1-H), 2.34 and 2.32 (3 H, 2 x s, ArMe), 2.17 and 2.13 (3 H, 2 x s, Ac), 1.52-1.56 (2 H, m, *J* 7.5 Hz, 2-H), 1.20-1.25 (4 H, m, *J* 7.5 Hz, 3,4-H), and 0.88 (3 H, t, *J* 6.9 Hz, 5-H); δ_C (2 stereoisomers) 171.09 and 170.66 (C=O), 134.45, 133.57, 132.21 and 129.93 (Ar-C), 129.49, 129.14, 127.99 and 125.42 (Ar-CH), 56.24, 51.69, 47.76 and 46.05 (CH_2N), 28.88 (2-C), 27.90 (3-C), 22.28 (4-C), 21.98 and 21.66 (MeCO), 21.30 and 21.20 (MeAr), and 13.87 (5-C); *m/z* 233.1783 [M^+ (18%), $C_{15}H_{23}NO$ requires 233.1780], 162 (9), 134 (17), 120 (33), 105 (100), 72 (9.9), and 43 (23).

(c) N-Acetyl-2-(2-phenylethyl)piperidine. Red oil (34%); ν_{max} /cm^{-1} 2936, 2862, 1634, 1604, 1548, 1496, 1423, 1371, 751, and 701; δ_H (2 isomers) 7.20-7.34 (5 H, m), 3.30 (1 H, m, piperidine 2-H), 3.18 and 2.89 (2 H, 2 x m, 6-H), 2.54-2.65 (2 H, m, Et 2-H), 2.07 and 2.03 (3 H, 2 s, MeCO), 1.93-2.00 (2 H, m, Et 1-H), and 1.58-1.66 (6 H, m, 3,4,5-H); δ_C (2 isomers) 165.82 (C=O), 132.82 and 132.55 (Ar-C), 128.27, 128.22, 128.56, 128.31, 125.86 and 125.76 (Ar-CH), 53.12 and 48.88 (CHN), 41.83 and 36.38 (CH_2N), 32.73 and 31.71 (Et 2-C) 28.27 (5-C), 26.25 (3-C), 21.99 and 21.51 (MeCO), and 19.05 (4-C); *m/z* 231.1623 [M^+ (7%), $C_{15}H_{21}NO$ requires 213.1623] 133 (15), 126 (38), 105 (30), 91 (48), 84 (100), 77 (11), and 55 (29).

Cyclisation of 4-Benzeneselenyl-*N*-(2-phenylcyclohexylidene)-1-butylamine (23a)

The imine from 4-benzeneselenylbutylamine (**8**, n = 1) (274 mg, 1.2 mmol) and 2-phenylcyclohexanone (209 mg, 1.2 mmol) was formed and reacted with Bu_3SnH (1.6 mmol) using the general procedure to yield an oil (165 mg). The crude product was purified by flash chromatography using TLC alumina as absorbent to yield *N*-(2-phenylcyclohexyl)pyrrolidine (**24a**) as the only product (55%, by ^{1}H NMR spectroscopy); yellow oil; ν_{max} /cm^{-1} 3025, 2926, 2763, 1634, 1601, 1496, 1454, 1224, 1172, 1121, and 1033; δ_H 7.28-7.34 (5 H, m), 3.40-3.48 (2 H, m, cyclohexyl 1-H and 2-H), 2.87-2.91 and 3.22-3.26 (4 H, 2 x m, pyrrolidine 2,5-H), 1.60-1.76, 1.92-2.10 and 2.15-2.25 (12 H, 3 x m); δ_C 144.88 (Ar-C), 128.62, 127.69 and 125.36 (Ph-*C*H), 67.09 (CHN), 52.63 (pyrrolidine 2,5-C), 45.11, (cyclohexyl 2-C), 30.11, 29.05, 24.31, 23.45 and 23.17; *m/z* 229.1817 [M^+ (27%), $C_{16}H_{23}N$ requires 229.1830], 130 (13), 117 (10), 110 (100), 91 (22), 84 (26), 70 (25), and 43 (44). The product was identical to an authentic sample prepared from 2-phenylcyclohexanone and pyrrolidine using the method for amine (**24b**).

Cyclisation of 4-benzeneselenyl-*N*-(1,2,3,4-tetrahydronaphth-2-ylidene)-1-butylamine (23b).

The imine from 4-benzeneselenylbutylamine (**8**, n = 1) (428 mg, 1.88 mmol) and 2-tetralone (274 mg, 1.88 mmol) was formed and reacted with Bu_3SnH using the general procedure to yield an oil (379 mg). GLC and ^{1}H NMR spectral analysis showed *exo* (**24b**) (19%) and 2-(1-butylamino)-1,2,3,4-tetrahydronaphthalene (20%).[51] Both were identical to authentic samples.

(a) 2-(1-Pyrrolidinyl)-1,2,3,4-tetrahydronaphthalene (**24b**). 2-(1-Pyrrolidinyl)-3,4-dihydronaphthalene was obtained from 2-tetralone and pyrrolidine (refluxing toluene with a Dean-Stark water separator) and reduced with $NaBH_4$ in ethanol in the presence of *p*-toluenesulfonic acid to yield the amine after flash chromatography using TLC alumina as absorbent; ν_{max} /cm^{-1} 2972, 1606, 1562, 1482, 1455, 1412, 1365, 1214, 908, 733, and 651; δ_H 7.03 (2 H, m), 6.77 (2 H, m), 3.39 (1 H, s, 2-H), 3.25 (4 H, t, *J* 6.8 Hz, pyrrolidine 2,5-H), 2.81 (2 H, t, *J* 7.5 Hz, 3-H), 2.68 (2 H, m, 1-H), 2.45 (2 H, t, *J* 7.5 Hz, 4-H), and 1.90 (4 H, t, *J* 6.8 Hz, pyrrolidine 3,4-H); δ_C 130.05 (Ar-C), 126.51, 125.73, 125.64 and 122.73 (Ar-CH), 121.59 (Ar-C), 60.95 (2-C), 51.72, (pyrrolidine 2,5-C), 47.30 (2-C), 26.25, 25.12, and 23.24 (1,3,4-C); *m/z* 201.1518 [M^+ (78%), $C_{14}H_{19}N$ requires 201.1518], 199 (55), 141 (16), 128 (39), 115 (31), 97 (34), 96 (100), 91 (26), and 84 (17).

(b) N-Butyl-1,2,3,4-tetrahydro-2-naphthylamine.[51] The amine was synthesised using method A from *n*-butylamine and 2-tetralone as a red oil; ν_{max} /cm^{-1} 3408, 3048, 2923, 2868, 1628, 1598, 1567, 1482, 1340, 1196, 787, and 649; δ_H 7.01-7.12 (4 H, m), 3.75 (1 H, s, NH), 3.03 (1 H, m, NH), 3.46 (1 H, m, 2-H) 3.04-3.07 (2 H, m, 1-H), 2.73-2.87 (4 H, m, ethyl 3,4-H), 1.56-1.65 (2 H, m, butyl 1-H), 1.32-1.38 (4 H, m, butyl 2,3-H), and 0.95 (3 H, t, *J* 7.5 Hz, butyl 4-H); δ_C 136.25 (Ar-C), 134.52, 129.32, 128.65 and 125.98 (Ar-

CH), 125.60 (Ar-C), 53.85 (CHN), 46.22 (CH_2N), 35.40, 31.22, 28.58, 28.01 and 20.49 (tetralin 1,3,4-C and butyl 2,3-C, and 13.91 (4-C); *m/z* 203.1635 [M^+ (47%), $C_{14}H_{21}N$ requires 203.1674], 160 (97), 131 (100), 115 (34), 104 (25), 91 (33), and 57 (47).

Synthesis of hydrazones

(a) 1-(5-Benzeneselenylpent-1-ylidene)-2-phenylhydrazine (**25a**). *General procedure for the synthesis of hydrazones*. Phenylhydrazine (179 mg, 1.66 mmol) and 5-benzeneselenylpentanal (400 mg, 1.66 mmol) were heated under reflux in dry toluene (50 cm^3) using a Dean-Stark water separator for 3 h. The solution was evaporated to dryness and the hydrazone purified by flash sinter chromatography to yield (**25a**) as an orange-red oil (495 mg, 90%); ν_{max} /cm^{-1} 3343, 3027, 2921, 1688, 1604, 1579, 1478, 1438, 1380, 1081, 1023, and 729; δ_H 7.43-7.49 (2 H, m, PhSe *o*-H), 7.18-7.26 (9 H, m, Ph-H, CH=N), 4.29 (1 H, brs, NH), 2.89 (2 H, t, 5-H), 2.38 (2 H, t, *J* 7.0, 2-H), and 1.70-1.76 (4 H, m, 3,4-H); δ_C 136.05, 132.62, 129.29, 128.20, 127.30, 126.95, 122.71, 121.09 (Ph-C), 113.51 (C=N), 43.23, 29.52, 27.27, and 25.47 (CH_2); *m/z* 332.0781 [M^+ (0.2%), $C_{17}H_{20}N_2Se$ requires 332.0791], 157 (38), 108 (30), 91 (45), 77 (100), 65 (40), 51 (60), and 39 (53).

(b) 1-(5-Benzeneselenylpentylidene)-2-benzoylhydrazine (**25b**). Yellow oil; ν_{max} /cm^{-1} 3307, 3058, 2933, 1656, 1603, 1578, 1478, 1437, 1288, 1073, 1023, 737, and 692; δ_H 7.72-7.85 (3 H, m, benzoyl-H, imine H), 7.47-7.53 (2 H, m, PhSe *o*-H),7.34-7.41 (3 H, m, benzoyl-H), 7.20-7.28 (3 H, m, PhSe), 3.45 (1 H, m, NH), 2.90 (2 H, t, *J* 7.4 Hz, 5-H), 2.35 (2 H, m, 2-H), and 1.49-1.75 (4 H, m, 3,4-H); δ_C 168.56 (C=O), 152.20 (C=N), 132.43, 132.16, 128.98 and 128.93 (Ar-CH), 128.62 and 126.83 (Ar-C), 126.70 and 126.61 (Ar-CH), 32.06, 28.97, 27.30, and 25.81 (CH_2); *m/z* (CI) 361.0819 [MH^+ (11%), $C_{18}H_{21}N_2OSe$ requires 361.0819], 239 (100), 225 (25), 205 (22), 139 (42), 122 (52), and 105 (14).

(c) 1-(5-Benzeneselenylpentylidene)semicarbazide (**25c**). A standard procedure for semicarbazide formation gave an oil; ν_{max} /cm^{-1} 3461, 3070, 2930, 2835, 1702, 1684, 1634, 1576, 1479, 1436, 1134, 731 and 690; δ_H (d^6-acetone) 7.41-7.46 (2 H, m, PhSe *o*-H), 7.18-7.24 (3 H, m, Ph-H), 7.15 (1 H, t, *J* 5.5 Hz, 1-H), 6.11 (1 H, s, NH), 3.41 (2 H, s, NH_2), 2.94 (2 H, m, 5-H), 2.14 (2 H, m, 2-H), 1.63-1.69 (2 H, m), and 1.38-1.43 (2 H, m); δ_C 161.96 (C=O), 148.14 (C=N), 136.47 (Ar-CH), 135.33 (Ar-C), 134.21 and 131.44 (Ar-CH), 35.06, 34.25, 31.41, and 31.15 (CH_2); *m/z* (CI) 300.0615 [MH^+ (37%), $C_{12}H_{19}N_3O$ requires 300.0615], 277 (18), 224 (76), 157 (62), 125 (100), 78 (83), 67 (87), 55 (93), and 41 (88).

(d) 1-(5-Benzeneselenylpentylidene)-2,2-diphenylhydrazine (**25d**). Oil; ν_{max} /cm^{-1} 3058, 2930, 2855, 1596, 1578, 1495, 1479, 1438, 1300, 1211, 1072, 748, and 638; δ_H 7.43-7.47 (2 H, m, PhSe *o*-H), 7.30-7.36 (4 H, m, Ph *o*-H), 7.19-7.23 (3 H, m, PhSe), 7.03-7.10 (6 H, m, Ph), 6.47 (1 H, t, *J* 4.3 Hz, CH=N), 2.90 (2 H, t, *J* 8.0 Hz, 5-H), 2.25 (2 H, m, 2-C), 1.65-1.71 (2 H, m), and 1.56-1.61 (2 H, m); δ_C 144.20 (C=N), 139.12, 132.34 and 129.64 (Ar-CH), 129.28 (Ar-C) 128.97 (Ar-CH), 126.62 (Ar-C), 123.85 and 122.29 (Ar-CH), 32.03, 29.01, 27.48 and 27.05 (CH_2); *m/z* 408.1107 [M^+ (12%), $C_{23}H_{24}N_2Se$ requires 408.1104], 183 (39), 168 (100), 91 (9.1), 77 (46), and 51 (35).

(e) 1-(6-Benzeneselenylhexylidene)-2-benzoylhydrazine (**25e**). Yellow oil (80%); ν_{max} /cm^{-1} 3236, 3063, 2935, 1656 , 1604, 1580, 1478, 1438, 1366, 1286, 1023, and 732; δ_H 9.20 (1 H, s, NH), 7.77-7.82 (3 H, m, benzoyl *o*-H, imine-H), 7.41-7.50 and 7.20-7.26 (8 H, m), 2.89 (2 H, t, *J* 7.0 Hz, 6-H), 2.35-2.42 (2 H, m, 2-H), and 1.45-1.55 (6 H, m, 3,4,5-H); δ_C 168.56 (C=O), 155.60 (C=N), 132.53 and 131.77 (Ar-CH), 130.15 (Ar-C), 128.98, 128.49, 127.20 and 126.67 (Ar-CH), 30.01, 29.45, 27.54, 25.94, and 25.15 (CH_2); *m/z* (CI) 375.0976 [MH^+ (100%), $C_{17}H_{19}NSe$ requires 375.0976], 256 (11), 219 (31), 139 (34), 122 (34), 105 (15).

(f) 1-(6-Benzeneselenylhexylidene)-2,2-diphenylhydrazine (**25f**). Oil; ν_{max} /cm^{-1} 3058, 2930, 1596, 1578, 1495, 1479, 1438, 1211, 1072, 748, and 638; δ_H 7.46-7.49 (2 H, m, PhSe *o*-H), 7.10-7.27 (13 H, m), 6.47 (1 H, t, *J* 7.0 Hz, 1-H), 2.91 (2 H, t, *J* 7.0 Hz, 6-H), 2.15-2.20 (2 H, m, 2-H), and 1.35-1.65 (6 H, m, 3,4,5-H); δ_C 144.31 (Ar-C), 139.65 (C=N), 132.34, (Ar-CH), 130.15 (Ar-C), 129.65, 129.16, 128.21, 128.82, and 122.34 (Ar-CH), 32.51, 29.85, 29.29, 27.75, and 27.43 (CH_2); *m/z* 422.1261 [M^+ (13%), $C_{24}H_{26}N_2Se$ requires 422.1261], 206 (6), 183 (20), 168 (100), 155 (8), 140 (4), 115 (7), 91 (8), and 77 (22).

Cyclisation of 1-(5-Benzeneselenylpentylidene)hydrazines.

(a) Cyclisation of 1-(5-Benzeneselenylpentylidene)-2-phenylhydrazine. The hydrazone (203 mg, 0.84 mmol) was reacted with Bu_3SnH using the general procedure and standard purification gave (**28a**) (26 mg, 18%), which was found to be identical to an authentic sample. Repeated cyclisations gave yields in the range of 6-18%.

1-Cyclopentyl-2-phenylhydrazine (**28a**).[52] The crude hydrazone from cyclopentanone and phenylhydrazine was reduced with lithium aluminium hydride in diethyl ether and the product purified using flash chromatography to yield (**28a**) as a red oil; ν_{max} /cm^{-1} 3054, 2929, 2855, 1617, 1517, 1422, 896, and 738; δ_H 7.47 (1 H, m, NH), 7.17-7.23 (3 H, m, Ph), 6.99-7.03 (2 H, m, Ph *o*-H), 6.80 (1 H, m, 1-H), 6.67 (1 H, s, NH), 2.42-4.48 (2 H, m, 2(5)-H), 2.19-2.24 [2 H, m, 5(2)-H] and 1.68-1.84 (4 H, m, 3,4-H); δ_C 129.45 (ArCH), 128.31 (ArC), 119.46, 112.96 (ArCH), 112.82 (1-C), 33.10, 26.45, and 24.95 (CH_2); *m/z* 176.1323 [M^+ (1.7%), $C_{11}H_{16}N_2$ requires 176.1313], 146 (100), 132 (50), 106 (44), 94 (26), 91 (51), 82 (27), 77 (45), and 65 (42).

(b) Cyclisation of 1-(5-Benzeneselenylpentylidene)-2-benzoylhydrazine (**25b**). Reaction of the hydrazone (480 mg, 0.98 mmol) with Bu_3SnH gave a crude oil (229 mg) which on purification gave (**28b**) (136 mg, 50%), which was identical to an authentic sample.

1-Benzoyl-2-cyclopentylhydrazine (**28b**). The hydrazone from benzoylhydrazine and cyclopentanone was reduced with sodium borohydride in ethanol to yield (**28b**) as a yellow oil; hydrazone: (Found: C, 71.28; H, 6.78; N, 13.56. $C_{12}H_{14}N_2O$ requires C, 71.29; H, 6.93; N, 14.86%); ν_{max} /cm^{-1} 3218, 2933, 1664, 1603, 1537, 1413, 1378, 1210, 1076, and 874; δ_H 8.57 (1 H, s, NH), 7.77-7.80 (2 H, m), 7.40-7.50 (3 H, m), 2.53-2.58 (2 H, m), 2.31-2.37 (2 H, m), and 1.74-1.96 (4 H, m); (**28b**): ν_{max} /cm^{-1} 3360, 2927, 1649, 1630, 1578, 1458, and 1438; δ_H 7.75-7.78 (2 H, m), 7.40-7.48 (3 H, m), 3.63 (1 H, t, *J* 6.5 Hz, cyclopentyl 1-H), 3.40-3.50 (2 H, brs, NH), 1.72-1.74 (4 H, m), and 1.30-1.52 (4 H, m); δ_C 167.80 (C=O), 131.74 and 128.59 (Ar-CH), 127.50 (Ar-C), 126.89 (Ar-CH), 61.75 (cyclopentyl 1-C), and 30.96 and 24.04 (CH_2); *m/z* 204.1261 [M^+ (6.8%), $C_{12}H_{16}N_2O$ requires 204.1263], 169 (10), 122 (42), 105 (100), 84 (48), 77 (49), 69 (25), and 41 (36).

(c) Cyclisation of 1-(5-Benzeneselenylpentylidene)semicarbazide (**25c**). Reaction of the hydrazone (160 mg, 0.54 mmol) using the standard procedure gave (**28c**) (46 mg, 60%), identical to an authentic sample.

1-Cyclopentylsemicarbazide (**28c**). The semicarbazone of cyclopentanone was reduced with sodium borohydride in ethanol and recrystallised (EtOAc/Et_2O) to yield crystals of (**28c**), m.p. 149-151 °C; hydrazone: (Found: C, 50.58; H, 7.83; N, 29.76. $C_6H_{11}N_3O$ requires C, 51.06; H, 7.80; N, 92.79%); ν_{max} (Nujol)/cm^{-1}, 3453, 1669 (C=N), 1409, 1239, 1163, and 722; δ_H (d^6-DMSO).7.56 (1 H, s NH), 5.31 (2 H, s, NH_2), 2.38 (2 H, t, *J* 7.5 Hz, 2(5)-H), 2.21 [2 H, t, *J* 7.5 Hz, 5(2)-H], and 1.69-1.88 (4 H, m, 3,4-H); hydrazine: (Found: C, 50.40; H, 9.43; N, 29.10. $C_6H_{13}N_3O$ requires C, 50.35; H, 9.09; N, 29.37%); ν_{max} (Nujol)/cm^{-1} 3430, 3290, 1691, 1584, and 722; δ_H 6.69 (1 H, s, NH), 5.63 (1.H, s, NH), 3.29-3.36 (1 H, m, cyclopentyl 1-H), 2.90-3.60 (2 H, brs, NH_2), and 1.33-1.71 (8 H, m, 2,3,4,5-C); δ_C 161.75 (C=O), 62.26 (CH), 30.63 and 23.94 (CH_2); *m/z* 143.1052 [M^+ (7.7%), $C_6H_{13}N_3O$ requires 143.1057], 144 (81), 97 (17), 84 (100), 71 (30), and 41 (63).

(d) Cyclisation of 1-(5-Benzeneselenylpentylidene)-2,2-diphenylhydrazine. The hydrazone (407 mg, 1.0 mmol) gave (**28d**) (70 mg, 32%), identical to an authentic sample.

1-Cyclopentyl-2,2-diphenylhydrazine (**28d**). The hydrazone from 1,1-diphenylhydrazine and cyclopentanone was reduced with lithium aluminium hydride in diethyl ether to yield (**28d**); ν_{max} /cm^{-1} 3305 3060, 2954, 1588, 1498, 1360, 1212, 1090, 1028, 749, and 692; δ_H 7.21-7.34 and 7.02, 7.14 (10 H, m), 3.25 (1 H, m, cyclopentyl 1-H), 2.90-3.00 (1 H, s, NH), 2.02-2.10 (2 H, m) 1.78-1.87 (2 H, m), and 1.40-1.61 (4 H, m, cyclopentyl); δ_C 129.16 (Ar-CH), 129.65 (Ar-C), 122.47 and 120.46 (Ar-CH), 65.58 (1-C), 33.70, and 28.83 (CH_2); *m/z* 252.1612 [M^+ (7.5%), $C_{17}H_{20}N_2$ requires 252.1626], 183 (75), 168 (100), 77 (46), and 51 (35).

(e) Attempted cyclisation of 1-(6-benzeneselenylhexylidene)-2-benzoylhydrazine. The hydrazone (261 mg, 0.70 mmol) gave the uncyclised 1-benzoyl-2-hexylidenehydrazine (64 mg, 42%) as the only isolable product, identical to an authentic sample.

1-Benzoyl-2-hexylidenehydrazine. Colourless crystals, m.p. 177-179 °C (EtOAc/Et_2O), from benzoylhydrazine and hexanal; (Found: C, 71.86; H, 8.38; N, 12.68. $C_{13}H_{18}N_2O$ requires C, 71.52; H, 8.31; N, 12.83%); ν_{max} /cm^{-1} 3300, 3050, 2952, 2884, 1747, 1643, 1604, 1534, 1450, and 1290; δ_H 7.82-7.85 (2.H, m, benzoyl *o*-H),

7.75 (1 H, t, *J* 4.8 Hz, 1-H), 7.28-7.43 (3 H, m), 2.20-2.31 (2 H, m, 2-H), 1.58-1.62 (2 H, m), 1.25-1.44 (4 H, m), and 0.88 (3 H, t, *J* 6.4 Hz, 6-H); δ_C 164.51 (C=O), 153.56 (C=N), 132.60, 131.56 (Ar-CH), 130.03 and 129.88 (Ar-C), 129.07, 128.28, 127.49, 126.61 (Ar-CH), 32.44, 31.33, 26.21 and 22.30 (CH_2), and 13.82 (6-C); *m/z* 218.1407 [M^+ (3.3%), $C_{13}H_{18}N_2O$ requires 218.1419], 217 (30), 186 (29), 163 (23), 155 (56), 132 (38), 124 (33), 113 (50), 70 (30), 51 (100), and 28 (89).

(f) Attempted cyclisation of 1-(5-benzeneselenylhexylidene)-2,2-diphenylhydrazine (**25f**). The hydrazone (358 mg, 0.85 mmol) was reacted with Bu_3SnH using the standard conditions to yield the uncyclised 1-hexylidene-2,2-diphenylhydrazine (46 mg, 20%), identical to an authentic sample, as the only isolable product. *1-Hexylidene-2,2-diphenylhydrazine*. Oil; ν_{max} /cm^{-1} 3061, 1687, 1596, 1496, 1456, 1300, 1211, 1091, 748, and 701; δ_H 7.31-7.38 and 7.05-7.12 (10 H, m), 6.53 (1 H, t, *J* 5.5 Hz, 1-H), 2.20-2.30 (2 H, m, 2-H), 1.41-1.52 (2 H, m), 1.28-1.33 (4 H, m), and 0.90 (3 H, t, *J* 7.2 Hz, 6-H); δ_C 144.27 (Ar-C), 140.32 (C=N), 129.57, 123.71 and 122.30 (Ar-CH), 32.64, 31.37, 26.67 and 22.40 (CH_2), and 13.94 (Me); *m/z* 266.1802 [M^+ (29%), $C_{18}H_{22}N_2$ requires 266.1783], 168 (100), 155 (15), 124 (9), 113 (15), 77 (28), and 51 (33).

1-[(5-Benzeneselenylpentylidene)amino]-2*S*-methoxymethylpyrrolidine.

(a) Synthesis. *S*-1-Amino-2-methoxymethylpyrrolidine (210 mg, 1.54 mmol) and 5-benzeneselenylpentanal (370 mg, 1.54 mmol) were reacted using the general procedure for the synthesis of hydrazones to give (**29a**) as an orange oil (480 mg, 88%); ν_{max} /cm^{-1} 3058, 3025, 2920, 1579, 1478, 1438, 1379, 1310, 1197, 1023, 731, and 694; δ_H 7.44-7.48 (2 H, m, PhSe *o*-H), 7.20-7.26 (3 H, m), 3.55-3.58 (1 H, m, pyrrolidine 2-H), 3.27-3.43 (3 H, m), 3.35 (3 H, s, MeO), 2.90 (2 H, t, *J* 7.2 Hz, CH_2Se), 2.66-2.70 (1 H, m), 2.15-2.22 (2 H, m, 2-H), 1.68-1.92 (6 H, m), and 1.54-1.60 (2 H, m); δ_C 138.18 (C=N), 132.40 (Ar-CH), 130.80 (Ar-C), 128.99 and 128.71 (Ar-CH), 74.82 (CH_2O), 63.41 (CH_3O), 59.15 (CHN), 50.36 (CH_2N), 32.43, 29.58, 27.86, 27.58, 26.55, and 22.12 (CH_2); *m/z* 354.1210 [M^+ (4.8%), $C_{17}H_{26}N_2OSe$ requires 354.1210], 325 (36), 281 (14), 211 (30), 181 (21), 157 (100), 114 (38), 91 (54), 77 (78), and 70 (76); $[\alpha]_D^{20}$(CH_2Cl_2) -37.5.

(b) Cyclisation of 1-[(5-benzeneselenylpentylidene)amino]-2S-methoxymethylpyrrolidine (**29a**). Reaction between the hydrazone (353 mg, 1.0 mmol) and Bu_3SnH gave the 5-*exo* product, 1-cyclopentylamino-2*S*-methoxymethylpyrrolidine (**31a**) (84 mg, 42%); ν_{max} /cm^{-1} 2929, 2872, 1672, 1451, 1380, 1195, and 1105; δ_H 3.67-3.71 (1 H, m, cyclopentyl CHN), 3,44-3.53 (3 H, m) 3.23-3.32 (2 H, m), 3.28 (3 H, s, MeO), 2.07-2.11 (1 H, m), and 1.59-1.86 (11 H, m); δ_C 74.90 (CH_2O), 60.65 (MeO), 59.15 (pyrrolidine 2-C), 56.11 (cyclopentyl 1-C), 50.36 (CH_2N), 33.44, 30.47, 23.99, and 20.80 (CH_2); *m/z* 198.1703 [M^+ (3.3%), $C_{11}H_{22}N_2O$ requires 198.1732], 197 (15), 169 (29), 130 (22), 94 (30), 84 (86), 69 (37), 55 (31), 45 (88), and 41 (100); $[\alpha]_D^{20}$(CH_2Cl_2) -46.7.

1-[(5-Benzeneselenyl-2-methylpentylidene)amino]-2*S*-methoxymethylpyrrolidine (29b).

Synthesis. (a) Diethyl 2-(3-benzeneselenylpropyl)-2-methylpropanedioate. Sodium hydride (100 mg of 60% suspension in mineral oil) was placed in a dried flask under nitrogen and washed with dry light petroleum. Dry and distilled DMF (20 cm^3), followed by a solution of diethyl methylmalonate (348 mg, 2 mmol) in DMF (5 cm^3), was added to the suspension. After stirring at 50 °C for 30 min 1-benzeneselenyl-3-iodopropane (633 mg, 2 mmol) in DMF (5 cm^3) was added dropwise over 10 min. The mixture was stirred at 50 °C for 8 h and on cooling, water (20 cm^3) and 2 M hydrochloric acid (10 cm^3) were added, and the organic products extracted into diethyl ether. The extracts were washed with water, dried, evaporated to dryness, and the crude product purified using flash sinter chromatography to yield diethyl 2-(3-benzeneselenylpropyl)-2-methylpropanedioate as a yellow oil (640 mg, 86%); ν_{max} /cm^{-1} 3057, 2938, 1737, 1580, 1479, 1439, 1379, 1251, 1175, 1023, 737, and 691; δ_H 7.45-7.48 (2 H, m, Ph *o*-H), 7.21-7.26 (3 H, m), 4.13 (4 H, q, *J* 7.2 Hz, MeCH_2), 2.88 (2 H, t, *J* 7.2 Hz, CH_2Se), 1.94-2.01 (2 H, m), 1.61-1.67 (2 H, m), 1.36 (3 H, s, 2-Me), and 1.21 (6 H, t, *J* 7.2 Hz, CH_2CH_3); δ_C 172.15 (C=O), 132.60 (Ar-CH), 130.15 (Ar-C), 129.01 and 126.81 (Ar-CH), 61.19 (MeCH_2), 53.37 (2-C), 33.70, 27.77, and 25.06 (3,4,5-C), 19.93 (2-Me), and 14.02 (CH_2CH_3); *m/z* 372.0852 [M^+ (14%), $C_{17}H_{24}O_4Se$ requires 372.0840], 215 (100), 187 (26), 157 (40), 141 (70), 123 (31), 113 (36), and 85 (45).

(b) Ethyl 5-benzeneselenyl-2-methylpentanoate. Diethyl 2-(3-benzeneselenylpropyl)-2-methylpropanedioate (325 mg, 0.87 mmol), dissolved in freshly dried and distilled DMSO (1 cm^3), was added to a solution of lithium

chloride (100 mg, 1.31 mmol) in DMSO (2 cm^3) containing water (100 mg, 1.75 mmol). The mixture was heated at 170 °C for 24 h, cooled to r.t., and water (20 cm^3) and dilute hydrochloric acid (5 cm^3) added. The product was extracted into diethyl ether, the extracts were washed with water, dried, and evaporated to dryness. The residue was purified by flash sinter chromatography to yield ethyl 5-benzeneselenyl-2-methylpentanoate was isolated as a light yellow oil (208 mg, 80%); ν_{max} /cm^{-1} 3057, 2933, 1731, 1579, 1477, 1438, 1378, 1242, 1182, 1022, 735, and 690; δ_H 7.44-7.50 (2.H, m, Ph *o*-H), 7.22-7.28 (3 H, m), 4.12 (2 H, q, *J* 7.0 Hz, $MeCH_2$), 2.90 (2 H, t, *J* 7.2 Hz, 5-H), 2.35-2.43 (1 H, m, 2-H), 1.52-1.78 (4 H, m, 3,4-H) 1.22 (3 H, d, *J* 7.0 Hz, 2-Me), and 1.13 (3 H, t, *J* 7.2 Hz, CH_2CH_3); δ_C 171.15 (C=O), 131.53 (Ar-CH), 129.90 (Ar-C), 129.18 and 127.72 (Ar-CH), 60.45 ($MeCH_2$), 39.11 (2-C), 33.61, 27.81 and 27.57 (3,4,5-C), 17.10 (2-Me) and 14.23 (CH_2CH_3); *m/z* 300.0638 [M^+ (16%), $C_{14}H_{20}O_2Se$ requires 300.0628], 157 (50), 143 (100), 115 (86), 97 (13), 91 (17), 77 (51), 69 (85), and 41 (49).

(c) 5-Benzeneselenyl-2-methylpentanal. The general procedure for the synthesis of aldehydes was used, except that a reaction time of 2.5 h was employed. Ethyl 5-benzeneselenyl-2-methylpentanoate (323 mg, 1.08 mmol) gave 5-benzeneselenyl-2-methylpentanal as a yellow oil (167 mg, 70%); ν_{max} /cm^{-1} 3071, 2928, 2854, 1723, 1579, 1478, 1437, 1073, 1022, 735, and 691; δ_H 9.57 (1 H, s, 1-H), 7.45-7.50 (2 H, m, Ph *o*-H), 7.21-7.27 (3 H, m), 2.90 (2 H, t, *J* 7.1 Hz, 5-H), 2.31-2.35 (2 H, m, 2-H), 1.68-1.77 (4 H, m, 3,4-H), and 1.06 (3 H, d, *J* 6.9 Hz, 2-Me); δ_C 204.56 (C=O), 132.65 (Ar-CH), 130.15 (Ar-C), 129.03 and 126.86 (Ar-CH), 45.76 (2-C), 30.36, 27.58 and 27.40 (3,4,5-C), and 16.48 (2-Me); *m/z* 256.0349 [M^+ (30%), $C_{12}H_{16}OSe$ requires 256.0366], 158 (98), 124 (21), 113 (33), 99 (66), 83 (51), 77 (100), 51 (66), and 41 (72).

(d) 1-[(5-Benzeneselenyl-2-methylpentylidene)amino]-2S-methoxymethylpyrrolidine (**29b**). *S*-1-Amino-2-methoxymethylpyrrolidine (102 mg, 0.78 mmol) and 5-benzeneselenyl-2-methylpentanal (200 mg, 0.78 mmol) were reacted using the general procedure for the synthesis of hydrazones to yield (**29b**) as an orange oil (274 mg, 96%); ν_{max} /cm^{-1} 2926, 2855, 1579, 1478, 1438, 1379, 1196, 1099, 1073, 1023, 736, and 691; δ_H (2 diastereoisomers) 7.43-7.51 and 7.21-7.27 (6 H, m, Ph-H, imine-H), 3.29-3.42 (6 H, m), 2.95-3.02 (2 H, m, CH_2Se), 2.89-2.93 (1 H, m), 2.15-2.34 (2 H, m), 1.96-2.08 and 1.82-1.88 (8 H, m), and 1.02 and 0.88 (3 H, 2 x d, *J* 7.0 Hz, 2-Me); δ_C (2 diastereoisomers) 143.52 (C=N), 132.47 (Ar-CH), 130.05 (Ar-C), 129.15 and 126.79 (Ar-CH), 67.90 (CH_2O), 63.48 (CH_3O), 59.16 (CHN), 50.43 (CH_2N), 36.60 (side chain 2-C), 35.54, 32.74, 30.19, 27.67, and 22.06 (CH_2), and 19.60 (Me); *m/z* 368.1367 [M^+ (24%), $C_{18}H_{28}N_2OSe$ requires 368.1367], 323 (81 M^+-$MeOCH_2$), 176 (19), 157 (22), 91 (28), 77 (32), and 70 (100); $[\alpha]_D^{20}$(CH_2Cl_2) -32.6.

(e) Cyclisation of 1-[(5-Benzeneselenyl-2-methylpentylidene)amino]-2S-methoxymethylpyrrolidine (**29b**). The hydrazone (199 mg, 0.54 mmol) was reacted with Bu_3SnH to yield the 5-*exo* product, 1-(2-methylcyclopentyl)amino-2*S*-methoxymethylpyrrolidine (**31b**) (46 mg, 40%); ν_{max} /cm^{-1} 3200, 2953, 2870, 1455, 1374, 1197, 1095, and 921; δ_H (2 diastereoisomers) 4.10 (1 H, s, NH), 3.68-3.72 (1 H, m, cyclopentyl CHN), 3.52-3.60 1 H, m), 3.43-3.47 (2 H, m), 3.33 and 3.35 (3 H, 2 x s, MeO), 3.21-3.24 (2 H, m), 2.43-2.47 (1 H, m, cyclopentyl 2-H), 2.14-2.21 (2 H, m), 1.71-2.02 (8 H, m), and 1.10 and 1.07 3 H, 2 x d, *J* 8.0 Hz, 2-Me); δ_C (2 diastereoisomers) 75.64 and 74.70 (CH_2O), 66.22 (MeO), 80.95 and 63.30 (cyclopentyl 1-C), 59.04 (pyrrolidine 2-C), 53.95 and 53.48 (pyrrolidine 5-C), 39.16 and 39.98 (cyclopentyl 2-C), 33.17, 30.20. 26.60, 22.18 and 22.03 (CH_2), and 19.13 and 17.36 (2-Me); *m/z* 212.1879 [M^+ (14%), $C_{12}H_{24}N_2O$ requires 212.1889], 155 (32), 149 (22), 132 (15), 124 (20), 113 (32), 83 (18), 69 (31), 57 (46), 51 (100), and 41 (54); $[\alpha]_D^{20}$(CH_2Cl_2) -30.0.

1-[(5-Benzeneselenyl-2-methylpentylidene)amino]-2*R*-methoxymethylpyrrolidine.

(a) Synthesis. *R*-1-Amino-2-methoxymethylpyrrolidine (111 mg, 0.85 mmol) and 5-benzeneselenyl-2-methylpentanal (217 mg, 0.85 mmol) were reacted using the general procedure for the synthesis of hydrazones to yield 1-[(5-benzeneselenyl-2-methylpentylidene)amino]-2*R*-methoxymethylpyrrolidine was isolated as an orange oil (305 mg, 98%) which was found to be spectroscopically identical to the *S* diastereoisomer (**29b**); $[\alpha]_D^{20}$ (CH_2Cl_2) +32.6.

(b) Cyclisation of 1-[(5-benzeneselenyl-2-methylpentylidene)amino]-2R-methoxymethylpyrrolidine. The hydrazone (190 mg, 0.52 mmol) was reacted with Bu_3SnH to yield the 5-*exo* product, 1-(2-methylcyclopentyl)-

amino-2*S*-methoxymethylpyrrolidine (43 mg, 39%) which was found to be spectroscopically identical to the *S* diastereoisomer (**31b**); $[\alpha]_D^{20}(CH_2Cl_2)$ +29.1.

1-(3-Benzeneselenylpropyl)-2-(3-phenylpropylidene)hydrazine (32).

Synthesis. (a) (3-Benzeneselenylpropyl)hydrazine. 1-Benzeneselenyl-3-iodopropane (650 mg, 2 mmol), synthesised by a literature procedure,[53] and hydrazine hydrate (500 mg, 10 mmol) were dissolved in ethanol (10 cm^3) and stirred at r.t. for 72 h. Water was added and the product extracted into dichloromethane. The hydrazine was isolated by extraction into 2 M hydrochloric acid, neutralised (Na_2CO_3, NaOH), and re-extracted into CH_2Cl_2. The organic extracts were dried and evaporated to dryness to yield (3-benzeneselenylpropyl)hydrazine as a yellow oil (344 mg, 75%); ν_{max} /cm^{-1} 3337, 3055, 2931, 1667, 1579, 1476, 1437, 1073, 1023, 735, and 691; δ_H 7.42-7.51 (2 H, m, Ph *o*-H), 7.20-7.26 (3 H, m, Ph-H), 4.13 (3 H, brs, NH, NH_2), 2.88-3.01 (4 H, m, 1,3-H), and 1.89-1.94 (2 H, m, 2-H); δ_C 132.54 (Ar-CH), 130.20 (Ar-C), 129.02 and 126.84 (Ar-CH), 60.88 (1-C), 28.50 (3-C), and 24.14 (2-C); *m/z* 230 (60%), 199 (22), 157 (79), 91 (48), 77 (100), and 51 (83).

(b) 1-(3-Benzeneselenylpropyl)-2-(3'-phenylpropylidene)hydrazine (**32**). The hydrazine (243 mg, 1.06 mmol) and 3-phenylpropanal (143 mg, 1.06 mmol) were reacted using the general procedure for the synthesis of hydrazones to yield (**32**) as a yellow oil (172 mg, 47%); ν_{max} /cm^{-1} 3420, 3027, 2927, 1653, 1603, 1579, 1496, 1477, 1454, 1437, 1217, 1023, and 736; δ_H 7.43-7.49 (2 H, m, PhSe *o*-H), 7.19-7.28 (9 H, m, Ph-H, imine H), 2.97 (2 H, t, *J* 7.2 Hz, 3-H), 2.88 (2 H, t, *J* 7.3 Hz, 1-H), 2.62-2.69 (4 H, m, 2',3'-H), and 2.01-2.05 (2 H, m, 2-H); δ_C 164.22 (C=N), 132.7 (Ar-CH), 131.46 and 129.86 (Ar-C), 129.04, 128.50, 128.36, 126.88, and 126.17 (Ar-CH) 34.27, 32.65, 30.16, 27.41, and 24.15 (CH_2).

(c) Attempted cyclisation of 1-(3-benzeneselenylpropyl)-2-(3'-phenylpropylidene)hydrazine (**32**). The hydrazone (212 mg, 0.62 mmol) was reacted with Bu_3SnH using the standard procedure to give a crude oil which on purification gave the acyclic hydrazone, 1-(3-phenylpropylidene)-2-propylhydrazine (**34**) as the only isolable product (30 mg, 26%); ν_{max} /cm^{-1} 2926, 2850, 1685, 1604, 1496, 1453, 1074, 1023, 739, and 699; δ_H 7.18-7.25, (6 H, m, Ph, imine-H), 2.64-2.72 (2 H, m, 1-H), 1.57-1.67 (2 H, m, 3'-H), 1.25-1.37 (4 H, m, 2,2'-H), and 0.92 (3 H, t, *J* 7.3 Hz, 3-H); δ_C 154.75 (C=N), 132.54 (Ar-C), 128.37, 128.27 and 126.01 (Ar-CH), 34.34, 29.57, 27.78 and 26.78 (CH_2), and 13.54 (Me); *m/z* 190 (M^+, 8%), 131 (17), 117 (38), 105 (34), 91 (100), and 77 (15).

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(*Received in UK* 10 *April* 1995; *revised* 19 *May* 1995; *accepted* 26 *May* 1995)