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Synthesis of Pyrrolizidines using Aminyl Radicals Generated from Sulfenamide Precursors

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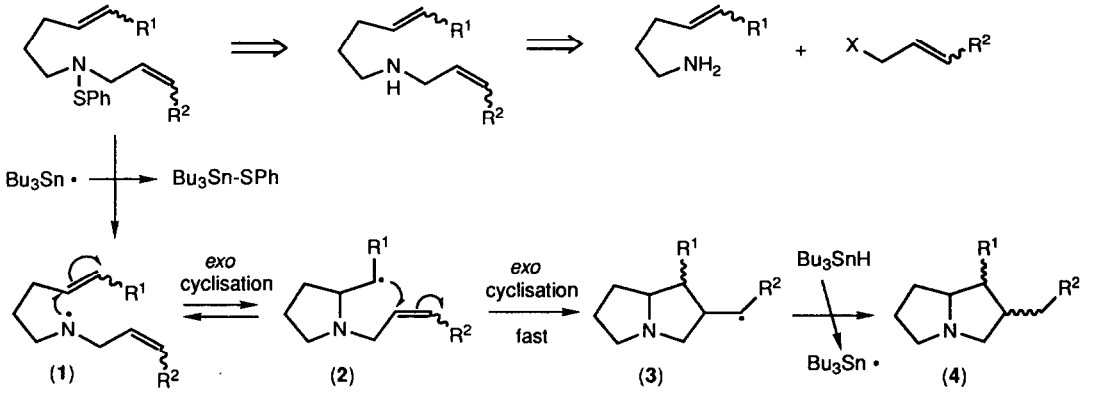
Abstract: Tandem radical cyclisations of aminyl radicals generated from sulfenamide precursors have been used for the synthesis of pyrrolizidines and other polycyclic nitrogen heterocycles. The aminyl radicals are generated by reaction between sulfenamide precursors and Bu_3SnH.

Sulfenamides have been shown to be excellent precursors of aminyl radicals, which are generated using tributyltin hydride (Bu_3SnH) for S_H2 abstraction of the benzenesulfenyl group.[1-4] Full details of the protocol using sulfenamides are described in the preceding paper.[4] In this paper we report the application of tandem cyclisation of aminyl radicals, generated from sulfenamides, to the synthesis of pyrrolizidines and other nitrogen heterocycles. The general scheme for synthesising pyrrolizidines is shown below (Scheme 1). A generalised retro-synthesis for the sulfenamide precursors is also shown.

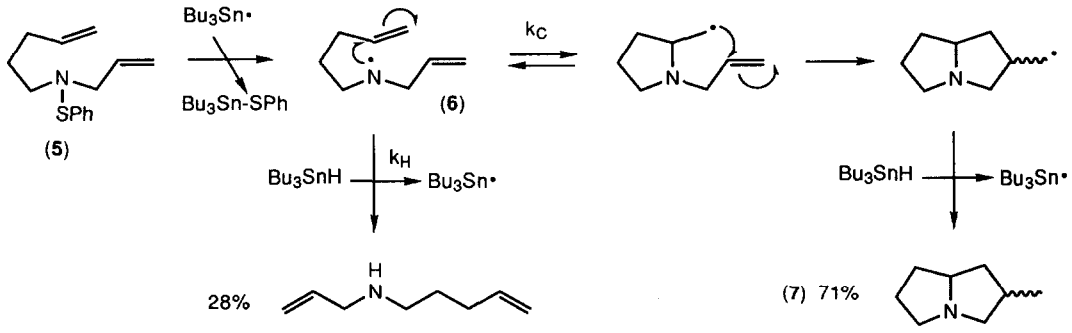


Unfortunately, the rate of cyclisation of neutral aminyl radicals is similar to the rate of ring opening which has limited their use for monocyclisation reactions.[4-6] In the preceding paper[4] we showed that this disadvantage could be partially overcome by using methods which force cyclisation, *e.g.* the use of aminyl radicals which cyclise rapidly and aminyls which cyclise to yield stable benzylic radicals. The third method to force cyclisation involves the trapping of the mono-cyclised carbon radical intermediates by further radical cyclisation. This tandem cyclisation also provides a route to the synthesis of pyrrolizidines and other nitrogen polycycles.[2,4]

The use of tandem radical cyclisations of carbon-centred radicals in synthetic reactions has been extensively reported[7] but there are only a few examples of the use of aminyl radicals.[2,3,5,8] These initial studies indicated the potential for applying our methodology using sulfenamides to the synthesis of a range of pyrrolizidines and further, to other polycylic nitrogen heterocycles. Pyrrolizidines have also been prepared by cyclisation of aminyl radicals derived from 2-alkenylpyrroles using *N*-hydroxypyridine-2-thione carbamates.[5] An indolizidine has been synthesised from the *N*-chloramine of of a 2-alkenylpiperidine.[9]

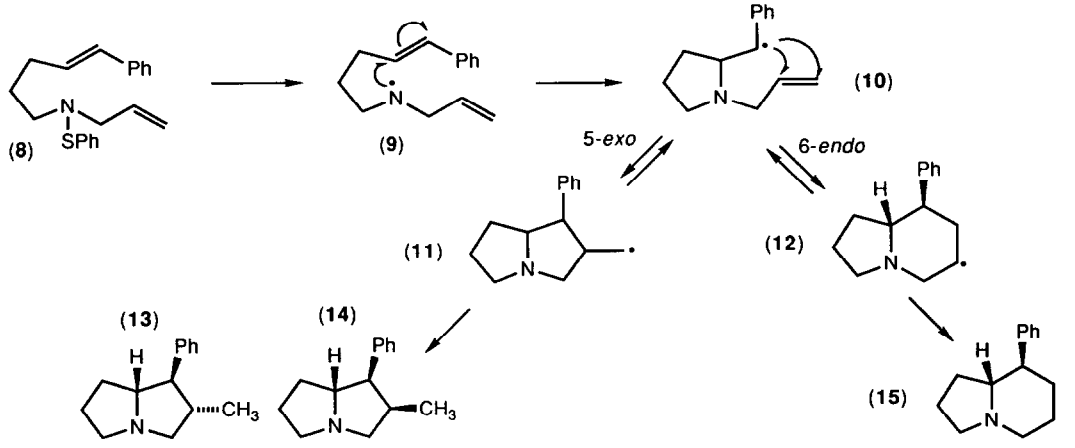
Our methodology relies on the rapid cyclisation (trapping) of the mono-cyclised radical intermediate (**2**) to yield radical (**3**) which is then trapped by hydrogen abstraction from Bu_3SnH to yield the pyrrolizidine product (**4**). The main competition in the sequence was as predicted, *i.e.* between trapping of the initial intermediate aminyl radical (**1**) by Bu_3SnH and cyclisation of (**1**). No monocyclisation products resulting from reaction between (**2**) and Bu_3SnH were detected. The trapping of (**2**) by cyclisation is obviously efficient because when *cis*-alkenes were used for the first cyclisation, reversible cyclisation/ring opening of the aminyl radical (**1**)/(**2**) would give isomerisation to the more stable *trans*-isomer of (**1**). The uncyclised product resulting from trapping of (**1**) by Bu_3SnH retained the *cis*-stereochemistry in each case.

A wide range of suitable precursors can be envisaged. Reactions between suitable alkenylamines and alkenylhalides provide a facile route to the starting amines. We initially studied the simplest system which has been previously reported,[3,5,8] the cyclisation of *N*-allylpent-4-enylaminyl radicals (**6**). Addition of Bu_3SnH over 6 h using a syringe pump gave a quantitative yield of products [2-methylpyrrolizidine (**7**) (72%),uncyclised *N*-allylpent-4-enylamine (28%)]. The 2-methylpyrrolizidine (**7**) was a mixture of two diasteroisomers in the ratio of 61% and 11%. The result indicates that the rate of reaction of (**6**) with Bu_3SnH (k_H) is fast compared with the the rate of cyclisation (k_C). The corresponding rates have been reported[6] for *N*-butylpent-4-enylamine as $k_H = 2 \times 10^5\ M^{-1}s^{-1}$ and $k_C = 1 \times 10^4\ s^{-1}$ respectively. Therefore, the trapping methodology only works well if the Bu_3SnH is kept at a very low concentration, best by using a syringe pump. When the reaction was carried out without a syringe pump, the ratios of (**7**):*N-allylpent-4-enylamine* were 36:64 (0.02 M Bu_3SnH) and 11:89 (0.11 M Bu_3SnH).[3] Tandem cyclisations via the aminium radical of (**6**) gave exclusively cyclisation.[5,8]

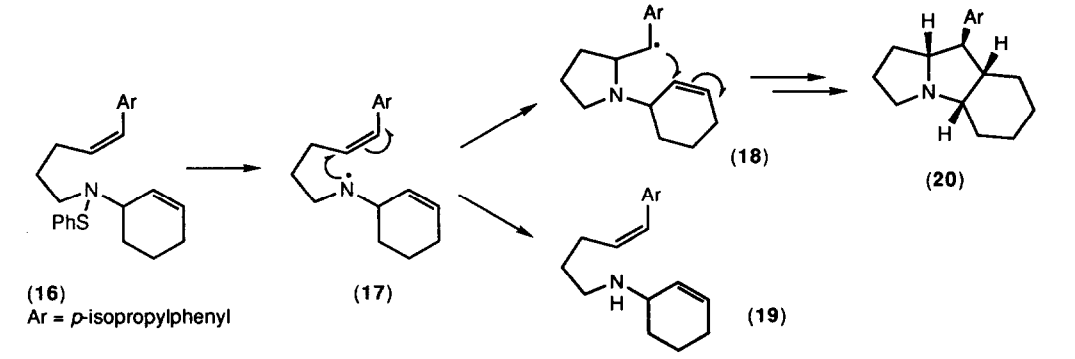


N-Allyl-*N*-(benzenesulfenyl)-5-phenylpent-4-enylamine (**8**) was used in the next experiment with a view to taking advantage of benzylic stabilisation to force the reaction to exclusive tandem cyclisation. The radical reaction between *N*-(benzenesulfenyl)-*N*-butyl-5-(4-isopropylphenyl)pent-4-enylamine and Bu_3SnH gave only cyclisation and therefore tandem cyclisation was also expected to be exclusive.[4] The tandem cyclisation (5-*exo*, 5-*exo*) gave the pyrrolizidines (49%), (**13**), (**14**), and a third minor diastereoisomer, the stereochemistry of which could not be assigned. No uncyclised material was observed. The aminyl radical (**9**) underwent 5-*exo* cyclisation to (**10**) which was efficiently trapped by 5-*exo* cyclisation, as well as 6-*endo* cyclisation via (**12**) to the indolizidine (**15**) (14% in THF). Stable carbon radical intermediates are known in certain cases to undergo reversible cyclisation/ring-opening and allow some thermodynamic control. The intermediate radical (**10**) has benzylic stabilisation which allows some of the thermodynamically more stable secondary radical (**12**) to be formed and not only the stereoelectronically favoured 5-*exo* radical (**11**). The stereochemistry of the pyrrolidines

(13) and (14) were determined using difference nOe and COSY 45 NMR spectroscopic techniques. The diastereoisomers were formed in the ratio of (13):(14):unknown diastereoisomer = 2.8:1.2:1 in THF. Repeating the experiment using benzene in place of THF gave the same yield (49%), but gave a different ratio (6.5:2.5:1) of pyrrolizidines and less indolizidine (8%). We could not determine any significance from the stereoselectivity observed in the cyclisations.

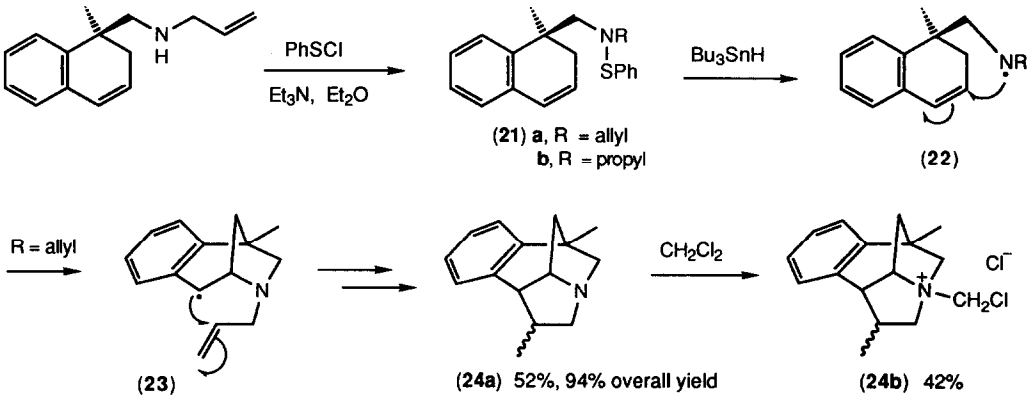


The potential of this system was extended by investigating the cyclohexenyl analogue (**16**), which by cyclisation of the intermediate aminyl radical (**17**) onto a cyclohexenyl alkene, would allow the synthesis of a tricyclic amine (**20**) containing the pyrrolizidine system. Reaction between (**16**) and Bu_3SnH gave a *ca.* 3:1 mixture of tandem cyclised product (**20**) (14% isolated) and the uncyclised amine (**19**) (6%, by ^1H NMR spectroscopic analysis of the crude product). The yields were not optimised. The alkene in the uncyclised amine (**19**) was in the *cis*-stereochemistry and no isomerisation had taken place indicating that it was formed by direct reduction of the intermediate aminyl radical (**17**) and that equilibration via (**18**) had not taken place. The *trans*-alkene would be expected if equilibration had taken place. The tricyclic product (**20**) was one diastereoisomer; assuming cyclisation of (**18**) to yield a *cis* ring-junction, molecular models indicate one favourable diastereoisomer as shown for (**20**). Interestingly, this stereochemistry is the same as the major product for cyclisation of sulfenamide (**8**) to pyrrolizidine (**13**). Unfortunately NMR spectroscopic studies could not confirm the stereochemistry.

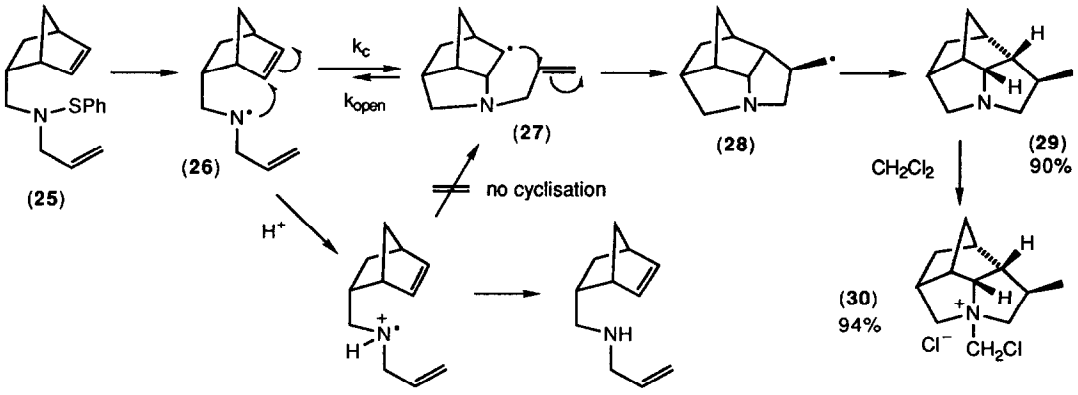


The reaction between the aphanorphine analogue (**21a**) and Bu_3SnH provides a further example of the use of benzylic stabilisation to assist exclusive tandem cyclisation; only the tandem cyclised product (**24a/24b**)

(94%) was obtained and no other products were detected. Determination of the structure of cyclised product (**24a**) using nOe studies showed two diastereoisomers (*exo*:*endo*-methyl in the ratio of 4:1). The methodology works particularly well for the compact cage-like product (**24a**) and indicates the potential for the synthesis of complex nitrogen heterocycles. The cyclised amine (**24a**) was strongly nucleophilic and the nitrogen reacted with CH_2Cl_2 to form the chloromethyl chloride salt of (**24b**) (42%). The first cyclisation is assisted by benzylic stabilisation and the second 5-*exo* cyclisation efficiently traps the intermediate aminyl radical (**23**). The effect of the trapping is shown by comparison[4] with the reaction between the *N*-propyl analogue (**21b**) and Bu_3SnH in which the mono-cyclised product and uncyclised amine were obtained in a ration of 4.6:1.

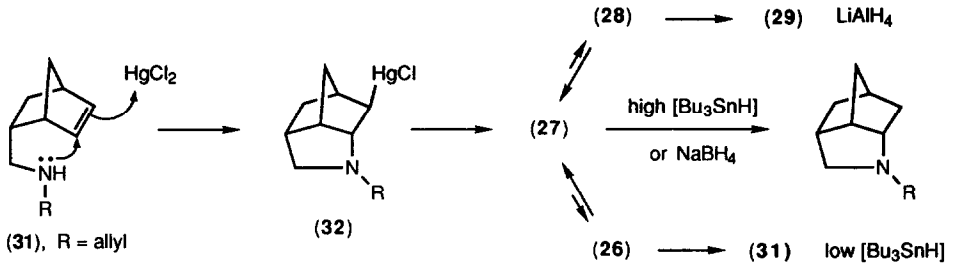


The reaction of *N*-(benzenesulfenyl)-*N*-allyl-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine (**25**) was used as a second test of the tandem methodology. The radical reaction between *N*-(benzenesulfenyl)-*N*-propyl-(bicyclo-[2.2.1]hept-5-en-2-yl)methylamine and Bu_3SnH gave a ratio of mono-cyclised product to uncyclised amine of 4:1,[4] and therefore, tandem cyclisation was expected to force the reaction towards exclusive cyclisation. As predicted, the Bu_3SnH radical reduction of sulfenamide (**25**) gave a 90% yield of the tandem product (**29**) and no uncyclised or mono-cyclised products. The cyclisation of the intermediate aminyl radical (**26**) to (**27**) is fast because of the strained alkene, buttressing effects, and close orientation of the aminyl to the alkene.[4] The tetracyclic pyrrolizidine product (**29**) is a strong nucleophile and gave the chloride salt (**30**) from a S_N2 type substitution reaction with CH_2Cl_2 during work-up. The cyclisation reaction was also attempted with added malonic acid[5] or $MgBr_2.Et_2O$[10] in order to give electrophilic aminium radical intermediates but no cyclisation was observed and only uncyclised amine was isolated (48% and 51% respectively). The absence of cyclisation is

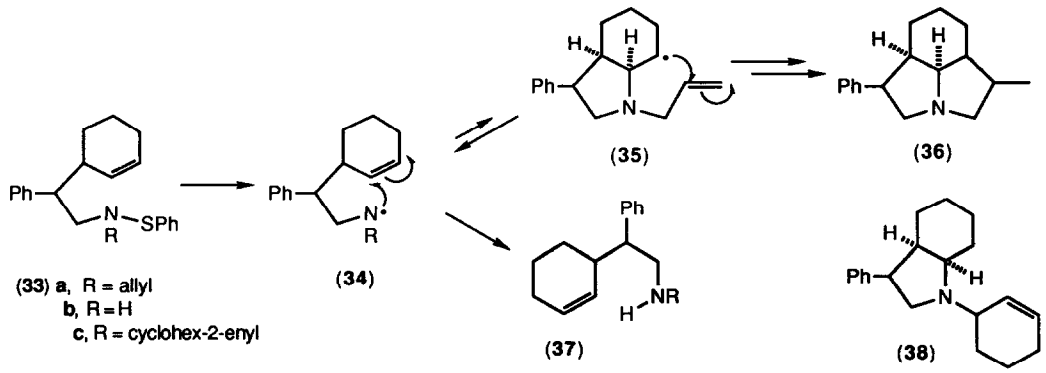


explained by the observation[5,11] that the rate of cyclisation of aminium radicals relative to their rate of reduction by the nucleophilic Bu_3SnH is considerably less than the same relative rates for aminyl radicals. Whereas the rate of cyclisation of (**26**) to (**27**) is faster than the rate of reduction of (**26**) by Bu_3SnH, the rate of reduction of the aminium cation of (**26**) by Bu_3SnH is faster than its rate of cyclisation..

In order to study the reversibility of the aminyl cyclisation step, *N*-allyl-(bicyclo[2.2.1]hept-5-en-2-yl)-methylamine (**31**, R = allyl) was cyclised using mercury(II) chloride[12] to yield the mono-cyclised mercury adduct (**32**) (56%). Reduction of (**32**, R = allyl) using reagents which would be predicted to proceed via radical mechanisms gave mixed results. Reduction using a high concentration of sodium borohydride[13] or Bu_3SnH gave the mono-cyclised amine, *i.e.* at high concentration, the intermediate radical (**27**) is trapped before further reaction (ring-opening or cyclisation). Surprisingly, reduction of (**32**) with Bu_3SnH using a syringe pump gave only ring-opened amine (**31**). Reduction with $LiAlH_4$ gave mostly the tandem product (**29**) with a small amount of the ring-opened amine (**31**) and the mono-cyclised amine. These results provide evidence for the reversibility of the aminyl radical cyclisation of (**26**) and (**27**) but that $k_c > k_{open}$ as opposed to the simple pent-4-enylaminyl system in which $k_c = k_{open}$.[6] Initial studies on the $HgCl_2$ cyclisation were carried out on the simpler *N*-propyl-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine (**31**, R = propyl) which gave the corresponding mercury adduct (**32**, R = propyl) (72%).

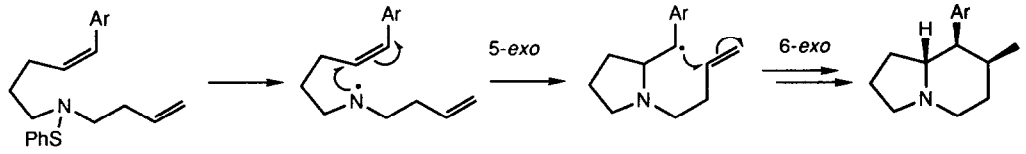


Attempts to synthesise hexahydroindolines by mono-cyclisation of an aminyl radical onto unactivated cyclohexenes failed and only uncyclised amine was formed.[4] These precursors provided a good model to test the tandem methodolgy. The *N*-allyl precursor (**33a**) gave a moderate yield (30%) of the tandem cyclised product (**36**) which was a mixture of three diastereoisomers in a ratio of 2:2:1. The aminyl radical (**34a**) cyclises to yield the hexahydroindoline radical (**35**) which is largely trapped by further 5-*exo* cyclisation. The first ring closure should give a *cis* stereochemistry at the ring-junction[7,8] but this could not be determined from ^1H NMR spectroscopic studies. Whereas the sulfenamide (**33b**) gave exclusively uncyclised amine (**37b**) in high yield,[4] the tandem reaction gave a ratio of bicyclised product (**36**):uncyclised amine (**37a**) (6%) of 5:1. Attempts to extend this series to give cyclisation of the intermediate aminyl radical (**34b**) onto a cyclohexene ring failed and a

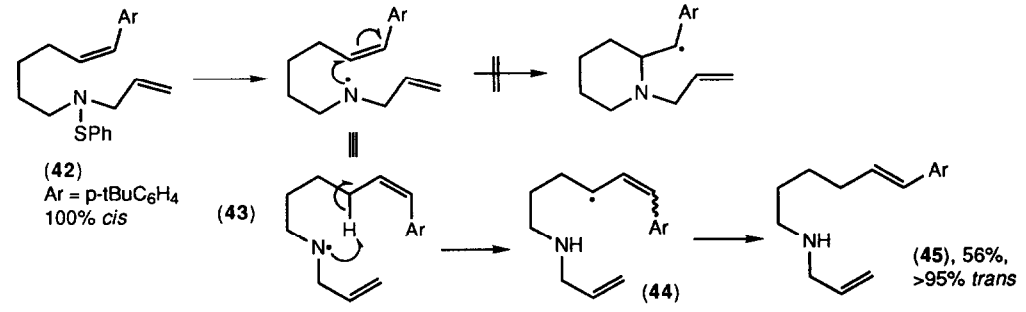


low yielding reaction unusually gave the mono-cyclised product (**38**) (16%, one diastereoisomer) and uncyclised amine (**33c**) (11%). Molecular models indicated that the second cyclisation onto the cyclohexene is not sterically favourable. A possible explanation for the mono-cyclisation is that the unfavourable equilibrium between (**34**) and (**35**) is overcome by 1,7- or bimolecular-hydrogen abstraction from the allylic position of the cyclohexene by the intermediate carbon-centred radical.

Attempts to apply the protocol to the synthesis of indolizidines were partially successful. The 5-*exo*, 6-*exo* cyclisation strategy proved successful; the reaction between sulfenamide (**39**) and Bu_3SnH gave a good yield of 7-methyl-8-(4-isopropylphenyl)indolizidine (**41**) (64%) and also the uncyclised amine (24%). Two isomers of (**41**) were formed and ^1H NMR spectroscopy using difference nOe and COSY45 techniques indicate they are invertomers (ratio of 55:45) rather than diastereoisomers. The major invertomer is shown (**41**) is shown in the scheme. The aminyl radical readily undergoes cyclisation and the carbon-radical is efficiently trapped in a 6-*exo* cyclisation. When the reduction was carried out using Ph_3SnH in place of Bu_3SnH mainly the uncyclised amine (75%) with only a trace of (**41**) was isolated. Ph_3SnH reacts slightly more rapidly with nucleophilic radicals than Bu_3SnH[14] and in this case is able to trap the intermediate aminyl radical prior to cyclisation. This result indicates the small difference in rate between cyclisation and ring-opening.



However, the 6-*exo*, 5-*exo* strategy for the synthesis of indolizidines failed, and the aminyl radical (**43**) generated from sulfenamide (**42**) underwent intramolecular H-abstraction to yield uncyclised amine (**45**). The use of $(Me_3Si)_3SiH$ showed no improvement and gave the same product (**45**) (84%, > 95% trans). Proof for the H-abstraction is provided by the loss of alkene geometry, presumably via styrryl radical (**44**), to yield the more stable *trans* diastereoisomer. Further evidence was provided by repeating the reaction using Bu_3SnD to yield (**45**) with a deuterium at 4-C. The abstraction would be unlikely if the 6-*exo* cyclisation was attempted onto an isolated alkene because aminyl radicals are not good H-abstractors and only occurs in the case of (**43**) because of the formation of a stable sryrryl radical.



In conclusion, we have shown that a variety of pyrrolizidines, hexahydroindolines, and indolizidines can be synthesised using the sulfenamide tandem methodology. Careful choice of precursors should also allow the synthesis of indolizidines by 6-*exo*, 5-*exo* cyclisation and quinolizidines by 6-*exo*, 6-*exo* cyclisation. Further synthetic studies using aminyl radicals generated from sulfenamides and from other precursors are underway.

Acknowledgements

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EXPERIMENTAL

General Procedures: The general procedures are fully reported in the preceding paper.[4]

N-Allyl-*N*-(Benzenesulfenyl)pent-4-enylamine (5)

N-*Allylpent-4-enylamine*. A solution of 5-bromopent-1-ene (5.21 g, 35 mmol) in diethyl ether (20 ml) was added to a solution of allylamine (20 g, 0.35 mol) in diethyl ether (20 ml). The solution was refluxed for 48 h, cooled, poured into aq. potassium carbonate solution made up to pH 14 with sodium hydroxide. The solution was extracted with diethyl ether, dried, and evaporated to dryness to yield a oil which was distilled to yield *N*-allylpent-4-enylamine; b.p. 150°C.

N-*Allyl*-N-*(benzenesulfenyl)pent-4-enylamine* (5). *General procedure for the synthesis of sulfenamides using* N-*(benzenesulfenyl)phthalimide*. A solution of *N*-allylpent-4-enylamine (600 mg, 4.8 mmol) and *N*-(benzenesulfenyl)phthalimide (1.00 g, 4 mmol) in toluene (10 ml) was refluxed for 12 h, cooled, diluted with light petroleum to precipitate the phthalimide, filtered, and evaporated to dryness. The resulting crude product was chromatographed using neutral alumina as absorbent and 20% diethyl ether/light petroleum as eluent to yield a pale yellow oil of N-*allyl*-N-*(benzenesulfenyl)pent-4-enylamine* (5) (797 mg, 86%); (Found: C, 71.9; H, 8.25; N, 5.95; S, 13.45. $C_{14}H_{19}NS$ requires C, 72.05; H, 8.2; N, 6.0; S, 13.45%); υ_{max} (neat)/cm^{-1} 3072, 2936, 1638, 1582, 1484, 1438, 1024, 914, 738, and 692; δ_H 1.72 (2 H, quintet, J = 7.5 Hz, 2-H), 2.05 (2 H, q, J = 7.5 Hz, 3-H), 2.91 (2 H, t, 1-H), 3.61 (2 H, d, J = 5.0 Hz, C*H*$_2$-allyl, 4.98 (2 H, m), 5.16 (2 H, m), 5.87 (2 H, m), 7.14 (1 H, m, Ar-H), and 7.30 (4 H, m, Ar-H); δ_C 26.0 (2-C), 29.6 (3-C), 54.8 (1-C), 60.6 (N*C*H$_2$CH=), 113.2 and 115.8 (=CH$_2$), 124.3, 124.4, 127.1, 134.1, 136.9 (Ar-CH), and 138.6 (Ar-C); m/z 233, 178 (100%), 150, 137, 124, 109, 82, 70, 65, and 55. The sulfenamide (5) was also synthesised using diphenyl disulfide and silver nitrate[4] in 87% yield.

Reaction between Bu$_3$SnH and N-*allyl*-N-*(benzenesulfenyl)pent-4-enylamine* (5). *General procedure for the radical reactions using Bu$_3$SnH*. A solution of Bu$_3$SnH (495 mg, 1.7 mmol) and AIBN (139 mg, 0.85 mmol) in deoxygenated dry THF was added using a syringe pump at a rate of 4 ml/h to a refluxing solution of the sulfenamide (5) (233 mg, 1 mmol) in THF (100 ml). When the addition was complete the solution was cooled and dil. hydrochloric acid (2 M) was added. The aqueous solution was washed with light petroleum (6 x) to remove tributyltin residues, basified to pH 14 with aq. sodium hydroxide solution (5 M) and extracted with diethyl ether. Normally the solution was evaporated to dryness and the residue purified using chromatography with neutral alumina as absorbent. In this case because of the volatility of the product, dry hydrogen chloride was passed through the ethereal solution to give a solid (169 mg, *ca.*100%). The solid was neutralised with 10% NaOD in D_2O and extracted into $CDCl_3$ and analysed using ^{1}H NMR (400 MHz); (5):*N*-allylpent-4-enylamine = 72%:28%; (7) showed an isomer ratio of 61%:11%. The data was identical to the literature data.[5]

trans-*N*-Allyl-*N*-(benzenesulfenyl)-5-phenylpent-4-enylamine (8)

5-Bromo-1-phenylpent-4-ene. Triphenylphosphine (3.38 g, 12.9 mmol) was added to a solution of 1-phenylpent-4-en-1-ol (1.39 g, 8.6 mmol) and CBr_4 (4.26 g, 12.9 mmol) in cyclohexane (90 ml). The mixture was stirred for 16 h, diluted with CH_2Cl_2, washed with brine, dried, and evaporated to dryness. The resulting oil was chromatographed on silica gel with 5% benzene in light petroleum to give 5-bromo-1-phenylpent-4-ene as an oil (1.20 g, 63%); υ_{max} (neat)/cm^{-1} 3024, 2952, 1596, 1492, 1304, 966, 742, and 694; δ_H 1.99 (2 H,

quintet, 4-H), 2.37 (2 H, q, 3-H), 3.41 (2 H, t, 5-H), 6.13 (1 H, dt, J = 16, 7 Hz, 2-H), 6.42 (1 H, d, J = 16 Hz, 1-H), and 7.23 (5 H, m, Ph-H); δ_C 31.2 (4-C), 32.1 (3-C), 33.1 (5-C), 126.0, 127.1, 128.4, 128.5, and 131.2 (Ph and alkene-CH), and 137.4 (Ph-C); m/z 224.0201 (M^+, $C_{11}H_{13}Br$ requires 224.0201), 226, 145, 128, 117 (100%), 102, 91, and 77. ^1H NMR indicated *ca.* 5% of the *cis*-isomer.

trans-N-*Allyl-5-phenylpent-4-enylamine*. Allylamine (5 ml) and *trans*-5-bromo-1-phenylpent-2-ene (1.205 g, 5.4 mmol) were refluxed in benzene for 4 h, cooled, and the solution evaporated to dryness. The residue was extracted with 2 M hydrochloric acid and the acid extract washed with light petroleum, neutralised with aq. sodium hydroxide solution, and extracted with diethyl ether. The ether extracts were washed with water, dried, and evaporated to dryness. The resulting oil was purified by chromatography using basic alumina as absorbent and 1% MeOH/$CHCl_3$ as eluent to yield a pale yellow oil of *trans-N*-allyl-5-phenylpent-4-enylamine (757 mg, 70%); υ_{max} (neat)/cm^{-1} 3308, 3024, 2924, 1640, 1596, 1492, 1646, 1118, 994, 964, 918, 742, and 694; δ_H (400 MHz) 1.69 (2 H, quintet, 2-H), 2.25 (2 H, q, 3-H), 2.67 (2 H, t, 1-H), 3.26 (2 H, d, =CHCH_2N), 5.09 (1 H, d, J = 10 Hz), 5.18 (1 H, d J = 17 Hz, 4-H), 5.90 (1 H, m), 6.21 (1 H, m), 6.39 (1 H, d, J = 17 Hz, 5-H), 7.20-7.30 (5 H, Ph-H); δ_C 29.4 (2-C), 30.6 (3-C), 48.6 (1-C), 52.2 (=CHCH_2N), 116.0 (=CH_2), 125.8, 126.7, 128.3, 130.0, 130.1, 136.4, and 137.5 (Ph- and alkene-C); m/z 202.1596 (MH^+, $C_{14}H_{19}N$+H requires 202.1596], 143, 129, 115, 102, 96, 91, 82, 77, and 70 (100%).

trans-N-*Allyl*-N-*(benzenesulfenyl)-5-phenylpent-4-enylamine* (**8**). A solution of *trans-N*-allyl-5-phenylpent-4-enylamine (500 mg, 2.5 mmol) and *N*-(benzenesulfenyl)phthalimide (593 mg, 2.4 mmol) were reacted using the general procedure (toluene, reflux, 6 h). The resulting oil was purified using chromatography on neutral alumina as absorbent with 5% diethyl ether/light petroleum as eluent to yield *trans-N*-allyl-*N*-(benzenesulfenyl)-5-phenylpent-4-enylamine (**8**) as a clear oil (595 mg, 80%); υ_{max} (neat)/cm^{-1} 3068, 3020, 2932, 2840, 1640, 1580, 1474, 1068, 964, 924, 738, and 692; δ_H (400 MHz) 1.81 (2 H, quintet, 2-H), 2.23 (2 H, q, 3-H), 2.95 (2 H, t, 1-H), 3.63 (2 H, d, =CHCH_2N), 5.17 (2 H, d, J = 10 Hz), 5.94 (1 H, m), 6.19 (1 H, dt J = 17, 7 Hz, 4-H), 6.36 (1 H, d, J = 17 Hz, 5-H), 7.18-7.33 (10 H, Ph-H); δ_C 27.8 (2-C), 30.2 (3-C), 56.1 (1-C), 62.0 (=CHCH_2N), 117.3 (=CH_2), 125.8, 125.9, 126.7, 128.3, 128.5, 130.1, 130.2, 135.4, 137.6, and 139.8 (Ph- and alkene-C); m/z 310.1629 [MH^+ (100%). $C_{20}H_{23}NS$+H requires 310.1629], 274, 256, 247, 235, 218, 202, 179, 166, 158, 148, 138, 126, and 93.

Reaction between Bu_3SnH and trans-N-*allyl*-N-*(benzenesulfenyl)-5-phenylpent-4-enylamine* (**8**). The sulfenamide (**8**) (310 mg, 1 mmol) was reacted with Bu_3SnH using the general procedure (5 h) to give an oil (213 mg). Chromatography using alumina as absorbent and MeOH/$CHCl_3$ as eluent gave 8-phenylindolizidine (**15**) (28 mg, 14%) and 1-phenyl-2-methylpyrrolizidine [98 mg, 49%, three diastereoisomers in the ratio of 2.8:1.2:1 for (**13**):(**14**):a third diastereoisomer (the stereochemistry could not be fully determined]. The structures were fully assigned using difference nOe, and COSY 45, and HETCOR NMR techniques (400 MHz) but some multiplets were overlapping between the three diastereoisomers and could not be fully determined.

8-Phenylindolizidine (**15**): υ_{max} (neat)/cm^{-1} 3028, 2930, 2782, 2640 (Bohlmann bands), 1683, 1602, 1495, 1164, 754, and 700; δ_H (400 MHz) 1.25-2.20 (12 H, m), 2.47 (1 H, ddd, J = 12.21, 9.85, 3.54 Hz, 8-H), 3.10 [2 H, m, 3, 4-H, the hydrogens are are the correct orientation (ca. 60°) to the nitrogen lone pair for deshielding]; δ_C (100 MHz) 20.3, 25.8, 29.3, and 32.9 (CH_2), 49.1 (8-C), 52.8 (4-C), 54.5 (3-C), 69.3 (8a-C), 126.3, 127.5, and 128.3 (Ph-CH), and 144.2 (Ph-C); m/z 201.1517 [M^+ (75%), $C_{14}H_{11}N$ requires 201.1517], 172 (5), 124 (5), 110 (15), 103 (8), 97 (98), 91 (12), 84 (100), 77 (5), and 69 (30)

1-Phenyl-2-methylpyrrolizidine mixture: υ_{max} (neat)/cm^{-1} 3028, 2957, 2801, 1602, 1493, 750, and 700; m/z 201.1517 [M^+ (25%), $C_{14}H_{11}N$ requires 201.1517], 130 (5), 117 (13), 103 (3), 97 (3), 91 (14), 83 (100), 77 (5), 70 (5), and 55 (35); (**13**): δ_H (400 MHz) 0.84 (3 H, d, Me), 1.62 (1 H, m, 7-H), 1.88 (3 H, m, 6-H_2, 7-H), 2.22 (1 H, dd, J = 10.1 Hz, 1-H), 2.30 (1 H, dd, J = 9.9 Hz, 3-H), 2.52 (1 H, m, 2-H), 2.71 (1 H, m, 5-H), 3.13 (1 H, m, 5-H), 3.60 (1 H, dd, J = 9.6, 6.2 Hz, 3-H), 3.82 (1 H, m, 7a-H), 7.18 (2 H, m, Ph-H), and 7.27 (2 H, m, Ph-H); δ_C (100 MHz) 14.56 (Me), 24.91 (6-C), 30.18 (7-C), 42.83 (2-C), 54.71 (5-C), 59.63 (1-C), 62.44 (3-C), 72.75 (7a-C), 126.81, 127.57,and 128.28 (Ph-CH), and 139.42 (Ph-C); (**14**) δ_H (400 MHz) 0.73 (3 H, d, Me), 1.54 (1 H, m, 7-H), 1.88 (2 H, m, 6-H), 2.07 (1 H, sestet, J = 16.4 Hz, 7-H),

2.52 (1 H, m, 2-H), 2.70 (1 H, m, 5-H), 2.83 (1 H, dd, J = 10.6, 6.0 Hz, 3-H), 3.02 (1 H, m, 1-H), 3.13 (1 H, m, 3-H), 3.30 (1 H, dt, J = 10.5, 5.9 Hz, 5-H), 4.08 (1 H, q, J = 7.2 Hz, 7a-H), 7.18 (2 H, m, Ph-H), and 7.27 (2 H, m, Ph-H); δ_C (100 MHz) 13.80 (Me), 25.81 (6-C), 31.47 (7-C), 38.36 (2-C), 54.21 (1-C), 55.70 (5-C), 61.11 (3-C), 67.74 (7a-C), 126.32, 128.11, and 128.18 (Ph-CH), and 138.84 (Ph-C); 3rd and minor diastereoisomer: δ_H (400 MHz) 0.97 (3 H, d, Me), 1.27 (1 H, m, 7-H), 1.62 (1 H, m, 6-H), 1.88 (2 H, m, 5, 6-H), 2.52 (2 H, m, 2, 5-H), 2.70 (1 H, m, 4-H), 3.02 (1 H, m, 1-H), 3.13 (1 H, m, 3-H), 3.53 (1 H, m, 4-H), 4.03 (1 H, m, 7a-H), 7.18 (2 H, m, Ph-H), and 7.27 (2 H, m, Ph-H); δ_C (100 MHz) 14.30 (Me), 23.61 (6-C), 28.25 (7-C), 32.30 (2-C), 53.46 (1-C), 56.68 (5-C), 60.78 (3-C), 69.54 (7a-C), 126.65, 127.88, and 128.34 (Ph-CH), and 137.11 (Ph-C).

***cis*-*N*-(Benzenesulfenyl)-*N*-(cyclohex-2-en-1-yl)-5-(4-isopropylphenyl)pent-4-enylamine (16)**

N-(Cyclohex-2-en-1-yl)-5-(4-isopropylphenyl)pent-4-enylamine. *cis*-5-(4-Isopropylphenyl)pent-4-enylamine was prepared as reported[4] and reacted with 3-bromocyclohexene (18 h reflux) to yield a crude oil (1.2 g) which was purified using a dry alumina column with diethyl ether/ethyl acetate as eluent to yield *N*-(cyclohex-2-en-1-yl)-5-(4-isopropylphenyl)pent-4-enylamine as an oil; υ_{max} (neat)/cm^{-1} 3402, 3021, 1459, and 842; δ_H 1.24 (6 H, d, Me), 1.65 (6 H, m, 2, 5' 6'-H), 1.94 (2 H, m, 4'-H), 2.33 (2 H, dt, 3-H), 2.65 (2 H, t, 1-H), 2.85 (1 H, q, C*H*Me$_2$), 3.09 (1 H, m, 1'-H), 5.71 (3 H, m, 4, 2', 3'-H), 6.40 (1 H, d, 5-H), and 7.17 (4 H, m, Ar-H); δ_C 20.25 (6'-C), 23.96 (Me), 25.29 (5'-C), 26.40 (2-C), 29.46 (4'-C), 30.65 (3-C), 33.61 (C*H*Me$_2$), 46.37 (1-C), 52.98 (1'-C), 127.63 (Ar-CH, 4, 5-C), 135.12 and 147.13 (Ar-C); m/z 284.2378 [MH$^+$ (100%). $C_{20}H_{29}N$+H requires 284.2378].

cis-N-*(Benzenesulfenyl)*-N-*(cyclohex-2-en-1-yl)-5-(4-isopropylphenyl)pent-4-enylamine* (**16**). *cis*-*N*-(Cyclohex-2-en-1-yl)-5-(4-isopropylphenyl)pent-4-enylamine was reacted with benzenesulfenylchloride using the general procedure (diethyl ether, room temperature, 2.5 h) to yield the sulfenamide (**16**) as a clear oil; υ_{max} (neat)/cm^{-1} 3005, 1581, 1477, 1439, 844, and 690; δ_H 1.26 (6 H, d, Me), 1.51 (4 H, m, 5', 6'-H), 1.72 (2 H, m, 2-H), 1.95 (2 H, m, 4'-H), 2.33 (2 H, dt, 3-H), 2.89 (1 H, q, C*H*Me$_2$), 3.00 (2 H, t, 1-H), 3.69 (1 H, m, 1'-H), 5.54 (3 H, m, 4, 2', 3'-H), 6.35 (1 H, d, 5-H), and 7.27 (9 H, m, Ar-H); δ_C 18.64 (5'-C), 21.29 (Me), 23.97 and 24.96 (2, 6'-C), 26.20 (4'-C), 28.89 (3-C), 33.81 (*C*HMe$_2$), 55.19 (1-C), 63.75 (1'-C), 127.69 (Ar and olefin-CH), 135.17 and 147.17 (Ar-C); m/z 392.2412 [MH$^+$ (100%). $C_{26}H_{33}NS$+H requires 392.2412], 316 (26), 284 (97), 150 (15), and 110 (22).

Reaction between Bu_3SnH and cis-N-*(benzenesulfenyl)*-N-*(cyclohex-2-en-1-yl)-5-(4-isopropylphenyl)-pent-4-enylamine* (**16**). The sulfenamide (**16**) was reacted with Bu_3SnH using the general procedure (benzene, reflux, syringe pump, 6 h) to yield a mixture of tricyclic amine (**20**) (ca. 14%) and uncyclised amine (**19**) (6%). No mono-cyclised material was observed. Purification using a dry alumina column with diethyl ether/light petroleum as eluent yielded the uncyclised amine, *N*-(cyclohex-2-en-yl)-5-(4-isopropylphenyl)pent-4-enylamine (**19**) (2 mg, 1%) and pure (**20**) (26 mg, 14%, one diastereoisomer); δ_H (400 MHz) 1.20-1.25 (6 H, d, Me), 1.41 (4 H, m, $CH_2CH_2CH_2CH_2$), 1.61 (4 H, m, 6-H, $CHCH_2$), 1.88 (2 H, m, $NCHCH_2$), 1.95 (2 H, m, 7-H), 2.70 (1 H, m, 2-H), 2.78 (1 H, m, $CHMe_2$), 2.88 (2 H, m, 5-H), 3.06 (1 H, m, 1-H), 3.25 (1 H, q, 3-H), 3.64 (1 H, q, 7a-H), and 7.12-7.26 (5 H, m, Ar-C); δ_C 21.00 ($CH_2CH_2CH_2$), 23.79 (Me), 24.08 ($CH_2CH_2CH_2$), 24.26 ($CHCH_2$), 27.00 (6-C), 28.62 ($NCHCH_2$), 31.99 (7-C), 33.59 (2-C), 45.78 ($CHMe_2$), 58.21 (5-C), 50.59 (1-C), 59.98 (3-C), 73.37 (7a-C), and 125.80-129.72 (Ar-C); m/z 283.2303 [M$^+$ (76%). $C_{20}H_{29}N$ requires 283.2300], 240 (100), 84 (63), and 49 (70).

***N*-Allyl-*N*-(benzenesulfenyl)-(1,2-dihydro-1-methylnaphth-1-yl)methylamine (21a).**

N-Allyl-(1,2-dihydro-1-methylnaphth-1-yl)methylamine. Allylamine (5.85 g, 0.10 mol) and CH_2Cl_2 (20 ml) were mixed with 4 Å molecular sieves. A solution of 1,2-dihydro-1-methyl-naphthalene-1-carboxaldehyde[4] (1.76, 10.3 mmol) in CH_2Cl_2 (10 ml) was added and stirred overnight. The sieves were filtered off, washed, and the filtrate evaporated to dryness to yield a pale yellow oil (1.875 g) which was used without purification; υ_{max} (neat)/cm^{-1} 1664, 1490, 1450, 920,786, and 756; δ_H 1.45 (3 H, s, 1-Me), 2.23 (1 H, d, J = 18.0 Hz, 2-H), 2.73 (1 H, d, J = 18.0 Hz, 2-H), 4.10 (2 H, m), 5.20 (2 H, m), 6.00 (2 H, m), 6.53 (1 H, d, J = 9 Hz),

7.20 (4 H, m, Ar-H), and 7.77 (1 H, s, CH=N). A solution of the imine (1.875 g, 10.3 mmol) in diethyl ether (10 ml) was added dropwise to a suspension of $LiAlH_4$ (1.74 g, 31 mmol). After 30 min the solution was diluted with diethyl ether and 1 M aq. sodium hydroxide solution added to destroy the excess hydride. The mixture was filtered and the filtrate dried and evaporated to give an oil which was chromatographed using neutral alumina as absorbent and 2% ethyl acetate/light petroleum as eluent to yield a light yellow oil of N-*allyl-(1,2-dihydro-1-methylnaphth-1-yl)methylamine* (1.68 g, 77%); (Found: C, 84.0; H, 9.0; N, 6.8. $C_{15}H_{19}N$ requires C, 84.45; H, 9.0; N, 6.6%); υ_{max} (neat)/cm^{-1} 3341, 3032, 2911, 1642, 1484, 1450, 1115, 994, 916, 786, and 755; δ_H 0.93 (1 H, brs, NH), 1.29 (3 H, s, 1-Me), 2.18 (1 H, ddd, J = 17.5, 3.9, 2.2 Hz, 2-H), 2.57 (1 H, ddd, J = 17.6, 4.9, 1.5 Hz, 2-H), 2.62 (1 H, d, J = 11.7 Hz, CC*H*N), 2.75 (1 H, d, J = 11.7 Hz, CC*H*N), 3.18 (2 H, dt, C=CHCH_2N), 5.06 (2 H, m, =CH_2), 5.84 (2 H, m, CH_2=C*H* and 3-H), 6.40 (1 H, m, 4-H), 7.04 (1 H, Ar-H), and 7.19 (3 H, Ar-H); δ_C 25.25 (Me), 34.75 (2-C), 37.53 (1-C), 52.97 (CCH_2N), 56.80 (C=C*H*CH_2), 115.42 (=CH_2), 124.69, 126.42, 126.69, 127.19, 127.33 (CH), 133.59 (8-C), 137.25 (4-C), and 140.96 (5-C); m/z 214.1596 [MH^+ (100%). $C_{15}H_{19}N$ requires 214.1596], 174 (2), 157 (2), 142 (10), 128 5), 115 (2), 70 (60), and 58 (5).

N-*Allyl*-N-*(benzenesulfenyl)-(1,2-dihydro-1-methylnaphth-1-yl)methylamine* (**21a**). *General procedure for the synthesis of sulfenamides using benzenesulfenylchloride.* A solution of benzenesulfenylchloride (867 mg, 6 mmol) in diethyl ether (10 ml) was added to a solution of *N*-allyl-(1,2-dihydro-1-methylnaphth-1-yl)methylamine (639 mg, 3 mmol) and Et_3N (6.06 g, 60 mmol) in diethyl ether (35 ml) and stirred for 30 min. The white precipitate was filtered, washed with diethyl ether, and the ether fractions evaporated to yield an oil (1.9 g). The oil was chromatographed using neutral alumina as absorbent and light petroleum as eluent to yield N-*allyl*-N-*(benzenesulfenyl)-(1,2-dihydro-1-methylnaphth-1-yl)methylamine* (**21a**) as a colourless oil (668 mg, 70%); (Found: C, 78.05; H, 7.05; N, 4.25. $C_{21}H_{23}N$ requires C, 78.5; H, 7.15; N, 4.35); υ_{max} (neat)/cm^{-1} 3060, 2964, 1640, 1477, 1438, 1023, 923, 788, 761, 737, and 692; δ_H 1.43 (3 H, s, 1-Me), 2.19 (1 H, ddd, J = 17.3 Hz, 2-H), 2.41 (1 H, dd, J = 17.5, 6.1 Hz, 2-H), 3.09 (1 H, d, J = 14.2 Hz, CC*H*N), 3.14 (1 H, d, J = 14.2 Hz, CC*H*N), 3.34 (1 H, dd, J = 14.3, 6.2 Hz, C=CHCH_2N), 3.45 (1 H, ddt, J = 14.3, 6.4, 1.2 Hz, C=CHCH_2N), 5.05 (2 H, m, =CH_2), 5.85 (2 H, m, CH_2=C*H* and 3-H), 6.44 (1 H, m, 4-H), and 7.20 (9 H, Ar-H); δ_C 23.83 (Me), 33.72 (2-C), 38.98 (1-C), 62.02 CCH_2N), 66.65 (C=C*H*CH_2), 117.41 (=CH_2), 125.04, 125.51, 126.51, 126.66, 127.00, 127.33, 127.71, 128.85 Ar-CH), 133.53 (8-C), 135.61 (4-C), 140.73, 140.80 (Ar-C); m/z 322.1630 [MH^+ (2%). $C_{21}H_{24}N$ requires 322.1629], 218 (35), 178 (22), 154 (7), 144 (17), 128 (12), 109 (52), 84 (43), 65 (27), and 49 (100).

Reaction between Bu_3SnH and N-*allyl*-N-*(benzenesulfenyl)-(1,2-dihydro-1-methylnaphth-1-yl)methylamine* (**21a**). The sulfenamide (**21a**) (321 mg, 1 mmol) was reacted with Bu_3SnH (495 mg, 1.7 mmol) using the general procedure (benzene, 4 h) to yield an oil (209 mg); ^1H NMR showed a 4:1 ratio of isomers of (**24a**) and no uncyclised or mono-cyclised product. Chromatography using neutral alumina as absorbent and MeOH/CH_2Cl_2 as eluent gave the tandem product (**24a**) (111 mg, 52%); mixture of diastereoisomers: υ_{max} (neat)/cm^{-1} 3063, 2957, 2908, 2859, 1486, 1454, 1377, 1068, 1043, 764, and 744; (the NMR spectral assignments were based on difference nOe, COSY, and HETCOR techniques) δ_H 1.16 (3 H, d, CHMe), 1.40 (3 H, s, 1-Me), 1.74 (1 H, dd, J = 11.6, 1.2 Hz, 2-H), 2.01 (1 H, J = 11.5, 5.3 Hz, 2-H), 2.36 (1 H, quintet, J = 6.6 Hz, C*H*Me), 2.51 (1 H, J = 10.8, 1.4 Hz, 1-CCH_2N), 2.61 (1 H, dd, J = 11.4, 7.2 Hz, MeCHCH_2N), 2.85 (1 H, dd, J = 11.4, 2.1 Hz, MeCHCH_2N), 3.07 (1 H, d, J = 4.2 Hz, 4-H), 3.24 (d, J = 10.8 Hz, 1-CCH_2N), 3.85 (1 H, t, J = 4.7 Hz, 3-H),and 7.15 (4 H, m, Ar-H); δ_C 20.38 (CH*Me*), 20.74 (1-Me), 41.34 (2-C), 45.72 (*C*HMe), 53.52 (4-C), 63.43 (MeCHCH_2N), 64.33 (3-C), 74.05 (1-CCH_2N), 122.41, 125.81, 126.30 and 128.59 (Ar-C), and 139.19 and 145.64 (Ar-C); m/z 213.1517 [M^+ (64%). $C_{15}H_{19}N$ requires 213.1517], 198 (88), 183 (4), 169 (10), 155 (20), 143 (71), 128 (100), 115 (33), 102 (4), 95 (20), 71 (28), and 57 (25); and the chloromethyl chloride salt (**24b**) (125 mg, 42%); υ_{max} (neat)/cm^{-1} 2969, 1459, 1038, 795, and 769; δ_H 1.20 (3 H, d, CHMe), 1.40 (3 H, s, 1-Me), 1.71 (1 H, d, J = 13.3 Hz, 2-H), 2.28 (1 H, quintet, J = 6.7 Hz, C*H*Me), 2.82 (1 H, J = 13.1, 5.5 Hz, 2-H), 3.41 (3 H, m, 4-H, 1-CCH_2N, MeCHCH_2N), 3.69 (1 H, dd, J = 13.20, 2.29, MeCHCH_2N), 4.00 (1 H, d, J = 12.4 Hz, 1-CCH_2N), 5.09 (1 H, t, J = 5.5 Hz, 3-H), 5.79 (1 H, d, J = 9.5 Hz, CH_2Cl), 5.96 (1 H, d, J = 9.5 Hz, CH_2Cl), and 6.93 (4 H, m, Ar-H); δ_C 19.05 (CH*Me*), 19.61 (1-Me),

38.62 (2-C), 42.60 (*C*HMe), 52.07 (4-C), 70.70 (MeCH*C*H$_2$N), 71.16 (*C*H$_2$Cl), 77.21 (3-C), 79.67 (1-C*C*H$_2$N), 123.19, 127.50, 127.91, and 128.48 (Ar-C), and 134.68 and 142.13 (Ar-C).

N-Allyl-N-(benzenesulfenyl)-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine (25).

N-*Allyl-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine.* Bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde (9.00 g, 74 mmol) in diethyl ether (10 ml) was added to a mixture of 4Å molecular sieves (6 g) and diethyl ether (10 ml) and cooled to 0°C. A solution of allylamine (8.44 g, 0.15 mol) in diethyl ether (10 ml) was added and stirred for 30 min. The mixture was filtered and evaporated to dryness to give the imine as an orange oil (10.30 g, 86%); υ_{max} (neat)/cm^{-1} 3056, 2968, 1662, 1494, 1334, 918, 730, and 696; δ_H 1.37 (3 H, m, 7-H, *exo*-3-H), 2.00 (1 H, ddd, J = 13, 9, 4 Hz, *endo*-3-H), 3.93 (2 H, d, J = 6 Hz, CH$_2$N), 5.10 (2 H, m, =CH$_2$), 5.90-6.50 (3 H, m, alkene-H), 7.26 (1 H, d, J = 6.5 Hz, CH=N); δ_C 30.4 (3-C), 42.7 and 44.8 (1, 4-C), 46.6 (2-C), 49.6 (7-C), 63.1 (CH$_2$N), 115.1 (=*C*H$_2$), 132.3, 136.1, 137.7 (alkene-C), and 170.3 (*C*H=N).

A solution of the crude imine (10.30 g, 74 mmol) in diethyl ether was added to a suspension of LiAlH$_4$ (4.22 g, 0.11 mol) in diethyl ether (70 ml) and stirred for 30 min. Aq. sodium hydroxide solution (1 M) was added dropwise until a grey granular precipitate had formed. The solution was stirred for 40 min, filtered, and the filtrate evaporated to dryness to yield an orange oil. Chromatography using basic alumina as absorbent and 10% MeOH in ethyl acetate as eluent gave a pale yellow oil of N-*allyl-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine.* (10.15 g, 84%); (perchlorate salt. Found: C, 50.10; H, 6.88; N, 5.31. $C_{11}H_{18}NO_4Cl$ requires C, 50.01; H, 6.88; N, 5.24%); υ_{max} (neat)/cm^{-1} 3340, 3056, 2960, 2864, 1640, 1334, 1116, 918, and 718; δ_H 0.52 (1 H, ddd, *endo*-3-H), 1.28 (1 H, m, 7-H), 1.42 (3 H, m, 7-H), 1.85 (1 H, ddd, *exo*-3-H), 2.34 (1 H, m, 2-H), 2.78 (1 H, brs, 4-H), 2.81 (2 H, m, CHC*H*$_2$N), 2.85 (1 H, brs, 1-H), 3.22 (2 H, d, J = 6.0 Hz, C*H*$_2$CH=), 5.11 (1 H, m), 5.92 (2 H, m), and 6.13 (1 H, m, 5-H); δ_C 30.8 (3-C), 39.25 (2-C), 42.31 (4-C), 44.33 (1-C), 49.55 (7-C), 52.76 (*C*H$_2$CH=), 53.80 (*C*H$_2$N), 115.65 (=CH$_2$), 132.04, 137.11, and 137.27; m/z 162, 148, 134, 122, 106, 96, 82, and 70 (100%).

N-*Allyl*-N-*(benzenesulfenyl)-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine* (**25**). *N*-allyl-(bicyclo[2.2.1]-hept-5-en-2-yl)methylamine (404 mg, 2.48 mmol) was reacted with *N*-(benzenesulfenyl)phthalimide (613 mg, 2.45 mmol) using the general procedure (5 h, toluene, reflux) to yield exo- and endo-N-*allyl*-N-*(benzenesulfenyl)-(bicyclo[2.2.1]-hept-5-en-2-yl)methylamine* (**25**) as a colourless oil (543 mg, 81%); (Found: C, 75.41; H, 7.76; N, 4.96. $C_{17}H_{21}NS$ requires C, 75.23; H, 7.80; N, 5.16%); υ_{max} (neat)/cm^{-1} 3056, 2964, 1582, 1474, 1338, 1336, 1092, 922, 738, and 692; δ_H 0.52 (1 H, ddd, J = 11.5, 4.3, 2.6 Hz, *endo*-3-H), 1.22 (1 H, m, 7-H), 1.39 (1 H, m, 7-H), 1.79 (1 H, ddd, J = 11.6, 8.8, 3.9 Hz, *exo*-3-H), 2.49 (1 H, m, 2-H), 2.61 (2 H, m, CHC*H*$_2$N), 2.75 (1 H, brs, 4-H), 2.85 (1 H, brs, 1-H), 3.59 (2 H, m, NC*H*$_2$C=), 5.90 (2 H, m, 6-H, C*H*=CH$_2$), 6.09 (1 H, dd, 5.7, 3.0 Hz, 5-H), 7.14-7.29 (5 H, m, Ph-H); δ_C 30.6 (3-C), 37.9 (2-C), 41.8 (4-C), 44.6 (1-C), 49.5 (7-C), 61.1 (*C*H$_2$CH=), 62.3 (*C*H$_2$N), 117.3 (=CH$_2$), 125.4, 125.5, 128.6, 132.7, 135.6, 137.1, and 140.0; m/z 271.1395 [M$^+$. $C_{17}H_{21}NS$ requires 271.1395], 178, 162, 148, 120, 109, 91, 79, 65, and 51. The data is for the *endo*-isomer but 30% of the *exo*-isomer was also present.

Reaction between Bu$_3$SnH and N-*allyl*-N-*(benzenesulfenyl)-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine* (**25**). The sulfenamide (**25**) (271 mg, 1.0 mmol) was reacted with Bu$_3$SnH (495 mg, 1.7 mmol) using the general procedure (syringe pump, THF, reflux, 12 h). The crude mixture was subjected to chromatography using neutral alumina as absorbent with 0.5% MeOH/CHCl$_3$ as eluent to yield the cyclic amine (**29**) as a yellow oil (103 mg, 63%; 90% allowing for the *exo*-isomer); υ_{max} (neat)/cm^{-1} 3360, 2944, 2860, 1464, and 1064; δ_H 0.98 (3 H, d, J = 6.6 Hz, Me), 1.33 (1 H, d, J = 12.8 Hz, *endo*-3-H), 1.63 (2 H, brs, 7-H), 1.76 (1 H, m, *exo*-3-H), 1.93 (2 H, m, 4-H, C*H*Me), 2.04 (1 H, m, 4-H), 2.15 (1 H, m, 2-H), 2.66 (1 H, m, 1-H), 2.77 (1 H, dd, J = 12.9, 8.4 Hz, MeCHC*H*$_2$N), 3.21 (1 H, dd, J = 12.9, 7.4 Hz, MeCHC*H*$_2$N), 3.32 (1 H, dd, J = 11.6, 5.0 Hz, CHC*H*$_2$N), 3.55 (1 H, dd, J = 8.2, 5.0 Hz, 6-H); δ_C 19.69 (Me), 31.87 (*C*HMe), 35.09 (3-C), 38.03 (2-C), 38.08 (5-C), 41.67 (7-C), 48.66 (1-C), 56.12 (4-C), 63.81 (CH*C*H$_2$N), 68.80 (MeCH*C*H$_2$N), and 73.11 (6-C); m/z 163.1360 [M$^+$ (14%). $C_{11}H_{17}N$ requires 163.1360], 148, 134, 120, 108, 96 (100%), 82, and 67.

In an initial reaction under the same conditions but extracted with CH_2Cl_2 to give a solid which was recrystallised from chloroform/ethyl acetate to yield colourless crystals of the chloromethyl chloride (**30**) (163 mg, 64%; 94 % allowing for the *exo*-isomer); m.p. 112-113°C; υ_{max} (neat)/cm^{-1} 3420, 1636, 1464, 1028, and 766; δ_H 1.26 (3 H, d, J = 6.6 Hz, Me), 1.79 (2 H, m, 7-H), 1.91 (2 H, m, 3-H), 2.33 (1 H, brs, 4-H), 2.51 (1 H, m, C*H*Me), 2.66 (1 H, m, 5-H), 2.76 (1 H, m, 2-H), 3.27 (1 H, m, 1-H), 3.72 (1 H, d, J = 13.4 Hz, CHC*H*$_2$N), 4.09 (1 H, dd, J = 11.3, 11.3 Hz, MeCHC*H*$_2$N), 4.31 (1 H, dd, J = 13.4, 6.9 Hz, CHC*H*$_2$N), 4.40 (1 H, dd, J = 7.5, 11.7 Hz, MeCHC*H*$_2$N), 4.97 (1 H, dd, J = 10.1, 4.7 Hz, 6-H), and 5.86 and 5.97 (2 H, ABq, CH_2Cl); δ_C 18.1 (Me), 30.7 (*C*HMe), 34.9 (3-C), 37.6 and 37.7 (1, 4-C), 41.7 (7-C), 47.9 (6-C), 53.7 (5-C), 69.6 (*C*H$_2$Cl), 70.6 (CHCH$_2$N), 73.8 (MeCHCH$_2$N), and 82.8 (6-C); m/z no M$^+$, 163, 148, 129, 96 (100%), 84, 67, and 49.

Reaction between N-*allyl-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine and HgCl*$_2$. A solution of *exo*- and *endo-N*-allyl-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine (163 mg, 1 mmol) in dry THF (5 ml) was added dropwise to a solution of mercury (II) chloride (272 mg, 1 mmol) in dry THF (10 ml) and the suspension stirred for 48 h. The mixture was filtered and the residue washed with THF to yield a white powder of the mercury adduct (**32**, R = allyl) (217 mg, 56%); m.p. 202-203°C (dec); υ_{max} (Nujol)/cm^{-1} 3039, 1464, 964, and 950; δ_H (CS_2/d$_6$-DMSO/$CDCl_3$) 1.18 (1 H, d, J = 12.6 Hz, *endo*-3-H), 1.51 (1 H, d, J = 10.4 Hz, 7-H), 1.90 (2 H, m, 7, *exo*-3-H), 2.52 (3 H, m, 1, 2, 4-H), 2.96 (1 H, m, 5-H), 3.14 (1 H, m, *exo*-C*H*$_2$N), 3.73 (2 H, m,*endo*-C*H*$_2$CH=CH$_2$), 4.03 (1 H, m, C*H*$_2$N), 4.56 (1 H, J = 5.0 Hz, 6-H), 5.50 (2 H, m, CH=C*H*$_2$), and 5.95 (1 H, m, C*H*=CH$_2$); δ_C (CS_2/d$_6$-DMSO/$CDCl_3$) 37.8 (2-C), 39.6 and 39.7 (7, 3-C), 40.4 (4-C), 46.3 (1-C), and 55.4 (6-C), 57.8 and 58.6 (*C*H$_2$N), 74.1 (3-C), 124.3 (CH=*C*H$_2$), and 128.1 (*C*H=CH$_2$); m/z 399.0632 [M$^+$(one set of isotopes), $C_{11}H_{16}NHgCl$ requires 399.0677], 202, 162 (100%), 120, 108, 91, and 77. The ^{1}H NMR spectrum indicated a ratio of isomers at 5-C-HgCl of 4:1. The data given is for the major isomer.

In a larger scale experiment, the mercury adduct resulting from *N*-allyl-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine (3.26 g, 12 mmol) was filtered and the filtrate purified by column chromatography using neutral alumina as absorbent and MeOH/chloroform as eluent to yield isomerically pure *exo-N*-allyl-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine as an oil (181 mg, 31% based on 30% of the *exo*-isomer in the starting material); υ_{max} (neat)/cm^{-1} 3311, 2963, 1678, 1644, 1117, 994, 917, and 707; δ_H 1.44 (6 H, m, NH, 2, 3, 7-H), 2.64 (3 H, m, 1, 4-H, C*H*$_2$N), 2.80 (1 H, C*H*$_2$N), 3.25 (2 H, d, J = 5.9 Hz, C*H*$_2$CH=CH$_2$), 5.21 (2 H, m, CH=C*H*$_2$), 5.92 (1 H, m, C*H*=CH$_2$), and 6.06 (2 H, m, 5, 6-H); δ_C 31.3 (3-C), 39.1, 41.5, and 44.4 (1, 2, 4-C), 45.0 (7-C), 52.6 (*C*H$_2$N), 55.0 (*C*H$_2$CH=CH$_2$), 115.6 (CH=*C*H$_2$), 136.3, 136.4, and 136.9 (alkene-CH); m/z 164.1440 (MH$^+$, $C_{11}H_{17}N$ requires 64.1439), 148, 122, 96, 91, 77, and 70 (100%).

Reaction between N-*propyl-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine and HgCl*$_2$. A solution of *exo*- and *endo-N*-propyl-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine (495 mg, 3 mmol) in dry THF (5 ml) was added dropwise to a solution of mercury (II) chloride (815 mg, 3 mmol) in dry THF (20 ml). The solvent was evaporated to dryness to yield a white solid which was chromatographed on neutral alumina using 1-4% MeOH/chloroform as eluent to give *exo-N*-propyl-(bicyclo[2.2.1]hept-5-en-2-yl)methylamine (85 mg, 17%); υ_{max} (neat)/cm^{-1} 3289, 2964, 1656, 1128, 903, and 706; δ_H 0.92 (3 H, t, Me), 1.12 (1 H, dt, J = 11.3, 3.6 Hz, *endo*-3-H), 1.30 (1 H, m, *exo*-3-H), 1.30 (2 H, m, 7-H), 1.55, (3 H, m, 2, C*H*$_2$Me), 1.64 (1 H, brs, NH), 2.62 (5 H, m, 1-H, C*H*$_2$N), 2.80 (1 H, brs, 4-H), 6.03 (1 H, m, J = 5.7, 2.9 Hz, 5-H), and 6.09 (1 H, dd, J = 5.7, 3.1 Hz, 6-H), the structure was confirmed using COSY NMR techniques; δ_C 11.8 (Me), 23.15 (*C*H$_2$Me), 31.5 (3-C), 39.2, 41.7, and 44.6 (1, 2, 4-C), 45.2 (7-C), 52.8 (*C*H$_2$N), 55.8 (*C*H$_2$CH=CH$_2$), 136.5, and 136.6 (5, 6-H); m/z 166.1590 (MH$^+$, $C_{11}H_{19}N$+H requires 166.1590), 149, 136, 98, 91, 79, and 72 (100%); and the mercury adduct (**32**, R = Pr) (864 mg, 72%); υ_{max} (neat)/cm^{-1} 2950, 1719, 1662, 1600, 1544, 1216, 1067, 937, 755, and 666; δ_H 0.92 (3 H, t, Me), 1.16 (1 H, d, J = 12.3 Hz, *endo*-3-H), 1.50 (3 H, m, C*H*$_2$Me 7-H), 1.75 (1 H, brd, 7-H), 2.02 (1 H, m, *exo*-3-H), 2.33 (1 H, m, 2-H), 2.48 (1 H, m, 4-H), 2.68 (5 H, m, 1, 5-H, *exo*-C*H*$_2$N, CH$_2$C*H*$_2$N), 3.01 (1 H, J = 10.0, 5.8 Hz, *endo*-C*H*$_2$N), and 3.79 (1 H, d, J = 4.8 Hz, 6-H), the assignments were confirmed using COSY techniques; δ_C 11.9 (Me), 22.3 (CH$_2$Me), 37.4 (2-C), 40.1 and 40.3 (7, 4-C), 41.9 (3-C), 46.9 (1-C), and 56.9 (CH$_2$CH$_2$N), 58.8 (5-C), 59.4 (*C*H$_2$N), 69.9 (6-C); m/z

401.0810 [M+ (31%). $C_{11}H_{18}NHgCl$ requires 401.0810], 372 (5), 199 (4), 164 (100), 149 (3), 136 (9), 122 (25), 110 (13), 91 (8), 80 (10), and 68 (10).

N-Allyl-N-(Benzenesulfenyl)-2-(cyclohex-2-en-1-yl)-2-phenylethylamine (33a)

N-*Allyl-2-(cyclohex-2-en-1-yl)-2-phenylethylamine*. 2-(Cyclohex-2-en-1-yl)-2-phenylethylamine and allyl bromide were reacted (reflux 15 h) to yield *N*-allyl-2-(cyclohex-2-en-1-yl)-2-phenylethylamine as a clear oil, (2.2 g, 92%); υ_{max} (neat)/cm^{-1} 3025, 1453, and 701; δ_H 1.56 (6 H, m, 4', 5', 6'-H), 2.39 (1 H, m, 1'-H), 2.95 (5 H, m, 1-H, 2-H, $CH_2CH{=}CH_2$), 5.03 (2 H, dt, 2', 3'-H), 5.79 (3 H, m, $CH{=}CH_2$), and 7.27 (5 H, m, Ph-H); δ_C 21.88 (6'-C), 25.22 (5'-C), 27.26 (4'-C), 38.96 (1'-C), 51.29 (2-C), 52.44 (1-C), 57.36 ($CH_2CH{=}CH_2$), 115.79 ($CH{=}CH_2$), 136.81 ($CH{=}CH_2$), and 127.99-142.24 (Ar-C, 2', 3'-C); m/z 242.1909 [MH^+ (100%). $C_{17}H_{23}N$+H requires 242.1909], 242 (100%), 202 (53), 102 (17), and 70 (43).

N-*Allyl*-N-*(benzenesulfenyl)-2-(cyclohex-2-en-1-yl)-2-phenylethylamine* (**33a**). *N*-Allyl-2-(cyclohex-2-en-1-yl)-2-phenylethylamine (**37a**) was reacted with benzenesulfenylchloride using the general procedure to yield the sulfenamide (**33a**) as a clear oil, (470 mg, 37%); υ_{max} (neat)/cm^{-1} 3028, 1580, 1476 and 1454, 691, and 689; δ_H 1.54 (6 H, m, 4', 5', 6'-H), 2.41 (1 H, m, 1'-H), 3.03 (1 H, m, 2-H), 3.23 (2 H, m, 1-H), 3.52 (2 H, d, $CH_2CH{=}CH_2$), 5.08 (2 H, dt, 2', 3'-H), 5.71 (3 H, m, $CH{=}CH_2$), and 7.31 (10 H, m, Ph-H); δ_C 21.89 (5'-C), 25.23 (6'-C), 27.24 (4'-C), 39.05 (1'-C), 49.49 (2-C), 59.41 (1-C), 62.23 ($CH_2CH{=}CH_2$), 117.42 ($CH{=}CH_2$), 135.40 ($CH{=}CH_2$), and 127.76-??? (Ar-C, 2', 3'-CH); m/z 350.1942 [MH^+ (100%). $C_{23}H_{27}NS$ +H requires 350.1942], 270 (81), 218 (38), 178 (25), and 109 (10).

Reaction between Bu_3SnH and N-*allyl*-N-*(benzenesulfenyl)-2-(cyclohex-2-en-1-yl)-2-phenylethylamine* (**33a**). The sulfenamide (**33a**) was reacted using the general procedure (benzene, reflux, syringe pump, 6 h) to yield (78 mg, 38%, prior to chromatography) of a mixture of ca. 5:1 of cyclised product, the tricyclic amine (**36**), to *N*-allyl-2-(cyclohex-2-en-1-yl)-2-phenylethylamine (**37a**). Purification using a dry alumina column with diethyl ether/light petroleum as eluent yielded the pure tricyclic amine (**36**) (3 diasteroisomers in the ratio 2:2:1) as a clear oil, (60 mg, 30%); δ_H 0.91-1.16 (3 x d, Me), 1.44-1.76 (6 H, m, $CH_2CH_2CH_2$), 2.29 (2 H, m, CH), 2.73-3.06 (4 H, m, CH_2N), 3.19 (1 H, m, PhC*H*), 3.87 (1H, m, C*H*N), and 7.10-7.38 (5 H, Ph-H); δ_C 12.03, 16.12, and 19.49 (Me), 21.87, 23.69, 24.46, 24.55, 25.10, 25.23, 25.54, and 30.18 (3 x $CH_2CH_2CH_2$), 37.73, 40.18, 41.13, 42.81, 43.99, and 44.98 (6 x CH), 49.49, 51.08, 51.24 (*C*HPh), 54.71, 55.16, 65.59, and 66.12 (CH_2N), 64.53, 65.98, and 66.84 (*C*HN), and 125.85-128.84 (Ph-C) (not all the resonances for the 3 diastereoisomers could be observed); m/z 242.1909 [MH^+ (89%). $C_{17}H_{23}N$+H requires 242.1909], 162 (100), and 70 (22).

N-(Benzenesulfenyl)-2,N-di-(cyclohex-2-en-1-yl)-2-phenylethylamine (33c)

2,N-*di-(cyclohex-2-en-1-yl)-2-phenylethylamine* (**37c**). 2-(Cyclohex-2-en-1-yl)-2-phenylethylamine was reacted with 3-bromocyclohexene (reflux, 15 h) to yield a crude oil which was purified using a dry alumina column with diethyl ether/ethyl acetate as eluent to yield 2,*N*-di-(cyclohex-2-en-1-yl)-2-phenylethylamine (**37c**) as a clear oil (861 mg); υ_{max} (neat)/cm^{-1} 3402, 3024, 1452, and 700; δ_H 1.51 (15 H, m), 2.76 (2 H, d, 1-H, CH_2N), 3.46 (1 H, m, CHN), 5.80 (4 H, dd, alkene-H), and 7.19 (5 H, m, Ar-H); δ_C 22.33, 25.28, 27.99, and 37.86 (cyclohexene-CH_2), 49.22 (2-C), 50.59 (CH_2N), 55.02 (*C*HN), and 129.82-143.84 (Ar and olefin-C); m/z 282.2222 [MH^+ (100%). $C_{20}H_{27}N$+H requires 282.2222], 202 (15), 190 (23), and 110 (17).

N-*(Benzenesulfenyl)-2,*N-*di-(cyclohex-2-en-1-yl)-2-phenylethylamine* (**33c**). Reaction between the amine (**37c**) and benzenesulfenylchloride using the general procedure (2.5 h) yielded the sulfenamide (**33c**) as a clear oil (788 mg, 71%); δ_H 1.31-1.98 (12 H, m, 4', 5', 6'-H), 2.59 (1 H, m, 1'H), 3.14 (1 H, m, 2-H), 3.40 (2 H, m, 1-H), 3.67 (1 H, m, CHN), 5.70 (4 H, m, olefin-H), and 6.99-7.29 (5 H, m, aromatic); δ_C 21.39, 22.29, 25.24 (4', 5', 6'-C, 6 resonances in total), 28.91 (1'-C), 32.13 (CHPh), 46.12 (1-C), 55.03 (*C*HN), and 125.57-136.58 (Ar and olefin-C); m/z 390.2255 [MH^+ (72%). $C_{26}H_{31}NS$+H requires 390.2255], 362 (69), 282 (93), 179 (100), and 110 (28).

Reaction between Bu_3SnH and N-*(benzenesulfenyl)-2,*N-*di-(cyclohex-2-en-1-yl)-2-phenylethylamine* (**33c**). The sulfenamide was reacted using the general procedure (benzene, reflux, syringe pump, 6 h) to yield the mono-cyclised product, 1-(cyclohex-2-en-1-yl)-4,5,6,7-hexahydro-3-phenylindoline (**38**) (one diastereoisomer, 16%) as a clear oil; δ_H 0.95 (2 H, dt, 5-H), 1.19 (2 H, m, 6-H), 1.36 (2 H, m, 5'-H), 1.43 (2 H, m, 4-H), 1.51 (2 H, 7-H), 1.78 (2 H, m, 6'-H), 1.93 (1 H, dt, 3-H), 1.95 (2 H, m, 4'-H), 2.41 (1 H, m, 3a-H), 2.70-2.92 (2 H, m, 2-H), 3.04 (1 H, m, 7a-H), 3.42 (1 H, m, 1'-H), 5.60-5.76 (2 H, m, 2' and 3'-H, olefin-H), and 7.05-7.26 (5 H, m, Ph-H); δ_C 22.00 (5-C), 25.52 (6-C), 28.00 (4-C), 28.61 (5'-C), 37.83 (6'-C), 38.01 (3a-C), 48.40 (4'-C), 49.00 (2-C), 55.43 (3-C), 69.49 (1'-C), and 125.61-132.49 (Ph and olefin-C); m/z 282.2222 [MH^+ (100%). $C_{20}H_{27}N$+H requires 282.2222], 202 (18), 190 (19), and 110 (32). The uncyclised amine (**37c**) (11%) was also obtained, as a clear oil, and no bicyclised material could be detected.

cis-N-(Benzenesulfenyl)-*N*-(but-3-enyl)-5-(4-isopropylphenyl)pent-4-enylamine (39)

cis-N-*(But-3-enyl)-5-(4-isopropylphenyl)pent-4-enylamine*. *cis*-5-(4-Isopropylphenyl)pent-4-enylamine was prepared as reported[4] and reacted with 4-bromobut-1-ene (ethyl acetate, reflux, 17 h) to yield a crude oil. The oil was purified using a flash alumina column with chloroform/methanol as eluent to yield the *cis-N*-(but-3-enyl)-5-(4-isopropylphenyl)pent-4-enylamine as a clear oil, (1.0 g, 79%); υ_{max} (neat)/cm^{-1} 3282, 3007, 1460, and 845; δ_H (300 MHz) 1.25 (6 H, d, Me), 1.62 (2 H, m, 2-H), 2.19 (2 H, q, 2'-H), 2.33 (2 H, m, 3-H), 2.61 (4 H, m, 1, 1'-H), 2.85 (1 H, q, C*H*Me_2), 5.07 (2 H, t, CH=CH_2), 5.58 (1 H, dt, 4-H), 5.77 (1 H, m, C*H*=CH_2), 6.41 (1 H, d, 5-H), and 7.17 (4 H, d, Ar-H); δ_C (75 MHz) 23.97 (Me), 29.63 (2-C), 30.84 (2'-C), 34.29 (3-C), 48.86 (1'-C), 49.32 (1-C), 116.33 (CH=*C*H_2), 136.47 (*C*H=CH_2), 127.06-131.25 (Ar, 4, 5-C), and 135.37 and 147.65 (Ar-C); m/z 258.2222 [MH^+ (100%). $C_{18}H_{27}N$+H requires 258.2222], 246 (42), 102 (20), and 85 (13).

cis-N-*(Benzenesulfenyl)*-N-*(but-3-enyl)-5-(4-isopropylphenyl)pent-4-enylamine* (**39**). *cis-N*-(But-3-enyl)-5-(4-isopropylphenyl)pent-4-enylamine (403 mg) was reacted with benzenesulfenylchloride using the general procedure (diethyl ether, room temperature, 2 h) to yield the sulfenamide (**39**) as a clear oil (532 mg, 93%); υ_{max} (neat)/cm^{-1} 3004, 1581, 1477, 1460, 844, and 689; δ_H 1.18 (6 H, d, Me), 1.50 (2 H, m, 3-H), 1.77 (2 H, m, 3-H), 2.17 (CH_2CH=CH_2), 2.86 (1 H, q, C*H*Me_2), 2.98 (4 H, m, NCH_2), 5.00 (2 H, d, CH=CH_2), 5.56 (1 H, m, 4-H), 5.60 (1 H, m, C*H*=CH_2), 6.35 (1 H, d, 5-H), 7.12-7.29 (9 H, m, Ar-H); δ_C 23.91 (Me), 26.05 (2-C), 28.72 (3-C), 32.96 (*C*H_2CH=CH_2), 33.75 (*C*HMe_2), 57.90 (2 x CH_2N), 115.96 (CH=*C*H_2), and 123.88-131.65 (Ar and olefin-C); m/z 366.2255 (MH^+, $C_{24}H_{31}NS$ requires 366.2255), 312 (100%), 258 (29), 210 (56), 182 (22), 124 (32), and 109 (8).

Reaction between Bu_3SnH and cis-N-*(Benzenesulfenyl)*-N-*(but-3-enyl)-5-(4-isopropylphenyl)pent-4-enylamine* (**39**). The sulfenamide (**39**) was reacted with Bu_3SnH using the general procedure (benzene, reflux, syringe pump, 6 h) to give a mixture of *cis-N*-(but-3-enyl)-5-(4-isopropylphenyl)pent-4-enylamine (24%) and 8-(4-isopropylphenyl)-7-methylindolizidine (**41**) (180 mg, 64%). Further purification using a dry alumina column with diethyl ether/light petroleum as eluent yielded the indolizidine (**41**) as a clear oil, (73 mg, 26%). ^1H NMR spectral analysis using difference nOe, HETCOR, and COSY45 techniques indicated two isomers which are invertomers (major isomer, 55%; minor isomer, 45%).

Major isomer (**41**): δ_H (400 MHz) 0.73 (3 H, d, Me), 1.20 (6 H, d, $CHMe_2$), 1.33 (1 H, m, 1-H), 1.61 (1 H, m, 6-H), 1.66 (1 H, m, 2-H), 1.80 (1 H, m, 2-H), 1.86 (1 H, m, 1-H), 2.04 (1 H, m, 7-H), 2.08 (1 H, m, 6-H), 2.31 (1 H, dt, 3-H), 2.39 (1 H, dt, 5-H), 2.57 (1 H, m, 8a-H), 2.80 (1 H, dd, 8-H), 2.87 (1 H, quintuplet, $CHMe_2$), 2.97 (1 H, ddd, 5-H), 3.19 (1 H, dt, 3-H), 7.02 (2 H, d, Ar-H), and 7.12 (2 H, d, Ar-H);

Minor isomer: δ_H (400 MHz) 0.69 (3 H, d, Me), 1.20 (6 H, d, $CHMe_2$), 1.27 (1 H, m, 8a-H), 1.42 (2 H, m, 1-H), 1.53 (1 H, m, 6-H), 1.57 (1 H, m, 2-H), 1.69 (1 H, m, 7-H), 1.78 (1 H, m, 2-H), 1.82 (1 H, m, 6-H), 2.06 (1 H, m, 8-H), 2.13 (1 H, m, 3-H), 2.17 (1 H, m, 5-H), 2.87 (1 H, quin, $CHMe_2$), 3.14 (1 H, m, 3-H), 3.18 (1 H, m, 5-H), 7.04 (2 H, d, Ar-H), and 7.10 (2 H, d, Ar-H);

Both isomers: δ_C (100 MHz) 20.29, 20.61 (Me), 23.85 (CH*Me*$_2$), 29.26 (6-C), 33.43 (2-C), 36.45 (1-C), 46.96 (7-C), 52.22 ($CHMe_2$), 54.02, 54.19 (8-C), 60.26 (3, 5-C), 69.53 (8a-C), and 126.00-128.11 (Ar-C); m/z 257.2144 [(M^+ (39%). $C_{18}H_{27}N$ requires 257.2144], 218 (32), 97 (100), 84 (82), and 69 (40).

***cis*-*N*-Allyl-*N*-(benzenesulfenyl)-6-(4-t-butylphenyl)hex-5-enylamine (42)**

4-Cyanobutylphosphonium bromide. 5-Bromovaleronitrile (25.0 g, 0.154 mol) and triphenylphosphine (37.0 g, 0.140 mol) in toluene (500 ml) were refluxed for 72 h. At the end of this time, colourless crystals of the product were filtered off and dried to yield 4-cyanobutylphosphonium bromide, (46.3 g, 78%), m.p. 231-233°C; δ_H (300 MHz) 1.68 (2 H, m, 3-H), 2.05 (2 H, dt, 2-H), 2.57 (2 H, t, 4-H), 3.91 (2 H, m, 1-H), and 7.60-7.85 (15 H, m, aromatic).

cis-*1-(4-t-Butylphenyl)-5-cyano-pent-5-ene.* 4-Cyanobutylphosphonium bromide (45.0 g, 0.106 mol) was added over a period of 20 min to a stirred solution of sodium hydride (4.24 g, 0.106 mol) in dry THF (200 ml) at room temperature under an atmosphere of nitrogen. The solution was stirred 1 h, a solution of 4-t-butylbenzaldehyde (6.88 g, 42 mmol) in THF (10 ml) added dropwise, and stirred at room temperature for a further 20 h. The solution was poured onto ice/water (200 ml) and acidified to pH 2 using 2 M hydrochloric acid, and extracted with diethyl ether. The ether extracts were dried, and evaporated to dryness to yield the crude product. Purification on a dry silica column using hexane and diethyl ether as eluent yielded the *cis*-5-cyano-1(4-t-butylphenyl)pent-5-ene as a clear oil, (8.0 g, 84%); δ_H (300 MHz) 1.31 (9 H, s, Me), 1.83 (2 H, q, 4-H), 2.35 (2 H, t, 3-H), 2.49 (2 H, dq, 5-H), 5.58 (1 H, m, 2-H), 6.51 (1 H, d, 1-H), and 7.20-7.40 (4 H, ABq, Ar-H); δ_C (75 MHz) 16.68 (4-C), 25.79 (3-C), 27.62 (5-C), 31.24 (Me), 34.76 (quart), 119.64 (CMe_3), 124.85-134.44 (Ar and olefin-C), and 150.42 (CN); m/z 227, 212 (100), 131 (45), 115 (23).

6-(4-t-butylphenyl)hex-5-enylamine. cis-1-(4-t-Butylphenyl)-5-cyanopent-1-ene (8.4 g, 37 mmol) in dry diethyl ether was added very slowly to a cooled solution of $LiAlH_4$ in dry diethyl ether and stirred at room temperature. After stirring for 30 min, water was added, the lithium salts filtered, and the solvent evaporated to dryness to yield pure cis-6-(4-t-butylphenyl)hex-5-enylamine as a clear oil, (8.5 g, 99%); δ_H 1.36 (9 H, s, Me), 1.35 (4 H, m, 2-H, 3-H), 1.49 (2 H, s, NH_2), 2.41 (2 H, t, 4-H), 2.73 (2 H, m, 1-H), 5.64 (1 H, m, 5-H), 6.40 (1 H, d, 6-H), and 7.20-7.40 (4 H, ABq, Ar-H); δ_C 27.34 (3-C), 28.56 (2-C), 31.59 (Me), 33.51 (4-C), 34.49 (CMe_3), 42.10 (1-C), 125.05-132.17 (Ar and olefin-CH), and 135.06 and 149.72 (Ar-C); m/z 231, 214 (31%), 199 (85), 188 (100), 129 (95), 115 (84). The amine was used without purification.

N-*Allyl-6-(4-t-butylphenyl)hex-5-enylamine.* A solution of allyl bromide (3.7 g, 31 mmol) in dry ethyl acetate (10 ml) was added dropwise to a stirred solution of 6-(4-t-butylphenyl)hex-5-enylamine (8.5 g, 37 mmol) and triethylamine (40 ml) in dry ethyl acetate (90 ml) at room temperature under an atmosphere of nitrogen. The solution was refluxed for 4 h, when TLC indicated that all of the starting material had been used up. The precipitate of triethylamine hydrobromide was filtered and the filtrate evaporated to dryness to yield the *N*-allyl-6-(4-t-butylphenyl)hex-5-enylamine as a clear oil, (9.8 g, 98%); δ_H (300 MHz) 1.19 (9 H, s, Me), 1.36 (4 H, m, 2, 3-H), 2.27 (2 H, m, 4-H), 2.36 (1 H, m, NH), 2.45 (2 H, t, 1-H), 3.09 (2 H, dd, $CH_2CH{=}CH_2$), 5.05 (2 H, m, $CH{=}CH_2$), 5.48 (1 H, m, 5-H), 5.78 (1 H, m, $CH{=}CH_2$), 6.27 (1 H, d, 6-H), and 7.09-7.32 (4 H, ABq, Ar-H); δ_C (75 MHz) 28.59 (4-C), 29.29 (3-C), 31.37 (Me), 34.51 (CMe_3), 49.08 (4-C), 52.36 (1-C), 56.84 ($CH_2CH{=}CH_2$), 116.17 ($CH{=}CH_2$), 136.52 ($CH{=}CH_2$), 125.06-132.33 (Ar-CH, 5, 6-C), 134.86 and 149.34 (Ar-C); m/z 272, 232 (71), 126 (17), 112 (16).

cis-N-*Allyl*-N-*(benzenesulfenyl)-6-(4-t-butylphenyl)hex-5-enylamine* (**42**). *cis-N*-Allyl-6-(4-t-butylphenyl)-hex-5-enylamine (1.9 g, 6.99 mmol) was reacted with *N*-(benzenesulfenyl)phthalimide (1.8 g, 6.99 mmol) using the general procedure (CH_2Cl_2, reflux, 4 h) to yield *cis-N*-allyl-*N*-(benzenesulfenyl)-6-(4-t-butylphenyl)hex-5-enylamine (**42**) as a clear oil (1.3 g, 49%); (Found C: 79.00, H: 8.75, N: 3.76; $C_{25}H_{31}NS$ requires C, 79.10; H, 8.76; N, 3.69%); δ_H 1.19 (9 H, s, Me), 1.35 (2 H, m, 3-H), 1.58 (2 H, m, 2-H), 2.25 (2 H, m, 4-H), 2.98 (1 H, d, $CH_2CH{=}CH_2$), 3.35 (1 H, d, $CH_2CH{=}CH_2$), 3.81 (2 H, dd, 1-H), 5.02 (2 H, m, $CH{=}CH_2$), 5.49 (1 H, m, 5-H), 5.78 (1 H, m, $CH{=}CH_2$), 6.28 (1 H, d, 6-H), and 7.15-7.28 (9 H, m, Ar-H); δ_C 27.38 (3-C), 28.54 (2-C), 31.39 (Me), 34.54 (CMe_3), 53.14 (4-C), 56.87 (1-C), 62.06 ($CH_2CH{=}CH_2$), 117.31 ($CH{=}CH_2$), 123.91-135.88 (Ar and olefin-CH), and 141.84 (Ar-C); m/z 380.2412 [MH^+ (45%). $C_{25}H_{33}NS$ +H requires 380.2412], 312 (100), 270 (27), 123 (21), 110 (39).

Reaction between Bu_3SnH and cis-N-*allyl*-N-*(benzenesulfenyl)-6-(4-t-butylphenyl)hex-5-enylamine* (**42**). The sulfenamide (**42**) (300 mg, 0.78 mmol) was reacted with Bu_3SnH using the general procedure (toluene, reflux, syringe pump, 6 h) to yield *trans-N*-allyl-6-(4-t-butylphenyl)hex-5-enylamine (**45**) (120 mg, 56%). The mass spectrum and ^1H NMR spectrum were very similar to the *cis*-isomer with the major exception that 6-H had shifted from δ 6.40 to 6.18 (1 H, dt) which is indicative of a *trans* double bond. None of the *cis*-isomer could be detected.

Reaction between the sulfenamide (**42**) (200 mg, 0.53 mmol) was carried out under the same conditions using tris(trimethylsilyl)silane in place of Bu_3SnH to yield *trans-N*-allyl-*N*-(benzenesulfenyl)-6-(4-t-butylphenyl)hex-5-enylamine (**45**) (120 mg, 84%) with no evidence of a cyclised product.

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