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Sequential Hydrostannylation-Cyclisation of δ- and ω-Allenyl Aryl Halides. Cyclisation at the Proximal Carbon.

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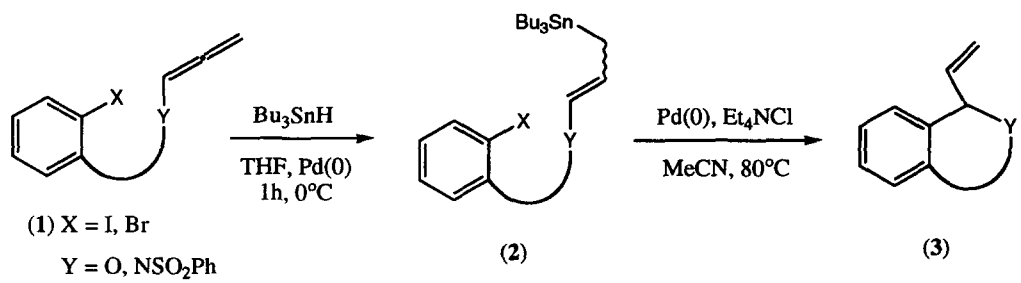
Abstract: Palladium catalysed hydrostannylation of (Bu_3SnH, THF, 0°C) of δ- and ω-allenyl aryl halides followed by mono- or bis-cyclisation (MeCN, 80°C) affords small (5-7), large (11-17) and spirocyclic rings in which cyclisation occurs at the proximal carbon of the original allene. The reaction proceeds via stereoselective allylstannane formation. The cyclisation products are α-vinyl oxygen- and nitrogen-heterocycles. Copyright © 1996 Elsevier Science Ltd

Cyclic carbopalladation can be achieved by a group of related reactions that provide versatile and powerful methodology for the construction of carbocyclic and heterocyclic rings.[1] These ring forming processes are marked by their tolerance of a wide range of functionality together with their ability to process a variety of starter species and to effect cyclisation onto all types of C-C unsaturated bonds. Substantial additional pre- and post- cyclisation functionality can be incorporated via cyclisation-anion capture[2] or polycomponent cascades.[3]

Cyclisation of aryl halides onto 1,2-dienes normally occurs at the centre carbon of the allene moiety generating a π-allylpalladium(II) species[1,4,5] except where such cyclisations involve three- versus 4-membered ring formation or other compelling stereoelectronic factors are operational.[6]

We now report simple synthetic methodology that is equivalent to carbopalladation of terminal heteroallenes at the α-carbon atom (proximal carbon) creating both small and large rings containing α-vinylheteroatom moieties (Scheme 1).



Scheme 1

A series of allenes (1a-f) were prepared by modification of known procedures.[7] The allenes underwent regiospecific, stereoselective hydrostannylation[8] on treatment with tri-n-butyltin hydride in anhydrous THF at 0°C over 1h in the presence of 10mol % $Pd(OAc)_2$ and 20mol % PPh_3. N.m.r. monitoring of the reaction showed that a mixture of alkene stereoisomers (2) was produced whose composition was dependant on the heteroatom Y [Z:E, 10:1.5 when Y=O (J_Z 5.8Hz, J_E12.0Hz), and 1:4 when Y=NSO_2Ph (J_Z5.8Hz, J_E14.0-14.3Hz)]. There mixtures were cyclised without further purification by evaporation of the solvent and addition of a 0.15M solution of $Et_4NCl.H_2O$ (1.5mol equiv) followed by stirring and heating the ca. 0.07 M solution of substrate (1a-f) whereupon cyclisation to (3) occurred. Reaction time and yields are collected in Table 1.

The cyclisation occurs rapidly and gives 5-7-membered rings in moderate to good yield (Table 1). Several attempts to cyclise (1f) to the corresponding 8-membered ring were unsuccessful. After 4-8h at 80°C all the starting material had been consumed producing a mixture of unidentified products. Monitoring the reaction by t.l.c. showed production of only baseline material.

The simplest mechanism for the cyclisation of the stannanes is illustrated for substrate (2c) in Scheme 2. This allows a common mechanism to operate for both E- and Z- stannanes and requires that elimination of Bu_3SnPdX leading to (3) be faster than β-hydride (HPdX) elimination leading to (4).

We have monitored the cyclisation of the 1:4 Z/E-mixture of stannanes (2c) (Table 2).

Table 2. Composition of Z/E-allyl stannane mixture (2c) during cyclisation to (3c)[a].

Time(min)	Z(%)[b]	E(%)[b]	Conversion (%) to (3c)[b]
0	20	80	-
2.5	9	91	27
5.0	<1	>99	34
10.0	<1	>99	75
30.0	-	-	>95

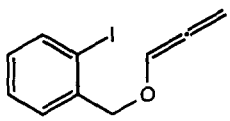
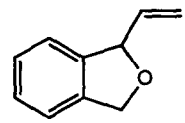
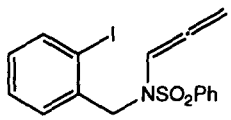
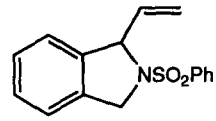
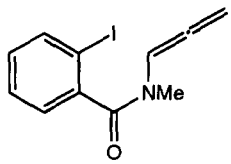
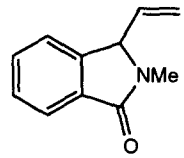
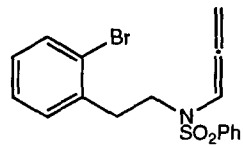
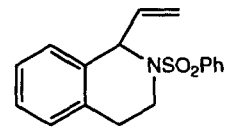
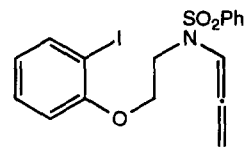
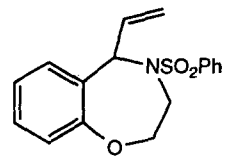
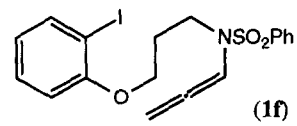
a. Reaction carried out at 80°C in MeCN using the standard catalyst system.

b. Determined by integration of the ^1H n.m.r. spectra.

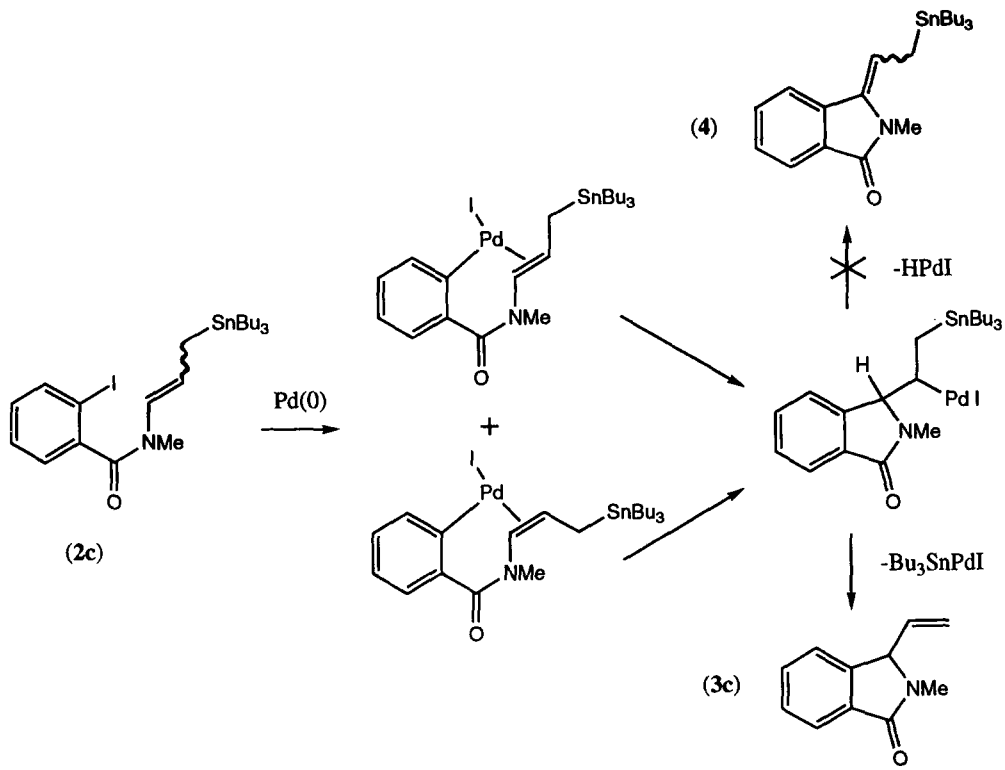
Thus the Z-isomer of (2c) cyclises faster than E-isomer. This observation, whilst not unequivocally establishing the mechanism outlined in Scheme 2, would accord with a mechanism in which coordination of Pd(O) to the alkene precedes the oxidative addition. The greater stability of Z-alkene complexes versus E-alkene complexes imparts a slight energetic advantage to the oxidative addition transition state involving the former. The suggestion (Scheme 2) that elimination of Bu_3SnPdX might be more facile than β-hydride elimination is lent credence by reports of related preferential elimination of HOPdX[9] and ROPdX[10].

Although the Pd(O) catalysed hydrostannylation of allenes[8,11] has been known for some time there has been little study of heteroallene substrates. Addition of Bu_3SnH to methoxyallenes has been studied by two groups.[12] The most recent study[12a] reports stereoselectivity for the Z-allylstanne in a number of cases. In our examples the substantial difference in E/Z-ratio between the allylstannes derived from (1a) and those from (1b) - (1f) indicate the importance of stereoelectronic effects in determining stereoselectivity.

Table 1. Sequential hydrostannylation-palladium catalysed cyclisation of (**1a-f**).

Substrate	Time (h)	Product	Yield(%)[a]
 (**1a**)	1	 (**3a**)	85[b]
 (**1b**)	1	 (**3b**)	66
 (**1c**)	1	 (**3c**)	72
 (**1d**)	4	 (**3d**)	52
 (**1e**)	3[c]	 (**3e**)	50
 (**1f**)	4-8	—	—

a. Overall yields from (**1**) of isolated materials.
b. Yield of crude material. Product decomposes on silica.
c. Concentration of (**1e**) was ca. 0.05M maintaining the concentration of $Et_4NCl.H_2O$ at 0.15M



Scheme 2

The effect of solvent and additives on the cyclisation of E/Z-(2c) was briefly examined (Table 3).

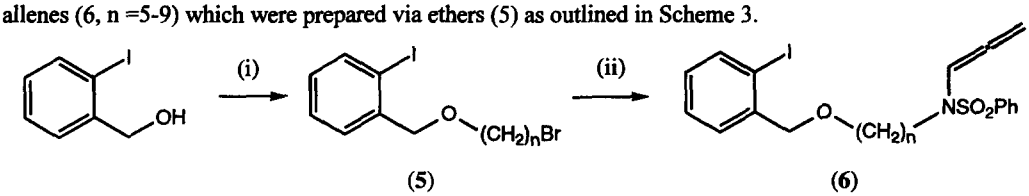
Table 3. Effect of solvent and additives on the cyclisation of E/Z-(2c).

Entry	Solvent	Additive(mol equiv)	T(°C))	Time(h)	3c(%)[a]
1	THF	-	66	24	-[b]
2	THF	NEt_3	66	24	-[b]
3	THF	K_2CO_3(1.5)	66	8	61
4	THF	$Et_4NCl.H_2O$(1.5)	66	8	61
5	Toluene	-	110	1	23
6	DMF	-	80	1	46
7	DMF	$Et_4NCl.H_2O$(1.5)	80	1	58
8	MeCN	-	80	7	59
9	MeCN	K_2CO_3(1.5)	80	4	60
10	MeCN	$Et_4NCl.H_2O$(0.5)	80	3.5	67
11	MeCN	$Et_4NCl.H_2O$(1.0)	80	1.75	69
12	MeCN	$Et_4NCl.H_2O$(1.5)	80	1	72
13	MeCN	$Et_4NCl.H_2O$(2.0)	80	0.75	72
14	MeCN	Et_4NCl(anhyd) (1.5)	80	1	72

a. Isolated yields.
b. Quantative recovery of (2c).

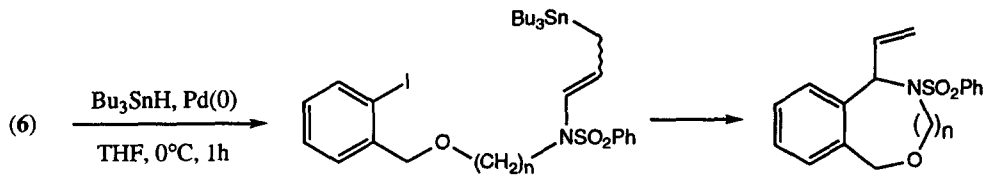
In the absence of added base the order of effectiveness of the solvents was MeCN > DMF > toluene >THF (Table 3, entries 1, 5, 6 and 8). When $Et_4NCl.H_2O$(1.5mol equiv) was added the order became MeCN > THF ~ DMF (Table 3, entries 4, 7 and 12). Varying the amount of $Et_4NCl.H_2O$ from 0.5 - 2.0 mol. equiv. in acetonitrile had minimal effect on the yield of (3c) (Table 3, entries 10 - 13) as did use of anhydrous Et_4NCl (Table 3, entry 14).

We have recently reported the first palladium catalysed sp^3 - sp^2 Stille macrocyclisations as part of a biscyclisation cascade[13] and have now extended these studies to a series of macrocyclisations starting from allenes (6, n =5-9) which were prepared via ethers (5) as outlined in Scheme 3.



(5) (6)

Scheme 3.(i) NaH, DMF, $Br(CH_2)_nBr$. (ii) DMF, NaH, $NHSO_2Ph$



(7) (8)

Sequential palladium catalysed hydrostannylation (THF, O°C) of (6) → (7) followed by high dilution ($5x10^{-3}$M) cyclisation in acetonitrile (80°C) afforded a series of macrocycles (8) in moderate yield (Table 4). The allylstannanes (7) again comprised a ca. 1:4 mixture of Z- and E-isomers.

Table 4. Sequential macrocyclisation (6) → (8)[a]

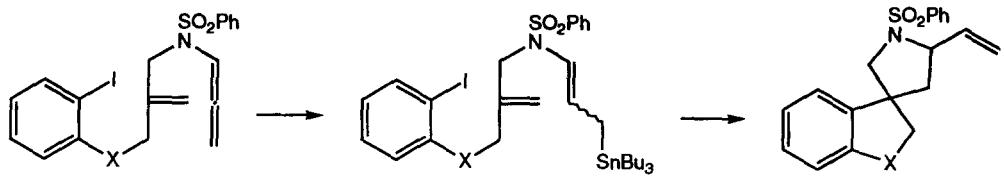
Substrate	n	Product	Ring size	Yield(%)[b]
6a	5	8a	11	40
6b	6	8b	12	44
6c	7	8c	13	43
6d	9	8d	15	46
6e	11	8e	17	46

a. The macrocyclisation employed $5x10^{-3}$M solutions of allyl stannanes whilst maintaining the concentration of $Et_4NCl.H_2O$ at 0.15M.

b. Isolated overall yields.

As part of our continuing studies on the scope of our palladium catalysed cyclisation-anion capture methodology we have explored several hydrostannylation-biscyclisation processes (Scheme 4).

The substrates (9a,b) were hydrostannylated in THF at 0°C as described above. The allylstannanes (10a,b) were obtained as ca. 1:4 mixtures of Z- and E-isomers and were cyclised, without isolation, to afford (11a) (41%) and (11b) (51%) respectively. The best results were obtained using a 0.15M solution of $Et_4NCl.H_2O$ (1.5mol. equiv.) in acetonitrile over 12h at 80°C and employing 3.5 x 10^{-2}M solutions of the vinyl stannanes. The addition of 1 mol. equiv. of either Ag_2CO_3 or Tl_2CO_3 failed to improve the yields of (11a,b).



(9) a. X = O
b. X = NSO_2Ph

(10)

(11) a. X = O
b. X = NSO_2Ph

Scheme 4

In summary, we have shown that sequential palladium catalysed hydrostannylation-cyclisation of δ- and ω-allenyl aryl halides allows cyclisation to be directed to the proximal carbon atom of the original allene. The sequential process can be applied to the synthesis of both small and large rings and to biscyclisation processes.

EXPERIMENTAL. Melting points were determined on a Koffler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on Perkin -Elmer Model 598 and 983G instruments and refer to films unless otherwise noted. Mass spectral data were obtained from VG AutoSpec operating at 70 eV. Nuclear magnetic resonance spectra were recorded on Bruker QE 300 and AM 400 machines operating at 300 and 400 MHz respectively. Unless otherwise specified, deuterochloroform was used as solvent with tetramethylsilane as internal standard (0.03%). Microanalyses were obtained using a Carlo Erba MOD 11016 instrument. Thin layer chromatography was carried out on Whatman PESIL G/UV polyester plates coated with a 0.2 mm layer of silica-gel and column chromatography was performed with silica-gel 60 (Merck 9385). Anhydrous DMF was commercially available (Aldrich), THF was sodium dried under a nitrogen atmosphere and *n*-hexane was distilled prior to use.

Synthesis of Allenes (1).

o-*Iodobenzyl 1,2-propadienyl ether (1a)* [4a]. A solution of *o*-iodobenzyl alcohol (2.81 g, 12 mmol) in dry DMF (25 ml) under a nitrogen atmosphere was treated with sodium hydride (60% dispersion in mineral oil, 576 mg, 14.4 mmol) at 0° C and the resulting mixture was stirred at room temperature for 30 min., then propargyl bromide (80% solution in toluene, 1.37 ml, 12.6 mmol) was added and the reaction mixture was stirred during 1.5 h at room temperature. DMF was evaporated under reduced pressure, the residue dissolved in dichloromethane (45 ml) and washed with water (45 ml). The organic layer was dried (Na_2SO_4) and evaporated to give the crude propargyl ether which was dissolved in dry THF (30 ml) and treated with potassium *t*-butoxide (1.51 g, 13.5 mmol). The suspension was stirred for 16 h at room temperature, THF was removed under vacuum and the residue was purified by flash chromatography (SiO_2) eluting with *n*-hexane to afford the **product** (2.29 g, 75%) as colourless needles, m.p. 85-86°C from *n*-hexane-ether; δ 4.51 (s, 2H, CH_2O), 5.88 (d, *J* 6.2 Hz, 2H, CH_2=C=C), 6.66 (t, *J* 6.2 Hz, 1H, C*H*=C=CH_2), 6.78 (t, *J* 7.5 Hz, 1H, ArH), 7.10-7.23 (m, 2H, ArH) and 7.56 (d, *J* 7.5 Hz, 1H, ArH); *m/z* (%) 272 (M^+, 18), 23 (76), 104 (100) and 69 (29); ν_{max} (CH_2Cl_2) 1960 and 845 cm^{-1}.

N-(o-*Iodobenzyl*)-N-(*phenylsulfonyl*)-*1,2-propadienylamine (1b).* A mixture of *o*-iodobenzyl alcohol (2.81 g, 12 mmol) and triethylamine (2.50 ml,18 mmol) in dichloromethane (50 ml) was cooled at 0°C and methanesulfonyl chloride (0.95 ml, 18 mmol) was added dropwise with stirring. The reaction was stirred for 2

h at this temperature and then washed with saturated aqueous sodium bicarbonate, dried (Na_2SO_4) and evaporated under reduced pressure. The crude mesylate (3.68 g, 98%) was dissolved in dry DMF (15 ml) under a nitrogen atmosphere and added to a solution of sodium *N*-propargylphenylsulfonamide (12 mmol) in DMF (25 ml), previously prepared from *N*-propargylphenylsulfonamide and excess of sodium hydride (1.5 eq.). The reaction was stirred for 1.5 h at room temperature, DMF was removed under reduced pressure and the residue dissolved in water (40 ml) and extracted with dichloromethane (2x25 ml). The organic layer was dried (Na_2SO_4), evaporated under reduced pressure and the residue was purified by flash chromatography (SiO_2) eluting with 98:2 v/v *n*-pentane-ether to afford the **product** (**1b**) (3.22 g, 66%) as colourless needles from *n*-pentane-ether, m.p. 87-88 °C (Found: C, 46.85; H, 3.7; N, 3.4; S, 7.7. $C_{16}H_{14}INO_2S$ requires: C, 46.75; H, 3.4; N, 3.4; S, 7.8%.); δ 4.31 (s, 2H, CH_2N), 5.08 (d, *J* 6.0 Hz, 2H, CH_2=C=C), 6.92 (t, *J* 6.0 Hz, 1H, C*H*=C=CH_2), 6.94 (t, *J* 9.0 Hz, 1H, ArH) and 7.32-7.89 (m, 8H, ArH); *m/z* (%) 411 (M^+, 5), 270 (58), 217 (73), 149 (52), 144 (38), 143 (100), 142 (40), 141 (22), 125 (38), 116 (32), 115 (52), 97 (29), 91 (27), 90 (70), 89 (44), 85 (20), 83 (28), 77 (74), 71 (74), 71 (22) and 69 (25); ν_{max} (CH_2Cl_2) 1960, 1350, 1165 and 850 cm^{-1}.

N-*(o-Iodobenzoyl)*-N-*methyl-1,2-propadienylamine (1c).*[4a] A solution of *o*-iodobenzoyl chloride (3.20 g, 12 mmol) in dichloromethane (15 ml) was added dropwise with stirring to a mixture of *N*-methylpropargylamine (828 mg, 12 mmol) and triethylamine (2.00 ml, 14.4 mmol) in dichloromethane (10 ml) at 0°C. The mixture was stirred at room temperature for 4 h, water (50 ml) was added, the organic layer decanted, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was immediately dissolved in DMF (25 ml) and treated with sodium hydroxide (pearls, 576 mg, 14.4 mmol) at room temperature for 16 h. DMF was removed under reduced pressure and the residue dissolved in water (40 ml) and extracted with dichloromethane (2x20 ml). The organic layer was dried (Na_2SO_4), evaporated, and the residue purified by flash chromatography (SiO_2) eluting with 7:3 v/v *n*-hexane-ether to give the **product** (**1c**) (2.85 g, 80%) as a pale yellow oil; δ 2.84, 3.15 (2xs, 3H, CH_3), 5.25, 5.33 (br. s and d, *J* 6.0 Hz, 2H, CH_2=C=C), 6.20, 7.45 (2xt, *J* 6.0 Hz, 1H, C*H*=C=CH_2), 6.78 (t, *J* 7.2 Hz, 1H, ArH), 7.05 (m, 1H, ArH), 7.20 (t, *J* 7.5 Hz, 1H, ArH) and 7.61 (d, *J* 7.2 Hz, 1H, ArH); *m/z* (%) 299 (M^+, 14), 231 (100), 104 (85) and 69 (31); ν_{max} (film) 1955, 1740 and 850 cm^{-1}.

N-*2-(o-Bromophenyl)ethyl*-N-*(phenylsulfonyl)-1,2-propadieylnamine (1d).* A solution of *o*-bromophenethyl alcohol (2.41 g, 12 mmol) and triethylamine (2.50 ml, 18 mmol) in THF (50 ml) was cooled at 0°C and methanesulfonyl chloride (1.14 ml, 14.4 mmol) was added dropwise with stirring. Stirring was continued for 2 h at the same temperature when lithium bromide (3.13 g, 36 mmol) was added and the resulting suspension was stirred for16 h at room temperature. Water (50 ml) and dichloromethane (50 ml) were then added, the organic layer decanted, dried (Na_2SO_4), and evaporated under reduced pressure. The crude bromide was dissolved in anhydrous DMF (10 ml) under a nitrogen atmosphere and added to a solution of sodium *N*-propargylphenylsulfonamide (12 mmol) in dry DMF (25 ml), previously prepared from *N*-propargylphenylsulfonamide and excess of sodium hydride (1.5 eq.). The mixture was stirred for 5 h, DMF was removed under reduced pressure and the residue was dissolved in water (50 ml) and extracted with dichloromethane (2x25 ml). The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure and the residue was purified by flash chromatography (SiO_2) eluting with 95:5 v/v *n*-hexane-ether to afford the **product** (**1d**) (3.06 g, 68%) as colourless needles from *n*-hexane-ether, m.p. 111-112°C (Found: C, 54.0;

H, 4.3; N, 3.8; S, 8.5. $C_{17}H_{16}BrNO_2S$ requires: C, 54.0; H, 4.25; N, 3.7; S, 8.5%.); δ 3.01, 3.38 (2xt, *J* 6.5 Hz, 4H, CH_2CH_2N), 5.34 (d, *J* 6.5 Hz, 2H, CH_2=C=C), 6.87 (t, *J* 6.5 Hz, 1H, C*H*=C=CH_2) and 7.04-7.83 (m, 9H, ArH); *m/z* (%) 380, 378 (M^++1, 7), 379, 377 (M^+, 29), 298 (31), 266 (22), 211 (31), 209 (34), 208 (32), 185 (28), 184 (46), 183 (29), 182 (45), 171 (25), 169 (26), 141 (58), 130 (32), 125 (63), 104 (30), 103 (29), 90 (20), 77 (100), 67 (21), 66 (28) and 51 (21); ν_{max} ($CDCl_3$) 1950, 1350, 1170 and 850 cm^{-1}.

N-*[2-(o-Iodophenoxy)ethyl]*-N*(phenylsulfonyl)-1,2-propadienylamine (1e)*. A suspension of *o*-iodophenol (2.20 g, 10 mmol) and sodium hydride (60% dispersion in mineral oil, 400 mg, 10 mmol) in dry DMF (20 ml) under a nitrogen atmosphere was stirred at room temperature for 30 min when 1,2-dibromoethane (2.60 ml, 30 mmol) was added in one portion. The mixture was stirred at room temperature for 4 h, then DMF removed under reduced pressure, water (40 ml) added and the mixture extracted with dichloromethane (2x25 ml). The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure giving an oil which was purified by flash chromatography (SiO_2) eluting with 98:2 v/v *n*-hexane-ether to afford the corresponding bromide (1.70 g, 52%). This product was dissolved in dry DMF (10 ml) and added to a solution of sodium *N*-propargylphenylsulfonamide (5.2 mmol) in anhydrous DMF (15 ml), previously prepared from *N*-propargylphenylsulfonamide and excess of sodium hydride (1.5 eq), and the resulting suspension was stirred at room temperature for 1.5 h. After the usual work-up the residual oil was purified by flash chromatography (SiO_2) eluting with 9:1 v/v *n*-hexane-ether giving the **product (1e)** (2.00 g, 87%) as a thick pale yellow oil (Found: C, 46.5; H, 3.8; N, 3.3; S, 7.1. $C_{17}H_{16}INO_3S$ requires: C, 46.3; H, 3.65; N, 3.2; S, 7.25%.); δ 3.60 (t, *J* 6.7 Hz, 2H, CH_2N), 4.16 (t, *J* 6.7 Hz, 2H, CH_2O), 5.37 (d, *J* 6.1 Hz, 2H, CH_2=C=C), 6.71 (t, *J* 7.1 Hz, 1H, ArH), 6.80 (d, *J* 8.0 Hz, 1H, ArH), 6.91 (t, *J* 6.1 Hz, 1H, C*H*=C=CH_2) and 7.26-7.86 (m, 7H, ArH); *m/z* (%) 441 (M^+, 3), 316 (59), 314 (23), 300 (23), 247 (42), 246 (30), 212 (27), 203 (42), 184 (26), 161 (23), 141 (42), 125 (72), 120 (28), 106 (26), 92 (29), 91 (31), 80 (22), 78 (25), 77 (100), 76 (35), 54 (23), 51 (31) and 39 (28); ν_{max} (film) 1950, 1355, 1170 and 865 cm^{-1}.

N-*[3-(o-Iodophenoxy)propyl]*-N-*(phenylsulfonyl)-1,2-propadienylamine (1f)*. Prepared from *o*-iodophenol and 1,3-dibromopropane employing the same procedure as that used for compound (**1e**) (above). The **product (1f)** (72% overall yield) was isolated as a thick pale yellow oil, (Found: C, 47.55; H, 4.0; N, 3.1; S, 7.0. $C_{18}H_{18}INO_3S$ requires: C, 47.5; H, 4.0; N, 3.1; S, 7.05%.); δ 2.10 (m, 2H, CH_2CH_2O), 3.41 (t, *J* 6.8 Hz, 2H, CH_2N), 4.05 (t, *J* 5.8 Hz, 2H, CH_2O), 5.29 (d, *J* 6.3 Hz, 2H, CH_2=C=C), 6.70 (t, *J* 7.5 Hz, 1H, ArH), 6.79 (d, *J* 8.0 Hz, 1H, ArH), 6.88 (t, *J* 6.3 Hz, 1H, C*H*=C=CH_2) and 7.26-7.85 (m, 7H, ArH); *m/z* (%) 455 (M^+, 26), 331 (39), 330 (100), 228 (32), 261 (50), 236 (41), 203 (48), 141 (46), 134 (61), 125 (80), 106 (39), 94 (58), 92 (36), 84 (71), 78 (44), 77 (84), 76 (36), 68 (59), 67 (50), 66 (37), 65 (34), 64 (32), 63 (31), 51 (49), 41 (70) and 39 (52); ν_{max} (film) 1960, 1350, 1165 and 850 cm^{-1}.

Synthesis of Vinyl-Heterocycles (3).

General Procedure. To a solution of 1,2-diene (**1**) (0.5 mmol) in anhydrous THF (4 ml) under a nitrogen atmosphere were added, at 0°C, tri-*n*-butyltin hydride (150 μl, 0.55 mmol), palladium acetate (11.2 mg, 0.05 mmol) and triphenylphosphine (26.2 mg, 0.10 mmol). After 1 h stirring for 1 h at this temperature, THF was evaporated under reduced pressure and the residue dissolved in a 0.15M solution of $Et_4NCl.H_2O$ in acetonitrile [7 ml, except in the case of product (**3e**) where 10 ml was used]. The reaction mixture was boiled under reflux for the time indicated in Table 1. After removing the solvent under reduced pressure, ethyl

acetate (5 ml) and a 2M aqueous solution of potassium fluoride (5 ml) were added and the corresponding emulsion was vigorously stirred for 1 h. The mixture was then filtered, the organic layer was decanted, dried (Na_2SO_4), and evaporated under reduced pressure. The resulting residue was purified by flash chromatography (SiO_2) eluting with mixtures of *n*-hexane-ether to afford the vinyl-heterocycles (**3**). Yields are collected in Table 1.

*1-Vinyl-1,3-dihydroisobenzofuran (**3a**)*. Colourless oil; δ 5.10, 5.18 (2xd, *J* 12.0 Hz, 2H, CH_2O), 5.25 (d, *J* 10.3 Hz, 1H, CH_2=C), 5.43 (d, *J* 17.8 Hz, 1H, CH_2=C), 5.58 (d, *J* 6.8 Hz, 1H, CHO), 5.94 (ddd, *J* 17.8, 10.3 and 6.8 Hz, 1H, C*H*=CH_2) and 7.13-7.40 (m, 4H, ArH); *m/z* (%) 146 (M^+, 18), 119 (100), 104 (33), 91 (60) and 77 (41); ν_{max} (film) 3075, 1665 and 800 cm^{-1}.

*1-Vinyl-2-phenylsulfonyl-1,3-dihydroisoindole (**3b**)*. Colourless prisms from *n*-hexane-ether, m.p. 79-80°C, (Found: C, 67.35; H, 5.45; N, 4.65; S, 11.3. $C_{16}H_{15}NO_2S$ requires: C, 67.35; H, 5.3; N, 4.9; S, 11.25%.); δ 4.66, 4.75 (2xd, *J* 13.5 Hz, 2H, CH_2N), 5.24 (d, *J* 7.8 Hz, 1H, CHN), 5.25 (d, *J* 9.8 Hz, 1H, CH_2=C), 5.43 (d, *J* 17.0 Hz, 1H, CH_2=C), 5.88 (ddd, *J* 17.0, 9.8 and 7.8 Hz, 1H, C*H*=CH_2) and 7.05-7.89 (m, 9H, ArH); *m/z* (%) 286 (M^++1, 1), 285 (M^+,3), 259 (26), 258 (100), 220 (38), 144 (65), 143 (33), 141 (46), 117 (27), 115 (29), 91 (23), 77 (90) and 51 (23); ν_{max} (film) 3080, 1670, 1350, 1165 and 810 cm^{-1}.

*2-Methyl-3-vinyl-2,3-dihydroisoindol-1-one (**3c**)*. Pale yellow oil, (Found: C, 76.5; H, 6.5; N, 8.0. $C_{11}H_{11}NO$ requires: C, 76.3; H, 6.4; N, 8.1%.); δ 3.07 (s, 3H, CH_3), 4.76 (d, *J* 7.5 Hz, 1H, CHN), 5.43-5.65 (m, 3H, CH_2=CH), 7.35 (d, *J* 7.4 Hz, 1H, ArH), 7.45, 7.53 (2xt, *J* 7.2 Hz, 2H, ArH) and 7.82 (d, *J* 7.4 Hz, 1H, ArH); *m/z* (%) 173 (M^+,94), 172 (35), 146 (100), 144 (24) and 91 (22); ν_{max} (film) 3080, 1690, 1640 and 830 cm^{-1}.

*1-Vinyl-2-phenylsulfonyl-1,2,3,4-tetrahydroisoquinoline (**3d**)*. Colourless oil, (Found: C, 67.9; H, 5.8; N, 4.55; S, 10.8. $C_{17}H_{17}NO_2S$ requires: C, 68.2; H, 5.75; N, 4.65; S, 10.7%.); δ 2.57-2.80 (m, 2H, C*H*$_2$Ar), 3.37 (ddd, *J* 13.5, 11.1 and 4.7 Hz, 1H, CH_2N), 3.87 (ddd, *J* 13.5, 6.2 and 2.6 Hz, 1H, CH_2N), 5.04 (d, *J* 17.0 Hz, 1H, CH_2=C), 5.15 (d, *J* 10.2 Hz, 1H, CH_2=C), 5.56 (d, *J* 5.6 Hz, 1H, CHN), 5.90 (ddd, *J* 17.0, 10.2 and 5.6 Hz, 1H, C*H*=CH_2) and 6.98-7.79 (m, 9H, ArH); *m/z* (%) 300 (M^++1, 1), 299 (M^+,3), 272 (87), 130 (36), 115 (25), 77 (100) and 51 (41); ν_{max} (film) 3080, 1645, 1330, 1165 and 840 cm^{-1}.

*1-Vinyl-2-phenylsulfonyl-1,2,3,4-tetrahydrobenzo[f]-1,4-oxazepine (**3e**)*. Colourless oil, (Found: C, 64.5; H, 5.1; N, 4.2; S, 10.0. $C_{17}H_{17}NO_3S$ requires: C, 64.7; H, 5.4; N, 4.4; S, 10.15%.); δ 3.67 (m, 2H CH_2N), 3.94, 4.21 (2xm, 2H, CH_2O), 4.87 (d, *J* 17.8 Hz, 1H, CH_2=C), 5.23 (d, *J* 10.3 Hz, 1H, CH_2C), 5.69 (d, *J* 4.6 Hz, 1H, CHN), 5.94 (ddd, *J* 17.8, 10.3 and 4.6 Hz, 1H, C*H*=CH_2) and 6.85-7.83 (m, 9H, ArH); *m/z* (%) 315 (M^+,8), 288 (100), 174 (47), 149 (48), 145 (29), 141 (37), 131 (31) and 77 (66); ν_{max} (film) 3080, 1640, 1350, 1160 and 795 cm^{-1}.

*General Procedure for Synthesis of Allenes (**6**)*.

To a stirred solution of *o*-iodobenzyl alcohol (2.81 g, 12 mmol) in anhydrous DMF (30 ml) was added portionwise sodium hydride (60% dispersion in mineral oil, 576 mg, 14.4 mmol) at 0°C under a nitrogen

atmosphere. The mixture was allowed to warm to room temperature and stirred at this temperature for 30 min. The resulting suspension was added *via* a syringe-pump during 30 min to a solution of the corresponding 1,ω-dibromoalkane (36 mmol) in dry DMF (25 ml). After 16 h stirring DMF was removed under reduced pressure and the residue purified by flash chromatography (SiO_2) to give the correspondig bromides (**5**) (70-63%). The reaction of these bromides with sodium *N*-propargylphenylsulfonamide was carried out according to the procedure previously described (above) to furnish allenes (**6**) as a pale yellow sticky oils (82-79%).

*1,2-Diene (**6a**) (n=5).* (Found: C, 50.95; H, 4.8; N, 2.75; S, 6.5. $C_{21}H_{24}INO_3S$ requires: C, 50.75; H, 4.8; N, 2.8; S, 6.45%.); δ 1.43, 1.62 (2xm, 6H, 3xCH_2), 3.12 (t, *J* 7.0 Hz, 2H, CH_2N), 3.53 (t, *J* 6.4 Hz, 2H, CH_2CH_2O), 4.46 (s, 2H, CH_2Ar), 5.28 (d, *J* 6.0 Hz, 2H, CH_2=C=C), 6.83 (t, *J* 6.0 Hz, 1H, C*H*=C=CH_2), 6.98 (t, *J* 7.5 Hz, 1H, ArH) and 7.32-7.82 (m, 8H, ArH); *m/z* (%) 497 (M^+, 0.2), 217 (100), 198 (39), 149 (45), 141 (51), 125 (34), 91 (49), 90 (46), 77 (83), 69 (25), 51 (25) and 41 (34); ν_{max} (film) 1960, 1360, 1170 and 850 cm^{-1}.

*1,2-Diene (**6b**) (n=6).* (Found: C, 51.8; H, 5.3; N, 2.7; S, 6.3. $C_{22}H_{26}INO_3S$ requires: C, 51.7; H, 5.15; N, 2.75; S, 6.3%.); δ 1.34 (m, 4H, 2xCH_2), 1.51-1.68 (m, 4H, 2xCH_2), 3.11 (t, *J* 7.2 Hz, 2H, CH_2N), 3.53 (t, *J* 6.4 Hz, 2H, CH_2CH_2O), 4.46 (s, 2H, CH_2Ar), 5.29 (d, *J* 6.2 Hz, 2H, CH_2=C=C), 6.83 (t, *J* 6.2 Hz, 1H, C*H*=C=CH_2), 6.97 (t, *J* 7.5 Hz, 1H, ArH) and 7.32-7.82 (m, 8H, ArH); *m/z* (%) 511 (M^+, 1), 217 (100), 170 (29), 141 (47), 128 (37), 91 (76), 90 (43), 78 (37), 77 (82) and 55(28); ν_{max} (film) 1950, 1350, 1160 and 855 cm^{-1}.

*1,2-Diene (**6c**) (n=7).* (Found: C, 52.35; H, 5.25; N, 2.5; S, 6.0. $C_{23}H_{28}INO_3S$ requires: C, 52.55; H, 5.35; N, 2.65; S, 6.1%.); δ 1.26-1.41 (m, 6H, 3xCH_2), 1.51-1.66 (m, 4H, 2xCH_2), 3.10 (t, *J* 7.2 Hz, 2H, CH_2N), 3.53 (t, *J* 6.5 Hz, 2H, CH_2CH_2O), 4.46 (s, 2H, CH_2Ar), 5.28 (d, *J* 6.2 Hz, 2H, CH_2=C=C), 6.83 (t, *J* 6.2 Hz, 1H, C*H*=C=CH_2), 6.97 (t, *J* 7.5 Hz, 1H, ArH) and 7.32-7.82 (m, 8H, ArH); *m/z* (%) 525 (M^+, 0.4), 384 (23), 282 (30), 217 (100), 142 (30), 141 (44), 97 (26), 91 (70), 90 (42), 78 (26), 77 (79), 55(35), 51 (25) and 41 (25); ν_{max} (film) 1960, 1350, 1165 and 855 cm^{-1}.

*1,2,Diene (**6d**) (n=9).* (Found: C, 54.05; H, 5.75; N, 2.4; S, 5.7. $C_{25}H_{32}INO_3S$ requires: C, 54.25; H, 5.8; N, 2.55; S, 5.8%.); δ 1.27 (m, 8H, 4xCH_2), 1.38, 1.53, 1.64 (3m, 6H, 3xCH_2), 3.10 (t, *J* 7.2 Hz, 2H, CH_2N), 3.54 (t, *J* 6.5 Hz, 2H, CH_2CH_2O), 4.47 (s, 2H, CH_2Ar), 5.29 (d, *J* 6.2 Hz, 2H, CH_2=C=C), 6.83 (t, *J* 6.2 Hz, 1H, C*H*=C=CH_2), 6.97 (td, *J* 7.5 and 1.5 Hz, 1H, ArH) and 7.26-7.82 (m, 8H, ArH); *m/z* (%) 553 (M^+, 1), 412 (22), 217 (100), 170 (23), 141 (30), 125 (25), 91 (48), 90 (34), 77 (61), 69 (26), 55(28) and 41 (28); ν_{max} (film) 1965, 1355, 1165 and 855 cm^{-1}.

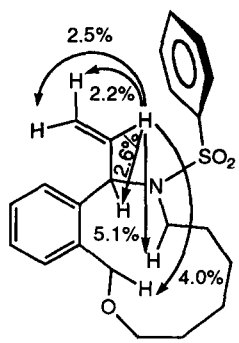
*1,2,Diene (**6e**) (n=11).* (Found: C, 56.05; H, 6.05; N, 2.4; S, 5.5. $C_{27}H_{36}INO_3S$ requires: C, 55.75; H, 6.25; N, 2.4; S, 5.5%.); δ 1.25 (m, 14H, 7xCH_2), 1.34-1.67 (m, 4H, 2xCH_2), 3.10 (t, *J* 7.3 Hz, 2H, CH_2N), 3.55 (t, *J* 6.5 Hz, 2H, CH_2CH_2O), 4.47 (s, 2H, CH_2Ar), 5.29 (d, *J* 6.2 Hz, 2H, CH_2=C=C), 6.83 (t, *J* 6.2 Hz, 1H, C*H*=C=CH_2), 6.98 (t, *J* 7.5 Hz, 1H, ArH) and 7.32-7.82 (m, 8H, ArH); *m/z* (%) 581 (M^+, 0.2), 217 (37), 206 (59), 196 (29), 141 (67), 121 (55), 91 (25), 77 (100), 69 (39), 68 (54), 67 (31), 55(69), 43 (42),41 (83) and 39 (32); ν_{max} (film) 1960, 1350, 1160 and 850 cm^{-1}.

General Procedure for Synthesis of Macrocycles (8).

These products were obtained by the same experimental procedure as that used for the synthesis of (**3**) but employing 0.15M solution of $Et_4NCl.H_2O$ in acetonitrile (50 ml instead of 7 ml). Conditions and yields are collected in Table 3.

*Vinylmacrocycle (**8a**) (n=5).* Colourless prisms from *n*-hexane-ether, m.p. 103-105 °C, (Found: C, 67.9; H, 6.65; N, 3.5; S, 8.5. $C_{21}H_{25}NO_3S$ requires: C, 67.9; H, 6.75; N, 3.75; S, 8.65%.); δ 1.43 (m, 2H, CH_2), 1.57 (m, 4H, 2xCH_2), 3.24 (t, *J* 6.4 Hz, 2H, CH_2N), 3.47 (t, *J* 5.0 Hz, 2H, CH_2CH_2O), 3.48 (d, *J* 6.6 Hz, 1H, CHN), 4.41 (s, 2H, CH_2Ar), 5.36 (ddd, *J* 14.1, 7.1 and 6.6 Hz, 1H, $CH{=}CH_2$), 6.28 (d, *J* 14.1 Hz, 1H, $CH_2{=}C$) and 7.19-7.80 (m with d at 7.54, *J* 7.1 Hz, 10H, ArH and 1H of $CH_2{=}C$); *m/z* (%) 371 (M^+, 9), 252 (26), 231 (39), 230 (100), 149 (26), 146 (31), 130 (38), 129 (40), 128 (30), 117 (39), 115 (45), 91 (27) and 77 (30); ν_{max} ($CDCl_3$) 3085, 1660, 1350, 1160 and 820 cm^{-1}.

*Vinylmacrocycle (**8b**) (n=6).* Colourless prisms from *n*-hexane-ether, m.p. 116-118 °C, (Found: C, 68.25; H, 7.3; N, 3.35; S, 8.2. $C_{22}H_{27}NO_3S$ requires: C, 68.55; H, 7.05; N, 3.65; S, 8.3%.); δ 1.31, 1.43, 1.55, 1.65 (4xm, 8H, 4xCH_2), 3.23 (t, *J* 6.9 Hz, 2H, CH_2N), 3.41 (d, *J* 6.9 Hz, 1H, CHN), 3.50 (t, *J* 5.3 Hz, 2H, CH_2CH_2O), 4.50 (s, 2H, CH_2Ar), 5.32 (ddd, *J* 14.2, 6.9 and 6.9 Hz, 1H, $CH{=}CH_2$), 6.71 (d, *J* 14.2 Hz, 1H, $CH_2{=}C$) and 7.17-7.86 (m with d at 7.54, *J* 6.9 Hz, 10H, ArH and 1H of $CH_2{=}C$); *m/z* (%) 385 (M^+, 10), 246 (30), 244 (100), 210 (40), 141 (41), 117 (26), 91 (63), 77 (72), 55 (35) and 41 (40); ν_{max} ($CDCl_3$) 3080, 1650, 1350, 1160 and 820 cm^{-1}.



(8b)

*Vinylmacrocycle (**8c**) (n=7).* Colourless prisms from *n*-hexane-ether, m.p. 99-102 °C, (Found: C, 69.3; H, 7.5; N, 3.8; S, 8.1. $C_{23}H_{29}NO_3S$ requires: C, 69.15; H, 7.3; N, 3.5; S, 8.05%.); δ 1.22-1.59 (m, 10H, 5xCH_2), 3.21 (t, *J* 7.2 Hz, 2H, CH_2N), 3.40 (d, *J* 7.2 Hz, 1H, CHN), 3.48 (t, *J* 5.0 Hz, 2H, CH_2CH_2O), 4.51 (s, 2H, CH_2Ar), 5.13 (ddd, *J* 14.3, 7.2 and 7.2 Hz, 1H, $CH{=}CH_2$), 6.77 (d, *J* 14.3 Hz, 1H, $CH_2{=}C$) and 7.10-7.79 (m with d at 7.53, *J* 7.2 Hz, 10H, ArH and 1H of $CH_2{=}C$); *m/z* (%) 399 (M^+, 3), 259 (25), 258 (100), 129 (25), 105 (26), 91 (35), 77 (36) and 55 (35); ν_{max} (film) 3080, 1640, 1350, 1160 and 820 cm^{-1}.

*Vinylmacrocycle (**8d**) (n=9).* Colourless prisms from *n*-hexane-ether, m.p. 104-105 °C, (Found: C, 69.95; H, 7.8; N, 3.1; S, 7.4. $C_{25}H_{33}NO_3S$ requires: C, 70.2; H, 7.8; N, 3.25; S, 7.5%.); δ 1.26 (m, 8H, 4xCH_2), 1.36 (m, 2H, CH_2), 1.51-1.64 (m, 4H,2xCH_2), 3.22 (t, *J* 7.9 Hz, 2H, CH_2N), 3.41 (d, *J* 7.2 Hz, 1H, CHN), 3.47 (t, *J* 5.7 Hz, 2H, CH_2CH_2O), 4.50 (s, 2H, CH_2Ar), 4.96 (ddd, *J* 14.2, 7.2 and 7.1 Hz, 1H,

C*H*=CH_2), 6.76 (d, *J* 14.2 Hz, 1H, CH_2=C) and 7.10-7.81 (m with d at 7.56, *J* 7.1 Hz, 10H, ArH and 1H of CH_2=C); *m/z* (%) 429 (M^++2, 19), 428 (M^++1, 47), 427 (M^+, 63), 287 (57), 286 (100), 285 (43), 217 (29), 170 (21), 156 (21), 141 (23), 129 (30), 128 (35), 117 (23), 91 (30), 77 (47), 69 (24), 55 (27) and 41 (27); ν_{max} (film) 3080, 1655, 1360, 1165 and 820 cm^{-1}.

Vinylmacrocycle (8e) (n=11). Colourless sticky oil, (Found: C, 70.9; H, 8.25; N, 2.9; S, 7.0. $C_{27}H_{37}NO_3S$ requires: C, 71.15; H, 8.2; N, 3.05; S, 7.05%.); δ 1.22-1.42 (m, 14H, 7xCH_2), 1.53-1.60 (m, 4H, 2xCH_2), 3.28 (t, *J* 7.5 Hz, 2H, CH_2N), 3.49 (d, *J* 6.0 Hz, 2H, CH_2CH_2O), 3.51 (t, *J* 7.0 Hz, 1H, CHN), 4.48 (s, 2H, CH_2Ar), 5.00 (ddd, *J* 14.0, 7.0 and 7.0 Hz, 1H, C*H*=CH_2), 6.65 (d, *J* 14.0 Hz, 1H, CH_2=C) and 7.06-7.80 (m with d at 7.57, *J* 7.0 Hz, 10H, ArH and 1H of CH_2=C); *m/z* (%) 455 (M^+, 6), 314 (49), 205 (31), 167 (83), 141 (40), 113 (35), 107 (40), 95 (29), 91 (63), 83 (43), 77 (61), 71 (80), 55 (83), 43 (89) and 41 (100); ν_{max} (film) 3080, 1660, 1360, 1165 and 805 cm^{-1}.

General Procedure for Synthesis of 1,2,6-Trienes (9a) and (9b).

The reaction of the corresponding allylic chlorides (X=O, NSO_2Ph)[13], readily availables by reaction of sodium *N*-(2-iodophenyl)phenylsulfonamide with 2-chloromethyl-3-chloro-1-propene in DMF over 24 h, with sodium *N*-propargylphenylsulfonamide was carried out in dry DMF over 24 h at room temperature using the same procedure as that used for the synthesis of (**6**) to afford compounds (**9a**) and (**9b**) in 74 and 79% yield respectively.

1,2,6-Triene (9a). Colourless sticky oil, (Found: C, 48.85; H, 3.8; N, 2.75; S, 6.8. $C_{19}H_{18}INO_3S$ requires: C, 48.85; H, 3.85; N, 3.0; S, 6.85%.); δ 3.91 (s, 2H, CH_2N), 4.57 (s, 2H, CH_2O), 5.22 (s, 1H, CH_2=C), 5.24 (d, *J* 6.3 Hz, 2H, CH_2=C=C), 5.48 (s, 1H, CH_2=C), 6.70-6.86 (m, 3H, NCH=C and 2H ArH) and 7.26-7.86 (m, 7H, ArH); *m/z* (%) 467 (M^+, 2), 238 (43), 220 (79), 146 (48), 141 (56), 131 (33), 84 (36), 77 (100), 65 (38), 51 (37), 49 (40) and 39 (31); ν_{max} (film) 3080, 1960, 1640, 1360, 1170, 850 and 820 cm^{-1}.

1,2,6-Triene (9b). Colourless prisms from *n*-hexane-ether, m.p. 59-60°C, (Found: C, 48.9; H, 4.05; N, 4.45; S, 10.5. $C_{25}H_{23}IN_2O_4S_2$ requires: C, 49.15; H, 3.85; N, 4.6; S, 10.15%.); δ 3.77, 3.87 (2d, *J* 16.3 Hz, 2H, CH_2NCH=C), 4.14, 4.28 (2d, *J* 15.0 Hz, 2H, CH_2NAr), 5.03, 5.11 (2s, 2H, CH_2=C), 5.19 (d, *J* 5.5 Hz, 2H, CH_2=C=C), 6.71 (t, *J* 5.5 Hz, 1H, NCH=C) and 7.00-7.90 (m, 14H, ArH); *m/z* (%) 606 (M^+, 0.7), 359 (35), 248 (31), 218 (33), 141 (27), 91 (33), 86(37), 84 (52), 79 (33), 77 (100) and 51 (43); ν_{max} (CH_2Cl_2) 3080, 1950, 1650, 1360, 1165, 855 and 810 cm^{-1}.

Synthesis of VinylSpirocycles (11a) and (11b).

Both compounds were obtained as 1:1 mixture of diastereoisomers following the same procedure as that used for the synthesis of (**3**) but using 0.15M solutions of $Et_4NCl.H_2O$ in acetonitrile (15 ml instead of 7 ml). Reaction conditions and yields are given in the text.

Vinylspirocycle (11a). Colourless oil,[Found (mixed diastereoisomers): C, 67.2; H, 5.5; N, 3.9; S, 9.7. $C_{19}H_{19}O_3S$ requires: C, 66.85; H, 5.55; N, 4.1; S, 9.4%]; δ (mixed diastereoisomers) 1.95 (dd, *J* 13.0 and 4.0 Hz, 1H, CH_2N), 2.20 (dd, *J* 13.0 and 5.6 Hz, 1H, CH_2CN), 3.30, 3.63 (2d, *J* 10.0 Hz, 2H, CH_2N), 4.32

(d, *J* 9.7 Hz, 1H, CH_2O), 4.38 (m, 1H, CHN), 4.47 (d, *J* 9.7 Hz, 1H, CH_2O), 5.20 (d, *J* 10.2 Hz, 1H, CH_2=C), 5.39 (d, *J* 17.2 Hz, 1H, CH_2=C), 5.85 (m, 1H, C*H*=CH_2) and 6.91-7.88 (m, 9H, ArH); *m/z* (%) 341 (M^+, 1), 86 (63), 84 (100), 77 (49), 51 (28), 49 (33), 47 (36) and 41 (22); ν_{max} (film) 3080, 1650, 1350, 1160 and 830 cm^{-1}.

Vinylspirocycle (11b). Colourless prisms from *n*-hexane-ether, m.p. 56-59°C, [Found (mixed diastereoisomers): C, 62.7; H, 5.0; N, 5.5; S, 13.1. $C_{25}H_{24}N_2O_4S_2$ requires: C, 62.5; H, 5.0; N, 5.8; S, 13.35%.]; δ (mixed diastereoisomers) 1.64 (dd, *J* 13.0 and 3.5 Hz, 1H, CH_2CN), 1.96 (dd, *J* 13.0 and 8.4 Hz, 1H, CH_2CN), 3.03,3.12 (2d, *J* 10.0 Hz, 2H, C*H*$_2$NAr), 3.79, 3.90 (2d, *J* 11.5 Hz, 2H, C*H*$_2$NCH), 4.28 (m, 1H,CHN), 5.20 (d, *J* 10.3 Hz, 1H, CH_2=C), 5.29 (d, *J* 17.0 Hz, 1H, CH_2=C), 5.82 (m, 1H, C*H*=CH_2) and 6.91-7.80 (m, 14H, ArH); *m/z* (%) 480 (M^+, 33), 234 (34), 233 (54), 210 (100), 168 (51), 141 (43), 130 (57), 118 (65), 91 (30), 77 (97), 68 (81) and 41 (32); ν_{max} ($CDCl_3$) 3080, 1660, 1350, 1165 and 820 cm^{-1}.

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