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Palladium Catalysed Tandem Cyclisation-Anion Capture Processes. Part 3.[1] Organoboron Anion Transfer Agents

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Abstract: The cyclisation-anion capture protocol has been applied to a wide range of starter and terminating species to effect regio- and stereo-specific mono- and bis-cyclisation processes in which a variety of organoboronderivatives function as anion transfer reagents. Direct capture (no cyclisation) is rarely a problem and it can usually be suppressed by modification of the reaction conditions. © 1997 Elsevier Science Ltd.

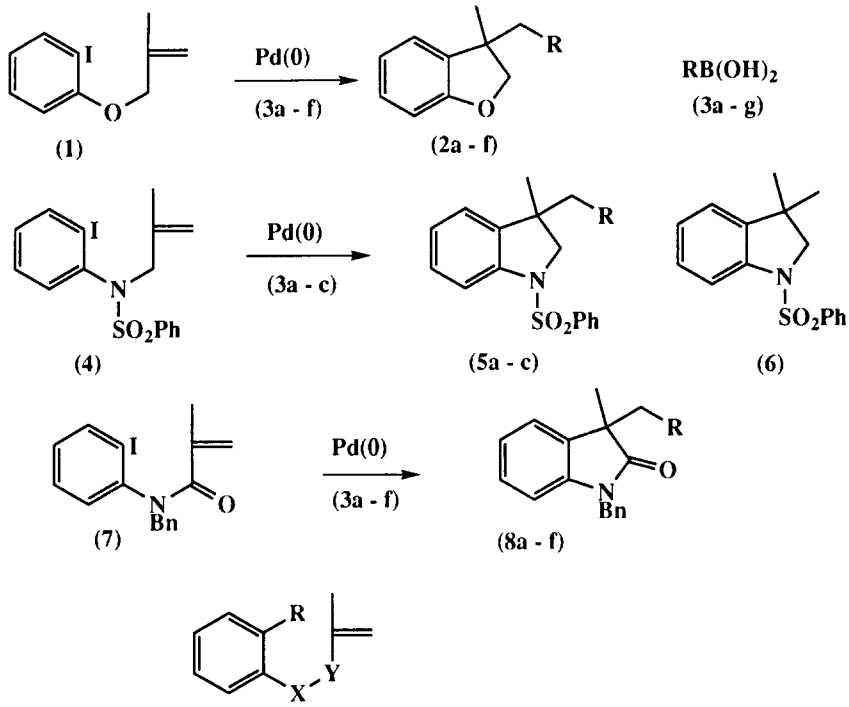
The previous two parts of this series of papers discussed mono- and bis-cyclisations involving a broad range of starter and terminating species with hydride as the anion capture agent.[1,2] This paper is concerned with analogous mono- and bis-cyclisations in which a range of organoboron derivatives function as anion capture agents.[3]

The use of organoboron reagents in palladium catalysed cross-coupling reactions was pioneered by Suzuki[4] who made the key observation of the importance of boron ate complexes in such processes. A further important advance by the same group was the demonstration that sp^3 - sp^3 coupling could be achieved.[5] The palladium catalysed organoboron cross-coupling reaction is now firmly established as an efficient method for C-C bond formation which tolerates a wide variety of functionality in the coupling partners. This versatility has engendered a multiplicity of applications.[6] In the context of our cyclisation-anion capture methodology it was important to survey a range of starter and terminating species and organoboron reagents to assess the likely importance of the deleterious shunt pathway[1,2] whereby replacement of X (X=halide, triflate) in the starter species by R from RBY_2 occurs without cyclisation.

All cyclisation-anion capture processes described in this paper employed a Pd(0) catalyst generated *in situ* from $Pd(OAc)_2$ and PPh_3 with the solvent and additives tailored to the particular organoboron reagent.

A. Aryl Halide Starter Species.

(i) 5-Exo-Trig Monocyclisations with Alkenes as Terminating Species. A range of organoboron reagents have been evaluated and are discussed in turn. Initial studies showed that aryl iodide (1) cyclised to (2a) (78%) on reaction with phenylboronic acid (3a) (1 mol eq) in the presence of 10 mol% $Pd(OAc)_2$, 20 mol% PPh_3, aq. Na_2CO_3 and Et_4NCl (1mol eq.) in toluene (110°C, 2 h). A more extensive study of 5-exo-trig cyclisations employing boronic acids (3b-f) as the capture agents was then undertaken.

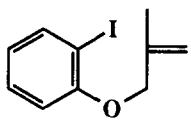
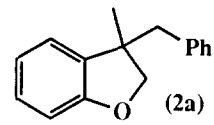
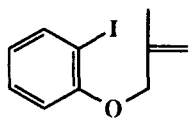
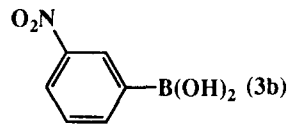
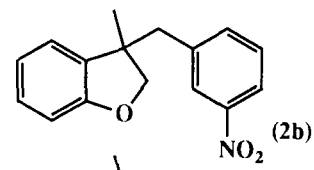
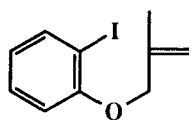
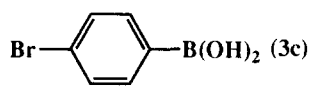
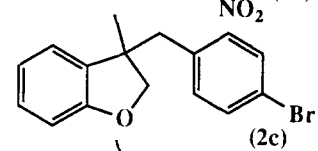
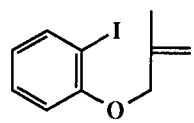
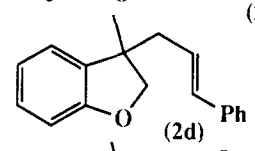
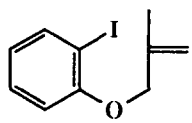
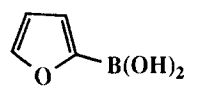
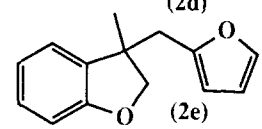
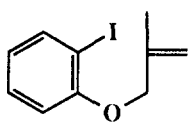
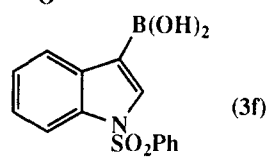
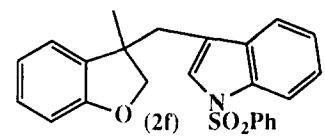
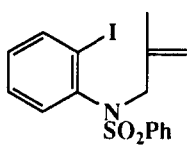
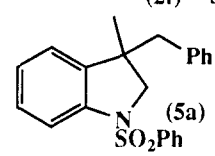
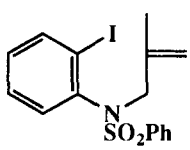
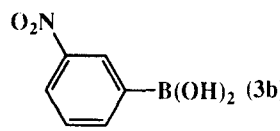
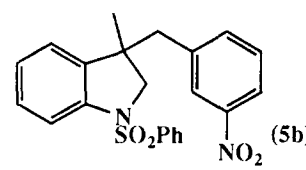
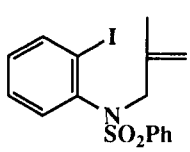
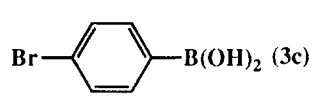
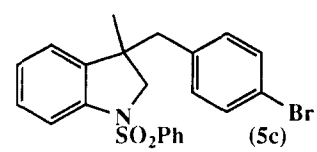


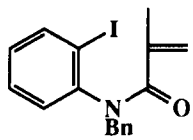
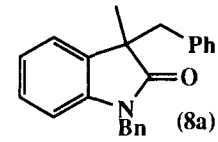
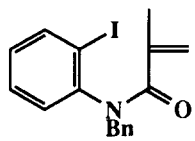
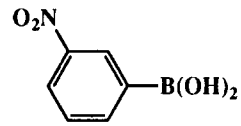
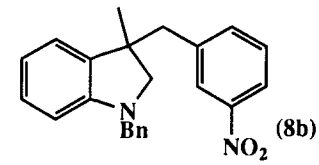
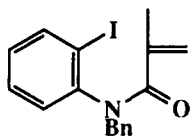
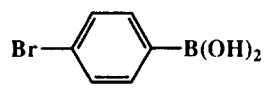
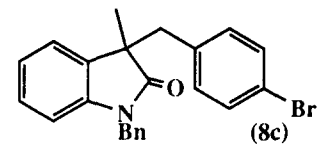
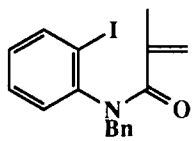
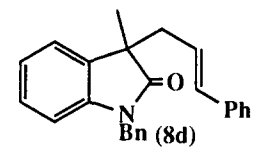
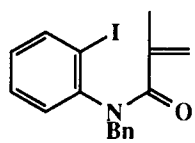
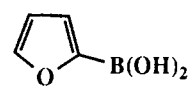
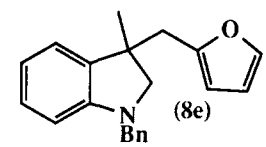
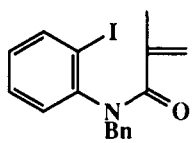
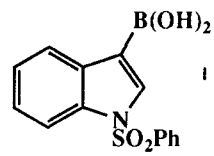
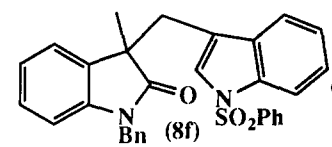
(9) a. X = O, Y = CH_2, R = CH=CHPh
b. X = O, Y = CH_2, R = 2 - furyl
c. X = O, Y = CH_2, R = 3 - (N - sulphonyl)lindolyl

Trial experiments established that 10 M aqueous Na_2CO_3 (2 mol eq.) in toluene (110°C, 8 h) in conjunction with 10 mol% $Pd(OAc)_2$, 20 mol% PPh_3 and 1.2 mol eq. of arylboronic acids (3a-c) were an effective combination. Cyclisation-anion capture was the sole reaction detected in most cases and (2a-c), (5a-c) and (8a-c) were obtained in good to excellent yield from (1), (4) and (7) respectively (Table 1). Reactions involving boronic acids (3d-f) were conducted in toluene at 90°C and employed 2 M Na_2CO_3 (2mol eq.) in combination with Et_4NCl (1mol eq.). Cyclisation-anion capture was the favoured reaction pathway with (2d-f) and (8d-f) being obtained in good yield from (1) and (7) respectively (Table 1). However, in reactions conducted at 90°C in toluene the mass balance was accounted for by formation of the appropriate direct capture product (9a-f) *via* the shunt pathway. In one example, the reaction of (1) with (3e), it was found that raising the reaction temperature to 110° C suppressed formation of (9b) and raised the yield of (2e) from 65% to 85% (Table 1).

With the arylboronic acids (3a-c) the use of less concentrated aqueous Na_2CO_3 solution and dimethoxyethane (DME) as solvent (Table 2) always led to varying amounts of cyclisation-hydride ion capture product (6) as illustrated by the reaction of (4) with (3a) (Table 2). The source of unexpected hydride products in palladium catalysed processes has been the subject of several studies[7] but is presently obscure.

Table 1 Cyclisation of aryl iodides (1), (4) and (7) with anion capture from boronic acids (3a - c)[a] and (3d - f)[b]

Aryl Iodide	Boronic acid	Product	Yield(%)
	$PhB(OH)_2$ (3a)	 (2a)	91
	 (3b)	 (2b)	93
	 (3c)	 (2c)	90
	t- $PhCH{=}CHB(OH)_2$ (3d)	 (2d)	67
	 (3e)	 (2e)	85[c]
	 (3f)	 (2f)	60
	$PhB(OH)_2$ (3a)	 (5a)	65
	 (3b)	 (5b)	63
	 (3c)	 (5c)	58

Aryl Iodide	Boronic acid	Product	Yield(%)
	$PhB(OH)_2$ (3a)	 (8a)	98
	 (3b)	 (8b)	95
	 (3c)	 (8c)	96
	t- $PhCH{=}CHB(OH)_2$ (3d)	 (8d)	72
	 (3e)	 (8e)	74
	 (3f)	 (8f)	65

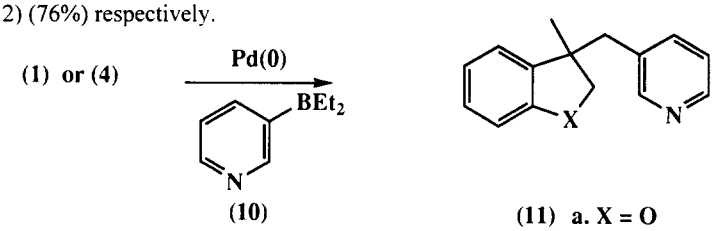
a. Reactions with arylboronic acids (3a - c) were carried out in boiling toluene using 10 M aqueous Na_2CO_3(2 mol eq.) as base
b. Reactions with boronic acids (3d - f) were carried out in toluene at 90°C using 1.5 mol eq. of (3d - f) ,2 M aqueous Na_2CO_3 (2 mol eq.) and Et_4NCl(1 mol eq.)
c. Reaction temperature 110°C

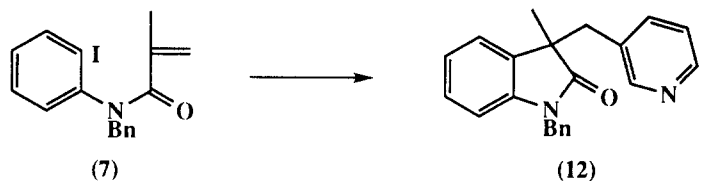
Table 2. Effect of solvent and additives on the reaction of (4) with (3a)[a]

Solvent[b]	Base[c]	Additive[d]	Time(h)	Product Ratio
DME	2M Na_2CO_3	-	35	4(2), 5a(14), 6(1)
DME	2M Na_2CO_3	Et_4NCl	8	5a(10), 6(1)
DME	2M $NaHCO_3$	Et_4NCl	12	4(1), 5a(1), 6(2)
DME	2M NaOAc	Et_4NCl	12	5a(2), 6(3)
Toluene	2M Na_2CO_3	Et_4NCl	10	5a(20), 6(1)

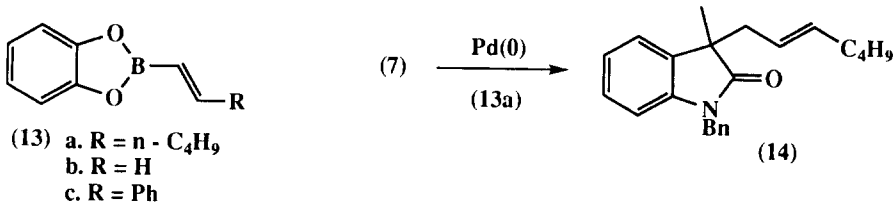
a. All reactions employed 10mol% Pd(OAc) and 20mol% PPh_3 as the catalyst precursor.
b. Reactions carried out in boiling solvent.
c. 2 mol eq. of base used in each case.
d. 1 mol eq. of Et_4NCl used where noted.

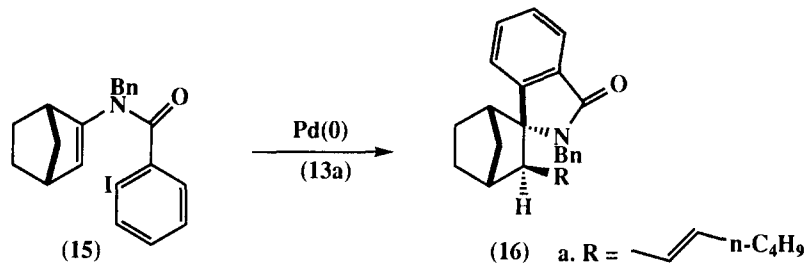
The three substrates (1), (4) and (7) also underwent cyclisation with anion capture from diethyl-3-pyridylborane (10) (1.3 mol eq.) (toluene, 110°C, 8 h) using the same catalyst/base/additive giving (11a) (72%), (11b) (70%) and (12) (76%) respectively.





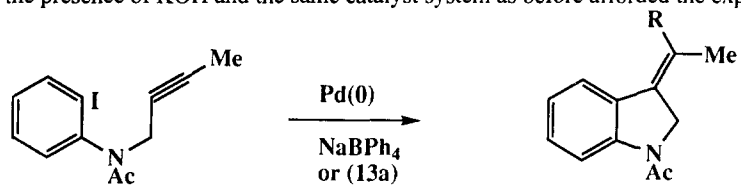
Two series of 5-exo-trig cyclisations employing vinyl catechol boranes (13a,b) as anion transfer agents were briefly investigated. The catalyst comprised 10mol% $Pd(OAc)_2$ and 20 mol% PPh_3 together with 2M NaOEt (2 mol eq.) in EtOH. Thus (7) and (13a) afforded (benzene, 80°C,5 h) the expected product (14) (35%) albeit in low yield. The norbornenyl substrate (15) underwent analogous cyclisation-anion capture with (13a) affording a mixture of (16a) (48%) and (16b) (48%). These reactions were carried out prior to those in Table 1 and have not been optimised.





(15) (16) a. R = b. R = H

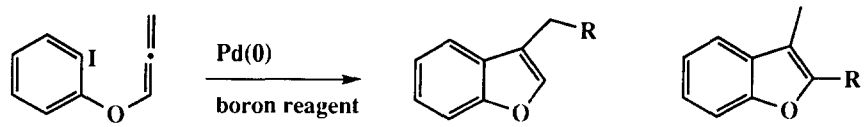
(ii) 5-Exo-Dig Monocyclisations with Alkynes as Terminating Species. Only two examples of this type of process have been studied both of which employed (17) as substrate. Reaction of (17) with $NaBPh_4$ (1mol.eq) in anisole (80°C, 1 h) in the presence of 10mol% $Pd(OAc)_2$ and 20mol% PPh_3 afford the desired product (18a) (31%) as a single stereoisomer. Although formally this reaction involves transfer of a phenyl group from the tetraphenylborate anion a more plausible mechanism involves NaPh, generated in low concentration, as the active phenyl transfer agent. Such a mechanism involving a low concentration of the NaPh in addition to the mandatory low concentration of the organopalladium(II) species favours the desired cyclisation-anion capture pathway rather than the unwanted shunt pathway. Reaction of (17) with catechol borane (13a) in THF (60°C, 1.5h) in the presence of KOH and the same catalyst system as before afforded the expected diene (18b) (41%).



(17) (18) a. R = Ph
b. R = $CH{=}CHC_4H_9$

(iii) 5-Exo-Dig Monocyclisations with Allenes as Terminating Species. Allenes have proved versatile terminating moieties in cyclisation-anion capture processes In the absence of geometrical constraints the cyclisation invariably occurs at the centre carbon atom of the allene generating a π-allylpalladium(II) species.[8] The formation of the latter intermediate allows access to a wide range of anion capture agents. Strategies for directing cyclisation to the proximal carbon atom of the allene include prior *in situ* hydrostannylation of the allenyl moiety[9] or geometrical constraints.[10,11]

The phenoxyallene (19) has been evaluated as a substrate with three types of organoboron(III) reagents.

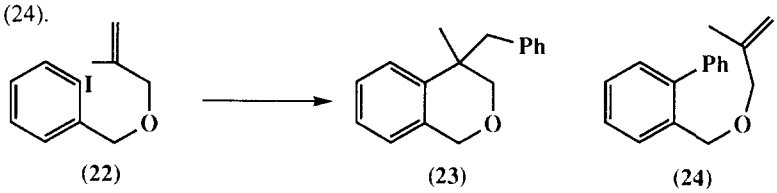


(19) (20) a. R = Ph
b. R = CH=CHPh
(21) a. R = Ph
b. R = CH=CHPh

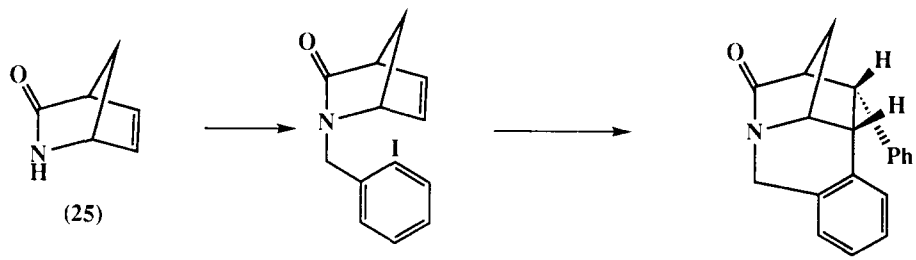
Thus (19) reacts (toluene, reflux, 1h) with sodium tetraphenylborate (1.2 mol.eq) in the presence of 5mol% $Pd(OAc)_2$ and 10mol% PPh_3 to give (20a) (65%) together with a trace amount of (21a). Using phenylboronic acid (3a) (1.2 mol.eq) as the anion capture agent, and Na_2CO_3 (2 mol.eq) as base together with the same catalyst system, the allene (19) reacts (2:1 toluene - H_2O, 90°C, 1h) to give (20a) (61%). A trace of (21a) was also detected. An analogous reaction was carried out under the same conditions replacing (3a) by the

(21a) was also detected. An analogous reaction was carried out under the same conditions replacing (3a) by the catechol boronate (13c). The product (20b) was isolated in 60% yield after 1.5h and again a trace of (21b) was detected.

(iv) 6-Exo-Trig Monocyclisations with Alkenes as Terminating Species. The iodoarene (22) reacts (anisole, 110°C) with sodium tetraphenylborate (1 mol.eq) to give the expected product (23) (60%). In this case the catalyst comprised 10mol% $Pd_2(dba)_3$ and 20mol% tri(2-furyl)phosphine. When the same substrate was reacted with phenylboronic acid (3a) the product (66%) comprised a 1:1 mixture of (23) and the premature capture product (24).



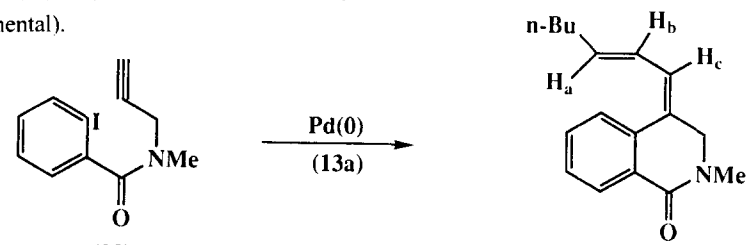
(22) (23) (24)



(25) (26) (27)

The chiral non-racemic *N*-(2-iodobenzyl) bicyclic lactam (26) was prepared by alkylation of (1*R*, 4*S*)-2-aza-3-oxobicyclo[2.2.1]hept-5-ene (25)[12] in 53% yield. Cyclisation - anion capture was effected by heating in anisole at 100°C for 24h in the presence of sodium tetraphenylborate (1.1mol.eq) using a catalyst system comprising 10mol% $Pd(OAc)_2$, 20mol% PPh_3 and Et_4NCl (1mol.eq). The enantiopure product (27) was isolated in 43% yield.

(v) 6-Exo-Dig Monocyclisations with Alkynes as Terminating Species. Only one example of this type has been studied. The iodoarene (28) reacted (benzene, 80°C, 16h) with the vinyl boronate (13a) in the presence of sodium ethoxide and a catalyst system comprising 10mol% $Pd(OAc)_2$ and 20mol% PPh_3 to afford the expected diene (29) (45%). The *E*-stereochemistry of the transferred alkene was confirmed by n.O.e. studies (see experimental).



(28) (29)

(vi) 6-Exo-Dig Monocyclisations with Allenes as the Terminating Species. Allene (30) was prepared by $KOBu^t$ isomerisation of (28) and subjected to a series of cyclisation-anion capture reactions (Table 3).

Table 3. Cyclisation of (30) with anion capture from sodium tetraphenylborate, boronic acids (3a) and (3g) and boronate (13c)[a]

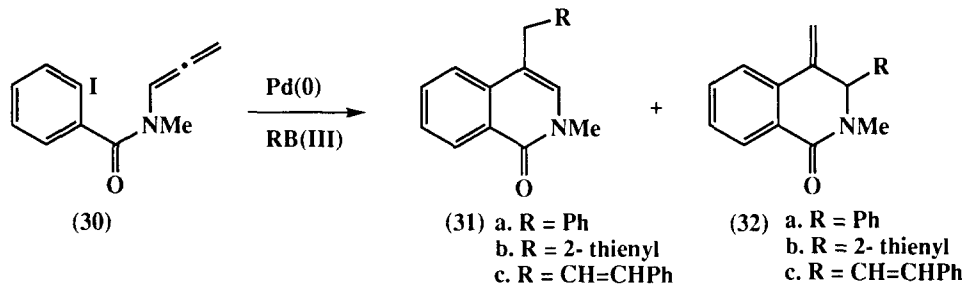
Boron Reagent(eq)	Base(eq)	Time(h)	Product(%)[b]
$NaBPh_4$(1.2)[c]	-	3.5	**31a** (71), **32a** (trace)
3a (1.2)	Na_2CO_3(2)	1	**31a** (34), **32a** (34)
3a (1.2)	Ag_2CO_3(2)	1	**31a** (61), **32a** (12)
3a (1.2)	Tl_2CO_3(2)	1	**31a** (56), **32a** (14)
3g (1.2)	Na_2CO_3(2)	16	**31b** (60), **32b** (trace)
13c (2.0)	Na_2CO_3(2)	1.5	**31c** (54), **32c** (21)[d]

a. Reactions carried out in 2:1 v/v toluene - H_2O unless otherwise noted. Catalyst system 5 mol% $Pd(OAc)_2$ and 10mol% PPh_3.

b. Isolated yields.

c. Reaction carried out in toluene. Using 2.5mol% $Pd_2(dba)_3$ and 10mol% PPh_3 as catalyst gave the same yield.

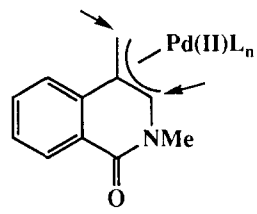
d. This yield includes 8% of (34).



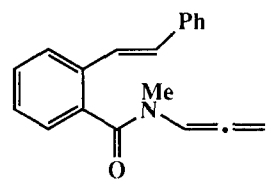
(30)

(31) a. R = Ph
b. R = 2- thienyl
c. R = CH=CHPh

(32) a. R = Ph
b. R = 2- thienyl
c. R = CH=CHPh



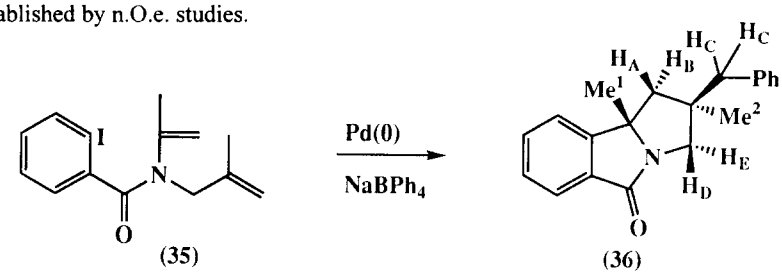
(33)



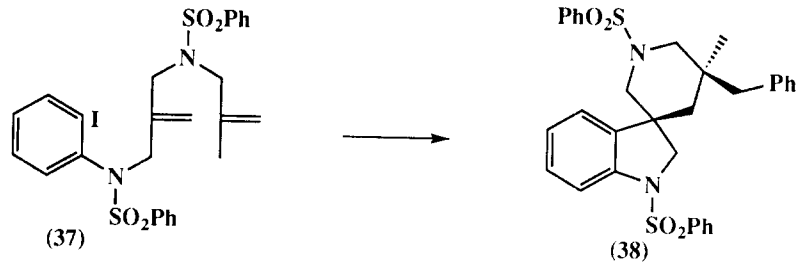
(34)

The series of cyclisation-anion capture processes (Table 3) were effected by Pd(0) generated *in situ* from 5 mol% $Pd(OAc)_2$ and 10 mol% PPh_3. Cyclisation generates the π-allyl species (33) with subsequent anion capture occurring predominantly at the least hindered exocyclic terminus. The effect of base was briefly studied for boronic acid (3a) and Ag(I) or Tl(I) carbonates were found to promote more selective formation of (31a) (Table 3). In the case (13c) a third product (34) (8%) was also detected.

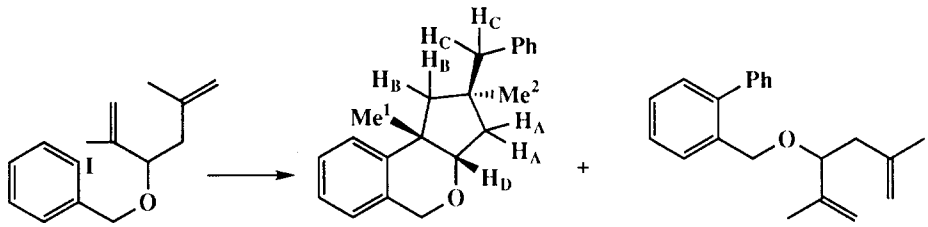
(vii) Biscyclisation Processes Employing Alkene Relay and Terminating Species. Several biscyclisations have been studied all with sodium tetraphenylborate as the anion transfer agent. Thus (35) reacts (anisole, 90°C, 16h) with sodium tetraphenylborate in the presence of 10 mol% $Pd(OAc)_2$ and 20 mol% PPh_3 to give the 6/5/5-fused system (36)(30%) as a single diastereomer. The relative stereochemistry of the two stereocentres was established by n.O.e. studies.



(35) (36)



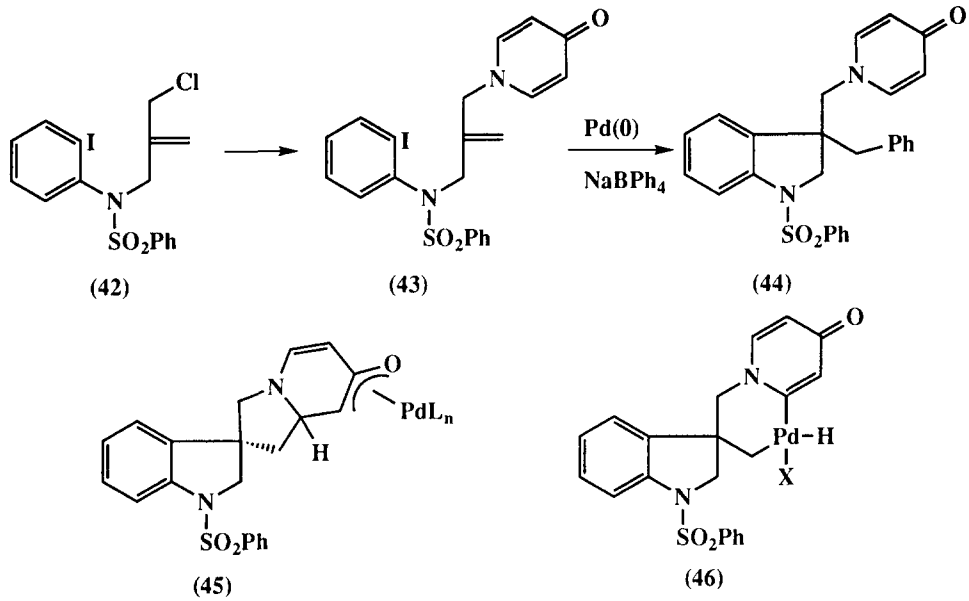
(37) (38)



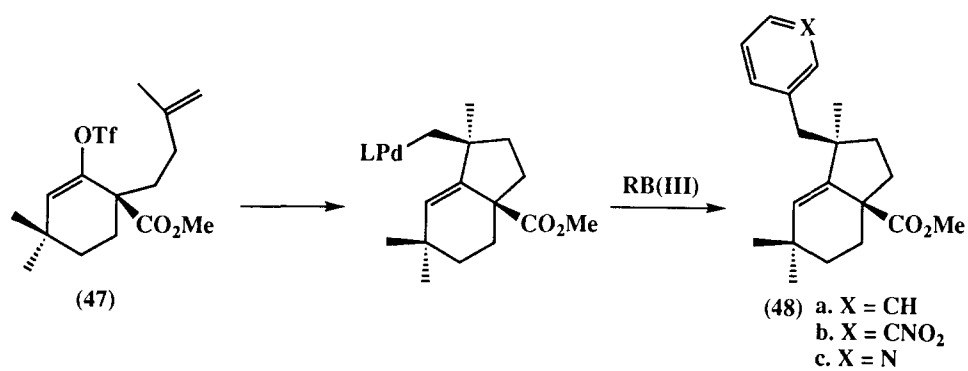
(39) (40) (41)

An analogous reaction (anisole, 110°C, 24h) of (37) with $NaBPh_4$ employing 10 mol% $Pd(dba)_2$ and 20 mol% tri(2-furyl)phosphine afforded the 6/5/6-spiro product (38) as a single diastereomer in 63% yield. The stereochemistry of (38) is provisional and is based on a chair-like pre-transition state conformer for the second cyclisation.[2] A third substrate (39) underwent cyclisation (anisole, 90°C, 16h) with anion capture from $NaBPh_4$ using 10 mol% $Pd(OAc)_2$ and 20 mol% PPh_3 to give a 2:1 mixture (70%) of the desired 6/6/5-fused product (40) and the premature capture product (41).

Aryl iodide (43) was prepared from (42) by reaction with the lithio derivative of 4-pyridone.[13] Cyclisation of (43) was effected in acetonitrile (80°C, 19h) using a catalyst system comprising 10 mol% $Pd(OAc)_2$, 20 mol% PPh_3 and Et_4NCl (1mol eq.) together with $NaBPh_4$ (1 mol eq.). The sole isolable product was (44) (56%). Products derived from the double cyclisation intermediate (45) (or its equivalent) were not detected although we have previously shown that products derivable from (45) are accessible in other reactions[13] However, it is possible that such products are derived from the Pd(IV) intermediate (46), rather oxo-π-allyl species (45), by insertion in the CH bond.



C. Vinyl Triflate Starter Species. The ready accessibility of vinyl triflates from aldehydes and ketones provides a large potential substrate base for our cyclisation-anion capture methodology. That enol triflates are excellent substrates for cyclisation with anion capture from B(III) species is illustrated by the application of such processes to (47). Enol triflate (47) was prepared in 72% yield from the corresponding ketone using N-(5-chloro-2-pyridyl)triflimide as the triflating agent.



Vinyl triflate (47) undergoes cyclisation-anion capture (DMF, 100% 8h) from $NaBPh_4$ (1eq) by a 5-exo-trig process to afford (48a) (90%) as a single diastereomer. Analogous reactions (toluene, 110°C, 8h) with m-nitrophenyl boronic acid (1.5 mol.eq) or diethyl-3-pyridyl borane (10) (1.5 mol.eq) affords (48b) (94%) and (48c) (92%) respectively. All reactions employed 10 mol% $Pd(OAc)_2$ and 20 mol% PPh_3 with the addition of Na_2CO_3 (2 mol eq) and Et_4NCl (1 mol eq) in the two latter cases. The stereochemistry of (48b) was established by X-ray crystallography (Figure 1) and that of (48a) and (48c) are assigned by analogy.

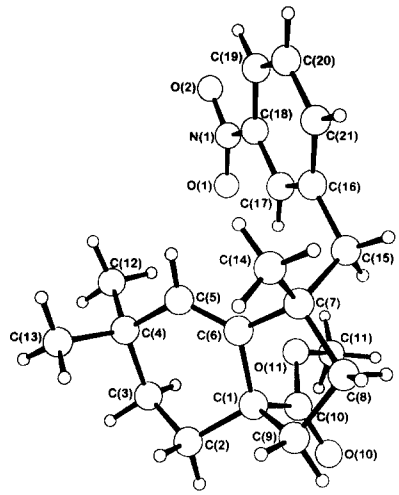
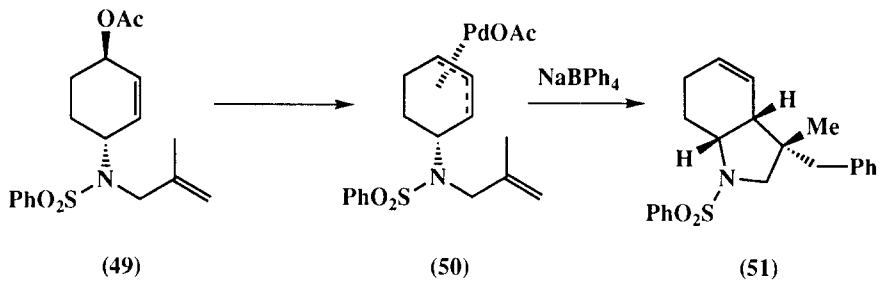
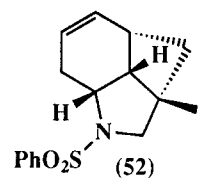


Figure 1. Molecular structure of **48b**

D. Allylic Acetate Starter Species. One example of a 5-exo-trig cyclisation with anion capture from $NaBPh_4$ have been studied using allylic acetate (49) as the starter species.



(49) (50) (51)



(52)

Substrate (49) reacts with $NaBPh_4$ in anisole at 60°C over 3h using 10 mol% $Pd(OAc)_2$/20 mol% PPh_3, *via* the π-allyl intermediate (50), to give a single diastereomer (51) (81%) in excellent yield. In the absence of the anion capture agent biscyclisation to the cyclobutyl product (52) occurs.[14]

Allenyl Starter Species. The first examples of cyclisation of allenyl species with anion capture from $NaBPh_4$ have recently been achieved[11] and will form the basis of a later paper in this series.

Conclusion. The cyclisation-anion capture methodology employing a wide range of organoboron(III) anion transfer reagents occurs with good regio- and stereo-selectivity usually in excellent yield. There are seldom any problems from the potentially competitive premature capture (shunt pathway) 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 983 G instruments and refer to potassium bromide discs unless otherwise noted. Mass spectral data were obtained from VG 7070 and Autospec instruments operating at 70 eV. Nuclear magnetic resonance spectra were recorded on Bruker WM 250, QE 300 and Bruker AM 400 instruments operating at 250, 300 and 400 Mhz, respectively. Unless otherwise specified deuteriochloroform was used as solvent. Microanalyses were obtained using a Carbo Erba MOD 11016 instrument. Preparative t.l.c. plates were prepared using silica gel 60 PF (Merck 7748). Column chromatography was performed with silica gel 60 (Merck 9385). Petroleum ether refers to the fraction with b.p. 40-60°C.

General procedure for cyclisation with capture from boronic acids (3a-c). The aryl iodide (1 mol. eq.) was added to a suspension of 10 mol% $Pd(OAc)_2$ and 20 mol% PPh_3 in dry toluene and the mixture was stirred for 10 min at room temperature. The arylboronic acid (1.5 eq) in a minimum amount of EtOH, Na_2CO_3 (2.6 M solution, 2.0 eq) and tetraethylammonium chloride (1 mol eq) were then added sequentially to this stirred solution and the mixture was boiled under reflux under a nitrogen atmosphere until tlc monitoring showed that all the starting material had been consumed. The mixture was cooled, filtered, and the filtrate evaporated under reduced pressure. The residue was partitioned between saturated NaCl solution and CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 and the combined CH_2Cl_2 extracts dried ($MgSO_4$) and evaporated. The residue was purified by crystallisation or column chromatography.

General procedure for cyclisation with capture from boronic acids (3d-f). A flask was charged with aryl iodide (1mmol), $Pd(OAc)_2$ (0.022g, 0.1mmol), PPh_3 (0.052g, 0.2mmol), boronic acid (1.5mmol in ethanol 0.5ml), Et_4NCl (0.165g, 1mmol), Na_2CO_3 [0.318g, 3mmol in H_2O(3ml)] and toluene (10ml) and heated under N_2 at 90°C for 8h. After cooling the reaction mixture the solvent was removed under reduced pressure to leave an oily residue which was dissolved in ether (30ml), washed with H_2O (20ml) and dried ($MgSO_4$). After removal of the ether, the residue was purified by column chromatography to yield the product.

3-Benzyl-3-methyl-2,3-dihydrobenzofuran (2a). A mixture of palladium acetate (0.044g, 0.2mmol), triphenylphosphine (0.104g, 2mmol), tetraethylammonium chloride (0.33g, 2mmol), phenylboronic acid (0.224g, 2mmol), aqueous sodium carbonate (0.53g in 2ml H_2O) and 2-iodophenyl methallyl ether (0.55g, 2mmol) in toluene (20ml) was boiled under reflux for 2h. After the usual work up the crude product was purified by column chromatography eluting with petroleum ether. The **product** (0.35g, 78%) was obtained as a colourless oil. (Found: C, 85.8; H, 7.2; $C_{16}H_{16}O$ requires C, 85.7; H, 7.2%), δ 7.21(m, 3H, ArH), 7.11(t, 1H, ArH), 6.92(m, 3H, ArH), 6.82(t, 1H, ArH), 6.74(d, 1H, J8.1Hz, ArH), 4.48 and 4.03(2xd, AB, 2x1H, J8.7Hz, OCH_2), 2.89 and 2.84(2xd, AB, 2x1H, J13.3Hz, $PhCH_2$) and 1.33(s, 3H, Me); m/z(%) 224(M^+,5), 133(100), 105(57), 91(18) and 77(12).

3-Methyl-3-(3'-nitrobenzyl)-2,3-dihydrobenzofuran (2b). A mixture of 2-iodophenyl methallyl ether (0.5g, 1.8mmol), palladium acetate (0.040g, 0.18mmol) and triphenylphosphine (0.095g, 0.36mmol) in toluene (20ml) was stirred for 10 min at room temperature. 3-Nitrophenylboronic acid (3b) (0.456g, 2.7mmol), Na_2CO_3 (0.386g, 3.6mmol), H_2O (0.5ml) and tetraethylammonium chloride (0.3g, 1.8mmol) were sequentially added to the stirred solution and the resulting mixture was boiled under reflux under a nitrogen atmosphere for 2h.

Workup in the usual way followed by preparative tlc eluting with 2:1 v/v ether-petroleum ether gave the **product** (0.45g, 93%) as pale yellow prisms, m.p. 97-99°C. (Found: C, 71.15; H, 5.6; N, 5.15. $C_{16}H_{15}NO_3$ requires C, 71.35; H, 5.6; N, 5.2%); δ 1.42(s, 3H, Me), 2.95(s, 2H, CH_2Ph), 4.11 and 4.45(d, 2x1H, J8 Hz, OCH_2), 6.71(d, 1H, J 8Hz, ArH), 6.88(d, 2H, J7 Hz, ArH), 7.16(m, 2H, ArH), 7.35(m, 1H, ArH), 7.79(s, 1H, ArH) and 8.06(d, 1H, J8 Hz, ArH); m/z(%) 269(M^+,4), 133(100), 91(5), 77(16) and 65(5); ν_{max}. (nujol) 2980, 1520, 1480, 1400 and 1010cm.$^{-1}$

3-(4'Bromobenzyl)-3-methyl-2,3-dihydrobenzofuran (2c). Prepared as above using 4-bromophenylboronic acid (3c) (1.5molar eq) and a reaction time of 4h. Standard workup followed by flash chromatography eluting with 1:9 v/v ether-petroleum ether gave the **product** (90%) as a colourless oil. (Found: C, 63.5; H, 5.0; Br, 26.2. $C_{16}H_{15}BrO$ requires C, 63.4; H, 5.0; Br, 26.35%); δ 1.30(s, 3H, Me), 2.77(s, 2H, CH_2Ph), 4.02 and 4.40(2xd, 2x1H, J9 Hz, OCH_2), 6.72-6.86(m, 5H, ArH), 7.10-7.20(m, 1H, ArH) and 7.30(d, 2H, J8 Hz, ArH); m/z(%) 304(M^+,98), 302(M^+,100), 170(20), 133(100), 91(15), 77(35) and 65(12); ν_{max} (film) 2850, 1630, 1510, 1250, 1100, 1030, 850 and 770cm.$^{-1}$

3-Methyl-3-styryl-2,3-dihydrobenzofuran (2d). Prepared as above from aryl iodide (1) (0.274g, 1mmol) and boronic acid (3d) (0.222g, 1.5mmol) but at 90°C in toluene for 8h. After workup followed by column chromatography eluting with 1:9 v/v ether-petroleum ether the **product** (0.167g, 67%) was obtained as a colourless oil. (Found: C, 86.35; H, 7.0. $C_{17}H_{16}O$ requires C, 86.4; H, 6.8%); δ7.30 -7.11(m, 7H, ArH), 6.89(t, 1H, J7 Hz, ArH), 6.8(d, 1H, J8Hz, ArH), 6.40(d, 1H, J16Hz,=CHPh), 6.12(m, 1H,CH=CHPh), 4.43 and 4.15(2xd, AB, 2x1H, J9Hz, OCH_2), 2.50(d, 2H, J7.5Hz, CH_2-CH=) and 1.39(s, 3H, Me); m/z(%) 250(M^+,1), 133(100), 105(50) and 77(8).

3-(2'-Furylmethyl)-3-methyl-2,3-dihydrobenzofuran (2e). Prepared as above from aryl iodide (1) (0.274g, 1mmol) and boronic acid (3e) (0.167g, 1mmol) in toluene at 110°C for 8h. The usual workup afforded the **product** (0.190g, 85%) as a colourless oil. (Found: C, 78.6; H, 6.7. $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.6%); δ7.31, 6.27 and 5.95(3xs, 3x1H, furan protons), 7.13(t, 1H, J8Hz, ArH), 7.02(d, 1H, J 7Hz, ArH), 6.86(t, 1H, J 7Hz, ArH) 6.77(d, 1H, J 8Hz, ArH), 4.55 and 4.13(2xd, AB, 2x1H, J 10Hz, OCH_2), 2.91(s, 2H, CH_2 furan), 1.34(s, 3H, Me); m/z(%) 214(M^+,3); 133(100) and 105(70).

3-Methyl-3-(N-sulphonylindol-3'-methyl)-2,3-dihydrobenzofuran (2f). Prepared as above from aryl iodide (1) (0.274g, 1mmol) and boronic acid (3f) (0.452g, 1.5mmol) but at 90°C in toluene for 8h. After workup followed by column chromatography eluting with 1:4 v/v ether-petroleum ether the **product** (0.243g, 60%) was obtained as colourless prisms, m.p. 88-89°C. (Found: C, 71.5; H, 5.4; N, 3.45. $C_{24}H_{21}NO_3S$ requires C, 71.45; H, 5.2; N, 3.45%); δ7.97-6.72(m, 14H, ArH), 4.39 and 4.06(2xd, AB, 2x1H, J 9Hz, OCH_2), 2.95(s, 2H, CH_2-Indole) and 1.40(s, 3H, Me); m/z(%): 403(11), 271(75), 133(100) and 77(78).

***N*-Phenylsulphonyl-3-benzyl-3-methylindoline (5a).** a. A mixture of *N*-phenylsulphonyl-(2'-methylprop-2'-enyl)-2-iodoaniline (0.5g, 1.2mmol), palladium acetate (0.027g, 0.12mmol) and PPh_3 (0.06g, 0.24mmol) in anhydrous toluene (5ml) was stirred for 10 min at room temperature. Phenylboronic acid (0.22g, 1.8mmol) in a minimum amount of EtOH(0.2ml), Na_2CO_3(0.256g, 2.4mmol 2M solution) and tetraethylammonium chloride

(0.20g, 1.2mmol) were added sequentially to this solution and the mixture was boiled under a nitrogen atmosphere for 8h. Workup in the usual way followed by preparative tlc eluting with 1:2 v/v ether-petroleum ether afforded the **product** (0.26g, 60%) as a pale yellow oil. HRMS: Found 363.1307. $C_{22}H_{21}NO_2S$ requires 363.1293. δ1.14(s, 3H Me), 2.61 and 2.72(2xd, 2x1H, J13Hz, CH_2), 3.38 and 3.95(2xd, 2x1H, J10Hz, NCH_2) and 6.8-7.8(m, 14H, ArH); m/z(%) 363(M^+,4), 272(100), 141(37), 91(52), 77(69) and 65(13); ν_{max}.(film) 2900, 1550, 1420, 1300, 1210, 1120 and 1020cm.$^{-1}$

b. A mixture of N-phenylsulphonyl-(2'-methylprop-2'-enyl)-2-iodoaniline (0.3g, 0.72mmol), palladium acetate (0.016g, 0.072mmol) and PPh_3 (0.38g, 0.145mmol) in anhydrous DME (5ml) was stirred for 10 min at room temperature. Phenylboronic acid (0.106g, 0.871mmol) in a minimum amount of EtOH (0.2ml), Na_2CO_3(0.153g, 1.45mmol), H_2O(0.75ml) and tetraethylammonium chloride (0.120g, 0.72mmol) were added sequentially to this solution and the mixture was boiled under a nitrogen atmosphere for 8h. Workup in the usual was followed by column chromatography eluting with 16:1 v/v petroleum ether-ether afforded (5a) (0.15g, 57%) and (6) (0.05g, 24%)[2] as colourless oils identical to those described previously.

N-Phenylsulphonyl-3-methyl-3-(3'-nitrobenzyl)indoline (5b). Prepared as above using 3-nitrophenylboronic acid (1.5 molar eq) and a reaction time of 8h. Workup and purification by preparative tlc eluting with 1:9 v/v ether-petroleum ether followed by crystallisation from ether-petroleum ether afforded the **product** (0.31g, 63%) as pale yellow prisms, m.p. 103-105°C (Found: C, 64.75; H, 4.95; N, 6.85; S, 8.0. $C_{22}H_{20}N_2O_4S$ requires C, 64.7; H, 4.9; N, 6.85; S, 7.85%); δ1.1(s, 3H, Me), 2.72 and 2.84(2xd, 2x1H, J13Hz, CH_2), 3.42 and 3.91(2xd, 2x1H, J10Hz, NCH_2) and 6.8-8.2(m, 13H, ArH); m/z(%): 408 (M^+,33), 272(100), 141(53), 136(22) and 77(72).

N-Phenylsulphonyl-3-(4'-bromobenzyl)-3-methylindoline (5c). Prepared as above using 4-bromophenylboronic acid (1.5 mol. eq) and a reaction time of 12h. Workup followed by purification by preparative tlc eluting with 4:1 v/v ether-petroleum ether afforded the **product** (0.31g, 58%) as a pale yellow oil. (Found: C, 59.45; H, 4.45; N, 2.85; S, 7.15, Br, 17.95. $C_{22}H_{20}BrNO_2S$ requires C, 59.75; H, 4.55; N, 3.15; S,7.25, Br, 18.1%); δ: 1.15(s, 3H, Me), 2.52 and 2.65(2xd, 2x1H, J13Hz, CH_2Ph), 3.42 and 3.91 (2xd, 2x1H, J10Hz, NCH_2) and 6.6-7.72(m, 13H, ArH); m/z(%): 443(M^+,2), 441(M^+,2), 272(100), 171(23), 141(37) and 77(63); ν_{max}.(film) : 2800, 1400, 1350 and 1150cm^{-1}

1.3-Dibenzyl-3-methyloxindole (8a). A mixture of N-benzyl-N-methacryloyl-2-iodoaniline (0.5g, 1.3mmol), palladium acetate (0.029g, 0.13mmol) and triphenylphosphine (0.069g, 0.26mmol) in toluene (5ml) was stirred for 10 min at room temperature. Phenylboronic acid (0.241g, 1.91mmol) dissolved in a minimum amount of EtOH (0.2ml), Na_2CO_3 (0.281g, 2.6mmol), H_2O (0.5ml) and tetraethylammonium chloride (0.219g, 1.3mmol) were added sequentially to this stirred solution and the mixture was boiled under a nitrogen atmosphere for 10h. Workup in the usual way followed by flash chromatography (SiO_2) eluting with 1:2 v/v ether-petroleum ether afforded the **product** (0.42g, 98%) as pale yellow needles, m.p. 95-97°C. (Found: C, 84.5; H, 6.5; N, 4.1. $C_{23}H_{21}NO$ requires C, 84.5; H, 6.4; N, 4.3%); δ 1.55(s, 3H, Me), 3.18 and 3.24(2xd, 2x1H, J13Hz, CH_2Ph), 4.47 and 5.00 (d, 2x1H, J16Hz, NCH_2), 6.41(m, 1H, ArH), 6.65(d, 2H, J6Hz, ArH) and 7.09-7.26(m, 11H, ArH); m/z(%) 327(M^+,55), 236(88), 91(100), 77(8) and 65(27); ν_{max}.(nujol) 2900, 1410, 1320, 1120 and 690cm.$^{-1}$

N-Benzyl-3-methyl-3-(3'-nitrobenzyl)oxindole (8b). Prepared as above using 3-nitrophenylboronic acid (1.5 mol. eq) and a reaction time of 8h. Workup and crystallisation of the residue from ether-petroleum ether afforded the **product** (0.469g, 95%) as pale yellow prisms, m.p. 103-105°C. (Found: C, 73.9; H, 5.25; N, 7.45. $C_{23}H_{20}N_2O_3$ requires: C, 74.2; H, 5.35; N, 7.5%); δ : 1.52(s, 3H, Me), 3.17 and 3.36(2xd, 2x1H, J13Hz, CH_2Ph), 4.52 and 4.87 (2xd, 2H, J15Hz, NCH_2) and 6.49-7.9(m, 13H, ArH); m/z(%): 372(M^+, 39), 236(100), 91(84) and 77(9); ν_{max}.(film): 2900, 1500, 1410, 1350 and 780cm.$^{-1}$

N-Benzyl-3-(4'-bromobenzyl)-3-methyloxindole (8c). Prepared as above using 4-bromophenylboronic acid (1.5 molar eq) and a reaction time of 8h. Workup followed by crystallisation of the residue from ether-petroleum ether afforded the **product** (0.48g, 90%) as pale yellow prisms, m.p. 115-118°C (Found: C, 68.25; H, 5.2; N, 3.25, Br, 19.95. $C_{23}H_{20}BrNO$ requires C, 68.0; H, 4.9; N 3.45; Br, 19.7%); δ 1.54(s, 3H, Me), 3.05 and 3.20(2xd, 2x1H, J13Hz, CH_2Ph), 4.42 and 5.04(2xd, 2x1H, J15Hz, NCH_2), 6.43(d, 1H, J6Hz, ArH), 6.64(s, 2H, ArH), 6.72(d, 2H, J8Hz, ArH) and 7.14-7.29(m, 8H, ArH); m/z(%) 407(M^+,8), 405(M^+,8), 236(98) 91(100), 77(8) and 65(16); ν_{max}.(nujol) 2900, 1700, 1630, 1470, 1350 and 1120cm.$^{-1}$

N-Benzyl-3-methyl-3-styryloxindole (8d). Prepared from aryl iodide (7) (0.377g, 1mmol) and boronic acid (3d) (0.222g, 1.5mmol). Workup followed by column chromatography eluting with 3:7 v/v ether-petroleum ether, afforded the **product** (0.254g, 72%) as a colourless prisms, mp 90-92°C. (Found: C, 85.0; H, 6.6; N, 3.95. $C_{25}H_{23}NO$ requires: C, 85.0; H, 6.5; N, 3.95%); δ7.30-6.96(m, 8H, ArH), 6.62(d, 1H, J5Hz, ArH), 6.4(d, 1H, J10Hz,=CHPh), 5.82(m, 1H, CH_2-CH=CH), 5.17 and 4.6(2xd. AB, 2x1H, J10Hz, NCH_2Ph), 2.81(m, 2H, CH_2-CH=) and 1.47(s, 3H, Me); m/z(%) 353(22), 236(61), 117(100) and 91(91).

N-Benzyl-3-(2'-furylmethyl)-3-methyloxindole (8e). Prepared from aryl iodide (7) (0.377g, 1mmol) and boronic acid (3e) (0.167g, 1.5mmol). Workup followed by column chromatography eluting with 3:7 v/v ether-petroleum ether afforded the **product** (0.234g, 74%), as colourless prisms, mp 89-91°C. (Found: C, 79.6; H, 6.1; N, 4.5. $C_{21}H_{19}NO_2$ requires C, 79.5; H, 6.0; N, 4.4%); δ 7.26-7.09(m, 8H, ArH and 1x furanH), 7.0(d, 1H, 7Hz, ArH), 6.60(d, 1H, J8Hz), 6.14 and 5.80(2xs, 2x1H, furanH), 5.04 and 4.72(2xd, AB, 2x1H, J16Hz, NCH_2Ph), 3.19(dd, 2H, J9Hz and 3Hz, CH_2 furan) and 1.5(s, 3H, Me); m/z(%) 317(M^+,30), 236(87) and 91(100).

N-Benzyl-3-methyl-3-(N'-phenylsulphonylindolyl-3'-methyl)oxindole (8f). Prepared from aryl iodide (7) (0.377g, 1mmol) and boronic acid (3f) (0.452g, 1.5mmol). Workup followed by column chromatography eluting with 2:3 v/v ether-petroleum ether afforded the **product** (0.344g, 68%) as colourless prisms, mp 169-171°C. (Found: C, 73.4; H, 5.05; N, 5.75. $C_{31}H_{26}N_2O_3S$ requires C, 73.5; H, 5.15; N, 5.55%); δ 7.84 and 7.54(2xd, 2x1H, J8Hz, ArH), 7.43-6.39(m, 17H, ArH and Indole 2-H), 4.86 and 4.33(2xd, AB, 2x1H, J16Hz, NCH_2), 3.47 and 3.16(2xd, AB, 2x1H, J14Hz, CH_2Indole) and 1.58(s, 3H, Me); m/z (%) 506(M^+,5), 270(100), 141(10) and 91(40).

3-Methyl-3-(pyridyl-3'-methyl)-2,3-dihydrobenzofuran (11a). A mixture of (1) (0.2g, 0.729mmol), $Pd(OAc)_2$, (0.016g, 0.0729mmol) and PPh_3(0.038g, 0.145mmol) in toluene (9ml) was stirred for 10 min at room temperature. Diethyl-3-pyridylborane (10) (0.16g, 1.09mmol), Na_2CO_3 (0.154g, 1.45mmol), Et_4NCl(0.12g,

0.729mmol) and H_2O(0.2ml) were added sequentially to this solution and the mixture was boiled under reflux for 10h. Standard workup followed by purification by preparative tlc eluting with 1:4 v/v ether-petroleum ether afforded the **product** (0.125g, 76%) as a colourless oil. (Found: C, 79.7; H, 6.85; N, 6.5. $C_{15}H_{15}NO$ requires: C, 79.95; H, 6.7; N, 6.2%); δ 1.24(s, 3H, Me), 2.72(s, 2H, CH_2Py), 3.97 and 4.32(2xd, 2x1H, J9Hz, OCH_2) and 6.60-8.34(m, 8H, ArH); m/z(%) 225(M^+,4), 133(100), 77(19) and 65(16); ν_{max}.(film) 2890, 1500, 1410 and 750cm.$^{-1}$

N-Phenylsulphonyl-3-methyl-3-(pyridyl-3'-methyl)indoline (11b). A mixture of N-phenylsulphonyl-N-(2'-methylpro-2'-enyl)-2-iodoaniline (4) (0.1g, 0.242mmol), $Pd(OAc)_2$ (0.005g, 0.024mmol) and PPh_3 (0.012g, 0.048mmol) in toluene (6ml) was stirred for 10 min at room temperature. Diethyl-3-pyridylborane (10). (0.053g, 0.363mmol), Na_2CO_3(0.0513g, 0.484mmol), Et_4NCl(0.04g, 0.242mmol) and H_2O(0.1ml) were added sequentially to this solution and the mixture was boiled under reflux for 8h. The solvent was then removed under reduced pressure and the residue partitioned between water (30ml) and dichloromethane (30ml). The water layer was extracted with dichloromethane (50ml) and the combined dichloromethane extracts dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography (SiO_2) eluting with 1:2 v/v ether-petroleum ether to afford the **product** (0.062g, 70%) as a pale yellow oil. (Found: C, 68.9; H, 5.4; N, 7.45; S, 8.65. $C_{21}H_{20}N_2O_2S$ requires: C, 69.2; H, 5.55; N, 7.65; S, 8.8%); δ: 1.1(s, 3H, Me), 2.52 and 2.62(2xd, 2x1H, J13Hz, CH_2Py), 3.34 and 3.82(2xd, 2x1H, J10Hz, NCH_2) and 6.68-8.36(m, 13H, ArH); m/z(%): 364(M^+1), 272(100), 141 (53), 77(82) and 65(56); ν_{max}.(film) : 2900, 1650, 1520, 1430, 1300, 1210, 1160 and 800cm.$^{-1}$

N-Benzyl-3-methyl-3-(pyridyl-3'-methyl)oxindole (12). A mixture of (7) (0.15g, 0.397mmol), $Pd(OAc)_2$, (0.009g, 0.04mmol) and PPh_3 (0.02g, 0.078mmol) in toluene (7ml) was stirred for 10 min at room temperature. Diethyl-3-pyridylborane (10) (0.087g, 0.596mmol), Na_2CO_3 (0.084g, 0.79mmol), Et_4NCl (0.065g, 0.397mmol) and H_2O(0.15ml) were added sequentially to this solution and the mixture was boiled under reflux for 9h. The solvent was then removed under reduced pressure and the residue partitioned between water (40ml) and dichoromethane (40ml). The water layer was extracted with dichloromethane (40ml) and the combined dichloromethane extracts dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography (SiO_2) eluting with 1:4 v/v ether-petroleum ether to afford the **product** (0.094g, 72%) as a pale yellow oil. (Found: C, 80.55; H, 6.25; N, 825. $C_{22}H_{20}N_2O$ required C, 80.5; H, 6.1; N, 8.55%). δ 1.45(s, 3H, Me), 3.01 and 3.17(2xd, 2x1H, J13Hz, CH_2Py), 4.47 and 4.8 (2xd, 2x1H, J16Hz, NCH_2Ph) and 6.38-8.27(m, 13H, ArH); m/z(%) 328(M^+,39), 236(93), 91(100), 77(11) and 65(19); ν_{max}. (nujol) 2900, 1715, 1440, 1380 and 720cm.$^{-1}$

N-Benzyl-3-[(E)-hept-2'-enyl]-3-methyloxindole (14). N-Benzyl-N-(2'-iodophenyl)methacrylamide(0.98 mmol) was added to a mixture of palladium acetate (10mol%) and triphenylphosphine (20mol%) in dry benzene (40ml) under a nitrogen atmosphere. After stirring for 10min *E*-hex-1-enyl-1,3,2-benzodioxaborole (1.48mmol), followed by sodium ethoxide (10ml of 2M solution in EtOH), were added. The resulting dark solution was boiled under reflux for 5h. The cooled solution was washed with water (50ml) dried ($MgSO_4$) and evaporated. The residue was purified by tlc eluting with 3:7 v/v ether-petroleum ether to afford the product as a pale brown oil (84mg, 32.5%). HRMS: 333.2101. $C_{23}H_{27}NO$ requires 333.2092. δ 0.78(t, 3H, J7Hz, $(CH_2)_2\underline{Me}$), 1.11(m, 4H, $2xCH_2$), 1.41(s, 3H, Me), 1.82(m, 2H, CH_2), 2.52(m, 2H, $\underline{CH_2}CH$=), 4.74 and 5.03(2xd, 2x1H, J15.7Hz, CH_2N), 5.05 and 5.4 (2xm, 2x1H, J15.1 and 7Hz, CH=CH), 6.66(d, 1H, J7.6Hz,

ArH) and 7.2(m, 8H, ArH); m/z(%) 333(M^+,19), 236(62), 237(100), 97(1) and 91(27); . ν_{max}.(film) 3029, 2923, 2867, 1711, 1610, 1486, 1464, 1451 and 939 $cm.^{-1}$

Norbornyl Spirocycles (16a) and (16b). A mixture of N-benzyl-N-(norborn-2'-enyl)-2-iodobenzamide (1mmol), palladium acetate (0.1mmol), triphenylphosphine (0.2mmol), E-hex-1-enyl-1,3,2-benzodioxaborole (1.48 mmol) and sodium ethoxide (2ml of 2M solution in EtOH) in dry benzene (30ml) was stirred and heated at 60°C for 6h. Work up followed by column chromatography (SiO_2) eluting with 1:1 v/v ether-petroleum ether afforded the **product** (16c) (48%) together with the hydride capture product (16b)(48%).[2]

16a. Found: C, 83.8; H, 7.9; N, 3.5. $C_{27}H_{31}NO$ requires C, 84.1; H, 8.1; N, 3.65%; δ 7.86-7.17(m, 9H, ArH), 5.4 and 4.9(2xm, 2H, CH=CH), 5.1 and 4.79(2xd, J15.9Hz, NCH_2), 2.6 and 2.5(2xd, 2x1H, 2xCH), 2.35 and 2.3(2xbr s, 2x1H, 2xCH), 2.0-1.0(m, 11H, 5xCH_2 and CH) and 0.8(t, 3H, Me); m/z(%) 385(M^+,73), 295(13), 294(69), 242(42), 91(100), 85(15) and 84(95).

16b. Spectroscopic data were identical to that reported previously.[2]

(E)-1-Acetyl-3-(1'-phenylethylidene)indoline (18a). A mixture of (17) (0.167g $5x10^{-4}$ mol), $Pd(OAc)_2$ (0.011g, 10mol%) and PPh_3(0.026g, 20mol%) in anisole (5ml) was stirred at room temperature for 15min, sodium tetraphenylborate (0.177g, $5x10^{-4}$ mol) was then added and the mixture heated at 80°C for 1h. The solvent was then evaporated under reduced pressure and the crude material purified by preparative tlc eluting with 1:1 v/v ether-petroleum ether to give the **product** (0.045g, 31%) which crystallised from ether-CH_2Cl_2 as colourless needles, m.p. 153-155°C. (Found: C, 82.05; H, 6.55; N, 5.1. $C_{18}H_{17}NO$ requires C, 82.1; H, 6.5; N, 5.3%); δ 8.31(d, 1H, J8.2Hz, ArH), 7.40 and 7.24(2xm, 3H and 2H, ArH), 7.06 and 6.62(2xt, 2x1H, ArH), 6.33(d, 1H, J7.8Hz, ArH), 4.68(d, 2H, J1.5Hz, NCH_2), 2.35(s, 3H, $COCH_3$) and 2.07(s, 3H, $C{=}CCH_3$), irradiation of the signal for the NCH_2 protons gave a 5.4% enhancement of the signal for the $C{=}CCH_3$ protons and 4.6% enhancement of the signal for the $COCH_3$ protons; m/z(%) 263(M^+,100), 221(38), 220(43), 206(98), 175(30), 144(38), 119(38), 105(34), 77(30) and 43(50); ν_{max}.(nujol) 1660, 1585, 760, 698 $cm.^{-1}$

(E)-1-Acetyl-3-(1'-hexenylethylidene)indoline (18b). A solution of (17) (0.313g, 0.001mol), $Pd(OAc)_2$ (0.022g, 10mol%) and PPh_3 (0.052g, 20mol%) in THF(7ml) was stirred at room temperature for 10min. Hexenylbenzodioxaborol (13b) (0.22g, 0.0011mol) was added followed by powdered KOH (0.112g, 0.002mol) and finally water (0.2ml). The reaction mixture was heated at 50°C for 2.5h and then the solvent evaporated off, water (10ml), added and the mixture extracted with ether (2x15ml). The combined ether layers were dried ($MgSO_4$) and evaporated. The residue was purified by preparative tlc eluting with 1:1 v/v ether-petroleum ether to give (18b) (0.11g, 41%) as pale yellow needles, m.p. 68-70°C HRMS: found 269.1780. $C_{18}H_{23}NO$ requires 269.1779. δ 8.28 and 7.57(2xd, 2x1H, J8 and 7.3Hz, ArH), 7.13 and 7.0(2xt, 2x1H, J7.1Hz, ArH), 6.86(d, 2H, J15Hz, CH=), 5.85(m, 1H, CH=), 2.53(m, 1H, $\underline{CH_2}CH{=}$), 4.52(s, 2H, NCH_2), 2.17 and 1.82(2xs, 2x3H, 2xMe), 1.3(m, 4H, 2xCH_2) and 0.85(t, 3H, Me); NOEDS(%): irradiation of the signal for NCH_2 effected enhancement of the signals for C=CMe(6.5) and COMe(4.4); m/z(%) 269(M^+,40) 187(65), 184(21), 145(30), 144(65), 130(100) and 43(48).

2-Iodophenyl propadienyl ether (19). A suspension of 2-iodophenol (2.20g, 10mmol), propargyl bromide (80%, 1.79g, 12mmol) and potassium carbonate (1.66g, 12mmol) in THF (25ml) was boiled under reflux for

16h. Water (50ml) and ethyl acetate (20ml) were then added and the organic layer separated, dried (Na_2SO_4), evaporated under reduced pressure and the residue dissolved in 3:1 v/v *t*-butyl alcohol - THF(20ml). Potassium *t*-butoxide(1.35g, 12mmol) was then added and the resulting mixture was stirred at room temperature for 16h. when the solvent was evaporated under reduced pressure and dichloromethane (20ml) added. The organic layer was separated and washed with water (20ml), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2) eluting with 4:1 v/v *n*-hexane-ether to give the **product**(2.20g, 85% overall yield) as a colourless oil (Found: C, 42.2; H, 2.85. C_9H_7IO requires C, 41.9; H, 2.75%); δ 5.44(d, J 6.06Hz, 2H, CH_2=C), 6.83(m, 2H, CHO and ArH), 7.08(dd, J8.1 and 1.1Hz, 1H, ArH), 7.31(td, J9.0 and 1.5Hz, 1H, ArH) and 7.79(dd, J9.0 and 1.3Hz, 1H, ArH); m/z(%) 258(M^+,37), 220(62), 131(100), 103(41), 92(52), 77(31), 65(30), 64(44), 63(46) and 39(39); ν_{max}.(film) 3060, 1955 and 840cm.$^{-1}$

General procedure for cyclisation onto allenes with capture by $NaBPh_4$. To a solution of allene (0.5mmol) in toluene (7ml) were added palladium acetate (5.6mg, 0.025mmol), triphenylphosphine (13.1mg, 0.05mmol) and $NaBPh_4$(205mg, 06mmol) and the reaction mixture was boiled under reflux for 1-3.5h. Ethyl acetate (5ml) and water (10ml) were added and 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 **products**.

General procedure for cyclisation onto allenes with capture by boronic acids. To a solution of allene (0.5mmol) in toluene (4ml) were added palladium acetate (5.6mg, 0.025mmol), triphenylphosphine (13.1mg, 0.05mmol), 0.5M aqueous solution of inorganic base (2ml) (see Table 3) and the corresponding boronic acid [0.6mmol, except when (*E*)-2-(2'-phenylethenyl)-1,3,2-benzodioxaborole was employed; in this case 1.0mmol was added]. The biphasic mixture was heated at 90°C for the time indicated in Table 3. Ethyl acetate (5ml) and water (10ml) were added and the organic phase was decanted, dried (Na_2SO_4) and evaporated. The resulting residue was purified by flash chromatography (SiO_2) eluting with mixtures of *n*-hexane-ether.

3-Benzylbenzofuran (20). After a reaction time of 1h and work up the **product** was obtained as a colourless oil (65%) (Found: C, 86.3; H, 5.7. $C_{15}H_{12}O$ requires C, 86.5; H, 5.8%); δ 4.01(s, 2H, CH_2) and 7.17-7.47(m, 10H, ArH); m/z(%) 209(M+1 ,27), 208(M^+,100), 209(88), 179(24), 178(35), 131(62) and 77(22); ν_{max}.(film) 3080, 1650 and 765cm.$^{-1}$

(E)-3-(3'-Phenylprop-2'-enyl)benzofuran (21b). After a reaction time of 1.5h at 90°C and workup the **product** was obtained as a thick colourless oil (Found: C, 87.6; H, 5.8. $C_{17}H_{14}O$ requires C, 87.2; H, 6.0%); δ 3.57(d, J6.5Hz, 2H, CH_2), 6.38(dt, J 15.7 and 6.5Hz, 1H, C=C<u>H</u>CH_2), 6.54 (d,J15.7Hz, 1H, PhCH=C) and 7.18-7.57(m, 10H, ArH); m/z(%) 235(M+1 ,34), 234(M^+,100), 233(36), 157(20), 131(40), 128(27), 115(30), 103(31), 91(23) and 77(28); ν_{max}.(film) 3080, 1650 and 965cm.$^{-1}$

4-Methyl-4-benzylisochroman (23). A mixture of palladium dibenzylidineacetone (0.11g, 0.2mmol), tri(2-furyl)phosphine (0.092g, 0.4mmol), tetraethylammonium chloride (0.33g, 2mmol), sodium tetraphenylborate (0.68g, 2mmol) and 2-iodobenzyl methallyl ether (0.58g, 2mmol) was heated in DMF at 110°C for 24h. After the usual work up the crude product was purified by column chromatography eluting with 1:1 v/v ether-petroleum ether. The **product** (0.28g, 60%) was obtained as a colourless oil. HRMS: 238.1364. $C_{17}H_{18}O$ requires 238.1357. δ 7.25-6.97(m, 9H, ArH), 4.84(br s, 2H, OCH_2), 3.78 and 3.38(2xd, AB, 2x1H, J11.4Hz,

OCH_2), 3.04 and 2.84(2xd, AB, 2x1H, J13.2Hz, CH_2Ph) and 1.13(s, 3H, Me); m/z(%) 238(M^+,7), 162(20), 147(100), 132(32), 119(85), 105(33), 91(63) and 77(23).

N-(2'-Iodobenzyl)-2-aza-3-oxobicyclo[2.2.1]hept-5-ene (26). Sodium hydride (1.0g of a 60% dispersion in mineral oil, 25mmol) was added portionwise to a solution of 1R, 4S-2-azabicyclo[2.2.1]hept-5-en-3-one (2.5g, 23mmol) in anhydrous THF (50ml) and the mixture stirred at room temperature for 1h. A solution of 2-iodobenzyl chloride (5.8g, 23mmol) in anhydrous THF (25ml) was then added and the mixture boiled under reflux for 12h. The solvent was then evaporated under reduced pressure and the residue partitioned between ether (120ml) and water (120ml). The aqueous layer was separated and extracted with ether (120ml). The combined ether extracts were dried (Na_2SO_4), the solvent removed under reduced pressure and the residue crystallised from ether-petroleum ether to afford the **product** (3.9g, 53%) as colourless prisms, m.p. 62-64°C; $[\alpha]_D$ -75.6 (c = 1, $CHCl_3$) (Found: C, 47.85; H, 3.6; N, 4.3. $C_{13}H_{12}INO$ requires C, 48.0; H, 3.7; N, 4.3%); δ 7.4-6.9(m, 4H, ArH), 6.7(m, 2H, CH=CH), 4.57 and 3.95(2xd, 2x1H, J15.4Hz, NCH_2), 4.15(s, 1H, NCH), 3.41(s, 1H, CHCO), and 2.36 and 2.13(2xd, 2x1H, J7.8 and 7.6Hz, CH_2) l; m/z(%) 326 (M+1,1), 217(21), 198(22), 90(29) and 66(100).

Cyclisation-anion capture product (27). A mixture of (26) (0.5g, 1.5mmol), palladium acetate (0.35g, 0.15mmol), triphenylphosphine (0.081g, 0.31mmol), Et_4NCl(0.26g, 1.5mmol) and $NaBPh_4$ (0.58g, 1.7mmol) in anisole (20ml) was stirred and heated at 100°C for 24h under a nitrogen atmosphere. After workup the residue was purified by flash chromatography (SiO_2) eluting with 2:1 v/v ether-petroleum ether to afford the **product** (0.18g, 43%) as pale brown needles, m.p. 182-185°C $[\alpha]_D$ -271.5 (c = 1, $CHCl_3$) (Found: C, 82.8; H, 6.35; N, 5.05. $C_{19}H_{17}NO$ requires C, 82.85; H, 6.2; N, 5.1%); δ7.1-6.7(m, 8H, ArH), 6.35(d, 1H, J7.7Hz, ArH), 5.03 and 4.19(2xd, 2x1H, J16.8Hz, NCH_2); 4.02(s, 1H, NCH), 3.83 and 3.67(2xm, 2x1H, 2xNCH), 3.01(s, 1H, COCH), 2.16 and 1.92(2xd, 2x1H, J9.95Hz, CH_2); m/z(%) 275(M^+, 100), 240(39), 184(58), 128(38), 115(46).

N-Methyl-4-[(E)-2'-heptenylidenyl]-3,4-dihydroisoquinolin-1-one (29). Prepared in an analogous manner to(14) from (28) (1.34mmol) and (13a) (0.3g, 1.48mmol) with a reaction time of 2h. The **product** (0.155g, 45%) was isolated as a yellow oil by preparative tlc eluting with 1:1 v/v ether-petroleum ether. HRMS: 255.1590. $C_{17}H_{17}NO$ requires 255.1623. δ0.9(t, 3H, J7Hz, Me), 1.37(m, 4H, $2xCH_2$), 2.16(m, 2H, CH_2), 3.15(s, 3H, NMe), 4.06(s, 2H, NCH_2), 5.95(m, 1H, J7.2 and 15Hz,=CH_a), 6.24(d, 1H, J11.1Hz,=CH_c), 6.59(dd, 1H, J11.1 and 14.9Hz,=CH_b), 7.41(m, 3H, ArH) and 8.41(d, 1H, J7.2Hz, ArH); NOEDS(%): irradiation of the signal for NCH_2 effected enhancement of H_C(13.6) and NMe(8.1); m/z(%) 255(M^+,99), 254(5), 212(23), 198(100), 172(30) and 159(50); ν_{max}.(film) 3030, 2917, 2856, 1638, 1597, 1397 and 895cm^{-1}

Compounds (31a-c), (32a) and (32c) were prepared by the general procedure (above) with reaction times, additives and yields as noted in Table 3.

N-Methyl-4-benzyl-1,2-dihydroisoquinolinyl-1-one (31a) Colourless needles from *n*-hexane-ether m.p. 96-97°C (Found: C, 82.0; H, 6.05; N, 5.5. $C_{17}H_{15}NO$ requires: C, 81.9; H, 6.05; N, 5.6%). δ 3.56(s, 3H, Me), 4.02(s, 2H, CH_2), 6.80(s, 1H, CH=C), 7.20-7.57(m, 8H, ArH) and 8.48(d, 1H,J7.8Hz, ArH); ν_{max}.(film) 3070, 1630-1670 and 800$cm.^{-1}$

N-Methyl-4-methylene-3-phenyl-1,2,3,4-tetrahydroisoquinolinyl-1-one (32a). Pale yellow oil, (Found: C, 82.15; H, 6.5; N, 5.5. $C_{17}H_{15}NO$ requires: C, 81.9; H, 6.05; N, 5.6%); δ 3.05(s, 3H, Me), 5.28, 5.45, 5.60(3xs,

3H, CH_2CCHN), 6.98-7.48(m, 8H, ArH) and 7.84(m, 1H, ArH), m/z(%) 249(M^+,35), 147(56), 146(100), 103(13), 91(24), 78(10) and 77(16); ν_{max}.(film) 3080, 1680, 1650 and 820cm.$^{-1}$

N-Methyl-4-(2-thienylmethyl)-1,2-dihydroisoquinolinyl-1-one (31b). Pale yellow oil (Found: C, 70.2;H, 5.0; N, 5.55, S, 12.7. $C_{15}H_{13}NOS$ requires: C, 70.55; H, 5.15; N, 5.5; S, 12.55%). δ 3.60(s, 3H, Me), 4.21(s, 2H, CH_2), 6.84-6.96(m, 3H, ArH), 7.16(d, J5.1Hz, 1H, ArH), 7.49(m, 1H, ArH), 7.62(d, J4.0Hz, 2H, ArH) and 8.49(d, J8.1Hz, 1H, ArH). m/z(%) 256(M+1,28), 255(M^+, 100), 254(41), 226(16), 184(14), 172(15), 115(12), 97(15) and 77(12); ν_{max}.(film) 3085, 1650-1600 and 845cm.$^{-1}$

(E)-N-Methyl-4-(3'-phenylprop-2'-enyl)-1,2-dihydroisoquinolinyl-1-one (31c). Colourless oil (Found: C, 82.55; H, 6.45; N, 4.95. $C_{19}H_{17}NO$ requires. C, 82.85; H, 6.2; N, 5.1%). δ 3.58(d, J6.0Hz, 2H, CH_2), 3.59(s, 3H, Me), 6.37(dt, J16.0 and 6.0Hz, 1H, $CH_2C\underline{H}$=CH), 6.49(d, J16.0Hz, 1H, PhCH), 6.93(s, 1H, CHN), 7.21-7.69(m, 8H, ArH) and 8.48(d, J8.1Hz, 1H, ArH). m/z(%)276(M+1, 28), 275(M^+,100), 274(34), 184(18), 173(19), 172(35), 146(25), 115(17), 91(21) and 77(15). ν_{max}.(film) 3080, 1660-1610, 960 and 810cm.$_{-1}$

(E)-N-Methyl-4-methylene-3-(2'-phenylethenyl)-1,2,3,4-tetrahydroisoquinolinyl-1-one (32c). Pale yellow oil (Found: C, 82.55; H, 5.85; N, 5.2. $C_{19}H_{17}NO$ requires: C, 82.85; H, 6.2; N, 5.1%). δ 3.07(s, 3H, Me), 4.75(d, J7.5Hz, 1H, CHN), 5.15, 5.30(2xs, 2H, CH_2=C), 5.44-5.64(m, 2H, CH=CH) and 7.21-7.88(m, 9H, ArH). m/z(%) 275(M^+,17), 173(48), 172(23), 146(100) 115(14), 91(26) and 77(14); ν_{max}.(film) 3085, 1690-1620 and 800cm.$^{-1}$

General procedure for biscyclisation-anion capture. A mixture of the cyclisation precursor (1mmol), palladium acetate (0.1mmol), triphenyphosphine (0.2mmol) and sodium tetraphenylborate (1mmol) in anisole (50ml) was stirred and heated 110°C until tlc monitoring showed all the starting material had been consumed (ca. 16h). The mixture was cooled, filtered, the filtrate evaporated under reduced pressure and the residue purified by flash chromatography.

Biscyclisation product (36). Flash chromatography eluting with 1:1 v/v ether-petroleum ether furnished the **product** (30%) as a colourless oil (Found: C, 82.2; H, 6.9; N, 4.5. $C_{20}H_{21}NO$ requires C, 82.45; H, 7.2; N, 4.8%); δ 7.75-7.16(m, 9H, ArH), 3.8 and 3.3(2xd, 2H, J11.9Hz, NCH_2), 2.8(s, 2H, $PhCH_2$), 2.1 and 1.7(2xd, J13.2Hz, 2H, CH_2) and 1.4 and 0.8(2xs, 2x3H, Me); NOEDS(%): irradiation of Me^1(δ0.8) effected enhancement of the signals for H_A(1.5), H_C(2) and H_D(1.5); m/z(%) 291(M^+, 37), 276(17), 215(19), 187(3), 159(100), 142(10), 95(10), 86(38) and 83(56).

Biscyclisation product (38). Flash chromatography eluting with 1:1 v/v ether-petroleum ether furnished the product (63%) which crystallised as colourless needles from ether-petroleum ether, m.p. 222-223°C (Found: C, 67.1, H, 5.65; H, 5.05. $C_{32}H_{32}N_2O_4S_2$ requires C,67.15, H, 5.6; N, 4.9%); δ 8.0-6.89(m, 19H, ArH), 4.6, 3.9, 3.7, 3.3, 3.2, and 2.3(6xd, 6x1H, 4xNCH and CH_2), 1.8 and 1.7(2xd, 2x1H, CH_2Ph), 1.6(d, 2H, CH_2) and 0.7(s, 3H, Me); m/z(%) 573(M+1,40), 433(100), 291(20) and 130(5).

Biscyclisation product (40) and direct capture product (41). The 2:1 mixture (70%) of (40) and (41) was separated by flash chromatography eluting with 9:1 v/v ether-petroleum ether.

40. Obtained as colourless plates from ether-petroleum ether, m.p. 60-62°C (Found: C, 86.15; H, 8.15. $C_{21}H_{24}O$ requires C, 86.3; H, 8.2%); δ 7.3-6.96(m, 9H, ArH), 4.7 and 4.62(2xd, 2H, J14.5Hz, OCH_2), 3.85(d,

1H, J1.2Hz, OCH), 2.71(2xd, 2H, J13Hz, $PhCH_2$), 2.45(dd, 1H, J5.5 and 14.3Hz, CH_A), 2.0 and 1.88(2xd, 2H, J13.4Hz, $2xH_B$), 1.73(d, 1H, J14.3Hz, CH_A), and 1.23 and 1.07(2xs, 2x3H, Me); m/z(%) 292(M^+,1), 201(24), 183(17), 146(41), 121(31), 91(24) and 40(100). NOEDS(%): irradiation of the benzyl methylene H_C protons effected enhancement of the signals for Me^1(1.7) (δ1.23) and Me^2(1.3) whilst irradiation of H_D effected enhancement of the signal for Me^1(4).

41. Obtained as a pale yellow oil (Found: C, 86.25; H, 8.3%); δ 8.0-6.8(m, 9H, ArH), 4.80, 4.76, 4.73 and 4.70(4xs, 4x1H, CH=), 4.4 and 4.2(2xd, 2H, OCH_2), 3.8(br dd, 1H, OCH), 2.4 and 2.2(2xdd, 2H, CH_2) and 1.86 and 1.84(2xs, 2x3H, Me); m/z(%) 237(4), 167(100), 165(29), 152(15), 55(8) and 41(11).

Cyclisation-anion capture product (44). A mixture of (43) (0.31g, 0.60mmol), palladium acetate (0.014g, 0.064mmol), triphenylphosphine (0.033g, 0.13mmol), tetraethylammonium chloride (0.10g, 0.62mol) and sodium tetraphenylborate (0.21g, 0.61mmol) in anhydrous acetonitrile (25ml) was boiled under reflux under an atmosphere of dry nitrogen for 19h. The solvent was then removed under reduced pressure and the residue partitioned between dichloromethane (50ml) and water (50ml). The aqueous layer was extracted with dichloromethane (50ml) and the combined dichloromethane extracts dried (Na_2SO_4) and the solvent removed under reduced pressure. The residue was purified by flash chromatography (SiO_2) eluting with 2:1 v/v ether-methanol to afford the **product** (0.16g, 56%) as yellow prisms, m.p. 98-100°C. HRMS: 457.157. $C_{27}H_{24}N_2O_3S$ requires 457.157; δ 7.8-6.8(m, 14H, ArH), 6.76(d, 2H, J7.6Hz, C=CHNCH=C), 6.10(d, 2H, J7.5Hz, CHCOCH), 4.04 and 3.73(2xd, 2x1H, J14.3Hz, CH_2), 3.81 and 3.59(2xd, 2x1H, J10.7Hz, CH_2) and 3.12 and 2.92(2xd, 2x1H, 14.1Hz, CH_2Ph); m/z(%) 456(M^+,3), 348(6), 207(7), 109(25) and 84(100).

3,3-Dimethyl-6-(3'-methylbut-3'-enyl)-6-methoxycarbonyl cyclohexenyl triflate (47). 2-Methoxylcarbonyl-2-(3'-methylbut-3'-enyl)-5,5-dimethylcyclohexanone (12g, 0.04mol) in dry THF (15ml) was added dropwise to a stirred solution of lithium diisopropylamide [from n-butyllithium (35.74ml, 1.6M solution in hexane, 0.057mol) and diisopropylamine (8.01mol, 0.057mol)] in freshly distilled THF (25ml) cooled to -78°C and the resulting solution was stirred at -78°C for a further 1h. N-(5-Chloro-2-pyridyl)triflimide (19.04g, 0.048mol) in THF (8ml) was then added dropwise at -78°C and the resulting mixture maintained at this temperature for 3h. The usual workup followed by distillation under reduced pressure gave the **product** (13.2g, 72%) as a colourless oil, b.p. 93-97°C/0.04mm Hg (Found: C, 50.3; H, 6.15; F, 14.85; S, 8.4. $C_{16}H_{23}F_3O_5S$ requires C,50.0; H, 6.05; F, 14.85; S, 8.35%); δ 1.06 and 1.10(2xs, 2x3H, 2xMe), 1.48-2.0(m, 8H, $4xCH_2$), 1.82(s, 3H,=CMe), 3.74(s, 3H, OMe), 4.71(d, 2H, J8Hz,=CH_2) and 5.63(s,1H,=CH); m/z(%) 384(M^+,1), 316(100), 69(83), 55(25) and 41(35); ν_{max}.(film) 3010, 1740, 1450, 1230, 920 and 830cm.$^{-1}$

Cyclisation-Anion capture product (48a). Enol triflate (47) (0.2g, 0.52mmol) was added to a stirred suspension of $Pd(OAc)_2$ (0.011g, 0.052mmol), PPh_3(0.027g, 0.104mmol) and $NaBPh_4$(0.21g, 0.062mmol) in DMF (8ml). The resulting mixture was boiled under reflux under a nitrogen atmosphere for 8h. Standard workup followed by column chromatography eluting with 1:8 v/v ether-petroleum ether afforded the **product** (0.15g, 90%) as a colourless oil. (Found: C, 80.6, H, 9.05. $C_{21}H_{28}O_2$ requires C, 80.75; H, 8.95%); δ 0.82, 0.94 and 0.97(3xs, 3x3H, 3xMe), 1.01-2.32(m, 8H, $4xCH_2$), 2.70(s, 2H, CH_2), 3.71(s, 3H, OMe), 4.64(s, 1H,=CH_2) and 7.1-7.25(m, 5H, ArH); m/z(%) 312(M^+,1), 253(3), 221(35), 161(100) and 91(19); ν_{max}.(film) 2900, 1760, 1490, 1400, 1300, 1220, 1180, 940 and 740cm.$^{-1}$

Cyclisation-anion capture product (48b). Enol triflate (47) (0.1g, 0.26mmol) was added to a stirred suspension of $Pd(OAc)_2$ (0.005g, 0.026mmol), PPh_3 (0.013g, 0.005mmol), 3-nitrophenylboronic acid (0.065g, 0.39mmol), Na_2CO_3 [0.05g, 0.052mmol in H_2O (0.1ml)] and $Et_4N^+Cl^-$ (0.04g, 0.26mmol) in toluene (8ml). The resulting mixture was boiled under reflux under a nitrogen atmosphere for 8h. The solvent was then removed under reduced pressure and the residue partitioned between water (40ml) and dichloromethane (40ml) and the combined dichloromethane extracts dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography (SiO_2) eluting with 1:10 v/v ether-petroleum ether to afford the **product** (0.088g, 94%) as colourless prisms, m.p. 84-85°C. (Found: C, 70.65; H, 7.55; N, 3.8. $C_{21}H_{27}NO_4$ requires: C, 70.55; H, 7.6; N, 3.9%); δ:0.92(s, 3H, Me), 0.96 and 1.03(2xs, 2x3H, 2xMe), 1.32-2.37(m, 8H, 4xCH_2), 2.78-2.84(m, 2H, CH_2), 3.75(s, 3H, OMe), 4.40(s, 1H,=CH) and 7.31-8.12(m, 4H, ArH); m/z(%): 357(M^+,7), 298(6), 221(54), 161(100) and 91(10); $\nu_{max.}$(nujol): 2900, 1540, 1410, 1360 and 880cm.$^{-1}$

Cyclisation-anion capture product (48c). Enol triflate (47) (0.265g, 0.69mmol) was added to a stirred suspension of $Pd(OAc)_2$ (0.0154g, 0.069mmol), PPh_3(0.036g, 0.13mmol), diethyl-3-pyridyl-borane (0.152g, 1.0mmol), Na_2CO_3 [0.146g, 1.3mmol in H_2O (0.2ml)] and $Et_4N^+Cl^-$(0.114g, 1.3mmol) in toluene (8ml). The resulting mixture was boiled under reflux under a nitrogen atmosphere for 8h. The solvent was then removed under reduced pressure and the residue partitioned between water (50ml) and dichloromethane (50ml). The water layer was extracted with dichloromethene (50ml) and the combined dichloromethane extracts dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography (SiO_2) eluting with 1:8 v/v ether-petroleum ether to afford the **product** (0.2g, 92%) as a colourless oil. (Found: C, 76.7; H, 8.8; N, 4.6. $C_{20}H_{27}NO_2$ requires C, 76.65; H, 8.6; N, 4.45%); δ 0.85(s, 3H, Me), 0.97(s, 6H, 2xMe), 1.32-2.34(m, 8H, 4xCH_2), 2.70(s, 2H, CH_2), 3.73(s, 3H, OMe), 4.53(s, 1H,=CH) and 7.14-8.45(m, 4H, ArH); m/z(%) 313(M^+,6), 298(1), 254(8), 221(22), 161(100) and 92(11); $\nu_{max.}$(film) 2900, 1760, 1490, 1410, 1180 and 750cm.$^{-1}$

Trans 1-acetoxy-4-(*N*-phenylsulphonyl-*N*-methallyl)cyclohex-2-ene (49). Sodium hydride (0.4g, 60% in mineral oil) was added portionwise to a stirred solution of *N*-phenylsulphonyl methallylamine (2.11g, 0.01mol) in dry DMF (50ml) at 0°C. The mixture was stirred for 1h when a solution of *cis*-1-acetoxy-4-chlorocyclohex-2-ene (1.74g, 0.01mol) in DMF (10ml) was added dropwise over 10min. The resulting mixture was stirred and heated at 70°C for 16h. Workup in the usual way followed by flash chromatography (SiO_2) eluting with 1:1 v/v ether-petroleum ether afforded the **product** (2.33g, 67%) as a pale yellow oil (Found: C, 62.0; H, 6.6, N, 4.0; S, 9.15. $C_{18}H_{23}NO_4S$ requires C, 61.9; H, 6.6; N, 4.05; S, 8.95%); δ 7.8-7.26(m, 5H, ArH), 5.65(dd, 1H, J1.8 and 11.35Hz,=CH), 5.23(m, 1H, CHO), 5.10(dd, 1H, J1.8 and 10.4Hz), 4.95 and 4.88(2xs, 2H,=CH_2), 4.6(m, 1H, NCH), 3.8 and 3.4(2xd, 2H, J18.6Hz, NCH_2), 2.0 and 1.8(2xs, 2x3H, Me) and 2.2 - 1.8(m, 4H, 2xCH_2); m/z(%) 349(M^+,19), 290(71), 289(68), 263(51), 237(38), 208(42), 170(42), 138(100), 122(50) and 95(40).

***N*-Phenylsulphonyl-3-benzyl-3-methyl-2,3,3a,6,7,7a-hexahydroindole (51).** 1-Acetoxy-4-(*N*-phenylsulphonyl-*N*-methallyl)cyclohex-2-ene (1mmol), palladium acetate (0.1mmol), triphenylphosphine (0.2mmol), sodium tetraphenylborate (1.1mmol) in anisole (30ml) was stirred and heated at 60°C for 3h. The mixture was then cooled, filtered and the filtrate evaporated to dryness under reduced pressure. The residue was purified by flash chromatography (SiO_2) eluting with 1:4 v/v ether-petroleum ether. The **product** (0.297g, 81%) was obtained as colourless prisms from ether-petroleum ether, m.p. 137-139°C (Found: C, 71.9; H, 7.1; N, 4.05. $C_{22}H_{25}NO_2S$ requires C, 71.95; H, 6.8; N, 3.8%); δ 7,8-7.0(m, 10H, ArH), 6.0(br, 1H,=CH), 5.69(dd, 1H,=CH),

3.8(m, 1H, NCH), 3.47 and 2.68(2xd, 2H, J9.95Hz, NCH_2), 2.8 and 2.4(2xd, 2H, J13.25Hz, $PhCH_2$), 2.2-2.0(m, 4H, $2xCH_2$), 0.6(s,3H, Me); m/z(%) 367(M^+,84), 287(20), 276(85), 226(62), 170(40), 134(60), 91(100), 77(85).

Single crystal X-ray diffraction analysis of 48b. All crystallographic measurements were carried out at 200K on a Stoe STADI4 diffractometer using graphite monochromated Copper K_α X-radiation (λ = 1.54184 Å) and an on-line profile fitting method.[15] Two equivalent sets of data were collected in the range $4.0° < 2\theta < 130.0°$. No significant variation was observed in the intensities of five standard reflections. Lorentz and polarisation corrections were applied to the data-set together with a semi-empirical absorption correction based on azimuthal ψ-scans. The structure was solved by direct methods using SHELXS-86[16] and was refined by full-matrix least-squares (using all the unique F^2 data) using SHELXL-93.[17] The weighting scheme was $w = [\sigma^2(F_o^2) + (0.0399P)^2 + 0.6708P]^{-1}$ where $P=(F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were constrained to idealised positions using a riding model with free rotation for methyl groups and fixed isotropic displacement parameters. Refinement included an isotropic extinction parameter x so that $F_c^* = k\,F_c\,[1 + 0.001 * x * F_c^2 * \lambda^3]^{-1/4}$ where k is the overall scale factor. The residuals wR_2 and R_1, given below, are defined as $wR_2=(\Sigma[w(F_O-F_C^2)^2] / \Sigma[wF_O^4])^{1/2}$ and $R_1=\Sigma||F_o|-|F_c|| / \Sigma|F_o|$. The latter is given for comparison with refinements based on F and uses reflections with $F_o^2 > 2\sigma(F_o^2)$.

Crystal data. $C_{21}H_{27}NO_4$, 0.53 x 0.42 x 0.34 mm, M = 357.44, monoclinic, space group $P2_1/a$, a = 13.1282(6), b = 9.5891(3), c = 15.2037(7) Å, β = 90.695(4)°, U = 1913.82(4) Å^3, Z = 4, D_X = 1.241 Mg m^{-3}, μ = 0.689 mm^{-1}, $F(000)$ = 768.

Data collection. Each scan divided into 30 steps, step size and width calculated from a learnt profile, scan speeds 0.4 - 1.5 seconds per step, $4.0 < 2\theta < 130.0°$, 6509 Data collected 3084 of which were unique, R_{int} = 0.0272. There were 2754 reflections with $F_o > 4.0\,\sigma(F_O)$.

Structure refinement. Isotropic extinction parameter x = 0.0089(4), wR_2 = 0.1030, R_1 = 0.0389, goodness of fit s = 1.061 for all F^2 values and 240 parameters.

Selected bond lengths and angles are listed in Table 4. Supplementary data, which includes atomic co-ordinates and all thermal parameters together with complete bond lengths and angles, has been deposited at the Cambridge Crystallographic Data Centre and is available on request.

Table 4. Selected bond lengths (Å) and angles (°) for **48b** with e.s.d.s in parentheses.

C(1)-C(6)	1.517(2)	C(1)-C(10)	1.529(2)
C(1)-C(2)	1.532(2)	C(1)-C(9)	1.534(2)
C(2)-C(3)	1.520(2)	C(3)-C(4)	1.537(2)
C(4)-C(5)	1.514(2)	C(4)-C(12)	1.527(2)
C(4)-C(13)	1.540(2)	C(5)-C(6)	1.325(2)
C(6)-C(7)	1.533(2)	C(7)-C(14)	1.528(2)
C(7)-C(15)	1.554(2)	C(7)-C(8)	1.556(2)
C(8)-C(9)	1.521(2)	C(10)-O(10)	1.201(2)
C(10)-O(11)	1.330(2)	O(11)-C(11)	1.449(2)
C(6)-C(1)-C(10)	113.70(12)	C(6)-C(1)-C(2)	110.54(11)
C(10)-C(1)-C(2)	107.99(12)	C(6)-C(1)-C(9)	101.20(12)
C(10)-C(1)-C(9)	108.45(12)	C(2)-C(1)-C(9)	115.00(13)
C(3)-C(2)-C(1)	110.20(12)	C(2)-C(3)-C(4)	112.64(12)
C(5)-C(4)-C(12)	109.18(12)	C(5)-C(4)-C(3)	110.46(11)
C(12)-C(4)-C(3)	109.59(13)	C(5)-C(4)-C(13)	109.02(12)
C(12)-C(4)-C(13)	108.85(13)	C(3)-C(4)-C(13)	109.71(13)

C(6)-C(5)-C(4)	125.40(13)	C(5)-C(6)-C(1)	122.65(13)
C(5)-C(6)-C(7)	127.23(13)	C(1)-C(6)-C(7)	109.36(12)
C(14)-C(7)-C(6)	110.81(11)	C(14)-C(7)-C(15)	110.43(13)
C(6)-C(7)-C(15)	113.10(12)	C(14)-C(7)-C(8)	110.97(13)
C(6)-C(7)-C(8)	102.84(13)	C(15)-C(7)-C(8)	108.44(12)
C(9)-C(8)-C(7)	106.29(12)	C(8)-C(9)-C(1)	103.44(12)
O(10)-C(10)-O(11)	122.61(14)	O(10)-C(10)-C(1)	123.59(14)
O(11)-C(10)-C(1)	113.73(12)	C(10)-O(11)-C(11)	116.00(12)

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