Pergamon

Tetrahedron 56 (2000) 7525–7539

TETRAHEDRON

Palladium Catalysed Tandem Cyclisation–Anion Capture Processes. Part 4: Organotin(IV) Transfer Agents

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Received 22 October 1999; revised 29 June 2000; accepted 20 July 2000

Abstract—Palladium(0) catalysed cascade mono- and bis-cyclisation–anion capture involving a wide variety of starter species, terminating species and organotin(IV) anion capture reagents are reported leading to a range of bridged, fused and spirocyclic products. The diastereoselectivity of the bis-cyclisation processes is explained in terms of steric effects in the transition states.

The previous paper in this series discussed mono- and bis-cyclisation reactions involving a broad range of starting and terminating species and boron anion capture reagents such as boronic acids and boranes.[1] In this work we report analogous mono- and bis-cyclisation reactions employing organotin(IV) reagents as anion capture agents.

The palladium catalysed intermolecular cross coupling of vinyl and aryl iodides and triflates with organotin reagents provides a versatile approach to the functionalisation of the vinyl and aryl species. A wide range of such processes have been developed,[2–4] with the Stille coupling reaction providing the most extensive and elegant methodology.[5]

Farina et al. studied the mechanism and the effects of additives in the Stille coupling reaction.[6] Cu(I) salts were found to increase the coupling rate engendering milder conditions using *N*-methylpyrrolidone (NMP) as solvent.[4,6] Recent work by Corey et al.[7] has demonstrated the rate accelerating effect of CuCl on Stille coupling of sterically congested substrates. Others found additives such as Ag_2O and CuO influence the coupling rates,[8] whilst Farina et al. showed that changing from triphenylphosphine to the softer ligands tri(2-furyl)phosphine or triphenylarsine, in NMP as solvent, effected a substantial rate increment.[9] Interest in the reaction remains high with reports of new tin(IV) reagents including fluorous tin(IV) derivatives,[10] new iminophosphine ligands[11] and a general method for Stille cross-coupling of aryl chlorides.[12]

The intramolecular Stille reaction has been extensively used in macrocyclic natural product synthesis,[5d,13] including Nicolau's rapamycin[14] and Danishefsky's dinemycin[15] syntheses because the reaction tolerates a great variety of functional groups and the organotin(IV) reagents are readily prepared.

Thus, organotin(IV) reagents are potentially a valuable anion capture reagent resource for our cyclisation–anion capture cascades. In this paper we described many successful applications of such reagents with a variety of starter species. Most of the cascades described herein employed a Pd(0) catalyst generated in situ from palladium acetate and triphenylphosphine with solvent and additives tailored to the particular organotin(IV) reagent. In some cases commercially available Pd(0) catalysts were also employed.

Aryl Halide as Starter Species

Mono-cyclisation with alkenes as terminating species

5-*exo-trig* Processes. Organotin(IV) reagents $RSnBu_3$ **1a**–**k**[15–18] have been evaluated as terminating species in a range of 5-*exo-trig* cyclisation processes of which Scheme 1 is a typical example.

The aryl iodide **2a** smoothly reacted with 10 mol% of palladium acetate, 20 mol% of triphenylphosphine, 1 equiv. of tetraethylammonium chloride and 1.1 equiv. of the organotin(IV) reagent in toluene at 90°C for 8 h affording products **4a**–**d** in 82–99% yield (Scheme 1 and Table 1). Similarly, **2b** reacted under analogous reaction conditions to give compounds **5a**–**d** and **5f** in 60–90% yield and **5e** in

Keywords: cascade reactions; palladium catalysis; Stille coupling; cyclisation.

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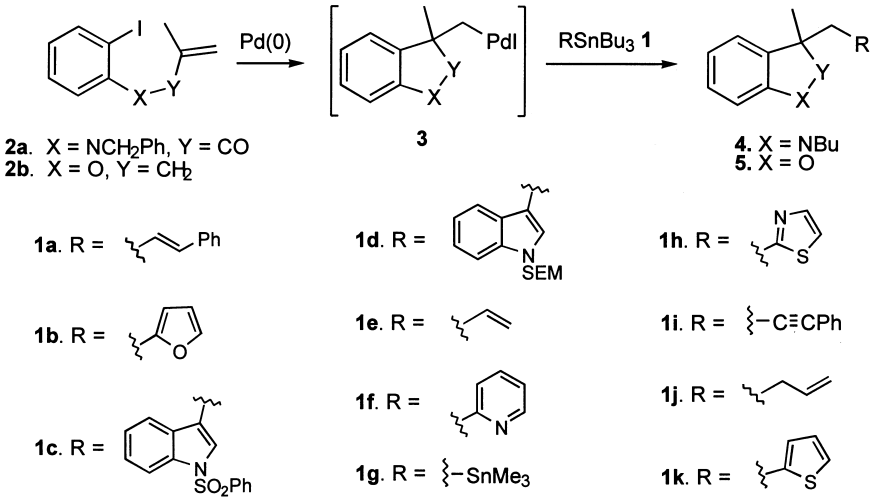
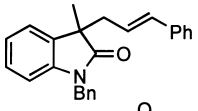
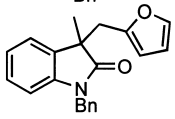
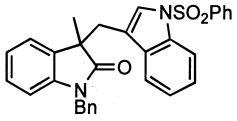
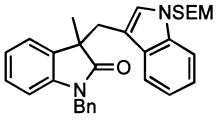
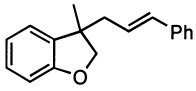
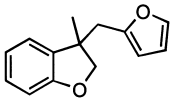
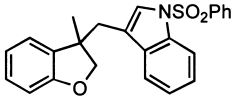
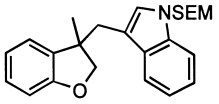
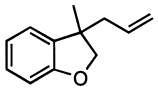
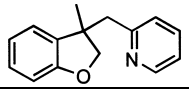
PII: S0040-4020(00)00659-1



Scheme 1.

Table 1. Cyclisation–anion capture of **2a**–**b** with **1a**–**j**. All reactions were carried out at 90°C in toluene using 10 mol% $Pd(OAc)_2$ and 20 mol% PPh_3 as the catalyst system

Aryl iodine **2**	$RSnBu_3$ **1**	Time (h)	Product		Yield (%)[a]
2a	**1a**	8		**4a**	89
2a	**1b**	8		**4b**	90
2a	**1c**	8		**4c**	80
2a	**1d**	6		**4d**	82
2b	**1a**	8		**5a**	90
2b	**1b**	8		**5b**	95
2b	**1c**	8		**5c**	86
2b	**1d**	8 6[b]		**5d**	65 92[b]
2b	**1e**	8		**5e**	45[c]
2b	**1f**	8		**5f**	60

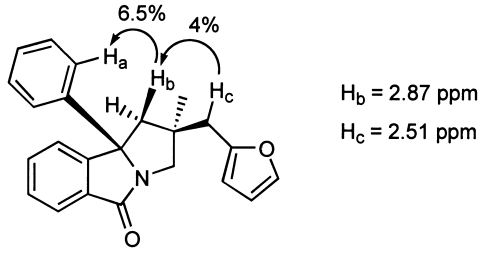
[a] Isolated yields.
[b] Reaction carried out at 110°C.
[c] A 1.6:1 mixture of **5e** and direct capture product **7** was obtained.

Table 2. Effect of additives on the reaction of **2b** and **1e**. Catalyst comprised 10 mol% $Pd(OAc)_2$ and 20 mol% PPh_3

Solvent (°C)	Additive (mol equiv.)	7:5**f**
Toluene (110)	Et_4NCl (1)	1:1.6
THF (60)	Et_4NCl (1)	1:0.9
Toluene (110)	–[a]	1:1.7
Toluene (110)	$TlNO_3$ (2)	1:2

[a] 5 mol % $Pd_2(dba)_3$ and no PPh_3.

45% yield (Scheme 1 and Table 1). The reaction of **2b** and the 2-trimethylsilylethoxymethyl (SEM) indolyl stannane **1d** in toluene at 90°C yielded product **5d** in 65% yield together with a ca. 25% of the direct capture product **6**. This result may reflect a slower rate of cyclisation of **2b** compared to **2a**, as a consequence of the conformationally more flexible allylic side chain relative to the amide moiety in **2a**. In addition, the SEM protected stannyl indole derivative may manifest increased reactivity due to the generation of an intramolecular ate-type complex by coordination between the SEM oxygen atom and tin(IV). Vedejs,[19] and Brown,[20] have shown that the Stille coupling reaction is faster if an intramolecular coordination between a nitrogen atom and tin(IV) takes place. The direct capture product **6** can be suppressed by raising the temperature to 110°C furnishing **5d** in 92% yield. A similar direct capture was observed with **2b**. Thus, treatment with **1j** under standard conditions at 110°C afforded a 1.6:1 mixture of **5f** and **7**. Attempts to suppress the direct capture process failed. Both omission of Et_4NCl in ligandless conditions and addition of $TlNO_3$ were ineffective (Table 2).



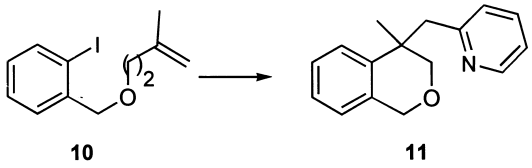
16c n.O.e. data

5-*exo-trig* Spirocyclisation. The enamide **8**[1] was prepared from norbornanone using conventional methodology. Enamide **8** reacted regio- and stereo-specifically in a cyclisation–anion capture process to give spirocycles **9** in the presence of 10 mol% of palladium acetate, 20 mol% of triphenylphosphine and $RSnBu_3$ **1** (1.1 mol equiv.) in acetonitrile at 80°C for 1 h to afford **9a**–**e** as single diastereomers

Table 3. Spirocyclisation–anion capture products from **8** and $RSnBu_3$. Catalyst system: 10 mol% $Pd(OAc)_2$ and 20 mol% PPh_3

$RSnBu_3$	Solvent	Temperature (°C)	Time (h)	Product **9** (%)[a]
1e	CH_3CN	80	2	**9a** (60)
1g	CH_3CN	80	2	**9b** (80)
1f	Toluene	110	2	**9c** (40)
1h	Toluene	110	2	**9d** (40)
1b	Toluene	90	2	**9e** (32)

[a] Isolated yields.



10 **11**

Scheme 3.

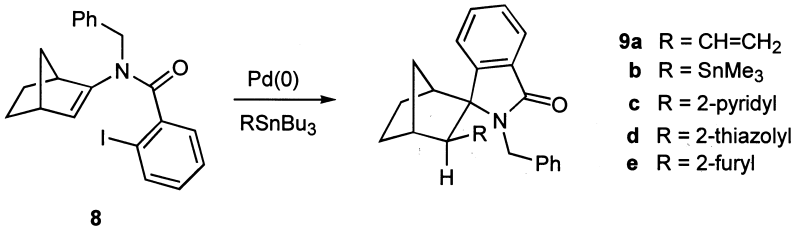
(Scheme 2 and Table 3). The stereochemistry of **9a**–**e** is based on analogy with previous studies with **8** involving boron reagents.[21] The lower yields of **9c**–**e** are presumed to be related to the size of the transferred group and its steric effect on the rate of transmetallation.

6-*exo-trig* Processes. Aryl iodide **10** was reacted with **1f** in the presence of 10 mol% of $Pd_2(dba)_3$ and 20 mol% of tri(2-furyl)phosphine and tetraethylammonium chloride (1 mol equiv.) in toluene at 110°C furnishing **11** in 60% yield (Scheme 3).

The availability of (*R*,*S*)-2-azabicyclo[2.2.1]hept-5-en-3-one (Vince's lactam) prompted us to investigate chiral substrate **12** as a precursor of chiral 6-*exo-trig* cascades. Compound **12** was prepared in 53% yield from Vince's lactam and *o*-iodobenzyl chloride using sodium hydride as a base in THF at 65°C (Scheme 4). When **12** and $RSnBu_3$ were subjected to a catalyst system consisting of 10 mol% of palladium acetate, 20 mol% of triphenylphosphine and Et_4NCl (1 mol equiv.) in toluene at 110°C for 16–24 h, **13a**–**d** were obtained in 30–88% yield as single diastereoisomers in a cascade that creates two new chiral centres and functionalises the *endo*-face of the bicyclic system.

Bis-cyclisations forming fused and spirocyclic rings

We and others have developed bis-cyclisation processes which generate fused, spirocyclic and bridged ring products through a β-hydride elimination step.[22–24] However, the



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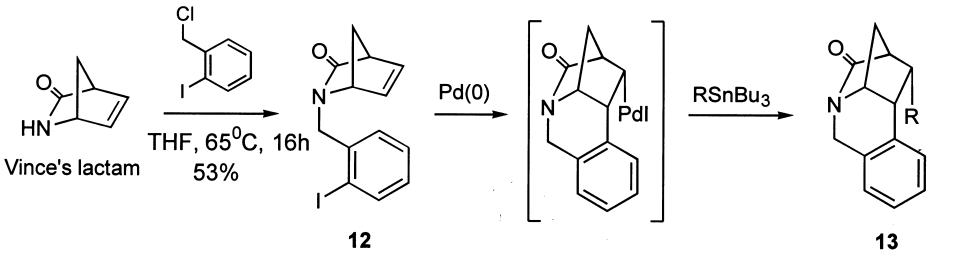
Scheme 2.



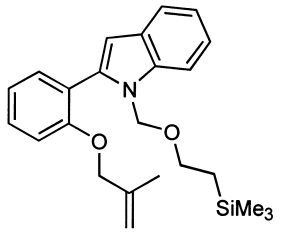
		Yield (%)
13a	R = 2-thienyl	88
b	R = 2-furyl	30
c	R = CH=CH$_2$	60
d	R = C≡CPh	66

Scheme 4.

bis-cyclisation–anion capture processes offer significant advantages over these processes because it allows addition of a wide variety of functional groups at the cyclisation terminus (Scheme 5). We have reported preliminary studies of such processes[2] and now present full details of this work.

Fused-ring systems. Enamides **14a**,**b** were prepared by acylation of the corresponding ketone imines with 2-iodobenzoyl chloride. These substrates have alkene relay and terminating species. Enamide **14a** was reacted with 2-furyltributyltin **1b** and the SEM-indolyl stannane **1d** using our standard catalyst system and Et_4NCl (1 mol equiv.) to afford 5:1 diastereomer mixtures of **16a**/**17a** and **16b**/**17b** in 74 and 66% yield respectively (Scheme 6).

The byproducts **15a** and **15b**, which arise from anion capture of the first alkylpalladium intermediate before the terminating step has engaged, were present in less than 10% yield in these two reactions. Similarly, the enamide **14b** reacts with the same stannanes yielding 3:1 diastereomer mixtures of **16c**/**17c** and **16d**/**17d** in 70 and 64% yield, respectively. When **14b** was treated with vinyltributyltin **1e** the reaction afforded 1.5:1 mixture of **16e**/**17e** in poor yield (30%) (Scheme 6). The stereochemistry of major isomer **16c** was determined by n.O.e. experiments as depicted below.



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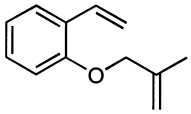

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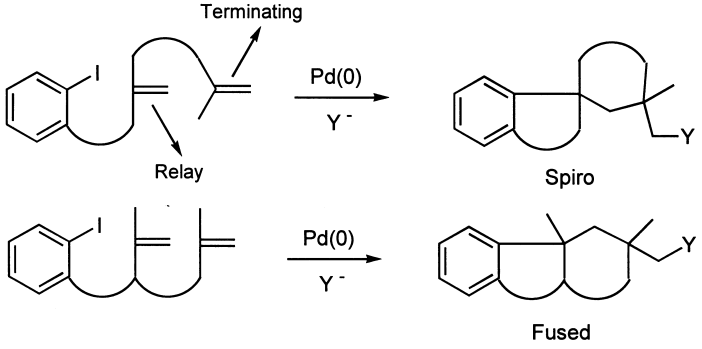
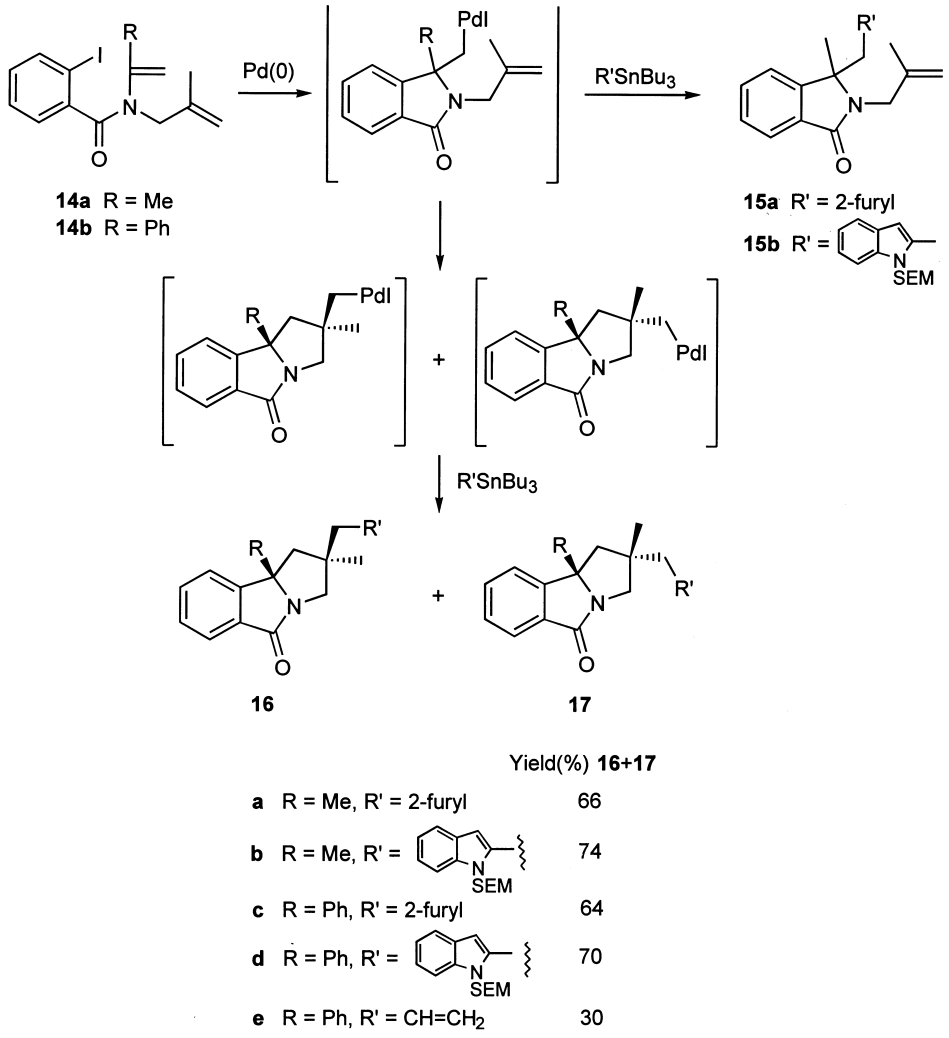
A possible explanation for the variation in diastereoselectivity is illustrated in Scheme 7. The first cyclisation of **14** generates an alkylpalladium intermediate **18**. The second cyclisation requires an eclipsed alignment of the Pd–C and olefinic C–C bonds. This arrangement creates a pseudo bicyclo[3.2.0] intermediate ring which can adopt either a chair-like or boat-like conformation. In the chair-like conformation **18** the R group and the methyl group are effectively *trans* to each other giving rise to the observed major isomer. On the other hand, boat conformation **19** has the R and methyl groups *cis* to one another. In this conformer, as the new C–C bond begins to form the two groups interact sterically, so disfavouring the cyclisation. In contrast, in the chair conformer **18** this steric interaction is absent due to the *trans* disposition of the two groups. Due to



Scheme 5.



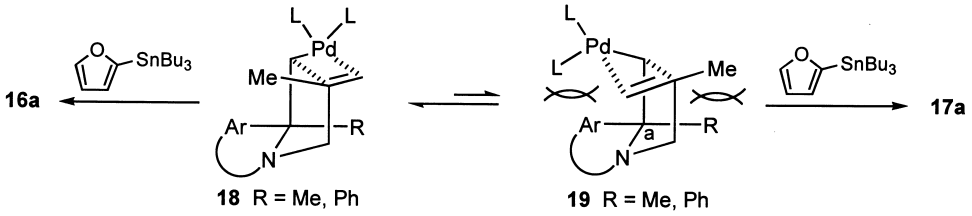
Scheme 6.

the geometrical anisotropy of the phenyl substituent, rotation around the C_a–R bond in **19** allows some diminution of the steric interaction and hence less diastereomeric discrimination.

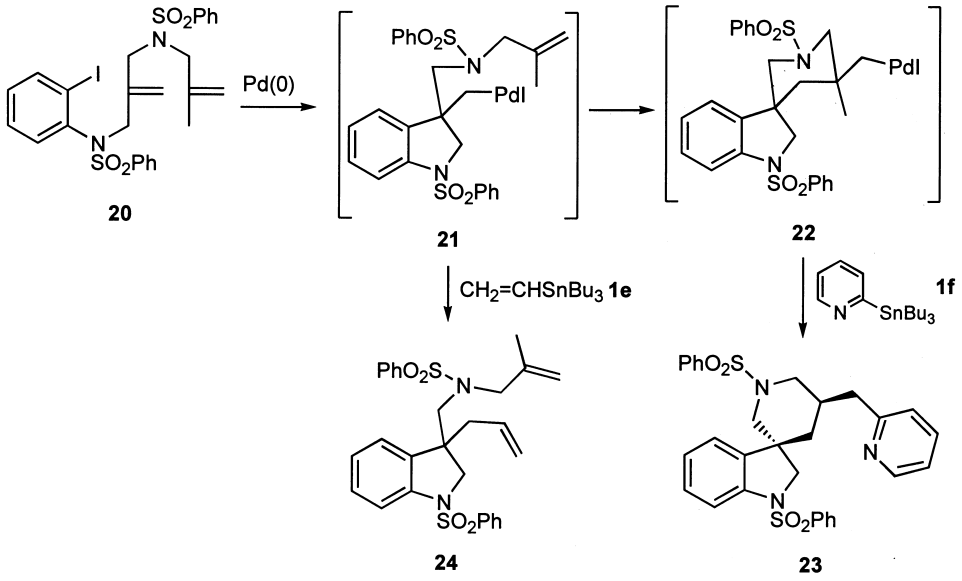
Spirocycles. The spirocyclic precursor **20**, previously synthesised by us,[21] underwent palladium catalysed bis-cyclisation anion capture which was treated with 10 mol% $Pd_2(dba)_3$, 20 mol% tri(2-furyl)phosphine and Et_4NCl (1 mol equiv.) in toluene at 110°C in the presence of 2-pyridyltributyltin **1f**. The spirocycle **23** was obtained as a single diastereoisomer in 48% yield. A chair-like pre-transition state conformer **21**, in which the bulky aryl and palladium groups are equatorial, is believed to be involved and this gives rise to the energetically most favourable equatorial CH_2PdI conformer **22** (Scheme 8). Under identical reaction conditions compound **20** was reacted with vinyltributyltin **1e** giving exclusively the monocyclised product **24** in 55% yield, due to the relatively fast coupling reaction of the alkylpalladium intermediate **21** with **1e** compared to a slower 6-*exo*-*trig* cyclisation.

Monocyclisations with alkynes as terminating species

5-*exo*-Dig processes. The aryl iodides **26a**–**c**, prepared from *N*-acetyl-*o*-iodoaniline **25** and the corresponding propargyl bromide at low temperatures using LDA as base,[21] underwent tandem palladium 5-*exo*-dig cyclisation–anion capture when treated with 10 mol% of palladium acetate and 20 mol% of triphenylphosphine in THF at



Scheme 7.



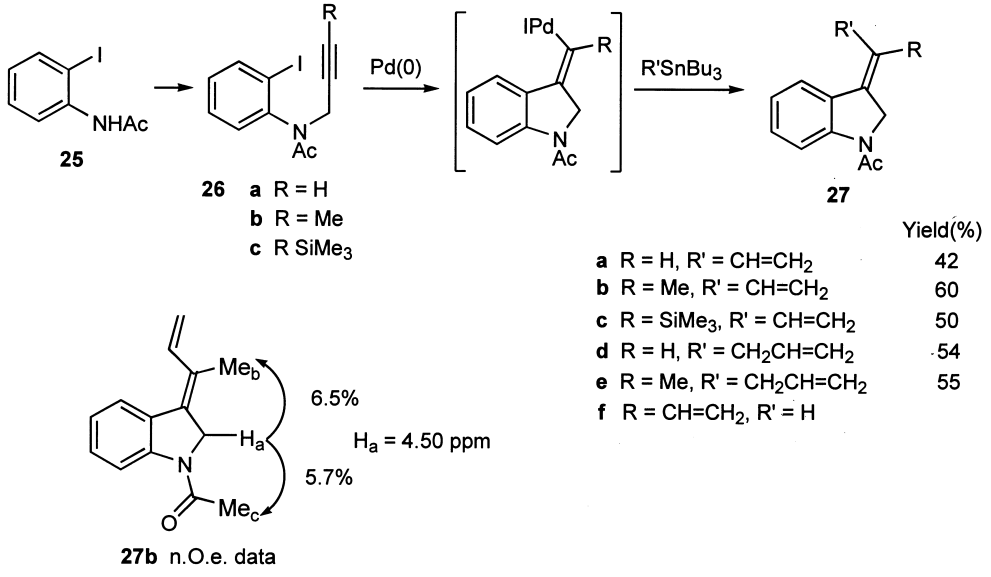
Scheme 8.

room temperature for 2–5 h in the presence of **1e** and **1j**. Compounds **27a**–**e** were obtained in 42–60% yield (Scheme 9) as single stereoisomers. The stereochemistry of **27a**–**e** was determined by n.O.e experiments and a typical example is shown in Scheme 9. However, higher reaction temperatures can cause stereomutation. Thus, the reaction of **26a** with vinyltributyltin **1e** under similar catalytic conditions but at 60°C for 1 h afforded a 1.4:1 mixture of **27a**/**27f**.

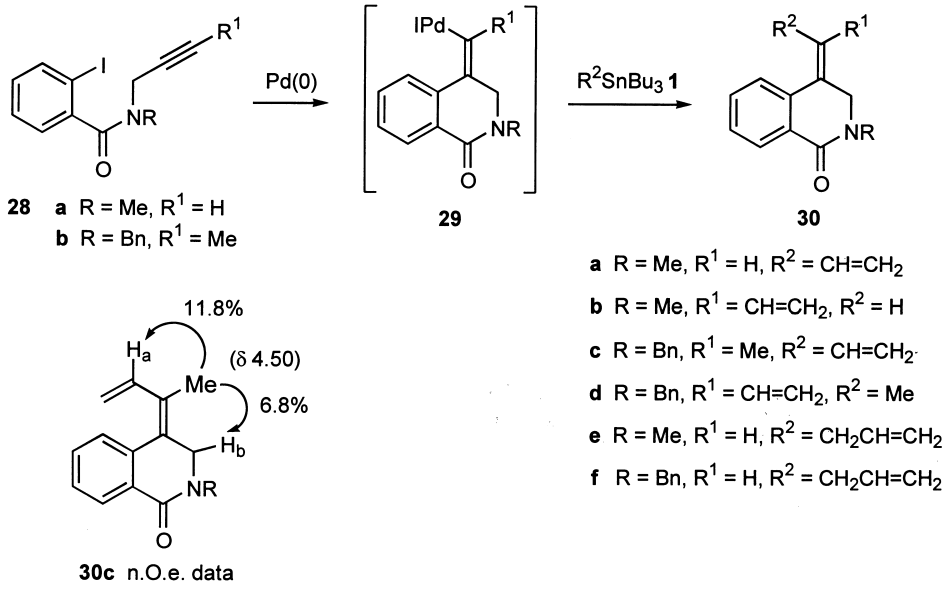
6-*exo*-Dig-process. Aryl iodides **28a**,**b** were prepared from *o*-iodobenzoyl chloride and the appropriate propargyl amines (Scheme 10), and immediately treated with vinyltributyltin **1e** in the presence of 10 mol% of palladium acetate, 20 mol% of triphenylphosphine and Et_4NCl (1 mol equiv.) in acetonitrile at 60°C, furnishing *E*/*Z*-mixtures of products (**30a**+**30b**) and (**30c**+**30d**) in 20 and 33% yield and 4:1 and 5:1 ratios, respectively. Stereomutated products are again observed due to the cyclisations were performed at 60°C. Amides **28a**,**b** cyclised with allyltributyltin **1j** to give **30e**, **f** in 50 and 29%, respectively. The *E*-configuration of the major isomer of the *E*/*Z*-mixtures **30**, as well as products **30e**,**f**, were established by n.O.e experiments and a typical example is shown in Scheme 10.

Monocyclisation with 1,2-dienes as terminating species

6-*exo*-*trig*-Process. Allenic amide **31**, prepared from **28a** in the presence of sodium hydride in DMF at room temperature, was treated with organostannanes **1b** and **1e** in the presence of 10 mol% of $Pd_2(dba)_3$, 40 mol% of tri(2-furyl)-phosphine in toluene at 110°C affording a 1.5:1 mixture of **33a**/**34a** and a 1:1 mixture of **33b**/**34b** in 70 and 60% yield, respectively (Scheme 11 and Table 4), via interception of the π-allylpalladium intermediate **32**.



Scheme 9.



Scheme 10.

Silver carbonate has been shown to be a very useful additive in controlling the regiochemical outcome of the reaction of π-allyl species with N nucleophiles.[25] However, in this series only became effective (employing 1 mol equiv. of silver salt) when 2-furyltributyltin **1b** was used as anion capture agent giving a 6:1 mixture of products **33a**/**34a** in the same yield (Table 4). This unexpected result can be justified by the high conjugation of **33a** which could induce a non-symmetrical π-allyl intermediate formation under basic reaction conditions.

Monocyclisations with 1,3-dienes as terminating species

Enamide **35** was prepared from verbenone by standard methodology[21] and then cyclised in acetonitrile at 80°C for 24 h using 10 mol% of palladium acetate, 20 mol% of triphenylphosphine and Et_4NCl (1 mol equiv.) in the presence of vinyltributyltin **1e**. The reaction afforded **36** regio- and stereo-specifically in 60% yield (Scheme 12).

Vinyl Bromides as Starter Species

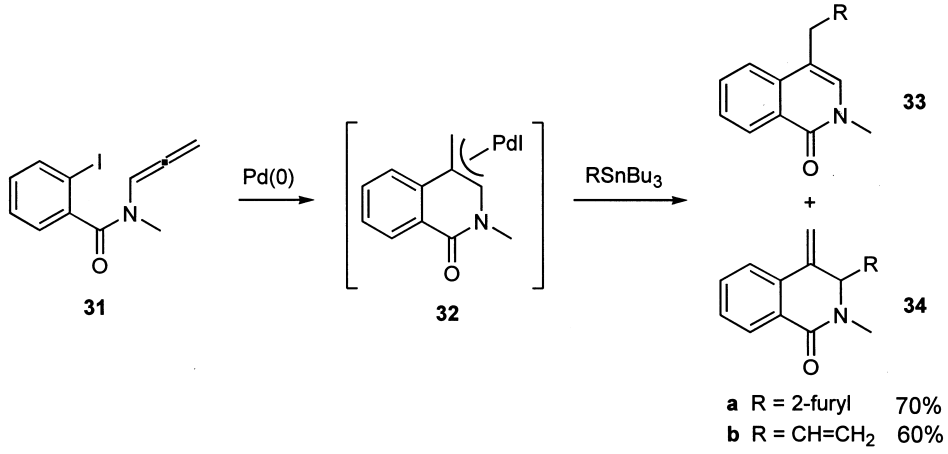
Monocyclisations with 1,3-dienes as terminating species

Trienes **37** and **38** were prepared according to standard procedures.[21] These trienes were reacted with vinyltributyltin **1e** in acetonitrile at 80°C for 24–48 h using as catalyst 10 mol% of palladium acetate, 20 mol% of triphenylphosphine and LiCl (1 mol equiv.) furnishing **39** (60%) and **40** (60%) (Scheme 13).

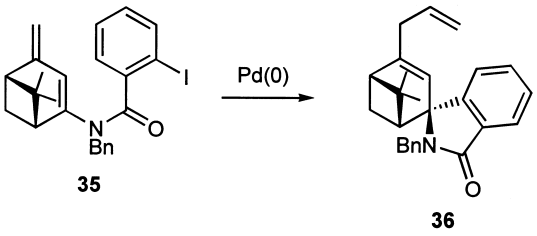
Table 4. Cyclisation–anion capture products from **31** and $RSnBu_3$. Catalyst system: 10 mol% $Pd(OAc)_2$ and 20 mol% PPh_3

$RSnBu_3$	Time (h)[a]	Additive (mol equiv.)	Products (%)[b]	
1b	2	–	**33a** (45)	**34a** (30)
1b	2.5	Ag_2CO_3 (1)	**33a** (61)	**34a** (10)
1e	12	–	**33b** (38)	**34b** (38)
1e	12	Ag_2CO_3 (1)	**33b** (38)	**34b** (38)

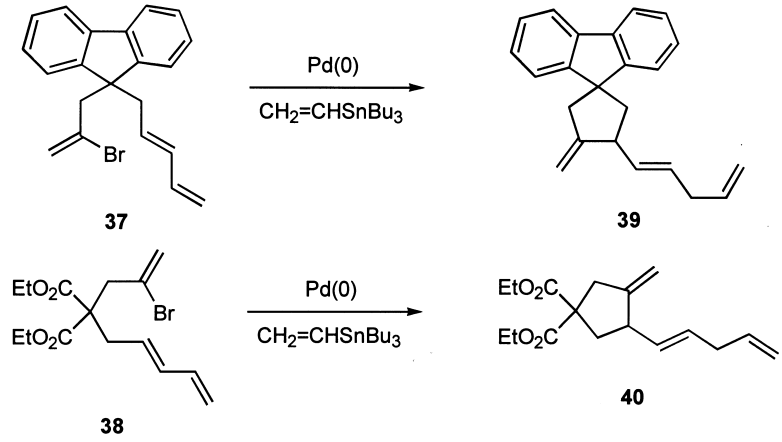
[a] Boiling toluene (110°C).
[b] Isolated yields.



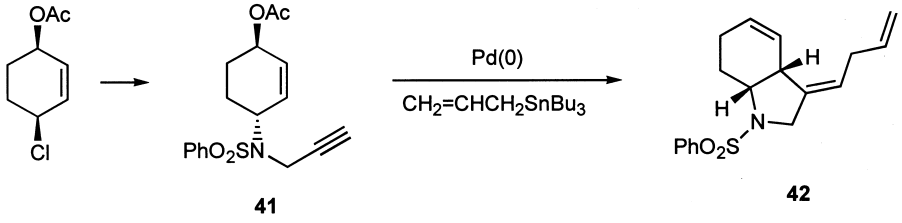
Scheme 11.



Scheme 12.



Scheme 13.



Scheme 14.

Allylic Acetates as Starter Species

Monocyclisations with alkynes as terminating species

Only one example involving monocyclisation combining an alkyne as terminating species has been studied so far. The allylic acetate **41** was prepared[26] as outlined in Scheme 14 employing Bäckvall's methodology.[27] Allylic acetate **41** was reacted with vinyltributyltin **1e** using our standard catalyst system [10 mol% of palladium acetate, 20 mol% of triphenylphosphine, LiCl (1 mol equiv.)] in THF at 60°C affording compound **42** in 42% yield. Recently, similar cyclisations–anion capture processes have also been published and it was noted that addition of $ZnCl_2$ improve the yields.[28]

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 films unless otherwise noted. Mass spectral data were obtained from a 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. Optical rotations were recorded on an AA100 Polarimeter at ambient temperature (ca 20°C). 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. Non-commercially available organotin(IV) compounds were synthesised according to known methods.[5]

General procedure for cyclisation–anion capture of 2a,b and organotin(IV) reagents

A stirred mixture of aryl iodide (1 mmol), organostannane (1.1 mmol), palladium acetate (0.022 g, 0.1 mmol), triphenylphosphine (0.052 g, 0.2 mmol) and tetraethylammonium chloride (0.165 g, 1 mmol) in toluene (10 ml) was heated at 90°C under a nitrogen atmosphere for 8–6 h (see Table 1). After cooling to room temperature, the solvent was removed under vacuum and the residue taken up into ether (15 ml). The ether layer was washed with water and then stirred with a saturated aqueous solution of potassium fluoride (2 ml) for 1 h. The layers were separated and the organic phase was filtered, dried ($MgSO_4$) and the solvent

evaporated. Column chromatography of the residue yielded **4** or **5**.

4a. Obtained from aryl iodide **2a** (0.377 g, 1 mmol) and tributylstannylstyrene **1a** (0.435 g, 1.1 mmol) after column chromatography eluting with 3:7 v/v ether/petroleum ether. The *product* (0.314 g, 89%) was obtained as colourless prisms from ether/petroleum ether, mp 90–92°C. (Found: C, 85.0; H, 6.6; N, 3.9. $C_{25}H_{23}NO$ requires: C, 85.0; H, 6.5; N, 3.9%); δ 7.30–6.96 (m, 13H ArH), 6.62 (d, 1H, *J*=5 Hz, Ar*H*), 6.40 (d, 1H, *J*=10 Hz, C═C*H*Ph), 5.82 (m, 1H, CH_2CH═CH), 5.17, 4.60 (2×d, 2H, *J*=10 Hz, NCH_2Ph), 2.81 (m, 2H, CH_2CH═C), and 1.47 (s, 3H, CH_3); *m*/*z* (%): 353 (M^+, 22), 236 (61), 117 (100), and 91 (91).

4b. Obtained from aryl iodide **2a** (0.377 g, 1 mmol) and 2-furyltributylstannane **1b** (0.393 g, 1.1 mmol) after column chromatography eluting with 3:7 v/v ether/petroleum ether. The *product* (0.285 g, 90%) was obtained as colourless prisms from ether/petroleum ether, 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), 7.00 (d, 1H, *J*=7 Hz, Ar*H*), 6.60 (d, 1H, *J*=8 Hz, ArH), 6.14, 5.80 (2×s, 2H, ArH), 5.04 and 4.72 (2×d, 2H, *J*=16 Hz, NCH_2Ph), 3.19 (dd, 2H, *J*=9 and 3 Hz, CH_2CO), and 1.50 (s, 3H, CH_3); *m*/*z* (%): 317 (M^+, 30), 236 (87), and 91 (100).

4c. Obtained from aryl iodide **2a** (0.377 g, 1 mmol) and 3-tributylstannylindole derivative **1c** (0.584 g, 1.1 mmol) after column chromatography eluting with 2:5 v/v ether/petroleum ether. The *product* (0.404 g, 80%) was obtained as colourless prisms from ether/petroleum ether, mp 169–171°C. (Found: C, 73.4; H, 5.1; N, 5.8. $C_{31}H_{26}N_2O_3S$ requires: C, 73.5; H, 5.1; N, 5.5%); δ 7.84, 7.54 (2×d, 2H, *J*=8 Hz, ArH), 7.43–6.39 (m, 17H, ArH), 4.86, 4.33 (2×d, 2H, *J*=16 Hz, NCH_2Ph), 3.47, 3.16 (2×d, 2H, *J*=14 Hz, CH_2CCN), and 1.58 (s, 3H, CH_3); *m*/*z* (%): 506 (M^+, 5), 270 (100), 141 (10), and 91 (41).

4d. Obtained from aryl iodide **2a** (0.377 g, 1 mmol) and 2-tributylstannylindole SEM-derivative **1d** (0.600 g, 1.1 mmol) after column chromatography eluting with 2:3 v/v ether/petroleum ether. The *product* (0.409 g, 82%) was obtained as a colourless thick oil. (Found HRMS: 496.2556. $C_{31}H_{36}N_2O_2Si$ requires: 496.2546); δ 7.33 (d, 2H, *J*=8 Hz, ArH), 7.28–6.97 (m, 8H, ArH), 6.67, 6.51 (d, 2H, *J*=8 Hz, ArH), 5.70 (s, 1H, ArH), 5.54–5.32 (2×d, 2H, *J*=7 Hz, NCH_2O), 5.10, 4.42 (2×d, 2H, *J*=15 Hz, NCH_2Ph), 3.54, 3.36 (2×d, 2H, *J*=14 Hz, CH_2CN), 3.40 (m, 2H, OCH_2CH_2), 1.60 (s, 3H, CH_3), 0.84 (m, 2H, CH_2Si), and −0.09 (s, 9H, $SiMe_3$); *m*/*z* (%): 496 (M^+, 24), 379 (21), 260 (40), 144 (100), 91 (28), and 73 (39).

5a. Obtained from aryl iodide **2b** (0.276 g, 1 mmol) and tributylstannylstyrene **1a** (0.435 g, 1.1 mmol) after column chromatography eluting with 1:9 v/v ether/petroleum ether. The *product* (0.167 g, 67%) was obtained as a colourless oil. (Found: C, 86.4; H, 7.0. $C_{17}H_{16}O$ requires: C, 86.4; H, 6.8%); δ 7.31–7.11 (m, 7H, ArH), 6.89 (t, 1H, *J*=7 Hz, ArH), 6.80 (d, 1H, *J*=8 Hz, Ar*H*), 6.40 (d, 1H, *J*=16 Hz, C═C*H*Ph), 6.12 (m, 1H, CH_2CH═CH), 4.43, 4.15 (2×d, 2H, *J*=9 Hz, OCH_2), 2.50 (d, 2H, *J*=7.5 Hz, CH_2CH═C), and 1.39 (s, 3H, CH_3); *m*/*z* (%): 250 (M^+, 1), 133 (100), 105 (50), and 77 (10).

5b. Obtained from aryl iodide **2b** (0.276 g, 1 mmol) and 2-furyltributylstannane (0.393 g, 1.1 mmol) after column chromatography eluting with 1:9 v/v ether/petroleum ether. The *product* (0.203 g, 95%) was obtained as a colourless oil. (Found: C, 78.4; H, 6.7. $C_{14}H_{14}O_2$ requires: C, 78.5; H, 6.5%); δ 7.31, 6.27, 5.95 (3s, 3H, ArH), 7.13 (t, 1H, *J*=8 Hz, ArH), 7.02 (d, 1H, *J*=7 Hz, ArH), 6.86 (t, 1H, *J*=7 Hz, ArH), 6.77 (d, 1H, *J*=8 Hz, ArH), 4.55, 4.13 (2×d, 2H, *J*=10 Hz, OCH_2), 2.91 (s, 2H, CH_2CO), and 1.34 (s, 3H, CH_3); *m*/*z* (%): 214 (M^+, 3), 133 (100), and 105 (70).

5c. Obtained from aryl iodide **2b** (0.276 g, 1 mmol) and 3-tributylstannylindole derivative **1c** (0.600 g, 1.1 mmol) after column chromatography eluting with 1:4 v/v ether/petroleum ether. The *product* (0.346 g, 86%) was obtained as colourless prisms from ether/petroleum ether, mp 88–90°C. (Found: C, 71.5; H, 5.4; N, 3.5. $C_{24}H_{21}NO_3S$ requires: C, 71.5; H, 5.2; N, 3.5%); δ 7.97–6.72 (m, 14H, ArH), 4.39, 4.06 (2×d, 2H, *J*=9 Hz, OCH_2), 2.95 (s, 2H, CH_2CCN), and 1.40 (s, 3H, CH_3); *m*/*z* (%): 403 (M^+, 11), 271 (75), 133 (100), and 77 (78).

5d. Obtained from aryl iodide **2b** (0.276 g, 1 mmol) and 2-tributylstannylindole SEM-derivative **1d** (0.589 g, 1.1 mmol) after column chromatography eluting with 1:19 v/v ether/petroleum ether. The *product* (0.255 g, 65%) was obtained as a colourless oil. (Found: C, 73.2; H, 7.8; N, 3.6. $C_{24}H_{31}NO_2Si$ requires: C, 73.3; H, 7.9; N, 3.6%); δ 7.64, 7.45 (2×d, 2H, *J*=8 Hz, ArH), 7.30–6.82 (m, 6H, ArH), 6.40 (s, 1H, ArH), 5.25, 4.88 (2×d, 2H, *J*=12 Hz, OCH_2N), 4.63, 4.31 (2×d, 2H, *J*=9 Hz, OCH_2), 3.45 (t, 2H, *J*=8 Hz, OCH_2CH_2), 3.33, 3.17 (2×d, 2H, *J*=15 Hz, CH_2CN), 1.58 (s, 3H, CH_3), 0.90 (t, 2H, *J*=8 Hz, CH_2Si), and 0.00 (s, 9H, $SiMe_3$); *m*/*z* (%): 393 (M^+, 7), 261 (29), 144 (68), 133 (100), 105 (37), and 73 (50).

5e. Obtained from aryl iodide **2b** (0.276 g, 1 mmol) and vinyltributylstannane **1e** (0.316 g, 1.1 mmol) after column chromatography eluting with 1:19 v/v ether/petroleum ether. The product was obtained as a colourless oil (71%) which comprised 1:1.6 mixture of **7** and **5e**. [Found (mixture) C, 82.45; H, 7.9. $C_{12}H_{14}O$ requires: C, 82.7; H, 8.1%]. **5e:** δ 7.10 (m, 2H, ArH), 6.88 (m, 1H, ArH), 6.80 (t, 1H, *J*=8 Hz, ArH), 5.68 (m, 1H, C═CH), 5.23(br s, 1H, C═CH), 5.05 (d, 1H, *J*=16 Hz, C═CH), 4.38, 4.11 (2×d, 2H, *J*=9 Hz, OCH_2), 2.34 (d, 2H, *J*=8 Hz, CH_2), and 1.32 (s, 3H, CH_3); *m*/*z* (%): 174 (M^+, 21), 261 (29), 133 (100), 105 (85), 91 (7), and 77 (15). **7:** δ 7.48 (d, 1H, *J*=8 Hz, ArH), 7.18 (m, 1H, ArH), 7.10 (m, 1H, C═CH_2), 6.98 (m, 1H, ArH), 6.83 (d, 1H, *J*=8 Hz, ArH), 5.73 (d, 1H, *J*=18 Hz, C═CH), 5.24 (d, 1H, *J*=11 Hz, C═CH), 5.09, 4.97 (2s, 2H, C═CH_2), 4.43 (s, 2H, OCH_2), and 1.83 (s, 3H, CH_3).

5f. Obtained from aryl iodide **2b** (0.276 g, 1 mmol) and 2-pyridyltributylstannane **1f** (0.400 g, 1.1 mmol) after column chromatography eluting with 2:3 v/v ether/petroleum ether. The *product* (0.134 g, 60%) was obtained as a pale yellow oil. The hydrochloride salt was prepared from

dry HCl gas in ether. (Found: C, 66.4; H, 5.9; N, 5.3. $C_{15}H_{15}NO{\cdot}HCl{\cdot}0.5H_2O$ requires: C, 66.5; H, 5.9; N, 5.2%); δ 8.53, 7.47 and 7.29 (3×m, 3×1H, ArH), 7.14–6.72 (m, 4H, ArH), 4.77, 4.12 (2×d, 2H, J=9 Hz, OCH_2), 3.07, 3.03 (2×d, 2H, J=13 Hz, CH_2Ar), and 1.39 (s, 3H, CH_3); m/z (%): 224 (M^+-1, 52), 218 (34), 133 (25), 117 (25), 93 (100), and 78 (12).

General procedure for cyclisation–anion capture of 8

A mixture of aryl iodide **8** (1 mmol), organostannane (1.1 mmol), palladium acetate (0.022 g, 0.1 mmol) and triphenylphosphine (0.052 g, 0.2 mmol) in an appropriate solvent was stirred and heated at 80–110°C under a nitrogen atmosphere for 2 h. After cooling to room temperature, the solvent was removed under vacuum and the residue taken up into ether (15 ml). The ether layer was washed with water and then stirred with a saturated aqueous solution of potassium fluoride (2 ml) for 1 h. The layers were separated and the organic phase was filtered, dried ($MgSO_4$) and the solvent evaporated. Column chromatography of the residue yielded **9a**–**e**.

9a. Obtained from **8** (0.429 g, 1 mmol) and vinyltributylstannane **1e** (0.134 g, 1 mmol) in acetonitrile at 80°C. After chromatography eluting with 2:3 v/v ether/petroleum ether, the *product* (0.197 g, 60%) was obtained as colourless prisms from ether/petroleum ether, mp 109–111°C. (Found: C, 83.5; H, 6.9; N, 4.6. $C_{23}H_{23}NO$ requires: C, 83.8; H, 7.2; N, 4.3%). δ 7.80–7.00 (m, 9H, ArH), 5.50 (m, 1H, CH═C), 5.30 (d, J=16.6 Hz, 1H, NCH), 4.75–4.50 (m, 3H, C═CH_2, NCH), 2.70 (d, J=10.4 Hz,1H, CH), 2.50 (m, 2H, 2×CH), 2.25 (s, 1H, CH), and 2.00–1.5 (m, 5H, 2×CH_2, C*H*CH═C). m/z (%): 329 (M^+, 40), 248 (12), 237 (30), 146 (55), 131 (27), 91 (100), and 78 (42).

9b. Obtained from **8** (0.429 g, 1 mmol) and hexamethylditin (0.620 g, 1.1 mmol) in acetonitrile at 80°C. After chromatography eluting with 2:3 v/v ether/petroleum ether, the *product* (0.373 g, 80%) was obtained as colourless prisms from ether/petroleum ether, mp 163–165°C. (Found: C, 62.0; H, 6.3; N, 3.3. $C_{24}H_{29}NOSn$ requires: C, 61.9; H, 6.2; N, 3.0%). δ 7.80–7.11 (m, 9H, ArH), 5.26, 4.65 (2×d, 2H, J=16 Hz, NCH_2), 2.42–1.46 (m, 9H, norbornyl-H), and 0.34 (s, 9H, $SnMe_3$). m/z (%): 467 (M^+, 14), 465 (10), 426 (16), 424 (12), 302 (14), 210 (19), 185 (16), 163 (14), 91 (100), and 59 (29).

9c. Obtained from **8** (0.429 g, 1 mmol) and 2-pyridyltributylstannane **1f** (0.400 g, 1 mmol) in toluene at 110°C. Crystallisation from methanol afforded *product* (0.150 g, 40%) as colourless plates, mp 143–145°C. (Found: C, 81.9; H, 6.4; N, 8.0. $C_{26}H_{24}N_2O$ requires: C, 82.0; H, 6.4; N, 7.4%). δ 8.40, 7.70 (2×d, 2H, J=7 Hz, ArH), 7.40–6.82 (m, 10H, ArH), 6.15 (d, 1H, ArH), 5.24, 4.94 (2×d, 2H, J=16 Hz, NCH_2), 3.52 (d, 1H, J=3 Hz, CH), 3.14 (d, 1H, J=1.5 Hz, CH), 3.00 (d, 1H, J=10 Hz, NCH), 2.30 (s, 1H, CH), and 2.10–1.50 (m, 5H, norbornyl-H). m/z (%): 380 (M^+, 0.5), 303 (100), 274 (10), 236 (20), 234 (40), 212 (53), 132 (23) and 65 (13).

9d. Obtained from **8** (0.429 g, 1 mmol) and 2-thiazolyltributylstannane **1h** (0.386 g, 1 mmol) in toluene at 110°C. Crystallisation from methanol afforded the *product* (0.154 g, 40%) as colourless plates, mp 270–271°C. (Found: C, 74.3; H, 5.7; N, 7.5. $C_{24}H_{22}N_2SO$ requires: C, 74.6; H, 5.7; N, 7.3%). δ 7.80 (d, 1H, J=7 Hz, ArH), 7.54 (d, 1H, J=3 Hz, ArH), 7.30–7.02 (m, 8H, ArH), 6.89 (d, 1H, J=3 Hz, ArH), 5.40, 4.77 (2×d, 2H, J=16 Hz, NCH_2), 3.64 (d, 1H, J=2.5 Hz, CH), 3.15 (d, 1H, J=3 Hz, CH), 2.90 (d, 1H, J=11 Hz, CH), 2.35 (s, 1H, CH), and 2.10–1.60 (m, 5H, norbornyl-H). m/z (%): 386 (M^+, 1), 304 (17), 303 (72), 302 (15), 262 (10), 248 (10), 212 (36), 132 (17), 91 (100), and 41 (10).

9e. Obtained from **8** (0.429 g. 1 mmol) and 2-furyltributylstannane **1b** (0.393 g, 1 mmol) in toluene at 90°C. After chromatography eluting with 2:3 v/v ether/petroleum ether the *product* (0.118 g, 32%) was obtained as colourless needles, mp 147–149°C. (Found: C, 81.1; H, 6.1; N, 3.7. $C_{25}H_{23}NO_2$ requires: C, 81.3; H, 6.2; N, 3.8%). δ 7.79 (d, 1H, J=7 Hz, ArH), 7.29–6.94 (m, 9H, ArH), 6.07, 5.86 (2s, 2H, ArH), 5.24, 4.83 (2×d, 2H, J=11 Hz, CH_2Ph), 3.34 (s, 1H, CHCO), 2.82 (s, 1H, CH), 2.69 (d, 1H, J=9 Hz, CH), 2.30, 1.97 (2×s, 2H, CH_2) and 1.96–1.55 (m, 4H, CH_2CH_2). m/z (%): 369 (M^+, 17), 303 (39), 277 (53), 115 (53), 91 (100), and 84 (81).

11. A mixture of palladium dibenzylidene acetone (0.011 g, 0.2 mmol), tri(2-furyl)phosphine (0.092 g, 0.4 mmol), tetraethylammonium chloride (0.33 g, 2 mmol), 2-pyridyltributylstannane **1f** (0.800 g, 2.2 mmol) and **10** (2 mmol) was stirred and heated in toluene (20 ml) at 110°C for 6 h. After the usual workup the crude product was purified by column chromatography eluting with 2:3 v/v ether/petroleum ether. The *product* was obtained as a pale yellow oil (0.230 g, 50%). (Found HRMS: 239.1303. $C_{16}H_{17}NO$ requires: 239.1310). δ 8.55 (d, 1H, J=5 Hz, ArH), 7.51 (m, 1H, ArH), 7.14 (m, 4H, ArH), 6.96 (m, 2H, ArH), 4.83 (s, 2H, OCH_2), 3.89, 3.48 (2×d, 2H, J=11 Hz, OCH_2), 3.22, 3.07 (2×d, 2H, J=12 Hz, CH_2Ar), and 1.23 (s, 3H, CH_3). m/z (%): 238 (M^+-1, 10), 194 (76), 147 (50), 131 (16), 93 (100), 78 (39), and 60 (44).

12. A 60% dispersion of sodium hydride in mineral oil (1.0 g, 25 mmol) was added portionwise to a solution of (*R*,*S*)-2-azabicyclo-[2,2,1]-hept-5-en-3-one (2.5 g, 23 mmol) in anhydrous THF (50 ml) and the mixture stirred at room temperature for 1 h. A solution of 2-iodobenzyl chloride (5.8 g, 23 mmol) in anhydrous THF (25 ml) was then added and the mixture boiled under reflux overnight. Water (10 ml) was then added and the solvent removed under reduced pressure. The residue was partitioned between diethyl ether (120 ml) and water (120 ml), the aqueous layer separated and extracted with diethyl ether (120 ml). The combined ether extracts were dried (Na_2SO_4) and the solvent removed under reduced pressure. The residue was crystallised from diethyl ether/petroleum ether to afford the *product* as colourless prisms (3.9 g, 53%), mp 62–64°C. (found C, 47.85; H, 3.6; N, 4.3. $C_{13}H_{12}INO$ requires C, 48.0; H, 3.7; N, 3%); δ 7.84 (d, 1H, J=8.0 Hz, ArH), 7.4–6.9 (m, 3H, ArH), 6.8–6.6 (m, 2H, CH═CH), 4.57 (d, 1H, J=15.4 Hz, NCHPh), 4.15 (s, 1H, NCHC═C), 3.95 (d, 1H, J=15.4 Hz, NCHPh), 3.41 (s, 1H, COCH) and 2.36 and 2.13 (2×d, 2×1H, J=7.8, 7.6 Hz, $COCCH_2$); m/z

(%) 326 (M^+1, 1), 217 (21), 198 (22), 90 (29) and 66 (100); $[\alpha]_D$=−75.6 (*c* 0.85, $CHCl_3$).

Cyclisation–anion capture of 12

13a. Obtained from aryl iodide **12** (0.300 g, 0.93 mmol) and 2-thiophenyltributylstannane **1k** (1.5 g, 4 mmol) after column chromatography eluting with ether. The *product* (0.520 g, 60%) was obtained as colourless needles from ether/petroleum ether, mp 166–169°C. (Found: C, 72.4; H, 8.5; N, 5.2. $C_{17}H_{15}NOS$ requires: C, 72.6; H, 8.5; N, 5.0%); $[\alpha]_D^{20}$=−189.3 (*c* 1.0, $CHCl_3$), δ 7.08–6.28 (m, 7H, ArH), 5.04, 4.24 (2×d, 2H, *J*=17 Hz, NCH_2), 4.20 (d, 1H, *J*=9.5 Hz, SCCHCCO), 4.06 (s, 1H, NCHC), 3.66 (d, 1H, *J*=9.5 Hz, PhCHCN), 3.05 (s, 1H, COCH), and 2.16, 1.92 (2×d, 2H, *J*=10, 10 Hz, $NCCH_2$); *m*/*z*(%) 282 (M^++1, 66), 281 (M^+, 100), 253 (67), 252 (75), 184 (58), 158 (49), 145 (44), 137 (52), and 128 (48).

13b. Obtained from aryl iodide **12** (0.300 g, 0.93 mmol) and 2-furyltributylstannane **1b** (0.39 g, 1 mmol) after column chromatography eluting with ether. The *product* (0.072 g, 30%) was obtained as colourless prisms from ether, mp 162–166°C. (Found: C, 76.9; H, 5.5; N, 5.5. $C_{17}H_{15}NO_2$ requires: C, 77.0; H, 5.7; N, 5.3%); $[\alpha]_D^{20}$=−154.8 (*c* 1.0, $CHCl_3$), δ 7.20–6.80 (m, 5H, ArH), 5.94–5.92 (m, 1H, ArH), 5.53 (d, 1H, *J*=3.5 Hz, ArH), 4.93, 4.11 (2×d, 2H, *J*=16.5, 16.5 Hz, NCH_2), 3.96–3.91 (m, 2H, NCHCC and PhCCHCO), 3.68 (d, 1H, *J*=10 Hz, PhCHCN), 3.05 (s, 1H, COCH), and 2.13, 1.85 (2×d, 2H, *J*=11.5, 10 Hz, $NCCH_2$); *m*/*z*(%) 265 (M^+, 100), 236 (59), 208 (37), 184 (18), and 121 (22).

13c. Obtained from aryl iodide **12** (0.300 g, 0.93 mmol) and vinyltributylstannane **1e** (0.339 g, 1 mmol) after column chromatography eluting with 2:1 v/v ether/petroleum ether. The *product* (0.130 g, 63%) was obtained as pale yellow needles from ether/petroleum ether, mp 99–101°C. (Found: C, 80.2; H, 6.7; N, 6.1. $C_{15}H_{15}NO$ requires: C, 80.0; H, 6.7; N, 6.2%); $[\alpha]_D^{20}$=−138.0 (*c* 1.0, $CHCl_3$), δ 7.30–6.90 (m, 4H, ArH), 5.20–4.80 (m, 4H, NCHPh and $CH{=}CH_2$), 4.09 (d, 1H, *J*=16.5 Hz, NCHPh), 3.90 (s, 1H, NCHCC), 3.47 (dd, 1H, *J*=10 Hz, PhCHCN), 3.24–3.19 (m, 1H, $CH_2{=}CCH$), 2.82 (s, 1H, COCH) and 2.06, 1.76 (2×d, 2H, *J*=10, 10 Hz, $NCCH_2$); *m*/*z*(%) 225 (M^+, 51), 196 (14), 128 (15), 117 (19), and 41 (100).

13d. Obtained from aryl iodide **12** (0.300 g, 0.93 mmol) and 2-phenylethynyltributylstannane **1i** (0.490 g, 1 mmol) after column chromatography eluting with 4:1 v/v ether/petroleum ether. The *product* (0.130 g, 63%) was obtained as light brown needles from ether/petroleum ether, mp 136–139°C. (Found: C, 84.2; H, 5.9; N, 4.5. $C_{21}H_{17}NO$ requires: C, 84.3; H, 5.7; N, 4.7%); $[\alpha]_D^{20}$=−109.6 (*c* 1.0, $CHCl_3$), δ 7.40–7.00 (m, 8H, ArH), 4.94, 4.11 (2×d, 2H, *J*=17, 16.5 Hz, NCH_2), 3.97 (s, 1H, NCHCC), 3.67–3.55 (m, 2H, PhCHCHCCPh), 3.09 (s, 1H, COCH), and 2.10, 1.76 (2×d, 2H, *J*=10, 10 Hz, $NCCH_2$); *m*/*z*(%) 299 (M^+, 75), 270 (100), 256 (38), 184 (35), and 115 (59).

Synthesis of enamide 14b

Obtained by reaction of the acetophenone imine of 2-methylallylamine (2.60 g, 15 mmol) and 2-iodobenzoylchloride (4.65 g, 15 mmol) in dichloromethane at room temperature for 24 h in the presence of triethylamine (2.02 g, 20 mmol). After column chromatography, eluting with 2:3 v/v ether/petroleum ether the *product* (4.53 g, 75%) was obtained as pale yellow prisms from ether/petroleum ether, mp 83–84°C. (Found: C, 56.3; H, 4.5; N, 3.3. $C_{19}H_{18}INO$ requires: C, 56.6; H, 4.5; N, 3.5%). δ 7.76 (d, 1H, *J*=8 Hz, ArH), 7.37 (m, 5H, ArH), 7.14 (m, 2H, ArH), 6.92 (m, 1H, ArH), 5.30, 5.21, 4.88, 4.78 (4×s, 4H, 2×C=CH_2) 4.29 (br s, 2H, NCH_2), and 1.90 (s, 3H, CH_3); *m*/*z*(%) 404 (M^++1, 0.6), 403 (M^+, 7), 276 (100), 221 (16), 103 (75), 97 (45), 91 (56), 77 (23), and 56 (21).

General procedure for bis-cyclisation–anion capture of 14[21] with organostannanes

A stirred mixture of enamine **14** (1 mmol), organostannane (1.1 mmol), palladium acetate (0.022 g, 0.1 mmol), triphenylphosphine (0.052 g, 0.2 mmol) and tetraethylammonium cloride (0.165 g, 1 mmol) in toluene (10 ml) was heated at 90°C under a nitrogen atmosphere for 8 h. After cooling to room temperature, the solvent was removed under vacuum and the residue taken up into ether (15 ml). The ether layer was washed with water and then stirred with a saturated aqueous solution of potassium fluoride (2 ml) for 1 h. The layers were separated and the organic phase was filtered, dried ($MgSO_4$) and the solvent evaporated. Column chromatography of the residue yielded **16** and **17**.

16a and 17a. Obtained as a colourless oily 5:1 mixture (0.185 g, 66%) from enamide **14a** (0.341 g, 1 mmol) and 2-furyltributylstannane **1b** (0.393 g, 1.1 mmol), after column chromatography eluting with 2:3 v/v ether/petroleum ether. [Found (mixed isomers): C, 76.7; H, 6.7; N, 5.0. $C_{18}H_{19}NO_2$ requires: C, 76.9; H, 6.7; N, 5.0%]; δ (major isomer **16a**) 7.77 (d, 1H, *J*=8 Hz, ArH), 7.57–7.27 (m, 4H, ArH), 6.19 (t, 1H, *J*=3 Hz, ArH), 6.09 (d, 1H, *J*=3 Hz, ArH), 2.88, 2.33 (2×d, 2H, *J*=12 Hz, NCH_2), 2.80 (s, 2H, $OCCH_2$), 2.10, 1.76 (2×d, 2H, *J*=13 Hz, CH_3CCH_2), and 1.42, 0.80 (2s, 6H, 2×CH_3); δ (minor isomer **17a**) 7.77–7.27 (m, 5H, ArH), 6.22, 5.91 (2s, 2H, ArH), 4.17, 3.08 (2×d, 2H, *J*=11 Hz, NH_2), 2.39 (dd, 2H, *J*=7, 7 Hz, CH_2CO), 1.98, 1.81 (2×d, 2H, *J*=13 Hz, CH_3CCH_2), and 1.58, 1.24 (2s, 6H, 2×CH_3); *m*/*z*(%) (mixed isomers) 281 (M^+, 28), 215 (30), 200 (39), 189 (39), and 159 (100).

16b and 17b. Obtained as a colourless oily 5:1 mixture (0.340 g, 70%) from enamine **14a** (0.341 g, 1 mmol) and 2-tributylstannylindole SEM derivative **1d** (0.589 g, 1.1 mmol) after column chromatography eluting with 2:3 v/v ether/petroleum ether. [Found (mixed isomers): C, 73.4; H, 7.9; N, 6.2. $C_{28}H_{36}N_2O_2Si$ requires: C, 73.1; H, 7.8; N, 6.1%]; δ (major isomer **16b**) 7.85 (d, 1H, *J*=7 Hz, ArH), 7.63–7.19 (m, 7H, ArH), 6.49 (s, 1H, ArH), 5.56 (s, 2H, NCH_2O), 4.09, 3.41 (2×d, 2H, *J*=12 Hz, NCH_2), 3.54 (t, 2H, *J*=8 Hz, OCH_2), 3.13 (s, 2H, CH_2CN), 2.23, 1.95 (2×d, 2H, *J*=13 Hz, CH_3CCH_2), 1.54, 0.95 (2s, 6H, 2×CH_3), 0.95 (m, 2H, CH_2SiMe_3), and 0.00 (s, 9H, $SiMe_3$); δ (minor isomer **17b**) 7.94 (d, 1H, *J*=7 Hz, ArH), 7.70–7.21 (m, 7H, ArH), 6.48 (s, 1H, ArH), 5.45, 5.29 (2×d, 2H, *J*=12 Hz, NCH_2O), 4.42, 3.25 (2×d, 2H, *J*=12 Hz, CH_2CN), 2.19, 2.01 (2×d, 2H, *J*=13 Hz, CH_3CCH_2), 1.78,

1.15 (2s, 6H, 2×CH_3), 0.82 (t, 2H, J=8 Hz, CH_2SiMe$_3$), and 0.00 (s, 9H, SiMe$_3$); m/z(%) (mixed isomers) 460 (M^+, 39), 272 (80), 261 (29), 145 (37), and 73 (100).

16c and 17c. Obtained as a colourless oily 3:1 mixture (0.219 g, 64%) from enamine **14b** (0.403 g, 1 mmol) and 2-furyltributylstannane **1b** (0.393 g, 1.1 mmol) after column chromatography eluting with 7:13 v/v ether/petroleum ether. [Found (mixed isomers): C, 80.5; H, 5.9; N, 4.1. $C_{23}H_{31}NO_2Sn$ requires: C, 80.5; H, 6.1; N, 4.1%]; δ (major isomer **16c**) 7.77 (d, 1H, J=9 Hz, ArH), 7.57–7.26 (m, 9H, ArH), 6.23 (d, 1H, J=2 Hz, ArH), 5.91 (d, 1H, J=3 Hz, ArH), 3.95, 3.29 (2×d, 2H, J=12 Hz, NCH_2), 2.87, 2.69 (2×d, 2H, J=13 Hz, CH_3CCH_2), 2.55 (s, 2H, CH_2CO), and 1.00 (s, 3H, CH_3); δ (minor isomer **17c**) 7.78–7.26 (m, 10H, ArH), 6.23 (s, 1H, ArH), 6.00 (d, 1H, J=3 Hz, ArH), 4.18, 3.06 (2×d, 2H, J=12 Hz, NCH_2), 2.64 (s, 2H, CH_2CO), 2.57, 2.09 (2×d, 2H, J=13 Hz, CH_3CCH_2), and 0.86 (s, 3H, CH_3); m/z(%) (mixed isomers) 343 (M^+, 65), 262 (25), 220 (100), and 165 (24).

16d and 17d. Obtained as a colourless oily 3:1 mixture (0.362 g, 70%) from enamine **14b** (0.403 g, 1 mmol) and 2-tributylstannylindole SEM derivative **1d** (0.589 g, 1.1 mmol) after column chromatography eluting with 7:13 v/v ether/petroleum ether. [Found (mixed isomers): C, 75.8; H, 7.4; N, 5.2. $C_{33}H_{38}N_2O_2Si$ requires: C, 75.9; H, 7.3; N, 5.4%]; δ (major isomer **16d**) 7.82–7.06 (m, 13H, ArH), 6.37 (s, 1H, ArH), 5.36 (dd, 2H, J=12 Hz, NCH_2O), 4.27, 3.15 (2×d, 2H, J=12 Hz, NCH_2), 3.34 (t, 2H, J=8 Hz, OCH_2), 2.88 (dd, 2H, J=12 Hz, CH_2CN), 2.69, 2.17 (2×d, 2H, J=13 Hz, CH_3CCH_2), 0.96 (s, 3H, CH_3), 0.79 (t, 2H, J=5 Hz, CH_2SiMe$_3$), and 0.15 (s, 9H, SiMe$_3$); δ (minor isomer **17b**) 7.82–7.06 (m, 13H, ArH), 6.30 (s, 1H, ArH), 5.36 (s, 2H, NCH_2O), 4.01, 3.40 (2×d, 2H, J=13 Hz, NCH_2), 3.34 (t, 2H, J=8 Hz, OCH_2), 2.88 (s, 2H, CH_2CN), 2.97, 2.07 (2×d, 2H, J=13 Hz, CH_3CCH_2), 1.11 (s, 3H, CH_3), 0.79 (t, 2H, J=5 Hz, CH_2SiMe$_3$), and 0.11 (s, 9H, SiMe$_3$); m/z(%) (mixed isomers) 522 (M^+, 26), 334 (71), 261 (68), 220 (100), 145 (71) and 73 (99).

23. A mixture of palladium acetate (0.044 g, 0.2 mmol), tri(2-furyl)phosphine (0.092 g, 0.4 mmol), tetraethylammonium chloride (0.330 g, 2 mmol), 2-pyridyltributylstannane **1f** (0.900 g, 2.2 mmol) and **20** (1.140 g, 2 mmol) was stirred and heated in toluene at 110°C for 16 h. The product **23** (0.550 g, 48%) was obtained, following the same workup described for **16**, as a colourless oil. (Found HRMS: 573.1756. $C_{31}H_{31}N_3O_4S_2$ requires: 573.1756). δ 8.46 (m, 1H, ArH), 7.97 (m, 2H, ArH), 7.69–7.42 (m, 11H, ArH), 7.21 and 7.14 (2×m, 2H, ArH), 6.91 (m, 2H, ArH), 4.57 and 4.28 (2×d, 2H, J=11 Hz, NCH_2), 3.76 and 3.43 (2×d, 2×1H, J=11.6 Hz, NCH_2), 3.07 and 2.88 (2×d, 2H, J=13 Hz, NCH_2), 1.90 and 1.30 (m, 4H, 2×CH_2), and 0.80 (s, 3H, CH_3). m/z(%) 574 (M^++1, 14), 512 (85), 432 (100), 292 (15), 263 (52), 130 (46), 93 (68) and 77 (60).

24. A mixture of aryl iodide **20** (0.31 g, 0.5 mmol), palladium acetate (0.011 g, 0.05 mmol), triphenylphosphine (0.026 g, 0.1 mmol), tetraethylammonium chloride (0.08 g, 0.5 mmol) and vinyltributylstannane **1e** (0.158 g, 0.5 mmol) in toluene (5 ml) was stirred and heated for 16 h at 110°C. The solvent was then removed, the residue dissolved in dichloromethane (25 ml), washed with water (25 ml) and the aqueous layer back extracted with dichloromethane (2×5 ml). The combined organic extracts were dried ($MgSO_4$), the solvent removed and the residue chromatographed eluting with 4:1 v/v petroleum ether/ether to afford the *product* (0.14 g, 55%) as a colourless oil. (Found: C, 64.5; H, 5.95; N, 5.35; S, 12.5. $C_{28}H_{30}N_2O_4S_2$ requires C, 64.35; H, 5.8; N, 5.35; S, 12.3%); δ 7.9 and 7.8 (2×d, 2×2H, J=6.2 Hz, ArH), 7.5(m, 5H, ArH), 7.2(br s, 3H, ArH), 6.96(br s, 2H, ArH), 5.3(m, 1H, CH=CH_2), 4.9(m, 2H, CH=CH_2); 4.63 and 4.29 (2×s, 2×1H, C=CH_2), 4.0 and 3.7 (2×d, 2×1H, J=11.2 Hz, NCH_2), 3.6, 3.4 (2×d, 2×1H, J=16.6 Hz, NCH_2), 3.2 and 3.0 (2×d, 2×1H, J=16.8 Hz), 2.3(m, 2H, CH_2C=C) and 1.1 (s, 3H, Me); m/z (%), 522(M^+, 2), 381(5), 298(77), 224(100), 157(50) and 77(72).

General procedure for bis-cyclisation–anion capture of 26 with organostannanes

A mixture of **26** (1 mmol), palladium acetate (0.022 g, 0.1 mmol) and triphenylphosphine (0.052 g, 0.2 mmol) in dry acetonitrile (10 ml) or THF (10 ml) was stirred at room temperature for 10–15 min. The organostannane (1 mmol) was then added slowly and the resulting mixture was stirred until no **26** remained. The solvent was evaporated, the residue dissolved in ether and treated with a saturated aqueous solution of potassium fluoride and the mixture stirred at room temperature for 1 h. The solution was then filtered, the ether layer separated, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative T.L.C eluting with 2:3 v/v of ether/petroleum ether.

27a. Obtained from **26a** and vinyltributylstannane **1e** according to the general procedure, in acetonitrile (2 h). The *product* (40%) was isolated as a pale yellow oil. (Found: C, 78.6; H, 6.6; N, 7.1. $C_{13}H_{13}NO$ requires: C, 78.4; H, 6.5; N, 7.0%); δ 8.25, 7.55 (2×d, 2H, J=8, 7.5 Hz, ArH), 7.25–6.95 (m, 3H, 2×ArH and CH=CH_2), 6.04 (d, 1H, C=CH), 5.21 (m, 2H, CH=CH_2), 4.53 (s, 2H, NCH_2), and 2.1 (s, 3H, $COCH_3$). m/z(%) 199 (M^+, 90), 157 (85), 156 (86), 130 (100), and 43 (39).

27b. Obtained from **26b** with vinyltributylstannane **1e** according to the general procedure, in acetonitrile (5°C, 1.5 h). The *product* (60%) crystallised as pale yellow needles from ether/petroleum ether, mp 106–108°C. (Found: C, 77.4; H, 7.1; N, 6.3. $C_{14}H_{15}NO.0.25H_2O$ requires: C, 77.1; H, 7.0; N, 6.4%); δ 8.29, 7.54 (2×d, 2H, J=8, 7.5 Hz, ArH), 7.24–7.11 (m, 2H, ArH and CH=CH_2), 6.96 (t, 1H, J=8 Hz, ArH), 5.35, 5.21 (2×d, 2H, J=17.5, 11 Hz, CH=CH_2), 4.50 (s, 2H, NCH_2), 2.16 (s, 3H, $NCOCH_3$), and 1.80 (s, 3H, C=CCH_3). m/z(%) 213 (M^+, 100), 198 (12), 196 (20), 171 (71), 156 (86), 144 (35), 130 (18) and 43 (38).

27c. Obtained from **26c** with vinyltributylstannane **1e** according to the general procedure, in acetonitrile (60°C, 2 h). The *product* (40%) crystallised as colourless needles from ether/petroleum ether, mp 138–140°C. (Found: C, 70.8; H, 7.9; N, 4.8. $C_{16}H_{21}NOSi$ requires: C, 70.8; H, 7.8; N, 5.2%); δ 8.25, 7.76 (2×d, 2H, J=8, 7.5 Hz, ArH),

7.15, 6.91 (2×t, 2H, J=8, 7,5 Hz, ArH), 6.55 (m, 1H, CH=CH_2), 5.21 (dd, 1H, J=11, 1.7 Hz, CH=CH_2), 4.99 (dd, 1H, J=18, 1.7 Hz, CH=CH_2), 4.57 (d, 2H, J=4 Hz, NCH_2), 2.16 (s, 3H, $NCOCH_3$), and 0.17 (s, 9H, $SiMe_3$). m/z(%) 271 (M^+, 4), 244 (10), 198 (63), 160 (100), 91 (14), 76 (10), and 73 (16)

27d. Obtained from **26a** and allyltributylstannane **1j** according to the general procedure, in acetonitrile (60°C, 2 h). The *product* (54%) crystallised as colourless needles from ether, mp 80–82°C. (Found: C, 75.4; H, 7.0; N, 6.2. $C_{14}H_{15}NO{\cdot}0.5H_2O$ requires: C, 75.7; H, 7.3; N, 6.3%); δ 8.27, 7.43 (2×d, 2H, J=8, 7.5 Hz, ArH), 7.16, 6.96 (2×t, 2H, J=8, 7.5 Hz, ArH), 5.84 (m, 1H, CH_2CH=CH_2), 5.49 (t, 1H, J=7.5 Hz, CH=CHCH_2), 5.08 (dd, 1H, J=17, 1.3 Hz, CH=CH_2), 5.00 (dd, 1H, J=10, 1.3 Hz, CH=CH_2), 4.54 (d, 2H, J=2 Hz, NCH_2), 3.13 (t, 2H, J=6.5 Hz, C=CCH_2C=C), and 2.12 (s, 3H, $NCOCH_3$); m/z(%) 213 (M^+, 80), 171 (21), 170 (19), 156 (19), 144 (16), 130 (100), and 43 (34).

27e. Obtained from **26b** and allyltributylstannane **1j** according to the general procedure, in THF (60°C, 5 h). The *product* (55%) crystallised as colourless needles from ether/petroleum ether, mp 102–109°C. (Found: C, 79.1; H, 7.5; N, 6.3. $C_{15}H_{17}NO$ requires: C, 79.3; H, 7.5; N, 6.2%); δ 8.39, 7.50 (2×d, 2H, J=8 Hz, ArH), 7.21, 7.04 (2×t, 2H, J=8, 7.5 Hz, ArH), 5.89 (m, 1H, CH_2CH=CH_2), 5.17–5.10 (m, 2H, CH=CH_2), 4.59 (s, 2H, NCH_2), 3.22 (d, 2H, J=5.6 Hz, C=CCH_2C=C), 2.27 (s, 3H, $NCOCH_3$), and 1.83 (s, 3H, C=CCH_3); m/z(%) 227 (M^+, 70), 184 (18), 170 (31), 145 (14), 144 (100), 130 (15), and 43 (49).

Synthesis of 28a and 28b

A solution of 2-iodobenzoyl chloride (2.665 g, 10 mmol) in dry dichloromethane was added dropwise over 1.5 h to a solution of the appropriate *N*-alkylated propargylamine (10 mmol) in dry dichloromethane (25 ml). After stirring at room temperature for 2 h, water was added and the organic phase was separated, dried (Na_2SO_4), and evaporated affording **28** as pale yellow prisms.

28a. Obtained as a colourless solid in 95% yield, mp 47–49°C. (Found: C, 44.3; H, 3.5; N, 4.7. $C_{11}H_{10}INO$ requires: C, 44.1; H, 3.4; N, 4.7%); δ 7.82 (m, 1H, ArH), 7.08–7.43 (m, 3H, ArH), 4.60 and 3.90 (2×d, 2×2H, J=2.4 Hz, NCH_2 rotamers), 3.2 and 2.92 (2×s, 2×3H, NCH_2 rotamers), and 2.32 (t, 1H, J=2.4 Hz, CH); m/z(%) 299 (M^+, 53), 231 (100), 203 (35), 172 (59), and 76 (44).

28b. Obtained as a colourless solid in 75% yield, mp 69–71°C. (Found: C, 55.7; H, 4.3; N, 3.8. $C_{18}H_{16}INO$ requires: C, 55.5; H, 4.1; N, 3.6%); δ (C_6D_6, 73°C) 7.82 (d, 1H, J=7 Hz, ArH), 7.45 (m, 1H, ArH), 7.10 (m, 6H, ArH), 6.60 (m, 1H, ArH), 4.40 (s, 2H, NCH_2Ph), 3.60 (s, 2H, NCH_2), and 1.50 (s, 3H, CH_3); m/z(%) 389 (M^+, 7), 336 (21), 298 (10), 262 (20), 231 (100), 203 (51), and 91 (90).

General procedure for cyclisation–anion capture of 28 with organotin reagents

The organotin(IV) reagent (1 mmol) was added slowly to a stirred mixture of **28** (1 mmol), palladium acetate (0.022 g, 0.1 mmol), triphenylphosphine (0.052 g, 0.2 mmol) and tetraethylammonium chloride (0.166, 1 mmol) in dry acetonitrile. The resulting mixture was stirred until no **28** remained (2–14 h). The solvent was evaporated, the residue dissolved in ether and treated with a saturated aqueous solution of potassium fluoride and the mixture stirred at room temperature for 1 h, filtered, the ethereal phase separated, dried ($MgSO_4$) filtered and the filtrate evaporated under reduced pressure. The residue was purified by preparative T.L.C eluting with 2:3 v/v ether/petroleum ether.

30a and 30b. Colourless oil (20%) which comprised a 4:1 mixture of **30a** and **30b**. [Found HRMS (mixed isomers): 199.0997. $C_{13}H_{13}NO$ requires: 199.0995]; m/z(%) (mixed isomers) 199 (M^+, 100), 198 (46), 184 (19), and 172 (25). **30a:** δ 8.14 (d, 1H, J=8 Hz, ArH), 7.40 (m, 3H, ArH), 6.90 (m, 1H, CH=CH_2), 6.29 (d, 1H, J=11 Hz, CH=CH_2), 5.47 (d, 1H, J=18 Hz, CH=CH_2), 5.33 (m, 1H, C=CH), 4.08 (s, 2H, CH_2), and 3.17 (s, 3H, NCH_3). **30b:** δ 8.15 (d, 1H, J=8 Hz, ArH), 7.40 (m, 3H, ArH), 6.64 (m, 1H, CH=CH_2), 6.29 (d, 1H, J=11 Hz, CH=CH_2), 5.47 (d, 1H, J=18 Hz, CH=CH_2), 5.33 (m, 1H, C=CH), 4.39 (s, 2H, CH_2), and 3.18 (s, 3H, NCH_3).

30c and 30d. Colourless oil (33%) which comprised a 5:1 mixture of **30c** and **30d**. [Found HRMS (mixed isomers): 289.1450. $C_{20}H_{19}NO$ requires: 289.1460]; m/z(%) (mixed isomers) 199 (M^+, 100), 289 (94), 274 (12), 198 (20), and 91 (100). **30c:** δ 8.08 (d, 1H, J=7.5 Hz, ArH), 7.32 (m, 8H, ArH), 6.82 (dd, 1H, J=17.5, 11 Hz, CH=CH_2), 5.33 (d, 1H, J=17.5 Hz, CH=CH_2), 5.18 (d, 1H, J=11 Hz, CH=CH_2), 4.76, 4.04 (2×s, 4H, 2×NCH_2), and 1.67 (s, 3H, CH_3).**30d** δ 8.08 (d, 1H, J=7.5 Hz, ArH), 7.32 (m, 8H, ArH), 6.45 (dd, 1H, J=17.5, 11 Hz, CH=CH_2), 5.31 (d, 1H, J=17.5 Hz, CH=CH_2), 5.17 (d, 1H, J=11 Hz, CH=CH_2), 4.77, 4.10 (2×s, 4H, 2×NCH_2), and 1.68 (s, 3H, CH_3).

30e. Colourless oil (50%). (Found HRMS: 213.1154. $C_{14}H_{15}NO$ requires: 213.1155); δ 8.08 (d, 1H, J=9 Hz, ArH), 7.32 (m, 3H, ArH), 5.83 (m, 1H, CH=CH_2), 5.66 (t, 1H, J=7.5 Hz, CH=CH_2), 5.05 (m, 1H, CH=CH_2), 5.01 (m, 1H, CH=C), 3.95 (s, 2H, NCH_2), 3.05 (s, 3H, NCH_3), and 3.00 (t, 2H, J=6 Hz, C=CHCH_2CH=C); m/z(%) 213 (M^+, 100), 212 (13), 198 (15), 172 (92), and 159 (26).

30f. Colourless oil (29%). (Found HRMS: 303.1635. $C_{21}H_{21}NO$ requires: 303.1623); δ 8.14 (d, 1H, J=9 Hz, ArH), 7.32 (m, 8H, ArH), 5.90 (m, 1H, CH=CH_2), 5.16 (d, 1H, J=10 Hz, CH=CH_2), 5.10 (d, 1H, J=17 Hz, CH=CH_2), 4.81 (s, 2H, PhCH_2N), 4.03 (s, 2H, NCH_2), 3.01 (d, 2H, J=5.5 Hz, C=CHCH_2CMe=C), and 1.59 (s, 3H, CH_3); m/z(%) 303 (M^+, 46), 262 (35), 160 (22), 91 (100), and 41 (11).

Synthesis of allene 31

A solution of *o*-iodobenzoyl chloride (3.20 g, 12 mmol) in dichloromethane (5 ml) was treated with *N*-methylpropargylamine (0.828 g, 12 mmol) and triethylamine (2.0 ml, 14.4 mmol) dissolved in dichloromethane (10 ml) at 0°C

and the resulting mixture was stirred at room temperature for 4 h. Water (50 ml) was then added and the organic layer separated, dried (Na_2SO_4) and evaporated. The residue was dissolved in DMF (25 ml) and treated with sodium hydroxide (pearls, 0.576 g, 14.4 mmol) at room temperature for 16 h. DMF was removed and the residue dissolved in dichloromethane (45 ml) and washed with water (45 ml). The organic layer was dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (SiO_2) eluting with 7:3 v/v *n*-hexane/ether to afford the *product* (2.85 g, 80%) as a pale yellow oil. (Found: C, 44.1; H, 3.5; N, 4.5. $C_{11}H_{10}INO$ requires: C, 44.0; H, 3.3; N, 4.7%); δ (mixture of rotomers) 7.61 (d, J=7.2 Hz, 1H, ArH), 7.20 (t, J=7.5 Hz, 1H, ArH), 7.05 (m, 1H, ArH), 6.78 (t, J=7.2 Hz, 1H, ArH), 6.20, 6.45 (2×t, J=6.0 Hz, 1H, C*H*═C═CH_2), 5.33, 5.25 (br s and d, J=6.0 Hz, 2H, CH_2═C═C) and 3.15, 2.84 (2×s, 3H, CH_3); *m*/*z* (%) 299 (M^+, 14), 231 (100), 104 (85) and 69 (31).

General procedure for cyclisation–anion capture of 31 with organotin(IV) reagents

The organostannane (0.6 mmol) and the additive (where required, see Table 4) were added to a stirred solution of allene **31** (150 mg, 0.5 mmol), $Pd_2(dba)_3$ (11.2 mg, 0.0125 mmol) and tri-(2-furyl)phosphine in toluene (7 ml). The resulting mixture was boiled under reflux for times depicted on Table 4. Treatment with a 2 M aqueous solution of KF and purification as described above, afforded a 1.5:1 mixture (75%) without silver carbonate or a 6:1 mixture (70%) using silver carbonate (1 mol equiv.) of **33a** and **34a** and a 1:1 mixture (60%) of **33b** and **34b**.

33a. Colourless prisms from *n*-hexane/ether, mp 128–130°C. (Found: C, 75.0; H, 5.65; N, 5.55. $C_{15}H_{13}NO_2$ requires: C, 75.3; H, 5.45; N, 5.85%). δ 8.48(d, J=8.1 Hz, ArH), 7.64–7.61 (m, 2H, ArH), 7.48(m, 1H, ArH), 7.34(s, 1H, ArH), 6.91(s, 1H, CHN), 6.02, 6.29(2×m, 2H, C*H*C*H*CHO), 4.01(s, 2H, CH_2) and 3.58 (s, 3H, Me); *m*/*z* (%) 239 (M^+, 100), 238 (24), 210 (33), 173 (28), 147 (26), 146 (62), 115 (28), 57 (32), 55 (21), 43 (24), and 42 (24).

34a. Colourless prisms from *n*-hexane/ether, mp 109–111°C. (Found: C, 75.1; H, 5.55; N, 5.55. $C_{15}H_{13}NO_2$ requires: C, 75.3; H, 5.45; N, 5.85%). δ 7.88, 7.46 and 7.33 (3×m, 5H, ArH), 6.24 (m, 2H, CHCO), 5.87 (s, 1H, C═CH_2), 5.81 (m, 1H, *CH*CHO), 5.34 (s, 1H, C═CH_2), 5.19 (s, 1H, CHN) and 3.04 (s, 3H, Me); *m*/*z* (%) 239 (M^+, 28), 174 (34), 146 (100), 91 (30), 77 (100), 65 (13), 42 (11), and 39 (12).

33b. Pale yellow oil. (Found: C, 78.0; H, 6.2; N, 6.9. $C_{13}H_{13}NO$ requires: C, 78.35; H, 6.55; N, 7.05%). δ 8.48 (d, J=8.3 Hz, 1H, ArH), 7.64 and 7.49 (2×m, 3H, ArH), 6.90 (s, 1H, C═CH), 5.98 (ddd, J=16.6, 10.5 and 6.0 Hz, 1H, C*H*═CH_2), 5.15 (d, J=10.5 Hz, 1H, C═CH_2), 5.14 (d, J=16.6 Hz, 1H, CH_2═CH), 3.59 (s, 3H, Me) and 3.43 (d, J=6.0 Hz, 2H, CH_2 C═C); *m*/*z* (%) 199 (M^+, 100), 198 (46), 172 (49), 146 (52), 115 (32), 103 (27), 77 (23), 42 (22), and 39 (34).

34b. Pale yellow oil. (Found: C, 78.0; H, 6.15; N, 6.9. $C_{13}H_{13}NO$ requires: C, 78.35; H, 6.55; N, 7.05%). δ 7.85 (d, J=7.1 Hz, 1H, ArH), 7.53 and 7.37 (m, 3H, ArH), 6.00 (dd, J=17.6 and 11.1 Hz, 1H, C*H*═CH_2), 5.45 (s, 1H, C═CH_2), 5.28 (d, J=17.6 Hz, 1H, C═CH_2), 5.25 (s, 1H, C═CH_2), 5.06 (d, J=11.1 Hz, 1H, CH═CH_2), 5.05 (s, 1H, CHN) and 3.03 (s, 3H, Me); *m*/*z* (%) 199 (M^+, 31), 147 (15), 146 (100), 115 (16), 91 (20), and 77 (15).

General procedure for monocyclisation–anion capture of 35,[21] 37,[21] 38,[21] and 41[25]

A mixture of the aryl or vinyl halide (1 mmol), palladium acetate (0.011 g, 0.1 mmol), triphenylphosphine (0.026 g, 0.2 mmol), tetraethylammonium chloride (0.170 g, 1 mmol) and vinyltributylstannane **1e** (0.320 g, 1 mmol) in acetonitrile (10 ml) was stirred and heated under reflux for 24 h. Treatment with 2 M aqueous solution of KF and purification, as described above, afforded the *products*.

36. Colourless oil (60%). (Found: C, 84.1; H, 7.3; N, 3.4. $C_{26}H_{27}NO$ requires: C, 84.5; H, 7.4; N, 3.8%). δ 7.80–7.19 (m, 9H, ArH), 5.63 (m, 1H, C*H*═CH_2), 5.23, 4.73 (2×d, 2H, J=16 Hz, NCH_2Ph), 5.06 (m, 2H, CH═CH_2), 4.98 (m, 1H, C═CH), 2.77 (d, 2H, J=6.5 Hz, CH_2CH═CH_2), 2.49 (m, 1H, CHCH_2CH), 2.35 (d, 1H, J=10 Hz, C*H*C═CH), 2.16 (m, 2H, CHCH_2CH and C*H*CH_2), 1.34, and 1.13 (2s, 6H, 2×CH_3); *m*/*z* (%) 370 (M^++1, 7), 369 (M^+, 10), 278 (86), 236 (25), 220 (14), 128 (22), 91 (100), and 41 (12).

39. Colourless oil (60%). (Found HRMS: 298.1722. $C_{23}H_{22}$ requires 298.1722); δ 7.49 (m, 8H, ArH), 5.86 (m, 1H, CH_2═C*H*), 5.55 (m, 2H, CHC*H*═CH_2 and CH_2═C), 5.04 (m, 4H, CH═CH_2, CHCH═C*H* and 1H of CH_2═CC), 3.70 (m, 1H, C*H*CH_2CH═C), 2.96, 2.67 (dd, 2H, J=10 Hz, CH_2CH═CH_2), 2.81 and 2.15 (2×m, 4H, CH═CHCH_2 and CH_2C); *m*/*z* (%) 299 (M^++1, 16), 298 (M^+, 60), 279 (14), 203 (19), 179 (24), 178 (100), 91 (11), and 55 (10).

40. Colourless oil (60%). (Found HRMS: 292.1674. $C_{17}H_{24}O_4$ requires 292.1674). δ 5.76 (m, 1H, CH_2C*H*═CH_2), 5.47 (m, 1 HC*H*═CHCH_2), 4.87 (m, 4H CH_2═CH and C═CH_2), 4.12 (m, 4H, 2×CH_2O), 3.06 (m, 1H, CH_2C*H*), 2.96, 2.89 (2×br s, 2H, CH_2C═CH_2), 2.71 (m, 2H, CH_2CH═CH_2), 2.50, 1.90 (2×m, 1H, CH_2CH), and 1.17 (m, 6H, 2×CH_3); *m*/*z* (%) 293 (M^++1, 4), 219 (27), 218 (98), 191 (23), 190 (41), 179 (21), 177 (33), 145 (100), 119 (22), 117 (77), 105 (29), 91 (55), 79 (32), 67 (30), and 29 (72).

42. In this case the reaction was carried out in THF at 60°C with lithium chloride (1 mol equiv.). The *product* (42%) was a thick yellow oil (42%). (Found: C, 68.2; H, 6.5; N, 4.5. $C_{18}H_{21}NO_2S$ requires: C, 68.6; H, 6.7; N, 4.4%); δ 7.80–7.60 (m, 5H, ArH), 5.80 (m, 1H, C*H*═CH_2), 5.60 (m, 1H, CH_2═C*H*), 5.30 (d, 1H, C*H*═CH), 5.12 (t, 1H, J=5 Hz, CH_2C*H*═CH), 4.83 (m, 2H, C═CH_2), 4.00 and 3.74 (2×d, J=9 Hz, NCH_2), 3.65 (br s, 1H, NCH), 3.21 (m, 1H, C*H*CH═CH_2), 2.62 (deform. t, 2H, J=4 Hz, C═CHCH_2CH═CH_2) and 2.30–1.64 (m, 4H, 2×CH_2); *m*/*z* (%) 315 (M^+, 26), 275 (10), 174 (31), 125 (28), 117 (10), 94 (12), 91 (23), 77 (100), and 51 (22).

Acknowledgements

We thank the EPSRC, the Spanish Government (MEC), Leeds University, Queen's University and Organon Laboratories for support.

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