Regiochemistry in aryl radical cyclisations (5-*exo versus* 6-*endo*) of *N*-vinylic 2-iodobenzamides

Hiroyuki Ishibashi,*[a] Kohei Ohata,[a] Michiyo Niihara,[b] Tatsunori Sato[b] and Masazumi Ikeda[b]

[a] *Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920-0934, Japan*
[b] *Kyoto Pharmaceutical University, Misasagi, Yamashina, Kyoto 607-8414, Japan*

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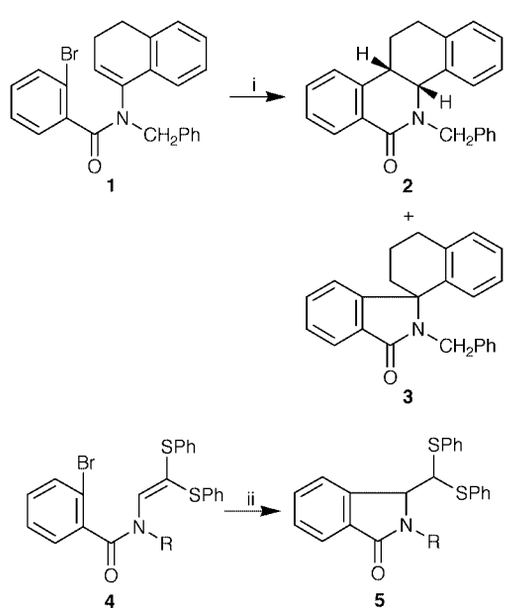
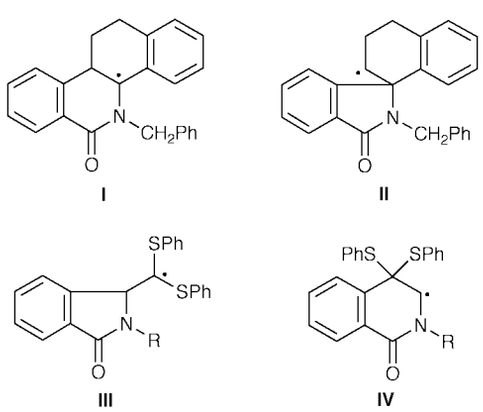
Bu_3SnH-mediated aryl radical cyclisations of a range of *N*-vinylic 2-iodobenzamides **10** were examined. The enamides **10a**–**d** gave exclusively the 5-*exo* cyclisation products **11a**–**d**, whereas the enamides **10e**,**f** having a phenyl substituent on the vinylic carbon atom α to the nitrogen atom gave predominantly the 6-*endo* cyclisation products **14** and **18**, respectively. The experiments on the effect of concentration of Bu_3SnH or temperature on the products distribution showed that the formation of the 6-*endo* cyclisation products **14** and **18** was a result of a 5-*exo* cyclisation of the aryl radicals formed from **10e**,**f** followed by neophyl rearrangement of the intermediate radicals.

Aryl radical cyclisation has recently emerged as a valuable tool for organic synthesis.[1] Many examples have been reported for the Bu_3SnH-mediated aryl radical cyclisation onto an enamide double bond.[2,3] The literature indicates that enamides having an alkenic bond at the 5-position relative to the aryl radical centre usually cyclise in a 6-*endo* manner exclusively or predominantly to give six-membered lactams.[2] For example, the enamide **1** gave the 6-*endo* cyclisation product **2** as the major product (38% yield) accompanied by the 5-*exo* cyclisation product **3** (27% yield).[2a] Quite recently, we found, however, that the enamides **4** underwent cyclisation in a 5-*exo* manner exclusively to give the isoindolone derivatives **5**.[4]



Scheme 1 *Reagents and conditions*: i, Bu_3SnH, AIBN, toluene, reflux; ii, Bu_3SnH, ACN, toluene, reflux.

At first glance, the difference between the structural features of the radical precursors **1** and **4** is that the enamide **1** has an aryl substituent on the vinylic carbon atom α to the nitrogen atom, whereas the enamides **4** have no substituent on the corresponding carbon atom. An additional feature of the enamides **4** is that they have two phenylthio groups at the terminus of their *N*-vinylic bond. Accordingly, one possible explanation for the predominant formation of **2** from **1** and **5** from **4** may be that the intermediate radicals **I** and **III** are much more stable than are the alternate intermediate radicals **II** and **IV**, respectively. The radical centre of **I** is flanked by the radical-stabilising aryl substituent and the nitrogen atom, and the radical **III** by two phenylthio groups. However, it is difficult to rule out the following possibility for the predominant formation of **2** and **5**. The aryl radicals formed from **1** and **4** may attack on the vinylic carbon atom so as to avoid the steric repulsion between the radical centre and the aryl or phenylthio substituents, to lead to the formation of **I** and **III**, respectively. Alternately, the formation of **I** may involve an initial 5-*exo* cyclisation of the radical formed from **1** followed by neophyl rearrangement[5] of the intermediate radical. Therefore, it forced us to examine in detail the cyclisations of a range of enamides **10** in order to see the exact reason for the predominant formation of **2** and **5**. Herein, we describe the results of our work in this area and show an example of the consecutive 5-*exo* cyclisation and neophyl rearrangement leading to the 6-*endo* products.



Results and discussion

The requisite radical precursors **10a**–**f** were prepared as follows. Acylation of *N*-methyl-2-(phenylthio)ethylamine with 2-iodobenzoyl chloride **6** gave the amide **7**, which was oxidised with MCPBA followed by heating of the resulting sulfoxide in boiling xylene to give **10a** as a result of the thermal *syn* elimination of benzenesulfenic acid. On the other hand, condensation of methylamine with phenylacetaldehyde, diphenylacetaldehyde,

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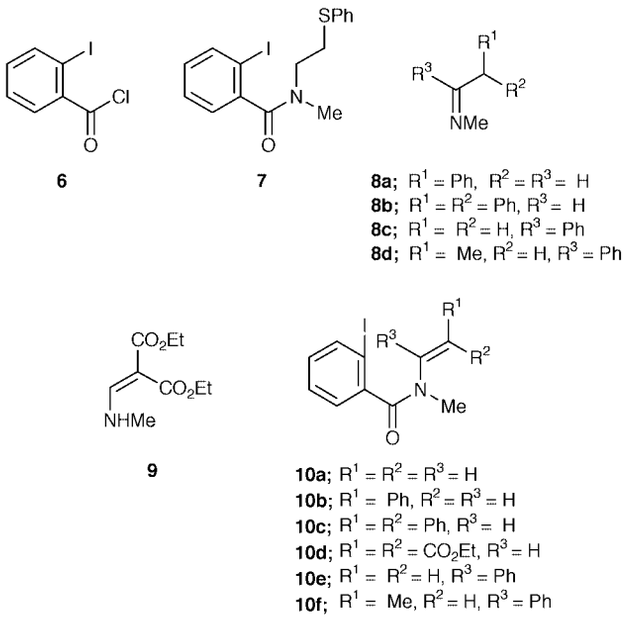
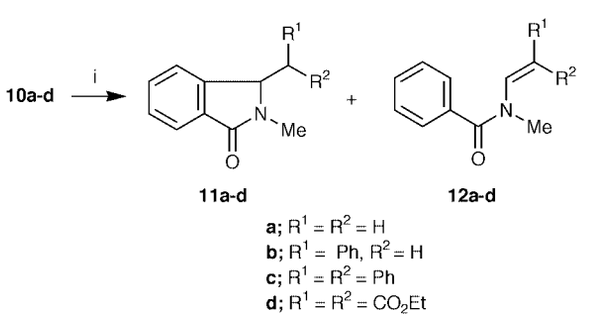


acetophenone or propiophenone gave the imines **8a**, **8b**, **8c** and **8d**, which were treated with acid chloride **6** to afford **10b**, **10c**, **10e** and **10f**, respectively. Similar treatment of the enamine **9**, prepared from *N*-methylamine and diethyl ethoxymethylenemalonate, with **6** afforded **10d**. The ^{1}H NMR spectra of **10a**–**e** showed the compounds **10a**,**b** to be mixtures of two rotamers of the amides, and the compounds **10c**–**e** to exist as single rotamers (see Experimental section). The geometry of the phenyl group (R^1 = Ph) of **10b** on the vinylic bond was proved to be *E*-configuration by the coupling constant (14.5 Hz) between the two alkenic protons. The ^{1}H NMR spectrum of **10f** also showed it to be a mixture of two components, but it is unknown whether the mixture consists of two rotamers or of two stereoisomers involving the methyl substituent (R^1 = Me).

We initiated our investigation by examining the cyclisation of the most simple enamide **10a**. When a mixture of Bu_3SnH (1.5 equiv.) and azobiscyclohexanecarbonitrile (ACN) (0.2 equiv.) in toluene was added slowly to a boiling solution of **10a** in toluene over a period of 1.5 h and the mixture was further heated for 1 h, the 5-*exo* cyclisation product **11a** was obtained in 60% yield, along with the reduction product **12a** (25% yield).

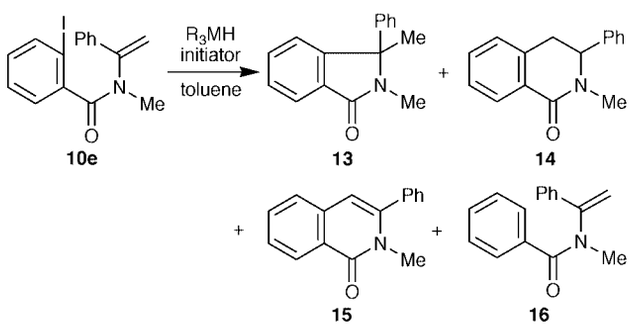


Scheme 2 *Reagents and conditions*: i, Bu_3SnH, ACN, toluene, reflux.

The structure of **11a** was readily confirmed by ^{1}H NMR spectroscopy which exhibited the signal due to the methyl group on the C-3 position at δ 1.47 as a doublet (J 6.5 Hz). This result clearly indicates that the general guideline for the aryl radical cyclisation, "a 5-*exo* cyclisation is preferred over a 6-*endo* cyclisation", is also applicable to the cyclisation onto the enamide double bond. The exclusive formation of the 5-*exo* cyclisation product **5** from **4** was not, therefore, assumed to be a result that the sterically more demanding two phenylthio groups prevented the 6-*endo* cyclisation.

Similarly, the enamides **10b**, **10c** and **10d**, having the substituents at the terminus of the *N*-vinylic bond, afforded exclusively the 5-*exo* cyclisation products **11b**, **11c** and **11d** in 55, 43, and 65% yields, respectively, along with the corresponding reduction products **12b** (35% yield), **12c** (16% yield) and **12d** (13% yield).

Our attention was next turned to the enamides **10e** and **10f** having a phenyl substituent on the vinylic carbon atom α to the nitrogen atom. When the compound **10e** was treated slowly with Bu_3SnH in the presence of ACN in boiling toluene, a mixture of the five-membered lactam **13** and the six-membered lactam **14** was obtained in 55% combined yield, together with the unsaturated six-membered lactam **15** and the reduction product **16** in 16 and 13% yields, respectively (Scheme 3). The



Scheme 3 *Reagents and conditions*: Bu_3SnH, ACN or Et_3B, toluene, reflux or room temp. or $(TMS)_3SiH$, ACN, toluene, reflux.

structures of **13** and **14** were confirmed by the spectroscopic evidence. Thus, the IR spectrum of the mixture of **13** and **14** showed the bands at 1680 and 1640 cm^{-1}, which were clearly indicative of five- and six-membered lactams, respectively. The ^{1}H NMR spectrum of the mixture exhibited a singlet due to the C-methyl protons of **13** at δ 1.88 and a double doublet (J 6.9 and 3.0 Hz) due to 3-H of **14** at δ 4.76. The integrated intensity of the peak heights of their signals indicated that the six-membered lactam **14** was the major product. The ratio of **13** to **14** was estimated to be *ca.* 1:5. Recrystallisation of the mixture from hexane–AcOEt gave **14** in pure form, mp 113.5–114 °C. On the other hand, the ^{1}H NMR spectrum of **15** showed the signal due to the alkenic 4-H at δ 6.46 as a singlet and the IR spectrum showed a band at 1650 cm^{-1} (a six-membered lactam).

Formation of **13** and **14** can be best explained in terms of an attack of Bu_3SnH on the intermediate radicals **VIa** and **VIIIa**, respectively (Scheme 4). The unsaturated lactam **15** might arise by an oxidation of the radical **VIIIa**.[6] One can imagine that the radical **VIIIa** might be formed directly by cyclisation of the aryl radical **Va** due probably to the higher stability of **VIIIa** over **VIa**. However, it has frequently been observed that a consecutive 5-*exo* cyclisation and neophyl rearrangement produces the 6-*endo* cyclisation products. We then examined the possibility of the neophyl rearrangement of the intermediate radical **VIa** to **VIIIa** *via* **VIIa** by carrying out the cyclisations of **10e** under various conditions. The results are summarised in Table 1.

First, Bu_3SnH was added rapidly (within 5 min) to a boiling solution of **10e** in toluene (entry 2 in Table 1). Under these conditions, the formation of the 5-*exo* cyclisation product **13** increased as compared with entry 1 (slow addition of Bu_3SnH). Thus, the ratios of **13**:(**14** + **15**) for entries 1 and 2 were estimated to be 1:6.9 and 1:3.4, respectively. A similar result was obtained by carrying out the reaction at room temperature in a high concentration of Bu_3SnH using triethylborane as a radical initiator,[7] in which the ratio of the products **13**:(**14** + **15**) was 1:3.0 (entry 3). These results suggest that the 5-*exo* cyclisation of **Va** giving **VIa** is a kinetically favoured process. It is assumed that at high concentration of Bu_3SnH (entries 2 and 3), the radical **VIa** is rapidly trapped by Bu_3SnH

Table 1 Radical cyclisation of **10e**[a]

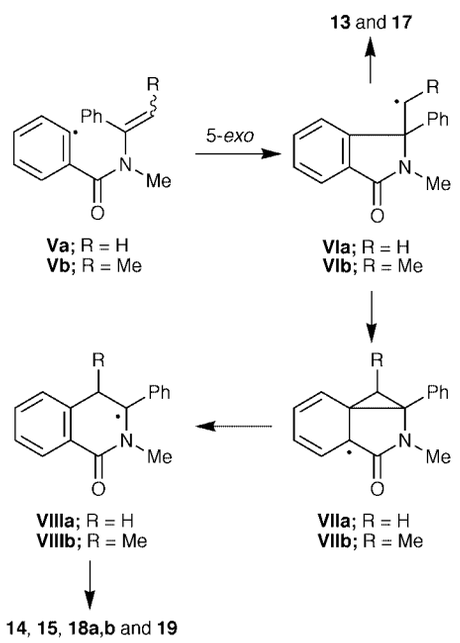
Entry	R_3MH[b]	Temp. (*T*/°C)	Time[c]	Yield of products (%)[d] **13**	**14**	**15**	**16**	Ratio of **13**:(**14** + **15**)
1	Bu_3SnH	110	4.5 h	9	46	16	13	1:6.9
2	Bu_3SnH	110	5 min[e]	18	55	6	13	1:3.4
3	Bu_3SnH	20	[f]	20	25	34	0	1:3.0
4	$(TMS)_3SiH$	110	4.5 h	8	11	47	0	1:7.3

[a] ACN was used as a radical initiator except for entry 3 (Et_3B). [b] For mol equiv. of R_3MH, see Experimental section. [c] Rate of addition of R_3MH. [d] Yields of **13** and **14** were estimated by the ratios of the mixtures of them, and isolated yields are indicated for **15** and **16**. [e] After addition of Bu_3SnH, the mixture was further heated for 30 min. [f] Et_3B was added to a mixture of enamide **10e** and Bu_3SnH, and the mixture was stirred for 20 h.

Table 2 Radical cyclisation of **10f**[a]

Entry	R_3MH[b]	Temp. (*T*/°C)	Time[c]	Yield of products (%)[d] **17**	**18a**,**b**	**19**	**20**	Ratio of **17**:(**18a**,**b** + **19**)
1	Bu_3SnH	110	4 h	8	40[e]	14	21	1:6.7
2	Bu_3SnH	110	10 min[f]	13	44[e]	8	30	1:4
3	Bu_3SnH	20	[g]	54	0	0	28	**17** only
4	$(TMS)_3SiH$	110	4.5 h	9	15[e]	48	5	1:7

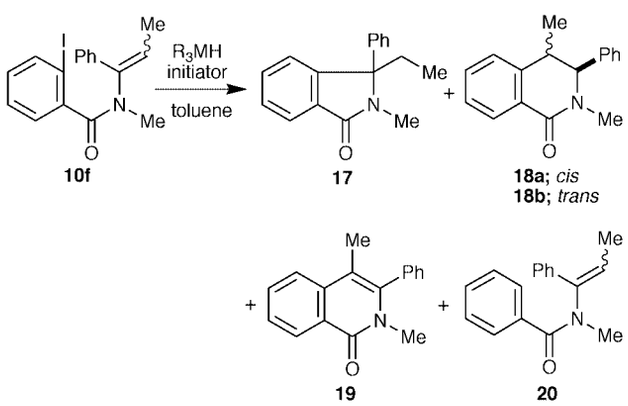
[a] ACN was used as a radical initiator except for entry 3 (Et_3B). [b] For mol equiv. of R_3MH, see Experimental section. [c] Rate of addition of R_3MH. [d] Yields of **17** and **18a**,**b** were estimated by the ratios of their mixtures, and isolated yields are indicated for **19** and **20**. [e] The ratios of **18a** and **18b** are 1.7:1 for entry 1, 1.9:1 for entry 2, and 2.8:1 for entry 4. [f] After addition of Bu_3SnH, the mixture was further heated for 30 min. [g] Et_3B was added to a solution of enamide **10f** and Bu_3SnH, and the mixture was stirred for 14 h.



Scheme 4

to result in an increase in the amount of the five-membered lactam **13**. On the other hand, at low concentrations of hydride (entry 1), a subsequent neophyl rearrangement of the radical **VIa** to **VIIIa** competes successfully with reduction by Bu_3SnH to result in an increase in the amount of the six-membered lactams **14** and **15**. When tris(trimethylsilyl)silane [$(TMS)_3SiH$] was used as a hydride in place of the Bu_3SnH used in entry 1, the ratio of **13**:(**14** + **15**) (1:7.3) was essentially the same as that (1:6.9) for entry 1, whereas an increase in the amount of the oxidation product **15** was observed (entry 4). $(TMS)_3SiH$ is a sterically more demanding hydride than Bu_3SnH, so that the radical **VIIIa** is resistant to an attack by $(TMS)_3SiH$, resulting in an increase in the amount of the oxidation product **15**.

The results obtained with the enamide **10f** strongly supported the assumption of the neophyl rearrangement of the radicals **VI** to **VIII**. Thus, treatment of the enamide **10f** with a high concentration of Bu_3SnH in the presence of triethylborane at room temperature gave only the 5-*exo* cyclisation product **17** in 54% yield along with **10f** (28% yield) (entry 3 in Table 2). By contrast, when the enamide **10f** was treated with a low concentration of Bu_3SnH (Scheme 5), a mixture of the 5-*exo* cyclisation product **17** and the 6-*endo* cyclisation products, 3,4-*cis* and -*trans* tetrahydroisoquinolinones **18a**,**b**, was obtained in 48% combined yield, together with the oxidation product **19** (16% yield) (entry 1 in Table 2). The structures of **18a**,**b** were confirmed by a comparison of the coupling constants between 3-H and 4-H with the reported values of the related compounds.[8] Thus, the *cis*-isomer **18a** had a relatively large coupling constant (6.3 Hz) and the *trans*-isomer had a small one (1.3 Hz). The ^1H NMR spectrum of the mixture of **17** and **18a**,**b** showed the ratio of **17**:**18a**,**b** to be 1:5, and hence the ratio of the 5-*exo* cyclisation product and the 6-*endo* cyclisation products, **17**:(**18a**,**b** + **19**), was estimated to be 1:6.7.



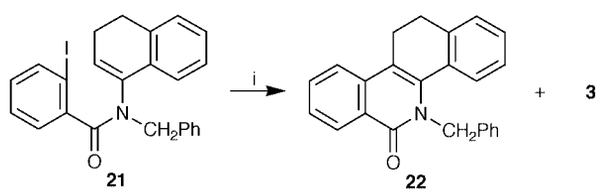
Scheme 5 *Reagents and conditions*: Bu_3SnH, ACN or Et_3B, toluene, reflux or room temp. or $(TMS)_3SiH$, ACN, toluene, reflux.

The exclusive formation of **17** from **10f** for entry 3 can be rationalised as follows. The radical **Vb** formed from **10f** cyclises in a kinetically favoured 5-*exo* manner to give **VIb** (Scheme 4). A subsequent neophyl rearrangement of **VIb** may be retarded for stereoelectronic reasons due probably to the presence of the methyl substituent (R = Me), and hence the radical **VIb** is

rapidly attacked by a high concentration of Bu_3SnH to give **17**. On the other hand, at high temperature and at low concentration of Bu_3SnH (entry 1) the radical **VIb** undergoes the neophyl rearrangement to give **VIIIb** *via* **VIIb**, thereby leading to the 6-*endo* cyclisation products **18a**,**b** and **19** as the major products. When Bu_3SnH was added rapidly (within 10 min) to a boiling solution of **10f** in toluene, the formation of the 5-*exo* cyclisation product **17** increased (entry 2 in Table 2) as compared with entry 1. As in the case of **10e**, when $(TMS)_3SiH$ was used in place of the Bu_3SnH used in entry 1, an increase in the amount of the oxidation product **19** was observed (entry 4).

Finally, in order to see the possibility of a consecutive 5-*exo* cyclisation and neophyl rearrangement for the formation of the 6-*endo* cyclisation product **2** from **1**, we examined the reaction of the enamide **21** having an iodine atom on the aryl group instead of the use of the bromide **1**.

When the enamide **21** was treated with Bu_3SnH under similar conditions to those described above for entry 3 in Table 2 (triethylborane, toluene, at room temperature), the unsaturated six-membered lactam **22** was obtained in 20% yield, along with a mixture of **3** and a considerable amount of an unidentified product (Scheme 6). Thus, it seems reasonable to assume that the direct *endo* cyclisation might be operating in the reactions of the enamide **21**. The 5-*exo* cyclisation leading to **3** might be retarded for stereoelectronic reasons caused by the formation of the spiro ring of **3**.



Scheme 6 *Reagents and conditions*: i, Bu_3SnH, Et_3B, toluene, room temp.

In summary, we revealed that the aryl radical cyclisations of the enamides **10a**–**f** usually occurred in a 5-*exo* manner, regardless of the presence of an aryl substituent on the vinylic carbon atom α to the nitrogen atom, and that at low concentration of hydride a consecutive 5-*exo* cyclisation and neophyl rearrangement took place to lead to the apparent formation of the 6-*endo* cyclisation products. The present results strongly suggest that the difference in the stability of the cyclised intermediate radicals is not always sufficient to explain the product distribution of the radical cyclisations. Exceptions may be the cases where severe steric repulsion exists in an alternative mode of cyclisation.

Experimental

Mps were measured on a Yanagimoto MP-S2 micro melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO-IR-A-100 spectrophotometer. ^1H NMR (60, 270 and 300 MHz) spectra were measured on a JEOL JNM-PMX 60, a JEOL JNM-EX 270 or a Varian XL-300 spectrometer for solutions in $CDCl_3$. δ Values quoted are relative to tetramethylsilane and *J* values are given in Hz. Exact mass determinations (EI and FAB mass spectra) were obtained on a JEOL-SX 102A instrument. Column chromatography was performed on silica gel 60 PF_{254} (Nacalai Tesque) under pressure.

2-Iodo-*N*-methyl-*N*-[2-(phenylthio)ethyl]benzamide 7

A solution of 2-iodobenzoyl chloride **6** (1.0 g, 3.75 mmol) in toluene (10 cm^3) was added to an ice-cooled solution of *N*-methyl-2-(phenylthio)ethylamine[9] (645 mg, 3.86 mmol), triethylamine (581 mg, 5.74 mmol) and 4-(dimethylamino)-pyridine (84 mg, 0.75 mmol) in toluene (30 cm^3), and the mixture was stirred at room temperature for 1 h. Water was added and the organic phase was washed successively with saturated aq. $NaHCO_3$, 10% aq. HCl, and brine, dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (2:1)] to give **7** (1.17 g, 79%) as an oil (Found: C, 49.1; H, 4.1; N, 3.4. $C_{16}H_{16}INOS$ requires C, 48.4; H, 4.1; N, 3.5%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1630; δ_H(270 MHz) 2.88 and 3.13 (total 3 H, both s, NMe), 2.9–4.0 (4 H, m) and 7.0–7.85 (9 H, m, ArH).

N-Ethenyl-2-iodo-*N*-methylbenzamide 10a

To a solution of **7** (2.33 g, 5.87 mmol) in dichloromethane (25 cm^3) was added dropwise a solution of MCPBA (1.11 g, 6.43 mmol) in dichloromethane (25 cm^3) at 0 °C during 1.5 h, and the mixture was stirred at the same temperature for 30 min. The reaction mixture was washed with saturated aq. $NaHCO_3$, dried ($MgSO_4$) and concentrated. The resulting crude sulfoxide was dissolved in xylene (50 cm^3) containing $NaHCO_3$ (1.0 g, 11.9 mmol), and the mixture was heated at reflux for 20 h. The precipitates were filtered off and the filtrate was concentrated. The crude material was chromatographed on silica gel [hexane–AcOEt (7:1)] to give **10a** (1.29 g, 77%) as an oil (Found: M^+, 286.9798. $C_{10}H_{10}INO$ requires *M*, 286.9807); $\nu_{max}(CCl_4)/cm^{-1}$ 1675 and 1620; δ_H(300 MHz) 2.94 (3 H × 1/4, s, NMe), 3.28 (3 H × 3/4, s, NMe), 4.28 (3/4 H, dd, *J* 9.0 and 1.3, one of CH=CH_2), 4.55 (3/4 H, dd, *J* 15.3 and 1.3, one of CH=CH_2), 4.629 (1/4 H, dd, *J* 9.0 and 1.1, one of CH=CH_2), 4.632 (1/4 H, dd, *J* 16.1 and 1.1, one of CH=CH_2), 6.42 (3/4 H, dd, *J* 15.3 and 9.0, C*H*=CH_2), 7.12 (1 H, td, *J* 7.6 and 1.7, ArH), 7.23 (3/4 H, dd, *J* 7.6 and 1.7, ArH), 7.24 (1/4 H, dd, *J* 7.6 and 1.7, ArH), 7.42 (1 H, td, *J* 7.5 and 1.1, ArH), 7.69 (1/4 H, dd, *J* 16.1 and 9.0, C*H*=CH_2) and 7.85 (1 H, dd, *J* 8.0 and 1.1, ArH).

(*E*)-2-Iodo-*N*-methyl-*N*-(2-phenylethenyl)benzamide 10b

To a solution of excess methylamine in diethyl ether (20 cm^3) were added phenylacetaldehyde (*ca.* 50% in diethyl phthalate) (1 g, 4.16 mmol for phenylacetaldehyde) and $MgSO_4$ (10 g), and the mixture was stirred at room temperature for 10 h. $MgSO_4$ was filtered off, the filtrate was concentrated, and the residue containing the imine **8a** was dissolved in dichloromethane (10 cm^3). To this were added successively triethylamine (870 mg, 8.6 mmol), 4-(dimethylamino)pyridine (DMAP) (100 mg, 0.82 mmol) and a solution of **6** (1.11 g, 4.17 mmol) in dichloromethane (5 cm^3) at 0 °C, and the mixture was stirred at room temperature for 5 h. Water was added and the reaction mixture was extracted with chloroform. The extract was washed successively with 5% aq. HCl, saturated aq. $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (5:1)] to give **10b** (362 mg, 24%), mp 113.5–114.5 °C (from hexane–AcOEt) (Found: C, 53.0; H, 3.9; N, 3.7. $C_{16}H_{14}INO$ requires C, 52.9; H, 3.9; N, 3.9%); $\nu_{max}(CCl_4)/cm^{-1}$ 1670 and 1635; δ_H(60 MHz) 3.08 and 3.41 (total 3 H, both s, NMe), 6.06 and 6.12 (total 1 H, both d, *J* 14.5, C*H*=Ph), 6.88 and 8.24 (total 1 H, both d, *J* 14.5, NCH=), 7.0–7.9 (9 H, m, ArH).

2-Iodo-*N*-methyl-*N*-(2,2-diphenylethenyl)benzamide 10c

A solution of diphenylacetaldehyde (981 mg, 5 mmol) in toluene (5 cm^3) was added to methylamine (5 cm^3) at −78 °C and the mixture was heated in a sealed tube at 100 °C for 2 h. The reaction vessel was cooled to −78 °C, the stopper was removed, and the reaction mixture was transferred carefully to a round-bottomed flask. After removal of any excess methylamine and solvent *in vacuo*, the residue containing the imine **8b** was dissolved in benzene (20 cm^3). Triethylamine (1.01 g, 10 mmol), DMAP (61 mg, 0.5 mmol) and a solution of acid chloride **6** (1.47 g, 5.5 mmol) in benzene (10 cm^3) were added to this solution at 0 °C, and the mixture was stirred at room temper-

ature for 1 h. The reaction mixture was washed successively with 5% aq. HCl, saturated aq. $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (8:1)] to give **10c** (1.60 g, 72%), mp 130.5–131 °C (from hexane–AcOEt) (Found: C, 59.8; H, 4.1; N, 3.1. $C_{22}H_{18}INO$ requires C, 60.15; H, 4.1; N, 3.2%); $\nu_{max}(CCl_4)$/cm^{-1} 1660; δ_H(60 MHz) 3.01 (3 H, s, NMe), 6.47 (1 H, s, CH=C) and 6.7–7.8 (14 H, m, ArH).

Diethyl [*N*-(2-iodobenzoyl)-*N*-methylaminomethylene]malonate 10d

A solution of diethyl ethoxymethylenemalonate (500 mg, 2.31 mmol) in toluene (5 cm^3) was added to anhydrous methylamine (5 cm^3) at −78 °C and the mixture was heated in a sealed tube at 100 °C for 2 h. A similar work-up to that described above for the preparation of **8a** gave diethyl methylaminomethylenemalonate **9** (465 mg, quant.), which was used immediately in the next step without further purification; δ_H(60 MHz) 1.28 (3 H, t, *J* 7.2, CMe), 1.31 (3 H, t, *J* 7.2, CMe), 3.13 (3 H, br s, NMe), 4.15 (2 H, q, *J* 7.2, OCH_2), 4.19 (2 H, q, *J* 7.2, OCH_2), 7.7–8.2 (1 H, br) and 8.5–9.5 (1 H, br).

A solution of **9** (465 mg, 2.31 mmol) in THF (10 cm^3) was added dropwise to a suspension of sodium hydride [60% dispersion in mineral oil (360 mg, 9.0 mmol), washed several times with hexane] in THF (10 cm^3) at 0 °C and the mixture was stirred at the same temperature for 30 min. To this was added a solution of acid chloride **6** (1.76 g, 6.6 mmol) in THF (10 cm^3) at 0 °C and the mixture was stirred at room temperature for 30 min. The solvent was evaporated off and the residue was dissolved in diethyl ether (30 cm^3). The organic phase was washed with brine and 10% aq. K_2CO_3, dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica gel [hexane–AcOEt (8:1)] to give **10d** as an oil (1.01 g, quant.) (Found: C, 44.8; H, 4.4; N, 3.1. $C_{16}H_{18}INO_5$ requires C, 44.6; H, 4.2; N, 3.3%); $\nu_{max}(CCl_4)$/cm^{-1} 1720, 1695 and 1615; δ_H(60 MHz) 1.19 (3 H, t, *J* 7.5, CMe), 1.34 (3 H, t, *J* 7.5, CMe), 3.26 (3 H, s, NMe), 4.11 (2 H, q, *J* 7.5, OCH_2), 4.28 (2 H, q, *J* 7.5, OCH_2) and 6.9–7.9 (5 H, m, ArH and CH=C).

2-Iodo-*N*-methyl-*N*-(1-phenylethenyl)benzamide 10e

Following the procedure described above for the preparation of **10c**, acetophenone (1.00 g, 8.32 mmol) was treated with anhydrous methylamine (5 cm^3), and the resulting crude imine **8c** was treated with acid chloride **6** (2.44 g, 9.15 mmol) in the presence of triethylamine (926 mg, 9.15 mmol) and DMAP (101 mg, 0.83 mmol) to give **10e** (2.28 g, 75%), mp 109–110 °C (from hexane–AcOEt) (Found: C, 52.95; H, 3.95; N, 3.7. $C_{16}H_{14}INO$ requires C, 52.9; H, 3.9; N, 3.9%); $\nu_{max}(CCl_4)$/cm^{-1} 1655; δ_H(60 MHz) 3.30 (3 H, s, NMe), 5.25 (2 H, s, C=CH_2) and 6.5–7.8 (9 H, m, ArH).

2-Iodo-*N*-methyl-*N*-(1-phenylprop-1-enyl)benzamide 10f

Following the procedure described above for the preparation of **10c**, propiophenone (1 g, 7.45 mmol) was treated with anhydrous methylamine (3 cm^3), and the resulting crude imine **8d** was treated with acid chloride **6** (2 g, 7.51 mmol) in the presence of triethylamine (1.01 g, 10 mmol) and DMAP (190 mg, 1.56 mmol) to give **10f** (815 mg, 29%), mp 70–72 °C (from hexane–AcOEt) (Found: C, 54.0; H, 4.4; N, 3.5. $C_{17}H_{16}INO$ requires C, 54.1; H, 4.3; N, 3.7%); $\nu_{max}(CHCl_3)$/cm^{-1} 1630; δ_H(270 MHz) 1.62 (3 H × 5/6, d, *J* 7.3, CMe), 1.89 (3 H × 1/6, d, *J* 7.3, CMe), 2.85 (3 H × 1/6, s, NMe), 3.37 (3 H × 5/6, s, NMe), 5.91 (5/6 H, q, *J* 7.3, MeC*H*=), 6.10 (1/6 H, q, *J* 7.3, MeC*H*=), 6.8–7.5 (8 H, m , ArH), 7.70 (5/6 H, d, *J* 7.9, ArH) and 7.84 (1/6 H, d, *J* 7.9, ArH).

Radical cyclisation of 10a

General procedure. To a boiling solution of **10a** (263 mg, 0.92 mmol) in toluene (37 cm^3) was added dropwise a solution of Bu_3SnH (400 mg, 1.37 mmol) and ACN (45 mg, 0.18 mmol) in toluene (37 cm^3) *via* a syringe during 1.5 h, and the mixture was further refluxed for 1 h. After evaporation of the solvent, diethyl ether (20 cm^3) and 8% aq. KF (20 cm^3) were added to the residue, and the whole was vigorously stirred at room temperature for 30 min. The organic phase was separated and the aqueous phase was further extracted with diethyl ether (3 × 10 cm^3). The combined organic phase was dried ($MgSO_4$) and concentrated, and the residue was chromatographed on silica gel [hexane–AcOEt (8:1)]. The first fraction gave *N-ethenyl-N-methylbenzamide* **12a** (37 mg, 25%) as an oil (Found: M$^+$, 161.0833. $C_{10}H_{11}NO$ requires *M*, 161.0841); $\nu_{max}(CCl_4)$/cm^{-1} 1665 and 1620; δ_H(300 MHz) 3.24 (3 H, br s, NMe), 4.20–4.34 (1 H, br, one of CH=CH_2), 4.51 (1 H, d, *J* 15.5, one of CH=CH_2), 6.68–6.92 (1 H, br, C*H*=CH_2) and 7.39–7.50 (5 H, m, ArH). The second fraction gave *2,3-dihydro-2,3-dimethyl-1H-isoindol-1-one* **11a** (88 mg, 60%) as an oil (Found: M$^+$, 161.0837); $\nu_{max}(CCl_4)$/cm^{-1} 1700; δ_H(60 MHz) 1.47 (3 H, d, *J* 6.5, 3-Me), 3.11 (3 H, s, NMe), 4.40 (1 H, q, *J* 6.5, 3-H) and 7.1–7.9 (4 H, m, ArH).

Radical cyclisation of 10b. Following the general procedure, **10b** (433 mg, 1.19 mmol) was treated with Bu_3SnH (520 mg, 1.79 mmol) and ACN (58 mg, 0.24 mmol). After work-up, the crude material was chromatographed on silica gel [hexane–AcOEt (7:1)]. The first fraction gave *(E)-N-methyl-N-(2-phenylethenyl)benzamide* **12b** (100 mg, 35%), mp 112.5–113 °C (from hexane–AcOEt) (Found: C, 80.9; H, 6.4; N, 5.9. $C_{16}H_{15}NO$ requires C, 81.0; H, 6.4; N, 5.9%); $\nu_{max}(CCl_4)$/cm^{-1} 1670 and 1635; δ_H(60 MHz) 3.31 (3 H, s, NMe), 5.98 (1 H, d, *J* 15, =C*H*Ph), 6.9–7.7 (11 H, m, ArH and NCH=). The second fraction gave *3-benzyl-2,3-dihydro-2-methyl-1H-isoindol-1-one* **11b** (154 mg, 55%) (Found: M$^+$, 237.1144. $C_{16}H_{15}NO$ requires *M*, 237.1154); $\nu_{max}(CCl_4)$/cm^{-1} 1700; δ_H(60 MHz) 2.82 (1 H, dd, *J* 14 and 7.5, one of CH_2Ph), 3.07 (3 H, s, NMe), 3.28 (1 H, dd, *J* 14 and 5.5, one of CH_2Ph), 4.58 (1 H, dd, *J* 7.5 and 5.5, 3-H) and 6.8–7.8 (9H, m, ArH).

Radical cyclisation of 10c. Following the general procedure, compound **10c** (250 mg, 0.57 mmol) was treated with Bu_3SnH (248 mg, 0.85 mmol) and ACN (27 mg, 0.11 mmol). After work-up, the crude material was chromatographed on silica gel [hexane–AcOEt (10:1)]. The first fraction gave *N-methyl-N-(2,2-diphenylethenyl)benzamide* **12c** (28 mg, 16%) as an oil (Found: M$^+$, 313.1461. $C_{22}H_{19}NO$ requires *M*, 313.1467); $\nu_{max}(CCl_4)$/cm^{-1} 1655; δ_H(60 MHz) 2.95 (3 H, s, NMe), 6.62 (1 H, s, CH=C) and 6.8–7.5 (15 H, m, ArH). The second fraction gave *2,3-dihydro-2-methyl-3-diphenylmethyl-1H-isoindol-1-one* **11c** (77 mg, 43%), mp 135.5–136.5 °C (from hexane–AcOEt) [Found: (M+H)$^+$, 314.1553. $C_{22}H_{20}NO$ requires *M*H$^+$, 314.1545]; $\nu_{max}(CCl_4)$/cm^{-1} 1700; δ_H(300 MHz) 2.89 (3 H, s, NMe), 4.59 (1 H, d, *J* 6.9, Ph_2CH), 5.19 (1 H, d, *J* 6.9, 3-H), 6.90–6.96 (2 H, m, ArH), 7.13–7.55 (11 H, m, ArH) and 7.76 (1 H, d, *J* 7.5, ArH).

Radical cyclisation of 10d. Following the general procedure, **10d** (800 mg, 1.85 mmol) was treated with Bu_3SnH (810 mg, 2.78 mmol) and ACN (90 mg, 0.37 mmol). After work-up, the crude material was chromatographed on silica gel [hexane–AcOEt (5:1)]. The first fraction gave *diethyl (N-benzoyl-N-methyl)aminomethylenemalonate* **12d** (76 mg, 13%) as an oil (Found: C, 63.15; H, 6.5; N, 4.4. $C_{16}H_{19}NO_5$ requires C, 62.9; H, 6.3; N, 4.6%); $\nu_{max}(CCl_4)$/cm^{-1} 1720, 1695 and 1615; δ_H(60 MHz) 1.19 (3 H, t, *J* 7, CMe), 1.34 (3 H, t, *J* 7, CMe), 3.30 (3 H, s, NMe), 4.14 (2 H, q, *J* 7, OCH_2), 4.34 (2 H, q, *J* 7, OCH_2), 7.28 (1 H, s, CH=C) and 7.47 (5 H, s, ArH). The second fraction gave *diethyl 2-(2,3-dihydro-2-methyl-1-oxo-1H-isoindol-3-yl)malonate* **11d** (367 mg, 65%) as an oil (Found: C, 62.6; H, 6.4; N, 4.6); $\nu_{max}(CCl_4)$/cm^{-1} 1740 and 1705; δ_H(300 MHz) 1.02 (3 H, t, *J* 7.1, CMe), 1.21 (3 H, t, *J* 7.1, CMe), 3.16 (3 H, s, NMe), 4.00 (2 H,

qd, *J* 7.1 and 1.8, one of OCH_2), 4.07 (1 H, d, *J* 3.5, 3-H), 4.22 (2 H, q, *J* 7.1, OCH_2), 5.14 (1 H, d, *J* 3.5, 3′-H), 7.42–7.60 (3 H, m, ArH) and 7.81 (1 H, d, *J* 7, ArH).

Radical cyclisation of 10e. *For entry 1 in Table 1.* To a boiling solution of **10e** (150 mg, 0.41 mmol) in toluene (50 cm^3) was added dropwise a solution of Bu_3SnH (205 mg, 0.71 mmol) and ACN (22 mg, 0.09 mmol) in toluene (50 cm^3) *via* a syringe during 4.5 h. After evaporation of the solvent, diethyl ether (80 cm^3) and 8% aq. KF (60 cm^3) were added to the residue, and the whole was vigorously stirred at room temperature for 5 h. The organic phase was separated and the aqueous phase was further extracted with diethyl ether (3 × 10 cm^3). The combined organic phase was dried ($MgSO_4$) and concentrated, and the residue was chromatographed on silica gel [hexane–AcOEt (4 : 1)]. The first fraction gave *N-methyl-N-(1-phenylethenyl)benzamide* **16** (13 mg, 13%) as an oil (Found: M^+, 237.1149. $C_{16}H_{15}NO$ requires *M*, 237.1154); $\nu_{max}(CHCl_3)/cm^{-1}$ 1630; δ_H(270 MHz) 3.24 (3 H, s, NMe), 4.85 (1 H, s, one of C=CH_2), 5.35 (1 H, s, one of C=CH_2) and 7.18–7.51 (10 H, m, ArH). The second fraction gave *1,2-dihydro-2-methyl-3-phenylisoquinolin-1-one* **15** (16 mg, 16%) as an oil (Found: M^+, 235.0994. $C_{16}H_{13}NO$ requires *M*, 235.0997); $\nu_{max}(CHCl_3)/cm^{-1}$ 1650 and 1620; δ_H(270 MHz) 3.43 (3 H, s, NMe), 6.46 (1 H, s, 4-H), 7.26–7.67 (8 H, m, ArH) and 8.46 (1 H, d, *J* 8.1, ArH). The third fraction gave a mixture of *2,3-dihydro-2,3-dimethyl-3-phenyl-1H-isoindol-1-one* **13** [$\nu_{max}(CHCl_3)/cm^{-1}$ 1680; δ_H(270 MHz) 1.88 (3 H, s, 3-Me), 2.86 (3 H, s, NMe), 6.98–7.39 (8 H, m, ArH) and 7.74–7.82 (1 H, m, ArH)] and *1,2,3,4-tetrahydro-2-methyl-3-phenylisoquinolin-1-one* **14** (54 mg) in a ratio of 1 : 5.1. Recrystallisation of this mixture from hexane–AcOEt gave pure **14**, mp 113.5–114 °C (from hexane–AcOEt) (Found: C, 80.9; H, 6.4; N, 5.8. $C_{16}H_{15}NO$ requires C, 81.0; H, 6.4; N, 5.9%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1640; δ_H(270 MHz) 3.03 (1 H, dd, *J* 15.8 and 3.0, one of 4-H_2), 3.10 (3 H, s, NMe), 3.66 (1 H, dd, *J* 15.8 and 6.9, one of 4-H_2), 4.76 (1 H, dd, *J* 6.9 and 3.0, 3-H), 6.98–7.39 (8 H, m, ArH) and 8.11–8.18 (1 H, m, ArH).

For entry 2 in Table 1. To a boiling solution of **10e** (150 mg, 0.41 mmol) in toluene (45 cm^3) was added dropwise a solution of Bu_3SnH (151 mg, 0.52 mmol) and ACN (21 mg, 0.09 mmol) in toluene (20 cm^3) *via* a syringe during 5 min, and the mixture was further heated at reflux for 30 min. After work-up, the crude material was chromatographed on silica gel [hexane–AcOEt (4 : 1)]. The first fraction gave **16** (13 mg, 13%). The second fraction gave **15** (6 mg, 6%). The third fraction gave a mixture of **13** and **14** (71 mg) in a ratio of 1 : 3.

For entry 3 in Table 1. To a stirred solution of **10e** (200 mg, 0.55 mmol) and Bu_3SnH (195 mg, 0.67 mmol) in toluene (55 cm^3) was added triethylborane (1.06 mol dm^{-3} solution in hexane; 2.1 cm^3, 2.22 mmol) at 0 °C, and the mixture was stirred at room temperature for 20 h. After evaporation of the solvent, a solution of the residue in diethyl ether (50 cm^3) was treated with 8% aq. KF (50 cm^3) in the usual manner. To the separated ethereal phase was added Al_2O_3 (10 g) and the whole was vigorously stirred at room temperature for 1 h. The inorganic materials were filtered off, the solvent was evaporated off and the residue was chromatographed on silica gel [hexane–AcOEt (4 : 1)]. The first fraction gave **15** (44 mg, 34%). The second fraction gave a mixture of **13** and **14** (59 mg) in a ratio of 1 : 1.2.

For entry 4 in Table 1. To a boiling solution of **10e** (150 mg, 0.41 mmol) in toluene (4 cm^3) was added dropwise a solution of $(TMS)_3SiH$ (201 mg, 0.81 mmol) and ACN (22 mg, 0.09 mmol) in toluene (40 cm^3) *via* a syringe during 4.5 h. After work-up, the crude material was chromatographed on silica gel [hexane–AcOEt (4 : 1)]. The first fraction gave **15** (45 mg, 47%). The second fraction gave a mixture of **13** and **14** (19 mg) in a ratio of 4 : 5.

Radical cyclisation of 10f. *For entry 1 in Table 2.* According to a procedure similar to that described above for entry 1 for the cyclisation of **10e**, **10f** (100 mg, 0.265 mmol) was treated with Bu_3SnH (100 mg, 0.34 mmol) and ACN (13 mg, 0.05 mmol). After work-up, the crude material was chromatographed on silica gel [hexane–AcOEt (4 : 1)]. The first fraction gave *N-methyl-N-(1-phenylprop-1-enyl)benzamide* **20** (14 mg, 21%), mp 138–139 °C (from hexane–AcOEt) (Found: C, 80.9; H, 6.9; N, 5.4. $C_{17}H_{17}NO$ requires C, 81.2; H, 6.8; N, 5.6%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1630; δ_H(270 MHz) 1.55 (3 H, d, *J* 7.3, CMe), 3.21 (3 H, s, NMe), 5.86 (1 H, q, *J* 7.3, MeC*H*=) and 7.13–7.50 (10 H, m, ArH). The second fraction gave *1,2-dihydro-2,4-dimethyl-3-phenylisoquinolin-1-one* **19** (10 mg, 14%), mp 101–102 °C (from hexane–AcOEt) (Found: C, 81.8; H, 6.2; N, 5.6. $C_{17}H_{15}NO$ requires C, 81.90; H, 6.1; N, 5.6%) (Found: M^+, 249.1155. $C_{17}H_{15}NO$ requires *M*, 249.1154); $\nu_{max}(CHCl_3)/cm^{-1}$ 1640; δ_H(270 MHz) 2.02 (3 H, s, 4-Me), 3.25 (3 H, s, NMe), 7.22–7.75 (8 H, m, ArH) and 8.54 (1 H, d, *J* 7.9, ArH). The third fraction gave a mixture of *3-ethyl-2,3-dihydro-2-methyl-3-phenyl-1H-isoindol-1-one* **17** and *cis*- and *trans-1,2,3,4-tetrahydro-2,4-dimethyl-3-phenylisoquinolin-1-ones* **18a**,**b** (total 32 mg, total 48%) in a ratio of 1 : 3.1 : 1.9. This mixture was further chromatographed on silica gel [hexane–AcOEt (8 : 1)] to give pure **18b**, **17** and **18a** in order of elution. Compound **18b**: mp 89.5–90.5 °C (Found: C, 81.2; H, 6.8; N, 5.5); $\nu_{max}(CHCl_3)/cm^{-1}$ 1640; δ_H(270 MHz) 1.48 (3 H, d, *J* 7.3, 4-Me), 3.07–3.20 (1 H, m, 4-H), 3.13 (3 H, s, NMe), 4.48 (1 H, d, *J* 1.3, 3-H), 6.95–7.40 (8 H, m, ArH) and 8.13–8.17 (1 H, m, ArH). Compound **17**: mp 138–138.5 °C (Found: C, 81.35; H, 6.9; N, 5.5) (Found: M^+, 251.1305. $C_{17}H_{17}NO$ requires *M*, 251.1310); $\nu_{max}(CHCl_3)/cm^{-1}$ 1680; δ_H(270 MHz) 0.49 (3 H, t, *J* 7.3, CMe), 2.39 (1 H, dq, *J* 14.2 and 7.3, one of CH_2), 2.57 (1 H, dq, *J* 14.2 and 7.3, one of CH_2), 2.81 (3 H, s, NMe), 7.10–7.50 (8 H, m, ArH) and 7.84–7.92 (1 H, m, ArH). Compound **18a**: mp 131–132 °C (Found: C, 81.3; H, 6.9; N, 5.5) (Found: M^+, 251.1307); $\nu_{max}(CHCl_3)/cm^{-1}$ 1640; δ_H(270 MHz) 1.19 (3 H, d, *J* 6.9, 4-Me), 3.07 (3 H, s, NMe), 3.79 (1 H, quintet, *J* 6.9, 4-H), 4.46 (1 H, d, *J* 6.3, 3-H), 6.88 (2 H, d, *J* 7.9, ArH), 7.06–7.47 (6 H, m, ArH) and 8.18 (1 H, dd, *J* 7.3 and 1.7, ArH).

For entry 2 in Table 2. According to a procedure similar to that described above for entry 2 for the cyclisation of **10e**, **10f** (100 mg, 0.265 mmol) was treated with Bu_3SnH (100 mg, 0.34 mmol) and ACN (13 mg, 0.05 mmol). After work-up, the crude material was chromatographed on silica gel [hexane–AcOEt (4 : 1)]. The first fraction gave **20** (20 mg, 30%). The second fraction gave **19** (5 mg, 8%). The third fraction gave a mixture **17** and **18a**,**b** (total 38 mg, total 57%) in a ratio of 1 : 2.2 : 1.2.

For entry 3 in Table 2. According to a procedure similar to that described above for entry 3 for the cyclisation of **10e**, **10f** (100 mg, 0.265 mmol) was treated with Bu_3SnH (100 mg, 0.34 mmol) and triethylborane (1.06 mol dm^{-3} solution in hexane; 1.5 cm^3, 1.6 mmol). After work-up, the crude material was chromatographed on silica gel [hexane–AcOEt (4 : 1)]. The first fraction gave **20** (19 mg, 28%). The second fraction gave **17** (36 mg, 54%).

For entry 4 in Table 2. According to a procedure similar to that described above for entry 4 for the cyclisation of **10e**, **10f** (100 mg, 0.265 mmol) was treated with $(TMS)_3SiH$ (105 mg, 0.42 mmol) and ACN (19 mg, 0.08 mmol). After work-up, the crude material was chromatographed on silica gel [hexane–AcOEt (4 : 1)]. The first fraction gave **20** (3 mg, 5%). The second fraction gave **19** (31 mg, 48%). The third fraction gave a mixture **17** and **18a**,**b** (total 16 mg, total 24%) in a ratio of 2.3 : 2.8 : 1.

N-Benzyl-*N*-(3,4-dihydro-1-naphthyl)-2-iodobenzamide 21

Using the procedure reported by Grigg,[10] compound **21** was prepared from 1-tetralone, benzylamine and acid chloride **6**, mp 113.5–114.5 °C (from hexane–AcOEt), lit.,[10] mp 115–116 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1635; δ_H(270 MHz) 1.72–1.90 (1 H, m), 1.90–2.09 (1 H, m), 2.25–2.42 (1 H, m), 2.42–2.60 (1 H, m), 4.05 (1 H, d, *J* 14.2, one of NCH_2), 5.69 (1 H, dd, *J* 5.3 and 4.3,

C=CH), 5.80 (1 H, d, *J* 14.2, one of NCH_2), 6.79–7.50 (12 H, m, ArH) and 7.72 (1 H, d, *J* 7.6, ArH).

Radical cyclisation of 21

To a stirred solution of **21** (100 mg, 0.21 mmol) and Bu_3SnH (77 mg, 0.26 mmol) in toluene (20 cm^3) was added triethylborane (1.06 mol dm^{-3} solution in hexane; 1.2 cm^3, 1.27 mmol) at 0 °C, and the mixture was stirred at room temperature for 4 h. After work-up as described above for entry 3 for **10e**, the crude material was chromatographed on silica gel [hexane–AcOEt (4:1)]. The first fraction gave 5-benzyl-11,12-dihydrobenzo[*c*]-phenanthridin-6(5*H*)-one **22**[11] (14 mg, 20%), mp 130–131 °C (from diethyl ether), lit.,[11] mp 129–131 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1640; δ_H(270 MHz) 2.84 (4 H, s, CH_2CH_2), 5.57 (2 H, s, NCH_2), 7.0–7.6 (12 H, m) and 8.48 (1 H, d, *J* 7.9, 4-H). The second fraction gave a mixture of **3**[2a] and a considerable amount of an unidentified product (9 mg).

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