Cathodic reduction of *N*-(2-iodophenyl)-*N*-alkylcinnamides: a novel sequential electrochemical radical cyclisation and hydroxylation

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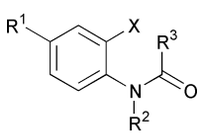
In recent years, intramolecular aryl radical cyclisation has emerged as a useful route for the synthesis of benzannulated heterocycles and carbocycles. The aryl radicals are generated *in situ* from aryl halides (iodides or bromides) with tributylstannyl hydride–AIBN, SmI_2, Co(I) or under photochemical conditions. The present work envisages the generation of aryl radicals by cathodic reduction of the carbon–iodine bond of *N*-(2-iodophenyl)-*N*-alkylcinnamides and their intramolecular cyclisation. The cathodic reduction of *N*-(2-iodophenyl)-*N*-alkylcinnamides under deaerated conditions in DMF gave 1-alkyl-3-benzylindolin-2-ones regioselectively and in the presence of oxygen yielded surprisingly 1-alkyl-3-hydroxy-3-benzylindolin-2-ones. Both these products were formed by a 5-*exo*-*trig* process in good yields. A mechanism for the formation of the products has been proposed through the use of cyclic voltammetry, coulometry and controlled-potential electrolysis as well as deuterium labelling.

Introduction

There continues to be an immense interest in intra- and intermolecular electrochemical cyclisation reactions of dicarbonyl, olefinic carbonyl and α,β-unsaturated carbonyl compounds with respect to the mechanistic details of the cyclisation processes and subsequent developments of practical electrosyntheses based on the electrolyses of these compounds.[1] The electrochemically induced intramolecular tethering of a variety of activated carbonyls,[2] and olefinic[3] and allenic groups[4] on to an aldehyde or a ketone and electrochemically induced Diels–Alder reactions[1,5] and electrocyclic ring[6] closure reactions are well known. The utility of tributylstannyl radical-mediated cyclisation in the syntheses of benzannulated carbocycles[7] and heterocycles[8] is well documented. Intramolecular cyclisation of *N*-(2-iodophenyl)-*N*-α,β-unsaturated carboxamides under Pd(II)-catalyzed,[9] Sm(II)[10] or Co(I)[11] and photochemically induced[12] conditions has been investigated. These reactions led to a mixture of products while the tributylstannyl radical-mediated cyclisation of *N*-(2-iodophenyl)-*N*-alkylcinnamides afforded 1-alkyl-3-benzylindolin-2-ones regioselectively.[13] Strangely, reports on the electrochemically induced aryl radical cyclisation are scarce and mainly confined to 2-halobenzanilides,[14] iodobenzylisoquinolinium salts[15] and enaminones.[16] The potential of this technique for radical cyclisation methodology has not been fully explored. It will be interesting to generate the aryl radical or aryl anion of *N*-(2-iodophenyl)-*N*-alkylcinnamides by cathodic reduction of the carbon–iodine bond and study the chemical behavior of these radicals/anions (Scheme 1), particularly in the light of published work on the intramolecular cyclisation of these amides under tributylstannyl radical-mediated (tributylstannyl hydride–AIBN) conditions.[13] *N*-(2-Iodophenyl)-*N*-alkylcinnamides undergo cathodic cyclisation and afforded 1-alkyl-3-benzylindolin-2-ones regioselectively. Surprisingly, electrolyses of *N*-(2-iodophenyl)-*N*-alkylcinnamides in DMF solutions in the presence of oxygen yielded 1-alkyl-3-hydroxy-3-benzylindolin-2-ones. This has prompted us to investigate the mechanism of this cathodic cyclisation and hydroxylation using deuterium-labelled substrates, which revealed that *N*-(2-iodophenyl)-*N*-alkylcinnamides in aerated media undergo reductive cyclisation to form 1-alkyl-3-benzylindolin-2-ones, which get oxidized to 1-alkyl-3-hydroxy-3-benzylindolin-2-ones by the superoxide generated *in situ* from the cathodic reduction of oxygen. Though α-hydroxylation of ketones[17] and indolin-2-ones[18] by oxygen in alkaline media and the anodic hydroxylations of carbonyl compounds[19] in methanol containing potassium iodide are known, the hydroxylation of carbonyl compounds under cathodic conditions in the presence of oxygen has not yet been reported.

Table 1 Various amides of *N*-(2-iodophenyl)-*N*-alkylanilines and α,β-unsaturated acids



Compound	R^1	R^2	R^3	X
1a	CH_3	$PhCH_2$	CH_3	I
1b	CH_3	$PhCH_2$	PhCH=CH	—
1c	CH_3	H	PhCH=CH	I
1d	CH_3	CH_3	PhCH=CH	I
1e	CH_3	CH_3CH_2	PhCH=CH	I
1f	CH_3	$PhCH_2$	PhCH=CH	I
1g	Cl	CH_3	PhCH=CH	I
1h	Cl	$PhCH_2$	PhCH=CH	I
1i	Br	$PhCH_2$	PhCH=CH	I
1j	H	CH_3	PhCH=CH	I
1k	H	$PhCH_2$	PhCH=CH	I

Results and discussion

Cyclic voltammetry of *N*-(2-iodophenyl)-*N*-alkylcinnamides

Various *N*-(2-iodophenyl)-*N*-alkylcinnamides were prepared according to the literature procedure[13] and characterised (Table 1). The cyclic voltammetric (CV) studies of **1a**–**1k** (5.0×10^{-3} M, Table 2) at a hanging mercury drop electrode (hmde) and at various sweep rates were performed in DMF containing

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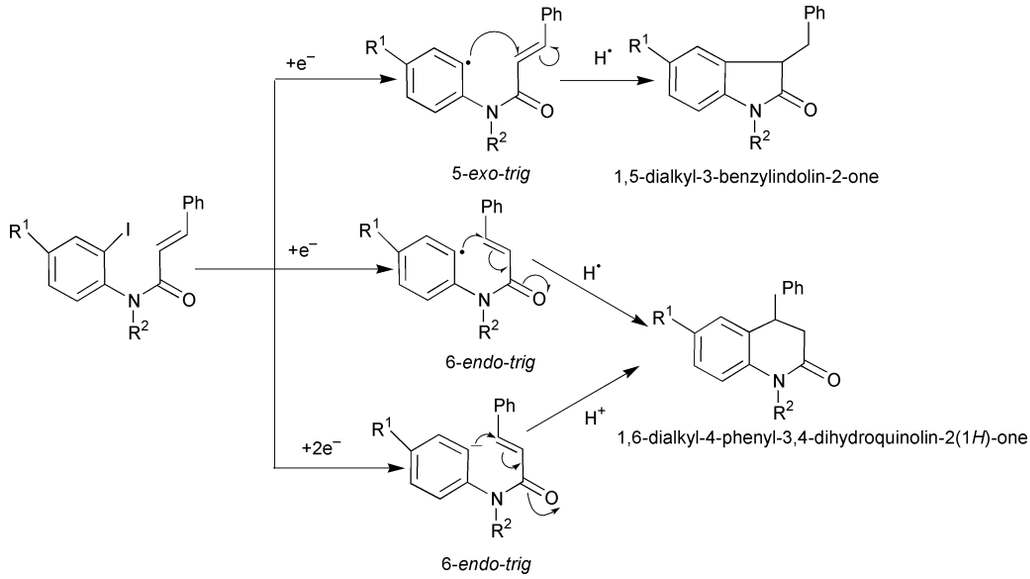


Scheme 1

Table 2 CV data of amides **1a**–**1k** (5.0×10^{-3} M) in DMF at 100 mV s^{-1} sweep rate

Compound	First cathodic peak		Second cathodic peak	
	Potential $-E_{p,cI}$/V [a]	Current $i_{p,cI}$/μA	Potential $-E_{p,cII}$/V [a]	Current $i_{p,cII}$/μA
1a	1.49	30.19	—	—
1b	1.69	24.10	2.12	15.33
1c	1.47	25.90	1.74	28.70
1d	1.59	47.10	1.75	24.10
1e	1.59	43.50	1.77	23.90
1f	1.48	40.90	1.68	20.30
1g	1.32	40.61	1.72	19.62
1h	1.20	31.30	1.64	25.50
1i	1.14	36.90	1.66	34.05
1j	1.57	52.46	1.74	24.42
1k	1.43	37.58	1.62	19.70

[a] Measured *versus* a silver quasi-reversible electrode.

tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. These studies were carried out to ascertain the reduction potentials of the C–I bond and C=C double bond in the substrates. The CV data obtained are presented in Table 2.

It may be pointed out that *N*-(2-iodo-4-methylphenyl)-*N*-benzylacetamide, **1a**, gave an irreversible peak at −1.49 V and *N*-(4-methylphenyl)-*N*-benzylcinnamide, **1b**, gave two irreversible cathodic peaks at −1.69 and −2.12 V, respectively. All the other amides, **1c**–**1k** showed two irreversible cathodic peaks. The first cathodic peak is due to the reduction of the C–I bond, whereas the second cathodic peak is due to C=C bond reduction. Linear plots of the square root of the sweep rates *versus* the cathodic peak currents of **1a**–**1k**, passing through the origin at all concentrations, suggest the diffusion-limited nature of the electrode processes. A typical cyclic voltammogram of **1f** is shown in Fig. 1.

While scanning in the reverse direction, a quasi-reversible anodic peak III (Fig. 1) appeared in the potential region of 0 to −0.4 V at all sweep rates. The anodic peak III appeared even when the potential scan was stopped and reversed at the potential of the first cathodic peak (C–I bond reduction). The appearance of anodic peak III in the reverse scan of **1f** in DMF is due to the oxidation of the species formed on the electrode surface at the end of the first cathodic peak. This observation has been confirmed by potential-hold experiments as described below. When the potential of the working electrode (hmde) in cyclic voltammetry at a given sweep rate was held at −1.55 V

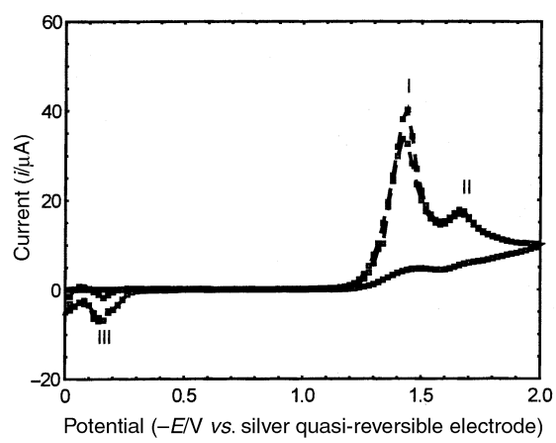


Fig. 1 Cyclic voltammogram of **1f** (5.0×10^{-3} M) in DMF at 100 mV s^{-1} sweep rate.

Table 3 Anodic peak currents $i_{p,aIII}$ of **1f** under cyclic voltammetric conditions during potential-hold experiments

Duration of holding/s	Anodic peak current $i_{p,aIII}$/μA
0	4.01
10	7.37
20	8.65
30	8.83
40	8.85
50	8.91
60	8.95
75	9.43
90	9.41

(called the switching potential after the first cathodic peak) for small intervals of time (0 to 90 s) and then the sweep reversed, the anodic peak currents $i_{p,aIII}$ were found to increase gradually with holding time (Table 3) and then reached a limiting value when the holding time was further increased to 90 s. These findings clearly indicate that the anodic peak III is due to the oxidation of the species generated at the cathodic potential corresponding to the first cathodic peak during the forward scan.

Microcoulometry

Microcoulometric studies of **1a**–**1d** (Table 4) were carried out

Table 4 Microcoulometric data of amides **1a**–**1d** in DMF

Substrate	Potential of electrolysis $-E$/V [a]	n [b]
1a	1.8	1.90
1b	1.8	2.00
1c	1.8	3.90
1d	1.8	2.00

[a] Measured *vs.* a silver quasi-reversible electrode. [b] No. of electrons transferred.

under polarographic conditions in DMF in order to find out the number of electrons transferred in the reduction process. The amides **1a** and **1b**, respectively, consumed two electrons each corresponding to the reduction of the C–I and C=C bonds. Although the amides **1c** and **1d**, as mentioned earlier, showed two cathodic peaks (irreversible) under cyclic voltammetric conditions, they displayed only a single wave in polarography. The microcoulometric studies of amide **1d** at the limiting region of the polarogram (corresponding to the second cathodic peak in cyclic voltammetry) indicate a transfer of two electrons, which is in contrast to **1c** for which a transfer of four electrons was observed in the reduction (Table 4). In the normal course of independent reduction of the C–I bond and reduction of the C=C bond, the number of electrons transferred would have been four, but microcoulometric experiments in the case of **1d** (at the end of the second wave, −1.80 V) showed a transfer of only two electrons. The number of electrons transferred for the reduction of the above amides in DMF (**1d**–**1k**) was further confirmed independently from current *vs.* time (*i*–*t*) curves under potentiostatic conditions and was found to be two.

Controlled-potential electrolysis

The controlled-potential electrolyses of **1c**–**1k** (10.0×10^{-3} M) were performed on a mercury pool cathode at −1.50 V in DMF under deaerated conditions (electrolytic hydrogen–argon). For example, the catholyte of **1d**, after work-up, afforded a viscous liquid in 90% yield (crude). According to Scheme 1, the electroreduction of the C–I bond leads to either the aryl radical or aryl anion depending on the number of electrons transferred, namely, one or two. The aryl radical/anion thus generated can undergo intramolecular cyclisation by either a 5-*exo*-*trig* or a 6-*endo*-*trig* process, as outlined in Scheme 1, to afford 1,5-dialkyl-3-benzylindolin-2-one or 1,6-dialkyl-3-phenyl-2-quinolone, respectively.

Thin layer chromatography of the crude product of electrolysis of **1d** (**6d** and **7d**, Table 5) showed two spots ($R_f = 0.70$ and 0.60), which were separated by flash column chromatography over silica. The major product, **7d** with $R_f = 0.70$, showed a molecular ion-peak at 251.131085 in the high resolution mass spectrum (HRMS). The molecular ion-peak observed at 251.131085 in HRMS was very close to that calculated for the molecular formula, $C_{17}H_{17}NO$. The ^{1}H NMR spectrum of **7d** showed signals at δ (ppm) 2.21 (3H, s, -CH_3), 2.77–2.92 (1H, dd, $J_{1,1'} = 13$ Hz, 8 Hz, -CHCH_2Ph), 3.12 (s, 3H, -NCH_3), 2.86 (1H, dd, $J_{1,1'} = 13$ Hz, $J_{1,2} = 4$ Hz, -CHCH_2Ph), 3.69 (1H, dd, $J_{1,2} = 4$ Hz, $J_{1,2} = 8$ Hz, -CHCH$_2$Ph), 6.65 (2H, m, Ph), 6.93–7.30 (6H, m, Ph). The ^{13}C NMR spectrum of **7d** exhibited signals at δ (ppm) 21.04 (q), 26.08 (q), 36.81 (t), 47.07 (d), 107.52 (d), 125.38 (d), 126.54 (s), 127.88 (s), 128.42 (d), 128.87 (d), 129.37 (d), 131.42 (d), 138.03 (s), 141.80 (s), 176.94 (C=O). The IR spectrum of **7d** showed a band at 1699 cm^{-1} due to the carbonyl group. A remarkable feature in the IR spectrum is that the band at 1619 cm^{-1} due to the C=C bond [which was present in the substrate (depolariser)] was absent and the band at 1654 cm^{-1}due to the C=O group was shifted to 1699 cm^{-1}. In the ^{13}C NMR spectrum, the signal due to the carbon of C=O of **1d** appears at 166.43 ppm, whereas that of the carbon of the C=O of the electrolysis product, **7d**, is shifted further downfield *viz*. to 176.94 ppm. The spectral data clearly indicate that the product **7d** is 1,5-dimethyl-3-benzylindolin-2-one and not 1,6-dimethyl-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one. The structures of the electrolysis products (**7d** and **7f**) in the cases of **1d** and **1f** have been further confirmed by comparison with respective authentic samples prepared independently by chemical methods.[13] The IR spectrum of the other electrolysis product with $R_f = 0.60$ showed a band at 1650 cm^{-1} due to C=O and another band at 1603 cm^{-1} due to the C=C bond. Furthermore, the signals at δ (ppm) 6.10 (1H, d, $J_{1,2} = 16$ Hz, -*N*COC*H*=CHPh) and 7.55–7.78 (1H, d, $J_{1,2} = 16$ Hz, -*N*COCH=C*H*Ph) in the ^{1}H NMR spectrum and 13 signals in the ^{13}C NMR spectrum revealed it to be the product of simple reduction of the C–I bond, namely **6d**, an observation which has been further confirmed by comparison with an authentic sample of **6d**.

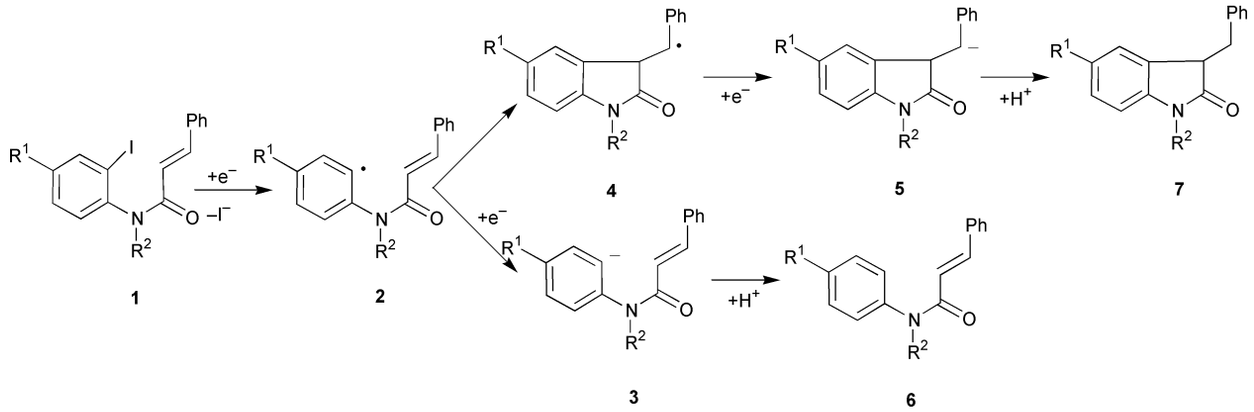
Table 5 Percentage yields of the electrolysis products 1-alkyl-3-benzylindolin-2-ones **7d**–**7k**

Compound	Cyclised compound **7c**–**7k**	Carbon–iodine reduction product **6c**–**6k**
1c	—	75
1d	70	10
1e	75	5
1f	85	—
1g	75	—
1h	80	—
1i	85	—
1j	75	10
1k	80	—

The cathodic cyclisation of the amides **1d**–**1k** was found to be highly regioselective. It may be pointed out that the compound **1c** on macroelectrolysis (at −1.5 V *vs.* a silver quasi-reversible electrode) afforded only the product of hydrogenolysis of the C–I bond, *viz*. *N*-(4-methylphenyl)cinnamide. A similar behavior was observed in tributylstannyl radical-mediated cyclisation of **1c**, which led only to simple reduction of the C–I bond instead of any cyclisation.[13] Since amides exhibit dynamic *E* and *Z* isomerism, a mechanistic rationale based on restricted rotation about the carbon–nitrogen bond was proposed to account for the failure of the cyclisation of **1c**.[13,14a] In the cathodic reactions reported here, single-electron reduction results in the formation of an aryl radical that tethers to the α-position of the C=C bond by a 5-*exo*-*trig* process (Scheme 1). The yield of 1-alkyl-3-benzylindolin-2-one is marginally influenced by the substituents on the aromatic ring and the alkyl group on the nitrogen atom. For example, when the *N*-methyl group (**1d**) was replaced by bulkier benzyl group (**1f**), the yield of the cyclised compound rose to 85% (Table 5) and the reaction was found to be general for all the amides studied.

Mechanism

The observation of a two electron-transfer in the reduction of amides **1a**, **1b** and **1d** and cathodic cyclisation of **1d**–**1k** to give the corresponding cyclised and C–I bond reduced products suggests an electrochemical and chemical reaction sequence. The first step is the generation of aryl radical **2** (Scheme 2) by single-electron reduction of the C–I bond. The subsequent step may involve either the intramolecular aryl radical cyclisation by a 5-*exo*-*trig* process to furnish **7** or transfer of another electron by a cathodic process to an anion, **3**, which is further protonated to give the C–I bond reduced product **6** (Scheme 2). Since these reactions are parallel reactions, the relative rates of intramolecular cyclisation of the aryl radical (**2** to **4**, Scheme 2) and the reduction of the aryl radical (**2** to **3**) will determine the ratio of the products. The proposed mechanism outlined in Scheme 2 for the formation of 1-alkyl-3-benzylindolin-2-ones is an ECEC



Scheme 2

Table 6 Percentage yields of the electrolysis products 1-alkyl-3-hydroxy-3-benzylindolin-2-ones **8d**–**8k**

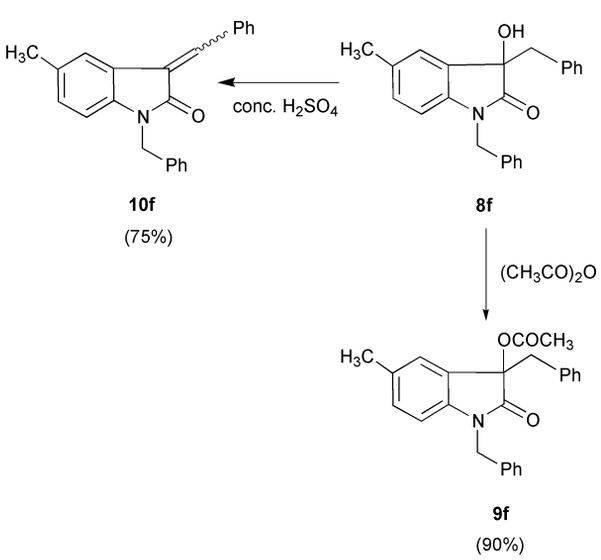
Substrate	Yield of **8** (%)
1d	75[a]
1f	85[a]
1g	80
1h	85
1i	85
1j	75
1k	85

[a] The dimers, **11d** and **11f**, respectively, were also isolated as minor products in the case of the cathodic reduction of **1d** and **1f** at higher concentrations.

(electrochemical–chemical–electrochemical–chemical) type process, whereas the formation of the C–I bond reduced product is of the EEC (electrochemical–electrochemical–chemical) type as outlined in Scheme 2.

Cathodic cyclisation and hydroxylation of *N*-(2-iodophenyl)-*N*-alkylcinnamides

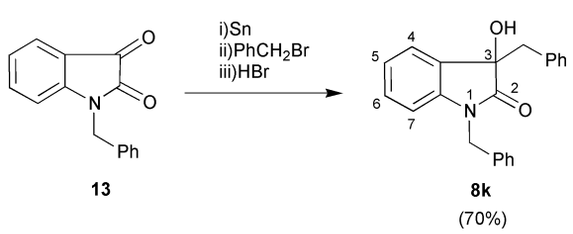
Cathodic cyclisation of *N*-(2-iodophenyl)-*N*-alkylcinnamides in the presence of oxygen. The controlled-potential electrolyses of the solutions of **1d**–**1k** (10.0×10^{-3} M) in DMF at −1.5 V *vs.* a silver quasi-reversible electrode were carried out using a mercury pool cathode in the presence of oxygen. For example, the catholyte of **1f**, after work-up, afforded a solid product (mp 213–214 °C), **8f**, in 85% yield which has not been reported in the literature (Scheme 3, Table 6). The product **8f** showed a molecular ion peak at 343.154184 in its high resolution mass spectrum (HRMS), close to that calculated for the molecular formula, $C_{23}H_{21}NO_2$. The IR spectrum of **8f** showed a sharp band at 1705 cm^{-1} due to the C=O group and, surprisingly, a band at 3328 cm^{-1} and also confirmed the absence of a C=C bond.



Scheme 3

The ^{1}H NMR spectrum of **8f** showed signals at δ (ppm) 2.25 (3H, s, -CH_3), 3.25–3.44 (3H, AB q and s, $J_{1,1'} = 13$ Hz, -C(OH)CH_2Ph), 4.41 (1H, d, $J_{1,1'} = 14$ Hz, -N CH_2Ph), 4.95 (1H, d, $J_{1,1'} = 13$ Hz, -N CH_2Ph), 6.30 (1H, d, $J_{1,2} = 7$ Hz, Ph), 6.66 (2H, m, Ph), 6.92 (2H, m, Ph), 7.1 (8H, m, Ph). The ^{13}C NMR spectrum of **8f** exhibited signals at δ (ppm) 21.06 (q), 43.69 (t), 44.82 (t), 76.36 (s), 109.30, 125.07, 126.63, 126.89, 127.24, 128.04, 128.59, 129.15, 129.96, 130.42, 132.53, 133.92, 135.02, 140.28, 177.61 (C=O). The broad signal at δ 3.25 ppm disappeared on shaking with D_2O indicating it to be due to an OH proton. This observation and the band at 3328 cm^{-1} in the IR spectrum suggest the presence of a hydroxy group in **8f**, which is further confirmed by the formation of 3-acetoxy-1,3-dibenzyl-5-methylindolin-2-one, **9f**, in 90% yield upon treatment with acetic anhydride (Scheme 3), while under acidic conditions, **8f** underwent dehydration to give a mixture of *E* and *Z* isomers of 1-benzyl-3-benzylidene-5-methylindolin-2-one, **10f**, in 75% yield.

In the case of **8k** (Table 6), the structure of the product was further confirmed by comparison with an authentic sample, which was synthesized independently by chemical methods as outlined in Scheme 4.[20]



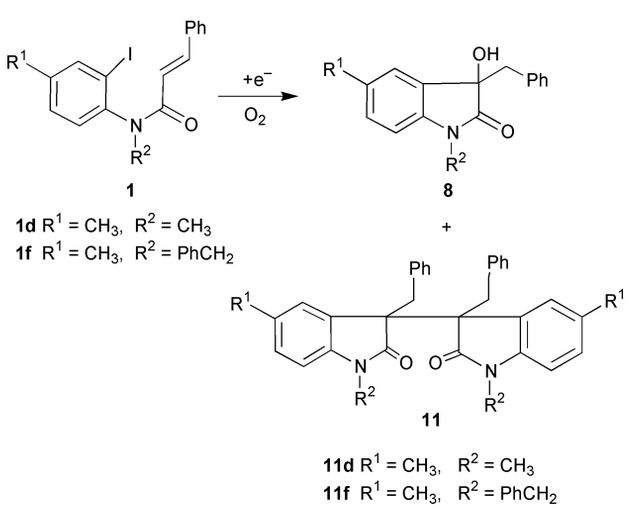
Scheme 4

The AB quartet centered at δ 3.25 ppm ($J_{1,1} = 13$ Hz) in the ^{1}H NMR spectrum is due to the diastereotopic benzylic protons at 3-C. The signal at δ 77.64 ppm (s) in the ^{13}C NMR spectrum of **8f** can be assigned to the carbon atom at the 3-position of the indole ring. All the amides (**1d**–**1k**, Table 6) on electrolysis afforded the corresponding 1-alkyl-3-hydroxy-3-benzylindolin-2-ones (**8d**–**8k**) in good yields. It is interesting to note that electrolyses of **1d** and **1f** in DMF solutions at higher concentrations (20 mM) afforded dimers, **11d** and **11f** (Scheme 5), respectively, in minor amounts together with the hydroxylated products, **8d** and **8f**. All the electrolysis products were isolated and thoroughly characterized by spectral means.

Mechanistic studies. While formation of the hydroxylated product in the present work under cathodic conditions is quite unprecedented, the formation of the tertiary alcohol **8** (Scheme 5) was even more intriguing as the sequential single-electron reduction of the C–I bond, 5-*exo*-*trig* cyclisation and hydroxylation of the resulting radical, **3**, should have led to secondary alcohol **14** and not to **8** (Scheme 6).

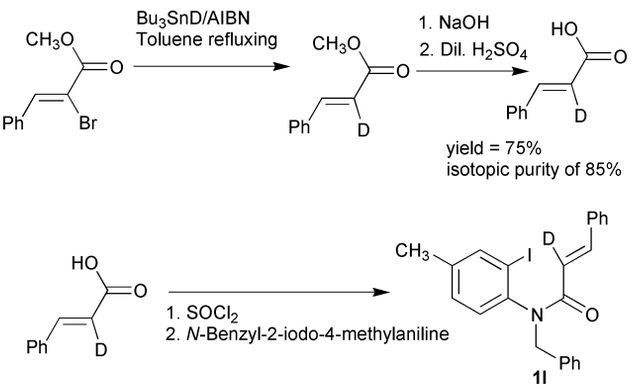
A mechanism involving the rearrangement of the secondary radical **4** to the more stable tertiary radical **12** was initially conceived to account for the formation of **8** and the dimer **11** (Scheme 6). Since 1,2-hydrogen shifts are rarely encountered in free radical rearrangements, it became imperative to establish the 1,2-hydrogen shift envisaged in Scheme 6 by labelling experiments.

(a) Isotope labelling experiments. The α-deuteriocinnamide, **1l** was synthesized as outlined in Scheme 7. Electrolysis of α-deuteriocinnamide **1l** was performed in DMF in the presence of oxygen. According to the mechanism speculated in Scheme 6, the cathodic reductive cyclisation of **1l** should have furnished 3-(α-deuterobenzyl)-3-hydroxyindolin-2-one, **8p** through a 1,2-deuterium shift (Scheme 8). However, characterisation of the electrolysis product by NMR spectroscopy and mass spectrometry showed the absence of deuterium in the product and confirmed it to be **8f** (Scheme 8).

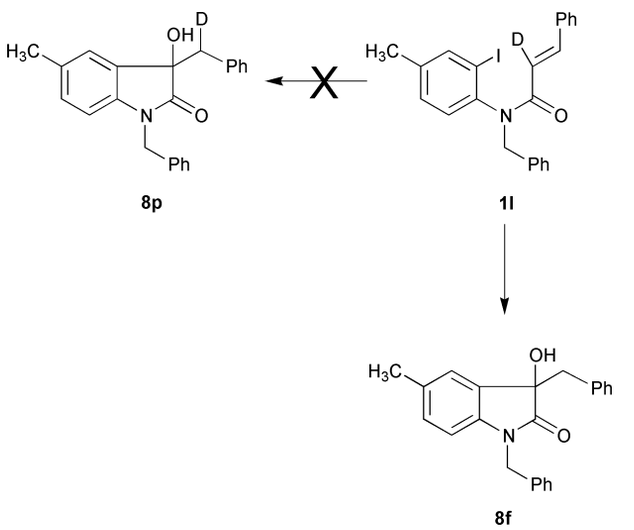


Scheme 5

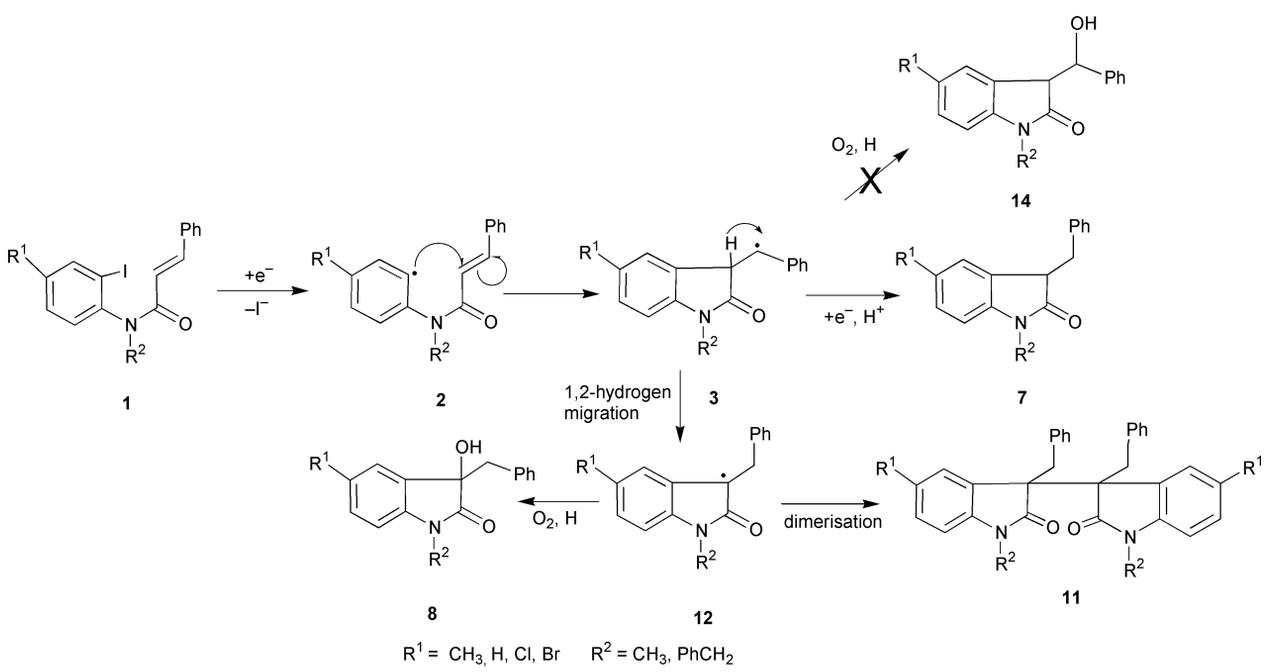
As the cathodic cyclisation *N*-(2-iodophenyl)-*N*-alkylcinnamides **1d**–**1k** (presented in Scheme 6) is very similar to tributylstannyl radical-mediated cyclisations,[13] we examined the radical cyclisation of **1f** (Table 6) with tributylstannyldeuteride–AIBN (Scheme 9) and that of **1l** with tributylstannyl hydride–AIBN (Scheme 10) in order to find out whether any



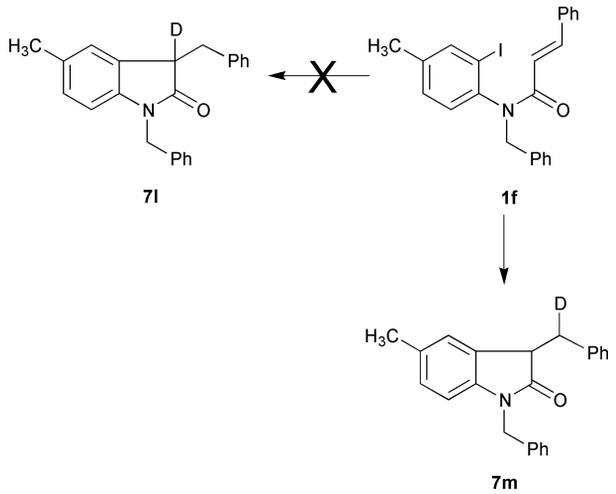
Scheme 7



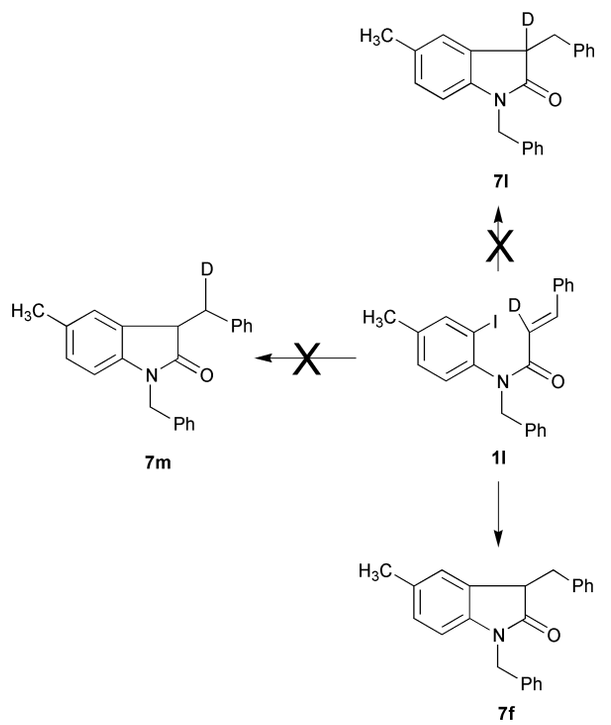
Scheme 8 Cathodic cyclisation of **1l** in DMF in the presence of oxygen.



Scheme 6



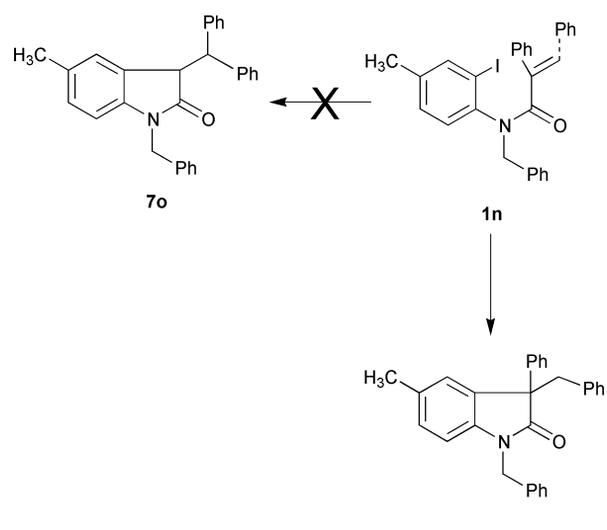
Scheme 9 Radical cyclisation of **1f** (Bu_3SnD–AIBN).



Scheme 10 Cathodic and radical cyclisation of **1l** (Bu_3SnH–AIBN).

1,2-hydrogen shift occurs in these radical cyclisation reactions. However, radical cyclisation of **1f** with tributylstannyl deuteride–AIBN furnished only **7m** (Scheme 9) and none of **7l**. The same outcome has been further confirmed by performing electrochemically induced cyclisations of compound **1l** (Scheme 10), which, after aqueous work-up, led only to the formation of product **7f** and not **7m**, thus ruling out the mechanism originally envisaged (Scheme 6). Likewise, tributylstannyl radical-mediated cyclisation of **1l** afforded only **7f** (Scheme 10) and none of **7l** or the product of 1,2-deuterium shift, *viz*. **7m**. The formation of the product **7f** was rather surprising. It was suspected that the deuterium-labelled product **7l**, formed by the cyclisation, might have undergone reverse exchange with water during work-up. To rule this out, the product of radical-mediated cyclisation of **1l** was isolated from a non-aqueous work-up by evaporating the toluene under vacuum and subjecting the crude product to column chromatographic purification. Characterization of the product by NMR spectroscopy revealed that it was nothing but **7f**. This could be possible only if the deuterium at 3-C is highly labile. Since the deuterium is bonded to a carbon that is α to the C=O group and aromatic ring, it can be expected to be acidic enough to undergo exchange by rapid enolisation–ketonisation under silica gel chromatographic conditions and thus **7l** might have undergone rapid exchange. This was apparent from the fact that when compound **7f** was dissolved in $CDCl_3$ and the solution of **7f** was allowed to equilibrate with D_2O and the NMR spectrum subsequently recorded, the ^1H NMR spectrum clearly revealed that the 3-C proton, α to the carbonyl group had undergone exchange. The spectrum exhibited signals at δ (ppm) 2.25 (3H, s, $-CH_3$), 3.15 (1H, d, $J_{1,1} = 14$ Hz, $-CDCH_2Ph$), 3.40 (d, 1H, $J_{1,1} = 14$ Hz, $-CDCH_2Ph$), 4.60 (d, 1H, $J_{1,1} = 16$ Hz, $-NCH_2Ph$), 4.98 (1H, d, $J_{1,1} = 16$ Hz, $-NCH_2Ph$), 6.40 (1H, d, $J_{1,2} = 8$ Hz, Ph), 6.80–6.90 (4H, m, Ph), 7.06–7.34 (8H, m, Ph). The signal at δ (ppm) 3.5 (dd), due to the hydrogen at 3-C, disappeared and so did the coupling of this hydrogen with neighboring protons at δ (ppm) 3.15 and 3.40. The ^{13}C NMR spectrum after exchange with D_2O exhibited signals at δ (ppm) 21.03 (q), 36.21 (t), 43.63 (t), 47.07 (deuterium-attached carbon), 109.06 (d), 125.24 (d), 126.64 (d), 126.74 (d), 127.29 (d), 128.19 (d), 128.58 (d), 129.59 (d), 132.07 (d), 135.07, 136.95, 140.56, 177.89 (C=O). The D_2O was removed from the NMR tube with the help of a syringe and water was added, the NMR solution shaken and the NMR spectrum was recorded again and was identical to that of **7f**. These studies confirm the labile nature of the deuterium at the 3-carbon of indolin-2-one **7l**.

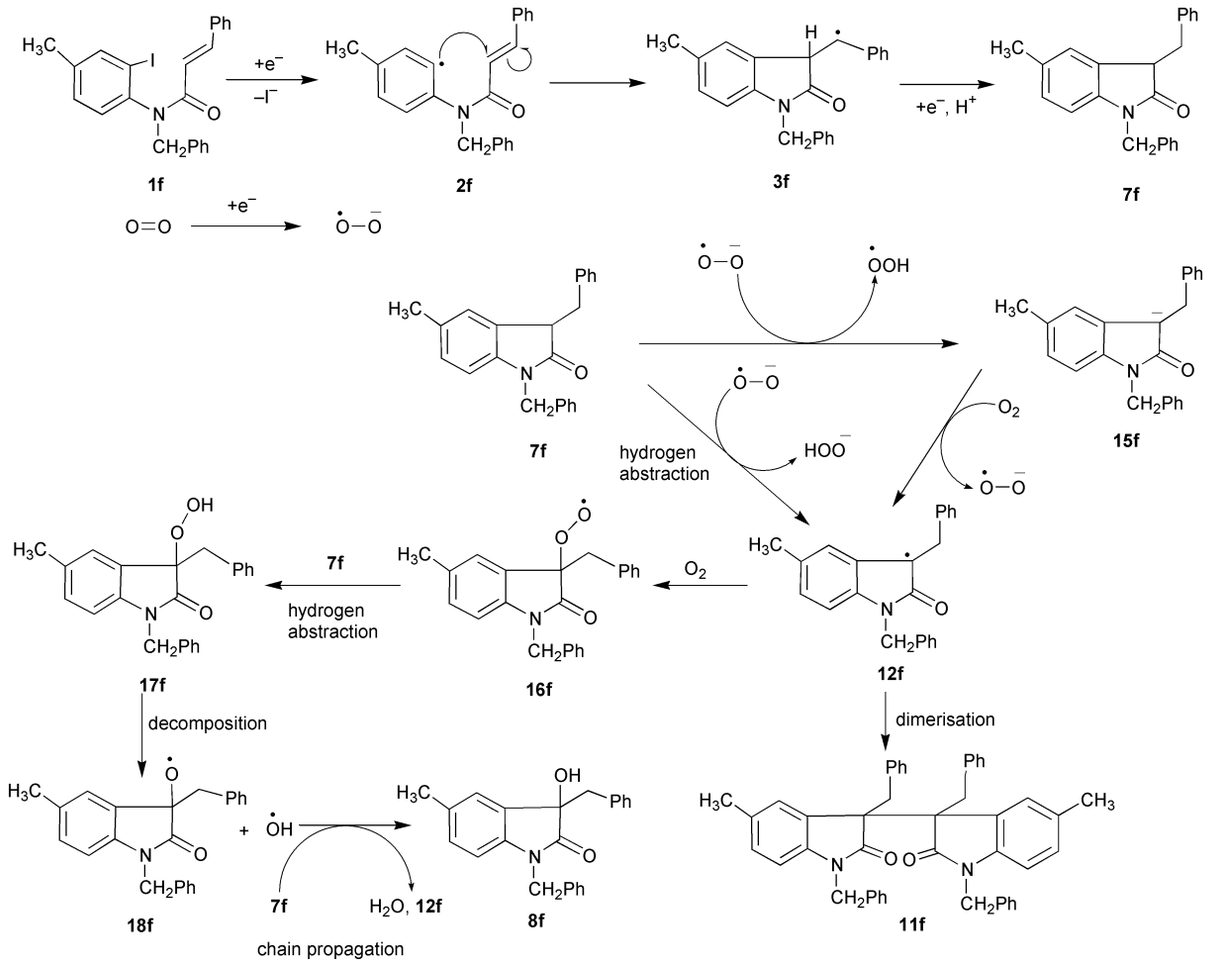
1,2-Hydrogen migrations in free radical reactions are much less prevalent and more important only for aryl[21] and halogen[22] migrating groups. The direction of the rearrangement is normally towards the formation of the more stable radical. Hence, the tributylstannyl radical-mediated cyclisation of **1n** (Scheme 11) was carried out in order to find out whether such



Scheme 11 Radical cyclisation of **1n** (Bu_3SnH–AIBN).

a 1,2-free radical rearrangement occurs when hydrogen is replaced by a phenyl group. This reaction afforded **7n** as the only product and not **7o** (Scheme 11), suggesting that there is no rearrangement of the radical formed during the cyclisation process.

(b) Electrolysis products and time of electrolysis. To follow the course of the above electrochemical cyclisation and hydroxylation reaction, controlled-potential electrolysis of **1f** (10.0×10^{-3} M) was carried out in DMF in the presence of oxygen at various time intervals and the yields of the products were determined (Table 7). It was found that at the beginning of the electrolysis 1,3-dibenzyl-5-methylindolin-2-one **7f**, is formed. The percentage yields of 1,3-dibenzyl-5-methylindolin-2-one, **7f** and 1,3-dibenzyl-3-hydroxy-5-methylindolin-2-one **8f** at different intervals of time are given in Table 7.



Scheme 12

Table 7 Percentage yields of **7f** and **8f** during the electrolysis of **1f** in DMF

Electrolysis time/min	Yield (%)	
	7f	**8f**
45	30	40
90	25	55
150	15	70
240	10	80
300	0	85

It can be seen from Table 7 that the product **7f**, which is formed immediately, undergoes hydroxylation to form **8f**. This observation suggests that the transformation of **1** to **8** occurs through the hydroxylation of an intermediate, **7** (Scheme 12), by oxygen to form **8**. The oxidation of **7** to **8** is found to be an electrochemical reaction and not a chemical reaction as shown by the following observations. In a controlled experiment, purging a solution of 1,3-dibenzyl-5-methylindolin-2-one **7f** in DMF (containing TBAP supporting electrolyte) with oxygen did not yield 1,3-dibenzyl-3-hydroxy-5-methylindolin-2-one, **8f**. On the other hand, electrolysis of **7f** under aerated conditions at −0.8 V *vs.* a silver quasi-reversible electrode in DMF solutions (in an H-shaped divided cell equipped with a mercury pool cathode and platinum foil anode) afforded **8f** in 85% yield.

(c) Cyclic voltammetry of 7f in the presence of oxygen. With a view to understanding the mechanism of the electrochemical hydroxylation reaction of **7** to **8** (Scheme 12), a cyclic voltammetric study of **7f** (5.0×10^{-3} M) in DMF was undertaken. The cyclic voltammogram of oxygen (saturated) in DMF solution at a hanging mercury drop electrode and 300 mV s^{-1} sweep rate showed a quasi-reversible cathodic peak (due to $O_2^{-\bullet}$ formation) at −0.75 V *vs.* a quasi-reversible silver electrode[23] (Fig. 2).

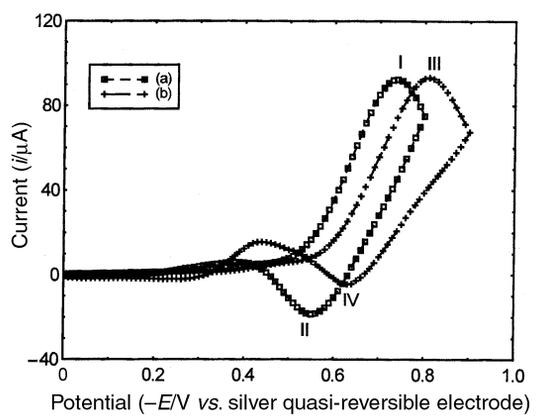


Fig. 2 Cyclic voltammograms of oxygen saturated in DMF (a) in the absence of 1,3-dibenzyl-5-methylindolin-2-one **7f** and (b) in the presence of 5.0×10^{-3} M of 1,3-dibenzyl-5-methylindolin-2-one **7f** at a sweep rate of 300 mV s^{-1}.

It may be mentioned that 1,3-dibenzyl-5-methylindolin-2-one, **7f** was not electro-active in the potential region from 0 to −1.5 V. During the reverse scan, the decrease in the anodic current in the cyclic voltammogram of oxygen in the presence of **7f** (Fig. 2) suggests the formation of an intermediate at the electrode/solution interface due to the interaction of the superoxide radical generated *in situ* (by reduction of oxygen) with 1,3-dibenzyl-5-methylindolin-2-one **7f**. The involvement of 1,3-dibenzyl-5-methylindolin-2-one **7f** in the depletion of superoxide from the mercury surface (electrode) is further

Table 8 CV data of oxygen for the first cathodic peak in the presence of various concentrations of 1,3-dibenzyl-5-methylindolin-2-one **7f** in DMF at 100 mV s^{-1} sweep rate

Concentration/ mM	Cathodic peak current $i_{p,cl}$/μA	Anodic peak current $i_{p,al}$/μA
0	94.3	27.2
5	93.9	8.9
7.5	93.4	4.4
10	92.0	3.4
15	93.2	1.5

Table 9 Percentage yields of **8f** during the electrolysis of **7f**

Quantity of electricity passed/ F $mole^{-1}$	Yield (%)
4.5	85
1.0	87
0.5	88
0.1	85

confirmed by the effect of varying the concentration of 1,3-dibenzyl-5-methylindolin-2-one **7f** on the anodic peak currents due to superoxide oxidation in cyclic voltammetry. Table 8 suggests that with an increase in the concentration of **7f**, the anodic peak currents due to the oxidation of superoxide to oxygen decreased substantially. The decrease in the anodic peak currents is attributed to the depletion of superoxide caused by the interaction of superoxide with 1,3-dibenzyl-5-methylindolin-2-one intermediate, **7f**, and hence is not available for oxidation (Table 8). The mechanism depicted in Scheme 12 would account for the observed sequential electrochemical reductive cyclisation and hydroxylation.

The hydroxylation reaction of 1,3-dibenzyl-5-methylindolin-2-one, **7f** with superoxide may proceed by abstraction of either hydrogen or a proton to form a radical, **12**, or an anion, **15** (Scheme 12). Enolates similar to **15** generated from 3-alkylindolin-2-ones are known to react with molecular oxygen to furnish 3-hydroxy-3-alkylindolin-2-ones.[17] In the present case also the anion of 1,3-disubstituted indolin-2-ones (generated in DMF by reaction of **7f** with NaH) underwent oxidation to give **8f** presumably through the radical, **12**.[18] With a view to finding out whether oxidation of **7f** is a chain reaction initiated by the electrochemically generated superoxide or a stoichiometric process involving superoxide, the electrolysis of a solution of **7f** was carried out by passing various amounts of current (nitrogen containing 3% oxygen was bubbled through the solution continuously at a flow rate of 100 mL min^{-1}). The percentage yields of **8f** obtained in the electrolysis are presented in Table 9. The yield of **8f** did not depend on the quantity of electricity passed, which suggests that a catalytic amount of electricity is sufficient for the completion of the reaction (Table 9).

The hydroxylation of **7f** by oxidation of its conjugate base **15f** (Scheme 12) was also investigated. The amount of base was varied and the yields of the hydroxylated product **8f** were estimated and the results are shown in Table 10. As can be seen from the data given in Table 10, the hydroxylation of **7f** occurs smoothly using a catalytic amount of NaH in the presence of oxygen. Further, the above observations clearly indicate that the hydroxylation reaction of **7f** is a chain reaction as shown in Scheme 12.

Conclusions

The cathodic cyclisation of *N*-(2-iodophenyl)-*N*-alkylcinnamides in DMF under deaerated conditions affords regioselectively the product of a 5-*exo*-*trig* process in good yields, whereas the photochemical and samarium(II)-induced cyclisations afford a mixture of products. The electrochemical method of cyclisation reported in the present work is not only novel, but also complementary to the existing radical cyclisation methodologies, *viz*. tributylstannyl radical-mediated cyclisation and SmI_2-mediated radical cyclisation for the synthesis of 1-alkyl-3-benzylindolin-2-ones. In the presence of oxygen, electrolyses of *N*-(2-iodophenyl)-*N*-alkylcinnamides afford 1-alkyl-3-hydroxy-3-benzylindolin-2-ones. The experimental evidence suggests a reaction pathway as outlined in Scheme 12, in which the formation of 1-alkyl-3-hydroxy-3-benzylindolin-2-ones involves the interaction of 1-alkyl-3-benzylindolin-2-one with the superoxide generated *in situ* from molecular oxygen by cathodic reduction. The transformation involving the sequential radical cyclisation and hydroxylation under cathodic conditions is novel, of mechanistic interest and also without precedence.

Table 10 Percentage yields of **8f** during the hydroxylation of **7f**

NaH : **7f** mole ratio	Yield (%)
2.00	85
1.00	88
0.50	87
0.15	85

Experimental

General

Solvents were dried by standard methods and freshly distilled prior to use. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Bruker spectrometer at room temperature using $CDCl_3$ as solvent and tetramethylsilane as the reference, unless otherwise mentioned. Mass spectral analyses were carried out using a Shimadzu mass detector model GCMS-QP 5000 at 70 eV. High resolution mass spectral data were obtained on a Finnigan Mat8230 spectrometer. Melting points are uncorrected. All the electrochemical studies were carried out with microprocessor-controlled potentiostat/galvanostat, EG&G, Princeton Applied Research Corporation, USA.

Preparation of *N*-(2-iodo-4-substituted-phenyl)-*N*-alkylcinnamides (1a–1k)

The substrate molecules (**1a**–**1k**, Table 1) were prepared by acylation of the corresponding 2-iodoanilines (2-iodo-4-methylaniline, 2-iodo-4-chloroaniline, 2-iodo-4-bromoaniline, and 2-iodoaniline, respectively) with cinnamoyl chloride, followed by alkylation of the resulting amides with NaH and the corresponding alkyl halide (CH_3I, $PhCH_2Br$ and EtBr) in DMF according to the procedure previously reported.[13] Likewise, deuterium-labelled *N*-(2-iodophenyl)-*N*-benzyl(α-deuterio)-cinnamide, **1k**, was prepared using PhCH=CDCOCl, 2-iodo-4-methylaniline and benzyl bromide.

Preparation of α-deuteriocinnamic acid

A mixture of 8.3×10^{-3} mol of methyl α-bromocinnamate, 1.0×10^{-2} mol of tributylstannyl deuteride and 1.0×10^{-4} mol of AIBN in toluene was left under a nitrogen atmosphere for 8 h. The toluene was distilled off under vacuum and the reaction mixture was dissolved in 25 mL of a water–methanol mixture (1 : 1 v/v). The reaction mixture was treated with 1.0 g of ammonium fluoride to convert the tributyltin compound into the tin fluoride. The product was extracted with ethyl acetate and the tin fluoride was removed as an insoluble solid. Methyl (α-deuterio)cinnamate was hydrolyzed by boiling with 20 mL of an aqueous 1 M NaOH solution under refluxing

conditions. The reaction was acidified with 25 mL of 1 M sulfuric acid and the product was precipitated. The product was recrystallised from methanol. This method gave α-deuteriocinnamic acid with 85% deuterium incorporation. The deuterium content was determined by integration of the ^{1}H NMR signal at δ (ppm) 6.47 ($J_{1,2}$ = 16.0 Hz) and 7.81 ($J_{1,2}$ = 16.0 Hz) relative to the α- (unlabelled) and β-protons, respectively, of the acid. The literature method[24] for the preparation of α-deuteriocinnamic acid by Dobner condensation of benzaldehyde with $CD_2(COOD)_2$ in boiling pyridine afforded α-deuteriocinnamic acid with an isotopic purity of 75%. Mp 130–131 °C. ^{1}H NMR (200 MHz; $CDCl_3$) δ (ppm) 6.50 (0.15H, $J_{1,2}$ = 16.0 Hz, isotopic impurity, PhCH=C*H*COOH), 7.25 (3H, m, Ph), 7.50 (2H, m, Ph), 7.80 (1H, s, PhC*H*=CDCOOH), 9.80 (1H, br signal, -COO*H*). ^{13}C NMR (50 MHz; $CDCl_3$) δ (ppm) 117.28, 128.34, 128.35, 128.53, 128.93, 130.71, 133.09, 133.99, 172.50 (C=O). MS (70 eV) *m*/*z* (%) 150 (6), 149 (53), 148 (78), 132 (16), 104 (48), 103 (37), 92 (24), 78 (38), 77 (48).

Cathodic cyclisation of 1d–1k under deaerated conditions

The cyclic voltammetric studies of **1d**–**1k** (5.0×10^{-3} M) in DMF at various sweep rates were carried out using a hanging mercury drop electrode (Metrohm, Switzerland) as working electrode, a quasi-reversible silver electrode as a reference electrode and a platinum electrode as the counter electrode. Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte throughout. The macroscale controlled-potential electrolyses of **1d**–**1k** (10.0×10^{-3} M) in DMF solutions were performed in an H-type divided cell at –1.5 V on a mercury pool cathode (10 cm^2 area) under deaerated conditions. For deaerating purposes, electrolytic hydrogen was used.

Cathodic cyclisation of *N*-(2-iodophenyl)-*N*-alkylcinnamides in the presence of oxygen

During the electrolyses of *N*-(2-iodophenyl)-*N*-alkylcinnamides (10.0×10^{-3} M) in DMF solutions in the presence of oxygen, the concentration of oxygen in the catholyte was maintained steady and low by purging the electrolyte with nitrogen containing 3% oxygen (flow rate 50 to 200 mL min^{-1}). The course of the reaction was monitored as a function of time by coulometry and thin layer chromatography. The electrolysis was stopped when the initial current (80 mA) reached a constant minimum value of 15 mA after about 8 to 10 h. The DMF was distilled off under vacuum and the products were isolated by flash column chromatography. A mixture of ethyl acetate and hexane was used as eluant.

Radical cyclisation of 1d, 1f, 1l and 1n

Reactant (1.0×10^{-2} mol) (**1d**, **1f**, **1l** and **1n**), $NaBH_4$ (2.0×10^{-2} mol), tributylstannyl chloride (3.5×10^{-4} mol) and AIBN (1.0×10^{-4} mol) were refluxed in 100 mL of a toluene–methanol mixture (20 : 1 v/v) under a nitrogen atmosphere for 8 h. The toluene–methanol was distilled off under vacuum and the residue was dissolved in 25 mL of a methanol–water mixture (1 : 1 v/v). The reaction mixture was treated with 0.5 g ammonium fluoride to convert the tributyltin compound to the tin fluoride. The products were extracted with ethyl acetate and purified by column chromatography. The yields of the products (**7d**, **7f**, **7l** and **7n**) were 80, 85, 85 and 85%, respectively. The spectral data of **7d** and **7f** obtained by electrochemical methods were compared with those of the chemically synthesized **7d** and **7f**.

Radical cyclisation of 1f with tributystannyl deuteride

A mixture of **1e** (1.0×10^{-2} mol), tributylstannyl deuteride (1.5×10^{-2} mol) and AIBN (3.5×10^{-4} mol) was refluxed in toluene under an inert atmosphere for 10 h. The toluene was distilled off under vacuum and the residue was dissolved in 25 mL of a methanol–water mixture (1 : 1). The reaction mixture was treated with 0. 5 g of ammonium fluoride to remove the tin compounds and the compound extracted with ethyl acetate and purified by column chromatography. The yield of the product **7i** was 85%.

Synthesis of 3-hydroxy-1,3-dibenzylindolin-2-one from indoline-2,3-dione

A mixture of 1-benzylindoline-2,3-dione (4.5×10^{-3} mol), benzyl bromide (5.0×10^{-3} mol), 0.50 mL of HBr (48% wt in water) and 1.0×10^{-2} mol of tin powder (100 mesh) in THF was refluxed for 10 h. The solvent was distilled off under vacuum and the product was extracted with ethyl acetate and purified by column chromatography.[20] The yield of the product **8k** was 75%. The spectral data of **8k** obtained by this method were compared with those for the electrolytically obtained **8k** and were found to be the same.

N-(2-Iodo-4-methylphenyl)-*N*-benzylacetamide, 1a

Viscous liquid; $\nu_{max}(CHCl_3)$/cm^{-1} 1680 (C=O); δ_H (200 MHz; $CDCl_3$) 1.75 (3H, s, -COCH_3), 2.30 (3H, s, -CH_3), 3.70 (1H, d, $J_{1,1'}$ = 16.0 Hz, -*N*CH_2Ph), 5.60 (1H, d, $J_{1,1'}$ = 16.0 Hz, -*N*CH_2Ph), 6.5–7.50 (m, 7H, Ph) and 7.70 (m, 1H, Ph).

N-(4-Methylphenyl)-*N*-benzylcinnamide, 1b

Mp 82–83 °C (methanol); $\nu_{max}(CHCl_3)$/cm^{-1} 1660 (conj. C=O) and 1619 (conj. C=C); $\lambda_{max}(CHCl_3)$/nm 284; δ_H (200 MHz; $CDCl_3$) 2.25 (3H, s, -CH_3), 4.90 (2H, s, -NCH_2Ph), 6.25 (1H, d, $J_{1,2}$ = 16 Hz, -*N*COC*H*=CHPh), 6.75 (2H, d, $J_{1,2}$ = 7 Hz, Ph), 7.50 (2H, d, $J_{1,2}$ = 7 Hz, Ph), 7.55–7.60 (10H, m, Ph) and 7.75 (1H, d, $J_{1,2}$ = 16 Hz, -*N*COCH=C*H*Ph); δ_C (50 MHz; $CDCl_3$) 21.04, 53.27, 118.79, 125.77, 127.22, 127.80, 127.99, 128.29, 128.57, 129.42, 130.00, 135.16, 137.50, 137.63, 139.26, 142.16, and 166.12.

N-(2-Iodo-4-methylphenyl)cinnamide, 1c

Mp 115–116 °C (methanol); $\nu_{max}(CHCl_3)$/cm^{-1} 1651 (conj. C=O) and 1628 (conj. C=C); $\lambda_{max}(CHCl_3)$/nm 280; δ_H (200 MHz; $CDCl_3$) 2.30 (3H, s, -CH_3), 6.57 (1H, d, $J_{1,2}$ = 16.0 Hz, -*N*COC*H*=CHPh), 7.20 (1H, d, $J_{1,2}$ = 7 Hz, Ph), 7.30–7.60 (8H, m, Ph), 7.70 (1H, d, $J_{1,2}$ = 16.0 Hz, -*N*COCH=C*H*Ph) and 8.20 (1H, m, Ph).

N-(2-Iodo-4-methylphenyl)-*N*-methylcinnamide, 1d

Starting from 5.0 g of 2-iodo-4-methylaniline, 5.8 g of **1d** were obtained (75%); mp 117–118 °C (methanol); $\nu_{max}(CHCl_3)$/cm^{-1} 1654 vs (conj. C=O) and 1619 vs (conj. C=C); $\lambda_{max}(CHCl_3)$/nm 285; δ_H (200 MHz; $CDCl_3$) 2.38 (3H, s -CH_3), 3.35 (s, 3H, -*N*CH_3), 6.10 (1H, d, $J_{1,2}$ = 16 Hz, -*N*COC*H*=CHPh), 7.06–7.33 (4H, m, Ph), 7.55–7.78 (7H, m, Ph), 7.70 (1H, d, $J_{1,2}$ = 16 Hz, -*N*COCH=C*H*Ph) and 7.95 (1H, d, $J_{1,3}$ = 3 Hz, Ph); δ_C (50 MHz; $CDCl_3$) 21.03 (q), 36.83 (q), 99.89, 118.65, 128.33, 129.04, 129.32, 129.94, 131.08, 135.64, 140.64, 140.96, 142.73, 143.50 and 166.43 (C=O).

N-(2-Iodo-4-methylphenyl)-*N*-ethylcinnamide, 1e

Starting from 5.0 g of 2-iodo-4-methylaniline, 6.1 g of **1e** were obtained (70%); mp 44-45 °C (hexane); $\nu_{max}(CHCl_3)$/cm^{-1} 1660 vs (conj. C=O) and 1625 vs (conj. C=C); $\lambda_{max}(CHCl_3)$/nm 283; δ_H (200 MHz; $CDCl_3$) 1.1 (3H, t, $J_{1,2}$ = 7 Hz, -*N*CH$_2$CH_3), 2.38 (3H, s, -CH_3), 3.35 (2H, q, $J_{1,2}$ = 7 Hz, -*N*CH_2CH$_3$), 6.10 (1H, d, $J_{1,2}$ = 16 Hz, -*N*COC*H*=CHPh), 7.06–7.33 (4H, m, Ph) and 7.55–7.78 (2H, d and m, $J_{1,2}$ = 16 Hz, -*N*COCH=C*H*Ph, Ph); δ_C (50 MHz; $CDCl_3$) 21.03 (q), 36.83 (q), 99.89, 118.65, 128.33, 129.32, 129.94, 131.08, 135.64, 140.64, 140.96, 142.73, 143.50 and 166.43 (C=O); *m*/*z* 265 (40%), 264 (100), 236 (18), 131 (70), 103 (55) and 77 (24).

***N*-(2-Iodo-4-methylphenyl)-*N*-benzylcinnamide, 1f**

Starting from 5.0 g of 2-iodo-4-methylaniline, 7.8 g of **1f** were obtained (80%); mp 157–158 °C (methanol); ν_{max}(KBr)/cm^{-1} 1651 vs (conj. C=O) and 1616 vs (conj. C=C); λ_{max}($CHCl_3$)/nm 282; δ_H (200 MHz; $CDCl_3$) 2.34 (3H, s, -CH_3), 4.05 (1H, d, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 5.70 (1H, d, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 6.03–6.20 (1H, d, $J_{1,2}$ = 16 Hz, -NCOCH=CHPh), 6.65 (1H, d, $J_{1,3}$ = 3 Hz, Ph), 7.05 (1H, m, Ph), 7.26–7.28 (10H, m, Ph) and 7.85 (2H, d, $J_{1,2}$ = 16 Hz, -NCOCH=CHPh); δ_C (50 MHz; $CDCl_3$) 20.54 (q), 51.96 (t), 100.26, 119.50, 127.44, 127.87, 128.31, 128.57, 129.44, 129.52, 129.89, 130.54, 135.10, 137.00, 140.18, 140.52, 140.83, 142.79 and 165.81 (C=O).

***N*-(2-Iodo-4-chlorophenyl)-*N*-methylcinnamide, 1g**

Starting from 5.0 g of 2-iodo-4-chloroaniline, 5.1 g of **1g** were obtained (70%); mp 122–123 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1667 vs (conj. C=O) and 1628 vs (conj. C=C); λ_{max}($CHCl_3$)/nm 280; δ_H (200 MHz; $CDCl_3$) 3.50 (3H, s, -NCH_3), 6.30 (1H, d, $J_{1,2}$ = 16 Hz, -NCOCH=CHPh), 7.37–7.54 (6H, m, Ph), 7.64–7.54 (2H, d, $J_{1,2}$ = 7 Hz, Ph), 7.86–7.90 (1H, d, $J_{1,2}$ = 16 Hz, -NCOCH=CHPh) and 8.18 (1H, d, $J_{1,4}$ = 1 Hz); δ_C (50 MHz; $CDCl_3$) 36.30 (q), 100.09, 117.56, 127.91, 128.66, 129.73, 129.92, 130.07, 134.65, 134.86, 139.50, 142.95, 144.43 and 165.67 (C=O). HRMS calculated: 396.972895, observed: 396.972282.

***N*-(2-Iodo-4-chlorophenyl)-*N*-benzylcinnamide, 1h**

Starting from 5.0 g of 2-iodo-4-chloroaniline, 7.0 g of **1h** were obtained (70%); mp 108–109 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1667 vs (conj. C=O), 1622 vs (conj. C=C); λ_{max}($CHCl_3$)/nm 284; δ_H (200 MHz; $CDCl_3$) 4.05 (1H, d, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 5.75 (1H, d, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 5.97–6.05 (1H, d, $J_{1,2}$ = 16 Hz, -NCOCH=CHPh), 6.70 (1H, d, $J_{1,2}$ = 7 Hz, Ph), 7.25–7.40 (12H, m, Ph), 7.80 (1H, d, J = 16 Hz, -NCOCH=CHPh) and 8.00 (1H, d, $J_{1,3}$ = 2 Hz, Ph); δ_C (50 MHz; $CDCl_3$) 51.80 (t), 100.99, 117.63, 127.70, 127.94, 128.44, 128.67, 129.34, 129.44, 131.54, 134.76, 134.83, 136.56, 139.52, 142.21, 143.60 and 165.49 (C=O); *m*/*z* 473 (4%), 131 (20), 103 (8) and 91 (100).

***N*-(2-Iodo-4-bromophenyl)-*N*-benzylcinnamide, 1i**

Starting from 5.0 g of 2-iodo-4-bromoaniline, 6.2 g of **1i** were obtained (70%); mp 126–127 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1648 vs (conj. C=O) and 1603 s (conj. C=C); λ_{max}($CHCl_3$)/nm 280; δ_H (200 MHz; $CDCl_3$) 4.05 (1H, d, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 5.75 (1H, d, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 5.97–6.05 (1H, d, $J_{1,2}$ = 16 Hz, -NCOCH=CHPh), 6.60 (d, 1H, $J_{1,2}$ = 7 Hz, Ph), 7.25–7.40 (12H, m, Ph), 7.80 (1H, d, $J_{1,2}$ = 16 Hz, -NCOCH=CHPh) and 8.12 (1H, d, $J_{1,3}$ = 2 Hz, Ph); δ_C (50 MHz; $CDCl_3$) 51.73 (t), 101.49, 117.57, 122.73, 127.67, 127.92, 128.44, 128.64, 129.40, 129.78, 131.94, 132.29, 134.78, 136.52, 142.18, 142.65, 143.58 and 165.36 (C=O); *m*/*z* 517 (2%), 131 (15), 103 (6) and 91 (100); HRMS calculated: 516.95417, observed: 516.95586.

***N*-(2-Iodophenyl)-*N*-methylcinnamide, 1j**

Starting from 5.0 g of 2-iodoaniline, 5.9 g of **1j** were obtained (70%); mp 108–109 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1654 vs (conj. C=O) and 1610 vs (conj. C=C); λ_{max}($CHCl_3$)/nm 280; δ_H (200 MHz; $CDCl_3$), 3.2 (3H, s, -NCH_3), 6.00 (1H, d, $J_{1,2}$ = 15 Hz, -NCOCH=CHPh), 6.97–7.38 (9H, m, Ph), 7.60 (1H, d, $J_{1,2}$ = 15 Hz, -NCOCH=CHPh) and 7.85 (1H, d, $J_{1,2}$ = 7 Hz, Ph); δ_C (50 MHz; $CDCl_3$) 26.16 (q), 117.87 (d), 127.68 (d), 127.93 (d), 128.46 (d), 128.67 (s), 129.28 (d), 129.42 (s), 129.78 (d), 134.86 (s), 140.02 (d), 142.29 (d), 145.41 (s) and 165.65 (C=O); *m*/*z* 364 (2), 237 (18), 236 (100), 208 (10), 131 (88), 103 (18) and 77 (14); HRMS: calculated: 364.019662, observed: 364.017677.

***N*-(2-Iodophenyl)-*N*-benzylcinnamide, 1k**

Starting from 5.0 g of 2-iodoaniline, 8.4 g of **1k** were obtained (80%); mp 88–89 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1664 vs (conj. C=O) and 1619 vs (conj. C=C); λ_{max}($CHCl_3$)/nm 280; δ_H (200 MHz; $CDCl_3$) 4.35 (1H, d, $J_{1,1'}$ = 14 Hz, -NCH_2Ph), 5.55 (1H, d, $J_{1,1'}$ = 14 Hz, -NCH_2Ph), 6.10 (1H, d, $J_{1,2}$ = 16 Hz, -NCOCH=CHPh), 6.95–7.10 (1H, m, Ph), 6.93–7.10 (1H, m, Ph), 7.36 (11H, m, Ph), 7.50–7.58 (2H, m, Ph), 7.71–7.84 (1H, d, $J_{1,2}$ = 16 Hz, -NCOCH=CHPh) and 7.99–8.04 (1H, m, Ph); δ_C (50 MHz; $CDCl_3$) 52.76, 117.45, 125.50, 127.74, 127.86, 128.49, 128.62, 129.21, 129.47, 129.80, 132.54, 133.72, 134.68, 134.86, 136.38, 143.64, 147.21 and 165.52 (C=O); *m*/*z* 438 (10), 312 (62), 180 (21), 131 (70), 103 (57), 91 (100) and 77 (45); HRMS: calculated: 442.06612 observed: ion not seen.

***N*-(2-Iodo-4-methylphenyl)-*N*-benzyl(α-deuterio)cinnamide, 1l**

Starting from 1.0 g of (α-deuterio)cinnamic acid 1.72 g of **1l** were obtained (80%); mp 110–111 °C (methanol); ν_{max}($CHCl_3$)/cm^{-1} 1651 (C=O) and 1616 (C=C); λ_{max}($CHCl_3$)/nm 282; δ_H (200 MHz; $CDCl_3$) 2.20 (3H, s, -CH_3), 4.00 (1H, d, $J_{1,1'}$ = 14 Hz, -NCH_2Ph), 5.67 (1H, d, $J_{1,1'}$ = 14 Hz, -NCH_2Ph), 6.65 (0.15H, d, $J_{1,2}$ = 16 Hz, -NCOCH=CHPh, isotopic impurity), 6.65 (1H, d, $J_{1,2}$ = 7 Hz, Ph), 6.94 (1H, dd, $J_{1,2}$ = 7 Hz, $J_{1,3}$ = 3 Hz, Ph), 7.10–7.35 (10H, m, Ph) and 7.70 (2H, m, Ph and -NCOCH=CHPh); δ_C (50 MHz; $CDCl_3$) 20.54 (q), 51.96 (t), 100.26, 118.24, 119.50, 127.44 (d), 127.87 (d), 128.31 (d), 128.57 (d), 129.44 (d), 129.52 (d), 129.89 (d), 130.54 (d), 135.10, 137.00, 140.18, 140.52 (d), 140.83, 142.79 (d) and 165.81 (C=O); *m*/*z* 454 (10%), 327 (54), 132 (62), 104 (15) and 91 (100).

***N*-(2-Iodo-4-methylphenyl)-*N*-benzyl(2-phenyl)cinnamide, 1n**

Starting from 5.0 g of 2-iodo-4-methylaniline, 8.57 g of **1n** were obtained (75%); mp 110–111 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1638 br (conj. C=O and conj. C=C); λ_{max}($CHCl_3$)/nm 290; δ_H (200 MHz; $CDCl_3$) 2.25 (3H, s, -CH_3), 4.24 (1H, d, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 5.75 (1H, d, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 6.14 (1H, d, $J_{1,2}$ = 7 Hz, Ph), 6.68 (1H, m, 1H, $J_{1,2}$ = 7 Hz, $J_{1,3}$ = 3 Hz, Ph), 6.75–7.38 (15H, m, Ph) and 7.74 (1H, d, $J_{1,3}$ = 3 Hz, Ph); δ_C (50 MHz; $CDCl_3$) 20.27 (q), 51.95 (t), 99.83, 127.35 (d), 127.49 (d), 127.76 (d), 128.05 (d), 128.19 (d), 128.70 (d), 128.80 (d), 129.26 (d), 129.35 (d), 131.27 (d), 132.99 (d), 135.41, 136.78, 138.08, 139.12, 139.91 (d), 140.46 and 170.81.

***N*-(4-Methylphenyl)-*N*-methylcinnamide, 6d**

Mp 76–77 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1607 vs (conj. C=O) and 1600 vs (conj. C=C); λ_{max}($CHCl_3$)/nm 280; δ_H (200 MHz; $CDCl_3$) 2.25 (3H, s, -CH_3), 3.30 (3H, s, -CH_3), 6.25 (1H, d, $J_{1,2}$ = 16.0 Hz, -NCOCH=CHPh), 6.75–7.40 (9H, m, Ph) and 7.50 (d, $J_{1,2}$ = 16.0 Hz, -NCOCH=CHPh); δ_C (50 MHz; $CDCl_3$) 21.01, 37.60, 118.68, 126.95, 127.77, 128.56, 129.40, 130.16, 135.11, 137.48, 140.84, 141.63 and 166.33; *m*/*z* 250 (2%), 131 (76), 103 (80), 91 (14) and 77 (100).

***N*-(4-Methylphenyl)-*N*-ethylcinnamide, 6e**

Mp 54–55 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1607 vs (conj. C=O) and 1600 vs (conj. C=C); λ_{max}($CHCl_3$)/nm 280; δ_H (200 MHz; $CDCl_3$) 1.05 (3H, t, $J_{1,2}$ = 7 Hz, -N$CH_2C$$H_3$), 2.25 (3H, s, -$CH_3$), 3.76 (2H, q, $J_{1,2}$ = 7 Hz, -N$CH_2$$CH_3$), 6.10 (1H, d, $J_{1,2}$ = 14 Hz, -NCOCH=CHPh), 6.95 (2H, d, $J_{1,2}$ = 7 Hz, Ph), 7.15 (7H, m, Ph) and 7.58 (1H, d, $J_{1,2}$ = 14 Hz, -NCOCH=CHPh); δ_C (50 MHz; $CDCl_3$) 13.05 (q), 21.10 (q), 44.45 (t), 119.31, 127.81, 128.15, 128.61, 129.33, 130.17, 135.38, 137.64, 139.31, 141.47 and 165.69 (C=O); *m*/*z* 250 (2%), 131 (76), 103 (80), 91 (14) and 77 (100).

***N*-(4-Chlorophenyl)-*N*-methylcinnamide, 6g**

Mp 77–78 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1630 vs (conj. C=O);

δ_H (200 MHz; $CDCl_3$) 3.45 (3H, s, -CH_3), 6.25 (1H, d, $J_{1,2}$ = 16.0 Hz, -*N*COC*H*=CHPh), 7.15–7.40 (9H, m, Ph) and 7.58 (1H, d, $J_{1,2}$ = 16.0 Hz, -*N*COCH=C*H*Ph); δ_C (50 MHz; $CDCl_3$) 37.52, 118.26, 127.86, 128.58, 128.70, 129.66, 129.80, 133.29, 135.00, 142.22, 142.30 and 166.02 (C=O).

1,5-Dimethyl-3-benzylindolin-2-one, 7d

0.50 g of **1d** were electrolysed; mp 91–92 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1699 vs (C=O); λ_{max}($CHCl_3$)/nm 260; δ_H (200 MHz; $CDCl_3$) 2.21 (3H, s, -CH_3), 2.77–2.92 (1H, dd, $J_{1,1'}$ = 13, $J_{1,2}$ = 8 Hz, -CHCH_2Ph), 3.12 (3H, s, -NCH_3), 2.86 (1H, dd, $J_{1,1'}$ = 13, $J_{1,2}$ = 4 Hz, -CHCH_2Ph), 3.69 (1H, dd, $J_{1,2}$ = 4, $J_{1,2}$ = 8 Hz, -CHCH_2Ph), 6.65 (2H, m, Ph) and 6.93–7.30 (6H, m, Ph); δ_C (50 MHz; $CDCl_3$) 21.04 (q), 26.08 (q), 36.81 (t), 47.07 (d), 107.52 (d), 125.38 (d), 126.54, 127.88, 128.42 (d), 128.87 (d), 129.37 (d), 131.42 (d), 138.03, 141.80 and 176.94 (C=O); *m*/*z* 251 (65%), 174 (4), 160 (100), 91 (20) and 77 (6). HRMS: calculated: 251.131015, observed: 251.131085.

1-Ethyl-3-benzyl-5-methylindolin-2-one, 7e

0.50 g of **1e** were electrolysed; mp 65–66 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1715 br (conj. C=O); λ_{max}($CHCl_3$)/nm 263; δ_H (200 MHz; $CDCl_3$) 1.00 (t, 3H, *J* = 7 Hz), 2.13 (s, 3H), 2.76–2.93 (dd, 1H, *J* = 14 Hz, *J* = 7 Hz), 3.35 (dd, 1H, *J* = 14 Hz, *J* = 5 Hz), 3.40–3.80 (m, 3H), (d + s, 2H, *J* = 7 Hz) and 6.90–7.20 (m, 6H); δ_C (50 MHz; $CDCl_3$) 12.40 (q), 21.00 (q), 34.42 (t), 36.76 (t), 46.99 (d), 107.65 (d), 125.48 (d), 125.83 (d), 126.48 (d), 128.06 (d), 128.67, 129.45 (d), 131.21, 137.73, 140.91 and 176.50 (C=O); *m*/*z* 265 (80%), 188 (7), 174 (100), 146 (10), 91 (30) and 77 (7).

1,3-Dibenzyl-5-methylindolin-2-one, 7f

0.50 g of **1f** were electrolysed; mp 110–111 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1718 vs (C=O); λ_{max}($CHCl_3$)/nm 270; δ_H (200 MHz; $CDCl_3$) 2.25 (3H, s, -CH_3), 3.00–3.10 (1H, q, $J_{1,1'}$ = 14, $J_{1,2}$ = 8 Hz, -CHCH_2Ph), 3.40–3.59 (1H, dd, $J_{1,1'}$ = 14, $J_{1,2}$ = 4 Hz, -CHCH_2Ph), 3.40–3.50 (q, 1H, $J_{1,2}$ = 8, $J_{1,2}$ = 4 Hz, -C*H*CH$_2$Ph), 4.57 (1H, d, $J_{1,1'}$ = 16 Hz, -*N*CH_2Ph), 5.05 (1H, d, $J_{1,1'}$ = 16 Hz -*N*CH_2Ph), 6.37 (1H, d, $J_{1,2}$ = 7 Hz, Ph), 6.78 (4H, m, Ph) and 7.08–7.34 (8H, m, Ph); δ_C (50 MHz; $CDCl_3$) 21.02 (q), 36.04 (t), 43.45t), 47.07 (d), 108.68 (d), 119.49, 125.22 (d), 126.55 (d), 126.83 (d), 127.19 (d), 128.05 (d), 128.17 (d), 128.54 (d), 129.61 (d), 131.48, 135.59, 137.37, 140.95 and 176.78 (C=O); *m*/*z* 327 (41%), 236 (63), 91 (100) and 77 (6); HRMS: calculated: 327.162315, observed: 327.159564.

1-Methyl-3-benzyl-5-chloroindolin-2-one, 7g

0.50 g of **1g** were electrolysed; mp 115–116 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1721 vs (conj. C=O); λ_{max}($CHCl_3$)/nm 260; δ_H (200 MHz; $CDCl_3$) 2.78–2.95 (1H, dd, $J_{1,1'}$ = 14, $J_{1,2}$ = 8 Hz, -CHCH_2Ph), 3.13 (3H, s, -*N*CH_3), 3.37–3.51 (1H, dd, $J_{1,1'}$ = 14, $J_{1,2}$ = 7 Hz, -CHCH_2Ph), 3.66–3.73 (1H, q, $J_{1,2}$ = 8, $J_{1,2}$ = 4 Hz -C*H*CH$_2$Ph), 6.63–6.80 (2H, m, Ph) and 7.11–7.40 (6H, m, Ph); δ_C (50 MHz; $CDCl_3$) 26.20 (q), 36.62 (t), 47.09 (d), 108.71 (d), 124.94 (d), 126.85 (d), 127.38, 127.83 (d), 128.39 (d), 129.29 (d), 129.93 and 137.29; *m*/*z* 273 (2.8%), 271 (9), 182 (4), 180 (12) and 91 (100); HRMS: calculated: 271.072423, observed: 271.07176.

1,3-Dibenzyl-5-chloroindolin-2-one, 7h

0.50 g of **1h** were electrolysed; mp 120–121 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1718 vs (C=O); λ_{max}($CHCl_3$)/nm 275; δ_H (200 MHz; $CDCl_3$) 3.00–3.10 (1H, dd, $J_{1,1'}$ = 14, $J_{1,2}$ = 8 Hz, -CHCH_2-Ph), 3.31–3.40 (1H, dd, $J_{1,1'}$ = 14, $J_{1,2}$ = 4 Hz, -CHCH_2Ph), 3.70–3.75 (1H, q, $J_{1,2}$ = 8, $J_{1,2}$ = 4 Hz, -C*H*CH$_2$Ph), 4.47 (1H, d, $J_{1,1'}$ = 16 Hz, -*N*CH_2Ph), 6.32 (1H, d, $J_{1,1'}$ = 7 Hz, Ph) and 6.77–7.25 (12H, m, Ph); δ_C (50 MHz; $CDCl_3$) 36.16 (t), 43.49 (t), 47.03 (d), 109.85 (d), 124.76 (d) 126.75 (d), 126.80 (d), 127.40 (d), 127.77 (d), 128.33 (d), 128.64 (d), 129.54 (d), 129.56, 129.77, 134.98 (d), 136.69, 141.87 and 176.21 (C=O); *m*/*z* 348 (3%), 346 (10), 131 (100), 103 (57) and 91 (78); HRMS: calculated: 347.107715, observed: 347.108165.

1,3-Dibenzyl-5-bromoindolin-2-one, 7i

0.50 g of **1i** were electrolysed; mp 114–115 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1724 vs (conj. C=O); λ_{max}($CHCl_3$)/nm 267; δ_H (200 MHz; $CDCl_3$) 3.10–3.20 (1H, dd, $J_{1,1'}$ = 14, $J_{1,2}$ = 8 Hz, -CHCH_2Ph), 3.40–3.59 (1H, dd, $J_{1,1'}$ = 14, $J_{1,2}$ = 4 Hz, -CHCH_2Ph), 3.80–3.85 (1H, dd, $J_{1,2}$ = 8, $J_{1,2}$ = 4 Hz, -CHCH_2-Ph), 4.57 (1H, d, $J_{1,1'}$ = 16 Hz, -*N*CH_2Ph), 6.37 (1H, d, $J_{1,1'}$ = 16 Hz, -*N*H$_2$Ph), 6.37 (1H, d, $J_{1,2}$ = 7 Hz, Ph), 6.88 (2H, m, Ph), and 7.08–7.34 (11H, m, Ph); δ_C (50 MHz; $CDCl_3$) 36.23 (t), 43.53 (d), 47.02 (t), 110.40 (d), 114.80, 125.80 (d), 126.79 (d), 127.44 (d), 127.57 (d), 128.36 (d), 128.67 (d), 129.58 (d), 130.21, 130.72 (d), 134.98, 136.72, 142.40 and 176.14 (C=O); *m*/*z* 393 (20%), 391 (20), 302 (10), 302 (10), 187 (10) and 91 (100); HRMS: 391.0577 observed: 391.058843.

1-Methyl-3-benzylindolin-2-one, 7j

0.50 g of **1j** were electrolysed; mp 67–68 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1705 vs (C=O); λ_{max}($CHCl_3$)/nm 258; δ_H (200 MHz; $CDCl_3$) 2.77–2.92 (1H, dd, $J_{1,1'}$ = 13, $J_{1,2}$ = 8 Hz, -CHCH_2Ph), 3.12 (3H, s, -*N*CH_3), 2.86 (1H, dd, $J_{1,1'}$ = 13, $J_{1,2}$ = 4 Hz, -CHCH_2Ph), 3.69 (1H, dd, $J_{1,2}$ = 4, $J_{1,2}$ = 8 Hz, -C*H*CH$_2$Ph), 6.65 (2H, d, $J_{1,2}$ = 7Hz, Ph), 6.85 (1H, t, $J_{1,2}$ = 7, $J_{1,3}$ = 2 Hz, Ph) and 6.93–7.30 (6H, m, Ph); δ_C (50 MHz; $CDCl_3$) 26.05 (q), 36.78 (t), 47.00 (d), 107.84, 121.98, 124.47, 126.55, 127.88, 128.22, 128.34, 129.34, 137.90, 144.15, 177.01 (C=O); *m*/*z* 237 (5%), 146 (12), 91 (100) and 77 (8).

1,3-Dibenzylindolin-2-one, 7k

0.50 g of **1k** were electrolysed; mp 98–99 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1718 br (C=O); λ_{max}($CHCl_3$)/nm 263; δ_H (200 MHz; $CDCl_3$) 3.00 (1H, dd, $J_{1,2}$ = 13, *J* = 8 Hz, -CHCH_2Ph), 3.36–3.45 (1H, dd, $J_{1,1'}$ = 13, $J_{1,2}$ = 4 Hz, -CHCH_2-Ph), 3.71–3.78 (1H, dd, $J_{1,2}$ = 8, $J_{1,2}$ = 4 Hz, -CHCH_2Ph), 4.52 (1H, d, $J_{1,1'}$ = 14 Hz, -*N*CH_2Ph), 4.93 (1H, d, $J_{1,1'}$ = 14 Hz, -*N*CH_2Ph), 6.44 (1H, d, $J_{1,2}$ = 7 Hz, Ph), 6.78–6.88 (4H, m, $J_{1,2}$ = 8, $J_{1,3}$ = 3 Hz, Ph) and 6.94–7.25 (9H, m, Ph); δ_C (50 MHz; $CDCl_3$) 36.36 (t), 43.40 (t), 46.97 (d), 108.94 (d), 122.00 (d), 124.35 (d), 126.55 (d), 126.81 (d), 127.22 (d), 127.80 (d), 128.09, 128.18, 128.54 (d), 129.57 (d), 135.45, 137.27, 143.30 and 176.80 (C=O); *m*/*z* 313 (35%), 222 (50) and 91 (100); HRMS: calculated: 313.146650, observed: 313.147285.

1,3-Dibenzyl-5-methyl-3-deuterioindolin-2-one, 7l

Mp 110–111 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1718 vs (C=O); λ_{max}($CHCl_3$)/nm 270; δ_H (200 MHz; $CDCl_3$) 2.45 (3H, s, -CH_3), 3.00 (1H, d, $J_{1,1'}$ = 14 Hz, -CDCH_2Ph), 3.45 (1H, d, $J_{1,1'}$ = 14 Hz, -CDCH_2Ph), 4.25 (1H, d, $J_{1,1'}$ = 13 Hz, -*N*CH_2Ph), 4.50 (1H, d, $J_{1,1'}$ = 13 Hz, -*N*CH_2Ph), 6.15 (1H, d, $J_{1,2}$ = 7 Hz, Ph), 6.40 (1H, m, Ph), 6.8 (4H, m, Ph) and 7.1–7.4 (8H, m, Ph); δ_C (50 MHz; $CDCl_3$) 21.02 (q), 36.04 (-CDCH$_2$Ph), 43.45 (t), 47.07 (d), 108.68 (d), 119.49, 125.22 (d), 126.55 (d), 126.83 (d), 127.19 (d), 128.05 (d), 128.17 (d), 128.54 (d), 129.61 (d), 131.48, 135.59, 137.37, 140.95 and 176.78 (C=O); *m*/*z* 328 (38%), 327 (38), 237 (27), 236 (38) and 91 (100).

1-Benzyl-3-(α-deuteriobenzyl)-5-methylindolin-2-one, 7m

Mp 110–111 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1718 vs (C=O); λ_{max}($CHCl_3$)/nm 270; δ_H (200 MHz; $CDCl_3$) 2.25 (3H, s, -CH_3), 3.00 (0.5H, d, $J_{1,2}$ = 7 Hz, -CHC*H*DPh), 3.45 (0.5H, d, $J_{1,2}$ = 7 Hz, -CHC*H*DPh), 3.85 (1H, m, $J_{1,3}$ = 3, $J_{1,2}$ = 7 Hz, -CHC*H*DPh), 4.25 (1H, d, $J_{1,1'}$ = 13 Hz, -*N*CH_2Ph), 4.50 (1H,

d, $J_{1,1'}$ = 13 Hz, -NCH_2Ph), 6.15 (1H, d, $J_{1,2}$ = 7 Hz, Ph), 6.40 (4H, m, Ph) and 7.25 (8H, m, Ph); δ_C (50 MHz; $CDCl_3$) 21.02 (q), 36.04 (3 equally intense signals), 43.45 (t), 47.07 (d), 108.68 (d), 119.49, 125.22 (d), 126.55 (d), 126.83 (d), 127.19 (d), 128.05 (d), 128.17 (d), 128.54 (d), 129.61 (d), 131.48, 135.59, 137.37, 140.95 and 176.78 (C=O); *m*/*z* 328 (50%), 237 (28), 236 (60), 92 (23) and 91 (100); HRMS: calculated: 328.17614, observed: 328.17543.

1,3-Dibenzyl-3-phenyl-5-methylindolin-2-one, 7n

Mp 116–117 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1718 vs (conj. C=O); λ_{max}($CHCl_3$)/nm 282; δ_H (200 MHz; $CDCl_3$) 2.25 (3H, s, -CH_3), 3.45 (1H, d, $J_{1,1'}$ = 13 Hz, -CH_2Ph), 3.85 (1H, d, $J_{1,1'}$ = 13 Hz, -CH_2Ph), 4.40 (d, 1H, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 4.80 (d, 1H, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 6.24 (1H, d, $J_{1,2}$ = 7 Hz, Ph), 6.56 (2H, t, $J_{1,2}$ = 7, $J_{1,3}$ = 3 Hz, Ph), 6.80 (3H, m, Ph) 6.94–7.14 (7H, m, Ph), 7.17–7.32 (3H, m, Ph) and 7.46 (2H, t, *J* = 7 Hz, Ph); δ_C (50 MHz; $CDCl_3$) 21.9 (q), 43.37 (t), 43.64 (t), 58.37 (q), 109.11 (d), 125.98 (d), 126.56 (d), 126.63 (d), 127.00 (d), 127.06 (d), 127.19 (d), 127.35 (d), 127.76 (d), 128.41 (d), 128.45 (d), 128.60 (d), 130.42 (d), 131.44, 131.65, 135.34, 135.83, 140.56 and 177.57 (C=O); *m*/*z* 403 (10%), 312 (18), 237 (82), 160 (45), 131 (100), 117 (25), 103 (54) and 91 (62); HRMS: calculated: 403.193615, observed: 403.195804.

3-Hydroxy-3-benzyl-1,5-dimethylindolin-2-one, 8d

0.50 g of **1d** were electrolysed; mp 139–140 °C (CCl_4); ν_{max}($CHCl_3$)/cm^{-1} 3376 w (O–H) and 1724 vs (C=O); λ_{max}($CHCl_3$)/nm 265; δ_H (200 MHz; $CDCl_3$) 2.25 (3H, s, -CH_3), 2.95 (3H, s, -NCH_3), 3.10–3.40 (2H, ABq, $J_{1,1'}$ = 13 Hz, -C(OH)-CH_2Ph), 5.70 (1H, br s, D_2O exchanged, -C(O*H*)CH_2Ph), 6.50 (1H, d, 1H, $J_{1,2}$ = 7 Hz, Ph) and 7.22 (7H, m, Ph); δ_C (50 MHz; $CDCl_3$) 21.08 (q), 25.82 (q), 44.80 (t), 77.63 (q), 107.78 (d), 125.19, 125.60 (d), 127.52 (d), 129.49 (d), 129.52, 130.17 (d), 132.26 (d), 134.17, 140.62 and 178.19 (C=O); *m*/*z* 267 (12%), 176 (100) and 91 (18).

3-Hydroxy-1,3-dibenzyl-5-methylindolin-2-one, 8f

0.50 g of **1f** were electrolysed; mp 213–214 °C ($CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 3328 s (O=H) and 1705 vs (C=O); λ_{max}($CHCl_3$)/nm 269; δ_H (200 MHz; $CDCl_3$) 2.25 (3H, s, -CH_3), 3.25–3.44 (3H, AB q and s, $J_{1,1'}$ = 13 Hz, 1H, D_2O exchanged, -C(O*H*)CH_2Ph), 4.41 (1H, d, $J_{1,1'}$ = 14 Hz, -NCH_2Ph), 4.95 (1H, d, $J_{1,1'}$ = 14 Hz, -NCH_2Ph), 6.30 (1H, d, $J_{1,2}$ = 7 Hz, Ph), 6.66 (2H, m, Ph), 6.92 (2H, m, Ph) and 7.1 (8H, m, Ph); δ_C (50 MHz; $CDCl_3$) 21.06 (q), 43.69 (t), 44.82 (t), 76.36 (q), 109.30, 125.07, 126.63, 126.89, 127.24, 128.04, 128.59, 129.15, 129.96, 130.42, 132.53, 133.92, 135.02, 140.28 and 177.61 (C=O); *m*/*z* 343 (18.8%), 251 (100) and 91 (94); HRMS: calculated: 343.157230, observed: 343.154184.

3-Hydroxy-1-methyl-3-benzyl-5-chloroindolin-2-one, 8g

0.50 g of **1g** were electrolysed; mp 170–171 °C ($CHCl_3$); λ_{max}($CHCl_3$)/nm 262; ν_{max}($CHCl_3$)/cm^{-1} 3532 w (OH) and 1721 vs (C=O); δ_H (200 MHz; $CDCl_3$) 2.95 (3H, s, -NCH_3), 3.24 (2H, AB q, $J_{1,1'}$ = 13 Hz, -C(OH)CH_2Ph), 4.22 (1H, br s, D_2O exchanged, -C(O*H*)CH_2Ph), 6.55 (1H, d, $J_{1,2}$ = 6 Hz), 6.90 (2H, m, Ph) and 7.15 (5H, m, Ph); δ_C (50 MHz; $CDCl_3$) 26.00 (q), 44.87 (t), 77.62 (q), 109.12 (d), 124.94 (d), 127.00 (d), 127.82 (d), 128.28, 129.37 (d), 130.11 (d), 131.03, 133.46, 141.57 and 177.67 (C=O); *m*/*z* 289 (3%), 287 (9), 197 (20), 196 (78), 195 (14) and 91 (100); HRMS: calculated: 287.070805, observed: 287.067525.

3-Hydroxy-1,3-dibenzyl-5-chloroindolin-2-one, 8h

0.50 g of **1h** were electrolysed; mp 218–219 °C ($CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 3350 w (OH) and 1718 vs (C=O); λ_{max} ($CHCl_3$)/nm 264; δ_H (200 MHz; $CDCl_3$) 2.65 (1H, d, $J_{1,1'}$ = 13 Hz, -C(OH)CH_2Ph), 2.84 (1H, d, $J_{1,1'}$ = 13 Hz, -C(OH)-CH_2Ph), 4.05 (d, 1H, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 4.31 (1H, d, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 6.01 (2H, m, Ph), 6.27 (2H, dd, $J_{1,2}$ = 7, $J_{1,3}$ = 2 Hz, Ph), 6.38 (2H, d, $J_{1,2}$ = 7 Hz, Ph), 6.57–6.7 (7H, m, Ph) and 6.90 (1H, d, $J_{1,3}$ = 2 Hz, Ph); δ_C (50 MHz; $CDCl_3$) 42.42 (t), 43.13 (t), 76.67 (q), 110.32 (d), 124.58 (d), 125.36 (d), 126.31, 126.59 (d), 127.05 (d), 127.78 (d), 128.38 (d), 128.74 (d), 130.09 (d), 132.51, 134.27, 135.32, 141.11 and 176.54 (C=O); *m*/*z* 365 (5%), 363 (15), 274 (8), 272 (24) and 91 (100); HRMS: calculated: 363.102105, observed: 363.10528.

3-Hydroxy-1,3-dibenzyl-5-bromoindolin-2-one, 8i

0.50 g of **1i** were electrolysed; mp 230–231 °C ($CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 3328 w (OH) and 1715 vs (C=O); λ_{max}($CHCl_3$)/nm 260; δ_H (200 MHz; $CDCl_3$) 2.61 (1H, d, $J_{1,1'}$ = 13 Hz, -C(OH)CH_2Ph), 2.90 (1H, d, $J_{1,1'}$ = 13 Hz, -C(OH)CH_2Ph), 4.04 (1H, d, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 4.31 (d, 1H, $J_{1,1'}$ = 16 Hz, -NCH_2Ph), 5.97 (2H, t, $J_{1,2}$ = 7, $J_{1,3}$ = 2 Hz, Ph), 6.27 (2H, dd, $J_{1,2}$ = 7, *J* = 3 Hz, Ph), 6.40 (2H, dd, *J* = 7, 2 Hz, Ph), 6.56–6.68 (6H, m, Ph), 6.79–6.84 (1H, dd, *J* = 7, *J* = 3 Hz, Ph) and 6.95 (1H, d, $J_{1,3}$ = 3 Hz, Ph); *m*/*z* 407 (10%), 405 (10), 315 (15), 313 (15), 131 (14) and 91 (100); HRMS: calculated: 407.05209, observed: 407.05654.

3-Hydroxy-1,3-dibenzylindolin-2-one, 8k

0.50 g of **1k** were electrolysed; mp 178–179 °C ($CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 3360 s (OH) and 1715 vs (C=O); λ_{max} ($CHCl_3$)/nm 260; δ_H (200 MHz; $CDCl_3$) 3.15–3.45 (2H, AB q, $J_{1,1'}$ = 13 Hz, -C(OH)CH_2Ph), 4.08 (1H, br s, D_2O exchanged, -C(O*H*)CH_2Ph), 4.31 (1H, d, $J_{1,1'}$ = 14 Hz, -NCH_2Ph), 4.89 (1H, d, $J_{1,1'}$ = 14 Hz, -NCH_2Ph), 6.36 (1H, d, $J_{1,2}$ = 7 Hz), 6.59 (2H, d, $J_{1,2}$ = 7 Hz, Ph), 6.85 (2H, d, $J_{1,2}$ = 7 Hz, Ph), 6.95–7.21 (8H, m, Ph) and 7.24–7.33 (1H, m, Ph); δ_C (50 MHz; $CDCl_3$) 43.68 (t), 44.73 (t), 77.66 (q), 109.54 (d), 122.96 (d), 124.39 (d), 126.60 (d), 126.84 (d), 127.25 (d), 128.02 (d), 128.60 (d), 129.34, 129.63 (d), 130.39 (d), 133.89, 134.85, 142.61 and 177.98 (C=O); *m*/*z* 329 (5%), 312 (23.57), 238 (59.28), 237 (35.54) and 91 (100); HRMS: calculated: 332.165055, observed: 332.165055.

3-Acetoxy-1,3-dibenzyl-5-methylindolin-2-one, 9f

Mp 132–133 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1753 (C=O) and 1728 (C=O); λ_{max}($CHCl_3$)/nm 264; δ_H (200 MHz; $CDCl_3$) 2.07 (3H, s, -OCO*C*H_3), 2.25 (3H, s, -CH_3), 3.25 (2H, ABq, $J_{1,1'}$ = 16 Hz, -C(OAc)CH_2Ph), 4.74 (2H, d, $J_{1,1'}$ = 13 Hz, -NCH_2Ph), 6.27 (1H, d, $J_{1,1'}$ = 7 Hz, Ph), 6.84–7.50 (12H, m, Ph); δ_C (50 MHz; $CDCl_3$) 20.74, 21.05, 42.61, 43.87, 80.77, 109.18, 123.86, 126.68, 127.10, 127.86, 128.53, 129.94, 130.78, 131.84, 132.71, 135.38, 140.77, 168.74 and 174.11.

1,1′,5,5′-Tetramethyl-3,3′-dibenzyl-3,3′-biindoline-2,2′-dione, 11d

Mp 240–241 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1696 vs (C=O); λ_{max}($CHCl_3$)/nm 268; δ_H (200 MHz; $CDCl_3$) 2.20 (3H, s, -CH_3), 3.52 (3H, s, -NCH_3), 3.85 (1H, d, $J_{1,1'}$ = 13 Hz, -CCH_2Ph), 4.18 (1H, d, $J_{1,1'}$ = 13 Hz, -C(OAc)CH_2Ph), 6.12 (1H, d, $J_{1,2}$ = 7 Hz, Ph), 6.75 (1H, m, Ph) and 7.05 (6H, m, Ph); δ_C (50 MHz; $CDCl_3$) 20.99 (q), 25.34 (q), 35.06 (t), 57.48 (s), 106.54 (d), 124.56, 124.66 (d), 125.77, 127.15 (d), 127.99 (d), 128.19 (d), 130.63 (d), 136.17, 140.62 and 176.78 (C=O); *m*/*z* 500 (8.21%), 251 (64.93), 250 (85), 222 (53.75) and 91 (100); HRMS: calculated: 508.30898, observed: 508.305358.

1,1′,3,3′-Tetrabenzyl-5,5′-dimethyl-3,3′-biindoline-2,2′-dione, 11f

Mp 144–145 °C (hexane); ν_{max}($CHCl_3$)/cm^{-1} 1720 (C=O), λ_{max}($CHCl_3$)/nm 268; δ_H (200 MHz; $CDCl_3$) 2.25 (3H, s, -CH_3), 3.85 (2H, d, $J_{1,1'}$ = 13 Hz, -CHCH_2Ph), 4.25 (2H, AB q,

$J_{1,1'}$ = 16 Hz, -NCH_2Ph), 4.99 (1H, d, $J_{1,1'}$ = 13 Hz, -CCH_2Ph), 5.85 (1H, d, $J_{1,2}$ = 6 Hz, Ph), 6.62 (3H, d, $J_{1,2}$ = 6 Hz, Ph) and 6.80–7.39 (9H, m, Ph); δ_C (50 MHz; $CDCl_3$) 21.16 (q), 35.47 (t), 45.38 (t), 57.78 (s), 108.30 (d), 125.03 (d), 126.11 (d), 126.56 (d), 126.98 (d), 127.58 (d), 128.15 (s), 128.31 (d), 128.44 (d), 130.88 (d), 135.01 (s), 136.06 (s), 140.30 (s) and 176.76 (C=O); *m/z* M (unobserved), 327 (58.62%), 326 (76.28), 146 (13.84) and 91 (100).

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