Synthesis of 3,4-Bridged Indoles by Photocyclisation Reactions. Part 2.[1] Photocyclisation of Halogenoacetyl Tryptophol Derivatives and α-Chloro Indol-3-ylalkanoate Esters

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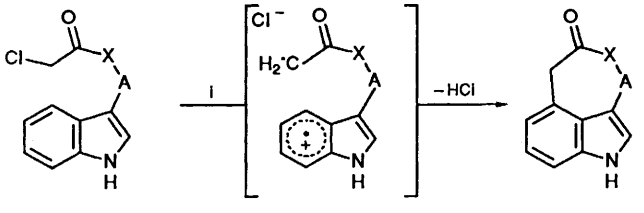
Irradiation of the trichloroacetates **2**, **4** and **5**, derived from the corresponding tryptophols, in methanolic acetonitrile results in photocyclisation to the indole 4-position, and the formation of the pyrrolobenzoxocines **9**–**11**. Attempted photocyclisation of the 'reversed' α-chloro esters **15a**, **15b** and **18** was thwarted by readily occurring elimination of HCl, although the dimethyl compound **15c** did cyclise to give the cycloheptaindole **20** upon irradiation in acetonitrile.

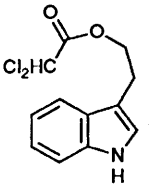
In the preceding paper we have described the photocyclisation reactions of various *N*-halogenoacetyl derivatives of tryptophan esters, tryptophanol and tryptamine.[1] These result in the formation of 3,4-bridged indoles in synthetically useful yields, and are thought to proceed by a mechanism which involves single-electron transfer from the excited state of the indole chromophore to the chlorocarbonyl moiety. This causes dissociation of the C–Cl bond and the ensuing acetamido radical subsequently collapses onto the indole 4-position. Loss of a proton results in the formation of the observed 3,4-bridged indole (Scheme 1, X = NH, A = CH_2CHCO_2Me in the case of tryptophan ester). The regiochemistry of this cyclisation is rationalised by application of SCF-MO theory, by which it is shown that the reactivity of the positions of the indole nucleus approximately correlate with the singly unoccupied molecular orbital (SUMO) electron-density values of the indole radical.[2] The key step in this mechanism is the electron/energy transfer from the excited aromatic chromophore to the chlorocarbonyl group. Evidence for this type of process comes from the fact that certain molecules such as chloroacetamide with no low lying singlet states efficiently quench the fluorescence of indoles.[3] Methyl chloroacetate has a similar effect, and therefore it seemed reasonable to expect that α-chloro esters might undergo similar photocyclisation reactions to their amide counterparts (Scheme 1, X = O). We have now investigated this possibility in detail, and report our results herein.



Scheme 1 *Conditions:* i, *hν*

Results and Discussion

Starting with the most plausible alternative to chloroacetyltryptophans, several chloroacetyl tryptophols were prepared and their photocyclisation studied. Thus, commercially available tryptophol and homotryptophol were readily converted into their dichloro- and trichloro-acetyl derivatives **1**, **2** and **6** by simple acylation. The *N*-(*tert*-butoxycarbonyl) (Boc) derivative **3** was prepared by treatment of ester **2** with di-*tert*-butyl pyrocarbonate (di-*tert*-butyl dicarbonate) [$(Boc)_2O$] in acetonitrile in the presence of 4-(dimethylamino)pyridine (DMAP). Attempts to prepare the *N*-methyl derivative **4** by methylation of ester **2** under basic conditions were unsuccessful, and therefore this *N*-methyl compound was obtained from ethyl *N*-methylindole-3-acetate by lithium aluminium hydride reduction (97%) to the *N*-methyltryptophol, followed by acylation with trichloroacetyl chloride (96%). The 5-methoxytryptophol derivative **5** was also prepared from the corresponding indole-3-acetic acid by esterification, reduction and acylation, all the steps proceeding in > 85% yield.



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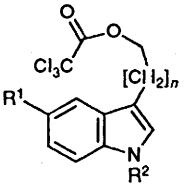

2 *n* = 2, $R^1 = R^2 = H$
3 *n* = 2, $R^1 = H$, R^2 = Boc
4 *n* = 2, $R^1 = H$, R^2 = Me
5 *n* = 2, R^1 = OMe, $R^2 = H$
6 *n* = 3, $R^1 = R^2 = H$

Initial photocyclisation studies were disappointing in that irradiation of (dichloroacetyl)tryptophol **1** in acetonitrile gave a black reaction mixture from which no single product could be isolated. However, repetition of the reaction in the presence of a nucleophile (methanol) led to a cleaner reaction mixture from which one product could be isolated. This was identified as the 3,4-disubstituted indole **8** (19%) which presumably arises from the initial photocyclisation product **7** by nucleophilic displacement of chloride with methanol followed by methanolysis of the 8-membered lactone (Scheme 2). Although no cyclic product results, this reaction can formally be considered a directed aromatic substitution whereby the electrophile is regioselectively delivered to the 4-position.

On the basis of previous results,[1] additional chlorines in the chlorocarbonyl compound were expected to increase the yield of photocyclisation product by further stabilising the radical intermediate, and indeed this proved to be the case. Irradiation of 2-(indol-3′-yl)ethyl trichloroacetate **2** in methanolic acetonitrile gave the pyrrolobenzoxocine **9**, a known ring system,[4] in 42% yield (Scheme 3). Although the yield of photocyclisation product was considerably better than that from the correspond-

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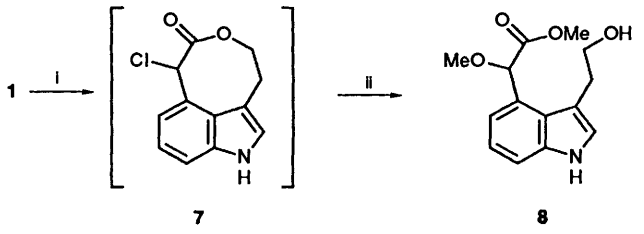
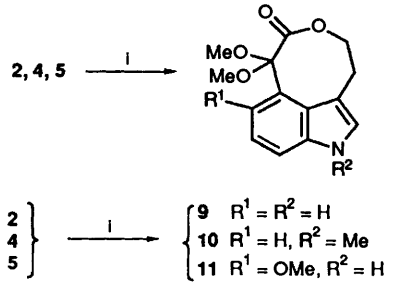


Scheme 2 *Reagents and conditions:* i, *hv*, MeCN; ii, MeOH

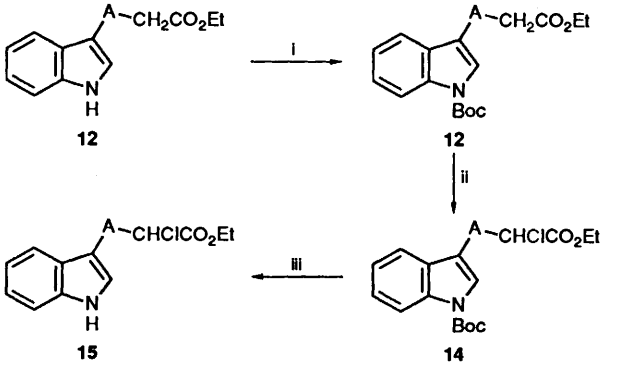
ing dichloroacetate, it was significantly poorer than the corresponding trichloroacetamide derivative.[1] It appears therefore that α-chloro ester photocyclisations are less efficient than their amide counterparts, possibly due to the greater stability of $^{\bullet}CH_2CONHR$ radicals over $^{\bullet}CH_2CO_2R$.



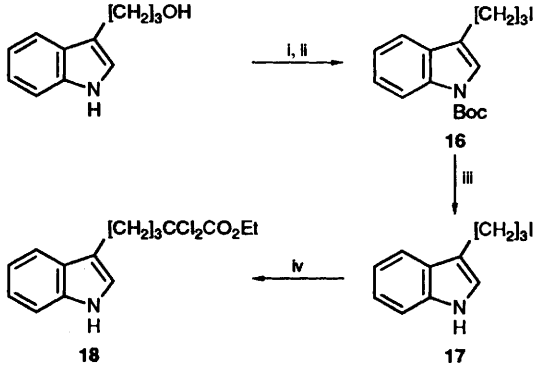
Scheme 3 *Reagents and conditions:* i, *hv*, MeCN, MeOH

The photocyclisation of 2-(indol-3′-yl)ethyl trichloroacetate **2** is effectively prevented by placing an electron-withdrawing substituent on the indole nitrogen. The *N*-Boc derivative **3** underwent merely acyl cleavage on irradiation in methanolic acetonitrile to give *N*-Boc-tryptophol in 77% yield. That photocyclisation was inhibited due to the electron-withdrawing nature of the indole nitrogen substituent, and consequent reduction of electron density in the ring, was shown by the successful cyclisation of the corresponding *N*-methyl derivative **4** which gave the pyrrolobenzoxocine **10** (36%) upon irradiation in methanolic acetonitrile (Scheme 3). Since the the presence of an electron-withdrawing group on the indole ring effectively prevents photocyclisation, an electron-releasing group might be expected to enhance the process, as is known to be the case for the analogous reaction involving simple benzene derivatives.[5] Indeed irradiation of 5-methoxytryptophyl trichloroacetate **5** in methanolic acetonitrile resulted in rapid consumption of starting material and formation of the photocyclised product **11** in 54% yield. Attempts to form an indole bridged by a nine-membered ring lactone by irradiation of the homotryptophol derivative **6** were unsuccessful; acyl cleavage occurred, and homotryptophol was reisolated in 58% yield.

We also investigated the photocyclisation of the 'reversed' α-chloro esters **15** and the dichloroester **18** in the hope that these would lead to cycloalka[*c*,*d*]indoles, although this cyclisation only proceeded poorly for the corresponding α-chloro amides.[1] The esters **15** were prepared from the corresponding ethyl esters **12a–c** of indole-3-alkanoic acids, obtained by reaction of indole with δ-valerolactone, ε-caprolactone and β,β-dimethyl-δ-valerolactone[6] respectively, using the general procedure described by Fritz.[7] The dimethyl compound **15c** was prepared for the specific purpose of blocking possible β-elimination of HCl. *N*-Protection, followed by chlorination of the ester enolate [generated using lithium isopropylcyclohexylamide (LiICA) as base] with tetrachloromethane gave the esters **14**, which were readily deprotected by treatment with trifluoroacetic acid (TFA) in dichloromethane (Scheme 4). The dichloro ester **18** was prepared from homotryptophol by conversion into the *N*-protected iodide **17** using standard methods, followed by reaction with the lithium enolate of ethyl dichloroacetate.[8] Work-up of the anion reaction gave the required ester **18**, deprotection having occurred during work-up (Scheme 5).

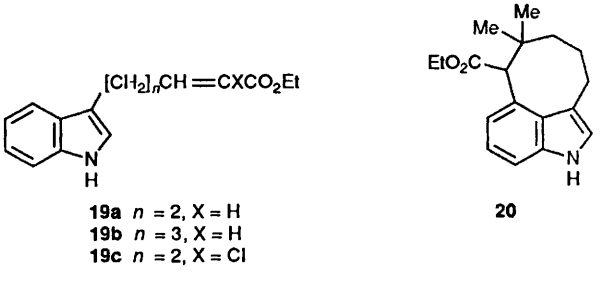


Scheme 4 (**a**, A = $[CH_2]_3$; **b**, A = $[CH_2]_4$; **c**, A = $[CH_2]_2CMe_2$). *Reagents and conditions:* i, $(Boc)_2O$, DMAP, MeCN; ii, LiICA, THF, −78 °C then CCl_4; TFA, CH_2Cl_2



Scheme 5 *Reagents and conditions:* i, TsCl, py, 0 °C, ii, NaI, acetone; iii, $(Boc)_2O$, DMAP, MeCN; iv, $LiCCl_2CO_2Et$, THF, HMPA, −78 °C

Irradiation of the α-chloro esters **15a** and **15b** led to photo elimination of HCl and the formation of the α,β-unsaturated esters **19a** and **19b** in 63 and 67% yield, respectively. No evidence for any cyclised product was found. Likewise the dichloro ester **18** also underwent photoelimination to give the unsaturated chloro ester **19c** (58%). However, the dimethyl chloro ester **15c**, in which elimination of HCl is blocked by the two methyl groups, did undergo photocyclisation, albeit in poor yield, to give the cycloheptaindole **20** (18%).



19a *n* = 2, X = H
19b *n* = 3, X = H
19c *n* = 2, X = Cl

20

In summary, we have shown that the photocyclisation reactions of tryptophan-derived chloroamides can be successfully extended to the related chloro esters, although in most cases the yields of cyclised products are reduced by competing photoelimination reactions. The analogous reactions of chloro ketones are currently under investigation.

Experimental

For general experimental details see ref. 1. NMR Coupling constants are given in Hz.

2-(*Indol-3'-yl*)*ethyl Dichloroacetate* **1**.—A solution of tryptophol (446 mg, 2.77 mmol) and pyridine (212 mg, 2.68 mmol) in dry dichloromethane (20 cm^3) was treated at 0 °C with a solution of dichloroacetyl chloride (435 mg, 2.95 mmol) in dichloromethane (1 cm^3). The reaction mixture was removed from the ice-bath and kept in the dark for 18 h. The solvent was evaporated off and the residue was chromatographed ($CHCl_3$) to give the *title compound* **1** (754 mg, 100%) as a viscous oil (Found: M^+, 271.0173. $C_{12}H_{11}Cl_2NO_2$ requires M, 271.0167); $\nu_{max}(CHCl_3)/cm^{-1}$ 3480 (NH), 3062, 3033, 3010, 2964, 1762 (C=O), 1622, 1558, 1490, 1458, 1421, 1388, 1354, 1338, 1303, 1168, 1129, 1093, 1049, 980, 848 and 819; λ_{max}(MeOH)/nm 221 (log ε 4.53), 281 (3.77) and 290infl; δ_H(270 MHz; [$^2H_6$]acetone) 3.17 (2 H, t, *J* 7.1, $ArCH_2$), 4.53 (2 H, t, *J* 7.1, CH_2O), 6.50 (1 H, s, $COCHCl_2$), 7.03 (1 H, t, *J* 7.4, 5-H), 7.10 (1 H, t, *J* 7.5, 6-H), 7.24 (1 H, s, 2-H), 7.39 (1 H, d, *J* 8.0, 7-H), 7.62 (1 H, d, *J* 7.2, 4-H) and 10.06 (1 H, br s, 1-H); *m/z* 271 (M^+, 26%), 223 (2), 149 (13), 144 (35, M − Cl_2CHCO_2), 143 (71, M − Cl_2CHCO_2H), 130 (100, $ArCH_2^{\bullet+}$), 115 (7), 103 (5) and 77 (7).

Irradiation of 2-(*Indol-3'-yl*)*ethyl Dichloroacetate* **1**.—A solution of (dichloroacetyl)tryptophol **1** (202 mg, 0.74 mmol) in 20% methanol–acetonitrile (100 cm^3) was irradiated for 25 min. The light yellow solution was evaporated and the residue was chromatographed (6% MeOH–CH_2Cl_2) to give *methyl* 2-[3'-(2-*hydroxyethyl*)*indol*-4'-*yl*]-2-*methoxyacetate* **8** (37 mg, 19%) as a yellow resin (Found: M^+, 263.1155. $C_{14}H_{17}NO_4$ requires M, 263.1158); $\nu_{max}(CHCl_3)/cm^{-1}$ 3477 (NH), 3011, 2954, 2884, 2830, 1746 (C=O), 1619, 1486, 1437, 1419, 1346, 1279, 1195, 1180, 1112, 1042, 1009, 947, 863 and 817; λ_{max}(MeOH)/nm 206 (log ε 4.24), 226 (4.40) and 293 (3.82); δ_H(270 MHz; [$^2H_6$]acetone) 3.18 (2 H, dt, $ArCH_2$), 3.39 (3 H, s, 2-OMe), 3,65 (3 H, s, CO_2Me), 3.85 (2 H, m, CH_2OH), 5.58 (1 H, s, 2-H), 7.06 (2 H, m, 5'-H and 6'-H), 7.23 (1 H, br s, 2'-H) and 7.37 (1 H, m, 7'-H; δ_C(67.9 MHz DEPT sequence experiment; $CDCl_3$) 30.3 ($ArCH_2$), 52.2 (CO_2Me), 57.1 (2-OMe), 63.0 (CH_2OH), 79.3 (C-2), 111.7 (3-3'), 112.2 (C-7'), 119.2 (C-5'), 121.8 (C-6'), 124.2 (C-2'), 125.0 (C-3'a), 128.1 (C-4'), 137.3 (C-7'a) and 171.8 (C-1); *m/z* 263 (M^+, 45%), 245 (4, M − H_2O), 232 (9, M − OMe), 231 (14, M − MeOH), 204 (100, M − CO_2Me), 186 (9, M − CO_2Me − H_2O), 172 (48), 158 (25), 154 (24), 144 (99), 130 (34), 115 (23, $Ar^{\bullet+}$), 103 (10) and 77 (16).

2-(*Indol-3'-yl*)*ethyl Trichloroacetate* **2**.—To a yellow solution of tryptophol (1.0 g, 6.20 mmol) and pyridine (0.49 g, 6.20 mmol) in dichloromethane (15 cm^3) at 0 °C was added trichloroacetyl chloride (1.24 g, 6.82 mmol), whereupon the solution darkened slightly. The mixture was removed from the cold-bath and kept in the dark for 2.5 h, after which time the solvent was evaporated off to give a brown oil. This was chromatographed (50% dichloromethane–light petroleum) to give the *title compound* **2** (1.82 g, 96%) as a pale yellow oil (Found: C, 47.3; H, 3.5; N, 4.4. $C_{12}H_{10}Cl_3NO_2$ requires C, 47.0; H, 3.3; N, 4.6%); ν_{max}(film)/cm^{-1} 3423 (indole NH), 1764 (C=O), 1458, 1422, 1255, 1226, 984, 864, 827, 743 and 680; λ_{max}(MeOH)/nm 275infl, 281 (log ε 3.74) and 290 (3.66); δ_H(200 MHz; $CDCl_3$) 3.24 (2 H, t, *J* 7.1, 2-H_2), 4.61 (2 H, t, *J* 7.1, 1-H_2), 7.09 (1 H, d, *J* 2.7, 2'-H), 7.10–7.25 (2 H, m, 5'- and 6'-H), 7.37 (1 H, d, *J* 7.4, 7'-H), 7.64 (1 H, d, *J* 7.5, 4'-H) and 8.04 (1 H, br s, 1'-H); *m/z* 305 (M^+, 8%), 144 (32), 143 (65), 130 (100, $ArCH_2^{\bullet+}$), 115 (8), 103 (5) and 77 (7).

Irradiation of 2-(*Indol-3'-yl*)*ethyl Trichloroacetate* **2**.—A solution of 2-(indol-3'-yl)ethyl trichloroacetate **2** (0.20 g, 0.652 mmol) in 20% methanol–acetonitrile (100 cm^3) was irradiated for 25 min. The golden brown solution was evaporated, and the residue was purified by chromatography (2% MeOH–CH_2Cl_2) to give, firstly, 1,3,4,7-*tetrahydro*-7,7-*dimethoxyoxocino*[4,5,6-cd]*indol*-6-*one* **9** (0.071 g, 42%) as a pale yellow solid, m.p. 196–198 °C (Found: C, 64.1; H, 5.6; N, 5.5. $C_{14}H_{15}NO_4$ requires C, 64.4; H, 5.8; N, 5.4%); ν_{max}(Nujol)/cm^{-1} 3422 (indole NH), 1752 (C=O), 1262, 1175, 1128, 1085, 1055, 1043 and 747; λ_{max}(MeOH)/nm 291infl, 296 (log ε 3.76) and 369 (3.24); δ_H(270 MHz; $CDCl_3$) 3.06 (1 H, d, *J* 16.1, 3-H), 3.35–3.48 (1 H, m, 3-H), 3.51 (3 H, s, OMe), 3.75 (3 H, s, OMe), 4.17 (1 H, dt, *J* 11.7 and 3.2, 4-H), 4.44 (1 H, t, *J* 11.8, 4-H), 7.00 (1 H, br s, 2-H), 7.13 (1 H, t, *J* 7.7, 9-H), 7.22 (1 H, d, *J* 7.1, 8-H), 7.30 (1 H, d, *J* 8.1, 10-H) and 8.25 (1 H, br s, 1-H); *m/z* 261 (M^+, 6%), 203 (11), 202 (83), 171 (14), 170 (100), 149 (11), 143 (11) and 115 (18).

This was followed by tryptophol (0.051 g, 48%), the spectroscopic properties of which were identical with those of an authentic sample.

2-[1'-(tert-*Butoxycarbonyl*)*indol*-3'-*yl*]*ethyl Trichloroacetate* **3**.—To a solution of 2-(indol-3'-yl)ethyl trichloroacetate **2** (0.46 g, 1.50 mmol) in dry acetonitrile (10 cm^3) were added di-*tert*-butyl dicarbonate (0.491 g, 2.25 mmol) and DMAP (0.018 g, 0.15 mmol). The suspension was stirred at ambient temperature for 15 h to give a clear yellow solution, which was then evaporated to leave a yellow, oily residue. This was purified by chromatography (CH_2Cl_2) to give the *title compound* **3** (0.458 g, 75%) as a yellow oil (Found: C, 50.4; H, 4.7; N, 3.35. $C_{17}H_{18}Cl_3NO_4$ requires C, 50.2; H, 4.5; N, 3.4%); ν_{max}(film)/cm^{-1} 1767 (ester C=O), 1736 (carbamate C=O), 1456, 1376, 1256, 1159, 1093, 829, 747 and 682; λ_{max}(MeOH)/nm 258 (log ε 4.00), 262 (3.99), 274infl, 285 (3.74) and 293 (3.76); δ_H(270 MHz; $CDCl_3$) 1.66 (9 H, s, Bu^t), 3.18 (2 H, td, *J* 6.8 and 1.1, 2-H_2), 4.62 (2 H, t, *J* 6.8, 1-H_2), 7.27 (1 H, td, *J* 7.5 and 1.2, 5'-H), 7.34 (1 H, td, *J* 7.5 and 1.3, 6'-H), 7.51 (1 H, s, 2'-H), 7.57 (1 H, dd, *J* 7.6 and 1.0, 4'-H) and 8.15 (1 H, br d, *J* 8.1, 7'-H); *m/z* 405 (M^+, 6%), 349 (8), 305 (3), 187 (22), 143 (39), 130 (24, $ArCH_2^{\bullet+}$) and 57 (100).

Irradiation of 2-[1'-(tert-*Butoxycarbonyl*)*indol*-3'-*yl*]*ethyl Trichloroacetate* **3**.—A solution of 2-[1'-*tert*-butoxycarbonyl)-indol-3'-yl]ethyl trichloroacetate **3** (0.20 g, 0.49 mmol) in 20% methanol–acetonitrile (100 cm^3) was irradiated for 5 min. The yellow-brown solution was evaporated, and the residue was purified by chromatography (2% MeOH–CH_2Cl_2) to give *tert-butyl* 3-(2-*hydroxyethyl*)*indole*-1-*carboxylate* (0.099 g, 77%) as a pale yellow oil (Found: C, 68.8; H, 7.5; N, 5.4. $C_{15}H_{19}NO_3$ requires C, 68.9; H, 7.3; N, 5.4%); ν_{max}(film)/cm^{-1} 3386 (OH), 1733 (C=O), 1455, 1381, 1310, 1256, 1159 and 1089; δ_H(270 MHz; $CDCl_3$) 1.54 (1 H, br s, OH), 1.67 (9 H, s, Bu^t), 2.97 (2 H, td, *J* 6.5 and 1.2, 3-CH_2), 3.93 (2 H, br t, *J* 6.1, CH_2OH), 7.24 (1 H, td, *J* 7.6 and 1.3, 5-H), 7.33 (1 H, td, *J* 7.8 and 1.4, 6-H), 7.47 (1 H, s, 2-H), 7.55 (1 H, d, *J* 7.8, 4-H) and 8.15 (1 H, br d, *J* 8.5, 7-H); *m/z* 261 (M^+, 26%), 205 (61), 174 (27), 149 (13), 131 (11), 130 (100, $ArCH_2^{\bullet+}$), 57 (97) and 41 (20).

Ethyl (1-*Methylindol*-3-*yl*)*acetate*.—Sodium hydride dispersion in mineral oil (60%; 0.217 g, 5.41 mmol) was washed with light petroleum (3 × 5 cm^3) and kept under nitrogen. Tetrahydrofuran (THF) (15 cm^3) was added, and the suspension was cooled to 0 °C. A solution of ethyl (indol-3-yl)acetate (1.0 g, 4.92 mmol) in THF (10 cm^3) was added dropwise, and the mixture was stirred at 0 °C for 30 min. After this time iodomethane (0.30 cm^3, 4.92 mmol) was added, and the mixture was stirred at 0 °C for 2 h before being allowed to warm to ambient temperature, and it was then stirred for a further 15 h. The resulting mixture was cautiously diluted with water (40 cm^3) and extracted with ether (3 × 50 cm^3), and the combined extracts were washed successively with water (2 × 30 cm^3) and brine (20 cm^3) before being dried ($MgSO_4$). Evaporation under reduced pressure gave a golden brown residue, which was purified by chromatography (CH_2Cl_2) to give the title compound[9] (0.546 g, 51%)

as a very pale yellow oil (Found: C, 71.6; H, 7.0; N, 6.6. Calc. for $C_{13}H_{15}NO_2$: C, 71.9; H, 7.0; N, 6.45%); ν_{max}(film)/cm^{-1} 3053, 1734 (C=O), 1475, 1376, 1332, 1250, 1151 and 741; δ_H(270 MHz; $CDCl_3$) 1.30 (3 H, t, *J* 7.1, OCH_2Me), 3.77 (3 H, s, NMe), 3.80 (2 H, td, *J* 4.3 and 0.8, CH_2CO_2Me), 4.20 (2 H, q, *J* 7.1, OCH_2Me), 7.07 (1 H, s, 2-H), 7.17 (1 H, td, *J* 7.2 and 1.1, 5-H), 7.28 (1 H, td, *J* 7.1 and 1.0, 6-H), 7.33 (1 H, d, *J* 7.6, 7-H) and 7.66 (1 H, d, *J* 8.1, 4-H); *m/z* 217 (M^+, 19%), 203 (7), 145 (11), 144 (100, $ArCH_2^{\bullet+}$), 143 (5), 102 (3), 77 (4) and 72 (3).

3-(2-*Hydroxyethyl*)-1-*methylindole*.—To a suspension of lithium aluminium hydride (0.035 g, 0.921 mmol) in dry ether (10 cm^3) was added a solution of ethyl 1-(methylindol-3′-yl)acetate (0.20 g, 0.921 mmol) in dry ether (5 cm^3) at a rate sufficient to maintain a gentle reflux. The resulting yellow-grey suspension was heated at reflux for a further 30 min, and was then allowed to cool. Water (0.2 cm^3) was cautiously added, followed by 15% aq. sodium hydroxide (0.6 cm^3). The resulting granular precipitate was filtered off from the very pale yellow solution, and it was then washed thoroughly with ether (3 × 20 cm^3). The combined ethereal solutions were dried ($MgSO_4$) and evaporated to leave a pale yellow oil, which was purified by chromatography (CH_2Cl_2) to give the title compound [9] (0.156 g, 97%) as an oil (Found: C, 75.5; H, 7.5; N, 7.8. Calc. for $C_{11}H_{13}NO$: C, 75.4; H, 7.5; N, 8.0%); ν_{max}(film)/cm^{-1} 1615 (C=O), 1474, 1425, 1378, 1328, 1046, 1012 and 741; δ_H(270 MHz; $CDCl_3$) 2.11 (1 H, br s, OH), 3.07 (2 H, td, *J* 6.5 and 0.7, CH_2CH_2OH), 3.77 (3 H, s, NMe), 3.92 (2 H, t, *J* 6.5, CH_2OH), 6.96 (1 H, s, 2-H), 7.22 (1 H, td, *J* 7.1 and 1.4, 5-H), 7.31 (1 H, td, *J* 7.1 and 1.2, 6-H), 7.37 (1 H, d, *J* 8.3, 7-H) and 7.68 (1 H, d, *J* 7.7, 4-H); *m/z* 175 (M^+, 26%), 145 (11), 144 (100, $ArCH_2^{\bullet+}$), 143 (6), 115 (4), 103 (3), 102 (3) and 77 (5).

2-(1′-*Methylindol*-3′-*yl*)*ethyl Trichloroacetate* **4**.—To a pale yellow solution of 3-(2-hydroxyethyl)-1-methylindole (0.156 g, 0.89 mmol) and pyridine (72 mm^3, 0.89 mmol) in dichloromethane (10 cm^3) at 0 °C was added trichloroacetyl chloride (109 mm^3, 0.979 mmol), whereupon the solution darkened slightly. The mixture was removed from the cold-bath and kept in the dark for 2.5 h, after which time the solvent was evaporated to give a brown oil. This was chromatographed (CH_2Cl_2) to give the *title compound* **4** (0.274 g, 97%) as a very pale yellow solid, m.p. 57–58 °C, which readily turned purple on storage at room temperature (Found: C, 48.9; H, 3.7; N, 4.3. $C_{13}H_{12}Cl_3NO_2$ requires C, 48.7; H, 3.8; N, 4.4%); ν_{max}(Nujol)/cm^{-1} 1762 (C=O), 1475, 1240, 986, 828, 741 and 682; λ_{max}(MeOH)/nm 281infl and 287 (log ε 3.75); δ_H(270 MHz; $CDCl_3$) 3.23 (2 H, td *J* 7.1 and 0.5, 2-H_2), 3.77 (3 H, s, Me), 4.59 (2 H, t, *J* 7.1, 1-H_2), 6.96 (1 H, s, 2′-H), 7.15 (1 H, td, *J* 7.2 and 1.3, 5′-H), 7.26 (1 H, td, *J* 7.2 and 1.2, 6′-H), 7.32 (1 H, d, *J* 8.4, 7′-H) and 7.64 (1 H, d, *J* 8.1, 4′-H); *m/z* 319 (M^+, 9%), 158 (21), 157 (30), 145 (11), 144 (100, $ArCH_2^{\bullet+}$), 143 (7), 115 (6) and 77 (5).

Irradiation of 2-(1′-*Methylindol*-3′-*yl*)*ethyl Trichloroacetate* **4**.—A solution of 2-(1′-methylindol-3′-yl)ethyl trichloroacetate **4** (0.10 g, 0.312 mmol) in 20% methanol–acetonitrile (50 cm^3) was irradiated for 20 min. The golden yellow solution was evaporated, and the residue was purified by chromatography (2% MeOH–CH_2Cl_2) to give 1,3,4,7-*tetrahydro*-7,7-*dimethoxy*-1-*methyloxocino*[4,5,6-cd]*indol*-6-*one* **10** (0.031 g, 36%) as a pale yellow solid, m.p. 141.5–143 °C (Found: M^+, 275.1158. $C_{15}H_{17}NO_4$ requires M, 275.1158); ν_{max}($CHCl_3$)/cm^{-1} 1745 (C=O), 1459, 1315, 1263, 1127, 1092 and 1044; λ_{max}(MeOH)/nm 299 (log ε 3.87) and 354infl; δ_H(270 MHz; $CDCl_3$) 3.05 (1 H, d, *J* 16.1, 3-H), 3.35–3.48 (1 H, m, 3-H), 3.50 (3 H, s, OMe), 3.74 (6 H, s, NMe and OMe), 4.16 (1 H, dt, *J* 11.7 and 3.3, 4-H), 4.44 (1 H, td, *J* 11.8 and 1.7, 4-H), 7.12 (1 H, s, 2-H), 7.33 (1 H, t, *J* 8.0, 9-H), 7.61 (1 H, dd, *J* 8.0 and 1.7, 8-H) and 8.01 (1 H, dd, *J* 7.4 and 1.7, 10-H); *m/z* 275 (M^+, 6%), 217 (12), 216 (82), 185 (16), 184 (100), 157 (15), 156 (10), 143 (8) and 115 (19).

Ethyl(5-*Methoxyindol*-3-*yl*)*acetate*.—A solution of triphenylphosphine (0.575 g, 2.19 mmol) and ethanol (0.2 cm^3, 3.41 mmol) in dry ether (10 cm^3) was added dropwise to a solution of diethyl azodicarboxylate (0.35 cm^3, 2.19 mmol) and (5-methoxyindol-3-yl)acetic acid (0.30 g, 1.46 mmol) in dry ether (10 cm^3). The mixture rapidly turned cloudy, followed some minutes later by the appearance of an oily material. The mixture was stirred for a further 30 min until all traces of the oily substance had disappeared, and then the resulting clear yellow solution was evaporated. The yellow-brown oily residue was purified by chromatography (CH_2Cl_2) to give the *title compound* (0.317 g, 93%) as a very pale solid, m.p. 89–91 °C (Found: C, 67.0; H, 6.4; N, 6.0. $C_{13}H_{15}NO_3$ requires C, 66.9; H, 6.5; N, 6.0%); ν_{max}(Nujol)/cm^{-1} 3349 (indole NH), 2863, 1712 (C=O), 1488, 1344, 1311, 1245, 1218, 1181 and 1027; δ_H(270 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.1, OCH_2Me), 3.74 (2 H, s, CH_2CO_2Et), 3.86 (3 H, s, OMe), 4.18 (2 H, q, *J* 7.1, OCH_2Me), 6.86 (1 H, dd, *J* 8.6 and 2.1, 6-H), 7.07–7.09 (2 H, m, 2- and 4-H), 7.20 (1 H, d, *J* 8.6, 7-H) and 8.12 (1 H, br s, 1-H); *m/z* 233 (M^+, 40%), 232 (5), 188 (6), 161 (12), 160 (100, $ArCN_2^{\bullet+}$), 159 (4), 145 (10) and 117 (6).

3-(2-*Hydroxyethyl*)-5-*methoxyindole*.—To a suspension of lithium aluminium hydride (0.033 g, 0.857 mmol) in dry ether (10 cm^3) was added a solution of ethyl (5-methoxyindol-3-yl)acetate (0.20 g, 0.857 mmol) in dry ether (5 cm^3) at a rate sufficient to maintain a gentle reflux. The resulting yellow-grey suspension was heated at reflux for a further 30 min, and then allowed to cool. Water (0.2 cm^3) was cautiously added, followed by 15% aq. sodium hydroxide (0.6 cm^3). The resulting granular precipitate was filtered off from the very pale yellow solution, and washed thoroughly with ether (3 × 20 cm^3). The combined ethereal solutions were dried ($MgSO_4$) and evaporated to leave a pale yellow oil, which was purified by chromatography (CH_2Cl_2) to give the *title compound* (0.140 g, 85%) as an oil (Found: C, 69.15; H, 6.8; N, 7.3. $C_{11}H_{13}NO_2$ requires C, 69.1; H, 6.85; N, 7.3%); ν_{max}(film)/cm^{-1} 3409 (indole NH), 1625 (C=O), 1585, 1486, 1456, 1215, 1172, 1068, 1044 and 798; δ_H(270 MHz; $CDCl_3$) 2.10 (1 H, br s, OH), 2.99 (2 H, t, *J* 6.3, CH_2CH_2OH), 3.87 (3 H, s, OMe), 3.98 (2 H, t, *J* 6.3, CH_2OH), 6.88 (1 H, dd, *J* 8.7 and 2.4, 6-H), 6.98 (1 H, d, *J* 2.1, 2-H), 7.07 (1 H, d, *J* 2.4, 4-H), 7.22 (1 H, d, *J* 8.9, 7-H) and 8.25 (1 H, br s, 1-H); *m/z* 191 (M^+, 24%), 173 (17), 161 (13), 160 (100, $ArCH_2^{\bullet+}$), 159 (8), 158 (9), 145 (15) and 117 (8).

2-(5′-*Methoxyindol*-3′-*yl*)*ethyl Trichloroacetate* **5**.—To a pale yellow solution of 3-(2-hydroxyethyl)-5-methoxyindole (0.135 g, 0.706 mmol) and pyridine (57 mm^3, 0.706 mmol) in dichloromethane (10 cm^3) at 0 ° C was added trichloroacetyl chloride (87 mm^3, 0.777 mmol), whereupon the solution darkened slightly. The mixture was removed from the cold-bath and kept in the dark for 2.5 h, after which time the solvent was evaporated off to give a yellow-brown oil. This was chromatographed (CH_2Cl_2) to give the *title compound* **5** (0.231 g, 97%) as an oil (Found: C, 46.2; H, 3.7; N, 4.25. $C_{13}H_{12}Cl_3NO_3$ requires C, 46.4; H, 3.6; N, 4.2%); ν_{max}(film)/cm^{-1} 3421 (indole NH), 1762 (C=O), 1487, 1456, 1256, 985, 828 and 681; δ_H(270 MHz; $CDCl_3$) 3.21 (2 H, td, *J* 7.1 and 0.7, 2-H_2), 3.89 (3 H, s, OMe), 4.61 (2 H, t, *J* 7.1, 1-H_2), 6.89 (1 H, dd, *J* 8.9 and 2.3, 6′-H), 7.08 (1 H, d, *J* 6.1, 4′-H), 7.09 (1 H, d, *J* 0.5, 2′-H), 7.27 (1 H, dd, *J* 8.8 and 0.5, 7′-H) and 7.98 (1 H, br s, 1′-H); *m/z* 335 (M^+, 11%), 174 (28), 173 (91), 172 (12), 160 (100, $ArCH_2^{\bullet+}$), 130 (23), 49 (13) and 36 (12).

Irradiation of 2-(5′-*Methoxyindol*-3′-*yl*)*ethyl Trichloroacetate* **5**.—A solution of 2-(5′-methoxyindol-3′-yl)ethyl trichloro-

acetate **5** (0.090 g, 0.267 mmol) in 20% methanol–acetonitrile (50 cm^3) was irradiated for 10 min. The golden brown solution was evaporated, and the residue was purified by chromatography (1% MeOH–CH_2Cl_2) to give 1,3,4,7-*tetrahydro*-7,7,8-*trimethoxyoxocino*[4,5,6-cd]*indol*-6-*one* **11** (0.042 g, 54%) as a very pale yellow solid, m.p. 149–152 °C (Found: M^+, 291.1107. $C_{15}H_{17}NO_5$ requires M, 291.1107); $\nu_{max}(CHCl_3)/cm^{-1}$ 3479 (indole NH), 1742 (C=O), 1263, 1243, 1105 and 1086; λ_{max}(MeOH)/nm 286 (log ε 3.56), 299infl, 319infl and 360 (3.57); δ_H(270 MHz; $CDCl_3$) 3.06 [1 H, d (with multiple fine splitting), *J* 17.3, 3-H], 3.22–3.34 (1 H, m, 3-H), 3.66 (3 H, s, 7-OMe), 3.74 (3 H, s, 7-OMe), 3.80 (3 H, s, 8-OMe), 4.14 (1 H, dt, *J* 11.7 and 3.7, 4-H), 4.30 (1 H, td, *J* 11.7 and 2.0, 4-H), 6.90 (1 H, d, *J* 8.8, 9-H), 7.03 (1 H, br s, 2-H), 7.30 (1 H, d, *J* 8.8, 10-H) and 8.01 (1 H, br s, 1-H); *m/z* 291 (M^+, 2%), 260 (5), 232 (67), 201 (13), 200 (74), 185 (20), 44 (27) and 28 (100).

3-(*Indol*-3′-*yl*)*propyl Trichloroacetate* **6**.—To a pale yellow solution of homotryptophol (1.0 g, 5.71 mmol) and pyridine (0.45 g, 5.71 mmol) in dichloromethane (15 cm^3) at 0 °C was added trichloroacetyl chloride (1.14 g, 6.28 mmol), whereupon the solution became a brighter yellow in colour. The mixture was removed from the cold-bath and kept in the dark for 2.5 h, after which time the solvent was evaporated off to give a green-brown oil. This was chromatographed (50% dichloromethane–light petroleum) to give the *title compound* **6** (1.78 g, 97%) as a pale yellow solid, m.p. 81.5–82.5 °C (Found: C, 48.5; H, 3.7; N, 4.3. $C_{13}H_{12}Cl_3NO_2$ requires C, 48.7; H, 3.8; N, 4.4%); ν_{max}(Nujol)/cm^{-1} 3408 (indole NH), 2954, 1750 (C=O), 1425, 1266, 1252, 1012, 998, 896, 828, 749 and 681; λ_{max}(MeOH)/nm 275infl, 282 (log ε 3.84) and 290 (3.76); δ_H(200 MHz; $CDCl_3$) 2.18 (2 H, quintet, *J* 7.0, 2-H_2), 2.93 (2 H, t, *J* 7.3, 3-H_2), 4.41 (2 H, t, *J* 6.3, 1-H_2), 7.01 (1 H, d, *J* 1.6, 2′-H), 7.16 (2 H, m, 5′- and 6′-H), 7.37 (1 H, d, *J* 7.4, 7′-H), 7.60 (1 H, d, *J* 7.5, 4′-H) and 7.98 (1 H, br s, 1′-H); *m/z* 319 (M^+, 10%), 158 (14), 130 (100, $ArCH_2^{\bullet+}$), 117 (3), 115 (3), 103 (4) and 77 (6).

Irradiation of 3-(*Indol*-3′-*yl*)*propyl Trichloroacetate* **6**.—A solution of 3-(indol-3′-yl)propyl trichloroacetate **6** (0.20 g, 0.624 mmol) in 20% methanol–acetonitrile (100 cm^3) was irradiated for 25 min. The golden brown solution was evaporated, and the residue was purified by chromatography (2% MeOH–CH_2Cl_2) to give, firstly, 3-(*indol*-3′-*yl*)*propyl methyl carbonate* (0.016 g, 11%) as a pale yellow oil (Found: C, 67.2; H, 6.7; N, 6.0. $C_{13}H_{15}NO_3$ requires C, 66.9; H, 6.5; N, 6.0%); ν_{max}(film)/cm^{-1} 3377 (indole NH), 1732 (C=O), 1444, 1317, 1286, 1008 and 748; δ_H(270 MHz; $CDCl_3$) 2.10 (2 H, quintet, *J* 7.1, 2-H_2), 2.87 (2 H, t, *J* 7.1, 3-H_2), 3.79 (3 H, s, OMe), 4.22 (2 H, t, *J* 7.1, 1-H_2), 7.00 (1 H, d, *J* 2.4, 2′-H), 7.11 (1 H, td, *J* 7.6 and 1.0, 5′-H), 7.20 (1 H, td, *J* 7.4 and 1.2, 6′-H), 7.36 (1 H, d, *J* 8.0, 7′-H), 7.59 (1 H, d, *J* 7.8, 4′-H) and 7.95 (1 H, br s, 1′-H); *m/z* 233 (M^+, 34%), 157 (25), 131 (13), 130 (100, $ArCH_2^{\bullet+}$), 86 (17), 84 (25), 51 (11) and 49 (33).

This was followed by homotryptophol (0.063 g, 58%) which was isolated as a pale yellow oil, the spectral properties of which were identical to those of an authentic sample.

Ethyl 5-(*Indol*-3′-*yl*)*pentanoate* **12a**.—To a suspension of 5-(indol-3′-yl)pentanoic acid (1.0 g, 4.60 mmol) in dry benzene (20 cm^3) was added oxalyl chloride (4 cm^3, 46 mmol) and the mixture was stirred at ambient temperature for 30 min. After this time, all the solid had dissolved, forming a red-brown solution. This was evaporated to leave a red-brown oil, which was cooled in an ice-bath whilst a mixture of ethanol (30 cm^3) and triethylamine (3 cm^3) was added dropwise. The mixture was stirred at 0 °C for 30 min, after which time it was diluted with water (75 cm^3) and extracted with ether (3 × 100 cm^3), and the combined extracts were washed successively with water (2 × 100 cm^3), saturated aq. sodium carbonate (2 × 75 cm^3), water (3 × 50 cm^3), and brine (30 cm^3) before being dried ($MgSO_4$), and evaporated to give a yellow oil. This was purified by chromatography (75% dichloromethane–light petroleum) to give the *title compound* **12a** (0.80 g, 71%) as a crystalline solid, m.p. 46.5–47.5 °C (Found: C, 73.4; H, 7.7; N, 5.6. $C_{15}H_{19}NO_2$ requires C, 73.4; H, 7.8; N, 5.7%); ν_{max}(film)/cm^{-1} 3320 (indole NH), 1718 (C=O), 1410, 1243, 1223, 1189, 1102, 785, 743 and 733; δ_H(270 MHz; $CDCl_3$) 1.24 (3 H, t, *J* 7.1, OCH_2Me), 1.73–177 (4 H, m, 3- and 4-H_2), 2.32–2.37 (2 H, m, 2-H_2), 2.76–2.81 (2 H, m, 5-H_2), 4.12 (2 H, q, *J* 7.1, OCH_2Me), 6.99 (1 H, d, *J* 2.4, 2′-H), 7.11 (1 H, td, *J* 6.9 and 1.2, 5′-H), 7.19 (1 H, td, *J* 7.5 and 1.2, 6′-H), 7.35 (1 H, d, *J* 8.1, 7′-H), 7.58–7.62 (1 H, m, 4′-H) and 7.91 (1 H, br s, 1′-H); *m/z* 245 (M^+, 29%), 200 (11), 156 (6), 144 (6), 143 (7), 131 (14) and 130 (100, $ArCH_2^{\bullet+}$).

Ethyl 5-[1′-(tert-*Butoxycarbonyl*)*indol*-3′-*yl*]*pentanoate* **13a**.—To a suspension of ethyl 5-(indol-3′-yl)pentanoate **12a** (0.76 g, 3.10 mmol) in dry acetonitrile (20 cm^3) were added di-*tert*-butyl dicarbonate (1.014 g, 4.65 mmol) and DMAP (0.038 g, 0.310 mmol). The suspension was stirred at room temperature for 15 h to give a clear pale yellow solution, which was then evaporated to leave a yellow-brown residue. This was purified by chromatography (1% MeOH–CH_2Cl_2) to give the *title compound* **13a** (1.008 g, 95%) as a pale yellow oil (Found: C, 69.7; H, 8.0; N, 4.1. $C_{20}H_{27}NO_4$ requires C, 69.5; H, 7.9; N, 4.05%); ν_{max}(film)/cm^{-1} 1734 (ester and carbamate C=O), 1455, 1377, 1256, 1162, 1091 and 747; δ_H(270 MHz; $CDCl_3$) 1.25 (3 H, t, *J* 7.2, OCH_2Me), 1.67 (9 H, s, Bu^t), 1.72–1.77 (4 H, m, 3- and 4-H_2), 2.33–2.38 (2 H, m, 2-H_2), 2.68–2.73 (2 H, m, 5-H_2), 4.13 (2 H, q, *J* 7.2, OCH_2Me), 7.22 (1 H, td, *J* 6.2 and 1.2, 5′-H), 7.3 (1 H, td, *J* 6.3 and 1.2, 6′-H), 7.35 (1 H, s, 2′-H), 7.51 (1 H, d, *J* 8.0, 4′-H) and 8.12 (1 H, br d, *J* 8.0, 7′-H); *m/z* 345 (M^+, 20%), 290 (1), 246 (10), 245 (59), 142 (6), 131 (15), 130 (100, $ArCH_2^{\bullet+}$) and 57 (81).

Ethyl 5-[1′-(tert-*Butoxycarbonyl*)*indol*-3′-*yl*]-2-*chloropentanoate* **14a**.—A solution of LiICA was prepared by the addition of butyllithium (1.5 mol dm^{-3} solution in hexanes; 1.2 cm^3, 1.74 mmol) to *N*-isopropylcyclohexylamine (286 mm^3, 1.74 mmol) in THF (50 cm^3) at −20 °C under nitrogen, and the solution was allowed to warm to 0 °C for 5 min before being cooled to −78 °C. A solution of ethyl 5-[1′-(*tert*-butoxycarbonyl)indol-3′-yl]pentanoate **13a** (0.50 g, 1.45 mmol) in THF (15 cm^3) was added dropwise to the LiICA solution. After a further 10 min, the mixture was allowed to warm slowly to −20 °C, and gave a clear orange solution. This was cooled again to −78 °C, and then added *via* a catheter to a solution of dry tetrachloromethane (15 cm^3) in THF (25 cm^3) at −78 °C under nitrogen. The solution was stirred at −78 °C for a further 10 min, and then allowed to warm slowly to ambient temperature to give a pale yellow solution. After a further 20 min, acetic acid (1.5 cm^3) was added, and the resulting solution was diluted with water (60 cm^3) and extracted with dichloromethane (3 × 75 cm^3). The combined extracts were dried ($MgSO_4$), evaporated, and purified by chromatography (1% MeOH–CH_2Cl_2) to give the *title compound* **14a** (0.314 g, 57%) as an oil (Found: M^+, 379.1550. $C_{20}H_{26}ClNO_4$ requires M, 379.1550); ν_{max}(film)/cm^{-1} 1733 (ester and carbamate C=O), 1455, 1372, 1256, 1159, 1092 and 747; δ_H(270 MHz; $CDCl_3$) 1.28 (3 H, t, *J* 7.1, OCH_2Me), 1.67 (9 H, s, Bu^t), 1.82–2.08 (4 H, m, 3- and 4-H_2), 2.74 (2 H, t, *J* 7.2, 5-H_2), 4.22 (2 H, qd, *J* 6.6 and 0.5, OCH_2Me), 4.30 (1 H, dd, *J* 7.8 and 5.9, 2-H), 7.23 (1 H, td, *J* 7.3 and 1.0, 5′-H), 7.31 (1 H, td, *J* 7.4 and 1.5, 6′-H), 7.37 (1 H, s, 2′-H), 7.50 (1 H, d, *J* 7.6, 4′-H) and 8.12 (1 H, br d, *J* 7.3, 7′-H); *m/z* 379 (M^+, 18%), 325 (13), 323 (33), 281 (14), 279 (42), 131 (16), 130 (100, $ArCH_2^{\bullet+}$) and 57 (46).

Ethyl 2-Chloro-5-(indol-3′-yl)pentanoate **15a**.—To a solution of ethyl 5-[1′-(*tert*-butoxycarbonyl)indol-3′-yl]-2-chloropentanoate **14a** (0.250 g, 0.658 mmol) in dichloromethane (25 cm^3) was added dropwise TFA (800 mm^3). The slightly red-brown solution was stirred at ambient temperature for 2 h, and then evaporated under reduced pressure to leave a brown oil. This was purified by chromatography (1% MeOH–CH_2Cl_2) to give the *title compound* **15a** (0.127 g, 69%) as an oil (Found: M^+, 279.1026. $C_{15}H_{18}ClNO_2$ requires M, 279.1026); ν_{max}(film)/cm^{-1} 3415 (indole NH), 1736 (C=O), 1619, 1458, 1371, 1340, 1181, 1095 and 743; λ_{max}(MeOH)/nm 274infl, 282 (log ε 3.73) and 290 (3.66); δ_H(270 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.2, OCH_2*Me*), 1.80–2.12 (4 H, m, 3- and 4-H_2), 2.81 (2 H, t, *J* 7.3, 5-H_2), 4.21 (2 H, qd, *J* 7.1 and 0.7, OCH_2Me), 4.30 (1 H, dd, *J* 7.8 and 5.9, 2-H), 7.00 (1 H, d, *J* 2.2, 2′-H), 7.11 (1 H, td, *J* 8.0 and 1.2, 5′-H), 7.19 (1 H, td, *J* 7.0 and 1.2, 6′-H), 7.35 (1 H, d, *J* 8.0, 7′-H), 7.58 (1 H, d, *J* 8.5, 4′-H) and 7.95 (1 H, br s, 1′-H); *m/z* 279 (M^+, 22%), 243 (3), 234 (2), 170 (9), 144 (6), 143 (12), 131 (11) and 130 (100, $ArCH_2^{\bullet+}$).

Irradiation of Ethyl 2-Chloro-5-(indol-3′-yl)pentanoate **15a**.—A solution of ethyl 2-chloro-5-(indol-3′-yl)pentanoate **15a** (0.030 g, 0.107 mmol) in acetonitrile (30 cm^3) was irradiated for 15 min. The brown solution was evaporated, and the residue was purified by chromatography (2% MeOH–CH_2Cl_2) to give *ethyl 5-(indol-3′-yl)pent-2-enoate* **19a** (0.016 g, 63%) as a golden brown oil (Found: M^+, 243.1259. $C_{15}H_{17}NO_2$ requires M, 243.1259); ν_{max}($CHCl_3$)/cm^{-1} 3481 (indole NH), 1713 (C=O), 1655, 1457, 1370, 1091 and 910; δ_H(270 MHz; $CDCl_3$) 1.28 (3 H, t, *J* 7.1, OCH_2*Me*), 2.93 (2 H, m, 5-H_2), 3.08–3.13 (2 H, m, 4-H_2), 4.17 (2 H, 2 × q, *J* 7.1, OCH_2Me), 5.78 (0.5 H, dt, *J* 11.5 and 1.7, *Z* 2-H), 5.88 (0.5 H, dt, *J* 15.8 and 1.6, *E* 2-H), 6.31 (0.5 H, dt, *J* 11.5 and 7.2, *Z* 3-H), 7.01 (1 H, d, *J* 2.2, 2′-H), 7.07 (0.5 H, dt, *J* 15.7 and 6.8, *E* 3-H), 7.12 (1 H, td, *J* 7.0 and 1.2, 5′-H), 7.20 (1 H, td, *J* 7.3 and 1.3, 6′-H), 7.37 (1 H, d, *J* 8.1, 7′-H), 7.61 (1 H, d, *J* 7.8, 4′-H) and 7.95 (1 H, br s, 1′-H); *m/z* 243 (M^+, 14%), 168 (5), 167 (4), 149 (8), 131 (11), 130 (100, $ArCH_2^{\bullet+}$), 129 (4) and 77 (4).

6-(Indol-3′-yl)hexanoic Acid.—Into a 3-necked flask equipped with overhead stirrer and Dean–Stark trap were placed indole (20 g, 0.171 mol), ε-caprolactone (22.37 g, 0.196 mol) and potassium hydroxide pellets (85% reagent; 16.90 g, 0.256 mol), together with *p*-cymene (100 cm^3). The mixture was stirred and heated to reflux, and this temperature was maintained until production of water had ceased (88 h). After this time the mixture was allowed to cool, to give a brown solution and a pale brown gum. Water (~300 cm^3) was added, and the mixture was stirred until the gummy substance had dissolved. The golden aqueous phase was separated and washed with light petroleum (3 × 30 cm^3), and the combined red organic extracts then furnished, on evaporation, mainly unchanged indole (12.10 g recovery). The aqueous phase was cautiously acidified with conc. hydrochloric acid, which produced a red-brown oil which gradually solidified. The mixture was kept below 4 °C for 2 days, after which time precipitation was complete. The solid material was dissolved in ether (~500 cm^3), and the acidic aqueous layer was extracted with ether (3 × 70 cm^3). The combined extracts were washed successively with water (3 × 150 cm^3), which removed much of the brownish colour, and brine (70 cm^3), dried ($MgSO_4$), and evaporated to leave a foul-smelling yellow solid. This was recrystallised from benzene to give the title compound (9.26 g, 23%) as a powdery solid, m.p. 141–143 °C (lit.,[7] 143–144 °C) (Found: C, 72.6; H, 7.5; N, 6.05. Calc. for $C_{14}H_{17}NO_2$: C, 72.7; H, 7.4; 6.1%); ν_{max}(Nujol)/cm^{-1} 2500–3500 (OH), 3372 (indole NH), 1695 (C=O), 1290, 1254, 1240, 1198, 741 and 731; δ_H(20 MHz; $CDCl_3$), 1.46 (2 H, m, 4-H_2), 1.72 (4 H, m, 3- and 5-H_2), 2.36 (2 H, t, *J* 7.3, 2-H_2), 2.76 (2 H, t, *J* 7.4, 6-H_2), 6.96 (1 H, s, 2′-H), 7.11 (1 H, t, *J* 7.3, 5′-H), 7.19 (1 H, t, *J* 7.4, 6′-H), 7.34 (1 H, d, *J* 7.3, 7′-H), 7.60 (1 H, d, *J* 7.5, 4′-H) and 7.91 (1 H, br s, 1′-H); *m/z* 231 (M^+, 29%), 158 (5), 144 (6), 130 (100, $ArCH_2^{\bullet+}$), 102 (19), 73 (52) and 55 (44).

Ethyl 6-(Indol-3′-yl)hexanoate **12b**.—To a suspension of 6-(indol-3′-yl)hexanoic acid (1.0 g, 4.32 mmol) in dry benzene (20 cm^3) was added oxalyl chloride (4 cm^3, 46 mmol) and the mixture was stirred at ambient temperature for 1 h. Work-up as for ester **12a** gave the *title compound* **12b** (0.795 g, 71%) as a crystalline solid, m.p. 60–61 °C (Found: C, 74.0; H, 8.3; N. 5.25. $C_{16}H_{21}NO_2$ requires C, 74.1; H, 8.2; N, 5.4%); ν_{max}(Nujol)/cm^{-1} 3342 (indole NH), 1710 (C=O), 1354, 1287, 1252, 1235, 1220, 1182, 1096, 1014, 748 and 668; δ_H(270 MHz; $CDCl_3$) 1.25 (3 H, t, *J* 7.2, OCH_2*Me*), 1.37–1.49 (2 H, m, 4-H_2), 1.63–1.79 (4 H, m, 3- and 5-H_2), 2.30 (2 H, t, *J* 7.3, 2-H_2), 2.76 (2 H, t, *J* 7.3, 6-H_2), 4.12 (2 H, q, *J* 7.1, OCH_2Me), 6.97 (1 H, d, *J* 2.2, 2′-H), 7.10 (1 H, td, *J* 6.7 and 1.2, 5′-H), 7.18 (1 H, td, *J* 6.7 and 1.2, 6′-H), 7.35 (1 H, d, *J* 6.7, 7′-H), 7.59 (1 H, d, *J* 7.7, 4′-H) and 7.91 (1 H, br s, 1′-H); *m/z* 259 (M^+, 25%), 214 (7), 144 (4), 143 (3), 131 (15), 130 (100, $ArCH_2^{\bullet+}$), 129 (3) and 77 (4).

Ethyl 6-[1′-(tert-butoxycarbonyl)indol-3′-yl]hexanoate **13b**.—To a suspension of ethyl 6-(indol-3′-yl)hexanoate **12b** (0.70 g, 2.70 mmol) in dry acetonitrile (20 cm^3) was added di-*tert*-butyl dicarbonate (0.884 g, 4.05 mmol) and DMAP (0.033 g, 0.270 mmol). The suspension was stirred at ambient temperature for 15 h to give a clear pale yellow solution, which was then evaporated to leave a yellow-brown residue. This was purified by chromatography (1% MeOH–CH_2Cl_2) to give the *title compound* **13b** (0.928 g, 97%) as a pale yellow oil (Found: C, 70.2; H, 8.1; N, 4.0. $C_{21}H_{29}NO_4$ requires C, 70.2; H, 8.1; N, 3.9%); ν_{max}(film)/cm^{-1} 1729 (ester and carbamate C=O), 1456, 1381, 1309, 1256, 1225, 1163, 1094 and 747; δ_H(270 MHz; $CDCl_3$) 1.25 (3 H, t, *J* 7.2, OCH_2*Me*), 1.40–1.49 (2 H, m, 4-H_2), 1.62–1.76 (4 H, m, 3- and 5-H_2), 1.67 (9 H, s, Bu^t), 2.31 (2 H, t, *J* 7.4, 2-H_2), 2.68 (2 H, t, *J* 7.3, 6-H_2), 4.12 (2 H, q, *J* 7.1, OCH_2Me), 7.22 (1 H, td, *J* 7.3 and 1.3, 5′-H), 7.31 (1 H, td, *J* 7.3 and 1.2, 6′-H), 7.34 (1 H, s, 2′-H), 7.51 (1 H, d, *J* 7.1, 4′-H) and 8.12 (1 H, br d, *J* 8.1, 7′-H); *m/z* 359 (M^+, 13%), 315 (1), 260 (11), 259 (61), 143 (4), 131 (18), 130 (100, $ArCH_2^{\bullet+}$) and 57 (46).

Ethyl 6-[1′-(tert-Butoxycarbonyl)indol-3′-yl]-2-chlorohexanoate **14b**.—A solution of LiICA was prepared by the addition of butyllithium (1.5 mol dm^{-3} solution in hexanes; 1.1 cm^3, 1.67 mmol) to *N*-isopropylcyclohexylamine (274 mm^3, 1.67 mmol) in THF (50 cm^3) at −20 °C under nitrogen, and the solution was then allowed to warm to 0 °C for 5 min before being cooled to −78 °C. A solution of ethyl 6-[1′-(*tert*-butoxycarbonyl)indol-3′-yl]hexanoate **13b** (0.50 g, 1.39 mmol) in THF (20 cm^3) was added dropwise to the LiICA solution. After a further 10 min, the mixture was allowed to warm slowly to −20 °C, and gave a clear orange solution. This was cooled again to −78 °C, and then added *via* a catheter to a solution of dry tetrachloromethane (15 cm^3) in THF (30 cm^3) at −78 °C under nitrogen. The solution was stirred at −78 °C for a further 10 min, and then worked up as for compound **14a** to give the *title compound* **14b** (0.290 g, 53%) as an oil (Found: M^+, 393.1707. $C_{21}H_{28}ClNO_4$ requires M, 393.1707); ν_{max}(film) cm^{-1} 1732 (ester and carbamate C=O), 1455, 1377, 1309, 1257, 1161, 1094 and 746; δ_H(270 MHz; $CDCl_3$) 1.29 (3 H, t, *J* 7.2, OCH_2*Me*), 1.42–2.08 (6 H, m, 3-, 4-, and 5-H_2), 1.67 (9 H, s, Bu^t), 2.70 (2 H, t, *J* 7.4, 6-H_2), 4.22 (2 H, q, *J* 7.2, OCH_2Me), 4.27 (1 H, t, *J* 6.1, 2-H), 7.23 (1 H, td, *J* 7.4 and 1.2, 5′-H), 7.31 (1 H, td, *J* 7.6 and 1.5, 6′-H), 7.35 (1 H, s, 2′-H), 7.50 (1 H, d, *J* 7.9, 4′-H) and 8.12 (1 H, br d, *J* 7.8, 7′-H); *m/z* 393 (M^+, 4%), 293 (20), 184 (9), 131 (16), 130 (100, $ArCH_2^{\bullet+}$), 57 (51), 44 (8) and 41 (16).

Ethyl 2-Chloro-6-(indol-3′-yl)hexanoate **15b**.—To a solution of ethyl 6-[1′-(*tert*-butoxycarbonyl)indol-3′-yl]-2-chlorohexanoate **14b** (0.250 g, 0.635 mmol) in dichloromethane (25 cm^3) was added dropwise TFA (800 mm^3). The slightly reddish solution was stirred at ambient temperature for 2 h, and then evaporated under reduced pressure to leave a brown oil. This was purified by chromatography (1% MeOH–CH_2Cl_2) to give the *title compound* **15b** (0.121 g, 65%) as an oil (Found: M^+, 293.1183. $C_{16}H_{20}ClNO_2$ requires M, 293.1183); $\nu_{max}(CHCl_3)$/cm^{-1} 3482 (indole NH), 1736 (C=O), 1457, 1266, 1227, 1178 and 707; λ_{max}(MeOH)/nm 277infl, 283 (log ε 4.01) and 291 (3.91); δ_H(270 MHz; $CDCl_3$) 128 (3 H, t, *J* 7.1, OCH_2Me), 1.43–1.63 (2 H, m, 4-H_2), 1.71–1.79 (2 H, m, 5-H_2), 1.95–2.07 (2 H, m, 3-H_2), 2.78 (2 H, t, *J* 7.6, 6-H_2), 4.22 (2 H, q, *J* 7.1, OCH_2Me), 4.25 (1 H, t, *J* 6.4, 2-H), 6.98 (1 H, d, *J* 2.4, 2′-H), 7.11 (1 H, td, *J* 6.4 and 1.1, 5′-H), 7.19 (1 H, td, *J* 6.3 and 1.2, 6′-H), 7.36 (1 H, d, *J* 7.8, 7′-H), 7.59 (1 H, d, *J* 7.8, 4′-H) and 7.93 (1 H, br s, 1′-H); *m/z* 293 (M^+, 21%), 212 (4), 149 (6), 131 (14), 130 (100, $ArCH_2^{\bullet+}$), 103 (3), 77 (7) and 57 (4).

Irradiation of Ethyl 2-Chloro-6-(indol-3′-yl)hexanoate **15b**.—A solution of ethyl 2-chloro-6-(indol-3′-yl)hexanoate **15b** (0.050 g, 0.170 mmol) in acetonitrile (50 cm^3) was irradiated for 15 min. The brown solution was evaporated, and the residue was purified by chromatography (2% MeOH–CH_2Cl_2) to give *ethyl 6-(indol-3′-yl)hex-2-enoate* **19b** (0.029 g, 67%) as a golden brown oil (Found: M^+, 257.1416. $C_{16}H_{19}NO_2$ requires M, 257.1416); $\nu_{max}(CHCl_3)$/cm^{-1} 3460 (indole NH), 1713 (C=O), 1369, 1319, 1301, 1220, 1187 and 1144; δ_H(270 MHz; $CDCl_3$) 1.29 (3 H, t, *J* 7.1, OCH_2Me), 1.87 (2 H, m, 5-H_2), 2.58–2.67 (2 H, m, 4-H_2), 2.93 (2 H, t, *J* 7.5, 6-H_2), 4.14 (2 H, q, *J* 7.1, OCH_2Me), 5.67–5.70 (1 H, m, 2-H), 6.87 (1 H, dt, *J* 16.2 and 7.1, 3-H), 7.00 (1 H, d, *J* 2.1, 2′-H), 7.10 (1 H, td, *J* 7.1 and 1.1, 5′-H), 7.18 (1 H, td, *J* 7.1 and 1.2, 6′-H), 7.35 (1 H, d, *J* 8.1, 7′-H), 7.61 (1 H, d, *J* 7.8, 4′-H) and 7.96 (1 H, br s, 1′-H); *m/z* 257 (M^+, 6%), 231 (25), 170 (53), 168 (26), 143 (31), 130 (100, $ArCH_2^{\bullet+}$), 86 (29) and 84 (44).

5-Hydroxy-3,3-dimethylpentanoic Acid Lactone.—To a suspension of sodium borohydride (4.0 g, 106 mmol) in THF (20 cm^3) at 0 °C was added, during 30 min, a solution of 3,3-dimethylglutaric anhydride (10.0 g, 70.35 mmol) in THF (50 cm^3). The resulting solution was allowed to warm to ambient temperature, and it was then stirred for 3.5 h. The solution was then recooled to 0 °C, and was quenched by the addition of 6 mol dm^{-3} hydrochloric acid (35 cm^3). The resulting solution was washed with brine (5 × 50 cm^3), and then extracted with ether (3 × 50 cm^3), the combined extracts being dried ($MgSO_4$) and evaporated to leave a pale yellow oil. Distillation of this in a Kugelrohr apparatus (oven temperature 155 °C; 24 mmHg) (lit.,[6] no b.p. given) gave the title compound (5.90 g, 65%) as a liquid, ν_{max}(film)/cm^{-1} 2959, 1746 (C=O), 1404, 1256, 1226,1175 and 1079; δ_H(270 MHz; $CDCl_3$) 1.05 (6 H, s, CMe_2), 1.66 (2 H, t, *J* 6.1, 4-H_2), 2.29 (2 H, s, 2-H_2) and 4.33 (2 H, t, *J* 6.1, 5-H_2); *m/z* 128 (M^+, 20%), 83 (7), 70 (17), 69 (100), 56 (58), 55 (16), 41 (60) and 39 (16).

Ethyl 5-(Indol-3′-yl)-3,3-dimethylpentanoate **12c**.—Into a 3-necked flask equipped with overhead stirrer and Dean–Stark trap were placed indole (3.74 g, 31.89 mmol), 5-hydroxy-3,3-dimethylpentanoic acid lactone (4.70 g, 36.67 mmol) and potassium hydroxide pellets (85% reagent; 3.16 g, 47.83 mmol), together with tetralin (100 cm^3). the mixture was stirred and heated to reflux, and this temperature was maintained until production of water had ceased (96 h). After this time the mixture was allowed to cool, and gave a brown solution and a pale brown gum. Water (~50 cm^3) was added, and the mixture was stirred until the gummy substance had dissolved. The aqueous phase was separated, and washed with light petroleum (3 × 30 cm^3), and the combined organic extracts furnished, on evaporation, mainly unchanged indole (1.3 g recovery). The aqueous phase was cautiously acidified with conc. hydrochloric acid, which produced a red-brown oil. The mixture was kept below 4 °C for 2 days, after which time the oil still had not solidified. The oil was dissolved in dry benzene (20 cm^3) and oxalyl chloride (4 cm^3, 46 mmol) was added. The mixture was stirred at ambient temperature for 30 min, and the resulting red-brown solution was evaporated to leave a red-brown oil. This was cooled in an ice-bath whilst a mixture of ethanol (30 cm^3) and triethylamine (3 cm^3) was added dropwise. The mixture was stirred at 0 °C for 30 min, after which time it was diluted with water (75 cm^3) and extracted with ether (3 × 100 cm^3); the combined extracts were washed successively with water (2 × 100 cm^3), saturated aq. sodium carbonate (2 × 75 cm^3), water (3 × 50 cm^3), and brine (30 cm^3) before being dried ($MgSO_4$) and evaporated to give a yellow oil. This was purified by chromatography (50% dichloromethane–light petroleum) to give the *title compound* **12c** (0.398 g, 5% from indole as an oil (Found: M^+, 273.1729. $C_{17}H_{23}NO_2$ requires M, 273.1729); ν_{max}(film)/cm^{-1} 3416 (indole NH), 1732 (C=O), 1458, 1369, 1337, 1230, 1115, 1036 and 741; δ_H(270 MHz; $CDCl_3$) 1.14 (6 H, s, CMe_2), 1.27 (3 H, t, *J* 7.2, OCH_2Me), 1.73–1.79 (2 H, m, 4-H_2), 2.34 (2 H, s, 2-H_2), 2.74–2.80 (2 H, m, 5-H_2), 4.15 (2 H, q, *J* 7.2, OCH_2Me), 6.97 (1 H, d, *J* 2.2, 2′-H), 7.12 (1 H, td, *J* 7.1 and 1.2, 5′-H), 7.19 (1 H, td, *J* 7.4 and 1.2, 6′-H), 7.35 (1 H, d, *J* 7.7, 7′-H), 7.63 (1 H, d, *J* 7.9, 4′-H) and 7.93 (1 H, br s, 1′-H); *m/z* 273 (M^+, 22%), 228 (8), 145 (5), 144 (41), 143 (8), 131 (11), 130 (100, $ArCH_2^{\bullet+}$) and 77 (5).

Ethyl 5-[1′-(tert-Butoxycarbonyl)indol-3′-yl]-3,3-dimethylpentanoate **13c**.—To a suspension of ethyl 5-(indol-3′-yl)-3,3-dimethylpentanoate **12c** (0.371 g, 1.36 mmol) in dry acetonitrile (20 cm^3) were added di-*tert*-butyl dicarbonate (0.44 g, 2.04 mmol) and DMAP (0.017 g, 0.136 mmol). The suspension was stirred at ambient temperature for 15 h to give a clear pale yellow solution, which was then evaporated to leave a yellow-brown residue. This was purified by chromatography (70% dichloromethane–light petroleum) to give the *title compound* **13c** (0.494 g, 97%) as an oil (Found: C, 70.7; H, 8.7; N, 3.65. $C_{22}H_{31}NO_4$ requires C, 70.75; H, 8.37; N, 3.75%); ν_{max}(film)/cm^{-1} 1729 (ester and carbamate C=O), 1455, 1371, 1353, 1256, 1162 and 1083; δ_H(270 MHz; $CDCl_3$) 1.13 (6 H, s, CMe_2), 1.27 (3 H, t, *J* 7.2, OCH_2Me), 1.67 (9 H, s, Bu^t), 1.68–1.77 (2 H, m, 4-H_2), 2.32 (2 H, s, 2-H_2), 2.65–2.72 (2 H, m, 5-H_2), 4.14 (2 H, q, *J* 7.2, OCH_2Me), 7.23 (1 H, td, *J* 7.6 and 1.3, 5′-H), 7.31 (1 H, td, *J* 8.2 and 1.3, 6′-H), 7.35 (1 H, s, 2′-H), 7.54 (1 H, d, *J* 7.6, 4′-H) and 8.12 (1 H, br d, *J* 7.8, 7′-H); *m/z* 373 (M^+, 1%), 273 (23), 228 (8), 144 (44), 143 (10), 131 (11), 130 (100, $ArCH_2^{\bullet+}$) and 57 (17).

Ethyl 5-[1′-(tert-Butoxycarbonyl)indol-3′-yl]-2-chloro-3,3-dimethylpentanoate **14c**.—A solution of LiICA was prepared by the addition of butyllithium (1.5 mol dm^{-3} solution in hexanes; 0.43 cm^3, 0.643 mmol) to *N*-isopropylcyclohexylamine (106 mm^3, 0.643 mmol) in THF (20 cm^3) at −20 °C under nitrogen, and the solution was allowed to warm to 0 °C for 5 min before being cooled to −78 °C. A solution of ethyl 5-[1′-(*tert*-butoxycarbonyl)indol-3′-yl]-3,3-dimethylpentanoate **13c** (0.20 g, 0.536 mmol) in THF (10 cm^3) was added dropwise to the LiICA solution. After a further 10 min, the mixture was allowed to warm slowly to −20 °C, to give a clear orange solution. This was cooled again to −78 °C, and then added *via* a catheter to a solution of dry tetrachloromethane (10 cm^3) in THF (25 cm^3) at −78 °C under nitrogen. The solution was stirred at −78 °C for a further 10 min, and was then worked up as for compound **14a** to give the *title compound* **14c** (0.083 g, 38%) as an oil (Found: C,

65.05; H, 7.6; N, 3.1. $C_{22}H_{30}ClNO_4$ requires C, 64.8; H, 7.4; N, 3.4%); ν_{max}(film)/cm^{-1} 1750 (ester C=O), 1733 (carbamate C=O), 1455, 1371, 1257, 1157, 1083 and 747; δ_H(270 MHz; $CDCl_3$) 1.20 (6 H, s, CMe_2), 1.31 (3 H, t, *J* 7.2, OCH_2Me), 1.68 (9 H, s, Bu^t), 1.69–1.92 (2 H, m, 4-H_2), 2.67–2.73 (2 H, m, 5-H_2), 4.25 (2 H, qd, *J* 7.1 and 0.7, OCH_2Me), 4.30 (1 H, s, 2-H), 7.24 (1 H, td, *J* 7.6 and 1.3, 5′-H), 7.29 (1 H, td, *J* 7.9 and 1.4, 6′-H), 7.36 (1 H, s, 2′-H), 7.53 (1 H, d, *J* 7.6, 4′-H) and 8.13 (1 H, br d, *J* 7.6, 7′-H); *m/z* 407 (M^+, 17%), 351 (36), 188 (32), 144 (36), 130 (100, $ArCH_2^{\bullet+}$), 84 (27), 57 (96) and 41 (22).

Ethyl 2-*Chloro*-5-(*indol*-3′-*yl*)-3,3-*dimethylpentanoate* **15c**.—To a solution of ethyl 5-[1′-(*tert*-butoxycarbonyl)indol-3′-yl]-2-chloro-3,3-dimethylpentanoate **14c** (0.052 g, 0.127 mmol) in dichloromethane (15 cm^3) was added dropwise TFA (200 mm^3). The pale purple solution was stirred at ambient temperature for 2 h, and then evaporated under reduced pressure to leave a brown oil. This was purified by chromatography (70% dichloromethane–light petroleum) to give the *title compound* **15c** (0.020 g, 52%) as an oil (Found: M^+, 307.1339. $C_{17}H_{22}ClNO_2$ requires M, 307.1339); ν_{max}($CHCl_3$)/cm^{-1} 3481 (indole NH), 1744 (C=O), 1457, 1371, 1335, 1269, 1181 and 1032; λ_{max}(MeOH)/nm 276infl, 282 (log ε 3.71) and 290 (3.65); δ_H(270 MHz; $CDCl_3$) 1.21 (6 H, s, CMe_2), 1.31 (3 H, t, *J* 7.1, OCH_2Me), 1.76–1.96 (2 H, m, 4-H_2), 2.78 (2 H, t, *J* 8.3, 5-H_2), 4.25 (2 H, qd, *J* 7.1 and 1.0, OCH_2Me), 4.32 (1 H, 2-H), 6.98 (1 H, d, *J* 2.2, 2′-H), 7.13 (1 H, td, *J* 7.5 and 1.1, 5′-H), 7.21 (1 H, td, *J* 7.5 and 1.1, 6′-H), 7.37 (1 H, d, *J* 6.8, 7′-H), 7.61 (1 H, d, *J* 7.9, 4′-H) and 7.94 (1 H, br s, 1′-H); *m/z* 307 (M^+, 8%), 223 (11), 213 (25), 149 (100), 144 (12), 130 (47, $ArCH_2^{\bullet+}$), 57 (22) and 41 (11).

Irradiation of Ethyl 2-*Chloro*-5-(*indol*-3′-*yl*)-3,3-*dimethylpentanoate* **15c**.—A solution of ethyl 2-chloro-5-(indol-3′-yl)-3,3-dimethylpentanoate **15c** (0.014 g, 45.5 μmol) in acetonitrile (10 cm^3) was irradiated for 30 min. The brown solution was evaporated, and the residue was purified by chromatography (2% MeOH–CH_2Cl_2) to give *ethyl* 3,4,5,6-*tetrahydro*-5,5-*dimethyl*-1H-*cyclohept*[cd]*indole*-6-*carboxylate* **20** (0.002 g, 18%) as a golden brown oil (Found: M^+, 271.1572. $C_{17}H_{21}NO_2$ requires M, 271.1572); ν_{max}(film)/cm^{-1} 3478 (indole NH), 1724 (C=O), 1457, 1423, 1370, 1227, 1035 and 705; δ_H(270 MHz; $CDCl_3$) 1.18 (6 H, s, CMe_2), 1.22 (3 H, t, *J* 7.1, OCH_2Me), 1.76–1.80 (2 H, m, 4-H_2), 2.65–2.87 (2 H, m, 3-H_2), 4.05 (2 H, q, *J* 7.1, OCH_2Me), 4.92–5.02 (1 H, m, 6-H), 6.98 (1 H, dd, *J* 7.8 and 1.2, 7-H), 7.03 (1 H, s, 2-H), 7.11 (1 H, t, *J* 7.8, 8-H), 7.21 (1 H, d, *J* 7.5, 9-H) and 8.09 (1 H, br s, 1-H); *m/z* 271 (M^+, 31%), 198 (16), 185 (15), 184 (100), 182 (16), 169 (15), 168 (16) and 130 (54).

3-(*Indol*-3′-*yl*)*propyl Toluene*-*p*-*sulfonate*.—To a yellow solution of homotryptophol (1.0 g, 5.71 mmol) in pyridine (5 cm^3) at 0 °C was added toluene-*p*-sulfonyl chloride (2.18 g, 11.4 mmol). Once all the toluene-*p*-sulfonyl chloride had dissolved, the golden mixture was kept at 0 °C for 24 h. After this time, crystals of pyridinium hydrochloride had formed, and the mixture was poured onto ice–water (~50 cm^3). The mixture was then extracted with ether (3 × 75 cm^3), and the combined extracts were washed successively with saturated aq. copper(II) sulfate (~4 × 30 cm^3), until no darkening of the copper sulfate solution was evident, followed by water (3 × 40 cm^3), and brine (30 cm^3), and were then dried ($MgSO_4$). The solution was evaporated at ambient temperature to leave a yellowish solid, which was purified by chromatography (CH_2Cl_2) to give the title compound (1.64 g, 87%) as a crystalline solid, m.p. 98–100 °C (lit.,[10] 97–98 °C) (Found: C, 65.4; H, 5.7; N, 4.5. Calc. for $C_{18}H_{19}NO_3S$: C, 65.6; H, 5.8; N, 4.25%); ν_{max}(Nujol)/cm^{-1} 3386 (indole NH), 1346, 1172, 923, 817, 781, 750 and 554; δ_H(270 MHz; $CDCl_3$) 2.04 (2 H, quintet, *J* 6.7, 2-H_2), 2.44 (3 H, s, Ar*Me*), 2.81 (2 H, t, *J* 7.1, 3-H_2), 4.09 (2 H, t, *J* 6.2, 1-H_2), 6.91 (1 H, d, *J* 2.5, 2′-H), 7.09 (1 H, td, *J* 7.1 and 1.4, 5′-H), 7.19 (1 H, td, *J* 7.5 and 1.4, 6′-H), 7.30–7.37 (3 H, m, 7′-H and Ar *o*-H), 7.51 (1 H, d, *J* 7.8, 4′-H), 7.78 (2 H, d, *J* 8.3, Ar *m*-H and 7.95 (1 H, br s, 1′-H); *m/z* 329 (M^+, 28%), 157 (26), 156 (12), 144 (5), 131 (12), 130 (100, $ArCH_2^{\bullet+}$), 91 (12, $C_7H_7^{\bullet+}$) and 77 (9).

3-(3-*Iodopropyl*)*indole* **16**.—*Method A*. To a solution of homotryptophol (0.50 g, 2.85 mmol) in dry toluene (20 cm^3) at ambient temperature were added triphenylphosphine (2.25 g, 8.56 mmol), imidazole (0.583 g, 8.56 mmol), and resublimed iodine (1.45 g, 5.71 mmol). The resulting solution was stirred at ambient temperature for 20 min, after which time some tarry material had precipitated out. The toluene was decanted from this, and the residue was washed with ether (3 × 50 cm^3). The combined organic solvents were washed successively with 5% aq. sodium thiosulfate (40 cm^3) and water (2 × 40 cm^3) before being dried ($MgSO_4$) and evaporated to leave a brown oily residue. This was purified by chromatography (50% dichloromethane–light petroleum) to give the *title compound* **16** (0.19 g, 23%) as a brown oil (Found: M^+, 285.0014. $C_{11}H_{12}IN$ requires M, 285.0013); ν_{max}(film)/cm^{-1} 3414 (indole NH), 1605, 1456, 1338, 1265, 1213, 1169, 1093, 1011 and 743; δ_H(270 MHz; $CDCl_3$) 2.20 (2 H, quintet, *J* 7.0, CH_2CH_2I), 2.90 (2 H, t, *J* 7.0, indole-CH_2), 3.22 (2 H, t, *J* 7.0, CH_2I), 7.05 (1 H, d, *J* 2.2, 2-H), 7.13 (1 H, td, *J* 7.1 and 1.0, 5-H), 7.21 (1 H, td, *J* 7.1 and 1.1, 6-H), 7.37 (1 H, d, *J* 8.0, 7-H), 7.62 (1 H, d, *J* 7.7, 4-H) and 7.98 (1 H, br s, 1-H); *m/z* 285 (M^+, 47%), 148 (5), 131 (11), 130 (100, $ArCH_2^{\bullet+}$), 129 (6), 103 (6), 102 (5) and 77 (10).

Method B. To a solution of 3-(indol-3′-yl)propyltoluene-*p*-sulfonate (0.30 g, 0.011 mmol) in acetone (20 cm^3) at ambient temperature was added sodium iodide (0.683 g, 4.55 mmol). The resulting suspension was stirred at ambient temperature for 2 days, after which time water (40 cm^3) was added to the pale yellow mixture. The resulting solution was extracted with ether (3 × 40 cm^3), and the combined extracts were washed with water (30 cm^3), dried ($MgSO_4$), and evaporated to leave a yellow oil. This was purified by chromatography (50% dichloromethane–light petroleum) to give the *title compound* **16** (0.247 g, 95%) as a brown oil, the spectroscopic properties of which were identical with those of material prepared by method A.

tert-*Butyl* 3-(3-*Iodopropyl*)*indole*-1-*carboxylate* **17**.—To a suspension of 3-(3-iodopropyl)indole **16** (0.240 g, 0.842 mmol) in dry acetonitrile (10 cm^3) were added di-*tert*-butyl dicarbonate (0.276 g, 1.26 mmol) and DMAP (0.010 g, 84.3 μmol). The suspension was stirred at ambient temperature for 15 h to give a clear yellow solution, which was then evaporated to leave a yellow-brown residue. This was purified by chromatography (CH_2Cl_2) to give the *title compound* **17** (0.301 g, 93%) as a yellow-brown oil which darkened on storage (Found: C, 49.8; H, 5.2; N, 3.6. $C_{16}H_{20}INO_2$ requires C, 49.9; H, 5.2; N, 3.6%); ν_{max}(film)/cm^{-1} 1733 (carbamate C=O), 1455, 1371, 1255, 1159, 1083 and 746; δ_H(270 MHz; $CDCl_3$) 1.67 (9 H, s, Bu^t), 2.15–2.26 (2 H, m, CH_2CH_2I), 2.82 (2 H, td, *J* 7.1 and 0.7, Indole-CH_2), 3.24 (2 H, t, *J* 6.7, CH_2I), 7.24 (1 H, td, *J* 7.6 and 1.3, 5-H), 7.32 (1 H, td, *J* 7.8 and 1.3, 6-H), 7.41 (1 H, s, 2-H), 7.54 (1 H, d, *J* 7.8, 4-H) and 8.13 (1 H, br d, *J* 7.8, 7-H); *m/z* 385 (M^+, 20%), 329 (60), 285 (14), 237 (12), 174 (18), 130 (80, $ArCH_2^{\bullet+}$), 57 (100) and 41 (22).

Ethyl 2,2-*Dichloro*-5-(*indol*-3′*yl*)*pentanoate* **18**.—A solution of LiICA was prepared by the addition of butyllithium (1.5 mol dm^{-3} solution in hexanes; 0.15 cm^3, 0.234 mmol) to *N*-isopropylcyclohexylamine (38 mm^3, 0.234 mmol) in a mixture of THF (20 cm^3) and hexamethylphosphoric triamide (HMPA) (0.1 cm^3) at −20 °C under nitrogen, and the solution was then allowed to warm to 0 °C for 5 min before being cooled to −78 °C. A solution of ethyl dichloroacetate (0.037 g, 0.234 mmol) in THF

(3 cm^3) was added to the LiICA solution, and the mixture was stirred at −78 °C for 15 min. A solution of *tert*-butyl 3-(3-iodopropyl)indole-1-carboxylate **17** (0.10 g, 0.26 mmol) in THF (5 cm^3) was added dropwise to the yellow solution, and the mixture was stirred at −78 °C for 2 h. After this time, acetic acid (2.0 cm^3) was added, and the resulting solution was diluted with water (30 cm^3) and extracted with dichloromethane (3 × 40 cm^3). The combined extracts were dried ($MgSO_4$), evaporated, and purified by chromatography (CH_2Cl_2) to give the *title compound* **18** (0.018 g, 24%) as a pale yellow oil (Found: C, 57.5; H, 5.4; N, 4.7. $C_{15}H_{17}Cl_2NO_2$ requires C, 57.3; H, 5.5; N, 4.5%); ν_{max}(film)/cm^{-1} 3417 (indole NH), 1743 (C=O), 1457, 1259, 1094, 1012 and 742; λ_{max}(MeOH)/nm 275infl, 282 (log ε 3.75) and 290 (3.68); δ_H(270 MHz; $CDCl_3$) 1.30 (3 H, t, *J* 7.1, OCH_2Me), 1.97–2.09 (2 H, m, 4-H_2), 2.50–2,56 (2 H, m, 3-H_2), 2.86 (2 H, t, *J* 7.3, 5-H_2), 4.28 (2 H, q, *J* 7.1, OCH_2Me), 7.02 (1 H, d, *J* 2.3, 2′-H), 7.12 (1 H, td, *J* 7.7 and 1.4, 5′-H), 7.20 (1 H, td, *J* 7.4 and 1.2, 6′-H), 7.36 (1 H, d, *J* 8.0, 7′-H), 7.60 (1 H, d, *J* 7.8, 4′-H) and 7.95 (1 H, br s, 1′-H); *m/z* 313 (M^+, 15%), 243 (33), 241 (39), 193 (31), 170 (89), 168 (45), 167 (38) and 130 (100, $ArCH_2^{\bullet+}$).

Irradiation of Ethyl 2,2-*Dichloro*-5-(*indol*-3′-*yl*)*pentanoate* **18**. —A solution of ethyl 2,2-dichloro-5-(indol-3′-yl)pentanoate **18** (0.012 g, 38.2 μmol) in acetonitrile (10 cm^3) was irradiated for 25 min. The brown solution was evaporated, and the residue was purified by chromatography (2% MeOH–CH_2Cl_2) to give *ethyl* 2-*chloro*-5-(*indol*-3′-*yl*)*pent*-2-*enoate* **19c** (0.006 g, 58%) as a golden brown oil (Found: M^+, 277.0870. $C_{15}H_{16}ClNO_2$ requires M, 277.0870); ν_{max}(film)/cm^{-1} 3480 (indole NH), 1630 (C=O), 1458, 1419, 1371, 1183, 1091 and 1049; δ_H(270 MHz; $CDCl_3$) 1.32 (3 H, t, *J* 7.2, OCH_2Me), 2.80 (2 H, td, *J* 7.0 and 1.0, 5-H_2), 2.93–3.00 (2 H, m, 4-H_2), 4.26 (2 H, q, *J* 7.1, OCH_2Me), 7.02 (1 H, d, *J* 2.4, 2′-H), 7.10–7.24 (3 H, m, 3-, 5′- and 6′-H), 7.37 (1 H, d, *J* 7.8, 7′-H), 7.61 (1 H, d, *J* 7.8, 4′-H) and 7.97 (1 H, br s, 1′-H); *m/z* 277 (M^+, 5%), 168 (3), 167 (3), 131 (10), 130 (100, $ArCH_2^{\bullet+}$), 129 (3), 108 (3) and 77 (4).

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