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# Palladium-catalyzed oxidative C–H bond coupling of indoles and benzaldehydes: a new approach to the synthesis of 3-benzoylindoles

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ABSTRACT

A palladium-catalyzed dehydrogenative acylation of indoles using easily accessible aldehydes as the acyl source is described. This reaction provides a new approach for the synthesis of 3-acylindoles.



## 1. Introduction

Indole derivatives exhibit a broad range of useful pharmacological effects, including antibiotic, anti-inflammatory, antihypertensive, and antitumor activities.[1]

3-Acylindoles have been found to exhibit various pharmaceutical activities like anticancer and antidiabetic effects and inhibition of HIV-1 integrase and antinociceptive (Fig. 1). In 1991, it was reported that an indole derivative, **1**, unexpectedly inhibited contractions of the electrically stimulated mouse vas deferens.[2] Later work revealed that **1**, and a number of related compounds are antinociceptive and interact with the cannabinoid CB1 receptor and exhibit typical cannabinoid pharmacology in vivo.[3] Aminoalkylindole **2** is not only potent in vivo, but has high affinity for both the cannabinoid CB1 and CB2 receptors. Since then various indole derivatives with similar structural skeleton have been synthesized and their pharmacological activities have been investigated. For example compound **3** was identified as a potent inhibitor of tubulin polymerization and also as a cytotoxic agent against B16 melanoma cells.[4]

Due to the need for efficient ways to synthesize more elaborate structures possessing biological activity, the development of novel and convenient methods for the preparation of indole derivatives, among, which 3-acylindoles with valuable pharmaceutical activities, is of considerable importance in organic chemistry.

Numerous synthetic methodologies for the construction of 3-acylindoles have been developed in the past decades.[5] The Friedel–Crafts reaction is the classic method for the preparation of 3-acylindoles and most of the other reported methods are also based on the use of acid chlorides and modification of this process.[6] Therefore, development of new methods using alternant acylating agents is of considerable importance.

Classical methods have several drawbacks, notably Manich-type indole oligomerization in the presence of Lewis acids and generation of side products caused by addition of indole to 3-acylindole. Toxicity, commercial nonavailability and handling difficulty of the reagents are some of the other disadvantages.

Direct C–H functionalization has emerged over the past few years as an attractive strategy, from both scientific and environmental points of view to install many different types of bonds, including carbon–oxygen, carbon–halogen, carbon–nitrogen, carbon–sulfur and carbon–carbon linkages.[7]

In recent years, building a carbon–carbon linkage directly from two simple carbon–hydrogen (C–H) bonds has emerged as an

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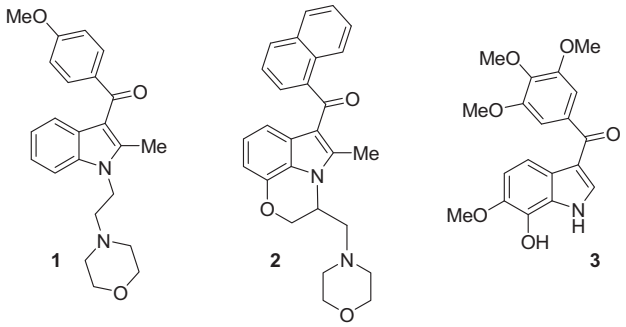


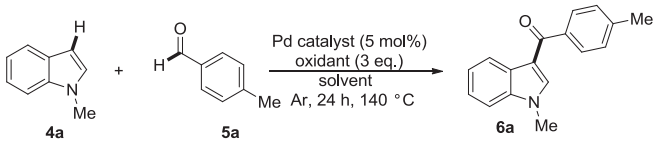

**Fig. 1.** Some bioactive compounds with a benzoylindole core structure.

attractive and challenging goal in catalysis.[8] This reaction is more atom economical and environmentally friendly than other cross-coupling reactions, and can be considered as a complementary strategy to the existing direct C–H bonds activations. Considerable advances in this field have recently been achieved.

## 2. Results and discussion

With an interest to develop catalytic C–H bond cross-coupling reactions, here we describe a versatile 3-acylindole synthesis by Pd catalyzed cross-coupling of indoles with aldehydes. *N*-methylindole (**4a**) and 4-methylbenzaldehyde (**5a**) were used as the substrates in the model reaction. In the initial trial, we were delighted that the desired product **6a** was obtained in 55% yield in the presence of oxidant TBHP (Table 1, entry 7).

**Table 1**
Optimization of the reaction conditions.[a]



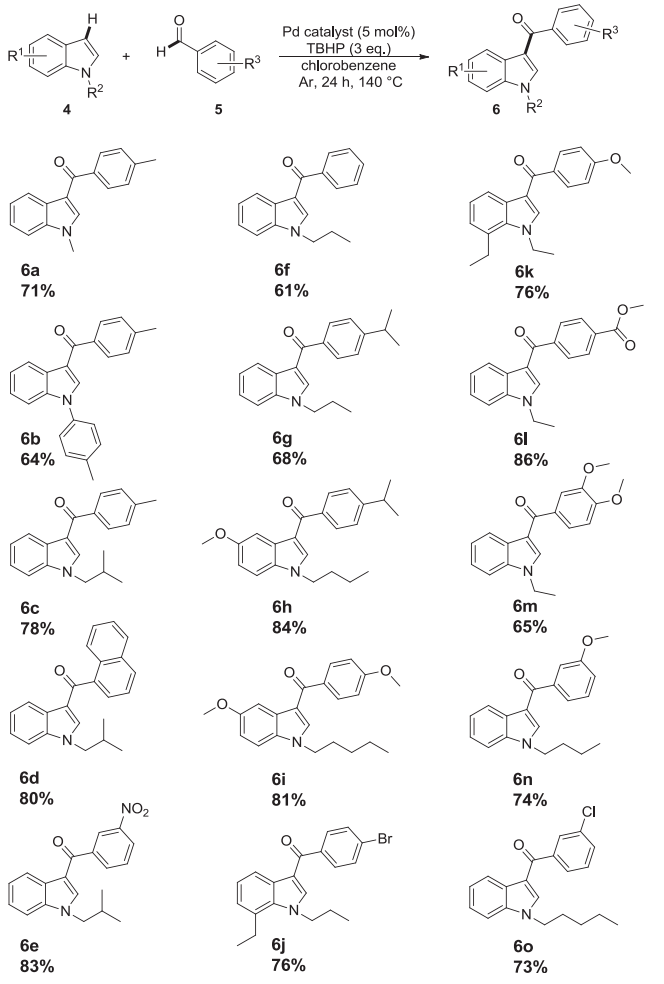

| Entry | Pd catalyst | Oxidant | Solvent[a] | Yield (%) |
|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ | TBHP | NMP | 0 |
| 2 | $Pd(OAc)_2$ | TBHP | $CH_3CN$ | 0 |
| 3 | $Pd(OAc)_2$ | TBHP | DMSO | 0 |
| 4 | $Pd(OAc)_2$ | TBHP | DMF | 0 |
| 5 | $Pd(OAc)_2$ | TBHP | DMAc | Trace |
| 6 | $Pd(OAc)_2$ | TBHP | DCE | 8 |
| 7 | $Pd(OAc)_2$ | TBHP | Toluene | 55 |
| 8 | $Pd(OAc)_2$ | TBHP | DME | 58 |
| 9 | $Pd(OAc)_2$ | TBHP | Diglyme | 60 |
| 10 | $Pd(OAc)_2$ | TBHP | Neat | 64 |
| 11 | $Pd(OAc)_2$ | TBHP | *tert*-Amyl alcohol | 61 |
| 12 | $Pd(OAc)_2$ | TBHP | 1,4-Dioxane | 67 |
| **13** | **$Pd(OAc)_2$** | **TBHP** | **PhCl** | **78** |
| 14 | $Pd(OAc)_2$ | DTBP | PhCl | 0 |
| 15 | $Pd(OAc)_2$ | $(PhCOO)_2$ | PhCl | 17 |
| 16 | $Pd(OAc)_2$ | $PhC(CH_3)_2OOH$ | PhCl | 34 |
| 17 | $PdCl_2$ | TBHP | PhCl | 22 |
| 18 | $Pd(COD)Cl_2$ | TBHP | PhCl | 31 |
| 19 | $Pd(PPh_3)_2Cl_2$ | TBHP | PhCl | 36 |
| 20[b] | $Pd(OAc)_2$ | TBHP | PhCl | 0 |
| 21[c] | $Pd(OAc)_2$ | TBHP | PhCl | 59 |
| 22[d] | $Pd(OAc)_2$ | TBHP | PhCl | 38 |

[a] NMP: *N*-methyl-2-pyrrolidinone; DMSO: dimethylsulfoxide; DMF: *N*,*N*-dimethylformamide; DMAc: *N*,*N*-dimethylacetamide; DCE: 1,1-dichloroethane; DME: 1,2-dimethoxyethane; COD: cyclooctadiene.
[b] The reaction was performed at 25 °C.
[c] The reaction was performed at 120 °C.
[d] The reaction was performed under air.

Different organic solvents were screened. Chlorobenzene gave the best yield while solvents, such as 1,4-dioxane, *tert*-amyl alcohol, diglyme and DME afforded moderate yields of the product and DCE, DMAc, DMF, DMSO, NMP, and $CH_3CN$ afforded poor results (Table 1, entries 1–13). The effectiveness of the oxidant was also examined. TBHP was the most suitable oxidant in this reaction. Other peroxides such as DTBP (di-*tert*-butylperoxide), $(PhCOO)_2$ and $PhC(CH_3)_2OOH$ were less effective (Table 1, entries 14–16), and no desired product was observed when oxygen was used as the sole oxidant. The optimal TBHP added to the reaction was 3 equiv. A screening of catalysts showed that $Pd(OAc)_2$ gave the best results while $PdCl_2$, $Pd(COD)Cl_2$ and $Pd(PPh_3)_2Cl_2$ were found to be inferior (Table 1, entries 17–19). The best activity was shown at 140 °C and the reaction provided a lower conversion at lower temperature (Table 1, entries 20 and 21).

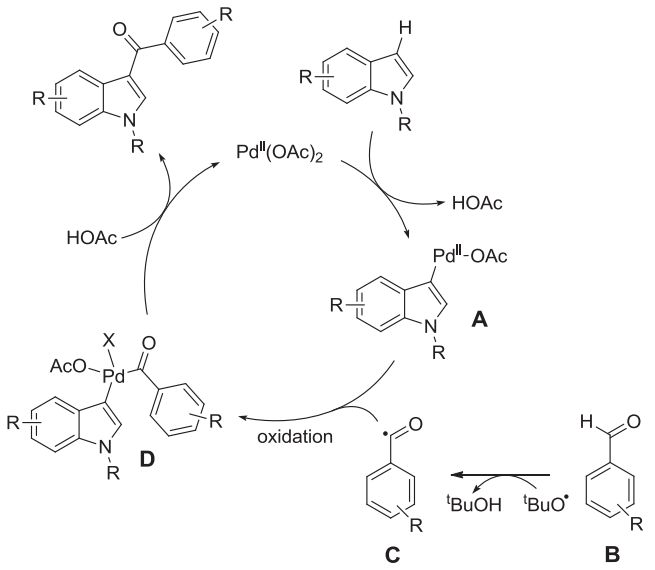
With the optimized reaction conditions in hand, we next tested the scope of the reaction (Scheme 1). Aldehydes with electron withdrawing groups and 1-naphthylaldehyde gave good yields of the corresponding products. The presence of bromine on the benzene ring did not change the reaction pathway, and moderate yields of the product were obtained using this moderately electron poor aldehyde. Aldehydes with electron-donating groups gave a slightly lower yield of the product presumably due to the difficult C–H bond cleavage of aldehyde.

Although the reaction mechanism is not clear at this stage, but on the basis of the previous chemistry,[9] it is believed that this




**Scheme 1.** Scope of direct 3-acylation indoles with aldehydes. Indole derivatives (1 mmol), aldehyde derivatives (3 mmol), TBHP 70% aq (3 mmol), $Pd(OAc)_2$ (5 mol %) in chlorobenzene at 140 °C for 24 h.

transformation begins with the 3-palladation of indole with $Pd(OAc)_2$. At the same time, the aldehyde is transferred to an acyl radical by TBHP. The Pd(II) intermediate **A** would react with the acyl radicals to afford the Pd(IV) intermediate **D**. The Pd(IV) intermediate **D** would undergo reductive elimination to produce the desired product and regenerate the Pd(II) species (Scheme 2).




**Scheme 2.** Tentative mechanism proposed for the 3-acylation of indoles (note: not all the neutral/anionic ligands around the Pd centers are shown).

## 3. Conclusion

In conclusion, we have developed a Pd-catalyzed protocol for a selective 3-acylation of indoles by oxidative coupling with aldehydes. This new methodology enabled cross-coupling with aromatic aldehydes in high yield and high regioselectivity. Investi gations into the Pd(II)/(IV) catalytic cycle along with characterization of postulated intermediates and extension of the scope are ongoing and will be reported in due course.

## 4. Experimental section

### 4.1. General

All reactions were performed under anhydrous conditions. Glassware was flame-dried and reactions were performed under an argon atmosphere. Catalytic reactions were performed employing microwave vials. Solvents were distilled before use. Chemicals were purchased from commercial sources and were used as received. Substituted indoles were prepared according to the literature.[10] Thin layer chromatography (TLC) analysis was performed using Silicycle precoated TLC plates (silica gel 60 $F_{254}$). The products were purified by preparative column chromatography on silica gel (0.063–0.200 mm; Merck). IR Spectra: Bruker Equinox 55 spectrometer; in $cm^{-1}$. $^1H$ and $^{13}C$ NMR Spectra: were recorded on Bruker DRX-500-Advance instrument; in $CDCl_3$ at 500.1 and 125.7 MHz, resp.; $\delta$ in parts per million, *J* in Hertz. EI-MS (70 eV): HP 5973 GC–MS instrument; in *m*/*z*. Melting points: Electrothermal 9200 apparatus.

### 4.2. General procedure for cyanoalkenylation of indoles

A 10 ml microwave vial equipped with a magnetic stirring bar and septum was flame-dried and then cooled under a stream of argon by venting through a needle in the septum. The vial was charged with indole derivatives (1 mmol), aldehyde derivatives (3 mmol), TBHP 70% aq (3 mmol, 0.4 ml) and $Pd(OAc)_2$ (0.05 mmol, 11 mg). The vial was sealed and flushed with argon for 2 min. Chlorobenzene (4 ml) was added via syringe. The reaction vessel was then immersed in an oil bath, which was preheated at 140 °C, for 24 h. After this time the reaction mixture was cooled to room temperature and diluted with ethyl acetate (15 ml). The mixture was washed with 10% NaOH solution (15 ml), and the organic extract was dried over sodium sulfate and filtered. Concentration of the solution by rotary evaporation under reduced pressure gave a residue, which was purified by using column chromatography.

*4.2.1. (1-Methyl-1H-indol-3-yl)(p-tolyl)methanone (**6a**).* The general procedure was followed using 1-methyl-1*H*-indole (1 mmol, 131 mg), 4-methylbenzaldehyde (3 mmol, 0.35 ml). Purification by column chromatography (20% $Et_2O$/hexane) gave the final product **6a** (177 mg, 71%) as a white solid, mp=136–137 °C; $R_f$ (20% $Et_2O$/hexane)=0.18; IR (KBr) $\nu_{max}$ 2920, 1609, 1521, 1461, 1368, 1228, 1121, 753 $cm^{-1}$; $^1H$ NMR (500.1 MHz, DMSO-$d_6$) $\delta$ 8.26 (d, *J*=7.7 Hz, 1H, =CH), 8.00 (s, 1H, =C*H*N), 7.70 (d, *J*=7.8 Hz, 2H, =CH), 7.58 (d, *J*=8.0 Hz, 1H, =CH), 7.35 (d, *J*=7.8 Hz, 2H, =CH), 7.28–7.33 (m, 2H, =CH), 3.88 (s, 3H, N*Me*), 2.41 (s, 3H, Ph*Me*) ppm; $^{13}C$ NMR (125.7 MHz, DMSO-$d_6$) $\delta$ 189.2, 141.0, 139.2, 137.3, 131.6, 128.9, 128.5, 126.7, 123.1, 122.2, 121.6, 113.9, 110.6, 33.1, 21.0 ppm; MS (EI, 70 eV): *m*/*z* (%)=249 ($M^+$, 61), 234 (5), 220 (5), 158 (100), 130 (12), 115 (5), 91 (19), 77 (19), 72 (29); Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62; Found: C, 81.67; H, 6.02; N, 5.65.

*4.2.2. p-Tolyl(1-p-tolyl-1H-indol-3-yl)methanone (**6b**).* The general procedure was followed using 1-*p*-tolyl-1*H*-indole (1 mmol, 207 mg), 4-methylbenzaldehyde (3 mmol, 0.35 ml). Purification by column chromatography (5% $Et_2O$/hexane) gave the final product **6b** (208 mg, 64%) as a yellow oil; $R_f$ (10% $Et_2O$/hexane)=0.24; IR (KBr) $\nu_{max}$ 2922, 1606, 1517, 1454, 1358, 1217, 1177, 744 $cm^{-1}$; $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 8.50 (d, *J*=7.3 Hz, 1H, =CH), 7.81 (d, *J*=8.0 Hz, 2H, =CH), 7.77 (s, 1H, =C*H*N), 7.51 (d, *J*=8.0 Hz, 1H, =CH), 7.34–7.41 (m, 6H, =CH), 7.31 (d, *J*=8.0 Hz, 2H, =CH), 2.47 (s, 3H, *Me*), 2.45 (s, 3H, *Me*) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 190.9, 141.8, 138.0, 137.9, 137.1, 136.5, 135.8, 130.4, 129.0, 127.5, 124.7, 124.0, 123.0, 122.8, 117.1, 110.8, 21.5, 21.1 ppm; MS (EI, 70 eV): *m*/*z* (%)=325 ($M^+$, 61), 310 (3), 234 (68), 219 (5), 191 (13), 167 (55), 149 (100), 119 (43), 91 (39), 57 (53), 43 (63); Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30; Found: C, 84.61; H, 5.92; N, 4.32.

*4.2.3. (1-Isobutyl-1H-indol-3-yl)(p-tolyl)methanone (**6c**).* The general procedure was followed using 1-isobutyl-1*H*-indole (1 mmol, 173 mg), 4-methylbenzaldehyde (3 mmol, 0.35 ml). Purification by column chromatography (10% $Et_2O$/hexane) gave the final product **6c** (227 mg, 78%) as a white solid, mp=104–106 °C, $R_f$ (20% $Et_2O$/hexane)=0.34; IR (KBr) $\nu_{max}$ 2958, 1612, 1520, 1461, 1382, 1212, 748 $cm^{-1}$; $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 8.41–8.43 (m, 1H, =CH), 7.75 (d, *J*=8.0 Hz, 2H, =CH), 7.56 (s, 1H, =C*H*N), 7.38–7.40 (m, 1H, =CH), 7.32–7.35 (m, 2H, =CH), 7.31 (d, *J*=8.0 Hz, 2H, =CH), 3.97 (d, *J*=7.3 Hz, 2H, NC$H_2$), 2.46 (s, 3H, Ph*Me*), 2.22–2.28 (m, 1H, C*H*Me$_2$), 0.96 (d, *J*=6.6 Hz, 6H, CH*Me*$_2$) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 190.7, 141.5, 138.2, 137.1, 128.9, 127.4, 123.4, 122.8, 122.5, 121.4, 115.5, 110.0, 54.7, 29.2, 21.5, 20.2 ppm; MS (EI, 70 eV): *m*/*z* (%)=291 ($M^+$, 64), 248 (100), 234 (2), 220 (4), 200 (17), 144 (11), 119 (28), 91 (20), 57 (3). Anal. Calcd for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81; Found: C, 82.26; H, 7.30; N, 4.78.

*4.2.4. (1-Isobutyl-1H-indol-3-yl)(naphthalen-1-yl)methanone (**6d**).* The general procedure was followed using 1-isobutyl-1*H*-indole (1 mmol, 173 mg), 1-naphthaldehyde (3 mmol, 0.41 ml). Purification by column chromatography (5% $Et_2O$/hexane) gave the

final product **6d** (262 mg, 80%) as an orange oil; $R_f$ (10% $Et_2O$/hexane)=0.19; IR (KBr) $\nu_{max}$ 2926, 1613, 1518, 1462, 1378, 1197, 1131, 747 $cm^{-1}$; $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 8.50–8.51 (m, 1H, =CH), 8.21 (d, $J$=8.4 Hz, 1H, =CH), 7.98 (d, $J$=8.2 Hz, 1H, =CH), 7.93 (d, $J$=7.9 Hz, 1H, =CH), 7.68 (d, $J$=7.0 Hz, 1H, =CH), 7.46–7.56 (m, 3H, =CH), 7.36–7.41 (m, 3H, =CH), 7.34 (s, 1H, =C*H*N), 3.88 (d, $J$=7.3 Hz, 2H, NC$H_2$), 2.16–2.22 (m, 1H, C*H*$Me_2$), 0.91 (d, $J$=6.7 Hz, 6H, CH*Me*$_2$) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 192.1, 139.1, 138.4, 137.3, 133.7, 130.8, 130.0, 128.1, 126.9, 126.7, 126.3, 126.0, 125.9, 124.5, 123.6, 122.9, 122.8, 117.4, 110.2, 54.7, 29.1, 20.1 ppm; MS (EI, 70 eV): $m/z$ (%)=327 ($M^+$, 65), 298 (2), 284 (88), 270 (14), 200 (38), 167 (47), 149 (60), 127 (33), 71 (33), 57 (57), 43 (100). Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28; Found: C, 84.16; H, 6.49; N, 4.30.

*4.2.5. (1-Isobutyl-1H-indol-3-yl)(3-nitrophenyl) methanone (**6e**).* The general procedure was followed using 1-isobutyl-1*H*-indole (1 mmol, 173 mg), 3-nitrobenzaldehyde (3 mmol, 453 mg). Purification by column chromatography (10% $Et_2O$/hexane) gave the final product **6e** (267 mg, 83%) as a white solid, mp=105–106 °C, $R_f$ (20% $Et_2O$/hexane)=0.32; IR (KBr) $\nu_{max}$ 3058, 2962, 1614, 1520, 1464, 1381, 1346, 1210, 1134, 713 $cm^{-1}$; $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 8.66 (s, 1H, =CH), 8.41–8.42 (m, 2H, =CH), 8.17 (d, $J$=7.6 Hz, 1H, =CH), 7.71 (t, $J$=7.9 Hz, 1H, =CH), 7.53 (s, 1H, =C*H*N), 7.37–7.44 (m, 3H, =CH), 4.00 (d, $J$=7.3 Hz, 2H, NC$H_2$), 2.23–2.30 (m, 1H, C*H*$Me_2$), 0.98 (d, $J$=6.6 Hz, 6H, CH*Me*$_2$) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 187.8, 148.0, 142.3, 137.4, 137.3, 134.5, 129.6, 127.1, 125.6, 124.0, 123.6, 123.1, 122.7, 114.8, 110.3, 54.9, 29.2, 20.2 ppm; MS (EI, 70 eV): $m/z$ (%)=322 ($M^+$, 55), 307 (3), 279 (100), 248 (16), 233 (9), 219 (3), 200 (20), 157 (3), 149 (27), 129 (13), 116 (8), 104 (8), 76 (8), 57 (21). Anal. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69; Found: C, 70.67; H, 5.61; N, 8.74.

*4.2.6. Phenyl(1-propyl-1H-indol-3-yl)methanone (**6f**).* The general procedure was followed using 1-propyl-1*H*-indole (1 mmol, 159 mg), benzaldehyde (3 mmol, 0.31 ml). Purification by column chromatography (10% $Et_2O$/hexane) gave the final product **6f** (160 mg, 61%) as an orange solid, mp=69–71 °C; $R_f$ (20% $Et_2O$/hexane)=0.34; IR (KBr) $\nu_{max}$ 3051, 2928, 1609, 1516, 1461, 1385, 1211, 1129, 721 $cm^{-1}$; $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 8.44–8.45 (m, 1H, =CH), 7.84 (d, $J$=7.2 Hz, 2H, =CH), 7.49–7.58 (m, 4H, =CH), 7.41–7.42 (m, 1H, =CH), 7.34–7.36 (m, 2H, =CH), 4.14 (t, $J$=7.0 Hz, 2H, NC$H_2$), 1.93 (sextet, $J$=7.2 Hz, 2H, C$H_2$Me), 0.97 (t, $J$=7.3 Hz, 3H, Me) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 190.9, 141.0, 137.0, 136.8, 131.0, 128.7, 128.3, 127.4, 123.5, 122.8, 122.6, 115.5, 109.8, 48.8, 23.2, 11.4 ppm; MS (EI, 70 eV): $m/z$ (%)=263 ($M^+$, 98), 234 (59), 220 (5), 186 (100), 167 (27), 158 (2), 149 (72), 144 (25), 116 (13), 105 (29), 77 (29), 43 (16); Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32; Found: C, 82.26; H, 6.54; N, 5.30.

*4.2.7. (4-Isopropylphenyl)(1-propyl-1H-indol-3-yl)methanone (**6g**).* The general procedure was followed using 1-propyl-1*H*-indole (1 mmol, 159 mg), 4-isopropylbenzaldehyde (3 mmol, 0.45 ml). Purification by column chromatography (10% $Et_2O$/hexane) gave the final product **6g** (208 mg, 68%) as an orange solid, mp=108–110 °C; $R_f$ (20% $Et_2O$/hexane)=0.36; IR (KBr) $\nu_{max}$ 3107, 2961, 1616, 1520, 1463, 1382, 1214, 1130, 758 $cm^{-1}$; $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 8.45–8.47 (m, 1H, =CH), 7.79 (d, $J$=8.1 Hz, 2H, =CH), 7.61 (s, 1H, =C*H*N), 7.40–7.42 (m, 1H, =CH), 7.32–7.36 (m, 4H, =CH), 4.14 (t, $J$=7.1 Hz, 2H, NC$H_2$), 3.01 (septet, $J$=6.9 Hz, 1H, C*H*$Me_2$), 1.93 (sextet, $J$=7.2 Hz, 2H, C$H_2$Me), 1.33 (d, $J$=6.9 Hz, 6H, CH*Me*$_2$), 0.97 (t, $J$=7.4 Hz, 3H, $CH_2$*Me*) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 190.7, 152.3, 138.6, 136.8, 129.3, 129.0, 127.4, 126.3, 123.4, 122.8, 122.5, 115.5, 109.8, 48.7, 34.1, 23.8, 23.2, 11.4 ppm; MS (EI, 70 eV): $m/z$ (%)=305 ($M^+$, 100), 276 (50), 262 (11), 186 (82), 157 (2), 144 (22), 129 (7), 116 (9), 104 (9), 77 (5), 43 (9); Anal. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59; Found: C, 82.41; H, 7.55; N, 4.57.

*4.2.8. (1-Butyl-5-methoxy-1H-indol-3-yl)(4-isopropylphenyl)methanone (**6h**).* The general procedure was followed using 1-butyl-5-methoxy-1*H*-indole (1 mmol, 203 mg), 4-isopropylbenzaldehyde (3 mmol, 0.45 ml). Purification by column chromatography (10% $Et_2O$/hexane) gave the final product **6h** (294 mg, 84%) as a white solid, mp=72–73 °C; $R_f$ (20% $Et_2O$/hexane)=0.44; IR (KBr) $\nu_{max}$ 3103, 2962, 1618, 1518, 1457, 1382, 1270, 1211, 1041, 843 $cm^{-1}$; $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 7.99 (d, $J$=2.5 Hz, 1H, =CH), 7.77 (d, $J$=8.1 Hz, 2H, =CH), 7.55 (s, 1H, =C*H*N), 7.36 (d, $J$=8.1 Hz, 2H, =CH), 7.28 (d, $J$=8.9 Hz, 1H, =CH), 6.98 (dd, $J$=2.5 Hz, $J$=8.9 Hz, 1H, =CH), 4.13 (t, $J$=7.2 Hz, 2H, NC$H_2$), 3.93 (s, 3H, O*Me*), 3.01 (septet, $J$=6.9 Hz, 1H, C*H*$Me_2$), 1.85 (quintet, $J$=7.4 Hz, 2H, NCH$_2$C$H_2$), 1.37 (sextet, $J$=7.6 Hz, 2H, C$H_2$Me), 1.33 (d, $J$=6.9 Hz, 6H CH*Me*$_2$), 0.95 (t, $J$=7.3 Hz, 3H, $CH_2$*Me*) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 190.7, 156.4, 152.2, 138.7, 136.8, 131.7, 128.9, 128.3, 126.4, 115.2, 114.1, 110.6, 103.9, 55.8, 47.1, 34.2, 32.0, 23.9, 20.1, 13.6 ppm; MS (EI, 70 eV): $m/z$ (%)=349 ($M^+$, 68), 334 (2), 306 (26), 291 (3), 279 (29), 262 (2), 230 (21), 202 (2), 167 (66), 159 (5), 149 (100), 132 (6), 104 (14), 71 (35), 57 (51), 43 (33); Anal. Calcd for $C_{23}H_{27}NO_2$: C, 79.05; H, 7.79; N, 4.01; Found: C, 79.11; H, 7.81; N, 3.99.

*4.2.9. (5-Methoxy-1-pentyl-1H-indol-3-yl)(4-methoxyphenyl)methanone (**6i**).* The general procedure was followed using 5-methoxy-1-pentyl-1*H*-indole (1 mmol, 217 mg), 4-methoxybenzaldehyde (3 mmol, 0.36 ml). Purification by column chromatography (20% $Et_2O$/hexane) gave the final product **6i** (285 mg, 81%) as an orange oil; $R_f$ (20% $Et_2O$/hexane)=0.22; IR (KBr) $\nu_{max}$ 2928, 1601, 1514, 1457, 1382, 1250, 1213, 1167, 1026, 842 $cm^{-1}$. $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 7.95 (d, $J$=2.2 Hz, 1H, =CH), 7.85 (d, $J$=8.6 Hz, 2H, =CH), 7.54 (s, 1H, =C*H*N), 7.28 (d, $J$=9.0 Hz, 1H, =CH), 7.00 (d, $J$=8.6 Hz, 2H, =CH), 6.98 (dd, $J$=2.2 Hz, $J$=9.0 Hz, 1H, =CH), 4.13 (t, $J$=7.1 Hz, 2H, NC$H_2$), 3.92 (s, 3H, O*Me*), 3.90 (s, 3H, O*Me*), 1.88 (quintet, $J$=7.2 Hz, 2H NCH$_2$C$H_2$), 1.31–1.36 (m, 4H, C$H_2$C$H_2$Me), 0.89 (t, $J$=7.1 Hz, 3H, $CH_2$*Me*) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 189.8, 162.1, 156.3, 136.3, 133.6, 131.7, 130.8, 128.3, 115.1, 114.0, 113.5, 110.6, 103.7, 55.8, 55.4, 47.3, 29.6, 29.0, 22.2, 13.9 ppm; MS (EI, 70 eV): $m/z$ (%)=351 ($M^+$, 12), 294 (6), 279 (51), 248 (7), 218 (5), 167 (88), 157 (3), 149 (100), 135 (20), 128 (4), 121 (18), 104 (16), 71 (49), 57 (71), 43 (47); Anal. Calcd for $C_{22}H_{25}NO_3$: C, 75.19; H, 7.17; N, 3.99; Found: C, 75.38; H, 7.15; N, 4.02.

*4.2.10. (4-Bromophenyl)(7-ethyl-1-propyl-1H-indol-3-yl)methanone (**6j**).* The general procedure was followed using 7-ethyl-1-propyl-1H-indole (1 mmol, 187 mg), 4-bromobenzaldehyde (3 mmol, 550 mg). Purification by column chromatography (5% $Et_2O$/hexane) gave the final product **6j** (281 mg, 76%) as a white solid, mp=126–127 °C; $R_f$ (20% $Et_2O$/hexane)=0.45; IR (KBr) $\nu_{max}$ 3027, 2924, 1607, 1527, 1467, 1384, 1255, 1210, 1112, 1065, 837 $cm^{-1}$; $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 8.33 (d, $J$=7.7 Hz, 1H, =CH), 7.69 (d, $J$=8.5 Hz, 2H, =CH), 7.63 (d, $J$=8.5 Hz, 2H, =CH), 7.47 (s, 1H, =C*H*N), 7.28 (t, $J$=7.5 Hz, 1H, =CH), 7.15 (d, $J$=7.1 Hz, 1H, =CH), 4.27 (t, $J$=7.3 Hz, 2H, NC$H_2$), 3.05 (quartet, $J$=7.5 Hz, 2H, C$H_2$Me), 1.87 (sextet, $J$=7.4 Hz, 2H, NCH$_2$C$H_2$), 1.37 (t, $J$=7.5 Hz, 3H, CH$_2$CH$_2$*Me*), 0.97 (t, $J$=7.5 Hz, 3H, $CH_2$*Me*) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 189.5, 139.8, 138.8, 134.6, 131.5, 130.3, 128.6, 127.8, 125.7, 125.0, 123.1, 120.6, 115.2, 51.5, 25.4, 25.2, 16.2, 11.1 ppm; MS (EI, 70 eV): $m/z$ (%)=371 [$(M+2)^+$, 13], 369 ($M^+$, 13), 340 (8), 291 (8), 246 (100), 214 (12), 202 (65), 183 (43), 167 (33), 157 (23), 149 (85), 115 (20), 105 (12), 71 (38), 57 (59), 43 (47); Anal. Calcd for $C_{20}H_{20}BrNO$: C, 64.87; H, 5.44; N, 3.78; Found: C, 65.02; H, 5.43; N, 3.80.

*4.2.11. (1,7-Diethyl-1H-indol-3-yl)(4-methoxyphenyl)methanone (**6k**).* The general procedure was followed using 1,7-diethyl-1H-

indole (1 mmol, 173 mg), 4-methoxybenzaldehyde (3 mmol, 0.36 ml). Purification by column chromatography (15% $Et_2O$/hexane) gave the final product **6k** (234 mg, 76%) as a white solid, mp=146–147 °C; $R_f$ (20% $Et_2O$/hexane)=0.22; IR (KBr) $\nu_{max}$ 2970, 1602, 1525, 1417,1376, 1247, 1180, 1101, 1026, 825 $cm^{-1}$; $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 8.31 (d, $J$=7.6 Hz, 1H, =CH), 7.85 (d, $J$=8.6 Hz, 2H, =CH), 7.54 (s, 1H, =C*H*N), 7.25 (t, $J$=7.6 Hz, 1H, =CH), 7.13 (d, $J$=7.1 Hz, 1H, =CH), 7.00 (d, $J$=8.6 Hz, 2H, =CH), 4.40 (quartet, $J$=7.2 Hz, 2H, NC$H_2$Me), 3.90 (s, 3H, O*Me*), 3.07 (quartet, $J$=7.5 Hz, 2H, C$H_2$Me), 1.50 (t, $J$=7.2 Hz, 3H, NCH$_2$*Me*), 1.38 (t, $J$=7.5 Hz, 3H, CH$_2$*Me*) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 189.7, 162.1, 137.3, 134.4, 133.6, 131.0, 128.8, 127.6, 124.5, 122.7, 120.6, 115.8, 113.5, 55.4, 44.4, 25.5, 17.3, 16.2 ppm; MS (EI, 70 eV): $m/z$ (%)=307 ($M^+$, 39), 292 (9), 279 (16), 263 (5), 250 (2), 200 (25), 167 (38), 156 (4), 149 (100), 143 (3), 135 (21), 104 (9), 77 (10), 71 (20), 57 (33), 43 (24); Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56; Found: C, 78.44; H, 6.86; N, 4.55.

*4.2.12. Methyl-4-[(1-ethyl-1H-indol-3-yl)carbonyl]benzoate (**6l**).* The general procedure was followed using 1-ethyl-1H-indole (1 mmol, 145 mg), methyl 4-formylbenzoate (3 mmol, 492 mg). Purification by column chromatography (15% $Et_2O$/hexane) gave the final product **6l** (264 mg, 86%) as a white solid, mp=144–145 °C; $R_f$ (20% $Et_2O$/hexane)=0.21; IR (KBr) $\nu_{max}$ 3120, 2978, 1708, 1604, 1516, 1461,1383, 1278, 1218, 1107, 734 $cm^{-1}$; $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 8.41–8.43 (m, 1H, =CH), 8.17 (d, $J$=8.2 Hz, 2H, =CH), 7.86 (d, $J$=8.2 Hz, 2H, =CH), 7.57 (s, 1H, =C*H*N), 7.42–7.44 (m, 1H, =CH), 7.34–7.39 (m, 2H, =CH), 4.24 (quartet, $J$=7.3 Hz, 2H, NC$H_2$), 3.98 (s, 3H, O*Me*), 1.53 (t, $J$=7.3 Hz, 3H, CH$_2$*Me*) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 189.9, 166.6, 144.8, 136.7, 136.4, 132.1, 129.6, 128.5, 127.2, 123.7, 122.9, 122.8, 115.6, 109.8, 52.4, 41.9, 15.2 ppm; MS (EI, 70 eV): $m/z$ (%)=307 ($M^+$, 49), 292 (5), 279 (10), 248 (4), 172 (100), 163 (12), 157 (4), 149 (70), 143 (6), 135 (13), 129 (10), 104 (12), 69 (66), 57 (51), 43 (49); Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56; Found: C, 74.12; H, 5.59; N, 4.59.

*4.2.13. (1-Ethyl-1H-indol-3-yl)(3,4-dimethoxyphenyl)methanone (**6m**).* The general procedure was followed using 1-ethyl-1*H*-indole (1 mmol, 145 mg), 3,4-dimethoxybenzaldehyde (3 mmol, 500 mg). Purification by column chromatography (25% $Et_2O$/hexane) gave the final product **6m** (201 mg, 65%) as an orange solid, mp=106–109 °C; $R_f$ (30% $Et_2O$/hexane)=0.16; IR (KBr) $\nu_{max}$ 3109, 2929, 1575, 1510, 1457, 1374, 1262, 1207, 1168, 1019, 744 $cm^{-1}$; $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 8.38 (m, 1H, =CH), 7.66 (s, 1H, =C*H*N), 7.47–7.48 (m, 2H, =CH), 7.42 (m, 1H, =CH), 7.31–7.36 (m, 2H, =CH), 6.94 (d, $J$=8.7 Hz, 1H, =CH), 4.25 (quartet, $J$=7.2 Hz, 2H NC$H_2$), 3.98 (s, 3H, O*Me*), 3.96 (s, 3H, O*Me*), 1.54 (t, $J$=7.2 Hz, 3H, CH$_2$*Me*) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 189.7, 151.8, 149.0, 136.6, 135.4, 133.6, 127.5, 123.4, 122.9, 122.8, 122.4, 115.7, 111.7, 109.9, 109.7, 56.0, 41.7, 15.2 ppm; MS (EI, 70 eV): $m/z$ (%)=309 ($M^+$, 48), 291 (21), 279 (40), 248 (32), 167 (83), 149 (100), 135 (6), 129 (13), 104 (15), 77 (10), 71 (43), 57 (64), 43 (49); Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53; Found: C, 73.93; H, 6.16; N, 4.51.

*4.2.14. (1-Butyl-1H-indol-3-yl)(3-methoxyphenyl)methanone (**6n**).* The general procedure was followed using 1-butyl-*1H*-indole (1 mmol, 173 mg), 3-methoxybenzaldehyde (3 mmol, 0.36 ml). Purification by column chromatography (5% $Et_2O$/hexane) gave the final product **6n** (227 mg, 74%) as an orange oil; $R_f$ (20% $Et_2O$/hexane)=0.38, IR (KBr) $\nu_{max}$ 2957, 1578, 1518, 1461, 1379, 1268, 1248, 1196, 1035, 745 $cm^{-1}$; $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 8.44–8.46 (m, 1H, =CH), 7.60 (s, 1H, =C*H*N), 7.33–7.42 (m, 6H, =CH), 7.14 (m, 1H, =CH), 4.17 (t, $J$=7.5 Hz, 2H, NC$H_2$), 3.88 (s, 3H, O*Me*), 1.87 (quintet, $J$=7.5 Hz, 2H, NCH$_2$C$H_2$), 1.38 (sextet, $J$=7.5 Hz, 2H, C$H_2$Me), 0.96 (t, $J$=7.5 Hz, 3H, CH$_2$*Me*) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 190.5, 159.5, 142.3, 137.0, 136.8, 129.2, 127.3, 123.5, 122.8, 122.6, 121.2, 117.3, 115.4, 113.4, 109.8, 55.4, 46.9, 31.9, 20.1, 13.6 ppm; MS (EI, 70 eV): $m/z$ (%)=307 ($M^+$, 94), 279 (20), 264 (42), 248 (7), 220 (4), 200 (83), 189 (47), 167 (42), 149 (100), 143 (5), 135 (55), 129 (9), 118 (85), 105 (24), 77 (43), 57 (31), 43 (30); Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56; Found: C, 78.08; H, 6.93; N, 4.53.

*4.2.15. (3-Chlorophenyl)(1-pentyl-1H-indol-3-yl)methanone (**6o**).* The general procedure was followed using 1-pentyl-1*H*-indole (1 mmol, 187 mg), 3-chlorobenzaldehyde (3 mmol, 0.34 ml). Purification by column chromatography (10% $Et_2O$/hexane) gave the final product **6o** (238 mg, 73%) as an orange oil; $R_f$ (20% $Et_2O$/hexane)=0.50; IR (KBr) $\nu_{max}$ 2929, 1620, 1519, 1462, 1380, 1226, 1189, 1130, 743 $cm^{-1}$; $^1H$ NMR (500.1 MHz, $CDCl_3$) $\delta$ 8.42–8.43 (m, 1H, =CH), 7.80 (m, 1H, =CH), 7.70 (d, $J$=7.6 Hz, 1H, =CH), 7.56 (s, 1H, =C*H*N), 7.52–7.54 (m, 1H, =CH), 7.41–7.45 (m, 2H, =CH), 7.34–7.38 (m, 2H, =CH), 4.17 (t, $J$=7.2 Hz, 2H, NC$H_2$), 1.89 (quintet, $J$=7.3 Hz, 2H, NCH$_2$C$H_2$), 1.32–1.39 (m, 4H, C$H_2$C$H_2$Me), 0.91 (t, $J$=7.1 Hz, 3H, CH$_2$*Me*) ppm; $^{13}C$ NMR (125.7 MHz, $CDCl_3$) $\delta$ 189.0, 142.5, 136.9, 136.8, 134.3, 130.9, 129.6, 128.7, 127.2, 126.7, 123.7, 122.8, 122.7, 115.1, 109.9, 47.2, 29.5, 28.9, 22.2, 13.9 ppm; MS (EI, 70 eV): $m/z$ (%)=327 [$(M+2)^+$,47], 325 ($M^+$, 89), 310 (6), 284 (18), 268 (56), 254 (9), 214 (100), 200 (9), 186 (16), 149 (35), 139 (39), 130 (25), 111 (25), 57 (15), 43 (27); Anal. Calcd for $C_{20}H_{20}ClNO$: C, 73.72; H, 6.19; N, 4.30; Found: C, 73.75; H, 6.18; N, 4.28.

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## Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.11.051.

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