



Synthesis of 3-substituted 3*H*-indol-3-ols by the reaction of 2-isocyanophenyl ketones with Grignard reagents

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ABSTRACT

A facile method for the synthesis of 3-substituted 3*H*-indol-3-ols has been developed. Thus, 2-isocyanophenyl ketones are allowed to react with various Grignard reagents to give the corresponding desired indolol derivatives in generally fair to good yields. The formation of 3-aryl-2,3-dimethylindolin-3-ols by the reaction of 2-isocyanobenzophenones with 2 M amounts of methylmagnesium bromide is also reported.

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1. Introduction

In the course of our studies on utilizations of 2-isocyanophenyl ketones for the synthesis of benzene-fused heterocycles,¹ we previously reported syntheses of 2,4-disubstituted quinolines,^{1a} 2-functionalized 4-alkylidene-4*H*-1,3-benzoxazines,^{1b,d} and 4-substituted quinoline-2(1*H*)-thiones.^{1c} In this paper, we wish to report that the reaction of 2-isocyanophenyl ketones with Grignard reagents provides an efficient route to 3-substituted 3*H*-indol-3-ols. 1*H*-Indoles are undoubtedly very important heterocycles in organic synthesis. 3*H*-Indoles are also an important class of heterocycles, because a number of molecules having this skeleton have been found in nature² and some 3*H*-indole derivatives have been utilized for the construction of indoline alkaloids.^{2a} Although a large number of methods to prepare 1*H*-indoles have been reported, the methodologies for the synthesis of 3*H*-indole are very limited.³ Therefore, development of new and convenient method for the synthesis of 3*H*-indoles is of considerable merit. 3*H*-Indol-3-ols are also of potential importance in organic synthesis. Liu and McWhorter, have reported a synthesis of 3-substituted 2-aryl-3*H*-indol-3-ols by the reaction of 2-aryl-3*H*-indol-3-ones with Grignard reagents.^{3a} They have also reported an elaboration of the 3*H*-indol-3-ol derivatives to more complex and important molecules.⁴ However, to the best of our

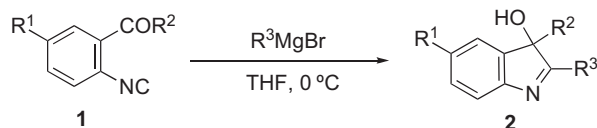
knowledge, few other reports on the methods for the general preparation of 3*H*-indol-3-ol derivatives have appeared so far.⁵

2. Results and discussion

The reactions for preparing 3-substituted 3*H*-indol-3-ols **2** from 2-isocyanophenyl ketones **1**, which can be easily prepared from the respective 2-aminophenyl ketones in two steps, were carried out as shown in Scheme 1. Thus, isocyano ketones **1** were allowed to react with an equimolar amount of Grignard reagents in THF at 0 °C. The reactions proceeded relative cleanly and completed within 10 min to give 3*H*-indol-3-ols **2** after usual aqueous workup followed by purification using column chromatography on silica gel using Et₂O–C₆H₆ (1:2, v/v) as an eluent.⁶ The results obtained from the reactions of various isocyano ketones **1** with aliphatic and aromatic Grignard reagents are summarized in Table 1, which indicates that yields of the desired products **2** were generally good to excellent. While the use of aryl Grignard reagents gave generally excellent yields of the desired products (entries 2–7 and 11), alkyl Grignard reagents, such as methyl- or ethyl-magnesium bromide, gave the corresponding desired products in rather diminished yields compared to those using aryl Grignard reagents (entries 1, 8–10, and 12). This is probably due to the formation of products arising from the initial addition of Grignard reagents to the carbonyl moiety. The reaction of **1a** with methylmagnesium bromide was attempted in a less polar solvent, such as toluene, resulted in the formation of a rather complex mixture of products containing the starting **1a**, and a considerable decrease in the yield of the desired product **2a**

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(29%) was observed. It should be noted that the use of organolithiums in place of Grignard reagents resulted in the formation of complex mixtures of products.



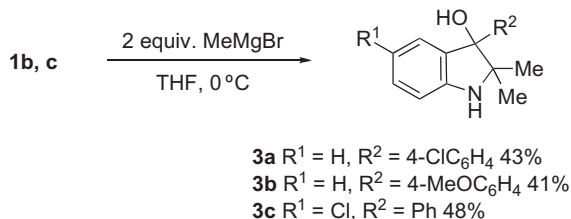
Scheme 1.

Table 1
Preparation of 3-substituted 3H-indol-3-ols **2**

Entry	1	R ³ in R ³ MgBr	2 (Yield/%) ^a
1	1a (R ¹ =H, R ² =Ph)	Me	2a (59)
2	1a	Ph	2b (88)
3	1a	4-MeC ₆ H ₄	2c (93)
4	1a	3-ClC ₆ H ₄	2d (96)
5	1a	4-ClC ₆ H ₄	2e (98)
6	1a	3-MeOC ₆ H ₄	2f (98)
7	1a	3,4-(MeO) ₂ C ₆ H ₃	2g (82)
8	1b (R ¹ =H, R ² =4-ClC ₆ H ₄)	Me	2h (57)
9	1c (R ¹ =H, R ² =4-MeOC ₆ H ₄)	Me	2i (58)
10	1d (R ¹ =Cl, R ² =Ph)	Me	2j (60)
11	1d	Ph	2k (68)
12	1e (R ¹ =Cl, R ² =Et)	Et	2l (50)

^a Isolated yields.

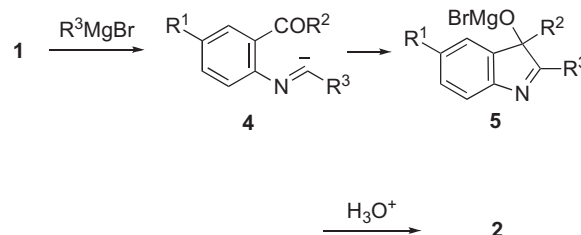
When 2 M amounts of methylmagnesium bromide were used, 3-substituted 2,2-dimethylindolin-3-ols **3** were obtained, as shown in Scheme 2. Yields of the products are moderate as indicated in Scheme 2 as well. 2-Ethyl- and 2-aryl-3H-indol-3-oxides intermediates (**5**; R³=Et and Ar, respectively) were found to be extremely stable toward excess ethyl- or aryl-magnesium bromide, and no formation of the corresponding 2,2-diethyl- or 2,2-diarylindolin-3-ols was observed even at elevating reaction temperatures. Addition of methylmagnesium bromide to the solution from the reaction of **1a** with phenylmagnesium bromide did not allow us to introduce a methyl group.



Scheme 2.

The pathway leading to 3-substituted 3H-indol-3-ols **2** from 2-isocyanophenyl ketones **1** and Grignard reagents is illustrated in Scheme 3. The first step of the present transformation is the addition of a Grignard reagent to the isocyano carbon of **1**, generating an imidoyl anion intermediate **4**. This intermediate cyclizes rapidly by the intramolecular attack of the imidoyl anion on the carbonyl carbon to give the 3H-indol-3-oxide intermediate **5**, which is protonated by aqueous workup to provide **2**.

As mentioned above, the reaction of 2-isocyanophenyl ketones with Grignard reagents under milder conditions has allowed preparing a range of 3-substituted 3H-indol-3-ols. The use of an excess amount of methylmagnesium bromide has also allowed preparing 3-substituted 2,2-dimethylindolin-3-ols. The present synthetic method may be of value in organic synthesis because it has advantages over the previous method;^{3a} the readily availability of the starting materials and the simplicity of the operations.



Scheme 3.

3. Experimental

3.1. General

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were determined with a Shimadzu FTIR-8300 spectrophotometer. The ¹H NMR spectra were determined in CDCl₃ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz. The ¹³C NMR spectra were determined using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. Low-resolution MS spectra (EI, 70 eV) were measured by a JEOL JMS AX505 HA spectrometer. TLC was carried out on a Merck Kieselgel 60 PF₂₅₄. Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

3.2. Starting materials

2-Isocyanophenyl ketones **1a**, **1c**, **1d**, and **1e** were prepared by the previously reported our method.^{1a,b} All other chemicals used in this study were commercially available.

3.2.1. N-[2-(4-Chlorobenzoyl)phenyl]formamide. This compound was prepared by treating 2-aminophenyl(4-chlorophenyl)methanone with excess HCO₂H in refluxing toluene under azeotropic conditions^{1a} in 93% yield; a yellow viscous oil; R_f 0.25 (1:2 AcOEt–hexane); IR (neat) 3312, 1697, 1643, 1603 cm⁻¹; ¹H NMR δ 7.15 (dd, J=7.8, 7.3 Hz, 1H), 7.48 (d, J=8.2 Hz, 2H), 7.54 (d, J=8.2 Hz, 1H), 7.60 (dd, J=8.2, 7.3 Hz, 1H), 7.67 (d, J=8.2 Hz, 2H), 8.49 (s, 1H), 8.67 (d, J=7.8 Hz, 1H), 10.61 (s, 1H); ¹³C NMR δ 122.33, 122.83, 123.22, 128.73, 131.31, 133.19, 134.49, 136.67, 139.17, 139.25, 159.56, 198.06. Anal. Calcd C₁₄H₁₀ClNO₂: C, 64.75; H, 3.88; N, 5.39. Found: C, 64.63; H, 4.00; N, 5.32.

3.2.2. 4-Chlorophenyl(2-isocyanophenyl)methanone (1b). This compound was prepared by dehydration of the above formamide with POCl₃–Et₃N in THF at 0 °C⁷ in 77% yield; yellow crystals; mp 85–88 °C (hexane–Et₂O); IR (KBr) 2130, 1661 cm⁻¹; ¹H NMR δ 7.48 (d, J=8.7 Hz, 2H), 7.51–7.55 (m, 3H), 7.59 (ddd, J=7.8, 7.3, 1.8 Hz, 1H), 7.76 (d, J=8.7 Hz, 2H); ¹³C NMR δ 127.93, 129.17 (two overlapped C's), 129.29, 129.35, 131.37, 131.67, 134.50, 135.73, 140.67, 169.34, 192.44. Anal. Calcd C₁₄H₈ClNO: C, 69.58; H, 3.34; N, 5.80. Found: C, 69.42; H, 3.32; N, 5.50.

3.3. General procedure for the reaction of 2-isocyanophenyl ketones **1** with Grignard reagents

To a stirred solution of one of 2-isocyanophenyl ketones (2.0 mmol) in THF (5 mL) at 0 °C was added one of Grignard reagents (Et₂O solution, 1.0 mmol for the preparation of **2** or 2.0 mmol for **3**) dropwise; the mixture was stirred for 10 min at the same temperature. Saturated aqueous NH₄Cl (10 mL) was added

and organic materials were extracted with Et₂O three times (10 mL each). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated by evaporation of the solvent. The residue was subjected to column chromatography on silica gel (1:2 Et₂O–C₆H₆) to give the desired products.

3.3.1. 2-Methyl-3-phenyl-3H-indol-3-ol (2a). Colorless needles; mp 179–184 °C (C₆H₆–THF); IR (KBr) 3208 cm^{−1}; ¹H NMR δ 1.93 (s, 3H), 4.25 (br s, 1H), 7.14 (t, *J*=7.3 Hz, 1H), 7.21 (d, *J*=7.3 Hz, 1H), 7.24–7.32 (m, 7H); ¹³C NMR δ 14.09, 87.09, 119.73, 123.68, 124.84, 126.44, 127.75, 128.55, 129.46, 138.60, 143.43, 153.07, 187.06; MS *m/z* 223 (M⁺, 100). Anal. Calcd C₁₅H₁₃NO: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.54; H, 5.94; N, 6.24.

3.3.2. 2,3-Diphenyl-3H-indol-3-ol (2b).⁸ A white solid; mp 195–197 °C (hexane–Et₂O) (lit.,⁸ mp 197–199 °C). The spectral (IR and ¹H NMR) data for this product were identical to those reported previously.⁹ ¹³C NMR δ 87.32, 121.12, 122.82, 124.17, 126.79, 127.58, 128.32, 128.76, 129.23, 129.72, 130.89, 131.16, 139.65, 143.87, 152.51, 180.27.

3.3.3. 2-(4-Methylphenyl)-3-phenyl-3H-indol-3-ol (2c). A white solid; mp 170–174 °C (hexane–Et₂O); IR (KBr) 3152, 1614 cm^{−1}; ¹H NMR δ 2.33 (s, 3H), 2.87 (s, 1H), 7.10–7.13 (m, 3H), 7.16 (dd, *J*=7.3, 0.9 Hz, 1H), 7.21 (tt, *J*=7.3, 1.4 Hz, 1H), 7.27 (dd, *J*=7.8, 7.3 Hz, 2H), 7.32 (td, *J*=7.3, 1.4 Hz, 1H), 7.38 (dd, *J*=7.8, 1.4 Hz, 2H), 7.56 (d, *J*=7.8 Hz, 1H), 7.92 (d, *J*=8.2 Hz, 2H); ¹³C NMR δ 21.58, 87.28, 120.95, 122.77, 124.17, 126.53, 127.52, 128.21, 128.72, 129.09, 129.25, 129.73, 139.85, 141.69, 143.78, 152.73, 180.21; MS *m/z* 299 (M⁺, 100). Anal. Calcd C₂₁H₁₇NO: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.10; H, 5.74; N, 4.69.

3.3.4. 2-(3-Chlorophenyl)-3-phenyl-3H-indol-3-ol (2d). A pale-yellow solid; mp 200–203 °C (hexane–Et₂O); IR (KBr) 3169 cm^{−1}; ¹H NMR δ 3.06 (s, 1H), 7.14 (td, *J*=7.3, 0.9 Hz, 1H), 7.17 (dd, *J*=7.3, 1.4 Hz, 1H), 7.21 (t, *J*=7.8 Hz, 1H), 7.24 (tt, *J*=7.3, 1.4 Hz, 1H), 7.28 (dd, *J*=7.3, 1.4 Hz, 2H), 7.31–7.36 (m, 4H), 7.54 (d, *J*=7.8 Hz, 1H), 7.83 (dd, *J*=7.8, 1.4 Hz, 1H), 8.09 (t, *J*=1.8 Hz, 1H); ¹³C NMR δ 87.29, 121.36, 122.85, 124.15, 127.24, 127.37, 127.77, 128.80, 128.85, 129.49, 129.89, 131.11, 132.63, 134.40, 139.01, 143.81, 152.22, 179.04; MS *m/z* 319 (M⁺, 100). Anal. Calcd C₂₀H₁₄ClNO: C, 75.12; H, 4.41; N, 4.38. Found: C, 74.96; H, 4.53; N, 4.41.

3.3.5. 2-(4-Chlorophenyl)-3-phenyl-3H-indol-3-ol (2e). A pale-yellow solid; mp 174–177 °C (hexane–Et₂O); IR (KBr) 3200 cm^{−1}; ¹H NMR δ 3.84 (s, 1H), 7.09 (t, *J*=7.3 Hz, 1H), 7.14 (d, *J*=7.3 Hz, 1H), 7.19–7.27 (m, 6H), 7.32 (dd, *J*=7.8, 1.4 Hz, 2H), 7.42 (d, *J*=7.8 Hz, 1H), 7.91 (d, *J*=8.7 Hz, 2H); ¹³C NMR δ 87.18, 121.12, 122.89, 124.15, 126.95, 127.68, 128.59, 128.80, 129.37, 129.82, 130.44, 137.36, 139.33, 143.87, 152.37, 179.38; MS *m/z* 319 (M⁺, 100). Anal. Calcd C₂₀H₁₄ClNO: C, 75.12; H, 4.41; N, 4.38. Found: C, 74.90; H, 4.59; N, 4.40.

3.3.6. 2-(3-Methoxyphenyl)-3-phenyl-3H-indol-3-ol (2f). A pale-yellow solid; mp 212–215 °C (hexane–THF); IR (KBr) 3169 cm^{−1}; ¹H NMR δ 3.18 (s, 1H), 3.74 (s, 3H), 6.90 (dd, *J*=8.2, 2.3 Hz, 1H), 7.11 (dd, *J*=7.8, 7.3 Hz, 1H), 7.15 (d, *J*=7.3 Hz, 1H), 7.18 (t, *J*=8.2 Hz, 1H), 7.21 (t, *J*=7.3 Hz, 1H), 7.25–7.30 (m, 3H), 7.36 (dd, *J*=7.3, 1.4 Hz, 2H), 7.52 (d, *J*=7.8 Hz, 1H), 7.55 (d, *J*=8.2 Hz, 1H), 7.58 (s, 1H); ¹³C NMR δ 55.22, 87.38, 113.14, 118.18, 121.25, 122.03, 122.81, 124.16, 126.91, 127.62, 128.78, 129.29, 129.84, 132.23, 139.65, 143.94, 152.68, 159.35, 180.09; MS *m/z* 315 (M⁺, 100). Anal. Calcd C₂₁H₁₇NO₂: C, 79.98; H, 5.43; N, 4.44. Found: C, 79.73; H, 5.52; N, 4.44.

3.3.7. 2-(3,4-Dimethoxyphenyl)-3-phenyl-3H-indol-3-ol (2g). A pale-yellow solid; mp 214–216 °C (hexane–THF); IR (KBr) 3140,

1603 cm^{−1}; ¹H NMR δ 3.56 (s, 1H), 3.83 (s, 3H), 3.84 (s, 3H), 6.66 (d, *J*=8.2 Hz, 1H), 7.05 (dd, *J*=7.8, 7.3 Hz, 1H), 7.11 (d, *J*=7.8 Hz, 1H), 7.19–7.22 (m, 2H), 7.26 (dd, *J*=7.8, 7.3 Hz, 2H), 7.34–7.37 (m, 3H), 7.45 (dd, *J*=8.2, 1.4 Hz, 1H), 7.59 (d, *J*=1.4 Hz, 1H); ¹³C NMR δ 55.73, 55.76, 87.09, 110.21, 111.20, 121.61, 122.76, 123.73, 123.84, 124.15, 126.24, 127.48, 128.68, 129.74, 140.27, 143.75, 148.52, 151.69, 152.72, 179.93; MS *m/z* 345 (M⁺, 100). Anal. Calcd C₂₂H₁₉NO₃: C, 76.50; H, 5.54; N, 4.06. Found: C, 76.13; H, 5.54; N, 4.10.

3.3.8. 3-(4-Chlorophenyl)-2-methyl-3H-indol-3-ol (2h). A yellow solid; mp 189–191 °C (hexane–Et₂O); IR (KBr) 3130 cm^{−1}; ¹H NMR δ 1.97 (s, 3H), 3.70 (br s, 1H), 7.14–7.19 (m, 3H), 7.27 (d, *J*=8.7 Hz, 2H), 7.31–7.34 (m, 3H); ¹³C NMR δ 14.12, 86.78, 119.94, 123.60, 126.39, 126.65, 128.79, 129.84, 133.74, 137.09, 142.80, 153.14, 186.42; MS *m/z* 257 (M⁺, 100). Anal. Calcd C₁₅H₁₂ClNO: C, 69.91; H, 4.69; N, 5.43. Found: C, 69.89; H, 4.71; N, 5.47.

3.3.9. 3-(4-Methoxyphenyl)-2-methyl-3H-indol-3-ol (2i). An orange solid; mp 176–179 °C (hexane–THF); IR (KBr) 3131, 1609 cm^{−1}; ¹H NMR δ 2.06 (s, 3H), 3.00 (s, 1H), 3.79 (s, 3H), 6.84 (d, *J*=8.7 Hz, 2H), 7.14–7.21 (m, 4H), 7.34 (ddd, *J*=7.8, 7.3, 1.4 Hz, 1H), 7.41 (d, *J*=7.8 Hz, 1H); ¹³C NMR δ 14.37, 55.23, 86.98, 114.00, 119.96, 123.50, 126.20, 126.38, 129.62, 130.42, 143.01, 153.45, 159.30, 186.60; MS *m/z* 253 (M⁺, 100). Anal. Calcd C₁₆H₁₅NO₂: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.71; H, 6.09; N, 5.31.

3.3.10. 5-Chloro-2-methyl-3-phenyl-3H-indol-3-ol (2j). A yellow solid; mp 131–134 °C (hexane–Et₂O); IR (KBr) 3128 cm^{−1}; ¹H NMR (500 MHz, CDCl₃) δ 2.08 (s, 3H), 2.91 (s, 1H), 7.17 (d, *J*=1.8 Hz, 1H), 7.24 (dd, *J*=7.8, 1.8 Hz, 1H), 7.30–7.36 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 14.45, 87.28, 120.64, 124.29, 124.70, 128.17, 128.79, 129.60, 132.36, 137.56, 144.92, 151.55, 187.35; MS *m/z* 257 (M⁺, 100). Anal. Calcd C₁₅H₁₂ClNO: C, 69.91; H, 4.69; N, 5.43. Found: C, 69.74; H, 4.94; N, 5.20.

3.3.11. 5-Chloro-2,3-diphenyl-3H-indol-3-ol (2k).⁶ A white solid; mp 224–227 °C (hexane–Et₂O) (lit.,⁶ mp 223–223.5 °C); IR (KBr) 3117 cm^{−1}; ¹H NMR δ 3.12 (s, 1H), 7.13 (d, *J*=2.3 Hz, 1H), 7.23–7.26 (m, 2H), 7.28–7.32 (m, 4H), 7.36 (d, *J*=7.3 Hz, 2H), 7.39 (tt, *J*=7.3, 1.4 Hz, 1H), 7.46 (d, *J*=7.8 Hz, 1H), 7.99 (dd, *J*=7.8, 1.4 Hz, 2H); ¹³C NMR δ 87.35, 121.99, 123.49, 124.09, 127.92, 128.39, 128.93, 129.26, 129.74, 130.41, 131.46, 132.52, 138.93, 145.37, 150.83, 180.61.

3.3.12. 5-Chloro-2,3-diethyl-3H-indol-3-ol (2l). A pale-yellow oil; *R*_f 0.28 (1:2 Et₂O–C₆H₆); IR (neat) 3219 cm^{−1}; ¹H NMR δ 0.57 (t, *J*=7.3 Hz, 3H), 1.34 (t, *J*=7.3 Hz, 3H), 1.82–1.89 (m, 1H), 2.02–2.09 (m, 1H), 2.12 (s, 1H), 2.42–2.50 (m, 1H), 2.65–2.73 (m, 1H), 7.30 (d, *J*=2.3 Hz, 1H), 7.34 (d, *J*=8.2 Hz, 1H), 7.38 (dd, *J*=8.2, 2.3 Hz, 1H); ¹³C NMR δ 7.18, 9.81, 21.63, 29.29, 87.18, 120.90, 123.09, 129.52, 131.59, 141.42, 151.83, 189.94; MS *m/z* 223 (M⁺, 100). Anal. Calcd C₁₂H₁₄ClNO: C, 64.43; H, 6.31; N, 6.26. Found: C, 64.36; H, 6.48; N, 6.48.

3.3.13. 3-(4-Chlorophenyl)-2,2-dimethylindolin-3-ol (3a). A yellow oil; *R*_f 0.29 (1:5 THF–hexane); IR (neat) cm^{−1}; ¹H NMR δ 0.72 (s, 3H), 1.32 (s, 3H), 2.14 (br s, 1H), 3.61 (br s, 1H), 6.66 (d, *J*=7.8 Hz, 1H), 6.74 (dd, *J*=7.8, 7.3 Hz, 1H), 7.04 (d, *J*=7.8 Hz, 1H), 7.12 (dd, *J*=7.8, 7.3 Hz, 1H), 7.25 (d, *J*=8.7 Hz, 2H), 7.37 (d, *J*=8.7 Hz, 2H); ¹³C NMR δ 21.29, 27.16, 68.27, 85.13, 110.93, 119.31, 125.39, 127.86, 128.98, 129.91, 132.47, 133.30, 138.93, 149.80; MS *m/z* 273 (M⁺, 7.3), 255 (100). Anal. Calcd C₁₆H₁₆ClNO: C, 70.20; H, 5.89; N, 5.12. Found: C, 70.28; H, 6.08; N, 5.06.

3.3.14. 3-(4-Methoxyphenyl)-2,2-dimethylindolin-3-ol (3b). A yellow oil; *R*_f 0.42 (1:8 AcOEt–C₆H₆); IR (neat) 3343, 1609 cm^{−1}; ¹H NMR δ 0.79 (s, 3H), 1.41 (s, 3H), 2.11 (s, 1H), 3.71 (br s, 1H), 3.83 (s, 3H), 6.75 (d, *J*=7.8 Hz, 1H), 6.81 (dd, *J*=7.8, 7.3 Hz, 1H), 6.89 (d,

$J=8.7$ Hz, 2H), 7.17 (d, $J=7.8$ Hz, 1H), 7.19 (dd, $J=7.8, 7.3$ Hz, 1H), 7.43 (d, $J=8.7$ Hz, 2H); ^{13}C NMR δ 21.13, 27.33, 55.19, 68.27, 85.15, 110.85, 113.04, 119.10, 125.56, 128.70, 129.60, 132.44, 133.07, 149.88, 158.85; MS m/z (%) 269 (M^+ , 7.3), 251 (100). Anal. Calcd $\text{C}_{17}\text{H}_{19}\text{NO}_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.78; H, 7.05; N, 5.44.

3.3.15. *5-Chloro-2,2-dimethyl-3-phenylindolin-3-ol (3c)*. Yellow crystals; mp 134–137 °C (hexane–AcOEt); IR (KBr) 3268, 1605 cm^{-1} ; ^1H NMR δ 0.79 (s, 3H), 1.41 (s, 3H), 2.13 (br s, 1H), 3.69 (br s, 1H), 6.67 (d, $J=8.2$ Hz, 1H), 7.12 (d, $J=1.8$ Hz, 1H), 7.15 (dd, $J=8.2, 1.8$ Hz, 1H), 7.33 (t, $J=7.3$ Hz, 1H), 7.38 (dd, $J=7.8, 7.3$ Hz, 2H), 7.49 (d, $J=7.8$ Hz, 2H); ^{13}C NMR δ 21.12, 27.18, 68.94, 85.42, 111.78, 123.59, 125.69, 127.38, 127.66, 127.89, 129.59, 134.72, 139.56, 148.38; MS m/z 273 (M^+ , 7.6), 255 (100). Anal. Calcd $\text{C}_{16}\text{H}_{16}\text{ClNO}$: C, 70.20; H, 5.89; N, 5.12. Found: C, 70.16; H, 5.84; N, 4.91.

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