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Synthesis of 1,2-Diaryl-1*H*-indol-4-ols and 1,2-Diaryl-7-ethoxy-1,5,6,7-tetrahydroindol-4-ones from Arylglyoxals and Enamines through Domino Reactions

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A series of 1,2-diaryl- and 1-alkyl-2-aryl-1*H*-indol-4-ols and 1,2-diaryl-7-ethoxy-1,5,6,7-tetrahydroindol-4-ones have been prepared by the domino reactions of arylglyoxals and enamines at reflux in non-nucleophilic and nucleophilic solvents such as acetonitrile and ethanol, respectively. The transformation occurs by annulation followed by aromatization without the use of any metal or catalyst.

Introduction

Indole heterocycles are present in many biologically active natural products as the core moiety.[1a] Indoles are also important molecules in drug discovery due to their ability to bind many receptors with high affinity.[1b] As a consequence, several methodologies have been developed to synthesize these heterocycles,[2] such as Fischer-type indole syntheses,[3] heteroannulations and the cyclization of 2-alkynylanilines,[4] reductive cyclization,[5] and metal-catalysed coupling/condensation cascades.[6] More precisely, indoles with oxygen-bearing substituents on the benzo moiety are known to be synthetic medicines and physiologically active substances, for example, serotonin, melatonin and psilocin.[7] In this series, serotonin is a key neurotransmitter in the central nervous system that regulates smooth muscle function in the cardiovascular and gastrointestinal systems and also controls platelet function.[7] This class of indole moiety have been synthesized by different approaches.[8]

Among the various known synthetic methodologies, the direct formation of C–X (X = heteroatom) bonds from allylic C–H bonds has attracted great attention in the field of organic chemistry.[9] These methodologies have a number of intrinsic advantages, such as higher atom economy, shorter synthetic routes and less energy and manpower usage, which leads to "benign by design".[10] Therefore the design of efficient allylic functionalization without the use of metal catalysts is a continuing challenge at the forefront of organic chemistry. In this context, the domino reaction is a powerful tool for the synthesis of multifunctionalized heterocycles.[10] Li and co-workers have recently reported a domino approach to the synthesis of dimeric 4-hydroxyindole derivatives by a microwave-assisted reaction in an acetic acid medium.[8c] Under the reported reaction conditions, two molecules of arylglyoxal monohydrates and two molecules of *N*-substituted 3-aminocyclohex-2-enones lead to the final polysubstituted bis-indoles. It was not possible to isolate the monomeric 4-hydroxyindole derivatives under the acidic reaction conditions. We report herein a two-component domino reaction for the synthesis of 1,2-diaryl-1*H*-indol-4-ols and 1-alkyl-2-aryl-1*H*-indol-4-ols from arylglyoxal monohydrates and *N*-substituted 3-aminocyclohex-2-enones under neutral conditions and in non-nucleophilic solvent without the use of any catalyst.

Results and Discussion

During our preliminary investigation, we observed that heating a mixture of 3-arylaminocyclohex-2-enones **1** and arylglyoxal monohydrates **2** at reflux in a non-nucleophilic solvent such as acetonitrile produced 1,2-diaryl-1*H*-indol-4-ol derivatives **3** within 6–8 h in moderate-to-good yields (Scheme 1). We subsequently investigated the scope of the reaction. Various 1,2-diaryl-1*H*-indol-4-ols **3a**–**s** were synthesized by this method by varying the enamine as well as arylglyoxal monohydrate (Table 1). 1-Alkyl-2-aryl-1*H*-indol-4-ols **4a**–**g** were also synthesized by a similar methodology by heating at reflux a mixture of 3-(alkylamino)cyclohex-2-enones **1** and arylglyoxal monohydrates **2** in acetonitrile (Table 2). The results showed that the reaction can tolerate various electron-donating and -withdrawing arylglyoxals and diverse amino-substituted enamines.

Subsequently we focused our attention on optimizing the reaction conditions in different non-nucleophilic as well as nucleophilic solvents. The reaction also proceeded well in non-nucleophilic dioxane and DMF, but the yields were very poor in THF and DCM (Table 3). The low boiling

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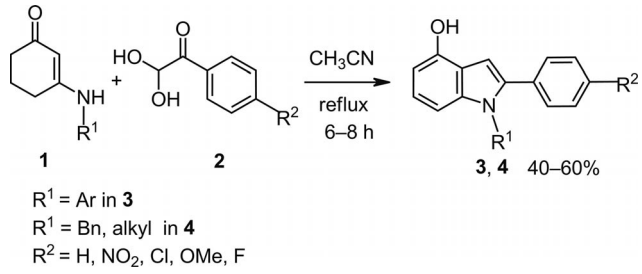


Scheme 1. Synthesis of 1,2-diaryl-1*H*-indol-4-ols **3** and 1-alkyl-2-aryl-1*H*-indol-4-ols **4**.

Table 1. Synthesis of 1,2-diaryl-1*H*-indol-4-ols **3a**–**s** in acetonitrile.

Entry	R^1	R^2	Product	Yield [%][a]
1	phenyl	H	**3a**	60
2	*p*-tolyl	H	**3b**	55
3	4-bromophenyl	H	**3c**	58
4	3-chlorophenyl	H	**3d**	54
5	3-methoxyphenyl	H	**3e**	44
6	phenyl	NO_2	**3f**	58
7	*p*-tolyl	NO_2	**3g**	60
8	4-bromophenyl	NO_2	**3h**	52
9	3-chlorophenyl	NO_2	**3i**	40
10	3-methoxyphenyl	NO_2	**3j**	50
11	phenyl	Cl	**3k**	55
12	3-chlorophenyl	Cl	**3l**	51
13	3-methoxyphenyl	Cl	**3m**	53
14	phenyl	OMe	**3n**	45
15	3-chlorophenyl	OMe	**3o**	42
16	3-methoxyphenyl	OMe	**3p**	41
17	phenyl	F	**3q**	50
18	3-chlorophenyl	F	**3r**	45
19	3-methoxyphenyl	F	**3s**	45

[a] Isolated yield.

Table 2. Synthesis of 1-alkyl-2-aryl-1*H*-indol-4-ols **4a**–**g** in acetonitrile.

Entry	R^1	R^2	Product	Yield [%][a]
1	benzyl	H	**4a**	41
2	benzyl	NO_2	**4b**	45
3	benzyl	Cl	**4c**	41
4	benzyl	OMe	**4d**	42
5	benzyl	F	**4e**	40
6	methyl	H	**4f**	43
7	cyclopropyl	H	**4g**	40

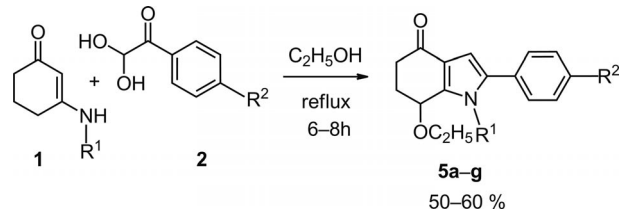
[a] Isolated yield.

Table 3. Synthesis of 1,2-diphenyl-1*H*-indol-4-ol (**3a**) in different solvents.[a]

Entry	Solvent	Reaction time [h]	Yield [%][b]
1	dichloromethane (DCM)	5	trace
2	THF	5	15
3	acetonitrile	5	60
4	dioxane	5	53
5	DMF	5	50

[a] Optimization of the reaction of 3-(phenylamino)cyclohex-2-enone (**1a**) with phenylglyoxal monohydrate (**2a**) in different solvents under heating at reflux for the indicated times. [b] Isolated yield.

points of THF and DCM are probably responsible for the poor yields. Surprisingly, completely different products were formed in a nucleophilic solvent such as ethanol, namely 7-ethoxy-1,2-diaryl-1,5,6,7-tetrahydroindol-4-ones **5** (Scheme 2, Table 4). The heating of arylglyoxal and enamine in ethanol at reflux produced 7-ethoxy-1,2-diaryl-1,5,6,7-tetrahydroindol-4-ones **5a**–**g** within 6–8 h in good

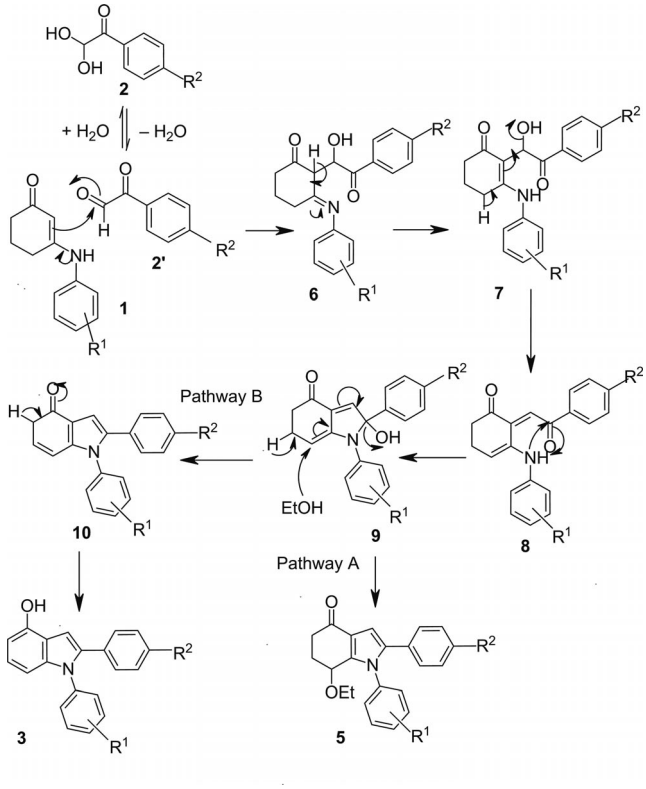


Scheme 2. Synthesis of 1,2-diaryl-7-ethoxy-1,5,6,7-tetrahydroindol-4-ones **5a**–**g**.

Table 4. Synthesis of 1,2-diaryl-7-ethoxy-1,5,6,7-tetrahydroindol-4-ones **5** in ethanol.

Entry	R^1	R^2	Product	Yield [%][a]
1	phenyl	H	**5a**	55
2	*p*-tolyl	H	**5b**	60
3	4-bromophenyl	H	**5c**	60
4	4-chlorophenyl	H	**5d**	50
5	3-methoxyphenyl	H	**5e**	60
6	benzyl	H	**5f**	50
7	3-methoxyphenyl	NO_2	**5g**	60

[a] Isolated yield.



Scheme 3. Plausible mechanism for the formation of indole derivatives **3**–**5**.

yields. In this case, the solvent molecule itself is incorporated into the product molecules.

The proposed reaction mechanism is depicted in Scheme 3. The initial nucleophilic attack of enamines **1** on the arylglyoxal (**2′**) affords intermediate **6**, which subsequently tautomerizes to form the hydroxy-enamine intermediate **7**. Allylic deprotonation of intermediate **7** leads to intermediate enamino-ketone **8**. Subsequently, intermediate **8** undergoes intramolecular cyclization to form intermediate **9**. In the presence of ethanol the intermediate **9** undergoes nucleophilic attack to produce compounds **5** (Scheme 3, Pathway A). In a non-nucleophilic solvent such as acetonitrile, the intermediate **8** undergoes 1,6-elimination of water to form intermediate **10**, which finally tautomerizes to produce aromatized compounds **3** and **4** (Scheme 3, Pathway B). All the compounds were fully characterized by ^{1}H and ^{13}C NMR and other analyses. X-ray crystal analysis of 2-(4-nitrophenyl)-1-phenyl-1*H*-indol-4-ol (**3f**) and 7-ethoxy-2-phenyl-1-(*p*-tolyl)-1,5,6,7-tetrahydroindol-4-one (**5b**) confirmed the structural assignments (Figure 1 and Figure 2).[11]

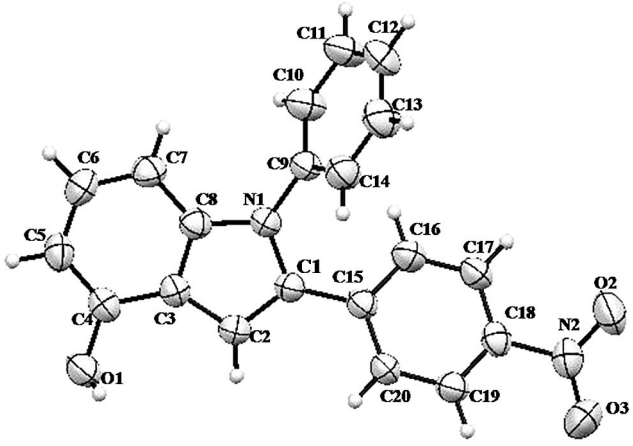


Figure 1. ORTEP diagram of the X-ray crystal structure of compound **3f** with the atomic numbering scheme. Thermal ellipsoids are shown at the 50% probability.

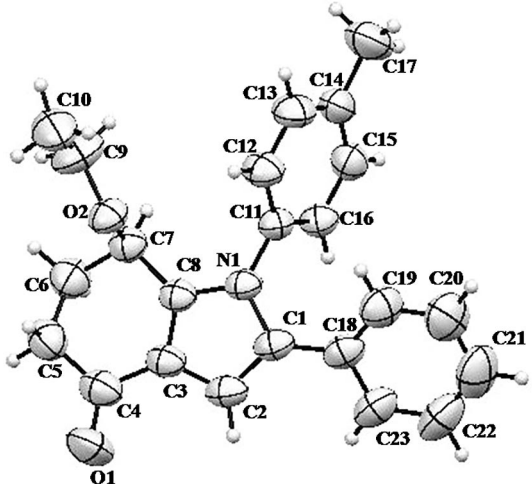


Figure 2. ORTEP diagram of the X-ray crystal structure of compound **5b** with the atomic numbering scheme. Thermal ellipsoids are shown at the 50% probability.

Conclusions

We have developed a convenient methodology for the synthesis of a diverse range of 1,2-diaryl-1*H*-indol-4-ols, 1-alkyl-2-aryl-1*H*-indol-4-ols and 1,2-diaryl-7-ethoxy-1,5,6,7-tetrahydroindol-4-ones from enamines and arylglyoxals without the use of any metals or expensive reagents. Non-nucleophilic and nucleophilic solvents such as acetonitrile and ethanol, respectively, play a key role in the formation of different indole derivatives. During the course of the reaction, the intermediate derived from the [3 + 2] heterocyclization of enamines and arylglyoxals undergoes different reactions depending upon the nature of the solvent leading to the products 1,2-diaryl-1*H*-indol-4-ols, 1-alkyl-2-aryl-1*H*-indol-4-ols and 1,2-diaryl-7-ethoxy-1,5,6,7-tetrahydroindol-4-ones.

Experimental Section

General: Enamines **1** and arylglyoxals **2** were prepared according to reported procedures.[8c] The solvents were purchased from commercial suppliers and used after distillation. Melting points were determined in open capillary tubes and are uncorrected. IR spectra were recorded with a Perkin-Elmer 782 spectrophotometer. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded with a Bruker 300 MHz instrument in $CDCl_3$ and [D_6]DMSO. Elemental analyses (C, H and N) were performed by using a Perkin-Elmer 240C elemental analyzer. The X-ray diffraction data for crystallized compounds were collected with Mo-K_α radiation at 296 K by using a Bruker APEX-II CCD system. The crystals were positioned at 50 mm from the CCD. Frames were measured with a counting time of 5 s. Data analyses were carried out with the Bruker APEX2 and Bruker SAINT programs. The structures were solved by using direct methods with the SHELXS97 program (G. M. Sheldrick, 2008).

General Procedure for the Preparation of 1,2-Diaryl-1*H*-indol-4-ols 3a–s and 1-Alkyl-2-aryl-1*H*-indol-4-ols 4a–g: A mixture of arylglyoxal **2** (4.0 mmol) and enamine **1** (5.0 mmol) was heated at reflux in acetonitrile (10 mL) for 6–8 h and the reaction was monitored by TLC analysis. After completion of the reaction, the solvent was evaporated in vacuo. The resulting residue was purified by column chromatography (ethyl acetate/hexane) on silica gel and crystallized from the same solvent system.

General Procedure for Preparation of 1,2-Diaryl-7-ethoxy-1,5,6,7-tetrahydroindol-4-ones 5a–g: A mixture of arylglyoxal **2** (4.0 mmol) and enamine **1** (5.0 mmol) was heated at reflux in ethanol (10 mL) for 6–8 h and the reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated in vacuo. The resulting residue was purified by column chromatography (ethyl acetate/hexane) on silica gel and crystallized from the same solvent system.

1,2-Diphenyl-1*H*-indol-4-ol (3a):[8a] Pale-yellow solid (684 mg, 60% yield); m.p. 152–154 °C. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 9.60 (s, 1 H), 7.46 (d, J = 8.1 Hz, 2 H), 7.29 (d, J = 7.2 Hz, 1 H), 7.17–7.10 (m, 7 H), 6.88 (t, J = 8.1 Hz, 1 H), 6.83 (s, 1 H), 6.55 (d, J = 8.1 Hz, 1 H), 6.44 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz,

[D$_6$]DMSO): δ = 150.7, 140.6, 138.3, 138.2, 132.2, 129.5, 128.6, 128.3, 127.8, 127.4, 127.2, 123.5, 117.9, 104.9, 101.7, 101.1 ppm.

2-Phenyl-1-(*p*-tolyl)-1*H*-indol-4-ol (3b): Pale-yellow solid (656 mg, 55% yield); m.p. 108–110 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.57 (s, 1 H), 7.19–7.11 (m, 7 H), 7.04 (d, J = 7.8 Hz, 2 H), 6.84 (t, J = 7.8 Hz, 1 H), 6.80 (s, 1 H), 6.52 (d, J = 8.1 Hz, 1 H), 6.43 (d, J = 7.5 Hz, 1 H), 2.26 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 150.7, 140.8, 138.2, 136.81, 135.8, 132.3, 129.9, 128.3, 128.3, 127.6, 127.1, 123.4, 117.9, 104.8, 101.8, 100.9, 20.7 ppm. IR (KBr): $\tilde{\nu}$ = 3237, 1460 cm^{-1}. $C_{21}H_{17}NO$ (299.37): calcd. C 84.25, H 5.72, N 4.68; found C 84.17, H 5.64, N 4.60.

1-(4′-Bromophenyl)-2-phenyl-1*H*-indol-4-ol (3c): Pale-yellow solid (844 mg, 58% yield); m.p. 116–118 °C. ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 9.63 (s, 1 H), 7.57 (d, J = 7.5 Hz, 2 H), 7.39–7.11 (m, 7 H), 6.88 (t, J = 7.8 Hz, 1 H), 6.83 (s, 1 H), 6.57 (d, J = 8.1 Hz, 1 H), 6.45 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 150.8, 140.4, 138.1, 137.6, 132.4, 131.9, 129.8, 128.5, 128.4, 127.3, 123.7, 120.1, 118.06, 105.1, 101.5, 101.5 ppm. IR (KBr): $\tilde{\nu}$ = 3230, 1450 cm^{-1}. $C_{20}H_{14}BrNO$ (364.24): calcd. C 65.95, H 3.87, N 3.85; found C 65.88, H 3.80, N 3.77.

1-(3′-Chlorophenyl)-2-phenyl-1*H*-indol-4-ol (3d): Pale-yellow solid (690 mg, 54% yield); m.p. 128–130 °C. ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 9.65 (s, 1 H), 7.40–7.37 (m, 2 H), 7.29 (s, 1 H), 7.23–7.12 (m, 6 H), 6.89 (t, J = 7.8 Hz, 1 H), 6.84 (s, 1 H), 6.58 (d, J = 8.4 Hz, 1 H), 6.46 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 150.8, 140.4, 139.7, 138.1, 133.5, 131.9, 131.0, 128.4, 128.4, 127.6, 127.5, 127.45, 126.7, 123.9, 118.0, 105.3, 101.7, 101.6 ppm. IR (KBr): $\tilde{\nu}$ = 3235, 1456 cm^{-1}. $C_{20}H_{14}ClNO$ (319.79): calcd. C 75.12, H 4.41, N 4.38; found C 75.03, H 4.33, N 4.29.

1-(3′-Methoxyphenyl)-2-phenyl-1*H*-indol-4-ol (3e): Pale-yellow solid (554 mg, 44% yield); m.p. 80–82 °C. ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 9.70 (s, 1 H), 7.36 (t, J = 8.1 Hz, 1 H), 7.34–7.10 (m, 6 H), 6.95 (t, J = 7.5 Hz, 2 H), 6.90 (s, 1 H), 679 (d, J = 7.8 Hz, 2 H), 6.70 (d, J = 7.5 Hz, 1 H), 3.69 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 159.8, 150.7, 140.5, 139.5, 138.2, 130.2, 129.3, 128.5, 128.3, 127.2, 123.5, 119.9, 118.0, 113.6, 113.1, 104.9, 101.8, 101.1, 55.0 ppm. IR (KBr): $\tilde{\nu}$ = 3235, 1440 cm^{-1}. $C_{21}H_{17}NO_2$ (315.37): calcd. C 79.98, H 5.43, N 4.44; found C 79.88, H 5.36, N 4.38.

2-(4′-Nitrophenyl)-1-phenyl-1*H*-indol-4-ol (3f): Brown solid (765 mg, 58% yield); m.p. 182–184 °C. ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 9.80 (s, 1 H), 8.05 (d, J = 7.8 Hz, 2 H), 7.48–7.37 (m, 5 H), 7.23 (d, J = 7.8 Hz, 2 H), 7.09 (s, 1 H), 6.94 (t, J = 7.8 Hz, 1 H), 6.58 (d, J = 8.4 Hz, 1 H), 6.47 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 151.2, 145.9, 141.5, 138.6, 137.9, 135.9, 129.8, 128.8, 127.9, 127.9, 124.9, 123.6, 118.0, 105.1, 104.1, 101.8 ppm. IR (KBr): $\tilde{\nu}$ = 3405, 1496 cm^{-1}. $C_{20}H_{14}N_2O_3$ (330.34): calcd. C 72.72, H 4.27, N 8.48; found C 72.63, H 4.21, N 8.40.

2-(4′-Nitrophenyl)-1-(*p*-tolyl)-1*H*-indol-4-ol (3g): Brown solid (825 mg, 60% yield); m.p. 180–182 °C: ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 9.78 (s, 1 H), 8.02 (d, J = 8.1 Hz, 2 H), 7.40 (d, J = 8.1 Hz, 2 H), 7.21 (d, J = 7.2 Hz, 1 H), 7.20–7.00 (m, 4 H), 6.91 (t, J = 7.8 Hz, 1 H), 6.46 (d, J = 7.2 Hz, 1 H), 6.36 (d, J = 7.2 Hz, 1 H), 2.27 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 151.2, 145.8, 141.6, 138.7, 137.2, 135.9, 135.3, 130.2, 128.7, 127.5, 124.8, 123.5, 118.0, 105.0, 103.9, 101.8, 20.7 ppm. IR (KBr): $\tilde{\nu}$ = 3419, 1515 cm^{-1}. $C_{21}H_{16}N_2O_3$ (344.37): calcd. C 73.24, H 4.68, N 8.13; found C 73.14, H 4.61, N 8.05.

1-(4′-Bromophenyl)-2-(4′-nitrophenyl)-1*H*-indol-4-ol (3h): Brown solid (850 mg, 52% yield); m.p. 190–192 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.82 (s, 1 H), 8.06 (d, J = 8.4 Hz, 2 H), 7.61 (d, J = 8.4 Hz, 2 H), 7.40 (d, J = 8.7 Hz, 2 H), 7.17 (d, J = 8.4 Hz, 2 H), 7.08 (s, 1 H), 6.94 (t, J = 8.1 Hz, 1 H), 6.59 (d, J = 8.1 Hz, 1 H), 6.47 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 151.7, 146.4, 141.6, 138.8, 137.6, 136.2, 133.2, 130.2, 129.3, 125.5, 124.1, 121.1, 118.5, 105.8, 105.0, 102.1 ppm. IR (KBr): $\tilde{\nu}$ = 3290, 1489 cm^{-1}. $C_{20}H_{13}BrN_2O_3$ (409.24): calcd. C 58.70, H 3.20, N 6.85; found C 58.66, H 3.15, N 6.79.

1-(3′-Chlorophenyl)-2-(4′-nitrophenyl)-1*H*-indol-4-ol (3i): Brown solid (583 mg, 40% yield); m.p. 178–180 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.82 (s, 1 H), 8.05 (d, J = 9.0 Hz, 2 H), 7.50–7.35 (m, 5 H), 7.20–7.05 (m, 2 H), 6.95 (t, J = 8.1 Hz, 1 H), 6.58 (d, J = 8.4 Hz, 1 H), 6.48 (d, J = 7.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 151.3, 146.0, 141.3, 139.3, 138.3, 135.8, 133.8, 131.3, 128.8, 127.9, 127.5, 126.7, 125.2, 123.6, 118.1, 105.5, 104.7, 101.6 ppm. IR (KBr): $\tilde{\nu}$ = 3409, 1492 cm^{-1}. $C_{20}H_{13}ClN_2O_3$ (364.79): calcd. C 65.85, H 3.59, N 7.68; found C 65.77, H 3.50, N 7.61.

1-(3′-Methoxyphenyl)-2-(4′-nitrophenyl)-1*H*-indol-4-ol (3j): Brown solid (720 mg, 50% yield); m.p. 196–198 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.63 (s, 1 H), 7.87 (d, J = 8.7 Hz, 2 H), 7.27 (d, J = 8.7 Hz, 2 H), 7.14 (t, J = 8.1 Hz, 1 H), 6.92 (s, 1 H), 6.80–6.75 (m, 2 H), 6.67 (t, J = 2.1 Hz, 1 H), 6.56 (d, J = 7.2 Hz, 1 H), 6.47 (d, J = 8.1 Hz, 1 H), 6.31 (d, J = 7.5 Hz, 1 H), 3.47 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 160.5, 151.6, 146.3, 141.8, 139.4, 139.1, 136.3, 130.9, 129.0, 125.3, 124.0, 120.3, 118.4, 113.9, 113.9, 105.6, 104.5, 102.3, 55.8 ppm. IR (KBr): $\tilde{\nu}$ = 3490, 1482 cm^{-1}. $C_{21}H_{16}N_2O_4$ (360.37): calcd. C 69.99, H 4.48, N 7.77; found C 69.92, H 4.43, N 7.71.

2-(4′-Chlorophenyl)-1-phenyl-1*H*-indol-4-ol (3k): Pale-yellow solid (703 mg, 55% yield); m.p. 184–186 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05–7.85 (m, 3 H), 7.75–7.56 (m, 6 H), 7.42 (t, J = 7.8 Hz, 1 H), 7.07 (d, J = 8.4 Hz, 1 H), 7.06 (s, 1 H), 6.50 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 149.1, 141.1, 138.5, 133.4, 131.1, 130.1, 129.5, 128.6, 128.5, 128.1, 127.6, 123.7, 118.0, 105.4, 104.0, 100.4 ppm. IR (KBr): $\tilde{\nu}$ = 3290, 1475 cm^{-1}. $C_{20}H_{14}ClNO$ (319.79): calcd. C 75.12, H 4.41, N 4.38; found C 75.05, H 4.33, N 4.30.

1-(3′-Chlorophenyl)-2-(4′-chlorophenyl)-1*H*-indol-4-ol (3l): Pale-yellow solid (722 mg, 51% yield); m.p. 144–146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26–6.94 (m, 10 H), 6.79 (d, J = 7.8 Hz, 2 H), 6.51 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.2, 140.9, 139.7, 138.4, 135.1, 133.7, 130.7, 130.5, 130.0, 128.7, 128.1, 127.9, 126.4, 124.0, 118.1, 105.8, 103.7, 101.1 ppm. IR (KBr): $\tilde{\nu}$ = 3295, 1495 cm^{-1}. $C_{20}H_{13}Cl_2NO$ (354.23): calcd. C 67.81, H 3.70, N 3.95; found C 67.74, H 3.62, N 3.88.

2-(4′-Chlorophenyl)-1-(3′-methoxyphenyl)-1*H*-indol-4-ol (3m): Pale-yellow solid (741 mg, 53% yield); m.p. 90–92 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.10 (m, 5 H), 6.97 (t, J = 7.8 Hz, 1 H), 6.84 (d, J = 8.4 Hz, 2 H), 6.77–6.72 (m, 3 H), 6.51 (d, J = 7.8 Hz, 1 H), 3.67 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.4, 149.1, 141.0, 139.6, 138.5, 133.4, 131.1, 130.2, 130.0, 128.6, 123.7, 120.5, 117.9, 113.8, 113.5, 105.4, 104.1, 100.4, 55.6 ppm. IR (KBr): $\tilde{\nu}$ = 3287, 1483 cm^{-1}. $C_{21}H_{16}ClNO_2$ (349.82): calcd. C 72.10, H 4.61, N 4.00; found C 72.01, H 4.54, N 3.91.

2-(4′-Methoxyphenyl)-1-phenyl-1*H*-indol-4-ol (3n):[8a] Pale-yellow solid (567 mg, 45% yield); m.p. 128–130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.30 (m, 3 H), 7.30–7.12 (m, 4 H), 6.98 (t, J = 7.8 Hz, 1 H), 6.86–6.72 (m, 4 H), 6.55 (d, J = 6.9 Hz, 1 H), 3.75 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9, 148.7, 140.6, 139.6, 138.7, 130.1, 129.2, 128.0, 127.2, 125.0, 122.8, 117.8, 113.7, 105.0, 103.7, 98.8, 55.2 ppm.

1-(3′-Chlorophenyl)-2-(4′-methoxyphenyl)-1*H*-indol-4-ol (3o): Pale-yellow solid (587 mg, 42% yield); m.p. 114–116 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.30 (m, 3 H), 7.15 (d, J = 8.1 Hz, 2 H), 7.05 (t, J = 8.1 Hz, 2 H), 6.90–6.75 (m, 4 H), 6.56 (d, J = 7.2 Hz, 1 H), 3.78 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 148.7, 140.4, 139.9, 139.4, 134.6, 130.1, 130.0, 128.0, 127.4, 126.3, 124.5, 123.1, 117.9, 113.8, 105.4, 103.5, 99.5, 55.2 ppm. IR (KBr): $\tilde{\nu}$ = 3220, 1479 cm^{-1}. $C_{21}H_{16}ClNO_2$ (349.82): calcd. C 72.10, H 4.61, N 4.00; found C 72.02, H 4.54, N 3.92.

2-(4′-Methoxyphenyl)-1-(3′-methoxyphenyl)-1*H*-indol-4-ol (3p): Pale-yellow solid (566 mg, 41% yield); m.p. 75–77 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.11 (m, 4 H), 6.90–6.68 (m, 7 H), 6.50 (d, J = 7.5 Hz, 1 H), 3.71 (s, 3 H), 3.65 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1, 158.9, 148.6, 140.5, 139.7, 139.6, 132.7, 130.0, 129.8, 122.8, 120.4, 117.8, 113.7, 113.6, 113.2, 105.0, 103.8, 98.8, 55.3, 55.2 ppm. IR (KBr): $\tilde{\nu}$ = 3220, 1479 cm^{-1}. $C_{22}H_{19}NO_3$ (345.40): calcd. C 76.50, H 5.54, N 4.06; found C 76.42, H 5.46, N 3.99.

2-(4′-Fluorophenyl)-1-phenyl-1*H*-indol-4-ol (3q): Pale-yellow solid (605 mg, 50% yield); m.p. 162–164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.55 (m, 3 H), 7.28–7.10 (m, 4 H), 6.97 (t, J = 7.2 Hz, 1 H), 6.90–6.80 (m, 4 H), 6.52 (d, J = 7.5 Hz, 1 H), 5.34 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.7, 148.8, 140.8, 138.7, 138.4, 130.5, 130.4, 129.3, 128.5, 128.0, 127.4, 123.3, 117.8, 115.3, 115.1, 105.2, 103.8, 99.7 ppm. IR (KBr): $\tilde{\nu}$ = 3220, 1493 cm^{-1}. $C_{20}H_{14}FNO$ (303.33): calcd. C 79.19, H 4.65, N 4.62; found C 79.08, H 4.58, N 4.54.

1-(3′-Chlorophenyl)-2-(4′-fluorophenyl)-1*H*-indol-4-ol (3r): Pale-yellow solid (603 mg, 45% yield); m.p. 136–138 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24–7.20 (m, 3 H), 7.13–7.08 (m, 2 H), 6.98–6.70 (m, 6 H), 6.50 (d, J = 7.8 Hz, 1 H), 5.35 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.9, 148.9, 140.5, 139.6, 138.5, 134.8, 130.5, 130.4, 130.2, 128.2, 128.1, 128.0, 127.6, 126.3, 123.6, 117.9, 115.5, 115.3, 105.6, 103.6, 100.5 ppm. IR (KBr): $\tilde{\nu}$ = 3220, 1493 cm^{-1}. $C_{20}H_{13}ClFNO$ (337.78): calcd. C 71.12, H 3.88, N 4.15; found C 71.03, H 3.81, N 4.08.

2-(4′-Fluorophenyl)-1-(3′-methoxyphenyl)-1*H*-indol-4-ol (3s): Pale-yellow solid (597 mg, 45% yield); m.p. 112–114 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (t, J = 7.8 Hz, 1 H), 7.12–7.07 (m, 2 H), 6.91 (t, J = 7.8 Hz, 2 H), 6.83–6.77 (m, 3 H), 6.68 (d, J = 8.4 Hz, 3 H), 6.47 (d, J = 7.5 Hz, 1 H), 5.75 (br. s, 1 H), 3.60 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.8, 160.2, 148.9, 140.7, 139.5, 138.6, 130.5, 130.3, 130.0, 128.6, 128.6, 123.3, 120.4, 117.9, 115.3, 115.1, 113.7, 113.3, 105.3, 103.9, 99.9, 55.4 ppm. IR (KBr): $\tilde{\nu}$ = 3220, 1493 cm^{-1}. $C_{21}H_{16}FNO_2$ (333.36): calcd. C 75.66, H 4.84, N 4.20; found C 75.57, H 4.76, N 4.11.

1-Benzyl-2-phenyl-1*H*-indol-4-ol (4a):[8f] Pale-yellow solid (490 mg, 41% yield); m.p. 96–98 °C (lit.:[8f] 96–98 °C). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.46 (s, 1 H), 7.42–7.30 (m, 5 H), 7.17–7.09 (m, 3 H), 6.85–6.80 (m, 3 H), 6.69 (d, J = 8.1 Hz, 1 H), 6.61 (s, 1 H), 6.37 (d, J = 7.5 Hz, 1 H), 5.31 (s, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 150.6, 139.6, 139.1, 138.4, 132.5, 128.8, 128.8, 128.5, 127.9, 127.0, 125.9, 122.9, 117.9, 104.3, 102.2, 99.7, 47.0 ppm.

1-Benzyl-2-(4′-nitrophenyl)-1*H*-indol-4-ol (4b): Brown solid (620 mg, 45% yield); m.p. 179–181 °C. ^{1}H NMR (300 MHz, [D$_6$]-DMSO): δ = 9.64 (s, 1 H), 8.18 (d, J = 8.7 Hz, 2 H), 7.68 (d, J = 8.7 Hz, 2 H), 7.20–7.06 (m, 3 H), 6.93–6.76 (m, 5 H), 6.41 (d, J = 7.5 Hz, 1 H), 5.40 (s, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 151.0, 146.4, 140.6, 138.9, 138.0, 136.8, 129.3, 128.6, 127.1, 125.9, 124.1, 123.9, 118.0, 104.5, 102.5, 102.3, 47.3 ppm. IR (KBr): $\tilde{\nu}$ = 3410, 1462 cm^{-1}. $C_{21}H_{16}N_2O_3$ (344.37): calcd. C 73.24, H 4.68, N 8.13; found C 73.15, H 4.60, N 8.06.

1-Benzyl-2-(4′-chlorophenyl)-1*H*-indol-4-ol (4c): Pale-yellow solid (547 mg, 41% yield); m.p. 58–60 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.10 (m, 7 H), 6.97–6.93 (m, 3 H), 6.71 (d, J = 8.1 Hz, 1 H), 6.48 (s, 1 H), 6.47 (d, J = 7.5 Hz, 1 H), 5.23 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.0, 140.0, 139.4, 137.8, 134.1, 131.0, 130.3, 128.8, 128.8, 127.3, 125.8, 123.1, 117.7, 104.8, 103.7, 98.9, 48.0 ppm. IR (KBr): $\tilde{\nu}$ = 3230, 1495 cm^{-1}. $C_{21}H_{16}ClNO$ (333.82): calcd. C 75.56, H 4.83, N 4.20; found C 75.48, H 4.75, N 4.12.

1-Benzyl-2-(4′-methoxyphenyl)-1*H*-indol-4-ol (4d): Pale-yellow solid (553 mg, 42% yield); m.p. 140–142 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.7 Hz, 2 H), 7.28–7.20 (m, 4 H), 7.01–6.95 (m, 3 H), 6.89 (d, J = 8.7 Hz, 2 H), 6.76 (d, J = 8.1 Hz, 1 H), 6.76 (d, J = 7.5 Hz, 1 H), 5.29 (s, 2 H), 3.80 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5, 148.7, 140.6, 139.7, 138.2, 130.5, 128.7, 127.1, 126.0, 125.0, 122.5, 117.7, 114.0, 104.6, 103.7, 97.7, 55.3, 47.9 ppm. IR (KBr): $\tilde{\nu}$ = 3220, 1493 cm^{-1}. $C_{22}H_{19}NO_2$ (329.40): calcd. C 80.22, H 5.81, N 4.25; found C 80.14, H 5.74, N 4.15.

1-Benzyl-2-(4′-fluorophenyl)-1*H*-indol-4-ol (4e): Pale-yellow solid (507 mg, 40% yield); m.p. 80–82 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.13 (m, 5 H), 6.99–6.89 (m, 5 H), 6.71 (d, J = 8.1 Hz, 1 H), 6.57 (s, 1 H), 6.46 (d, J = 7.5 Hz, 1 H), 5.30–5.20 (br. s, 1 H), 5.19 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3, 148.9, 139.8, 139.6, 137.9, 131.0, 130.9, 128.8, 128.6, 127.2, 125.9, 123.0, 117.7, 115.7, 115.4, 104.8, 103.7, 98.6, 47.9 ppm. IR (KBr): $\tilde{\nu}$ = 3220, 1493 cm^{-1}. $C_{21}H_{16}FNO$ (317.36): calcd. C 79.48, H 5.08, N 4.41; found C 79.40, H 5.01, N 4.35.

1-Methyl-2-phenyl-1*H*-indol-4-ol (4f): Yellow gummy mass (383 mg, 43% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57–7.44 (m, 5 H), 7.17 (t, J = 7.8 Hz, 1 H), 7.02 (d, J = 8.1 Hz, 1 H), 6.68 (s, 1 H), 6.63 (d, J = 7.8 Hz, 1 H), 3.76 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.9, 140.3, 132.8, 129.6, 128.8, 128.3, 123.7, 121.6, 117.5, 105.5, 103.9, 99.1, 30.7 ppm. IR (KBr): $\tilde{\nu}$ = 3225, 1499 cm^{-1}. $C_{15}H_{13}NO$ (223.27): calcd. C 80.69, H 5.87, N 6.27; found C 80.58, H 5.79, N 6.18.

1-Cyclopropyl-2-phenyl-1*H*-indol-4-ol (4g): Yellow gummy mass (398 mg, 40% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, J = 6.9 Hz, 2 H), 7.49–7.40 (m. 3 H), 7.26 (d, J = 8.4 Hz, 1 H), 7.13 (t, J = 7.5 Hz, 1 H), 6.62 (s, 1 H), 6.59 (d, J = 7.8 Hz, 1 H), 5.40 (br. s, 1 H), 3.47–3.35 (m, 1 H), 0.98–0.89 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.8, 140.8, 133.3, 129.7, 128.5, 127.6, 123.5, 121.5, 117.2, 105.4, 103.3, 99.0, 27.5, 9.1 ppm. IR (KBr): $\tilde{\nu}$ = 3225, 1499 cm^{-1}. $C_{17}H_{15}NO$ (249.31): calcd. C 81.90, H 6.06, N 5.62; found C 81.81, H 6.00, N 5.53.

7-Ethoxy-1,2-diphenyl-1,5,6,7-tetrahydroindol-4-one (5a): Pale-yellow solid (730 mg, 55% yield); m.p. 116–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.30 (m, 4 H), 7.02–7.05 (m, 6 H), 6.76 (s, 1 H), 4.25 (t, J = 2.6 Hz, 1 H), 3.55–3.48 (m, 1 H), 3.19–3.11 (m, 1 H), 2.99–2.87 (m, 1 H), 2.48–2.36 (m, 2 H), 2.19–2.09 (m, 1 H), 1.20 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.6, 142.7, 137.5, 137.3, 131.7, 129.0, 128.4, 128.3, 128.1, 128.0, 127.1, 121.6, 105.6, 67.7, 64.5, 33.4, 27.7, 15.4 ppm. IR (KBr): $\tilde{\nu}$ = 1678, 1512 cm^{-1}. $C_{22}H_{21}NO_2$ (331.41): calcd. C 79.73, H 6.39, N 4.23; found C 79.62, H 6.30, N 4.16.

7-Ethoxy-2-phenyl-1-(*p*-tolyl)-1,5,6,7-tetrahydroindol-4-one (5b): Pale-yellow solid (828 mg, 60% yield); m.p. 152–154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.08 (m, 9 H), 6.76 (s, 1 H), 4.25 (t, J = 3 Hz, 1 H), 3.57–3.51 (m, 1 H), 3.20–3.15 (m, 1 H), 2.94–2.90

(m, 1 H), 2.46–2.38 (m, 5 H), 2.17–2.12 (m, 1 H), 1.14 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.6, 142.9, 138.3, 137.3, 134.8, 131.8, 129.6, 128.4, 128.1, 127.7, 127.1, 121.5, 105.5, 67.7, 64.5, 33.4, 27.7, 21.1, 15.4 ppm. IR (KBr): $\tilde{\nu}$ = 1680, 1516 cm^{-1}. $C_{23}H_{23}NO_2$ (345.44): calcd. C 79.97, H 6.71, N 4.05; found C 79.88, H 6.63, N 3.98.

1-(4′-Bromophenyl)-7-ethoxy-2-phenyl-1,5,6,7-tetrahydroindol-4-one (5c): Pale-yellow solid (983 mg, 60% yield); m.p. 115–117 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.40 (m, 2 H), 7.19–6.98 (m, 7 H), 6.68 (t, J = 1.2 Hz, 1 H), 4.16 (t, J = 2.7 Hz, 1 H), 3.52–3.50 (m, 1 H), 3.16–3.11 (m, 1 H), 2.90–2.85 (m, 1 H), 2.49–2.33 (m, 2 H), 2.06–1.98 (m, 1 H), 1.12–1.10 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.4, 142.5, 137.2, 136.6, 132.1, 131.4, 129.6, 128.5, 128.3, 127.4, 122.2, 121.9, 106.0, 67.8, 64.4, 33.3, 27.5, 15.4 ppm. IR (KBr): $\tilde{\nu}$ = 1678, 1513 cm^{-1}. $C_{22}H_{20}BrNO_2$ (410.31): calcd. C 64.40, H 4.91, N 3.41; found C 64.28, H 4.83, N 3.32.

1-(4′-Chlorophenyl)-7-ethoxy-2-phenyl-1,5,6,7-tetrahydroindol-4-one (5d): Pale-yellow solid (730 mg, 50% yield); m.p. 88–90 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.30 (m, 3 H), 7.19–7.12 (m, 4 H), 7.10–7.04 (m, 2 H), 6.75 (s, 1 H), 4.23 (t, J = 2.6 Hz, 1 H), 3.63–3.53 (m, 1 H), 3.24–3.14 (m, 1 H), 2.97–2.86 (m, 1 H), 2.48–2.38 (m, 2 H), 2.18–2.06 (m, 1 H), 1.15–1.13 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.5, 142.6, 137.3, 136.0, 134.3, 131.4, 129.3, 128.9, 128.4, 128.2, 127.7, 121.9, 105.9, 67.7, 64.5, 33.3, 27.5, 15.4 ppm. IR (KBr): $\tilde{\nu}$ = 1670, 1517 cm^{-1}. $C_{22}H_{20}ClNO_2$ (365.86): calcd. C 72.22, H 5.51, N 3.83; found C 72.14, H 5.42, N 3.76.

7-Ethoxy-1-(3′-methoxyphenyl)-2-phenyl-1,5,6,7-tetrahydroindol-4-one (5e): Pale-yellow solid (867 mg, 60% yield); m.p. 144–146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19 (s, 1 H), 7.13–7.01 (m, 6 H), 6.84 (dd, J_1 = 8.4, J_2 = 2.4 Hz, 2 H), 6.69 (s, 1 H), 4.21 (t, J = 3.0 Hz, 1 H), 3.65 (s, 3 H), 3.51–3.46 (m, 1 H), 3.16–3.11 (m, 1 H), 2.95–2.80 (m, 1 H), 2.40–2.30 (m, 2 H), 2.15–2.06 (m, 1 H), 1.08 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.8, 160.0, 142.7, 138.3, 137.2, 131.6, 129.6, 128.7, 128.0, 127.1, 121.5, 120.2, 114.0, 113.8, 105.6, 67.5, 64.4, 55.34, 33.2, 27.5, 15.3 ppm. IR (KBr): $\tilde{\nu}$ = 1676, 1508 cm^{-1}. $C_{23}H_{23}NO_3$ (361.44): calcd. C 76.43, H 6.41, N 3.88; found C 76.34, H 6.32, N 3.81.

1-Benzyl-7-ethoxy-2-phenyl-1,5,6,7-tetrahydroindol-4-one (5f): Pale-yellow solid (690 mg, 50% yield); m.p. 125–127 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.20 (m, 8 H), 6.94 (d, J = 6.9 Hz, 2 H), 6.64 (s, 1 H), 5.25 (s, 2 H), 4.38 (t, J = 3.6 Hz, 1 H), 3.68–3.63 (m, 1 H), 3.36–3.29 (m, 1 H), 2.89–2.79 (m, 1 H), 2.45–2.29 (m, 2 H), 2.19–2.12 (m, 1 H), 1.22 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.2, 141.5, 137.9, 137.7, 131.9, 129.1, 129.2, 128.7, 128.0, 127.4, 125.6, 121.5, 105.5, 68.6, 64.5, 48.1, 33.8, 27.8, 15.5 ppm. IR (KBr): $\tilde{\nu}$ = 1677, 1510 cm^{-1}. $C_{23}H_{23}NO_2$ (345.44): calcd. C 79.97, H 6.71, N 4.05; found C 79.91, H 6.63, N 3.97.

7-Ethoxy-1-(3′-methoxyphenyl)-2-(4′-nitrophenyl)-1,5,6,7-tetrahydroindol-4-one (5g): Pale-yellow solid (974 mg, 60% yield); m.p. 170–172 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (dd, J_1 = 9.0, J_2 = 2.4 Hz, 2 H), 7.20–7.15 (m, 4 H), 6.92–6.83 (m, 2 H), 6.55 (s, 1 H), 4.21 (t, J = 2.5 Hz, 1 H), 3.69 (s, 3 H), 3.68–3.67 (m, 1 H), 3.52–3.47 (m, 1 H), 2.84–2.80 (m, 1 H), 2.40–2.33 (m, 2 H), 2.10–2.05 (m, 1 H), 1.07 (t, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.3, 160.3, 146.3, 144.3, 138.1, 137.9, 134.7, 130.1, 128.2, 123.5, 121.9, 120.0, 114.3, 114.0, 108.0, 67.4, 64.5, 55.4, 33.3, 27.4, 15.3 ppm. IR (KBr): $\tilde{\nu}$ = 1669, 1519 cm^{-1}. $C_{23}H_{22}N_2O_5$ (406.44): calcd. C 67.97, H 5.46, N 6.89; found C 67.88, H 5.37, N 6.82.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of **3a**–**3s**, **4a**–**4g** and **5a**–**g**.

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[11] CCDC-903273 (for **3f**) and -903896 (for **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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