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Substituted Benzo[*a*]carbazoles and Indoleacetic Acids from Arylglyoxals and Enamines through Domino Condensation, Thermal Cyclization, and Aromatization

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Keywords: Synthetic methods / Domino reactions / Cyclization / Nitrogen heterocycles / Aromatization

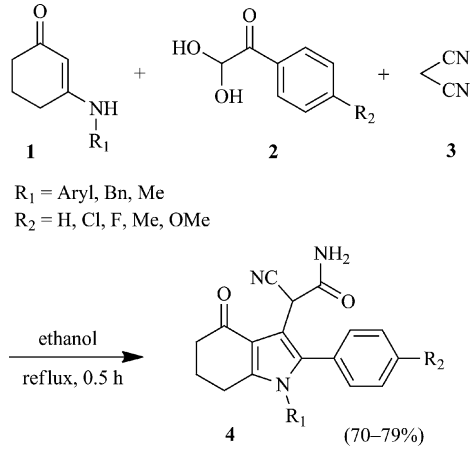
A two-step method has been developed in which cyclohexanone-fused 2-(3-pyrrolyl)-2-cyanoacetamides, the condensation products of enamines, arylglyoxals, and malononitrile, are converted into highly substituted benzo[*a*]carbazoles through a one-step thermal cyclization and palladium-catalyzed aromatization. The biologically important indoleacetic acid derivatives are also obtained in good yields from the hydrolysis and aromatization of the same cyanoacetamides.

Introduction

The carbazole core is present in a number of naturally occurring molecules that exhibit remarkable biological activity in living cells.[1] Carbazole ring compounds also have wide applicability in materials science as organic light-emitting materials as a result of their wide band gap, high luminescent activity, and flexibility with regard to the chemical manipulation of the parent carbazole framework.[2] Among various carbazole derivatives, the aryl- and heteroaryl-annulated[*a*]carbazoles have drawn significant biological and pharmacological interest that has ensued from their affinity toward nucleic acids.[3] Particularly, the benzo[*a*]carbazole frameworks may exhibit antitumor activity,[4a] antiestrogenic properties[4b] or kinase inhibitory activities.[4c] Hence, these are appealing targets for organic chemists. A number of useful synthetic methods for the preparation of carbazole derivatives are available that utilize metal-mediated C–C and C–N bond formation[5] as well as thermal and photochemical cyclization reactions of different substituted indoles or arylamines.[6] Although these methods are useful to synthesize carbazole derivatives, there are some significant limitations, such as most of them require multistep reaction protocols and demonstrate poor atom economy. Therefore, a simple, efficient, regiocontrolled, and diversified synthesis for carbazole derivatives that contain specific substitution patterns is still highly attractive. On the other hand, the indoleacetic acid derivatives, the analogues of plant growth regulatory hormones,[7a,7b] are also important target molecules to synthetic chemists.[7c–7f] However, until now there has been no report of the synthesis of highly functionalized indoleacetic acids, such as (4-hydroxy-1,2-diphenyl-1*H*-3-indolyl)acetic acids. Therefore, we wish to report, herein, an efficient synthesis for both highly substituted benzo[*a*]carbazoles and indoleacetic acid derivatives from a common intermediate that follows reaction protocols with a minimum number of steps.

Results and Discussion

Recently, some reports have shown that the domino condensation of arylglyoxals and enamines can produce densely substituted pyrrole derivatives.[8] Similarly, when a mixture of the enamine 3-(phenylamino)cyclohex-2-enone (**1**, R_1 = phenyl), phenylglyoxal monohydrate (**2**, R_2 = H), and malononitrile (**3**) was heated at reflux in ethanol, the new compound 2-cyano-2-(4-oxo-1,2-diphenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl)acetamide (**4a**) was formed in high yield through a domino condensation (see Scheme 1). Inter-



Scheme 1. Synthesis of pyrrole-substituted 2-cyanoacetamide derivatives **4**.

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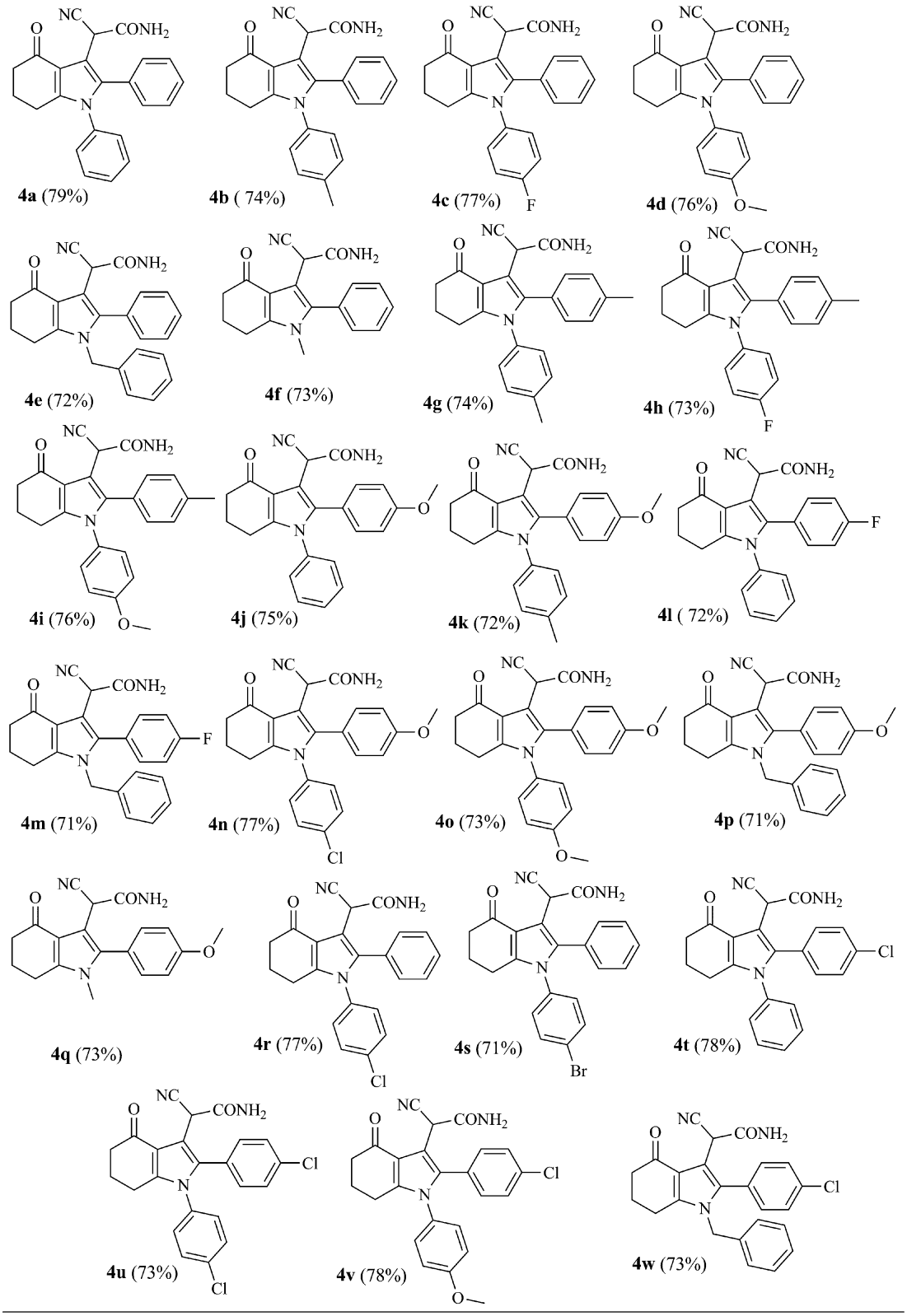
estingly, under the reaction conditions, one of the two cyano groups of malononitrile was selectively hydrolyzed into an amide group. By using this approach, a series of 2-(1,2-diaryl-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl)-2-cyano-

Table 1. Synthesis of pyrrole-substituted 2-cyanoacetamide derivatives **4**.[a]



[a] Isolated yield.

acetamides **4a**–**4w** were synthesized by varying the starting enamine as well as the arylglyoxal monohydrate (see Scheme 1 and Table 1). All of the compounds **4a**–**4w** were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, and the X-ray crystal structure analysis of 2-[1,2-bis(4-chlorophenyl)-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl]-2-cyanoacetamide (**4u**) further confirmed the structural assignments (see Figure 1).[9] The synthesis of **4a** by using the same starting materials, as described above, but with other solvents such as acetonitrile, dioxone, and *N*,*N*-dimethylformamide (DMF) also afforded a good yield of product (69–77%) within 0.5 h when the reaction mixture was heated at reflux (see Supporting Information, Table S1). Some cyclohexanone-fused pyrrole derivatives have also been synthesized by using a different approach.[10]

A proposed mechanism for the formation of compound **4a** is shown in Scheme 2.[8e,11] Initially, arylglyoxal monohydrate **2** undergoes a Knoevenagel condensation with malononitrile to produce α,β-unsaturated nitrile intermediate **5**. Then, a Michael-type 1,4-addition of enamine **1** with intermediate **5** produces imminium intermediate **6**, which subsequently tautomerizes to give **7**. Intermediate **7** the undergoes a tandem cyclization to form fused furano-pyrrole intermediate **8**. Finally, the rearrangement of intermediate **8** leads to pyrrole-substituted cyanoacetamides **4**, which results in the selective hydrolysis of one of the two nitrile groups.

After the successful synthesis of compounds **4a**–**4w**, we thought that the fused cyclohexanone ring of **4a**–**4w** could be aromatized to produce biologically important 4-hydroxyindole derivatives. Therefore, 2-cyano-2-(4-oxo-1,2-di-

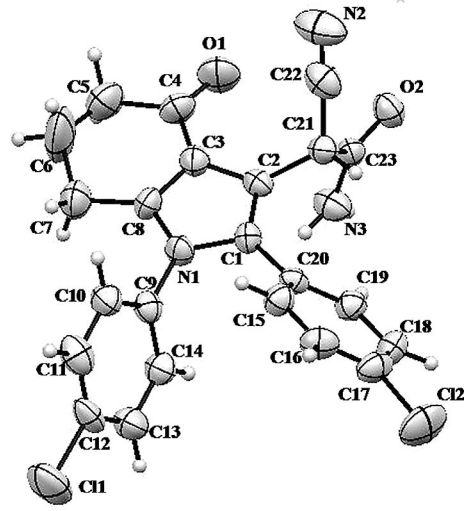
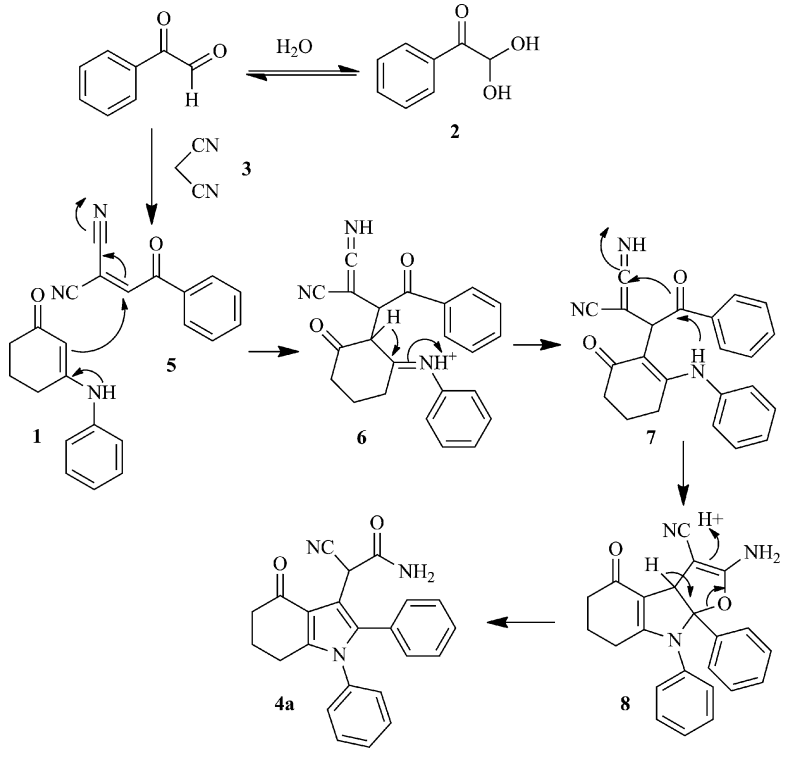


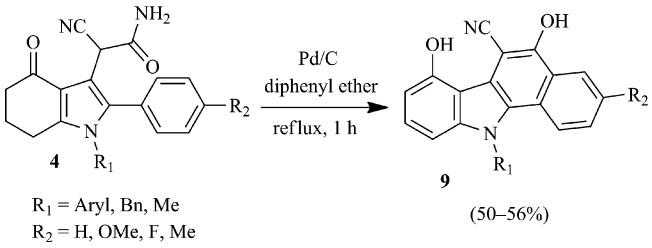
Figure 1. ORTEP diagram of X-ray crystal structure of **4u**.

phenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl)acetamide (**4a**) was heated at reflux in diphenyl ether in the presence of palladium on carbon (Pd/C) for 1 h. Surprisingly, the highly substituted carbazole derivative 5,7-dihydroxy-11-phenyl-11*H*-benzo[*a*]carbazole-6-carbonitrile (**9a**) was formed instead of a hydroxy indole derivative. The reaction proceeded through an intramolecular thermal cyclization between the amide carbonyl and the adjacent aromatic ring carbon of **4a** followed by an aromatization step to produce carbazole derivative **9a**. The reaction is very significant from an atom economy point of view, as it liberates only one molecule of



Scheme 2. Plausible mechanism for the formation of cyanoacetamide derivatives **4**.

ammonia during the course of reaction. By using this method, different substituted 11-aryl-5,7-dihydroxy-11*H*-benzo[*a*]carbazole-6-carbonitriles **9a**–**9l** were synthesized in moderate yields (see Scheme 3 and Table 2). The results demonstrate that the reaction can tolerate various electron-donating and electron-withdrawing groups on the 2-aryl moiety as well as on the *N*-aryl and -alkyl substituents of compounds **4**. All of the compounds **9a**–**9l** were fully characterized by ^{1}H and ^{13}C NMR spectroscopic analyses. The X-ray crystal structure determination of 11-(4-fluorophenyl)-5,7-dihydroxy-11*H*-benzo[*a*]carbazole-6-carbonitrile (**9c**) further confirmed the formation of the product (see Figure 2).[9] When compound **4k** was heated at reflux in diphenyl ether for 1 h without the Pd/C catalyst, the cyclized product **10k** was formed in good yield (see Scheme 4), which confirms that the cyclization is a thermal process.



Scheme 3. Synthesis of benzo[*a*]carbazole derivatives **9**.

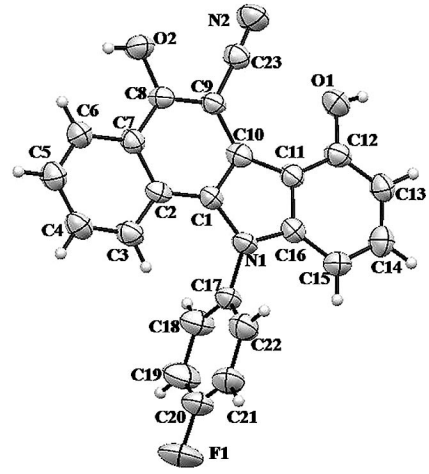
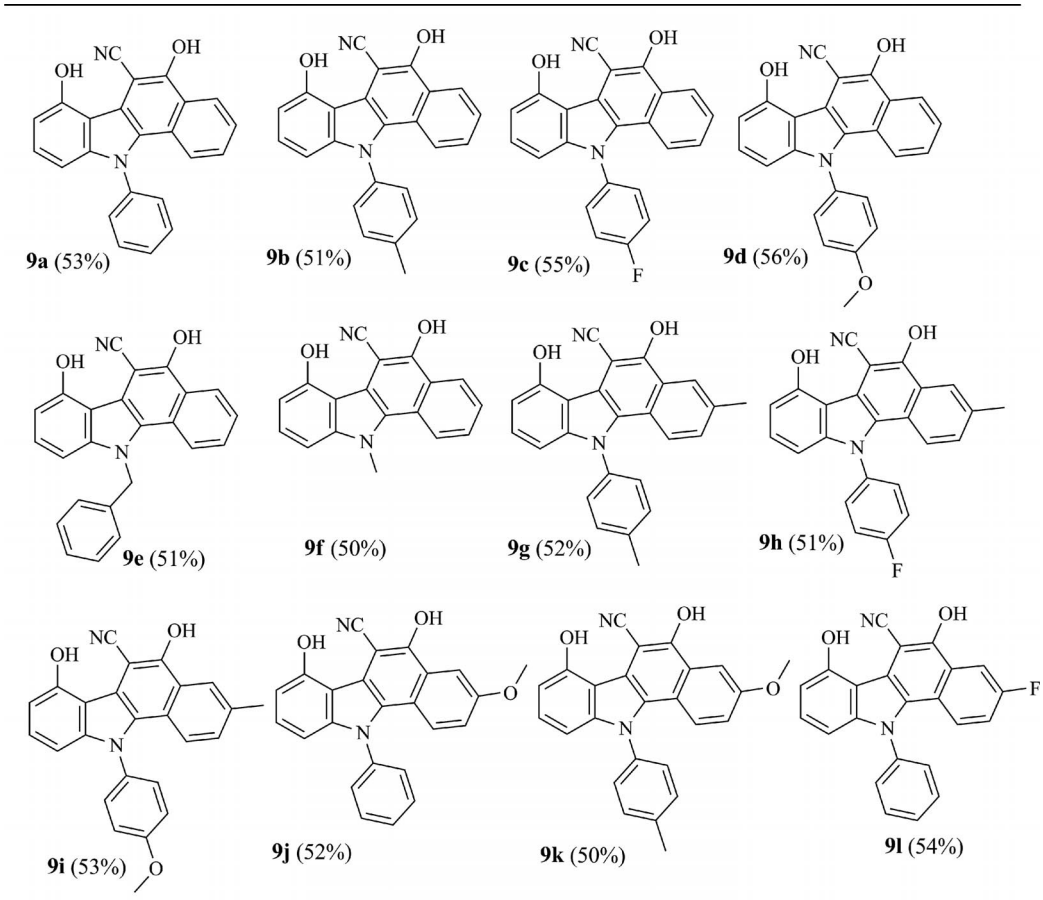
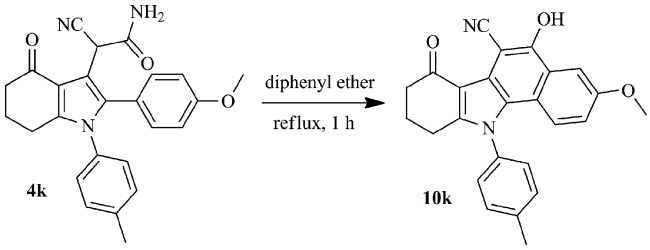


Figure 2. ORTEP diagram of X-ray crystal structure of **9c**.

Table 2. Synthesis of benzo[*a*]carbazole derivatives **9**.[a]

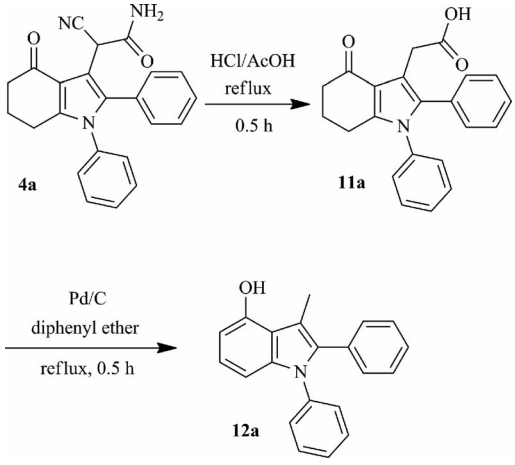


[a] Isolated yield.

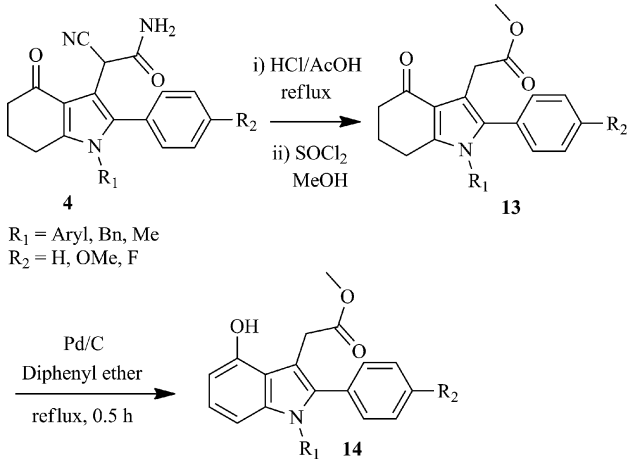


Scheme 4. Synthesis of compound **10k**.

After the syntheses of benzo[*a*]carbazoles **9a**–**9l**, we focused our attention on the preparation of the analogues of biologically important plant growth regulatory hormones,[7] the indoleacetic acid derivatives, from cyanoacetamides **4**. Thus, acetamide **4a** was initially heated to reflux in a mixture of concentrated HCl and acetic acid (1:1) for 0.5 h to afford (4-oxo-1,2-diphenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl)-acetic acid (**11a**) through hydrolysis and decarboxylation (see Scheme 5). Subsequently, acetic acid derivative **11a** was heated at reflux in diphenyl ether with Pd/C in anticipation that it would produce the indoleacetic acid derivative. The reaction, however, produced only 3-methyl-1,2-diphenyl-1*H*-indol-4-ol (**12a**) through decarboxylation (see Scheme 5).



Scheme 5. Synthesis of 3-methyl-1,2-diphenyl-1*H*-indol-4-ol (**12a**).



Scheme 6. Synthesis of indoleacetic acid derivatives **14**.

To overcome the difficulties, the carboxyl group of **11a** was protected as a methyl ester through a reaction with thionyl chloride and dry methanol to produce methyl (4-oxo-1,2-diphenyl-4,5,6,7-tetrahydro-1*H*-indol-3-yl)acetate (**13a**). Then, ester **13a** was heated at reflux with Pd/C in diphenyl ether for 0.5 h to produce the desired methyl (4-hydroxy-1,2-diphenylindol-3-yl)acetate (**14a**) in good yield (see Scheme 6 and Table 3). It is interesting to note that no benzo[*a*]carbazole derivative was formed through a thermal cyclization between the ester carbonyl and the adjacent aromatic ring, as previously observed in the case of **4a**. By using this method, several methyl (1,2-diaryl-4-hydroxyindol-3-yl)acetates **14** were synthesized (see Scheme 6 and Table 3). All of the compounds were fully characterized by ^{1}H and ^{13}C NMR spectroscopic analysis. The X-ray crystal structure of methyl (1-benzyl-2-phenyl-4-hydroxyindol-3-yl)acetate (**14e**) is shown in Figure 3.[9]

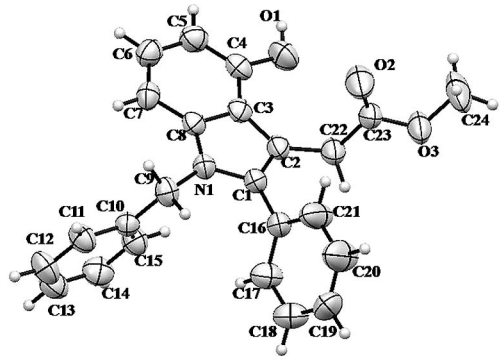


Figure 3. ORTEP diagram of X-ray crystal structure of **14e**.

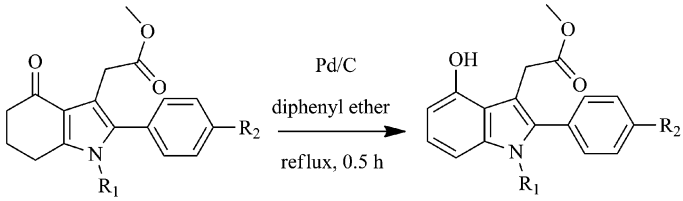
Conclusions

In summary, we have successfully developed a simple and concise two-step method for the synthesis of highly substituted benzo[*a*]carbazole derivatives that proceeds with high atom economy from easily available precursors. Furthermore, the syntheses of biologically important indoleacetic acid derivatives and other indole derivatives from the same intermediate demonstrate the diversity of the approach.

Experimental Section

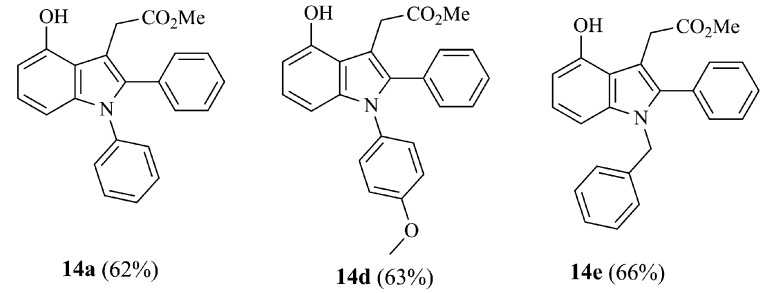
General Methods: All reagents for the reactions were purchased from commercial sources and used without further purification. Solvents were used after distillation. Enamines **1** and arylglyoxals **2** were prepared according to the literature procedure.[8a] Reactions with Pd/C were performed under dry N_2. The ^{1}H NMR spectroscopic data were recorded at 300 MHz, and and chemical shifts are reported in ppm. The ^{13}C NMR spectroscopic data were recorded at 75 MHz with a Bruker AVANCE 300 spectrometer, and the samples were dissolved in $CDCl_3$ or deuterated dimethyl sulfoxide {[D_6]DMSO}. Elemental analyses were performed with a Perkin–Elmer instrument. X-ray crystallography was performed with a Bruker APEX-II instrument.

Table 3. Synthesis of indoleacetic acid derivatives **14**.[a]

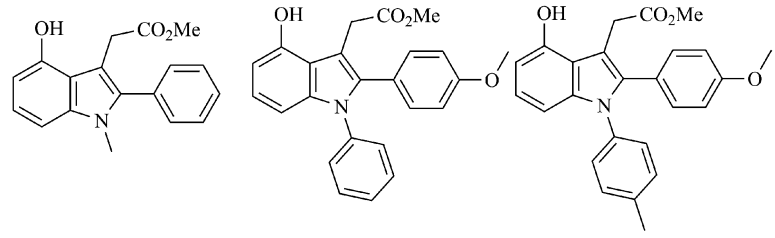


13 **14** (60–66%)

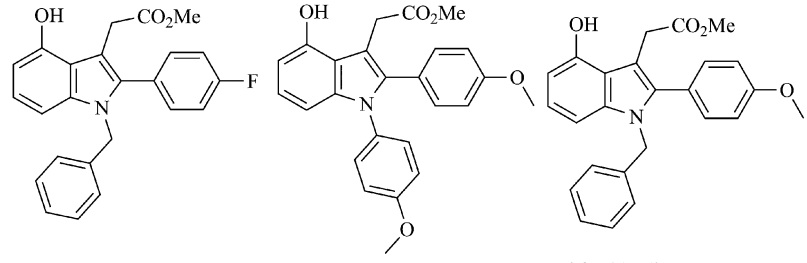
R_1 = Aryl, Bn, Me
R_2 = H, OMe, F



14a (62%) **14d** (63%) **14e** (66%)



14f (60%) **14j** (61%) **14k** (60%)



14m (61%) **14o** (63%) **14p** (64%)

[a] Isolated yield.

Synthesis of 2-(1,2-Diaryl-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl)-2-cyanoacetamides 4: A mixture of enamine **1** (2.0 mmol), arylglyoxal monohydrate **2** (2.0 mmol), and malononitrile (2.2 mmol) in ethanol (15 mL) was heated at reflux for 0.5 h. Upon completion of the reaction, the crude mass was poured into a saturated brine solution. A white precipitate formed, and this was isolated by filtration and then dried. Recrystallization (ethanol/chloroform) afforded **4** as colorless crystals.

Synthesis of 11-Aryl-5,7-dihydroxy-11*H*-benzo[*a*]carbazole-6-carbonitriles 9: A mixture of 2-(1,2-diaryl-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl)-2-cyanoacetamide **4** (1 mmol) and Pd/C (20 mol-%) in diphenyl ether (10 mL) was heated at reflux for 1 h under N_2. Upon completion of reaction, the crude mass was filtered through a bed of Celite (ethyl acetate), and the filtrate was concentrated. The crude residue was purified by chromatography on a silica gel column (EtOAc/hexane, 1:3) to give pure **9** as a yellow solid.

Synthesis of 5-Hydroxy-3-methoxy-7-oxo-11-*p*-tolyl-8,9,10,11-tetrahydro-7*H*-benzo[*a*]carbazole-6-carbonitrile (10k): 2-Cyano-2-[2-(4-methoxyphenyl)-4-oxo-1-*p*-tolyl-4,5,6,7-tetrahydro-1*H*-3-indolyl]-acetamide (**4k**, 1 mmol) in diphenyl ether (10 mL) was heated at reflux for 1 h under N_2. Upon completion of the reaction, the crude mass was purified by chromatography on a silica gel column (EtOAc/hexane, 1:1) to give pure **10k** as a yellow solid.

Synthesis of 2-(4-Oxo-1,2-diphenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl)-acetic Acid (11a): 2-Cyano-2-(4-oxo-1,2-diphenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl)acetamide (**4a**, 1 mmol) in concentrated HCl/AcOH (1:1, 10 mL) was heated at reflux for 1 h. Upon completion

of the reaction, the mixture was poured into water. A white solid precipitate formed, and this was isolated by filtration and then dried to produce **11a** as a white powdery product.

Synthesis of 3-Methyl-1,2-diphenyl-1*H*-3-indol-4-ol (12a): 2-(4-Oxo-1,2-diphenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl)acetic acid (**11a**, 0.5 mmol) and Pd/C (20 mol-%) in diphenyl ether (7 mL) was heated at reflux for 0.5 h under N_2. Upon completion of reaction, the crude mass was filtered through a bed of Celite (ethyl acetate), and the filtrate was concentrated. The crude residue was purified by chromatography on a silica gel column (EtOAc/hexane, 1:4) to produce **12a** as a white solid.

Synthesis of Methyl (1,2-Diaryl-4-oxo-4,5,6,7-tetrahydro-1*H*-indol-3-yl)acetates 13: 2-(1,2-Diaryl-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl)-2-cyanoacetamide **4** (1 mmol) in concentrated HCl/AcOH (1:1, 10 mL) was heated at reflux for 1 h. Upon completion of reaction, the mixture was poured into water. A white solid precipitate formed, and this was isolated by filtration and then dried to produce **11** as a white powdery product. The white crude product **11** was dissolved in dry methanol (10 mL), and thionyl chloride (1.5 mmol) was added under ice-cold conditions. The reaction mixture was then kept at room temperature for 1 h. Upon completion of the reaction, the methanol was removed, and the reaction mixture was neutralized by the addition of aqueous $NaHCO_3$. The resulting mixture was extracted with ethyl acetate, and the organic phase was dried and concentrated to produce **13** as a white solid.

Synthesis of Methyl (1,2-Diaryl-4-hydroxyindol-3-yl)acetates 14: A mixture of compound methyl (1,2-diaryl-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl)acetate **13** (0.5 mmol) and Pd/C (20 mol-%) in diphenyl ether (7 mL) was heated at reflux for 0.5 h under N_2. Upon completion of the reaction, the crude mass was filtered through a bed of Celite (ethyl acetate), and the filtrate was concentrated. The crude residue was purified by chromatography on silica gel column (EtOAc/hexane, 1:4) to produce **14** as a yellow solid.

2-Cyano-2-(4-oxo-1,2-diphenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl)acetamide (4a): White solid (582 mg, 79% yield); m.p. 216–218 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.53 (s, 1 H), 7.40–7.34 (m, 4 H), 7.27–7.25 (m, 5 H), 7.18–7.16 (m, 2 H), 5.03 (s, 1 H), 2.69–2.59 (m, 2 H), 2.49–2.45 (m, 2 H), 2.08–2.04 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 193.9, 165.8, 145.4, 136.5, 135.0, 130.7, 129.1, 128.5, 128.3, 128.2, 127.9, 116.9, 109.2, 37.8, 35.7, 23.1, 22.3 ppm. IR (KBr): $\tilde{\nu}$ = 2244, 1709, 1676 cm^{-1}. $C_{23}H_{19}N_3O_2$ (369.41): calcd. C 74.78, H 5.18, N 11.37; found C 74.70, H 5.12, N 11.29.

2-Cyano-2-(4-oxo-2-phenyl-1-*p*-tolyl-4,5,6,7-tetrahydro-1*H*-3-indolyl)acetamide (4b): White solid (566 mg, 74% yield); m.p. 138–140 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.41 (s, 1 H), 7.22–7.17 (m, 4 H), 7.10–7.03 (m, 6 H), 4.92 (s, 1 H), 2.54–2.49 (m, 2 H), 2.41–2.35 (m, 2 H), 2.1 (s, 3 H), 1.98–1.89 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 193.9, 165.7, 145.5, 137.9, 135.0, 133.9, 130.6, 129.6, 129.1, 128.3, 128.2, 127.6, 116.9, 116.8, 109.0, 37.8, 35.6, 23.0, 22.3, 20.6 ppm. IR (KBr): $\tilde{\nu}$ = 2251, 1708, 1661 cm^{-1}. $C_{24}H_{21}N_3O_2$ (383.44): calcd. C 75.18, H 5.52, N 10.96; found C 75.09, H 5.45, N 10.87.

2-Cyano-2-[1-(4-fluorophenyl)-4-oxo-2-phenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl]acetamide (4c): White solid (596 mg, 77% yield); m.p. 88–90 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.50 (s, 1 H), 7.42–7.17 (m, 8 H), 7.15–7.12 (m, 2 H), 4.97 (s, 1 H), 2.65–2.57 (m, 2 H), 2.42–2.36 (m, 2 H), 2.11–2.03 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 193.8, 165.7, 162.8, 159.7, 145.5, 135.5, 132.8, 130.7, 130.2, 128.9, 128.4, 128.2, 116.8, 116.1, 115.8, 109.1, 37.8, 35.6, 23.0, 22.2 ppm. IR (KBr): $\tilde{\nu}$ = 2255, 1705, 1664 cm^{-1}. $C_{23}H_{18}FN_3O_2$ (387.40): calcd. C 71.31, H 4.68, N 10.85; found C 71.20, H 4.59, N 10.77.

2-Cyano-2-[1-(4-methoxyphenyl)-4-oxo-2-phenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl]acetamide (4d): White solid (606 mg, 76% yield); m.p. 140–142 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.52 (s, 1 H), 7.32–7.26 (m, 4 H), 7.21–7.17 (m, 4 H), 6.92 (d, J = 8.7 Hz, 2 H), 5.01 (s, 1 H), 3.72 (s, 3 H), 2.62–2.57 (m, 2 H), 2.45–2.44 (m, 2 H), 2.07–2.03 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 193.8, 165.8, 158.8, 145.7, 135.2, 130.7, 129.2, 129.1, 128.3, 128.2, 116.9, 116.7, 114.2, 108.9, 55.3, 37.8, 35.7, 23.0, 22.3 ppm. IR (KBr): $\tilde{\nu}$ = 2246, 1707, 1667 cm^{-1}. $C_{24}H_{21}N_3O_3$ (399.44): calcd. C 72.16, H 5.30, N 10.52; found C 72.08, H 5.23, N 10.41.

2-(1-Benzyl-4-oxo-2-phenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl)-2-cyanoacetamide (4e): White solid (572 mg, 72% yield); m.p. 200–202 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.42–7.41 (m, 4 H), 7.29–7.23 (m, 6 H), 6.91 (d, J = 6.9 Hz, 2 H), 5.05 (s, 3 H), 2.69–2.67 (m, 2 H), 2.40–2.39 (m, 2 H), 2.06–2.02 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 194.3, 166.1, 145.3, 137.3, 135.2, 131.2, 129.5, 129.3, 129.1, 129.0, 127.8, 126.4, 117.4, 117.1, 109.4, 47.7, 38.1, 35.8, 23.4, 22.1 ppm. IR (KBr): $\tilde{\nu}$ = 2249, 1711, 1669 cm^{-1}. $C_{24}H_{21}N_3O_2$ (383.44): calcd. C 75.18, H 5.52, N 10.96; found C 75.10, H 5.46, N 10.87.

2-Cyano-2-(1-methyl-4-oxo-2-phenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl)acetamide (4f): White solid (448 mg, 73% yield); m.p. 196–198 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.50–7.48 (m, 3 H), 7.41–7.39 (m, 3 H), 7.25 (s, 1 H), 4.99 (s, 1 H), 3.35 (s, 3 H), 2.85–2.82 (m, 2 H), 2.40–2.38 (m, 2 H), 2.11–2.10 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 194.0, 166.3, 145.4, 134.9, 131.1, 129.5, 129.2, 129.0, 117.3, 116.6, 108.8, 38.8, 35.9, 32.1, 23.2, 21.8 ppm. IR (KBr): $\tilde{\nu}$ = 2247, 1701, 1660 cm^{-1}. $C_{18}H_{17}N_3O_2$ (307.34): calcd. C 70.34, H 5.58, N 13.67; found C 70.25, H 5.50, N 13.59.

2-Cyano-2-(4-oxo-1,2-di-*p*-tolyl-4,5,6,7-tetrahydro-1*H*-3-indolyl)acetamide (4g): White solid (587 mg, 74% yield); m.p. 76–78 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.48 (s, 1 H), 7.28 (s, 1 H), 7.18–7.13 (m, 4 H), 7.10–7.01 (m, 4 H), 4.96 (s, 1 H), 2.58–2.52 (m, 2 H), 2.42–2.32 (m, 2 H), 2.26 (s, 3 H), 2.22 (s, 3 H), 2.10–2.01 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 194.1, 166.1, 145.7, 138.2, 138.0, 135.4, 134.3, 130.8, 129.9, 129.5, 128.0, 126.5, 117.3, 117.1, 109.2, 38.2, 36.0, 23.4, 22.6, 21.1, 20.9 ppm. IR (KBr): $\tilde{\nu}$ = 2250, 1705, 1669 cm^{-1}. $C_{25}H_{23}N_3O_2$ (397.46): calcd. C 75.54, H 5.83, N 10.57; found C 75.45, H 5.73, N 10.48.

2-Cyano-2-[1-(4-fluorophenyl)-4-oxo-2-*p*-tolyl-4,5,6,7-tetrahydro-1*H*-3-indolyl]acetamide (4h): White solid (585 mg, 73% yield); m.p. 108–110 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.47 (s, 1 H), 7.29–7.23 (m, 2 H), 7.22–7.19 (m, 3 H), 7.04–7.00 (m, 4 H), 4.92 (s, 1 H), 2.54–2.45 (m, 2 H), 2.42–2.39 (m, 2 H), 2.19 (s, 3 H), 2.01–1.94 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 194.2, 166.2, 163.2, 145.9, 138.2, 135.6, 133.3, 130.9, 130.5, 129.3, 126.4, 117.4, 116.6, 116.3, 109.4, 38.2, 36.1, 23.4, 22.6, 21.2 ppm. IR (KBr): $\tilde{\nu}$ = 2254, 1703, 1654 cm^{-1}. $C_{24}H_{20}FN_3O_2$ (401.43): calcd. C 71.81, H 5.02, N 10.47; found C 71.70, H 4.92, N 10.36.

2-Cyano-2-[1-(4-methoxyphenyl)-4-oxo-2-*p*-tolyl-4,5,6,7-tetrahydro-1*H*-3-indolyl]acetamide (4i): White solid (628 mg, 76% yield); m.p. 90–92 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.46 (s, 1 H), 7.25 (s, 1 H), 7.15 (d, J = 4.8 Hz, 2 H), 7.11–7.01 (m, 4 H), 6.88 (d, J = 8.1 Hz, 2 H), 4.92 (s, 1 H), 3.68 (s, 3 H), 2.54–2.52 (m, 2 H), 2.45–2.38 (m, 2 H), 2.19 (s, 3 H), 2.02–1.94 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 194.2, 166.3, 159.2, 145.9, 138.2, 135.6, 133.3, 130.9, 129.5, 129.2, 126.6, 117.4, 117.0, 114.6, 109.1, 55.7, 38.2, 36.1, 23.4, 22.7, 21.2 ppm. IR (KBr): $\tilde{\nu}$ = 2248, 1701,

1669 cm^{-1}. $C_{25}H_{23}N_3O_3$ (413.46): calcd. C 72.62, H 5.61, N 10.16; found C 72.54, H 5.52, N 10.03.

2-Cyano-2-[2-(4-methoxyphenyl)-4-oxo-1-phenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl]acetamide (4j): White solid (598 mg, 75% yield); m.p. 198–200 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.41 (s, 1 H), 7.33–7.28 (m, 3 H), 7.22 (s, 1 H), 7.17 (d, J = 6.6 Hz, 2 H), 6.99 (d, J = 8.7 Hz, 2 H), 6.74 (d, J = 8.7 Hz, 2 H), 4.92 (s, 1 H), 3.61 (s, 3 H), 2.52–2.49 (m, 2 H), 2.36–2.35 (m, 2 H), 1.98–1.94 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 194.3, 166.2, 159.5, 145.5, 137.0, 135.4, 132.5, 129.5, 128.8, 128.4, 121.5, 117.4, 117.2, 114.1, 109.3, 55.4, 38.2, 36.1, 23.5, 22.7 ppm. IR (KBr): $\tilde{\nu}$ = 2244, 1710, 1670 cm^{-1}. $C_{24}H_{21}N_3O_3$ (399.44): calcd. C 72.16, H 5.30, N 10.52; found C 72.07, H 5.22, N 10.43.

2-Cyano-2-[2-(4-methoxyphenyl)-4-oxo-1-*p*-tolyl-4,5,6,7-tetrahydro-1*H*-3-indolyl]acetamide (4k): White solid (594 mg, 72% yield); m.p. 178–180 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.48 (s, 1 H), 7.29 (s, 1 H), 7.19–7.07 (m, 6 H), 6.82 (d, J = 8.7 Hz, 2 H), 4.98 (s, 1 H), 3.68 (s, 3 H), 2.58–2.57 (m, 2 H), 2.43–2.42 (m, 2 H), 2.26 (s, 3 H), 2.05–2.01 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 193.8, 165.8, 159.1, 145.2, 137.8, 135.0, 134.0, 132.0, 129.6, 127.6, 121.2, 116.9, 116.7, 113.6, 108.8, 55.0, 37.8, 35.7, 23.0, 22.3, 20.6 ppm. IR (KBr): $\tilde{\nu}$ = 2247, 1708, 1669 cm^{-1}. $C_{25}H_{23}N_3O_3$ (413.46): calcd. C 72.62, H 5.61, N 10.16; found C 72.52, H 5.53, N 10.07.

2-Cyano-2-[2-(4-fluorophenyl)-4-oxo-1-phenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl]acetamide (4l): White solid (557 mg, 72% yield); m.p. 80–82 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.51 (s, 1 H), 7.39–7.31 (m, 4 H), 7.24 (d, J = 8.1 Hz, 2 H), 7.19 (d, J = 8.4 Hz, 2 H), 7.13–7.05 (m, 2 H), 5.11 (s, 1 H), 2.61–2.54 (m, 2 H), 2.47–2.40 (m, 2 H), 2.04–2.01 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 194.4, 166.1, 164.0, 160.7, 145.7, 136.7, 134.3, 133.5, 133.4, 129.6, 128.9, 128.4, 126.0, 117.3, 115.7, 115.4, 109.8, 38.2, 36.0, 23.5, 22.7 ppm. IR (KBr): $\tilde{\nu}$ = 2255, 1705, 1664 cm^{-1}. $C_{23}H_{18}FN_3O_2$ (387.40): calcd. C 71.31, H 4.68, N 10.85; found C 71.23, H 4.58, N 10.75.

2-[1-Benzyl-2-(4-fluorophenyl)-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl]-2-cyanoacetamide (4m): White solid (569 mg, 71% yield); m.p. 74–76 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.46 (s, 1 H), 7.31–7.21 (m, 8 H), 6.90 (d, J = 6.9 Hz, 2 H), 5.14 (s, 1 H), 5.03 (s, 2 H), 2.71–2.69 (m, 2 H), 2.41–2.38 (m, 2 H), 2.05–2.04 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 194.4, 166.1, 161.3, 145.2, 137.2, 133.9, 133.6, 129.1, 127.8, 126.4, 117.0, 116.0, 115.7, 109.7, 47.7, 38.1, 35.7, 23.3, 22.1 ppm. IR (KBr): $\tilde{\nu}$ = 2249, 1711, 1669 cm^{-1}. $C_{24}H_{20}FN_3O_2$ (401.43): calcd. C 71.81, H 5.02, N 10.47; found C 71.70, H 4.91, N 10.33.

2-[1-(4-Chlorophenyl)-2-(4-methoxyphenyl)-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl]-2-cyanoacetamide (4n): White solid (668 mg, 77% yield); m.p. 186–188 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.41–7.37 (m, 3 H), 7.23–7.20 (m, 3 H), 7.01 (d, J = 8.4 Hz, 2 H), 6.77 (d, J = 7.8 Hz, 2 H), 4.91 (s, 1 H), 3.62 (s, 3 H), 2.54–2.52 (m, 2 H), 2.41–2.35 (m, 2 H), 1.98–1.97 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 193.8, 165.8, 159.2, 145.2, 135.5, 134.9, 133.0, 132.1, 129.8, 129.2, 120.8, 116.9, 113.8, 109.1, 55.0, 37.8, 35.7, 23.0, 22.2 ppm. IR (KBr): $\tilde{\nu}$ = 2251, 1708, 1671 cm^{-1}. $C_{24}H_{20}ClN_3O_3$ (433.88): calcd. C 66.44, H 4.65, N 9.68; found C 66.34, H 4.57, N 9.60.

2-Cyano-2-[1,2-bis(4-methoxyphenyl)-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl]acetamide (4o): White solid (626 mg, 73% yield); m.p. 140–142 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.48 (s, 1 H), 7.29 (s, 1 H), 7.18 (d, J = 8.7 Hz, 2 H), 7.09 (d, J = 8.7 Hz, 2 H), 6.91 (d, J = 9.0 Hz, 2 H), 6.83 (d, J = 8.7 Hz, 2 H), 4.98 (s, 1 H), 3.72 (s, 3 H), 3.69 (s, 3 H), 2.57–2.56 (m, 2 H), 2.43–2.42 (m, 2 H), 2.05–2.01 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 193.8, 165.9, 159.1, 158.8, 145.4, 135.2, 132.0, 129.2, 129.1, 121.2, 117.0, 116.5, 114.2, 113.6, 108.6, 55.3, 55.0, 37.8, 35.7, 23.0, 22.2 ppm. IR (KBr): $\tilde{\nu}$ = 2254, 1710, 1670 cm^{-1}. $C_{25}H_{23}N_3O_4$ (429.46): calcd. C 69.92, H 5.40, N 9.78; found C 69.82, H 5.32, N 9.71.

2-[1-Benzyl-2-(4-methoxyphenyl)-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl]-2-cyanoacetamide (4p): White solid (586 mg, 71% yield); m.p. 150–152 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.17 (s, 1 H), 7.08–6.96 (m, 6 H), 6.74–6.67 (m, 4 H), 4.81 (s, 1 H), 4.79 (s, 2 H), 3.52 (s, 3 H), 2.43–2.42 (m, 2 H), 2.15–2.14 (m, 2 H), 1.81–1.79 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 193.8, 165.8, 159.7, 144.6, 137.0, 134.7, 132.2, 128.7, 127.3, 125.9, 120.8, 117.0, 116.6, 114.0, 108.9, 55.1, 47.2, 37.7, 35.5, 22.9, 21.7 ppm. IR (KBr): $\tilde{\nu}$ = 2247, 1709, 1664 cm^{-1}. $C_{25}H_{23}N_3O_3$ (413.46): calcd. C 72.62, H 5.61, N 10.16; found C 72.52, H 5.53, N 10.07.

2-Cyano-2-[2-(4-methoxyphenyl)-1-methyl-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl]acetamide (4q): White solid (484 mg, 73% yield); m.p. 180–182 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.40 (s, 1 H), 7.33 (d, J = 8.7 Hz, 2 H), 7.25 (s, 1 H), 7.06 (d, J = 8.7 Hz, 2 H), 5.00 (s, 1 H), 3.81 (s, 3 H), 3.33 (s, 3 H), 2.86–2.82 (m, 2 H), 2.41–2.37 (m, 2 H), 2.11–2.07 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 194.0, 166.4, 160.0, 145.2, 134.8, 132.5, 121.5, 117.4, 116.5, 114.5, 108.6, 55.6, 38.1, 35.9, 32.0, 23.2, 21.8 ppm. IR (KBr): $\tilde{\nu}$ = 2250, 1709, 1669 cm^{-1}. $C_{19}H_{19}N_3O_3$ (337.37): calcd. C 67.64, H 5.68, N 12.46; found C 67.55, H 5.61, N 12.38.

2-[1-(4-Chlorophenyl)-4-oxo-2-phenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl]-2-cyanoacetamide (4r): White solid (622 mg, 77% yield); m.p. 232–234 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.52 (s, 1 H), 7.47 (d, J = 8.7 Hz, 2 H), 7.39–7.29 (m, 6 H), 7.16 (t, J = 3.6 Hz, 2 H), 5.0 (s, 1 H), 2.67–2.60 (m, 2 H), 2.50–2.44 (m, 2 H), 2.08–2.06 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 193.8, 165.7, 145.4, 135.4, 135.0, 133.1, 130.7, 129.8, 129.2, 128.9, 128.5, 128.3, 117.0, 116.9, 109.4, 37.8, 35.6, 23.0, 22.2 ppm. IR (KBr): $\tilde{\nu}$ = 2255, 1710, 1664 cm^{-1}. $C_{23}H_{18}ClN_3O_2$ (403.86): calcd. C 68.40, H 4.49, N 10.40; found C 68.31, H 4.43, N 10.32.

2-[1-(4-Bromophenyl)-4-oxo-2-phenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl]-2-cyanoacetamide (4s): White solid (636 mg, 71% yield); m.p. 196–198 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.59–7.50 (m, 3 H), 7.27–7.22 (m, 6 H), 7.16–7.13 (m, 2 H), 4.99 (s, 1 H), 2.65–2.58 (m, 2 H), 2.44–2.43 (m, 2 H), 2.08–2.03 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 194.0, 165.9, 145.7, 136.1, 135.2, 132.4, 130.9, 130.3, 129.1, 128.7, 128.6, 121.8, 117.3, 117.1, 109.6, 38.1, 35.9, 23.3, 22.5 ppm. IR (KBr): $\tilde{\nu}$ = 2252, 1704, 1659 cm^{-1}. $C_{23}H_{18}BrN_3O_2$ (448.31): calcd. C 61.62, H 4.05, N 9.37; found C 61.53, H 3.97, N 9.30.

2-[2-(4-Chlorophenyl)-4-oxo-1-phenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl]-2-cyanoacetamide (4t): White solid (628 mg, 78% yield); m.p. 236–238 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.53 (s, 1 H), 7.43–7.32 (m, 6 H), 7.27 (d, J = 7.2 Hz, 2 H), 7.19–7.16 (dd, J_1 = 7.2 Hz, J_2 = 1.8 Hz, 2 H), 5.17 (s, 1 H), 2.62–2.60 (m, 2 H), 2.45–2.43 (m, 2 H), 2.07–2.04 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 194.0, 165.7, 145.5, 136.2, 133.6, 133.3, 132.5, 129.3, 128.6, 128.2, 128.1, 127.9, 116.9, 109.6, 37.8, 35.4, 23.0, 22.3 ppm. IR (KBr): $\tilde{\nu}$ = 2243, 1708, 1664 cm^{-1}. $C_{23}H_{18}ClN_3O_2$ (403.86): calcd. C 68.40, H 4.49, N 10.40; found C 68.29, H 4.40, N 10.33.

2-[1,2-Bis(4-chlorophenyl)-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl]-2-cyanoacetamide (4u): White solid (640 mg, 73% yield); m.p. 199–201 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.53–7.47 (m, 3 H),

7.39–7.31 (m, 5 H), 7.19 (d, J = 8.1 Hz, 2 H), 5.15 (s, 1 H), 2.68–2.63 (m, 2 H), 2.51–2.45 (m, 2 H), 2.08–2.06 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 193.9, 165.6, 145.6, 135.2, 133.6, 133.4, 133.2, 132.5, 129.8, 129.3, 128.4, 127.9, 117.1, 116.8, 109.8, 37.8, 35.4, 23.0, 22.2 ppm. IR (KBr): $\tilde{\nu}$ = 2252, 1709, 1668 cm^{-1}. $C_{23}H_{17}Cl_2N_3O_2$ (438.30): calcd. C 63.03, H 3.91, N 9.59; found C 62.96, H 3.82, N 9.51.

2-[2-(4-Chlorophenyl)-1-(4-methoxyphenyl)-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl]-2-cyanoacetamide (4v): White solid (676 mg, 78% yield); m.p. 115–117 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.52 (s, 1 H), 7.35 (d, J = 8.4 Hz, 3 H), 7.22–7.17 (m, 4 H), 6.95–6.92 (m, 2 H), 5.15 (s, 1 H), 3.74 (s, 3 H), 2.61–2.57 (m, 2 H), 2.46–2.42 (m, 2 H), 2.07–2.03 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 194.0, 165.7, 158.9, 145.8, 133.8, 133.2, 132.5, 129.1, 128.8, 128.2, 116.9, 116.7, 114.3, 109.3, 55.4, 37.8, 35.5, 23.0, 22.7 ppm. IR (KBr): $\tilde{\nu}$ = 2249, 1706, 1675 cm^{-1}. $C_{24}H_{20}ClN_3O_3$ (433.88): calcd. C 66.44, H 4.65, N 9.68; found C 66.36, H 4.58, N 9.61.

2-[1-Benzyl-2-(4-chlorophenyl)-4-oxo-4,5,6,7-tetrahydro-1*H*-3-indolyl]-2-cyanoacetamide (4w): White solid (610 mg, 73% yield); m.p. 157–159 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.39–7.36 (m, 3 H), 7.22–7.14 (m, 6 H), 6.81 (d, J = 6.9 Hz, 2 H), 5.11 (s, 1 H), 4.95 (s, 2 H), 2.61–2.59 (m, 2 H), 2.32–2.30 (m, 2 H), 1.97–1.93 (m, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 194.4, 166.0, 145.4, 137.2, 134.4, 133.7, 133.1, 129.1, 129.0, 128.3, 127.8, 126.3, 117.3, 117.1, 109.9, 47.7, 38.1, 35.6, 23.3, 22.1 ppm. IR (KBr): $\tilde{\nu}$ = 2254, 1709, 1671 cm^{-1}. $C_{24}H_{20}ClN_3O_2$ (417.88): calcd. C 68.98, H 4.82, N 10.06; found C 68.88, H 4.73, N 9.97.

5,7-Dihydroxy-11-phenyl-11*H*-benzo[*a*]carbazole-6-carbonitrile (9a): White solid (185 mg, 53% yield); m.p. 238–240 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.57 (s, 1 H), 10.43 (s, 1 H), 8.38 (d, J = 8.1 Hz, 1 H), 7.65–7.60 (m, 3 H), 7.51–7.47 (m, 3 H), 7.33 (t, J = 6.9 Hz, 1 H), 7.21 (d, J = 8.4 Hz, 1 H), 7.13 (t, J = 8.1 Hz, 1 H), 6.61 (d, J = 7.5 Hz, 1 H), 6.41 (d, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 154.9, 153.4, 144.0, 139.5, 130.5, 129.3, 129.0, 128.8, 128.2, 127.0, 125.1, 124.2, 124.0, 123.4, 121.7, 117.4, 115.4, 110.4, 105.5, 101.0, 91.0 ppm. IR (KBr): $\tilde{\nu}$ = 3358, 2215 cm^{-1}. $C_{23}H_{14}N_2O_2$ (350.36): calcd. C 78.84, H 4.03, N 8.00; found C 78.76, H 3.96, N 7.92.

5,7-Dihydroxy-11-*p*-tolyl-11*H*-benzo[*a*]carbazole-6-carbonitrile (9b): White solid (186 mg, 51% yield); m.p. 220–222 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.61 (s, 1 H), 10.47 (s, 1 H), 8.43 (d, J = 8.4 Hz, 1 H), 7.55–7.48 (m, 3 H), 7.38–7.29 (m, 3 H), 7.20–7.04 (m, 2 H), 6.65 (d, J = 7.8 Hz, 1 H), 6.44 (d, J = 8.1 Hz, 1 H), 2.48 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 155.2, 153.8, 144.6, 139.2, 137.3, 131.4, 130.5, 129.8, 128.8, 128.4, 127.3, 125.4, 124.6, 123.9, 122.1, 117.9, 115.7, 110.8, 105.8, 101.5, 91.4, 21.1 ppm. IR (KBr): $\tilde{\nu}$ = 3357, 2213 cm^{-1}. $C_{24}H_{16}N_2O_2$ (364.39): calcd. C 79.11, H 4.43, N 7.69; found C 79.02, H 4.34, N 7.61.

11-(4-Fluorophenyl)-5,7-dihydroxy-11*H*-benzo[*a*]carbazole-6-carbonitrile (9c): White solid (202 mg, 55% yield); m.p. 262–264 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.49 (br. s, 2 H), 8.42 (d, J = 8.4 Hz, 1 H), 7.63–7.52 (m, 5 H), 7.44 (t, J = 7.2 Hz, 1 H), 7.27 (d, J = 8.4 Hz, 1 H), 7.18 (t, J = 8.1 Hz, 1 H), 6.66 (d, J = 7.8 Hz, 1 H), 6.45 (d, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 164.1, 160.8, 155.4, 153.8, 144.6, 136.3, 131.5, 129.4, 128.8, 127.5, 125.5, 124.7, 124.5, 123.8, 122.0, 118.0, 117.7, 115.9, 110.9, 106.0, 101.4, 91.3 ppm. IR (KBr): $\tilde{\nu}$ = 3356, 2214 cm^{-1}. $C_{23}H_{13}FN_2O_2$ (368.35): calcd. C 74.99, H 3.56, N 7.60; found C 74.90, H 3.47, N 7.51.

5,7-Dihydroxy-11-(4-methoxyphenyl)-11*H*-benzo[*a*]carbazole-6-carbonitrile (9d): White solid (213 mg, 56% yield); m.p. 280–282 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.57 (br. s, 1 H), 10.44 (s, 1 H), 8.41 (d, J = 8.1 Hz, 1 H), 7.53–7.51 (m, 1 H), 7.45–7.33 (m, 4 H), 7.25–7.13 (m, 3 H), 6.66–6.62 (dd, ^1J = 7.8 Hz, ^2J = 2.1 Hz, 1 H), 6.45–6.41 (dd, J_1 = 8.1 Hz, J_2 = 2.4 Hz, 1 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 160.0, 155.1, 153.8, 144.8, 132.3, 130.3, 129.6, 128.6, 127.2, 125.4, 124.6, 124.5, 123.9, 122.1, 117.9, 116.0, 115.5, 110.7, 105.8, 101.5, 91.4, 56.0 ppm. IR (KBr): $\tilde{\nu}$ = 3358, 2217 cm^{-1}. $C_{24}H_{16}N_2O_3$ (380.39): calcd. C 75.78, H 4.24, N 7.36; found C 75.70, H 4.16, N 7.25.

11-Benzyl-5,7-dihydroxy-11*H*-benzo[*a*]carbazole-6-carbonitrile (9e): White solid (184 mg, 51% yield); m.p. 226–228 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.50 (s, 1 H), 10.43 (s, 1 H), 8.40 (t, J = 5.4 Hz, 1 H), 8.33 (t, J = 5.4 Hz, 1 H), 7.58–7.55 (m, 2 H), 7.29–7.20 (m, 5 H), 7.06 (d, J = 8.1 Hz, 2 H), 6.64 (d, J = 7.8 Hz, 1 H), 6.04 (s, 2 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 154.8, 153.8, 143.7, 138.1, 130.7, 129.3, 129.1, 127.6, 127.4, 126.3, 126.2, 125.4, 124.6, 123.9, 122.7, 117.9, 115.4, 110.5, 105.6, 101.0, 91.6, 49.6 ppm. IR (KBr): $\tilde{\nu}$ = 3358, 2217 cm^{-1}. $C_{24}H_{16}N_2O_2$ (364.39): calcd. C 79.11, H 4.43, N 7.69; found C 79.02, H 4.36, N 7.60.

5,7-Dihydroxy-11-methyl-11*H*-benzo[*a*]carbazole-6-carbonitrile (9f): Yellow solid (144 mg, 50% yield); m.p. 272–274 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.45 (s, 1 H), 10.34 (s, 1 H), 8.82 (d, J = 8.4 Hz, 1 H), 8.45 (d, J = 8.4 Hz, 1 H), 7.79 (t, J = 7.2 Hz, 1 H), 7.66 (t, J = 7.5 Hz, 1 H), 7.27 (t, J = 7.8 Hz, 1 H), 7.17 (d, J = 8.1 Hz, 1 H), 6.61 (d, J = 7.5 Hz, 1 H), 4.31 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 154.4, 153.7, 143.4, 129.7, 128.9, 126.9, 125.4, 124.5, 124.4, 123.1, 118.0, 114.7, 110.3, 105.0, 101.0, 91.5, 35.0 ppm. IR (KBr): $\tilde{\nu}$ = 3353, 2210 cm^{-1}. $C_{18}H_{12}N_2O_2$ (288.30): calcd. C 74.99, H 4.20, N 9.72; found C 74.90, H 4.12, N 9.63.

5,7-Dihydroxy-3-methyl-11-*p*-tolyl-11*H*-benzo[*a*]carbazole-6-carbonitrile (9g): Yellow solid (197 mg, 52% yield); m.p. 228–230 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.43 (s, 1 H), 10.38 (s, 1 H), 8.18 (s, 1 H), 7.48 (d, J = 7.5 Hz, 2 H), 7.36 (d, J = 7.8 Hz, 2 H), 7.21–7.09 (m, 3 H), 6.61 (d, J = 7.5 Hz, 1 H), 6.42 (d, J = 8.1 Hz, 1 H), 2.48 (s, 3 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 154.8, 153.6, 144.4, 139.1, 137.3, 134.9, 131.4, 130.4, 130.1, 129.6, 128.8, 127.9, 127.0, 124.6, 123.6, 122.1, 122.0, 117.9, 105.8, 101.4, 91.5, 21.6, 21.3 ppm. IR (KBr): $\tilde{\nu}$ = 3357, 2213 cm^{-1}. $C_{25}H_{18}N_2O_2$ (378.42): calcd. C 79.35, H 4.79, N 7.40; found C 79.25, H 4.70, N 7.32.

11-(4-Fluorophenyl)-5,7-dihydroxy-3-methyl-11*H*-benzo[*a*]carbazole-6-carbonitrile (9h): White solid (195 mg, 51% yield); m.p. 251–253 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.43 (br. s, 2 H), 8.20 (s, 1 H), 7.57–7.53 (m, 4 H), 7.28 (d, J = 6.0 Hz, 1 H), 7.16 (t, J = 8.1 Hz, 2 H), 6.65 (d, J = 7.5 Hz, 1 H), 6.45 (d, J = 8.1 Hz, 1 H), 2.45 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 154.9, 153.7, 144.4, 135.0, 131.4, 131.3, 130.6, 129.6, 127.2, 124.7, 123.7, 122.0, 118.0, 117.7, 115.2, 110.9, 106.0, 101.3, 91.4, 21.6 ppm. IR (KBr): $\tilde{\nu}$ = 3360, 2221 cm^{-1}. $C_{24}H_{15}FN_2O_2$ (382.38): calcd. C 75.38, H 3.95, N 7.33; found C 75.30, H 3.88, N 7.24.

5,7-Dihydroxy-11-(4-methoxyphenyl)-3-methyl-11*H*-benzo[*a*]carbazole-6-carbonitrile (9i): Yellow solid (209 mg, 53% yield); m.p. 240–242 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.44 (br. s, 1 H), 10.38 (s, 1 H), 8.19 (s, 1 H), 7.42 (d, J = 7.8 Hz, 2 H), 7.24–7.21 (m, 4 H), 7.14 (t, J = 7.8 Hz, 1 H), 6.62 (d, J = 7.8 Hz, 1 H), 6.43 (d, J = 8.4 Hz, 1 H), 3.91 (s, 3 H), 2.45 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 159.9, 154.7, 153.6, 144.6, 134.9, 132.3, 130.5, 130.3, 129.8, 127.0, 124.7, 123.6, 122.0, 118.0, 116.0, 114.8, 110.7, 105.7, 101.4, 91.7, 56.0, 21.6 ppm. IR (KBr): $\tilde{\nu}$ = 3361,

2227 cm^{-1}. $C_{25}H_{18}N_2O_3$ (394.42): calcd. C 76.13, H 4.60, N 7.10; found C 76.05, H 4.51, N 7.01.

5,7-Dihydroxy-3-methoxy-11-phenyl-11*H*-benzo[*a*]carbazole-6-carbonitrile (9j): Yellow solid (198 mg, 52% yield); m.p. 230–232 °C. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 10.47 (s, 1 H), 10.39 (s, 1 H), 7.79 (s, 1 H), 7.75–7.66 (m, 3 H), 7.51 (d, J = 7.8 Hz, 2 H), 7.23–7.01 (m, 3 H), 6.64 (d, J = 7.8 Hz, 1 H), 6.43 (d, J = 8.4 Hz, 1 H), 3.88 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 157.1, 154.2, 153.5, 144.2, 140.0, 131.0, 129.9, 129.7, 129.2, 128.2, 126.9, 125.9, 119.8, 118.7, 117.9, 114.1, 110.9, 106.0, 104.4, 101.3, 91.8, 55.8 ppm. IR (KBr): $\tilde{\nu}$ = 3360, 2228 cm^{-1}. $C_{24}H_{16}N_2O_3$ (380.39): calcd. C 75.78, H 4.24, N 7.36; found C 75.69, H 4.17, N 7.28.

5,7-Dihydroxy-3-methoxy-11-*p*-tolyl-11*H*-benzo[*a*]carbazole-6-carbonitrile (9k): Yellow solid (197 mg, 50% yield); m.p. 170–172 °C. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 10.45 (s, 1 H), 10.38 (s, 1 H), 7.49 (d, J = 8.1 Hz, 2 H), 7.36 (d, J = 8.1 Hz, 2 H), 7.26–7.01 (m, 3 H), 6.86 (d, J = 8.7 Hz, 1 H), 6.63 (d, J = 7.5 Hz, 1 H), 6.41 (d, J = 8.1 Hz, 1 H), 3.84 (s, 3 H), 2.49 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 157.1, 154.1, 153.5, 144.3, 139.2, 137.3, 131.9, 130.1, 128.9, 127.9, 126.8, 125.9, 123.9, 119.7, 118.8, 117.9, 114.4, 110.8, 105.9, 104.3, 101.4, 55.8, 21.3 ppm. IR (KBr): $\tilde{\nu}$ = 3354, 2231 cm^{-1}. $C_{25}H_{18}N_2O_3$ (394.42): calcd. C 76.13, H 4.60, N 7.10; found C 76.05, H 4.51, N 7.02.

3-Fluoro-5,7-dihydroxy-11-phenyl-11*H*-benzo[*a*]carbazole-6-carbonitrile (9l): Yellow solid (199 mg, 54% yield); m.p. 248–250 °C. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 10.70 (s, 1 H), 10.50 (s, 1 H), 8.11 (d, J = 2.4 Hz, 1 H), 7.82–7.70 (m, 3 H), 7.52 (d, J = 7.5 Hz, 2 H), 7.37–7.14 (m, 3 H), 6.66 (d, J = 7.8 Hz, 1 H), 6.44 (d, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 161.4, 154.3, 153.8, 144.4, 139.7, 131.1, 129.9, 129.1, 127.7, 125.7, 124.9, 120.9, 118.2, 117.9, 117.5, 115.5, 110.7, 108.6, 106.1, 101.4, 92.7 ppm. IR (KBr): $\tilde{\nu}$ = 3354, 2205 cm^{-1}. $C_{23}H_{13}FN_2O_2$ (368.35): calcd. C 74.99, H 3.56, N 7.60; found C 74.91, H 3.47, N 7.52.

5-Hydroxy-3-methoxy-7-oxo-11-*p*-tolyl-8,9,10,11-tetrahydro-7*H*-benzo[*a*]carbazole-6-carbonitrile (10k): Yellow solid (225 mg, 57% yield); m.p >300 °C. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 10.63 (s, 1 H), 7.70 (s, 1 H), 7.48–7.41 (m, 4 H), 7.03–6.94 (m, 2 H), 3.82 (s, 3 H), 2.60–2.57 (m, 2 H), 2.47 (s, 3 H), 2.05–1.97 (m, 2 H), 1.31–1.21 (m, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 3342, 2201 cm^{-1}. $C_{25}H_{20}N_2O_3$ (396.43): calcd. C 75.74, H 5.08, N 7.07; found C 75.64, H 5.01, N 6.96.

2-(4-Oxo-1,2-diphenyl-4,5,6,7-tetrahydro-1*H*-3-indolyl)acetic Acid (11a): White solid (310 mg, 90% yield); m.p. 198–200 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.30 (m, 3 H), 7.27–7.17 (m, 5 H), 7.08–7.06 (m, 2 H), 3.61 (s, 2 H), 2.74–2.64 (m, 4 H), 2.07–2.16 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.1, 172.3, 147.0, 136.9, 135.7, 130.7, 129.3, 129.0, 128.5, 128.2, 127.9, 127.5, 118.8, 112.5, 37.6, 33.9, 23.6, 23.0 ppm. IR (KBr): $\tilde{\nu}$ = 2943, 1706 cm^{-1}. $C_{22}H_{19}NO_3$ (345.39): calcd. C 76.50, H 5.54, N 4.06; found C 76.41, H 5.47, N 3.97.

3-Methyl-1,2-diphenyl-1*H*-3-indol-4-ol (12a): White solid (209 mg, 70% yield); m.p. 136–138 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.19 (m, 6 H), 7.18–7.13 (m, 4 H), 6.96 (d, J = 7.8 Hz, 1 H), 6.86 (d, J = 8.4 Hz, 1 H), 6.48–6.45 (dd, J_1 = 7.5 Hz, J_2 = 1.0 Hz, 1 H), 2.60 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.7, 139.8, 138.7, 136.1, 131.9, 130.7, 128.9, 127.9, 127.8, 127.1, 126.7, 123.0, 117.6, 109.8, 105.1, 103.6, 11.6 ppm. IR (KBr): $\tilde{\nu}$ = 3450 cm^{-1}. $C_{21}H_{17}NO$ (299.36): calcd. C 84.25, H 5.72, N 4.68; found C 84.17, H 5.65, N 4.60.

Methyl (4-Oxo-1,2-diphenyl-4,5,6,7-tetrahydro-1*H*-indol-3-yl)acetate (13a): White solid (294 mg, 82% yield); m.p. 180–182 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.26 (m, 3 H), 7.20–7.18 (m, 3 H), 7.09–7.05 (m, 4 H), 3.75 (s, 2 H), 3.72 (s, 3 H), 2.69–2.65 (m, 2 H), 2.53–2.49 (m, 2 H), 2.15–2.10 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.9, 172.9, 144.3, 137.3, 134.2, 130.5, 129.0, 128.1, 128.0, 127.9, 127.7, 127.4, 119.1, 113.5, 51.7, 38.3, 31.2, 23.4, 23.1 ppm. IR (KBr): $\tilde{\nu}$ = 1739, 1642 cm^{-1}. $C_{23}H_{21}NO_3$ (359.41): calcd. C 76.86, H 5.89, N 3.90; found C 76.78, H 5.81, N 3.82.

Methyl [1-(4-Methoxyphenyl)-4-oxo-2-phenyl-4,5,6,7-tetrahydro-1*H*-indol-3-yl]acetate (13d): White solid (334 mg, 86% yield); m.p. 62–64 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.21–7.19 (m, 3 H), 7.08–7.05 (m, 2 H), 7.01 (d, J = 9.0 Hz, 2 H), 6.81 (d, J = 9.0 Hz, 2 H), 3.78 (s, 3 H), 3.74 (s, 2 H), 3.71 (s, 3 H), 2.66–2.62 (m, 2 H), 2.52–2.48 (m, 2 H), 2.14–2.10 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.9, 172.9, 158.9, 144.6, 134.4, 130.5, 130.4, 130.1, 128.7, 128.0, 127.4, 118.9, 114.1, 113.2, 55.4, 51.7, 38.3, 31.2, 23.6, 23.0 ppm. IR (KBr): $\tilde{\nu}$ = 1737, 1644 cm^{-1}. $C_{24}H_{23}NO_4$ (389.44): calcd. C 74.02, H 5.95, N 3.60; found C 73.93, H 5.87, N 3.52.

Methyl (1-Benzyl-4-oxo-2-phenyl-4,5,6,7-tetrahydro-1*H*-indol-3-yl)acetate (13e): White solid (302 mg, 81% yield); m.p. 98–100 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.27 (m, 5 H), 7.24–7.20 (m, 3 H), 6.89 (d, J = 6.6 Hz, 2 H), 4.98 (s, 2 H), 3.68 (s, 3 H), 3.67 (s, 2 H), 2.64–2.60 (m, 2 H), 2.48–2.44 (m, 2 H), 2.15–2.09 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.6, 172.9, 143.6, 137.2, 134.4, 130.7, 130.3, 128.8, 128.5, 128.3, 127.4, 125.7, 118.9, 113.2, 51.6, 47.9, 38.1, 31.0, 23.5, 22.3 ppm. IR (KBr): $\tilde{\nu}$ = 1735, 1640 cm^{-1}. $C_{24}H_{23}NO_3$ (373.44): calcd. C 77.19, H 6.21, N 3.75; found C 77.10, H 6.13, N 3.66.

Methyl (1-Methyl-4-oxo-2-phenyl-4,5,6,7-tetrahydro-1*H*-indol-3-yl)-acetate (13f): White solid (238 mg, 81% yield); m.p. 100–102 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.35 (m, 3 H), 7.31–7.26 (m, 2 H), 3.67 (s, 3 H), 3.63 (s, 2 H), 3.38 (s, 3 H), 2.82–2.78 (m, 2 H), 2.49–2.44 (m, 2 H), 2.21–2.15 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.3, 172.9, 143.5, 134.0, 130.6, 130.5, 128.5, 128.2, 118.3, 112.7, 51.7, 38.0, 31.6, 31.0, 23.3, 22.1 ppm. IR (KBr): $\tilde{\nu}$ = 1733, 1641 cm^{-1}. $C_{18}H_{19}NO_3$ (297.34): calcd. C 72.71, H 6.44, N 4.71; found C 72.62, H 6.36, N 4.63.

Methyl [2-(4-Methoxyphenyl)-4-oxo-1-phenyl-4,5,6,7-tetrahydro-1*H*-indol-3-yl]acetate (13j): White solid (338 mg, 87% yield); m.p. 136–138 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.28 (m, 3 H), 7.09–7.07 (m, 2 H), 6.99 (d, J = 8.7 Hz, 2 H), 6.73 (d, J = 8.7 Hz, 2 H), 3.74 (s, 3 H), 3.73 (s, 2 H), 3.72 (s, 3 H), 2.67–2.63 (m, 2 H), 2.52–2.48 (m, 2 H), 2.16–2.09 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.9, 173.0, 158.9, 144.0, 137.4, 134.1, 131.6, 128.9, 127.8, 127.6, 122.7, 119.0, 113.5, 113.1, 55.1, 51.7, 38.3, 31.2, 23.6, 23.1 ppm. IR (KBr): $\tilde{\nu}$ = 1735, 1646 cm^{-1}. $C_{24}H_{23}NO_4$ (389.44): calcd. C 74.02, H 5.95, N 3.60; found C 73.92, H 5.86, N 3.53.

Methyl [2-(4-Methoxyphenyl)-4-oxo-1-*p*-tolyl-4,5,6,7-tetrahydro-1*H*-indol-3-yl]acetate (13k): White solid (338 mg, 84% yield); m.p. 140–142 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.10 (d, J = 7.8 Hz, 2 H), 7.00–6.94 (m, 4 H), 6.74 (d, J = 8.7 Hz, 2 H), 3.75 (s, 2 H), 3.72 (s, 6 H), 2.66–2.62 (m, 2 H), 2.51–2.47 (m, 2 H), 2.33 (s, 3 H), 2.15–2.07 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.9, 173.0, 158.9, 144.1, 137.7, 134.8, 134.1, 131.7, 129.5, 127.4, 122.8, 118.9, 113.6, 112.9, 55.1, 51.7, 38.3, 31.2, 23.6, 23.1, 21.0 ppm. IR (KBr): $\tilde{\nu}$ = 1738, 1644 cm^{-1}. $C_{25}H_{25}NO_4$ (403.47): calcd. C 74.42, H 6.25, N 3.47; found C 74.34, H 6.17, N 3.36.

Methyl [1-Benzyl-2-(4-fluorophenyl)-4-oxo-4,5,6,7-tetrahydro-1*H*-indol-3-yl]acetate (13m): White solid (317 mg, 81% yield); m.p. 79–81 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.25 (m, 3 H), 7.19–7.17 (m, 2 H), 7.01 (t, J = 8.7 Hz, 2 H), 6.87 (d, J = 7.2 Hz, 2 H),

4.95 (s, 2 H), 3.68 (s, 3 H), 3.63 (s, 2 H), 2.65–2.61 (m, 2 H), 2.49–2.45 (m, 2 H), 2.16–2.08 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.5, 172.7, 143.5, 137.0, 133.1, 132.5, 132.4, 128.8, 127.4, 126.2, 125.5, 118.7, 115.6, 115.3, 113.4, 51.6, 47.6, 38.0, 30.8, 23.4, 22.1 ppm. IR (KBr): $\tilde{\nu}$ = 1733, 1645 cm^{-1}. $C_{24}H_{22}FNO_3$ (391.43): calcd. C 73.64, H 5.66, N 3.58; found C 73.57, H 5.58, N 3.50.

Methyl [1,2-Bis(4-methoxyphenyl)-4-oxo-4,5,6,7-tetrahydro-1*H*-indol-3-yl]acetate (13o): White solid (343 mg, 82% yield); m.p. 148–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.01–6.98 (m, 4 H), 6.82 (d, J = 8.7 Hz, 2 H), 6.74 (d, J = 8.7 Hz, 2 H), 3.78 (s, 3 H), 3.75 (s, 3 H), 3.72 (s, 5 H), 2.64–2.60 (m, 2 H), 2.51–2.47 (m, 2 H), 2.13–2.09 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.9, 173.0, 158.9, 144.3, 134.2, 131.7, 130.2, 128.8, 122.8, 118.8, 114.1, 113.6, 113.5, 112.8, 55.4, 55.1, 51.7, 38.3, 31.2, 23.6, 23.0 ppm. IR (KBr): $\tilde{\nu}$ = 1740, 1642 cm^{-1}. $C_{25}H_{25}NO_5$ (419.46): calcd. C 71.58, H 6.01, N 3.34; found C 71.47, H 5.94, N 3.25.

Methyl [1-Benzyl-2-(4-methoxyphenyl)-4-oxo-4,5,6,7-tetrahydro-1*H*-indol-3-yl]acetate (13p): White solid (322 mg, 80% yield); m.p. 110–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.24 (m, 3 H), 7.13 (d, J = 8.7 Hz, 2 H), 6.90–6.83 (m, 4 H), 4.96 (s, 2 H), 3.78 (s, 3 H), 3.70 (s, 3 H), 3.64 (s, 2 H), 2.63–2.59 (m, 2 H), 2.47–2.43 (m, 2 H), 2.14–2.10 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.6, 173.0, 159.7, 143.4, 137.3, 134.2, 132.0, 128.8, 127.4, 125.7, 122.4, 118.4, 114.0, 113.0, 55.2, 51.6, 47.8, 38.1, 31.1, 23.5, 22.2 ppm. IR (KBr): $\tilde{\nu}$ = 1738, 1643 cm^{-1}. $C_{25}H_{25}NO_4$ (403.47): calcd. C 74.42, H 6.25, N 3.47; found C 74.33, H 6.17, N 3.38.

Methyl (4-Hydroxy-1,2-diphenylindol-3-yl)acetate (14a): White solid (110 mg, 62% yield); m.p. 186–188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (s, 1 H), 7.34–7.20 (m, 8 H), 7.16–7.14 (m, 2 H), 7.07 (d, J = 8.4 Hz, 1 H), 6.86 (d, J = 8.4 Hz, 1 H), 6.74 (d, J = 7.2 Hz, 1 H), 3.82 (s, 2 H), 3.83 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.1, 150.3, 139.8, 138.2, 137.9, 130.9, 130.8, 129.0, 128.1, 128.0, 127.9, 127.8, 127.1, 123.9, 108.2, 105.2, 103.5, 52.9, 32.0 ppm. IR (KBr): $\tilde{\nu}$ = 3480, 1745 cm^{-1}. $C_{23}H_{19}NO_3$ (357.40): calcd. C 77.29, H 5.36, N 3.92; found C 77.20, H 5.28, N 3.82.

Methyl [4-Hydroxy-1-(4-methoxyphenyl)-2-phenylindol-3-yl]acetate (14d): White solid (122 mg, 63% yield); m.p. 188–190 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.36 (s, 1 H), 7.29–7.20 (m, 5 H), 7.07 (d, J = 6.6 Hz, 3 H), 6.83 (d, J = 6.9 Hz, 3 H), 6.71 (d, J = 7.5 Hz, 1 H), 3.87 (s, 2 H), 3.82 (s, 3 H), 3.78 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.0, 158.4, 150.3, 140.1, 138.1, 131.0, 130.9, 129.1, 128.0, 127.8, 123.7, 117.7, 114.2, 107.9, 104.7, 103.6, 55.3, 52.8, 32.1 ppm. IR (KBr): $\tilde{\nu}$ = 3482, 1748 cm^{-1}. $C_{24}H_{21}NO_4$ (387.42): calcd. C 74.40, H 5.46, N 3.62; found C 74.32, H 5.36, N 3.54.

Methyl (1-Benzyl-4-hydroxy-2-phenylindol-3-yl)acetate (14e): White solid (122 mg, 66% yield); m.p. 189–191 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (s, 1 H), 7.40 (t, J = 7.8 Hz, 3 H), 7.32–7.29 (dd, J_1 = 6.6 Hz, J_2 = 2.7 Hz, 2 H), 7.22–7.17 (m, 3 H), 7.03 (t, J = 3.0 Hz, 1 H), 6.93–6.90 (m, 2 H), 6.77 (d, J = 8.4 Hz, 1 H), 6.68 (d, J = 7.8 Hz, 1 H), 5.14 (s, 2 H), 3.77 (s, 2 H), 3.76 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.0, 150.4, 139.0, 138.5, 137.9, 130.9, 130.7, 128.7, 128.6, 128.4, 127.1, 126.1, 123.6, 117.8, 107.5, 104.1, 103.4, 52.8, 47.9, 32.1 ppm. IR (KBr): $\tilde{\nu}$ = 3488, 1751 cm^{-1}. $C_{24}H_{21}NO_3$ (371.42): calcd. C 77.61, H 5.70, N 3.77; found C 77.50, H 5.62, N 3.69.

Methyl (4-Hydroxy-1-methyl-2-phenylindol-3-yl)acetate (14f): White solid (88 mg, 60% yield); m.p. 116–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (s, 1 H), 7.53–7.38 (m, 5 H), 7.13 (t, J = 8.1 Hz, 1 H), 6.91 (d, J = 7.8 Hz, 1 H), 6.69 (d, J = 7.5 Hz, 1 H), 3.77 (s, 3 H), 3.75 (s, 2 H), 3.55 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.1, 150.4, 139.3, 138.3, 130.9, 128.5, 123.4, 117.5, 107.3, 103.3, 102.4, 52.8, 32.0, 31.2 ppm. IR (KBr): $\tilde{\nu}$ = 3489, 1752 cm^{-1}. $C_{18}H_{17}NO_3$ (295.33): calcd. C 73.20, H 5.80, N 4.74; found C 73.11, H 5.72, N 4.65.

Methyl [4-Hydroxy-2-(4-methoxyphenyl)-1-phenylindol-3-yl]acetate (14j): White solid (118 mg, 61% yield); m.p. 160–162 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.40 (s, 1 H), 7.34–7.23 (m, 3 H), 7.16–7.12 (m, 4 H), 7.04 (t, J = 8.1 Hz, 1 H), 6.85–6.79 (m, 3 H), 6.73 (d, J = 7.2 Hz, 1 H), 3.86 (s, 2 H), 3.84 (s, 3 H), 3.79 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.1, 159.2, 150.3, 139.6, 138.3, 137.8, 132.1, 129.0, 128.1, 127.0, 123.7, 123.0, 117.9, 113.6, 108.0, 104.8, 103.5, 55.1, 52.9, 32.1 ppm. IR (KBr): $\tilde{\nu}$ = 3486, 1754 cm^{-1}. $C_{24}H_{21}NO_4$ (387.42): calcd. C 74.40, H 5.46, N 3.62; found C 74.31, H 5.35, N 3.55.

Methyl [4-Hydroxy-2-(4-methoxyphenyl)-1-*p*-tolylindol-3-yl]acetate (14k): White solid (120 mg, 60% yield); m.p. 148–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (s, 1 H), 7.15–7.10 (m, 4 H), 7.03 (t, J = 8.1 Hz, 3 H), 6.82 (d, J = 8.4 Hz, 3 H), 6.71 (d, J = 7.5 Hz, 1 H), 3.85 (s, 2 H), 3.81 (s, 3 H), 3.78 (s, 3 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.1, 159.2, 150.2, 139.8, 137.9, 136.8, 135.7, 132.1, 129.6, 127.8, 123.5, 123.2, 117.8, 113.5, 107.9, 104.5, 103.6, 55.1, 52.8, 32.1, 21.0 ppm. IR (KBr): $\tilde{\nu}$ = 3483, 1755 cm^{-1}. $C_{25}H_{23}NO_4$ (401.45): calcd. C 74.79, H 5.77, N 3.49; found C 74.70, H 5.69, N 3.38.

Methyl [1-Benzyl-2-(4-fluorophenyl)-4-hydroxyindol-3-yl]acetate (14m): White solid (119 mg, 61% yield); m.p. 116–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (s, 1 H), 7.29–7.20 (m, 5 H), 7.12–7.02 (m, 3 H), 6.90 (d, J = 7.2 Hz, 2 H), 6.78 (d, J = 8.1 Hz, 1 H), 6.68 (d, J = 7.8 Hz, 1 H), 5.12 (s, 2 H), 3.76 (s, 2 H), 3.74 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.8, 164.6, 161.3, 150.4, 138.9, 137.8, 137.3, 132.8, 128.6, 127.2, 126.7, 126.0, 123.7, 117.7, 115.7, 115.4, 107.6, 104.4, 103.3, 52.8, 47.9, 32.0 ppm. IR (KBr): $\tilde{\nu}$ = 3490, 1756 cm^{-1}. $C_{24}H_{20}FNO_3$ (389.41): calcd. C 74.02, H 5.18, N 3.60; found C 73.93, H 5.10, N 3.51.

Methyl [4-Hydroxy-1,2-bis(4-methoxyphenyl)indol-3-yl]acetate (14o): White solid (131 mg, 63% yield); m.p. 120–122 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (s, 1 H), 7.14 (d, J = 8.7 Hz, 2 H), 7.09–7.02 (m, 3 H), 6.88–6.77 (m, 5 H), 6.71 (d, J = 7.5 Hz, 1 H), 3.85 (s, 2 H), 3.82 (s, 3 H), 3.79 (s, 3 H), 3.78 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.2, 159.2, 158.4, 150.2, 132.2, 131.1, 129.2, 123.5, 123.1, 117.7, 114.2, 113.5, 107.9, 104.2, 103.5, 55.3, 55.1, 52.8, 32.1 ppm. IR (KBr): $\tilde{\nu}$ = 3479, 1746 cm^{-1}. $C_{25}H_{23}NO_5$ (417.45): calcd. C 71.93, H 5.55, N 3.36; found C 71.85, H 5.47, N 3.27.

Methyl [1-Benzyl-4-hydroxy-2-(4-methoxyphenyl)indol-3-yl]acetate (14p): White solid (128 mg, 64% yield); m.p. 116–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (s, 1 H), 7.24–7.17 (m, 5 H), 7.02 (t, J = 7.8 Hz, 1 H), 6.94–6.91 (m, 4 H), 6.75 (d, J = 7.5 Hz, 1 H), 6.67 (d, J = 7.5 Hz, 1 H), 5.13 (s, 2 H), 3.82 (s, 2 H), 3.76 (s, 3 H), 3.75 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.2, 159.9, 150.3, 138.8, 138.4, 138.0, 132.1, 128.6, 127.1, 126.1, 123.4, 122.8, 117.8, 113.9, 107.5, 103.8, 103.3, 55.3, 52.8, 47.9, 32.1 ppm. IR (KBr): $\tilde{\nu}$ = 3487, 1750 cm^{-1}. $C_{25}H_{23}NO_4$ (401.45): calcd. C 74.79, H 5.77, N 3.49; found C 74.70, H 5.69, N 3.41.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of all synthesized compounds.

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[9] CCDC-960635 (for **4u**), -983375 (for **9c**), and -983376 (for **14e**) 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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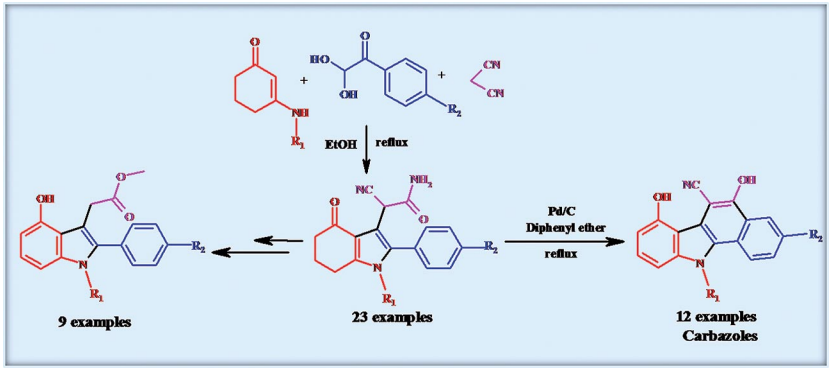
Carbazole Synthesis



The domino condensation of enamines, arylglyoxals, and malononitrile produced cyclohexanone-fused 2-(3-pyrrolyl)-2-cyanoacetamides, which were transformed into highly substituted benzo[*a*]carbazoles through a one-step thermal cyclization and aromatization. The cyanoacetamides also underwent hydrolysis and aromatization reactions to give the biologically important indoleacetic acid derivatives.

Keywords: Synthetic methods / Domino reactions / Cyclization / Nitrogen heterocycles / Aromatization

