Author(s): Zhang, Jingyu; Li, Jing; Ward, Jas S; Truong, Khai-Nghi; Rissanen, Kari; Albrecht, Markus

Title: Iron(III) chloride as mild catalyst for the dearomatizing cyclization of N-acylindoles

Year: 2020

Version: Published version

Please cite the original version:

Zhang, J., Li, J., Ward, J. S., Truong, K.-N., Rissanen, K., & Albrecht, M. (2020). Iron(III) chloride as mild catalyst for the dearomatizing cyclization of N-acylindoles. Journal of Organic Chemistry, 85(19), 12160-12174. https://doi.org/10.1021/acs.joc.0c01373

JOC The Journal of Organic Chemistry

Article

Iron(III) chloride as mild catalyst for the dearomatizing cyclization of N-acylindoles

Jingyu Zhang, Jing Li, Jas S Ward, Khai-Nghi Truong, Kari Rissanen, and Markus Albrecht

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.0c01373 • Publication Date (Web): 28 Aug 2020

Just Accepted

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

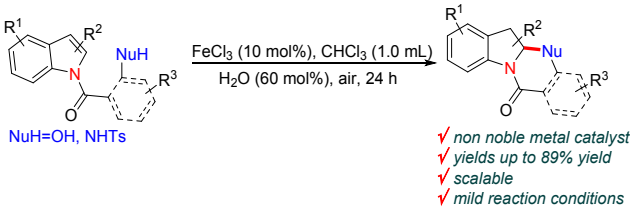
Iron(III) chloride as mild catalyst for the dearomatizing cyclization of *N*-acylindoles

Jingyu Zhang,[a] Jing Li,[a] Jas S. Ward,[b] Khai-Nghi Truong,[b] Kari Rissanen[b] and Markus Albrecht*[a]

[a] Institut für Organische Chemie, RWTH Aachen University, Landoltweg 1, Aachen 52074, Germany

[b] University of Jyvaskyla, Department of Chemistry, P.O. Box 35, FIN-40014 Jyväskylä, Finland

Supporting Information Placeholder



ABSTRACT: A catalytic approach for the preparation of indolines by dearomatizing cyclization is presented. $FeCl_3$ acts as a catalyst to afford tetracyclic 5a,6-dihydro-12*H*-indolo[2,1-*b*][1,3]benzoxazin-12-ones in good yields. The cyclization also proceeds with tosylamides forming C-N bonds in 53 % yield.

■ INTRODUCTION

Indole is a basic heterocyclic motif found in important natural (e.g. alkaloids) or non-natural organic derivatives (e.g. dyes). The parent molecule is rather old and its chemistry is well explored. Functionalization at the heterocyclic part usually proceeds in 3-position while 2-functionalization is possible utilizing e.g. C-H activation approaches.[1] Just recently dearomatization reactions at the indole skeleton came into the focus of attention.[2-3] This is of special interest due to the importance of indolines in natural products or as bioactives,[4] e.g. in case of the Strychnos alkaloids (Figure 1).

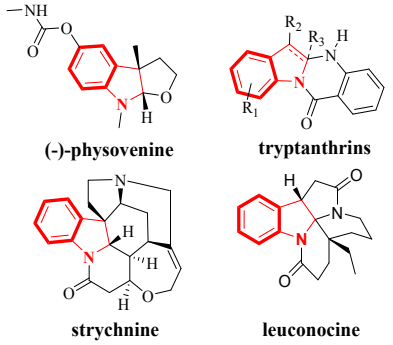
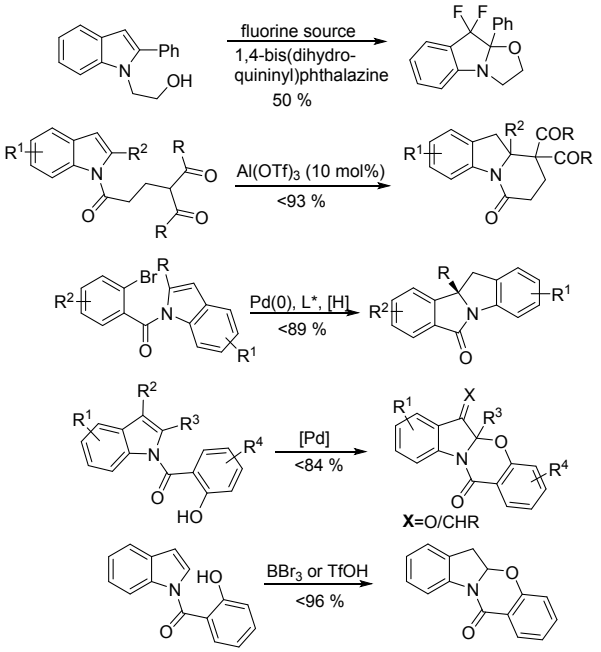


Figure 1. Indoline based natural products and bioactive molecules.

Consequently, the search for synthetic methodologies to make indoline derivatives easily available has been in the focus of attention for several decades.[5] The dearomatization reaction of indoles is a facile approach to access indolines. Many methods have been developed via intramolecular dearomatization and intermolecular dearomatization.[2,6] To date, some cases of the use of *N*-substituted indoles to prepare indolines via dearomatization cyclization have been shown (Scheme 1).[7-8] Respective dearomatizing cyclizations have been achieved applying either a quinine organocatalyst in the presence of a fluorine source, aluminium triflate or palladium catalysts. The cyclizations hereby proceed by C-C or C-O bond formation.

Scheme 1. Cyclizing intramolecular dearomatization reactions at the indole skeleton.

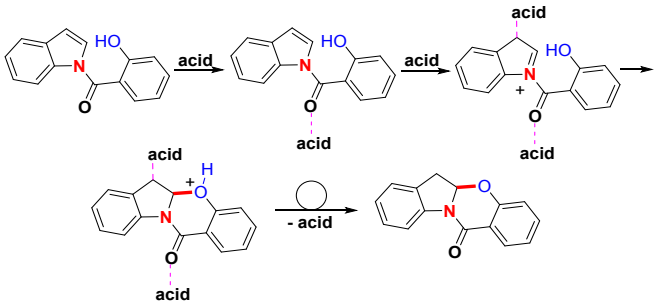


Just recently we introduced a protocol for the synthesis of tri- and tetracyclic indolines from acyl-indoles using relatively harsh reaction conditions by applying BBr_3 or triflic acid to

facilitate the cyclization.[8] However it is desired to develop milder and more effective reaction conditions in order to obtain the target molecules easily in high yields.

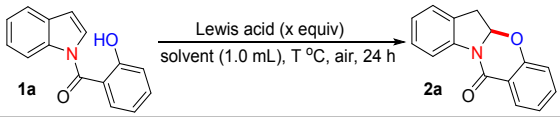
The dearomatizing cyclization follows a proposed mechanism as outlined in Scheme 2.[9] The carbonyl group is activated by an acid and then the addition of an acid to the 3-position of the indole activates the 2-position for nucleophilic attack. After cyclization the acid dissociates and the proton at oxygen migrates to the 3-position.

Scheme 2. Proposed mechanism of the acid catalysed dearomatising cyclization of hydroxybenzoylindole to the corresponding indoline.



RESULTS AND DISCUSSION

Table 1. Lewis acid catalysts for the dearomatizing cyclization of acyl indole 1a to indoline 2a.[a]



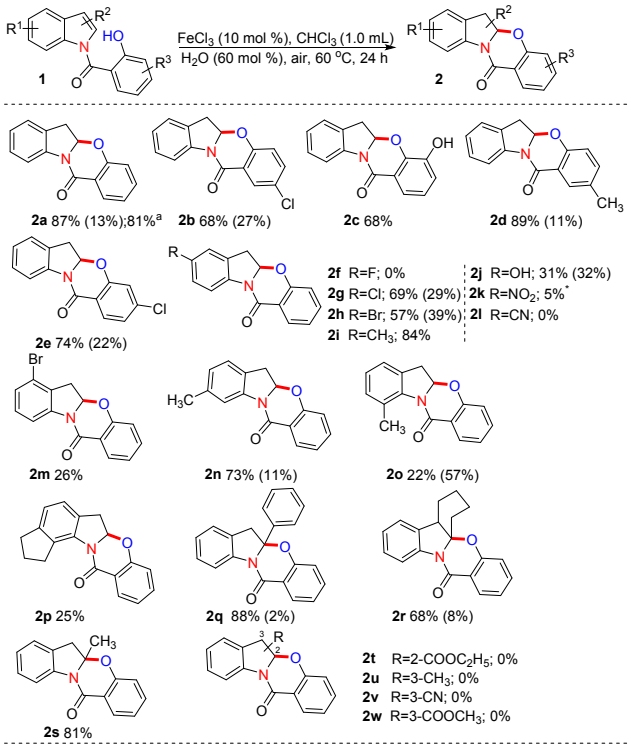
Entry	Lewis acid (x eq)	Solvent	T (°C)	2a/1a (%) [b]
1	$TiCl_4$ (1.0)	DCM	rt	0/98
2	$B(OH)_3$ (1.0)	DCM	rt	8/78
3	$MnCl_2 \cdot 4H_2O$ (1.0)	DCM	rt	13/81
4	$CuCl_2 \cdot 2H_2O$ (1.0)	DCM	rt	23/76
5	$FeCl_2 \cdot 4H_2O$ (1.0)	DCM	rt	20/74
6	$AlCl_3$ (1.0)	DCM	rt	31/66
7	$Ga(OTf)_3$ (1.0)	DCM	rt	90/9
8	$Y(OTf)_3$ (1.0)	DCM	rt	25/73
9	$Yb(OTf)_3$ (1.0)	DCM	rt	26/68
10	$Fe(OTf)_3$ (1.0)	DCM	rt	73/27
11	$FeCl_3 \cdot 6H_2O$ (1.0)	DCM	rt	77/17
12	$FeCl_3$ (1.0)	DCM	rt	99/0
13	$FeCl_3$ (0.1)	DCM	rt	67/28
14	$FeCl_3$ (0.1)	$CHCl_3$	rt	73/22
15	$FeCl_3$ (0.1)	$CHCl_3$	40	79/17
16	$FeCl_3$ (0.1)	$CHCl_3$	60	85/14
17[c]	$FeCl_3$ (0.1)	$CHCl_3$	60	86/14
18[d]	**$FeCl_3$ (0.1)**	**$CHCl_3$**	**60**	**87/13**
19[e]	$FeCl_3$ (0.1)	$CHCl_3$	60	85/13
20[f]	$FeCl_3$ (0.1)	$CHCl_3$	60	86/14
21[d]	$FeCl_3$ (0.01)	$CHCl_3$	60	10/87

[a] Unless otherwise noted, all reactions were performed on a 0.5 mmol scale, solvent (1.0 mL) in a sealed tube under air for 24 h. [b] Isolated yield. [c] 20 mol% H_2O was added. [d] 60 mol% H_2O was added. [e] 100 mol% H_2O was added. [f] 140 mol% H_2O was added.

In earlier studies Bronsted acids as well as BBr_3 were used to ~~initiate the cyclization. However, with those reagents it was not~~ possible to perform the reaction in a catalytic fashion.[8] Initially the reaction of acyl indole **1a** to the indoline **2a** was done using one equivalent of different Lewis acids in dichloromethane at room temperature for 24 hours. One equivalent of the "classical" Lewis acid $TiCl_4$ did not yield any product, while $B(OH)_3$, $MnCl_2 \cdot 4H_2O$, $CuCl_2 \cdot 2H_2O$, $FeCl_2 \cdot 4H_2O$, $AlCl_3$ as well as $Y(OTf)_3$ and $Yb(OTf)_3$ afforded only small amounts of the desired cyclization product. However, with $Ga(OTf)_3$ the product **2a** was obtained in 90 % yield and with $Fe(OTf)_3$, $FeCl_3 \cdot 6H_2O$ in 73 %, 77 % yields, respectively.[10] Finally, the use of $FeCl_3$ resulted in the quantitative formation of the indoline **2a** (Table 1). Following this, $FeCl_3$ was applied in catalytic amounts (10 mol%) yielding **2a** in 67 %. Switching of the solvent to chloroform led to the product **2a** in 73 % which could be increased to 85 % at 60 °C. Addition of water (up to 140 mol%) did not significantly influence the reaction. The use of only 1 mol% of catalyst reduced the yield of **2a** to 10 %.

In recently published studies dearomatizing reactions at the indole utilizing $FeCl_3$ followed a radical mechanism.[11] Addition of 1 eq. 2,6-di-*tert*-butyl-4-methylphenol (**BHT**) as a radical inhibitor during the cyclization of **1a** with $FeCl_3$ did not alter the yields of the reaction (88 % of **2a**). Moreover, another proposed mechanism is also possible. The carbonyl group be activated by $FeCl_3$ and then protonation of the C3-position of the indole activates the C2-position for nuclephilic attack. After cyclization the $FeCl_3$ dissociates from the carbonyl group and the proton at oxygen dissociates.[12]

Scheme 3. Scope of the dearomatizing cyclization of indoles 1 to indolines 2 catalysed by $FeCl_3$.



Reaction conditions: **1** (0.5 mmol), $FeCl_3$ (10 mol%), H_2O (60 mol%) in $CHCl_3$ (1.0 mL) at 60 °C (oil bath) under air for 24 h. The

yield of starting material recovery is given in brackets. [a] The yield of gram reaction. * NMR yield.

To evaluate the applicability of this transformation, the reaction was performed at 60 °C using 10 mol % $FeCl_3$ with 60 mol % H_2O in 1.0 mL of chloroform for 24 h of reaction time (standard conditions). The scope of the reaction was shown in Scheme 3. The cyclization reaction seems to be more or less independent of the substituents at the *N*-benzoyl unit (**2a-2e**, 68-89 % yield). Electron donating groups in 5- or 6-position of the indole (**2g-2j, 2n**) do not affect the cyclization dramatically. However, electron withdrawing groups in 5-position destabilize a positive charge in 2-position and thus suppress the cyclization. Only 5 % of product were obtained with a nitro group (**2k**) while with fluorine or nitrile no target product **2f**, **2l** formation has been observed. Obviously, the bromine in 4-position of indole has a negative effect compared with the bromine in 5-position of indole (**2h, 2m**). With the 7-methyl and the 6,7-cycloalkane indole derivatives, only small amounts (22 %, 25 %) of **2o**, **2p** were obtained due to steric interaction of the substitutents with the amide carbonyl oxygen. Substituents in 2-position of the indole heterocycle (**2q-2s**) result in good cyclization yields (68-88 %) if the substituent does not destabilize a positive charge (**2t**, no product observed). Substituents in 3-position (**2u-2w**) suppress the attack of the Lewis acid and thus do not result in product formation. **2u** was obtained earlier with TfOH, while BBr_3 as sterically demanding Lewis acid did not afford the cyclization product.[8] In the light of this observation, the formation of **2r** seems to be a surprise. Here the electronic activation of the 2-position seems to override the steric blocking of the 3-position.

It was possible to crystallize representative compounds and to perform X-ray structural analyses (Figure 2). As starting material, the benzoyl indole **1i** could be structurally characterized. It is found that in the crystal the phenolic oxygen shows a distance of only 2.96 Å to the 2-position of indole and a dihedral angle N-C(O)-C-C(OH) of 53.3°. Only a slight rotation around the $C_{carbonyl}$-C_{phenol} bond has to occur to enable cyclization resulting in a dihedral angle N-C(O)-C-C(O) of 18.4° with an O-C2 distance of 1.42 Å. In general, the obtained tetracyclic systems **2** adopt a more or less wavy planar structure. In the 2-substituted derivatives the phenyl (**2q**) or cyclohexyl units (**2r**) stick out vertical to this plane.

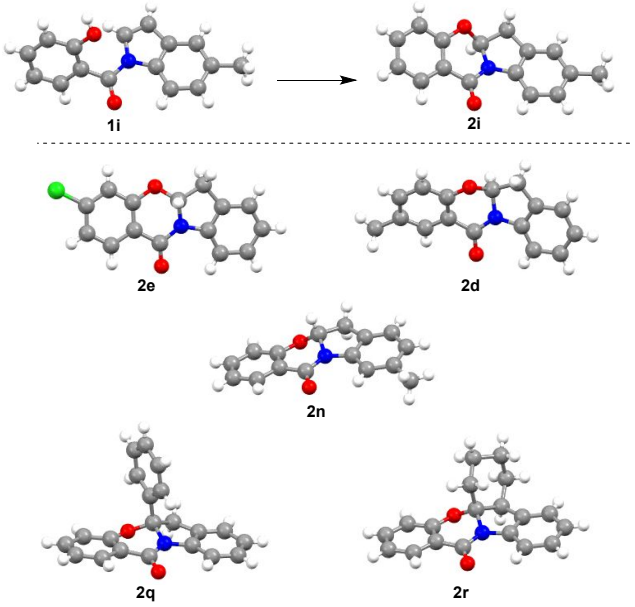
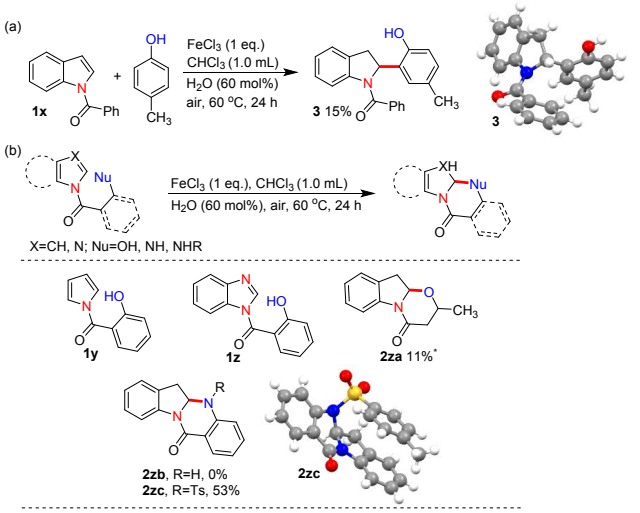


Figure 2. Molecular structures of 1i, 2i 2e, 2d, 2n, 2q and 2r.

The corresponding intermolecular reaction between **1x** and 4-methyl phenol[13] only proceeds with stoichiometric amounts of $FeCl_3$ and as described earlier[14] results in 15 % yield of the C-C coupling product **3** (Scheme 4, (a)). Cyclizations of the pyrrole **1y**, benzimidazole **1z** or amine derivative **1zb** do not proceed. However, C-N bond formation can be accomplished even with catalytic amounts of $FeCl_3$ if the tosylated amine **1zc** is used for the reaction. The N-H coupled product **2zc** was characterized by X-ray diffraction. The reaction of 3-hydroxybutyryl indole under standard conditions gave tricyclic product **2za** in 11 % yield.

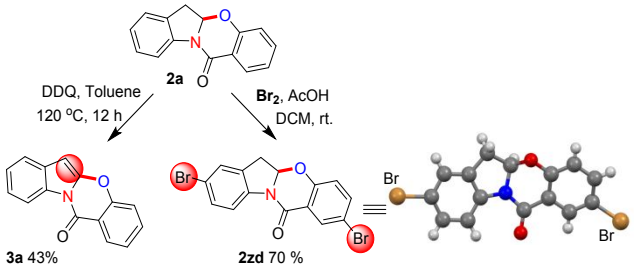


Scheme 4. (a) Attempts to perform the $FeCl_3$ catalyzed reaction intermolecularly (**3**, 15 %, 1 eq. $FeCl_3$). (b) Pyrrole (**1y**), benzimidazole (**1z**) and amine (**1zb**) do not cyclize. C-N bond formation proceeds, if the amine is tosylated (**2zc**). * NMR yield. The structure of **3**, **2zc** in the crystal.

Some orientating reactions have been performed at the tetracyclic 5a,6-dihydro-12*H*-indolo[2,1-*b*][1,3]benzoxazin-12-one **2a**. The skeleton is fairly stable in the presence of acid or base. However, **2a** can be aromatized by reaction with DDQ (43 % of **3a**) and it can be doubly brominated to obtain **2zd** in

70 % yield. The latter could be characterized by X-ray diffraction showing the obtained substitution pattern (Scheme 5).

Scheme 5. Rearomatization and bromination of the indoline 2a.



CONCLUSIONS

In conclusion in here a versatile reaction catalyzed by $FeCl_3$ has been studied which affords 5a,6-dihydro-12*H*-indolo[2,1-*b*][1,3]benzoxazin-12-ones in a dearoamtizing cyclization at indole in good yields. The reaction has a broad scope and affords the hitherto rarely described 2-oxo substituted indoline skeleton. As already indicated with example **2zc** in the future the method even can be expanded further and natural product synthesis is envisaged.[15]

EXPERIMENTAL SECTION

General information. Chemicals and solvents were obtained from commercial sources and used as received without further treatment. Chemicals were purchased from Acros Organics, Alfa Aesar, Sigma Aldrich, TCI. Air and moisture sensitive reactions were carried out by using air free techniques under nitrogen. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60, F254 precoated aluminium foil plates, visualized by UV irradiation. Fluka silica gel (40-60 µm) was used for column chromatography. Melting points were determined with a Büchi B-540 melting-point apparatus. NMR spectra were measured with VNMRS 400, VNMRS 600 instruments. EI mass spectra were measured with a Finnigan SSQ 7000. HR-ESI mass spectra were measured with a ThermoFisher Scientific LTQ Orbitrap XL of samples in acidified methanol. FTIR spectra were measured with a PerkinElmer Spectrum 100 via ATR. Elemental analysis was performed by using Vario EL and Vario EL cube instruments from Elementar.

Genernal procedure 1 - synthesis of N-acylindoles: Prepared according to literature procedure.[16a] A solution of indole (5.0 mmol), tetrabutylammonium hydrogensulfate (30.6 mg, 0.09 mmol), powdered NaOH (600 mg, 15.0 mmol), 2-methoxybenzoyl chloride (1.116 mL, 7.5 mmol), in CH_2Cl_2 (20 mL) were stirred in a flask under air at room temperature for 5 h. The reaction mixture was washed with water (30 mL) and extracted with CH_2Cl_2 (3×30 mL). The combined organic layer was dried with Na_2SO_4. Then the solvent was evaporated under vacuum. The residue was purified by flash chromatography on silica gel with n-pentane/ethyl acetate as the solvent to afford the pure product.

Genernal procedure 2 - synthesis of (2-hydroxyphenyl)(1*H*-indol-1-yl)methanones: Prepared according to literature procedure.[8] To a solution of N-acylindole (3.0 mmol) in CH_2Cl_2 (30 mL) under nitrogen was added BBr_3 solution (1.0 M in CH_2Cl_2) (3.6 mL, 3.6 mmol) at -78°C and the reaction mixture was stirred 3 h. Then MeOH (1.0 mL) was added to quench the reaction. The solution was added water (30 mL) and extracted with CH_2Cl_2 (20 mL) three times. The combined organic layer was dried with Na_2SO_4. Then the solvent was evaporated under vacuum. The residue was purified by flash chromatography on silica gel with n-pentane/ethyl acetate as the solvent to afford the pure product.

General procedure 3 - the dearomatizing cyclization of (2-hydroxyphenyl)(1*H*-indol-1-yl)methanones: A solution of the (2-hydroxyphenyl)(1*H*-indol-1-yl)methanone (0.5 mmol), $FeCl_3$ (8.2 mg, 10 mol %), H_2O (5.4 µL, 60 mol%) in $CHCl_3$ (1.0 mL) was stirred in a sealed reaction tube under an atmosphere of air at 60 °C for 24 h. After being cooled to room temperature, the reaction mixture was washed with water (10 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was dried with Na_2SO_4. Then the solvent was evaporated under vacuum. The residue was purified by flash chromatography on silica gel with n-pentane/ethyl acetate as the solvent to afford the pure product.

Gram-Scale Reaction: a solution of (2-Hydroxyphenyl)(1*H*-indol-1-yl)methanone (**1a**, 1.0 g, 4.21 mmol), $FeCl_3$ (68.1 mg, 0.42 mmol) and H_2O (45.5 µL, 2.53 mmol) in chloroform (8.5 mL) were stirred in a flask under air at 60 °C for 24 h. The reaction mixture was washed with water (30 mL) and extracted with CH_2Cl_2 (3×30 mL). The combined organic layer was dried with Na_2SO_4. Then the solvent was evaporated under vacuum. The residue was purified by flash chromatography on silica gel with n-pentane/ethylacetate = 40:1 as the solvent to afford the pure product **2a** in a yield of 81% (805 mg).

(1H-indol-1-yl)(2-methoxyphenyl)methanone ***(1A).*** [8] Purified by silica gel column chromatography; White solid; Isolated yield: 483 mg, 96%; Rf (n-pentane/ethyl acetate = 30/1) = 0.13; mp 68-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.45 (d, *J* = 6.8 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.11-7.02 (m, 3H), 6.55 (d, *J* = 3.6 Hz, 1H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 167.4, 156.5, 135.7, 132.3, 131.1, 129.2, 127.6, 125.0, 125.0, 124.0, 120.9, 120.9, 116.7, 111.6, 108.8, 55.8; MS (EI$^+$, 70 eV): m/z (%) = 252.0 (10), 251.0 (47) [M]+, 136.0 (9), 135.0 (100), 134.3 (2), 120.0 (1), 116.0 (4), 92.1 (7), 89.1 (4), 79.2 (2), 77.2 (12), 76.2 (1), 64.2 (2), 63.2 (3); IR (ATR) ν (cm−1) = 3330, 3151, 3123, 3006, 2976, 2934, 2837, 2496, 2326, 2162, 2085, 2047, 1951, 1911, 1789, 1745, 1672, 1598, 1538, 1487, 1454, 1430, 1382, 1345, 1291, 1244, 1205, 1148, 1113, 1069, 1016, 934, 890, 871, 747, 677. Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.44; H, 4.93; N, 5.59. HRMS (ESI) m/z : [M+Na]$^+$ calcd for $C_{16}H_{13}NO_2Na$, 274.0839; found, 274.0836.

(5-Chloro-2-methoxyphenyl)(1H-indol-1-yl)methanone ***(1B).*** Purified by silica gel column chromatography; Colorless solid; Isolated yield: 1.194 g, 84%; R_f (n-pentane/ethyl acetate = 30/1) = 0.30; mp 89-92 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.43 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.39-7.36 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.09 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.02 (d, *J* = 1.8 Hz, 2H), 6.56 (d, *J* = 3.6 Hz, 1H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 166.3, 157.2, 138.0, 135.7, 131.1, 130.2, 127.2, 125.2, 124.2, 123.5, 121.2, 121.0, 116.6, 112.5, 109.1, 56.2; MS (EI$^+$, 70 eV): m/z (%) = 287.2 (12), 286.2 (7), 285.1 (45) [M]$^+$, 256.2 (16), 254.3 (5), 251.2 (9), 250.2 (50), 231.2 (8), 228.1 (6), 225.2 (6), 195.2 (11), 182.2 (6), 171.1 (34), 170.1 (11), 169.1 (100), 140.2 (8), 135.2 (32), 126.2 (11), 125.2 (16), 116.2 (5), 111.2 (6), 105.2 (6), 97.3 (6), 91.2 (15), 85.2 (9), 83.2 (14), 77.3 (17), 51.4 (5); IR (ATR) ν (cm^{-1}) = 3353, 3078, 3008, 2974, 2941, 2854, 2658, 2502, 2342, 2190, 2107, 2044, 2005, 1920, 1677, 1590, 1540, 1486, 1446, 1397, 1334, 1249, 1201, 1149, 1122, 1095, 1060, 1020,

938, 887, 822, 755, 717; Anal. Calcd for $C_{16}H_{12}ClNO_2$: C, 67.26; H, 4.23; N, 4.90. Found: C, 67.03; H, 4.17; N, 4.89.

(2,3-Dimethoxyphenyl)(1H-indol-1-yl)methanone ***(1C).***[8] Purified by silica gel column chromatography; Brown oil; Isolated yield: 1.38 g, 98%; R_f (n-pentane/ethyl acetate =30/1) = 0.15; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.47 (br s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 8.1 Hz, 1H), 7.09-7.07 (m, 2H), 7.01 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.55 (d, *J* = 3.6 Hz, 1H), 3.93 (s, 3H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 166.9, 153.0, 146.3, 135.7, 131.2, 130.3, 127.6, 125.0, 124.6, 124.2, 121.0, 120.0, 116.7, 114.7, 108.9, 61.9, 56.1; MS (EI$^+$, 70 eV): m/z (%) = 283.1 (2), 282.1 (12), 281.1 (54) [M]$^+$, 166.0 (13), 165.0 (100), 164.3 (3), 150.0 (4), 122.1 (11), 121.1 (5), 120.1 (2), 116.1 (4), 107.1 (5), 92.2 (3), 89.2 (4), 79.2 (2), 77.3 (5), 63.3 (2), 51.4 (2); IR (ATR) ν (cm^{-1}) = 2939, 2836, 2163, 2017, 1917, 1691, 1583, 1536, 1475, 1448, 1378, 1336, 1266, 1235, 1202, 1082, 1047, 999, 930, 878, 828, 747, 669; Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.62; H, 5.23; N, 5.15.

(1H-indol-1-yl)(2-methoxy-5-methylphenyl)methanone ***(1D).*** Purified by silica gel column chromatography; White solid; Isolated yield: 947 mg, 89%; R_f (n-pentane/ethyl acetate = 20/1) = 0.38; mp 87-89 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.45 (s, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.31-7.29 (m, 2H), 7.25 (s, 1H), 7.08 (d, *J* = 3.0 Hz, 1H), 8.92 (d, *J* = 9.0 Hz, 1H), 6.54 (d, *J* = 3.6 Hz, 1H), 3.75 (s, 3H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 167.6, 154.4, 135.7, 132.7, 131.1, 130.4, 129.6, 127.7, 125.0, 124.7, 124.0, 120.8, 116.7, 111.6, 108.7, 55.9, 20.5; MS (EI$^+$, 70 eV): m/z (%) = 266.3 (15), 265.2 (100) [M]$^+$, 264.1 (3), 246.2 (4), 150.3 (15), 149.2 (89), 134.2 (3), 130.2 (4), 116.2 (8), 106.2 (7), 105.2 (6), 91.3 (16), 89.2 (9), 78.3 (5), 77.3 (4), 66.1 (3), 64.4 (3); IR (ATR) ν (cm^{-1}) = 3416, 3144, 3113, 3047, 3004, 2929, 2836, 2498, 2323, 2053, 1923, 1670, 1609, 1584, 1536, 1496, 1449, 1408, 1337, 1290, 1252, 1205, 1149, 1121, 1088, 1066, 1021, 934, 879, 816, 746, 680; Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 77.24; H, 5.49; N, 5.04.

(4-Chloro-2-methoxyphenyl)(1H-indol-1-yl)methanone ***(1E).*** Purified by silica gel column chromatography; Light yellow solid; Isolated yield: 1.28 g, 90%; R_f (n-pentane/ethyl acetate =30/1) = 0.45; mp 95-97 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.42 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.09 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.03 (d, *J* = 1.2 Hz, 2H), 6.56 (d, *J* = 3.6 Hz, 1H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 166.3, 157.2, 138.0, 135.7, 131.1, 130.2, 127.2, 125.2, 124.2, 123.5, 121.2, 121.0, 116.6, 112.4, 109.1, 56.2; MS (EI$^+$, 70 eV): m/z (%) = 288.0 (3), 287.0 (14), 286.0 (9), 285.0 (43) [M]$^+$, 246.0 (3), 172.0 (3), 171.0 (37), 170.0 (10), 169.0 (100), 154.0 (2), 130.1 (5), 128.0 (3), 126.0 (10), 116.1 (6), 113.0 (3), 111.1 (7), 98.1 (2), 89.2 (5), 77.2 (3), 75.2 (3), 63.3 (5); IR (ATR) ν (cm^{-1}) = 3380, 3117, 3072, 2932, 2853, 2656, 2325, 2094, 1978, 1894, 1693, 1591, 1534, 1483, 1449, 1397, 1332, 1292, 1251, 1205, 1179, 1150, 1120, 1089, 1059, 1022, 950, 891, 816, 756, 718; Anal. Calcd for $C_{16}H_{12}ClNO_2$: C, 67.26; H, 4.23; N, 4.90. Found: C, 67.49; H, 3.92; N, 5.00.

(5-Chloro-1H-indol-1-yl)(2-methoxyphenyl)methanone ***(1F).*** Purified by silica gel column chromatography; White solid; Isolated yield: 1.4 g, 99%; R_f (n-pentane/ethyl acetate = 10/1) = 0.30; mp 105-107 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.38 (br s, 1H), 7.54-7.51 (m, 2H), 7.44 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.32 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.10-7.08 (m, 2H), 7.03 (d, *J* = 9.0 Hz, 1H), 6.48 (d, *J* = 3.6 Hz, 1H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 167.2, 156.5, 134.0, 132.6, 132.3, 129.5, 129.3, 128.8, 125.1, 124.4, 121.0, 120.5, 117.6, 111.6, 108.0, 55.9; MS (EI$^+$, 70 eV): m/z (%) = 288.0 (3), 287.0 (12), 286.0 (8), 285.0 (39) [M]$^+$, 150.0 (3), 136.1 (10), 135.1 (100), 120.0 (2), 92.1 (8), 77.2 (12), 64.2 (2), 63.2 (2); IR (ATR) ν (cm^{-1}) = 3350, 3146, 3110, 3074, 3021, 2975, 2939, 2840, 2508, 2324, 2162, 2043, 2000, 1952, 1894, 1810, 1759, 1681, 1597, 1536, 1486, 1443, 1367, 1333, 1292, 1256, 1192, 1117, 1094, 1061, 1020, 943, 878, 816, 787, 755, 718; Anal. Calcd for $C_{16}H_{12}ClNO_2$: C, 67.26; H, 4.23; N, 4.90. Found: C, 67.30; H, 4.33; N, 4.77.

(5-Bromo-1H-indol-1-yl)(2-methoxyphenyl)methanone ***(1G).*** Purified by silica gel column chromatography; White solid; Isolated yield: 1.634 g, 99%; R_f (n-pentane/ethyl acetate = 30/1) = 0.24; mp 90-91 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.33 (s, 1H), 7.70 (s, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 8.8 Hz, 2H), 7.10-7.07 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.48 (d, *J* = 4.8 Hz, 1H), 3.78 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 167.3, 156.5, 134.3, 132.8, 132.6, 129.3, 128.7, 127.8, 124.4, 123.6, 121.0, 118.0, 117.3, 111.6, 107.9, 55.9; MS (EI$^+$, 70 eV): m/z (%) = 330.9 (16), 330.0 (3), 329.0 (15) [M]$^+$, 195.9 (2), 193.9 (2), 136.0 (9), 135.1 (100), 134.3 (2), 115.1 (5), 114.1 (2), 92.1 (8), 88.2 (2), 77.2 (14), 64.3 (2), 63.3 (2), 51.4 (2); IR (ATR) ν (cm^{-1}) = 3352, 3120, 3076, 3005, 2925, 2853, 2705, 2328, 2198, 2092, 2045, 1978, 1919, 1757, 1680, 1598, 1534, 1487, 1444, 1369, 1332, 1245, 1191, 1113, 1021, 942, 874, 753; Anal. Calcd for $C_{16}H_{12}BrNO_2$: C, 58.20; H, 3.66; N, 4.24. Found: C, 58.09; H, 3.48; N, 4.25.

(2-Methoxyphenyl)(5-methyl-1H-indol-1-yl)methanone ***(1H).*** Purified by silica gel column chromatography; White solid; Isolated yield: 1.278 g, 96%; R_f (n-pentane/ethyl acetate = 10/1) = 0.30; mp 79-81 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.30 (s, 1H), 7.52-7.49 (m, 1H), 7.44-7.42 (m, 1H), 7.36 (s, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.47 (d, *J* = 4.2 Hz, 1H), 3.78 (s, 3H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 167.2, 156.5, 133.9, 133.6, 132.2, 131.4, 129.2, 127.6, 126.3, 125.0, 120.9, 120.8, 116.3, 111.6, 108.6, 55.8, 21.6; MS (EI$^+$, 70 eV): m/z (%) = 267.0 (2), 266.1 (12), 265.1 (61) [M]$^+$, 136.0 (10), 135.1 (100), 134.3 (2), 130.1 (5), 103.1 (2), 102.1 (2), 92.1 (7), 77.2 (14), 64.2 (2), 63.2 (2), 51.3 (2); IR (ATR) ν (cm^{-1}) = 3366, 3164, 3115, 3021, 2920, 2847, 2330, 2206, 2164, 2077, 1983, 1950, 1913, 1690, 1593, 1541, 1488, 1459, 1365, 1332, 1292, 1253, 1213, 1187, 1126, 1060, 1018, 941, 882, 814, 753, 661; Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.78; H, 5.66; N, 5.19.

(5-Methoxy-1H-indol-1-yl)(2-methoxyphenyl)methanone ***(1I).***[16b] Purified by silica gel column chromatography; Yellow solid; Isolated yield: 476 mg, 85%; R_f (n-pentane/ethyl acetate = 8/1) = 0.30; mp 91-92 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.35 (s, 1H), 7.52-7.49 (m, 1H), 7.43 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.04-7.01 (m, 3H), 6.97 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.48 (d, *J* = 3.6 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 167.0, 156.8, 156.5, 132.2, 132.1, 130.4, 129.2, 128.2, 124.9, 120.9, 117.4, 113.2, 111.6, 108.7, 103.8, 55.8; MS (EI$^+$, 70 eV): m/z (%) = 282.0 (8), 281.0 (40) [M]$^+$, 145.9 (12), 136.0 (9), 134.9 (100), 131.0 (4), 117.0 (4), 102.9 (10), 92.0 (17), 77.0 (24), 76.0 (8), 64.0 (5), 63.0 (5), 51.1 (4); IR (ATR) ν (cm^{-1}) = 3321, 3151, 3122, 3045, 2983, 2944, 2827, 2658, 2491, 2323, 2220, 2173, 2107, 2051, 1992, 1945, 1911, 1855, 1794, 1665, 1598, 1538, 1467, 1380, 1340, 1287, 1243, 1189, 1110, 1064, 1021, 937, 882, 858, 799, 751, 721, 664; Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.70; H, 5.45; N, 5.09.

(2-Methoxyphenyl)(5-nitro-1H-indol-1-yl)methanone ***(1J).***[16b] Purified by silica gel column chromatography; White solid; Isolated yield: 1.466 g, 99%; R_f (n-pentane/ethyl acetate = 10/1) =

0.46; mp 153-155 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.54 (d, *J* = 9.0 Hz, 1H), 8.49 (s, 1H), 8.26 (d, *J* = 9.0 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 3.6 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 9.0 Hz, 1H), 6.69 (d, *J* = 3.6 Hz, 1H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 167.4, 156.6, 144.5, 138.7, 133.1, 131.0, 130.5, 129.5, 123.7, 121.2, 120.3, 117.1, 116.7, 111.7, 108.9, 55.9; MS (EI$^+$, 70 eV): m/z (%) = 297.1 (5), 296.1 (23) [M]$^+$, 136.1 (8), 135.1 (100), 115.1 (2), 92.2 (7), 77.2 (10), 64.3 (2); IR (ATR) ν (cm^{-1}) = 3123, 3006, 2925, 2847, 2503, 2204, 2158, 2038, 1979, 1908, 1775, 1688, 1601, 1513, 1442, 1381, 1320, 1249, 1195, 1137, 1070, 1042, 1016, 945, 915, 885, 828, 746, 709; Anal. Calcd for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.46. Found: C, 64.52; H, 3.94; N, 9.27.

1-(2-Methoxybenzoyl)-1H-indole-5-carbonitrile ***(1K).*** Purified by silica gel column chromatography; White solid; Isolated yield: 1.307 g, 95%; R_f (n-pentane/ethyl acetate = 10/1) = 0.13; mp 143-144 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.53 (d, *J* = 8.4 Hz, 1H), 7.90 (s, 1H), 8.7 (dd, *J* = 1.5 Hz, 1H), 7.57-7.54 (m, 1H), 7.46 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.20 (d, *J* = 3.6 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 4.2 Hz, 1H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 167.4, 156.5, 137.5, 133.0, 131.1, 129.7, 129.4, 128.2, 125.6, 123.9, 121.1, 119.8, 117.3, 111.7, 108.1, 107.3, 55.8; MS (EI$^+$, 70 eV): m/z (%) = 277.1 (6), 276.1 (32) [M]$^+$, 141.1 (3), 136.1 (8), 135.1 (100), 134.3 (1), 120.1 (1), 114.1 (4), 92.1 (8), 79.2 (1), 77.2 (11), 64.2 (3), 63.2 (2), 51.3 (1); IR (ATR) ν (cm^{-1}) = 3355, 3207, 3124, 3012, 2952, 2842, 2501, 2325, 2225, 2040, 1996, 1952, 1915, 1810, 1766, 1683, 1600, 1539, 1460, 1432, 1367, 1330, 1247, 1212, 1187, 1110, 1067, 1040, 1011, 944, 882, 816, 752, 661; Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C,74.01; H, 4.43; N, 9.86.

(4-Bromo-1H-indol-1-yl)(2-methoxyphenyl)methanone ***(1L).*** Purified by silica gel column chromatography; White solid; Isolated yield: 1.529 g, 93%; R_f (n-pentane/ethyl acetate = 35/1) = 0.15; mp 129-130 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.42 (d, *J* = 7.2 Hz, 1H), 7.54-7.52 (m, 1H), 7.47-7.44 (m, 2H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.12-7.09 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 3.6 Hz, 1H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 167.5, 156.5, 136.0, 132.6, 131.7, 129.3, 128.2, 126.9, 126.1, 124.4, 121.0, 115.7, 114.6, 111.6, 108.4, 55.8; MS (EI$^+$, 70 eV): m/z (%) = 330.9 (12), 328.9 (13) [M]$^+$, 195.8 (5), 193.8 (5), 135.9 (9), 134.9 (100), 114.9 (13), 113.9 (5), 91.9 (18), 87.9 (5), 77.0 (29), 64.0 (7), 63.0 (7), 62.0 (5), 51.0 (5); IR (ATR) ν (cm^{-1}) = 3380, 3148, 3113, 3059, 3014, 2926, 2838, 2515, 2325, 2074, 1986, 1901, 1837, 1747, 1682, 1597, 1533, 1489, 1463, 1415, 1375, 1332, 1258, 1171, 1119, 1062, 1021, 947, 883, 817, 747, 675; Anal. Calcd for $C_{16}H_{12}BrNO_2$: C, 58.20; H, 3.66; N, 4.24. Found: C, 58.27; H, 3.65; N, 4.23.

(2-Methoxyphenyl)(6-methyl-1H-indol-1-yl)methanone ***(1M).*** Purified by silica gel column chromatography; Light brown solid; Isolated yield: 1.312 g, 99%; R_f (n-pentane/ethyl acetate = 20/1) = 0.21; mp 85-88 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.35 (s, 1H), 7.52-7.49 (m, 1H), 7.45-7.43 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.10-7.07 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 3.6 Hz, 1H), 6.49 (d, *J* = 3.6 Hz, 1H), 3.79 (s, 3H), 2.52 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 167.4, 156.5, 136.1, 135.1, 132.1, 129.1, 128.8, 127.0, 125.4, 125.1, 120.9, 120.4, 117.0, 111.6, 108.7, 55.8, 22.1; MS (EI$^+$, 70 eV): m/z (%) = 266.3 (19), 265.2 (89) [M]$^+$, 144.1 (5), 136.2 (13), 135.1 (100), 134.0 (2), 130.1 (13), 128.0 (3), 120.1 (3), 103.2 (5), 102.0 (6), 92.1 (15), 79.2 (2), 78.3 (3), 77.1 (29), 64.2 (3), 63.1 (4); IR (ATR) ν (cm^{-1}) = 3355, 3150, 3109, 3018, 2919, 2855, 2725, 2326, 2076, 1873, 1741, 1677, 1598, 1534, 1487, 1460, 1428, 1379, 1340, 1295, 1255, 1202, 1164, 1119, 1061, 1043, 1018, 937, 879, 803, 746, 665; Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.86; H, 5.72; N, 5.25.

(2-Methoxyphenyl)(7-methyl-1H-indol-1-yl)methanone ***(1N).*** Purified by silica gel column chromatography; Purple oil; Isolated yield: 1.258 g, 95%; R_f (n-pentane/ethyl acetate = 10/1) = 0.46; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.58 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.55-7.52 (m, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.04-7.03 (m, 2H), 6.52 (d, *J* = 3.6 Hz, 1H), 3.81 (s, 3H), 2.61 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 166.0, 157.8, 135.3, 133.2, 132.4, 130.9, 129.0, 127.9, 126.7, 124.6, 124.1, 120.8, 118.5, 111.9, 108.1, 56.0, 22.5; MS (EI$^+$, 70 eV): m/z (%) = 267.0 (2), 266.1 (15), 265.1 (63) [M]$^+$, 264.4 (2), 136.0 (14), 135.1 (100), 134.4 (2), 130.1 (5), 120.0 (2), 103.1 (2), 102.1 (2), 92.1 (8), 79.2 (2), 77.2 (16), 76.2 (2), 64.2 (2), 63.2 (2), 51.3 (2); IR (ATR) ν (cm^{-1}) = 3375, 3049, 2933, 2839, 2332, 2161, 2046, 1919, 1692, 1595, 1545, 1484, 1457, 1406, 1322, 1252, 1214, 1171, 1108, 1078, 1021, 947, 876, 785, 754, 722, 682; Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.66; H, 5.85; N, 5.66.

(7,8-Dihydrocyclopenta[g]indol-1(6H)-yl)(2-methoxphenyl)methanone ***(1O).*** Purified by silica gel column chromatography; White solid; Isolated yield: 1.237 g, 85%; R_f (n-pentane/ethyl acetate = 40/1) = 0.20; mp 120-121 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.52-7.49 (m, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 3.6 Hz, 1H), 6.49 (d, *J* = 3.6 Hz, 1H), 3.80 (s, 3H), 3.47 (t, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.5 Hz, 2H), 2.14-2.09 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 166.2, 157.2, 142.9, 132.9, 132.7, 131.1, 130.5, 130.2, 127.8, 125.0, 120.9, 120.8, 118.7, 111.7, 108.6, 55.9, 35.2, 33.7, 25.7; MS (EI$^+$, 70 eV): m/z (%) = 292.1 (3), 291.0 (16) [M]$^+$, 156.0 (6), 154.9 (6), 153.9 (18), 136.0 (9), 134.9 (100), 129.0 (6), 127.9 (9), 126.9 (7), 91.9 (19), 77.0 (37), 76.0 (4), 64.0 (6), 63.0 (5), 51.1 (6); IR (ATR) ν (cm^{-1}) = 3360, 3106, 3068, 3007, 2944, 2842, 2287, 2031, 1857, 1753, 1683, 1599, 1541, 1490, 1464, 1436, 1410, 1335, 1247, 1215, 1186, 1108, 1073, 1018, 949, 872, 804, 752, 722, 669; Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.09; H, 5.78; N, 4.78.

(2-Methoxyphenyl)(2-phenyl-1H-indol-1-yl)methanone ***(1P).***[7a] Purified by silica gel column chromatography; Green solid; Isolated yield: 994 mg, 76%; R_f (n-pentane/ethyl acetate = 40/1) = 0.11; mp 130-132 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.11 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 6.6 Hz, 1H), 7.34-7.28 (m, 2H), 7.26 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.24-7.23 (m, 2H), 7.19-7.16 (m, 1H), 7.12-7.07 (m, 3H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.63 (s, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 3.64 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 168.4, 157.1, 141.3, 138.0, 133.2, 133.1, 130.8, 129.5, 128.8, 127.6, 127.5, 125.9, 124.7, 123.5, 120.5, 120.2, 115.2, 110.9, 110.3, 55.4; MS (EI$^+$, 70 eV): m/z (%) = 327.9 (7), 326.8 (35) [M]$^+$, 191.9 (13), 190.9 (10), 189.9 (12), 165.9 (5), 164.9 (32), 163.9 (7), 162.9 (6), 136.0 (8), 134.9 (100), 92.1 (21), 77.1 (29), 64.2 (6), 63.2 (7); IR (ATR) ν (cm^{-1}) = 3338, 3054, 2934, 2838, 2658, 2503, 2323, 2104, 1992, 1901, 1806, 1673, 1592, 1446, 1313, 1255, 1148, 1072, 1020, 920, 882, 829, 745, 699; Anal. Calcd for $C_{22}H_{17}NO_2$: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.69; H, 5.26; N, 4.25.

(2-Methoxyphenyl)(1,2,3,4-tetrahydro-9H-carbazol-9-yl)methanone ***(1Q).***[7a] Purified by silica gel column chromatography; Colorless solid; Isolated yield: 1.48 g, 97%; R_f (n-pentane/ethyl acetate =30/1) = 0.24; mp 118-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.50 (t, *J* = 7.0 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 3.75 (s, 3H), 2.66 (t, *J* = 5.6

Hz, 2H), 2.49 (m, 2H), 1.81-1.75 (m, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ (ppm) 167.4, 156.9, 136.5, 135.9, 132.3, 130.5, 129.1, 127.0, 123.8, 123.1, 121.0, 118.3, 117.6, 115.3, 111.8, 55.9, 25.4, 23.8, 22.2, 21.3; MS (EI$^+$, 70 eV): m/z (%) = 306.2 (11), 305.1 (48) $[M]^+$, 170.1 (4), 169.1 (1), 168.1 (4), 167.1 (2), 140.1 (1), 136.1 (9), 135.1 (100), 134.4 (1), 120.1 (1), 115.1 (3), 92.2 (6), 79.3 (1), 77.2 (10), 76.3 (1); IR (ATR) ν (cm^{-1}) = 3314, 3065, 2949, 2843, 2656, 2322, 2033, 1914, 1660, 1600, 1490, 1454, 1362, 1325, 1243, 1211, 1161, 1118, 1068, 1016, 930, 871, 832, 800, 751, 666; Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.33; H, 6.16; N, 4.56.

(2-Methoxyphenyl)(2-methyl-1H-indol-1-yl)methanone ***(1R).***[7a] Purified by silica gel column chromatography; Yellow solid; Isolated yield: 1.19 g, 90%; R_f (n-pentane/ethyl acetate = 30/1) = 0.23; mp 81-84 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.52 (t, *J* = 8.7 Hz, 1H), 7.44-7.41 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.09-7.05 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.36 (s, 1H), 3.70 (s, 3H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 168.0, 157.1, 137.8, 137.1, 132.8, 129.9, 129.5, 126.5, 123.3, 123.1, 121.1, 119.6, 114.9, 111.8, 109.4, 55.9, 16.3; MS (EI$^+$, 70 eV): m/z (%) = 266.1 (10), 265.1 (49) $[M]^+$, 264.3 (2), 137.0 (1), 136.0 (10), 135.1 (100), 134.4 (3), 130.1 (4), 128.0 (1), 120.0 (1), 103.1 (3), 102.1 (1), 92.1 (7), 89.1 (1), 79.2 (2), 78.2 (1), 77.2 (14), 76.2 (1), 64.2 (2), 63.2 (2), 51.3 (2); IR (ATR) ν (cm^{-1}) = 3019, 2972, 2937, 2836, 2209, 2160, 2018, 1959, 1918, 1670, 1595, 1490, 1445, 1359, 1331, 1301, 1252, 1204, 1159, 1111, 1018, 973, 942, 884, 838, 800, 754; Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.58; H, 5.71; N, 5.25.

Ethyl 1-(2-methoxybenzoyl)-1H-indole-2-carboxylate ***(1S).*** Purified by silica gel column chromatography; Colorless oil; Isolated yield: 1.183 g, 73%; R_f (n-pentane/ethyl acetate = 20/1) = 0.16; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.01 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.49-7.40 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.23 (s, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 3.90 (q, *J* = 7.2 Hz, 2H), 3.73 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 167.4, 161.4, 158.0, 138.6, 133.7, 131.7, 131.1, 127.6, 127.4, 125.4, 123.8, 122.3, 120.6, 115.8, 115.0, 111.8, 61.3, 55.9, 14.1; MS (EI$^+$, 70 eV): m/z (%) = 324.1 (8), 323.1 (38) $[M]^+$, 278.0 (3), 144.0 (2), 143.0 (1), 137.0 (1), 136.0 (11), 135.0 (100), 134.3 (2), 120.0 (1), 116.1 (2), 115.1 (2), 114.1 (1), 105.0 (1), 92.2 (8), 92.1 (8), 89.1 (3), 79.2 (2), 77.1 (14), 64.2 (2), 63.2 (1); IR (ATR) ν (cm^{-1}) = 3071, 2978, 2840, 2167, 2040, 1919, 1714, 1599, 1545, 1486, 1443, 1372, 1314, 1254, 1153, 1116, 1089, 1018, 960, 912, 884, 863, 749; Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.47; H, 5.11; N, 5.15. HRMS (ESI) m/z : $[M+Na]^+$ calcd for $C_{19}H_{17}NO_4Na$, 346.1050; found, 346.1047.

(2-Methoxyphenyl)(3-methyl-1H-indol-1-yl)methanone ***(1T).***[8] Purified by silica gel column chromatography; White solid; Isolated yield: 1.277 g, 96%; R_f (n-pentane/ethyl acetate = 30/1) = 0.23; mp 112-114 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.43 (s, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6,83 (s, 1H), 3.80 (s, 3H), 2.22 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 166.9, 156.4, 136.0, 132.2, 132.0, 128.9, 125.3, 125.1, 124.2, 123.8, 120.8, 118.9, 118.0, 116.7, 111.6, 55.9, 9.9; MS (EI$^+$, 70 eV): m/z (%) = 266.0 (10), 265.1 (45) $[M]^+$, 264.4 (2), 136.0 (9), 135.0 (100), 134.2 (2), 130.1 (4), 120.0 (1), 103.1 (2), 92.1 (7), 79.2 (1), 78.2 (1), 77.2 (13), 76.2 (2), 64.2 (2), 63.2 (2), 51.3 (2); IR (ATR) ν (cm^{-1}) = 3352, 3051, 2933, 2834, 2324, 2044, 1915, 1793, 1683, 1599, 1490, 1452, 1369, 1344, 1297, 1249, 1214, 1172, 1114, 1044, 1021, 939, 876, 748, 660; Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.93; H, 5.77; N, 5.28.

1-(2-Methoxybenzoyl)-1H-indole-3-carbonitrile ***(1U).*** Purified by silica gel column chromatography; Light yellow solid; Isolated yield: 1.354 g, 98%; R_f (n-pentane/ethyl acetate = 10/1) = 0.20; mp 141-144 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.46 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.61-7.58 (m, 2H), 7.52-7.44 (m, 3H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 166.9, 156.5, 135.1, 134.8, 133.6, 129.8, 128.4, 127.0, 125.4, 122.9, 121.4, 119.8, 117.0, 114.2, 111.8, 93.6, 56.0; MS (EI$^+$, 70 eV): m/z (%) = 277.1 (4), 276.1 (22) $[M]^+$, 141.1 (3), 136.1 (8), 135.1 (100), 120.2 (1), 114.2 (3), 105.2 (1), 92.2 (7), 79.3 (1), 77.3 (10), 64.4 (2), 63.3 (2), 51.4 (1); IR (ATR) ν (cm^{-1}) = 3376, 3147, 3072, 3002, 2945, 2841, 2494, 2224, 2118, 2039, 1982, 1926, 1808, 1746, 1693, 1600, 1546, 1491, 1448, 1332, 1294, 1249, 1216, 1152, 1123, 1055, 1020, 946, 873, 749, 709, 659; Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 72.54; H, 4.31; N, 9.58. HRMS (ESI) m/z : $[M+Na]^+$ calcd for $C_{17}H_{12}N_2O_2Na$, 299.0791; found, 299.0790.

Methyl 1-(2-methoxybenzoyl)-1H-indole-3-carboxylate ***(1V).*** Purified by silica gel column chromatography; White solid; Isolated yield: 1.514 g, 98%; R_f (n-pentane/ethyl acetate =30/1) = 0.31; mp 148-149 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.48 (d, *J* = 7.8 Hz, 1H), 8.16 (dd, *J* = 6.6, 1.8 Hz, 1H), 7.76 (s, 1H), 7.58-7.55 (m, 1H), 7.47 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.45-7.40 (m, 2H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 3H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 167.6, 164.7, 156.6, 136.1, 133.8, 133.1, 129.6, 127.9, 125.9, 125.1, 123.7, 121.7, 121.2, 116.6, 113.6, 111.8, 55.9, 51.7; MS (EI$^+$, 70 eV): m/z (%) = 310.1 (8), 309.0 (34) $[M]^+$, 278.0 (2), 146.1 (3), 143.1 (2), 137.0 (1), 136.0 (10), 135.1 (100), 134.4 (2), 120.0 (2), 115.1 (3), 114.1 (1), 103.1 (1), 92.2 (8), 88.2 (1), 79.3 (2), 78.3 (1), 77.2 (14), 76.3 (2), 64.3 (2), 63.3 (2), 51.4 (2); IR (ATR) ν (cm^{-1}) = 3152, 2951, 2846, 2343, 2038, 1904, 1791, 1712, 1677, 1600, 1565, 1445, 1376, 1329, 1279, 1254, 1191, 1144, 1049, 1016, 951, 873, 742, 706, 656; Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. Found: C, 69.94; H, 4.85; N, 4.46.

(2-Methoxyphenyl)(1H-pyrrol-1-yl)methanone ***(1W).***[16c] Purified by silica gel column chromatography; Yellow oil; Isolated yield: 1.990 g, 99%; R_f (n-pentane/ethyl acetate =30/1) = 0.31; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.51-7.48 (m, 1H), 7.39 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.16 (br s, 2H), 7.06-7.03 (m, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.28 (t, *J* = 2.1 Hz, 2H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 166.5, 156.9, 132.4, 129.3, 123.7, 120.7, 120.6, 113.2, 111.6, 55.9; MS (EI$^+$, 70 eV): m/z (%) = 202.1 (4), 201.0 (28) $[M]^+$, 182.3 (1), 165.1 (2), 155.1 (5), 148.2 (3), 136.1 (8), 135.1 (100), 134.3 (3), 132.2 (6), 120.1 (2), 118.2 (2), 105.2 (2), 92.2 (12), 91.2 (14), 79.3 (2), 78.3 (2), 77.3 (18), 76.3 (2), 66.4 (2), 65.4 (3), 64.4 (4), 63.4 (4), 51.5 (3), 50.5 (2); IR (ATR) ν (cm^{-1}) = 3385, 3146, 3008, 2942, 2840, 2332, 2159, 2039, 1921, 1700, 1599, 1463, 1400, 1330, 1250, 1166, 1117, 1077, 1044, 1020, 975, 879, 741, 663; Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 70.19; H, 5.24; N, 7.75. HRMS (ESI) m/z : $[M+Na]^+$ calcd for $C_{12}H_{11}NO_2Na$, 224.0682; found, 224.0681.

*(1H-benzo[d]imidazol-1-yl)(2-methoxyphenyl)methanone****(1X).***[16d] Purified by silica gel column chromatography; White oil; Isolated yield: 1.001 g, 79%; R_f (n-pentane/ethyl acetate =4/1) = 0.15; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.26 (d, *J* = 8.4Hz, 1H), 7.97 (s, 1H), 7.81-7.80 (m, 1H), 7.61-7.58 (m, 1H), 7.54 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.46-7.40 (m, 2H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 166.0, 156.7, 144.3, 143.8, 133.7, 131.8, 130.1, 125.9, 125.3, 123.1, 121.3, 120.5, 115.7, 111.8, 55.9; MS (EI$^+$, 70 eV): m/z (%) = 253.3 (8), 252.3 (41) $[M]^+$, 136.2 (7), 135.2 (100), 120.1 (3), 92.1 (18), 90.1 (7), 79.2 (3), 77.2 (29), 76.1 (3), 64.2 (9), 63.1 (8), 51.1 (4), 50.1 (3); IR (ATR) ν (cm^{-1}) = 3414, 3077, 2943, 2841, 2169,

2045, 1919, 1702, 1600, 1506, 1447, 1359, 1286, 1250, 1196, 1148, 1111, 1085, 1016, 941, 903, 875, 749, 680; Anal. Calcd for $C_{15}H_{12}N_2O_2$: C, 71.42; H, 4.79; N, 11.10. Found: C, 70.53; H, 4.87; N, 10.81. HRMS (ESI) m/z : $[M+H]^+$ calcd for $C_{15}H_{13}N_2O_2$, 253.0972; found, 253.0971.

(2-Hydroxyphenyl)(1H-indol-1-yl)methanone ***(1a).***[8] Purified by silica gel column chromatography; White solid; Isolated yield: 1.225 g, 89%; R_f (n-pentane/ethyl acetate = 30/1) = 0.21; mp 108-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.97 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.64-7.60 (m, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 3.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 3.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ (ppm) 170.7, 161.5, 136.1, 135.4, 131.3, 130.8, 127.9, 125.1, 124.3, 121.2, 119.3, 118.6, 116.2, 116.1, 109.2; MS (EI^+, 70 eV): m/z (%) = 238.0 (5), 237.0 (31) $[M]^+$, 236.1 (1), 135.1 (2), 122.1 (2), 121.0 (23), 120.1 (1), 118.1 (10), 117.1 (100), 116.2 (6), 93.1 (7), 92.1 (3), 91.2 (1), 90.1 (9), 89.1 (9), 77.2 (1), 75.2 (1), 65.2 (12), 64.3 (3), 63.2 (5), 62.3 (1), 53.3 (1), 51.1 (1); IR (ATR) ν (cm^{-1}) = 3200, 2952, 2855, 2704, 2563, 2324, 2213, 2086, 1940, 1795, 1748, 1639, 1602, 1539, 1499, 1452, 1387, 1349, 1299, 1252, 1207, 1154, 1106, 1039, 1015, 936, 891, 833, 748, 714; Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.98; H, 4.32; N, 5.71.

(5-Chloro-2-hydroxyphenyl)(1H-indol-1-yl)methanone ***(1b).*** Purified by silica gel column chromatography; White solid; Isolated yield: 949 mg, 84%; R_f (n-pentane/ethyl acetate = 15/1) = 0.40; mp 161-162 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.21 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.41-7.38 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 1.8 Hz, 1H), 6.97 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.71 (d, *J* = 3.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 170.0, 162.3, 141.4, 136.0, 132.2, 130.8, 127.4, 125.2, 124.4, 121.3, 119.9, 118.8, 116.2, 114.6, 109.6; MS (EI^+, 70 eV): m/z (%) = 273.0 (11), 272.0 (7), 271.0 (34) $[M]^+$, 156.9 (6), 155.0 (18), 127.0 (3), 118.1 (10), 117.1 (100), 116.2 (8), 99.1 (7), 90.1 (7), 89.1 (9), 63.2 (6), 62.2 (2), 53.3 (1); IR (ATR) ν (cm^{-1}) = 3079, 2926, 2746, 2325, 2165, 2084, 1985, 1905, 1794, 1625, 1587, 1544, 1496, 1450, 1416, 1350, 1245, 1203, 1149, 1083, 1016, 911, 861, 824, 745, 719; Anal. Calcd for $C_{15}H_{10}ClNO_2$: C, 66.31; H, 3.71; N, 5.16. Found: C, 66.08; H, 3.78; N, 5.06.

(2,3-Dihydroxyphenyl)(1H-indol-1-yl)methanone ***(1c).***[8] Purified by silica gel column chromatography; Brown oil; Isolated yield: 1.121 g, 97%; R_f (n-pentane/ethyl acetate = 8/1) = 0.24; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.09 (s, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 3.6 Hz, 1H), 7.42-7.40 (m, 1H), 7.36-7.34 (m, 1H), 7.20 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.16-7.14 (m, 1H), 6.90 (t, *J* = 8.1 Hz, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 6.14 (s, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 170.4, 148.3, 145.8, 136.0, 130.8, 127.9, 125.0, 124.3, 122.1, 121.1, 119.8, 119.6, 116.4, 116.3, 109.2; MS (EI^+, 70 eV): m/z (%) = 255.3 (4), 254.3 (24), 253.1 (100) $[M]^+$, 138.2 (3), 137.2 (34), 136.1 (7), 118.2 (14), 117.2 (77), 116.2 (6), 109.2 (3), 107.2 (3), 90.3 (8), 89.2 (11), 81.3 (7), 64.3 (5), 56.5 (3), 55.7 (4), 45.3 (2); IR (ATR) ν (cm^{-1}) = 3388, 2161, 1912, 1646, 1590, 1538, 1449, 1386, 1336, 1263, 1186, 1099, 1073, 1017, 964, 878, 848, 786, 743, 669; Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 70.15; H, 4.27; N, 5.60.

(2-Hydroxy-5-methylphenyl)(1H-indol-1-yl)methanone ***(1d).*** Purified by silica gel column chromatography; White solid; Isolated yield: 485 mg, 64%; R_f (n-pentane/ethyl acetate = 30/1) = 0.31; mp 131-133 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.71 (s, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 3.6 Hz, 1H), 7.40-7.37 (m, 2H), 7.34-7.31 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 3.6 Hz, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 170.8, 159.3, 136.3, 136.1, 131.1, 130.8, 128.6, 128.0, 125.0, 124.2, 121.2, 118.4, 116.2, 115.9, 109.0, 20.7; MS (EI^+, 70 eV): m/z (%) = 252.2 (11), 251.1 (73) $[M]^+$, 136.2 (3), 118.2 (8), 117.2 (100), 116.3 (8), 107.2 (6), 106.3 (3), 105.2 (3), 90.3 (7), 89.3 (11), 79.3 (4), 78.3 (5), 77.3 (17), 64.4 (5), 56.5 (4), 55.0 (4), 45.4 (4); IR (ATR) ν (cm^{-1}) = 3855, 3241, 2915, 2867, 2715, 2565, 2481, 2323, 2099, 1923, 1774, 1652, 1604, 1538, 1507, 1444, 1344, 1257, 1201, 1119, 1061, 1008, 929, 885, 820, 737, 681; Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.45; H, 5.16; N, 5.71.

(4-Chloro-2-hydroxyphenyl)(1H-indol-1-yl)methanone ***(1e).*** Purified by silica gel column chromatography; White solid; Isolated yield: 878 mg, 74%; R_f (n-pentane/ethyl acetate = 15/1) = 0.40; mp 161-163 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.20 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.42-7.38 (m, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 1.8 Hz, 1H), 6.97 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.71 (d, *J* = 3.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 170.0, 162.3, 141.4, 136.0, 132.2, 130.8, 127.5, 125.3, 124.4, 121.3, 120.0, 118.9, 116.2, 114.6, 109.6; MS (EI^+, 70 eV): m/z (%) = 273.0 (11), 272.0 (6), 271.0 (34) $[M]^+$, 156.9 (6), 156.0 (2), 155.0 (18), 129.0 (1), 127.0 (3), 118.1 (10), 117.1 (100), 116.2 (7), 101.1 (2), 99.1 (7), 91.1 (1), 90.1 (7), 89.2 (8), 73.1 (2), 63.2 (6); IR (ATR) ν (cm^{-1}) = 3113, 2957, 2746, 2333, 2190, 2086, 2004, 1905, 1794, 1625, 1588, 1544, 1496, 1450, 1417, 1350, 1246, 1204, 1149, 1083, 1016, 910, 861, 824, 745, 718. Anal. Calcd for $C_{15}H_{10}ClNO_2$: C, 66.31; H, 3.71; N, 5.16. Found: C, 65.88; H, 3.64; N, 5.06. HRMS (ESI) m/z : $[M+]^+$ calcd for $C_{15}H_{10}ClNO_2$, 271.0400.; found, 271.0395.

(5-Fluoro-1H-indol-1-yl)(2-hydroxyphenyl)methanone ***(1f).*** Purified by silica gel column chromatography; Gray solid; Isolated yield: 505 mg, 50%; R_f (n-pentane/ethyl acetate = 8/1) = 0.40; mp 139-141 °C; ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) 9.87 (s, 1H), 8.25 (dd, *J* = 9.0, 4.2 Hz, 1H), 7.58 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.55-7.52 (m, 1H), 7.50 (d, *J* = 4.2 Hz, 1H), 7.28 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.14-7.10 (m, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 3.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) 170.4, 161.5, 160.8, 159.2, 135.5, 132.5, 131.9, 131.8, 131.2, 129.4, 119.4, 118.7, 117.4, 117.3, 115.8, 113.0, 112.8, 108.9, 106.9, 106.7; MS (EI^+, 70 eV): m/z (%) = 256.1 (16), 255.0 (100) $[M]^+$, 136.1 (8), 135.0 (93), 133.9 (11), 122.1 (4), 121.0 (51), 108.1 (8), 107.0 (15), 93.1 (8), 65.2 (13), 63.1 (4); IR (ATR) ν (cm^{-1}) = 3306, 2924, 2853, 2720, 2507, 2324, 2266, 2201, 2171, 2142, 2071, 2008, 1977, 1941, 1856, 1736, 1657, 1599, 1541, 1460, 1384, 1326, 1260, 1201, 1128, 1096, 949, 885, 856, 801, 755, 719; Anal. Calcd for $C_{15}H_{10}FNO_2$: C, 70.58; H, 3.95; N, 5.49. Found: C, 70.69; H, 4.01; N, 5.40.

(5-Chloro-1H-indol-1-yl)(2-hydroxyphenyl)methanone ***(1g).*** Purified by silica gel column chromatography; Brown solid; Isolated yield: 1.175 g, 99%; R_f (n-pentane/ethyl acetate = 15/1) = 0.21; mp 132-135 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.86 (s, 1H), 8.19 (d, *J* = 9.0 Hz, 1H), 7.59-7.57 (m, 2H) 7.54 (t, *J* = 7.8 Hz, 1H), 7.49 (dd, *J* = 3.6, 1.8 Hz, 1H), 7.34 (d, *J* = 9.0 Hz, 1H), 7.13 (d, *J* =8.4 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 3.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 170.5, 161.5, 135.6, 134.5, 132.0, 131.2, 129.8, 129.1, 125.3, 120.8, 119.4, 118.7, 117.2, 115.8, 108.4; MS (EI^+, 70 eV): m/z (%) = 271.9 (11), 270.8 (69) $[M]^+$, 152.8 (34), 151.9 (12), 150.9 (100), 149.9 (9), 122.9 (6), 122.0 (5), 120.9 (64), 93.1 (11), 89.1 (6), 65.2 (19), 63.2 (6); IR (ATR) ν (cm^{-1}) = 3852, 3284, 2923, 2850, 2669, 2330, 2173, 2084, 1991, 1873, 1730, 1652, 1593, 1533, 1444, 1375, 1331, 1250, 1189, 1070, 943, 875, 797, 758, 712, 660; Anal. Calcd for $C_{15}H_{10}ClNO_2$: C, 66.31; H, 3.71; N, 5.16. Found: C, 66.08; H, 3.78; N, 5.06.

(5-Bromo-1H-indol-1-yl)(2-hydroxyphenyl)methanone ***(1h).*** Purified by silica gel column chromatography; Light red solid; Isolated yield: 1.246 g, 99%; R_f (n-pentane/ethyl acetate = 20/1) = 0.29; mp 134-136 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.86 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 1.8 Hz, 1H), 7.57 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.55-7.52 (m, 1H), 7.49-7.47 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.00-6.97 (m, 1H), 6.62 (d, *J* = 3.6 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 170.5, 161.6, 135.6, 134.8, 132.5, 131.2, 129.0, 127.9, 123.9, 119.4, 118.7, 117.6, 117.5, 115.8, 108.3; MS (EI$^+$, 70 eV): m/z (%) = 315.0 (52) [M]$^+$, 236.3 (3), 235.2 (4), 198.2 (7), 197.0 (100), 195.0 (91), 193.9 (4), 122.2 (6), 121.1 (78), 116.2 (17), 115.0 (26), 93.0 (18), 92.1 (3), 89.2 (7), 88.2 (3), 87.0 (3), 65.1 (26), 63.2 (8), 62.0 (5); IR (ATR) ν (cm^{-1}) = 3922, 3846, 3683, 3284, 3156, 3121, 3071, 2963, 2924, 2852, 2740, 2624, 2514, 2330, 2229, 2187, 2163, 2109, 2045, 2000, 1969, 1923, 1880, 1818, 1747, 1648, 1606, 1574, 1533, 1480, 1441, 1370, 1328, 1253, 1178, 1111, 1084, 1056, 1036, 979, 942, 882, 752, 692; Anal. Calcd for $C_{15}H_{10}BrNO_2$: C, 56.99; H, 3.19; N, 4.43. Found: C, 56.70; H, 3.23; N, 4.34.

(2-Hydroxyphenyl)(5-methyl-1H-indol-1-yl)methanone ***(1i).*** Purified by silica gel column chromatography; White solid; Isolated yield: 849 mg, 78%; R_f (n-pentane/ethyl acetate = 20/1) = 0.41; mp 143-144 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.95 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.59 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.53-7.50 (m, 1H), 7.43-7.41 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 3.6 Hz, 1H), 2.48 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 170.5, 161.4, 135.2, 134.3, 134.0, 131.3, 131.1, 128.0, 126.4, 121.1, 119.3, 118.6, 116.2, 115.9, 109.1, 21.6; MS (EI$^+$, 70 eV): m/z (%) = 252.2 (12), 251.1 (77) [M]$^+$, 235.1 (2), 132.2 (14), 131.2 (70), 130.6 (100), 129.2 (2), 128.1 (3), 122.2 (2), 121.1 (33), 103.2 (7), 102.0 (5), 93.0 (10), 92.0 (1), 78.2 (1), 77.2 (7), 76.2 (2), 65.2 (13), 64.3 (1), 63.1 (4), 51.0 (1); IR (ATR) ν (cm^{-1}) = 3181, 2916, 2858, 2710, 2181, 2087, 2022, 1897, 1638, 1604, 1539, 1458, 1383, 1340, 1256, 1209, 1139, 1092, 1065, 1039, 1000, 953, 891, 834, 811, 760, 718; Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.10; H, 4.98; N, 5.50.

(5-Hydroxy-1H-indol-1-yl)(2-hydroxyphenyl)methanone ***(1j).*** Purified by silica gel column chromatography; Gray solid; Isolated yield: 304 mg, 53%; R_f (n-pentane/ethyl acetate = 8/1) = 0.08; mp 175-177 °C; ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) 9.26 (s, 1H), 8.28 (s, 1H), 8.22 (d, *J* = 9.0 Hz, 1H), 7.51 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.48-7.45 (m, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.08-7.05 (m, 1H), 7.04-7.03 (m, 2H), 6.91 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.54 (d, *J* = 3.6 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) 167.4, 155.6, 155.5, 154.2, 154.1, 132.6, 132.4, 129.7, 129.6, 128.5, 121.8, 121.7, 119.7, 116.8, 116.7, 116.6, 113.2, 113.1, 108.1, 105.7, 105.7; MS (EI$^+$, 70 eV): m/z (%) = 254.1 (18), 253.0 (84) [M]$^+$, 150.1 (10), 134.1 (10), 133.1 (100), 132.0 (13), 121.1 (49), 105.1 (5), 104.1 (7), 93.1 (7), 77.2 (6), 76.1 (4), 65.2 (12), 63.2 (4), 51.2 (8); IR (ATR) ν (cm^{-1}) = 3281, 2927, 2852, 2782, 2623, 2553, 2476, 2323, 2172, 2048, 2007, 1947, 1915, 1869, 1795, 1652, 1605, 1549, 1450, 1370, 1261, 1228, 1184, 1144, 1106, 1063, 949, 888, 855, 828, 808, 717; Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 70.91; H, 4.32; N, 5.55.

(2-Hydroxyphenyl)(5-nitro-1H-indol-1-yl)methanone ***(1k).*** Purified by silica gel column chromatography; Yellow solid; Isolated yield: 700 mg, 50%; R_f (n-pentane/ethyl acetate = 5/1) = 0.20; mp 191-193 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.83 (s, 1H), 8.56 (d, *J* = 2.4 Hz, 1H), 8.33 (d, *J* = 9.0 Hz, 1H), 8.28 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.64 (d, *J* = 3.6 Hz, 1H), 7.60-7.57 (m, 2H), 7.16 (dd, *J* = 8.7, 0.9 Hz, 1H), 7.03-7.01 (m, 1H), 6.84 (d, *J* = 3.6 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 170.7, 161.9, 144.6, 139.2, 136.4, 131.2, 130.8, 130.6, 120.2, 119.7, 119.0, 117.5, 116.3, 115.2, 109.2; MS (EI$^+$, 70 eV): m/z (%) = 282.1 (4) [M]$^+$, 163.2 (9), 162.1 (100), 161.2 (3), 146.0 (2), 132.1 (12), 121.0 (13), 117.1 (4), 116.1 (52), 115.1 (4), 114.1 (4), 104.1 (13), 91.2 (1), 90.2 (4), 89.1 (29), 88.1 (3), 87.1 (3), 86.1 (2), 77.2 (3), 76.2 (3), 65.2 (3), 64.3 (2), 63.2 (10), 62.1 (5), 57.2 (2), 51.4 (2); IR (ATR) ν (cm^{-1}) = 3802, 3691, 3356, 3098, 3028, 2922, 2854, 2629, 2553, 2412, 2287, 2212, 2159, 2107, 2032, 1992, 1940, 1846, 1741, 1665, 1599, 1510, 1447, 1383, 1326, 1193, 1074, 949, 883, 824, 743; Anal. Calcd for $C_{15}H_{10}N_2O_4$: C, 63.83; H, 3.57; N, 9.93. Found: C, 63.76; H, 3.70; N, 9.89.

1-(2-Hydroxybenzoyl)-1H-indole-5-carbonitrile ***(1l).*** Purified by silica gel column chromatography; Yellow solid; Isolated yield: 571 mg, 48%; R_f (n-pentane/ethyl acetate = 5/1) = 0.13; mp 159-161 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.83 (s, 1H), 8.32 (d, *J* = 9.0 Hz, 1H), 7.97 (s, 1H), 7.64 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.60 (d, *J* = 3.6 Hz, 1H), 7.58-7.56 (m, 2H), 7.16-7.14 (m, 1H), 7.02-7.00 (m, 1H), 6.75 (d, *J* = 3.6 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 170.7, 161.8, 138.0, 136.2, 131.1, 130.8, 130.0, 128.1, 126.1, 119.7, 119.6, 118.9, 117.0, 115.3, 108.4, 107.5; MS (EI$^+$, 70 eV): m/z (%) = 263.2 (14), 262.1 (84) [M]$^+$, 143.2 (4), 142.1 (39), 135.1 (10), 122.2 (8), 121.0 (100), 120.1 (6), 115.1 (4), 114.1 (4), 93.1 (10), 92.1 (5), 65.2 (12), 64.2 (2), 63.2 (3); IR (ATR) ν (cm^{-1}) = 3854, 3320, 3158, 3064, 2923, 2853, 2727, 2535, 2324, 2171, 2104, 2014, 1985, 1935, 1898, 1857, 1655, 1606, 1577, 1540, 1459, 1371, 1330, 1250, 1193, 1158, 1090, 1032, 889, 819, 761, 724, 665; Anal. Calcd for $C_{16}H_{10}N_2O_2$: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.39; H, 3.83; N, 11.25. HRMS (ESI) m/z : [M+Na]$^+$ calcd for $C_{16}H_{10}N_2O_2Na$, 285.0635; found, 285.0631.

(4-Bromo-1H-indol-1-yl)(2-hydroxyphenyl)methanone ***(1m).*** Purified by silica gel column chromatography; White solid; Isolated yield: 663 mg, 59%; R_f (n-pentane/ethyl acetate = 40/1) = 0.20; mp 114-116 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.89 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.56-7.52 (m, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.27-7.24 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 3.6 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 170.8, 161.7, 136.4, 135.8, 131.5, 131.3, 128.5, 127.1, 126.1, 119.5, 118.8, 115.7, 115.2, 115.0, 108.8; MS (EI$^+$, 70 eV): m/z (%) = 317.9 (8), 316.9 (48), 315.9 (9), 314.9 (84) [M]$^+$, 197.9 (9), 196.9 (96), 195.9 (12), 194.9 (100), 120.9 (85), 115.9 (20), 114.9 (20), 113.9 (8), 92.9 (17), 91.9 (7), 89.0 (9), 87.9 (8), 65.0 (29), 64.0 (6), 63.0 (10); IR (ATR) ν (cm^{-1}) = 3254, 3111, 3057, 2923, 2854, 2660, 2325, 2200, 2114, 1995, 1926, 1854, 1784, 1725, 1646, 1606, 1578, 1529, 1471, 1421, 1380, 1329, 1278, 1237, 1150, 1053, 966, 878, 743, 680; Anal. Calcd for $C_{15}H_{10}BrNO_2$: C, 56.99; H, 3.19; N, 4.43. Found: C, 57.19; H, 3.28; N, 4.43.

(2-Hydroxyphenyl)(6-methyl-1H-indol-1-yl)methanone ***(1n).*** Purified by silica gel column chromatography; Light brown solid; Isolated yield: 909 mg, 91%; R_f (n-pentane/ethyl acetate = 40/1) = 0.15; mp 86-89 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.98 (s, 1H), 8.13 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.53-7.49 (m, 2H), 7.38 (d, *J* = 3.6 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* =8.4 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 3.6 Hz, 1H), 2.52 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 170.8, 161.4, 136.5, 135.3, 131.3, 128.5, 127.4, 125.7, 120.8, 119.3, 118.6, 116.5, 116.3, 109.1, 22.1; MS (EI$^+$, 70 eV): m/z (%) = 252.3 (16), 251.1 (72) [M]$^+$, 249.9 (2), 235.1 (2), 196.2 (2), 132.3 (16), 130.9 (100), 130.1 (40), 129.2 (2), 128.1 (5), 122.2 (3), 121.1 (40), 103.2 (9), 102.0 (8), 93.0 (14), 78.2 (2), 77.1 (12), 75.2 (2), 65.1 (21), 63.0 (7), 52.9 (2), 50.8 (3); IR (ATR) ν (cm^{-1}) = 3271, 3068, 3022, 2919, 2854, 2691, 2555, 2328, 2188, 2112, 1992, 1916, 1878, 1751, 1716, 1647, 1602, 1540, 1487, 1452, 1389, 1347, 1254, 1204, 1129, 1100, 1032, 937, 890, 807, 750, 713, 667; Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.11; H, 5.20; N, 5.47.

(2-Hydroxyphenyl)(7-methyl-1H-indol-1-yl)methanone ***(1o).*** Purified by silica gel column chromatography; Light yellow solid; Isolated yield: 899 mg, 82%; R_f (n-pentane/ethyl acetate = 15/1) = 0.60; mp 95-96 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.72 (s, 1H), 7.76 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.58-7.55 (m, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 3.6 Hz, 1H), 7.28-7.26 (m, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.99-6.97 (m, 1H), 6.67 (d, *J* = 4.2 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 171.4, 162.9, 136.4, 135.7, 132.1, 131.9, 129.4, 127.6, 125.8, 124.2, 119.5, 119.0, 118.7, 115.5, 108.6, 21.5; MS (EI$^+$, 70 eV): m/z (%) = 251.9 (10), 250.8 (47) [M]$^+$, 250.1 (2), 132.0 (10), 131.0 (100), 130.0 (30), 129.0 (1), 127.9 (2), 122.0 (2), 120.9 (29), 103.0 (5), 102.0 (3), 93.1 (7), 92.1 (2), 77.2 (5), 65.2 (11), 63.2 (3), 51.3 (2); IR (ATR) ν (cm^{-1}) = 3838, 3677, 3471, 3131, 3063, 2951, 2651, 2319, 2205, 2154, 2039, 1930, 1734, 1644, 1533, 1477, 1406, 1338, 1259, 1195, 1075, 1042, 960, 886, 801, 765, 695; Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.55; H, 5.30; N, 5.47.

(7,8-Dihydrocyclopenta[g]indol-1(6H)-yl)(2-hydroxyphenyl)methanone ***(1p).*** Purified by silica gel column chromatography; White solid; Isolated yield: 620 mg, 60%; R_f (n-pentane/ethyl acetate = 20/1) = 0.70; mp 87-88 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.60 (s, 1H), 7.70 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.56-7.53 (m, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 3.6 Hz, 1H), 7.27-7.26 (m, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 3.6 Hz, 1H), 3.10-3.05 (m, 4H), 2.16-2.11 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 170.7, 162.6, 143.0, 136.0, 133.3, 132.0, 130.3, 129.9, 128.0, 120.9, 119.4, 119.1, 118.6, 115.6, 108.9, 34.0, 33.4, 25.7; MS (EI$^+$, 70 eV): m/z (%) = 278.1 (11), 277.0 (51) [M]$^+$, 158.1 (13), 157.0 (100), 156.0 (28), 155.0 (5), 154.0 (13), 129.0 (7), 128.0 (7), 127.0 (5), 120.9 (24), 92.9 (6), 65.0 (10); IR (ATR) ν (cm^{-1}) = 3875, 3436, 3125, 3058, 2959, 2925, 2870, 2834, 2322, 2170, 2089, 2019, 1995, 1967, 1867, 1812, 1741, 1645, 1606, 1535, 1483, 1413, 1383, 1340, 1260, 1234, 1196, 1152, 1096, 1063, 1034, 954, 933, 882, 806, 767, 722, 671; Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.56; H, 5.44; N, 4.98.

(2-Hydroxyphenyl)(2-phenyl-1H-indol-1-yl)methanone ***(1q).***[7a] Purified by silica gel column chromatography; Yellow solid; Isolated yield: 712 mg, 76%; R_f (n-pentane/ethyl acetate = 20/1) = 0.62; mp 135-137 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.56 (s, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.44-7.40 (m, 2H), 7.38-7.37 (m, 2H), 7.30-7.27 (m, 3H), 7.25-7.21 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.85 (s, 1H), 6.70 (t, *J* = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 173.9, 162.4, 141.4, 138.3, 136.8, 132.7, 129.6, 128.7, 128.0, 124.3, 123.2, 121.1, 119.4, 118.1, 116.9, 113.9, 109.5; MS (EI$^+$, 70 eV): m/z (%) = 314.2 (5), 313.2 (21) [M]$^+$, 194.2 (23), 193.1 (100), 192.3 (11), 191.2 (5), 190.1 (4), 166.2 (3), 165.1 (18), 164.3 (3), 121.1 (27), 93.2 (9), 90.3 (4), 89.2 (5), 65.2 (15), 63.2 (4); IR (ATR) ν (cm^{-1}) = 3869, 3196, 3051, 2696, 2488, 2323, 2185, 2101, 1996, 1883, 1800, 1745, 1646, 1609, 1575, 1478, 1450, 1364, 1324, 1291, 1239, 1189, 1159, 1111, 1026, 965, 899, 864, 785, 752, 692, 664; Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47. Found: C, 79.60; H, 4.65; N, 4.30. HRMS (ESI) m/z : [M+Na]$^+$ calcd for $C_{21}H_{15}NO_2Na$, 336.0995; found, 336.0997.

(2-Hydroxyphenyl)(1,2,3,4-tetrahydro-9H-carbazol-9-yl)methanone ***(1r).***[7a] Purified by silica gel column chromatography; Yellow oil; Isolated yield: 971 mg, 74%; R_f (n-pentane/ethyl acetate = 30/1) = 0.16; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.38 (s, 1H), 7.54-7.51 (m, 1H), 7.50 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.13-7.09 (m, 2H), 6.88-6.86 (m, 1H), 2.86-2.61 (m, 4H), 1.89-1.87 (m, 4H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 172.2, 161.8, 136.7, 136.2, 136.2, 132.8, 130.1, 123.2, 122.7, 119.2, 118.4, 118.1, 118.1, 116.9, 114.1, 25.2, 23.5, 22.5, 21.2; MS (EI$^+$, 70 eV): m/z (%) = 292.4 (8), 291.1 (63) [M]$^+$, 172.3 (14), 171.2 (100), 170.2 (8), 168.2 (7), 167.2 (5), 154.2 (2), 144.2 (5), 143.2 (46), 142.3 (4), 140.2 (2), 128.2 (2), 121.2 (19), 116.0 (2), 115.2 (5), 93.2 (5), 66.0 (7), 45.4 (3); IR (ATR) ν (cm^{-1}) = 3283, 3054, 2932, 2849, 2161, 1933, 1643, 1605, 1479, 1454, 1363, 1307, 1247, 1203, 1150, 1110, 1054, 1032, 958, 926, 882, 821, 742, 659; Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 77.94; H, 5.53; N, 4.87.

(2-Hydroxyphenyl)(2-methyl-1H-indol-1-yl)methanone ***(1s).***[7a] Purified by silica gel column chromatography; Yellow oil; Isolated yield: 351 mg, 82%; R_f (n-pentane/ethyl acetate = 20/1) = 0.67; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.56 (s, 1H), 7.57-7.54 (m, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.45 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.18-7.14 (m, 2H), 7.11-7.06 (m, 2H), 6.88-6.85 (m, 1H), 6.48 (s, 1H), 2.48 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 173.3, 162.4, 137.7, 137.4, 136.8, 133.0, 129.6, 122.8, 122.7, 120.1, 119.4, 118.5, 116.6, 113.6, 108.5, 15.1; MS (EI$^+$, 70 eV): m/z (%) = 252.2 (9), 251.1 (50) [M]$^+$, 132.2 (11), 131.2 (100), 130.2 (34), 121.1 (21), 103.2 (5), 93.1 (6), 77.2 (4), 65.2 (11), 63.3 (3); IR (ATR) ν (cm^{-1}) = 3283, 3057, 2967, 2924, 2750, 2322, 2085, 1929, 1645, 1608, 1480, 1453, 1372, 1311, 1252, 1199, 1111, 1029, 972, 890, 857, 812, 745, 710, 659; Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 74.39; H, 4.96; N, 6.05. HRMS (ESI) m/z : [M+Na]$^+$ calcd for $C_{16}H_{13}NO_2Na$, 274.0839; found, 274.0834.

Ethyl 1-(2-hydroxybenzoyl)-1H-indole-2-carboxylate ***(1t).*** Purified by silica gel column chromatography; Colorless solid; Isolated yield: 340 mg, 23%; R_f (n-pentane/ethyl acetate = 20/1) = 0.37; mp 103-104 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.63 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.54-7.51 (m, 2H), 7.45 (s, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.26 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 4.13-4.12 (m, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 173.6, 162.4, 160.8, 138.7, 137.0, 131.2, 130.9, 127.4, 127.2, 123.4, 122.9, 119.8, 118.5, 117.6, 115.6, 113.3, 61.6, 14.0; MS (EI$^+$, 70 eV): m/z (%) = 310.3 (11), 309.0 (99) [M]$^+$, 264.0 (8), 236.2 (3), 190.2 (12), 189.1 (100), 144.2 (7), 143.2 (41), 121.1 (19), 116.2 (3), 115.2 (9), 93.3 (5), 92.2 (2), 89.2 (4), 66.0 (8). 45.3 (3); IR (ATR) ν (cm^{-1}) = 3231, 3066, 2992, 2958, 2655, 2322, 2166, 2076, 1827, 1701, 1654, 1614, 1580, 1530, 1479, 1443, 1381, 1327, 1280, 1239, 1197, 1156, 1023, 962, 893, 860, 812, 752, 698; Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. Found: C, 69.34; H, 4.79; N, 4.38. HRMS (ESI) m/z : [M+Na]$^+$ calcd for $C_{18}H_{15}NO_4Na$, 332.0893; found, 332.0892.

(2-Hydroxyphenyl)(3-methyl-1H-indol-1-yl)methanone ***(1u).***[8] Purified by silica gel column chromatography; White solid; Isolated yield: 844 mg, 84%; R_f (n-pentane/ethyl acetate = 20/1) = 0.41; mp 154-156 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.95 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.61 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 8.4 Hz, 1H), 7.41-7.39 (m, 1H), 7.36-7.34 (m, 1H), 7.25 (s, 1H), 7.11 (dd, *J* = 8.4, 0.6 Hz, 1H), 6.99 (t, *J* = 8.1 Hz, 1H), 2.30 (d, *J* = 1.2 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 170.2, 161.2, 136.4, 135.0, 131.9, 131.2, 125.2, 124.7, 124.1, 119.2, 119.2, 118.6, 118.5, 116.5, 116.4, 9.9; MS (EI$^+$, 70 eV): m/z (%) = 252.3 (9), 251.1 (61) [M]$^+$, 132.2 (10), 131.2 (100), 130.2 (59), 129.2 (2), 128.2 (3), 122.2 (2), 121.2 (22), 103.2 (6), 102.2 (4), 93.3 (7), 92.3 (2), 77.3 (8), 76.3 (2), 66.0 (12), 65.3 (2), 64.4 (3), 54.9 (2), 45.4 (6); IR (ATR) ν (cm^{-1}) = 3232, 2915, 2858, 2714, 2569, 2320, 2078, 1915, 1650, 1598, 1449, 1355, 1254, 1213, 1099, 1044, 932, 875, 742. Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.06; H, 5.25; N, 5.47.

1-(2-Hydroxybenzoyl)-1H-indole-3-carbonitrile ***(1v).*** Purified by recrystal (a mixture of n-pentane and ethyl acetate used as the recrystallization solvent); White solid; Yield: 575 mg, 47%; R_f (n-pentane/ethyl acetate = 8/1) = 0.21; mp 161-164 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.68 (s, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.98 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.62-7.59 (m, 1H), 7.52-7.46 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.06-7.03 (m, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 170.0, 161.9, 136.8, 135.2, 134.8, 131.0, 128.2, 126.9, 125.6, 120.1, 120.0, 119.1, 116.3, 114.8, 113.9, 93.9; MS (EI$^+$, 70 eV): m/z (%) = 264.2 (7), 263.3 (35), 262.6 (22), 262.0 (100) [M]$^+$, 235.1 (5), 207.2 (6), 143.2 (4), 142.2 (29), 141.2 (6), 122.2 (15), 121.1 (98), 120.2 (6), 115.2 (5), 114.2 (10), 93.2 (13), 92.2 (7), 66.0 (19), 64.3 (5), 45.3 (10); IR (ATR) ν (cm^{-1}) = 3779, 3314, 3143, 3068, 2924, 2689, 2233, 2079, 1989, 1919, 1803, 1765, 1703, 1605, 1547, 1499, 1453, 1343, 1309, 1257, 1205, 1153, 1123, 1097, 1025, 945, 882, 848, 744, 704, 658; Anal. Calcd for $C_{16}H_{10}N_2O_2$: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.27; H, 3.84; N, 10.75.

Methyl 1-(2-hydroxybenzoyl)-1H-indole-3-carboxylate ***(1w).*** Purified by silica gel column chromatography; White solid; Isolated yield: 433 mg, 49%; R_f (n-pentane/ethyl acetate = 10/1) = 0.20; mp 145-147 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.85 (s, 1H), 8.22-8.19 (m, 2H), 8.12 (s, 1H), 7.59-7.56 (m, 2H), 7.44-7.43 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 3.94 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 170.9, 164.5, 161.9, 136.4, 136.3, 133.6, 131.2, 127.7, 125.8, 125.2, 122.0, 119.9, 118.9, 115.9, 115.2, 113.8, 51.8; MS (EI$^+$, 70 eV): m/z (%) = 296.3 (10), 295.0 (82) [M]$^+$, 264.0 (6), 176.3 (13), 175.2 (100), 174.4 (4), 146.2 (4), 145.2 (6), 144.2 (57), 143.3 (4), 121.2 (32), 116.2 (8), 115.2 (4), 93.3 (6), 89.2 (5), 66.0 (8), 64.4 (2), 45.4 (3); IR (ATR) ν (cm^{-1}) = 3408, 3150, 3053, 2952, 2319, 2165, 2088, 2015, 1917, 1667, 1609, 1552, 1483, 1446, 1362, 1325, 1278, 1245, 1188, 1151, 1033, 970, 933, 883, 812, 758, 658; Anal. Calcd for $C_{17}H_{13}NO_4$: C, 69.15; H, 4.44; N, 4.74. Found: C, 69.12; H, 4.29; N, 4.43.

(2-Hydroxyphenyl)(1H-pyrrol-1-yl)methanone ***(1y).*** Purified by silica gel column chromatography; Light yellow oil; Isolated yield: 867 mg, 93%; R_f (n-pentane/ethyl acetate = 15/1) = 0.50; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.01 (s, 1H), 7.67 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.54-7.51 (m, 1H), 7.34 (t, *J* = 2.4 Hz, 2H), 7.10 (dd, *J* = 8.4, 0.6 Hz, 1H), 6.98- 6.96 (m, 1H), 6.40 (t, *J* = 2.4 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 170.0, 161.8, 135.8, 131.4, 121.8, 119.3, 118.5, 115.0, 113.6; MS (EI$^+$, 70 eV): m/z (%) = 188.3 (12), 187.2 (100) [M]$^+$, 185.9 (3), 170.1 (2), 130.1 (1), 122.2 (7), 121.0 (88), 120.1 (7), 94.1 (1), 93.2 (13), 92.1 (11), 77.2 (1), 68.2 (2), 67.2 (32), 66.3 (2), 65.1 (21), 64.2 (2), 63.0 (7), 53.0 (2); IR (ATR) ν (cm^{-1}) = 3880, 3319, 3150, 2665, 2334, 2083, 1992, 1927, 1652, 1609, 1580, 1464, 1406, 1339, 1242, 1183, 1154, 1082, 1036, 972, 885, 816, 740, 711, 671; Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 69.63; H, 4.81; N, 7.67. HRMS (ESI) m/z : [M+]$^+$ calcd for $C_{11}H_9NO_2$, 187.0628; found, 187.0632.

(1H-benzo[d]imidazol-1-yl)(2-hydroxyphenyl)methanone ***(1z).*** Purified by recrystal; White solid; Isolated yield: 76 mg, 16%; R_f (n-pentane/ethyl acetate = 4/1) = 0.09; mp 120-122 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.94 (s, 1H), 8.34 (s, 1H), 8.09-8.07 (m, 1H), 7.87-7.86 (m, 1H), 7.63-7.60 (m, 2H), 7.48-7.44 (m, 2H), 7.19-7.19 (m, 1H), 7.05 (t, *J* = 7.5 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 169.5, 162.0, 144.1, 143.0, 136.8, 132.2, 131.0, 126.0, 125.6, 120.9, 120.0, 119.0, 115.3, 115.0; MS (EI$^+$, 70 eV): m/z (%) = 239.4 (3), 238.3 (30) [M]$^+$, 237.4 (3), 122.2 (5), 121.2 (100), 120.2 (29), 119.2 (3), 118.2 (52), 93.2 (13), 92.2 (21), 91.2 (4), 90.2 (10), 65.2 (21), 64.2 (9), 63.2 (11); IR (ATR) ν (cm^{-1}) = 3371, 3124, 3060, 2921, 2855, 2696, 2589, 2321, 2176, 2083, 2007, 1926, 1795, 1689, 1599, 1513, 1451, 1395, 1350, 1308, 1252, 1208, 1145, 1088, 1008, 916, 881, 837, 740; Anal. Calcd for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.54; H, 4.46; N, 11.15. HRMS (ESI) m/z : [M+H]$^+$ calcd for $C_{14}H_{11}N_2O_2$, 239.0815; found, 239.0813.

(1H-indol-1-yl)(2-nitrophenyl)methanone ***(1Y).***[16e] Prepared according to literature procedure.[1] A solution of indole (1.172 g, 10.0 mmol), tetrabutylammonium hydrogensulfate (61.2 mg, 0.18 mmol), powdered NaOH (1.2 g, 30.0 mmol), 2-nitrobenzoyl chloride (1.98 mL, 15.0 mmol), in CH_2Cl_2 (30 mL) were stirred in a flask under air at room temperature for 5 h. The reaction mixture was washed with water (30 mL) and extracted with CH_2Cl_2 (3×30 mL). The combined organic layer was dried with Na_2SO_4. Then the solvent was evaporated under vacuum. The residue was purified by flash chromatography on silica gel with n-pentane/ethyl acetate (10:1) as the solvent to afford the pure product. Brown solid; Isolated yield: 2.18 g, 82%; R_f (n-pentane/ethyl acetate = 10/1) = 0.14; mp 110-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.59 (br s, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 7.4 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.64-7.59 (m, 2H), 7.41-7.32 (m, 2H), 6.82 (br s, 1H), 6.61 (s, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 164.9, 145.6, 135.8, 134.6, 131.4, 131.3, 130.8, 128.9, 125.6, 125.5, 125.0, 124.5, 121.2, 116.7, 110.3; MS (EI$^+$, 70 eV): m/z (%) = 267.4 (10), 266.4 (62) [M]$^+$, 233.3 (3), 220.3 (3), 191.2 (4), 190.2 (4), 165.2 (3), 163.1 (3), 151.2 (8), 150.2 (100), 135.2 (4), 134.1 (5), 133.1 (3), 132.2 (34), 117.2 (5), 116.1 (32), 104.1 (18), 92.1 (3), 90.1 (5), 89.1 (25), 79.2 (3), 78.2 (9), 77.1 (6), 76.2 (30), 75.1 (5), 74.1 (3), 64.1 (4), 63.2 (14), 62.1 (3), 52.1 (7), 51.2 (35), 50.1 (12); IR (ATR) ν (cm^{-1}) = 3869, 3364, 3151, 3121, 3049, 2922, 2856, 2659, 2323, 2203, 2174, 2018, 1912, 1737, 1686, 1583, 1521, 1476, 1448, 1382, 1344, 1242, 1208, 1150, 1097, 1055, 1013, 985, 871, 846, 746, 710; Anal. Calcd for $C_{15}H_{10}N_2O_3$: C, 67.67; H, 3.79; N, 10.52. Found: C, 67.77; H, 3.65; N, 10.37.

(2-Aminophenyl)(1H-indol-1-yl)methanone ***(1zb).***[16f] A solution of (1*H*-indol-1-yl)(2-nitrophenyl)methanone (532 mg, 2.0 mmol), iron dust (560 mg, 10.0 mmol), 32% HCl (2.0 mL) in CH_3CH_2OH (8 mL) were stirred in a flask under air at 120 ℃ for 2 h. The solvent was removed in vacuo. The mixture was washed with water (10 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was dried with Na_2SO_4. Then the solvent was evaporated under vacuum. The residue was purified by flash chromatography on silica gel with n-pentane/ethyl acetate (4:1) as the solvent to afford the pure product. Yellow oil; Isolated yield: 417 mg, 88%; R_f (n-pentane/ethyl acetate = 4/1) = 0.80; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.30 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.39-7.35 (m, 3H), 7.34-7.29 (m, 2H), 6.79 (t, *J* = 8.4 Hz, 1H), 6.76-6.73 (m, 1H), 6.61 (d, *J* = 4.2 Hz, 1H), 5.05 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 169.4, 149.1, 136.2, 133.4, 131.5, 131.0, 128.2, 124.7, 123.8, 121.0, 117.2, 116.8, 116.3, 108.1; MS (EI$^+$, 70 eV): m/z (%) = 237.4 (8), 236.4 (41) [M]$^+$, 235.5 (2), 121.2 (8), 120.2 (100), 119.3 (3), 117.2 (14), 116.2 (56), 92.2 (27), 91.2 (3), 90.2 (6), 89.2 (29), 65.3 (19), 64.3 (4), 63.2 (13), 62.3 (3), 52.3 (3); IR (ATR) ν (cm^{-1}) = 3873, 3475, 3378, 3117, 3044, 2649, 2495, 2320, 2172, 2084, 2004, 1901, 1748, 1659, 1616, 1565, 1529, 1486, 1445, 1380, 1318, 1242, 1205, 1145, 1123, 1016, 976, 940, 913, 878, 857, 857, 822, 745, 675; Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 75.78; H, 4.82; N, 11.88.

N-(2-(1H-indole-1-carbonyl)phenyl)-4-methylbenzenesulfonamide ***(1zc).*** A solution of (2-aminophenyl)(1*H*-indol-1-yl)methanone (449 mg, 1.90 mmol), pyridine(0.19 mL, 2.28 mmol), 4-Methylbenzenesulfonyl chloride (2.28 mmol, 435 mg) in CH_2Cl_2 (12 mL) were stirred in a flask under air at room temperature for 8 h. The mixture was washed with water (20 mL) and extracted with CH_2Cl_2 (3×20 mL). The

combined organic layer was dried with Na_2SO_4. Then the solvent was evaporated under vacuum. The residue was purified by flash chromatography on silica gel with n-pentane/ethyl acetate (8:1) as the solvent to afford the pure product. White solid; Isolated yield: 408 mg, 55%; R_f (n-pentane/ethyl acetate = 8/1) = 0.25; mp 140-141 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.54 (s, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.59-7.56 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.39-7.33 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 2H), 6.64 (d, *J* = 4.2 Hz, 1H), 6.46 (d, *J* = 3.6 Hz, 1H), 2.06 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 167.5, 144.0, 137.4, 135.8, 135.7, 133.1, 130.7, 130.3, 129.5, 127.4, 127.1, 126.6, 126.0, 125.4, 125.0, 124.6, 121.0, 116.7, 108.9, 21.4; MS (EI$^+$, 70 eV): m/z (%) = 391.4 (4), 390.4 (13) [M]$^+$, 275.3 (4), 274.3 (25), 273.2 (10), 236.4 (9), 235.4 (54), 234.3 (8), 210.3 (15), 209.3 (22), 208.2 (5), 195.3 (3), 180.3 (5), 167.2 (6), 166.1 (3), 155.2 (4), 119.1 (20), 118.1 (11), 117.2 (100), 116.1 (3), 92.2 (19), 91.1 (32), 90.1 (5), 89.1 (7), 65.2 (8), 64.2 (4), 63.2 (4); IR (ATR) ν (cm^{-1}) = 3879, 3276, 3152, 3054, 2922, 2855, 2668, 2322, 2173, 2087, 1978, 1916, 1809, 1744, 1650, 1595, 1539, 1484, 1448, 1399, 1334, 1275, 1243, 1201, 1183, 1157, 1089, 1062, 1016, 954, 914, 861, 807, 759, 713, 675; Anal. Calcd for $C_{22}H_{18}N_2O_3S$: C, 67.68; H, 4.65; N, 7.17. Found: C, 67.81; H, 4.64; N, 7.05.

5a,6-Dihydro-12H-benzo[5,6][1,3]oxazino[3,2-a]indol-12-one ***(2a).***[8] Purified by silica gel column chromatography; White solid; Isolated yield: 103 mg, 87%; R_f (n-pentane/ethyl acetate = 30/1) = 0.12; mp 127-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.30-7.24 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.09-7.04 (m, 2H), 6.06-6.01 (m, 1H), 3.57 (dd, *J* = 16.6, 8.2 Hz, 1H), 3.45 (dd, *J* = 16.4, 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 159.2, 156.8, 140.5, 134.5, 128.5, 127.2, 124.9, 124.3, 123.4, 119.9, 116.9, 115.4, 89.6, 35.3; MS (EI$^+$, 70 eV): m/z (%) = 238.1 (21), 237.1 (100) [M]$^+$, 121.1 (13), 120.1 (30), 118.2 (9), 117.1 (71), 116.3 (3), 92.2 (17), 90.2 (9), 89.2 (9), 77.2 (1), 76.1 (1), 65.3 (2), 64.3 (5), 63.3 (6); IR (ATR) ν (cm^{-1}) = 3882, 3324, 3196, 3049, 2922, 2855, 2656, 2317, 2171, 2090, 2007, 1890, 1819, 1659, 1600, 1474, 1315, 1225, 1184, 1149, 1081, 1021, 938, 857, 798, 746, 689; Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 74.81; H, 4.29; N, 6.04; HRMS (ESI) m/z : [M+Na]$^+$ calcd for $C_{15}H_{11}NO_2Na$, 260.0682; found, 260.0680.

2-Chloro-5a,6-dihydro-12H-benzo[5,6][1,3]oxazino[3,2a]indol-12-one ***(2b).*** Purified by silica gel column chromatography; White solid; Isolated yield: 92 mg, 68%; R_f (n-pentane/ethyl acetate = 10/1) = 0.56; mp 159-161 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.10 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.30-7.26 (m, 2H), 7.17 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.11-7.08 (m, 2H), 6.06 (t, *J* = 7.8 Hz, 1H), 3.59 (dd, *J* = 16.5, 8.1 Hz, 1H), 3.46 (dd, *J* = 16.5, 6.9 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 158.5, 157.3, 140.4, 140.2, 129.6, 128.6, 127.0, 125.0, 124.5, 124.0, 118.4, 117.4, 115.5, 90.0, 35.2; MS (EI$^+$, 70 eV): m/z (%) = 273.2 (40), 272.3 (28), 271.0 (100) [M]$^+$, 269.9 (3), 157.1 (3), 156.2 (5), 155.2 (9), 154.1 (13), 128.1 (3), 126.1 (9), 118.2 (7), 117.2 (65), 98.2 (3), 90.3 (12), 89.3 (12), 64.3 (8); IR (ATR) ν (cm^{-1}) = 3881, 3326, 3057, 2926, 2851, 2674, 2324, 2176, 2108, 1993, 1897, 1722, 1659, 1594, 1477, 1430, 1304, 1224, 1172, 1072, 947, 866, 752, 662; Anal. Calcd for $C_{15}H_{10}ClNO_2$: C, 66.31; H, 3.71; N, 5.16. Found: C, 65.77; H, 3.68; N, 4.97; HRMS (ESI) m/z: [M+Na]$^+$ calcd for $C_{15}H_{10}ClNO_2Na$, 294.0292; found, 294.0292.

4-Hydroxy-5a,6-dihydro-12H-benzo[5,6][1,3]oxazino[3,2a]indol-12-one ***(2c).***[8] Purified by silica gel column chromatography; White solid; Isolated yield: 86 mg, 68%; R_f (n-pentane/ethyl acetate = 8/1) = 0.08; mp 231-233 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.15 (d, *J* = 7.8 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.32-7.28 (m, 2H), 7.16-7.15 (m, 1H), 7.12-7.08 (m, 2H), 6.11 (t, *J* = 7.5 Hz, 1H), 5.47 (s, 1H), 3.63 (dd, *J* = 16.8, 8.4 Hz, 1H), 3.53 (dd, *J* = 16.8, 6.6Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 159.1, 144.4, 144.1, 140.5, 128.6, 126.8, 124.9, 124.5, 123.7, 120.4, 120.3, 119.7, 115.5, 90.4, 35.3; MS (EI$^+$, 70 eV): m/z (%) = 254.3 (14), 253.1 (100) [M]$^+$, 251.9 (3), 137.2 (7), 136.2 (42), 119.3 (4), 118.3 (46), 117.3 (68), 108.2 (10), 107.2 (5), 91.3 (4), 90.3 (15), 89.3 (15), 80.3 (8), 79.3 (4), 64.5 (4), 56.5 (3), 55.8 (13), 54.9 (7), 54.2 (3), 45.4 (4); IR (ATR) ν (cm^{-1}) = 3858, 3626, 3218, 2919, 2851, 2681, 2507, 2326, 2077, 1987, 1918, 1777, 1645, 1588, 1463, 1335, 1297, 1255, 1172, 1065, 978, 923, 890, 849, 805, 736, 672; Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 71.61; H, 4.59; N, 5.41; HRMS (ESI) m/z: [M+Na]$^+$ calcd for $C_{15}H_{11}NO_3Na$, 276.0631; found, 276.0631.

2-Methyl-5a,6-dihydro-12H-benzo[5,6][1,3]oxazino[3,2-a]indol-12-one ***(2d).*** Purified by silica gel column chromatography; White solid; Isolated yield: 112 mg, 89%; R_f (n-pentane/ethyl acetate = 30/1) = 0.19; mp 139-142 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.14 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 1.8 Hz, 1H), 7.30-7.26 (m, 3H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.02 (t, *J* = 7.5 Hz, 1H), 3.58 (dd, *J* = 16.8 Hz, 1H), 3.45 (dd, *J* = 16.5 Hz, 1H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 159.5, 154.8, 140.6, 135.3, 133.0, 128.5, 128.3, 127.3, 124.9, 124.2, 119.5, 116.6, 115.5, 89.6, 35.3, 20.8; MS (EI$^+$, 70 eV): m/z (%) = 252.3 (14), 251.2 (100) [M]$^+$, 135.3 (12), 134.2 (47), 125.6 (3), 118.3 (5), 117.2 (58), 106.3 (10), 105.3 (9), 90.3 (9), 89.3 (10), 78.3 (9), 77.3 (4), 55.8 (4), 54.9 (3); IR (ATR) ν (cm^{-1}) = 3857, 3309, 3196, 3033, 2918, 2858, 2727, 2324, 2086, 1990, 1867, 1653, 1604, 1483, 1426, 1306, 1229, 1143, 1069, 1031, 913, 856, 817, 745, 706, 663; Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.46; H, 5.13; N, 5.45; HRMS (ESI) m/z: [M+Na]$^+$ calcd for $C_{16}H_{13}NO_2Na$, 274.0839; found, 274.0838.

3-Chloro-5a,6-dihydro-12H-benzo[5,6][1,3]oxazino[3,2-a]indol-12-one ***(2e).*** Purified by silica gel column chromatography; White solid; Isolated yield: 100 mg, 74%; R_f (n-pentane/ethyl acetate = 10/1) = 0.56; mp 158-159 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.10 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.31-7.26 (m, 2H), 7.17 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.11-7.08 (m, 2H), 6.06 (t, *J* = 7.8 Hz, 1H), 3.59 (dd, *J* = 16.5, 8.1 Hz, 1H), 3.47 (dd, *J* = 16.5, 6.9 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 158.5, 157.3, 140.4, 140.2, 129.6, 128.6, 127.0, 125.0, 124.5, 124.0, 118.4, 117.4, 115.5, 90.0, 35.2; MS (EI$^+$, 70 eV): m/z (%) = 272.8 (12), 271.9 (6), 270.8 (39) [M]$^+$, 155.9 (6), 154.9 (12), 153.8 (17), 127.9 (8), 125.9 (24), 118.0 (9), 117.0 (100), 116.0 (7), 98.0 (9), 91.1 (6), 90.1 (26), 89.1 (29), 63.2 (24), 62.2 (6); IR (ATR) ν (cm^{-1}) = 3882, 3327, 3061, 2924, 2681, 2322, 2180, 2106, 1993, 1920, 1788, 1728, 1659, 1597, 1479, 1429, 1305, 1223, 1177, 1071, 944, 867, 751, 662; Anal. Calcd for $C_{15}H_{10}ClNO_2$: C, 66.31; H, 3.71; N, 5.16. Found: C, 65.52; H, 3.51; N, 5.10; HRMS (ESI) m/z: [M+Na]$^+$ calcd for $C_{15}H_{10}ClNO_2Na$, 294.0292; found, 294.0291.

8-Chloro-5a,6-dihydro-12H-benzo[5,6][1,3]oxazino[3,2a]indol-12-one ***(2g).*** Purified by silica gel column chromatography; White solid; Isolated yield: 94 mg, 69%; R_f (n-pentane/ethyl acetate = 30/1) = 0.10; mp 148-151 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.06-8.04 (m, 2H), 7.52-7.49 (m, 1H), 7.26-7.24 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.05 (t, *J* = 7.5 Hz, 1H), 3.57 (dd, *J* = 16.8, 7.8 Hz, 1H), 3.45 (dd, *J* = 16.8, 7.2 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 159.1, 156.8, 139.2, 134.7, 129.2, 129.1, 128.5, 125.2, 123.5, 119.6, 117.0, 116.2, 89.6, 35.1; MS (EI$^+$, 70 eV): m/z (%) = 272.3 (28), 271.0 (100) [M]$^+$, 153.1 (11), 152.3 (3), 151.1 (32), 121.2 (12), 120.2 (31), 116.2 (4), 92.2 (15), 89.2 (9), 65.2 (3), 64.3 (6); IR (ATR) ν (cm^{-1}) = 3313, 3131, 3071, 2921, 2659, 2332, 2056, 2013, 1881, 1736, 1659, 1603, 1469, 1431, 1403, 1359, 1330, 1308, 1241, 1216, 1188, 1150, 1109,

1070, 1026, 951, 864, 819, 789, 729, 698, 656; Anal. Calcd for $C_{15}H_{10}ClNO_2$: C, 66.31; H, 3.71; N, 5.16. Found: C, 66.11; H, 3.64; N, 4.75; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{15}H_{10}ClNO_2Na$, 294.0292; found, 294.0293.

8-Bromo-5a,6-dihydro-12H-benzo[5,6][1,3]oxazino[3,2-a]indol-12-one ***(2h).*** Purified by silica gel column chromatography; White solid; Isolated yield: 89 mg, 57%; R_f (n-pentane/ethyl acetate = 40/1) = 0.24; mp 164-167 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.06 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.53-7.51 (m, 1H), 7.42-7.40 (m, 2H), 7.21 (t, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.06 (t, *J* = 7.5 Hz, 1H), 3.59 (dd, *J* = 16.8, 7.8 Hz, 1H), 3.47 (dd, *J* = 16.5, 6.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 159.2, 156.8, 139.6, 134.7, 131.4, 129.5, 128.5, 128.1, 123.6, 119.6, 117.0, 116.7, 89.6, 35.0; MS (EI^+, 70 eV): m/z (%) = 316.1 (2), 315.0 (85) $[M]^+$, 314.2 (3), 236.2 (2), 198.1 (3), 197.0 (41), 196.2 (2), 195.1 (39), 121.2 (14), 120.1 (44), 116.1 (17), 93.2 (2), 92.1 (18), 89.1 (10), 65.3 (2), 64.3 (5), 63.3 (7), 62.2 (3), 50.2 (2); IR (ATR) ν (cm^{-1}) = 3314, 3131, 3069, 2917, 2655, 2328, 2174, 2087, 1986, 1879, 1658, 1602, 1469, 1428, 1401, 1359, 1329, 1307, 1241, 1216, 1187, 1150, 1110, 1083, 1025, 933, 869, 818, 789, 757, 729, 697, 655; Anal. Calcd for $C_{15}H_{10}BrNO_2$: C, 56.99; H, 3.19; N, 4.43. Found: C, 56.58; H, 3.15; N, 4.35; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{10}BrNO_2Na$, 337.9787; found, 337.9787.

8-Methyl-5a,6-dihydro-12H-benzo[5,6][1,3]oxazino[3,2-a]indol-12-one ***(2i).*** Purified by silica gel column chromatography; White solid; Isolated yield: 105 mg, 84%; R_f (n-pentane/ethyl acetate = 40/1) = 0.05; mp 175-177 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.07 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.51-7.48 (m, 1H), 7.21-7.18 (m, 1H), 7.11-7.09 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.03 (t, *J* = 7.5 Hz, 1H), 3.55 (dd, *J* = 16.5, 8.1 Hz, 1H), 3.44 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 159.0, 156.8, 138.2, 134.3, 134.1, 128.9, 128.4, 127.3, 125.6, 123.4, 120.0, 116.9, 115.2, 89.7, 35.3, 21.4; MS (EI^+, 70 eV): m/z (%) = 252.2 (14), 251.1 (86) $[M]^+$, 249.9 (2), 132.2 (7), 130.9 (73), 130.0 (16), 125.6 (2), 121.1 (7), 120.1 (11), 102.9 (7), 93.2 (2), 92.1 (9), 78.2 (3), 77.1 (5), 65.3 (2), 64.3 (3), 63.0 (3); IR (ATR) ν (cm^{-1}) = 3305, 3036, 2958, 2914, 2325, 2164, 2047, 2003, 1928, 1893, 1847, 1733, 1652, 1609, 1491, 1461, 1408, 1367, 1334, 1312, 1249, 1222, 1166, 1150, 1109, 1075, 1029, 948, 930, 897, 868, 818, 783, 697, 658; Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.01; H, 5.07; N, 5.07; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{13}NO_2Na$, 274.0839; found, 274.0838.

8-Hydroxy-5a,6-dihydro-12H-benzo[5,6][1,3]oxazino[3,2-a]indol-12-one ***(2j).*** Purified by silica gel column chromatography; White solid; Isolated yield: 39 mg, 31%; R_f(n-pentane/ethyl acetate = 8/1) = 0.06; mp 260-262 °C; ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ (ppm) 8.32 (s, 1H), 7.97 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.59-7.56 (m, 1H), 7.24 (t, *J* = 8.1 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.86 (s, 1H), 6.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.16 (t, *J* = 7.5 Hz, 1H), 3.64 (dd, *J* = 16.8, 7.8 Hz, 1H), 3.37 (dd, *J* = 16.2, 6.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $(CD_3)_2CO$): δ (ppm) 157.6, 156.8, 154.4, 134.1, 133.2, 129.2, 127.7, 123.0, 120.0, 116.7, 115.4, 113.9, 112.4, 89.8, 34.8; MS (EI^+, 70 eV): m/z (%) = 254.0 (9), 253.0 (48) $[M]^+$, 134.0 (5), 132.9 (55), 122.0 (7), 119.9 (13), 104.9 (10), 103.9 (16), 93.0 (8), 91.9 (29), 78.0 (13), 77.0 (13), 76.0 (5), 65.0 (13), 63.0 (18), 53.1 (5), 52.0 (10), 51.0 (14), 50.0 (7); IR (ATR) ν (cm^{-1}) = 3204, 2923, 2853, 2324, 2175, 2097, 1991, 1919, 1838, 1736, 1613, 1576, 1499, 1463, 1347, 1261, 1216, 1154, 1109, 1087, 1027, 977, 939, 894, 857, 827, 802, 753, 692, 657; Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 69.92; H, 4.54; N, 5.21; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{11}NO_3Na$, 276.0631; found, 276.0628.

7-Bromo-5a,6-dihydro-12H-benzo[5,6][1,3]oxazino[3,2-a]indol-12-one ***(2m).*** Purified by silica gel column chromatography; White solid; Isolated yield: 41 mg, 26%; R_f (n-pentane/ethyl acetate = 40/1) = 0.18; mp 165-166 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.07 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.24-7.17 (m, 3H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.08 (t, *J* = 7.5 Hz, 1H), 3.61 (dd, *J* = 17.4, 8.4 Hz, 1H), 3.43 (dd, *J* = 17.4, 6.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 159.4, 156.8, 141.5, 134.8, 130.3, 128.6, 128.2, 127.1, 123.6, 119.6, 119.4, 117.1, 114.0, 88.9, 36.7; MS (EI^+, 70 eV): m/z (%) = 316.0 (6), 315.0 (38) $[M]^+$, 196.9 (30), 194.9 (32), 121.0 (30), 119.9 (100), 117.0 (8), 115.9 (21), 93.0 (7), 91.9 (69), 89.0 (25), 65.1 (8), 64.0 (26), 63.0 (37), 62.0 (9), 51.0 (8); IR (ATR) ν (cm^{-1}) = 3326, 3042, 2923, 2854, 2320, 2169, 2082, 2022, 1993, 1924, 1842, 1662, 1600, 1478, 1452, 1413, 1364, 1319, 1239, 1178, 1152, 1110, 1085, 1026, 938, 886, 850, 814, 759, 706, 659; Anal. Calcd for $C_{15}H_{10}BrNO_2$: C, 56.99; H, 3.19; N, 4.43. Found: C, 57.46; H, 3.13; N, 4.37; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{10}BrNO_2Na$, 337.9787; found, 337.9789.

9-Methyl-5a,6-dihydro-12H-benzo[5,6][1,3]oxazino[3,2-a]indol-12-one ***(2n).*** Purified by silica gel column chromatography; Colorless solid; Isolated yield: 92 mg, 73%; R_f (n-pentane/ethyl acetate = 20/1) = 0.39; mp 166-169 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.07 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.99 (s, 1H), 7.51-7.48 (m, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.03 (t, *J* = 7.5 Hz, 1H), 3.54 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.41 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 159.2, 156.9, 140.6, 138.6, 134.4, 128.5, 125.0, 124.5, 124.2, 123.3, 119.9, 116.9, 116.2, 89.9, 35.0, 21.8; MS (EI^+, 70 eV): m/z (%) = 252.2 (37), 251.1 (100) $[M]^+$, 250.1 (5), 132.2 (18), 131.2 (85), 130.2 (77), 128.1 (3), 125.6 (4), 121.2 (23), 120.1 (34), 104.2 (4), 103.2 (16), 102.1 (7), 93.2 (6), 92.1 (36), 89.1 (3), 78.3 (8), 77.2 (15), 76.2 (3), 65.3 (6), 63.2 (14), 62.4 (3), 51.3 (6), 50.2 (4); IR (ATR) ν (cm^{-1}) = 3318, 2920, 2851, 2329, 2162, 2078, 2043, 1895, 1819, 1762, 1657, 1608, 1496, 1443, 1418, 1359, 1317, 1245, 1219, 1185, 1150, 1083, 1034, 952, 915, 859, 813, 752, 690, 656; Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.26; H, 5.16; N, 5.47; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{13}NO_2Na$, 274.0839; found, 274.0839.

10-Methyl-5a,6-dihydro-12H-benzo[5,6][1,3]oxazino[3,2-a]indol-12-one ***(2o).*** Purified by silica gel column chromatography; White solid; Isolated yield: 28 mg, 22%; R_f (n-pentane/ethyl acetate = 30/1) = 0.09; mp 85-86 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.04 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.11-7.08 (m, 2H), 7.06-7.02 (m, 2H), 6.01 (t, *J* = 7.8 Hz, 1H), 3.52 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.45 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.67 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 158.4, 156.5, 139.2, 134.1, 132.1, 128.7, 128.6, 126.8, 125.1, 123.2, 122.3, 120.6, 116.5, 90.5, 35.9, 23.2; MS (EI^+, 70 eV): m/z (%) = 253.3 (3), 252.3 (18), 251.2 (100) $[M]^+$, 250.2 (2), 132.3 (6), 131.2 (58), 130.2 (31), 121.2 (12), 120.2 (14), 103.3 (5), 102.3 (2), 93.3 (2), 92.3 (9), 78.3 (2), 77.3 (4), 66.1 (2), 65.3 (2), 64.4 (3); IR (ATR) ν (cm^{-1}) = 3859, 3629, 3349, 3045, 2924, 2855, 2676, 2500, 2328, 2197, 2086, 1991, 1937, 1748, 1679, 1603, 1462, 1407, 1308, 1262, 1226, 1186, 1147, 1108, 1060, 1022, 953, 913, 871, 837, 764, 722, 692; Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.35; H, 5.58; N, 5.41; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{13}NO_2Na$, 274.0839; found, 274.0838.

2,3,6,6a-tetrahydro-1H,12H-benzo[5,6][1,3]oxazino[3,2-a]cyclopenta[g]indol-12-one ***(2p).*** Purified by silica gel column chromatography; Yellow solid; Isolated yield: 35 mg, 25%; R_f (n-pentane/ethyl acetate = 20/1) = 0.50; mp 147-148 °C; ^{1}H NMR (600

MHz, $CDCl_3$): δ (ppm) 8.06 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.50-7.47 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.06-7.02 (m, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 5.99-5.95 (m, 1H), 3.54-3.51 (m, 3H), 3.44-3.40 (m, 1H), 2.93-2.87 (m, 2H), 2.07-1.98 (m, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 158.4, 156.8, 147.0, 136.8, 134.3, 130.9, 128.7, 125.6, 123.2, 122.7, 120.8, 120.1, 116.6, 90.3, 35.6, 35.2, 33.5, 25.6; MS (EI^+, 70 eV): m/z (%) = 278.1 (22), 277.0 (100) $[M]^+$, 158.0 (12), 157.0 (97), 156.0 (54), 155.0 (4), 153.9 (11), 130.0 (7), 129.0 (15), 128.0 (13), 126.9 (7), 120.9 (15), 119.9 (8), 114.9 (6), 92.9 (3), 91.9 (15), 65.0 (4), 64.0 (6), 63.0 (6); IR (ATR) ν (cm^{-1}) = 3351, 3068, 3015, 2956, 2897, 2841, 2323, 2161, 2096, 1993, 1962, 1885, 1679, 1610, 1416, 1363, 1328, 1225, 1182, 1148, 1117, 1082, 1039, 974, 946, 861, 814, 756, 725, 701, 682, 661; Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.76; H, 5.41; N, 5.02; HRMS (ESI) m/z : $[M+Na]^+$ calcd for $C_{18}H_{15}NO_2Na$, 300.0995; found, 300.0990.

5a-Phenyl-5a,6-dihydro-12H-benzo[5,6][1,3]oxazino[3,2-a]indol-12-one ***(2q).*** Purified by silica gel column chromatography; White solid; Isolated yield: 138 mg, 88%; R_f (n-pentane/ethyl acetate = 40/1) = 0.10; mp 144-145 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.34 (d, *J* = 16.2 Hz, 1H), 7.93 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.41-7.35 (m, 4H), 7.23-7.17 (m, 4H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.05-7.02 (m, 2H), 4.02 (d, *J* = 15.6 Hz, 1H), 3.49 (d, *J* = 15.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 159.5, 155.4, 141.8, 141.5, 134.6, 128.8, 128.8, 128.6, 128.2, 126.1, 125.5, 125.2, 124.7, 123.0, 119.6, 117.5, 115.4, 98.3, 45.9; MS (EI^+, 70 eV): m/z (%) = 314.1 (4), 313.2 (19) $[M]^+$, 287.2 (2), 286.2 (2), 260.2 (2), 244.2 (2), 236.1 (2), 194.2 (16), 193.1 (100), 192.3 (9), 191.2 (3), 190.1 (2), 166.2 (3), 165.1 (14), 164.2 (2), 128.2 (2), 121.3 (3), 120.1 (7), 116.2 (2), 115.1 (3), 114.2 (2), 102.2 (2), 92.1 (16), 90.3 (13), 89.2 (24), 77.3 (4), 76.3 (2), 75.3 (2), 74.2 (2), 65.4 (2), 64.4 (8), 63.3 (10), 51.4 (3), 50.4 (2); IR (ATR) ν (cm^{-1}) = 3320, 3044, 2961, 2922, 2852, 2327, 2188, 2162, 2031, 1902, 1822, 1739, 1661, 1604, 1479, 1458, 1398, 1318, 1261, 1221, 1158, 1110, 1018, 966, 924, 870, 808, 752, 699, 664; Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.05; H, 4.80; N, 4.40; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{15}NO_2Na$, 336.0995; found, 336.0993.

2,3,4,4a-Tetrahydro-1H,10H-benzo[5,6][1,3]oxazino[2,3-k]carbazol-10-one ***(2r).*** Purified by silica gel column chromatography; Light yellow solid; Isolated yield: 98 mg, 68%; R_f (n-pentane/ethyl acetate = 20/1) = 0.40; mp 111-114 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.18 (d, *J* = 7.8 Hz, 1H), 8.08 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.50-7.48 (m, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.17-7.13 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 3.69 (d, *J* = 6.0 Hz, 1H), 2.33 (dd, *J* = 14.7, 2.7 Hz, 1H), 2.21 (d, *J* = 9.6 Hz, 1H), 2.14-2.08 (m, 1H), 1.71-1.68 (m, 1H), 1.46-1.40 (m, 3H), 1.32-1.28 (m, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 158.3, 155.1, 139.8, 134.4, 131.0, 128.4, 128.2, 124.4, 122.7, 122.7, 118.6, 117.6, 116.6, 97.3, 46.8, 29.8, 22.6, 20.8, 20.5; MS (EI^+, 70 eV): m/z (%) = 292.0 (23), 290.9 (100) $[M]^+$, 290.9 (4), 248.9 (11), 247.8 (67), 234.8 (3), 172.0 (7), 170.9 (62), 169.9 (11), 167.9 (3), 166.9 (3), 143.9 (4), 142.9 (36), 141.9 (3), 130.0 (3), 128.0 (3), 120.9 (4), 119.9 (4), 115.0 (4), 92.0 (6), 77.1 (2), 64.2 (2), 63.2 (2); IR (ATR) ν (cm^{-1}) = 3315, 3051, 2930, 2858, 2657, 2325, 2098, 1993, 1919, 1808, 1655, 1604, 1464, 1405, 1326, 1277, 1232, 1154, 1028, 932, 854, 749, 682; Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 77.26; H, 5.69; N, 4.67; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{17}NO_2Na$, 314.1152; found, 314.1149.

5a-Methyl-5a,6-dihydro-12H-benzo[5, 6][1, 3]oxazino[3, 2-a]indol-12-one ***(2s).*** Purified by silica gel column chromatography; Pink solid; Isolated yield: 102 mg, 81%; R_f (n-pentane/ethyl acetate = 40/1) = 0.10; mp 89-92 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.19 (d, *J* = 8.4 Hz, 1H), 8.07 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.32-7.28 (m, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 3.65 (d, *J* = 13.8 Hz, 1H), 3.33 (d, *J* = 13.8 Hz, 1H), 1.60 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 158.5, 155.1, 140.3, 134.6, 128.4, 128.2, 126.9, 125.0, 124.4, 122.8, 118.6, 117.5, 116.2, 96.7, 43.4, 23.9; MS (EI^+, 70 eV): m/z (%) = 252.2 (15), 251.2 (93) $[M]^+$, 250.5 (2), 237.3 (9), 236.2 (73), 135.1 (5), 132.2 (9), 131.0 (100), 130.2 (42), 125.7 (2), 121.2 (9), 120.1 (20), 116.1 (2), 103.2 (4), 102.0 (2), 92.1 (24), 90.3 (12), 89.2 (20), 77.3 (5), 65.3 (3), 64.3 (10), 63.1 (14), 51.0 (3); IR (ATR) ν (cm^{-1}) = 3858, 3622, 3321, 3055, 2972, 2924, 2702, 2491, 2325, 2238, 2145, 2094, 2062, 1999, 1967, 1929, 1737, 1659, 1603, 1483, 1461, 1401, 1321, 1261, 1229, 1150, 1125, 1075, 1022, 957, 927, 871, 842, 757, 697, 664; Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.42; H, 5.30; N, 5.53; HRMS (ESI^+) m/z: $[M+Na]^+$ calcd for $C_{16}H_{13}NO_2Na$, 274.0839; found, 274.0839.

Phenyl(2-(p-tolyloxy)indolin-1-yl)methanone ***(3).*** Purified by silica gel column chromatography; Yellow solid; Isolated yield: 25 mg, 15%; R_f (n-pentane/ethyl acetate = 5/1) = 0.19; mp 179-181 °C; ^1H NMR (600 MHz, DMSO-d_6): δ (ppm) 9.30 (br, 1H), 7.39-7.03 (m, 9H), 6.79 (br, 1H), 6.61-6.57 (m, 2H), 5.60 (br, 1H), 3.73-3.69 (m, 1H), 2.76 (d, *J* = 16.2 Hz, 1H), 2.05 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6): δ (ppm) 169.4, 151.7, 143.5, 137.4, 131.8, 130.2, 129.3, 128.7, 128.6, 127.5, 127.4, 126.9, 125.8, 125.7, 124.5, 116.9, 115.5, 59.9, 46.1, 20.8; MS (EI^+, 70 eV): m/z (%) = 330.4 (9), 329.4 (34) $[M]^+$, 225.3 (10), 224.4 (60), 223.2 (14), 208.3 (34), 207.2 (34), 194.2 (3), 180.2 (4), 118.2 (4), 117.1 (8), 106.1 (8), 105.1 (100), 97.2 (4), 91.1 (7), 85.2 (4), 78.2 (4), 77.2 (52), 71.3 (6), 69.2 (4), 65.2 (5), 57.2 (9), 55.1 (4), 51.1 (6); IR (ATR) ν (cm^{-1}) = 3307, 3065, 3027, 2921, 2854, 2729, 2319, 2167, 2036, 1980, 1943, 1903, 1737, 1625, 1590, 1506, 1472, 1394, 1330, 1266, 1215, 1179, 1157,1104, 1068, 1026, 1001, 972, 935, 876, 820, 786, 749, 696; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{19}NO_2Na$, 352.1308; found, 352.1301.

5-Tosyl-5a,6-dihydroindolo[2,1-b]quinazolin-12(5H)-one ***(2zc).*** Purified by silica gel column chromatography; Gray solid; Isolated yield: 103 mg, 53%; R_f (n-pentane/ethyl acetate = 5/1) = 0.25; mp 212-213 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.01 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.78 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.65 (td, *J* = 7.8, 1.8 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.52-7.49 (m, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.12-7.05 (m, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.84 (dd, *J* = 10.8, 6.0 Hz, 1H), 4.80 (dd, *J* = 18.6, 6.0 Hz, 1H), 3.55 (dd, *J* = 18.3, 11.1 Hz, 1H), 2.22 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 159.4, 144.7, 140.7, 140.5, 134.5, 132.9, 129.4, 128.9, 128.6, 128.3, 128.1, 127.6, 127.5, 127.0, 124.6, 115.1, 75.5, 30.6, 21.6; MS (EI^+, 70 eV): m/z (%) = 392.5 (5), 391.5 (12), 390.5 (48) $[M]^+$, 274.3 (14), 273.4 (12), 236.4 (15), 235.4 (100), 234.3 (34), 233.3 (7), 210.4 (4), 209.4 (12), 208.3 (6), 206.3 (11), 205.3 (12), 180.3 (8), 179.3 (3), 155.2 (5), 132.2 (5), 118.2 (5), 117.2 (48), 92.2 (3), 91.2 (23), 90.1 (9), 89.1 (7), 77.2 (4), 65.2 (8), 63.2 (3); IR (ATR) ν (cm^{-1}) = 3878, 3302, 3050, 2925, 2855, 2651, 2322, 2233, 2167, 2087, 1984, 1913, 1656, 1598, 1485, 1457, 1416, 1352, 1314, 1257, 1227, 1194, 1162, 1111, 1072, 1030, 956, 938, 891, 811, 772, 746, 705, 669; Anal. Calcd for $C_{22}H_{18}N_2O_3S$: C, 67.68; H, 4.65; N, 7.17. Found: C, 67.46; H, 4.53; N, 7.03; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{18}N_2O_3SNa$, 413.0930; found, 413.0933.

12H-benzo[5,6][1,3]oxazino[3,2-a]indol-12-one ***(3a).***[16g] Purified by silica gel column chromatography; Yellow solid; Isolated yield: 10 mg, 43%; R_f (n-pentane/ethyl acetate = 30/1) = 0.50; mp 151-153 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.58 (d, *J* = 7.8 Hz, 1H), 8.30 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.71-7.68 (m, 1H), 7.56 (d, *J* = 6.6 Hz, 1H), 7.38-7.33 (m, 4H), 6.15 (s, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ (ppm) 156.9, 154.1, 145.9, 135.7, 129.2, 128.3,

128.0, 124.9, 124.2, 122.8, 119.7, 116.6, 116.1, 114.5, 84.4; MS (EI$^+$, 70 eV): m/z (%) = 236.2 (18), 235.2 (100) $[M]^+$, 234.3 (3), 180.2 (3), 179.1 (19), 178.1 (10), 177.1 (3), 152.1 (6), 151.1 (4), 146.1 (3), 121.1 (7), 120.0 (12), 117.5 (5), 103.9 (3), 103.1 (3), 92.0 (7), 89.1 (4), 76.0 (13), 75.0 (4), 64.1 (4), 63.0 (5), 50.1 (5); IR (ATR) ν (cm^{-1}) = 3208, 3066, 2925, 2855, 2318, 2164, 1765, 1697, 1599, 1462, 1368, 1294, 1248, 1199, 1154, 1095, 1031, 1001, 956, 904, 871, 822, 747, 683; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{10}NO_2$, 236.0706; found, 236.0696.

2,8-Dibromo-5a,6-dihydro-12H-benzo[5,6][1,3]oxazino[3,2-a]indol-12-one ***(2zd).*** Purified by silica gel column chromatography; White solid; Isolated yield: 59 mg, 70%; R_f (n-pentane/ethyl acetate = 9/1) = 0.60; mp 157-158 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.17 (d, *J* = 2.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.60 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.42-7.40 (m, 2H), 6.97 (d, *J* = 9.0 Hz, 1H), 6.05-6.03 (m, 1H), 3.59 (dd, *J* = 16.8, 8.4 Hz, 1H), 3.47 (dd, *J* = 16.8, 6.6 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ (ppm) 157.8, 155.8, 139.4, 137.5, 131.6, 131.1, 129.3, 128.2, 121.2, 118.9, 117.1, 116.8, 116.2, 89.8, 34.9; MS (EI$^+$, 70 eV): m/z (%) = 395.3 (100), 394.4 (10), 393.3 (50) $[M]^+$, 201.2 (8), 200.2 (62), 199.3 (10), 198.2 (67), 197.2 (70), 196.2 (5), 195.2 (71), 172.2 (27), 170.2 (32), 116.3 (31), 89.3 (16), 63.3 (21), 62.2 (4); IR (ATR) ν (cm^{-1}) = 3861, 3311, 3057, 2924, 2854, 2659, 2322, 2204, 2110, 2026, 1992, 1887, 1756, 1709, 1657, 1598, 1476, 1439, 1401, 1332, 1300, 1245, 1215, 1155, 1067, 1033, 953, 921, 893, 864, 818, 772, 739, 704, 657; Anal. Calcd for $C_{15}H_9Br_2NO_2$: C, 45.61; H, 2.30; N, 3.55. Found: C, 44.46; H, 2.28; N, 3.34; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_9Br_2NO_2Na$, 415.8892; found, 415.8879.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://

Crystal structure information (CCDC numbers 1977486, 1977487, 1977488, 1977489, 1977490, 1977491, 1977492, 1977493, 1977494 and 1977495), and copies of ^{1}H and ^{13}C{^{1}H} NMR spectra (PDF)

Crystallographic data for **1i**, **2d**, **2e**, **2i**, **2n**, **2q**, **2r**, **2zd**, **2zc** and **3** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

Markus Albrecht
* E-mail: markus.albrecht@oc.rwth-aachen.de;

ORCID

Markus Albrecht：0000-0002-3501-1477

Kari Rissanen：0000- 0002-7282-8419

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENT

Jingyu Zhang gratefully acknowledges support by the Chinese Scholarship Council.

■ REFERENCES

(1) (a) Cacchi, S.; Fabrizi, G. Synthesis and functionalization of Indoles through palladium-catalyzed reactions. *Chem. Rev.* **2005**, *105*, 2873. (b) Bandini, M.; Eichholzer, A. Catalytic Functionalization of Indoles in a New Dimension. *Angew. Chem. Int. Ed.* **2009**, *48*, 9608.

(2) For selected examples on dearomatization of indole, see: (a) Bera, S.; Daniliuc, C. G.; Studer, A. Oxidative N-Heterocyclic Carbene Catalyzed Dearomatization of Indoles to Spirocyclic Indolenines with a Quaternary Carbon Stereocenter. *Angew. Chem. Int. Ed.* **2017**, *56*, 7402. (b) Huang, L.; Cai, Y.; Zhang, H.-J.; Zhang, C.; Dai, L.-X.; You, S.-L. Highly Diastereo-and Enantioselective Synthesis of Quinuclidine Derivatives by an Iridium-Catalyzed Intramolecular Allylic Dearomatization Reaction. *CCS Chem.* **2019**, *1*, 106. (c) Cera, G.; Crispino, P.; Monari, M.; Bandini, M. Stereoselective synthesis of tetracyclic indolines via gold-catalyzed cascade cyclization reactions. *Chem. Commun.* **2011**, *47*, 7803. (d) Liu, Y.; Xu, W.; Wang, X. Gold(I)-Catalyzed Tandem Cyclization Approach to Tetracyclic Indolines. *Org. Lett.* **2010**, *12*, 1448. (e) Noey, E. L.; Wang, X.; Houk, K. N. Selective Gold(I)-Catalyzed Formation of Tetracyclic Indolines: A Single Transition Structure and Bifurcations Lead to Multiple Products. *J. Org. Chem.* **2011**, *76*, 3477. (f) Schröder, F.; Sharma, U. K.; Mertens, M.; Devred, F.; Debecker, D. P.; Luque, R.; Van der Eycken, E. V. Silver-Nanoparticle-Catalyzed Dearomatization of Indoles toward 3-Spiroindolenines via a 5-exo-dig Spirocyclization. *ACS Catal.* **2016**, *6*, 8156. (g) Wang, Y.; Zheng, C.; You, S.-L. Iridium-Catalyzed Asymmetric Allylic Dearomatization by a Desymmetrization Strategy. *Angew. Chem. Int. Ed.* **2017**, *56*, 15093. (h) Zheng, C.; Xia, Z.-L.; You, S.-L. Unified Mechanistic Understandings of Pictet-Spengler Reactions. *Chem* **2018**, *4*, 1952. (i) Zhu, M.; Zheng, C.; Zhang, X.; You, S.-L. Synthesis of Cyclobutane-Fused Angular Tetracyclic Spiroindolines via Visible-Light-Promoted Intramolecular Dearomatization of Indole Derivatives. *J. Am. Chem. Soc.* **2019**, *141*, 2636.

(3) For selected reviews, see: (a) Bariwal, J.; Voskressensky, L. G.; Van der Eycken, E. V. Recent advances in spirocyclization of indole derivatives. *Chem. Soc. Rev.* **2018**, *47*, 3831. (b) Ramachandran, G.; Sathiyanarayanan, K. I. Dearomatization Strategies of Heteroaromatic Compounds. *Curr. Organocatal.* **2015**, *2*, 14. (c) Saya, J. M.; Ruijter, E.; Orru, R. V. A. Total Synthesis of Aspidosperma and Strychnos Alkaloids through Indole Dearomatization. *Chem. Eur. J.* **2019**, *25*, 8916. (d) Zhuo, C. X.; Zheng, C.; You, S.-L. Transition-metal-catalyzed asymmetric allylic dearomatization reactions. *Acc. Chem. Res.* **2014**, *47*, 2558. (e) Zi, W. W.; Zuo, Z. W.; Ma, D. W. Intramolecular Dearomative Oxidative Coupling of Indoles: A Unified Strategy for the Total Synthesis of Indoline Alkaloids. *Acc. Chem. Res.* **2015**, *48*, 702. (f) Roche, S. P.; Tendoung, J.-J. Y.; Treguier, B. Advances in dearomatization strategies of indoles. *Tetrahedron* **2015,** *71*, 3549.

(4) Zhang, D.; Song, H.; Qin, Y. Total Synthesis of Indoline Alkaloids: A Cyclopropanation Strategy. *Acc. Chem. Res.* **2011**, *44*, 447.

(5) For selected examples, see: (a) Galliford, C. V.; Scheidt, K. A. Pyrrolidinyl-spirooxindole natural products as inspirations for the development of potential therapeutic agents. *Angew. Chem. Int. Ed.* **2007**, *46*, 8748. (b) Griebel, G.; Simiand, J.; Gal, C. S.-L.; Wagnon, J.; Pascal, M.; Scatton, B.; Maffrand, J.-P.; Soubrie, P. Anxiolytic- and antidepressant-like effects of the non-peptide vasopressin V-1b receptor antagonist, SSR149415, suggest an innovative approach for the treatment of stress-related disorders. *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 6370. (c) Kitamura, H.; Kato, A.; Esaki, T. AG-041R, a novel indoline-2-one derivative, induces systemic cartilage hyperplasia in rats. *Eur. J. Pharmacol.* **2001**, *418*, 225. (d) Li, G.-Y.; Li, B.-G.; Yang, T.; Yan, J.-F.; Liu, G.-Y.; Zhang, G.-L. Chaetocochins A-C, epipolythiodioxopiperazines from Chaetomium cochliodes. *J. Nat. Prod.* **2006**, *69*, 1374. (e) Rottmann, M.; McNamara, C.; Yeung, B. K. S.; Lee, M. C. S.; Zou, B.; Russell, B.; Seitz, P.; Plouffe, D. M.; Dharia, N. V.; Tan, J.; Cohen, S. B.; Spencer, K. R.; Gonzalez-Paez, G. E.; Lakshminarayana, S. B.; Goh, A.; Suwanarusk, R.; Jegla, T.; Schmitt, E. K.; Beck, H. P.; Brun, R.; Nosten, F.; Renia, L.; Dartois, V.; Keller, T. H.; Fidock, D. A.; Winzeler, E. A.; Diagana, T. T. Spiroindolones, a Potent Compound Class for the Treatment of Malaria. *Science* **2010**, *329*, 1175. (f) Zeeli, S.; Weill, T.; Finkin-Groner, E.; Bejar, C.; Melamed, M.; Furman, S.; Zhenin, M.; Nudelman, A.; Weinstock, M. Synthesis and Biological Evaluation of Derivatives of Indoline as

Highly Potent Antioxidant and Anti-inflammatory Agents. *J. Med. Chem.* **2018**, *61*, 4004. (g) Cera, G.; Chiarucci, M.; Mazzanti, A.; Mancinelli, M.; Bandini, M. Enantioselective Gold-Catalyzed Synthesis of Polycyclic Indolines. *Org. Lett.* **2012**, *14*, 1350. (h) He, W.; Griffiths, B. M.; Wang, W.; Wang, X. Diastereoselective synthesis and biological evaluation of enantiomerically pure tricyclic indolines. *Org. Biomol. Chem.* **2017**, *15*, 4241. (i) Lian, Y.; Davies, H. M. L. Rhodium-Catalyzed [3+2] Annulation of Indoles. *J. Am. Chem. Soc.* **2010**, *132*, 440. (j) Podoll, J. D.; Liu, Y.; Chang, L.; Walls, S.; Wang, W.; Wang, X. Bio-inspired synthesis yields a tricyclic indoline that selectively resensitizes methicillin-resistant Staphylococcus aureus (MRSA) to beta-lactam antibiotics. *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 15573. (k) Xiong, H.; Xu, H.; Liao, S.; Xie, Z.; Tang, Y. Copper-Catalyzed Highly Enantioselective Cyclopentannulation of Indoles with Donor-Acceptor Cyclopropanes. *J. Am. Chem. Soc.* **2013**, *135*, 7851.

(6) For selected examples on intermolecular dearomatization of indole, see: (a) Zhang, H.-J.; Gu, Q.; You, S.-L. Ni-Catalyzed Intermolecular Allylic Dearomatization Reaction of Tryptophols and Tryptamines. *Org. Lett.* **2019**, *21*, 9420. (b) Kubota, K.; Haya ma, K.; Iwamoto, H.; Ito, H. Enantioselective Borylative Dearomatization of Indoles through Copper(I) Catalysis. *Angew. Chem. Int. Ed.* **2015**, *54*, 8809. (c) Liu, K.; Xu, G.; Sun, J. Gold-catalyzed stereoselective dearomatization/metal-free aerobic oxidation: access to 3-substituted indolines/oxindoles. *Chem. Sci.* **2018**, *9*, 634. (d) Mei, G. J.; Tang, X.; Tasdan, Y.; Lu, Y. Enantioselective Dearomatization of Indoles by an Azoalkene-Enabled (3+2) Reaction: Access to Pyrroloindolines. *Angew. Chem. Int. Ed.* **2020**, *59*, 648. (e) Romano, C.; Jia, M.; Monari, M.; Manoni, E.; Bandini, M. Metal-free enantioselective electrophilic activation of allenamides: stereoselective dearomatization of indoles. *Angew. Chem. Int. Ed.* **2014**, *53*, 13854. (f) Ryzhakov, D.; Jarret, M.; Guillot, R.; Kouklovsky, C.; Vincent, G. Radical-Mediated Dearomatization of Indoles with Sulfinate Reagents for the Synthesis of Fluorinated Spirocyclic Indolines. *Org. Lett.* **2017**, *19*, 6336. (g) Shao, W.; Li, H.; Liu, C.; Liu, C. J.; You, S.-L. Copper-catalyzed intermolecular asymmetric propargylic dearomatization of indoles. *Angew. Chem. Int. Ed.* **2015**, *54*, 7684. (h) Wu, J.; Dou, Y. C.; Guillot, R.; Kouklovsky, C.; Vincent, G. Electrochemical Dearomative 2,3-Difunctionalization of Indoles. *J. Am. Chem. Soc.* **2019**, *141*, 2832. (i) Xu, W. Q.; Wang, W.; Wang, X. Gold-Catalyzed Cyclization Leads to a Bridged Tetracyclic Indolenine that Represses beta-Lactam Resistance. *Angew. Chem. Int. Ed.* **2015**, *54*, 9546. (j) Wu, J.; Nandi, R. K.; Guillot, R.; Kouklovsky, C.; Vincent, G. Dearomative Diallylation of N-Acylindoles Mediated by $FeCl_3$. *Org. Lett.* **2018**, *20*, 1845.

(7) Seleced examples see: (a) Fang, X.; Gao, S.; Wu, Z.; Yao, H.; Lin, A. Pd(II)-Catalyzed oxidative dearomatization of indoles: substrate-controlled synthesis of indolines and indolones. *Org. Chem. Front.* **2017**, *4*, 292. (b) Lozano, O.; Blessley, G.; del Campo, T. M.; Thompson, A. L.; Giuffredi, G. T.; Bettati, M.; Walker, M.; Borman, R.; Gouverneur, V. Organocatalyzed Enantioselective Fluorocyclizations. *Angew. Chem. Int. Ed.* **2011**, *50*, 8105. (c) Wang, J.-J.; Zhou, A.-X.; Wang, G.-W.; Yang, S.-D. An Aluminum Triflate-Catalyzed Intramolecular Reaction Sequence Toward Concise Construction of the Tetrahydropyrido[1,2-a]indol-6-one Skeleton. *Adv. Synth. Catal.* **2014**, *356*, 3356. (d) Shen, C.; Liu, R.-R.; Fan, R.-J.; Li, Y.-L.; Xu, T.-F.; Gao, J.-R.; Jia, Y.-X. Enantioselective Arylative Dearomatization of Indoles via Pd-Catalyzed Intramolecular Reductive Heck Reactions. *J. Am. Chem. Soc.* **2015,** *137*, 4936. (e) Flanagan, S. R.; Harrowven, D. C.; Bradley, M. Radical cyclisation reactions with indoles. *Tetrahedron Lett.* **2003**, *44*, 1795. (f) Liang, R.-X.; Wang, K.; Song, L.-J.; Sheng, W.-J.; Jia, Y.-X. Synthesis of tetracyclic indolin-3-ones through Pd-catalyzed intramolecular deacetylative dearomatization of 3-acetoxy-indoles. *RSC Adv.* **2019**, *9*, 13959. (g) Zhao, L.; Li, Z.; Chang, L.; Xu, J.; Yao, H.; Wu, X. Efficient Construction of Fused Indolines with a 2-Quaternary Center via an Intramolecular Heck Reaction with a Low Catalyst Loading. *Org. Lett.* **2012**, *14*, 2066. (h) Mei, L.-Y.; Wei, Y.; Tang, X.-Y.; Shi, M. Catalyst-Dependent Stereodivergent and Regioselective Synthesis of Indole-Fused Heterocycles through Formal Cycloadditions of Indolyl-Allenes. *J. Am. Chem. Soc.* **2015**, *137*, 8131.

(8) Hartmann, J. M.; de Groot, M.; Schäringer, K.; Henke, K.; Rissanen, K.; Albrecht, M. 2H-[1,3]Oxazino[3,2-]indolin-4(3H)-ones: A Class Of Polyheterocyclic Indole-Based Compounds. *Eur. J. Org. Chem.* **2018**, *2018*, 901.

(9) (a) Bubnov, Y. N.; Zhun, I. V.; Klimkina, E. V.; Ignatenko, A. V.; Starikova, Z. A. Reductive 1,2-allylboration of indoles by triallyl- and triprenylborane - Synthesis of 2-allylated indolines. *Eur. J. Org. Chem.* **2000**, *2000*, 3323. (b) Nowrouzi, F.; Batey, R. A. Regio- and Stereoselective Allylation and Crotylation of Indoles at C2 Through the Use of Potassium Organotrifluoroborate Salts. *Angew. Chem. Int. Ed.* **2013**, *52*, 892. (c) Alam, R.; Diner, C.; Jonker, S.; Eriksson, L.; Szabo, K. J. Catalytic Asymmetric Allylboration of Indoles and Dihydroisoquinolines with Allylboronic Acids: Stereodivergent Synthesis of up to Three Contiguous Stereocenters. *Angew. Chem. Int. Ed.* **2016**, *55*, 14415. (d) Han, B.; Xiao, Y. C.; Yao, Y. A.; Chen, Y. C. Lewis Acid Catalyzed Intramolecular Direct Ene Reaction of Indoles. *Angew. Chem. Int. Ed.* **2010***, 49,* 10189.

(10) (a) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. Direct C-H Transformation via Iron Catalysis. *Chem. Rev.* **2011**, *111*, 1293. (b) Bauer, I.; Knolker, H. J. Iron Catalysis in Organic Synthesis. *Chem. Rev.* **2015**, *115*, 3170. (c) Bauer, E. *Iron Catalysis II*; Springer International Publishing: Switzerland, 2015**.**

(11) Tomakinian, T.; Guillot, R.; Kouklovsky, C.; Vincent, G. Direct Oxidative Coupling of N-Acetyl Indoles and Phenols for the Synthesis of Benzofuroindolines Related to Phalarine. *Angew. Chem. Int. Ed.* **2014**, *53*, 11881.

(12) Beaud, R.; Nandi, R. K.; Perez-Luna, A.; Guillot, R.; Gori, D.; Kouklovsky, C.; Ghermani, N. E.; Gandon, V.; Vincent, G. Revealing the electrophilicity of N-Ac indoles with $FeCl_3$: a mechanistic study. *Chem. Commun.* **2017**, *53*, 5834.

(13) Liu, K.; Tang, S.; Huang, P.; Lei, A. External oxidant-free electrooxidative [3+2] annulation between phenol and indole derivatives. *Nature Commun.* **2017**, *8*, 775.

(14) Nandi, R. K.; Ratsch, F.; Beaud, R.; Guillot, R.; Kouklovsky, C.; Vincent, G. Intermolecular dearomative C2-arylation of N-Ac indoles activated by $FeCl_3$. *Chem. Commun.* **2016**, *52*, 5328.

(15) Ghosh, S. K.; Nagarajan, R. Total synthesis of cruciferane via epoxidation/tandem cyclization sequence. *RSC Adv.* **2014**, *4*, 63147.

(16) (a) Pan, S.; Ryu, N.; Shibata, T. Ir(I)-Catalyzed C-H Bond Alkylation of C2-Position of Indole with Alkenes: Selective Synthesis of Linear or Branched 2-Alkylindoles. *J. Am. Chem. Soc.* **2012**, *134*, 17474. (b) Bremner, J. B.; Samosorn, S.; Ambrus, J. I. N-acylation of 5-substituted indoles with carboxylic acids via DCC coupling. *Synthesis* **2004**, 2653. (c) Ho, S.; Bondarenko, G.; Rosa, D.; Dragisic, B.; Orellana, A. Synthesis of Acyl Pyrroles via Palladium-Catalyzed Carbonylative Amination of Aryl and Alkenyl Iodides. *J. Org. Chem.* **2012**, *77*, 2008. (d) Zhao, J.; Li, P.; Xia, C.; Li, F. Direct N-acylation of azoles via a metal-free catalyzed oxidative cross-coupling strategy. *Chem. Commun.* **2014**, *50*, 4751. (e) Gao, K.; Wu, B.; Yu, C.-B.; Chen, Q.-A.; Ye, Z.-S.; Zhou, Y.-G. Iridium Catalyzed Asymmetric Hydrogenation of Cyclic Imines of Benzodiazepinones and Benzodiazepines. *Org. Lett.* **2012**, *14*, 3890. (f) Zhou, Y.; Li, J. A.; Ji, X.; Zhou, W.; Zhang, X.; Qian, W.; Jiang, H.; Liu, H. Silver- and Gold-Mediated Domino Transformation: A Strategy for Synthesizing Benzo[e]indolo[1,2-a]pyrrolo/pyrido[2,1-c][1,4]-diazepine-3,9-diones. *J. Org. Chem.* **2011**, *76*, 1239. (g) Xia, Z.; Wang, K.; Zheng, J.; Ma, Z.; Jiang, Z.; Wang, X.; Lv, X. Copper-catalyzed domino intramolecular cyclization: a facile and efficient approach to polycyclic indole derivatives. *Org. Biomol. Chem.* **2012**, *10*, 1602.