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Tetrahedron
Tetrahedron 63 (2007) 474–491

Simple route to 3-(2-indolyl)-1-propanones via a furan recyclization reaction

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Received 12 July 2006; revised 29 September 2006; accepted 19 October 2006
Available online 15 November 2006

Abstract—A simple route to 1-*R*-3-(2-indolyl)-1-propanones has been elaborated based on recyclization of 2-(2-aminobenzyl)furan derivatives. Being a modification of the Reissert indole synthesis, our approach employs the furan ring as a source of carbonyl function. This approach is general and allows varying of substituents in aromatic ring as well as in 3-position of indole nucleus.

1. Introduction

The indole framework is a structural feature of a vast number of natural and synthetic biologically active compounds. This fact calls forth the elaboration of new methods for the synthesis of indole ring system as well as to modifications of the known general approaches to this class of compounds.[1] One of the oldest synthesis, the Reissert method, based on the reductive cyclization of *ortho*-nitrophenylpyruvate derivatives into indole-2-carboxylic acids, is still important today. On its own[2] as well as with its closest modifications,[3] the method is widely used in the synthesis of natural and unnatural compounds possessing different kinds of biological activity. It is based on the spontaneous cyclization of *ortho*-aminobenzylcarbonyl compounds **A** generated in situ (Fig. 1).

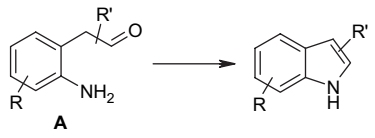

Figure 1. The cyclization of *ortho*-aminobenzylcarbonyl compounds into indole derivatives.

Two methods are known for the generation of compounds **A**. The first way, perhaps used most widely, includes the reduction of nitro group in *ortho*-nitrobenzylcarbonyl compounds[4] or their analogs, for example, Leimgruber–Batcho indole synthesis.[5] Another one consists in a generation of the carbonyl group by the oxidation of 2-aminophenethyl alcohols[6] or oxidative cleavage of appropriate olefins.[7] The carbonyl function can also be obtained by partial reduction of the nitrile group usually in *o*-nitrophenylacetonitriles with simultaneous generation of carbonyl and amino functions.[8]

Methods of indole synthesis employing recyclization of a heterocyclic fragment which can serve as a source of a carbonyl group are also very interesting. Thus, Ogasawara elaborated an original method for the synthesis of indole-3-acetic acid derivatives based on recyclization of 3-(2-aminoaryl)-2,3-dihydro-2,5-dimethoxyfurans in methylene chloride in the presence of trifluoroacetic acid (Scheme 1).[9] The methodology was employed later in the synthesis of psilocin.[10] Another interesting indole synthesis based on recyclization of 5-aminocoumarines upon treatment with sulfuric acid in boiling methanol was reported by Alper and Nguyen (Scheme 2).[11] In the known recyclization of 4-amino-2-methylbenzofuran derivatives into 4-hydroxy-2-methylindoles under strong acidic conditions, the furan ring formally acts as a source of carbonyl function (Scheme 3).[12]

It is well known that alkylfurans can be hydrolyzed into 1,4-dicarbonyl compounds[13] under acidic conditions. This property is widely exploited in organic synthesis. In particular, during last years we developed a general approach to the synthesis of benzoannelated heterocyclic compounds based on recyclization of *ortho*-substituted benzylfurans.[14] In a preliminary publication we reported on a novel approach to indole synthesis (Scheme 4).[15]

Keywords: Furan; Recyclization; Indoles.
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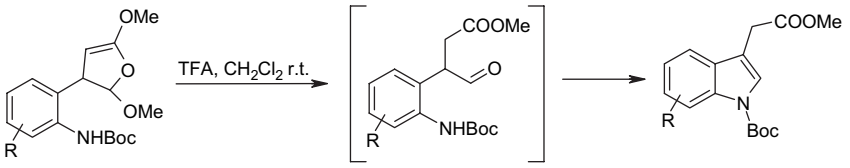
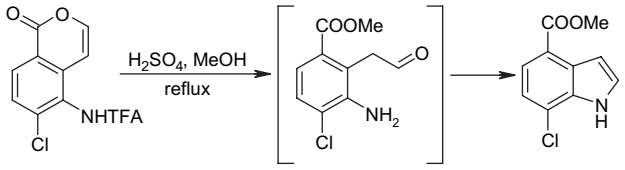
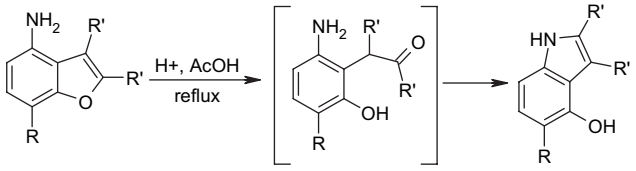
doi:10.1016/j.tet.2006.10.056



Scheme 1.



Scheme 2.



Scheme 3.

The problem of the highly functionalized indole synthesis always attracts the attention of researchers. Our method allows construction of the indole nucleus with oxopropyl substituent at the 2-position making these compounds suitable for further synthetic use. Few ways of indole synthesis with similar structure are known[16] and the most popular one employs Michael addition.[17] At the same time, limited numbers of 3-(2-indolyl)-1-propanones can be obtained by this method. The main drawback of this approach is the impossibility of synthesis of indoles unsubstituted at the 3-position due to its susceptibility to electrophilic attack. On the other hand, 3-substituted indoles usually react sluggishly with α,β-enones to give Michael products and require the search for more efficient catalysts.[17f] Recently it was reported that the direction of electrophilic attack can be changed by preliminary reduction of indole into 4,7-dihydroindole via Birch procedure.[18] Subsequent Michael addition with suitable electrophiles and reoxidation leads to the desired indole system. Although this multistep reaction sequence is regioselective, it proceeds in low overall yields.[18]

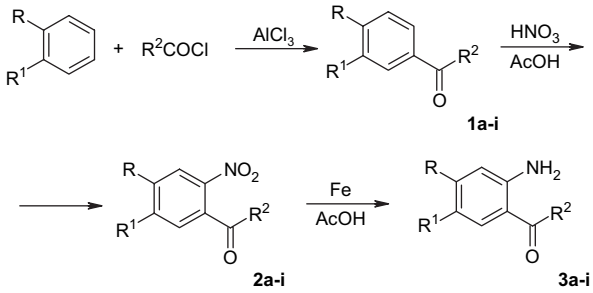
The method proposed by us is more general than all existing approaches to 3-(2-indolyl)-1-propanones. We report here detailed results on the indole synthesis published in our preliminary article.[15]

2. Results and discussion

2.1. Synthesis of starting materials

2-Aminobenzylfurans were the starting compounds for our synthesis of indole derivatives. One of the general approaches to benzylfurans is the alkylation of furans with benzylalcohols,[19] which can be obtained by reduction of the corresponding ketones.

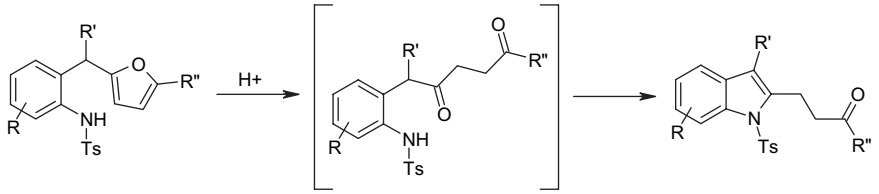
Acylation of veratrol or 1,4-benzodioxane with acyl chlorides under the Friedel–Crafts conditions furnished ketones **1a–i** in 75–85% yields. They were further nitrated with fuming nitric acid in acetic acid[20] giving nitroderivatives **2a–i**. The reduction of the latter with iron powder in water in the presence of acetic acid afforded the desired ketones **3a–i** (Scheme 5, Table 1). Ketones **3j**,**k** were obtained from



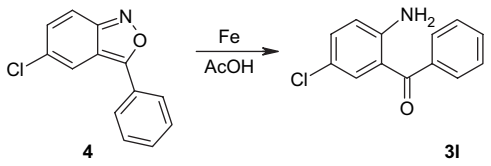
Scheme 5.

Table 1. Synthesis of the ketones **2** and **3**

Entry	R	R^1	R^2	Product	Yield (%)	Product	Yield (%)
a	OMe	OMe	5-Me-Fur	**2a**	65	**3a**	85
b	OMe	OMe	Me	**2b**	57	**3b**	72
c	OMe	OMe	Et	**2c**	65	**3c**	68
d	OMe	OMe	CH_2Ph	**2d**	63	**3d**	66
e	OCH_2CH_2O		Me	**2e**	56	**3e**	65
f	OMe	OMe	Ph	**2f**	83	**3f**	90
g	OMe	OMe	4-MeC_6H_4	**2g**	68	**3g**	73
h	OMe	OMe	4-ClC_6H_4	**2h**	77	**3h**	67
i	OCH_2CH_2O		Ph	**2i**	78	**3i**	74
j	H	H	Ph	—	—	**3j**	82
k	H	H	4-BrC_6H_4	—	—	**3k**	85
l	H	Cl	Ph	—	—	**3l**	75



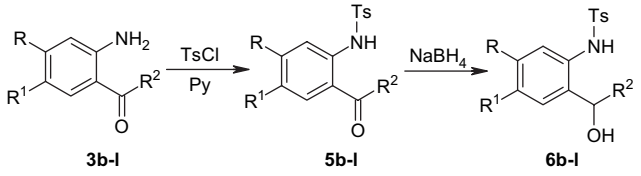
Scheme 4.



Scheme 6.

N-tosylanthranilic acid by the known method[21] and compound **3l** was obtained via reduction of benzisoxazole **4**[22] (Scheme 6, Table 1).

Aminobenzylalcohols failed to react with furans under the alkylation conditions employed. This fact can be rationalized by protonation of amino group leading to instability of the corresponding benzyl cation. To overcome such problems and reduce the basicity of the amino group, the ketones **3b–l** were transformed into compounds **5b–l** and then into benzylalcohol derivatives **6b–l** (Scheme 7, Table 2).



Scheme 7.

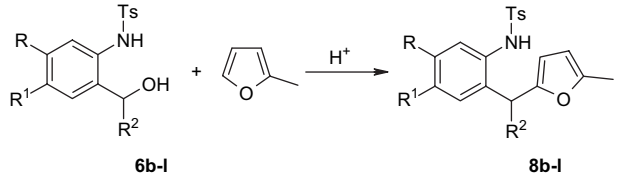
Table 2. Synthesis of the compounds **5** and **6**

Entry	R	R^1	R^2	Product	Yield (%)	Product	Yield (%)
b	OMe	OMe	Me	**5b**	79	**6b**	69
c	OMe	OMe	Et	**5c**	74	**6c**	72
d	OMe	OMe	CH_2Ph	**5d**	77	**6d**	68
e	OCH_2CH_2O		Me	**5e**	72	**6e**	70
f	OMe	OMe	Ph	**5f**	81	**6f**	85
g	OMe	OMe	4-MeC_6H_4	**5g**	80	**6g**	84
h	OMe	OMe	4-ClC_6H_4	**5h**	78	**6h**	86
i	OCH_2CH_2O		Ph	**5i**	79	**6i**	83
j	H	H	Ph	**5j**	70	**6j**	85
k	H	H	4-BrC_6H_4	**5k**	72	**6k**	89
l	H	Cl	Ph	**5l**	69	**6l**	89

The reduction of the ketone **3a** with $NaBH_4$ in the presence of a two-fold excess of $AlCl_3$ according to the published procedure[23] afforded 2-aminobenzylfuran **7**, which after tosylation gave compound **8a** (Scheme 8, Table 3). 2-Tosylaminobenzylfuran derivatives **8b–l** were prepared by alkylation of 2-methylfuran with corresponding alcohols **6b–l** in the presence of *para*-toluenesulfonic acid with azeotropical removal of water in boiling CH_2Cl_2 for compounds **8b–i** or in boiling benzene for compounds **8j–l** (Scheme 9, Table 3).

Table 3. Synthesis of compounds **8** and **9**

Entry	R	R^1	R^2	Product	Yield (%)	Product	Yield (%)
a	OMe	OMe	H	**8a**	82	**9a**	67
b	OMe	OMe	Me	**8b**	69	**9b**	78
c	OMe	OMe	Et	**8c**	75	**9c**	69
d	OMe	OMe	CH_2Ph	**8d**	42	**9d**	67
e	OCH_2CH_2O		Me	**8e**	75	**9e**	85
f	OMe	OMe	Ph	**8f**	82	**9f**	80
g	OMe	OMe	4-MeC_6H_4	**8g**	78	**9g**	84
h	OMe	OMe	4-ClC_6H_4	**8h**	78	**9h**	81
i	OCH_2CH_2O		Ph	**8i**	79	**9i**	71
j	H	H	Ph	**8j**	80	**9j**	82
k	H	H	4-BrC_6H_4	**8k**	78	**9k**	81
l	H	Cl	Ph	**8l**	62	**9l**	66



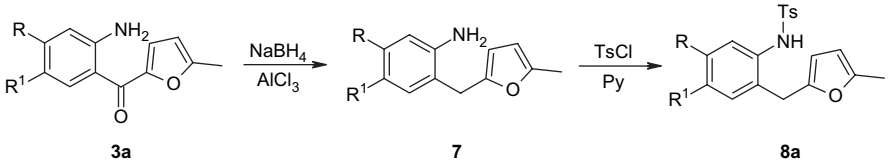
Scheme 9.

2.2. Synthesis of indole derivatives

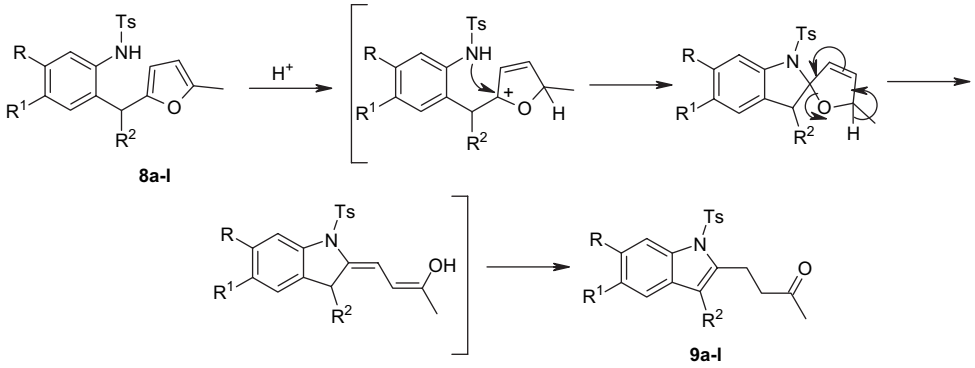
Refluxing benzylfurans **8a**,**b**,**e–l** in ethanolic solution saturated with hydrogen chloride (Scheme 10, Table 2) leads to indole ketones **9a**,**b**,**e–l** (Scheme 10, Table 3). The recyclization reaction starts with furan ring protonation and subsequent nucleophilic attack of the nitrogen atom lone pair onto the furyl cation. Reaction times ranged from 20 to 40 min, except for benzylfurans **8j–l**, which required 1.5–2 h. It should be noted that the recyclization of benzylfurans **8c** (R^2=Et) and **8d** (R^2=CH_2Ph) under the same conditions proceeded with formation of considerable amounts of unidentified by-products. We found that optimal conditions for the transformation **8c**,**d**→**9c**,**d** were in acetic acid solution at room temperature in the presence of hydrochloric acid (Scheme 10, Table 3). Moreover, it was found that this method also worked well for other indoles **9a**,**b**,**e–l**.

Indole derivatives **9a–l** were fully characterized by spectral methods. For unambiguous proof of structure, X-ray analysis was performed for **9j** (Fig. 2).[24]

To establish the reaction scope, we studied the influence of the substituents in the 5-position of the furan ring on the reaction course. For this purpose, benzylfurans **8m–p** were obtained by alkylation of corresponding furan derivatives with alcohol **6f** (Scheme 11). It is appeared that the nature of the alkyl substituent in the 5-position of the furan ring had no influence on the recyclization process. Corresponding indoles **9m**,**n** were obtained in high yield from benzylfurans **8m**,**n**



Scheme 8.



Scheme 10.

by refluxing in ethanolic hydrogen chloride solution (Scheme 11). Any attempts to recyclize compound **8o** failed and resulted in tarry materials. We found that even prolonged heating (12 h) of the benzylfuran **8p** bearing aromatic substituent in 5-position with ethanolic hydrogen chloride resulted in isolation of intact starting material. Optimized conditions for **8p** appeared to be in acetic acid solution in the presence of sufficient amount of 70% perchloric acid at room temperature. Despite the reaction requiring five days for completion it gave pure indole **9p** in 60% yield (Scheme 11).

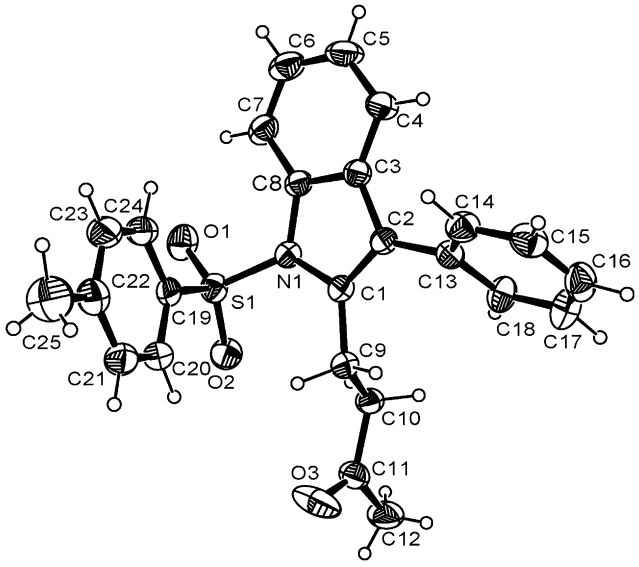
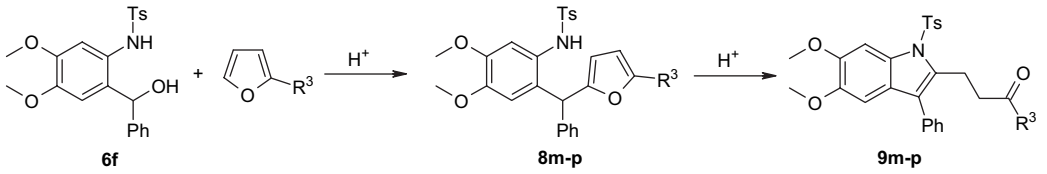


Figure 2. ORTEP diagram of **9j**.

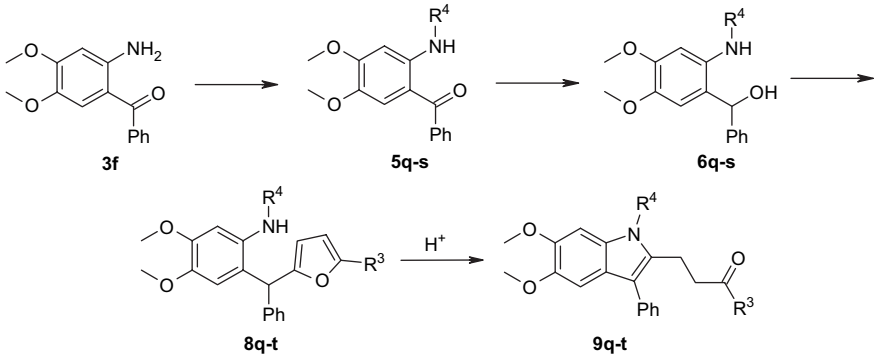
We also studied the influence of the protective group at nitrogen on the course of the recyclization. Starting benzylfurans **8q–t** were prepared according to Scheme 12. As it was expected, replacement of the tosyl group with mesyl one had no influence and corresponding indole **9q** was obtained from **8q** in refluxing ethanol saturated with hydrogen chloride. An attempt to recyclize benzylfuran **8r** under the same conditions failed due to resinification of the reaction mixture. We obtained indole **9r** from a mixture of acetic and hydrochloric acids at room temperature. Unlike **8q** and **8r**, acetylated amine **8s** did not give desired indole **9s**. Only resinification of the reaction mixture was observed.

The failure in the preparation of indoles **9r**,**s** under drastic reflux conditions can be attributed to the hydrolysis of amide function,[25] and subsequent side reactions. Most probably recyclization of compounds **8r** and **8s** in ethanolic hydrogen chloride solution gives indoles **10** unsubstituted at nitrogen. The loss of the electron withdrawing protecting group then favors intramolecular cyclization onto the 3-position with the formation of compound **11**. The instability of this intermediate under acidic conditions seems to be a reason for the observed resinification. Scheme 13 presents a plausible explanation and the nature of this transformation will be studied in future.



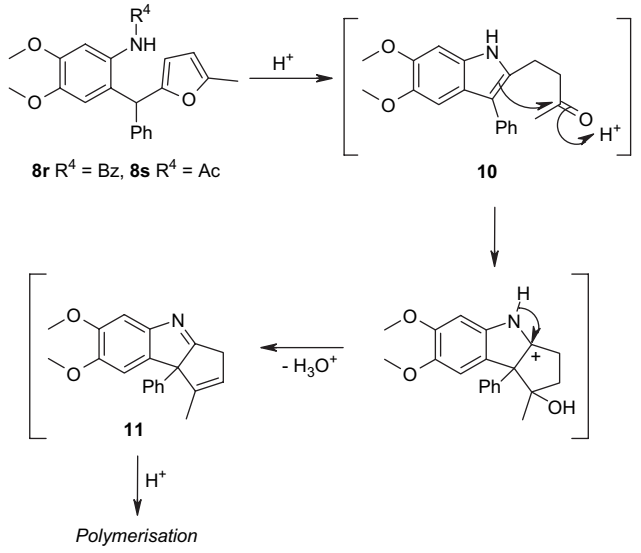
Entry	R^3	Product	Yield (%)	Product	Yield (%)
m	Et	**8m**	62	**9m**	72
n	*t*-Bu	**8n**	48	**9n**	79
o	H	**8o**	24	**9o**	-
p	4-MeC_6H_4	**8p**	59	**9p**	60

Scheme 11.



Entry	R^3	R^4	Product	Yield (%)	Product	Yield (%)
q	Me	Ms	**8q**	74	**9q**	84
r	Me	Bz	**8r**	66	**9r**	63
s	Me	Ac	**8s**	68	**9s**	-
t	*t*-Bu	Ac	**8t**	58	**9t**	-

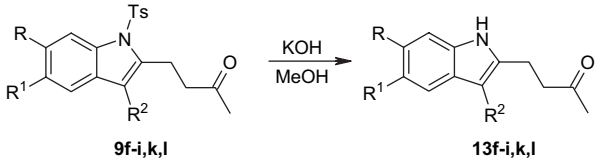
Scheme 12.



Scheme 13.

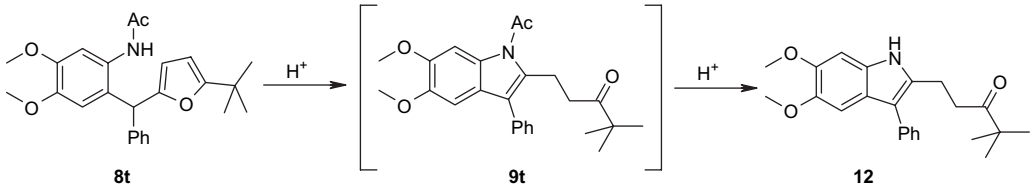
Indirect support for this hypothesis comes from the isolation of ketone **12** instead of the expected product **9t** upon treatment of **8t** with ethanolic hydrogen chloride solution or the mixture of acetic and hydrochloric acids at room temperature (Scheme 14). However it is not clear whether the loss of the protective group occurs after the ketone **9t** formation or before it. In our opinion, the isolation of ketone **12** was possible due to retarding of secondary cyclization by the bulky tertiary butyl group next to carbonyl function (Scheme 14).

Our method of indole synthesis is limited to aryl amines protected with a sulfonyl or a benzoyl group with the exception of the isolation of unsubstituted indole **12** (Scheme 14). In order to access such indoles, we attempted detosylation reaction. We have found that refluxing of indoles **9f–i**,**k**,**l** in a methanolic solution of potassium hydroxyde[26,27] smoothly leads to compounds **13f–i**,**k**,**l** (Scheme 15). Indole **12** was prepared from compound **9n** according to this procedure in 60% yield. However this method is applicable only to indoles **9** bearing an aromatic ring in the 3-position and failed with indoles **9a–e** substituted with hydrogen or alkyl group. The search for optimal conditions of detosylation of indoles **9a–e** is in progress.



Entry	R	R^1	R^2	Product	Yield (%)
f	OMe	OMe	Ph	**13f**	90
g	OMe	OMe	4-MeC_6H_4	**13g**	86
h	OMe	OMe	4-ClC_6H_4	**13h**	91
i	OCH_2CH_2O		Ph	**13i**	81
k	H	H	4-BrC_6H_4	**13k**	54
l	H	Cl	Ph	**13l**	62

Scheme 15.



Scheme 14.

3. Conclusion

In conclusion, we would like to note that we have developed a novel modification of Reissert's indole synthesis employing furan rings as a masked 1,4-dicarbonyl compound. Our methodology is very simple with yields ranging from good to high at every stage and allows variation of the substituents in final products and is scalable up to a pilot production. Furthermore, it gives highly functionalized indoles attractive for the further synthetic employment.

4. Experimental

4.1. General

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and in DMSO-d_6 on a Bruker AC 200, Bruker WM 250 and Bruker AM 300 spectrometers. Chemical shifts are reported in parts per million relative to tetramethylsilane as an internal standard and coupling constants (J) are given in absolute values in hertz to the nearest 0.1 Hz. Mass spectra were recorded on a Kratos MS-30 instrument with 70 eV electron impact ionization at 200 °C. IR spectra were recorded on InfraLUM FT-02 and InfraLUM FT-801. Column chromatography was carried out using silica gel KSK (50–160 μm) and KSK (5–40 μm) manufactured by LTD Sorbpolymer. A single crystal of **9j** suitable for X-ray crystallography was grown from ethanol.

4.1.1. General procedure for the synthesis of ketones 1a–i. Anhydrous $AlCl_3$ (57.4 g, 430 mmol) was added to a mixture of the corresponding acyl chloride (31.2 g, 400 mmol) and benzene (200–240 mL) under vigorous stirring keeping the temperature below 0 °C. Veratrole or 1,4-benzodioxane (300 mmol) was added successively keeping the temperature below 10 °C. The resulted reaction mixture was brought to 55–60 °C and maintained for 2.5 h at this temperature under vigorous stirring. After completion of the reaction, the mixture was poured into crushed ice (500 g) containing 13 mL of concentrated hydrochloric acid. The benzene layer was separated and evaporated to dryness. The crystalline residue was washed successively with $NaHCO_3$ solution, water, filtered off, and air dried. Recrystallization from EtOH or hexane afforded compounds **1a–i** in 75–85% yields.

WARNING: Care should be taken when handling benzene as a solvent due to its carcinogenic properties.

4.1.2. General procedure for the nitration of compounds 1a–i. Fuming nitric acid (3.0 mL, 70 mmol) was added dropwise to a solution of corresponding ketone **1** (10 mmol) in AcOH (7 mL) at 0 °C. The reaction mixture was maintained at 0 °C for 10 min and at room temperature for 20 min. Then it was poured into ice and the separated residue was filtered off and washed with a water solution of $NaHCO_3$ until pH=7 was reached. Recrystallization from EtOH–acetone afforded compounds **2a–i**.

4.1.2.1. 4,5-Dimethoxy-2-nitrophenyl-5-methyl-2-furylmethanone (2a). Yield 1.89 g, 65% as a yellow solid, mp 128–129 °C [Found: C, 57.79; H, 4.42; N, 4.77. $C_{14}H_{13}NO_6$ requires C, 57.73; H, 4.50; N, 4.81%]; ν_{max}(KBr) 1653, 1577, 1522, 1275, 1075, 1016, 878, 812, 784, 758 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.68 (1H, s, H_{Ar}), 6.98 (1H, s, H_{Ar}), 6.95 (1H, d, J 3.2 Hz, 4-H_{Fur}), 6.14 (1H, d, J 3.2 Hz, 3-H_{Fur}), 4.03 (3H, s, O*Me*), 3.97 (3H, s, O*Me*), 2.35 (3H, s, *Me*).

4.1.2.2. 1-(4,5-Dimethoxy-2-nitrophenyl)-1-ethanone (2b). Yield 1.28 g, 57% as yellow needles, mp 135–137 °C [Found: C, 53.54; H, 5.04; N, 6.37. $C_{10}H_{11}NO_5$ requires C, 53.33; H, 4.92; N, 6.22%]; ν_{max}(KBr) 1701, 1576, 1518, 1463, 1327, 1284, 1225, 1183, 1046, 883, 790 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.59 (1H, s, H_{Ar}), 6.74 (1H, s, H_{Ar}), 3.96 (6H, s, O*Me*), 2.48 (3H, s, *Me*).

4.1.2.3. 1-(4,5-Dimethoxy-2-nitrophenyl)-1-propanone (2c). Yield 1.55 g, 65% as pale yellow needles, mp 132–133 °C [Found: C, 55.03; H, 5.21; N, 5.99. $C_{11}H_{13}NO_5$ requires C, 55.23; H, 5.48; N, 5.85%]; ν_{max}(KBr) 1699, 1578, 1524, 1098, 1060, 1016, 871, 854, 837, 789 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.64 (1H, s, H_{Ar}), 6.71 (1H, s, H_{Ar}), 3.98 (6H, s, O*Me*), 2.72 (2H, q, J 7.2 Hz, CH_2Me), 1.25 (3H, t, J 7.2 Hz, CH$_2$*Me*).

4.1.2.4. 1-(4,5-Dimethoxy-2-nitrophenyl)-2-phenyl-1-ethanone (2d). Yield 1.90 g, 63% as a pale yellow solid, mp 166–167 °C [Found: C, 63.97; H, 5.13; N, 4.74. $C_{16}H_{15}NO_5$ requires C, 63.78; H, 5.02; N, 4.65%]; ν_{max}(KBr) 1709, 1577, 1509, 1450, 1396, 1332, 1282, 1226, 1176, 1082, 1010, 879, 791, 774, 722, 695 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.58 (1H, s, H_{Ar}), 7.22 (5H, s, Ph), 6.42 (1H, s, H_{Ar}), 3.97 (2H, s, CH_2Ph), 3.88 (3H, s, O*Me*), 3.73 (3H, s, O*Me*).

4.1.2.5. 1-(7-Nitro-2,3-dihydro-1,4-benzodioxin-6-yl)-1-ethanone (2e). Yield 1.25 g, 56% as a yellow solid, mp 118–120 °C [Found: C, 54.05; H, 4.14; N, 6.40. $C_{10}H_9NO_5$ requires C, 53.82; H, 4.06; N, 6.28%]; ν_{max}(KBr) 1694, 1616, 1578, 1525, 1351, 1302, 1060, 919, 899, 869, 829, 752, 706 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.64 (1H, s, H_{Ar}), 6.86 (1H, s, H_{Ar}), 4.36–4.33 (4H, m, CH_2CH_2), 2.48 (3H, s, *Me*).

4.1.2.6. 4,5-Dimethoxy-2-nitrophenyl-phenylmethanone (2f). Yield 2.38 g, 83% as pale yellow needles, mp 136–138 °C [Found: C, 62.88; H, 4.68; N, 4.98. $C_{15}H_{13}NO_5$ requires C, 62.72; H, 4.56; N, 4.88%]; ν_{max}(KBr) 1671, 1576, 1519, 1447, 1390, 1334, 1290, 1225, 1180, 1064, 994, 875, 833, 790, 758, 720, 689, 633, 616 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.77–7.74 (2H, m, Ph), 7.74 (1H, s, H_{Ar}), 7.60–7.55 (1H, m, Ph), 7.47–7.42 (2H, m, Ph), 6.87 (1H, s, H_{Ar}), 4.04 (3H, s, O*Me*), 3.97 (3H, s, O*Me*).

4.1.2.7. 4,5-Dimethoxy-2-nitrophenyl-4-methylphenylmethanone (2g). Yield 2.05 g, 68% as pale yellow needles, mp 139–140 °C [Found: C, 63.97; H, 5.15; N, 4.77. $C_{16}H_{15}NO_5$ requires C, 63.78; H, 5.02; N, 4.65%]; ν_{max}(KBr) 1670, 1606, 1575, 1520, 1469, 1456, 1393, 1331, 1287, 1222, 1177, 1064, 868, 783, 754, 615 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.73 (1H, s, H_{Ar}), 7.65 (2H, d, J 8.0 Hz, H_{Ar}), 7.24 (2H, d, J 8.0 Hz, H_{Ar}), 6.85 (1H, s, H_{Ar}), 4.03 (3H, s, O*Me*), 3.97 (3H, s, O*Me*), 2.42 (3H, s, *Me*).

4.1.2.8. 4-Chlorophenyl-4,5-dimethoxy-2-nitrophenylmethanone (2h). Yield 2.47 g, 77% as pale yellow

needles, mp 149–150 °C [Found: C, 55.85; H, 3.93; N, 4.51. $C_{15}H_{12}ClNO_5$ requires C, 56.00; H, 3.76; N, 4.35%]; ν_{max}(KBr) 1679, 1577, 1520, 1468, 1321, 1285, 1263, 1226, 1065, 864, 823, 787, 756 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.74 (1H, s, H_{Ar}), 7.68 (2H, d, *J* 8.5 Hz, H_{Ar}), 7.42 (2H, d, *J* 8.5 Hz, H_{Ar}), 6.84 (1H, s, H_{Ar}), 4.04 (3H, s, O*Me*), 3.98 (3H, s, O*Me*).

4.1.2.9. 7-Nitro-2,3-dihydro-1,4-benzodioxin-6-yl-phenylmethanone (2i). Yield 2.22 g, 78% as pale yellow needles, mp 188–189 °C [Found: C, 63.36; H, 3.77; N, 5.12. $C_{15}H_{11}NO_5$ requires C, 63.16; H, 3.89; N, 4.91%]; ν_{max}(KBr) 1670, 1577, 1525, 888, 873, 732 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.82 (1H, s, H_{Ar}), 7.78–7.74 (2H, m, H_{Ar}), 7.62–7.56 (1H, m, H_{Ar}), 7.49–7.41 (2H, m, H_{Ar}), 6.94 (1H, s, H_{Ar}), 4.41 (4H, s, CH_2CH_2).

4.1.3. General procedure for the reduction of compounds 2a–i. A mixture of corresponding compound **2** (36 mmol), iron powder (20 g), AcOH (70 mL), water (100 mL), and AcOEt (20 mL) was stirred under reflux for 6 h. After completion of the reaction, the mixture was neutralized with $NaHCO_3$ until pH=7 and filtered off. The residue was washed on the filter with AcOEt (3×150 mL). The organic layer was separated and the water layer was extracted with AcOEt (3×150 mL). Combined extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was recrystallized from AcOEt–hexane afforded compounds **3a–i**.

4.1.3.1. 2-Amino-4,5-dimethoxyphenyl-5-methyl-2-furylmethanone (3a). Yield 7.99 g, 85% as yellow needles, mp 120 °C [Found: C, 64.39; H, 5.66; N, 5.47. $C_{14}H_{15}NO_4$ requires C, 64.36; H, 5.79; N, 5.36%]; ν_{max}(KBr) 3415, 3301, 1626, 1590, 1577, 1525, 1493, 1467, 1392, 1253, 1211, 1139, 817, 802, 775, 582 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.56 (1H, s, H_{Ar}), 7.04 (1H, d, *J* 3.2 Hz, 4-H_{Fur}), 6.20 (1H, s, H_{Ar}), 6.18 (1H, d, *J* 3.2 Hz, 3-H_{Fur}), 5.96 (2H, s, NH_2), 3.90 (3H, s, O*Me*), 3.82 (3H, s, O*Me*), 2.42 (3H, s, *Me*).

4.1.3.2. 1-(2-Amino-4,5-dimethoxyphenyl)-1-ethanone (3b). Yield 5.05 g, 72% as a pale yellow solid, mp 106–107 °C [Found: C, 61.76; H, 6.83; N, 7.24. $C_{10}H_{13}NO_3$ requires C, 61.53; H, 6.71; N, 7.17%]; ν_{max}(KBr) 3446, 3338, 1634, 1590, 1541, 1510, 1456, 1423, 1397, 1246, 1208, 1191, 1164, 1057, 948, 851, 834, 562 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.12 (1H, s, H_{Ar}), 6.24 (2H, br s, NH_2), 6.11 (1H, s, H_{Ar}), 3.87 (3H, s, O*Me*), 3.84 (3H, s, O*Me*), 2.52 (3H, s, *Me*).

4.1.3.3. 1-(2-Amino-4,5-dimethoxyphenyl)-1-propanone (3c). Yield 5.12 g, 68% as a yellow solid, mp 128–129 °C [Found: C, 63.33; H, 7.35; N, 6.78. $C_{11}H_{15}NO_3$ requires C, 63.14; H, 7.23; N, 6.69%]; ν_{max}(KBr) 3440, 3329, 1632, 1593, 1543, 1510, 937, 838 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.18 (1H, s, H_{Ar}), 6.24 (2H, br s, NH_2), 6.12 (1H, s, H_{Ar}), 3.87 (3H, s, O*Me*), 3.84 (3H, s, O*Me*), 2.90 (2H, q, *J* 7.3 Hz, CH_2Me), 1.22 (3H, t, *J* 7.3 Hz, CH_2*Me*).

4.1.3.4. 1-(2-Amino-4,5-dimethoxyphenyl)-2-phenyl-1-ethanone (3d). Yield 6.44 g, 66% as a deep yellow solid, mp 91–92 °C [Found: C, 71.04; H, 6.45; N, 5.27. $C_{16}H_{17}NO_3$ requires C, 70.83; H, 6.32; N, 5.16%]; ν_{max}(KBr) 3449, 3315, 1629, 1577, 1539, 1509, 1465, 1242, 1149, 852, 845, 830, 723, 700, 553 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.18 (5H, s, Ph), 7.08 (1H, s, H_{Ar}), 6.17 (1H, s, H_{Ar}), 6.13 (2H, br s, NH_2), 4.07 (2H, s, CH_2Ph), 3.73 (3H, s, O*Me*), 3.67 (3H, s, O*Me*).

4.1.3.5. 1-(7-Amino-2,3-dihydro-1,4-benzodioxin-6-yl)-1-ethanone (3e). Yield 4.52 g, 65% as a deep yellow solid, mp 125 °C [Found: C, 62.36; H, 5.65; N, 7.34. $C_{10}H_{11}NO_3$ requires C, 62.17; H, 5.74; N, 7.25%]; ν_{max}(KBr) 3435, 3321, 1640, 1623, 1587, 1546, 1499, 1303, 1289, 1249, 1230, 1203, 1068, 952, 897, 862 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.23 (1H, s, H_{Ar}), 6.12 (1H, s, H_{Ar}), 5.97 (2H, br s, NH_2), 4.30–4.27 (2H, m, CH_2), 4.21–4.18 (2H, m, CH_2), 2.49 (3H, s, *Me*).

4.1.3.6. 2-Amino-4,5-dimethoxyphenyl-phenylmethanone (3f). Yield 8.33 g, 90% as a yellow solid, mp 78–80 °C [Found: C, 70.24; H, 5.99; N, 5.52. $C_{15}H_{15}NO_3$ requires C, 70.02; H, 5.88; N, 5.44%]; ν_{max}(KBr) 3426, 3314, 1627, 1588, 1530, 1510, 1461, 1446, 1396, 1320, 1249, 1126, 832, 699 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.63–7.61 (2H, m, Ph), 7.53–7.43 (3H, m, Ph), 6.94 (1H, s, H_{Ar}), 6.22 (2H, br s, NH_2), 6.21 (1H, s, H_{Ar}), 3.91 (3H, s, O*Me*), 3.66 (3H, s, O*Me*).

4.1.3.7. 2-Amino-4,5-dimethoxyphenyl-4-methylphenylmethanone (3g). Yield 7.12 g, 73% as a yellow solid, mp 103–104 °C [Found: C, 71.01; H, 6.43; N, 5.25. $C_{16}H_{17}NO_3$ requires C, 70.83; H, 6.32; N, 5.16%]; ν_{max}(KBr) 3446, 3339, 1631, 1593, 1552, 1514, 1467, 1447, 1411, 1384, 1279, 1257, 1230, 1209, 1172, 1120, 868, 836, 767, 577 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.54 (2H, d, *J* 7.6 Hz, H_{Ar}), 7.25 (2H, d, *J* 7.6 Hz, H_{Ar}), 6.97 (1H, s, H_{Ar}), 6.21 (1H, s, H_{Ar}), 6.16 (2H, br s, NH_2), 3.90 (3H, s, O*Me*), 3.67 (3H, s, O*Me*), 2.43 (3H, s, *Me*).

4.1.3.8. 2-Amino-4,5-dimethoxyphenyl-4-chlorophenylmethanone (3h). Yield 7.02 g, 67% as yellow needles, mp 140–141 °C [Found: C, 61.93; H, 4.91; N, 4.87. $C_{15}H_{14}ClNO_3$ requires C, 61.76; H, 4.84; N, 4.80%]; ν_{max}(KBr) 3453, 3317, 1624, 1606, 1580, 1533, 1394, 1260, 1219, 1126, 864, 842, 768 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.53 (2H, d, *J* 8.1 Hz, H_{Ar}), 7.43 (2H, d, *J* 8.1 Hz, H_{Ar}), 6.85 (1H, s, H_{Ar}), 6.20 (2H, br s, NH_2), 6.18 (1H, s, H_{Ar}), 3.89 (3H, s, O*Me*), 3.66 (3H, s, O*Me*).

4.1.3.9. 7-Amino-2,3-dihydro-1,4-benzodioxin-6-yl-phenylmethanone (3i). Yield 6.79 g, 74% as a pale yellow solid, mp 144–145 °C [Found: C, 70.77; H, 5.21; N, 5.58. $C_{15}H_{13}NO_3$ requires C, 70.58; H, 5.13; N, 5.49%]; ν_{max}(KBr) 3432, 3324, 1640, 1583, 1549, 1500, 1304, 1255, 1237, 1206, 1072, 934, 880, 832, 749, 704 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.63–7.58 (2H, m, Ph), 7.50–7.43 (3H, m, Ph), 7.00 (1H, s, H_{Ar}), 6.22 (1H, s, H_{Ar}), 5.93 (2H, br s, NH_2), 4.31–4.26 (2H, m, CH_2), 4.19–4.14 (2H, m, CH_2).

4.1.3.10. 2-Amino-5-chlorophenyl-phenylmethanone (3l). Compound **3l** was obtained similarly to **3a–i** from compound **4** in 75% yield as yellow needles.

4.1.4. General procedure for the tosylation of ketones 3b,d–i. *p*-Toluenesulfonyl chloride (10.67 g, 56 mmol) was added to a solution of corresponding compound **3** (47 mmol) in pyridine (36 mL) at room temperature and the mixture was left for 1 h. Then it was poured into excess of water and the precipitate was filtered off, washed with water, and dried. Recrystallization from CH_2Cl_2–hexane afforded products **5b**,**d–i**.

4.1.4.1. 2-Acetyl-4,5-dimethoxy-1-(4-methylphenylsulfonamido)benzene (5b). Yield 12.96 g, 79% as a pale yellow solid, mp 144–146 °C [Found: C, 58.76; H, 5.56; N, 4.09. $C_{17}H_{19}NO_5S$ requires C, 58.44; H, 5.48; N, 4.01%]; ν_{max}(KBr) 3257, 1631, 1578, 1518, 1002, 961, 917, 863, 848, 811, 726, 706, 677, 659, 575, 546 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 11.51 (1H, s, N*H*), 7.68 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.31 (1H, s, H_{Ar}), 7.21 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.13 (1H, s, H_{Ar}), 3.93 (3H, s, O*Me*), 3.85 (3H, s, O*Me*), 2.48 (3H, s, *Me*), 2.37 (3H, s, *Me*).

4.1.4.2. 4,5-Dimethoxy-1-(4-methylphenylsulfonamido)-2-propionylbenzene 5c. Compound **5c** was obtained similarly to **5b**,**d–i** but *p*-toluenesulfonyl chloride was added at 0 °C and the mixture maintained at this temperature for 20 min before pouring into water. Yield 12.63 g, 74% as colorless needles, mp 143–144 °C [Found: C, 59.62; H, 5.97; N, 3.99. $C_{18}H_{21}NO_5S$ requires C, 59.49; H, 5.82; N, 3.85%]; ν_{max}(KBr) 3257, 1638, 1612, 1577, 1517, 1162, 951, 911, 861, 818, 682, 575 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 11.50 (1H, s, N*H*), 7.67 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.31 (1H, s, H_{Ar}), 7.20 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.16 (1H, s, H_{Ar}), 3.93 (3H, s, O*Me*), 3.84 (3H, s, O*Me*), 2.82 (2H, q, *J* 7.2 Hz, CH_2Me), 2.36 (3H, s, *Me*), 1.11 (3H, t, *J* 7.2 Hz, CH_2*Me*).

4.1.4.3. 4,5-Dimethoxy-1-(4-methylphenylsulfonamido)-2-(2-phenylacetyl)benzene (5d). Yield 15.38 g, 77% as a white solid, mp 153–154 °C [Found: C, 65.19; H, 5.53; N, 3.36. $C_{23}H_{23}NO_5S$ requires C, 64.92; H, 5.45; N, 3.29%]; ν_{max}(KBr) 3280, 1627, 1573, 1516, 1464, 1425, 1400, 1346, 1160, 982, 912, 718, 698, 675, 655, 583, 567, 545, 512 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 11.44 (1H, s, N*H*), 7.66 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.33–7.09 (9H, m, Ph+H_{Ar}+H_{Ts}), 4.12 (2H, s, CH_2Ph), 3.92 (3H, s, O*Me*), 3.76 (3H, s, O*Me*), 2.38 (3H, s, *Me*).

4.1.4.4. 7-Acetyl-6-(4-methylphenylsulfonamido)-2,3-dihydro-1,4-benzodioxine (5e). Yield 11.74 g, 72% as colorless cubes, mp 179–181 °C [Found: C, 58.97; H, 5.02; N, 4.11. $C_{17}H_{17}NO_5S$ requires C, 58.78; H, 4.93; N, 4.03%]; ν_{max}(KBr) 3260, 1639, 1578, 1514, 1468, 1409, 930, 901, 875, 813, 730, 707, 682, 663, 643, 563, 551, 516 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 11.25 (1H, s, N*H*), 7.71 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.22 (2H, s, H_{Ar}), 7.21 (2H, d, *J* 8.1 Hz, H_{Ts}), 4.31–4.28 (2H, m, CH_2), 4.23–4.20 (2H, m, CH_2), 2.43 (3H, s, *Me*), 2.37 (3H, s, *Me*).

4.1.4.5. 2-Benzoyl-4,5-dimethoxy-1-(4-methylphenylsulfonamido)benzene (5f). Yield 15.65 g, 81% as a white solid, mp 171–172 °C [Found: C, 64.46; H, 5.04; N, 3.31. $C_{22}H_{21}NO_5S$ requires C, 64.22; H, 5.14; N, 3.40%]; ν_{max}(KBr) 3248, 1642, 1600, 1575, 1514, 1450, 1384, 1346, 1266, 1211, 1161, 1109, 1092, 1001, 902, 697 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 10.23 (1H, s, N*H*), 7.53 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.55–7.52 (1H, m, Ph), 7.39–7.27 (5H, m, H_{Ar}+Ph), 7.03 (2H, d, *J* 8.2 Hz, H_{Ts}), 6.80 (1H, s, H_{Ar}), 4.00 (3H, s, O*Me*), 3.67 (3H, s, O*Me*), 2.23 (3H, s, *Me*).

4.1.4.6. 4,5-Dimethoxy-2-(4-methylbenzoyl)-1-(4-methylphenylsulfonamido)benzene (5g). Yield 15.98 g, 80% as a white solid, mp 195–196 °C [Found: C, 65.17; H, 5.53; N, 3.36. $C_{23}H_{23}NO_5S$ requires C, 64.92; H, 5.45; N, 3.29%]; ν_{max}(KBr) 3269, 1635, 1605, 1518, 1388, 1356, 1269, 1254, 1213, 1174, 1158, 1111, 1006, 899, 768, 688, 669, 562 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 10.15 (1H, s, N*H*), 7.53 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.38 (1H, s, H_{Ar}), 7.26 (2H, d, *J* 8.1 Hz, H_{Ar}), 7.19 (2H, d, *J* 8.1 Hz, H_{Ar}), 7.02 (2H, d, *J* 8.1 Hz, H_{Ts}), 6.83 (1H, s, H_{Ar}), 3.99 (3H, s, O*Me*), 3.69 (3H, s, O*Me*), 2.44 (3H, s, *Me*), 2.23 (3H, s, *Me*).

4.1.4.7. 2-(4-Chlorobenzoyl)-4,5-dimethoxy-1-(4-methylphenylsulfonamido)benzene (5h). Yield 16.31 g, 78% as a white solid, mp 201 °C [Found: C, 59.53; H, 4.78; N, 3.02. $C_{22}H_{20}ClNO_5S$ requires C, 59.26; H, 4.52; N, 3.14%]; ν_{max}(KBr) 3262, 1636, 1605, 1590, 1519, 1356, 1159, 772, 688, 671, 590, 580, 545, 514 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 10.08 (1H, s, N*H*), 7.53 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.37 (1H, s, H_{Ar}), 7.36 (2H, d, *J* 8.5 Hz, H_{Ar}), 7.28 (2H, d, *J* 8.5 Hz, H_{Ar}), 7.03 (2H, d, *J* 8.2 Hz, H_{Ts}), 6.74 (1H, s, H_{Ar}), 4.00 (3H, s, O*Me*), 3.69 (3H, s, O*Me*), 2.25 (3H, s, *Me*).

4.1.4.8. 7-Benzoyl-6-(4-methylphenylsulfonamido)-2,3-dihydro-1,4-benzodioxine (5i). Yield 15.19 g, 79% as a yellow solid, mp 194 °C [Found: C, 64.75; H, 4.40; N, 3.59. $C_{22}H_{19}NO_5S$ requires C, 64.53; H, 4.68; N, 3.42%]; ν_{max}(KBr) 3182, 1621, 1600, 1572, 1500, 1399, 1339, 1310, 1246, 1157, 1065, 881, 815, 740, 710, 693, 671 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 10.09 (1H, s, N*H*), 7.60 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.59–7.53 (1H, m, Ph), 7.34 (1H, s, H_{Ar}), 7.44–7.32 (4H, m, Ph), 7.07 (2H, d, *J* 8.1 Hz, H_{Ts}), 6.90 (1H, s, H_{Ar}), 4.35–4.31 (2H, m, CH_2), 4.24–4.20 (2H, m, CH_2), 2.25 (3H, s, *Me*).

4.1.4.9. 2-Benzoyl-1-(4-methylphenylsulfonamido)benzene (5j). Compound **5j** was obtained similarly to **5b**,**d–i** but the reaction mixture was refluxed for 25–30 min after the addition of *p*-toluenesulfonyl chloride. Yield 11.55 g, 70% as colorless cubes, mp 128–129 °C [Found: C, 68.50; H, 4.96; N, 4.07. $C_{20}H_{17}NO_3S$ requires C, 68.36; H, 4.88; N, 3.99%]; ν_{max}(KBr) 3245, 1646, 1596, 1482, 1450, 1396, 1325, 1316, 1295, 1283, 1258, 1211, 1165, 1092, 941, 898, 883, 768, 749, 725, 709 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 9.99 (1H, s, N*H*), 7.82–7.79 (1H, m, H_{Ar}), 7.60–7.50 (4H, m, H_{Ar}+H_{Ts}), 7.41–7.38 (5H, m, H_{Ar}), 7.13–7.04 (3H, m, H_{Ar}+H_{Ts}), 2.25 (3H, s, *Me*).

4.1.4.10. 2-(4-Bromobenzoyl)-1-(4-methylphenylsulfonamido)benzene (5k). Compound **5k** was obtained similarly to **5j**. Yield 14.55 g, 72% as colorless needles, mp 145–146 °C [Found: C, 55.99; H, 3.85; N, 3.31. $C_{20}H_{16}BrNO_3S$ requires C, 55.82; H, 3.75; N, 3.25%]; ν_{max}(KBr) 3266, 1644, 1600, 1582, 941, 895, 814, 787, 757, 736, 728, 689, 559, 544 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 9.84 (1H, s, N*H*), 7.82–7.78 (1H, m, H_{Ar}), 7.58–7.50 (5H,

m, H_{Ar}+H_{Ts}), 7.36–7.33 (1H, m, H_{Ar}), 7.27 (2H, d, *J* 8.5 Hz, H_{Ar}), 7.15–7.08 (1H, m, H_{Ar}), 7.05 (2H, d, *J* 8.1 Hz, H_{Ts}), 2.26 (3H, s, *Me*).

4.1.4.11. 2-Benzoyl-4-chloro-1-(4-methylphenylsulfonamido)benzene (5l). Compound **5l** was obtained similarly to **5j**. Yield 12.49 g, 69% as colorless needles, mp 125–126 °C [Found: C, 62.49; H, 4.27; N, 3.74. $C_{20}H_{16}ClNO_3S$ requires C, 62.25; H, 4.18; N, 3.63%]; ν_{max}(KBr) 3267, 1637, 1593, 1470, 1381, 1337, 1292, 1165, 807, 710, 691 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 9.70 (1H, s, N*H*), 7.77 (1H, d, *J* 8.8 Hz, H_{Ar}), 7.55 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.62–7.33 (7H, m, H_{Ar}+Ph), 7.04 (2H, d, *J* 8.1 Hz, H_{Ts}), 2.24 (3H, s, *Me*).

4.1.4.12. *N*-(2-Benzoyl-4,5-dimethoxyphenyl)methanesulfonamide 5q. Compound **5q** was obtained similarly to **5b**,**d–i**, employing mesylchloride instead of *p*-toluenesulfonyl chloride. Yield 11.49 g, 73% as a yellow solid, mp 116–117 °C [Found: C, 57.31; H, 4.88; N, 4.42. $C_{16}H_{17}NO_5S$ requires C, 57.30; H, 5.11; N, 4.18%]; ν_{max}(KBr) 3255, 1611, 1576, 1523, 1344, 1265, 1151, 966, 937, 879, 835, 763, 741, 702, 520 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 10.50 (1H, s, N*H*), 7.72–7.47 (5H, m, Ph), 7.44 (1H, s, H_{Ar}), 7.09 (1H, s, H_{Ar}), 4.01 (3H, s, O*Me*), 3.75 (3H, s, O*Me*), 3.00 (3H, s, *Me*).

4.1.4.13. 2-Benzoyl-4,5-dimethoxy-1-phenylcarboxamidobenzene (5r). Benzoylchloride (10.0 g, 71 mmol) was added to a solution of ketone **3f** (8.23 g, 32 mmol) in pyridine (26 mL). The reaction mixture was left for 1 h at room temperature and then poured into excess of water. The clotted precipitate was filtered off, washed with water, and recrystallized from CH_2Cl_2–hexane. Yield 9.01 g, 78% as yellow needles, mp 190 °C [Found: C, 73.30; H, 5.45; N, 3.99. $C_{22}H_{19}NO_4$ requires C, 73.12; H, 5.30; N, 3.88%]; ν_{max}(KBr) 3255, 1662, 1615, 1591, 1524, 751, 703 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 12.52 (1H, s, N*H*), 8.76 (1H, s, H_{Ar}), 8.12–8.08 (2H, m, Ph), 7.72–7.69 (2H, m, Ph), 7.62–7.48 (6H, m, Ph), 7.12 (1H, s, H_{Ar}), 4.08 (3H, s, O*Me*), 3.74 (3H, s, O*Me*).

4.1.4.14. *N*-(2-Benzoyl-4,5-dimethoxyphenyl)acetamide (5s). A mixture of the compound **3f** (7 g, 27 mmol) and Ac_2O (5.5 g, 54 mmol) was refluxed for 10 min, cooled to room temperature, poured into water and brought to pH=7 with $NaHCO_3$. The precipitate was filtered off and recrystallized from CH_2Cl_2–hexane. Yield 5.89 g, 73% as yellow cubes, mp 140–141 °C [Found: C, 68.39; H, 5.83; N, 4.75. $C_{17}H_{17}NO_4$ requires C, 68.22; H, 5.72; N, 4.68%]; ν_{max}(KBr) 3232, 1685, 1617, 1526, 1468, 1346, 1261, 1210, 1117, 1010, 881, 836, 771, 745, 706 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 11.42 (1H, s, N*H*), 8.46 (1H, s, H_{Ar}), 7.69–7.48 (5H, m, Ph), 7.03 (1H, s, H_{Ar}), 4.00 (3H, s, O*Me*), 3.72 (3H, s, O*Me*), 2.25 (3H, s, *Me*).

4.1.5. General method of reduction of compounds 5b–l,q. Finely ground $NaBH_4$ (3.8 g, 100 mmol) was added portionwise to a solution of corresponding compound **5** (50 mmol) in EtOH (50 mL). The reaction mixture was brought to reflux and left for 1 h at room temperature. Then it was poured into water and neutralized with 10% hydrochloric acid until pH=7. The precipitate was filtered off, washed with water, and recrystallized from EtOH–acetone mixture affording compounds **6b–l**,**q**.

4.1.5.1. 2-(1-Hydroxyethyl)-4,5-dimethoxy-1-(4-methylphenylsulfonamido)benzene (6b). Yield 12.11 g, 69% as a white solid, mp 144–146 °C [Found: C, 58.34; H, 6.13; N, 4.10. $C_{17}H_{21}NO_5S$ requires C, 58.10; H, 6.02; N, 3.99%]; ν_{max}(KBr) 3447, 3148, 1522, 1452, 1389, 1335, 1271, 1214, 1200, 1155, 1130, 1087, 1015, 991, 564 cm^{-1}; δ_H (250 MHz, DMSO-d_6) 9.22 (1H, s, N*H*), 7.60 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.39 (2H, d, *J* 8.1 Hz, H_{Ts}), 6.96 (1H, s, H_{Ar}), 6.19 (1H, s, H_{Ar}), 5.04 (1H, br s, O*H*), 4.98 (1H, q, *J* 6.3 Hz, C*H*Me), 3.73 (3H, s, O*Me*), 3.43 (3H, s, O*Me*), 2.38 (3H, s, *Me*), 1.16 (3H, d, *J* 6.3 Hz, CH*Me*).

4.1.5.2. 2-(1-Hydroxypropyl)-4,5-dimethoxy-1-(4-methylphenylsulfonamido)benzene (6c). Yield 13.14 g, 72% as a white solid, mp 159–160 °C [Found: C, 59.35; H, 6.50; N, 3.99. $C_{18}H_{23}NO_5S$ requires C, 59.16; H, 6.34; N, 3.83%]; ν_{max}(KBr) 3458, 3227, 1519, 1466, 1453, 1382, 1338, 1266, 1204, 1182, 1162, 1124, 1091, 1074, 1011, 989, 917, 693, 559, 544 cm^{-1}; δ_H (250 MHz, DMSO-d_6) 9.20 (1H, s, N*H*), 7.60 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.38 (2H, d, *J* 8.1 Hz, H_{Ts}), 6.90 (1H, s, H_{Ar}), 6.28 (1H, s, H_{Ar}), 5.04 (1H, br s, O*H*), 4.72–4.66 (1H, m, C*H*CH_2Me), 3.71 (3H, s, O*Me*), 3.46 (3H, s, O*Me*), 2.38 (3H, s, *Me*), 1.39 (2H, dq, *J* 7.2, 6.3 Hz, CHC*H*$_2$Me), 0.76 (3H, t, *J* 7.2 Hz, $CHCH_2$*Me*).

4.1.5.3. 2-(1-Hydroxy-2-phenylethyl)-4,5-dimethoxy-1-(4-methylphenylsulfonamido)benzene (6d). Yield 14.52 g, 68% as a white solid, mp 118–119 °C [Found: C, 64.88; H, 5.97; N, 3.35. $C_{23}H_{25}NO_5S$ requires C, 64.62; H, 5.89; N, 3.28%]; ν_{max}(KBr) 3481, 3265, 1614, 1597, 1518, 1496, 1456, 1394, 1341, 1268, 1211, 1161, 1112, 1089, 1012, 985, 900, 699, 662 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.66 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.41 (1H, s, N*H*), 7.26–7.21 (5H, m, Ph+H_{Ts}), 6.97–6.94 (2H, m, Ph), 6.82 (1H, s, H_{Ar}), 6.54 (1H, s, H_{Ar}), 4.78 (1H, t, *J* 7.6 Hz, C*H*CH_2Ph), 3.75 (6H, s, O*Me*), 2.88–2.69 (2H, m, CHC*H*$_2$Ph), 2.38 (3H, s, *Me*), 2.27 (1H, br s, O*H*).

4.1.5.4. 7-(1-Hydroxyethyl)-6-(4-methylphenylsulfonamido)-2,3-dihydro-1,4-benzodioxine (6e). Yield 12.22 g, 70% as a white solid, mp 144–145 °C [Found: C, 58.67; H, 5.57; N, 4.13. $C_{17}H_{19}NO_5S$ requires C, 58.44; H, 5.48; N, 4.01%]; ν_{max}(KBr) 3452, 3174, 1587, 1506, 1462, 1427, 1377, 1323, 1288, 1176, 1161, 1127, 1078, 1067, 921, 893, 812, 658, 569, 554, 532 cm^{-1}; δ_H (250 MHz, DMSO-d_6) 9.30 (1H, s, N*H*), 7.62 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.39 (2H, d, *J* 8.1 Hz, H_{Ts}), 6.84 (1H, s, H_{Ar}), 6.26 (1H, s, H_{Ar}), 5.06 (1H, br s, O*H*), 4.87 (1H, q, *J* 6.3 Hz, C*H*Me), 4.19–4.14 (4H, m, CH_2CH_2), 2.39 (3H, s, *Me*), 1.12 (3H, d, *J* 6.3 Hz, CH*Me*).

4.1.5.5. 2-Hydroxy(phenyl)methyl-4,5-dimethoxy-1-(4-methylphenylsulfonamido)benzene (6f). Yield 17.55 g, 85% as a white solid, mp 194–195 °C [Found: C, 58.44; H, 5.48; N, 4.01. $C_{22}H_{23}NO_5S$ requires C, 63.91; H, 5.61; N, 3.39%]; ν_{max}(KBr) 3489, 3185, 1513, 1394, 1350, 1166, 1014, 992, 902, 869, 720, 674, 575 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.53 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.34–7.27 (4H, m, Ph+N*H*), 7.21 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.17–7.12 (2H, m,

Ph), 6.83 (1H, s, H_{Ar}), 6.46 (1H, s, H_{Ar}), 5.52 (1H, s, C*H*), 3.78 (3H, s, O*Me*), 3.69 (3H, s, O*Me*), 2.58 (1H, br s, O*H*), 2.42 (3H, s, *Me*).

4.1.5.6. 2-Hydroxy(4-methylphenyl)methyl-4,5-dimethoxy-1-(4-methylphenylsulfonamido)benzene (6g). Yield 17.93 g, 84% as colorless cubes, mp 179–180 °C [Found: C, 64.83; H, 6.01; N, 3.36. $C_{23}H_{25}NO_5S$ requires C, 64.62; H, 5.89; N, 3.28%]; ν_{max}(KBr) 3482, 3164, 1513, 1464, 1398, 1353, 1272, 1206, 1179, 1164, 1094, 1016, 992, 907, 868, 817, 760, 736, 709, 690, 674, 579, 559 cm^{-1}; δ_H (200 MHz, DMSO-d_6) 9.17 (1H, s, N*H*), 7.55 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.34 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.10 (2H, d, *J* 8.8 Hz, H_{Ar}), 7.06 (2H, d, *J* 8.8 Hz, H_{Ar}), 6.87 (1H, s, H_{Ar}), 6.20 (1H, s, H_{Ar}), 6.01 (1H, s, C*H*), 5.81 (1H, br s, O*H*), 3.64 (3H, s, O*Me*), 3.41 (3H, s, O*Me*), 2.37 (3H, s, *Me*), 2.27 (3H, s, *Me*).

4.1.5.7. 2-[4-Chlorophenyl(hydroxy)methyl]-4,5-dimethoxy-1-(4-methylphenylsulfonamido)benzene (6h). Yield 19.22 g, 86% as a white solid, mp 174–175 °C [Found: C, 59.13; H, 5.24; N, 3.01. $C_{22}H_{22}ClNO_5S$ requires C, 58.99; H, 4.95; N, 3.13%]; ν_{max}(KBr) 3474, 3173, 1518, 1489, 1464, 1441, 1400, 1354, 1275, 1209, 1182, 1167, 1092, 1022, 1011, 993, 907, 816, 762, 745, 689, 675, 583 cm^{-1}; δ_H (200 MHz, DMSO-d_6) 9.20 (1H, s, N*H*), 7.55 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.33 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.30 (2H, d, *J* 8.8 Hz, H_{Ar}), 7.22 (2H, d, *J* 8.8 Hz, H_{Ar}), 6.89 (1H, s, H_{Ar}), 6.20 (1H, s, H_{Ar}), 6.08 (1H, s, C*H*), 5.97 (1H, br s, O*H*), 3.67 (3H, s, O*Me*), 3.47 (3H, s, O*Me*), 2.37 (3H, s, *Me*).

4.1.5.8. 7-Hydroxy(phenyl)methyl-6-(4-methylphenylsulfonamido)-2,3-dihydro-1,4-benzodioxine (6i). Yield 17.06 g, 83% as a white solid, mp 90–91 °C [Found: C, 64.50; H, 5.32; N, 3.65. $C_{22}H_{21}NO_5S$ requires C, 64.22; H, 5.14; N, 3.40%]; ν_{max}(KBr) 3492, 3228, 1589, 1506, 1459, 1414, 1383, 1311, 1158, 1091, 1067, 1040, 1012, 912, 888, 818, 733, 702, 684 cm^{-1}; δ_H (200 MHz, DMSO-d_6) 9.27 (1H, s, N*H*), 7.58 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.35 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.29–7.16 (5H, m, Ph), 6.63 (1H, s, H_{Ar}), 6.28 (1H, s, H_{Ar}), 5.92 (1H, s, C*H*), 5.82 (1H, br s, O*H*), 4.11 (4H, s, CH_2CH_2), 2.37 (3H, s, *Me*).

4.1.5.9. 2-Hydroxy(phenyl)methyl-1-(4-methylphenylsulfonamido)benzene (6j). Yield 15.00 g, 85% as a white solid, mp 147–148 °C [Found: C, 68.21; H, 5.49; N, 3.88. $C_{20}H_{19}NO_3S$ requires C, 67.97; H, 5.42; N, 3.96%]; ν_{max}(KBr) 3450, 3112, 1322, 1154, 740, 698, 569 cm^{-1}; δ_H (250 MHz, DMSO-d_6) 9.42 (1H, s, N*H*), 7.53 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.37–7.15 (8H, m, H_{Ar}+H_{Ts}), 7.13–7.06 (2H, m, H_{Ar}), 7.01–6.95 (1H, m, H_{Ar}), 6.23 (1H, br s, O*H*), 6.01 (1H, s, C*H*), 2.37 (3H, s, *Me*).

4.1.5.10. 2-[4-Bromophenyl(hydroxy)methyl]-1-(4-methylphenylsulfonamido)benzene (6k). Yield 19.22 g, 89% as pale yellow cubes, mp 142–143 °C [Found: C, 55.73; H, 4.30; N, 3.32. $C_{20}H_{18}BrNO_3S$ requires C, 55.56; H, 4.20; N, 3.24%]; ν_{max}(KBr) 3420, 3136, 1595, 1488, 1461, 1401, 1325, 1234, 1156, 1087, 1003, 926, 817, 796, 765, 693, 562 cm^{-1}; δ_H (250 MHz, DMSO-d_6) 9.40 (1H, s, N*H*), 7.51 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.45 (2H, d, *J* 8.4 Hz, H_{Ar}), 7.30 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.31–7.25 (1H, m, H_{Ar}), 7.20–7.10 (4H, m, H_{Ar}), 7.00–6.95 (1H, m, H_{Ar}), 6.30 (1H, br s, O*H*), 6.03 (1H, s, C*H*), 2.37 (3H, s, *Me*).

4.1.5.11. 4-Chloro-2-hydroxy(phenyl)methyl-1-(4-methylphenylsulfonamido)benzene (6l). Yield 17.22 g, 89% as a white solid, mp 120–122 °C [Found: C, 62.19; H, 4.77; N, 3.68. $C_{20}H_{18}ClNO_3S$ requires C, 61.93; H, 4.68; N, 3.61%]; ν_{max}(KBr) 3428, 3143, 1485, 1323, 1159, 1088, 1007, 698, 670, 574 cm^{-1}; δ_H (250 MHz, DMSO-d_6) 9.51 (1H, br s, N*H*), 7.53 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.34–7.19 (9H, m, H_{Ar}+H_{Ts}), 6.89 (1H, d, *J* 8.6 Hz, H_{Ar}), 6.27 (1H, br s, O*H*), 6.07 (1H, s, C*H*), 2.37 (3H, s, *Me*).

4.1.5.12. *N*-[2-Hydroxy(phenyl)methyl-4,5-dimethoxyphenyl]methanesulfonamide (6q). Yield 14.15 g, 84% as a white solid, mp 173–174 °C [Found: C, 57.23; H, 5.90; N, 4.41. $C_{16}H_{19}NO_5S$ requires C, 56.96; H, 5.68; N, 4.15%]; ν_{max}(KBr) 3470, 3271, 1514, 1456, 1439, 1395, 1334, 1265, 1203, 1146, 1119, 1024, 996, 976, 921, 873, 749, 733, 516 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.60 (1H, s, N*H*), 7.40–7.29 (5H, m, Ph), 7.21 (1H, s, H_{Ar}), 6.76 (1H, s, H_{Ar}), 5.92 (1H, d, *J* 3.0 Hz, C*H*), 3.87 (3H, s, O*Me*), 3.86 (3H, s, O*Me*), 3.09 (1H, d, *J* 3.0 Hz, O*H*), 2.20 (3H, s, *Me*).

4.1.5.13. 2-Hydroxy(phenyl)methyl-4,5-dimethoxy-1-phenylcarboxamidobenzene (6r). Finely ground $NaBH_4$ (3.41 g, 90 mmol) was added portionwise to a solution of compound **5r** (16.2 g, 45 mmol) in EtOH (200 mL). The reaction mixture was brought to reflux and then left for 1 h at room temperature. Then it was poured into water and neutralized with 10% hydrochloric acid until pH=7. The precipitate was filtered off, washed with water, and recrystallized from ethanol–acetone mixture. Yield 11.92 g, 73% as a white solid, mp 173–174 °C [Found: C, 72.97; H, 5.70; N, 3.96. $C_{22}H_{21}NO_4$ requires C, 72.71; H, 5.82; N, 3.85%]; ν_{max}(KBr) 3461, 3364, 1659, 1616, 1539, 1508, 1464, 1454, 1414, 1377, 1331, 1259, 1235, 1213, 1203, 1138, 1090, 733, 696 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 9.20 (1H, br s, N*H*), 8.02 (1H, s, H_{Ar}), 7.69–7.66 (2H, m, Ph), 7.50–7.30 (8H, m, Ph), 6.64 (1H, s, H_{Ar}), 5.94 (1H, d, *J* 3.2 Hz, C*H*), 3.94 (3H, s, O*Me*), 3.79 (3H, s, O*Me*), 3.15 (1H, d, *J* 3.2 Hz, O*H*).

4.1.5.14. *N*-[2-Hydroxy(phenyl)methyl-4,5-dimethoxyphenyl]acetamide (6s). Finely ground $NaBH_4$ (0.15 g, 16 mmol) was added portionwise to a solution of compound **5s** (1.9 g, 4.2 mmol) in ethanol (22 mL). The reaction mixture was refluxed for 5 min, cooled, poured into water, and neutralized with 10% hydrochloric acid until pH=7. The precipitate was filtered off, washed with water, and recrystallized from EtOH–acetone. Yield 0.86 g, 68% as colorless needles, mp 176–177 °C [Found: C, 67.94; H, 6.45; N, 4.72. $C_{17}H_{19}NO_4$ requires C, 67.76; H, 6.36; N, 4.65%]; ν_{max}(KBr) 3421, 3361, 1657, 1614, 1527, 1509, 1452, 1412, 1253, 1234, 1203, 1116, 1035, 1016, 864, 728, 696, 605, 593, 550 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 8.18 (1H, br s, N*H*), 7.52 (1H, s, H_{Ar}), 7.37–7.31 (5H, m, Ph), 6.67 (1H, s, H_{Ar}), 5.85 (1H, d, *J* 3.0 Hz, C*H*), 3.88 (3H, s, O*Me*), 3.80 (3H, s, O*Me*), 3.51 (1H, d, *J* 3.0 Hz, O*H*), 1.95 (3H, s, *Me*).

4.1.5.15. 4,5-Dimethoxy-2-(5-methyl-2-furylmethyl)-aniline (7). A mixture of compound **3a** (7 g, 27 mmol),

THF (250 mL), $NaBH_4$ (4.2 g, 110 mmol), and anhydrous $AlCl_3$ (8 g, 60 mmol) was stirred at room temperature until full consumption of starting material **3a** (TLC monitoring). The reaction mixture was poured into ice–water mixture and extracted with AcOEt (3×150 mL). Combined extracts were dried over anhydrous Na_2SO_4 and evaporated at reduced pressure. The compound **7** was used at the next step without additional purification. Yield 5.34 g, 80% as a yellow solid, mp 55 °C (AcOEt–hexane) [Found: C, 68.19; H, 7.01; N, 5.75. $C_{14}H_{17}NO_3$ requires C, 68.00; H, 6.93; N, 5.66%]; ν_{max}(KBr) 3396, 3318, 1612, 1519, 1467, 1447, 1256, 1218, 1019, 1002, 856, 849, 795, 764, 747, 653 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.66 (1H, s, H_{Ar}), 6.31 (1H, s, H_{Ar}), 5.85 (2H, s, H_{Fur}), 3.83 (3H, s, O*Me*), 3.81 (3H, s, O*Me*), 3.77 (2H, s, CH_2), 3.50 (2H, br s, NH_2), 2.26 (3H, s, *Me*).

4.1.5.16. 4,5-Dimethoxy-2-(5-methyl-2-furylmethyl)-1-(4-methylphenylsulfonamido)benzene (8a). *p*-Toluenesulfonyl chloride (4.43 g, 23 mmol) was added to a solution of compound **7** (4.79 g, 19.4 mmol) in pyridine (19 mL) and the reaction mixture was left for 1 h at room temperature and then poured into water. The precipitated compound was filtered off, air dried, and recrystallized from CH_2Cl_2–hexane. Yield 4.9 g, 63% as a white solid, mp 115–116 °C [Found: C, 63.05; H, 5.89; N, 3.41. $C_{21}H_{23}NO_5S$ requires C, 62.83; H, 5.77; N, 3.49%]; ν_{max}(KBr) 3221, 1519, 1420, 1327, 1216, 1162, 992, 679 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.59 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.23 (2H, d, *J* 8.1 Hz, H_{Ts}), 6.92 (1H, s, H_{Ar}), 6.59 (1H, s, H_{Ar}), 6.56 (1H, s, N*H*), 5.82 (1H, d, *J* 3.0 Hz, 4-H_{Fur}), 5.74 (1H, d, *J* 3.0 Hz, 3-H_{Fur}), 3.82 (3H, s, O*Me*), 3.81 (3H, s, O*Me*), 3.37 (2H, s, CH_2), 2.41 (3H, s, *Me*), 2.24 (3H, s, *Me*).

4.1.6. General procedure for the synthesis of compounds 8b–i. A mixture of corresponding compound **6** (10 mmol), *p*-TsOH (0.1 g, 6 mmol), and 2-methylfuran (1.64 g, 20 mmol) in CH_2Cl_2 (70 mL) was refluxed with azeotropic removal of water for 2–3 h (TLC monitoring). The reaction mixture was neutralized with a solution of $NaHCO_3$ and organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Then it was reduced in volume to 5–10 mL and diluted with hexane up to 50–60 mL. The resulted solution was passed through a pad of silica gel and left for crystallization or evaporated to dryness and used in further steps.

4.1.6.1. 4,5-Dimethoxy-2-[1-(5-methyl-2-furyl)ethyl]-1-(4-methylphenylsulfonamido)benzene (8b). Yield 2.86 g, 69% as a white solid, mp 109–110 °C [Found: C, 63.83; H, 6.17; N, 3.48. $C_{22}H_{25}NO_5S$ requires C, 63.60; H, 6.06; N, 3.37%]; ν_{max}(KBr) 3275, 1514, 1160, 1010, 900, 868, 816, 787, 675, 554 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.60 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.23 (2H, d, *J* 8.2 Hz, H_{Ts}), 6.87 (1H, s, H_{Ar}), 6.62 (1H, s, H_{Ar}), 6.52 (1H, s, N*H*), 5.80 (1H, d, *J* 3.0 Hz, 4-H_{Fur}), 5.73 (1H, d, *J* 3.0 Hz, 3-H_{Fur}), 3.81 (3H, s, O*Me*), 3.79 (3H, s, O*Me*), 3.76 (1H, q, *J* 7.2 Hz, C*H*Me), 2.40 (3H, s, *Me*), 2.21 (3H, s, *Me*), 1.22 (3H, d, *J* 7.2 Hz, CH*Me*).

4.1.6.2. 4,5-Dimethoxy-2-[1-(5-methyl-2-furyl)propyl]-1-(4-methylphenylsulfonamido)benzene (8c). Compound **8c** was obtained as a pale yellow oil and used as such at the next step without additional purification. Yield 3.22 g, 75%.

4.1.6.3. 4,5-Dimethoxy-2-[1-(5-methyl-2-furyl)-2-phenylethyl]-1-(4-methylphenylsulfonamido)benzene (8d). Compound **8d** was obtained as a pale yellow oil and used as such at the next step without additional purification. Yield 2.06 g, 42%.

4.1.6.4. 7-[1-(5-Methyl-2-furyl)ethyl]-6-(4-methylphenylsulfonamido)-2,3-dihydro-1,4-benzodioxine (8e). Yield 3.10 g, 75% as a white solid, mp 136–138 °C [Found: C, 64.22; H, 5.79; N, 3.50. $C_{22}H_{23}NO_5S$ requires C, 63.91; H, 5.61; N, 3.39%]; ν_{max}(KBr) 3270, 1504, 1392, 1332, 1311, 1161, 1068, 898, 681, 580, 550 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.62 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.25 (2H, d, *J* 8.2 Hz, H_{Ts}), 6.89 (1H, s, H_{Ar}), 6.65 (1H, s, H_{Ar}), 6.50 (1H, s, N*H*), 5.80 (1H, d, *J* 3.0 Hz, 4-H_{Fur}), 5.75 (1H, d, *J* 3.0 Hz, 3-H_{Fur}), 4.23 (4H, s, CH_2CH_2), 3.70 (1H, q, *J* 7.2 Hz, C*H*Me), 2.41 (3H, s, *Me*), 2.21 (3H, s, *Me*), 1.23 (3H, d, *J* 7.2 Hz, CH*Me*).

4.1.6.5. 4,5-Dimethoxy-2-[5-methyl-2-furyl(phenyl)-methyl]-1-(4-methylphenylsulfonamido)benzene (8f). Yield 3.91 g, 82% as a white solid, mp 134–135 °C [Found: C, 68.24; H, 5.19; N, 2.82. $C_{27}H_{27}NO_5S$ requires C, 67.90; H, 5.07; N, 2.93%]; ν_{max}(KBr) 3283, 1513, 1450, 1384, 1345, 1288, 1263, 1210, 1164, 1091, 1018, 902, 720, 710, 677, 567, 548 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.63 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.30 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.26–7.20 (3H, m, Ph), 7.00 (1H, s, H_{Ar}), 6.75–6.69 (2H, m, Ph), 6.22 (1H, s, H_{Ar}), 6.12 (1H, s, N*H*), 5.84 (1H, d, *J* 3.0 Hz, 4-H_{Fur}), 5.58 (1H, d, *J* 3.0 Hz, 3-H_{Fur}), 4.75 (1H, s, C*H*), 3.85 (3H, s, O*Me*), 3.62 (3H, s, O*Me*), 2.47 (3H, s, *Me*), 2.23 (3H, s, *Me*).

4.1.6.6. 4,5-Dimethoxy-2-[5-methyl-2-furyl(4-methylphenyl)methyl]-1-(4-methylphenylsulfonamido)benzene (8g). Yield 3.83 g, 78% as a white solid, mp 143–145 °C [Found: C, 68.66; H, 6.13; N, 2.97. $C_{28}H_{29}NO_5S$ requires C, 68.41; H, 5.95; N, 2.85%]; ν_{max}(KBr) 3252, 1512, 1462, 1446, 1393, 1340, 1289, 1204, 1164, 1093, 1018, 909, 813, 782, 756, 672, 552 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.61 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.28 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.04 (2H, d, *J* 8.0 Hz, H_{Ar}), 7.01 (1H, s, H_{Ar}), 6.62 (2H, d, *J* 8.0 Hz, H_{Ar}), 6.24 (1H, s, H_{Ar}), 6.07 (1H, s, N*H*), 5.83 (1H, d, *J* 3.0 Hz, 4-H_{Fur}), 5.55 (1H, d, *J* 3.0 Hz, 3-H_{Fur}), 4.67 (1H, s, C*H*), 3.84 (3H, s, O*Me*), 3.63 (3H, s, O*Me*), 2.45 (3H, s, *Me*), 2.32 (3H, s, *Me*), 2.22 (3H, s, *Me*).

4.1.6.7. 2-[4-Chlorophenyl(5-methyl-2-furyl)methyl]-4,5-dimethoxy-1-(4-methylphenylsulfonamido)benzene (8h). Yield 3.89 g, 76% as a white solid, mp 138–139 °C [Found: C, 63.52; H, 5.28; N, 2.89. $C_{27}H_{26}ClNO_5S$ requires C, 63.34; H, 5.12; N, 2.74%]; ν_{max}(KBr) 3243, 1518, 1492, 1331, 1161, 790, 674, 567, 549 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.62 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.28 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.20 (2H, d, *J* 8.4 Hz, H_{Ar}), 6.92 (1H, s, H_{Ar}), 6.69 (2H, d, *J* 8.4 Hz, H_{Ar}), 6.25 (1H, s, H_{Ar}), 6.06 (1H, s, N*H*), 5.85 (1H, d, *J* 3.0 Hz, 4-H_{Fur}), 5.61 (1H, d, *J* 3.0 Hz, 3-H_{Fur}), 4.93 (1H, s, C*H*), 3.81 (3H, s, O*Me*), 3.64 (3H, s, O*Me*), 2.45 (3H, s, *Me*), 2.24 (3H, s, *Me*).

4.1.6.8. 7-[5-Methyl-2-furyl(phenyl)methyl]-6-(4-methylphenylsulfonamido)-2,3-dihydro-1,4-benzodioxine (8i). Yield 3.75 g, 79% as a white solid, mp 200 °C [Found: C, 68.03; H, 5.44; N, 3.07. $C_{27}H_{25}NO_5S$ requires C, 68.19; H, 5.30; N, 2.95%]; ν_{max}(KBr) 3269, 1499, 1375, 1335, 1315, 1165, 1069, 901, 679, 563 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.65 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.33 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.28–7.25 (3H, m, Ph), 7.00 (1H, s, H_{Ar}), 6.78–6.72 (2H, m, Ph), 6.24 (1H, s, H_{Ar}), 6.04 (1H, s, N*H*), 5.84 (1H, d, *J* 3.0 Hz, 4-H_{Fur}), 5.58 (1H, d, *J* 3.0 Hz, 3-H_{Fur}), 4.71 (1H, s, C*H*), 4.26–4.21 (4H, m, CH_2CH_2), 2.47 (3H, s, *Me*), 2.23 (3H, s, *Me*).

4.1.6.9. 2-[5-Methyl-2-furyl(phenyl)methyl]-1-(4-methylphenylsulfonamido)benzene (8j). A mixture of the compound **6j** (3.53 g, 10 mmol), 2-methylfuran (1.64 g, 20 mmol), and $BF_3 \cdot OEt_2$ (0.01 mL) in benzene (50 mL) was refluxed with azeotropic removal of water within 20–60 min (TLC monitoring). The reaction mixture was neutralized with $NaHCO_3$ solution in water and organic layer was separated, washed with water and dried over anhydrous Na_2SO_4. The benzene solution was reduced in volume to 5–7 mL and diluted with hexane up to 50–60 mL. The resultant solution was passed through a pad of silica gel and left for crystallization. Yield 3.34 g, 80% as a white solid, mp 128–129 °C [Found: C, 71.77; H, 5.70; N, 3.48. $C_{25}H_{23}NO_3S$ requires C, 71.92; H, 5.55; N, 3.35%]; ν_{max}(KBr) 3271, 1489, 1452, 1385, 1338, 1168, 1090, 907, 784, 752, 702, 669, 566, 548 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.58 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.50–7.47 (1H, m, H_{Ar}), 7.28–7.21 (6H, m, H_{Ar}+H_{Ts}), 7.13–7.07 (1H, m, H_{Ar}), 6.81–6.73 (3H, m, H_{Ar}), 6.28 (1H, s, N*H*), 5.86 (1H, d, *J* 3.0 Hz, 4-H_{Fur}), 5.60 (1H, d, *J* 3.0 Hz, 3-H_{Fur}), 4.88 (1H, s, C*H*), 2.44 (3H, s, *Me*), 2.24 (3H, s, *Me*).

WARNING: Care should be taken when handling benzene as a solvent due to its carcinogenic properties.

4.1.6.10. 2-[4-Bromophenyl(5-methyl-2-furyl)methyl]-1-(4-methylphenylsulfonamido)benzene (8k). Compound **8k** was obtained similarly to compounds **8j**. Yield 3.87 g, 78% as colorless cubes, mp 137–138 °C [Found: C, 60.73; H, 4.59; N, 2.74. $C_{25}H_{22}BrNO_3S$ requires C, 60.49; H, 4.47; N, 2.82%]; ν_{max}(KBr) 3288, 1486, 1378, 1338, 1164, 1091, 785, 660, 566, 548 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.58 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.47–7.43 (1H, m, H_{Ar}), 7.37 (2H, d, *J* 8.2 Hz, H_{Ar}), 7.28–7.21 (3H, m, H_{Ar}+H_{Ts}), 7.14–7.08 (1H, m, H_{Ar}), 6.76–6.73 (1H, m, H_{Ar}), 6.65 (2H, d, *J* 8.2 Hz, H_{Ar}), 6.25 (1H, s, N*H*), 5.86 (1H, d, *J* 3.0 Hz, 4-H_{Fur}), 5.61 (1H, d, *J* 3.0 Hz, 3-H_{Fur}), 4.97 (1H, s, C*H*), 2.44 (3H, s, *Me*), 2.25 (3H, s, *Me*).

4.1.6.11. 4-Chloro-2-[5-methyl-2-furyl(phenyl)methyl]-1-(4-methylphenylsulfonamido)benzene (8l). Compound **8l** was obtained similarly to compounds **8j**. Yield 2.80 g, 62% as a white solid, mp 123–124 °C [Found: C, 66.29; H, 4.76; N, 3.17. $C_{25}H_{22}ClNO_3S$ requires C, 66.44; H, 4.91; N, 3.10%]; ν_{max}(KBr) 3334, 1488, 1401, 1322, 1156, 1115, 1089, 931, 890, 814, 777, 702, 657, 583, 544 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.58 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.42 (1H, d, *J* 8.6 Hz, H_{Ar}), 7.30–7.23 (5H, m, Ph+H_{Ts}), 7.22 (1H, dd, *J* 8.6, 2.4 Hz, H_{Ar}), 6.81–6.78 (2H, m, Ph), 6.74 (1H, d, *J* 2.4 Hz, H_{Ar}), 6.22 (1H, s, N*H*), 5.87 (1H, d, *J* 3.0 Hz, 4-H_{Fur}), 5.63 (1H, d, *J* 3.0 Hz, 3-H_{Fur}), 4.83 (1H, s, C*H*), 2.45 (3H, s, *Me*), 2.25 (3H, s, *Me*).

4.1.6.12. 2-[5-Ethyl-2-furyl(phenyl)methyl]-4,5-dimethoxy-1-(4-methylphenylsulfonamido)benzene (8m). Compound **8m** was obtained similarly to compounds **8b–i** employing 2-ethylfuran instead of 2-methylfuran. Yield 3.04 g, 62% as colorless cubes, mp 137–138 °C [Found: C, 68.66; H, 6.11; N, 2.97. $C_{28}H_{29}NO_5S$ requires C, 68.41; H, 5.95; N, 2.85%]; ν_{max}(KBr) 3278, 1613, 1599, 1561, 1520, 1494, 1466, 1448, 1381, 1348, 898, 809, 756, 718, 706, 670, 640, 565, 547 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.63 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.30 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.27–7.21 (3H, m, Ph), 7.00 (1H, s, H_{Ar}), 6.77–6.71 (2H, m, Ph), 6.22 (1H, s, H_{Ar}), 6.12 (1H, s, N*H*), 5.85 (1H, d, *J* 3.2 Hz, 4-H_{Fur}), 5.58 (1H, d, *J* 3.2 Hz, 3-H_{Fur}), 4.72 (1H, s, C*H*), 3.86 (3H, s, O*Me*), 3.62 (3H, s, O*Me*), 2.58 (2H, q, *J* 7.2 Hz, CH_2Me), 2.45 (3H, s, *Me*), 1.20 (3H, t, *J* 7.2 Hz, CH_2*Me*).

4.1.6.13. 2-[5-(*tert*-Butyl)-2-furyl(phenyl)methyl]-4,5-dimethoxy-1-(4-methylphenylsulfonamido)benzene (8n). A mixture of compound **6f** (2 g, 5 mmol), 2-*tert*-butylfuran (1.0 g, 8 mmol), and 70% $HClO_4$ (0.2 mL) in 1,4-dioxane (7 mL) was maintained at 65–70 °C for 20–25 min (TLC monitoring). Then the reaction mixture was poured into water, neutralized with $NaHCO_3$, and extracted with CH_2Cl_2 (3×50 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was recrystallized from hexane. Yield 1.25 g, 48% as a white solid, mp 68–70 °C [Found: C, 69.50; H, 6.27; N, 2.94. $C_{30}H_{33}NO_5S$ requires C, 69.34; H, 6.40; N, 2.70%]; ν_{max}(KBr) 3259, 1599, 1513, 1461, 1344, 1207, 1189, 1162, 1092, 1007, 907, 815, 722, 703, 664, 564, 548 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.61 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.29 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.30–7.24 (3H, m, Ph), 6.99 (1H, s, H_{Ar}), 6.83–6.80 (2H, m, Ph), 6.22 (1H, s, H_{Ar}), 6.01 (1H, s, N*H*), 5.81 (1H, d, *J* 3.1 Hz, 4-H_{Fur}), 5.51 (1H, d, *J* 3.1 Hz, 3-H_{Fur}), 4.72 (1H, s, C*H*), 3.84 (3H, s, O*Me*), 3.63 (3H, s, O*Me*), 2.43 (3H, s, *Me*), 1.22 (9H, s, *t-Bu*).

4.1.6.14. 2-[2-Furyl(phenyl)methyl]-4,5-dimethoxy-1-(4-methylphenylsulfonamido)benzene (8o). Compound **8o** was obtained similarly to compounds **8n** employing furan instead of 2-*tert*-butylfuran. Yield 0.56 g, 24% as a white solid, mp 160–161 °C [Found: C, 67.58; H, 5.60; N, 3.13. $C_{26}H_{25}NO_5S$ requires C, 67.37; H, 5.44; N, 3.02%]; ν_{max}(KBr) 3269, 1515, 1451, 1347, 1211, 1179, 1164, 1091, 1008, 726, 681, 569 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.63 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.35–7.24 (6H, m, Ph+H_{Ts}+5-H_{Fur}), 6.94 (1H, s, H_{Ar}), 6.81–6.77 (2H, m, Ph), 6.28 (1H, dd, *J* 3.2, 1.9 Hz, 4-H_{Fur}), 6.26 (1H, s, H_{Ar}), 6.00 (1H, br s, N*H*), 5.74 (1H, d, *J* 3.2 Hz, 3-H_{Fur}), 4.91 (1H, s, C*H*), 3.82 (3H, s, O*Me*), 3.63 (3H, s, O*Me*), 2.45 (3H, s, *Me*).

4.1.6.15. 4,5-Dimethoxy-2-[5-(4-methylphenyl)-2-furyl(phenyl)methyl]-1-(4-methylphenylsulfonamido)-benzene (8p). A mixture of compound **6f** (0.99 g, 2.4 mmol), 2-(4-methylphenyl)furan (0.42 g, 2.7 mmol), and concentrated hydrochloric acid (10 mL) in 30 mL of AcOH was maintained at 55–60 °C for 2 min. Then the reaction mixture was poured into water, neutralized with $NaHCO_3$, and

extracted with CH_2Cl_2 (3×50 mL). The organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was recrystallized from hexane. Yield 0.78 g, 59% as a white solid, mp 113–114 °C [Found: C, 71.48; H, 5.80; N, 2.75. $C_{33}H_{31}NO_5S$ requires C, 71.59; H, 5.64; N, 2.53%]; ν_{max}(KBr) 3233, 1514, 1327, 1162, 703, 672, 569, 548 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.64 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.44 (2H, d, *J* 8.1 Hz, H_{Ar}), 7.29 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.28–7.23 (3H, m, Ph), 7.16 (2H, d, *J* 8.1 Hz, H_{Ar}), 6.97 (1H, s, H_{Ar}), 6.89–6.86 (2H, m, Ph), 6.46 (1H, d, *J* 3.2 Hz, 4-H_{Fur}), 6.34 (1H, s, H_{Ar}), 6.06 (1H, br s, N*H*), 5.76 (1H, d, *J* 3.2 Hz, 3-H_{Fur}), 4.91 (1H, s, C*H*), 3.84 (3H, s, O*Me*), 3.62 (3H, s, O*Me*), 2.38 (3H, s, *Me*), 2.36 (3H, s, *Me*).

4.1.6.16. *N*-{4,5-Dimethoxy-2-[5-methyl-2-furyl(phenyl)methyl]phenyl}methanesulfonamide (8q). Compound **8q** was obtained similarly to the compounds **8b–i** from **6q** as a pale yellow oil and used as such in further steps.

4.1.6.17. 4,5-Dimethoxy-2-[5-methyl-2-furyl(phenyl)-methyl]-1-phenylcarboxamidobenzene (8r). A mixture of compound **6r** (6.2 g, 17 mmol), 2-methylfuran (2.8 g, 34 mmol), and 70% $HClO_4$ (0.5 mL) in 1,4-dioxane (20 mL) was maintained at 70–75 °C for 20–25 min. The reaction mixture was poured into water, neutralized with $NaHCO_3$, and left overnight at room temperature. The crystalline precipitate was filtered off, washed with water, and recrystallized from CH_2Cl_2–hexane. Yield 4.79 g, 66% as a white solid, mp 143–144 °C [Found: C, 76.13; H, 6.02; N, 3.37. $C_{27}H_{25}NO_4$ requires C, 75.86; H, 5.89; N, 3.28%]; ν_{max}(KBr) 3232, 1643, 1513, 1212, 1091, 1023, 699 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.72–7.68 (2H, m, Ph+N*H*), 7.52–7.47 (m, 3H, H_{Ph}), 7.40–7.28 (5H, m, Ph+H_{Ar}), 7.19–7.17 (2H, m, Ph), 6.53 (1H, s, H_{Ar}), 5.93 (1H, d, *J* 3.0 Hz, 4-H_{Fur}), 5.89 (1H, d, *J* 3.0 Hz, 3-H_{Fur}), 5.47 (1H, s, C*H*), 3.93 (3H, s, O*Me*), 3.75 (3H, s, O*Me*), 2.25 (3H, s, *Me*).

4.1.6.18. *N*-{4,5-Dimethoxy-2-[5-methyl-2-furyl(phenyl)-methyl]phenyl}acetamide (8s). A mixture of compound **6s** (3.3 g, 11 mmol), 2-methylfuran (1.8 g, 22 mmol), and 70% $HClO_4$ (0.32 mL) in 1,4-dioxane (12 mL) was maintained at 70–75 °C for 15–20 min. The reaction mixture was poured into water, neutralized with $NaHCO_3$, and extracted with CH_2Cl_2 (3×50 mL). The extract was dried over anhydrous Na_2SO_4 and evaporated to dryness. The obtained product was recrystallized from CH_2Cl_2–hexane. Yield 2.73 g, 68% as a white solid, mp 127–128 °C [Found: C, 72.40; H, 6.22; N, 3.94. $C_{22}H_{23}NO_4$ requires C, 72.31; H, 6.34; N, 3.83%]; ν_{max}(KBr) 3280, 1655, 1528, 1519, 1212, 1020, 788, 757, 737, 702 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.35–7.28 (4H, m, Ph+H_{Ar}), 7.17–7.14 (2H, m, Ph), 6.94 (1H, br s, N*H*), 6.52 (1H, s, H_{Ar}), 5.93 (1H, d, *J* 3.0 Hz, 4-H_{Fur}), 5.83 (1H, d, *J* 3.0 Hz, 3-H_{Fur}), 5.42 (1H, s, C*H*), 3.88 (3H, s, O*Me*), 3.75 (3H, s, O*Me*), 2.29 (3H, s, *Me*), 1.94 (3H, s, *Me*).

4.1.6.19. *N*-{2-[5-(*tert*-Butyl)-2-furyl(phenyl)methyl]-4,5-dimethoxyphenyl}acetamide (8t). 2-*tert*-Butylfuran (0.48 g, 3.9 mmol) was added to a solution of compound **6s** (0.78 g, 2.6 mmol) in AcOH (30 mL) followed by hydrochloric acid (11 mL) under cooling in water bath. The resulted reaction mixture was maintained at room temperature for 24 h (TLC monitoring), poured into water, neutralized with $NaHCO_3$, and extracted with AcOEt (3×50 mL). The extract was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified on silica gel (5–40 μm) column with AcOEt–hexane (2:3) as an eluent. The solvent was removed in a rotatory evaporator and the residue was recrystallized from hexane. Yield 0.61 g, 58% as a white solid, mp 133–134 °C [Found: C, 73.81; H, 7.29; N, 3.55. $C_{25}H_{29}NO_4$ requires C, 73.69; H, 7.17; N, 3.44%]; ν_{max}(KBr) 3321, 1659, 1535, 1513, 1260, 1216, 783, 759, 734, 698 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.35–7.29 (4H, m, Ph+H_{Ar}), 7.14–7.16 (2H, m, Ph), 6.84 (1H, br s, N*H*), 6.50 (1H, s, H_{Ar}), 5.89 (1H, d, *J* 3.0 Hz, 4-H_{Fur}), 5.78 (1H, d, *J* 3.0 Hz, 3-H_{Fur}), 5.39 (1H, s, C*H*), 3.87 (3H, s, O*Me*), 3.74 (3H, s, O*Me*), 1.90 (3H, s, *Me*), 1.26 (9H, s, *t-Bu*).

4.1.7. General procedure for the synthesis of compounds 9a,b,e–n. Ethanolic HCl (10 mL) prepared by saturation of 200 g of EtOH with 100 g of gaseous HCl was added to a solution of corresponding compound **8** (2 mmol) in EtOH (10 mL). The reaction mixture was refluxed until all starting compound was consumed (TLC monitoring). The reaction mixture was poured into water and the precipitate obtained was filtered off, washed with water and recrystallized from ethanol.

4.1.7.1. 4-[5,6-Dimethoxy-1-(4-methylphenylsulfonyl)-1*H*-2-indolyl]-2-butanone (9a). Yield 0.54 g, 67% as a white solid, mp 174–175 °C [Found: C, 62.96; H, 5.94; N, 3.70. $C_{21}H_{23}NO_5S$ requires C, 62.83; H, 5.77; N, 3.49%]; ν_{max}(KBr) 1721, 1488, 1157, 1053, 918, 855, 815, 667, 607, 541 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.75 (1H, s, H_{Ind}), 7.56 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.16 (2H, d, *J* 8.2 Hz, H_{Ts}), 6.82 (1H, s, H_{Ind}), 6.26 (1H, s, H_{Ind}), 3.95 (3H, s, O*Me*), 3.85 (3H, s, O*Me*), 3.22–3.18 (2H, m, CH_2), 2.91–2.87 (2H, m, CH_2), 2.32 (3H, s, *Me*), 2.15 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 207.5, 147.5, 147.2, 144.9, 139.2, 135.7, 131.5, 129.9(2C), 126.2(2C), 122.7, 110.2, 101.9, 99.2, 56.4, 56.1, 43.6, 30.0, 23.6, 21.6; MS: *m*/*z* (%) 401 (M^+, 78), 246 (69), 205 (23), 204 (100), 203 (57), 190 (22), 189 (96), 188 (18), 174 (16), 145 (15), 91 (67).

4.1.7.2. 4-[5,6-Dimethoxy-3-methyl-1-(4-methylphenylsulfonyl)-1*H*-2-indolyl]-2-butanone (9b). Yield 0.65 g, 78% as a white solid, mp 147–148 °C [Found: C, 63.84; H, 6.18; N, 3.49. $C_{22}H_{25}NO_5S$ requires C, 63.60; H, 6.06; N, 3.37%]; ν_{max}(KBr) 1716, 1489, 1361, 1347, 1214, 1164 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.78 (1H, s, H_{Ind}), 7.50 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.15 (2H, d, *J* 8.2 Hz, H_{Ts}), 6.77 (1H, s, H_{Ind}), 3.99 (3H, s, O*Me*), 3.89 (3H, s, O*Me*), 3.19–3.11 (2H, m, CH_2), 2.93–2.85 (2H, m, CH_2), 2.32 (3H, s, *Me*), 2.16 (3H, s, *Me*), 2.09 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 207.8, 147.5, 147.1, 144.5, 135.4, 134.0, 130.6, 129.6(2C), 126.0(2C), 124.4, 117.9, 100.2, 99.4, 56.3, 56.0, 43.9, 29.9, 21.4, 20.8, 9.0; MS: *m*/*z* (%) 415 (M^+, 26), 261 (22), 260 (100), 218 (64), 217 (59), 204 (15), 203 (70), 202 (29), 188 (17), 174 (16), 159 (26), 91 (22).

4.1.7.3. 4-[3-Ethyl-5,6-dimethoxy-1-(4-methylphenylsulfonyl)-1*H*-2-indolyl]-2-butanone (9c). Concentrated hydrochloric acid (10 mL) was added to a solution of

compound **8c** (2.1 g, 4.9 mmol) in AcOH (40 mL) under cooling in water bath. The resulted reaction mixture was maintained at room temperature for 2 h (TLC monitoring), poured into water, neutralized with $NaHCO_3$, and extracted with CH_2Cl_2 (3×50 mL). The extract was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified on silica gel (50–160 μm) column with acetone–CH_2Cl_2–hexane (5:3:20) as an eluent. The solvent was removed in rotatory evaporator and residue was recrystallized from CH_2Cl_2–hexane. Yield 1.45 g, 69% as a white solid, mp 90 °C [Found: C, 64.62; H, 6.51; N, 3.07. $C_{23}H_{27}NO_5S$ requires C, 64.31; H, 6.34; N, 3.26%]; ν_{max}(KBr) 1713, 1489, 1469, 1358, 1277, 1215, 1194, 1177, 1157, 1016, 852, 676 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.79 (1H, s, H_{Ind}), 7.48 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.14 (2H, d, *J* 8.2 Hz, H_{Ts}), 6.80 (1H, s, H_{Ind}), 3.97 (3H, s, O*Me*), 3.91 (3H, s, O*Me*), 3.17–3.12 (2H, m, CH_2), 2.92–2.87 (2H, m, CH_2), 2.57 (2H, q, *J* 7.5 Hz, CH_2Me), 2.32 (3H, s, *Me*), 2.17 (3H, s, *Me*), 1.10 (3H, t, *J* 7.5 Hz, CH$_2$*Me*); δ_C (50 MHz, $CDCl_3$) 208.0, 147.6, 147.2, 144.6, 135.5, 133.8, 131.1, 129.7(2C), 126.1(2C), 124.3, 123.6, 100.4, 99.7, 56.5, 56.2, 44.7, 30.0, 21.6, 20.9, 17.6, 14.8; MS: *m*/*z* (%) 429 (M^+, 20), 275 (20), 274 (100), 232 (32), 231 (42), 218 (16), 217 (41), 216 (68), 202 (21), 91 (20).

4.1.7.4. 4-[3-Benzyl-5,6-dimethoxy-1-(4-methylphenylsulfonyl)-1*H*-2-indolyl]-2-butanone (9d). Compound **9d** was obtained similarly to compounds **9c**. Yield 1.61 g, 67% as a white solid, mp 135–136 °C [Found: C, 68.65; H, 6.12; N, 2.96. $C_{28}H_{29}NO_5S$ requires C, 68.41; H, 5.95; N, 2.85%]; ν_{max}(KBr) 1717, 1489, 1459, 1351, 1286, 1212, 1175, 1147, 1087, 1021, 895, 853, 736, 689, 655 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.81 (1H, s, H_{Ind}), 7.49 (2H, d, *J* 8.3 Hz, H_{Ts}), 7.16–7.14 (5H, m, Ph+H_{Ts}), 6.95–6.92 (2H, m, Ph), 6.63 (1H, s, H_{Ind}), 3.97 (3H, s, O*Me*), 3.95 (2H, s, CH_2Ph), 3.77 (3H, s, O*Me*), 3.18–3.13 (2H, m, CH_2), 2.80–2.75 (2H, m, CH_2), 2.36 (3H, s, *Me*), 2.09 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 207.7, 147.8, 147.4, 144.7, 139.5, 135.7, 135.3, 131.3, 129.8(2C), 128.4(2C), 128.0(2C), 126.2(2C), 126.1, 124.2, 121.3, 100.8, 99.8, 56.5, 56.1, 44.1, 30.0, 21.6, 21.1; MS: *m*/*z* (%) 491 (M^+, 63), 336 (100), 279 (18), 278 (15), 190 (16), 91(39).

4.1.7.5. 4-[8-Methyl-6-(4-methylphenylsulfonyl)-2,3-dihydro-6*H*-[1,4]dioxino[2,3-*f*]indol-7-yl]-2-butanone (9e). Yield 0.70 g, 85% as colorless cubes, mp 122–123 °C [Found: C, 64.20; H, 5.77; N, 3.28. $C_{22}H_{23}NO_5S$ requires C, 63.91; H, 5.61; N, 3.39%]; ν_{max}(KBr) 1720, 1579, 1477, 1353, 1168, 1145, 1113, 1067, 916, 885, 810, 670, 647, 574 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.72 (1H, s, H_{Ind}), 7.54 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.16 (2H, d, *J* 8.2 Hz, H_{Ts}), 6.78 (1H, s, H_{Ind}), 4.29–4.25 (4H, m, CH_2CH_2), 3.17–3.11 (2H, m, CH_2), 2.91–2.85 (2H, m, CH_2), 2.33 (3H, s, *Me*), 2.15 (3H, s, *Me*), 2.05 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 208.0, 144.5, 141.8, 141.4, 135.5, 134.8, 131.3, 129.7(2C), 126.3(2C), 125.9, 117.5, 105.6, 104.2, 64.5, 64.3, 43.9, 30.0, 21.6, 20.9, 9.1; MS: *m*/*z* (%) 413 (M^+, 15), 259 (34), 258 (100), 216 (76), 215 (69), 202 (50), 201 (20), 159 (30), 145 (20), 101 (18), 91 (29).

4.1.7.6. 4-[5,6-Dimethoxy-1-(4-methylphenylsulfonyl)-3-phenyl-1*H*-2-indolyl]-2-butanone (9f). Yield 0.76 g, 80% as colorless needles, mp 175–176 °C [Found: C, 68.14; H, 5.81; N, 2.80. $C_{27}H_{27}NO_5S$ requires C, 67.90; H, 5.70; N, 2.93%]; ν_{max}(KBr) 1715, 1488, 1469, 1439, 1362, 1309, 1232, 1183, 1156, 1088, 1021, 946, 850, 816, 769, 708, 690, 663, 603 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.86 (1H, s, H_{Ind}), 7.59 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.50–7.38 (3H, m, Ph), 7.29–7.25 (2H, m, Ph), 7.19 (2H, d, *J* 8.2 Hz, H_{Ts}), 6.72 (1H, s, H_{Ind}), 4.02 (3H, s, O*Me*), 3.81 (3H, s, O*Me*), 3.23–3.14 (2H, m, CH_2), 2.98–2.89 (2H, m, CH_2), 2.36 (3H, s, *Me*), 2.13 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 207.4, 147.9, 147.4, 144.8, 135.3, 134.8, 132.9, 130.8, 129.8(2C), 129.6(2C), 128.8(2C), 127.6, 126.1(2C), 124.7, 123.5, 100.8, 99.3, 56.4, 56.0, 44.8, 29.7, 21.5, 21.4; MS: *m*/*z* (%) 477 (M^+, 33), 323 (28), 322 (60), 280 (25), 279 (21), 276 (31), 266 (21), 265 (36), 264 (77), 234 (39), 232 (16), 219 (25), 218 (100), 217 (24), 204 (19), 91 (26).

4.1.7.7. 4-[5,6-Dimethoxy-3-(4-methylphenyl)-1-(4-methylphenylsulfonyl)-1*H*-2-indolyl]-2-butanone (9g). Yield 0.82 g, 84% as a white solid, mp 154–155 °C [Found: C, 68.67; H, 6.13; N, 2.96. $C_{28}H_{29}NO_5S$ requires C, 68.41; H, 5.95; N, 2.85%]; ν_{max}(KBr) 1714, 1490, 1465, 1444, 1365, 1295, 1230, 1216, 1181, 1156, 1088, 1034, 1017, 850, 774, 663, 632, 576, 544 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.83 (1H, s, H_{Ind}), 7.58 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.25 (2H, d, *J* 7.8 Hz, H_{Ar}), 7.18 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.14 (2H, d, *J* 7.8 Hz, H_{Ar}), 6.71 (s, 1H, H_{Ind}), 4.01 (3H, s, O*Me*), 3.80 (3H, s, O*Me*), 3.20–3.12 (2H, m, CH_2), 2.94–2.86 (2H, m, CH_2), 2.41 (3H, s, *Me*), 2.32 (3H, s, *Me*), 2.12 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 207.4, 147.8, 147.4, 144.8, 137.4, 135.3, 134.7, 130.7, 129.8(2C), 129.7(2C), 129.5(2C), 129.4, 126.1(2C), 124.7, 123.7, 100.9, 99.3, 56.4, 56.0, 44.8, 29.7, 21.5, 21.4, 21.2; MS: *m*/*z* (%) 491 (M^+, 27), 337 (21), 336 (73), 294 (31), 293 (22), 280 (25), 279 (52), 278 (100), 264 (22), 234 (23), 218 (41), 91 (43).

4.1.7.8. 4-[3-(4-Chlorophenyl)-5,6-dimethoxy-1-(4-methylphenylsulfonyl)-1*H*-2-indolyl]-2-butanone (9h). Yield 0.83 g, 81% as a white solid, mp 123–124 °C [Found: C, 63.53; H, 5.22; N, 2.99. $C_{27}H_{26}ClNO_5S$ requires C, 63.34; H, 5.12; N, 2.74%]; ν_{max}(KBr) 1711, 1489, 1441, 1363, 1288, 1267, 1219, 1185, 1157, 1089, 1039, 1015, 852, 837, 678, 657, 613, 572, 548 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.83 (1H, s, H_{Ind}), 7.58 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.42 (2H, d, *J* 8.0 Hz, H_{Ar}), 7.20 (2H, d, *J* 8.0 Hz, H_{Ar}), 7.18 (2H, d, *J* 8.2 Hz, H_{Ts}), 6.66 (1H, s, H_{Ind}), 4.01 (3H, s, O*Me*), 3.80 (3H, s, O*Me*), 3.19–3.10 (2H, m, CH_2), 2.94–2.85 (2H, m, CH_2), 2.36 (3H, s, *Me*), 2.13 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 207.2, 148.1, 147.6, 145.0, 135.3, 135.1, 133.7, 131.5, 131.1(2C), 130.8, 129.9(2C), 129.1(2C), 126.2(2C), 123.6, 123.3, 100.6, 99.4, 56.5, 56.1, 44.7, 29.8, 21.6, 21.4; MS: *m*/*z* (%) 513/511 (M^+, 25/58), 358 (24), 357 (100), 356 (71), 314 (27), 313 (27), 301 (21), 300 (75), 299 (42), 298 (59), 265 (25), 221 (16), 220 (24), 91 (77).

4.1.7.9. 4-[6-(4-Methylphenylsulfonyl)-8-phenyl-2,3-dihydro-6*H*-[1,4]dioxino[2,3-*f*]indol-7-yl]-2-butanone (9i). Yield 0.67 g, 71% as a white solid, mp 186–188 °C [Found: C, 68.32; H, 5.48; N, 3.27. $C_{27}H_{25}NO_5S$ requires C, 68.19; H, 5.30; N, 2.95%]; ν_{max}(KBr) 1712, 1471, 1358, 1332, 1156, 1084, 1064, 1035, 1016, 938, 844, 703, 681, 660, 588, 548 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.79 (1H, s, H_{Ind}), 7.62 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.44–7.34 (3H, m, Ph), 7.25–7.23 (2H, m, Ph), 7.20 (2H, d, *J* 8.2 Hz, H_{Ts}),

6.75 (1H, s, H_{Ind}), 4.29–4.27 (2H, m, CH_2), 4.25–4.23 (2H, m, CH_2), 3.21–3.16 (2H, m, CH_2), 2.92–2.87 (2H, m, CH_2), 2.36 (3H, s, *Me*), 2.11 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 207.4, 144.8, 142.2, 141.7, 135.6, 135.4, 132.8, 131.4, 129.9(2C), 129.7(2C), 128.8(2C), 127.7, 126.4(2C), 124.9, 124.3, 106.5, 104.2, 64.5, 64.3, 44.8, 29.8, 21.6, 21.5; MS: *m/z* (%) 475 (M^+, 19), 321 (100), 320 (80), 278 (71), 277 (21), 276 (21), 264 (80), 262 (64), 91 (24).

4.1.7.10. 4-[1-(4-Methylphenylsulfonyl)-3-phenyl-1*H*-2-indolyl]-2-butanone (9j). Yield 0.68 g, 82% as colorless cubes, mp 119–120 °C [Found: C, 72.31; H, 5.70; N, 3.49. $C_{25}H_{23}NO_3S$ requires C, 71.92; H, 5.55; N, 3.35%]; ν_{max}(KBr) 1713, 1449, 1408, 1363, 1272, 1233, 1215, 1172, 1091, 1040, 1022, 778, 740, 707, 659, 575, 546 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.26–8.22 (1H, m, H_{Ind}), 7.63 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.49–7.24 (8H, m, H_{Ind}+Ph), 7.18 (2H, d, *J* 8.2 Hz, H_{Ts}), 3.30–3.21 (2H, m, CH_2), 2.99–2.90 (2H, m, CH_2), 2.32 (3H, s, *Me*), 2.13 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 207.2, 144.9, 136.6, 136.3, 135.5, 132.6, 130.5, 129.8(2C), 129.7(2C), 128.7(2C), 127.7, 126.3(2C), 124.7, 124.4, 123.9, 119.5, 115.2, 44.7, 29.7, 21.5, 21.3; MS: *m/z* (%) 417 (M^+, 26), 263 (33), 262 (82), 221 (25), 220 (84), 219 (44), 218 (79), 217 (48), 206 (17), 205 (61), 204 (100), 91 (46).

4.1.7.11. 4-[3-(4-Bromophenyl)-1-(4-methylphenylsulfonyl)-1*H*-2-indolyl]-2-butanone (9k). Yield 0.80 g, 81% as a white solid, mp 119–120 °C [Found: C, 60.75; H, 4.66; N, 2.94. $C_{25}H_{22}BrNO_3S$ requires C, 60.49; H, 4.47; N, 2.82%]; ν_{max}(KBr) 1713, 1486, 1453, 1409, 1363, 1238, 1172, 1090, 1067, 1039, 1008, 748, 706, 665, 577, 547 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.30–6.97 (12H, m, H_{Ar}+H_{Ind}+H_{Ts}), 3.37–3.07 (2H, m, CH_2), 2.92–2.60 (2H, m, CH_2), 2.22 (3H, s, *Me*), 2.00 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 207.0, 145.0, 136.6, 136.5, 135.4, 131.9(2C), 131.7, 131.4(2C), 130.1, 129.9(2C), 126.3(2C), 124.9, 124.0, 123.1, 121.8, 119.2, 115.2, 44.6, 29.8, 21.6, 21.2; MS: *m/z* (%) 497/495 (M^+, 15/14), 342/340 (60/61), 300 (42), 298 (53), 284 (68), 282 (76), 219 (35), 218 (100), 217 (89), 216 (18), 205 (34), 204 (59), 203 (20), 91 (73).

4.1.7.12. 4-[5-Chloro-1-(4-methylphenylsulfonyl)-3-phenyl-1*H*-2-indolyl]-2-butanone (9l). Yield 0.60 g, 66% as a white solid, mp 175–176 °C [Found: C, 66.73; H, 5.09; N, 3.26. $C_{25}H_{22}ClNO_3S$ requires C, 66.44; H, 4.91; N, 3.10%]; ν_{max}(KBr) 1712, 1492, 1446, 1415, 1360, 1303, 1286, 1236, 1166, 1130, 1090, 1070, 1045, 1022, 808, 780, 708, 674, 585, 537 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.18 (1H, d, *J* 9.5 Hz, H_{Ar}), 7.62 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.48–7.39 (3H, m, H_{Ar}), 7.29–7.23 (4H, m, H_{Ar}), 7.22 (2H, d, *J* 8.2 Hz, H_{Ts}), 3.25–3.20 (2H, m, CH_2), 2.94–2.89 (2H, m, CH_2), 2.37 (3H, s, *Me*), 2.13 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 206.9, 145.2, 137.8, 135.2, 135.0, 132.0, 131.8, 130.0(2C), 129.8, 129.7(2C), 128.9(2C), 128.0, 126.3(2C), 124.8, 123.7, 119.1, 116.2, 44.5, 29.7, 21.6, 21.3; MS: *m/z* (%) 453/451 (M^+, 6/15), 298 (34), 297 (25), 296 (78), 256 (22), 255 (18), 254 (69), 253 (20), 252 (18), 240 (49), 239 (26), 238 (100), 219 (24), 218 (66), 217 (66), 204 (31), 91 (61).

4.1.7.13. 1-[5,6-Dimethoxy-1-(4-methylphenylsulfonyl)-3-phenyl-1*H*-2-indolyl]-3-pentanone (9m). Yield 0.71 g, 72% as colorless cubes, mp 149–150 °C [Found: C, 68.63; H, 6.11; N, 2.98. $C_{28}H_{29}NO_5S$ requires C, 68.41; H, 5.95; N, 2.85%]; ν_{max}(KBr) 1714, 1491, 1465, 1441, 1415, 1360, 1309, 1285, 1225, 1186, 1163, 1114, 1088, 1046, 1026, 951, 841, 820, 767, 705, 687, 656, 603, 566, 545 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.85 (1H, s, H_{Ind}), 7.59 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.49–7.36 (3H, m, Ph), 7.29–7.25 (2H, m, Ph), 7.19 (2H, d, *J* 8.2 Hz, H_{Ts}), 6.72 (1H, s, H_{Ind}), 4.02 (3H, s, O*Me*), 3.80 (3H, s, O*Me*), 3.22–3.13 (2H, m, CH_2), 2.93–2.84 (2H, m, CH_2), 2.42 (2H, q, *J* 7.2 Hz, CH_2Me), 2.35 (3H, s, *Me*), 1.05 (3H, t, *J* 7.2 Hz, CH_2*Me*); δ_C (50 MHz, $CDCl_3$) 210.0, 147.8, 147.3, 144.7, 135.2, 135.0, 132.8, 130.7, 129.7(2C), 129.5(2C), 128.7(2C), 127.6, 126.1(2C), 124.6, 123.4, 100.7, 99.2, 56.3, 55.9, 43.4, 35.6, 21.4(2C), 7.7; MS: *m/z* (%) 491 (M^+, 14), 336 (100), 280 (22), 279 (97), 266 (30), 265 (17), 264 (66), 234 (20), 220 (20), 139 (15), 91 (54).

4.1.7.14. 1-[5,6-Dimethoxy-1-(4-methylphenylsulfonyl)-3-phenyl-1*H*-2-indolyl]-4,4-dimethyl-3-pentanone (9n). Yield 0.82 g, 79% as a white solid, mp 135 °C [Found: C, 69.50; H, 6.67; N, 2.89. $C_{30}H_{33}NO_5S$ requires C, 69.34; H, 6.40; N, 2.70%]; ν_{max}(KBr) 1702, 1491, 1363, 1179, 1160, 1088, 1048, 1026, 953, 851, 706, 687, 656, 606, 573, 547 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.87 (1H, s, H_{Ind}), 7.59 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.47–7.34 (3H, m, Ph), 7.28–7.25 (2H, m, Ph), 7.18 (2H, d, *J* 8.2 Hz, H_{Ts}), 6.73 (1H, s, H_{Ind}), 4.01 (3H, s, O*Me*), 3.80 (3H, s, O*Me*), 3.16–3.07 (2H, m, CH_2), 3.00–2.92 (2H, m, CH_2), 2.35 (3H, s, *Me*), 1.13 (9H, s, *t-Bu*); δ_C (50 MHz, $CDCl_3$) 214.6, 148.0, 147.6, 144.8, 135.6, 133.1, 130.9, 129.8, 129.7(4C), 128.8(2C), 127.6, 126.2(2C), 124.5, 123.7, 101.0, 99.5, 56.5, 56.2, 44.0, 38.2, 26.4(3C), 21.9, 21.6; MS: *m/z* (%) 519 (M^+, 27), 366 (43), 365 (100), 280 (41), 265 (36), 264 (27).

4.1.7.15. 3-[5,6-Dimethoxy-1-(4-methylphenylsulfonyl)-3-phenyl-1*H*-2-indolyl]-1-(4-methylphenyl)-1-propanone (9p). $HClO_4$ (70%, 16.3 mL) was added dropwise to a solution of compound **8p** (0.50 g, 0.9 mmol) in AcOH (40 mL) under cooling with water. The resultant reaction mixture was left for five days at room temperature until completion of the reaction (TLC monitoring), then poured into water, neutralized with $NaHCO_3$, and extracted with CH_2Cl_2 (3×50 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified on silica gel (50–160 μm) column with AcOEt–hexane (1:5) as an eluent. The solvent was removed in rotatory evaporator and residue was recrystallized from CH_2Cl_2–hexane. Yield 0.30 g, 60% as a white solid, mp 187 °C [Found: C, 71.70; H, 5.99; N, 2.75. $C_{33}H_{31}NO_5S$ requires C, 71.59; H, 5.64; N, 2.53%]; ν_{max}(KBr) 1676, 1488, 1049, 1029, 955, 856, 703, 683, 659, 605, 566, 550 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.90 (1H, s, H_{Ind}), 7.83 (2H, d, *J* 7.9 Hz, H_{Ar}), 7.62 (2H, d, *J* 8.0 Hz, H_{Ts}), 7.46–7.18 (9H, m, H_{Ar}+H_{Ts}), 6.76 (1H, s, H_{Ind}), 4.02 (3H, s, O*Me*), 3.81 (3H, s, O*Me*), 3.43–3.34 (4H, m, CH_2CH_2), 2.40 (3H, s, *Me*), 2.34 (3H, s, *Me*); δ_C (75 MHz, $CDCl_3$) 198.4, 147.9, 147.5, 144.9, 143.8, 135.4, 135.3, 134.2, 133.0, 130.9, 129.8(2C), 129.7(2C), 129.2(2C), 128.9(2C), 128.2(2C), 127.7, 126.3(2C), 124.8, 123.6, 100.9, 99.4, 56.5, 56.1, 40.2, 22.1, 21.7, 21.6; MS: *m/z* (%) 553 (M^+, 7), 399 (15), 398 (17), 264 (18), 220 (16), 155 (14), 139 (16), 120 (23), 119 (91), 91 (100).

4.1.7.16. 4-(5,6-Dimethoxy-1-methylsulfonyl-3-phenyl-1*H*-2-indolyl)-2-butanone (9q). Compound **9q** was obtained similarly to compounds **9a**,**b**,**e**–**n**. Yield 0.67 g, 84% as a white solid, mp 126–127 °C [Found: C, 62.65; H, 5.80; N, 3.60. $C_{21}H_{23}NO_5S$ requires C, 62.83; H, 5.77; N, 3.49%]; ν_{max}(KBr) 1712, 1490, 1470, 1441, 1357, 1300, 1235, 1216, 1179, 1153, 1025, 765, 705, 555, 520 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.69 (1H, s, H_{Ind}), 7.55–7.36 (5H, m, Ph), 6.83 (1H, s, H_{Ind}), 3.99 (3H, s, O*Me*), 3.85 (3H, s, O*Me*), 3.22–3.14 (2H, m, CH_2), 2.90–2.82 (2H, m, CH_2), 2.30 (3H, s, *Me*), 2.10 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 207.2, 148.3, 147.8, 134.8, 132.9, 130.4, 129.7(2C), 129.0(2C), 127.8, 124.4, 123.5, 101.4, 98.7, 56.5, 56.3, 44.6, 39.7, 29.7, 21.2; MS: *m*/*z* (%) 401 (M^+, 27), 322 (32), 280 (24), 265 (61), 263 (100), 248 (18), 221 (18).

4.1.7.17. 4-(1-Benzoyl-5,6-dimethoxy-3-phenyl-1*H*-2-indolyl)-2-butanone (9r). Hydrochloric acid (18 mL) was added dropwise to a solution of compound **8r** (0.8 g, 1.9 mmol) in AcOH (54 mL) under cooling with water. The resulted reaction mixture was maintained at 30 °C for 1.5 h (TLC monitoring), then poured into water, neutralized with $NaHCO_3$, and extracted with CH_2Cl_2 (3×50 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified on silica gel (50–160 μm) column with acetone–CH_2Cl_2–hexane (5:3:20) as an eluent. The solvent was removed in rotatory evaporator and residue was recrystallized from CH_2Cl_2–hexane. Yield 0.50 g, 63% as a yellow solid, mp 114–115 °C [Found: C, 76.19; H, 6.01; N, 3.40. $C_{27}H_{25}NO_4$ requires C, 75.86; H, 5.89; N, 3.28%]; ν_{max}(KBr) 1715, 1678, 1488, 1442, 1357, 1321, 1289, 1160, 1098, 845, 798, 765, 715, 695 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.82–7.79 (2H, m, Ph), 7.68–7.63 (1H, m, Ph), 7.57–7.40 (7H, m, Ph), 6.87 (1H, s, H_{Ind}), 6.35 (1H, s, H_{Ind}), 3.82 (3H, s, O*Me*), 3.53 (3H, s, O*Me*), 3.21–3.16 (2H, m, CH_2), 2.72–2.67 (2H, m, CH_2), 2.00 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 207.2, 169.8, 146.9, 146.7, 135.6, 135.2, 133.6, 133.1, 130.6, 129.8(4C), 129.0(2C), 128.9(2C), 127.5, 122.7, 122.5, 100.9, 98.7, 56.3, 55.8, 44.1, 29.6, 21.2; MS: *m*/*z* (%) 427 (M^+, 37), 306 (27), 106 (17), 105 (100), 77 (51).

4.1.7.18. 1-(5,6-Dimethoxy-3-phenyl-1*H*-2-indolyl)-4,4-dimethyl-3-pentanone (12). A solution of compound **8t** (0.45 g, 1.1 mmol) in EtOH (75 mL) and ethanolic HCl (15 mL) (prepared by saturation of 200 g of ethanol with 100 g of gaseous HCl) was refluxed until the starting compound **8t** was consumed (TLC monitoring). The reaction mixture was poured into water, neutralized with $NaHCO_3$, and extracted with AcOEt (3×150 mL). Combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified on silica gel (50–160 μm) column with AcOEt–hexane (1:3) as an eluent. The solvent was removed in a rotatory evaporator and residue was recrystallized from hexane. Yield 0.77 g, 19% as a white solid, mp 60 °C [Found: C, 75.37; H, 7.53; N, 4.01. $C_{23}H_{27}NO_3$ requires C, 75.59; H, 7.45; N, 3.83%]; ν_{max}(KBr) 3371, 1700, 1483, 1129, 703 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.69 (1H, br s, N*H*), 7.48–7.47 (4H, m, Ph), 7.35–7.31 (1H, m, Ph), 7.09 (1H, s, H_{Ind}), 6.90 (1H, s, H_{Ind}), 3.93 (3H, s, O*Me*), 3.88 (3H, s, O*Me*), 3.09–3.05 (2H, m, CH_2), 2.91–2.87 (2H, m, CH_2), 1.15 (9H, s, *t-Bu*); δ_C (75 MHz, $CDCl_3$) 214.1, 146.9, 145.2, 135.7, 134.0(2C), 129.5(2C), 128.6(2C), 125.9, 120.3, 114.2, 101.2, 94.6, 56.6, 56.3, 44.3, 37.5, 26.6(3C), 20.1; MS: *m*/*z* (%) 365 (M^+, 78), 350 (15), 267 (19), 266 (100).

4.1.8. General procedure for the synthesis of compounds 13f–i,k,l. Compounds **9f–i**,**k**,**l** (2 mmol) were added to a solution of KOH (5.6 g, 100 mmol) in MeOH (23 mL) and the mixture was refluxed for 4 h. After completion of the reaction (TLC monitoring), the mixture was poured into 200 mL of water and the product was extracted with CH_2Cl_2. The organic layer was washed with water (3× 100 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was recrystallized from CH_2Cl_2–hexane.

4.1.8.1. 4-(5,6-Dimethoxy-3-phenyl-1*H*-2-indolyl)-2-butanone (13f). Yield 0.58 g, 90% as a beige solid, mp 103–105 °C [Found: C, 74.52; H, 6.67; N, 4.45. $C_{20}H_{21}NO_3$ requires C, 74.28; H, 6.55; N, 4.33%]; ν_{max}(KBr) 3363, 1713, 1487, 1464, 1133, 848, 757, 708 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 8.64 (1H, br s, N*H*), 7.51–7.43 (4H, m, Ph), 7.36–7.30 (1H, m, Ph), 7.06 (1H, s, H_{Ind}), 6.88 (1H, s, H_{Ind}), 3.92 (3H, s, O*Me*), 3.87 (3H, s, O*Me*), 3.07–3.03 (2H, m, CH_2), 2.88–2.84 (2H, m, CH_2), 2.19 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 210.0, 146.9, 145.2, 135.7, 133.7(2C), 129.5(2C), 128.8(2C), 126.0, 120.3, 114.3, 101.2, 94.6, 56.6, 56.3, 44.2, 30.1, 19.8; MS: *m*/*z* (%) 323 (M^+, 68), 266 (100), 235 (16), 222 (20).

4.1.8.2. 4-[5,6-Dimethoxy-3-(4-methylphenyl)-1*H*-2-indolyl]-2-butanone (13g). Yield 0.58 g, 86% as a yellow solid, mp 130–131 °C [Found: C, 74.63; H, 6.91; N, 4.27. $C_{21}H_{23}NO_3$ requires C, 74.75; H, 6.87; N, 4.15%]; ν_{max}(KBr) 3372, 1708, 1012, 933, 841, 828, 766, 741, 675 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 8.60 (1H, br s, N*H*), 7.34 (2H, d, *J* 8.1 Hz, H_{Ar}), 7.28 (2H, d, *J* 8.1 Hz, H_{Ar}), 7.04 (1H, s, H_{Ind}), 6.88 (1H, s, H_{Ind}), 3.92 (3H, s, O*Me*), 3.86 (3H, s, O*Me*), 3.06–3.02 (2H, m, CH_2), 2.88–2.83 (2H, m, CH_2), 2.43 (3H, s, *Me*), 2.18 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 210.0, 146.9, 145.2, 135.6, 133.5(2C), 132.7, 129.5(2C), 129.4(2C), 120.4, 114.1, 101.2, 94.6, 56.5, 56.3, 44.2, 30.1, 21.3, 19.8; MS: *m*/*z* (%) 337 (M^+, 100), 322 (15), 281 (26), 280 (92), 265 (15), 249 (28), 236 (23), 221 (16).

4.1.8.3. 4-[3-(4-Chlorophenyl)-5,6-dimethoxy-1*H*-2-indolyl]-2-butanone (13h). Yield 0.65 g, 91% as a beige solid, mp 122–123 °C [Found: C, 67.41; H, 5.74; N, 3.99. $C_{20}H_{20}ClNO_3$ requires C, 67.13; H, 5.63; N, 3.91%]; ν_{max}(KBr) 3367, 1705, 1485, 1468, 1333, 1236, 1180, 1159, 1131, 1014, 836, 767 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 8.67 (1H, br s, N*H*), 7.44 (2H, d, *J* 8.4 Hz, H_{Ar}), 7.36 (2H, d, *J* 8.4 Hz, H_{Ar}), 6.99 (1H, s, H_{Ind}), 6.88 (1H, s, H_{Ind}), 3.92 (3H, s, O*Me*), 3.86 (3H, s, O*Me*), 3.04–2.98 (2H, m, CH_2), 2.89–2.83 (2H, m, CH_2), 2.19 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 210.0, 147.0, 145.4, 134.2, 133.8, 131.7, 130.7(2C), 129.4, 128.9(2C), 120.0, 113.1, 100.7, 94.6, 56.5, 56.3, 44.2, 30.1, 19.6; MS: *m*/*z* (%) 359/357 (M^+, 35/100), 302 (24), 301 (18), 300 (72), 266 (17), 265 (44), 221 (22).

4.1.8.4. 4-(8-Phenyl-2,3-dihydro-6*H*-[1,4]dioxino[2,3-*f*]-indol-7-yl)-2-butanone (13i). Yield 0.52 g, 81% as a beige

solid, mp 197–198 °C [Found: C, 74.96; H, 6.12; N, 4.48. $C_{20}H_{19}NO_3$ requires C, 74.75; H, 5.96; N, 4.36%]; ν_{max}(KBr) 3367, 1705, 1468, 1377, 1337, 1167, 1065, 704 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 8.47 (1H, br s, N*H*), 7.49–7.24 (5H, m, Ph), 7.08 (1H, s, H_{Ind}), 6.84 (1H, s, H_{Ind}), 4.30–4.23 (4H, m, CH_2CH_2), 3.08–3.01 (2H, m, CH_2), 2.90–2.83 (2H, m, CH_2), 2.18 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 210.0, 140.8, 139.2, 135.5, 134.8, 130.5, 129.4(2C), 128.6(2C), 125.9, 122.1, 113.7, 105.5, 98.2, 64.7, 64.4, 44.1, 30.1, 19.7; MS: *m*/*z* (%) 321 (M^+, 57), 278 (17), 265 (25), 264 (100), 208 (20), 180 (18).

4.1.8.5. 4-[3-(4-Bromophenyl)-1*H*-2-indolyl]-2-butanone (13k). Yield 0.37 g, 54% as a white solid, mp 138–139 °C [Found: C, 63.40; H, 4.83; N, 4.22. $C_{18}H_{16}BrNO$ requires C, 63.17; H, 4.71; N, 4.09%]; ν_{max}(KBr) 3355, 1707, 1488, 1369, 748, 714 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.82 (1H, br s, N*H*), 7.56 (2H, d, *J* 8.0 Hz, H_{Ar}), 7.57–7.53 (1H, m, H_{Ind}), 7.33 (2H, d, *J* 8.0 Hz, H_{Ar}), 7.36–7.29 (1H, m, H_{Ind}), 7.18–7.14 (1H, m, H_{Ind}), 7.10–7.06 (1H, m, H_{Ind}), 3.06–3.02 (2H, m, CH_2), 2.88–2.84 (2H, m, CH_2), 2.18 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 209.8, 135.3, 135.2, 134.4, 131.8(2C), 131.3(2C), 127.3, 122.1, 120.1, 119.9, 118.7, 113.3, 110.9, 44.0, 30.1, 19.6; MS: *m*/*z* (%) 343/341 (M^+, 47/49), 325/323 (24/24), 310/308 (13/16), 300/298 (22/24), 271 (15), 218 (27), 217 (21), 206 (17), 205 (100), 204 (60), 203 (16).

4.1.8.6. 4-(5-Chloro-3-phenyl-1*H*-2-indolyl)-2-butanone (13l). Yield 0.37 g, 62% as a beige solid, mp 129–131 °C [Found: C, 72.87; H, 5.55; N, 4.57. $C_{18}H_{16}ClNO$ requires C, 72.60; H, 5.42; N, 4.70%]; ν_{max}(KBr) 3389, 1703, 794, 769, 734, 706 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.89 (1H, br s, N*H*), 7.55 (1H, d, *J* 1.5 Hz, H_{Ind}), 7.51–7.30 (5H, m, Ph), 7.25 (1H, d, *J* 6.8 Hz, H_{Ind}), 7.14 (1H, dd, *J* 6.8, 1.5 Hz, H_{Ind}), 3.10–3.06 (2H, m, CH_2), 2.91–2.86 (2H, m, CH_2), 2.21 (3H, s, *Me*); δ_C (50 MHz, $CDCl_3$) 210.2, 136.7(2C), 134.7, 133.6, 129.7(2C), 128.8(2C), 126.4, 125.6, 122.0, 118.4, 114.3, 111.8, 43.9, 30.1, 19.6; MS: *m*/*z* (%) 299/297 (M^+, 29/77), 256 (19), 254 (63), 240 (47), 219 (20), 218 (23), 217 (23), 206 (21), 205 (100), 204 (94), 203 (20).

Acknowledgements

Financial support was provided by Bayer HealthCare AG and the Russian Foundation of Basic Research (Grant 03-03-32759). The authors would like to emphasize their special thanks to Dr. Valery E. Zavodnik for X-ray analysis.

References and notes

1. See the following reviews: (a) Moody, C. J. *Synlett* **1994**, 681–688; (b) Sundberg, R. J. *Indoles*; Academic: London, 1996; (c) Gilchrist, T. L. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2849–2866; (d) Gribble, G. W. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1045–1075; (e) Gilchrist, T. L. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2491–2515.
2. (a) Taga, M.; Ohtsuka, H.; Inoune, I.; Kawaguchi, T.; Nomura, S.; Yamada, K.; Date, T.; Hiramutsu, H.; Sato, Y. *Heterocycles* **1996**, *42*, 251–263; (b) Shin, C.; Yamada, Y.; Hayashi, K.; Yonezawa, Y.; Umemura, K.; Tanji, T.; Yoshimura, J. *Heterocycles* **1996**, *43*, 891–898; (c) Wang, Z.; Jimenez, L. S. *J. Org. Chem.* **1996**, *61*, 816–818; (d) Dong, W.; Jimenez, L. S. *J. Org. Chem.* **1999**, *64*, 2520–2523; (e) Katayama, S.; Ae, N.; Nagata, R. *J. Org. Chem.* **2001**, *66*, 3474–3483.
3. (a) Cushing, T. D.; Sanz-Cervera, J. F.; Williams, R. M. *J. Am. Chem. Soc.* **1996**, *118*, 557–579; (b) Kozmin, S. A.; Rawal, V. H. *J. Am. Chem. Soc.* **1998**, *120*, 13523–13524; (c) Alvarez, M.; Bros, M. A.; Joule, J. A. *Tetrahedron Lett.* **1998**, *39*, 679–680; (d) Wong, A.; Kuethe, J. T.; Davies, I. W.; Hughes, D. L. *J. Org. Chem.* **2004**, *69*, 7761–7764.
4. (a) Iwama, T.; Birman, V. B.; Kozmin, S. A.; Rawal, V. H. *Org. Lett.* **1999**, *1*, 673–676; (b) Suzuki, H.; Gyoutoku, H.; Yokoo, H.; Shibna, M.; Sato, Y.; Yamada, H.; Murakami, Y. *Synlett* **2000**, 1196–1198; (c) Rutherford, J. L.; Rainka, M. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 15168–15169; (d) Banwell, M. G.; Kelly, B. D.; Kokas, O. J.; Lupton, D. W. *Org. Lett.* **2003**, *5*, 2497–2500; (e) Gallou, F.; Yee, N.; Qiu, F.; Senanayake, C.; Linz, G.; Schnaubelt, J.; Soyka, R. *Synlett* **2004**, 883–885.
5. (a) Ochi, M.; Kataoka, K.; Ariki, S.; Iwatsuki, C.; Kodama, M.; Fukuyama, Y. *J. Nat. Prod.* **1998**, *61*, 1043–1045; (b) Hume, W. E.; Tokunaga, T.; Nagata, R. *Tetrahedron* **2002**, *58*, 3605–3611; (c) Faul, M. M.; Grutsch, J. L.; Kobierski, M. E.; Kopach, M. E.; Krumrich, C. A.; Staszak, M. A.; Udodong, U.; Vicenzi, J. T.; Sullivan, K. A. *Tetrahedron* **2003**, *59*, 7215–7229; (d) Fetter, J.; Bertha, F.; Poszavacz, L.; Simig, G. *J. Heterocycl. Chem.* **2005**, *42*, 137–139.
6. (a) Tsuji, Y.; Kotachi, S.; Huh, K.-T.; Watanabe, Y. *J. Org. Chem.* **1990**, *55*, 580–584; (b) Webb, R. R.; Venuti, M. C.; Eigenbrot, C. *J. Org. Chem.* **1991**, *56*, 4706–4713; (c) Aoyagi, Y.; Mizusaki, T.; Ohta, A. *Tetrahedron Lett.* **1996**, *37*, 9203–9206; (d) Fujita, K.-I.; Yamomoto, K.; Yamaguchi, R. *Org. Lett.* **2002**, *4*, 2691–2694.
7. (a) Danishefsky, S. J.; Phillips, G. B. *Tetrahedron Lett.* **1984**, *25*, 3159–3162; (b) Maehr, H.; Smallheer, J. *J. Am. Chem. Soc.* **1985**, *107*, 2943–2945; (c) Ziegler, F. E.; Berlin, M. Y. *Tetrahedron Lett.* **1998**, *39*, 2455–2458; (d) Banfield, S. C.; England, D. B.; Kerr, M. A. *Org. Lett.* **2001**, *3*, 3325–3327; (e) Zawada, P. V.; Banfield, S. C.; Kerr, M. A. *Synlett* **2003**, 971–974.
8. (a) Makoza, M.; Stalewski, J. *Tetrahedron* **1995**, *51*, 7263–7276; (b) Makoza, M.; Stalewski, J.; Maslennikova, O. S. *Synthesis* **1997**, 1131–1133; (c) Belley, M.; Scheigetz, J.; Dube, P.; Dolman, S. *Synlett* **2001**, 222–225; (d) Walkington, A.; Gray, M.; Hossner, F.; Kitteringham, J.; Voyle, M. *Synth. Commun.* **2003**, *33*, 2229–2233.
9. Samizu, K.; Ogasawara, K. *Synlett* **1994**, 499–500.
10. Sakagami, H.; Ogasawara, K. *Heterocycles* **1999**, *51*, 1131–1135.
11. Alper, P. B.; Nguyen, K. T. *J. Org. Chem.* **2003**, *68*, 2051–2053.
12. Cnilin, A.; Rodighiero, P.; Guiotto, A. *Synthesis* **1998**, 309–312.
13. See the following reviews: (a) Dean, F. M. *Adv. Heterocycl. Chem.* **1982**, *30*, 167–238; (b) Dean, F. M. *Adv. Heterocycl. Chem.* **1982**, *31*, 237–344; (c) Piancatelli, G.; D'Auria, M.; D'Onofrio, F. *Synthesis* **1994**, 867–889.
14. (a) Abaev, V. T.; Gutnov, A. V.; Butin, A. V. *Khim. Geterotsikl. Soedin* **1998**, 603–607; (b) Abaev, V. T.; Osipova, A. A.; Butin, A. V. *Khim. Geterotsikl. Soedin.* **2001**, 849–850; (c) Gutnov, A. V.; Abaev, V. T.; Butin, A. V.; Dmitriev, A. S. *J. Org. Chem.* **2001**, *66*, 8685–8686; (d) Butin, A. V.;

Abaev, V. T.; Mel'chin, V. V.; Dmitriev, A. S. *Tetrahedron Lett.* **2005**, *46*, 8439–8441; See the following review: (e) Butin, A. V.; Abaev, V. T. *Izv. Akad. Nauk, Ser. Khim.* **2001**, 1436–1443.
15. Butin, A. V.; Stroganova, T. A.; Lodina, I. V.; Krapivin, G. D. *Tetrahedron Lett.* **2001**, *42*, 2031–2033.
16. (a) Ziegler, F. E.; Spitzner, E. B.; Wilkins, C. K. *J. Org. Chem.* **1971**, *36*, 1759–1764; (b) Vedachalam, M.; Mohan, B.; Srinivasan, P. C. *Tetrahedron Lett.* **1983**, *24*, 3531–3532; (c) Sadanandan, E. V.; Vedachalam, M.; Srinivasan, P. C. *Indian J. Chem., Sect. B* **1993**, *32B*, 481–483; (d) Lee, J.; Ha, J. D.; Cha, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 8127–8128.
17. (a) Garnick, R. L.; Levery, S. B.; Le Quesne, P. W. *J. Org. Chem.* **1978**, *43*, 1226–1229; (b) Iqbal, Z.; Jackson, A. H.; Rao, K. R. N. *Tetrahedron Lett.* **1988**, *29*, 2577–2580; (c) Dujardin, G.; Poirier, J.-M. *Bull. Soc. Franc* **1994**, *131*, 900–909; (d) Srivastava, N.; Banik, B. K. *J. Org. Chem.* **2003**, *68*, 2109–2114; (e) Bartoli, G.; Bartolacci, M.; Bosco, M.; Foglia, G.; Giuliani, A.; Marcantoni, E.; Sambri, L.; Torregiani, E. *J. Org. Chem.* **2003**, *68*, 4594–4597; (f) Arcadi, A.; Bianchi, G.; Chiarini, M.; D'Annibale, G.; Marinelli, F. *Synlett* **2004**, 944–950.
18. Cavdar, H.; Saracoglu, N. *Tetrahedron* **2005**, *61*, 2401–2405.
19. (a) Kul'nevich, V. G.; Zhuravlev, S. V. *Khim. Geterotsikl. Soedin* **1984**, 307–308; (b) Gutnov, A. V.; Butin, A. V.; Abaev, V. T.; Krapivin, G. D.; Zavodnik, V. E. *Molecules* **1999**, *4*, 204–218; See the following review: (c) Butin, A. V.; Stroganova, T. A.; Kul'nevich, V. G. *Khim. Geterotsikl. Soedin* **1999**, 867–901.
20. As a typical procedure, see: (a) Kamath, H. V.; Dhekne, V. V.; Kulkarni, S. N. *Indian J. Chem., Sect. B* **1982**, *21B*, 911–913.
21. *Org. Synth.* **1952**, *32*, 8–13.
22. Davis, R. B.; Pizzini, L. C. *J. Org. Chem.* **1960**, *25*, 1884–1888.
23. Ono, A.; Suzuki, N.; Kamimura, J. *Synthesis* **1987**, 736–738.
24. Crystal data of compound **9j**: $C_{18}H_{14}O_2$, monoclinic, space group $P2(1)/c$; a=9.312(2) Å, b=12.490(2) Å, c=18.634(4) Å, α=90°, β=95.60(3)°, γ=90°, V=2156.9(7) Å^3, Z=4, D_{calcd}=1.286 Mg/m^3, $F(000)$=880; 1958 reflections collected, 1839 unique (R_{int}=0.0225); final R indices (1839 observed collections $I>2\sigma I$): R_1=0.0299, wR_2=0.0800; final R indices (all data): R_1=0.0299, wR_2=0.0800. Crystallographic data (excluding structure factors) for the structure in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 601089. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk]. Each request should be accompanied by the complete citation of this paper.
25. Butin, A. V.; Smirnov, S. K.; Stroganova, T. A. *J. Heterocycl. Chem.* **2006**, *43*, 623–628.
26. (a) Itoh, T.; Yokoya, M.; Miyauchi, K.; Nagata, K.; Ohsawa, A. *Org. Lett.* **2003**, *5*, 4301–4304; (b) Haskins, C. M.; Knight, D. W. *Tetrahedron Lett.* **2004**, *45*, 599–601; (c) Strekowski, L.; Aken, K. V.; Gulevich, Y. *J. Heterocycl. Chem.* **2000**, *37*, 1495–1499; (d) Fresneda, P. M.; Molina, P.; Bleda, J. A. *Tetrahedron* **2001**, *57*, 2355–2363; (e) Tanaka, K.; Katsumura, S. *J. Am. Chem. Soc.* **2002**, *124*, 9660–9661; (f) McClenaghan, N. D.; Passalacqua, R.; Loiseau, F.; Campagna, S.; Verheyde, B.; Hameurlaine, A.; Dehaen, W. *J. Am. Chem. Soc.* **2003**, *125*, 5356–5365.
27. (a) Cheng, K.-F.; Wong, T.-T.; Wong, W.-T.; Lai, T.-F. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2487–2496; (b) Phisalaphong, C.; Takayama, H.; Sakai, S.-I. *Tetrahedron Lett.* **1993**, *34*, 4035–4038.