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Furan Ring-Opening/Indole Ring-Closure: Pictet–Spengler-Like Reaction of 2-(*o*-Aminophenyl)furans with Aldehydes

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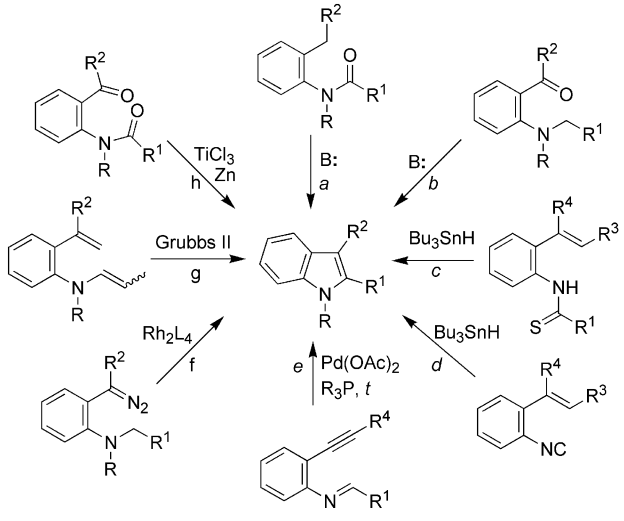
A new simple approach to 3-(2-acylvinyl)-2-(hetero)arylindoles has been developed. The method is based on the acid-catalysed interaction of 2-(2-aminophenyl)furans with (hetero)aromatic aldehydes. The reactions proceed under very mild conditions and lead to indoles containing a reactive α,β-unsaturated ketone moiety, which is suitable for further transformations, in moderate to good yields.

Introduction

For many years indoles have attracted unremitting attention due to the broad range of their biological activity.[1] The numerous methods for indole synthesis have been discussed in multiple publications and summarized in a number of books and reviews.[2] However, the preparation of 2,3-disubstituted indoles is a challenge to organic chemists, at least those indoles with substituents at the 2- and/or 3-positions that have reactive functional groups suitable for further transformations. The synthesis of indoles by the formation of the C2–C3 bond is a promising approach to the solution of this problem. The first of these syntheses was realized in 1886 when indole was obtained by the distillation of *N*-acetyl-*o*-toluidine in the presence of zinc dust.[3] This method is not preparative, however; Madelung later demonstrated that the same transformation can be realized by heating *o*-alkylanilides with a base at 400 °C.[4] For a long time the Madelung reaction (path a in Scheme 1) was the main route to the indole unit by C2–C3 bond formation in spite of the incompatibility of many functional groups to strong basic conditions.[5] An analogous cyclization reaction proceeded when a benzylic carbanion was generated in the *ortho* position to an imine or isocyanide group.[6] Deprotonation of *N*-alkylanilines bearing an *ortho* substituent with an electrophilic α-carbon atom (Scheme 1, path b) leads to indoles by a similar mechanism.[7] Other methods for the synthesis of indoles by C2–C3 bond formation include the radical cyclization of *N*-(*o*-vinylaryl)-thioamides (path c)[8] or aryl isocyanides (path d),[9] transition-metal-catalysed interaction of a double or triple bond with *ortho*-isocyanide or imine groups (path e),[10] intramolecular carbene insertion into the C–H bond of *N*-alkylanilines (path f),[11] ring-closing metathesis (path g)[12] and the McMurry reaction (path h)[13] among others.[14]



Scheme 1.

However, a few reports describing the acid-catalysed C2–C3 bond formation of indoles have been published.[15] The electrophilic N=C$^+$ or N–C$^+$ moieties are usually the key intermediates in these reactions.

Similarly, the Pictet–Spengler reaction and related processes proceed through the formation of iminium ions. This stimulated us to design a new approach to 2-arylindoles bearing a 2-acylvinyl substituent at the C3 atom based on the recyclization of 2-(2-aminophenyl)furans[15f] under

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Pictet–Spengler-like conditions. These compounds are interesting both in themselves and as precursors to other indoles (in the first place, by the modification of the α,β-unsaturated ketone moiety) with a broad range of biological activity. Herein we describe this new method of indole generation by C2–C3 bond formation. In contrast, the formation of the N–C2 bond is a key step in the previous furan-to-indole recyclizations.[16]

Results and Discussion

We first screened the reaction conditions for the model reaction between 2-(5-methylfuran-2-yl)aniline (**1a**) and benzaldehyde (**2a**). We found that the target indole **3a** was formed by heating at reflux a benzene solution of the starting compounds with weak Brønsted acids such as Amberlyst-15 or CCl_3CO_2H. However, the yield of **3a** was low under these conditions. Thus, we tried to use acidic systems that had been found to be effective in other furan recyclizations: $HClO_4$ in dioxane,[16e] HCl(g) in EtOH,[16f] aq. HCl/AcOH[16h] and $TsOH/C_6H_6$.[17] Indeed, we obtained indole **3a** in yields of 70–80% by using these acid catalysts. The product structure was unambiguously proven by X-ray analysis (Figure 1).[18]

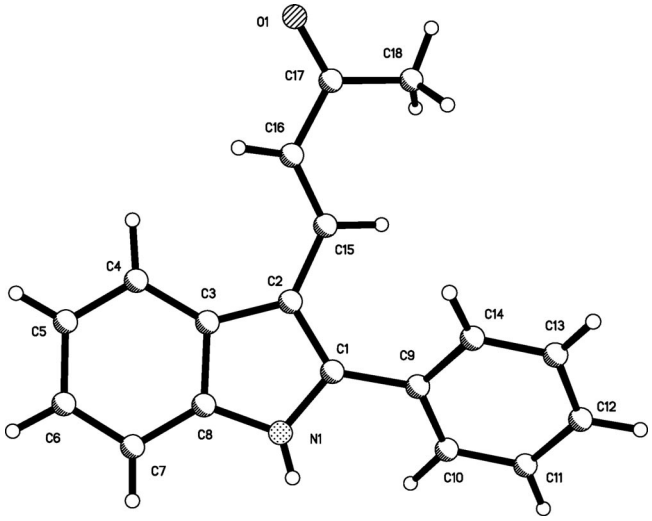
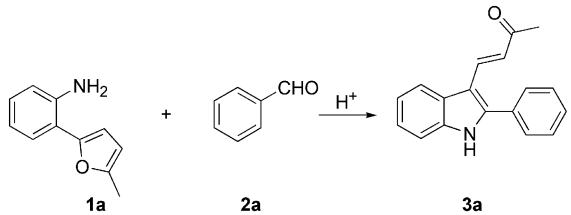


Figure 1. Single-crystal X-ray structure of **3a**.

The systems HCl(g)/EtOH and aq. HCl/AcOH were found to be effective both under reflux and at room temperature. The full conversion of the starting furan was found to proceed after only 1–3 min at reflux. An increase in the reaction time led to a decrease in the yield due to the formation of a tar. In contrast, at room temperature the reaction proceeded to completion after 18–24 h. Heating at 30–35 °C can be considered a good compromise between these two limits as a similar yield can be obtained after 1.5 h. A good yield was also obtained when the reaction was performed with anhydrous *p*-TsOH in C_6H_6. The use of $TsOH·H_2O$ led, however, to a complex mixture of products. The results of the experiments performed to optimize the reaction conditions are summarized in Table 1.

Table 1. Optimization of the reaction conditions for the model reaction of the Pictet–Spengler-like indole synthesis by the interaction of **1a** with **2a**.



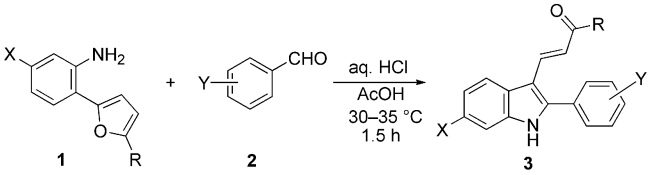
1a **2a** **3a**

Entry	Solvent	Acid	*T* [°C]	Time	Yield [%][a]
1	C_6H_6	Amberlyst-15	reflux	24 h	20
2	C_6H_6	Cl_3CCOOH	reflux	8 h	15
3	C_6H_6	$TsOH·H_2O$	reflux	8 h	20
4	C_6H_6	TsOH	reflux	9 min	77
5	C_6H_6	TsOH	30–35	18 h	79
6	dioxane	$HClO_4$	30–35	24 h	15
7	dioxane	$HClO_4$	reflux	1 min	72
8	EtOH	HCl	30–35	1.5 h	76
9	EtOH	HCl	reflux	3 min	70
10	AcOH	aq. HCl	30–35	1.5 h	78
11	AcOH	aq. HCl	reflux	1 min	74

[a] Isolated yields.

A broad range of 2,3-disubstituted and 2,3,6-trisubstituted indoles were synthesized in 53–79% isolated yields from various 2-furylanilines and substituted benzaldehydes (Table 2) under the optimized reaction conditions (aq. HCl/AcOH, 30–35 °C).

Table 2. Synthesis of 3-(2-acylvinyl)-2-arylindoles **3** from 2-(2-furyl)anilines **1** and benzaldehydes **2**.



1 **2** **3**

1a X = H, R = Me
1b X = H, R = Et
1c X = Cl, R = Me
1d X = Me, R = Me

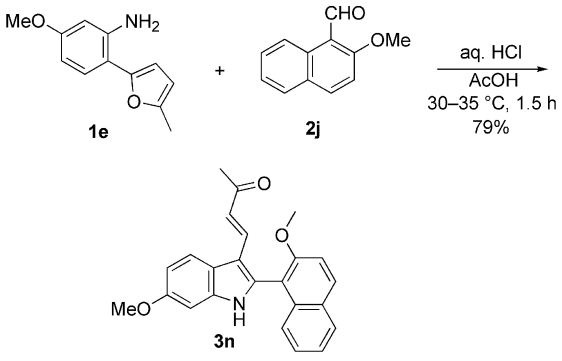
2a Y = H
2c Y = 4-F
2e Y = 3-O_2N
2g Y = 2-HO-5-Cl
2i Y = 4-EtO

2b Y = 3,4-$(MeO)_2$
2d Y = 4-O_2N
2f Y = 2-O_2N
2h Y = 4-Br

Entry	Product	X	R	Y	Yield [%][a]
1	**3a**	H	Me	H	78
2	**3b**	H	Me	3,4-$(MeO)_2$	72
3	**3c**	H	Me	4-F	70
4	**3d**	H	Me	4-O_2N	79
5	**3e**	H	Me	3-O_2N	62
6	**3f**	H	Me	2-O_2N	53
7	**3g**	H	Et	2-HO-5-Cl	70
8	**3h**	H	Et	4-EtO	66
9	**3i**	Me	Me	3,4-$(MeO)_2$	77
10	**3j**	Me	Me	4-Br	74
11	**3k**	Me	Me	4-F	60
12	**3l**	Cl	Me	3,4-$(MeO)_2$	76
13	**3m**	Cl	Me	4-O_2N	74

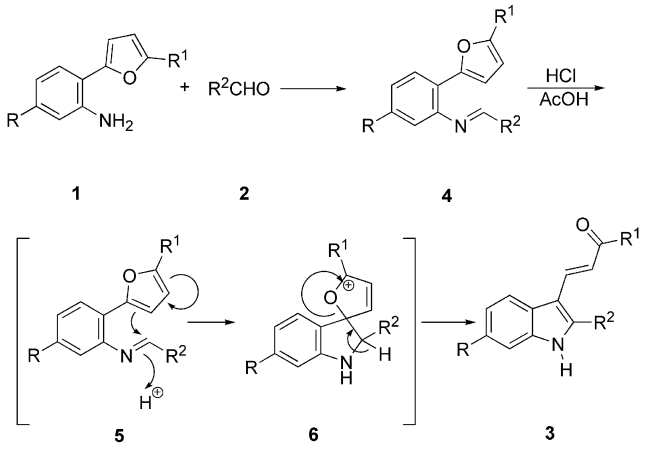
[a] Isolated yields.

The lowest yield was observed with 2-nitrobenzaldehyde (**2f**). This result cannot be explained by only the steric demands of the *ortho* substituent as 5-chlorosalicylaldehyde (**2g**) gave the corresponding indole in 70% yield. Moreover, the reaction of 2-methoxynaphthalene-1-carbaldehyde (**2j**) with **1e** led to the indole **3n** in 79% yield (Scheme 2).



Scheme 2.

The possible mechanism of this reaction is given in Scheme 3. The first step of the process is the formation of the Schiff base **4**. We isolated this intermediate when the reaction was performed at a lower temperature as well as when the starting compounds **1** and **2** were mixed in HCl-free acetic acid. The protonation of **4** yields the acyliminium ion **5**, which attacks the C2 atom of the furan ring to yield the cation **6**. Subsequent furan ring-opening leads to the indole **3**.

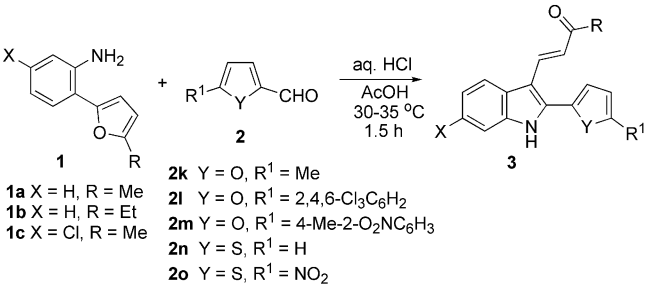


Scheme 3.

This kind of reactivity is specific to furan derivatives as it is known that other 2-(heteroaryl)anilines react with aldehydes in the presence of acids by the common Pictet–Spengler reaction to form quinoline derivatives annulated to the corresponding heterocycles.[19]

We next studied the reactivity of heterocyclic aldehydes and found that furfural and thiophene-2-carbaldehyde derivatives reacted efficiently with 2-(2-furyl)anilines to yield the corresponding 2-(heteroaryl)indoles in yields of 43–80% (Table 3).

Table 3. Synthesis of indoles **3** from **1** and heteroarenecarbaldehydes **2**.



1a X = H, R = Me
1b X = H, R = Et
1c X = Cl, R = Me

2k Y = O, R^1 = Me
2l Y = O, R^1 = 2,4,6-$Cl_3C_6H_2$
2m Y = O, R^1 = 4-Me-2-$O_2NC_6H_3$
2n Y = S, R^1 = H
2o Y = S, R^1 = NO_2

Entry	Product	X	R	Y	R^1	Yield [%][a]
1	**3o**	Cl	Me	O	Me	80
2	**3p**	H	Me	O	2,4,6-$Cl_3C_6H_2$	75
3	**3q**	H	Me	O	4-Me-2-$O_2NC_6H_3$	65
4	**3r**	Cl	Me	S	H	75
5	**3s**	H	Et	S	NO_2	43

[a] Isolated yields.

In contrast, pyridinecarbaldehydes failed to give the target indoles in this process. Similarly, acetaldehyde was not found to be efficient in indole formation under these reaction conditions, possibly due to the reversibility of the formation of imine **4** and, as a result, competitive furan ring-opening leading to various byproducts.

Conclusions

A few approaches to 2-(hetero)arylindoles bearing an α,β-unsaturated ketone moiety at the C3 position have previously been reported, namely, aldol condensation of indole-3-carbaldehyde,[20] palladium-catalysed processes[21] and Friedel–Crafts-like reactions.[22] We have developed a new synthetic route to these compounds based on an acid-catalysed imine formation/indole ring-closure/furan ring-opening sequence. The synthesized compounds can be further modified to give various bioactive compounds by simple procedures similar to the known transformations of other 3-(2-acylvinyl)indoles.[23] The optimization of the reaction conditions for the synthesis of the analogous 3-(2-acylvinyl)-2-alkylindoles is under investigation.

Experimental Section

General: NMR spectra were recorded with a Bruker DPX 300 (300 MHz for ^{1}H and 75 MHz for ^{13}C NMR) spectrometer at room temperature. The chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$: ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.13 ppm; [D_6]DMSO: ^{1}H: δ = 2.50 ppm, ^{13}C: δ = 39.7 ppm). Coupling constants (J) are given in Hz. The multiplicities of the signals are described as follows: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, dd = double doublet, br. = broadened. IR spectra were measured as KBr plates with InfraLUM FT-02 and InfraLUM FT-801 instruments. Mass spectra were recorded with a Kratos MS-30 instrument with 70 eV electron-impact ionization at 200 °C. Melting points (uncorrected) were determined in capillaries with an Electrothermal 9100 capillary melting-point

apparatus. Column chromatography was performed on silica gel KSK (50–160 μm, LTD Sorbpolymer). The 2-(5-alkylfuran-2-yl)-anilines **1** were prepared according to published procedures.[15f] All the reactions were carried out by using freshly distilled and dry solvents.

General Procedure for the Synthesis of Indoles 3:[24] 2-Furylaniline **1** (3 mmol) and aldehyde **2** (3 mmol) were mixed with a solution of hydrochloric acid (0.01 mL) in acetic acid (5 mL). The resulting mixture was stirred at 30–35 °C for 1.5 h, poured into H_2O (200 mL) and neutralized with $NaHCO_3$. The resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic fractions were dried with Na_2SO_4, treated with activated charcoal and concentrated under reduced pressure. The residue was purified by column chromatography on SiO_2. Non-polar admixtures were first removed by using a CH_2Cl_2/hexane (1:4) mixture followed by product isolation with acetone as an eluent. Indoles **3** were purified by recrystallization using the specified solvents.

(3*E*)-4-(2-Phenyl-1*H*-indol-3-yl)but-3-en-2-one (3a): Brown-green solid. Yield: 0.61 g, 78%. M.p. 224–225 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.27 (s, 3 H, CH_3), 6.90 (d, ^3J = 16.2 Hz, 1 H, =CH), 7.21–7.31 (m, 2 H, H_{Ar}), 7.49–7.67 (m, 6 H, H_{Ar}), 7.77 (d, ^3J = 16.2 Hz, 1 H, =CH), 8.01–8.03 (m, 1 H, H_{Ar}), 12.18 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 28.0, 108.3, 112.2, 120.7, 121.4, 122.3, 123.1, 125.8, 129.0 (2 C), 129.1, 129.6 (2 C), 131.1, 136.8, 136.9, 143.9, 197.2 ppm. IR (KBr): $\tilde{\nu}$ = 3215, 1600, 1570, 1451, 1426, 1269, 1231, 776, 738 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 261 (45) [M]$^+$, 246 (45), 218 (100), 217 (62), 189 (17), 108 (16). $C_{18}H_{15}NO$ (261.33): calcd. C 82.73, H 5.79, N 5.36; found C 82.58, H 5.75, N 5.22.

(3*E*)-4-[2-(3,4-Dimethoxyphenyl)-1*H*-indol-3-yl]but-3-en-2-one (3b): Yellow solid. Yield: 0.69 g, 72%. M.p. 215–216 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.27 (s, 3 H), 3.86 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 6.85 (d, ^3J = 16.2 Hz, 1 H, =CH), 7.14–7.28 (m, 5 H, H_{Ar}), 7.47–7.50 (m, 1 H, H_{Ar}), 7.83 (d, ^3J = 16.2 Hz, 1 H, =CH), 7.96–7.99 (m, 1 H, H_{Ar}), 12.06 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 27.8, 55.6 (2 C), 107.8, 111.9, 112.0, 112.6, 120.5, 121.3, 121.9, 122.4, 122.9, 123.3, 125.9, 136.7, 137.3, 144.2, 148.9, 149.7, 197.2 ppm. IR (KBr): $\tilde{\nu}$ = 3306, 1587, 1282, 1247, 1181, 1134, 1021, 975 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 321 (100) [M]$^+$, 306 (20), 290 (32), 278 (68), 263 (77), 247 (90), 233 (27), 45 (18). $C_{20}H_{19}NO_3$ (321.38): calcd. C 74.75, H 5.96, N 4.36; found C 74.78, H 6.01, N 4.20.

(3*E*)-4-[2-(4-Fluorophenyl)-1*H*-indol-3-yl]but-3-en-2-one (3c): Yellow solid. Yield: 0.59 g, 70%. M.p. >250 °C (dec.; EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.26 (s, 3 H, CH_3), 6.87 (d, ^3J = 16.0 Hz, 1 H, =CH), 7.19–7.30 (m, 2 H, H_{Ar}), 7.43–7.51 (m, 3 H, H_{Ar}), 7.63–7.73 (m, 3 H, =CH + H_{Ar}), 7.99–8.02 (m, 1 H, H_{Ar}), 12.18 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 27.9, 108.4, 112.2, 116.1 (d, $^2J_{CF}$ = 21.8 Hz, 2 C), 120.6, 121.4, 122.5, 123.1, 125.7, 127.5 (d, $^4J_{CF}$ = 3.0 Hz), 131.7 (d, $^3J_{CF}$ = 8.5 Hz, 2 C), 136.5, 136.7, 142.8, 162.6 (d, $^1J_{CF}$ = 246.9 Hz), 197.2 ppm. IR (KBr): $\tilde{\nu}$ = 3234, 1602, 1572, 1457, 1267, 1232, 844 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 279 (54) [M]$^+$, 264 (68), 236 (100), 118 (18), 43 (18). $C_{18}H_{14}FNO$ (279.32): calcd. C 77.40, H 5.05, N 5.01; found C 77.58, H 4.97, N 5.16.

(3*E*)-4-[2-(4-Nitrophenyl)-1*H*-indol-3-yl]but-3-en-2-one (3d): Red solid. Yield: 0.73 g, 79%. M.p. 257–258 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.30 (s, 3 H, CH_3), 6.94 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.23–7.28 (m, 1 H, H_{Ar}), 7.30–7.35 (m, 1 H, H_{Ar}), 7.53–7.55 (m, 1 H, H_{Ar}), 7.73 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.91 (d, ^3J = 9.0 Hz, 2 H, H_{Ar}), 8.04–8.06 (m, 1 H, H_{Ar}), 8.45 (d, ^3J = 9.0 Hz, 2 H, H_{Ar}), 12.40 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 27.9, 110.0, 112.5, 120.9, 121.7, 123.9, 124.0, 124.1 (2 C), 125.7, 130.5 (2 C), 135.8, 137.3, 137.4, 140.4, 147.2, 197.5 ppm. IR (KBr): $\tilde{\nu}$ = 3248, 1631, 1602, 1520, 861, 745 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 306 (2) [M]$^+$, 217 (26), 109 (11), 63 (17), 43 (100). $C_{18}H_{14}N_2O_3$ (306.32): calcd. C 70.58, H 4.61, N 9.15; found C 70.47, H 4.51, N 9.31.

(3*E*)-4-[2-(3-Nitrophenyl)-1*H*-indol-3-yl]but-3-en-2-one (3e): Red solid. Yield: 0.57 g, 62%. M.p. 227–228 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.29 (s, 3 H, CH_3), 6.92 (d, ^3J = 16.0 Hz, 1 H, =CH), 7.23–7.28 (m, 1 H, H_{Ar}), 7.29–7.35 (m, 1 H, H_{Ar}), 7.52–7.55 (m, 1 H, H_{Ar}), 7.72 (d, ^3J = 16.0 Hz, 1 H, =CH), 7.88–7.94 (m, 1 H, H_{Ar}), 8.03–8.05 (m, 1 H, H_{Ar}), 8.07–8.11 (m, 1 H, H_{Ar}), 8.35–8.39 (m, 1 H, H_{Ar}), 8.44–8.45 (m, 1 H, H_{Ar}), 12.42 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 27.8, 109.3, 112.4, 120.8, 121.6, 123.5, 123.6, 123.7, 123.8, 125.6, 130.6, 132.5, 135.8, 135.9, 137.0, 140.4, 148.1, 197.4 ppm. IR (KBr): $\tilde{\nu}$ = 3238, 1631, 1610, 1523, 1452, 1349, 1255, 1231, 738 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 306 (2) [M]$^+$, 216 (37), 189 (14), 63 (19), 51 (15), 43 (100). $C_{18}H_{14}N_2O_3$ (306.32): calcd. C 70.58, H 4.61, N 9.15; found C 70.64, H 4.56, N 9.27.

(3*E*)-4-[2-(2-Nitrophenyl)-1*H*-indol-3-yl]but-3-en-2-one (3f): Red solid. Yield: 0.49 g, 53%. M.p. 251–252 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.20 (s, 3 H, CH_3), 6.78 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.23–7.33 (m, 2 H, H_{Ar}), 7.36 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.47–7.50 (m, 1 H, H_{Ar}), 7.72–7.75 (m, 1 H, H_{Ar}), 7.82–7.87 (m, 1 H, H_{Ar}), 7.91–7.97 (m, 1 H, H_{Ar}), 8.02–8.05 (m, 1 H, H_{Ar}), 8.24–8.27 (m, 1 H, H_{Ar}), 12.27 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 28.0, 109.7, 112.3, 120.6, 121.5, 122.3, 123.3, 125.0, 125.2, 125.4, 131.1, 133.6, 133.7, 135.0, 136.9, 139.3, 149.1, 197.1 ppm. IR (KBr): $\tilde{\nu}$ = 3201, 1613, 1524, 1445, 783, 748, 699 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 306 (2) [M]$^+$, 218 (20), 76 (20), 63 (22), 51 (20), 43 (100). $C_{18}H_{14}N_2O_3$ (306.32): calcd. C 70.58, H 4.61, N 9.15; found C 70.64, H 4.56, N 9.27.

(1*E*)-1-[2-(5-Chloro-2-hydroxyphenyl)-1*H*-indol-3-yl]pent-1-en-3-one (3g): Brown solid. Yield: 0.68 g, 70%. M.p. 208–209 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.02 (t, ^3J = 7.4 Hz, 3 H, CH_3), 2.60 (q, ^3J = 7.4 Hz, 2 H, CH_2), 6.84 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.08 (d, ^3J = 8.7 Hz, 1 H, H_{Ar}), 7.18–7.28 (m, 2 H, H_{Ar}), 7.33 (d, ^4J = 2.4 Hz, 1 H, H_{Ar}), 7.41 (dd, ^3J = 8.7, ^4J = 2.4 Hz, 1 H, H_{Ar}), 7.45–7.48 (m, 1 H, H_{Ar}), 7.58 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.99–8.01 (m, 1 H, H_{Ar}), 10.33 (s, 1 H, OH), 11.98 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 8.5, 33.8, 109.5, 112.1, 117.8, 119.9, 120.2, 120.5, 121.1, 122.4, 122.7, 125.3, 130.2, 131.2, 136.1, 136.8, 140.1, 154.5, 199.7 ppm. IR (KBr): $\tilde{\nu}$ = 3296, 1611, 1441, 1203, 1181, 749, 727 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 327/325 (1/3) [M]$^+$, 233 (25), 204 (40), 117 (45), 102 (45), 88 (30), 75 (27), 63 (30), 57 (100). $C_{19}H_{16}ClNO_2$ (325.80): calcd. C 70.05, H 4.95, N 4.30; found C 70.31, H 4.94, N 4.28.

(1*E*)-1-[2-(4-Ethoxyphenyl)-1*H*-indol-3-yl]pent-1-en-3-one (3h): Brown solid. Yield: 0.63 g, 66%. M.p. 135–136 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.03 (t, ^3J = 7.5 Hz, 3 H, CH_3), 1.38 (t, ^3J = 7.1 Hz, 3 H, CH_3), 2.62 (q, ^3J = 7.5 Hz, 2 H, CH_2), 4.13 (q, ^3J = 7.1 Hz, 2 H, CH_2O), 6.90 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.15 (d, ^3J = 8.7 Hz, 2 H, H_{Ar}), 7.18–7.27 (m, 2 H, H_{Ar}), 7.45–7.48 (m, 1 H, H_{Ar}), 7.53 (d, ^3J = 8.7 Hz, 2 H, H_{Ar}), 7.76 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.97–8.00 (m, 1 H, H_{Ar}), 12.03 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 8.5, 14.7, 33.7, 63.3, 107.8, 112.0, 114.9 (2 C), 120.5, 120.7, 121.3, 122.8, 123.2, 125.9, 130.9 (2 C), 135.9, 136.7, 144.2, 159.3, 199.7 ppm. IR (KBr): $\tilde{\nu}$ = 3265, 1608, 1573, 1497, 1454, 1279, 1250, 1208, 1201, 1180, 1045 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 319 (100) [M]$^+$, 291 (25), 290 (76), 262 (71), 233 (59), 206 (41), 205 (52), 204 (94), 59 (21).

$C_{21}H_{21}NO_2$ (319.41): calcd. C 78.97, H 6.63, N 4.39; found C 79.08, H 6.48, N 4.24.

(3*E*)-4-[2-(3,4-Dimethoxyphenyl)-6-methyl-1*H*-indol-3-yl]but-3-en-2-one (3i): Yellow solid. Yield: 0.77 g, 77%. M.p. 216–217 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.25 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 6.80 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.04 (dd, ^3J = 8.1, ^4J = 1.2 Hz, 1 H, H_{Ar}), 7.12–7.26 (m, 4 H, H_{Ar}), 7.79 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.84 (d, ^3J = 8.4 Hz, 1 H, H_{Ar}), 11.91 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 21.3, 27.7, 55.6, 55.7, 107.8, 111.8, 111.9, 112.6, 120.2, 121.7, 122.3, 122.9, 123.5, 123.8, 132.2, 137.2, 137.4, 143.8, 148.6, 149.6, 197.2 ppm. IR (KBr): $\tilde{\nu}$ = 3208, 1605, 1569, 1486, 1464, 1456, 1259, 1247, 1236, 1224, 1144, 1030, 816 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 335 (74) [M]$^+$, 320 (28), 292 (73), 277 (20), 262 (49), 261 (100), 246 (24), 218 (57), 217 (31), 204 (45), 191 (21), 101 (23), 83 (33), 43 (68). $C_{21}H_{21}NO_3$ (335.41): calcd. C 75.20, H 6.31, N 4.18; found C 75.42, H 6.27, N 4.02.

(3*E*)-4-[2-(4-Bromophenyl)-6-methyl-1*H*-indol-3-yl]but-3-en-2-one (3j): Yellow solid. Yield: 0.79 g, 74%. M.p. 266–267 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.26 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 6.85 (d, ^3J = 16.0 Hz, 1 H, =CH), 7.06 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, H_{Ar}), 7.28 (d, ^4J = 1.5 Hz, 1 H, HAr), 7.55 (d, ^3J = 8.4 Hz, 2 H, H_{Ar}), 7.67 (d, ^3J = 16.0 Hz, 1 H, =CH), 7.79 (d, ^3J = 8.4 Hz, 2 H, H_{Ar}), 7.87 (d, ^3J = 8.1 Hz, 1 H, H_{Ar}), 12.06 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 21.3, 27.9, 108.6, 112.0, 120.4, 122.5, 122.6, 123.1, 123.6, 130.3, 131.3 (2 C), 131.9 (2 C), 132.7, 136.5, 137.4, 141.9, 197.2 ppm. IR (KBr): $\tilde{\nu}$ = 3261, 1611, 1453, 1273, 1000, 829 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 356/354 (1/1) [M]$^+$, 231 (33), 115 (22), 102 (13), 75 (14), 43 (100). $C_{19}H_{16}BrNO$ (354.25): calcd. C 64.42, H 4.55, N 3.95; found C 64.48, H 4.42, N 3.96.

(3*E*)-4-[2-(4-Fluorophenyl)-6-methyl-1*H*-indol-3-yl]but-3-en-2-one (3k): Yellow solid. Yield: 0.53 g, 60%. M.p. >250 °C (dec.; EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.25 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 6.84 (d, ^3J = 16.0 Hz, 1 H, =CH), 7.05 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, H_{Ar}), 7.27 (m, 1 H, H_{Ar}), 7.42–7.49 (m, 2 H, H_{Ar}), 7.62–7.70 (m, 3 H, =CH + H_{Ar}), 7.87 (d, ^3J = 8.1 Hz, 1 H, H_{Ar}), 12.03 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 21.3, 27.9, 108.4, 112.0, 116.0 (d, $^2J_{CF}$ = 21.7 Hz, 2 C), 120.4, 122.2, 123.1, 123.6, 127.6 (d, $^4J_{CF}$ = 3.1 Hz), 131.6 (d, $^3J_{CF}$ = 8.5 Hz, 2 C), 132.5, 136.6, 137.2, 142.4, 162.5 (d, $^1J_{CF}$ = 247.0 Hz), 197.2 ppm. IR (KBr): $\tilde{\nu}$ = 3187, 1601, 1569, 1483, 1453, 1276, 1235, 1162, 1001, 839 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 293 (86) [M]$^+$, 279 (26), 278 (56), 251 (78), 250 (100), 249 (37), 248 (34), 236 (25), 235 (76), 234 (36), 77 (24), 59 (48), 43 (61). $C_{19}H_{16}FNO$ (293.34): calcd. C 77.80, H 5.50, N 4.77; found C 77.76, H 5.32, N 4.89.

(3*E*)-4-[6-Chloro-2-(3,4-dimethoxyphenyl)-1*H*-indol-3-yl]but-3-en-2-one (3l): Yellow solid. Yield: 0.81 g, 76%. M.p. 237–238 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.27 (s, 3 H, CH_3), 3.86 (s, 6 H, OCH_3), 6.84 (d, ^3J = 16.2 Hz, 1 H, =CH), 7.13–7.23 (m, 4 H, H_{Ar}), 7.47 (d, ^4J = 1.8 Hz, 1 H, H_{Ar}), 7.77 (d, ^3J = 16.2 Hz, 1 H, =CH), 7.98 (d, ^3J = 8.4 Hz, 1 H, H_{Ar}), 12.18 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 27.8, 55.7 (2 C), 107.8, 111.5, 111.9, 112.5, 121.4, 121.8, 122.4, 122.6, 122.9, 124.7, 127.3, 136.5, 137.2, 144.8, 148.9, 149.8, 197.2 ppm. IR (KBr): $\tilde{\nu}$ = 3228, 1611, 1455, 1255, 1237, 1026, 1003 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 357/355 (1/3) [M]$^+$, 277 (5), 191 (6), 113 (5), 96 (6), 43 (100). $C_{20}H_{18}ClNO_3$ (355.82): calcd. C 67.51, H 5.10, N 3.94; found C 67.57, H 5.01, N 3.95.

(3*E*)-4-[6-Chloro-2-(4-nitrophenyl)-1*H*-indol-3-yl]but-3-en-2-one (3m): Red solid. Yield: 0.75 g, 74%. M.p. >250 °C (dec.; EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.30 (s, 3 H, CH_3), 6.92 (d, ^3J = 16.0 Hz, 1 H, =CH), 7.25 (dd, ^3J = 8.7, ^4J = 2.1 Hz, 1 H, H_{Ar}), 7.54 (d, ^4J = 2.1 Hz, 1 H, H_{Ar}), 7.67 (d, ^3J = 16.0 Hz, 1 H, =CH), 7.90 (d, ^3J = 9.0 Hz, 2 H, H_{Ar}), 8.07 (d, ^3J = 8.7 Hz, 1 H, H_{Ar}), 8.45 (d, ^3J = 9.0 Hz, 2 H, H_{Ar}), 12.53 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 27.9, 110.0, 111.9, 121.8, 122.3, 124.1 (2 C), 124.4, 124.6, 128.3, 130.4 (2 C), 135.1, 136.9, 137.7, 140.9, 147.3, 197.4 ppm. IR (KBr): $\tilde{\nu}$ = 3277, 1630, 1606, 1515, 1349, 1262, 1231, 857 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 342/340 (1/3) [M]$^+$, 251 (24), 216 (25), 113 (22), 108 (40), 94 (26), 75 (31), 43 (100). $C_{18}H_{13}ClN_2O_3$ (340.77): calcd. C 63.44, H 3.85, N 8.22; found C 63.32, H 3.71, N 8.27.

(3*E*)-4-[2-(2-Ethoxy-1-naphthyl)-6-methoxy-1*H*-indol-3-yl]but-3-en-2-one (3n): Yellow solid. Yield: 0.91 g, 79%. M.p. 116–117 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.16 (t, ^3J = 6.9 Hz, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 4.19 (q, ^3J = 6.9 Hz, 2 H, CH_2), 6.67 (d, ^3J = 15.9 Hz, 1 H, =CH), 6.88 (dd, ^3J = 8.6, ^4J = 2.1 Hz, 1 H, H_{Ar}), 6.92 (d, ^4J = 2.1 Hz, 1 H, H_{Ar}), 7.19 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.23–7.28 (m, 1 H, H_{Ar}), 7.38–7.45 (m, 2 H, H_{Ar}), 7.63 (d, ^3J = 9.0 Hz, 1 H, H_{Ar}), 7.92 (d, ^3J = 8.6 Hz, 1 H, H_{Ar}), 7.95–8.01 (m, 1 H, H_{Ar}), 8.15 (d, ^3J = 9.0 Hz, 1 H, H_{Ar}), 11.89 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 14.8, 27.9, 55.3, 64.5, 95.1, 110.6, 110.7, 115.1, 119.6, 120.4, 121.0, 123.9, 124.2, 127.4, 128.2, 128.3, 128.4, 131.4, 133.8, 136.7, 138.2, 138.6, 154.9, 156.2, 196.8 ppm. IR (KBr): $\tilde{\nu}$ = 3234, 1603, 1575, 1456, 1262, 1160, 809 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 385 (1) [M]$^+$, 150 (5), 129 (5), 121 (7), 115 (8), 75 (10), 43 (100). $C_{25}H_{23}NO_3$ (385.47): calcd. C 77.90, H 6.01, N 3.63; found C 78.17, H 6.05, N 3.46.

(3*E*)-4-[6-Chloro-2-(5-methyl-2-furyl)-1*H*-indol-3-yl]but-3-en-2-one (3o): Brown solid. Yield: 0.72 g, 80%. M.p. 267–268 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.34 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 6.39 (d, ^3J = 3.3 Hz, 1 H, H_{Fur}), 6.80 (d, ^3J = 16.2 Hz, 1 H, =CH), 6.98 (d, ^3J = 3.3 Hz, 1 H, H_{Fur}), 7.17 (dd, ^3J = 8.4, ^4J = 2.1 Hz, 1 H, H_{Ind}), 7.43 (d, ^4J = 2.1 Hz, 1 H, H_{Ind}), 7.93 (d, ^3J = 8.7 Hz, 1 H, H_{Ind}), 8.17 (d, ^3J = 16.2 Hz, 1 H, =CH), 12.17 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 13.5, 27.4, 107.4, 108.8, 111.4, 112.5, 121.5, 121.9, 123.5, 124.4, 127.7, 133.3, 135.9, 137.7, 144.2, 154.1, 197.4 ppm. IR (KBr): $\tilde{\nu}$ = 3250, 1634, 1600, 1569, 1265, 1234, 1169, 1006, 959 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 301/299 (4/13) [M]$^+$, 221 (35), 193 (13), 178 (13), 96 (15), 43 (100). $C_{17}H_{14}ClNO_2$ (299.76): calcd. C 68.12, H 4.71, N 4.67; found C 67.96, H 4.61, N 4.72.

(3*E*)-4-{2-[5-(2,4,6-Trichlorophenyl)-2-furyl]-1*H*-indol-3-yl}but-3-en-2-one (3p): Red solid. Yield: 0.97 g, 75%. M.p. 276–277 °C (EtOH/dioxane). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.30 (s, 3 H, CH_3), 6.86 (d, ^3J = 16.2 Hz, 1 H, =CH), 7.04 (d, ^3J = 3.6 Hz, 1 H, H_{Fur}), 7.18–7.23 (m, 1 H, H_{Ar}), 7.25–7.31 (m, 1 H, H_{Ar}), 7.27 (d, ^3J = 3.6 Hz, 1 H, H_{Fur}), 7.47–7.49 (m, 1 H, H_{Ar}), 7.93 (s, 2 H, H_{Ar}), 7.96–7.98 (m, 1 H, H_{Ar}), 8.27 (d, ^3J = 15.6 Hz, 1 H, =CH), 12.21 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 27.3, 108.8, 111.7, 112.2, 115.3, 120.9, 121.6, 123.8, 123.9, 125.5, 127.3, 128.7 (2 C), 131.3, 135.5, 135.9 (2C), 136.3, 137.3, 146.9, 147.1, 197.4 ppm. IR (KBr): $\tilde{\nu}$ = 3208, 1623, 1599, 1573, 1455, 1265, 1237, 735 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 435/433/431/429 (2/15/44/44) [M]$^+$, 322 (86), 288 (73), 209 (61), 207 (100), 178 (32), 101 (38), 59 (52). $C_{22}H_{14}Cl_3NO_2$ (430.72): calcd. C 61.35, H 3.28, N 3.25; found C 61.34, H 3.26, N 3.38.

(3*E*)-4-{2-[5-(4-Methyl-2-nitrophenyl)-2-furyl]-1*H*-indol-3-yl}but-3-en-2-one (3q): Red solid. Yield: 0.75 g, 65%. M.p. 272–273 °C (EtOH/dioxane). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.34 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 6.85 (d, ^3J = 16.2 Hz, 1 H, =CH), 7.00 (d, ^3J = 3.9 Hz, 1 H, H_{Fur}), 7.18–7.24 (m, 1 H, H_{Ar}), 7.22 (d,

^3J = 3.9 Hz, 1 H, H_{Fur}), 7.26–7.32 (m, 1 H, H_{Ar}), 7.47–7.50 (m, 1 H, H_{Ar}), 7.47–7.50 (m, 1 H, H_{Ar}), 7.65 (dd, ^3J = 8.1, ^4J = 1.8 Hz, 1 H, H_{Ar}), 7.84 (d, ^4J = 1.8 Hz, 1 H, H_{Ar}), 7.94 (d, ^3J = 8.1 Hz, 1 H, H_{Ar}), 7.96–7.97 (m, 1 H, H_{Ar}), 8.20 (d, ^3J = 16.2 Hz, 1 H, =CH), 12.20 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 20.4, 27.1, 108.9, 111.8, 112.2, 112.8, 119.7, 120.9, 121.6, 123.9, 124.2, 124.4, 125.5, 128.9, 131.2, 133.4, 136.3, 137.4, 140.3, 146.8, 147.2, 149.0, 197.6 ppm. IR (KBr): $\tilde{\nu}$ = 3287, 1626, 1602, 1573, 1518, 1434, 1271, 1236 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 386 (100) [M]$^+$, 357 (22), 356 (55), 327 (20), 268 (24), 254 (23), 225 (23), 210 (26), 184 (61), 182 (23), 167 (20), 166 (25), 154 (25), 101 (24), 43 (42). $C_{23}H_{18}N_2O_4$ (386.41): calcd. C 71.49, H 4.70, N 7.25; found C 71.67, H 4.60, N 7.22.

(3*E*)-4-[6-Chloro-2-(2-thienyl)-1*H*-indol-3-yl]but-3-en-2-one (3r): Yellow solid. Yield: 0.68 g, 75%. M.p. 237–238 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.32 (s, 3 H, CH_3), 6.87 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.21 (dd, ^3J = 8.7, ^4J = 2.1 Hz, 1 H, H_{Ind}), 7.33 (dd, ^3J = 5.1, ^3J = 3.6 Hz, 1 H, H_{Th}), 7.47 (d, ^4J = 2.1 Hz, 1 H, H_{Ind}), 7.56 (dd, ^4J = 1.2, ^3J = 3.6 Hz, 1 H, H_{Th}), 7.87 (dd, ^4J = 1.2, ^3J = 5.1 Hz, 1 H, H_{Th}), 7.96 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.98 (d, ^3J = 8.7 Hz, 1 H, H_{Ind}), 12.29 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 27.9, 108.7, 111.6, 121.6, 121.9, 123.7, 124.5, 127.9, 128.5, 128.7, 129.4, 131.4, 135.3, 137.3, 137.5, 197.3 ppm. IR (KBr): $\tilde{\nu}$ = 3258, 1628, 1602, 1263, 1238, 706 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 303/301 (2/7) [M]$^+$, 223 (55), 112 (40), 87 (14), 75 (15), 63 (21), 43 (100). $C_{16}H_{12}ClNOS$ (301.80): calcd. C 63.68, H 4.01, N 4.64; found C 63.65, H 3.98, N 4.64.

(1*E*)-1-[2-(5-Nitro-2-thienyl)-1*H*-indol-3-yl]pent-1-en-3-one (3s): Violet solid. Yield: 0.42 g, 43%. M.p. 227–228 °C (EtOH/acetone). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.06 (t, ^3J = 7.4 Hz, 3 H, CH_3), 2.74 (q, ^3J = 7.4 Hz, 2 H, CH_2), 7.05 (d, ^3J = 15.9 Hz, 1 H, =CH), 7.23–7.28 (m, 1 H, H_{Ind}), 7.33–7.38 (m, 1 H, H_{Ar}), 7.51–7.53 (m, 1 H, H_{Ind}), 7.60 (d, ^3J = 4.5 Hz, 1 H, H_{Th}), 7.96 (d, ^3J = 15.9 Hz, 1 H, =CH), 8.03–8.05 (m, 1 H, H_{Ind}), 8.30 (d, ^3J = 4.5 Hz, 1 H, H_{Th}), 12.47 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 8.2, 33.9, 111.8, 112.4, 121.1, 121.9, 124.7, 124.8, 125.5, 127.2, 130.7, 132.6, 132.9, 137.4, 139.6, 150.9, 199.9 ppm. IR (KBr): $\tilde{\nu}$ = 3240, 1627, 1612, 1452, 1423, 1334, 1193, 813, 745, 730 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 326 (60) [M]$^+$, 297 (100), 294 (69), 251 (65), 239 (50), 235 (61), 222 (47), 208 (34), 178 (28), 59 (24). $C_{17}H_{14}N_2O_3S$ (326.38): calcd. C 62.56, H 4.32, N 8.58; found C 62.36, H 4.19, N 8.50.

5-Chloro-2-(5-methyl-2-furyl)-*N*-(4-nitrobenzylidene)aniline (4m): Aniline **1c** (500 mg, 2.4 mmol) and *p*-nitrobenzaldehyde (**2d**; 364 mg, 2.4 mmol) were dissolved in acetic acid (5 mL) and stirred at room temperature for 2 h. The mixture was cooled to 5–7 °C, and the residue was removed by filtration and recrystallized from glacial acetic acid. The product **4m** was isolated as a red solid (0.59 g, 72%). M.p. 164–165 °C. IR (KBr): $\tilde{\nu}$ = 3440, 1634, 1601, 1519, 1103, 1021, 908, 859, 769, 735, 686 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 342/340 (33/100) [M]$^+$, 299/297 (17/51), 283/281 (14/42), 215 (16), 44 (19). $C_{18}H_{13}ClN_2O_3$ (340.77): calcd. C 63.44, H 3.85, N 8.22; found C 63.36, H 3.76, N 8.07. Owing to the instability of **4m** in solution we failed to record its NMR spectra. To prove the structure of **4m**, it was reduced with $NaBH_4$ and characterized as the corresponding amine.

5-Chloro-2-(5-methyl-2-furyl)-*N*-(4-nitrobenzyl)aniline: $NaBH_4$ (0.25 g, 6.4 mmol) was added portionwise to a solution of **4m** (1.1 g, 3.2 mmol) in a mixture of ethanol (20 mL) and 1,4-dioxane (10 mL) at room temperature. The resulting mixture was heated at reflux for 10 min, poured into H_2O (200 mL) and neutralized with NH_4Cl. The residue formed was removed by filtration and purified by column chromatography (eluent: CH_2Cl_2/hexane, 1:3). The title product was obtained as a yellow solid (0.62 g, 56%). M.p. 99–100 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 4.52 (d, ^3J = 3.9 Hz, 2 H, CH_2), 5.71 (br. t, ^3J = 3.9 Hz, 1 H, NH), 6.09 (d, ^3J = 3.3 Hz, 1 H, H_{Fur}), 6.45 (m, 2 H, H_{Ar} + H_{Fur}), 6.71 (dd, ^3J = 8.1, ^4J = 2.1 Hz, 1 H, H_{Ar}), 7.34 (d, ^3J = 8.1 Hz, 1 H, H_{Ar}), 7.53 (d, ^3J = 8.7 Hz, 2 H, H_{Ar}), 8.21 (d, ^3J = 8.7 Hz, 2 H, H_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 47.2, 107.5, 108.1, 111.2, 115.1, 117.6, 123.9 (2 C), 127.5 (2 C), 128.6, 134.3, 144.5, 146.5, 147.2, 150.5, 151.6 ppm. MS (EI, 70 eV): *m*/*z* (%) = 344/342 (33/100) [M]$^+$, 274/272 (19/57), 220 (56), 143 (90), 115 (63), 89 (83), 45 (46). $C_{18}H_{15}ClN_2O_3$ (342.78): calcd. C 63.07, H 4.41, N 8.17; found C 63.28, H 4.28, N 8.14.

Supporting Information (see footnote on the first page of this article): General experimental procedures for the synthesis of the indoles and ^{1}H and ^{13}C NMR spectra of the synthesized compounds.

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[24] Other procedures studied for the transformation of furans **1** into indoles **3** are given in the Supporting Information.

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