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Oxidative Rearrangement of 2-(2-Aminobenzyl)furans: Synthesis of Functionalized Indoles and Carbazoles

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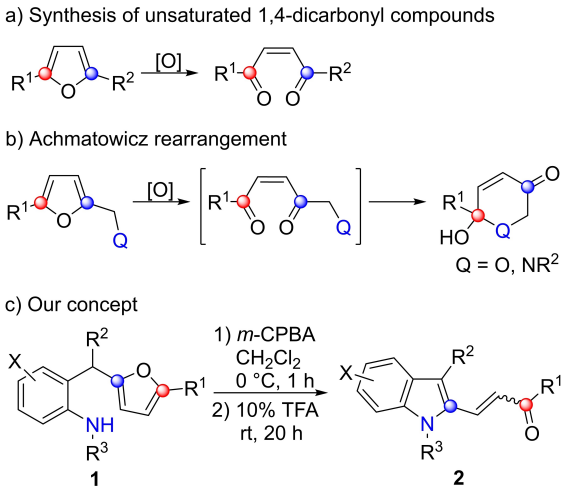
2-(2-Acylvinyl)indoles obtained by oxidative rearrangement of substituted 2-(2-aminobenzyl)furans could be used to construct structural analogues of antifungal alkaloids caulindoles A–D as well as other indole-derived molecules and substituted carbazoles by introducing new reaction centers into the structure of starting materials or by synthetic manipulation with functional groups of the obtained compounds.

Introduction

The oxidative transformation of furans into various functionalized compounds is a powerful instrument in modern organic chemistry.[1] A strong interest in studying such processes is certified by a number of diverse pathways developed annually,[2] being stimulated, among others, by availability of starting furans through biomass processing.[3] Due to the combination of accessibility and versatile reactivity under oxidative conditions, substituted furans serve as convenient and inexpensive building blocks for the synthesis of a broad range of valuable products.

The most studied oxidative transformation of furans is their conversion into 2,3-unsaturated 1,4-dicarbonyl compounds (Scheme 1a), which are widely applied in modern synthetic organic chemistry for the preparation of various acyclic, alicyclic, and heterocyclic molecules, including natural products. Usually the construction of the desired molecules proceeds in a stepwise manner and includes: a) synthesis of a starting furan, b) its oxidation to the corresponding enedione, c) cyclization, d) subsequent functionalization. However, the use of this sequence not only requires the isolation of multiple intermediary products, but can also be accompanied by diverse side processes.



Scheme 1. Oxidative transformations of furans.

The effective solution to this problem is based on the design of a starting furan containing a nucleophilic moiety at the appropriate position aiming for the interception of the unsaturated 1,4-dicarbonyl compound formed during the furan oxidation. This strategy was for the first time applied 50 years ago when Achmatowicz *et al.* reported the oxidation of furfuryl alcohols affording, after subsequent acidic treatment, substituted dihydropyran-3-ones (Scheme 1b).[4] Multiple investigations of this reaction made the Achmatowicz rearrangement a well-studied oxidative transformation of substituted furans into functionalized heterocycles such as pyran and pyridine derivatives.[5]

In the Achmatowicz rearrangement, a nucleophile, located at the α-position of a side chain at the C(2) atom of the furan ring, attacks the distal carbonyl group of the intermediate enedione, furnishing a six-membered heterocycle. Oppositely, the intramolecular nucleophilic attack on the proximal carbonyl group, resulted from the oxidation of substituted furan, is represented only by scarce transformations affording the

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corresponding spirocyclic ketals or hemiaminals.[6] Recently we described an oxidative rearrangement of 2-(2-amino-benzyl) furans **1** into 2-(2-acylvinyl)indoles **2** that proceeded in high yields and excellent stereocontrol affording exclusively either *E*- or *Z*-arrangement of substituents at C=C bond (Scheme 1c).[7]

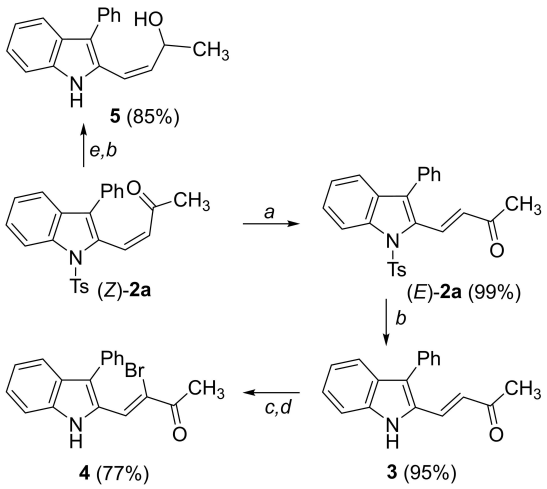
Herein, we present the continuation of our research of the oxidative rearrangement of substituted furans and further transformations of the obtained products into important heterocyclic motifs.

Results and Discussion

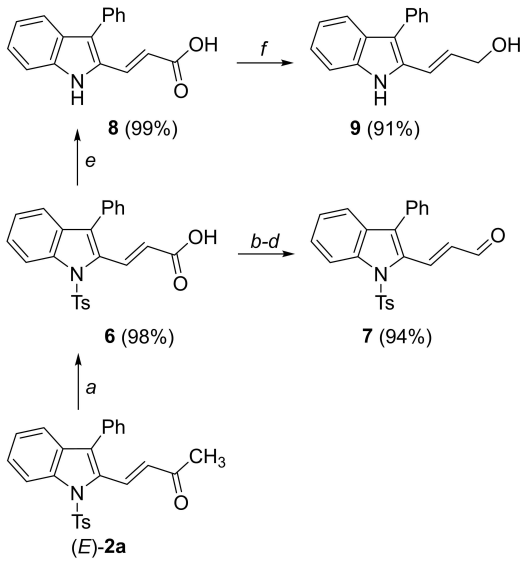
Unlike Achmatowicz rearrangement, in our approach the furan core provides only one carbon atom for the construction of a new heterocycle, while the remaining carbons are released as the reactive α,β-unsaturated ketone moiety. In the combination with high reactivity of the indole scaffold toward diverse reagents, this ensures a wide synthetic value of the obtained 2-(2-acylvinyl)indoles **2**.[8]

We started this work by exploring the reactivity of indoles **2** aiming to demonstrate their potential as versatile building blocks for the synthesis of various indole-containing molecules. We found that the quantitative isomerization of (*Z*)-**2a** into (*E*)-**2a** could be achieved by heating in the presence of molecular iodine (Scheme 2). Subsequent treatment of (*E*)-**2a** with methanolic KOH led to the *NH*-indole **3** in a near quantitative yield; the sequential treatment of the obtained **3** with Oxone/NH_4Br in MeOH and HCl in $CHCl_3$ afforded brominated product **4** in high yield. The reduction of (*Z*)-**2a** with $NaBH_4$ in EtOH afforded the corresponding alcohol in quantitative yield, further deprotection of which produced *N*-unsubstituted allyl alcohol **5** in high yield.

Next, we oxidized (*E*)-**2a** with NaBrO to the corresponding β-(2-indolyl)acrylic acid **6** in quantitative yield (Scheme 3). This acid was smoothly converted to the corresponding α,β-unsaturated aldehyde **7**, which could be a convenient precursor



Scheme 2. Synthesis of indoles **2**–**5**. a) I_2, toluene, 150 °C, MW; b) KOH, MeOH, 60 °C; c) Oxone, NH_4Br, MeOH 20 °C; d) HCl, $CHCl_3$, rt; e) $NaBH_4$, EtOH.



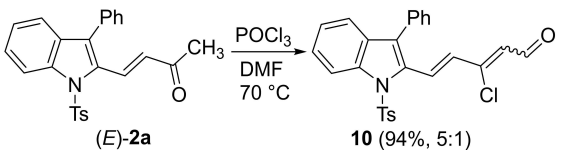
Scheme 3. Synthesis of indoles **6**–**9**. a) NaOH, Br_2, H_2O, 1,4-dioxane, rt; b) MeI, Cs_2CO_3, acetone, 60 °C; c) $LiAlH_4$, $AlCl_3$, Et_2O, 0 °C; d) MnO_2, CH_2Cl_2, rt; e) KOH, MeOH, 60 °C; f) EtOCOCl, TEA, THF, 0 °C then $NaBH_4$.

in the synthesis of analogues of antilipidemic fluvastatin.[9] We also found that the quantitative deprotection of acrylic acid **6**, its transformation to a mixed anhydride followed by reduction with $NaBH_4$ led to the corresponding (*E*)-allyl alcohol **9** in high yield.

Finally, treatment of indole (*E*)-**2a** with Vilsmeier-Haack reagent provided indolyldienal **10** in excellent yield (Scheme 4). This compound could be involved in a large variety of transformations furnishing diverse useful polycyclic compounds.[10]

In 2004 Nkunya and co-workers isolated caulindoles A–D from the *Isolona cauliflora* (Figure 1).[11] These dimeric indoles showed antifungal and mild antimalarial activity. The isolated caulindoles A–D could be accessed through the Diels–Alder reaction of corresponding (*E*)-5-(3-methylbuta-1,3-dien-1-yl)-1*H*-indoles.[12] We suggested that the obtained indole (*E*)-**2a** could be smoothly converted into the corresponding diene, which should afford [4 + 2]-cyclodimers that can be considered as caulindoles analogues.

Reaction of (*E*)-**2a** with MeMgI furnished tertiary allyl alcohol **11**. The sequential treatment of allyl alcohol **11** with MsCl and TEA led to the corresponding diene **12** in high yield (Scheme 5). The key Diels–Alder reaction of the obtained diene **12** in the presence of $Cu(OTf)_2$ in CH_2Cl_2 afforded the mixture of dimeric indoles **13** in 45 % yield.[13]



Scheme 4. Synthesis of indolyldienal **10**.

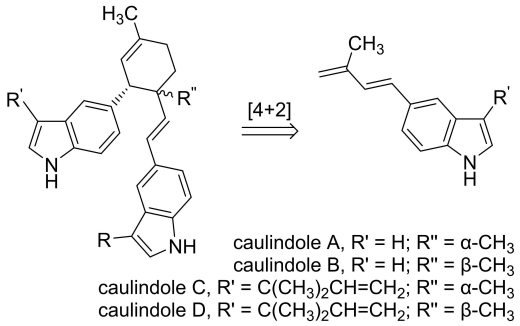
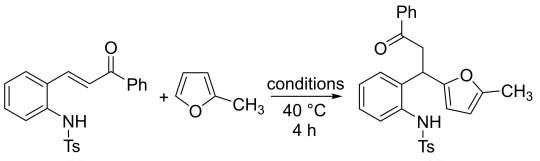


Figure 1. Antifungal alkaloids caulindoles A–D and known approach for their synthesis.

Carbazoles form an important class of nitrogen-containing heterocycles; this tricyclic scaffold is an integral part of diverse natural products and a wide range of bioactive compounds including approved drugs. Moreover, carbazoles are frequently used as building blocks for the preparation of a variety of functional organic materials.[14] Many approaches for the synthesis of functionalized carbazoles have been developed up to now.[15] The commonly used route is based on various processes of the benzene ring fusion to readily available indoles.[16] Having obtained the efficient method for the synthesis of 3-substituted indoles bearing α,β-unsaturated ketone moiety at the C(2) atom, we designed a new simple approach to functionalized carbazole derivatives. To implement this idea, a substituent at the C(3) atom of the indole ring should have a CH-acid moiety at the α-position that can be involved into aldol condensation with unsaturated ketone functionality at the indole C(2) atom. Retrosynthetic analysis revealed that the appropriate substrates could be synthesized by Michael addition of 2-alkylfurans to 2-aminochalcones (Scheme 6).

We began this part of our work by searching for the optimal reaction conditions for Michael addition of 2-methylfuran **15** to 2-(tosylamino)chalcone **14a** as model compounds (Table 1). We found that $CuBr_2$, $Cu(OTf)_2$ and I_2 in DCE or CH_3CN were barely effective (Table 1, entries 1–6). The good yields of 2-(2-aminobenzyl)furan **16a** were observed when we used TMSCl in DCE and HCl in CH_3CN (Table 1, entries 7,8). Finally, we found that the desired product **16a** was formed in quantitative yield when TsOH in DCE and TMSCl in CH_3CN were applied (Table 1, entries 9,10). In both cases, the reaction can be efficiently scaled up; the yield of **16a** being slightly dropped to 89% using TsOH in DCE (Table 1, entry 11), while TMSCl provided the target product in 95% yield (Table 1, entry 12). Oppositely, the use of TfOH in DCE led to the partial cyclisation of the starting chalcone **14a** affording 2-substituted quinoline *via* Friedländer-like reaction.[17]

Table 1. Optimization of reaction conditions for the Michael addition of 2-methylfuran **15** to chalcone **14a**[a].

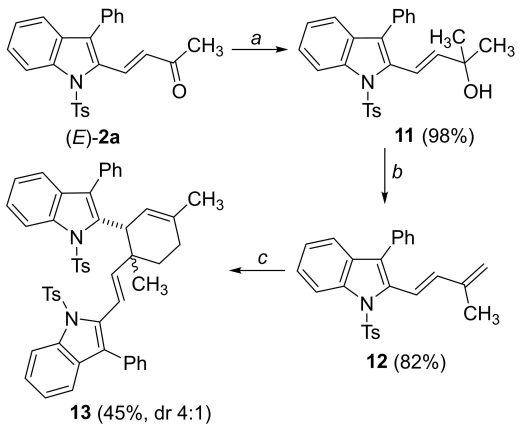


14a **15** **16a**

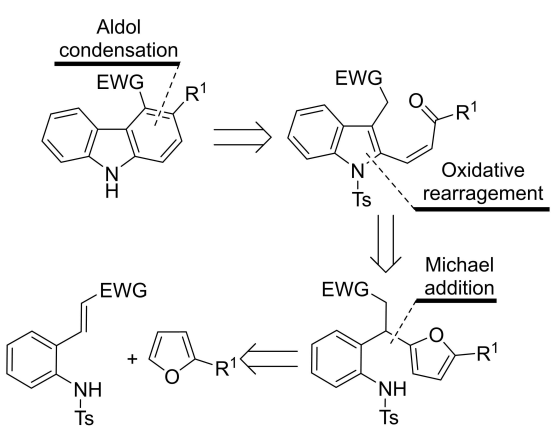
Entry	Solvent	Cat. [% mol]	Yield, [%][b]
1	DCE	$CuBr_2$ (20)	15
2	DCE	$Cu(OTf)_2$ (20)	35
3	DCE	I_2 (20)	35
4[c]	CH_3CN	$CuBr_2$ (20)	–
5[c]	CH_3CN	I_2 (20)	–
6	CH_3CN	$Cu(OTf)_2$ (20)	20
7	DCE	TMSCl (20)	70
8	CH_3CN	HCl (20)	65
9	DCE	TsOH (20)	99
10	CH_3CN	TMSCl (20)	99
11[d]	DCE	TsOH (20)	89[e]
12[d]	CH_3CN	TMSCl (20)	95[e]

[a] All reactions performed at 0.1 mmol scale. [b] NMR yields. [c] Decomposition. [d] Reaction performed at 0.5 mmol scale at 50 °C for 24 h. [e] Isolated yield.

Using the optimized reaction conditions, we synthesized a series of substituted 2-(2-aminobenzyl)furans **16a–h** in high yields and studied their oxidative rearrangement (Table 2). We found that the desired indoles **17a–h** were formed in high

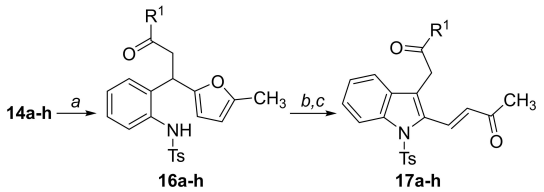


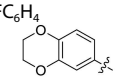
Scheme 5. Synthesis of dimeric indole **13**. a) MeMgI, Et_2O, toluene, rt; b) MsCl, TEA, THF, 60 °C; c) $Cu(OTf)_2$, CH_2Cl_2, reflux.



Scheme 6. The retrosynthetic scheme for the synthesis of 3,4-substituted carbazoles.

Table 2. Scope of the Oxidative Rearrangement of 2-(2-Aminobenzyl) furans **16** to 2-(2-Acylvinyl)indoles **17**.[a]



14,16,17	R^1	Yield, [%][b] 16	17
a	Ph	92	86
b	4-$CH_3C_6H_4$	86	84
c	4-$CH_3OC_6H_4$	88	89
d	4-ClC_6H_4	87	92
e	4-FC_6H_4	84	88
f		85	84
g	2-naphthyl	89	83
h	2-thienyl	82	85

[a] Reaction conditions: a) 2-methylfuran **15**, TMSCl, CH_3CN, 50 °C; b) *m*-CPBA, CH_2Cl_2, 0 °C, 1 h; c) 10% TFA, rt, 20 h. [b] Isolated yields.

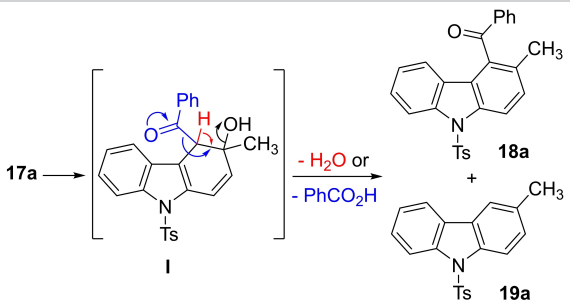
yields, the substituents at the carbonyl group had no influence on the reaction outcome.[13] Remarkably, (*E*)-isomers were exclusively formed in all reactions.

Finally, we optimized the reaction conditions for the intramolecular aldol condensation of the obtained 2-(2-acylvinyl) indoles **17** aiming to synthesize the desired carbazoles. Initially screened $Cu(OTf)_2$ and TfOH (Table 3, entries 1,2) gave rise to the formation of the mixture of the anticipated product **18a** and unexpected carbazole **19a** with a 1:1 ratio in *ca.* 80% total yield. Both were formed from the same intermediate hydroxyketone **I** *via* elimination of water or benzoic acid, respectively. Heating the solution of the starting indole **17a** in acetic acid led to the formation of the desired carbazole **18a** exclusively in high yield (Table 3, entry 3). Supposingly, the different chemoselectivity of these reactions resulted from the change of the elimination mechanism. Triflic acid and copper(II) triflate induce E1 reaction *via* the carbocation generation from the intermediate **I**; this cation can eject either proton or acyl cation. Oppositely, acetic acid has too weak acidity and can promote only E2 dehydration.

Fortunately, aldol condensation could be induced not only by acids but also by bases. We found that heating of the starting indole with methanolic KOH resulted in the formation of a mixture of the desired product **18a** and the corresponding *NH*-carbazole **20a** with a total yield of 45% and a ratio of *ca.* 1:1 (Table 4, entry 1). A prolonged heating of the reaction mixture led exclusively to *NH*-carbazole **20a** in moderate yield (Table 4, entry 2). The reaction time could be significantly reduced by heating the indole **20a** in methanolic KOH at 110 °C under microwave irradiation; however, the yield of *NH*-carbazole **20a** was significantly lower (Table 4, entry 3). On the other hand, the treatment of **17a** with methanolic KOH at room temperature produced carbazole **18a** in quantitative yield (Table 4, entry 4). In other words, the intramolecular aldol condensation itself should be performed under mild reaction conditions while *N*-deprotection required elevated temperature. Indeed, *one-pot* version of the total process including aldol condensation at room temperature overnight followed by heating the reaction mixture under microwave irradiation provided desired carbazole **20a** in high yield (Table 4, entry 5). It should be noted that the (*E*)-**17a** was used as the starting material for intramolecular aldol condensation; however, it is obvious that the *Z*-isomer **17a** enters the aldol condensation, which was formed through isomerization of the *E*-isomer **17a**. Thus, the *Z*/*E*-isomerization is the important act of the developed process.

Next, we studied the scope of this tandem intramolecular aldol condensation/deprotection under the optimized reaction conditions (Table 5). We found that the aryl substituent in the aroylmethyl moiety had not influence the reaction efficiency;

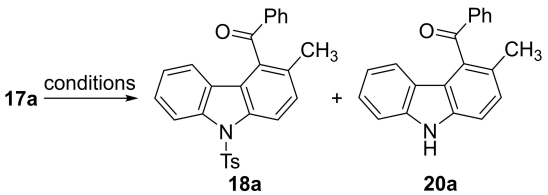
Table 3. Optimization of reaction conditions for intramolecular aldol condensation[a].



Entry	Reaction conditions	Yield, [%][b] 18a	19a
1	$Cu(OTf)_2$ (5 mol%), DCE, 85 °C	40	38
2	TfOH (5 mol%), toluene, 85 °C	41	39
3	AcOH, 120 °C	89	traces

[a] All reactions performed at 0.1 mmol scale. [b] Yields determined by NMR using internal standard.

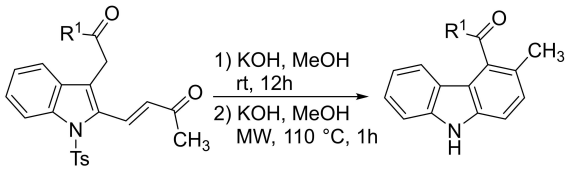
Table 4. Optimization of reaction conditions for the intramolecular aldol condensation[a].



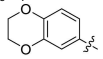
Entry	Reaction conditions	Yield, [%][b] 18a	20a
1	KOH, MeOH, 60 °C, 4 h	24	21
2	KOH, MeOH, 60 °C, 50 h	traces	47
3	KOH, MeOH 110 °C, MW, 1 h	traces	27
4	KOH, MeOH, rt, 12 h	95	–
5	KOH, MeOH, rt, 12 h, then 110 °C, MW, 1 h	–	93 (89)

[a] All reactions performed at 0.1 mmol scale. [b] NMR yields. Isolated yield is given in parentheses.

Table 5. Scope of tandem intramolecular aldol condensation/deprotection affording carbazoles **20**.



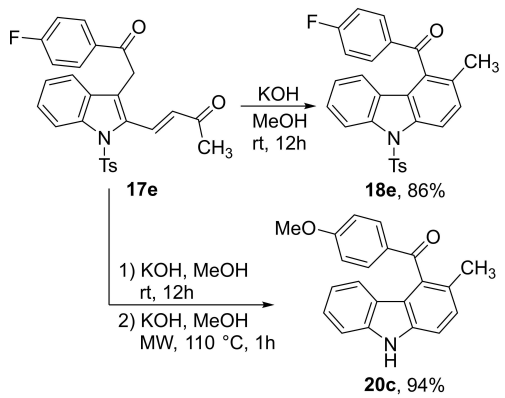
17a-d,f-h **20a-d,f-h**

17,20	R^1	Yield of **20**, [%][a]
a	Ph	89
b	4-$CH_3C_6H_4$	86
c	4-$CH_3OC_6H_4$	85
d	4-ClC_6H_4	91
f		82
g	2-naphthyl	83
h	2-thienyl	84

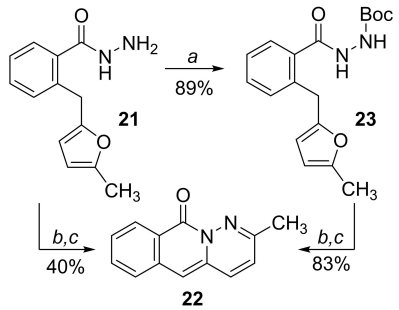
[a] Isolated yields.

the functionalized carbazoles **20a–d,f–h** were formed invariably in high yields.

It should be noted that the intramolecular aldol condensation and deprotection of indole **17e** afforded carbazole **20c** in a high yield as a result of competing nucleophilic aromatic substitution (Scheme 7).



Scheme 7. Tandem Intramolecular aldol condensation and deprotection affording carbazoles **18e** and **20c**.



Scheme 8. Synthesis of pyridazino[1,6-*b*]isoquinoline **22**. a) Boc_2O, CH_2Cl_2, rt; b) *m*-CPBA, CH_2Cl_2, 0 °C, 1 h; c) HCl, rt, 20 h.

To expand the scope of the oxidative rearrangement, we studied the transformation of 2-benzylfurans bearing a nucleophilic moiety separated from the phenyl group by one or more atoms. We were pleased to find that the oxidative rearrangement of the benzohydrazide **21** and subsequent cyclodehydration afforded pyridazino[1,6-*b*]isoquinoline **22**, whilst in low yield (Scheme 8). The reduced yield of **22** is presumably associated with the competitive oxidation of hydrazide moiety. To overcome this problem, we protected the compound **21** with Boc group and used the obtained hydrazide **23** for the title rearrangement. Indeed, the oxidation of **23** provided the target pyridazino[1,6-*b*]isoquinoline **22** in 83 % yield.

Conclusion

We showed that the oxidative transformation of benzylfurans developed by us earlier could be used to access various heterocyclic scaffolds via simple structural modifications of starting materials or manipulations with acylvinyl substituent at C(2) of obtained products.

Experimental Section

General information

^1H and ^{13}C NMR spectra were recorded with a «Bruker Avance III HD 400» (400 MHz for ^1H and 100 MHz for ^{13}C NMR) spectrometer at room temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$, ^1H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm; [D_6] DMSO, ^1H: δ = 2.50 ppm, ^{13}C: δ = 39.52 ppm). Coupling constants (*J*) are given in Hertz. Splitting patterns of an apparent multiplets associated with an averaged coupling constants were designated as s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet), dd (doublet of doublets) and br (broadened). IR spectra were measured in nujol or CaF_2 using a «FSM 1202» spectrophotometer. High-resolution mass measurements were carried out using a BrukermicroTOF-QTM ESI-TOF (Electro Spray Ionization/Time of Flight) mass spectrometer. GC/MS analysis was performed on an «Agilent 7890B» interfaced to an «Agilent 5977A» mass selective detector. Melting points were determined with a «Stuart SMP 30. Data sets for X-Ray diffraction were collected with a «New Xcalibur, Ruby» diffractometer. All reactions under microwave radiation were performed in Anton Paar® Microwave Synthesis Reactor «Monowave 300». Column chromatography was performed on silica gel Macherey Nagel (40–63 μm). All the reactions were carried out using freshly distilled and dry solvents from solvent stills.

(*Z*)-4-(3-Phenyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one (2a) was synthesized according to the reported procedure.[7]

(*E*)-4-(3-Phenyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one ((*E*)-2a)[18] was synthesized according to the reported procedure.[7]

Synthesis of (*E*)-4-(3-Phenyl-1*H*-indol-2-yl)but-3-en-2-one (3). To a stirred solution of indole *(E)*-**2a** (528 mg, 1.22 mmol) in MeOH (12 mL) was added KOH (276 mg, 4.9 mmol). The reaction mixture was stirred at room temperature until full dissolution of the solid. Then the reaction mixture was stirred at 60 °C in the aluminium block for 48 hours (The same result might be achieved by heating of the reaction mixture at 110 °C for 5 hours under microwave irradiation). After that, the reaction mixture was concentrated *in*

vacuo and the residue was purified by flash column chromatography (silica gel, eluent – ethyl acetate/petroleum ether = 1:10) to afford the compound **3**. Yield: 302 mg, 95%; pale beige solid; mp 216–217 °C (CH_2Cl_2/hexane = 1:9), lit 218–219 °C;[19] ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.80 (s, 1H), 7.60–7.40 (m, 8H), 7.31–7.28 (m, 1H), 7.11–7.07 (m, 1H), 6.89 (d, ^3J = 16.1 Hz, 1H), 2.28 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 197.1, 137.6, 133.5, 131.1, 130.1, 129.8 (2 C), 128.9 (2 C), 127.0, 126.7, 125.3, 124.9, 122.8, 120.3, 119.7, 111.7, 27.7 ppm.

Synthesis of (*Z*)-3-Bromo-4-(3-phenyl-1*H*-indol-2-yl)but-3-en-2-one (4). To the solution of indole **3** (131 mg, 0.5 mmol) and NH_4Br (65 mg, 1.2 equiv., 0.6 mmol) in methanol (4 mL) was added Oxone® (185 mg, 1.2 equiv., 0.6 mmol) in 4 equal portions within 20 min, and the resulting suspension was stirred at room temperature for 3 h (TLC control). After that, the reaction mixture was diluted with water (30 mL), extracted with ethyl acetate (2× 50 mL), washed with water (3×50 mL), brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue after concentration was dissolved in $CHCl_3$ (10 mL), treated with HCl (12 M, 45 μL, 1 equiv., 0.5 mmol) and stirred at room temperature for 5 min (TLC control). Upon completion, the reaction mixture was treated with crystalline $NaHCO_3$ (42 mg, 1 equiv., 0.5 mmol) and concentrated *in vacuo*. The product was purified by gradient column chromatography (basic aluminium oxide, eluent – petroleum ether/CH_2Cl_2 10:1 to 2:1). NOTE: *partial decomposition was detected when silica gel was used for column chromatography*. Yield: 131 mg, 77%; pale green solid; mp 137–138 °C (CH_2Cl_2/petroleum ether = 1:9); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.98 (br s, 1H), 8.16 (s, 1H), 7.75–7.73 (m, 1H), 7.57–7.42 (m, 6H), 7.42–7.38 (m, 1H), 7.24–7.17 (m, 1H), 2.48 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 137.3, 133.5, 130.6 (2 C), 130.0, 129.0 (2 C), 128.1, 128.0, 127.9, 126.7, 126.4, 121.4, 121.0, 119.7, 112.0, 26.3; HRMS (ESI$^+$): *m/z* calcd for $C_{18}H_{15}NBrO^+$: 340.0332 $[M+H]^+$; found: 340.0342.

Synthesis of (*Z*)-4-(3-Phenyl-1*H*-indol-2-yl)but-3-en-2-ol (5). To a stirred solution of indole *(Z)*-**2a** (208 mg, 0.5 mmol) in ethanol (20 mL) was added $NaBH_4$ portionwise at 0 °C. After addition was complete, the reaction mixture was heated at 80 °C in the aluminium block until yellow color of the solution disappeared (takes about 5–10 min). Upon completion, the reaction mixture was poured into water (50 mL), extracted with ethyl acetate (2× 50 mL), washed with water (50 mL), brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was dissolved in methanol (10 mL), and KOH (112 mg, 4 equiv., 2 mmol) was added at room temperature. The formed suspension was stirred at 60 °C in the aluminium block for 5 h. Upon completion, the reaction mixture was poured into water (50 mL), extracted with ethyl acetate (2×50 mL), washed with water (50 mL), brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2, passed through a pad of silica and concentrated *in vacuo*. Yield: 112 mg, 85%; pale beige oil; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.10 (br s, 1H), 7.57–7.55 (m, 1H), 7.49–7.44 (m, 5H), 7.32–7.29 (m, 1H), 7.18–7.15 (m, 1H), 7.06–7.03 (m, 1H), 6.39 (d, ^3J = 12.1 Hz, 1H), 5.75–5.68 (m, 1H), 5.30 (d, ^3J = 4.6 Hz, 1H), 4.71–4.65 (m, 1H), 1.20 (d, ^3J = 6.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 137.0, 136.2, 134.7, 131.3, 129.4 (2 C), 128.5 (2 C), 126.5, 126.0, 122.3, 119.7, 118.6, 118.4, 116.2, 111.7, 63.3, 23.6 ppm; HRMS (ESI$^+$): *m/z* calcd for $C_{18}H_{18}NO^+$: 264.1383 $[M+H]^+$; found: 264.1381.

(*E*)-3-(1-Tosyl-3-phenyl-1*H*-indol-2-yl)prop-2-enoic acid (6) was synthesized according to the reported procedure.[20]

Synthesis of (*E*)-3-(3-Phenyl-1-tosyl-1*H*-indol-2-yl)acrylaldehyde (7). To a stirred mixture of the acrylic acid **6** (292 mg, 0.7 mmol) and $CsCO_3$ (228 mg, 1 equiv.) in acetone (20 mL) was added methyl iodide (44 μL, 1 equiv.), and the formed suspension was stirred at 50 °C in the aluminium block for 4 h (TLC control). Upon completion, the reaction mixture was poured into water (50 mL), extracted with ethyl acetate (2×50 mL), washed with water (50 mL), brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to afford the ester. To a suspension of $LiAlH_4$ (30 mg, 1.12 equiv., 0.8 mmol) in Et_2O (20 mL) was added $AlCl_3$ (35 mg, 0.38 equiv., 0.27 mmol) in one portion at 0 °C. The resulting suspension was stirred for 5 min followed by the addition of obtained ester (300 mg, 0.71 mmol) portionwise at the same temperature. The reaction mixture was further stirred until full consumption of the starting ester (TLC control, ca. 1 h). Upon completion, the reaction mixture was diluted with water (20 mL) and extracted with Et_2O (2×20 mL). Combined organic fractions were washed with water (30 mL), brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. To the solution of alcohol (300 mg, 0.7 mmol) in CH_2Cl_2 (30 mL) was added MnO_2 (620 mg, 10 equiv., 7 mmol). The resulting suspension was stirred at room temperature for 24 h (TLC control). Upon completion, the reaction mixture was filtered through paper filter and concentrated to afford the final product with high NMR purity. If needed, the product could be recrystallized from ethyl acetate/petroleum ether mixture. Yield: 264 mg, 94%; pale yellow prisms; mp 140–141 °C (ethyl acetate/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.61 (d, ^3J = 7.8 Hz, 1H), 8.32–8.30 (m, 1H), 8.19 (d, ^3J = 16.1 Hz, 1H), 7.60 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.47–7.41 (m, 4H), 7.29–7.23 (m, 4H), 7.18 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 6.07 (dd, ^3J = 16.1 Hz, ^3J = 7.8 Hz, 1H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 145.5, 141.1, 137.9, 135.1, 133.0, 132.3, 131.2, 131.1, 130.2, 130.0 (2 C), 129.6 (2 C), 129.4 (2 C), 128.8, 127.4, 126.8 (2 C), 124.8, 121.2, 115.9, 21.7 ppm; HRMS (ESI$^+$): *m/z* calcd for $C_{24}H_{20}NSO_3^+$: 402.1158 $[M+H]^+$; found: 402.1170.

Synthesis of (*E*)-3-(3-Phenyl-1*H*-indol-2-yl)acrylic acid (8). To the solution of the acrylic acid **6** (417 mg, 1 mmol) in methanol/1,4-dioxane (1:1, 10 mL) was added KOH (224 mg, 4 equiv., 4 mmol) The resulting solution was stirred at 60 °C in the aluminium block for 5 h (TLC control). Upon completion, the reaction mixture was poured into water (50 mL), extracted with ethyl acetate (2× 50 mL), washed with water (50 mL), brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to afford the acid **8**. Yield: 260 mg, 99%; white solid; mp 226–227 °C (ethyl acetate/petroleum ether = 1:10); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.28 (br s, 1H), 11.72 (br s, 1H), 7.57–7.53 (m, 4H), 7.47–7.40 (m, 4H), 7.29–7.25 (m, 1H), 7.10–7.06 (m, 1H), 6.57 (d, ^3J = 15.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.6, 137.3, 133.5, 132.3, 130.0, 129.7 (2 C), 128.8 (2 C), 126.9, 126.6, 124.5, 121.7, 120.1, 119.6, 117.4, 111.5 ppm; HRMS (ESI$^+$): *m/z* calcd for $C_{17}H_{14}NO_2^+$: 264.1019 $[M+H]^+$; found: 264.1020.

Synthesis of (*E*)-3-(3-Phenyl-1*H*-indol-2-yl)prop-2-en-1-ol (9). To a solution of acrylic acid **8** (66 mg, 0.25 mmol) in THF (10 mL) was added TEA (3.5 μL, 1 equiv.) and ethyl chloroformate (24 μL, 1 equiv.) at 0 °C. The formed suspension was stirred for 20 min at the same temperature. Then $NaBH_4$ (30 mg, 3 equiv., 0.75 mmol) was added in one portion, and the formed suspension was stirred at room temperature for 20 h (TLC control). Upon completion, the reaction mixture was diluted with water (20 mL), treated with HCl (1 M, 3 mL) and extracted with CH_2Cl_2 (2×30 mL). Combined organic fractions were washed with water (30 mL), brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by column chromatography (silica gel, eluent – CH_2Cl_2/ethyl acetate, 2:1). Yield: 57 mg, 91%; beige oil; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.33 (br s, 1H), 7.52–7.44 (m, 5H), 7.40–7.37 (m, 1H), 7.35–7.31 (m, 1H), 7.16–7.12 (m, 1H), 7.02–6.99 (m, 1H), 6.69 (br d, ^3J = 16.1 Hz, 1H), 6.51 (dt, ^3J = 16.1 Hz, ^2J = 4.8 Hz, 1H), 4.86 (t, ^3J = 5.5 Hz, 1H), 4.16 (t, ^3J = 4.4 Hz, 2H) ppm; ^{13}C NMR

(100 MHz, DMSO-d_6): δ = 136.4, 134.6, 132.4, 131.0, 129.4 (2 C), 128.5 (2 C), 127.1, 125.9, 122.3, 119.4, 118.4, 117.9, 115.1, 110.9, 61.3 ppm; HRMS (ESI$^+$): *m/z* calcd for $C_{17}H_{16}NO^+$: 250.1226 [*M* + H]$^+$; found: 250.1225.

Synthesis of (4*E*)-3-Chloro-5-(3-phenyl-1-tosyl-1*H*-indol-2-yl) penta-2,4-dienal (10). $POCl_3$ was added to DMF (4 mL) at 0 °C, and the resulting mixture was stirred for 10 min. Indole *(E)*-**2a** (210 mg, 0.5 mmol) was added to the solution of Vilsmeier reagent at 0 °C, the formed solution was brought to 70 °C in the aluminium block and stirred for 1.5 h (TLC control). Upon completion, the reaction mixture was diluted with water (5 mL), treated with saturated aqueous solution of $NaHCO_3$ (1 mL), extracted with ethyl acetate (2 × 50 mL), washed with water (3 × 50 mL), brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by column chromatography (silica gel, eluent – petroleum ether/CH_2Cl_2 10:1 to 5:1). Yield: 217 mg, 94%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.13 (d, ^3J = 7.2 Hz, 1H), 8.33–8.31 (m, 1H), 8.14 (d, ^3J = 15.4 Hz, 1H), 7.63 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.46–7.40 (m, 4H), 7.33–7.25 (m, 4H), 7.19 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 6.28 (d, ^3J = 15.4 Hz, 1H), 5.80 (d, ^3J = 7.2 Hz, 1H), 2.35 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 148.9, 145.4, 137.7, 135.4, 132.8, 132.2, 131.0, 130.6, 130.0, 129.9 (2 C), 129.5, 129.3 (2 C), 128.5, 128.2, 127.0, 126.9, 126.8 (3 C), 124.7, 120.8, 115.8, 21.7 ppm; HRMS (ESI$^+$): *m/z* calcd for $C_{26}H_{21}NSClO_3^+$: 462.0925 [*M* + H]$^+$; found: 462.0926.

(*E*)-2-Methyl-4-(3-phenyl-1-tosyl-1*H*-indol-2-yl)but-3-en-2-ol (11) was synthesized according to the reported procedure.[7]

Synthesis of (*E*)-2-(3-Methylbuta-1,3-dien-1-yl)-3-phenyl-1-tosyl-1*H*-indole (12). To the solution of allyl alcohol **11** (100 mg, 0.24 mmol) and Et_3N (0.2 mL, 1.45 mmol) in anhydrous THF (0.5 mL) at 0 °C MsCl (0.05 mL, 0.73 mmol) was slowly added dropwise. The solution was allowed to warm to room temperature over 1.5 h and then refluxed for 30 min. The formed precipitate was filtered off and washed with ethyl acetate. Concentrated filtrate was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:10) to afford the diene **12**. Yield: 81 mg, 82%; pale beige oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30–8.28 (m, 1H), 7.62 (AA'BB'-system, ^3J = 8.3 Hz, 2H), 7.43–7.39 (m, 2H), 7.35–7.31 (m, 5H), 7.23–7.19 (m, 1H), 7.15 (AA'BB'-system, ^3J = 8.3 Hz, 2H), 7.06 (d, ^3J = 16.3 Hz, 1H), 6.16 (d, ^3J = 16.3 Hz, 1H), 4.96 (s, 1H), 4.69 (s, 1H), 2.33 (s, 3H), 1.97 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 142.1, 139.2, 136.9, 135.7, 134.8, 133.7, 131.3, 130.2 (2 C), 129.7 (2 C), 128.8 (2 C), 127.4, 127.0 (2 C), 125.2, 124.1, 123.7, 119.9, 118.4, 117.9, 115.5, 21.7, 18.4 ppm; HRMS (ESI$^+$): *m/z* calcd for $C_{26}H_{24}NSO_2^+$: 414.1522 [*M* + H]$^+$; found: 414.1535.

Synthesis of (*E*)-2-{2-[1,4-Dimethyl-2-(3-phenyl-1-tosyl-1*H*-indol-2-yl)cyclohex-3-en-1-yl]vinyl}-3-phenyl-1-tosyl-1*H*-indole (13). To the solution of diene **12** (104 mg, 0.25 mmol) in CH_2Cl_2 (5 mL) was added $Cu(OTf)_2$ (37 mg, 0.5 equiv., 0.125 mmol). The resulting mixture was stirred at 40 °C in the aluminium block for 120 h (TLC control). Upon completion, the reaction mixture was dry-loaded onto silica gel. The product was purified by gradient column chromatography (silica gel, petroleum ether/CH_2Cl_2 10:1 to 5:1). If needed, the product could be recrystallized from benzene/MeOH mixture. Yield: 93 mg, 45%; colorless plates; mp 258–259 °C (benzene/MeOH). Product was obtained as a mixture of two diastereomers in 4:1 ratio. NMR data for the major isomer are given. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18–8.16 (m, 1H), 8.12–8.10 (m, 1H), 7.66 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.47 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.36–7.35 (m, 1H), 7.29–7.27 (m, 2H), 7.22–7.20 (m, 2H), 7.19–7.16 (m, 3H), 7.15–7.12 (m, 3H), 7.11–7.06 (m, 1H), 7.03 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 6.96–6.87 (m, 6H), 6.81–6.79 (m, 1H), 5.91 (d, ^3J = 16.4 Hz, 1H), 4.82 (br s, 1H), 4.42 (br s, 1H), 2.34 (s, 3H), 2.29 (s, 3H), 1.38–1.30 (m, 2H), 1.22 (s, 3H), 1.21 (s, 3H), 1.12–1.05 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.4, 144.5, 144.3, 137.7, 136.8, 136.5, 136.1, 135.9, 135.6, 134.3, 134.2, 133.7, 133.6, 131.9, 130.2 (2C), 129.9 (2C), 129.7 (4C), 128.5 (2C), 127.7, 127.1 (2C), 126.9, 126.7, 126.3 (4C), 124.8, 124.5, 123.9, 123.7, 122.9, 121.7, 120.0, 119.6, 116.2, 115.8, 115.2, 43.4, 40.7, 31.2, 26.6, 24.2, 23.3, 21.7 (2C) ppm; HRMS (ESI$^+$): *m/z* calcd for $C_{52}H_{47}N_2S_2O_4^+$: 827.2972 [*M* + H]$^+$; found: 827.2975.

Synthesis of 2-tosylaminochalcones 14a–h. The 2-tosylaminochalcones **14** were synthesized according to the reported procedures.[17]

(*E*)-*N*-{2-[3-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-3-oxoprop-1-en-1-yl]phenyl}-4-methylbenzenesulfonamide (14f). Yield: 539 mg, 62%; white solid; mp 151–152 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, ^3J = 15.4 Hz, 1H), 7.35 (AA'BB'-system, ^3J = 8.1 Hz, 2H), 7.32–7.26 (m, 4H), 7.18–7.14 (m, 1H), 7.12 (br s, 1H), 7.05–7.01 (m, 1H), 6.95–6.89 (m, 3H), 6.71–6.69 (m, 1H), 4.12–4.10 (m, 2H), 4.08–4.06 (m, 2H), 1.96 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.1, 148.3, 143.9, 143.6, 138.4, 136.3, 135.5, 131.6, 131.1, 131.0, 129.8 (2 C), 127.7, 127.4 (2 C), 127.3, 127.1, 124.4, 122.9, 118.2, 117.5, 64.9, 64.3, 21.4 ppm; IR (nujol) ν_{max} = 3167, 1647, 1610, 1578, 1510, 1329, 1290, 1167 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{24}H_{22}NSO_5^+$: 436.1213 [*M* + H]$^+$; found: 436.1208.

(*E*)-4-Methyl-*N*-{2-[3-(naphthalen-2-yl)-3-oxoprop-1-en-1-yl] phenyl}benzenesulfonamide (14g). Yield: 632 mg, 74%; white solid; mp 158–159 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (br s, 1H), 8.03–8.00 (m, 1H), 7.98–7.96 (m, 1H), 7.91–7.88 (m, 1H), 7.87–7.85 (m, 1H), 7.79 (d, ^3J = 15.5 Hz, 1H), 7.66–7.64 (m, 1H), 7.62–7.53 (m, 4H), 7.49–7.47 (m, 1H), 7.41–7.34 (m, 3H), 7.30–7.27 (m, 1H), 7.10 (AA'BB'-system, ^3J = 8.0 Hz, 2H), 2.11 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.1, 144.0, 139.3 (2 C), 136.1, 135.7, 135.5, 135.1, 132.7, 131.2 (2 C), 130.4, 129.8 (2 C), 129.7, 128.8, 128.7, 127.9, 127.8, 127.4 (2 C), 127.3, 127.0, 124.6, 124.5, 21.4 ppm; IR (nujol) ν_{max} = 3188, 1649, 1589, 1330, 1280 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{26}H_{22}NSO_3^+$: 428.1315 [*M* + H]$^+$; found: 428.1332.

General Procedure for the Synthesis of 2-(2-Aminobenzyl)furans 16. To a solution of corresponding 2-tosylaminochalcone **14** (1 mmol) and 2-methylfuran **15** (265 μL, 3 mmol) in CH_3CN (4 mL) was added TMSCl (25 μL, 0.2 mmol). The resulting solution was stirred at 50 °C in the aluminium block for 24 h (TLC control). Upon completion, the reaction mixture was concentrated *in vacuo*. The product was purified by column chromatography (silica gel, petroleum ether/CH_2Cl_2, 3:1). The products were recrystallized from appropriate solvents mixture.

4-Methyl-*N*-(2-(1-(5-methylfuran-2-yl)-3-oxo-3-phenylpropyl) phenyl)benzenesulfonamide (16a). Yield: 422 mg, 92%; white solid; mp 174–175 °C (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (br s, 1H), 7.93–7.91 (m, 2H), 7.69 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.57–7.52 (m, 2H), 7.45–7.41 (m, 2H), 7.25–7.23 (m, 1H), 7.20–7.16 (m, 1H), 7.12–7.10 (m, 3H), 5.76 (d, ^3J = 2.8 Hz, 1H), 5.51 (d, ^3J = 2.8 Hz, 1H), 4.59 (dd, ^3J = 9.4 Hz, ^3J = 3.7 Hz, 1H), 3.72 (dd, ^2J = 18.4 Hz, ^3J = 3.7 Hz, 1H), 3.51 (dd, ^2J = 18.4 Hz, ^3J = 9.4 Hz, 1H), 2.28 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.9, 153.9, 151.2, 143.2, 137.8, 136.4, 136.0, 134.6, 133.8, 129.7 (2 C), 128.8 (2 C), 128.7, 128.4 (2 C), 127.8, 127.3 (2 C), 126.5, 126.4, 107.2, 106.2, 44.6, 33.9, 21.5, 13.6 ppm; IR (nujol) ν_{max} = 3244, 1666, 1327, 1281, 1221, 1155 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{27}H_{26}NSO_4^+$: 460.1577 [*M* + H]$^+$; found: 460.1578.

4-Methyl-*N*-(2-(1-(5-methylfuran-2-yl)-3-oxo-3-(4-methylphenyl)-propyl)phenyl)benzenesulfonamide (16b). Yield: 406 mg, 86%; pale yellow solid; mp 171–172 °C (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (br s, 1H), 7.82 (AA'BB'-system, ^3J =

8.2 Hz, 2H), 7.69 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.54–7.52 (m, 1H), 7.24–7.22 (m, 3H), 7.19–7.16 (m, 1H), 7.12–7.08 (m, 3H), 5.76 (d, ^3J = 2.8 Hz, 1H), 5.50 (d, ^3J = 2.8 Hz, 1H), 4.57 (dd, ^3J = 9.6 Hz, ^3J = 3.7 Hz, 1H), 3.69 (dd, ^2J = 18.3 Hz, ^3J = 3.7 Hz, 1H), 3.49 (dd, ^2J = 18.3 Hz, ^3J = 9.6 Hz, 1H), 2.39 (s, 3H), 2.29 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.5, 154.0, 151.2, 144.8, 143.2, 137.9, 136.1, 134.6, 133.9, 129.7 (2 C), 129.5 (2 C), 128.7, 128.5 (2 C), 127.7, 127.3 (2 C), 126.5, 126.4, 107.2, 106.1, 44.6, 33.9, 21.8, 21.5, 13.6 ppm; IR (nujol) ν_{max} = 3259, 1663, 1607, 1560, 1321, 1283, 1221, 1153 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{28}H_{28}NSO_4^+$: 474.1734 $[M+H]^+$; found: 474.1734.

***N*-(2-(3-(4-Methoxyphenyl)-1-(5-methylfuran-2-yl)-3-oxopropyl)-phenyl)-4-methylbenzenesulfonamide (16c).** Yield: 430 mg, 88%; pale yellow solid; mp 208–209 °C (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (br s, 1H), 7.90 (AA'BB'-system, ^3J = 8.8 Hz, 2H), 7.69 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.54–7.52 (m, 1H), 7.23–7.21 (m, 1H), 7.19–7.14 (m, 1H), 7.11–7.07 (m, 3H), 6.89 (AA'BB'-system, ^3J = 8.8 Hz, 2H), 5.75 (d, ^3J = 2.8 Hz, 1H), 5.49 (d, ^3J = 2.8 Hz, 1H), 4.56 (dd, ^3J = 9.7 Hz, ^3J = 3.6 Hz, 1H), 3.85 (s, 3H), 3.66 (dd, ^2J = 18.2 Hz, ^3J = 3.6 Hz, 1H), 3.47 (dd, ^2J = 18.2 Hz, ^3J = 9.7 Hz, 1H), 2.29 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.4, 164.2, 154.1, 151.1, 143.1, 137.9, 136.2, 134.6, 130.7 (2 C), 129.6 (2 C), 129.4, 128.7, 127.7, 127.3 (2 C), 126.4, 126.3, 114.0 (2 C), 107.1, 106.1, 55.6, 44.4, 33.9, 21.5, 13.6 ppm; IR (nujol) ν_{max} = 3225, 1661, 1601, 1319, 1267, 1221, 1173, 1151 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{28}H_{28}NSO_5^+$: 490.1683 $[M+H]^+$; found: 490.1681.

***N*-{2-[3-(4-Chlorophenyl)-1-(5-methylfuran-2-yl)-3-oxopropyl] phenyl}-4-methylbenzenesulfonamide (16d).** Yield: 430 mg, 87%; white solid; mp 164–165 °C (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (br s, 1H), 7.85 (AA'BB'-system, ^3J = 8.5 Hz, 2H), 7.67 (AA'BB'-system, ^3J = 8.1 Hz, 2H), 7.51–7.49 (m, 1H), 7.40 (AA'BB'-system, ^3J = 8.5 Hz, 2H), 7.24–7.22 (m, 1H), 7.20–7.16 (m, 1H), 7.12–7.10 (m, 3H), 5.76 (d, ^3J = 2.8 Hz, 1H), 5.51 (d, ^3J = 2.8 Hz, 1H), 4.59 (dd, ^3J = 9.4 Hz, ^3J = 4.0 Hz, 1H), 3.69 (dd, ^2J = 18.3 Hz, ^3J = 4.0 Hz, 1H), 3.47 (dd, ^2J = 18.3 Hz, ^3J = 9.4 Hz, 1H), 2.29 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 153.6, 151.3, 143.3, 140.4, 137.8, 135.9, 134.7, 134.5, 129.8 (2 C), 129.7 (2 C), 129.1 (2 C), 128.7, 127.9, 127.3 (2 C), 126.6, 126.5, 107.3, 106.2, 44.5, 34.0, 21.5, 13.6 ppm; IR (nujol) ν_{max} = 3294, 1689, 1595, 1497, 1321, 1209, 1159, 1094 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{27}H_{25}NSClO_4^+$: 494.1187 $[M+H]^+$; found: 494.1189.

***N*-{2-[3-(4-Fluorophenyl)-1-(5-methylfuran-2-yl)-3-oxopropyl] phenyl}-4-methylbenzenesulfonamide (16e).** Yield: 400 mg, 84%; white solid; mp 167–168 °C (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (br s, 1H), 7.97–7.93 (m, 2H), 7.68 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.52–7.50 (m, 1H), 7.25–7.23 (m, 1H), 7.20–7.16 (m, 1H), 7.12–7.08 (m, 5H), 5.76 (d, ^3J = 2.8 Hz, 1H), 5.50 (d, ^3J = 2.8 Hz, 1H), 4.58 (dd, ^3J = 9.5 Hz, ^3J = 3.7 Hz, 1H), 3.70 (dd, ^2J = 18.3 Hz, ^3J = 3.7 Hz, 1H), 3.49 (dd, ^2J = 18.3 Hz, ^3J = 9.5 Hz, 1H), 2.29 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.3, 166.3 (d, $^1J_{CF}$ = 256.0 Hz), 153.7, 151.3, 143.3, 137.8, 136.0, 134.6, 132.8 (d, $^4J_{CF}$ = 2.9 Hz), 131.1 (d, $^3J_{CF}$ = 9.4 Hz, 2 C), 129.7 (2 C), 128.7, 127.9, 127.3 (2 C), 126.6, 126.5, 115.9 (d, $^2J_{CF}$ = 21.9 Hz, 2 C), 107.3, 106.2, 44.5, 34.0, 21.5, 13.6 ppm; IR (nujol) ν_{max} = 3275, 1688, 1593, 1489, 1325, 1286, 1238, 1213, 1163, 1092 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{27}H_{25}NSFO_4^+$: 478.1483 $[M+H]^+$; found: 478.1484.

***N*-{2-[3-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-1-(5-methylfuran-2-yl)-3-oxopropyl]phenyl}-4-methylbenzenesulfonamide (16f).** Yield: 439 mg, 85%; pale yellow solid; mp 201–202 °C (ethyl acetate/1.4-dioxane = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (br s, 1H), 7.68 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.54–7.52 (m, 1H), 7.45–7.44 (m, 2H), 7.22–7.20 (m, 1H), 7.18–7.14 (m, 1H), 7.11–7.07 (m, 3H), 6.87–6.85 (m, 1H), 5.75 (d, ^3J = 2.8 Hz, 1H), 5.48 (d, ^3J = 2.8 Hz, 1H), 4.54 (dd, ^3J = 9.6 Hz, ^3J = 3.7 Hz, 1H), 4.29–4.28 (m, 2H), 4.25–4.24 (m, 2H), 3.62 (dd, ^2J = 18.2 Hz, ^3J = 3.7 Hz, 1H), 3.42 (dd, ^2J = 18.2 Hz, ^3J = 9.6 Hz, 1H), 2.29 (s, 3H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.3, 154.0, 151.1, 148.7, 143.5, 143.1, 137.8, 136.1, 134.6, 130.2, 129.6 (2 C), 128.7, 127.7, 127.3 (2 C), 126.4, 126.3, 122.5, 117.9, 117.4, 107.1, 106.1, 64.9, 64.2, 44.4, 33.9, 21.5, 13.6 ppm; IR (nujol) ν_{max} = 3248, 1655, 1603, 1583, 1510, 1489, 1317, 1296, 1213, 1149, 1088, 1067 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{29}H_{28}NSO_6^+$: 518.1632 $[M+H]^+$; found: 518.1642.

4-Methyl-*N*-{2-[1-(5-methylfuran-2-yl)-3-(naphthalen-2-yl)-3-oxopropyl]phenyl}benzenesulfonamide (16g). Yield: 453 mg, 89%; white solid; mp 178–179 °C (decomp.) (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 8.44 (br s, 1H), 7.98–7.93 (m, 2H), 7.87–7.85 (m, 2H), 7.69 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.62–7.58 (m, 1H), 7.56–7.53 (m, 2H), 7.29–7.27 (m, 1H), 7.21–7.17 (m, 1H), 7.14–7.10 (m, 3H), 5.77 (d, ^3J = 2.8 Hz, 1H), 5.52 (d, ^3J = 2.8 Hz, 1H), 4.63 (dd, ^3J = 9.6 Hz, ^3J = 3.7 Hz, 1H), 3.86 (dd, ^2J = 18.3 Hz, ^3J = 3.7 Hz, 1H), 3.66 (dd, ^2J = 18.3 Hz, ^3J = 9.6 Hz, 1H), 2.27 (s, 3H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.8, 153.9, 151.2, 143.2, 137.7, 136.1, 136.0, 134.5, 133.6, 132.5, 130.3, 129.8, 129.7 (2 C), 129.0, 128.8, 128.7, 127.9, 127.8, 127.3 (2 C), 127.1, 126.6, 126.5, 123.8, 107.3, 106.2, 44.8, 33.9, 21.5, 13.7 ppm; IR (nujol) ν_{max} = 3284, 1670, 1626, 1601, 1582, 1560, 1491, 1323, 1288, 1157, 1090 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{31}H_{28}NSO_4^+$: 510.1734 $[M+H]^+$; found: 510.1743.

4-Methyl-*N*-{2-[1-(5-methylfuran-2-yl)-3-oxo-3-(thiophen-2-yl) propyl]phenyl}benzenesulfonamide (16h). Yield: 381 mg, 82%; white solid; mp 170–171 °C (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (br s, 1H), 7.70 (d, ^3J = 3.8 Hz, 1H), 7.68 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.63 (d, ^3J = 4.8 Hz, 1H), 7.51–7.49 (m, 1H), 7.24–7.22 (m, 1H), 7.19–7.16 (m, 1H), 7.13–7.08 (m, 4H), 5.76 (d, ^3J = 2.8 Hz, 1H), 5.53 (d, ^3J = 2.8 Hz, 1H), 4.57 (dd, ^3J = 9.4 Hz, ^3J = 4.1 Hz, 1H), 3.67 (dd, ^2J = 17.8 Hz, ^3J = 4.1 Hz, 1H), 3.41 (dd, ^2J = 17.8 Hz, ^3J = 9.4 Hz, 1H), 2.29 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 153.6, 151.3, 143.4, 143.2, 137.8, 135.8, 134.5 (2C), 132.7, 129.7 (2 C), 128.7, 128.3, 127.9, 127.3 (2 C), 126.6, 126.5, 107.3, 106.2, 45.0, 34.0, 21.5, 13.6 ppm; IR (nujol) ν_{max} = 3238, 1641, 1412, 1325, 1285, 1153 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{25}H_{24}NS_2O_4^+$: 466.1141 $[M+H]^+$; found: 466.1137.

General Procedure for the Synthesis of 2-(2-Acylvinyl)indoles (17a–h)[7]. *m*-CPBA (77% w/w, 135 mg, 0.6 mmol) was added to a solution of a corresponding 2-(2-aminobenzyl)furan **16** (0.5 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 1 h. Then TFA (3.8 μL, 0.05 mmol) was added. The reaction mixture was allowed to reach room temperature and stirred for 20 h. Thereafter, the reaction mixture was cooled to −10 °C for 15 min. This was accompanied by precipitation of *m*-chlorobenzoic acid. Precipitate was filtered off using rapid vacuum filtration and washed with cooled CH_2Cl_2 (2 × 2 mL). The combined filtrates were concentrated *in vacuo* and the residue was purified by flash column chromatography (silica gel, eluent – petroleum ether/CH_2Cl_2, 9:1 to 1:1) to afford the corresponding indoles. The products were recrystallized from ethyl acetate.

(*E*)-4-[3-(2-Oxo-2-phenylethyl)-1-tosyl-1*H*-indol-2-yl]but-3-en-2-one (17a). Yield: 196 mg, 86%; white solid; mp 168–169 °C (decomp.) (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20–8.18 (m, 1H), 8.06 (d, ^3J = 16.5 Hz, 1H), 8.00–7.98 (m, 2H), 7.63–7.59 (m, 1H), 7.56 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.51–7.47 (m, 2H), 7.38–7.34 (m, 1H), 7.31–7.29 (m, 1H), 7.23–7.21 (m, 1H), 7.16 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 6.26 (d, ^3J = 16.5 Hz, 1H), 4.40 (s, 2H), 2.40 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 195.6, 145.3, 137.4, 136.5, 135.1, 134.2, 133.9, 133.8, 131.7, 130.9, 129.9 (2 C), 129.0 (2 C), 128.4 (2 C), 126.8 (2 C), 126.6, 124.5, 120.2,

120.1, 115.5, 35.6, 27.0, 21.7 ppm; IR (nujol) ν_{max} = 1670, 1618, 1595, 1362, 1259, 1223, 1171 cm^{-1}; HRMS (ESI^+): *m/z* calcd for $C_{27}H_{24}NSO_4^+$: 458.1421 $[M+H]^+$; found: 458.1421.

(*E*)-4-{3-[2-Oxo-2-(p–tolyl)ethyl]-1-tosyl-1*H*-indol-2-yl}but-3-en-2-one (17b). Yield: 198 mg, 84%; gray solid; mp 141–142 °C (decomp.) (ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.19–8.17 (m, 1H), 8.07 (d, ^3J = 16.5 Hz, 1H), 7.89 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.56 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.37–7.33 (m, 1H), 7.31–7.27 (m, 3H), 7.22–7.18 (m, 1H), 7.16 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 6.27 (d, ^3J = 16.5 Hz, 1H), 4.38 (s, 2H), 2.43 (s, 3H), 2.41 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.3, 195.2, 145.3, 144.8, 137.4, 135.0, 134.1, 134.0, 133.9, 131.7, 131.0, 129.9 (2 C), 129.7 (2 C), 128.6 (2 C), 126.8 (2 C), 126.6, 124.4, 120.5, 120.1, 115.4, 35.5, 27.0, 21.8, 21.7 ppm; IR (nujol) ν_{max} = 1689, 1663, 1605, 1325, 1250, 1173, 1130 cm^{-1}; HRMS (ESI^+): *m/z* calcd for $C_{28}H_{26}NSO_4^+$: 472.1577 $[M+H]^+$; found: 472.1580.

(*E*)-4-{3-[2-(4-Methoxyphenyl)-2-oxoethyl]-1-tosyl-1*H*-indol-2-yl}but-3-en-2-one (17c). Yield: 217 mg, 89%; pale yellow solid; mp 193–195 °C (decomp.) (ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.19–8.16 (m, 1H), 8.07 (d, ^3J = 16.5 Hz, 1H), 7.97 (AA'BB'-system, ^3J = 8.8 Hz, 2H), 7.56 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.36–7.33 (m, 1H), 7.31–7.29 (m, 1H), 7.22–7.18 (m, 1H), 7.16 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 6.95 (AA'BB'-system, ^3J = 8.8 Hz, 2H), 6.28 (d, ^3J = 16.5 Hz, 1H), 4.35 (s, 2H), 3.88 (s, 3H), 2.41 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 194.1, 164.1, 145.3, 137.3, 135.0, 134.1, 134.0, 131.6, 131.0, 130.8 (2 C), 129.9 (2 C), 129.4, 126.7 (2 C), 126.6, 124.4, 120.7, 120.2, 115.4, 114.2 (2 C), 55.7, 35.3, 27.0, 21.7 ppm; IR (nujol) ν_{max} = 1682, 1599, 1576, 1364, 1319, 1248, 1219, 1186, 1175, 1138 cm^{-1}; HRMS (ESI^+): *m/z* calcd for $C_{28}H_{26}NSO_5^+$: 488.1526 $[M+H]^+$; found: 488.1536.

(*E*)-4-{3-[2-(4-Chlorophenyl)-2-oxoethyl]-1-tosyl-1*H*-indol-2-yl}but-3-en-2-one (17d). Yield: 226 mg, 92%; pale yellow solid; mp 137–138 °C (decomp.) (ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.20–8.18 (m, 1H), 8.05 (d, ^3J = 16.5 Hz, 1H), 7.91 (AA'BB'-system, ^3J = 8.6 Hz, 2H), 7.55 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.45 (AA'BB'-system, ^3J = 8.6 Hz, 2H), 7.38–7.34 (m, 1H), 7.29–7.27 (m, 1H), 7.23–7.20 (m, 1H), 7.16 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 6.23 (d, ^3J = 16.5 Hz, 1H), 4.36 (s, 2H), 2.41 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 194.5, 145.4, 140.4, 137.4, 135.1, 134.7, 134.2, 133.9, 131.9, 130.8, 130.0 (2 C), 129.8 (2 C), 129.4 (2 C), 126.8 (2 C), 126.7, 124.5, 120.0, 119.8, 115.5, 35.7, 26.9, 21.7 ppm; IR (nujol) ν_{max} = 1678, 1587, 1250, 1213, 1173, 1088 cm^{-1}; HRMS (ESI^+): *m/z* calcd for $C_{27}H_{23}NSClO_4^+$: 492.1031 $[M+H]^+$; found: 492.1041.

(*E*)-4-{3-[2-(4-Fluorophenyl)-2-oxoethyl]-1-tosyl-1*H*-indol-2-yl}but-3-en-2-one (17e). Yield: 209 mg, 88%; gray solid; mp 169–170 °C (decomp.) (ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.26–8.24 (m, 1H), 8.12 (d, ^3J = 16.5 Hz, 1H), 8.09–8.06 (m, 2H), 7.62 (AA'BB'-system, ^3J = 8.0 Hz, 2H), 7.44–7.41 (m, 1H), 7.36–7.32 (m, 1H), 7.30–7.28 (m, 1H), 7.24–7.19 (m, 4H), 6.30 (d, ^3J = 16.5 Hz, 1H), 4.43 (s, 2H), 2.48 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 194.0, 165.3 (d, $^1J_{CF}$ = 256 Hz), 145.4, 137.4, 135.1, 134.2, 133.9, 132.9 (d, $^4J_{CF}$ = 3.0 Hz), 131.8, 131.1 (d, $^3J_{CF}$ = 9.4 Hz, 2 C), 130.8, 130.0 (2 C), 126.8 (2 C), 126.7, 124.5, 120.1, 120.0, 116.2 (d, $^2J_{CF}$ = 22.0 Hz, 2 C), 115.5, 35.6, 26.9, 21.7 ppm; IR (nujol) ν_{max} = 1695, 1663, 1597, 1508, 1364, 1327, 1256, 1232, 1215, 1173, 1132 cm^{-1}; HRMS (ESI^+): *m/z* calcd for $C_{27}H_{23}NSFO_4^+$: 476.1326 $[M+H]^+$; found: 476.1327.

(*E*)-4-{3-[2-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-oxoethyl]-1-tosyl-1H-indol-2-yl}but-3-en-2-one (17f). Yield: 216 mg, 84%; gray solid; mp 171–172 °C (decomp.) (ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.18–8.16 (m, 1H), 8.06 (d, ^3J = 16.5 Hz, 1H), 7.56–7.51 (m, 4H), 7.36–7.32 (m, 1H), 7.31–7.29 (m, 1H), 7.22–7.18 (m, 1H), 7.16 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 6.93–6.91 (m, 1H), 6.26 (d, ^3J = 16.5 Hz, 1H), 4.32 (s, 2H), 4.33–4.31 (m, 2H), 4.29–4.27 (m, 2H), 2.41 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 193.9, 148.7, 145.3, 143.7, 137.4, 135.1, 134.1, 134.0, 131.7, 131.0, 130.2, 129.9 (2 C), 126.8 (2 C), 126.6, 124.4, 122.6, 120.6, 120.2, 118.0, 117.6, 115.4, 64.9, 64.3, 35.3, 27.0, 21.7 ppm; IR (nujol) ν_{max} = 1672, 1578, 1506, 1364, 1321, 1286, 1261, 1213, 1175, 1119 cm^{-1}; HRMS (ESI^+): *m/z* calcd for $C_{29}H_{26}NSO_6^+$: 516.1475 $[M+H]^+$; found: 516.1477.

(*E*)-4-{3-[2-(Naphthalen-2-yl)-2-oxoethyl]-1-tosyl-1*H*-indol-2-yl}but-3-en-2-one (17g). Yield: 212 mg, 83%; pale beige solid; mp 170–171 °C (decomp.) (ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.55 (s, 1H), 8.21–8.19 (m, 1H), 8.10 (d, ^3J = 16.5 Hz, 1H), 8.03–8.01 (m, 1H), 7.98–7.96 (m, 1H), 7.92–7.88 (m, 2H), 7.65–7.56 (m, 4H), 7.38–7.34 (m, 2H), 7.24–7.20 (m, 1H), 7.15 (AA'BB'-system, ^3J = 8.1 Hz, 2H), 6.34 (d, ^3J = 16.5 Hz, 1H), 4.55 (s, 2H), 2.42 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 195.6, 145.3, 137.3, 136.0, 134.9, 134.1, 134.0, 133.6, 132.6, 131.7, 130.9, 130.3, 129.9 (2 C), 129.8, 129.0, 128.9, 128.0, 127.2, 126.7 (2 C), 126.6, 124.5, 123.9, 120.4, 120.2, 115.4, 35.7, 27.0, 21.7 ppm; IR (nujol) ν_{max} = 1678, 1595, 1358, 1279, 1248, 1167, 1132 cm^{-1}; HRMS (ESI^+): *m/z* calcd for $C_{31}H_{26}NSO_4^+$: 508.1577 $[M+H]^+$; found: 508.1586.

(*E*)-4-{3-[2-Oxo-2-(thiophen-2-yl)ethyl]-1-tosyl1*H*-indol-2-yl}but-3-en-2-one (17h). Yield: 197 mg, 85%; gray solid; mp 179–180 °C decomp. (ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.19–8.17 (m, 1H), 8.07 (d, ^3J = 16.5 Hz, 1H), 7.80 (d, ^3J = 3.7 Hz, 1H), 7.68 (d, ^3J = 4.9 Hz, 1H), 7.55 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.38–7.34 (m, 2H), 7.24–7.20 (m, 1H), 7.17–7.15 (m, 3H), 6.35 (d, ^3J = 16.5 Hz, 1H), 4.32 (s, 2H), 2.43 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.3, 188.4, 145.4, 143.3, 137.2, 134.9, 134.7, 134.3, 133.9, 132.6, 131.8, 130.8, 130.0 (2 C), 128.5, 126.7 (2 C), 126.6, 124.5, 120.2, 119.7, 115.4, 36.3, 27.1, 21.7 ppm; IR (nujol) ν_{max} = 1657, 1618, 1593, 1558, 1515, 1411, 1364, 1263, 1242, 1227, 1169 cm^{-1}; HRMS (ESI^+): *m/z* calcd for $C_{25}H_{22}NS_2O_4^+$: 464.0985 $[M+H]^+$; found: 464.0990.

General Procedure for the Synthesis of (3-Methyl-9-tosyl-9*H*-carbazol-4-yl)(aryl)methanones 18. To a solution of (*E*)-4-[3-(2-oxo-2-arylethyl)-1-tosyl-1*H*-indol-2-yl]but-3-en-2-one **17** (0.2 mmol) in MeOH (4 mL) was added KOH (44.2 mg, 0.8 mmol) at room temperature. The resulting solution was stirred at the same temperature overnight (TLC control). After completion of the reaction, saturated aqueous solution of NH_4Cl (1 mL) was added dropwise. After that, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography (silica gel, eluent – petroleum ether/CH_2Cl_2, 9:1) to afford the *N*-tosylcarbazoles **18**.

(3-Methyl-9-tosyl-9*H*-carbazol-4-yl)(phenyl)methanone (18a). Yield: 83 mg, 95% yield; gray oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, ^3J = 8.5 Hz, 1H), 8.32 (d, ^3J = 8.5 Hz, 1H), 7.84 (AA'BB'-system, ^3J = 7.6 Hz, 2H), 7.69 (AA'BB'-system, ^3J = 8.1 Hz, 2H), 7.59–7.56 (m, 1H), 7.43–7.40 (m, 2H), 7.39–7.37 (m, 2H), 7.35–7.33 (m, 1H), 7.12 (AA'BB'-system, ^3J = 8.1 Hz, 2H), 7.10–7.06 (m, 1H), 2.29 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.0, 145.2, 139.0, 137.0, 136.8, 135.1, 134.3, 133.4, 130.2, 129.9 (2 C), 129.8 (2 C), 129.5, 129.2 (2 C), 127.5, 126.7 (2 C), 124.8, 124.1, 123.3, 122.1, 115.8, 115.2, 21.6, 18.8 ppm; IR (nujol) ν_{max} = 1666, 1595, 1421, 1312, 1277, 1219, 1173, 1155 cm^{-1}; HRMS (ESI^+): *m/z* calcd for $C_{27}H_{22}NSO_3^+$: 440.1315 $[M+H]^+$; found: 440.1310.

(4-Fluorophenyl)(3-methyl-9-tosyl-9*H*-carbazol-4-yl)methanone (18e). Yield: 78 mg, 86%; transparent oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, ^3J = 8.6 Hz, 1H), 8.32 (d, ^3J = 8.4 Hz, 1H), 7.87–7.84 (m, 2H), 7.69 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 7.42–7.37 (m, 2H), 7.32–7.30 (m, 1H), 7.14–7.05 (m, 5H), 2.30 (s, 3H), 2.25 (s, 3H)

ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.4, 166.6 (d, $^1J_{CF}$ = 257.1 Hz), 145.2, 139.1, 137.0, 135.1, 133.3 (d, $^4J_{CF}$ = 2.8 Hz), 133.0, 132.6 (d, $^3J_{CF}$ = 9.6 Hz, 2 C), 130.2, 129.9 (2 C), 129.6, 127.7, 126.7 (2 C), 124.7, 124.1, 123.2, 122.0, 116.5 (d, $^2J_{CF}$ = 22.1 Hz, 2 C), 115.9, 115.3, 21.6, 18.8 ppm; HRMS (ESI$^+$): *m/z* calcd for $C_{27}H_{21}FNSO_3^+$: 458.1221 $[M+H]^+$; found: 458.1220.

Synthesis of 3-Methyl-9-tosyl-9*H*-carbazole (19 a). To the solution of (*E*)-4-(3-(2-oxo-2-phenylethyl)-1-tosyl-1*H*-indol-2-yl)but-3-en-2-one **17 a** (0.15 mmol) in DCE (4 mL) was added $Cu(OTf)_2$ (2.7 mg, 0.0075 mmol) at room temperature. The reaction mixture was heated to 85 °C in the aluminium block and stirred for 24 h (TLC control). After that, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography (silica gel, petroleum ether/CH_2Cl_2, 25 : 1) to afford the carbazole **19 a**. Yield: 19 mg, 38 %; pale gray oil;[21] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, ^3J = 8.4 Hz, 1H), 8.20 (d, ^3J = 8.4 Hz, 1H), 7.87–7.85 (m, 1H), 7.68–7.66 (m, 3H), 7.48–7.44 (m, 1H), 7.35–7.32 (m, 1H), 7.30–7.28 (m, 1H), 7.08 (AA'BB'-system, ^3J = 8.2 Hz, 2H), 2.48 (s, 3H), 2.25 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 138.9, 136.8, 135.4, 133.8, 129.7 (2 C), 128.7, 127.3, 126.8, 126.7 (3 C), 123.9, 120.2, 120.0, 115.4, 115.1, 21.6, 21.4 ppm.

General Procedure for the Synthesis of Carbazoles 20. 30 mL Microwave reaction vessel was charged with corresponding 2-(2-acylvinyl)indole **17 a-h** (0.2 mmol), KOH (22.1 mg, 0.4 mmol) and MeOH (4 mL) at 0 °C. The reaction mixture was allowed to reach room temperature and stirred for 12 h (TLC control). Upon completion, to a resulting solution was additionally added KOH (22.1 mg, 0.4 mmol) and stirred at 110 °C under microwave irradiation for 1 hour (TLC control). After completion of the reaction, saturated aqueous solution of NH_4Cl (0.5–1.0 mL) was added dropwise. After that, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography (silica gel, petroleum ether/CH_2Cl_2, 9 : 1) to afford the carbazoles **20**.

(3-Methyl-9*H*-carbazol-4-yl)(phenyl)methanone (20 a). Yield: 51 mg, 89 %; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (br s, 1H), 7.96–7.94 (m, 2H), 7.59–7.55 (m, 1H), 7.48 (d, ^3J = 8.0 Hz, 1H), 7.45–7.38 (m, 3H), 7.36–7.28 (m, 3H), 6.98–6.94 (m, 1H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.0, 140.2, 138.1, 137.3, 133.9, 133.3, 130.0 (2 C), 129.1 (2 C), 128.2, 126.1, 125.5, 122.2, 121.8, 120.3, 119.7, 111.4, 110.7, 18.9 ppm; IR (nujol) ν_{max} = 3312, 1649, 1319, 1263 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{20}H_{16}NO^+$: 286.1226 $[M+H]^+$; found: 286.1233.

(3-Methyl-9*H*-carbazol-4-yl)(4-methylphenyl)methanone (20 b). Yield: 51 mg, 86 %; pale gray oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (br s, 1H), 7.84 (AA'BB'-system, ^3J = 8.0 Hz, 2H), 7.49 (d, ^3J = 8.0 Hz, 1H), 7.38 (d, ^3J = 8.0 Hz, 1H), 7.35–7.33 (m, 1H), 7.31–7.27 (m, 2H), 7.22 (AA'BB'-system, ^3J = 8.0 Hz, 2H), 6.98–6.94 (m, 1H), 2.39 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.0, 144.9, 140.2, 138.1, 134.9, 133.6, 130.1 (2C), 129.8 (2C), 128.2, 126.0, 125.4, 122.2, 121.9, 120.2, 119.7, 111.3, 110.7, 21.9, 18.9 ppm; IR (nujol) ν_{max} = 3267, 1654, 1599, 1315, 1285, 1261, 1176 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{21}H_{18}NO^+$: 300.1383 $[M+H]^+$; found: 300.1391.

(4-Methoxyphenyl)(3-methyl-9*H*-carbazol-4-yl)methanone (20 c). Yield: 53 mg, 85 %; pale beige oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (br s, 1H), 7.92–7.90 (m, 2H), 7.50 (d, ^3J = 8.0 Hz, 1H), 7.41–7.39 (m, 1H), 7.36 (d, ^3J = 8.0 Hz, 1H), 7.32–7.28 (m, 2H), 6.99–6.95 (m, 1H), 6.90 (AA'BB'-system, ^3J = 8.9 Hz, 2H), 3.84 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 164.3, 140.1, 138.0, 133.7, 132.4, 130.6, 128.2 (2 C), 126.0, 125.4, 122.3, 122.0, 120.3, 119.8, 114.3 (2 C), 111.2, 110.6, 55.6, 18.8 ppm; IR (nujol) ν_{max} = 3400, 1647, 1595, 1572, 1493, 1310, 1258, 1169, 1153 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{21}H_{18}NO_2^+$: 316.1332 $[M+H]^+$; found: 316.1341.

(4-Chlorophenyl)(3-methyl-9*H*-carbazol-4-yl)methanone (20 d). Yield: 58 mg, 91 %; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (br s, 1H), 7.88 (AA'BB'-system, ^3J = 8.4 Hz, 2H), 7.44 (d, ^3J = 8.2 Hz, 1H), 7.41–7.39 (m, 3H), 7.37–7.35 (m, 1H), 7.33–7.31 (m, 1H), 7.29 (d, ^3J = 8.2 Hz, 1H), 7.00–6.96 (m, 1H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.8, 140.6, 140.2, 138.0, 135.7, 132.7, 131.3 (2 C), 129.5 (2 C), 128.3, 126.2, 125.4, 122.0, 121.6, 120.1, 119.8, 111.7, 110.8, 18.9 ppm; IR (nujol) ν_{max} = 3420, 1666, 1649, 1585, 1568, 1398, 1313, 1286, 1256 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{20}H_{15}ClNO^+$: 320.0837 $[M+H]^+$; found: 320.0842.

(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)(3-methyl-9*H*-carbazol-4-yl) methanone (20 f). Yield: 56 mg, 82 %; pale beige oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (br s, 1H), 7.53–7.45 (m, 3H), 7.39–7.35 (m, 2H), 7.33–7.31 (m, 1H), 7.28 (br s, 1H), 7.00–6.97 (m, 1H), 6.86 (d, ^3J = 8.4 Hz, 1H), 4.29–4.28 (m, 2H), 4.24–4.23 (m, 2H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 148.9, 143.8, 140.1, 138.0, 133.5, 131.3, 128.2, 126.0, 125.4, 124.3, 122.3, 122.0, 120.2, 119.7, 119.3, 117.8, 111.2, 110.6, 64.9, 64.2, 18.8 ppm; IR (nujol) ν_{max} = 3402, 1651, 1599, 1576, 1502, 1310, 1288, 1261, 1175, 1115 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{22}H_{18}NO_3^+$: 344.1281 $[M+H]^+$; found: 344.1290.

(3-Methyl-9*H*-carbazol-4-yl)(naphthalen-2-yl)methanone (20 g). Yield: 55 mg, 83 %; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (br s, 1H), 8.19 (d, ^3J = 8.6 Hz, 1H), 8.14 (br s, 1H), 7.94 (d, ^3J = 8.6 Hz, 1H), 7.88 (d, ^3J = 8.2 Hz, 1H), 7.77 (d, ^3J = 8.2 Hz, 1H), 7.60–7.56 (m, 1H), 7.51–7.45 (m, 3H), 7.38–7.33 (m, 2H), 7.30–7.28 (m, 1H), 6.94–6.90 (m, 1H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.9, 140.2, 138.1, 136.3, 134.7, 133.5, 133.0, 132.7, 130.0, 129.1, 128.9, 128.3, 128.0, 126.8, 126.1, 125.6, 124.7, 122.3, 121.9, 120.5, 119.8, 111.4, 110.7, 19.0 ppm; IR (nujol) ν_{max} = 3238, 1649, 1624, 1310, 1265, 1231 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{24}H_{18}NO^+$: 336.1383 $[M+H]^+$; found: 336.1391.

(3-Methyl-9*H*-carbazol-4-yl)(thiophen-2-yl)methanone (20 h). Yield: 49 mg, 84 %; pale gray oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (br s, 1H), 7.69 (dd, ^3J = 4.9 Hz, ^4J = 0.9 Hz, 1H), 7.57 (d, ^3J = 8.0 Hz, 1H), 7.35–7.28 (m, 4H), 7.25–7.23 (m, 1H), 6.99–6.96 (m, 2H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 144.8, 140.1, 138.0, 135.9, 135.6, 132.9, 128.7, 128.2, 126.1, 125.5, 122.1, 121.6, 120.1, 119.7, 111.7, 110.8, 18.8 ppm; IR (nujol) ν_{max} = 3281, 1630, 1516, 1493, 1410, 1352, 1319, 1265, 1240, 1227 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd for $C_{18}H_{14}NSO^+$: 292.0791 $[M+H]^+$; found: 292.0793.

Synthesis of 2-[(5-Methylfuran-2-yl)methyl]benzohydrazide (21). The mixture of 2-[(5-methylfuran-2-yl)methyl]benzoic acid (200 mg, 0.93 mmol) and K_2CO_3 (257 mg, 1.86 mmol) in acetone (5 mL) was reflux for 15–20 minutes. Then the reaction mixture was cooled to room temperature and MeI (290 μL, 4.65 mmol) was added dropwise. The resulting solution was stirred at the same temperature for 3 h (TLC control). Upon completion, the reaction mixture was concentrated *in vacuo*. The obtained methyl 2-[(5-methylfuran-2-yl)methyl]benzoate was purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1 : 3). The solution of hydrazine hydrate (1.84 mL, 37.2 mmol) and obtained methyl 2-[(5-methylfuran-2-yl)methyl]benzoate (277 mg, 1.2 mmol) in *n*-butyl alcohol (1.86 mL, 20.4 mmol) was reflux for 20–30 minutes (TLC control). Upon completion, the reaction mixture was poured into water (50 mL). The obtained solid product **21** was filtered under reduced pressure and dried in the air. Yield: 262 mg, 95 %; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.43 (m, 1H), 7.34–7.30 (m, 1H), 7.22–7.20 (m, 1H), 7.17–7.13 (m, 1H), 6.51 (br s, 3H), 5.83 (d, ^3J = 2.8 Hz, 1H), 5.79 (d, ^3J = 2.8 Hz,

1H), 4.06 (s, 2H), 2.17 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.0, 152.1, 151.3, 137.7, 132.8, 131.1, 130.8, 128.1, 126.9, 107.6, 106.3, 31.9, 13.6 ppm; HRMS (ESI^+): *m/z* calcd for $C_{13}H_{15}N_2O_2^+$: 231.1128 $[M+H]^+$; found: 231.1127.

Synthesis of 2-methyl-10*H*-pyridazino[1,6-*b*]isoquinolin-10-one (22). *m*-CPBA (77% w/w, 135 mg, 0.6 mmol) was added to a solution of a 2-[(5-methylfuran-2-yl)methyl]benzohydrazide **21** (115 mg, 0.5 mmol) or *tert*-butyl 2-{2-[(5-methylfuran-2-yl)methyl] benzoyl}hydrazine-1-carboxylate **23** (165 mg, 0.5 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 1 h. Then HCl (3.07 μL, 0.1 mmol) was added. The reaction mixture was allowed to reach room temperature and stirred for 20 h. Thereafter, the reaction mixture was cooled to −10 °C for 15 min. This was accompanied by precipitation of *m*-chlorobenzoic acid. Precipitate was filtered off using rapid vacuum filtration and washed with cooled CH_2Cl_2 (2×2 mL). The combined filtrates were concentrated *in vacuo* and the residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether, 1:3) to afford the corresponding 2-methyl-10*H*-pyridazino[1,6-*b*]isoquinolin-10-one **22**. Yield: 42 mg, 40% (for **21**), 87 mg, 83% (for **23**); dark green oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69–8.67 (m, 1H), 7.72–7.68 (m, 1H), 7.63–7.61 (m, 1H), 7.54–7.50 (m, 1H), 7.40 (d, ^3J = 9.3 Hz, 1H), 6.65 (s, 1H), 6.55 (d, ^3J = 9.3 Hz, 1H), 2.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 152.3, 135.5, 134.0, 133.1, 132.5, 129.1, 126.5, 125.9, 124.2, 120.0, 102.5, 22.7 ppm; HRMS (ESI^+): *m/z* calcd for $C_{13}H_{11}N_2O^+$: 211.0866 $[M+H]^+$; found: 211.0865.

Synthesis of *tert*-butyl 2-{2-[(5-methylfuran-2-yl)methyl] benzoyl}hydrazine-1-carboxylate (23). The mixture of 2-[(5-methylfuran-2-yl)methyl]benzohydrazide **21** (230 mg, 1 mmol) and di-*tert*-butyl dicarbonate (689 μL, 3 mmol) in CH_2Cl_2 (5 mL) was reflux under a argon atmosphere (TLC control). Upon completion, the reaction mixture was concentrated *in vacuo*. The product **23** was purified by column chromatography (silica gel, petroleum ether). Yield: 293 mg, 89%; yellow solid; mp 87–88 °C (CH_2Cl_2/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (br s, 1H), 7.54–7.52 (m, 1H), 7.41–7.37 (m, 1H), 7.30–7.27 (m, 2H), 6.61 (br s, 1H), 5.92 (d, ^3J = 2.8 Hz, 1H), 5.84 (d, ^3J = 2.8 Hz, 1H), 4.16 (s, 2H), 2.22 (s, 3H), 1.51 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.9, 155.5, 152.2, 151.4, 137.3, 133.4, 131.1, 130.9, 128.2, 126.9, 107.5, 106.3, 82.1, 31.9, 28.3 (3C), 13.6 ppm; HRMS (ESI^+): *m/z* calcd for $C_{18}H_{23}N_2O_4^+$: 331.1652 $[M+H]^+$; found: 331.1654.

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Conflicts of interest

There are no conflicts to declare.

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