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Furan ring opening–indole ring closure: recyclization of 2-(2-aminophenyl)furans into 2-(2-oxoalkyl)indoles

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ABSTRACT

The acid-catalyzed rearrangement of 5-alkyl-2-[2-(sulfonylamino)phenyl]furans into 2-(2-oxoalkyl)indoles is described. When the *N*-sulfonyl group in the starting compounds was displaced by an *N*-acyl group, the corresponding indoles were not formed under the same reaction conditions due to the in situ indole deacylation and decomposition. The presence of an alkyl group at the C5 position of the furan ring is also crucial for the efficiency of the process. The discussed rearrangement provides a simple and efficient approach to 2-(2-oxoalkyl)indoles.

1. Introduction

For many years indoles have been among the most studied compounds due to their significant role in biology and medicine as well as high reactivity in various chemical reactions.[1] There are thousands of natural and synthetic physiologically active compounds containing the indole scaffold.[2] Many indole derivatives, such as indomethacin, vinblastine, indoramin, pindolol, etc., are commercial medicines. The broad application of various indoles stimulates organic chemists to develop novel methodologies for indole core formation and functionalization. One of the approaches toward synthesis of indoles possessing the required pharmacophores and/or functional groups involves the modification of the pre-existing indole core. Alternatively, these indoles can be assembled from the appropriately functionalized starting materials. The last approach is realized, for example, when indoles are prepared by recyclization of other heterocyclic compounds. It allows for selective introduction of various functional groups at the definite positions.[3]

In recent years we have investigated acid-catalyzed furan recyclizations as a general method for the synthesis of a broad range of heterocycles.[4] In these recyclizations, furans can be considered as synthetic equivalents of dicarbonyl synthons. One of the latent carbonyl groups participates in the formation of the new heterocycle, while the second one is transformed from the latent form into its genuine entity. Alternatively, it can further react with the appropriate functional group if it is present in the started compound. In particular, we used this approach to synthesize 2-(3-oxoalkyl)indoles **2** (reaction *a* in Fig. 1),[5] 2-(2-acylvinyl)indoles **4** (reaction *b*),[6] 3-(2-acylvinyl)indoles **6** (reaction *c*),[7] and 2-(2-oxoalkyl)indoles **8** (reaction *d*)[8] from the corresponding furans **1**, **3**, **5**, **7**, respectively.

The processes *a* and *d* seem to be very similar but they have two principal distinctions. Firstly, in reaction *a* furan provided only one out of four carbon atoms of the furan ring and is incorporated into the formed pyrrole ring of the indole. In contrast, in process *d*, the furan ring provides two carbon atoms for the indole ring formation (Fig. 1). Secondly, in the recyclization of 2-(2-aminobenzyl)furans the furan ring reacts as a synthetic equivalent of 1,4-diketone (Fig. 2), which is a typical behavior for furans in ring-opening transformations. On the other hand, in recyclization of 2-(2-aminophenyl)furans, the furan ring can be considered as

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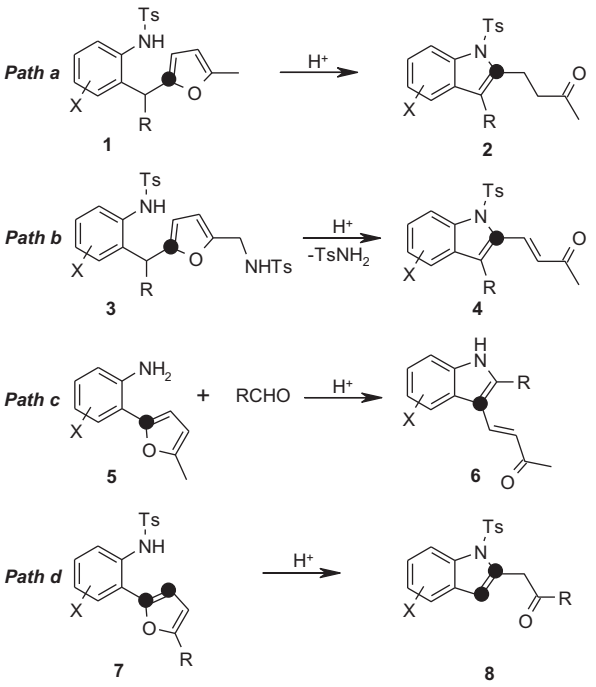
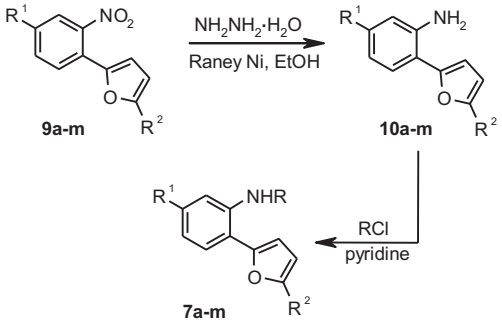


Fig. 1. Furans into indoles recyclizations.

Table 1
Synthesis of sulfonamides **7a**–**m**



Entry	R	R^1	R^2	Yield [%]	
				10	**7**
a	Ts	CH_3	CH_3	89	65
b	Ts	CH_3O	CH_3	82	57
c	Ts	Cl	CH_3	82	69
d	Ts	Cl	C_2H_5	90	73
e	Ts	H	CH_3	85	65
f	Ts	H	C_2H_5	83	68
g	Ts	H	Bn	89	72
h	Ts	H	4-$CH_3C_6H_4CH_2$	89	78
i	Ts	H	$CO_2C_2H_5$	80	75
j	Ts	H	H	85	70
k	Ts	Cl	$CH_2CH_2CO_2CH_3$	77	62
l	Ts	CH_3	$CH_2CH_2CO_2CH_3$	80	64
m	Ms	CH_3	CH_3	89	55

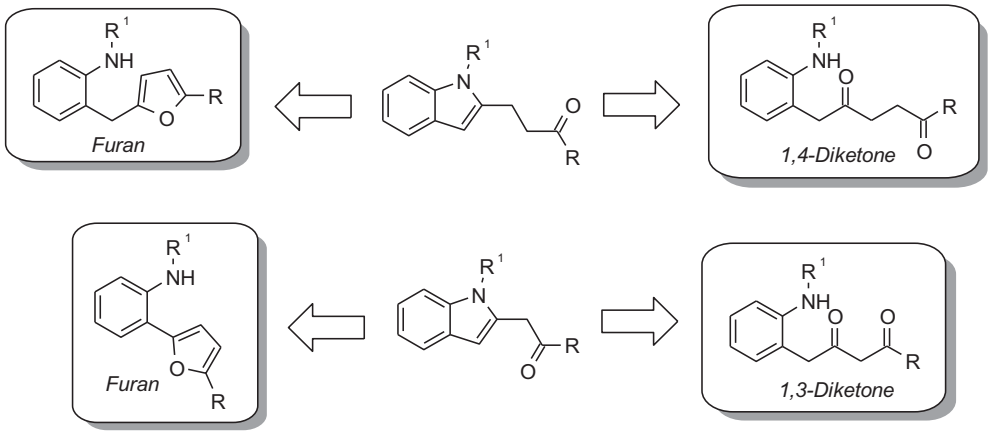


Fig. 2. Furans as synthetic equivalents of 1,4- and 1,3-diketones in the indole synthesis.

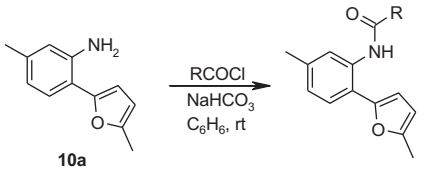
a synthetic equivalent of 1,3-diketone. Indeed, reaction *d* is quite similar to the indole synthesis from 1-(2-aminobenzyl)-1,3-diketones, which is generated by reduction of the corresponding nitrobenzenes (Fig. 2).[9]

This unusual reactivity of 2-(2-aminophenyl)furans stimulated us to study their transformations in more depth. Herein, we report more detailed study of this promising recyclization reaction.

2. Results and discussion

The parent sulfonamides **7a**–**m** were synthesized by reduction of the corresponding 2-(2-nitrophenyl)furans **9** with hydrazine hydrate in the presence of Raney nickel, followed by treatment of the formed anilines **10** with sulfonyl chlorides (Table 1). Treatment of the aniline **10a** with acyl chloride in benzene afforded amides **7n**,**o** (Scheme 1).

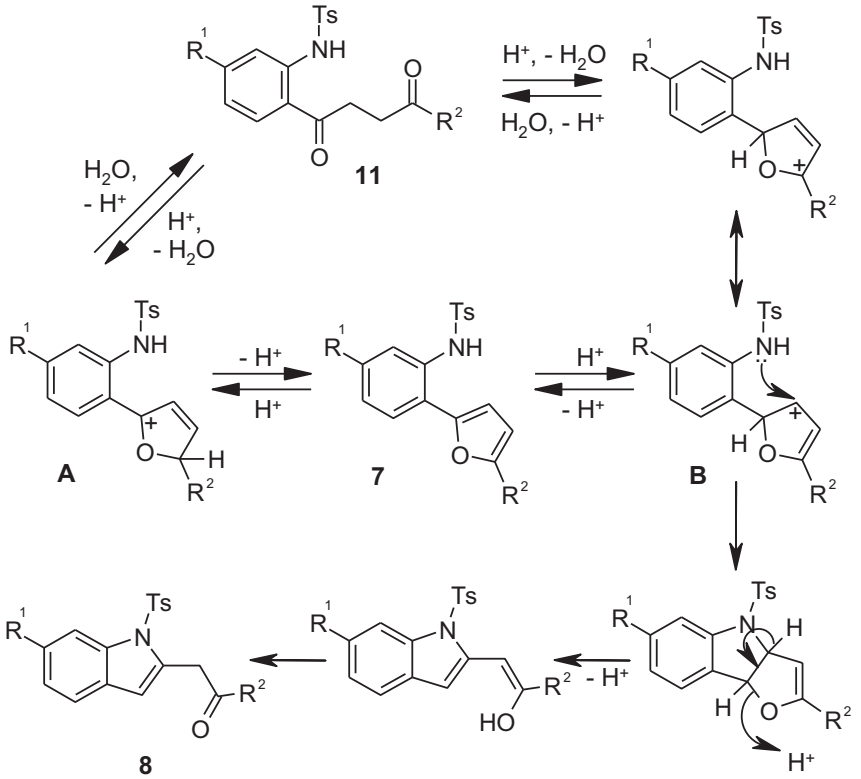
Initially, we started our investigation of the title recyclization by testing the reaction conditions, which were earlier applied for the recyclization of 2-[2-(tosylamino)benzyl]furans **1** into 2-(3-oxoalkyl)indoles **2**. This process was found to efficiently proceed when **1** was heated to reflux in ethanolic HCl solution for 10–40 min.[5b] However, under the same reaction conditions, the conversion of **7** was incomplete even after prolonged heating producing indoles **8** in low yields only. Thus, when **7a**–**c** were



Scheme 1. Synthesis of *N*-acylanilides **7n**,**o**.

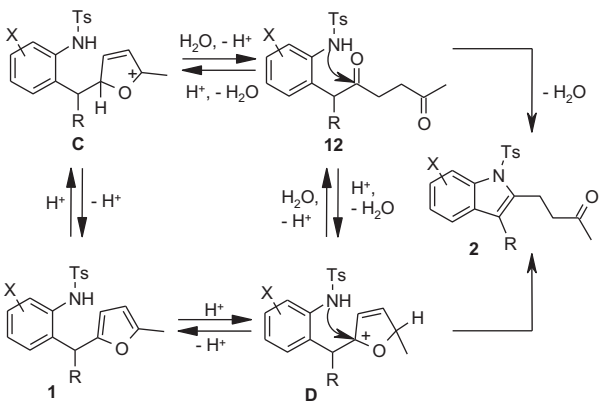
refluxed in saturated ethanolic HCl for 6 h, the target products **8a**–**c** were obtained in 27, 42, and 30% yields, respectively. Along with **8a**–**c**, the side-products, diketones **11a**–**c**, were isolated in 43, 32, and 25% yields, respectively (Scheme 2). The unreacted starting compounds **7a**–**c** were also found in the reaction mixtures.

a direct precursor of the target indole **2**, in the reaction mixture is sufficient enough, thus providing high efficiency of recyclization of benzylfurans **1**. Moreover, both **C** and **D** can be transformed under the reaction conditions into the diketone **12**, which undergoes cyclization into indole **2** (Scheme 3).



Scheme 2. Plausible mechanism for recyclization of arylfurans **7**.

The differences in behavior of **7** and **1** could be understood by comparison of mechanistic schemes for these two recyclizations. Both reactions proceed via protonation of the furan ring leading to cations **A** and **B** in reactions of arylfurans **7** (Scheme 2) and cations **C** and **D** in reactions of benzylfurans **1** (Scheme 3). Most likely, the stabilities of the cations **C** and **D** are very similar, which originate from the protonation of both α-positions in benzylfurans **1**, are quite similar. Therefore, the concentration of the cation **D**, which is



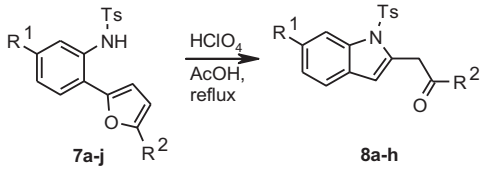
Scheme 3. The proposed mechanism for recyclization of benzylfurans **1**.

In contrast, the benzylic cation **A**, which is formed by protonation of 2-[2-(tosylamino)aryl]-5-alkylfuran **7** at C(5) position, is much more stable than the cation **B**. Thus, the concentration of **B** in reaction mixture is low. It leads to the low yield of the product and a significant decrease of reaction rate as this cation is a direct precursor of indole **8**. At the same time, under used reaction conditions both **A** and **B** are transformed into diketone **11**, formation of which was observed in our experiments. In the presence of acid, this side-product cyclizes slowly into furan **7**, as the furan ring opening into 1,4-diketone is a reversible process. Therefore, a small concentration of cation **B** should be permanently present under equilibrium conditions, what allows for the smooth formation of indole **8**. Therefore, it is possible to suppose that the formation of **8** should be more efficient if harsher reaction conditions were used, at which equilibrium between furan **7** and diketone **11** could be achieved.

Indeed, treatment of furan **7a** solution in glacial acetic acid with 70% $HClO_4$ under reflux allowed us to both increase significantly indole yield and decrease reaction time. The best yield of indole **8a** was obtained when the ratio of perchloric and acetic acids was 1:10 and reaction time was 10–15 min. Furthermore, a decrease of the process duration, as well as utilization of a lower loading of $HClO_4$ afforded the target indole **8a** together with diketone **11a**. The control experiments showed that treatment of diketones **11a**–**c** under these reaction conditions afforded indoles **8a**–**c** in high yields.

Next, the scope of this recyclization using a series of furans **7** under the optimized reaction conditions was studied (Table 2). Formation of the indole **8** was found to be efficient for the

Table 2
Recyclization of 2-[2-(tosylamino)phenyl]furans **7** into indoles **8**



Entry	R^1	R^2	Yield of **8** [%]
a	CH_3	CH_3	75
b	CH_3O	CH_3	64
c	Cl	CH_3	85
d	Cl	C_2H_5	73
e	H	CH_3	83
f	H	C_2H_5	80
g	H	Bn	56
h	H	4-$CH_3C_6H_4CH_2$	60
i	H	$CO_2C_2H_5$	—
j	H	H	—

substrates containing various substituents at the aniline moiety and alkyl groups at C(5) position of the furan ring. However, the attempts of recyclization of furans **7i**,**j** into the corresponding indoles were not successful. In reaction of **7i**, the starting furan stayed intact after refluxing for 40 min. The possible reason for the low reactivity of **7i** toward protonation is its deactivation by the electron-withdrawing ester group. Oppositely, protonation at the unsubstituted C(5) position of the furan ring in **7j** is too fast, leading to full destruction of the substrate in 5 min.

Structures of indoles **8** were determined using ^{1}H and ^{13}C NMR, mass spectrometry, and elemental analysis data. For compound **8e** it was unambiguously proved by single-crystal X-ray diffraction data (Fig. 3).

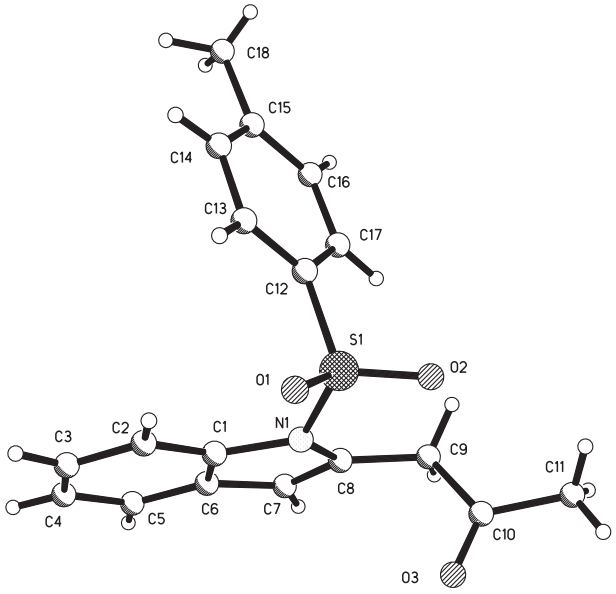
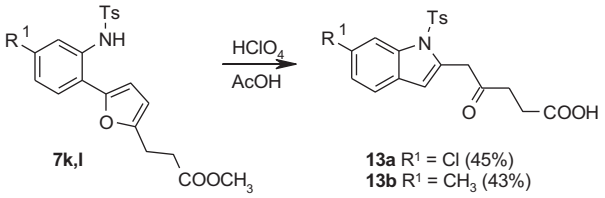


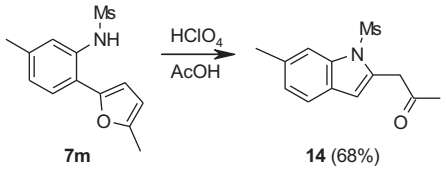
Fig. 3. Single-crystal X-ray structure of **8e**.

It was found that recyclization of 3-{5-[2-(tosylamino)phenyl]-2-furyl}propionates **7k**,**l** into indoles is accompanied by hydrolysis of the ester moiety furnishing 6-(2-indolyl)-4-oxopentanoic acids **13a**,**b** in moderate yields (Scheme 4).

At last, we investigated the effect of the *N*-protecting group on the efficiency of recyclization reaction. We found that 2-furyl-*N*-mesyl aniline **7m** was smoothly rearranged into the corresponding *N*-mesylindole (Scheme 5). In contrast, heating *N*-acetyl- and *N*-benzoyl-2-(2-furyl)anilines **7n**,**o** in both $HClO_4$/AcOH mixture and ethanolic HCl solution resulted in total decomposition of the starting materials only. We believe that indoles formed from these substrates, undergo fast deacylation leading to *N*-unsubstituted derivatives, which are unstable under these reaction conditions.[5b,d]



Scheme 4. Recyclization of 3-{5-[2-(tosylamino)phenyl]-2-furyl}propionates **7k**,**l**.



Scheme 5. Recyclization of mesylate **7m**.

3. Conclusion

In summary, we have developed a simple and efficient approach to 2-(2-oxoalkyl)indoles by acid-catalyzed recyclization of 2-(2-aminophenyl)furans. This method was shown to be efficient for 2-furylanilines containing alkyl substituent at the C(5) position of the furan ring and sulfonyl group at the nitrogen atom of aniline moiety. The obtained 2-(2-oxoalkyl)indoles are interesting both themselves and as potent precursors in syntheses of the more complex indole derivatives,[10] such as alkaloids vindorosine,[11] ibogain, and isoibogain.[12] Nevertheless, there are only a few investigations of 2-(2-oxoalkyl)indoles nowadays due to, mainly, the absence of the general approaches to these compounds.[13–16] So, we believe that the method described herein would be useful for organic chemists as a simple and convenient route to these ketoindoles.

4. Experimental section

4.1. General

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DPX 300 and Bruker AM 360 spectrometers at room temperature; the chemical shifts δ were measured in parts per million with respect to the solvent ($CDCl_3$, 1H: δ=7.26 ppm, 13C: δ=77.0 ppm; DMSO-d_6, 1H: δ=2.50 ppm, 13C: δ=39.5 ppm). Coupling constants (J) are given in hertz. Splitting patterns of an apparent multiplet associated with an averaged coupling constants were designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets) and br (broadened). IR spectra were measured as KBr plates on InfraLUM FT-02 and InfraLUM FT-801 instruments. Mass spectra were recorded on a Kratos MS-30 instrument with 70 eV electron impact ionization at 200 °C. Column chromatography was performed on silica gel KSK (50–160 μm, LTD Sorbpolymer). The synthesis of compounds **9** is described in Supplementary data. All the reactions were carried out using freshly distilled and dry solvents from solvent stills. Crystallographic data (excluding structure factors) for compound **8e** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 832947. Copies of the data can be obtained, free of charge, on

application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.2. Synthesis of 2-[2-(tosylamino)phenyl]furans 7a–l

Hydrazine hydrate (10 mL) and Raney nickel (4 g) were added to solution of nitroarene **9** (38 mmol) in ethanol (100 mL). Mixture was refluxed for 2 h (TLC monitoring). Nickel was filtered off. Evaporation of filtrate afforded 2-(2-aminophenyl)furan **10**. This product (13 mmol) was dissolved in pyridine (15 mL) and cooled to 0 °C. Then TsCl (5 g, 26 mmol) was added. The reaction mixture was stirred at room temperature for 12 h (TLC monitoring) and poured into 6 M HCl (200 mL). Residue was filtered, washed with water, and air-dried. Product was purified by column chromatography on silica gel using benzene/petroleum ether (1:3) mixture as an eluent.

*4.2.1. 4-Methyl-N-[5-methyl-2-(5-methyl-2-furyl)phenyl]benzenesulfonamide (**7a**).* White solid; yield 65% (2.88 g); mp 92–93 °C (benzene/petroleum ether). Found: C, 67.09; H, 5.74; N, 3.96. $C_{19}H_{19}NO_3S$ requires C, 66.84; H, 5.61; N, 4.10%. R_f=0.61 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3271, 1572, 1493, 1397, 1336, 1172, 1092, 1024, 896, 816 cm^{-1}; δ_H (360 MHz, $CDCl_3$) 7.79 (1H, br s, NH), 7.47–7.44 (3H, m, H_{Ar}+$2H_{Ts}$), 7.18 (1H, d, *J* 8.3 Hz, H_{Ar}), 7.07 (2H, d, *J* 8.0 Hz, H_{Ts}), 6.90 (1H, d, *J* 8.3 Hz, H_{Ar}), 6.12 (1H, d, *J* 3.2 Hz, H_{Fur}), 5.95 (1H, d, *J* 3.2 Hz, H_{Fur}), 2.34 (3H, s, CH_3), 2.32 (3H, s, CH_3), 2.30 (3H, s, CH_3); δ_C (90 MHz, $CDCl_3$) 151.9, 150.2, 143.4, 138.6, 136.0, 132.5, 129.2 (2C), 127.1, 126.9 (2C), 126.3, 124.2, 120.3, 108.3, 107.5, 21.4, 21.2, 13.6; *m*/*z* (EI, 70 eV) 341 (M^+, 100), 186 (78), 171 (14), 158 (29), 143 (19), 91 (32), 43 (20%).

*4.2.2. 4-Methyl-N-[5-methoxy-2-(5-methyl-2-furyl)phenyl]benzenesulfonamide (**7b**).* White solid; yield 57% (2.65 g); mp 82–83 °C (benzene/petroleum ether). Found: C, 64.13; H, 5.50; N, 3.82. $C_{19}H_{19}NO_4S$ requires C, 63.85; H, 5.36; N, 3.92%. R_f=0.58 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3324, 1583, 1502, 1449, 1336, 1238, 1160, 1090, 1029, 972, 894 cm^{-1}; δ_H (360 MHz, $CDCl_3$) 7.87 (1H, br s, NH), 7.51 (2H, d, *J* 8.3 Hz, H_{Ts}), 7.20 (1H, d, *J* 8.7 Hz, H_{Ar}), 7.17 (1H, d, *J* 2.5 Hz, H_{Ar}), 7.09 (2H, d, *J* 8.3 Hz, H_{Ts}), 6.62 (1H, dd, *J* 8.7, 2.5 Hz, H_{Ar}), 6.08 (1H, d, *J* 3.2 Hz, H_{Fur}), 5.96 (1H, d, *J* 3.2 Hz, H_{Fur}), 3.79 (3H, s, OCH_3), 2.34 (3H, s, CH_3), 2.30 (3H, s, CH_3); δ_C (90 MHz, $CDCl_3$) 159.6, 151.6, 149.9, 143.6, 136.0, 134.0, 129.3 (2C), 128.5, 127.0 (2C), 115.5, 111.7, 107.7, 107.6, 107.4, 55.4, 21.4, 13.6; *m*/*z* (EI, 70 eV) 357 (M^+, 65), 202 (100), 187 (22), 174 (33), 171 (32), 170 (25), 162 (18), 159 (27), 131 (17), 116 (17), 91 (29), 65 (24), 59 (20), 43 (18%).

*4.2.3. 4-Methyl-N-[5-chloro-2-(5-methyl-2-furyl)phenyl]benzenesulfonamide (**7c**).* White solid; yield 69% (3.24 g); mp 131–132 °C (benzene/petroleum ether). Found: C, 60.02; H, 4.45; N, 3.77. $C_{18}H_{16}ClNO_3S$ requires C, 59.75; H, 4.46; N, 3.87%. R_f=0.60 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3332, 1595, 1574, 1490, 1397, 1334, 1294, 1154, 1091, 1032, 940, 869, 820, 782 cm^{-1}; δ_H (360 MHz, $CDCl_3$) 7.88 (1H, br s, NH), 7.63 (1H, d, *J* 2.2 Hz, H_{Ar}), 7.52 (2H, d, *J* 8.3 Hz, H_{Ts}), 7.23 (1H, d, *J* 8.3 Hz, H_{Ar}), 7.12 (2H, d, *J* 8.3 Hz, H_{Ts}), 7.04 (1H, dd, *J* 8.3, 2.2 Hz, H_{Ar}), 6.23 (1H, d, *J* 3.6 Hz, H_{Fur}), 6.00 (1H, d, *J* 3.6 Hz, H_{Fur}), 2.36 (3H, s, CH_3), 2.32 (3H, s, CH_3); δ_C (90 MHz, $CDCl_3$) 152.6, 149.1, 143.9, 135.8, 133.8, 133.7, 129.5 (2C), 128.1, 127.0 (2C), 125.4, 123.0, 121.0, 109.4, 107.8, 21.4, 13.7; *m*/*z* (EI, 70 eV) 363/361 (M^+, 24/72), 208/206 (33/100), 191 (38), 178 (63), 171 (56), 163 (40), 143 (71), 91 (86), 69 (35), 57 (37), 43 (47%).

*4.2.4. 4-Methyl-N-[5-chloro-2-(5-ethyl-2-furyl)phenyl]benzenesulfonamide (**7d**).* White solid; yield 73% (3.56 g); mp 132–134 °C (benzene/petroleum ether). Found: C, 60.68; H, 4.71; N, 3.76. $C_{19}H_{18}ClNO_3S$ requires C, 60.71; H, 4.83; N, 3.73%. R_f=0.62 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3315, 1573, 1491, 1399, 1339, 1160, 1090, 1038, 935, 906, 870, 818 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.91 (1H, br s, NH), 7.53 (1H, d, *J* 2.1 Hz, H_{Ar}), 7.41 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.13 (1H, d, *J* 8.7 Hz, H_{Ar}), 7.02 (2H, d, *J* 8.4 Hz, H_{Ts}), 6.94 (1H, dd, *J* 8.7, 2.1 Hz, H_{Ar}), 6.15 (1H, d, *J* 3.3 Hz, H_{Fur}), 5.91 (1H, d, *J* 3.3 Hz, H_{Fur}), 2.61 (2H, q, *J* 7.5 Hz, CH_2), 2.22 (3H, s, CH_3), 1.20 (3H, t, *J* 7.5 Hz, CH_3); δ_C (75 MHz, $CDCl_3$) 158.2, 148.9, 143.9, 135.6, 133.7, 133.6, 129.5 (2C), 128.0, 126.9 (2C), 125.3, 122.7, 120.9, 109.1, 106.3, 21.5, 21.4, 12.2; *m*/*z* (EI, 70 eV) 377/375 (M^+, 9/27), 222/220 (33/100), 193 (25), 192 (87), 177 (30), 163 (27), 157 (65), 128 (20), 91 (36), 65 (20), 59 (15%).

*4.2.5. 4-Methyl-N-[2-(5-methyl-2-furyl)phenyl]benzenesulfonamide (**7e**).* White solid; yield 65% (2.76 g); mp 88–89 °C (benzene/petroleum ether). Found: C, 66.13; H, 5.27; N, 4.15. $C_{18}H_{17}NO_3S$ requires C, 66.03; H, 5.23; N, 4.28%. R_f=0.65 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3312, 1597, 1577, 1445, 1415, 1334, 1304, 1218, 1167, 1091, 1024, 896, 818 cm^{-1}; δ_H (360 MHz, $CDCl_3$) 7.85 (1H, br s, NH), 7.62–7.60 (1H, m, H_{Ar}), 7.46 (2H, d, *J* 8.3 Hz, H_{Ts}), 7.35–7.30 (1H, m, H_{Ar}), 7.24–7.19 (1H, m, H_{Ar}), 7.12–7.07 (3H, m, H_{Ar}+$2H_{Ts}$), 6.21 (1H, d, *J* 3.2 Hz, H_{Fur}), 5.98 (1H, d, *J* 3.2 Hz, H_{Fur}), 2.36 (3H, s, CH_3), 2.30 (3H, s, CH_3); δ_C (90 MHz, $CDCl_3$) 152.3, 150.0, 143.5, 136.0, 132.7, 129.3 (2C), 128.3, 127.2, 126.9 (2C), 125.4, 123.7, 123.0, 109.0, 107.7, 21.4, 13.7; *m*/*z* (EI, 70 eV) 327 (M^+, 97), 172 (100), 144 (90), 129 (23), 115 (17), 91 (34), 77 (17), 43 (25%).

*4.2.6. 4-Methyl-N-[2-(5-ethyl-2-furyl)phenyl]benzenesulfonamide (**7f**).* White solid; yield 68% (3.01 g); mp 89–90 °C (benzene/petroleum ether). Found: C, 66.99; H, 5.73; N, 4.00. $C_{19}H_{19}NO_3S$ requires C, 66.84; H, 5.61; N, 4.10%. R_f=0.65 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3253, 1593, 1538, 1488, 1392, 1328, 1154, 1091, 1017, 905, 763 cm^{-1}; δ_H (360 MHz, $CDCl_3$) 7.94 (1H, br s, NH), 7.63–7.61 (1H, m, H_{Ar}), 7.46 (2H, d, *J* 8.3 Hz, H_{Ts}), 7.33–7.30 (1H, m, H_{Ar}), 7.24–7.19 (1H, m, H_{Ar}), 7.11–7.06 (3H, m, H_{Ar}+$2H_{Ts}$), 6.22 (1H, d, *J* 3.3 Hz, H_{Fur}), 6.00 (1H, d, *J* 3.3 Hz, H_{Fur}), 2.70 (2H, q, *J* 7.6 Hz, CH_2), 2.30 (3H, s, CH_3), 1.30 (3H, t, *J* 7.6 Hz, CH_3); δ_C (90 MHz, $CDCl_3$) 157.9, 150.0, 143.5, 136.0, 132.7, 129.3 (2C), 128.3, 127.2, 126.9 (2C), 125.3, 123.4, 122.9, 108.8, 106.1, 21.4 (2C), 12.3; *m*/*z* (EI, 70 eV) 341 (M^+, 36), 186 (70), 158 (100), 143 (18), 130 (21), 129 (35), 91 (36), 43 (34%).

*4.2.7. 4-Methyl-N-[2-(5-benzyl-2-furyl)phenyl]benzenesulfonamide (**7g**).* White solid; yield 72% (3.78 g); mp 108–109 °C (benzene/petroleum ether). Found: C, 71.12; H, 5.19; N, 3.36. $C_{24}H_{21}NO_3S$ requires C, 71.44; H, 5.25; N, 3.47%. R_f=0.63 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3364, 3315, 1580, 1537, 1490, 1420, 1336, 1302, 1224, 1161, 1089, 1030, 908 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.92 (1H, br s, NH), 7.66–7.63 (1H, m, H_{Ar}), 7.44–7.19 (9H, m, $7H_{Ar}$+$2H_{Ts}$), 7.11–7.06 (1H, m, H_{Ar}), 6.97 (2H, d, *J* 8.1 Hz, H_{Ts}), 6.25 (1H, d, *J* 3.0 Hz, H_{Fur}), 6.08 (1H, d, *J* 3.0 Hz, H_{Fur}), 4.02 (2H, s, CH_2), 2.27 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 154.6, 150.7, 143.3, 137.3, 135.6, 132.5, 129.2 (2C), 128.8 (2C), 128.6 (2C), 128.3, 128.2, 127.1, 126.7 (2C), 125.2, 123.4, 122.5, 108.6, 108.0, 34.6, 21.3; *m*/*z* (EI, 70 eV) 403 (M^+, 14), 248 (22), 220 (38), 91 (100), 65 (25), 39 (17%).

*4.2.8. 4-Methyl-N-{2-[5-(4-methylbenzyl)-2-furyl]phenyl}benzenesulfonamide (**7h**).* White solid; yield 78% (4.23 g); mp 76–77 °C (benzene/petroleum ether). Found: C, 72.24; H, 5.65; N, 3.29. $C_{25}H_{23}NO_3S$ requires C, 71.92; H, 5.55; N, 3.35%. R_f=0.64 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3368, 3344, 1600, 1488, 1346, 1336, 1164, 1092, 1024, 892, 800 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.92 (1H, br s, NH), 7.66–7.63 (1H, m, H_{Ar}), 7.33–7.30 (3H, m, H_{Ar}+$2H_{Ts}$), 7.24–7.19 (5H, m, H_{Ar}), 7.11–7.06 (1H, m, H_{Ar}), 6.99 (2H,

d, *J* 8.1 Hz, H_{Ts}), 6.25 (1H, d, *J* 3.3 Hz, H_{Fur}), 6.06 (1H, d, *J* 3.3 Hz, H_{Fur}), 3.98 (2H, s, CH_2), 2.36 (3H, s, CH_3), 2.29 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 155.0, 150.6, 143.3, 136.3, 135.7, 134.2, 132.6, 129.5 (2C), 129.2 (2C), 128.5 (2C), 128.3, 127.1, 126.8 (2C), 125.2, 123.4, 122.5, 108.6, 107.8, 34.2, 21.3, 20.9; *m/z* (EI, 70 eV) 417 (M^+, 18), 262 (64), 234 (27), 145 (28), 105 (100), 91 (22), 59 (21), 43 (27%).

*4.2.9. Ethyl 5-(4-methyl-2-{[(4-methylphenyl)sulfonyl]amino}phenyl)-2-furoate (**7i**).* White solid; yield 75% (3.75 g); mp 108–109 °C (benzene/petroleum ether). Found: C, 62.22; H, 4.83; N, 3.43. $C_{20}H_{19}NO_5S$ requires C, 62.32; H, 4.97; N, 3.63%. R_f=0.52 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3247, 1720, 1485, 1442, 1385, 1335, 1298, 1213, 1157, 1020, 813 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.96 (1H, br s NH), 7.66–7.63 (1H, m, H_{Ar}), 7.50 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.42–7.39 (1H, m, H_{Ar}), 7.33–7.28 (1H, m, H_{Ar}), 7.16–7.13 (1H, m, H_{Ar}), 7.12 (1H, d, *J* 3.9 Hz, H_{Fur}), 7.04 (2H, d, *J* 8.4 Hz, H_{Ts}), 6.45 (1H, d, *J* 3.9 Hz, H_{Fur}), 4.40 (2H, q, *J* 7.1 Hz, CH_2), 2.28 (3H, s, CH_3), 1.43 (3H, t, *J* 7.1 Hz, CH_3); δ_C (75 MHz, $CDCl_3$) 158.1, 154.9, 143.9, 143.6, 135.7, 133.4, 130.1, 129.3 (2C), 127.9, 126.9 (2C), 125.7, 124.7, 121.5, 119.0, 109.5, 61.2, 21.4, 14.3; *m/z* (EI, 70 eV) 385 (M^+, 2), 202 (43), 178 (21), 155(44), 156 (45), 129 (57), 114 (28), 102 (34), 91 (100), 77 (43), 65 (44), 51 (27), 39 (31%).

*4.2.10. N-[2-(2-Furyl)phenyl]-4-methylbenzenesulfonamide (**7j**).* White solid; yield 70% (2.85 g); mp 130–131 °C (benzene/petroleum ether). Found: C, 65.41; H, 4.91; N, 4.37. $C_{17}H_{15}NO_3S$ requires C, 65.16; H, 4.82; N, 4.47%. R_f=0.59 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3339, 1593, 1507, 1458, 1417, 1336, 1291, 1167, 1089, 1006, 890, 809 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.88 (1H, br s, NH), 7.64–7.61 (1H, m, H_{Ar}), 7.48–7.44 (3H, m, H_{Fur}+2H_{Ts}), 7.36–7.33 (1H, m, H_{Ar}), 7.28–7.23 (1H, m, H_{Ar}), 7.14–7.09 (1H, m, H_{Ar}), 7.07 (2H, d, *J* 8.3 Hz, H_{Ts}), 6.41 (1H, dd, *J* 3.2, 1.8 Hz, H_{Fur}), 6.32 (1H, dd, *J* 3.2, 0.7 Hz, H_{Fur}), 2.31 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 151.9, 143.5, 142.3, 136.0, 133.1, 129.4 (2C), 128.9, 127.7, 126.9 (2C), 125.4, 123.7, 122.6, 111.6, 108.0, 21.4; *m/z* (EI, 70 eV) 313 (M^+, 19), 158 (70), 130 (100), 102 (13), 91 (27), 77 (17), 43 (14%).

*4.2.11. Methyl 3-[5-(4-chloro-2-{[(4-methylphenyl)sulfonyl]amino}phenyl)-2-furyl]propanoate (**7k**).* White solid; yield 62% (3.49 g); mp 75–76 °C (benzene/petroleum ether). Found: C, 58.07; H, 4.42; N, 3.39. $C_{21}H_{20}ClNO_5S$ requires C, 58.13; H, 4.65; N, 3.23%. R_f=0.52 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3240, 1736, 1332, 1160, 828 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.86 (1H, br s, NH), 7.62 (1H, d, *J* 2.1 Hz, H_{Ar}), 7.53 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.23 (1H, d, *J* 8.7 Hz, H_{Ar}), 7.13 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.05 (1H, dd, *J* 8.7, 2.1 Hz, H_{Ar}), 6.23 (1H, d, *J* 3.3 Hz, H_{Fur}), 6.07 (1H, d, *J* 3.3 Hz, H_{Fur}), 3.72 (3H, s, OCH_3), 3.04–3.00 (2H, m, CH_2), 2.73–2.68 (2H, m, CH_2), 2.33 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 172.6, 154.7, 143.9, 135.7, 134.0, 133.8, 129.5 (2C), 128.3, 126.9 (2C), 125.4 (2C), 122.9, 120.8, 109.2, 107.7, 51.9, 32.2, 23.4, 21.5; *m/z* (EI, 70 eV) 435/433 (M^+, 2/6), 280/278 (33/100), 91 (20%).

*4.2.12. Methyl 3-[5-(4-methyl-2-{[(4-methylphenyl)sulfonyl]amino}phenyl)-2-furyl]propanoate (**7l**).* White solid; yield 64% (3.44 g); mp 81–82 °C (benzene/petroleum ether). Found: C, 64.29; H, 5.82; N, 3.37. $C_{22}H_{23}NO_5S$ requires C, 63.91; H, 5.61; N, 3.39%. R_f=0.53 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3180, 1712, 1360, 1284, 1256, 1172, 1140, 1084, 1052, 828 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.75 (1H, br s, NH), 7.44 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.41 (1H, d, *J* 1.2 Hz, H_{Ar}), 7.16 (1H, d, *J* 7.8 Hz, H_{Ar}), 7.06 (2H, d, *J* 8.1 Hz, H_{Ts}), 6.89 (1H, dd, *J* 7.8, 1.2 Hz, H_{Ar}), 6.11 (1H, d, *J* 3.3 Hz, H_{Fur}), 6.00 (1H, d, *J* 3.3 Hz, H_{Fur}), 3.69 (3H, s, OCH_3), 3.00–2.96 (2H, m, CH_2), 2.70–2.65 (2H, m, CH_2), 2.30 (3H, s, CH_3), 2.28 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 172.6, 153.9, 150.5, 143.4, 138.8, 136.0, 132.5, 129.3 (2C), 127.2, 126.8 (2C), 126.4, 124.3, 120.3, 108.1, 107.4, 51.8, 32.3, 23.4, 21.4, 21.2; *m/z* (EI, 70 eV) 413 (M^+, 4), 258 (100), 226 (13), 198 (18), 184 (15), 170 (20), 144 (16), 91 (29), 65 (15%).

4.3. *N*-[5-Methyl-2-(5-methyl-2-furyl)phenyl] methanesulfonamide (7m)

This compound was synthesized from **9a** and methanesulfonyl chloride using procedure described in Section 4.2. White solid; yield 55% (1.90 g); mp 71–72 °C (benzene/petroleum ether). Found: C, 59.09; H, 5.58; N, 5.32. $C_{13}H_{15}NO_3S$ requires C, 58.85; H, 5.70; N, 5.28%. R_f=0.54 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3336, 1612, 1576, 1396, 1336, 1328, 1152, 1132, 1036, 976, 900, 808, 800 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.62 (1H, br s, NH), 7.43 (1H, d, *J* 0.9 Hz, H_{Ar}), 7.38 (1H, d, *J* 8.1 Hz, H_{Ar}), 6.98 (1H, dd, *J* 8.1, 0.9 Hz, H_{Ar}), 6.49 (1H, d, *J* 3.3 Hz, H_{Fur}), 6.10 (1H, d, *J* 3.3 Hz, H_{Fur}), 2.87 (3H, s, CH_3), 2.38 (3H, s, CH_3), 2.36 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 152.3, 150.1, 139.0, 132.4, 127.4, 126.4, 123.2, 119.8, 108.9, 107.8, 39.0, 21.2, 13.6; *m/z* (EI, 70 eV) 265 (M^+, 57), 186 (100), 171 (32), 158 (68), 143 (49), 115 (22), 43 (44%).

4.4. General procedure for synthesis of *N*-acyl-5-methyl-2-(5-methyl-2-furyl)anilines 7n,o

Solution of acyl chloride (15 mmol) in benzene (25 mL) was added under stirring to solution of aniline **10a** (1.87 g, 10 mmol) in benzene (30 mL). The reaction mixture was stirred at room temperature for 1 h (TLC control), poured into cold water (100 mL), and neutralized with $NaHCO_3$. The mixture was kept for 2 h, then organic layer was separated and aqueous layer was extracted with ethyl acetate (2×30 mL). The combined organic fractions were dried with anhydrous Na_2SO_4 and filtered. Solvent was evaporated to dryness under reduced pressure. Residue was purified by chromatography on silica gel using benzene/petroleum ether (1:3) mixture as an eluent.

*4.4.1. N-[5-Methyl-2-(5-methyl-2-furyl)phenyl]acetamide (**7n**).* White solid; yield 52% (1.19 g); mp 148–149 °C (benzene/petroleum ether). Found: C, 73.29; H, 6.71; N, 6.06. $C_{14}H_{15}NO_2$ requires C, 73.34; H, 6.59; N, 6.11%. R_f=0.47 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3225, 1656, 1576, 1536, 1028, 820 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.42 (1H, br s, NH), 8.10 (1H, s, H_{Ar}), 7.37 (1H, d, *J* 8.1 Hz, H_{Ar}), 6.92 (1H, d, *J* 8.1 Hz, H_{Ar}), 6.42 (1H, d, *J* 3.0 Hz, H_{Fur}), 6.09 (1H, d, *J* 3.0 Hz, H_{Fur}), 2.38 (3H, s, CH_3), 2.35 (3H, s, CH_3), 2.18 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 168.1, 151.7, 150.7, 138.4, 133.7, 126.9, 125.1, 122.5, 118.0, 108.3, 107.6, 24.9, 21.4, 13.6; *m/z* (EI, 70 eV) 229 (M^+, 47), 187 (26), 144 (63), 115 (12), 43 (100%).

*4.4.2. N-[5-Methyl-2-(5-methyl-2-furyl)phenyl]benzamide (**7o**).* Beige solid; yield 68% (1.99 g); mp 104–105 °C (benzene/petroleum ether). Found: C, 78.56; H, 5.72; N, 4.64. $C_{19}H_{17}NO_2$ requires C, 78.33; H, 5.88; N, 4.81%. R_f=0.63 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3420, 3400, 1684, 1576, 1544, 1420, 1304, 1036, 800 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 9.63 (1H, br s, NH), 8.45 (1H, d, *J* 0.9 Hz, H_{Ar}), 7.97–7.93 (2H, m, H_{Ar}), 7.58–7.46 (3H, m, H_{Ar}), 7.42 (1H, d, *J* 8.1 Hz, H_{Ar}), 6.95 (1H, dd, *J* 8.1, 0.9 Hz, H_{Ar}), 6.48 (1H, d, *J* 3.3 Hz, H_{Fur}), 6.12 (1H, d, *J* 3.3 Hz, H_{Fur}), 2.41 (3H, s, CH_3), 2.40 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 165.0, 151.5, 151.3, 138.5, 135.2, 134.0, 131.7, 128.6 (2C), 126.9 (2C), 126.8, 125.0, 121.9, 117.6, 108.3, 107.9, 21.5, 13.6; *m/z* (EI, 70 eV) 291 (M^+, 31), 143 (12), 105 (100), 77 (79)51 (33), 43 (19%).

4.5. Recyclization of 2-[2-(tosylamino)phenyl]furans 7 into indoles 8, 13, 14

To the refluxing solution of compound **7** (9 mmol) in acetic acid (30 mL) was added 70% $HClO_4$ (3 mL). The reaction mixture was refluxed for 10–15 min (TLC control) and poured into cold water

(300 mL). The formed precipitate was filtered off, washed subsequently with $NaHCO_3$ solution and water, air-dried, and purified by column chromatography on silica gel using benzene/petroleum ether (1:3) mixture as an eluent.

*4.5.1. 1-{6-Methyl-1-[(4-methylphenyl)sulfonyl]-1H-indol-2-yl}acetone (**8a**).* White solid; yield 75% (2.30 g); mp 119–120 °C (benzene/petroleum ether). Found: C, 67.02; H, 5.90; N, 4.02. $C_{19}H_{19}NO_3S$ requires C, 66.84; H, 5.61; N, 4.10%. R_f=0.52 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 1720, 1424, 1364, 1263, 1172, 1135, 1050, 826 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.76 (1H, d, *J* 1.2 Hz, H_{Ar}), 7.64 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.32 (1H, d, *J* 7.8 Hz, H_{Ar}), 7.19 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.02 (1H, dd, *J* 7.8, 1.2 Hz, H_{Ar}), 6.45 (1H, s, H_{Ind}), 4.07 (2H, s, CH_2), 2.43 (3H, s, CH_3), 2.33 (3H, s, CH_3), 2.28 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 204.4, 144.8, 137.0, 135.9, 134.4, 133.3, 129.8 (2C), 126.9, 126.5 (2C), 125.0, 120.1, 114.5, 112.2, 43.6, 29.5, 22.0, 21.5; *m/z* (EI, 70 eV) 341 (M^+, 70), 298 (77), 234 (73), 144 (100), 143 (69), 91 (56), 65 (14), 43 (14%).

*4.5.2. 1-{6-Methoxy-1-[(4-methylphenyl)sulfonyl]-1H-indol-2-yl}acetone (**8b**).* White solid; yield 64% (2.06 g); mp 176–177 °C (benzene/petroleum ether). Found: C, 64.19; H, 5.34; N, 3.91. $C_{19}H_{19}NO_4S$ requires C, 63.85; H, 5.36; N, 3.92%. R_f=0.48 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 1720, 1616, 1490, 1364, 1280, 1173, 1055, 972, 819 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.65 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.47 (1H, d, *J* 2.4 Hz, H_{Ar}), 7.31 (1H, d, *J* 8.7 Hz, H_{Ar}), 7.20 (2H, d, *J* 8.4 Hz, H_{Ts}), 6.82 (1H, dd, *J* 8.7, 2.4 Hz, H_{Ar}), 6.42 (1H, s, H_{Ind}), 4.06 (2H, s, CH_2), 3.82 (3H, s, OCH_3), 2.33 (3H, s, CH_3), 2.28 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 204.6, 157.6, 144.9, 137.6, 135.7, 132.7, 129.8 (2C), 126.5 (2C), 122.9, 121.0, 112.5, 112.1, 98.9, 55.6, 43.7, 29.5, 21.5; *m/z* (EI, 70 eV) 357 (M^+, 47), 315 (23), 314 (92), 250 (21), 160 (100), 144 (39), 117 (19), 91 (31), 43 (19%).

*4.5.3. 1-{6-Chloro-1-[(4-methylphenyl)sulfonyl]-1H-indol-2-yl}acetone (**8c**).* White solid; yield 85% (2.76 g); mp 117–118 °C (benzene/petroleum ether). Found: C, 60.04; H, 4.28; N, 3.88. $C_{18}H_{16}ClNO_3S$ requires C, 59.75; H, 4.46; N, 3.87%. R_f=0.49 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 1721, 1592, 1457, 1424, 1372, 1328, 1273, 1173, 1091, 1048, 948, 830 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.96 (1H, d, *J* 1.8 Hz, H_{Ar}), 7.65 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.34 (1H, d, *J* 8.1 Hz, H_{Ar}), 7.23 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.17 (1H, dd, *J* 8.1, 1.8 Hz, H_{Ar}), 6.47 (1H, s, H_{Ind}), 4.10 (2H, s, CH_2), 2.35 (3H, s, CH_3), 2.29 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 203.9, 145.3, 136.9, 135.4, 134.7, 130.3, 130.0 (2C), 127.6, 126.6 (2C), 124.1, 121.3, 114.5, 111.8, 43.5, 29.6, 21.6; *m/z* (EI, 70 eV) 363/361 (M^+, 20/60), 320/318 (33/100), 256/254 (18/56), 219 (17), 206 (22), 166 (28), 164 (58), 91 (54), 43 (16%).

*4.5.4. 1-{6-Chloro-1-[(4-methylphenyl)sulfonyl]-1H-indol-2-yl}butan-2-one (**8d**).* White solid; yield 73% (2.46 g); mp 131–132 °C (benzene/petroleum ether). Found: C, 60.52; H, 4.78; N, 3.72. $C_{19}H_{18}ClNO_3S$ requires C, 60.71; H, 4.83; N, 3.73%. R_f=0.55 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 1721, 1454, 1365, 1168, 1092, 1050, 952, 816 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.97 (1H, d, *J* 1.8 Hz, H_{Ar}), 7.65 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.33 (1H, d, *J* 8.4 Hz, H_{Ar}), 7.22 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.17 (1H, dd, *J* 8.4, 1.8 Hz, H_{Ar}), 6.46 (1H, s, H_{Ind}), 4.07 (2H, s, CH_2), 2.59 (2H, q, *J* 7.5 Hz, CH_2), 2.35 (3H, s, CH_3), 1.10 (3H, t, *J* 7.5 Hz, CH_3); δ_C (75 MHz, $CDCl_3$) 206.4, 145.3, 136.9, 135.5, 134.8, 130.2, 129.9 (2C), 127.7, 126.6 (2C), 124.1, 121.2, 114.5, 111.8, 42.5, 35.5, 21.5, 7.6; *m/z* (EI, 70 eV) 377/375 (M^+, 11/33), 320/318 (12/36), 254 (64), 219 (27), 164 (57), 128 (22), 91 (50), 57 (100%).

*4.5.5. 1-{1-[(4-Methylphenyl)sulfonyl]-1H-indol-2-yl}acetone (**8e**).* White solid; yield 83% (2.44 g); mp 97–98 °C (benzene/petroleum ether). Found: C, 66.38; H, 5.11; N, 4.18. $C_{18}H_{17}NO_3S$ requires C, 66.03; H, 5.23; N, 4.28%. R_f=0.56 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 1722, 1452, 1361, 1250, 1170, 1121, 1053, 814 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.94–7.91 (1H, m, H_{Ar}), 7.67 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.46–7.43 (1H, m, H_{Ar}), 7.27–7.16 (4H, m, $2H_{Ar}$+$2H_{Ts}$), 6.51 (1H, s, H_{Ind}), 4.13 (2H, s, CH_2), 2.32 (3H, s, CH_3), 2.30 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 204.3, 144.9, 136.5, 135.7, 134.0, 129.8 (2C), 129.1, 126.6 (2C), 124.3, 123.4, 120.6, 114.3, 112.3, 43.6, 29.6, 21.5; *m/z* (EI, 70 eV) 327 (M^+, 100), 284 (82), 220 (54), 172 (26), 130 (57), 91 (47%).

*4.5.6. 1-{1-[(4-Methylphenyl)sulfonyl]-1H-indol-2-yl}butan-2-one (**8f**).* White solid; yield 80% (2.46 g); mp 111–112 °C (benzene/petroleum ether). Found: C, 67.02; H, 5.67; N, 3.94. $C_{19}H_{19}NO_3S$ requires C, 66.84; H, 5.61; N, 4.10%. R_f=0.60 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 1715, 1594, 1450, 1366, 1172, 1111, 809 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.95–7.92 (1H, m, H_{Ar}), 7.66 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.46–7.43 (1H, m, H_{Ar}), 7.26–7.16 (4H, m, $2H_{Ar}$+$2H_{Ts}$), 6.50 (1H, s, H_{Ind}), 4.10 (2H, s, CH_2), 2.60 (2H, q, *J* 7.4 Hz, CH_2), 2.32 (3H, s, CH_3), 1.10 (3H, t, *J* 7.4 Hz, CH_3); δ_C (75 MHz, $CDCl_3$) 206.7, 144.8, 136.5, 135.7, 134.1, 129.7 (2C), 129.2, 126.5 (2C), 124.2, 123.4, 120.5, 114.3, 112.2, 42.6, 35.4, 21.5, 7.6; *m/z* (EI, 70 eV) 341 (M^+, 94), 285 (47), 284 (76), 220 (100), 186 (30), 130 (79), 129 (25), 91 (29), 57 (24), 43 (28%).

*4.5.7. 1-{1-[(4-Methylphenyl)sulfonyl]-1H-indol-2-yl}-3-phenylacetone (**8g**).* White solid; yield 56% (2.03 g); mp 115–116 °C (benzene/petroleum ether). Found: C, 71.22; H, 5.21; N, 3.44. $C_{24}H_{21}NO_3S$ requires C, 71.44; H, 5.25; N, 3.47%. R_f=0.61 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 1730, 1452, 1358, 1172, 1088, 1051 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.96–7.93 (1H, m, H_{Ar}), 7.64 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.45–7.42 (1H, m, H_{Ar}), 7.39–7.16 (9H, m, $7H_{Ar}$+$2H_{Ts}$), 6.46 (1H, s, H_{Ind}), 4.11 (2H, s, CH_2), 3.90 (2H, s, CH_2), 2.31 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 203.7, 144.9, 136.6, 135.8, 133.9, 133.8, 129.8 (2C), 129.7 (2C), 129.2, 128.7 (2C), 127.1, 126.6 (2C), 124.3, 123.4, 120.6, 114.3, 112.4, 49.6, 42.2, 21.5; *m/z* (EI, 70 eV) (%) 403 (M^+, 21), 284 (49), 220 (71), 205 (21), 130 (89), 102 (22), 91 (100), 77 (17), 65 (66%).

*4.5.8. 1-(4-Methylphenyl)-3-{1-[(4-methylphenyl)sulfonyl]-1H-indol-2-yl}acetone (**8h**).* White solid; yield 60% (2.25 g); mp 109–110 °C (benzene/petroleum ether). Found: C, 72.03; H, 5.63; N, 3.25. $C_{25}H_{23}NO_3S$ requires C, 71.92; H, 5.55; N, 3.35%. R_f=0.63 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 1724, 1456, 1386, 1256, 1192, 1180, 1088, 1068, 1052, 808 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.98–7.95 (1H, m, H_{Ar}), 7.66 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.46–7.43 (1H, m, H_{Ar}), 7.28–7.16 (8H, m, $6H_{Ar}$+$2H_{Ts}$), 6.46 (1H, s, H_{Ind}), 4.13 (2H, s, CH_2), 3.88 (2H, s, CH_2), 2.36 (3H, s, CH_3), 2.31 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 203.9, 144.8, 136.6, 136.5, 135.8, 133.9, 130.8, 129.7 (2C), 129.5 (2C), 129.3 (2C), 129.1, 126.6 (2C), 124.2, 123.4, 120.5, 114.2, 112.4, 49.2, 42.1, 21.5, 21.0; *m/z* (EI, 70 eV) 417 (M^+, 13), 284 (57), 220 (70), 130 (71), 105 (100), 91 (62), 77(26), 65 (21%).

*4.5.9. 5-{6-Chloro-1-[(4-methylphenyl)sulfonyl]-1H-indol-2-yl}-4-oxopentanoic acid (**13a**).* White solid; yield 45% (1.70 g); mp 147–148 °C (benzene/petroleum ether). Found: C, 56.84; H, 4.15; N, 3.13. $C_{20}H_{18}ClNO_5S$ requires C, 57.21; H, 4.32; N, 3.34%. R_f=0.02 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3430, 1712, 1424, 1360, 1276, 1260, 1172, 1088, 948 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 9.92 (1H, br s, OH), 7.97 (1H, s, H_{Ar}), 7.63 (2H, d, *J* 8.2 Hz, H_{Ts}), 7.34–7.14 (4H, m, $2H_{Ar}$+$2H_{Ts}$), 6.49 (1H, s, H_{Ind}), 4.11 (2H, s, CH_2), 2.89–2.87 (2H, m, CH_2), 2.69–2.66 (2H, m, CH_2), 2.33 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 203.9, 178.5, 145.3, 136.9, 135.4, 134.2, 130.3, 130.0 (2C), 127.6, 126.5 (2C), 124.2, 121.3, 114.5, 112.2, 42.7, 36.4, 27.8, 21.5; *m/z* (EI, 70 eV) 421/419 (M^+, 2/6), 319 (33), 164 (100), 155(18), 101 (27), 91 (84) 65 (44%).

*4.5.10. 5-{6-Methyl-1-[(4-methylphenyl)sulfonyl]-1H-indol-2-yl}-4-oxopentanoic acid (**13b**).* White solid; yield 43% (1.54 g); mp

170–171 °C (benzene/petroleum ether). Found: C, 63.28; H, 5.20; N, 3.36. $C_{21}H_{21}NO_5S$ requires C, 63.14; H, 5.30; N, 3.51%. R_f=0.02 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 3472, 1712, 1360, 1264, 1224, 1172, 1140, 1084, 1052, 828 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 9.98 (1H, br s, OH), 7.77 (1H, s, H_{Ar}), 7.62 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.31 (1H, d, *J* 7.8 Hz, H_{Ar}), 7.19 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.02 (1H, d, *J* 7.8 Hz, H_{Ar}), 6.48 (1H, s, H_{Ind}), 4.09 (2H, s, CH_2), 2.89–2.86 (2H, m, CH_2), 2.68–2.65 (2H, m, CH_2), 2.43 (3H, s, CH_3), 2.32 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 204.3, 178.2, 144.8, 137.2, 135.9, 134.5, 132.8, 129.8 (2C), 126.9, 126.5 (2C), 125.0, 120.2, 114.6, 112.6, 42.9, 36.3, 27.8, 21.9, 21.5; *m*/*z* (EI, 70 eV) 399 (M^+, 3), 299 (12), 234 (13), 144 (100), 115 (10), 91 (31), 65 (17%).

*4.5.11. 1-(1-Methanesulfonyl-6-methyl-1H-indol-2-yl)acetone (**14**).* White solid; yield 68% (1.62 g); mp 159–160 °C (benzene/petroleum ether). Found: C, 59.08; H, 5.66; N, 5.32. $C_{13}H_{15}NO_3S$ requires C, 58.85; H, 5.70; N, 5.28%. R_f=0.51 (CH_2Cl_2/acetone/petroleum ether=1:1:2); ν_{max} (KBr) 1720, 1452, 1423, 1354, 1330, 1268, 1167, 1060, 974, 810 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.39 (1H, d, *J* 8.1 Hz, H_{Ar}), 7.18 (1H, d, *J* 0.9 Hz, H_{Ar}), 7.08 (1H, dd, *J* 8.1, 0.9 Hz, H_{Ar}), 6.41 (1H, s, H_{Ind}), 4.10 (2H, s, CH_2), 3.11 (3H, s, CH_3), 2.48 (3H, s, CH_3), 2.29 (3H, s, CH_3); δ_C NMR (75 MHz, $CDCl_3$) 205.5, 136.7, 134.6, 133.3, 126.7, 124.9, 120.3, 113.6, 111.3, 43.6, 39.1, 29.5, 21.9; *m*/*z* (EI, 70 eV) 265 (M^+, 2), 222 (26), 142 (49), 143 (74), 115 (22), 43 (100), 39 (20%).

4.6. Transformation of 2-[2-(tosylamino)phenyl]furans 7a–c induced by ethanolic HCl

Compound **7** (3 mmol) was added to HCl ethanolic solution (20 mL) prepared by dissolution of 100 g of gaseous HCl in 200 g of ethanol. The reaction mixture was refluxed for 6 h. Then it was poured into cold water. The formed precipitate was filtered off, washed subsequently with $NaHCO_3$ solution and water, air-dried. Residue was purified by column chromatography on silica gel using AcOEt/petroleum ether (1:4) mixture as an eluent affording compounds **8** and **11**. Reaction of **7a** (R_f=0.34) affords 27% **8a** (R_f=0.16) and 43% **11a** (R_f=0.05); **7b** (R_f=0.29) gives 42% **8b** (R_f=0.14) and 32% **11b** (R_f=0.04); **7c** (R_f=0.29) gives 30% **8c** (R_f=0.09) and 25% **11c** (R_f=0.05).

*4.6.1. N-[5-Methyl-2-(4-oxopentanoyl)phenyl]-4-methylbenzenesulfonamide (**11a**).* White solid; yield 43% (0.46 g); mp 111–112 °C (AcOEt/petroleum ether). Found: C, 63.78; H, 6.11; N, 3.83. $C_{19}H_{21}NO_4S$ requires C, 63.49; H, 5.89; N, 3.90%. R_f=0.05 (AcOEt/petroleum ether=1:4); ν_{max} (KBr) 3089, 1716, 1652, 1596, 1494, 1402, 1163, 931, 874, 820 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 11.42 (1H, br s, NH), 7.73 (1H, d, *J* 8.1 Hz, H_{Ar}), 7.69 (2H, d, *J* 8.1 Hz, H_{Ts}), 7.43 (1H, d, *J* 1.2 Hz, H_{Ar}), 7.21 (2H, d, *J* 8.1 Hz, H_{Ts}), 6.83 (1H, dd, *J* 8.1, 1.2 Hz, H_{Ar}), 3.20–3.16 (2H, m, CH_2), 2.80–2.76 (2H, m, CH_2), 2.35 (3H, s, CH_3), 2.30 (3H, s, CH_3), 2.26 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 207.1, 201.8, 146.2, 143.8, 140.0, 136.4, 130.9, 129.6 (2C), 127.2 (2C), 123.5, 119.4, 119.1, 36.7, 33.1, 30.1, 22.0, 21.5; *m*/*z* (EI, 70 eV) 359 (M^+, 33), 288 (65), 223 (40), 204 (26), 161 (70), 134 (57), 91 (100), 77 (32), 65 (33), 59 (47), 43(27%).

*4.6.2. N-[5-Methoxy-2-(4-oxopentanoyl)phenyl]-4-methylbenzenesulfonamide (**11b**).* White solid; yield 32% (0.36 g); mp 114–115 °C (AcOEt/petroleum ether). Found: C, 60.88; H, 5.63; N, 3.69. $C_{19}H_{21}NO_5S$ requires C, 60.78; H, 5.64; N, 3.73%. R_f=0.04 (AcOEt/petroleum ether=1:4); ν_{max} (KBr) 3402, 1719, 1635, 1571, 1510, 1158, 898 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.80 (1H, br s, NH), 7.79 (1H, d, *J* 9.0 Hz, H_{Ar}), 7.71 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.23 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.11 (1H, d, *J* 2.7 Hz, H_{Ar}), 6.53 (1H, dd, *J* 9.0, 2.7 Hz, H_{Ar}), 3.79 (3H, s, OCH_3), 3.19–3.15 (2H, m, CH_2), 2.81–2.77 (2H, m, CH_2), 2.35 (3H, s, CH_3), 2.26 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 207.2, 200.6, 164.3, 143.9, 142.5, 136.3, 133.0, 129.6 (2C), 127.2 (2C), 115.0, 109.0, 102.6, 55.5, 36.7, 32.9, 30.1, 21.5; *m*/*z* (EI, 70 eV) 375 (M^+, 52), 304 (83), 239 (90), 220 (34), 176 (100), 149 (46), 91 (56), 43 (53%).

*4.6.3. N-[5-Chloro-2-(4-oxopentanoyl)phenyl]-4-methylbenzenesulfonamide (**11c**).* White solid; yield 25% (0.28 g); mp 115–116 °C (AcOEt/petroleum ether). Found: C, 56.72; H, 4.61; N, 3.49. $C_{18}H_{18}ClNO_4S$ requires C, 56.92; H, 4.78; N, 3.69. R_f=0.05 (AcOEt/petroleum ether=1:4); ν_{max} (KBr) 3113, 1716, 1649, 1616, 1397, 1158, 906, 818 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 11.47 (1H, br s, NH), 7.80 (1H, d, *J* 8.4 Hz, H_{Ar}), 7.72 (2H, d, *J* 8.4 Hz, H_{Ts}), 7.66 (1H, d, *J* 1.8 Hz, H_{Ar}), 7.26 (2H, d, *J* 8.4 Hz, H_{Ts}), 6.99 (1H, dd, *J* 8.4, 1.8 Hz, H_{Ar}), 3.20–3.16 (2H, m, CH_2), 2.83–2.79 (2H, m, CH_2), 2.37 (3H, s, CH_3), 2.26 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 206.8, 201.5, 144.2, 141.0, 140.9, 136.0, 132.1, 129.8 (2C), 127.2 (2C), 122.6, 119.8, 118.3, 36.6, 33.3, 30.0, 21.5; *m*/*z* (EI, 70 eV) 381/379 (M^+, 12/36), 338/336 (6/18), 310/308 (24/72), 243 (28), 224 (57), 182 (30), 180 (44), 155 (52), 91 (100), 65 (32), 55 (31), 43 (32%).

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Supplementary data

Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2011.10.114.

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