DOI 10.1007/s10593-024-03309-z
Chemistry of Heterocyclic Compounds **2024**, *60*(3/4), 138–142

An efficient synthesis of (*E*)-3-[(dimethylamino)methylidene]furan-2(3*H*)-thiones and transamination reactions thereof

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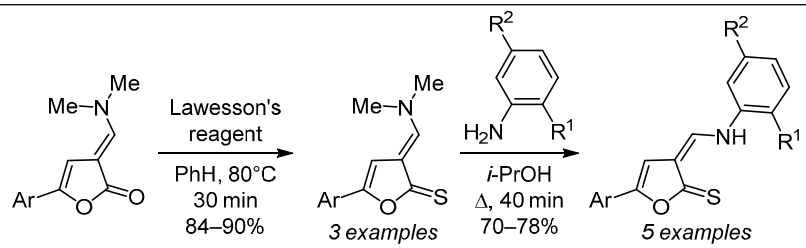
Translated from Khimiya Geterotsiklicheskikh Soedinenii, 2024, *60*(3/4), 138–142

Submitted April 1, 2024
Accepted after revision May 9, 2024



Ar = Ph, 4-MeC$_6$H$_4$, 4-ClC$_6$H$_4$; R^1 = OH, R^2 = H; R^1 = OH, R^2 = Me

The conditions were developed and the optimal temperature regime was selected for a selective thionation of 5-aryl-3-[(dimethylamino)-methylidene]furan-2(3*H*)-ones with Lawesson's reagent. The stereochemistry of the synthesized 3-[(dimethylamino)methylidene]furan-2(3*H*)-thiones was established. Based on this, a number of 3-arylaminomethylidenefuran-2(3*H*)-thiones were synthesized *via* transamination reaction.

Keywords: *N*,*N*-dimethylformamide dimethyl acetal, furan-2(3*H*)-ones, Lawesson's reagent, push-pull furan-2(3*H*)-thiones, transamination reaction.

Recently, in the field of organic synthesis, interest in enamine systems, particularly dimethylaminomethylidene derivatives of various classes of compounds, has been steadily increasing. Due to the pronounced push-pull nature of the C=C double bond,[1,2] these structures act as electrophilic substrates. The presence of a sterically unhindered β-position of the C=C bond makes it possible to functionalize such systems in various ways. These structures are widely used as platform compounds in the design and creation of new ligands with antitumor,[3–6] anti-inflammatory,[3] antibacterial[7,8] activity. They also exhibit anti-glycation and α-glucosidase inhibiting properties.[9]

The synthetic potential of noncyclic enamine derivatives was studied in reactions with N-nucleophilic reagents of varying nucleophilicities, differing in the number and nature of nucleophilic centers, which resulted in the construction of new polyheterocyclic compounds containing pyrimidine,[10–12] pyridine,[13,14] pyrazole[15–17] heterocycles. Such systems are used as starting substrates in reactions with active methylene reagents to obtain complex heterocyclic building blocks containing pyran[18–20] and chromene[21] fragments.

Transamination reactions present an effective tool in the field of modern organic synthesis and contribute to the creation of new multifunctional substrates. These starting compounds include aminomethylidene derivatives, which are highly active synthetically due to the presence of several reaction centers.

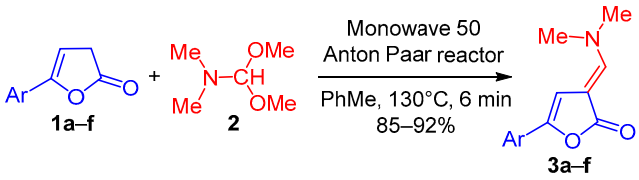
Methods for the synthesis of 3-[((het)arylamino)-methylidene]furan-2(3*H*)-ones[22,23] were previously developed based on a three-component reaction of 5-aryl-substituted furan-2(3*H*)-ones, ortho ester, and aromatic and heterocyclic amines. The transamination reaction of dimethylaminomethylidene derivatives of various heterocycles with amines (aliphatic, aromatic, heterocyclic) is the best known method in the literature for preparing aminomethylidene derivatives.

The synthesis of the only enamine derivative of furan-2(3*H*)-one, 3-[(dimethylamino)methylidene]-5-phenylfuran-2(3*H*)-one (**3a**), was previously described, which involved the aminoformylation reaction of the oxo derivative of the five-membered heterocycle 5-phenylfuran-2(3*H*)-one.[24]

A previous study[25] demonstrated the possibility of synthesizing enamine derivatives employing the enamination reaction of 5-arylfuran-2(3*H*)-ones **1a**–**f** with the single-carbon dimethylformamide dimethyl acetal synthon (**2**) in a Monowave 50 synthesis reactor (Anton Paar) under elevated pressure conditions. The anomalous

inertness of compounds **3a–f** toward N-nucleophilic reagents was established, which was explained on the basis of X-ray structural analysis data (Scheme 1).

Scheme 1

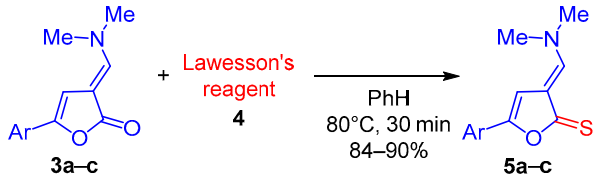


a Ar = Ph, **b** Ar = 4-MeC_6H_4, **c** Ar = 4-ClC_6H_4, **d** Ar = 3,4-$Me_2C_6H_3$, **e** Ar = 4-BrC_6H_4, **f** Ar = 4-$MeOC_6H_4$

A single example of dimethylaminomethylidene derivatives of sulfur-containing analogs of oxo derivatives of five-membered heterocycles is known. Their synthesis involved the formation of the 5-chloro-4-formyl derivative of the corresponding furanone from 3-[(dimethylamino)-methylidene]-5-phenylfuran-2(3*H*)-one (**3a**), followed by substitution of the chlorine atom by the mercaptide ion.[24]

We propose a simpler and more effective method for the synthesis of thio analogs of 5-aryl-3-[(dimethylamino)-methylidene]furan-2(3*H*)-ones **5a–c** using selective thionation with Lawesson's reagent **4** of the resulting dimethylaminomethylidene derivatives of furan-2(3*H*)-ones **3a–c** (Scheme 2).

Scheme 2



a Ar = Ph, **b** Ar = 4-MeC_6H_4, **c** Ar = 4-ClC_6H_4

The optimization of the conditions for thionation was carried out using the example of 5-(4-chlorophenyl)-3-[(dimethylamino)methylidene]furan-2(3*H*)-one (**3c**). It is known that nonpolar solvents such as PhH and PhMe are most commonly used, which is due to their ability to dissolve Lawesson's reagent **4**. It was found that thionation depends on the temperature regime (Table 1). Carrying out the reaction under reflux (110°C) in PhMe led to resinification of the reaction mixture, and the target product could not be isolated. This was also observed when the temperature was decreased to 100°C. At 95 and 90°C, the formation of the target product 5-(4-chlorophenyl)-3-[(dimethylamino)methylidene]furan-2(3*H*)-thione (**5c**) was observed in yields of 45 and 50%, respectively. The best result was achieved when the reaction was carried out under reflux in PhH; the product was isolated in 84% yield. These conditions were chosen as optimal and used to carry out the reactions of other 5-aryl-substituted 3-[(dimethyl-amino)methylidene]furan-2(3*H*)-ones.

The ^{1}H NMR spectra of the synthesized dimethyl-aminomethylidene-substituted furan-2(3*H*)-thiones **5a–c** exhibit the characteristic signals corresponding to the protons at the exocyclic C=C bond, as well as methyl and furan-2(3*H*)-thione protons (Fig. 1). The signals of the protons of the exocyclic C=C bond are shifted downfield (8.05–8.09 ppm) compared to the corresponding signals of the starting 5-aryl-3-[(dimethylamino)methylidene]furan-2(3*H*)-ones **3a–c** (7.19–7.28 ppm), which could probably be due to steric interaction between the sulfur atom and the hydrogen atom at the C=C double bond. This fact suggests an increase in the electron density in the enamine fragment of 5-aryl-substituted 3-[(dimethylamino)methylidene]furan-2(3*H*)-thiones **5a–c**, which makes the dimethylamino group a good leaving group in elimination processes.

Table 1. The yield of product **5c** *vs* the reaction temperature

Temperature, °C	Solvent	Yield, %
110	PhMe	–*
105	PhMe	–*
100	PhMe	–*
95	PhMe	45
90	PhMe	50
80	PhH	84

* Resinification of the reaction mixture was observed.

In the NOESY spectrum of 5-(4-chlorophenyl)-3-[(di-methylamino)methylidene]furan-2(3*H*)-thione (**5c**), upon selective excitation of the proton of the furan-2(3*H*)-thione ring, a cross peak is observed at 7.26/3.48 ppm, showing correlation with the methyl group of the enamine fragment, and excitation of the proton at the C=C bond produces a cross peak at 8.08/3.55 ppm, which corresponds to correlation with the second methyl group, indicating the *E*-configuration of the double bond (Fig. 1).

Previously, the direct amination method with aromatic amines containing only electron-withdrawing substituents was used for the synthesis of aminomethylidene deri-vatives.[26] It was shown that it was impossible to introduce electron-donating aromatic amines into the amination reaction. This lack of reactivity is explained by their higher basicity compared to electron-withdrawing aromatic amines, which further confirms the effectiveness of using transamination reactions in the synthesis of amino-methylidene derivatives (Scheme 3).

In continuation of our research on the development of methods for the preparation of new furan-2(3*H*)-thiones aminomethylidene derivatives and the study of the chemical properties of the resulting push-pull dimethylamino-

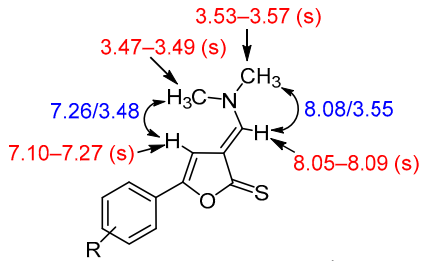
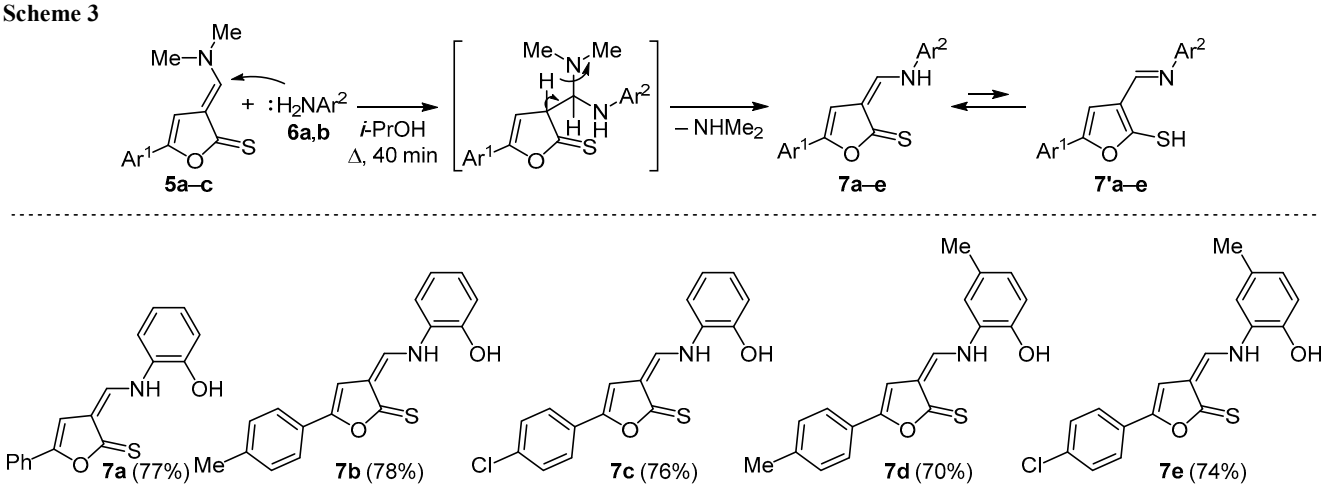


Figure 1. The characteristic signals in the ^{1}H NMR spectra of compounds **5a–c** (red) and cross peaks in the NOESY spectrum of compound **5c** (δ in ppm) (blue).

Scheme 3



methylidene-substituted 5-arylfuran-2(3*H*)-thiones, we carried out their transamination reactions with aromatic amines **6a**,**b** containing electron-donating substituents (2-aminophenol and 2-amino-4-methylphenol). We found that heating the reaction mixture in *i*-PrOH under reflux in the absence of a catalyst proved to be suitable conditions for carrying out the transamination. The reaction proceeds as a primary Michael addition of the amino group of the amine, followed by elimination of the dimethylamine molecule to form 5-aryl-3-{[(2-R-phenyl)amino]methylidene}furan-2(3*H*)-thiones **7a**–**e** in 82–90% yields (Scheme 3). The structure of the obtained 5-aryl-3-{[(2-R-phenyl)amino]methylidene}furan-2(3*H*)-thiones **7a**–**e** was established based on IR and NMR spectroscopy data.

For 5-aryl-3-{[(2-R-phenyl)amino]methylidene}furan-2(3*H*)-thiones **7a**–**e**, the existence of various tautomeric forms is possible as a result of thione–thiol tautomerism (Scheme 3). The IR spectra recorded for samples in the KBr matrix contain absorption bands of the thiocarbonyl group at 1091–1100 cm^{-1}, as well as stretching vibrations of the NH group, which appear in the region of 3280–3473 cm^{-1}, and stretching vibrations of the C=C double bond at 1635–1657 cm^{-1}, which indicates the existence of the synthesized compounds **7a**–**e** in the aminomethylidene thione form (Scheme 3).

The ^{1}H NMR spectrum of 5-aryl-3-{[(2-R-phenyl)-amino]methylidene}furan-2(3*H*)-thiones **7a**–**e** recorded in DMSO-d_6 is characterized by the signals of the protons of the furan-2(3*H*)-thione ring in the region of 6.87–6.94 ppm, protons of the exocyclic C=C bond in the region of 8.89–8.95 ppm as doublets with SSCC J = 12.0–14.1 Hz, protons of the NH group also as doublets at 13.16–13.24 ppm with SSCC J = 12.0–14.2 Hz.

The presence of the C=C double bond in the structure of compounds **7a**–**e** makes it possible for such systems to exist in the form of a mixture of *Z*- and *E*-isomers. Transamination yielded compounds **7a**–**e** in the form of the isomer with the *Z*-configuration of the C=C double bond. This can probably be proven by the downfield shift of the signal of the proton of the NH group (13.16–13.24 ppm), as well as the observation of the coupling constant of the H-bonded proton (J = 12.0–14.2 Hz), which confirms the existence of the obtained compounds **7a**–**e** in the form of the *cis*-enamine with an intramolecular hydrogen bond of the NH···S type. This observation, using the example of aminomethylidene structures, is well documented in the literature.[24] The substitution of the bulky methyl groups with a phenyl substituent and its probable deshielding of the proton at the exocyclic C=C bond due to ring currents leads to a downfield shift of this proton in the ^{1}H NMR spectra compared with the chemical shifts of this proton in the spectra of the starting compounds **5a**–**c**.

A NOESY experiment on 3-{[(2-hydroxyphenyl)amino]-methylidene}-5-(*p*-tolyl)furan-2(3*H*)-thione (**7b**) as an example shows the spatial proximity of the protons of the NH and OH groups, which corresponds to the cross peak at 10.62/13.20 ppm, and also shows the absence of correlation between the proton of the furan-2(3*H*)-thione ring and the proton of the NH group, which present further evidence in favor of the *Z*-configuration (Fig. 2).

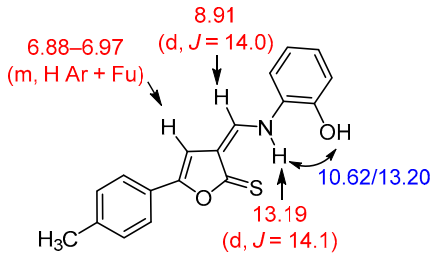


Figure 2. The characteristic signals in the ^{1}H NMR spectrum (red) and cross peak in the NOESY spectrum (blue) of compound **7b** (δ in ppm, J in Hz).

To conclude, selective thionation of 5-aryl-3-[(dimethylamino)methylidene]furan-2(3*H*)-ones has been carried out yielding their thio analogs. The latter present a platform for the synthesis of 5-aryl-3-{[(2-R-phenyl)amino]-methylidene}furan-2(3*H*)-thiones containing electron-donating substituents in the aromatic fragment.

Experimental

IR spectra were registered on a Nicolet 6700 (Thermo Scientific, USA) Fourier transform spectrophotometer in 4000–40 cm^{-1} range with samples in KBr pellets. ^{1}H and ^{13}C

NMR spectra (400 and 100 MHz, respectively) were acquired on a Varian (Agilent) 400 spectrometer in acetone-d_6 and DMSO-d_6, with TMS as internal standard. Elemental analysis was performed on an Elementar vario MICRO cube CHNS-analyzer. Melting points were determined on a StuartTM SMP10 instrument in open capillaries. The progress of the reactions and the purity of the resulting compounds were monitored by TLC on ALUGRAM SIL G/UV254 plates, eluent hexane–EtOAc–acetone, 2:2:1, visualization under UV light.

The starting (*E*)-5-aryl-3-[(dimethylamino)methylidene]-furan-2(3*H*)-ones **3a**–**c** were synthesized using a previously developed procedure.[23]

Synthesis of (*E*)-5-aryl-3-[(dimethylamino)methylidene]furan-2(3*H*)-thione 5a–c (General method). A mixture of 5-aryl-3-[(dimethylamino)methylidene]furan-2(3*H*)-one **3a**–**c** (1 mmol), Lawesson's reagent **4** (1 mmol), and PhH (10 ml) was charged into a flat-bottom flask, and the mixture was heated at 80°C for 30 min. The formed precipitate was filtered off, washed with PhH, and purified by recrystallization from EtOH.

(*E*)-3-[(Dimethylamino)methylidene]-5-phenylfuran-2(3*H*)-thione (5a). Yield 190 mg (84%), yellow crystals, mp 158–160°C. IR spectrum, ν, cm^{-1}: 1634 (C=C), 1350 (CH_3), 1209 (C=S). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 3.48 (3H, s, CH_3); 3.55 (3H, s, CH_3); 7.19 (1H, s, 4-CH furan); 7.24–7.29 (1H, m, H Ph); 7.37–7.41 (2H, m, H Ph); 7.69 (2H, d, *J* = 8.0, H Ph); 8.07 (1H, s, =CH). ^{13}C NMR spectrum (acetone-d_6), δ, ppm: 39.7 (CH_3); 47.4 (CH_3); 101.8 (C-4 furan); 114.6 (C-3 furan); 123.4; 127.4; 128.6; 129.7; 151.3 (C-5 furan); 154.7 (C=C exo); 198.9 (C=S). Found, %: C 67.85; H 6.05; N 6.43; S 14.05. $C_{13}H_{13}NOS$. Calculated, %: C 67.50; H 5.67; N 6.06; S 13.86.

(*E*)-3-[(Dimethylamino)methylidene]-5-(*p*-tolyl)furan-2(3*H*)-thione (5b). Yield 210 mg (86%), yellow crystals, mp 199–200°C. IR spectrum, ν, cm^{-1}: 1632 (C=C), 1347 (CH_3), 1215 (C=S). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 2.33 (3H, s, CH_3 tolyl); 3.47 (3H, s, CH_3); 3.54 (3H, s, CH_3); 7.12 (1H, s, 4-CH furan); 7.21 (2H, d, *J* = 8.0, H Ar); 7.58 (2H, d, *J* = 8.0, H Ar); 8.05 (1H, s, =CH). ^{13}C NMR spectrum (acetone-d_6), δ, ppm: 20.3 (CH_3 tolyl); 39.7 (CH_3); 47.4 (CH_3); 100.9 (C-4 furan); 114.6 (C-3 furan); 123.5; 127.1; 129.3; 137.3; 151.6 (C-5 furan); 154.5 (C=C exo); 198.8 (C=S). Found, %: C 68.03; H 6.44; N 6.11; S 13.55. $C_{14}H_{15}NOS$. Calculated, %: C 68.54; H 6.16; N 5.71; S 13.07.

(*E*)-5-(4-Chlorophenyl)-3-[(dimethylamino)methylidene]-furan-2(3*H*)-thione (5c). Yield 230 mg (90%), yellow crystals, mp 190–191°C. IR spectrum, ν, cm^{-1}: 1623 (C=C), 1343 (CH_3), 1213 (C=S). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 3.49 (3H, s, CH_3); 3.57 (3H, s, CH_3); 7.27 (1H, s, 4-CH furan); 7.42 (2H, d, *J* = 8.0, H Ar); 7.69 (2H, d, *J* = 12.0, H Ar); 8.09 (1H, s, =CH). ^{13}C NMR spectrum (acetone-d_6), δ, ppm: 39.8 (CH_3); 47.7 (CH_3); 102.7 (C-4 furan); 114.5 (C-3 furan); 125.0; 128.8; 150.1 (C-5 furan); 155.1 (C=C exo); 198.6 (C=S). Found, %: C 58.59; H 4.05; N 5.73; S 13.21. $C_{13}H_{12}ClNOS$. Calculated, %: C 58.75; H 4.55; N 5.27; S 12.96.

Synthesis of (*Z*)-5-aryl-3-{[(2-R-phenyl)amino]methylidene}furan-2(3*H*)-thiones 7a–e (General method). 5-Aryl-3-[(dimethylamino)methylidene]furan-2(3*H*)-thione **5a**–**c** (1 mmol), the corresponding aromatic amine **6a**,**b** (2-aminophenol, 2-amino-4-methylphenol) (1 mmol), and *i*-PrOH (10 ml) were charged into a round-bottom flask equipped with a reflux condenser. The reaction mixture was heated under reflux for 40 min. After the completion of the reaction, the solvent was evaporated on a rotary evaporator and the residue was triturated in H_2O. The solid was filtered off, washed with H_2O, and purified by recrystallization in PhMe.

(*Z*)-3-{[(2-Hydroxyphenyl)amino]methylidene}-5-phenylfuran-2(3*H*)-thione (7a). Yield 227 mg (77%), red crystals, mp 213–215°C. IR spectrum, ν, cm^{-1}: 3375 (NH), 3306 (OH), 1640 (C=C), 1098 (C=S). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 6.94–7.10 (5H, m, H Ar, 4-CH furan); 7.30–7.67 (5H, m, H Ar); 8.94 (1H, d, *J* = 14.1, =CH); 10.63 (1H, s, OH); 13.22 (1H, d, *J* = 14.1, NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 105.6 (C-4 furan); 115.4 (C-3 furan); 116.5; 116.8; 120.5; 123.8; 126.6; 127.3; 128.3; 129.4; 145.3 (C=C exo); 147.7 (C–OH); 151.5 (C-5 furan); 188.4 (C=S). Found, %: C 69.50; H 4.97; N 5.11; S 11.21. $C_{17}H_{13}NO_2S$. Calculated, %: C 69.13; H 4.44; N 4.74; S 10.85.

(*Z*)-3-{[(2-Hydroxyphenyl)amino]methylidene}-5-(*p*-tolyl)furan-2(3*H*)-thione (7b). Yield 241 mg (78%), red crystals, mp 219–221°C. IR spectrum, ν, cm^{-1}: 3471 (NH), 3416 (OH), 1635 (C=C), 1093 (C=S). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.31 (3H, s, CH_3); 6.88–6.97 (2H, m, H Ar, 4-CH furan); 6.98 (1H, dd, *J* = 8.1, *J* = 1.4, H Ar); 7.05–7.14 (1H, m, H Ar); 7.24 (2H, d, *J* = 7.9, H Ar); 7.56 (2H, d, *J* = 7.8, H Ar); 7.67 (1H, d, *J* = 8.1, H Ar); 8.91 (1H, d, *J* = 14.0, =CH); 10.62 (1H, s, OH); 13.19 (1H, d, *J* = 14.1, NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 21.3 (CH_3); 104.7 (C-4 furan); 115.5 (C-3 furan); 116.5; 116.7; 120.5; 123.8; 126.6; 126.7; 127.1; 130.0; 137.8; 145.1 (C=C exo); 147.7 (C–OH); 151.8 (C-5 furan); 188.4 (C=S). Found, %: C 70.13; H 5.14; N 4.91; S 10.82. $C_{18}H_{15}NO_2S$. Calculated, %: C 69.88; H 4.89; N 4.53; S 10.36.

(*Z*)-5-(4-Chlorophenyl)-3-{[(2-hydroxyphenyl)amino]-methylidene}furan-2(3*H*)-thione (7c). Yield 250 mg (76%), red crystals, mp 220–221°C. IR spectrum, ν, cm^{-1}: 3473 (NH), 3412 (OH), 1639 (C=C), 1091 (C=S). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 6.92–6.99 (2H, m, H Ar); 7.04 (1H, s, 4-CH furan); 7.11 (1H, t, *J* = 8.0, H Ar); 7.48 (2H, d, *J* = 8.0, H Ar); 7.68–7.72 (3H, m, H Ar); 8.95 (1H, d, *J* = 12.0, =CH); 10.65 (1H, br. s, OH); 13.24 (1H, d, *J* = 12.0, NH). ^{13}C NMR spectrum DMSO-d_6), δ, ppm: 106.5 (C-4 furan); 115.4 (C-3 furan); 116.5; 116.9; 120.5; 125.5; 126.5; 127.4; 128.3; 129.5; 132.5; 145.7 (C=C exo); 147.8 (C–OH); 150.3 (C-5 furan); 188.4 (C=S). Found, %: C 62.39; H 4.07; N 4.78; S 10.21. $C_{17}H_{12}ClNO_2S$. Calculated, %: C 61.91; H 3.67; N 4.25; S 9.72.

(*Z*)-3-{[(2-Hydroxy-5-methylphenyl)amino]methylidene}-5-(*p*-tolyl)furan-2(3*H*)-thione (7d). Yield 226 mg (70%), red crystals, mp 205–206°C. IR spectrum, ν, cm^{-1}: 3473 (NH), 3211 (OH), 1642 (C=C), 1319 (CH_3), 1100 (C=S). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz):

2.26 (3H, s, CH_3); 2.31 (3H, s, CH_3); 6.85–6.91 (3H, m, H Ar, 4-CH furan); 7.23 (2H, d, J = 7.8, H Ar); 7.49–7.59 (3H, m, H Ar); 8.89 (1H, d, J = 14.0, =CH); 10.35 (1H, s, OH); 13.16 (1H, d, J = 14.0, NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 20.8 (CH_3); 21.3 (CH_3); 104.6 (C-4 furan); 115.5 (C-3 furan); 116.3; 116.9; 123.8; 126.2; 126.7; 127.6; 129.4; 130.0; 137.8; 145.0 (C=C exo); 145.4 (C–OH); 151.7 (C-5 furan); 188.2 (C=S). Found, %: C 69.98; H 5.87; N 4.91; S 10.22. $C_{19}H_{17}NO_2S$. Calculated, %: C 70.56; H 5.30; N 4.33; S 9.91.

(*Z*)-5-(4-Chlorophenyl)-3-{[(2-hydroxy-5-methylphenyl)amino]methylidene}furan-2(3*H*)-thione (7e). Yield 253 mg (74%), red crystals, mp 209–210°C. IR spectrum, ν, cm^{-1}: 3469 (NH), 3225 (OH), 1650 (C=C), 1326 (CH_3), 1092 (C=S). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (J, Hz): 2.26 (3H, s, CH_3); 6.85–6.92 (2H, m, H Ar); 7.02 (1H, s, 4-CH furan); 7.47 (2H, d, J = 8.2, H Ar); 7.53 (1H, s, H Ar); 7.68 (2H, d, J = 8.1, H Ar); 8.95 (1H, d, J = 14.1, =CH); 10.40 (1H, s, OH); 13.21 (1H, d, J = 14.2, NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 20.8 (CH_3); 106.5 (C-4 furan); 115.4 (C-3 furan); 116.4; 117.1; 125.5; 126.1; 127.8; 128.3; 129.4; 129.5; 132.5; 145.5 (C=C exo); 150.3 (C-5 furan); 188.2 (C=S). Found, %: C 63.21; H 4.59; N 4.61; S 9.82. $C_{18}H_{14}ClNO_2S$. Calculated, %: C 62.88; H 4.10; N 4.07; S 9.32.

Supplementary file containing ^{1}H and ^{13}C NMR spectra of all synthesized compounds as well as NOESY spectra of compounds **5c** and **7a–e** is available at the journal website http://link.springer.com/journal/10593.

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