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PII: S0040-4020(17)30979-1

DOI: 10.1016/j.tet.2017.09.043

Reference: TET 28994

To appear in: *Tetrahedron*

Received Date: 29 June 2017

Revised Date: 18 September 2017

Accepted Date: 25 September 2017

Please cite this article as: Merkushev AA, Strel'nikov VN, Uchuskin MG, Trushkov IV, A simple synthesis of benzofurans by acid-catalyzed domino reaction of salicyl alcohols with *N*-tosylfurfurylamine, *Tetrahedron* (2017), doi: 10.1016/j.tet.2017.09.043.

Graphical Abstract

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A simple synthesis of benzofurans by acid-catalyzed domino reaction of salicyl alcohol with *N*-tosylfurfurylamine

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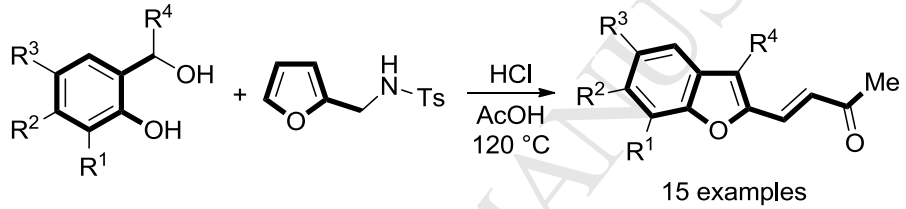

Tetrahedron
journal homepage: www.elsevier.com

A Simple Synthesis of Benzofurans by Acid-Catalyzed Domino Reaction of Salicyl Alcohols with *N*-Tosylfurfurylamine

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Furan
Benzofurans
Domino reaction
Salicyl alcohols
Bronsted acid catalysis

ABSTRACT

A simple route to polysubstituted benzofurans based on the domino reaction of commercial or easily available salicyl alcohols with *N*-protected furfurylamine has been designed and developed. The reaction was found to proceed with reasonable yields under heating of substrates in acetic acid in the presence of catalytic amount of conc. HCl when tosyl was used as protecting group.

1. Introduction

An increasing attention towards furan chemistry during past few decades is dictated by several reasons. Firstly, the furan core is the key structural element of a large number of organic materials, natural products and drugs.[1] Secondly, simple furans are easily available via processing of renewable sources such as agricultural wastes and other carbohydrate-containing raw materials.[2] This allows one to use furans as inexpensive starting materials for the synthesis of various useful products. The huge diversity of such products is provided by the versatile reactivity of the furan ring; thereby furans can serve as unique building blocks in organic and medicinal chemistry research.[3] They are widely used as synthetic equivalents of 1,4-dicarbonyl compounds for the preparation of various acyclic, carbocyclic and heterocyclic compounds.[4] What is more, processes wherein only a single masked carbonyl groups is involved into new ring formation, second one being released in a free form, were developed for the synthesis of diverse heterocyclic products.[5] Similarly, containing two C=C bonds, furans can react as either 2π- or 4π-component depending on the reaction partner and conditions. Namely, furans appear as activated alkenes in [2+4]-, [2+3]-, [2+2]-, and [2+1]-cycloadditions.[6] At the same time, furans exhibit the reactivity of 1,3-dienes in [4+2]-, [4+3]- and [4+4]-cycloadditions[7] as well as affording 1,4-addition products in reaction with methanolic bromine and some other electrophiles.[8]

Bearing a leaving group at the α-position of the side chain, furans can behave as synthetic equivalents of 1,3-dienes also in reactions with nucleophiles affording products of nucleophilic attack at the C(5) atom of the furan ring rather than typical nucleophilic substitution (Scheme 1a). Since the first announcement of this abnormal reactivity almost 90 years ago,[9] a number of examples of such reactions with various nucleophiles (alkoxide, phenoxide, sodium diethyl phosphite, CH-acids, ketene S,S-acetals, indoles etc.) were reported.[10] It was shown that this reaction proceeds through the initial leaving group departure followed by attack of nucleophile onto the furan C(5) atom producing 2-methylene-2,5-dihydrofuran intermediate.[11] The same two steps are also involved in the Piancatelli rearrangement.[12] The intramolecular version of this anomalous nucleophilic substitution furnishing substituted spirans was also investigated (Scheme 1b).[13] In some cases, the corresponding spiroketal derivatives were isolated and it was showed that under acidic conditions they undergo further rearrangement producing the corresponding Piancatelli products.[14] Wu and Yin used this transformation in the total synthesis of antifeeding natural compound tonghaosu and its structural analogues.[15]

Recently, we described an unusual domino reaction of *N*-tosylfurfurylamine with 2-(tosylamino)benzyl alcohols providing direct access to 2-(2-acylvinyl)indoles,[16] an important class of organic molecules, which could be used as versatile building blocks for the synthesis of bioactive compounds (Scheme 1c). This reaction proceeds through the acid-induced elimination of

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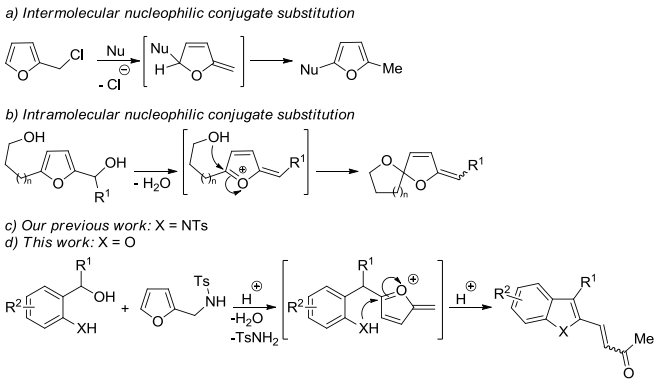
tosylamide, intramolecular nucleophilic attack on the formed oxonium providing 5-methylene-5*H*-spiro[furan-2,2'-indoline], subsequent acid-promoted furan ring opening, and aromatization of the indole core. We proposed that the use of 2-hydroxybenzyl alcohols in this domino reaction should provide benzofurans that would allow for further extending the synthetic concept toward another class of internal nucleophiles. Herein we report our development of the general protocol for the synthesis of densely substituted 2-(2-acylvinyl)benzofurans in a highly stereoselective manner.

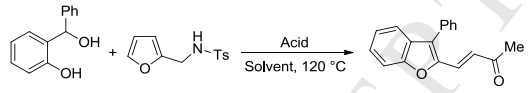
Scheme 1. Nucleophilic Conjugate Substitution of furfuryl derivatives



2. Results/Discussion

The reaction of 2-hydroxybenzhydryl alcohol **1a** with *N*-tosylfurfurylamine **2a** was selected as a model process for the optimization of reaction conditions. Based on our previous findings, benzofuran **3a** was expected to be formed under acidic conditions.[16] The initial experiment showed that heating of starting compounds with H_3PO_4 in toluene under reflux afforded target product **3a** in low yield (Table 1, entry 1). Encouraged by this result, we have screened various Brønsted and Lewis acids using the same solvent and temperature regime and found that the yield of product could be improved to 40% when TMSCl was used (Table 1, entry 5).

Table 1. Screening of reaction conditions



1a 2a 3a

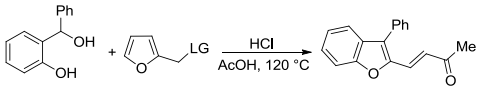
Entry[a]	Acid	Solvent	Time (h)	Yield of **3a** (%)[b]
1	H_3PO_4	Toluene	0.5	16
2	AcOH	Toluene	12	25
3	TFA	Toluene	12	32
4	H_2SO_4	Toluene	0.5	22
5	TMSCl	Toluene	24	40
6[c]	$Yb(OTf)_3$	Toluene	6	33
7[c]	$CuBr_2$	Toluene	3	30
8[c]	$Cu(OTf)_2$	Toluene	0.5	28
9[c]	$PdCl_2$	Toluene	3	21
10[c]	AgOTf	Toluene	0.5	26
11	-	AcOH	1	16
12	$2\text{-}O_2NC_6H_4CO_2H$	AcOH	6	24
13	TSA	AcOH	0.5	27
14	Amberlyst 15	AcOH	6	25
15	H_2SO_4	AcOH	0.5	21
16	HCl	AcOH	1	58

[a]Reaction was performed at 0.1 mmol scale of **1a** with 1.2 eq. of **2a** and 1 eq. of acid. [b]Conversion and yield was detected by GS-MS with an internal standard. [c]20 mol. % of catalyst was used.

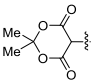
Metal halides and trifluoromethanesulfonates were found to be less efficient in the initiation of the studied transformation (entries 6-10). In the attempt to achieve a better yield of the desired benzofuran **3a**, we have changed the solvent to acetic acid and screened several Bronsted acids again (entries 11-16). We found that the best yield of **3a** was observed when conc. HCl was applied for the transformation (entry 16). Further variation of the ratio of the reacting compounds, temperature and HCl loading had no positive influence on the yield of the target benzofuran **3a**.

Under the optimized conditions, we have screened a series of furans containing leaving groups of a different nature. The furfurylamine **2b** and its derivatives **2c-e**, furfuryl alcohol **2f** and its derivatives **2g-j** and 5-(furan-2-ylmethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione **2k** applied to this reaction. We have found that only *N*-tosylfurfurylamine **2a** has a good balance between the stability in the first step of the domino reaction (Friedel-Crafts alkylation) and reactivity in the leaving group elimination. On the contrary, furans **2b-k** gave either products of Piancatelli rearrangement or significant tarring of the reaction mixture. Therefore, the optimal reaction procedure can be summarized as follows: 2-hydroxybenzyl alcohol **1** is heated under reflux with *N*-tosylfurfurylamine **2a** (1.2 eq.) in acetic acid containing conc. HCl (1 eq.) for 1 h under air atmosphere. Furthermore, we have successfully carried out the studied reaction using 1 mmol of starting alcohol **1** and obtained the desired product **3a** in 56% yield. Thus, the reaction can be easily scaled up without the loss of efficiency. It is worth noting that the benzofuran **3a** was obtained as a single (*E*)-isomer as deduced on the basis of ^3J values for the olefinic protons.[17]

Table 2. Screening of leaving groups in furfuryl derivatives



1a 2a 3a

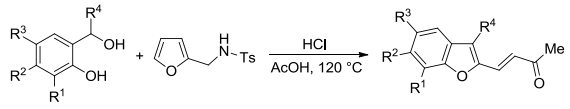
Entry[a]	Furan **2**	LG	Yield of **3a** (%)[b]
1	**2a**	TsNH	58 (56[c])
2	**2b**	NH_2	traces
3	**2c**	PhNH	ND
4	**2d**	BnNH	traces
5	**2e**	Bn_2N	traces
6	**2f**	HO	20
7	**2g**	PhO	27
8	**2h**	$4\text{-}MeC_6H_4O$	29
9	**2i**	$4\text{-}ClC_6H_4O$	30
10	**2j**	TsO	ND
11	**2k**		ND

[a]Reaction was performed at 0.1 mmol scale of **1a** with 1.2 eq. of **2a** and 1 eq. of acid. [b]Conversion and yield was detected by GS-MS with an internal standard. [c]Reaction was performed at 1 mmol scale. Isolated yield.

With the optimized conditions in hand, we next examined the scope of the reaction. We have found that the reaction of various salicyl alcohols **1** with **2a** led to the formation of benzofurans **3a-o** in moderate to good yields (Table 3). Various functional groups at the *para*-, *meta*- or *ortho*-positions of the starting salicyl alcohols (**1a-c**,**e-j**,**l-n**) were found to be well tolerated under the optimized reaction conditions. More electron-deficient salicylic alcohol **1k** (R^3 = Cl) afforded benzofuran **3k** in moderate yield. A similar effect was previously observed in the reaction of *N*-tosylfurfurylamine with 2-(tosylamino)benzyl alcohols and could be explained by the reduced nucleophilicity of the corresponding

substrate.[16] Salicyl alcohol **1d** bearing branched alkyl substituent at the α-position was found to be unsuitable substrate for the discussed reaction on the contrary to benzhydryl alcohols; the corresponding benzofuran **3d** was isolated in 35% yield only. The moderate yield of product **3d** could be explained by the side intramolecular cyclodehydration affording to 2,2-dimethyl-2,3-dihydro-1-benzofuran.[18] Nevertheless, 3-alkyl-2-(2-acylvinyl)-benzofuran **3o** was obtained in reasonable yield starting from salicyl alcohol **1o** possessing electron-donating substituents.

Table 3. Scope of the acid-catalyzed synthesis of benzofurans[a]



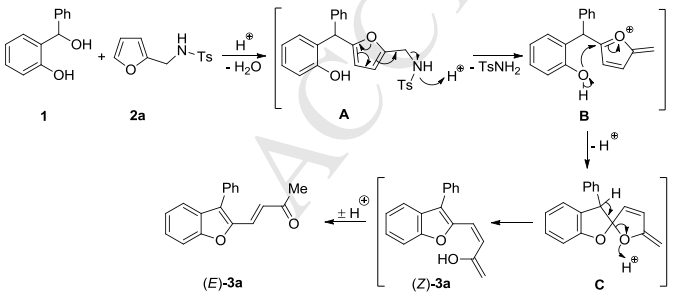
1a-o 2a 3a-o

Entry	**1**,**3**	R^1	R^2	R^3	R^4	Yield of **3** (%)[b]
1	**a**	H	H	H	Ph	56
2	**b**	H	H	H	4-MeC_6H_4	55
3	**c**	H	H	H	4-MeOC_6H_4	54
4	**d**	H	H	H	*i*-Pr	35
5	**e**	Me	H	Br	Ph	60
6	**f**	Me	H	Br	4-MeC_6H_4	58
7	**g**	Me	Me	H	Ph	55
8	**h**	Me	Me	H	4-MeC_6H_4	58
9	**i**	H	Me	Me	Ph	58
10	**j**	H	Me	Me	4-MeC_6H_4	57
11	**k**	H	H	Cl	Ph	46
12	**l**	H	H	Me	Ph	55
13	**m**	H	H	Me	4-MeC_6H_4	60
14	**n**	H	H	Br	Ph	53
15	**o**	H	H	MeO	Me	57

[a]Reaction was performed at 1 mmol scale. [b] Isolated yield.

The proposed reaction mechanism for rearrangement is given in Scheme 2. This includes Friedel-Crafts alkylation of *N*-tosylfurfurylamine **2a** with 2-hydroxybenzyl alcohol **1** to form intermediate 2-(2-hydroxybenzyl)furan **A**. Then subsequent acid-initiated elimination of $TsNH_2$ produces intermediate **B**; intramolecular nucleophilic attack of the phenolic hydroxyl moiety onto the *ipso*-carbon atom of the furan ring affords spiro-conjugated species **C**, protonation of which induces dihydrofuran ring opening and aromatization of the benzofuran core. Fast acid-catalyzed isomerization of (*Z*)-**3** to (*E*)-isomer accomplishes the formation of (*E*)-**3**.

Scheme 2. Proposed reaction mechanism



3. Conclusion

In conclusion, we have developed an acid-catalyzed domino reaction of salicylic alcohols with *N*-tosylfurfurylamine to afford 2-(2-acylvinyl)benzofurans. This novel and simple method provides easily accessible starting compounds, a general and straightforward route to prepare densely substituted benzofurans via Friedel-Crafts alkylation step, acid-induced leaving group elimination followed by intramolecular nucleophilic attack of the appropriately located amine moiety on the *ipso* carbon atom of the furan ring, dihydrofuran ring opening and benzofuran aromatization.

4. Experimental

4.1. General Information

NMR spectra were recorded with a «Bruker Avance III HD 400» (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR) spectrometer at room temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$, ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm; DMSO-d_6, ^{1}H: 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 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», the values are uncorrected. Column chromatography was performed on silica gel Macherey Nagel (40-63 μm). Starting furans **2** were synthesized according to published procedures.[17b,19] All the reactions were carried out using freshly distilled and dry solvents from solvent stills.

*4.2. General procedure for the synthesis of starting salicylic alcohols **1**.*

To a solution of Grignard reagent (4 mmol) in dry ether (4 mL) a solution of corresponding salicylaldehyde (2 mmol) in dry ether (2 mL) was added dropwise. The mixture was stirred for 60 minutes (TLC control) and then a saturated solution of aq. NH_4Cl (5 mL) was added slowly. The layers were separated and the aqueous layer was extracted with ethyl acetate (2 × 3 mL). The combined organic fractions washed with water (2 × 5 mL), brine (2 × 5 mL), dried with Na_2SO_4 and evaporated to dryness. The residue was dissolved in ethyl acetate/petroleum ether mixture, passed through thin layer of silica gel and left to crystallization.

*4.2.1. 2-[Hydroxy(phenyl)methyl]phenol (**1a**)*[20]

White solid (340 mg, 85% yield); mp 90–91 °C (ethyl acetate/petroleum ether), lit. 84–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (br.s, 1H, OH), 7.40–7.30 (m, 5H, H_{Ar}), 7.21–7.17 (m, 1H, H_{Ar}), 6.90–6.87 (m, 2H, H_{Ar}), 6.84–6.80 (m, 1H, H_{Ar}), 6.00 (s, 1H, CH), 3.03 (br.s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 142.1, 129.4, 128.9 (2C), 128.4, 128.3, 127.0 (2C), 126.9, 120.1, 117.4, 77.1.

*4.2.2. 2-[Hydroxy(4-methylphenyl)methyl]phenol (**1b**)*[20]

White solid (368 mg, 86% yield); mp 104–105 °C (ethyl acetate/petroleum ether), lit. 94–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (br.s, 1H, OH), 7.32–7.28 (m, 3H, H_{Ar}), 7.21–7.19 (m, 2H, H_{Ar}), 6.94–6.88 (m, 2H, H_{Ar}), 6.84–6.81 (m, 1H, H_{Ar}), 6.02 (s, 1H, CH), 2.73 (br.s, 1H, OH), 2.38 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 139.2, 138.3, 129.6 (2C), 129.4, 128.4, 127.0 (2C), 126.8, 120.0, 117.5, 77.3, 21.3.

*4.2.3. 2-[Hydroxy(4-methoxyphenyl)methyl]phenol (**1c**)*[21]

Colorless oil (396 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (br.s, 1H, OH), 7.28–7.23 (m, 2H, H_{Ar}), 6.98–6.95 (m, 2H, H_{Ar}), 6.89–6.87 (m, 4H, H_{Ar}), 5.65 (s, 1H, CH), 3.79 (s, 3H, OCH_3), 2.75 (br.s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ

159.8, 154.9, 131.9, 129.8, 129.4, 129.0 (2C), 128.5 (2C), 120.6, 117.4, 114.4, 77.1, 55.4.

*4.2.4. 2-(1-Hydroxy-2-methylpropyl)phenol (**1d**)*[22]

White solid (282 mg, 85% yield); mp 50–51 °C (ethyl acetate/petroleum ether), lit. 48–49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (br.s, 1H, OH), 7.18–7.14 (m, 1H, H_{Ar}), 6.92–6.89 (m, 1H, H_{Ar}), 6.86–6.79 (m, 2H, H_{Ar}), 4.51 (d, ^3J = 6.8 Hz, 1H, CH), 2.73 (br.s, 1H, OH), 2.11 (m, 1H, CH), 1.05 (d, ^3J = 6.8 Hz, 3H, CH_3), 0.86 (d, ^3J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 128.9, 128.4, 126.3, 119.5, 117.3, 82.2, 34.5, 19.4, 18.3.

*4.2.5. 4-Bromo-2-[hydroxy(phenyl)methyl]-6-methylphenol (**1e**)*

White solid (504 mg, 86% yield); mp 126–127 °C (ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (br.s, 1H, OH), 7.38–7.31 (m, 5H, H_{Ar}), 7.19 (s, 1H, H_{Ar}), 6.83 (s, 1H, H_{Ar}), 5.93 (s, 1H, CH), 2.88 (br.s, 1H, OH), 2.22 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 141.4, 133.2, 129.1 (2C), 128.8, 128.7, 128.5, 127.8, 126.9 (2C), 111.5, 77.0, 15.8; IR (nujol, v/cm^{-1}): 3382, 3288, 1496, 1418, 1333, 1254, 1217, 1204, 1036; HRMS (ESI) calcd for $C_{14}H_{12}BrO^+$ [M-OH]$^+$ 275.0066, found 275.0067.

*4.2.6. 4-Bromo-2-[hydroxy(4-methylphenyl)methyl]-6-methylphenol (**1f**)*

White solid (mg, 87% yield); mp 121–122 °C (ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (br.s, 1H, OH), 7.28–7.26 (m, 2H, H_{Ar}), 7.21–7.19 (m, 3H, H_{Ar}), 6.83–6.82 (m, 1H, H_{Ar}), 5.90 (s, 1H, CH), 2.81 (br.s, 1H, OH), 2.38 (s, 3H, CH_3), 2.24 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 138.6, 138.5, 133.1, 129.7 (2C), 128.7, 128.5, 127.9, 126.9 (2C), 111.4, 77.0, 21.3, 15.8; IR (nujol, v/cm^{-1}): 3410, 3208, 1512, 1253, 1213, 1177, 1033; HRMS (ESI) calcd for $C_{15}H_{14}BrO^+$ [M-OH]$^+$ 289.0223, found 289.0223.

*4.2.7. 6-[Hydroxy(phenyl)methyl]-2,3-dimethylphenol (**1g**)*

White solid (365 mg, 80% yield); mp 101–103 °C (ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.73 (br.s, 1H, OH), 7.38–7.36 (m, 2H, H_{Ar}), 7.31–7.27 (m, 2H, H_{Ar}), 7.22–7.18 (m, 1H, H_{Ar}), 6.89 (d, ^3J = 7.8 Hz, 1H, H_{Ar}), 6.62 (d, ^3J = 7.8 Hz, 1H, H_{Ar}), 6.41 (br.s, 1H, OH), 5.96 (s, 1H, CH), 2.16 (s, 3H, CH_3), 2.07 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.3, 144.7, 135.7, 127.8 (2C), 127.6, 126.6, 126.2 (2C), 124.0, 123.0, 120.5, 72.0, 19.6, 11.6; IR (nujol, v/cm^{-1}): 3432, 3185, 1687, 1667, 1595, 1294, 1262, 1244, 1206, 1165, 1080; HRMS (ESI) calcd for $C_{15}H_{15}O^+$ [M-OH]$^+$ 211.1117, found 211.1118.

*4.2.8. 6-[Hydroxy(4-methylphenyl)methyl]-2,3-dimethylphenol (**1h**)*

White solid (411 mg, 85% yield); mp 122–123 °C (ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.72 (br.s, 1H, OH), 7.23 (d, ^3J = 7.4 Hz, 2H, H_{Ar}), 7.09 (d, ^3J = 7.4 Hz, 2H, H_{Ar}), 6.84 (d, ^3J = 7.7 Hz, 1H, H_{Ar}), 6.59 (d, ^3J = 7.7 Hz, 1H, H_{Ar}), 6.38 (br.s, 1H, OH), 5.89 (s, 1H, CH), 2.26 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.05 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.3, 141.7, 135.6, 135.5, 128.3 (2C), 127.5, 126.2 (2C), 124.0, 122.9, 120.4, 72.1, 20.5, 19.6, 11.5; IR (nujol, v/cm^{-1}): 3399, 3317, 1580, 1511, 1249, 1224, 1172, 1082, 1029; HRMS (ESI) calcd for $C_{16}H_{17}O^+$ [M-OH]$^+$ 225.1274, found 225.1271.

*4.2.9. 2-[Hydroxy(phenyl)methyl]-4,5-dimethylphenol (**1i**)*

White solid (369 mg, 81% yield); mp 124–125 °C (ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (br.s, 1H, OH), 7.41–7.29 (m, 5H, H_{Ar}), 6.69 (s, 1H, H_{Ar}), 6.64 (s, 1H, H_{Ar}), 5.93 (s, 1H, CH), 2.96 (br.s, 1H, OH), 2.20 (s, 3H, CH_3), 2.12 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 142.5, 137.8, 129.3, 128.8 (2C), 128.2, 127.9, 126.9 (2C), 124.1, 118.6, 76.9, 19.6, 18.8; IR (nujol, v/cm^{-1}): 3337, 3168, 1618, 1494, 1408, 1281, 1227, 1198, 1186, 1069, 1007; HRMS (ESI) calcd for $C_{15}H_{15}O^+$ [M-OH]$^+$ 211.1117, found 211.1113.

*4.2.10. 2-[Hydroxy(4-methylphenyl)methyl]-4,5-dimethylphenol (**1j**)*

White solid (407 mg, 84% yield); mp 89–91 °C (ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.91 (br.s, 1H, OH), 7.21 (d, ^3J = 7.8 Hz, 2H, H_{Ar}), 7.05 (d, ^3J = 7.8 Hz, 2H, H_{Ar}), 7.02 (s, 1H, H_{Ar}), 6.53 (s, 1H, H_{Ar}), 5.88 (s, 1H, CH), 5.49 (br.s, 1H, OH), 2.24 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.07 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.5, 142.8, 135.0, 134.7, 128.7, 128.1 (2C), 127.8, 126.0 (2C), 125.7, 116.3, 68.3, 20.5, 19.0, 18.5; IR (nujol, v/cm^{-1}): 3341, 3102, 1508, 1339, 1277, 1188, 1072, 1000; HRMS (ESI) calcd for $C_{16}H_{17}O^+$ [M-OH]$^+$ 225.1274, found 225.1271.

*4.2.11. 4-Chloro-2-(hydroxy(phenyl)methyl)phenol (**1k**)*[23]

White solid (427 mg, 86% yield); mp 87–88 °C (ethyl acetate/petroleum ether), lit. 89–90.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (br.s, 1H, OH), 7.40–7.32 (m, 5H, H_{Ar}), 7.15–7.12 (m, 1H, H_{Ar}), 6.84–6.82 (m, 2H, H_{Ar}), 5.97 (s, 1H, CH), 2.80 (br.s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 141.4, 129.3, 129.1 (2C), 128.8, 128.2, 128.1, 127.0 (2C), 125.0, 118.9, 76.9.

*4.2.12. 2-[Hydroxy(phenyl)methyl]-4-methylphenol (**1l**)*[24]

White solid (360 mg, 84% yield); mp 96–97 °C (ethyl acetate/petroleum ether), lit 98–100 °C;[24] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (br.s, 1H, OH), 7.41–7.30 (m, 5H, H_{Ar}), 6.99 (br.d, ^3J = 8.2 Hz, 1H, H_{Ar}), 6.80 (d, ^3J = 8.2 Hz, 1H, H_{Ar}), 6.70 (br.s, 1H, H_{Ar}), 5.96 (s, 1H, CH), 2.82 (br.s, 1H, OH), 2.21 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 142.2, 129.9, 129.3, 128.9 (2C), 128.8, 128.3, 127.0 (2C), 126.5, 117.3, 77.2, 20.6.

*4.2.13. 2-[Hydroxy(4-methylphenyl)methyl]-4-methylphenol (**1m**)*

White solid (410 mg, 90%); mp 93–94 °C (ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.04 (br.s, 1H, OH), 7.24 (d, ^3J = 7.9 Hz, 2H, H_{Ar}), 7.12 (d, ^4J = 1.6 Hz, 1H, H_{Ar}), 7.06 (d, ^3J = 7.9 Hz, 2H, H_{Ar}), 6.82 (dd, ^3J = 8.1 Hz, ^4J = 1.6 Hz, 1H, H_{Ar}), 6.65 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 5.93 (d, ^3J = 3.8 Hz, 1H, CH), 5.54 (d, ^3J = 3.8 Hz, 1H, OH), 2.25 (s, 3H, CH_3), 2.17 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.4, 142.6, 135.2, 131.4, 128.2 (2C), 127.6, 127.2, 127.0, 126.1 (2C), 114.8, 68.3, 20.5, 20.3; IR (nujol, v/cm^{-1}): 3375, 3325, 1598, 1512, 1499, 1418, 1239, 1224, 1197, 1174, 1144, 1035; HRMS (ESI) calcd for $C_{15}H_{15}O^+$ [M-OH]$^+$ 211.1117, found 211.1119.

*4.2.14. 4-Bromo-2-[hydroxy(phenyl)methyl]phenol (**1n**)*

White solid (452 mg, 81% yield); mp 104–105 °C (ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (br.s, 1H, OH), 7.40–7.33 (m, 5H, H_{Ar}), 7.29–7.27 (m, 1H, H_{Ar}), 6.99–6.98 (m, 1H, H_{Ar}), 6.80–6.78 (m, 1H, H_{Ar}), 5.98 (s, 1H, CH), 2.74 (br.s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 141.4, 132.2, 131.0, 129.2 (2C), 128.9, 128.6, 127.0 (2C), 119.4, 112.0, 76.5; IR (nujol, v/cm^{-1}): 3434, 3220, 1580, 1485, 1238, 1165, 1108, 1078, 1037, 1023; HRMS (ESI) calcd for $C_{13}H_{10}BrO^+$ [M-OH]$^+$ 260.9910, found 260.9912.

*4.2.15. 2-(1-Hydroxyethyl)-4-methoxyphenol (**1o**)*[20]

Yellow oil (289 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (br.s, 1H, OH), 6.79 (d, ^3J = 8.8 Hz, 1H, H_{Ar}), 6.72 (dd, ^3J = 8.8 Hz, ^4J = 2.9 Hz, 1H, H_{Ar}), 6.57 (d, ^4J = 2.9 Hz, 1H, H_{Ar}), 5.02 (q, ^3J = 6.6 Hz, 1H, CH), 3.74 (s, 3H, OCH_3), 2.46 (br.s, 1H, OH), 1.58 (d, ^3J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 149.4, 129.4, 117.8, 114.0, 112.6, 71.6, 56.0, 23.5.

4.3. General procedure for synthesis of benzofurans ***3***.

A conc. HCl (12 M, 30 µl) was added to a solution of salicyl alcohol **1** (1 mmol) and *N*-(furan-2-ylmethyl)-4-methylbenzenesulfonamide **2a** (1.1 mmol, 276 mg) in glacial AcOH (5 ml). The reaction mixture was stirred at 120 °C for 1 h (TLC control), then evaporated to dryness under reduced pressure. After purification by column chromatography on silica gel using CH_2Cl_2/petroleum ether mixture (1:9) as an eluent, products was obtained as oils.

*4.3.1. (3E)-4-(3-Phenyl-1-benzofuran-2-yl)but-3-en-2-one (**3a**)*

Yellow oil (147 mg, 56% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65–7.62 (m, 2H, H_{Ar}), 7.60–7.54 (m, 4H, H_{Ar}), 7.52–7.49 (m, 1H, H_{Ar}), 7.47–7.45 (m, 1H, H_{Ar}), 7.36 (d, ^3J = 15.8 Hz, 1H, CH), 7.31–7.29 (m, 1H, H_{Ar}), 6.85 (d, ^3J = 15.8 Hz, 1H, CH), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.9, 154.2, 147.6, 130.2, 129.3 (2C), 129.2 (2C), 128.5, 127.5, 127.4, 127.1, 127.0, 125.8, 123.8, 120.7, 111.5, 28.2; IR (nujol, v/cm^{-1}): 1688, 1664, 1614, 1597, 1572, 1359, 1281, 1250, 1204, 1165; HRMS (ESI) calcd. for $C_{18}H_{15}O_2^+$ $[M+H]^+$ 263.1067, found 263.1071.

*4.3.2. (3E)-4-[3-(4-Methylphenyl)-1-benzofuran-2-yl]but-3-en-2-one (**3b**)*

Yellow oil (152 mg, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.64 (m, 1H, H_{Ar}), 7.53–7.50 (m, 1H, H_{Ar}), 7.51 (d, ^3J = 15.7 Hz, 1H, CH), 7.44–7.40 (m, 3H, H_{Ar}), 7.36–7.34 (m, 2H, H_{Ar}), 7.30–7.28 (m, 1H, H_{Ar}), 6.96 (d, ^3J = 15.7 Hz, 1H, CH), 2.46 (s, 3H, CH_3), 2.35 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 155.1, 148.3, 138.6, 130.0 (2C), 129.5 (2C), 128.7, 128.6, 128.3, 127.2, 127.0, 126.9, 123.6, 121.2, 111.6, 28.5, 21.5; IR (nujol, v/cm^{-1}): 1686, 1661, 1599, 1360, 1281, 1254, 1205, 1186, 1167; HRMS (ESI) calcd. for $C_{19}H_{17}O_2^+$ $[M+H]^+$ 277.1223, found 277.1221.

*4.3.3. (3E)-4-[3-(4-Methoxyphenyl)-1-benzofuran-2-yl]but-3-en-2-one (**3c**)*

Pale orange oil (158 mg, 54% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 (d, ^3J = 8.2 Hz, 2H, H_{Ar}), 7.55–7.53 (m, 2H, H_{Ar}), 7.52–7.48 (m, 1H, H_{Ar}), 7.39 (d, ^3J = 15.8 Hz, 1H, CH), 7.35–7.33 (m, 1H, H_{Ar}), 7.17 (d, ^3J = 8.2 Hz, 2H, H_{Ar}), 6.86 (d, ^3J = 15.8 Hz, 1H, CH), 3.86 (s, 3H, CH_3), 2.32 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.8, 159.5, 154.2, 147.3, 130.5 (2C), 127.6, 127.3, 127.2, 126.6, 125.7, 123.7, 122.3, 120.7, 114.8 (2C), 111.4, 55.2, 28.1; IR (nujol, v/cm^{-1}): 1691, 1601, 1570, 1556, 1510, 1360, 1288, 1271, 1248, 1207, 1165, 1113, 1034, 1014; HRMS (ESI) calcd. for $C_{19}H_{17}O_3^+$ $[M+H]^+$ 293.1172, found 293.1174.

*4.3.4. (3E)-4-[3-(1-Methylethyl)-1-benzofuran-2-yl]but-3-en-2-one (**3d**)*

Pale orange oil (80 mg, 35% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85–7.83 (m, 1H, H_{Ar}), 7.64 (d, ^3J = 15.8 Hz, 1H, CH), 7.58–7.56 (m, 1H, H_{Ar}), 7.43–7.39 (m, 1H, H_{Ar}), 7.29–7.25 (m, 1H, H_{Ar}), 6.68 (d, ^3J = 15.8 Hz, 1H, CH), 3.51–3.44 (m, 1H, CH), 2.37 (s, 3H, CH_3), 1.41 (d, ^3J = 7.0 Hz, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.4, 154.5, 146.3, 131.3, 127.4, 127.1, 126.8, 126.0, 123.0, 121.9, 111.5, 27.6, 24.7, 22.3 (2C); IR (nujol, v/cm^{-1}): 1688, 1664, 1605, 1273, 1258, 1165, 1040; HRMS (ESI) calcd. for $C_{15}H_{17}O_2^+$ $[M+H]^+$ 229.1223, found 229.1219.

*4.3.5. (3E)-4-(5-Bromo-7-methyl-3-phenyl-1-benzofuran-2-yl)but-3-en-2-one (**3e**)*

Yellow oil (212 mg, 60% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.61–7.52 (m, 6H, H_{Ar}), 7.49 (br.s, 1H, H_{Ar}), 7.36 (d, ^3J = 15.8 Hz, 1H, CH), 6.92 (d, ^3J = 15.8 Hz, 1H, CH), 2.53 (s, 3H, CH_3), 2.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.9, 152.0, 148.5, 130.3, 129.7, 129.3 (2C), 129.1 (2C), 128.9, 128.6, 127.8, 126.7, 125.1, 123.9, 120.2, 116.0, 28.1, 14.1; IR (nujol, v/cm^{-1}): 1688, 1605, 1553, 1356, 1325, 1300, 1261, 1200, 1167; HRMS (ESI) calcd. for $C_{19}H_{16}BrO_2^+$ $[M+H]^+$ 355.0328, found 355.0324.

*4.3.6. (3E)-4-[5-Bromo-7-methyl-3-(4-methylphenyl)-1-benzofuran-2-yl]but-3-en-2-one (**3f**)*

Pale orange oil (213 mg, 58% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.55 (br.s, 1H, H_{Ar}), 7.48–7.37 (m, 5H, H_{Ar}), 7.35 (d, ^3J = 15.8 Hz, 1H, CH), 6.89 (d, ^3J = 15.8 Hz, 1H, CH), 2.52 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.32 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.9, 152.0, 148.3, 138.3 (2C), 130.3, 129.9 (2C), 129.0 (2C), 127.6, 126.9, 126.8, 125.2, 123.9, 120.3, 116.0, 28.1, 20.8, 14.1; IR (nujol, v/cm^{-1}): 1690, 1607, 1508, 1402, 1354, 1323, 1300, 1263, 1196, 1169, 1115; HRMS (ESI) calcd. for $C_{20}H_{18}BrO_2^+$ $[M+H]^+$ 369.0485, found 369.0485.

*4.3.7. (3E)-4-(6,7-Dimethyl-3-phenyl-1-benzofuran-2-yl)but-3-en-2-one (**3g**)*

Yellow oil (160 mg, 55% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.61–7.55 (m, 4H, H_{Ar}), 7.52–7.49 (m, 1H, H_{Ar}), 7.40–7.36 (m, 2H, H_{Ar}+CH), 7.16–7.14 (m, 1H, H_{Ar}), 6.89 (d, ^3J = 15.6 Hz, 1H, CH), 2.45 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.32 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.8, 153.6, 146.9, 135.9, 130.5, 129.1 (2C), 129.0 (2C), 128.4, 127.3, 126.4, 126.3, 125.9, 124.9, 119.5, 117.2, 28.1, 18.9, 11.2; IR (nujol, v/cm^{-1}): 1667, 1595, 1294, 1242, 1206, 1165, 1079; HRMS (ESI) calcd. for $C_{20}H_{19}O_2^+$ $[M+H]^+$ 291.1380, found 291.1382.

*4.3.8. (3E)-4-[6,7-Dimethyl-3-(4-methylphenyl)-1-benzofuran-2-yl]but-3-en-2-one (**3h**)*

Pale orange oil (176 mg, 58% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.47–7.45 (m, 2H, H_{Ar}), 7.41–7.35 (m, 4H, H_{Ar}+CH), 7.16–7.14 (m, 1H, H_{Ar}), 6.87 (d, ^3J = 15.7 Hz, 1H, CH), 2.45 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.32 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.8, 153.6, 146.7, 137.9, 135.8, 129.7 (2C), 129.0 (2C), 127.6, 127.5, 126.4, 126.2, 125.8, 125.0, 119.5, 117.3, 28.0, 20.7, 18.9, 11.2; IR (nujol, v/cm^{-1}): 1674, 1607, 1589, 1311, 1261, 1162; HRMS (ESI) calcd. for $C_{21}H_{21}O_2^+$ $[M+H]^+$ 305.1536, found 305.1533.

*4.3.9. (3E)-4-(5,6-Dimethyl-3-phenyl-1-benzofuran-2-yl)but-3-en-2-one (**3i**)*

Yellow oil (168 mg, 58% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62–7.56 (m, 4H, H_{Ar}), 7.53–7.49 (m, 1H, H_{Ar}), 7.46 (s, 1H, H_{Ar}), 7.42 (s, 1H, H_{Ar}), 7.36 (d, ^3J = 15.8 Hz, 1H, CH), 6.82 (d, ^3J = 15.8 Hz, 1H, CH), 2.37 (s, 3H, CH_3), 2.30 (s, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.8, 153.2, 146.9, 137.0, 132.4, 130.5, 129.2 (2C), 129.1 (2C), 128.4, 127.2, 126.2, 125.8, 125.4, 120.4, 111.6, 28.1, 20.1, 19.3; IR (nujol, v/cm^{-1}): 1664, 1593, 1302, 1254, 1221, 1167; HRMS (ESI) calcd. for $C_{20}H_{19}O_2^+$ $[M+H]^+$ 291.1380, found 291.1376.

*4.3.10. (3E)-4-[5,6-Dimethyl-3-(4-methylphenyl)-1-benzofuran-2-yl]but-3-en-2-one (**3j**)*

Yellow oil (173 mg, 57% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.48–7.46 (m, 3H, H_{Ar}), 7.41–7.40 (m, 3H, H_{Ar}), 7.35 (d, ^3J = 15.8 Hz, 1H, CH), 6.80 (d, ^3J = 15.8 Hz, 1H, CH), 2.41 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.30 (s, 6H, 2 × CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.8, 153.2, 146.8, 137.9, 137.0, 132.4, 129.8 (2C), 129.0 (2C), 127.5, 127.4, 126.0, 125.9, 125.5, 120.5, 111.6, 28.0, 20.7, 20.1, 19.4; IR (nujol, v/cm^{-1}): 1663, 1612, 1593, 1304, 1256, 1167; HRMS (ESI) calcd. for $C_{21}H_{21}O_2^+$ $[M+H]^+$ 305.1536, found 305.1534.

*4.3.11. (3E)-4-(5-Chloro-3-phenyl-1-benzofuran-2-yl)but-3-en-2-one (**3k**)*

Pale orange oil (136 mg, 46% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74–7.72 (m, 1H, H_{Ar}), 7.65 (br.s, 1H, H_{Ar}), 7.62–

7.59 (m, 4H, H_{Ar}), 7.53–7.51 (m, 1H, H_{Ar}), 7.38–7.34 (m, 2H, H_{Ar}+CH), 6.90 (d, ^3J = 15.8 Hz, 1H, CH), 2.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.0, 152.7, 149.1, 129.6, 129.4 (2C), 129.3 (2C), 129.0, 128.8, 128.5, 128.0, 127.4, 126.7, 125.0, 120.0, 113.3, 28.3; IR (nujol, v/cm^{-1}): 1671, 1607, 1259, 1164, 1064; HRMS (ESI) calcd. for $C_{18}H_{14}ClO_2^+$ $[M+H]^+$ 297.0677, found 297.0677.

*4.3.12. (3E)-4-(5-Methyl-3-phenyl-1-benzofuran-2-yl)but-3-en-2-one (**3l**)*

Pale orange oil (152 mg, 55% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62–7.56 (m, 5H, H_{Ar}), 7.54–7.52 (m, 1H, H_{Ar}), 7.45 (br.s, 1H, H_{Ar}), 7.36 (d, ^3J = 15.8 Hz, 1H, CH), 7.32–7.30 (m, 1H, H_{Ar}), 6.85 (d, ^3J = 15.8 Hz, 1H, CH), 2.40 (s, 3H, CH_3), 2.31 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.8, 152.7, 147.7, 133.1, 130.3, 129.2 (2C), 129.1 (2C), 128.7, 128.4, 127.6, 127.1, 126.8, 125.6, 120.2, 111.0, 28.1, 20.7; IR (nujol, v/cm^{-1}): 1664, 1628, 1607, 1491, 1356, 1277, 1254, 1200; HRMS (ESI) calcd. for $C_{19}H_{17}O_2^+$ $[M+H]^+$ 277.1223, found 277.1228.

*4.3.13. (3E)-4-[5-Methyl-3-(4-methylphenyl)-1-benzofuran-2-yl]but-3-en-2-one (**3m**)*

Pale orange oil (174 mg, 60% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.54 (d, ^3J = 8.4 Hz, 1H, H_{Ar}), 7.47 (d, ^3J = 8.0 Hz, 2H, H_{Ar}), 7.44 (br.s, 1H, H_{Ar}), 7.41 (d, ^3J = 8.0 Hz, 2H, H_{Ar}), 7.36 (d, ^3J = 15.8 Hz, 1H, CH), 7.30 (br.d, ^3J = 8.4 Hz, 1H, H_{Ar}), 6.84 (d, ^3J = 15.8 Hz, 1H, CH), 2.41 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.31 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.8, 152.7, 147.6, 138.0, 133.0, 129.8 (2C), 129.0 (2C), 128.6, 127.6, 127.4, 127.2, 126.6, 125.7, 120.3, 111.0, 28.1, 20.7 (2C); IR (nujol, v/cm^{-1}): 1604, 1592, 1286, 1253, 1204, 1169; HRMS (ESI) calcd. for $C_{20}H_{19}O_2^+$ $[M+H]^+$ 291.1380, found 291.1378.

*4.3.14. (3E)-4-(5-Bromo-3-phenyl-1-benzofuran-2-yl)but-3-en-2-one (**3n**)*

Yellow oil (180 mg, 53% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78 (br.s, 1H, H_{Ar}), 7.69–7.65 (m, 2H, H_{Ar}), 7.63–7.58 (m, 4H, H_{Ar}), 7.56–7.54 (m, 1H, H_{Ar}), 7.36 (d, ^3J = 15.8 Hz, 1H, CH), 6.91 (d, ^3J = 15.8 Hz, 1H, CH), 2.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.9, 153.0, 148.9, 129.9, 129.6, 129.5, 129.3 (2C), 129.2 (2C), 128.7, 128.0, 126.6, 124.8, 122.9, 116.2, 113.6, 28.2; IR (nujol, v/cm^{-1}): 1686, 1601, 1447, 1358, 1298, 1275, 1254, 1207, 1165, 1051; HRMS (ESI) calcd. for $C_{18}H_{14}BrO_2^+$ $[M+H]^+$ 341.0172, found 341.0173.

*4.3.15. (3E)-4-(5-Methoxy-3-methyl-1-benzofuran-2-yl)but-3-en-2-one (**3o**)*

Pale orange oil (131 mg, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, ^3J = 15.6 Hz, 1H, CH), 7.32 (d, ^3J = 8.9 Hz, 1H, H_{Ar}), 6.98 (dd, ^3J = 8.9 Hz, ^4J = 2.4 Hz, 1H, H_{Ar}), 6.94 (d, ^3J = 2.4 Hz, 1H, H_{Ar}), 6.82 (d, ^3J = 15.6 Hz, 1H, CH), 3.86 (s, 3H, OCH_3), 2.37 (s, 3H, CH_3), 2.35 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 156.4, 150.1, 149.4, 130.5, 127.4, 125.0, 121.9, 116.3, 112.0, 102.3, 56.1, 28.8, 8.6; IR (nujol, v/cm^{-1}): 1658, 1624, 1257, 1221, 1179, 1024; HRMS (ESI) calcd. for $C_{14}H_{15}O_3^+$ $[M+H]^+$ 231.1016, found 231.1011.

Acknowledgments

The work was supported by the Ministry of Education and Science of the Russian Federation (Project № 4.5371.2017/8.9 and Agreement № 02.a03.0008).

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