





Synthetic strategy toward furyl- and benzofuryl-containing building blocks for organic materials

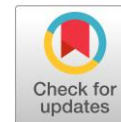
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Abstract

A synthetic approach to furyl- and benzofuryl-containing building blocks utilizing easily accessible substrates is reported. Cascade acid-catalyzed reactions of 2-methylfuran with α,β -unsaturated carbonyl compounds or salicyl alcohols followed by oxidation afford functionalized furans and benzofurans, respectively. Synthetic potential of the obtained products was demonstrated by synthesizing hetaryl-substituted heterocycles, which may find an application in materials chemistry.

Keywords

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heterocycle
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1. Introduction

Organic molecules have an opportunity for replacing the traditional inorganic compounds in functional materials due to their low cost, flexibility in designing physical and chemical properties, and simplicity of the manufacturing processes [1, 2]. The possibility for the organic compounds to act as active components of solar cells [3], optoelectronic devices [4], sensors [5, 6] and other materials [7, 8] has been the focus of extensive research.

The functional properties of heterocyclic architectures, which have certain advantages over carbocyclic counterparts [9], have been intensively studied [10, 11]. Historically, thiophene derivatives were among the first to be used as substrates to obtain functional materials for organic electronics [12]. In turn, furans, being oxygen-containing analogs with better solubility as well as with other suitable physicochemical features [13] could compete with thiophenes; however, their use as integral parts of functional materials started to be investigated just recently. Thus, the potential applications of furans and benzofurans in photovoltaics [14–16] and optoelectronics [17, 18] are being evaluated currently with a specific focus on hetaryl-substituted systems (Figure 1).

To date, there are few general synthetic strategies toward furyl- and benzofuryl-containing heterocycles. Usual-

ly, benzofurans are accessed via transition metal-catalyzed inter- or intramolecular cyclizations of phenols or their O-protected derivatives with alkenes and alkynes [19]. Suzuki-Miyaura cross-coupling is used to obtain target heterocyclic motifs possessing both benzofuran [20] and furan [21, 22] moieties. The conjugate addition/cyclization has also been successfully utilized for the synthesis of substituted furan-indol conjugates [23]. Heterogeneous catalysis with Cu@imine/Fe₃O₄ nanoparticles [24], graphene oxide with cascade addition/cyclization [25] was applied to obtain complex heterocyclic molecules with furyl substituents.

Acid-catalyzed domino reaction of accessible alkylfurans [26] with ambiphilic compounds, comprehensively explored by Butin et al., serves as a convenient tool for constructing functionalized heterocyclic compounds [27]. The Butin reaction yields a wide range of heterocycles that possess alkanone fragments, including furans and benzofurans. In the present work, we propose a way for the utilization of the Butin reaction products as building blocks for construction hetaryl-substituted furans [28] and benzofurans [29] as potential functional molecules. The synthetic design relies on the possibility for the oxidation of the alkanone side chain followed by chemical engagement of the formed α,β -unsaturated ketone fragment into chemical transformations to obtain novel heterocyclic systems [30, 31, 32] (Scheme 1).

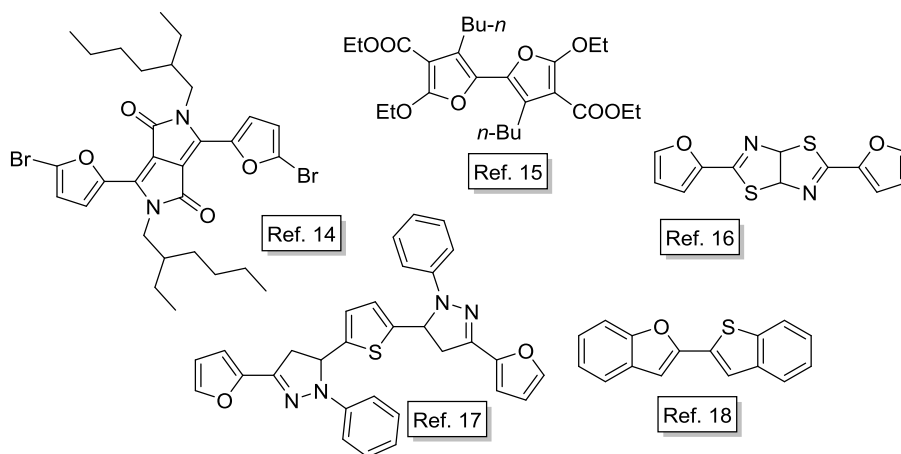
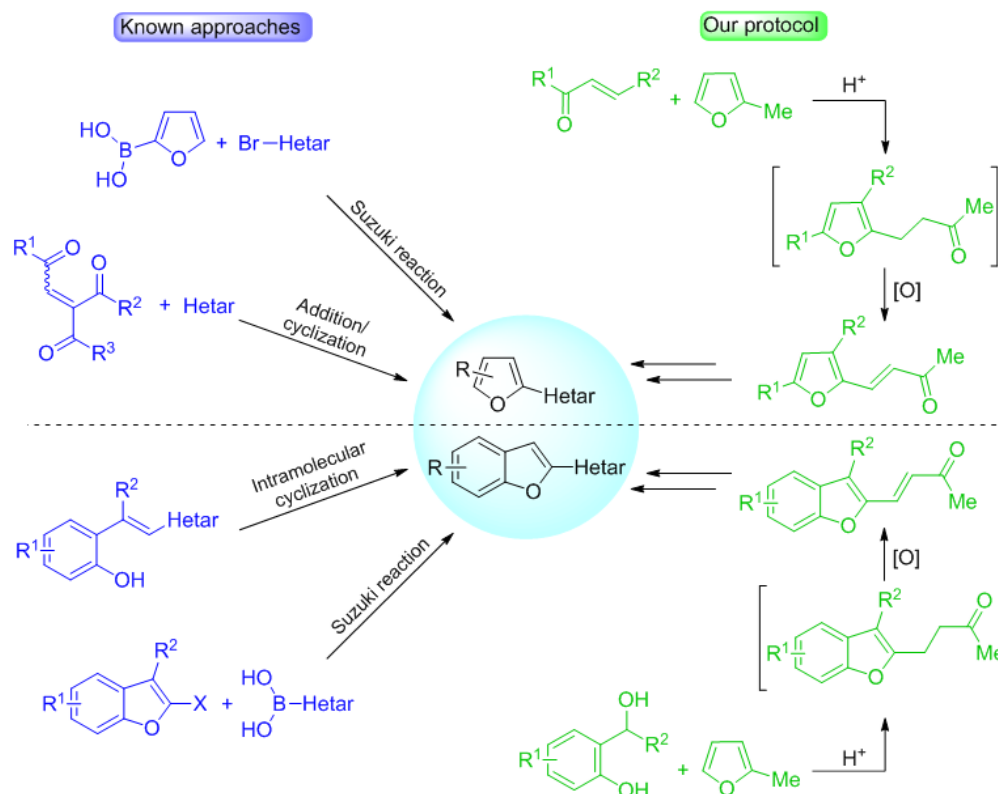


Figure 1 Furan-based molecules for material chemistry.



Scheme 1 Known synthetic strategies toward hetaryl-substituted furans and benzofurans and our protocol.

2. Experimental

^1H and ^{13}C NMR spectra were recorded with a «Bruker Avance III HD 400» (400 MHz for ^1H and 101 MHz for ^{13}C NMR) spectrometer at room temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent (CDCl_3 , ^1H : $\delta = 7.26$ ppm, ^{13}C : $\delta = 77.16$ ppm). Coupling constants (J) are given in Hertz. Splitting patterns of apparent multiplets associated with an averaged coupling constants were designated as *s* (singlet), *d* (doublet), *t* (triplet), *m* (multiplet), and *br* (broadened). 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». Column chromatography was performed on silica gel Macherey Nagel

(40–63 μm). Reaction progress was monitored by GC/MS analysis and thin layer chromatography (TLC) on aluminum backed plates with Merck Kiesel 60 F254 silica gel. The TLC plates were visualized either by UV radiation at a wavelength of 254 nm. All the reactions were carried out using dried and freshly distilled solvent.

2.1. General method for synthesis of furans

A 5 mL microreaction vial equipped with a stirring bar and a Teflon cap was charged with unsaturated ketone **1** (1 mmol), 2-methylfuran (**2**) (1.5 mmol, 123 mg, 1.5 equiv), AcOH (5 mL), and 48% aq. HBr (8.4 mg, 5.6 μL , 5% mol). The vial was closed and placed into an aluminum heating block preheated to 80 $^\circ\text{C}$, and the mixture was stirred for 12 h (TLC control). Upon completion, the reaction mixture was filtered through a thin layer of silica gel. The solvent

was evaporated, and the residue was dissolved in dichloromethane (2 ml) and DDQ (1.2 mmol, 272 mg, 1.2 equiv.) was added. The mixture was stirred at room temperature until full consumption of the starting material (TLC control). Upon completion, the reaction mixture was subjected to column chromatography on silica gel (eluent: dichloromethane/petroleum ether, 1:1).

2.1.1. (*E*)-4-(3,5-diphenylfuran-2-yl)but-3-en-2-one (3a)

Yellow needles. Yield 265 mg (92%); $m_p = 112\text{--}113\text{ }^\circ\text{C}$ (ethanol). $R_f = 0.45$ (petroleum ether/ethyl acetate, 3:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.82–7.75 (*m*, 2H), 7.51–7.32 (*m*, 9H), 6.90 (*s*, 1H), 6.84 (*d*, $J = 15.6$ Hz, 1H), 2.34 (*s*, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 197.6, 155.7, 146.1, 134.3, 132.5, 129.7, 129.1 (2C), 129.0 (2C), 128.9, 128.5 (2C), 128.3, 128.1, 124.6 (2C), 124.3, 108.8, 28.1 ppm. GC-LRMS (EI, m/z): 288 (M^+ , 100%), 273 ($[\text{M}-\text{CH}_3]^+$), 245 ($[\text{M}-\text{CH}_3\text{CO}]^+$).

2.1.2. (*E*)-4-(5-(4-methoxyphenyl)-3-phenylfuran-2-yl)but-3-en-2-one (3b)

Orange solid. Yield 264 mg (83%); $m_p = 142\text{--}143\text{ }^\circ\text{C}$ (ethanol). $R_f = 0.40$ (petroleum ether/ethyl acetate, 3:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.73–7.68 (*m*, 2H), 7.50–7.37 (*m*, 6H), 6.98–6.94 (*m*, 2H), 6.79 (*d*, $J = 15.8$ Hz, 1H), 6.76 (*s*, 1H), 3.85 (*s*, 3H), 2.33 (*s*, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 197.7, 160.4, 155.9, 145.4, 134.6, 132.6, 129.1 (2C), 128.5 (2C), 128.3, 128.3, 126.2 (2C), 123.7, 122.6, 114.5 (2C), 107.4, 55.5, 28.1 ppm. GC-LRMS (EI, m/z): 318 (M^+ , 100%), 303 ($[\text{M}-\text{CH}_3]^+$), 275 ($[\text{M}-\text{CH}_3\text{CO}]^+$).

2.1.3. (*E*)-4-(3,5-bis(4-methoxyphenyl)furan-2-yl)but-3-en-2-one (3c)

Brown solid. Yield 261 mg (75%); $m_p = 137\text{--}139\text{ }^\circ\text{C}$ (ethanol). $R_f = 0.28$ (petroleum ether/ethyl acetate, 4:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.73–7.68 (*m*, 2H), 7.44 (*d*, $J = 15.6$ Hz, 1H), 7.41–7.37 (*m*, 2H), 7.02–6.93 (*m*, 4H), 6.77 (*d*, $J = 15.6$ Hz, 1H), 6.73 (*s*, 1H), 3.86 (*s*, 3H), 3.858 (*s*, 3H), 2.32 (*s*, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 197.6, 160.4, 159.9, 155.9, 145.2, 134.5, 129.8 (2C), 128.4, 126.27 (2C), 125.1, 123.3, 122.8, 114.7 (2C), 114.6 (2C), 107.5, 55.5 (2C), 28.1 ppm. GC-LRMS (EI, m/z): 348 (M^+ , 100%), 333 ($[\text{M}-\text{CH}_3]^+$), 305 ($[\text{M}-\text{CH}_3\text{CO}]^+$).

2.2. General method for synthesis of benzofurans

To a solution of salicyl alcohol **4** (0.5 mmol) in dichloroethane (2 mL) was added 2-methylfuran (**2**) (0.75 mmol, 61.5 mg, 1.5 equiv.) and trifluoromethanesulfonic acid (0.05 mmol, 7.5 mg, 0.1 equiv.). The resulting mixture was stirred at 80 $^\circ\text{C}$ until full consumption of the starting material (TLC control, ca. 1 h). Upon completion, the reaction mixture was filtered through a thin layer of silica gel, and DDQ (0.6 mmol, 136 mg, 1.2 equiv.) was added. The mixture was stirred at room temperature until full consumption of the starting material (TLC control). Upon completion, the reaction mixture was subjected to column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:20).

2.2.1. (*E*)-4-(3-phenylbenzofuran-2-yl)but-3-en-2-one (5a)

Orange solid. Yield 127 mg (97%); $m_p = 102\text{--}104\text{ }^\circ\text{C}$ (ethanol). $R_f = 0.56$ (petroleum ether/ethyl acetate, 1:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.67–7.63 (*m*, 1H), 7.56–7.40 (*m*, 8H), 7.31–7.26 (*m*, 1H), 6.98 (*d*, $J = 15.7$ Hz, 1H), 2.35 (*s*, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 197.6, 155.2, 148.5, 131.3, 129.7 (2C), 129.3 (2C), 128.6, 128.6, 128.5, 127.3, 127.2, 126.9, 123.7, 121.1, 111.7, 28.6 ppm. GC-LRMS (EI, m/z): 262 (M^+), 247 ($[\text{M}-\text{CH}_3]^+$), 219 ($[\text{M}-\text{CH}_3\text{CO}]^+$, 100%) [33].

2.2.2. (*E*)-4-(4,7-dimethoxy-3-phenylbenzofuran-2-yl)but-3-en-2-one (5b)

Yellow solid. Yield 135 mg (84%); $m_p = 166\text{--}167\text{ }^\circ\text{C}$ (ethanol). $R_f = 0.49$ (petroleum ether/ethyl acetate, 1:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.42–7.33 (*m*, 5H), 7.26 (*d*, $J = 15.7$ Hz, 1H), 6.91 (*d*, $J = 15.7$ Hz, 1H), 6.76 (*d*, $J = 8.6$ Hz, 1H), 6.47 (*d*, $J = 8.6$ Hz, 1H), 3.94 (*s*, 3H), 3.60 (*s*, 3H), 2.22 (*s*, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 197.7, 149.3, 148.4, 145.6, 140.2, 131.4, 130.9 (2C), 128.4, 128.2, 127.9 (2C), 127.5, 126.7, 119.9, 110.0, 104.1, 57.1, 56.0, 28.7 ppm. GC-LRMS (EI, m/z): 322 (M^+ , 100%), 307 ($[\text{M}-\text{CH}_3]^+$), 279 ($[\text{M}-\text{CH}_3\text{CO}]^+$).

2.2.3. (*E*)-4-(5-methoxy-7-methyl-3-phenylbenzofuran-2-yl)but-3-en-2-one (5c)

Brown solid. Yield 133 mg (87%); $m_p = 135\text{--}136\text{ }^\circ\text{C}$ (ethanol). $R_f = 0.55$ (petroleum ether/ethyl acetate, 1:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.57–7.44 (*m*, 6H), 6.96 (*d*, $J = 15.7$ Hz, 1H), 6.88–6.85 (*m*, 2H), 3.80 (*s*, 3H), 2.55 (*s*, 3H), 2.35 (*s*, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 197.7, 156.8, 149.4, 148.9, 131.7, 129.6 (2C), 129.3 (2C), 128.8, 128.5, 128.4, 127.4, 126.8, 122.9, 117.6, 100.2, 56.1, 28.3, 15.2 ppm. GC-LRMS (EI, m/z): 306 (M^+), 291 ($[\text{M}-\text{CH}_3]^+$), 263 ($[\text{M}-\text{CH}_3\text{CO}]^+$, 100%).

2.3. General method for synthesis of pyrroles

To a solution of furan **3a** or benzofuran **5a** (0.4 mmol) in dioxane (3 mL) was added TosMIC (0.8 mmol, 156 mg, 2 equiv.) and Cs_2CO_3 (0.8 mmol, 260 mg, 2 equiv.). The resulting suspension was stirred at 60 $^\circ\text{C}$ until full consumption of the starting material (TLC control, ca. 24 h). Upon completion, the reaction mixture was poured into water (200 mL) and extracted with ethyl acetate (3 \times 20 mL). Combined organic phase was dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. Crude concentrated extract was subjected to column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, graduate elution from 1:5 to 1:2).

2.3.1. 1-(4-(3,5-diphenylfuran-2-yl)-1H-pyrrol-3-yl)ethan-1-one (6)

Colorless oil. Yield 116 mg (89%). $R_f = 0.41$ (petroleum ether/ethyl acetate, 1:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.57 (*br. s*, 1H), 7.77–7.70 (*m*, 2H), 7.45–7.36 (*m*, 5H), 7.31–7.25 (*m*, 3H), 7.24–7.19 (*m*, 1H), 6.96 (*s*, 1H), 6.79 (*t*, $J = 2.3$ Hz, 1H), 2.23 (*s*, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 194.7, 153.0, 143.5, 133.9, 130.8, 128.8 (2C),

128.5 (2C), 127.5, 127.3 (2C), 126.7, 125.3, 125.3, 124.9, 123.8 (2C), 121.8, 114.0, 106.8, 28.1 ppm. GC-LRMS (EI, m/z): 327 (M^+ , 100%), 312 ($[M-CH_3]^+$), 284 ($[M-CH_3CO]^+$).

2.3.2. 1-(4-(3-phenylbenzofuran-2-yl)-1H-pyrrol-3-yl)ethan-1-one (7)

Colorless oil. Yield 114 mg (95%). R_f = 0.33 (petroleum ether/ethyl acetate, 1:1). 1H NMR (400 MHz, $CDCl_3$) δ 9.42 (br. s, 1H), 7.56–7.50 (*m*, 1H), 7.38–7.33 (*m*, 1H), 7.33–7.27 (*m*, 2H), 7.25–7.09 (*m*, 6H), 6.58–6.51 (*m*, 1H), 2.10 (*s*, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 154.7, 146.9, 133.1, 129.2 (2C), 128.9, 128.7 (2C), 127.1, 125.8, 124.6, 124.5, 122.9, 122.0, 120.1, 119.0, 113.7, 111.4, 28.3 ppm. GC-LRMS (EI, m/z): 301 (M^+ , 100%), 286 ($[M-CH_3]^+$), 258 ($[M-CH_3CO]^+$).

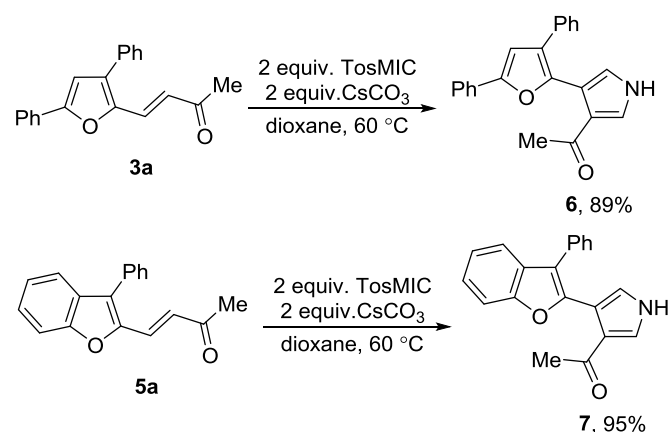
3. Results and discussion

We began our research with evaluating the possibility of synthesizing the target α,β -unsaturated carbonyl compounds with furyl substituent at β -position. To this end, we utilized a recently reported acid-catalyzed domino reaction of 2-methylfuran (**2**) with unsaturated ketones **1** that led to the formation of furylalkanones **A** (Scheme 2). We screened various oxidants in order to obtain respective unsaturated products **3** from alkanones **A** [34–36] and found that DDQ in the amount of 1.2 equiv. effectively induced the desired transformation affording compounds **3** with high yields. The oxidation step could be coupled with the acid-catalyzed domino reaction with the only requirement to change the solvent after passing the initial reaction mixture through a pad of silica gel. The developed method was evaluated by synthesizing three examples of the target molecular architecture.

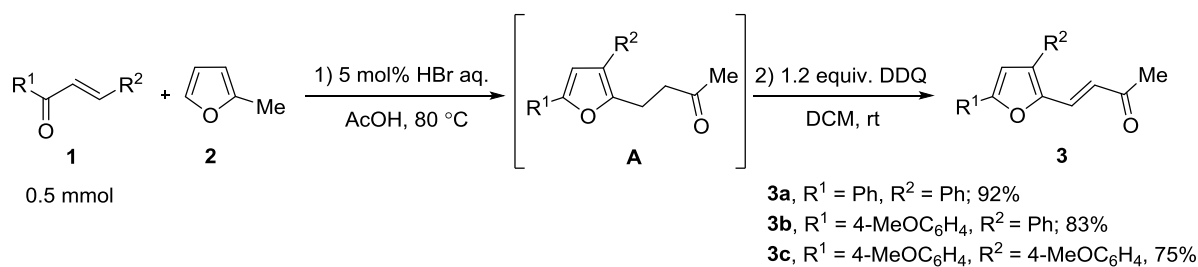
In order to obtain the target benzofuryl-containing unsaturated ketones **5**, we employed another acid-catalyzed

domino reaction, namely, a reaction of salicyl alcohols **4** with 2-methylfuran (**2**) [29] (Scheme 3). The oxidative conditions found for the synthesis of compounds **3** from alkanone intermediates appeared to be suitable for obtaining the benzofuran counterparts **5**. The oxidation step was also integrated into the process without the need to switch the solvent, and the resulting products **5a–c** were obtained with high yields.

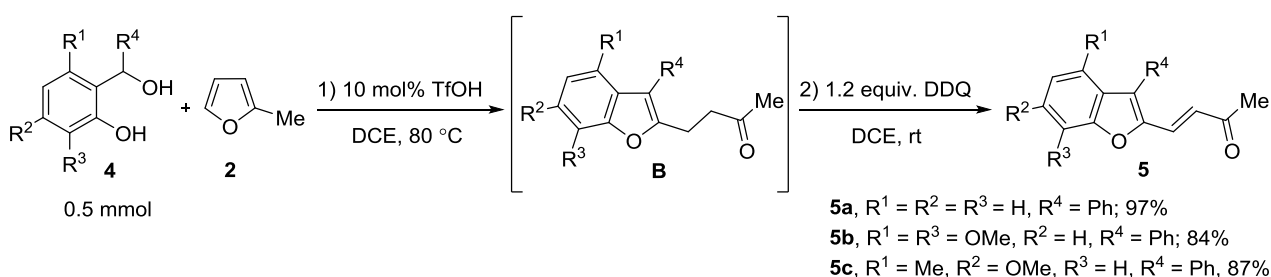
The presence of a highly reactive α,β -unsaturated ketone fragment in the structure of the synthesized compounds opens prospect for applying the products **3** and **5** as building blocks for obtaining the furyl- and benzofuryl-containing heterocycles. To demonstrate this possibility, we performed the reaction of the compounds **3a** and **5a** with TosMIC upon activation with a base [37–40]. The reaction afforded respective pyrroles **6** and **7** with high yields (Scheme 4). The structure of the compounds **6** and **7** represents a general furyl/benzofuryl-substituted heterocyclic motif. Importantly, well-explored chemical behaviour of the acetyl group and free pyrrolic nitrogen possessed by the final compounds could be utilized for further structural modifications.



Scheme 4 Synthesis of pyrroles **6** and **7**.



Scheme 2 Synthesis of furans **3**.



Scheme 3 Synthesis of benzofurans **5**.

4. Conclusions

We developed a protocol for the synthesis of functionalized furans and benzofurans starting from easily available precursors. The obtained products could serve as building blocks for designing potential furan- and benzofuran-based heterocyclic functional molecules for organic electronics.

Supplementary materials

No supplementary materials are available.

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Author contributions

Conceptualization: D.A.M.

Data curation: Y.A.V.

Formal Analysis: D.A.M., Y.A.V.

Funding acquisition: Y.A.V.

Investigation: D.A.E., D.K.V.

Methodology: D.A.E., D.K.V.

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Software: D.A.M., Y.A.V.

Supervision: D.A.M.

Validation: D.A.M., Y.A.V.

Visualization: Y.A.V., D.A.M.

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Conflict of interest

The authors declare no conflict of interest.

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