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## SYNTHESIS OF 9,9'-(FURAN-2,5-DIYLBIS(4,1-PHENYLENE))BIS-9H-CARBAZOLE

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A two-step synthetic route to 9,9'-(furan-2,5-diylbis(4,1-phenylene))bis-9H-carbazole was developed. On the first stage, by arylation of furan with 4-bromophenyldiazonium chloride under the Meerwein reaction conditions 2,5-bis(4-bromophenyl)furan was obtained. The Ullmann reaction between carbazole and 2,5-bis(4-bromophenyl)furan led to the formation of 9-(4-(5-(4-bromophenyl)-2-furyl)phenyl)-9H-carbazole and 9,9'-(furan-2,5-diylbis(4,1-phenylene))bis-9H-carbazole.

*Keywords:* carbazole, 2,5-bis(4-bromophenyl)furan, arylation, Meerwein reaction, Ullmann reaction.

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### 1. Introduction

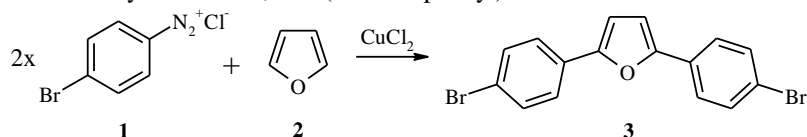
Over the past few decades, the studies, synthesis and investigation of  $\pi$ -conjugated organic materials drew considerable research attention owing to their possible applications in the field of organic optoelectronics. One of important advantages of low-molar-mass organic semiconductors is the fact that the energy of levels of their peripheral orbitals and subsequent energy gaps of organic molecules can be easily modified by molecular design and as a result photoelectronic and electrochemical properties can be finely adjusted. Presently, the conjugated compounds are of a special attention because of their applicability in optoelectronic and electronic devices, such as organic light emitting diodes (OLEDs) [1-3], solar cells [4, 5] and organic thin-film transistors [6].

Commercialization of materials for organic electronics for the manufacturing purposes requires simple synthetic routes and readily available synthetic precursors. Carbazole is cheap and at the same time is one of the most popular building blocks for organic optoelectronic materials due to high triplet energy levels, good hole transporting properties and thermal stability [7, 8]. On the other hand, diarylfuran structural motif also often appears in structures of semiconducting materials and compounds showing prominent photophysical properties [9, 10]. In this light, combination of carbazole and diarylfuran moieties is a promising tool for the preparation of practically valuable materials. Herein, we report on the two-step synthetic approach to the preparation of 9,9'-(furan-2,5-diylbis(4,1-phenylene))bis-9H-carbazole based on the subsequent copper-mediated Meerwein and Ullmann reactions.

## 2. Results and discussion

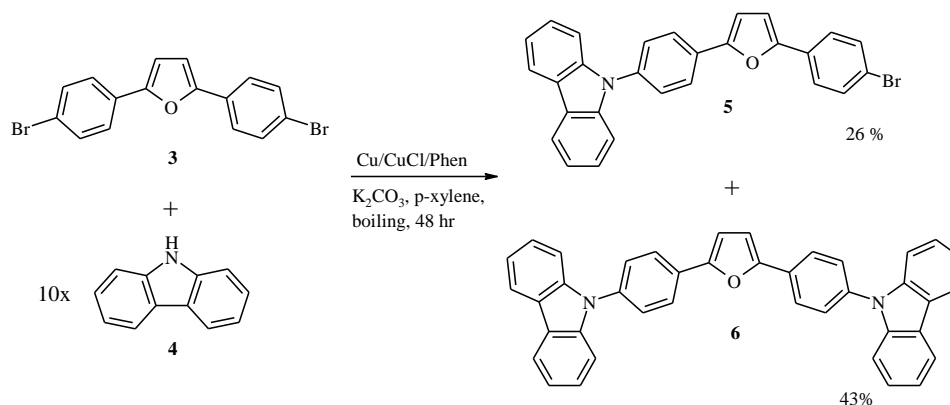
On the first step for the preparation of 2,5-bis(4-bromophenyl)furan **3** we applied the Meerwein arylation reaction. The reaction of two equivalents of 4-bromophenyldiazonium chloride **1** with furan **2** proceeds in water-acetone medium in the presence of catalytic amounts of copper (II) chloride.

Scheme 1. Synthesis of 2,5-bis(4-bromophenyl)furan



Then, 2,5-bis(4-bromophenyl)furan **3** was studied in the reaction with carbazole **4** under the Ullmann reaction conditions. The reactions were carried out in refluxing p-xylene during 48 h. Meanwhile, Cu/CuCl/phenantroline and potassium carbonate was used as a catalytic system and base respectively.

Scheme 2. The Ullmann reaction



It was found that application of stoichiometric ratio (2:1) of carbazole **4** and diarylfuran **3** under the chosen reaction conditions led to predominant formation of monoarylated product **5** in 72 % yield, while compound **6** was formed in trace amounts. In its turn, increasing of reagents ratio to 10:1 resulted in formation of the mixture of compounds **5** and **6** with yields 26 and 43 % respectively. Further increasing of reagents ratio found to be unsuitable in terms of complication of isolation procedure. Solutions of carbazole-containing compounds show strong blue fluorescence under exposure to sunlight. In general, the reaction yields are rather poor nevertheless starting materials and catalysts are cheap and commercially available.

## 3. Conclusion

In summary, practically oriented a two-step approach to the synthesis of carbazole-decorated diarylfurans was developed. Further detailed investigation of photophysical properties of obtained compounds is on the way.

#### 4. Experimental details

$^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra of the solutions in DMSO- $d_6$  were obtained using Bruker DRX 400 spectrometer (400 MHz ( $^1\text{H}$ ), 100 MHz ( $^{13}\text{C}$ )). Chemical shifts ( $\delta$ ) are reported in ppm referenced to tetramethylsilane (TMS). Column chromatography was carried out on Fluka Silica Gel 60. Thin layer chromatography (TLC) was performed on silica gel (Merck TLC Silica Gel 60 F<sub>254</sub>) and visualized with UV-lamp.

##### 2,5-Bis(4-bromophenyl)furan **3**

A mixture of furan **2** (1.0 g, 14.7 mmol) and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.2 g) in 25 ml of acetone was placed in a flask with magnetic stirrer, dropping funnel and bubble counter and stirred vigorously. The solution of arenediazonium salt obtained by diazotation of 4-bromoaniline (5.1 g, 29.4 mmol) was added dropwise during 15 min and the stirring continued for about 2 hr. After the nitrogen evolution caused the semisolid was filtered and recrystallized from ethanol. The compound **3** obtained as white needles, yield 36 % (2.0 g), mp = 196–197 °C.

##### The Ullmann reaction procedure

A mixture of carbazole **4** (2.2 g, 13.2 mmol), 2,5-bis(4-bromophenyl)furan **3** (0.5 g, 1.3 mmol), copper (0.02 g, 0.3 mmol), copper (I) chloride (0.03 g, 0.3 mmol), 1,10-phenanthroline (0.06 g, 0.3 mmol) and  $\text{K}_2\text{CO}_3$  (1.8 g, 13.2 mmol) were added to 20 ml of p-xylene and heated at 155 °C for 48 h. After cooling to room temperature, the mixture was poured into water and extracted with ethyl acetate. The organic extracts were washed with water and dried over anhydrous sodium sulfate. After the solvent was removed, the residue was purified by column chromatography on silica gel with hexane/dichloromethane (5:1) as the eluent to give the desired products **5** and **6**.

**9-(4-(5-(4-Bromophenyl)-2-furyl)phenyl)-9H-carbazole **5**** was obtained as white needles,  $R_f$  = 0.4 (5:1 hexane/DCM), yield 26 %.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.22 (d,  $J$  = 3.4 Hz, 1H), 7.24 (d,  $J$  = 3.4 Hz, 1H), 7.28–7.34 (m, 2H), 7.42–7.49 (m, 4H), 7.67 (d,  $J$  = 8.4 Hz, 2H), 7.71 (d,  $J$  = 8.4 Hz, 2H), 7.82 (d,  $J$  = 8.4 Hz, 2H), 8.11 (d,  $J$  = 8.3 Hz, 2H), 8.26 (d,  $J$  = 7.7 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  109.59, 109.76, 110.17 (2C), 120.65 (2C), 121.03 (2C), 121.04, 123.30 (2C), 125.69 (2C), 125.96 (2C), 126.78 (2C), 127.63 (2C), 129.50, 129.69, 132.37 (2C), 136.50, 140.51 (2C), 152.43, 152.86.

**9,9'-(Furan-2,5-diylbis(4,1-phenylene))bis-9H-carbazole **6**** was obtained as off-white solid,  $R_f$  = 0.2 (5:1 hexane/DCM), yield 43 %.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.28–7.36 (m, 6H), 7.43–7.51 (m, 8H), 7.75 (d,  $J$  = 8.2 Hz, 4H), 8.17 (d,  $J$  = 8.2 Hz, 4H), 8.28 (d,  $J$  = 7.7 Hz, 4H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  109.70 (2C), 110.20 (4C), 120.65 (4C), 121.03 (4C), 123.31 (4C), 125.68 (4C), 126.80 (4C), 127.70 (4C), 129.63 (2C), 136.49(2C), 140.54 (4C), 152.90 (2C).

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## СИНТЕЗ 9,9'-(ФУРАН-2,5-ДИЛБІС(4,1-ФЕНІЛЕН))БІС-9Н-КАРБАЗОЛУ

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Протягом останніх десятиліть синтез та дослідження  $\pi$ -кон'югованих органічних матеріалів привернули значну увагу дослідників у зв'язку з активним застосуванням їх в органічній оптоелектроніці. Однією з важливих переваг низькомолекулярних органічних напівпровідників є те, що енергії рівнів периферійних орбіталей та відповідні енергії переходів в органічних молекулах легко модифікуються за допомогою молекулярного дизайну, внаслідок чого фотоелектронні та електрохімічні властивості таких сполук можна легко скорегувати. З іншого боку, комерціалізація матеріалів для виробничих цілей потребує простих синтетичних шляхів та дешевих і легкодоступних синтетичних прекурсорів. У цій праці ми вирішили поєднати в одній молекулі фрагменти карбазолу та діарилфурану, які є часто вживаними структурними фрагментами органічних напівпровідникових матеріалів. З цією метою ми розробили двостадійний метод синтезу діарилфуранів, декорованих фрагментами карбазолу, який ґрунтується на купрум каталітичних реакціях Мервейна та Ульмана. Спочатку ми одержали 2,5-біс(4-бромфеніл)фуран арилюванням фурану 4-бромфенілдіазоній

хлоридом, який на наступній стадії ввели в реакцію Ульмана з карбазолом, унаслідок чого отримали 9-(4-(5-(4-бромфеніл)-2-фурил)феніл)-9*H*-карбазол та 9,9'-(біс-2,5-діілбіс(4,1-фенілен))біс-9*H*-карбазол з виходами 26 і 43 %, відповідно. Будову отриманих сполук доведено за допомогою  $^1\text{H}$  та  $^{13}\text{C}$  ЯМР спектроскопії. Спектр ЯМР  $^1\text{H}$  сполуки **6** внаслідок симетрії молекули є відносно простим і містить 5 груп сигналів з інтегральними інтенсивностями 4:4:4:8:6. Найбільш слабкопольний дублет (8,3 м.ч.) належить протонам карбазолу у положеннях 1 та 8. Протони феніленових груп дають два дублети при 8,2 і 7,8 м.ч. Сигнали протонів у позиціях 2, 3, 6, 7 карбазолу злились у мультиплет при 7,4–7,5 м.ч., а мультиплет при 7,3–7,4 м.ч. належить сигналам протонів карбазолу у положеннях 4 та 5 і протонів фуранового ядра.

Отже, розроблено двостадійний та синтетично привабливий метод синтезу діарилфуранів, декорованих фрагментами карбазолу – перспективних матеріалів для органічної оптоелектроніки.

*Ключові слова:* карбазол, 2,5-біс(4-бромфеніл)фуран, арилювання, реакція Месрвейна, реакція Ульмана.

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