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New monomers for (bi)pyridine-containing polymers

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Abstract. Convenient methods for the synthesis of three monomers based on functionalized (bi)pyridines with using "1,2,4-triaizine" methodology have been developed.

Keywords: monomers; 1,2,4-triazines; (bi)pyridines; inverse demand Diels-Alder reaction

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Introduction

(2,2′-Bi)pyridine containing polymers are of interest from the point of view of creating OLED [1, 2] for redox catalytic reactions [3], as electrolyte membrane fuel cell application [4] or anode materials components [5]. In this regard, the development of convenient methods for the synthesis of compounds with the (poly) pyridine fragment and suitable for using as monomers, is an actual purpose. In this article we propose the convenient methods for the synthesis of three potential monomers of the (bi)pyridine series.

Experimental part

^{1}H NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 MHz), the internal standard was $SiMe_4$. Mass-spectra (ionization type — electrospray) were recorded on a MicrOTOF-Q II instrument from Bruker Daltonics (Bremen, Germany). Elemental analysis was performed on a Perkin Elmer PE 2400 II CHN analyzer. The starting 4-bromophenylhydrazone **2** was obtained according to the described method [11].

General procedure for the synthesis of 1,2,4-triazines 3

Hydrazone **2** (605 mg, 2.5 mmol) was solved in ethanol (30 ml) and solution of the corresponding carbaldehyde **1** (2.5 mmol) in ethanol (25 ml) was added. The resulting mixture was kept at room temperature for 12 h. The precipitate was filtered off, washed with ethanol and dried. Then the obtained intermediate was suspended in acetic acid (30 ml) and mixture was heated to reflux two times. Solvent was removed under reduced pressure.

Ethanol (30 ml) was added to the residue; the resulting crystals of **3** were filtered off, washed with ethanol and dried. The crude triazines were used directly in the next step without additional purification.

6-(4-Bromophenyl)-3-(5-bromopyridin-2-yl)-1,2,4-triazine (3a). Yield 630 mg (1.60 mmol, 64%). NMR ^{1}H (DMSO-d_6, δ, ppm): 7.75–7.79 (m, 2H, C_6H_4Br), 8.23 (dd, 1H, ^3J 8.4 Hz, ^4J 2.4 Hz, H-4(py)), 8.25–8.29 (m, 2H, C_6H_4Br), 8.49 (d, 1H, ^3J 8.4 Hz, H-5(py)), 8.89 (d, 1H, ^4J 2.4 Hz, H-6(py)), 9.52 (s, 1H, H-5). ESI–MS, m/z: 390.92 $(M+H)^+$.

6-Bromo-2-(6-(4-bromophenyl)-1,2,4-triazin-3-yl)quinoline (3b). Yield 800 mg (1.80 mmol, 72%). NMR ^{1}H (DMSO-d_6, δ, ppm): 7.77–7.83 (m, 2H, C_6H_4Br), 7.92 (dd, 1H, ^3J 8.0 Hz, ^4J 2.0 Hz, H-7(qui)), 8.15–8.20 (m, 2H, H-5,8(qui)), 8.30–8.35 (m, 2H, C_6H_4Br), 8.56 and 8.70 (both d, 1H, ^3J 8.4 Hz, H-3 and H-4 (qui)), 9.61 (s, 1H, H-5). ESI–MS, m/z: 440.94 $(M+H)^+$.

3-(4-Bromophenyl)-6-(thiophen-2-yl)-1,2,4-triazine (7). A mixture of 349 mg (1.7 mmol) of 2-bromo-1-(thiophen-2-yl)ethanone **5**, 732 mg (3.4 mmol) of hydrazide **6** and 25 mL of DMF was heated at 120 °C under argon for 10 h. The solvent was distilled off under reduced pressure, the residue was treated with ethanol, and the precipitate was filtered off. The crude triazine was used directly in the next step without addition purification. Yield 343 mg (1.08 mmol, 63%). NMR ^{1}H (DMSO-d_6, δ, ppm): 7.27 (dd, 1H, ^3J 5.2 Hz, 3.8 Hz, H-4(thio)), 7.70–7.76 (m, 2H, C_6H_4Br), 7.27 (dd, 1H, ^3J 5.2 Hz, ^4J 0.8 Hz, H-5 (thio)), 8.10 (dd, 1H, ^3J 3.8 Hz, ^4J 0.8 Hz, H-3(thio)), 8.37–8.42 (m, 2H, C_6H_4Br), 9.43 (s, 1H, H-5).

A general procedure for the synthesis of (bi)pyridines 4 and 8

The mixture of corresponding 1,2,4-triazine **3** or **7** (0.8 mmol) and 1-morpholinocyclo-pentene (0.64 ml, 4.0 mmol) was stirred at 200 °C for 2 h under argon atmosphere. Then, the additional portion of 1-morpholinocyclopentene (0.32 ml, 2.0 mmol) was added and the resulting mixture was stirred for additional 1 h at the same conditions. The reaction mass was cooled to room temperature. The products were purified by flash chromatography (DCM as eluent) and then by recrystallization (ethanol).

4-(4-Bromophenyl)-1-(5-bromopyridin-2-yl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine (4a). Yield 270 mg (0.63 mmol, 78%). NMR ^{1}H (DMSO-d_6, δ, ppm): 2.08 (m, 2H, CH_2-6), 3.04 (t, 2H, ^3J 7.6 Hz, CH_2-7), 3.46 (t, 2H, ^3J 7.6 Hz, CH_2-5), 7.48–7.54 (m, 2H, C_6H_4Br), 7.64–7.70 (m, 2H, C_6H_4Br), 8.11 (dd, 1H, ^3J 8.4 Hz, ^4J 1.6 Hz, H-4′), 8.30 (d, 1H, ^3J 8.4 Hz, H-5′), 8.47 (s, 1H, H-3), 8.75 (d, 1H, ^4J 1.6 Hz, H-6′). ESI–MS, m/z: 428.96 $(M+H)^+$. Found, %: C 53.19, H 3.39, N 6.40. $C_{19}H_{14}Br_2N_2$. Calculated, %: C 53.05, H 3.28, N 6.51.

6-Bromo-2-(4-(4-bromophenyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridin-1-yl)quinoline (4b). Yield 290 mg (0.60 mmol, 75%). NMR ^{1}H (DMSO-d_6, δ, ppm): 2.14 (m, 2H, CH_2-6), 3.08 (t, 2H, ^3J 7.6 Hz, CH_2-7), 3.69 (t, 2H, ^3J 7.6 Hz, CH_2-5), 7.51–7.57 (m, 2H, C_6H_4Br), 7.66–7.71 (m, 2H, C_6H_4Br), 7.86 (dd, 1H, ^3J 8.8 Hz, ^4J 1.6 Hz, H-7(qui)), 8.02 (d, 1H, ^3J 8.8 Hz, H-8(qui)), (d, 1H, ^4J 1.6 Hz, H-5(qui)), 8.40 and 8.56 (both d, 1H, ^3J 8.8 Hz, H-3 and H-4 (qui)), 8.54 (s, 1H, H-3). ESI–MS, m/z: 478.98 $(M+H)^+$. Found, %: C 57.41, H 3.22, N 8.67. $C_{23}H_{16}Br_2N_2$. Calculated, %: C 57.53, H 3.36, N 8.53.

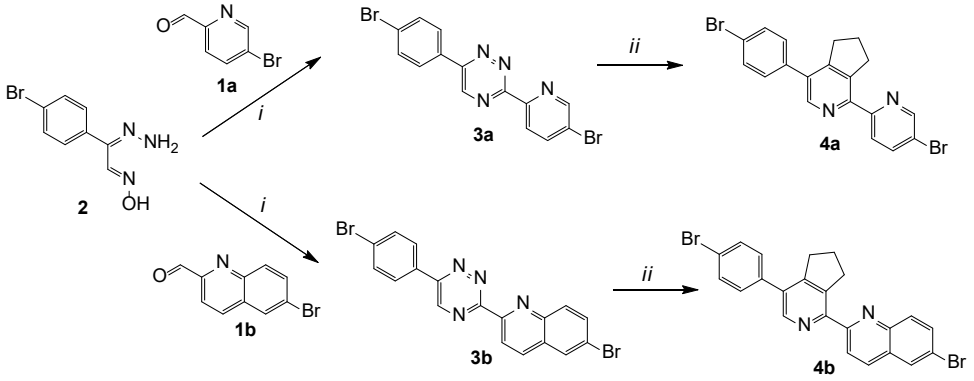
1-(4-Bromophenyl)-4-(thiophen-2-yl)-6,7-dihydro-5*H*-cyclopenta[c] pyridine (8). Yield 228 mg (0.64 mmol, 80%). NMR ^{1}H (DMSO-d_6, δ, ppm): 2.14 (m, 2H, CH_2-6), 3.15 (t, 2H, ^3J 7.6 Hz, CH_2-7), 3.20 (t, 2H, ^3J 7.6 Hz, CH_2-5), 7.16 (dd, 1H, ^3J 5.2 Hz, 3.8 Hz, H-4(thio)), 7.33 (dd, 1H, ^3J 3.8 Hz, ^4J 0.8 Hz, H-3(thio)), 7.41 (dd, 1H, ^3J 5.2 Hz, ^4J 0.8 Hz, H-5(thio)), 7.57–7.62 (m, 2H, C_6H_4Br), 7.65–7.70 (m, 2H, C_6H_4Br), 8.73 (s, 1H, H-3). ESI–MS, m/z: 356.01 $(M+H)^+$. Found, %: C 60.53, H 3.81, N 4.07. $C_{18}H_{14}BrNS$. Calculated, %: C 60.68, H 3.96, N 3.93.

1-(4-Bromophenyl)-4-(5-bromothiophen-2-yl)-6,7-dihydro-5*H*-cyclopenta[*c*] pyridine (9). Pyridine **8** (307 mg, 0.86 mmol) was dissolved in DMF (30 mL). *N*-Bromosuccinimide (184 mg, 1.0 mmol) was added and the resulting mixture was stirred for 8 h at 50 °C. Then water (100 mL) was added to the mixture and precipitate formed was filtered off. The analytical sample was obtained by recrystallization (ethanol). Yield 329 mg (0.76 mmol, 88%). NMR ^{1}H ($CDCl_3$, δ, ppm): 2.19 (m, 2H, CH_2-6), 3.17 (t, 2H, ^3J 7.6 Hz, CH_2-7), 3.20 (t, 2H, ^3J 7.6 Hz, CH_2-5), 7.10 and 7.13 (d, 1H, ^3J 3.8 Hz, H-3 and H-4 (thio)), 7.61–7.65 (m, 2H, C_6H_4Br), 7.67–7.71 (m, 2H, C_6H_4Br), 8.69 (s, 1H, H-3). ESI–MS, m/z: 433.92 $(M+H)^+$. Found, %: C 49.53, H 3.14, N 3.39. $C_{18}H_{13}Br_2NS$. Calculated, %: C 49.68, H 3.01, N 3.22.

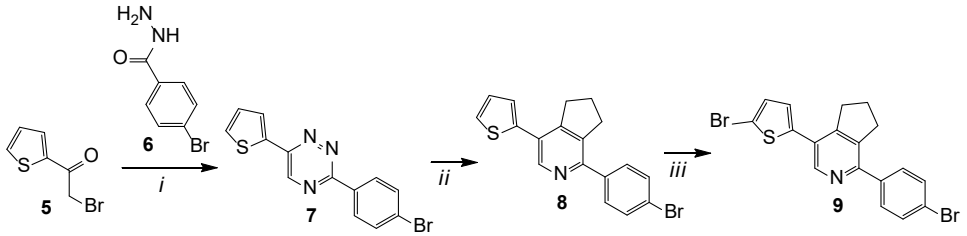
Results and discussion

The "1,2,4-triazine" methodology has been used for the preparation of the target compounds [7–9]. In particular, we used the modified synthetic route previously used for preparation of the luminophores of 2,2'-bipyridine [10] and 2-(2-pyridyl) quinoluine series [11]. Namely, heterocyclization [6] of the corresponding commercially available aldehydes **1a,b** and hydrazone of 4'-bromoisonitrosoacetophenone **2** [11] allowed to obtain the 1,2,4-triazine precursors **3**, which are also of interest as monomers (Scheme 1). The further solvent-free inverse demand Diels-Alder reaction with 1-morpholinocyclopentene [12] allowed to synthesize compounds **4** of 2,2'-bipyridine and 2-(2-pyridyl)quinoluine series.

We have also suggested an approach for obtaining the monomer of monopyridine series. In this case we also used the "1,2,4-triazine" methodology. Namely,



Scheme 1. Reagents and conditions: *i*) 12 h, r.t. / EtOH, then AcOH, 118 °C, 5 min; *ii*) 1-morpholinocyclopentene, 200 °C, neat, 3 h.



Scheme 2. Reagents and conditions: *i*) DMF, 120 °C, 10 h; *ii*) 1-morpholinocyclopentene, 200 °C, neat, 3 h; *iii*) NBS, 50 °C, 8 h.

the condensation of 2-bromoacetylthiophene **5** with two equivalents of hydrazide of 4-bromobenzoic acid **6** allowed to obtain the triazine precursor **7** (Scheme 2). This heterocyclization has been known for a long time [13]. In this case reaction was realized during heating in DMF with no sodium acetate [14, 15]. The further solvent-free inverse demand Diels-Alder reaction [12] with 1-morpholinocyclopentene allowed to obtain the condendes pyridine **8**. For preparation of monomer **9** we used the bromination of thiophene ring of compound **8** at position C5 by *N*-bromosuccinimide in DMF. This reaction is a well-known effective method [16, 17]. For the full conversion of compound **8** to **9** it is necessary the heating reaction mass at 50 °C.

The structure of compounds **4** and **9** was confirmed by data of NMR ^{1}H, mass-spectrometry and elemental analysis. The characteristics of compounds **4** correlate with ones for the previously published similar compounds [10, 11]. For compound **9** there are the signals of protons of thiophene ring as two doublets, protons of cyclopentene fragment, protons of 4-bromophenyl moiety, as well as proton of 6,7-dihydro-5*H*-cyclopenta[*c*]pyridine as singlet.

Conclusions

In conclusion, we have reported herein effective synthetic protocols for the preparation of functionalized (bi)pyridines as potential monomers for the further synthesis of (bi)pyridines-based polymers for different applications.

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