

**Ionic liquid-mediated synthesis of (1*H*-1,2,3-triazol-1-yl)furoxans by
[3+2] cycloaddition of azidofuroxans to acetylenes**

**Leonid L. Fershtat, Salavat S. Ashirbaev, Alexander S. Kulikov, Vadim V. Kachala, and
Nina N. Makhova**

Experimental

All reactions were carried out in well-cleaned oven-dried glassware with magnetic stirring. ¹H and ¹³C NMR spectra were recorded on a Bruker AM-300 (300.13 and 75.47 MHz, respectively) spectrometer and referenced to residual solvent peak. The chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Elemental analyses were performed by the CHN Analyzer Perkin-Elmer 2400. The melting points were determined on a Kofler melting point apparatus and are uncorrected. Analytical TLC was carried out on Merck 25 TLC silica gel 60 F₂₅₄ aluminum sheets. The visualization of the TLC plates was accomplished with a UV light.

High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were done in a positive ion mode (interface capillary voltage – 4500 V) or in a negative ion mode (3200 V); mass range from *m/z* 50 to *m/z* 3000 Da; external or internal calibration was performed with Electrospray Calibrant Solution (Fluka). A syringe injection was used for solutions in acetonitrile, methanol, or water (flow rate 3 μl/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.

4-Azido-3-phenylfuroxan 1a. Yield 1.93 g (95%), mp 94-95 °C (lit.¹⁴ 95 °C). ¹H NMR (CDCl₃, δ, ppm): 7.47-7.50 (m, 3H, Ph), 8.02 (d, 2H, Ph, ³*J* 3.6 Hz). ¹³C NMR (CDCl₃, δ, ppm): 108.62 (C-3 furoxan), 121.30, 126.42, 128.79, 130.71 (C Ph), 152.54 (C-4 furoxan). ¹⁴N NMR (CDCl₃, δ, м.д.): -145.92 (N₃). Found (%): C, 47.33; H, 2.44; N, 34.45. Calc. for C₈H₅N₅O₂ (%): C, 47.30; H, 2.48; N, 34.47.

4-Azido-3-propylfuroxan 1b. Yield 1.50 g (89%). Yellow oil. ¹H NMR (CDCl₃, δ, ppm): 0.94 (t, 3H, CH₃CH₂CH₂, ³J 7.4 Hz), 1.56-1.72 (m, 2H, CH₃CH₂CH₂), 2.41 (t, 2H, CH₃CH₂CH₂, ³J 7.4 Hz). ¹³C NMR (CDCl₃, δ, ppm): 12.73 (CH₃CH₂CH₂), 19.46 (CH₃CH₂CH₂), 24.21 (CH₃CH₂CH₂), 108.14 (C-3 furoxan), 152.67 (C-4 furoxan). ¹⁴N NMR (CDCl₃, δ, m.d.): -145.30 (N₃). Found (%): C, 35.47; H, 4.16; N, 41.43. Calc. for C₅H₇N₅O₂ (%): C, 35.50; H, 4.17; N, 41.41.

4-[4,5-Bis(hydroxymethyl)-1H-1,2,3-triazol-1-yl]-3-phenylfuroxan 4b. Yield 0.118 g (41%), mp 97-99 °C. ¹H NMR (CDCl₃, δ, ppm): 3.88 (br. s, 2H, 2CH₂OH), 4.24 (br. s, 2H, CH₂OH), 4.46 (br. s, 2H, CH₂OH), 7.34-7.42 (m, 5H, Ph). ¹³C NMR (CDCl₃, δ, ppm): 53.26 (CH₂OH), 55.07 (CH₂OH), 111.44 (C-3 furoxan), 120.18, 126.76, 129.02, 131.54 (C Ph), 130.84 (C-4 triazole), 135.72 (C-5 triazole), 150.92 (C-4 furoxan). Found (%): C, 49.80; H, 3.82; N, 24.23. Calc. for C₁₂H₁₁N₅O₄ (%): C, 49.83; H, 3.83; N, 24.21.

4-[4,5-Bis(hydroxymethyl)-1H-1,2,3-triazol-1-yl]-3-propylfuroxan 4d. Yield 0.163 g (64%). Non-distillable oil. ¹H NMR (CDCl₃, δ, ppm): 1.03 (t, 3H, CH₃CH₂CH₂, ³J 7.3 Hz), 1.65-1.72 (m, 2H, CH₃CH₂CH₂), 2.97 (t, 2H, CH₃CH₂CH₂, ³J 7.3 Hz), 3.86 (br. s, 2H, 2CH₂OH), 4.35 (br. s, 2H, CH₂OH), 4.53 (br. s, 2H, CH₂OH). ¹³C NMR (CDCl₃, δ, ppm): 12.97 (CH₃CH₂CH₂), 18.87 (CH₃CH₂CH₂), 24.96 (CH₃CH₂CH₂), 53.14 (CH₂OH), 55.66 (CH₂OH), 111.76 (C-3 furoxan), 130.99 (C-4 triazole), 135.83 (C-5 triazole), 150.54 (C-4 furoxan). HRMS (ESI), *m/z*: 256.1027 [M + H]⁺ (calc. for C₉H₁₃N₅O₄, *m/z*: 256.1041). Found (%): C, 42.32; H, 5.15; N, 27.47. Calc. for C₉H₁₃N₅O₄ (%): C, 42.35; H, 5.13; N, 27.44.

4-[4-(Hydroxymethyl)-1H-1,2,3-triazol-1-yl]-3-phenylfuroxan 4f and *4-[5-(hydroxymethyl)-1H-1,2,3-triazol-1-yl]-3-phenylfuroxan 4'f*. Yield 0.07 g (27%) – mixture of regioisomers, **4f**:**4'f** ratio = 3:1. Compound **4f**. ¹H NMR (CDCl₃, δ, ppm): 3.94 (br. s, 1H, CH₂OH), 4.49 (br. s, 2H, CH₂OH), 7.55 (br. s, 5H, Ph). ¹³C NMR (CDCl₃, δ, ppm): 54.37 (CH₂OH), 111.16 (C-3 furoxan), 120.23, 126.84, 129.26, 131.59 (C Ph), 130.96 (C-4 triazole), 135.82 (C-5 triazole), 151.06 (C-4 furoxan). Compound **4'f**. ¹H NMR (CDCl₃, δ, ppm): 3.79 (br. s, 1H, CH₂OH), 4.27 (br. s, 2H, CH₂OH), 7.32-7.41 (m, 5H, Ph). ¹³C NMR (CDCl₃, δ, ppm): 53.23 (CH₂OH), 110.92 (C-3 furoxan), 119.74, 126.52, 129.02, 131.86 (C Ph), 130.78 (C-4 triazole), 137.71 (C-5 triazole), 150.28 (C-4 furoxan). Found (%): C, 50.99; H, 3.48; N, 26.99. Calc. for C₁₁H₉N₅O₃ (%): C, 50.97; H, 3.50; N, 27.02.

4-[4-(Acetyl)-1H-1,2,3-triazol-1-yl]-3-phenylfuroxan **4g** and 4-[5-(acetyl)-1H-1,2,3-triazol-1-yl]-3-phenylfuroxan **4'g**. Yield 0.071 g (26%) – mixture of regioisomers, **4g:4'g** ratio = 6:1. Compound **4g**. ¹H NMR (CDCl₃, δ, ppm): 2.77 (s, 3H, COCH₃), 7.51 (br. s, 5H, Ph), 8.64 (s, 1H, CH triazole). ¹³C NMR (CDCl₃, δ, ppm): 29.51 (COCH₃), 110.63 (C-3 furoxan), 120.12, 127.97, 129.10, 131.09 (C Ph), 130.91 (C-4 triazole), 134.33 (C-5 triazole), 148.93 (C-4 furoxan), 191.52 (COCH₃). Compound **4'g**. ¹H NMR (CDCl₃, δ, ppm): 2.51 (s, 3H, COCH₃), 7.36-7.42 (m, 5H, Ph), 8.32 (s, 1H, CH triazole). ¹³C NMR (CDCl₃, δ, ppm): 28.16 (COCH₃), 109.84 (C-3 furoxan), 125.97, 126.83, 128.81, 130.05 (C Ph), 132.07 (C-4 triazole), 136.95 (C-5 triazole), 149.46 (C-4 furoxan), 189.62 (COCH₃). Found (%): C, 53.12; H, 3.33; N, 25.84. Calc. for C₁₂H₉N₅O₃ (%): C, 53.14; H, 3.34; N, 25.82.

3-Phenyl-4-[4-phenyl-1H-1,2,3-triazol-1-yl]furoxan **4h** and 3-phenyl-4-[5-phenyl-1H-1,2,3-triazol-1-yl]furoxan **4'h**. Yield 0.125 g (41%) – mixture of regioisomers, **4h:4'h** ratio = 4:1. Compound **4h**. ¹H NMR (CDCl₃, δ, ppm): 7.30-7.52 (m, 10H, 2C₆H₅), 8.33 (s, 1H, CH triazole). ¹³C NMR (CDCl₃, δ, ppm): 110.53 (C-3 furoxan), 119.98, 124.09, 126.47, 128.73, 129.08, 129.26, 129.84, 130.55 (C Ph), 134.13 (C-4 triazole), 138.51 (C-5 triazole), 151.16 (C-4 furoxan). Compound **4'h**. ¹H NMR (CDCl₃, δ, ppm): 7.14-7.19 (m, 2H, Ph), 7.30-7.42 (m, 8H, H-3,4,5 Ph, C₆H₅), 7.94 (s, 1H, CH triazole). ¹³C NMR (CDCl₃, δ, ppm): 111.06 (C-3 furoxan), 119.98, 124.09, 126.47, 128.73, 129.08, 129.26, 129.84, 130.55 (C Ph), 132.80 (C-4 triazole), 140.43 (C-5 triazole), 148.93 (C-4 furoxan). Found (%): C, 62.93; H, 3.64; N, 22.95. Calc. for C₁₆H₁₁N₅O₂ (%): C, 62.95; H, 3.63; N, 22.94.

4-[4-(Hydroxymethyl)-1H-1,2,3-triazol-1-yl]-3-propylfuroxan **4j** and 4-[5-(hydroxymethyl)-1H-1,2,3-triazol-1-yl]-3-propylfuroxan **4'j**. Yield 0.054 g (24%) – mixture of regioisomers, **4j:4'j** ratio = 5:1. Compound **4j**. ¹H NMR (CDCl₃, δ, ppm): 1.08 (t, 3H, CH₃CH₂CH₂, ³J 7.4 Hz), 1.62-1.73 (m, 2H, CH₃CH₂CH₂), 2.97 (t, 2H, CH₃CH₂CH₂, ³J 7.4 Hz), 3.92 (br. s, 1H, CH₂OH), 4.56 (br. s, 2H, CH₂OH). ¹³C NMR (CDCl₃, δ, ppm): 12.88 (CH₃CH₂CH₂), 18.93 (CH₃CH₂CH₂), 24.75 (CH₃CH₂CH₂), 54.62 (CH₂OH), 110.87 (C-3 furoxan), 130.86 (C-4 triazole), 135.74 (C-5 triazole), 150.93 (C-4 furoxan). Compound **4'j**. ¹H NMR (CDCl₃, δ, ppm): 0.96 (t, 3H, CH₃CH₂CH₂, ³J 7.5 Hz), 1.42-1.48 (m, 2H, CH₃CH₂CH₂), 3.03 (t, 2H, CH₃CH₂CH₂, ³J 7.5 Hz), 3.81 (br. s, 1H, CH₂OH), 4.31 (br. s, 2H, CH₂OH). ¹³C NMR (CDCl₃, δ, ppm): 13.08 (CH₃CH₂CH₂), 19.26 (CH₃CH₂CH₂), 24.99 (CH₃CH₂CH₂), 53.22 (CH₂OH), 111.26 (C-3 furoxan), 131.24 (C-4 triazole), 137.90 (C-5 triazole), 149.35 (C-4 furoxan). Found (%): C, 42.68; H, 4.89; N, 31.07. Calc. for C₈H₁₁N₅O₃ (%): C, 42.67; H, 4.92; N, 31.10.

4-[4-(Acetyl)-1H-1,2,3-triazol-1-yl]-3-propylfuroxan **4k** and 4-[5-(acetyl)-1H-1,2,3-triazol-1-yl]-3-propylfuroxan **4'k**. Yield 0.135 g (57%) – mixture of regioisomers, **4k:4'k** ratio = 3.5:1. Compound **4k**. ¹H NMR (CDCl₃, δ, ppm): 1.02 (t, 3H, CH₃CH₂CH₂, ³J 7.4 Hz), 1.64-1.79 (m, 2H, CH₃CH₂CH₂), 2.76 (s, 3H, COCH₃), 2.93 (t, 2H, CH₃CH₂CH₂, ³J 7.4 Hz), 8.81 (s, 1H, CH triazole). ¹³C NMR (CDCl₃, δ, ppm): 13.15 (CH₃CH₂CH₂), 18.99 (CH₃CH₂CH₂), 24.90 (CH₃CH₂CH₂), 27.31 (COCH₃), 111.03 (C-3 furoxan), 125.50 (C-4 triazole), 136.92 (C-5 triazole), 147.74 (C-4 furoxan), 191.21 (COCH₃). Compound **4'k**. ¹H NMR (CDCl₃, δ, ppm): 0.84 (t, 3H, CH₃CH₂CH₂, ³J 7.3 Hz), 1.41-1.52 (m, 2H, CH₃CH₂CH₂), 2.65 (s, 3H, COCH₃), 3.06-3.16 (m, 2H, CH₃CH₂CH₂), 8.31 (s, 1H, CH triazole). ¹³C NMR (CDCl₃, δ, ppm): 13.27 (CH₃CH₂CH₂), 20.34 (CH₃CH₂CH₂), 25.77 (CH₃CH₂CH₂), 28.43 (COCH₃), 109.71 (C-3 furoxan), 124.05 (C-4 triazole), 135.12 (C-5 triazole), 150.26 (C-4 furoxan), 190.63 (COCH₃). Found (%): C, 45.54; H, 4.70; N, 29.49. Calc. for C₉H₁₁N₅O₃ (%): C, 45.57; H, 4.67; N, 29.52.

3-Propyl-4-[4-phenyl-1H-1,2,3-triazol-1-yl]furoxan **4l** and 3-propyl-4-[5-phenyl-1H-1,2,3-triazol-1-yl]furoxan **4'l**. Yield 0.133 g (49%) – mixture of regioisomers, **4l:4'l** ratio = 5:1. Compound **4l**. ¹H NMR (CDCl₃, δ, ppm): 0.88 (t, 3H, CH₃CH₂CH₂, ³J 7.3 Hz), 1.44-1.54 (m, 2H, CH₃CH₂CH₂), 2.54 (t, 2H, CH₃CH₂CH₂, ³J 7.3 Hz), 7.40-7.57 (m, 5H, Ph), 8.53 (s, 1H, CH triazole). ¹³C NMR (CDCl₃, δ, ppm): 13.25 (CH₃CH₂CH₂), 18.41 (CH₃CH₂CH₂), 24.11 (CH₃CH₂CH₂), 110.85 (C-3 furoxan), 117.49, 126.02, 128.99, 129.89 (C Ph), 129.98 (C-4 triazole), 133.18 (C-5 triazole), 150.06 (C-4 furoxan). Compound **4'l**. ¹H NMR (CDCl₃, δ, ppm): 1.03 (t, 3H, CH₃CH₂CH₂, ³J 7.4 Hz), 1.66-1.76 (m, 2H, CH₃CH₂CH₂), 3.02 (t, 2H, CH₃CH₂CH₂, ³J 7.4 Hz), 7.40-7.57 (m, 5H, Ph), 7.94 (s, 1H, CH triazole). ¹³C NMR (CDCl₃, δ, ppm): 13.38 (CH₃CH₂CH₂), 19.12 (CH₃CH₂CH₂), 25.17 (CH₃CH₂CH₂), 111.24 (C-3 furoxan), 125.84, 127.46, 128.62, 129.21 (C Ph), 130.40 (C-4 triazole), 137.23 (C-5 triazole), 149.54 (C-4 furoxan). Found (%): C, 57.58; H, 4.81; N, 25.79. Calc. for C₁₃H₁₃N₅O₂ (%): C, 57.56; H, 4.83; N, 25.82.