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Synthesis of N-Substituted Methyl 4*H*-Thieno[3,2-*b*]pyrrole-5-carboxylates

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Abstract—The alkylation of methyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate with methyl iodide and allyl, propargyl, and benzyl bromides in the presence of sodium hydride in THF afforded the corresponding N-substituted derivatives. Some reactions of the alkylation products were studied.

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Derivatives of methyl and ethyl 4*H*-thieno[3,2-*b*]-pyrrole-5-carboxylates [1, 2] can be used for the synthesis of biologically active compounds of the thienopyrrole series [3–8]; they also provide basic scaffolds for the construction of π-conjugated fused systems for optoelectronics [9–12].

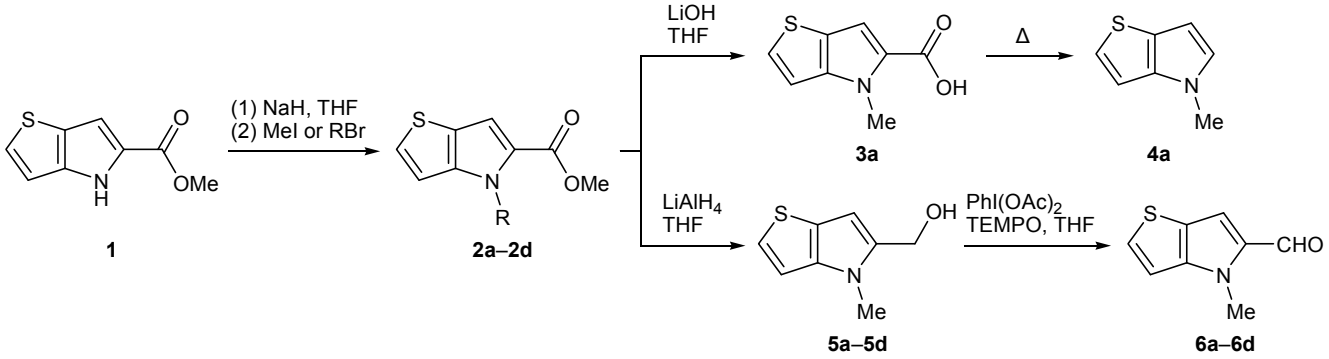
By alkylation of ester **1** with methyl iodide and allyl, propargyl, and benzyl bromides we obtained compounds **2a**–**2d** with the goal of studying their chemical properties and converting to simpler monomers or more complex cross-conjugated structures.

The hydrolysis of ester **2a** in aqueous alkali gave carboxylic acid **3a** with a high yield. Decarboxylation of **3a** afforded monomer **4a** which was intended for further polymerization. The reduction of **2a**–**2d** with $LiAlH_4$ in THF gave alcohols **5a**–**5d** which were oxidized with (diacetoxy-λ^3-iodanyl)benzene in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) [13]; as a result, aldehydes **6a**–**6d** were isolated in good yields (Scheme 1).

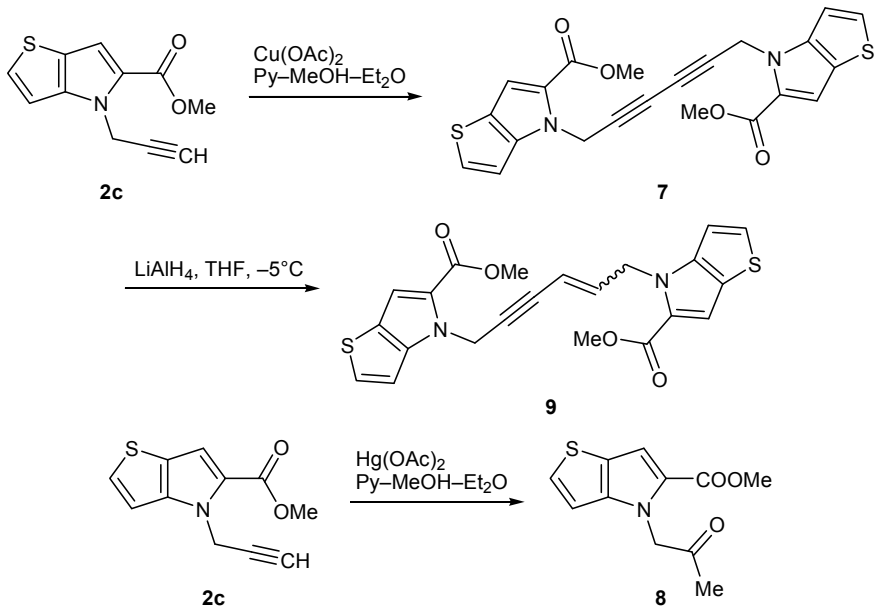
Using *N*-propargyl derivative **2c** we obtained dimeric structures. The Glaser coupling [14] of **2c** led to the formation of dimer **7** in a moderate yield. Attempts to improve the yield of dimer **7** by using $Hg(OAc)_2$ [15] instead of $Cu(OAc)_2$ resulted in the formation of hydration product **8**. Enyne **9** was synthesized by the reduction of diacetylenic compound **7** under mild conditions (Scheme 2).

Esters **2** and their derivatives are planned to use as initial compounds for the synthesis of other structures.

Scheme 1.



Scheme 2.



EXPERIMENTAL

The IR spectra were recorded on a Shimadzu Prestige-21 IR spectrometer from samples prepared as thin films. The ^{1}H and ^{13}C NMR spectra were measured on Bruker AM-300 (300.13 and 75.47 MHz, respectively) and Bruker Avance-500 spectrometers (500.13 and 125.77 MHz) using tetramethylsilane as internal standard. The mass spectra were obtained using Thermo Finnigan MAT 95XP (electron impact, 70 eV; ion source temperature 200°C; sample injection temperature 5–270°C, heating rate 22 deg/min) and Shimadzu LCMS-2010EV instruments (samples were dissolved in chloroform–acetonitrile and introduced with a syringe; eluent acetonitrile–water, 95:5; flow rate 0.1 mL/min; positive ion detection, needle electrode voltage 4.5 kV, capillary voltage 5 V, capillary temperature 250°C). The elemental compositions were determined with a Euro EA-2000 CHN analyzer. The progress of reactions was monitored by TLC on Sorbfil plates (Russia); spots were detected by treatment with a solution of 4-methoxybenzaldehyde in ethanol acidified with sulfuric acid, followed by heating at 120–150°C. The products were isolated by column chromatography on silica gel using 30–60 g of the sorbent per gram of substrate.

Methyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (1) was synthesized according to [1, 2]; its spectral parameters coincided with those given therein.

Methyl 4-methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (2a). A solution of 0.20 g (1.10 mmol) of methyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (**1**) in 2 mL of THF was added dropwise with stirring under argon to a suspension of 55.0 mg (2.29 mmol) of sodium hydride (a 55% suspension of NaH in mineral oil was preliminarily washed with anhydrous hexane) in 10 mL of anhydrous THF. The mixture was stirred for 15 min, 0.14 mL (2.19 mmol) of methyl iodide was added dropwise, and the mixture was stirred on heating until initial compound **1** disappeared (TLC). The mixture was cooled to room temperature, treated with a saturated aqueous solution of ammonium chloride, and extracted with methylene chloride (3×20 mL). The extract was evaporated, and the residue was purified by silica gel column chromatography using petroleum ether–ethyl acetate (5:1) as eluent. Yield 0.14 g (65%), light yellow crystals, mp 62–63°C. IR spectrum, ν, cm^{-1}: 1710, 1695, 1532, 1464, 1445, 1378, 1369, 1235, 1209, 1179, 1095, 1075, 962, 728. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz), δ, ppm: 3.86 s (3H, OCH_3), 4.06 s (3H, NCH_3), 6.95 d (1H, 3-H, J = 5.4 Hz), 7.18 s (1H, 6-H), 7.34 d (1H, 2-H, J = 5.4 Hz). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δ_C, ppm: 51.27 (NCH_3, OCH_3), 109.00 (C^6), 110.04 (C^3), 114.83 (C^{6a}), 121.90 (C^5), 129.13 (C^2), 138.00 (C^{3a}), 164.60 (C=O).

Compounds **2b**–**2d** were synthesized in a similar way.

Methyl 4-(prop-2-en-1-yl)-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (2b) was synthesized from 0.06 g (0.33 mmol) of compound **1** and 79.9 mg (0.66 mmol) of allyl bromide using 9.5 mg (0.39 mmol) of NaH and

6 mg of Bu_4NI as phase-transfer catalyst. After appropriate treatment and chromatographic purification (SiO_2, petroleum ether–ethyl acetate, 5:1), we isolated 0.7 g (95%) of **2b** as oily material. IR spectrum, ν, cm^{-1}: 2948, 1703, 1699, 1532, 1464, 1441, 1395, 1303, 1256, 1216, 1175, 1103, 759, 719. ^1H NMR spectrum ($CDCl_3$, 500 MHz), δ, ppm: 3.86 s (3H, OMe), 4.98 d.d (1H, $=CH_2$, J = 17.1, 1.1 Hz), 5.13 d.d (1H, $=CH_2$, J = 16.6, 1.2 Hz), 5.14–5.16 m (2H, NCH_2), 6.01 q.d.q (1H, =CH, J = 5.3, 5.1, 17.0 Hz), 6.92 d (1H, 3-H, J = 5.5 Hz), 7.21 s (1H, 6-H), 7.33 d (1H, 2-H, J = 5.3 Hz). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δ_C, ppm: 49.38 (NCH_2), 51.31 (OMe), 109.51 (C^6), 110.44 ($=CH_2$), 116.34 (C^3), 122.24 (C^{6a}), 125.86 (C^5), 129.32 (C^2), 133.95 (=CH), 145.14 (C^{3a}), 161.92 (C=O). Found: m/z 221.0505 $[M]^+$. $C_{11}H_{11}NO_2S$. Calculated: M 221.0510.

Methyl 4-(prop-2-yn-1-yl)-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (2c) was synthesized from 0.37 g (2.04 mmol) of compound **1** and 0.45 mL (4.10 mmol) of a 80% solution of propargyl bromide in toluene. Yield 0.42 g (94%), bright yellow crystals, mp 83–86°C. IR spectrum, ν, cm^{-1}: 3106, 3265, 2953, 1692, 1534, 1492, 1464, 1438, 1394, 1377, 1306, 1261, 1220, 1181, 1171, 1111, 776, 732, 659. ^1H NMR spectrum ($CDCl_3$, 500 MHz), δ, ppm: 2.32 t (1H, ≡CH, J = 2.3 Hz), 3.88 s (3H, OMe), 5.38 d (2H, CH_2, J = 2.4 Hz), 7.09 d (1H, 3-H, J = 5.2 Hz), 7.22 s (1H, 6-H), 7.38 d (1H, 2-H, J = 5.2 Hz). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δC, ppm: 36.13 (NCH_2), 51.46 (OMe), 72.52 (≡CH), 78.41 (≡C), 110.10 (C^6), 110.54 (C^3), 122.60 (C^{6a}), 125.47 (C^5), 129.73 (C^2), 144.60 (C^{3a}), 163.0 (C=O). Found: m/z 219.0349 $[M]^+$. $C_{11}H_9NO_2S$. Calculated: M 219.0354.

Methyl 4-benzyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (2d) was synthesized from 0.06 g (0.33 mmol) of compound **1** and 0.084 g (0.66 mmol) of benzyl bromide. Yield 82 mg (92%), yellowish crystals, mp 81–83°C. IR spectrum, ν, cm^{-1}: 2950, 1703, 1532, 1490, 1464, 1441, 1395, 1303, 1257, 1216, 1175, 1103, 1085, 991, 918, 781, 759, 719, 666. ^1H NMR spectrum ($CDCl_3$, 500 MHz), δ, ppm: 3.83 s (3H, OMe), 5.76 s (1H, NCH_2), 6.86 d (1H, 3-H, J = 5.4 Hz), 7.13 d (2H, Ph, J = 7.4 Hz), 7.25 s (1H, 6-H), 7.23–7.28 m (3H, Ph), 7.32 d (1H, 2-H, J = 5.7 Hz). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δ_C, ppm: 50.39 (NCH_2), 51.28 (OMe), 109.78 (C^6), 110.58 (C^3), 122.39 (C^{6a}), 126.09 (C^5), 126.65 (C_{arom}), 127.34 (C_{arom}), 128.56 (C_{arom}), 129.44 (C^2), 137.94 (C_{arom}), 145.43 (C^{3a}), 161.90 (C=O). Found: m/z 271.0662 $[M]^+$. $C_{15}H_{13}NO_2S$. Calculated: M 271.0667.

4-Methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylic acid (3a). mp 172–174°C; published data [16]: mp 154°C. IR spectrum, ν, cm^{-1}: 3445, 3094, 3080, 272, 2655, 2593, 1657, 1545, 1493, 1417, 1366, 1249, 1176, 1080, 908, 717. ^1H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 4.04 s (3H, NCH_3), 7.05 d (1H, 3-H, J = 5.1 Hz), 7.16 s (1H, 6-H), 7.42 d (1H, 2-H, J = 5.3 Hz). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δ_C, ppm: 33.37 (NCH_3), 108.73 (C^6), 109.81 (C^3), 121.47 (C^{6a}), 126.75 (C^5), 128.66 (C^2), 134.80 (C^{3a}), 163.31 (C=O). Mass spectrum, m/z (I_{rel}, %): 180 $[M - H]^+$ (100), 221 $[M - H + MeCN]^+$ (26). $C_8H_7NO_2S$. Calculated: M 181.0197.

4-(Prop-2-en-1-yl)-4*H*-thieno[3,2-*b*]pyrrol-5-ylmethanol (5b). A solution of 60 mg (0.27 mmol) of compound **2b** in 5 mL of anhydrous THF was added dropwise with stirring under argon to a suspension of 12 mg (0.32 mmol) of $LiAlH_4$ in 10 mL of anhydrous THF. The mixture was stirred until the initial compound disappeared (TLC) and treated with a solution of ammonium chloride. Tetrahydrofuran was distilled off, and the residue was extracted with methylene chloride (3×10 mL). The combined extracts were washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography on silica gel using petroleum ether–ethyl acetate (5:1) as eluent. Yield 38 mg (72%), oily material. IR spectrum, ν, cm^{-1}: 2948, 1703, 1699, 1532, 1464, 1441, 1395, 1303, 1256, 1216, 1175, 1103, 759, 719. ^1H NMR spectrum ($CDCl_3$, 500 MHz), δ, ppm: 1.82 br.s (1H, OH), 4.65 s (2H, OCH_2), 4.75 d (2H, NCH_2, J = 4.8 Hz), 4.99 d (1H, $=CH_2$, J = 17.1 Hz), 5.16 d (1H, $=CH_2$, J = 10.1 Hz), 5.99 d.d.d (1H, =CH, J = 5.1, 10.2, 5.3 Hz), 6.38 s (1H, 6-H), 6.89 d (1H, 3-H, J = 5.1 Hz), 7.09 d (1H, 2-H, J = 5.3 Hz). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ_C, ppm: 48.04 (NCH_2), 57.51 (OCH_2), 101.17 (C^6), 110.46 ($=CH_2$), 116.57 (C^3), 121.94 (C^{6a}), 122.01 (C^5), 123.78 (C^2), 134.06 (=CH), 141.47 (C^{3a}). Found, %: C 62.48; H 5.49; N 7.46; S 16.98. $C_{10}H_{11}NOS$. Calculated, %: C 62.15; H 5.74; N 7.25; S 16.59.

Compounds **5a**, **5c**, and **5d** were synthesized in a similar way.

4-Methyl-4*H*-thieno[3,2-*b*]pyrrol-5-ylmethanol (5a) was synthesized from 70 mg (0.36 mmol) of compound **2a** using 40.0 mg (1.05 mmol) of $LiAlH_4$. Yield 38 mg (63%), mp 71–73°C. IR spectrum, ν, cm^{-1}: 3527, 3230, 2727, 1530, 1377, 1366, 1337, 1295, 1241, 1135, 1078, 987, 975, 823, 763, 713, 654. ^1H NMR spectrum (acetone-d_6, 300 MHz), δ, ppm: 2.86 s (1H, OH), 3.79 s (3H, NCH_3), 4.64 d (2H,

OCH_2, J = 5.5 Hz), 6.27 s (1H, 6-H), 7.02 d (1H, 3-H, J = 5.3 Hz), 7.11 d (1H, 2-H, J = 5.2 Hz). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δ_C, ppm: 31.28 (NCH_3), 56.29 (OCH_2), 99.58 (C^6), 110.23 (C^3), 120.70 (C^{6a}), 121.30 (C^5), 122.18 (C^2), 138.36 (C^{3a}). Mass spectrum, m/z (I_{rel}, %): 168 $[M + H]^+$ (10), 150 $[M - OH]^+$ (100). C_8H_9NOS. Calculated: M 167.0405.

4-(Prop-2-yn-1-yl)-4*H*-thieno[3,2-*b*]pyrrol-5-ylmethanol (5c) was synthesized by the reduction of 60 mg (0.27 mmol) of compound **2c** with 12.4 mg (0.33 mmol) of $LiAlH_4$ in THF. Yield 42 mg (81%), light yellow crystals, mp 66–68°C. IR spectrum, ν, cm^{-1}: 3312, 3270, 3203, 2950, 1462, 1400, 1438, 1377, 1364, 1330, 1295, 1013, 782, 721, 682, 655. ^1H NMR spectrum (acetone-d_6, 500 MHz), δ, ppm: 2.79 s (1H, OH), 2.87 t (1H, ≡CH, J = 2.3 Hz), 4.73 s (2H, OCH_2), 5.06 d (2H, CH_2, J = 2.3 Hz), 6.33 s (1H, 6-H), 7.12 d (1H, 3-H, J = 5.3 Hz), 7.15 d (2H, 2-H, J = 5.3 Hz). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δ_C, ppm: 34.40 (CH_2), 56.38 (OCH_2), 73.08 (≡CH), 78.91 (≡C), 100.47 (C^6), 110.72 (C^3), 122.10 (C^{6a}), 122.77 (C^2), 125.86 (C^5), 144.10 (C^{3a}). Found, %: C 62.46; H 4.49; N 7.46; S 16.49. $C_{10}H_9NOS$. Calculated, %: C 62.80; H 4.74; N 7.32; S 16.77.

4-Benzyl-4*H*-thieno[3,2-*b*]pyrrol-5-ylmethanol (5d) was synthesized from 60 mg (0.22 mmol) of compound **2d** using 10.0 mg (0.27 mmol) of $LiAlH_4$. Yield 34 mg (64%), oily material. ^1H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 2.17 s (1H, OH), 4.65 s (2H, OCH_2), 5.39 s (1H, NCH_2), 6.45 s (1H, 6-H), 6.78 d (1H, 3-H, J = 5.3 Hz), 7.06 d (1H, 2-H, J = 5.2 Hz), 7.09 d (2H, Ph, J = 7.1 Hz), 7.23–7.29 m (3H, Ph). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δ_C, ppm: 49.24 (CH_2), 57.68 (OCH_2), 101.56 (C^6), 110.50 (C^3), 122.60 (C^{6a}), 123.93 (C^2), 126.10 (C^5), 126.44 (C_{arom}), 127.56 (C_{arom}), 128.80 (C_{arom}), 136.98 (C_{arom}), 137.70 (C^{3a}). Mass spectrum, m/z (I_{rel}, %): 244 $[M + H]^+$ (5), 226 $[M - OH]^+$ (100). Found, %: C 69.10; H 5.39; N 5.76; S 13.18. $C_{10}H_9NOS$. Calculated, %: C 68.89; H 5.47; N 5.44; S 13.44.

4-Methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carbaldehyde (6a). Alcohol **5a**, 30.0 mg (0.18 mmol), was dissolved in 5 mL of methylene chloride, 87.10 mg (0.27 mmol) of $PhI(OAc)_2$ and 0.3 mg (0.003 mmol) of TEMPO were added in one portion under argon, and the mixture was stirred at room temperature until initial compound **5a** disappeared (~3 h; TLC). The solvent was evaporated, and the residue was purified by column chromatography on silica gel using ethyl acetate–petroleum ether (1:5) as eluent. Yield 20 mg (68%), oily material. IR spectrum, ν, cm^{-1}: 1662, 1539, 1472, 1382, 1291, 1154, 1135, 1085, 846, 835, 763, 726, 669, 601. ^1H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 4.09 s (3H, CH_3), 6.96 d (1H, 3-H, J = 5.4 Hz), 7.10 s (1H, 6-H), 7.48 d (1H, 2-H, J = 5.4 Hz), 9.64 s (1H, CHO). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δ_C, ppm: 34.47 (NCH_3), 109.82 (C^6), 115.39 (C^3), 123.15 (C^{6a}), 132.33 (C^2), 136.10 (C^{3a}), 147.82 (C^5), 180.69 (CHO). Mass spectrum, m/z (I_{rel}, %): 166 $[M + H]^+$ (56), 183 $[M + H + H_2O]^+$ (17), 207 $[M + H + MeCN]^+$ (50). C_8H_7NOS. Calculated: M 165.0248.

Compounds **6b**–**6d** were synthesized in a similar way.

4-(Prop-2-en-1-yl)-4*H*-thieno[3,2-*b*]pyrrole-5-carbaldehyde (6b) was synthesized by oxidation of 60 mg (0.31 mmol) of compound **5b** with 0.15 g (0.47 mmol) of $PhI(OAc)_2$ in the presence of a catalytic amount of TEMPO. The product was purified by column chromatography on silica gel using ethyl acetate–petroleum ether (1:5) as eluent. Yield 0.048 g (82%), oily material. IR spectrum, ν, cm^{-1}: 2924, 2850, 1730, 1652, 1648, 1533, 1472, 1409, 1388, 1298, 831, 726. ^1H NMR spectrum ($CDCl_3$, 500 MHz), δ, ppm: 5.02 d (1H, $=CH_2$, J = 17.1 Hz), 5.15–5.16 m (1H, $=CH_2$), 5.17 d (2H, NCH_2, J = 4.9 Hz), 5.97–6.10 m (1H, =CH), 6.94 d (1H, 3-H, J = 5.4 Hz), 7.13 s (1H, 6-H), 7.46 d (1H, 2-H, J = 5.4 Hz), 9.63 s (1H, CHO). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ_C, ppm: 49.43 (NCH_2), 110.29 (C^6), 115.84 (C^3), 116.81 ($=CH_2$), 123.65 (C^{6a}), 132.35 (=CH), 133.48 (C^2), 135.54 (C^{3a}), 150.52 (C^5), 180.36 (CHO). Found: m/z 191.0399 $[M]^+$. $C_{10}H_9NOS$. Calculated: M 191.0405.

4-(Prop-2-yn-1-yl)-4*H*-thieno[3,2-*b*]pyrrole-5-carbaldehyde (6c) was synthesized by oxidation of 60 mg (0.31 mmol) of compound **5c** with 0.15 g (0.47 mmol) of $PhI(OAc)_2$ in the presence of a catalytic amount of TEMPO. Yield 46 mg (78%), light yellow crystals, mp 60–62°C. IR spectrum, ν, cm^{-1}: 3215, 3102, 2828, 2798, 2112, 1651, 1534, 1467, 1387, 1337, 1295, 1248, 1188, 1134, 1055, 968, 776, 728, 675, 601. ^1H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 2.35 s (1H, ≡CH), 5.41 d (2H, CH_2, J = 7.3 Hz), 7.12 d (1H, 3-H, J = 5.8 Hz), 7.13 s (1H, 6-H), 7.51 d (1H, 2-H, J = 5.4 Hz), 9.63 s (1H, CHO). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δ_C, ppm: 36.19 (CH_2), 73.09 (≡CH), 76.99 (≡C), 110.55 (C^6), 116.47 (C^3), 124.60 (C^{6a}), 127.40 (C^5), 132.77 (C^2), 146.80 (C^{3a}), 180.56 (CHO). Found: m/z 189.0243 $[M]^+$. $C_{10}H_7NOS$. Calculated: M 189.0248.

4-Benzyl-4*H*-thieno[3,2-*b*]pyrrole-5-carbaldehyde (6d) was synthesized by oxidation of 0.034 g (0.14 mmol) of crude alcohol **5d** with 68.7 mg

(0.21 mmol) of $PhI(OAc)_2$ in the presence of 0.25 mg (0.0015 mmol) of TEMPO. The product was purified by column chromatography on silica gel using ethyl acetate–petroleum ether (1:5) as eluent. Yield 23.3 mg (68%), oily material. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz), δ, ppm: 4.86 s (2H, OCH_2), 6.54 d (1H, 6-H, J = 5.0 Hz), 7.28–7.38 m (6H, 3-H, Ph), 7.43 d (1H, 2-H, J = 5.5 Hz), 7.89 d (1H, CHO, J = 5.0 Hz). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δ_C, ppm: 45.69 (CH_2), 105.10 (C^6), 113.55 (C^3), 124.60 (C^{6a}), 127.0 (C^5), 127.71 (C_{arom}), 128.36 (C_{arom}), 128.58 (C_{arom}), 129.10 (C^2), 134.50 (C_{arom}), 143.76 (C^{3a}), 161.50 (CO_2Me). Found, %: C 69.29; H 4.36; N 5.68; S 13.66. $C_{14}H_{11}NOS$. Calculated, %: C 69.68; H 4.59; N 5.80; S 13.29.

Dimethyl 4,4′-(hexa-2,4-diyne-1,6-diyl)bis(4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate) (7). Compound **2c**, 40 mg (0.18 mmol), was dissolved in 10 mL of a 1:1:3 pyridine–methanol–diethyl ether mixture, 8 mg of copper(II) acetate was added, and the mixture was refluxed for 2 h with stirring. The mixture was cooled, acidified with 5% aqueous HCl, and extracted with methylene chloride (3 × 5 mL). The combined extracts were dried over $MgSO_4$ and evaporated, and the residue was purified by column chromatography on silica gel using petroleum ether–ethyl acetate (first 5:1 and then 2:1) as eluent. Yield 15 mg (38%), colorless crystals, mp 182–184°C. IR spectrum, ν, cm^{-1}: 3306, 3210, 1712, 1688, 1465, 1436, 1391, 1377, 1342, 1303, 1259, 1253, 1211, 1173, 1105, 714. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz), δ, ppm: 3.85 s (6H, OCH_3), 5.42 s (4H, CH_2), 7.00 d (2H, 3-H, 3′-H, J = 5.5 Hz), 7.18 s and 7.26 s (2H, 6-H, 6′-H), 7.36 d (1H, 2-H, 2′-H, J = 5.4 Hz). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δ_C, ppm: 36.68 (CH_2), 51.46 (OMe), 68.36, 73.60 (C≡C), 110.35 (C^6), 110.26 (C^3), 122.85 (C^{6a}), 125.41 (C^5), 129.93 (C^2), 144.69 (C^{3a}), 161.83 (CO_2Me). Mass spectrum, m/z (I_{rel}, %): 437 $[M + H]^+$ (100), 405 $[M - OCH_3]^+$. $C_{22}H_{18}N_2O_4S_2$. Calculated: M 436.0551.

Dimethyl 4,4′-(hex-2-en-4-yne-1,6-diyl)bis(4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate) (9). A solution of 100 mg (0.25 mmol) of dimer **7** in 5 mL of anhydrous THF was added dropwise with stirring under argon to a suspension of 60 mg (1.01 mmol) of $LiAlH_4$ in 20 mL of anhydrous THF cooled to –5°C. The mixture was stirred until initial compound **7** disappeared (TLC) and was then treated as described above for the synthesis of **7**. The product was purified by column chromatography on silica gel using petroleum ether–ethyl acetate (5:1) as eluent. Yield 50 mg (50%), white crystals, mp 122–124°C. IR spectrum, ν, cm^{-1}: 3101, 3085, 2722, 1709, 1490, 1436, 1377, 1339, 1303, 1259, 1209, 1174, 1107, 1085, 1057, 1042, 971, 937, 823, 773, 757, 721, 664. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz), δ, ppm: 3.84 s (3H, OCH_3), 3.86 s (3H, OCH_3), 5.28 d (2H, CH_2, J = 6.8 Hz), 5.59 s (2H, CH_2), 5.61 d (1H, =CH, J = 1.6 Hz), 6.05–6.10 m (1H, =CH), 6.68 d (1H, 3-H, J = 5.4 Hz), 7.11 d (1H, 3′-H, J = 5.3 Hz), 7.14 d (1H, 2-H, J = 5.3 Hz), 7.14 s and 7.24 s (1H each, 6-H, 6′-H), 7.38 d (1H, 2′-H, J = 5.3 Hz). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δ_C, ppm: 37.07 and 46.27 (NCH_2), 51.34 and 51.50 (OMe), 80.00 and 90.03 (C≡C), 109.60 (C^6), 110.21 ($C^{6'}$), 110.48 (C^3), 110.80 ($C^{3'}$), 110.86 (=CH), 122.20 (C^{6a}), 122.86 ($C^{6a'}$), 125.53 (C^5), 125.57 ($C^{5'}$), 129.22 (C^2), 129.95 ($C^{2'}$), 138.93 (=C), 144.86 (C^{3a}), 145.08 ($C^{3a'}$), 161.95 and 162.01 (C=O). Mass spectrum, m/z (I_{rel}, %): 439 $[M + H]^+$ (10), 407 $[M - OCH_3]^+$ (4), 391 (100), 281 (10). $C_{22}Hz_{20}N_2O_4S_2$. Calculated: M 438.0708.

Methyl 4-(2-oxopropyl)-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (8). A solution of 0.07 g (0.23 mmol) of compound **2c** and 0.11 g (0.34 mmol) of $Hg(OAc)_2$ in 5 mL of methanol was refluxed for 1 h with stirring. The resulting orange–red solution was cooled to 0°C, 20 mL of methylene chloride, 0.5 mL of a 1 M solution of sodium hydroxide, and 21.0 mg (0.58 mmol) of $NaBH_4$ were added, and the mixture was stirred for 1 h. Excess $NaBH_4$ was decomposed with 3 mL of water, and the aqueous phase was extracted with methylene chloride (3 × 10 mL). The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and evaporated, and the residue was purified by column chromatography on silica gel using petroleum ether–ethyl acetate (1:1) as eluent. Yield 60 mg (79%). IR spectrum, ν, cm^{-1}: 2880, 2820, 1729, 1699, 1491, 1469, 1441, 1398, 1376, 1347, 1304, 1256, 1234, 1189, 1174, 1116, 723. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz), δ, ppm: 2.19 s (3H, CH_3CO), 3.83 s (3H, OMe), 5.21 s (2H, CH_2), 6.83 d (1H, 3-H, J = 5.4 Hz), 7.25 s (1H, 6-H), 7.36 d (1H, 2-H, J = 5.4 Hz). ^{13}C NMR spectrum ($CDCl_3$, 125 MHz), δ_C, ppm: 26.87 (**C**H_3CO), 56.59 (CH_2), 51.45 (OMe), 109.53 (C^6), 109.97 (C^3), 122.57 (C^{6a}), 125.91 (C^5), 130.05 (C^2), 145.39 (C^{3a}), 162.22 (**C**O_2Me), 202.64 (CH_3**C**O). Found: m/z 237.0454 $[M]^+$. $C_{11}H_{11}NO_3S$. Calculated: M 237.0459.

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REFERENCES

1. Hemetsberger, H. and Knittel, D., *Monatsh. Chem*., 1972, vol. 103, p. 194.
2. Yarovenko, V.N., Semenov, S.L., Zavarzin, I.V., Ignatenko, A.V., and Krayushkin, M.M., *Russ. Chem. Bull., Int. Ed*., 2003, vol. 52, p. 451.
3. Ching, K.-Ch., Kam, Y.-W., Merits, A., Ng, L.F.P., and Chai, Ch.L.L., *J. Med. Chem*., 2015, vol. 58, p. 9196.
4. Ching, K.-Ch., Tran, T.N.Q., Amrun, S.N., Kam, Y.-W., Ng, L.F.P., and Chai, Ch.L.L., *J. Med. Chem*., 2017, vol. 60, p. 3165.
5. Sartori, L., Mercurio, C., Amigoni, F., Cappa, A., Faga, G., Fattori, R., Legnaghi, E., Ciossani, G., Mattevi, A., Meroni, G., Moretti, L., Cecatiello, V., Pasqualato, S., Romussi, A., Thaler, F., Trifiro, P., Villa, M., Vultaggio, S., Botrugno, O.A., Dessanti, P., Minucci, S., Zagarri, E., Carettoni, D., Iuzzolino, L., Varasi, M., and Vianello, P., *J. Med. Chem*., 2017, vol. 60, p. 1673.
6. Ashok, D., Goud, P., Shravani, D., Rajaiah, J., Sarasija, M., and Bhaskar, K., *Indian J. Heterocycl. Chem*., 2010, vol. 20, p. 81.
7. Ilyin, A.P., Dmitrieva, I.G., Kustova, V.A., Manaev, A.V., and Ivachtchenko, A.V., *J. Comb. Chem*., 2007, vol. 9, p. 96.
8. Sindac, J.A., Yestrepsky, B.D., Barraza, S.J., Bolduc, K.L., Blakely, P.K., Keep, R.F., Irani, D.N., Miller, D.J., and Larsen, S.D., *J. Med. Chem*., 2012, vol. 55, p. 3535.
9. Verbitskiy, E.V., Slepukhin, P.A., Valova, M.S., Cheprakova, E.M., Schepochkin, A.V., Rusinov, G.L., and Charushin, V.N., *Eur. J. Org. Chem*., 2014, p. 8133.
10. Krayushkin, M.M., Yarovenko, V.N., Semenov, S.L., Zavarzin, I.V., Ignatenko, A.V., Martynkin, A.Yu., and Uzhinov, B.M., *Org. Lett*., 2002, vol. 4, p. 3879.
11. Jones, C., Boudinet, D., Xia, Y., Denti, M., Das, A., Facchetti, A., and Driver, T.G., *Chem. Eur. J*., 2014, vol. 20, p. 5938.
12. Jiang, X.-D., Zhang, H., Zhang, Y., and Zhao, W., *Tetrahedron*, 2012, vol. 68, p. 9795.
13. De Mico, A., Margarita, R., Parlanti, L., Vescovi, A., and Piancatelli, G., *J. Org. Chem*., 1997, vol. 62, p. 6974.
14. Li, J.J., *Name reactions: A Collection of Detailed Reaction Mechanisms*, New York: Springer, 2003, 2nd ed. Translated under the title *Mekhanizmy organicheskikh reaktsii*, Moscow: BINOM, 2006, p. 101.
15. Vostrikov, N.S., Abutkov, A.V., and Miftakhov, M.S., *Russ. Chem. Bull., Int. Ed*., 2001, vol. 50, p. 1238.
16. Lotz, S., Landman, M., Goerls, H., Crause, Ch., Nienaber, H., and Olivier, A., *Z. Naturforsch. B: Chem. Sci*., 2007, vol. 62, no. 3, p. 419.