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Self-condensation of N-substituted (4*H*-thieno[3,2-*b*]-pyrrol-5-yl)methanols into bis(thienopyrrolyl)methanes

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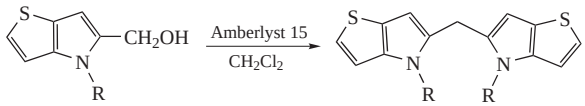
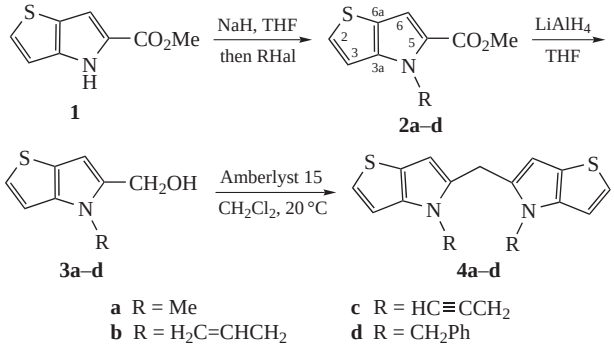
N-Substituted (4*H*-thieno[3,2-*b*]pyrrol-5-yl)methanols were obtained by alkylation of methyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate followed by reduction with $LiAlH_4$. These compounds on contact with Amberlyst 15 (H-form) in CH_2Cl_2 undergo self-condensation to produce bis(4*H*-thieno[3,2-*b*]-pyrrol-5-yl)methanes.



R = Me, allyl, propargyl, CH_2Ph

4*H*-Thieno[3,2-*b*]pyrrole-5-carboxylic derivatives[1,2] are of interest in search for bioactive thienopyrrole compounds,[3–8] as well as base matrices in preparation of π-condensed systems for optoelectronics.[9–12] In this study, we performed N-alkylation of methyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate **1** with iodomethane, allyl, propargyl or benzyl bromides and obtained the corresponding N-derivatives **2a**–**d**, which were further reduced ($LiAlH_4$) into the corresponding alcohols **3a**–**d** (Scheme 1).† We anticipated of using alcohols **3** to access more complex structures of bis(thienopyrrolyl)methane type **4** by means of self-condensation reaction. Choice of alcohols **3** for this purpose was based on known precedents of acid[13(*a*),(*b*)] or ion-exchange Montmorillonite resin[13(*c*)] catalyzed syntheses of pyrromethanes (dipyrrolylmethanes) from monomeric acetoxymethylpyrroles and 5-unsubstituted pyrroles. Bis(thienopyrrolyl)methanes[14] are the valuable intermediates in the synthesis of porphyrins *via* pyrromethenes.[15] The data on self-condensation of such compounds are scarce[13(*a*),(*c*)] and relate to pyrroles with NH group.[12,13(*c*),14(*e*),16] In the case of N-substituted pyrroles, the possibilities of acid-catalyzed **3** → **4** route are not obvious and hence they require experimental confirmation. In addition, bis(thienopyrrolyl)methanes **4** seem promising in creation of cross-conjugation involving their methylene fragment.

On the way to methanes **4**, reactions of alcohol **3a** in SiO_2–CH_2Cl_2 and TsOH–benzene systems were studied at room temperature and on heating. In all cases, the reactions were sluggish and conversion of alcohol **3a** was never complete even after several hours. Meanwhile, in the Amberlyst 15 (H-form)–CH_2Cl_2 system, alcohol **3a** was fully converted into a new product whose



1 **2a–d** **3a–d** **4a–d**

a R = Me
b R = H_2C=$CHCH_2$
c R = HC≡CCH_2
d R = CH_2Ph

Scheme 1

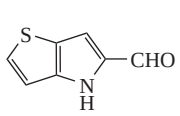
† The IR spectra were recorded from thin films on a Shimadzu IR Prestige-21 spectrometer. The ^1H and ^{13}C NMR spectra were recorded on Bruker AM-300 (300.13 and 75.47 MHz, respectively) and Bruker Avance-500 instruments (500.13 and 125.77 MHz, respectively) using tetramethylsilane as internal standard. The mass spectra (EI, 70 eV) were obtained on Thermo Finnigan MAT 95XP and Shimadzu LCMS-2010EV mass spectrometers (sample solutions in chloroform–acetonitrile were injected by a syringe at a flow rate of 0.1 ml min^{-1}, eluent acetonitrile–water, 95:5) in the register mode of positive ions with the ionizing potential of needle electrode 4.5 kV, temperature of capillary interface 250 °C, voltage of capillary interface 5 V, flow rate of atomizing gas (nitrogen) 1.5 dm^3 min^{-1} (for chemical ionization at atmospheric pressure). The reaction course was monitored by TLC on 'Sorbphil' plates with visualization of compounds in the ethanol solution of anisaldehyde acidified with sulfuric acid with subsequent heating at 120–150 °C. The products were isolated by column chromatography on silica gel (30–60 g of adsorbent per 1 g of compound); freshly distilled solvents were used as eluents.

Methyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate **1** was obtained according to published procedure,[1,2] the spectral characteristics conformed to those given in literature.

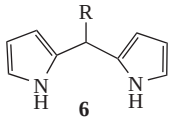
*Methyl 4-methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate* **2a**.[18] A solution of pyrrole **1** (0.20 g, 1.10 mmol) in anhydrous THF (2 ml) was added to a stirred suspension of NaH (55.0 mg, 2.29 mmol) (pre-rinsed with anhydrous hexane from a 55% dispersion in mineral oil) in anhydrous THF (10 ml) under an argon atmosphere, and the mixture was stirred for 30 min. Then a solution of iodomethane (0.14 ml, 2.19 mmol) in THF (5 ml) was added dropwise, and the mixture was stirred at 40 °C until the starting pyrrole was consumed (TLC control). The mixture was cooled and quenched with saturated NH_4Cl solution, the product was extracted with CH_2Cl_2 (3×20 ml). The solvent was evaporated, the residue was purified by column chromatography on SiO_2 (light petroleum–ethyl acetate, 5:1) to give 0.17 g (79%) of compound **2a** as slightly yellow crystals, mp 62–63 °C. IR (ν/cm^{-1}): 1710, 1695, 1532, 1464, 1445, 1378, 1369, 1235, 1209, 1179, 1095, 1075, 962, 728. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.86 (s, 3H, OMe), 4.06 (s, 3H, NMe), 6.95 (d, 1H, H-3, *J* 5.4 Hz), 7.18 (s, 1H, H-6), 7.34 (d, 1H, H-2, *J* 5.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 51.3 (NMe, OMe), 109.0 (C^6), 110.0 (C^3), 114.8 (C^{6a}), 121.9 (C^5), 129.13 (C^2), 138.0 (C^{3a}), 164.6 (CO_2Me).

spectra were in accordance with structure **4a** (see Scheme 1). In the same manner, alcohols **3b**–**d** underwent self-condensation into bis(thienopyrrolyl)methanes **4b**–**d**.‡

To our knowledge, symmetric bis(thienopyrrolyl)methanes of type **4** are not documented. The most close precedent is condensation of aldehyde **5** with C(5)-unsubstituted pyrroles leading to unsymmetrical (thienopyrrolyl)methanes used for the preparation of BODIPY complexes.[16] At the same time, syntheses of more simple dipyrromethanes **6** are well developed [see, *e.g.*, refs. 14(*d*),17].

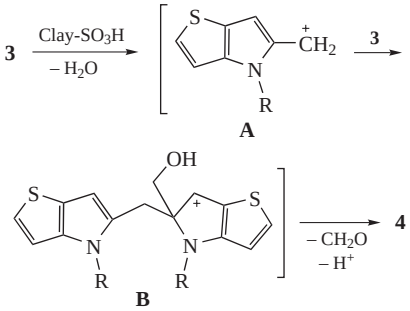


5



6

R = H, Alk, Ar, *etc.*



Scheme 2

The tentative mechanism of the self-condensation is outlined in Scheme 2. Alcohol **3** on contact with highly acidic Amberlyst 15 is converted into carbocation **A** which would regioselectively attack C(2) site of the second molecule of **3**. The thus formed adduct **B** with secondary carbocation centre is supposed to

*Methyl 4-allyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate* **2b** was prepared analogously from pyrrole **1** (0.06 g, 0.33 mmol), NaH (9.5 mg, 0.39 mmol) and allyl bromide (79.9 mg, 0.66 mmol) using Bu_4NI (6 mg) as the phase transfer catalyst. The purification by column chromatography on SiO_2 (light petroleum–ethyl acetate, 5:1) gave 0.70 g (95%) of **2b** as an oily substance. IR (ν/cm^{-1}): 2948, 1703, 1699, 1532, 1464, 1441, 1395, 1303, 1256, 1216, 1175, 1103, 759, 719. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.86 (s, 3H, OMe), 4.98 (dd, 1H, =CH_2, *J* 17.1 and 1.1 Hz), 5.13 (dd, 1H, =CH_2, *J* 10.4 and 1.1 Hz), 5.15 (m, 2H, NCH_2), 6.01 (m, 1H, =CH, *J* 17.0, 1.5, 10.4 and 5.3 Hz), 6.92 (d, 1H, H-3, *J* 5.5 Hz), 7.21 (s, 1H, H-6), 7.33 (d, 1H, H-2, *J* 5.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 49.4 (CH_2), 51.3 (OMe), 109.5 (C^6), 110.4 (=CH_2), 116.3 (C^3), 122.2 (C^{6a}), 125.9 (C^5), 129.3 (C^2), 133.9 (=CH), 145.1 (C^{3a}), 161.9 (*C*O_2Me). HRMS (ESI), *m*/*z*: 221.0505 $[M]^+$ (calc. for $C_{11}H_{11}NO_2S$, *m*/*z*: 221.0510).

*Methyl 4-(prop-2-yn-1-yl)-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate* **2c** was prepared in a similar manner from pyrrole **1** (0.37 g, 2.04 mmol) and 80% solution of propargyl bromide (0.45 ml, 4.10 mmol) in toluene. Bright yellow crystals, mp 83–86 °C. Yield 0.42 g (94%). IR (ν/cm^{-1}): 3106, 3265, 2953, 1692, 1534, 1492, 1464, 1438, 1394, 1377, 1306, 1261, 1220, 1181, 1171, 1111, 776, 732, 659. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.32 (t, 1H, ≡CH, *J* 2.3 Hz), 3.88 (s, 3H, OMe), 5.38 (d, 2H, NCH_2, *J* 2.4 Hz), 7.09 (d, 1H, H-3, *J* 5.2 Hz), 7.22 (s, 1H, H-6), 7.38 (d, 1H, H-2, *J* 5.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 36.1 (CH_2), 51.5 (OMe), 72.5 (≡CH), 78.4 (≡C), 110.1 (C^6), 110.5 (C^3), 122.6 (C^{6a}), 125.5 (C^5), 129.7 (C^2), 145.3 (C^{3a}), 162.3 (*C*O_2Me). HRMS (ESI), *m*/*z*: 219.0349 $[M]^+$ (calc. for $C_{11}H_9NO_2S$, *m*/*z*: 219.0354).

*Methyl 4-benzyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate* **2d** was prepared similarly from pyrrole **1** (0.06 g, 0.33 mmol) and benzyl bromide (0.084 g, 0.66 mmol). Yellowish crystals, mp 81–83 °C. Yield 80 mg (92%). IR (ν/cm^{-1}): 2950, 1703, 1532, 1490, 1464, 1441, 1395, 1303, 1257, 1216, 1175, 1103, 1085, 991, 918, 781, 759, 719, 666. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.83 (s, 3H, OMe), 5.76 (s, 2H, NCH_2), 6.86 (d, 1H, H-3, *J* 5.4 Hz), 7.13 (d, 2H, Ph, *J* 7.4 Hz), 7.25 (s, 1H, H-6), 7.23–7.28 (m, 3H, Ph), 7.32 (d, 1H, H-2, *J* 5.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 50.4 (CH_2), 51.3 (OMe), 109.8 (C^6), 110.6 (C^3), 122.4 (C^{6a}), 126.1 (C^5), 126.6 (C_{Ar}), 127.3 (C_{Ar}), 128.6 (C_{Ar}), 129.4 (C^2), 137.9 (C_{Ar}), 145.4 (C^{3a}), 161.9 (*C*O_2Me). HRMS (ESI), *m*/*z*: 271.0662 $[M]^+$ (calc. for $C_{15}H_{13}NO_2S$, *m*/*z*: 271.0667).

*(4-Methyl-4*H*-thieno[3,2-*b*]pyrrol-5-yl)methanol* **3a**. A solution of ester **2a** (70 mg, 0.36 mmol) in anhydrous THF (5 ml) was added to a stirred suspension of $LiAlH_4$ (40.0 mg, 1.05 mmol) in anhydrous THF (10 ml) under an argon atmosphere. The mixture was stirred until the starting ester was consumed (TLC control), then quenched with saturated solution of NH_4Cl, THF was evaporated and the product was extracted with CH_2Cl_2 (3×20 ml). The combined extracts were washed with brine, dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (EtOAc–light petroleum, 1:5) to isolate 38.0 mg (63%) of white powder, mp 71–73 °C. IR (ν/cm^{-1}): 3527, 3230, 2727, 1530, 1377, 1366, 1337, 1295, 1241, 1135, 1078, 987, 975, 823, 763, 713, 654. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.86 (s, 1H, OH), 3.79 (s, 3H, NMe), 4.64 (d, 2H, OCH_2, *J* 5.5 Hz), 6.27 (s, 1H, H-6), 7.02 (d, 1H, H-3, *J* 5.3 Hz), 7.11 (d, 1H, H-2, *J* 5.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 31.3 (NMe), 56.3 (OCH_2), 99.6 (C^6), 110.2 (C^3), 120.7 (C^{6a}), 121.3 (C^5), 122.2 (C^2), 138.4 (C^{3a}). MS (EI), *m*/*z* (%): 168 $[M+H]^+$ (10), 150 $[M-OH]^+$ (100).

*(4-Allyl-4*H*-thieno[3,2-*b*]pyrrol-5-yl)methanol* **3b** was prepared similarly from **2b** (60 mg, 0.27 mmol) and $LiAlH_4$ (12 mg, 0.32 mmol). Purification by column chromatography on SiO_2 (light petroleum–EtOAc, 5:1) gave 0.38 g (72%) of compound **3b** as an oil. IR (ν/cm^{-1}): 2948, 1703, 1699, 1532, 1464, 1441, 1395, 1303, 1256, 1216, 1175, 1103, 759, 719. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 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 (ddd, 1H, =CH, *J* 5.1, 10.2, 5.3 Hz), 6.38 (s, 1H, H-6), 6.89 (d, 1H, H-3, *J* 5.1 Hz), 7.09 (d, 1H, H-2, *J* 5.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 48.0 (NCH_2), 57.5 (OCH_2), 101.2 (C^6), 110.5 (=CH_2), 116.6 (C^3), 121.9 (C^{6a}), 122.0 (C^5), 123.7 (C^2), 134.1 (=CH), 141.5 (C^{3a}). Found (%): C, 62.48; H, 5.49; N, 7.46; S, 16.98. Calc. for $C_{10}H_{11}NOS$ (%): C, 62.15; H, 5.74; N, 7.25; S, 16.59.

*{4-(Prop-2-yn-1-yl)-4*H*-thieno[3,2-*b*]pyrrol-5-yl}methanol* **3c** was prepared analogously from **2c** (60 mg, 0.27 mmol) and $LiAlH_4$ (12.4 mg, 0.33 mmol). Yield 81% (42 mg). Light yellow crystals, mp 66–68 °C. IR (ν/cm^{-1}): 3312, 3270, 3203, 2950, 1462, 1400, 1438, 1377, 1364, 1330, 1295, 1013, 782, 721, 682, 655. ^{1}H NMR (500 MHz, acetone-d_6) δ: 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, H-6), 7.12 (d, 1H, H-3, *J* 5.3 Hz), 7.15 (d, 2H, H-2, *J* 5.3 Hz). ^{13}C NMR (125 MHz, acetone-d_6) δ: 34.4 (CH_2), 56.4 (OCH_2), 73.1 (≡CH), 78.9 (≡C), 100.5 (C^6), 110.7 (C^3), 122.1 (C^{6a}), 122.8 (C^2), 125.9 (C^5), 144.1 (C^{3a}). Found (%): C, 62.46; H, 4.49; N, 7.46; S, 16.49. Calc. for $C_{10}H_9NOS$ (%): C, 62.80; H, 4.74; N, 7.32; S, 16.77.

*(4-Benzyl-4*H*-thieno[3,2-*b*]pyrrol-5-yl)methanol* **3d** was prepared similarly from **2d** (60 mg, 0.22 mmol) and $LiAlH_4$ (10.0 mg, 0.27 mmol). Yield 34.0 mg (64%), oil. IR (ν/cm^{-1}): 3537, 2931, 2873, 1526, 1476, 1452, 1405, 1375, 1356, 1336, 1294, 1241, 1218, 1137, 1080, 1048, 995, 935, 826, 801, 776, 743, 592. ^{1}H NMR (500 MHz, acetone-d_6) δ: 2.90 (s, 1H, OH), 4.64 (s, 2H, OCH_2), 5.44 (s, 2H, NCH_2), 6.38 (s, 1H, H-6), 6.87 (d, 1H, H-3, *J* 5.2 Hz), 7.06 (d, 1H, H-2, *J* 5.3 Hz), 7.16 (d, 2H, Ph, *J* 7.2 Hz), 7.23–7.29 (m, 3H, Ph). ^{13}C NMR (125 MHz, acetone-d_6) δ: 48.7 (CH_2), 56.5 (OCH_2), 100.2 (C^6), 110.8 (C^3), 122.5 (C^{6a}), 122.6 (C^2), 126.6 (C_{Ar}), 127.1 (C_{Ar}), 128.5 (C^5), 128.5 (C_{Ar}), 138.6 (C_{Ar}), 138.4 (C^{3a}). MS (EI), *m*/*z* (%): 244 $[MH]^+$ (5), 226 $[M-OH]^+$ (100). Found (%) C, 68.89; H, 5.47; N, 5.44; S, 13.44. Calc. for $C_{14}H_{15}NOS$ (%): C, 69.10; H, 5.39; N, 5.76; S, 13.18.

‡ *Bis(4-methyl-4*H*-thieno[3,2-*b*]pyrrol-5-yl)methane* **4a**. Amberlyst 15 (0.15 g) was added to a stirred solution of **3a** (0.14 g, 0.84 mmol) in CH_2Cl_2 (10 ml), the reaction mixture was stirred until the starting alcohol was consumed (5–6 h, TLC control). Amberlyst was filtered off, the CH_2Cl_2 filtrate was concentrated, and the residue was purified by column chromatography on silica gel (EtOAc–light petroleum, 1:5) to isolate 70.0 mg (58%) of product **4a** as an oil. IR (ν/cm^{-1}): 3097, 3083, 2953, 2853, 1662, 1537, 1471, 1438, 1382, 1334, 1291, 1133, 1083, 845, 765, 725. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.68 (s, 6H, NMe), 4.13 (s, 2H, CH_2), 6.14 (s, 2H, H-6), 6.90 (d, 2H, H-3, *J* 5.3 Hz), 7.03 (d, 2H, H-2, *J* 5.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 26.2 (CH_2), 32.2 (NMe), 100.1 ($C^{6'}$), 109.9 ($C^{3'}$), 121.6 ($C^{6a'}$), 121.9 ($C^{2'}$), 134.7 ($C^{5'}$), 140.1 ($C^{3a'}$). MS (EI), *m*/*z* (%): 287 $[MH]^+$ (100). Found (%): C, 63.16; H, 4.66; N, 9.49; S, 22.76. Calc. for $C_{15}H_{14}N_2S_2$ (%): C, 62.90; H, 4.93; N, 9.78; S, 22.39.

release formaldehyde molecule and proton affording final stable bis(thienopyrrolyl)methane **4**.

In total, the herein obtained bis(4*H*-thieno[3,2-*b*]pyrrol-5-yl)-methanes **4** seem promising as new scaffolds in search for new bioactive compounds and design of new cross-conjugated structures. The mechanistic aspects of the chemical transformations can also be of interest.

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*Bis(4-allyl-4*H*-thieno[3,2-*b*]pyrrol-5-yl)methane* **4b** was prepared similarly from alcohol **3b**, reaction time 8 h, oil, yield 55%. IR (ν/cm^{-1}): 3099, 3081, 3009, 2982, 2954, 2919, 2867, 1517, 1476, 1442, 1395, 1345, 1337, 1298, 1285, 1082, 988, 921, 798, 773, 648. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.07 (s, 2H, CH_2), 4.60 (dd, 2H, NCH_2, *J* 1.6, 3.4 Hz), 4.61 (d, 2H, NCH_2, *J* 1.6, 3.4 Hz), 4.92 (dd, 2H, $=CH_2$, *J* 1.2, 17.1 Hz), 5.13 (dd, 2H, $=CH_2$, *J* 1.2, 10.2 Hz), 5.88 (m, 2H, =CH, *J* 5.1, 10.1 Hz), 6.15 (s, 2H, H-6′), 6.85 (d, 1H, H-3′, *J* 5.3 Hz), 6.87 (d, 1H, H-3′, *J* 5.2 Hz), 7.01 (d, 2H, H-2′, *J* 5.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 26.0 (CH_2), 47.9 (NCH_2), 100.5 ($C^{6'}$), 110.3 ($C^{3'}$), 116.5 ($=CH_2$), 122.2 ($C^{6a'}$), 122.0 ($C^{2'}$), 133.7 (=CH), 134.5 ($C^{5'}$), 140.5 ($C^{3a'}$). HRMS (ESI), *m*/*z*: 338.0906 $[M]^+$ (calc. for $C_{19}H_{18}N_2S_2$, *m*/*z*: 338.0911). Found (%): C, 67.81; H, 5.47; N, 8.43; S, 18.66. Calc. for $C_{19}H_{18}N_2S_2$ (%): C, 67.42; H, 5.36; N, 8.28; S, 18.95.

*Bis{4-(prop-2-yn-1-yl)-4*H*-thieno[3,2-*b*]pyrrol-5-yl}methane* **4c** was prepared analogously from alcohol **3c**, reaction time 8 h, oil, yield 43%. IR (ν/cm^{-1}): 3285, 3259, 3106, 3081, 2954, 2923, 2850, 2125, 1661, 1647, 1531, 1517, 1472, 1436, 1394, 1334, 1296, 1248, 1133, 1086, 1055, 1042, 910, 773, 715, 653. ^{1}H NMR (300 MHz, acetone-d_6) δ: 2.33 (s, 2H, ≡CH), 4.32 (s, 2H, CH_2), 4.75 (d, 4H, NCH_2, *J* 2.5 Hz), 6.23 (s, 2H, H-6′), 6.98 (d, 2H, H-2′, *J* 5.3 Hz), 7.06 (d, 2H, H-3′, *J* 5.3 Hz). ^{13}C NMR (125 MHz, acetone-d_6) δ: 34.4 (CH_2), 56.4 (NCH_2), 73.1 (≡CH), 78.9 (≡C), 101.4 ($C^{6'}$), 110.1 ($C^{3'}$), 121.5 ($C^{6a'}$), 122.8 ($C^{2'}$), 133.8 ($C^{5'}$), 140.3 ($C^{3a'}$). HRMS (ESI), *m*/*z*: 334.0593 $[M]^+$ (calc. for $C_{19}H_{14}N_2S_2$, *m*/*z*: 334.0598). Found (%): C, 68.60; H, 4.53; N, 8.47; S, 19.56. Calc. for $C_{19}H_{14}N_2S_2$ (%): C, 68.23; H, 4.22; N, 8.38; S, 19.17.

*Bis(4-benzyl-4*H*-thieno[3,2-*b*]pyrrol-5-yl)methane* **4d** was prepared in a similar manner from alcohol **3d**, reaction time 9–10 h, oil, yield 62%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.92 (s, 2H, CH_2), 5.13 (s, 4H, NCH_2), 6.19 (s, 2H, H-6), 6.77 (d, 2H, H-3, *J* 5.3 Hz), 6.99 (d, 2H, H-2, *J* 5.2 Hz), 6.89 (m, 4H, Ph), 7.21 (m, 6H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 37.6 (CH_2), 48.5 (NCH_2), 99.1 ($C^{3'}$), 110.0 ($C^{6'}$), 121.0 ($C^{2'}$), 121.9 ($C^{6a'}$), 125.6 (C_{Ar}), 126.0 (C_{Ar}), 127.1 (C_{Ar}), 128.0 (C_{Ar}), 128.1 (C_{Ar}), 128.5 (C_{Ar}), 134.2 ($C^{5'}$), 137.5 (C_{Ar}), 139.9 (C_{Ar}), 141.5 ($C^{3a'}$). HRMS (ESI), *m*/*z*: 438.1219 $[M]^+$ (calc. for $C_{27}H_{22}N_2S_2$, *m*/*z*: 438.1224). Found (%): C, 73.59; H, 5.13; N, 6.54; S, 14.98. Calc. for $C_{27}H_{22}N_2S_2$ (%): C, 73.94; H, 5.06; N, 6.39; S, 14.62.

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