SYNTHESES OF BROMINATED BITHIAZOLES AND ETHYNYLATION *VIA* PALLADIUM-CATALYZED CROSS-COUPLING

Thomas Nußbaumer and Richard Neidlein*

Pharmazeutisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 364, 69120 Heidelberg, Germany

Dedicated on the 73rd birthday of Teruaki Mukaiyama, Department of Chemistry, University of Tokyo, Japan

Abstract - The syntheses of brominated 2,2'- and 4,4'-bithiazoles and related 2,2'-bithiazole-5,5'-dicarbaldehyde are described. Palladium-catalyzed cross-coupling of the readily available brominated bithiazoles with acetylenes yields the desired alkynylated bithiazoles. The terminally unprotected ethynyl derivatives can be obtained after removal of the Me_3Si protecting groups under basic conditions.

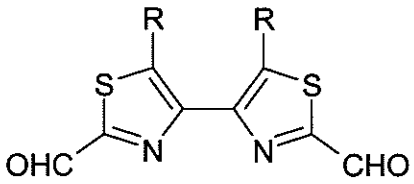
INTRODUCTION

The synthesis of novel porphyrins, porphycenes and related conjugated macrocycles continues to be the topic of intense investigations because of their aromatic properties as annulene derivatives[1] as well as their potential use as photosensitizers.[2] In the recent years, a number of studies have been conducted regarding the use of porphyrinoids for biomedical applications such as fluorescence detection, viral inhibition, and photodynamic tumor therapy (PDT).[3] Therefore, many attempts have been made to modify the porphyrin ring system to generate new chromophores.[4]

In earlier works, we investigated the syntheses of sulfur-containing porphycene analogs, namely 21,23-dithiaporphycene and tetrathiaporphycene,[5] and observed remarkable changes in the structural and chemical properties of these compounds. Stimulated by the observation of Vogel, Schaffner and coworkers,[6] which showed the potential use of acetylenic and cumulenic porphycene derivatives as PDT agents, we investigated the syntheses of brominated and alkynylated tetrathiaporphycenes.[7]

However, the effects of introducing a heteroatom into the position of the β-carbon in porphycenes are unknown. One particularly interesting class of heterocycles, the bithiazoles, have been reported to show luminescence, DNA-cleaving activity, and to inhibit platelet aggregation.[8] Therefore, we became

interested in the syntheses of thiazole-containing porphycene analogs and related brominated and alkynylated porphycene derivatives.



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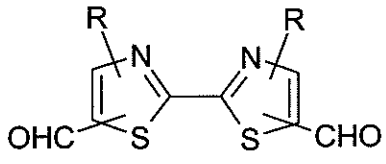

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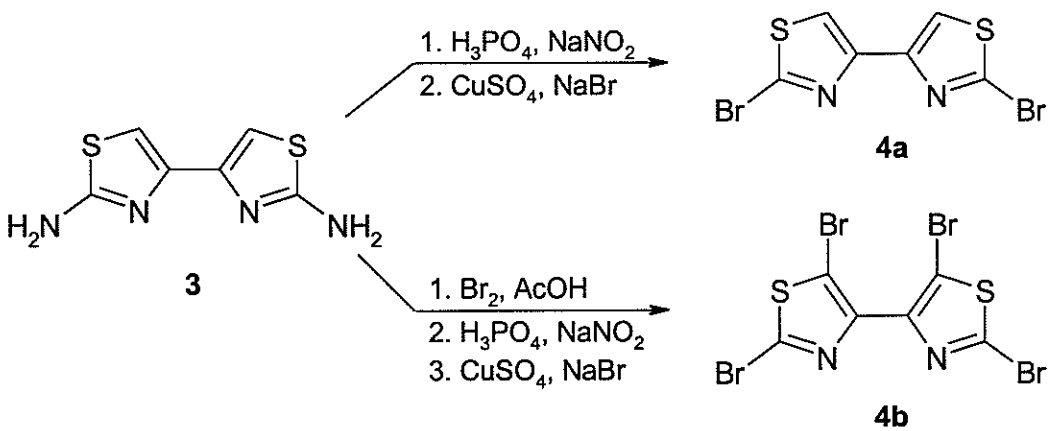
R = H, Br, C≡C—R'

The reductive intermolecular coupling of dicarbonyl compounds with low-valent titanium under McMurry conditions has been established as the most efficient route for the preparation of porphycenes and related macrocycles.[5-7,9] Therefore, various substituted bisformylated bithiazoles, like **1** or **2**, seemed to be suitable precursors for the syntheses of thiazole-containing macrocycles. The preparation of brominated and formylated bithiazole derivatives has not received much attention. To the best of our knowledge, only the synthesis of 4,4' bithiazol-5,5'-dicarbaldehyde (**1**) (R = H) has been reported.[10] Thus, our first task was to develop simple routes for the syntheses of brominated, ethynylated, and formylated bithiazoles.

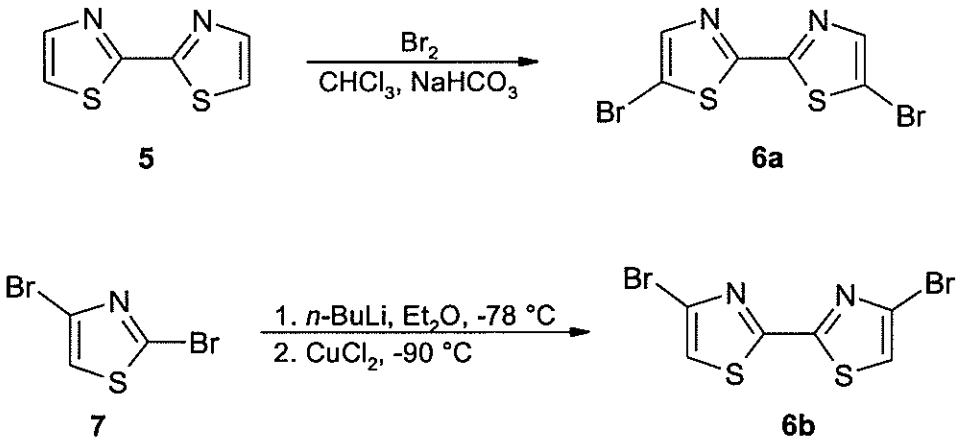
RESULTS AND DISCUSSION

Aminothiazole can be converted in good yields into the related bromothiazole *via* diazotization and treatment of the resulting diazonium salt with NaBr in the precence of $CuSO_4$.[11] This methodology was applied to the 2,2'-amino-4,4'-bithiazole (**3**) (Scheme 1).[12] By this route, 2,2'-dibromo-4,4'-bithiazole (**4a**) was obtained in moderate yield under Sandmeyer conditions. The 2,2',5,5'-tetrabromo-4,4'-bithiazole (**4b**) was obtained in the same way, after treatment of **3** with bromine in acetic acid.



Scheme 1

Due to the different reactivity of 4- and 5-positions in thiazole, a different synthetic route had to be developed for the synthesis of the brominated 2,2'-bithiazoles **6a,b** (Scheme 2). 5,5'-dibromo-2,2'-bithiazole (**6a**) was prepared in good yields from the readily available 2,2'-bithiazole (**5**)[13] by treatment with an excess of bromine in chloroform in the presence of $NaHCO_3$.

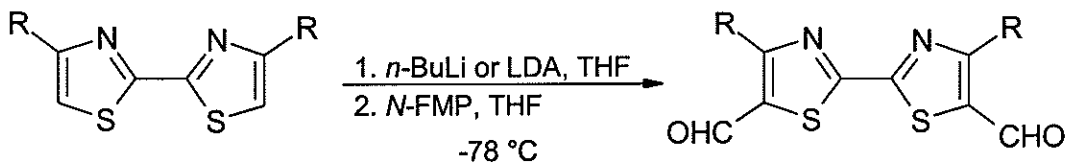


5 **6a** **7** **6b**

Scheme 2

4,4'-Dibromo-2,2'-bithiazole (**6b**) was prepared in good yields by oxidative coupling of regioselectively 2-lithiated 2,4-dibromothiazole (**7**) with $CuCl_2$ in ether at –90 °C. Similar conditions had previously been used for the syntheses of related bithiophenes.[14] Although 4,5-dibromothiazole derivatives are known,[15] attempts to introduce additional bromine into **6a** or **6b** to generate the 4,4',5,5'-tetrabromo-2,2'-bithiazole failed.

The introduction of two formyl substituents into the 5,5'-position of the 2,2'-bithiazoles (**5**) and (**6b**) can be accomplished from the corresponding 5,5'-dilithiated 2,2'-bithiazoles using *N*-formylmorpholine (*N*-FMP) as formylating agent (Scheme 3).[16] Thus, we could obtain the 2,2'-bithiazole-5,5'-dicarbaldehyde (**8a**) in good yield by regioselective 5,5'-lithiation of **5** with two equivalents of *n*-butyllithium in THF followed by treatment with *N*-FMP at –78 °C. The related 4,4'-dibromo-2,2'-bithiazole-5,5'-dicarbaldehyde (**8b**) was prepared by deprotonation of **6b** with lithium diisopropylamide (LDA) and quenching of the resulting 4,4'-dibromo-2,2'-bithiazol-5,5'-yllithium compound with *N*-FMP under the conditions described above.



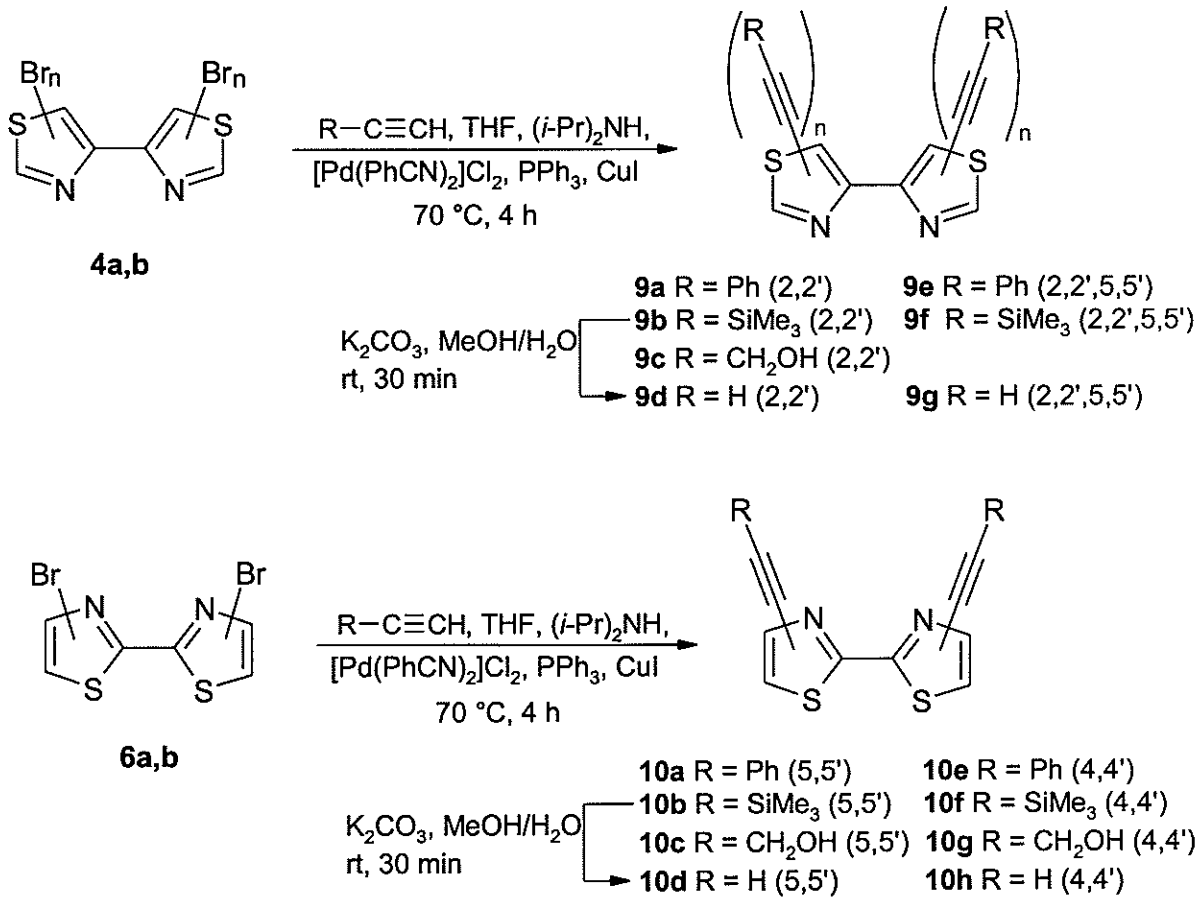
5, 6b

8a R = H
8b R = Br

Scheme 3

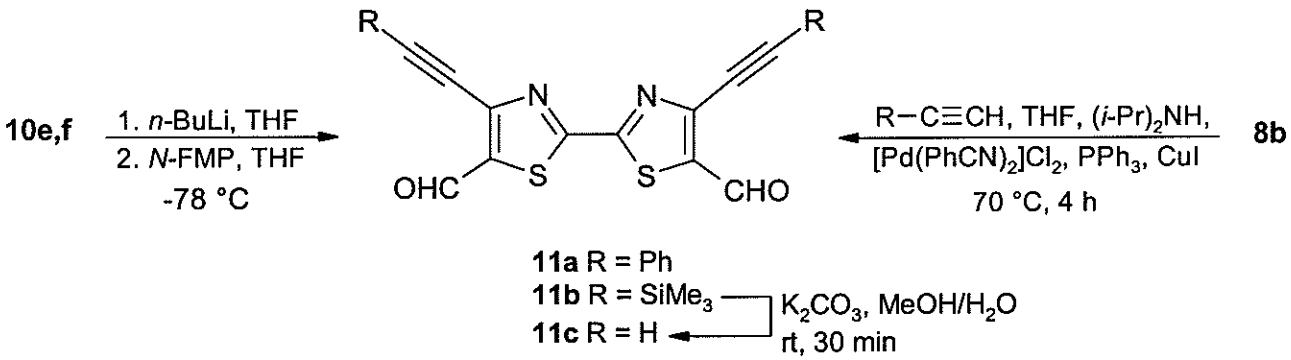
In contrast, the reaction of **6b** with two equivalents of *n*-butyllithium in THF followed by treatment with *N*-FMP at –78 °C did not yield the desired 2,2'-bithiazole-4,4'-dicarbaldehyde. In this case, the dehalogenated compound (**5**) (20 %) and compound (**8a**) (40 %) were isolated as major products. This can be attributed to the effect of a nitrogen lone pair on N-3 which destabilizes negative charge at C-4.[17] However, attempts to transform the 2,2',5,5'-tetrabromo-4,4'-bithiazole (**4b**) into the related 5,5'-dibromo-4,4'-bithiazole-2,2'-dicarbaldehyde (**1**) (R = Br) failed, too.

The brominated bithiazole derivatives (**4a,b**) and (**6a,b**) provided excellent starting materials for the preparation of polyethynylbithiazoles of structure (**1**) and (**2**). The most powerful method to introduce ethynyl groups into aromatic nuclei, like thiazole, is the palladium-catalyzed cross-coupling of aryl halides with terminal acetylenes. Using the conditions of the modified *Heck*-coupling[18] reaction as published by *Sonogashira et al.*,[19] however, the desired products were obtained only in moderate yields. Applying a method developed by *Neenan* and *Whitesides*[20] who prepared polyethynylthiazoles using a dichlorobis(benzonitrile)palladium(II)/CuI/PPh_3 catalyst system in diisopropylamine $(i\text{-Pr})_2NH$, the desired products were obtained in moderate yields, too. In our studies, best results were obtained using the catalyst system $[Pd(PhCN)_2]Cl_2$/CuI/PPh_3 (1:1:2) in a mixture of THF and $(i\text{-Pr})_2NH$ as solvent.



Scheme 4

Under these reaction conditions, the phenylethynyl- and trimethysilylethynyl-substituted bithiazoles (**9a,b,e,f**, **10a,b,e,f** and **11a,b**) were obtained in good yields. When propargyl alcohol was used as alkynylation partner for the brominated bithiazoles (**4a**) and (**6a,b**), compounds (**9c**) and (**10c,g**) were obtained in moderate yields. The alkynylated 2,2'-bithiazole-5,5'-dicarbaldehydes (**11a,b**) could be synthesized by two different pathways (Scheme 5). The formyl group could be introduced in good yields into **10e,f** using the formylating procedure described above. **11a,b** were also available by reaction of the brominated 2,2'-bithiazole-5,5'-dicarbaldehydes (**8b**) with the corresponding acetylene derivatives.



Scheme 5

The terminally unprotected ethynylbithiazoles could easily be prepared by protodesilylation with K_2CO_3 in degassed methanol (Scheme 4,5).[21] Because of the instability of the polyethynylated bithiazoles (**9d,g**, **10d,h** and **11c**), isolation and complete characterization were difficult.

In conclusion, we have shown that the brominated bithiazoles (**4a,b**) and (**6a,b**) can be obtained using simple starting materials. **4a,b** and **6a,b** can be converted to the polyethynylbithiazoles (**9a-g**, **10a-h** and **11a,b**) by palladium-catalyzed coupling reactions.

EXPERIMENTAL

All reactions requiring anhydrous and anaerobic conditions were carried out under argon in flame-dried glassware. Solvents were purified and dried according to standard procedures.[22] Diisopropylamine was freshly distilled from KOH; THF was distilled from potassium benzophenone before use. Silica gel (60-200 mesh) for column chromatography (CC) was obtained from E. Merck, KGaA, Darmstadt. Melting points were determined on a Reichert hotstage and are uncorrected. UV/Vis spectra were recorded on a Hewlett Packard HP 8452A Diode Array spectrophotometer. IR spectra were obtained as KBr pellets on a Perkin-Elmer PE 1600 FT-IR spectrophotometer. ^{1}H-NMR spectra were recorded at 250 MHz on a Bruker WM-250 or at 360 MHz on a Bruker AM-360. ^{13}C-NMR spectra were measured at 62.9 MHz or at 90.6 MHz on the Bruker spectrometer described above. δ values are reported in ppm downfield from internal TMS. The degree of carbon substitution was determined by *J*-modulated spin echo experiments.

MS spectra were obtained on a Varian MAT-311 A mass spectrometer. Elemental analyses were performed on a Foss-Heraeus Vario EL.

2,2'-Dibromo-4,4'-bithiazole (4a): To a mixture of 4.00 g (20.0 mmol) of 2,2'-diamino-4,4'-bithiazole (**3**) in 20 mL of 85 % phosphoric acid and 10 mL of 65 % nitric acid was added a solution of 3.60 g (52.0 mmol) of sodium nitrite in water (10 mL) at –10 °C. After stirring for 45 min at –10 °C, the dark brown solution was added in one portion to a solution of 8.40 g (52.0 mmol) of $CuSO_4$ and 11.00 g (100.0 mmol) of NaBr in 300 mL of water at 0 °C. The foaming mixture was stirred for 30 min at 0 °C and for an additional 3 h at 50 °C. Then the black solution was neutralized with 2 N NaOH and extracted with $CHCl_3$ (5 × 70 mL). The organic layer was washed with water, dried over $MgSO_4$ and evaporated. Purification of the residue by column chromatography with chloroform yielded 1.90 g (30 %) of **4a** as colorless needles, mp 213-215 °C (*n*-hexane/ethyl acetate). IR (KBr): $\tilde{\nu}$ = 3122 cm^{-1} (s, CH), 1453 (s), 1399 (s), 1223 (m), 1048 (m), 1016 (s), 1007 (s), 878 (w), 767 (m), 745 (m). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 230 nm (4.08), 260 (4.16). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.75 (s, 2H, 5,5'-H). ^{13}C-NMR ($CDCl_3$, 63 MHz): δ = 149.6 (C), 136.7 (C), 119.4 (C-5,5'). MS (EI, 70 eV): *m/z* (%) = 326 (100) [M^+], 347 (36) [M^+- ^{79}Br], 345 (33) [M^+- ^{81}Br], 166 (28) [M^+- 2Br], 140 (56) [166^+- CN], 114 (16) [140^+- CN], 96 (24), 82 (36), 69 (54) [114^+- CHS], 45 (78) [CHS^+]. HRMS calcd for $C_{12}H_2N_2{}^{79}Br^{81}BrS_2$: 325.8006. Found: 325.8007. *Anal.* Calcd for $C_6H_2N_2Br_2S_2$: C, 22.10; H, 0.62; N, 8.59; S, 19.67. Found: C, 22.20; H, 0.72; N, 8.72; S, 19.75.

2,2',5,5'-Tetrabromo-4,4'-bithiazole (4b): To a solution of 2.00 g (10.0 mmol) of 2,2'-diamino-4,4'-bithiazole (**3**) in acetic acid (50 mL) was added a solution of 4.80 g (30.0 mmol) bromine in acetic acid (20 mL) at 80 °C. After stirring for 5 h at 80 °C the mixture was allowed to cool to rt. The precipitate was collected, washed with acetic acid and dried in vacuum. The crude product (4.28 g) was added to a mixture of 85 % phosphoric acid (20 mL) and of 65 % nitric acid (10 mL). The solution was cooled to -10 °C and a solution of 1.72 g (25.0 mmol) of sodium nitrite in water (10 mL) was added. After stirring for 45 min at –10 °C, the dark brown solution was added in one portion to a solution of 4.20 g (25.0 mmol) of $CuSO_4$ and 2.57 g (25.0 mmol) of NaBr in 200 mL of water at 0 °C. The foaming mixture was stirred for 30 min at 0 °C and additional 3 h at 50 °C. Then the black solution was neutralized with 2 N NaOH and extracted with $CHCl_3$ (5 × 70 mL). The organic layer was washed with water, dried over $MgSO_4$ and evaporated. Purification of the residue by column chromatography with chloroform yielded 1.93 g (40 %) of **4b** as colorless needles, mp 134-136 °C (*n*-hexane). IR (KBr): $\tilde{\nu}$ = 1450 cm^{-1} (s), 1394 (s), 1182 (m), 1009 (s), 989 (s), 757 (m). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 230 nm (4.15), 246 (sh, 4.05), 274 (4.03). ^{13}C-NMR ($CDCl_3$, 63 MHz): δ = 145.5 (C-4,4'), 135.2 (C-2,2'), 111.2 (C-5,5'). MS (EI, 70

eV): *m/z* (%) = 484 (61) [M^+], 405 (71) [M^+- ^{79}Br], 403 (67) [M^+- ^{81}Br], 298 (39) [M^+- 2Br, -CN], 193 (37) [298^+- ^{79}Br, -CN], 191 (32) [298^+- ^{81}Br, -CN], 112 (100) [193^+-^{81}Br], 94 (85). HRMS calcd for $C_6N_2{}^{79}Br_2{}^{81}Br_2S_2$: 483.6195. Found: 483.6194. *Anal.* Calcd for $C_6N_2Br_4S_2$: C, 14.89; N, 5.79; S, 13.25. Found: C, 14.89; N, 5.88; S, 13.55.

5,5'-Dibromo-2,2'-bithiazole (6a): To a solution of 1.68 g (10.0 mmol) of 2,2'-bithiazole (**5**) in $CHCl_3$ (20 mL) was added dropwise a solution of 6.40 g (40.0 mmol) of bromine in $CHCl_3$ (10 mL) within 30 min. The mixture was stirred for 48 h at rt. Each 10 h, 0.42 g (5.0 mmol) of solid $NaHCO_3$ was added. Then the suspension was diluted with $CHCl_3$ (150 mL), and the organic phase was washed with saturated aqueous $NaHCO_3$ (50 mL), and with water (2 × 50 mL). The organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure. Recrystallization of the crude product from ethyl acetate yielded 2.40 g (77 %) of **6a** as colorless needles, mp 148 °C. IR (KBr): $\tilde{\nu}$ = 3089 cm^{-1} (w, CH), 1466 (s), 1378 (s), 1133 (m), 1000 (m), 917 (s), 850 (s), 744 (w), 606 (m). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 236 nm (3.58), 332 (sh, 4.26), 342 (4.30), 360 (sh, 4.11). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.75 (s, 2H, 4,4'-H). ^{13}C-NMR ($CDCl_3$, 63 MHz): δ = 161.6 (C-2,2'), 144.9 (C-4,4'), 111.8 (C-5,5'). MS (EI, 70 eV): *m/z* (%) = 326 (92) [M^+], 347 (54) [M^+- ^{79}Br], 345 (53) [M^+- ^{81}Br], 166 (8) [M^+- 2Br], 109 (16) [166^+- C_2HS], 83 (25) [C_3HNS^+], 57 (100) [C_2HS^+]. HRMS calcd for $C_6H_2N_2{}^{79}Br{}^{81}BrS_2$: 325.8006. Found: 325.8007. *Anal.* Calcd for $C_6H_2N_2Br_2S_2$: C, 22.11; H, 0.62; N, 8.59; S, 19.67. Found: C, 22.07; H, 0.67; N, 8.79; S, 19.94.

4,4'-Dibromo-2,2'-bithiazole (6b): To a solution of 2.43 g (10.0 mmol) of 2,4-dibromothiazole (**7**) in dry ether (150 mL) was added dropwise *n*-BuLi (6.3 mL (10.0 mmol) of a 1.6 M solution in *n*-hexane) within 15 min at –78 °C. The mixture was stirred for 1 h at –78 °C, then cooled to –90 °C, and 2.0 g (15.0 mmol) of anhydrous $CuCl_2$ was added. After stirring for 2 h at –78 °C, the suspension was allowed to warm to rt over night and then treated with 2N HCl (100 mL). The organic phase was diluted with $CHCl_3$ (300 mL) and washed several times with aqueous ammonia (12 %). After drying over $MgSO_4$, the solvent was evaporated, and the residue was recrystallized from ethyl acetate to afford 1.12 g (69 %) of **6b** as yellow needles, mp 261-263 °C. IR (KBr): $\tilde{\nu}$ = 3076 cm^{-1} (s, CH), 1444 (s), 1380 (s), 1287 (w), 1264 (s), 1216 (w), 1096 (s), 953 (s), 940 (m), 863 (s), 818 (s), 765 (s). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 232 nm (3.53), 338 (3.95), 352 (sh, 3.83). ^{1}H-NMR (DMSO-d_6, 250 MHz): δ = 8.09 (s, 5,5'-H). ^{13}C-NMR (DMSO-d_6, 91 MHz): δ = 160.2 (C-2,2'), 125.4 (C-4,4'), 121.5 (C-5,5'). MS (EI, 70 eV): *m/z* (%) = 326 (100) [M^+], 247 (2) [M^+- ^{79}Br], 245 (2) [M^+- ^{81}Br], 208 (13) [247^+- CHCN], 206 (13) [245^+- CHCN], 163 (4) [$M^+/2$], 138 (54) [163^+- CN], 136 (56) [163^+- CN], 83 (23) [C_3HNS^+], 57 (86) [C_2HS^+], 45 (57) [CHS^+]. HRMS calcd for $C_6H_2N_2{}^{79}Br{}^{81}BrS_2$: 325.8006. Found: 325.8007. *Anal.* Calcd for $C_6H_2N_2Br_2S_2$: C, 22.10; H, 0.62; N, 8.59; S, 19.67. Found: C, 22.34; H, 0.74; N, 8.58; S, 19.97.

General procedure for the preparation of 2,2'-bithiazolyl-5,5'-dicarbaldehydes (8a,b): To a solution of **5** or **6b** (5.0 mmol) in dry THF (150 mL) was added dropwise *n*-BuLi (6.9 mL (11.0 mmol) of a 1.6 M solution in *n*-hexane) or in the case of **6b** LDA (5.5 mL (11.0 mmol) of a 2.0 M solution in THF) within 15 min at –78 °C. After stirring for 30 min at –78 °C, a solution of 1.38 g (12.0 mmol) of *N*-formylmorpholine in THF (5 mL) was added. After additional 2 h at –78 °C, the mixture was allowed to warm to rt over night, and then hydrolyzed with 2 N HCl (100 mL). The aqueous phase was extracted with methylene chloride (3 × 70 mL). The combined organic phases were washed with water (2 × 40 mL), dried over $MgSO_4$, and the solvent was evaporated. The remaining solid was recrystallized.

2,2'-Bithiazole-5,5'-dicarbaldehyde (8a): Recrystallization from benzene, 0.89 g (80 %) of colorless needles, mp 250-252 °C. IR (KBr): $\tilde{\nu}$ = 3081 cm^{-1} (w, CH), 2863 (w, C*H*O), 1663 (s, CH*O*), 1495 (m), 1395 (m), 1359 (m), 1278 (w), 1226 (s), 1167 (m), 936 (m), 892 (m), 774 (m), 660 (m). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 244 nm (3.92), 266 (3.91), 342 (4.40), 356 (4.45), 372 (sh, 4.27). ^{1}H NMR (DMSO-d_6, 300 MHz): δ = 10.13 (s, 2H, CHO), 8.89 (s, 2H, 4,4'-H). ^{13}C NMR (DMSO-d_6, 76 MHz): δ = 184.5 (CHO), 164.4 (C-2,2'), 153.2 (C-4,4'), 141.4 (C-5,5'). MS (EI, 70 eV): *m/z* (%) = 224 (100) [M^+], 195 (25) [M^+- CHO], 86 (12), 58 (32), 57 (59). HRMS calcd for $C_8H_4N_2O_2S_2$: 223.9714. Found: 223.9715. *Anal.* Calcd for $C_8H_4N_2O_2S_2$: C, 42.84; H, 1.79; N, 12.49; S, 28.59. Found: C, 43.12; H, 1.94; N, 12.53; S, 28.37.

4,4'-Dibromo-2,2'-bithiazole-5,5'-dicarbaldehyde (8b): Recrystallization from *n*-hexane/ethyl acetate (1:1), 1.34 g (70 %) of colorless flakes, mp 241-243 °C. IR (KBr): $\tilde{\nu}$ = 2855 cm^{-1} (w, C*H*O), 1663 (s, CH*O*), 1648 (s, CH*O*), 1460 (s), 1382 (s), 1357 (m), 1314 (w), 1246 (s), 1196 (s), 958 (s), 849 (w). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 240 nm (4.25), 270 (3.83), 360 (sh, 4.29), 374 (4.39), 388 (sh, 4.28). ^{1}H NMR (DMSO-d_6, 250 MHz): δ = 9.98 (s, 2H, CHO). ^{13}C NMR (DMSO-d_6, 91 MHz): δ = 183.4 (CHO), 163.4 (C-2,2'), 135.7 (C), 134.3 (C). MS (EI, 70 eV): *m/z* (%) = 382 (100) [M^+], 353 (10) [M^+- CHO], 236 (6), 137 (46), 135 (40), 57 (55). HRMS calcd for $C_8H_2N_2O_2{}^{79}Br^{81}BrS_2$: 381.7904. Found: 381.7902. *Anal.* Calcd for $C_8H_2N_2O_2Br_2S_2$: C, 25.15; H, 0.53; N, 7.33; S, 16.79. Found: C, 25.25; H, 0.61; N, 7.46; S, 17.08.

General procedure for the alkynylation of the brominated bithiazoles via palladium-catalyzed coupling: Brominated bithiazole (0.5 mmol) was dissolved in a mixture of freshly distilled dry THF (50 mL) and dry diisopropylamin (10 mL). To this clear solution were added dichlorobis(benzonitrile)palladium(II) (78.0 mg, 0.2 mmol), PPh_3 (106.0 mg, 0.4 mmol), and CuI (38 mg, 0.2 mmol). Then an excess of the corresponding acetylene (1.5 equiv. per bromine atom) was added at rt, and the solution was heated under

reflux for 4 h. During this time, the color of the solution turned from bright yellow to dark brown, with a formation of a precipitate. Then the solution was allowed to cool to rt, and filtered. The filtrate was evaporated and the residue was chromatographed.

2,2'-Bis(phenylethynyl)-4,4'-bithiazole (9a): CC (*n*-hexane/$CHCl_3$, 1:2) and recrystallization from *n*-hexane/ethyl acetate (2:1), 110.0 mg (60 %) of colorless flakes, mp 260-262 °C. IR (KBr): $\tilde{\nu}$ = 3120 cm^{-1} (s, CH), 3046 (w, CH), 2211 (w, C≡C), 1495 (s), 1454 (s), 1399 (m), 1279 (m), 1236 (w), 1112 (s), 1053 (s), 756 (s), 689 (s). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 230 nm (4.36), 276 (4.54), 312 (4.52), 336 (sh, 4.27). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.96 (s, 2H, 5,5'-H), 7.63 (m, 4H, phenyl-H), 7.41 (m, 6H, phenyl-H). ^{13}C-NMR ($CDCl_3$, 63 MHz): δ = 150.7 (C), 149.0 (C), 132.1 (CH), 129.7 (CH), 128.5 (CH), 121.3 (C), 117.8 (C-5,5'), 94.5 (C≡C), 82.2 (C≡C). MS (EI, 70 eV): *m/z* (%) = 368 (100) [M^+], 241 (35) [M^+- $C_6H_5C_2CN$], 145 (34) [$C_6H_5C_2CS^+$], 114 (43) [M^+- $2C_6H_5C_2CN$], 70 (22), 69 (26) [114^+- CHS]. HRMS calcd for $C_{22}H_{12}N_2S_2$: 368.0442. Found: 368.0442. *Anal.* Calcd for $C_{22}H_{12}N_2S_2$: C, 71.73; H, 3.28; N, 7.60; S, 17.40. Found: C, 71.50; H, 3.37; N, 7.72; S, 17.70.

2,2',5,5'-Tetrakis(phenylethynyl)-4,4'-bithiazole (9e): CC ($CHCl_3$) and recrystallization from benzene, 194.0 mg (68 %) of yellow needles, mp 241-244 °C (decomp). IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1} (w, CH), 2210 (m, C≡C), 1595 (w), 1497 (s), 1453 (m), 1441 (m), 1288 (w), 1213 (w), 1158 (w), 1103 (m), 1023 (w), 914 (w), 816 (w), 766 (w), 755 (s), 688 (s), 638 (s). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 237 nm (4.65), 318 (4.65), 375 (4.65). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.62-7.53 (m, 8H, phenyl-H), 7.42-7.36 (m, 6H, phenyl-H), 7.31-7.24 (m, 6H, phenyl-H). ^{13}C-NMR ($CDCl_3$, 91 MHz): δ = 150.8 (C-2,2'), 146,8 (C-4,4'), 132.1 (CH), 131.6 (CH), 129.8 (CH), 128.9 (CH), 128.6 (CH), 128.3 (CH), 122.6 (C), 121.3 (C), 119.3 (C-5,5'), 100.7 (C≡C), 94.9 (C≡C), 82.4 (C≡C), 80.2 (C≡C). MS (EI, 70 eV): *m/z* (%) = 568 (100) [M^+], 491 (4) [M^+- C_6H_5], 467 (7) [M^+- $C_6H_5C_2$], 440 (6) [467^+- CN], 284 (2) [$M^+/2$]. HRMS calcd for $C_{38}H_{20}N_2S_2$: 568.1068. Found: 568.1071. *Anal.* Calcd for $C_{38}H_{20}N_2S_2$: C, 80.25; H, 3.54; N, 4.92; S, 11.27. Found: C, 79.92; H, 3.55; N, 4.91; S, 11.51.

5,5'-Bis(phenylethynyl)-2,2'-bithiazole (10a): CC (*n*-hexane/$CHCl_3$, 1:1) and recrystallization from *n*-hexane/ethyl acetate (2:1), 125.0 mg (68 %) of yellow needles, mp 230 °C. IR (KBr): $\tilde{\nu}$ = 3077 cm^{-1} (w, CH), 2199 (m, C≡C), 1502 (s), 1475 (m), 1441 (m), 1387 (m), 923 (s), 866 (s), 756 (s), 684 (s), 610 (s). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 240 nm (4.39), 274 (4.06), 290 (sh, 3.68), 394 (4.63). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.98 (s, 2H, 4,4'-H), 7.55 (m, 4H, phenyl-H), 7.38 (m, 6H, phenyl-H). ^{13}C-NMR ($CDCl_3/CS_2$ (1:1), 91 MHz): δ = 160.5 (C), 147.7 (C-4,4'), 131.6 (CH), 129.2 (CH), 128.5 (CH), 122.1 (C), 121.1 (C), 98.5 (C≡C), 79.1 (C≡C). MS (EI, 70 eV): *m/z* (%) = 368 (100) [M^+], 184 (16) [$M^+/2$], 158

(28) [184$^+$- CN], 145 (14), 114 (42). HRMS calcd for $C_{22}H_{12}N_2S_2$: 368.0442. Found: 368.0442. *Anal.* Calcd for $C_{22}H_{12}N_2S_2$: C, 71.73; H, 3.28; N, 7.60; S, 17.40. Found: C, 71.43; H, 3.29; N, 7.76; S, 17.70.

4,4'-Bis(phenylethynyl)-2,2'-bithiazole (10e): CC ($CHCl_3$) and recrystallization from *n*-hexane/ethyl acetate (2:1), 138.0 mg (75 %) of yellow needles, mp 264-266 °C. IR (KBr): $\tilde{\nu}$ = 3117 cm^{-1} (s, CH), 3045 (w, CH), 2222 (w, C≡C), 1596 (s), 1500 (s), 1469 (m), 1440 (m), 1416 (s), 1300 (w), 1226 (w), 1112 (w), 1068 (w), 981 (w), 885 (s), 756 (s), 689 (s). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 254 nm (4.43), 284 (4.62), 300 (sh, 4.50), 350 (4.11). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.63 (s, 2H, 5,5'-H), 7.61-7.57 (m, 4H, phenyl-H), 7.38-7.35 (m, 6H, phenyl-H). ^{13}C NMR ($CDCl_3$, 91 MHz): δ = 160.3 (C-2,2'), 138.7 (C-4,4'), 131.9 (CH), 128.9 (CH), 128.4 (CH), 124.9 (C-5,5'), 122.1 (C), 89.9 (C≡C), 82.6 (C≡C). MS (EI, 70 eV): *m/z* (%) = 368 (100) [M$^+$], 184 (11) [M$^+$/2], 158 (57) [184$^+$- CN], 114 (33) [$C_4H_2S_2^+$]. HRMS calcd for $C_{22}H_{12}N_2S_2$: 368.0442. Found: 368.0442. *Anal.* Calcd for $C_{22}H_{12}N_2S_2$: C, 71.71; H, 3.28; N, 7.60; S, 17.41. Found: C, 71.73; H, 3.42; N, 7.61; S, 17.60.

2,2'-Bis[(trimethylsilyl)ethynyl]-4,4'-bithiazole (9b): CC (*n*-hexane/ethyl acetate, 1:1) and recrystallization from acetonitrile, 99.2 mg (55 %) of colorless crystals, mp 202-205 °C. IR (KBr): $\tilde{\nu}$ = 3119 cm^{-1} (s, CH), 2958 (s, CH), 2898 (m, CH), 2162 (s, C≡C), 1449 (s), 1414 (w), 1252 (s), 1245 (s), 1226 (m), 1162 (s), 1137 (m), 1055 (s), 977 (w), 839 (s), 792 (s), 761 (s), 735 (s), 702 (m), 640 (s). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 232 nm (sh, 4.31), 254 (4.55), 278 (4.38), 292 (4.36). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.92 (s, 2H, 5,5'-H), 0.34 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C-NMR ($CDCl_3$, 91 MHz): δ = 150.4 (C-2,2'), 148.7 (C-4,4'), 117.7 (C-5,5'), 101.4 (C≡C), 96.4 (C≡C), -0.5 (Si(CH$_3$)$_3$). MS (EI, 70 eV): *m/z* (%) = 360 (100) [M$^+$], 345 (86) (M$^+$- CH$_3$], 237 (16) [M$^+$- C$_2$Si(CH$_3$)$_3$, - CN], 222 (8) [237$^+$- CH$_3$], 165 (41), 97 (8) [C$_2$Si(CH$_3$)$_3^+$], 73 (31) [Si(CH$_3$)$_3^+$], 69 (16) [C$_3$HS$^+$]. HRMS calcd for $C_{16}H_{20}N_2S_2Si_2$: 360.0607. Found: 360.0607. *Anal.* Calcd for $C_{16}H_{20}N_2S_2Si_2$: C, 53.28; H, 5.59; N, 7.76; S, 17.78. Found: C, 52.99; H, 5.59; N, 7.80; S, 18.02.

2,2',5,5'-Tetrakis[(trimethylsilyl)ethynyl]-4,4'-bithiazole (9f): CC (*n*-hexane/ethyl acetate, 20:1) and recrystallization from petroleum ether (40-60), 152.0 mg (55 %) of yellow needles, mp 203 °C. IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1} (s, CH), 2897 (m, CH), 2150 (s, C≡C), 1451 (s), 1404 (m), 1252 (s), 1159 (s), 1144 (s), 841 (s), 782 (s), 757 (s), 738 (m), 700 (m), 642 (w), 628 (m). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 240 nm (4.31), 284 (4.50), 342 (4.45), 354 (sh, 4.37). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 0.24 (s, 36H, Si(CH$_3$)$_3$). ^{13}C-NMR ($CDCl_3$, 91 MHz): δ = 150.9 (C-2,2'), 145.9 (C-4,4'), 118.9 (C-5,5'), 107.1 (C≡C), 101.5 (C≡C), 96.2 (C≡C), 93.8 (C≡C), -0.37 (Si(CH$_3$)$_3$), -0.59 (Si(CH$_3$)$_3$). MS (EI, 70 eV): *m/z* (%) = 552 (75) [M$^+$], 537 (24) [M$^+$- CH$_3$], 479 (53) [M$^+$- Si(CH$_3$)$_3$], 276 (9) [M$^+$/2], 73 (100) [Si(CH$_3$)$_3^+$]. HRMS calcd

for $C_{26}H_{36}N_2S_2Si_4$: 552.1397. Found: 552.1399. *Anal.* Calcd for $C_{26}H_{36}N_2S_2Si_4$: C, 56.47; H, 6.56; N, 5.06; S, 11.59. Found: C, 56.56; H, 6.65; N, 5.01; S, 11.43.

5,5'-Bis[(trimethylsilyl)ethynyl]-2,2'-bithiazole (10b): CC (*n*-hexane/ethyl acetate, 5:1) and recrystallization from acetonitrile,122.6 mg (68 %) of colorless flakes, mp 166-168 °C. IR (KBr): $\tilde{\nu}$ = 3088 cm^{-1} (w, CH), 2957 (m, CH), 2897 (w, CH), 2149 (m, C≡C), 1480 (s), 1411 (w), 1377 (s), 1283 (m), 1252 (s), 1244 (s), 1178 (w), 1157 (m), 924 (s), 842 (s), 759 (s), 733 (m), 699 (m), 640 (m). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 258 nm (sh, 3.92), 364 (sh, 4.47), 376 (4.53), 390 (sh, 4.39). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.88 (s, 2H, 4,4'-H), 0.25 (s, 18H, $Si(CH_3)_3$). ^{13}C-NMR ($CDCl_3$, 91 MHz): δ = 160.4 (C-2,2'), 148.4 (C-4,4'), 121.4 (C-5,5'), 105.3 (C≡C), 93.3 (C≡C), -0.3 ($Si(CH_3)_3$). MS (EI, 70 eV): *m/z* (%) = 360 (100) [M^+], 345 (83) [M^+- CH_3], 165 (30), 139 (6). HRMS calcd for $C_{16}H_{20}N_2S_2Si_2$: 360.0607. Found: 360.0607. *Anal.* Calcd for $C_{16}H_{20}N_2S_2Si_2$: C, 53.28; H, 5.58; N, 7.76; S, 17.78. Found: C, 52.99; H, 5.58; N, 7.70; S, 18.05.

4,4'-Bis[(trimethylsilyl)ethynyl]-2,2'-bithiazole (10f): CC (*n*-hexane/$CHCl_3$, 5:1) and recrystallization from acetonitrile,126.0 mg (70 %) of colorless flakes, mp 257-259 °C. IR (KBr): $\tilde{\nu}$ = 3106 cm^{-1} (m, CH), 2957 (m, CH), 2898 (w, CH), 2166 (m, C≡C), 1512 (w), 1468 (s), 1427 (w), 1406 (m), 1275 (m), 1253 (s), 1245 (s), 1149 (m), 983 (s), 882 (s), 867 (s), 842 (s), 757 (s), 722 (w). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 238 nm (4.68), 240 (sh, 4.63), 324 (sh, 3.97), 343 (4.12), 354 (sh, 4.03). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.57 (s, 2H, 5,5'-H), 0.27 (s, 18H, $Si(CH_3)_3$). ^{13}C-NMR ($CDCl_3$, 91 MHz): δ = 159.9 (C-2,2'), 138.5 (C-4,4'), 125.8 (C-5,5'), 97.4 (C≡C), 95.9 (C≡C), -0.3 ($Si(CH_3)_3$). MS (EI, 70 eV): *m/z* (%) = 360 (99) [M^+], 345 (100) [M^+- CH_3], 191 (5), 165 (28), 139 (17), 107 (7), 73 (16) [$Si(CH_3)_3^+$]. HRMS calcd for $C_{16}H_{20}N_2S_2Si_2$: 360.0607. Found: 360.0607. *Anal.* Calcd for $C_{16}H_{20}N_2S_2Si_2$: C, 53.28; H, 5.58; N, 7.76; S, 17.78. Found: C, 53.01; H, 5.69; N, 7.70; S, 17.69.

2,2'-Bis(3-hydroxyprop-1-ynyl)-4,4'-bithiazole (9c): CC (ethyl acetate/methanol, 20:2) and recrystallization from ethyl acetate/methanol, 75.0 mg (54 %) of colorless needles, mp 259 °C (decomp). IR (KBr): $\tilde{\nu}$ = 3407 cm^{-1} (m, OH), 3259 (s, OH), 3107 (s, CH), 2226 (w, C≡C), 1466 (s), 1362 (m), 1253 (w), 1228 (w), 1200 (s), 1080 (m), 1034 (s), 761 (w), 642 (w). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 232 nm (sh, 3.94), 248 (4.08), 276 (sh, 3.91), 284 (sh, 3.87), 290 (sh, 3.85). ^{1}H-NMR (DMSO-d_6, 250 MHz): δ = 8.14 (s, 2H, 5,5'-H), 5.56 (t, ^3J = 6.12 Hz, 2H, -OH), 4.39 (d, ^3J = 6.12 Hz, 4H, -CH_2OH). ^{13}C-NMR (DMSO-d_6, 91 MHz): δ = 149.5 (C), 147.9 (C), 118.8 (C-5,5'), 95.4 (C≡C), 76.7 (C≡C), 49.3 (CH_2OH). MS (EI, 70 eV): *m/z* (%) = 276 (100) [M^+], 247 (12), 195 (11) [M^+- C_4H_3NO], 114 (18) [$C_4H_2S_2^+$], 70

(16), 69 (25) [C_3HS^+]. HRMS calcd for $C_{12}H_8N_2O_2S_2$: 276.0027. Found: 276.0027. *Anal.* Calcd for $C_{12}H_8N_2O_2S_2$: C, 52.16; H, 2.92; N, 10.14; S, 23.21. Found: C, 51.91; H, 3.19; N, 10.02; S, 23.59.

5,5'-Bis(3-hydroxyprop-1-ynyl)-2,2'-bithiazole (10c): CC (ethyl acetate) and recrystallization from toluene, 50.0 mg (36 %) of colorless crystals, mp 200-203 °C (decomp). IR (KBr): $\tilde{\nu}$ = 3361 cm^{-1} (s, OH), 3244 (s, OH), 3078 (m, CH), 2219 (w, C≡C), 1495 (s), 1451 (w), 1414 (m), 1387 (s), 1289 (m), 1153 (m), 1026 (s), 935 (m), 854 (m), 762 (w), 669 (w). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 355 nm (4.35), 369 (4.42), 385 (4.27). ^{1}H-NMR (DMSO-d_6, 250 MHz): δ = 8.16 (s, 2H, 4,4'-H), 5.51 (t, ^3J = 6.0 Hz, 2H, -OH), 4.38 (d, ^3J = 6.0 Hz, -CH_2OH). ^{13}C NMR (DMSO-d_6, 91 MHz): δ = 159.4 (C-2,2'), 148.2 (C-4,4'), 120.4 (C-5,5'), 99.6 (C≡C), 72.9 (C≡C), 49.5 (CH_2OH). MS (EI, 70 eV): m/z (%) = 276 (100) [M^+], 259 (6) [M^+- OH], 182 (10), 138 (8) [M^+/2], 112 (25) [$C_4S_2^+$]. HRMS calcd for $C_{12}H_8N_2O_2S_2$: 276.0027. Found: 276.0027. *Anal.* Calcd for $C_{12}H_8O_2N_2S_2$: C, 52.16; H, 2.92; N, 10.14; S, 23.21. Found: C, 52.33; H, 3.16; N, 9.85; S, 22.87.

4,4'-Bis(3-hydroxyprop-1-ynyl)-2,2'-bithiazole (10g): CC (ethyl acetate/methanol, 20:1) and recrystallization from ethyl acetate, 55.0 mg (40 %) of colorless crystals, mp 280-283 °C (decomp). IR (KBr): $\tilde{\nu}$ = 3341 cm^{-1} (s, OH), 3063 (s, CH), 2912 (m, CH), 1485 (s), 1437 (w), 1404 (m), 1355 (s), 1221 (w), 1039 (s), 1016 (s), 965 (m), 925 (m), 882 (m), 828 (w), 806 (m). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 341 nm (3.15). ^{1}H-NMR (DMSO-d_6, 250 MHz): δ = 8.15 (s, 2H, 5,5'-H), 5.43 (t, ^3J = 6.0 Hz, 2H, OH), 4.33 (d, ^3J = 6.0 Hz, 4H, -CH_2OH). ^{13}C-NMR (DMSO-d_6, 91 MHz): δ = 159.5 (C-2,2'), 137.2 (C-4,4'), 126.6 (C-5,5'), 90.1 (C≡C), 77.5 (C≡C), 49.2 (CH_2OH). MS (EI, 70 eV): *m/z* (%) = 276 (100) [M^+], 247 (30), 229 (16), 219 (6), 135 (12), 111 (11), 95 (41), 83 (18), 69 (17), 58 (18), 51 (25), 45 (34), 43 (20). HRMS calcd for $C_{12}H_8N_2O_2S_2$: 276.0027. Found: 276.0027. *Anal.* Calcd for $C_{12}H_8N_2O_2S_2$: C, 52.16; H, 2.92; N, 10.14; S, 23.21. Found: C, 52.30; H, 3.10; N, 10.12; S, 23.43.

General procedure for the preparation of 4,4'-diethynyl-2,2'-bithiazolyl-5,5'-dicarbaldehydes (11a,b): To a solution of **10e,f** (1.0 mmol) in dry THF (50 mL) was added dropwise *n*-BuLi (1.3 mL (2.1 mmol) of a 1.6 M solution in *n*-hexane) within 15 min at –78 °C. After stirring for 30 min at –78 °C, a solution of 254.0 mg (2.2 mmol) of *N*-formylmorpholine in THF (5 mL) was added. After additional 2 h at –78 °C, the mixture was allowed to warm to rt within 6 h, and then poured into saturated aqueous NH_4Cl solution (100 mL). The aqueous phase was extracted with methylene chloride (3 × 70 mL). The combined organic phases were washed with water (3 × 40 mL), dried over $MgSO_4$, and the solvent was evaporated. The remaining solid was recrystallized.

4,4'-Bis(phenylethynyl)-2,2'-bithiazolyl-5,5'-dicarbaldehyde (11a): Recrystallization from toluene, 297.0 mg (70 %) of yellow flakes, mp 316 °C (decomp). IR (KBr): $\tilde{\nu}$ = 3048 cm^{-1} (w, CH), 2833 (w, C*H*O), 2208 (m, C≡C), 1663 (s, CH*O*), 1500 (m), 1470 (m), 1443 (m), 1400 (m), 1334 (m), 1213 (m), 1185 (m), 911 (w), 748 (m), 681 (m). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 230 nm (4.28), 292 (sh, 4.62), 306 (4.64), 388 (4.21). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 10.32 (s, 2H, CHO), 7.68-7.64 (m, 4H, phenyl-H), 7.46-7.42 (m, 6H, phenyl-H). ^{13}C-NMR ($CDCl_3/CF_3CO_2D$ (1:1), 63 MHz): δ = 186.3 (CHO), 165.5 (C-2,2'), 148.0 (C), 140.4 (C), 132.6 (CH), 131.2 (CH), 129.0 (CH), 100.4 (C≡C), 79.1 (C≡C). MS (EI, 70 eV): *m/z* (%) = 424 (73) [M^+], 396 (7) [M^+- CHO], 212 (3) [M^+/2], 185 (31), 158 (100), 114 (50) [$C_4H_2S_2^+$], 102 (26) [$C_8H_6^+$]. HRMS calcd for $C_{24}H_{12}N_2O_2S_2$: 424.0340. Found: 424.0342. *Anal.* Calcd for $C_{24}H_{12}N_2O_2S_2$: C, 67.91; H, 2.85; N, 6.59; S, 15.10. Found: C, 67.97; H, 3.07; N, 6.56; S, 15.33.

4,4'-Bis[(trimethylsilyl)ethynyl]-2,2'-bithiazolyl-5,5'-dicarbaldehyde (11b): Recrystallization from petroleum ether (bp 40-60), 325.0 mg (78 %) of yellow needles, mp 249-250 °C. IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1} (m, CH), 2900 (m, CH), 2853 (w, C*H*O), 2159 (w, C≡C), 1683 (s, CH*O*), 1472 (s), 1396 (m), 1370 (m), 1315 (s), 1253 (s), 1194 (s), 1041 (s), 890 (s), 849 (s), 718 (m), 662 (m). UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 268 (4.76), 377 (4.32), 397 (4.21). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 10.19 (s, 2H, CHO), 0.33 (s, 18H, $Si(CH_3)_3$). ^{13}C-NMR ($CDCl_3$, 91 MHz): δ = 182.7 (CHO), 164.0 (C), 144.9 (C), 142.5 (C), 104.7 (C≡C), 94.6 (C≡C), -0.6 ($Si(CH_3)_3$). MS (EI, 70 eV): *m/z* (%) = 416 (95) [M^+], 401 (100) [M^+- CH_3], 387 (8) [M^+- CHO], 372 (10) [M^+- CHO, -CH_3], 219 (22), 193 (21), 139 (67), 109 (14), 95 (11), 73 (43) [$Si(CH_3)_3^+$]. HRMS calcd for $C_{18}H_{20}N_2O_2S_2Si_2$: 416.0505. Found: 416.0505. *Anal.* Calcd for $C_{18}H_{20}N_2O_2S_2Si_2$: C, 51.89; H, 4.84; N, 6.72; S, 15.39. Found: C, 51.79; H, 4.88; N, 6.80; S, 15.69.

General procedure for the removal of $SiMe_3$ protecting groups. To a suspension of poly[trimethylsilyl-ethynyl]bithiazoles (0.4 mmol) in deoxygenated methanol (50 mL) was added saturated aqueous K_2CO_3 solution (0.5 mL). The mixture was stirred for 30 min at rt. The solution was diluted with methylene chloride (100 mL), washed several times with water, dried over $MgSO_4$, and concentrated under reduced pressure. The remaining solid was recrystallized.

2,2'-Diethynyl-4,4'-bithiazole (9d): Recrystallization from nitromethane, 78.0 mg (90 %) of colorless needles, mp 170-175 °C (decomp). IR (KBr): $\tilde{\nu}$ = 3188 cm^{-1} (s, C≡CH), 3116 (s, CH), 2102 (m, C≡C), 1454 (s), 1248 (w), 1151 (s), 1131 (m), 1064 (m), 789 (m), 752 (s), 684 (m). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.91 (s, 2H, 5,5'-H), 3.53 (s, 2H, C≡CH). ^{13}C-NMR ($CDCl_3$, 63 MHz): δ = 150.4 (C-2,2'), 147.8 (C-4,4'), 118.0 (C-5,5'), 82.6 (C≡*C*H), 76.3 (*C*≡CH). MS (EI, 70 eV): *m/z* (%) = 216 (100) [M^+], 165 (30) [M^+- CN, -C_2H]), 114 (34) [$C_2H_2S_2^+$], 70 (26), 69 (50) [114^+- CHS], 45 (10) [CHS^+]. HRMS

calcd for $C_{18}H_{12}N_4S_2$: 215.9814. Found: 215.9815.

2,2',5,5'-Tetraethynyl-4,4'-bithiazole (9g): Yield: 85.0 mg (80 %) of brown crystals, mp 85 °C (decomp). IR (KBr): $\tilde{\nu}$ = 3294 cm^{-1} (s, C≡C*H*), 3220 (m, C≡C*H*), 2103 (m, C≡C), 1451 (s), 1138 (s), 783 (m), 700 (w), 668 (s), 618 (s). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 3.66 (s, 2H, C≡CH), 3.51 (s, 2H, C≡CH). ^{13}C-NMR ($CDCl_3$, 91 MHz): δ = 150.8 (C-2,2'), 146.3 (C-4,4'), 118.8 (C-5,5'), 89.0 (C≡*C*H), 83.4 (C≡*C*H), 75.7 (*C*≡CH); 73.0 (*C*≡CH). MS (EI, 70 eV): *m/z* (%) = 264 (100) [M^+], 240 (11), 213 (11), 169 (10), 93 (20), 83 (16). HRMS calcd for $C_{14}H_4N_2S_2$: 263.9814. Found: 263.9815.

5,5'-Diethynyl-2,2'-bithiazole (10d): Recrystallization from nitromethane, 76.0 mg (88 %) of colorless needles, mp 125-126 °C (decomp). IR (KBr): $\tilde{\nu}$ = 3295 cm^{-1} (s, C≡C*H*), 3194 (s, CH), 2095 (w, C≡C), 1482 (s), 1374 (s), 1155 (s), 932 (s), 880 (m), 866 (s), 764 (s), 685 (s), 675 (m), 607 (s). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.96 (s, 2H, 4,4'-H), 3.57 (s, 2H, C≡CH). ^{13}C-NMR ($CDCl_3$, 91 MHz): δ = 160.8 (C-2,2'), 148.8 (C-4,4'), 120.3 (C-5,5'), 86.5 (C≡*C*H), 73.1 (*C*≡CH). MS (EI, 70 eV): *m/z* (%) = 216 (79) [M^+], 82 (100) [C_3NS^+], 81 (26), 70 (13), 69 (25). HRMS calcd for $C_{18}H_{12}N_4S_2$: 215.9814. Found: 215.9815.

4,4'-Diethynyl-2,2'-bithiazole (10h): Recrystallization from methanol, 42.0 mg (48 %) of colorless needles, mp 192-193 °C (decomp). IR (KBr): $\tilde{\nu}$ = 3218 cm^{-1} (s, C≡C*H*), 3114 (s, CH), 2112 (C≡C), 1469 (s), 1403 (m), 1282 (w), 1133 (w), 986 (2), 890 (s), 761 (s), 746 (m). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 7.62 (s, 2H, 5,5'-H), 3.18 (s, 2H, C≡CH). ^{13}C-NMR ($CDCl_3$, 91 MHz): δ = 160.1 (C-2,2'), 137.5 (C-4,4'), 126.2 (C-5,5'), 78.2 (C*C*H), 76.9 (*C*CH). MS (EI, 70 eV): *m/z* (%) = 216 (98) [M^+], 166 (2) [M^+- $2C_2H$], 108 (4) [M^+/2], 82 (100) [$C_3NS]^+$. HRMS calcd for $C_{10}H_4N_2S_2$: 215.9816. Found: 215.9815.

4,4'-Diethynyl-2,2'-bithiazolyl-5,5'-dicarbaldehyde (11c): Recrystallization from toluene, 92.0 mg (85 %) of colorless flakes, mp 175 °C (decomp). IR (KBr): $\tilde{\nu}$ = 3249 cm^{-1} (s, C≡C*H*), 2849 (w, C*H*O), 2115 (m, C≡C), 1660 (s, CH*O*), 1475 (s), 1395 (m), 1317 (s), 1205 (s), 1022 (s), 700 (m), 694 (m). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 10.22 (s, 2H, CHO), 3.61 (s, 2H, C≡CH). ^{13}C-NMR ($CDCl_3$, 63 MHz): δ = 182.3 (CHO), 164.1 (C-2,2'), 143.8 (C), 143.5 (C), 85.1 (C≡*C*H), 74.6 (C≡*C*H). MS (EI, 70 eV): *m/z* (%) = 272 (80) [M^+], 110 (80) [$C_5H_2SO^+$], 82 (100) [110^+- CO], 81 (92) [110^+- CHO]. HRMS calcd for $C_{12}H_4N_2O_2S_2$: 271.9714. Found: 271.9714.

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