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A facile S-transalkylation of 2,2′-bipyridine alkyl sulfides—a new tool for the synthesis of annulated biheterocycles☆

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Abstract—A simple and efficient synthesis of annulated 2,2′-bipyridinium salts with attached dihydrothiazole or dihydro-1,3-thiazine rings has been developed through tandem S-transalkylation/intramolecular ring closure of 2,2′-bipyridine alkyl sulfides. The structures were confirmed by X-ray crystallographic analysis.

2,2′-Bipyridine and its fused analogues have been shown to exhibit important applications in coordination and supramolecular chemistry.[1] Also the diquaternary 2,2′-bipyridinium salts such as diquat dibromide (Fig. 1, R = H) have aroused much interest owing to their valuable herbicidal activity.[2]

Although a great variety of substituted diquaternary 2,2′-bipyridinium salts have been prepared and tested as herbicides,[3] the chemistry of their condensed derivatives with attached cycloalkene rings has received little attention. During the course of our investigations into symmetrical and unsymmetrical cycloalkeno[*c*]fused 2,2′-bipyridine alkyl sulfides,[4a–g] we became interested in the synthesis of their bridged diquaternary salts by reaction with 1,2- or 1,3-dihalides. Herein, we wish to report the finding that the reaction between 2,2′-bipyridines (**2a**,**b**) and symmetrical or unsymmetrical cycloalkeno[*c*]fused 2,2′-bipyridines (**5a**–**e**) and (**7a**–**d**) containing alkylsulfanyl functionalities at the α and α′ positions, and 1,2-dibromoethane or 1,3-dibromopropane takes a different course, not leading to the formation of the corresponding diquat derivatives (Fig. 1, R = SCH_3), but to annulated 2,2′-bipyridinium salts **4**, **6** and **8** in synthetically useful yields (see Scheme 1).

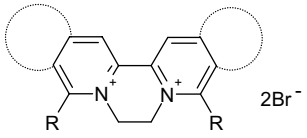

Figure 1. Diquat and its annulated analogues.

The required 2,2′-bipyridines **2a**,**b**, **5a**–**e** and **7a**–**d** are directly available from the Diels–Alder reaction of 3,3′-dimethylsulfanyl-5,5′-bi-1,2,4-triazine **1**, and norbornadiene or cyclic enamines according to our published methods.[4c,g] When **2a** (R = CH_3) was treated with an excess of 1,2-dibromoethane (**3a**) under reflux for 25 h, 2,2′,3,3′-tetrahydro-5,5′-bithiazolo[3,2-*a*]pyridinium dibromide **4a** ($n = 1$) was obtained in 69% yield. The formation of **4a** by the reaction of **2b** [R = $CH(CH_3)_2$] with **3a** was less favourable, and needed more time (90 h) for completion. The reaction of **2a** with 1,3-dibromopropane (**3b**) proceeded in the same manner giving the corresponding 3,3′4,4′-tetrahydro-2*H*,2*H*′-6,6′-bipyrido-[2,1-*b*][1,3]thiazinium dibromide (**4b**) ($n = 2$). Also symmetrical and unsymmetrical cycloalkeno[*c*]-fused 2,2′-bipyridines (**5a**–**e**) reacted efficiently with **3a** and **3b** giving dimeric dihydrothiazolopyridinium dibromides **6a**–**e** ($n = 1$) or pyridodihydro-1,3-thiazinium dibromides **6f**–**j** ($n = 2$) in excellent yields. Extending this study by using mixed 2,2′-bipyridines **7a**–**d** consisting of two different heterocyclic units, clearly showed the generality of this reaction, since unsymmetrical diquaternary bipyridinium salts **8a**–**d** were obtained in good yields (Scheme 1 and Table 1).

Keywords: S-Transalkylation; Annulated diquaternary 2,2′-bipyridinium salts.

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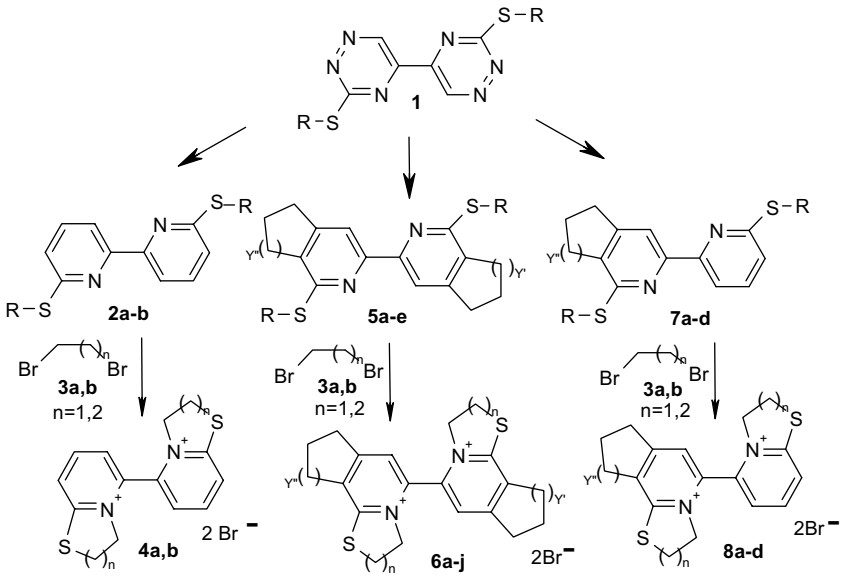


Scheme 1. Synthesis of annulated 2,2′-bipyridinium salts.

Table 1. Synthesis of 2,2′-bipyridinium salts with attached dihydrothiazole or dihydro-1,3-thiazine rings

No.	*Y*	*Y′*	*n*	Time (h)	Yield (%)	Mp (°C)
4a	—	—	1	25	69	360[a]
4b	—	—	2	13	64	313[a]
6a	1	1	1	6	84	274[a]
6b	2	2	1	14	94	315[a]
6c	3	3	1	10	86	289[a]
6d	4	4	1	14	82	252[a]
6e	3	4	1	21	96	235[a]
6f	3	4	2	21	94	285[a]
6g	1	1	2	12	90	304[a]
6h	2	2	2	16	89	266[a]
6i	3	3	2	12	96	291[a]
6j	4	4	2	12	89	244[a]
8a	3	—	1	36	95	334[a]
8b	4	—	1	37	96	339[a]
8c	1	—	2	32	88	240[a]
8d	2	—	2	32	96	235[a]

[a] Decomposition.

Evidence for the structures of **4a**,**b** and their condensed analogues **6a**–**j** and **8a**–**d** was provided by ^{1}H NMR and HR-ESI spectroscopy.[5] The structures of **4a**,**b** were fully determined by X-ray crystallographic analysis.[6] The X-ray investigation suggested that the positive charges in **4a** and **4b** are strongly localized at the N1 atoms and rather slightly delocalized in the N11–C16–S17 areas. The pyridine rings in both molecules are twisted relative to each other by 69.7(2)° and 75.1(2)° for **4a** and **4b**, respectively (Figs. 2 and 3). This conformation is constrained by electrostatic repulsion between positive charges at the adjacent pyridine rings and steric interaction of the hydrogen atoms from the methylene groups. Distortions of the ring geometries are comparable with those in other 2,2′-bipyridinium compounds.[7]

Mechanistically, the formation of the 2,2′-bipyridinium dibromides **4a**,**b** and their annulated analogues by the reaction of **2a** with 1,2-dibromoethane (**3a**) or 1,3-dibromopropane (**3b**) is thought to proceed via the reactive sulfonium salts **9a**,**b** followed by demethylation of

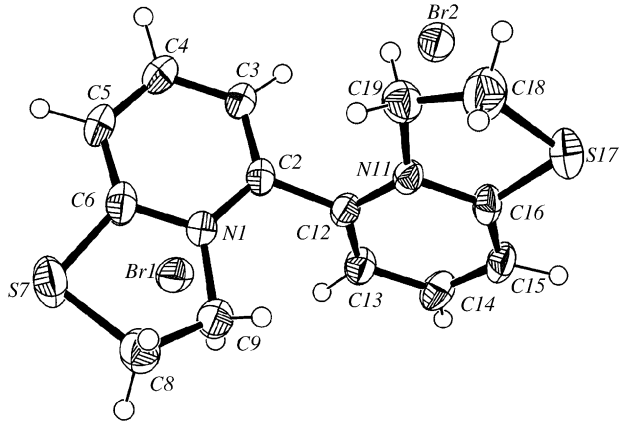


Figure 2. X-ray of 2,2′3,3′-tetrahydro-[5,5′]bithiazolo[3,2-*a*]pyridinium dibromide **4a**.

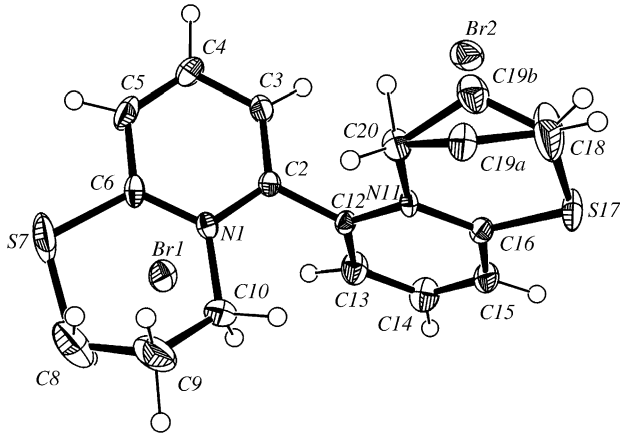
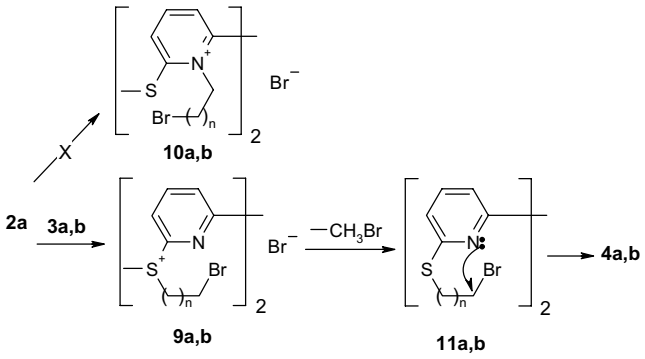
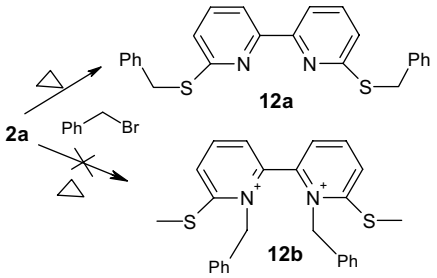


Figure 3. X-ray of 3,3′,4,4′-tetrahydro-2*H*,2*H*′-[6,6′]-bipyrido[2,1-*b*]-1,3-thiazinium dibromide **4b**.



Scheme 2. A proposed mechanism for the S-transalkylation reaction.



Scheme 3. S-Transalkylation of 2,2′-bipyridine methylsulfide with benzyl bromide.

the resulting intermediates.[8] This leads to 6,6′-bis(2-bromoethylsulfanyl)-2,2′-bipyridine (**11a**) or 6,6′-bis(3-bromopropylsulfanyl)-2,2′-bipyridine (**11b**). Cyclization of the latter compounds involving nucleophilic replacement of the bromine by the ring nitrogen afforded **4a** and **4b**, respectively (see Scheme 2).

It is reasonable to assume that the formation of the sulfonium salts **9a**,**b** occurs in preference to the pyridinium salts **10a**,**b** as a consequence of the enhanced nucleophilicity of sulfur and the higher affinity of a sulfide group for soft electrophiles in comparison with the ring nitrogen.[9] To prove this, compound **2a** ($R = CH_3$) was refluxed with benzyl bromide for 2 h. Under these conditions no trace of bipyridinium dibromide **12b** was observed; compound **2a** formed the corresponding 6,6′-bis-(benzylsulfanyl)-2,2′-bipyridine **12a**, exclusively (Scheme 3).

In summary we have prepared several annulated diquaternary, 2,2′-bipyridinium salts containing dihydrothiazine and dihydro-1,3-thiazole rings by tandem reactions between the corresponding 2,2′-bipyridine alkyl sulfides and 1,2- or 1,3-dihalides. The ease and efficiency of this approach makes it an attractive process for the preparation of functionalized biheterocycles and macrocycles.

Acknowledgements

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5. General procedure for the synthesis of compounds **4a**–**b**, **6a**–**j** and **8a**–**d**. A solution of the 2,2′-bipyridine derivative (1 mmol) in 1,2-dibromoethane or 1,3-dibromopropane (2 ml) was heated at 136–140 °C for a number of hours as indicated in Table 1. After cooling, the precipitated solid was filtered off and washed with diethyl ether. The crude products **4a**–**b** were recrystallized from methanol to give light yellow solids. The crude products **6a**–**j** and **8a**–**d** were recrystallized from dichloromethane/methanol mixtures.
Compound **4a** mp 360 °C; IR (KBr) cm^{-1} 1107, 1455, 1560, 2970, 3403. ^1H NMR (D_2O, 200 MHz) δ (ppm) 3.95 (t, $2\times2H$, $J = 8.3$ Hz), 4.99–5.14 (m, $2\times2H$), 7.95 (dd, $2\times1H$, $J = 1.0$, 7.7 Hz), 8.28 (dd, $2\times1H$, $J = 1.0$, 8.0 Hz), 8.49 (t, $2\times1H$, $J = 8.1$ Hz); ^{13}C NMR (D_2O, 50 MHz) δ (ppm) 31.77, 62.48, 127.54, 128.61, 143.47, 147.37, 167.78; HR-ESI calcd for $C_{14}H_{14}N_2S_2$ 274.0587; found 274.0562.
Compound **4b** mp 313 °C; IR (KBr) cm^{-1} 1107, 1455, 1560, 2970, 3406. ^1H NMR (D_2O, 200 MHz) δ (ppm) 2.48 (quin, $2\times2H$, $J = 6.0$ Hz), 3.46 (t, $2\times2H$, $J = 6.3$ Hz), 4.22–4.45 (m, $2\times2H$), 7.79 (dd, $2\times1H$, $J = 1.4$, 7.4 Hz), 8.10 (dd, $2\times1H$, $J = 1.6$, 8.6 Hz), 8.26 (t, $2\times1H$, $J = 7.6$ Hz); ^{13}C NMR (D_2O, 50 MHz) δ (ppm) 20.91, 27.41, 53.36, 126.00, 131.10, 141.80, 143.90, 162.10; HR-ESI calcd for $C_{16}H_{18}N_2S_2$ 302.0900; found 302.0902.
Compound **6a** mp 274 °C; IR (KBr) cm^{-1} 1207, 1459, 1557, 1601, 2943, 3445. ^1H NMR (D_2O, 200 MHz) δ (ppm) 2.45 (quin, $2\times2H$, $J = 7.7$ Hz), 3.13 (t, $2\times2H$, $J = 7.6$ Hz), 3.30 (t, $2\times2H$, $J = 7.6$ Hz), 3.92 (t, $2\times2H$, $J = 7.5$ Hz), 4.80–5.05 (m, $2\times2H$), 7.79 (s, $2\times1H$); HR-ESI calcd for $C_{20}H_{22}N_2S_2$ 354.1213 found 354.1222.
Compound **6b** mp 315 °C; IR (KBr) cm^{-1} 1211,1447, 1556, 1596, 2937, 3443. ^1H NMR (D_2O, 200 MHz) δ (ppm) 1.72–1.96 (m, $4\times2H$), 2.68 (t, $2\times2H$, $J = 7.4$ Hz), 2.93 (t, $2\times2H$, $J = 7.5$ Hz), 3.77 (t, $2\times2H$, $J = 7.6$ Hz), 4.72–4.98 (m, $2\times2H$), 7.51 (s, $2\times1H$); HR-ESI calcd for $C_{22}H_{26}N_2S_2$ 382.1526 found 382.1552.
Compound **6c** mp 289 °C; IR (KBr) cm^{-1} 1221, 1444, 1553, 1595, 2926, 3400. ^1H NMR (D_2O, 200 MHz) δ (ppm)

2.05–2.15 (m, 2 × 2H), 2.15–2.21 (m, 2 × 2H), 2.65–2.80 (m, 2 × 2H), 3.22–3.36 (m, 2 × 2H), 3.42 (t, 2 × 2H, $J = 4.5$ Hz), 3.61 (t, 2 × 2H, $J = 5.5$ Hz), 4.18–4.28 (m, 2 × 2H), 7.07 (s, 2 × 1H); HR-ESI calcd for $C_{24}H_{30}N_2S_2$ 438.2128; found 438.2168.

Compound **6d** mp 252 °C; IR (KBr) cm^{-1} 1235, 1453, 1552, 1559, 2921, 3400. ^1H NMR (D_2O, 200 MHz) δ (ppm) 1.15–1.28 (m, 4 × 2H), 1.78–2.15 (m, 4 × 2H), 3.07 (q, 4 × 2H, $J = 6.2$ Hz), 3.88 (t, 2 × 2H, $J = 7.5$ Hz), 4.82–5.15 (m, 2 × 2H), 7.73 (s, 2 × 1H); HR-ESI calcd for $C_{26}H_{34}N_2S_2$ 438.2152; found 438.2150.

Compound **6e** mp 235 °C; IR (KBr) cm^{-1} 1205, 1453, 1550, 1559, 2920, 3405. ^1H NMR (D_2O, 200 MHz) δ (ppm) 1.10–1.25 (m, 2 × 2H), 1.30–1.45 (m, 5 × 2H), 2.48–2.58 (m, 4 × 2H), 3.28–3.43 (m, 2 × 2H), 4.40–4.58 (m, 2 × 2H), 7.22 (s, 1H), 7.25 (s, 1H); HR-ESI calcd for $C_{25}H_{32}N_2S_2$ 424.1996; found 424.2010.

Compound **6f** mp 285 °C; IR (KBr) cm^{-1} 1235, 1450, 1552, 1559, 2921, 3400. ^1H NMR (D_2O, 200 MHz) δ (ppm) 1.12–1.22 (m, 2 × 2H), 1.30–1.55 (m, 5 × 2H), 1.95–2.05 (m, 2 × 2H), 2.45–2.55 (m, 2 × 2H), 2.57–2.70 (m, 2 × 2H), 2.90–3.05 (m, 2 × 2H), 3.80–4.05 (m, 2 × 2H), 7.23 (s, 1H), 7.35 (s, 1H); HR-ESI calcd for $C_{27}H_{36}N_2S_2$ 452.2309; found 452.2326.

Compound **6g** mp 304 °C; IR (KBr) cm^{-1} 1206, 1429, 1559, 1563, 2932, 3487. ^1H NMR (D_2O, 200 MHz) δ (ppm) 2.20–2.39 (m, 4 × 2H), 2.99 (t, 2 × 2H, $J = 7.6$ Hz), 3.15 (t, 2 × 2H, $J = 7.6$ Hz), 3.35 (t, 2 × 2H, $J = 6.2$ Hz), 4.08–4.22 (m, 2 × 2H), 7.56 (s, 2 × 1H); HR-ESI calcd for $C_{22}H_{26}N_2S_2$ 382.1526; found 382.1552.

Compound **6h** mp 266 °C; IR (KBr) cm^{-1} 1248, 1420, 1556, 1602, 2934, 3441. ^1H NMR (D_2O, 200 MHz) δ (ppm) 1.75–1.90 (m, 2 × 4H), 2.27–2.33 (m, 2 × 2H), 2.70 (t, 2 × 2H, $J = 6.0$ Hz), 2.88 (t, 2 × 2H, $J = 6.0$ Hz), 3.34 (t, 2 × 2H, $J = 6.4$ Hz), 4.01–4.18 (m, 2 × 2H), 7.42 (s, 2 × 1H); HR-ESI calcd for $C_{24}H_{30}N_2S_2$ 410.1815; found 410.1848.

Compound **6i** mp 291 °C; IR (KBr) cm^{-1} 1206, 1429, 1566, 1604, 2989, 3431. ^1H NMR (D_2O, 200 MHz) δ (ppm) 1.50–1.70 (m, 4 × 2H), 1.75–1.90 (m, 2 × 2H), 2.20–2.30 (m, 2 × 2H), 2.85–2.98 (m, 2 × 2H), 3.07 (t, 2 × 2H, $J = 5.8$ Hz), 3.27 (t, 2 × 2H, $J = 6.8$ Hz), 4.02–4.20 (m, 2 × 2H), 7.44 (s, 2 × 1H); HR-ESI calcd for $C_{26}H_{34}N_2S_2$ 438.2152; found 438.2160.

Compound **6j** mp 244 °C; IR (KBr) cm^{-1} 1125, 1453, 1552, 1599, 2920, 3458. ^1H NMR (D_2O, 200 MHz) δ (ppm) 1.21–1.43 (m, 4 × 2H), 1.58–1.85 (m, 4 × 2H), 2.28–2.38 (m, 2 × 2H), 2.94 (t, 2 × 2H, $J = 5.6$ Hz), 3.11 (t, 2 × 2H, $J = 5.2$ Hz), 3.34 (t, 2 × 2H, $J = 6.6$ Hz), 4.10–4.25 (m, 2 × 2H), 7.55 (s, 2 × 1H); HR-ESI calcd for $C_{28}H_{38}N_2S_2$ 466.2465; found 466.2490.

Compound **8a** mp 334 °C; IR (KBr) cm^{-1} ^1H NMR (D_2O, 200 MHz) δ (ppm) 1.71–1.80 (m, 2 × 2H), 1.90–2.10 (m, 2H), 3.00–3.13 (m, 2 × 2H), 3.38 (t, 2H, $J = 7.5$ Hz), 3.91 (t, 2H, $J = 7.5$ Hz), 4.95–5.15 (m, 2 × 2H), 7.70 (s, 1H), 7.88 (dd, 1H, $J = 1.2$, 7.5 Hz), 8.23 (dd, 1H, $J = 1.2$, 8.6 Hz), 8.45 (t, 1H, $J = 8.6$ Hz); HR-ESI calcd 342.1212 for $C_{19}H_{22}N_2S_2$ found 342.1206.

Compound **8b** mp 339 °C; ^1H NMR (D_2O, 200 MHz) δ (ppm) 1.30–1.45 (m, 2 × 2H), 1.68–1.89 (m, 2 × 2H), 2.85–3.00 (m, 2 × 2H), 3.72 (t, 2H, $J = 7.7$ Hz), 3.85 (t, 2H, $J = 7.8$ Hz), 4.81–4.98 (m, 2 × 2H), 7.61 (s, 1H), 7.80 (dd, 1H, $J = 1.0$, 8.2 Hz), 8.15 (dd, 1H, $J = 1.1$, 8.4 Hz), 8.37 (t, 1H, $J = 8.5$ Hz); HR-ESI calcd 356.1370 for $C_{20}H_{24}N_2S_2$ found 356.1354.

Compound **8c** mp 240 °C; ^1H NMR (D_2O, 200 MHz) δ (ppm) 2.30–2.50 (m, 3 × 2H), 3.09 (t, 2H, $J = 7.6$ Hz), 3.25 (t, 2H, $J = 7.4$ Hz), 3.45 (t, 2 × 2H, $J = 7.0$ Hz), 4.20–4.41 (m, 2 × 2H), 7.68 (s, 1H), 7.77 (dd, 1H, $J = 1.5$, 7.5 Hz), 8.10 (dd, 1H, $J = 1.5$, 8.7 Hz), 8.26 (t, 1H, $J = 8.6$ Hz); HR-ESI calcd 342.1213 for $C_{19}H_{22}N_2S_2$ found 342.1208.

Compound **8d** mp 235 °C; ^1H NMR (D_2O, 200 MHz) δ (ppm) 1.78–2.05 (m, 2 × 2H), 2.35–2.58 (m, 2 × 2H), 2.80 (t, 2H, $J = 5.7$ Hz), 2.98 (t, 2H, $J = 6.2$ Hz), 3.46 (t, 2H, $J = 6.2$ Hz), 3.44 (t, 2H, $J = 6.4$ Hz), 4.15–4.42 (m, 2 × 2H), 7.55 (s, 1H), 7.77 (dd, 1H, $J = 1.6$, 7.5 Hz), 8.10 (dd, 1H, $J = 1.5$, 8.6 Hz), 8.27 (t, 1H, $J = 7.4$ Hz); HR-ESI calcd 356.137 for $C_{20}H_{24}N_2S_2$ found 356.1354.

Compound **12a** mp 143 °C; IR (KBr) cm^{-1} 1138, 1417, 1556, 2927, 3057. ^1H NMR ($CDCl_3$, 200 MHz) δ (ppm) 4.58 (s, 2 × 2H), 7.17–7.34 (m, 2 × 5H), 7.44 (dd, 2 × 1H, $J = 1.4$, 7.6 Hz), 7.60 (t, 2 × 1H, $J = 7.6$ Hz), 8.16 (dd, 2 × 1H, $J = 1.2$, 7.8 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) 34.27, 116.80, 122.12, 127.06, 2 × C 128.49, 2 × C 128.76, 136.81, 138.23, 155.26, 157.80. HR-ESI calcd for $C_{24}H_{21}N_2S_2$ $(M+H)^+$ 401.1141; found 401.1164. Anal. Calcd for $C_{24}H_{20}N_2S_2$: C 71.78; H 5.27; N 6.97. Found: C 71.87; H 5.23; N 7.13.

6. X-ray measurements were performed on an Enraf-Nonius MACH 3 four-circle diffractometer at the Institute of Organic Chemistry Polish Academy of Sciences in Warsaw. Crystal data of **4a**: monoclinic, space group $P2_1/n$, $a = 13.2170(5)$ Å, $b = 7.1624(3)$ Å, $c = 16.5787(9)$ Å, $\beta = 96.945(4)°$, $V = 1557.9(1)$ Å^3, $Z = 4$. Crystal data of **4b**: monoclinic, space group $P2_1/n$, $a = 14.1037(10)$ Å, $b = 7.4756(6)$ Å, $c = 16.7277(14)$ Å, $\beta = 96.961(6)°$, $V = 1750.7(2)$ Å^3, $Z = 4.3244$ for **4a** and 3692 reflections for **4b** were collected at room temperature. Both structures were solved by direct methods and refined by full-matrix least-squares methods, final R of 0.0496 and 0.0506 for 2376 and 2584 reflections with $I > 2\sigma(I)$ for **4a** and **4b**, respectively. More crystallographic data for the structures in this letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 278673 and CCDC 278666. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].
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