Versatile Route to Functionalized 1*H*-2-Benzothiopyrans and 1*H*-2-Naphthothiopyrans by Electrophilic Cyclization of Bis(arylmethylthio)acetylenes: 2-Benzo- and 2-Naphthothiopyrylium Salts

Thomas R. Klein, Marco Bergemann, Nasser A. M. Yehia, and Egon Fanghänel*,†

Department of Chemistry, Martin-Luther-University, Halle-Wittenberg, D-06099 Halle, Germany

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Substituted 1*H*-2-benzothiopyrans find applications as pharmaceutically active compounds or synthons for more complex sulfur heterocycles. However, restricted variability in their synthesis limits the application for research or industrial purposes. To develop a direct and fast route to substituted and functionalized 1*H*-2-benzothiopyrans, we investigated the ring closure of symmetrical bis(arylmethylthio)acetylenes with iodine monochloride or bromine. This facile reaction yielded 1*H*-3-halo-4-arylmethylthio-2-benzo- and 2-naphthothiopyrans via postulated vinyl cations in yields of 47−86%. Substituted 2-benzo- and 2-naphthothiopyrylium salts were prepared by hydride abstraction with triphenylcarbenium tetrafluoroborate from the products, further enhancing the synthetic potential of the found cyclization reaction.

Introduction

1*H*-2-Benzothiopyrans both show and promise interesting biological properties.[1] They represent a more or less rigid and polarizable ring system,[2] which should be capable of interacting with receptor proteins like, but different from, the isomeric 2*H*-1-benzothiopyrans. The latter have already been tested and applied as drugs.[3] 1*H*-2-Benzothiopyrans can be easily converted into isothiochromans in high yields by catalytic reduction.[4] Certain 1-substituted and 1,1-disubstituted isothiochromans show pharmacological (antitussive, sedative, muscle relaxating, neuroleptic) activity,[5] as well.

The value of 1*H*-2-benzothiopyrans as synthons is given by the formation of highly reactive 2-benzothiopyrylium salts with trityl tetrafluoroborate ($TrBF_4$).[6] A wide variety of substituted and fused heterocyclic systems can be formed from the 2-benzothiopyrylium salts, for example, by using them as dienophiles in hetero Diels−Alder reactions.[7]

In contrast to the high synthetic and pharmacologic potential of 1*H*-2-benzothiopyrans, a very limited variability exists for preparation of these compounds.[8] Our aim was to develop a fast and efficient synthesis that allows a specific substitution pattern of the product by selecting appropriate educts. Symmetric bis(arylmethylthioacetylenes) **2** were chosen as starting material for cyclization due to the ease of preparation and high variability. Electrophilic attack of iodine monochloride and to a limited extent bromine gave 1*H*-3-halo-4-arylmethylthio-2-benzothiopyrans **3** in good yields (47−

† Address correspondence to this author at Institute of Organic Chemistry; Martin-Luther-University Halle-Wittenberg; D-06099 Halle. Tel: 0049-3461-462086. Fax: 0049-3461-462080. E-mail: Fanghaenel@chemie.uni-halle.de.

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(2) Schneller, S. W. *Adv. Heterocycl. Chem.* **1975**, *18*, 59.

(3) (a) Antifungal: Nakib, T. A.; Bezjak, V.; Rashid, S.; Fullam, B.; Meegan, M. J. *Eur. J. Med. Chem. Chim. Ther.* **1991**, *26*, 221. (b) Antimicrobial: Obi, K.; Saito, T.; Kojima, A.; Fukuda, H.; Hirai, K.; Suzue, S. *J. Antibiot. Tokyo* **1995**, *48*, 274 and 278. (c) Analgesic: Hori, M.; Kataoka, T.; Shimizu, H.; Imai, E.; Iwata, N.; Kawamura, N.; Kurono, M.; Nakano, K.; Kido, M. *Chem. Pharm. Bull. Tokyo* **1989**, *37*, 1282. (d) Antikonvulsant and sedative hypnotic: Arnoldi, A.; Bonsignori, A.; Melloni, P.; Merlini, L.; Quadri, M. L.; Rossi, A. C.; Valsecchi, M. *J. Med. Chem.* **1990**, *33*, 2865. (e) Platelet antiaggregating: Bargagna, A.; Longobardi, M.; Mariani, E.; Schenone, P.; Losasso, C.; Esposito, G.; Falzarano, C.; Marmo, E. *Farmaco* **1990**, *45*, 405. (f) Anticancer (tyrosin protein kinase inhibitor): Geissler, J. F.; Roesel, J. L.; Meyer, T.; Trinks, U. P.; Traxler, P.; Lydon, N. B. *Cancer Res.* **1992**, *52*, 4492.

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(8) (a) 1-Phenyl-3,4-substituted; from thiobenzophenone, activated acetylenes; 3 days Na_D irradiation, 20−60% yield: Ohno, A.; Koizumi, T.; Ohnishi, Y.; Tsuchihashi, G. *Tetrahedron Lett.* **1970**, *23*, 2025. (b) 4-Substituted; from isothiochroman-4-one, Grignard compounds; dehydratization, 30% yield: Padwa, A.; Au, A.; Lee, G. A.; Owens, W. *J. Org. Chem.* **1975**, *40*, 1142. (c) 3,4-Substituted; from 2-iodobenzyl chloride, *tert*-butyl-SH, base, $Pd(dba)_2$, asymmetric substituted acetylenes, $AgBF_4$, PhCl reflux; 5 steps, 47−54% yield: see ref 6a. (d) 1-Phenyl-3,4-substituted; from thiobenzophenone, activated acetylenes, 61−97% yield: Rapp, J.; Huisgen, R. *Tetrahedron* **1997**, *53*, 961. See also: Ingall, A. H. *Compr. Heterocycl. Chem* **1994**, *3*, 885. Ingall, A. H. *Compr. Heterocycl. Chem. II* **1996**, *5*, 501.

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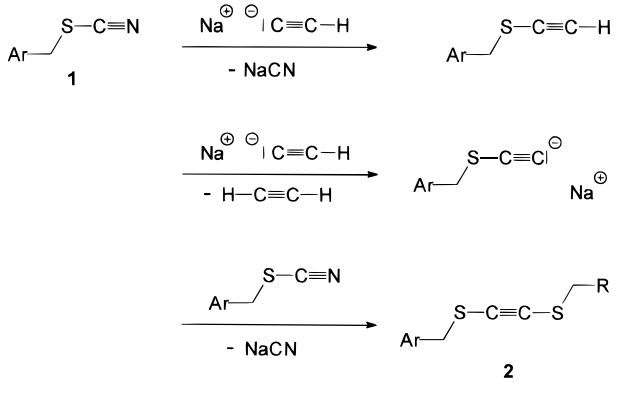
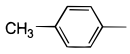
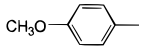
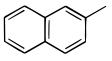
Table 1. Symmetrical Bis(arylmethylthio)acetylenes 2 from Arylmethyl Thiocyanates 1



substance number	Ar	yield(%)
2a		89
2b		68
2c		74
2d		62
2e		62
2f		69

86% isolated). The simple addition of halogen onto the triple bond played no role under the appropriate reaction conditions.

A preliminary description of this new reaction has been given for the unsubstituted starting compound.[9]

Results

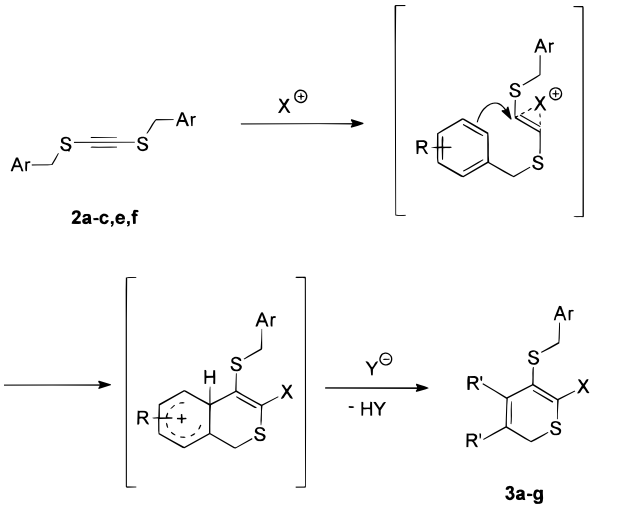
Choice and Preparation of Starting Compounds. To test the influence of substituents on the electrophilic ring closure reaction, several symmetric bis(arylmethylthio)acetylenes **2** have been prepared via arylmethyl thiocyanates **1** and sodium acetylide. Commercially available arylmethyl halides yielded thiocyanates **1** nearly quantitatively using the SiO_2-supported, solvent-free technique of Kodomari et al.[10] The reaction of the thiocyanates with sodium acetylide in liquid ammonia[11] gave acetylenes **2** in 60−90% yields (Table 1). ^{1}H NMR signals (singlets) of the methylene groups were at 3.79−3.89 ppm in chloroform-*d* as expected, with the exception of **2d** and **2e** (4.19 ppm; 4.25 ppm). Compounds **2b**−**f** have not yet been described in the literature and are therefore characterized in detail.

(9) Bergemann, M.; Fanghänel, E. 16th International Symposium on the Organic Chemistry of Sulfur (ISOCS), abstract book, R. 318, poster, Martin-Luther-Universität Halle-Wittenberg 1994, ISBN 3-924763-46-1.

(10) Kodomari, M.; Kuzuoka, T.; Yoshitomi, S. *Synthesis* **1983**, 141.

(11) Brandsma, L. *Preparative Acetylenic Chemistry*, reprint of the 2nd ed.; Elsevier: Amsterdam-Oxford-New York-Tokyo, 1992.

Table 2. Synthesis of 1*H*-2-Benzothiopyrans 3 from 2 and Iodine Monochloride or Bromine



substance	R', R'	Ar	X	yield (%)
3a		C_6H_5	I	86
3b		C_6H_5	Br	70
3c		4-CH_3-C_6H_4	I	71
3d		4-CH_3-C_6H_4	Br	47
3e		4-CH_3O-C_6H_4	I	84
3f		1-naphthyl	I	63
3g		2-naphthyl	I	55

Compounds **2a**−**d** have been chosen to study the electronic effect of a donor (**2b**,**c**) or an acceptor (**2d**) in the aryl group and of the type of the aromatic system (**2a**,**e**,**f**) on the electrophilic cyclization reaction.

Electrophilic Cyclization of 2a−f with Iodine Monochloride or Bromine. The acetylenes **2** were rapidly converted into 1*H*-2-benzothiopyrans **3**, via a vinyl cation as postulated intermediate, by reaction with equimolar amounts of iodine monochloride or bromine at −70 °C in methanol or methanol/chloroform (Table 2). The products precipitated from the cold reaction mixture. A second fraction could be obtained after neutralization of the filtrate with solid sodium bicarbonate, filtration, removal of the solvent, and recrystallization from ethanol. In general iodine monochloride gave higher yields than bromine. Some acetylenes (**2c**,**e**,**f**) could only be cyclized with iodine monochloride. The structure of the reaction products has been confirmed spectroscopically and by X-ray crystal structure analysis of **3a**. The ORTEP plot of **3a** is shown in Figure 1.

Two ^{1}H NMR signals (singlets) for the methylene groups of **3** were found: for the 4-substituents almost unchanged at 3.66−3.92 ppm in chloroform-*d* (4.28 ppm

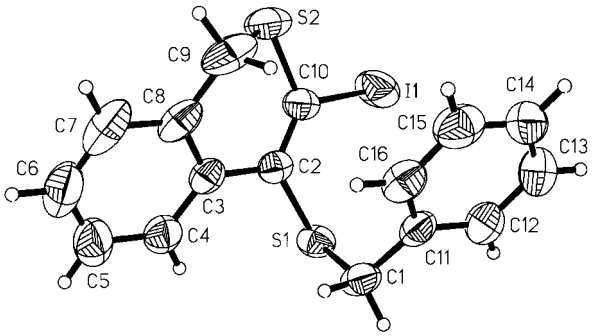
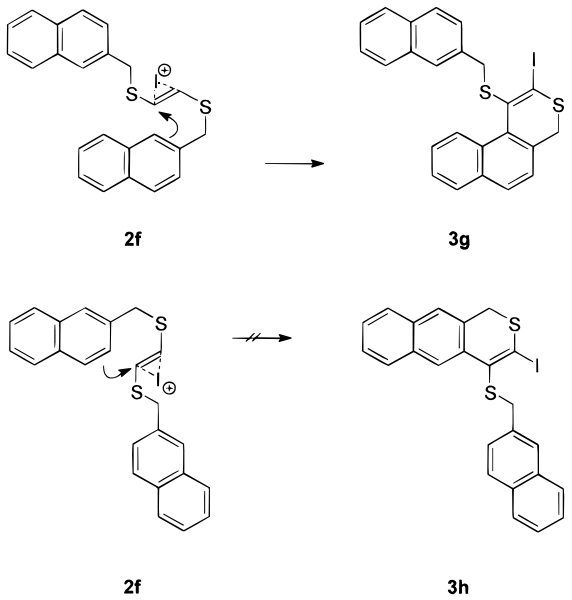


Figure 1. ORTEP plot of **3a**.

Scheme 1

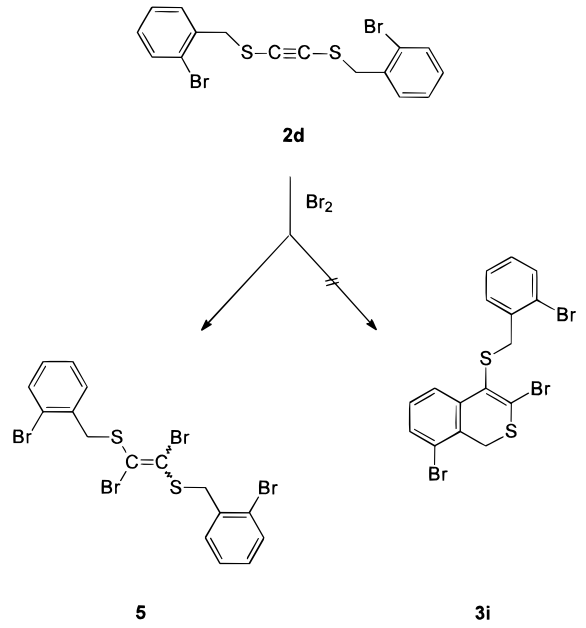


for **3f**) and the ring-methylene group shifted about 0.3 ppm upfield (with the exception of **3g**, where an upfield shift of 0.94 ppm was recorded).

From **2f** two different cyclization products may be formed (Scheme 1). The ^{1}H NMR spectra of the resulting substance from the reaction of **1f** with iodine monochloride showed 11 signals, which can be predicted for each of the possible isomers alone but not for a mixture of both. Due to the existence of only one singlet in the aromatic region, structure **3g** is likely. The ^{1}H−^{1}H COSY spectra of **3g** and the interpretation of all cross-peaks proved the postulated formula (Figure 2, Supporting Information).

Limitations of the new cyclization reaction were seen in the attempt to generate the 1*H*-2-benzothiopyran ring from **2d**, which failed (Scheme 2). Instead of ring closure to **3i** halogen addition to **5** was observed with bromine. Iodine monochloride yielded a complex reaction mixture from which no cyclization product could be isolated. The electronic effect of the *ortho* Br substituent made the stabilization of the postulated vinyl cation by intramolecular substitution less favorable and the intermolecular addition of a nucleophile more so. The isolated addition product **5** showed high selectivity toward one of the possible *E*/*Z* isomers as deduced from the ^{1}H NMR signal of the methylene group (4.19 ppm, 95%; 4.08 ppm, 5%). Most probably the *E* isomer was formed in excess, because bromine is known to prefer *anti* over *syn* addition if an ionic mechanism is involved.[12]

Scheme 2



Conversion of 3 into Thiopyrylium Salts 4. To extend the synthetic variability of the ring closure products, **3a**−**g** were treated with $TrBF_4$ in dry CH_2Cl_2 (or CH_2Cl_2/CH_3NO_2). $TrBF_4$ acts as hydride extractor,[13] forming triphenylmethane and the desired 2-benzothiopyrylium salts **4**. All compounds **3** investigated except **3g** provided the salts **4** in yields between 37% and 85% yields (Table 3). In the case of **3g** the starting material was recovered unchanged, possibly by sterical hindrance of the hydride abstraction by the bulky tritylium cation.

The salts **4** were deeply colored (λ_{max} in CH_3CN, 422−450 nm; ϵ = 1300−8800 l/mol cm) hydrolysis-sensitive crystals, which were stored in a desiccator. The ^{1}H NMR signal (singlet) of the methylene group of the substituent was shifted downfield to 4.26 ppm (**4a**, $CDCl_3$) and 4.19−4.72 ppm (**4b**,**c**,**e**,**f**, CD_3CN). The disappearance of the singlet of the ring-methylene group and a new resonance at 10.08−10.93 ppm (singlet) confirmed the formation of the thiopyrylium salt.

Discussion

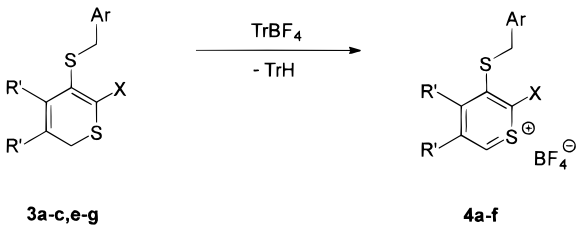
1*H*-2-Benzothiopyrans **3**, which are important for their use as synthons and pharmacologically active compounds, could be obtained in good yields in a flexible and easy reaction from bis(arylmethylthio)acetylenes **2**. The preparation of the acetylenes was achieved by modifying standard reactions using commercial arylmethyl halides as starting material and proceeded without difficulties.

The electrophilic addition of halogens to acetylenes is normally catalyzed by Lewis acids and yields (*E*)-1,2-dihaloalkenes stereoselectively.[12] In polar solvents the stabilization of polar intermediates and transition states could also be expected in the absence of catalysts. In this way the preformed cations (X = iodonium, bromonium) attack the electron rich triple bond of **2** by forming a vinyl

(12) (a) *Houben-Weyl Methoden der organischen Chemie*, 4th ed.; Georg Thieme Verlag: Stuttgart, 1960; Vol. V/4, pp 92−95. (b) Al-Hassan, M. I. *J. Organomet. Chem.* **1989**, *372*, 183. (c) König, J.; Wolf, V. *Tetrahedron Lett.* **1970**, *19*, 1629. (d) Schmid, G. H.; Modro, A.; Yates, K. *J. Org. Chem.* **1980**, *45*, 665.

(13) (a) Dauben, H. J.; Gadecki, F. A.; Harmon, K. M.; Pearson, D. L. *J. Am. Chem. Soc.* **1957**, *79*, 4558. (b) Bonthrone, W. Reid, D. H. *J. Chem. Soc.* **1959**, 2773.

Table 3. Conversion of 3 into 2-Benzo- and 2-Naphthothiopyrylium Salts 4



3a-c,e-g **4a-f**

number	R', R'	Ar	X	yield (%)
4a		C_6H_5	I	47
4b		C_6H_5	Br	37
4c		4-CH_3-C_6H_4	I	61
4e		4-CH_3O-C_6H_4	I	60
4f		1-naphthyl	I	85
		2-naphthyl	I	no reaction

cation which can react with nucleophiles/anions to equilibrate its charge. Because of the reduced nucleophilicity of the halogen anions (Y = chloride, bromide) in methanol, which is due to strong hydrogen bonding, the vinyl cation attacks intramolecularly the aromatic π-system forming a σ-complex and finally the 1*H*-2-benzothiopyran ring. This reaction corresponds to the intramolecular formation of indenes via a benzyl vinyl cation[14] as an intermediate. It is furthermore plausible that vinyl cations **6** were stabilized by electronic interaction with the nucleophilic, easily polarizable sulfur (Scheme 3).

The bridged structure **6c** is expected to be the most stable.[15] Low concentration of the acetylene, low temperatures, and slow addition of the halogen favored the intramolecular course of reaction. Higher reactivity and larger yields were observed with iodine monochloride as compared to bromine due to the strongly polarized bond between the two halogens in iodine monochloride. Some acetylenes (**2c**,**e**,**f**) reacted only with this reagent. The proposed mechanism (Table 2) is in agreement with the superiority of iodine monochloride over bromine in the reaction described.

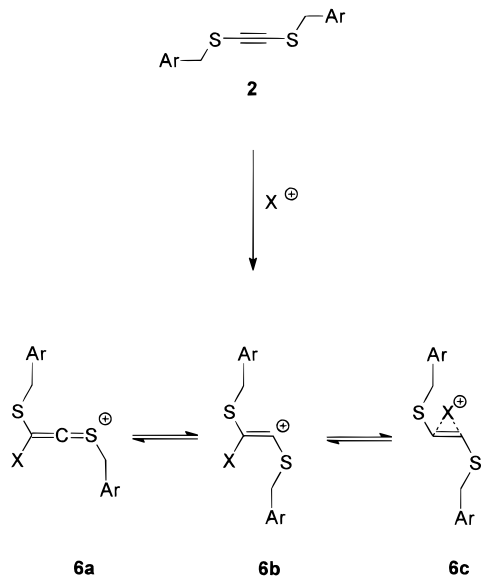
From the two possible cyclization products of **2f**, only **3g** was found. This high selectivity of ring closure toward the 1- and not the 3-position of the 2-substituted naphthalene ring corresponds to the favored electrophilic substitution of the 1-position of naphthalene under kinetic control.

No ring closure but *trans* addition of halogen onto the triple bond was found in case of acetylene **2d**. The *ortho*

(14) (a) Maroni, R.; Melloni, G. *Tetrahedron Lett.* **1972**, 2869. (b) Marcuzzi, F.; Melloni, G. *Tetrahedron Lett.* **1975**, 2771.

(15) Hanack, M. *Angew. Chem.* **1978**, *90*, 346; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 333.

Scheme 3



Br substitution of the benzene ring blocked one of two *ortho* positions (statistical factor) and deactivated the aromatic ring for electrophilic substitution. Therefore, the addition of bromide is favored in comparison to intramolecular cyclization.

The potential of the ring closure reaction previously described has not been exploited totally with the use of iodine monochloride or bromine as electrophiles and the symmetric bis(arylmethylthio)acetylenes as educts. Both directions, that is, other electrophiles and different substitution patterns of the educts (especially unsymmetrical acetylenes **2** and bis(arylmethylseleno)acetylenes) will be followed by the authors. The halogen in the 3-position of the 2-benzothiopyran ring in **3** opens the way to further derivatization and intramolecular cyclization to fused sulfur heterocycles.

Conclusion

We have shown that substituted 1*H*-2-benzothiopyrans **3** with a new substitution pattern were readily accessible by electrophilically induced ring closure of acetylenes **2**. The synthetic versatility of **3** was demonstrated by their conversion into 2-benzo- and 2-naphthothiopyrylium salts **4** with $TrBF_4$. Compounds **3** and **4** open routes for synthesizing fused heterocycles and for potential applications in medicine and in material science.

Experimental Section

Melting points were determined on a micro melting point apparatus and are corrected. NMR spectra at 300 MHz (^1H) and 75 MHz (^{13}C) were obtained in $CDCl_3$ (**1**, **2**, **3**, **4a**) and in CD_3CN (**4b**,**c**,**e**,**f**), respectively (ppm; ^{13}C off-resonance), with TMS as internal standard unless stated otherwise. UV−vis absorptions are given as [λ in nm (ϵ in L/mol cm)]. All elemental analyses reported were averaged from two independent determinations. HPLC analysis was performed with CH_3CN (no gradient) on an RP-18 column connected to a UV array detector. The peak area for accumulated absorption in the range of 210−370 nm was utilized as a purity criterion. For the described compounds of type **1**, **2**, and **3**, a purity of more than 98% was determined.

Arylmethyl halides, potassium thiocyanate, and iodine monochloride and bromine used were obtained from commercial sources. Ammonia and acetylene of highest commercial purity from gas cylinders were purified/washed as described in the individual experiments.

General Procedure: Arylmethyl Thiocyanates 1 from Arylmethyl Halides. SiO_2-supported active KSCN (75 mmol), prepared as described by Kodomari,[10] was placed in a 100 mL Erlenmeyer flask and the arylmethyl halide (25 mmol) was added. If the latter was a solid at room temperature, the flask was immersed into a steam bath until all arylmethyl halide was liquified and absorbed. The flask was placed in the dark for 16 h and shaken from time to time. The product was extracted with toluene and filtered to remove all solids, and the toluene was evaporated. The pure thiocyanate was isolated in near quantitative yield.

Benzyl thiocyanate (1a): 3.35 g from 3.16 g (25 mmol) of benzyl chloride (90%); clear, odorless crystals, mp 39−40 °C (39.4 °C[16]).

4-Methylbenzyl thiocyanate (1b): 3.84 g from 3.51 g (25 mmol) of 4-methylbenzyl chloride (93%); clear, odorless liquid, bp 151 °C/20 mbar (110−112 °C/6 Torr,[17] 148−150 °C/14 Torr[17]).

4-Methoxybenzyl thiocyanate (1c): 2.20 g from 1.96 g (12.5 mmol) of 4-methoxybenzyl chloride (98%); slightly yellow liquid with anise-like smell, bp 134 °C/1 mbar (135−139 °C/0.7 Torr[18]).

2-Bromobenzyl thiocyanate (1d): 5.40 g from 6.25 g (25 mmol) of 1-bromobenzyl bromide (96%); slightly brownish liquid with pungent odor, bp 113 °C/0.1 mbar, $n^{20}_D = 1.6102$; ^{1}H NMR δ 4.23 (s, 2H), 7.21 (d, 1H, 7.5 Hz), 7.33 (t, 1H, 7.4 Hz), 7.41 (t, 1H, 8.6 Hz), 7.61 (d, 1H, 8.0 Hz). Anal. Calcd for C_8H_6BrNS: C, 42.12; H, 2.65; S, 14.05; N, 6.14; Br, 35.03. Found: C, 42.20; H, 2.80; S, 14.29; N, 6.48; Br, 32.11.

1-Naphthylmethyl thiocyanate (1e): 2.59 g from 2.18 g (12.5 mmol) of 1-chloromethylnaphthalene (99%); clear, odorless crystals, mp 91 °C (91−91.5 °C[17]).

2-Naphthylmethyl thiocyanate (1f): 2.46 g from 2.74 g (12.5 mmol) of 2-bromomethylnaphthalene (95%); clear, odorless crystals, mp 101 °C (101−101.5 °C[19]).

General Procedure: Symmetric Bis(arylmethylthio)-acetylenes 2 from Arylmethyl Thiocyanates 1. Ammonia (dried by passing through a KOH-filled column) was liquified (10 mL) under an argon atmosphere using a reflux condenser filled with solid CO_2 and ethanol. After sodium (575 mg; 25 mmol) was added, acetylene gas (passed through H_2SO_4 and an active carbon filter) was bubbled into the deep blue solution until the color disappeared. Dry CH_2Cl_2 (2 mL) was added, and by stirring, a concentrated solution of the thiocyanate (20 mmol) in CH_2Cl_2 was slowly introduced through a dropping funnel. After stirring was continued for 30 min and the ammonia evaporated, 3 mL of CH_2Cl_2 followed by 20 mL of H_2O was added to dissolve all solids. The phases were separated, and the water layer was extracted with CH_2Cl_2 (3 × 12 mL). It now contained only NaCN, which was destroyed with alkaline H_2O_2. The unified organic phases were washed with water and dried and the solvent removed. The products were pure after recrystallization from diethyl ether.

Bis(benzylthio)acetylene (2a): 12.0 g from 15.0 g (100 mmol) of benzyl thiocyanate **1a** (89%); clear crystals, mp (ethanol) 54 °C (54 °C[17]); ^{1}H NMR δ 3.80 (s, 4H), 7.25 (m, 10H); ^{13}C NMR δ 41.42, 87.95, 127.59, 128.46, 129.04, 136.46; UV−vis (CH_3CN) 228 (20 100). Anal. Calcd for $C_{16}H_{14}S_2$: C, 71.07; H, 5.22; S, 23.71. Found: C, 71.43; H, 5.55; S, 23.73.

Bis(4-methylbenzylthio)acetylene (2b): 1.96 g from 3.26 g (20 mmol) of 4-methylbenzyl thiocyanate **1b** (68%); flat, clear crystals, mp (ethanol) 78.5 °C; ^{1}H NMR δ 2.33 (s, 6H), 3.82 (s, 4H), 7.13 (s, 8H); ^{13}C NMR δ 21.09, 41.23, 87.93, 128.90, 129.13, 133.38, 137.25; UV−vis (CH_3CN) 231 (29 300). Anal. Calcd for $C_{18}H_{18}S_2$: C, 72.48; H, 6.04; S, 21.48. Found: C, 72.15; H, 5.84; S, 21.68.

Bis(4-methoxybenzylthio)acetylene (2c): 1.49 g from 2.15 g (12 mmol) of 4-methoxybenzyl thiocyanate **1c** (74%); orange plates, mp (ethanol) 81−82 °C; ^{1}H NMR δ 3.79 (s, 6H), 3.82 (s, 4H), 6.85 (d, 4H, 8.6 Hz), 7.18 (d, 4H, 8.6 Hz); ^{13}C NMR δ 41.02, 55.20, 87.98, 113.90, 128.48, 130.21, 159.12; UV−vis (CH_3CN) 239 (28 900). Anal. Calcd for $C_{18}H_{18}S_2O_2$: C, 65.45; H, 5.46; S, 19.39. Found: C, 64.99; H, 5.40; S, 19.76.

Bis(2-bromobenzylthio)acetylene (2d): 2.35 g from 2.0 g (8.9 mmol) of 2-bromobenzyl thiocyanate **1d** (62%); clear crystals, mp (ethanol) 80 °C; ^{1}H NMR δ 3.91 (s, 4H), 7.11 (d, 8H, 7.1 Hz), 7.18 (d, 4H, 7.3 Hz), 7.52 (d, 4H, 7.6 Hz); ^{13}C NMR δ 41.66, 88.25, 124.42, 127.28, 129.29, 131.42, 132.96, 135.61; UV−vis (CH_3CN) 233 (19 800). Anal. Calcd for $C_{16}H_{12}S_2Br_2$: C, 44.88; H, 2.82; S, 14.97; Br, 37.22. Found: C, 44.85; H, 3.06; S, 15.03; Br, 37.35.

Bis(1-naphthylmethylthio)acetylene (2e): 1.38 g from 2.39 g (12 mmol) of 1-naphthylmethyl thiocyanate **1e** (62%); yellow crystals, mp (ethanol) 76−79 °C; ^{1}H NMR δ 4.25 (s, 4H), 7.18 (d, 2H, 6.9 Hz), 7.31 (t, 2H, 7.6 Hz), 7.52 (m, 4H), 7.78 (d, 2H, 8.1 Hz), 7.87 (d, 2H, 9.0 Hz), 8.01 (d, 2H, 7.6 Hz); ^{13}C NMR δ 39.19, 88.87, 123.56, 125.04, 125.80, 126.20, 128.12, 128.65, 128.76, 131.10, 131.65, 133.83; UV−vis (CH_3CN) 287 (17 500). Anal. Calcd for $C_{24}H_{18}S_2$: C, 77.80; H, 4.90; S, 17.31. Found: C, 77.55; H, 5.11; S, 17.58.

Bis(2-naphthylmethylthio)acetylene (2f): 2.39 g from 3.70 g (19 mmol) of 2-naphthylmethyl thiocyanate **1f** (69%); yellow crystals, mp (ethanol) 128−129 °C; ^{1}H NMR δ 3.89 (s, 4H), 7.32 (d, 2H), 7.47 (t, 4H), 7.55 (s, 2H), 7.77 (m, 6H); ^{13}C NMR δ 41.67, 88.27, 126.01, 126.20, 126.84, 127.65, 127.76, 128.04, 128.29, 132.71, 133.15, 133.70; UV−vis (CH_3CN) 263 (sh) (15 600). Anal. Calcd for $C_{24}H_{18}S_2$: C, 77.80; H, 4.90; S, 17.31. Found: C, 77.24; H, 5.18; S, 17.41.

General Procedure: 1*H*-2-Benzothiopyrans 3 from Bis(arylmethylthio)acetylenes 2. Acetylene **2** (1 mmol) was dissolved in 2 mL of $CHCl_3$, and 8 mL of CH_3OH was added. The suspension was cooled to −70 °C, and by stirring, the halogen (Br_2 or ICl; 1.1 mmol) in 1 mL of $CHCl_3$ was slowly added. Stirring was continued for 10 min at −70 °C. After the solution was warmed to room temperature, all solids were dissolved. When the solution was immersed into solid CO_2/ethanol, most of the product precipitated and was filtered. A second fraction was obtained by neutralization with solid $NaHCO_3$, removal of the solvents at low temperatures (35 °C), and purification of the dark residue by precipitation from CH_2Cl_2 with cyclohexane. The products were pure after one or two recrystallizations from ethanol.

1*H*-3-Iodo-4-benzylthiobenzothiopyran (3a): 279 mg from 270 mg (1 mmol) of **2a** (84%); slightly yellow needles, mp (ethanol) 81.0 °C; ^{1}H NMR δ 3.49 (s, 2H), 3.84 (s, 2H), 7.20 (m, 8H), 7.92 (d, 1H, 8.0 Hz); ^{13}C NMR δ 35.78, 39.66, 97.09, 126.48, 127.01, 127.16, 127.84, 128.11, 128.47, 129.08, 130.41, 132.24, 135.06, 136.72; UV−vis (CH_2Cl_2) 253 (14 400), 337 (6900); (CH_3CN) 250 (13 200), 337 (6580); EI-MS *m*/*z* (relative intensity) 396 (M^+, 100), 305 ($C_9H_6S_2I^+$, 22), 269 ($C_{16}H_{13}S_2^+$, 12), 178 ($C_9H_6S_2^+$, 58), 91 ($C_7H_7^+$, 59). Anal. Calcd for $C_{16}H_{13}S_2I$: C, 48.49; H, 3.31; S, 16.18. Found: C, 48.74; H, 3.86; S, 16.20.

1*H*-3-Bromo-4-benzylthiobenzothiopyran (3b): 245 mg from 270 mg (1 mmol) of **2a** (70%); clear needles, mp (ethanol) 59.5 °C; ^{1}H NMR δ 3.55 (s, 2H), 3.83 (s, 2H), 7.18 (m, 8H), 7.88 (d, 1H); ^{13}C NMR δ 34.72, 39.12, 123.37, 126.38, 127.05, 127.16, 127.82, 128.17, 128.35, 129.04, 130.10, 130.18, 133.43, 136.97; UV−vis (CH_2Cl_2) 248 (14 000), 332 (7200); (CH_3CN) 332 (5000); EI-MS *m*/*z* (relative intensity) 349 (M^+, 57), 269 ($C_{16}H_{13}S_2^+$, 9), 258 ($C_9H_6S_2Br^+$, 14), 178 ($C_9H_6S_2^+$, 50), 91 ($C_7H_7^+$, 100). Anal. Calcd for $C_{16}H_{13}S_2Br$: C, 55.02; H, 3.95; S, 18.36; Br, 22.88. Found: C, 55.20; H, 4.38; S, 18.16; Br, 22.46.

1*H*-3-Iodo-4-(4-methylbenzylthio)-6-methylbenzothiopyran (3c): 303 mg from 298 mg (1 mmol) of **2b** (71%); clear needles, mp (ethanol) 67.7 °C; ^{1}H NMR δ 2.30 (s, 3H), 2.39 (s, 3H), 3.51 (s, 2H), 3.81 (s, 2H), 7.01 (m, 6H), 7,71 (s, 1H); ^{13}C NMR δ 21.09, 21.29, 35.61, 39.60, 96.87, 126.36, 127.66, 127.93, 128.83, 128.97, 129.07, 132.16, 133.82, 135.33, 136.64, 137.50; UV−vis (CH_3CN) 250 (12 600), 335 (4300); EI-MS *m*/*z* (relative intensity) 424 (M^+, 53), 297 ($C_{18}H_{17}S_2^+$, 7), 264 ($C_{18}H_{16}S^+$, 14), 192 ($C_{10}H_8S_2^+$, 16), 148 ($C_9H_8S^+$, 8), 105 ($C_8H_9^+$,

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100). Anal. Calcd for $C_{18}H_{17}S_2I$: C, 50.94; H, 4.01; S, 15.09. Found: C, 50.69; H, 4.21; S, 15.15.

1*H*-3-Bromo-4-(4-methylbenzylthio)-6-methylbenzothiopyran (3d): 89 mg from 149 mg (0.5 mmol) of **2b** (47%); clear crystals, mp (ethanol) 79−80 °C; ^{1}H NMR δ 2.30 (s, 3H), 2.39 (s, 3H), 3.59 (s, 2H), 3.81 (s, 2H), 6.99 (m, 6H), 7.66 (s, 1H); ^{13}C NMR δ 20.96, 21.17, 34.38, 38.87, 123.17, 126.36, 127.31, 127.92, 128.92, 128.95, 128.98, 130.41, 133.28, 134.08, 136.71, 137.53; UV−vis (CH_3CN) 248 (16 500), 331 (7800). Anal. Calcd for $C_{18}H_{17}S_2Br$: C, 57.29; H, 4.54; S, 16.99. Found: C, 57.66; H, 4.78; S, 17.32.

1*H*-3-Iodo-4-(4-methoxybenzylthio)-6-methoxybenzothiopyrane (3e): 1.16 g from 1.0 g (3 mmol) of **2c** (84%); clear crystals, mp (ethanol) 97.5 °C; ^{1}H NMR δ 3.50 (s, 2H), 3.76 (s, 3H), 3.81 (s, 2H), 3.82 (s, 3H), 6.73 (d, 2H, 8.5 Hz), 6.82 (d, 1H, 8.2 Hz), 6.97 (s, 1H), 6.98 (d, 2H, 8.4 Hz), 7.49 (d, 1H, 2.5 Hz); ^{13}C NMR δ 35.36, 39.22, 55.24, 55.47, 97.99, 113.04, 113.56, 113.88, 122.77, 127.48, 128.86, 130.18, 133.42, 135.07, 158.62, 159.35; UV−vis (CH_3CN) 228 (32 800), 253 (16 600), 320 (6500), 334 (5800); EI-MS *m*/*z* (relative intensity) 455 (M^+, 100), 330 ($C_{18}H_{17}S_2^+$, 7), 264 ($C_{18}H_{17}S_2O_2^+$, 48), 208 ($C_{10}H_8S_2O^+$, 22), 121 ($C_8H_9O^+$, 100). Anal. Calcd for $C_{18}H_{17}S_2O_2I$: C, 47.37; H, 3.75; S, 14.05. Found: C, 47.52; H, 3.70; S, 14.54.

1*H*-3-Iodo-4-(1-naphthylmethylthio)naphtho[1,2-*c*]thiopyran (3f): 158 mg from 185 mg (0.5 mmol) of **2e** (63%); yellow crystals, mp (ethanol) 167.5−168.5 °C; ^{1}H NMR δ 3.92 (s, 2H), 4.28 (s, 2H), 6.90 (d, 1H), 7.17 (t, 1H), 7.45 (m, 2H), 7.54 (m, 2H), 7.68 (d, 1H), 7.80 (m, 2H), 7.87 (d, 1H), 7.96 (d, 1H), 8.10 (t, 1H), 8.19 (d, 1H); ^{13}C NMR δ 30.56, 37.71, 97.75, 123.31, 124.09, 124.76, 125.35, 125.73, 126.01, 126.04, 126.73, 127.45, 127.54, 127.65, 128.26, 128.61, 128.66, 129.57, 130.72, 131.50, 132.14, 132.40, 133.57, 133.77; UV−vis (CH_3CN) 245 (sh) (12 100), 288 (8170), 363 (2860); EI-MS *m*/*z* (relative intensity) 496 (M^+, 95), 369 ($C_{24}H_{17}S_2^+$, 12), 336 ($C_{24}H_{16}S^+$, 33), 254 (I_2^+, 6), 227 ($C_{13}H_7S_2^+$, 13), 184.5 ($C_{24}H_{17}S_2^{2+}$, 9), 141 ($C_{11}H_9^+$, 100). Anal. Calcd for $C_{24}H_{17}S_2I$: C, 58.07; H, 3.45; S, 12.92. Found: C, 58.12; H, 3.63; S, 13.04.

1*H*-3-Iodo-4-(2-naphthylmethylthio)naphtho[2,1-*c*]thiopyran (3g): 275 mg from 370 mg (1 mmol) of **2f** (55%); yellow crystals, mp (ethanol) 106−108 °C; ^{1}H NMR δ 2.95 (s, 2H), 3.66 (s, 2H), 6.71 (s, 1H), 7.04 (d, 1H), 7.17 (d, 1H), 7.39 (m, 2H), 7.55 (m, 4H), 7.72 (m, 1H), 7.78 (d, 1H), 7.86 (d, 1H), 9.03 (d, 1H); ^{13}C NMR δ 37.83, 39.95, 95.63, 124.24, 125.72, 125.98, 126.14, 126.98, 127.50, 127.74, 128.37, 129.20, 132.24, 132.59, 133.53, 133.95, 134.09, 135.43; UV−vis (CH_3CN) 250 (sh) (27 300), 363 (5890); EI-MS *m*/*z* (relative intensity) 496 (M^+, 18), 369 ($C_{24}H_{17}S_2^+$, 5), 336 ($C_{24}H_{16}S^+$, 12), 254 (I_2^+, 6), 227 ($C_{13}H_7S_2^+$, 8), 192 (IS_2H^+, 30), 141 ($C_{11}H_9^+$, 54), 91 ($C_7H_7^+$, 100). Anal. Calcd for $C_{24}H_{17}S_2I$: C, 58.07; H, 3.45; S, 12.92. Found: C, 58.08; H, 3.67; S, 12.99.

General Procedure: 2-Benzothiopyrylium Salts 4 by Hydride Abstraction with $TrBF_4$ from Benzothiopyrans 3. **3** (0.5 mmol) was dissolved in 1 mL of dry CH_2Cl_2 and added in one portion to a solution of $TrBF_4$[20] (231 mg; 0.7 mmol) in 2 mL of CH_2Cl_2. The resulting dark liquid was stirred for 30 min and then poured into the 3-fold volume of dry diethyl ether with vigorous stirring. The formed solid was collected, washed twice with diethyl ether, and dried in a vacuum desiccator. Every step was carried out under argon and with exclusion of moisture. If necessary, recrystallization was possible in acetic anhydride with some loss of material (incomplete precipitation).

1*H*-3-Iodo-4-benzylthiobenzothiopyrylium tetrafluoroborate (4a): 135 mg from 199 mg (0.5 mmol) of **3a** (47%); orange powder, mp >155 °C (dec); ^{1}H NMR δ 4.26 (s, 2H), 7.03 (d, 1H), 7.14 (d, 2H), 7.27 (d, 2H), 8.17 (t, 1H), 8.42 (t, 1H), 8.51 (d, 1H), 9.03 (d, 1H), 10.66 (s, 1H); UV−vis (CH_3CN) 276 (14 000), 324 (sh) (5200), 436 (2600); IR (KBr) ν_{max} 1066 cm^{-1} (BF_4^-). Anal. Calcd for $C_{16}H_{12}S_2I^+BF_4^-$: C, 39.84; H, 2.70; S, 13.28. Found: C, 39.86; H, 2.91; S, 13.23.

1*H*-3-Bromo-4-benzylthiobenzothiopyrylium tetrafluoroborate (4b): 97 mg from 175 mg (0.5 mmol) of **3b** (37%); orange powder, mp >95 °C (dec); ^{1}H NMR δ 4.28 (s, 2H), 7.06 (d, 2H, 4.7 Hz), 7.13 (d, 1H, 2.6 Hz), 7.27 (m, 2H), 8.18 (t, 1H), 8.45 (t, 1H), 8.56 (d, 1H, 8.2 Hz), 9.03 (d, 1H, 8.6 Hz), 10.58 (s, 1H); UV−vis (CH_3CN) 254 (9300), 273 (7900), 320 (4200), 436 (1360); IR (KBr) ν_{max} 1061 cm^{-1} (BF_4^-). Anal. Calcd for $C_{16}H_{12}S_2Br^+BF_4^-$: C, 44.07; H, 3.00; S, 14.70; Br, 18.30. Found: C, 44.59; H, 3.21; S, 14.46; Br, 18.25.

1*H*-3-Iodo-4-(4-methylbenzylthio)-6-methylbenzothiopyrylium tetrafluoroborate (4c): 46 mg from 62 mg (0.15 mmol) of **3c** (61%); yellow crystals, mp >148 °C (dec); ^{1}H NMR δ 2.19 (s, 3H), 2.68 (s, 3H), 4.19 (s, 2H), 6.88 (s, 4H), 7.98 (d, 1H, 8.3 Hz), 8.37 (d, 1H, 8.4 Hz), 8.68 (s, 1H), 10.47 (s, 1H); UV−vis (CH_3CN) 220 (24 700), 280 (18 600), 334 (5900), 434 (2700); EI-MS *m*/*z* (relative intensity) 423 ($M - BF_4^+$, 25), 297 ($C_{18}H_{16}S_2^+$, 5), 105 ($C_8H_9^+$, 100); IR (KBr) ν_{max} 1060 cm^{-1} (BF_4^-). Anal. Calcd for $C_{18}H_{16}S_2I^+BF_4^-$: C, 42.38; H, 3.16; S, 12.57. Found: C, 41.95; H, 3.06; S, 12.33.

1*H*-3-Iodo-4-(4-methoxybenzylthio)-6-methoxybenzothiopyrylium tetrafluoroborate (4e): 42 mg from 60 mg (0.13 mmol) of **3e** (60%); yellow crystals, mp >143 °C (dec); ^{1}H NMR δ 3.67 (s, 3H), 4.17 (s, 2H), 4.23 (s, 3H), 6.66 (d, 2H, 8.3 Hz), 6.94 (d, 2H, 8.3 Hz), 7.63 (d, 1H, 9.1 Hz), 8.24 (s, 1H), 8.37 (d, 1H, 9.1 Hz), 10.09 (s, 1H); UV−vis (CH_3CN) 232 (22 200), 281 (24 200), 306 (14 300), 371 (7900), 421 (6800); EI-MS *m*/*z* (relative intensity) 455 ($M - BF_4^+$, 55), 329 ($C_{18}H_{16}S_2O_2^+$, 33), 254 ($C_{12}H_{12}S_2O_2^+$, 60),121 ($C_8H_9O^+$, 100); IR (KBr) ν_{max} 1033 cm^{-1} (BF_4^-). Anal. Calcd for $C_{18}H_{16}S_2O_2I^+BF_4^-$: C, 39.88; H, 2.97; S, 11.83. Found: C, 39.90; H, 3.36; S, 11.75.

1*H*-3-Iodo-4-(1-naphthylmethylthio)naphtho[1,2-*c*]thiopyrylium tetrafluoroborate (4f): 41 mg from 41 mg (0.08 mmol) of **3f** (85%); bright orange powder, mp >185 °C (dec); ^{1}H NMR δ 4.72 (s, 2H), 6.81 (d, 1H, 6.9 Hz), 7.00 (t, 1H, 7.7 Hz), 7.49 (m, 2H), 7.59 (d, 1H, 8.3 Hz), 7.70 (d, 1H, 7.6 Hz), 8.08 (m, 3H), 8.21 (d, 1H, 7.5 Hz), 8.45 (d, 1H, 9.3 Hz), 8.66 (d, 1H, 9.3 Hz), 8.80 (d, 1H, 8.0 Hz), 10.93 (s, 1H); UV−vis (CH_3CN) 285 (28 900), 450 (8800); IR (KBr) ν_{max} 1054 cm^{-1} (BF_4^-). Anal. Calcd for $C_{24}H_{16}S_2I^+BF_4^-$: C, 49.51; H, 2.77; S, 11.01. Found: C, 49.95; H, 2.33; S, 11.02.

Reaction between Bis(2-bromobenzylthio)acetylene (2d) and Halogens: Formation of 1,2-Bis(2-bromobenzylthio)-1,2-dibromoethylene (5). Following the general procedure for the preparation of benzothiopyrans **3** (see above), to 1 mmol of **2d** (584 mg) was added an equimolar amount of ICl or Br_2. Only educt and a mixture of decomposition products could be isolated from the reaction with ICl. With bromine, 208 mg (28%) of a new compound was formed. The analytical data confirm the formation of the addition product 1,2-bis(2-bromobenzylthio)-1,2-dibromoethylene **5** and not the corresponding benzothiopyran **3i**.

5: clear crystals; mp (ethanol) 75−77 °C; ^{1}H NMR δ 4.14 (s, 4H), 7.12 (t, 2H, 6.9 Hz), 7.22 (t, 2H, 7.4 Hz), 7.30 (d, 2H, 7.3 Hz), 7.54 (d, 2H, 7.8 Hz); EI-MS *m*/*z* (relative intensity) 585 (M^+, 65), 426 ($M - Br_2^+ = C_{16}H_{12}S_2Br_2^+$, 7), 337 ($C_9H_6S_2$-$Br_2^+$, 71), 258 ($C_9H_6S_2Br^+$, 44), 170 ($C_7H_6Br^+$, 100), 89 ($C_7H_6^+$, 16). Anal. Calcd for $C_{16}H_{12}S_2Br_4$: C, 32.68; H, 2.68; S, 10.90; Br, 54.36. Found: C, 33.07; H, 2.20; S, 11.03; Br, 53.91.

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Supporting Information Available: ^{1}H−^{1}H COSY spectra of **3g** with interpretation of the aromatic cross-peaks (Figure 2). Further X-ray crystal structure data for **3a** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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