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SYNTHESIS OF ISOTHIOCHROMENES AND 1,3-DIHYDROBENZO[*c*]THIOPHENES BY IODINE- AND HYDROBROMIC ACID-MEDIATED CYCLIZATIONS OF *o*-[(*tert*-BUTYLSULFANYL)METHYL)]STYRENES

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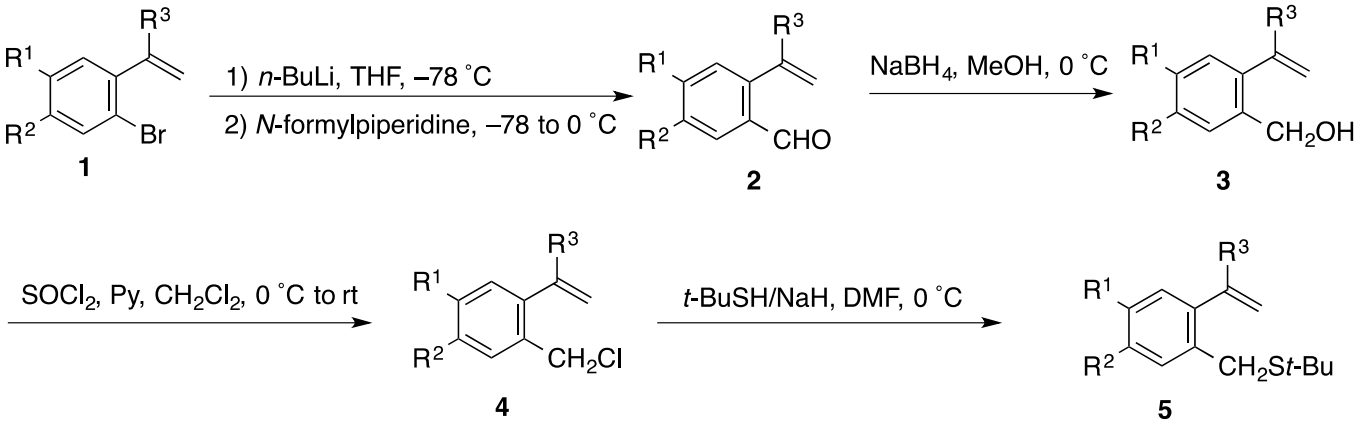
Abstract – Methods for the syntheses of 4-substituted isothiochromenes and 1,1-disubstituted 1,3-dihydrobenzo[*c*]thiophenes have been developed. Thus, treatment of α-substituted *o*-[(*tert*-butylsulfanyl)methyl]styrenes, derived from α-substituted *o*-bromostyrenes using an easily operated four-step sequence, with iodine in the presence of sodium hydrogencarbonate gave isothiochromene derivatives. These *tert*-butyl sulfides were treated with concentrated hydrobromic acid to give 1,3-dihydrobenzo[*c*]thiophene derivatives.

INTRODUCTION

Some compounds with the isothiochromene (1*H*-2-benzothiopyran) structure have been reported to exhibit biological activity.[1] To date, construction of this skeleton has been commonly performed *via* the reaction of isothiochroman-4-one with Grignard reagents followed by dehydration with concentrated sulfuric acid.[2] This method, however, suffers from low yields and limited generality. Therefore, some different methods have recently been reported.[3] On the other hand, previous studies in our laboratory have revealed that α-substituted 2-lithiostyrenes serve, through reactions with a variety of electrophile followed by cyclizations of the resulting precursors, as versatile intermediates for the preparation of heterocyclic derivatives.[4-8] In the present paper, we wish to describe a convenient synthesis of 4-substituted isothiochromenes (**8**) by iodine-mediated cyclization of α-substituted *o*-[(*tert*-butylsulfanyl)methyl]styrenes (**5**), derived through formylation of α-substituted 2-lithiostyrenes. We also report that 1,1-disubstituted 1,3-dihydrobenzo[*c*]thiophenes (**13**) can be prepared by hydrobromic

acid-mediated cyclization of **5**. 1,3-Dihydrobenzo[*c*]thiophene 2,2-dioxide, prepared by oxidation of 1,3-dihydrobenzo[*c*]thiophene, has been used as a precursor for the generation of *o*-quinone dimethides, which has been utilized as useful intermediates for the preparation of polycyclic compounds.[9] The reaction of *o*-xylene dihalides with disodium sulfide has been used to prepare 1,3-dihydrobenzo[*c*]thiophenes,[10] though an efficient method based on the Ga-promoted cycloaddition of alkynyl enynes have recently been reported[11] and we recently have reported a synthesis of 1-aryl-1,3-dihydrobenzo[*c*]thiophenes by acid mediated cyclization of 1-[aryl(methoxy)methyl-2-[(*tert*-butylsulfanyl)methyl]benzenes.[12] However, few general methods for the preparation of 1,1-disubstituted 1,3-dihydrobenzo[*c*]thiophenes have been reported; Nishio reported the formation of 1,1-dimethyl-1,3-dihydrobenzo[*c*]thiophene by a Lawesson's reagent-mediated cyclization of 1-[(2-hydroxymethyl)phenyl]-1-methylethanol.[13]

RESULTS AND DISCUSSION



Scheme 1

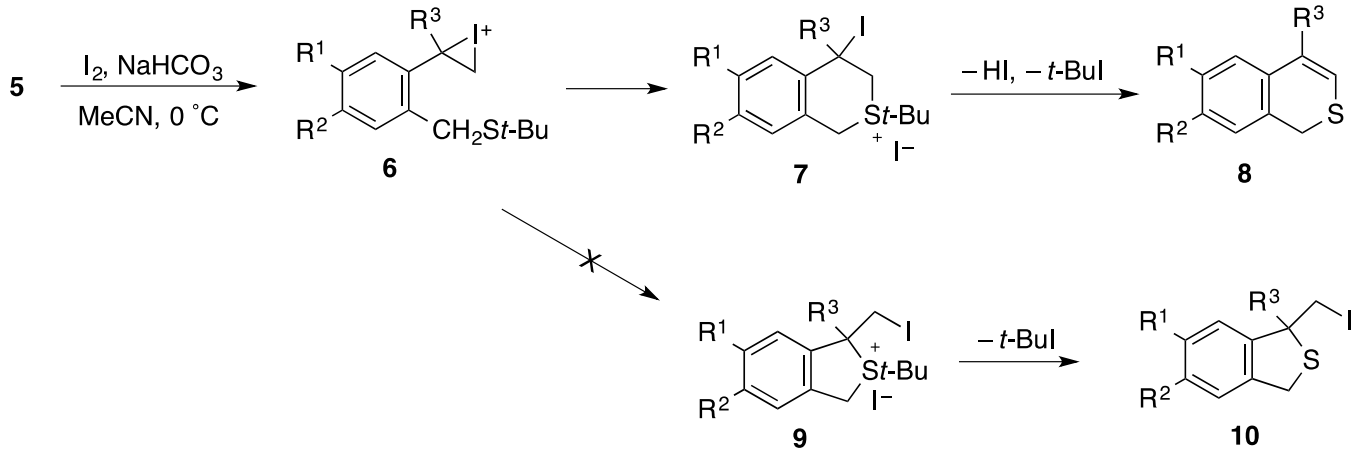
The synthesis of the precursor sulfides (**5**) was accomplished according to the sequence illustrated in Scheme 1. Thus, α-substituted 2-bromostyrenes **1**, which were easily prepared from 2-bromobenzaldehydes as described previously,[3b,4-7] were treated with butyllithium in THF at –78 ˚C and the resulting α-substituted 2-lithiostyrenes were allowed to react with *N*-formylpiperidine at –78 to 0 ˚C to afford α-substituted 2-vinylbenzaldehydes (**2**) in generally good yields as compiled in Table 1. Initially, the bromine/lithium exchange between **1** and butyllithium was carried out in diethyl ether at 0 ˚C as described previously.[4-8] However, after reactions with *N*-formylpiperidine only low-to-moderate yields of **2** were obtained. The reduction of **2** with sodium borohydride in methanol at 0 ˚C provided α-substituted *o*-vinylbenzyl alcohols (**3**) in good to excellent yields. Treatment of these alcohols with thionyl chloride in dichloromethane at 0 ˚C to rt in the presence of pyridine produced the corresponding α-substituted

o-vinylbenzyl chlorides (**4**), which were used in the next step without purification after aqueous workup. The resultant crude chlorides were allowed to react with *tert*-butyl mercaptide, generated from *tert*-butyl mercaptan and sodium hydride, in DMF at 0 ˚C to give α-substituted *o*-[(*tert*-butylsulfanyl)methyl]styrenes (**5**) in good overall yields from **3**.

Table 1. Preparation of the precursor sulfides (**5**)

Entry	**1**	R^1	R^2	R^3	**2**	Yield/%[a]	**3**	Yield/%[a]	**5**	Yield/%[a,b]
1	**1a**	H	H	Ph	**2a**	83	**3a**	82	**5a**	64
2	**1b**	H	H	4-MeC_6H_4	**2b**	80	**3b**	90	**5b**	69
3	**1c**	H	H	4-ClC_6H_4	**2c**	85	**3c**	88	**5c**	64
4	**1d**	H	H	4-$MeOC_6H_4$	**2d**	87	**3d**	98	**5d**	53
5	**1e**	H	H	naphthalen-1-yl	**2e**	87	**3e**	93	**5e**	89
6	**1f**	H	H	Me	**2f**	94	**3f**	88	**5f**	77
7	**1g**	Cl	H	Ph	**2g**	89	**3g**	88	**5g**	92
8	**1h**	MeO	H	Ph	**2h**	79	**3h**	96	**5h**	93
9	**1i**	MeO	MeO	Ph	**2i**	93	**3i**	95	**5i**	75

[a] Yields of isolated products. [b] Overall yields from **3**.



Scheme 2

We hoped that these *tert*-butyl sulfides (**5**) would produce 4-substituted isothiochromenes (**8**) on treatment with iodine. In practice, it was found that compounds (**5**) reacted with three equivalents of iodine in acetonitrile at 0 ˚C in the presence of three equivalents of sodium hydrogencarbonate to result in the isolation of the corresponding desired products (**8**) as the sole products, as depicted in Scheme 2. The synthetic material (**8a**) gave IR and ^{1}H NMR data, which were identical to those reported for 4-phenylisothiochromene.[2] As shown in Table 2, the yields of the products (**8**) are generally moderate to good, though the yield of 4-methylisothiochromene (**8f**) was only low. Yields of the products (**8**) decreased somewhat if two equivalent each of iodine and sodium hydrogencarbonate were used. In Scheme 2, the pathway to these products from **5** is also shown. Thus, the iodonium ion intermediate (**6**) is

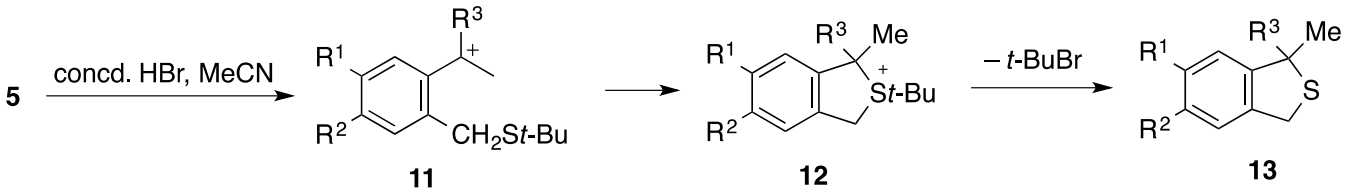
formed on treatment with iodine. The 6-endo cyclization by the attack of one of the lone pairs of the sulfur atom on the β-position of the styryl moiety of **6** occurs exclusively to produce the benzopyranium ion intermediate (**7**). The subsequent eliminations of hydrogen iodide and *tert*-butyl iodide give rise to **8**. 1-(Iodomethyl)-1,3-dihydrobenzo[*c*]thiophenes (**10**), which might be produced *via* the dihydrobenzo[*c*]thiophenium ion intermediate (**9**), generated by the attack of the sulfur atom lone pair on the benzylic carbon of the iodonium ion intermediate (**6**) were not detected at all. Unfavorableness of this pathway may be ascribed to the steric crowd at the reaction center.

Table 2. Preparation of isothiochromenes (**8**) and 1,3-dihydrobenzo[*c*]thiophenes (**13**)

Entry	**5**	R^1	R^2	R^3	**8**	Yield/%[a]	**13**	Temp	Yield/%[a]
1	**5a**	H	H	Ph	**8a**	67	**13a**	rt	78
2	**5b**	H	H	4-MeC_6H_4	**8b**	81	**13b**	rt	83
3	**5c**	H	H	4-ClC_6H_4	**8c**	63	**13c**	rt	52
4	**5d**	H	H	4-$MeOC_6H_4$	**8d**	82	**13d**	0 ˚C	67
5	**5e**	H	H	naphthalen-1-yl	**8e**	35	**13e**	rt	83
6	**5f**	H	H	Me	**8f**	17	**13f**	rt	86
7	**5g**	Cl	H	Ph	**8g**	50	**13g**	rt	63
8	**5h**	MeO	H	Ph	**8h**	63	**13h**	rt	76
9	**5i**	MeO	MeO	Ph	**8i**	53	**13i**	0 ˚C	88

[a] Yields of isolated products.

We also found that when *tert*-butyl sulfides (**5**) were treated with concentrated hydrobromic acid in acetonitrile at 0 ˚C or rt, 1,1-disubstituted 1,3-dihydrobenzo[*c*]thiophenes (**13**) were obtained, as illustrated in Scheme 3. As compiled in Table 2 as well, the yields of the products were generally good, while those of the products carrying an electron-withdrawing chloro substituent on each of the benzene rings were only moderate (Entries 3 and 7). The precursors (**5**) carrying a methoxy group at 4-position on each of the benzene rings (**5d**) and (**5i**) found to be more reactive than the others; therefore, the reaction of these precursors with hydrobromic acid can be conducted at 0 ˚C. Scheme 3 also shows the pathway to the products (**13**). The Markovnikov addition of a proton to the vinyl moiety of **5** generates the benzyl cation intermediate (**11**), which intramolecularly cyclizes by the attack of the sulfur lone pair on the cation center to produce the dihydrobenzo[*c*]thiophenium ion intermediate (**12**). A loss of *tert*-butyl bromide from this intermediate affords **13**. The use of catalytic amounts of the acid resulted in recovery of considerable amounts of the starting materials.



Scheme 3

In summary, the results reported above demonstrate that 4-substituted isothiochromene and 1,1-disubstituted 1,3-dihydrobenzo[*c*]thiophene derivatives, which are hard to prepare by previous methods, can be tunably prepared from readily available starting materials. Work on further applications utilizing *o*-functionalized (*tert*-butylsulfanyl)alkylbenzenes for the preparation of related heterocycles is now in progress in our laboratory. Results of those efforts will be described in due course.

EXPERIMENTAL

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were recorded with a Perkin–Elmer Spectrum 65 FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 and 125 MHz, respectively. High-resolution MS spectra were measured by a JEOL JMS-T100GCV (EI or FI, TOF; 70 eV or 2100 V, respectively) or a Thermo Scientific Exactive (ESI, positive) spectrometer. Elemental analyses were performed with an Elementar Vario EL II instrument. TLC was carried out on Merck Kieselgel 60 PF_{254}. Column chromatography was performed using WAKO GEL C-200E. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

Starting Materials. (2-Bromo-5-chlorophenyl)(phenyl)methanone,[14] (2-bromophenyl)(naphthalen-1-yl)methanone,[15] 2-(1-arylethenyl)-1-bromobenzenes **1a**,[4] **1b**,[5] **1c**,[3b] **1d**,[6] **1f**,[4] **1h**,[5] and **1i**[7] were prepared according to the previously reported method. Butyllithium was supplied by Asia Lithium Corporation. All other chemicals used in this study were commercially available.

1-[1-(2-Bromophenyl)ethenyl]naphthalene (1e). This compound was prepared in 94% yield from (2-bromophenyl)(naphthalen-1-yl)methanone as described for the preparation of **1a**.[4] A pale-yellow oil; R_f 0.64 (CH_2Cl_2/hexane 1:10); IR (neat) 1612 cm^{-1}; ^{1}H NMR δ 5.73 (d, J = 1.1 Hz, 1H), 5.82 (d, J = 1.1 Hz, 1H), 7.13 (td, J = 6.9, 1.7 Hz, 1H), 7.24–7.34 (m, 3H), 7.36–7.50 (m, 3H), 7.58 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.84 (dd, J = 9.2, 2.9 Hz, 1H), 8.23 (dd, J = 9.2, 2.3 Hz, 1H), ^{13}C NMR δ 122.09, 122.53, 125.06, 125.61, 125.96, 126.18, 126.70, 127.21, 127.97, 128.34, 128.75, 131.29, 131.41, 133.51, 134.00, 139.38, 143.43, 147.12. HR-MS (EI). Calcd for $C_{18}H_{13}Br$ (M): 308.0201. Found: *m/z* 308.0190.

1-Bromo-4-chloro-2-(1-phenylethenyl)benzene (1g). This compound was prepared in 68% yield from (2-bromo-5-chlorophenyl)(phenyl)methanone as described for the preparation of **1a**.[4] A colorless oil; R_f

0.64 (CH_2Cl_2/hexane 1:10); IR (neat) 1616 cm^{-1}; ^1H NMR δ 5.27 (s, 1H), 5.85 (s, 1H), 7.19 (dd, J = 7.4, 1.1 Hz, 1H), 7.25–7.33 (m, 6H), 7.51 (d, J = 8.6 Hz, 1H); ^{13}C NMR δ 116.67, 121.26, 126.48, 127.98, 128.43, 129.04, 131.34, 133.27, 134.02, 138.86, 144.19, 147.91. Anal. Calcd for $C_{14}H_{10}BrCl$: C, 57.28; H, 3.43. Found: C, 57.39; H, 3.68.

Typical Procedure for the Preparation of 2-(1-Arylethenyl)benzaldehydes (2). 2-(1-Phenylethenyl)benzaldehyde (2a). To a stirred solution of **1a** (1.2 g, 4.6 mmol) in THF (10 mL) at –78 ˚C was added *n*-BuLi (1.6 M in hexane; 4.6 mmol) dropwise. After 15 min, 1-formylpiperidine (0.57 g, 5.1 mmol) was added and the temperature was gradually raised to 0 ˚C. Saturated aqueous NH_4Cl (20 mL) was added and the mixture was extracted with AcOEt (3 × 15 mL). The combined extracts were washed with brine (20 mL), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by column chromatography on SiO_2 (Et_2O/hexane 1:10) to give **2a** (0.79 g, 83%); a pale-yellow oil; R_f 0.45. The spectral data (IR and ^1H NMR) were identical to those reported previously.[16]

2-[1-(4-Methylphenyl)ethenyl]benzaldehyde (2b): a pale-yellow oil; R_f 0.41 (AcOEt/hexane 1:25); IR (neat) 2848, 2752, 1696 cm^{-1}; ^1H NMR δ 2.34 (s, 3H), 5.22 (s, 1H), 5.94 (s, 1H), 7.12 (d, J = 8.6 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 7.4 Hz, 1H), 7.47 (td, J = 7.4, 1.1 Hz, 1H), 7.58 (td, J = 7.4, 1.1 Hz, 1H), 7.98 (dd, J = 7.4, 1.1 Hz, 1H); 10.04 (s, 1H); ^{13}C NMR δ 21.10, 117.03, 126.77, 127.35, 128.00, 129.31, 130.85, 133.62, 134.45, 138.00, 138.23, 145.57, 145.80, 192.10. HR-MS (EI). Calcd for $C_{16}H_{14}O$ (M): 222.1045. Found: *m/z* 222.1040.

2-[1-(4-Chlorophenyl)ethenyl]benzaldehyde (2c): a colorless oil; R_f 0.47 (AcOEt/hexane 1:25); IR (neat) 2846, 2753, 1697 cm^{-1}; ^1H NMR δ 5.30 (s, 1H), 5.96 (s, 1H), 7.21 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 7.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.99 (d, J = 7.4 Hz, 1H), 10.02 (s, 1H); ^{13}C NMR δ 118.27, 127.85, 128.13, 128.34, 129.79, 130.84, 133.81, 134.23, 134.33, 139.18, 144.78, 144.85, 191.70. HR-MS (EI). Calcd for $C_{15}H_{11}ClO$ (M): 242.0498. Found: *m/z* 242.0504.

2-[1-(4-Methoxyphenyl)ethenyl]benzaldehyde (2d): a colorless oil; R_f 0.26 (AcOEt/hexane 1:25). The spectral data (IR and ^1H NMR) were identical to those reported previously.[17]

2-[1-(Naphthalen-1-yl)ethenyl]benzaldehyde (2e): a pale-yellow solid; mp 55–58 ˚C (hexane/CH_2Cl_2); IR (neat) 2843, 2751, 1690, 1657 cm^{-1}; ^1H NMR δ 5.60 (s, 1H), 5.89 (s, 1H), 7.23 (d, J = 6.9 Hz, 1H), 7.31 (d, J = 6.9 Hz, 1H), 7.38–7.46 (m, 5H), 7.81 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.97–8.00 (m, 2H), 10.40 (s, 1H); ^{13}C NMR δ 124.46, 125.23, 125.46, 125.89, 126.47, 127.62, 127.90, 128.04, 128.59, 128.61, 130.07, 131.09, 133.42, 134.09, 134.27, 139.45, 144.51, 146.52, 191.98. HR-MS (EI). Calcd for $C_{19}H_{14}O$ (M): 258.1045. Found: *m/z* 258.1042.

2-(1-Methylethenyl)benzaldehyde (2f):[18] a colorless liquid; R_f 0.44 (CH_2Cl_2/hexane 1:2). The ^1H NMR data for this compound was identical to those reported previously.[19]

4-Chloro-2-(1-phenylethenyl)benzaldehyde (2g): a pale-yellow oil; R_f 0.29 (AcOEt/hexane 1:25); IR (neat) 2848, 2754, 1693, 1614 cm^{-1}; ^1H NMR δ 5.31 (s, 1H), 6.00 (s, 1H), 7.26 (dd, J = 8.6, 1.7 Hz, 2H), 7.32–7.35 (m, 4H), 7.46 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 9.97 (s, 1H); ^{13}C NMR δ 118.56, 126.79, 128.55, 128.76, 129.00, 130.76 (2 overlapped Cs), 132.77 (2 overlapped Cs), 140.05, 144.65, 146.96, 190.70. Anal. Calcd for $C_{15}H_{11}ClO$: C, 74.23; H, 4.57. Found: C, 74.17; H, 4.75.

4-Methoxy-2-(1-phenylethenyl)benzaldehyde (2h): a colorless liquid; R_f 0.26 (AcOEt/hexane 1:15); IR (neat) 2841, 2759, 1684 cm^{-1}; ^1H NMR δ 3.87 (s, 3H), 5.30 (s, 1H), 5.96 (s, 1H), 6.81 (d, J = 2.9 Hz, 1H), 6.99 (dd, J = 8.6, 2.9 Hz, 1H), 7.27–7.33 (m, 5H), 7.98 (d, J = 8.6 Hz, 1H), 9.90 (s, 1H); ^{13}C NMR δ 55.58, 114.05, 115.46, 117.42, 126.70, 127.91, 128.24, 128.60, 129.87, 140.44, 145.75, 147.99, 163.81, 190.67. HR-MS (EI). Calcd for $C_{16}H_{14}O_2$ (M): 238.0994. Found: *m/z* 238.0990.

4,5-Dimethoxy-2-(1-phenylethenyl)benzaldehyde (2i): a pale-yellow oil; R_f 0.23 (AcOEt/hexane 1:8); IR (neat) 2851, 1769, 1679 cm^{-1}; ^1H NMR δ 3.91 (s, 3H), 3.97 (s, 3H), 5.27 (s, 1H), 5.98 (s, 1H), 6.74 (s, 1H), 7.31 (s, 5H), 7.51 (s, 1H), 9.92 (s, 1H); ^{13}C NMR δ 56.05, 56.18, 108.46, 112.50, 117.89, 126.85, 127.86, 128.26, 128.59, 140.73, 140.88, 145.10, 148.90, 153.55, 190.78. HR-MS (EI). Calcd for $C_{17}H_{16}O_3$ (M): 268.1099. Found: *m/z* 268.1099.

Typical Procedure for the Preparation of 2-(1-Arylethenyl)benzyl Alcohols (3). [2-(1-Phenylethenyl)phenyl]methanol (3a). To a stirring solution of **2a** (0.66 g, 3.2 mmol) in MeOH (6 mL) at 0 ˚C was added $NaBH_4$ (0.12 g, 3.2 mmol) in several portions. After 5 min, 1% aqueous HCl (v/v) (20 mL) was added and the organic solvent was removed by evaporation. The mixture was extracted with AcOEt (3 × 15 mL), and the combined extracts were washed with brine (20 mL), dried (Na_2SO_4) and concentrated by evaporation. The residue was purified by column chromatography on SiO_2 (Et_2O/hexane 1:1) to give **3a** (0.55 g, 82%); a pale-yellow oil; R_f 0.35. The spectral data (IR and ^1H NMR) were identical to those reported previously.[20]

{2-[1-(4-Methylphenyl)ethenyl]phenyl}methanol (3b): a colorless oil; R_f 0.28 (AcOEt/hexane 1:5); IR (neat) 3351, 1610 cm^{-1}; ^1H NMR δ 1.59 (br s, 1H), 2.33 (s, 3H), 4.43 (s, 2H), 5.19 (s, 1H), 5.75 (s, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 7.4 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.48 (d, J = 7.4 Hz, 1H); ^{13}C NMR δ 21.11, 63.23, 114.68, 126.42, 127.55, 127.94, 128.11, 129.21, 130.16, 137.80, 137.90, 138.65, 140.71, 148.13. HR-MS (EI). Calcd for $C_{16}H_{16}O$ (M): 224.1201. Found: *m/z* 224.1195.

{2-[1-(4-Chlorophenyl)ethenyl]phenyl}methanol (3c): a colorless oil; R_f 0.24 (AcOEt/hexane 1:5); IR (neat) 3334, 1615 cm^{-1}; ^1H NMR δ 1.54 (br s, 1H), 4.43 (s, 2H), 5.26 (s, 1H), 5.78 (s, 1H), 7.19–7.23 (m, 3H), 7.26 (d, J = 8.6 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.50 (d, J = 7.4 Hz, 1H);

^{13}C NMR δ 63.05, 116.03, 127.66, 127.81, 127.98, 128.20, 128.63, 130.13, 133.82, 138.56, 138.97, 139.86, 147.12. HR-MS (EI). Calcd for $C_{15}H_{13}ClO$ (M): 244.0655. Found: *m/z* 244.0662.

{2-[1-(4-Methoxyphenyl)ethenyl]phenyl}methanol (3d): a colorless oil; R_f 0.24 (AcOEt/hexane 1:5); IR (neat) 3887, 1606 cm^{-1}; ^{1}H NMR δ 1.56 (br, 1H), 3.79 (s, 3H), 4.44 (s, 2H), 5.14 (s, 1H), 5.70 (s, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 55.25, 63.21, 113.67, 113.82, 127.55, 127.72, 127.93, 128.05, 130.10, 133.14, 138.61, 140.74, 147.60, 159.43. HR-MS (EI). Calcd for $C_{16}H_{16}O_2$ (M): 240.1150. Found: *m/z* 240.1158.

{2-[1-(Naphthalen-1-yl)ethenyl]phenyl}methanol (3e): a colorless oil; R_f 0.51 (AcOEt/hexane 1:7); IR (neat) 3363 cm^{-1}; ^{1}H NMR δ 1.37 (br s, 1H), 4.46 (s, 2H), 5.67 (d, *J* = 1.7 Hz, 1H), 5.74 (d, *J* = 1.7 Hz, 1H), 7.28–7.46 (m, 8H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR δ 63.26, 121.10, 125.19, 125.61, 125.78, 126.22, 126.82, 127.72, 127.95, 128.16, 128.52, 128.55, 130.07, 131.02, 134.05, 138.19, 140.01, 141.89, 147.33. HR-MS (EI). Calcd for $C_{19}H_{16}O$ (M): 260.1201. Found: *m/z* 260.1189.

[2-(1-Methylethenyl)phenyl]methanol (3f):[21] a colorless liquid; R_f 0.57 (AcOEt/hexane 1:2). The ^{1}H NMR data for this compound was identical to those reported previously.[22]

[4-Chloro-2-(1-phenylethenyl)phenyl]methanol (3g): a colorless oil; R_f 0.32 (AcOEt/hexane 1:5); IR (neat) 3335, 1615 cm^{-1}; ^{1}H NMRδ 1.52 (br s, 1H), 4.38 (d, *J* = 5.7 Hz, 2H), 5.26 (d, *J* = 1.1 Hz, 1H), 5.80 (d, *J* = 1.1 Hz, 1H), 7.24–7.33 (m, 6H), 7.35 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR δ 62.43, 116.22, 126.46, 128.02, 128.23, 128.62, 129.35, 129.91, 133.15, 137.21, 139.87, 141.97, 147.14. HR-MS (EI). Calcd for $C_{15}H_{13}ClO$ (M): 244.0655. Found: *m/z* 244.0659.

[4-Methoxy-2-(1-phenylethenyl)phenyl]methanol (3h): a colorless oil; R_f 0.62 (AcOEt/hexane 2:3); IR (neat) 3378, 1606 cm^{-1}; ^{1}H NMR δ 1.37 (br s, 1H), 3.82 (s, 3H), 4.36 (s, 2H), 5.27 (d, *J* = 1.1 Hz, 1H), 5.79 (d, *J* = 1.1 Hz, 1H), 6.81 (d, *J* = 2.9 Hz, 1H), 6.91 (dd, *J* = 8.6, 2.9 Hz, 1H), 7.26–7.29 (m, 5H), 7.38 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR δ 55.30, 62.82, 113.23, 115.52, 115.74, 126.52, 128.02, 128.52, 129.99, 131.05, 140.47, 142.09, 148.24, 158.96. HR-MS (EI). Calcd for $C_{16}H_{16}O_2$ (M): 240.1150. Found: *m/z* 240.1147.

[4,5-Dimethoxy-2-(1-phenylethenyl)phenyl]methanol (3i): a white solid; mp 64–66 ˚C (hexane/CH_2Cl_2); IR (neat) 3491, 1606 cm^{-1}; ^{1}H NMR δ 1.41 (br s, 1H), 3.86 (s, 3H), 3.93 (s, 3H), 4.38 (s, 2H), 5.24 (s, 1H), 5.78 (s, 1H), 6.75 (s, 1H), 7.03 (s, 1H), 7.28–7.30 (m, 5H); ^{13}C NMR δ 55.93, 56.02, 62.99, 111.53, 113.29, 115.48, 126.56, 127.97, 128.50, 131.13, 133.04, 140.92, 148.02, 148.11, 148.62. HR-MS (EI). Calcd for $C_{17}H_{18}O_3$ (M): 270.1256. Found: *m/z* 270.1261.

Typical Procedure for the Preparation of *tert*-Butyl Sulfides (5). 1-{[(1,1-Dimethylethyl)sulfanyl]methyl}-2-(1-phenylethenyl)benzene (5a). To a stirred solution of **3a** (0.55 g, 2.6 mmol) in CH_2Cl_2 (8 mL) containing pyridine (0.21 g, 2.6 mmol) at 0 ˚C was added $SOCl_2$ (0.31 g, 2.6 mmol) dropwise and temperature was raised to rt. After 4 h, the mixture was diluted by adding CH_2Cl_2 (20 mL) and treated with H_2O (20 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic layers were washed with brine (15 mL), dried (Na_2SO_4) and concentrated by evaporation. The crude product **4a** (0.46 g) was used in the next reaction without purification. Thus, to a stirred suspension of NaH (60% in mineral oil; 88 mg, 2.2 mmol) in DMF (3 mL) at 0 ˚C was added *t*-BuSH (0.20 g, 2.2 mmol) dropwise. After evolution of H_2 gas had ceased, a DMF (2 mL) solution of the above **4a** was added. After 5 min, saturated aqueous NH_4Cl (20 mL) was added and the mixture was extracted with AcOEt (3 × 15 mL). The combined extracts were washed with brine (20 mL), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by column chromatography on SiO_2 (CH_2Cl_2/hexane 1:3) to give **5a** (0.47 g, 64%); a white solid; mp 80–81 ˚C (hexane); IR (KBr) 1615 cm^{-1}; ^1H NMR δ 1.21 (s, 9H), 3.55 (s, 2H), 5.33 (s, 1H), 5.82 (d, *J* = 1.4 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.22 (dd, *J* = 7.8, 7.3 Hz, 1H), 7.25–7.31 (m, 6H), 7.47 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR δ 30.64, 30.68, 42.75, 115.78, 126.61, 126.71, 127.69, 127.74, 128.32, 130.07, 130.36, 136.14, 140.74, 141.32, 148.04. HR-MS (EI). Calcd for $C_{19}H_{22}S$ (M): 282.1442. Found: *m/z* 282.1453.

1-{[(1,1-Dimethylethyl)sulfanyl]methyl}-2-[1-(4-methylphenyl)ethenyl]benzene (5b): a yellow oil; R_f 0.21 (AcOEt/hexane 1:100); IR (neat) 1610 cm^{-1}; ^1H NMR δ 1.21 (s, 9H), 2.33 (s, 3H), 3.56 (s, 2H), 5.26 (s, 1H), 5.78 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.14–7.19 (m, 4H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR δ 21.11, 30.69 (2 overlapped Cs), 42.75, 114.84, 126.51, 126.66, 127.64, 129.01, 130.03, 130.31, 136.22, 137.50, 137.98, 141.55, 147.85. HR-MS (FI). Calcd for $C_{20}H_{24}S$ (M): 296.1599. Found: *m/z* 296.1603.

1-[1-(4-Chlorophenyl)ethenyl]-2-{[(1,1-dimethylethyl)sulfanyl]methyl}benzene (5c): a colorless oil; R_f 0.20 (AcOEt/hexane 1:100); IR (neat) 1615 cm^{-1}; ^1H NMR δ 1.22 (s, 9H), 3.53 (s, 2H), 5.33 (s, 1H), 5.80 (s, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.21–7.32 (m, 6H), 7.46 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 33.63, 33.67, 116.19, 126.86, 127.94, 127.96, 128.46, 130.26, 130.31, 133.54, 135.54, 136.08, 139.23, 140.84, 146.98. HR-MS (FI). Calcd for $C_{19}H_{21}ClS$ (M): 316.1052. Found: *m/z* 316.1068.

1-{[(1,1-Dimethylethyl)sulfanyl]methyl}-2-[1-(4-methoxyphenyl)ethenyl]benzene (5d): a pale-yellow oil; R_f 0.30 (CH_2Cl_2/hexane 1:4); IR (neat) 1607 cm^{-1}; ^1H NMR δ 1.14 (s, 9H), 3.49 (s, 2H), 3.72 (s, 3H), 5.13 (s, 1H), 5.65 (s, 1H), 6.74 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 7.14–7.20 (m, 3H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 30.62, 30.68, 42.75, 55.27, 113.66, 113.86, 126.67,

127.65, 127.81, 130.03, 130.27, 133.44, 136.19, 141.58, 147.39, 159.28. HR-MS (FI). Calcd for $C_{20}H_{24}OS$ (M): 312.1548. Found: *m/z* 312.1548.

1-[(2-{[(1,1-Dimethylethyl)sulfanyl]methyl}phenyl)ethenyl]naphthalene (5e): a pale-yellow oil; R_f 0.46 (CH_2Cl_2/hexane 1:3); IR (neat) 1607 cm^{-1}; ^1H NMR δ 1.17 (s, 9H), 3.67 (s, 2H), 5.69 (s, 1H), 5.87 (d, *J* = 1.1 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 6.9 Hz, 1H), 7.38–7.46 (m, 5H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR δ 30.63, 30.91, 42.78, 121.06, 125.21, 125.60, 125.97, 126.00, 126.81, 126.95, 127.64, 127.87, 128.38, 130.12, 130.79, 131.21, 134.08, 135.34, 140.25, 142.72, 147.16. HR-MS (FI). Calcd for $C_{23}H_{24}S$ (M): 332.1599. Found: *m/z* 333.1593.

1-{[(1,1-Dimethylethyl)sulfanyl]methyl}-2-(1-methylethenyl)benzene (5f): a colorless liquid; R_f 0.44 (CH_2Cl_2/hexane 1:5); IR (neat) 1639 cm^{-1}; ^1H NMR δ 1.35 (s, 9H), 2.11 (s, 3H), 3.79 (s, 2H), 4.98 (d, *J* = 1.1 Hz, 1H), 5.23 (q, *J* = 1.7 Hz, 1H), 7.11 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.17–7.20 (m, 2H), 7.39 (dd, *J* = 7.4, 1.1 Hz, 1H); ^{13}C NMR δ 25.24, 30.49, 30.73, 42.89, 115.09, 126.60, 126.97, 128.05, 130.26, 134.46, 143.75, 144.75. HR-MS (ESI). Calcd for $C_{14}H_{20}S$ (M+H): 221.1364. Found: *m/z* 221.1360.

1-Chloro-4-{[(1,1-dimethylethyl)sulfanyl]methyl}-3-(1-phenylethenyl)benzene (5g): a pale-yellow oil; R_f 0.53 (CH_2Cl_2/hexane 1:4); IR (neat) 1615 cm^{-1}; ^1H NMR δ 1.19 (s, 9H), 3.49 (s, 2H), 5.33 (s, 1H), 5.83 (s, 1H), 7.19 (d, *J* = 1.7 Hz, 1H), 7.26–7.30 (m, 6H), 7.41 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR δ 30.12, 30.63, 42.92, 116.40, 126.55, 127.82, 127.97, 128.46, 130.07, 131.45, 132.30, 134.94, 140.03, 142.93, 147.02. HR-MS (FI). Calcd for $C_{19}H_{21}ClS$ (M): 316.1052. Found: *m/z* 316.1061.

1-{[(1,1-Dimethylethyl)sulfanyl]methyl}-4-methoxy-2-(1-phenylethenyl)benzene (5h): a pale-yellow oil; R_f 0.54 (AcOEt/hexane 1:10); IR (neat) 1604 cm^{-1}; ^1H NMR δ 1.20 (s, 9H), 3.49 (s, 2H), 3.78 (s, 3H), 5.33 (s, 1H), 5.81 (s, 1H), 6.73 (d, *J* = 2.3 Hz, 1H), 6.85 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.25–7.31 (m, 5H), 7.37 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR δ 30.07, 30.67, 42.61, 55.27, 113.39, 115.59, 115.67, 126.60, 127.72, 128.14, 128.32, 131.18, 140.50, 142.49, 148.00, 158.20. HR-MS (FI). Calcd for $C_{20}H_{24}OS$ (M): 312.1548. Found: *m/z* 312.1545.

1-{[(1,1-Dimethylethyl)sulfanyl]methyl}-4,5-dimethoxy-2-(1-phenylethenyl)benzene (5i): a colorless oil; R_f 0.59 (AcOEt/hexane 1:4); IR (neat) 1604 cm^{-1}; ^1H NMR δ 1.21 (s, 9H), 3.53 (s, 2H), 3.82 (s, 3H), 3.92 (s, 3H), 5.33 (s, 1H), 5.80 (s, 1H), 6.67 (s, 1H), 6.99 (s, 1H), 7.26–7.31 (m, 5H); ^{13}C NMR δ 30.60, 30.69, 42.70, 55.91, 55.94, 112.76, 113.30, 115.61, 126.67, 127.70, 128.25, 128.31, 133.59, 140.87, 147.52, 147.86, 148.38. HR-MS (FI). Calcd for $C_{21}H_{26}O_2S$ (M): 342.1654. Found: *m/z* 342.1667.

Typical Procedure for the Preparation of 1*H*-2-Benzothiopyrans (8). 4-Phenyl-1*H*-2-benzothiopyran (8a).[2] To a stirred solution of **5a** (0.24 g, 0.85 mmol) in MeCN (5 mL) containing $NaHCO_3$ (0.21 g, 2.6 mmol) at 0 ˚C was added I_2 (0.65 g, 2.6 mmol) in portions. The temperature was

raised to rt, and the mixture was stirred for 15 min before 10% aqueous $Na_2S_2O_3$ (15 mL) was added. After evaporation of MeCN, the organic materials were extracted with AcOEt (3 × 15 mL), and the combined extracts were washed with saturated aqueous $NaHCO_3$ and brine (20 mL each), and dried over anhydrous K_2CO_3. Evaporation of the solvent gave a residue, which was purified by column chromatography on SiO_2 to afford **8a** (0.12 g, 67%); a pale-yellow oil; R_f 0.45 (CH_2Cl_2/hexane 1:4). The spectral data (IR and ^1H NMR) were identical to those reported previously.[2]

4-(4-Methylphenyl)-1*H*-2-benzothiopyran (8b): a white solid; mp 94–96 ˚C (hexane/CH_2Cl_2); IR (KBr) 1595, 1509, 1485 cm^{-1}; ^1H NMR δ 2.38 (s, 3H), 3.85 (s, 2H), 6.51 (s, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 7.14–7.25 (m, 7H); ^{13}C NMR δ 21.16, 31.19, 120.69, 126.29, 126.70, 127.27, 128.19, 128.52, 129.15, 129.60, 134.41, 137.06, 137.50, 138.79. HR-MS (EI). Calcd for $C_{16}H_{14}S$ (M): 238.0816. Found: *m/z* 238.0814. Anal. Calcd for $C_{16}H_{14}S$: C, 80.63; H, 5.92; S, 13.45. Found: C, 80.41; H, 5.91; S, 13.16.

4-(4-Chlorophenyl)-1*H*-2-benzothiopyran (8c): a white solid; mp 166–168 ˚C (hexane/CH_2Cl_2); IR (KBr) 1535, 1487 cm^{-1}; ^1H NMR δ 3.86 (s, 2H), 6.54 (s, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 7.16–7.20 (m, 2H), 7.25–7.29 (m, 3H), 7.35 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR δ 31.12, 121.92, 126.03, 126.87, 127.43, 128.49, 128.68, 129.47, 129.94, 133.17, 133.93, 137.66, 138.81. HR-MS (EI). Calcd for $C_{15}H_{11}ClS$ (M): 258.0270. Found: *m/z* 258.0259.

4-(4-Methoxyphenyl)-1*H*-2-benzothiopyran (8d): a white solid; mp 80–83 ˚C (hexane/CH_2Cl_2); IR (KBr) 1608, 1543, 1505 cm^{-1}; ^1H NMR δ 3.84 (s, 3H), 3.85 (s, 2H), 6.49 (s, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR δ 31.16, 55.29, 113.81, 120.22, 126.27, 126.70, 127.27, 128.20, 129.63, 129.73, 132.86, 134.43, 138.46, 158.92. HR-MS (EI). Calcd for $C_{16}H_{14}OS$ (M): 254.0765. Found: *m/z* 254.0758. Anal. Calcd for $C_{16}H_{14}OS$: C, 75.56; H, 5.55; S, 12.60. Found: C, 75.34; H, 5.53; S, 12.46.

4-(Naphthalen-1-yl)-1*H*-2-benzothiopyran (8e): reaction time: 15 h; a white solid; mp 128–129 ˚C (hexane/CH_2Cl_2); IR (KBr) 1505, 1483 cm^{-1}; ^1H NMR δ 3.84 (d, *J* = 13.7 Hz, 1H), 4.09 (d, *J* = 13.7 Hz, 1H), 6.50 (s, 1H), 6.51 (d, *J* = 6.9 Hz, 1H), 6.91–6.95 (m, 1H), 7.15–7.17 (m, 2H), 7.28 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.38 (t, *J* = 6.9 Hz, 2H), 7.44 (dd, *J* = 8.0, 6.9 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR δ 31.08, 123.21, 125.69, 125.84, 125.94, 126.00, 126.07, 126.76, 127.44, 127.58, 127.88, 128.07, 128.20, 128.24, 131.97, 133.62, 134.95, 136.68, 138.19. HR-MS (EI). Calcd for $C_{19}H_{14}S$ (M): 274.0816. Found: *m/z* 274.0806. Anal. Calcd for $C_{19}H_{14}S$: C, 83.17; H, 5.14. Found: C, 83.00; H, 5.24.

4-Methyl-1*H*-2-benzothiopyran (8f):[23] a pale- yellow oil; R_f 0.41 (CH_2Cl_2/hexane 1:4); IR (neat) 1600, 1487 cm^{-1}; ^1H NMR δ 2.11 (s, 3H), 3.68 (s, 2H), 6.16 (s, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 7.15 (td, *J* = 7.4,

1.7 Hz, 1H), 7.17–7.23 (m, 2H); ^{13}C NMR δ 20.43, 30.84, 118.57, 123.27, 126.70, 127.44, 127.93, 129.29, 131.16, 134.58.

6-Chloro-4-phenyl-1*H*-2-benzothiopyran (8g): colorless needles; mp 114–115 ˚C (hexane/CH_2Cl_2); IR (KBr) 1586, 1475 cm^{-1}; ^{1}H NMR δ 3.82 (s, 2H), 6.61 (s, 1H), 6.98 (d, *J* = 1.7 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.23 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.33–7.42 (m, 5H); ^{13}C NMR δ 30.60, 122.96, 126.04, 127.65, 127.96, 128.05, 128.51, 128.69 (2 overlapped Cs), 133.16, 135.91, 138.02, 139.62. HR-MS (EI). Calcd for $C_{15}H_{11}ClS$ (M): 258.0270. Found: *m/z* 258.0272. Anal. Calcd for $C_{15}H_{11}ClS$: C, 69.63; H, 4.29. Found: C, 69.56; H, 4.28.

6-Methoxy-4-phenyl-1*H*-2-benzothiopyran (8h):[24] a white solid; mp 74–77 ˚C (hexane); IR (KBr) 1604, 1489 cm^{-1}; ^{1}H NMR δ 3.67 (s, 3H), 3.83 (s, 2H), 6.57 (br s, 2H), 6.81 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.31–7.39 (m, 5H); ^{13}C NMR δ 30.55, 55.26, 112.49, 112.99, 121.96, 122.02, 127.34, 127.57, 128.48, 128.58, 135.34, 138.66, 140.25, 158.78.

6,7-Dimethoxy-4-phenyl-1*H*-2-benzothiopyran (8i): a white solid; mp 101 ˚C (hexane); IR (KBr) 1602, 1514 cm^{-1}; ^{1}H NMR δ 3.65 (s, 3H), 3.82 (s, 2H), 3.92 (s, 3H), 6.46 (s, 1H), 6.56 (s, 1H), 6.73 (s, 1H), 7.33–7.38 (m, 5H); ^{13}C NMR δ 30.81, 55.92, 56.00, 110.01, 110.22, 118.86, 122.38, 127.12, 127.36, 128.45 (2 overlapped Cs), 138.69, 140.32, 147.76, 148.71. Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.56; H, 5.69.

General Procedure for the Preparation of 1,3-Dihydrobenzo[*c*]thiophenes (13). To a stirred solution of **5** (1.0 mmol) in MeCN (5 mL) at 0 ˚C was added concentrated HBr (0.18 g, 1.0 mmol). Stirring was continued at the temperature indicated in Table 2 until disappearance of the starting materials had been confirmed by TLC analyses on silica gel. Saturated aqueous $NaHCO_3$ (20 mL) was added, and MeCN was removed by evaporation. The mixture was extracted with AcOEt (3 × 15 mL), and the combined extracts were washed with water and brine (20 mL each), and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by preparative TLC on silica gel to afford **13**.

1-Methyl-1-phenyl-1,3-dihydrobenzo[*c*]thiophene (13a): a pale-yellow oil; R_f 0.29 (CH_2Cl_2/hexane 1:5); IR (neat) 1485, 1445 cm^{-1}; ^{1}H NMR δ 2.11 (s, 3H), 4.30 (d, *J* = 15.4 Hz, 1H), 4.32 (d, *J* = 15.4 Hz, 1H), 6.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.22–7.30 (m, 5H), 7.33 (dd, *J* = 7.8, 1.4 Hz, 2H); ^{13}C NMR δ 30.80, 36.74, 63.63, 124.45, 124.72, 126.63, 126.73, 126.97, 127.11, 128.08, 140.40, 147.53, 148.94. HR-MS (EI). Calcd for $C_{15}H_{14}S$ (M): 226.0816. Found: *m/z* 226.0817.

1-Methyl-1-(4-methylphenyl)-1,3-dihydrobenzo[*c*]thiophene (13b): a pale-yellow oil; R_f 0.25 (CH_2Cl_2/hexane 1:10); IR (neat) 1510, 1483, 1452 cm^{-1}; ^{1}H NMR δ 2.09 (s, 3H), 2.30 (s, 3H), 4.29 (d, *J* = 14.3 Hz, 1H), 4.30 (d, *J* = 14.3 Hz, 1H), 6.98 (d, *J* = 6.9 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.19–7.25 (m, 5H), 7.28 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR δ 20.91, 30.87, 36.49, 63.24, 124.38, 124.66, 126.64, 126.83,

127.03, 128.75, 136.21, 140.43, 144.78, 149.25. HR-MS (EI). Calcd for $C_{16}H_{16}S$ (M): 240.0973. Found: *m/z* 240.0981.

1-(4-Chlorophenyl)-1-methyl-1,3-dihydrobenzo[*c*]thiophene (13c): a pale-yellow oil; R_f 0.27 (CH_2Cl_2/hexane 1:10); IR (neat) 1592, 1481 cm^{-1}; ^1H NMR δ 2.08 (s, 3H), 4.30 (s, 2H), 6.95 (d, J = 6.9 Hz, 1H), 7.20–7.30 (m, 7H); ^{13}C NMR δ 30.78, 36.55, 62.91, 124.28, 124.80, 127.12, 127.21, 128.13, 128.28, 132.40, 140.38, 146.37, 148.71. HR-MS (EI). Calcd for $C_{15}H_{13}ClS$ (M): 260.0427. Found: *m/z* 260.0415.

1-(4-Methoxyphenyl)-1-methyl-1,3-dihydrobenzo[*c*]thiophene (13d): a pale-yellow oil; R_f 0.34 (CH_2Cl_2/hexane 3:10); IR (neat) 1608, 1581, 1508 cm^{-1}; ^1H NMR δ 2.08 (s, 3H), 3.77 (s, 3H), 4.30 (s, 2H), 6.80 (d, J = 8.6 Hz, 2H), 6.96 (dd, J = 8.6, 1.1 Hz, 1H), 7.20–7.23 (m, 2H), 7.25–7.29 (m, 3H); ^{13}C NMR δ 31.05, 36.43, 55.21, 63.12, 113.30, 124.31, 124.68, 126.82, 127.04, 128.02, 139.80, 140.31, 149.47, 158.10. HR-MS (EI). Calcd for $C_{16}H_{16}OS$ (M): 256.0922. Found: *m/z* 256.0932.

1-Methyl-1-(naphthalen-1-yl)-1,3-dihydrobenzo[*c*]thiophene (13e): a pale-yellow solid; mp 119–120 ˚C (hexane/ CH_2Cl_2); IR (neat) 1598, 1510, 1482, 1455 cm^{-1}; ^1H NMR δ 2.27 (s, 3H), 4.38 (d, J = 14.3 Hz, 1H), 4.47 (d, J = 14.3 Hz, 1H), 6.88 (d, J = 7.4 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 7.24–7.48 (m, 6H), 7.76 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1H); ^{13}C NMR δ 33.93, 36.81, 63.22, 124.33, 124.49, 124.67, 125.03 (2 overlapped Cs), 125.27, 126.95, 127.10, 127.26, 129.02, 129.09, 130.85, 135.16, 139.52, 140.54, 150.10. HR-MS (EI). Calcd for $C_{19}H_{16}S$ (M): 276.0973. Found: *m/z* 276.0966. Anal. Calcd for $C_{19}H_{16}S$: C, 82.57; H, 5.84. Found: C, 82.33; H, 5.81.

1-Methyl-1-phenyl-1,3-dihydrobenzo[*c*]thiophene (13f): a colorless liquid; R_f 0.32 (hexane). The ^1H and ^{13}C NMR data for this compound were identical to those reported previously.[14]

6-Chloro-1-methyl-1-phenyl-1,3-dihydrobenzo[*c*]thiophene (13g): a pale-yellow oil; R_f 0.59 (Et_2O/hexane 1:20); IR (neat) 1592, 1481 cm^{-1}; ^1H NMR δ 2.09 (s, 3H), 4.26 (s, 2H), 6.94 (s, 1H), 7.21–7.23 (m, 3H), 7.29–7.34 (m, 4H); ^{13}C NMR δ 30.64, 35.98, 63.12, 124.57, 125.68, 126.73, 126.89, 127.15, 128.21, 133.00, 139.01, 146.80, 151.26. HR-MS (EI). Calcd for $C_{15}H_{13}ClS$ (M): 260.0427. Found: *m/z* 260.0435. Anal. Calcd for $C_{15}H_{13}ClS$: C, 69.09; H, 5.02. Found: C, 68.90; H, 5.24.

5-Methoxy-1-methyl-1-phenyl-1,3-dihydrobenzo[*c*]thiophene (13h): a pale-yellow oil; R_f 0.48 (AcOEt/hexane 1:10); IR (neat) 1607, 1580, 1494, 1443 cm^{-1}; ^1H NMR δ 2.10 (s, 3H), 3.73 (s, 3H), 4.21 (d, J = 13.2 Hz, 1H), 4.25 (d, J = 13.2 Hz, 1H), 6.49 (d, J = 2.3 Hz, 1H), 6.80 (dd, J = 8.6, 2.3 Hz, 1H), 7.18 (d, J = 8.6 Hz, 1H), 7.19 (t, J = 7.4 Hz, 1H), 7.27 (dd, J = 8.0, 7.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ 30.63, 35.84, 55.44, 63.26, 109.61, 112.93, 125.13, 126.59, 126.68, 128.08, 132.53, 147.56, 150.64, 159.09. HR-MS (EI). Calcd for $C_{16}H_{16}OS$ (M): 256.0922. Found: *m/z* 256.0921. Anal. Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29. Found: C, 74.80; H, 6.24.

5,6-Dimethoxy-1-methyl-1-phenyl-1,3-dihydrobenzo[*c*]thiophene (13i): a white solid; mp 69–70 ˚C (hexane/ CH_2Cl_2); IR (KBr) 1603,1505 cm^{-1}; ^1H NMR δ 2.11 (s, 3H), 3.76 (s, 3H), 3.89 (s, 3H), 4.24 (d, *J* = 15.5 Hz, 1H), 4.26 (d, *J* = 15.5 Hz, 1H), 6.44 (s, 1H), 6.77 (s, 1H), 7.20 (td, *J* = 7.4, 1.1 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.32 (dd, *J* = 7.4, 1.1 Hz, 2H); ^{13}C NMR δ 30.82, 36.55, 55.98, 56.03, 63.46, 106.92, 107.02, 126.50, 126.52, 128.11, 132.10, 140.76, 148.04, 148.42, 148.56. HR-MS (FI). Calcd for $C_{17}H_{18}O_2S$ (M): 286.1028. Found: *m/z* 286.1034. Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34. Found: C, 70.95; H, 6.22.

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REFERENCES

1. D. Kaminsky, A. Kryshchyshyn, I. Nektegayev, O. Vasylenko, P. Grellier, and R. Lesyk, *Eur. J. Med. Chem.*, 2014, **75**, 57.
2. A. Padwa, A. Au, G. A. Lee, and W. Owens, *J. Org. Chem.*, 1975, **40**, 1142.
3. (a) T. R. Appel, N. A. M. Yehia, U. Baumeister, H. Hratung, R. Kluge, D. Ströhl, and E. Fanghänel, *Eur. J. Org. Chem.*, 2003, 47; (b) K. Kobayashi, S. Fujita, M. Hase, O. Morikawa, and H. Konishi, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 763; (c) G. Mloston, P. Grzelak, M. Mikina, A. Linden, and H. Heimgartner, *Beilstein J. Org. Chem.*, 2015, **11**, 576.
4. K. Kobayashi, M. Hase, K. Hashimoto, S. Fujita, M. Tanmatsu, O. Morikawa, and H. Konishi, *Synthesis*, 2006, 2493.
5. S. Fukamachi, H. Konishi, and K. Kobayashi, *Heterocycles*, 2009, **78**, 169.
6. K. Kobayashi, M. Horiuchi, M. Tanmatsu, and H. Konishi, *Heterocycles*, 2008, **75**, 1779.
7. S. Fukamachi, M. Tanmatsu, H. Konishi, and K. Kobayashi, *Heterocycles*, 2009, **78**, 2077.
8. (a) K. Kobayashi, K. Shikata, S. Fukamachi, and H. Konishi, *Heterocycles*, 2008, **75**, 599; (b) K. Kobayashi, T. Kozuki, S. Fukamachi, and H. Konishi, *Heterocycles*, 2010, **81**, 163; (c) K. Kobayashi, K. Shikata, Y. Fujii, S. Fukamachi, M. Tanmatsu, and H. Konishi, *Heterocycles*, 2010, **81**, 1459.
9. (a) M. P. Cava and J. McGrady, *J. Org. Chem.*, 1975, **40**, 72; (b) A. M. S. Silva, A. M. G. Silva, A. C. Tome, and J. A. S. Cavaleiro, *Eur. J. Org. Chem.*, 1999, 135; (c) D. T. Patoilo, A. M. S. Silva, D. C. G. A. Pinto, A. C. Tome, and J. A. S. Cavaleiro, *J. Heterocycl. Chem.*, 2007, **44**, 1345; (d) S. Kotha and P. Khedkar, *J. Org. Chem.*, 2009, **74**, 5667; (e) E. U. Mughal, J. Ebenhard, and D. Kuck, *Chem. Eur. J.*, 2010, **75**, 2706; (f) G. da Silva, V. L. M. Silva, and A. M. S. Silva, *Synthesis*, 2016,

48, 4519.

10. R. Neidlein and H. Doert, *Liebigs Ann. Chem.*, 1980, 1540.
11. H. Zhou, D. Zhu, Y. Xie, H. Huang, and K. Wang, *J. Org. Chem.*, 2010, **75**, 2706.
12. K. Kobayashi and Y. Shigemura, *Heterocycles*, 2016, **92**, 2261.
13. T. Nishio, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1113.
14. K. Kobayashi, W. Miyatani, and N. Matsumoto, *Helv. Chim. Acta*, 2013, **96**, 239.
15. K. Kobayashi, K. Hashimoto, T. Ukon, S. Fukamachi, O. Morikawa, and H. Konishi, *Synthesis*, 2008, 584.
16. K. Kundu, J. V. McCullagh, and A. T. Morehead, Jr., *J. Am. Chem. Soc.*, 2005, **127**, 16042.
17. J. Yang and N. Yoshikai, *J. Am. Chem. Soc.*, 2014, **136**, 16748.
18. R. F. C. Brown and M. Butcher, *Aust. J. Chem.*, 1969, **22**, 1457.
19. W. T. Spencer and A. J. Frontier, *J. Org. Chem.*, 2012, **77**, 7730.
20. J. M. Hornback, L. G. Mawhorter, S. E. Carlson, and R. A. Bedont, *J. Org. Chem.*, 1979, **44**, 3698.
21. M. Jimenez-Estrada, A. Navarro, M. V. Flores, R. R. Chilpa, B. Hernandez, A. L. Anaya, and B. Lotina-Hennsen, *J. Agric. Food Chem.*, 1996, **44**, 2346.
22. P. I. Fedrov, T. P. Fedorova, V. P. Sheverdov, and A. V. Eremkin, *Russ. J. Org. Chem.*, 2016, **52**, 806.
23. F. Krolipfeiffer, H. Schultze, E. Schlumbohm, and E. Sommermeyer, *Ber*, 1925, **58B**, 1654.
24. L. Benati, L. Capella, P. C. Montevecchi, and P. Spagnolo, *J. Org. Chem.*, 1994, **59**, 2818.