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ONE-POT SYNTHESIS OF 4-SUBSTITUTED ISOTHIOCHROMAN-1-THIONES FROM α-SUBSTITUTED 2-BROMOSTYRENES AND CARBON DISULFIDE

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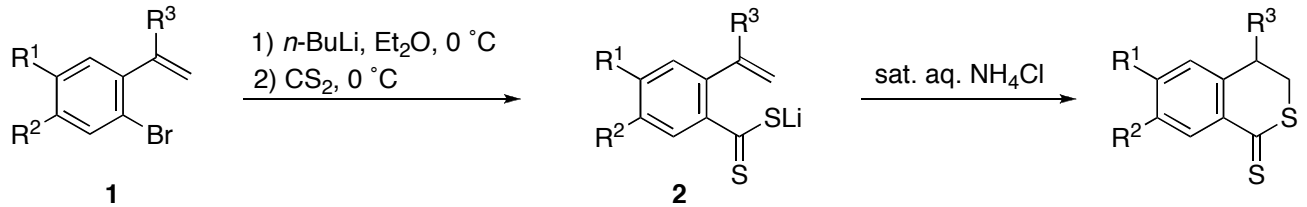
Abstract - A facile method for the preparation of isothiochroman-1-thiones has been developed. Thus, treatment of α-substituted 2-lithiostyrenes, generated in situ from bromine-lithium exchange between the respective 2-bromostyrenes and butyllithium, with carbon disulfide, followed by workup with saturated aqueous ammonium chloride, affords 4-substituted isothiochroman-1-thiones in reasonable yields.

We previously described that the reaction of α-substituted 2-lithiostyrenes, generated by bromine-lithium exchange between α-substituted 2-bromostyrenes and butyllithium, with carbon disulfide generated α-substituted lithium 2-(vinyl)dithiobenzoates, which were then treated with iodine to give 4-substituted isothiochromene-1-thiones together with the corresponding 3-iodomethylbenzo[*c*]thiophene-1(3*H*)-thione derivatives.[1] As a continuation of this study, we now wish to report that 4-substituted 3,4-dihydroisothiochroman-1-thiones (**3**) can be obtained by simply working up α-substituted lithium 2-(vinyl)dithiobenzoates (**2**) with saturated aqueous ammonium chloride. Isothiochroman-1-thione (3,4-dihydro-2-benzothiopyran-1-thione) derivatives may be of interest from a biological point of view, because some of compounds having the related isothiochroman skeleton have been reported to exhibit biological activity.[2] Although a few methods have been reported to prepare this class of heterocycles,[3] these are suffered from quite limited generality and unavailability of the starting materials. Thus, Campora et al. have prepared 4,4-dimethylisothiochroman-1-thione by reacting the respective nickelabenzocyclopentane complex with carbon disulfide.[3a,c] Isothiochroman-1-thione has been prepared by successive treatment of 1-bromo-2-(2-chloroethyl)benzene with butyllithium and carbon disulfide by Gade et al.[3b]

The one-pot preparation of 4-substituted isothiochroman-1-thiones (**3**) from α-substituted 2-bromostyrenes (**1**) was conducted as illustrated in Scheme 1. Thus, compounds (**1**) were treated with butyllithium in diethyl ether at 0 ˚C to generate the corresponding α-substituted 2-lithiostyrenes, which were allowed to react with carbon disulfide to give α-substituted lithium 2-(vinyl)dithiobenzoates (**2**). Then, addition of saturated aqueous ammonium chloride to the reaction mixtures caused cyclization of the resulting α-substituted 2-(vinyl)dithiobenzoic acids to afford 4-substituted isothiochroman-1-thiones (**3**). The yields of the products are also indicated in Scheme 1. When the substrates carrying a methyl group at the α-position (i.e., **1a** and **1e**) were used as the starting materials, the expected products (**2a** and **2e**, respectively) were obtained in rather lower yields. The substrates carrying a 4-chlorophenyl group at the α-position (i.e., **1d** and **1h**) gave somewhat lower yields of the expected products (**2d** and **2h**, respectively). It was found that methoxy group(s) on the benzene nuclei improved the yields of the expected products. Higher electron density of the vinyl moiety may facilitate the cyclization.



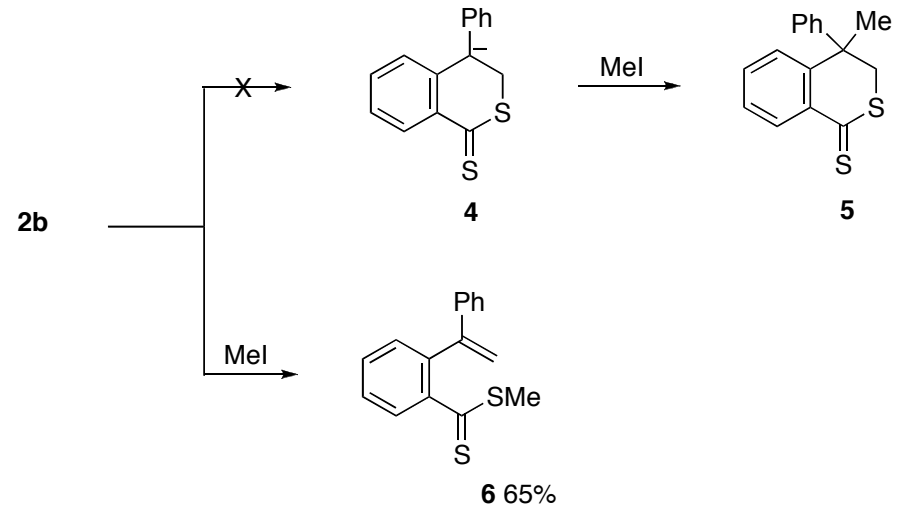
1 **2**

a $R^1 = R^2 = H$, $R^3 = Me$
b $R^1 = R^2 = H$, $R^3 = Ph$
c $R^1 = R^2 = H$, $R^3 = p$-Tol
d $R^1 = R^2 = H$, $R^3 = 4\text{-}ClC_6H_4$
e $R^1 = OMe$, $R^2 = H$, $R^3 = Me$
f $R^1 = OMe$, $R^2 = H$, $R^3 = Ph$
g $R^1 = OMe$, $R^2 = H$, $R^3 = p$-Tol
h $R^1 = OMe$, $R^2 = H$, $R^3 = 4\text{-}ClC_6H_4$
i $R^1 = OMe$, $R^2 = H$, $R^3 = 4\text{-}MeOC_6H_4$
j $R^1 = R^2 = OMe$, $R^3 = Ph$

3a 12%
3b 46%
3c 44%
3d 28%
3e 19%
3f 58%
3g 54%
3h 35%
3i 56%
3j 51%

Scheme 1

Unfortunately, we cannot make any explanation of the mechanism for the formation of 4-substituted isothiochroman-1-thiones (**3**) from the α-substituted 2-(vinyl)dithiobenzoic acids. The cyclization, giving a benzyl anion intermediate (**4**), does not occur before workup, because addition of iodomethane to the reaction mixture from **1b** resulted in the formation of methyl 2-(1-phenylethenyl)benzenedithioate (**6**) in high yields, and no trace of 4-methyl-4-phenyl-3,4-dihydroisothiochroman-1-thione (**5**) was detected. It should be noted that workup of α-substituted lithium 2-(vinyl)dithiobenzoates (**2**) under more acidic conditions using 10% hydrochloric acid gave intractable mixtures of products, from which no trace of the desired products could not be isolated.



Scheme 2

In conclusion, we have shown that the reaction described here offers a convenient synthesis of 4-substituted isothiochroman-1-thiones. This is the first method for the general synthesis of isothiochroman-1-thiones. The present method may be of value in organic synthesis, because it is of simple manipulations and the starting α-substituted 2-bromostyrenes are readily available.

EXPERIMENTAL

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were determined with a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H NMR spectra were determined in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz. The ^{13}C NMR spectra were determined in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. Low-resolution MS spectra (EI, 70 eV) were measured by a JEOL JMS AX505 HA spectrometer. TLC was carried out on a Merck Kieselgel 60 PF_{254}. Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

Starting Materials. 1-Bromo-2-(1-methylethenyl)benzene (**1a**),[4] 1-bromo-2-(1-phenylethenyl)benzene (**1b**),[5] 1-bromo-2-[1-(4-methylphenyl)ethenyl]benzene (**1c**),[6] 1-bromo-2-[1-(4-chlorophenyl)ethenyl]benzene (**1d**),[7] 1-bromo-4-methoxy-2-(1-methylethenyl)benzene (**1e**),[8] 1-bromo-4-methoxy-2-(1-phenylethenyl)benzene (**1f**),[7] 1-bromo-2-[1-2-(4-chlorophenyl)ethenyl]-4-methoxybenzene (**1h**),[6] 1-bromo-4-methoxy-2-[1-(4-methoxyphenyl)ethenyl]benzene (**1i**),[6] 2-bromo-5-methoxybenzaldehyde,[4] and (2-bromo-4,5-dimethoxyphenyl)phenylmethanone[9] were prepared by the appropriate reported procedures. All other chemicals used in this study were commercially available.

(2-Bromo-5-methoxyphenyl)(4-methylphenyl)methanol. This compound was prepared by reacting

2-bromo-5-methoxybenzaldehyde with 4-methylphenylmagnesium bromide in Et_2O at 0 ˚C in 82% yield; a white solid; mp 54–56 ˚C (hexane–Et_2O); IR (KBr) 3292 cm^{-1}; ^1H NMR δ 2.27 (1H, d, *J* = 3.7 Hz), 2.33 (3H, s), 3.79 (3H, s), 6.09 (1H, d, *J* = 3.7 Hz), 6.71 (1H, dd, *J* = 8.7, 3.2 Hz), 7.14 (2H, d, *J* = 8.2 Hz), 7.20 (1H, d, *J* = 3.2 Hz), 7.28 (2H, d, *J* = 8.2 Hz), 7.40 (1H, d, *J* = 8.7 Hz). Anal. Calcd for $C_{15}H_{15}BrO_2$: C, 58.65; H, 4.92. Found: C, 58.54; H, 4.84.

(2-Bromo-5-methoxyphenyl)(4-methylphenyl)methanone. This compound was prepared by the PCC oxidation of (2-bromo-5-methoxyphenyl)(4-methylphenyl)methanol in CH_2Cl_2 at room temperature for 79 % yield; a white solid; mp 79–83 ˚C (hexane–Et_2O); IR (KBr) 1663 cm^{-1}; ^1H NMR δ 2.43 (3H, s), 3.80 (3H, s), 6.86 (1H, d, *J* = 3.2 Hz), 6.90 (1H, dd, *J* = 8.7, 3.2 Hz), 7.27 (2H, d, *J* = 8.2 Hz), 7.50 (1H, d, *J* = 8.7 Hz), 7.73 (2H, d, *J* = 8.2 Hz). Anal. Calcd for $C_{15}H_{13}BrO_2$: C, 59.04; H, 4.29. Found: C, 59.15; H, 4.24.

1-Bromo-4-methoxy-2-[1-(4-methylphenyl)ethenyl]benzene (1g). This compound was prepared by reacting (2-bromo-5-methoxyphenyl)(4-methylphenyl)methanone with methylenetriphenylphosphorane in THF at 0 ˚C in 99% yield; a white solid; mp 50–51 ˚C (pentane); IR (KBr) 1589 cm^{-1}; ^1H NMR δ 2.34 (3H, s), 3.80 (3H, s), 5.20 (1H, s), 5.79 (1H, s), 6.77 (1H, dd, *J* = 8.7, 2.7 Hz), 6.86 (1H, d, *J* = 2.7 Hz), 7.11 (2H, d, *J* = 8.2 Hz), 7.17 (2H, d, *J* = 8.2 Hz), 7.46 (1H, d, *J* = 8.7 Hz). Anal. Calcd for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99. Found: C, 63.19; H, 5.14.

3.2.4. 1-Bromo-4,5-dimethoxy-2-(1-phenylethenyl)benzene (1j). This compound was prepared by reacting (2-bromo-4,5-dimethoxyphenyl)phenylmethanone[9] with methylenetriphenylphosphorane in THF at 0 ˚C in 86% yield; a white solid; mp 87–89 ˚C (hexane–Et_2O); IR (KBr) 1599 cm^{-1}; ^1H NMR δ 3.86 (3H, s), 3.90 (3H, s), 5.27 (1H, d, *J* = 0.9 Hz), 5.83 (1H, d, *J* = 0.9 Hz), 6.80 (1H, s), 7.07 (1H, s), 7.28–7.33 (5H, m). Anal. Calcd for $C_{16}H_{15}BrO_2$: C, 60.21; H, 4.74. Found: C, 60.23; H, 5.03.

Typical Procedure for the Preparation of 3,4-Dihydro-2-benzothiopyran-1-thiones (3). 4-Phenyl-3,4-dihydro-2-benzothiopyran-1-thione (3b). To a stirred solution of **1b** (0.26 g, 1.0 mmol) in Et_2O (3 mL) at 0 ˚C was added *n*-BuLi (1.6 M in hexane; 1.0 mmol) dropwise; the mixture was stirred for 1 h. To the resulting mixture freshly distilled CS_2 (76 mg, 1.0 mmol) was added. After 30 min, saturated aqueous NH_4Cl (10 mL) was added, and the mixture was extracted with CH_2Cl_2 three times (10 mL each). The combined extracts was washed with brine, dried over anhydrous Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel to afford **3b** (0.12 g, 46%); a red oil; R_f 0.38 (1:10 THF–hexane); IR (neat) 1233, 1026 cm^{-1}; ^1H NMR δ 3.40 (1H, dd, *J* = 12.8, 7.8 Hz), 3.52 (1H, dd, *J* = 12.8, 3.7 Hz), 4.61 (1H, dd, *J* = 7.8, 3.7 Hz), 6.98 (1H, d, *J* = 7.8 Hz), 7.13 (2H, d, *J* = 7.3 Hz), 7.30 (1H, tt, *J* = 7.3, 1.4 Hz), 7.34–7.37 (2H, m), 7.40 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 7.49 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 8.42 (1H, dd, *J* = 7.8, 1.4 Hz); ^{13}C NMR δ 37.22, 45.40, 127.49, 127.83, 128.30, 128.80, 128.85, 128.96, 133.39, 137.17, 138.78, 139.81, 224.37; MS *m*/*z* 256 (M^+, 100). Anal. Calcd for $C_{15}H_{12}S_2$: C, 70.27; H, 4.72. Found: C, 70.03; H, 4.83.

4-Methyl-3,4-dihydro-2-benzothiopyran-1-thione (3a): a red liquid; R_f 0.39 (1:10 THF–hexane); IR (neat) 1225, 1024 cm^{-1}; ^1H NMR δ 1.48 (3H, d, *J* = 6.9 Hz), 2.93 (1H, dd, *J* = 12.8, 5.5 Hz), 3.38–3.42 (1H, m), 3.44 (1H, dd, *J* = 12.8, 3.7 Hz), 7.23 (1H, d, *J* = 7.8 Hz), 7.34 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 7.53 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 8.33 (1H, dd, *J* = 7.8. 1.4 Hz); MS *m/z* 194 (M^+, 100). Anal. Calcd for $C_{10}H_{10}S_2$: C, 61.81; H, 5.19. Found: C, 61.81; H, 5.48.

4-(4-Methylphenyl)-3,4-dihydro-2-benzothiopyran-1-thione (3c): red needles; mp 113–115 ˚C (hexane); IR (KBr) 1236, 1022 cm^{-1}; ^1H NMR δ 2.35 (3H, s), 3.38 (1H, dd, *J* = 12.8, 6.3 Hz), 3.50 (1H, dd, *J* = 12.8, 3.7 Hz), 4.57 (1H, dd, *J* = 6.3, 3.7 Hz), 6.98 (1H, d, *J* = 7.8 Hz), 7.02 (2H, d, *J* = 8.2 Hz), 7.16 (2H, d, *J* = 8.2 Hz), 7.38 (1H, ddd, *J* = 8.2, 7.3, 1.4 Hz), 7.48 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 8.41 (1H, dd, *J* = 8.2, 1.4 Hz); MS *m/z* 270 (M^+, 100). Anal. Calcd for $C_{16}H_{14}S_2$: C, 71.07; H, 5.22. Found: C, 70.81; H, 5.46.

4-(4-Chlorophenyl)-3,4-dihydro-2-benzothiopyran-1-thione (3d): a red solid; mp 140–142 ˚C (hexane–Et_2O); IR (KBr) 1231, 1022 cm^{-1}; ^1H NMR δ 3.34 (1H, dd, *J* = 12.8, 6.9 Hz), 3.55 (1H, dd, *J* = 12.8, 3.7 Hz), 4.60 (1H, dd, *J* = 6.9, 3.7 Hz), 6.99 (1H, d, *J* = 7.8 Hz), 7.05 (2H, d, *J* = 8.2 Hz), 7.32 (2H, d, *J* = 8.2 Hz), 7.42 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 7.51 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 8.41 (1H, dd, *J* = 7.8, 1.4 Hz); MS *m/z* 290 (M^+, 100). Anal. Calcd for $C_{15}H_{11}ClS$: C, 61.95; H, 3.81. Found: C, 61.73; H, 3.73.

6-Methoxy-4-methyl-3,4-dihydro-2-benzothiopyran-1-thione (3e): a red liquid; R_f 0.25 (1:2 Et_2O–hexane); IR (neat) 1599, 1229, 1015 cm^{-1}; ^1H NMR δ 1.47 (3H, d, *J* = 7.3 Hz), 2.89 (1H, dd, *J* = 12.8, 5.5 Hz), 3.31–3.37 (1H, m), 3.44 (1H, dd, *J* = 12.8, 3.2 Hz), 3.89 (3H, s), 6.69 (1H, d, *J* = 2.7 Hz), 6.85 (1H, dd, *J* = 9.2, 2.7 Hz), 8.40 (1H, d, *J* = 9.2 Hz); MS *m/z* (%) 224 (M^+, 100). Anal. Calcd for $C_{11}H_{12}OS_2$: C, 58.89; H, 5.39. Found: C, 58.72; H, 5.52.

6-Methoxy-4-phenyl-3,4-dihydro-2-benzothiopyran-1-thione (3f): a red solid; mp 142–144 ˚C (hexane–CH_2Cl_2); IR (KBr) 1594, 1219, 1016 cm^{-1}; ^1H NMR δ 3.66 (1H, dd, *J* = 12.8, 7.3 Hz), 3.50 (1H, dd, *J* = 12.8, 3.8 Hz), 3.78 (3H, s), 4.55 (1H, dd, *J* = 7.3, 3.8 Hz), 6.44 (1H, d, *J* = 2.7 Hz), 6.90 (1H, dd, *J* = 9.2, 2.7 Hz), 7.14 (2H, d, *J* = 7.3 Hz), 7.30 (1H, tt, *J* = 7.3, 1.4 Hz), 7.35 (2H, t, *J* = 7.3 Hz), 8.48 (1H, d, *J* = 9.2 Hz); MS *m/z* 286 (M^+, 100). Anal. Calcd for $C_{16}H_{14}OS_2$: C, 67.10; H, 4.93. Found: C, 67.06; H, 4.71.

6-Methoxy-4-(4-methylphenyl)-3,4-dihydro-2-benzothiopyran-1-thione (3g): a red solid; mp 130–132 ˚C (hexane–CH_2Cl_2); IR (KBr) 1595, 1229, 1013 cm^{-1}; ^1H NMR δ 2.34 (3H, s), 3.34 (1H, dd, *J* = 12.8, 7.8 Hz), 3.47 (1H, dd, *J* = 12.8, 3.7 Hz), 3.78 (3H, s), 4.51 (1H, dd, *J* = 7.8, 3.7 Hz), 6.44 (1H, d, *J* = 2.3 Hz), 6.89 (1H, dd, *J* = 8.7, 2.3 Hz), 7.02 (2H, d, *J* = 7.8 Hz), 7.15 (2H, d, *J* = 7.8 Hz), 8.47 (1H, d, *J* = 8.7 Hz); MS *m/z* 300 (M^+, 100). Anal. Calcd for $C_{17}H_{16}OS_2$: C, 67.96; H, 5.37. Found: C, 68.02; H, 5.53.

4-(4-Chlorophenyl)-6-methoxy-3,4-dihydro-2-benzothiopyran-1-thione (3h): a red solid; mp 124–126 ˚C (hexane–Et_2O); IR (KBr) 1599, 1230, 1015 cm^{-1}; ^1H NMR δ 3.29 (1H, dd, *J* = 13.3, 7.3 Hz), 3.52 (1H,

dd, *J* = 13.3, 3.7 Hz), 3.81 (3H, s), 4.54 (1H, dd, *J* = 7.3, 3.7 Hz), 6.43 (1H, d, *J* = 2.7 Hz), 6.92 (1H, dd, *J* = 9.2, 2.7 Hz), 7.06 (2H, d, *J* = 9.2 Hz), 7.32 (2H, d, *J* = 9.2 Hz), 8.48 (1H, d, *J* = 9.2 Hz); ^{13}C NMR δ 37.13, 45.10, 55.60, 113.48, 113.74, 129.01, 129.58, 132.22, 133.06, 133.42, 138.26, 139.05, 164.11, 221.81; MS *m/z* 320 (M^+, 100). Anal. Calcd for $C_{16}H_{13}ClOS_2$: C, 59.89; H, 4.08. Found: C, 59.85; H, 4.09.

6-Methoxy-4-(4-methoxyphenyl)-3,4-dihydro-2-benzothiopyran-1-thione (3i): a red solid; mp 95–97 ˚C (hexane–CH_2Cl_2); IR (KBr) 1597, 1251, 1022 cm^{-1}; ^{1}H NMR δ 3.32 (1H, dd, *J* = 12.8, 7.8 Hz), 3.46 (1H, dd, *J* = 12.8, 3.7 Hz), 3.78 (3H, s), 3.80 (3H, s), 4.50 (1H, dd, *J* = 7.8, 3.7 Hz), 6.44 (1H, d, *J* = 2.7 Hz), 6.87–6.90 (3H, m), 7.05 (2H, d, *J* = 8.7 Hz), 8.47 (1H, d, *J* = 9.2 Hz); MS *m/z* 316 (M^+, 100). Anal. Calcd for $C_{17}H_{16}O_2S_2$: C, 64.52; H, 5.10. Found: C, 64.54; H, 4.85.

6,7-Dimethoxy-4-phenyl-3,4-dihydro-2-benzothiopyran-1-thione (3j): a red solid; mp 119–121 ˚C (hexane–CH_2Cl_2); IR (KBr) 1601, 1263, 1020 cm^{-1}; ^{1}H NMR δ 3.30 (1H, dd, *J* = 12.8, 6.4 Hz), 3.59 (1H, dd, *J* = 12.8, 3.6 Hz), 3.80 (3H, s), 3.98 (3H, s), 4.56 (1H, dd, *J* = 6.4, 3.6 Hz), 6.43 (1H, s), 7.13 (2H, d, *J* = 7.3 Hz), 7.30 (1H, tt, *J* = 7.3, 1.8 Hz), 7.35 (2H, t, *J* = 7.3 Hz), 8.07 (1H, s); MS *m/z* 316 (M^+, 100). Anal. Calcd for $C_{17}H_{16}O_2S_2$: C, 64.52; H, 5.10. Found: C, 64.27; H, 4.97.

Methyl 2-(1-Phenylethenyl)dithiobenzoate (6). Compound **1b** (0.26 g, 1.0 mmol) was treated successively with butyllithium (1.0 mmol) and CS_2 (1.0 mmol) as described in the above Typical Procedure. Iodomethane (0.14 g, 1.0 mmol) was added to the resulting mixture, and stirring was continued for 1 h before a similar workup. The crude product was purified by column chromatography on silica gel to afford **6** (0.18 g, 65%); an orange oil; R_f 0.25 (hexane); IR (neat) 1047 cm^{-1}; ^{1}H NMR δ 2.52 (3H, s), 5.34 (1H, d, *J* = 1.4 Hz), 5.60 (1H, d, *J* = 1.4 Hz), 7.22–7.29 (6H, m), 7.34 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 7.39 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 7.41 (1H, dd, *J* = 7.8, 1.4 Hz); MS *m/z* 270 (M^+, 100). Anal. Calcd for $C_{16}H_{14}S_2$: C, 71.07; H, 5.22. Found: C, 71.86; H, 5.35.

REFERENCES

1. S. Fukamachi, H. Konishi, and K. Kobayashi, *Heterocycles,* 2009, **78**, 169.
2. (a) C. Petixoto, P. Laurin, M. Klich, C. Dupuis-Hamelin, P. Mauvais, P. Lassigne, A. Bonnefoy, and B. Musicki, *Tetrahedron Lett.*, 2000, **41**, 1742. (b) J. Liu, E. T. Birzin, W. Chan, Y. T. Yang, L.-Y. Pai, C. DaSilva, E. C. Hayes, R. T. Mosley, F. DiNinno, S. P. Rohrer, J. M. Schaeffer, and M. L. Hammond, *Bioorg. Med. Chem. Lett.*, 2005, **15**, 715. (c) X. Wang, G. Zhao, Y. Chen, X. Xu, W. Zhang, L. Wang, and S. Li, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 770.
3. (a) J. Campora, E. Carmona, E. Gutierrez-Puebla, M. L. Poveda, and C. Ruiz, *Organometallics,* 1988, **7**, 2577. (b) T. Gade, M. Streek, and J. Voss, *Chem. Ber.*, 1992, **125**, 127. (c) J. Campora, A. Monge, P. Palma, M. L. Poveda, C. Ruiz, and E. Carmona, *Organometallics,* 1994, **13**, 1728.
4. I. Fleming and M. Woolias, *J. Chem. Soc., Perkin Trans. 1,* 1979, 829.
5. M. E. Jason, *Tetrahedron Lett.*, 1982, **23**, 1635.

6. K. Kobayashi, S. Fukamachi, D. Nakamura, O. Morikawa, and H. Konishi, *Heterocycles,* 2008, **75**, 95.
7. K. Kobayashi, S. Fujita, M. Hase, O. Morikawa, and H. Konishi, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 763.
8. G. W. Morrow, T. M. Marks, and D. L. Sear, *Tetrahedron,* 1995, **51**, 10115.
9. V. J. Bauer, B. J. Duffy, D. Hoffmann, S. S. Klioze, R. W. Kosely, Jr., A. R. McFadden, L. L. Martin, H. H. Ong, and H. M. Geyer, III, *J. Med. Chem.*, 1976, **19**, 1315.