Studies in sulfur heterocycles. Part 16.[1,2] Use of 7-hydroxy-1-benzothiophene in the synthesis of substituted benzothiophene derivatives and tricyclic compounds incorporating a fused thiophene ring

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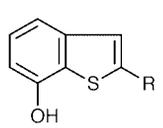
Heteroatom directed *ortho*-metallation on *N*,*N*-diethyl-7-carbamoyloxy-1-benzothiophene, readily available from 7-hydroxy-1-benzothiophene enabled regioselective substitution in the 6-position. Both 7- and 4-hydroxy-1-benzothiophene were used in the annelation of 5- or 6-membered oxygen heterocycles onto the 1-benzothiophene molecule through sequential Claisen rearrangement–ring closure reactions. The nature of the annelated ring depends upon the reaction conditions.

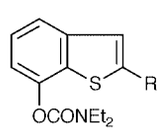
Tricyclic compounds consisting of six-membered oxygen heterocycles fused to a 1-benzothiophene core were initially synthesized as sulfur analogues of naturally occurring furocoumarins and furochromones.[3] There are other examples in the literature of five-,[4] six-[5] and seven-membered[6] oxygenated rings fused to the benzene ring of 1-benzothiophene. Compounds in which the oxygen heterocycle is fused to the thiophene moiety are fewer in number and their history is relatively recent.

Synthesis of this class of compounds is accomplished either by introducing a suitable substituent *ortho*- to the hydroxy function followed by annelation or *O*-alkylation and subsequent rearrangement–ring closure.

Difficult accessibility[7] has limited the use of 7-hydroxy-1-benzothiophene (**1**) as an intermediate in these syntheses, and



1 R = H
2 R = $SiMe_3$



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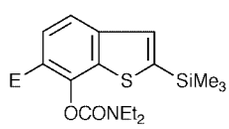
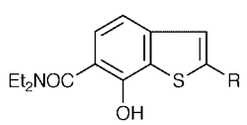
the reactions of this compound have not been studied in any detail. Several expedient syntheses[8,9] of **1** recently reported by us have made this compound readily available and we report herein its use in the regioselective functionalisation of the benzene ring in 1-benzothiophene and in annelating five- and six-membered oxygen heterocycles onto the 1-benzothiophene core.

Results and discussion

Conversion of the hydroxy function in **1** to a suitable "directed metallating group" (DMG) would allow regioselective functionalisation of the benzene ring in **1** through directed metallation.[10] We have noted earlier[11] that in 1-benzothiophene, silyl protection of the position α to the ring sulfur atom is necessary before carrying out metallation elsewhere in the molecule. In one of the syntheses of **1** developed by us, compound **2** is obtained in the penultimate step and has built-in silyl protection. The hydroxy function in **2** was converted into the *O*-carbamate and the resulting compound **3** was deprotonated in the 6-position under standard directed metallation conditions (Bu^tLi–TMEDA–THF, −78 °C) followed by quenching the lithio derivative with a number of representative electrophiles, *viz*. methyl iodide, *N*,*N*-dimethylformamide and tributyltin chloride to afford **4a**–**c**.



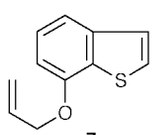
4a E = Me
4b E = CHO
4c E = $SnBu_3$



5 R = $SiMe_3$
6 R = H

Upon leaving the deprotonated species to attain room temperature, rather than quenching with an electrophile, and stirring at that temperature for five hours, it underwent anionic Fries rearrangement,[12] affording the salicylamide **5** in 80% yield. Removal of the trimethylsilyl group was carried out in the usual way with tetrabutylammonium fluoride to afford **6** in 82% yield.

The ready availability of **1** also allows its use in the angular annelation of five- or six-membered oxygen heterocycles through thermally induced Claisen rearrangement of its allyl or propargyl ethers and cyclisation of the resulting *ortho*-alkenyl or *ortho*-alkynyl phenols. Thus **1** afforded the allyl ether **7** in



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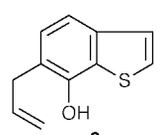

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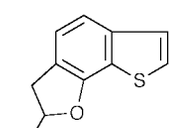

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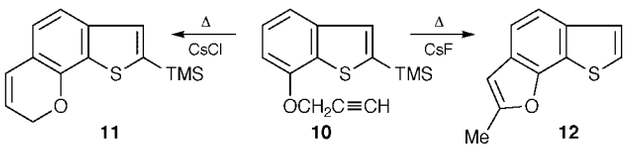
high yield upon reacting with allyl bromide in dry acetone in the presence of anhydrous potassium carbonate. The latter upon heating in *N*,*N*-dimethylaniline afforded the rearranged product as a brown oil, which upon short path distillation gave an oil which from IR and NMR data was shown to be the *o*-allylphenol **8**. The product was sufficiently pure for the next step, which consists of polyphosphoric acid (PPA) mediated

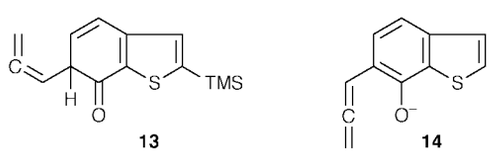
cyclisation to the tricyclic compound **9** in 82% yield. The propargyl ether **10** obtained similarly from **2** and propargyl bromide was also subjected to Claisen rearrangement. The size of the third oxygenated ring depended upon the reaction conditions (Scheme 1).



Scheme 1

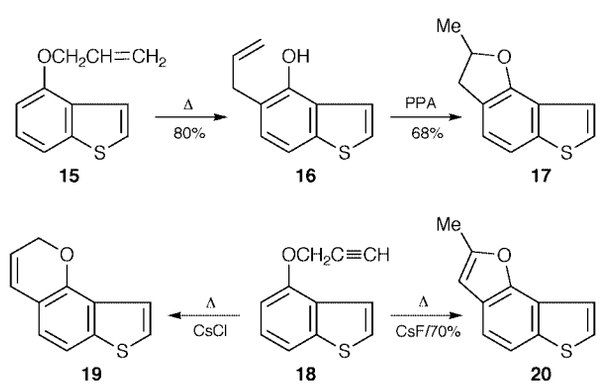
Heating **10** in *N*,*N*-dimethylaniline resulted in the annelation of a pyran ring. Use of caesium chloride as additive afforded **11** in better yield. The rearrangement of the propargyl ether, when carried out in the presence of caesium fluoride, gave a five-membered ring, resulting in the tricyclic compound **12** in excellent yield.

The results can be explained in terms of the mechanism[13] of the rearrangement–cyclisation. The use of additives in Claisen rearrangement of primary ethers has been reported.[13] Caesium chloride and caesium fluoride when used as additives play two different roles. The α-allenyl ketone **13** formed during the [3,3] sigmatropic rearrangement undergoes enolisation followed by hydrogen shift prior to ring closure leading to the annelation of a six-membered ring **11**; caesium chloride apparently facilitates this process. Caesium fluoride, on the other hand, abstracts the α-hydrogen atom from the allenyl ketone leading to the intermediate **14** which then undergoes ring closure to afford **12**,



with simultaneous desilylation mediated by caesium fluoride (because of the high nucleophilicity of the fluoride ion towards the silicon atom).

The usefulness of additives in this type of annelation could further be demonstrated in successfully annelating five- and six-membered oxygenated rings through Claisen rearrangement–cyclisation of 4-allyloxy-1-benzothiophene (**15**), as shown in Scheme 2.



Scheme 2

Jeffrey and co-workers[4] carried out the rearrangement, but failed to cyclise the rearranged product **16**, which in our hands was cyclised with PPA to afford **17** in 68% yield. The propargyl ether **18** upon heating in *N*,*N*-dimethylaniline in the presence of caesium chloride and caesium fluoride afforded **19** and **20** in 64% and 53% yields respectively.

Experimental

Melting points (uncorrected) were recorded in open capillaries on a hot stage apparatus. IR spectra were recorded on a Perkin-Elmer 298 Spectrometer, for solids in potassium bromide discs, and for liquids by placing a thin layer of the sample between two potassium bromide discs. ^{1}H NMR spectra were recorded in $CDCl_3$ solutions unless otherwise stated, on Varian EM-360, JEOL FX-100 and Bruker DPX-300 Spectrometers. Chemical shifts (δ) are expressed in ppm using tetramethylsilane as internal standard. Coupling constant (J) values are given in Hz.

Commercially available solvents were distilled prior to use. Light petroleum (bp 60–80 °C) was used. Tetrahydrofuran was dried by the benzophenone ketyl method.

N,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) and *N*,*N*-dimethylformamide were freshly distilled over calcium hydride prior to use. All lithiation reactions were carried out under an argon atmosphere. Anhydrous sodium sulfate was used as drying agent.

2-Trimethylsilyl-7-(*N*,*N*-diethylcarbamoyloxy)-1-benzothiophene 3

A solution of 2-trimethylsilyl-7-hydroxy-1-benzothiophene (350 mg, 0.00157 mol) and *N*,*N*-diethylcarbamoyl chloride (0.204 g, 0.0015 mol) in anhydrous pyridine (2 ml) was placed in a pressure-capped glass bottle and was heated for about 5 h on a steam bath. The mixture was poured over ice and extracted with ether; the ether phase was sequentially washed with 10% hydrochloric acid, sodium bicarbonate solution, and finally with water and dried. The colourless viscous liquid obtained after removal of solvent was purified by column chromatography (ethyl acetate–petroleum ether 1:9 as eluent). Yield 360 mg (70%). Found: C, 60.00; H, 7.26; N, 4.59. $C_{16}H_{23}NO_2SSi$ requires C, 59.81; H, 7.16; N, 4.36%. ν_{max}/cm^{-1} 1700 (OCONEt$_2$). ^{1}H NMR: δ 7.63 (d, 1H, H-4, J 7.8), 7.45 (s, 1H, H-3), 7.33 (dd, 1H, H-5, J 7.5, 8.1), 7.18 (d, 1H, H-6, J 7.8), 3.54 (q, 2H, CH_2CH$_3$, J 6.6), 3.43 (q, 2H, CH_2CH$_3$, J 6.6), 1.35 (t, 3H, CH$_2$CH_3), 1.24 (t, 3H, CH$_2$CH_3), 0.36 [s, 9H, Si(CH_3)$_3$].

General procedure for metallation of 3 and subsequent reaction with electrophiles to afford compounds 4

tert-Butyllithium (1.5 M, 1.2 equiv.) was slowly added by syringe to a well stirred mixture of tetrahydrofuran (20 ml) and TMEDA (1.2 equiv.) at −78 °C. When a yellow colour developed (after about 30 min) the substrate **3** (1 equiv.) was added slowly by syringe at that temperature. After stirring the reaction mixture for 30 min at a temperature between −20 and −10 °C, it was cooled again to −78 °C. The electrophile (1 equiv.) was slowly added to the reaction mixture by syringe and kept for 10–15 min with the cooling bath in place, followed by stirring at room temperature for 12 h. Work-up consisted of neutralising the reaction mixture with saturated ammonium chloride solution (25 ml) and water (100 ml), extraction with ether (3 × 25 ml), washing the organic layer with water and drying. Evaporation of the solvent afforded the crude material.

2-Trimethylsilyl-6-methyl-7-(*N*,*N*-diethylcarbamoyloxy)-1-benzothiophene 4a. Light yellow oil, purified by column chromatography (ethyl acetate–petroleum ether 10:90 as eluent). Yield 41%. Found: C, 61.00; H, 7.72; N, 4.27. $C_{17}H_{25}NO_2SSi$ requires C, 60.85; H, 7.50; N, 4.17%. ν_{max}/cm^{-1} 1700 (OCONEt$_2$). ^{1}H NMR: δ 7.53 (d, 1H, H-5, J 7.5), 7.39 (s, 1H, H-3), 7.17 (d, 1H, H-4, J 7.5), 3.56 (q, 2H, CH_2CH$_3$), 3.44 (q, 2H, CH_2CH$_3$), 2.31 (s, 3H, 6-CH_3), 1.38 (t, 3H, CH$_2$CH_3), 1.25 (t, 3H, CH$_2$CH_3), 0.36 [s, 9H, Si(CH_3)$_3$].

2-Trimethylsilyl-6-formyl-7-(*N*,*N*-diethylcarbamoyloxy)-1-benzothiophene 4b. Viscous liquid, purified by column chromatography (ethyl acetate–petroleum ether 20:80 as eluent). Yield

46%. Found: C, 58.32; H, 6.34; N, 4.20. $C_{17}H_{23}NO_3SSi$ requires C, 58.59; H, 6.6; N, 4.01%. ν_{max}/cm^{-1} 1680 (CHO), 1700 ($OCONEt_2$). ^1H NMR: δ 9.96 (s, 1H, C*H*O), 7.50 (d, 1H, H-5, *J* 7.8), 7.38 (s, 1H, H-3), 7.19 (d, 1H, H-4, *J* 7.8), 3.54 (q, 2H, CH_2CH_3), 3.43 (q, 2H, CH_2CH_3), 1.37 (t, 3H, CH_2CH_3), 1.24 (t, 3H, CH_2CH_3), 0.35 [s, 9H, $Si(CH_3)_3$].

2-Trimethylsilyl-6-tributylstannyl-7-(*N*,*N*-diethylcarbamoyloxy)-1-benzothiophene 4c. Colourless liquid, purified by column chromatography (ethyl acetate–petroleum ether 5 : 95 as eluent). Yield 61%. Found: C, 55.00; H, 8.23; N, 2.10. $C_{28}H_{49}NO_2SSiSn$ requires C, 55.10; H, 8.03; N, 2.29%. ν_{max}/cm^{-1} 1700 ($OCONEt_2$). ^1H NMR: δ 7.63 (d, 1H, H-5, *J* 7.5), 7.42 (s, 1H, H-3), 7.36 (d, 1H, H-4, *J* 7.5), 3.55 (q, 2H, CH_2CH_3), 3.44 (q, 2H, CH_2CH_3), 1.66 (t, 3H, CH_2CH_3), 1.62 (t, 3H, CH_2CH_3), 1.39–0.87 [m, 27H, $Sn(C_4H_9)_3$], 0.35 [s, 9H, $Si(CH_3)_3$].

2-Trimethylsilyl-6-(*N*,*N*-diethylcarbamoyl)-7-hydroxy-1-benzothiophene 5

To a well stirred solution of tetrahydrofuran (50 ml) and TMEDA (1.2 equiv.), 1.5 M *tert*-butyllithium (1.2 equiv.) was slowly added by syringe at −78 °C and kept for 30 min. After a yellow colour developed, a solution of **2** (0.25 g, 1 mmol) in tetrahydrofuran (10 ml) was added. The reaction mixture was stirred for 12 h after it was allowed to attain room temperature keeping the cooling bath in place. Work-up as in the reaction of compound **3** with ammonium chloride afforded crude **5** as a light brown gummy liquid which was purified by column chromatography to a light brown oil. Yield 200 mg (80%). ν_{max}/cm^{-1} 1645 ($CONEt_2$), 3360 (br, OH). ^1H NMR: δ 10.9 (-OH proton), 7.42 (s, 1H, H-3), 7.27 (d, 1H, H-5, *J* 8.5), 7.10 (d, 1H, H-4, *J* 8.5), 3.60–3.46 (q, 4H, CH_2CH_3), 1.83–1.2 (t, 6H, CH_2CH_3).

6-(*N*,*N*-Diethylcarbamoyl)-7-hydroxy-1-benzothiophene 6

Compound **5** (160 mg, 0.5 mmol) and tetrabutylammonium fluoride (1.2 equiv.) were stirred for 16 h at room temperature in THF solution (20 ml). Work-up as in the reaction of compound **3** afforded **6** as a light yellow oil. Yield 96 mg (82%). Found: C, 62.61; H, 6.00; N, 5.55. $C_{13}H_{15}NO_2S$ requires C, 62.65; H, 6.02; N, 5.62%. ν_{max}/cm^{-1} 1645 ($CONEt_2$), 3360 (br, OH). ^1H NMR: δ 7.79–7.16 (m, 4H, H-2, H-3, H-4 and H-5), 3.66–3.39 (q, 4H, CH_2CH_3), 1.46–1.23 (t, 6H, CH_2CH_3).

7-Allyloxy-1-benzothiophene 7

A mixture of 7-hydroxy-1-benzothiophene (200 mg, 1.3 mmol) and freshly distilled allyl bromide (160 mg, 1.33 mmol) was refluxed for 4 h under anhydrous conditions in dry acetone (10 ml) in the presence of anhydrous potassium carbonate (190 mg, 1.33 mmol). After cooling, the reaction mixture was poured into cold water. Extraction with ether, drying and removal of the solvent left an oil which was purified by short path distillation (bp 80 °C/0.05 mmHg). Yield 240 mg (95%). Found: C, 69.25; H, 5.06. $C_{11}H_{10}OS$ requires C, 69.47; H, 5.26. ν_{max}/cm^{-1} 1255 (C-O-C). ^1H NMR: δ 7.43–6.59 (5H, m, aromatic protons), 6.46–5.82 (1H, m, -C*H*=CH_2), 5.56–5.16 (2H, m, -CH=CH_2), 4.76–4.62 (2H, m, OCH_2).

6-Allyl-7-hydroxy-1-benzothiophene 8

7-Allyloxy-1-benzothiophene **7** (200 mg, 1.05 mmol) in *N*,*N*-dimethylaniline (4 ml) was refluxed for 5 h under nitrogen. After cooling, the reaction mixture was poured into cold hydrochloric acid (10%). Upon extraction with ether, drying and removal of the solvent **8** was obtained as a light brown liquid, which was purified by short path distillation (bp 95–98/0.05 mmHg). Yield 150 mg (78%). ν_{max}/cm^{-1} 3500 (br, phenolic -OH). ^1H NMR: δ 7.39–6.96 (4H, m, aromatic protons) 6.29–5.73 (1H, m, CH_2CH=CH_2), 5.36–5.0 (2H, m, CH_2CH=CH_2), 3.56–3.39 (2H, m, -CH_2CH=CH_2).

2-Methyl-2,3-dihydrothieno[3,2-*g*][1] benzofuran 9

The solution of **8** (190 mg, 0.001 mol) in chlorobenzene (5 ml) and PPA (200 mg) was refluxed for 3 h. After cooling, the reaction mixture was filtered and diethyl ether was added. Washing with brine, drying and removal of solvent gave crude **9** which was purified by column chromatography (using petroleum ether as eluent) to afford the pure compound. Yield 160 mg (82%). Mp 47–48 °C. Found: C, 69.74; H, 5.14. $C_{11}H_{10}OS$ requires C, 69.47; H, 5.26%. ^1H NMR: δ 7.41–7.10 (4H, m, aromatic protons), 5.18–5.07 (1H, m, H-2), 3.51 (1H, m, H-3), 2.91 (1H, m, H-3), 1.56 (3H, d, -CH_3, *J* 9.0).

2-Trimethylsilyl-7-propargyloxy-1-benzothiophene 10

2-Trimethylsilyl-7-hydroxy-1-benzothiophene (222 mg, 0.001 mol) and propargyl bromide (120 mg, 0.001 mol) were stirred at room temperature under anhydrous conditions in dry acetone (25 ml) in the presence of anhydrous potassium carbonate (170 mg, 0.001 mol) for 12 h. After filtering the reaction mixture, the acetone was distilled off. Extraction with chloroform, washing with brine and drying afforded the product which was purified by short path distillation (bp 80–90 °C). Yield 210 mg (80%). Found: C, 64.64; H, 6.31. $C_{14}H_{16}OSSi$ requires C, 64.61; H, 6.15%. ^1H NMR: δ 7.46 (d, 1H, H-6, *J* 8), 7.44 (s, 1H, H-3), 7.28 (t, 2H, H-5), 6.86 (d, 1H, H-4, *J* 8), 4.87 (d, 2H, O-CH_2, *J* 2.4), 2.52 (t, 1H, -C≡C*H*), 0.34 [s, 9H, $Si(CH_3)_3$].

8-Trimethylsilylthieno[3,2-*h*][1]benzopyran 11

The compound **10** (260 mg, 0.001 mol) in *N*,*N*-dimethylaniline (5 ml) and CsCl (235 mg, 0.0014 mol) were refluxed for 6 h under a nitrogen atmosphere. After cooling, it was filtered and diethyl ether (20 ml) was added to the filtrate. The reaction mixture, upon washing with brine and removal of solvent, gave the desired product as a colourless liquid which was purified by column chromatography using light petroleum as eluent. Yield 180 mg (70%). Found: C, 64.54; H, 6.31. $C_{14}H_{16}OSSi$ requires C, 64.61; H, 6.15%. ^1H NMR: δ 6.95 (d, 1H, H-6, *J* 9), 6.89 (s, 1H, H-7), 6.61 (d, 1H, H-5, *J* 9), 6.17 (dt, 1H, H-4, *J* 9.9, 1.8), 5.38 (m, 1H, H-3), 4.63 (m, 2H, H-2), 0.30 [s, 9H, $Si(CH_3)_3$].

2-Methylthieno[3,2-*g*][1]benzofuran 12

The compound **10** (260 mg, 0.001 mol) in *N*,*N*-dimethylaniline (5 ml) and CsF (1.5 g, 0.01 mol) were refluxed for 6 h under nitrogen. After cooling, the mixture was filtered and diethyl ether (20 ml) was added to the filtrate. Upon washing with brine, drying and removal of solvent, the desired product was obtained which was purified by column chromatography using petroleum ether as eluent. Yield 170 mg (90%). mp 40–41 °C. Found: C, 70.41; H, 4.20. $C_{11}H_8OS$ requires C, 70.21; H, 4.25%. ^1H NMR: δ 7.65 (d, 1H, H-5, *J* 8.1), 7.48 (d, 1H, H-4, *J* 8.1), 7.44 (d, 1H, H-7, *J* 5.1), 7.36 (d, 1H, H-6, *J* 5.4), 66.50 (s, 1H, H-3), 2.55 (s 3H, -CH_3).

4-Allyloxy-1-benzothiophene 15

A mixture of 4-hydroxy-1-benzothiophene (1 g, 0.0066 mol) and freshly distilled allyl bromide (810 mg, 0.006 mol) was refluxed for 4 h under anhydrous conditions in dry acetone (10 ml) in the presence of anhydrous potassium carbonate (1 g). After cooling, the reaction mixture was poured into cold water. Extraction with ether, drying and removal of solvent left an oil which was purified by short path distillation (bp 80–82 °C/0.05 mmHg). Yield 1.1 g (95%). Found: C, 69.27; H, 5.21. $C_{11}H_{10}OS$ requires C, 69.47; H, 5.26%. ν_{max}/cm^{-1} 1255 (C-O-C). ^1H NMR: δ 7.6–6.6 (m, 5H, H-2, H-3, H-5, H-6 and H-7), 5.8–6.4 (m, 1H, OCH_2CHCH_2), 5.6–5.1 (m, 2H, -OCH_2CHCH_2), 4.7 (d, 2H, -OCH_2CHCH_2, *J* 4).

5-Allyl-4-hydroxy-1-benzothiophene 16

4-Allyloxy-1-benzothiophene (**15**) (600 mg, 0.0034 mol) in *N*,*N*-dimethylaniline (8 ml) was refluxed for 5 h under nitrogen. After cooling, the reaction mixture was poured into cold hydrochloric acid (10%). Extraction with ether, drying and removal of the solvent yielded a light yellow oil. Yield 450 mg (75%). Found: C, 69.30; H, 5.16. $C_{11}H_{10}OS$ requires C, 69.47; H, 5.26%. ν_{max}/cm^{-1} 3500 (br, phenolic -OH). ^1H NMR: δ 7.47 (d, 1H, H-2, *J* 5.7), 7.42 (d, 1H, H-7, *J* 8.7), 7.34 (d, 1H, H-3, *J* 5.4), 7.10 (d, 1H, H-6, *J* 8.1), 6.10 (m, 1H, CH_2CHCH_2), 5.47 (s, 1H, -O*H*), 5.25 (m, 2H, $-CH_2-CH=CH_2$), 3.54 (d, 2H, benzylic proton, *J* 6.3).

2-Methyl-2,3-dihydrothieno[2,3-*g*][1]benzofuran 17

A solution of **16** (190 mg, 0.001 mol) in chlorobenzene (5 ml) and PPA (200 mg) were refluxed for 3 h. After cooling, the reaction mixture was filtered and diethyl ether was added, the mixture was washed with brine and dried and the solvent removed to give crude **17** which was purified by column chromatography (using petroleum ether as eluent). Yield 130 mg (68%). mp 57–60 °C. Found: C, 69.21; H, 5.01. $C_{11}H_{10}OS$ requires C, 69.47; H, 5.26%. ^1H NMR: δ 7.39–7.00 (m, 4H, H-4, H-5, H-6 and H-7), 5.09 (m, 1H, H-2), 3.44 (m, 1H, H-3), 2.98 (m, 1H, H-3), 1.55 (d, 3H, $CHCH_3CH_2$, *J* 9.0).

4-Propargyloxy-1-benzothiophene 18

4-Hydroxy-1-benzothiophene (500 mg, 0.003 mol) and propargyl bromide (360 mg, 0.003 mol) were stirred at room temperature under anhydrous conditions in dry acetone (30 ml) in the presence of anhydrous potassium carbonate (500 mg, 0.003 mol) for 12 h. After the usual work-up **18** was obtained as an oily liquid which was purified by short path distillation (bp 70 °C/0.05 mmHg). Yield 460 mg (74%). Found: C, 69.76; H, 4.56. $C_{11}H_8OS$ requires C, 70.21; H, 4.25%. ^1H NMR: δ 7.56–7.26 (m, 4H, H-2, H-3, H-6, H-7), 6.89 (d, 1H, H-5, *J* 7.8), 4.87 (d, 2H, CH_2CCH, *J* 2.1), 2.56 (t, 1H, CH_2CCH).

Thieno[2,3-*h*][1]benzofuran 19

The compound **18** (188 mg, 0.001 mol) in *N*,*N*-dimethylaniline (4 ml) and CsCl (235 mg, 0.0014 mol) was refluxed for 6 h under a nitrogen atmosphere. After cooling, the mixture was filtered and 20 ml of diethyl ether was added to the filtrate. The reaction mixture upon washing with brine and removal of solvent gave the desired product as a solid with a low melting point which was purified by column chromatography using petroleum ether as eluent. Yield 120 mg (64%). Found: C, 70.31; H, 4.05. $C_{11}H_8OS$ requires C, 70.21; H, 4.25%. ^1H NMR: δ 7.38–7.26 (m, 3H, H-6, H-7 and H-8), 6.98 (d, 1H, H-5, *J* 8.1), 6.52 (dt, 1H, H-4), *J* 9.9, 1.8), 5.75 (m, 1H, H-3), 4.96 (m, 2H, H-2). ^{13}C NMR: δ 65.90 (CH_2), 114.82 (CH), 119.0 (CH), 120 (CH), 123.39 (CH), 125.24 (CH), 125.74 (CH), 126 (C), 130 (C), 141 (C), 150 (C).

2-Methylthieno[2,3-*g*][1]benzofuran 20

The compound **18** (188 mg, 0.001 mol) in *N*,*N*-dimethylaniline (3 ml) and CsF (210 mg, 0.0014 mol) were refluxed for 6 h under nitrogen. After cooling, the mixture was filtered and 20 ml of diethyl ether was added to the filtrate, which was washed with brine, and the solvent removed to give the desired product as a white crystalline solid which was purified by column chromatography using petroleum ether as eluent. Yield 100 mg (53%). Mp 39–40 °C. Found: C, 70.00; H, 4.30. $C_{11}H_8OS$ requires C, 70.21; H, 4.25%. ^1H NMR: δ 7.68 (d, 1H, H-5, *J* 8.4), 7.65 (d, 1H, H-6, *J* 5.4), 7.49 (d, 1H, H-7, *J* 6), 7.46 (d, 1H, H-4, *J* 8.7), 6.48 (d, 1H, H-3, *J* 1.2), 2.56 (s, 3H), -C*H*$_3$). ^{13}C NMR: δ 14.01 (CH_3), 103.14 (C-3), 116.78 (C-4), 117.05 (C-8), 118.06 (C-5), 126.35 (C-7), 124.60 (C), 125.07 (C), 136.32 (C), 149.29 (C), 153.73 (C).

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