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FACILE SYNTHESIS OF SUBSTITUTED 5-HYDROXYTHIO-7H-THIENO[3,2-g] [1]BENZOTHIOPYRAN-7-ONES

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Lewis acid ($BF_3(OEt)_2$) in dry diethyl ether mediated cyclization and demethylation of substituted 2-(2-methyl-3-methylsulfanyl-phenylsulfanyl)-1,2-diphenyl-ethanones (3a–e) at ambient temperature gave 7-methyl-2,3-diphenyl-6-thio-benzo[b]thiophenes (4a–e). Treatment of (4a–e) with substituted malonic acids furnishes the corresponding substituted 5-hydroxythio-7H-thieno[3,2-g][1] benzothiopyran-7-ones. These were characterized by their elemental, IR, ^{1}H NMR and mass spectral analysis.

Keywords: Friedel-Crafts cyclization; Demethylation; Condensation; Benzothiophenes; Benzothiopyranones

INTRODUCTION

5-Hydroxy-thio-coumarins and their derivatives are of interest in many pharmaceutical areas, since they exhibit a variety of biological activities, such as anti-coagulant [1] and anti-HIV protease activity.

Although there is a general method by which substituted hydroxy coumarins are normally synthesized by the condensation of a phenol with malonic acid in the presence of $ZnCl_2$, and $POCl_3$ [2, 3], in this communication we report an expedient and convenient procedure for the preparation of substituted 5-hydroxy-thio-coumarins by condensation of S-methyl-2-methyl-benzene 1,3-dithiol (1) with desyl halides [4] (2a–e) in order to produce 2-(2-methyl-3-methylsulfanyl-phenylsulfanyl)-1,2-diphenylethanones (3a–e). The (3a–e) cyclization and demethylation with Lewis acid BF_3 $(OEt)_2$ in dry diethyl ether at ambient temperature gave 7-methyl-2,3-diphenyl-6-thio-benzo[b]thiophenes (4a–e). Treatment of (4a–e) with different substituted malonic acids in presence of $AlCl_3$ in dry dichloromethane at room temperature resulted in the formation of the title compounds. All these compounds have been confirmed by their elemental and spectral analysis. The study on their biological activity is in progress.

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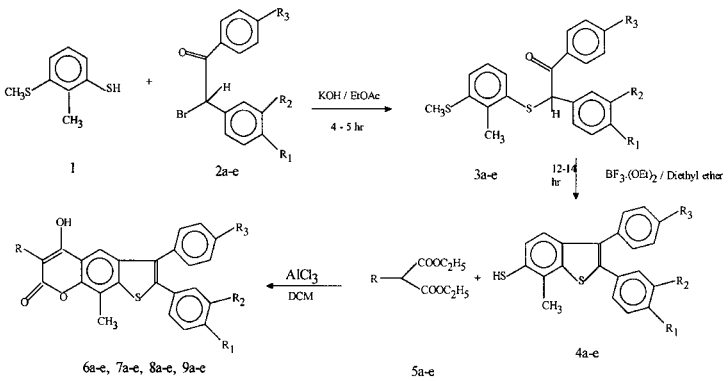


6a $R=R_1=R_2=R_3=H$ 6b $R=R_1=R_2=H,R_3=Br$ 6c $R=R_1=R_2=H,R_3=CH_3$

6d $R=R_1=R_2=H$, $R_3=Cl$ 6e $R=H,R_1=R_2=Cl,R_3=H$

7a $R=C_2H_5,R_1=R_2=R_3=H$ 7b $R=C_2H_5$ $R_1=R_2=H,R_3=Br$ 7c $R=C_2H_5,R_1=R_2=H,R_3=CH_3$

7d $R=C_2H_5,R_1=R_2=H$, $R_3=Cl$ 7e $R=C_2H_5$, $R_1=R_2=Cl$, $R_3=H$

8a $R=C_3H_7,R_1=R_2=R_3=H$ 8b $R=C_3H_7,R_1=R_2=H,R_3=Br$ 8c $R=C_3H_7,R_1=R_2=H,R_3=CH_3$

8d $R=C_3H_7,R_1=R_2=H$, $R_3=Cl$ 8e $R=C_3H_7,R_1=R_2=Cl$, $R_3=H$

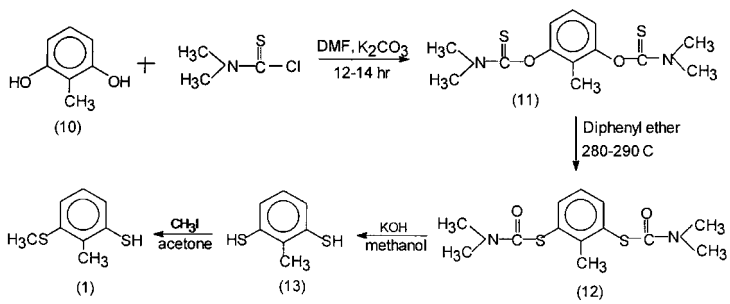
9a $R=C_5H_{11},R_1=R_2=R_3=H$ 9b $R=C_5H_{11},R_1=R_2=H,R_3=Br$ 9c $R=C_5H_{11},R_1=R_2=H,R_3=CH_3$

9d $R=C_5H_{11},R_1=R_2=H$, $R_3=Cl$ 9e $R=C_5H_{11},R_1=R_2=Cl$, $R_3=H$

SCHEME 1

RESULTS AND DISCUSSION

The required starting substance for the above synthetic route, namely S-methyl-2-methyl-1,3-benzenedithiol [10, 11], was obtained by treatment of 2-methyl-resorcinol (10) with dimethyl thiocarbomyl chloride in the presence of DMF at 80 °C for 12 hours, to give 2-methyl bis-1,3-(O,O′-dimethylthiocarbamato)benzene (11) in 75% yield. Treatment of (11) in diphenyl ether solution at 250–280 °C under a nitrogen atmosphere, gave the rearrangement product 2-methylbis-1,3-(S,S′-dimethylthiocarbamato)benzene (12). This compound was converted into 2-methyl-benzene-1,3-dithiol (13) in 80% yield in the presence of methanolic KOH. Treatment of (13) with methyl iodide in 0.8 mole ratio at room temperature produced S-methyl-2-methyl-benzene-1,3-dithiol (1) in 23% yield.



SCHEME 2

The reactions of (1) with desyl halides (2a–e) proceeded at room temperature in the system of KOH in EtOAc to furnish 2-(2-methyl-3-methylsulfanyl-phenylsulfanyl)-1,2-diphenyletanones (3a–e) respectively in 70–89% yields. This reaction is also carried out by refluxing for 14–15 hours, but the produced yields were less efficient. The cyclization and demethylation [5–9] of (3a–e) with the Lewis acid $AlCl_3$ in dry DCM at room temperature gave 7-methyl-2,3-diphenyl-(6)-thio-benzo[b]thiophenes (4a–e) in lower yields, hence we carried out the reaction in BF_3 $(OEt)_2$ in dry diethyl ether solvent at ambient temperature, which furnished the compounds (4a–e) in better yields. Treatment of (4a–e) with different substituted malonic acids (5a–e) in the presence of $ZnCl_2$ and $POCl_3$ produced substituted 5-hydroxy-7H-thieno[3,2-g][1]benzothiopyran-7-ones (6a–e, 7a–e, 8a–e, 9a–e) in lower yields. The same reaction produced greater yields in $AlCl_3$/DCM at room temperature.

The IR spectra of all the final products exhibit a broad band in the region of 3430–3450 cm^{-1} due to —OH stretching vibrations. A sharp peak in the region of 1680–1720 cm^{-1} confirms the presence of C═O group. The peak at 750 cm^{-1} is for C—S stretching vibrations.

The ^1H NMR spectra of all the final products (6a–e), (7a–e), (8a–e) and (9a–e), having a hydroxy group at C—S position exhibited a singlet at δ 12.4, and a singlet was observed at δ 5.34–5.42 due to the H-6 proton. The prominent peaks indicating the usual fragmentation pattern are observed in mass spectra of all compounds (6a–e) to (9a–e), molecular ion peaks are in accordance with their molecular weights.

Experimental

All the melting points are uncorrected. The purity was checked by thin layer chromatography and characterized by spectral studies. The IR spectra were recorded on Shimadzu FTIR model 8010 Spectrophotometer and are given in cm^{-1} in KBr. The ^1H NMR spectra in $CDCl_3$ were recorded on a C17-20-ZM-390 200 MHz NMR Spectrometer instrument using TMS as an internal standard (chemical shifts in δ units ppm), and mass spectra of the compounds described are recorded on Jeol TMS-D300 at 70 eV. Compounds were obtained in 70–80% yields. Compounds were recrystallized from alcohol. C, H, and S analysis were conducted on a Carlo Erba EA 1108-Elemental Analyzer Instrument.

S-Methyl-2-methyl-benzene 1,3-dithiol (1)

A mixture of 2-methyl-benzene-1,3-dithiol (13) (0.01 mol) was dissolved in acetone (30 ml). Methyl iodide (0.5 mol) was added to this mixture at room temperature. The reaction mixture was stirred for 7–8 hours. Excess of acetone was distilled off and the pH was adjusted to 5.5. The mixture was filtered and the filtrate was extracted with EtOAc. The residue was concentrated *in vacuo* in order to produce the desired compound (1).

2-(2-Methyl-3-methylsulfanyl-phenylsulfanyl)-1,2-diphenylethanones (3a–e)

Compound (1) (0.01 mol) was dissolved in EtOAc (30 ml), to this was added KOH pellets (0.2 mol) and the mixture was stirred for 1 hour. To the above mixture was added the desyl halides (0.01 mol) and the mixture was stirred at room temperature for 4–5 hours. The mixture was poured into water and then extracted with ethyl acetate. The solvents were concentrated *in vacuo* to produce the desired compound (3a–e) which was later purified by coloumn chromatography (EtOAc/pet. ether = 3:7).

TABLE I Physical and Analytical Data.

Entry	*Yield %*	*MP*	*Molecular formula*	*C*	*H*	*S*	*Cl*	*Br*
6a	61	214–216	$C_{24}H_{16}O_2S_2$	72.00 (71.98)	4.00 (4.01)	16.00 (15.98)	–	–
6b	59	200–202	$C_{24}H_{15}O_2S_2Br$	60.12 (60.10)	3.13 (3.12)	13.36 (13.40)		16.70 (16.68)
6c	62	218–220	$C_{25}H_{18}O_2S_2$	72.46 (72.42)	4.35 (4.32)	15.46 (15.48)		
6d	59	215–217 (d)	$C_{24}H_{15}O_2S_2Cl$	66.28 (66.26)	3.45 (3.43)	14.73 (14.70)	8.17 (8.14)	
6e	60	205–207	$C_{24}H_{15}O_2S_2Cl_2$	61.54 (61.53)	2.99 (2.97)	13.65 (13.68)	15.14 (15.13)	
7a	61	230–232	$C_{26}H_{20}O_2S_2$	72.89 (72.86)	4.67 (4.64)	14.95 (14.93)		
7b	59	235–237 (d)	$C_{26}H_{19}O_2S_2Br$	61.53 (61.50)	3.75 (3.78)	12.62 (12.58)		15.78 (15.76)
7c	62	215–218	$C_{27}H_{21}O_2S_2$	73.47 (73.45)	4.76 (4.72)	14.51 (14.50)		
7d	59	212–214	$C_{26}H_{19}O_2S_2Cl$	67.46 (67.42)	4.11 (4.09)	13.84 (13.80)	7.68 (7.62)	
7e	60	215–217 (d)	$C_{26}H_{18}O_2S_2Cl_2$	62.78 (62.76)	3.62 (3.60)	12.88 (12.91)	14.82 (14.79)	
8a	61	155–157	$C_{27}H_{20}O_2S_2$	73.64 (73.62)	4.55 (4.50)	14.54 (14.58)		
8b	59	160–162	$C_{27}H_{19}O_2S_2Br$	62.43 (62.40)	3.66 (3.63)	12.33 (12.29)		15.41 (15.40)
8c	62	159–161	$C_{28}H_{22}O_2S_2$	74.01 (73.98)	4.85 (4.86)	14.09 (14.06)		
8d	59	149–151 (d)	$C_{27}H_{19}O_2S_2Cl$	68.28 (68.26)	4.00 (3.99)	13.48 (13.46)	7.48 (7.50)	
8e	60	152–154	$C_{27}H_{18}O_2S_2Cl_2$	63.65 (63.62)	3.54 (3.53)	12.57 (12.59)	13.95 (13.93)	
9a	61	180–182	$C_{29}H_{26}O_2S_2$	74.04 (74.02)	5.53 (5.50)	13.62 (13.66)		
9b	59	185–187	$C_{29}H_{25}O_2S_2Br$	63.39 (63.36)	4.55 (4.52)	11.66 (11.62)		14.57 (14.55)
9c	62	179–181 (d)	$C_{30}H_{28}O_2S_2$	74.38 (74.36)	5.78 (5.76)	13.22 (13.20)		
9d	59	192–193	$C_{29}H_{25}O_2S_2Cl$	68.98 (68.96)	4.95 (4.93)	12.68 (12.66)	7.04 (7.00)	
9e	60	185–187	$C_{29}H_{24}O_2S_2Cl_2$	64.56 (64.54)	4.45 (4.43)	11.87 (11.86)	13.17 (13.14)	

TABLE II Spectral Data.

Entry	R_1	R_2	R_3	*MP*	*IR, cm^{-1}*	*^1H NMR ($CDCl_3$, δ, ppm)*	*MS, m/z (M^+)*
3a	H	H	H	100–112	3430 (br, −OH), 1720 (C=O)	2.49 (s, 3H, CH_3), 2.95 (s, 3H, $-SCH_3$), 6.74–6.83 (m, 5H, Ar−H), 6.95–7.01 (m, 5H, Ar−H), 7.21 (dd, 1H, Ar−H), 7.32 (dd, 1H, Ar−H), 7.41 (dd, 1H, Ar−H)	364
3b	H	H	Br	115–117	3430 (br, −OH), 1720 (C=O)	2.48 (s, 3H, CH_3), 2.95 (s, 3H, $-SCH_3$), 6.76–6.86 (m, 4H, Ar−H), 6.91–7.00 (m, 5H, Ar−H), 7.21–7.28 (dd, 1H, Ar−H), 7.32–7.36 (dd, 1H, Ar−H), 7.41 (dd, 1H, Ar−H)	443
3c	H	H	CH_3	110–112 (d)	3430 (br, −OH), 1720 (C=O)	2.47 (s, 3H, CH_3), 2.51–2.59 (s, 3H, CH_3), 2.95 (s, 3H, $-SCH_3$), 6.78–6.89 (m, 4H, Ar−H), 6.90–7.05 (m, 5H, Ar−H), 7.21–7.28 (dd, 1H, Ar−H), 7.32–7.36 (dd, 1H, Ar−H), 7.41–7.48 (dd, 1H, Ar−H)	378
3d	H	H	Cl	120–122	3432 (br, −OH), 1720 (C=O)	2.48 (s, 3H, CH_3), 2.95 (s, 3H, $-SCH_3$), 6.76–6.86 (m, 4H, Ar−H), 6.91–7.01 (m, 5H, Ar−H), 7.21–7.28 (dd, 1H, Ar−H), 7.32–7.36 (dd, 1H, Ar−H), 7.41–7.48 (dd, 1H, Ar−H)	398
3e	Cl	Cl	H	119–121	3430 (br, −OH), 1720 (C=O)	2.45 (s, 3H, CH_3), 2.95 (s, 3H, $-SCH_3$), 6.70–6.89 (m, 5H, Ar−H), 7.43–7.52 (dd, 2H, Ar−H), 7.54–7.58 (dd, 1H, Ar−H), 7.61–7.66 (dd, 1H, Ar−H), 7.73–7.78 (dd, 1H, Ar−H), 7.82 (s, 1H, Ar−H)	433
4a	H	H	H	123–125 (d)	3430 (br, −OH), 1720 (C=O)	2.49 (s, 3H, CH_3), 5.42 (s, 1H, −SH), 6.74–6.83 (m, 5H, Ar−H), 6.95–7.01 (m, 5H, Ar−H), 7.35–7.42 (dd, 1H, Ar−H), 7.43–7.49 (dd, 1H, Ar−H)	346
4b	H	H	Br	118–120	3432 (br, −OH), 1720 (C=O)	2.48 (s, 3H, CH_3), 5.42 (s, 1H, −SH), 6.76–6.86 (m, 4H, Ar−H), 6.91–7.00 (m, 5H, Ar−H), 7.35–7.42 (dd, 1H, Ar−H), 7.43–7.49 (dd, 1H, Ar−H)	429
4c	H	H	CH_3	128–130	3430 (br, −OH), 1720 (C=O)	2.49 (s, 3H, CH_3), 2.51–2.59 (s, 3H, CH_3), 5.42 (s, 1H, −SH), 6.78–6.89 (m, 4H, Ar−H), 6.90–7.05 (m, 5H, Ar−H), 7.35–7.42 (dd, 1H, Ar−H), 7.43–7.49 (dd, 1H, Ar−H)	360
4d	H	H	Cl	110–112 (d)	3432 (br, −OH), 1720 (C=O)	2.48 (s, 3H, CH_3), 5.43 (s, 1H, −SH), 6.76–6.86 (m, 4H, Ar−H), 6.91–7.01 (m, 5H, Ar−H), 7.35–7.42 (dd, 1H, Ar−H), 7.43–7.49 (dd, 1H, Ar−H)	380
4e	Cl	Cl	H	130–132	3430 (br, −OH), 1720 (C=O)	2.45 (s, 3H, CH_3), 5.40 (s, 1H, −SH), 6.70–6.89 (m, 5H, Ar−H), 7.35–7.43 (dd, 1H, Ar−H), 7.45–7.52 (dd, 1H, Ar−H), 7.63–7.68 (dd, 1H, Ar−H), 7.70–7.82 (dd, 1H, Ar−H), 7.86 (s, 1H, Ar−H)	415

TABLE III Spectral Data.

Entry	*R*	R_1	R_2	R_3	*IR, cm^{-1}*	*^1H NMR ($CDCl_3$, δ, ppm)*	*MS, m/z (M^+)*
6a	H	H	H	H	3430 (br, −OH), 1720 (C=O)	2.49–2.52 (s, 3H, CH_3), 5.42 (s, 1H, 6−H), 6.74–6.83 (m, 5H, Ar−H), 6.95–6.99 (m, 5H, Ar−H), 7.48 (s, 1H, Ar−H), 12.42 (s, 1H, −OH)	400
6b	H	H	H	Br	3430 (br, −OH), 1720 (C=O)	2.48–2.52 (s, 3H, CH_3), 5.43 (s, 1H, 6−H), 6.76–6.86 (m, 4H, Ar−H), 6.91–7.00 (m, 5H, Ar−H), 7.40 (s, 1H, Ar−H), 12.43 (s, 1H, −OH)	479
6c	H	H	H	CH_3	3430 (br, −OH), 1720 (C=O)	2.42 (s, 3H, CH_3), 2.51–2.59 (s, 3H, CH_3), 5.42 (s, 1H, 6−H), 6.78–6.89 (m, 4H, Ar−H), 6.90–7.05 (m, 5H, Ar−H), 7.47 (s, 1H, Ar−H), 12.42 (s, 1H, −OH)	414
6d	H	H	H	Cl	3432 (br, −OH), 1720 (C=O)	2.48–2.52 (s, 3H, CH_3), 5.43 (s, 1H, 6−H), 6.76–6.86 (m, 4H, Ar−H), 6.91–7.00 (m, 5H, Ar−H), 7.43 (s, 1H, Ar−H), 12.43 (s, 1H, −OH)	434
6e	H	Cl	Cl	H	3430 (br, −OH), 1720 (C=O)	2.45 (s, 3H, CH_3), 5.40 (s, 1H, 6−H), 6.70–6.89 (m, 5H, Ar−H), 7.43–7.52 (dd, 2H, Ar−H), 7.71–7.82 (s, 1H, Ar−H), 7.82 (s, 1H, Ar−H), 12.40 (s, 1H, −OH)	469
7a	*Et	H	H	H	3430 (br, −OH), 1720 (C=O)	2.21 (s, 3H, CH_3), 2.49–2.52 (s, 3H, CH_3), 4.21–4.42 (q, 2H, CH_2), 6.74–6.83 (m, 5H, Ar−H), 6.95–6.83 (m, 5H, Ar−H), 7.49 (s, 1H, Ar−H), 12.42 (s, 1H, −OH)	428
7b	*Et	H	H	Br	3432 (br, −OH), 1720 (C=O)	2.23 (s, 3H, CH_3), 2.48–2.52 (s, 3H, CH_3), 4.23–4.46 (q, 2H, CH_2), 6.76–6.86 (m, 4H, Ar−H), 6.9–7.00 (m, 5H, Ar−H), 7.40 (s, 1H, Ar−H), 12.43 (s, 1H, −OH)	507
7c	*Et	H	H	CH_3	3430 (br, −OH), 1720 (C=O)	2.24 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.51–2.59 (s, 3H, CH_3), 4.20–4.45 (q, 2H, CH_2), 6.78–6.89 (m, 4H, Ar−H), 6.90–7.05 (m, 5H, Ar−H), 7.42 (s, 1H, Ar−H), 12.42 (s, 1H, −OH)	441
7d	*Et	H	H	Cl	3432 (br, −OH), 1720 (C=O)	2.20 (s, 3H, CH_3), 2.48–2.52 (s, 3H, CH_3), 4.21–4.42 (q, 2H, CH_2), 6.76–6.86 (m, 4H, Ar−H), 6.91–7.00 (m, 5H, Ar−H), 7.40 (s, 1H, Ar−H), 12.43 (s, 1H, −OH)	462
7e	*Et	Cl	Cl	H	3430 (br, −OH), 1720 (C=O)	2.18 (s, 3H, CH_3), 2.45–2.54 (s, 3H, CH_3), 4.19–4.38 (q, 2H, CH_2), 6.70–6.89 (m, 5H, Ar−H), 7.43–7.52 (dd, 2H, Ar−H), 7.71–7.82 (s, 1H, Ar−H), 7.85 (s, 1H, Ar−H), 12.40 (s, 1H, −OH)	497
8a	*Pr	H	H	H	3430 (br, −OH), 1720 (C=O)	1.20–1.25 (d, 6H, CH_3), 2.21–2.36 (m, 1H, CH), 2.49–2.52 (s, 3H, CH_3), 6.74–6.83 (m, 5H, Ar−H), 6.95–6.83 (m, 5H, Ar−H), 7.45 (s, 1H, Ar−H), 12.42 (s, 1H, −OH)	440
8b	*Pr	H	H	H	3432 (br, −OH), 1720 (C=O)	1.23–1.26 (d, 6H, CH_3), 2.25–2.34 (m, 1H, CH), 2.48–2.52 (s, 3H, CH_3), 6.76–6.86 (m, 4H, Ar−H), 6.91–7.00 (m, 5H, Ar−H), 7.40 (s, 1H, Ar−H), 12.43 (s, 1H, −OH)	519
8c	*Pr	H	H	H	3430 (br, −OH), 1720 (C=O)	1.20–1.24 (d, 6H, CH_3), 2.24–2.38 (m, 1H, methyne), 2.42 (s, 3H, CH_3), 2.51–2.59 (s, 3H, CH_3), 6.78–6.89 (m, 4H, Ar−H), 6.90–7.05 (m, 5H, Ar−H), 7.42 (s, 1H, Ar−H), 12.42 (s, 1H, −OH)	454

8d	*Pr	H	H	H	3432 (br, −OH), 1720 (C=O)	1.21–1.25 (d, 6H, CH_3), 2.26–2.32 (m, 1H, CH), 2.48–2.52 (s, 3H, CH_3), 6.76–6.86 (m, 4H, Ar−H), 6.91–7.00 (m, 5H, Ar−H), 7.45 (s, 1H, Ar−H), 12.43 (s, 1H, −OH)	474
8e	*Pr	H	H	H	3430 (br, −OH), 1720 (C=O)	1.24–1.28 (d, 6H, CH_3), 2.24–2.36 (m, 1H, CH), 2.45–2.54 (s, 3H, CH_3), 6.70–6.89 (m, 5H, Ar−H), 7.43–7.52 (dd, 2H, Ar−H), 7.71–7.82 (s, 1H, Ar−H), 7.85 (s, 1H, Ar−H), 12.40 (s, 1H, −OH)	509
9a	*Pn	H	H	H	3430 (br, −OH), 1720 (C=O)	1.18–1.40 (t, 3H, CH_3), 1.80–1.98 (m, 2H, CH_2), 2.49–2.52 (s, 3H, CH_3), 3.26 (q, 2H, CH_2), 3.32 (q, 2H, CH_2), 4.19–4.32 (t, 2H, CH_2), 6.74–6.83 (m, 5H, Ar−H), 6.95–6.83 (m, 5H, Ar−H), 7.45 (s, 1H, Ar−H), 12.42 (s, 1H, −OH)	470
9b	*Pn	H	H	H	3432 (br, −OH), 1720 (C=O)	1.22–1.46 (t, 3H, CH_3), 1.82–1.94 (m, 2H, CH_2), 2.48–2.52 (s, 3H, CH_3), 3.20 (q, 2H, CH_2), 3.36 (q, 2H, CH_2), 4.24–4.34 (t, 2H, CH_2), 6.76–6.86 (m, 4H, Ar−H), 6.91–7.00 (m, 5H, Ar−H), 7.40 (s, 1H, Ar−H), 12.43 (s, 1H, −OH)	549
9c	*Pn	H	H	H	3430 (br, −OH), 1720 (C=O)	1.26–1.48 (t, 3H, CH_3), 1.84–1.96 (m, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.51–2.59 (s, 3H, CH_3), 3.19 (q, 2H, CH_2), 3.32 (q, 2H, CH_2), 2.21–4.35 (t, 2H, CH_2), 6.78–6.89 (m, 4H, Ar−H), 6.90–7.05 (m, 5H, Ar−H), 7.45 (s, 1H, Ar−H), 12.42 (s, 1H, −OH)	484
9d	*Pn	H	H	H	3432 (br, −OH), 1720 (C=O)	1.20–1.41 (t, 3H, CH_3), 1.82–1.94 (m, 2H, CH_2), 2.48–2.52 (s, 3H, CH_3), 3.24 (q, 2H, CH_2), 3.36 (q, 2H, CH_2), 4.19–4.36 (t, 2H, CH_2), 6.76–6.86 (m, 4H, Ar−H), 6.91–7.00 (m, 5H, Ar−H), 7.40 (s, 1H, Ar−H), 12.43 (s, 1H, −OH)	504
9e	*Pn	H	H	H	3430 (br, −OH), 1720 (C=O)	1.24–1.45 (t, 3H, CH_3), 1.82–1.96 (m, 2H, CH_2), 2.46–2.52 (s, 3H, CH_3), 3.22 (q, 2H, CH_2), 3.38 (q, 2H, CH_2), 4.24–4.34 (t, 2H, CH_2), 6.70–6.89 (m, 5H, Ar−H), 7.43–7.52 (dd, 2H, Ar−H), 7.75 (s, 1H, Ar−H), 12.40 (s, 1H, −OH)	539

*Et – C_2H_5
*Pr – C_3H_7
*Pn – C_5H_{11}

7-Methyl-2,3-diphenyl-6-thio-benzo[b]thiophenes (4a–e)

A mixture of 2-(2-methyl-3-methylsulfanyl-phenylsulfanyl)-1,2-diphenylethanone (3a–e) (0.01 mol) was dissolved in dry diethyl ether (30 ml) to obtain a clear solution. $BF_3(OEt)_2$ (0.5 ml) was added to this solution and stirred under N_2 atmosphere for 10–12 hrs at room temperature and washed with water (20 ml), dried with Na_2SO_4 and concentrated *in vacuo* to produce a light brown oil, which was separated by column chromatography (EtOAc/pet. ether = 1:9) to give the desired compound.

Substituted 5-hydroxythio-7H-thieno[3,2-g][1] benzothiopyran-7-ones (6a–e)

Mixture of compounds (4a–e) (0.01 mol) and substituted malonic acids (0.01 mol) was dissolved in dry DCM (10 ml) to obtained a clear solution. To this was added $AlCl_3$ (26.0 g) in small portions and the resulting solution was stirred under a N_2 atmosphere for 12–14 h at room temperature. The mixture was poured onto crushed ice containing conc. HCl. The organic layer was separated out with DCM and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford a reddish crude product which was purified by coloumn chromotography (EtOAc:pet. ether = 2:8).

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