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Application of directed metalation in synthesis. Part 4: Expedient synthesis of substituted benzo[*b*]thiophene and naphthothiophene☆

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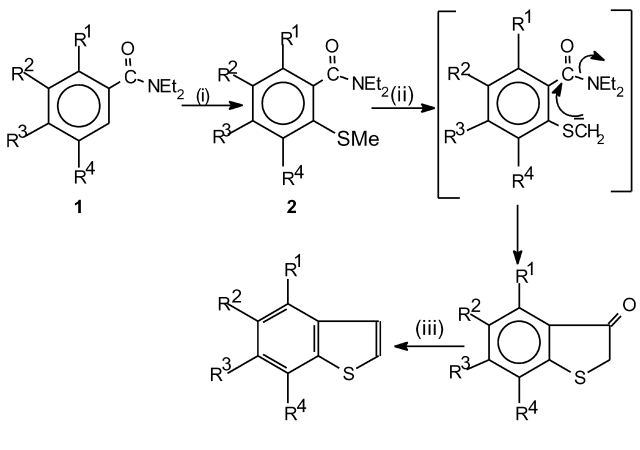
Abstract—A short, simple and inexpensive synthesis of several diversely substituted benzo[*b*]thiophenes and one naphthothiophene is described. The method involves introduction of methylsulfanyl group *ortho*- to the amide function of readily available *N*,*N*-diethylamides of aryl carboxylic acid by directed metalation. Thioindoxyls, obtained in high yields through side-chain deprotonation and cyclisation in one pot, are reduced to benzo[*b*]thiophene or napthothiophene. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

We have recently reported[2] a short and expedient route to various methoxybenzo[*b*]thiophenes. The method consisting of sequential directed *ortho*-lithiation, side chain deprotonation, cyclisation using tertiary amide function as internal electrophile[3] and borohydride reduction compares favourably with earlier reported[4,5] synthesis of these compounds. Since the publication of our results,[2] a paper[6] appeared describing the synthesis of the key intermediate used by us, by a procedure which is essentially a modification of our method. The only difference is in the use of ester instead of amide as the internal electrophile. Importance of benzo[*b*]thiophene can be appreciated from the numerous reports in the literature[7] since the chemistry[4,5] and the biological activities of these compounds were reviewed. Thus benzo[*b*]thiophene derivatives have exhibited[7] biological activities e.g. anti-inflammatory, analgesic, antiexudative, antipsychotic and enzyme inhibiting properties. Benzo[*b*]thiophene and naphtho[2,1-*b*]thiophene based diphosphanes have been developed[7] as C_1-symmetric ligands for homogeneous stereoselective catalysis. Diaryl substituted benzo[*b*]thiophenes have been developed[7] as novel photochromic materials. Substituted benzo[*b*]thiophenes and partially hydrogenated benzo-[*b*]thiophenes have been used as building blocks in the synthesis[2,8] of polycondensed systems which include sulfur analogues[1,9] of bioactive natural products. Expedient access to substituted benzo[*b*]thiophenes, preferably avoiding as much possible use of expensive and environmentally offensive thiols, is thus important. Some time ago we developed a multistep synthesis[10] of substituted benzo-[*b*]thiophenes that did not use thiols as starting materials.

We report here the further application of the method[2] developed by us in the synthesis of other substituted benzo[*b*]thiophenes and naphthothiophene establishing the generality of this procedure.



Scheme 1. *Reagents and condition*: (i) *sec*-BuLi/TMEDA/THF/−78° C/Me−S−S−Me, (ii)LDA/THF/−78°C. (iii) $NaBH_4$/MeOH/10% NaOH/reflux for 10 h.

☆ See Ref. 1.

Keywords: benzo[*b*]thiophene; directed metalation; thioindoxyl; naphthothiophene; intramolecular cyclisation.

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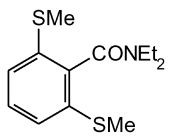
2. Results and discussion

The starting materials used in the synthesis (Scheme 1) were easily available *N*,*N*-diethylamides (**1**) of arylcarboxylic acids. Methoxy benzamides were synthesized from commercially available hydroxybenzoic acids. Under standard directed metalation condition[11] (*sec*-BuLi/TMEDA/THF/−78°C in argon atmosphere), deprotonation takes place in the *ortho*-position of the tertiary amide function. Deprotonation took place exclusively in the *ortho*-position of the tertiary amide, when the molecule also contained methoxy substituents reflecting the greater directing power[11] of tertiary amides. Even when a particular position of the aromatic ring was under the simultaneous influence of two methoxy groups as in the case of *N*,*N*-diethyl-2,4-dimethoxybenzamide, exclusive deprotonation was observed in the 6-position when 1.1 molar equiv. of *sec*-BuLi was used. As expected, *N*,*N*-diethyl-3-methoxybenzamide was deprotonated in the 2-position under the reinforcing effect of the directing influences of tertiary amide and methoxy functions.

The lithio derivatives were quenched at −78°C with dimethyl disulphide[12] (2 molar equiv.) followed by stirring at room temperature for 5 h. When *N*,*N*-diethyl benzamide was treated with 2.5 molar equiv. of *sec*-BuLi and the reaction mixture was stirred for 10 h at room temperature methyl sulfanyl function was introduced in both the *ortho*-position of the tertiary amide function along with the formation of some mono substituted product (54:22). Close R_f values of the starting tertiaryamides (**1**) (R^1=R^2=R^3=R^4=H) and the methylsulfanyl substituted products (**5**) necessitated repeated column chromatography for the preparation of analytically pure sample of the product. However even with partially pure **5**, one could smoothly proceed to the next step. For introduction of methylsulfanyl group in the 3-position of *N*,*N*-diethylthiophene-2-carboxamide, silyl protection of the free α-position was necessary. *N*,*N*-diethyl-3-methylsulfanyl-5-trimethylsilylthiophene-2-carboxamide (**2k**) was obtained from *N*,*N*-diethyl-5-trimethylsilylthiophene-2-carboxamide[13] in 78% yield. Table 1 summarises the compounds obtained by introducing methyl sulfanyl substituents *ortho*- to $CONEt_2$.



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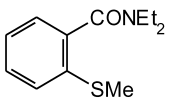
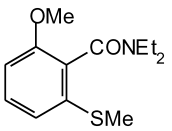
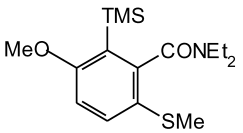
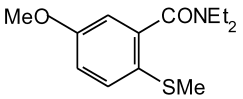
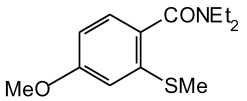
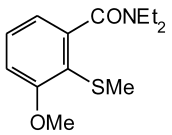
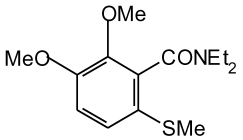
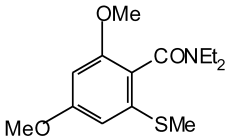
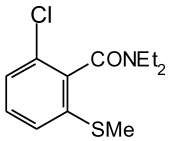
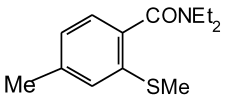
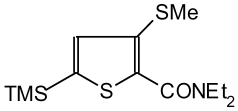
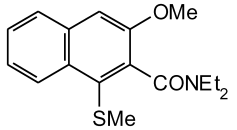
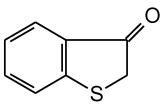
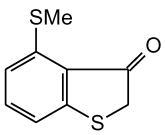
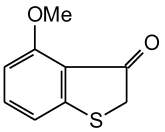
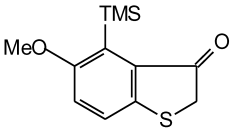
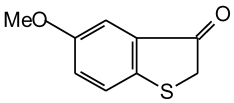
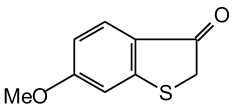
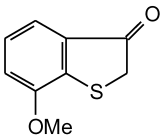
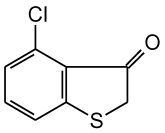
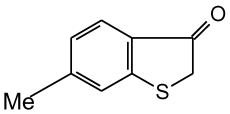
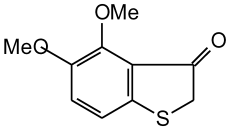
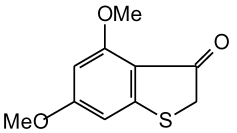
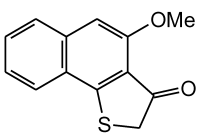
Side chain deprotonation of **2** with 2.5 molar equiv. of LDA[11,14] was instantaneously followed by cyclisation to afford the thioindoxyls **3**. Our attempts to cyclise **2k** for access to a thienothiophene system, however, failed and we got the starting material back. Cyclisation of *N*,*N*-diethyl-2-methylsulfanyl-4-methoxy-5-trimethylsilylbenzamide (**2c**) proceeded to give an extremely poor yield of the thioindoxyl (**3d**) accompanied mostly by unreacted starting material and some intractable decomposition product. Since the desilylated product, (**2d**) cyclised smoothly to afford **3e**, it is presumed that the presence of a bulky trimethylsilyl group in the *ortho*-position might force the tertiary amide into a position not easily accessible for the SCH_2^- anion for a nucleophilic attack on the carbonyl carbon. Cyclisation of *N*,*N*-diethyl-1-methylsulfanyl-3-methoxy-napthalene-3-carboxamide (**2l**) afforded 2,3-dihydro-4-methoxy-naptho[1,2-*b*]thiophen-3-one (**3l**) in 69% yield.

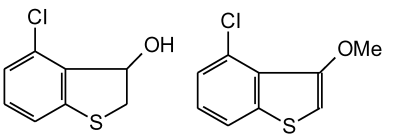
Table 1.

No.	Compound	Yield (%)	Nature
2a		77	Gummy liquid
2b		72	Solid
2c		79	Solid
2d		90	Oil
2e		62	Oil
2f		85	Viscous liquid
2g		72	Gummy liquid
2h		70	Solid
2j		75	Solid
2k		71	Viscous liquid
2l		79	Gummy liquid
2m		69	Gummy liquid

Though the thioindoxyls (Table 2) were susceptible to slow decomposition upon prolonged exposure to air, they could be kept under argon in the refrigerator with no visible sign of deterioration and were fully characterized by analytical and spectral data. As expected, the IR data of these compounds do not show the presence of enol tautomers. It was observed[15] earlier that in solid state thioindoxyls exist entirely in the keto form. Borohydride reduction[16] of the thioindoxyls in hot methanolic sodium hydroxide afforded the substituted benzo[*b*]thiophenes in all but one case. ^{1}H NMR data and mpt/bpt of the benzo[*b*]thiophenes which were earlier reported in the literature corresponded with those of the compounds reported in this paper.Work up consists of treatment with sulfuric acid (10%) after removal of methanol. While reducing **3i** (R^1=R^2=R^4=H, R^3=Me) more concentrated sulfuric acid (20%) and prolonged stirring were required during work up.

Table 2.

No.	Compound	Yield (%)	Nature
3a		67	Solid
3b		66	Solid
3c		65	Solid
3d		10	Solid
3e		69	Solid
3f		78	Solid
3g		69	Solid
3h		68	Solid
3i		77	Solid
3j		89	Solid
3k		81	Solid
3l		73	Solid



6 **7**

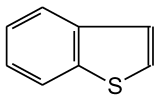
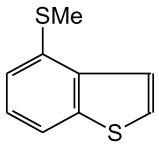
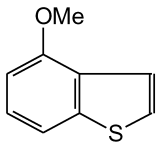
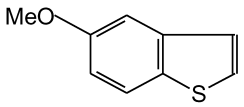
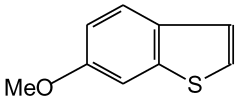
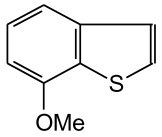
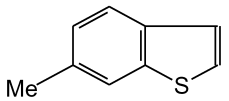
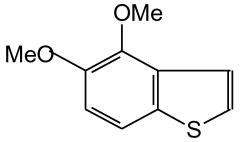
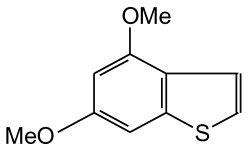
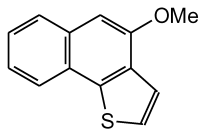
Table 3 summarises the benzo[*b*]thiophenes synthesized. Melting/boiling points and ^{1}H NMR data of the benzo-[*b*]thiophenes earlier reported corresponded with the data on the same compounds synthesized by us. However, all our attempts to prepare 4-chlorobenzo[*b*]thiophene from 2,3-dihydro-4-chlorobenzo[*b*]thiophene-3-one (**3h**) completely failed.

Conversion of thioindoxyl to benzo[*b*]thiophene through borohydride reduction should involve initial formation of carbinol followed by dehydration. Borohydride reduction of **3h** afforded 2,3-dihydro-3-hydroxy-4-chloro benzo[*b*]thiophene (**6**) in 75% yield which was fully characterized. However attempts to dehydrate it with *p*-toluene sulphonic acid resulted in the formation of an intractable mixture of unidentifiable products and no trace of 4-chlorobenzo-[*b*]thiophene was found. Methylation of **3h** with aqueous potassium hydroxide (20%) and dimethylsulphate afforded 3-methoxy-4-chlorobenzo[*b*]thiophene (**7**) in 72% yield. Reduction of **3l** afforded 4-methoxy-naptho[1,2-*b*]thiophene (**4j**), as expected, in 85% yield.

3. Conclusion

The procedure described above provides an expedient access to diversely substituted benzo[*b*]thiophenes and its simplicity constitutes a significant improvement over earlier methods. Thioindoxyls which are key intermediates in the present synthesis of benzo[*b*]thiophenes are obtained from much simpler and readily available starting materials than were needed earlier.[4] The method also compares favorably with a short and expedient synthesis[17] of benzo[*b*]thiophene which is elegant but uses thiols as starting material. The present work is yet another demonstration of the power of directed metalation in the regiocontrolled functionalisation of aromatic nuclei and the subsequent utilisation of the introduced functionalities for annelation purposes.

Table 3.

No.	Compound	Yield (%)	Nature
4a		67	Solid
4b		45	Liquid
4c		82	Oil
4d		77	Solid
4e		73	Oil
4f		71	Oil
4g		92	Solid
4h		73	Oil
4i		85	Solid
4j		79	Solid

4. Experimental

4.1. General

Commercially available solvents were distilled prior to use. Light petroleum ether (bp 60–80°C) was used for column chromatography. Anhydrous sodium sulfate was used as drying agent. THF, *n*-hexane, cyclohexane were dried by the usual sodium-benzophenone-ketyl method. ^{1}H NMR spectra (300 MHz) and ^{13}C, DEPT (75.5 MHz) were recorded in $CDCl_3$ solution on Bruker DPX-300 spectrometer. Chemical shift (δ) are expressed in ppm using tetramethylsilane as internal standard. Coupling constant (J) values are given in Hz. Melting points (uncorrected) were recorded in open capillaries on a hot stage apparatus. IR spectra were recorded on a FTIR-8300, SHIMADZU spectrometer, for solids in potassium bromide discs and for liquids by placing a thin layer of the sample between two potassium bromide discs. *n*-BuLi and *sec*-BuLi were prepared in our laboratory by reacting molecularised lithium with 1-chlorobutane in *n*-hexane (in the case of *n*-BuLi) or 2-chlorobutane in cyclohexane (in the case of *sec*-BuLi). Molecularisation of lithium was done either by heating the lithium in heavy paraffin liquid and then vigorous stirring with a mechanical stirrer or under sonication. Strength of the alkyl lithium was determined by titration against diphenyl acetic acid.

4.1.1. Synthesis of 2-methylsulfanylbenzamides. To a stirred solution of TMEDA (0.92 mL, 1.1 equiv.) and *sec*-BuLi [6.21 mL, 1.1 equiv. of 1 M solution in cyclohexane] in THF (15 mL) at −78°C, *N*,*N*-diethyl benzamide (**1**) (R^1=R^2=R^3=R^4=H) (1 g, 5.6 mmol) was added through a needle syringe system. Stirring was continued for 30 min and dimethyl disulfide (1 mL, 2 equiv.) in THF (5 mL) was added to the reaction mixture kept at −78°C. After stirring the reaction mixture at the same teperature for 15 min it was allowed to attain room temperature and kept for 6 h at that temperature. After removal of the solvent under reduced pressure, saturated solution of ammonium chloride was added to the reaction mixture and it was extracted with diethyl ether. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. Removal of solvent afforded compound **2a** (R^1=R^2=R^3=R^4=H) which was purified by column chromatography using ethyl acetate–light petroleum (3:17) as eluant. Gummy liquid (980 mg, 77%); (Found C, 65.81; H, 6.00; N, 6.40. $C_{12}H_{13}OSN$ requires C, 65.75; H, 5.93; N, 6.39%); ν_{max} (NEAT): 1629 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.96 (3H, t, J=7.1 Hz, $-CH_2CH_3$), 1.19 (3H, t, J=7.1 Hz, $-CH_2CH_3$), 2.34 (3H, s, −SMe), 3.05 (2H, q, J=7.1 Hz, $-CH_2CH_3$), 3.5 (2H, q, J=7.1 Hz, $-CH_2CH_3$), 7.09–7.11 (2H, m, Ar-3, 4H), 7.22–7.24 (2H, m, Ar-5, 6H); δ_C (75.5 MHz, $CDCl_3$) 13.0, 14.3, 16.7, 39.2, 43.1, 125.8, 126.5, 127.5, 129.4, 135.2, 137.8, 169.6.

4.1.2. *N*,*N*-Diethyl-2-methylsulfanyl-6-methoxybenzamide (2b, R^1=OMe, R^2=R^3=R^4=H). Compound **2b** (R^1=OMe, R^2=R^3=R^4=H) was synthesized following the same procedure as stated above with (1 g, 4.8 mmol) of 2-methoxybenzamide, TMEDA (1.8 ml, 2.5 equiv.), *sec*-BuLi [9.7 mL, 2.5 equiv. of 1.25 M solution in cyclohexane], dimethyl disulfide (0.87 mL, 2 equiv.) and stirring at room temperature for 10 h. Colourless needles, crystalised from CCl_4–petroleum ether (880 mg, 72%); mp 61–63°C; (Found C, 61.65; H, 7.39; N, 5.51. $C_{13}H_{19}O_2SN$ requires C, 61.66; H, 7.50; N, 5.53%); ν_{max} (KBr): 1633 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.98 (3H, t, J=7.1 Hz, $-CH_2CH_3$), 1.20 (3H, t, J=7.1 Hz, $-CH_2CH_3$), 2.38 (3H, s, −SMe), 3.05 (2H, q, J=7.1 Hz, $-CH_2CH_3$), 3.34 (2H, q, J=7.1 Hz, $-CH_2CH_3$), 3.72 (3H, s, −OMe), 6.65 (1H, dd, J=8.30 Hz, 1.5, Ar-3H), 6.82 (1H, dd, J=8.0, 1.5 Hz, Ar-5H), 7.20 (1H, dd, J=8.3, 8.0 Hz, Ar-4H); δ_C (75.5 MHz, $CDCl_3$) 12.9, 14.3, 16.7, 39.0, 42.9, 56.0, 108.5, 119.6, 129.9, 136.8, 155.9, 167.0.

4.1.3. *N*,*N*-Diethyl-2-methylsulfanyl-5-methoxy-6-trimethylsilylbenzamide[12] (2c, R^1=TMS, R^2=OMe,

R^3=R^4=H). Prepared in the same way as before. Purification by column chromatography [eluant: ethyl acetate–light petroleum (1:9)]; colourless solid (79%), mp 79–81°C. (Found C, 59.18; H, 8.50; N, 4.21. $C_{16}H_{27}O_2NSSi$ requires C, 59.07; H, 8.30; N, 4.30%); ν_{max} (NEAT): 1631 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.80 (9H, s, $-SiMe_3$), 0.91 (3H, t, J=7.2 Hz, $-CH_2CH_3$), 1.04 (3H, t, J=7.2 Hz, $-CH_2CH_3$), 2.12 (3H, s, –SMe), 2.81–2.93 (2H, m, $-CH_2CH_3$), 3.53 (3H, s, –OMe), 3.64–3.71 (2H, m, $-CH_2CH_3$), 6.57 (1H, d, J=8.7 Hz, Ar-3H), 7.15 (1H, d, J=8.7 Hz, Ar-4H); δ_C (75.5 MHz, $CDCl_3$) 0.5, 11.6, 12.7, 18.6, 38.1, 42.4, 54.7, 110.0, 124.5, 124.8, 133.6, 145.5, 163.4, 168.6.

4.1.4. *N*,*N*-Diethyl-2-methylsulfanyl-5-methoxybenzamide (2d, R^1=H, R^2=OMe, R^3=R^4=H). Desilylation was done by refluxing the compound (370 mg, 1.33 mmol) with CsF (350 mg, 2 equiv.) in DMF–water mixture (10:1). After cooling, the mixture was evaporated to dryness in vaccuo and the residue was extracted with ether, washed with brine water. Drying and removal of solvent afforded compound **2d** (R_1=H, R_2=OMe, R_3=R_4=H) which was purified by column chromatography [eluant: ethyl acetate–light petroleum (3:17)]; colourless oil (260 mg, 90%);(Found C, 61.65; H, 7.80; N, 5.48. $C_{13}H_{19}O_2NS$ requires C, 61.66; H, 7.50; N, 5.53%); ν_{max} (NEAT): 1631 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.03 (3H, t, J=7.0 Hz, $-CH_2CH_3$), 1.25 (3H, t, J=7.0 Hz, $-CH_2CH_3$), 2.38 (3H, s, –SMe), 3.11 (2H, q, J=7.0 Hz, $-CH_2CH_3$), 3.50–3.60 (2H, m, $-CH_2CH_3$), 3.76 (3H, s, –OMe), 6.72 (1H, d, J=2.8 Hz, Ar-6H), 6.84 (1H, dd, J=8.6, 2.8 Hz, Ar-4H), 7.31 (1H, d, J=8.6 Hz, Ar-3H); δ_C (75.5 MHz, $CDCl_3$) 12.9, 14.3, 19.1, 39.1, 43.1, 55.8, 112.0, 112.2, 115.6, 118.7, 125.0, 129.9, 133.0, 141.2, 159.0, 169.5.

4.1.5. *N*,*N*-Diethyl-2-methylsulfanyl-4-methoxybenzamide (2e, R^1=R^2=H, R^3=OMe, R^4=H). Compound **2e** (R^1=R^2=H, R^3=OMe, R^4=H) was synthesized following the general procedure with 1.2 equiv. of *sec*-BuLi. Purification by column chromatography [eluant: ethyl acetate–light petroleum (3:17)]; Yellowish oil (62%); (Found C, 61.55; H, 7.81; N, 5.58. $C_{13}H_{19}O_2NS$ requires C, 61.66; H, 7.50; N, 5.53%); ν_{max} (NEAT): 1627 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.08 (3H, t, J=7.1 Hz, $-CH_2CH_3$), 1.27 (3H, t, J=7.1 Hz, $-CH_2CH_3$), 2.44 (3H, s, –SMe), 3.14 (2H, q, J=7.1 Hz, $-CH_2CH_3$), 3.58 (2H, q, J=7.1 Hz, $-CH_2CH_3$), 3.81 (3H, s, –OMe), 6.70 (1H, dd, J=8.4, 2.3 Hz, Ar-5H), 6.80 (1H, d, J=2.3 Hz, Ar-3H), 7.10 (1H, d, J=8.4 Hz, Ar-6H); δ_C (75.5 MHz, $CDCl_3$) 13.0, 14.4, 16.5, 39.3, 43.2, 55.7, 110.5, 113.3, 127.8, 130.2, 137.1, 160.3, 169.7.

4.1.6. *N*,*N*-Diethyl-2-methylsulfanyl-3-methoxybenzamide (2f, R^1=R^2=R^3=H, R^4=OMe). Prepared in the same way as before. Purification by column chromatography [eluant: ethyl acetate–light petroleum (3:17)]; colourless viscous liquid (85%); (Found C, 61.95; H, 7.61; N, 5.50. $C_{13}H_{19}O_2NS$ requires C, 61.66; H, 7.50; N, 5.53%); ν_{max} (NEAT): 1631 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.96 (3H, t, J=7.2 Hz, $-CH_2CH_3$), 1.20 (3H, t, J=7.2 Hz, $-CH_2CH_3$), 2.30 (3H, s, –SMe), 3.03 (2H, q, J=7.2 Hz, $-CH_2CH_3$), 3.28–3.39 (1H, m, $-CH_2CH_3$), 3.62–3.74 (1H, m, $-CH_2CH_3$), 3.84 (3H, s, –OMe), 6.74 (1H, dd, J=7.9, 1.0 Hz, Ar-4H), 6.81 (1H, dd, J=8.3, 1.0 Hz, Ar-6H), 7.24 (1H, dd, J=8.3, 7.9 Hz, Ar-5H); δ_C (75.5 MHz, $CDCl_3$) 12.9, 14.2, 18.5, 39.0, 43.0, 56.3, 111.3, 118.6, 120.6, 130.3, 144.0, 160.5, 169.6.

4.1.7. *N*,*N*-Diethyl-2-methylsulfanyl-5,6-dimethoxybenzamide (2g, R^1=R^2=OMe, R^3=R^4=H). Prepared in the same way as before. Purification by column chromatography [eluant: ethyl acetate–light petroleum (3:17)]; Gummy liquid (72%); (Found C, 59.55; H, 7.49; N, 4.96. $C_{14}H_{21}O_3NS$ requires C, 59.36; H, 7.42; N, 4.94%); ν_{max} (NEAT): 1631 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.07 (3H, t, J=7.1 Hz, $-CH_2CH_3$), 1.27 (3H, t, J=7.1 Hz, $-CH_2CH_3$), 2.42 (3H, s, –SMe), 3.13 (2H, q, J=7.1 Hz, $-CH_2CH_3$), 3.50–3.60 (2H, m, $-CH_2CH_3$), 3.84 (3H, s, –OMe), 3.86 (3H, s, –OMe), 6.87 (1H, d, J=8.5 Hz, Ar-3H), 7.09 (1H, d, J=8.5 Hz, Ar-4H); δ_C (75.5 MHz, $CDCl_3$) 12.8, 14.1, 18.7, 39.0, 43.2, 56.2, 61.9, 113.1, 126.0, 126.5, 134.6, 145.4, 151.9, 166.6.

4.1.8. *N*,*N*-Diethyl-2-methylsulfanyl-4,6-dimethoxybenzamide (2h, R^1=OMe, R^2=H, R^3=OMe, R^4=H). Prepared in the same way as before; colourless solid (ether–petroleum ether) (70%); mp 78–80°C. (Found C, 59.65; H, 7.59; N, 4.86. $C_{14}H_{21}O_3NS$ requires C, 59.36; H, 7.42; N, 4.94%); ν_{max} (KBr): 1637 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.01 (3H, t, J=7.1 Hz, $-CH_2CH_3$), 1.23 (3H, t, J=7.1 Hz, $-CH_2CH_3$), 2.42 (3H, s, –SMe), 3.24 (4H, q, J=7.1 Hz, $-CH_2CH_3$), 3.76 (3H, s, –OMe), 3.78 (3H, s, –OMe), 6.26 (1H, d, J=2.0 Hz, Ar-3H), 6.40 (1H, d, J=2.0 Hz, Ar-5H); δ_C (75.5 MHz, $CDCl_3$) 13.0, 14.2, 16.7, 39.1, 43.0, 55.8, 56.0, 96.0, 104.3, 119.7, 137.7, 157.1, 161.1, 167.1.

4.1.9. *N*,*N*-Diethyl-2-methylsulfanyl-6-chlorobenzamide (2i, R^1=Cl, R^3=R^4=R^5=H). Prepared in the same way as before; Crystaline colourless solid (ether–petroleum ether) (75%); mp 56–57°C. (Found C, 56.05; H, 6.49; N, 5.32. $C_{12}H_{16}ONSCl$ requires C, 56.03; H, 6.22; N, 5.44%); ν_{max} (KBr): 1624 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.12 (3H, t, J=7.1 Hz, $-CH_2CH_3$); 1.28 (3H, t, J=7.1 Hz, $-CH_2CH_3$), 2.46 (3H, s, –SMe), 3.15 (2H, q, J=7.1 Hz, $-CH_2CH_3$), 3.61 (2H, q, J=7.1 Hz, $-CH_2CH_3$), 7.17–7.26 (3H, m, Ar-3, 4, 5H); δ_C (75.5 MHz, $CDCl_3$) 13.0, 14.1, 16.8, 39.1, 43.0, 125.5, 126.7, 129.9, 131.2, 136.1, 137.9, 166.1.

4.1.10. *N*,*N*-Diethyl-2-methylsulfanyl-4-methylbenzamide (2j, R^1=R^2=H, R^3=Me, R^4=H). Prepared in the same way as before. Purification by column chromatography [eluant: ethyl acetate–light petroleum (1:9)]; Viscous liquid (71%); (Found C, 65.80; H, 7.99; N, 5.96. $C_{13}H_{19}ONS$ requires C, 65.82; H, 8.01; N, 5.90%); ν_{max} (NEAT): 1631 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.98 (3H, t, J=7.0 Hz, $-CH_2CH_3$), 1.06 (3H, t, J=7.0 Hz, $-CH_2CH_3$), 2.36 (3H, s, –Me), 2.37 (3H, s, –SMe), 3.29 (2H, q, J=7.0 Hz, $-CH_2CH_3$), 3.36 (2H, q, J=7.0 Hz, $-CH_2CH_3$), 7.22 (1H, d, J=3.0 Hz, Ar-3H), 7.27 (1H, dd, J=8.0, 3.0 Hz, Ar-5H), 7.67 (1H, d, J=8.0 Hz, Ar-6H); δ_C (75.5 MHz, $CDCl_3$) 13.0, 16.8, 14.1, 21.7, 39.23, 93.0, 126.5, 126.6, 128.2, 134.9, 135.0, 139.3, 169.9.

4.1.11. *N*,*N*-Diethyl-3-methylsulfanyl-5-trimethylsilylthiophene-2-carboxamide (2k). Prepared in the same

way as before. Purification by column chromatography [eluant: ethyl acetate–light petroleum (3:17)]; Gummy liquid (79%); (Found C, 57.85; H, 8.59; N, 5.46. $C_{13}H_{23}ONSSi$ requires C, 57.99; H, 8.55; N, 5.20%); ν_{max} (NEAT): 1633 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.08 (9H, s, $-SiMe_3$); 1.00 (6H, t, J=7.1 Hz, $-CH_2CH_3$), 2.20 (3H, s, –SMe), 3.20 (4H, q, J=7.1 Hz, $-CH_2CH_3$), 6.70 (1H, s, Ar-4H); δ_C (75.5 MHz, $CDCl_3$) 0.2, 13.9, 18.5, 41.8, 134.0, 135.3, 138.0, 141.4, 164.5.

4.1.12. *N*,*N*-Diethyl-1-methylsulfanyl-3-methoxynaphthalene-2-carboxamide (2l). Prepared in the same way. Purification by column chromatography [eluant: ethyl acetate–light petroleum (3:17)]; Gummy liquid (69%); (Found C, 65.85; H, 8.00; N, 5.96. $C_{13}H_{19}ONS$ requires C, 65.82; H, 8.01; N, 5.90%); ν_{max} (NEAT): 1735 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.03 (3H, t, J=7.1 Hz, $-CH_2CH_3$), 1.31 (3H, t, J=7.1 Hz, $-CH_2CH_3$), 2.42 (3H, s, –SMe), 3.07–3.15 (2H, m, $-CH_2CH_3$), 3.48–3.88 (2H, m, $-CH_2CH_3$), 3.92 (3H, s, –OMe), 7.19 (1H, s, Ar-4H), 7.47–7.51 (2H, m, Ar-6, 7H), 7.75–7.78 (1H, m, Ar-5H), 8.52–8.53 (1H, m, Ar-8H); δ_C (75.5 MHz, $CDCl_3$): 12.8, 13.9, 20.5, 39.0, 43.0, 56.0, 107.7, 125.4, 126.6, 127.4, 127.8, 130.1, 131.7, 135.1, 135.3, 153.7, 167.3.

4.1.13. Synthesis of thioindoxyl. To a stirred solution of THF (10 ml) and *n*-BuLi (1.37 mL, 1.5 equiv.) at −78°C, diisopropylamine (0.8 mL, 2.5 equiv.), was added through needle syringe system. The mixture was allowed to reach −30°C and kept at that temperature for 1 h. Then it was cooled again to −78°C and compound **2a** (R^1=R^2=R^3=R^4=H) (510 mg, 2.3 mmol) in THF (5 mL) was added dropwise and stirring was continued for 30 min at that temperature. The reaction mixture was then allowed to attain ambient temperature and kept at that temperature for 10 h. Usual ammonium chloride work up afforded 2,3-dihydrobenzo[*b*]thiophene-3-one (**3a**, R^1=R^2=R^3=R^4=H) which was purified by column chromatography [eluant: ethyl acetate–light petroleum (1:9)]; colourless needles, crystalised from EtOH (230 mg, 67%); mp 62–64°C; (Found C, 64.10; H, 4.30. C_8H_6OS requires C, 64.00; H, 4.00%); ν_{max} ($CHCl_3$): 1689 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.70 (2H, s, $-SCH_2-$); 7.14 (1H, ddd, J=7.5, 7.0, 1.2 Hz, Ar-6H), 7.35 (1H, dd, J=7.5, 1.2 Hz, Ar-7H), 7.47 (1H, ddd, J=7.7, 7.0, 1.2 Hz, Ar-5H), 7.70 (1H, dd, J=7.7, 1.2 Hz, Ar-4H); δ_C (75.5 MHz, $CDCl_3$) 39.6, 124.9, 125.1, 127.0, 131.3, 136.0, 154.6, 200.4.

4.1.14. 2,3-Dihydro-4-methylsulfanylbenzo[*b*]thiophene-3-one (3b, R^1=SMe, R^2=R^3=R^4=H). Colourless solid, crystalised from EtOH (66%); mp 121–123°C; (Found C, 55.32; H, 4.21. $C_9H_8OS_2$ requires C, 55.10; H, 4.08%); ν_{max} ($CHCl_3$): 1689 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.39 (3H, s, –SMe), 3.72 (2H, s, $-SCH_2-$), 6.84 (1H, dd, J=7.8, 1.5 Hz, Ar-5H), 7.03 (1H, dd, J=7.7, 1.5 Hz, Ar-7H), 7.34 (1H, dd, J=7.8, 7.7 Hz, Ar-6H); δ_C (75.5 MHz, $CDCl_3$) 14.1, 39.2, 119.3, 119.8, 126.7, 135.2, 145.1, 156.5, 199.8.

4.1.15. 2,3-Dihydro-4-methoxybenzo[*b*]thiophene-3-one (3c, R^1=OMe, R^2=R^3=R^4=H). Light yellow solid crystalised from EtOH (65%); (Found C, 60.22; H, 4.49. $C_9H_8O_2S$ requires C, 60.00; H, 4.44%); mp 101–104°C; ν_{max} ($CHCl_3$): 1683 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.76 (2H, s, $-SCH_2-$), 3.95 (3H, s, –OMe), 6.63 (1H, d, J=8.0 Hz, Ar-5H), 6.96 (1H, d, J=7.9 Hz, Ar-7H), 7.45 (1H, dd, J=8.0, 7.9 Hz, Ar-6H); δ_C (75.5 MHz, $CDCl_3$) 40.6, 57.2, 107.9, 120.3, 120.7, 138.3, 158.2, 161.7, 199.2.

4.1.16. 2,3-Dihydro-4-trimethylsilyl-5-methoxybenzo-[*b*]thiophene-3-one (3d, R^1=TMS, R^2=OMe, R^3=R^4=H). Obtained as mixture with an extremely poor yield of the thioindoxyl accompanied mostly by unreacted starting material and some intractable decomposition product, ν_{max} (NEAT): 1693 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.12 {s, 9H, $-Si(CH_3)_3$}, 3.54 (s, 3H, $-SH_2$), 3.55 (s, 3H, OMe), 7.13 (d, 1H, J=8.5 Hz, Ar-6H), 7.20 (d, 1H, J=8.5 Hz, Ar-5H).

4.1.17. 2,3-Dihydro-5-methoxysulfanylbenzo[*b*]thiophene-3-one (3e, R^1=H, R^2=OMe, R^3=R^4=H). Greenish solid, crystalised from EtOH (69%); (Found C, 60.18; H, 4.49. $C_9H_8O_2S$ requires C, 60.00; H, 4.44%); mp 94–95°C; ν_{max} (KBr): 1689 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.82 (3H, s, –OMe), 3.83 (2H, s, $-SCH_2-$), 7.16 (1H, d, J=2.7 Hz, Ar-4H), 7.21 (1H, dd, J=8.5, 2.7 Hz, Ar-6H), 7.30 (1H, d, J=8.5 Hz, Ar-7H); δ_C (75.5 MHz, $CDCl_3$) 40.5, 55.8, 108.3, 125.5, 125.9, 129.9, 146.6, 158.1, 200.3.

4.1.18. 2,3-Dihydro-6-methoxybenzo[*b*]thiophene-3-one (3f, R^1=R^2=H, R^3=OMe, R^4=H). Yellowish solid, crystalised from EtOH (78%); mp 112–113°C; (Found C, 60.21; H, 4.57. $C_9H_8O_2S$ requires C, 60.00; H, 4.44%); ν_{max} ($CHCl_3$): 1681 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.81 (2H, s, $-SCH_2-$), 3.88 (3H, s, –OMe), 6.75 (1H, dd, J=8.5, 2.2 Hz, Ar-5H), 6.85 (1H, d, J=2.2 Hz, Ar-7H), 7.70 (1H, d, J=8.5 Hz, Ar-4H); δ_C (75.5 MHz, $CDCl_3$) 40.0, 56.2, 107.8, 113.7, 124.7, 128.4, 157.6, 166.3, 198.4.

4.1.19. 2,3-Dihydro-7-methoxybenzo[*b*]thiophene-3-one (3g, R^1=R^2=R^3=H, R^4=OMe). Yellowish solid, crystalised from EtOH (69%); (Found C, 60.14; H, 4.79. $C_9H_8O_2S$ requires C, 60.00; H, 4.44%); mp 99–101°C; ν_{max} ($CHCl_3$): 1716 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.78 (2H, s, $-SCH_2-$), 3.94 (3H, s, –OMe), 7.01 (1H, dd, J=7.8, 1.0 Hz, Ar-6H), 7.19 (1H, dd, J=7.8, 7.7 Hz, Ar-5H), 7.40 (1H, dd, J=7.7, 1.0 Hz, Ar-4H); δ_C (75.5 MHz, $CDCl_3$) 39.8, 56.3, 115.5, 118.6, 126.7, 132.8, 143.8, 155.5, 200.7.

4.1.20. 2,3-Dihydro-4-chlorobenzo[*b*]thiophene-3-one (3h, R^1=Cl, R^2=R^3=R^4=H). Colourless solid, crystalised from EtOH (68%); mp 109–110°C; (Found C, 52.17; H, 2.99. C_8H_5OSCl requires C, 52.03; H, 2.71%); ν_{max} (KBr): 1687 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.83 (2H, s, $-SCH_2-$), 7.09 (1H, dd, J=7.0, 1.0 Hz, Ar-5H), 7.24 (1H, dd, J=7.5, 1.0 Hz, Ar-7H), 7.35 (1H, dd, J=7.5, 7.0 Hz, Ar-6H); δ_C (75.5 MHz, $CDCl_3$) 40.1, 123.5, 127.2, 135.8, 136.9, 157.4, 197.4.

4.1.21. 2,3-Dihydro-6-methylbenzo[*b*]thiophene-3-one (3i, R^1=R^2=H, R^3=Me, R^4=H). Pale yellow fluffy solid, crystalised from EtOH (77%); (Found C, 65.93; H, 4.86. C_9H_8OS requires C, 65.85; H, 4.87%); mp 80–81°C; ν_{max} (KBr): 1708 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.33 (3H, s, $-CH_3$), 3.69 (2H, s, $-SCH_2-$), 6.93 (1H, dd, J=7.9, 1.9 Hz, Ar-5H), 7.14 (1H, d, J=1.9 Hz, Ar-7H), 7.58 (1H, d,

J=7.9 Hz, Ar-4H); δ_C (75.5 MHz, $CDCl_3$) 22.4, 39.7, 125.0, 126.6, 126.7, 129.1, 147.6, 155.0, 199.9.

4.1.22. 2,3-Dihydro-4, 5-dimethoxybenzo[*b*]thiophene-3-one (3j, R¹=R²=OMe, R³=R⁴=H). White solid, crystalised from EtOH (89%); (Found C, 57.26; H, 4.99. $C_{10}H_{10}O_3S$ requires C, 57.14; H, 4.76%); mp 63–64°C; ν_{max} ($CHCl_3$): 1693 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.73 (2H, s, $-SCH_2-$), 3.79 (3H, s, –OMe), 3.89 (3H, s, –OMe), 6.97 (1H, d, J=8.5 Hz, Ar-6H), 7.10 (1H, d, J=8.5 Hz, Ar-7H); δ_C (75.5 MHz, $CDCl_3$) 39.1, 56.2, 60.7, 117.9, 118.1, 120.9, 122.9, 144.8, 148.8, 196.9.

4.1.23. 2,3-Dihydro-4, 6-dimethoxybenzo[*b*]thiophene-3-one (3k, R¹=OMe, R²=H, R³=OMe, R⁴=H). Colourless needles, crystalised from EtOH (81%); (Found C, 57.16; H, 4.89. $C_{10}H_{10}O_3S$ requires C, 57.14; H, 4.76%); mp 97–98°C; ν_{max} (NEAT): 1680 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.68 (2H, s, $-SCH_2-$), 3.79 (3H, s, –OMe), 3.83 (3H, s, OMe), 6.07 (1H, d, J=1.8 Hz, Ar-6H), 6.37 (1H, d, J=1.8 Hz, Ar-5H); δ_C (75.5 MHz, $CDCl_3$) 40.1, 56.2, 56.3, 96.0, 100.2, 113.9, 160.0, 161.8, 167.7, 196.4,

4.1.24. 2,3-Dihydro-4-methoxynaphtho[1,2-*b*]thiophene-3-one (3l). Yellowish solid, crystalised from EtOH (73%); mp 103–105°C; (Found C, 67.86; H, 4.59. $C_{13}H_{10}O_2S$ requires C, 67.82; H, 4.34%); ν_{max} ($CHCl_3$): 1681 (C=O) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.87 (2H, s, $-SCH_2-$), 3.99 (3H, s, –OMe), 6.81 (1H, s, Ar-5H), 7.39 (1H, ddd, J=8.2, 7.0, 1.0 Hz, Ar-7H), 7.59 (1H, ddd, J=8.2, 7.0, 1.2 Hz, Ar-8H), 7.70 (1H, dd, J=8.2, 1.2 Hz, Ar-6H), 7.86 (1H, dd, J=8.2, 1.0 Hz, Ar-9H); δ_C (75.5 MHz, $CDCl_3$) 40.2, 56.0, 103.1, 119.9, 124.7, 124.9, 127.7, 131.1, 138.0, 150.0, 156.4, 161.3, 198.3.

4.2. General procedure for the synthesis of benzo[*b*]thiophene

To a solution of compound **3a** (R¹=R²=R³=R⁴=H) in MeOH and 10% NaOH (6:1), $NaBH_4$ (2 equiv.) in MeOH and 10% NaOH solution (10:3) was added. This mixture was heated to reflux for 1 h on steam bath and then allowed to stand just under boiling condition for 12 h. After removal of MeOH, the reaction mixture was acidified with 10% sulfuric acid and extracted with ether. The organic layer was washed with water and dried. Removal of solvent afforded compound **4a** (R¹=R²=R³=R⁴=H) which was purified by column chromatography [eluant: ethyl acetate–light petroleum (1:9)]; colourless solid (67%), mp 32–33°C (lit[4b,d] mp 31–31.5°C). All the compounds reported below were synthesized in the same way.

4.2.1. 4-Methylsulfanylbenzo[*b*]thiophene (4b, R¹=SMe, R²=R³=R⁴=H). Purified by column chromatography [eluant: ethyl acetate–light petroleum (1:9)]; Light yellow gummy liquid (45%); (Found C, 59.98; H, 4.44. $C_{10}H_{10}O_3S$ requires C, 60.00; H, 4.47%); δ_H (300 MHz, $CDCl_3$) 2.57 (3H, s, –SMe), 7.23 (1H, dd, J=8.0, 7.4 Hz, Ar-6H), 7.44–7.53 (3H, m, Ar-2, 3, 5H), 7.80 (1H, d, J=8.0 Hz, Ar-7H); δ_C (75.5 MHz, $CDCl_3$) 16.5, 122.9, 123.1, 125.0, 127.5, 127.6, 131.5, 140.2, 140.7.

4.2.2. 4-Methoxybenzo[*b*]thiophene (4c, R¹=OMe, R²=R³=R⁴=H). Purified by column chromatography [eluant: ethyl acetate–light petroleum (1:9)]; colourless oil (82%), bp 80°C/0.05 mm (lit[18] bp 141°C/17 mm).

4.2.3. 5-Methoxybenzo[*b*]thiophene (4d, R¹=H, R²=OMe, R³=R⁴=H). Purified by column chromatography [eluant: ethyl acetate–light petroleum (1:9)]; colourless solid (77%); mp 44–45°C (lit[17] mp 43–44°C).

4.2.4. 6-Methoxybenzo[*b*]thiophene (4e, R¹=R²=H, R³=OMe, R⁴=H). Purified by column chromatography [eluant: ethyl acetate–light petroleum (1:9)]; colourless oil (73%); bp 82–83°C/0.1 mm (lit[4b,d] bp 80°C/0.1 mm).

4.2.5. 7-Methoxybenzo[*b*]thiophene (4f, R¹=R²=R³=H, R⁴=OMe). Purified by column chromatography [eluant: ethyl acetate–light petroleum (1:9)]; colourless oil (71%); bp 87°C/0.1 mm (lit[19] bp 80–90°C/0.1 mm).

4.2.6. 6-Methylbenzo[*b*]thiophene (4g, R¹=R²=H, R³=Me, R⁴=H). Purified by column chromatography [eluant: ethyl acetate–light petroleum (1:4)]; Low melting white solid (92%); (Found C, 72.98; H, 5.50. C_9H_8S requires C, 72.97; H, 5.40%); δ_H (300 MHz, $CDCl_3$) 7.66 (1H, dd, J=8.2, 3.0 Hz, Ar-3H), 7.62 (1H, d, J=3.0 Hz, Ar-6H), 7.29 (1H, d, J=5.4 Hz, Ar-5H), 7.23 (1H, d, J=5.4 Hz, Ar-2H), 7.14 (1H, d, J=8.2 Hz, Ar-4H), 2.43 (3H, s, $-CH_3$); δ_C (75.5 MHz, $CDCl_3$) 21.9, 122.6, 123.5, 123.9, 125.5, 126.6, 134.5, 137.7, 140.4.

4.2.7. 4,5-Dimethoxybenzo[*b*]thiophene (4h, R¹=R²=OMe, R³=R⁴=H). Purified by column chromatography [eluant: ethyl acetate–light petroleum (1:9)]; Yellowish oil (73%); (Found C, 61.76; H, 5.11. $C_{10}H_{10}O_2S$ requires C, 61.85; H, 5.15%); bp 91–95°C/0.1 mm; δ_H (300 MHz, $CDCl_3$) 3.93 (3H, s, –OMe), 3.99 (3H, s, –OMe), 7.07 (1H, d, J=8.7 Hz, Ar-6H), 7.37 (1H, d, J=5.5 Hz, Ar-2H), 7.42 (1H, d, J=5.5 Hz, Ar-3H), 7.53 (1H, d, J=8.7 Hz, Ar-7H); δ_C (75.5 MHz, $CDCl_3$) 57.6, 61.6, 113.2, 118.1, 120.7, 127.3, 134.2, 135.6, 144.2, 148.9.

4.2.8. 4,6-Dimethoxybenzo[*b*]thiophene (4i, R¹=OMe, R²=H, R³=OMe, R⁴=H). Purified by column chromatography [eluant: ethyl acetate–light petroleum (1:9)]; colourless crystals (85%); (Found C, 61.98; H, 4.35. $C_{10}H_{10}O_2S$ requires C, 61.85; H, 5.15%); mp 75–76°C; δ_H (300 MHz, $CDCl_3$) 3.75 (3H, s, –OMe), 3.81 (3H, s, –OMe), 6.31 (1H, d, J=1.7 Hz, Ar-5H), 6.83 (1H, d, J=1.7 Hz, Ar-7H), 7.05 (1H, d, J=5.5 Hz, Ar-2H), 7.28 (1H, d, J=5.5 Hz, Ar-3H); δ_C (75.5 MHz, $CDCl_3$) 55.8, 56.0, 96.2, 96.6, 120.6, 122.2, 125.4, 142.5, 155.7, 159.2.

4.2.9. 2,3-Dihydro-3-hydroxy-4-chlorobenzo[*b*]thiophene (6). Compound **6** was synthesized following the general procedure of preparation of benzo[*b*]thiophene as stated above. Purified by column chromatography [eluant: ethyl acetate–light petroleum (1:4)]; Reddish white solid (75%); mp 155–156°C; (Found C, 51.89; H, 3.80. C_8H_7ClOS requires C, 51.47; H, 3.75%); ν_{max} (KBr): 3226 (–OH) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.27 (1H, dd, J=12.5 Hz, 1.3, $-SCH_2-$), 3.59 (1H, dd, J=12.5, 6.03 Hz, $-SCH_2-$), 5.50 {1H, dd, J=6.03, 1.3 Hz, $-SCH_2-CH(OH)-$}, 6.97–7.15 (3H, m, Ar-5, 6, 7H); δ_C

(75.5 MHz, $CDCl_3$) 40.8, 76.1, 121.5, 125.4, 131.5, 138.7, 144.0, 146.0.

4.2.10. 3-Methoxy-4-chlorobenzo[*b*]thiophene (7). To a stirred solution of 2,3-dihydro-4-chlorobenzo[*b*]thiophene-3-one **3h** (R^1=Cl, R^2=R^3=R^4=H): equiv.) in 20% aqueous potassium hydroxide solution, kept at room temperature, dimethylsulphate (3 equiv.) was added through a pressure equalizing dropping funnel. After stirring for 45 min the reaction mixture was warmed to 60–70°C for 1 h then cooled and extracted with ether. The ether layer was washed with water, dried and solvent removed to afford compound **7** which was purified by column chromatography [eluant: ethyl acetate–light petroleum (1:4)]; colourless solid (88%); mp 146–147°C; (Found C, 54.39; H, 3.79. C_9H_7ClOS requires C, 54.40; H, 3.52%); δ_H (300 MHz, $CDCl_3$) 3.97 (3H, s, –OMe), 7.17 (1H, s, Ar-2H), 7.19 (1H, dd, *J*=8.0, 7.8 Hz, Ar-6H), 7.33 (1H, d, *J*=7.8 Hz, Ar-5H), 7.56 (1H, d, *J*=8.0 Hz, Ar-7H); δ_C (75.5 MHz, $CDCl_3$) 65.3, 77.6, 123.5, 126.9, 128.0, 131.4, 131.4, 140.3, 149.6.

4.2.11. 4-Methoxynaphtho[*b*]thiophene (4j). Purified by column chromatography [eluant: ethyl acetate–light petroleum (1:9)]; colourless crystals (79%); mp 66–67°C; (Found C, 72.91; H, 4.65. $C_{13}H_{10}OS$ requires C, 72.89; H, 4.67%); δ_H (300 MHz, $CDCl_3$) 3.97 (3H, s, –OMe), 6.87 (1H, s, Ar-5H), 7.33 (2H, m, Ar-7, 8H), 7.37 (1H, d, *J*=5.3 Hz, Ar-2H), 7.54 (1H, d, *J*=5.3 Hz, Ar-3H), 7.73 (1H, dd, *J*=8.1, 1.5 Hz, Ar-6H), 7.96 (1H, dd, *J*=8.1, 1.5 Hz, Ar-9H); δ_C (75.5 MHz, $CDCl_3$) 55.7, 101.5, 122.2, 123.8, 124.5, 124.8, 125.3, 126.3, 127.9, 131.6, 132.9, 139.9, 153.9.

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