Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron
Tetrahedron 60 (2004) 5215–5224

Application of directed metalation in synthesis. Part 6: A novel anionic rearrangement under directed metalation conditions leading to heteroannulation☆

Tarun Kanti Pradhan, Chandrani Mukherjee, Sukanta Kamila and Asish De*

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

Received 8 January 2004; revised 24 March 2004; accepted 14 April 2004

Dedicated to Professor Victor Snieckus

Abstract—A short and efficient synthesis of condensed 1,4-oxathiin-2-ones from easily available phenols is described. The key step in this synthesis is a hitherto unreported anionic rearrangement under directed metalation conditions. The rearrangement occurs after side chain deprotonation of a methyl sulfanyl group by an *O*-carbamate directed metalating group and the reaction mixture is kept at room temperature for 8–12 h. Acid-mediated cyclisation of the rearranged product affords [1,4]oxathiin-2-one.
© 2004 Elsevier Ltd. All rights reserved.

1. Introduction

The variety of rearrangements undergone by aromatic or heteroaromatic molecules after *ortho*-deprotonation under standard directed metalation conditions[2] have contributed to the ubiquitous nature of applications of heteroatom directed *ortho*-metalation[2] (Directed Metalation; DoM). When DoM is carried out with *O*-carbamate as the directed metalating group (DMG), the *ortho*-deprotonated species, in the absence of electrophile quench, was found to be susceptible to three types of rearrangements. All of these rearrangements using *O*-carbamate as DMG were reported by Snieckus who was the first to show the possibilities of anionic rearrangements under directed metalation conditions and also demonstrated their usefulness in organic synthesis. The first of these rearrangements is an anionic version of the *ortho*-Fries rearrangement[3,4] involving 1,3-carbamoyl transfer and christened as 'Snieckus rearrangement' by Gawley.[5] This rearrangement takes place after DMG mediated deprotonation at −78 °C, if the deprotonated species is allowed to reach room temperature instead of being quenched with an electrophile.

The second type of anionic rearrangement[6] termed as 'remote anionic *ortho*-Fries rearrangement' involving ring to ring carbamoyl transfer, provides regioselective entry into sterically encumbered biaryls as well as substituted and condensed dibenzo[*b,d*]pyranones and fluorenones.

The third type of anionic rearrangement[7] called 'anionic homologous *ortho*-Fries rearrangement' involves side chain deprotonation of *ortho*-alkyl substituents by an *O*-carbamate DMG followed by intramolecular anionic rearrangement. Subsequent acid mediated cyclisation of the rearranged product results in heteroannulation leading to benzofuranones. All these three types of anionic rearrangements are summarised in Scheme 1.

A fourth variety of anionic rearrangement under directed metalation condition, recently reported by us[1] involves the side chain deprotonation of *ortho*-methylsulfanyl substituents by an *O*-carbamate DMG followed by rearrangement. In common with the rearrangements described above, this rearrangement also provides access to interesting target molecules. Thus acid mediated cyclisation of the rearranged products affords condensed 1,4-oxathiin-2-ones in excellent yields, thereby providing an easy access to this heterocyclic system since the substrate for rearrangement can be obtained from phenols via successive *O*-carbamoylation and directed metalation.

Since publication of our preliminary findings, we have examined the scope of this rearrangement:

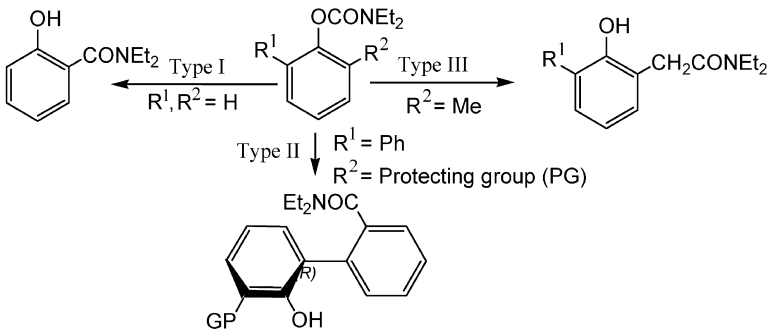
(a) by utilising new phenolic compounds as starting materials in the synthesis of condensed 1,4-oxathiin-2-ones in order to establish the generality of this synthesis

☆ For Part 5 see Ref. 1.

Keywords: Directed metalation; Anionic rearrangement; [1; 4]Oxathiin-2-one.

* Corresponding author. Tel.: +91-33-473-4971x246/253; fax: +91-33-473-2805; e-mail address: ocad@mahendra.iacs.res.in

0040–4020/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2004.04.033



Scheme 1. Reagents and conditions: *s*-BuLi/THF/TMEDA/−78 °C to rt.

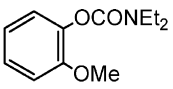
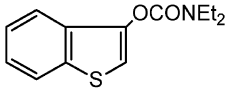
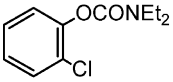
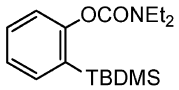
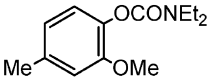
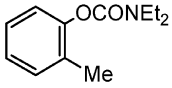
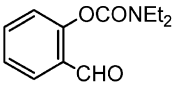
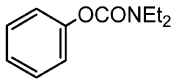
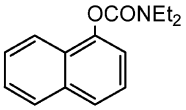
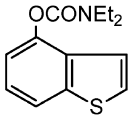
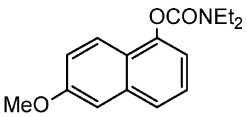
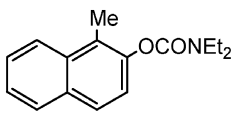
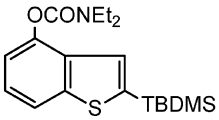
(b) by examining the selectivity of this rearrangement viz a viz other types of rearrangements reported by Snieckus through examining substrates where other types of rearrangement could also take place.

The results which we have obtained so far are presented herein.

2. Results and discussion

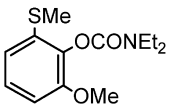
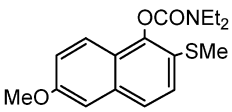
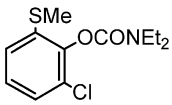
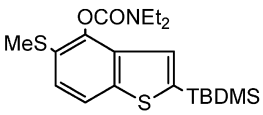
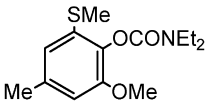
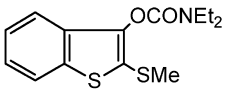
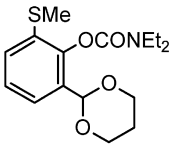
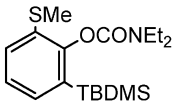
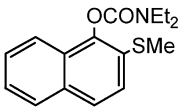
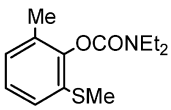
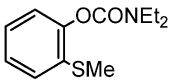
For heteroannulation we have chosen benzene, naphthalene and benzo[*b*]thiophene as basic aromatic cores. The corresponding starting materials were phenols (parent compound as well as substituted phenols), α- and β-naphthol (with and without substituents) and hydroxybenzo[*b*]thiophenes. *O*-Carbamates were prepared in good yields by treating the corresponding hydroxy compounds with *N*,*N*-diethylcarbamoyl chloride in tetrahydrofuran (THF) in the presence of sodium hydride (Table 1). Compound **1h** was prepared from 2,3-dihydrobenzo[*b*]thiophene-3-one which was synthesised via an expedient route reported[8,9] earlier by us. *Ortho*-deprotonation of *O*-carbamates with 2.5 equiv. of *s*-BuLi in THF in the presence of tetramethylethylenediamine (TMEDA) followed by

Table 1. Aryl *O*-carbamate

Entry	Compound	Yield (%)	Reference	Entry	Compound	Yield (%)	Reference
1a		90	2e	**1h**		87	—
1b		94	2e	**1i**		86	—
1c		95	2e	**1j**		93	2e,3,7a
1d		85	—	**1k**		96	2e,3,14
1e		89	2e,13,14	**1l**		95	10
1f		96	15	**1m**		87	2e,7a
1g		73	10				

Note: introduction of TBDMS group in compounds **1g** and **1i** done from **11** and **1k**, respectively using *s*-BuLi/TMEDA/THF/TBDMSC1.

Table 2. *N*,*N*-Diethyl *ortho*-methylsulfanyl aryl carbamates

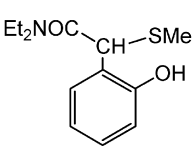
Entry	Compound	Yield (%)	Entry	Compound	Yield (%)
2a		81	**2f**		84
2b		92	**2g**		75
2c		96	**2h**		93
2d		80	**2i**		55
2e		82	**2j**[a]		92
			2k		92

[a] See Scheme 3.

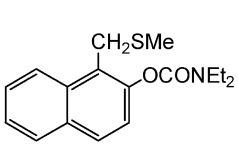
quenching with dimethyl disulfide afforded the corresponding *ortho*-methylsulfanyl derivatives in excellent yields (Table 2).

In the case of parent *N*,*N*-diethyl carbamoyloxy benzene (**1k**) it was necessary to protect one of the two free *ortho*-positions of the *O*-carbamate function as a *t*-butyl dimethyl silyl (TBDMS) derivative, by quenching the deprotonated species with TBDMSCl in order to prevent anionic *ortho*-Fries rearrangement which occurs in preference to the desired rearrangement (vide infra) when a substrate can undergo both. Similar silyl protection of the 2-position of *N*,*N*-diethyl-4-carbamyloxybenzo[*b*]thiophene (**1l**) was needed because it was preferentially deprotonated in the 2-position.[10] Not unexpectedly[2e] attempts to introduce a methylsulfanyl function in the 2-position of *N*,*N*-diethyl-2-methyl carbamoyloxy benzene (**1j**) and the 3-position of *N*,*N*-diethyl-1-methyl-2-carbamyloxy naphthalene (**1m**) by directed lithiation resulted in the formation of **9** and **10**, respectively. It is apparent that DMG induced lateral deprotonation in **9** was followed by electrophile quench and anionic homologus *ortho*-Fries rearrangement because of the use of 2 equiv. of *s*-BuLi and 1 equiv. of dimethyldisulfide.

8

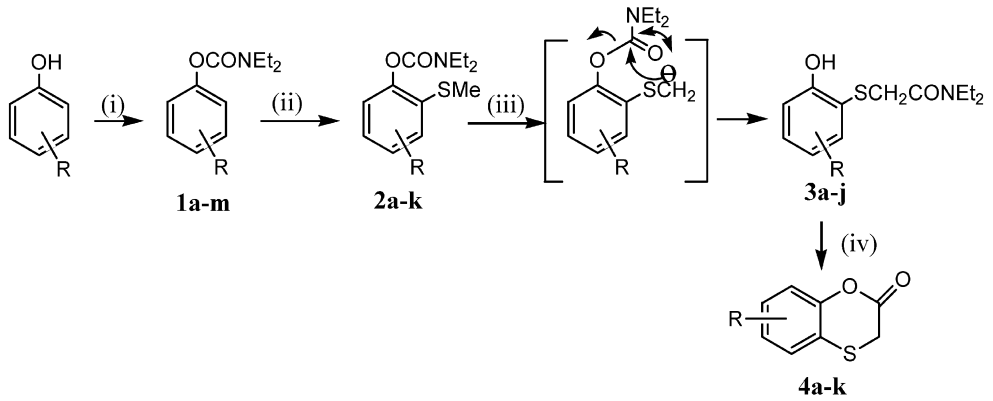


9



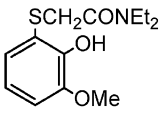
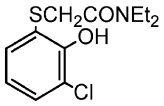
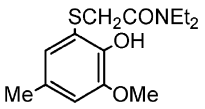
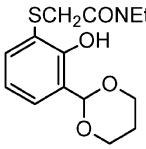
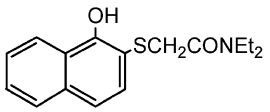
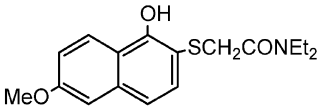
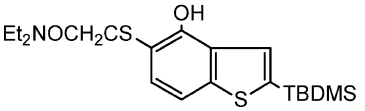
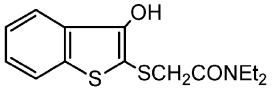
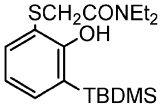
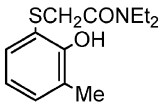
10

While side chain deprotonation of the methylsulfanyl group in the presence of an *ortho*-tertiary amide was earlier accomplished with LDA, all attempts to generate SCH_2^- anion in the presence of the *ortho*-*O*-carbamate DMG by LDA resulted in the recovery of starting materials. Use of *s*-BuLi at −78 °C instead of LDA was however successful in generating the anion. Allowing the reaction mixture to attain room temperature and maintaining that temperature for 8–12 h resulted in anionic rearrangement (Scheme 2) affording *N*,*N*-diethyl-2-hydroxy aryl thioacetamides in good to excellent yields (Table 3). We have reported[1] earlier that when **2k** was subjected to rearrangement conditions, the only product obtained was *N*,*N*-diethyl-2-hydroxy-3-methylsulfanyl benzamide (**8**) from a 'normal' anionic *ortho*-Fries rearrangement. It was conjectured[1] that the preferential ring deprotonation was due to the use of *s*-BuLi instead of LDA for generating the SCH_2^- anion (vide supra). It thus appears that 'normal' anionic *ortho*-Fries rearrangement occurs in preference to the desired rearrangement. After one of the two free *ortho*-positions was protected as a *t*-butyldimethylsilyl (TBDMS) derivative (**2i**), deprotonation and rearrangement afforded *N*,*N*-diethyl-2-hydroxy-3-*t*-butyldimethylsilyl phenyl thioacetamide (**3i**) in 64% yield. The substrate *ortho*-carbamate **2j** needed for examining the selectivity between an anionic homologous *ortho*-Fries rearrangement versus the desired rearrangement in its simplest form could not be obtained in a straightforward way. Compound **2j** was ultimately synthesised from **2d** in several steps as shown in Scheme 3. Under rearrangement conditions (*s*-BuLi/TMEDA/THF/−78 °C to rt/8–10 h) compound **2j** afforded *N*,*N*-diethyl-2-hydroxy-3-methyl phenyl



Scheme 2. Reagents and conditions: (i) NaH/THF/ClCONEt$_2$; (ii) *s*-BuLi/TMEDA/THF/dimethyldisulfide/−78 °C; (iii) *s*-BuLi/TMEDA/THF/−78 °C to rt; (iv) aceticacid/reflux.

Table 3. *N*,*N*-Diethyl-2-hydroxy aryl thioacetamide

Entry	Compound	Yield (%)
3a		93
3b		75
3c		85
3d		72
3e		92
3f		90
3g		83
3h		78
3i		64
3j		63

thioacetamide (**3j**) as the exclusive reaction product indicating that carbamoyl transfer to the methylsulfanyl side chain took place in preference to the methyl substituent.

Heating the rearranged products with glacial acetic acid under reflux for 18–20 h resulted in the annulation of [1,4]-oxathiin ring (Scheme 2) to the existing aromatic core in excellent yields (Table 4). Compound **4k** was obtained after desilylation of **4i** with tetrabutylammonium fluoride in 89% yield.

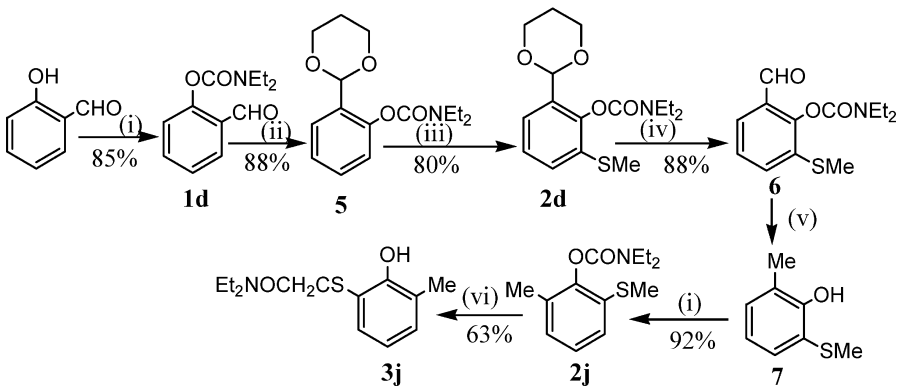
3. Conclusion

The high yielding anionic rearrangement reported above, characterised by its wide scope and selectivity with respect to anionic homologous *ortho*-Fries rearrangement is yet another example of the power of directed metalation as a synthetic tool. This is further corroborated by the key role which this rearrangement plays in the short and efficient synthesis of condensed [1,4]oxathiin-2-ones, which compares favourably with the earlier reported[11,12] synthesis of this class of compounds.

4. Experimental

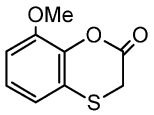
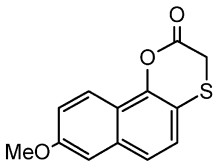
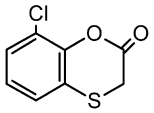
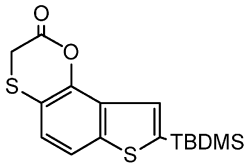
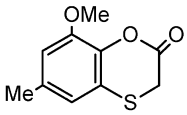
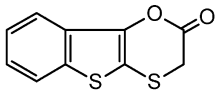
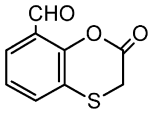
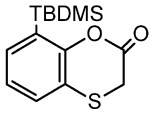
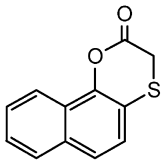
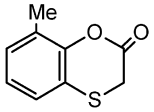
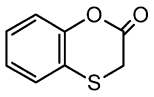
4.1. General

Melting points (uncorrected) were recorded in open capillaries on a hot stage apparatus. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on Bruker DPX-300 spectrometer. Chemical shifts (δ) are expressed in ppm using tetramethylsilane as internal standard. IR spectra were recorded on FTIR-8300, SHIMADZU spectrometer, for solids in KBr discs and for liquids by placing a thin layer of the sample between two KBr discs. Commercially available solvents were purified by distillation. Diethyl ether and tetrahydrofuran, after keeping overnight over potassium hydroxide were further purified by benzophenone ketyl method. Both *n*- and *s*-butyl lithium were prepared by slow addition of the appropriate halide to the freshly prepared dispersion of granular lithium or lithium chips in *n*-hexane (for *n*-butyl lithium) or cyclohexane (for *s*-butyl lithium). Petroleum ether has boiling point 60–80 °C.



Scheme 3. Reagents and conditions: (i) NaH/THF/$ClCONEt_2$; (ii) 1,3-propanediol/C_6H_6/$FeCl_3$; (iii) *s*-BuLi/THF/TMEDA/ dimethyldisulfide/−78 °C; (iv) 1:1 aq. MeOH/$FeCl_3$; (v) hydrazenehydrate/DIGOL/KOH; (vi) *s*-BuLi/TMEDA/THF/−78 °C to rt.

Table 4. Annulated oxathiin-2-one

Entry	Compound	Yield (%)	Entry	Compound	Yield (%)
4a		82	**4f**		84
4b		81	**4g**		90
4c		83	**4h**		91
4d		92	**4i**		81
4e		86	**4j**		89
			4k		89

For compounds **2c**, **3c** and **4c** see Ref. 1.

Silicagel (60–120 mesh) was used for column chromatography.

4.1.1. *N,N*-Diethyl-1-carbamoyloxybenzene-2-carboxaldehyde (1d). Prepared by dropwise addition of the solution of salicylaldehyde (4.88 g, 40 mmol) in THF (15 mL) to the stirred mixture of NaH (60%) (4 g, 100 mmol) in THF (30 mL). Stirring was continued for 1 h at room temperature and *N,N*-diethylcarbamoylchloride (7 mL, 50 mmol) in THF (10 mL) was added. The mixture was left under stirring for 10 h. After removal of most of the solvent, residue decomposed with water and extracted with diethyl ether. The ethereal layer was washed with water, dried over Na_2SO_4 and evaporated to afford the crude product. Purified by column chromatography [eluent: ethyl acetate–light petroleum (1:9)].

Colourless oil, yield 6.36 g, 72%. [Found: C, 65.26; H, 6.91; N, 6.38. $C_{12}H_{15}NO_3$ requires C, 65.14; H, 6.83; N, 6.33%]; ν_{max} (Neat) 1726.2, 1679 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 10.17 (1H, s, C*H*O), 7.84 (1H, d, *J*=7.5 Hz), 7.60–7.54 (1H, m, ArH), 7.32–7.24 (1H, m), 7.19 (1H, d, *J*=8.1 Hz), 3.56–3.34 (4H, m, CH_2CH_3), 1.36–1.17 (6H, m, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 188.5, 153.4, 153.0, 134.9, 129.4, 128.5, 125.5, 123.4, 42.3, 41.9, 14.1, 13.1.

4.1.2. *N*,*N*-Diethyl-3-carbamoyloxybenzo[*b*]thiophene (1h). Prepared from 2,3-dihydrobenzo[*b*]thiophene-3-one (1.5 g, 10 mmol) in THF (15 mL), NaH (60%) (0.8 g, 20 mmol) in THF (30 mL) and *N*,*N*-diethylcarbamoyl-chloride (2.7 mL, 20 mmol) following the same procedure. Purified by column chromatography [eluent: ethyl acetate–light petroleum (7.5: 92.5)], colourless oil, yield 2.16 g, 87%. [Found: C, 62.83; H, 6.26; N, 5.34. $C_{13}H_{15}NO_2S$ requires C, 62.62; H, 6.06; N, 5.62%]; ν_{max} (Neat) 1720 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.81–7.78 (1 H, m), 7.71–7.68 (1H, m), 7.41–7.34 (3H, m), 3.54–3.40 (4H, m, CH_2CH_3), 1.36–1.22 (6H, m, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 153.0, 141.2, 136.8, 132.5, 124.8, 124.0, 122.8, 120.2, 110.6, 42.4, 42.1, 14.2, 13.3.

4.1.3. *N*,*N*-Diethyl-2-*t*-butyldimethylsilyl carbamoyloxybenzene (1i). To a well stirred solution of TMEDA (0.33 mL, 2.2 mmol) in anhydrous THF (10 mL) kept under argon, *s*-BuLi (2 M, 1.1 mL, 2.2 mmol) was added through syringe at −78 °C. After 10 min **1k** (0.5 g, 2 mmol) in THF (5 mL) was added in the same way. After stirring for 20 min at that temperature TBDMSCl (0.36 g, 2.4 mmol) in THF (3 mL) was added. The reaction mixture was allowed to attain room temperature and stirred at that temperature for 10 h. After this period saturated ammonium chloride solution was added and the mixture was stirred for 5 min. After removal of most of the THF under reduced pressure, the residue was extracted with diethyl ether. The ethereal extract was washed with water and dried (Na_2SO_4). The residue left after removal of the solvent was purified by column chromatography [eluent: ethylacetate–petroleum (1:9)], colourless oil, yield 0.68 g, 86%. [Found: C, 66.53; H, 9.72; N, 4.42. $C_{17}H_{29}NO_2Si$ requires C, 66.40; H, 9.51; N, 4.55%]; ν_{max} (Neat) 1722 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.22–7.14 (2 H, m), 6.96–6.91 (1H, m), 6.78 (1H, d, *J*=7.2 Hz), 3.60–3.42 (2H, m, CH_2CH_3), 3.23–3.08 (2H, m, CH_2CH_3), 1.24–1.20 (3H, t, *J*=7.1 Hz, CH_2CH_3), 1.01–0.91 (12H, m, CH_2CH_3, $SiCCH_3$), 0.20 (6H, br s, $SiCH_3$); δ_C (75 MHz, $CDCl_3$) 168.9, 150.9, 129.6, 129.4, 127.7, 121.2, 119.1, 42.7, 39.0, 25.5, 17.9, 13.9, 13.0, −4.2, −4.6.

4.1.4. General procedure for the synthesis of *N*,*N*-diethyl-1-carbamoyloxy-2-methylsulfanyl arenes. *N*,*N*-Diethyl-1-carbamoyloxy-2-methylsulfanyl-6-methoxy benzene (2a). To a well-stirred solution of TMEDA (3.4 mL, 22 mmol) at −78 °C *s*-BuLi (14 mL of 1.6 M solution, 22 mmol) was added through needle syringe system. After 5 min **1a** (2 g, 9 mmol) in THF (15 mL) was added and kept at that temperature for 30 min. Then dimethyl disulfide (1.8 mL, 20 mmol) was added and the reaction mixture was allowed to reach room temperature followed by stirring at that temperature for 10 h. Ammonium chloride work up as described before afforded the compound **2a**. Purification by crystallisation (ethyl acetate–petroleum) afforded colourless solid, yield 1.9 g, 81%, mp 65–67 °C. [Found: C, 58.00; H, 7.20; N, 5.30. $C_{13}H_{19}O_3NS$ requires C, 57.99; H, 7.06; N, 5.20%]; ν_{max} (Neat) 1724 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.06 (1 H, dd, *J*=8.0, 8.1 Hz), 6.68 (2H, m), 3.74 (3H s, O*Me*), 3.37 (4H, q, *J*=7.0 Hz, CH_2CH_3), 2.34 (3H, s, S*Me*), 1.19 (6H, t, *J*=7.0 Hz, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 153.5, 152.6, 137.9, 133.9, 126.5 118.2, 109.6, 56.5, 42.5, 42.4, 15.4, 14.5, 13.8.

4.1.5. *N*,*N*-Diethyl-1-carbamoyloxy-2-chloro-6-methylsulfanyl benzene (2b). Prepared in the same way from *N*,*N*-Diethyl-1-carbamoyloxy-2-chlorobenzene (1.8 g, 8 mmol), using TMEDA (2.6 mL, 18 mmol), *s*-BuLi (9.2 mL of 1.9 M solution, 18 mmol), dimethyl disulfide (1.6 mL, 18 mmol). Purified by column chromatography [eluent: ethyl acetate–petroleum (3:17)] to afforded yellowish gummy material, yield 2 g, 92%. [Found: C, 52.33; H, 6.1; N, 5.3. $C_{12}H_{16}O_2ClNS$ requires C, 52.65; H, 5.85; N, 5.11%]; ν_{max} (Neat) 1732 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.18 (1H, dd, *J*=2.3, 7.3 Hz) 7.12–7.01 (2H, m), 3.52–3.40 (4H, q, *J*=7.1 Hz, CH_2CH_3), 2.39 (3H, s, S*Me*), 1.31 (3H, t, *J*=7.1 Hz, CH_2CH_3), 1.19 (3H, t, *J*=7.1 Hz, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 152.5, 144.8, 135.5, 128.8, 126.9, 126.7, 126.6, 42.9, 42.6, 15.4, 14.6, 13.7.

4.1.6. 2-(*N*,*N*-Diethyl-1-carbamoyloxy-2-methylsulfanyl-phenyl-6-)-1,3-dioxane (2d). Prepared from 2-(*N*,*N*-diethyl-1-carbamoyloxy phenyl-2-)-1,3-dioxane (**5**) (1.11 g, 4 mmol), THF (10 mL), *s*-BuLi [1.9 M (4 mL, 8 mmol)], TMEDA (1.2 mL, 8 mmol) and dimethyldisulfide (0.7 mL, 8 mmol) following the same procedure. Purified by column chromatography over alumina [eluent: ethyl acetate–petroleum (1:4)], crystallised from ether, yield 1.03 g, 80%, mp 97–99 °C. [Found: C, 59.16; H, 7.23; N, 4.48. $C_{16}H_{23}NO_4S$ requires C, 59.05; H, 7.12; N, 4.30%]; ν_{max} (KBr) 1724.2 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.47–7.44 (1H, m), 7.23–7.17 (2H, m), 5.53 (1H, s, OC*H*O), 4.19–3.86 (4H, m, OCH_2CH_2), 3.47 (2H, q, *J*=7.0 Hz, NCH_2), 3.37 (2H, q, *J*=7.0 Hz, NCH_2), 2.39 (3H, s, S*Me*), 2.39–2.12 (2H, m, $CH_2CH_2CH_2$), 1.30 (3H, t, *J*=7.0 Hz, CH_2CH_3), 1.19 (3H, t, *J*=7.0 Hz, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 152.8, 146.0, 132.7, 131.7, 127.2, 125.9, 123.8, 97.9, 67.3, 42.5, 41.9, 25.5, 15.3, 14.2, 13.3.

4.1.7. *N*,*N*-Diethyl-2-methylsulfanyl-1-carbamoyloxy naphthalene (2e). Prepared in the same way from **1e** (1.9 g, 8 mmol), *s*-BuLi [2.3 M (4 mL, 10 mmol)] in THF (10 mL), TMEDA (1.5 mL, 10 mmol) and dimethyl-disulfide (1 mL, 12 mmol). Purified by column chromatography [eluent: ethyl acetate–petroleum (1:8)], crystallised from petroleum, white solid, yield 1.8 g, 82%, mp 83–85 °C. [Found: C, 66.61; H, 6.79; N, 4.96. $C_{16}H_{19}NO_2S$ requires C, 66.40; H, 6.62; N, 4.84%]; ν_{max} (KBr) 1708.8 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.97–7.82 (2H, m), 7.70 (1H, d, *J*=7.9 Hz), 7.54–7.40 (3H, m), 3.62 (2H, q, *J*=7.1 Hz, CH_2CH_3), 3.49 (2H, q, *J*=7.1 Hz, CH_2CH_3), 2.52 (3H, s, S*Me*), 1.41 (3H, t, *J*=7.1 Hz, CH_2CH_3), 1.25 (3H, t, *J*=7.1 Hz, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 153.7, 144.7, 133.0, 128.5, 128.3, 128.2, 127.3, 126.4, 126.0, 125.1, 121.4, 42.9, 42.6, 16.1, 14.9, 13.8.

4.1.8. *N*,*N*-Diethyl-1-carbamoyloxy-2-methylsulfanyl-6-methoxynaphthalene (2f). Prepared in the same way

from **1f** (2 g, 7.3 mmol), TMEDA (2.73 mL, 18 mmol), *s*-BuLi (11.4 mL of 1.6 M solution, 18 mmol) and dimethyl disulfide (1.44 mL, 18 mmol). Purified by crystallisation (ethyl acetate–petroleum). White powder, yield 1.98 g, 84%, mp 64–65 °C. [Found: C, 64.00; H, 6.66; N, 4.27. $C_{17}H_{21}O_3NS$ requires C, 63.90; H, 6.58; N, 4.38%]; ν_{max} (Neat) 1718 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.6 (1H, d, *J*=9.1 Hz), 7.5 (1H, d, *J*=8.6 Hz), 7.35 (1H, d, *J*=8.6 Hz), 7.08 (1H, dd, *J*=2.4, 9.1 Hz), 7.02 (1H, d, *J*=2.4 Hz), 3.82 (3H, s, O*Me*), 3.56 (2H, q, *J*=7.1 Hz, CH_2CH_3), 3.38 (2H, q, *J*=7.1 Hz, CH_2CH_3), 2.4 (3H, s, S*Me*), 1.34 (6H, t, *J*=7.1 Hz, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 166.3, 158.0, 153.8, 145.6, 134.6, 126.8, 125.2 124.1, 123.2, 120.1, 106.2, 55.7, 42.8 42.6, 16.8, 14.8, 13.7.

4.1.9. *N*,*N*-Diethyl-2-*t*-butyldimethylsilyl-5-methylsulfunyl-4-carbamolyloxy benzo[*b*]thiophene (2g). Prepared in the same way from **1g** (0.363 g, 1 mmol), *s*-BuLi [2 M (1 mL, 2 mmol)] in THF (7 mL), TMEDA (0.3 mL, 2 mmol) and dimethyldisulfide (0.2 mL, 2 mmol). Purified by column chromatography [eluent: ethyl acetate–petroleum ether (7.5:82.5)], yield 0.30 g, 75%, mp 77–79 °C. [Found: C, 58.58; H, 7.60; N, 3.33. $C_{20}H_{31}NO_2S_2Si$ requires C, 58.63; H, 7.63; N, 3.42%]; ν_{max} (Neat) 1728.1 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.52 (1H, d, *J*=8.7 Hz), 7.20–7.15 (2H, m), 3.50–3.30 (4H, m, CH_2CH_3), 2.33 (3H, s, S*Me*), 1.28–1.10 (6H, m, CH_2CH_3), 0.83 (9H, s, CCH_3], 0.20 (6H, s, $SiCH_3$); δ_C (75 MHz, $CDCl_3$) 153.6, 144.7, 143.9, 141.5, 136.3, 127.9, 126.2, 126.0, 42.9, 42.7, 26.7, 17.5, 17.2, 17.1, 13.8, −4.6.

4.1.10. *N*,*N*-Diethyl-2-methylsulfanyl-3-carbamoyloxy-benzo[*b*]thiophene (2h). Prepared in the same way as before starting from **1h** (2.5 g, 10 mmol), *s*-BuLi [2 M (10 mL, 20 mmol), TMEDA (3 mL, 20 mmol) and dimethyldisulfide (2 mL, 22 mmol). Purified by column chromatography [eluent: ethyl acetate–petroleum (1:9)], to afford colorless oil, yield 2.7 g, 93%. [Found: C, 56.84; H, 5.68; N, 4.86. $C_{14}H_{17}NO_2S_2$ requires C, 56.92; H, 5.80; N, 4.74%]; ν_{max} (Neat) 1726 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.67 (1H, dd, *J*=2.0, 6.9 Hz), 7.53 (1H, dd, *J*=2.0, 6.9 Hz), 7.38–7.31 (2H, m), 3.52 (2H, q, *J*=7.0 Hz, NCH_2), 3.40 (2H, q, *J*=7.0 Hz, NCH_2), 2.50 (3H, s, S*Me*), 1.35 (3H, t, *J*=7.0 Hz, CH_2CH_3), 1.23 (3H, t, *J*=7.0 Hz, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 152.9, 142.6, 137.2, 133.2, 125.0, 124.9, 122.3, 120.3, 42.5, 42.2, 19.9, 14.2, 13.3.

4.1.11. *N*,*N*-Diethyl-2-methylsulfanyl-6-*t*-butyldimethylsilyl carbamoyloxy benzenes (2i). Prepared by the same procedure from **1i** (0.8 g, 2.6 mmol) *s*-BuLi [1.3 M (4 mL, 5 mmol)], in THF (10 mL), TMEDA (0.8 mL, 5 mmol) and dimethyldisulfide (0.5 mL, 5 mmol). Purified by column chromatography [eluent: ethyl acetate–petroleum (12.5:87.5)], colourless oil, yield 0.50 g, 55%. [Found: C, 61.36; H, 8.63; N, 3.81. $C_{18}H_{31}NO_2SSi$ requires C, 61.14; H, 8.84; N, 3.96%]; ν_{max} (Neat) 1726.2 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.03 (1H, dd, *J*=8.4, 7.8 Hz), 6.76 (1H, d, *J*=7.8 Hz), 6.53 (1H, d, *J*=8.4 Hz), 3.31–3.22 (2H, m, NCH_2), 3.10–3.01 (2H, m, NCH_2), 1.16 (3H, t, *J*=7.2 Hz, CH_2CH_3), 0.96 (3H, d, *J*=7.2 Hz, CH_2CH_3), 0.87 (9H, s, CCH_3), 0.17–0.15 (6H, d, $SiCH_3$); δ_C (75 MHz, $CDCl_3$) 166.5, 151.4, 136.6, 126.3, 125.5, 119.1, 115.8, 42.6, 38.9, 25.4, 14.8, 13.9, 13.0, 12.7, −4.1, −4.7.

4.1.12. *N*,*N*-Diethyl-2-methylsulfanyl-6-methyl carbamoyloxybenzene (2j). Compound **6** (0.267 g, 1 mmol) was heated at 160 °C with hydrazenehydrate (0.2 g, 4 mmol) in DIGOL (5 mL) for 30 min. Then KOH (0.392 g, 8 mmol) in DIGOL (3 mL) was added to the reaction mixture and heated at 170 °C for 1 h. The reaction mixture was allowed to attain room temperature and poured in to ice water, extracted with diethyl ether (3×30 mL), organic layer washed with water and dried over Na_2SO_4. Evaporation of the solvent left a gummy mass, which did not show any carbonyl peak in the IR, but showed a broad peak at 3390 cm^{-1} (OH) indicating the hydrolysis of *O*-carbamate function. The crude phenol was reconverted into *O*-carbamate in the same way which was purified by column chromatography [eluent: ethyl acetate–petroleum ether (1:9)]. Colourless liquid, overall yield 0.17 g, 68%. [Found: C, 61.72; H, 7.72; N, 5.59. $C_{13}H_{19}NO_2S$ requires C, 61.63; H, 7.56; N, 5.53%]; ν_{max} (Neat) 1722.3 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.12–6.99 (3H, m), 3.47 (2H, q, *J*=6.6 Hz, NCH_2), 3.36 (2H, q, *J*=6.6 Hz, NCH_2), 2.40 (3H, s, S*Me*), 2.19 (3H, s, $ArCH_3$), 1.30 (3H, t, *J*=6.6 Hz, CH_2CH_3), 1.19 (3H, t, *J*=6.6 Hz, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 152.8, 146.8, 132.1, 131.4, 127.3, 125.8, 123.7, 42.2, 41.9, 16.2, 14.9, 14.2, 13.3.

4.1.13. *N*,*N*-Diethyl-1-carbamoyloxy-2-methylsulfanyl-benzene (2k). Prepared in the same way starting from **1k** (1.2 g, 6.5 mmol), TMEDA (2.45 mL, 15 mmol), in dry THF (10 mL), *s*-BuLi (8.6 mL of 1.9 M, 15 mmol) and dimethyl disulfide (1.2 mL, 15 mmol). Purified by column chromatography [eluent: ethyl acetate–petroleum (3:17)]. Yellowish oil, yield 1.38 g, 92%. [Found: C, 62.9; H, 7.5; N, 6.3. $C_{12}H_{17}O_2NS$ requires C, 62.88; H, 7.42; N, 6.11%]; ν_{max} (Neat) 1722 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.18–7.03 (4H, m), 3.39–3.34 (4H, m, CH_2CH_3), 2.35 (3H, s, S*Me*), 1.18–1.15 (6H, m, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 153.9, 148.9, 132.2, 126.8, 126.4, 126.3, 123.2, 42.6, 42.5, 15.4, 14.6, 13.9.

4.1.14. General procedure for the synthesis of substituted *N*,*N*-diethyl-2-hydroxy aryl thioacetamides. *N*,*N*-Diethyl-2-hydroxy-3-methoxy phenyl thioacetamide (3a). To a well stirred solution of dry THF (10 mL), TMEDA (0.75 mL, 4 mmol), *s*-BuLi (2.6 mL of 1.6 M solution, 4 mmol), **2a** (0.45 g, 1.6 mmol) in dry THF (10 mL) was added at −78 °C and kept at that temperature for 30 min. Stirring at room temperature for 10 h and ammonium chloride work up as described before afforded compound **3a** which was purified by column chromatography [eluent: ethyl acetate–petroleum ether (1:8)], oily liquid, yield 0.42 g, 93%. [Found: C, 58.04; H, 7.20; N, 5.31. $C_{13}H_{19}O_3NS$ requires C, 57.90; H, 7.06; N, 5.20%]; ν_{max} (Neat) 3244, 1622 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.96 (1H, d, *J*=8.1 Hz), 6.78 (1H, dd, *J*=8.0, 8.1 Hz), 6.67 (1H, d, *J*=8.0 Hz), 3.75 (3H, s, O*Me*), 3.55 (2H, s, SCH_2), 3.36–3.13 (4H, m, CH_2CH_3), 1.16–1.00 (6H, m, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 168.3, 153.2, 124.8, 124.6, 122.6, 119.2, 111.6, 56.3, 42.9, 40.9, 35.8, 14.3, 12.9.

4.1.15. *N*,*N*-Diethyl-2-hydroxy-3-chloro phenyl thioacetamide (3b). Prepared following the same procedure from **2b** (0.26 g, 1 mmol), *s*-BuLi [2 M (1 mL, 2 mmol)] using THF (8 mL), TMEDA (0.3 mL, 2 mmol). An oily

mass, difficult to separate from the unreacted starting material was obtained. But its formation was confirmed from IR and ^{1}H NMR and was sufficiently pure for the next step; ν_{max} (Neat) 3226, 1623 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.41–7.31 (2H, m), 6.72 (1H, dd, J=7.7, 7.8 Hz), 3.63 (2H, s, SCH_2), 3.44 (4H, m, CH_2CH_3), 1.15 (6H, t, J=6.9 Hz, CH_2CH_3).

4.1.16. 2-(*N*,*N*-Diethyl-1-acetamido-2-hydroxyphenyl-3-)-1,3-dioxane (3d). Prepared by the same procedure from **2d** (0.33 g, 1 mmol), *s*-BuLi (2 M, 1 mL, 2 mmol) in THF (8 mL), TMEDA (0.3 mL, 2 mmol). Purified by column chromatography over alumina; [eluent: ethyl acetate–petroleum (1:3)], yield 0.23 g, 72%, Crystallised from ether, mp 76–77 °C. [Found: C, 59.04; H, 7.32; N, 4.42. $C_{16}H_{23}NO_4S$ requires 59.05; H, 7.12; N, 4.30%]; ν_{max} (KBr) 3072, 1622 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 9.82 (1H, s, O*H*), 7.54–7.45 (2H, m), 6.84–6.79 (1H, m), 5.90 (1H, s, OC*H*O), 4.26–4.20 (2H, m, OCH_2CH_2), 4.05–3.96 (2H, m, OCH_2CH_2), 3.60 (2H, s, SCH_2), 3.33 (2H, q, J=7.1 Hz, CH_2CH_3), 3.21 (2H, q, J=7.1 Hz, CH_2CH_3), 2.28–2.16 (1H, m, $CH_2CH_2CH_2$), 1.45–1.40 (1H, m, $CH_2CH_2CH_2$), 1.20–1.08 (6H, m, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 169.1, 156.1, 136.9, 129.1, 125.7, 119.7, 98.0, 67.4, 42.3, 41.3, 39.1, 25.7, 14.0, 12.7.

4.1.17. *N*,*N*-Diethyl-1-hydroy naphthyl-2-thioacetamide (3e). Prepared in the same way from **2e** (0.29 g, 1 mmol), *s*-BuLi (2 M, 1 mL, 2 mmol) in THF (8 mL), TMEDA (0.3 mL, 2 mmol). Purified by column chromatography [eluent: ethyl acetate–petroleum ether (1:7)], crystallised from ether–petroleum ether, yield 0.26 g, 92%, mp 88–90 °C. [Found: C, 66.32; H, 6.48; N, 4.89. $C_{16}H_{19}NO_2S$ requires C, 66.40; H, 6.62; N, 4.84%]; ν_{max} (KBr) 3049, 1624 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 10.63 (1H, s, O*H*), 8.36 (1H, m), 7.71 (1H, m), 7.51–7.43 (3H, m), 7.25 (1H, d, J=8.4 Hz), 3.63 (2H, s, SCH_2), 3.36 (2H, q, J=7.2 Hz, NCH_2), 3.18 (2H, q, J=7.2 Hz, NCH_2), 1.13–1.07 (6H, m, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 170.1, 157.3, 135.9, 133.4, 127.8, 126.6, 125.7, 125.6, 124.0, 119.7, 112.0, 42.8, 41.1, 40.5, 14.5, 13.2.

4.1.18. *N*,*N*-Diethyl-1-hydroxy-6-methoxy naphthyl-2-thioacetamide (3f). Prepared in the same way from **2f** (0.5 g, 1.6 mmol), TMEDA (0.58 mL, 4 mmol), THF (8 mL) and *s*-BuLi (2.4 mL of 1.6 M solution, 4 mmol). Purified by column chromatography [eluent: ethyl acetate–petroleum ether (3:17)], liquid oil, yield 0.45 g, 90%. [Found: C, 64.06; H, 6.66; N, 4.29. $C_{17}H_{21}O_3NS$ requires C, 63.90; H, 6.58; N, 4.38%]; ν_{max} (Neat) 3062, 1730 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.2 (1H, d, J=9.1 Hz), 7.38 (1H, d, J=8.6 Hz), 7.09 (1H, d, J=8.6 Hz), 7.03 (1H, dd, J=2.4, 9.1 Hz), 6.96 (1H, d, J=2.4 Hz), 3.83 (3H, s, O*Me*), 3.56 (2H, s, SCH_2), 3.50–3.15 (4H, m, CH_2CH_3), 1.27–1.03 (6H, m, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 159.3, 158.0, 137.5, 134.2, 133.0, 121.2, 118.6, 117.9, 105.9, 55.6, 42.8, 42.1, 40.6, 14.6, 13.2.

4.1.19. *N*,*N*-Diethyl-5-(2-*t*-butyldimethylsilyl-4-hydroxy-benzo[*b*]thienyl) thioacetamide (3g). Prepared in the same way from **2g** (0.4 g, 1 mmol), *s*-BuLi [2 M (1 mL, 2 mmol)], THF (10 mL) using TMEDA (0.3 mL, 2 mmol). Purified by column chromatography [eluent: ethyl acetate–petroleum (1:8)], yield 0.33 g, 83%, mp 35–39 °C. [Found: C, 58.78; H, 7.75; N, 3.38. $C_{20}H_{31}NO_2S_2Si$ requires C, 58.63; H, 7.63; N, 3.42%]; ν_{max} (Neat) 3307, 1641.3 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.72 (1H, s), 7.38 (1H, d, J=8.6 Hz), 7.31 (1H, d, J=8.6 Hz), 3.61 (2H, s, SCH_2), 3.04 (2H, q, J=7.2 Hz, NCH_2), 3.23 (2H, q, J=7.2 Hz, NCH_2), 1.69–1.15 (6H, m, CH_2CH_3), 0.95 (9H, s, CCH_3), 0.33 (6H, s, $SiCH_3$); δ_C (75 MHz, $CDCl_3$) 170.2, 155.8, 147.9, 138.5, 133.0, 132.3, 130.2, 113.8, 112.3, 42.8, 42.1, 40.8, 26.8, 17.3, 14.5, 13.2, −4.5.

4.1.20. *N*,*N*-Diethyl-2-(3-hydroxybenzo[*b*]thienyl)thioacetamide (3h). Prepared in the same way from **2h** (0.3 g, 1 mmol), *s*-BuLi [2 M (1 mL, 2 mmol)], THF (10 mL) using TMEDA (0.3 mL, 2 mmol). Purified by column chromatography [eluent: ethyl acetate–petroleum (3:17)], gummy liquid, yield 0.23 g, 78%. [Found: C, 56.89; H, 5.58; N, 4.48. $C_{14}H_{17}NO_2S_2$ requires C, 56.92; H, 5.80; N, 4.74%]; ν_{max} (Neat) 3130, 1605 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 10.74 (1H, s, O*H*), 7.76–7.72 (1H, m), 7.55–7.52 (1H, m), 7.25–7.22 (2H, m), 3.49 (2H, s, SCH_2), 3.28 (2H, q, J=7.2 Hz, NCH_2), 3.12 (2H, q, J=7.2 Hz, NCH_2), 1.05–0.97 (6H, m, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 169.5, 154.7, 138.4, 135.5, 132.1, 124.6, 123.7, 122.1, 121.9, 42.1, 41.8, 40.6, 13.9, 12.7.

4.1.21. *N*,*N*-Diethyl-2-hydroxy-3-*t*-butyldimethylsilyl-phenyl thioacetamide (3i). Prepared in the same way from **2i** (0.35 g, 1 mmol), *s*-BuLi [2 M (1 mL, 2 mmol) in THF (8 mL), TMEDA (0.3 mL, 2 mmol). Purified by column chromatography [eluent: ethyl acetate–petroleum (1:5)], mp 30–33 °C, yield 0.22 g, 64%. [Found: C, 61.34; H, 8.92; N, 3.88. $C_{18}H_{31}NO_2SSi$ requires C, 61.14; H, 8.84; N, 3.96%]; ν_{max} (Neat) 3325, 1595 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.38 (2 H, m), 7.28 (1H, d, J=8.0 Hz), 3.61 (2H, s, SCH_2), 3.38 (2H, q, J=7.1 Hz, NCH_2), 3.21 (2H, q, J=7.1 Hz, NCH_2), 1.15–1.09 (6H, m, CH_2CH_3), 0.95 (9H, s, CCH_3), 0.33 (6H, s, Si*Me*); δ_C (75 MHz, $CDCl_3$) 170.2, 155.8, 147.9, 133.0, 132.3, 130.3, 113.8, 112.3, 42.8, 42.1, 40.0, 26.8, 17.3, 14.5, 13.2, −4.59.

4.1.22. *N*,*N*-Diethyl-2-hydroxy-3-methylphenylthioacetamide (3j). Prepared in the same way from **2j** (0.25 g, 1 mmol), *s*-BuLi [2 M (0.5 mL, 1 mmol) in THF (8 mL), TMEDA (0.15 mL, 1 mmol). Purified by column chromatography [eluent: ethyl acetate–petroleum (1:5)], mp 30–35 °C, yield 0.16 g, 63%. [Found: C, 61.81; H, 7.38; N, 5.73. $C_{13}H_{19}NO_2S$ requires C, 61.63; H, 7.56; N, 5.53%; ν_{max} (Neat) 3168, 1620 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 10.19 (1H, s, O*H*), 7.18–7.04 (1H, m), 6.84 (1H, d, J=7.4 Hz), 6.77–6.72 (1H, m), 3.63 (2H, s, SCH_2), 3.43–3.29 (4H, m, NCH_2), 2.34 (3H, s, $ArCH_3$), 1.26–1.03 (6H, m, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 173.6, 159.3, 133.3, 132.4, 123.7, 121.6, 121.3, 54.3, 45.9, 44.3, 17.5, 17.1, 15.2.

4.1.23. General procedure of synthesis of oxathiin-2-ones. 8-Methoxy benz[1,4]oxathiin-2-one (4a). The hydroxy compound **3a** (0.25 g, 9.3 mmol) was heated with 7 mL of glacial acetic acid for 18 h under magnetic stirring condition. Cooling, the reaction mixture was extracted with dichloromethane (2×20 mL). The organic layer was washed with water, dried (Na_2SO_4). Removal of solvent afforded the

crude 8-Methoxy benz[1,4]oxathiin-2-one, which was purified by crystallisation (ethyl acetate–petroleum) to afford colourless crystal, yield 0.15 g, 82%, mp 68–71 °C. [Found: C, 55.03; H, 4.06. $C_9H_8O_3S$ requires C, 55.10; H, 4.08%]; ν_{max} (KBr) 1760 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.99 (1H, dd, *J*=7.9, 8.0 Hz), 6.84 (1H, dd, *J*=1.1, 7.9 Hz), 6.78 (1H, dd, *J*=1.1, 8.0 Hz), 3.83 (3H, s, O*Me*), 3.39 (2H, s, SCH_2); δ_C (75 MHz, $CDCl_3$) 162.9, 149.2, 140.6, 124.9, 121.3, 119.8, 111.0, 56.5, 29.0.

4.1.24. 8-Chloro benz[1,4]oxathiin-2-one (4b). The crude product **3b** (0.5 g, 1.8 mmol) was heated with 10 mL glacial acetic acid for 20 h. Purified by crystallisation [ethyl acetate–petroleum ether]. White powder, yield 0.24 g, 81%, mp 94–96 °C. [Found: C, 47.63; H, 2.22. $C_8H_5O_2ClS$ requires C, 47.80; H, 2.50%]; ν_{max} (KBr) 1772 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.34 (1H, dd, *J*=1.1, 8.0 Hz), 7.25 (1H, dd, *J*=1.1, 7.8 Hz), 7.04 (1H, dd, *J*=8.0, 7.8 Hz), 3.49 (2H, s, SCH_2); δ_C (75 MHz, $CDCl_3$) 162.1, 146.9, 129.3, 126.8, 125.2, 124.2, 122.2, 30.1.

4.1.25. 8-Formyl benz[1,4]oxathiin-2-one (4d). Prepared in the same way from **3d** (0.16 g, 0.5 mmol) by heating with acetic acid (5 mL). Simultaneous deprotection of the aldehyde function took place during cyclisation affording **4d** which was purified by crystallisation from diethyl ether, yield 0.09 g, 92%, solid, mp 106–108 °C. [Found: C, 55.66; H, 3.14. $C_9H_6O_3S$ requires C, 55.66; H, 3.11%]; ν_{max} (KBr) 1716.5, 1641.3 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 9.83 (1H, s, C*H*O), 7.62 (1H, dd, *J*=1.5, 6.1 Hz), 7.46 (1H, dd, *J*=1.5, 6.1 Hz), 6.91 (1H, d, *J*=7.68 Hz), 3.63 (2H, s, SCH_2); δ_C (75 MHz, $CDCl_3$) 196.3, 174.8, 160.5, 140.0, 136.5, 133.5, 121.0, 120.4, 34.6.

4.1.26. Naphtho[1,2-*b*][1,4]oxathiin-2-one (4e). Prepared in the same way as stated above from **3e** (0.4 g, 1.3 mmol) acetic acid (10 mL). Purified by column chromatography [eluent: ethyl acetate–light petroleum (1:4)], crystallised from petroleum ether, yield 0.26 g, 86%, mp 62–64 °C. [Found: C, 66.73; H, 3.62. $C_{12}H_8O_2S$ requires C, 66.65; H, 3.73%]; ν_{max} (KBr) 1755 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.20–8.16 (1H, m), 7.82–7.78 (1H, m), 7.60–7.49 (3H, m), 7.36–7.25 (1H, m), 3.55 (2H, s, SCH_2); δ_C (75 MHz, $CDCl_3$) 165.0, 148.1, 135.4, 130.2, 129.7, 129.1, 127.0, 126.9, 126.8, 123.0, 117.0, 31.2.

4.1.27. 8-Methoxy naphtho[1,2-*b*][1,4]oxathiin-2-one (4f). Prepared in the same way from **3f** (0.4 g, 1.25 mmol) and glacial acetic acid (10 mL). Purified by crystallisation (ethyl acetate–petroleum ether). Colourless shinny crystals, yield 0.26 g, 84%, mp 82–84 °C. [Found: C, 63.2; H, 4.09. $C_{13}H_{10}O_3S$ requires C, 63.4; H, 4.06%]; ν_{max} (KBr) 1755 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.02 (1H, d, *J*=9.2 Hz), 7.41 (1H, d, *J*=8.6 Hz), 7.23 (1H, d, *J*=8.6 Hz), 7.14 (1H, dd, *J*=2.5, 9.2 Hz), 7.03 (1H, d, *J*=2.5 Hz), 3.86 (3H, s, O*Me*), 3.46 (2H, s, SCH_2); δ_C (75 MHz, $CDCl_3$) 163.2, 158.7, 146.4, 135.0, 125.7, 123.7, 122.7, 120.3, 120.2, 112.3, 106.4, 55.8, 29.3.

4.1.28. 8-*t*-Butyldimethylsilyl[1]benzo[5,4-*b*]thieno[1,4]-oxathiin-2-one (4g). Prepared by same way from **3g** (0.2 g, 0.5 mmol) in aceteic acid (10 mL). Purified by column chromatography [eluent: ethyl acetate–light petroleum (1:9)], yield 0.15 g, 90%, mp 122–124 °C. [Found: C, 57.23; H, 5.86. $C_{16}H_{20}O_2S_2Si$ requires C, 57.10; H, 5.99%]; ν_{max} (KBr) 1750.7 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.62 (1H, s), 7.57 (1H, d, *J*=8.4 Hz), 7.21 (1H, d, *J*=8.4 Hz), 3.53 (2H, s, SCH_2), 0.95 (9H, s, CCH_3), 0.36 (6H, s, SiCH_3); δ_C (75 MHz, $CDCl_3$) 161.8, 144.6, 143.2, 141.2, 130.7, 125.9, 117.2, 112.5, 112.2, 28.0, 25.3, 15.8, −6.0.

4.1.29. [1]Benzo[3,2-*b*]thieno[1,4]oxathiin-2-one (4h). Prepared by same way from **3h** (0.295 g, 1 mmol) and acetic acid (10 mL). Purified by crystallisation (ethyl acetate–petroleum ether), yield 0.20 g, 91%, mp 72–74 °C. [Found: C, 54.48; H, 2.54. $C_{10}H_6O_2S_2$ requires C, 54.03; H, 2.72%]; ν_{max} (KBr) 1754 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.70–7.67 (1H, m), 7.48–7.43 (1H, m), 7.35–7.32 (1H, m), 7.15–7.09 (1H, m), 3.70 (2H, s, SCH_2); δ_C (75 MHz, $CDCl_3$) 169.5, 154.7, 138.5, 135.5, 132.1, 123.8, 123.7, 122.1, 121.9, 41.8.

4.1.30. 8-*t*-Butyldimethylsilyl benz[1,4]oxathiin-2-one (4i). Prepared from **3i** (0.1 g, 0.3 mmol) and acetic acid (7 mL) in the same way. Purified by column chromatography [eluent: ethyl acetate–light petroleum (1:9)], yield 0.07 g, 86%, solid, mp 60–62 °C. [Found: C, 59.83; H, 7.28. $C_{14}H_{20}O_2SSi$ requires C, 59.96; H, 7.19%]; ν_{max} (KBr) 1768 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.62–7.57 (2H, m), 7.21 (1H, d, *J*=8.4 Hz), 3.53 (2H, s, SCH_2), 0.95 (9H, s, CCH_3), 0.36 (6H, s, SiCH_3); δ_C (75 MHz, $CDCl_3$) 161.8, 143.2, 141.2, 125.9, 122.5, 117.2, 112.2, 28.0, 25.3, 15.8, −6.0.

4.1.31. 8-Methyl benz[1,4]oxathiin-2-one (4j). Prepared from **3j** (0.06 g, 0.24 mmol) and acetic acid (5 mL) in the same way. Purified by column chromatography [eluent: ethyl acetate–petroleum (1:9)], solid, mp 58–50 °C, yield 0.04 g, 89%. [Found: C, 59.73; H, 4.63. $C_9H_8O_2S$ requires C, 59.98; H, 4.47%]; ν_{max} (KBr) 1768 cm^{-1}; δ_H (300MH_Z, $CDCl_3$) 7.59–7.56 (1H, m), 7.18–7.14 (1H, m), 6.94–6.92 (1H, m), 3.69 (2H, s, SCH_2), 2.33 (3H, s, ArCH_3); δ_C (75 MHz, $CDCl_3$) 170.6, 155.0, 147.6, 129.1, 126.7, 126.6, 125.1, 39.8, 22.4.

4.1.32. Benz[1,4]oxathiin-2-one (4k). Compound **4i** (0.166 g, 1 mmol) and tetrabutyl ammonium fluoride (Bu_4NF) trihydrate (0.315 g, 1 mmol) in THF (10 mL) were stirred for 24 h at room temperature. After this period the reaction mixture was diluted with diethyl ether, washed with water (3×30 mL) and dried over Na_2SO_4. Removal of solvent afforded crude **4k**. Purified by column chromatography [eluent: ethyl acetate–petroleum (1:9)], solid, mp 48–50 °C, yield 0.09 g, 89%. [Found: C, 57.88; H, 3.85. $C_8H_6O_2S$ requires C, 57.81; H, 3.64%]; ν_{max} (KBr) 1741 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.70–7.67 (1H, m), 7.46–7.43 (1H, m), 7.35–7.32 (1H, m), 7.15–7.09 (1H, m), 3.70 (2H, s, SCH_2); δ_C (75 MHz, $CDCl_3$) 170.1, 154.1, 135.5, 130.8, 126.5, 124.6, 124.4, 39.1.

4.1.33. 2-(*N*,*N*-Diethyl-1-carbamoyloxyphenyl-2-)-1,3-dioxane (5). Compound **1d** (4.42 g, 20 mmol), 1,3-propanediol (3.04 g, 40 mmol) and anhydrous $FeCl_3$ (10%) in dry C_6H_6 (50 mL) were refluxed with continuous distilling of water for 10 h. Then most of the solvent distilled off, diluted with ether (50 mL), washed with water (3×50 mL) and dried (Na_2SO_4). Evaporation of the solvent left a

viscous liquid which was purified by column chromatography over alumina. [eluent: ethyl acetate–light petroleum (1:9)], colourless oily liquid, yield 4.9 g, 88%. [Found: C, 64.63; H, 4.60; N, 5.11. $C_{15}H_{21}NO_4$ requires C, 64.50; H, 7.58; N, 5.01%]; ν_{max} (Neat) 1720.4 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.67–7.65 (1H, m), 7.36–7.31 (1H, m), 7.23–7.12 (2H, m), 5.64 (1H, s, OC*H*O), 4.26–4.21 (2H, m, OC$H_2$$CH_2$), 3.97–3.89 (2H, m, OC$H_2$$CH_2$), 3.49–3.39 (4H, m, C$H_2$$CH_3$), 2.27–2.13 (2H, m, CH_2C$H_2$$CH_2$), 1.43–1.20 (6H, m, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 155.7, 148.7, 130.5, 129.4, 126.9, 125.1, 122.6, 97.7, 67.3, 42.3, 34.7, 25.6, 14.2, 13.2.

4.1.34. *N*,*N*-Diethyl-6-formyl-2-methylsulfanyl carbamoyloxybenzene (6). Compound **2d** (0.650 g, 2 mmol) was heated under refluxed with 1:1 aq. MeOH (8 mL) and $FeCl_3$ (0.32 g, 0.2 mmol) for 1 h. After distilling off most of the MeOH the compound extracted with dichloromethane (3×30 mL), washed with water (3×20 mL) and dried over Na_2SO_4. The oily residue was purified by column chromatography [eluent: ethyl acetate–light petroleum (1:4)], oily liquid, yield 0.47 g, 88%. [Found: C, 58.53; H, 6.52; N, 5.38. $C_{13}H_{17}NO_3S$ requires C, 58.40; H, 6.41; N, 5.24%]; ν_{max} (Neat) 1772, 1724 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 10.07 (1H, s, C*H*O), 7.61 (1H, dd, *J*=1.8, 7.5 Hz), 7.41 (1H, dd, *J*=1.5, 6.3 Hz), 7.25 (1H, dd, *J*=7.5, 6.3 Hz), 3.50 (2H, q, *J*=7.2 Hz, NCH_2), 3.49 (2H, q, *J*=7.2 Hz, NCH_2), 2.42 (3H, s, S*Me*), 1.27 (3H, t, *J*=7.2 Hz, CH_2CH_3), 1.18 (3H, t, *J*=7.2 Hz, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 188.5, 152.7, 149.8 134.4, 131.6, 129.3, 126.2, 125.8, 42.5, 42.1, 14.9, 14.1, 13.1.

4.1.35. *N*,*N*-Diethyl-1-[2-hydroxyphenyl]-1-methylsulfanylacetamide (9). Prepared from **1j** (2.07 g, 10 mmol), *s*-BuLi [2 M, 10 mL, 20 mmol)], TMEDA (3 mL, 20 mmol), THF (15 mL) and dimethyl disulfide (2 mL, 22 mmol) following the same procedure. White crystalline solid. Purified by crystallisation from diethyl ether, mp 130–132 °C, yield 1.71 g, 83%. [Found: C, 61.83; H, 7.64; N, 5.64. $C_{13}H_{19}NO_2S$ requires C, 61.63; H, 7.56; N, 5.53%]; ν_{max} (KBr) 3170, 1620 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 10.41 (1H, s, O*H*), 7.20–7.15 (1H, m), 7.00–6.92 (2H, m), 6.79–6.74 (1H, m), 4.73 (1H, s, C*H*SMeCONEt$_2$), 3.52–3.27 (4H, m, C$H_2$$CH_3$), 1.98 (3H, s, SC$H_3$), 1.23 (3H, t, *J*=6.2 Hz, CH_2CH_3), 1.11 (3H, t, *J*=6.2 Hz, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 173.6, 159.3, 133.4, 132.4, 123.1, 121.6, 121.3, 54.3, 45.9, 44.3, 17.5, 17.1, 15.20.

4.1.36. *N*,*N*-Diethyl-1-thiomethyl methyl-2-carbamyloxynaphthalene (10). Compound **1m** (2.57 g, 10 mmol) deprotonated with *s*-BuLi [2 M (5.5 mL, 11 mmol)] in THF (5 mL) using TMEDA (1.6 mL, 11 mmol) and dimethyldisulfide (1 mL, 12 mmol) following the general procedure compound **10** was obtained as an oil. Purification by column chromatography [eluent: ethyl acetate–petroleum (12.5:87.5)], afforded a colourless oily liquid, yield 2.3 g, 78%. [Found: C, 64.84; H, 6.83; N, 5.23. $C_{17}H_{21}NO_2S$ requires C, 67.42; H, 6.90; N, 4.48]; ν_{max} (Neat) 1718 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.96 (1H, d, *J*=8.0 Hz), 7.77 (1H, d, *J*=8.0 Hz), 7.71–7.68 (1H, m), 7.54–7.48 (1H, m), 7.37–7.32 (1H, m), 7.13–7.09 (1H, m), 4.23 (2H, s, CH_2SCH_3), 3.58–3.45 (4H, m, C$H_2$$CH_3$), 2.07 (3H, s, S*Me*), 1.36–1.26 (6H, m, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 159.7, 152.6, 133.0, 129.2, 129.2, 128.6, 126.6, 123.2, 122.3, 118.3, 114.6, 44.6, 44.4, 27.9, 16.8, 15.8, 14.6.

Acknowledgements

Thanks for financial assistance are due to Council of Scientific and Industrial Research (New Delhi) under the project No. 01(1573)/99/EMR-II and Royal Society of Chemistry for a Research Fund Grant to A. D. T. K. P and S. K. thank Council of Scientific and Industrial Research (New Delhi) for Senior Research Fellowships.

References and notes

1. Part 5. Mukherjee, C.; Kamila, S.; De, A. *Synlett* **2003**, 1474.
2. (a) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1. (b) Snieckus, V. *Heterocycles* **1980**, *14*, 1649. (c) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306. (d) Snieckus, V. *Bull. Soc. Chim. Fr.* **1988**, 67. (e) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879.
3. Sibi, M. P.; Snieckus, V. *J. Org. Chem.* **1983**, *48*, 1935.
4. Seebach, D.; Bauer, V. W. *Helv. Chim. Acta* **1984**, *67*, 1972.
5. Zhang, P.; Gawley, R. E. *J. Org. chem.* **1993**, *58*, 3223.
6. Wang, W.; Snieckus, V. *J. Org. Chem.* **1992**, *57*, 424.
7. (a) Kalinin, A. V.; Jalil Miah, M. A.; Chattopadhay, S.; Tsukazaki, M.; Wicki, M.; Nguyen, T.; Coelho, A. L.; Kerr, M.; Snieckus, V. *Synlett* **1997**, 839. (b) Focken, T.; Hopf, H.; Snieckus, V.; Dix, I.; Jones, P. G. *Eur. J. Org. Chem.* **2001**, 2221.
8. Mukherjee, C.; De, A. *Synlett* **2002**, 325.
9. Mukherjee, C.; Kamila, S.; De, A. *Tetrahedron* **2003**, *59*, 4767.
10. Mondal, S. S.; Samanta, S. S.; Deb, C.; De, A. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2559.
11. Greenwood, D.; Stevenson, H. A. *J. Chem. Soc.* **1953**, 1514.
12. Horner, L.; Sturm, K. *Liebigs Ann. Chem.* **1955**, *597*, 1.
13. Beaulieu, F.; Snieckus, V. *Synthesis* **1992**, 112.
14. Sibi, M. P.; Chattopadhay, S.; Dankwardt, J. W.; Snieckus, V. *J. Am. Chem. Soc.* **1985**, *107*, 6312.
15. Kamila, S.; Mukherjee, C.; Mondal, S. S.; De, A. *Tetrahedron* **2003**, *59*, 1339.