Synthesis of 2-Benzylthio-5-phenyl-3,4-disubstituted Thiophenes by Intramolecular Condensation of α-Oxo Ketene Dibenzylthioacetals

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A facile route to 2-benzylthio-5-phenyl-3,4-disubstituted thiophenes was described. Catalyzed by sodium hydroxide, the title compounds were synthesized in moderate to good yields simply from the intramolecular aldol type condensation of α-oxo ketene dibenzylthioacetals. The chemical selectivity for this annulation reaction was studied and discussed.

Keywords α-oxo ketene dithioacetals, α-oxo ketene dibenzylthioacetals, multisubstituted thiophenes, intramolecular aldol type condensation

Introduction

As a kind of versatile intermediates, α-oxo ketene dithioacetals **1** (Fig. 1) are important in organic synthesis[1] and most works are focused on the α-oxo ketene dimethylthioacetals.[2] In our studies, it is found that some reactions upon these kind of intermediates are modulated by the dialkylthio groups.[3] It is well known that thiophene derivatives serve as a very important heterocycles core to pharmaceuticals[4] and fragrance compounds,[5] and providing useful properties in the new conducting polymers[6] or nonlinear optical materials as well.[7] Among the various synthetic routes for substituted thiophenes, two common approaches are often adopted. One is the functionallization of the thiophene ring via the α-metalation or β-halogenation,[4] and the other is the annulation of suitably substituted acyclic precursors.[8] The latter becomes more attractive for its flexibilities, companying with the readily available starting materials.

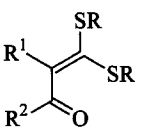

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Fig. 1 Structure of α-oxo ketene dithioacetals.

Recently, we found that assisted by sodium hydroxide, multisubstituted thiophenes were easily constructed from the corresponding α-oxo ketene dibenzylthioacetals **2** via an intramolecular annulation process (Scheme 1).[9] However, the corresponding α-oxo ketene dimethylthioacetals failed to give thiophenes under the same conditions. Marino and co-workers[10] found that some α-oxo ketene dimethylthioacetals underwent deprotonation on the methylthio group by LDA at −78 ℃ and thus thiophenes were produced by a subsequent intramolecular aldol type condensation. 2-Alkylthio-5-aryl thiophenes and related compounds, patented as miticides and insecticides in 1979,[11] were prepared by treatment of 2-phenyl thio-

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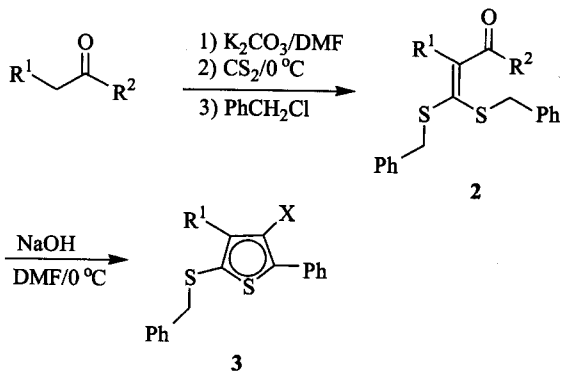
phenes with alkylsulfenyl chlorides in the presence of Ferro. However, the method used has the shortcomings as poor yields and long reaction time. Comparatively, our method presented provides a much simpler route for the unreported 2-benzylthio-5-phenyl-3, 4-disubstituted thiophenes from convenient acyclic precursors **2**.

Scheme 1



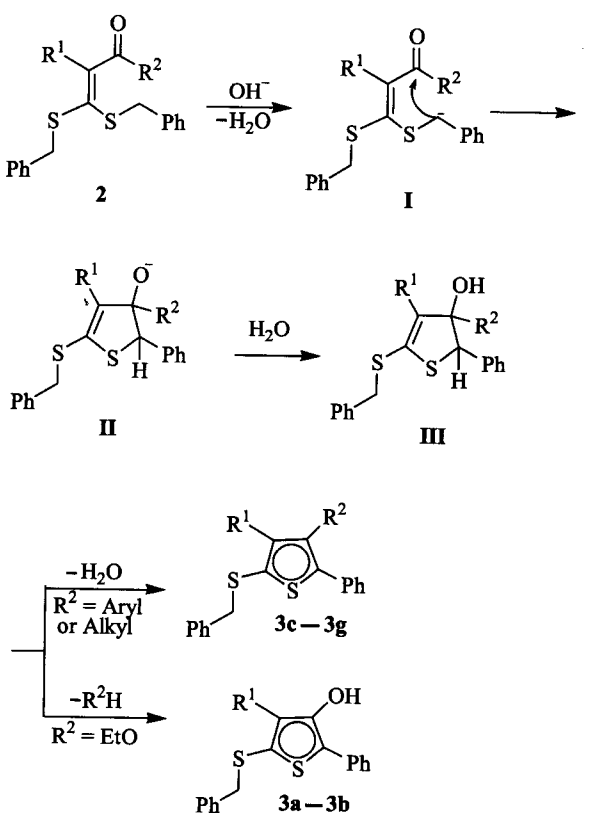
2 **3**

Results and discussion

Compounds **2** (except **2e**) were prepared conveniently in high yields via the reaction of corresponding β-dicarbonyl substrates with carbon disulfide and benzyl chloride in the presence of anhydrous potassium carbonate in DMF (Table 1). Under the optimized condition, 2-benzylthio-3-acetyl-4-hydroxy-5-phenyl thiophene (**3a**) was produced when **2a** was stirred for fifteen minutes in DMF at 0 ℃ catalyzed by NaOH. The homologous **3b**—**3g** were obtained similarly in 33.7%—73.7% yields (Table 2). In the identical conditions, the inseparable mixture was produced from **2h**.

The mechanism about the conversion of **2** to **3** is proposed in Scheme 2. In aprotic polar solvent DMF, compounds **2** can be readily deprotonated by NaOH on the methylene moiety of the benzylthio group. Then α-carbonyl is then attacked by the anions **I** to yield intermediates **II** which is transferred into intermediates **III** by protonation. When R^2 is aryl or alkyl group, the elimination of H_2O from **III** drives this reaction to products **3c**—**3g**. Similarly, when R^2 is ethoxy group, EtOH was released to yield **3a**—**3b**. In all cases, including α, α′-dioxo ketene dibenzylthioacetals **2a**—**2d**, **2g**, the dibenzylthioacetal **2f** and α-oxo ketene dibenzylthioacetal (**2e**), the reactions proceeded smoothly to afford the corresponding multisubstituted thiophenes in moderate to good yields. When the reaction was performed in alcoholic solvents, thiophenes **3** could not be obtained even though the sodium alkoxide was used as base. It is probably due to the inefficiency in the deprotonation process at the methylene moiety in protic solvents.

Scheme 2

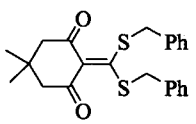


2 **I** **II** **III** **3c—3g** **3a—3b**

Compound **3b′** is resulted from the transesterification with sodium methoxide in DMF as the solvent. Whereas, when the bulky sodium isopropoxide or sodium tertiary butanoxide was used, few transesterification products were observed on ^1H NMR spectra though the reaction can be accelerated by strong bases (Table 2, Entry 4).

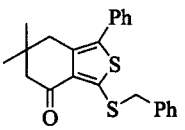
The selectivity of the nucleophilic addition at the α-carbonyl of **I** by the carbanion was observed. It follows the order aroyl > ethoxycarbonyl > acetyl. Hard-soft nucleophilicity can be used to explain this order. The carbanion **I** is a soft nucleophile due to its efficient dispersion of the negative charge on both sulfur atom and phenyl ring. The electrophilicity of ethoxycarbonyl is softer than acetyl because of the additional electron-donating p-π conjungation among the alkoxyl and the carbonyl group.

Table 1 The experimental results of compounds **2**[a]

Entry	Compound	R^1	R^2	Reaction time (h)	Yield (%)[c]
1	**2a**	CH_3CO	EtO	12	86.7
2	**2b**	EtOCO	EtO	12	92.1
3	**2c**	CH_3CO	p-$CH_3C_6H_4$	18	88.1
4	**2d**	PhCO	Ph	18	88.0
5[b]	**2e**	H	CH_3	0.5	93.0
6	**2f**			18	90.4
7	**2g**	EtOCO	Ph	18	84.0
8	**2h**	CH_3CO	CH_3	12	92.0

[a] (1) β-Dicarbonyl compounds/K_2CO_3/DMF; (2) CS_2/0 ℃; (3) $PhCH_2Cl$/DMF. [b] **2h**, t-BuONa-t-BuOH, r.t.. [c] Isolated yield.

Table 2 Intramolecular aldol type condensation of compounds **2** under base condition[a]

Entry	Substrate	Product	R^1	X	Reaction time (min)	Yield (%)[d]
1	**2a**	**3a**	CH_3CO	HO	15	50.0
2	**2b**	**3b**	EtOCO	HO	50	73.7
3[b]	**2b**	**3b′**	MeOCO	HO	10	51.8
4[c]	**2b**	**3b**	EtOCO	HO	10	83.5
5	**2c**	**3c**	CH_3CO	p-$CH_3C_6H_4$	10	33.7
6	**2d**	**3d**	PhCO	Ph	10	55.5
7	**2e**	**3e**	H	CH_3	40	50.3
8	**2f**	**3f**			20	56.1
9	**2g**	**3g**	EtOCO	Ph	15	40.5
10	**2g**	**3g′**	Ph	HO	15	5.0[e]

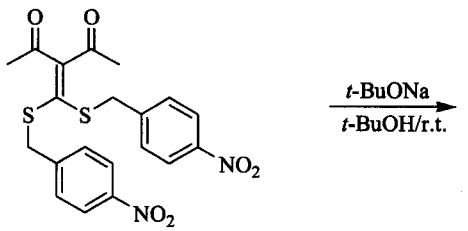
[a] NaOH as base. [b] NaOMe as base. [c] $NaOPr^i$ as base. [d] Isolated yield. [e] Based on ^1H NMR.

So ethoxycarbonyl is preferentially attacked by the softer carbanion. The conversion of **2a** to **3a** was a circumstantial evidence for such a proposal (Table 2, Entry 1). The electrophilicity of aroyl is comparatively the softest owing to the strong π-π conjungation so that the carbanion derived from **2c** and **2g** preferred to attack at the aroyl carbon rather than the ethoxycarbonyl carbon and the acetyl carbon to afford **3c** and **3g** respectively (Table 2, Entries 5 and 9). When with **2c** as the substrate, no product attacked at the acetyl was observed. Whereas in the case of **2g**, competitive reactions of carbanion attacking on both α-aroyl and α-ethoxycarbonyl were observed and resulted in the formation of **3g** and **3g′** with the ratio of 10∶1 according to the ^1H NMR spectrum.

In fact, in all of the above cases, no evidence for the formation of thienothiophenes was detected even if the reaction time was prolonged enough. However, when substrate **4** was treated with t-BuOH-t-BuONa, thienothio-

phenes **5** was obtained in high yield (Scheme 3). This is probably due to the easy deprotonation on the methylene moiety for there is a strong electron-withdrawing nitro group on the phenyl ring. Different result was observed when compound **2h** was tested. In the similar conditions, only the deacetylation product **2e** was obtained in 93.0% yield (Scheme 4).

Scheme 3



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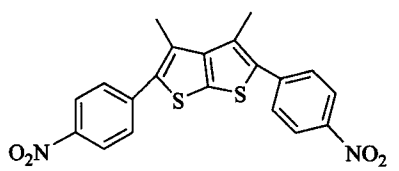

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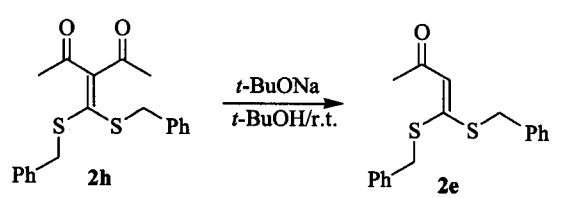
Scheme 4



2h **2e**

In summary, here a facile method to synthesize 2-benzylthio-5-phenyl-3,4-disubstituted thiophenes is described. Compared with the other routes, this method can be well performed under much milder conditions. The investigation for the bioactivities of these new multisubstituted thiophenes is in progress.

Experimental

Melting points were uncorrected. IR spectra (KBr) were measured on a MAGNA-IR 560 spectrometer. ^{1}H NMR spectra were determined on a Bruker AC spectrometer (80 MHz) or a Varian Unity spectrometer (400 MHz) in $CDCl_3$ and with TMS as internal standard. Elemental analyses were obtained on a PE 2400 analyzer. The mass spectra were recorded on an HP MS 5973 spectrometer. Unless otherwise noted materials were obtained from commercially available sources and used without further purification. β-Dicarbonyl compounds are all commercial compounds except diphenyl formacyl methane and phenyl formacyl acetic ether.[12]

General procedure for compounds **2** *(except* **2e***)*

To a flask containing DMF (15 mL) and β-dicarbonyl compound (10 mmol) was added anhydrous K_2CO_3 (30 mmol). After stirring for 30 min at room temperature, the mixture was cooled to 0 ℃ and then CS_2 (10 mmol) was added. Stirring for another one hour, a solution of $PhCH_2Cl$ (20 mmol) in DMF (5 mL) was added dropwise. After substrates consumed, the reaction was quenched by saturated NH_4Cl solution (100 mL). Dilute HCl was added to acidify the solution to pH 7. The precipitates were collected and compounds **2** were obtained after recrystallized from anhydrous ethanol.

2-(1,1-*Dibenzylthio*)*methylene acetacetic ether* (**2a**) Yellow crystal, m.p. 87—89 ℃; ^{1}H NMR δ: 1.26 (t, J = 7.1 Hz, 3H, CH_3), 2.14 (s, 3H, O=C-CH_3), 4.07 (s, 4H, 2×SCH_2), 4.23 (q, J = 7.1 Hz, 2H, OCH_2), 7.20—7.34 (m, 10H, 10×ArH); IR (KBr) ν: 3037, 3011, 1706, 1698, 1600, 1513 cm^{-1}. Anal. calcd for $C_{21}H_{22}O_3S_2$: C 65.26, H 5.74; found C 65.11, H 5.58.

2-(1,1-*Dibenzylthio*)*methylene malonic ether* (**2b**) Light yellow crystal, m.p. 38—40 ℃; ^{1}H NMR δ: 1.27 (t, J = 7.1 Hz, 6H, 2×CH_3), 4.09 (s, 4H, 2×SCH_2), 4.21 (q, J = 7.1 Hz, 4H, 2×OCH_2), 7.28 (s, 10H, 10×ArH); IR (KBr) ν: 3045, 3012, 1726, 1600, 1498 cm^{-1}; MS (20 eV) m/z (%): 416 (M^+, 5), 91 (100). Anal. calcd for $C_{22}H_{24}O_4S_2$: C 63.44, H 5.81; found C 63.31, H 5.67.

1-(1,1-*Dibenzylthio*)*methylene-*(*p-methyl*)*phenyl formacyl acetone* (**2c**) Yellow crystal, m.p. 96—98 ℃; ^{1}H NMR δ: 2.07 (s, 3H, O=C-CH_3), 2.40 (s, 3H, $ArCH_3$), 3.91 (s, 2H, SCH_2), 4.11 (s, 2H, SCH_2), 7.05—7.30 (m, 12H, 12×ArH), 7.62 (d, J = 8.8 Hz, 2H, 2×ArH); IR (KBr) ν: 3024, 1650, 1601, 1497 cm^{-1}. Anal. calcd for $C_{26}H_{24}O_2S_2$: C 72.19, H 5.59; found C 72.25, H 5.69.

(1,1-*Dibenzylthio*)*methylene-diphenyl formacyl methane* (**2d**) Light yellow crystal, m.p. 149—151

℃; ^{1}H NMR δ: 3.95 (s, 4H, 2 × SCH_2), 7.18—7.78 (m, 20H, 20 × ArH); IR (KBr) ν: 3059, 3030, 1661, 1595 cm^{-1}. Anal. calcd for $C_{30}H_{24}O_2S_2$: C 74.97, H 5.03; found C 74.82, H 5.01.

2-(1,1-*Dibenzylthio*) *methylene*-5,5-*dimethyl*-1,3-*cyclohexan-dione* (**2f**) Yellow crystal, m.p. 107—109 ℃; ^{1}H NMR δ: 1.05 (s, 6H, 2 × CH_3), 2.48 (s, 4H, 2 × CH_2), 4.14 (s, 4H, 2 × SCH_2), 7.28 (s, 10H, 10 × ArH); IR (KBr) ν: 3054, 3020, 1621, 1600, 1497 cm^{-1}. Anal. calcd for $C_{23}H_{24}O_2S_2$: C 69.66, H 6.10; found C 70.02, H 6.28.

2-(1,1-*Dibenzylthio*) *methylene-phenyl formacyl acetic ether* (**2g**) Orange viscous oil, ^{1}H NMR δ: 1.09 (t, J = 7.2 Hz, 3H, CH_3), 3.94 (s, 2H, SCH_2), 4.14 (q, J = 7.2 Hz, 2H, OCH_2), 4.17 (s, 2H, SCH_2), 7.05—7.70 (m, 15H, 15 × ArH); IR (KBr) ν: 3085, 3061, 3029, 1704, 1668, 1597, 1452, 1267, 1222 cm^{-1}. Anal. calcd for $C_{26}H_{24}O_3S_2$: C 69.61, H 5.39; found C 69.36, H 5.11.

3-(1,1-*Dibenzylthio*) *methylene*-2,4-*pentanedione* (**2h**) Light yellow crystal, m.p. 110—112 ℃; ^{1}H NMR δ: 2.04 (s, 6H, 2 × CH_3), 4.06 (s, 4H, 2 × SCH_2), 7.27 (s, 10H, 10 × ArH); IR (KBr) ν: 3040, 3013, 1701, 1592, 1500 cm^{-1}. Anal. calcd for $C_{20}H_{20}O_2S_2$: C 67.38, H 5.65; found C 67.46, H 5.74.

Synthesis of 1-(1,1-*dibenzylthio*) *methylene acetone* (**2e**)

To a solution of compound **2h** (1 mmol) in 10 mL of *t*-BuOH was added *t*-BuONa-*t*-BuOH solution (0.2 mol/mL, 5 mL) at room temperature. The reaction mixture was stirred for 5 min to starting material consumed (monitored by TLC). The mixture was then quenched by saturated NH_4Cl solution (20 mL) and was adjusted to pH 7 with dilute HCl solution. Thus, compound **2e** was obtained as white solid in 93.0% yield after filtration. M. p. 96—98 ℃, ^{1}H NMR δ: 2.13 (s, 3H, CH_3), 4.11 (s, 4H, 2 × SCH_2), 4.21 (s, 1H, = CH), 7.25—7.34 (m, 10H, 10 × ArH); IR (KBr) ν: 3036, 1739, 1636, 1555, 1475 cm^{-1}. Anal. calcd for $C_{18}H_{18}OS_2$: C 68.75, H 5.77; found C 68.87, H 5.86.

Preparation of 3-(1,1-*di*(*p-nitro benzylthio*)) *methylene*-2,4-*pentanedione* (**4**)

To a flask with DMF (15 mL) and 2,4-pentanedione (10 mmol) was added anhydrous K_2CO_3 (30 mmol). Stirred for 30 min at room temperature and then CS_2 (10 mmol) was added at 0 ℃. Stirring for another one hour, the solution of *p*-$NO_2C_6H_4CH_2Br$ (22 mmol) in DMF (5 mL) was added dropwise. Reacted for overnight to substrates consumed, the reaction was quenched by adding saturated NH_4Cl solution (100 mL). Product **4** as a brown solid was obtained in 76.8% yield after recrystallization from anhydrous ethanol. M. p. 112.0—113.0 ℃, ^{1}H NMR δ: 2.10 (s, 6H, 2 × CH_3), 4.13 (s, 4H, 2 × CH_2), 7.45 (d, J = 8.8 Hz, 4H, 4 × ArH), 8.19 (d, J = 8.8 Hz, 4H, 4 × ArH); IR (KBr) ν: 3028 1680, 1600, 1520, 1350 cm^{-1}. Anal. calcd for $C_{20}H_{18}N_2O_6S_2$: C 53.80, H 4.06, N 6.27; found C 53.69, H 4.13, N 6.18.

General procedure for compounds **3**

To a solution of compound **2** in 10 mL of DMF was added NaOH (4 mmol) at 0 ℃. The reaction mixture was stirred and monitored by TLC to the substrate consumed and then quenched with saturated NH_4Cl solution (10 mL). Dilute HCl was added to acidify the solution to pH 7. The precipitate was collected and purified by column chromatography on silica gel to yield **3**.

2-*Benzylthio*-3-*acetyl*-4-*hydroxy*-5-*phenyl thiophene* (**3a**) Deep yellow crystal, m.p. 108—110 ℃; ^{1}H NMR δ: 2.56 (s, 3H, O = C - CH_3), 4.23 (s, 2H, SCH_2), 7.30—7.79 (m, 10H, 10 × ArH), 11.21 (s, 1H, OH); IR (KBr) ν: 3500—2500, 1627, 1600, 1428, 1300 cm^{-1}. Anal. calcd for $C_{19}H_{16}O_2S_2$: C 67.03, H 4.74; found C 67.15, H 4.79.

2-*Benzylthio*-3-*ethoxycarbonyl*-4-*hydroxy*-5-*phenyl thiophene* (**3b**) Yellow green crystal, m.p. 104—106 ℃; ^{1}H NMR δ: 1.40 (t, J = 7.1 Hz, 3H, CH_3), 4.24 (s, 2H, SCH_2), 4.40 (q, J = 7.1 Hz, 2H, CH_2), 7.25—7.80 (m, 10H, 10 × ArH), 9.79 (s, 1H, OH); ^{13}C NMR δ: 14.119 (CH_3), 38.902 (SCH_2), 61.464 (OCH_2), 114.013, 114.991 (= C - S - C =), 125.711, 125.885, 127.706, 128.457, 128.555, 129.018, 132.447, 134.935, 145.609 (C - C = O), 151.526 (C - OH), 165.803 (C = O); IR (KBr) ν: 3300—2500, 1722, 1455, 1371, 1241 cm^{-1}. Anal. calcd for $C_{20}H_{18}O_3S_2$: C 64.84, H 4.90, found C 67.61, H 4.69.

2-*Benzylthio*-3-*methoxycarbonyl*-4-*hydroxy*-5-*phenyl thiophene* (**3b′**) Yellow green crystal, m.p. 160—

161 ℃; ^{1}H NMR δ: 3.92 (s, 3H, OCH_3), 4.42 (s, 2H, SCH_2), 7.26—7.90 (m, 10H, 10 × ArH), 9.72 (s, 1H, OH); MS (20 eV) *m/z* (%): 356 (M^+, 64), 91 (100); IR (KBr) ν: 3300—2500, 1724, 1418, 1302 cm^{-1}. Anal. calcd for $C_{19}H_{16}O_3S_2$: C 64.02, H 4.52; found C 64.15, H 4.38.

2-Benzylthio-3-acetyl-4-(p-methyl)phenyl-5-phenyl thiophene (**3c**) Colorless crystal, m.p. 112—114 ℃; ^{1}H NMR δ: 1.82 (s, 3H, O = C - CH_3), 2.34 (s, 3H, $ArCH_3$), 4.21 (s, 2H, SCH_2), 7.07—7.33 (m, 14H, 14 × ArH); IR (KBr) ν: 3057, 3032, 1689, 1475, 1324 cm^{-1}. Anal. calcd for $C_{26}H_{22}OS_2$: C 75.33, H 5.35; found C 75.25, H 5.51.

2-Benzylthio-3-phenyl formacyl-4,5-diphenyl thiophene (**3d**) Light yellow solid, m.p. 170—173 ℃; ^{1}H NMR δ: 4.06 (s, 2H, SCH_2), 7.05—7.74 (m, 20H, 20 × ArH); IR (KBr) ν: 3059, 3031, 1698, 1596, 1419, 1224 cm^{-1}. Anal. calcd for $C_{30}H_{22}OS_2$: C 77.89, H 4.79; found C 77.70, H 4.55.

2-Benzylthio-4-methyl-5-phenyl thiophene (**3e**) Yellow oil, ^{1}H NMR δ: 2.21 (s, 3H, CH_3), 4.00 (s, 2H, SCH_2), 6.77 (s, 1H, CH), 7.18—7.32 (m, 5H, 5 × ArH), 7.32—7.42 (m, 5H, 5 × ArH); IR (KBr) ν: 3085, 3060, 3025, 1600, 1490, 1450 cm^{-1}. Anal. calcd for $C_{18}H_{16}S_2$: C 72.93, H 5.44; found C 72.80, H 5.36.

2-Benzylthio-5-phenyl-3,4-thieno(4,4-dimethyl-2-oxo)cyclohexane (**3f**) Yellow crystal, m.p. 175—177 ℃; ^{1}H NMR δ: 1.02 (s, 6H, 2 × CH_3), 2.41 (s, 2H, CH_2), 2.74 (s, 2H, CH_2), 4.27 (s, 2H, SCH_2), 7.28—7.39 (m, 10H, 10 × ArH); IR (KBr) ν: 3029, 1654, 1490 cm^{-1}. Anal. calcd for $C_{23}H_{22}OS_2$: C 72.98, H 5.86; found C 72.88, H 5.72.

2-Benzylthio-3-ethoxycarbonyl-4,5-diphenyl-thiophene (**3g**) Pure **3g** was obtained by recrystallization in ethanol from a mixture of **3g** and **3g′** after purification by column chromatography. Yellow solid, m.p. 80—81 ℃; ^{1}H NMR δ: 0.97 (t, J = 7.2 Hz, 3H, CH_3), 4.05 (q, J = 7.2 Hz, 2H, OCH_2), 4.26 (s, 2H, SCH_2), 7.08—7.46 (m, 15H, 15 × ArH); IR (KBr) ν: 3082, 3051, 3026, 1718, 1595, 1494, 1442, 1375, 1212 cm^{-1}; MS (20 eV) *m/z* (%): 430 (M^+, 100), 91 (100). Anal. calcd for $C_{26}H_{22}O_2S_2$: C 72.53, H 5.15; found C 72.39, H 5.01.

2-Benzylthio-3-phenylformacyl-4-hydroxyl-5-phenyl thiophene (**3g′**) Pure **3g′** could not be completely isolated from **3g** by column chromatography and recrystallization. ^{1}H NMR δ: 3.95 (s, 2H, SCH_2), 7.08—7.77 (m, 15H, 15 × ArH), 9.74 (s, 1H, OH).

Preparation of 2,2′-di(p-nitro phenyl)-3,3′-dimethyl-thienothiophene (**5**)

To a solution of compound **4** (1 mmol) in *t*-BuOH (15 mL) was added *t*-BuONa-*t*-BuOH (0.5 mol/mL, 2.0 mL) at room temperature. The mixture was stirred for eight hours and then the reaction was quenched by adding saturated NH_4Cl solution (10 mL). Dilute HCl was added to acidify the solution to pH 7. The brown solid **5** was filtered and purified by crystallization from ethanol in 79.5% yield. M.p. 148.0—149.0 ℃; ^{1}H NMR δ: 2.69 (s, 6H, 2 × CH_3), 7.41—8.37 (m, 8H, 8 × ArH); IR (KBr) ν: 3120, 3070, 1590, 1520, 1349 cm^{-1}. Anal. calcd for $C_{20}H_{14}N_2O_4S_2$: C 58.52, H 3.44, N 6.82; found C 58.73, H 3.40, N 6.95.

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