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REACTIONS OF NINHYDRIN WITH BENZO[*b*]THIOPHENES

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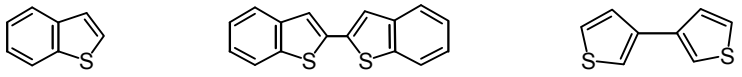
Abstract – The reaction of ninhydrin with benzo[*b*]thiophene in acetic acid in the presence of a small amount of sulfuric acid afforded a novel fluorenone compound fused to benzo[*b*]thiophene rings. In the reaction using 2,2'-bibenzo[*b*]thiophene, phthalide conjoined in a spiro framework was unexpectedly isolated along with an isocoumarin derivative which is fused to benzo[*b*]thiophene and benzene rings. The product related to the latter was obtained in the reaction of 3,3'-bithiophene with ninhydrin. The structures of these novel heterocycles were supported by spectroscopic studies and X-ray crystallography.

INTRODUCTION

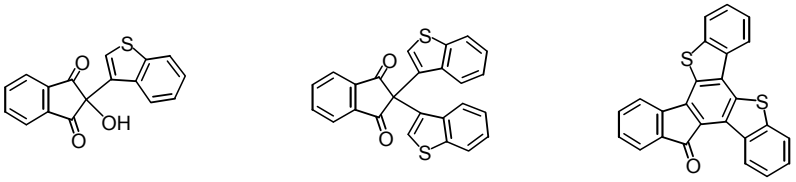
Ninhydrin is known as a highly electrophilic compound because of its activated ketone functional group at the 2-position.[1] It reacts with a variety of nucleophiles, such as amines,[2] alkenes,[3] and methylene compounds activated by neighboring carbonyl groups.[4] The reactions are in most cases acid-catalyzed. Arenes also enter into a Friedel-Crafts-type reaction with ninhydrin, affording 2-monoaryl- and/or 2,2-diaryl-1,3-indandiones.[5] Phenols undergo *ortho*-selective substitution to give 2-(2-hydroxyphenyl)-2-hydroxy-1,3-indandiones, which actually equilibrate to intramolecular hemiacetal structures.[6] Despite the versatility of the reactions of ninhydrin investigated thus far, studies of reactions with heteroaromatic compounds have been extremely limited. Musgrave et al. have reported the reaction of ninhydrin with thiophene in aqueous 75% v/v sulfuric acid.[7] Other than this paper, to the best of our knowledge, none has reported the reactions of ninhydrin with thiophene derivatives. Herein, we report the results of our investigation on the reactions of benzo[*b*]thiophene derivatives with ninhydrin, demonstrating the formation of unexpected compounds.

RESULTS AND DISCUSSION

The thiophene compounds as illustrated below were used in the reactions with ninhydrin.

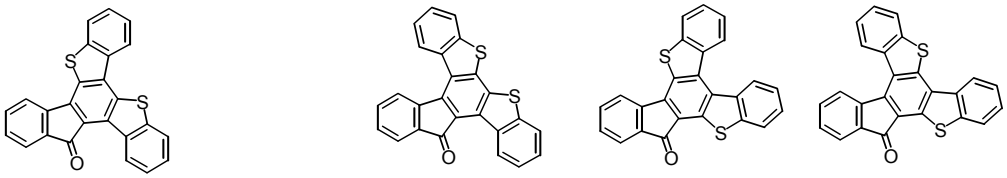


The reaction of benzo[*b*]thiophene was carried out in acetic acid under reflux by adding a small amount of sulfuric acid as a catalyst. At the outset, the substitution of one and/or two thiophene rings at the 2-position of ninhydrin was anticipated because of the high reactivity to electrophiles of the carbon at this position. In addition to such substituted products, **1** and **2**, a novel product **3** was obtained.



1 **2** **3**

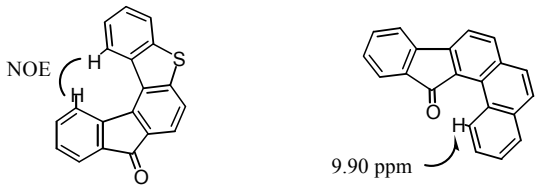
Compound **3** was isolated in 68% yield as an orange solid. Its ^{1}H NMR spectrum is composed of six doublets and six triplets in aromatic regions, indicating the existence of three sets of *ortho*-disubstituted benzene rings. In the ^{13}C NMR spectrum, twenty five signals were observed, among which twenty four are assignable to aromatic carbons and one to a carbonyl carbon. On the basis of these data together with the mass spectrum (m/e M^{+} 392) and IR spectrum (1703 cm^{-1}), four isomeric structures **3A-3D** are conceivable.



3A (3) **3B** **3C** **3D**

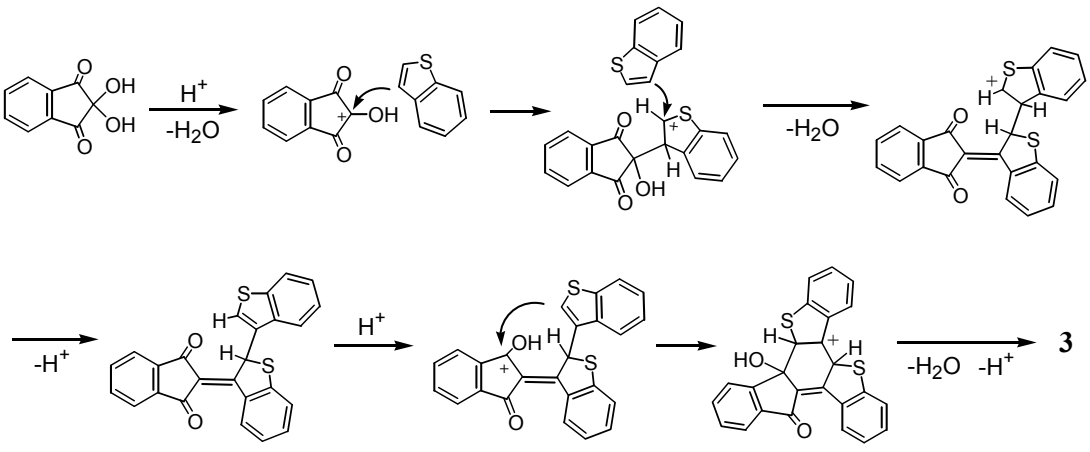
The most characteristic feature in the ^{1}H NMR spectrum is the occurrence of one doublet at a low magnetic field of 9.95 ppm. This proton should be located in close proximity to the carbonyl functionality and be subject to the anisotropic effect. This suggestion was supported by the NMR measurements in the presence of the shift reagent, $Eu(fod)_4$. With increasing sift reagent concentration, the signal at 9.95 ppm significantly moves downfield, whereas the other signals are not affected except for the *peri*-proton at 7.75 ppm, which shows a slight downfield shift. On the basis of these observations, **3A** and **3B** are the most plausible structures among the four isomers. Then, **3B** is excluded, because the compound in question showed no NOE effects between any protons, indicating that there are

no protons close to each other through space. The protons separated spatially by a bay region, as shown in compound **4**, have been reported to exhibit NOE.[8] The chemical shifts of 9.95 ppm and others are consistent with those observed for protons in similar environments structurally, for example, in compound **5**.[9] Thus, the structure of the orange product was identified as **3**.



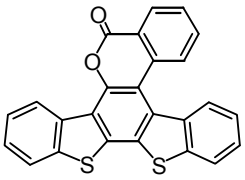
4 **5**

The formation of **3** is formally a result of dehydration from two benzo[*b*]thiophenes and one ninhydrin molecule. A possible mechanism for the formation of **3** is depicted in Scheme 1. Benzo[*b*]thiophene is known to undergo electrophilic attack at the β-carbon atom. Thus, it is reasonable that the reaction of benzo[*b*]thiophene with ninhydrin affords **1** and **2**. The cationic intermediate yielding these substituted products is capable of entering into a reaction with a second molecule of benzo[*b*]thiophene, followed by intramolecular condensation to connect the carbonyl carbon and the α-carbon. An analogous thiophene-condensed fluorenone product has been isolated in the reaction of ninhydrin with thiophene,[7] whereas the condensation pattern of the thiophene rings is different from the case in question. This is not unusual, because benzo[*b*]thiophene undergoes electrophilic attack at the β-position, whereas thiophene undergoes it at the α-position.

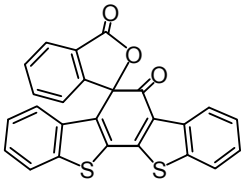


Scheme 1

The results obtained for benzo[*b*]thiophene prompted us to examine the reaction of ninhydrin with 2,2'-bibenzo[*b*]thiophene, since this might form **3B**. Unexpectedly, actual products were lactone compounds **6** (70%) and **7** (5%). Products due to substitution at the 2-carbon of ninhydrin were not obtained.

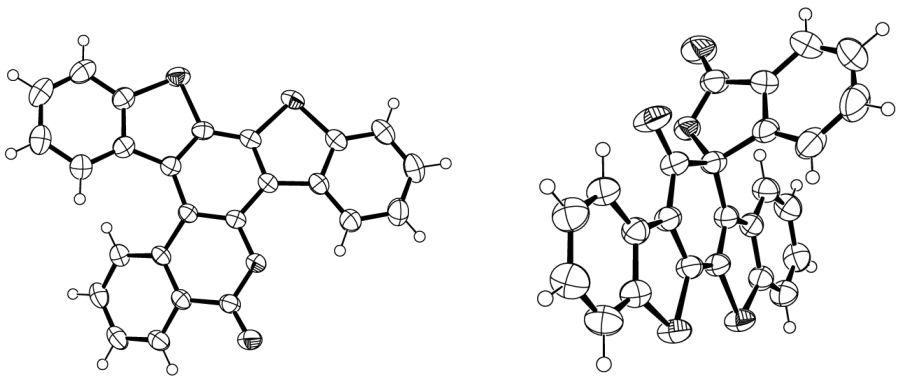


6



7

Compound **6**, a colorless solid, is formulated as $C_{25}H_{12}O_2S_2$ on the basis of the mass spectrum and combustion data. The IR spectrum of **6** displays carbonyl absorption at 1743 cm^{-1}, and the ^{1}H-NMR spectrum has three sets of doublet-triplet-triplet-doublet patterns. The structure of **6** was eventually established by X-ray crystallographic analysis for a single crystal obtained by recrystallization from chloroform (Figure 1). The molecule is not planar but significantly twisted. The isocoumarin substructure deviates more significantly from planarity than the benzobis(benzothiophene) ring. Because of this chiral structure, the crystal of **6** includes a pair of *dl* molecules and, that is a racemic crystal of space group $Pca2_1$. Compound **7** is a yellow colored solid, showing a UV/Vis absorption maximum at 418 nm. The structure of spirolactone **7** was also elucidated by X-ray crystallographic analysis for a single crystal obtained by recrystallization from chlorobenzene (Figure 1).

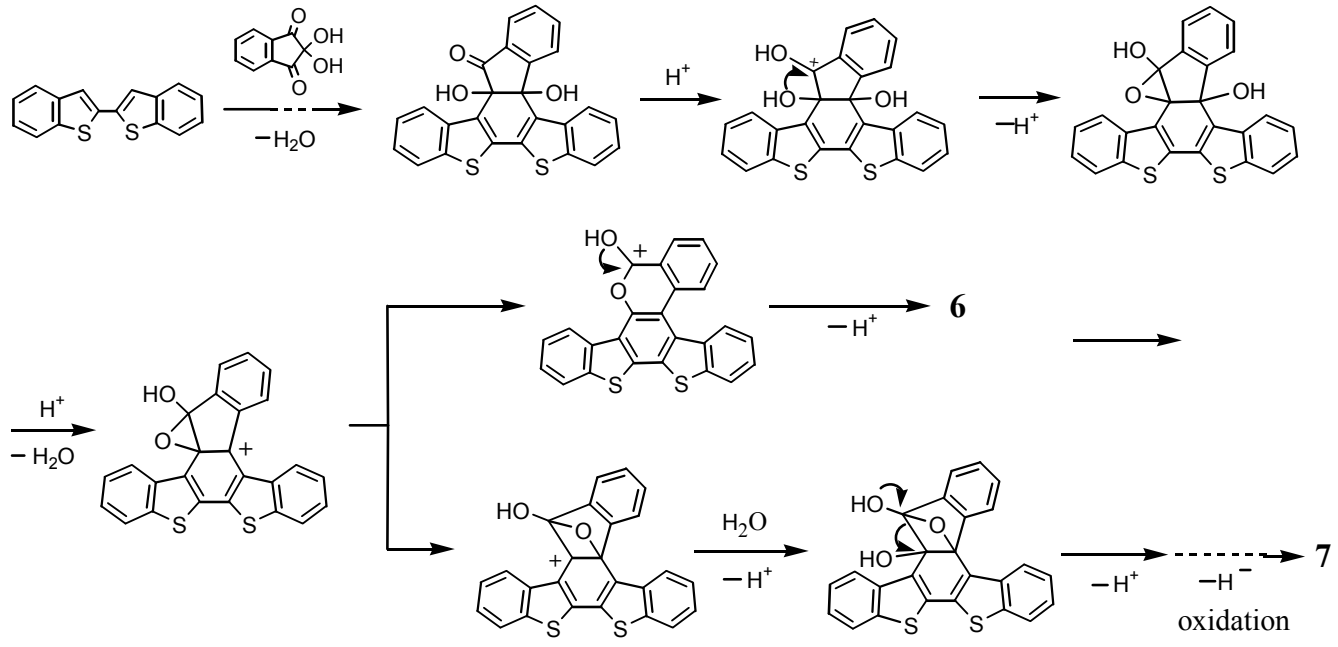


(a) (b)

Figure 1 (a) ORTEP drawing of **6**. (b) ORTEP drawing of **7**.

The formation of **6** is interpreted as a result of dehydration accompanied by ring expansion. We assume a possible mechanism of the formation of **6** as shown in Scheme 2, with reference to the analogous formation of indole-condensed isocoumarin using ninhydrin as the starting compound, as reported by Bullington.[10] The acid-promoted addition of benzo[*b*]thiophene to ninhydrin would lead to the formation of an α, β-dihydroxyketone and subsequently to a hydroxyl epoxide intermediate. The latter could undergo dehydration followed by ring expansion through the opening of the epoxide ring to

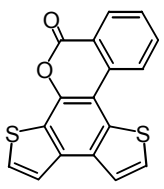
neutralize the positive charge. The literature indicates the formation of isocoumarin compounds from hemiacetals derived from ninhydrin and phenols. [11]



Scheme 2

The rationale for the formation of spirolactone **7** is more difficult because it must involve oxidation. We assume that oxygen in the air participates in the oxidation process, since the reaction under nitrogen atmosphere extremely lowered the yield of **7**. At this stage, however, the detailed mechanism for the formation of **7** is not confirmative.

Likewise in the formation of **6** and/or **7** from 2,2'-bibenzo[*b*]thiophene, 3,3'-bithiophene is considered to form intramolecular cyclization products because the reactive α-positions of two thiophene units are open for electrophilic attack. As anticipated, compound **8** was isolated as a colorless solid in 64% yield. The spirolactone product corresponding to **7** was not detected this time. The formation of **8** may be consistently explained by the intervention of an epoxide as an intermediate. It is, therefore, reasonable that in this reaction, the two thiophene rings are condensed with the isocoumarin ring in different orientation from that in the case of **6**.



8

In conclusion, we have demonstrated that ninhydrin shows the high electrophilic reactivity to benzo[*b*]thiophenes. Principally, three types of reaction were observed: substitution at the 2-carbon by the thiophenes, condensation by dehydration to give benzo[*b*]thiophene-fused fluorene, and the rearrangements of the cationic intermediate to give novel isocoumarin and spirolactone compounds, **6** and **7**.

EXPERIMENTAL

All melting points were determined using a Yanaco MS-500V apparatus and uncorrected. The IR spectra were obtained using a Shimadzu FT-IR 8200PC spectrometer. The UV spectra were recorded by Shimadzu FTUV-2200PC. The ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) spectra were recorded using a JEOL α-500 spectrometer. Chemical shifts are given in δ values (ppm) using TMS as the internal standard. The mass spectra were taken on a Shimadzu GCMS-QP5050A mass spectrometer. Elementary combustion analyses were performed using a Yanaco CHN CORDER MT-6 analyzer. All reactions were monitored by TCL employing a 0.25 mm silica gel plate (Merck 60F 254). Column chromatography was carried out on silica gel (Merck 60N spherical). The yields of products are based on the initial weights of ninhydrin used.

*(a) Reaction with benzo[b]thiophene***.** A solution of ninhydrin (0.89 g, 5 mmol) and benzo[*b*]thiophene (1.32 g, 10 mmol) in acetic acid (60 mL) was refluxed with conc H_2SO_4 (0.2 mL) for 6 h. The usual workup and chromatography of the reaction mixture gave the fraction of **2** first, followed by the fraction of **1** and lastly the fraction of **3**. Compound **3** was recrystallized from hot toluene or EtOAc.

2-Hydroxy-2-benzo[*b*]thien-3-yl-1,3-indandione (1): 0.29 g, 20%. yellow crystals. mp 212-214 ºC. UV λ_{max} ($CHCl_3$) 358 nm (log ε=3.08); ^{1}H-NMR ($CDCl_3$) δ 3.44 (1H, s, OH), 7.19 (1H, s), 7.38 (1H, ddd, *J*=8.2, 7.0, 0.9 Hz), 7.46 (1H, ddd, *J*=8.2, 7.3, 1.2 Hz), 7.80 (1H, dd, *J*=7.9, 0.9 Hz), 7.93 (2H, m), 8.06 (2H, m), 8.57 (1H, dd, *J*=7.9, 0.9 Hz); ^{13}C-NMR ($CDCl_3$) δ 122.54, 124.34, 124.68, 125.05, 125.30, 127.18, 130.80, 136.71, 136.80, 140.11, 140.49, 196.75; MS *m/Z*=294 (100%, M), 266 (19%, M-CO); IR (KBr) 3360, 1705 cm^{-1}; Anal. Calcd for $C_{17}H_{10}O_3S$: C, 69.37; H, 3.42; S, 10.89%. Found: C, 69.42; H, 3.50, S, 10.71%.

2,2-Bisbenzo[*b*]thien-3-yl-1,3-indandione (2): 0.33 g, 16%. yellow crystals. mp 195-198 ºC. UV λ_{max} (CH_3Cl) 370 nm (log ε=3.31); ^{1}H-NMR ($CDCl_3$) δ 7.17 (1H, t, *J*=8.2 Hz), 7.26 (2H, s), 7.28 (2H, t, *J*=8.2 Hz), 7.64 (2H, d, *J*=8.2 Hz), 7.81 (2H, d, *J*=8.2 Hz), 7.95 (2H, m), 8.12 (2H, m); ^{13}C-NMR ($CDCl_3$) δ 122.68, 124.20, 124.35, 124.40, 124.43, 124.54, 127.40, 129.82, 136.52, 137.12, 140.44, 140.59, 197.35, MS *m/Z*=410 (100%, M), 365 (24%, M-CO-OH), 353 (23%, M-CO-CHO); IR (KBr) 1708 cm^{-1}; Anal. Calcd for $C_{25}H_{14}O_2S_2$: C, 73.17; H, 3.41; S, 15.61%. Found: C, 73.42; H,3.53, S,

15.71%.

Indeno[2,3-*i*]benzo[1,2-*b*:3,4-*b'*]bis[1]benzothiophen-6-one (3): 1.32 g, 68%. orange solid. mp 414-416 ºC. UV λ_{max} ($CHCl_3$) 478 nm (log ε=2.82); ^{1}H-NMR ($CDCl_3$) δ 7.37 (1H, t, *J*=6.7 Hz), 7.57 (1H, t), 7.59 (1H, t), 7.61 (1H, t), 7. 63 (1H, t), 7.69 (1H, t, *J*=7.3 Hz), 7.75 (1H, d, *J*=7.3 Hz), 7.80 (1H, d, *J*=7.3 Hz), 7. (1H, d, *J*=7.9 Hz), 8.05 (1H, d, *J*= 7.9 Hz), 8.60 (1H, d, *J*=7.9 Hz), 9.95 (1H, d, *J*=8.6 Hz); ^{13}C-NMR ($CDCl_3$) δ 121.84, 122.18, 123.10, 124.17, 125.10, 125.29, 125.61, 127.43, 127.79, 127.93, 129.01, 130.94, 132.59, 133.63, 133.65, 134.19, 134.69, 134.85, 135.30, 135.46, 136.48, 138.82, 141.48, 142.85, 195.00; MS *m/Z*=392 (100%, M), 364 (19%, M-CO), 362 (20%, M-H_2CO); IR (KBr) 1703 cm^{-1}; Anal. Calcd for $C_{25}H_{12}OS_2$: C, 76.50; H, 3.08; S, 16.34%. Found: C, 76.20; H, 3.16, S, 15.75%.

(b) Reaction with 2,2'-bibenzo[b]thiophene. A solution of ninhydrin (0.89 g, 5 mmol), 2,2'-bibenzo[*b*]thiophene (2.66 g, 10 mmol) in acetic acid (70 mL) was refluxed with conc H_2SO_4 (0.2 mL) was refluxed for 5 h and treated in a manner similar to that described above. The fraction of **6** was eluted faster than that of **7**. Single crystals of **6** and **7** suited for X-ray analyses were obtained by recrystallization from hot toluene and chlorobenzene, respectively.

7*H*-Bis[1]benzothieno[3,2-*a*:2',3'-*c*]dibenzo[*b*,*d*]pyran-7-one (6): 1.43 g, 70%. colorless solid. mp 344.2-346 ºC. ^{1}H-NMR ($CDCl_3$) δ 7.39 (1H, t, *J*=7.6 Hz), 7.50 (1H, t, *J*=7.6 Hz), 7.56 (1H, t, *J*=7.3 Hz), 7.63 (1H, t, *J*=8.0 Hz), 7.66 (1H, t, *J*=7.3 Hz), 7.79 (1H, t, *J*=7.3 Hz), 7.95 (1H, d, *J*=8.0 Hz), 7.98 (1H, d, *J*=7.6 Hz), 8.52 (1H, d, *J*=8.0 Hz), 8.51 (1H, d, *J*=8.0 Hz), 8.65 (1H, d, *J*=8.2 Hz), 9.10 (1H, d, *J*=7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 121.48, 122.61, 122.77, 123.52, 123.71, 124.94, 124.82, 125.44, 125.84, 126.64, 126.96, 126.99, 127.09, 128.72, 129.27, 130.19, 133.25, 134.41, 134.65, 135.81, 135.93, 138.95, 140.45, 147.72, 177.81, MS *m/Z*=408 (100%, M), 380 (10%, M-CO), 351 (26%, M-CO-CHO); IR (KBr) 1743 cm^{-1}; Anal. Calcd for $C_{25}H_{12}O_2S_2$: C, 73.53; H, 2.94; S, 15.68%. Found: C, 73.42; H, 3.21, S, 16.10%.

Spiro[6,7-dihydro-6-oxobenzo[2,1-*b*:3,4-*b'*]bis[1]benzothiophene-7,1'-3'-oxoisobenzofuran] (7): 0.11 g, 5%. yellow crystals. mp 294.5-296 ºC. UV λ_{max}($CHCl_3$) 418 nm (log ε = 3.21); ^{1}H-NMR ($CDCl_3$) δ 7.10 (1H, d, *J*=7.6 Hz), 7.22 (1H, d, *J*=7.0 Hz), 7.23 (1H, t, *J*=8.2 Hz), 7.35 (1H, t, *J*=8.2 Hz), 7.46 (1H, t), 7.48 (1H, t), 7.50 (1H, t), 7.58 (1H, t, *J*=7.3 Hz), 7.85 (1H, d, *J*=7.9 Hz), 7.90 (1H, d, *J*=7.3 Hz), 8.13 (1H, d, *J*=7.6 Hz), 8.50 (1H, d, *J*=6.7 Hz); MS *m/Z*=424 (100%, M), 408 (81%, M-O), 380 (78%, M-CO_2), 351 (58%, M-CO_2-CHO); Anal. Calcd for $C_{25}H_{12}O_3S_2$: C, 70.75; H, 2.83; S, 15.09%. Found: C, 70.02; H, 3.01, S, 14.81%.

(c) Reaction with 3,3'-bithiophene. A solution of ninhydrin (0.89 g, 5 mmol) and 3,3'-bithiophene (2.66

g, 10 mmol) was refluxed in acetic acid (70 mL) with conc H_2SO_4 (0.2 mL) for 3 h. The usual workup and chromatography of the reaction mixture gave **8**.

8*H*-Bisthieno[2,3-*a*:3',2'-*c*]dibenzo[*b*,*d*]pyran-8-one (8): 0.98 g, 64 %. colorless solid. mp 244 ºC. ^{1}H-NMR ($CDCl_3$) δ 7.65 (1H, t, *J*=7.0 Hz), 7.67 (1H, d, *J*=5.5 Hz), 7.73 (1H, d, *J*=9.2 Hz), 7.74 (1H, d, *J*=9.2 Hz), 7.81（1H, d, *J*=5.5 Hz), 7.98 (1H, t, *J*=7.8 Hz), 8.57 (1H, d, *J*=7.9 Hz), 8.68 (1H, d, *J*=8.2 Hz); ^{13}C-NMR ($CDCl_3$) δ 108.89, 121.07, 121.77, 122.29, 124.79, 125.64, 126.76, 128.15, 130.01, 131.22, 131.66, 132.45, 134.83, 135.20, 136.50, 145.49, 160.42; IR (KBr) 1740 cm^{-1}; MS *m/Z*=308 (100%, M), 280 (31%, M-CO), 251 (22%, M-CO-CHO); Anal. Calcd for $C_{17}H_8O_2S_2$: C, 66.21; H, 2.61; S, 20.80%. Found: C,66.49; H,2.99, S, 20.76%.

X-Ray crystal data of 6. $C_{25}H_{12}O_2S_2$, M=408.49. orthorhombic, $Pca2_1$ (#29), *a*=20.2280(7), *b*=11.4336(3), *c*=7.7505(2) Å, *U*=1792.53(9) Å^3, *Z*=4, D_{calc}=1.514 g/cm^3, μ (Mo-Kα)=3.176 cm^{-1}, 4828 reflections ($2\theta \leq 59.1^o$), R_{int} 0.028, R_1 ($I > 2.00\sigma(I)$) 0.0274, wR_2 ($I > 2.00\sigma(I)$) 0.0479. CCDC reference number 704947.

X-Ray crystal data of 7. $C_{25}H_{12}O_3S_2$, M=424.49. monoclinic, C2/c (#15), *a*=24.7951(11), *b*=10.2854(3), *c*=15.0316(5) Å, β = 90.9718(15), *U*=3832.9(2) Å^3, *Z*=8, D_{calc}=1.471 g/cm^3, μ (Mo-Kα)=3.038 cm^{-1}, 4384 reflections ($2\theta \leq 54.9^o$), R_1 ($I > 2.00\sigma(I)$) 0.0312, wR_2 ($I > 2.00\sigma(I)$) 0.0526. CCDC reference number 704948.

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