# Syntheses of 2*H*-1-Benzothiopyran-2-ones (Thiocoumarins) and Related Compounds from Benzenethiols and Diketene

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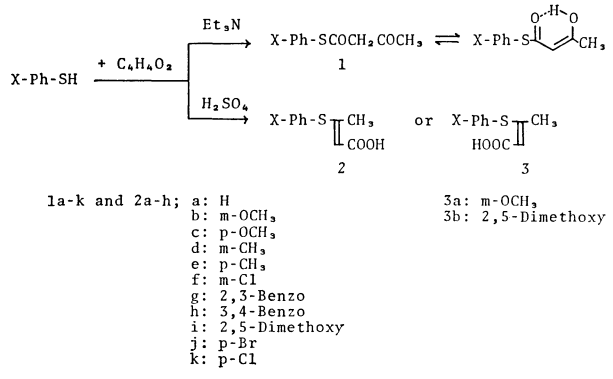
(Received December 14, 1979)

The products formed by the reaction of benzenethiols with diketene in the presence of $H_2SO_4$ are (*E*)-β-(arylthio)crotonic acids (**2**) and/or isomeric (*Z*)-β-(arylthio)crotonic acids and not, as has been reported, *S*-phenyl 3-oxobutanethioates (**1**). Compounds **1a**—**k**, as the precursor of thiocoumarins, were prepared from benzenethiols and diketene in the presence of triethylamine. The reaction of **1** with various condensing agents has been examined to prepare 2*H*-1-benzothiopyran-2-ones (thiocoumarins). It is found that 4-methyl(thiocoumarins) were conveniently prepared by the reaction of **1** with anhydrous aluminium chloride in yields of 16—48%. When **1** was treated with PPA, isomeric 2-methyl(thiochromones) were preferentially obtained in yields of 5—66%, and compound **2** was isolated as an intermediate. The spectral characteristics of 4-methyl(thiocoumarins) have also been described.

It is well known that 2*H*-1-benzothiopyran-2-ones (thiocoumarins) can not be obtained by the Pechmann reaction of benzenethiols.[1] Thiocoumarins are generally prepared from the unstable 2-mercaptobenzaldehydes which require multistage processes from benzenethiols.[2] Although Konishi *et al.* reported the convenient method to prepare thiocoumarins by the cyclization of *S*-phenyl 3-oxobutanethioates with PPA,[3] the products are mostly not thiocoumarins, but isomeric thiochromones (4*H*-1-benzothiopyran-4-ones).[4] Furthermore, recently we found that the *S*-phenyl 3-oxobutanethioates, described in our previous paper,[4] were really isomeric (*E*)-β-(arylthio)crotonic acids (**2**) and/or (*Z*)-β-(arylthio)crotonic acids (**3**).

We have now prepared a number of *S*-(substituted phenyl) 3-oxobutanethioates (**1**) from benzenethiols and diketene, and studied the cyclization of **1** with various condensing agents to prepare thiocoumarin derivatives. These works were reported in a preliminary form,[5] but in this paper we wish to report further details of these reactions. We also wish to report the spectral characteristics of 4-methyl(thiocoumarins), compared with those of isomeric 2-methyl(thiochromones).




Scheme 1.

## Results and Discussion

*Preparation of* S-*Phenyl 3-Oxobutanethioates.* Recently Yaggi and Douglas reported that the product obtained from the reaction between benzenethiols and diketene in the presence of sulfuric acid was (*E*)-β-(arylthio)crotonic acid **2** (X=H or *p*-Cl).[6] A number of authentic (*E*)-β-(arylthio)crotonic acids (**2**) were prepared from sodium (*E*)-β-chlorocrotonate and sodium benzenethiolates by a similar method to that for **2a**.[7] The IR spectra and mp's of previously reported products, obtained by the reaction of benzenethiols with diketene in the presence of $H_2SO_4$, were in agreement with those of authentic samples (**2**), except for *m*-methoxy (**3a**) and 2,5-dimethoxy (**3b**) derivatives. No depression in melting point was observed in admixture of any pair of those samples. However, the melting points and IR spectra of *m*-methoxy and 2,5-dimethoxy derivatives are quite different from those of authentic samples. These compounds were assigned to (*Z*)-β-(arylthio)crotonic acid derivatives (**3**), as isomers of **2**, on the basis of NMR spectra of (*Z*)- and (*E*)-β-thio-substituted crotonates.[8] That is, the chemical shifts for the vinylic methyl group and vinylic proton for **3a** and **3b** showed upfield chemical shift of *ca.* 0.5 ppm for vinylic methyl group and downfield chemical shift of *ca.* 0.65 ppm for vinylic proton, compared to the corresponding values for authentic samples. From the results, the products obtained from the reaction of benzenethiols with diketene in the presence of $H_2SO_4$ are not **1**, described in previous paper, but the isomeric **2** and/

Table 1. The NMR spectra of *S*-phenyl 3-oxobutanethioates (**1**)

| Compound No. | X | NMR in $CCl_4$ (ppm) |
|---|---|---|
| **1f** | *m*-Cl | 1.95 and 2.25 (total 3H, each s), 3.65 and 5.50 (total *ca.* 1.2H, each s), 7.20—7.60 (4H, m), 12.20 (broad) |
| **1g** | 2,3-Benzo | 1.90 and 2.15 (total 3H, each s), 3.68 and 5.45 (total *ca.* 1.4H, each s), 7.20—8.20 (7H, m) |
| **1i** | 2,5-Dimethoxy | 1.90 and 2.18 (total 3H, each s), 3.73(3H, s), 3.75(3H, s), 3.52 and 5.36 (total *ca.* 1.2H, each s), 6.50—7.00 (3H, m) |
| **1j** | *p*-Br | 1.92 and 2.20 (total 3H, each s), 3.58 and 5.32 (total *ca.* 1.3H, each s), 7.00—7.55 (4H, m) 12.50 (broad) |

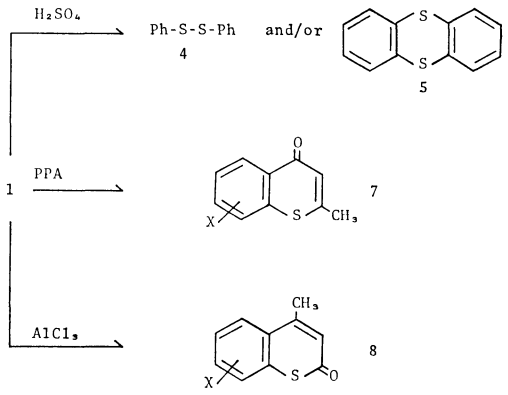
See Ref. 5 for **1a**—**e** and **1h**.

Table 2. Spectral data of 4-methyl(thiocoumarins) (**8**)

| Compound | X | NMR (ppm) in CDCl | $\nu_{CO}$ ($cm^{-1}$) | UV $\lambda_{max}$ ($\varepsilon \times 10^{-4}$) (nm) in EtOH | *m/e* (rel. intensity) |
|---|---|---|---|---|---|
| **8a** | H | 2.58 (3H, s)<br>6.62 (1H, s)<br>7.45—7.56 (3H, m)<br>7.95 (1H, m) | 1635 | 235 (2.5), 241 (2.5)<br>289 (0.7), 298 (0.7)<br>342 (0.29) | 176 (M, 46), 148 (M−28, 76)<br>147 (M−29, 100) |
| **8d** | 7-$CH_3$ | 2.44 (3H, s)<br>2.52 (3H, s)<br>6.53 (1H, s)<br>7.20—7.30 (2H, m)<br>7.78 (1H, d, $J$=10 Hz) | 1645 | 230 (2.4), 239 (2.4)<br>295 (0.8), 303 (0.9)<br>343 (0.4) | 190 (M, 45), 162 (M−28, 100)<br>161 (M−29, 100) |
| **8e** | 6-$CH_3$ | 2.50 (3H, s)<br>2.54 (3H, s)<br>6.62 (1H, s)<br>7.44 (2H, s)<br>7.78 (1H, s) | 1635 | 237 (2.8), 243 (3.0)<br>290 (0.8), 298 (0.8)<br>350 (0.3) | 190 (M, 48) 162 (M−28, 95)<br>161 (M−29, 100) |
| **8f** | 7-Cl | 2.54 (3H, s)<br>6.57 (1H, s)<br>7.20—7.50 (2H, m)<br>7.80 (1H, d, $J$=10 Hz) | 1645 | 233 (2.8), 241 (2.9)<br>266 (1.1), 290 (1.2)<br>301 (1.0), 337 (0.3) | 212 (M+2, 9), 210 (M, 24)<br>184 (40), 183 (47)<br>182 (M−28, 100), 181 (M−29, 90) |
| **8g** | 7,8-Benzo | 2.65 (3H, s)<br>6.68 (1H, s)<br>7.48—8.37 (6H, m) | 1650<br>1630 | 275 (2.6), 286 (2.5)<br>319 (0.6), 333 (0.6)<br>373 (0.24), 390 s (0.19) | 226 (M, 43), 198 (M−28, 100)<br>197 (M−29, 79) |
| **8h** | 5,6-Benzo | 2.60 (3H, s)<br>6.48 (1H, s)<br>7.25—8.30 (6H, m) | 1650 s<br>1630 | 246 (5.4), 281 (2.2)<br>295 (2.3), 333 (1.2)<br>380 b (0.2) | 226 (M, 64), 198 (M−28, 100)<br>197 (M−29, 57) |
| **8j** | 6-Br | 2.50 (3H, s)<br>6.50 (1H, s)<br>7.30—7.65 (2H, m)<br>7.88 (1H, d, $J$=2 Hz) | 1625 | 248 (4.5), 287 (0.65)<br>298 (0.60), 351 (0.28) | 256 (M+2, 71), 254 (M, 68),<br>228 (100), 227 (83),<br>226 (M−28, 98), 225 (M−29, 72) |
| **8k** | 6-Cl | 2.50 (3H, s)<br>6.50 (1H, s)<br>7.35 (2H, s)<br>7.74 (1H, s) | 1625 | 246 (4.5), 287 (0.65),<br>298 (0.60), 350 (0.29) | 212 (M+2, 28), 210 (M, 73)<br>184 (38), 183 (45),<br>182 (M−28, 100), 181 (M−29, 96) |

or **3**.

*S*-Phenyl 3-oxobutanethioates (**1**), precursor of thiocoumarins, were quantitatively prepared by the reaction of benzenethiols with diketene in the presence of triethylamine for 5—20 h at room temperature, and existed in a mixture of the keto-enol tautomeric forms, NMR spectra of which were shown in Table 1.




Scheme 2.

*The Reaction of* S-*Phenyl 3-Oxobutanethioates (**1**) with Various Condensing Agents.* The reaction of **1a** with sulfuric acid gave diphenyl disulfide (**4**) which was formed by decomposition of **1a**, and/or thianthrene derivatives (**5** and thianthrene 5,10-bis(dioxide) **6**) as oxidized products of **4**.

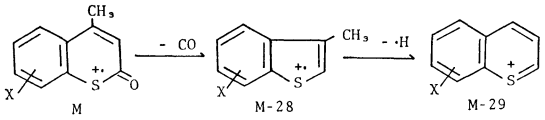
2-Methyl(thiochromone) derivatives (**7**), as the isomeric product of thiocoumarin, were preferentially obtained by treating **1** with polyphosphoric acid (PPA) at 70 °C. In the case of *m*-methoxy derivative (**1b**), only thiocoumarin **8b** was obtained. Compound **8b** also could be obtained from **2b** (X=*m*-$OCH_3$) and PPA. However, the other *S*-phenyl 3-oxobutanethioates, even with substituents such as methoxyl group(s) (**1c** and **1i**) gave the thiochromone **7** in yields of 10—79%. At lower temperatures of 5—10 °C, the same reaction of **1** afforded (*E*)-*β*-(arylthio)crotonic acid **2** (X=H, *m*-$CH_3$, or *p*-$CH_3$) in a low yield (4—10%). It is also known that the reaction of **1a** or **1d** with concd $H_2SO_4$ (1 equivalent) in $Et_2O$ gave **2** (X=H or *m*-$CH_3$) in a yield of 21%.[9] It is concluded that compound **2** will be an intermediate to give **7**.

In the case of the use of anhydrous aluminium chloride as a condensing agent, some of 4-methyl(thiocoumarins) (**8**) were conveniently obtained in yields of 10—48% and no 2-methyl(thiochromones) (**7**) were obtained. However, the reaction of all methoxy derivatives of **1** with $AlCl_3$ gave only an oily undetermined material, and none of thiocoumarins was isolated. As the direct reaction of **1** with $AlCl_3$, without solvent, was favorable as regards to yield.[5] some of **8** were prepared by this method. In the cases of reaction of **1a**, **1j**, and **1k** with the suspension

of $AlCl_3$, carbon disulfide or benzene was used as the solvent.

When $ZnCl_2$ was used as a condensing agents for **1a**, **4** was obtained in 11% yield. In the cases of other condensing agents such as $PCl_5$, $P_2O_5$, and $Ac_2O$, oily undetermined materials were obtained.

*Spectral Characteristics.* The NMR, IR, UV, and mass spectra of **8** are summarized in Table 2. In the mass spectra, the major fragmentation was initial loss of carbon monoxide from the molecular ion, followed by the loss of a hydrogen atom leading to the formation of the ring-expanded thianaphthalenium ion as shown in Scheme 3. There was not the M−40 fragment ion, which was found characteristically in the mass spectra of 2-methyl(thiochromones) (**7**).[4] The base peak of **8** was the M−28 or M−29 fragment ion (Table 2).




Scheme 3.

In the NMR spectra, the benzenoid proton at the 5-position of **8** showed the chemical shift in the range of 7.78—8.00 ppm. The difference between the proton at the 5-position and other aromatic protons was 0.34—0.53 ppm, whereas that of **7** was *ca.* 1.00 ppm.

In the IR spectra, the carbonyl bands of **8** were found in the range 1635—1650 $cm^{-1}$ and higher by 10—35 $cm^{-1}$ than those of the corresponding thiochromones, except for **8j** and **8k**.

The fluorescent spectra of **8** and **7** were generally very weak, compared to those of the corresponding coumarins.

## Experimental

All the melting points are uncorrected. IR spectra were recorded on a Hitachi ESI-S2 spectrophotometer using KBr pellts. $^1$H-NMR spectra were taken on a Hitachi R-24A spectrometer with tetramethylsilane as an internal standard. Mass spectra were recorded on a Hitachi RMU-6E mass spectrometer operating at 80 eV. The fluorescent spectra were recorded on a Hitachi MPF-2A fluorescent spectrophotometer. Elemental analyses were recorded on a Yanaco CHN recorder MT-2.

(E)-*β-(Arylthio)crotonic Acid Derivatives (2).* *Method A*: Concd $H_2SO_4$ (9.0 g) was added dropwise to $Et_2O$ (50 ml) solution of benzenethiol (5.0 g) at 30 °C. Diketene (5.0 g) was then added to this mixture. After 2 h, ether was removed *in vacuo* at 20 °C, and the residue was poured into an ice-water solution. White solid was separated, collected by filtration and recrystallized from EtOH to give **2a** (5.3 g). Other compounds **2** were prepared by a similar method. **2a**: 60%, mp 174.5—175.5 °C; **2c**: 5%, mp 172—175 °C; **2d**: 65%, mp 165—166 °C; **2e**: 60%, mp 204—205 °C; **2f**: 29%, mp 154—155 °C; **2g**: 10%, mp 198—202 °C; **2h**: 65%, mp 191—195 °C.

The NMR and IR spectra of these compounds corresponded to data of Table 3 described in previous paper.[4]

*Method B*: NaOH (1.2 g) was added to a solution of (*E*)-*β*-chlorocrotonic acid (2.0 g) in EtOH (10 ml). To the mixture, a solution of sodium *m*-methoxybenzenethiolate (*m*-methoxybenzenethiol (2.0 g)+NaOH (1.6 g)) in EtOH (5 ml) was added dropwise at 50 °C and stirred for 2 h. After cooling, dilute HCl was added to this solution until the pH was 1. The resulting solid was separated, and recrystallized from EtOH to give **2b** (X=*m*-$OCH_3$), yield 62%, mp 119—121 °C; NMR ($CDCl_3$): $\delta$=2.40 (3H, s), 3.80 (3H, s), 5.28 (1H, s), 6.90—7.30 (4H, m), and 10.2 (1H, b); $\nu_{CO}$: 1680 $cm^{-1}$. Found: C, 58.76; H, 5.48%. Calcd for $C_{11}H_{12}O_3S$: C, 58.93; H, 5.36%. **2i** (X=2,5-Dimethoxy): yield 50%, mp 126—128 °C; NMR ($CDCl_3$): $\delta$=2.40 (3H, s), 3.80 (3H, s), 3.83 (3H, s), 5.23 (1H, s), 6.95—7.10 (3H, m), and 10.80 (1H, b); $\nu_{CO}$: 1680 $cm^{-1}$. Found: C, 56.53; H, 5.59%. Calcd for $C_{12}H_{14}O_4S$: C, 56.69; H, 5.51%. Other compounds **2a** and **2c—h** were also prepared by a similar method in yields of 10—51%.

*(Z)-β-(Arylthio)crotonic Acid Derivatives (3).* Compound **3b** (X=2,5-dimethoxy) was prepared by the method A for **2a**: yield 22%, mp 169—171 °C; NMR ($CDCl_3$): $\delta$=1.90 (3H, s), 3.78 (3H, s), 3.83 (3H, s), 5.90 (1H, s), and 6.90—7.10 (3H, m); $\nu_{CO}$: 1675 $cm^{-1}$. Compound **3a** (X=*m*-$OCH_3$) was prepared by a similar method and isolated from the isomer mixture (**2b** and **3a**) by repeated recrystallization from EtOH. **3a**: mp 170—171 °C; NMR ($CDCl_3$): $\delta$=1.90 (3H, s), 3.80 (3H, s), 5.90 (1H, s), and 7.00—7.30 (4H, m).

*S-Phenyl 3-Oxobutanethioates (1).* Compound **1a** was quantitatively obtained from benzenethiol and diketene in the presence of $Et_3N$ in dichloromethane at room temperature for 20 h.[6] Other compounds **1b—k** were prepared similarly. All of compounds **1a—i** were colorless liquid, and **1j** and **1k** were recrystallized from $Et_2O$; **1j**: mp 51—53 °C; **1k**: mp 45 °C (lit,[6] 45—46 °C). Liquid **1** was used without purification for the cyclization with condensing agents.

*The Reaction of 1 with Concd $H_2SO_4$.* *Method I*: The mixed acid of 30% fuming $H_2SO_4$ (1.0 g) and concd $H_2SO_4$ (10 g) was added dropwise to **1a** (5.5 g) under stirring at 0 °C. The mixture was stirred at room temperature for 5 h, and was poured into an ice-water solution. The resulting solid was separated and recrystallized from EtOH to give diphenyl disulfide **4** (1.9 g): yield 61%, mp 58—59 °C.

*Method II*: Compound **1a** (5.0 g) was added dropwise to concd $H_2SO_4$ (20 ml) at 15 °C. The mixture was stirred for 5 h at 15 °C and was poured into an ice-water solution. The resulting solid was separated, washed with EtOH and acetone, and purified by acid-pasting to give thianthrene

Table 3. Elemental analyses of 4-methyl-(thiocoumarins) (**8**)

| Compound | Formula (MW) | Analysis (%) Calcd (Found) C | H |
|---|---|---|---|
| **8f** | $C_{10}H_7OSCl$ (210.5) | 57.01 (56.76) | 3.33 (3.28) |
| **8g** | $C_{14}H_{10}OS$ (226) | 74.34 (74.96) | 4.42 (4.51) |
| **8h** | $C_{14}H_{10}OS$ (226) | 74.34 (74.30) | 4.42 (4.49) |
| **8j** | $C_{10}H_7OSBr$ (254.9) | 47.08 (47.07) | 2.75 (2.69) |
| **8k** | $C_{10}H_7OSCl$ (210.5) | 57.01 (57.25) | 3.33 (3.40) |

5,10-bis(dioxide) **6** in 56% yield (mp>320 °C, lit,[10]> 360 °C). Found: C, 51.67; H, 2.97%. From the first filtrate in EtOH, thianthrene **5** was isolated in 4% yield; mp 152—154 °C (lit,[11] 157—159 °C).

*The Reaction of **1** with PPA.* Compound **1a** (3.0 g) was added to PPA (60 g) at 70 °C and stirred for 1—2 h. After cooling, the mixture was poured into an ice-water solution. The resulting solid was separated and recrystallized from EtOH–water mixture to give **7a** (1.8 g, 66%). Other **7** were similarly prepared. **7c**: X=6-$OCH_3$, 10%, mp 102—103 °C; **7d**: X=7-$CH_3$, 23%, mp 98—100 °C; **7e**: X=6-$CH_3$, 53%, mp 120 °C; **7f**: X=7-Cl, 25%, mp 165—166 °C; **7g**: X=7,8-benzo, 25%, mp 194—195 °C; **7h**: X=5,6-benzo, 15%, mp 126—128 °C; **7i**: X=5,8-dimethoxy, 79%, mp 146—148 °C; **7j**: X=6-Br, 23%, mp 181—182 °C (lit,[12] 176 °C); NMR ($CDCl_3$): $\delta$=2.43 (3H, s), 6.79 (1H, s), 7.23—7.70 (2H, m), and 8.55 (1H, d, $J$=2 Hz); $\nu_{co}$: 1623 $cm^{-1}$, Found: C, 46.87; H, 2.81%. $\lambda_{max}$ (EtOH): 224 ($\varepsilon$ $1.8\times10^4$), 252 ($2.5\times10^4$), 281 ($0.3\times10^4$), 292 ($0.3\times10^4$), and 342b nm ($0.8\times10^4$); **7k**: X=6-Cl, 34%, mp 164—166 °C (lit,[12] 170 °C); NMR ($CDCl_3$): $\delta$=2.46 (3H, s), 6.81 (1H, s), 7.48 (2H, s), and 8.43 (1H, s); $\nu_{co}$: 1628 $cm^{-1}$. Found: C, 57.13; H, 3.46%. $\lambda_{max}$ (EtOH): 223 ($\varepsilon$ $1.7\times10^4$), 250 ($2.4\times10^4$), 280 ($0.5\times10^4$), 291 ($0.4\times10^4$), and 342b nm ($0.9\times10^4$).

From the same reaction of **1a**, **1d**, and **1e** at 5—10 °C, **2a** (yield, 4%), **2d** (4%), and **2e** (10%) were isolated, respectively. Under the same conditions at 70 °C, **8b** (X=7-$OCH_3$) was obtained in 54% yield from **1b**.

*The Reaction of **1** with Aluminium Chloride.* *Method (i)*: Compound **1a** (3.0 g, 15 mmol) was added to a suspension of $AlCl_3$ (20 g) in $CS_2$ (20 ml). After reflux for 5 h, the mixture was poured into cold water. The resulting solid was separated and recrystallized from EtOH to give **8a** (1.0 g) in 38% yield, mp 126—127 °C (lit,[2] 124 °C). When benzene was used in the place of $CS_2$, **8j** and **8k** were obtained; **8j**: 27%, mp 184—185 °C; **8k**: 23%, mp 177—179 °C.

*Method (ii)*: Compound **1a** (3.0 g, 15 mmol) was added to $AlCl_3$ (20 g), and stirred at 80—90 °C for 2 h. After cooling, the mixture was poured into cold water. The resulting solid was separated and recrystallized from EtOH to give **8a** in 48% yield. The others of **8** were similarly obtained by the method (ii); **8d**: 42%, mp 108—109 °C (lit,[2] 110 °C); **8e**: 31%, mp 114—115 °C (lit,[2] 120 °C); **8f**: 22%, mp 157—158 °C; **8g**: 16%, mp 169—171 °C; **8h**: trace, mp 133—134 °C.

The elemental analyses of those compounds were shown in Table 3.

*The Fluorescent Spectra.* **8b**: $F_{max}$ (EtOH): 402 nm (rel. intensity based on **8b** as a standard); **8g**: $F_{max}$: 467 nm (1.5); **8h**: $F_{max}$: 405 (0.74) and 435 nm (0.66); **7b**[4] (X=7-$OCH_3$): $F_{max}$: 382 nm (2.0); **7g**: $F_{max}$: 398 nm (0.73); **7h**: $F_{max}$: 402 nm (0.6); **7i**; $F_{max}$: 494 nm ($2.9\times10$); 7-MeO-4-methylcoumarin: $F_{max}$: 410 nm ($2.7\times10^2$); 7,8-benzo-4-methylcoumarin:[3] $F_{max}$: 418 nm ($9.1\times10$); 5,6-benzo-4-methylcoumarin:[3] $F_{max}$: 403 nm ($9.6\times10^2$). The other thiocoumarins and thiochromones which were prepared herein showed no detectable fluorescence.

This work was supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education (No. 475675).

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