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Dedicated to the Memory of Professor Raymond N. Castle

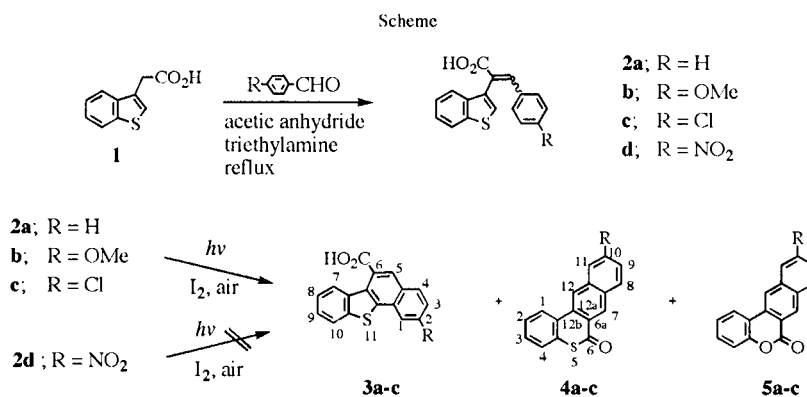
Naphtho[1,2-*b*][1]benzothiophene-6-carboxylic acids, 6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-ones and 6*H*-benzo[*b*]naphtho[2,3-*d*]pyran-6-ones were synthesized in one step by the photocyclization reaction of 3-aryl-2-([1]benzothien-3-yl)propenoic acids. The photocyclization reaction did not occur when the 3-aryl group contained the electron-withdrawing nitro group. The assignment of the ¹H and ¹³C nmr spectra of 6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one and 6*H*-benzo[*b*]naphtho[2,3-*d*]pyran-6-one by two-dimensional nmr methods is described. The difference between the chemical shift values of H12 for these two compounds is attributed to different molecular geometries.

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Stilbene-type compounds have been widely utilized as versatile intermediates for the synthesis of polycyclic derivatives in photocyclization reactions [1-3]. While the photocyclization of thiophene derivatives was being studied, it was found that a general oxidative reaction along with a new unexpected photocyclization reaction occurred. Previously one of our groups performed the photocyclization of 3-(4-methoxyphenyl)-2-(5-methyl[1]benzothien-3-yl)propenoic acid as a stilbene type derivative upon irradiation in a mixture of cyclohexane and benzene in the presence of iodine and air to afford the expected product, 2-methoxy-8-methylbenzo[*b*]naphtho[2,1-*d*]thiophene-6-carboxylic acid together with two unexpected rearrangement products, 10-methoxy-2-methyl-6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one and 10-methoxy-2-methyl-6*H*-benzo[*b*]naphtho[2,3-*d*]pyran-6-one [4]. Among these products benzonaphthothiophene-6-carboxylic acid was the expected photocyclized product, however, the latter two compounds were unusual rearrangement products. A similar photocyclization reaction was also performed employing 2-([1]benzothien-3-yl)-3-phenylpropenoic acid **2a** and its 5-methyl derivative as a starting material and corresponding benzonaphthothiophene-6-carboxylic acids (**3a** and its 5-methyl derivative)

and 6*H*-benzonaphthothiopyran-6-ones (**4a** and its 5-methyl derivative) were respectively obtained [4]. But in that case the corresponding pyran-6-one derivatives could not be obtained [4]. As a similar photo-rearrangement reaction only Riche *et al.* [5] had reported that irradiation of 2-(3-indolyl)-3-(4-pyridyl)propenitrile or its methyl ester gave the expected cyclized products, 11*H*-pyrido[3,4-*a*]carbazoles along with pyrido[3,4-*j*]phenanthridines. In their case the pyran-6-one derivative was not reported. Some groups have reported the synthesis of 6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one derivatives [6] or 6*H*-benzo[*b*]naphtho[2,3-*d*]pyran-6-one derivatives [7,8], however, no report using the photocyclization reaction for preparation of these compounds could be found. In this paper we described the study on the reactivity of this photocyclization rearrangement reaction. The total assignments of the ¹H and ¹³C nmr spectra of thiopyran and pyran derivatives were also determined.

The synthetic pathway to thiopyrans **4** and pyrans **5** is illustrated in the Scheme. 3-Aryl-2-([1]benzothien-3-yl)propenoic acids **2** [4] was employed as a key intermediate for the photocyclization. The reaction of [1]benzothien-3-ylacetic acid **1** [9] with the appropriate aldehyde in acetic



anhydride in the presence of triethylamine gave the corresponding **2**. In the ^1H nmr spectrum of **2** the methylene resonance at 3.88 ppm, which was observed in **1**, is not observed and a new resonance corresponding to the methine proton at about 8.1 ppm is observed, as expected for compound **2**. Irradiation of **2a** in a mixture of cyclohexane and benzene (9:1, v/v) containing iodine and air with a 500 watt high pressure mercury vapor lamp gave the desired cyclized products **3a** (73%) [4], **4a** (6%) [4] and **5a** (2%) [7,8] which could not be obtained in the previous report [4]. Similar irradiation of **2b,c** also gave the corresponding separable mixture of three compounds **3-5**. However, photocyclization of **2d** containing the electron withdrawing nitro group, on phenyl did not produce the desired cyclized product. The only product obtained showed the presence of a carboxyl group in its ir spectrum and was not identified.

Nmr Spectral Assignments for **4a** and **5a**.

Total nmr spectral assignments for **4a** and **5a** were performed as follows using 2D nmr spectroscopy. Some of the 2D experiments were acquired at a very low resolution in F1 (especially the pfg-HMBC experiment of the compound **4a**) because of the very small quantities of **4a** and **5a** obtained. The 2D analysis for compounds **4a** and **5a** required very long acquisition times even at low resolution.

Compound **4a** showed two singlets and two four-spin systems which allows the assignment from the ^1H - ^1H COSY spectrum using a pulsed field gradient probe (^1H - ^1H pfg-COSY) as shown in Figure 1. The most downfield shifted signal in these four-spin systems is the double doublet proton resonating at 8.33 ppm. Considering the structure of **4a**, this signal can be assigned as H1 based on its chemical shift which is typical of bay-region protons. The pfg-COSY shows that H1 is a member of the four-spin system consisting of signals resonating at 7.30 ppm, 7.34 ppm, 7.39 ppm and 8.33 ppm. Based on this observation, the assignment of these signals are easily performed and are H4 (7.30 ppm), H3 (7.34 ppm), H2 (7.39 ppm) and H1 (8.33 ppm). From the HMQC spectrum (pfg-HMQC) of **4a** shown in Figure 2 the corresponding protonated carbons (C1-C4) can be assigned directly. For compound **4a**, the carbon signal resonating at 186.8 ppm can be assigned to the carbonyl carbon at position 6. Both singlets (8.61 ppm and 8.82 ppm) showed a long range coupling with the carbonyl carbon in the pfg-HMBC shown in Figure 3. The correlation between the proton signal at 8.82 ppm and C6 carbonyl carbon signal is stronger than that between the signal at 8.61 ppm and C6. As a result, the signal at 8.82 ppm could be tentatively assigned to H7, which shows a three bond coupling with C6, and the other signal at 8.61

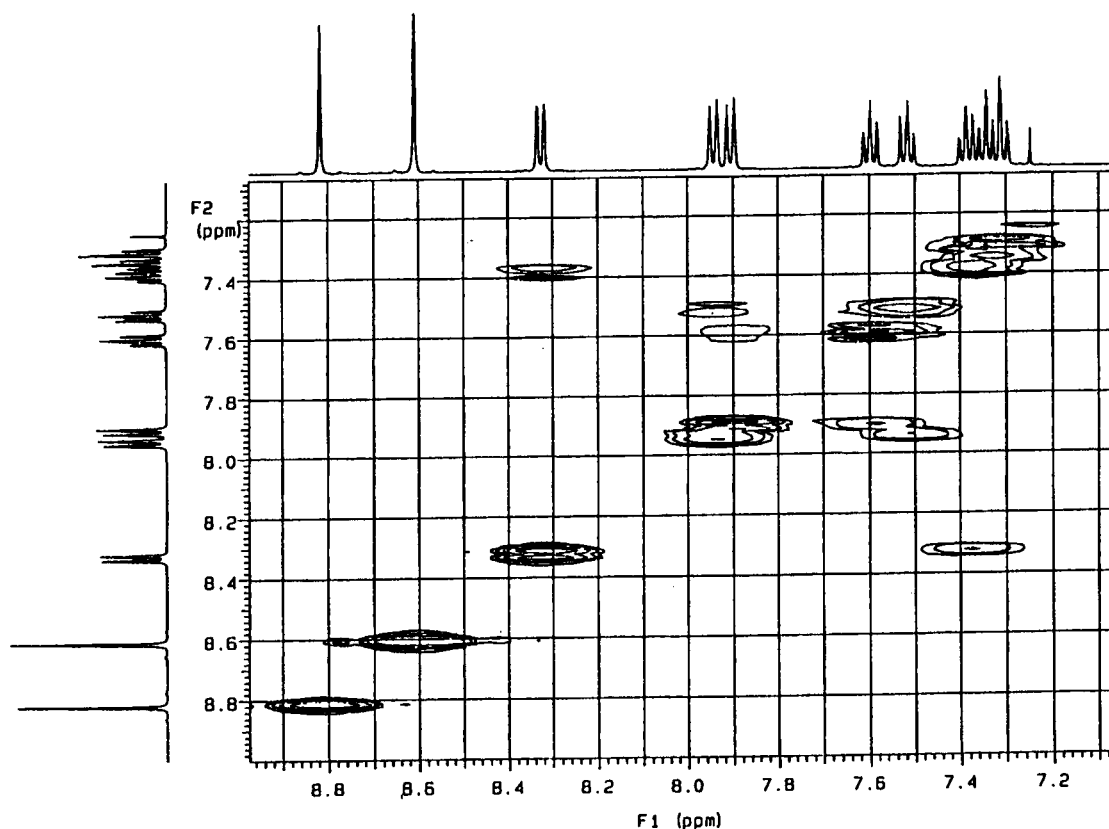


Figure 1. ^1H - ^1H pfg-COSY Spectrum of **4a**.

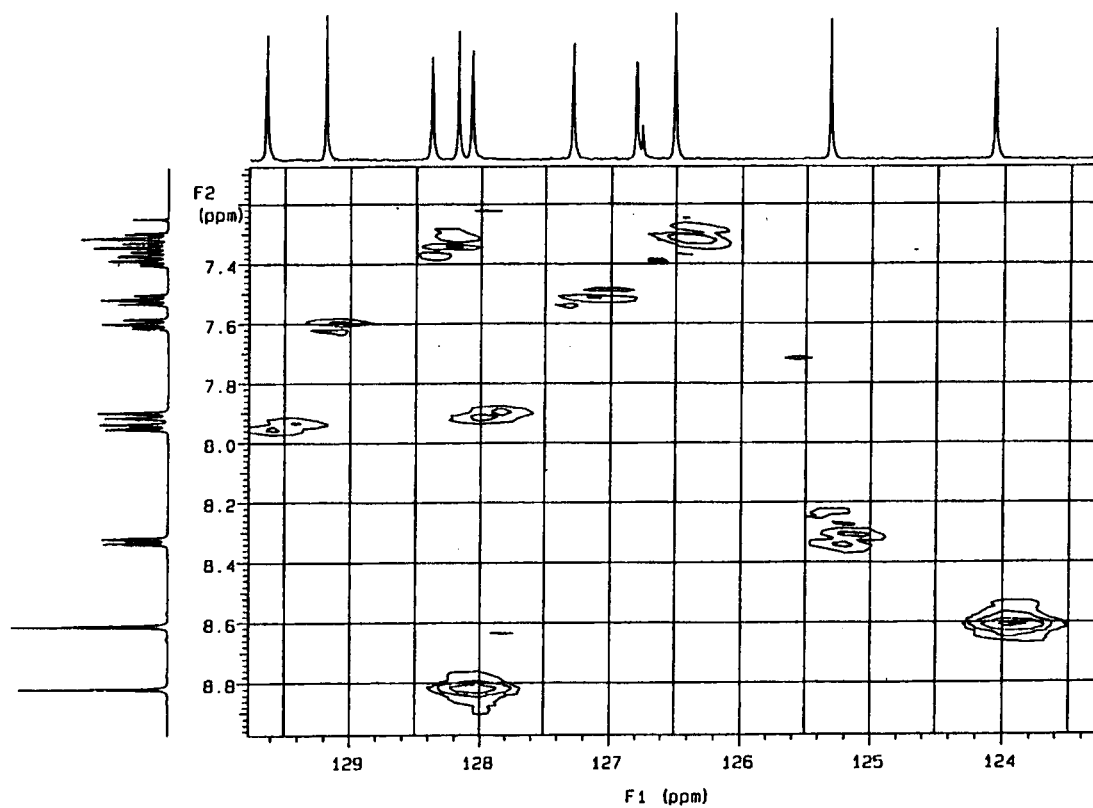


Figure 2. pfg-HMQC Spectrum of 4a.

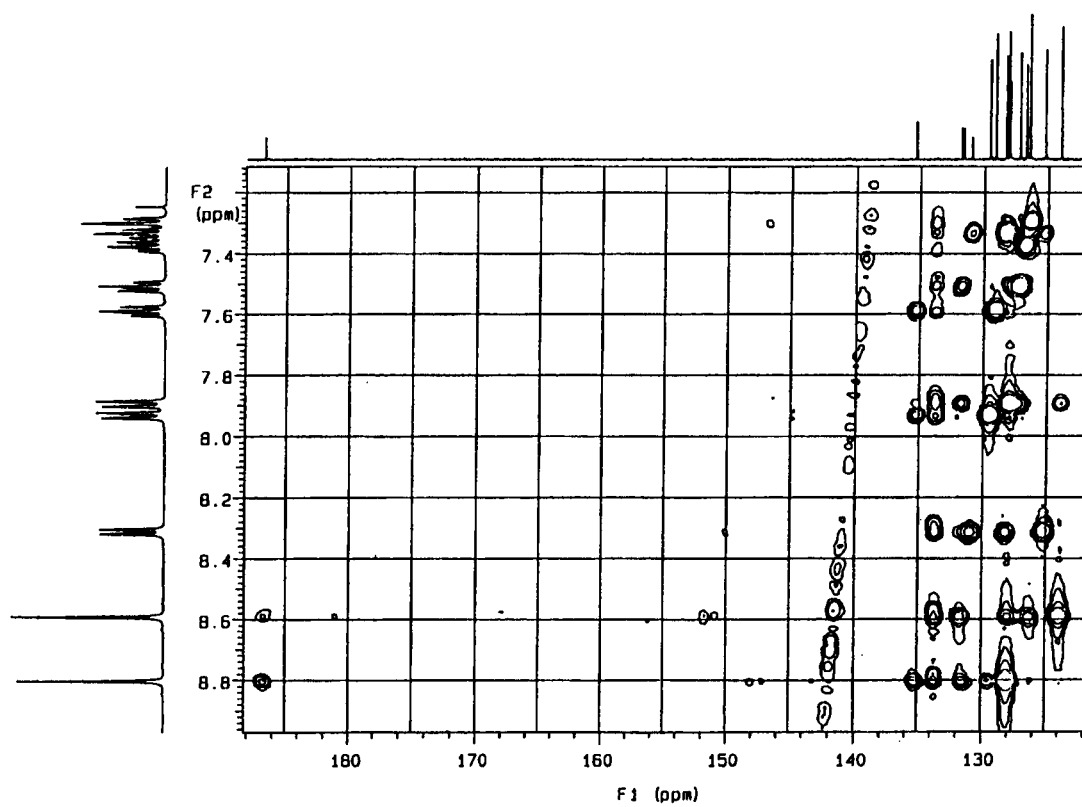


Figure 3. pfg-HMBC Spectrum of 4a.

ppm could be assigned as H12. The carbon signals that have correlation with H7 are observed at 135.4 ppm, 131.7 ppm and 129.6 ppm except C6 and C7. Among these signals only the signal at 129.6 ppm correspondings to a protonated carbon. Therefore this signal could be attributed to C8. From this assignment, H8 (7.94 ppm) could be automatically assigned from the pfg-HMQC spectrum, and H9-H11 which are members of the four-spin system that includes H8 could be also assigned directly from the ^1H - ^1H pfg-COSY spectrum as H9 (7.52 ppm), H10 (7.60 ppm), H11 (7.90 ppm) respectively. A nuclear Overhauser enhancement (nOe) experiment was also performed to differentiate between H7 and H12 unequivocally, and indeed, saturation of the signal resonating at 8.61 ppm enhanced signals corresponding to H1 and H11. Therefore, the signal at 8.61 ppm could be unequivocally assigned as H12. At this stage one can complete the assignment of the ^1H nmr spectrum. All protonated carbons were also easily assigned by use of the pfg-HMQC spectrum. With the protons and protonated carbons assigned, the quaternary carbons can easily be assigned. As described above, in the pfg-HMBC spectrum, the quaternary carbon signals that have correlation with H7 are observed at 135.4 ppm and 131.7 ppm, and are attributed to C11a and C12a, both of which have three bond couplings with H7. Of these two signals, the carbon resonating at 135.4 ppm has a correlation with H8 in the pfg-HMBC spectrum. Therefore the quaternary carbon resonating at 135.4 corresponds to C11a, and the other carbon resonance at 131.7 ppm corresponds to C12a. The quaternary carbon at 131.8 ppm showed couplings to H9, H11 and H12 in the pfg-HMBC spectrum, so that, this carbon could be assigned to C7a. The carbon at 131.0 ppm that correlates with H1 and H3 was assigned as C4a. The number of carbon signals shown in the ^{13}C nmr spectrum of **4a** is 16, however, the number of the carbon of **4a** is 17. This means one carbon signal is completely overlapped on another one. At this point, the unassigned signal in the ^{13}C nmr spectrum is the quaternary carbon resonating at 126.8 ppm, and the unidentified carbons of **4a** are C12b and C6a. Both C6a and C12b should have the correlations with H7 (H7-C6a is two bonds, and H7-C12b is four bonds and zigzag pattern) and H12 (both H12-C6a and H12-C12b are three bonds), respectively. So, the attention was paid to the protonated carbon resonating at 126.5 ppm for assignment of these two carbons. This signal has already been assigned as C4 from the consideration of the pfg-HMQC spectrum. It is impossible for C4 to have the correlations with H7 (H7-C4 is six bonds and non-zigzag pattern) and H12 (H12-C4 is five bonds and non-zigzag pattern) in the pfg-HMQC spectrum. However, the "protonated" carbon resonating at 126.5 ppm shows an obvious long range correlation with H12 and also a weak long range correlation with H7 in the pfg-HMQC spectrum of **4a**. Therefore the signals corresponding to C6a or C12b are overlapped with that of C4. Furthermore, we postulate that the signal resonating at

126.5 ppm corresponds to C6a and the other carbon at 126.8 ppm to C12b, based on the fact that the correlation between H12 (8.61 ppm) and the signal resonating at 126.5 ppm is obviously stronger than the correlation between H12 and the signal at 126.8 ppm. This observation is consistent with the relation between H12 and C12b being three bonds in a non-zigzag pattern whereas that between H12 and C6a is three bonds and a zigzag pattern. Hence, the correlation between H12 and C6a should be stronger than that of in H12 and C12b. Proton and ^{13}C chemical shifts assignments for **4a** are listed in Table 1.

Table 1
 ^1H and ^{13}C Chemical Shifts, Coupling Pattern, Coupling Constants (Hz) and Long Range Correlation of 6*H*-Benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one (**4a**)

Position	δH	δC	Long Range Correlation
1	8.33 (dd, $J = 7.9, 1.5$)	125.3	H3
2	7.39 (td, $J = 7.9, 1.5$)	126.8	H4
3	7.34 (td, $J = 7.9, 1.5$)	128.4	H1
4	7.30 (dd, $J = 7.9, 1.5$)	126.5	H2
4a		131.0	H1, H3
6		186.8	H7
6a		126.5	H12
7	8.82 (s)	128.2	H8
7a		131.8	H9, H11, H12
8	7.94 (d, $J = 8.2$)	129.6	H7, H10
9	7.52 (ddd, $J = 8.2, 7.0, 1.2$)	127.3	H11
10	7.60 (ddd, $J = 8.2, 7.0, 1.2$)	129.2	H8
11	7.90 (d, $J = 8.2$)	128.1	H9, H12
11a		135.4	H7, H8, H10
12	8.61 (s)	124.1	H11
12a		131.7	H1, H7
12b		126.8	H2, H4, H12

The assignments of all ^1H and ^{13}C nmr of **5a** were performed in a similar manner as described above. At first, the most downfield shifted proton of double doublet resonating at 8.19 ppm in its ^1H nmr spectrum was assigned as H1. The pfg-COSY spectrum of **5a** (Figure 4) shows that this proton is a member of the four-spin system composed of signals resonating at 7.35 ppm, 7.36 ppm, 7.46 ppm and 8.19 ppm. With H1 identified, the assignment of the remaining protons in this four-spin system can be achieved through the consideration of their orientation relative to one another in the molecular framework. The corresponding protonated carbons C1-C4 could be assigned based on correlation observed in the pfg-HMQC spectrum shown in Figure 5. In the ^{13}C nmr spectrum of **5a**, the most downfield shifted quaternary carbon is assigned as the carbonyl carbon C6. The pfg-HMBC spectrum (Figure 6) shows that this carbon only correlates with the proton resonating at 8.99 ppm, and the only hydrogen that is separated from C6 by three bonds distance is H7. Therefore, this proton corresponds to H7,

and the other unassigned singlet, resonating at 8.50 ppm, then must correspond to H12. After assignment of these two singlet protons C7 and C12 were assigned directly from correlations observed in the pfg-HMQC spectrum. Furthermore, the pfg-HMBC spectrum showed that H7 has correlations with two quaternary and two protonated carbons other than C6. One of these two protonated carbons is C7 (one bond coupling) and the other should be C8. Two quaternary carbons are C11a and C12a but it is impossible to differentiate between them at this stage. The assignment of C8 (129.6 ppm) showed that the proton of broad doublet resonating at 8.02 ppm corresponds to H8 by use of the pfg-HMQC spectrum. Assignments of the remaining three protons (H9, H10 and H11) in the four-spin system including H8 are made by correlations observed in the ^1H - ^1H pfg-COSY spectrum. Carbons 9-11 were also assigned directly from correlations with protons 9-11 in the pfg-HMQC spectrum. As described for **4a**, an nOe experiment was performed to unequivocally differentiate between H7 and H12. Saturation of the signal resonating at 8.50 ppm enhanced signals corresponding to H1 and H11. Therefore, this signal at 8.50 ppm could be unequivocally assigned as H12. At this stage, all protons and protonated carbons are completely assigned.

The protons at positions 2 and/or 4 and 12 all correlate with the quaternary carbon resonating at 118.4 ppm showing that this carbon corresponds to C12b. On the other hand, this fact (the correlation with C12b and the subsequent correlations of C12b with H2 and H4) also could prove the identity of H12. The quaternary carbon resonating at 150.9 ppm showed obvious couplings with H1 and H3 and a weak coupling to H4 (or H2). As a result, this carbon could be assigned as C4a. Similarly the carbon at 136.2 ppm having obvious couplings with H7, H8 and H10 was easily assigned to C11a. Likewise, the carbon resonating at 132.5 ppm showed couplings with H12, H11 and H9 and was assigned to C7a. At this stage, two unassigned carbon signals remain (129.7 ppm and 119.3 ppm) and the unidentified quaternary carbons in the structure of **5a** are C6a and C12a. The pfg-HMBC spectrum shows that of these two signals, the carbon resonating at 119.3 ppm correlates with H12. On the other hand the coupling of the carbon resonating at 129.7 ppm with H1 or H7 is ambiguous because the correlations of C3 and C8 with H1 and H7 respectively inhibited the accurate analysis of the coupling of that carbon. However this quaternary carbon did not show a correlation with H12. Therefore, the carbon at 129.7 ppm is assigned as C12a and the other carbon resonating at 119.3

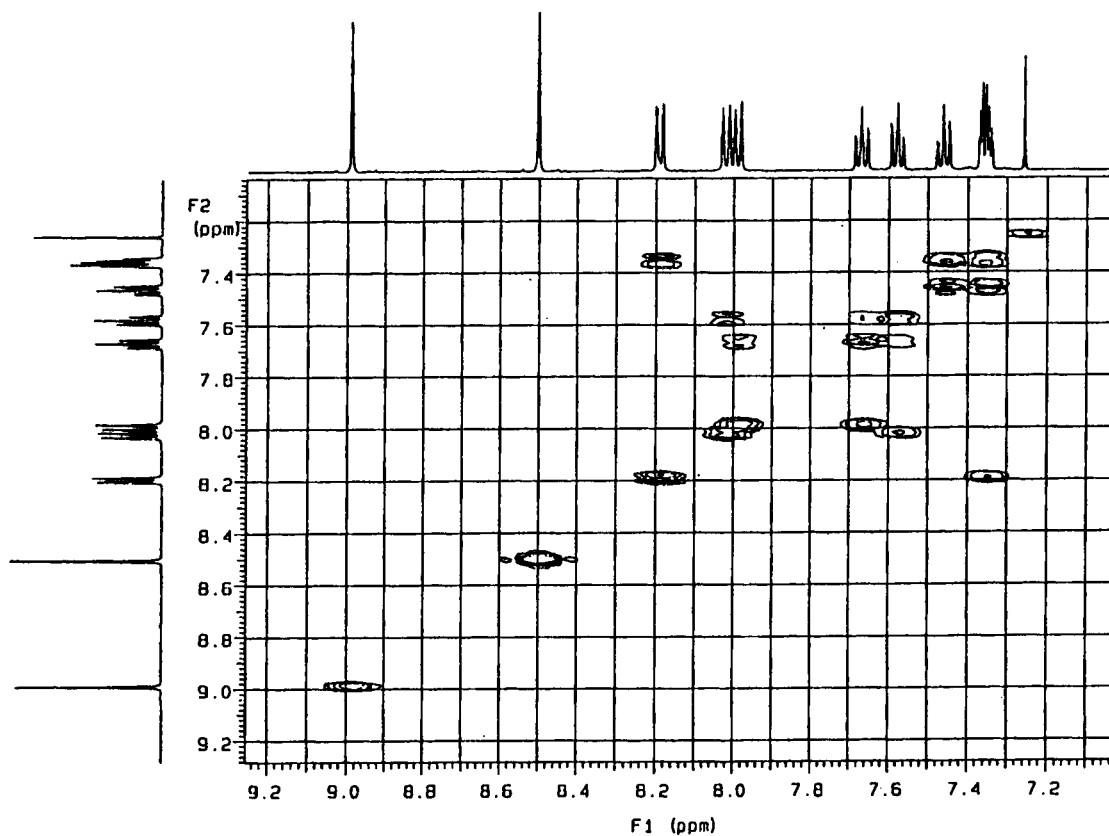


Figure 4. ^1H - ^1H pfg-COSY Spectrum of **5a**.

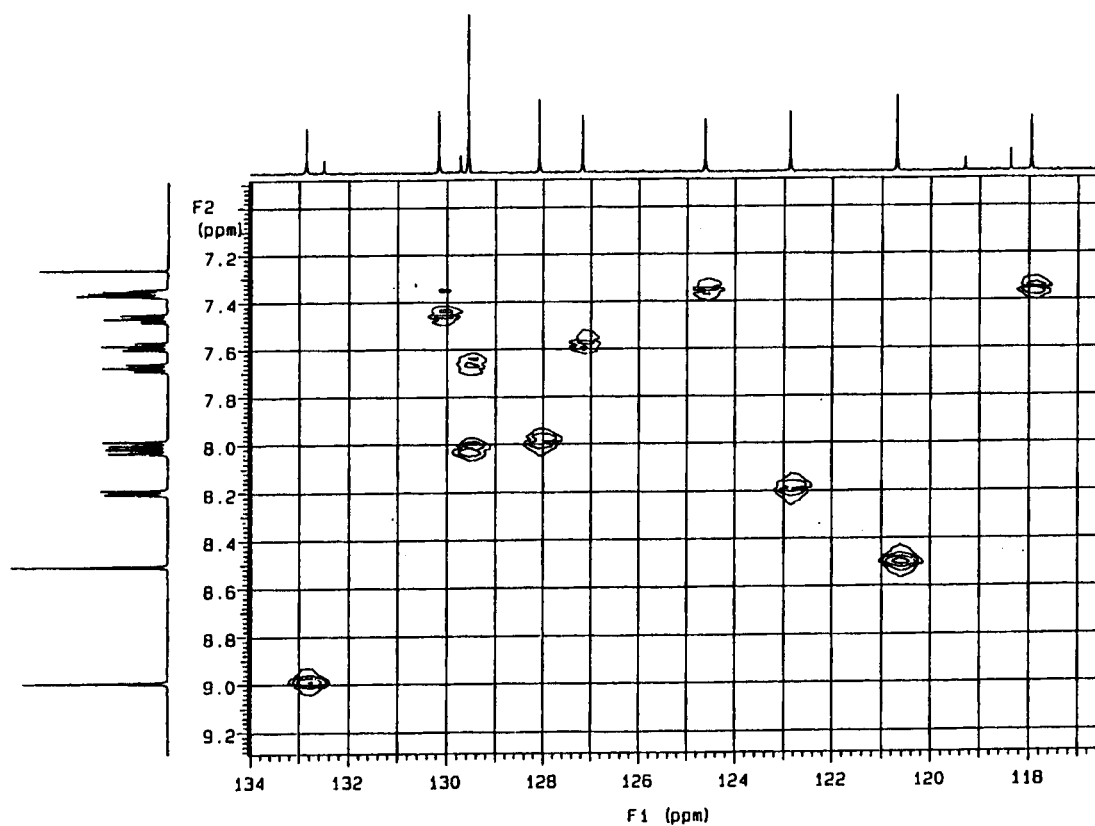


Figure 5. pfg-HMQC Spectrum of 5a.

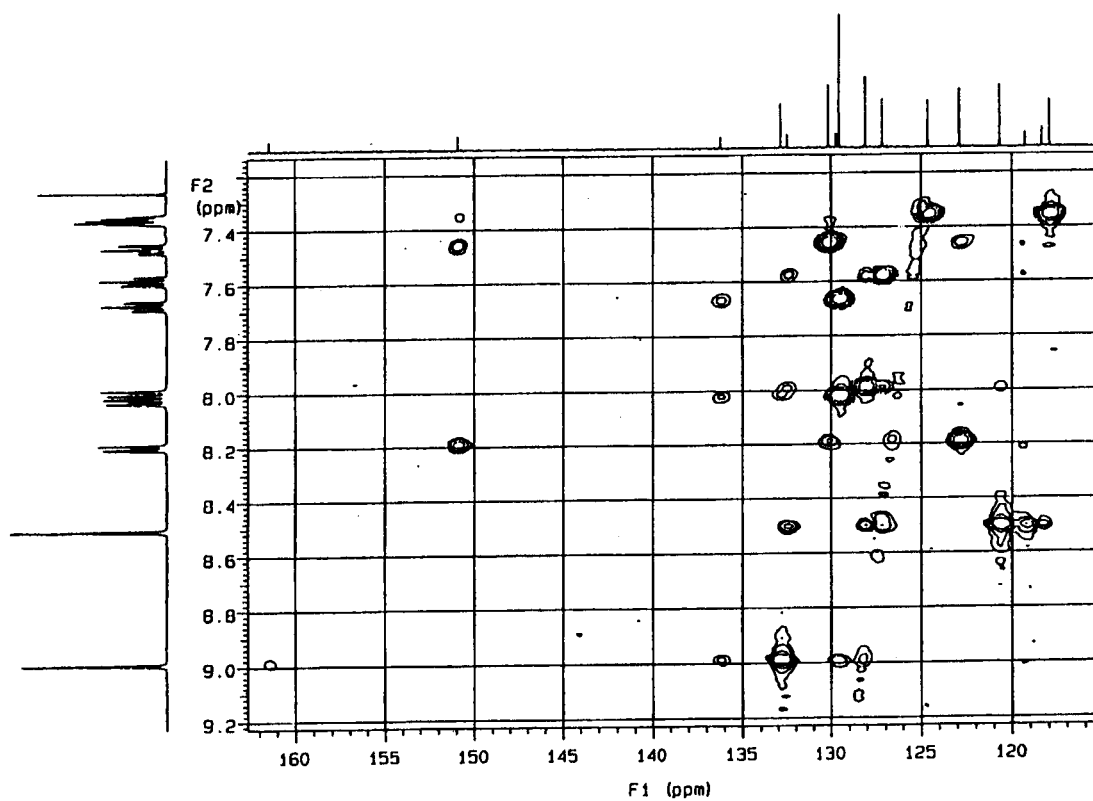


Figure 6. pfg-HMBC Spectrum of 5a.

Table 2
¹H and ¹³C Chemical Shifts, Coupling Pattern,
 Coupling Constants (Hz) and Long Range Correlation of
 6*H*-Benzo[*b*]naphtho[2,3-*d*]pyran-6-one (5a)

Position	δH	δC	Long Range Correlation
1	8.19 (dd, <i>J</i> = 7.9, 1.2)	122.9	H3
2	7.35 (td, <i>J</i> = 7.9, 1.2)	124.6	H4
3	7.46 (td, <i>J</i> = 7.9, 1.2)	130.2	H1
4	7.36 (dd, <i>J</i> = 7.9, 1.2)	117.9	H2
4a		150.9	H1, H3
6		161.4	H7
6a		119.3	H12
7	8.99 (s)	132.9	H8
7a		132.5	H9, H11, H12
8	8.02 (br d, <i>J</i> = 8.2)	129.6	H7, H10
9	7.58 (ddd, <i>J</i> = 8.2, 7.0, 1.2)	127.2	H11
10	7.67 (ddd, <i>J</i> = 8.2, 7.0, 1.2)	129.6	H8
11	7.99 (br d, <i>J</i> = 8.2)	128.1	H9, H12
11a		136.2	H7, H8, H10
12	8.50 (s)	120.7	H11
12a		129.7	H1, H7
12b		118.4	H2, H4, H12

ppm is assigned as C6a. Finally these chemical shift assignments are presented in Table 2.

The geometrical structures of **4a** and **5a** have been investigated by the use of semiempirical calculations using PM3 parameters [10]. The PM3 calculations give distances between H1 and H12 of 1.720 Å for **4a** and 1.847 Å for **5a**, that is to say, the distance in **4a** is closer than that in **5a**. Furthermore the dihedral angle of O6-C6-C7-H7 is 3.816° for **4a** and 0.467° for **5a**. That is, the angle of **5a** is smaller than that of **4a**. These results are consistent with the data of their ¹H nmr spectra, in which H1 and H12 of **4a** experiences the anisotropic effect of the benzene ring to a greater extent than those of **5a** and hence resonate further downfield. The proton at position 7 of **5a** also experiences a greater anisotropic effect from the carbonyl group than that of **4a** and as a result resonates farther downfield.

EXPERIMENTAL

All melting points were determined on a Yanagimoto micro-melting point apparatus, and are uncorrected. The ir spectra were recorded on a Japan Spectroscopic IRA-102 diffraction grating infrared spectrophotometer and frequencies are expressed in cm⁻¹. The FAB-mass spectra was measured on a VG 70 mass spectrometer. Elemental analyses were performed on a Yanagimoto MT-5 CHN Corder elemental analyzer. The ¹H nmr spectrum at 60 MHz was recorded on a Hitachi R-1500 FT-nmr spectrometer and the ¹H nmr spectra at 200 MHz and 500 MHz were acquired on a Varian VXR-200 and -500 instruments in the solvent indicated with tetramethylsilane as the internal standard. All experiments were taken at 45 °C. Chemical shifts are given in ppm (δ) and *J* values in Hz, and the signals are designated as follow; s, singlet; d, doublet; dd, doublet doublet; ddd, doublet doublet doublet; t, triplet; td, triplet doublet; m, multiplet. The ¹H-¹H COSY, HMQC, and HMBC experiments were performed using a pulsed field gradient probe (proton 90 ° pulse = 14.5, carbon 90 ° pulse =

16.5). The pfg-HMQC experiment was performed using Varian pulse program optimized for direct coupling (140 Hz, ¹J_{CH}). The pfg-HMBC experiment was performed using the Varian pulse program optimized for 8 Hz ³J_{CH} coupling. The semiempirical PM3 calculation was carried out with the use of CAChe MOPAC system (ver. 94). The ground-state structure was minimized until a gradient norm of less than 0.01 kcal mol⁻¹ Å⁻¹ was achieved.

General Procedure for Preparation of 3-Aryl-2-([1]benzothien-3-yl)propenoic Acids (2).

To a solution of [1]benzothien-3-ylacetic acid (**1**, 1.92 g, 10 mmol) [**9**] in acetic anhydride (2 ml) were added triethylamine (1 ml) and aldehyde (11 mmol), and the mixture was refluxed under stirring. When the crystals were precipitated in this step the crystals were collected *in vacuo*. Otherwise, the reaction mixture was poured into ice water (50 ml) and the mixture was extracted with ether. The organic layer was washed with 10% hydrochloric acid and extracted with 10% aqueous sodium hydroxide. The aqueous layer was acidified with 10% hydrochloric acid. After the mixture stood for a while crystals precipitated and were collected *in vacuo* and recrystallized to give the title compound.

2-([1]Benzothien-3-yl)-3-phenylpropenoic Acid (**2a**).

Benzaldehyde was used as aldehyde. The reaction time was 4 hours. Recrystallization from chloroform-*n*-hexane (1:3, v/v) gave **2a** (1.65 g, 59%) as colorless prisms, mp 154.5-156 °C (lit. [4] 148-150 °C). Ir: 3000 (OH), 1675 (CO) cm⁻¹; ¹H-nmr (60 MHz, deuteriochloroform): δ 7.11 (5H, br s, H-phenyl), 6.97-7.56 (4H, m, H2', H4', H5' and H6'), 7.81-7.93 (1H, m, H7'), 8.18 (1H, s, H3), near 9.0 (1H, br, OH). FAB-ms *m/z*: 281 [MH]⁺, 280 [MH-H]⁺.

2-([1]Benzothien-3-yl)-3-(4-methoxyphenyl)propenoic Acid (**2b**).

4-Methoxybenzaldehyde was used as aldehyde. The reaction time was 18 hours. Recrystallization from benzene gave **2b** (1.74 g, 56%) as yellow needles, mp 170-171 °C (sublim. around 150 °C). Ir: 3000 (OH), 1675 (CO) cm⁻¹; ¹H-nmr (60 MHz, deuteriochloroform): δ 3.66 (3H, s, OCH₃), 6.59 (2H, d, *J*_{3',2'} = *J*_{5',6'} = 9 Hz, H3" and H5"), 7.00 (2H, d, *J*_{2',3'} = *J*_{6',5'} = 9 Hz, H2" and H6"), 7.18-7.52 (4H, m, H2', H4', H5' and H6'), 7.80-7.94 (1H, m, H7'), 8.13 (1H, s, H3), near 10.6 (1H, br, OH). FAB-ms *m/z*: 311 [MH]⁺, 310 [MH-H]⁺.

Anal. Calcd. for C₁₈H₁₄O₃S·1/10C₆H₆: C, 70.21; H, 4.63. Found: C, 70.32; H, 4.80.

2-([1]Benzothien-3-yl)-3-(4-chlorophenyl)propenoic Acid (**2c**).

4-Chlorobenzaldehyde was used as aldehyde. The reaction time was 20 hours. Recrystallization from benzene gave **2c** (1.63 g, 52%) as yellow prisms, mp 183-184 °C (sublim. around 164 °C). Ir: 3000 (OH), 1675 (CO) cm⁻¹; ¹H-nmr (200 MHz, deuteriochloroform): δ 6.98 (2H, d, *J*_{3',2'} = *J*_{5',6'} = 8.8 Hz, H3" and H5"), 7.00 (2H, d, *J*_{2',3'} = *J*_{6',5'} = 8.8 Hz, H2" and H6"), 7.23-7.40 (2H, m, H5' and H6'), 7.32 (1H, s, H2'), 7.47 (1H, dd, *J*_{4',5'} = 7.5 Hz, *J*_{4',6'} = 1.4 Hz, H4'), 7.90 (1H, dd, *J*_{7,6'} = 7.7 Hz, *J*_{7,5'} = 1.4 Hz, H7'), 8.11 (1H, s, H3). FAB-ms *m/z*: 317 [(M+2)H]⁺ (7%), 316 [(M+2)H-H]⁺ (18%), 315 [MH]⁺ (21%), 314 [MH-H]⁺ (100%).

Anal. Calcd. for C₁₇H₁₁ClO₂S·1/20C₆H₆: C, 65.20; H, 3.57. Found: C, 65.23; H, 3.88.

2-([1]Benzothien-3-yl)-3-(4-nitrophenyl)propenoic Acid (**2d**).

4-Nitrobenzaldehyde was used as aldehyde. The reaction time was 15 minutes. Recrystallization from chloroform-*n*-hexane (1:3, v/v) gave **2d** (2.08 g, 64%) as yellow powder, mp 194-195 °C

(sublim. around 178 °C). ir (Nujol): 3000 (OH), 1680 (CO), 1520 (NO₂) cm⁻¹; ¹H-nmr (60 MHz, DMSO-*d*₆): δ 7.18 (2H, d, *J*_{2',3'} = *J*_{6',5'} = 9 Hz, H2'' and H6''), 7.31-7.47 (4H, m, H2', H4', H5'' and H6'), 7.96 (3H, d, *J*_{7,6'} = 9 Hz, *J*_{3'',2''} = *J*_{5'',6''} = 9 Hz, H7', H3'' and H5''), 8.18 (1H, s, H3), 9.9 (1H, br s, OH). FAB-*m/z*: 326 [MH]⁺, 325 [MH-H]⁺.

Anal. Calcd. for C₁₇H₁₁NO₄S·1/4H₂O: C, 61.90; H, 3.51; N, 4.25. Found: C, 61.76; H, 3.42; N, 4.11.

General Procedure for Preparation of Cyclized Products.

A solution of **2** (500 mg) in proper solvent (500 ml) containing iodine (100 mg, 0.39 mmol) was irradiated for 1 hour with a 500 watt high pressure mercury lamp under bubbling of air. Precipitated crystalline solid was collected *in vacuo*. The filtrate was evaporated *in vacuo*. The residue was combined with the precipitated solid and chromatographed on silica gel to give cyclized products **3**, **4** and **5**.

Photocyclization Reaction of **2a** (500 mg, 1.79 mmol).

A mixture of cyclohexane and benzene (9:1, v/v) was used as the solvent.

(Naphtho[1,2-*b*][1]benzothiophene-6-carboxylic Acid (**3a**)).

This compound was eluted with *n*-hexane-ethyl acetate (15:1, v/v). Recrystallization from benzene to give **3a** (363 mg, 73%) as yellow powder, mp 238-240 °C (lit. [4] 236-239 °C) (sublim. around 185 °C). Ir: 3000 (OH), 1690 (CO) cm⁻¹; ¹H-nmr (200 MHz, DMSO-*d*₆): δ 7.54-7.62 and 7.69-7.84 (each 2H, each m, H2, H3, H8 and H9), 8.17-8.24 (2H, m, H7 and H10), 8.30 (1H, s, H5), 8.42-8.46 (1H, m, H1), near 13.7 (1H, br, OH). FAB-*m/z*: 279 [MH]⁺, 278 [MH-H]⁺.

Anal. Calcd. for C₁₇H₁₀O₂S·1/4H₂O: C, 72.20; H, 3.74. Found: C, 72.15; H, 4.00.

6*H*-Benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one (**4a**)).

This compound was eluted with *n*-hexane-ethyl acetate (150:1, v/v). Recrystallization from methanol to give **4a** (28 mg, 6%) as yellow needles, mp 174-175 °C (lit. [4] 170-172 °C) (sublim. around 154 °C). Ir: 1740, 1720, 1685 (CO) cm⁻¹. FAB-*m/z*: 263 [MH]⁺.

Anal. Calcd. for C₁₇H₁₀OS·1/5H₂O: C, 76.78; H, 3.94. Found: C, 76.87; H, 4.08.

6*H*-Benzo[*b*]naphtho[2,3-*d*]pyran-6-one (**5a**)).

This compound was eluted with *n*-hexane-ethyl acetate (100:1, v/v). Recrystallization from ethanol to give **5a** (9 mg, 2%) as yellow needles, mp 185-186 °C (lit. [7] 186 °C, [8] 177-178 °C) (sublim. around 151 °C). Ir: 1730 (CO) cm⁻¹. FAB-*m/z*: 247 [MH]⁺.

Anal. Calcd. for C₁₇H₁₀O₂·1/5C₂H₅OH: C, 81.80; H, 4.42. Found: C, 82.08; H, 4.64.

Photocyclization Reaction of **2b** (500 mg, 1.61 mmol).

A mixture of cyclohexane and benzene (4:1, v/v) was used as the solvent.

2-Methoxynaphtho[1,2-*b*][1]benzothiophene-6-carboxylic Acid (**3b**)).

This compound was eluted with *n*-hexane-ethyl acetate (10:1, v/v). Recrystallization from benzene to give **3b** (307 mg, 62%) as yellow needles, mp 238-239 °C (sublim. around 206 °C). Ir: 3000 (OH), 1695 (CO) cm⁻¹; ¹H-nmr (200 MHz, DMSO-*d*₆): δ 4.01

(3H, s, OCH₃), 7.31-7.41 and 7.52-7.56 (each 2H, each m, H3, H4, H8 and H9), 8.10-8.14 (2H, m, H1 and H7), 8.26 (1H, s, H5), 8.49-8.53 (1H, m, H10), near 13.5 (1H, br, OH). FAB-*m/z*: 309 [MH]⁺, 308 [MH-H]⁺.

Anal. Calcd. for C₁₈H₁₂O₃S: C, 70.11; H, 3.92. Found: C, 69.93; H, 4.23.

10-Methoxy-6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one (**4b**)).

This compound was eluted with *n*-hexane-ethyl acetate (150:1, v/v). Recrystallization from ethyl acetate to give **4b** (24 mg, 5%) as yellow prisms, mp 212-213 °C (sublim. around 186 °C). Ir: 1730, 1710, 1690 (CO) cm⁻¹; ¹H-nmr (200 MHz, deuteriochloroform): δ 4.00 (3H, s, OCH₃), 7.22-7.27 and 7.41-7.49 (each 2H, each m, H2, H3, H4 and H9), 7.42 (1H, s, H11), 7.95 (1H, d, *J*_{8,9} = 9.9 Hz, H8), 8.44-8.49 (1H, m, H1), 8.66 (1H, s, H12), 8.88 (1H, s, H7). FAB-*m/z*: 293 [MH]⁺.

Anal. Calcd. for C₁₈H₁₂O₂S·1/4H₂O: C, 72.83; H, 4.24. Found: C, 73.00; H, 4.32.

10-Methoxy-6*H*-benzo[*b*]naphtho[2,3-*d*]pyran-6-one (**5b**)).

This compound was eluted with *n*-hexane-ethyl acetate (100:1, v/v). Recrystallization from ethanol to give **5b** (27 mg, 6%) as yellow needles, mp 196-198 °C (sublim. around 173 °C). Ir: 1720 (CO) cm⁻¹; ¹H-nmr (200 MHz, deuteriochloroform): δ 4.01 (3H, s, OCH₃), 7.22-7.53 (5H, m, H2, H3, H4, H9 and H11), 7.94 (1H, d, *J*_{8,9} = 9.9 Hz, H8), 8.20 (1H, dd, *J*_{1,2} = 8.0 Hz, *J*_{1,3} = 1.8 Hz, H1), 8.41 (1H, s, H12), 8.93 (1H, s, H7). FAB-MS *m/z*: 277 [MH]⁺.

Anal. Calcd. for C₁₈H₁₂O₃: C, 78.25; H, 4.38. Found: C, 78.50; H, 4.33.

Photocyclization Reaction of **2c** (500 mg, 1.59 mmol).

A mixture of cyclohexane and benzene (4:1, v/v) was used as the solvent.

2-Chloronaphtho[1,2-*b*][1]benzothiophene-6-carboxylic Acid (**3c**)).

This compound was eluted with *n*-hexane-ethyl acetate (10:1, v/v). Recrystallization from benzene to give **3c** (263 mg, 53%) as brown powder, mp 283-284 °C (sublim. around 210 °C). Ir: 3000 (OH), 1700 (CO) cm⁻¹; ¹H-nmr (200 MHz, DMSO-*d*₆): δ 7.55-7.60 (2H, m, H8 and H9), 7.74 (1H, dd, *J*_{3,4} = 8.8 Hz, *J*_{3,1} = 1.0 Hz, H3), 8.19-8.30 (3H, m, H1, H4 and H7), 8.33 (1H, s, H5), 8.44-8.46 (1H, m, H10), near 13.8 (1H, br, OH). FAB-MS *m/z*: 315 [(M+2)H]⁺, 314 [(M+2)H-H]⁺, 313 [MH]⁺, 312 [MH-H]⁺.

Anal. Calcd. for C₁₇H₉ClO₂S·1/4H₂O: C, 64.36; H, 3.02. Found: C, 64.47; H, 3.42.

10-Chloro-6*H*-benzo[*b*]naphtho[2,3-*d*]thiopyran-6-one (**4c**)).

This compound was eluted with *n*-hexane-ethyl acetate (500:1, v/v). Recrystallization from ethyl acetate to give **4c** (38 mg, 8%) as yellow needles, mp 259-260 °C (sublim. around 209 °C). Ir: 1735, 1715, 1705 (CO) cm⁻¹; ¹H-nmr (200 MHz, CDCl₃): δ 7.32-7.57 (4H, m, H2, H3, H4 and H9), 7.99-8.03 (2H, m, H8 and H11), 8.20-8.25 (1H, m, H1), 8.49 (1H, s, H12), 9.01 (1H, s, H7). FAB-MS *m/z*: 297 [MH]⁺.

Anal. Calcd. for C₁₇H₉ClOS·1/2H₂O: C, 66.78; H, 3.30. Found: C, 66.49; H, 3.57.

10-Chloro-6*H*-benzo[*b*]naphtho[2,3-*d*]pyran-6-one (**5c**)).

This compound was eluted with *n*-hexane-ethyl acetate (200:1, v/v). Recrystallization from ethyl acetate to give **5c** (22 mg, 5%)

as yellow prisms, mp 263.5-264 °C (sublim. around 207 °C). Ir: 1720 (CO) cm^{-1} ; ^1H -nmr (200 MHz, deuteriochloroform): δ 7.44-7.57 (4H, m, H2, H3, H4 and H9), 8.01-8.05 (2H, m, H8 and H11), 8.45-8.49 (1H, m, H1), 8.73 (1H, s, H12), 8.95 (1H, s, H7). FAB-MS m/z : 281 $[\text{MH}]^+$.

Anal. Calcd. for $\text{C}_{17}\text{H}_9\text{ClO}_2 \cdot 1/2\text{H}_2\text{O}$: C, 70.48; H, 3.48. Found: C, 70.82; H, 3.84.

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