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An efficient novel synthesis of β-(azuleno[1,2-*b*]benzothienyl)- and β-(azuleno[2,1-*b*]benzothienyl)-α,β-unsaturated ketones by the tropylium ion-mediated intramolecular furan ring-opening reaction and X-ray investigation of methyl ketone derivative† [1]

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Intramolecular reaction of 2-tropylio-3-(5-substituted 2-furyl)benzothiophenes (**3**), prepared from the corresponding 2-cycloheptatrienyl-3-(5-substituted 2-furyl)benzothiophenes (**2**), afforded the β-(azuleno[1,2-*b*]benzothienyl)-α,β-unsaturated ketones (**4**), which are otherwise difficult to obtain, in moderate yields. The reaction involves a ring-opening process of the furan ring by intramolecular attack of the tropylium ion onto the 2-position of the furan ring. Similarly, β-(azuleno[2,1-*b*]benzothienyl)-α,β-unsaturated ketones (**8**) were obtained from the corresponding 3-tropylio-2-(5-substituted 2-furyl)benzothiophenes (**7**) albeit in lower yields. The molecular and crystal structures of the methyl ketone derivative, **8a**, are discussed on the basis of X-ray structure analysis.

Introduction

Azulene and its derivatives, which are typical bicyclic non-benzenoid aromatic hydrocarbons, are of interest not only from the fundamental viewpoint, but also for pharmaceutical and physiological activities, and as advanced materials. Hetero-aromatic fused ring systems containing azulene fragments are also of interest and several kinds of such compounds have been prepared.[2] The synthetic methods were restricted to the hetero-aromatization of the azulene or the application of Takase and Yasunami's azulene-synthesis using 2*H*-cyclohepta[*b*]furan-2-one and suitable enamines.[3] These methods generally suffered from tedious multistage procedures and/or low yields, and the synthetic difficulties have impeded progress in this area. During our studies on the intramolecular cyclization reaction by the tropylium ion,[4] we recently found a novel, one-pot synthetic method for tricyclic benz[*a*]azulenes having an α,β-unsaturated ketone group from the corresponding *o*-[(2-furyl)cycloheptatrienyl]benzenes.[5] This reaction seems to involve a furan ring-opening reaction by intramolecular electrophilic attack of the initially formed tropylium ion derivatives onto the 2-position of the furan ring (Scheme 1).

Although it is well-known that 2-substituted furan derivatives react with protic acid to give the corresponding 1,4-diketones by a ring-opening reaction[6] and a few tropylium ion-mediated azulene syntheses have been reported[7], this is the first case of a tropylium ion-mediated furan-ring-opening reaction to give the benz[*a*]azulene ring. The successful preparation of benz[*a*]azulenic enones opened a route to the synthesis of a variety of aromatic fused azulenic enones. Hence, we applied such a type of reaction to see the scope and limitations of the reaction and to construct novel heteroaromatic fused azulene rings. Now, this paper will report a new, facile, one-pot synthesis of azuleno[1,2-*b*]benzothiophenic enones (**4**) and azuleno[2,1-*b*]benzothiophenic enones (**8**), which include the novel tetracyclic π-conjugated azulene nuclei cata-condensed with the benzothiophene ring, from the corresponding 3-(2-furyl)-2-tropyliobenzothiophenes (**3**) and 2-(2-furyl)-3-tropyliobenzothiophenes (**7**), respectively. Since much attention is currently focused on benzo[*b*]thiophenes due to their biological activities,[8] compounds **4** and **8** are expected to display the interesting biological activities. The X-ray structure of methyl ketone derivative (**8a**) will be also described.

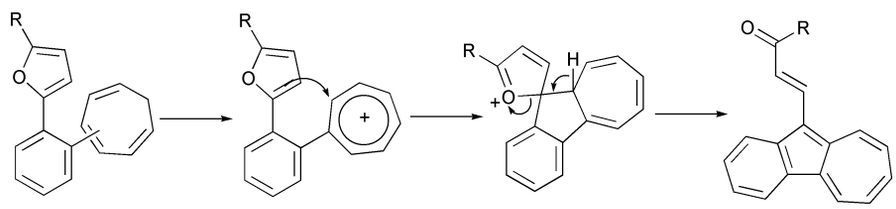
Results and discussion

Synthesis of β-(azuleno[1,2-*b*]benzothienyl)-α,β-unsaturated ketones (4) and β-(azuleno[2,1-*b*]benzothienyl)-α,β-unsaturated ketones (8)

The synthetic sequence leading to **4** from the readily available 3-bromobenzothiophene[9] is depicted in Scheme 2.

3-Bromobenzothiophene was treated with LDA in tetrahydrofuran at −78 °C, followed by addition of powdered tropylium tetrafluoroborate to give 3-bromo-2-cycloheptatrienylbenzothiophene (**1**) in 68% yield. The palladium(II)-catalyzed Stille coupling reaction[10] of **1** with 5-substituted 2-trimethylstannylfurans, which were readily obtained from the 2-substituted furans according to the previously reported method,[5a] gave the corresponding 2-cycloheptatrienyl-3-(2-furyl)benzothiophenes (**2a**–**f**) as a pale yellow oil. The formyl derivative (**2g**) was prepared from **2f** and pyridinium *p*-toluene-

† Electronic supplementary information (ESI) available: physical properties and the results of elementary analyses of **1**, **2a**–**2h**, **5a**, **5b**, **6a** and **6b**. See http://www.rsc.org/suppdata/ob/b4/b401579g/



Scheme 1

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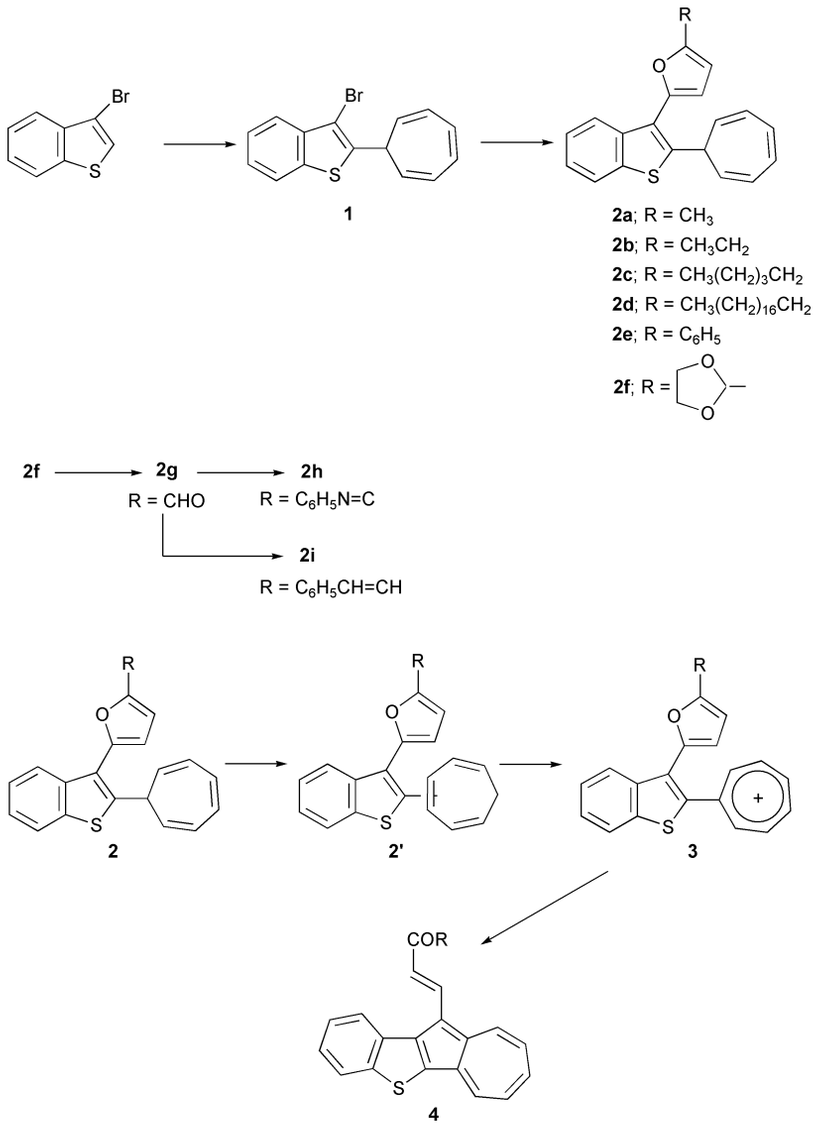
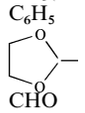


Scheme 2

sulfonate.[11] The (phenylimino)methyl and styryl derivatives (**2h** and **2j**) were prepared from the formyl derivative (**2g**). In order to decrease the steric hindrance at the subsequent hydride-abstraction process, **2** was then thermally isomerized by sigmatropic rearrangement to an isomeric mixture of **2** and **2′**.

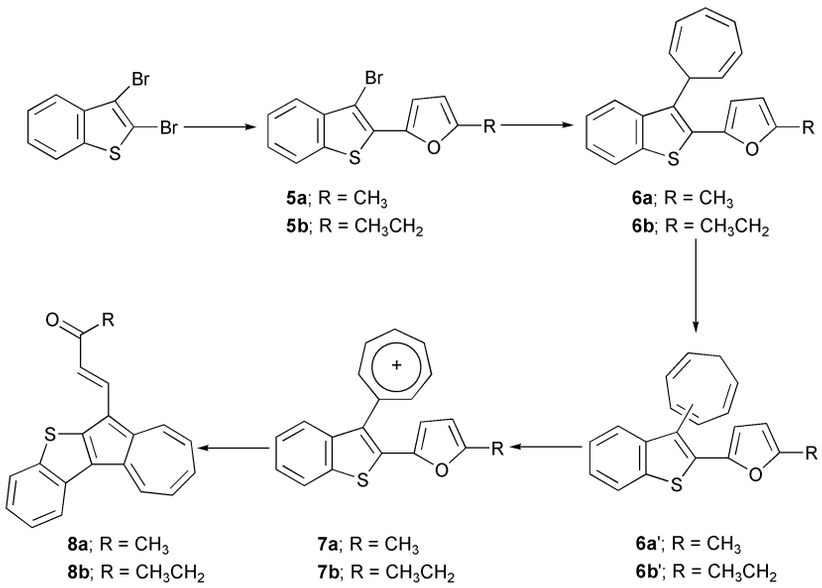
With the exception of **2f** and **2f′**, the isomeric mixture **2** and **2′** was treated with an equimolar amount of triphenylmethyl tetrafluoroborate at ambient temperature for 10 min., followed by addition of dry ether, to give the corresponding 3-(2-furyl)-2-tropyliobenzothiophenes (**3**) as dark-colored precipitates. With **2f** and **2f′**, the 1,3-dioxolane ring reacted with triphenylmethyl tetrafluoroborate to afford a complex mixture,[12] and no tropylium ion derivatives were obtained. The structure of 3-(5-methyl-2-furyl)-2-tropyliobenzothiophene (**3a**) was established by the ^{1}H NMR spectrum and elemental analysis.[13] The spectra of other tropylium ion derivatives **3** were not measured and **3** were used for the next step without further purification. Conversion of the tropylium ion derivatives **3** to the desired azuleno[1,2-*b*]benzothiophenic enones (**4**) was achieved by refluxing a dichloromethane solution of **3**. The results are shown in Table 1. The described yields are based on the cycloheptatrienyl derivatives **2**. When the substituent on the furan ring is an alkyl group such as methyl, ethyl, pentyl or octadecyl group, the corresponding azuleno[1,2-*b*]benzothiophenic enone **4** was obtained in fairly good yields. When the substituent is phenyl or styryl group, the azulenoid analogues of chalcone and dibenzylideneacetone (DBA), **4e** and **4i**, respectively, were obtained in slightly lower yield. With **3g** and **3h**, however, the starting materials were recovered unchanged after prolonged reaction time. The non-reactivity of **3g** and **3h** in this type of reaction could be attributed to decreased nucleophilicity of the 2-position in the furan ring due to the electron-withdrawing groups such as the (phenylimino)methyl or formyl groups.

Table 1

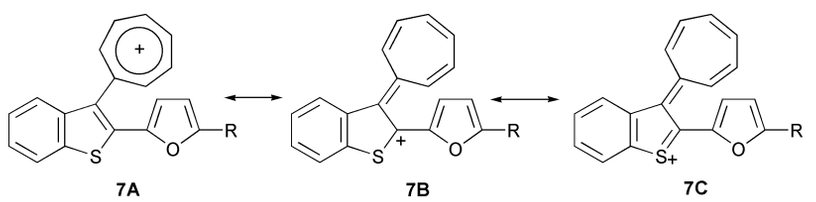
Cycloheptatriene (**2′**)	R	Azulenes	Yield[a]
2a′	CH_3	**4a**	64%
2b′	CH_3CH_2	**4b**	66%
2c′	$CH_3(CH_2)_3CH_2$	**4c**	65%
2d′	$CH_3(CH_2)_{16}CH_2$	**4d**	68%
2e′	C_6H_5	**4e**	54%
2f′		—	—
2g′	CHO	—	—
2h′	C_6H_5N=CH	—	—
2i′	C_6H_5CH=CH	**4i**	51%

[a] Yields are of isolated and purified products.

The structures of these β-(azuleno[1,2-*b*]benzothiophene derivatives (**4**) were established by their ^{1}H NMR and mass spectra as well as elemental analyses. Moreover, the present single-crystal X-ray analysis showed that the methyl ketone



Scheme 3



Scheme 4

Table 2

Cycloheptatriene (**6′**)	R	Azulenes	Yield[a]
6a′	CH_3	**8a**	31%
6b′	CH_3CH_2	**8b**	30%

[a] Yields are of isolated and purified products.

derivative **4a** had an (*E*)-4-(11-azuleno[1,2-*b*]benzothiophenyl)-3-buten-2-one skeleton, although the α,β-unsaturated carbonyl group suffered some disorder to result in a somewhat ambiguous structure of the moiety.[14]

The coupling constants between the olefinic protons on **4** were *ca.* 16 Hz. This shows that the *trans* configuration is between the azuleno[1,2-*b*]benzothiophene ring and the carbonyl group. X-ray crystallographic analysis of **4a** also supports the *trans* configuration. If the above-mentioned mechanism for the formation of **4** is correct, the azuleno[1,2-*b*]benzothiophene ring and the carbonyl group should be *cis* to each other. This can be explained by the assumption that the initially formed *cis* isomer changes into the more stable *trans* isomer by the acid generated in the course of the reaction and/or by the post-treatment for the isolation and purification of the products.

In a similar manner as described above, other isomers, β-azuleno[2,1-*b*]benzothienyl-α,β-unsaturated ketones (**8**), could be obtained from the corresponding tropylium ion derivatives (**7**) (Scheme 3). The results are shown in Table 2.

However, the yields of **8** are lower than those of **4**. Although the reason for the lower yield is not yet clear at present, a likely explanation is that, for **7**, the heptafulvene-type structures (**7B** and **7C**) contribute appreciably to the structure (Scheme 4) and, therefore, the electrophilicity of the tropylium ion is decreased.

The coupling constants between the olefinic protons on **8a** and **8b** show that the azuleno[2,1-*b*]thiophene ring and the carbonyl group are also *trans* to each other. A single-crystal X-ray analysis of **8a** also supports *trans* configuration between the azuleno[2,1-*b*]thiophene ring and the carbonyl group (*vide infra*).

Molecular and crystal structures of 8a

Fig. 1 shows the X-ray structure of **8a** with atom labeling.

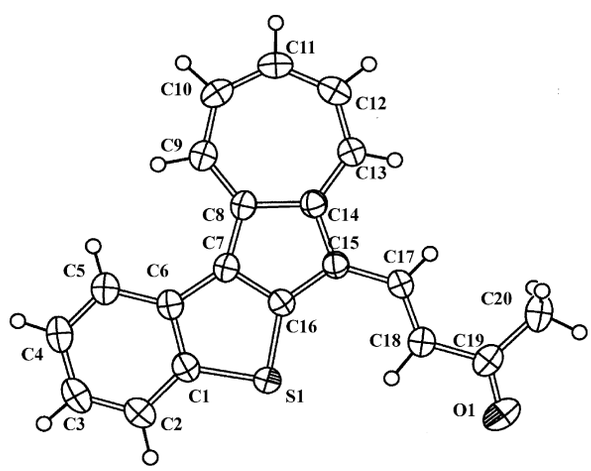
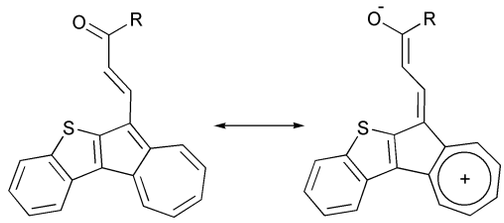


Fig. 1 X-ray structure of **8a** with atom labeling.

The result of the X-ray analysis confirmed the molecular structure of **8a**. The molecule has C_s symmetry. The C8–C9, C9–C10, C10–C11, C11–C12, C12–C13, and C13–C14 bond lengths in the seven-membered ring of **8a** are 1.387(3), 1.389(4), 1.382(4), 1.376(4), 1.385(4), and 1.387(3) Å, respectively. Thus, these bond lengths do not exhibit such clear bond-length alternation as those found for azuleno[1,2-*b*]thiophene,[15] 9-phenylbenz[*a*]azulene[16], and 4-(10-benz[*a*]azulenyl)-1,1,1-triphenyl-2-butanone.[17] Similar to the case of 4-(10-benz[*a*]azulenyl)-1,1,1-triphenyl-3,4-buten-2-one,[18] conjugation between the enone moiety and the seven-membered ring seems to result in the absence of a distinct bond-length alternation (Scheme 5).

Molecular stacking of two **8a** molecules is shown in Fig. 2. The inter-plane distance of the stacking is *b*/2 (*ca.* 3.38 Å). The close contact suggests a certain π–π interaction between the stacked molecules resulting in the dark greenish-brown colour



Scheme 5

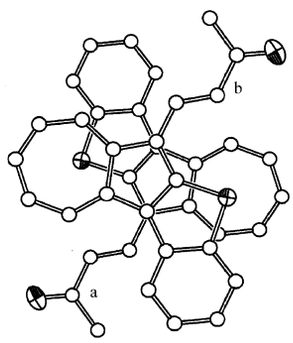


Fig. 2 Stacking of **8a** molecules viewed along the *b* axis. Symmetry codes: *a*: *x*, *y*, *z*; *b*: $-x$, $y + 0.5$, $-z$.

of the crystal that is clearly different from the yellow colour of the solution.

Conclusion

We have developed an efficient synthetic method for β-(azuleno-[1,2-*b*]benzothienyl-α,β-unsaturated ketones (**4**) and β-(azuleno[2,1-*b*]benzothienyl-α,β-unsaturated ketones (**8**) which are difficult to synthesize by other methods because of the inaccessibility of suitable precursors. The X-ray structure of **8a** was determined. Compound **8a** shows a short intermolecular face-to-face packing in the crystal.

Experimental

All melting points were determined with a Yanaco MO JP-3 apparatus and are uncorrected. ^{1}H NMR spectra were obtained on a Brucker DPX-250 spectrometer (250 MHz) using tetramethylsilane as an internal reference. For all NMR spectra, δ values are given in ppm and *J* values in Hz. The mass spectra were determined with a Shimazdu GC-MS QP200A spectrometer. All dry solvents were freshly distilled over an appropriate drying agent before use. Column chromatography was performed on silica gel (Wako-gel, C-200). The elemental analyses were performed by Miss Masuko Nishinaka, Department of Chemistry, Faculty of Science, Kobe University.

The physical properties and the results of elementary analyses of **1**, **2a**–**2h**, **5a**, **5b**, **6a**, and **6b** have been deposited as ESI.†

Preparation of 3-bromo-2-cycloheptatrienylbenzothiophene (1)

To a stirred solution of 3-bromobenzothiophene (7.0 g, 33 mmol) in dry tetrahydrofuran (200 cm^3) was added slowly 19.8 ml of lithium diisopropylamide (2.0 M solution in heptane/tetrahydrofuran/ethylbenzene, 39 mmol) under a nitrogen atmosphere at −78 °C. After the addition was complete, the reaction mixture was stirred at −78 °C for 2 h. Then powdered tropylium tetrafluoroborate (6.2 g, 35 mmol) was added in limited amounts. The mixture was allowed to warm to room temperature and stirred overnight. After addition of 300 ml of ether, the solution was then neutralized with 10% aqueous ammonium chloride solution. The ether layer was separated, dried over anhydrous sodium sulfate, and the solvent was evaporated. The residue was purified by column chromatography (silica gel, hexane) to give **1** (6.8 g, 68%) as colourless crystals.

General procedure for the synthesis of 2-cycloheptatrienyl-3-(2-furyl)benzothiophenes (2a–2f)

All of these reactions were carried out under a nitrogen atmosphere. The mixture of **1** (4.5 g, 14.8 mmol), 2-substituted 5-trimethylstannylfuran[5] (21 mmol), bis(triphenylphosphine)palladium(II) chloride (5.0 g, 7.1 mmol) and dry tetrahydrofuran (200 cm^3) was refluxed for 8 h. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, hexane–benzene (1 : 1)) to give the corresponding 2-cycloheptatrienyl-3-(2-furyl)benzothiophenes (**2**); The yields of **2a**, **2b**, **2c**, **2d**, **2e**, and **2f** were 77, 80, 62, 79, 78, and 52%, respectively.

2-Cycloheptatrienyl-3-(5-formyl-2-furyl)benzothiophene (2g)

A solution of **2f** (3.00 g, 8.29 mmol) and pyridinium *p*-toluenesulfonate (0.63 g, 2.49 mmol) in acetone (50 cm^3) and H_2O (5 cm^3) was heated at reflux for 3 h. The solvent was evaporated and the residue was dissolved in 100 cm^3 of ether. The ether solution was washed with 10% aqueous sodium carbonate solution, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was purified by short column chromatography over silica gel using benzene as eluent to give **2g** (2.06 g, 78%).

2-Cycloheptatrienyl-3-[5-(phenylimino)methyl-2-furyl]-benzothiophene (2h)

A mixture of **2g** (1.00 g, 3.14 mmol), aniline (0.35 g, 3.77 mmol), and benzene (10 cm^3) was heated at reflux for 1 h under a nitrogen atmosphere. The reaction mixture was purified by column chromatography over silica gel using benzene as eluent to give **2h** (2.06 g, 96%) as yellow needles.

2-Cycloheptatrienyl-3-(5-styryl-2-furyl)benzothiophene (2i)

To an ice-cooled mixture of **2g** (0.64 g, 2.02 mmol), benzyltriphenylphosphonium bromide (0.88 g, 2.02 mmol), 18-crown-6 (0.052 g, 0.20 mmol), and dichloromethane (20 cm^3), powdered potassium hydroxide (0.22 g, 4.00 mmol) was added and then the mixture was stirred for 3 h at ambient temperature. After the filtration of insoluble materials, the filtrate was washed with water, and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was purified by column chromatography over silica gel using hexane as eluent to give **2i** as the mixture of geometrical isomers (0.49 g, 62%), which was used for the next step without separation; *m*/*z*: 392 (M^+); Found: C, 82.81; H, 5.26. $C_{27}H_{20}OS$ requires C, 82.62; H, 5.14%.

3-Bromo-2-(5-methyl-2-furyl)benzothiophene (5a)

A mixture of 2,3-dibromobenzothiophene[19](5.0 g, 17 mmol), 2-methyl-5-trimethylstannylfuran (5.15 g, 21 mmol), bis(triphenylphosphine)palladium(II) (1.5 g, 2.14 mmol), and dry tetrahydrofuran (50 cm^3) was refluxed for 8 h under a nitrogen atmosphere. The solvent was evaporated and the residue was purified by column chromatography over silica gel using hexane as eluent to give **5a** (2.58 g, 52%).

3-Bromo-2-(5-ethyl-2-furyl)benzothiophene (5b)

The procedure described above was used yielding **5b** (42%).

3-Cycloheptatrienyl-2-(5-methyl-2-furyl)benzothiophene (6a)

To a solution of **5a** (2.00 g, 6.83 mmol) in 150 cm^3 of dry ether, 5.10 ml of butyllithium (1.6 M solution in hexane, 8.16 mmol) was added slowly under a nitrogen atmosphere. After the addition was complete, the reaction mixture was stirred at −78 °C for 2 h. Then powdered tropylium tetrafluoroborate (1.80 g, 10.0 mmol) was added in limited amounts. The mixture was allowed to warm to room temperature and stirred overnight.

After addition of 100 cm^3 of ether, the solution was then neutralized with 10% aqueous ammonium chloride solution. The ether layer was separated, dried over anhydrous sodium sulfate, and the solvent was evaporated. The residue was purified by column chromatography (silica gel, hexane) to give **6a** (1.20 g, 58%) as colourless crystals.

3-Cycloheptatrienyl-2-(5-ethyl-2-furyl)benzothiophenes (6b)

The procedure described above was used yielding **6b** (82%) as colourless crystals.

Thermal isomerization of 2 and 6 to 2′ and 6′, respectively

The xylene solution of **2** was refluxed for 5 h. The solvent was evaporated *in vacuo* and the residue was short-chromatographed over silica gel to give the isomeric mixture **2′** in almost quantitative yield. In a similar manner, **6** was thermally isomerized to the isomeric mixture **6′**.

General procedure for the synthesis of azuleno[1,2-*b*]benzothiophenic enones (4) and azuleno[2,1-*b*]benzothiophenic enones (8)

A solution of **2′** (0.526 mmol) in 5 cm^3 of dry dichloromethane was added to a solution of triphenylmethyl tetrafluoroborate (180 mg, 0.545 mmol) in dry dichloromethane (10 cm^3) at 0 °C and was stirred for 10 min. Then, 200 cm^3 of dry ether was added and stirred for 10 min. 3-(2-Furyl)2-tropyliobenzothiophene (**3**), which separated out as dark-colored precipitates, was collected by filtration and washed with dry ether. This product was dissolved in 80 cm^3 of dichloromethane and the solution was refluxed for 1 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexane-ethyl acetate (3 : 1)) and recrystallization from toluene to afford **4**. In a similar manner, **8** was obtained from the corresponding 3-cycloheptatrienyl-2-(2-furyl)benzothiophenes **6′**.

(*E*)-4-(11-Azuleno[1,2-*b*]benzothiophenyl)-3-buten-2-one (4a)

This compound was obtained as black prisms in 64% yield; mp 166–169 °C (Found: C, 79.29; H, 4.77. $C_{20}H_{14}OS$ requires C, 79.44; H, 4.67%); $\delta_H(CDCl_3)$ 8.63 (1H, d, *J* 9.8, seven-membered ring), 8.43 (1H, d, *J* 16.0, olefin), 8.45–8.39 (1H, m, six-membered ring), 8.27 (1H, d, *J* 9.2, seven-membered ring), 7.94–7.87 (1H, m, six-membered ring), 7.60 (1H, dd, *J* 10.2, 9.8, seven-membered ring), 7.53–7.46 (2H, m, six-membered ring), 7.29 (2H, dd, *J* 10.2, 9.8, seven-membered ring), 6.91 (1H, d, *J* 16.0, olefin), 2.49 (3H, s, methyl); *m*/*z*: 302 (M^+).

(*E*)-5-(11-Azuleno[1,2-*b*]benzothiophenyl)-4-penten-3-one (4b)

This compound was obtained as dark green prisms in 66% yield; mp 138–141 °C (Found: C, 79.58; H, 5.22. $C_{21}H_{16}OS$ requires C, 79.71; H, 5.10%); δ_H ($CDCl_3$) 8.67 (1H, d, *J* 10.0, seven-membered ring), 8.56 (1H, d, *J* 16.0, olefin), 8.50–8.43 (1H, m, six-membered ring), 8.37 (1H, d, *J* 9.2, seven-membered ring), 8.02–7.92 (1H, m, six-membered ring), 7.66 (1H, dd, *J* 10.0, 9.7, seven-membered ring), 7.59–7.49 (2H, m, six-membered ring), 7.38–7.22 (2H, m, seven-membered ring), 7.00 (1H, d, *J* 16.0, olefin), 2.82 (2H, q, *J* 7.3, methylene), 1.28 (3H, t, *J* 7.3, methyl); *m*/*z*: 316 (M^+).

(*E*)-1-(11-Azuleno[1,2-*b*]benzothiophenyl)-1-octen-3-one (4c)

This compound was obtained as dark green needles in 65% yield; mp 65–70 °C (Found: C, 80.28; H, 6.38. $C_{24}H_{22}OS$ requires C, 80.41; H, 6.19%); $\delta_H(CDCl_3)$ 8.60 (1H, d, *J* 10.2, seven-membered ring), 8.51 (1H, d, *J* 15.9, olefin), 8.46–8.41 (1H, m, six-membered ring), 8.36 (1H, d, *J* 9.2, seven-membered ring), 7.96–7.90 (1H, m, six-membered ring), 7.62 (1H, dd, *J* 9.9, 9.8, seven-membered ring), 7.53–7.46 (2H, m, six-membered ring), 7.30–7.18 (2H, m, seven-membered ring), 6.95 (1H, d, *J* 15.9, olefin), 2.98–2.72 (2H, m, methylene), 1.86–1.78 (2H, m, methylene), 1.48–1.38 (4H, m, methylene), 0.98 (3H, t, *J* 6.4); *m*/*z*: 358 (M^+).

(*E*)-1-(11-Azuleno[1,2-*b*]benzothiophenyl)-1-henicosen-3-one (4d)

This compound was obtained as dark brown needles in 68% yield; mp 82–84 °C (Found: C, 82.36; H, 9.05. $C_{37}H_{48}OS$ requires C, 82.17; H, 8.95%); $\delta_H(CDCl_3)$ 8.67 (1H, d, *J* 10.0, seven-membered ring), 8.56 (1H, d, *J* 16.0, olefin), 8.50–8.43 (1H, m, six-membered ring), 8.35 (1H, d, *J* 9.3, seven-membered ring), 7.98–7.89 (1H, m, six-membered ring), 7.63 (1H, dd, *J* 9.8, 9.7, seven-membered ring), 7.56–7.48 (2H, m, six-membered ring), 7.38–7.25 (2H, m, seven-membered ring), 6.99 (1H, d, *J* 16.0, olefin), 2.78 (2H, t, *J* 7.5, methylene), 1.80 (2H, m, methylene), 1.40–1.18 (30H, m, methylene), 0.88 (3H, t, *J* 7.2); *m*/*z*: 540 (M^+).

(*E*)-3-(11-Azuleno[1,2-*b*]benzothiophenyl)-1-phenyl-2-propen-1-one (4e)

This compound was obtained as dark green needles in 54% yield; mp 140–142 °C (Found: C, 82.51; H, 4.30. $C_{25}H_{16}OS$ requires C, 82.39; H, 4.42%); δ_H ($CDCl_3$) 8.85 (1H, d, *J* 16.0, olefin), 8.76 (1H, d, *J* 10.2, seven-membered ring), 8.60–8.57 (1H, m, six-membered ring), 8.39 (1H, d, *J* 9.5, seven-membered ring), 8.10 (2H, dd, *J* 8.3, 7.8, phenyl), 7.98–7.94 (1H, m, six-membered ring), 7.78 (1H, d, *J* 16.0, olefin), 7.68 (1H, dd, *J* 9.9, 9.8, seven-membered ring), 7.59–7.48 (5H, m, six-membered ring & phenyl), 7.36–7.22 (2H, m, seven-membered ring); *m*/*z*: 364 (M^+).

1-(11-Azuleno[1,2-*b*]benzothiophenyl)-5-phenyl-1,4-pentadien-3-one (4i)

This compound was obtained as dark reddish-brown needles in 51% yield; mp 52–54 °C (Found: C, 82.88; H, 4.43. $C_{27}H_{18}OS$ requires C, 83.05; H, 4.65%); δ_H ($CDCl_3$) 8.78 (1H, d, *J* 15.3, olefin), 8.77 (1H, d, *J* 11.2, seven-membered ring), 8.62–8.56 (1H, m, six-membered ring), 8.41 (1H, d, *J* 9.2, seven-membered ring), 8.01–7.96 (1H, m, six-membered ring), 7.82 (1H, d, *J* 15.9, olefin), 7.75–7.63 (3H, m, seven-membered ring & phenyl), 7.57–7.53 (2H, m, six-membered ring), 7.47–7.31 (5H, m, seven-membered ring & phenyl), 7.35 (1H, d, *J* 15.9, olefin), 7.17 (1H, d, *J* 15.9, olefin); *m*/*z*: 390 (M^+).

(*E*)-4-(11-Azuleno[2,1-*b*]benzothiophenyl)-3-buten-2-one (8a)

This compound was obtained as dark greenish-brown prisms in 31% yield; mp 119–121 °C (Found: C, 79.26; H, 4.43. $C_{20}H_{14}OS$ requires C, 79.44; H, 4.67%); δ_H ($CDCl_3$) 8.82 (1H, d, *J* 9.5, seven-membered ring), 8.59 (1H, d, *J* 10.1, seven-membered ring), 8.35 (1H, d, *J* 7.7, six-membered ring), 8.32 (1H, d, *J* 15.6, olefin), 7.96 (1H, d, six-membered ring), 7.73 (1H, dd, *J* 9.8, 9.8, seven-membered ring), 7.55 (dd, 1H, *J* = 10.0, 7.3 Hz, seven-membered ring), 7.44 (dd, 1H, *J* = 9.8, 9.6 Hz, seven-membered ring), 7.57–7.40 (2H, m, six-membered ring), 6.70 (1H, d, *J* 15.6, olefin), 2.47 (3H, s, methyl); *m*/*z*: 302 (M^+).

(*E*)-5-(11-Azuleno[2,1-*b*]benzothiophenyl)-4-penten-3-one (8b)

This compound was obtained as dark green prisms in 30% yield; mp 91–93 °C (Found: C, 79.88; H, 5.08. $C_{21}H_{16}OS$ requires C, 79.71; H, 5.10%); δ_H ($CDCl_3$) 8.78 (1H, d, *J* 8.6, seven-membered ring), 8.58 (1H, d, *J* 10.2, seven-membered ring), 8.37 (1H, d, *J* 15.3, olefin), 8.33 (1H, d, *J* 7.3, six-membered ring), 7.94 (1H, d, *J* 7.9, six-membered ring), 7.70–7.39 (5H, m, six- & seven-membered rings), 6.71 (1H, d, *J* 15.5, olefin), 2.77 (2H, q, *J* 7.4, methylene), 1.27 (3H, t, *J* 7.4, methyl); *m*/*z*: 316 (M^+).

X-ray analysis of 8a

Dark greenish-brown prismatic crystals of **8a** ($C_{20}H_{14}OS$, FW = 302.4) were grown from a toluene solution of the compound and a single crystal having dimensions of 0.06 × 0.18 × 0.26 mm^3 was used for the single crystal X-ray diffraction experiment. A SMART 1000 diffractometer and Mo-Kα radiation (λ = 0.71073 Å, $2\theta_{min}$ = 4.2° and $2\theta_{max}$ = 54.2°) were used for the experiment. Crystal structure analysis was carried out by using a program package SHELXL-97.[20] At first, we assumed four space groups, $P2_1/m$, $P2_1$, Pm and $P\bar{1}$ to solve the structure. In the cases of the last three space groups, the structures could be solved by direct methods and subsequent refinements of them by methods similar to that described below gave the following results: $R(F)$ for data with $I > 2\sigma(I)$, w$R2$ for all reflections and S were 0.0412, 0.1152, and 1.041 for $P2_1$-model; 0.0437, 0.1216, and 1.035 for Pm-model; 0.0477, 0.1255, and 1.041 for $P\bar{1}$-model. In the case of the first space group ($P2_1/m$), the direct method failed to solve the structure. Then, an initial structure for this space group was derived by the following method; the y coordinates of the non-hydrogen atom in the $P2_1$-model were replaced by 1/4, since the model showed pseudo mirror symmetry. In this trial, subsequent refinements by full matrix least-squares method gave reasonable positions of the non-hydrogen atoms. Then, all of the hydrogen positions were determined from different Fourier maps. Non-hydrogen and hydrogen atoms were included in the refinement by applying anisotropic and isotropic displacement parameters, respectively, to give the final results given below. Monoclinic space group of $P2_1/m$ with a = 10.287(2) Å, b = 6.764(1) Å, c = 11.472(2) Å, β = 111.162(3)°, V = 744.3(2) Å^3, Z = 2, D_{calc} = 1.349 g cm^{-3}, μ = 0.216 mm^{-1}. Out of 3962 total data (R(int) = 0.0322) with absorption correction by SADABS, unique 1608 reflections were used, parameters being 173. $R(F)$ = 0.0413 for 1315 data with $I > 2\sigma(I)$, w$R2$ = 0.1173 and S = 1.027 for all reflections. Although the R factors of the $P2_1$-model were comparable with those of the $P2_1/m$-model, the benzene moiety and the positions of the H atoms in the former model exhibited significant deformations. Therefore, the $P2_1/m$-mode was adopted. ‡

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‡ CCDC reference numbers 226170 (**8a**) and 232411 (**4a**). See http://www.rsc.org/suppdata/ob/b4/b401579g/ for crystallographic data in.cif or other electronic format.

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13 Mp > 200 °C (Found: C, 61.28; H, 4.08. $C_{20}H_{15}BF_4OS$ requires C, 61.56; H, 3.87%); δ_H (CD_2Cl_2) 8.94–8.82 (6H, m, tropylium ring), 8.22–8.19 (1H, m, six-membered ring), 8.08–8.02 (1H, m, six-membered ring), 7.67–7.55 (2H, m, six-membered ring), 6.85 (1H, d, *J* 3.3, furan ring), 6.33 (1H, d, *J* 3.3, furan ring), 2.20 (3H, s, methyl).
14 Crystal data for **4a**. Orthorhombic, space group $Pca2_1$, a = 18.905(3), b = 4.772(1), c = 33.799(5) Å, V = 3049.0(8) Å^3, Z = 8. Final $R(F)$ = 0.0829 for 2635 data >2$\sigma(I)$ and $R(F^2)$ = 0.2371 for all 5720 reflections.
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