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Novel and facile synthesis of β-(4-azuleno[1,2-*b*]thienyl)- and β-(4-azuleno[2,1-*b*]thienyl)-α,β-unsaturated ketones by intramolecular tropylium ion-mediated furan ring-opening reaction

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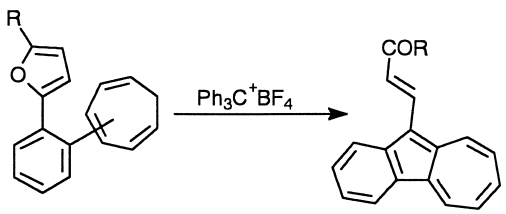
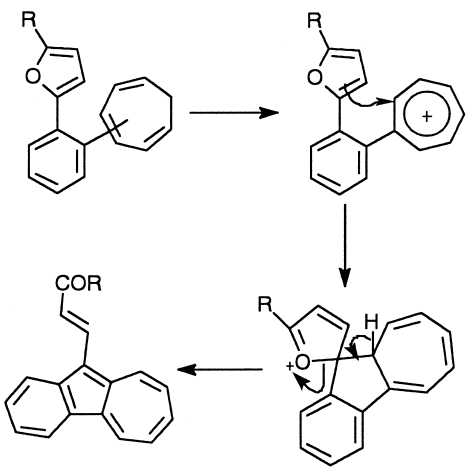
Abstract—The novel and efficient methods for the synthesis of β-(4-azuleno[1,2-*b*]thienyl)-α,β-unsaturated ketones (**1**) and β-(4-azuleno[2,1-*b*]thienyl)-α,β-unsaturated ketones (**2**) have been described. Refluxing the dichloromethane solutions of 2-tropylio-3-(2-furyl)thiophene tetrafluoroborates (**3**) or 3-tropylio-2-(2-furyl)thiophene tetrafluoroborates (**4**) afforded (**1**) and (**2**), respectively, in moderate yields. The reaction involves an intramolecular tropylium ion-mediated furan ring-opening reaction.

1. Introduction

Azulene and its derivatives, which are typical polycyclic non-benzenoid aromatic hydrocarbons, are of interest not only from the fundamental viewpoint of their chemical and physical properties,[1] but also in terms of their pharmaceutical and physiological activities and as advanced materials.[2] Heteroaromatic fused ring systems containing azulene nuclei are also interesting compounds, and several azulene derivatives condensed with heteroaromatics such as thiophene, furan, pyrrole, pyridine, thiapyran, pyrimidine, thiazole or porphyrin have been prepared and investigated.[3] Synthetic methods of these heteroaromatic fused azulene nuclei were restricted to the heteroaromatization of the azulene derivatives or the Takase and Yasunami reaction between 2*H*-cyclohepta[*b*]furan-2-one and suitable enamines. Most of the reported heteroaromatic fused azulenes were restricted to the parent compounds and alky-, aryl- or alkoxycarbonyl-substituted derivatives. The synthetic difficulties of heteroaromatic fused azulenes have precluded progress in this area, unlike the case of azulenes. Recently, we have developed a novel approach to the synthesis of benz[*a*]azulenic enones based on the triphenylmethyl (trityl) salt-promoted intramolecular reaction of *o*-(2-furyl)cycloheptatrienylbenzenes (Scheme 1).[4] This reaction apparently involves an intramolecular electrophilic attack of the initially formed tropylium ion derivatives onto the electron-rich 2-position of the furan ring, followed by a ring-opening reaction and synchronous aromatization (Scheme 2).[4] Although a few tropylium ion-mediated azulene syntheses have been reported,[5–7] this is the first case of a tropylium ion-mediated furan-ring-opening



Scheme 1.



Scheme 2.

Keywords: azulene; azuleno[1,2-*b*]thiophene; azuleno[2,1-*b*]thiophene; α,β-unsaturated ketone; tropylium ion; furan ring-opening reaction.

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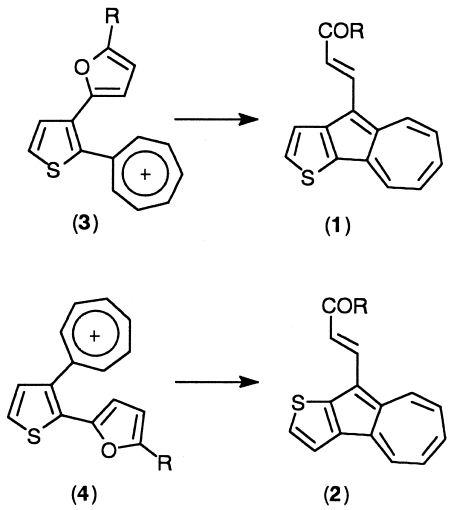
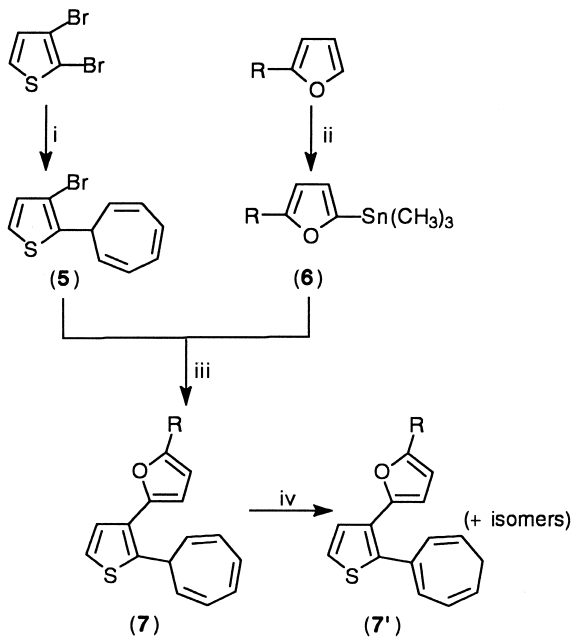


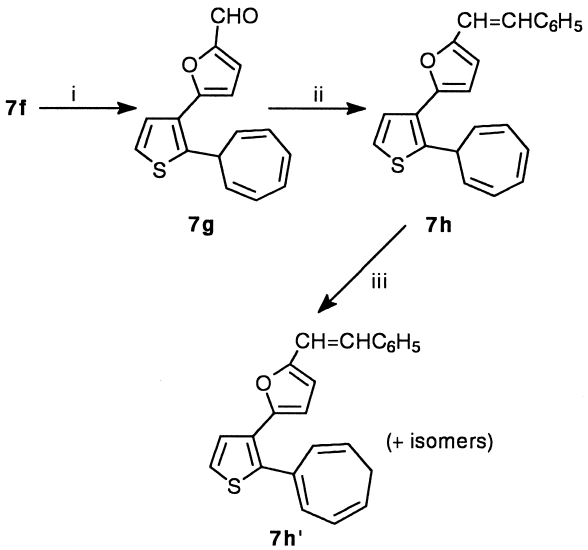
Scheme 3.

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. In this paper we wish to report a novel, facile synthesis of β-(4-azuleno[1,2-*b*]thienyl)-α,β-unsaturated ketones (**1**)[8] and β-(4-azuleno[2,1-*b*]thienyl)-α,β-unsaturated ketones (**2**) from the corresponding 2-tropylio-3-(2-furyl)thiophene tetrafluoroborates (**3**) and 3-tropylio-2-(2-furyl)thiophene tetrafluoroborates (**4**), respectively (Scheme 3). Although



6a, **7a**, **7a'**; R = CH_3
6b, **7b**, **7b'**; R = CH_2CH_3
6c, **7c**, **7c'**; R = $C(CH_3)_3$
6d, **7d**, **7d'**; R = C_6H_5
6e, **7e**, **7e'**; R = H
6f, **7f**, **7f'**; R = $CHOCH_2CH_2O$

Scheme 4. *Reagents and conditions* (i) BuLi, $C_7H_7^+BF_4^-$, THF, −78°C; (ii) BuLi, $(CH_3)_3SnCl$, THF, −78°C; (iii) $PdCl_2(PPh_3)_2$, THF, reflux; (iv) xylene, reflux.



Scheme 5. *Reagents and conditions* (i) PPTS, H_2O–acetone; (ii) $Ph_3P^{+-}CH_2C_6H_5Br^-$, KOH, 18-*crown*-6; (iii) xylene, reflux.

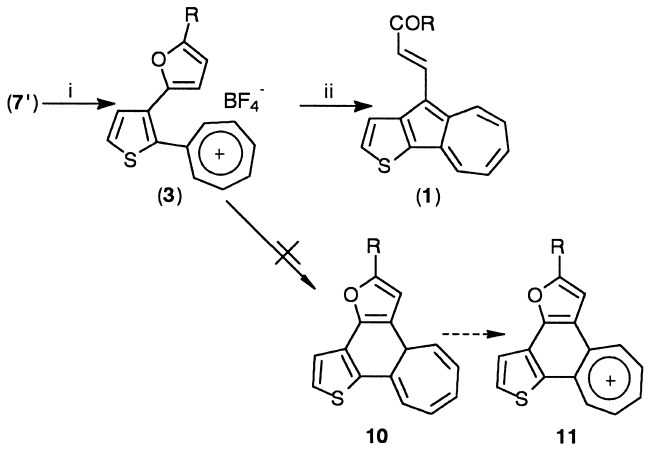
benzenoid α,β-unsaturated ketones, such as benzalacetone and chalcone, have been known for a long time and investigated extensively from the chemical and physical point of view, the studies of azulenoid analogues, especially heteroaromatic fused azulenoid ones, have been sparse.

2. Results and discussions

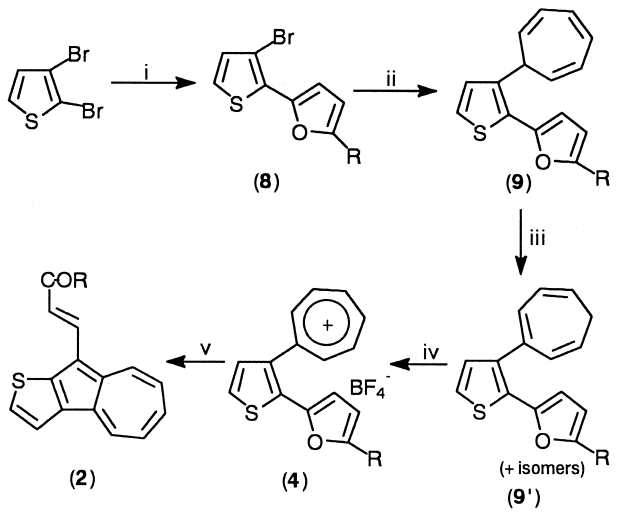
2.1. Synthesis of β-(4-azuleno[1,2-*b*]thienyl)-α,β-unsaturated ketones 1

The synthetic sequence leading to the precursors for **1**, 2-cycloheptatrienyl-3-(2-furyl)thiophenes (**7′**), from the readily available compounds, 2,3-dibromothiophene and 2-substituted furans, is depicted in Schemes 4 and 5.

2,3-Dibromothiophene was treated with butyllithium in THF at −78°C, followed by addition of powdered tropylium tetrafluoroborate to give 3-bromo-2-cycloheptatrienylthiophene (**5**), the common starting material for the synthesis of **1**, in 74% yield. 5-Substituted 2-trimethylstannylfurans (**6**) were prepared from the corresponding 2-substituted furans, according to the well-known method.[4b,9] The palladium(II)-catalyzed Stille coupling reaction[10] of **5** with **6** gave the corresponding 2-cycloheptatrienyl-3-(2-furyl)thiophenes **7** as a pale yellow oil. The other desired precursor having a styryl group was prepared from 2-cycloheptatrienyl-3-[5-(1,3-dioxolan-2-yl)-2-furyl]thiophene (**7f**). Thus, **7f** was treated with pyridinium *p*-toluenesulfonate in aqueous acetone[11] to afford 2-cycloheptarienyl-3-(5-formyl-2-furyl)-thiophene (**7g**) in 94% yield. Then, treatment of **7g** with an equimolar amount of benzyltriphenylphosphonium bromide in the presence of 18-*crown*-6 and potassium hydroxide gave 2-cycloheptatrieny-3-(5-styryl-2-furyl)thiophene (**7h**) as a mixture of geometrical isomers, which could be separated successfully into *E*- and *Z*-isomers by column chromatography, in good yield. In order to diminish the steric hindrance in the subsequent hydride-abstraction process, **7** was thermally isomerized[12] by 1,5-hydride shift



Scheme 6. *Reagents and conditions* (i) $Ph_3C^+BF_4^-$, CH_2Cl_2; (ii) CH_2Cl_2, reflux.

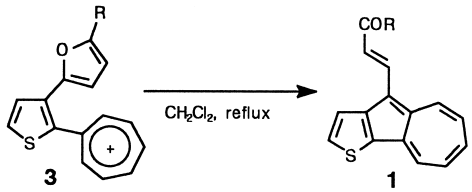


8a, 9a, 9a'; R = H, **2a, 4a**; R = CPh_3
8b, 9b, 9b', 4b, 2b; R = CH_3
8c, 9c, 9c'; **4c, 2c**; R = C_6H_5

Scheme 7. *Reagents and conditions* (i) **6**, $PdCl_2(PPh_3)_2$, THF, reflux; (ii) BuLi, $C_7H_7^+BF_4^-$, THF, −78°C; (iii) xylene, reflux; (iv) $Ph_3C^+BF_4^-$, CH_2Cl_2; (v) CH_2Cl_2, reflux.

to the isomeric mixture **7′**. With the exception of **7f′**, the isomeric mixture **7′** was treated with an equimolar amount of trityl tetrafluoroborate in dichloromethane at ambient temperature to afford 3-(2-furyl)-2-tropyliothiophenes **3** as dark-colored crystals. With **7e′**, which has no substituent on the furan ring, triphenylmethyl-substituted derivative **3e** was obtained instead of 3-(2-furyl)-2-tropyliothiophene itself. Apparently, the trityl salt acts as not only a hydride abstraction reagent but also as an electrophile in the reaction.[13] With **7f′**, the 1,3-dioxolane ring reacted with trityl tetrafluoroborate[14] to afford a complex mixture, and any tropylium ion derivatives were not obtained. Conversion of the tropylium ion derivatives **3** to the desired β-(4-azuleno[1,2-*b*]thienyl)-α,β-unsaturated ketones **1** was achieved by refluxing a dichloromethane solution of **3** for 4–7 h (Scheme 6).[15] The results are given in Table 1. It might be expected that intramolecular electrophilic attack on the 3-position of the furan ring gave the six-membered compounds, **10** and/or **11**.[16] However, the formation of these compounds were not confirmed. The use of methyltrimethoxysilane as an acid scavenger[5] did not bring about the increase in the yield. When the substituent on the furan ring is alkyl (entry 1, 2, 3 and 5), phenyl (entry 4) or alkenyl group (entry 7), the reactivity of **3** was apparently minimally influenced. With **3h**, (*E*)- and (*Z*)-isomers gave the same sole azulenic enones **1h**, the configuration of the olefin moiety of which is *trans*. In contrast to the case of the compounds having alkyl, phenyl or alkenyl subsituents on the furan ring, an attempted conversion of the formyl derivative **3g** into the corresponding azulenic enone was unsuccessful. The starting material was recovered unchanged after prolonged reaction times (entry 6). Presumably, the non-reactivity of the formyl derivative in this type of reaction is a reflection of the decreased nucleophilicity of the 2-position in the furan ring due to the electrophilicity of the formyl group, and therefore, the tropylium ion cannot attack the 2-position of the furan ring. The structures of the obtained β-(4-azuleno[1,2-*b*]thienyl)-α,β-unsaturated ketones **1** were confirmed by their ^1H NMR, and mass spectra as well as elemental analysis. Moreover, the structure of **1a** was established by X-ray crystallography.[17] The coupling constants between the olefinic protons of **1** are ca. 15 Hz, indicating that the azuleno[1,2-*b*]thiophene ring and the carbonyl group are *trans* to each other. X-Ray crystallographic analysis of **1a** also supports the *trans* configuration. If the above mentioned mechanism for the formation of benz[*a*]azulenic enones (Scheme 2) is correct, the azuleno[1,2-*b*]thiophene 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 spontaneously into the more stable *trans* isomer by the acid generated in the course of the reaction.

Table 1. Synthesis of β-(4-azuleno[1,2-*b*]thienyl)-α,β-unsaturated ketones (**1**) from tropylium ion derivatives (**3**)



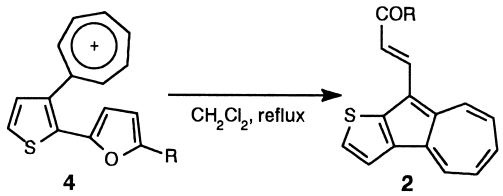
Entry	R	Starting material (**3**)	Time (h)	Product (**1**)	Yield[a] (%)
1	CH_3	**3a**	6	**1a**	57
2	C_2H_5	**3b**	7	**1b**	47
3	$C(CH_3)_3$	**3c**	7	**1c**	48
4	C_6H_5	**3d**	4	**1d**	52
5	$C(C_6H_5)_3$	**3e**	6	**1e**	42
6	CHO	**3g**	50		–[b]
7	CH=CH–C_6H_5	**3h**	7	**1h**	54–65

[a] Yields are of isolated and purified products.
[b] Starting material (**3g**) was recovered unchanged.

2.2. Synthesis of β-(4-azuleno[2,1-*b*]thienyl)-α,β-unsaturated ketones 2

Other isomers, β-(4-azuleno[2,1-*b*]thienyl)-α,β-unsaturated ketones **2** could be successfully obtained from the corresponding 2-(2-furyl)-3-tropyliothiophene tetrafluoroborates (**4**) in a similar manner as described above. The

Table 2. Synthesis of β-(4-azuleno[2,1-*b*]thienyl)-α,β-unsaturated ketones (**2**) from tropylium ion derivatives (**4**)



Entry	R	Starting material (**4**)	Time (h)	Product (**2**)	Yield[a] (%)
1	$C(C_6H_5)_3$	**4a**	5	**2a**	52
2	CH_3	**4b**	9	**2b**	55
3	C_6H_5	**4c**	12	**2c**	54

[a] Yields are of isolated and purified products.

synthetic sequence leading to β-(4-azuleno[2,1-*b*]thienyl)-α,β-unsaturated ketones **2** from the readily available compounds is depicted in Scheme 7. The palladium(II) catalyzed Stille coupling reaction of 2,3-dibromothiophene with 5-substituted 2-trimethylstannylfuran (**6**) gave the corresponding 2-furyl-3-bromothiophene derivative (**8**). The compound **8** was treated with butyllithium in THF at −78°C, followed by addition of powdered tropylium tetrafluoroborate to give the corresponding 3-cyclohepta-trienyl-2-(2-furyl)thiophene (**9**). Thermal sigmatropic rearrangement of **9** to **9′** and subsequent hydride abstraction using trityl tetrafluoroborate gave the corresponding 2-(2-furyl)-3-tropyliothiophene tetrafluoroborate (**4**) as dark colored crystals. Refluxing the dichloromethane solution of **4** gave the desired β-(4-azuleno[2,1-*b*]thienyl)-α,β-unsaturated ketone **2**. The results are shown in Table 2. The structures of the obtained β-(4-azuleno[2,1-*b*]thienyl)-α,β-unsaturated ketones **2** were confirmed by their ^{1}H NMR, and mass spectra as well as elemental analysis. The

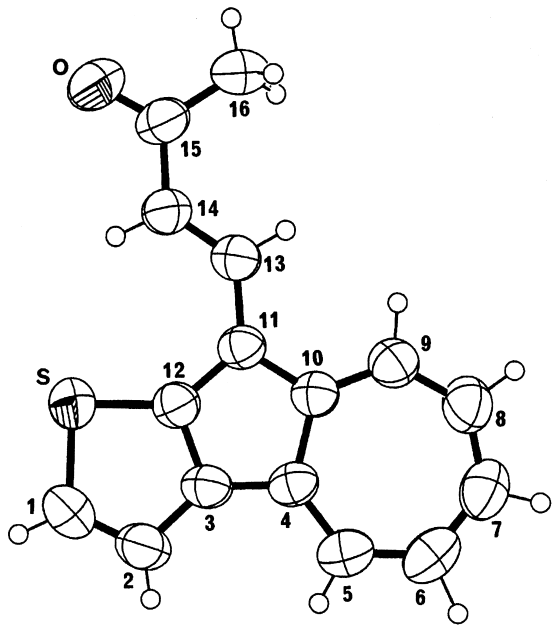


Figure 1. X-Ray structure of **2b** with the atom numbering scheme. The seven-membered ring shows very weak bond-length alternation as shown by the related bond lengths: C(4)–C(5)=1.382(3); C(5)–C(6)=1.395(4); C(6)–C(7)=1.368(4); C(7)–C(8)=1.382(4); C(8)–C(9)=1.370(4); C(9)–C(10)=1.384(3); C(4)–C(10)=1.487(3) Å.

coupling constants (ca. 15 Hz) between the olefinic protons of **2** show that the azuleno[2,1-*b*]thiophene ring and the carbonyl group are *trans* to each other as well as **1**. Moreover, the molecular structure of **2b** was unequivocally determined by a single-crystal X-ray analysis (Fig. 1). The details of the crystal structure of **2b** have been deposited at the Cambridge Crystallographic Data Center (CCDC 189654).

3. Conclusion

We have developed an efficient synthetic method of β-(4-azuleno[1,2-*b*]thienyl)-α,β-unsaturated ketones (**1**) and β-(4-azuleno[2,1-*b*]thienyl)-α,β-unsaturated ketones (**2**). This synthetic methodology is considered to be valuable to lead a diversity of β-(4-azuleno[1,2-*b*]thienyl)- and β-(4-azuleno[2,1-*b*]thienyl)-α,β-unsaturated ketones. The reasons are: (1) the starting materials are readily available, (2) the procedure is simple and easy, (3) yields are moderate, and (4) the formation of the azuleno[1,2-*b*]-thiophene ring and azuleno[2,1-*b*] thiophene ring is difficult by other synthetic methods.

4. Experimental

All melting points were uncorrected. ^{1}H NMR spectra were obtained on a Brucker DPX-250 spectrometer (250 MHz) using tetramethylsilane as an internal reference. The mass spectra were determined with Shimazdu GC–MS QP200A spectrometer. All reagents are of commercial quality. All dry solvents were freshly distilled over an appropriate drying agent before use. Column chromatography was performed on silica-gel (Wako-gel, C-200).

4.1. X-Ray structure determination

$C_{16}H_{12}OS$, FW 252.33, monoclinic space group $P2_1/c$, Z=4, T=297°C (570 K), a=7.989(2), b=9.433(3), c=17.029(3) Å, β=100.98(2)°, V=1259.8(5) Å^3, D_c=1.330 g/cm^3, $F(000)$=528, graphite monochromated Cu Kα radiation with λ=1.5418 Å, μ=2.133 mm^{-1}. The intensities of 2158 (1998 independent, R_{int}=0.024) were measured on a Rigaku AFC5R automatic four-circle diffractometer ($\theta/2\theta$ scan, $4.68<\theta<60.08°$). Absorption correction was made by using Ψ-scan method (T_{min}=0.710, T_{max}=1.000). The structure was solved by the direct method using a program package teXsan.[18] The positions of the non-hydrogen atoms were refined against F^2 by the full matrix least-squares calculations applying anisotropic displacement parameters. The hydrogen atoms were included in the refinement with constraints. The Structure refinements (1566 reflection with $I>2\sigma(I)$, 164 parameters) gave R=0.0889 and wR=0.1160, goodness of fit=2.000, $(\Delta/\sigma)_{max}<0.000$. $\Delta\rho_{max}$=0.28, $\Delta\rho_{min}$=−0.22 e/Å^{-3}.

4.1.1. Preparation of 2-cycloheptatrienyl-3-bromothiophene (5). To a solution of 2,3-dibromothiophene (20.7 mmol, 5.01 g) in 30 mL of dry terahydrofuran, 15.3 mL of butyllithium (1.6 M solution in hexane, 24.5 mmol) was added dropwise under nitrogen at −78°C. The mixture was stirred for 1 h at −78°C. Then, powdered

tropylium tetrafluoroborate (24.8 mmol, 4.41 g) was added in limited amounts. The mixture was stirred for 8 h, warmed to room temperature and stirred for 1 h. The usual work-up gave **5** (3.87 g, 74%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 3.21 (1H, t, J=5.6 Hz, seven-membered ring), 5.41 (2H, dd, J=5.6, 8.8 Hz, seven-membered ring), 6.18–6.30 (2H, m, seven-membered ring), 6.70–6.78 (2H, m, seven-membered ring), 6.97 (1H, d, J=5.4 Hz, thiophene ring), 7.19 (1H, d, J=5.4 Hz, thiophene ring). m/z: 254 (M^++2), 252 (M^+). Anal. calcd for $C_{11}H_9SBr$: C, 52.19; H, 3.58. Found: C, 52.48; H, 3.47.

4.2. General procedure for the synthesis of 2-cycloheptatrienyl-3-(2-furyl)thiophenes (7)

A mixture of **5** (1.47 g, 5.83 mmol), 2-trimethylstannylfuran derivatives (**6**) (8.19 mmol), bis(triphenylphosphine)palladium(II) chloride (0.275 g, 0.400 mmol) and 50 mL of THF was refluxed for 20 h under nitrogen atmosphere. The usual work-up gave the corresponding 2-cycloheptatrienyl-3-(2-furyl)thiophenes (**7**).

4.2.1. 2-Cycloheptatrienyl-3-(5-methyl-2-furyl)thiophene (7a). 2-Cycloheptatrienyl-3-(5-methyl-2-furyl)thiophene (**7a**) was obtained as a pale yellow oil in 85% yield. ^{1}H NMR ($CDCl_3$): δ 2.27 (3H, s, CH_3), 3.33 (1H, t, J=5.5 Hz, seven-membered ring), 5.48 (2H, dd, J=9.1, 5.5 Hz, seven-membered ring), 5.95 (1H, d, J=3.2 Hz, furan ring), 6.11 (1H, d, J=3.2 Hz, furan ring), 6.23–6.31 (2H, m, seven-membered ring), 6.76 (2H, dd, J=3.0, 3.0 Hz, seven-membered ring), 7.19 (1H, d, J=5.3 Hz, thiophene ring), 7.31 (1H, d, J=5.3 Hz, thiophene ring); m/z: 254 (M^+). Anal. calcd for $C_{16}H_{14}OS$: C, 75.56; H, 5.55. Found: C, 75.48; H, 5.62.

4.2.2. 2-Cycloheptatrienyl-3-(5-ethyl-2-furyl)thiophene (7b). 2-Cycloheptatrienyl-3-(5-ethyl-2-furyl)thiophene (**7b**) was obtained as a pale yellow oil in 46% yield. ^{1}H NMR ($CDCl_3$): δ 1.21 (3H, t, J=7.4 Hz, CH_3), 2.62 (2H, q, J=7.4 Hz, CH_2), 3.38 (1H, t, J=5.5 Hz, seven-membered ring), 5.48 (2H, dd, J=9.1, 5.5 Hz, seven-membered ring), 5.96 (1H, d, J=3.3 Hz, furan ring), 6.14 (1H, d, J=3.3 Hz, furan ring), 6.20–6.30 (2H, m, seven-membered ring), 6.70–6.76 (2H, m, seven-membered ring), 7.19 (1H, d, J=5.3 Hz, thiophene ring), 7.29 (1H, d, J=5.3 Hz, thiophene ring); m/z: 268 (M^+). Anal. calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01. Found: C, 76.26; H, 5.83.

4.2.3. 2-Cycloheptatrienyl-3-(5-*t*-butyl-2-furyl)thiophene (7c). 2-Cycloheptatrienyl-3-(5-*t*-butyl-2-furyl)thiophene (**7c**) was obtained as a pale yellow oil in 47% yield. ^{1}H NMR ($CDCl_3$): δ 1.23 (9H, s, CH_3), 3.50 (1H, t, J=5.4 Hz, seven-membered ring), 5.48 (2H, dd, J=9.1, 5.4 Hz, seven-membered ring), 5.93 (1H, d, J=3.2 Hz, furan ring), 6.17 (1H, d, J=3.2 Hz, furan ring), 6.20–6.30 (2H, m, seven-membered ring), 6.70–6.76 (2H, m, seven-membered ring), 7.16 (1H, d, J=5.4 Hz, thiophene ring), 7.24 (1H, d, J=5.4 Hz, thiophene ring); m/z: 296 (M^+). Anal. calcd for $C_{19}H_{20}OS$: C, 76.99; H, 6.76. Found: C, 77.12; H, 6.64.

4.2.4. 2-Cycloheptatrienyl-3-(5-phenyl-2-furyl)thiophene (7d). 2-Cycloheptatrienyl-3-(5-phenyl-2-furyl)thiophene (**7d**) was obtained as a yellow powder in 70% yield. ^{1}H NMR ($CDCl_3$): δ 3.56 (1H, t, J=5.5 Hz, seven-membered ring), 5.40 (2H, dd, J=9.1, 5.5 Hz, seven-membered ring), 6.14–6.28 (2H, m, seven-membered ring), 6.30 (1H, d, J=3.5 Hz, furan ring), 6.52 (1H, d, J=3.5 Hz, furan ring), 6.68–6.78 (2H, m, seven-membered ring), 6.99 (1H, d, J=5.4 Hz, thiophene ring), 7.02–7.30 (4H, m, thiophene ring and phenyl), 7.45 (2H, d, J=7.7 Hz, phenyl); m/z: 316 (M^+). Anal. calcd for $C_{21}H_{16}OS$: C, 79.71; H, 5.10. Found: C, 79.82; H, 5.31.

4.2.5. 2-Cycloheptatrienyl-3-(2-furyl)thiophene (7e). 2-Cycloheptatrienyl-3-(2-furyl)thiophene (**7e**) was obtained as a pale yellow oil in 65% yield. ^{1}H NMR ($CDCl_3$): δ 3.34 (1H, t, J=5.5 Hz, seven-membered ring), 5.47 (2H, dd, J=8.8, 5.5 Hz, seven-membered ring), 6.23 (1H, dd, J=3.4, 0.6 Hz, furan ring), 6.20–6.30 (2H, m, seven-membered ring), 6.37 (1H, dd, J=3.4, 1.8 Hz, furan ring), 6.70–6.80 (2H, m, seven-membered ring), 7.20 (1H, d, J=5.3 Hz, thiophene ring), 7.33 (1H, d, J=5.3 Hz, thiophene ring), 7.36 (1H, dd, J=1.8, 0.6 Hz, furan ring); m/z: 240 (M^+). Anal. calcd for $C_{15}H_{12}OS$: C, 74.97; H, 5.03. Found: C, 74.76; H, 5.21.

4.2.6. 2-Cycloheptatrienyl-3-[5-(1,3-dioxolan-2-yl)-2-furyl]thiophene (7f). 2-Cycloheptatrienyl-3-[5-(1,3-dioxolan-2-yl)-2-furyl]thiophene (**7f**) was obtained as a yellow oil in 81% yield. ^{1}H NMR ($CDCl_3$): δ 3.38 (1H, t, J=5.5 Hz, seven-membered ring), 3.82–4.01 (4H, m, dioxolane ring), 5.35 (2H, dd, J=8.9, 5.5 Hz, seven-membered ring), 5.80 (1H, s, dioxolane ring), 6.08 (1H, d, J=3.4 Hz, furan ring), 6.15–6.26 (2H, m, seven-membered ring), 6.30 (1H, d, J=3.4 Hz, furan ring), 6.60–6.76 (2H, m, seven-membered ring), 7.08 (1H, d, J=5.4 Hz, thiophene ring), 7.20 (1H, d, J=5.4 Hz, thiophene ring); m/z: 312 (M^+). Anal. calcd for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16. Found: C, 69.02; H, 5.22.

4.2.7. Synthesis of 2-cycloheptatrienyl-3-(5-formyl-2-furyl)thiophene (7g). A mixture of **7f** (4.29 g, 13.7 mmol), pyridinium *p*-toluenesulfonate (1.04 g, 4.12 mmol), 5 mL of H_2O and 60 mL of acetone was refluxed for 1 h. The solvent was evaporated in vacuo and the residue was dissolved in ether. The ether solution was washed with aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by short column chromatography over silica gel using toluene as eluent to give **7g** (3.45 g) as a yellow oil in 94% yield. ^{1}H NMR ($CDCl_3$): δ 3.38 (1H, t, J=5.5 Hz, seven-membered ring), 5.47 (2H, dd, J=9.0, 5.5 Hz, seven-membered ring), 6.28–6.34 (2H, m, seven-membered ring), 6.41 (1H, d, J=3.8 Hz, furan ring), 6.75–6.85 (2H, m, seven-membered ring), 7.23 (1H, d, J=3.8 Hz, furan ring), 7.28 (1H, d, J=5.4 Hz, thiophene ring), 7.47 (1H, d, J=5.4 Hz, thiophene ring), 9.58 (1H, s, formyl); m/z: 268 (M^+). Anal. calcd for $C_{16}H_{12}O_2S$: C, 71.62; H, 4.51. Found: C, 71.56; H, 4.66.

4.2.8. Synthesis of 2-cycloheptatrienyl-3-(5-styryl-2-furyl)-thiophene (7h). A mixture of **7g** (5.00 g, 18.6 mmol), benzyltriphenylphosphonium bromide (8.64 g, 18.6 mmol), 18-*crown*-6 (180 mg, 10 mmol) and 100 mL of CH_2Cl_2 was ice-cooled. To this solution, powdered KOH (2.08 g, 37.1 mmol) was added and the mixture was stirred

for 1 h at ambient temperature. After the filtration of insoluble materials, the filtrate was washed with water, and dried over Na_2SO_4. The solvent was evaporated in vacuo. The residue was purified by column chromatography over silica gel using hexane as eluent to give **7h** (5.72 g), which is a mixture of geometrical isomers (*E*/*Z*=ca. 2:1), as a pale yellow oil in 90% yield. *E*-isomer: ^{1}H NMR ($CDCl_3$): δ 3.58 (1H, t, *J*=5.5 Hz, seven-membered ring), 5.49 (2H, dd, *J*=9.0, 5.5 Hz, seven-membered ring), 6.25–6.31 (2H, m, seven-membered ring), 6.29 (1H, d, *J*=3.4 Hz, furan ring), 6.33 (1H, d, *J*=3.4 Hz, furan ring), 6.78 (1H, d, *J*=16.0 Hz, olefin), 6.72–6.80 (2H, m, seven-membered ring), 6.91 (1H, d, *J*=16.0 Hz, olefin), 7.18 (1H, d, *J*=5.2 Hz, thiophene ring), 7.31 (1H, d, *J*=5.2 Hz, thiophene ring), 7.20–7.44 (5H, m, phenyl); *m*/*z*: 342 (M^+). Anal. calcd for $C_{23}H_{18}OS$: C, 80.67; H, 5.30. Found: C, 80.52; H, 5.55. *Z*-isomer: ^{1}H NMR ($CDCl_3$): δ 3.22 (1H, t, *J*=5.5 Hz, seven-membered ring), 5.47 (2H, dd, *J*=9.0, 5.5 Hz, seven-membered ring), 6.11 (1H, d, *J*=3.8 Hz, furan ring), 6.23 (1H, d, *J*=3.8 Hz, furan ring), 6.21–6.25 (2H, m, seven-membered ring), 6.27 (1H, d, *J*=11.3 Hz, olefin), 6.42 (1H, d, *J*=11.3 Hz, olefin), 6.56–6.70 (2H, m, seven-membered ring), 7.09 (2H, d, *J*=2.0 Hz, phenyl), 7.27 (1H, d, *J*=5.0 Hz, thiophene ring), 7.32 (1H, d, *J*=5.0 Hz, thiophene ring), 7.22–7.46 (3H, m, phenyl); *m*/*z*: 342 (M^+). Anal. calcd for $C_{23}H_{18}OS$: C, 80.67; H, 5.30. Found: C, 80.50; H, 5.18.

4.3. General procedure for the synthesis of 3-bromo-2-(2-furyl)thiophene (8)

A mixture of 2-trimethylstannylfuran derivatives (**6**) (16.4 mmol), 2,3-dibromothiophene (21.3 mmol), bis-(triphenylphosphine)palladium(II) chloride (0.550 g, 0.800 mmol) and 50 mL of dry THF was refluxed for 20 h under nitrogen atmosphere. The usual work-up gave the corresponding 3-bromo-2-(2-furyl)thiophene (**8**).

4.3.1. 3-Bromo-2-(2-furyl)thiophene (8a). 3-Bromo-2-(2-furyl)thiophene (**8a**) was obtained as a pale yellow oil in 63% yield. ^{1}H NMR ($CDCl_3$): δ 6.48 (1H, dd, *J*=3.5, 1.7 Hz, furan ring), 6.98 (1H, d, *J*=5.3 Hz, thiophene ring), 7.05 (1H, d, *J*=3.5 Hz, furan ring), 7.16 (1H, d, *J*=5.3 Hz, thiophene ring), 7.42 (1H, d, *J*=1.7 Hz, furan ring); *m*/*z*: 230 (M^++2), 228 (M^+). Anal. calcd for C_8H_5OSBr: C, 41.94; H, 2.20. Found: C, 42.21; H, 2.33.

4.3.2. 3-Bromo-2-(5-methyl-2-furyl)thiophene (8b). 3-Bromo-2-(5-methyl-2-furyl)thiophene (**8b**) was obtained as a pale yellow oil in 53% yield. ^{1}H NMR ($CDCl_3$): δ 2.34 (3H, s, CH_3), 6.09 (1H, d, *J*=3.3 Hz, furan ring), 6.95 (1H, d, *J*=3.3 Hz, furan ring), 6.98 (1H, d, *J*=5.3 Hz, thiophene ring), 7.14 (1H, d, *J*=5.3 Hz, thiophene ring); *m*/*z*: 244 (M^++2), 242(M^+). Anal. calcd for C_9H_7OSBr: C, 44.46; H, 2.90. Found: C, 44.65; H, 3.10.

4.3.3. 3-Bromo-2-(5-phenyl-2-furyl)thiophene (8c). 3-Bromo-2-(5-phenyl-2-furyl)thiophene (**8c**) was obtained as pale yellow plates in 41% yield. Mp 66°C. ^{1}H NMR ($CDCl_3$): δ 6.76 (1H, d, *J*=3.6 Hz, furan ring), 7.03 (1H, d, *J*=5.3 Hz, thiophene ring), 7.13 (1H, d, *J*=3.6 Hz, furan ring), 7.22 (1H, d, *J*=5.3 Hz, thiophene ring), 7.28–7.33 (1H, m, phenyl), 7.38–7.48 (2H, m, phenyl), 7.73 (2H, m, phenyl); *m*/*z*: 306 (M^++2), 304(M^+). Anal. calcd for $C_{14}H_9OSBr$: C, 55.10; H, 2.97. Found: C, 55.28; H, 3.12.

4.4. General procedure for the synthesis of 3-cycloheptatrienyl-2-(2-furyl)thiophenes (9)

To a solution of **8** (4.11 mmol) in 20 mL of dry ether, 3.10 mL of butyllithium (1.6 M solution in hexane, 4.96 mmol) was added at −78°C under nitrogen atmosphere. The mixture was stirred for 1 h at −78°C. Then powdered tropylium tetrafluoroborate (998 mg, 5.61 mmol) was added in limited amounts. The mixture was stirred for 5 h at −78°C. Then, the mixture was quenched with 5% NH_4Cl solution and extracted with ether. The ether solution was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography to give **9**.

4.4.1. 3-Cycloheptatrienyl-2-(2-furyl)thiophene (9a). 3-Cycloheptatrienyl-2-(2-furyl)thiophene (**9a**) was obtained as a pale yellow oil in 84% yield. ^{1}H NMR ($CDCl_3$): δ 3.10 (1H, t, *J*=5.4 Hz, seven-membered ring), 5.39 (2H, dd, *J*=9.0, 5.4 Hz, seven-membered ring), 6.22 (1H, d, *J*=3.4 Hz, furan ring), 6.23–6.33 (2H, m, seven-membered ring), 6.36 (1H, dd, *J*=3.4, 1.8 Hz, furan ring), 6.73 (2H, dd, *J*=3.1, 3.1 Hz, seven-membered ring), 7.20 (1H, d, *J*=5.3 Hz, thiophene ring), 7.28 (1H, d, *J*=5.3 Hz, thiophene ring), 7.35 (1H, d, *J*=1.8 Hz, furan ring); *m*/*z*: 240(M^+). Anal. calcd for $C_{15}H_{12}OS$: C, 74.97; H, 5.03. Found: C, 75.22; H, 5.12.

4.4.2. 3-Cycloheptatrienyl-2-(5-methyl-2-furyl)thiophene (9b). 3-Cycloheptatrienyl-2-(5-methyl-2-furyl)thiophene (**9b**) was obtained as a pale yellow oil in 66% yield. ^{1}H NMR ($CDCl_3$): δ 2.29 (3H, s, CH_3), 3.07 (1H, t, *J*=5.5 Hz, seven-membered ring), 5.41 (2H, dd, *J*=8.9, 5.5 Hz, seven-membered ring), 5.96 (1H, d, *J*=3.2 Hz, furan ring), 6.09 (1H, d, *J*=3.2 Hz, furan ring), 6.23–6.35 (2H, m, seven-membered ring), 6.75 (2H, dd, *J*=3.1, 3.1 Hz, seven-membered ring), 7.20 (1H, d, *J*=5.2 Hz, thiophene ring), 7.27 (1H, d, *J*=5.2 Hz, thiophene); *m*/*z*: 254 (M^+). Anal. calcd for $C_{16}H_{14}OS$: C, 75.56; H, 5.55. Found: C, 75.68; H, 5.69.

4.4.3. 3-Cycloheptatrienyl-2-(5-phenyl-2-furyl)thiophene (9c). 3-Cycloheptatrienyl-2-(5-phenyl-2-furyl)thiophene (**9c**) was obtained as a pale yellow oil in 87% yield. ^{1}H NMR ($CDCl_3$): δ 3.28 (1H, t, *J*=5.5 Hz, seven-membered ring), 5.44 (2H, dd, *J*=8.9, 5.5 Hz, seven-membered ring), 6.26–6.33 (2H, m, seven-membered ring), 6.35 (1H, d, *J*=3.5 Hz, furan ring), 6.63 (1H, d, *J*=3.5 Hz, furan ring), 6.75–6.85 (2H, dd, *J*=3.1, 3.1 Hz, seven-membered ring), 7.21–7.26 (2H, m, phenyl and thiophene ring), 7.30 (1H, d, *J*=5.3 Hz, thiophene ring), 7.35 (2H, m, phenyl), 7.62 (2H, m phenyl); *m*/*z*: 316 (M^+). Anal. calcd for $C_{21}H_{16}OS$: C, 79.71; H, 5.05. Found: C, 79.57; H, 4.88.

4.5. Thermal isomerization of 7 and 9

A xylene solution of **7** was refluxed for 3 h. The solvent was evaporated in vacuo and then the residue was subjected to short column chromatography over silica gel to give **7′** in almost quantitative yield. In a similar manner, thermal isomerization of **9** to **9′** was achieved.

4.6. General procedure for the synthesis of 3-(2-furyl)-2-tropyliothiophene tetrafluoroborates (3) from 7′

A solution of **7′** (0.786 mmol) in 3 mL of dry dichloromethane was added to a solution of triphenylmethyl tetrafluoroborate (259 mg, 0.786 mmol) in dry dichloromethane (2 mL) at ambient temperature and was stirred for 5 min. After addition of 100 mL of dry ether, the resulting precipitates were collected, washed with dry ether, and dried in vacuo to yield 3-(2-furyl)-2-tropyliothiophene tetrafluoroborates (**3**) as dark colored precipitates.

4.6.1. 2-Tropylio-3-(5-methyl-2-furyl)thiophene tetrafluoroborate (3a). 2-Tropylio-3-(5-methyl-2-furyl)thiophene tetrafluoroborate (**3a**) was obtained as purple powder in 87% yield. ^{1}H NMR (CD_2Cl_2): δ 2.22 (3H, s, CH_3), 6.20 (1H, d, J=3.3 Hz, furan ring), 6.75 (1H, d, J=3.3 Hz, furan ring), 7.43 (1H, d, J=5.2 Hz, thiophene ring), 7.95 (1H, d, J=5.2 Hz, thiophene ring), 8.69–8.99 (6H, m, tropylium). Anal. calcd for $C_{16}H_{13}BF_4OS$: C, 56.50; H, 3.85. Found: C, 56.75; H, 3.70.

4.6.2. 2-Tropylio-3-(5-ethyl-2-furyl)thiophene tetrafluoroborate (3b). 2-Tropylio-3-(5-ethyl-2-furyl)thiophene tetrafluoroborate (**3b**) was obtained as blue powder in 82% yield. ^{1}H NMR (CD_2Cl_2): δ 1.12 (3H, d, J=7.6 Hz, CH_3), 2.55 (2H, q, J=7.6 Hz, CH_2), 6.17 (1H, d, J=3.5 Hz, furan ring), 6.71 (1H, d, J=3.5 Hz, furan ring), 7.39 (1H, d, J=5.4 Hz, thiophene ring), 7.88 (1H, d, J=5.4 Hz, thiophene ring), 8.88–8.97 (6H, m, tropylium). Anal. calcd for $C_{17}H_{15}BF_4OS$: C, 57.65; H, 4.27. Found: C, 57.46; H, 4.12.

4.6.3. 2-Tropylio-3-(5-*t*-butyl-2-furyl)thiophene tetrafluoroborate (3c). 2-Tropylio-3-(5-*t*-butyl-2-furyl)thiophene tetrafluoroborate (**3c**) was obtained as purple powder in 88% yield. ^{1}H NMR (CD_2Cl_2): δ 1.13 (9H, s, CH_3), 6.17 (1H, d, J=3.6 Hz, furan ring), 6.72 (1H, d, J=3.6 Hz, furan ring), 7.39 (1H, d, J=5.0 Hz, thiophene ring), 7.91 (1H, d, J=5.0 Hz, thiophene ring), 8.83–8.96 (6H, m, tropylium). Anal. calcd for $C_{19}H_{19}BF_4OS$: C, 59.71; H, 5.01. Found: C, 59.56; H, 4.88.

4.6.4. 2-Tropylio-3-(5-phenyl-2-furyl)thiophene tetrafluoroborate (3d). 2-Tropylio-3-(5-phenyl-2-furyl)thiophene tetrafluoroborate (**3d**) was obtained as deep-green powder in 64% yield. ^{1}H NMR (CD_2Cl_2): δ 6.93 (1H, d, J=3.7 Hz, furan ring), 6.98 (1H, d, J=3.7 Hz, furan ring), 7.20–7.34 (5H, m, phenyl), 7.56 (1H, d, J=5.3 Hz, thiophene ring), 8.03 (1H, d, J=5.3 Hz, thiophene ring), 8.69–8.82 (4H, m, tropylium), 9.10–9.15 (2H, m, tropylium). Anal. calcd for $C_{21}H_{15}BF_4OS$: C, 62.71; H, 3.76. Found: C, 62.56; H, 3.66.

4.6.5. 2-Tropylio-3-(5-triphenylmethyl-2-furyl)thiophene tetrafluoroborate (3e). 2-Tropylio-3-(5-triphenylmethyl-2-furyl)thiophene tetrafluoroborate (**3e**) was obtained as reddish-purple powder in 76% yield (2 equiv. of triphenylmethyl tetrafluoroborate was used). ^{1}H NMR (CD_3CN): δ 6.21 (1H, d, J=3.5 Hz, furan ring), 6.81–6.87 (6H, m, phenyl), 6.92 (1H, d, J=3.5 Hz, furan ring), 7.17–7.31 (9H, m, phenyl), 7.52 (1H, d, J=5.3 Hz, thiophene ring), 7.96 (1H, d, J=5.3 Hz, thiophene ring), 8.19 (2H, ddd, J=10.3, 7.0, 3.9 Hz, tropylium), 8.51 (2H, dd, J=7.0, 3.9 Hz, tropylium), 8.92 (2H, d, J=10.3 Hz, tropylium). Anal. calcd for $C_{34}H_{25}BF_4OS$: C, 71.84; H, 4.43. Found: C, 71.66; H, 4.28.

4.6.6. 2-Tropylio-3-(5-formyl-2-furyl)thiophene tetrafluoroborate (3g). 2-Tropylio-3-(5-formyl-2-furyl)thiophene tetrafluoroborate (**3g**) was obtained as red powder in 65% yield. ^{1}H NMR (CD_3CN): δ 7.00 (1H, d, J=3.7 Hz, furan ring), 7.41 (1H, d, J=3.7 Hz, furan ring), 7.65 (1H, d, J=5.3 Hz, thiophene ring), 8.07 (1H, d, J=5.3 Hz, thiophene ring), 8.87–8.99 (4H, m, tropylium), 9.16 (2H, br d, J=9.0 Hz, tropylium), 9.59 (1H, s, formyl). Anal. calcd for $C_{16}H_{11}BF_4O_2S$: C, 54.27; H, 3.13. Found: C, 54.02; H, 3.29.

4.6.7. (*E*)-2-Tropylio-3-(5-styryl-2-furyl)thiophene tetrafluoroborate (3h-*E*). (*E*)-2-Tropylio-3-(5-styryl-2-furyl)-thiophene tetrafluoroborate (**3h**-*E*) was obtained as blue powder in 62% yield. ^{1}H NMR (CD_2Cl_2): δ 6.32 (1H, d, J=13.0 Hz, olefin), 6.43 (1H, d, J=13.0 Hz, olefin), 6.62 (1H, d, J=3.7 Hz, furan ring), 7.02 (1H, d, J=3.7 Hz, furan ring), 6.93–7.03 (2H, m, phenyl), 7.15 (2H, d, J=7.9 Hz, phenyl), 7.34 (1H, d, J=4.3 Hz, phenyl), 7.53 (1H, d, J= 5.4 Hz, thiophene ring), 8.02 (1H, d, J=5.4 Hz, thiophene ring), 8.37–9.23 (6H, m, tropylium). Anal. calcd for $C_{23}H_{17}BF_4OS$: C, 64.51; H, 3.97. Found: C, 64.76; H, 4.12.

4.6.8. (*Z*)-2-Tropylio-3-(5-styryl-2-furyl)thiophene tetrafluoroborate (3h-*Z*). (*Z*)-2-Tropylio-3-(5-styryl-2-furyl)-thiophene tetrafluoroborate (**3h**-*Z*) was obtained as blue powder in 68% yield. ^{1}H NMR (CD_2Cl_2): δ 6.50 (1H, d, J=3.5 Hz, furan ring), 6.72 (1H, d, J=5.0 Hz, olefin), 6.84 (1H, d, J=3.5 Hz, furan ring), 7.26–7.32 (6H, m, phenyl and tropylium), 7.35 (1H, d, J=5.0 Hz, olefin), 7.46 (1H, d, J=5.2 Hz, thiophene ring), 7.91 (1H, d, J=5.2 Hz, thiophene ring), 8.84 (3H, m, tropylium), 9.05–9.09 (2H, m, tropylium). Anal. calcd for $C_{23}H_{17}BF_4OS$: C, 64.51; H, 3.97. Found: C, 64.39; H, 3.88.

4.7. General procedure for the synthesis of 2-(3-furyl)-3-tropyliothiophene tetrafluoroborates 4 from 9′

Following the procedure for the preparation of compounds **3**, **4** was obtained as deep-colored precipitation.

4.7.1. 2-(5-Triphenylmethyl-3-furyl)-3-tropyliothiophene tetrafluoroborate (4a). From **9′a** and 2 equiv. of trityl tetrafluoroborate, 2-(5-triphenylmethyl-3-furyl)-3-tropyliothiophene tetrafluoroborate (**4a**) was obtained as reddish-purple powder in 82% yield. ^{1}H NMR (CD_3CN): δ 6.16 (1H, d, J=3.6 Hz, furan ring), 6.80 (1H, d, J=3.6 Hz, furan ring), 6.81–6.87 (6H, m, phenyl), 7.17–7.30 (10H, m, phenyl and thiophene ring), 7.60 (1H, d, J=5.3 Hz, thiophene ring), 8.32–8.45 (2H, m, tropylium), 8.64 (2H, dd, J=6.6, 4.4 Hz, tropylium), 8.97 (2H, d, J=10.3 Hz, tropylium). Anal. calcd for $C_{34}H_{25}BF_4OS$: C, 71.84; H, 4.43. Found: C, 71.68; H, 4.55.

4.7.2. 2-(5-Methyl-3-furyl)-3-tropyliothiophene tetrafluoroborate (4b). 2-(5-Methyl-3-furyl)-3-tropyliothiophene tetrafluoroborate (**4b**) was obtained as dark-purple powder in 78% yield. ^{1}H NMR (CD_3CN): δ 2.18 (3H, s, CH_3), 6.13 (1H, d, J=3.3 Hz, furan ring), 6.59 (1H, d, J=3.3 Hz, furan ring), 7.41 (1H, d, J=5.3 Hz, thiophene

ring), 7.52 (1H, d, J=5.3 Hz, thiophene ring), 8.85–9.11 (6H, m, tropylium). Anal. calcd for $C_{16}H_{13}BF_4OS$: C, 56.50; H, 3.85. Found: C, 56.72; H, 3.68.

4.7.3. 2-(5-Phenyl-3-furyl)-3-tropyliothiophene tetrafluoroborate (4c). 2-(5-Phenyl-3-furyl)-3-tropyliothiophene tetrafluoroborate (**4c**) was obtained as violet powder in 72% yield. ^{1}H NMR (CD_3CN): δ 6.82 (1H, d, J=3.7 Hz, furan ring), 6.89 (1H, d, J=3.7 Hz, furan ring), 7.25–7.38 (5H, m, phenyl), 7.43 (1H, d, J=5.3 Hz, thiophene ring), 7.68 (1H, d, J=5.3 Hz, thiophene ring), 8.85–8.97 (4H, m, tropylium), 9.18–9.24 (2H, m, tropylium). Anal. calcd for $C_{21}H_{15}BF_4OS$: C, 62.71; H, 3.76. Found: C, 62.58; H, 3.58.

4.8. General procedure for the synthesis of β-(4-azuleno[1,2-*b*]thienyl)-α,β-unsaturated ketones (1) and β-(4-azuleno[2,1-*b*]thienyl)-α,β-unsaturated ketones (2)

A solution of **3** or **4** (1.00 mmol) in 100 mL of dry CH_2Cl_2 was refluxed, and the solvent was evaporated in vacuo. The product was purified by column chromatography over silica gel and recrystallized from toluene.

4.8.1. 4-(4-Azuleno[1,2-*b*]thienyl)but-3-en-2-one (1a). 4-(4-Azuleno[1,2-*b*]thienyl)but-3-en-2-one (**1a**) was obtained from **3a** as deep-bluish green needles in 57% yield; without isolation of **3a**, **1a** was also obtained immediately from **7a**′ in 36% yield. Mp 144–145.5°C. ^{1}H NMR ($CDCl_3$): δ 2.46 (3H, s, CH_3), 6.90 (1H, d, J=15.6 Hz, olefin), 7.25 (1H, dd, J=10.4, 9.6 Hz, seven-membered ring), 7.26 (1H, dd, J=10.1, 9.2 Hz, seven-membered ring), 7.62 (1H, dd, J=10.1, 9.6 Hz, seven-membered ring), 7.73 (1H, d, J=5.1 Hz, thiophene ring), 7.89 (1H, d, J=5.1 Hz, thiophene ring), 8.28 (1H, d, J=15.6 Hz, olefin), 8.29 (1H, d, J=9.2 Hz, seven-membered ring), 8.49 (1H, d, J=10.4 Hz, seven-membered ring); m/z: 252 (M^+). Anal. calcd for $C_{16}H_{12}OS$: C, 76.16; H, 4.79. Found: C, 76.30; H, 4.63.

4.8.2. 5-(4-Azuleno[1,2-*b*]thienyl)pent-4-en-3-one (1b). 5-(4-Azuleno[1,2-*b*]thienyl)pent-1-en-3-one (**1b**) was obtained from **3b** as dark-green needles in 47% yield. Mp 127°C. ^{1}H NMR ($CDCl_3$): δ 1.25 (3H, t, J=7.4 Hz, CH_3), 2.77 (2H, q, J=7.4 Hz, CH_2), 6.96 (1H, d, J=15.5 Hz, olefin), 7.31 (2H, t, J=9.9 Hz, seven-membered ring), 7.62 (1H, t, J=9.9 Hz, seven-membered ring), 7.78 (1H, d, J=5.1 Hz, thiophene ring), 7.92 (1H, d, J=5.1 Hz, thiophene ring), 8.38 (1H, d, J=7.1 Hz, seven-membered ring), 8.39 (1H, d, J=15.5 Hz, olefin), 8.62 (1H, d, J=10.5 Hz, seven-membered ring); m/z: 266 (M^+). Anal. calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30. Found: C, 76.48; H, 5.38.

4.8.3. 1-(4-Azuleno[1,2-*b*]thienyl)-4,4-dimethyl-pent-1-en-3-one (1c). 1-(4-Azuleno[1,2-*b*]thienyl)-4,4-dimethyl-pent-1-en-3-one (**1c**) was obtained from **3c** as deep bluish-green needles in 48% yield. Mp 126°C. ^{1}H NMR ($CDCl_3$): δ 1.32 (9H, s, CH_3), 7.22 (2H, t, J=9.8 Hz, seven-membered ring), 7.28 (1H, d, J=15.2 Hz, olefin), 7.54 (1H, t, J=10.1 Hz, seven-membered ring), 7.70 (1H, d, J=5.1 Hz, thiophene ring), 7.89 (1H, d, J=5.1 Hz, thiophene ring), 8.26 (1H, d, J=9.1 Hz, seven-membered ring), 8.46 (1H, d, J=15.1 Hz, olefin), 8.57 (1H, d, J=10.6 Hz, seven-membered ring); m/z: 294 (M^+). Anal. calcd for $C_{19}H_{18}OS$: C, 77.51; H, 6.16. Found: C, 77.43; H, 6.25.

4.8.4. 1-(4-Azuleno[1,2-*b*]thienyl)-3-phenyl-prop-1-en-3-one (1d). 1-(4-Azuleno[1,2-*b*]thienyl)-3-phenyl-prop-1-en-3-one (**1d**) was obtained from **3d** as deep bluish-green needles in 52% yield. Mp 224.5–225.5°C. ^{1}H NMR ($CDCl_3$): δ 7.31–7.39 (2H, m, seven-membered ring), 7.52–7.65 (4H, m, phenyl and seven-membered ring), 7.72 (1H, d, J=15.0 Hz, olefin), 7.85 (1H, d, J=5.1 Hz, thiophene ring), 7.96 (1H, d, J=5.1 Hz, thiophene ring), 8.11 (2H, dd, J=8.0, 1.7 Hz, phenyl), 8.38 (1H, d, J=9.1 Hz, seven-membered ring), 8.67 (1H, d, J=15.0 Hz, olefin), 8.70 (1H, d, J=10.4 Hz, seven-membered ring); m/z: 314 (M^+). Anal. calcd for $C_{21}H_{14}OS$: C, 80.23; H, 4.49. Found: C, 80.15; H, 4.58.

4.8.5. 1,1,1-Triphenyl-4-(4-azuleno[1,2-*b*]thienyl)but-3-en-2-one (1e). 1,1,1-Triphenyl-4-(4-azuleno[1,2-*b*]thienyl)-but-3-en-2-one (**1e**) was obtained from **3e** as deep bluish-green needles in 42% yield. Mp >300°C. ^{1}H NMR ($CDCl_3$): 6.88 (1H, d, J=15.2 Hz, olefin), 6.95 (1H, d, J=5.1 Hz, thiophene ring), 7.21–7.42 (17H, m, phenyl and seven-membered ring), 7.60 (1H, dd, J=9.8, 9.8 Hz, seven-membered ring), 7.72 (1H, d, J=5.1 Hz, thiophene ring), 8.31 (1H, d, J=9.0 Hz, seven-membered ring), 8.50 (1H, d, J=15.2 Hz, olefin), 8.60 (1H, d, J=10.3 Hz, seven-membered ring); m/z: 480 (M^+). Anal. calcd for $C_{34}H_{24}OS$: C, 84.97; H, 5.03. Found: C, 85.15; H, 4.88.

4.8.6. 1-(4-Azuleno[1,2-*b*]thienyl)-5-phenyl-penta-1,4-dien-3-one (1h). 1-(4-Azuleno[1,2-*b*]thienyl)-5-phenyl-pent-1,4-dien-3-one (**1h**) was obtained from **3h**-(*E*) or **3h**-(*Z*) as deep-green needles in 54% yield from **3h**-(*E*), 65% from **3h**-(*Z*). Mp 176–177°C. ^{1}H NMR ($CDCl_3$): 7.17 (1H, d, J=15.9 Hz, olefin), 7.23 (1H, d, J=15.3 Hz, olefin), 7.29–7.41 (5H, m, phenyl and seven-membered ring), 7.66 (2H, d, J=7.8 Hz, phenyl), 7.64 (1H, t, J=9.5 Hz, seven-membered ring), 7.79 (1H, d, J=15.9 Hz, olefin), 7.84 (1H, d, J=5.1 Hz, thiophene ring), 7.94 (1H, d, J=5.1 Hz, thiophene ring), 8.37 (1H, d, J=9.1 Hz, seven-membered ring), 8.57 (1H, d, J=15.3 Hz, olefin), 8.69 (1H, d, J=10.3 Hz, seven-membered ring); m/z: 340 (M^+). Anal. calcd for $C_{23}H_{16}OS$: C, 81.15; H, 4.74. Found: C, 81.33; H, 4.82.

4.8.7. 1,1,1-Triphenyl-4-(4-azuleno[2,1-*b*]thienyl)but-3-en-2-one (2a). 1,1,1-Triphenyl-4-(4-azuleno[2,1-*b*]thienyl)-but-3-en-2-one (**2a**) was obtained from **4a** as deep-green needles in 52% yield. Mp 283–285°C. ^{1}H NMR ($CDCl_3$): 6.77 (1H, d, J=14.9 Hz, olefin), 7.16–7.62 (19H, m, phenyl, seven-membered and thiophene ring), 7.68 (1H, d, J=5.2 Hz, thiophene ring), 8.42 (1H, d, J=9.0 Hz, seven-membered ring), 8.51 (1H, d, J=14.9 Hz, olefin), 8.60 (1H, d, J=10.3 Hz, seven-membered ring); m/z: 480 (M^+). Anal. calcd for $C_{34}H_{24}OS$: C, 84.97; H, 5.03. Found: C, 84.76; H, 5.16.

4.8.8. 4-(4-Azuleno[2,1-*b*]thienyl)but-3-en-2-one (2b). 4-(4-Azuleno[2,1-*b*]thienyl)but-3-en-2-one (**2b**) was obtained from **3a** as deep bluish-green prisms in 54% yield. Mp 151–152°C. ^{1}H NMR ($CDCl_3$): δ 2.47 (3H, s, CH_3), 6.73 (1H, d, J=15.5 Hz, olefin), 7.36 (1H, dd, J=10.4, 9.6 Hz, seven-membered ring), 7.38 (1H, dd, J=10.0, 9.3 Hz,

seven-membered ring), 7.56 (1H, d, J=5.2 Hz, thiophene ring), 7.66 (1H, dd, J=10.0, 9.6 Hz, seven-membered ring), 7.77 (1H, d, J=5.2 Hz, thiophene ring), 8.35 (1H, d, J=15.5 Hz, olefin), 8.49 (1H, d, J=9.3 Hz, seven-membered ring), 8.60 (1H, d, J=10.4 Hz, seven-membered ring); m/z: 252 (M^+). Anal. calcd for $C_{16}H_{12}OS$: C, 76.16; H, 4.79. Found: C, 76.29; H, 4.88.

4.8.9. 1-(4-Azuleno[2,1-*b*]thienyl)-3-phenyl-prop-1-en-3-one (2c). 1-(4-Azuleno[2,1-*b*]thienyl)-3-phenyl-prop-1-en-3-one (**2c**) was obtained from **3c** as deep-green needles in 54% yield. Mp 249.5–250.5°C. ^{1}H NMR ($CDCl_3$); δ 7.39–7.47 (2H, m, seven-membered ring), 7.51–7.64 (3H, m phenyl), 7.57 (1H, d, J=15.0 Hz, olefin), 7.61 (1H, d, J=5.2 Hz, thiophene ring), 7.72 (1H, dd, J=9.9, 9.9 Hz, seven-membered ring), 7.83 (1H, d, J=5.2 Hz, thiophene ring), 8.16 (2H, dd, J=7.9, 1.7 Hz, phenyl), 8.55 (1H, d, J=9.1 Hz, seven-membered ring), 8.75 (1H, d, J=15.0 Hz, olefin), 8.76 (1H, d, J=10.0 Hz, seven-membered ring); m/z: 314 (M^+). Anal. calcd for $C_{21}H_{14}OS$: C, 80.23; H, 4.49. Found: C, 80.44; H, 4.38.

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