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Azulenesulfonium and azulenebis(sulfonium) salts: Formation by interrupted Pummerer reaction and subsequent derivatisation by nucleophiles

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ABSTRACT

Azulenes undergo either single or dual S_EAr reactions depending on the nature of the sulfur(IV) electrophile employed. These electrophiles are generated *in situ* from either sulfoxides or sulfides. The resultant cationic or dicationic azulene products can undergo further derivatisation by means of nucleophilic attack at the sulfonium α-carbon. In the case of cycloalkyl azulenylsulfonium salts, this leads to ring-opened azulenylsulfide products.

1. Introduction

Sulfonium salts, trivalent cationic sulfur(IV) species, have a rich chemistry which has seen them exploited in various applications. They are used as photoacid generators [1], for purposes including microlithography [2], initiation of polymerisation [3], optical data storage [4], and oxygen-independent photodynamic therapy [5]. In organic synthesis, sulfonium salts may be employed in cross-coupling, where they have been shown to be competent pseudo-halide electrophilic coupling partners [6–12]. They have been used to enable versatile derivatisation reactions using photoredox catalysis [11b,c], [13–22], as well as via S_NAr processes and/or aryne intermediates [23,24], and via sulfurane intermediates [46,47]. Synthetic applications of sulfonium salts (and other sulfur(IV) species derived from them, such as sulfur ylides) have been reviewed [25].

Methods for preparing sulfonium salts have been reviewed [26], and include approaches such as the direct alkylation of thiols and sulfides [27]. One strategy is to employ a sulfoxide starting material in a so-called "Interrupted Pummerer" reaction [25,28,29]. As shown in Scheme 1, a sulfoxide **1** may be activated with an electrophilic activating agent **2** (commonly an acid anhydride) to give cationic intermediate **3**. In a classical Pummerer reaction, intermediate **3** undergoes deprotonation α-to sulfur, with concomitant S–O bond cleavage to give thionium ion **4**. This in turn undergoes addition of the carboxylate nucleophile to give α-acyloxysulfide **5** as the final product. However, in the presence of a sufficiently nucleophilic additive, the reaction pathway may be "interrupted", with nucleophilic substitution at sulfur occurring in preference to deprotonation, thereby forming sulfonium salt **6**. The interrupted Pummerer reaction has been utilised in [3,3]-sigmatropic reaction cascades [30], in carbohydrate synthesis [31], and in heterocycle synthesis [32].

If an aromatic ring is sufficiently electron-rich, it may act as the nucleophile in the interrupted Pummerer reaction, by an S_EAr mechanism. Azulene (**7**), a bicyclic, non-alternant arene, fulfils this criterion. Known for its blue colour [33] and anomalous fluorescence [34], azulene has a dipole of 1.08 D, unusually high for a hydrocarbon. This may be rationalised through considerations of resonance, with the resonance structures **7′**-**7‴** shown in Scheme 2 all possessing a seven-membered ring that is itself aromatic (6π tropylium cation). It follows from these resonance structures that

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E-mail address: s.e.lewis@bath.ac.uk (S.E. Lewis).
[1] Dedicated to the memory of Prof. Jonathan M. J. Williams, mentor and friend, from whom I learned a great deal.

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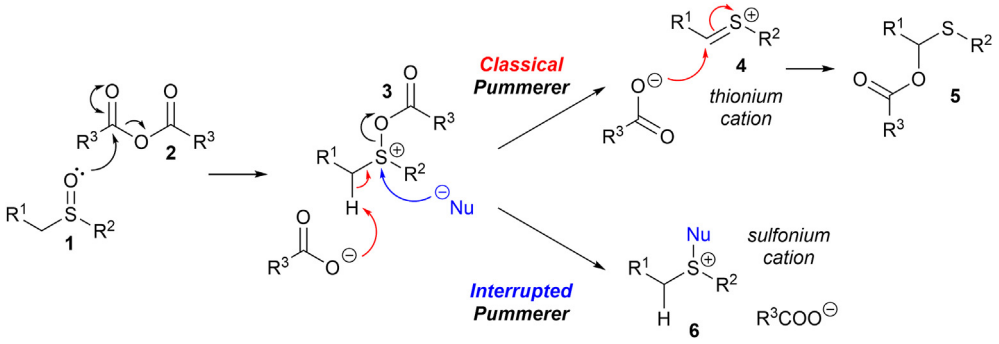
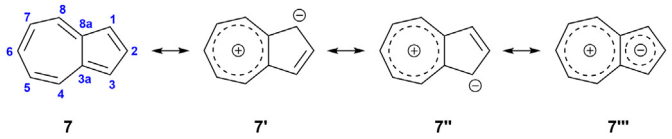


Scheme 1. Classical and Interrupted variants of the Pummerer reaction.



Scheme 2. Resonance structures of azulene.

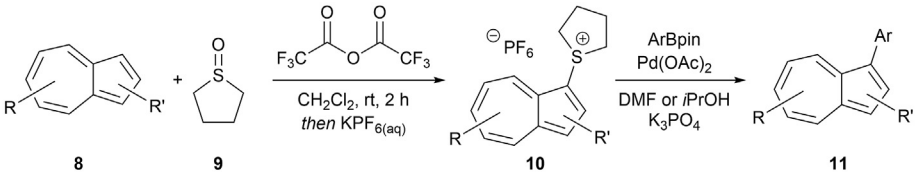
the 1- and 3-positions of azulene are the most electron rich and hence the preferred sites for S_EAr reactions.

Formation of a sulfonium salt by an interrupted Pummerer reaction with azulenes was first reported by Shoji, Ito, Morita and co-workers [35]. As part of our ongoing interest in the chemistry of azulene [36,48,49], we previously reported the synthesis of *cyclic* sulfonium salts bearing an azulene substituent. These were highly stable and applicable in cross-coupling (Scheme 3) [10]. The cross-coupling of azulenes had previously been difficult, due to instability of most azulenyl halides; this necessitated other approaches [37]. We now wish to report on the scope of the interrupted Pummerer reaction of azulenes, on a variant employing sulfide starting materials, as well as on reactions of azulenesulfonium salts other than in cross-coupling.

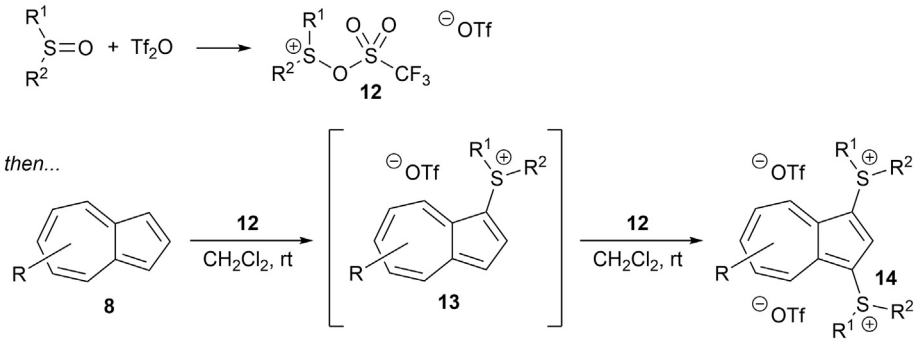
2. Results and discussion

2.1. Azulenebis(sulfonium) dications

Both the 1- and 3-positions of azulene are highly nucleophilic (*c.f.* Scheme 2), which can lead to problems of over-reaction in S_EAr reactions. For example, electrophilic halogenation of azulene with *N*-halosuccinimides inevitably leads to mixtures of 1-halo- and 1,3-dihaloazulenes. In contrast, the interrupted Pummerer reaction shown in Scheme 3 provides monosubstitution product **10** cleanly, with no second S_EAr reaction occurring. The introduction of a (positively charged) sulfonium substituent in **10** strongly deactivates the azulene ring towards further S_EAr reactions. Nevertheless, Shoji, Ito, Morita and co-workers have previously demonstrated [35a] that a second interrupted Pummerer reaction may be induced by use of a stronger activating agent, thereby producing an azulenebis(sulfonium) dication. Specifically, use of a sulfonic acid anhydride (triflic anhydride) instead of a carboxylic acid anhydride can provide a Pummerer intermediate **12** (Scheme 4) which is electrophilic enough to react a second time with monosulfonium salts such as **13**. (Use of triflic anhydride to activate DMSO for S_EAr reactions with arenes was first reported by Balenkova [38]).



Scheme 3. Synthesis of azulenesulfonium salts by Interrupted Pummerer reaction.



Scheme 4. Synthesis of azulenebis(sulfonium) salts by Interrupted Pummerer reaction.

Table 1
Synthesis of azulenebis(sulfonium) salts.[a]

Entry	Substrate	Sulfoxide	Product	Yield
1	Azulene	DMSO	**15**•2OTf	95%[b]
2	Azulene	**9**	**16**•2OTf	90%
3	4,6,8-Trimethylazulene	DMSO	**17**•2OTf	69%
4	4,6,8-Trimethylazulene	**9**	**18**•2OTf	77%

[a] Reaction conditions: 14 eq. sulfoxide, 2.4 eq. Tf_2O, CH_2Cl_2, rt, 2 h.
[b] Yield previously reported [35a] for this product.

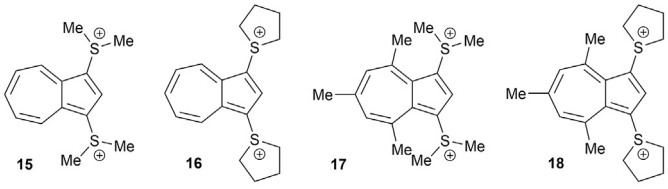


Fig. 1. Structures of dications $\mathbf{15}^{2+}$ - $\mathbf{18}^{2+}$.

We have employed triflic anhydride with other azulenes and sulfoxides to obtain novel azulenebis(sulfonium) dications **16**–**18** that have been characterised crystallographically, as shown in Table 1 and Figs. 1–3. While the procedure in Scheme 4 provides the products as their triflate salts in the first instance, a salt swap with aqueous KPF_6 may be readily effected to give the corresponding hexafluorophosphate salts.

In order to expand further the synthetic accessibility of azulenebis(sulfonium) salts, we investigated other ways to generate reactive electrophiles such as **3** (Scheme 1). Species of type **3** can react with azulenes to give the desired products as they are trivalent sulfur(IV) species bearing a good leaving group. Generation of **3** from a sulfoxide is redox-neutral with respect to sulfur, *i.e.* starting material **1** is also a sulfur(IV) species. We considered the alternative possibility of generating a reactive sulfur(IV) species in an oxidative process from a sulfur(II) precursor (Scheme 5). In order to activate a sulfide such as **19**, selection of the correct activating agent is crucial. Whereas an acylating agent such as **20** (*e.g. carboxylic* acid anhydride) is the most common choice for sulfoxide activation in interrupted Pummerer reactions, this is not a productive pathway for sulfides. Although acylsulfonium salts such as **21** are known species [39], they would not be expected to undergo the desired S_EAr process at sulfur as the acyl group is not a viable leaving group. Rather, nucleophiles reportedly effect addition/elimination at the carbonyl of **21**, and/or attack on the R^1/R^2 substituents α-to sulfur. In contrast, a *sulfonic* acid anhydride such as **22** will activate sulfide **19** to give a disulfur species **23**, in which a viable leaving group (the sulfone) is attached to the sulfonium. In this case, attack of a nucleophile at the sulfonium centre leads to S–S bond cleavage and loss of a sulfinate anion to give **24**.

Reaction of arenes with electrophiles of type **23** in an S_EAr process was first reported by Balenkova and co-workers [40], but to date has not been reported for azulenes. At the outset it was unclear whether sulfonylsulfonium electrophiles of type **23** would be sufficiently electrophilic to react twice and form an azulenebis(sulfonium) dication (as is the case for sulfonyloxysulfonium electrophiles **12**) or whether only a single S_EAr reaction would occur. We first attempted formation of the monosubstitution product by treating a mixture of azulene and excess 1,4-oxathiane **25** with only 1.25 eq. of triflic anhydride (Scheme 6A). This provided the expected product **26**, thus demonstrating the viability of this alternative approach to the preparation of azulenesulfonium salts. The reaction was repeated with 2.2 eq. of triflic anhydride (Scheme 6B), which led to the formation of azulenebis(sulfonium) dication **27**, thereby showing that sulfonylsulfonium electrophiles (**23**) can indeed effect a second S_EAr reaction on azulene. However, the yield of **27** was low, and a second product predominated, unexpected trifluoromethyl sulfoxide **28**. We rationalise the formation of **28** on the basis of the sulfinate anion produced by the first S_EAr process reacting with triflic anhydride to produce mixed sulfonic/sulfinic anhydride **31** [41], which is itself a viable electrophile for a second S_EAr process that introduces the sulfoxide at the azulene 3-position (Scheme 6C). A somewhat analogous process was proposed by Gunji and co-workers to explain the unexpected formation of a sulfoxide upon the attempted sulfonylation of 2-aminoazulene [42]. The structures of **26**–**28** were confirmed crystallographically (Fig. 4).

We also evaluated 1,4-dithiane **33** as the sulfide in this process, for which an additional mechanistic pathway can operate. It has

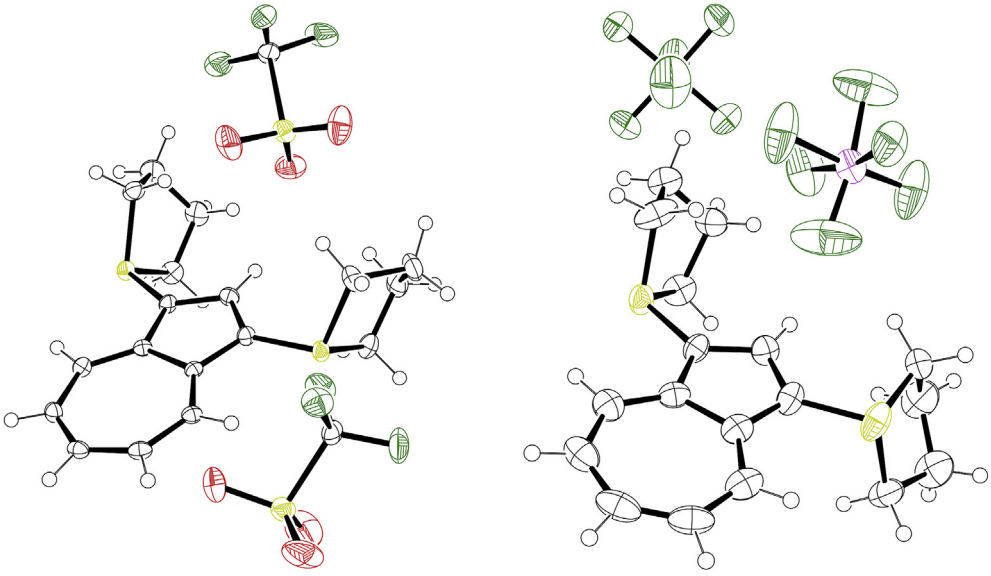


Fig. 2. Solid state structures of **16**•2OTf (*left*) and **16**•$2PF_6$ (*right*), crystallised from EtOH. Ellipsoids are represented at 50% probability. H atoms are shown as spheres of arbitrary radius. CCDC 2007946 and 2007947.

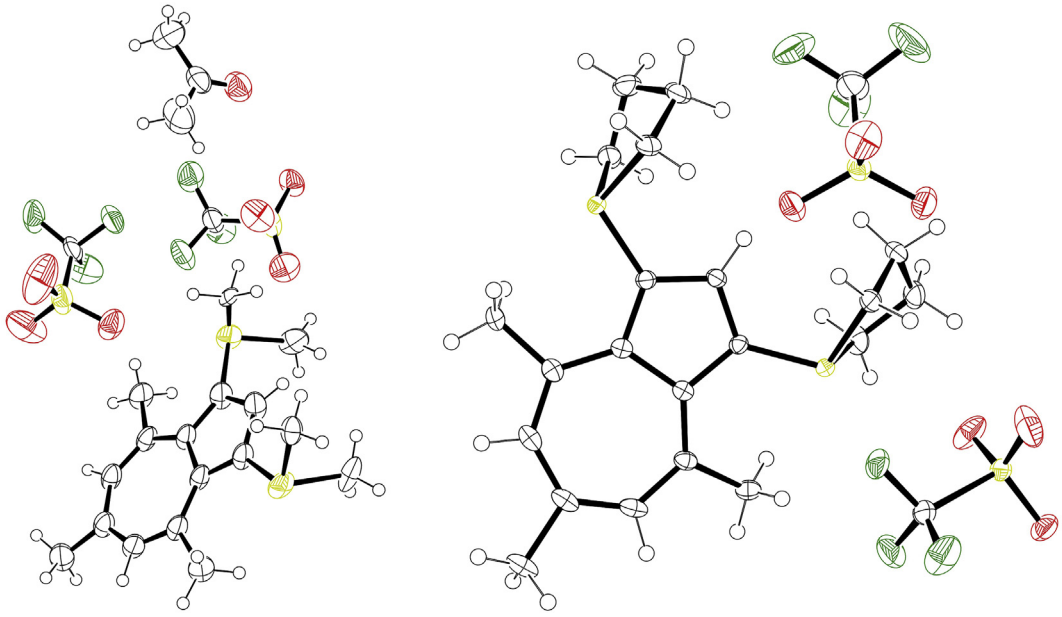
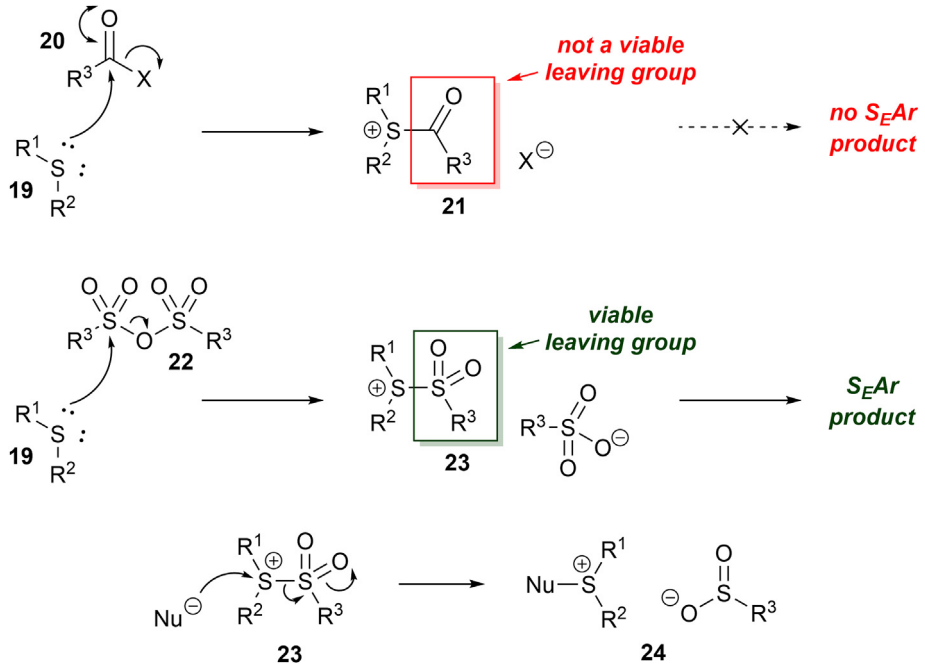


Fig. 3. Solid state structures of **17**•2OTf•acetone (*left*), crystallised from acetone and **18**•2OTf (*right*), crystallised from EtOH. Ellipsoids are represented at 50% probability. H atoms are shown as spheres of arbitrary radius. CCDC 2007948 and 2007949.

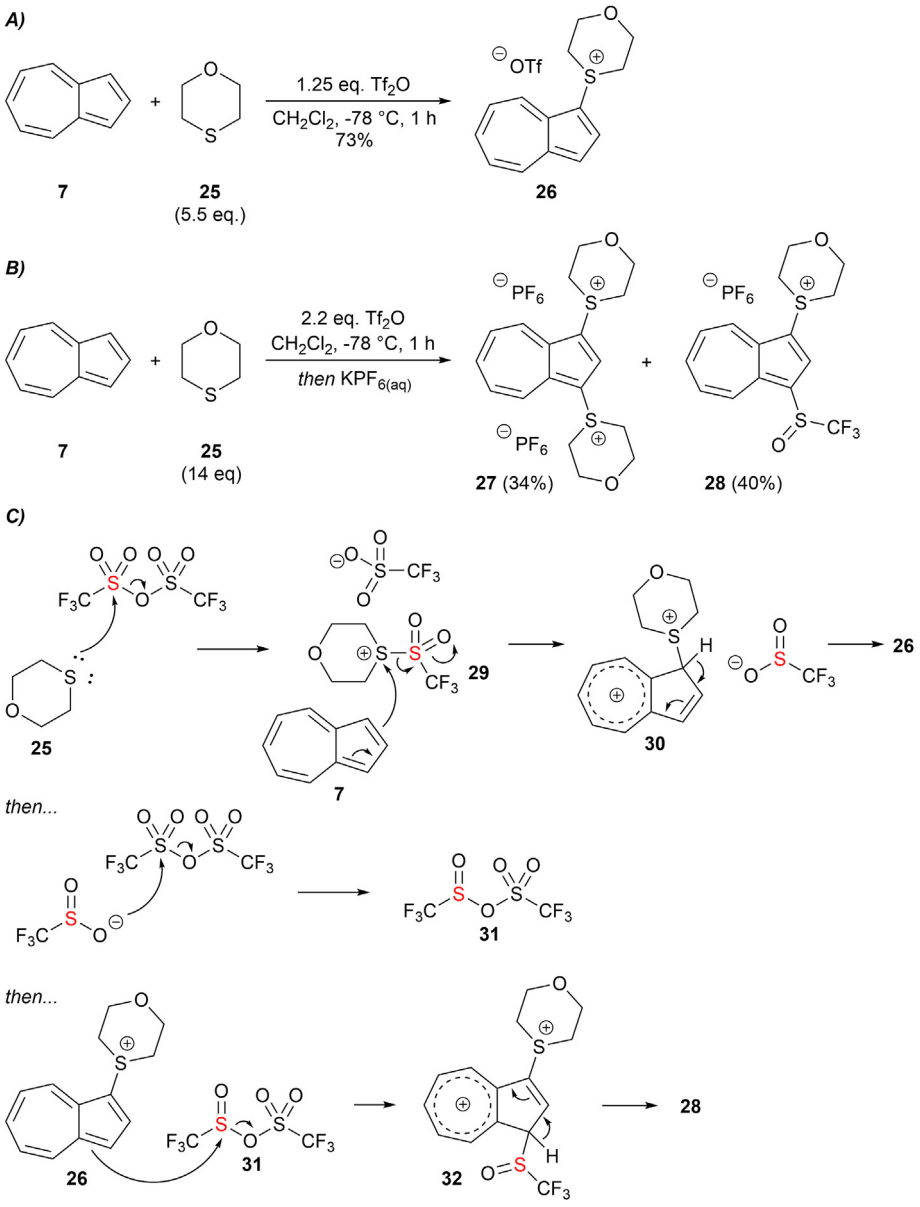


Scheme 5. Oxidative activation of a sulfide **19** gives a viable electrophile **23** for S_EAr.

been reported that cyclic bis(sulfides) can undergo electrophilic activation and transannular reaction to give disulfonium dications and this pathway operates even for **33**, when the product is the highly strained bicyclo[2.2.0] dication **35** [43]. The mechanism proceeding via **35** is depicted in Scheme 7A, although both **34** and **35** would be viable electrophiles for the S_EAr step and we have not attempted to determine whether this mechanism is operative or the one in Scheme 5. Regardless, these reaction conditions are able to effect either monosubstitution (Scheme 7B-C) or disubstitution (Scheme 7D), depending on stoichiometry with respect to triflic anhydride, as was the case for 1,4-oxathiane in Scheme 6. In contrast to the 1,4-oxathiane case, no sulfoxide-containing by-product was isolated from the disubstitution reaction, although its formation is mechanistically viable in this case also [42]. The structures of **37** and **39** were confirmed crystallographically (Fig. 5).

2.2. Sulfonium ring-opening

It has previously been shown that azulenyl dimethyl sulfonium salts react readily with amine nucleophiles at the methyl group, undergoing demethylation to afford the corresponding azulenyl methyl sulfides (Scheme 8A) [35]. As the azulenesulfonium salts we



Scheme 6. Synthesis of 1,4-oxathiane-derived azulene(sulfonium) salts and unexpected sulfoxide by-product.

report here are all cycloalkyl structures, the corresponding transformation would effect a ring opening, as opposed to dealkylation, in these cases [44]. We applied this procedure to a selection of azulene monosulfonium and bis(sulfonium) salts, using phenylthiolate as a model nucleophile, as shown in Scheme 8B. In each instance the reaction proceeded to give products **45**–**50** in good to excellent yield; no chromatography was necessary. The structure of **48** was confirmed crystallographically (Fig. 6).

We also evaluated representative nitrogen nucleophiles (benzhydrylamine, potassium phthalimide) in the azulenesulfonium ring-opening process and found them to be equally competent nucleophiles (Scheme 9), giving **51**–**52** (Scheme 9A). In contrast, reaction with sodium ethoxide did not effect nucleophilic substitution to give **53**, but instead gave a small amount of impure material tentatively assigned as homoallyl sulfide **54**, which could arise from an elimination/ring-opening process (Scheme 9B).

3. Conclusions

This work describes the synthesis of cyclic azulenesulfonium and azulenebis(sulfonium) salts having diversity in both the azulene and the cyclic sulfonium motifs. Two different methods are exploited to synthesise these compounds, namely the redox-neutral interrupted Pummerer process employing sulfoxides, and the oxidative direct electrophilic activation of sulfides. Either of these processes can be made to favour either the mono- or bis(-sulfonium) product, through appropriate choice of reaction stoichiometry and/or activating agent. The cyclic sulfonium salts are bench-stable, highly crystalline and readily prepared in good yield. They also undergo facile ring-opening when treated with a variety of nucleophiles, introducing a third point of diversity into the final products (Schemes 8 and 9).

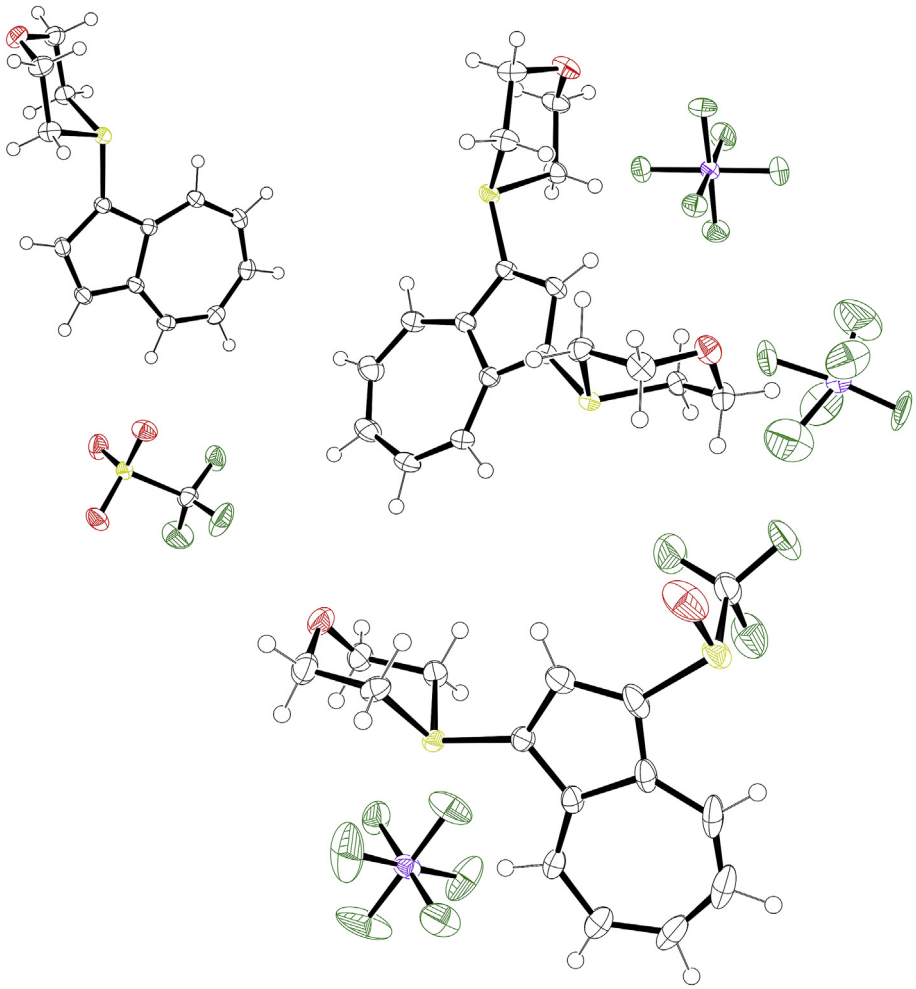


Fig. 4. Solid state structures of **26**•OTf (*top left*), **27**•2PF_6 (*top right*), and **28**•PF_6 (*bottom*). Ellipsoids are represented at 50% probability. H atoms are shown as spheres of arbitrary radius. CCDC 2007950, 2007951 and 2007952.

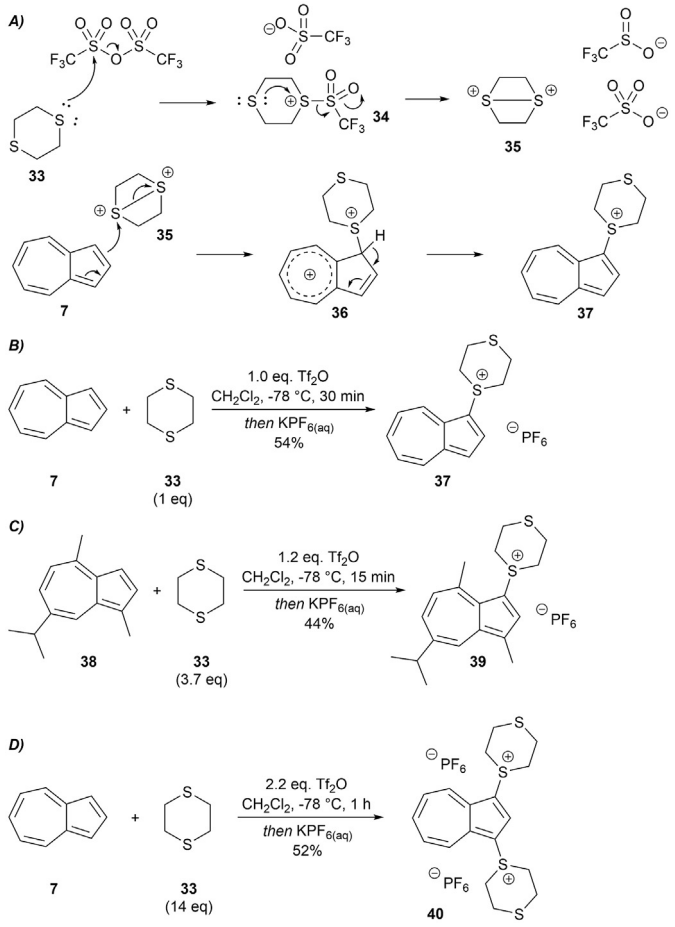
4. Experimental section

4.1. General information

Reactions were carried out under an atmosphere of nitrogen unless stated otherwise. Petrol refers to petroleum ether, bp 40–60 °C. Dichloromethane was dried and degassed by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. *N*,*N*-Dimethylformamide was supplied stored under argon, over 4 Å molecular sieves; no further drying was performed. TLCs were performed using aluminium-backed plates precoated with Alugram®SIL G/UV or aluminium backed plates precoated with Alugram®ALOX N/UV 254 nm and visualised by the naked eye (for coloured azulene compounds) UV light (254 nm). Flash column chromatography was carried out using Davisil LC 60 Å silica gel (35–70 μm) purchased from Sigma Aldrich. All reagents were purchased from Sigma-Aldrich Chemical Co., Fluorochem Ltd, or Fisher Scientific Ltd.; all reagents were used as received without further purification. IR spectra were recorded on a Perkin-Elmer Spectrum 1600 FT IR spectrometer with universal ATR sampling accessory, with absorbances quoted as ν in cm^{-1}. NMR spectra were run on an Agilent ProPulse 500 MHz instrument or Bruker Avance 500 MHz instruments at 298 K, unless otherwise specified. In tabulated NMR data, "p" refers to a pentet/quintet, "hept" refers to a heptet, and "app" is an abbreviation of "apparent". Capillary melting points were recorded on a Büchi 535 melting point apparatus, and are uncorrected. High resolution mass spectrometry (HRMS) was carried out using a micrOTOF ESI-TOF spectrometer coupled to an Agilent 1200 LC system for autosampling. X-ray crystallography was carried out at 150 K on a RIGAKU SuperNova, Dual, Cu at zero, EosS2 single crystal diffractometer using a microfocus sealed X-ray tube with Cu-Kα radiation $\lambda = 1.51484$ Å and a Rigaku New Xcalibur, EosS2 using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å).

4.2. General procedure A: synthesis of azulenebis(sulfonium) salts by interrupted Pummerer reaction

The required azulene (1.0 eq.) and sulfoxide (14.0 eq.) were added to a 100 mL round bottomed flask. The flask was sealed, evacuated and filled with N_2. 10 mL of CH_2Cl_2 was added and the reaction mixture stirred for 5 min. Triflic anhydride (2.4 eq.) was diluted in 10 mL of CH_2Cl_2, then this solution was added dropwise to the reaction flask. The reaction was stirred at room temperature for 2 h, then solvent was removed *in vacuo*. The crude product was dissolved in the minimum amount of CH_2Cl_2 and precipitated after addition excess of Et_2O. The precipitate was then recrystallised from EtOH to give the desired product.



Scheme 7. Azulenesulfonium salt formation via bicyclo[2.2.0] dicationic electrophile **35**.

4.2.1. 1,1'-(Azulene-1,3-diyl)bis(tetrahydro-1H-thiophen-1-ium) bis(trifluoromethanesulfonate) - ***16*•2OTf**

Using *General Procedure A* with azulene **7** (128.0 mg, 1.00 mmol), tetrahydrothiophene-*S*-oxide (1.26 mL, 14.0 mmol) and triflic anhydride (0.40 mL, 2.40 mmol) gave **16**•2OTf as fluffy orange crystals (542 mg, 0.90 mmol, 90%); m.p. 160–164 °C (dec.). ^{1}H-NMR (500 MHz, Acetone-d_6) δ = 9.36 (d, J = 9.5 Hz, 2H), 9.14 (s, 1H), 8.60 (t, J = 10.0 Hz, 1H), 8.31 (t, J = 10.1 Hz, 2H), 4.34–4.29 (m, 4H), 4.09–4.04 (m, 4H), 2.95–2.86 (m, 4H), 2.59–2.51 (m, 4H) ppm. ^{13}C-NMR (126 MHz, Acetone-d_6) δ = 146.3, 144.6, 140.3, 138.3, 133.6, 110.5, 51.4, 30.2 ppm. IR (neat): ν = 3018, 2959, 1583 cm^{-1}. HRMS (ESI+) *m/z* calcd for $[C_{18}H_{22}S_2]^{2+}$ 151.0576, found 151.0593.

4.2.2. (4,6,8-Trimethylazulene-1,3-diyl)bis(dimethylsulfonium) bis(trifluoromethanesulfonate) - ***17*•2OTf**

Using *General Procedure A* with 4,6,8-trimethylazulene [45] (170.0 mg, 1.00 mmol), dimethylsulfoxide (0.99 mL, 14.0 mmol) and triflic anhydride (0.40 mL, 2.40 mmol) gave **17**•2OTf as fluffy yellow crystals (402.4 mg, 0.68 mmol, 69%); m.p. 144–146 °C (dec.). ^{1}H-NMR (300 MHz, Acetone-d_6) δ 9.56 (s, 1H), 8.07 (s, 2H), 3.63 (s, 12H), 3.43 (s, 6H), 2.84 (s, 3H) ppm. ^{13}C-NMR (126 MHz, Acetone-d_6) δ 157.5, 154.3, 141.8, 140.5, 139.5, 110.6, 33.8, 31.8, 29.5 ppm. IR (neat): ν = 3027, 2937, 1593 cm^{-1}. HRMS (ESI+) *m/z* calculated for $C_{17}H_{24}S_2^{2+}$ $[M]^{2+}$ 146.0654, found 146.0647.

4.2.3. 1,1'-(4,6,8-trimethylazulene-1,3-diyl)bis(tetrahydro-1H-thiophen-1-ium) bis(trifluoromethanesulfonate) - ***18*•2OTf**

Using *General Procedure A* with 4,6,8-trimethylazulene [45] (170.0 mg, 1.00 mmol), tetrahydrothiophene-*S*-oxide (1.26 mL, 14.0 mmol) and triflic anhydride (0.40 mL, 2.40 mmol) gave **18**•2OTf as orange crystals (492.5 mg, 0.77 mmol, 77%); m.p. 126–129 °C (dec.). ^{1}H-NMR (500 MHz, Acetone-d_6) δ 8.65 (s, 1H), 8.06 (s, 2H), 4.37–4.32 (m, 4H), 4.12–4.07 (m, 4H), 3.47 (s, 6H), 2.90–2.83 (m, 4H), 2.85 (s, 3H), 2.54–2.46 (m, 4H) ppm. ^{13}C-NMR (126 MHz, Acetone-d_6) δ 156.5, 153.3, 141.5, 139.5, 137.9, 110.2, 52.6, 31.5, 30.1, 28.5 ppm. IR: ν = 3015, 2962, 1696, 1589 cm^{-1}. HRMS (ESI+) *m/z* calculated for $[C_{21}H_{28}S_2]^{2+}$ 172.0811, found 172.0809.

4.3. General procedure B: synthesis of azulenesulfonium or azulenebis(sulfonium) salts by electrophilic activation of a sulfide

The required sulfide and azulene were dissolved in CH_2Cl_2 under a nitrogen atmosphere and cooled to −78 °C in an acetone/dry ice bath. The required quantity of triflic anhydride was dissolved in 5 mL of dry CH_2Cl_2 and added dropwise to the reaction mixture. After vigorous stirring for the specified period, the reaction mixture was allowed to warm to room temperature, then worked up as specified.

4.3.1. 4-(Azulen-1-yl)-1,4-oxathian-4-ium trifluoromethanesulfonate - ***26*•OTf**

General Procedure B was used, with azulene **7** (100 mg, 0.78 mmol, 1.0 eq.), 1,4-oxathiane **25** (0.40 mL, 4.29 mmol, 5.5 eq.) and triflic anhydride (0.16 mL, 0.98 mmol, 1.25 eq.) in 15 mL of CH_2Cl_2. Reaction time 1 h. The reaction mixture was concentrated under reduced pressure until 2/3 of the solvent was removed, then

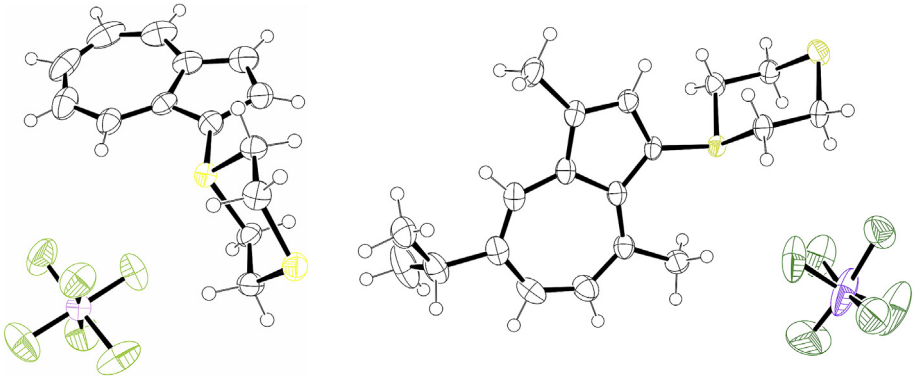
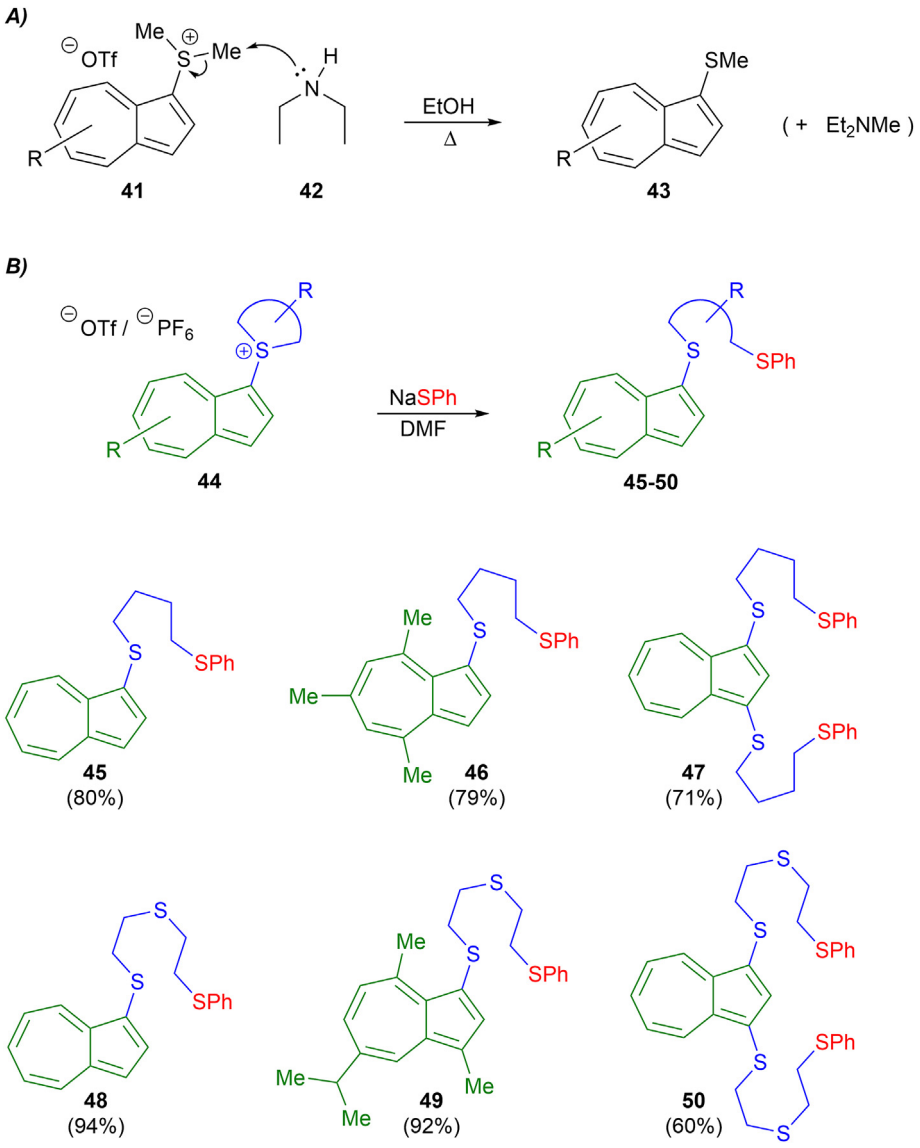


Fig. 5. Solid state structures of **37**•PF_6 (*left*) and **39**•PF_6 (*right*). Ellipsoids are represented at 50% probability. H atoms are shown as spheres of arbitrary radius. CCDC 2007953 and 2007954.



Scheme 8. Ring opening of cycloalkyl sulfonium salts by a thiolate nucleophile.

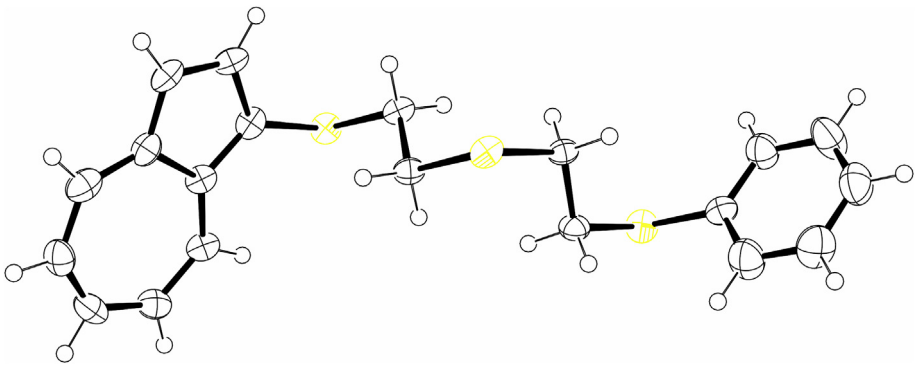
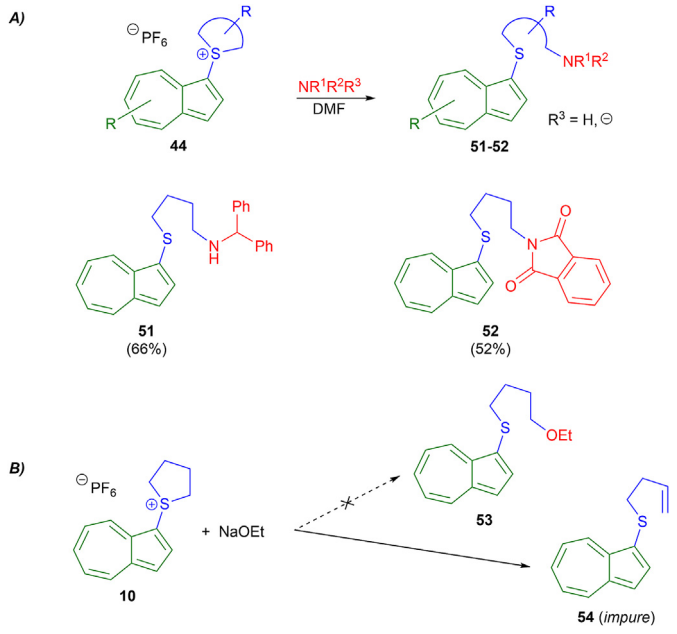


Fig. 6. Solid state structures of **48**. Ellipsoids are represented at 50% probability. H atoms are shown as spheres of arbitrary radius. CCDC 2007955.

Et_2O (20 mL) was added, forming a precipitate. This was filtered and recrystallised from EtOAc/Et_2O to give **26**•OTf as a red solid (215 mg, 73%). m.p. 259–261 °C (dec.). ^{1}H-NMR (500 MHz, Acetonitrile-d_3) δ 8.88 (d, J = 9.9 Hz, 1H), 8.80 (d, J = 9.6 Hz, 1H), 8.47 (d, J = 4.5 Hz, 1H), 8.17 (app t, J = 9.9 Hz, 1H), 7.88 (app t, J = 9.9 Hz, 1H), 7.83 (app t, J = 9.8 Hz, 1H), 7.73 (d, J = 4.6 Hz, 1H), 4.47 (app dt, J = 14.0, 3.2 Hz, 2H), 4.05 (ddd, J = 13.6, 11.3, 1.5 Hz, 2H), 3.82 (ddd, J = 12.6, 11.1, 3.4 Hz, 2H), 3.62 (dd, J = 12.7, 2.5 Hz, 2H) ppm. ^{13}C-



Scheme 9. Ring-opening of cyclic sulfoniums with nitrogen nucleophiles.

NMR (126 MHz, Acetonitrile-d_3) δ 145.6, 143.5, 143.1, 142.2, 137.0, 136.7, 130.6, 130.1, 122.0, 100.7, 66.1, 43.1 ppm. IR (neat): ν = 3082, 2995, 2962, 1586 cm^{-1}. HRMS (ESI+) calcd for $[C_{14}H_{15}SO]^+$ 231.0838; found 231.0844.

4.3.2. 1,1'-(Azulene-1,3-diyl)bis(1,4-oxathian-4-ium) bis(hexafluorophosphate) - **27**•2PF$_6$ and 4-(3-((Trifluoromethyl) sulfinyl)azulen-1-yl)-1,4-oxathian-4-ium hexafluorophosphate - **28**•PF$_6$

General Procedure B was used, with azulene **7** (110 mg, 0.86 mmol, 1.0 eq.), 1,4-oxathiane **25** (1.12 mL, 12.1 mmol, 14 eq.) and triflic anhydride (0.32 mL, 1.88 mmol, 2.2 eq.) in 15 mL of CH_2Cl_2. Reaction time 1 h. The reaction mixture was poured into Et_2O (100 mL) and washed with water (3 × 100 mL). The combined aqueous phases were collected and washed with Et_2O (3 × 20 mL). After this, KPF_6 (2.00 g, 10.84 mmol, 12.6 eq.) was added to the aqueous phase, and an orange precipitate formed. This was filtered, and the precipitate was recrystallised with EtOAc/Et_2O to give **27**•2PF$_6$ as an orange solid (142 mg, 34%). The aqueous filtrate was then extracted with EtOAc (2 × 50 mL). The combined EtOAc phases were dried over Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure to give **28**•PF$_6$ as an orange solid (212 mg, 40%). **27**•2PF$_6$: m.p. 159–161 °C (dec.). ^{1}H-NMR (500 MHz, Acetonitrile-d_3) δ 9.14 (d, J = 9.4 Hz, 2H), 9.11 (s, 1H), 8.56 (t, J = 9.9 Hz, 1H), 8.28 (t, J = 9.9 Hz, 2H), 4.53 (app dt, J = 13.7, 3.0 Hz, 4H), 4.10 (ddd, J = 14.1, 10.8, 1.7 Hz, 4H), 3.88 (ddd, J = 12.6, 10.8, 3.4 Hz, 4H), 3.78–3.75 (m, 4H) ppm. ^{13}C-NMR (126 MHz, Acetonitrile-d_3) δ 147.3, 145.1, 140.8, 139.7, 134.9, 106.0, 65.8, 42.9 ppm. IR (neat): ν = 3345, 2961, 2922, 1578 cm^{-1}. HRMS (ESI+) calcd for $[C_{18}H_{22}S_2O_2]^{2+}$ 167.0525; found 167.0514. **28**•PF$_6$: m.p. 202–204 °C (dec.). ^{1}H-NMR (500 MHz, Acetonitrile-d_3) δ 9.25 (d, J = 9.9 Hz, 1H), 9.09 (dd, J = 9.9, 1.0 Hz, 1H), 9.03 (s, 1H), 8.48 (app td, J = 10.0, 1.0 Hz, 1H), 8.20 (app t, J = 10.0 Hz, 1H), 8.15 (app t, J = 10.0 Hz, 1H), 4.51–4.46 (m, 2H), 4.07 (app ddt, J = 14.0, 12.7, 1.4 Hz, 2H), 3.90 (app td, J = 11.4 Hz, 6.5 Hz, 2H), 3.72–3.68 (m, 2H) ppm. ^{13}C-NMR (126 MHz, Acetonitrile-d_3) δ 146.4, 146.0, 143.5, 140.6, 140.0, 138.4, 134.4, 134.0, 126.4 (q, $^1J_{CF}$ = 334 Hz), 104.3, 65.9, 42.8, 42.7 ppm. One azulene carbon was not observed. IR (neat): ν = 3345, 3083, 3065, 2963, 2923, 1578 cm^{-1}. HRMS (ESI+) calcd for $[C_{15}H_{14}F_3S_2O_2]^+$ 347.0382; found 347.0500.

4.3.3. 1-(Azulen-1-yl)-1,4-dithian-1-ium hexafluorophosphate - **37**•PF$_6$

General Procedure B was used, with azulene **7** (50 mg, 0.39 mmol, 1.25 eq.), 1,4-dithiane **33** (39 mg, 0.32 mmol, 1.0 eq.) and triflic anhydride (55 μL, 0.32 mmol, 1.0 eq.) in 5 mL of CH_2Cl_2. Reaction time 30 min. The reaction mixture was poured into Et_2O (100 mL) and washed with water (3 × 100 mL). The combined aqueous phases were collected and washed with Et_2O (3 × 20 mL). After this, KPF_6 (1.50 g, 8.0 mmol, 35 eq.) was added to the aqueous phase, and a small amount of orange precipitate formed, which was filtered off. The aqueous filtrate was then extracted with EtOAc (2 × 50 mL). The combined EtOAc phases were dried over Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The crude product was recrystallised from EtOAc/Et_2O to give **37**•PF$_6$ as a red solid (82 mg, 54%). m.p. 212–218 °C. ^{1}H-NMR (500 MHz, Acetonitrile-d_3) δ 8.84 (d, J = 9.9 Hz, 1H), 8.80 (d, J = 9.7 Hz, 1H), 8.47 (d, J = 4.6 Hz, 1H), 8.17 (app t, J = 9.9 Hz, 1H), 7.87 (app t, J = 9.9 Hz, 1H), 7.82 (app t, J = 9.8 Hz, 1H), 7.72 (d, J = 4.6 Hz, 1H), 3.96 (dd, J = 12.5, 11.4, 2.4 Hz, 2H), 3.88–3.84 (m, 2H), 3.45 (ddd, J = 16.1, 11.7, 2.0 Hz, 2H), 3.28–3.23 (m, 2H) ppm. ^{13}C-NMR (126 MHz, Acetonitrile-d_3) δ 145.4, 143.3, 143.1, 142.1, 137.2, 136.7, 130.6, 130.0, 122.0, 100.9, 45.7, 27.2 ppm. IR (neat): ν = 1458 cm^{-1}. HRMS (ESI+) calcd for $[C_{14}H_{15}S_2]^+$ 247.0610; found 247.0600.

4.3.4. 1-(5-iso-Propyl-3,8-dimethylazulen-1-yl)-1,4-dithian-1-ium hexafluorophosphate - **39**•PF$_6$

General Procedure B was used, with guaiazulene **38** (100 mg, 0.50 mmol, 1.0 eq.), 1,4-dithiane **33** (222 mg, 1.84 mmol, 3.7 eq.) and triflic anhydride (0.17 mL, 0.61 mmol, 1.2 eq.) in 5 mL of CH_2Cl_2. Reaction time 15 min. The reaction mixture was poured into Et_2O (100 mL) and washed with water (3 × 100 mL). The combined aqueous phases were collected and washed with Et_2O (3 × 20 mL). After this, KPF_6 (1.50 g, 8.0 mmol, 16 eq.) was added to the aqueous phase. The aqueous phase was then extracted with EtOAc (3 × 25 mL). The combined EtOAc phases were dried over Na_2SO_4 and filtered; the filtrate was concentrated under reduced pressure. The crude product was recrystallised from EtOAc/Et_2O to give **39**•PF$_6$ as a pink solid (103 mg, 44%). m.p. 137–139 °C. ^{1}H-NMR (500 MHz, Acetonitrile-d_3) δ 8.56 (d, J = 2.2 Hz, 1H), 8.18 (s, 1H), 7.93 (dd, J = 10.8, 2.1 Hz, 1H), 7.63 (d, J = 10.8 Hz, 1H), 3.93–3.83 (m, 4H), 3.45 (ddd, J = 14.6, 11.7, 2.3 Hz, 2H), 3.27 (hept, J = 7.0 Hz, 1H), 3.23–3.17 (m, 2H), 3.19 (s, 3H), 2.66 (s, 3H), 1.39 (d, J = 6.9 Hz, 6H) ppm. ^{13}C-NMR (126 MHz, Acetonitrile-d_3) δ 149.7, 148.3, 143.1, 140.7, 140.0, 138.8, 136.6, 135.2, 130.1, 97.4, 47.7, 38.8, 29.2, 27.7, 24.6, 13.2 ppm. IR (neat): ν = 3046, 2960, 2922, 1578 cm^{-1}. HRMS (ESI+) calcd for $[C_{19}H_{25}S_2]^+$ 317.1392; found 317.1523.

4.3.5. 1,1'-(Azulene-1,3-diyl)bis(1,4-dithian-1-ium) bis(hexafluorophosphate) - **40**•2PF$_6$

General Procedure B was used, with azulene **7** (140 mg, 1.09 mmol, 1.0 eq.), 1,4-dithiane **33** (1.83 g, 15.3 mmol, 14 eq.) and triflic anhydride (0.41 mL, 2.40 mmol, 2.2 eq.) in 15 mL of CH_2Cl_2. Reaction time 40 min. The reaction mixture was poured into Et_2O (100 mL) and washed with water (3 × 100 mL). The combined aqueous phases were collected and washed with Et_2O (3 × 20 mL). After this, KPF_6 (2.00 g, 10.84 mmol, 10.0 eq.) was added to the aqueous phase, and an orange precipitate formed. This was filtered, and the precipitate was recrystallised with EtOAc/Et_2O to give **40**•2PF$_6$ as an orange solid (373 mg, 52%). m.p. 189–191 °C (dec.). ^{1}H-NMR (500 MHz, Acetonitrile-d_3) δ 9.12 (s, 1H), 9.10 (d, J = 9.4 Hz, 2H), 8.56 (t, J = 10.0 Hz, 1H), 8.28 (app t, J = 10.1 Hz, 2H), 4.05–3.98 (m, 8H), 3.49 (ddd, J = 15.9, 9.7, 4.1 Hz, 4H), 3.36–3.31 (m, 4H) ppm.

^{13}C-NMR (126 MHz, Acetonitrile-d_3) δ 147.4, 144.8, 140.8, 140.1, 134.8, 106.1, 45.7, 27.0 ppm. IR (neat): ν = 2952, 1583 cm^{-1}. HRMS (ESI+) calcd for $[C_{18}H_{22}S_4]^{2+}$ 183.0297; found 183.0288.

4.4. General procedure C: nucleophilic ring-opening of cyclic sulfonium salts

The required sulfonium salt and nucleophile were added to a 50 mL round bottomed flask with a magnetic stirrer bar. The flask was evacuated and filled N_2 gas. 5 mL of DMF was added to the flask and the reaction mixture was stirred at the specified temperature for the specified time. The reaction mixture was diluted with diethyl ether (30 mL), and washed with water (2 × 30 mL) and 5% $LiCl_{(aq)}$ solution (30 mL). The organic layer was dried over $MgSO_4$ and filtered. The filtrate was concentrated *in vacuo* and if necessary, the crude product was purified as indicated.

4.4.1. Azulen-1-yl(4-(phenylthio)butyl)sulfide - ***45***

General Procedure C was used, with azulenesulfonium salt **10**•PF_6 (R = H, 100 mg, 0.278 mmol, 1.0 eq.) [10] and sodium thiophenolate (44 mg, 0.333 mmol, 1.2 eq.). Reaction time 2 h at room temperature. Product **45** was obtained as a dark-blue oil (70.4 mg, 0.217 mmol, 80%); no chromatography was required. ^{1}H-NMR (500 MHz, Chloroform-*d*) δ 8.69 (dd, *J* = 9.8, 2.5 Hz, 1H), 8.30 (d, *J* = 9.5 Hz, 1H), 7.96 (d, *J* = 3.9 Hz, 1H), 7.64 (app t, *J* = 9.9 Hz, 1H), 7.39 (d, *J* = 3.9 Hz, 1H), 7.32–7.22 (m, 5H), 7.21 (app t, *J* = 10.0 Hz, 1H), 7.17 (tt, *J* = 6.7, 1.9 Hz, 1H), 2.88 (t, *J* = 7.3 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 1.78 (p, *J* = 7.4 Hz, 2H), 1.67 (p, *J* = 7.1 Hz, 2H) ppm. ^{13}C-NMR (126 MHz, Chloroform-*d*) δ 141.9, 140.6, 138.4, 137.0, 136.7, 135.7, 129.3, 129.2, 129.0, 125.9, 124.0, 123.6, 119.5, 117.4, 37.2, 33.4, 29.1, 28.2 ppm. IR (neat): ν = 3018, 2928, 2845, 1573 cm^{-1}. HRMS (ESI+) *m/z* calcd. for $C_{20}H_{20}S_2$ $[M+Na]^+$ 347.0899, found 347.0912.

4.4.2. Phenyl(4-((4,6,8-trimethylazulen-1-yl)thio)butyl)sulfide - ***46***

General Procedure C was used, with azulenesulfonium salt **10**•PF_6 (R = 4,6,8-$(Me)_3$, 50 mg, 0.124 mmol, 1.0 eq.) [10] and sodium thiophenolate (22 mg, 0.167 mmol, 1.35 eq.). Reaction time 10 min at room temperature. Product **46** was obtained as a dark-blue oil (36 mg, 79%); no chromatography was required. ^{1}H-NMR (500 MHz, Chloroform-*d*) δ = 7.61 (d, *J* = 4.1 Hz, 1H), 7.33–7.24 (m, 6H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.93 (s, 1H), 6.92 (s, 1H), 3.26 (s, 3H), 2.92–2.89 (m, 4H), 2.80 (s, 3H), 2.56 (s, 3H), 1.82–1.73 (m, 4H) ppm; ^{13}C-NMR (126 MHz, Chloroform-*d*) δ = 148.8, 147.1, 145.8, 137.9, 137.5, 136.7, 134.3, 129.7, 129.3, 129.0, 127.3, 126.0, 120.5, 115.9, 37.4, 33.4, 28.6, 28.5, 28.3, 28.2, 25.6 ppm. IR (neat): ν = 2958, 1574 cm^{-1}. HRMS calcd for $[C_{23}H_{26}S_2]^+$ 366.1470; found 366.1486.

4.4.3. 1,3-Bis((4-(phenylthio)butyl)thio)azulene - ***47***

General Procedure C was used, with azulenesulfonium salt **16**•2PF_6 (100 mg, 0.169 mmol, 1.0 eq.) and sodium thiophenolate (54 mg, 0.405 mmol, 2.4 eq.). Reaction time 2.5 h at room temperature. Product **47** was obtained as a dark-blue oil (63 mg, 71%); no chromatography was required. ^{1}H-NMR (500 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 9.2 Hz, 2H), 7.99 (s, 1H), 7.66 (t, *J* = 9.8 Hz, 1H), 7.30–7.24 (m, 10H), 7.18–7.14 (m, 2H), 2.87 (t, *J* = 7.2 Hz, 4H), 2.82 (t, *J* = 7.2 Hz, 4H), 1.77 (app p, *J* = 6.9 Hz, 4H), 1.66 (app p, *J* = 7.1 Hz, 4H) ppm. ^{13}C-NMR (126 MHz, Chloroform-*d*) δ = 145.6, 141.9, 139.2, 136.6, 135.8, 129.1, 128.9, 125.8, 124.4, 119.0, 36.9, 33.3, 28.9, 28.0 ppm. IR (neat): ν = 3050, 2925, 2847, 1572 cm^{-1}. HRMS calcd for $[C_{30}H_{32}S_4+O_2+Na]^+$ 575.1177; found 575.1209.

4.4.4. Azulen-1-yl(2-((2-(phenylthio)ethyl)thio)ethyl)sulfide - ***48***

General Procedure C was used, with azulenesulfonium salt **37**•PF_6 (100 mg, 0.255 mmol, 1.0 eq.) and sodium thiophenolate (40 mg, 0.303 mmol, 1.2 eq.). Reaction time 2 h at room temperature. Product **48** was obtained as a dark-blue solid (85 mg, 94%); no chromatography was required. m.p. 53–57 °C. ^{1}H-NMR (500 MHz, Chloroform-*d*) δ = 8.71 (d, *J* = 9.7 Hz, 1H), 8.32 (d, *J* = 9.5 Hz, 1H), 7.95 (d, *J* = 4.0 Hz, 1H), 7.67 (app t, *J* = 9.8 Hz, 1H), 7.38 (d, *J* = 3.9 Hz, 1H), 7.34–7.17 (m, 7H), 2.98–2.91 (m, 4H), 2.67–2.61 (m, 4H) ppm. ^{13}C-NMR (126 MHz, Chloroform-*d*) δ = 142.2, 142.2, 141.1, 138.6, 137.3, 135.8, 135.3, 130.0, 129.2, 126.6, 124.3, 124.0, 118.0, 117.5, 37.5, 34.1, 32.3, 31.5 ppm. IR (neat): ν = 3069, 3050, 3016, 3001, 2928, 1672, 1572 cm^{-1}. HRMS (ESI+) calcd for $[C_{20}H_{20}S_3+Na]^+$ 379.0619; found 379.0609.

4.4.5. (5-iso-Propyl-3,8-dimethylazulen-1-yl)(2-((2-(phenylthio) ethyl)thio)ethyl)sulfide - ***49***

General Procedure C was used, with azulenesulfonium salt **39**•PF_6 (100 mg, 0.216 mmol, 1.0 eq.) and sodium thiophenolate (40 mg, 0.303 mmol, 1.4 eq.). Reaction time 2 h at room temperature. Product **49** was obtained as a blue oil (85 mg, 92%); no chromatography was required. ^{1}H-NMR (500 MHz, Chloroform-*d*) δ = 8.05 (d, *J* = 2.2 Hz, 1H), 7.58 (s, 1H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.37–7.22 (m, 4H), 7.18 (*t*, J = 7.2 Hz, 1H), 6.91 (d, *J* = 10.8 Hz, 1H), 3.23 (s, 3H), 3.07–2.97 (m, 5H), 2.71–2.67 (m, 4H), 2.58 (s, 3H), 1.34 (d, *J* = 6.9 Hz, 6H) ppm. ^{13}C-NMR (126 MHz, Chloroform-*d*) δ = 147.4, 142.4, 140.8, 139.1, 135.8, 134.0, 130.0, 129.21, 129.19, 128.3, 127.7, 127.3, 126.6, 125.3, 38.2, 37.9, 34.1, 31.7, 31.6, 27.3, 24.7, 13.0 ppm. IR (neat): ν = 2960, 2922, 1578 cm^{-1}. HRMS (ESI+) calcd for $[C_{25}H_{30}S_3+Na]^+$ 449.1402; found 449.1629.

4.4.6. 1,3-Bis((2-((2-(phenylthio)ethyl)thio)ethyl)thio)azulene - ***50***

General Procedure C was used, with azulenesulfonium salt **40**•2PF_6 (85 mg, 0.129 mmol, 1.0 eq.) and sodium thiophenolate (82 mg, 0.620 mmol, 4.8 eq.). Reaction time 2 h at room temperature. Product **50** was obtained as a blue solid (45 mg, 60%); no chromatography was required. m.p. 83–85 °C. ^{1}H- NMR (500 MHz, Chloroform-*d*) δ = 8.67 (d, *J* = 9.7 Hz, 2H), 8.01 (s, 1H), 7.72 (*t*, J = 9.8 Hz, 1H), 7.35 (app t, *J* = 9.0 Hz, 2H), 7.30–7.24 (m, 8H), 7.19 (t, *J* = 7.1 Hz, 2H), 3.01–2.98 (m, 4H), 2.94–2.91 (m, 4H), 2.68–2.62 (m, 8H). ppm. ^{13}C-NMR (126 MHz, Chloroform-*d*) δ = 146.6, 142.7, 139.8, 136.3, 135.3, 130.1, 129.2, 126.7, 125.2, 117.9, 37.4, 34.2, 32.4, 31.6. ppm. IR (neat): ν = 2923, 1578 cm^{-1}. HRMS (ESI+) calcd for $[C_{30}H_{32}S_6+H]^+$ 607.0720; found 607.0818.

4.4.7. 4-(Azulen-1-ylthio)-N-benzhydrylbutyl-1-amine - ***51***

General Procedure C was used, with azulenesulfonium salt **10**•PF_6 (R = H, 100 mg, 0.278 mmol, 1.0 eq.) [10] and benzhydrylamine (0.24 mL, 1.39 mmol, 5.0 eq.). Reaction time 16 h at 50 °C. The crude product was purified by column chromatography (silica gel, 3:1 Pet Ether:EtOAc) to give **51** as a dark-turquoise oil (74 mg, 66%). ^{1}H-NMR (500 MHz, Chloroform-*d*) δ = 8.69 (d, *J* = 9.7 Hz, 1H), 8.29 (d, *J* = 9.3 Hz, 1H), 7.96 (d, *J* = 3.9 Hz, 1H), 7.64 (t, *J* = 9.9 Hz, 1H), 7.38–7.34 (m, 4H), 7.29–7.25 (m, 4H), 7.23–7.18 (m, 3H), 4.76 (s, 1H), 2.81 (t, *J* = 6.9 Hz, 2H), 2.53 (t, *J* = 6.5 Hz, 2H), 1.66–1.56 (m, 4H) ppm. ^{13}C-NMR (126 MHz, Chloroform-*d*) δ = 144.4, 141.8, 140.6, 138.4, 137.0, 135.7, 128.6, 127.4, 127.0, 126.7, 123.9, 123.5, 119.8, 117.4, 67.7, 47.8, 37.6, 29.3, 27.9 ppm. IR (neat): ν = 2925, 1638, 1575 cm^{-1}. HRMS (ESI+) calcd for $[C_{27}H_{27}NS + H]^+$ 398.1937; found 398.2019.

4.4.8. 2-(4-(Azulen-1-ylthio)butyl)isoindoline-1,3-dione - 52

General Procedure C was used, with azulenesulfonium salt **10**•PF_6 (R = H, 50 mg, 0.139 mmol, 1.0 eq.) [10] and potassium phthalimide (30 mg, 0.161 mmol, 1.2 eq.). Reaction time 2 h at room temperature. The crude product was purified by column chromatography (silica gel, 1:1 Pet Ether:EtOAc) to give **52** as a dark blue oil (26 mg, 52%). ^{1}H-NMR (500 MHz, Chloroform-*d*) δ = 8.67 (d, *J* = 9.7 Hz, 1H), 8.26 (d, *J* = 9.5 Hz, 1H), 7.94 (d, *J* = 3.9 Hz, 1H), 7.81 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.62 (t,

J = 9.9 Hz, 1H), 7.33 (d, J = 3.9 Hz, 1H), 7.27 (t, J = 9.7 Hz, 1H), 7.18 (t, J = 9.7 Hz, 1H), 3.63 (t, J = 7.2 Hz, 2H), 2.83 (t, J = 7.2 Hz, 2H), 1.81 (app p, J = 7.4 Hz, 2H), 1.54 (app p, J = 7.4 Hz, 2H) ppm. ^{13}C-NMR (126 MHz, Chloroform-d) δ = 168.5, 142.0, 141.9, 140.8, 138.4, 137.0, 135.8, 134.0, 132.2, 124.0, 123.7, 123.3, 119.2, 117.4, 37.7, 37.2, 27.6, 27.2 ppm (one aromatic carbon was not observed). IR (neat): ν = 1719 cm^{-1}. HRMS (ESI+) calcd for $[C_{22}H_{19}NO_2S + Na]^+$ 384.1029; found 384.1075.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2020.131700.

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