Diazadithiafulvalenes as electron donor reagents

Toshio Koizumi,† Nadeem Bashir, Alan R. Kennedy and John A. Murphy *

Department of Pure and Applied Chemistry, The University of Strathclyde, 295 Cathedral Street, Glasgow, UK G1 1XL

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Diazadithiafulvalenes act as excellent electron donors to arenediazonium salts. The diazadithiafulvalenium radical cations trap primary carbon radicals successfully. However, the diazadithiafulvalenium salts which form, undergo rapid ring fragmentation in contrast to their tetrathia counterparts.

Introduction

The radical-polar crossover reaction affords a means of performing radical and ionic chemistry in one pot.[1] Specifically, an arenediazonium salt **1** acts as electron acceptor from tetrathiafulvalene‡ (TTF) liberating dinitrogen and forming an aryl radical. This can cyclise onto an appropriately placed alkene to yield a secondary radical. This combines with the radical-cation of tetrathiafulvalene affording a sulfonium salt **2** which can then undergo substitution by oxygen or nitrogen nucleophiles (Scheme 1). This reaction has recently been used in the key step of a novel synthesis of the complex alkaloid aspidospermidine.[2]

It has recently been shown electrochemically that diazadithiafulvalenes‡ **3** (DDTFs) are more powerful electron donors than TTF,[3] and so they are good candidates for second generation catalysts to extend the scope of the radical-polar crossover reaction. Specifically, the radical-cations of these compounds may display different kinetics for coupling to carbon radicals than $TTF^{+\bullet}$, since the *N*-linked R groups could retard approach to sulfur. This could permit slower carbon radical cyclisations to occur prior to the radical termination step. This paper describes their reactions with arenediazonium salts.[4]

Results and discussion

The diazadithiafulvalene **7** was prepared by literature procedures.[5] Thus benzothiazole was reacted with diethyl sulfate to afford **4** or with iodoethane to form the corresponding iodide salt. The ethyl product **4** was isolated and treated with triethylamine to obtain the ylide **5**, which dimerised to **7**. Diazadithiafulvalene **7** was isolated when air was rigorously excluded. However, this compound is highly oxygen-sensitive and a solution in deuterochloroform rapidly turned red on exposure to air, indicating its ease of oxidation and afforded a broad ^{1}H NMR spectrum differing from that reported[5] for **7** by Wanzlick *et al.* Repeating the preparation in acetonitrile led to a yellow solution once again, but the solution slowly went red over 24 h and after work-up in air and chromatography without exclusion of air, one major (colourless) compound was isolated, the oxalamide **9**. The ^{1}H NMR spectrum of this compound featured two doublets of quartets consistent with the C_2 symmetry which was ultimately confirmed by X-ray crystallography (Fig. 1).

Baldwin and Walker[6] reported the oxidative rearrangement

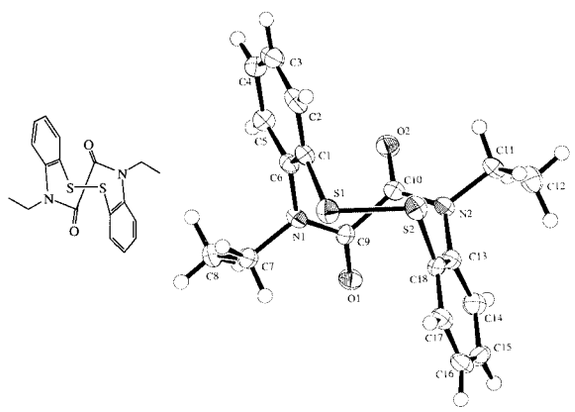


Fig. 1 Molecular Structure of $C_{18}H_{18}N_2O_2S_2$ **9** drawn with 50% probability ellipsoids and with H atoms as small spheres of arbitrary size. S1–S2 2.060(1) Å; C1–S1–S2–C18 −106.1(2), S1–S2–C18–C17 −84.8(3), S2–S1–C1–C2 −89.6(3), O1–C9–C10–O2 111.9(4), O1–C9–N1–C7 1.7(5) and O2–C10–N2–C11 0.0(5)° (see ref. 13).

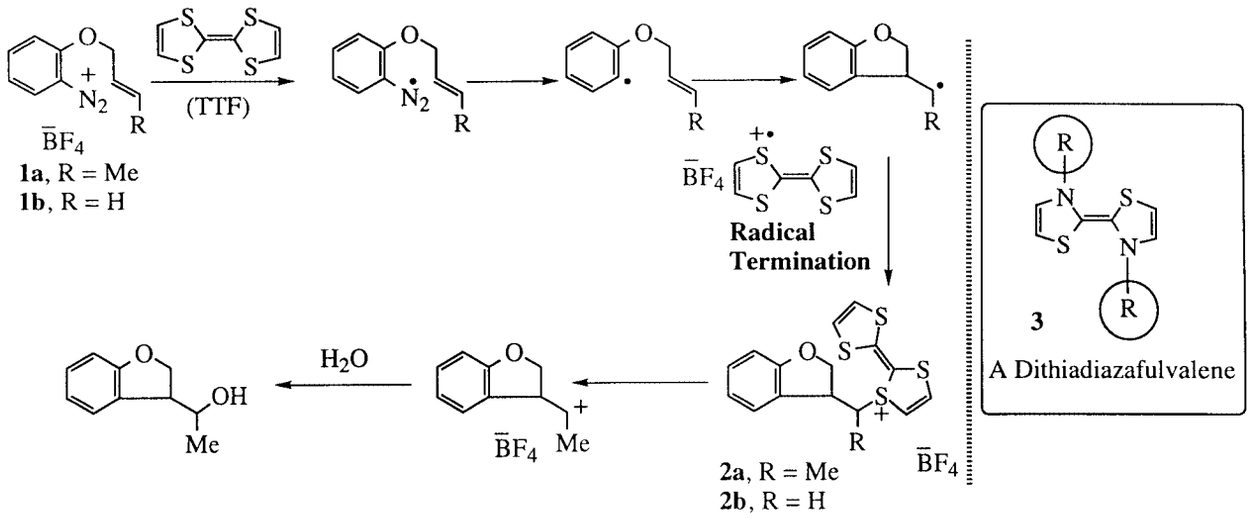
of the methyl compound **6** in air, establishing the product structure as **8** by desulfurisation with Raney nickel to afford *N*-phenyl-*N*-methyloxalamide. The same compound has subsequently been formed by other means.[7] On the other hand, Wanzlick *et al.* had reported that **7** was oxidised to the macrocycle **10** in air. Our results support the findings of Baldwin and Walker. The mechanism may involve the initial reaction with dioxygen to form the superoxide radical-anion, followed by reaction to form a dioxetane **11**. Cleavage of the weak O–O bond to form a diradical and fragmentation to the bis-thiyl radical **12** leads ultimately to macrocycle formation.

The products **16** and **17** were prepared by the route of Tormos *et al.*[3] Reaction of dimethyl acetylenedicarboxylate with the dithio-imine **13**, (R′ = Me or Ph) afforded the thiocarbonyl product **14**. Conversion to the selenocarbonyl compound **15** followed by reaction with trimethyl phosphite afforded **16** or **17** (Scheme 2). Although these compounds are substituted with electron-withdrawing ester groups, they are still more powerful electron-donors than TTF.[3]

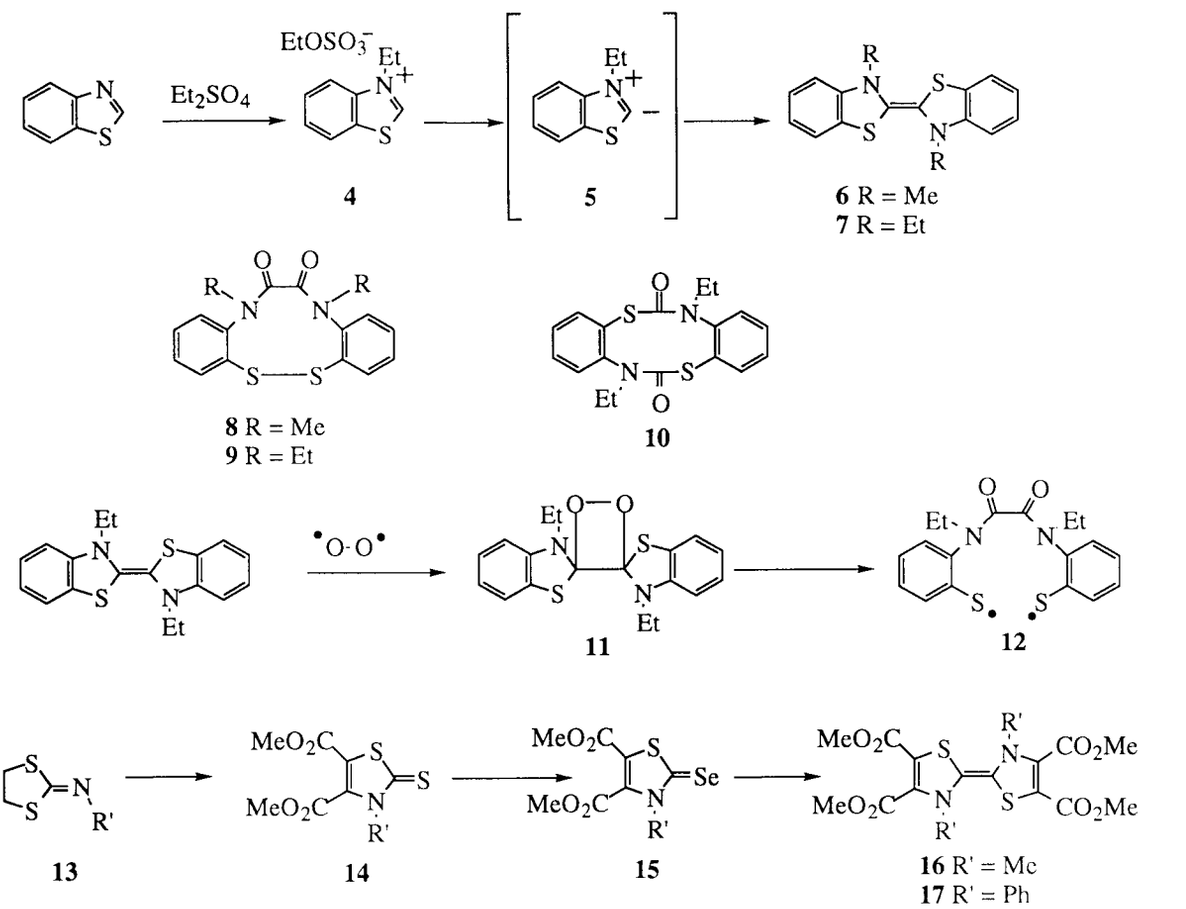
Compounds **16** and **17** were firstly reacted with the diazonium salts **1a** and **1b**. Surprisingly it was not possible to isolate clean products from **1b**, in marked contrast to its reaction with TTF, but **1a** afforded a single major product on reaction with both **16** and **17**. These were identified as the formamides **18** (70%) and **19** (69%) respectively (Scheme 3). When heterocycle **7** was reacted with **1a**, the formamide **20** (39%) was isolated. No product featuring an intact diazadithiafulvalenium ring system [the analogue of **2**] was detected. Similarly, when **6** was reacted with **1a**, the formamide **21** was isolated.

† *Current address*: National Defense Academy, Hashirimizu, Yokosuka 239, Japan.

‡ IUPAC names for tetrathiafulvalene and diazadithiafulvalene are 2,2′-bi(1,3-dithiol-2-ylidene) and 2,2′-bi(1,3-thiazol-2-ylidene), respectively.



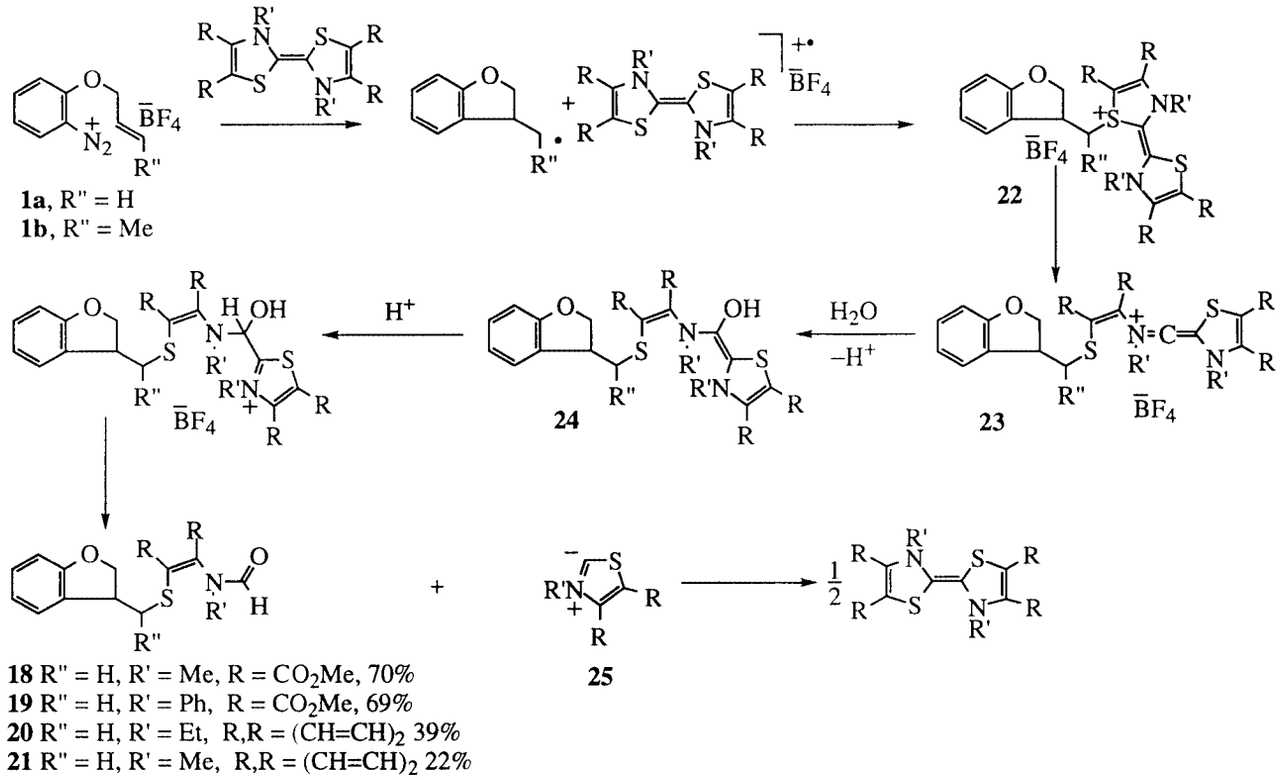
Scheme 1



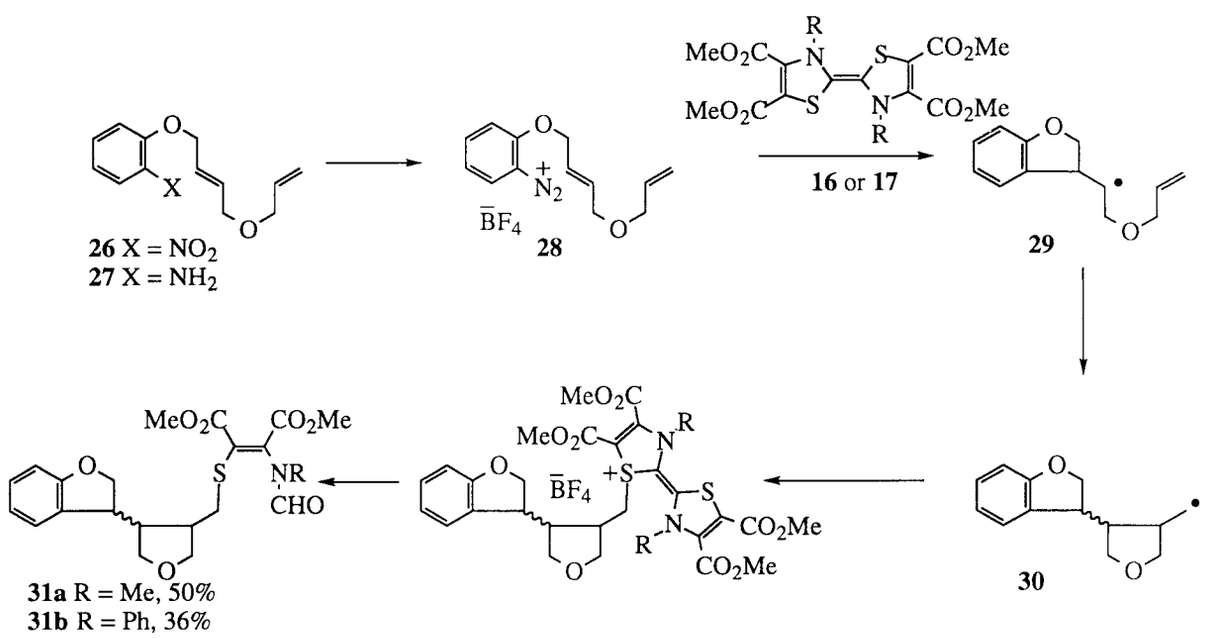
Scheme 2

The isolation of products **18**, **19**, **20** and **21** shows that there is a marked difference in the reactivity of intermediates formed from diazadithiafulvalenes compared to tetrathiafulvalene. The proposed mechanism for formation of the observed products is shown below. The products may be rationalised by a spontaneous opening of the initially formed salt **22** arising from the better stabilisation of positive charge by the nitrogen than by the sulfur in TTF salts. Once the ring has cleaved, the salt **23** will readily trap water to afford the enol **24**. Protonation and fragmentation afford the thiazolium salt **25** and the formamide product. An alternative to the mechanism shown features direct attack by water on the salt **22**. We have shown that nucleophiles attack tetrathiafulvalenium salts at the internal carbons[8] and the regiochemistry of attack (at the carbon adjacent to the positive charge) could lead to the products observed here.

It is noteworthy that the dithiadiazafulvalenes afford better reactions with substrate **1a** than **1b**. This suggests that the dithiadiazafulvalene radical-cations combine much more effectively with primary radicals than with secondary radicals, and hence their sensitivity to steric factors may be greater than anticipated. If this is the case, then it could be probed by a tandem radical cyclisation. Two substrates were prepared, **28** and **36** as shown below. Compound **28** should form a secondary radical **29** after the first cyclisation; if trapping by the radical-cations of diazadithiafulvalenes is slow then the second cyclisation



Scheme 3

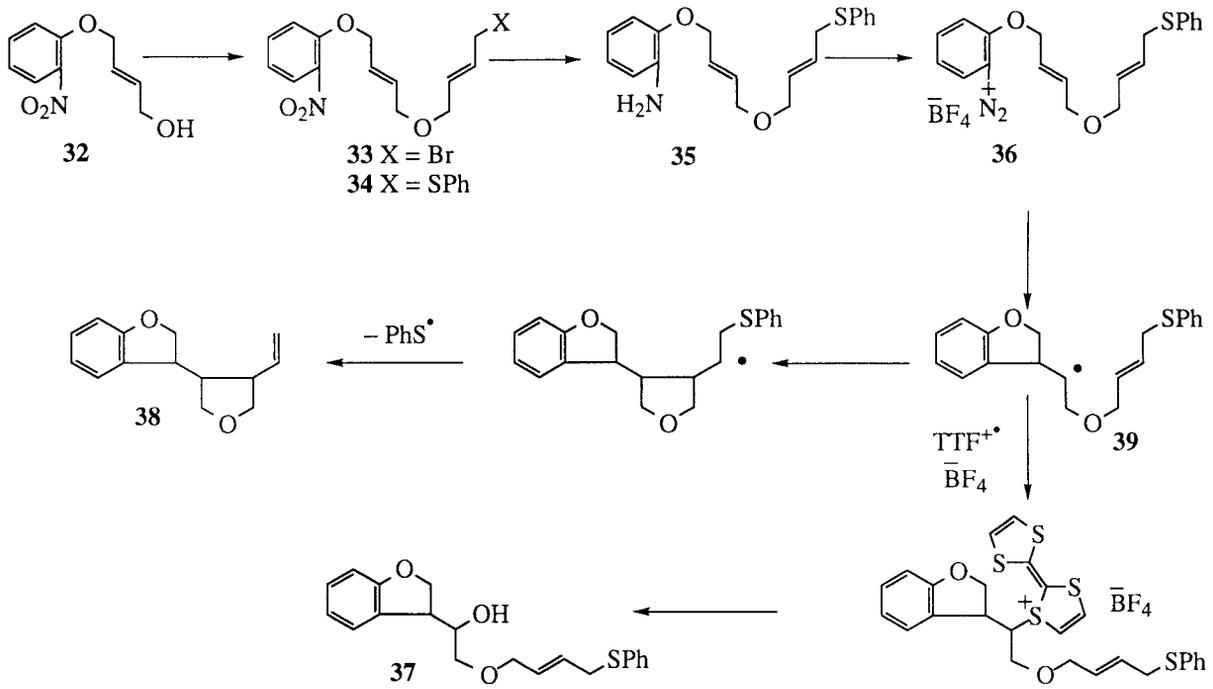


Scheme 4

should occur affording the final radical **30**, which is primary, and should therefore be efficiently converted into the corresponding formamide **31**. This is in effect what occurred, with **31a** being isolated in 50% yield and **31b** being isolated in 36% yield (Scheme 4).

The second substrate **36** should allow for a different termination, by the expulsion of a phenylthiyl radical. In this case, a comparison with the reactions of tetrathiafulvalene was made. Reaction with TTF led to isolation of 19% of monocyclised alcohol **37** and 48% of the bicyclised product **38**. Diazadithiafulvalene **16** led to a higher yield of bicyclised product **37** (72%) and no product of monocyclisation was isolated; this is consistent with the radical **39** produced after the initial cyclisation having a greater lifetime to cyclise (Scheme 5). This supports the proposal that the rate constants for coupling of secondary radical to $DDTF^{+\bullet}$ are lower than to $TTF^{+\bullet}$.

In conclusion, diazadithiafulvalenes are more powerful electron donors than TTF. Their radical-cations afford isolable products from coupling to primary carbon radicals. These products all feature cleavage of the DDTF ring system. The diazadithiafulvalene radical-cations apparently couple more slowly with secondary carbon radicals than tetrathiafulvalenium radical-cations. This suggests that modification of the TTF nucleus could also usefully alter the rates of coupling and extend the scope of the radical-polar crossover reaction to allow slower radical cyclisations to occur.



Scheme 5

Experimental

Melting points were carried out on a Kofler hot stage apparatus and are uncorrected. Microanalyses were determined using a Perkin-Elmer 240B elemental analyser. Infrared spectra were obtained on a Perkin-Elmer 1720-X FTIR or a Pye-Unicam SP3-100 spectrometer. Ultraviolet spectra were recorded on a Philips PU8700 series instrument. ^{1}H NMR spectra were recorded at 250 MHz on a Bruker WM250, at 270 MHz on a JEOL EX270 or at 400 MHz on a Bruker AM400 machine. ^{13}C NMR spectra were recorded at 67.5 MHz on a JEOL EX270 or at 100 MHz on a Bruker AM400 machine. NMR experiments were carried out in deuterochloroform, d_4-methanol, d_6-acetone, d_3-acetonitrile or d_6-dimethyl sulfoxide with tetramethylsilane as an internal reference. Chemical shifts are quoted in parts per million (ppm). The following abbreviations are used for multiplicities: s, singlet; d, doublet, t, triplet, q, quartet; m, multiplet. Coupling constants are reported in Hertz (Hz). In cases where superimposition of the signals of two, or more, isomers occurred, the signals have been reported as multiplets (m), unless the coupling constants of each isomer could be ascertained. Mass spectra were recorded at the EPSRC Mass Spectrometry Service Centre, Swansea.

Where necessary, solvents were dried and/or distilled before use. Tetrahydrofuran was distilled from sodium–benzophenone. Acetonitrile was distilled from phosphorus(v) oxide. Dichloromethane was distilled from calcium hydride. Diethyl ether, toluene and benzene were dried over sodium wire. Unless otherwise stated all petrol was of boiling range 40–60 °C and was distilled before use. Chromatography was performed using Sorbsil C60 (May and Baker), Kieselgel 60 (Art 9385) or Kieselgel HF254 silica gels.

3-Ethylbenzothiazolium iodide[5]

Iodoethane (27.70 g, 178.0 mmol, 4.00 equiv.) was added to a solution of benzothiazole (6.00 g, 44.4 mmol, 1.00 equiv.) in dry dimethylformamide (10 ml). The resultant solution was refluxed under nitrogen for 2 h. The formation of a precipitate was noted. The reaction mixture was diluted with ether and cooled in an ice bath to completely precipitate the product. The product was thoroughly washed with ether. The title compound was obtained as a creamy solid (9.08 g, 70.2%). No further purification was required. δ_H (250 MHz; d_6-DMSO) 1.59 (3H, t, *J* 7.2, Me), 4.88 (2H, q, *J* 7.2, NCH_2), 7.86–7.95 (2H, m, ArH), 8.40–8.44 (1H, m, ArH), 8.50–8.57 (1H, m, ArH) and 10.6 (1H, s, CH).

3-Ethylbenzothiazolium ethyl sulfate 4[9]

To a solution of benzothiazole (4.00 g, 29.6 mmol, 1.00 equiv.) in freshly distilled toluene (20 ml) was added dropwise a solution of diethyl sulfate (11.63 ml, 88.8 mmol, 3.00 equiv.). The resultant solution was heated to 60 °C for 6 h. The formation of a precipitate was noted. The creamy solid was filtered, washed with ether and dried under vacuum to give the title compound (6.60 g, 77%); mp 124–126 °C (lit.[9] 126.5 °C). δ_H (250 MHz; $CDCl_3$) 1.17 (3H, t, *J* 7.1, Me), 1.68 (3H, t, *J* 7.2, Me), 4.01 (2H, q, *J* 7.1, OCH_2), 4.95 (2H, q, *J* 7.2, NCH_2), 7.70–7.85 (2H, m, ArH), 8.18 (1H, d, *J* 7.6, ArH), 8.34 (1H, d, *J* 8.3, ArH) and 10.95 (1H, s, CH).

3,3′-Diethyl-2,2′-bi(2,3-dihydrobenzothiazol-2-ylidene) 7[3a]

Triethylamine (1.28 ml, 9.2 mmol, 2.00 equiv.) was added to a suspension of 3-ethylbenzothiazolium ethyl sulfate (1.33 g, 4.6 mmol, 1.00 equiv.) in dry acetonitrile (4.5 ml) in one flush. Initially a dark orange coloured solution was observed which gradually turned a pale yellow colour. On heating the reaction mixture to 60 °C, a yellow coloured solution was observed. The reaction mixture was allowed to cool to room temperature. Formation of a precipitate was noted. Further cooling with an ice–water bath ensured complete product precipitation. Filtration under nitrogen gave the title compound **7** as a bright yellow crystalline solid (0.53 g, 70%). This air-sensitive solid was stored under argon. Found: C, 66.37; H, 5.40; N, 8.74. $C_{18}H_{18}N_2S_2$ requires C, 66.25; H, 5.55; N, 8.60%; *m*/*z* (EI^+) 326 (M^+) and 43 (100).

5,8-Diethyldibenzo[*c*:*i*][1,2,5,8]dithiadiazecine-6,7(5*H*,8*H*)-dione 9[5]

Dry triethylamine (0.14 g, 1.4 mmol) was added, in one flush, to a solution of 3-ethylbenzothiazolium iodide **4b** (0.20 g, 0.7 mmol, 1.00 equiv.) in dry acetonitrile (3 ml) under nitrogen. A yellow coloured solution was noted after 30 min of stirring at room temperature. No product precipitated. The reaction mix-

ture was left stirring under nitrogen overnight. A red coloured solution was observed. Thin layer chromatography employing hexane–ethyl acetate (1:1) as the eluent revealed one major product. The reaction mixture was evaporated to dryness and purified by chromatography (dichloromethane) affording the title compound **9** (125 mg, 100%) as colourless plates, mp 168–169 °C (lit.[5] 166–168 °C). ν_{max}(film)/cm^{-1} 1669, 1640, 1461, 1377, 1273, 766 and 725; δ_H (250 MHz; CD_3CN) 0.94 (6H, t, *J* 7.2, 2 × Me), 3.19 (2H, dq, *J* 13.6, 7.2, N-CH), 3.62 (2H, dq, *J* 13.6, 7.2, N-CH), 7.4–7.6 (6H, m, ArH) and 7.75–7.85 (2H, m, ArH); δ_C (62.5 MHz; CD_3CN) 12.7, 44.7, 131.0, 132.3, 134.7, 138.1, 139.0, 143.5 and 164.5; *m*/*z* (EI$^+$) 358 (M$^+$, 12%) and 136 (100).

1-(2,3-Dihydrobenzofuran-3-yl)methylthio-2-(*N*-methyl-*N*-formylamino)-1,2-bis(methoxycarbonyl)ethene 18

Arenediazonium tetrafluoroborate **1b** (57 mg, 0.24 mmol) was dissolved in degassed acetone (5 ml). To this, the dithiadiazafulvalene[3] **16** (99 mg, 0.23 mmol) was added. Rapid nitrogen evolution was observed. The solution was stirred for 24 h and evaporated to dryness. The residue was subjected to column chromatography on silica gel (hexane–ethyl acetate, 1:1) to give *1-(2,3-dihydrobenzofuran-3-yl)methylthio-2-(N-methyl-N-formylamino)-1,2-bis(methoxycarbonyl)ethene* **18** (59 mg, 70%) (Found: M$^+$, 365.0936. $C_{17}H_{19}NO_6S$ requires *M*, 365.0933). ν_{max}(film)/cm^{-1} 3017, 2953, 2890, 1737, 1687, 1582, 1235 and 753; δ_H (400 MHz; $CDCl_3$) 2.91 (1H, dd, *J* 12.8 and 9.2, CH_2S), 2.95 [3H (minor), s, NCH_3], 3.02 [3H (major), s, NCH_3], 3.05–3.13 (1H, m, CH_2S), 3.60–3.70 (1H, m, CHAr), 3.76 [3H (minor), s, OCH_3], 3.77 [3H (major), s, OCH_3], 3.92 [3H (minor), s, OCH_3], 3.94 [3H (major), s, OCH_3], 4.35 (1H, dd, *J* 9.4, 5.0, OCH_2), 4.58–4.63 (1H, m, OCH_2), 6.82 (1H, d, *J* 8.0, ArH), 6.88 (1H, t, *J* 7.4, ArH), 7.16–7.21 (2H, m, ArH), 7.98 [1H (major), s, C(=O)H] and 8.10 [1H (minor), s, C(=O)H]; δ_C (100 MHz; $CDCl_3$) 30.4, 32.2, 33.6, 41.8, 42.0, 42.2, 52.8, 53.0, 53.5, 53.4, 75.5, 75.7, 110.1, 110.2, 121.0, 124.6, 125.4, 127.9, 129.4, 129.5, 149.1, 160.0, 162.2, 163.2, 163.4 and 163.8.

1-(2,3-Dihydrobenzofuran-3-yl)methylthio-2-(*N*-phenyl-*N*-formylamino)-1,2-bis(methoxycarbonyl)ethene 19

The procedure was carried out as for the preparation of **18**, using dithiadiazafulvalene **17**,[3] (99 mg, 0.18 mmol) and affording *1-(2,3-dihydrobenzofuran-3-yl)methylthio-2-(N-phenyl-N-formylamino)-1,2-bis(methoxycarbonyl)ethene* **19** (53 mg, 69%) (Found: M$^+$, 427.1133. $C_{22}H_{21}NO_6S$ requires *M* 427.1090). ν_{max}(film)/cm^{-1} 3019, 2953, 2892, 1732, 1690, 1594, 1259 and 753; δ_H (400 MHz; $CDCl_3$) 2.77 (1H, dd, *J* 13.3 and 9.5, CH_2S), 3.02 (1H, dd, *J* 13.3 and 5.0, CH_2S), 3.45–3.52 (1H, m, ArCH), 3.76 (3H, s, Me), 3.95 (3H, s, Me), 4.13 (1H, dd, *J* 9.4 and 5.0, $ArOCH_2$), 4.33 (1H, dd, *J* 9.4 and 9.4, $ArOCH_2$), 6.77 (1H, d, *J* 8.0, ArH), 6.81–6.87 (1H, m, ArH), 7.05 (1H, d, *J* 7.4, ArH), 7.12–7.16 (1H, m, ArH), 7.23–7.25 (1H, m, ArH), 7.31–7.46 (4H, m, ArH), 8.27 [1H (minor), s, CHO] and 8.53 [1H (major), s, CHO]; δ_C (100 MHz; $CDCl_3$) 36.6, 42.6, 53.1, 53.5, 75.6, 110.2, 120.9, 122.9, 124.0, 125.5, 127.2, 128.3, 129.2, 129.4, 129.9, 139.1, 146.4, 160.0, 161.8, 162.2 and 164.1.

N-{2-[(2-,3-Dihydro-1-benzofuran-3-yl)methylsulfanyl]phenyl}-*N*-ethylformamide 20

A solution of bi(2,3-dihydrobenzothiazol-2-ylidene) **7** (145 mg, 0.44 mmol, 1.02 equiv.) in acetone (1.5 ml) was added to a solution of 2-allyloxybenzenediazonium tetrafluoroborate (100 mg, 0.43 mmol, 1.00 equiv.) in acetone. The reaction mixture bubbled vigorously and nitrogen evolution occurred. The reaction mixture was left stirring under nitrogen for 1 h. The formation of a precipitate was noted. The reaction mixture was evaporated to dryness and the residue adsorbed onto silica gel (employing dichloromethane). Flash chromatography [hexane–ethyl acetate (4:1)] gave *N-{2-[(2,3-dihydro-1-benzofuran-3-yl)methylsulfanyl]phenyl}-N-ethylformamide* **20** (53 mg, 39%) as a red oil [Found: (M + H)$^+$, 314.1212. $C_{18}H_{18}NO_2S$ requires *M* + *H*, 314.1215]. ν_{max}(film)/cm^{-1} 3063, 2957, 2926, 2871, 2853, 1677, 1650, 1474, 1480 and 753; δ_H (250 MHz; $CDCl_3$) 1.14 (3H, t, *J* 7.3, CH_3), 3.01 (1H, dd, *J* 12.4, 9.8, SCH_2), 3.30 (1H, dd, *J* 12.4, 5.0, SCH_2), 3.68 (1H, m, ArCH), 3.79 (2H, q, *J* 7.3, NCH_2), 4.43 (1H, dd, *J* 9.3, 5.3, OCH_2), 4.63 (1H, dd, *J* 9.3, 9.3, OCH_2), 6.75–6.95 (2H, m, ArH), 7.10–7.40 (6H, m, ArH) and 8.09 and 8.38 (1H, s, HC=O); δ_C (67.8 MHz; $CDCl_3$) 13.1, 37.4, 40.4, 41.4, 76.1, 110.2, 120.9, 124.7, 126.6, 128.0, 129.0, 129.3, 130.0, 128.9, 136.7, 138.7, 160.0 and 163.0; *m*/*z* (CI) 331 [(M + NH_4)$^+$ 75%], 314 [(M + H), 100].

N-{2-[(2,3-Dihydro-1-benzofuran-3-yl)methylsulfanyl]phenyl}-*N*-methylformamide 21

Diazonium salt **1a** (114 mg, 0.46 mmol) was dissolved in degassed acetone (10 ml) under nitrogen. To this solution, dithiadiazafulvalene **6** (137 mg, 0.46 mmol) was added. The solution was stirred for 24 h and evaporated to dryness. The residue was subjected to column chromatography on silica gel (hexane–ethyl acetate, 7:3) to give the *monocyclised product*, **21**, as a brown oil (30 mg, 22%) [Found: (M + H)$^+$, 300.1066. $C_{17}H_{17}NO_2S$ requires *M* + H, 300.1058]. ν_{max}(film)/cm^{-1} 3060, 3010, 2925, 2886, 1680 (C=O) and 753; δ_H (250 MHz; $CDCl_3$) 3.00 (1H, dd, *J* 9.6 and 5.6, SCH_2), 3.24–3.32 (4H, m, NCH_3 and SCH_2), 3.59–3.70 (1H, m, ArCH), 4.42 (1H, dd, *J* 9.2 and 5.4, OCH_2), 4.62 (1H, dd, *J* 9.2, 9.0, OCH_2), 6.78–6.91 (2H, m, ArH), 7.14–7.52 (6H, m, ArH) and 8.13 and 8.31 (1H, 2 × s, HC=O); δ_C (100 MHz; $CDCl_3$) 33.1 (q), 37.7 (t), 41.5 (d), 76.1 (t), 110.2 (d), 120.9 (d), 124.7 (d), 127.2 (d), 128.81 (d), 128.85 (s), 128.9 (d), 129.28 (d), 129.32 (d), 135.8 (s), 140.7 (s), 160.1 (s) and 163.3 (d); *m*/*z* (EI) 300 [(M + H)$^+$ 9%], 91 (100%).

2-(5-Oxaocta-2,7-dien-1-yloxy)nitrobenzene 26

Diethyl azodicarboxylate (7.2 ml, 8.00 g, 45.9 mmol) was added dropwise, at 0 °C, to a solution of 2-nitrophenol (6.38 g, 45.9 mmol), 4-(allyloxy)but-2-enol[10] (4.0 g, 31.2 mmol) and triphenylphosphine (12.0 g, 45.9 mmol) in tetrahydrofuran (70 ml) over a period of 0.5 h. After stirring for 16 h at rt the mixture was evaporated to dryness, redissolved in dichloromethane (250 ml) and subsequently washed with sodium hydroxide (2 M, 200 ml), hydrochloric acid (2 M, 200 ml), saturated sodium carbonate (200 ml) and water (2 × 200 ml). The mixture was dried over anhydrous sodium sulfate, filtered and the solvent removed *in vacuo*. Column chromatography [hexane–ethyl acetate (9:1)] of the residue gave *2-(5-oxaocta-2,7-dien-1-yloxy)nitrobenzene* **26** as a yellow oil (4.10 g, 36%) (Found: C, 62.45; H, 6.22; N, 5.64. $C_{13}H_{15}NO_4$ requires C, 62.45; H, 6.22; N, 5.64%). ν_{max}(film)/cm^{-1} 2857, 1607, 1583, 1526, 1353, 1281 and 745; δ_H (250 MHz; $CDCl_3$) 4.01 (2H, ddd, *J* 5.6, 1.3, 1.3, OCH_2), 4.13 (2H, d, *J* 3.8, OCH_2), 4.80 (2H, d, *J* 3.5, OCH_2), 5.25 (2H, m, $=CH_2$), 5.58–5.97 (3H, m, =CH), 7.00–7.16 (2H, m, ArH), 7.51 (1H, ddd, *J* 7.2, 7.2, 1.7, ArH) and (1H, dd, *J* 8.1, 1.5, ArH); δ_C (100 MHz; $CDCl_3$) 66.0, 66.2, 71.6, 115.1, 117.5, 120.7, 125.8, 126.8, 130.9, 134.1, 134.7, 140.5 and 152.0.

2-(5-Oxaocta-2,7-dien-1-yloxy)aniline 27

A slurry of sodium borohydride (0.60 g, 15.8 mmol) in ethanol (30 ml) was added in one flush to a suspension of copper(II) acetylacetonate (0.88 g, 3.3 mmol) in ethanol (30 ml). The reaction mixture was left to stir until a clumpy solid had formed and the evolution of hydrogen gas ceased. 2-(5-Oxaocta-2,7-dien-1-yloxy)nitrobenzene **26** (3.95 g, 15.8 mmol) was added as a solution in ethanol (30 ml), followed by addition of sodium borohydride (1.20 g, 31.6 mmol) in ethanol (30 ml). The mixture was stirred for 3 h, carefully poured onto water (140 ml) and evaporated to one quarter of its original volume. The mixture was

diluted with more water (35 ml) and extracted with dichloromethane (3 × 60 ml). The combined organic phase was dried over anhydrous sodium sulfate, filtered and evaporated to dryness. Column chromatography [petroleum ether–diethyl ether (1:1)] of the crude oil gave *2-(5-oxaocta-2,7-dien-1-yloxy)-aniline* **27** as a yellow oil (1.61 g, 47%) (Found: C, 71.17; H, 8.11; N, 6.35. $C_{13}H_{17}NO_2$ requires C, 71.21; H, 7.81; N, 6.39%). ν_{max}(film)/cm^{-1} 3467, 3368, 2856, 1615, 1505, 1216 and 741; δ_H (250 MHz; $CDCl_3$) 3.77 (2H, s, NH_2), 3.99 (2H, ddd, *J* 5.6, 1.4, 1.4, OCH_2), 4.10 (2H, d, *J* 5.6, OCH_2), 4.62 (2H, d, *J* 6.2, OCH_2), 5.19 (1H, m, $=CH_2$), 5.28 (1H, ddd, *J* 17.2, 1.6, 1.6, $=CH_2$), 5.76–5.97 (3H, m, =CH) and 6.65–6.85 (4H, m, ArH); δ_C (100 MHz; $CDCl_3$) 64.6 (t), 66.0 (t), 71.5 (t), 112.1 (d), 115.4, 117.4, 118.5, 121.6, 128.5, 129.8, 134.7, 136.6 and 146.3.

2-(5-Oxaocta-2,7-dien-1-yloxy)benzenediazonium tetrafluoroborate 28

A solution of 2-(5-oxaocta-2,7-dien-1-yloxy)aniline **27** (0.60 g, 2.7 mmol) in dichloromethane (9 ml) was added dropwise, at −20 °C, to a suspension of nitrosonium tetrafluoroborate (0.35 g, 3.0 mmol) in dichloromethane (9 ml) over a period of 0.5 h. After stirring for a further 40 min the solvent was removed *in vacuo* with cooling (dry ice–methanol bath employed). The residue was washed with diethyl ether (2 × 50 ml), dissolved in acetone (5 ml) and subsequently poured onto cold diethyl ether (100 ml). The resultant precipitate was carefully filtered under nitrogen to give *2-(5-oxaocta-2,7-dien-1-yloxy)benzenediazonium tetrafluoroborate* **28** (0.58 g, 67%) as a light brown solid (Found: C, 48.69; H, 4.74; N, 8.60. $C_{13}H_{15}BF_4N_2O_2$ requires C, 40.09; H, 4.75; N, 8.81%). ν_{max}(film)/cm^{-1} 2249, 1591 and 1083; δ_H (250 MHz; $CDCl_3$) 4.00 (2H, dd, *J* 4.2, 1.1, OCH_2), 4.13 (2H, d, *J* 5.0, OCH_2), 5.07 (2H, d, *J* 5.5, OCH_2), 5.16–5.31 (2H, m, $=CH_2$), 5.76–5.97 (3H, m, =CH), 7.22–7.28 (1H, m, ArH), 7.39 (1H, d, *J* 8.7, ArH) and 8.01 (1H, dd, *J* 7.5, 8.8, ArH); δ_C (62.9 MHz; $CDCl_3$) 66.36, 68.25, 71.83, 101.09, 115.21, 117.68, 123.43, 124.54, 132.66, 132.91, 134.49, 144.38 and 162.55.

Reaction of the arenediazonium tetrafluoroborate 28 with the dithiadiazafulvalene 16 and 17

A typical procedure is as follows: arenediazonium tetrafluoroborate **28**[11] (0.11 g, 0.35 mmol) was dissolved in degassed acetone (5 ml). To this, the dithiadiazafulvalene **16** (0.15 g, 0.35 mmol) or **17** (0.19 g, 0.35 mmol) was added. Rapid nitrogen evolution was observed. The solution was stirred for 20 h and evaporated to dryness. The residue was subjected to column chromatography on silica gel (hexane–ethyl acetate, 4:5 [for the reaction with **16**] or 1:1 [for the reaction with **17**]) to give the bicyclisation product as a mixture of stereoisomers. *1-[4-(2,3-dihydrobenzo[b]furan-3-yl)tetrahydrofuran-3-yl]methylthio-2-(N-methyl-N-formylamino)-1,2-bis(methoxycarbonyl)ethene* **31a**: (76 mg, 50%) (Found: M^+ 435.1323. $C_{21}H_{25}NO_7S$ requires *M*, 435.1352). ν_{max}(film)/cm^{-1} 3012, 2952, 2872, 1733, 1687, 1592, 1234 and 753. *1-[4-(2,3-Dihydrobenzo[b]furan-3-yl)tetrahydrofuran-3-yl]methylthio-2-(N-phenyl-N-formylamino)-1,2-bis(methoxycarbonyl)ethene* **31b** (63 mg, 36%) (Found: M^+, 497.1469. $C_{26}H_{27}NO_7S$ requires *M* 497.1508). ν_{max}(film)/cm^{-1} 3014, 2952, 2885, 1732, 1691, 1593, 1235 and 754.

2-(9-Bromo-5-oxanona-2,7-dien-1-yloxy)nitrobenzene 33

To a solution of 2-(4-hydroxybut-2-en-1-yloxy)nitrobenzene **32**[12] (10.0 g, 48 mmol) and 1,4-dibromobut-2-ene (20.5 g, 96 mmol) in dry tetrahydrofuran (300 ml), sodium hydride (2.69 g, 67 mmol) was added slowly in an ice–methanol bath. The mixture was stirred for 2 h in the ice–methanol bath and poured into hydrochloric acid (2 M, 400 ml). The solution was extracted with dichloromethane (3 × 150 ml). The extracts were washed with brine (100 ml), dried over magnesium sulfate, and evaporated to dryness. The crude product was chromatographed (hexane–ethyl acetate, 7:3 to 1:1) to afford *2-(9-bromo-5-oxanona-2,7-dien-1-yloxy)nitrobenzene* **33** (4.00 g, 24%) (Found: C, 49.17; H, 4.50; N, 4.09. $C_{14}H_{16}BrNO_4$ requires C, 49.14; H, 4.71; N, 4.09%). ν_{max}(film)/cm^{-1} 3078, 3030, 2924, 2854, 1731, 1607, 1583, 1525, 1353, 1106 and 745; δ_H (250 MHz; $CDCl_3$) 3.96 (2H, d, *J* 7.1, OCH_2), 4.02 (2H, d, *J* 6.4, OCH_2), 4.13 (2H, d, *J* 4.5, CH_2Br), 4.79 (2H, d, *J* 4.2, $ArOCH_2$), 5.78–6.03 (4H, m, 2 × CH=CH), 7.01–7.11 (2H, m, ArH), 7.48–7.56 (1H, m, ArH) and 7.82 (1H, d, *J* 8.1, ArH); δ_C (67.8 MHz; $CDCl_3$) 32.0, 65.87, 66.3, 69.8, 115.0, 120.4, 125.7, 126.9, 129.1, 130.7, 131.49, 134.1, 140.3 and 151.9.

2-(9-Phenylthio-5-oxanona-2,7-dien-1-yloxy)nitrobenzene 34

A suspension of sodium hydride (0.45 g of 60% in oil, 11.3 mmol) in dry tetrahydrofuran (50 ml) was treated with thiophenol (0.956 g, 8.7 mmol) and stirred under nitrogen for 30 min in an ice bath. The fresh sodium thiophenoxide suspension was added slowly to an ice-cold solution of 2-(9-bromo-5-oxanona-2,7-dien-1-yloxy)nitrobenzene **33** (2.97 g, 8.7 mmol) in tetrahydrofuran (45 ml). The mixture was allowed to warm to rt and stirred for 3 h. The reaction mixture was poured into water (210 ml) and extracted with dichloromethane (3 × 100 ml). The extracts were washed with saturated Na_2CO_3 solution (2 × 130 ml), brine (100 ml), dried over magnesium sulfate, and evaporated to dryness. The residue was subjected to column (silica gel, hexane–ethyl acetate, 4:1) to give *2-(9-phenylthio-5-oxanona-2,7-dien-1-yloxy)nitrobenzene* **34** (2.82 g, 88%) (Found: C, 64.60; H, 5.77; N, 4.06. $C_{20}H_{21}NO_4S$ requires C, 64.67; H, 5.70; N, 3.77%). ν_{max}(film)/cm^{-1} 3075, 3032, 2916, 2854, 1607, 1583, 1525, 1482, 1353, 1280, 1090, 743 and 691; δ_H (250 MHz; $CDCl_3$) 3.55 (2H, d, *J* 6.6, CH_2S), 3.93 (2H, d, *J* 5.5, CH_2O), 4.00 (2H, d, *J* 4.5, CH_2O), 4.74 (2H, d, *J* 4.6, CH_2OAr), 5.59–5.87 (4H, m, 2 × CH=CH), 7.02–7.07 (2H, m, ArH), 7.16–7.34 (5H, m, ArH), 7.46–7.53 (1H, m, ArH), 7.81 (1H, dd, *J* 8.0 and 1.5, ArH); δ_C (67.8 MHz; $CDCl_3$) 36.4, 66.3, 70.8, 115.4, 121.1, 126.2, 126.9, 127.3, 129.4, 129.5, 130.1, 130.3, 131.1, 134.5, 136.3, 140.8 and 152.3.

2-(9-Phenylthio-5-oxanona-2,7-dien-1-yloxy)aniline 35

Copper(II) acetylacetonate (1.72 g, 6.6 mmol) was added to ethanol (20 ml) under nitrogen. To the suspension, sodium borohydride (0.208 g, 5.5 mmol) was added using ethanol (20 ml). The mixture was stirred until a clumpy solid was formed. To this mixture, a solution of the 2-(9-phenylthio-5-oxanona-2,7-dien-1-yloxy)nitrobenzene **32** (2.045 g, 5.5 mmol) in ethanol (20 ml) was added, followed by further sodium borohydride (0.416 g, 11.0 mmol) flushed in with ethanol (20 ml). The solution was stirred for 2.5 h. And then sodium borohydride (0.260 g, 6.9 mmol) was added to the mixture. The solution was stirred overnight at rt. The reaction mixture was filtered and the filtrate was poured into water (90 ml). The solution was evaporated to remove the solvent and extracted with dichloromethane (3 × 70 ml). The combined extracts were washed with brine (50 ml), dried over magnesium sulfate, and evaporated to dryness. The crude product was purified by column chromatography on silica gel (dichloromethane) to give *2-(9-phenylthio-5-oxanona-2,7-dien-1-yloxy)aniline* **35** (1.17 g, 62%) as a yellow oil (Found: C, 70.09; H, 7.04; N, 3.98. $C_{20}H_{23}NO_2S$ requires C, 70.35; H, 6.79; N, 4.10%). ν_{max}(film)/cm^{-1} 3466, 3368, 3057, 3029, 2918, 2854, 1614, 1505, 1277, 1216, 1041, 1024 and 739; δ_H (250 MHz; $CDCl_3$) 3.53 (2H, d, *J* 6.5, CH_2S), 3.78 (2H, s, NH_2), 3.91 (2H, d, *J* 5.5, CH_2), 3.98 (2H, d, *J* 6.0, CH_2O), 4.58 (2H, d, *J* 5.9, CH_2OAr), 5.58–5.91 (4H, m, 2 × CH=CH), 6.66–6.83 (4H, m, ArH) and 7.13–7.34 (5H, m, ArH); δ_C (67.8 MHz; $CDCl_3$) 35.9, 64.4, 65.6, 70.2, 112.0, 115.3, 118.4, 121.6, 126.3, 128.4, 128.9, 129.7, 129.7, 129.9, 135.8, 136.6 and 146.2.

2-(9-Phenylthio-5-oxanona-2,7-dien-1-yloxy)benzenediazonium tetrafluoroborate 36

A suspension of nitrosonium tetrafluoroborate (0.244 g, 2.1 mmol) in dichloromethane (7 ml) under nitrogen was cooled to −20 °C. To this, a solution of 2-(9-phenylthio-5-oxanona-2,7-dien-1-yloxy)aniline **35** (0.650 g, 1.9 mmol) in dichloromethane (7 ml) was added dropwise over 0.5 h. The solution was stirred for 60 min. The solvent was removed under reduced pressure. The residue was washed with cold ether (50 ml) twice and dissolved with acetone (5 ml). The acetone solution was poured into ether (100 ml) below −20 °C. The ether was removed by decantation and the residual oil was dissolved with acetone followed by pouring into ether (100 ml). After decantation, the oily product was dried under reduced pressure to afford *2-(9-phenylthio-5-oxanona-2,7-dien-1-yloxy)benzenediazonium tetrafluoroborate* **36** (0.71 g, 85%) as a brown oil (Found: M^+, 353.13208. $C_{20}H_{21}N_2O_2S$ requires *M*, 353.13237). ν_{max}(film)/cm^{-1} 2261, 1592, 1488, 1296, 1059 and 753. δ_H (250 MHz; $CDCl_3$) 3.55 (2H, d, *J* 6.4, CH_2S), 3.94 (2H, d, *J* 5.6, CH_2O), 4.01 (2H, d, *J* 4.3, CH_2O), 5.03 (2H, d, *J* 4.7, CH_2OAr), 5.60–5.88 (4H, m, 2 × CH=CH), 7.12–7.35 (7H, m, ArH), 7.95–8.02 (1H, m, ArH) and 8.40 (1H, dd, *J* 8.4 and 1.4, ArH); δ_C (67.8 MHz; $CDCl_3$) 35.8, 66.1, 68.2, 70.6, 101.1, 115.1, 123.4, 124.5, 126.4, 129.0, 129.2, 129.5, 129.7, 132.4, 133.0, 135.9, 144.2 and 162.5.

Reaction of 2-(9-phenylthio-5-oxanona-2,7-dien-1-yloxy)-benzenediazonium tetrafluoroborate 36 with dithiadiazafulvalene 16

The diazonium salt **36** (0.14 g, 0.32 mmol) was dissolved in degassed acetone (8 ml) under nitrogen. To this solution, dithiadiazafulvalene **16** (0.32 mmol) was added. The solution was stirred for 4 h and evaporated to dryness. The residue was subjected to column chromatography on silica gel (hexane–ethyl acetate, 9:1) to give the bicyclised product *4-(2,3-dihydrobenzo[b]furan-3-yl)tetrahydrofuran-3-yl-ethene* **38** (50 mg, 72%) and diphenyl disulfide (11 mg, 31%) **38** (Found: M^+, 216.1150. $C_{14}H_{16}O_2$ requires *M*, 216.1150). ν_{max}(film)/cm^{-1} 3076, 2975, 2929, 2859, 1639, 1594, 1482, 1459, 1231, 1056, 997, 921 and 752; δ_H (400 MHz; $CDCl_3$) 2.32–3.14 (2H, m, CHCHC=C), 3.39–4.65 (7H, m, 3 × CH_2 and ArCH), 4.99–5.32 (2H, m, C=CH_2), 5.62–5.97 (1H, m, CH=C), 6.79–6.87 (2H, m, ArH) and 7.02–7.29 (2H, m, ArH); δ_C (100 MHz; $CDCl_3$) 41.2, 42.0, 42.3, 44.3, 46.0, 46.6, 47.9, 48.2, 48.7, 49.1, 49.2, 49.8, 69.7, 70.3, 70.7, 72.0, 73.4, 73.5, 73.6, 73.9, 74.7, 75.1, 75.8, 109.9, 109.9, 110.0, 110.0, 116.5, 116.6, 116.8, 116.9, 117.4, 117.7, 120.6, 126.6, 120.6, 124.6, 124.7, 124.7, 125.1, 128.6, 128.7, 128.7, 128.8, 128.8, 129.0, 129.7, 130.0, 130.7, 136.7, 137.9, 138.4, 160.1, 160.2 and 160.5; *m/z* (EI) 216 [$(M)^+$ 8%], 119 (100%). Diphenyl disulfide: δ_H (250 MHz; $CDCl_3$) 7.22–7.34 (6H, m, ArH) and 7.48–7.52 (4H, m, ArH).

Reaction of 2-(9-phenylthio-5-oxanona-2,7-dien-1-yloxy)-benzenediazonium tetrafluoroborate 36 with dithiadiazafulvalene 6

Diazonium salt **36** (154 mg, 0.35 mmol) was dissolved in degassed acetone (8 ml) under nitrogen. To this solution, dithiadiazafulvalene **6** (104 mg, 0.35 mmol) was added. The solution was stirred for 4 h and evaporated to dryness. The residue was subjected to column chromatography on silica gel (hexane–ethyl acetate, 9:1) to give the bicyclised product, *4-(2,3-dihydrobenzo[b]furan-3-yl)tetrahydrofuran-3-ylethene* **38** (55 mg, 72%) (data as above) and diphenyl disulfide (16 mg, 42%).

Reaction of 2-(9-phenylthio-5-oxanona-2,7-dien-1-yloxy)-benzenediazonium tetrafluoroborate 36 with TTF

TTF (72 mg, 0.35 mmol) was added in one flush to a solution of 2-(9-phenylthio-5-oxanona-2,7-dien-1-yloxy)benzenediazonium tetrafluoroborate (0.154 g, 0.35 mmol) in degassed acetone (8 ml). After stirring at room temperature for 4 h the mixture was evaporated to dryness. Column chromatography [hexane–ethyl acetate (9:1 to 4:1)] gave the monocyclised product, *1-(2,3-dihydrobenzo[b]furan-3-yl)-7-phenylthio-3-oxahept-5-enol* **37** (23 mg, 19%), bicyclised product, *4-(2,3-dihydrobenzo[b]furan-3-yl)tetrahydrofuran-3-ylethene* **38** (36 mg, 48%) (data as above), and diphenyl disulfide (7 mg, 18%). **37** [Found: $(M + NH_4)^+$ 360.1633]. $C_{20}H_{26}NO_3S$ requires *M* + NH_4, 360.1633; ν_{max}(film)/cm^{-1} 3459, 3011, 2898, 2864, 1610, 1595, 1482, 1460, 1233, 1114, 968 and 754; δ_H (250 MHz; $CDCl_3$) 3.28 [1H (minor), dd, *J* 9.6 and 3.5, ArCH], 3.36 [1H (major), dd, *J* 9.6 and 6.7, ArCH], 3.47–3.58 (4H, m, OCH_2 and SCH_2), 3.88–3.99 (3H, m, OCH_2 and CHOH), 4.43 [1H (minor), dd, *J* 9.3 and 5.4, $ArOCH_2$], 4.52 [1H (minor), dd, *J* 9.2 and 9.2, $ArOCH_2$], 4.53 [1H (major), dd, *J* 9.1 and 9.1 $ArOCH_2$], 4.67 [1H (major), dd, *J* 9.1 and 5.1, $ArOCH_2$], 5.60–5.69 (1H, m, CH=CH), 5.72–5.83 (1H, m, CH=CH), 6.80–6.82 (1H, m, ArH), 6.87 (1H, ddd, *J* 7.4, 7.4 and 0.9, ArH), 7.14–7.22 (3H, m, ArH) and 7.26–7.36 (4H, m, ArH); δ_C (67.8 MHz; $CDCl_3$) 36.1, 45.1, 45.5, 71.4, 71.7, 71.9, 72.5, 73.0, 73.1, 109.9, 110.0, 120.6, 120.7, 125.4, 126.0, 126.6, 126.9, 129.0, 129.1, 129.3, 129.5, 130.3, 135.8 and 160.9.

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