Cycloaddition of benzo[*b*]thiophene-*S*,*S*-dioxide – a route to substituted dibenzothiophenes and dibenzothiophene *S*,*S*-dioxides

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Benzo[*b*]thiophene *S*,*S*-dioxide can be transformed by cycloaddition with tetraarylthiophene *S*-oxides to tetraaryldibenzothiophene *S*,*S*-dioxides. An analogous cycloaddition of benzo[*b*]thiophene *S*,*S*-dioxide, albeit at higher temperatures, leads directly to tetraaryldibenzothiophenes.

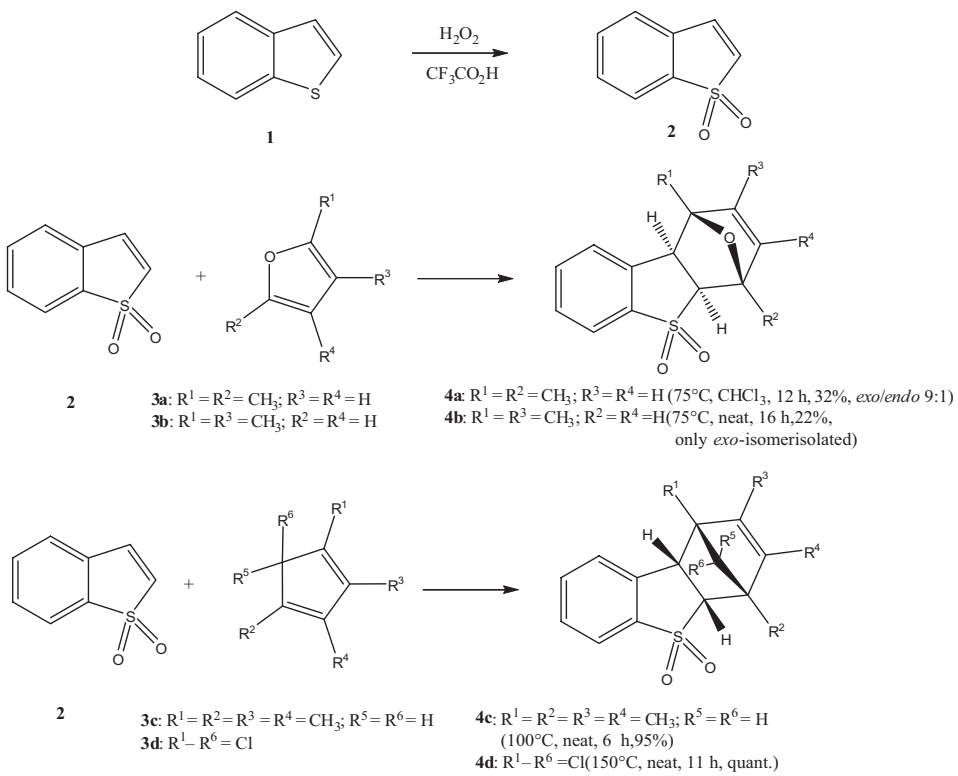
Keywords: [4+2]-cycloaddition, benzo[*b*]thiophene-*S*,*S*-dioxide, dibenzothiophenes, thiophene-*S*-oxide, tetracyclone, desulfurisation

Dibenzothiophenes are ubiquitious constituents of fossil fuels.[1,2] Their removal by desulfurisation of the molecules is a crucial step in lowering the sulfur content in fuels further. Interesting substrates for such desulfurisation reactions are alkylated and arylated dibenzothiophenes as these are known to undergo desulfurisation least readily. For our own desulfurisation studies[3,4] of thiophenes, benzothiophenes and dibenzothiophenes we were in need of multi-substituted dibenzothiophenes and their oxygenated derivatives as substrates.

In the following, the preparation of multi-substituted dibenzothiophenes and their *S*,*S*-dioxide derivatives by cycloaddition reactions of benzothiophene *S*,*S*-dioxide as the ene component is described. Benzothiophene-*S*,*S*-dioxide has been used as ene-component in [3+2]-cycloaddition reactions,[5-10] where azomethine ylides,[5] diazomethane,[6] diphenyl nitrone,[6] nitrile oxides,[8-10] and nitrile imides[11,12] have been used as reactants. Much less studied is benzo[*b*]thiophene-*S*,*S*-dioxide or its substituted derivatives as ene components in [4 + 2]-cycloaddition reactions.[13-16]

Results and discussion

Initially, we examined cyclopentadienes and furans as dienes to gather further information on the reactivity of benzothiophene *S*,*S*-dioxide (**2**) as ene in the Diels–Alder reaction. It was found that both 1,2,3,4-tetramethylcyclopentadiene (**3c**) and hexachlorocyclopentadiene (**3d**) react with **2** (Scheme 1). The reaction with hexachlorocyclopentadiene (**3d**) had already been reported[14] but without the spectroscopic data of the cycloadduct. We chose to repeat this reaction in order to study the stereoselectivity of the cycloaddition. In fact, the cycloadduct formed as one isomer only. An X-ray crystal structural analysis of **4d** was carried out and it showed **4d** to be the *endo*-isomer (Fig. 1) (T. Thiemann, J. Iniesta and T. Matsumoto, submitted). This is in accord with the fact that many cyclopentadienes, including hexachlorocyclopentadiene,



Scheme 1

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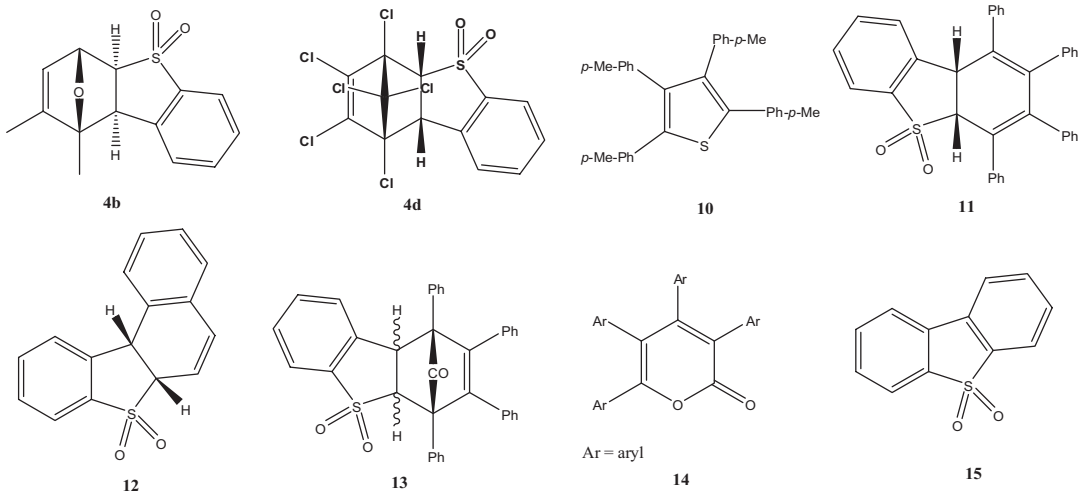
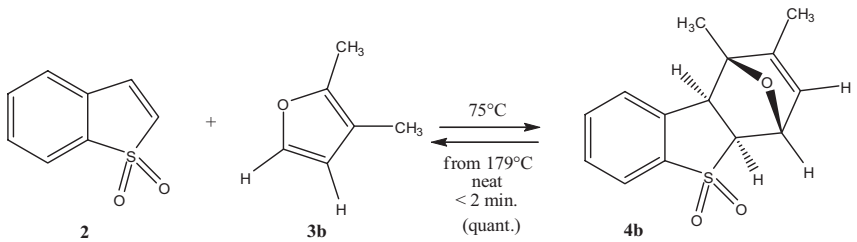


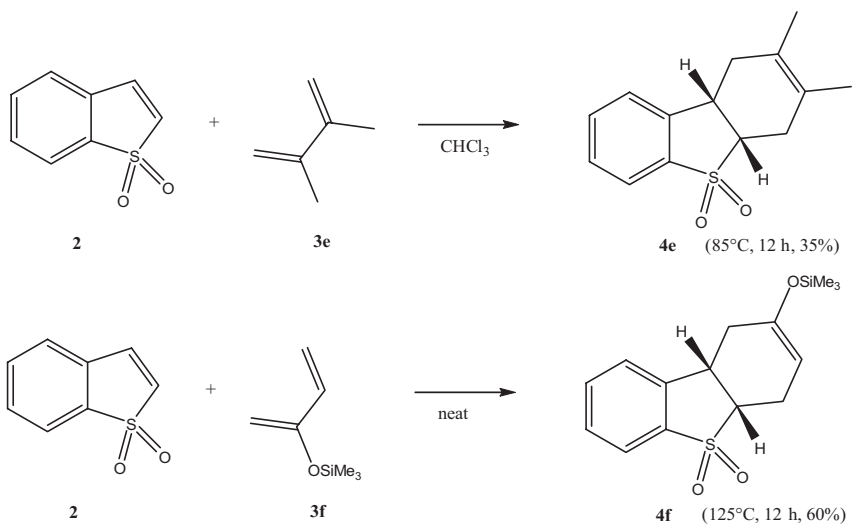
Fig. 1

form *endo*-isomers preferentially.[17] Also, 2,5-dimethylfuran (**3a**) and 2,3-dimethylfuran (**3b**) formed the respective cycloadducts with **2** as predominately one isomer. The regio- and stereochemistry of isolated **4b** was determined by X-ray crystal structural analysis (T. Thiemann, J. Iniesta and T. Matsumoto, submitted). It showed it to be the *exo*-isomer (Fig. 1). The tendency of furans to form predominantly *exo*-isomers is well documented (see refs 18–20 and refs cited in ref 20). As these cycloadducts can undergo a back reaction to the products, the thermodynamic *exo*-product is preferred (see refs 18–20 and refs cited in ref 20), while for the other cycloalkadienes discussed above the kinetically favoured *endo*-isomer is formed. When heated, cycloadduct **4b** undergoes cleanly a retro-Diels–Alder reaction to the starting materials, benzo[*b*]thiophene-*S*,*S*-dioxide (**2**) and 2,3-dimethylfuran (**3b**) (Scheme 2).

For the actual preparation of the substituted dibenzothiophene *S*,*S*-dioxides reactive non-cyclic dienes were needed or cyclic dienes that would provide the cycloadduct with an extrudable bridge. As non-cyclic diene, 2,3-dimethylbuta-1,3-diene (**3e**) was chosen. **2** reacts with **3e** to form the expected cycloadduct **4e** [see also ref. 14]. The reaction, however, is sluggish and when the reaction is carried out in chloroform at 60°C unreacted **2** remains even after 12 h. Also, 2-trimethylsilyloxybutadiene (**3f**) was used as diene, where **2** and **3f** were reacted in a neat mixture for 12 h to give **4f** as predominantely one regioisomer in 60% yield (Scheme 3).



Scheme 2



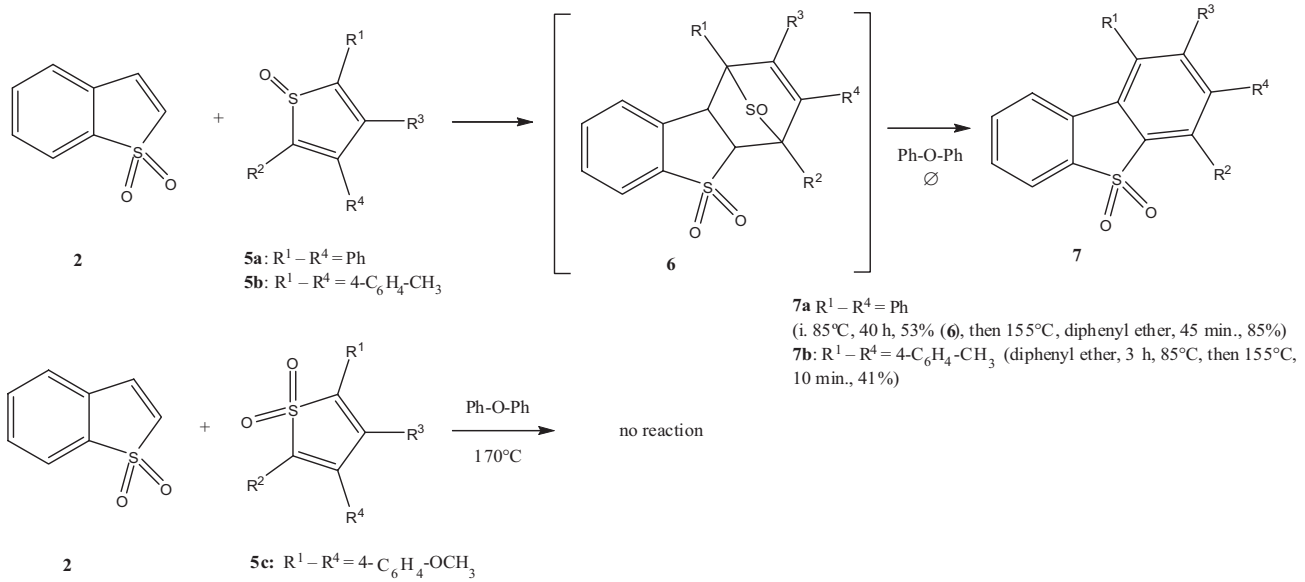
Scheme 3

Tetraarylthiophene-*S*-oxides, tetraarylthiophene-*S*,*S*-dioxides and tetracyclones (tetraarylcyclopentadienones) were chosen as cyclic dienes that in the reaction with **2** would lead to cycloadducts with a bridge, which could be thermally extruded. It is known that 7-thiabicyclo[2.2.1]heptadiene-*S*-oxides and *S*,*S*-dioxides as well as bicyclo[2.2.1]heptadien-7-ones as the primary cycloadducts are not stable in these reactions and extrude the C1/S1-bridge at the reaction temperatures needed for the cycloaddition reactions or at subsequent, more elevated temperatures (see refs 22–24 and refs cited in refs 23 and 24). Thiophene-*S*-oxides are known to be *endo*-selective in [4 + 2] cycloaddition reactions.[21] In the present case, the *exo*-/*endo*-selectivity could not be ascertained due to the subsequent formation of the SO-bridge in the primary cycloadduct.

Both tetraphenylthiophene-*S*-oxide (**5a**) and tetrakis(*p*-methylphenyl)thiophene *S*-oxide (**5b**) were reacted with **2** and the desired tetraaryldibenzothiophene *S*,*S*-dioxides **7** could be isolated in acceptable yield (Scheme 4). Nevertheless, in the reaction some of the thiophene *S*-oxide was deoxygenated and especially in the case of **5b** also appreciable amounts of tetrakis(*p*-tolyl)thiophene (**10**) (Fig. 1) were formed. Initially, the reaction was run at 85°C, and thereafter, at the end of the reaction, the reaction temperature was raised to 155°C for a short time. After the initial reaction at 85°C, the reaction mixture contained a number of products. Apart from the desired products **7**, also intermediate **6** and **11** could be identified. Intermediate **6** can be transformed cleanly to **7** by thermolysis.

Much more difficult is the reaction with tetraarylthiophene *S*,*S*-dioxides. Thus, tetrakis(*p*-methoxyphenyl)thiophene *S*,*S*-dioxide (**5c**) does not cycloadd to benzo[*b*]thiophene dioxide (**2**), even at temperatures as high as 170°C with diphenyl ether used as solvent. Rather, in this case benzothiophene dioxide dimerises to the well known **11**[25-27] (Fig. 1).

A number of substituted tetracyclones **8a**–**e** were reacted with **2** in diphenyl ether at 150°C. Here, the dibenzothiophenes **9** were obtained directly in acceptable yield (Scheme 5). It is believed that the deoxygenation of the sulfur moiety occurs at the stage of the primary adduct **13** (Fig. 1), perhaps concurrent with the extrusion of carbon monoxide and the aromatisation of the adduct. Tetracyclones are known not to be *exo*-/*endo*-selective at higher reaction temperatures.[28] In the present case, the *exo*-/*endo*-selectivity could not be ascertained due to the subsequent extrusive decarbonylation of the primary cycloadduct. The extruded species are reductants. Also, the tetracyclones that were used as the diene component, may react as reductant of the primary cycloadducts. α-Pyrones **14** (Fig. 1) form as by-products in the reactions. It is known, however, that tetracyclones **8** are air-oxidised to α-pyrones **14** when heated in diphenyl ether at elevated temperatures



2

5a: $R^1 - R^4 = Ph$
5b: $R^1 - R^4 = 4\text{-}C_6H_4\text{-}CH_3$

6

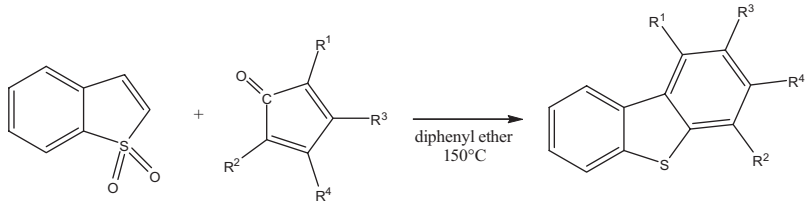
7

7a $R^1 - R^4 = Ph$
(i. 85°C, 40 h, 53% (**6**), then 155°C, diphenyl ether, 45 min., 85%)
7b: $R^1 - R^4 = 4\text{-}C_6H_4\text{-}CH_3$ (diphenyl ether, 3 h, 85°C, then 155°C, 10 min., 41%)

2

5c: $R^1 - R^4 = 4\text{-}C_6H_4\text{-}OCH_3$

Scheme 4

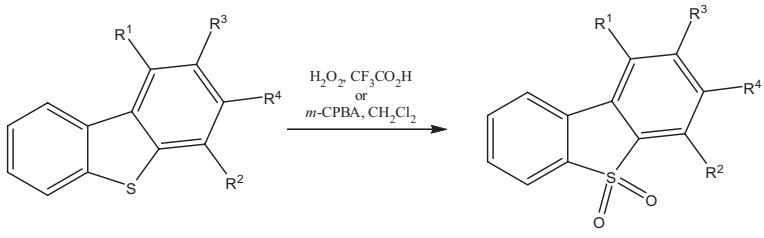


2

8a: R^1 - R^4 = Ph
8b: $R^1 = R^2 = Ph$; $R^3 = R^4 = 4\text{-}C_6H_4\text{-}OCH_3$
8c: $R^1 = R^2 = Ph$; $R^3 = R^4 = 4\text{-}C_6H_4\text{-}CH_3$
8d: $R^1 = R^2 = Ph$; $R^3 = R^4 = 4\text{-}C_6H_4\text{-}Br$
8e: $R^1 = R^2 = Ph$; $R^3 = R^4 = 4\text{-}C_6H_4\text{-}F$

9a: $R^1 - R^4 = Ph$ (150°C, 45 h, 45%)
9b: $R^1 = R^2 = Ph$; $R^3 = R^4 = 4\text{-}C_6H_4\text{-}OCH_3$ (150 °C, 45 h, 45%)
9c: $R^1 = R^2 = Ph$; $R^3 = R^4 = 4\text{-}C_6H_4\text{-}CH_3$ (150 °C, 36 h, 46%)
9d: $R^1 = R^2 = Ph$; $R^3 = R^4 = 4\text{-}C_6H_4\text{-}Br$ (150 °C, 18 h, 50%)
9e: $R^1 = R^2 = Ph$; $R^3 = R^4 = 4\text{-}C_6H_4\text{-}F$ (150°C, 20 h, 49%)

Scheme 5



9a: $R^1 - R^4$ = Ph
9d: $R^1 = R^2$ = Ph; $R^3 = R^4$ = 4-C_6H_4-Br
9e: $R^1 = R^2$ = Ph; $R^3 = R^4$ = 4-C_6H_4-F

7a: $R^1 - R^4$ = Ph (87%, H_2O_2)
7c: $R^1 = R^2$ = Ph; $R^3 = R^4$ = 4-C_6H_4-Br (85%, *m*-CPBA)
7d: $R^1 = R^2$ = Ph; $R^3 = R^4$ = 4-C_6H_4-F (88%, H_2O_2)

Scheme 6

(see T. Thiemann, J. Iniesta and D.J. Walton, submitted). It has been confirmed that benzo[*b*]thiophene (**1**) itself does not react with tetracyclones **8** under the conditions, so that a deoxygenation of benzo[*b*]thiophene-*S*,*S*-dioxide (**2**) to benzo[*b*]thiophene (**1**) prior to the cycloaddition can be excluded. Also, while tetracyclones **8** are easily oxidised to α-pyrones **14**, at elevated temperatures even with molecular oxygen (*vide supra*), no oxygen transfer can be noted during a prolonged heating of a mixture of tetracyclone **8** and dibenzothiophene *S*,*S*-dioxide (**13**) (Fig. 1), showing that tetracyclone does not act as a reductant to **7** produce **9**, even at 150°C.

The tetraaryldibenzothiophenes **9** can be converted into the corresponding tetraaryldibenzothiophene *S*,*S*-dioxides **7** by reaction with H_2O_2/CF_3CO_2H or with *m*-chloroperoxybenzoic acid (*m*-CPBA) (Scheme 6). On the other hand, it is known that dibenzothiophene *S*,*S*-dioxides can be reduced to dibenzothiophenes.[29]

In conclusion, it could be shown that benzo[*b*]thiophene *S*,*S*-dioxide (**2**) reacts as the ene component with a number of dienes in [4 + 2] cycloaddition reactions. Cyclopentadienes provide *endo*-cycloadducts, while predominantely *exo*-cycloadducts are obtained with furans. In the reaction of **2** with tetracyclones, substituted dibenzothiophenes are produced directly. These are interesting candidates for desulfurisation studies of highly congested dibenzothiophenes.

Experimental

General

Tetracyclone (**8a**) (TCI), 2,3-dimethylbuta-1,3-diene (**3e**) (TCI), 2-trimethylsilyloxybuta-1,3-diene (**3f**) (Aldrich), 2,5-dimethylfuran (**3a**) (TCI), and 2,3-dimethylfuran (**3b**) (Aldrich) were acquired commercially. Substituted tetracyclones **8b–e** were obtained from substituted benzils and diphenylacetone by Weiss reactions. Tetraphenylthiophene *S*-oxides **5a** and **5b** were obtained via published procedures from diphenylacetylene (tolane) and bis(4-methylphenyl)acetylene, respectively, via the corresponding tetraarylzirconacyclopentadienes.[30] Benzothiophene-*S*,*S*-dioxide (**2**)[31] and dibenzothiophene *S*,*S*-dioxide (**15**) were prepared by trifluoroacetic acid catalysed H_2O_2 oxidation of commercially available benzo[*b*]thiophene (**1**) (TCI) (vide infra) and dibenzothiophene (Acros), respectively. Melting points are uncorrected. IR spectra, ^1H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer. The chemical shifts are relative to TMS (solvent $CDCl_3$, unless noted otherwise). Mass spectra were measured with a JMS-01-SG-2 spectrometer (EI, 70 eV or FAB-modus). Column chromatography was carried out with Wakogel 300.

Typical preparation of benzo[b]thiophene S,S-dioxide (**2**) [see ref. 31]: To a mixture of trifluoroacetic acid (3.0 ml) and benzo[*b*]thiophene (**1**, 750 mg, 5.6 mmol) was added at 0°C a solution of hydrogen peroxide in trifluoroacetic acid (from a 4 M stock solution prepared from mixing 30% hydrogen peroxide (4.3 ml) and trifluoroacetic acid (8.5 ml). After the addition, the reaction temperature was raised to room temperature and kept until the starting material was almost consumed (TLC, chloroform). The mixture was neutralised with 10w% aq. $NaHCO_3$ solution. Then, the solution was extracted with chloroform (5 x 20 ml), the organic phase dried over anhydrous $MgSO_4$ and concentrated under reduced pressure at rt until a few ml solution remained. Column chromatography of this solution on silica gel (chloroform/ether 2:1) gave **2** in high purity. The benzo[*b*]thiophene-*S*,*S*-dioxide concentration in solution was determined by ^1H NMR.

Alternatively, water (20 ml) was added to the reaction mixture after completion of the reaction. Then the mixture was filtered after neutralisation with the $NaHCO_3$ solution. The dried solid was taken up in chloroform and subjected to column chromatography on silica gel (chloroform/ether 2:1). The pure fractions were concentrated under reduced pressure to give **2** as a colourless solid (820 mg, 88%); (Found: 166.0091. $C_8H_6O_2S$ requires M, 166.0089); δ_H (270 MHz, $CDCl_3$) 6.71 (1H, d, ^3J = 6.7 Hz), 7.22 (1H, d, ^3J = 6.7 Hz), 7.35–7.38 (1H, m), 7.50–7.57 (2H, m), 7.69–7.72 (1H, m); δ_C (67.8 MHz, $CDCl_3$) 121.3 (CH), 125.4 (CH), 130.5 (CH), 130.7 (CH), 131.1 (C_{quat}), 132.4 (CH), 133.6 (CH), 136.6 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 166 (39) [M^+], 150 (38), 137 (100), 118 (17), 109 (48), 90 (16), 89 (14), 76 (12), 75 (11), 74 (11), 58 (20).

exo-1,11-Dimethyl-14-oxa-3-thiatetracyclo[9.2.0^{2,10}.0^{4,9}]tetradeca-3,5,7,12-tetraene S,S-dioxide (**4a**): A solution of **2** (361 mg, 2.18 mmol) in chloroform (3 ml) and 2,5-dimethylfuran (**3a**, 4.27 g, 43.6 mmol, 20 equiv.) was stirred at 75°C for 12 h. Then the product mixture was concentrated under reduced pressure and the residue subjected to column chromatography on silica gel (hexane: chloroform:ether 5:1:1) to give the product **4a** (100 mg, 0.38 mmol, 29% yield) as a colourless solid; m.p. 137°C; (Found: 263.0747. $C_{14}H_{15}O_3S(MH^+)$ requires 263.0742); ν_{max} (KBr)/cm^{-1} 3082, 2980, 2936, 1474, 1449, 1384, 1341, 1290, 1257, 1221, 1183, 1149, 1122, 1084, 1069, 869, 770, 751, 578; δ_H (270 MHz, $CDCl_3$) 1.84 (3H, s, CH_3), 1.85 (3H, s, CH_3), 3.91 (1H, d, ^3J = 8.4 Hz), 4.15 (1H, d, ^3J = 8.4 Hz), 5.66 (1H, d, ^3J = 5.7 Hz), 6.34 (1H, d, ^3J = 5.7 Hz), 7.36 (1H, d, ^3J = 7.8 Hz), 7.60–7.40 (3H, m); δ_C (67.8 MHz, $CDCl_3$) 18.7 (CH_3), 19.0 (CH_3), 56.3 (CH), 70.2 (CH), 87.7 (C), 89.0 (C), 122.0 (CH), 124.8 (CH), 129.5 (CH), 133.29 (CH), 136.74 (CH), 137.87 (CH), 138.00 (C), 141.24 (C); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 263 (24) [MH^+], 262 (5) [M^+]; (Found: C, 64.0; H, 5.4. $C_{14}H_{14}O_3S$ requires C, 64.10%; H, 5.38).

exo-11,12-Dimethyl-14-oxa-3-thiatetracyclo[9.2.0^{2,10},0^{4,9}]tetradeca-4,6,8,12-tetraene S,S-dioxide (**4b**): A solution of **2** (380 mg, 2.29 mmol) in chloroform (3 ml) and 2,3-dimethylfuran (**3b**, 2.12 g, 22.1 mmol) was stirred at 75°C for 16 h. Then, the product mixture was subjected to column chromatography on silica gel (initially, hexane to remove the excess 2,3-dimethylfuran, thereafter hexane: chloroform:ether 4:1:1) to give **4b** (133 mg 0.508 mmol, 22% yield) as a colourless solid; m.p. 179–180°C; (Found: 262.0671. $C_{14}H_{14}O_3S$ requires M, 262.0664); ν_{max} (KBr)/cm^{-1} 3080, 2966, 2932, 1476, 1444, 1387, 1300, 1199, 1155, 1124, 994, 938, 871, 802, 768, 593, 567, 657, 513; δ_H (270 MHz, $CDCl_3$) 1.43 (3H, s, CH_3), 1.89 (3H, s, CH_3), 3.61 (2H, m), 5.40 (1H, bs), 6.08 (1H, bs), 7.39 (1H, d, ^3J = 7.8 Hz), 7.49–7.55 (1H, m), 7.58–7.64 (1H, m), 7.72 (1H, d, ^3J = 7.8 Hz); δ_C (67.8 MHz, $CDCl_3$) δ 12.0 (CH_3), 14.5 (CH_3), 50.3 (CH), 67.4 (CH), 78.5 (CH), 89.3 (C), 121.8 (CH), 128.2 (CH), 128.4 (CH), 129.6 (CH), 132.6 (CH), 135.0 (C), 142.2 (C), 150.9 (C); MS (EI, 70 eV) *m/z* (%) = 262 (4.8) [M^+], 201 (9), 199 (7), 198 (44), 197 (11), 183 (14). 166 (13), 165 (11), 156 (13), 155 (91), 154 (14), 153 (30), 152 (26), 141 (12), 139 (12), 137 (37), 129 (17), 128 (39), 127 (17), 115 (46), 109 (26), 102 (20), 97 (39), 96 (100), 95 (77), 91 (10), 89 (16), 81 (62), 77 (20), 76 (14), 67 (16); (Found: C, 63.8; H, 5.2. $C_{14}H_{14}O_3S$ requires C, 64.10; H, 5.38).

endo-1,11,12,13-Tetramethyl-3-thiatetracyclo[9.2.1^{1,11}.0^{2,10},0^{4,9}] tetradeca-4,6,8,12-tetraene S,S-dioxide (**4c**): A solution containing

2 (528 mg, 3.2 mmol) and tetramethylcyclopentadiene (**3c**, 1.0 g. 8.2 mmol) was stirred at 100°C for 6 h. Then, the product mixture was subjected to column chromatography on silica gel (first, hexane for the removal of excess tetramethylcyclopentadiene, thereafter hexane: chloroform:ether 4:1:1) to give **4c** (702 mg 2.44 mmol, 95%) as a colourless solid; m.p. 185°C; (Found: 288.1182. $C_{17}H_{20}O_2S$ requires M, 288.1184); ν_{max} (KBr)/cm^{-1} 2962, 2922, 2862, 1470, 1445, 1384, 1311, 1286, 1223, 1152, 1147, 1120, 1060, 761, 586, 547; δ_H (270 MHz, $CDCl_3$) 0.97 (3H, s, CH_3), 1.44 (1H, d, ^2J = 8.4 Hz) 1.50 (3H, s, CH_3), 1.51 (3H, s, CH_3), 1.60 (1H, d, ^2J = 8.4 Hz), 1.68 (3H, s, CH_3), 3.77 (1H, d, ^3J = 8.1 Hz), 4.01 (1H, d, ^3J = 8.1 Hz), 7.35–7.60 (4H, m); δ_C (67.8 MHz, $CDCl_3$) 10.9 (CH_3), 11.7 (CH_3), 17.2 (CH_3), 17.5 (CH_3), 54.8 (CH_2), 55.4 (C), 56.7 (C), 64.2 (CH), 72.2 (CH), 121.3 (CH), 125.8 (CH), 128.7 (CH), 132.3 (CH), 137.7 (C), 138.2 (C), 138.7 (C), 141.3 (C); MS (EI, 70 eV) *m/z* (%) = 288 (2) [M$^+$], 209 (6), 179 (4), 123 (10), 122 (100), 107 (21). 91 (9); (Found: C, 70.8; H, 7.0. $C_{17}H_{20}O_25$ requires, C, 70.80; H, 6.99).

endo-1,11,12,13,14,14-Hexachlorotetracyclo[9.2.1^{1,11}.0^{2,10},0^{4,9}] tetradeca-4,6,8,12-tetraene-S,S-dioxide (**4d**): A solution containing **2** (612 mg, 3.67 mmol) and hexachlorocyclopentadiene (**3d**, 5.9 ml, ca. 10 g) was stirred at 150°C for 11 h. Then, the product mixture was subjected to column chromatography on silica gel (first, hexane for the removal of excess hexachlorocyclopentadiene, thereafter hexane:chloroform:ether 2:1:1) to give **4d** (1.57 g 3.68 mmol, quant.) as a colourless solid; (Found: 438.8269. $C_{13}H_7O_2{}^{37}Cl^{35}Cl_5S$ (MH$^+$) requires 438.8269 [FAB]); ν_{max} (KBr)/cm^{-1} 3074, 2974, 1600, 1478, 1452, 1313, 1247, 1183, 1155, 1132, 1101, 1081, 1067, 1008, 885, 737, 717, 541; δ_H (270 MHz, $CDCl_3$) 4.63 (1H, d, ^3J = 8.4 Hz), 4.82 (1H, d, ^3J = 8.4 Hz), 7.56–7.81 (4H, m); δ_C (67.8 MHz, $CDCl_3$) 53.5 (C), 68.7 (C), 79.0 (C), 81.4 (CH), 104.5 (CH), 122.2 (CH), 126.8 (CH), 131.0 (CH), 131.2 (CH), 131.6 (C), 132.1 (C), 134.0 (C), 140.7 (C); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 439 (7.5) [M$^+$].

12,13-Dimethyl-1,2,10,11-tetrahydrodibenzo[b,d]thiophene S,S-dioxide (**4e**): A solution of **1** in chloroform (166 mg, 1.0 mmol) and 2,3-dimethylbutadiene (**3e**, 1.68 g, 20 equivalents) was stirred at 60°C for 12 h. Then, the product mixture was concentrated under reduced pressure and subjected to column chromatography on silica gel (hexane:chloroform:ether 2:1:1) to give product **4e** (87 mg, 0.35 mmol, 35% yield) as a colourless solid, m.p. 90°C; (Found: 248.0868. $C_{14}H_{16}O_2S$ requires M, 248.0871); ν_{max} (KBr)/cm^{-1} 2916, 1465, 1448, 1299, 1277, 1152, 1131, 1106, 766, 747, 615, 573, 561, 507, 494, 464; δ_H (270 MHz, $CDCl_3$) 1.67 (3H, s, CH_3), 1.70 (3H, s, CH_3), 2.33–2.54 (4H, m), 3.63–3.73 (2H, m), 7.28–7.49 (2H, m), 7.55–7.61 (1H, m), 7.75 (1H, d, ^3J = 8.1 Hz); δ_C (67.8 MHz, $CDCl_3$) 18.8 (CH_2), 19.3 (CH_2), 28.9 (CH_3), 33.9 (CH_3), 36.9 (CH), 59.3 (CH), 122.1 (CH), 123.5 (CH), 124.7 (CH), 125.6 (CH), 128.6 (C), 133.4 (C), 138.3 (C), 141.5 (C); MS (EI, 70 eV) *m/z* (%) = 249 (8) [MH$^+$], 248 (49) [M$^+$], 230 (36), 215 (26), 214 (18), 213 (100), 212 (15), 199 (11), 198 (65), 197 (15), 182 (12), 167 (10), 165 (13), 152 (10), 128 (12), 115 (15), 91 (13).

12-Trimethylsiloxy-1,2,10,11-tetrahydrodibenzo[b,d]thiophene S,S-dioxide (**4f**): A neat mixture of **2** (356 mg, 2.15 mmol) and 2-trimethylsilyloxybuta-1,3-diene (**3f**, 1.5 g, 10.6 mmol) was stirred for 12 h at 125°C. Column chromatography of the cooled reaction mixture on silica gel (hexane/ether/$CHCl_3$ 3:1:1) gave **4f** (399 mg, 60%) as a colourless oil; (Found: 308.0903. $C_{15}H_{20}O_3SiS$ requires M, 308.0902); δ_H (270 MHz, $CDCl_3$) 0.16 (9H, s, $SiMe_3$), 2.16–2.62 (4H, m), 3.62 (1H, m), 3.80 (1H, m), 4.86 (1H, t ^3J = 3.8 Hz), 7.40–7.62 (3H, m), 7.77 (1H, d, ^3J = 7.0 Hz); δ_C (67.8 MHz, $CDCl_3$) 0.0 (3C), 19.6, 31.7, 37.1, 58.0, 99.2, 122.3, 125.2, 128.7, 128.8, 133.3, 140.8, 148.6; MS (EI, 70 eV) *m/z* (%) = 308 (3.0) [M$^+$], 191 (100).

1,2,3,4-Tetraphenyldibenzothiophene S,S-dioxide (**7a**): *Method A:* reaction with tetraphenylthiophene *S*-oxide. A solution of **4** in 560 mg of diphenylether (18 mg, 3.15 10^{-5} mol) was stirred at 135°C for 45 min. Then, the mixture was concentrated under reduced pressure and subjected to column chromatography on silica gel (initially hexane to elute the diphenyl ether, thereafter hexane:chloroform: ether 1:1:1) to give **7a** (14 mg, 85%) as a colourless solid; m.p. 369°C; IR (KBr) ν 1488, 1467, 1442, 1300, 1163, 1125, 785, 749, 698, 578, 558 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.25 (d, 1H, ^3J = 7.6 Hz), 6.77–6.89 (m, 10H), 7.16–7.38 (m, 12H), 7.72 (d, 1H, ^3J = 7.3 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 121.6, 125.1, 126.1, 126.2, 126.8 (2C), 126.9 (2C), 127.3 (2C), 127.8, 127.9, 128.7 (2C), 129.5, 129.7 (2C), 130.5 (2C), 130.7 (2C), 130.8 (2C), 131.3, 133.1 (2C), 134.1, 135.6, 137.7, 138.0, 138.1, 138.2, 138.4, 138.8, 144.0, 147.5; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 521 (MH$^+$, 18.6), 520 (M$^+$, 12.4). HRMS Found: 521.1575. Calcd. for $C_{36}H_{25}O_2S$: 521.1575 (MH$^+$, FAB).

1,2,3,4-Tetrakis(p-methylphenyl)dibenzothiophene S,S-dioxide (**7b**): A mixture of tetrakis(4-methylphenyl)thiophene *S*-oxide (**5b**, 83 mg, 0.18 mmol) and dibenzothiophene S,S-dioxide (**2**, 94 mg, 0.57 mmol) in diphenyl ether (1 g) was heated at 85°C for 12 h. Thereafter, the reaction temperature was raised to 155°C for 10 min. Column chromatography of the cooled mixture on silica gel (initially hexane to elute diphenylether, then hexane/$CHCl_3$/ether 3:1:1) gave **7b** (42 mg, 41%) as a colourless solid, m.p. 377°C; (Found: 576.2121. $C_{40}H_{32}O_2S$ requires M, 576.2123); ν_{max} (KBr)/cm^{-1} 1519, 1462, 1413, 1300, 1157, 1124, 1062, 1021, 821, 751, 591, 553, 531; δ_H (270 MHz, $CDCl_3$) 2.09 (6H, s, 2 CH_3), 2.28 (3H, s, CH_3), 2.34 (3H, s, CH_3), 6.25 (1H, d, ^3J = 8.1 Hz), 6.62–6.70 (8H, m), 7.02–7.35 (10H, m), 7.68 (1H, d, ^3J = 8.1 Hz); δ_C (67.8 MHz, $CDCl_3$) 21.1 (2C), 21.3, 21.4, 121.5, 125.1, 127.5 (3C), 127.6 (2C), 128.0 (2C), 129.2, 129.3 (2C), 129.6 (2C), 130.3 (2C), 130.6 (2C), 130.7 (2C), 131.4, 132.9, 135.0, 135.4, 135.4, 135.5, 137.2, 137.3, 138.2, 138.5, 138.9, 144.3, 147.8; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 576 (5) [M$^+$].

1,2,3,4-Tetraphenyldibenzothiophene (**9a**); *Method A:* benzo [*b*]thiophene in excess. A solution containing **2** (614 mg, 3.70 mmol) and tetracyclone (**8a**) (364 mg, 0.948 mmol) in diphenyl ether (10 ml) was stirred at 150°C for 45 h. Then, the mixture was subjected to column chromatography on silica gel (initially, hexane to remove diphenylether, thereafter hexane:chloroform:ether 4:1:1) to give **9a** (214 mg 0.44 mmol, 45% yield), m.p. 265°C; (Found: 488.1600. $C_{36}H_{24}S$ requires M, 488.1599); ν_{max} (KBr)/cm^{-1} 3056, 1488, 1467, 1400, 1301, 1163, 1125, 785, 749, 698, 578, 558; δ_H (270 MHz, $CDCl_3$) 6.62 (1H, d, ^3J = 8.6 Hz), 6.95–6.75 (10H, m), 7.01 (1H, dd, ^3J = 8.6 = Hz, ^3J = 8.6 = Hz), 7.40–7.10 (11H, m), 7.73 (1H, d, ^3J = 7.8 Hz); δ_C (67.8 MHz, $CDCl_3$) 122.3, 123.7, 125.1, 125.4, 125.6, 126.0, 126.5 (2C), 126.7 (2C), 127.0, 127.2, 128.1 (2C), 128.3 (2C), 130.0 (2C), 130.2 (2C), 131.4 (2C), 131.5 (2C), 132.4, 135.2, 136.3, 137.3, 138.7, 139.0, 139.7, 139.7, 139.9, 140.1, 140.4; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 488 (3.6) [M$^+$]; and dimerisation product, 10,11-dihydro-9-thia-3:4-benzofluorene *S,S*-dioxide (**5**), (208 mg, 42% yield) as a colourless solid; ν_{max} (KBr)/cm^{-1} 3672, 1455, 1297, 1200, 1147, 1110, 1056, 762, 727, 544; δ_H (270 MHz, $CDCl_3$) 4.53 (1H, ddd, ^3J = 7.3 Hz, ^3J = 2.7 Hz, ^4J = 2.7 Hz), 4.82 (1H, d, ^3J = 7.3 Hz), 6.08 (1H, dd, ^3J = 9.7 Hz, ^3J = 2.7 Hz), 6.58 (1H, dd, ^3J = 9.7 Hz, ^4J = 2.7 Hz), 7.07 (1H, m), 7.16 (1H, m), 7.31–7.50 (5H, m), 7.76 (1H, m); δ_C (67.8 MHz, $CDCl_3$) 40.6 (CH), 63.7 (CH), 118.9 (CH), 121.5 (CH), 126.9 (CH), 128.3 (CH), 128.5 (CH), 128.7 (CH), 129.1 (CH), 129.4 (CH), 130.5 (CH), 131.0 (CH), 131.2 (C), 133.5 (C), 136.9 (C), 139.3 (C); MS (EI, 70 eV) *m/z* (%) = 268 (34) [M$^+$], 250 (18), 204 (48), 203 (100), 202 (79). 201 (14). 200 (12). 128 (10). 101 (30).

2,3-Bis(4-fluorophenyl)-1,4-diphenyldibenzothiophene (**9e**); *Method B:* equimolar amounts of reactants. A solution of **2** (210 mg, 1.26 mmol) and **8e** (526 mg, 1.25 mmol) in diphenyl ether (3.5 ml) was heated at 150 C for 20 h. Direct chromatography of the cooled mixture on silica gel (initially hexane to remove diphenyl ether, then hexane/ether/$CHCl_3$ 5:1:1) gave **9e** (323 mg, 49%) as a colourless solid; m.p. 280°C; (Found: 524.1412. $C_{36}H_{22}F_2S$ requires M, 524.1410); δ_H (270 MHz, $CDCl_3$) 6.57–6.65 (5H, m), 6.78–6.85 (4H, m), 7.01 (1H, dd, ^3J = 7.6 Hz, ^3J = 7.6 Hz), 7.20–7.33 (11H, m), 7.73 (1H, d, ^3J = 7.6 Hz); δ_C (67.8 MHz, $CDCl_3$) 113.7 (2C, d, $^2J_{CF}$ = 14.5 Hz), 114.0 (2C, d, $^2J_{CF}$ = 15.1 Hz), 122.3, 123.9, 125.1, 126.1, 127.2, 127.4, 128.2 (2C), 128.4 (2C), 129.9 (2C), 130.1 (2C), 135.6 (m, 2C), 132.7, 132.7 (2C, d, $^3J_{CF}$ = 7.3 Hz), 132.8 (2C, d, $^3J_{CF}$ = 7.3 Hz), 135.8, 136.1, 137.5, 137.7, 137.9, 139.6, 139.8, 140.5, 140.7, 160.7 (d, $^1J_{CF}$ = -244 Hz), 160.8 (d, $^1J_{CF}$ = -245 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 524 (10) [M$^+$].

2,3-Bis(4-methylphenyl)-1,4-diphenyldibenzothiophene (**9c**) (analogous to the preparation of **9e**): colourless solid, m.p. 261°C; (Found: 516.1911. $C_{38}H_{28}S$ requires M, 516.1912); ν_{max} (KBr)/cm^{-1} 3020, 2916, 1515, 1442, 1419, 1373, 1336, 1299, 1260, 1213, 1141, 1109, 1070, 1022, 837, 794, 730, 701, 531; δ_H (270 MHz, $CDCl_3$) 2.10 (6H, s, 2 CH_3), 6.56 (1H, d, ^3J = 8.4 Hz), 6.67–6.77 (8H, m), 6.99 (1H, m), 7.21–7.34 (11H, m), 7.71 (1H, d, ^3J = 7.8 Hz); δ_C (67.8 MHz, $CDCl_3$) 122.2, 123.7, 125.1, 125.8, 126.9, 127.1, 127.2 (2C), 127.4 (2C), 128.0 (2C), 128.2 (2C), 130.0 (2C), 130.2 (2C), 131.2 (2C), 131.3 (2C), 132.3, 134.5, 134.8, 135.3, 136.3 (2C), 136.7, 137.5, 138.9, 139.1, 140.1, 140.3, 140.4, 140.5; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 516 (18) [M$^+$].

2,3-Bis(4-methoxyphenyl)-1,4-diphenyldibenzothiophene (**9b**) (analogous to the preparation of **9e**): colourless solid, m.p. 235°C; (Found: 548.1814. $C_{38}H_{28}O_2S$ requires M, 548.1810); ν_{max} (KBr)/cm^{-1} 3048, 2927, 1603, 1512, 1459, 1440, 1419, 1375, 1288, 1249, 1173, 1032, 839, 758, 731, 700, 547 cm; δ_H (270 MHz, $CDCl_3$) 3.63 (6H,

s, 2 OCH_3), 6.44 (2H, m, J^* = 8.9 Hz), 6.45 (2H, m, J^* = 8.9 Hz), 6.57 (1H, d, ^3J = 8.3 Hz), 6.75 (2H, m, J^* = 8.9 Hz), 6.77 (2H, m, J^* = 8.9 Hz), 7.00 (1H, m); 7.22–7.34 (11H, m), 7.72 (1H, d, ^3J = 8.3 Hz) [for AA'XX' system $J^* = J_{23} + J_{25}$]; δ_C (67.8 MHz, $CDCl_3$) 54.9 (2C), 112.2 (2C), 112.3 (2C), 122.3, 123.7, 125.1, 125.8, 126.9, 127.1, 128.1 (2C), 128.3 (2C), 130.0 (2C), 130.2 (2C), 132.2, 132.3, 132.4 (2C), 132.5 (2C), 135.4, 136.3, 137.7, 136.3, 137.7, 138.7, 138.8, 140.1, 140.4, 140.5, 157.0, 157.2; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 548 (11) [M^+].

2,3-Bis(4-bromophenyl)-1,4-diphenyldibenzothiophene (**9d**) (analogous to the preparation of **9e**): Chromatography on silica gel (hexane/ether/$CHCl_3$ 5:1:1) gave **9d** as a colourless solid; m.p. 306°C; (Found: 645.9794. $C_{36}H_{22}{}^{79}Br^{81}BrS$ requires M, 645.9791); δ_H (270 MHz, $CDCl_3$) 6.59 (1H, d, ^3J = 7.8 Hz), 6.71–6.75 (4H, m), 7.02–7.08 (5H, m), 7.19–7.33 (11H, m), 7.73 (1H, d, ^3J = 7.6 Hz); δ_C (67.8 MHz, $CDCl_3$) 119.9, 120.2, 122.3, 123.9, 125.2, 126.2, 127.4, 127.6, 128.3 (2C), 128.5 (2C), 130.0 (2C), 130.2 (2C), 132.8, 132.9 (2C), 133.0 (2C), 135.3, 136.0, 137.1, 137.3, 137.4, 138.5, 138.5, 139.4, 139.6, 140.5, 141.0; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 648 (23) {[$^{81}Br_2$]M^+}, 646 (40) {[$^{81}Br^{79}Br$]M^+}, 644 (19) {[$^{79}Br_2$]M^+}, 568 (7.4), 566 (7.7).

1,2,3,4-Tetraphenyldibenzothiophene S,S-dioxide (**7a**); *Method B*: To a suspension of **9a** (45 mg, 0.092 mmol) in trifluoroacetic acid (1 ml) was added slowly at 0°C a mixture of H_2O_2 (1.4 ml, 30w% aq.) and trifluoroacetic acid (3 ml). The resulting mixture was stirred for 10 h at room temperature. Thereafter, water (15 ml) was added and the mixture was extracted with CH_2Cl_2 (3 × 15 ml). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel to yield **7a** (42 mg, 87%).

2,3-Bis(4-bromophenyl)-1,4-diphenyldibenzothiophene S,S-dioxide (**7c**): To a solution of **9d** (50 mg, 0.077 mmol) in CH_2Cl_2 (4 ml) was added *m*-CPBA (400 mg, 70 wt%, 1.5 mmol) and the resulting mixture was stirred for 10 h at room temperature. Then, the mixture was poured into aq. sat. $NaHCO_3$ (15 ml) and stirred for 30 min. It was extracted with $CHCl_3$ (3 × 15 ml). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (ether/$CHCl_3$ 1:1) to give **7c** (45 mg, 85%) as a colourless solid; m.p. 402°C (dec.); δ_H (270 MHz, $CDCl_3$) 6.24 (1H, d, ^3J = 8.1 Hz), 6.65 (2H, m, J^* = 7.6 Hz), 6.71 (2H, m, J^* = 7.6 Hz), 6.90 (2H, m, J^* = 7.6 Hz), 7.05 (2H, m, J^* = 7.6 Hz), 7.14–7.20 (2H, m), 7.26–7.40 (10H, m), 7.72 (1H, d, ^3J = 7.6 Hz) [for AA'XX' system $J^* = J_{23} + J_{25}$]; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 680 (0.1) {[$^{81}Br]_2M^+$}, 678 (0.13) {[$^{81}Br^{79}Br$]M^+}, 676 (0.06) {[$^{79}Br]_2M^+$}.

2,3-Bis(4-fluorophenyl)-1,4-diphenyldibenzothiophene S,S-dioxide (**7d**): The reaction was carried out analogous to the preparation of **7a** (method B). Column chromatography on silica gel (hexane/$CHCl_3$/ether 1:1:1) gave **7d** as a colourless solid; m.p. 347°C; (Found: 557.1392. $C_{36}H_{23}O_2F_2S$ requires MH, 557.1387 [FAB]); ν_{max} (KBr)/cm^{-1} 1515, 1160, 1058; δ_H (270 MHz, $CDCl_3$) 6.26 (1H, d, ^3J = 7.8 Hz), 6.58–6.64 (4H, m), 6.72–6.77 (4H, m), 7.14–7.39 (12H, m), 7.72 (1H, d, ^3J = 7.8 Hz); δ_C (67.8 MHz, $CDCl_3$) 114.2 (2C, d, $^2J_{CF}$ = 21.8 Hz), 114.3 (2C, d, $^2J_{CF}$ = 21.3 Hz), 121.7, 125.1, 127.5 (2C), 128.0, 128.1, 128.9 (2C), 129.0, 129.6 (2C), 129.7, 130.6 (2C), 131.0, 132.0 (2C, d, ^3J = 8.3 Hz), 132.3 (2C, d, $^3J_{CF}$ = 8.3 Hz), 133.2, 133.6 (d, $^4J_{CF}$ = 2.2 Hz), 133.8, 134.1 (d, $^4J_{CF}$ = 3.3 Hz), 135.8, 137.9, 138.2, 138.5, 138.8, 143.1, 146.5, 161.0 (d, $^1J_{CF}$ = –246 Hz), 161.1 (d, $^1J_{CF}$ = –247 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 557 (62) [MH^+].

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