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### Synthesis of New Lipophilic Sulfones and Their Use in Cyclization Reactions

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## Synthesis of New Lipophilic Sulfones and Their Use in Cyclization Reactions

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*Analytically pure novel dibenzylsulfanes **2a,b** were synthesized by established reactions. Their oxidation by hydrogen peroxide resulted in the formation of the corresponding sulfones **3a,b**, which were isolated in high yields. Analogously, the new bis-sulfone **7** was prepared starting from bis-bromo derivative **4** via bis-sulfane **6**. The sulfones obtained reacted readily with bis-imidoylchlorides **8**, yielding highly substituted dihydrothiophene-S,S-dioxides of type **9** and **10**. Due to their vicinal amino-imino substructures, these cyclic sulfones proved to be excellent chelating ligands, exemplified by the preparation of the palladium complex **11**.*

**Keywords** Bis-imidoyl chlorides; cyclization reaction; oxidation; sulfanes; sulfones; thiophene-S, S-dioxides

## INTRODUCTION

Among organic sulfur compounds, sulfones have become increasingly useful and important in organic synthesis. The sulfone group, incorporated into an organic compound, efficiently stabilizes negative charges on an adjacent carbon center. This property is especially important in the development of new methods for the formation of C-C bonds

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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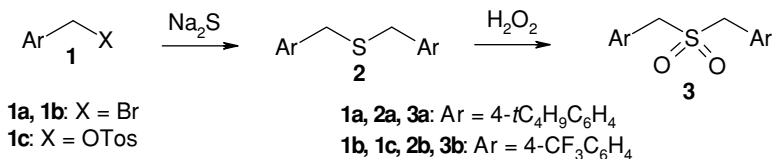
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(Ramberg–Bäcklund reaction, Julia olefination, and others). In addition, some derivatives of sulfones show biological activity: Sulfonal and diaminodiphenyl sulfones were used as active pharmaceutical ingredients. Recently, we focused our interest towards benzyl sulfones, which are easily accessible and can be employed as starting materials for sulfur-containing heterocycles.<sup>1</sup> Thus, we used the reaction between dibenzyl sulfone and *bis*-electrophiles, derived from oxalic acid, for the synthesis of highly substituted derivatives of dihydrothiophene-S,S-dioxides.<sup>2</sup> These derivatives show interesting acidochromism, can be regarded as precursor molecules for diamino dienes, and, in addition, offer good requirements for the formation of metal complexes. However, due to the low solubility of most substituted benzyl sulfones, the cyclization reaction is restricted to only few examples.<sup>2</sup>

Therefore our aim was to involve such benzyl sulfones into this cyclization reaction that possess substituents leading to a better solubility, easier signal sets in their NMR spectra, and, probably, higher biological activity.

## RESULTS AND DISCUSSION

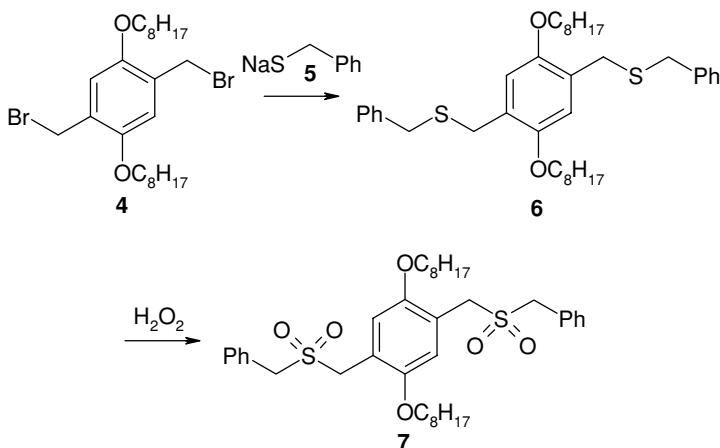
As synthetic entry, we employed the oxidation of symmetric sulfanes, which can easily be prepared starting from the corresponding benzyl halides and sodium sulphide. By adapting a procedure in the literature,<sup>1a</sup> the sulfanes **2a,b** could be isolated as colorless crystals in very good yields by the reaction of benzyl bromides **1a,b** with sodium sulfide (Scheme 1). Surprisingly, the sulfanes **2a,b** are not described in literature despite their simple structure. Alternatively, **2b** can be prepared starting from 4-trifluoromethylbenzyl tosylate **1c** instead of from bromide **1b**.



**SCHEME 1**

The oxidation of a thioether can yield either the corresponding sulfoxide, the corresponding sulfone, or both, depending on the method used. As standard method for the preparation of dibenzylsulfones, the oxidation of dibenzylsulfanes with hydrogen peroxide was therefore used. The sulfones **3a,b** could be isolated as

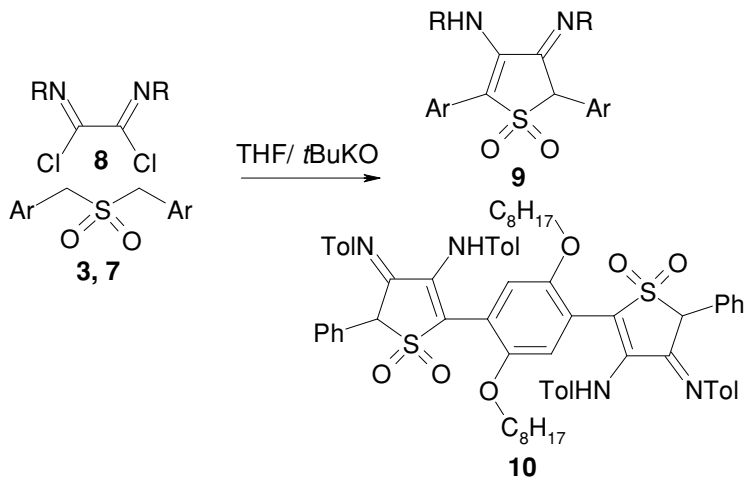
colorless crystals in very good yields (Scheme 1). Whereas the sulfone **3a** was not previously known, **3b** was already prepared earlier by the reaction of *p*-trifluoromethyl benzyl bromide **1b** and sodium hydroxymethanesulfinate.<sup>3</sup> It is noteworthy that the overall yield for **3b** following our protocol is higher than in the literature cited above.



**SCHEME 2**

We were also interested in the synthesis of *bis*-sulfone **7**. With this aim in view, the *bis*-benzyl bromide **4**<sup>4</sup> was converted with the sodium salt of benzyl mercaptane **5** into the sulfane **6** (Scheme 2). This bi-functional sulfane, which forms colorless crystals, could be isolated in excellent yield. Its oxidation with hydrogen peroxide finally resulted in the *bis*-sulfone **7**, which was isolated nearly quantitatively as colorless crystals. Elemental analysis and MS data confirmed the molecular composition for **6** and **7**. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **6** and **7** confirm the high symmetry of these molecules.

In order to test the reactivity of newly synthesized sulfones, they were cyclized with *bis*-electrophiles of type **8**. In the course of our past work, we demonstrated that *bis*-arylimidoyl chlorides **2** are excellent (and selective) *bis*-electrophiles that can be employed in a wide range as C<sub>2</sub>-building blocks for heterocyclic as well as for carbocyclic compounds.<sup>5</sup> Under quite mild conditions (THF in the presence of *t*BuOK at -20°C), **3** reacted with *bis*-electrophile **8**. Single products (TLC) were formed and could be isolated in high yields in the form of yellow crystals. Elemental analysis



SCHEME 3

and MS data confirmed the presence of 1:1 cyclization products **9** (Scheme 3, Table I).

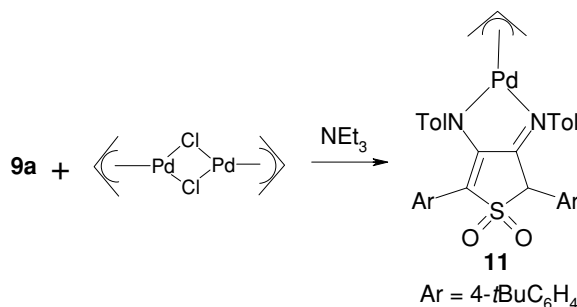
Evidence for the structure of amino-imino substituted 2,3-dihydrothiophene-dioxides of type **9** is the presence of double signal sets in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The NH proton of compound **9c** absorbs in the  $^1\text{H}$  NMR spectra at 7.7 ppm, whereas the cyclic CH proton could be detected as singlet at approx. 5.4 ppm. Generally, the chemical behavior of **9** is identical to that of derivatives reported earlier.<sup>2</sup> Due to the presence of donor–acceptor substitution, solutions of compounds **9** are dark yellow (**9a** in  $\text{CHCl}_3$ :  $\lambda_{\text{max}} = 361 \text{ nm}$ ,  $\log \varepsilon 4.0$ ). In addition, **9** shows an amphoteric character upon treatment with acids (HCl) and bases ( $t\text{BuOK}$ ,  $n\text{BuLi}$ ). In each case, the color changes reversibly to deep red with formation of cations/anions. The neutral dihydrothiophene dioxide **9** is regenerated upon treatment with acid (or base). The

TABLE I Isolated Yields of the Cyclic Sulfones of Type 9

	Ar	R	Yield (%)
<b>9a</b>	4- <i>t</i> BuC <sub>6</sub> H <sub>4</sub>	4-Tol	88
<b>9b</b>	4- <i>t</i> BuC <sub>6</sub> H <sub>4</sub>	4-BrC <sub>6</sub> H <sub>4</sub>	79
<b>9c</b>	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	4-Tol	83
<b>9d</b>	4-Tol	4-Tol	67
<b>9e</b>	4-Tol	Ph	63
<b>9f</b>	4-BrC <sub>6</sub> H <sub>4</sub>	Ph	72

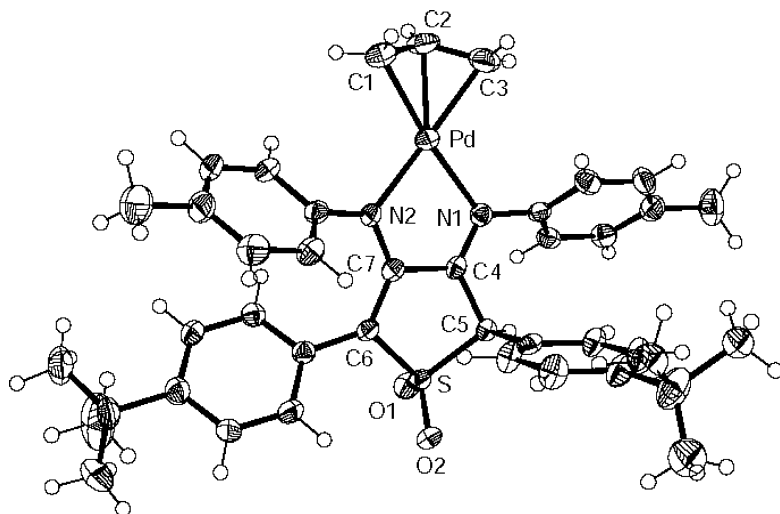
*bis*-sulfone **7** could be successfully cyclized twice under the same conditions used for the preparation of **9**. The corresponding *bis*-heterocycle **10** was isolated after purification by column chromatography as a yellow solid in an acceptable yield. In the MS spectra, the molpeak at  $m/z = 1134$  and an additional one at  $m/z = 1070$  [ $M-SO_2^+$ ], which resulted from sulfur dioxide elimination, could be observed. The  $^1H$  as well as the  $^{13}C$  NMR spectra of derivative **10** display complex sets of signals mainly in the part of aromatic protons/carbons. However, the NH as well as the cyclic CH protons could be detected at about 9.2 and 5.08 ppm, respectively.

The application of this cyclization reaction to other sulfones, e.g., dimethyl sulfone or diethyl sulfonyldiglycolate, failed and resulted only in the formation of complex product mixtures.



**SCHEME 4**

As a result of its vicinal amino-imino substructures, compounds of type **9** are capable of the preparation of metal complexes. Thus, **9a** reacts readily with allyl palladium chloride in the presence of triethylamine with formation of a red solution in which only one product could be detected by TLC. Upon purification by flash chromatography, the palladium complex **11** was isolated in the form of red crystals. MS data and  $^1H$  and  $^{13}C$  NMR spectra confirmed the molecular structure of complex **11** (Scheme 4). In the  $^1H$  NMR of **11**, the signals of the cyclic CH proton (5.32 ppm) and the signal of the methyl moiety of the tolylamino group (2.07) are shifted to higher fields compared to the signals of the ligand **9a**. Due to the oxonole-like character of the anion of **9a**, the solutions of complex **11** are dark red (THF:  $\lambda_{max} = 478$ ,  $\log \epsilon$  3.7). Derivative **11** is electrochemically active and can be oxidized reversibly. By employing square wave measurements, one peak at 1.064 V was observed. The quasi-reversibility of the oxidation was confirmed by cyclic voltammetric measurements  $\Delta E_{RED,OX} = 0.090$  V. The solid-state structure of **11** was established by single-crystal X-ray diffraction studies (Figure 1).



**FIGURE 1** ORTEP-plot (50% probability ellipsoids) of the solid state molecular structure of **11**, selected bond lengths in Å: Pd-N1 2.106(3), Pd-N2 2.091(3), Pd-C1 2.112(4), Pd-C2 2.114(4), Pd-C3 2.119(5), S-O1 1.451(3), S-O2 1.445(3), S-C5 1.807(4), S-C6 1.747(4), N1-C4 1.285(5), N2-C7 1.340(5), C4-C5 1.512(5), C4-C7 1.484(5), C6-C7 1.397(5).

Compound **11** is a monomer in the solid state, and according to our expectation, one thiophene-*S,S*-dioxide molecule is coordinated at the palladium(II) center. The second ligand, an allyl anion, is  $\eta^3$ -bonded, which causes a square planar environment of the palladium(II) center (Figure 1). The new synthesized Pd complex **11** shows high stability as a solid as well as in solution, and can be handled under normal aerobic conditions. The bond lengths and angles for the Pd complex **11** lie in the expected ranges.

## CONCLUSIONS

The novel dibenzylsulfanes **2a,b** were synthesized in high yields and were analytically pure. Their oxidation by hydrogen peroxide resulted in the formation of the sulfones **3a,b**, which were isolated as stable crystalline compounds. This method has been adapted for the preparation of the new *bis*-sulfone **7**.

The sulfones **3a,b** as well as **7** can easily be cyclized with *bis*-electrophiles of type **8** forming highly substituted thiophene-*S,S*-dioxides **9** and **10**. Due to their vicinal amino-imino substructures,

these derivatives proved to be excellent chelating ligands, exemplified by the preparation of palladium complex **11**.

## EXPERIMENTAL

### General

The reagents described in the following section were purchased from commercial sources and used directly unless otherwise stated in the text. The *bis*-imidoyl chlorides **8**,<sup>6</sup> the sulfones **3c,d**,<sup>1a</sup> and the *bis*-benzyl bromide **4**<sup>4</sup> were synthesized by procedures in the literature. All solvents were reagent grade, were dried by standard practices, and were distilled prior to use. Reactions were monitored by TLC (0.2 mm Merck silica gel plates; 60, F<sub>254</sub>), and <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AVANCE 250 and 400 spectrometers; shifts are given relative to solvent signals. Melting points were measured on a Galen III apparatus (Boetius system) and are uncorrected.

### Preparation of 4-Trifluoromethylbenzyl Tosylate (**1c**)

To a solution of 4-trifluoromethylbenzyl alcohol (5.00 g, 28 mmol) in dry THF (50 mL), triethylamine (3.60 g, 35 mmol) and tosyl chloride (5.70 g, 30 mmol) were added. The reaction mixture was stirred at 70°C for 4 h. The mixture was filtered, and the solvent was removed under reduced pressure; the remaining oil was dissolved in chloroform, and the solution was washed twice with saturated sodium carbonate solution and with water. The organic phase was dried over sodium sulphate, the solvent was removed, and the crude product was purified by column chromatography on silica gel (chloroform/*n*-heptane). The product was obtained as colorless oil. Yield: 7.95 g (84%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 7.92 (d, *J* = 8 Hz, 2H, CH-Ar), 7.79–7.30 (m, 6H, CH-Ar), 4.62 (s, 2H, CH<sub>2</sub>), 2.49 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>): δ = 146.8, 131.3, 130.8, 128.8, 128.2 (q, <sup>2</sup>*J* = 30 Hz, C-CF<sub>3</sub>), 127.0, 126.8, 125.6 (q, <sup>3</sup>*J* = 4 Hz), 123.9 (q, <sup>1</sup>*J* = 270 Hz, CF<sub>3</sub>), 45.1, 21.8. MS (neg. DCI in water): *m/z* (%) = 329 (10) [M-H<sup>-</sup>], 172 (20) [C<sub>7</sub>H<sub>8</sub>SO<sub>3</sub><sup>-</sup>], 171 (100) [C<sub>7</sub>H<sub>7</sub>SO<sub>3</sub><sup>-</sup>]. Elemental analysis calculated for C<sub>15</sub>H<sub>13</sub>F<sub>3</sub>O<sub>3</sub>S (330.30): C 54.54, H 3.97, S 9.71, Found: C 54.12, H 3.83, S 9.28%.

### Preparation of Dibenzylsulfanes **2a,b**: General Procedure

To a solution of the corresponding benzyl bromides **1a,b** or tosylate **1c** (50 mmol) in methanol (30 mL), a solution of sodium sulphide trihydrate (5.20 g, 40 mmol) in 20 mL of water was added at rt. The reaction



mixture was stirred at 80°C for 3 h. The mixture was cooled down to rt and was then extracted with chloroform (three times). The organic phase was dried over sodium sulphate, the solvent was removed in vacuo, and the crude product was recrystallized from pentane (at –16°C) to yield **2a,b** as colorless crystals.

### ***Di(4-tert-butyl)benzyl Sulfane (2a)***

Colorless crystals, yield: 7.68 g (94%), mp 55°C. <sup>1</sup>H NMR (250 MHz, DMSO-d<sub>6</sub>): δ = 7.32 (d, *J* = 8 Hz, 4H, CH-Ar), 7.22 (d, *J* = 8 Hz, 4H, CH-Ar), 3.60 (s, 4H, CH<sub>2</sub>), 1.25 (s, 18H, CH<sub>3</sub>). <sup>13</sup>C NMR (63MHz, DMSO-d<sub>6</sub>): δ = 149.6, 135.7, 128.9, 125.6, 35.4, 34.6, 31.4. IR (ATR): ν<sub>max</sub> = 3024, 2908, 1667, 1514, 1461, 1415, 1360, 1106, 831, 707, 655 cm<sup>-1</sup>. MS (EI): *m/z*(%) = 326 (60) [M<sup>+</sup>], 179 (80), 147 (100), 117 (50). Elemental analysis calculated for C<sub>22</sub>H<sub>30</sub>S (326.55): C 80.92, H 9.26, S 9.82, Found: C 80.96, H 9.01, S 9.75%.

### ***Di(4-trifluoromethyl)benzyl Sulfane (2b)***

Colorless crystals, yield: 7.70 g (88%, from **1b**) 7.10 g (81%, from **1c**), mp 19°C (pentane). <sup>1</sup>H NMR (250 MHz, DMSO-d<sub>6</sub>): δ = 7.62 (d, *J* = 8 Hz, 4H, CH-Ar), 7.47 (d, *J* = 8 Hz, 4H, CH-Ar), 3.77 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (63MHz, DMSO-d<sub>6</sub>): δ = 143.7, 131.2, 127.9 (q, <sup>2</sup>*J* = 30 Hz, C-CF<sub>3</sub>), 125.6 (q, <sup>3</sup>*J* = 4 Hz), 124.6 (q, <sup>1</sup>*J* = 270 Hz, CF<sub>3</sub>), 35.2. IR (ATR): ν<sub>max</sub> = 2923, 1619, 1424, 1325, 1165, 1124, 1165, 1019, 850 cm<sup>-1</sup>. MS (EI): *m/z*(%) = 350 (30) [M<sup>+</sup>], 191 (40), 159 (100), 109 (40). Elemental analysis calculated for C<sub>16</sub>H<sub>12</sub>F<sub>6</sub>S (350.33): C 54.86, H 3.45, S 9.15, Found: C 54.93, H 3.57, S 9.13%.

## **Preparation of the Bis-sulfane 6**

To a solution of sodium hydroxide (1.00 g, 25 mmol) in 5 mL of water and 40 mL of DMF, benzyl mercaptan (3.00 g, 24 mmol) was added. The mixture was stirred at rt for 10 min, and bis-benzyl bromide **5** (5.00 g, 9.6 mmol) was added. The solution was stirred at 60°C for 3 h and was cooled down to rt. The slurry was added into 200 mL of water; the solid was filtered off and washed with water. The crude product was recrystallized from ethanol to yield **6** as colorless crystals. Yield 4.92 g (84%), mp 61°C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 7.27 (m, 10H, CH-Ar), 6.79 (s, 2H, CH-Ar), 3.91 (t, *J* = 6.5 Hz, 4H, O-CH<sub>2</sub>), 3.71 (s, 4H, S-CH<sub>2</sub>), 3.68 (s, 4H, S-CH<sub>2</sub>), 1.8–1.7 (m, 4H, CH<sub>2</sub>), 1.5–1.3 (m, 20H, CH<sub>2</sub>), 1.0–0.9 (m, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (63MHz, CDCl<sub>3</sub>): δ = 150.7, 138.6, 128.9, 128.4, 126.8, 126.3, 114.4, 69.1, 36.3, 31.9, 30.2, 29.5, 29.4, 29.3, 26.2, 22.7, 14.1. MS (EI): *m/z*(%) = 606 (5) [M<sup>+</sup>], 484 (10), 167 (10), 137 (25), 91

(100), 43 (60). Elemental analysis calculated for  $C_{38}H_{54}S_2O_2$  (606.90): C 75.20, H 8.97, S 10.57, Found: C 75.17, H 8.40, S 10.96%.

### Oxidation of the Sulfanes 2a,b and 6: General Procedure

For this oxidation reaction, the crude sulfanes were used. To the solution of 25 mmol of sulfane **2a,b** (or 9 mmol of **6**) in 25–60 mL of acetic acid at 60°C (temperature maximum 90°C), 7.3 mL of hydrogen peroxide (8.30 g, 80 mmol, 35% in water) was slowly added. Then the reaction mixture was stirred at 80°C for 3 h. The mixture was cooled to rt, and 200 mL of water was added; the colorless solid that formed was filtered off and washed with water. After recrystallization from ethanol, the products **3a,b** and **7** were obtained as colorless crystals.

#### Di(4-tert-butyl)benzyl Sulfone (3a)

Colorless crystals, yield: 7.44 g (83%), mp 182°C.  $^1H$  NMR (250 MHz, DMSO- $d_6$ ):  $\delta$  = 7.41 (d,  $J$  = 8 Hz, 4H, CH-Ar), 7.29 (d,  $J$  = 8 Hz, 4H, CH-Ar), 4.41 (s, 4H,  $CH_2$ ), 1.27 (s, 18H,  $CH_3$ ).  $^{13}C$  NMR (63 MHz, DMSO- $d_6$ ):  $\delta$  = 151.2, 131.3, 125.8, 125.5, 58.5, 34.8, 31.5. IR (ATR):  $\nu_{max}$  = 2959, 2903, 2866, 1508, 1396, 1310, 1252 ( $SO_2$ ), 1106 ( $SO_2$ ), 867, 839  $cm^{-1}$ . MS (EI):  $m/z$ (%) = 358 (10) [ $M^+$ ], 343 (20), 294 (80), 147 (100) 117 (100). Elemental analysis calculated for  $C_{22}H_{30}SO_2$  (358.55): C 73.70, H 8.43, S 8.94, Found: C 73.57, H 8.28, S 8.77%.

#### Di(4-trifluoromethyl)benzyl Sulfone (3b)

Colorless crystals, yield: 8.79 g (92%) mp 207°C (chloroform, Lit.<sup>3</sup> 207°C).  $^1H$  NMR (250 MHz, DMSO- $d_6$ ):  $\delta$  = 7.73 (d,  $J$  = 8 Hz, 4H, CH-Ar), 7.60 (d,  $J$  = 8 Hz, 4H, CH-Ar), 4.67 (s, 4H,  $CH_2$ ).  $^{13}C$  NMR (63 MHz, DMSO- $d_6$ ):  $\delta$  = 133.3, 132.4, 129.4 (q,  $^2J$  = 30 Hz C- $CF_3$ ), 125.7 (q,  $^3J$  = 4 Hz), 124.6 (q,  $^1J$  = 270 Hz,  $CF_3$ ), 57.8. IR (ATR):  $\nu_{max}$  = 2934, 1623, 1420, 1321, 1290 ( $SO_2$ ), 1162, 1117 ( $SO_2$ ), 1064, 1018, 830, 711  $cm^{-1}$ . MS (EI):  $m/z$ (%) = 382 (10) [ $M^+$ ], 362 (20), 159 (100), 109 (40). Elemental analysis calculated for  $C_{16}H_{12}F_6S$  (382.33): C 50.27, H 3.16, S 8.39, Found: C 50.24, H 3.12, S 8.34%.

#### Bis-sulfone 7

Colorless crystals, yield: 5.31 g (88%), mp 162°C (ethanol/ chloroform).  $^1H$  NMR (250 MHz,  $CDCl_3$ ):  $\delta$  = 7.37 (m, 10H, CH-Ar), 7.07 (s, 2H, CH-Ar), 4.37 (s, 4H, S- $CH_2$ ), 4.16 (s, 4H, S- $CH_2$ ), 3.99 (t,  $J$  = 6,5 Hz, 4H, O- $CH_2$ ), 1.75 (m, 4H,  $CH_2$ ), 1.30 (m, 20H,  $CH_2$ ), 0.88 (m, 6H,  $CH_3$ ).  $^{13}C$  NMR (63 MHz,  $CDCl_3$ ):  $\delta$  = 150.9, 131.0, 128.9, 128.8, 127.0, 118.2, 116.0, 69.3, 58.4, 53.0, 31.8, 29.4, 29.3, 29.2, 26.1, 22.6, 14.1. MS

(EI):  $m/z(\%) = 671$  (1) [ $M^+$ ], 452 (5), 359 (15), 137 (20), 91 (100), 43 (50). Elemental analysis calculated for  $C_{38}H_{54}S_2O_6$  (670.98): C 68.02, H 8.11, S 9.56, Found: C 67.90, H 7.99, S 9.80%.

### Preparation of Cyclic Sulfones 9a–f: General Procedure

To a solution of 6 mmol of sulfone **3a** or **3b** in 50 mL of dry THF (for the sulfones **3c** and **3d** 100 mL of dry THF), *t*-BuOK (3.00 g, 27 mmol) was added and the solution was stirred for 5 min. The light yellow solution was cooled to  $-20^\circ\text{C}$  and the corresponding *bis*-imidoylchloride **8** (6.5 mmol) was added. The deep red reaction mixture was stirred at  $20^\circ\text{C}$  for 30 min and was then acidified (pH 6) by dropwise addition of HCl/isopropanol. The mixture was concentrated in vacuo to dryness, and the residue was treated with 100 mL of chloroform/*n*-heptane (1:1). The slurry was filtered over  $\text{SiO}_2$ , and upon removal of the solvent in vacuo, the crude product was recrystallized from chloroform/*n*-heptane to yield **9a–f** as yellow crystals.

#### 4-(4-Tolylamino)-3-(4-tolylimino-2,5-di(4-tert-butylphenyl)-2,3-dihydrothiophene-1,1-dioxide (9a)

Yellow crystals, yield: 2.82 g (88%), mp  $201^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta = 8.32$  (s, 1H, NH), 7.17–7.10 (m, 4H, CH-Ar), 6.93 (d,  $J = 8$  Hz, 2H, CH-Ar), 6.87 (d,  $J = 8$  Hz, 2H, CH-Ar), 6.76–6.66 (m, 6H, CH-Ar), 6.54 (d,  $J = 8$  Hz, 2H, CH-Ar), 5.45 (s, 1H, CH-ring), 2.13 (s, 3H,  $\text{CH}_3$ ), 2.09 (s, 3H,  $\text{CH}_3$ ), 1.20 (s, 18H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (63 MHz,  $\text{DMSO}-d_6$ ):  $\delta = 158.3$  (C-3), 151.9, 151.5, 145.8, 138.5, 134.6, 134.4, 133.6, 130.1, 129.4, 129.1, 128.8, 128.5, 127.2, 125.4, 124.7, 124.0, 122.1, 119.2, 65.2 (C-2), 34.7, 34.6, 31.2, 20.8, 20.7. IR (ATR):  $\nu_{\text{max}} = 3312$  (NH), 3024, 2952, 1633 (C=C), 1603 (C=N), 1519, 1500,  $1300 + 1296$  ( $\text{SO}_2$ ), 1169, 1130, 828, 812,  $757\text{ cm}^{-1}$ . MS (EI)  $m/z$ : 590 (30) [ $M^+$ ], 526 (15) [ $M-\text{SO}_2^+$ ], 264 (30), 248 (90), 57 (100) [ $\text{C}_4\text{H}_9^+$ ]. Elemental analysis calculated for  $\text{C}_{38}\text{H}_{42}\text{N}_2\text{SO}_2$  (590.83): C 77.25, H 7.17, N 4.74, S 5.43, Found: C 76.89, H 6.88, N 4.47, S 5.13%.

#### 4-(4-Bromophenylamino)-3-(4-bromophenylimino-2,5-di(4-tert-butylphenyl)-2,3-dihydrothiophene-1,1-dioxide (9b)

Yellow crystals, yield 3.41 g (79%), mp  $206^\circ\text{C}$ .  $^1\text{H}$  NMR (250 MHz,  $\text{DMSO}-d_6$ ):  $\delta = 8.30$  (s, 1H, NH), 7.18–6.89 (m, 12H, CH-Ar), 6.70–6.66 (m, 4H CH-Ar), 5.99 (s, 1H, CH-ring), 1.22; 1.21 (m, 18H, CH-*t*Bu).  $^{13}\text{C}$  NMR (63 MHz,  $\text{DMSO}-d_6$ ):  $\delta = 158.9$  (C-3), 152.1, 151.2, 147.8, 139.6, 138.0, 131.3, 130.9, 130.6, 128.6, 126.3, 125.2, 124.9, 124.5, 122.2, 120.4, 117.1, 115.4, 79.6, 65.6 (C-2), 34.9, 34.6, 31.4. MS (EI)  $m/z$ : 722 (5) +

720 (10) + 718 (5) [ $M^+$ ], 656 (5) [ $M-SO_2^+$ ], 520 (5), 314 (20), 57 (100) [ $C_4H_9^+$ ]. Elemental analysis calculated for  $C_{36}H_{36}Br_2N_2SO_2(720.57)$ : C 60.01, H 5.04, N 3.89, S 4.45, Found: C 59.63, H 4.93, N 3.53, S 4.14%.

**4-(4-Tolylamino)-3-(4-tolylimino-2,5-di(4-trifluoromethylphenyl))-2,3-dihydrothiophene-1,1-dioxide (9c)**

Yellow crystals, yield: 3.04 g (83%), mp 193°C.  $^1H$  NMR (400MHz,  $CDCl_3$ ):  $\delta$  = 7.77 (s, 1H, NH), 7.42 (d,  $J$  = 8 Hz, 2H, CH-Ar), 7.32 (s, 4H CH-Ar), 7.36 (d,  $J$  = 8 Hz, 2H, CH-Ar), 7.09 (d,  $J$  = 8 Hz, 2H, CH-Ar), 6.92 (d,  $J$  = 8 Hz, 2H, CH-Ar), 6.78 (d,  $J$  = 8 Hz, 2H, CH-Ar), 6.66 (d,  $J$  = 8 Hz, 2H, CH-Ar), 6.49 (d,  $J$  = 8 Hz, 2H, CH-Ar), 5.44 (s, 1H, CH-ring), 2.23 (s, 3H,  $CH_3$ ), 2.17 (s, 3H,  $CH_3$ ).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 156.6 (C-3), 145.1, 139.9, 135.6, 135.4, 134.0, 133.7, 131.1, 130.6 (q,  $^2J$  = 30 Hz), 130.2, 129.8, 129.5 (q,  $^2J$  = 30 Hz), 129.0, 125.5 (q,  $^3J$  = 4 Hz), 124.6 (q,  $^3J$  = 4 Hz), 123.8 (q,  $^1J$  = 270 Hz), 123.7 (q,  $^1J$  = 270 Hz), 123.2, 119.8, 119.2, 117.5, 65.0 (C-2), 20.8, 20.6. MS (EI) m/z: 614 (30) [ $M^+$ ], 550 (30) [ $M-SO_2^+$ ], 275 (100), 91 (80) [ $C_7H_7^+$ ]. Elemental analysis calculated for  $C_{32}H_{26}F_6N_2SO_2(614.61)$ : C 62.54, H 3.94, N 4.56, S 5.22, Found: C 62.42, H 4.24, N 4.54, S 4.85%.

**4-(4-Tolylamino)-3-(4-tolylimino-2,5-di(4-tolyl))-2,3-dihydrothiophene-1,1-dioxide (9d)**

Yellow crystals, yield: 2.06 g (67%), mp 240°C.  $^1H$  NMR (250 MHz,  $CDCl_3$ ):  $\delta$  = 7.72 (s, 1H, NH), 7.22–6.81 (m, 12H, CH-Tol), 6.68 (d,  $J$  = 8 Hz, 2H, CH-Tol), 6.52 (d,  $J$  = 8 Hz, 2H, CH-Tol), 5.30 (s, 1H, CH-ring), 2.39 (s, 3H,  $CH_3$ ), 2.27 (m, 6H,  $CH_3$ ), 2.21 (s, 3H, CH-Tol).  $^{13}C$  NMR (63 MHz,  $CDCl_3$ ):  $\delta$  = 158.0 (C-3), 145.6, 138.8, 138.6, 138.1, 135.3, 134.8, 130.4, 129.9, 129.6, 129.3, 129.2, 128.9, 128.7, 127.5, 121.6, 120.4, 119.8, 119.3, 65.1 (C-2), 21.35, 21.33, 21.23, 21.21. MS (EI) m/z: 506 (10) [ $M^+$ ], 357 (10), 268 (20), 107 (100), 91 (40) [ $C_7H_7^+$ ]. Elemental analysis calculated for  $C_{32}H_{30}N_2SO_2(506.67)$ : C 75.86, H 5.97, N 5.53, S 6.33, Found: C 75.46, H 5.68, N 5.41, S 6.03%.

**4-(4-Phenylamino)-3-(4-phenylimino-2,5-di(4-tolyl))-2,3-dihydrothiophene-1,1-dioxide (9e)**

Yellow crystals, yield: 1.81 g (63%), mp 167°C.  $^1H$  NMR (250 MHz,  $CDCl_3$ ):  $\delta$  = 7.80 (s, 1H, NH), 7.26–6.79 (m, 16H, CH-Ar), 6.62–6.59 (m, 2H, CH-Ph), 5.30 (s, 1H, CH-ring), 2.27 (s, 3H,  $CH_3$ ), 2.26 (s, 3H,  $CH_3$ ).  $^{13}C$  NMR (63 MHz,  $CDCl_3$ ):  $\delta$  = 158.5 (C-3), 148.1 (C-4), 139.1, 138.7, 137.5, 137.3, 130.0, 128.8, 128.75, 128.7, 128.2, 127.2, 125.0, 124.0, 123.8, 121.5, 119.2, 65.1 (C-2), 21.4 ( $CH_3$ ), 21.2 ( $CH_3$ ). MS (DEI) m/z: 478 (20) [ $M^+$ ], 414 (10) [ $M-SO_2^+$ ], 413 (20), [ $M-HSO_2^+$ ], 207 (40), 77

(100). Elemental analysis calculated for  $C_{30}H_{26}N_2SO_2$  (478.62): C 75.29, H 5.48, N 5.85, S 6.70, Found: C 74.73, H 5.50, N 5.87, S 6.83%.

**4-(4-Phenylamino)-3-(4-phenylimino-2,5-di(4-bromophenyl)-2,3-dihydrothiophene-1,1-dioxide (9f)**

Yellow crystals, yield: 2.63 g (72%), mp 193°C.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.80 (s, 1H, NH), 7.29–7.00 (m, 12H, CH-Ar), 6.85–6.81 (m, 4H CH-Ph), 6.62–6.60 (m, 2H CH-Ph), 5.33 (s, 1H, CH-ring).  $^{13}C$  NMR (63 MHz,  $CDCl_3$ ):  $\delta$  = 157.7 (C-3), 147.9 (C-4), 138.3, 136.8, 132.4, 132.3, 131.9, 131.2, 130.4, 129.3, 128.8, 128.2, 125.7, 125.4, 124.8, 123.4, 122.2, 119.6, 119.0, 64.7 (C-2). MS (EI)  $m/z$ : 610 (10) + 608 (20) + 606 (10)  $[M^+]$ , 544 (10)  $[M-SO_2^+]$ , 349 (20), 77 (60), 32 (100). Elemental analysis calculated for  $C_{28}H_{20}N_2SO_2$  (608.36): C 55.28, H 3.31, N 4.60, S 5.27, Found: C 54.91, H 3.18, N 4.49, S 5.20%.

**Preparation of Cyclic Bis-sulfone 10**

To a solution of **7** (1.00 g, 1.5 mmol) in 50 mL of dry THF, *t*-BuOK (1.00 g, 9 mmol) was added, and the solution was stirred for 5 min at 0°C. The light yellow solution was cooled down to –20°C, and the *bis*-tolylimidoylechloride **8** (1.20 g, 4 mmol) was added. The deep red reaction mixture was stirred at 20°C for 30 min and was then acidified (pH 6) by HCl/isopropanol. The mixture was concentrated in vacuo to dryness, and the residue was treated with 100 mL of chloroform/*n*-heptane (1:1). The slurry was filtered over  $SiO_2$ , and upon removal of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (chloroform/*n*-heptane) to yield **10** as yellow solid. Yield: 590 mg (35%).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 9.23 (s, 2H, NH), 7.48–7.05 (m, 28H, CH-Ar), 5.08 (s, 2H, CH-ring), 3.90 (m, 4H, O-CH<sub>2</sub>), 2.27 (m, 6H), 2.08 (m, 6H), 1.7–1.6 (m, 4H, CH<sub>2</sub>), 1.35–1.11 (m, 20H, CH<sub>2</sub>), 0.82–0.76 (m, 6H, CH<sub>3</sub>).  $^{13}C$  NMR (63 MHz,  $CDCl_3$ ):  $\delta$  = 157.5, 135.3, 133.8, 131.1, 131.3, 130.9, 130.3, 129.7, 129.6, 129.5, 128.9, 128.8, 128.7, 128.3, 128.2, 127.9, 121.5, 121.4, 121.3, 119.7, 119.8, 69.3, 69.2, 66.7 (C-ring), 58.6, 58.4, 54.7, 53.2, 53.0, 31.8, 29.4, 29.3, 29.2, 26.1, 25.9, 22.6, 20.9, 20.7, 14.1. MS (micro-ESI in chloroform/methanol)  $m/z$ : 1173 (1)  $[M+K^+]$ , 1157 (1)  $[M+Na^+]$ , 1134 (1)  $[M^+]$ , 1170 (15)  $[M-SO_2^+]$ , 1169  $[M-HSO_2^+]$ , 925 (60), 837 (100), 786 (60). Elemental analysis calculated for  $C_{70}H_{80}N_4S_2O_6$  (1137.55): C 73.91, H 7.09, N 4.93, S 5.64, Found: C 73.74, H 7.18, N 4.68, S 5.30%.

**Preparation of Palladium Complex 11**

To a solution of **9a** (400 mg, 0.68 mmol) in 10 mL of dry THF, allyl palladium chloride (130 mg, 0.71 mmol) and 0.2 mL of triethylamine

were added. The deep red solution was stirred for 2 h at 60°C. The reaction mixture was filtered over SiO<sub>2</sub>, and upon removal of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (chloroform/*n*-heptane) to yield **11** as red solid. Red crystals were obtained by recrystallization from toluene/chloroform/*n*-heptane. Yield: 380 mg (76%). <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>): δ = 7.13–7.10 (m, 2H, CH-Ar), 6.93–6.72 (m, 10H, CH-Ar), 6.60 (d, *J* = 8 Hz, 2H, CH-Tol), 6.53 (d, *J* = 8 Hz, 2H, CH-Tol), 5.6–5.4 (m, 1H, CH-allyl), 5.32 (s, 1H, CH-ring), 3.96–3.94 (m, 1H, CH-allyl), 2.95–2.79 (m, 3H, CH-allyl), 2.30 (s, 3H, CH<sub>3</sub>), 2.22 (s, 3H, CH<sub>3</sub>), 1.26 (s, 9H, CH<sub>3</sub>), 1.22 (s, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, THF-d<sub>8</sub>): δ = 150.9, 150.6, 150.5, 150.0, 148.0, 135.4, 129.8, 128.8, 128.7, 128.6, 127.2, 127.0, 124.6, 123.5, 123.4, 123.2, 120.9, 120.8, 117.4, 114.9, 114.8, 110.7, 67.4 (C-2), 61.4 (C-allyl), 59.5 (C-allyl), 34.1, 31.0, 20.0, 19.9. MS (EI) *m/z*: 734 (20) + 735 (50) + 736 (50) + 737 (30) + 738 (50) + 739 (20) + 740 (20) + 741 (10) [M<sup>+</sup>], 364 (100) calculated and measured isotope pattern for C<sub>41</sub>H<sub>46</sub>N<sub>2</sub>O<sub>2</sub>PdS are in agreement.

## Crystal Structure Determination for **11**

The intensity data for the compound were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo-K<sub>α</sub> radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.<sup>8</sup>

The structure was solved by direct methods (SHELXS<sup>9</sup>) and refined by full-matrix least squares techniques against F<sub>o</sub><sup>2</sup> (SHELXL-97<sup>10</sup>). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen and non-solvent atoms were refined anisotropically.<sup>10</sup> XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

## Crystal Data for **11**

C<sub>41</sub>H<sub>46</sub>N<sub>2</sub>O<sub>2</sub>PdS · 0.5 C<sub>7</sub>H<sub>8</sub>, *M* = 783.33 g mol<sup>−1</sup>, red prism, size 0.04 × 0.04 × 0.04 mm<sup>3</sup>, triclinic, space group Pī, *a* = 10.8286(4), *b* = 12.8989(7), *c* = 15.4064(7) Å, α = 69.731(2), β = 76.060(2), γ = 87.698(3)°, *V* = 1957.00(16) Å<sup>3</sup>, *T* = −90°C, *Z* = 2, ρ<sub>calcd.</sub> = 1.329 g cm<sup>−3</sup>, μ (Mo-K<sub>α</sub>) = 5.66 cm<sup>−1</sup>, *F*(000) = 818, 13447 reflections in h(−14/14), k(−15/16), l(−17/19), measured in the range 1.80° ≤ 2θ ≤ 27.50°, completeness Θ<sub>max</sub> = 97.9%, 8797 independent reflections, *R*<sub>int</sub> = 0.0420, 6309 reflections with *F*<sub>o</sub> > 4σ(*F*<sub>o</sub>), 457 parameters, 0 restraints, *R*<sub>1obs</sub> = 0.0582, *wR*<sub>2obs</sub><sup>2</sup> = 0.1269, *R*<sub>1all</sub> = 0.0953, *wR*<sub>2all</sub><sup>2</sup> = 0.1451, GOOF = 1.032, largest difference peak and hole: 1.021 / −0.532 e Å<sup>−3</sup>.

CCDC-670265 (**11**) contains the supplementary crystallographic data for this article. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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