# Synthesis of 2-Aryl-3-arylsulfonylindoles and 2-Anilino-3-arylsulfonylindoles from 2-(Arylsulfonyl)methylanilines Using the Aza-Wittig Reaction of Iminophosphoranes

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**Abstract:** 2-(Arylsulfonyl)methyl-*N*-(triphenylphosphoranylidene)anilines **5** were prepared starting from 2-(arylsulfonyl)methylanilines **2**. The aza-Wittig reaction of iminophosphoranes **5** with acyl cyanides gave *N*-[aryl(cyano)methylene]-2-(arylsulfonyl)methylanilines **6**, which were cyclized by sodium hydroxide to 2-aryl-3-arylsulfonylindoles **7**. The iminophosphoranes **5** reacted with phenyl isocyanate to give the corresponding carbodiimides **11**, which were cyclized in a similar manner to 2-anilino-3-arylsulfonylindoles **12**.

**Key words:** sulfones, iminophosphoranes, acyl cyanides, aza-Wittig reaction, indoles

The synthesis of heterocycles using the aza-Wittig reaction of iminophosphoranes is now one of the most useful methods for preparing nitrogen-containing heterocycles.<sup>1</sup> The versatility of the heterocyclic synthesis comes from the ready accessibility of iminophosphoranes and their high reactivity towards heterocumulenes and carbonyl compounds. We are interested in the synthesis of heterocycles using sulfur compounds and have used iminophosphorane-containing sulfur compounds for this purpose. We obtained 2-substituted 1,3-benzothiazoles from 2methylsulfanylaniline<sup>2</sup> and 2-substituted 1,4-benzothiazine-3-thiones<sup>3</sup> from 2-(substituted methylsulfanyl)anilines via the corresponding iminophosphoranes. As a continuation of this study, we chose the iminophosphoranes 5 as the starting sulfur-containing compounds. We report here the unexpected formation of 2-aryl-3-aryl-sulfonylindoles from 5 and some related results.

The iminophosphoranes 5 have an active methylene group adjacent to a sulfonyl group<sup>4</sup> and appear to serve as a good building block for heterocycles (Scheme 1). They can be easily synthesized from the readily available aryl 2-nitrobenzyl sulfones 1.<sup>5</sup> 2-(Arylsulfonyl)methylanilines 2a-c were obtained by reduction of the nitro group in 1 with tin in hydrochloric acid.<sup>6</sup> In a preliminary experiment, **2c** ( $\mathbf{R} = \mathbf{Cl}, \mathbf{R}^1 = p$ -Tol) was diazotized, neutralized by alkali, and then treated with sodium azide. However, the product was 5-chloro-3-(p-tolyl)sulfonyl-1H-indazole (3) instead of the expected azide 4c. Direct addition of sodium azide to the diazotized 2 without neutralization by alkali gave the desired azides 4a-c in 76-87% yield (Tables 1 and 2). The iminophosphoranes **5a–c** were readily prepared in 82–95% yield from the azides 4 and triphenylphosphane in dichloromethane at 0-5°C to room temperature (Staudinger reaction<sup>1b</sup>).

The preparation of 4-phenylsulfonylquinoline derivatives by condensation of the iminophosphorane group of **5** with benzil or methyl phenylglyoxalate followed by cyclization in the presence of a base was unsuccessful, because



Scheme 1

Table 1. Azides 4 and Iminophosphoranes 5 Prepared

Product <sup>a</sup>	R	$\mathbb{R}^1$	Yield (%)	mp (°C)
4a	Н	4-MeC <sub>6</sub> H <sub>4</sub>	76	124–126
4b	Cl	Ph	87	159–161
4c	Cl	$4-MeC_6H_4$	87	154-156
5a	Н	$4-\text{MeC}_6H_4$	82	174-175
5b	Cl	Ph	95	220-222
5c	Cl	$4-\text{MeC}_6\text{H}_4$	93	240-242

<sup>a</sup> Satisfactory microanalyses obtained: C  $\pm$  0.28, H  $\pm$  0.30, N  $\pm$  0.26.

the condensation of the iminophosphorane moiety of **5** with such ketones was difficult. A report<sup>7</sup> about the formation of 2-cyano-1-azadienes by the condensation of iminophosphoranes with cinnamoyl cyanide prompted us to use aroyl cyanides as the substrate. In fact, **5** readily condensed with aroyl cyanides in refluxing toluene to form **6a–f** in 48–74% yield (Scheme 2 and Tables 3 and 4).

Cyclization of the anions **8** generated by basic treatment of **6** was expected to give 3-amino-4-phenylsulfonylquinoline derivatives **10** through 6-*exo*-digonal cyclization.<sup>8</sup> However, treatment of **6** with sodium hydroxide in warm DMSO unexpectedly yielded 2-aryl-3-arylsulfonylindoles **7a–f** in 56–83% yield. Recently, Ichikawa et al.<sup>9</sup> reported that the "disfavored" 5-*endo*-trigonal cyclization<sup>10</sup> occurred during the nucleophilic addition– elimination of  $\beta$ , $\beta$ -difluoro-(*o*-tosylamino)styrene and  $\beta$ , $\beta$ -difluoro-(*o*-hydroxy)styrene to give 2-fluoroindoles

Fable 2. MS, IR, and	<sup>1</sup> H NMR Data of	Azides 4 and	Iminophosphoranes 5
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Product	MS <i>m</i> / <i>z</i> (%)	$\frac{\text{IR (KBr)}}{v (\text{cm}^{-1})}$	$^{1}$ H NMR (CDCl <sub>3</sub> /TMS) $\delta$
<b>4</b> a	287 (M <sup>+</sup> , 7), 194 (50), 180 (28), 132 (28), 104 (100)	2070, 1590, 1480, 1440, 1400, 1280, 1145, 1120, 1080	2.41 (s, 3H), 4.37 (s, 2H), 6.97–7.53 (m, 8H)
4b	307 (M <sup>+</sup> , 10), 214 (46), 180 (40), 138 (31), 102 (69), 77 (100)	2100, 1410, 1290, 1145, 1130, 1080	4.33 (s, 2H), 6.90–7.70 (m, 8H)
4c	321 (M <sup>+</sup> , 8), 228 (35), 214 (22), 194 (19), 138 (23), 91 (100)	2070, 1590, 1480, 1395, 1290, 1240, 1130	2.43 (s, 3H), 4.29 (s, 2H), 6.91–7.57 (m, 7H)
5a	521 (M <sup>+</sup> , 4), 366 (100), 212 (2), 183 (25), 152 (2), 108 (5)	1580, 1480, 1445, 1430, 1345, 1295, 1270, 1105, 1080	2.22 (s, 3H), 4.94 (s, 2H), 6.21–7.54 (23H)
5b	541 (M <sup>+</sup> , 6), 400 (100), 214 (8), 183 (41), 108 (8)	1570, 1460, 1330, 1295, 1110, 1010	4.90 (s, 2H), 6.10–7.70 (m, 23H)
5c	555 (M <sup>+</sup> , 6), 400 (100), 214 (9), 183 (45), 152 (5), 108 (8)	1580, 1465, 1340, 1305, 1295, 1105	2.25 (s, 3H), 4.87 (s, 2H), 6.10–7.43 (m, 22H)



 Table 3. Nitriles 6 and Indoles 7 Prepared

Product <sup>a</sup>	R	$\mathbb{R}^1$	$\mathbb{R}^2$	Yield (%)	mp (°C)
6a	Н	4-MeC <sub>6</sub> H <sub>4</sub>	Ph	49	115-118
6b	Н	$4 - MeC_6H_4$	$4 - MeC_6H_4$	64	162–164
6c	Cl	Ph	Ph	61	197–199
6d	Cl	Ph	$4 - MeC_6H_4$	67	156-158
6e	Cl	$4 - MeC_6H_4$	Ph	74	170-171
6f	Cl	$4 - \text{MeC}_{6}H_{4}$	$4 - MeC_6H_4$	48	170-172
7a	Н	$4 - \text{MeC}_{6}H_{4}$	Ph	74	204-205
7b	Н	$4 - \text{MeC}_{6}H_{4}$	$4 - MeC_6H_4$	83	227-228
7c	Cl	Ph	Ph	81	189–190
7d	Cl	Ph	$4 - MeC_6H_4$	66	215-216
7e	Cl	$4 - MeC_6H_4$	Ph	56	173-175
7f	Cl	$4 - \text{MeC}_6^0 \text{H}_4^2$	$4-MeC_6H_4$	74	220-221

<sup>a</sup> Satisfactory microanalyses obtained:  $C \pm 0.32$ ,  $H \pm 0.28$ ,  $N \pm 0.28$ . Compounds **7a–c**, **7e**, and **7f** contained occluded water to an extent of 0.5 H<sub>2</sub>O, 1 H<sub>2</sub>O, and 0.25 H<sub>2</sub>O, respectively. and 2-fluorobenzo[b]furans, respectively. These types of reactions seem to be the same as our method of preparation of indoles 7. However, the formation of 7 may also be explained by a 2,3-sigmatropic rearrangement of the anion 8 to the next intermediate 9 followed by aromatization upon elimination of hydrogen cyanide (Scheme 2).

Carbodiimide formation from iminophosphoranes and isocyanates followed by intramolecular nucleophilic cyclization is a useful methodology for the synthesis of fivemembered nitrogen heterocycles such as pyrazoles, 1,3oxazoles, imidazoles, 1,3,4-oxadiazoles, 1,3,4-thiadiazoles, and 1,3,4-triazoles and has been well-reviewed.<sup>1d,g</sup> However, studies on the preparation of a pyrrole ring by such a cyclization process are limited.<sup>11</sup> We realized that cyclization by attack of a sulfone-stabilized carbanion at the carbodiimide moiety produces indoles. The iminophosphoranes **5a–c** were treated with phenyl isocyanate in refluxing dichloromethane to give carbodiimides **11a–c** in 66–98% yield (Scheme 3 and Tables 5 and 6). 5-exo-Trig-





Table 4. MS, IR, and <sup>1</sup> H NMR Dat	a of Nitriles 6 and Indoles 7
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Product	MS <i>m</i> / <i>z</i> (%)	$\frac{\text{IR (KBr)}}{v (\text{cm}^{-1})}$	<sup>1</sup> H NMR (CDCl <sub>3</sub> /TMS) $\delta$
6a	374 (M <sup>+</sup> , 7), 219 (100), 165 (6), 116 (14)	2210, 1600, 1565, 1450, 1315, 1290, 1255, 1160, 1130, 1085	2.29 (s, 3H), 4.60 (s, 2H), 6.94–7.98 (m, 13H)
6b	388 (M <sup>+</sup> , 10), 233 (100), 218 (3), 116 (10)	2200, 1590, 1550, 1310, 1285, 1245, 1180, 1160, 1125, 1080	2.32 (s, 3H), 2.52 (s, 3H), 4.61 (s, 2H), 6.94–7.87 (m, 12H)
6c	394 (M <sup>+</sup> , 12), 253 (100), 218 (15), 190 (4), 165 (4), 150 (8)	2200, 1585, 1440, 1315, 1300, 1280, 1155, 1130, 1080	4.53 (s, 2H), 7.10–8.00 (m, 13H),
6d	408 (M <sup>+</sup> , 12), 267 (100), 232 (14), 150 (5), 123 (9)	2220, 1595, 1445, 1320, 1285, 1190, 1135, 1085	2.48 (s, 3H), 4.55 (s, 2H), 7.08–7.89 (m, 12H)
6e	408 (M <sup>+</sup> , 12), 253 (100), 208 (17), 150 (7), 123 (9)	2200, 1590, 1300, 1280, 1245, 1130, 1080	2.30 (s, 3H), 4.55 (s, 2H), 6.94–7.96 (m, 12H)
6f	422 (M <sup>+</sup> , 13), 267 (100), 232 (12), 150 (5), 123 (7)	2200, 1585, 1555, 1475, 1405, 1310, 1280, 1180, 1130, 1080	2.32 (s, 3H), 2.48 (s, 3H), 4.53 (s, 2H), 6.97–7.85 (m, 11H)
7a	347 (M <sup>+</sup> , 100), 283 (10), 267 (14), 208 (27), 165 (15), 139 (8)	3250, 1595, 1535, 1475, 1440, 1395, 1285, 1160, 1130, 1080	2.30 (s, 3H), 7.08–8.23 (m, 13H), 8.82 (br s, 1H)
7b	361 (M <sup>+</sup> , 100), 297 (7), 281 (11), 222 (17), 207 (6), 139 (6)	3320, 1600, 1500, 1450, 1395, 1300, 1160, 1130, 1080	2.32 (s, 3H), 2.43 (s, 3H), 7.10–8.23 (m, 12H), 8.67 (br s, 1H)
7c	367 (M <sup>+</sup> , 100), 303 (10), 267 (29), 242 (29), 199 (14), 191 (20)	3250, 1570, 1440, 1385, 1300, 1130, 1065	7.23–7.63 (m, 12H), 8.29 (s, 1H), 8.96 (br s, 1H)
7d	381 (M <sup>+</sup> , 100), 281 (12), 256 (15), 241 (7), 204 (8), 125 (6)	3260, 1610, 1575, 1495, 1445, 1390, 1300, 1160, 1135, 1085	2.40 (s, 3H), 7.19–7.68 (m, 11H), 8.26 (s, 1H), 8.83 (br s, 1H)
7e	381 (M <sup>+</sup> , 100), 317 (10), 281 (27), 242 (25), 191 (12), 139 (12)	3250, 1440, 1390, 1295, 1130, 1080	2.32 (s, 3H), 7.08–7.56 (m, 11H), 8.28 (s, 1H), 8.53 (br s, 1H)
7f	395 (M <sup>+</sup> , 100), 295 (20), 281 (10), 256 (19), 204 (12), 139 (11)	3250, 1600, 1495, 1445, 1410, 1390, 1300, 1135, 1085	2.32 (s, 3H), 2.41 (s, 3H), 7.10–7.55 (m, 10H), 8.25 (s, 1H), 8.83 (br s, 1H)

Table 5. Carbodiimides 11 and Indoles 12 Prepared

Product <sup>a</sup>	R	R <sup>1</sup>	Yield (%)	mp (°C)
11a	H	$\begin{array}{c} \text{4-MeC}_6\text{H}_4\\ \text{Ph}\\ \text{4-MeC}_6\text{H}_4\\ \text{4-MeC}_6\text{H}_4\\ \text{Ph}\\ \text{4-MeC}_4\text{H}_4\\ \end{array}$	66	114–117
11b	Cl		98	133–135
11c	Cl		97	133–135
12a	H		83	164–166
12b	Cl		72	168–170
12c	Cl		68	229–230

 $^a$  Satisfactory microanalyses obtained: C  $\pm$  0.24, H  $\pm$  0.13, N  $\pm$  0.31. Compound 12b contained one mole of occluded MeOH.

onal cyclization of **11** to 2-anilino-3-arylsulfonylindoles **12a–c** was accomplished in 68–83% yield upon treatment with sodium hydroxide in dimethyl sulfoxide at room temperature (Tables 5 and 6).

The reaction of iminophosphorane **5b** with carbon disulfide<sup>12</sup> in refluxing toluene gave the dimer **14** in 68% yield, probably through further condensation of the intermediate isothiocyanate **13** with the starting **5b** (Scheme 3).

Wojciechowski and Makosza synthesized 2-alkyl-3-arylsulfonylindoles by the condensation of **2** with trialkyl orthoformate.<sup>6</sup> They also prepared 2-unsubstituted 3-phenylsulfonylindoles via the vicarious substitution of *m*-isocyanatonitrobenzene with chloromethyl phenyl sulfone.<sup>13</sup> In contrast to these methods, we could introduce aryl groups and an anilino group into the C-2 position of the 3arylsulfonylindoles. Thus, we have shown that iminophosphoranes **5** are useful building blocks for 2-aryl- and 2anilino-3-arylsulfonylindoles which are otherwise inaccessible and, furthermore, a rarely known class of indoles.<sup>11</sup>

Melting points were determined using a MRK MEL-TEMP II and are uncorrected. IR spectra were recorded on a JASCO A-102 spectrophotometer. Mass and <sup>1</sup>H NMR spectra were taken with a JEOL JMS DX-300 spectrometer and a JEOL GSX-400 spectrometer, respectively. Microanalyses were performed with a YANACO CHN-Coder MT-5.

# Aryl 2-Nitrobenzyl Sulfones 1a-c:

Compound  $\mathbf{1a}^{14}$  (R = H, R<sup>1</sup> = *p*-Tolyl) was prepared by stirring a mixture of sodium *p*-toluenesulfinate (8.9 g, 50 mmol) and commercially available 2-nitrobenzyl bromide (10.8 g, 50 mmol) in DMSO (100 mL) at r.t. for 1 h followed by pouring the mixture into ice-water (500 mL). The sulfones **1b** (R = Cl, R<sup>1</sup> = Ph) and **1c** (R = Cl, R<sup>1</sup> = *p*-

Fable 6. MS, IR, and	<sup>1</sup> H NMR Data of	Carbodiimides 1	1 and Indoles 12
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Product	MS <i>m</i> / <i>z</i> (%)	IR (KBr) v (cm <sup>-1</sup> )	$^{1}$ H NMR (CDCl <sub>3</sub> /TMS) $\delta$
11a	362 (M <sup>+</sup> , 9), 207 (100), 180 (1), 132 (2)	2100, 1575, 1480, 1300, 1245, 1205, 1130, 1085	2.39 (s, 3H), 4.52 (s, 2H), 7.06–7.55 (m, 13H)
11b	382 (M <sup>+</sup> , 19), 241 (83), 206 (100), 102 (4)	2150, 1570, 1485, 1305, 1240, 1220, 1160, 1130, 1085	4.50 (s, 2H), 7.05–7.74 (m, 13H)
11c	396 (M <sup>+</sup> , 14), 241 (65), 206 (100), 102 (5)	2130, 1595, 1485, 1319, 1250, 1160, 1140, 1090	2.42 (s, 3H), 4.46 (s, 2H), 7.03–7.71 (m, 12H)
12a	362 (M <sup>+</sup> , 100), 298 (8), 223 (9), 207 (36), 206 (41), 180 (7)	3360, 1630, 1605, 1575, 1520, 1505, 1480, 1465, 1375, 1280	2.36 (s, 3H), 7.02–7.88 (m, 13H), 8.20 (br s, 1H), 8.40 (br s, 1H)
12b	382 (M <sup>+</sup> , 100), 318 (5), 282 (3), 257 (9), 242 (16), 206 (38)	3500, 3340, 1625, 1600, 1570, 1500, 1460, 1365, 1265, 1145	6.99–8.01 (m, 13H), 8.28 (br s, 1H), 8.39 (br s, 1H)
12c	396 (M <sup>+</sup> , 100), 332 (7), 257 (9), 241 (20), 206 (41)	3360, 1630, 1600, 1580, 1495, 1460, 1370, 1270, 1145, 1125	2.39 (s, 3H), 6.98–7.90 (m, 12H), 8.19 (br s, 1H), 8.40 (br s, 1H)

Tolyl) were prepared according to the literature<sup>5</sup> from 4-chloronitrobenzene and aryl chloromethyl sulfones.

## 2-Aminobenzyl Aryl Sulfones 2a-c:

The sulfone **2c** (R = Cl, R<sup>1</sup> = *p*-Tolyl) was prepared according to the literature<sup>6</sup> by reduction of the corresponding aryl 2-nitrobenzyl sulfone with tin in HCl. Sulfones **2a** (R = H, R<sup>1</sup> = *p*-Tolyl) and **2b** (R = Cl, R<sup>1</sup> = Ph) were prepared similarly.

*Compound* **2a:** yield: 87%; white powder; mp 140–141 °C. IR (KBr): v = 3470, 3380, 1620, 1595, 1575, 1490, 1275, 1135 cm<sup>-1</sup>.MS: <math>m/z (%) = 261 (M<sup>+</sup>, 6), 106 (100). Anal. Calcd for C<sub>14</sub>H<sub>15</sub>NO<sub>2</sub>S (261.3): C, 64.34; H, 5.79; N, 5.36. Found: C, 64.39; H, 5.78; N, 5.43.

Compound 2b: yield: 90%; white powder; mp 131-133°C.

IR (KBr):  $v = 3440, 3360, 1630, 1575, 1480, 1400, 1280, 1140 \text{ cm}^{-1}$ . MS: m/z (%) = 281 (M<sup>+</sup>, 7), 140 (100).

Anal. Calcd for C<sub>13</sub>H<sub>12</sub>NO<sub>2</sub>SCl (281.8): C, 55.42; H, 4.29; N, 4.97. Found: C, 55.36; H, 4.29; N, 4.93.

#### 5-Chloro-3-(p-tolyl)sulfonyl-1H-indazole (3):

A solution of NaNO<sub>2</sub> (520 mg, 7.5 mmol) in H<sub>2</sub>O (3 mL) was added to a stirred solution of **2c** (1.48 g, 5.0 mmol) in 4 M HCl (250 mL) at 0-5 °C. After stirring for 30 min at the same temperature, the mixture was neutralized with 10% aq NaOH solution. The resulting precipitate was collected by filtration, then dissolved in CHCl<sub>3</sub>. The CHCl<sub>3</sub> solution was dried (MgSO<sub>4</sub>), filtered and the solvent was evaporated. The residue obtained was recrystallized from EtOAc/hexane to give **3** (1.35 g, 88%) as a white powder; mp 242–244 °C.

IR (KBr):  $v = 3260, 1585, 1470, 1315, 1140 \text{ cm}^{-1}$ 

MS: m/z (%) = 306 (M<sup>+</sup>, 55), 242 (43), 155 (15), 139 (22), 91 (100). Anal. Calcd for C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>SCl (306.8): C, 54.81; H, 3.61; N, 9.13. Found: C, 54.65; H, 3.62; N, 9.37.

#### Aryl 2-Azidobenzyl Sulfones 4a-c; General Procedure:

A solution of NaNO<sub>2</sub> (5.18 g, 75 mmol) in H<sub>2</sub>O (25 mL) was added dropwise to a stirred solution of **2** (50 mmol) in 4 M HCl (250 mL) at 0-5 °C. After stirring the mixture at the same temperature for 30 min, a solution of NaN<sub>3</sub> (3.25 g, 50 mmol) in H<sub>2</sub>O (50 mL) was slowly added to the mixture. During the addition, a vigorous foam was formed. The stirring was continued for 30 min below 5 °C, and then for 5 h at r.t. The mixture was extracted with CHCl<sub>3</sub>, the organic layer was dried (MgSO<sub>4</sub>), and the solvent was removed in vacuo. The residue was recrystallized from  $CHCl_3$ /hexane to give light tan plates (4a) or light tan needles (4b and 4c).

## 2-(Arylsulfonyl)methyl-N-(triphenylphosphoranylidene)anilines 5a–c; General Procedure:

To a cooled (0–5 °C) and stirred solution of Ph<sub>3</sub>P (7.86 g, 30 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (150 mL) was added a solution of **4** (30 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (150 mL) under N<sub>2</sub>. The mixture was stirred at 0–5 °C for 1 h and then slowly warmed to r.t. The solvent was removed in vacuo and the residue was treated with benzene to precipitate the product, which was collected by filtration and recrystallized from benzene/hexane to give a white powder (**5a**) or from CHCl<sub>3</sub>/hexane to give white needles (**5b** and **5c**).

## *N*-[Aryl(cyano)methylene]-2-(arylsulfonyl)methylanilines 6a–f; General Procedure:

A mixture of **5** (4.0 mmol) and aroyl cyanide (4.0 mmol) in anhyd toluene (50 mL) was refluxed for 20 h under  $N_2$ . After cooling, the precipitate (unreacted **5**) was filtered off and the filtrate was evaporated. In the cases of **6c** and **6e**, the resulting solid residue was recrystallized from CHCl<sub>3</sub>/hexane to give the products as yellow needles. In the other cases, the resulting oily residue was chromatographed on silica gel with CHCl<sub>3</sub> as eluent to give **a** solid product, which was recrystallized from CHCl<sub>3</sub>/hexane to give **6** as yellow needles.

#### 2-Aryl-3-arylsulfonylindoles 7a–f; General Procedure:

To a stirred solution of **6** (1.0 mmol) dissolved in warm DMSO (3 mL) was added powdered NaOH (200 mg, 5.0 mmol). The mixture was stirred at 80–90 °C for 1 h. After cooling, the mixture was neutralized with 10% NH<sub>4</sub>Cl solution (ca. 50 mL) [*Caution!* The evolution of HCN began at pH 8–9]. The resulting precipitate was collected by filtration and dissolved in CHCl<sub>3</sub>. The CHCl<sub>3</sub> solution was dried (MgSO<sub>4</sub>) and the solvent was removed in vacuo. The residue was recrystallized from CHCl<sub>3</sub>/hexane to give **7** as a white powder.

## *N*-[2-(Arylsulfonylmethyl)phenyl]*N*'-phenylcarbodiimides 11ac; General Procedure:

To a stirred solution of **5** (4.0 mmol) in  $CH_2Cl_2$  (50 mL) was added phenyl isocyanate (480 mg, 4.0 mmol) at r.t. under N<sub>2</sub>. After the mixture was refluxed for 12 h, the solvent was removed in vacuo. The residue was washed with hexane and then recrystallized from  $CH_2Cl_2$ /hexane to give white needles (**11a** and **11b**) or a white powder (**11c**).

## 2-Anilino-3-arylsulfonylindoles 12a-c; General Procedure:

To a stirred solution of 11 (1.0 mmol) dissolved in warm DMSO (3 mL) was added powdered NaOH (200 mg, 5.0 mmol). After stir-

ring at r.t. for 30 min, the mixture was neutralized with 10% aq NH<sub>4</sub>Cl solution (ca. 50 mL). The resulting precipitate was collected by filtration and dissolved in CHCl<sub>3</sub>. The solution was dried (MgSO<sub>4</sub>) and evaporated in vacuo to give an oily product. In the case of **12a**, the residue was purified by column chromatography on silica gel with CHCl<sub>3</sub>/EtOAc as eluent to give a brown oil, which took a long time to crystallize. The products **12b** and **12c** were obtained by the addition of a small amount of MeOH to the oily residue followed by collection of the resulting precipitate by filtration. Recrystallization from MeOH gave a white powder (**12a**) or white plates (**12b** and **12c**).

#### *N*,*N*<sup>2</sup>Bis[4-chloro-2-(phenylsulfonylmethyl)phenyl]carbodiimide (14):

A mixture of **5b** (1.63 g, 3.0 mmol) and excess  $CS_2$  (1.0 mL) in anhyd toluene (40 mL) was refluxed for 20 h under N<sub>2</sub>. After cooling, the solvent was removed in vacuo and benzene was added to the residue to give the precipitate, which was collected by filtration and recrystallized from  $CH_2Cl_2$ /hexane to afford **14** (360 mg, 68%) as a white powder; mp 186–188 °C.

IR (KBr): v = 2100, 1475, 1300, 1125 cm<sup>-1</sup>.

MS: m/z (%) = 570 (M<sup>+</sup>, 11), 429 (26), 287 (90), 252 (50), 166 (41), 77 (100).

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 4.45 (s, 4 H), 7.03–7.74 (m, 16 H).

Anal. Calcd for  $C_{27}H_{20}N_2O_4S_2Cl_2$  (571.5): C, 56.75; H, 3.53; N, 4.90. Found: C, 56.49; H, 3.54; N, 5.02.

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