### **Copper-Mediated Cross-Coupling Reaction of N-Protected Sulfonimidamides and Aryl Halides**

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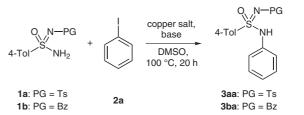
**Abstract:** Copper-mediated cross-coupling reactions of N-protected sulfonimidamides with aryl iodides and aryl bromides provide N-protected *N'*-aryl sulfonimidamides in moderate to good yields.

**Key words:** N-arylation, aryl halides, copper, cross-coupling, sulfonimidamide

Sulfonimidamides are the aza-analogues of sulfonamides. They are potent reagents in nitrene transfer chemistry<sup>1</sup> as exemplified by diastereoselective C–H aminations.<sup>2</sup> Preparation of various chiral sulfonimidoylguanidines have recently been carried out by the reaction of sulfonimidamides with uronium reagents.<sup>3</sup> Since both sulfonimidamides and guanidine moities occur in several biologically active molecules, we became interested in the preparation of compounds that contain both of these interesting functional groups. From a more fundamental point of view, we wanted to design new compounds, which contained the sulfonimidamide moiety as a basic module to be incorporated into chiral ligands for asymmetric catalysis.

Metal-catalyzed C–N cross-coupling reactions are powerful tools in organic synthesis and offer the possibility of versatile structural modifications of a nitrogen containing substrate. The use of palladium-based catalysts in C–N cross-coupling has extensively been studied by Buchwald and Hartwig, who also developed robust and sustainable procedures for efficient couplings of several substrates.<sup>4</sup> Copper-mediated reactions provide a low cost alternative to palladium-catalyzed cross-coupling protocols and exhibit improved functional group tolerance in some cases. Cross-coupling reactions using stoichiometric and catalytic amounts of copper have extensively been examined during the last decade,<sup>5</sup> which resulted in improvements with respect to the choice of copper salt, base, ligand, and additive.

Stimulated by our findings on the ligand-free copper-promoted N-arylation of sulfoximines, which gave the desired products in high yields starting from *S*-alkyl-*S*arylsulfoximines and aryl iodides or aryl bromides,<sup>6,7</sup> we wondered, if similar N-arylation conditions would also be applicable in sulfonimidamide cross-couplings. Herein, we confirm this hypothesis and report on the preparation  
 Table 1
 Reaction Conditions Tested for the Copper-Mediated N-Arylation of Sulfonimidamides 1a and 1b with Phenyl Iodide (2a)<sup>a</sup>



Entry	Substrate	Copper salt	Base	Yield (%) <sup>b</sup>
1	1a	CuI	Cs <sub>2</sub> CO <sub>3</sub>	32
2	1a	CuBr	Cs <sub>2</sub> CO <sub>3</sub>	22
3	1a	CuCl	Cs <sub>2</sub> CO <sub>3</sub>	35
4	1b	CuCl	Cs <sub>2</sub> CO <sub>3</sub>	54
5	1b	CuCl	K <sub>2</sub> CO <sub>3</sub>	65

<sup>a</sup> Reaction conditions: sulfonimidamide (1.0 equiv), phenyl iodide (2.0 equiv), base (2.5 equiv), and copper salt (1.0 equiv) in DMSO (0.4 M with respect to the sulfonimidamide) at 100 °C.

<sup>b</sup> Determined after column chromatography.

of N-protected N'-aryl sulfonimidamides by copperpromoted cross-coupling reactions. The protocol is easy to perform and all starting materials, except for the sulfonimidamides, are commercially available. The products were obtained in moderate to good yields, and several derivatives became accessible.

As test reactions, the cross-couplings between sulfonimidamides 1 and phenyl iodide (2a) were chosen. To identify the best reaction conditions, the effects of different solvents, copper salts, and bases were studied. The results of the initial screening are summarized in Table 1.

A solvent screening showed that performing the crosscoupling in dimethyl sulfoxide gave the product in higher yield than in 1,4-dioxane. Unsatisfactory results were obtained with toluene, N,N-dimethylformamide, and Nmethyl-2-pyrrolidone. To our delight, several copper salts promoted the N-arylation yielding N-phenyl sulfonimidamides **3**, and the best results were obtained with copper(I) halides, especially copper(I) chloride (Table 1, entries 3– 5). Changing the N-protecting group of the sulfonimidamide from N-tosyl to N-benzoyl led to a significant increase in yield (entries 3 and 4). Moreover, potassium

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 Table 2
 Copper-Mediated Cross-Coupling of Sulfonimidamide 1b

 with Aryl Halides 2b-k<sup>a</sup>
 1

0 \ 4-Tol	N—Bz S <sup>V</sup> NH <sub>2</sub>	+	X CuCl, K <sub>3</sub> CC DMSO, 100 °C, 20 2		N-Bz NH
Entry	ArX	X	Aryl	Product	Yield (%) <sup>b</sup>
1	2b	Ι	4-MeOC <sub>6</sub> H <sub>4</sub>	3bb	70
2	2c	Ι	$4-FC_6H_4$	3bc	59
3	2d	Ι	$4-ClC_6H_4$	3bd	67
4	2e	Ι	3-ClC <sub>6</sub> H <sub>4</sub>	3be	62
5	2f	Ι	$2-ClC_6H_4$	3bf	68
6	2g	Ι	$4-IC_6H_4$	3bg	66
7	2h	Ι	$4-MeC_6H_4$	3bh	55
8	2i	Ι	$3-MeC_6H_4$	3bi	55
9	2j	Ι	2-naphthyl	3bj	75
10	2k	Br	4-MeOC <sub>6</sub> H <sub>4</sub>	3bb	50

<sup>a</sup> Reaction conditions: sulfonimidamide (1.0 equiv), aryl halide (2.0 equiv),  $K_2CO_3$  (2.5 equiv), and CuCl (1.0 equiv) in DMSO (0.4 M with respect to the sulfonimidamide) at 100 °C.

<sup>b</sup> Determined after column chromatography.

carbonate proved to be superior to cesium carbonate as base (entry 5).

Next, the substrate scope using various aryl iodides and bromides was investigated. The results are summarized in Table 2.

The optimized conditions for the cross-coupling of 1a and 1b with phenyl iodide (2a) proved to be effective for all other substrates as well, and the corresponding arylated sulfonimidamides 3 were isolated in moderate to good yields. The electronic properties of the substituents of the aryl iodide 2 appeared to have no significant influence on the yield regardless of whether the substituents were electron-donating or -withdrawing. Substituents in ortho or *meta* position did not hamper the coupling (Table 2, entries 3–5, 7, and 8). Both aryl iodide 2b and aryl bromide 2k were suitable aryl sources as the direct comparison showed, but in the case of the aryl bromide the isolated yield was somewhat lower (entries 1 and 10). Furthermore, the reaction seemed to proceed more rapidly for aryl iodides. When 1-bromo-4-iodobenzene was used as aryl source a mixture of N-(4-bromo) and N-(4-iodophenyl) sulfonimidamide was isolated, and to our surprise no chemoselectivity was observed. In the case of 1,4-diiodobenzene (2g) only the monoarylated product 3bg was isolated (entry 6). No diarylation was observed even when 2 equivalents of the sulfonimidamide (with respect to the aryl iodide 2g) were used.

In conclusion, we have developed a copper-mediated cross-coupling method for the synthesis of various N-arylated sulfonimidamides. This synthetic pathway is highly flexible, allowing the coupling of several aryl iodides and bromides with sulfonimidamides.

All reactions were carried out under argon using standard Schlenk techniques. The sulfonimidamides **1** were prepared according to literature protocols.<sup>1</sup> All other starting materials were obtained from commercial suppliers and used without further purification. NMR spectra were recorded in CDCl<sub>3</sub> containing TMS as an internal standard on a Varian Mercury 300 spectrometer (300 and 75 MHz for <sup>1</sup>H and <sup>13</sup>C NMR spectra, respectively) or a Varian Inova 400 spectrometer (400 and 100 MHz for <sup>1</sup>H and <sup>13</sup>C NMR spectra, respectively). IR spectra were measured on a Perkin-Elmer PE-1760 FT instrument as KBr pellets and MS spectra were recorded on a Varian MAT 212 using EI as an ionization technique. TLC was carried out on silica gel 60 F<sub>254</sub> aluminum sheets (Merck) with spot detection under UV light.

### N-Benzoyl N'-Aryl Sulfonimidamides; General Procedure

A dry, sealable vial was charged with sulfonimidamide **1** (1.0 equiv), aryl halide **2** (2.0 equiv), CuCl (1.0 equiv),  $K_2CO_3$  (2.5 equiv), and degassed DMSO (1 mL per 0.4 mmol of the sulfonimidamide). After heating to 100 °C for 20 h, the heterogeneous mixture was cooled to r.t., taken up in CH<sub>2</sub>Cl<sub>2</sub>, and the CH<sub>2</sub>Cl<sub>2</sub> layer was washed with 25% aq ammonia, aq sat. NaHCO<sub>3</sub>, and brine. The organic layer was dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. The products were purified by column chromatography on silica gel affording the N-protected *N*'-aryl sulfonimidamides **3**.

# $N\mbox{-}(4\mbox{-}Toluene sulfonyl)\mbox{-}4\mbox{-}tolue ne sulfonimid\mbox{-}N'\mbox{-}phenylamide\mbox{(3aa)}$

Solid; mp 149–150 °C;  $R_f = 0.13$  (pentane–EtOAc, 5:2).

IR (KBr): 3182, 1490, 1306, 1265, 1148, 1068, 756, 540 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.36 (s, 3 H, CH<sub>3</sub>), 2.40 (s, 3 H, CH<sub>3</sub>), 7.01–7.11 (m, 3 H<sub>arom</sub>), 7.15–7.27 (m, 6 H<sub>arom</sub>), 7.76–7.80 (m, 2 H<sub>arom</sub>), 7.86–7.90 (m, 2 H<sub>arom</sub>), 8.39 (s, 1 H, NH).

 $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 21.5 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 122.5 (2 CH), 125.8 (CH), 126.7 (2 CH), 127.8 (2 CH), 129.1 (2 CH), 129.1 (2 CH), 129.6 (2 CH), 134.5 (C), 135.1 (C), 139.9 (C), 142.8 (C), 144.7 (C).

MS (EI, 70 eV): m/z (%) = 400 (52, [M<sup>+</sup>]), 308 (57), 247 (16), 183 (19), 155 (100), 139 (22), 91 (51).

Anal. Calcd for  $C_{20}H_{20}N_2O_3S_2$ : C, 59.98; H, 5.03; N, 6.99. Found: C, 59.75; H, 4.98; N, 6.98.

### N-Benzoyl-4-toluenesulfonimid-N'-phenylamide (3ba)

Solid; mp 140–141 °C;  $R_f = 0.19$  (pentane–EtOAc, 3:1).

IR (KBr): 3107, 1634, 1490, 1329, 1288, 1223, 1160, 840, 705, 635, 526 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.37 (s, 3 H, CH<sub>3</sub>), 7.10–7.18 (m, 3 H<sub>arom</sub>), 7.24 (d, *J* = 8.0 Hz, 4 H<sub>arom</sub>), 7.40–7.44 (m, 2 H<sub>arom</sub>), 7.50–7.56 (m, 1 H<sub>arom</sub>), 7.79–7.83 (m, 2 H<sub>arom</sub>), 8.18–8.22 (m, 2 H<sub>arom</sub>), 10.41 (br s, 1 H, NH).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.5 (CH<sub>3</sub>), 122.0 (2 CH), 125.3 (CH), 127.0 (2 CH), 127.9 (2 CH), 129.3 (2 CH), 129.4 (2 CH), 129.7 (2 CH), 132.4 (CH), 135.1 (C), 135.6 (C), 135.9 (C), 144.3 (C), 172.6 (C).

MS (EI, 70 eV): m/z (%) = 350 (45, [M<sup>+</sup>]), 258 (71), 155 (27), 105 (100), 77 (19).

Anal. Calcd for  $C_{20}H_{18}N_2O_2S$ : C, 68.55; H, 5.18; N, 7.99. Found: C, 68.22; H, 5.18; N, 7.88.

# *N*-Benzoyl-4-toluenesulfonimid-*N'*-(4-methoxyphenyl)amide (3bb)

Low-melting, glassy product;  $R_f = 0.24$  (pentane-EtOAc, 3:1).

IR (KBr): 3166, 1607, 1573, 1509, 1448, 1320, 1284, 1250, 1217, 1174, 1145, 1029, 954, 861, 830, 715, 528  $\rm cm^{-1}.$ 

 $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.37 (s, 3 H, CH<sub>3</sub>), 3.74 (s, 3 H, CH<sub>3</sub>), 6.72–6.79 (m, 2 H<sub>arom</sub>), 7.03–7.09 (m, 2 H<sub>arom</sub>), 7.20–7.25 (m, 2 H<sub>arom</sub>), 7.38–7.45 (m, 2 H<sub>arom</sub>), 7.49–7.55 (m, 1 H<sub>arom</sub>), 7.73–7.78 (m, 2 H<sub>arom</sub>), 8.17–8.22 (m, 2 H<sub>arom</sub>), 9.90 (s, 1 H, NH).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 21.8 (CH<sub>3</sub>), 55.4 (CH<sub>3</sub>), 114.6 (2 CH), 125.9 (2 CH), 127.3 (2 CH), 127.7 (C), 128.1 (2 CH), 129,6 (2 CH), 129.8 (2 CH), 132.5 (CH), 135.4 (C), 136.0 (C), 144.4 (C), 158.0 (C), 173.1 (C).

MS (EI, 70 eV): m/z (%) = 380 (88, [M<sup>+</sup>]), 258 (7), 227 (17), 155 (4), 122 (100), 105 (35), 77 (12).

Anal. Calcd for  $C_{21}H_{20}N_2O_3S$ : C, 66.29; H, 5.30; N, 7.36. Found: C, 65.89; H, 5.58; N, 7.23.

## *N*-Benzoyl-4-toluenesulfonimid-*N'*-(4-fluorophenyl)amide (3bc)

Solid; mp 129–130 °C;  $R_f = 0.25$  (pentane–EtOAc, 4:1).

IR (KBr): 3121, 3062, 2921, 2844, 1603, 1572, 1509, 1467, 1330, 1284, 1258, 1212, 1176, 1156, 1092, 957, 817, 711, 642, 584, 531, 503  $\rm cm^{-1}$ .

 $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.38 (s, 3 H, CH<sub>3</sub>), 6.89–6.97 (m, 2 H<sub>arom</sub>), 7.08–7.15 (m, 2 H<sub>arom</sub>), 7.22–7.27 (m, 2 H<sub>arom</sub>), 7.39–7.45 (m, 2 H<sub>arom</sub>), 7.50–7.56 (m, 1 H<sub>arom</sub>), 7.74–7.79 (m, 2 H<sub>arom</sub>), 8.16–8.21 (m, 2 H<sub>arom</sub>), 10.26 (s, 1 H, NH).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 21.6 (CH<sub>3</sub>), 116.3 (d, J = 23 Hz, 2 CH), 125.2 (d, J = 8 Hz, 2 CH), 127.2 (2 CH), 128.1 (2 CH), 129.6 (2 CH), 129.9 (2 CH), 131.4 (C), 132.6 (CH), 135.2 (C), 135.8 (C), 144.7 (C), 160.7 (d, J = 247 Hz, C), 173.0 (C).

<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 115.5.

MS (EI, 70 eV): m/z (%) = 368 (45, [M<sup>+</sup>]), 269 (46), 155 (27), 105 (100), 77 (29).

Anal. Calcd for  $C_{20}H_{17}FN_2O_2S;$  C, 65.20; H, 4.65; N, 7.60. Found: C, 65.26; H, 4.81; N, 7.54.

### *N*-Benzoyl-4-toluenesulfonimid-*N'*-(4-chlorophenyl)amide (3bd)

Solid; mp 143–144 °C;  $R_f = 0.25$  (pentane–EtOAc, 4:1).

IR (KBr): 1618, 1483, 1396, 1317, 1289, 1253, 1155, 911, 769, 708, 669, 646, 535 cm<sup>-1</sup>.

 $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.38 (s, 3 H, CH<sub>3</sub>), 7.06–7.11 (m, 2 H\_{arom}), 7.17–7.22 (m, 2 H\_{arom}), 7.22–7.28 (m, 2 H\_{arom}), 7.38–7.45 (m, 2 H\_{arom}), 7.50–7.56 (m, 1 H\_{arom}), 7.76–7.81 (m, 2 H\_{arom}), 8.15–8.21 (m, 2 H\_{arom}), 10.40 (s, 1 H, NH).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 21.6 (CH<sub>3</sub>), 123.5 (2 CH), 127.1 (2 CH), 128.1 (2 CH), 129.5 (2 CH), 129.6 (2 CH), 130.0 (2 CH), 131.1 (C), 132.7 (CH), 134.4 (C), 135.1 (C), 135.8 (C), 144.8 (C), 172.9 (C).

MS (EI, 70 eV): m/z (%) = 384 (41, [M<sup>+</sup>]), 258 (54), 155 (35), 126 (5), 105 (100), 77 (26).

Anal. Calcd for  $C_{20}H_{17}ClN_2O_2S$ : C, 62.41; H, 4.45; N, 7.28. Found: C, 62.19; H, 4.51; N, 7.19.

## *N*-Benzoyl-4-toluenesulfonimid-*N'*-(3-chlorophenyl)amide (3be)

Solid; mp 167–168 °C;  $R_f = 0.25$  (pentane–EtOAc, 4:1).

IR (KBr): 3116, 2834, 1598, 1472, 1323, 1277, 1152, 1091, 959, 860, 809, 782, 711, 681, 643, 520  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.38 (s, 3 H, CH<sub>3</sub>), 7.01–7.09 (m, 2 H<sub>arom</sub>), 7.15 (d, *J* = 7.9 Hz, 1 H<sub>arom</sub>), 7.17–7.20 (m, 1 H<sub>arom</sub>), 7.24–7.29 (m, 2 H<sub>arom</sub>), 7.38–7.45 (m, 2 H<sub>arom</sub>), 7.50–7.56 (m, 1 H<sub>arom</sub>), 7.79–7.84 (m, 2 H<sub>arom</sub>), 8.15–8.29 (m, 2 H<sub>arom</sub>), the NH signal was not resolved.

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 21.6 (CH<sub>3</sub>), 119.6 (CH), 121.7 (CH), 125.4 (CH), 127.1 (2 CH), 128.1 (2 CH), 129.6 (2 CH), 130.0 (2 CH), 130.4 (CH), 132.7 (CH), 135.0 (C), 135.1 (C), 135.9 (C), 144.9 (C), 172.9 (C).

MS (EI, 70 eV): *m*/*z* (%) = 384 (26, [M<sup>+</sup>]), 258 (81), 155 (33), 105 (100), 77 (24).

Anal. Calcd for  $C_{20}H_{17}CIN_2O_2S$ : C, 62.41; H, 4.45; N, 7.28. Found: C, 62.71; H, 4.39; N, 7.27.

# *N*-Benzoyl-4-toluenesulfonimid-*N'*-(2-chlorophenyl)amide (3bf)

Solid; mp 62–65 °C;  $R_f = 0.36$  (pentane–EtOAc, 5:1).

IR (KBr): 3147, 3064, 1605, 1573, 1490, 1320, 1292, 1145, 1093, 951, 813, 713, 649, 559, 535, 503 cm<sup>-1</sup>.

 $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.35 (s, 3 H, CH<sub>3</sub>), 6.98–7.05 (m, 1 H<sub>arom</sub>), 7.12–7.18 (m, 1 H<sub>arom</sub>), 7.20–7.25 (m, 2 H<sub>arom</sub>), 7.31–7.35 (m, 1 H<sub>arom</sub>), 7.38–7.45 (m, 2 H<sub>arom</sub>), 7.49–7.58 (m, 2 H<sub>arom</sub>), 7.80–7.85 (m, 2 H<sub>arom</sub>), 8.19–8.24 (m, 2 H<sub>arom</sub>), 11.00 (s, 1 H, NH).

 $^{13}\text{C}$  NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 21.6 (CH<sub>3</sub>), 122.2 (CH), 125.1 (C), 125.8 (CH), 127.0 (2 CH), 127.7 (CH), 128.1 (2 CH), 129.7 (2 CH), 129.9 (2 CH), 132.6 (CH), 133.6 (C), 135.1 (C), 136.2 (C), 144.7 (C), 172.5 (C).

MS (EI, 70 eV): m/z (%) = 384 (21, [M<sup>+</sup>]), 258 (81), 155 (32), 105 (100), 77 (28).

Anal. Calcd for  $C_{20}H_{17}ClN_2O_2S$ : C, 62.41; H, 4.45; N, 7.28. Found: C, 62.43; H, 4.33; N, 7.24.

### *N*-Benzoyl-4-toluenesulfonimid-N'-(4-iodophenyl)amide (3bg) Low-melting, glassy product; $R_f = 0.27$ (pentane–EtOAc, 4:1).

IR (KBr): 1606, 1485, 1319, 1292, 1147, 951, 814, 713, 540 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.38 (s, 3 H, CH<sub>3</sub>), 6.89–6.93 (m, 2 H<sub>arom</sub>), 7.23–7.27 (m, 2 H<sub>arom</sub>), 7.39–7.45 (m, 2 H<sub>arom</sub>), 7.50–7.56 (m, 3 H<sub>arom</sub>), 7.77–7.81 (m, 2 H<sub>arom</sub>), 8.15–8.19 (m, 2 H<sub>arom</sub>); the NH signal was not resolved.

 $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 21.7 (CH<sub>3</sub>), 89.4 (C), 123.6 (2 CH), 127.1 (2 CH), 128.0 (2 CH), 129.5 (2 CH), 129.9 (2 CH), 132.6 (CH), 135.0 (C), 135.7 (C), 135.8 (C), 138.3 (2 CH), 144.7 (C), 172.7 (C).

MS (EI, 70 eV): m/z (%) = 476 (28, [M<sup>+</sup>]), 258 (32), 155 (23), 105 (100), 77 (35).

HRMS (EI): m/z calcd for  $C_{20}H_{17}IN_2O_2S$ : 476.0055; found: 476.0057.

### N-Benzoyl-4-toluenesulfonimid-N'-4-tolylamide (3bh)

Solid; mp 151 °C;  $R_f = 0.24$  (pentane–EtOAc, 4:1).

IR (KBr): 3057, 1600, 1569, 1512, 1385, 1326, 1251, 1148, 957, 863, 817, 712, 584, 506  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.26 (s, 3 H, CH<sub>3</sub>), 2.36 (s, 3 H, CH<sub>3</sub>), 7.03 (s, 4 H<sub>arom</sub>), 7.19–7.25 (m, 2 H<sub>arom</sub>), 7.38–7.45 (m, 1 H<sub>arom</sub>), 7.49–7.55 (m, 1 H<sub>arom</sub>), 7.76–7.82 (m, 2 H<sub>arom</sub>), 8.16–8.21 (m, 2 H<sub>arom</sub>), 10.19 (s, 1 H, NH).

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<sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ = 20.8 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 122.7 (CH), 127.2 (2 CH), 128.1 (2 CH), 129.6 (2 CH), 129.8 (2 CH), 130.0 (2 CH), 132.5 (CH), 132.8 (C), 135.4 (C), 135.6 (C), 136.1 (C), 144.4 (C), 172.9 (C).

MS (EI, 70 eV): *m*/*z* (%) = 364 (67, [M<sup>+</sup>]), 258 (51), 211 (20), 155 (23), 105 (100), 77 (28).

Anal. Calcd for  $C_{21}H_{20}N_2O_2S$ : C, 69.20; H, 5.52; N, 7.69. Found: C, 69.15; H, 5.61; N, 7.66.

#### N-Benzoyl-4-toluenesulfonimid-N'-3-tolylamide (3bi)

Solid; mp 151–152 °C;  $R_f = 0.27$  (pentane–EtOAc, 4:1).

IR (KBr): 3121, 1600, 1569, 1475, 1324, 1280, 1246, 1144, 1093, 1018, 960, 827, 724, 644, 531 cm<sup>-1</sup>.

 $^1H$  NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.27 (s, 3 H, CH<sub>3</sub>), 2.36 (s, 3 H, CH<sub>3</sub>), 6.88–7.00 (m, 3 H<sub>arom</sub>), 7.07–7.14 (m, 1 H<sub>arom</sub>), 7.21–7.25 (m, 2 H<sub>arom</sub>), 7.38–7.45 (m, 1 H<sub>arom</sub>), 7.49–7.55 (m, 1 H<sub>arom</sub>), 7.78–7.84 (m, 2 H<sub>arom</sub>), 8.16–8.21 (m, 2 H<sub>arom</sub>), 10.37 (s, 1 H, NH).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 21.3 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 118.9 (CH), 122.7 (CH), 126.3 (CH), 127.2 (2 CH), 128.1 (2 CH), 129.1 (CH), 129.6 (2 CH), 129.8 (2 CH), 132.5 (CH), 135.3 (C), 135.7 (C), 136.2 (C), 139.5 (C), 144.4 (C), 172.8 (C).

MS (EI, 70 eV): *m*/*z* (%) = 364 (47, [M<sup>+</sup>]), 258 (76), 211 (14), 155 (30), 105 (100), 77 (35).

HRMS (EI): m/z calcd for  $C_{21}H_{20}N_2O_2S$ : 364.1246; found: 364.1246.

#### *N*-Benzoyl-4-toluenesulfonimid-*N*'-naphthalen-1-amide (3bj) Solid; mp 146–147 °C; $R_f = 0.23$ (pentane–EtOAc, 6:1).

IR (KBr): 3293, 3056, 1602, 1570, 1401, 1292, 1259, 1145, 1089, 942, 802, 713, 644, 538, 499  $\rm cm^{-1}.$ 

 $^1\text{H}$  NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.29 (s, 3 H, CH<sub>3</sub>), 7.11–7.15 (m, 2 H\_{arom}), 7.29–7.35 (m, 1 H\_{arom}), 7.42–7.60 (m, 6 H\_{arom}), 7.63–7.66 (m, 1 H\_{arom}), 7.75–7.79 (m, 2 H\_{arom}), 7.79–7.83 (m, 1 H\_{arom}), 8.18–8.22 (m, 1 H\_{arom}), 8.25–8.29 (m, 2 H\_{arom}), 11.41 (s, 1 H, NH).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 21.6 (CH<sub>3</sub>), 120.2 (CH), 121.5 (CH), 125.3 (CH), 126.2 (CH), 126.3 (CH), 126.9 (CH), 127.0 (2 CH), 127.4 (C), 128.1 (2 CH), 128.4 (CH), 129.6 (4 CH), 131.3

(C), 132.5 (CH), 134.1 (C), 135.3 (C), 136.1 (C), 144.4 (C), 173.1 (C).

MS (EI, 70 eV): *m*/*z* (%) = 400 (69, [M<sup>+</sup>]), 258 (5), 247 (13), 155 (15), 115 (28), 105 (100), 77 (18).

Anal. Calcd for  $C_{24}H_{20}N_2O_2S$ : C, 71.98; H, 5.03; N, 6.99. Found: C, 72.15; H, 5.18; N, 6.69.

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