SUPPORTING INFORMATION FOR

Synthesis of Sulfonimidamides from Sulfinamides by Oxidation with N-
Chlorosuccinimide

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General: 1H and 13C NMR spectra were recorded in CDCl3, CD3OD or acetone-d6 on a Varian Inova 400 or a Varian Mercury 300 spectrometer (400 and 100 MHz, and 300 and 75 MHz, respectively). Chemical shifts are given in ppm and spin-spin coupling constants, J, are given in Hz. Melting points were determined in open-end capillary tubes on a Büchi B-540 melting point apparatus and are uncorrected. Microanalyses were obtained with a Vario EL element analyzer. Mass spectra were acquired on a Varian MAT 212 spectrometer. IR spectra were taken on a Perkin-Elmer FT/IR 1760 and were recorded as KBr pellets or in solution. All reagents were purchased from commercial suppliers and used without further purification. Amide sodium salts were obtained upon treatment of the corresponding sulfonamide with NaH (1 equiv, 60% in mineral oil). Sulfinamides 1a-c were prepared according to literature procedures from NH2-free p-tolylsulfinamide 5 using n-BuLi and the corresponding anhydride,[1] or 1b by reaction of p-tolylsulfinyl chloride with BnNH2.

General procedure for the synthesis of sulfonimidamides 3:
To a stirring solution of sulfinamide 1 (1.0 mmol) and amine/amino salt (2.0-5.0 mmol) or H2NCN (88.2 mg, 2.1 mmol) and t-BuOK (235.6 mg, 2.0 mmol) in dry acetonitrile
under argon at room temperature, NCS (160.3 mg, 1.2 mmol) was added. Once the starting material was consumed (monitored by TLC), the reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography.

**N-(Benzoyl)-p-toluenesulfonyl chloride (2a):** [2]

Pale yellow solid. Mp. 102-104 °C (Lit.[2] mp. 105-106 °C); 1H NMR (300 MHz, CDCl3): δ 8.18-8.10 (m, 4H), 7.58 (tt, J = 7.4, 1.4 Hz, 1H), 7.50-7.42 (m, 4H), 2.53 (s, 3H); 13C NMR (75 MHz, CDCl3): δ 170.9 (C=O), 146.9 (C), 140.2 (C), 134.2 (C), 133.3 (CH), 130.4 (2 x CH), 129.8 (2 x CH), 128.4 (2 x CH), 127.2 (2 x CH), 21.9 (CH3); MS (EI+), m/z (relative intensity): 294 [M +, 18], 258 [M+Cl, 5], 190 [(M+H)+-Bz, 28], 155 [40], 105 [100].

**N-(Benzoyl)-N’-(p-methylbenzenenesulfonyl)-p-toluenesulfonylimidamide (3a):**

Following the general procedure, the reaction of sulfinamide 1a with NCS and TsNHNa gave 3a as a white solid (94%). Chromatography: gradient of ethyl acetate/pentane 1:4 to 1:1. Mp. >200 °C (decomp.); 1H NMR (400 MHz, acetone-d6): δ 7.84 (d, J = 7.4 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.16 (t, J = 7.4 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.5 Hz, 2H), 2.20 (s, 3H), 2.11 (s, 3H); 13C NMR (100 MHz, acetone-d6): δ 173.1 (C=O), 142.6 (C), 141.5 (C), 141.0 (C), 139.8 (C), 136.7 (C), 131.5 (CH), 129.2 (2 x CH), 128.9 (2 x CH), 128.6 (2 x CH), 127.5 (2 x CH), 126.8 (2 x CH), 126.4 (2 x CH), 20.6 (CH3), 20.5 (CH3); IR (KBr): ν 3257, 1596, 1419, 1311, 1263, 1152, 1079 cm⁻¹; MS (ESI-), m/z: 427 [(M-H)-]; Calcd. for C21H20N2O4S2·H2O: C, 56.48; H, 4.97 N, 6.27; found C, 56.31; H, 4.83; N, 5.90.

**N-(Benzyl)-N’-(p-methylbenzenenesulfonyl)-p-toluenesulfonylimidamide (3b):**

Following the general procedure, the reaction of sulfinamide 1b with NCS and TsNHNa gave 3b as a white solid (50%). Chromatography: gradient of ethyl acetate/pentane 1:4 to 1:1. Mp. 135-137 °C; 1H NMR (400 MHz, acetone-d6): δ 7.78 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.32-7.24 (m, 6H), 4.18 (AB system, J = 14.5 Hz, 1H), 4.12 (AB system, J = 14.5 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H); 13C NMR (100 MHz, acetone-d6): δ 144.2 (C), 142.2 (C), 141.7 (C), 136.6 (C), 136.3 (C), 129.6 (2 x CH), 128.9 (2 x CH), 128.3 (CH), 128.0 (2 x CH), 127.5 (4 x CH), 126.5 (2 x CH), 46.1 (CH2), 20.7 (CH3), 20.6 (CH3); IR (KBr): ν 3256, 1596, 1419, 1311, 1263, 1152, 1079 cm⁻¹; MS (EI+), m/z (relative intensity): 415 [(M+H)+, 1], 309 [M⁺-
N-[tert-Butoxycarbonylamino]-N’-(p-methylbenzenesulfonyl)-p-toluenesulfonimidamide (3c):

Following the general procedure, the reaction of sulfinamide 1c with NCS and TsNHNa gave 3c as a white solid (78%). Chromatography: gradient of ethyl acetate/pentane 1:1 to ethyl acetate. Mp. >147 °C (decomp.); \(^1\)H NMR (300 MHz, CD\(_3\)OD): \(\delta\) 7.57 (d, \(J = 8.2\) Hz, 2H), 7.53 (d, \(J = 8.2\) Hz, 2H), 7.11 (d, \(J = 7.8\) Hz, 2H), 7.08 (d, \(J = 7.8\) Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 1.23 (s, 9H); \(^{13}\)C NMR (75 MHz, CD\(_3\)OD): \(\delta\) 159.0 (C=O), 142.2 (C), 141.8 (C), 140.5 (C), 139.1 (C), 128.4 (2 x CH), 128.3 (2 x CH), 127.1 (2 x CH), 126.4 (2 x CH), 79.7 (C), 27.0 (3 x CH\(_3\)), 20.0 (CH\(_3\)); IR (KBr): \(\nu\) 2979, 1646, 1299, 1152, 1091, 1050 cm\(^{-1}\); MS (ESI-), \(m/z\): 423 [(M-H)-]; Calcd. for C\(_{19}\)H\(_{24}\)N\(_2\)O\(_5\)S\(_2\)·5/3H\(_2\)O: C, 50.20; H, 6.06 N, 6.16; found C, 50.13; H, 5.71 N, 5.76.

N-(Benzoyl)-N’-(p-nitrobenzenesulfonyl)-p-toluenesulfonimidamide (3d):

Following the general procedure, the reaction of sulfinamide 1a with NCS and NsNHNa gave 3d as a white solid (86%). Chromatography: gradient of dichloromethane/acetone 4:1 to 1:1. Mp. >240 °C (decomp.); \(^1\)H NMR (400 MHz, acetone-d\(_6\)): \(\delta\) 7.90 (s, 4H), 7.73 (d, \(J = 8.5\) Hz, 2H), 7.71 (d, \(J = 8.5\) Hz, 2H), 7.28 (t, \(J = 8.5\) Hz, 2H), 7.16-7.06 (m, 4H), 2.21 (s, 3H); \(^{13}\)C NMR (100 MHz, acetone-d\(_6\)): \(\delta\) 172.8 (C=O), 150.1 (C), 148.8 (C), 142.5 (C), 140.2 (C), 136.7 (C), 131.3 (CH), 129.0 (2 x CH), 128.8 (2 x CH), 128.2 (2 x CH), 127.4 (2 x CH), 126.5 (2 x CH), 123.3 (2 x CH), 20.6 (CH\(_3\)); IR (KBr): \(\nu\) 3103, 2924, 1605, 1531, 1325, 1152, 1048 cm\(^{-1}\); MS (ESI-), \(m/z\): 458 [(M-H)-]; Calcd. for C\(_{20}\)H\(_{17}\)N\(_3\)O\(_6\)S\(_2\)·3/2H\(_2\)O: C, 50.20; H, 6.06 N, 6.16; found C, 50.13; H, 5.71 N, 5.76.

N-(Benzoyl)-N’-(2-thiophenesulfonyl)-p-toluenesulfonimidamide (3e):

Following the general procedure, the reaction of sulfinamide 1a with NCS and ThphSO\(_2\)NHNa gave 3e as a white solid (94%). Chromatography: gradient of dichloromethane/acetone 4:1 to 1:1. Mp. >230 °C (decomp.); \(^1\)H NMR (300 MHz, acetone-d\(_6\)): \(\delta\) 7.98 (d, \(J = 8.4\) Hz, 2H), 7.78 (d, \(J = 8.4\) Hz, 2H), 7.49 (dd, \(J = 5.0, 1.5\) Hz, 1H), 7.45-7.39 (m, 2H), 7.34-7.28 (br t, \(J = 7.4\) Hz, 2H), 7.18 (d, \(J = 8.2\) Hz, 2H), 6.83 (dd, \(J = 5.0, 3.7\) Hz, 1H), 2.34 (s, 3H); \(^{13}\)C NMR (75 MHz, acetone-d\(_6\)): \(\delta\) 173.5 (C=O), 145.8 (C), 142.8 (C), 139.8 (C), 136.8 (C), 131.6 (CH), 130.7 (CH), 130.1 (CH), 129.3 (2 x CH), 129.0 (2 x CH), 127.7 (2 x CH), 126.4 (2 x CH), 126.2 (CH), 20.5 (CH\(_3\)); IR (KBr): \(\nu\) 1606, 1571, 1327, 1286, 1050 cm\(^{-1}\); MS (ESI-), \(m/z\): 419 [M\(^-\)].
Calcd. for C_{18}H_{16}N_{2}O_{4}S_{3}·4/3 H_{2}O: C, 48.63; H, 4.23 N, 6.30; found C, 48.86; H, 4.25; N, 6.01.

**N-(Benzoyl)-N'-(tert-butylsulfonyl)-p-toluenesulfonimidamide (3f):**

Following the general procedure, the reaction of sulfinamide 1a with NCS and BusNHNa gave 3f as a white solid (50%) and sulfonimidoyl chloride 2a (28%). Chromatography: gradient of dichloromethane/acetone 4:1 to 1:1. Mp. >200 °C (decomp.); 

{\textsuperscript{1}}H NMR (400 MHz, acetone-d_{6}): \(\delta\) 8.11 (d, \(J = 8.2\) Hz, 2H), 8.02 (d, \(J = 8.2\) Hz, 2H), 7.45 (t, \(J = 7.1\) Hz, 1H), 7.39-7.30 (m, 4H), 2.40 (s, 3H), 2.31 (s, 9H); 

{\textsuperscript{13}}C NMR (100 MHz, acetone-d_{6}): \(\delta\) 173.0 (C=O), 142.7 (C), 141.0 (C), 136.9 (C), 131.5 (CH), 129.2 (2 x CH), 129.1 (2 x CH), 127.7 (2 x CH), 126.1 (2 x CH), 58.9 (C), 23.8 (3 x CH_{3}), 20.1 (CH_{3}); IR (KBr): ν 2929, 1598, 1556, 1346, 1100 cm\(^{-1}\); MS (ESI-), \(m/z\): 393 [(M-H)-]; Calcd. for C_{18}H_{22}N_{2}O_{4}S_{2}·5/3H_{2}O: C, 50.92; H, 6.01; N, 6.60; found C, 50.53; H, 5.69; N, 6.26.

**N-(Benzoyl)-N'-(cyano)-p-toluenesulfonimidamide (3g):**

Following the general procedure, the reaction of sulfinamide 1a with NCS, H_{2}NCN and t-BuOK gave 3g as a white solid (85%). Chromatography: gradient of dichloromethane/acetone 4:1 to 1:1. Mp. >126 °C (decomp.); 

{\textsuperscript{1}}H NMR (300 MHz, acetone-d_{6}): \(\delta\) 8.11 (d, \(J = 8.2\) Hz, 2H), 7.92 (d, \(J = 8.2\) Hz, 2H), 7.45 (t, \(J = 7.3\) Hz, 1H), 7.39-7.28 (m, 4H), 2.37 (s, 3H); 

{\textsuperscript{13}}C NMR (75 MHz, acetone-d_{6}): \(\delta\) 173.1 (C=O), 142.2 (C), 140.8 (C), 137.5 (C), 131.1 (CH), 129.1 (2 x CH), 129.0 (2 x CH), 127.6 (2 x CH), 126.6 (2 x CH), 116.0 (CN), 20.5 (CH_{3}); IR (KBr): ν 2183, 1603, 1567, 1328 cm\(^{-1}\); MS (ESI-), \(m/z\): 298 [(M-H)-]; Calcd. for C_{15}H_{13}N_{3}O_{2}S·5/3H_{2}O: C, 50.92; H, 6.01; N, 6.60; found C, 50.53; H, 5.69; N, 6.26.

**N-(Benzoyl)-N'-(phenyl)-p-toluenesulfonimidamide (3h):**

Following the general procedure, the reaction of sulfinamide 1a with NCS and aniline gave 3h as a white solid (94%). Chromatography: gradient of ethyl acetate/pentane 1:10 to 1:4. Mp. 169-172 °C (Lit.[3] mp. 173-174 °C); 

{\textsuperscript{1}}H NMR (400 MHz, acetone-d_{6}): \(\delta\) 9.69 (br s, 1H, NH), 8.08 (d, \(J = 8.5\) Hz, 2H), 7.87 (d, \(J = 8.5\) Hz, 2H), 7.52 (t, \(J = 7.4\) Hz, 1H), 7.41 (t, \(J = 7.6\) Hz, 2H), 7.34 (d, \(J = 8.5\) Hz, 2H), 7.27-7.19 (m, 4H), 7.10-7.04 (m, 1H), 2.35 (s, 3H); 

{\textsuperscript{13}}C NMR (100 MHz, acetone-d_{6}): \(\delta\) 171.4 (C=O), 144.1 (C), 136.6 (C), 136.1 (C), 131.9 (CH), 129.7 (2 x CH), 129.2 (2 x CH), 129.0 (2 x CH), 127.9 (2 x CH), 127.8 (2 x CH), 124.9 (CH), 121.5 (2 x CH), 20.6 (CH_{3}); IR (KBr): ν 3420, 1602, 1329, 1286, 954 cm\(^{-1}\); MS (EI+), \(m/z\) (relative intensity): 350 [M\(^{+}\), 63], 258
N-(Benzoyl)-N',N'-dimethyl-p-toluenesulfonimidamide (3i):
Following the general procedure, the reaction of sulfamidate 1a with NCS and dimethylamine gave 3i as a white solid (97%). Chromatography: gradient of ethyl acetate/pentane 1:4 to 1:1. Mp. 95-96 °C; \(^1\)H NMR (300 MHz, acetone-\(d_6\)): \(\delta\) 8.15 (d, \(J = 8.2\) Hz, 2H), 7.86 (d, \(J = 8.2\) Hz, 2H), 7.55 (t, \(J = 7.3\) Hz, 1H), 7.50-7.41 (m, 4H), 2.84 (s, 6H), 2.45 (s, 3H); \(^1\)C NMR (75 MHz, acetone-\(d_6\)): \(\delta\) 171.4 (C=O), 144.0 (C), 136.5 (C), 133.0 (C), 131.8 (CH), 129.8 (2 x CH), 129.1 (2 x CH), 128.0 (2 x CH), 127.9 (2 x CH), 36.8 (2 x CH3), 20.6 (CH3); MS (EI+), \(m/z\) (relative intensity): 303 [M+, 8], 259 [M+-NMe2, 40], 105 [100]; Calcd. for C\(_{16}\)H\(_{18}\)N\(_2\)O\(_2\)S: C, 63.55; H, 6.00 N, 9.26; found C, 63.66; H, 5.79; N, 9.24.

N-(Benzoyl)-p-toluenesulfonimidamide (3j):
Following the general procedure, the reaction of sulfamidate 1a with NCS and hexamethyldisilazane gave 3j as a white solid (89%). Chromatography: gradient of ethyl acetate/pentane 1:4 to 1:1. Mp. 137-138 °C (Lit.[3] mp. 139-141 °C); \(^1\)H NMR (400 MHz, acetone-\(d_6\)): \(\delta\) 8.05 (d, \(J = 8.5\) Hz, 2H), 7.91 (d, \(J = 8.5\) Hz, 2H), 7.49 (t, \(J = 7.3\) Hz, 1H), 7.42-7.35 (m, 4H), 7.20 (br s, 2H), 2.40 (s, 3H); \(^1\)C NMR (100 MHz, acetone-\(d_6\)): \(\delta\) 171.7 (C=O), 143.4 (C), 139.8 (C), 136.4 (C), 131.6 (CH), 129.4 (2 x CH), 128.9 (2 x CH), 127.8 (2 x CH), 126.8 (2 x CH), 20.6 (CH3); MS (EI+), \(m/z\) (relative intensity): 275 [(M+H)+, 7], 197 [7], 108 [100].

General procedure for the cleavage of the N-benzoyl group:
To a solution of 3 (0.15 mmol) in MeOH (0.6 mL), a 10% HCl aq. solution (0.6 mL) was added at room temperature. The mixture was heated at 120 °C in a sealed tube for 16 h. Saturated aqueous Na\(_2\)HCO\(_3\) was added, extracted with CH\(_2\)Cl\(_2\) (3 x 1 mL), dried over MgSO\(_4\) and concentrated to dryness. The residue was purified by flash chromatography.

N-(p-Toluene-sulfonyl)-p-toluene-sulfonimidamide (4):
Following the general procedure, the reaction of sulfonimidamide 3a with 10% HCl solution in MeOH gave 4 as a white solid (73%). Chromatography: ethyl acetate/pentane 1:1. Mp. 164-165 °C (Lit.[4] mp. 164-164.5 °C); \(^1\)H NMR (400 MHz,
acetone-$d_6$): $\delta$ 7.64 (d, $J = 8.2$ Hz, 2H), 7.52 (d, $J = 8.2$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 6.92 (br s, 2H, NH$_2$), 2.29 (s, 3H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 143.8 (C), 142.0 (C), 141.7 (C), 139.3 (C), 129.4 (2 x CH), 128.8 (2 x CH), 126.8 (2 x CH), 126.4 (2 x CH), 20.6 (CH$_3$), 20.5 (CH$_3$); MS (EI$^+$), $m/z$ (relative intensity): 325 [(M+H)$^+$, 7], 308 [M$^+$-NH$_2$, 4], 261 [100], 154 [91], 108 [86].

$p$-Tolylsulfinamide (5):[5,6]

Following the general procedure, the reaction of sulfonimidamide 3i with 10% HCl solution in MeOH gave 5 as a white solid (87%). Chromatography: ethyl acetate/pentane 1:1. Mp. 113-114 ºC (Lit.[5] mp. 113 ºC); $^1$H NMR (300 MHz, acetone-$d_6$): $\delta$ 7.78 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 6.47 (br s, 2H, NH$_2$), 2.41 (s, 3H); $^{13}$C NMR (75 MHz, acetone-$d_6$): $\delta$ 142.4 (C), 141.6 (C), 129.3 (2 x CH), 126.0 (2 x CH), 20.4 (CH$_3$).

References
400 MHz, acetone-$d_6$

100 MHz, acetone-$d_6$
400 MHz, acetone-$d_6$

100 MHz, acetone-$d_6$
$^{3d}$

$400$ MHz, acetone-$d_6$

$100$ MHz, acetone-$d_6$
$^{1}H$ NMR spectra of compound 3e recorded at 300 MHz and 75 MHz in acetone-$d_{6}$.
300 MHz, acetone-d$_6$

75 MHz, acetone-d$_6$
400 MHz, acetone-\textit{d}_6

100 MHz, acetone-\textit{d}_6
300 MHz, acetone-$d_6$

75 MHz, acetone-$d_6$
$\text{SO}_3\text{NBz}$

400 MHz, acetone-$d_6$

100 MHz, acetone-$d_6$
400 MHz, acetone-d$_6$

100 MHz, acetone-d$_6$
300 MHz, acetone-$d_6$

75 MHz, acetone-$d_6$