Supporting Information

Zinc Chloride Catalyzed Ring Opening of N-arylsulfonyl Aziridines by Thioamides: A New Approach to the Synthesis of Amidines

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1. General Information
The chemicals used in this work were purchased from Fluka and Merck chemical companies. The progress of the reaction was monitored by TLC using 0.25 μm pre-coated silica gel plates. Melting points were determined using Stuart Scientific SMP2 apparatus and are uncorrected. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on Bruker-Avance 400.

Preparation of phosphinimine TsN=PPh$_3$:
Solutions of the triphenyl phosphine (2.63 g, 10 mmol) and anhydrous chloramine-T (2.28 g, 10 mmol), each in hot absolute alcohol (40 ml), were mixed. The mixture was boiled for 1 hour under reflux in a dry apparatus closed with a calcium chloride tube. The solution was then filtered, concentrated by direct distillation, and the resulting crystals were finally taken to dryness in a vacuum desiccator. The complete dry residue was thrice recrystallized from benzene and gave triphenylphosphine-$p$-toluenesulphonyl imine (m. p. 187 °C) as white crystals. [1]

Preparation of $p$-toluenesulfonyl azide:
A solution of sodium azide (7.15 g, 0.11 mol) in water (20 ml) was placed in a 250 ml Erlenmeyer flask and diluted with aqueous ethanol (90%, 40 ml). To this solution was added with stirring a warm (45°C) solution of $p$-toluenesulfonyl chloride (19.05 g, 0.10 mol) in ethanol (99%, 100 ml). The reaction mixture was stirred at room temperature for 2.5 h. Then, most of the solvent was removed at 35°C under vacuum. The residue was mixed with water (120 ml) in a separatory funnel, and the oily $p$-toluenesulfonyl azide was separated. The oily product was washed with water (2×10 ml) and dried over anhydrous magnesium sulfate. Filtration, gave the pure $p$-toluenesulfonyl azide as colorless crystals in good yield (16–17 g, 81–86%). [2]

Preparation of (N-$p$-toluenesulfonyl)iminophenyl iodonane:
The compound was prepared according to the procedure of Yamada et al [3]. To a solution of KOH (8.4 g, 150 mmol) and $p$-toluene sulfonamide (10.2 g, 60 mmol) in MeOH (200 ml) at 0°C was added diacetoxyiodobenzene (19.2 g, 60.0 mmol). A yellow color developed within 5 min. The cooling bath was removed and the solution allowed to warm to room temperature as it was stirred for 3 h. Water (200 ml) was added and the solution was refrigerated at 0°C overnight. The precipitate was collected by filtration and air dried to yield 18.6 g of a light yellow powder.

Procedure for the large-scale preparation of $p$-toluenesulfonyl aziridine:
To a mixture of iodine (2.54 g, 10 mmol), hydrated chloramine-T (28.2 g, 100 mmol), and HTAB (3.64 g, 10 mmol) in distilled water (300 mL) was added styrene (200 mmol). The mixture was stirred at room temperature for 1.5 h. After the decantation of water, the crude product was obtained as a brown solid. The resultant solid was purified by recrystallization from methanol (100 mL) to give the corresponding aziridine as a white solid (23.48 g, 86%) [4].

Preparation of N-arylsulfonfyl amidines; General Procedure:
A suspension of anhydrous ZnCl$_2$ (33 mg, 0.24 mmol, 2 mol %) in dry DCM (20 ml) was refluxed for 5 min and a solution of 2-phenyl-1-(arylsulfonyl) aziridine (12 mmol) in dry DCM (10 ml) was added slowly and stirred at 40 °C for a further 5 min. After that, morpholino(aryl) methanethione (10 mmol) was added to the reaction mixture and stirred in
the same temperature for 2 h. Then the reaction mixture was tritivated well with water (50 ml) to remove ZnCl₂ and extracted with DCM (3×50 ml). The combined organic layers were dried over MgSO₄, and concentrated in vacuo. Finally, the residue was subjected to column chromatography on silica-gel and elusion with petroleum ether/ethyl acetate (1:1) furnished the N-aryl sulfonfyl amidines product as white solids in good to excellent yields (67-91%)

4-methyl-N-(morpholino(phenyl)methylene)benzenesulfonamide (3a): white solid (98%); m.p. 166-167 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 8 Hz, 2H), 7.36-7.32 (m, 2H), 7.29-7.25 (m, 2H), 7.07-7.02 (m, 3H), 3.85 (t, J = 4.8 Hz, 2H), 3.69 (t, J = 4.8 Hz, 2H), 3.46 (t, J = 4.8 Hz, 2H), 3.04 (t, J = 4.8 Hz, 2H), 2.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.9, 141.7, 140.6, 130.3, 130.0, 128.8, 128.4, 127.3, 126.5, 66.7, 66.3, 48.2, 45.2, 21.4; Anal. Calcd. for C₁₈H₂₀N₂O₃S: C, 62.77; H, 5.85; N, 8.13; S, 9.31 Found: C, 62.69; H, 5.91; N, 8.07; S, 9.36.

4-methyl-N-(morpholino(p-tolyl)methylene)benzenesulfonamide (3b): white solid (96%); m.p. 148-150 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 8 Hz, 2H), 7.10 (d, J = 8 Hz, 2H), 7.06 (d, J = 8 Hz, 2H), 6.98 (d, J = 8 Hz, 2H), 3.83 (t, J = 4.8 Hz, 2H), 3.68 (t, J = 4.8 Hz, 2H), 3.47 (t, J = 4.8 Hz, 2H), 3.07 (t, J = 4.8 Hz, 2H), 2.31 (s, 3H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.8, 141.7, 141.2, 139.7, 130.6, 128.9, 128.6, 126.8, 126.5, 66.7, 66.3, 48.2, 45.1, 21.4, 21.4; Anal. Calcd. for C₁₉H₂₂N₂O₃S: C, 63.66; H, 6.19; N, 7.82; S, 8.95 Found: C, 63.60; H, 6.24; N, 7.77; S, 9.03.
7\textsuperscript{2}-(4-(dimethylamino)phenyl)(morpholino)methylene)-4-methylbenzenesulfonamide (3c): white solid (82\%); m.p. 129-132 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.50 (d, \(J = 8\) Hz, 2H), 7.06-7.02 (m, 4H), 6.55 (d, \(J = 8\) Hz, 2H), 3.77-3.49 (m, 6H), 3.18-3.17 (m, 2H), 2.92 (s, 6H), 2.28 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 167.2, 151.4, 141.4, 140.3, 129.6, 129.4, 128.9, 128.8, 127.3, 66.7, 66.5, 48.4, 45.2, 40.1, 21.4; Anal. Calcd. for C\textsubscript{29}H\textsubscript{25}N\textsubscript{5}O\textsubscript{5}S: C, 61.99; H, 6.50; N, 10.84; S, 8.27 Found: C, 61.89; H, 6.57; N, 10.77; S, 8.23.

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\text{N-((4-isopropylphenyl)(morpholino)methylene)-4-methylbenzenesulfonamide (3d): white solid (78\%); m.p. 120-122 °C;} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.35 (d, \(J = 8\) Hz, 2H), 7.09 (d, \(J = 8\) Hz, 2H), 7.00 (d, \(J = 8\) Hz, 2H), 6.94 (d, \(J = 8\) Hz, 2H), 3.87 (t, \(J = 4.8\) Hz, 2H), 3.70 (t, \(J = 4.8\) Hz, 2H), 3.47 (t, \(J = 4.8\) Hz, 2H), 3.06 (t, \(J = 4.8\) Hz, 2H), 2.84 (sep, \(J = 6.8\) Hz, 1H), 2.28 (S, 3H), 1.19 (d, \(J = 6.8\) Hz, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 166.2, 150.9, 141.6, 140.5, 128.8, 128.4, 126.6, 126.4, 126.3, 66.7, 66.4, 48.3, 45.1, 33.9, 23.8, 21.4; Anal. Calcd. for C\textsubscript{21}H\textsubscript{18}N\textsubscript{5}O\textsubscript{3}S: C, 65.26; H, 6.78; N, 7.25; S, 8.30 Found: C, 65.19; H, 6.79; N, 7.19; S, 8.26.

4-methyl-N-(morpholino(naphthalen-2-yl)methylene)benzenesulfonamide (3e): white solid (85\%); m.p. 92-93\textsuperscript{3}C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.73 (d, \(J = 8\) Hz, 2H), 7.44 (d, \(J = 8.4\) Hz, 2H), 7.28-7.19 (m, 4H), 7.09-7.04 (m, 3H), 3.84 (t, \(J = 4.8\) Hz, 2H), 3.69 (t, \(J = 4.8\) Hz, 2H), 3.48 (t, \(J = 4.8\) Hz, 2H), 3.06 (t, \(J = 4.8\) Hz, 2H), 2.31 (S, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 164.7, 143.5, 142.2, 140.4, 139.2, 129.7, 129.0, 128.9, 128.5, 128.4, 127.9, 127.6, 127.4, 126.5, 126.4, 66.6, 66.3, 48.2, 45.2, 21.5; Anal. Calcd. for C\textsubscript{22}H\textsubscript{22}N\textsubscript{5}O\textsubscript{3}S: C, 66.98; H, 5.62; N, 7.10; S, 8.13 Found: C, 66.89; H, 5.70; N, 7.07; S, 8.06.
**4-methyl-N-(morpholino(quinolin-2-yl)methylene)benzenesulfonamide (3f):** white solid (85%); m.p. 123-127 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.20 (d, $J = 8.4$ Hz, 1H), 7.87 (d, $J = 8$ Hz, 1H), 7.81 (d, $J = 8$ Hz, 1H), 7.70-7.67 (m, 1H), 7.57-7.53 (m, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 6.97 (d, $J = 8$ Hz, 2H), 3.91 (t, $J = 4.8$ Hz, 2H), 3.75 (t, $J = 4.8$ Hz, 2H), 3.51 (t, $J = 4.8$ Hz, 2H), 3.02 (t, $J = 4.8$ Hz, 2H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.0, 142.0, 140.1, 136.7, 130.9, 130.3, 129.5, 128.9, 128.8, 128.0, 127.9, 127.9, 126.7, 121.1, 66.5, 66.3, 48.0, 45.1, 21.4; Anal. Calcd. for C$_{23}$H$_{21}$N$_3$O$_3$: C, 63.78; H, 5.35; N, 10.63; S, 8.11 Found: C, 63.72; H, 5.41; N, 10.51; S, 8.03.

**N-([1,1'-biphenyl]-4-yl(morpholino)methylene)-4-methylbenzenesulfonamide (3g):** white solid (75%); m.p. 152-156 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.51-7.44 (m, 5H), 7.41-7.38 (m, 2H), 7.34-7.30 (m, 2H), 7.15 (d, $J = 8.4$ Hz, 2H), 7.04 (d, $J = 8$ Hz, 2H), 3.88 (t, $J = 4.8$ Hz, 2H), 3.71 (t, $J = 4.8$ Hz, 2H), 3.50 (t, $J = 4.8$ Hz, 2H), 3.12 (t, $J = 4.8$ Hz, 2H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.8, 142.9, 141.8, 140.6, 139.9, 130.9, 130.1, 129.7, 128.9, 127.9, 127.1, 127.1, 126.6, 66.8, 66.4, 48.3, 45.2, 21.5; Anal. Calcd. for C$_{24}$H$_{24}$N$_3$O$_3$: C, 68.55; H, 5.75; N, 6.66; S, 7.63 Found: C, 68.47; H, 5.71; N, 6.58; S, 7.59.

**N-((4-hydroxyphenyl)(morpholino)methylene)benzenesulfonamide (3h)**

N-((3,4-dimethoxyphenyl)(morpholino)methylene)-4-methylbenzenesulfonamide (3i): white solid (87%); m.p. 68-69 °C; 1H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8 Hz, 2H), 7.06 (d, J = 8 Hz, 2H), 6.77 (d, J = 8.4 Hz, 1H), 6.72 (dd, J = 8.2 Hz, J = 1.6 Hz, 1H), 6.50 (d, J = 1.6 Hz, 1H), 3.89-3.84 (m, 5H), 3.81-3.70 (m, 5H), 3.49 (t, J = 4.8 Hz, 2H), 3.13 (t, J = 4.8 Hz, 2H), 2.29 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 165.9, 150.4, 148.8, 141.7, 140.7, 130.9, 128.8, 126.6, 123.3, 120.7, 110.6, 66.8, 66.4, 55.9, 55.8, 48.5, 45.3, 21.4; Anal. Calcd. for C₂₀H₂₄N₂O₅S: C, 59.39; H, 5.98; N, 6.93; S, 7.93 Found: C, 59.31; H, 6.04; N, 6.88; S, 7.87.

N-((4-chlorophenyl)(morpholino)methylene)-4-methylbenzenesulfonamide (3j)

N-((4-bromophenyl)(morpholino)methylene)-4-methylbenzenesulfonamide (3k)
\(N\)-((3-bromophenyl)(morpholino)methylene)-4-methylbenzenesulfonamide (3l)


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\begin{align*}
&\text{O}_2\text{N} \\
&\text{N} \\
&\text{O} \\
&\text{N} \\
&\text{S} \\
&\text{O} \\
&\text{N} \\
&\text{O}
\end{align*}
\]

4-methyl-\(N\)-(morpholino(4-nitrophenyl)methylene)benzenesulfonamide (3m)

white solid (69%); m.p. 170-172°C (ref [5] 171-173 °C)

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\begin{align*}
&\text{NO}_2 \\
&\text{N} \\
&\text{O} \\
&\text{N} \\
&\text{S} \\
&\text{O} \\
&\text{N} \\
&\text{O}
\end{align*}
\]

\(N\)-((4-isopropylphenyl)(morpholino)methylene)-4-nitrobenzenesulfonamide (3n): white solid (65%); m.p. 206-207 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.16 (d, \(J = 8.8\) Hz, 2H), 7.77 (d, \(J = 8.8\) Hz, 2H), 7.22 (d, \(J = 8\) Hz, 2H), 7.07 (d, \(J = 8\) Hz, 2H), 3.98 (t, \(J = 4.8\) Hz, 2H), 3.82 (t, \(J = 4.8\) Hz, 2H), 3.60 (t, \(J = 4.8\) Hz, 2H), 3.21 (t, \(J = 4.8\) Hz, 2H), 2.98-2.92 (sep, \(J = 6.8\) Hz, 1H), 1.29 (d, \(J = 6.8\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.6, 151.7, 149.1, 140.1, 128.2, 127.9, 127.3, 126.7, 123.5, 66.7, 66.3, 48.6, 45.4, 34.0, 23.8; Anal. Calcd. for C\(_{20}\)H\(_{22}\)N\(_2\)O\(_5\): C, 57.54; H, 5.55; N, 10.07; S, 7.68 Found: C, 57.50; H, 5.47; N, 10.06; S, 7.77.

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\begin{align*}
&\text{NO}_2 \\
&\text{N} \\
&\text{O} \\
&\text{N} \\
&\text{S} \\
&\text{O} \\
&\text{N} \\
&\text{O}
\end{align*}
\]

\(N\)-(morpholino(naphthalen-2-yl)methylene)-4-nitrobenzenesulfonamide (3o): white solid (68%); m.p. 192-196 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 (d, \(J = 8.8\) Hz, 2H), 7.89 (t, \(J = 8.4\) Hz, 2H), 7.75 (d, \(J = 8\) Hz, 1H), 7.72 (d, \(J = 8.8\) Hz, 2H), 7.65-7.56 (m, 3H), 7.25 (dd, \(J = 8.4\) Hz, \(J = 1.6\) Hz, 2H), 4.04 (t, \(J = 4.8\) Hz, 2H), 3.86 (t, \(J = 4.8\) Hz, 2H), 3.60 (t, \(J = 4.8\) Hz, 2H), 3.24 (t, \(J = 4.8\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.3, 149.1, 148.9, 133.5,
132.2, 128.7, 128.3, 128.1, 128.0, 128.0, 127.8, 127.4, 127.4, 123.6, 123.4, 66.7, 66.3, 48.6, 45.5; Anal. Calcd. for C$_{21}$H$_{19}$N$_3$O$_3$S: C, 59.28; H, 4.50; N, 9.88; O, 18.80; S, 7.54 Found: C, 59.34; H, 4.47; N, 10.02; S, 7.59.

![Chemical Structure](image)

$N$-(2-((1,1'-biphenyl)-4-yl)-1-morpholinoethylidene)-4-methylbenzenesulfonamide (3p)

white solid (70%); m.p. 140-143°C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, $J = 8$ Hz, 2H), 7.58 (d, $J = 8$ Hz, 2H), 7.54 (d, $J = 8$ Hz, 2H), 7.46 (t, $J = 8$ Hz, 2H), 7.39-7.36 (m, 1H), 7.25 (d, $J = 8$ Hz, 4H), 4.50 (s, 2H), 3.84 (t, $J = 4.8$ Hz, 2H), 3.67 (t, $J = 4.8$ Hz, 2H), 3.41 (s, 4H), 2.40 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.8, 142.9, 141.8, 140.5, 139.8, 130.9, 130.1, 129.7, 128.9, 127.9, 127.2, 127.1, 126.4, 66.3, 66.1, 46.3, 44.2, 36.4, 21.5; Anal. Calcd. for C$_{25}$H$_{26}$N$_3$O$_3$S: C, 69.10; H, 6.03; N, 6.45; S, 7.38 Found: C, 69.04; H, 5.97; N, 6.50; S, 7.46.
4-methyl-N-(morpholino(phenyl)methylene)benzenesulfonamide (3a)
4-methyl-N-(morpholino(p-tolyl)methylene)benzenesulfonamide

N-((4-(dimethylamino)phenyl)(morpholino)methylene)-4methylbenzenesulfonamide(3c)
$N\text{-}(4\text{-isopropylphenyl})(\text{morpholino})\text{methylene}\text{-}4\text{-methylbenzenesulfonamide (3d)}$
4-methyl-N-(morpholino(naphthalen-2-yl)methylene)benzenesulfonamide (3e)
4-methyl-N-(morpholino(quinolin-2-yl)methylene)benzenesulfonamide (3f)
$N\text{-}([1,1\text{'-biphenyl}]\text{-}4\text{-yl(morpholino)methylene})\text{-}4\text{-methylbenzenesulfonamide (3g)}$
\(N-((3,4\text{-dimethoxyphenyl})(\text{morpholino})\text{methylene})-4\text{-methylbenzenesulfonamide (3i)}\)
$N$-((4-isopropylphenyl)(morpholino)methylene)-4-nitrobenzenesulfonamide (3n)
$N$-(morpholino(naphthalen-2-yl)methylene)-4-nitrobenzenesulfonamide(3o)
N-(2-([1,1'-biphenyl]-4-yl)-1-morpholinoethylidene)-4-methylbenzenesulfonamide (3p)
References


