SUPPLEMENTARY MATERIAL

Regioselective Synthesis of 2, 5-Disubstituted Pyrroles via Stepwise Iododesilylation and Coupling Reactions

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General Information:

All the reactions were carried out under N2. The starting chemicals and reagents are used without further purification. n-Hexane was distilled over CaH2, DMF was distilled under reduced pressure over BaO, and THF was distilled over sodium and benzophenone ketyl. The reactions were monitored by thin-layer chromatography (TLC) using silica gel plates. Column chromatography were carried out using silica gel (200-300 mesh size). The eluent are selected in different proportions of n-hexane, ether and ethyl acetate. All products were characterized by NMR, GC-MS spectra. 1H and 13C NMR were recorded on a Bruker Avance (500 MHz for 1H and 125 MHz for 13C). Chemical shifts (δ) are given in part per million (ppm) on the δ scale, referenced to the residual proton resonance of the solvents (7.26 for CDCl3; 2.05 for (CD3)2CO) or to the residual carbon resonance of the solvent (206.26 for (CD3)2CO).
Experimental Section

*N, N-Dimethyl-1H-pyrrole-1-sulfonamide (2)*

\[ \begin{align*}
&\text{NaH (1.73 g, 43.2 mmol) was washed with } n\text{-hexane (3×10 mL) and DMF (70 mL) was added. This NaH-DMF mixture was cooled to 0°C, and a solution of pyrrole (1) (2.42 g, 36 mmol) in DMF (20 mL) was added dropwise. After addition, the reaction was stirred at 0°C for 2.5 h. ClSO2NMe2 (3.86 ml, 36 mmol) in DMF (20 mL) was added dropwise, and the mixture allowed to warm to room temperature in 2 h. The resulting mixture was then poured into ice-water (200 mL), and Et2O (200 mL) was added. The aqueous layer was extracted with Et2O (2×100 mL). The combined ethereal solutions washed with water (2×200 mL) and brine (200 mL) and dried over MgSO4. The solvent was removed in vacuo and the crude mixture was purified by chromatography using } n\text{-hexane : ether (30:1) as eluent in 70% yield (4.39 g) of white crystals; mp: 61-62 °C; }^1\text{H NMR (500 MHz, CDCl}_3\text{) }\delta 2.79 \text{ (s, 6H), 6.31 (t, 1H, } J = 2 \text{ Hz), 7.09 (t, 1H, } J = 2 \text{ Hz);} ^13\text{C NMR (125 MHz, CDCl}_3\text{) }\delta 38.3, 111.7, 120.9. \text{ HRMS (ESI-TOF) for C}_6\text{H}_{10}\text{N}_2\text{O}_2\text{S }[\text{M+H}]^+: \text{calcd, 175.0536. found 175.0536.}
\end{align*} \]

*N, N-Dimethyl-2, 5-bis(trimethylsilyl)-1H-pyrrole-1-sulfonamide (3)*

\[ \begin{align*}
&\text{A solution of 2,2,6,6-tetramethylpiperidine (TMP) (8.05 mL, 47.4 mmol) in THF (60 mL) was cooled to -78°C and n-butyllithium (18.5 ml/2.5 M, 46.8 mmol) was slowly added, keeping temperature under -65°C. The resulting mixture was stirred for 1 h at -78°C. N, N-Dimethyl-1H-pyrrole-1-sulfonamide (2) (3.14 g, 18 mmol) in THF (20 mL) was then slowly added and the mixture stirred for 1.5 h at -78°C. Trimethylchlorosilane (6 mL, 46.8 mmol) in THF (15 mL) was slowly added. And the reaction mixture stirred for 30 min at -78°C, then two hours at room temperature. The reaction mixture was diluted with ether (100 mL) and poured into water (100 mL). The aqueous layer was extracted with ether (3×50 mL) and the combined ethereal solution washed with water (2×100 mL) and brine (100 mL) and dried over MgSO4. The solvent was removed in vacuo and the crude mixture was purified by chromatography using } n\text{-hexane : ether (30:1) as eluent in 98% yield (5.62 g) of white crystals; mp: 81-83°C; }^1\text{H NMR (500 MHz, CDCl}_3\text{) }\delta 0.30 \text{ (s, 18H), 2.62 (s, 6H), 6.56 (s, 2H);} ^13\text{C NMR (125 MHz, CDCl}_3\text{) }\delta 0.6, 37.7, 125.2, 142.8. \text{ HRMS (ESI-TOF) for C}_12\text{H}_26\text{N}_2\text{O}_2\text{SSi}_2\text{ [M+H]}^+: \text{calcd, 319.1326. found 319.1326.}
\end{align*} \]

General Procedure for the Synthesis of Compound 4a-4b

2
2-Iodo-\(N\)-dimethyl-5-(trimethylsilyl)-1\(H\)-pyrrole-1-sulfonamide (4a)

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{N} & \quad \text{I} \\
& \quad \text{SO}_2\text{NMe}_2
\end{align*}
\]

A mixture of 3 (159 mg, 0.5 mmol), NIS (138 mg, 0.6 mmol), \(\text{AgNO}_3\) (15 mg, 0.09 mmol) and \(\text{CH}_2\text{Cl}_2\) (20 mL) was stirred at room temperature for 15 h. The reaction mixture was diluted with ether (20 mL) and poured into water (10 mL). The aqueous layer was extracted with ether (3×20 mL), and the resulting organic layers were washed with sodium thiosulfate (20 mL), water (2×40 mL) and brine (40 mL) and dried over \(\text{Na}_2\text{SO}_4\). The solvent was removed in vacuo and the crude mixture was purified by chromatography using \(n\)-hexane : ether (30:1) as eluent in 84% yield (156 mg) of white crystals; mp: 48-49°C; \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.30 (s, 9H), 2.88 (s, 6H), 6.43 (d, \(J = 3.5\) Hz, 1H), 6.60 (d, \(J = 3.5\) Hz, 1H); \(^{13}\text{C}\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 0.6, 37.9, 125.2, 126.3, 144.5. HRMS (ESI-TOF) for C\(_9\)H\(_{17}\)IN\(_2\)O\(_2\)SSi [\(\text{M}+\text{H}\)^+] : calcd, 372.9897. found 372.9893.

2-Bromo-\(N\)-dimethyl-5-(trimethylsilyl)-1\(H\)-pyrrole-1-sulfonamide (4b)

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{N} & \quad \text{Br} \\
& \quad \text{SO}_2\text{NMe}_2
\end{align*}
\]

A mixture of 3 (159 mg, 0.5 mmol), NBS (107 mg, 0.6 mmol) and THF (20 mL) was stirred at 0°C for 6 h. The reaction mixture was diluted with ether (20 mL) and poured into water (10 mL). The aqueous layer was extracted with ether (3×20 mL), and the resulting organic layers were washed with sodium thiosulfate (20 mL), water (2×40 mL) and brine (40 mL) and dried over \(\text{Na}_2\text{SO}_4\). The solvent was removed in vacuo and the crude mixture was purified by chromatography using \(n\)-hexane : ether (30:1) as eluent in 62% yield (101 mg) of colorless oil; \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.30 (s, 9H), 2.91 (s, 6H), 6.38 (d, \(J = 3.5\) Hz, 1H), 6.42 (d, \(J = 3.5\) Hz, 1H); \(^{13}\text{C}\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 0.5, 37.8, 103.6, 117.6, 123.2, 141.7. HRMS (ESI-TOF) for C\(_9\)H\(_{17}\)BrN\(_2\)O\(_2\)SSi [\(\text{M}+\text{H}\)^+] : calcd, 325.0036. found 325.0034.

**General Procedure for the Synthesis of Compound 5a-5b**

A mixture of compound 4a (37.2 mg, 0.1 mmol), terminal alkynes (0.15 mmol), \(\text{CuI}\) (5 mg, 0.03 mmol), \(\text{PdCl}_2(\text{PPh}_3)_2\) (8 mg, 0.01 mmol), \(\text{Et}_3\text{N}\) (1 mL) and THF (1 mL) was stirred at 30°C for 2 h. The reaction mixture was diluted with ether (10 mL) and poured into water (10 mL). The aqueous layer was extracted with ether (3×10 mL), and the resulting organic layers were washed with water and brine and dried over \(\text{Na}_2\text{SO}_4\). The solvent was removed in vacuo and the crude mixture was purified by chromatography using suitable solvent as eluent.

\(N, N\)-Dimethyl-2-(trimethylsilyl)-5-(2-(trimethylsilyl)ethynyl)-1\(H\)-pyrrole-1-
sulfonamide (5a)

\[
\text{Me}_3\text{Si} \quad \text{N} \quad \equiv \quad \text{Si} \quad \text{SO}_2\text{NMe}_2
\]

75% yield of white crystals; mp: 84-85°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.24 (s, 9H), 0.30 (s, 9H), 2.91 (s, 6H), 6.36 (d, \(J = 3.5\) Hz, 1H), 6.63 (d, \(J = 3.5\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) -0.2, 0.5, 38.2, 95.4, 101.0, 118.8, 122.0, 122.1, 141.2. HRMS (ESI-TOF) for C\(_{14}\)H\(_{26}\)N\(_2\)O\(_2\)SSi \([\text{M+H]}^+\): calcd, 343.1326. found 343.1327.

2-(3-Hydroxy-3-methylbut-1-yn-1-yl)-N, N-dimethyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (5b)

\[
\text{Me}_3\text{Si} \quad \text{N} \quad \equiv \quad \text{OH} \quad \text{SO}_2\text{NMe}_2
\]

80% yield of white crystals; mp: 84-85°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.30 (s, 9H), 1.60 (s, 6H), 2.90 (s, 6H), 6.39 (d, \(J = 3.5\) Hz), 6.56 (d, \(J = 3.5\) Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 0.4, 31.1, 38.2, 65.6, 73.5, 99.6, 118.5, 121.1, 121.2, 140.9. HRMS (ESI-TOF) for C\(_{14}\)H\(_{24}\)N\(_2\)O\(_3\)SSi \([\text{M+H]}^+\): calcd, 329.1350. found 329.1350.

**General Procedure for the Synthesis of Compound 6a-6g**

A mixture of compound 4a (37.2 mg, 0.1 mmol), aromatic boronic acid (0.15 mmol), 2M Na\(_2\)CO\(_3\) (0.2 mL), Pd(PPh\(_3\))\(_4\) (12 mg, 0.01 mmol) and the mixture solvent of toluene: methanol (1:1, 3.5 mL) was stirred at 100°C for 2 h. (O\(_2\) in the reaction system was strictly removed by nitrogen purging for 30 minutes or vacuum degassing under N\(_2\) filling cycles before the reaction started). The reaction mixture was diluted with ether (20 mL) and poured into water (10 mL). The aqueous layer was extracted with ether (3×20 mL), and the resulting organic layers were washed with water and brine and dried over Na\(_2\)SO\(_4\). The solvent was removed in vacuo and the crude mixture was purified by chromatography using suitable organic solvent as eluent.

\(N, N\)-Dimethyl-2-phenyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6a)

\[
\text{Me}_3\text{Si} \quad \text{N} \quad \equiv \quad \text{SO}_2\text{NMe}_2
\]

84% yield of white crystals; mp: 74-75°C; \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)CO) \(\delta\) 0.33 (s, 9H), 2.29 (s, 6H), 6.26 (d, \(J = 3.5\) Hz, 1H), 6.53 (d, \(J = 3\) Hz, 1H), 7.43 (ddd, \(J = 8.0\) Hz, \(J = 5.0\) Hz, \(J = 3.0\) Hz, 3H), 7.49 (dt, \(J = 5\) Hz, \(J = 2\) Hz, 2H); \(^{13}\)C NMR (125 MHz, (CD\(_3\))\(_2\)CO) \(\delta\) 0.9, 36.5, 115.9, 122.9, 128.4, 129.0, 131.2, 133.3, 139.6, 139.9.
HRMS (ESI-TOF) for C_{15}H_{22}N_{2}O_{2}SSi [M+H]^+: calcd, 323.1244. found 323.1240.

2-(4-Methoxyphenyl)-N, N-dimethyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6b)

78% yield of white crystals; mp: 169-170°C; ^1H NMR (500 MHz, CDCl_3) δ 0.34 (s, 9H), 2.30 (s, 6H), 3.83 (s, 3H), 6.19 (d, J = 3 Hz, 1H), 6.48 (d, J = 3 Hz, 1H), 6.91 (d, J = 9 Hz, 2H), 7.41 (d, J = 9 Hz, 2H); ^13C NMR (125 MHz, CDCl_3) δ 0.7, 36.5, 55.3, 113.0, 115.1, 122.0, 124.9, 131.9, 138.4, 139.8, 159.6. HRMS (ESI-TOF) for C_{16}H_{24}N_{2}O_{3}SSi [M+H]^+: calcd, 353.1350. found 353.1351.

2-(4-Chlorophenyl)-N, N-dimethyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6c)

73% yield of white crystals; mp: 169-170°C; ^1H NMR (500 MHz, CDCl_3) δ 0.34 (s, 9H), 2.32 (s, 6H), 6.24 (d, J = 3.5 Hz, 1H), 6.49 (d, J = 3.5 Hz, 1H), 7.36 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H); ^13C NMR (125 MHz, (CD_3)_2CO) δ 0.9, 36.7, 116.5, 123.1, 128.5, 132.1, 132.8, 134.6, 138.3, 140.6. HRMS (ESI-TOF) for C_{15}H_{21}ClN_{2}O_{2}SSi [M+H]^+: calcd, 357.0854. found 357.0853.

2-(4-Acetylphenyl)-N, N-dimethyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6d)

75% yield of white crystals; mp: 114-115°C; ^1H NMR (500 MHz, CDCl_3) δ 0.36 (s, 9H), 2.29 (s, 6H), 2.63 (s, 3H), 6.30 (d, J = 3.5 Hz, 1H), 6.52 (d, J = 3.5 Hz, 1H), 7.61 (d, J = 8.5 Hz, 2H), 7.98 (d, J = 8.5 Hz, 2H); ^13C NMR (125 MHz, CDCl_3) δ 0.7, 26.7, 36.7, 116.2, 122.4, 127.6, 130.5, 136.4, 137.4, 137.7, 141.5, 197.6. HRMS (ESI-TOF) for C_{17}H_{24}N_{2}O_{3}SSi [M+H]^+: calcd, 365.1350. found 365.1352.

2-(4-Hydroxyphenyl)-N, N-dimethyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6e)

70% yield of white crystals; mp: 126-127°C; ^1H NMR (500 MHz, CDCl_3) δ 0.34 (s, 9H), 2.31 (s, 6H), 6.19 (d, J = 3.5 Hz, 1H), 6.47 (d, J = 3.5 Hz, 1H), 6.84 (d, J = 8.5
Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H); 13C NMR (125 MHz, CDCl3) δ 0.7, 36.5, 114.5, 115.1, 122.0, 125.1, 132.1, 138.3, 139.9, 155.7. HRMS (ESI-TOF) for C15H22N2O3SSi [M+H]+: calcd, 339.1193. found 339.1194.

2-(4-Cyanophenyl)-N,N-dimethyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6f)

72% yield of white crystals; mp: 167-168°C; 1H NMR (500 MHz, CDCl3) δ 0.35 (s, 9H), 2.31 (s, 6H), 6.31 (d, J = 3.5 Hz, 1H), 6.52 (d, J = 3.5 Hz, 1H), 7.62 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H); 13C NMR (125 MHz, CDCl3) δ 0.6, 36.7, 111.7, 116.7, 118.6, 122.5, 130.8, 131.3, 136.9, 137.2, 142.0. HRMS (ESI-TOF) for C16H21N3O2SSi [M+H]+: calcd, 348.1197. found 348.1196.

N,N-Dimethyl-2-(3-nitrophenyl)-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6g)

60% yield of white crystals; mp: 138-141°C; 1H NMR (500 MHz, CDCl3) δ 0.36 (s, 9H), 2.36 (s, 6H), 6.35 (d, J = 3.5 Hz, 1H), 6.54 (d, J = 3.5 Hz, 1H), 7.57 (t, J = 8 Hz, 1H), 7.87 (dt, J = 8 Hz, J = 1.5 Hz, 1H), 8.22 (ddd, J = 8 Hz, J = 2 Hz, J = 1.5 Hz, 1H), 8.32 (t, J = 2 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ 0.6, 36.9, 116.8, 122.5, 122.9, 124.9, 128.5, 134.3, 136.2, 136.8, 141.8, 147.6. HRMS (ESI-TOF) for C15H21N3O4SSi [M+H]+: calcd, 368.1095. found 368.1093.

Representative Procedure for the Synthesis of Compound 7a-7d

A mixture of 2-aryl-N,N-dimethyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (1 mmol), NIS (292.5 mg, 1.3 mmol), AgNO3 (34 mg, 0.2 mmol) and CH3CN (30 mL) was stirred at 35°C for 1 h. The reaction mixture was diluted with ether (20 mL) and poured into water (10 mL). The aqueous layer was extracted with ether (3×20 mL), and the resulting organic layers were washed with sodium thiosulfate, water and brine and dried over Na2SO4. The solvent was removed in vacuo and the crude mixture was purified by chromatography using suitable organic solvent as eluent.

2-Iodo-N,N-dimethyl-5-phenyl-1H-pyrrole-1-sulfonamide (7a)

71% yield of white crystals; mp: 86-87°C; 1H NMR (500 MHz, CDCl3) δ 2.62 (s, 6H),

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6.17 (d, J = 3.5 Hz, 1H), 6.65 (d, J = 3.5 Hz, 1H), 7.34-7.39 (m, 3H), 7.40-7.42 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 37.9, 116.9, 125.9, 127.5, 128.2, 130.2, 133.4, 141.6. HRMS (ESI-TOF) for C$_{12}$H$_{13}$IN$_2$O$_2$S $[M+H]^+$: calcd, 376.9815. found 376.9823.

2-Iodo-5-(4-methoxyphenyl)-N, N-dimethyl-1H-pyrrole-1-sulfonamide (7b)

86% yield of white crystals; mp: 199-200°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 2.62 (s, 6H), 3.83 (s, 3H), 6.12 (d, J = 3.5 Hz, 1H), 6.63 (d, J = 3.5 Hz, 1H), 6.89 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 37.9, 55.3, 112.9, 116.6, 125.8, 125.9, 131.6, 159.6. HRMS (ESI-TOF) for C$_{13}$H$_{15}$IN$_2$O$_3$S $[M+H]^+$: calcd, 406.9921. found 406.9911.

2-(4-Chlorophenyl)-5-iodo-N, N-dimethyl-1H-pyrrole-1-sulfonamide (7c)

84% yield of white crystals; mp: 111-112°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 2.67 (s, 6H), 6.16 (d, J = 3.5 Hz, 1H), 6.66 (d, J = 3.5 Hz, 1H), 7.33 (s, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 38.1, 117.2, 126.1, 127.7, 131.4, 131.9, 134.3, 140.5. HRMS (ESI-TOF) for C$_{12}$H$_{12}$ClIN$_2$O$_2$S $[M+H]^+$: calcd, 410.9425. found 410.9422.

2-(4-Acetylphenyl)-5-iodo-N, N-dimethyl-1H-pyrrole-1-sulfonamide (7d)

70% yield of white crystals; mp: 182-184°C; $^1$H NMR (500 MHz, CDCl$_3$) δ 2.62 (s, 3H), 2.69 (s, 6H), 6.23 (d, J = 3.5 Hz, 1H), 6.69 (d, J = 3.5 Hz, 1H), 7.51 (d, J = 8.5 Hz, 2H), 7.95 (d, J = 8.5 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 26.6, 38.2, 117.8, 126.4, 127.5, 130.1, 136.3, 138.1, 140.9, 197.5. HRMS (ESI-TOF) for C$_{14}$H$_{15}$IN$_2$O$_3$S $[M+H]^+$: calcd, 418.9921. found 418.9918.

General Procedure for the Synthesis of Compound 8a-8j

A mixture of 2-iodo-N, N-dimethyl-5-aryl-1H-pyrrole-1-sulfonamide (0.1 mmol), aromatic boronic acid (0.15 mmol), 2M Na$_2$CO$_3$ (0.2 mL), Pd(PPh$_3$)$_4$ (12 mg, 0.01 mmol) and toluene: methanol (1:1, 3.5 mL) was stirred at 100°C for 2 h (O$_2$ in the reaction system was strictly removed by nitrogen purging for 30 minutes or vacuum degassing under N$_2$ filling cycles before the reaction started). The reaction mixture
was diluted with ether (20 mL) and poured into water (10 mL). The aqueous layer was extracted with ether (3 x 20 mL), and the resulting organic layers were washed with water and brine and dried over Na₂SO₄. The solvent was removed in vacuo and the crude mixture was purified by chromatography using suitable organic solvent as eluent.

2,5-Bis(4-methoxyphenyl)-N, N-dimethyl-1H-pyrrole-1-sulfonamide (8a)

![Structure of 2,5-Bis(4-methoxyphenyl)-N, N-dimethyl-1H-pyrrole-1-sulfonamide (8a)](image)

83% yield of white crystals; mp: 192-193°C; ¹H NMR (500 MHz, CDCl₃) δ 2.33 (s, 6H), 3.84 (s, 6H), 6.21 (s, 2H), 6.93 (d, J = 9 Hz, 4H), 7.48 (d, J = 9 Hz, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 37.2, 55.2, 113.2, 113.8, 126.4, 130.5, 139.2, 159.2. HRMS (ESI-TOF) for C₂₀H₂₂N₂O₄S [M+H]^+: calcd, 387.1373. found 387.1372.

2-(4-Hydroxyphenyl)-5-(4-methoxyphenyl)-N, N-dimethyl-1H-pyrrole-1-sulfonamide (8b)

![Structure of 2-(4-Hydroxyphenyl)-5-(4-methoxyphenyl)-N, N-dimethyl-1H-pyrrole-1-sulfonamide (8b)](image)

86% yield of white crystals; mp: 233-234°C; ¹H NMR (500 MHz, CDCl₃) δ 2.33 (s, 6H), 3.84 (s, 3H), 4.98 (s, 1H), 6.21 (s, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 37.2, 55.3, 113.2, 113.8, 114.7, 126.4, 126.5, 130.5, 130.7, 139.2, 155.3, 159.2. HRMS (ESI-TOF) for C₁⁹H₂₀N₂O₄S [M+H]^+: calcd, 373.1217. found 373.1229.

2,5-Bis(4-chlorophenyl)-N, N-dimethyl-1H-pyrrole-1-sulfonamide (8c)

![Structure of 2,5-Bis(4-chlorophenyl)-N, N-dimethyl-1H-pyrrole-1-sulfonamide (8c)](image)

81% yield of white crystals; mp: 126-127°C; ¹H NMR (500 MHz, CDCl₃) δ 2.34 (s, 6H), 6.30 (s, 2H), 7.38 (d, J = 8.5 Hz, 4H), 7.49 (d, J = 8.5 Hz, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 37.2, 114.9, 128.0, 130.4, 131.9, 133.8, 139.1. HRMS (ESI-TOF) for C₁₈H₁₆Cl₂N₂O₂S [M+H]^+: calcd, 395.0382. found 395.0382.

2-(4-Chlorophenyl)-5-(4-methoxyphenyl)-N,N-dimethyl-1H-pyrrole-1-sulfonamide (8d)

![Structure of 2-(4-Chlorophenyl)-5-(4-methoxyphenyl)-N,N-dimethyl-1H-pyrrole-1-sulfonamide (8d)](image)
75% yield of white crystals; mp: 211-212°C; ¹H NMR (500 MHz, CDCl₃) δ 2.33 (s, 6H), 3.85 (s, 3H), 6.24 (d, J = 1.5 Hz, 1H), 6.27 (d, J = 1.5 Hz, 1H), 6.94 (d, J = 9 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.49 (dd, J = 8.5 Hz, J = 5 Hz, 4H), ¹³C NMR (125 MHz, CDCl₃) δ 37.2, 55.3, 113.3, 113.9, 114.8, 125.8, 127.9, 130.3, 130.7, 132.4, 133.4, 138.5, 139.9, 159.4. HRMS (ESI-TOF) for C₁₉H₁₉ClN₂O₃S [M+H]⁺: calcd, 391.0878. found 391.0878.

2-(4-Chlorophenyl)-5-(4-cyanophenyl)-N,N-dimethyl-1H-pyrrole-1-sulfonamide (8e)

66% yield of white crystals; mp: 193-195°C; ¹H NMR (500 MHz, CDCl₃) δ 2.34 (s, 6H), 6.35 (d, J = 3.5 Hz, 1H), 6.40 (d, J = 3.5 Hz, 1H), 7.40 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.64-7.69 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 37.3, 110.9, 115.2, 116.3, 118.9, 128.2, 129.4, 130.5, 131.2, 131.6, 134.3, 138.0, 138.8, 139.9. HRMS (ESI-TOF) for C₁₉H₁₆ClN₃O₂S [M+Na]⁺: calcd, 408.0544. found 408.0540.

2-(4-Acetylphenyl)-5-(4-chlorophenyl)-N,N-dimethyl-1H-pyrrole-1-sulfonamide (8f)

68% yield of white crystals; mp: 199-200°C; ¹H NMR (500 MHz, CDCl₃) δ 2.34 (s, 6H), 2.63 (s, 3H), 6.34 (d, J = 3.5 Hz, 1H), 7.39 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 8.00 (d, J = 8.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 26.7, 37.3, 115.1, 115.8, 127.9, 128.2, 129.1, 130.5, 131.6, 134.0, 135.9, 138.0, 139.5, 139.8, 197.6. HRMS (ESI-TOF) for C₂₀H₁₉ClN₃O₃S [M+H]⁺: calcd, 403.0878. found 403.0871.

2-(4-Chlorophenyl)-5-(2-methoxyphenyl)-N,N-dimethyl-1H-pyrrole-1-sulfonamide (8g)

76% yield of colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 2.32(s, 6H), 3.88 (s, 3H), 6.25 (d, J = 3.5 Hz, 1H), 6.30 (d, J = 3.5 Hz, 1H), 6.94 (dd, J = 8 Hz, J = 1 Hz, 1H), 6.99 (dt, J = 7.5 Hz, J = 1 Hz, 1H), 7.33-7.38 (m, 4H), 7.53 (d, J = 8.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 36.9, 55.5, 110.4, 113.7, 114.5, 119.9, 123.2, 127.9, 129.5, 131.0, 131.1, 132.0, 133.7, 136.0, 136.6, 157.7. HRMS (ESI-TOF) for C₁₉H₁₉ClN₃O₃S [M+H]⁺: calcd, 391.0878. found 391.0890.
2-(4-Acetylphenyl)-N,N-dimethyl-5-phenyl-1H-pyrrole-1-sulfonamide (8h)

92% yield of white crystals; mp: 193-194°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.30 (s, 6H), 2.63 (s, 3H), 6.34 (d, \(J = 3.5\) Hz, 1H), 6.39 (d, \(J = 3.5\) Hz, 1H), 7.35-7.38 (m, 1H), 7.41-7.44 (m, 2H), 7.60 (dd, \(J = 8.5\) Hz, \(J = 1.5\) Hz, 2H), 7.67 (d, \(J = 8.5\) Hz, 2H), 8.00 (d, \(J = 8.5\) Hz, 2H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 26.6, 37.2, 37.4, 114.7, 115.6, 127.9, 128.1, 128.9, 129.3, 133.0, 135.7, 138.4, 139.3, 140.8, 197.6. HRMS (ESI-TOF) for C\(_{21}\)H\(_{22}\)N\(_2\)O\(_4\)S [M+H]\(^+\): calcd, 369.1267. Found 369.1276.

2-(4-Acetylphenyl)-5-(4-methoxyphenyl)-N,N-dimethyl-1H-pyrrole-1-sulfonamide (8i)

68% yield of white crystals; mp: 195-196°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.33 (s, 6H), 2.63 (s, 3H), 3.85 (s, 3H), 6.28 (d, \(J = 3.5\) Hz, 1H), 6.37 (d, \(J = 3.5\) Hz, 1H), 6.96 (d, \(J = 9\) Hz, 2H), 7.53 (d, \(J = 9\) Hz, 2H), 7.65 (d, \(J = 8.5\) Hz, 2H), 7.99 (d, \(J = 8.5\) Hz, 2H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 26.6, 37.2, 55.3, 113.4, 114.1, 115.7, 125.6, 127.9, 128.8, 130.7, 135.6, 138.6, 138.9, 140.6, 159.6, 197.6. HRMS (ESI-TOF) for C\(_{21}\)H\(_{22}\)N\(_2\)O\(_4\)S [M+H]\(^+\): calcd, 399.1373. Found 399.1377.

2-(4-Acetylphenyl)-5-(2-methoxyphenyl)-N,N-dimethyl-1H-pyrrole-1-sulfonamide (8j)

65% yield of white crystals; mp: 140-141°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.31 (s, 6H), 2.63 (s, 3H), 2.89 (s, 3H), 6.30 (d, \(J = 3.5\) Hz, 1H), 6.39 (d, \(J = 3.5\) Hz, 1H), 6.94-7.01 (m, 2H), 7.34-7.40 (m, 2H), 7.69 (d, \(J = 8.5\) Hz, 2H), 7.99 (d, \(J = 8.5\) Hz, 2H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 26.6, 37.0, 55.5, 110.5, 114.2, 115.4, 120.0, 122.9, 127.8, 129.5, 129.7, 131.2, 135.8, 136.7, 137.2, 138.3, 157.6, 197.7. HRMS (ESI-TOF) for C\(_{21}\)H\(_{22}\)N\(_2\)O\(_4\)S [M+H]\(^+\): calcd, 399.1373. Found 399.1374.

**General Procedure for the Synthesis of Compound 9a, 9c**

A mixture of 2, 5-diarly-N, N-dimethyl-1H-pyrrole-1-sulfonamide (0.2 mmol), TBAF (126 mg, 0.4 mmol) and DMF (5mL) was stirred at 130°C for 8 h. (O\(_2\) in the reaction system was strictly removed by nitrogen purging for 30 minutes or vacuum
degassing under N₂ filling cycles before the reaction started). The reaction mixture
was diluted with ether (20 mL) and poured into water (10 mL). The aqueous layer was
extracted with ether (3×15 mL), and the resulting organic layers were washed with
water and brine and dried over Na₂SO₄. The solvent was removed in vacuo and the
crude mixture was purified by chromatography using suitable organic solvent as
eluent.

2,5-Bis(4-methoxyphenyl)-\(N, N\)-dimethyl-1\(H\)-pyrrole-3-sulfonamide (9a)

\[
\text{SO}_2\text{NMe}_2
\]

52% yield of colorless oil; ¹H NMR (500 MHz, (CD₃)₂CO) δ 2.48 (s, 6H), 3.82 (s, 3H), 3.84 (s, 3H), 6.76 (d, \(J = 3\) Hz, 1H), 6.98 (dd, \(J = 9\) Hz, \(J = 7\) Hz, 4H), 7.66 (d, \(J = 9\) Hz, 2H), 7.72 (d, \(J = 9\) Hz, 2H), 10.93 (s, 1H); ¹³C NMR (125 MHz, (CD₃)₂CO) δ 37.8, 55.3, 108.1, 113.7, 114.8, 116.7, 124.3, 124.9, 126.3, 132.0, 135.2, 159.6, 160.5. HRMS (ESI-TOF) for C₂₀H₂₂N₂O₄S [2M+Na]⁺: calcd, 795.9212. found 795.2583.

2,5-Bis(4-chlorophenyl)-\(N, N\)-dimethyl-1\(H\)-pyrrole-3-sulfonamide (9c)

\[
\text{Cl}\text{SO}_2\text{NMe}_2
\]

54% yield of colorless oil; ¹H NMR (500 MHz, (CD₃)₂CO) δ 2.51 (s, 6H), 6.97 (d, \(J = 3\) Hz, 1H), 7.46 (dd, \(J = 11\) Hz, \(J = 8.5\) Hz, 4H), 7.77 (d, \(J = 8.5\) Hz, 2H), 7.83 (d, \(J = 8.5\) Hz, 2H), 11.28 (s, 1H); ¹³C NMR (125 MHz, (CD₃)₂CO) δ 37.8, 110.0, 118.2, 126.7, 128.5, 129.6, 130.6, 130.8, 131.7, 132.5, 132.9, 134.6, 134.7. HRMS (ESI-TOF) for C₁₈H₁₆Cl₂N₂O₂S [2M+Na]⁺: calcd, 813.5852. found 813.0473.
$N, N$-Dimethyl-$1H$-pyrrole-$1$-sulfonamide (2)
$N, N$-Dimethyl-2, 5-bis(trimethylsilyl)-$1H$-pyrrole-1-sulfonamide (3)
2-Iodo-\(N\), \(N\)-dimethyl-5-(trimethylsilyl)-1\(H\)-pyrrole-1-sulfonamide (4a)
2- Bromo -N, N-dimethyl-5-( trimethylsilyl)-1H-pyrrole-1- sulfonamide (4b)
$N, N$-Dimethyl-2-(trimethylsilyl)-5-(2-(trimethylsilyl)ethynyl)-1$H$-pyrrole-1-sulfonamide (5a)
2-(3-Hydroxy-3-methylbut-1-yn-1-yl)-N, N-dimethyl-5-(trimethylsilyl)-1H-pyrrole-1-Sulfonamide (5b)
$N,N$-Dimethyl-2-phenyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6a)
2-(4-Methoxyphenyl)-N, N-dimethyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6b)
2-(4-Chlorophenyl)-N, N-dimethyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6c)
2-(4-Acetylphenyl)-N, N-dimethyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6d)
2-(4-Hydroxyphenyl)-N, N-dimethyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6e)
2-(4-Cyanophenyl)-N, N-dimethyl-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6f)
$\text{N, N-Dimethyl-2-(3-nitrophenyl)-5-(trimethylsilyl)-1H-pyrrole-1-sulfonamide (6g)}$
2-Iodo-\(N, N\)-dimethyl-5-phenyl-1\(H\)-pyrrole-1-sulfonamide (7a)
2-Iodo-5-(4-methoxyphenyl)-N,N-dimethyl-1H-pyrrole-1-sulfonamide (7b)
2-(4-Chlorophenyl)-5-iodo-N,N-dimethyl-1\textit{H}-pyrrole-1-sulfonamide (7e)
2-(4-Acetylphenyl)-5-iodo-N,N-dimethyl-1H-pyrrole-1-sulfonamide (7d)
2, 5-Bis(4-methoxyphenyl)-N, N-dimethyl-1H-pyrrole-1-sulfonamide (8a)
2-(4-Hydroxyphenyl)-5-(4-methoxyphenyl)-N,N-dimethyl-1H-pyrrole-1-sulfonamide (8b)
2, 5-Bis(4-chlorophenyl)-N, N-dimethyl-1H-pyrrole-1-sulfonamide (8c)
2-(4-Chlorophenyl)-5-(4-methoxyphenyl)-N,N-dimethyl-1H-pyrrole-1-sulfonamide (8d)
2-(4-Chlorophenyl)-5-(4-cyanophenyl)-N, N-dimethyl-1H-pyrrole-1-sulfonamide (8e)
2-(4-Acetylphenyl)-5-(4-chlorophenyl)-N, N-dimethyl-1H-pyrrole-1-sulfonamide (8f)
2-(4-Chlorophenyl)-5-(2-methoxyphenyl)-N,N-dimethyl-1H-pyrrole-1-sulfonamide (8g)
2-(4-Acetylphenyl)-N, N-dimethyl-5-phenyl-1H-pyrrole-1-sulfonamide (8h)
2-(4-Acetylphenyl)-5-(4-methoxyphenyl)-N,N-dimethyl-1H-pyrrole-1-sulfonamide (8i)
2-(4-Acetylphenyl)-5-(2-methoxyphenyl)-N,N-dimethyl-1H-pyrrole-1-sulfonamide (8j)
2, 5-Bis(4-methoxyphenyl)-N, N-dimethyl-1H-pyrrole-3-sulfonamide (9a)
$^{1}H-^{1}H$ COSY of 9a, (CD$_3$)$_2$CO, 400 MHz
2, 5-Bis(4-chlorophenyl)-N, N'-dimethyl-1H-pyrrole-3-sulfonamide (9c)
HMBC spectrum of 9c, (CD$_3$)$_2$CO, 400 MHz

$\text{HMBC spectrum of } 9c, \text{ (CD}_3\text{)}_2\text{CO, 400 MHz}$

$9c$

$\text{1H-1H COSY of } 9c, \text{ (CD}_3\text{)}_2\text{CO, 400 MHz}$

$\text{1H-1H COSY of } 9c, \text{ (CD}_3\text{)}_2\text{CO, 400 MHz}$