Supporting Information

Facile One-Pot Synthesis of Aromatic and Heteroaromatic Sulfonamides

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Characterization Data for Sulfonamides

General. ¹H NMR spectral data are indicated in the form: δ value of signal (peak multiplicity, coupling constants in the form *J* and integrated number of protons). Splitting patterns are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet. For infra-red spectral data only major absorptions are indicated.

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General Experimental.

ⁱPrMgCl in THF (2.0M) was purchased from the Aldrich Chemical Co. and titrated with 1,10-phenanthroline as the indicator in dry THF at room temperature against 2-pentanol in PhMe (0.909 M). Most aryl and heteroaryl bromides and Et₂NH were purchased from the Aldrich Chemical Co. and used as received. Ethyl 5-bromothiophene-2-carboxylate was purchased from Avocado and used as received. THF was dried over Na/Ph₂CO prior to distillation. SO₂Cl₂ was purchased from the Aldrich Chemical Co. and fractionally redistilled directly before use. All reactions were carried out under a positive pressure of Argon using standard Schlenck techniques. Flash chromatography was carried out on silica (eluants are given in parentheses).

N,N-Diethylbenzenesulfonamide (9a).¹

Procedure GP 1: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9a** (170 mg, 80%) as a white solid: mp 41-42 °C (from Et₂O/hexanes) (Lit. mp 42 °C); R_f = 0.30 (EtOAc : hexanes 1 : 5); IR (film) 1446, 1351, 1161, 1090 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.82 - 7.79 (m, 2H), 7.57 - 7.46 (m, 3H), 3.24 (q, *J* = 7.1 Hz, 4H), 1.12 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (75 MHz) δ 140.3, 132.3, 128.9, 127.0, 42.0, 14.1; MS (CI) *m/z* 231 (M + NH₄)⁺, 214 (M + H)⁺; HRMS (CI) calcd for C₁₀H₁₅NO₂S (M + H)⁺ 214.0901, found 214.0904. Anal. calcd for C₁₀H₁₅NO₂S: C, 56.31; H, 7.09; N, 6.57. Found: C, 56.28; H, 7.00; N, 6.45.

1-Benzenesulfonylpiperidine (9b).²

Procedure GP 1: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9b** (191 mg, 85%) as a white solid: mp 91-92 °C (from Et₂O/hexanes) (Lit. mp 91 °C); R_f = 0.35 (EtOAc : hexanes 1 : 3); IR (film) 1443, 1333, 1144, 929 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.62 - 7.51 (m, 3H), 2.98 (d, *J* = 5.3 Hz, 4H), 1.68 - 1.56 (m, 4H), 1.45 - 1.40 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 136.4, 132.5, 128.9, 127.7, 47.0, 25.2, 23.5; MS (CI) *m/z* 226 (M + H)⁺; HRMS (CI) calcd for C₁₁H₁₅NO₂S: (M + H)⁺ 226.0901, found 226.0893.

4-Benzenesulfonylmorpholine (9c).³

Procedure GP 1: chromatography (CH₂Cl₂ : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9c** (199 mg, 88%) as a white solid: mp 118 °C (from Et₂O/hexanes) (Lit. mp 118-119 °C); *R_f* = 0.42 (EtOAc); IR (film) 1448, 1347, 1165, 936 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.78 - 7.75 (m, 2H), 7.67 - 7.54 (m, 3H), 3.74 (app t, *J* = 4.7 Hz, 4H), 3.00 (app t, *J* = 4.5 Hz, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 135.1, 133.1, 129.2, 127.9, 66.1, 46.0; MS (CI) *m/z* 227 (M + H)⁺; HRMS (CI) calcd for C₁₀H₁₃NO₃S: (M + H)⁺ 228.0694, found 228.0695.

1-Methyl-4-phenylsulfonylpiperazine (9d).⁴

Procedure GP 1: chromatography (CH₂Cl₂ : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9d** (84 mg, 35%) as a white solid: mp 129-130 °C (from Et₂O/hexanes) (Lit. mp 129-130 °C); *R_f* = 0.21 (EtOAc); IR (film) 1449, 1347, 1331, 1171 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.76 (d, *J* = 7.0 Hz, 2H), 7.64 - 7.52 (m, 3H), 3.13 (br s, 4H), 2.61 (br s, 4H), 2.35 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 135.2, 132.9, 129.1, 127.8, 54.0, 45.9, 45.7; MS (CI) *m/z* 241 (M + H)⁺; HRMS (CI) calcd for C₁₁H₁₆N₂O₂S: (M + H)⁺ 241.1010, found 241.1005.

***N,N*-Diethyl-4-methylbenzenesulfonamide (9e).⁵**

Procedure GP 1: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9e** (796 mg, 60%) as a white waxy solid: mp 58-59 °C (from Et₂O/hexanes) (Lit. mp 59-60 °C); *R_f* = 0.27 (EtOAc : hexanes 1 : 5); IR (film) 1305, 1200, 1155, 1090, 1019 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.20 (q, *J* = 7.1 Hz, 4H), 2.39 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (75 MHz) δ 142.9, 137.4, 129.6, 127.0, 42.0, 21.5, 14.2; MS (CI) *m/z* 228 (M + H)⁺, 212; HRMS (CI) calcd for C₁₁H₁₇NO₂S: (M + H)⁺ 228.1058, found 228.1052.

***N,N*-Diethyl-4-(tert-butyl)benzenesulfonamide (9f).**

Procedure GP 1: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9f** (831 mg, 61%) as a white solid: mp 126-127 °C (from Et₂O/hexanes); *R_f* = 0.28 (EtOAc : hexanes 1 : 9); IR (film) 1329, 1196, 1158 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 3.25 (q, *J* = 7.1 Hz, 4H), 1.35 (s, 9H), 1.16 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 155.9, 137.2, 126.9, 125.9, 42.2, 35.1, 31.1,

14.3; MS (CI) m/z 270 ($M + H$)⁺; HRMS (CI) calcd for C₁₄H₂₃NO₂S: ($M + H$)⁺ 270.1527, found 270.1537. Anal. calcd for C₁₄H₂₃NO₂S: C, 62.42; H, 8.61; N, 5.20. Found: C, 62.26; H, 8.62; N, 5.12.

***N,N*-Diethyl-4-phenylbenzenesulfonamide (9g).**⁶

Procedure GP 1: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9g** (769 mg, 62%) as a white solid: mp 83-84 °C (from Et₂O/hexanes) (Lit. mp 83–85 °C); R_f = 0.31 (EtOAc : hexanes 1 : 5); IR (film) 1561, 1333, 1156, 889 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.89 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H), 7.52 - 7.40 (m, 3H), 3.30 (q, J = 7.1 Hz, 4H), 1.18 (t, J = 7.1 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 145.1, 139.4, 138.9, 129.1, 128.4, 127.6, 127.3, 127.1, 42.2, 14.3 ; MS (CI) m/z 290 ($M + H$)⁺; HRMS (CI) calcd for C₁₆H₁₉NO₂S: ($M + H$)⁺ 290.1214, found 290.1210.

***N,N*-Diethyl-2-methoxybenzenesulfonamide (9h).**

Procedure GP 1: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9h** (948 mg, 73%) as a colorless oil: R_f = 0.27 (EtOAc : hexanes 1 : 4), IR (film) 2937, 1347, 1150, 759 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.94 (d, J = 7.2 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.04 - 6.97 (m, 2H), 3.93 (s, 3H), 3.38 - 3.31 (q, J = 7.0 Hz, 4H), 1.11 (t, J = 7.1 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 156.7, 134.0, 131.3, 129.0, 120.2, 112.0, 55.8, 41.8, 14.3; MS (CI) m/z 244 ($M + H$)⁺; HRMS (CI) calcd for C₁₁H₁₇NO₃S: ($M + H$)⁺ 244.1007, found 244.1002.

***N,N*-Diethyl-4-methoxybenzenesulfonamide (9i).**⁷

Procedure GP 1: chromatography (hexanes : Et₂O, 1 : 0 to 9 : 1) gave sulfonamide **9i** (974 mg, 75%) as a yellow oil: R_f = 0.29 (EtOAc/hexanes 1 : 4); IR (film) 1596, 1497, 1333, 1256, 1154, 1019 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.75 (d, J = 8.7 Hz, 2H), 6.97 (t, J = 8.7 Hz, 2H), 3.87 (s, 3H), 3.25 (q, J = 7.1 Hz, 4H), 1.16 (t, J = 7.1 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 162.6, 132.0, 129.0, 114.1, 55.6, 41.9, 14.1; MS (CI) m/z 244 ($M + H$)⁺; HRMS (CI) calcd for C₁₁H₁₇NO₃S: ($M + H$)⁺ 244.1007, found 244.1006.

***N,N*-Diethyl-4-phenoxybenzenesulfonamide (9j).**

Procedure GP 1: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9j** (710 mg, 58%) as a white waxy solid: mp 81-82 °C (from Et₂O/hexanes); R_f = 0.33 (EtOAc :

hexanes 1 : 5); IR (film) 1580, 1486, 1333, 1241, 1152 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.76 (d, $J = 8.7$ Hz, 2H), 7.42 (t, $J = 8.0$ Hz, 2H), 7.23 (t, $J = 7.4$ Hz, 1H), 7.09 - 7.02 (m, 4H), 3.25 (q, $J = 7.1$ Hz, 4H), 1.16 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 161.2, 155.3, 134.0, 130.8, 129.4, 124.9, 120.2, 117.6, 42.1, 14.2; MS (CI) m/z 306 ($\text{M} + \text{H}$) $^+$; HRMS (CI) calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_3\text{S}$: ($\text{M} + \text{H}$) $^+$ 306.1163, found 306.1163. Anal. calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_3\text{S}$: C, 62.93; H, 6.27; N, 4.59. Found: C, 62.83; H, 6.20; N, 4.39.

***N,N*-Diethyl-4-(dimethylamino)benzenesulfonamide (9k).**

Procedure GP 1: chromatography (hexanes : Et_2O 1 : 0 to 9 : 1) gave sulfonamide **9k** (716 mg, 56%) as a white solid: mp 119–120 $^\circ\text{C}$ (from Et_2O /hexanes); $R_f = 0.24$ (EtOAc : hexanes 1 : 4); IR (film) 1317, 1197, 1014, 926, 820 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.65 (d, $J = 8.9$ Hz, 2H), 6.68 (d, $J = 8.9$ Hz, 2H), 3.21 (q, $J = 7.1$ Hz, 4H) 3.05 (s, 6H), 1.13 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR δ 128.8, 111.0, 41.9, 40.1, 14.2; MS (CI) m/z 257 ($\text{M} + \text{H}$) $^+$; HRMS (CI) calcd for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$: ($\text{M} + \text{H}$) $^+$ 257.1323, found 257.1322. Anal. calcd for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$: C, 56.22; H, 7.86; N, 10.93. Found: C, 56.35; H, 8.00; N, 10.83.

Ethyl 4-(diethylaminosulfonyl)benzoate (9l).⁸

Procedure GP 2: chromatography (hexanes : EtOAc 9 : 1) gave sulfonamide **9l** (304 mg, 53%) as an oil: $R_f = 0.31$ (EtOAc : hexanes 1 : 9); IR (film) 1723, 1274, 1158 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 8.17 (d, $J = 8.3$ Hz, 2H), 7.89 (d, $J = 8.4$ Hz, 2H), 4.43 (m, 2H), 3.28 (q, $J = 7.1$ Hz, 4H), 1.43 (t, $J = 7.1$ Hz, 4H), 1.15 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.1, 144.3, 133.8, 130.2, 126.9, 61.6, 42.0, 14.2, 14.1; MS (CI) m/z 303 ($\text{M} + \text{NH}_4$) $^+$; HRMS (CI) calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_4\text{S}$: ($\text{M} + \text{H}$) $^+$ 286.1112, found 286.1120.

***N,N*-Diethyl-4-cyanobenzenesulfonamide (9m).⁹**

Procedure GP 2: chromatography (hexanes : EtOAc 9 : 1) gave sulfonamide **9m** (319 mg, 67%) as a white solid: mp 93–94 $^\circ\text{C}$ (from Et_2O /hexanes) (Lit. mp 94 $^\circ\text{C}$); $R_f = 0.33$ (EtOAc : hexanes 1 : 9); IR (film) 2233, 1335, 1156 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.94 (d, $J = 7.5$ Hz, 2H), 7.81 (d, $J = 7.6$ Hz, 2H), 3.28 (q, $J = 7.0$ Hz, 4H), 1.15 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 144.9, 132.9, 127.6, 117.4, 116.0, 42.2, 14.1; MS (CI) m/z 256 ($\text{M} + \text{NH}_4$) $^+$; HRMS (CI) calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$: ($\text{M} + \text{H}$) $^+$ 239.0854, found 239.0863.

***N,N*-Diethyl-4-bromobenzenesulfonamide (9n).**¹⁰

Procedure GP 2: chromatography (hexanes : EtOAc 9 : 1) gave sulfonamide **9n** (282 mg, 48%) as an oil: R_f = 0.40 (EtOAc : hexanes 1 : 9); IR (film) 1574, 1468, 1383, 1335, 1178 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.49 (m, 4H), 3.24 (q, J = 7.1 Hz, 4H), 1.14 (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 139.6, 132.3, 128.5, 127.1, 42.1, 14.1; MS (CI) m/z 311 ($\text{M}^{81} + \text{NH}_4$)⁺, 309 ($\text{M}^{79} + \text{NH}_4$)⁺; HRMS (CI) calcd for $\text{C}_{10}\text{H}_{14}\text{BrNO}_2\text{S}$: ($\text{M}^{81} + \text{H}$)⁺ 293.9986, ($\text{M}^{79} + \text{H}$)⁺ 292.0007, found ($\text{M}^{81} + \text{H}$)⁺ 293.9984, ($\text{M}^{79} + \text{H}$)⁺ 292.0003.

***N,N*-Diethyl-3-pyridinesulfonamide (9o).**¹¹

Procedure GP 2: chromatography (hexanes : Et_2O 1 : 0 to 9 : 1) gave sulfonamide **9o** (460 mg, 68%) as a solid: mp 45 °C (from Et_2O /hexanes); R_f = 0.26 (EtOAc : hexanes 1 : 5); IR (film) 1572, 1466, 1336, 1162 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 9.0 (s, 1H), 8.76 (d, J = 3.7 Hz, 1H), 8.07 (d, J = 7.9 Hz, 1H), 7.46 - 7.42 (m, 1H), 3.25 (q, J = 7.1 Hz, 4H), 1.13 (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 152.9, 147.8, 137.0, 134.6, 123.8, 42.1, 14.2; MS (CI) m/z 215 ($\text{M} + \text{H}$)⁺; HRMS (CI) calcd for $\text{C}_9\text{H}_{14}\text{N}_2\text{O}_2\text{S}$: ($\text{M} + \text{H}$)⁺ 215.0854, found 215.0858.

3-(1-Pyrrolidinosulfonyl)pyridine (9p).¹²

Procedure GP 2: chromatography (hexanes : Et_2O 1 : 0 to 9 : 1) gave sulfonamide **9p** (342 mg, 51%) as a white solid: mp 74-75 °C (from Et_2O /hexanes) (Lit. mp 78 °C); R_f = 0.20 (EtOAc : hexanes 1 : 5); IR (film) 2979, 2880, 1346, 1008 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 9.07 (s, 1H), 8.88 (s, 1H), 8.15 (d, J = 7.9 Hz, 1H), 7.53 - 7.48 (m, 1H), 3.30 - 3.28 (m, 4H), 1.86 - 1.79 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 153.2, 148.2, 135.1, 133.5, 123.7, 47.9, 25.3; MS (CI) m/z 213 ($\text{M} + \text{H}$)⁺; HRMS (CI) calcd for $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_2\text{S}$: ($\text{M} + \text{H}$)⁺ 213.0697, found 213.0705.

***N,N*-Diethyl-2-pyridinesulfonamide (9q).**¹³

Procedure GP 2: chromatography (hexanes : Et_2O 1 : 0 to 9 : 1) gave sulfonamide **9q** (379 mg, 56%) as a yellow oil: R_f = 0.15 (EtOAc : hexanes 1 : 5); IR (film) 1334, 1202, 1173, 1116, 1019, 938 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 8.67 (d, J = 4.6 Hz, 1H), 7.96 - 7.85 (m, 2H), 7.47 - 7.43 (m, 1H), 3.39 (q, J = 7.1 Hz, 4H), 1.14 (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 158.5, 150.0, 137.9, 126.3, 122.2, 42.8, 14.4; MS (CI) m/z 215 ($\text{M} + \text{H}$)⁺; HRMS (CI) calcd for $\text{C}_9\text{H}_{14}\text{N}_2\text{O}_2\text{S}$: ($\text{M} + \text{H}$)⁺ 215.0854, found 215.0853.

***N,N*-Diethyl-6-bromo-2-pyridinesulfonamide (9r).**

Procedure GP 2: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9r** (214 mg, 35%) as a white solid: mp 51-52 °C (from Et₂O/hexanes); *R_f* = 0.22 (EtOAc : hexanes 1 : 5); IR (film) 1338, 1202, 1177, 1155, 1130, 1018 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.87 (d, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.1 Hz, 1H); 3.37 (q, *J* = 7.2 Hz, 4H), 1.14 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 159.1, 142.1, 139.8, 131.0, 121.0, 42.9, 14.2; MS (CI) *m/z* 295 (M⁸¹ + H)⁺, 293 (M⁷⁹ + H)⁺; HRMS (CI) calcd for C₉H₁₃BrN₂O₂S: (M⁸¹ + H)⁺ 294.9939, (M⁷⁹ + H)⁺ 292.9959, found (M⁸¹ + H)⁺ 294.9943, (M⁷⁹ + H)⁺ 292.9964. Anal. calcd for C₉H₁₃BrN₂O₂S: C, 36.87; H, 4.47; N, 9.55. Found: C, 36.94; H, 4.46; N, 9.48.

2-Bromo-6-(piperidinosulfonyl)pyridine (9s).

Procedure GP 2: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9s** (308 mg, 48%) as a white solid: mp 121-122 °C (from Et₂O/hexanes); *R_f* = 0.2 (EtOAc : hexanes 1 : 4); IR (film) 1552, 1411, 1347, 1177 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.90 (d, *J* = 7.5 Hz, 1H), 7.75 (t, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 3.35 (t, *J* = 4.8 Hz, 4H), 1.67 - 1.55 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 157.2, 142.1, 140.1, 131.3, 121.7, 47.5, 25.4, 23.6; MS (CI) *m/z* 324 (M + NH₄)⁺, 307 (M + H)⁺; HRMS (CI) calcd for C₁₀H₁₃BrN₂O₂S: (M⁸¹ + H)⁺ 306.9939, (M⁷⁹ + H)⁺ 304.9959, found (M⁸¹ + H)⁺ 306.9953, (M⁷⁹ + H)⁺ 304.9973. Anal. calcd for C₁₀H₁₃BrN₂O₂S: C, 39.36; H, 4.29; N, 9.19. Found: C, 39.32; H, 4.47; N, 9.30.

***N,N*-Diethyl-4-isoquinolinesulfonamide (9t).**

Procedure GP 2: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9t** (330 mg, 52%) as a white solid: mp 119-120 °C (from Et₂O/hexanes); *R_f* = 0.22 (EtOAc : hexanes 1 : 3); IR (film) 1316, 1136, 1019 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 9.40 (s, 1H), 9.02 (s, 1H), 8.63 (d, *J* = 8.6 Hz, 1H), 8.10 (d, *J* = 8 Hz, 1H), 7.91 - 7.84 (m, 1H), 7.75 (app t, *J* = 7.5 Hz, 1H), 3.47 - 3.38 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 157.4, 144.3, 132.5, 131.3, 128.7, 128.4, 124.4, 41.3, 14.0; MS (CI) *m/z* 265 (M + NH₄)⁺; HRMS (CI) calcd for C₁₃H₁₆N₂O₂S: (M + H)⁺ 265.1010, found 265.1015. Anal. calcd for C₁₃H₁₆N₂O₂S: C, 59.07; H, 6.10; N, 10.60. Found: C, 59.17; H, 5.93; N, 10.39.

4-(Piperidinosulfonyl)isoquinoline (9u).

Procedure GP 2: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9u** (293 mg, 47%) as a beige solid: mp 105-106 °C (from Et₂O/hexanes); R_f = 0.20 (EtOAc : hexanes 1 : 3); IR (film) 1331, 1158, 932 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 9.33 (s, 1H), 8.98 (s, 1H), 8.64 (d, J = 8.6 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.81 (t, J = 7.3 Hz, 1H), 7.66 (t, J = 7.9 Hz, 1H), 3.13 (t, J = 4.1 Hz, 4H), 1.52 (d, J = 7.5 Hz, 4H), 1.40 - 1.37 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 157.6, 145.5, 132.4, 131.5, 128.8, 128.6, 128.3, 128.0, 124.4, 46.4, 25.3, 23.5; MS (CI) m/z 277 (M + NH₄)⁺; HRMS (CI) calcd for C₁₄H₁₆N₂O₂S: (M + NH₄)⁺ 277.1010, found 277.1021. Anal. calcd for C₁₄H₁₆N₂O₂S: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.93; H, 5.63; N, 10.14.

N,N-Diethyl-5-bromo-2-thiophenesulfonamide (9v).¹⁴

Procedure GP 2: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9v** (293 mg, 48%) as an orange oil: R_f = 0.47 (EtOAc/hexanes 1 : 3); IR (film) 1342, 1152, 1017, 704 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.24 (d, J = 3.2 Hz, 1H), 7.01 (d, J = 3.5 Hz, 1H), 3.16 (q, J = 6.9 Hz, 4H), 1.11 (t, J = 7.0 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 141.8, 131.4, 130.5, 118.7, 42.8, 14.3; MS (CI) m/z 300 (M + H)⁺, 317 (M⁸¹ + NH₄)⁺, 315 (M⁷⁹ + NH₄)⁺; HRMS (CI) calcd for C₈H₁₂BrNO₂S₂: (M⁸¹ + H)⁺ 299.9551, (M⁷⁹ + H)⁺ 297.9571, found (M⁸¹ + H)⁺ 299.9549, (M⁷⁹ + H)⁺ 297.9563. Anal. calcd for C₈H₁₂BrNO₂S₂: C, 32.22; H, 4.06; N, 4.70. Found: C, 32.31; H, 3.94; N, 4.68.

1-(5-Bromo-2-thienylsulfonyl)piperidine (9w).¹⁴

Procedure GP 2: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9w** (190 mg, 30%) as a white solid: mp 83-84 °C (from Et₂O/hexanes); R_f = 0.24 (EtOAc : hexanes 1 : 5); IR (film) 1344, 1208, 1165, 720 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.24 (d, J = 3.9 Hz, 1H), 7.10 (d, J = 3.9 Hz, 1H), 3.01 (t, J = 5.4 Hz, 4H), 1.69 - 1.62 (m, 4H), 1.49 - 1.44 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 137.7, 132.2, 130.7, 119.5, 46.9, 25.1, 23.4; MS (CI) m/z 329 (M⁸¹ + NH₄)⁺, 327 (M⁷⁹ + NH₄)⁺, 312 (M⁸¹ + H)⁺, 310 (M⁷⁹ + H)⁺; HRMS (CI) calcd for C₉H₁₂BrNO₂S₂: (M⁸¹ + H)⁺ 311.9551, (M⁷⁹ + H)⁺ 309.9571, found (M⁸¹ + H)⁺ 311.9547, (M⁷⁹ + H)⁺ 309.9572. Anal. calcd for C₉H₁₂BrNO₂S₂: C, 34.84; H, 3.90; N, 4.51. Found: C, 35.00; H, 4.04; N, 4.53.

Ethyl 5-(diethylaminosulfonyl)-2-thiophenecarboxylate (9x).

Procedure GP 2: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9x** (129 mg, 21%) as a yellow oil: R_f = 0.43 (EtOAc : hexanes 1 : 4); IR (film) 1717, 1459, 1353, 1252, 1151, 1094, 1015 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.72 (d, J = 3.8 Hz, 1H), 7.49 (d, J = 3.8 Hz, 1H), 4.38 (q, J = 6.9 Hz, 2H), 3.29 (t, J = 7.0 Hz, 4H), 1.39 (t, J = 7.2 Hz, 3H), 1.26 - 1.17 (t, J = 7.0 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 162.0, 145.7, 138.3, 132.5, 130.8, 62.0, 42.7, 29.7, 14.2; MS (CI) m/z 292 (M + H)⁺, 309 (M + NH₄)⁺; HRMS (CI) calcd for C₁₁H₁₇NO₄S₂: (M + H)⁺ 292.0677, found 292.0687. Anal. calcd for C₁₁H₁₇NO₄S₂: C, 45.34; H, 5.88; N, 4.80. Found: C, 45.19; H, 5.76; N, 4.84. The yield of **9x** was increased to 35% on using an inverse addition of the Grignard reagent **6x** to sulfur dioxide in THF.

Ethyl 5-(piperidinosulfonyl)-2-thiophenecarboxylate (9y).

Procedure GP 2: chromatography (hexanes : Et₂O 1 : 0 to 9 : 1) gave sulfonamide **9y** (290 mg, 47%) as a white solid: mp 84 °C (from Et₂O/hexanes); R_f = 0.24 (EtOAc : hexanes 1 : 5); IR (film) 1719, 1358, 1249, 1162 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.77 (d, J = 3.4 Hz, 1H), 7.46 (d, J = 3.9 Hz, 1H), 4.39 (q, J = 7.0 Hz, 2H), 3.07 (t, J = 5.4 Hz, 4H), 1.51 - 1.37 (m, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 161.2, 142.5, 139.1, 132.7, 131.5, 62.0, 47.0, 25.1, 23.4, 14.3; MS (CI) m/z 304 (M + H)⁺, 321 (M + NH₄)⁺; HRMS (CI) calcd for C₁₂H₁₇NO₄S₂: (M + H)⁺ 304.0677, found 304.0687. Anal. calcd for C₁₂H₁₇NO₄S₂: C, 47.51; H, 5.65; N, 4.64. Found: C, 47.66; H, 5.32; N, 4.76.

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^1H and ^{13}C NMR spectra for 9h.