

SUPPORTING INFORMATION

Triflic Acid Controlled Successive Annulation of Aromatic Sulfonamides: An Efficient One-Pot Synthesis of N-Sulfonyl Pyrroles, Indoles and Carbazoles

Mohammed Abid, Liliana Teixeira and Béla Török*

MATERIALS. All the starting chemicals were purchased from Aldrich and used without any purification. CDCl_3 used as a solvent (99.8%) for NMR studies was an Aldrich product. Other solvents used in synthesis with minimum purity of 99.5% were Fisher products.

NMR ANALYSIS. The ^1H , and ^{13}C spectra were obtained on a 300 MHz Varian NMR spectrometer, in CDCl_3 solvent with tetramethylsilane as internal standards or the residual solvent signal of CDCl_3 . The temperature was 25 °C (accuracy ± 1 °C) and controlled by the Varian control unit.

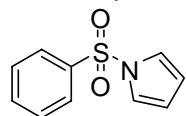
GC-MS ANALYSIS: The mass spectrometric identification of the products have been carried out by an Agilent 6850 gas chromatograph- 5973 mass spectrometer system (70 eV electron impact ionization) using a 30m long DB-5 type column (J&W Scientific).

All the melting points are uncorrected and recorded on a MEL-TEMP apparatus.

GENERAL PROCEDURE FOR SYNTHESIS OF N-SULFONYL PYRROLES, INDOLES AND CARBAZOLES: Sulfonamide (100 mg, 0.636 mmol) and 2,5-dimethoxytetrahydrofuran (420 mg, 3.18 mmol) were placed in a round bottom flask with 2 ml of CH_2Cl_2 . This mixture was cooled to 0°C for 10-15 min and TfOH (0.05 eqv. for pyrroles, 1.0 eqv. for indoles and 3.5 eqv. for carbazoles) was added slowly drop wise to the reactants. After addition the mixture was stirred at room temperature for an additional 2 hrs. Acid was quenched with water and the product was extracted with CH_2Cl_2 . Combined organic layers were dried over sodium sulfate. Solvent was evaporated *in vacuo* and the residue was subjected to flash chromatography. The pure products were characterized by GCMS and NMR as shown below.

CHARACTERIZATION OF PRODUCTS:

1-(Phenylsulfonyl)-1H-pyrrole. (Table-2, Entry-1)



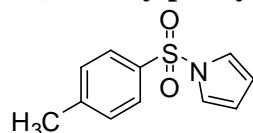
M.P : 85.3-87 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 7.84 (m, 2H), 7.57 (m, 1H), 7.48 (m, 2H), 7.15 (t, *J* = 2.4 Hz, 2H), 6.28 (t, *J* = 2.4 Hz, 2H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 139.3, 134.0, 129.5, 126.9, 121.0, 113.8

MS-C₁₀H₉NO₂S (207), m/z (%): 207 (M⁺, 98), 141 (85), 115 (30), 77 (100).

1-(4-Methylphenylsulfonyl)-1H-pyrrole. (Table-2, Entry-2)



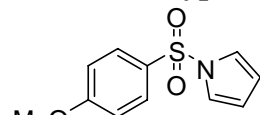
M.P : 96.9-97.5 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 7.61 (td, *J* = 8.0, 1.2 Hz, 1H), 7.46 (td, *J* = 7.6, 1.2 Hz, 1H), 7.27 (m, 2H), 7.14 (t, *J* = 2.0 Hz, 2H), 6.30 (t, *J* = 2.0 Hz, 2H), 2.56 (s, 3H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 138.1, 133.5, 128.3, 126.9, 121.8, 112.5, 20.3

MS-C₁₁H₁₁NO₂S (221), m/z (%): 221 (M⁺, 30), 155 (25), 91 (100), 65 (15)

1-(4-Methoxyphenylsulfonyl)-1H-pyrrole. (Table-2, Entry-3)



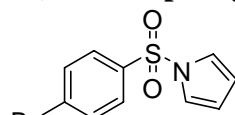
M.P : 100.1-102.7 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 7.81 (dd, *J* = 2.0, 7.0 Hz, 2H), 7.14 (t, *J* = 2.4 Hz, 2H), 6.93 (dd, *J* = 2.0, 7.0 Hz, 2H), 6.27 (t, *J* = 2.4 Hz, 2H), 3.84 (s, 3H)

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 128.1, 125.3, 124.7, 121.9, 113.5, 110.8, 54.8

MS- C₁₁H₁₁NO₃S (237), m/z (%): 237 (M⁺, 80), 171 (100), 107 (40), 92 (20), 77 (25).

1-(4-Bromophenylsulfonyl)-1H-pyrrole. (Table-2, Entry-4)



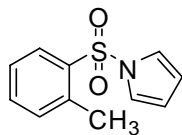
M.P : 75.8-76.9 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 7.71 (m, 2H), 7.41 (m, 2H), 7.21 (t, *J* = 2.4 Hz, 2H), 6.31 (t, *J* = 2.4 Hz, 2H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 136.1, 143.8, 130.5, 128.1, 121.9, 113.2

MS-C₁₀H₈BrNO₂S (285), m/z (%): 285 (M⁺, 30), 206 (80), 155 (100).

1-(2-Methylphenylsulfonyl)-1H-pyrrole. (Table-2, Entry-5)



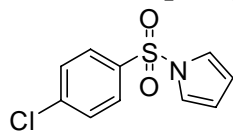
M.P : 91-92.8 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 7.71 (m, 2H), 7.27 (m, 2H), 7.13 (t, *J* = 2.4 Hz, 2H), 6.26 (t, *J* = 2.4 Hz, 2H), 2.38 (s, 3H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 145.1, 136.3, 130.1, 130.0, 127.0, 120.9, 113.7, 21.7

MS-C₁₁H₁₁NO₂S (221), m/z (%): 221 (M⁺, 30), 156 (15), 91 (100), 65 (30)

1-(4-Chlorophenylsulfonyl)-1H-pyrrole. (Table-2, Entry-6)



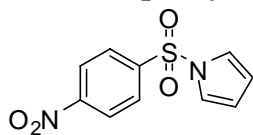
M.P : 82.8-84 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 7.73 (m, 2H, Ar), 7.43 (m, 2H, Ar), 7.23 (t, *J* = 2.4 Hz, 2H), 6.33 (t, *J* = 2.4 Hz, 2H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 136.0, 134.7, 130.4, 128.0, 121.8, 113.1

MS-C₁₀H₈ClNO₂S (241), m/z (%): 241 (M⁺, 15), 206 (60), 111 (100).

1-(4-Nitrophenylsulfonyl)-1H-pyrrole. (Table-2, Entry-7)



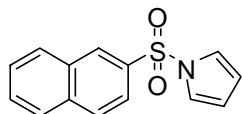
M.P : 135.1-138.5 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.35 (m, 3H), 8.13 (m, 2H), 6.72 (t, *J* = 2.4 Hz, 2H), 6.28 (t, *J* = 2.4 Hz, 2H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 146.1, 136.8, 128.6, 125.1, 124.2, 116.3

MS-C₁₀H₈N₂O₄S (252), m/z (%): 252 (M⁺, 100), 186 (30), 156 (50), 122 (75), 76 (20).

1-(2-Naphthylsulfonyl)-1H-pyrrole. (Table-2, Entry-8)



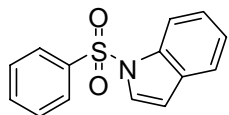
M.P : 116.3-118.1 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.46 (d, *J* = 1.6 Hz, 3H), 7.89 (m, 3H), 7.76 (dd, *J* = 2.0, 8.7 Hz, 1H), 7.62 (m, 2H), 7.21 (t, *J* = 2.4 Hz, 2H), 6.27 (t, *J* = 2.4 Hz, 2H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 136.1, 135.4, 132.1, 130.0, 129.6, 129.6, 128.7, 128.1, 128.0, 121.7, 121.0, 113.8

MS-C₁₄H₁₁NO₂S (257), m/z (%): 257 (M⁺, 20), 191 (10), 127 (100).

1-(Phenylsulfonyl)-1H-indole. (Table-3, Entry-1)



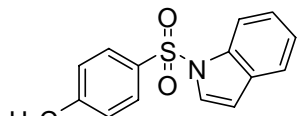
M.P : 78.1-79.9 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 7.99 (dt, *J* = 0.8, 8.0 Hz, 1H), 7.87 (m, 2H), 7.58 (d, *J* = 3.59 Hz, 1H), 7.50 (m, 2H), 7.41 (m, 2H), 7.30 (m, 1H), 7.21 (m, 1H), 6.64 (d, *J* = 3.59 Hz, 1H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 138.4, 133.9, 130.9, 129.4, 126.9, 126.5, 124.8, 123.5, 121.6, 115.3, 113.7, 109.4

MS-C₁₄H₁₁NO₂S (257), m/z (%): 257 (M⁺, 45), 141 (25), 116 (80), 77 (100).

1-(4-Methylphenylsulfonyl)-1H-indole. (Table-3, Entry-2)



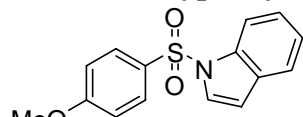
M.P : 88.4-90 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 7.98 (d, *J* = 8.4 Hz, 1H), 7.74 (m, 2H), 7.56 (d, *J* = 3.6 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.22 (m, 4H), 6.64 (d, *J* = 3.6 Hz, 1H), 2.30 (s, 3H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 145.1, 130.1, 130.0, 127.0, 126.5, 124.7, 124.1, 123.4, 121.5, 120.9, 113.7, 109.2, 21.7

MS-C₁₅H₁₃NO₂S (271), m/z (%): 271 (M⁺, 70), 155 (40), 116 (60), 91 (100).

1-(4-Methoxyphenylsulfonyl)-1H-indole. (Table-3, Entry-3)



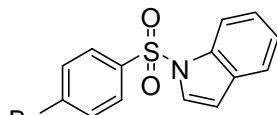
M.P : 109.7-111.1 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 7.99 (d, *J* = 8.4 Hz, 1H), 7.79 (m, 3H), 7.52 (m, 1H), 7.26 (m, 1H), 7.13 (t, *J* = 2.4 Hz, 1H), 6.93 (m, 1H), 6.84 (m, 1H), 6.63 (t, *J* = 2.4 Hz, 1H), 3.74 (s, 3H)

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 128.7, 128.3, 127.6, 126.4, 124.3, 123.9, 123.5, 121.5, 120.9, 120.1, 114.2, 109.1, 55.8

MS-C₁₅H₁₃NO₃S (287), m/z (%): 287 (M⁺, 70), 171 (100), 116 (20), 107 (30), 77 (30).

1-(4-Bromophenylsulfonyl)-1H-indole. (Table-3, Entry-4)



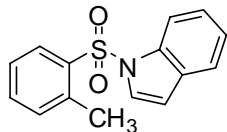
M.P : 72.3-74.1 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.08 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.76 (d, *J* = 3.6 Hz, 1H), 7.65 (m, 1H), 7.40 (m, 3H), 7.22 (m, 3H), 6.66 (d, *J* = 3.6 Hz, 1H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 136.2, 134.9, 131.5, 130.5, 128.3, 128.0, 124.5, 123.5, 121.9, 121.7, 113.2, 107.6

MS-C₁₄H₁₀BrNO₂S (335), *m/z* (%): 335 (M⁺, 25), 256 (10), 191 (15), 116 (100).

1-(2-Methylphenylsulfonyl)-1H-indole. (Table-3, Entry-5)



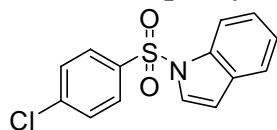
M.P : 81.2-83 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 7.84 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.65 (d, *J* = 3.6 Hz, 1H), 7.43 (m, 2H), 7.20 (m, 5H), 6.88 (d, *J* = 3.6 Hz, 1H), 2.57 (s, 3H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 138.2, 134.9, 134.0, 133.2, 130.6, 129.2, 128.4, 127.1, 126.8, 124.6, 123.3, 121.3, 113.0, 107.7, 20.4

MS-C₁₅H₁₃NO₂S (271), *m/z* (%): 271 (M⁺, 65), 206 (25), 116 (80), 91 (100).

1-(4-Chlorophenylsulfonyl)-1H-indole. (Table-3, Entry-6)



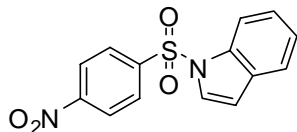
M.P : 78.5-79.9 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.11 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.79 (d, *J* = 3.6 Hz, 1H), 7.63 (m, 2H), 7.38 (m, 3H), 7.23 (m, 2H), 6.68 (d, *J* = 3.6 Hz, 1H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 136.1, 134.4, 131.7, 130.3, 128.0, 127.9, 122.3, 121.9, 121.8, 121.6, 113.1, 107.5

MS-C₁₄H₁₀ClNO₂S (291), *m/z* (%): 291 (M⁺, 50), 116 (100), 111 (15), 77 (10).

1-(4-Nitrophenylsulfonyl)-1H-indole. (Table-3, Entry-7)



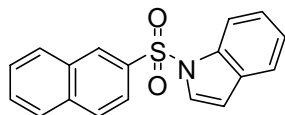
M.P : 65.6-68.3 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.31 (m, 4H), 8.02 (m, 3H), 7.54 (m, 1H), 7.15 (t, *J* = 2.4 Hz, 1H), 6.35 (t, *J* = 2.4 Hz, 1H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 143.8, 131.2, 128.1, 126.0, 125.3, 124.7, 124.2, 121.9, 121.0, 115.0, 113.5, 110.8

MS-C₁₄H₁₀N₂O₄S (302), *m/z* (%): 302 (M⁺, 40), 156 (10), 116 (100), 89 (20), 76 (10).

1-(2-Naphthylsulfonyl)-1H-indole. (Table-3, Entry-8)



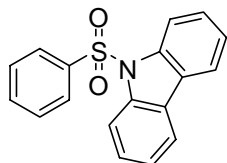
M.P : 72.3-74.1 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.52 (d, *J* = 1.6 Hz, 1H), 8.05 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.91 (m, 1H), 7.84 (m, 1H), 7.73 (m, 3H), 7.61 (m, 3H), 7.30 (m, 1H), 7.21 (m, 1H), 6.65 (d, *J* = 3.6 Hz, 1H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 135.4, 135.1, 130.0, 129.9, 129.7, 129.6, 128.7, 128.1, 128.1, 127.9, 126.6, 124.8, 124.1, 123.5, 121.6, 121.0, 113.8, 109.4

MS-C₁₈H₁₃NO₂S (307), m/z (%): 307 (M⁺, 40), 241 (5), 191 (20), 127 (100), 116 (25).

9-(Phenylsulfonyl)-9H-carbazole. (Table-4, Entry-1)



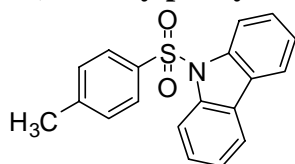
M.P : 116.7-119.1 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.40 (dd, *J* = 0.6, 8.0 Hz, 2H), 7.88 (dd, *J* = 0.6, 8.0 Hz, 2H), 7.68 (m, 4H), 7.52 (m, 5H)

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 138.4, 135.3, 129.5, 129.2, 127.5, 126.4, 124.0, 121.3, 120.1, 115.2

MS-C₁₈H₁₃NO₂S (307), m/z (%): 307 (M⁺, 24), 166 (100), 77 (30).

9-(4-Methylphenylsulfonyl)-9H-carbazole. (Table-4, Entry-2)



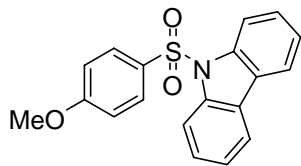
M.P : 130.3-133.2 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.32 (d, *J* = 8.4 Hz, 2H), 7.89 (dq, *J* = 0.8, 7.6 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.47 (td, *J* = 1.2, 7.2 Hz, 2H), 7.34 (td, *J* = 1.2, 8.0 Hz, 2H), 7.07 (d, *J* = 8Hz, 2H), 2.24 (s, 3H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 145.0, 138.6, 135.2, 129.8, 127.5, 126.6, 126.5, 124.0, 120.1, 115.3, 21.6

MS- C₁₉H₁₅NO₂S (321), m/z (%): 321 (M⁺, 35), 254 (1), 166 (100), 91 (40).

9-(4-Methoxyphenylsulfonyl)-9H-carbazole. (Table-4, Entry-3)



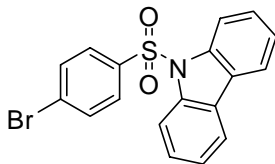
M.P : 160.1-162.3 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.31 (m, 2H), 7.89 (m, 2H), 7.52 (dd, *J* = 2.0, 6.9 Hz, 2H), 7.48 (m, 2H), 7.35 (m, 2H), 6.75 (m, 2H), 3.70 (s, 3H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 163.7, 128.7, 127.4, 126.4, 123.9, 120.0, 115.2, 114.3, 55.7

MS-C₁₉H₁₅NO₃S (337), m/z (%): 337 (M⁺, 60), 166 (100), 140 (15), 107 (15), 77 (10).

9-(4-Bromophenylsulfonyl)-9H-carbazole. (Table-4, Entry-4)



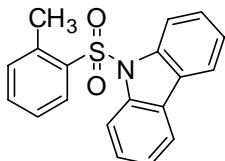
M.P : 125.9-128 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.02 (m, 4H), 7.66 (m, 1H), 7.57 (m, 1H), 7.38 (m, 5H), 7.22 (m, 1H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 138.9, 136.1, 134.5, 131.6, 127.7, 127.3, 125.7, 123.8, 120.3, 115.2

MS-C₁₈H₁₂BrNO₂S (385), m/z (%): 385 (M⁺, 20), 166 (100).

9-(2-Methylphenylsulfonyl)-9H-carbazole. (Table-4, Entry-5)



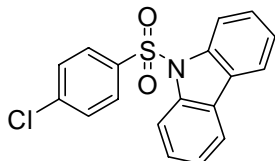
M.P : 119.2-121.6 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.07 (dq, *J* = 0.4, 8.0 Hz, 2H), 7.97 (dq, *J* = 0.8, 8.0 Hz, 2H), 7.75 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.38 (m, 5H), 7.17 (m, 2H), 2.36 (s, 3H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 138.8, 138.4, 138.1, 133.6, 133.1, 129.0, 127.4, 126.4, 125.6, 123.7, 120.3, 115.0, 20.7

MS-C₁₉H₁₅NO₂S (321), m/z (%): 321 (M⁺, 20), 256 (2), 166 (100), 91 (25).

9-(4-Chlorophenylsulfonyl)-9H-carbazole. (Table-4, Entry-6)



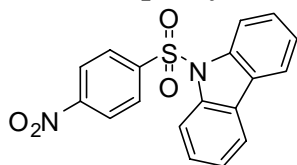
M.P : 135.6-138.3 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.05 (m, 5H), 7.62 (m, 2H), 7.42 (m, 5H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 138.7, 136.1, 134.4, 131.5, 128.2, 127.9, 123.7, 120.2, 115.0, 107.5

MS- C₁₈H₁₂ClNO₂S (341), m/z (%): 341 (M⁺, 55), 166 (100), 111 (10), 77 (25).

9-(4-Nitrophenylsulfonyl)-9H-carbazole. (Table-4, Entry-7)



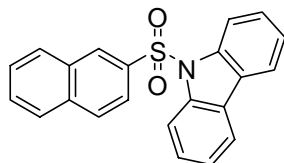
M.P : 112.1-114.8 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.26 (m, 4H), 8.01 (m, 4H), 7.53 (m, 2H), 7.32 (m, 1H), 7.16 (m, 1H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 139.8, 130.6, 129.2, 120.8, 118.3, 117.1, 114.6, 113.5

MS-C₁₈H₁₂N₂O₄S (352), m/z (%): 352 (M⁺, 20), 166 (100), 156 (10), 77 (30), 122 (5).

9-(2-Naphthylsulfonyl)-9H-carbazole. (Table-4, Entry-8)



M.P : 156.5-158.9 °C

¹H NMR (300.128 MHz, CDCl₃), δ (ppm) 8.47 (s, 1H), 8.39 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.0 Hz, 3H), 7.70 (m, 3H), 7.51 (m, 4H), 7.33 (td, J = 0.8, 8.0 Hz, 2H).

¹³C NMR (75.474 MHz, CDCl₃), δ (ppm) 138.6, 135.4, 135.1, 131.9, 129.6, 129.3, 128.4, 128.0, 127.8, 127.6, 126.6, 124.1, 121.4, 1120.2, 115.3

MS-C₂₂H₁₅NO₂S (357), m/z (%): 357 (M⁺, 40), 166 (100), 127 (45).

¹H and ¹³C NMR SPECTRA OF PRODUCTS

