Section A:

Experimental

All reagents and solvents were purchased and used as received, with the exception of CH_2Cl_2 which was dried over CaH_2 using standard procedures. Dry THF was purchased from Aldrich. No efforts were made to optimize the experimental procedures, apart from those detailed within the discussion. Merck Silica Gel 60 was used for chromatography and filtrations. NMR spectra were obtained using Bruker AC-200, Varian 300-AMX and Bruker WH-400 spectrometers. Melting points were recorded using an adapted BristolScope apparatus and stand uncorrected.

Benzyl-1-*tert*-butoxycarbonyl-3,5-dimethylpyrrole-2-carboxylate 3

Pyrrole **2** (2.29 g, 10.0 mmol), DMAP (122 mg, 1.0 mmol) and dry CH_2Cl_2 (25 mL) were stirred at room temperature overnight. The reaction mixture was then filtered through a short plug of silica, eluting with CH_2Cl_2 and then the solvent removed *in vacuo*. Purification *via* column chromatography on silica gel eluting with 95:5 hexanes:ethyl acetate gave the title compound as a colourless oil which solidified upon standing (3.21 g, 97 %), mp 67 °C; δ_H(200 MHz; $CDCl_3$) 1.48 (9H, s), 2.17 (3H, s), 2.29 (3H, s), 5.27 (2H, s), 5.74 (1H, s), 7.25 – 7.42 (5H, m); Anal. Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.28; H, 7.11; N, 4.29; *m/z* EI 329 (14 %, M^+), 229 (100, $(MH - CO_2{}^tBu)^+$), 91 (86, $(CH_2Ph)^+$), (Found: (M^+), 329.1625. $C_{19}H_{23}NO_4$ requires 329.1627).

Benzyl-1-methanesulfonyl-3,5-dimethylpyrrole-2-carboxylate 4

To a solution of pyrrole **2** (344 mg, 1.5 mmol) in dry THF (2 mL) under a flow of N_2 at room temperature was added NaH (47 mg, 1.95 mmol) and the reaction mixture stirred under N_2 for 15 minutes. Methanesulfonyl chloride (151 μL, 1.95 mmol) was then added dropwise and the reaction mixture stirred for 4 hours. Cautious addition of water (0.5 mL) to quench was followed by removal of the solvents *in vacuo*. A solution of the resulting crude material in CH_2Cl_2 was extracted with $NaHCO_3$ (sat.), water and brine (3 x 10 mL). The organic solution was then dried over $MgSO_4$ and the solvent removed *in vacuo*. The product was purified by column chromatography on silica gel eluting with 93:7 hexanes:ethyl acetate to give the title compound as a white solid (400 mg, 87 %), mp 127 °C; δ_H(200 MHz; $CDCl_3$) 2.13 (3H, s), 2.38 (3H, s), 3.43 (3H, s), 5.28 (2H, s), 5.81 (1H, s), 7.26 – 7.45 (5H, m); Anal. Calcd for $C_{15}H_{17}NO_4S$: C, 58.61; H, 5.57; N, 4.56. Found: C, 58.79; H, 5.54; N, 4.55; *m/z* EI 307 (55 %, M^+), 173 (100, $(MH - CO_2CH_2Ph)^+$), 91 (84, $(CH_2Ph)^+$), (Found: (M^+), 307.0880. $C_{15}H_{17}NO_4S$ requires 307.0878).

Benzyl-3,5-dimethyl-4-nitropyrrole-2-carboxylate 6

A suspension of finely ground ammonium nitrate (320 mg, 4.0 mmol) and trifluoro methanesulfonic anhydride (338 μL, 2.0 mmol) in CH_2Cl_2 (5 mL) was stirred at 0 ° C for 1 hour. Benzyl-3,5-dimethylpyrrole-2-carboxylate **2** (229 mg, 1.0 mmol) was then added After stirring at 0 °C for 20 minutes, the solution was quenched by the addition of phosphate pH 7 buffer solution (5 mL). The crude product was then extracted with CH_2Cl_2 (3 x 10 mL) and dried over $MgSO_4$ before the solvents were removed *in vacuo*. Purification by column chromatography on silica gel eluting with 95:5 hexanes:ethyl acetate gave the title compound (41 mg, 15 %), δ_H(200 MHz; $CDCl_3$) 2.61 (6H, s), 5.37 (1H, s), 7.29 – 7.48 (5H, m), 9.11 (1H, br s); *m/z* EI 274 (17 %, M^+), 91 (100, CH_2Ph^+). (Found: (M^+), 274.0952. $C_{14}H_{14}N_2O_4$ requires 274.0954).

Ethyl-1-*tert*-butoxycarbonyl-3,5-dimethylpyrrole-2-carboxylate 8

Prepared according to the procedure for pyrrole **3**. δ_H(200 MHz; $CDCl_3$) 1.33 (3H, t, *J* 7.5 Hz), 1.55 (9H, s) 2.18 (3H, s), 2.30 (3H, s), 4.28 (2H, q, *J* 7.5 Hz), 5.74 (1H, s); Anal. Calcd for $C_{14}H_{21}NO_4$: C, 62.90; H, 7.92; N, 5.24. Found: C, 63.11; H, 7.84; N, 5.11; *m/z* EI 267 (15 %, M^+), 167 (87), 57 (100), (Found: (M^+), 267.1470, $C_{14}H_{21}NO_4$ requires 267.1471).

Ethyl-1-methanesulfonyl-3,5-dimethylpyrrole-2-carboxylate 9

Prepared according to the procedure for pyrrole **4**. δ_H(200 MHz; $CDCl_3$) 1.36 (3H, t, *J* 7.5 Hz), 2.16 (3H, s), 2.40 (3H, s), 3.57 (3H, s), 4.33 (2H, q, *J* 7.5 Hz), 5.81 (1H, s); *m/z* EI 245 (61 %, M^+), 200 (34, $(M - 3CH_3)^+$), 167 (90),120 (100), (Found: (M^+) 245.0719, $C_{10}H_{15}SO_4N$ requires 245.0722).

Ethyl-1-*tert*-butoxycarbonyl-3-ethyl-5-methylpyrrole carboxylate 11

Prepared according to the procedure for pyrrole **3**. δ_H(200 MHz; $CDCl_3$) 1.20 (3H, t, *J* 7.5 Hz), 1.33 (3H, t, *J* 7.5 Hz), 1.51 (9H, s) 2.20 (3H, s), 2.70 (2H, q, *J* 7.5 Hz), 4.28 (2H, q, *J* 7.5 Hz), 5.77 (1H, s); *m/z* EI 281 (10 %, M^+), 181 (91), 57 (100), (Found: (M^+), 281.1628. $C_{15}H_{23}NO_4$ requires 281.1627).

Ethyl-3-ethyl-1-methanesulfonyl-5-methylpyrrole carboxylate 12

Prepared according to the procedure for pyrrole **4**. δ_H(200 MHz; $CDCl_3$) 1.21 (3H, t, *J* 7.5 Hz), 1.35 (3H, t, *J* 7.5 Hz), 2.18 (3H, s), 2.84 (2H, q, *J* 7.5 Hz), 3.47 (3H, s), 4.37 (2H, q, *J* 7.5 Hz), 5.89 (1H, s); Anal. Calcd for $C_{11}H_{17}NSO_4$: C, 50.95; H, 6.61; N, 5.40. Found: C, 51.17; H, 6.84; N, 5.57; *m/z* EI 259 (37 %, M^+), 214 (27), 180 (54), 134 (100), (Found: (M^+), 259.0876. $C_{11}H_{17}NO_4S$ requires 259.0878).

Section B: Table B1. Crystal data and structure refinement for 2, 3, 4 and 5.

Identification code	2	3	4	5
Empirical formula	C19 H23 N O4	C14 H15 N O2	C15 H17 N O4 S	C15 H14 F3 N S O4
Formula weight	329.38	229.27	307.36	361.34
Temperature	293(2) K	150(2) K	293(2) K	173(12) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71069 Å
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	P1	*C2/c*	P21/c	$P\bar{1}$ (#2)
Unit cell dimensions	a = 7.6712(10) Å	a = 31.763(9) Å	a = 5.740 Å	a = 7.8836(5)Å
	b = 9.6611(12) Å	b = 7.2968(9) Å	b = 22.730 Å	b = 8.7241(9)Å
	c = 13.495(2) Å	c = 10.5463(11) Å	c = 11.291Å	c = 12.485(1)Å
	alpha = 101.897(11) deg			alpha = 100.351(4)deg
	beta = 97.135(11) deg	beta = 96.953(14) deg	beta = 96.14 deg	beta = 106.051(4)deg
	gamma = 110.793(11) deg			gamma = 98.346(6)deg
Volume	893.4(2) A^3	2426.3(8) A^3	1464.7 A^3	794.4(1) $Å^3$
Z	2	8	4	2
F(000)	352	976	648	372.00
Crystal size	0.5 x 0.5 x 0.4 mm	0.3 x 0.3 x 0.3 mm	0.2 x 0.2 x 0.5 mm	0.35 x 0.15 x 0.07
Theta range for data collection	1.58 to 25.17 deg.	2.58 to 25.17 deg.	2.55 to 25.15 deg.	-19.0 to 23.0 deg.
Reflections collected	3400	2391	2607	6097
Independent reflections	3202 [R_{int} = 0.0062]	2191 [R_{int} = 0.0156]	2607 [R_{int} = 0.0000]	2616 [R_{int} = 0.045]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.132	1.027	1.003	1.61
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0979	R1 = 0.0458, wR2 = 0.1124	R1 = 0.0412, wR2 = 0.0946	R1 = 0.044, wR2 = 0.068 [I>3sigma(I)]
R indices (all data)	R1 = 0.0433, wR2 = 0.1060	R1 = 0.0960, wR2 = 0.1348	R1 = 0.0916, wR2 = 0.1059	0.072, wR2 = 0.123

Table B2. Selected bond lengths [Å] for pyrroles 2, 3, 4 and 5.

Bond		2	3	4	5
N(1)	C(2)	1.384(3)	1.403(2)	1.420(3)	1.427(3)
N(1)	C(5)	1.351(3)	1.393(2)	1.407(3)	1.428(3)
C(2)	C(3)	1.391(3)	1.369(2)	1.375(3)	1.368(4)
C(3)	C(4)	1.409(3)	1.418(2)	1.415(4)	1.424(4)
C(4)	C(5)	1.380(3)	1.357(2)	1.353(4)	1.353(4))
C(3)	C(7)	1.497(3)	1.499(2)	1.502(4)	1.503(4)
C(5)	C(6)	1.491(3)	1.486(2)	1.495(4)	1.489(4)
O(9)	C(8)	1.221(2)	1.202(2)	1.216(3)	1.208(3)
O(10)	C(8)	1.344(2)	1.342(2)	1.337(3)	1.344(3)
O(10)	C(11)	1.443(3)	1.450(2)	1.465(3)	1.464(3)
C(11)	C(12)	1.499(3)	1.499(2)	1.498(4)	1.497(4)
C(12)	C(13)	1.387(3)	1.379(2)	1.384(4)	1.382(4)
C(12)	C(17)	1.388(3)	1.388(2)	1.389(4)	1.390(4)
C(13)	C(14)	1.383(3)	1.382(2)	1.388(4)	1.383(4)
C(14)	C(15)	1.374(3)	1.365(2)	1.382(4)	1.367(5)
C(15)	C(16)	1.381(4)	1.371(3)	1.376(4)	1.385(5)
C(16)	C(17)	1.384(3)	1.380(2)	1.383(4)	1.384(4)
N(1)	C(18)		1.417(2)		
C(21)	C(22)		1.510(2)		
C(21)	C(24)		1.512(2)		
O(18)	C(19)		1.196(2)		
O(218)	C(20)		1.320(2)		
O(20)	C(21)		1.493(2)		
C(21)	C(23)		1.515(2)		
S(18)	N(1)			1.687(2)	1.649(2))
S(18)	O(19)			1.427(2)	1.412(2)
S(18)	O(20)			1.427(2)	1.418(2)
S(18)	C(21)			1.745(3)	1.844(3)
C(2)	C(8)	1.436(3)	1.469(2)	1.463(3)	1.474(3)

	2	3	4	5
C(2) N(1) C(5)	110.0(2)	108.50(11)	108.1(2)	107.8(2)
C(4) C(5) N(1)	107.3(2)	106.91(12)	106.8(2)	106.5(2)
C(4) C(5) C(6)	130.8(2)	128.86(14)	128.8(2)	127.3(2)
N(1) C(5) C(6)	121.8(2)	124.17(14)	124.5(2)	126.2(2)
C(5) C(4) C(3)	109.0(2)	109.89(13)	110.7(2)	110.5(2)
C(2) C(3) C(4)	106.0(2)	106.55(13)	106.7(2)	107.4(2)
C(2) C(3) C(7)	128.0(2)	127.97(14)	128.4(2)	128.0(2)
C(4) C(3) C(7)	125.9(2)	125.32(14)	124.9(2)	124.6(2)
C(3) C(2) N(1)	107.7(2)	108.12(12)	107.8(2)	107.7(2)
C(3) C(2) C(8)	133.4(2)	130.07(13)	128.7(2)	127.1(2)
N(1) C(2) C(8)	118.9(2)	120.43(12)	121.9(2)	124.0(2)
O(9) C(8) O(10)	121.9(2)	123.28(12)	124.6(2)	124.3(2)
O(9) C(8) C(2)	124.7(2)	125.47(12)	124.7(2)	126.1(2)
O(10) C(8) C(2)	113.3(2)	111.24(11)	110.6(2)	109.5(2)
O(10) C(11) C(12)	109.2(2)	107.89(11)	108.0(2)	107.6(2)
C(13) C(12)C(17)	118.7(2)	118.01(14)	118.5(2)	118.8(3)
C(13) C(12) C(11)	118.1(2)	120.09(14)	120.5(2)	120.9(2)
C(17) C(12) C(11)	123.2(2)	121.89(14)	120.9(2)	120.3(3)
C(12) C(13) C(14)	120.8(2)	120.8(2)	120.8(2)	120.6(3)
C(15) C(14) C(13)	120.2(2)	120.5(2)	119.9(3)	120.5(3)
C(14) C(15) C(16)	119.6(2)	119.6(2)	119.8(3)	119.7(3)
C(15) C(16) C(17)	120.6(2)	120.2(2)	120.2(3)	120.0(3)
C(16) C(17) C(12)	120.2(2)	120.9(2)	120.8(3)	120.4(3)
C(8) O(10) C(11)	115.5(2)	115.58(11)	118.0(2)	114.9(2)
O(19) C(18) O(20)		128.04(14)		
O(19) C(18) N(1)		122.57(13)		
O(20) C(18) N(1)		109.36(11)		
O(20) C(21) C(22)		109.31(12)		
O(20) C(21) C(24)		110.25(12)		
C(22) C(21) C(24)		113.13(13)		
O(20) C(21) C(23)		101.02(11)		
C(22) C(21) C(23)		111.15(14)		
C(24) C(21) C(23)		111.31(14)		
C(5) N(1) C(18)		123.53(12)		
C(2) N(1) C(18)		125.93(11)		
C(18) O(20) C(21)		121.56(10)		
O(19) S(18) O(20)			119.08(11)	121.7(1)
O(19) S(18) N(1)			107.08(10)	110.1(1)
O(20) S(18) N(1)			106.56(10)	108.7(1)
O(19) S(18) C(21)			108.53(12)	108.0(1)
O(20) S(18) C(21)			110.15(12)	103.4(1)
N(1) S(18) C(21)			104.41(12)	103.3(1)

Section C:

Table C1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 2. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(9)	404(1)	1498(2)	3842(1)	31(1)
O(10)	1098(1)	2052(2)	4364(1)	24(1)
N(1)	467(1)	2582(2)	1317(2)	24(1)
C(5)	588(1)	3218(3)	214(2)	26(1)
C(4)	1013(1)	3665(3)	455(2)	27(1)
C(3)	1156(1)	3283(3)	1744(2)	24(1)
C(2)	807(1)	2607(3)	2271(2)	22(1)
C(6)	291(1)	3275(4)	-993(2)	33(1)
C(7)	1603(1)	3481(3)	2372(2)	29(1)
C(8)	743(1)	2007(3)	3530(2)	22(1)
C(11)	1048(1)	1510(3)	5653(2)	27(1)
C(12)	1466(1)	1681(3)	6473(2)	24(1)
C(13)	1467(1)	1692(3)	7788(2)	28(1)
C(14)	1843(1)	1801(3)	8595(2)	35(1)
C(15)	2223(1)	1886(4)	8100(2)	43(1)
C(16)	2227(1)	1878(4)	6792(3)	43(1)
C(17)	1852(1)	1770(3)	5979(2)	33(1)

Table C2. Anisotropic displacement parameters (A^2 x 10^3) for 2. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
O(9)	21(1)	45(1)	28(1)	8(1)	2(1)	3(1)
O(10)	21(1)	32(1)	20(1)	1(1)	1(1)	1(1)
N(1)	19(1)	29(1)	23(1)	0(1)	1(1)	2(1)
C(5)	30(1)	25(1)	23(1)	0(1)	2(1)	6(1)
C(4)	30(1)	27(1)	26(1)	2(1)	6(1)	1(1)
C(3)	25(1)	21(1)	26(1)	-1(1)	2(1)	2(1)
C(2)	20(1)	22(1)	22(1)	0(1)	1(1)	2(1)
C(6)	36(1)	39(2)	23(1)	0(1)	2(1)	7(1)
C(7)	24(1)	30(1)	33(1)	1(1)	4(1)	3(1)
C(8)	20(1)	22(1)	24(1)	1(1)	1(1)	2(1)
C(11)	29(1)	32(1)	21(1)	4(1)	3(1)	3(1)
C(12)	25(1)	24(1)	23(1)	0(1)	1(1)	1(1)
C(13)	32(1)	27(1)	24(1)	1(1)	1(1)	2(1)
C(14)	41(1)	36(1)	26(1)	-2(1)	6(1)	3(1)
C(15)	32(1)	55(2)	37(2)	-5(1)	10(1)	7(1)
C(16)	27(1)	62(2)	39(2)	-5(1)	1(1)	4(1)
C(17)	28(1)	46(2)	24(1)	-5(1)	1(1)	5(1)

Table C3. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 2.

	y	y	z	U(iso)
H(1)	209(1)	2208(2)	1415(2)	29
H(4)	1181(1)	4153(3)	-151(2)	33
H(6A)	431(2)	3867(18)	-1664(4)	50
H(6B)	37(2)	3972(18)	-853(4)	50
H(6C)	210(4)	2023(4)	-1256(8)	50
H(7A)	1766(1)	4222(17)	1829(7)	44
H(7B)	1733(2)	2267(3)	2497(13)	44
H(7C)	1602(1)	4085(18)	3202(7)	44
H(11A)	947(1)	226(3)	5660(2)	33
H(11B)	835(1)	2301(3)	5993(2)	33
H(13)	1205(1)	1623(3)	8139(2)	34

Section D:

Table D1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	5541(2)	8798(1)	6206(1)	42(1)
O(9)	6013(2)	10067(1)	8439(1)	59(1)
O(10)	6716(2)	12362(1)	8111(1)	53(1)
O(19)	3354(2)	6409(1)	6131(1)	71(1)
O(20)	2843(1)	8560(1)	6753(1)	44(1)
C(5)	6210(2)	8558(2)	5299(1)	46(1)
C(4)	7618(2)	9909(2)	5326(1)	51(1)
C(3)	7866(2)	11035(2)	6251(1)	47(1)
C(2)	6550(2)	10338(2)	6779(1)	42(1)
C(6)	5404(3)	7087(2)	4465(1)	63(1)
C(7)	9393(2)	12629(2)	6595(1)	66(1)
C(8)	6378(2)	10858(2)	7851(1)	43(1)
C(11)	6571(3)	12988(2)	9155(1)	56(1)
C(12)	6968(2)	14660(2)	9297(1)	47(1)
C(13)	8186(2)	15735(2)	10183(1)	55(1)
C(14)	8537(3)	17277(2)	10335(1)	64(1)
C(15)	7681(3)	17766(2)	9609(1)	63(1)
C(16)	6469(3)	16717(2)	8722(1)	63(1)
C(17)	6110(2)	15174(2)	8566(1)	59(1)
C(18)	3810(2)	7772(2)	6361(1)	45(1)
C(21)	1114(2)	7824(2)	7156(1)	47(1)
C(22)	-488(2)	6719(2)	6261(1)	68(1)
C(23)	705(3)	9210(2)	7629(2)	68(1)
C(24)	1588(3)	7074(2)	7971(1)	65(1)

Table D2. Anisotropic displacement parameters (A^2 x 10^3) for 3. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12
N(1)	46(1)	39(1)	42(1)	9(1)	11(1)	18(1)
O(9)	82(1)	47(1)	45(1)	17(1)	12(1)	20(1)
O(10)	77(1)	39(1)	44(1)	10(1)	22(1)	20(1)
O(19)	76(1)	37(1)	99(1)	9(1)	36(1)	20(1)
O(20)	47(1)	38(1)	49(1)	14(1)	15(1)	17(1)
C(5)	50(1)	54(1)	41(1)	11(1)	11(1)	29(1)
C(4)	55(1)	61(1)	47(1)	20(1)	19(1)	29(1)
C(3)	48(1)	46(1)	51(1)	18(1)	13(1)	20(1)
C(2)	46(1)	38(1)	44(1)	10(1)	9(1)	18(1)
C(6)	68(1)	65(1)	51(1)	-1(1)	10(1)	31(1)
C(7)	63(1)	53(1)	78(1)	22(1)	26(1)	13(1)
C(8)	45(1)	38(1)	44(1)	10(1)	7(1)	14(1)
C(11)	74(1)	48(1)	43(1)	9(1)	21(1)	19(1)
C(12)	51(1)	48(1)	43(1)	9(1)	18(1)	21(1)
C(13)	66(1)	54(1)	48(1)	6(1)	9(1)	32(1)
C(14)	72(1)	51(1)	61(1)	-2(1)	8(1)	26(1)
C(15)	75(1)	51(1)	73(1)	17(1)	30(1)	33(1)
C(16)	73(1)	71(1)	63(1)	27(1)	20(1)	41(1)
C(17)	59(1)	63(1)	48(1)	8(1)	6(1)	23(1)
C(18)	50(1)	38(1)	45(1)	8(1)	9(1)	17(1)
C(21)	47(1)	46(1)	51(1)	17(1)	16(1)	16(1)
C(22)	51(1)	70(1)	69(1)	17(1)	7(1)	12(1)
C(23)	71(1)	64(1)	80(1)	20(1)	36(1)	33(1)
C(24)	64(1)	71(1)	66(1)	36(1)	19(1)	23(1)

Table D3. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 3.

	x	y	z	U(iso)
H(4)	8317(2)	10072(2)	4815(1)	61
H(6A)	4045(3)	6764(8)	4269(7)	94
H(6B)	5694(16)	6315(4)	4714(3)	94
H(6C)	5955(14)	7234(4)	3875(4)	94
H(7A)	9533(13)	13053(6)	6012(2)	99
H(7B)	10580(5)	12592(2)	6882(9)	99
H(7C)	9044(9)	13263(4)	7113(7)	99
H(11A)	7489(3)	12866(2)	9657(1)	68
H(11B)	5301(3)	12452(2)	9257(1)	68
H(13)	8778(2)	15418(2)	10683(1)	66
H(14)	9363(3)	17988(2)	10936(1)	77
H(15)	7919(3)	18805(2)	9716(1)	75
H(16)	5887(3)	17045(2)	8224(1)	76
H(17)	5282(2)	14471(2)	7963(1)	71
H(22A)	-1635(5)	6319(12)	6510(2)	101
H(22B)	-156(8)	5888(8)	5946(7)	101
H(22C)	-693(13)	7248(4)	5757(5)	101
H(23A)	-440(11)	8881(2)	7890(10)	102
H(23B)	542(20)	9726(9)	7109(3)	102
H(23C)	1754(9)	9902(8)	8187(7)	102
H(24A)	513(7)	6715(13)	8284(7)	97
H(24B)	2672(12)	7809(5)	8493(5)	97
H(24C)	1879(18)	6220(9)	7654(2)	97

Section E:

Table E1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 4. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(18)	4069(1)	3889(1)	70(1)	18(1)
O(9)	5782(3)	4565(1)	-2181(2)	26(1)
O(10)	8490(3)	3948(1)	-2803(2)	24(1)
O(19)	3258(3)	3528(1)	975(2)	26(1)
O(20)	6454(3)	4078(1)	193(2)	24(1)
N(1)	3651(4)	3507(1)	-1216(2)	16(1)
C(5)	2369(5)	2981(1)	-1381(2)	20(1)
C(4)	3176(5)	2698(1)	-2310(2)	23(1)
C(3)	4993(5)	3025(1)	-2755(2)	19(1)
C(2)	5270(4)	3529(1)	-2083(2)	16(1)
C(6)	458(5)	2800(1)	-656(2)	25(1)
C(7)	6252(5)	2846(1)	-3799(2)	29(1)
C(8)	6508(4)	4071(1)	-2331(2)	19(1)
C(11)	9621(5)	4423(1)	-3406(2)	26(1)
C(12)	9585(5)	4261(1)	-4694(2)	20(1)
C(13)	11481(5)	3980(1)	-5104(2)	25(1)
C(14)	11438(5)	3817(1)	-6291(2)	30(1)
C(15)	9463(5)	3925(1)	-7073(3)	31(1)
C(16)	7567(5)	4204(1)	-6676(2)	31(1)
C(17)	7626(5)	4373(1)	-5496(3)	27(1)
C(21)	2203(5)	4494(1)	-160(2)	24(1)

Table E2. Anisotropic displacement parameters (A^2 x 10^3) for 4. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + 2 h k a* b* U12].

U11	*U22*	**U33**	**U23**	**U13**	**U12**	
S(18)	20(1)	19(1)	17(1)	-2(1)	4(1)	1(1)
O(9)	28(1)	20(1)	32(1)	0(1)	11(1)	-1(1)
O(10)	24(1)	23(1)	27(1)	1(1)	13(1)	-4(1)
O(19)	39(1)	24(1)	17(1)	1(1)	7(1)	-2(1)
O(20)	17(1)	31(1)	24(1)	-6(1)	1(1)	-1(1)
N(1)	18(1)	16(1)	16(1)	0(1)	5(1)	1(1)
C(5)	20(1)	15(1)	24(1)	4(1)	2(1)	0(1)
C(4)	28(2)	16(1)	25(2)	-4(1)	3(1)	-3(1)
C(3)	22(2)	19(1)	18(1)	-2(1)	3(1)	3(1)
C(2)	14(1)	19(1)	15(1)	2(1)	2(1)	0(1)
C(6)	24(2)	24(2)	27(2)	2(1)	7(1)	-3(1)
C(7)	36(2)	28(2)	26(2)	-10(1)	13(1)	-2(1)
C(8)	18(1)	24(2)	13(1)	-1(1)	1(1)	1(1)
C(11)	26(2)	28(2)	28(2)	1(1)	12(1)	-11(1)
C(12)	22(2)	18(1)	22(1)	-1(1)	8(1)	-7(1)
C(13)	20(2)	29(2)	25(2)	1(1)	-1(1)	0(1)
C(14)	27(2)	30(2)	33(2)	-4(1)	11(1)	2(1)
C(15)	36(2)	33(2)	24(2)	-2(1)	6(1)	-7(2)
C(16)	26(2)	37(2)	28(2)	5(1)	-5(1)	-6(1)
C(17)	18(2)	27(2)	36(2)	0(1)	10(1)	-1(1)
C(21)	22(2)	20(1)	28(2)	-5(1)	6(1)	4(1)

Table E3. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 4.

	x	y	z	U(iso)
H(4)	2614(5)	2339(1)	-2614(2)	28
H(6A)	-467(18)	3137(2)	-500(13)	37
H(6B)	1133(5)	2634(7)	84(7)	37
H(6C)	-520(18)	2512(6)	-1088(7)	37
H(7A)	5696(23)	2468(4)	-4083(10)	44
H(7B)	7905(6)	2825(8)	-3556(5)	44
H(7C)	5961(26)	3132(4)	-4424(6)	44
H(11A)	11224(5)	4473(1)	-3052(2)	32
H(11B)	8788(5)	4789(1)	-3328(2)	32
H(13)	12802(5)	3900(1)	-4578(2)	30
H(14)	12735(5)	3636(1)	-6560(2)	35
H(15)	9417(5)	810(1)	-7866(3)	37
H(16)	6242(5)	4280(1	-7202(2)	37
H(17)	6339(5)	4563(1)	-5236(3)	32
H(21A)	2612(19	4715(4)	-831(9)	35
H(21B)	2359(21)	4739(4)	537(6)	35
H(21C)	613(5)	4360(1)	-312(15)	35

Section F: Pyrrole 5

Empirical Formula C15H14F3NSO4

Formula Weight 361.34

Crystal Color, Habit clear , platelet

Crystal Dimensions 0.35 X 0.15 X 0.07 mm

Crystal System triclinic

Lattice Type Primitive

Lattice Parameters a = 7.8836(5)A

b = 8.7241(9) A

c = 12.485(1) A

a = 100.351(4)0

{3 = 106.051(4)0

'Y = 98.346(6)0

V = 794.4(1) A3

Space Group pI (#2)

Z value 2

Dcalc 1.511 g/cm3

Fooo 372.00

JL(MoKa) 2.56 cm-l

B. Intensity Measurements

Diffractometer Rigaku/ ADSC CCD

Radiation MoKa ()., = 0.71069 A)

graphite monochromated

Detector Aperture 94 mm x 94 mm

Data Images 464 exposures @ 35.0 seconds

4> oscillation Range (X=-90.0) 0.0 -190.0°

(.; oscillation Range (X=-90.0) -19.0-23.0°

Detector Position 40.49 mm

Detector Swing Angle -5.52°

2fJmax 50.2°

No. of Reflections Measured Total: 6097

Unique: 2616 (Rint = 0.045)

Corrections Lorentz- polarization

Absorption

(trans. factors: 0.6313 -1.0000)

C. Structure Solution and Refinement

Structure Solution Direct Methods (SIR97)

Refinement FUll-matrix least-squares

FUnction Minimized Ew(Fo2 -FC2)2

2

Least Squares Weights w = ~ = [0";(F02) + TFo2]-1

p-factor 0.0000

Anomalous Dispersion All non-hydrogen atoms

No. Observations (1>0.000"(1)) 2616	No. Observations (1>30"(1)) 2016
No. Variables 217	Residuals (refined on F, 1>30"(1)): R;
Reflection/Parameter Ratio 12.06	Rw 0.044 ; 0.068
Residuals (refined on F2, all data): R;	Maximum peak in Final Diff. Map 0.35
Rw 0.072 ; 0.123	e- /A3
Goodness of Fit Indicator 1.61	Minimum peak in Final Diff. Map -0.49
Max Shift/Error in Final Cycle 0.00	e- / A3

Data Collection

A clear platelet crystal of C15H14F3NSO4 having approximate dimensions of 0.35 x 0.15 x 0.07 mm was mounted on a glass fiber. All measurements were made on a Rigaku/ ADSC CCD area detector with graphite monochromated Mo-Ka radiation. Cell constants and an orientation matrix for data collection, derived from 3847 reflections (2{} = 7.0 - 50.2°), corresponded to a triclinic cell with dimensions:

a = 7.8836(5) 11 a = 100.351(4)0

b = 8.7241(9) 11 .8 = 106.051(4)0

c = 12.485(1) 11 'Y = 98.346(6)

V = 794.4(1) 113

For Z = 2 and F .W .= 361.34, the calculated density is 1.51 g/cm3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: pI (#2)

The data were collected at a temperature of -100 :t. 1°C to a maximum 2{} value of 50.2°. Data were collected in 0.50° oscillations with 35.0 second exposures. A sweep of data was done using f/J oscillations from 0.0 to 190.0° at X=-90.0° and a second sweep was performed using UJ oscillations between -19.0 and 23.0° at X=-90.0°. The crystal-to-detector distance was 40.49 mm .The detector swing angle was -5.52°. Data Reduction

Of the 6097 reflections which were collected, 2616 were unique (~nt = 0.045); equivalent reflections were merged. Data were collected and processed using the d*TREK programlO .Net intensities and sigmas were derived as follows: m F2 = [L(Pi -mBatle)] .Lp i=l where Pi is the value in counts of the ith pixel m is the number of pixels in the integration area Batle is the background average Lp is the Lorentz and polarization factor Ej=l Bj Batle = n where n is the number of pixels in the background area Bj is the value of the jth pixel in counts ~ E~-l(Bave -Bj)2 a2(F~kl) = [(L... Pi) + m(J- n- 1)1 .Lp .errmul + (erradd .F2)2 i=l where erradd = 0.05 errmul = 1.20

The linear absorption coefficient, 11, for Mo-Ka radiation is 2.6 cm-l. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods and expanded using Fourier techniques2. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement3 was based on 2616 observed reflections (I > O.OOa(I)) and 217 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

Rl = EIIFol-IFcll = 0.072

EIFor

fE(Fo2 -Fc2)2

wR2 = V Ew(Fo2)2 = 0.123

The standard deviation of an observation of unit weight4 was 1.61. The weighting scheme was based oil counting statistics. Plots of Ew(IFol -IFcl)2 versus IFol, reflection order in data collection, sin O / >. and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.35 and -0.49 e- / A3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber5 .Anomalous dispersion effects were included in Fcalc6; the values for ~f' and ~r' were those of Creagh and McAuley7. The values for the mass attenuation coefficients are those of Creagh and Hubbel18. All calculations were performed using the teXsan9 crystallographic software package of Molecular Structure Corporation.

References

(1) ~: Altomare, A., Burla, M.C., Cammalli, G., Cascarano, M., Giacovazzo, C., Guagliardi, A., Moliterni, A.G.G., Polidori, G., Spagna, A. SIR97: a new tool for crystal structure determination and refinement. (1998). Submitted.

(2) DIRQIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M. (1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands,

(3) Least-Squares: Function minimized: Ew(Fo2 -FC2)2

(4) Standard deviation of an observation of unit weight: !Ew(Fo2 -F~2)2

V (No-Nv) where: No = number of observations Nv = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

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(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

(10) d*TREK: Area Detector Software. Version 4.13. Molecular Structure Corporation. (1996-1998).

Table F1. Atomic coordinates and Biso/Beq

atom	x	y	z	Beq
S(18)	0.32844(7)	0.50062(6)	0.68245(4)	1.55(1)
F(22)	0.4809(2)	0.2818(2)	0.7718(1)	4.00(4)
F(23)	0.5621(2)	0.5166(2)	0.8763(2)	4.95(4)
F(24)	0.3049(2)	0.3767(3)	0.8543(2)	4.98(5)
0(9)	0.4221(2)	0.1930(2)	0.5380(1)	1.94(3)
0(10)	0.2342(2)	0.1460(2)	0.3573(1)	1.58(3)
0(19)	0.4529(2)	0.5155(2)	0.6206(1)	2.19(3)
0(20)	0.2755(2)	0.6353(2)	0.7358(1)	2.34(3)
N(l)	0.1457(2)	0.3666(2)	0.6041(1)	1.28(3)
C(2)	0.1271(3)	0.2522(2)	0.5020(2)	1.23(4)
C(3)	-0.0522(3)	0.1837(2)	0.4532(2)	1.37(4)
C(4)	-0.1462(3)	0.2557(2)	0.5242(2)	1.60(4)
C(5)	-0.0303(3)	0.3686(2)	0.6136(2)	1.49(4)
C(6)	-0.0758(3)	0.4770(3)	0.7033(2)	2.16(5)
C(7)	-0.1397(3)	0.0543(2)	0.3462(2)	1.76(4)
C(8)	0.2798(3)	0.1978(2)	0.4716(2)	1.29(4)
C(ll)	0.3649(3)	0.0683(2)	0.3169(2)	1.69(4)
C(12)	0.2773(3)	-0.0102(2)	0.1927(2)	1.63(4)
C(13)	0.3377(3)	0.0436(3)	0.1095(2)	2.49(5)
C(14)	0.2600(4)	-0.0330(3)	-0.0048(2)	3.38(6)
C(15)	0.1200(4)	-0.1613(3)	-0.0375(2)	3.50(6)
C(16)	0.0575(4)	-0.2170(3)	0.0446(2)	3.33(5)

C(17)	0.1367(3)	-0.1425(3)	0.1593(2)	2.52(5)
C(21)	0.4248(3)	0.4110(3)	0.8025(2)	2.27(4)
H(l)	-0.2764	0.2270	0.5107	1.9667
H(2)	-0.0071	0.4665	0.7793	2.6233
H(3)	-0.0454	0.5873	0.6972	2.6233
H(4)	-0.2052	0.4481	0.6930	2.6233
H(5)	-0.2399	-0.0168	0.3574	2.0598
H(6)	-0.1876	0.1011	0.2818	2.0598
H(7)	-0.0517	-0.0073	0.3311	2.0598
H(8)	0.3979	-0.0117	0.3603	2.0147
H(9)	0.4726	0.1474	0.3266	2.0147
H(10)	0.4374	0.1364	0.1319	3.0767
H(ll)	0.3047	0.0051	-0.0629	4.0699
H(12)	0.0629	-0.2145	-0.1185	4.2925
H(13)	-0.0409	-0.3099	0.0218	3.9751
H(14)	0.0922	-0.1828	0.2167	3.0676

Beq = ~7r2(Ull(aa*)2 + U22(bb*)2 + U33(CC*)2 + 2U12aa*bb* cos'Y + 2U13aa*cc* cos/3 + 2U23bb*cc* cosa)

Table F2. Anisotropic Displacement Parameters

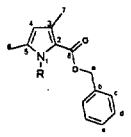
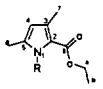
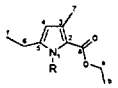
Atom	U11	U22	U33	U12	U13	U23
S(18)	0.0190(3)	0.0168(3)	0.0180(3)	-0.0001(2)	0.0021(2)	0.0005(2)
F(22)	0.077(1)	0.0450(8)	0.0286(8)	0.0362(8)	0.0022(8)	0.0076(6)
F(23)	0.061(1)	0.0479(9)	0.040(1)	-0.0079(7)	-0.0304(9)	-0.0002(7)
F(24)	0.052(1)	0.114(1)	0.048(1)	0.03i(l)	0.0262(9)	0.052(1)
0(9)	0.0171(7)	0.0360(8)	0.0177(8)	0.0100(6)	0.0009(6)	0.0021(6)
0(10)	0.0176(7)	0.0266(7)	0.0145(7)	0.0085(6)	0.0035(6)	0.0003(6)
0(19)	0.0216(8)	0.0275(8)	0.0312(9)	-0.0027(6)	0.0096(7)	0.0038(6)
0(20)	0.0318(9)	0.0195(7)	0.0299(9)	0.0041(6)	0.0044(7)	-0.0044(6)
N(I)	0.0139(8)	0.0181(8)	0.0143(9)	0.0025(6)	0.0036(7)	0.0002(6)
C(2)	0.0166(9)	0.0166(9)	0.013(1)	0.0044(7)	0.0035(8)	0.0026(7)
C(3)	0.0160(9)	0.018(1)	0.016(1)	0.0034(7)	0.0023(8)	0.0038(7)
C(4)	0.015(1)	0.026(1)	0.020(1)	0.0042(7)	0.0053(8)	0.0046(8)
C(5)	0.0158(9)	0.022(1)	0.021(1)	0.0054(7)	0.0082(8)	0.0069(7)
C(6)	0.028(1)	0.031(1)	0.024(1)	0.0095(9)	0.011(1)	0.0018(9)
C(7)	0.015(1)	0.024(1)	0.021(1)	0.0003(8)	0.0000(9)	-0.0003(8)
C(8)	0.0171(9)	0.0154(9)	0.0161(9)	0.0026(7)	0.0051(7)	0.0030(7)
C(ll)	0.017(1)	0.027(1)	0.021(1)	0.0089(8)	0.0073(9)	0.0023(8)
C(12)	0.019(1)	0.021(1)	0.022(1)	0.0080(7)	0.0070(8)	-0.0005(8)
C(13)	0.031(1)	0.036(1)	0.024(1)	-0.002(1)	0.012(1)	0.0003(9)
C(14)	0.047(2)	0.055(2)	0.022(1)	0.001(1)	0.016(1)	0.000(1)
C(15)	0.046(2)	0.049(1)	0.024(1)	0.003(1)	0.007(1)	-0.015(1)
C(16)	0.043(2)	0.032(1)	0.036(1)	-0.008(1)	0.009(1)	-0.012(1)
C(17)	0.037(1)	0.027(1)	0.030(1)	-0.0017(9)	0.015(1)	0.0013(9)
C(21)	0.027(1)	0.033(1)	0.018(1)	0.0054(8)	-0.0037(8)	0.0022(8)

The general temperature factor expression:

exp(-27r2(a*2U11h2 + b*2U22k2 + c*2U3312 + 2a*b*U12hk + 2a*c*U13hl + 2b*c*U23kl»

Section G:

Table G1. ^{13}C Chemical shifts for pyrroles 2, 3, 4, 5, 7, 8, 9, 10, 11 and 12.

	Pyrrole R	C^2	C^3	C^4	C^5	C^6	C^7	C^8	a	b	c, d, e	others
	**2** H	117.47	129.64	111.56	133.32	13.13	13.03	161.78	65.55	136.71	127.98 128.05 128.58	
	3 Boc	120.88	131.04	113.08	135.99	14.03	12.67	161.22	66.09	136.20	128.03 128.20 128.45	$C(CH_3)_3$ 27.55 $C(CH_3)_3$ 84.32 $CO_2{}^tBu$ 149.69
	4 Ms	122.92	131.55	115.09	137.72	14.98	12.53	160.95	66.77	135.33	128.21 128.39 128.49	SO_2CH_3 43.18
	5 Tf	124.99	133.19	118.30	138.43	14.68	12.34	160.13	67.48	135.17	128.44 128.53 128.77	CF_3 119.40, q, J 323 Hz
	**7** H	117.77	128.93	111.29	133.06	12.90	12.90	162.30	59.72	14.50		
	8 Boc	121.23	130.02	112.81	135.28	(13.70)	12.20	161.14	59.90	(13.74)		$C(CH_3)_3$ 27.13 $C(CH_3)_3$ 83.80 $CO_2{}^tBu$ 149.49
	9 Ms	123.60	131.15	115.17	137.63	14.22	12.68	161.49	60.94	15.26		SO_2CH_3 43.56
	**10** H	117.69	128.69	109.69	139.59	20.45	(13.03)	162.45	59.72	14.52		f (13.49)
	11 Boc	121.06	129.48	110.74	141.10	20.50	12.17	160.86	59.63	14.09		$C(CH_3)_3$ 26.13 $C(CH_3)_3$ 84.42 $CO_2{}^tBu$ 149.33 f 13.62
	12 Ms	123.69	130.91	113.25	143.81	21.76	(12.56)	161.51	60.87	14.20		SO_2CH_3 43.43 f (12.96)

Section H:

Figure: Crystal structures of 2, 3, 4 and 5.

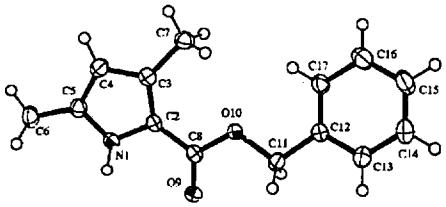


Figure 1. Crystal structure of 2.

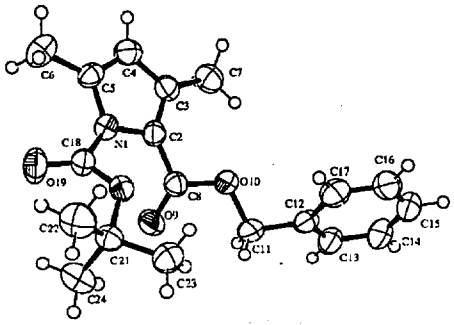


Figure 2. Crystal structure of 3.

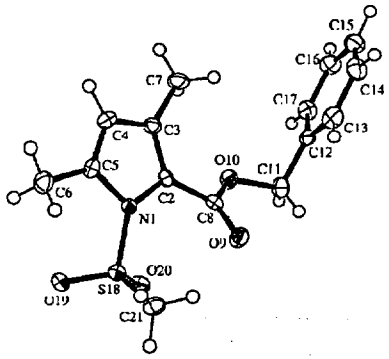


Figure 3. Crystal structure of 4.

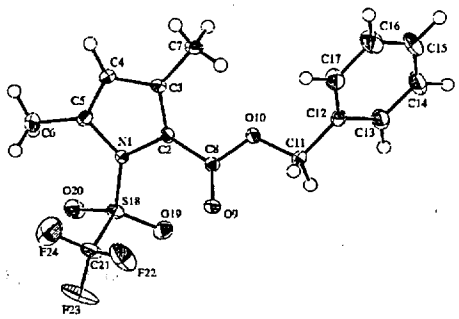


Figure 4. Crystal structure of 5.