Supplementary Information: Hunter and McNab

Chemical and spectroscopic properties of the 3-hydroxythiophene [thiophen-3(2*H*)-one] system.

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Supplementary Information

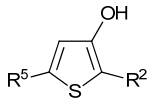


Table S1. ^{1}H NMR parameters of 3-hydroxythiophenes for solutions in $CDCl_3$ unless otherwise stated.

R^2	R^5	$\delta_H(2)$	$\delta_H(4)$	$\delta_H(5)$	$^3J_{4,5}$/Hz	$^4J_{2,4}$/Hz	$^4J_{2,5}$/Hz
H	H[a]	6.29	6.71	7.10	5.1	1.6	3.2
Me	H		6.59	6.84	5.4		
Ph	H		6.74	7.08	5.4		
CO_2Et	H		6.69	7.31	5.4		
H	Me[a]	5.95	6.38[b]			1.7	
H	Ph[a]	6.27	7.06			1.7	
H	SMe[a]	6.24	6.66			1.8	

[a] d_6-DMSO solution; [b] $^4J_{H4,Me}$ 1.1 Hz

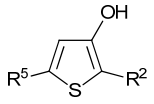


Table S2. ^{13}C NMR parameters of 3-hydroxythiophenes for solutions in $CDCl_3$ unless otherwise stated; $^1J_{CH}$ values shown in parentheses are quoted in Hz.

R^2	R^5	$\delta_C(2)$ ($^1J_{H2}$)	$\delta_C(3)$	$\delta_C(4)$ ($^1J_{H4}$)	$\delta_C(5)$ ($^1J_{H5}$)
H	H[a]	98.0 (184.1)	155.1	119.9 (167.1)	124.4 (187.2)
Me	H	113.2	148.9	119.9 (163.0)	119.5 (188.7)
Ph	H	117.8	148.7	120.5 (169.6)	122.3 (188.4)
CO_2Et	H[b]	103.8	164.4	118.9	131.1
H	Me[a]	95.2 (184.0)	154.1	118.6 (166.0)	137.2
H	Ph[a]	98.2 (185.4)	155.4	116.4 (166.1)	140.9
H	SMe[a]	100.1 (185.9)	154.4	122.5 (168.6)	134.6

[a] d_6-DMSO solution; [b]coupling constants not measured

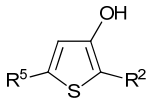


Table S3. Long range ^{13}C-^{1}H coupling constants of 3-hydroxythiophenes for solutions in $CDCl_3$ unless otherwise stated; (m = multiplet; s = singlet); J_{CH} values quoted in Hz.

R^2	R^5	$^3J_{C2\text{-}H4}$	$^3J_{C2\text{-}H5}$	$^3J_{C3\text{-}H5}$	$^2J_{C3\text{-}H4} = {}^2J_{C3\text{-}H2}$	$^3J_{C4\text{-}H2}$	$^2J_{C4\text{-}H5}$	$^3J_{C5\text{-}H2}$	$^2J_{C5\text{-}H4}$
H	H[a,b]	7.6	3.8	11.6	1.8	7.4	4.7	6.3	6.3
Me	H[a]	m	m	m	m		3.8		5.1
Ph	H	m	m	10.7	2.0		2.5		4.0
H	Me[a]	7.4			s	5.4		m	m
H	Ph[a]	7.5				6.8		m	m
H	SMe[a]	7.2				6.7		m	m

[a] d_6-DMSO solution; [b] additional couplings to OH observed – see Fig. 1 in main paper.

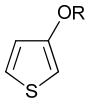


Table S4. ^{1}H NMR parameters of 3-hydroxy-, 3-methoxy- and 3-acetoxythiophene for solutions in $CDCl_3$.

R	$\delta_H(2)$	$\delta_H(4)$	$\delta_H(5)$	$^3J_{4,5}$/Hz	$^4J_{2,4}$/Hz	$^4J_{2,5}$/Hz
H	6.29	6.71	7.10	5.1	1.6	3.2
Me	6.28	6.79	7.20	5.2	1.6	3.1
Ac	7.09	6.90	7.23	5.3	1.4	3.3

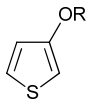


Table S5. ^{13}C NMR parameters of 3-hydroxy-, 3-methoxy- and 3-acetoxythiophene for solutions in $CDCl_3$; $^1J_{CH}$ values shown in parentheses are quoted in Hz.

R	$\delta_C(2)$ ($^1J_{H2}$)	$\delta_C(3)$	$\delta_C(4)$ ($^1J_{H4}$)	$\delta_C(5)$ ($^1J_{H5}$)
H	98.0 (184.1)	155.1	119.9 (167.1)	124.4 (187.2)
Me	96.5 (183.2)	158.7	119.2 (166.9)	124.7 (187.2)
Ac	110.7 (188.5)	146.9	121.7 (172.0)	124.0 (188.6)

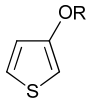


Table S6. Long range ^{13}C-^1H coupling constants of 3-hydroxy-, 3-methoxy- and 3-acetoxythiophene for solutions in $CDCl_3$ (m = multiplet; s = singlet); J_{CH} values quoted in Hz.

R	$^3J_{C2\text{-}H4}$	$^3J_{C2\text{-}H5}$	$^3J_{C3\text{-}H5}$	$^2J_{C3\text{-}H4}$ = $^2J_{C3\text{-}H2}$	$^3J_{C4\text{-}H2}$	$^2J_{C4\text{-}H5}$	$^3J_{C5\text{-}H2}$	$^2J_{C5\text{-}H4}$
H	7.6	3.8	11.6	1.8	7.4	4.7	6.3	6.3
Me	6.8	3.9	m	m	6.6	6.6	5.4	5.4
Ac	6.8	2.7	12.6	[a]	6.9	4.1	5.7	6.5

[a]undetected

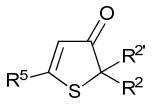


Table S7. ^{1}H NMR parameters of thiophen-3(2*H*)-ones for solutions in $CDCl_3$.

R^2	$R^{2'}$	R^5	$\delta_H(2)$	$\delta_H(4)$	$\delta_H(5)$	$^3J_{4,5}$/Hz
H	H	H	3.58	6.22	8.36	5.7
Me	H	H	3.61	6.14	8.34	5.8
Me	Me	H		5.98	8.24	6.0
-$(CH_2)_5$-		H		6.03	8.27[a]	5.9
Me	Ph	H		6.16	8.48	6.0
H	H	Me	3.63	5.98		
H	H	Ph	3.81	6.56		
H	H	SMe	3.61	5.88		
H	H	4-t-BuC_6H_4	3.77	6.53		

[a]Additional coupling to one proton of the cyclohexyl ring, ^5J 0.7 Hz.

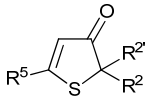


Table S8. ^{13}C NMR parameters of thiophen-3(2*H*)-ones for solutions in $CDCl_3$; $^1J_{CH}$ values shown in parentheses are quoted in Hz

R^2	$R^{2'}$	R^5	$\delta_C(2)$ ($^1J_{H2}$)	$\delta_C(3)$	$\delta_C(4)$ ($^1J_{H4}$)	$\delta_C(5)$ ($^1J_{H5}$)
H	H	H	38.6 (143.6)	203.4	123.4 (176.2)	164.9 (180.3)
Me	H	H	48.3 (138.4)	207.2	121.9 (175.8)	164.5 (178.2)
Me	Me	H	56.6	207.7	120.3 (175.4)	161.4 (179.2)
-$(CH_2)_5$-		H	65.5	207.3	121.6 (173.8)	161.9 (179.1)
Me	Ph	H	62.3	206.3	119.6 (176.2)	162.5 (180.3)
H	H	Me	41.4 (143.6)	202.5	121.7 (172.3)	180.1
H	H	Ph	40.6 (143.6)	202.4	118.3 (170.8)	178.7
H	H	SMe	40.6 (141.3)	197.9	115.7 (174.1)	182.5
H	H	4-t-BuC_6H_4	40.4	202.8	117.7	178.4

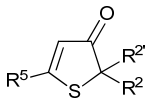
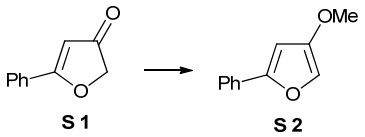


Table S9. Long range ^{13}C-^{1}H coupling constants of thiophen-3(2*H*)-ones for solutions in $CDCl_3$ (m = multiplet); J_{CH} values quoted in Hz. Couplings to C3 usually too complex for assignment.

R^2	$R^{2'}$	R^5	$^3J_{C2\text{-}H4}$	$^3J_{C2\text{-}H5}$	$^2J_{C4\text{-}H5}$	$^2J_{C5\text{-}H4}$
H	H	H	6.7	2.7	4.0	8.0[a]
Me	H	H	m	m	3.3	m
Me	Me	H	m	m	3.9	7.0
-$(CH_2)_5$-		H	m	m	2.8	7.2
Me	Ph	H	m	m	2.8	7.8
H	H	Me	6.7		[b]	m
H	H	Ph	5.7			m
H	H	SMe	6.6			m

[a]Additional coupling to C2, ^3J 2.6 Hz; [b]additional coupling to 5-methyl group, ^3J 4.2 Hz.

3-Methoxy-5-phenylfuran S2



The conditions used for the alkylation of the thiophen-3(2*H*)-ones were also applicable to 5-phenylfuran-3(2*H*)-one[1] **S1** to give 3-methoxy-5-phenylfuran **S2** (52%) bp 152-154 °C (0.2 Torr) (Found: C, 75.6; H, 5.95. $C_{11}H_{10}O_2$ requires C, 75.9; H, 5.75%), δ_H 7.65-7.30 (5H, m), 7.14 (1H, d, ^4J 1.0), 6.48 (1H, d, ^4J 1.0) and 3.75 (3H, s); δ_C 151.40 (quat), 130.68 (quat), 128.45, 127.40, 126.45 (quat), 123.53, 122.60, 98.58 and 57.85; *m/z* 174 (M^+, 100%), 145 (9), 131 (31), 105 (46), 103 (37), 102 (18) and 77 (35).

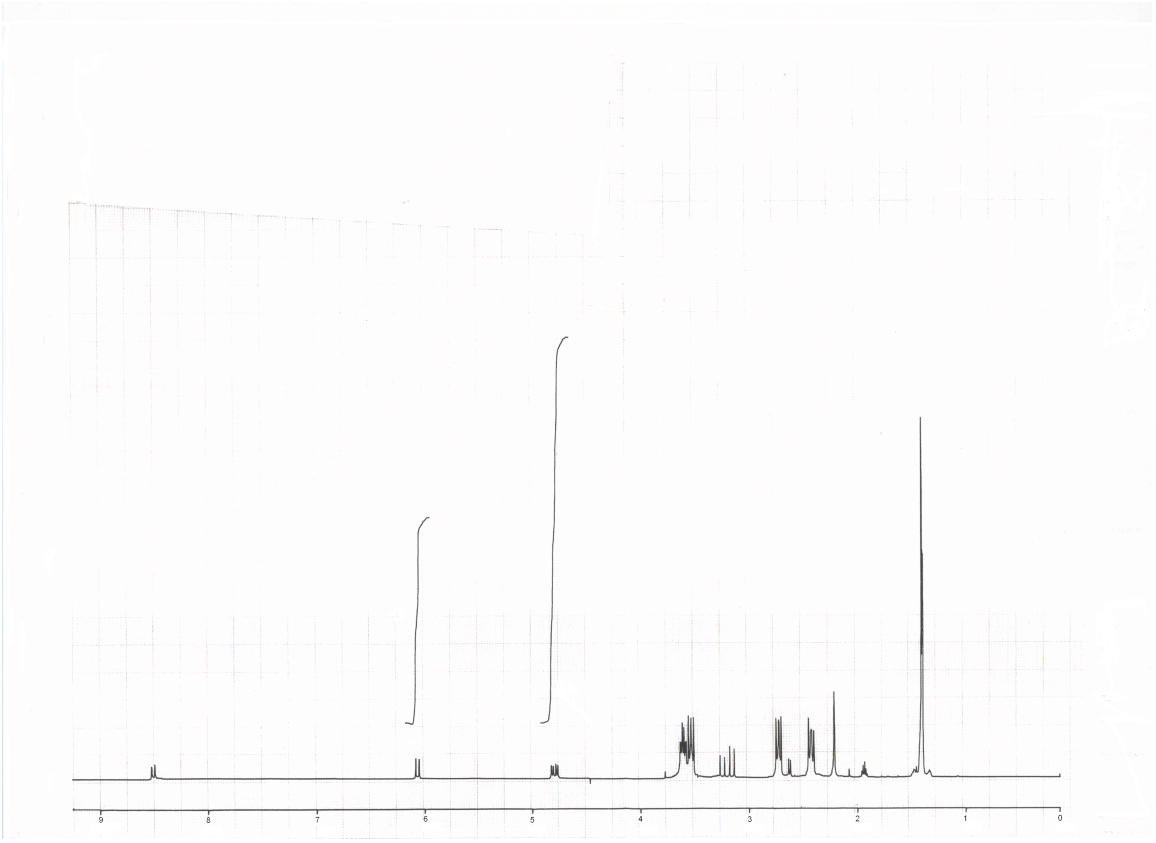


Figure S1. ^{1}H NMR spectrum (80 MHz) of adduct **24** formed from 2,2-dimethylthiophen-3(2*H*)-one **11** and morpholine in CD_3CN. The precursor **11** (34% of mixture) is characterised by signals at δ_H 8.51 and 6.06 and the product **24** (66% of mixture) by two protons of an AMX system at δ_H 4.79 (^3J 8.4 and 3.4 Hz) and 3.20 (^2J 17.7 and ^3J 8.4 Hz) (the third proton is overlapping).

References

1. J. P. Bouchet, J. F. Robert and J. J. Panouse, *C. R. Acad. Sci., Ser.* 2, 1982, **294**, 249-252.