Supporting Information

Vinyl sulfone building blocks in covalently reversible reactions with thiols

Thomas H. Schneider,[a] Max Rieger,[b] Kay Ansorg,[b] Alexandre N. Sobolev,[c] Tanja Schirmeister,[a] Bernd Engels,[b] Simon Grabowsky[c,d*]

[a] University of Mainz, Institute of Pharmacy and Biochemistry, Staudingerweg 5, 55128 Mainz, Germany

[b] University of Würzburg, Institute of Physical and Theoretical Chemistry, Emil-Fischer-Str. 42, 97074 Würzburg, Germany

[c] The University of Western Australia, School of Chemistry and Biochemistry, M310, 35 Stirling Highway, Crawley WA 6009, Australia

[d] Universität Bremen, Fachbereich 2 – Biologie/Chemie, Leobener Str. NW2, 28359 Bremen, Germany

* Corresponding author: Dr. S. Grabowsky, simon.grabowsky@uni-bremen.de, +49 421 218 63152.

Contents: Crystallographic details, summary of hydrogen bonds in the crystals, electrostatic potentials mapped onto the Hirshfeld surfaces of all compounds **1**-**9**.

Table S1: Crystallographic Details

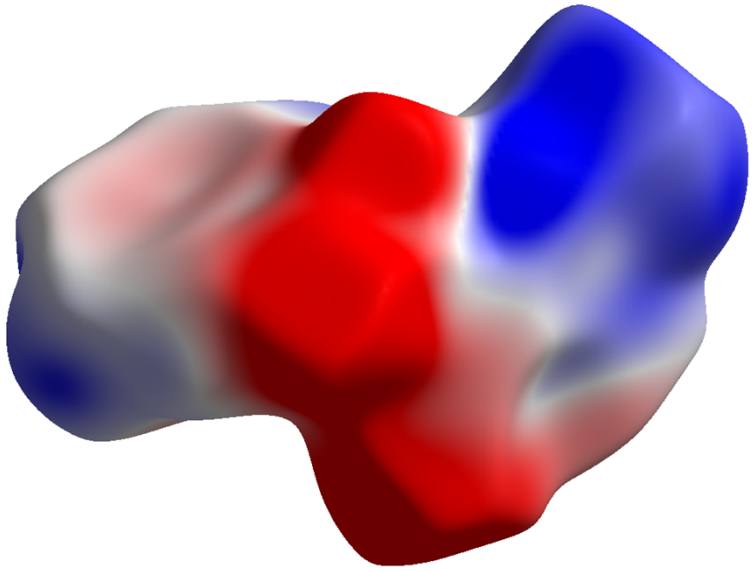
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Empirical formula	$C_{11}H_{12}N_2O_2S_2$	$C_{12}H_{14}N_2O_2S_2$	$C_{17}H_{16}N_2O_2S_2$	$C_{17}H_{16}N_2O_2S_2$	$C_{16}H_{13}FN_2O_2S_2$	$C_{16}H_{13}N_3O_4S_2$	$C_{17}H_{16}N_2O_3S_2$	$C_{16}H_{13}IN_2O_2S_2$	$C_{16}H_{14}N_2O_2S_2$
Formula mass [gmol^{-1}]	268.35	282.37	344.44	344.44	348.40	375.41	360.44	456.30	330.41
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
λ ($Mo_{K\alpha}$) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group (no.)	$P2_1/n$ (14)	$P\bar{1}$ (2)	$P2_1/c$ (14)	C2/c (15)	$P2_1/c$ (14)	$P2_1/n$ (14)	$P2_1/c$ (14)	C 2/c (15)	$P\bar{1}$ (2)
a [Å]	7.9295(16)	8.0971(1)	8.4275(2)	29.3586(16)	8.3288(2)	11.226(2)	8.6156(2)	28.3814(8)	11.0502(3)
b [Å]	11.306(2)	12.4447(2)	16.8324(4)	5.6119(2)	11.2945(2)	10.807(2)	20.5840(4)	6.2777(1)	11.5540(4)
c [Å]	14.113(3)	13.3768(3)	11.6886(2)	24.1160(15)	17.1609(4)	14.909(3)	9.6518(2)	21.5020(7)	13.7697(4)
α [°]	90.00	87.181(2)	90.0	90.0	90.0	90.00	90.0	90.0	66.109(3)
β [°]	99.94(3)	80.232(1)	97.869(2)	122.985(8)	100.643(2)	110.24(3)	101.108(2)	117.043	84.184(2)
γ [°]	90.00	88.150(1)	90.0	90.0	90.0	90.00	90.0	90.0	77.048(2)
V [Å^3]	1246.3(4)	1326.39(4)	1642.47(6)	3332.8(3)	1586.55(6)	1697.2(6)	1679.62(6)	3412.15(16)	1566.40(8)
Z	4	4	4	8	4	4	4	8	4
ρ_{calcd} [gcm^{-3}]	1.430	1.414	1.393	1.373	1.459	1.469	1.425	1.777	1.401
μ [mm^{-1}]	0.418[1]	0.397[2]	0.335[2]	0.330[2]	0.356[2]	0.341[2]	0.335[2]	2.131[2]	0.348[2]
F_{000}	560	592	720	1440	720	776	752	1792	688
Crystal dimensions [mm]	0.37×0.36×0.20	0.36×0.27×0.26	0.33×0.25×0.09	0.70×0.45×0.15	0.32×0.20×0.12	0.34×0.14×0.08	0.37×0.15×0.13	0.40 ×0.25×0.14	0.41 ×0.27×0.06
θ range [°]	2.93–52.16	3.69–45.74	3.52–41.03	3.97–45.75	3.01–45.47	2.80–49.12	3.66–37.69	2.95–45.49	3.69–37.57
No. of collected reflections	407484	92204	77724	54264	56056	129050	33211	107459	54281
No. of independent reflections	14320	22625	10664	14231	13383	17254	8593	14388	15966
No. of reflections > 2σ(I)	12324	15703	5529	7127	8950	14297	5829	11464	9736
R_{int}	0.0498	0.0318	0.0707	0.0646	0.0576	0.0357	0.0381	0.0423	0.0567
completeness of data [%]	100.0	99.5	98.3	99.5	99.8	97.7	95.9	99.7	96.4
Number of parameters	262	437	272	272	260	283	281	260	509
Goodness-of-fit	1.707	1.004	1.004	1.005	1.001	1.127	1.006	1.001	1.007
Final R indices (I>2σ(I))	R1=0.0265, wR2=N/A	R1=0.0320, wR2=0.0834	R1=0.0394, wR2=0.0794	R1=0.0444, wR2=0.0866	R1=0.0612, wR2=0.1231	R1=0.0460, wR2=0.1073	R1=0.0342, wR2=0.0756	R1=0.0316, wR2=0.0746	R1=0.0397, wR2=0.0798
R indices (all data)	R1=N/A, wR2=N/A	R1=0.0510, wR2=0.0867	R1=0.0952, wR2=0.0854	R1=0.1011, wR2=0.0915	R1=0.0992, wR2=0.1402	R1=0.0572, wR2=0.1126	R1=0.0600, wR2=0.0790	R1=0.0449, wR2=0.0815	R1=0.0783, wR2=0.0841
max./min. residual electron density [e Å^{-3}]	0.310/–0.250	0.908/–0.606	0.442/–0.363	0.919/–0.441	0.757/–0.319	1.021/–0.257	0.492/–0.377	1.550/–0.587	0.636/–0.524
CCDC entry	852449	897056	897057	897058	897059	897060	897061	897062	897063

[1] analytical absorption correction, [2] empirical 'multi-scan' absorption correction.

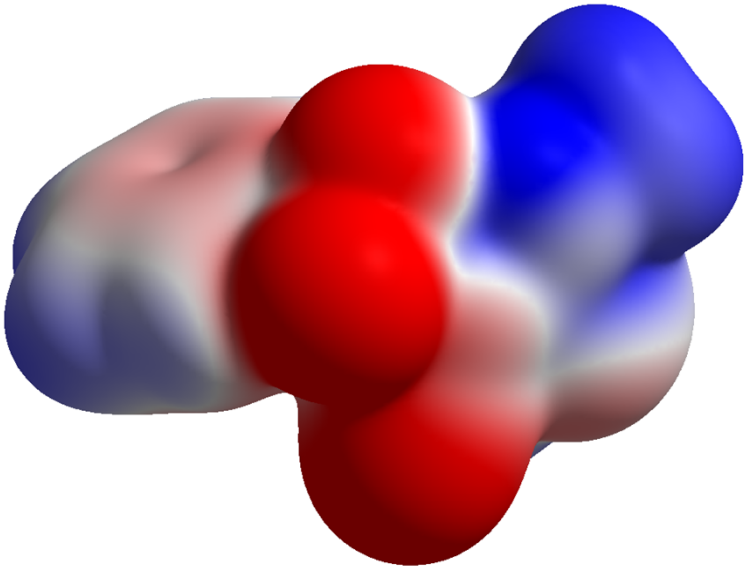
Table S2: Summary of hydrogen bonds. Hydrogen atom positions were freely refined in all the determinations.

D-H…A	d(H…A) / Å	d(D…A) / Å	a(D-H…A) / °	symmetry
compound **1**:				
N2-H2...O1	2.139(8)	2.7866(8)	122.0(6)	intramolecular
N2-H2...O1	2.264(8)	3.1271(8)	146.0(7)	-x,1-y,-z
C4-H4A...N1	2.541(11)	3.3478(9)	132.3(7)	-1/2-x,1/2+y,1/2-z
C6-H6...N1	2.366(8)	3.4055(9)	161.5(6)	-1/2-x,1/2+y,1/2-z
C8-H8...O2	2.555(9)	3.2879(9)	124.9(6)	1/2+x,1/2-y,1/2+z
C9-H9...O1	2.481(8)	3.3936(9)	142.5(6)	1/2-x,-1/2+y,1/2-z
C11-H11C...O2	2.521(15)	3.3116(9)	133.5(8)	-x,1-y,-z
compound **2**:				
N2A-H2A...O1A	2.308(11)	2.8768(7)	128.0(9)	intramolecular
N2A-H2A...N1B	2.607(11)	3.2160(8)	133.3(9)	1-x,1-y,-z
N2B-H2B...O1B	2.151(10)	2.7621(7)	128.6(9)	intramolecular
N2B-H2B...O2B	2.403(10)	3.0777(7)	136.7(9)	2-x,1-y,-z
C4B-H4BC...N1A	2.596(12)	3.4159(10)	140.2(9)	1-x,1-y,1-z
C7A-H7A...O1B	2.417(12)	3.3103(9)	147.9(10)	-1+x,y,z
C7B-H7B...O2A	2.435(10)	3.1750(8)	132.1(8)	1-x,1-y,1-z
C8B-H8B...O1A	2.452(10)	3.2872(8)	147.5(8)	1+x,-1+y,z
C12B-H12F...O2B	2.572(13)	3.4299(9)	134.1(9)	2-x,1-y,-z
compound **3**:				
N2-H2...O1	2.095(13)	2.7780(11)	137.4(10)	intramolecular
C4-H4C...O2	2.355(11)	3.3086(12)	160.3(9)	1-x,-y,1-z
C7-H7...N1	2.555(13)	3.4012(16)	154.0(11)	x,1/2-y,-1/2+z
C9-H9...O1	2.503(13)	3.3024(14)	142.6(11)	x,1/2-y,1/2+z
compound **4**:				
N2-H2...O1	2.254(14)	2.7826(12)	128.2(13)	intramolecular
N2-H2...O1	2.265(12)	2.8801(10)	139.7(13)	1-x,1-y,1-z
C6-H6...N1	2.610(15)	3.5299(15)	164.4(11)	x,1+y,z
C8-H8...N1	2.535(14)	3.3610(15)	149.3(11)	1/2-x,1/2+y,1/2-z
compound **5**:				
N2-H2...O1	2.152(17)	2.8097(12)	136.3(16)	intramolecular
C4-H4A...N1	2.556(17)	3.4606(19)	157.5(15)	-x,1-y,1-z
C4-H4C...O2	2.37(2)	3.2747(15)	167.4(19)	1-x,1-y,1-z
C13-H13...N1	2.505(19)	3.3961(15)	149.2(14)	x,-1+y,z
C16-H16...F1	2.478(18)	3.2706(16)	142.3(14)	-x,1/2+y,1/2-z
compound **6**:				
N2-H2...O1	2.190(17)	2.7581(10)	123.0(13)	intramolecular
N2-H2...N1	2.507(15)	3.1758(10)	134.8(13)	1-x,-y,2-z
C4-H4B...O2	2.440(14)	3.1678(11)	134.1(12)	1-x,-y,2-z
C8-H8...O2	2.580(15)	3.4272(12)	146.8(12)	3/2-x,1/2+y,3/2-z
C7-H7...O3	2.546(15)	3.4308(12)	151.4(12)	-x,-y,1-z
C6-H6...O4	2.565(14)	3.3888(11)	143.1(11)	-x,-y,1-z
C16-H16...N1	2.600(13)	3.2868(10)	128.2(10)	-1/2+x,1/2-y,-1/2+z
compound **7**:				
N2-H2...O1	2.108(13)	2.7957(10)	135.3(11)	intramolecular
C4-H4A...N1	2.478(14)	3.4025(14)	164.4(10)	-x,1-y,2-z
C4-H4C...O2	2.380(14)	3.3089(13)	156.1(10)	1-x,1-y,2-z
C9-H9...N1	2.456(12)	3.4112(13)	168.8(10)	x,3/2-y,-1/2+z
compound **8**:				
N2-H2...O1	2.03(3)	2.7265(15)	136(2)	intramolecular
N2-H2...O1	2.38(2)	3.1041(13)	141(2)	-x,y,1/2-z
C15-H15...O1	2.52(3)	3.3339(16)	142(2)	-x,1+y,1/2-z

compound **9**:				
N2A-H2A...O1A	2.095(16)	2.7932(14)	139.1(14)	intramolecular
N2B-H2B...O1B	2.040(16)	2.7655(14)	136.8(13)	intramolecular
C4A-H4AA...N1B	2.579(16)	3.4614(17)	152.8(12)	1-x,2-y,-z
C4A-H4AC...O2A	2.548(15)	3.1304(15)	120.7(11)	1-x,2-y,-z
C6B-H6B...O1A	2.520(14)	3.1749(14)	124.3(11)	1-x,1-y,1-z

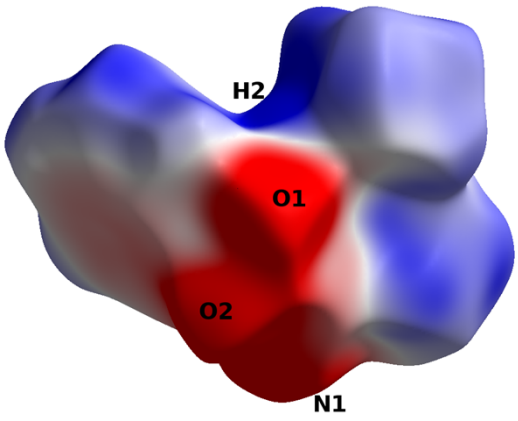


(a)

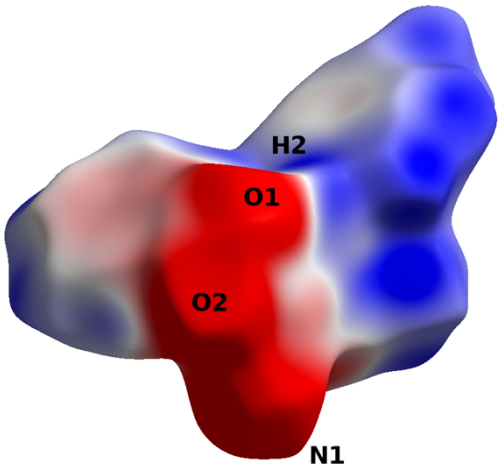


(b)

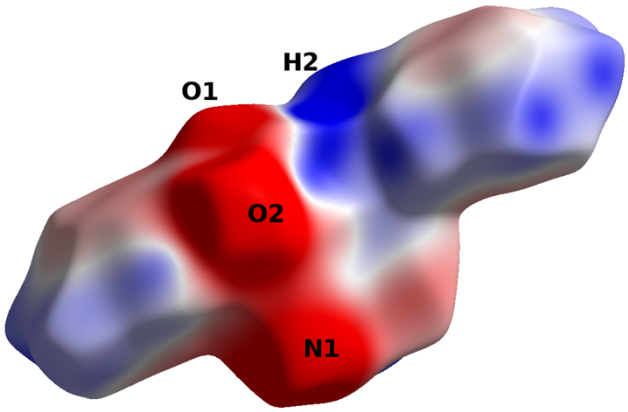
Figure S1: Electrostatic potential (-0.05 to 0.05 a.u.) mapped onto (a) the Hirshfeld surface and (b) the 0.001 a.u. electron-density isosurface of compound **1**.



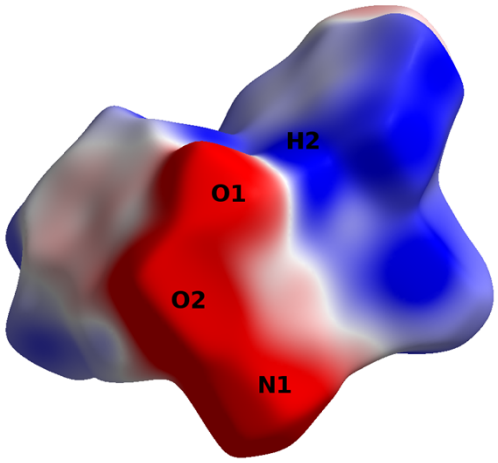
(a)



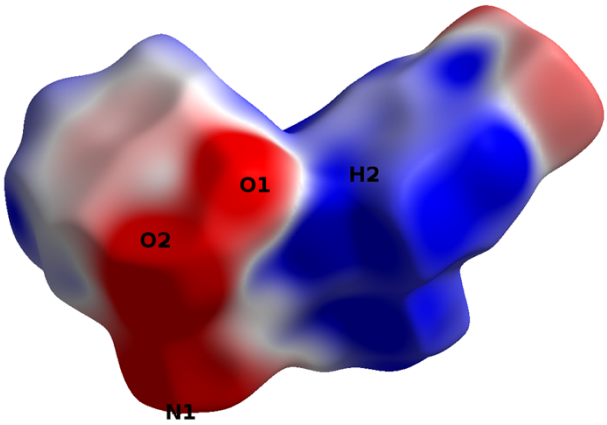
(b)



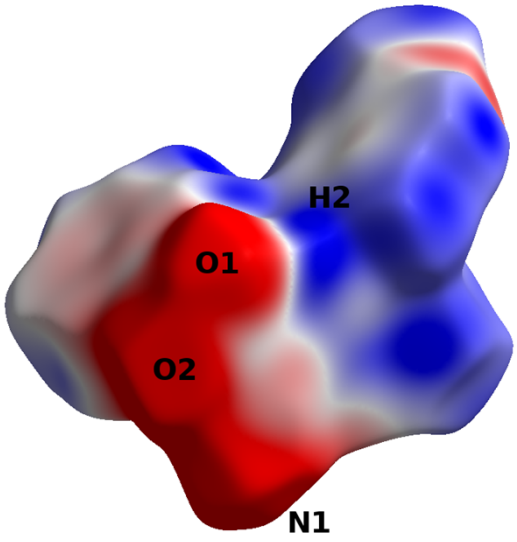
(c)



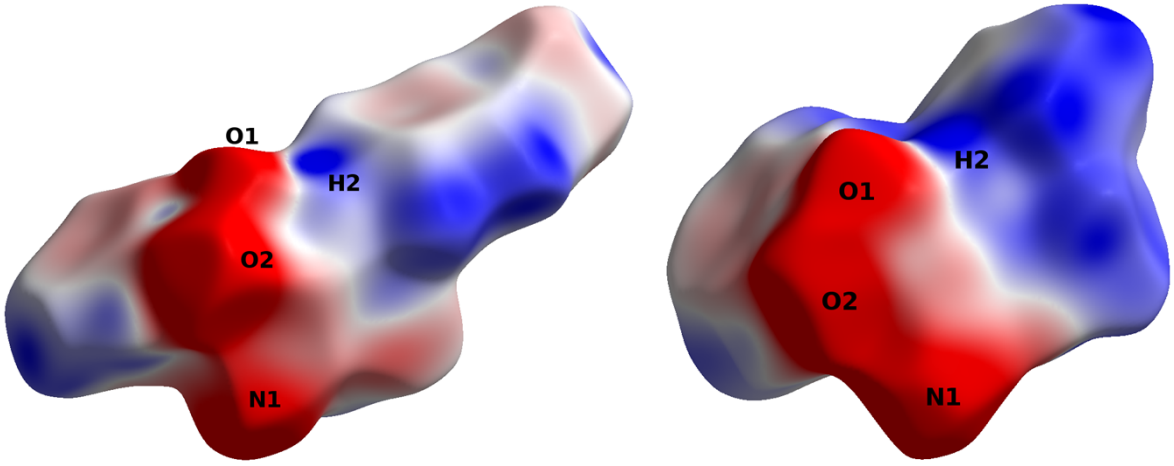
(d)



(e)



(f)



(g) (h)

Figure S2: Electrostatic potential mapped onto the Hirshfeld Surfaces of (a) **2**, (b) **3**, (c) **4**, (d) **5**, (e) **6**, (f) **7**, (g) **8**, (h) **9**, for **1** see Figures S1 and 6(d). All molecules are in the same orientation as defined in Figure 5. Colour scale -0.05 (red) to 0 (white) to 0.05 a.u. (blue). Wavefunction used for the ESP calculation is at the BLYP/6-31G(d) level calculated with the programs Gaussian 03 and CrystalExplorer, except for the iodophenyl substituted compound **8** (g), where it is BLYP/3-21G because of size restrictions. For **2** (a) and **9** (h) only independent molecule A of the asymmetric unit is shown.