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Electronic Supplementary Information

Experimental and theoretical investigation of conformational states and noncovalent interactions in crystalline sulfonamides with methoxyphenyl moiety

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1. Physicochemical characterization

1.1. **Mass spectrometry**

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1. Physicochemical characterization

1.1. Mass spectrometry

The mass spectra of **1a**, **1b**, **2a** and **2b** are shown in Figures S1-S4.

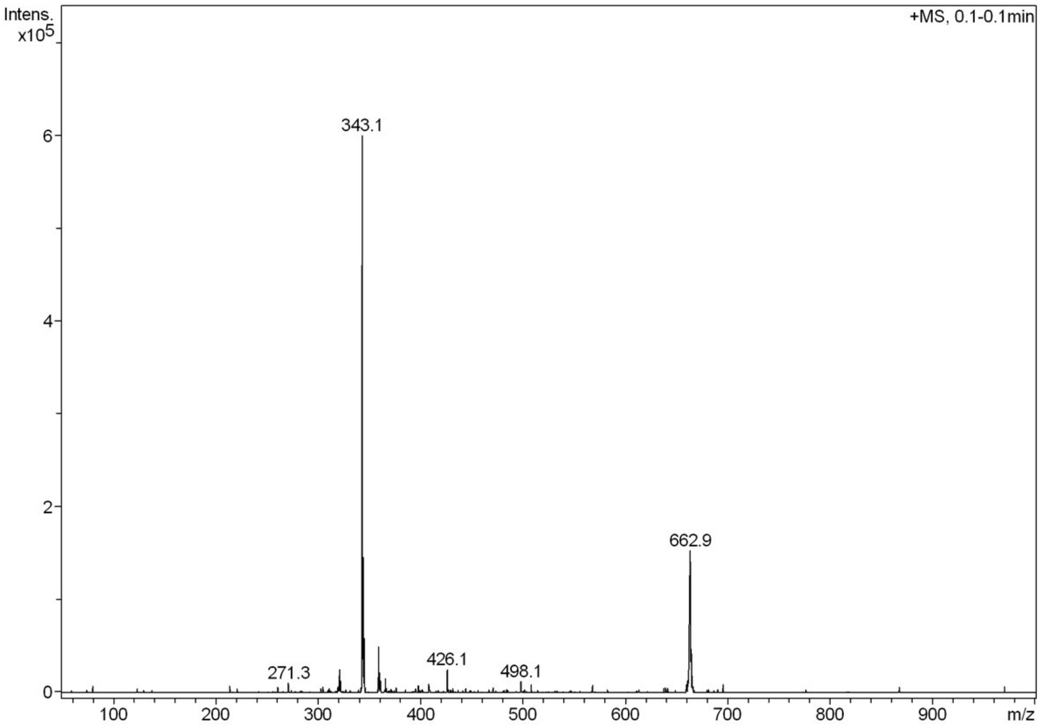


Figure S1. Mass spectrum for **1a**.

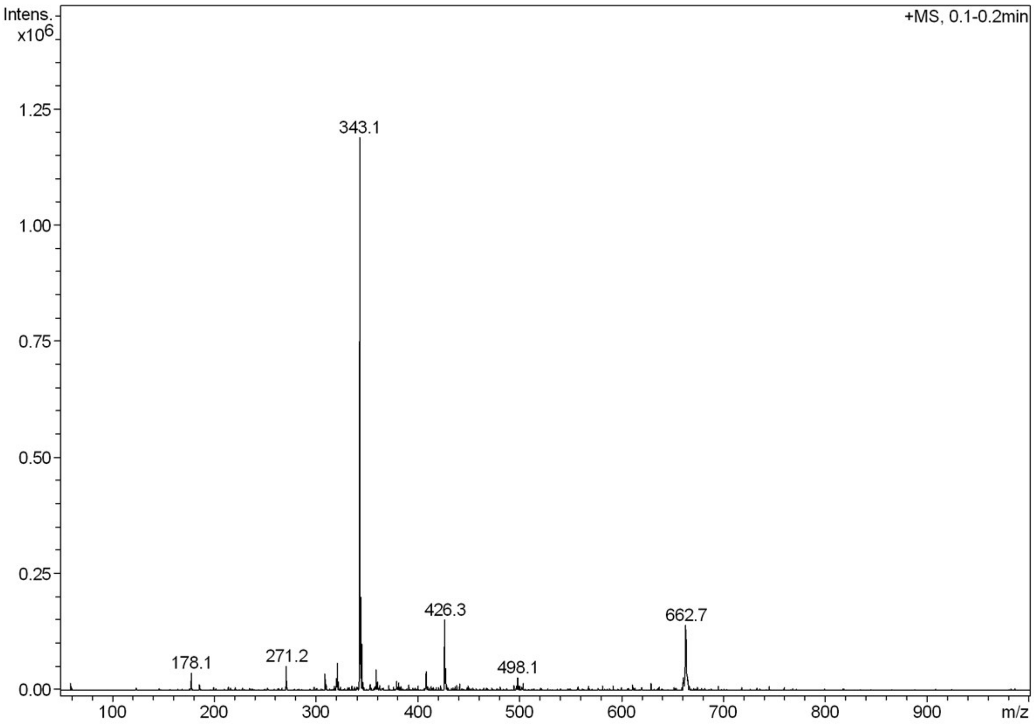


Figure S2. Mass spectrum for **1b**.

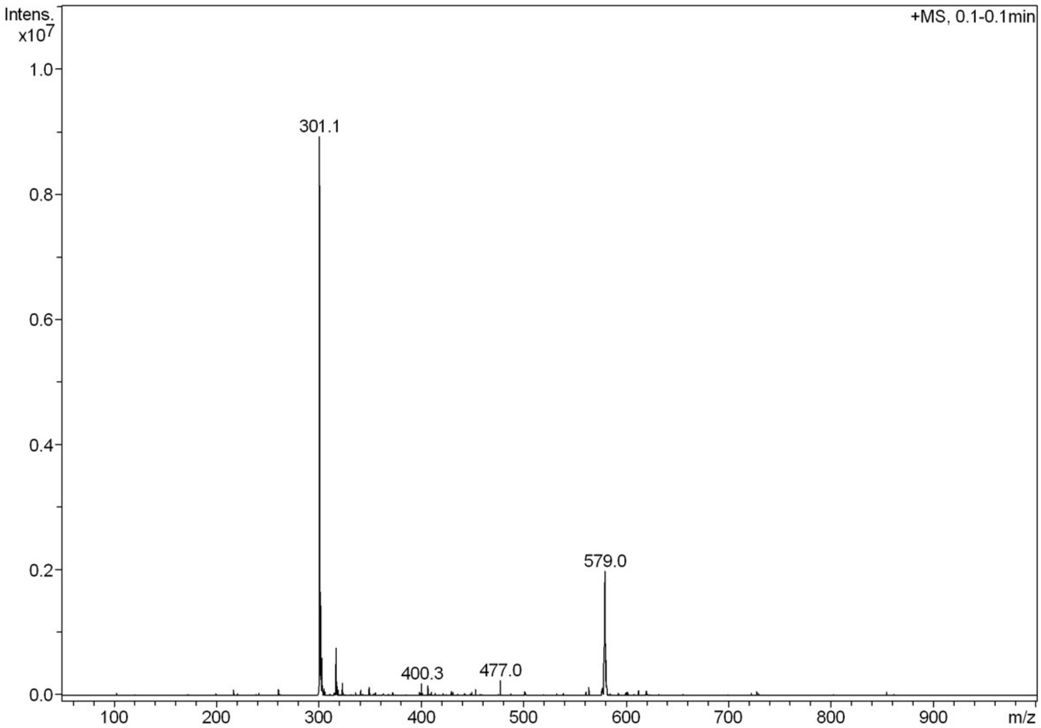


Figure S3. Mass spectrum for **2a**.

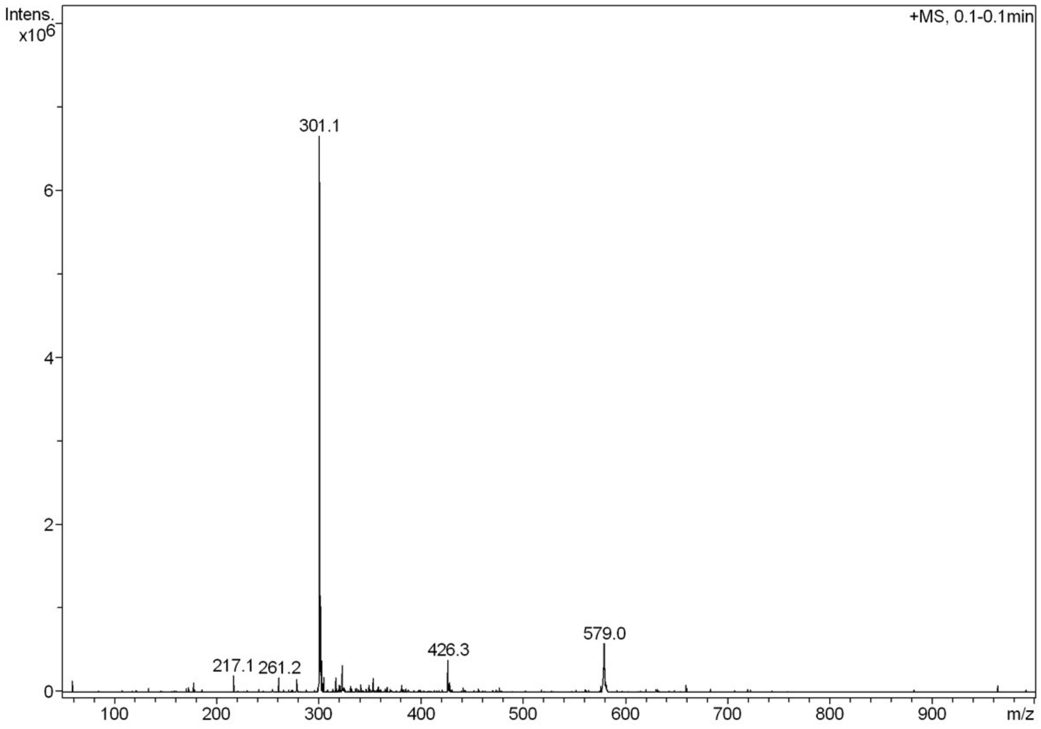


Figure S4. Mass spectrum for **2b**.

1.2. Powder X-ray diffraction

The PXRD measurements were used to check the phase purity of synthesized sulfonamides **1a**, **2a**, **1b** and **2b**. The results showed that the PXRD patterns of the products are different from the pattern of starting substrate, *N*-acetylsulfanilyl chloride (Figure S5). It clearly indicates that new crystalline solids were yielded. Additionally, all of the reflections displayed in the measured patterns from the as-synthesized compounds match with those in the simulated patterns generated from the single-crystal diffraction data, confirming the formation of the corresponding molecular structures of **1a**, **2a**, **1b** and **2b** in high phase purity.

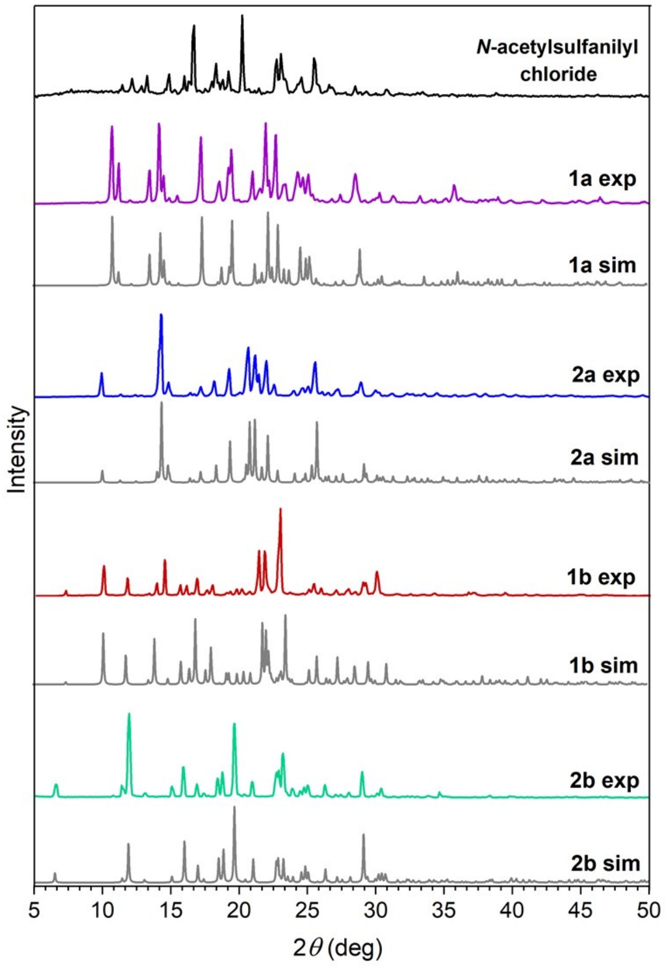


Figure S5. Experimental (exp) and simulated (sim) PXRD patterns of sulfonamides **1a**, **2a**, **1b** and **2b**. Simulated patterns were calculated in Mercury using single-crystal diffraction data.

1.3. FT-IR spectroscopy

The FT-IR spectra for the compounds are compared in Figure S6 and the most characteristic IR bands are summarized in Table S1. The spectra of synthesized sulfonamides contains some characteristic bands of the vibrations of sulfonamide group –SO_2NH–, amine group –NH_2, amide group –CONH– and methoxyphenyl fragment C_{Ar}–O–C_{Alif}. The most characteristic SO_2 asymmetric and symmetric stretching vibrations appeared in the range of 1320÷1310 cm^{-1} and 1155÷1143 cm^{-1}, respectively. The S–N bond is a bridge between S-side and N-side of sulfonamide molecules. The stretching ν(S–N) vibrations are visible as bands appearing in the region 914÷895 cm^{-1}. In compounds **1a** and **1b** there is an acetylamide group in the fourth position of benzene ring connected with S atom of sulfonamide group. In the IR spectra there can be observed bands assigned to the ν(N–H) vibrations at 3263÷3231 cm^{-1} and δ(N–H) at 1533÷1523 cm^{-1} (II amide band), as well as bands assigned to the ν(C=O) vibrations at 1707 cm^{-1} and 1680 cm^{-1} (I amide band) for **1a** and **1b**, respectively. In turn, compounds **2a** and **2b** contain at the same position an amine group. Therefore, the IR spectra of **2a** and **2b** showed two strong bands in the range of 3459÷3338 cm^{-1} which are assigned to the N–H stretching vibrations and single bands in the range of 1639÷1635 cm^{-1} assigned to the N–H bending vibrations of primary aromatic amine. The ν(N–H) vibrations in sulfonamide groups occurred in the region 3349÷3144 cm^{-1}. The stretching vibrations bands of aromatic rings ν(C=C) appeared in the region of 1594÷1489 cm^{-1}. The presence of methoxyphenyl moiety in all the synthesized sulfonamides is reflected in the IR spectra as two bands corresponded to the asymmetric stretching vibrations of C_{Ar}–O–C_{Alif} fragment in the range of 1286÷1254 cm^{-1} and symmetric stretching vibrations in the range of 1056÷1022 cm^{-1}.

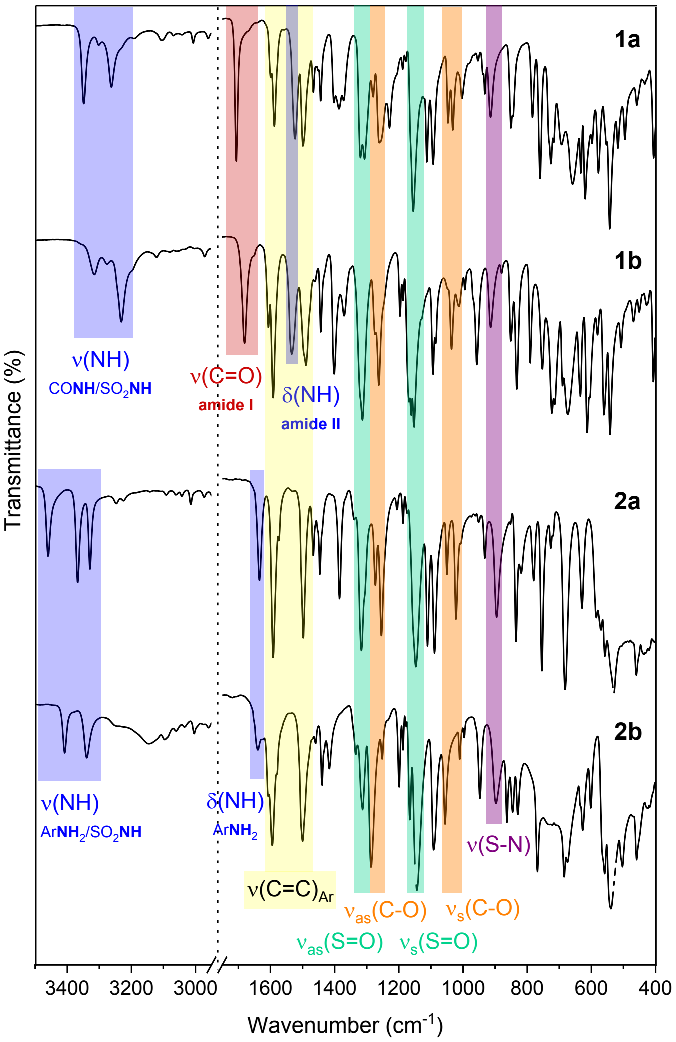


Figure S6. Experimental ATR FT-IR spectra of sulfonamides **1a**, **1b**, **2a** and **2b**.

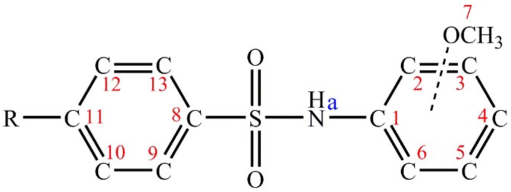
Table S1. Experimental vibrational frequencies (cm^{-1}) for the characteristic FT-IR bands.

Vibration type	1a	2a	1b	2b
ν(NH$_2$)	–	3459, 3367	–	3408, 3338
ν(NH)	3349, 3263	3328	3315, 3231	3144
ν(C=O) amide I	1706	–	1680	–
δ(NH$_2$)	–	1635	–	1639
ν(C=C)$_{Ar}$	1588, 1499	1592, 1498	1591, 1489	1594, 1499
δ(NH) amide II	1523	–	1533	–
ν$_{as}$(SO$_2$)	1320	1317	1313	1313
ν$_{as}$(C–O–C)	1261	1254	1262	1286
ν$_s$(SO$_2$)	1155	1147	1152	1143
ν$_s$(C–O–C)	1032	1022	1035	1056
ν(S–N)	914	895	914	897

1.4. ^{1}H and ^{13}C NMR spectroscopy

The ^{1}H and ^{13}C NMR data for all sulfonamides are given in Figures S7–S14 and Table S2. The ^{1}H NMR spectra of **1a, 1b, 2a** and **2b** showed one singlet peak at about 3.6 ppm corresponding to the methyl protons of the methoxy group. The spectra also showed singlet peak at 10.27 ppm for **1a** and 10.29 ppm for **1b** derived from protons of the amide –CONH– group. The presence of acetyl –CH_3 protons in the structure of **1a** and **1b** was observed as singlet peak at 2.07/2.06 ppm in ^{1}H NMR spectra. After hydrolysis of the acetamide group, the singlets at 2.07/2.06 ppm were absent in the spectra of **2a** and **2b**. It was also observed the appearance of singlet peaks at 5.92 ppm for **2a** and 5.97 ppm for **2b** which is assigned to protons of the primary amine group. The proton of sulfonamide –SO_2NH– group manifests its presence in the analyzed structures as singlet peak between 8.78 and 10.15 ppm. The aromatic protons of all the sulfonamide derivatives showed signals in the region between 6.51 and 7.70 ppm (Figures S7–S10, Table S2). The structure analysis of the prepared compounds was also supported by ^{13}C NMR measurements which displayed the characteristic signals of the obtained compounds. The signal of the carbonyl carbon atom from the amide group appeared at 169.42 and 169.47 ppm for **1a** and **1b**, respectively. The signal at about 24.58 and 24.57 ppm is attributed to carbon atom of –CH_3 in acetamide group for **1a** and **1b**, respectively. The carbon atoms from the methoxy group for all prepared compounds occurred in the range of 55.39÷56.06 ppm. The aromatic carbons of all derivatives showed signals in the region between 111.83 and 160.11 ppm in ^{13}C NMR spectra (Figures S11–S14, Table S2).

Table S2. Experimental ^{1}H NMR and ^{13}C NMR chemical shifts (ppm) for **1a**, **1b**, **2a** and **2b**.

Atoms numbering	**1a**, **1b** R = -NHC(O)CH$_3$ **2a**, **2b** R = -NH$_2$			
	1a	**1b**	**2a**	**2b**
^{1}H NMR				
Ha	9.28	10.15	8.78	9.86
Hb	10.27	10.29	–	–
Hc	–	–	5.92	5.97
H2	–	6.64÷6.70	–	6.63÷6.66
H3	6.89	–	6.90	–
H4	7.09	6.58	7.04	6.52÷6.56
H5	6.85	7.11	6.83	7.09
H6	7.19	6.64÷6.70	7.20	6.63÷6.66
H9, H13	7.67	7.70	7.35	7.40
H10, H12	7.62	7.70	6.51	6.52÷6.56
H7	3.51	3.66	3.60	3.66
H15	2.07	2.06	–	–
^{13}C NMR				
C1	126.01	139.56	125.65	140.20
C2	143.29	112.27	153.14	111.83
C3	112.22	160.11	112.11	160.06
C4	126.86	109.33	125.87	108.70
C5	120.84	130.41	120.79	130.23
C6	125.12	106.04	123.37	105.50
C7	55.91	55.43	56.06	55.39
C8	134.54	133.46	126.86	124.81
C9, C13	128.33	128.43	129.17	129.21
C10, C12	118.64	119.03	112.75	113.02
C11	152.59	143.58	151.74	153.32
C14	169.42	169.47	–	–
C15	24.58	24.57	–	–

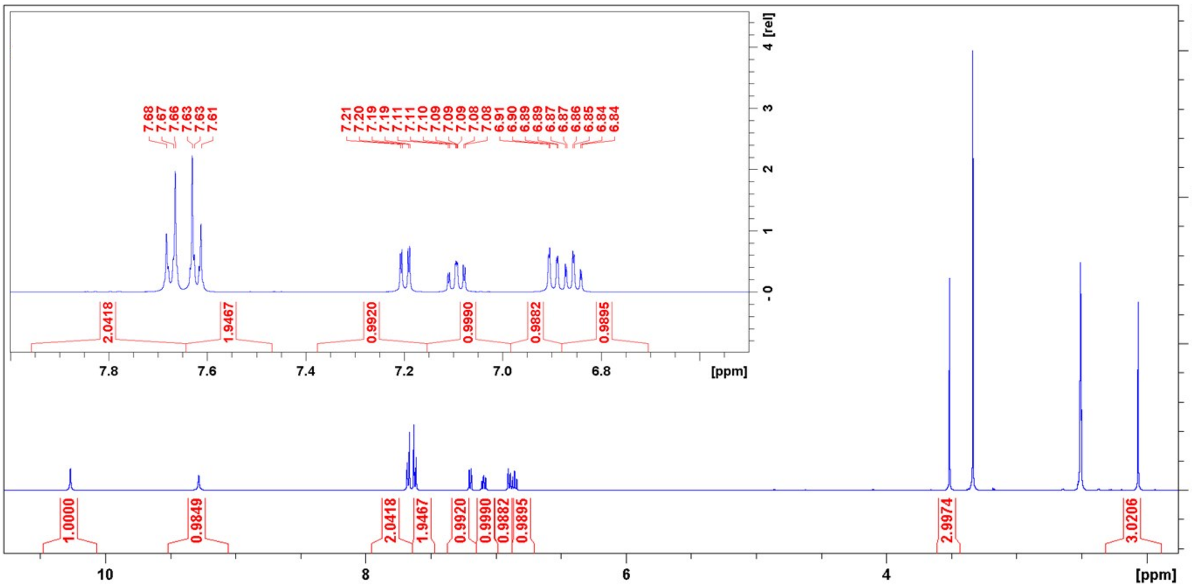


Figure S7. ^{1}H NMR spectrum for **1a**.

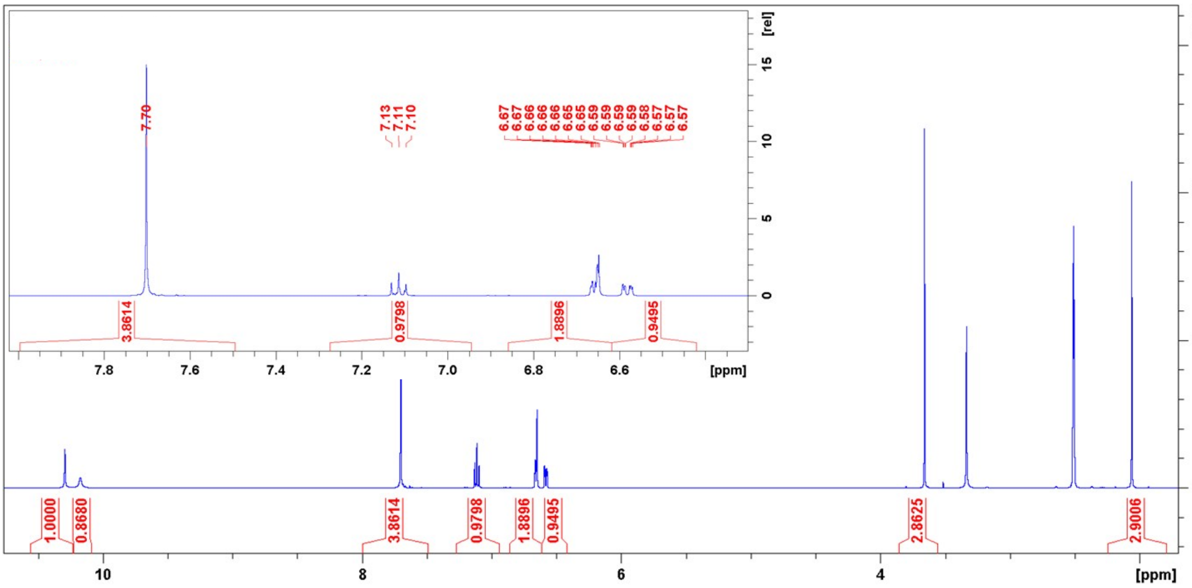


Figure S8. ^{1}H NMR spectrum for **1b**.

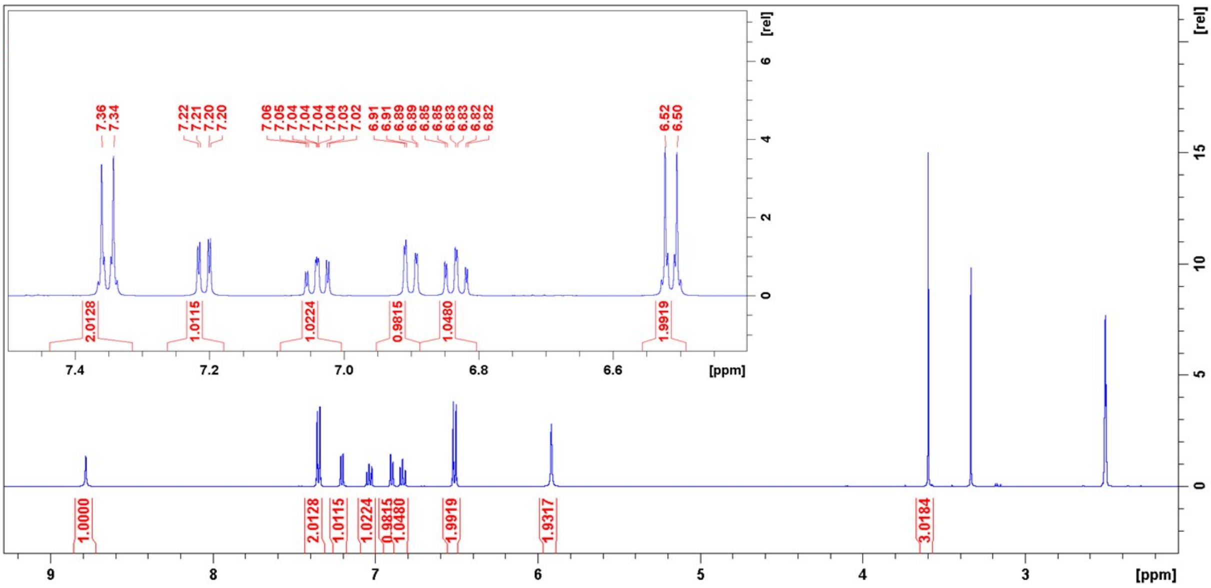


Figure S9. ^{1}H NMR spectrum for **2a**.

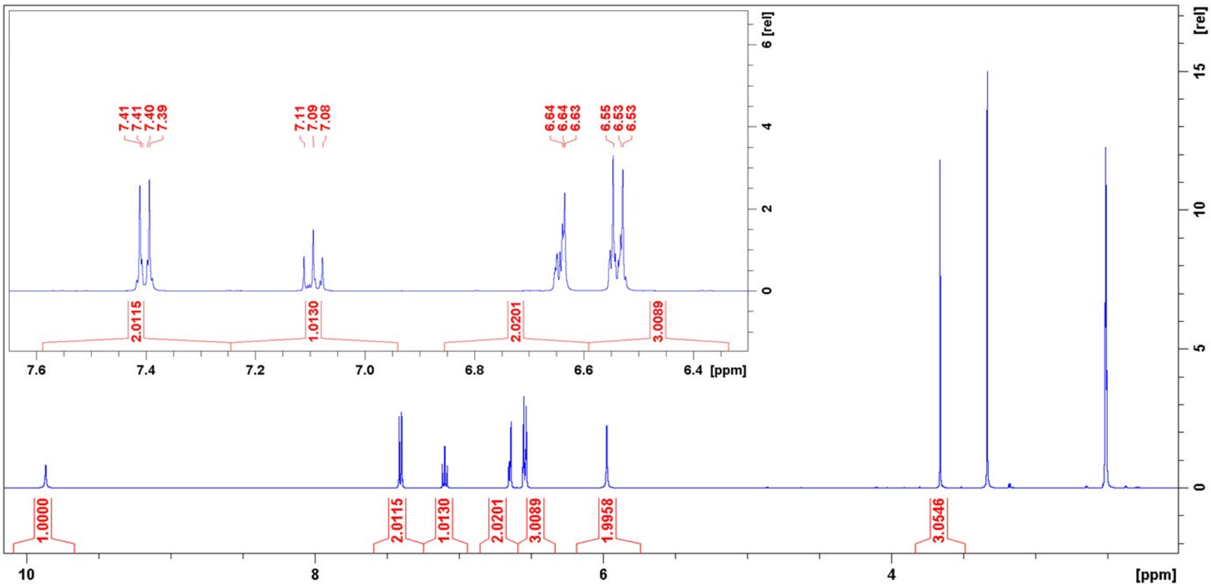


Figure S10. ^{1}H NMR spectrum for **2b**.

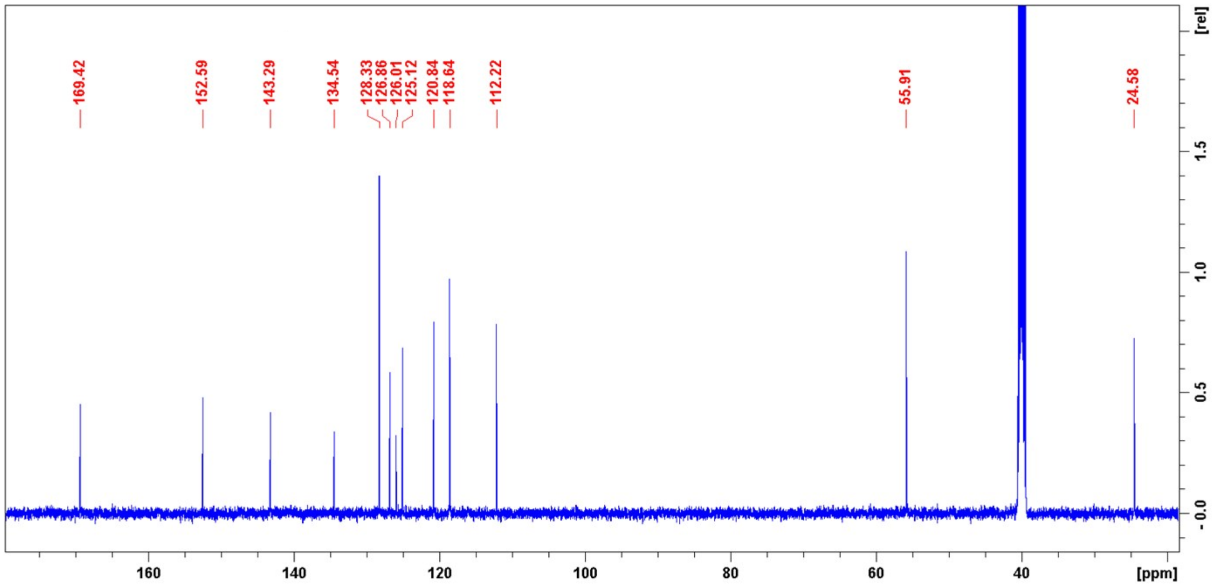


Figure S11. ^{13}C NMR spectrum for **1a**.

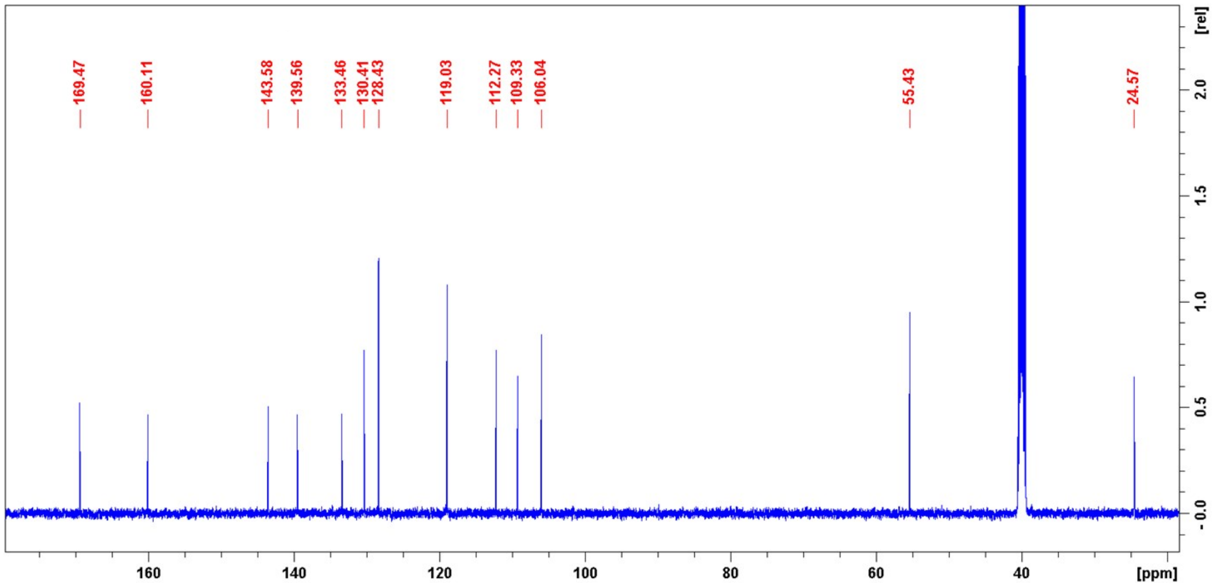


Figure S12. ^{13}C NMR spectrum for **1b**.

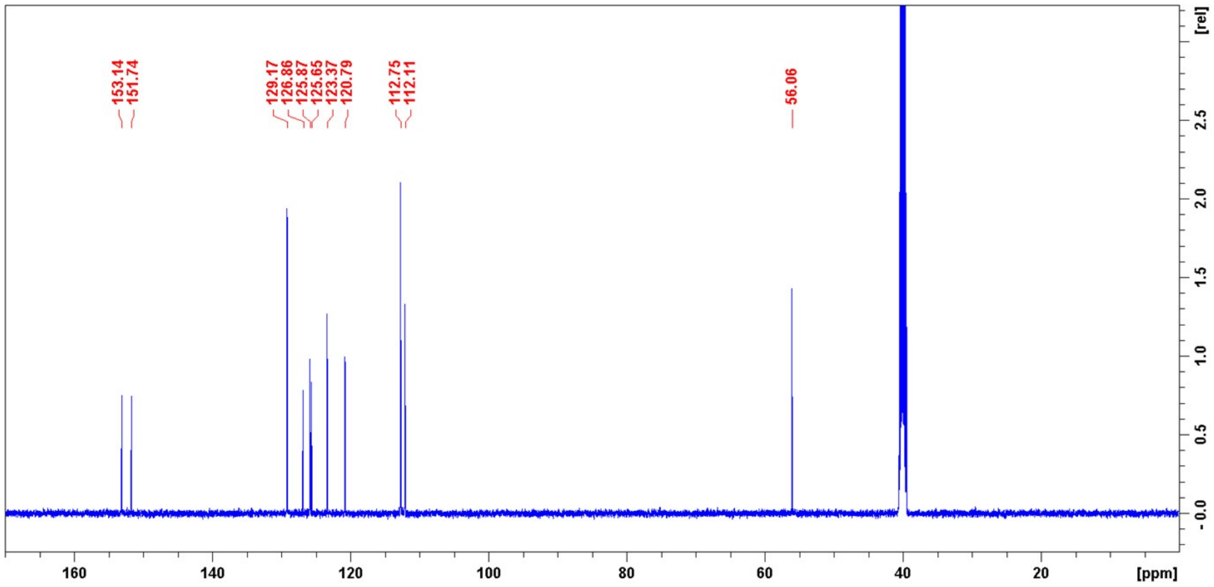


Figure S13. ^{13}C NMR spectrum for **2a**.

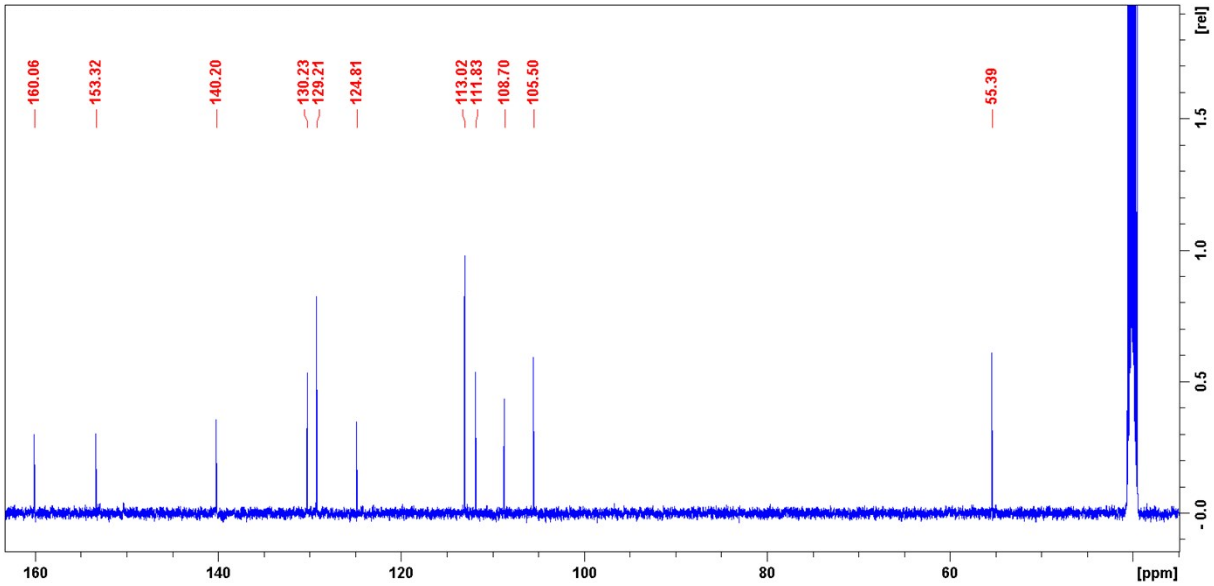
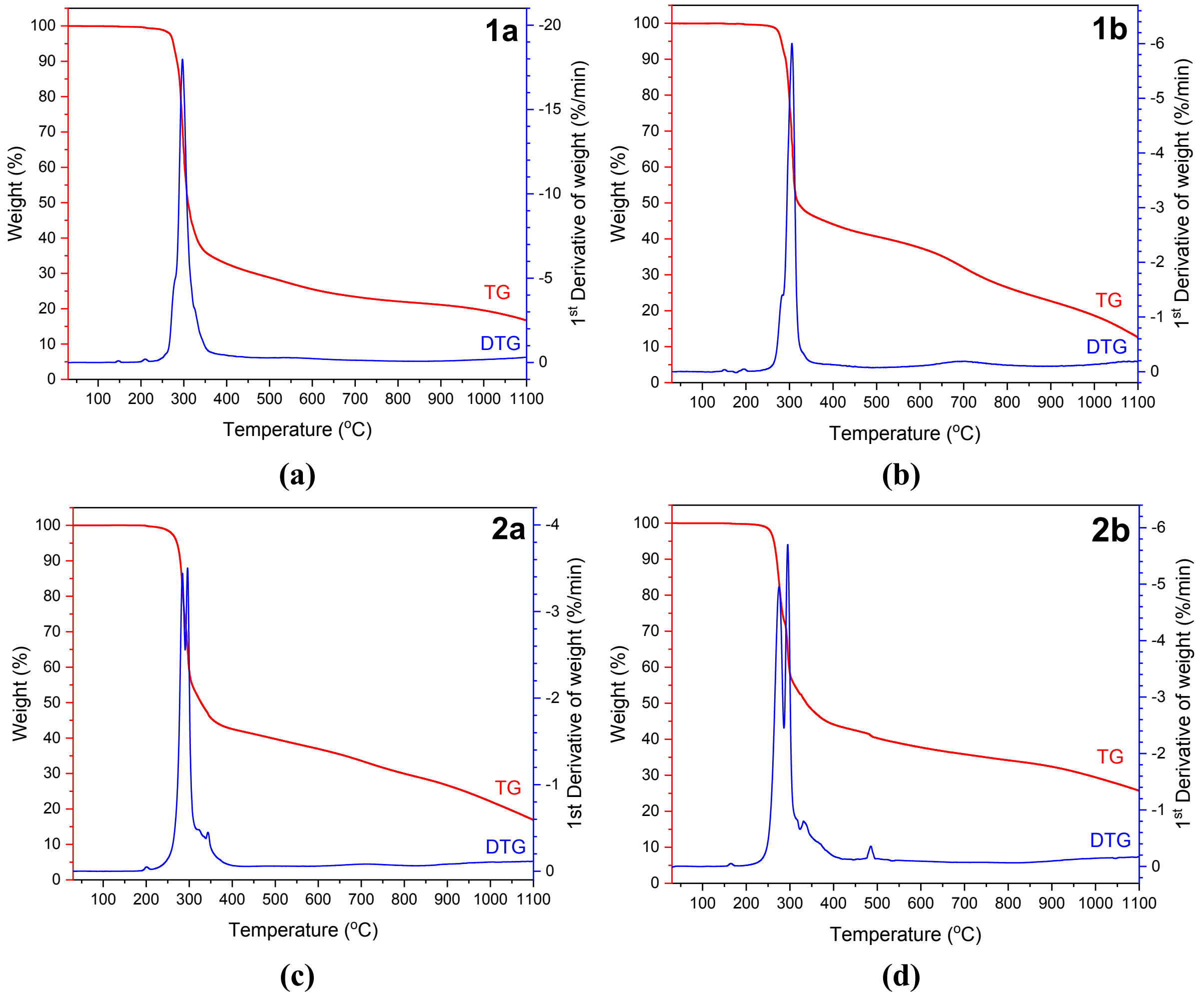


Figure S14. ^{13}C NMR spectrum for **2b**.

1.5. Thermogravimetry

The thermal behaviour of compounds **1a**, **1b**, **2a** and **2b** was evaluated by thermogravimetric analysis (TGA). The TG curves are given in Figure S15. The first step indicative to thermal decomposition of sulfonamides obtained takes place over 250 ºC for **1a** and **1b** and over 220 ºC for **2a** and **2b**. The DTG curves in this range revealed single peak for **1a** and **1b** with peak temperature of 297 ºC and 306 ºC, respectively. Analogous DTG peak for **2a** and **2b** is partially separated and occurs as double peak with peak temperatures 284/296 ºC and 275/295 ºC, respectively. The highest thermal decomposition rate slows down at about 350 ºC. The final degradation step is characterized by low weight loss rate without distinct maximum on DTG curves. The TG curves do not reach the values near to zero even at 1100 ºC indicating the formation of ashy residue.



(a) (b) (c) (d)

Figure S15. TG/DTG curves for (**a**) **1a**, (**b**) **1b**, (**c**) **2a** and (**d**) **2b**.

Table S3. Bond lengths (Å), angles (º) and torsion angles (º) for **1a**.

S(1)–O(1)	1.4396(8)	C(9)–C(10)	1.4001(15)	C(5)–H(5)	0.9500
S(1)–O(2)	1.4411(8)	C(1)–C(6)	1.3917(14)	C(3)–H(3)	0.9500
S(1)–N(2)	1.6325(9)	C(1)–C(2)	1.3922(14)	C(8)–H(8A)	0.9800
S(1)–C(1)	1.7538(10)	C(2)–C(3)	1.3839(15)	C(8)–H(8B)	0.9800
O(3)–C(10)	1.3593(14)	C(2)–H(2A)	0.9500	C(8)–H(8C)	0.9800
O(3)–C(15)	1.4255(15)	C(4)–C(3)	1.3996(14)	C(13)–C(12)	1.380(2)
N(2)–C(9)	1.4338(13)	C(4)–C(5)	1.4008(15)	C(13)–H(13)	0.9500
N(2)–H(2)	0.864(17)	C(10)–C(11)	1.3954(16)	C(11)–C(12)	1.391(2)
O(4)–C(7)	1.2144(15)	C(14)–C(13)	1.3966(17)	C(11)–H(11)	0.9500
N(1)–C(7)	1.3724(14)	C(14)–H(14)	0.9500	C(15)–H(15A)	0.9800
N(1)–C(4)	1.4031(13)	C(6)–C(5)	1.3859(15)	C(15)–H(15B)	0.9800
N(1)–H(1)	0.8800	C(6)–H(6)	0.9500	C(15)–H(15C)	0.9800
C(9)–C(14)	1.3879(15)	C(7)–C(8)	1.5064(16)	C(12)–H(12)	0.9500

O(1)–S(1)–O(2)	118.24(5)	C(3)–C(4)–C(5)	119.73(10)	C(7)–C(8)–H(8A)	109.5
O(1)–S(1)–N(2)	105.69(5)	C(3)–C(4)–N(1)	116.97(9)	C(7)–C(8)–H(8B)	109.5
O(2)–S(1)–N(2)	107.71(5)	C(5)–C(4)–N(1)	123.30(10)	H(8A)–C(8)–H(8B)	109.5
O(1)–S(1)–C(1)	109.40(5)	O(3)–C(10)–C(11)	125.34(11)	C(7)–C(8)–H(8C)	109.5
O(2)–S(1)–C(1)	107.17(5)	O(3)–C(10)–C(9)	115.18(9)	H(8A)–C(8)–H(8C)	109.5
N(2)–S(1)–C(1)	108.29(5)	C(11)–C(10)–C(9)	119.48(11)	H(8B)–C(8)–H(8C)	109.5
C(10)–O(3)–C(15)	117.44(10)	C(9)–C(14)–C(13)	119.68(12)	C(12)–C(13)–C(14)	119.87(12)
C(9)–N(2)–S(1)	118.60(7)	C(9)–C(14)–H(14)	120.2	C(12)–C(13)–H(13)	120.1
C(9)–N(2)–H(2)	115.2(11)	C(13)–C(14)–H(14)	120.2	C(14)–C(13)–H(13)	120.1
S(1)–N(2)–H(2)	111.6(11)	C(5)–C(6)–C(1)	120.24(10)	C(12)–C(11)–C(10)	119.60(13)
C(7)–N(1)–C(4)	128.28(10)	C(5)–C(6)–H(6)	119.9	C(12)–C(11)–H(11)	120.2
C(7)–N(1)–H(1)	115.9	C(1)–C(6)–H(6)	119.9	C(10)–C(11)–H(11)	120.2
C(4)–N(1)–H(1)	115.9	O(4)–C(7)–N(1)	123.88(11)	O(3)–C(15)–H(15A)	109.5
C(14)–C(9)–C(10)	120.43(10)	O(4)–C(7)–C(8)	122.43(11)	O(3)–C(15)–H(15B)	109.5
C(14)–C(9)–N(2)	121.05(10)	N(1)–C(7)–C(8)	113.68(10)	H(15A)–C(15)–H(15B)	109.5
C(10)–C(9)–N(2)	118.47(9)	C(6)–C(5)–C(4)	119.42(10)	O(3)–C(15)–H(15C)	109.5
C(6)–C(1)–C(2)	120.82(10)	C(6)–C(5)–H(5)	120.3	H(15A)–C(15)–H(15C)	109.5
C(6)–C(1)–S(1)	119.23(8)	C(4)–C(5)–H(5)	120.3	H(15B)–C(15)–H(15C)	109.5
C(2)–C(1)–S(1)	119.94(8)	C(2)–C(3)–C(4)	120.80(10)	C(13)–C(12)–C(11)	120.90(11)
C(3)–C(2)–C(1)	118.97(10)	C(2)–C(3)–H(3)	119.6	C(13)–C(12)–H(12)	119.6
C(3)–C(2)–H(2A)	120.5	C(4)–C(3)–H(3)	119.6	C(11)–C(12)–H(12)	119.6
C(1)–C(2)–H(2A)	120.5				

O(1)–S(1)–N(2)–C(9)	173.91(8)	C(14)–C(9)–C(10)–C(11)	1.76(16)
O(2)–S(1)–N(2)–C(9)	–58.83(9)	N(2)–C(9)–C(10)–C(11)	–175.74(10)
C(1)–S(1)–N(2)–C(9)	56.76(9)	C(10)–C(9)–C(14)–C(13)	–0.30(16)
S(1)–N(2)–C(9)–C(14)	69.60(12)	N(2)–C(9)–C(14)–C(13)	177.14(10)
S(1)–N(2)–C(9)–C(10)	–112.92(10)	C(2)–C(1)–C(6)–C(5)	–1.50(17)
O(1)–S(1)–C(1)–C(6)	–37.46(10)	S(1)–C(1)–C(6)–C(5)	177.33(9)
O(2)–S(1)–C(1)–C(6)	–166.78(9)	C(4)–N(1)–C(7)–O(4)	–3.4(2)
N(2)–S(1)–C(1)–C(6)	77.28(10)	C(4)–N(1)–C(7)–C(8)	175.33(11)
O(1)–S(1)–C(1)–C(2)	141.38(9)	C(1)–C(6)–C(5)–C(4)	0.27(18)
O(2)–S(1)–C(1)–C(2)	12.05(10)	C(3)–C(4)–C(5)–C(6)	1.15(17)
N(2)–S(1)–C(1)–C(2)	–103.88(9)	N(1)–C(4)–C(5)–C(6)	–179.31(11)
C(6)–C(1)–C(2)–C(3)	1.27(17)	C(1)–C(2)–C(3)–C(4)	0.18(17)
S(1)–C(1)–C(2)–C(3)	–177.55(9)	C(5)–C(4)–C(3)–C(2)	–1.38(17)
C(7)–N(1)–C(4)–C(3)	–166.82(11)	N(1)–C(4)–C(3)–C(2)	179.05(10)
C(7)–N(1)–C(4)–C(5)	13.63(18)	C(9)–C(14)–C(13)–C(12)	–1.50(17)
C(15)–O(3)–C(10)–C(11)	–1.79(17)	O(3)–C(10)–C(11)–C(12)	178.92(11)
C(15)–O(3)–C(10)–C(9)	178.55(11)	C(9)–C(10)–C(11)–C(12)	–1.44(17)
C(14)–C(9)–C(10)–O(3)	–178.56(10)	C(14)–C(13)–C(12)–C(11)	1.83(18)
N(2)–C(9)–C(10)–O(3)	3.94(14)	C(10)–C(11)–C(12)–C(13)	–0.35(19)

Table S4. Bond lengths (Å), angles (º) and torsion angles (º) for **2a**.

C(1)–C(6)	1.393(3)	C(7)–C(8)	1.386(3)	C(12)–O(3)	1.367(2)
C(1)–C(2)	1.396(3)	C(7)–C(12)	1.404(3)	C(13)–O(3)	1.429(3)
C(1)–S(1)	1.743(2)	C(7)–N(2)	1.436(2)	C(13)–H(13A)	0.9800
C(2)–C(3)	1.380(3)	C(8)–C(9)	1.389(3)	C(13)–H(13B)	0.9800
C(2)–H(2)	0.9500	C(8)–H(8)	0.9500	C(13)–H(13C)	0.9800
C(3)–C(4)	1.409(3)	C(9)–C(10)	1.385(3)	N(1)–H(1A)	0.97(3)
C(3)–H(3)	0.9500	C(9)–H(9)	0.9500	N(1)–H(1B)	0.82(3)
C(4)–N(1)	1.367(3)	C(10)–C(11)	1.397(3)	N(2)–S(1)	1.6494(19)
C(4)–C(5)	1.405(3)	C(10)–H(10)	0.9500	N(2)–H(2A)	0.81(3)
C(5)–C(6)	1.379(3)	C(11)–C(12)	1.386(3)	O(1)–S(1)	1.4368(15)
C(5)–H(5)	0.9500	C(11)–H(11)	0.9500	O(2)–S(1)	1.4401(15)
C(6)–H(6)	0.9500				

C(6)–C(1)–C(2)	120.37(18)	C(8)–C(7)–N(2)	121.83(19)	O(3)–C(13)–H(13B)	109.5
C(6)–C(1)–S(1)	120.37(15)	C(12)–C(7)–N(2)	118.46(18)	H(13A)–C(13)–H(13B)	109.5
C(2)–C(1)–S(1)	119.21(15)	C(7)–C(8)–C(9)	120.4(2)	O(3)–C(13)–H(13C)	109.5
C(3)–C(2)–C(1)	119.89(18)	C(7)–C(8)–H(8)	119.8	H(13A)–C(13)–H(13C)	109.5
C(3)–C(2)–H(2)	120.1	C(9)–C(8)–H(8)	119.8	H(13B)–C(13)–H(13C)	109.5
C(1)–C(2)–H(2)	120.1	C(10)–C(9)–C(8)	120.1(2)	C(4)–N(1)–H(1A)	116.5(19)
C(2)–C(3)–C(4)	120.57(19)	C(10)–C(9)–H(9)	120.0	C(4)–N(1)–H(1B)	112(2)
C(2)–C(3)–H(3)	119.7	C(8)–C(9)–H(9)	120.0	H(1A)–N(1)–H(1B)	123(3)
C(4)–C(3)–H(3)	119.7	C(9)–C(10)–C(11)	120.02(19)	C(7)–N(2)–S(1)	119.61(14)
N(1)–C(4)–C(5)	121.08(19)	C(9)–C(10)–H(10)	120.0	C(7)–N(2)–H(2A)	117(2)
N(1)–C(4)–C(3)	120.48(18)	C(11)–C(10)–H(10)	120.0	S(1)–N(2)–H(2A)	106(2)
C(5)–C(4)–C(3)	118.43(18)	C(12)–C(11)–C(10)	120.0(2)	C(12)–O(3)–C(13)	116.60(17)
C(6)–C(5)–C(4)	121.04(19)	C(12)–C(11)–H(11)	120.0	O(1)–S(1)–O(2)	118.63(9)
C(6)–C(5)–H(5)	119.5	C(10)–C(11)–H(11)	120.0	O(1)–S(1)–N(2)	107.69(9)
C(4)–C(5)–H(5)	119.5	O(3)–C(12)–C(11)	124.72(19)	O(2)–S(1)–N(2)	104.62(9)
C(5)–C(6)–C(1)	119.65(18)	O(3)–C(12)–C(7)	115.39(17)	O(1)–S(1)–C(1)	107.71(9)
C(5)–C(6)–H(6)	120.2	C(11)–C(12)–C(7)	119.87(19)	O(2)–S(1)–C(1)	109.98(9)
C(1)–C(6)–H(6)	120.2	O(3)–C(13)–H(13A)	109.5	N(2)–S(1)–C(1)	107.71(9)
C(8)–C(7)–C(12)	119.66(19)				

C(6)–C(1)–C(2)–C(3)	0.5(3)	C(8)–C(7)–C(12)–O(3)	177.29(18)
S(1)–C(1)–C(2)–C(3)	–176.78(16)	N(2)–C(7)–C(12)–O(3)	–0.2(3)
C(1)–C(2)–C(3)–C(4)	0.5(3)	C(8)–C(7)–C(12)–C(11)	–1.0(3)
C(2)–C(3)–C(4)–N(1)	178.64(19)	N(2)–C(7)–C(12)–C(11)	–178.56(18)
C(2)–C(3)–C(4)–C(5)	–2.3(3)	C(8)–C(7)–N(2)–S(1)	54.5(2)
N(1)–C(4)–C(5)–C(6)	–177.9(2)	C(12)–C(7)–N(2)–S(1)	–128.06(17)
C(3)–C(4)–C(5)–C(6)	3.1(3)	C(11)–C(12)–O(3)–C(13)	6.9(3)
C(4)–C(5)–C(6)–C(1)	–2.1(3)	C(7)–C(12)–O(3)–C(13)	–171.36(18)
C(2)–C(1)–C(6)–C(5)	0.2(3)	C(7)–N(2)–S(1)–O(1)	–61.34(17)
S(1)–C(1)–C(6)–C(5)	177.51(16)	C(7)–N(2)–S(1)–O(2)	171.57(15)
C(12)–C(7)–C(8)–C(9)	0.9(3)	C(7)–N(2)–S(1)–C(1)	54.57(17)
N(2)–C(7)–C(8)–C(9)	178.38(19)	C(6)–C(1)–S(1)–O(1)	15.33(19)
C(7)–C(8)–C(9)–C(10)	–0.1(3)	C(2)–C(1)–S(1)–O(1)	–167.37(16)
C(8)–C(9)–C(10)–C(11)	–0.7(3)	C(6)–C(1)–S(1)–O(2)	145.97(17)
C(9)–C(10)–C(11)–C(12)	0.6(3)	C(2)–C(1)–S(1)–O(2)	–36.72(19)
C(10)–C(11)–C(12)–O(3)	–177.90(19)	C(6)–C(1)–S(1)–N(2)	–100.57(18)
C(10)–C(11)–C(12)–C(7)	0.3(3)	C(2)–C(1)–S(1)–N(2)	76.73(18)

Table S5. Bond lengths (Å), angles (º) and torsion angles (º) for **1b**.

C(1)–C(2)	1.3849(16)	C(7)–N(1)	1.3615(15)	C(12)–H(12)	0.9500
C(1)–C(6)	1.3878(16)	C(7)–C(8)	1.5031(17)	C(13)–O(3)	1.3673(16)
C(1)–S(1)	1.7558(12)	C(8)–H(8A)	0.9800	C(13)–C(14)	1.3916(18)
C(2)–C(3)	1.3849(17)	C(8)–H(8B)	0.9800	C(14)–H(14)	0.9500
C(2)–H(2)	0.9500	C(8)–H(8C)	0.9800	C(15)–O(3)	1.4262(18)
C(3)–C(4)	1.3919(16)	C(9)–C(10)	1.3847(17)	C(15)–H(15A)	0.9800
C(3)–H(3)	0.9500	C(9)–C(14)	1.3949(17)	C(15)–H(15B)	0.9800
C(4)–C(5)	1.3950(16)	C(9)–N(2)	1.4361(16)	C(15)–H(15C)	0.9800
C(4)–N(1)	1.4070(15)	C(10)–C(11)	1.396(2)	N(1)–H(1)	0.8800
C(5)–C(6)	1.3857(17)	C(10)–H(10)	0.9500	N(2)–S(1)	1.6389(11)
C(5)–H(5)	0.9500	C(11)–C(12)	1.378(2)	N(2)–H(2A)	0.841(18)
C(6)–H(6)	0.9500	C(11)–H(11)	0.9500	O(1)–S(1)	1.4312(9)
C(7)–O(4)	1.2256(15)	C(12)–C(13)	1.3944(19)	O(2)–S(1)	1.4377(9)

C(2)–C(1)–C(6)	120.69(11)	C(7)–C(8)–H(8B)	109.5	C(13)–C(14)–H(14)	120.7
C(2)–C(1)–S(1)	120.27(9)	H(8A)–C(8)–H(8B)	109.5	C(9)–C(14)–H(14)	120.7
C(6)–C(1)–S(1)	118.99(9)	C(7)–C(8)–H(8C)	109.5	O(3)–C(15)–H(15A)	109.5
C(1)–C(2)–C(3)	119.16(11)	H(8A)–C(8)–H(8C)	109.5	O(3)–C(15)–H(15B)	109.5
C(1)–C(2)–H(2)	120.4	H(8B)–C(8)–H(8C)	109.5	H(15A)–C(15)–H(15B)	109.5
C(3)–C(2)–H(2)	120.4	C(10)–C(9)–C(14)	121.44(12)	O(3)–C(15)–H(15C)	109.5
C(2)–C(3)–C(4)	120.72(11)	C(10)–C(9)–N(2)	118.88(11)	H(15A)–C(15)–H(15C)	109.5
C(2)–C(3)–H(3)	119.6	C(14)–C(9)–N(2)	119.57(11)	H(15B)–C(15)–H(15C)	109.5
C(4)–C(3)–H(3)	119.6	C(9)–C(10)–C(11)	118.73(13)	C(7)–N(1)–C(4)	127.54(10)
C(3)–C(4)–C(5)	119.72(11)	C(9)–C(10)–H(10)	120.6	C(7)–N(1)–H(1)	116.2
C(3)–C(4)–N(1)	116.85(10)	C(11)–C(10)–H(10)	120.6	C(4)–N(1)–H(1)	116.2
C(5)–C(4)–N(1)	123.43(11)	C(12)–C(11)–C(10)	120.97(13)	C(9)–N(2)–S(1)	120.84(8)
C(6)–C(5)–C(4)	119.52(11)	C(12)–C(11)–H(11)	119.5	C(9)–N(2)–H(2A)	113.6(12)
C(6)–C(5)–H(5)	120.2	C(10)–C(11)–H(11)	119.5	S(1)–N(2)–H(2A)	106.8(12)
C(4)–C(5)–H(5)	120.2	C(11)–C(12)–C(13)	119.59(13)	C(13)–O(3)–C(15)	117.11(11)
C(5)–C(6)–C(1)	120.17(11)	C(11)–C(12)–H(12)	120.2	O(1)–S(1)–O(2)	118.54(6)
C(5)–C(6)–H(6)	119.9	C(13)–C(12)–H(12)	120.2	O(1)–S(1)–N(2)	104.81(5)
C(1)–C(6)–H(6)	119.9	O(3)–C(13)–C(14)	124.07(12)	O(2)–S(1)–N(2)	108.16(6)
O(4)–C(7)–N(1)	123.10(11)	O(3)–C(13)–C(12)	115.31(12)	O(1)–S(1)–C(1)	110.42(6)
O(4)–C(7)–C(8)	122.58(11)	C(14)–C(13)–C(12)	120.61(12)	O(2)–S(1)–C(1)	107.92(5)
N(1)–C(7)–C(8)	114.31(10)	C(13)–C(14)–C(9)	118.64(12)	N(2)–S(1)–C(1)	106.31(5)
C(7)–C(8)–H(8A)	109.5				

C(6)–C(1)–C(2)–C(3)	0.98(19)	N(2)–C(9)–C(14)–C(13)	–176.79(11)
S(1)–C(1)–C(2)–C(3)	–176.35(10)	O(4)–C(7)–N(1)–C(4)	–5.0(2)
C(1)–C(2)–C(3)–C(4)	–0.2(2)	C(8)–C(7)–N(1)–C(4)	173.79(11)
C(2)–C(3)–C(4)–C(5)	–1.2(2)	C(3)–C(4)–N(1)–C(7)	–159.25(12)
C(2)–C(3)–C(4)–N(1)	179.46(12)	C(5)–C(4)–N(1)–C(7)	21.4(2)
C(3)–C(4)–C(5)–C(6)	1.8(2)	C(10)–C(9)–N(2)–S(1)	116.16(12)
N(1)–C(4)–C(5)–C(6)	–178.88(12)	C(14)–C(9)–N(2)–S(1)	–67.43(14)
C(4)–C(5)–C(6)–C(1)	–1.1(2)	C(14)–C(13)–O(3)–C(15)	4.7(2)
C(2)–C(1)–C(6)–C(5)	–0.3(2)	C(12)–C(13)–O(3)–C(15)	–176.34(14)
S(1)–C(1)–C(6)–C(5)	177.02(11)	C(9)–N(2)–S(1)–O(1)	–168.63(9)
C(14)–C(9)–C(10)–C(11)	–0.8(2)	C(9)–N(2)–S(1)–O(2)	64.00(10)
N(2)–C(9)–C(10)–C(11)	175.54(12)	C(9)–N(2)–S(1)–C(1)	–51.68(11)
C(9)–C(10)–C(11)–C(12)	1.3(2)	C(2)–C(1)–S(1)–O(1)	–133.64(10)
C(10)–C(11)–C(12)–C(13)	–0.5(2)	C(6)–C(1)–S(1)–O(1)	48.99(12)
C(11)–C(12)–C(13)–O(3)	–179.84(13)	C(2)–C(1)–S(1)–O(2)	–2.63(12)
C(11)–C(12)–C(13)–C(14)	–0.8(2)	C(6)–C(1)–S(1)–O(2)	179.99(10)
O(3)–C(13)–C(14)–C(9)	–179.77(12)	C(2)–C(1)–S(1)–N(2)	113.21(11)
C(12)–C(13)–C(14)–C(9)	1.29(19)	C(6)–C(1)–S(1)–N(2)	–64.16(11)
C(10)–C(9)–C(14)–C(13)	–0.48(19)		

Table S6. Bond lengths (Å), angles (º) and torsion angles (º) for **2b**.

C(1)–C(6)	1.3931(15)	C(7)–C(12)	1.3853(15)	C(12)–H(12)	0.9500
C(1)–C(2)	1.3967(15)	C(7)–C(8)	1.3972(15)	C(13)–O(3)	1.4267(14)
C(1)–S(1)	1.7511(11)	C(7)–N(2)	1.4289(14)	C(13)–H(13A)	0.9800
C(2)–C(3)	1.3828(16)	C(8)–C(9)	1.3872(16)	C(13)–H(13B)	0.9800
C(2)–H(2)	0.9500	C(8)–H(8)	0.9500	C(13)–H(13C)	0.9800
C(3)–C(4)	1.4051(16)	C(9)–C(10)	1.3931(17)	N(1)–H(1B)	0.904(19)
C(3)–H(3)	0.9500	C(9)–H(9)	0.9500	N(1)–H(1A)	0.853(19)
C(4)–N(1)	1.3944(15)	C(10)–C(11)	1.3913(16)	N(2)–S(1)	1.6344(10)
C(4)–C(5)	1.4038(16)	C(10)–H(10)	0.9500	N(2)–H(2A)	0.865(18)
C(5)–C(6)	1.3870(16)	C(11)–O(3)	1.3618(14)	O(1)–S(1)	1.4405(9)
C(5)–H(5)	0.9500	C(11)–C(12)	1.4008(15)	O(2)–S(1)	1.4382(9)
C(6)–H(6)	0.9500				

C(6)–C(1)–C(2)	120.72(10)	C(12)–C(7)–N(2)	121.52(10)	O(3)–C(13)–H(13B)	109.5
C(6)–C(1)–S(1)	120.15(9)	C(8)–C(7)–N(2)	117.75(10)	H(13A)–C(13)–H(13B)	109.5
C(2)–C(1)–S(1)	119.13(8)	C(9)–C(8)–C(7)	119.02(11)	O(3)–C(13)–H(13C)	109.5
C(3)–C(2)–C(1)	119.49(10)	C(9)–C(8)–H(8)	120.5	H(13A)–C(13)–H(13C)	109.5
C(3)–C(2)–H(2)	120.3	C(7)–C(8)–H(8)	120.5	H(13B)–C(13)–H(13C)	109.5
C(1)–C(2)–H(2)	120.3	C(8)–C(9)–C(10)	121.46(11)	C(4)–N(1)–H(1B)	114.1(12)
C(2)–C(3)–C(4)	120.61(11)	C(8)–C(9)–H(9)	119.3	C(4)–N(1)–H(1A)	115.1(12)
C(2)–C(3)–H(3)	119.7	C(10)–C(9)–H(9)	119.3	H(1B)–N(1)–H(1A)	111.4(17)
C(4)–C(3)–H(3)	119.7	C(11)–C(10)–C(9)	118.68(11)	C(7)–N(2)–S(1)	123.34(8)
N(1)–C(4)–C(5)	120.42(10)	C(11)–C(10)–H(10)	120.7	C(7)–N(2)–H(2A)	115.4(11)
N(1)–C(4)–C(3)	120.40(11)	C(9)–C(10)–H(10)	120.7	S(1)–N(2)–H(2A)	111.5(11)
C(5)–C(4)–C(3)	119.15(10)	O(3)–C(11)–C(10)	125.14(10)	C(11)–O(3)–C(13)	117.96(10)
C(6)–C(5)–C(4)	120.35(10)	O(3)–C(11)–C(12)	114.05(10)	O(2)–S(1)–O(1)	118.53(5)
C(6)–C(5)–H(5)	119.8	C(10)–C(11)–C(12)	120.80(11)	O(2)–S(1)–N(2)	108.66(5)
C(4)–C(5)–H(5)	119.8	C(7)–C(12)–C(11)	119.34(10)	O(1)–S(1)–N(2)	104.08(5)
C(5)–C(6)–C(1)	119.67(10)	C(7)–C(12)–H(12)	120.3	O(2)–S(1)–C(1)	107.64(5)
C(5)–C(6)–H(6)	120.2	C(11)–C(12)–H(12)	120.3	O(1)–S(1)–C(1)	109.46(5)
C(1)–C(6)–H(6)	120.2	O(3)–C(13)–H(13A)	109.5	N(2)–S(1)–C(1)	108.05(5)
C(12)–C(7)–C(8)	120.69(10)				

C(6)–C(1)–C(2)–C(3)	0.97(16)	N(2)–C(7)–C(12)–C(11)	–178.40(10)
S(1)–C(1)–C(2)–C(3)	–178.63(9)	O(3)–C(11)–C(12)–C(7)	–179.70(10)
C(1)–C(2)–C(3)–C(4)	–0.52(17)	C(10)–C(11)–C(12)–C(7)	1.18(17)
C(2)–C(3)–C(4)–N(1)	–178.51(10)	C(12)–C(7)–N(2)–S(1)	–39.58(15)
C(2)–C(3)–C(4)–C(5)	–0.30(17)	C(8)–C(7)–N(2)–S(1)	142.58(9)
N(1)–C(4)–C(5)–C(6)	178.90(11)	C(10)–C(11)–O(3)–C(13)	3.58(17)
C(3)–C(4)–C(5)–C(6)	0.69(16)	C(12)–C(11)–O(3)–C(13)	–175.50(10)
C(4)–C(5)–C(6)–C(1)	–0.25(17)	C(7)–N(2)–S(1)–O(2)	65.08(10)
C(2)–C(1)–C(6)–C(5)	–0.59(17)	C(7)–N(2)–S(1)–O(1)	–167.73(9)
S(1)–C(1)–C(6)–C(5)	179.01(9)	C(7)–N(2)–S(1)–C(1)	–51.43(10)
C(12)–C(7)–C(8)–C(9)	–0.51(17)	C(6)–C(1)–S(1)–O(2)	–10.68(11)
N(2)–C(7)–C(8)–C(9)	177.35(10)	C(2)–C(1)–S(1)–O(2)	168.93(8)
C(7)–C(8)–C(9)–C(10)	1.13(17)	C(6)–C(1)–S(1)–O(1)	–140.77(9)
C(8)–C(9)–C(10)–C(11)	–0.59(17)	C(2)–C(1)–S(1)–O(1)	38.84(10)
C(9)–C(10)–C(11)–O(3)	–179.59(11)	C(6)–C(1)–S(1)–N(2)	106.50(10)
C(9)–C(10)–C(11)–C(12)	–0.58(17)	C(2)–C(1)–S(1)–N(2)	–73.90(10)
C(8)–C(7)–C(12)–C(11)	–0.62(16)		

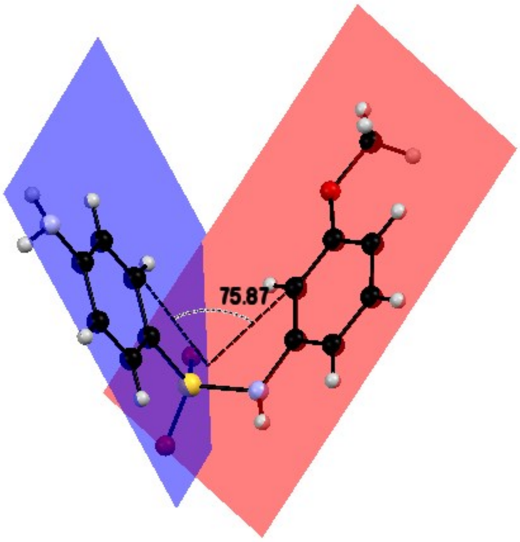
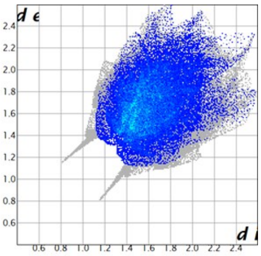
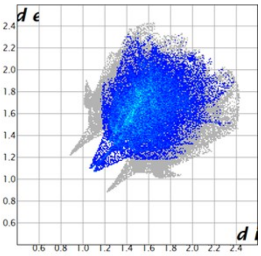
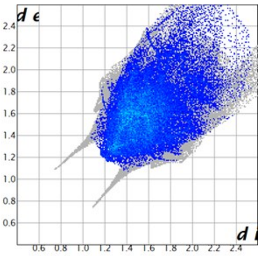
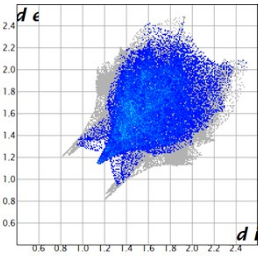
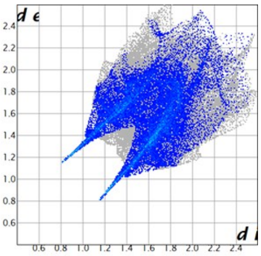
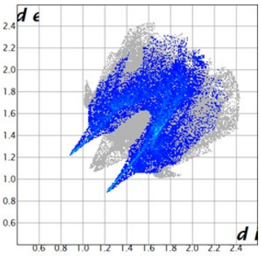
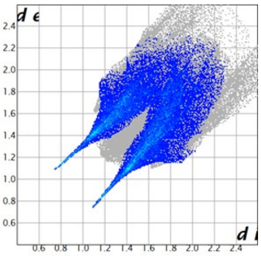
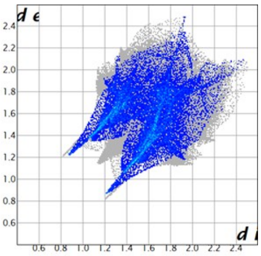
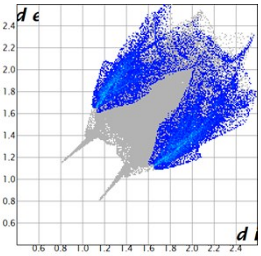
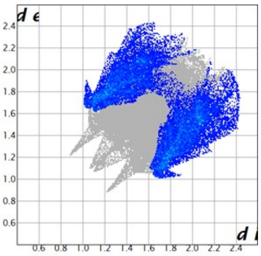
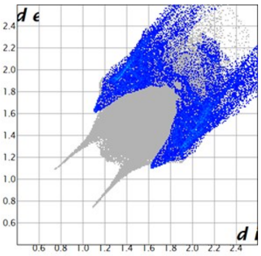
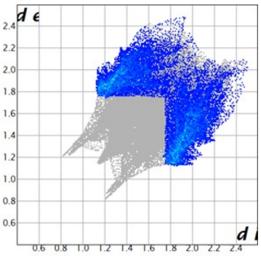
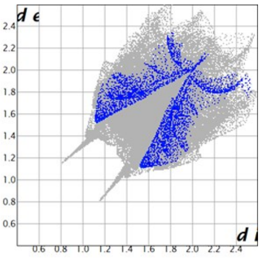
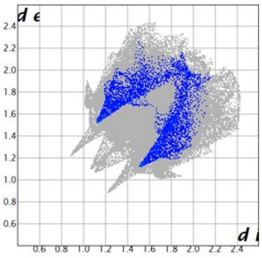
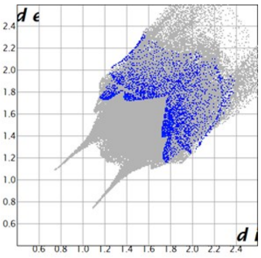
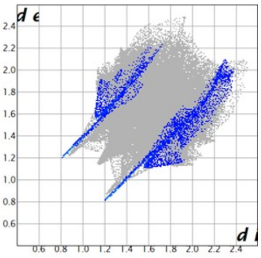
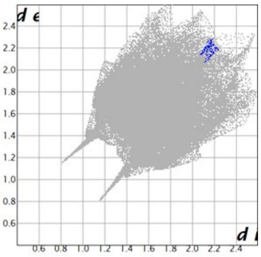
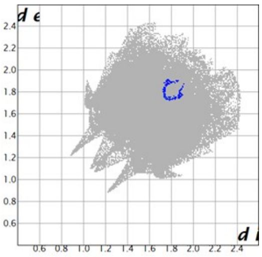
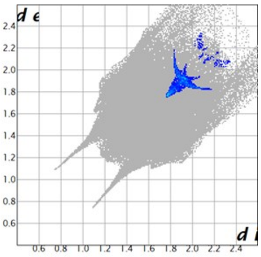
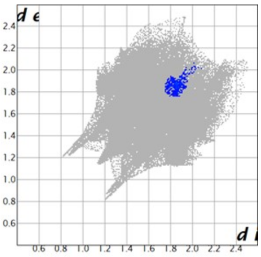
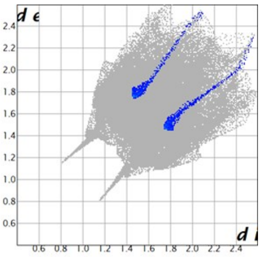
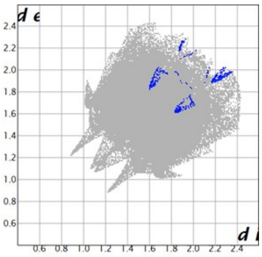
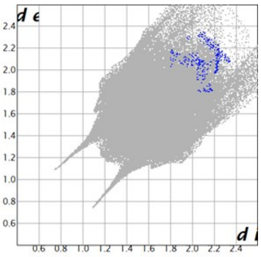
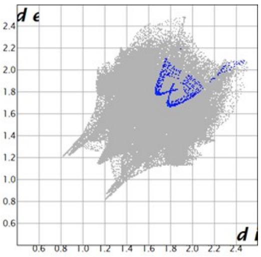
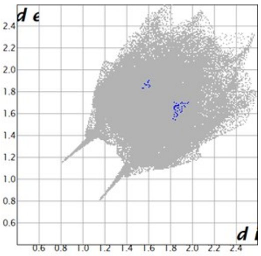
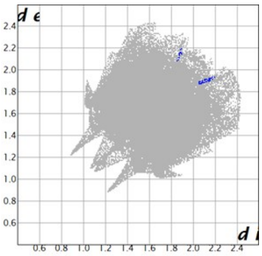
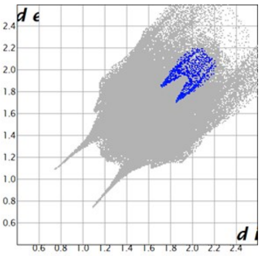
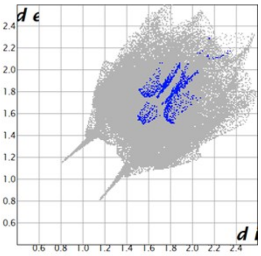
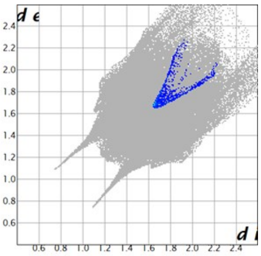
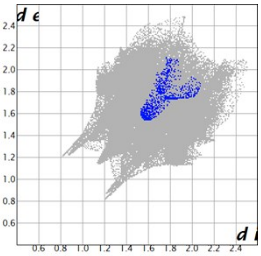


Figure S16. The experimental geometry of V-shaped **2b** molecule with marked dihedral angle between phenyl rings.

Table S7. 2D fingerprint plots of particular interactions observed in the crystal structure of sulfonamides **1a**, **2a**, **1b** and **2b** (d_e and d_i are expressed in Å)

	1a	**2a**	**1b**	**2b**
H···H	 **42.9%**	 **38.7%**	 **40.3%**	 **36.9%**
O···H	 **26.2%**	 **25.1%**	 **32.2%**	 **26.1%**
C···H	 **23.5%**	 **29.4%**	 **19.2%**	 **29.5%**

N···H	 **4.4%**	 **5.9%**	 **3.2%**	 **5.1%**
C···C	 **0.1%**	 **0.2%**	 **2.4%**	 **0.6%**
C···O	 **1.4%**	 **0.6%**	 **0.3%**	 **0.6%**
C···N	 **0.1%**	 **0.1%**	 **1.1%**	**------**
O···O	 **1.3%**	**------**	 **1.1%**	 **1.0%**

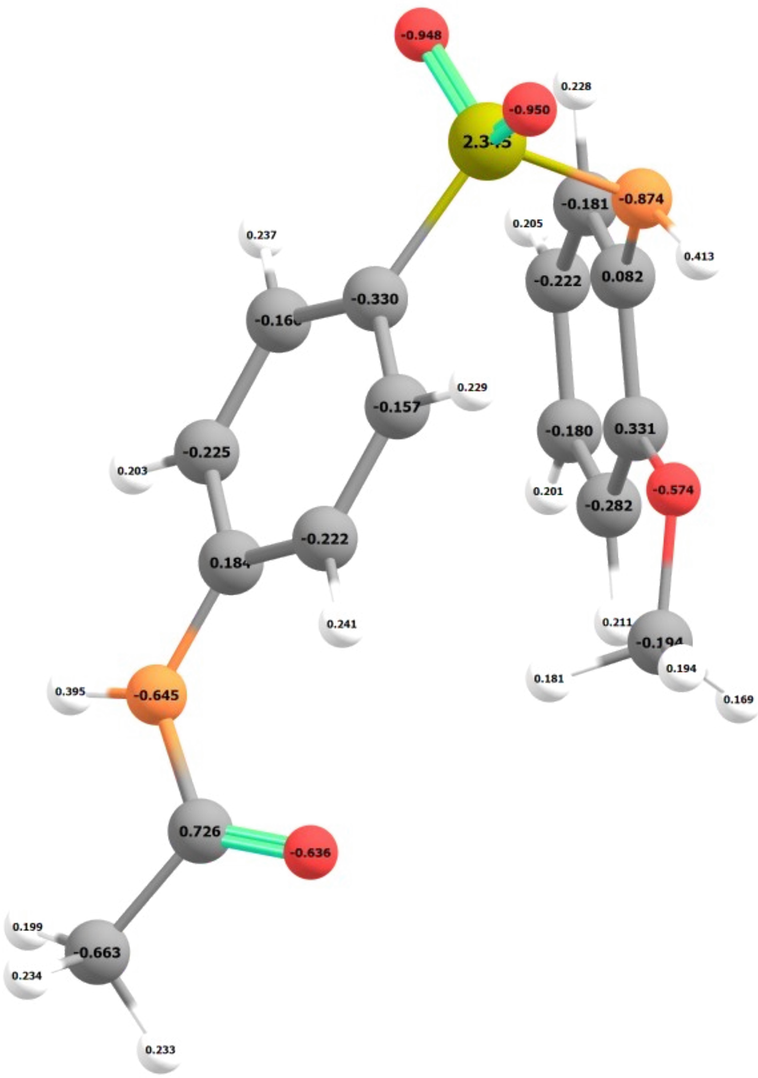


Figure S17. Partial atomic charges derived from NBO analysis corresponding to global minimum for **1a**.

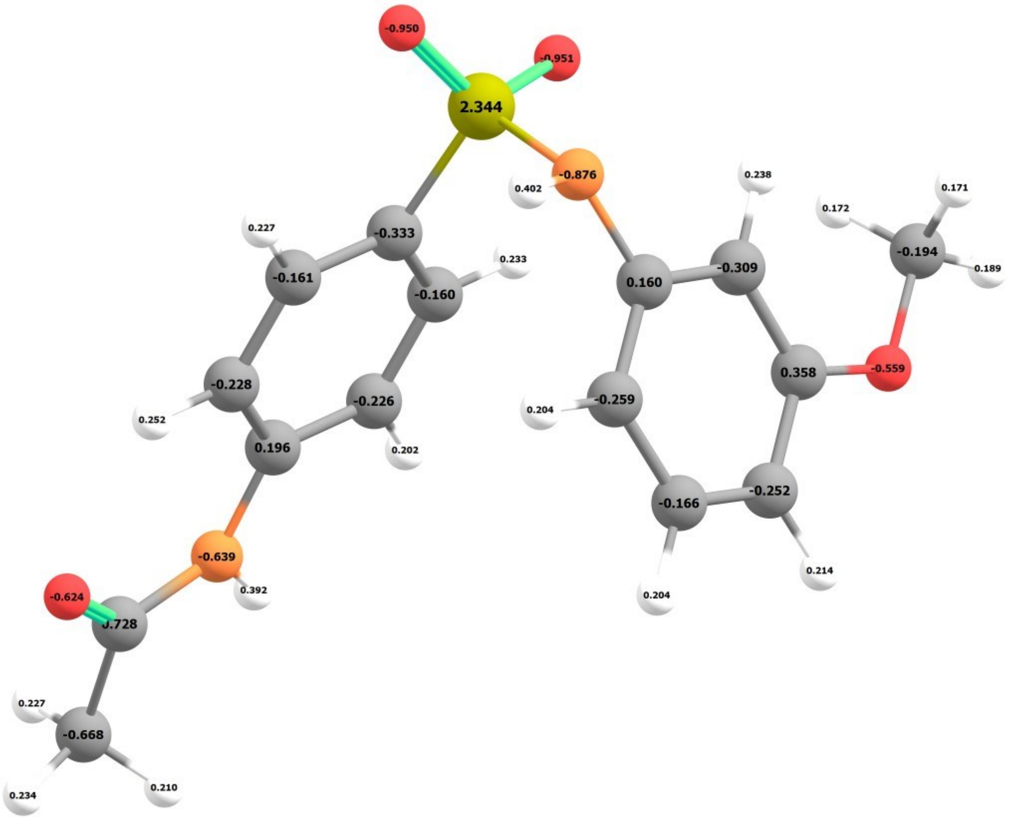


Figure S18. Partial atomic charges derived from NBO analysis corresponding to global minimum for **1b**.

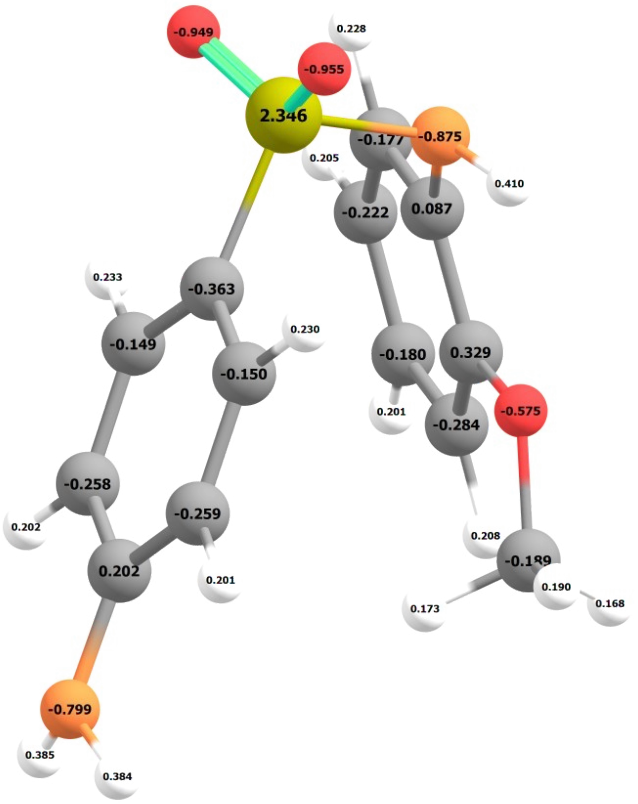


Figure S19. Partial atomic charges derived from NBO analysis corresponding to global minimum for **2a**.

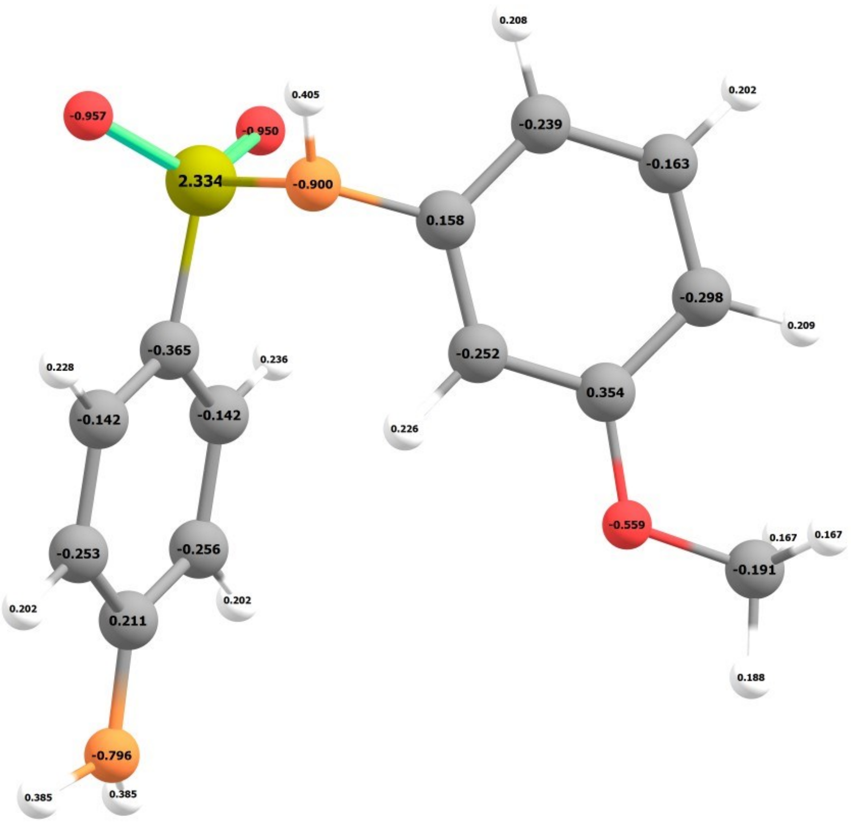
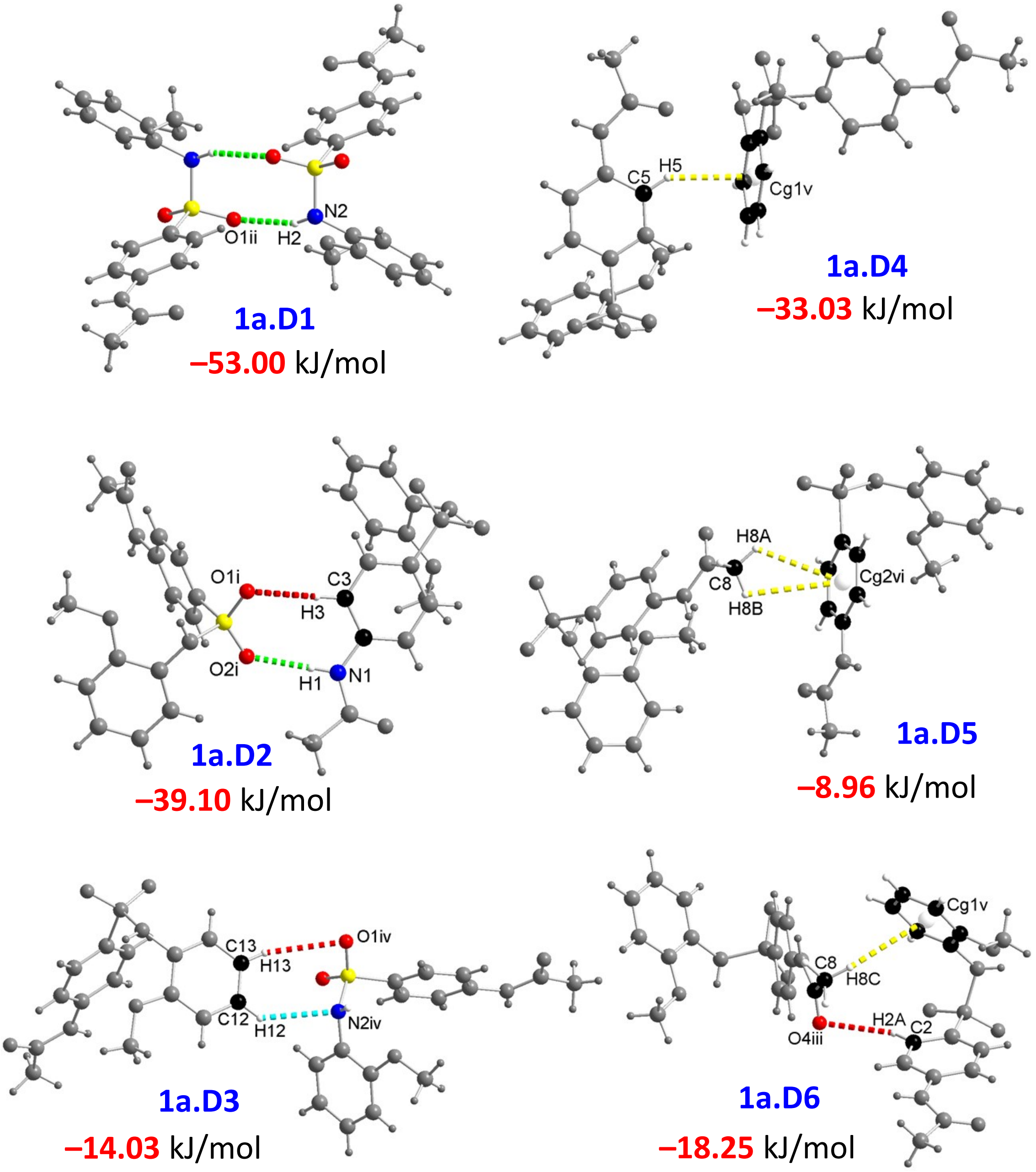


Figure S20. Partial atomic charges derived from NBO analysis corresponding to global minimum for **2b**.



1a.D1 –53.00 kJ/mol

1a.D4 –33.03 kJ/mol

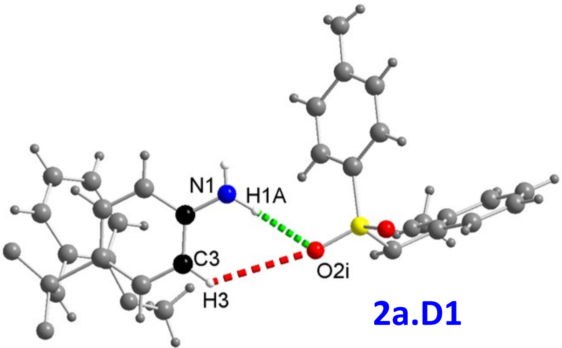
1a.D2 –39.10 kJ/mol

1a.D5 –8.96 kJ/mol

1a.D3 –14.03 kJ/mol

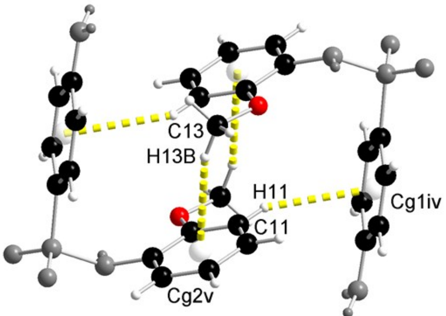
1a.D6 –18.25 kJ/mol

Figure S21. The structures of dimers of **1a** with calculated energies.



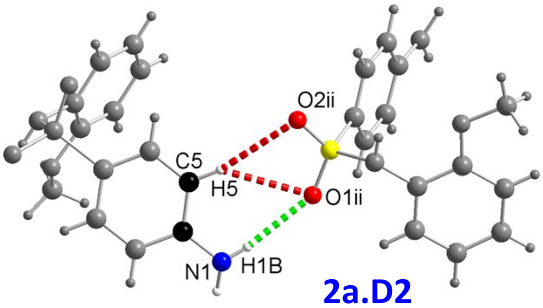
2a.D1

–29.27 kJ/mol



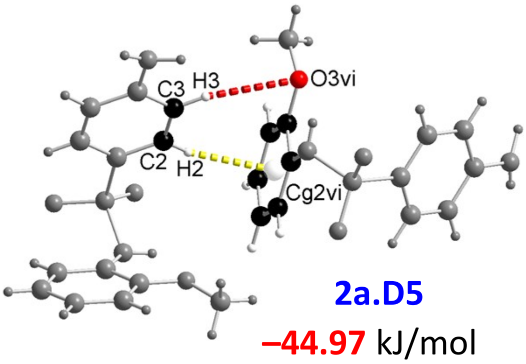
2a.D4

–78.04 kJ/mol



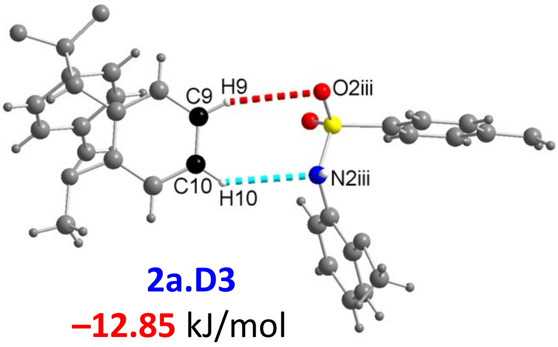
2a.D2

–25.71 kJ/mol



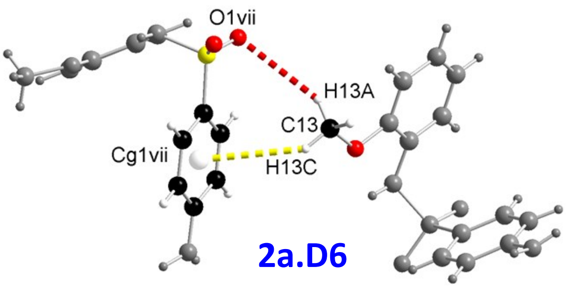
2a.D5

–44.97 kJ/mol



2a.D3

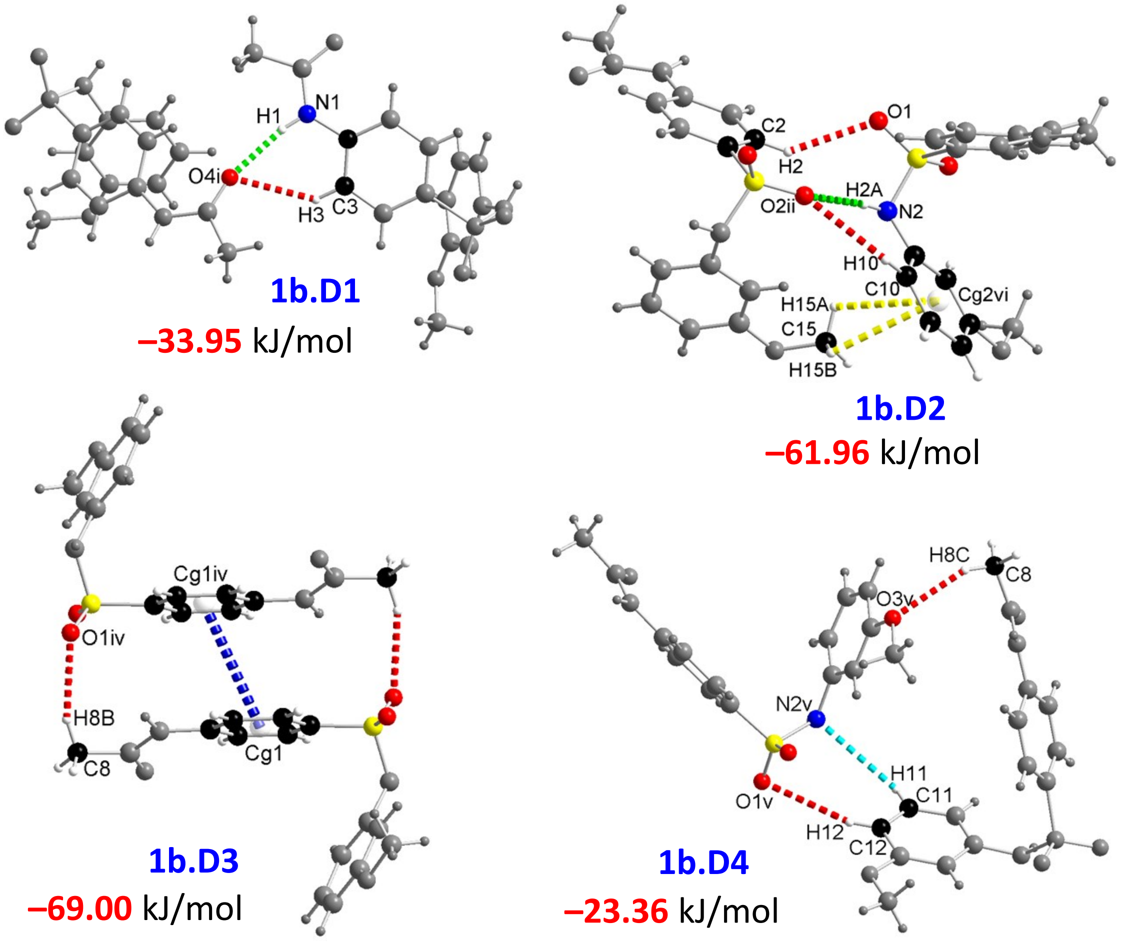
–12.85 kJ/mol



2a.D6

–20.22 kJ/mol

Figure S22. The structures of dimers of **2a** with calculated energies.



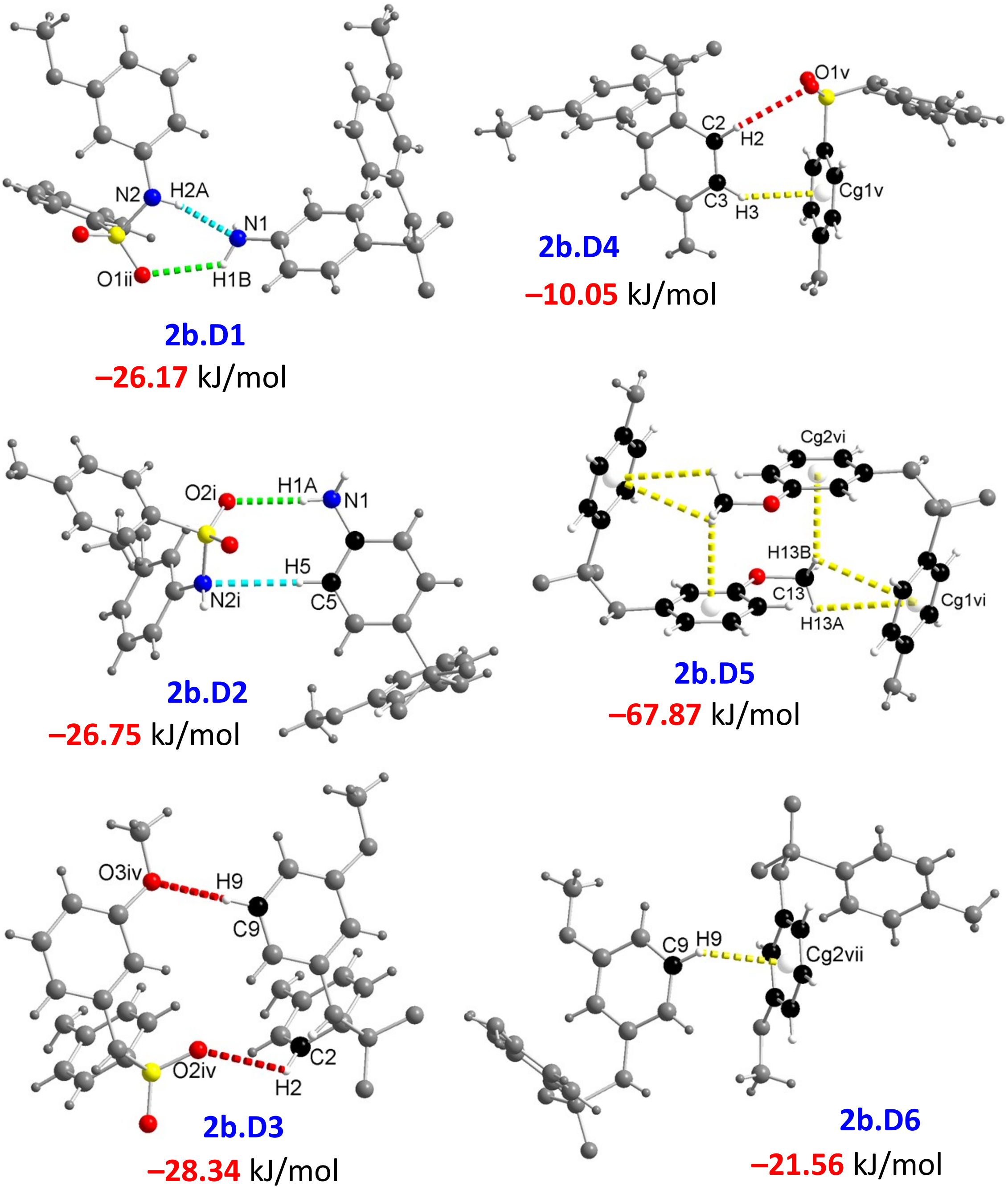
1b.D1
–33.95 kJ/mol

1b.D2
–61.96 kJ/mol

1b.D3
–69.00 kJ/mol

1b.D4
–23.36 kJ/mol

Figure S23. The structures of dimers of **1b** with calculated energies.



2b.D1
–26.17 kJ/mol

2b.D4
–10.05 kJ/mol

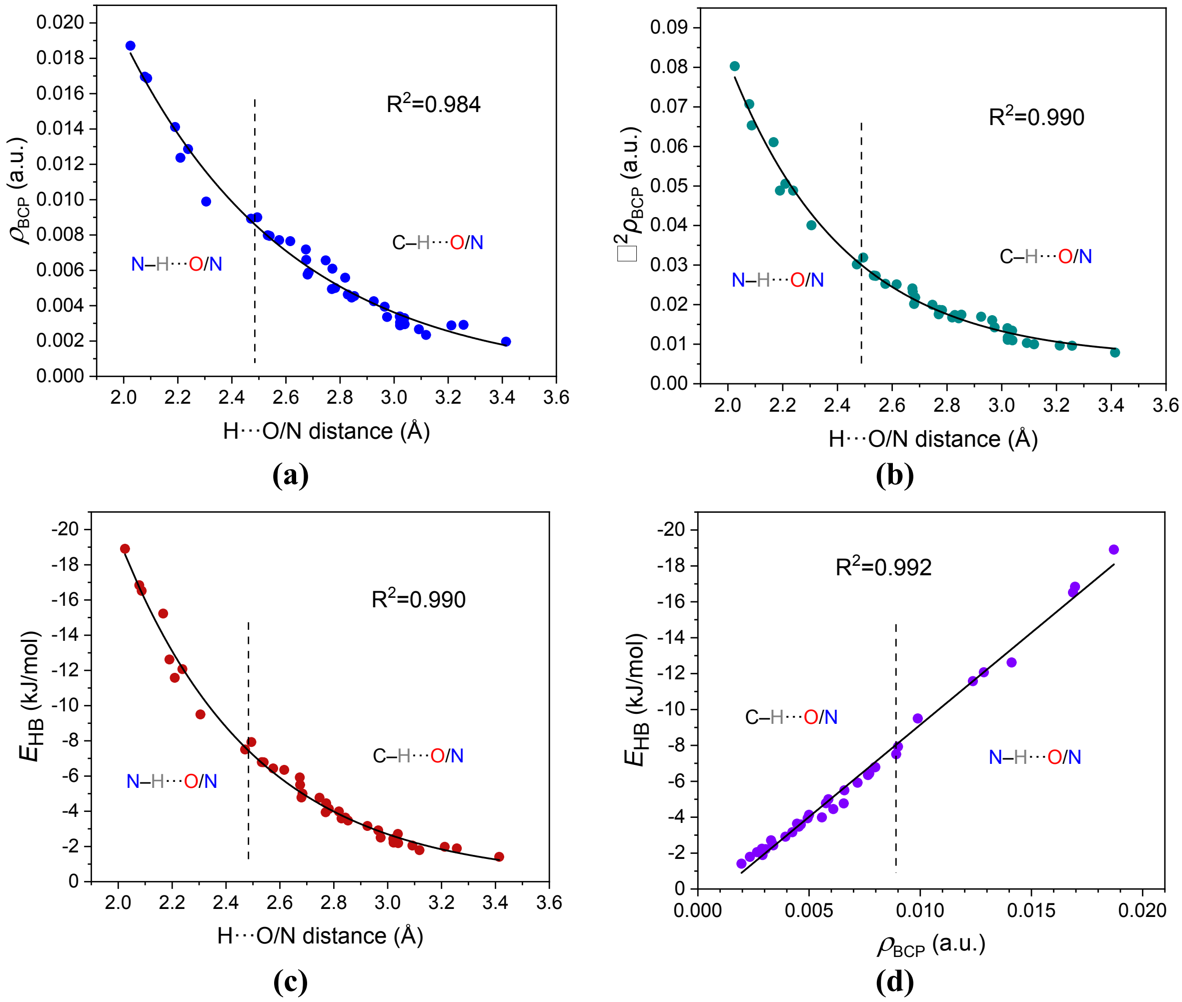
2b.D2
–26.75 kJ/mol

2b.D5
–67.87 kJ/mol

2b.D3
–28.34 kJ/mol

2b.D6
–21.56 kJ/mol

Figure S24. The structures of dimers of **2b** with calculated energies.



(a) **(b)**

(c) **(d)**

Figure S25. Relationship between the H···O/N distance and QTAIM parameters at the BCPs: (**a**) the electron density (ρ_{BCP}), (**b**) the Laplacian of the electron density ($\nabla^2\rho_{BCP}$) and (**c**) the calculated H-bond energy (E_{HB}) and (**d**) the relationship between the electron density (ρ_{BCP}) and the calculated H-bond energy (E_{HB}) for N–H···O/N and C–H···O/N hydrogen bonds considered together.