Supporting Information

Development of Selective Colorimetric Probes for Hydrogen Sulfide Based on Nucleophilic Aromatic Substitution

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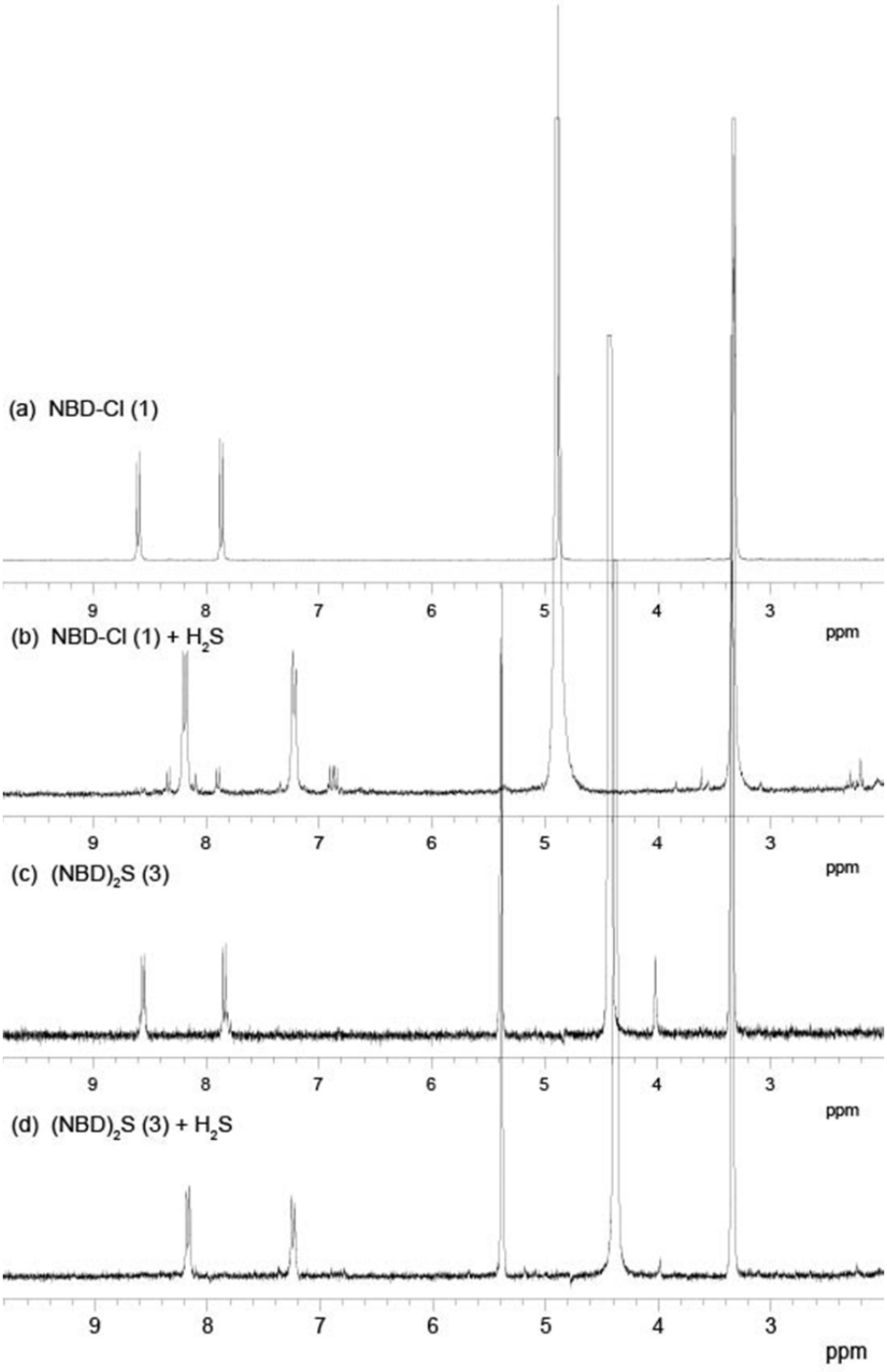

Figure S1. ^{1}H NMR spectra of (a) **1**, (b) **1** upon treatment with 1 equiv of NaSH, (c) **3**, and (d) **3** upon treatment with 2 equiv of NaSH. Conditions: 10 mM **1** (a) or **3** (c), reacting with 10 mM NaSH (b) or 20 mM NaSH (d), 3 DCM: 2 MeOD solvent.

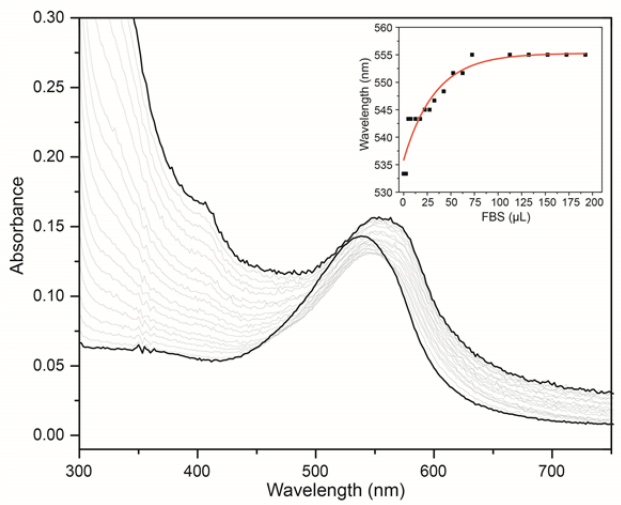

Figure S2. Change in absorbance of **2** as a function of added FBS. UV-vis absorption spectra showing the titration of **2** with FBS. Conditions: 22.1 µM of **2**, 50 mM PIPES, 100 mM KCl, 25 °C. Insert: UV-vis absorbance changes during the course of the titrations with FBS.

NMR Spectra

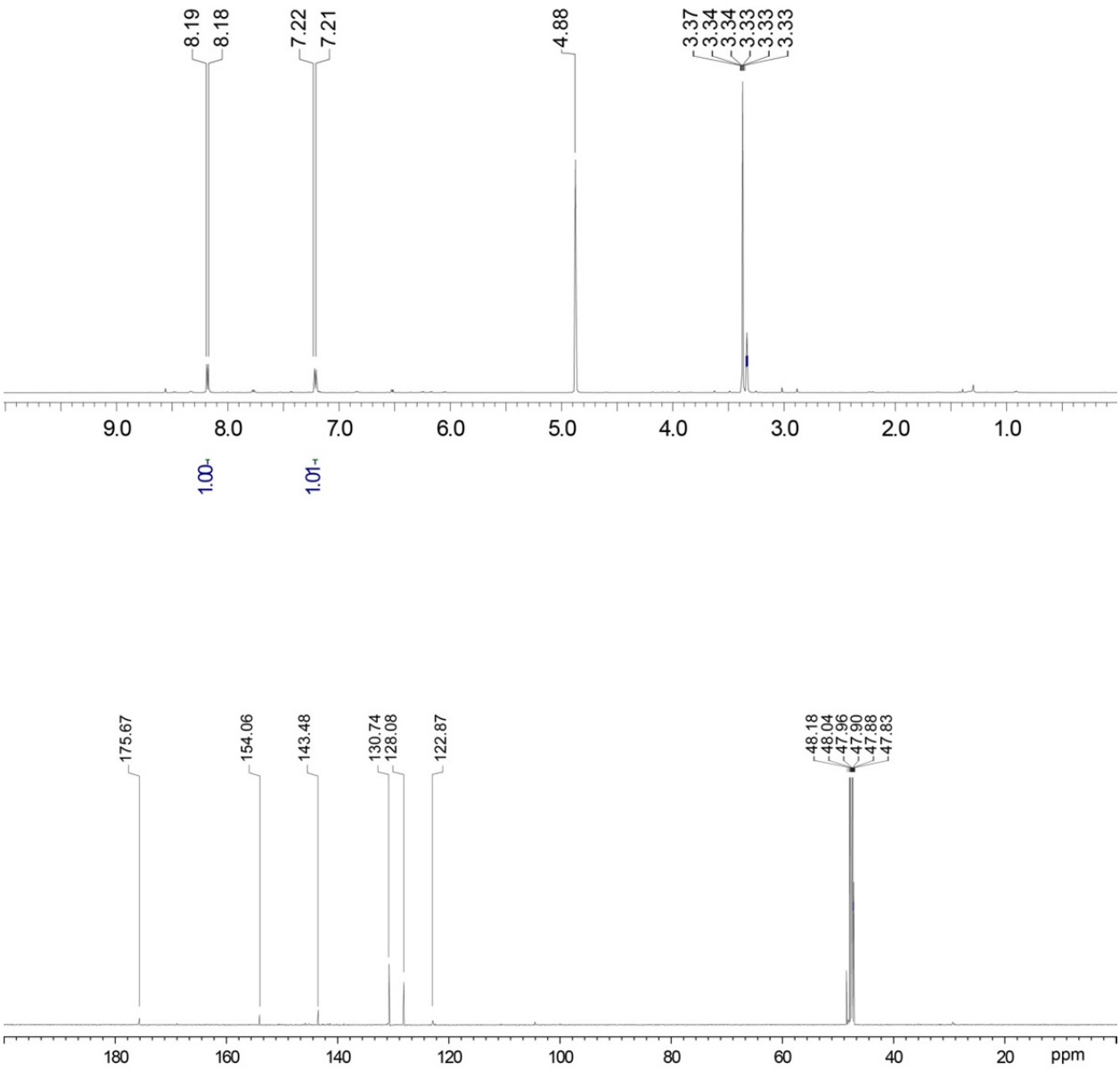

Figure S3. ^{1}H (600 MHz, MeOD) and $^{13}C\{^{1}H\}$ (150 MHz, MeOH) NMR spectra of **2**.

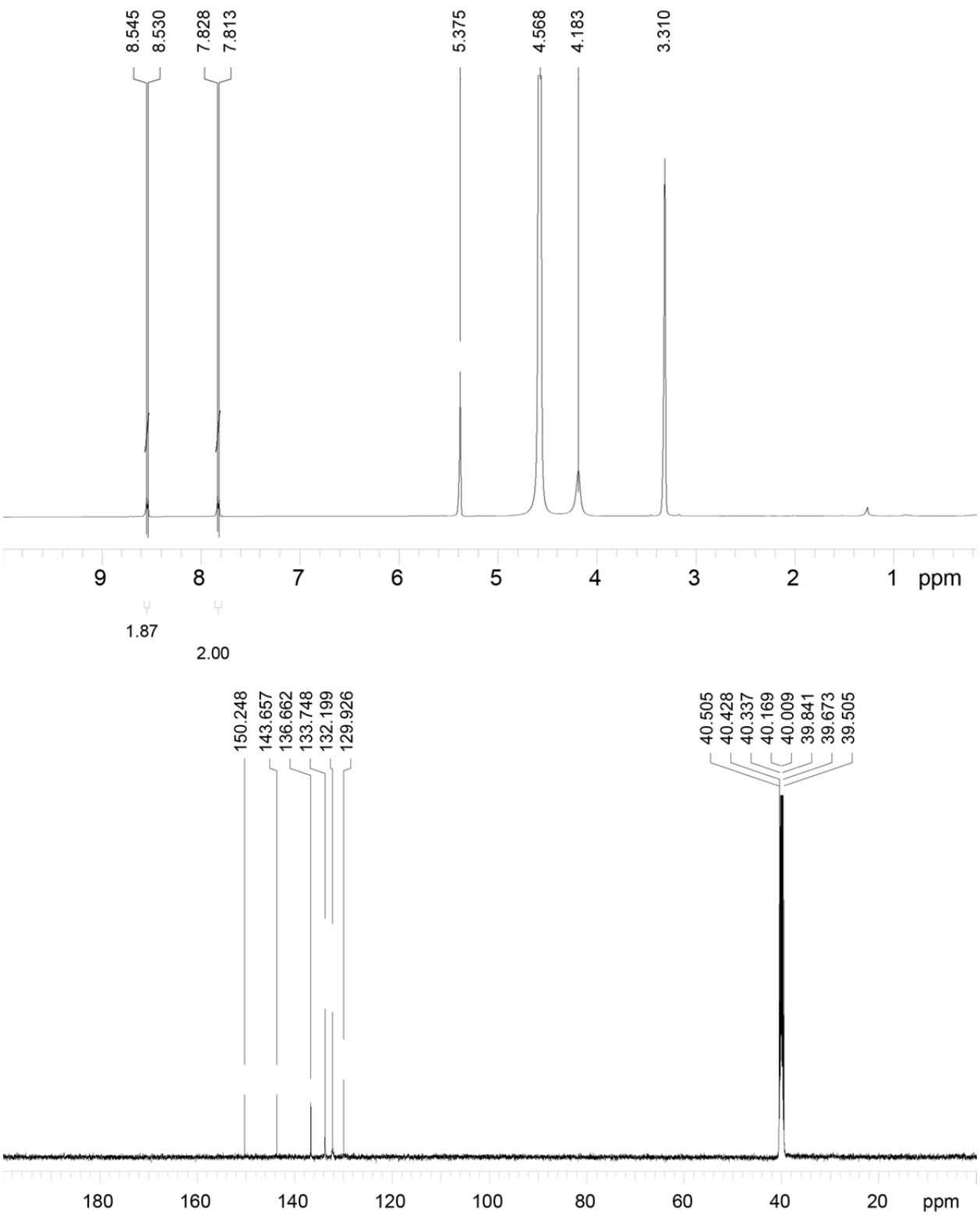

Figure S4. ^{1}H (500 MHz, 3:2 CD_2Cl_2:MeOD) and $^{13}C\{^{1}H\}$ (125 MHz, DMSO) NMR spectra of **3**.

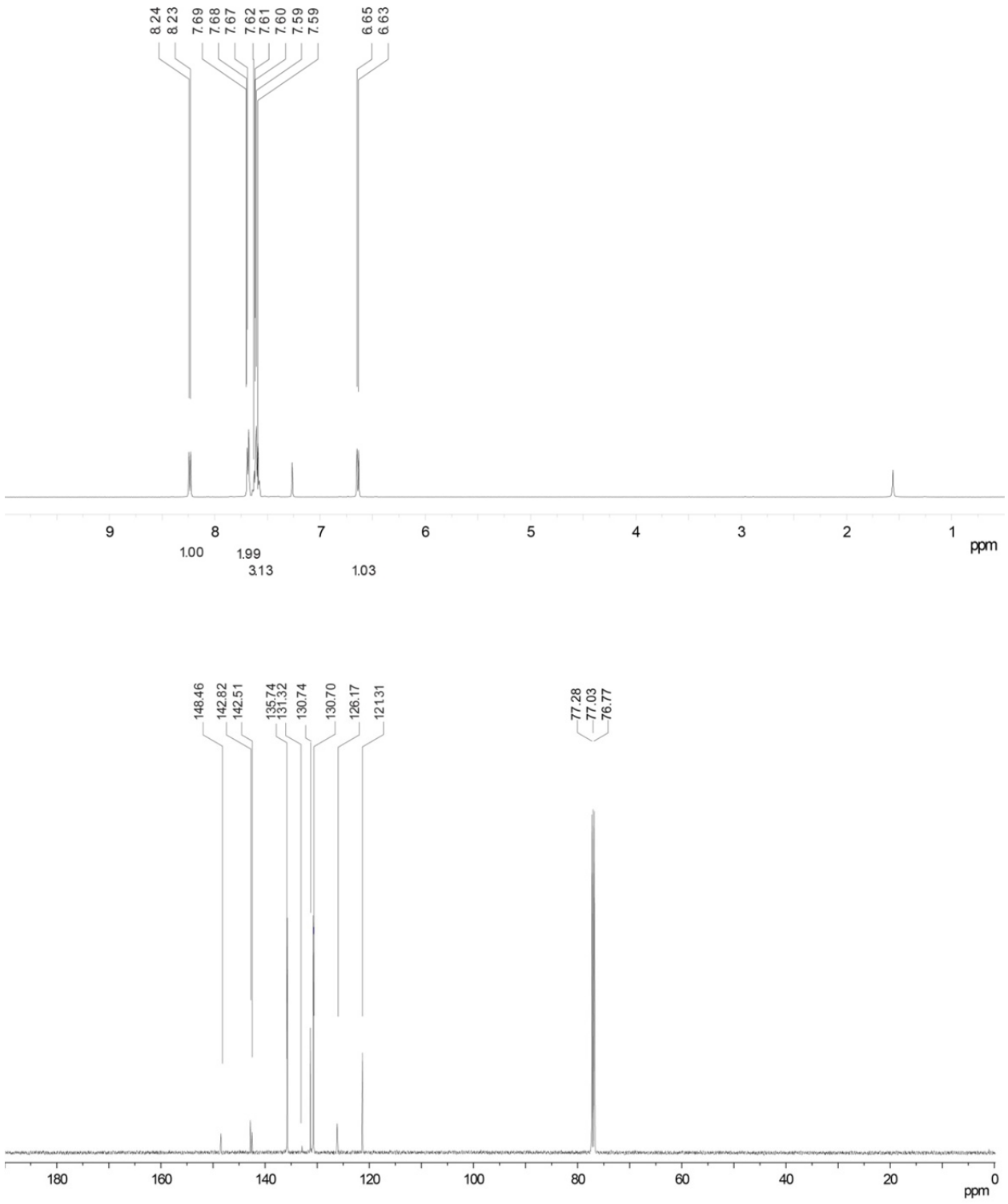

Figure S5. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **4**.

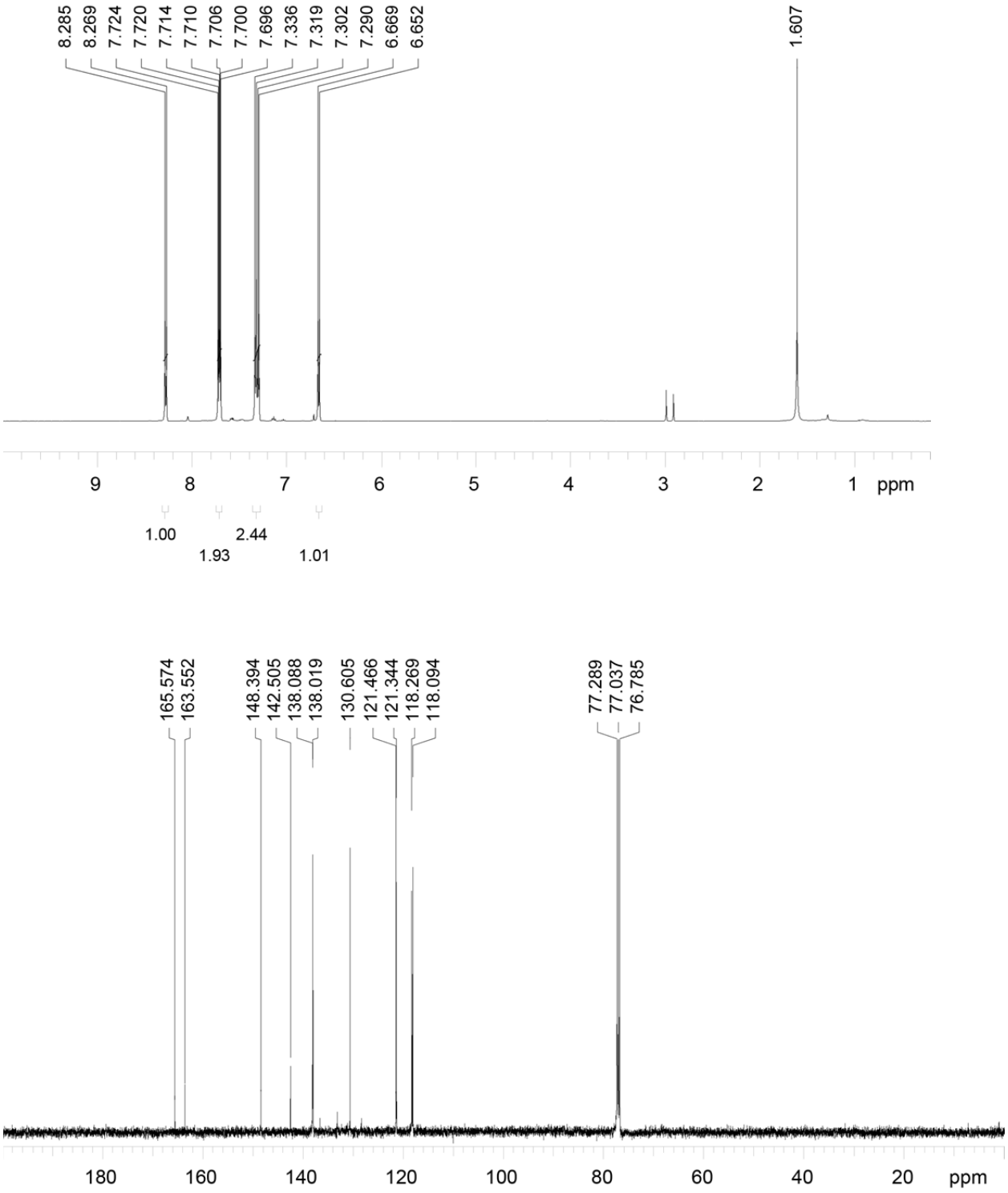

Figure S6. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **5**.

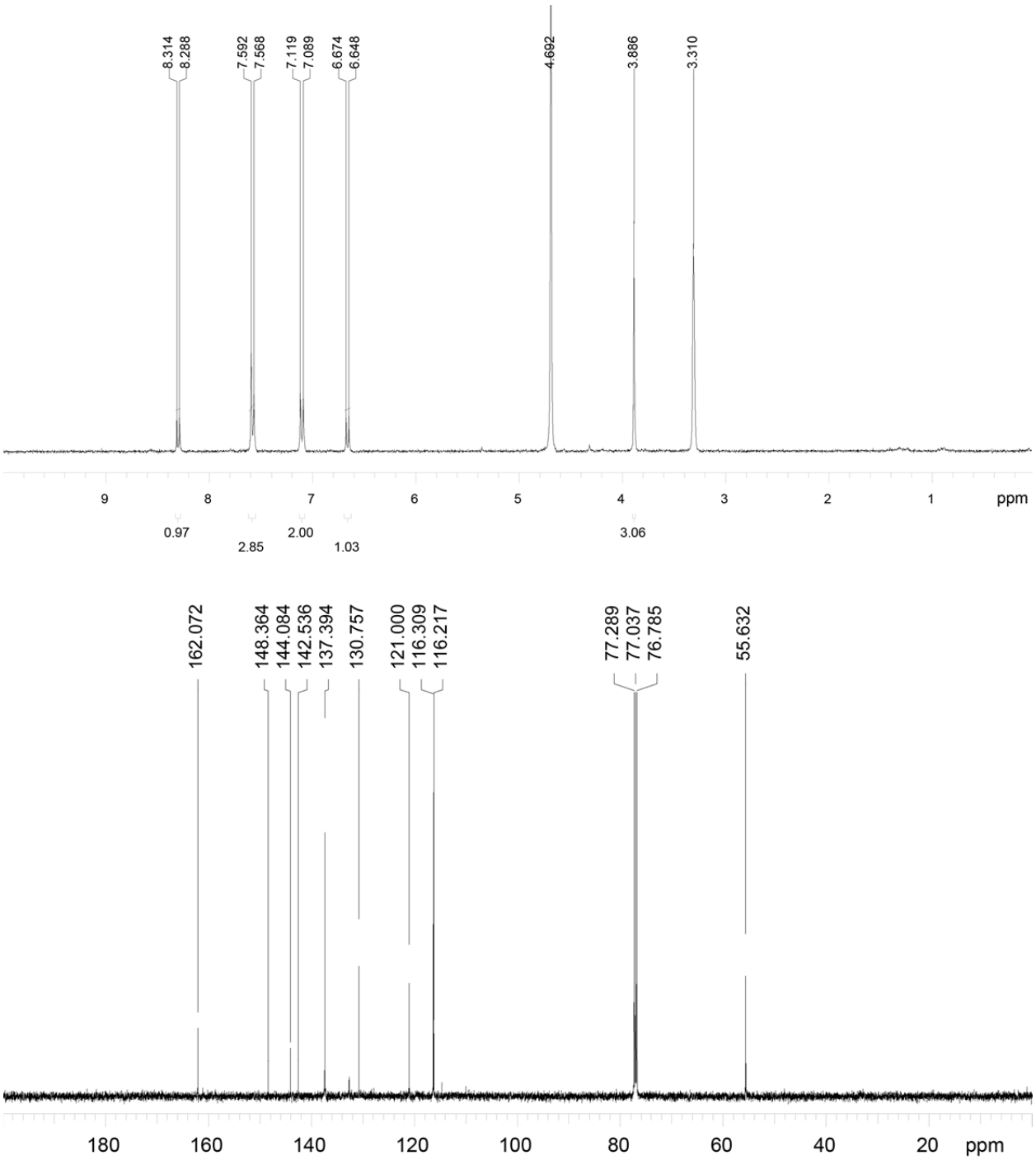

Figure S7. ^{1}H (500 MHz, 3:1 MeOD:$CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **6**.

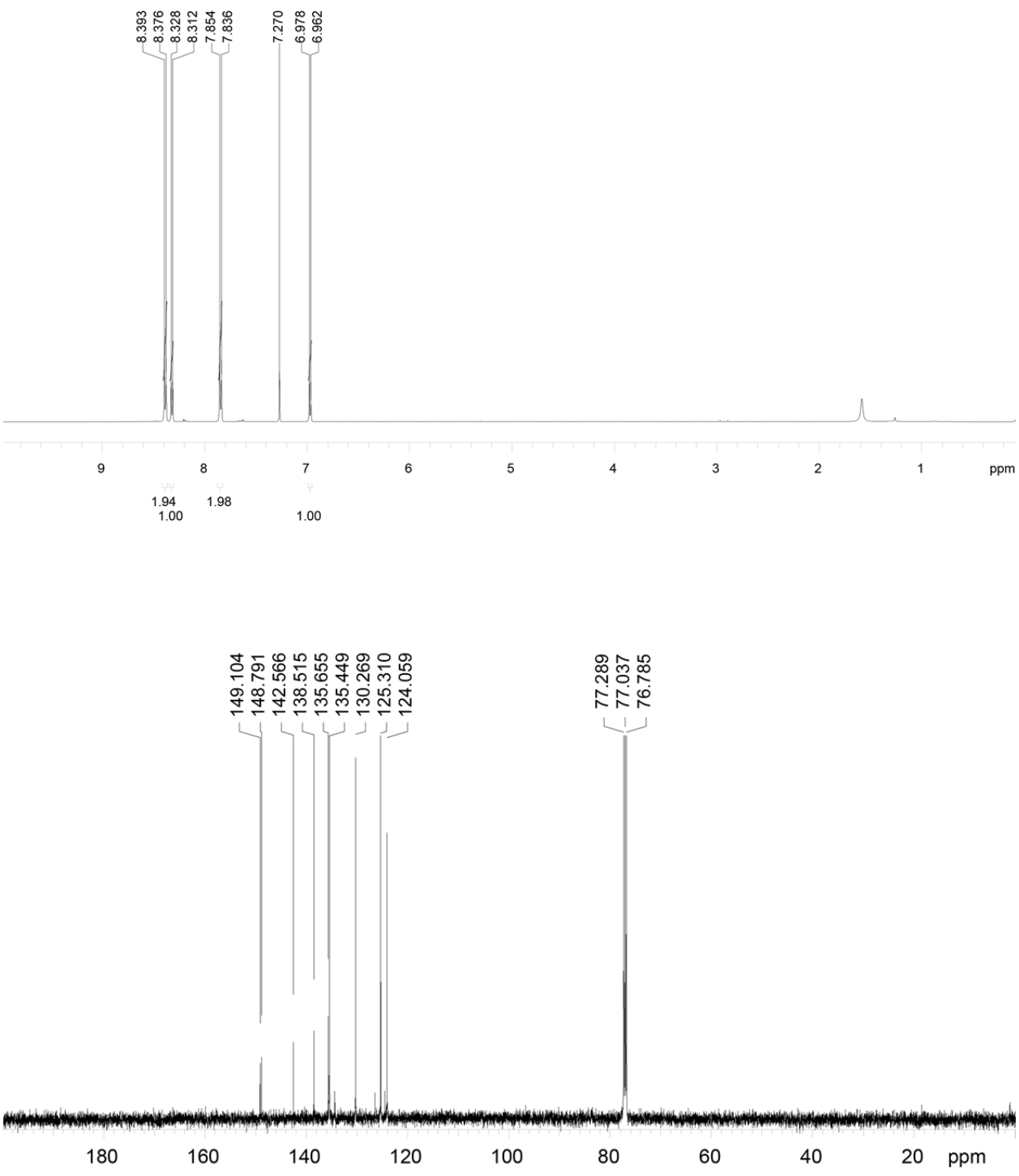

Figure S8. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **7**.

Table S1. Crystallographic parameters for the X-ray structural refinement for **3**.[a]

Empirical formula	$C_{12}H_4N_6O_6S$
Formula weight	360.27
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 13.1415(13) Å
	b = 11.4080(11) Å, β = 107.601(2)°
	c = 9.3240(9) Å
Volume (Å^3)	1332.4(2)
Z	4
Density (calculated)	1.796 Mg/m^3
Absorption coefficient	0.296 mm^{-1}
F(000)	728
Crystal size (mm)	0.39 x 0.11 x 0.10
Theta range for data collection (deg.)	1.63 - 27.00
Limiting indices	$-16 \le h \le 16$, $-14 \le k \le 14$, $-11 \le l \le 11$
Reflections collected / unique	14609 / 2897 [R_{int} = 0.0213]
Completeness to θ (%)	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9710 and 0.8934
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2897 / 0 / 242
Goodness-of-fit on F^2	1.054
Final R indices [$I>2\sigma(I)$]	R1 = 0.0319, wR2 = 0.0825
R indices (all data)	R1 = 0.0360, wR2 = 0.0863
Largest diff. peak and hole (e/Å^3)	0.385 and -0.176

[a] Refinement method was full-matrix least squares on F^2; $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3**. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
S(1)	8585(1)	9624(1)	9929(1)	25(1)
O(1)	10096(1)	6488(1)	12457(1)	32(1)
O(2)	8537(1)	3723(1)	9741(1)	42(1)
O(3)	7520(1)	4072(1)	7467(2)	41(1)
O(4)	4959(1)	9301(1)	8575(1)	29(1)
O(5)	4013(1)	11486(1)	4924(1)	40(1)
O(6)	5152(1)	12470(1)	4139(1)	42(1)
N(1)	9755(1)	7564(1)	11848(1)	27(1)
N(2)	9595(1)	5566(1)	11544(2)	31(1)
N(3)	8074(1)	4393(1)	8713(2)	31(1)
N(4)	6046(1)	9260(1)	9218(1)	26(1)
N(5)	4648(1)	10050(1)	7366(1)	26(1)
N(6)	4924(1)	11801(1)	5022(1)	30(1)
C(1)	8402(1)	8134(1)	9471(2)	21(1)
C(2)	9035(1)	7325(1)	10554(2)	22(1)
C(3)	8940(1)	6080(1)	10357(2)	24(1)
C(4)	8205(1)	5644(1)	9002(2)	25(1)
C(5)	7626(1)	6417(1)	7975(2)	25(1)
C(6)	7721(1)	7652(1)	8202(2)	23(1)
C(7)	7509(1)	10262(1)	8531(2)	22(1)
C(8)	6421(1)	9988(1)	8410(2)	21(1)
C(9)	5550(1)	10486(1)	7261(2)	22(1)
C(10)	5787(1)	11316(1)	6254(2)	24(1)
C(11)	6814(1)	11604(1)	6427(2)	28(1)
C(12)	7680(1)	11073(1)	7560(2)	27(1)

Table S3. Bond lengths [Å] and angles [°] for **3**.

S(1)-C(1)	1.7513(14)
S(1)-C(7)	1.7652(14)
O(1)-N(1)	1.3707(16)
O(1)-N(2)	1.3871(17)
O(2)-N(3)	1.2326(18)
O(3)-N(3)	1.2261(18)
O(4)-N(5)	1.3756(16)
O(4)-N(4)	1.3728(15)
O(5)-N(6)	1.2272(18)
O(6)-N(6)	1.2243(17)
N(1)-C(2)	1.3169(18)
N(2)-C(3)	1.3166(19)
N(3)-C(4)	1.4522(19)
N(4)-C(8)	1.3139(18)
N(5)-C(9)	1.3166(19)
N(6)-C(10)	1.4572(19)
C(1)-C(6)	1.3651(19)
C(1)-C(2)	1.4337(19)
C(2)-C(3)	1.432(2)
C(3)-C(4)	1.429(2)
C(4)-C(5)	1.354(2)
C(5)-C(6)	1.424(2)
C(5)-H(5)	0.937(18)
C(6)-H(6)	0.937(18)
C(7)-C(12)	1.359(2)
C(7)-C(8)	1.4342(19)
C(8)-C(9)	1.4276(19)
C(9)-C(10)	1.431(2)
C(10)-C(11)	1.352(2)
C(11)-C(12)	1.432(2)
C(11)-H(11)	0.957(18)
C(12)-H(12)	0.949(18)
C(1)-S(1)-C(7)	101.52(6)
N(1)-O(1)-N(2)	112.94(10)
N(5)-O(4)-N(4)	112.96(10)
C(2)-N(1)-O(1)	104.37(12)
C(3)-N(2)-O(1)	104.25(12)
O(3)-N(3)-O(2)	124.28(14)
O(3)-N(3)-C(4)	118.20(13)
O(2)-N(3)-C(4)	117.52(13)
C(8)-N(4)-O(4)	104.50(11)
C(9)-N(5)-O(4)	104.20(11)
O(6)-N(6)-O(5)	124.34(14)
O(6)-N(6)-C(10)	118.52(14)
O(5)-N(6)-C(10)	117.12(12)
C(6)-C(1)-C(2)	116.08(13)
C(6)-C(1)-S(1)	127.48(11)
C(2)-C(1)-S(1)	116.44(10)
N(1)-C(2)-C(3)	109.47(12)
N(1)-C(2)-C(1)	127.92(13)
C(3)-C(2)-C(1)	122.59(13)
N(2)-C(3)-C(4)	133.10(14)
N(2)-C(3)-C(2)	108.96(13)
C(4)-C(3)-C(2)	117.94(13)
C(5)-C(4)-C(3)	118.89(13)
C(5)-C(4)-N(3)	119.96(14)
C(3)-C(4)-N(3)	121.15(13)
C(4)-C(5)-C(6)	122.30(14)
C(4)-C(5)-H(5)	119.1(11)
C(6)-C(5)-H(5)	118.6(11)
C(1)-C(6)-C(5)	122.17(13)
C(1)-C(6)-H(6)	122.5(11)
C(5)-C(6)-H(6)	115.4(11)
C(12)-C(7)-C(8)	117.23(13)
C(12)-C(7)-S(1)	121.04(11)
C(8)-C(7)-S(1)	121.68(11)
N(4)-C(8)-C(9)	109.09(12)
N(4)-C(8)-C(7)	129.12(13)
C(9)-C(8)-C(7)	121.74(12)
N(5)-C(9)-C(8)	109.25(12)
N(5)-C(9)-C(10)	132.62(13)
C(8)-C(9)-C(10)	118.13(13)
C(11)-C(10)-C(9)	119.30(13)
C(11)-C(10)-N(6)	120.84(13)
C(9)-C(10)-N(6)	119.81(13)
C(10)-C(11)-C(12)	121.85(13)
C(10)-C(11)-H(11)	119.8(10)
C(12)-C(11)-H(11)	118.2(11)
C(7)-C(12)-C(11)	121.62(14)
C(7)-C(12)-H(12)	120.6(10)
C(11)-C(12)-H(12)	117.7(10)

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	20(1)	23(1)	29(1)	-4(1)	1(1)	-1(1)
O(1)	29(1)	34(1)	28(1)	5(1)	2(1)	5(1)
O(2)	57(1)	25(1)	48(1)	6(1)	25(1)	3(1)
O(3)	35(1)	31(1)	54(1)	-16(1)	10(1)	-5(1)
O(4)	22(1)	33(1)	33(1)	6(1)	9(1)	2(1)
O(5)	35(1)	44(1)	34(1)	5(1)	-1(1)	7(1)
O(6)	62(1)	33(1)	31(1)	11(1)	14(1)	12(1)
N(1)	22(1)	30(1)	26(1)	1(1)	4(1)	4(1)
N(2)	30(1)	31(1)	33(1)	4(1)	9(1)	4(1)
N(3)	29(1)	25(1)	43(1)	-5(1)	18(1)	-2(1)
N(4)	21(1)	28(1)	27(1)	3(1)	7(1)	1(1)
N(5)	24(1)	27(1)	27(1)	2(1)	6(1)	4(1)
N(6)	44(1)	22(1)	22(1)	0(1)	6(1)	10(1)
C(1)	17(1)	24(1)	23(1)	-1(1)	6(1)	2(1)
C(2)	17(1)	27(1)	23(1)	-1(1)	7(1)	1(1)
C(3)	22(1)	25(1)	28(1)	3(1)	11(1)	3(1)
C(4)	22(1)	24(1)	32(1)	-3(1)	13(1)	-2(1)
C(5)	18(1)	29(1)	27(1)	-7(1)	7(1)	-2(1)
C(6)	20(1)	26(1)	24(1)	0(1)	5(1)	3(1)
C(7)	21(1)	20(1)	25(1)	-3(1)	5(1)	-1(1)
C(8)	23(1)	19(1)	21(1)	-2(1)	5(1)	2(1)
C(9)	23(1)	19(1)	21(1)	-3(1)	5(1)	4(1)
C(10)	32(1)	18(1)	21(1)	-2(1)	6(1)	4(1)
C(11)	39(1)	19(1)	28(1)	1(1)	13(1)	-2(1)
C(12)	27(1)	23(1)	32(1)	-2(1)	10(1)	-4(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^3$x 10^3) for **3**.

	x	y	z	U_{eq}
H(5)	7135(14)	6133(16)	7090(20)	31(4)
H(6)	7286(13)	8108(16)	7419(19)	28(4)
H(11)	6981(13)	12136(16)	5738(19)	31(4)
H(12)	8385(14)	11274(15)	7580(19)	27(4)

Table S6. Torsion angles [°] for **3**.

N(2)-O(1)-N(1)-C(2)	0.36(15)	S(1)-C(1)-C(6)-C(5)	-178.47(11)
N(1)-O(1)-N(2)-C(3)	0.07(15)	C(4)-C(5)-C(6)-C(1)	0.0(2)
N(5)-O(4)-N(4)-C(8)	0.01(15)	C(1)-S(1)-C(7)-C(12)	-121.06(12)
N(4)-O(4)-N(5)-C(9)	-0.38(15)	C(1)-S(1)-C(7)-C(8)	61.66(12)
C(7)-S(1)-C(1)-C(6)	10.51(14)	O(4)-N(4)-C(8)-C(9)	0.34(14)
C(7)-S(1)-C(1)-C(2)	-169.12(10)	O(4)-N(4)-C(8)-C(7)	-177.27(13)
O(1)-N(1)-C(2)-C(3)	-0.62(14)	C(12)-C(7)-C(8)-N(4)	-178.78(14)
O(1)-N(1)-C(2)-C(1)	178.28(13)	S(1)-C(7)-C(8)-N(4)	-1.4(2)
C(6)-C(1)-C(2)-N(1)	179.08(13)	C(12)-C(7)-C(8)-C(9)	3.88(19)
S(1)-C(1)-C(2)-N(1)	-1.25(19)	S(1)-C(7)-C(8)-C(9)	-178.74(10)
C(6)-C(1)-C(2)-C(3)	-2.15(19)	O(4)-N(5)-C(9)-C(8)	0.57(14)
S(1)-C(1)-C(2)-C(3)	177.52(10)	O(4)-N(5)-C(9)-C(10)	-179.61(14)
O(1)-N(2)-C(3)-C(4)	179.30(14)	N(4)-C(8)-C(9)-N(5)	-0.60(16)
O(1)-N(2)-C(3)-C(2)	-0.45(15)	C(7)-C(8)-C(9)-N(5)	177.21(12)
N(1)-C(2)-C(3)-N(2)	0.71(16)	N(4)-C(8)-C(9)-C(10)	179.55(12)
C(1)-C(2)-C(3)-N(2)	-178.26(12)	C(7)-C(8)-C(9)-C(10)	-2.64(19)
N(1)-C(2)-C(3)-C(4)	-179.08(12)	N(5)-C(9)-C(10)-C(11)	179.80(14)
C(1)-C(2)-C(3)-C(4)	1.95(19)	C(8)-C(9)-C(10)-C(11)	-0.40(19)
N(2)-C(3)-C(4)-C(5)	179.57(15)	N(5)-C(9)-C(10)-N(6)	-2.8(2)
C(2)-C(3)-C(4)-C(5)	-0.70(19)	C(8)-C(9)-C(10)-N(6)	177.03(11)
N(2)-C(3)-C(4)-N(3)	-0.5(2)	O(6)-N(6)-C(10)-C(11)	0.5(2)
C(2)-C(3)-C(4)-N(3)	179.25(12)	O(5)-N(6)-C(10)-C(11)	178.96(13)
O(3)-N(3)-C(4)-C(5)	7.6(2)	O(6)-N(6)-C(10)-C(9)	-176.90(12)
O(2)-N(3)-C(4)-C(5)	-172.89(13)	O(5)-N(6)-C(10)-C(9)	1.57(19)
O(3)-N(3)-C(4)-C(3)	-172.33(13)	C(9)-C(10)-C(11)-C(12)	2.1(2)
O(2)-N(3)-C(4)-C(3)	7.2(2)	N(6)-C(10)-C(11)-C(12)	-175.29(13)
C(3)-C(4)-C(5)-C(6)	-0.2(2)	C(8)-C(7)-C(12)-C(11)	-2.2(2)
N(3)-C(4)-C(5)-C(6)	179.81(13)	S(1)-C(7)-C(12)-C(11)	-179.57(11)
C(2)-C(1)-C(6)-C(5)	1.2(2)	C(10)-C(11)-C(12)-C(7)	-0.8(2)