Electronic Supplementary Material (ESI) for Analyst.

Colorimetric Detection of Hg^{2+} with an Azulene-Containing Chemodosimeter via Dithioacetal Hydrolysis

Carlos M. López-Alled, Lloyd C. Murfin, Gabriele Kociok-Köhn, Tony D. James,* Jannis Wenk* and Simon E. Lewis.*

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General Details

Reactions were carried out under an atmosphere of N_2, through the use of a Schlenk line. Anhydrous dichloromethane was purified through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. Solvent was deoxygenated by channelling a stream of N_2 through the liquid (sparging). "Pet" refers to petroleum ether (boiling point 40-60 °C). Thin layer chromatography (TLC) was carried out on aluminium plates coated with silica gel (Alugram®SIL G/UV 254 nm), and visualisation was achieved by the naked eye (for coloured azulene compounds) and with UV light. Solvents were removed using Büchi rotary evaporators and with high vacuum on a Schlenk line. Flash column chromatography was carried out using Davisil LC 60 Å silica gel (35-70 micron) purchased from Sigma-Aldrich. NMR spectra were run in $CDCl_3$ unless otherwise stated, on an Agilent A500a instrument. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR instrument. Capillary melting points were recorded on a Büchi 535 melting point apparatus and are uncorrected. High resolution mass spectrometry (HRMS) was carried out using a micrOTOF ESI-TOF spectrometer coupled to an Agilent 1200 LC system for autosampling. X-ray crystallography was carried out on a Nonius Kappa CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å).

Synthesis of 2-(azulen-1-yl)-1,3-dithiolane (3)

Under an atmosphere of nitrogen, azulene-1-carbaldehyde **2** (13 mg, 0.083 mmol, 1.0 eq., prepared as described previously)[1] was dissolved in CH_2Cl_2 (10 mL) and combined with 4 Å molecular sieves, into which $BF_3.Et_2O$ (5 µL, 0.04 mmol, 0.5 eq.) and ethane-1,2-dithiol (13 µL, 0.166 mmol, 2.0 eq.) were added. The mixture was stirred for 28 hours at room temperature, after which saturated $Na_2CO_{3(aq)}$ (10 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 20 mL), and the organic phase was dried over $MgSO_4$, filtered, then concentrated under reduced pressure to give a blue solid. The crude was purified *via s*ilica column chromatography (petroleum ether/ ethyl acetate, 80:20, v/v) to give **3** (12.5 mg, 65 %, R_f = 0.60) as a blue solid and unreacted **2** (3.5 mg, 27%) as a red solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 8.48 (d, *J* = 9.8 Hz, 1H), 8.28 (d, *J* = 9.8 Hz, 1H), 8.19 (d, *J* = 4.0 Hz, 1H), 7.59 (t, *J* = 9.8 Hz, 1H), 7.34 (d, *J* = 3.9 Hz, 1H), 7.21 (t, *J* = 9.8 Hz, 1H), 7.16 (t, *J* = 9.8 Hz, 1H), 6.46 (s, 1H), 3.65-3.59 (m, 2H), 3.48-3.41 (m, 2H) ppm; ^{13}C-NMR (126 MHz, $CDCl_3$) δ = 142.07, 137.86, 137.17, 136.87, 135.46, 133.27, 126.32, 123.57, 122.70, 117.32, 49.64, 40.18 ppm; IR: *v* = 2923, 2903, 1574, 1455, 1434, 1412, 1391, 1303, 1273, 1247, 1191, 966, 948, 789, 751, 728, 696, 675 cm^{-1}. HRMS (-ve ESI) calculated mass: $[M-H]^+$ = 233.0453, observed mass: $[M-H]^+$= 233.0457; m. pt. 103.5-106.5 °C.

Limit of Detection

UV-Vis limit of detection (LOD) was calculated using **Equation S1**.[2]

$$LOD = \frac{3\sigma}{m} \quad \text{(S1)}$$

Where ***σ*** is the standard deviation of the blank and ***m*** is the gradient of the line of best fit.

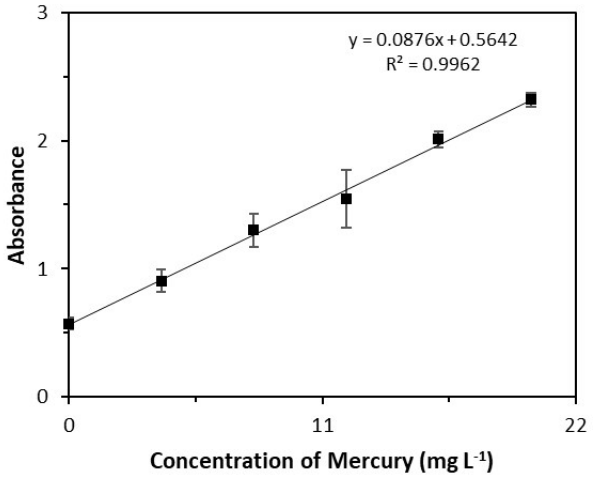


Figure S1. LOD of **3** (100 µM) with NaOH (1 mM) to $Hg(NO_3)_2$ in MeCN/ H_2O (2:8, v/v) determined by UV-vis absorption at λ_{max} = 307 nm, calculated to be 1.65 mg L^{-1} using Equation S1. Displayed errors calculated by standard deviation (n = 3). Incubation time 30 min.

Fluorescence data

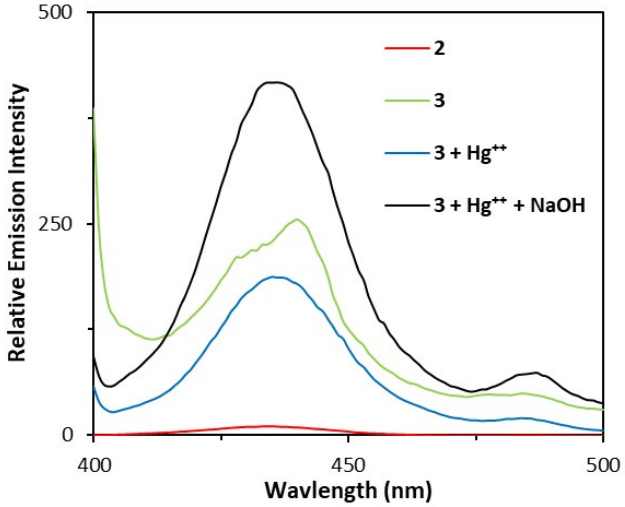
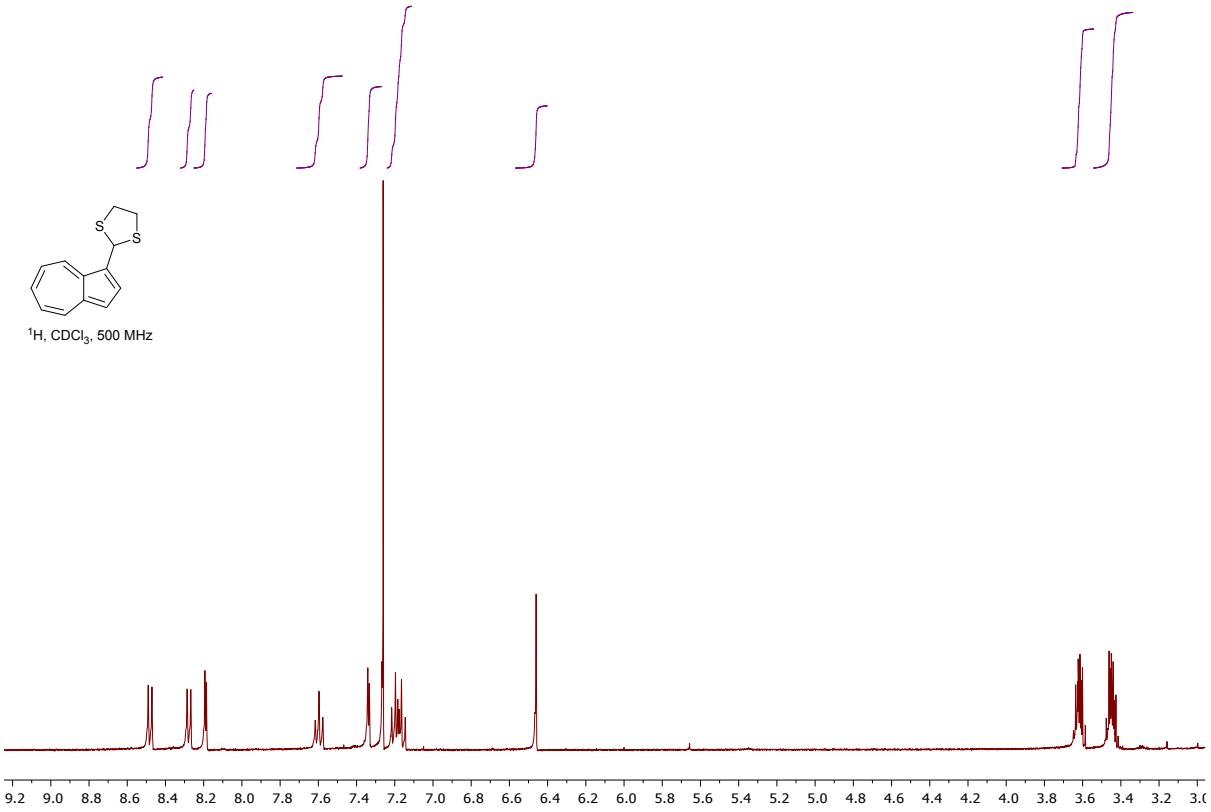
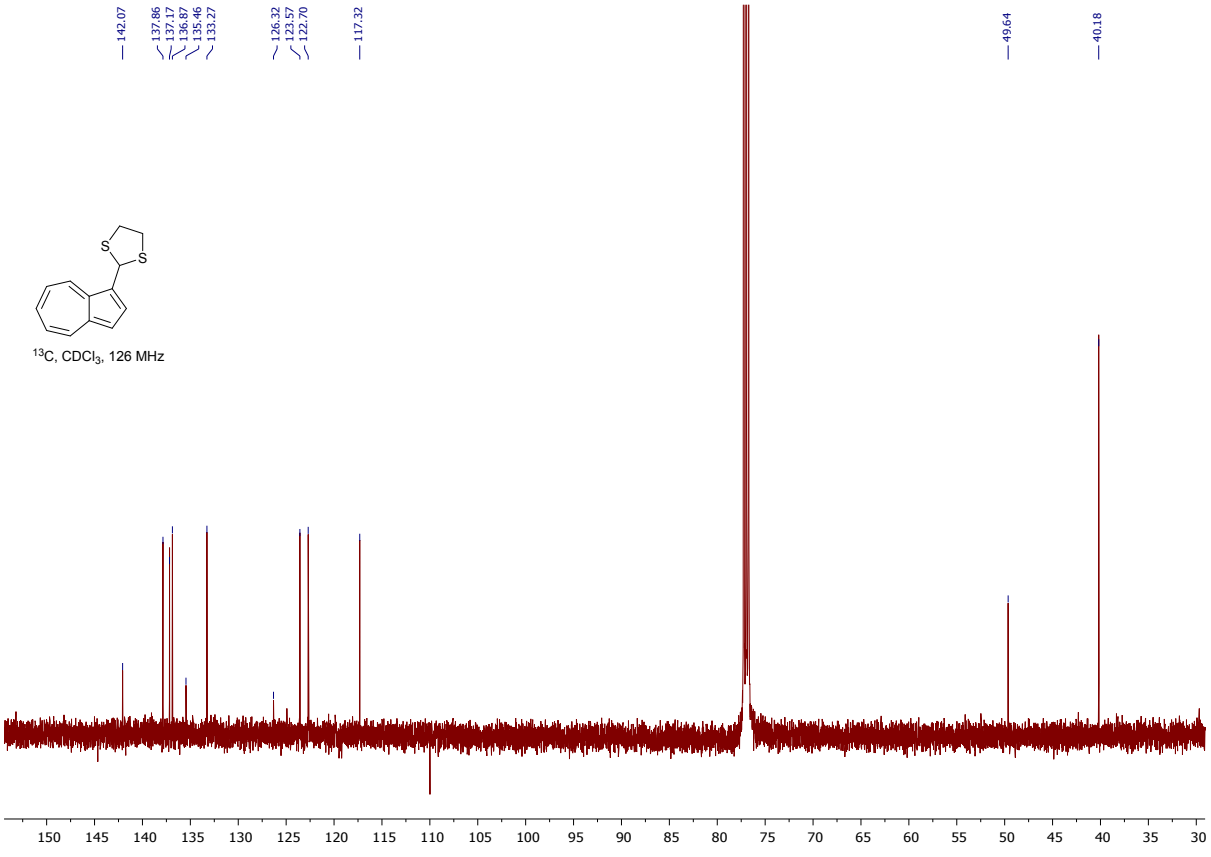
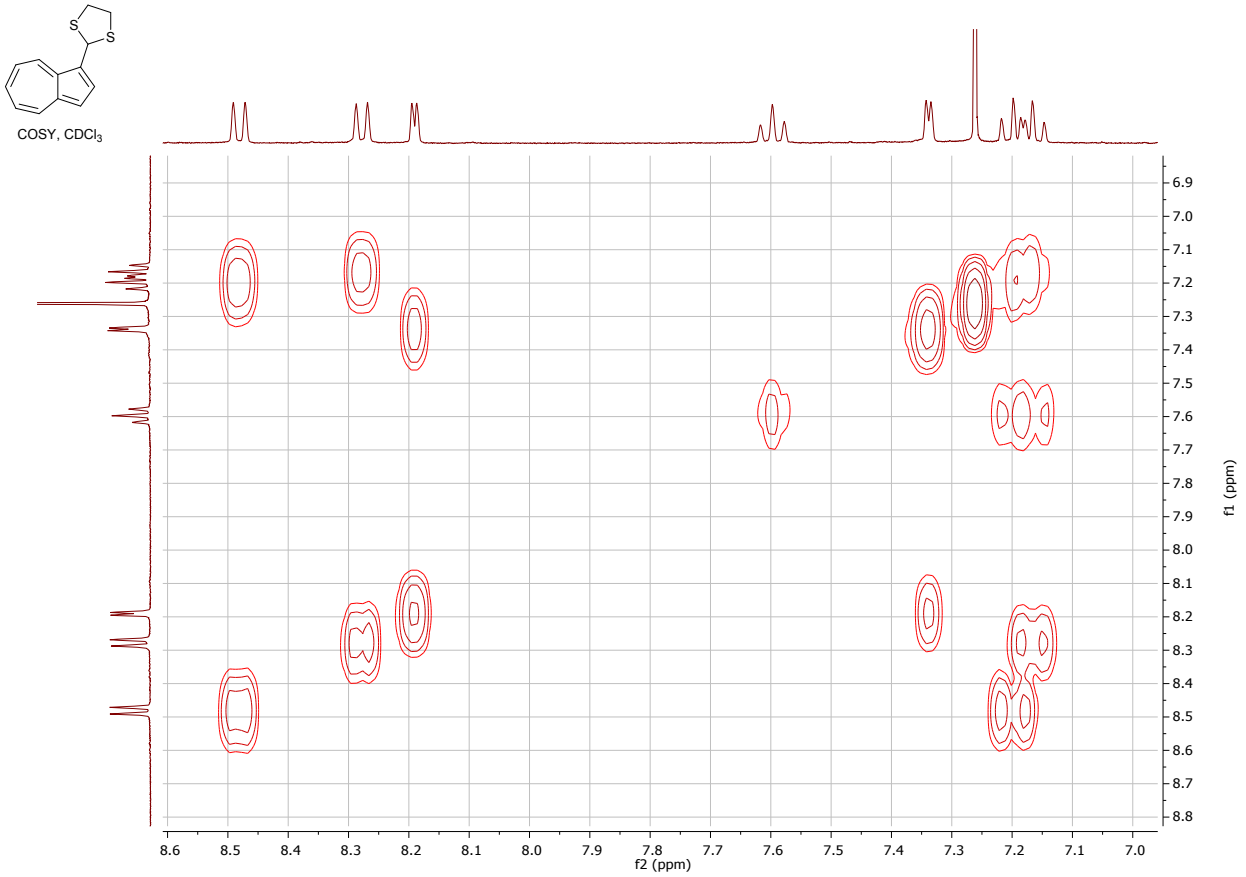


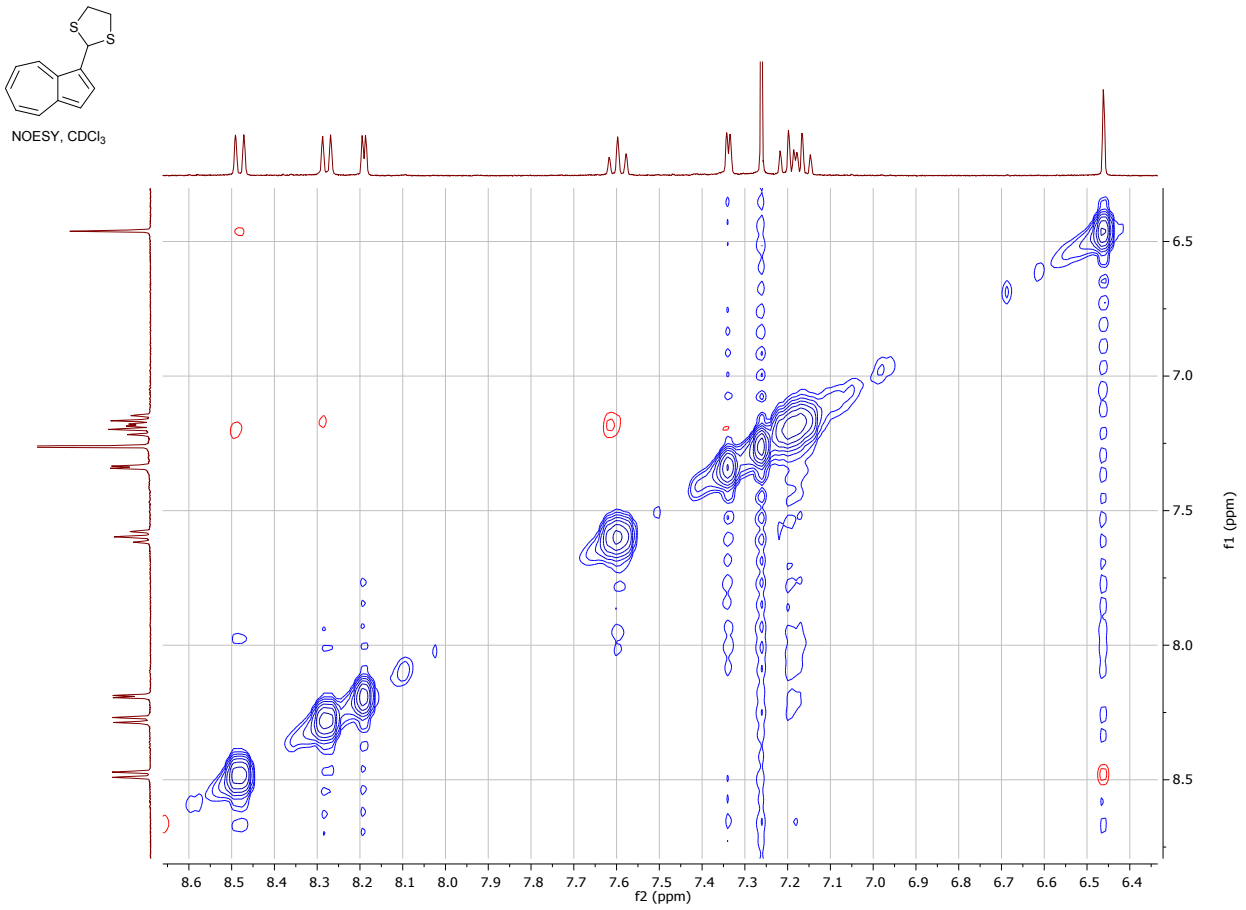
Figure S2. Comparison of fluorescence emission spectra of **2** (500 µM), **3** (500 µM), **3** (500 µM) + $Hg(NO_3)_2$ (500 µM), and **3** (500 µM) + $Hg(NO_3)_2$ (500 µM) + NaOH (10 mM) in MeCN/H_2O (2:8, v/v). Fluorescence intensities were measured with λ_{ex} = 375 nm (ex. slit 20, em. slit 20) nm on an Agilent Technologies Cary Eclipse Fluorescence Spectrometer.

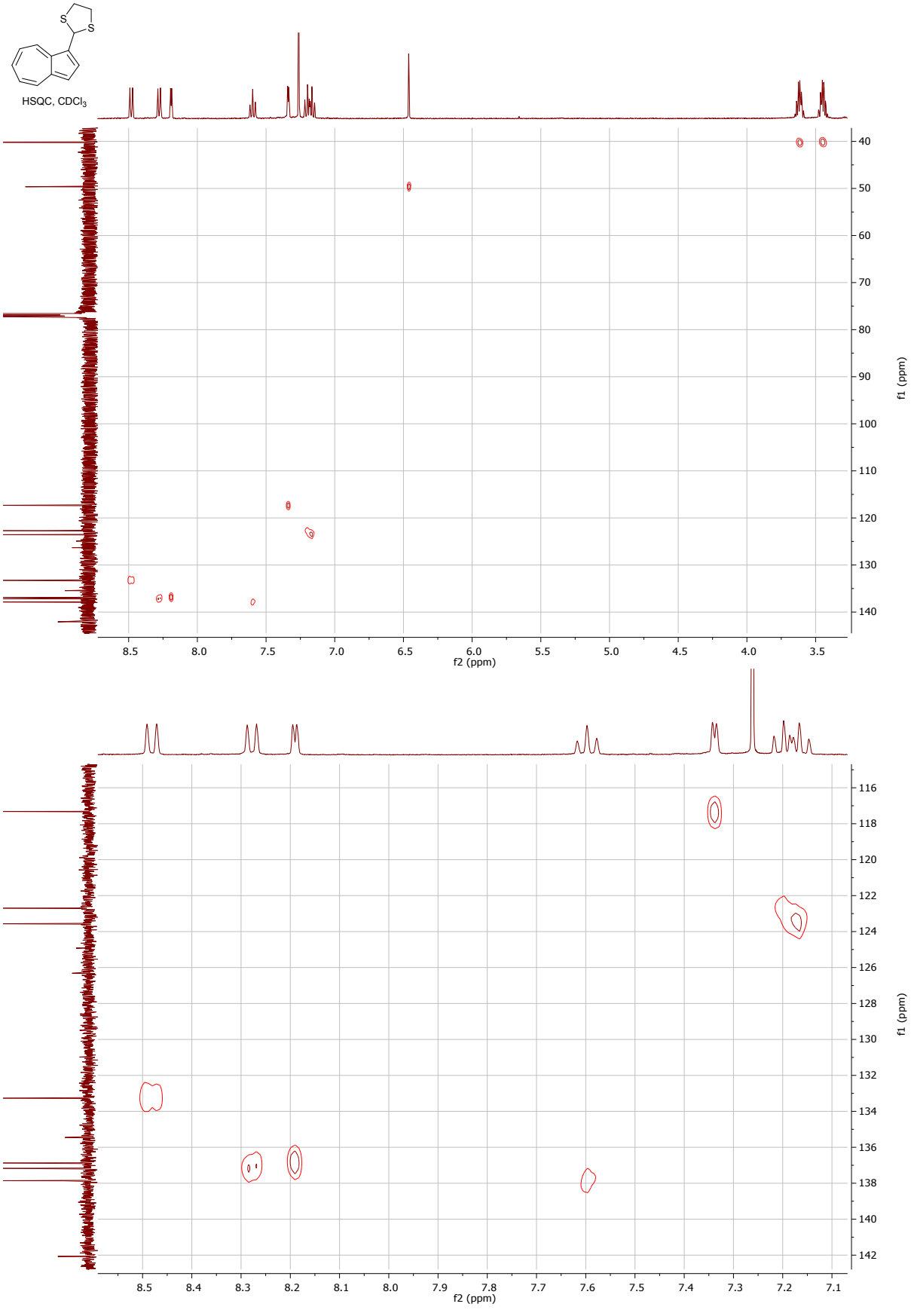
NMR spectra of 3






S
S
COSY, CDCl3
f2 (ppm)
f1 (ppm)


S
S
NOESY, CDCl3
f2 (ppm)
f1 (ppm)


HSQC, CDCl3
f2 (ppm)
f1 (ppm)
f2 (ppm)
f1 (ppm)

X-ray crystallographic data for 3

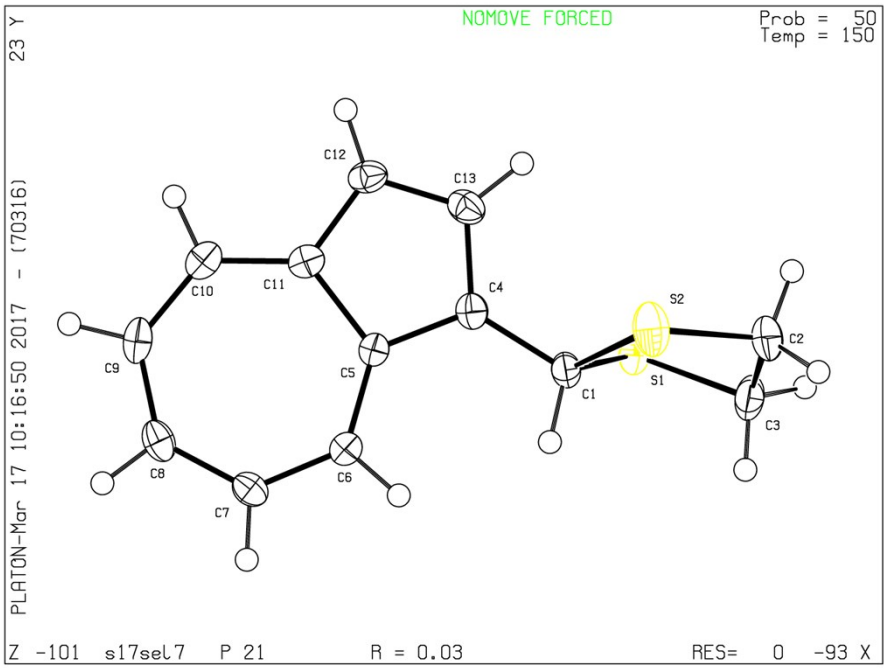


Table S1. Crystal data and structure refinement for 3.

CCDC code	1958284	
Empirical formula	$C_{13}H_{12}S_2$	
Formula weight	232.35	
Temperature	150.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 6.0305(2) Å	α= 90°.
	b = 7.7775(2) Å	β= 101.799(3)°.
	c = 12.0577(4) Å	γ = 90°.
Volume	553.58(3) $Å^3$	
Z	2	
Density (calculated)	1.394 Mg/m^3	
Absorption coefficient	4.016 mm^{-1}	
F(000)	244	
Crystal size	0.300 x 0.100 x 0.030 mm^3	
Theta range for data collection	3.745 to 72.961°.	
Index ranges	-7<=h<=4, -9<=k<=9, -14<=l<=14	
Reflections collected	3962	
Independent reflections	2126 [R(int) = 0.0308]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.64349	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2126 / 1 / 136	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0887	

R indices (all data)	R1 = 0.0344, wR2 = 0.0894
Absolute structure parameter	-0.03(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.221 and -0.197 e.Å^{-3}

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)	1400(1)	3398(1)	8685(1)	23(1)
S(2)	3792(2)	6700(1)	8807(1)	35(1)
C(1)	2026(5)	5182(4)	7823(2)	21(1)
C(2)	3085(6)	5935(5)	10116(3)	32(1)
C(3)	1013(6)	4776(5)	9830(3)	32(1)
C(4)	3204(5)	4575(4)	6920(3)	20(1)
C(5)	2315(5)	4571(4)	5741(2)	17(1)
C(6)	251(5)	5235(4)	5185(3)	19(1)
C(7)	-685(5)	5237(4)	4025(3)	22(1)
C(8)	210(6)	4580(4)	3134(3)	24(1)
C(9)	2247(6)	3757(4)	3148(3)	26(1)
C(10)	3973(5)	3380(5)	4076(3)	23(1)
C(11)	4068(5)	3718(4)	5210(3)	20(1)
C(12)	5878(5)	3286(5)	6099(3)	24(1)
C(13)	5352(5)	3801(4)	7114(3)	24(1)

Table S3. Bond lengths [Å] for **3**.

S(1)-C(3)	1.801(4)
S(1)-C(1)	1.818(3)
S(2)-C(2)	1.818(4)
S(2)-C(1)	1.849(3)
C(1)-C(4)	1.493(4)
C(1)-H(1)	1.0000
C(2)-C(3)	1.522(5)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(13)	1.404(4)
C(4)-C(5)	1.413(4)
C(5)-C(6)	1.387(4)
C(5)-C(11)	1.498(4)
C(6)-C(7)	1.398(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.393(5)
C(7)-H(7)	0.9500
C(8)-C(9)	1.382(5)
C(8)-H(8)	0.9500
C(9)-C(10)	1.395(4)
C(9)-H(9)	0.9500

C(10)-C(11)	1.382(5)
C(10)-H(10)	0.9500
C(11)-C(12)	1.406(4)
C(12)-C(13)	1.385(5)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500

Table S4. Bond angles [°] for **3**.

C(3)-S(1)-C(1)	93.36(17)	C(4)-C(5)-C(11)	106.0(3)
C(2)-S(2)-C(1)	98.12(15)	C(5)-C(6)-C(7)	128.5(3)
C(4)-C(1)-S(1)	111.1(2)	C(5)-C(6)-H(6)	115.7
C(4)-C(1)-S(2)	111.8(2)	C(7)-C(6)-H(6)	115.7
S(1)-C(1)-S(2)	106.30(15)	C(8)-C(7)-C(6)	129.1(3)
C(4)-C(1)-H(1)	109.2	C(8)-C(7)-H(7)	115.5
S(1)-C(1)-H(1)	109.2	C(6)-C(7)-H(7)	115.5
S(2)-C(1)-H(1)	109.2	C(9)-C(8)-C(7)	130.1(3)
C(3)-C(2)-S(2)	108.9(2)	C(9)-C(8)-H(8)	115.0
C(3)-C(2)-H(2A)	109.9	C(7)-C(8)-H(8)	115.0
S(2)-C(2)-H(2A)	109.9	C(8)-C(9)-C(10)	128.5(3)
C(3)-C(2)-H(2B)	109.9	C(8)-C(9)-H(9)	115.8
S(2)-C(2)-H(2B)	109.9	C(10)-C(9)-H(9)	115.8
H(2A)-C(2)-H(2B)	108.3	C(11)-C(10)-C(9)	128.8(3)
C(2)-C(3)-S(1)	107.3(2)	C(11)-C(10)-H(10)	115.6
C(2)-C(3)-H(3A)	110.3	C(9)-C(10)-H(10)	115.6
S(1)-C(3)-H(3A)	110.3	C(10)-C(11)-C(12)	125.3(3)
C(2)-C(3)-H(3B)	110.3	C(10)-C(11)-C(5)	128.1(3)
S(1)-C(3)-H(3B)	110.3	C(12)-C(11)-C(5)	106.6(3)
H(3A)-C(3)-H(3B)	108.5	C(13)-C(12)-C(11)	108.8(3)
C(13)-C(4)-C(5)	108.3(3)	C(13)-C(12)-H(12)	125.6
C(13)-C(4)-C(1)	125.0(3)	C(11)-C(12)-H(12)	125.6
C(5)-C(4)-C(1)	126.6(3)	C(12)-C(13)-C(4)	110.3(3)
C(6)-C(5)-C(4)	127.1(3)	C(12)-C(13)-H(13)	124.8
C(6)-C(5)-C(11)	126.9(3)	C(4)-C(13)-H(13)	124.8

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	29(1)	23(1)	18(1)	0(1)	7(1)	-2(1)
S(2)	51(1)	28(1)	26(1)	-6(1)	6(1)	-14(1)
C(1)	26(1)	22(2)	16(1)	-1(1)	3(1)	1(1)
C(2)	38(2)	39(2)	19(2)	-7(1)	2(1)	0(2)
C(3)	38(2)	40(2)	19(1)	-6(1)	10(1)	-1(2)
C(4)	24(1)	16(1)	19(1)	3(1)	5(1)	-2(1)
C(5)	20(1)	13(1)	18(1)	1(1)	6(1)	-3(1)
C(6)	21(1)	16(1)	21(1)	0(1)	6(1)	-1(1)
C(7)	21(1)	20(1)	22(2)	2(1)	1(1)	-2(1)

C(8)	31(2)	21(2)	19(1)	0(1)	0(1)	-5(1)
C(9)	39(2)	22(2)	18(1)	-3(1)	11(1)	-5(1)
C(10)	28(1)	17(1)	27(1)	1(1)	12(1)	-1(1)
C(11)	20(1)	15(2)	25(1)	2(1)	7(1)	-2(1)
C(12)	20(1)	23(2)	29(2)	5(1)	9(1)	1(1)
C(13)	22(1)	27(2)	24(2)	6(1)	2(1)	0(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3**.

	x	y	z	U(eq)
H(1)	578	5762	7462	25
H(2A)	4378	5287	10562	39
H(2B)	2762	6923	10576	39
H(3A)	-376	5475	9599	38
H(3B)	865	4079	10499	38
H(6)	-643	5759	5655	23
H(7)	-2134	5758	3813	26
H(8)	-726	4719	2404	29
H(9)	2505	3401	2431	31
H(10)	5258	2814	3906	28
H(12)	7239	2731	6017	28
H(13)	6308	3651	7838	29

Table S7. Torsion angles [°] for **3**.

C(3)-S(1)-C(1)-C(4)	161.3(2)
C(3)-S(1)-C(1)-S(2)	39.38(17)
C(2)-S(2)-C(1)-C(4)	-140.4(2)
C(2)-S(2)-C(1)-S(1)	-18.97(19)
C(1)-S(2)-C(2)-C(3)	-14.1(3)
S(2)-C(2)-C(3)-S(1)	43.2(3)
C(1)-S(1)-C(3)-C(2)	-51.2(3)
S(1)-C(1)-C(4)-C(13)	-63.8(4)
S(2)-C(1)-C(4)-C(13)	54.9(4)
S(1)-C(1)-C(4)-C(5)	111.7(3)
S(2)-C(1)-C(4)-C(5)	-129.6(3)
C(13)-C(4)-C(5)-C(6)	-178.9(3)
C(1)-C(4)-C(5)-C(6)	4.9(5)
C(13)-C(4)-C(5)-C(11)	0.5(3)
C(1)-C(4)-C(5)-C(11)	-175.7(3)
C(4)-C(5)-C(6)-C(7)	-179.3(3)
C(11)-C(5)-C(6)-C(7)	1.4(5)
C(5)-C(6)-C(7)-C(8)	-0.2(6)
C(6)-C(7)-C(8)-C(9)	-0.1(6)
C(7)-C(8)-C(9)-C(10)	-0.7(6)
C(8)-C(9)-C(10)-C(11)	0.7(6)

C(9)-C(10)-C(11)-C(12)	179.7(3)
C(9)-C(10)-C(11)-C(5)	0.6(6)
C(6)-C(5)-C(11)-C(10)	-1.8(5)
C(4)-C(5)-C(11)-C(10)	178.8(3)
C(6)-C(5)-C(11)-C(12)	179.0(3)
C(4)-C(5)-C(11)-C(12)	-0.4(3)
C(10)-C(11)-C(12)-C(13)	-179.0(3)
C(5)-C(11)-C(12)-C(13)	0.2(4)
C(11)-C(12)-C(13)-C(4)	0.1(4)
C(5)-C(4)-C(13)-C(12)	-0.3(4)
C(1)-C(4)-C(13)-C(12)	175.9(3)

References

[1] (a) K. Hafner and C. Bernhard, *Justus Liebigs Ann. Chem*., 1959, **625**, 108. (b) W. Treibs, H.-J. Neupert and J. Hiebsch, *Chem. Ber.*, 1959, **92**, 141.

[2] Analytical Methods Committee, *Analyst*, 1987, **112**, 199.