Supplementary Material

Synthesis, solid-state structure, and electrochemical properties of thienodipyrimidine-2,4,5,7-tetra(thi)ones

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1. General Methods and Instrumentation

UV-Vis spectroscopy. Solution phase absorption spectra were recorded on an Agilent Cary 5000 UV-Vis-NIR spectrophotometer, using a quartz cell with a path length of 1 cm.

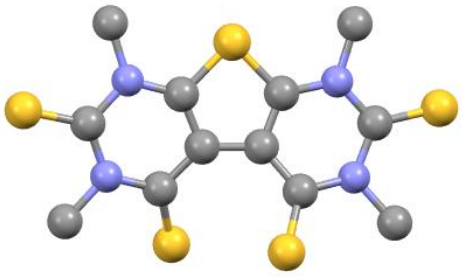
Cyclic voltammetry. Cyclic voltammetry was performed in CH_2Cl_2 under nitrogen with a three-electrode PGSTAT204 potentiostat from Metrohm Autolab. Glassy carbon disk was used as the working electrode (diameter = 5 mm), platinum wire as the counter electrode, and a silver wire as the pseudo reference electrode. An analyte of concentration of 1 mM was used with $n Bu_4NPF_6$ (100 mM) as the supporting electrolyte. Redox potentials relative to saturated calomel electrode (SCE) are reported, using ferrocene/ferrocenium ($E_{1/2}$ = 0.46 V) as an internal standard.[1]

Single-crystal X-ray diffraction. Single crystals were grown; crystallization details for each sample can be found in the synthetic details. X-ray diffraction data were collected on a Rigaku Oxford Diffraction SuperNova dual source diffractometer with a mirror monochromator using Mo or Cu Kα radiation. The crystal was kept at 296(3) K during data collection. The structures were solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using least squares minimization using Olex2.[4]

Irradiation Details. Photocyclization reactions were irradiated with EvoluChem 6200K (λ_{irrad} = 415–725 nm; white light) or EvoluChem 365 PF (λ_{rrad} = 355–385 nm; ultraviolet) LEDs.

2. Single-Crystal Structural Characterization

Table S1. Crystal data and structure refinement for **1a-S$_4$**.[a]

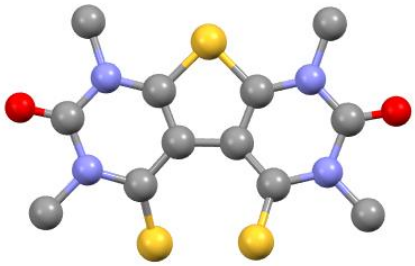


Empirical formula	$C_{12}H_{12}N_4S_5$	a	8.5159(5) Å	α	90 °
Formula weight	372.56	b	11.3808(8) Å	β	96.173(7) °
Temperature	296(2) K	c	16.2386(12) Å	γ	90 °
Crystal system	monoclinic				
Space group	Pc				

Volume	1564.68(19) Å^3
Z	4
ρ_{calc}	1.582 g cm^{-3}
μ	0.737 mm^{-1}
F(000)	768.0
Crystal size	0.216 mm × 0.179 mm × 0.038 mm
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection	6.588 ° to 59.164 °
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -22 ≤ l ≤ 22
Reflections collected	14228
Independent reflections	6668 [R_{int} = 0.0615, R_{sigma} = 0.1782]
Data/restraints/parameters	6668/2/387
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0661, wR_2 = 0.1646
Final R indexes [all data]	R_1 = 0.1121, wR_2 = 0.1729
Largest diff. peak/hole	0.78/-1.30 e Å^{-3}
CCDC Number	2244092

[a] Hydrogen atoms and one **1a-S$_4$** molecule omitted for clarity.

Table S2. Crystal data and structure refinement for **2a-O_2S_2**.[a]

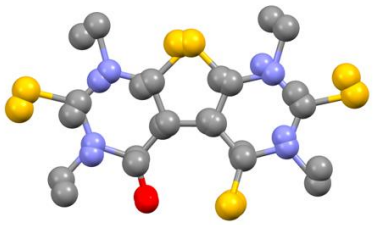


Empirical formula	$C_{12}H_{12}N_4O_2S_3$	a	10.8682(5) Å	α	90 °
Formula weight	340.453	b	8.5926(4) Å	β	90 °
Temperature	298 K	c	15.0316(10) Å	γ	90 °
Crystal system	orthorhombic				
Space group	$Pca2_1$				

Volume	1403.74(13) $Å^3$
Z	4
ρ_{calc}	1.611 g cm^{-3}
μ	0.537 mm^{-1}
F(000)	705.7
Crystal size	0.35 mm × 0.26 mm × 0.16 mm
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection	6.62 º to 59.34 º
Index ranges	0 ≤ h ≤ 15, 0 ≤ k ≤ 11, -20 ≤ l ≤ 15
Reflections collected	13559
Independent reflections	3041 [R_{int} = 0.0460, R_{sigma} = 0.0339]
Data/restraints/parameters	3041/1/230
Goodness-of-fit on F2	1.121
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1005
Final R indexes [all data]	R_1 = 0.0652, wR_2 = 0.1192
Largest diff. peak/hole	0.25/-0.34 e $Å^{-3}$
CCDC Number	2244099

[a] Hydrogen atoms are omitted for clarity.

Table S3. Crystal data and structure refinement for **3a-OS$_3$**.[a]

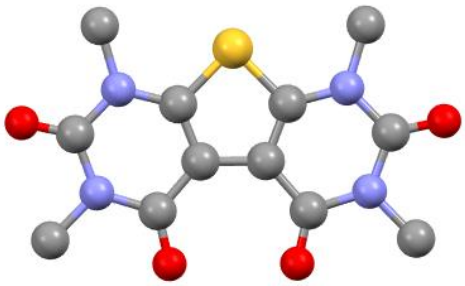


Empirical formula	$C_{12}H_{12}N_4OS_4$	a	9.5240(4) Å	α	90 °
Formula weight	356.50	b	8.4921(3) Å	β	98.988(4) °
Temperature	293(2) K	c	18.4678(8) Å	γ	90 °
Crystal system	monoclinic				
Space group	$P2_1/n$				

Volume	1475.31(10) Å^3
Z	4
ρ_{calc}	1.605 g cm^{-3}
μ	5.955 mm^{-1}
F(000)	736.0
Crystal size	0.16 mm × 0.07 mm × 0.04 mm
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection	9.698 ° to 144.82 °
Index ranges	-11 ≤ h ≤ 11, -10 ≤ k ≤ 10, -21 ≤ l ≤ 22
Reflections collected	5911
Independent reflections	2869 [R_{int} = 0.0283, R_{sigma} = 0.0366]
Data/restraints/parameters	2869/313/274
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0709, wR_2 = 0.2023
Final R indexes [all data]	R_1 = 0.0892, wR_2 = 0.2227
Largest diff. peak/hole	0.87/-0.77 e Å^{-3}
CCDC Number	2251143

[a] Hydrogen atoms are omitted for clarity.

Table S4. Crystal data and structure refinement for **4a-O$_4$**.[a]

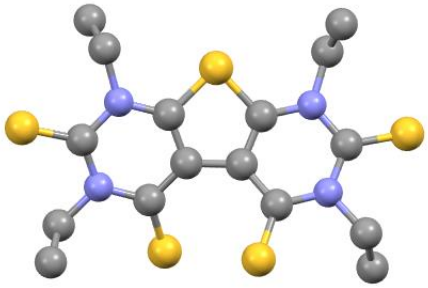


Empirical formula	$C_{12}H_{12}N_4O_4S$	a	6.7836(2) Å	α	90 °
Formula weight	308.32	b	8.4663(2) Å	β	98.143(3) °
Temperature	296(2) K	c	21.9949(6) Å	γ	90 °
Crystal system	monoclinic				
Space group	$P2_1/n$				

Volume	1250.47(6) Å^3
Z	4
ρ_{calc}	1.638 g cm^{-3}
μ	2.548 mm^{-1}
F(000)	640.0
Crystal size	0.22 mm × 0.06 mm × 0.05 mm
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection	8.122 ° to 145.972 °
Index ranges	-8 ≤ h ≤ 7, -10 ≤ k ≤ 10, -24 ≤ l ≤ 27
Reflections collected	8484
Independent reflections	2481 [R_{int} = 0.0299, R_{sigma} = 0.0248]
Data/restraints/parameters	2481/1107/384
Goodness-of-fit on F^2	1.105
Final R indexes [I>=2σ (I)]	R_1 = 0.0530, wR_2 = 0.1447
Final R indexes [all data]	R_1 = 0.0589, wR_2 = 0.1492
Largest diff. peak/hole	0.44/-0.31 e Å^{-3}
CCDC Number	2247147

[a] Hydrogen atoms and one **4a-O$_4$** unit are omitted for clarity.

Table S5. Crystal data and structure refinement for **1b-S_4**.[a]

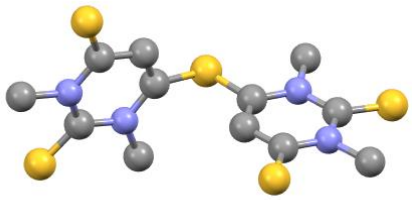


Empirical formula	$C_{16}H_{20}N_4S_5$	a	11.8534(2) Å	α	90 °
Formula weight	428.66	b	17.1645(3) Å	β	90 °
Temperature	293(2) K	c	18.8475(3) Å	γ	90 °
Crystal system	orthorhombic				
Space group	Pbca				

Volume	3834.67(11) $Å^3$
Z	8
ρ_{calc}	1.485 g cm^{-3}
μ	5.631 mm^{-1}
F(000)	1792.0
Crystal size	0.14 mm × 0.11 mm × 0.04 mm
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection	9.384 ° to 145.956 °
Index ranges	-14 ≤ h ≤ 12, -21 ≤ k ≤ 19, -23 ≤ l ≤ 18
Reflections collected	26895
Independent reflections	3813 [R_{int} = 0.0470, R_{sigma} = 0.0246]
Data/restraints/parameters	3813/0/230
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.1034
Final R indexes [all data]	R_1 = 0.0482, wR_2 = 0.1149
Largest diff. peak/hole	0.37/-0.29 e $Å^{-3}$
CCDC Number	2246037

[a] Hydrogen atoms are omitted for clarity.

Table S6. Crystal data and structure refinement for **5**.[a]

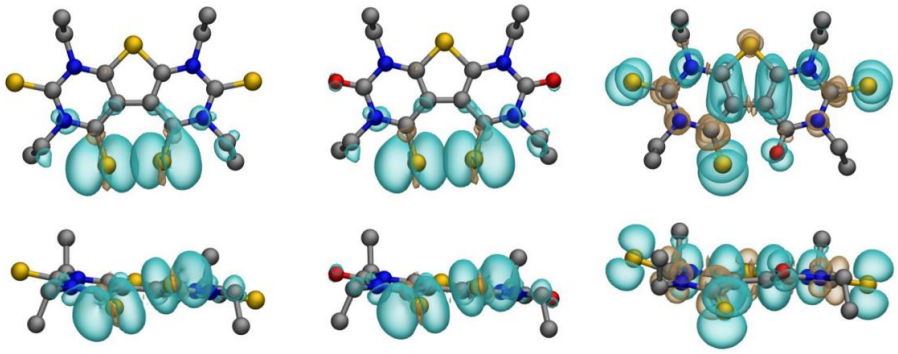


Empirical formula	$C_{12}H_{12}N_4O_3S_3$	a	5.6075(4) Å	α	113.098(8) °
Formula weight	374.56	b	11.9838(10) Å	β	99.865(6) °
Temperature	296 K	c	13.2276(11) Å	γ	93.093(6) °
Crystal system	triclinic				
Space group	P $\bar{1}$				

Volume	798.30(12)
Z	2
ρ_{calc}	1.558 g cm^{-3}
μ	0.723 mm^{-1}
F(000)	368.9
Crystal size	0.56 mm× 0.12 mm × 0.04 mm
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection	6.84 º to 59.14 º
Index ranges	-7 ≤ h ≤ 7, -16 ≤ k ≤ 15, -14 ≤ l ≤ 18
Reflections collected	6731
Independent reflections	3709 [R_{int} = 0.0246, R_{sigma} = 0.0481]
Data/restraints/parameters	3709/0/194
Goodness-of-fit on F2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0477, wR_2 = 0.1057
Final R indexes [all data]	R_1 = 0.0759, wR_2 = 0.1238
Largest diff. peak/hole	0.43/-0.40 e Å^{-3}
CCDC Number	2244101

[a] Hydrogen atoms are omitted for clarity.

3. Electron Spin Density Plots



1b-$S_4^{\bullet+}$ **2b-$O_2S_2^{\bullet+}$** **3b-$OS_3^{\bullet+}$**

Figure S1. Electron spin density distributions (isosurface value 0.001 a.u.) for radical cations **1b-$S_4^{\bullet+}$**, **2b-$O_2S_2^{\bullet+}$**, and **3b-$OS_3^{\bullet+}$** (top view above and side view below). Atoms color code: C grey, N blue, O red, S yellow; geometry optimized at the UωB97X-D/6-31G(d,p) level.

4. Cartesian Coordinates for Optimized Geometries

1a-S_4

C	3.49020	0.38533	-0.06100
N	2.99912	-0.88500	-0.02451
C	1.64075	-1.20565	0.32301
C	0.72568	-0.17050	0.01002
C	1.22550	1.12299	-0.07051
N	2.57775	1.40663	0.05451
S	0.00000	2.33743	0.00000
C	-1.22550	1.12299	0.07052
C	-0.72568	-0.17050	-0.01001
C	-1.64075	-1.20565	-0.32301
N	-2.99912	-0.88499	0.02451
C	-3.49020	0.38533	0.06100
N	-2.57775	1.40663	-0.05451
C	-2.98906	2.80549	-0.09636
C	-3.92578	-1.99815	0.23281
C	2.98906	2.80549	0.09635
C	3.92578	-1.99815	-0.23280
S	1.27231	-2.62361	1.15259
S	-1.27231	-2.62361	-1.15259
S	-5.14643	0.70932	0.23352
S	5.14643	0.70932	-0.23352
H	-3.99832	2.86838	-0.49239
H	-2.31052	3.35025	-0.75660
H	-2.96776	3.24538	0.90570
H	-3.33741	-2.88739	0.44374
H	-4.53590	-2.17387	-0.65691
H	-4.57989	-1.76203	1.07065
H	2.31053	3.35025	0.75661
H	2.96774	3.24539	-0.90570
H	3.99833	2.86838	0.49237
H	4.57989	-1.76203	-1.07065
H	3.33741	-2.88739	-0.44374
H	4.53590	-2.17387	0.65691

[1a-S_4]$^{+1}$

C	-3.49386	0.42363	0.06219
N	-2.99113	-0.88057	0.00990
C	-1.66442	-1.19916	-0.12720
C	-0.72614	-0.14163	0.01849
C	-1.22694	1.14284	0.05815
N	-2.54939	1.43395	0.06366
S	0.00000	2.37652	-0.00000
C	1.22694	1.14284	-0.05815
C	0.72614	-0.14163	-0.01849
C	1.66442	-1.19916	0.12720
N	2.99113	-0.88057	-0.00990
C	3.49386	0.42363	-0.06219
N	2.54939	1.43395	-0.06366
C	3.01984	2.82683	-0.06714
C	3.98178	-1.97111	-0.00995
C	-3.01984	2.82683	0.06714
C	-3.98179	-1.97111	0.00995
S	-1.21261	-2.77471	-0.55617
S	1.21261	-2.77471	0.55617
S	5.11535	0.76293	-0.08143
S	-5.11535	0.76293	0.08143
H	3.62228	3.00595	0.82259
H	2.16637	3.50104	-0.06972
H	3.62130	3.00130	-0.95826
H	3.50079	-2.8738	-0.37736
H	4.35951	-2.12996	1.00166
H	4.80121	-1.69002	-0.66454
H	-2.16637	3.5010	0.06971
H	-3.62129	3.00131	0.95826
H	-3.62229	3.00595	-0.82259
H	-4.80121	-1.69003	0.66454
H	-3.50079	-2.87383	0.37735
H	-4.35951	-2.12996	-1.00166

2a-O_2S_2

C	1.22009	1.16933	0.09117
N	2.54478	1.47729	0.15528
C	3.48667	0.45927	0.21970
N	2.99866	-0.83108	0.00040
C	1.68191	-1.14454	-0.32060
C	0.72693	-0.10880	0.00765
S	-0.00000	2.41314	-0.00000
C	-1.22009	1.16933	-0.09117
C	-0.72693	-0.10880	-0.00765
N	-2.54478	1.47729	-0.15528
C	-3.48667	0.45927	-0.21970
N	-2.99866.	-0.83108	-0.00040
C	-1.68191.	-1.14454	0.32060
S	-1.30121	-2.54772	1.12479
O	-4.66673	0.69033	-0.41047
O	4.66673	0.69033	0.41047
S	1.30121	-2.54772	-1.12479
C	2.99431	2.86491	0.23749
C	4.02280	-1.87500	-0.08621
C	-4.02280	-1.87501	0.08622
C	-2.99431	2.86491	-0.23749
H	4.07858	2.85697	0.30199
H	2.58158	3.34119	1.13008
H	4.89913	-1.52700	0.45233
H	4.27986	-2.07110	-1.12942
H	-4.89913	-1.52700	-0.45232
H	-4.27985	-2.07110	1.12942
H	-2.68429	3.40917	0.65768
H	-4.07858	2.85696	-0.30199
H	2.68429	3.40917	-0.65768
H	3.63147	-2.78784	0.35947
H	-3.63147	-2.78784	-0.35947
H	-2.58159	3.34119	-1.13008

[2a-O_2S_2]$^{+1}$

C	1.22044	1.20783	0.05454
N	2.53478	1.52584	0.08113
C	3.49972	0.52862	0.08008
N	3.00618	-0.78816	-0.01169
C	1.68643	-1.13167	-0.08874
C	0.72907	-0.08115	0.01882
S	-0.00000	2.44473	-0.00000
C	-1.22044	1.20783	-0.05454
C	-0.72907	-0.08115	-0.01883
N	-2.53478	1.52584	-0.08113
C	-3.49972	0.52862	-0.08008
N	-3.00618	-0.78816	0.01169
C	-1.68643	-1.13167	0.08874
S	-1.29470	-2.75508	0.37192
O	-4.68341	0.77320	-0.13704
O	4.68341	0.77320	0.13704
S	1.29470	-2.75508	-0.37192
C	2.97266	2.92503	0.11069
C	4.03297	-1.83901	-0.07566
C	-4.03297	-1.83901	0.07566
C	-2.97266	2.92503	-0.11069
H	4.05771	2.93131	0.14925
H	2.57343	3.41595	1.00033
H	4.99501	-1.37433	0.11218
H	4.02772	-2.29883	-1.06536
H	-4.99501	-1.37433	-0.11218
H	-4.02771	-2.29884	1.06536
H	-2.63565	3.43413	0.79481
H	-4.05771	2.93131	-0.14924
H	2.63565	3.43413	-0.79481
H	3.82131	-2.59219	0.68380
H	-3.82131	-2.59219	-0.68380
H	-2.57343	3.41595	-1.00033

3a-OS_3

C	-3.42200	-0.35370	-0.11812
N	-2.96069	0.94957	-0.08835
C	-1.64539	1.32032	0.22922
C	-0.68390	0.26735	0.01633
C	-1.15343	-1.02034	0.05168
N	-2.48252	-1.33873	0.08655
S	0.10466	-2.22557	0.09599
C	1.30071	-0.95665	0.00996
C	0.76000	0.29793	-0.04972
C	1.65586	1.38713	-0.39564
N	3.03042	1.07542	-0.19620
C	3.54851	-0.18285	-0.02120
N	2.64281	-1.22419	-0.02746
C	3.10021	-2.61469	0.03605
C	3.95965	2.20463	-0.29236

C	-2.89743	-2.73808	0.21569
C	-3.95345	2.01829	-0.25344
S	-1.27665	2.80118	0.87065
O	1.32677	2.46973	-0.83368
S	5.19298	-0.45516	0.16762
S	-5.03666	-0.73990	-0.34603
H	4.06512	-2.69044	-0.45704
H	2.38416	-3.24587	-0.49157
H	3.19835	-2.93821	1.07447
H	3.36379	3.10644	-0.39530
H	4.60875	2.08389	-1.16101
H	4.57341	2.24485	0.60695
H	-2.11467	-3.29071	0.73476
H	-3.08080	-3.17414	-0.76808
H	-3.81005	-2.78298	0.80474
H	-4.64304	1.72837	-1.04198
H	-3.42630	2.93100	-0.51540
H	-4.50832	2.17068	0.67476

[3a-OS_3]$^{+1}$

C	-3.40430	-0.32594	-0.13558
N	-2.93594	0.96752	-0.09830
C	-1.63034	1.32674	0.25973
C	-0.65979	0.26714	0.05605
C	-1.14870	-1.05588	0.10117
N	-2.44842	-1.34258	0.10622
S	0.10237	-2.26641	0.13864
C	1.29255	-0.99192	0.00092
C	0.73732	0.29084	-0.05895
C	1.63181	1.40179	-0.39488
N	3.00164	1.09514	-0.24038
C	3.52632	-0.15662	-0.04364
N	2.60609	-1.23049	-0.03946
C	3.11578	-2.61082	0.01311
C	3.93548	2.22177	-0.36727
C	-2.89813	-2.73878	0.23463
C	-3.91987	2.04246	-0.29545
S	-1.25252	2.76744	0.94840
O	1.26536	2.48353	-0.79063
S	5.13928	-0.44006	0.16430
S	-4.98002	-0.72571	-0.41564
H	3.97384	-2.69397	-0.64792
H	2.33863	-3.28845	-0.33685
H	3.40916	-2.85820	1.03341
H	3.34505	3.11754	-0.53178
H	4.60449	2.05117	-1.21138
H	4.52141	2.30906	0.54735
H	-2.12716	-3.30873	0.75069
H	-3.09091	-3.15642	-0.75385
H	-3.80798	-2.75962	0.82769
H	-4.55604	1.77578	-1.13608
H	-3.38176	2.96202	-0.50428
H	-4.52980	2.16567	0.60150

4a-O_4

C	-1.22726	0.88920	0.00833
N	-2.55589	1.21563	0.01284
C	-3.52041	0.21651	0.01431
N	-3.03365	-1.08214	-0.00200
C	-1.68301	-1.48635	-0.03510
C	-0.72589	-0.38474	0.00172
S	0.00000	2.12531	-0.00000
C	1.22726	0.88920	-0.00833
C	0.72589	-0.38474	-0.00172
N	2.55589	1.21563	-0.01284
C	3.52041	0.21651	-0.01431
N	3.03365	-1.08214	0.00200
C	1.68300	-1.48635	0.03510
O	1.42586	-2.67370	0.09320
O	4.71187	0.47950	-0.02661
C	2.98201	2.61116	-0.02091
C	4.01309	-2.16854	0.01831
C	-2.98201	2.61116	0.02091
C	-4.01309	-2.16854	-0.01830
O	-4.71187	0.47950	0.02661
O	-1.42586	-2.67370	-0.09320
H	2.62017	3.12106	0.87577
H	2.60585	3.11485	-0.91522
H	4.06825	2.62305	-0.02978
H	5.00405	-1.73130	-0.05593
H	3.82826	-2.83757	-0.82260
H	3.91928	-2.73695	0.94487
H	-2.62017	3.12107	-0.87577
H	-2.60585	3.11485	0.91522
H	-4.06825	2.62305	0.02978
H	-5.00406	-1.73130	0.05593
H	-3.82826	-2.83757	0.82261
H	-3.91928	-2.73695	-0.94487

[4a-O_4]$^{+1}$

C	-1.21760	0.93198	0.00172
N	-2.51396	1.22260	0.00977
C	-3.49655	0.18301	0.01863
N	-3.01003	-1.10494	-0.00022
C	-1.66361	-1.49779	-0.05060
C	-0.69956	-0.38014	-0.00497
S	0.00000	2.17684	0.00000
C	1.21760	0.93198	-0.00172
C	0.69956	-0.38014	0.00497
N	2.51396	1.22260	-0.00977
C	3.49655	0.18301	-0.01863
N	3.01003	-1.10494	0.00022
C	1.66361	-1.49779	0.05060
O	1.37627	-2.66843	0.12932
O	4.66845	0.47044	-0.03925
C	2.98132	2.61430	-0.01711
C	3.98857	-2.20045	0.01465
C	2.98132	2.61430	0.01711
C	-3.98857	-2.20045	-0.01465
O	-4.66845	0.47044	0.03925
O	-1.37627	-2.66843	-0.12932
H	2.62517	3.12101	0.88198
H	2.61561	3.11498	-0.91585
H	4.06675	2.59869	-0.02318
H	4.97969	-1.77274	-0.09790
H	3.77232	-2.88087	-0.80811
H	3.91485	-2.74091	0.95851
H	-2.62517	3.12101	-0.88198
H	-2.61561	3.11498	0.91585
H	-4.06675	2.59869	0.02318
H	-4.97969	-1.77274	0.09790
H	-3.77232	-2.88087	0.80811
H	-3.91485	-2.74091	-0.95851

1b-S_4

C	-1.21349	1.02754	-0.16050
N	-2.54677	1.31372	-0.19042
C	-3.46196	0.31491	0.07337
N	-2.97551	-0.97958	0.04626
C	-1.63519	-1.32270	-0.17788
C	-0.70860	-0.23478	0.01317
S	0.01118	2.24537	-0.42608
C	1.23959	1.01827	-0.23743
C	0.73943	-0.22201	0.06550
N	2.56932	1.29644	-0.33419
C	3.49173	0.27672	-0.19866
N	3.01140	-0.91645	0.30475
C	1.66799	-1.16523	0.63171
S	1.20114	-2.37328	1.66814
S	5.10420	0.51938	-0.59760
S	-5.07296	0.68044	0.36414
S	-1.17668	-2.81882	-0.72685
C	-2.97706	2.71684	-0.36364
C	-2.98811	3.49360	0.94571
C	-3.95623	-2.08444	0.16672
C	-4.63625	-2.41784	-1.15364
C	3.98159	-2.00795	0.55261
C	4.03745	-2.96240	-0.63094
C	3.00309	2.68373	-0.59814
C	3.29944	3.43098	0.69334
H	-3.96848	2.68996	-0.81061
H	-2.29990	3.16512	-1.09564
H	-3.70277	3.05254	1.64266
H	-3.28850	4.52442	0.74450
H	-2.00136	3.51251	1.41573
H	-4.68326	-1.77468	0.91513
H	-3.40089	-2.94181	0.54212
H	-5.18627	-1.55761	-1.54067
H	-5.34704	-3.23172	-0.98861
H	-3.90395	-2.74295	-1.89483
H	3.65025	-2.51710	1.45448
H	4.94778	-1.54778	0.73876
H	3.05881	-3.41423	-0.81404
H	4.74916	-3.76297	-0.41495
H	4.36522	-2.44361	-1.53511
H	2.21243	3.16794	-1.17565

H	3.88194	2.62899	-1.23666
H	2.42271	3.46582	1.34547
H	3.59356	4.45599	0.45686
H	4.12066	2.95140	1.23071

[1b-S_4]$^{+1}$

C	-1.23250	1.04632	-0.12360
N	-2.55377	1.33874	-0.14739
C	-3.49576	0.34404	0.04355
N	-2.99459	-0.96354	0.08407
C	-1.66475	-1.29253	0.02694
C	-0.72647	-0.22450	0.04392
S	-0.01321	2.26372	-0.38004
C	1.21823	1.04063	-0.23787
C	0.72640	-0.22091	0.02269
N	2.53440	1.33497	-0.33513
C	3.49012	0.35270	-0.14231
N	3.00252	-0.89336	0.26716
C	1.67424	-1.21867	0.37630
S	1.21052	-2.72874	0.99460
S	5.10675	0.65573	-0.36566
S	-5.11224	0.69361	0.18222
S	-1.18956	-2.90967	-0.16109
C	-2.97782	2.75225	-0.29656
C	-3.05426	3.47114	1.04214
C	-3.99168	-2.06634	0.13717
C	-4.46132	-2.47755	-1.25075
C	4.00826	-1.94254	0.58776
C	4.33335	-2.79895	-0.62652
C	2.94735	2.72874	-0.63101
C	3.20695	3.52232	0.64035
H	-3.94399	2.73861	-0.79569
H	-2.26726	3.22653	-0.97768
H	-3.79509	2.99880	1.68960
H	-3.35681	4.50559	0.86722
H	-2.08896	3.48074	1.55472
H	-4.81881	-1.70717	0.74376
H	-3.51423	-2.89300	0.66079
H	-4.95425	-1.64614	-1.75866
H	-5.18175	-3.29196	-1.14773
H	-3.63148	-2.83180	-1.86651
H	3.59779	-2.53691	1.40292
H	4.89042	-1.42675	0.95737
H	3.44428	-3.30809	-1.00507
H	5.06306	-3.55716	-0.33402
H	4.76762	-2.19272	-1.42379
H	2.15857	3.17393	-1.24109
H	3.83817	2.66754	-1.25216
H	2.31701	3.57676	1.27238
H	3.49508	4.53936	0.36677
H	4.02221	3.07507	1.21226

2b-O_2S_2

C	-1.21278	1.07804	-0.11288
N	-2.54064	1.37877	-0.10137
C	-3.46178	0.37656	0.16755
N	-2.97592	-0.92961	0.12347
C	-1.65459	-1.27830	-0.13382
C	-0.71122	-0.19194	0.02868
S	0.00345	2.29052	-0.43257
C	1.23230	1.05597	-0.30678
C	0.74475	-0.18660	0.01695
N	2.55302	1.34056	-0.45489
C	3.49263	0.32764	-0.30931
N	3.02146	-0.87432	0.21644
C	1.69462	-1.13860	0.54714
S	1.27047	-2.37906	1.57329
O	4.66609	0.51247	-0.58025
O	-4.63571	0.63201	0.37187
S	-1.23897	-2.78488	-0.70417
C	-3.03712	2.76089	-0.17843
C	-3.07572	3.43725	1.18541
C	-4.02271	-1.96638	0.21443
C	-4.74618	-2.18618	-1.10722
C	4.06694	-1.88011	0.48738
C	4.18367	-2.87164	-0.66170
C	3.04329	2.68788	-0.78189
C	3.37843	3.49035	0.46772
H	-4.03379	2.70730	-0.61347
H	-2.39894	3.30098	-0.88294
H	-3.74839	2.89628	1.85405
H	-3.44411	4.45975	1.07488
H	-2.08267	3.47854	1.64114
H	-4.71788	-1.63399	0.98462
H	-3.53021	-2.87784	0.54821
H	-5.24756	-1.27102	-1.43007
H	-5.50330	-2.96418	-0.97946
H	-4.04724	-2.50776	-1.88211
H	3.79587	-2.38029	1.41515
H	4.99790	-1.33702	0.63218
H	3.23995	-3.40144	-0.81613
H	4.95764	-3.60846	-0.43248
H	4.45814	-2.35959	-1.58743
H	2.28119	3.18163	-1.39007
H	3.92424	2.55190	-1.40722
H	2.50531	3.60562	1.11555
H	3.72686	4.48502	0.18014
H	4.17232	2.99671	1.03281

[2b-O_2S_2]$^{+1}$

C	-1.22802	1.10536	-0.12105
N	-2.54463	1.40841	-0.13779
C	-3.49050	0.41339	0.06271
N	-2.99339	-0.90020	0.13837
C	-1.67288	-1.23800	0.06844
C	-0.72816	-0.17096	0.04439
S	-0.00977	2.31898	-0.39384
C	1.21839	1.09225	-0.26344
C	0.73019	-0.17269	0.00099
N	2.53044	1.39116	-0.37188
C	3.48853	0.40562	-0.17628
N	3.00258	-0.85507	0.21067
C	1.68194	-1.18307	0.32253
S	1.25031	-2.71879	0.90530
O	4.67189	0.62779	-0.30713
O	-4.67420	0.65866	0.13704
S	-1.23627	-2.87198	-0.08029
C	-3.03978	2.79378	-0.27291
C	-3.15508	3.48889	1.07584
C	-4.05014	-1.93650	0.22605
C	-4.57101	-2.33472	-1.14755
C	4.06578	-1.85445	0.47746
C	4.43173	-2.62424	-0.78272
C	3.01653	2.75698	-0.65824
C	3.30038	3.53740	0.61684
H	-4.00876	2.72406	-0.76368
H	-2.36384	3.31871	-0.95222
H	-3.86394	2.96032	1.71628
H	-3.52007	4.50658	0.92298
H	-2.18959	3.54494	1.58541
H	-4.84338	-1.50807	0.83494
H	-3.62146	-2.78472	0.75827
H	-5.01910	-1.47685	-1.65339
H	-5.33937	-3.10145	-1.02676
H	-3.77457	-2.74374	-1.77374
H	3.70395	-2.51295	1.26603
H	4.91877	-1.29899	0.86051
H	3.56892	-3.16067	-1.18461
H	5.20782	-3.35394	-0.54182
H	4.82097	-1.94745	-1.54628
H	2.26767	3.24683	-1.28476
H	3.91820	2.63962	-1.25683
H	2.40569	3.63921	1.23625
H	3.64917	4.53770	0.35209
H	4.08071	3.04371	1.19945

3b-OS_3

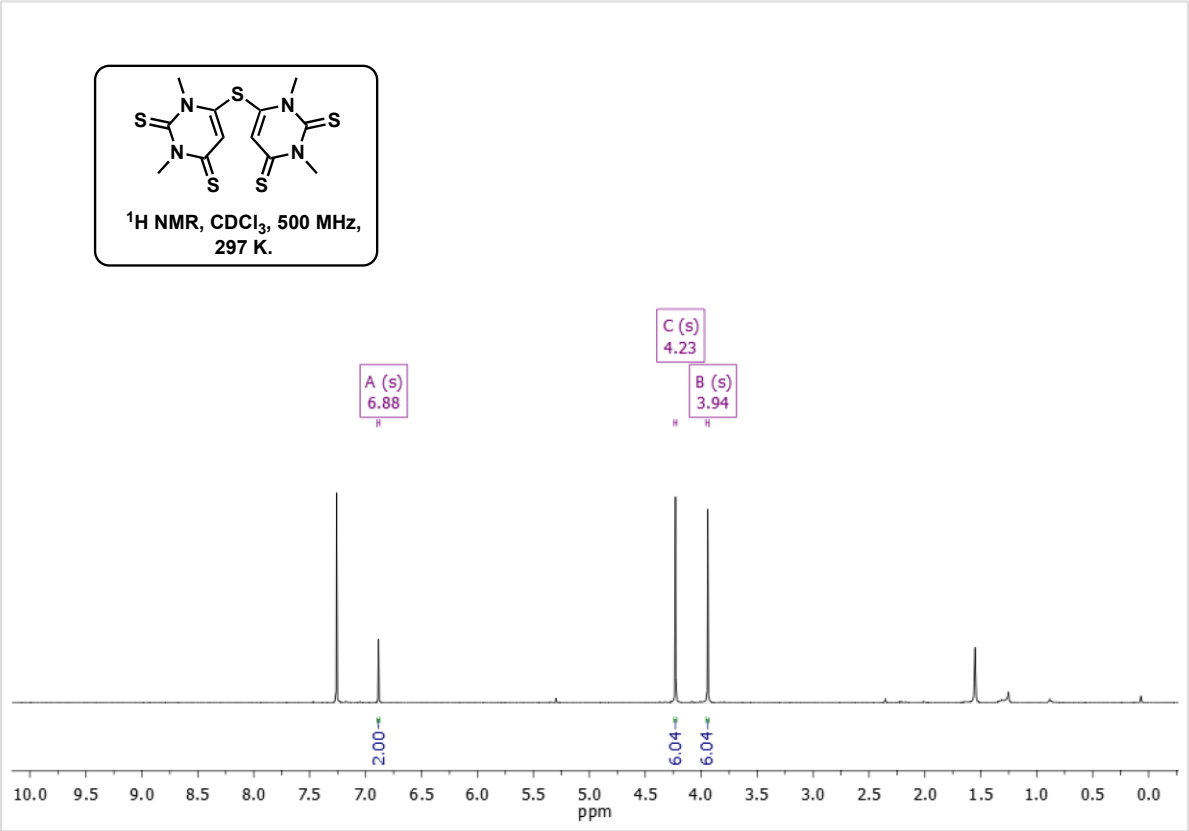
C	-1.17697	0.95038	-0.30130
N	-2.50308	1.26892	-0.36563
C	-3.44764	0.28511	-0.17168
N	-2.99081	-1.02080	-0.21486
C	-1.64614	-1.40189	-0.34824
C	-0.70473	-0.32856	-0.15376
S	0.07942	2.15045	-0.44225
C	1.27923	0.89876	-0.22649
C	0.73904	-0.34350	-0.04137
N	2.61891	1.17717	-0.21068
C	3.53099	0.16423	0.01134
N	3.00925	-1.05658	0.35626
C	1.62520	-1.37216	0.47293
O	1.28157	-2.41103	0.99833
S	5.18501	0.44393	-0.11634
S	-5.06063	0.68262	0.07137
S	-1.18754	-2.93702	-0.78289
C	-2.89435	2.68842	-0.49054
C	-2.93711	3.40615	0.85160

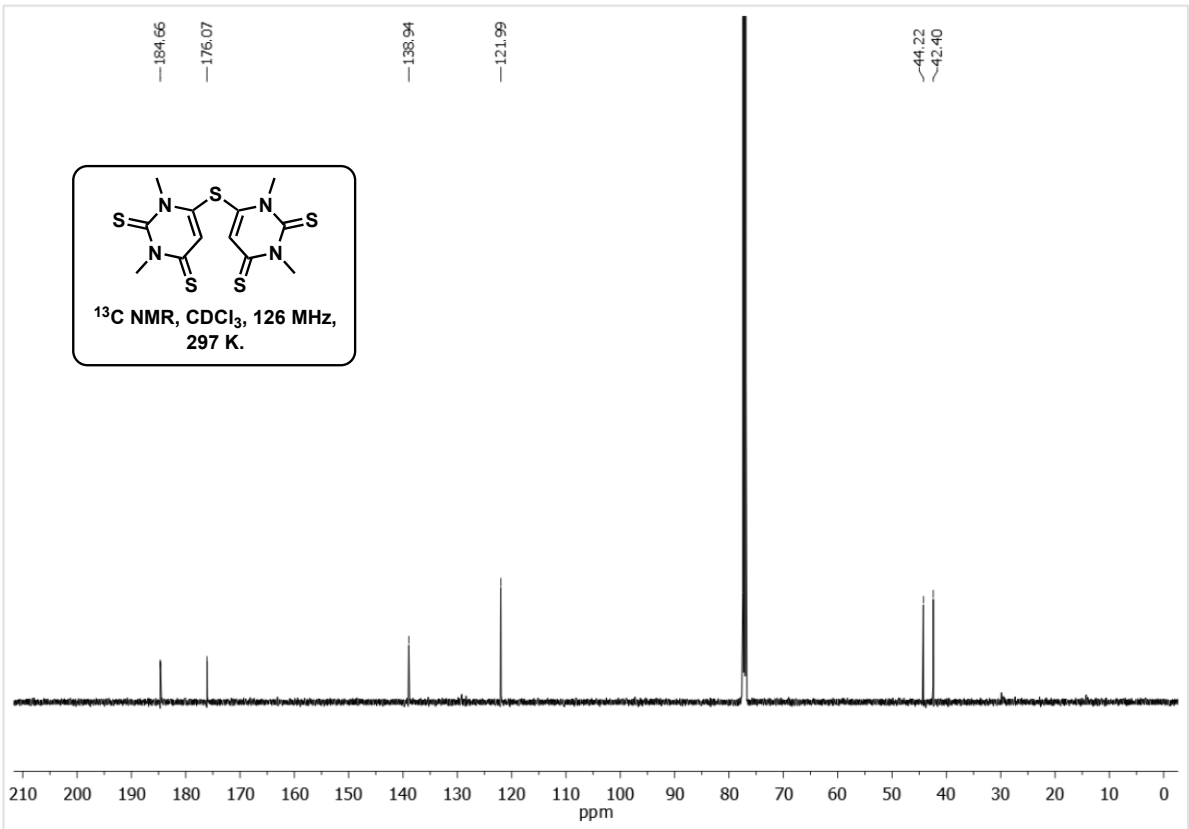
C	-3.99914	-2.10314	-0.13633
C	-4.17214	-2.59125	1.29428
C	3.91657	-2.17320	0.69161
C	4.20396	-3.03835	-0.52722
C	3.06610	2.57052	-0.40792
C	3.20369	3.31566	0.91166
H	-3.86905	2.70508	-0.97344
H	-2.18032	3.15172	-1.17664
H	-3.68942	2.95379	1.50014
H	-3.20382	4.45250	0.68641
H	-1.96936	3.37776	1.35908
H	-3.64415	-2.90165	-0.78345
H	-4.92912	-1.70773	-0.53490
H	-3.23226	-2.98595	1.68876
H	-4.91428	-3.39317	1.31327
H	-4.52063	-1.78323	1.94202
H	3.41571	-2.74859	1.46696
H	4.82888	-1.74234	1.09708
H	3.28019	-3.46819	-0.92297
H	4.86871	-3.85805	-0.24328
H	4.69107	-2.45508	-1.31250
H	2.34628	3.05218	-1.07404
H	4.01572	2.52874	-0.93687
H	2.25782	3.34332	1.45933
H	3.51537	4.34390	0.71427
H	3.96056	2.83946	1.53885

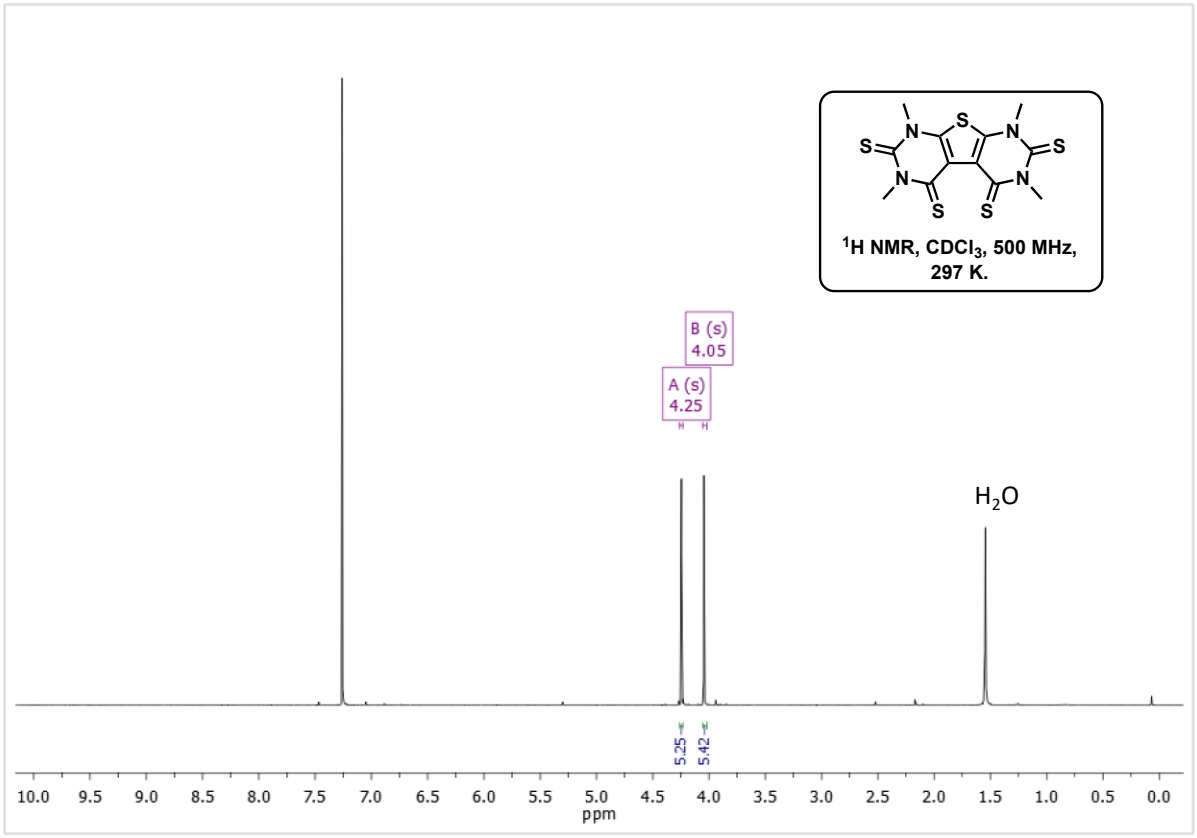
[3b-OS$_3$]$^{+1}$

C	-1.17468	0.98795	-0.35002
N	-2.47144	1.27873	-0.36540
C	-3.42943	0.26343	-0.12555
N	-2.97531	-1.03279	-0.23493
C	-1.63467	-1.40394	-0.39344
C	-0.68447	-0.32701	-0.20224
S	0.07552	2.19409	-0.47654
C	1.26632	0.93701	-0.22015
C	0.71126	-0.33289	-0.03760
N	2.57733	1.18922	-0.20738
C	3.50496	0.14461	0.01976
N	2.97407	-1.06133	0.39938
C	1.59943	-1.38106	0.47034
O	1.22853	-2.42516	0.95518
S	5.12843	0.41718	-0.14989
S	-4.98858	0.67352	0.23348
S	-1.15802	-2.91042	-0.86052
C	-2.90065	2.69550	-0.51357
C	-2.92296	3.44172	0.81335
C	-3.98551	-2.12041	-0.18088
C	-4.12836	-2.67617	1.22734
C	3.88067	-2.17154	0.77670
C	4.20003	-3.06032	-0.41617
C	3.05672	2.58166	-0.39925
C	3.20905	3.31043	0.92693
H	-3.88567	2.67545	-0.97359
H	-2.21278	3.14942	-1.23106
H	-3.66273	3.00739	1.48669
H	-3.19788	4.47988	0.61674
H	-1.94774	3.43661	1.30578
H	-3.64994	-2.88554	-0.87727
H	-4.92223	-1.70643	-0.54427
H	-3.18397	-3.09575	1.58303
H	-4.87398	-3.47428	1.21868
H	-4.46019	-1.90217	1.92312
H	3.36359	-2.73032	1.55368
H	4.77894	-1.72683	1.19870
H	3.28985	-3.51002	-0.82018
H	4.86502	-3.86520	-0.09479
H	4.70072	-2.49495	-1.20555
H	2.34624	3.07672	-1.06460
H	4.00294	2.51733	-0.93041
H	2.26297	3.36626	1.47113
H	3.55017	4.32842	0.72835
H	3.95199	2.81484	1.55494

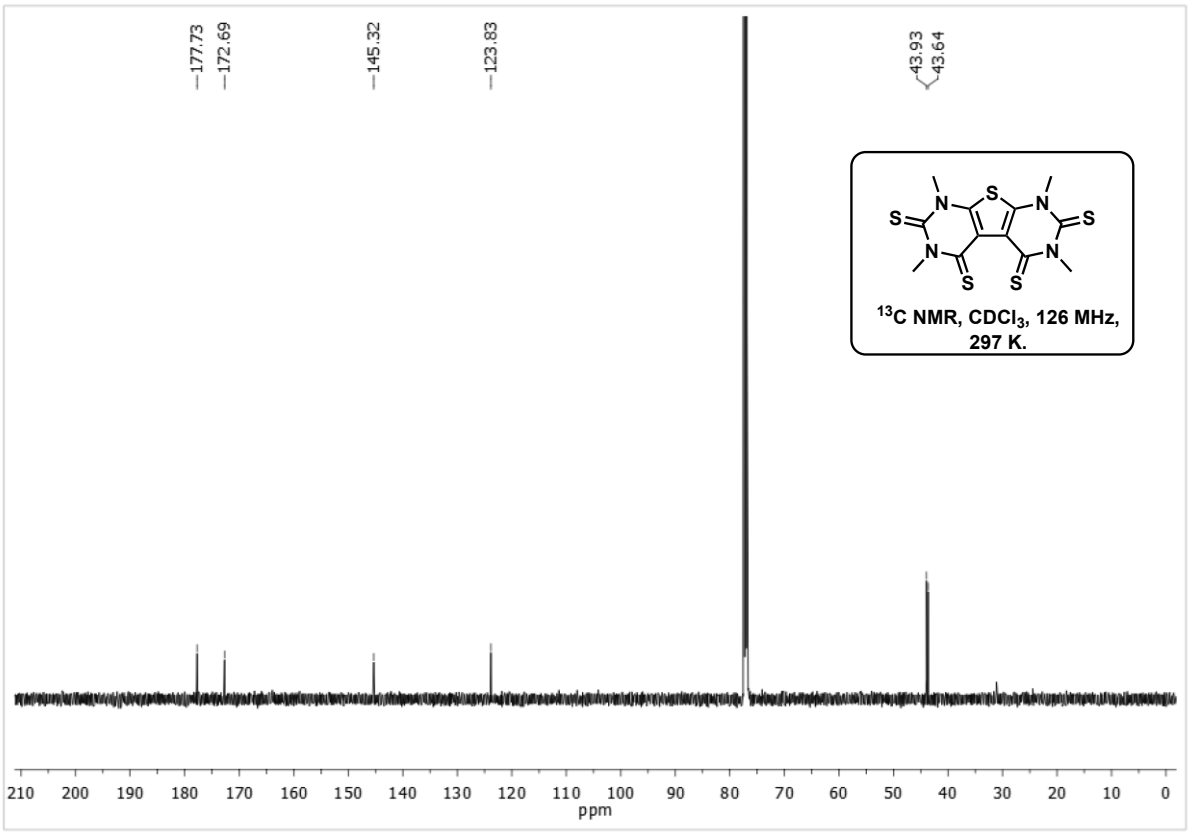
5. ^{1}H and ^{13}C NMR Spectra



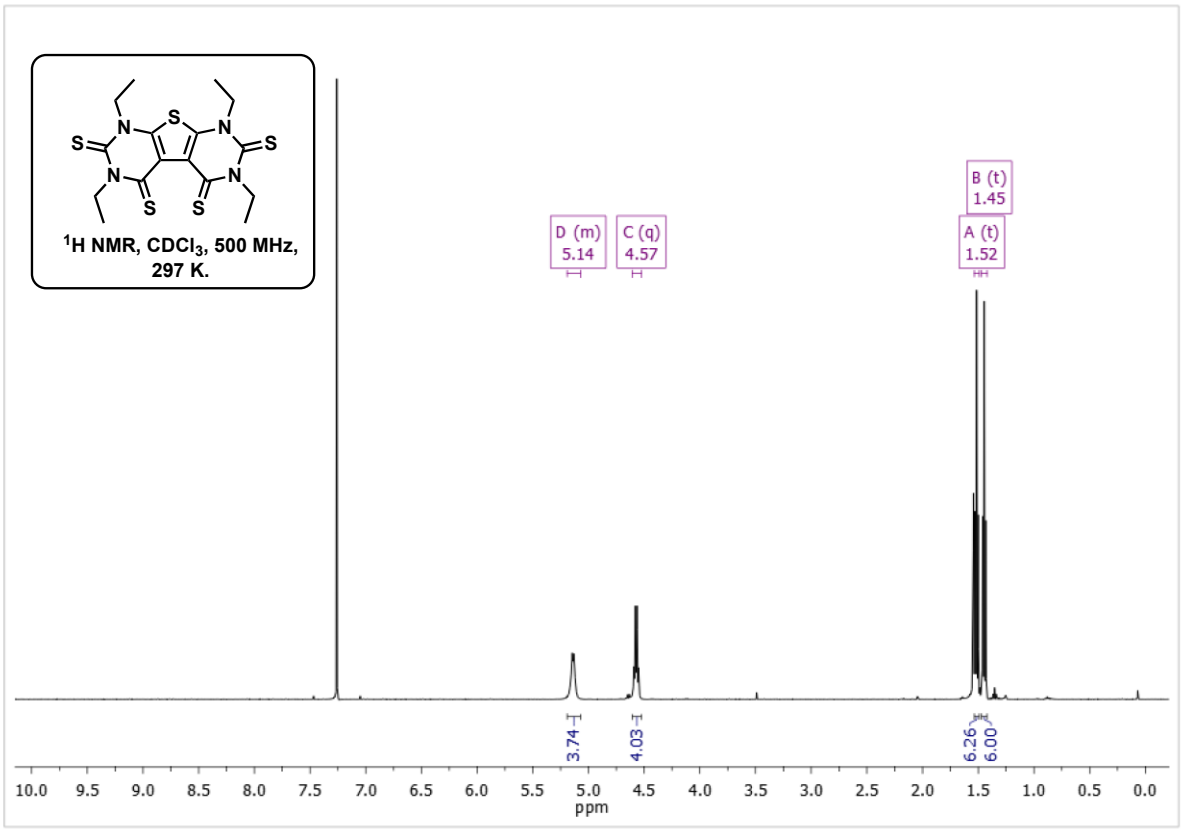


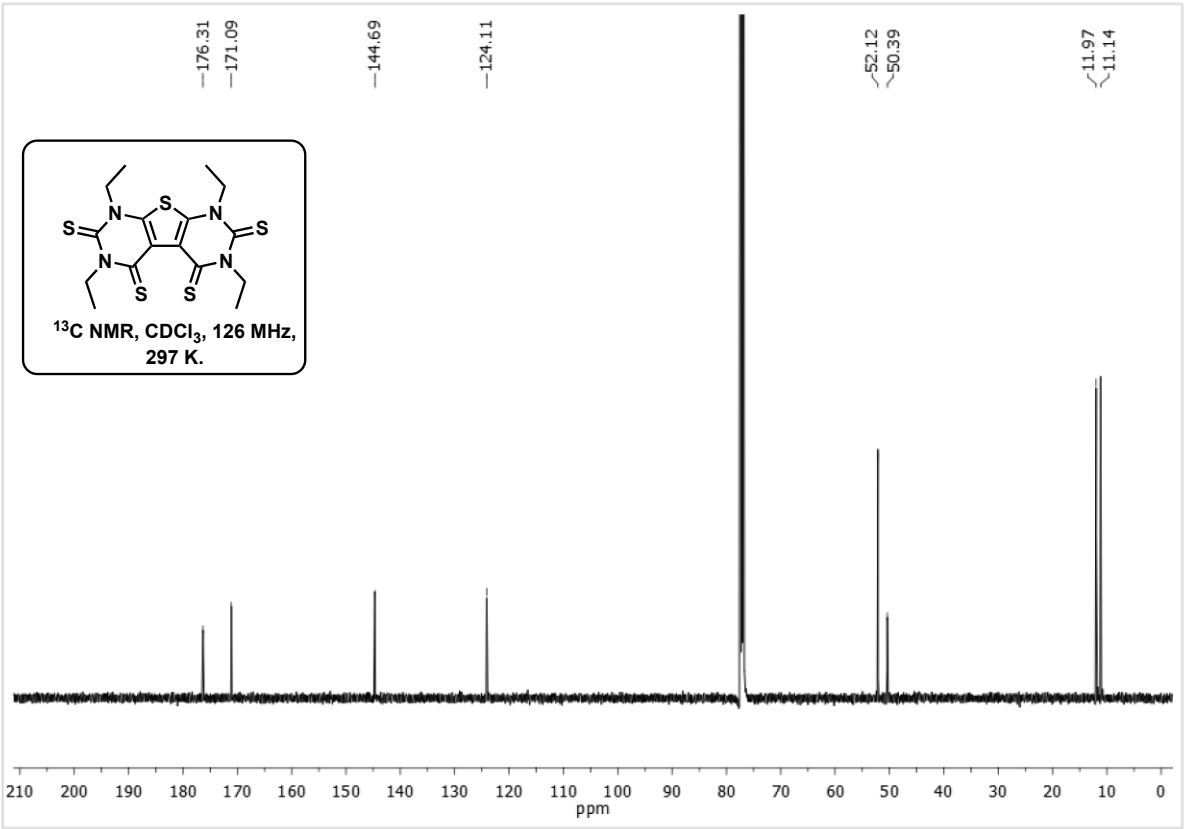


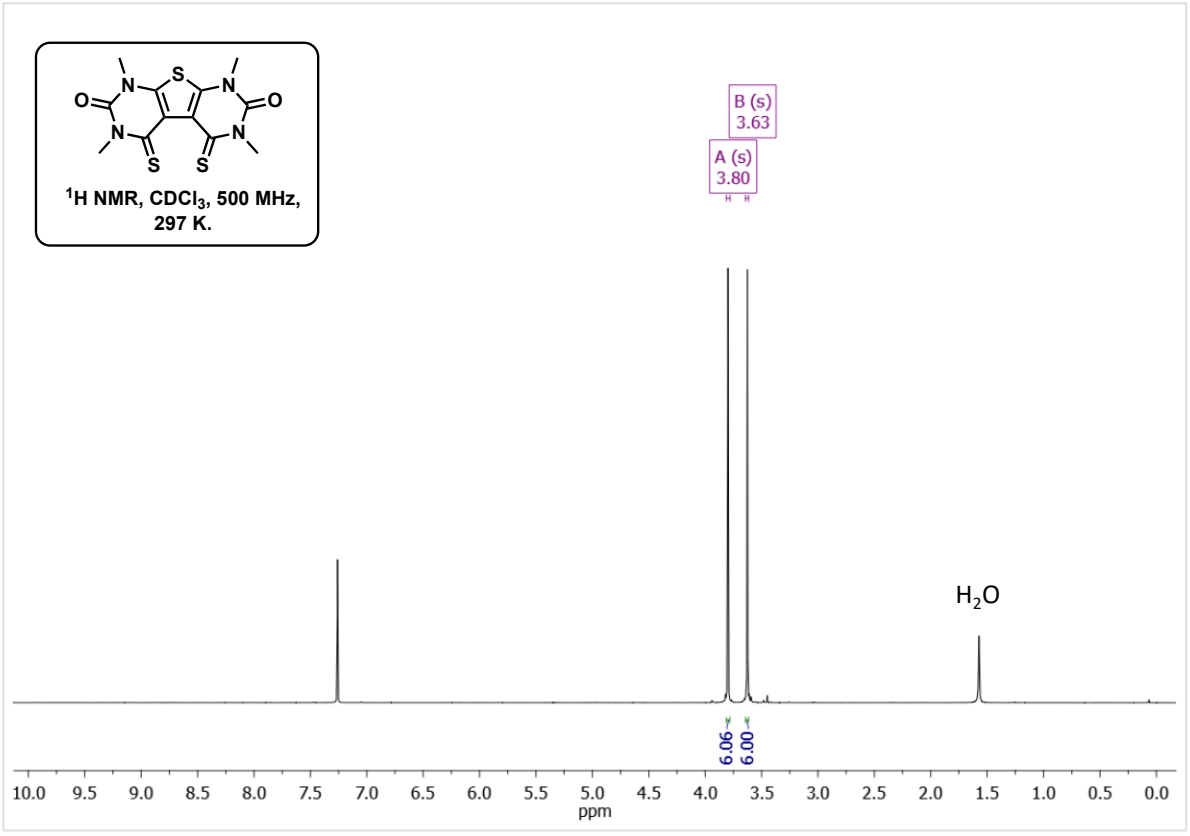
^{1}H NMR, $CDCl_3$, 500 MHz, 297 K.



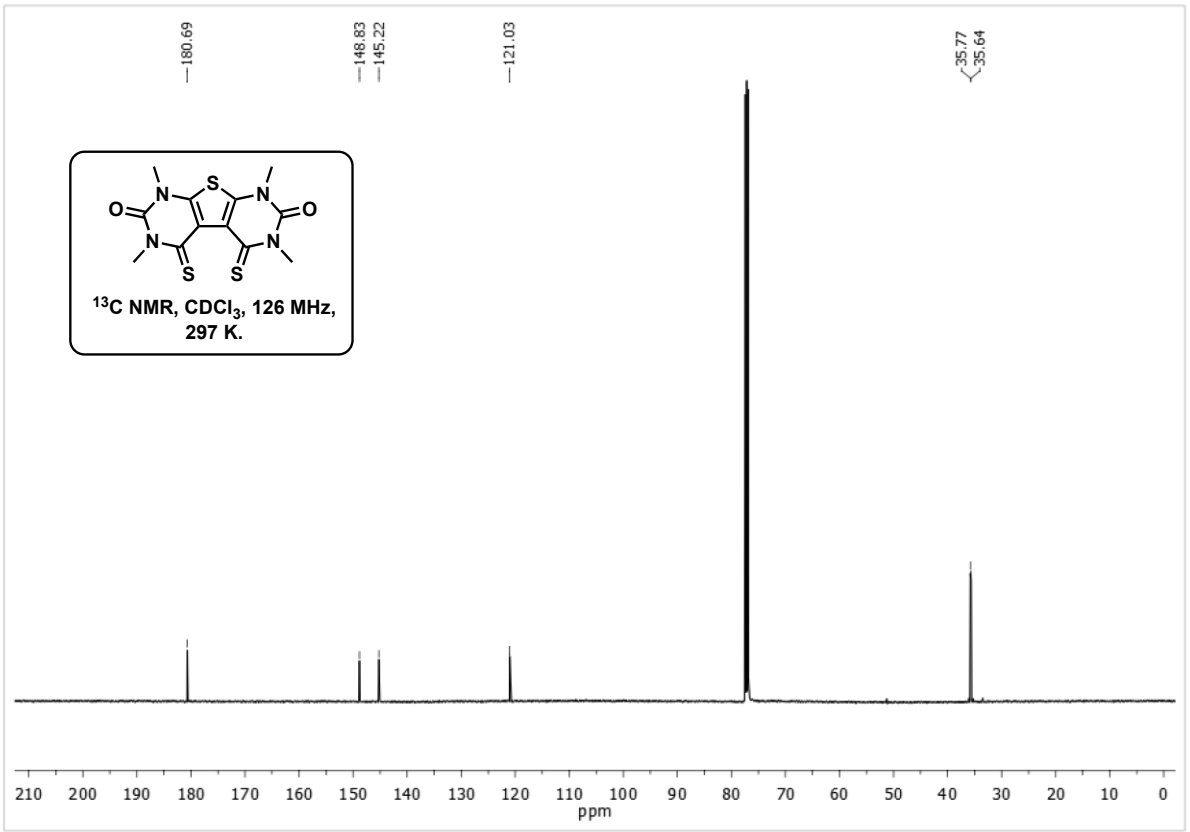
^{13}C NMR, $CDCl_3$, 126 MHz, 297 K.


^{1}H NMR, $CDCl_3$, 500 MHz, 297 K.
D (m) 5.14
C (q) 4.57
B (t) 1.45
A (t) 1.52
3.74
4.03
6.26
6.00
ppm

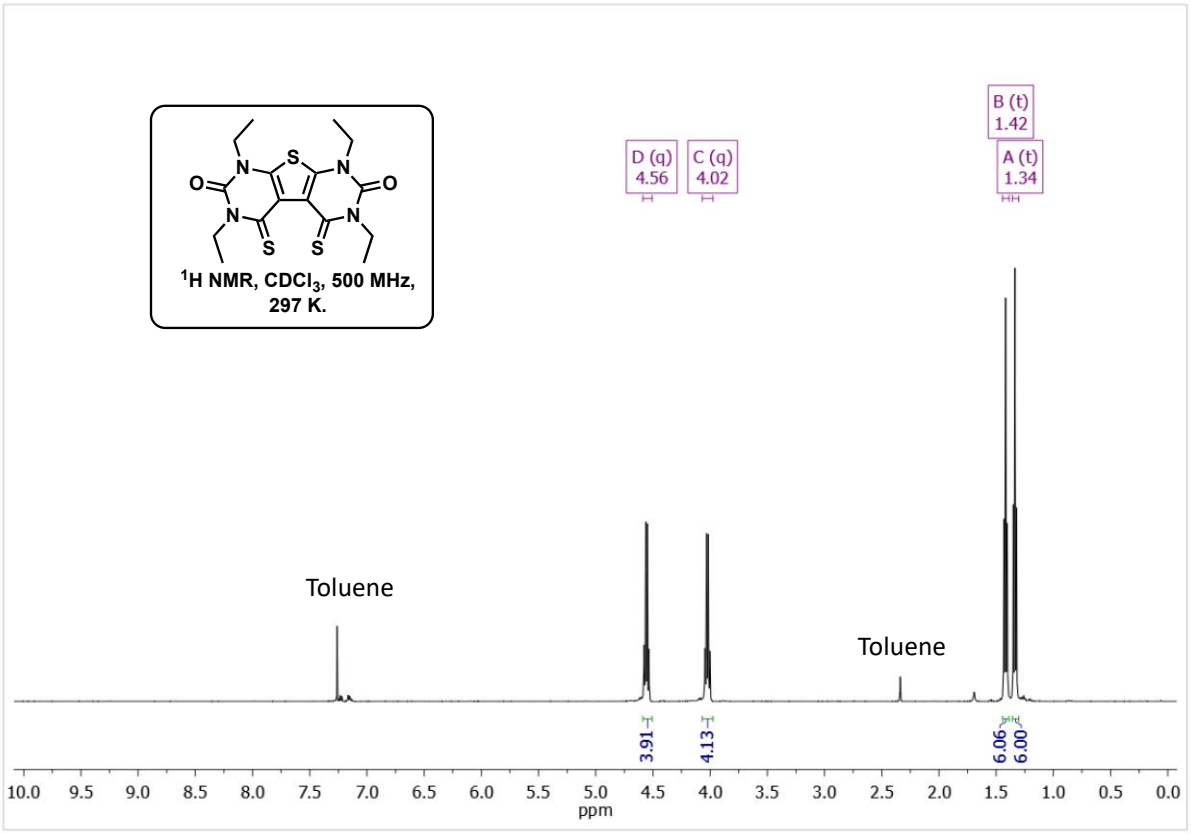

176.31
171.09
144.69
124.11
52.12
50.39
11.97
11.14
^{13}C NMR, $CDCl_3$, 126 MHz, 297 K.
ppm

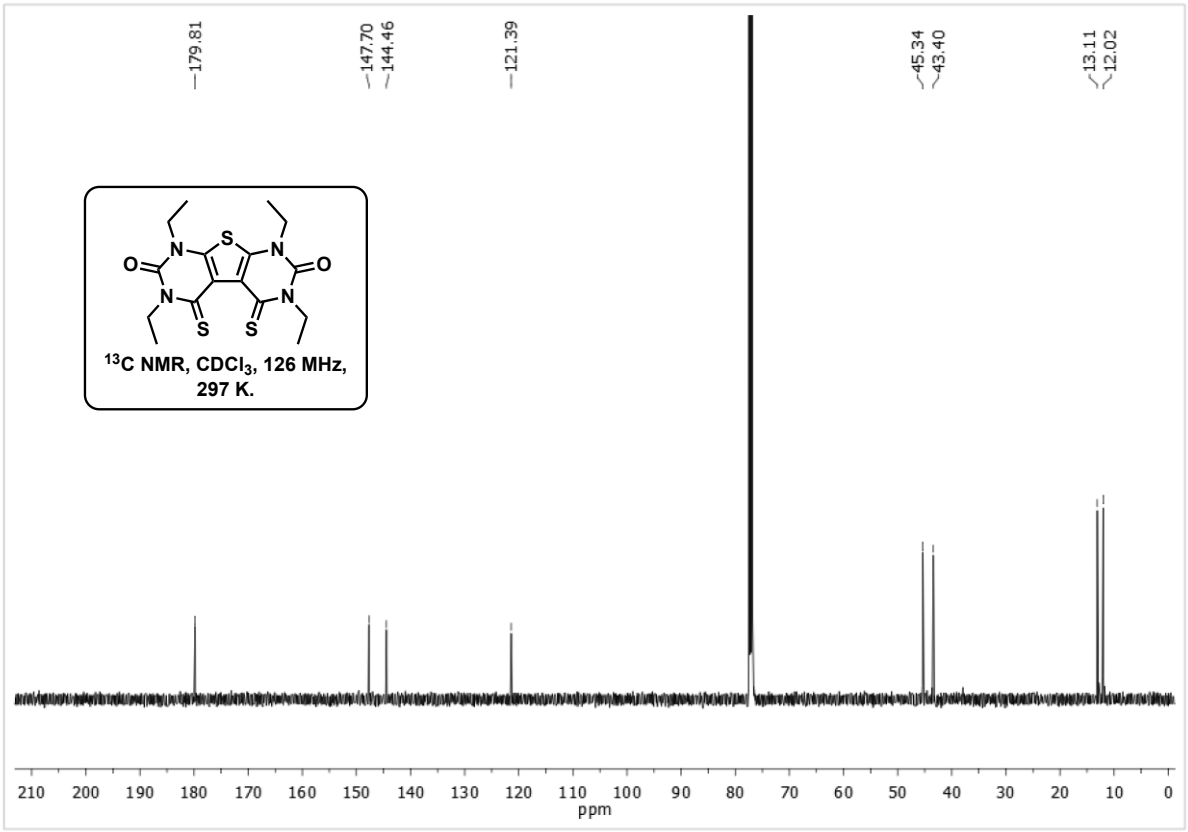


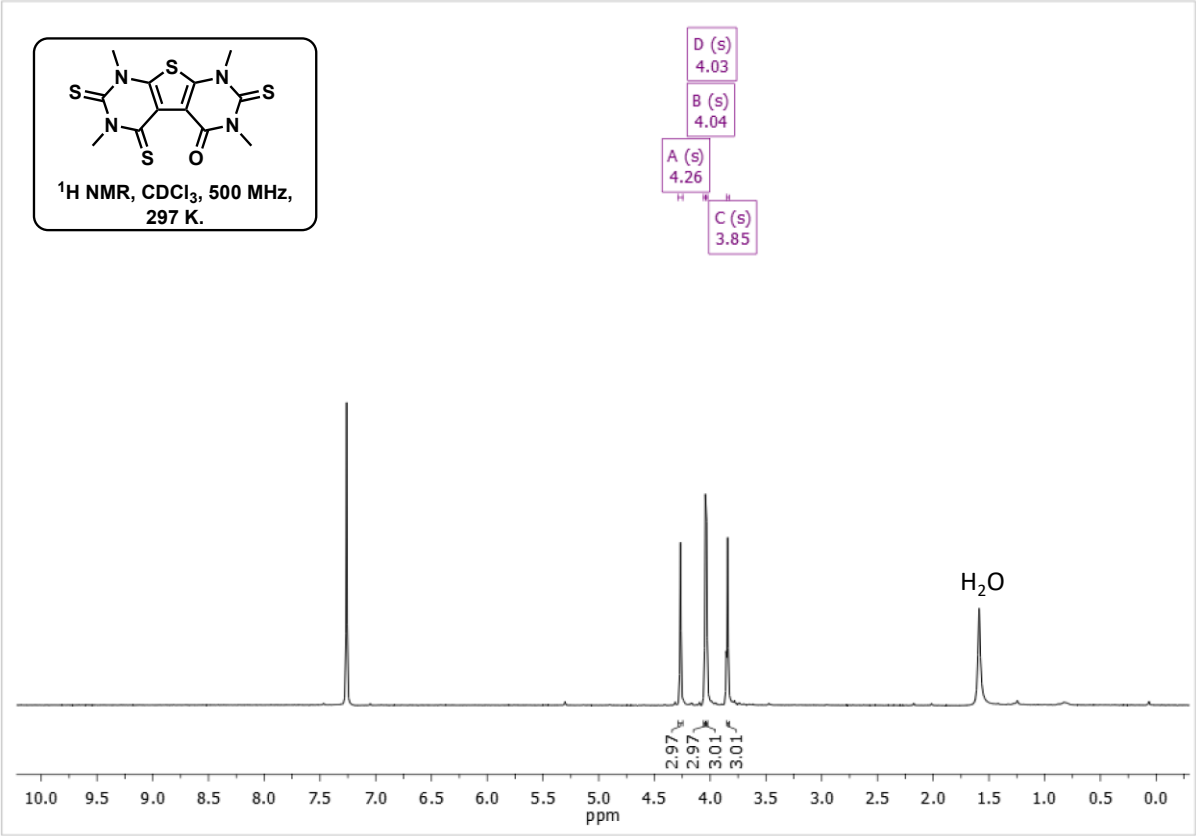
^{1}H NMR, $CDCl_3$, 500 MHz, 297 K.



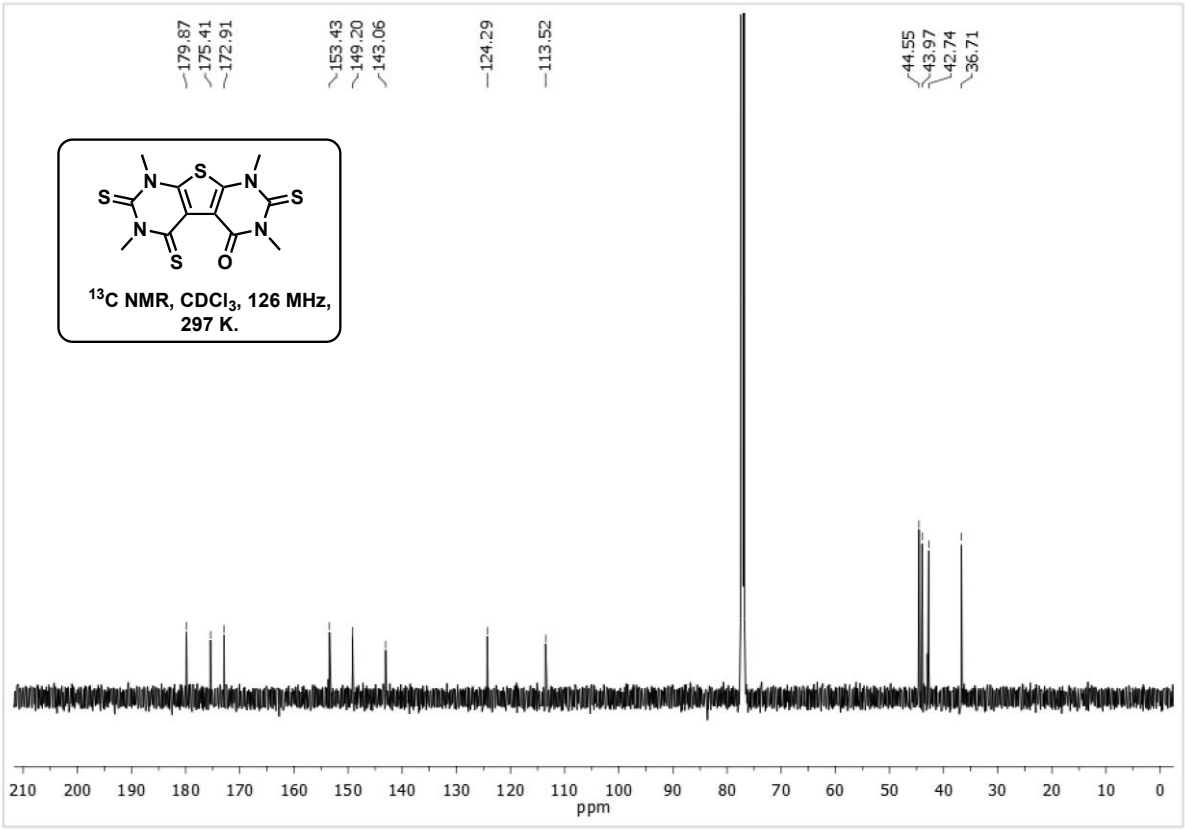
^{13}C NMR, $CDCl_3$, 126 MHz, 297 K.


^{1}H NMR, CDCl$_3$, 500 MHz, 297 K.
D (q) 4.56
C (q) 4.02
B (t) 1.42
A (t) 1.34
Toluene
Toluene
3.91
4.13
6.06
6.00
ppm

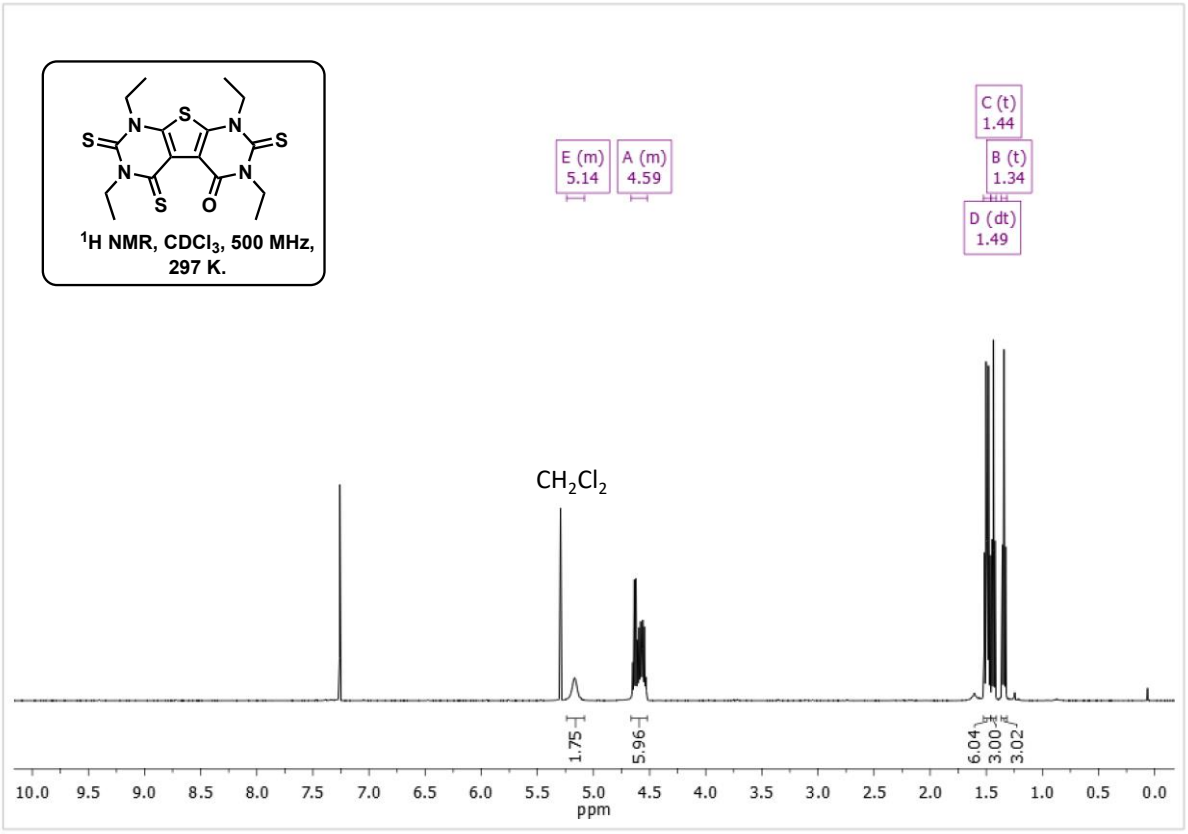

179.81
147.70
144.46
121.39
45.34
43.40
13.11
12.02
^{13}C NMR, CDCl$_3$, 126 MHz, 297 K.
ppm

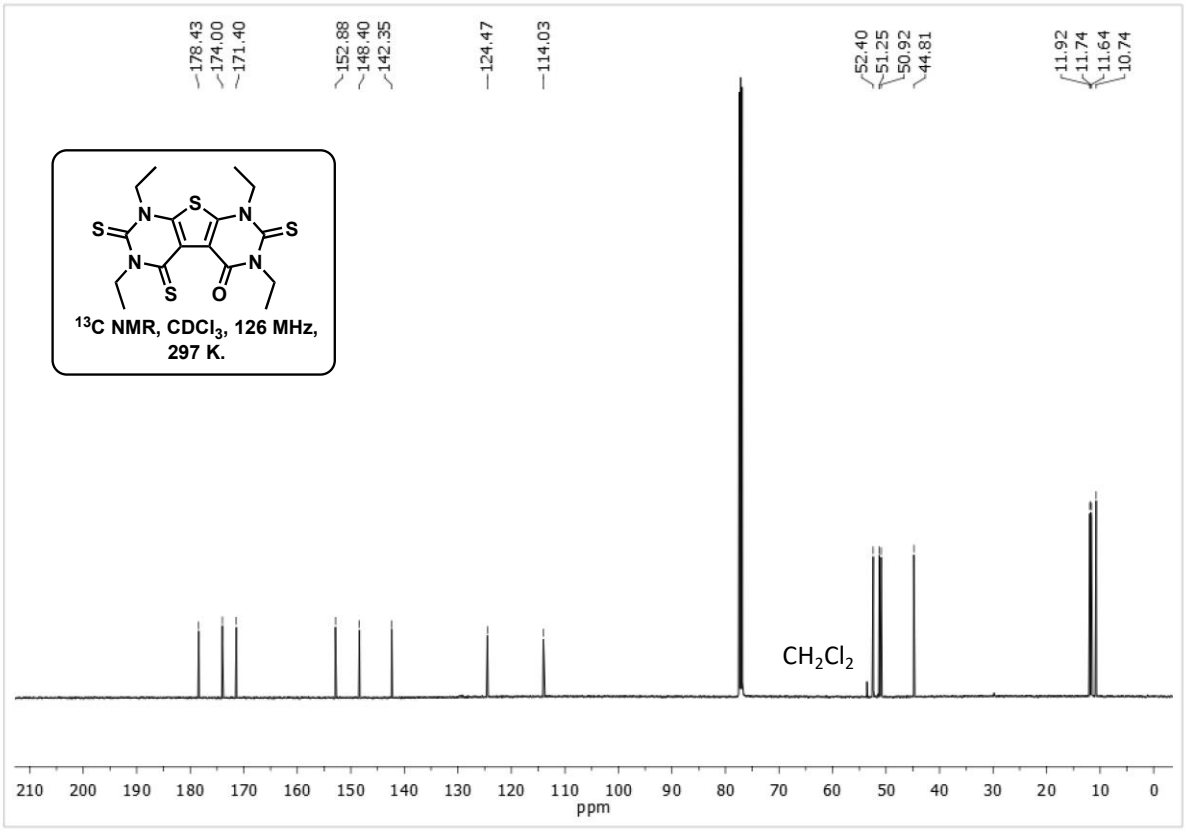


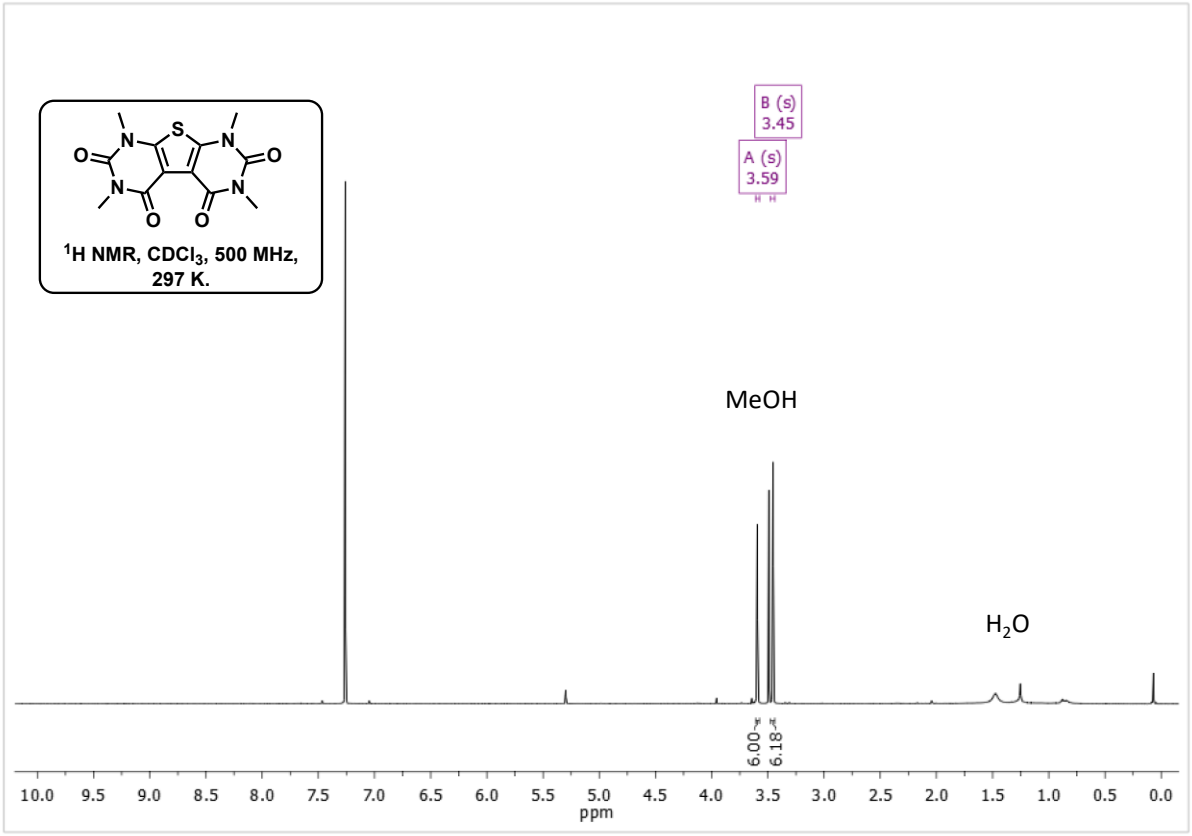
^{1}H NMR, $CDCl_3$, 500 MHz, 297 K.



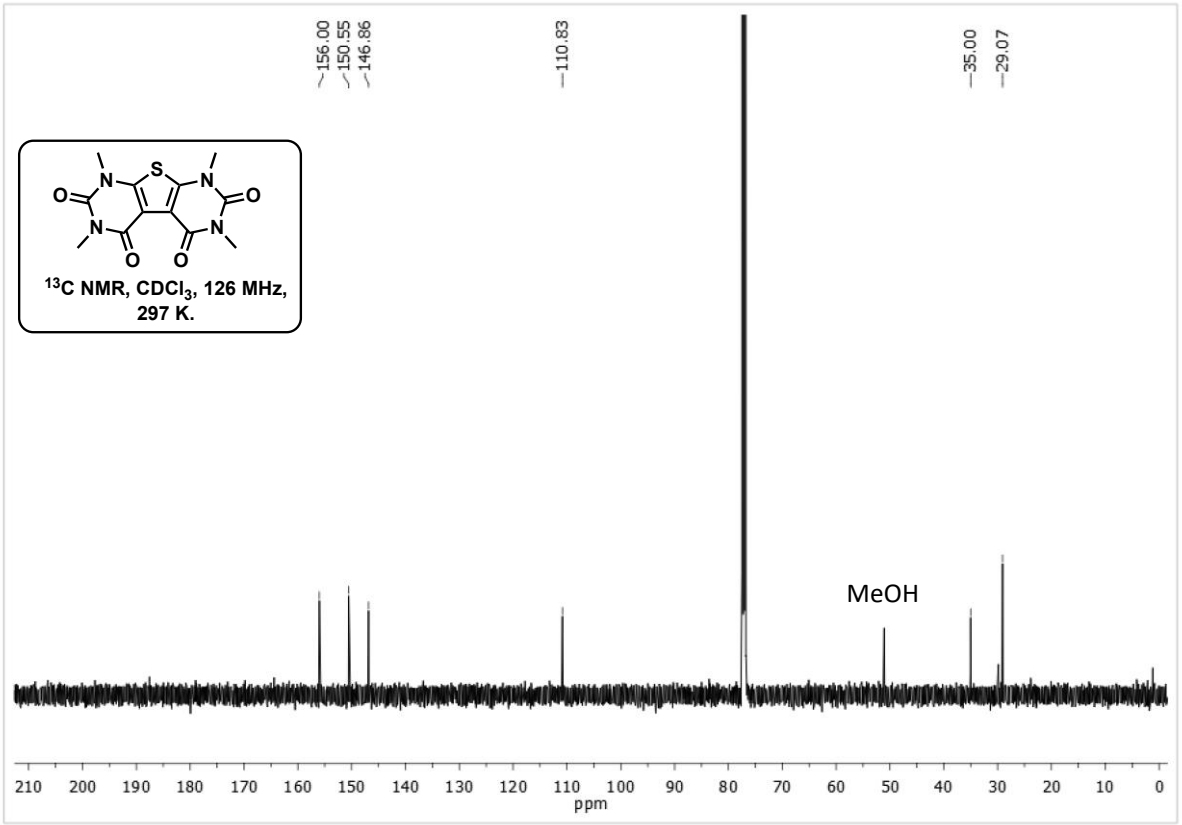
^{13}C NMR, $CDCl_3$, 126 MHz, 297 K.


^{1}H NMR, $CDCl_3$, 500 MHz, 297 K.
E (m) 5.14
A (m) 4.59
C (t) 1.44
B (t) 1.34
D (dt) 1.49
CH_2Cl_2
1.75
5.96
6.04
3.00
3.02
ppm


178.43
174.00
171.40
152.88
148.40
142.35
124.47
114.03
52.40
51.25
50.92
44.81
11.92
11.74
11.64
10.74
^{13}C NMR, $CDCl_3$, 126 MHz, 297 K.
CH_2Cl_2
ppm

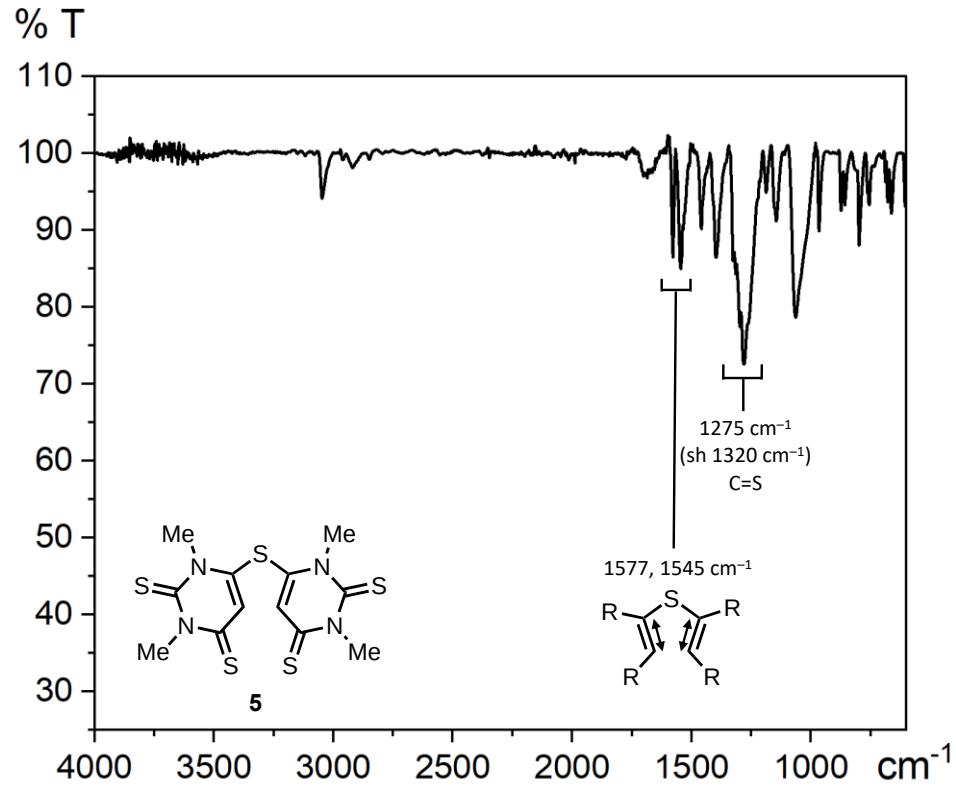


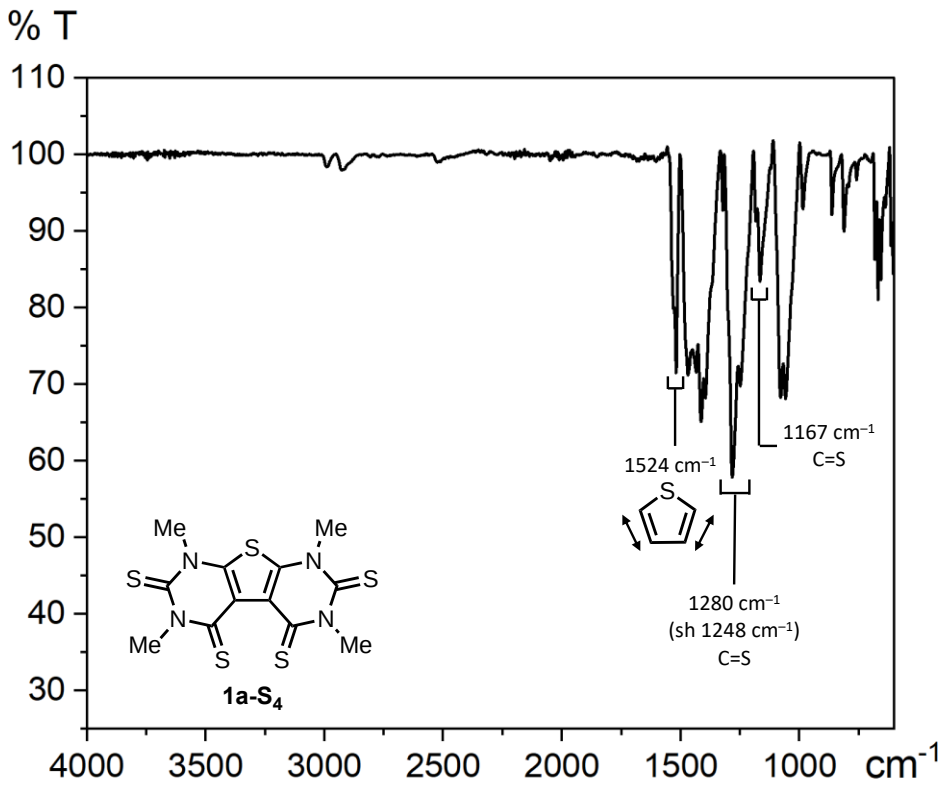
^{1}H NMR, $CDCl_3$, 500 MHz, 297 K.

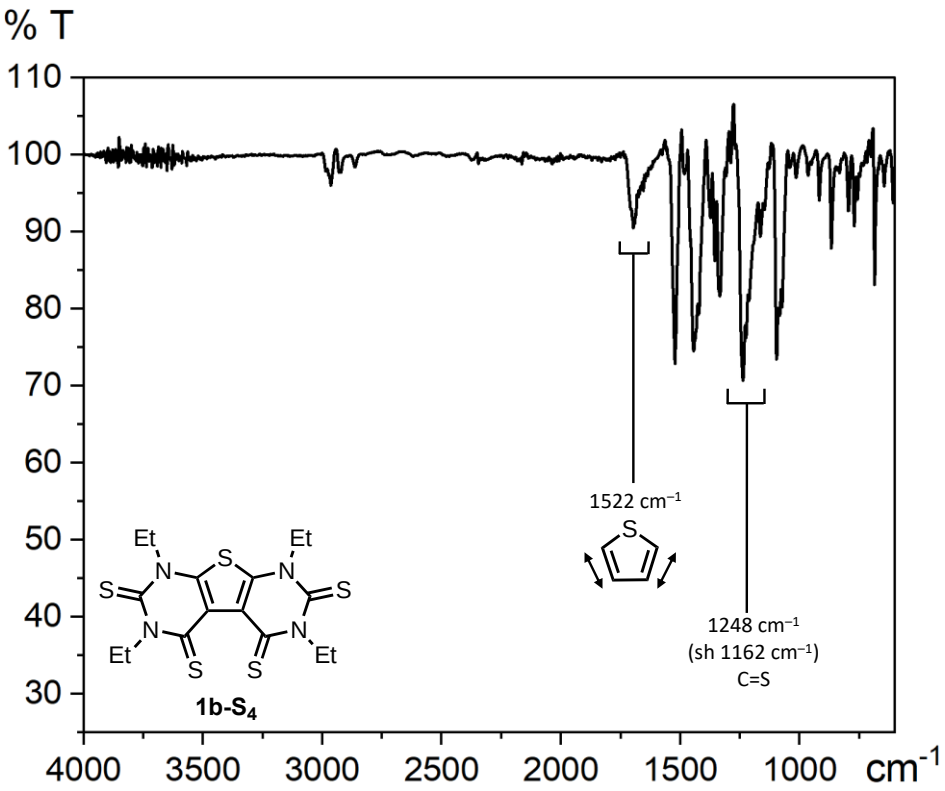


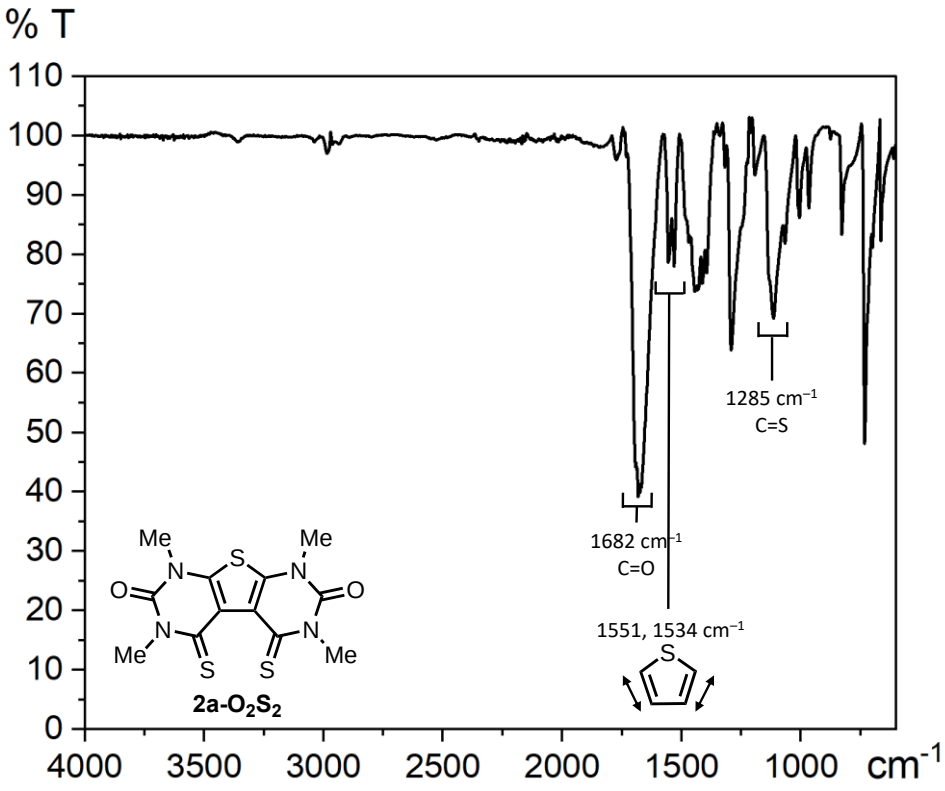
^{13}C NMR, $CDCl_3$, 126 MHz, 297 K.

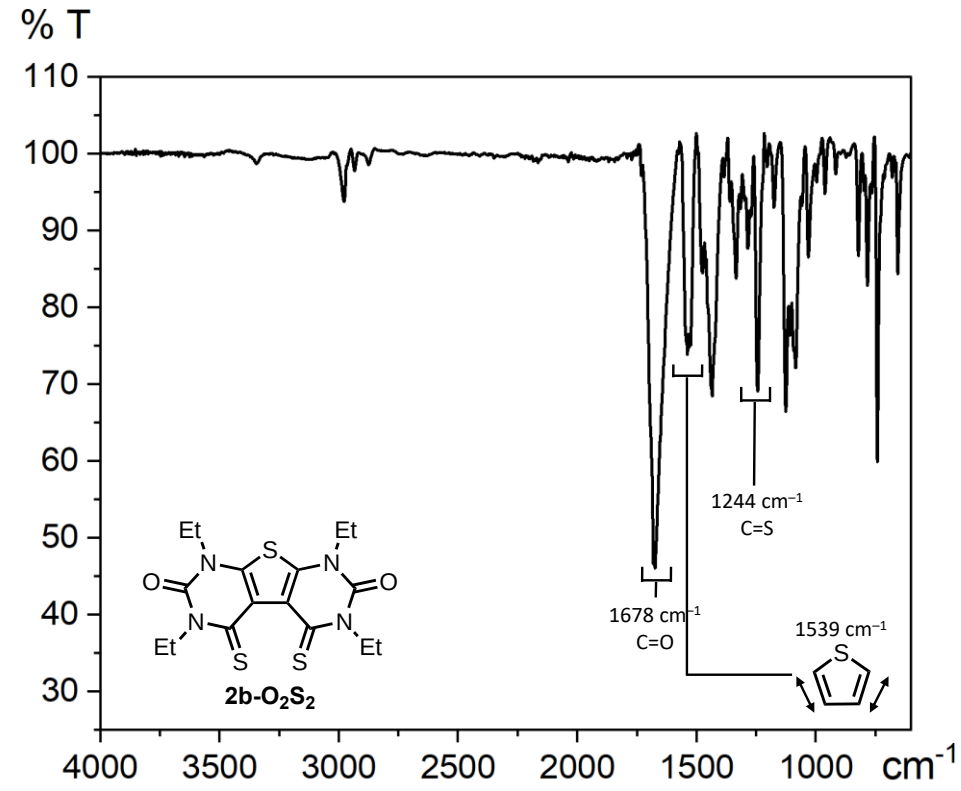
6. Infrared Spectra

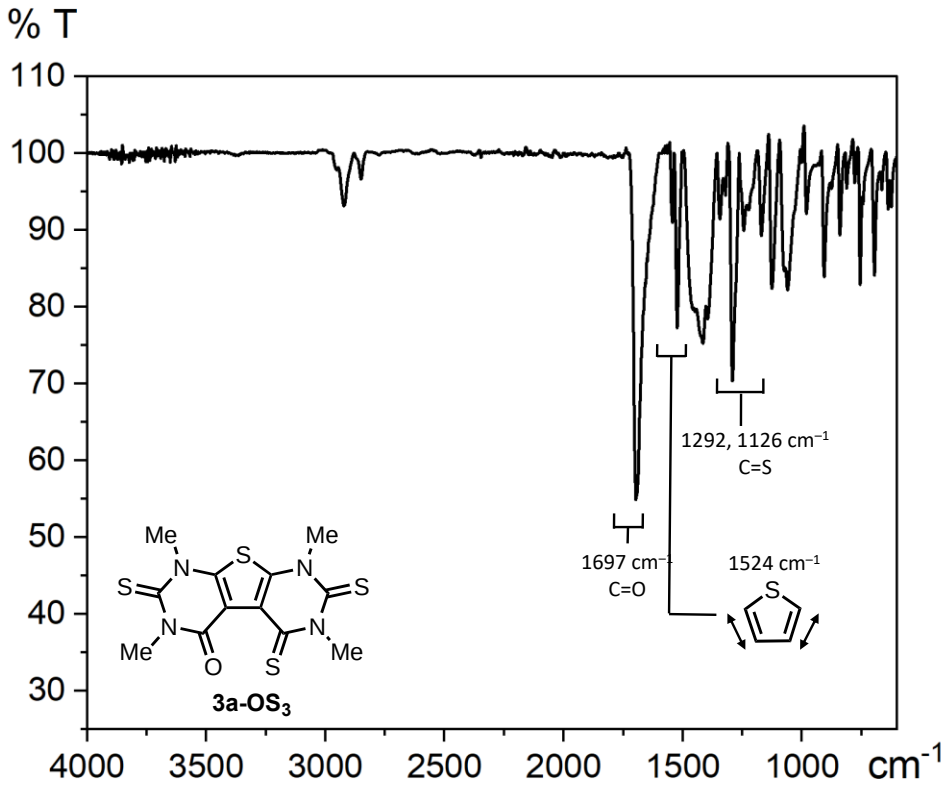


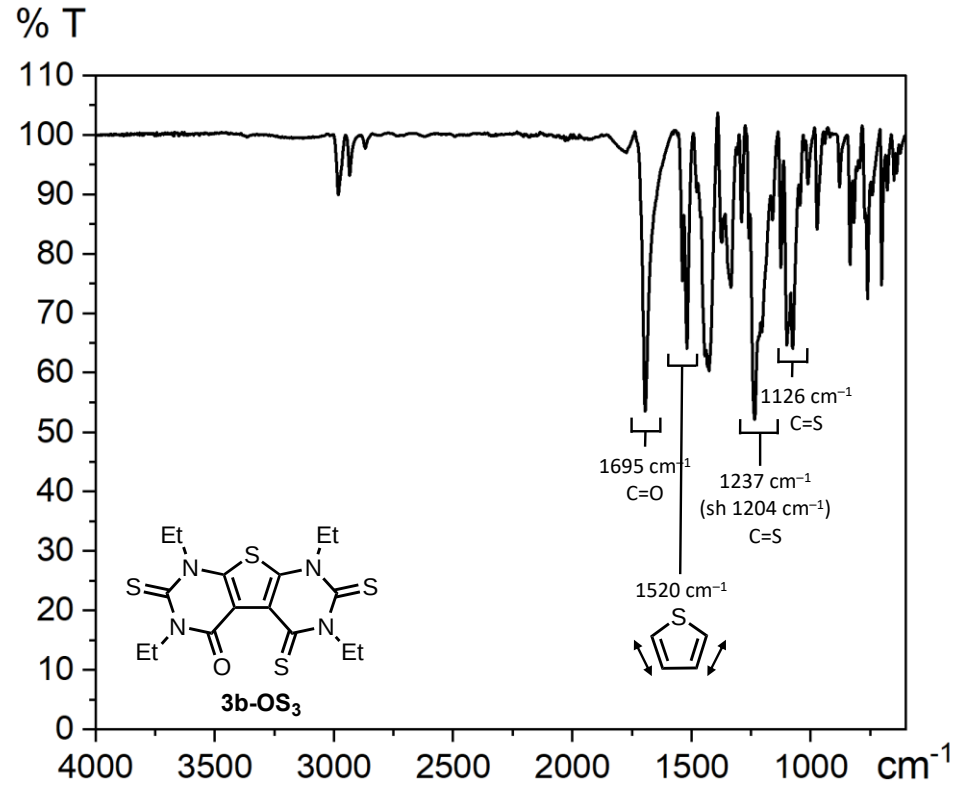


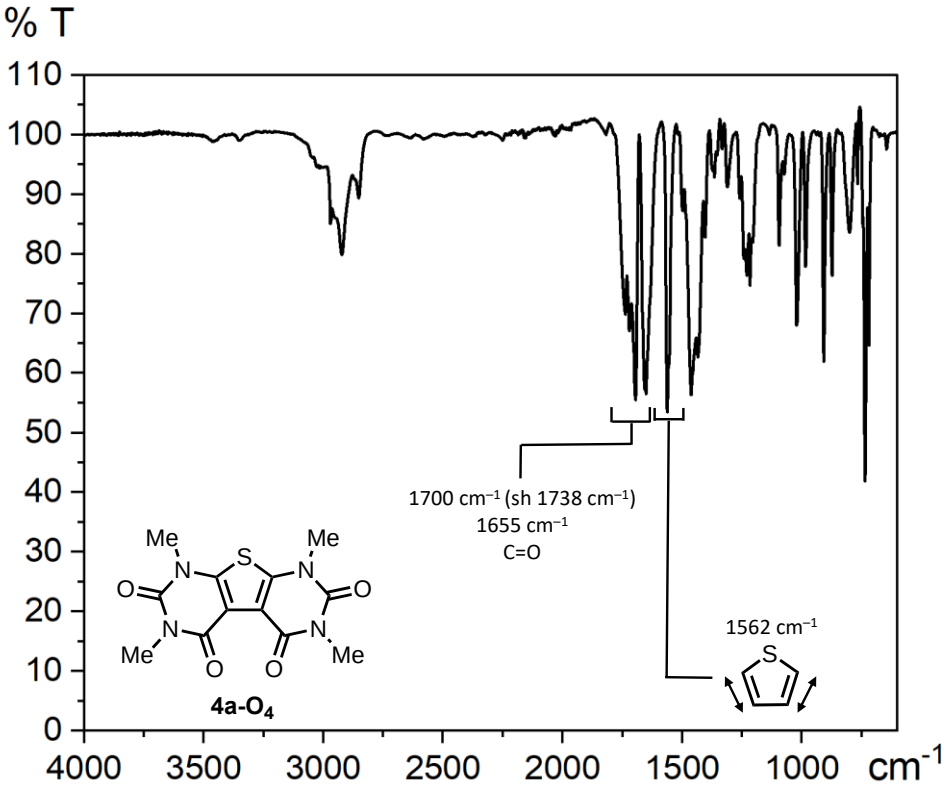

% T
110
100
90
80
70
60
50
40
30
4000
3500
3000
2500
2000
1500
1000
cm-1
1522 cm–1
1248 cm–1
(sh 1162 cm–1)
C=S
Et
N
S
S
Et
1b-S4


% T
110
100
90
80
70
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
1500
1000
cm-1
1285 cm–1
C=S
1682 cm–1
C=O
1551, 1534 cm–1
Me
N
O
S
2a-O2S2


% T
110
100
90
80
70
60
50
40
30
4000
3500
3000
2500
2000
1500
1000
cm-1
1678 cm−1
C=O
1244 cm−1
C=S
1539 cm−1
2b-O2S2


% T
110
100
90
80
70
60
50
40
30
4000
3500
3000
2500
2000
1500
1000
cm-1
1697 cm−1
C=O
1292, 1126 cm−1
C=S
1524 cm−1
3a-OS3


% T
110
100
90
80
70
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
1500
1000
cm-1
1695 cm-1
C=O
1520 cm-1
1126 cm-1
C=S
1237 cm-1
(sh 1204 cm-1)
C=S
Et
N
S
S
N
Et
Et
N
S
S
N
Et
O
S
3b-OS3


% T
110
100
90
80
70
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
1500
1000
cm-1
1700 cm-1 (sh 1738 cm-1)
1655 cm-1
C=O
1562 cm-1
Me
N
S
N
Me
O
O
N
N
Me
O
O
4a-O4

7. References

1. Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.
2. Sheldrick, G. M. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3.
3. Sheldrick, G. M. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2015**, *71*, 3.
4. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, A. K.; Puschmann, J. H. *Appl. Crystallogr.* **2009**, *42*, 339.

