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Supplementary Materials for

A reversible single-molecule switch based on activated antiaromaticity

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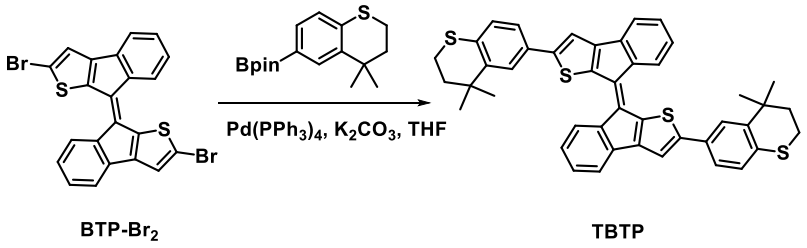
This PDF file includes:

Synthetic details

2,2'-bis(4,4-dimethylthiochroman-6-yl)-8,8'-biindeno[2,1-b]thiophenylidene (**TBTP**)



BTP-Br$_2$ **TBTP**

2,2'-dibromo-8,8'-biindeno[2,1-b]thiophenylidene (BTP-Br$_2$)(*25*) 0.2 g 0.41 mmol and 2-(4,4-dimethylthiochroman-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Thiocroman-Bpin)(*26*) 0.273 g 0.90 mmol (2.2 eqv.) were added into a 50 mL schlenk flask, followed by the addition of 10 mL THF/H_2O = 4:1. The mixture was purged with N_2 for 20 min, and then, a suspension of K_2CO_3 (0.21g 1.5 mmol) in 1 mL water was added. While stirring the mixture under nitrogen for another 10 min, $Pd(PPh_3)_4$ (60 mg, 0.05 mmol) was added in one portion, and the mixture was heated to reflux for 12h. The reaction was monitored by thin-layer chromatography (TLC). After the starting materials were consumed, the mixture was cooled to room temperature. The mixture was diluted with 50 mL of dichloromethane and washed with DI-water (100 mL×3). The organic phase was dried with $MgSO_4$, filtered, and the solvent was removed under vacuum. The crude product was further purified by recrystallization to obtain the pure product as a black solid (0.18 g, 63%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.53 (d, *J* = 7.1 Hz, 2H), 7.67 (d, *J* = 2.0 Hz, 2H), 7.51 (d, *J* = 6.8 Hz, 2H), 7.42 (s, 2H), 7.36 – 7.26 (m, 6H), 7.11 (d, *J* = 8.2 Hz, 2H), 3.14 – 3.00 (m, 4H), 2.05 – 1.93 (m, 4H), 1.40 (s, 12H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 150.55, 150.34, 143.18, 141.72, 138.04, 137.59, 133.43, 130.51, 129.40, 127.36, 126.17, 125.54, 124.05, 123.75, 120.04, 114.72, 37.79, 33.49, 30.18, 23.59. Mass Spectrum: *m/z*= 693.1764 (calcd for $C_{44}H_{37}S_4$ ($[M+H]^+$) 693.1778).

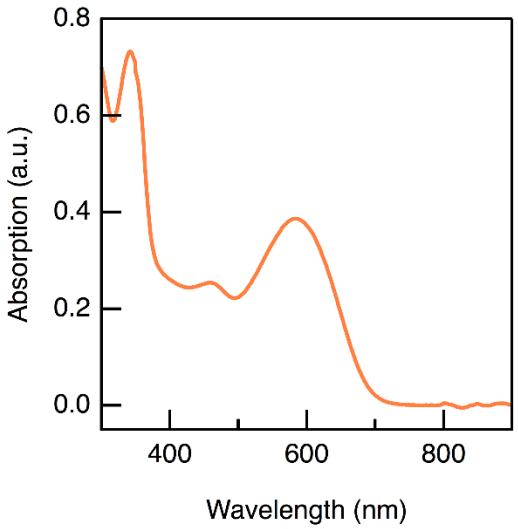


fig. S1. UV-vis spectrum of TBTP. UV-Vis spectrum of **TBTP** in dichloromethane (1×10^{-5} M).

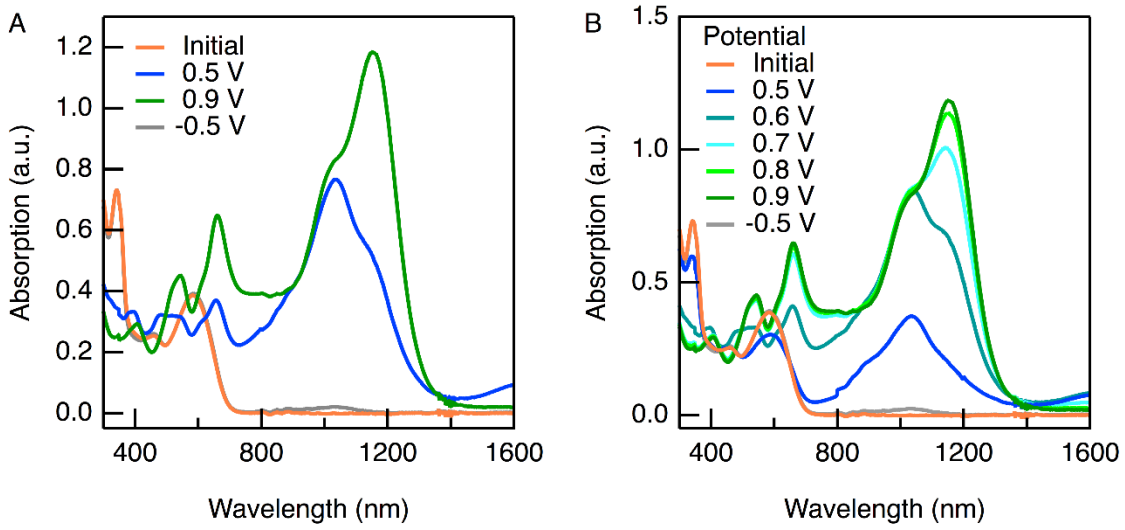


fig. S2. Steady-state linear absorption spectroscopy of TBTP obtained in a spectroelectrochemical setup. Steady-state linear absorption of **TBTP** in dichloromethane (1×10^{-4} M) obtained in a spectroelectrochemical setup, using a gold honeycomb electrode as the working electrode, a Pt plate as the counter electrode (Au electrode and Pt electrodes are built on a single chip with a Teflon frame), Ag/AgCl electrode as the reference, and tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The absorption spectra were recorded as a function of potential applied to the working electrode relative to the reference electrode. A) Select spectra at key applied potentials. B) All recorded spectra showing reversible switching. All the potentials are reported versus ferrocene [Fc+/0].

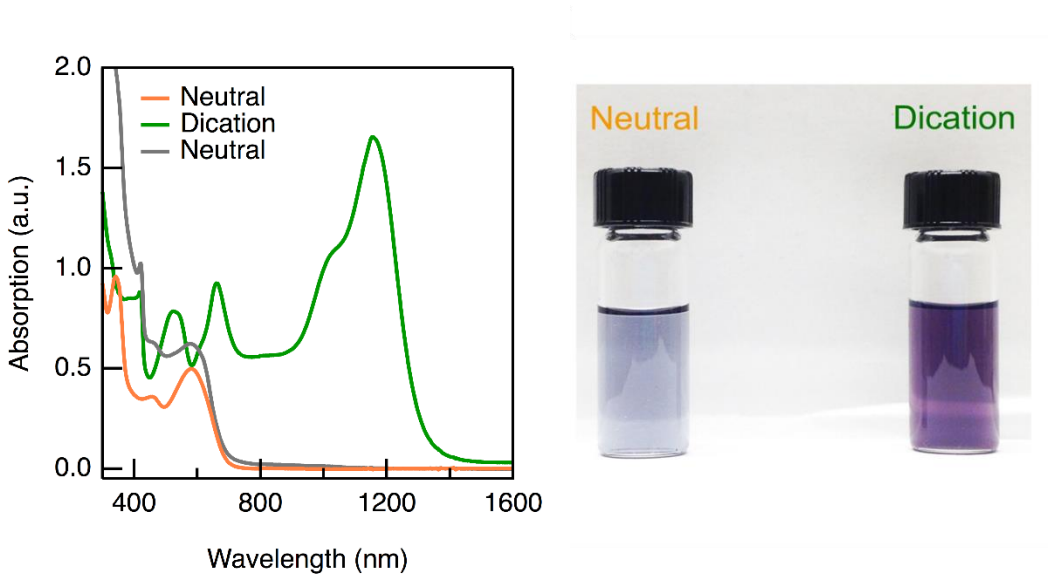


fig. S3. Steady-state linear absorption spectroscopy of TBTP and chemically oxidized TBTP dication. Steady-state linear absorption spectroscopy of neutral **TBTP** (orange) and chemically oxidized **TBTP** dication (green) in DCM (1×10^{-5} M). $AgSbF_6/I_2$ is used as the oxidant to obtain the dication, and ferrocene is used as reductant reversibly switch back to the neutral species (grey). Also shown are photograph of the neutral and dication solutions of **TBTP** in dichloromethane (1×10^{-4} M).

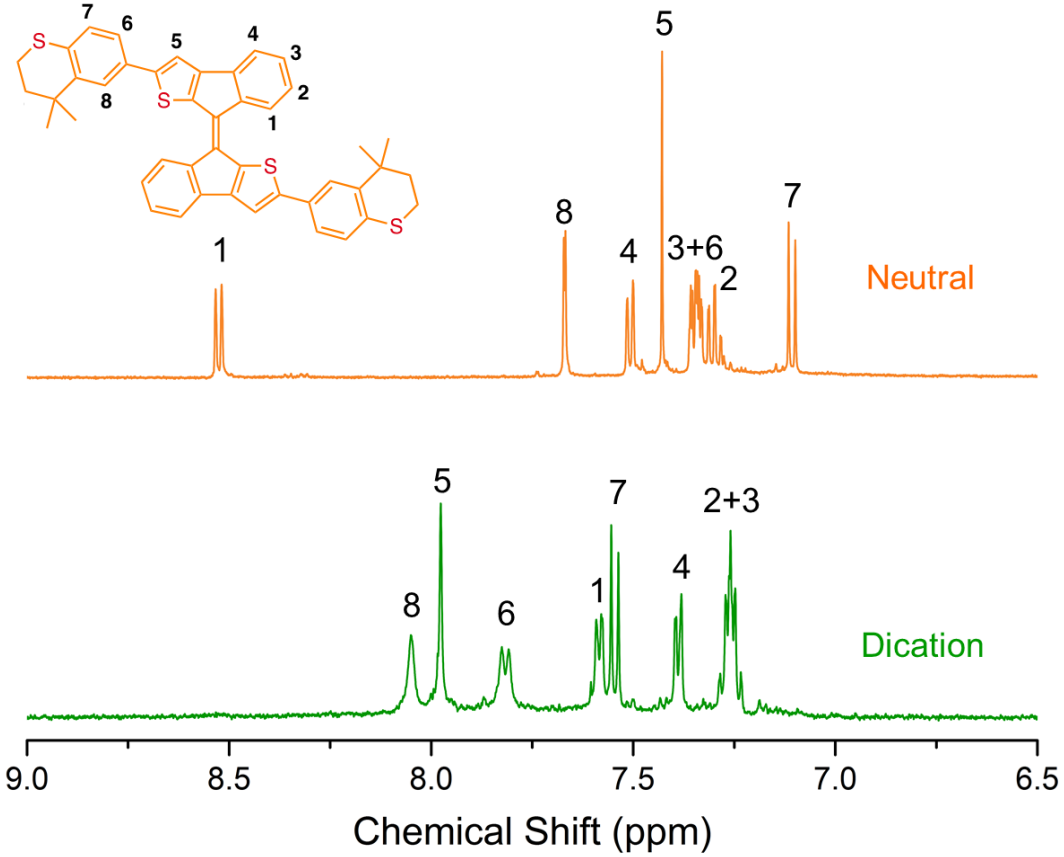


fig. S4. ^{1}H NMR of the neutral TBTP and dication obtained by chemical oxidation. ^{1}H NMR of the neutral **TBTP** (orange) and dication (green) obtained by chemical oxidation using $AgSbF_6/I_2$ in CD_2Cl_2. after oxidation to the dication, the peak at ~8.5 ppm in the neutral **TBTP** drastically shifts upfield to ~7.6 ppm in the +2 state, while the other protons on the same benzene ring also exhibit a slight upshield shift. The aromatic proton signals on thiophene and thiocroman in the +2 state are slightly shifted downfield, likely due to the positive charge on the molecule, as observed in other systems. The proton assignments were corroborated by 2D-NMR (COSY) shown below.

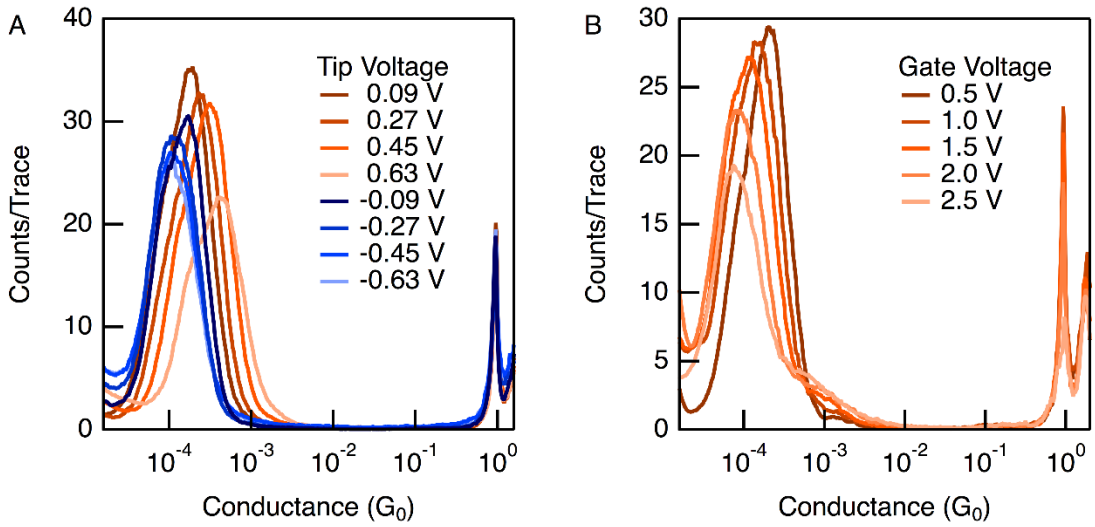


fig. S5. STM-BJ measurements of TBTP. (**A**) Logarithm-binned 1D histograms (100 bins/decade) for **TBTP** in propylene carbonate with tetrabutylammonium perchlorate (0.1 M) at tip biases ranging from -0.63 V to 0.63 V in steps of 0.18 V (tip relative to substrate). (**B**) Logarithm-binned 1D histograms for **TBTP** in propylene carbonate with tetrabutylammonium perchlorate (0.1 M) at different gate voltages (relative to substrate) as indicated in the figure.

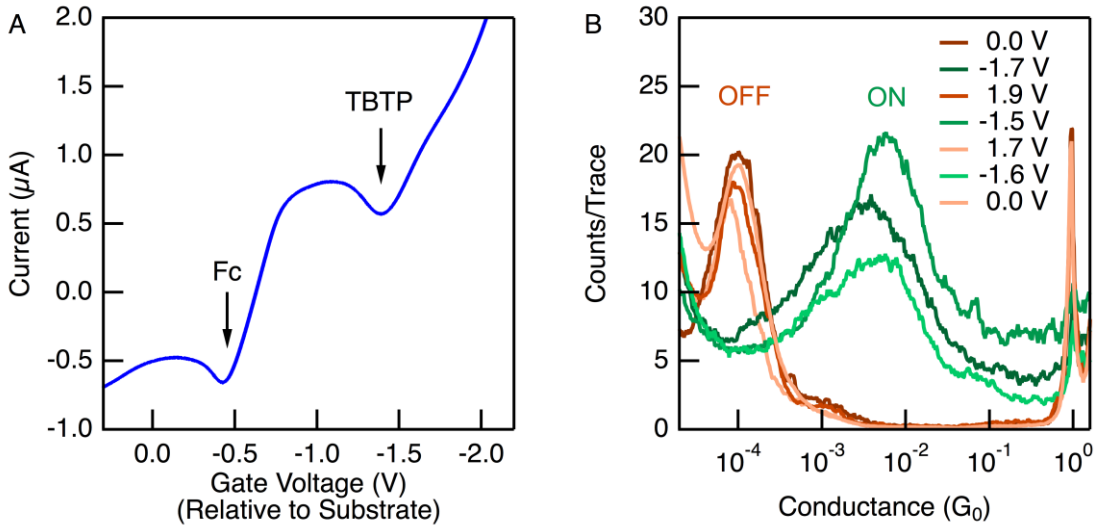


fig. S6. STM-BJ measurements of a reversible single-molecule switch and in situ LSV. (A) Logarithm-binned 1D histograms for **TBTP** in propylene carbonate with tetrabutylammonium perchlorate (0.1 M) as a function of gate voltage (applied relative to the substrate) showing reversible switching of the molecular junction conductance. **(B)** Linear Sweep Voltammetry of **TBTP** in propylene carbonate (~100 μM) with tetrabutylammonium perchlorate (0.1 M) as the electrolyte, and ferrocene (~10 μM) as internal reference. The data was recorded on the STM set up used for conductance measurement with a gold tip, coated with Apiezon wax as the working electrode, and a Pt gate electrode. As the gate potential is swept relative to substrate, the oxidation of ferrocene and **TBTP** were observed, and found at -0.4 V and -1.4 V, respectively as indicated by the arrows in the figure.

table S1. DFT calculation (GIAO-B3LYP/6-31G) of ^{1}H NMR of TBTP and TBTP^{2+}.** The ^{1}H NMR peak at carbon 1 moves largely upfield from 8.65 ppm to 7.35 ppm upon oxidation, while the others (carbon 2 through 7) move slightly downfield.

Label of protons	Chemical Shift (ppm)	
	Neutral	Dication
1	8.65	7.35
2	7.24	7.44
3	7.29	7.45
4	7.41	7.48
5	7.26	7.47
6	7.48	7.57
7	7.18	7.72
8	7.81	7.80

table S2. DFT-based NICS calculations of the aromaticity of rings. a, b and c as indicated in table S1. We see in general that the NICS value becomes more positive for all four rings (labeled a, b c and d in the figure adjacent to table S1) and is most positive for ring b, which is at the core of the **BTP** unit.

Type	**Redox States**	**a**	**b**	**c**	**d**
NICS(1)_zz	Neutral	-18.46	11.54	-13.70	-20.20
	Dication	-6.88	33.05	2.40	-12.34
NICS(0)	Neutral	-5.73	4.15	-16.55	-5.08
	Dication	-0.95	13.23	-10.64	-3.98

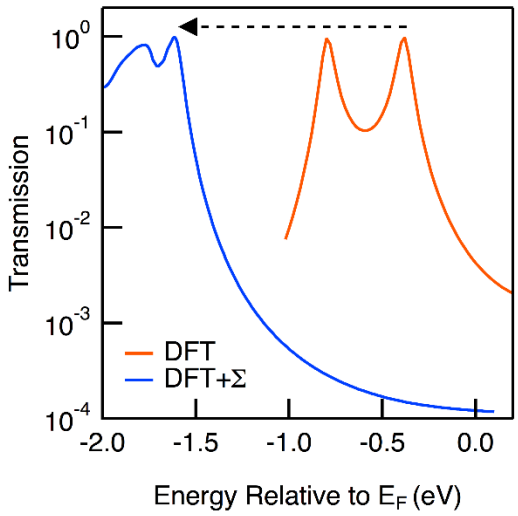


fig. S7. Transmission calculations for the neutral TBTP molecule using standard DFT methods and with DFT + Σ. Transmission as a function of energy for the neutral **TBTP** molecule using standard DFT (orange) methods and with DFT+Σ (blue). The zero-bias conductance for the PBE calculation is 4.8×10^{-3} G_0 while DFT+Σ yields a conductance of 1.2×10^{-4} G_0, in good agreement with experimental value of about 2×10^{-4} G_0 at a low bias. The good agreement on conductance suggests that our modeling of the junction geometry is realistic and can be compared to the experiment.

DFT-optimized coordinates

Cartesian Coordinates for Optimized Structures with Gaussian 09 at B3LYP/6-31G** for **TBTP** and **TBTP** dication.

TBTP

Element	Coordinates (angstroms)			Element	Coordinates (angstroms)		
	X	Y	Z		X	Y	Z
C	1.77444	-0.79019	-0.85003	C	-9.59047	-1.59036	1.2594
C	0.36283	-0.5882	-1.14857	C	-10.55483	-0.41131	1.25146
C	-0.15943	-1.96886	-1.35954	S	-9.80573	1.06609	2.02407
C	0.88253	-2.90828	-1.12313	C	7.43596	2.64628	0.65386
C	-0.36282	0.58844	-1.1485	C	8.71836	1.40072	-1.11413
C	0.15943	1.96914	-1.35929	C	-7.43562	-2.64649	0.65385
C	-0.88254	2.90852	-1.12283	C	-8.71847	-1.40102	-1.11386
C	-2.07386	2.14885	-0.75757	H	3.79488	-3.42157	-0.19188
C	-1.77444	0.79039	-0.84998	H	-3.79491	3.42169	-0.19166
C	3.37785	-2.42657	-0.29258	H	-2.16331	-1.72441	-2.13392
C	4.09363	-1.28121	0.00141	H	-2.54402	-4.14396	-2.40911
S	3.12236	0.16298	-0.29108	H	-0.7546	-5.77452	-1.88681
C	-3.37788	2.4267	-0.29244	H	1.47695	-4.98178	-1.12007
C	-4.09369	1.2813	0.00139	H	2.16338	1.7248	-2.13354
S	-3.12238	-0.16285	-0.29121	H	2.54411	4.1444	-2.40834
C	-1.37902	-2.419	-1.85972	H	0.75464	5.77487	-1.88595
C	-1.58677	-3.79433	-2.03435	H	-1.47697	4.98202	-1.1195
C	-0.577	-4.71245	-1.74566	H	-5.80767	-0.78001	-0.30122
C	0.67621	-4.27079	-1.30235	H	-7.82368	2.9787	2.15519
C	1.37907	2.41935	-1.8593	H	-5.4872	3.13175	1.42128
C	1.58683	3.79471	-2.03371	H	5.80791	0.77978	-0.30158
C	0.57704	4.71278	-1.74497	H	7.82321	-2.97858	2.15595
C	-0.67622	4.27106	-1.30182	H	5.48672	-3.13146	1.42194
C	5.47025	-1.17711	0.48701	H	9.29156	1.79299	2.29383
C	-5.47033	1.17714	0.4869	H	10.12347	2.48093	0.90221
C	-6.2499	0.03293	0.26438	H	11.44272	0.62796	1.85086
C	-7.57196	-0.10647	0.70965	H	10.88916	0.16295	0.23985
C	-8.14443	0.99228	1.3856	H	-9.29089	-1.7931	2.2943
C	-7.37423	2.14561	1.62198	H	-10.12292	-2.48155	0.903
C	-6.06181	2.23941	1.19583	H	-11.44239	-0.62872	1.85164
C	6.24999	-0.03307	0.26426	H	-10.8895	-0.16407	0.2403
C	7.57203	0.10627	0.70963	H	7.06536	2.64855	1.68354
C	8.14429	-0.9924	1.38587	H	6.57323	2.69717	-0.01499
C	7.37391	-2.14556	1.6225	H	8.01654	3.56232	0.49936
C	6.06151	-2.23928	1.19628	H	9.36114	0.55153	-1.36361
C	8.32667	1.41096	0.38365	H	9.24925	2.32258	-1.37943

C	9.59087	1.58995	1.25891	H	7.82904	1.32922	-1.74736
C	10.55489	0.41063	1.25103	H	-7.06488	-2.64879	1.68347
S	9.80559	-1.06629	2.02435	H	-6.57299	-2.69729	-0.01513
C	-8.32648	-1.41125	0.38383	H	-8.01616	-3.56257	0.49938
H	-9.24945	-2.32286	-1.37906	H	-9.36127	-0.5518	-1.36323
H	-7.82927	-1.32954	-1.74725				

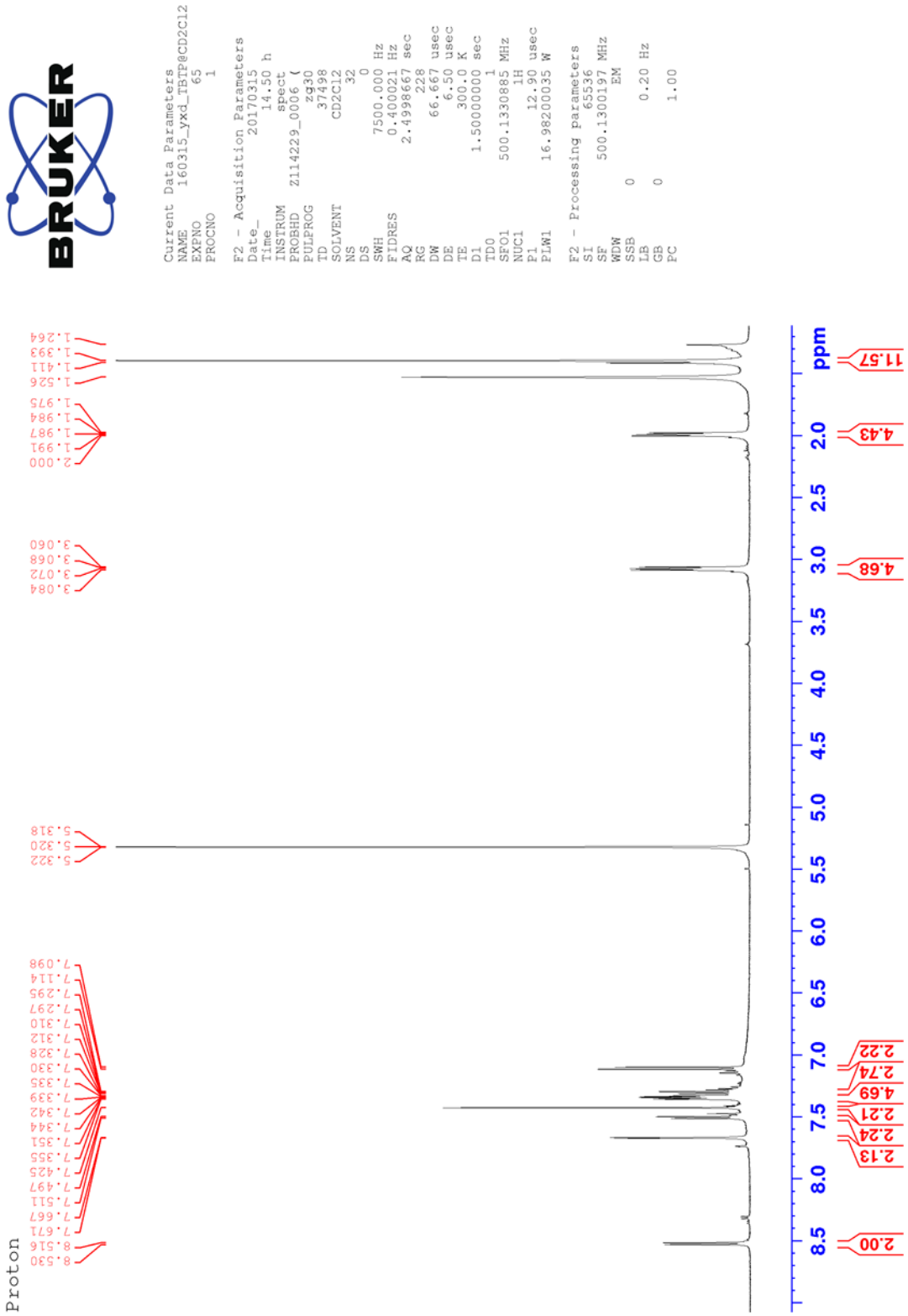
TBTP Dication

Element	Coordinates (angstroms)			Element	Coordinates (angstroms)		
	X	Y	Z		X	Y	Z
C	1.70455	-0.77494	-1.23423	C	8.65833	1.42946	2.78662
C	0.38613	-0.60556	-1.63643	C	9.89418	0.57365	2.54907
C	-0.10877	-1.96585	-2.01189	S	9.48568	-1.13547	2.02021
C	0.92124	-2.91471	-1.7741	C	-7.71195	-1.56439	1.56728
C	-0.38612	0.6056	-1.63643	C	-8.65832	-1.42951	2.78659
C	0.10876	1.9659	-2.01188	C	-9.89418	-0.57371	2.54906
C	-0.92125	2.91475	-1.77406	S	-9.48567	1.13543	2.02024
C	-2.06603	2.17099	-1.25165	C	6.60689	2.56576	1.96237
C	-1.70455	0.77497	-1.23422	C	8.47517	2.12235	0.3392
C	3.32171	-2.42369	-0.76176	C	-6.60688	-2.56581	1.96233
C	3.99874	-1.24378	-0.32696	C	-8.47516	-2.12235	0.33916
S	2.99326	0.19607	-0.55436	H	3.76307	-3.40853	-0.68842
C	-3.32171	2.42371	-0.76171	H	-3.76307	3.40854	-0.68836
C	-3.99874	1.24379	-0.32694	H	-2.07474	-1.65227	-2.85288
S	-2.99326	-0.19605	-0.55436	H	-2.40548	-4.05327	-3.36611
C	-1.29704	-2.36501	-2.60258	H	-0.63352	-5.70625	-2.89012
C	-1.47679	-3.731	-2.90696	H	1.53418	-4.98023	-1.90454
C	-0.47848	-4.66124	-2.64437	H	2.07472	1.65233	-2.8529
C	0.74648	-4.25443	-2.08057	H	2.40545	4.05333	-3.3661
C	1.29702	2.36506	-2.60258	H	0.63349	5.70631	-2.89006
C	1.47677	3.73106	-2.90694	H	-1.53419	4.98026	-1.90447
C	0.47846	4.66129	-2.64433	H	-5.27742	-0.9679	0.5325
C	-0.74649	4.25447	-2.08052	H	-7.94003	3.16301	1.06098
C	5.30332	-1.16956	0.22977	H	-5.71711	3.31443	0.08953
C	-5.30331	1.16955	0.22979	H	5.27743	0.96789	0.53252
C	-5.87029	-0.06831	0.64911	H	7.94003	-3.16303	1.06091
C	-7.13478	-0.19007	1.19498	H	5.71711	-3.31443	0.08946
C	-7.895	1.01553	1.34661	H	8.09783	1.0385	3.64364
C	-7.34722	2.26245	0.93518	H	9.00565	2.43003	3.06702
C	-6.09413	2.3451	0.39101	H	10.4718	0.44636	3.46796
C	5.87029	0.0683	0.6491	H	10.55692	1.00144	1.79326
C	7.13479	0.19005	1.19498	H	-8.09783	-1.03858	3.64362

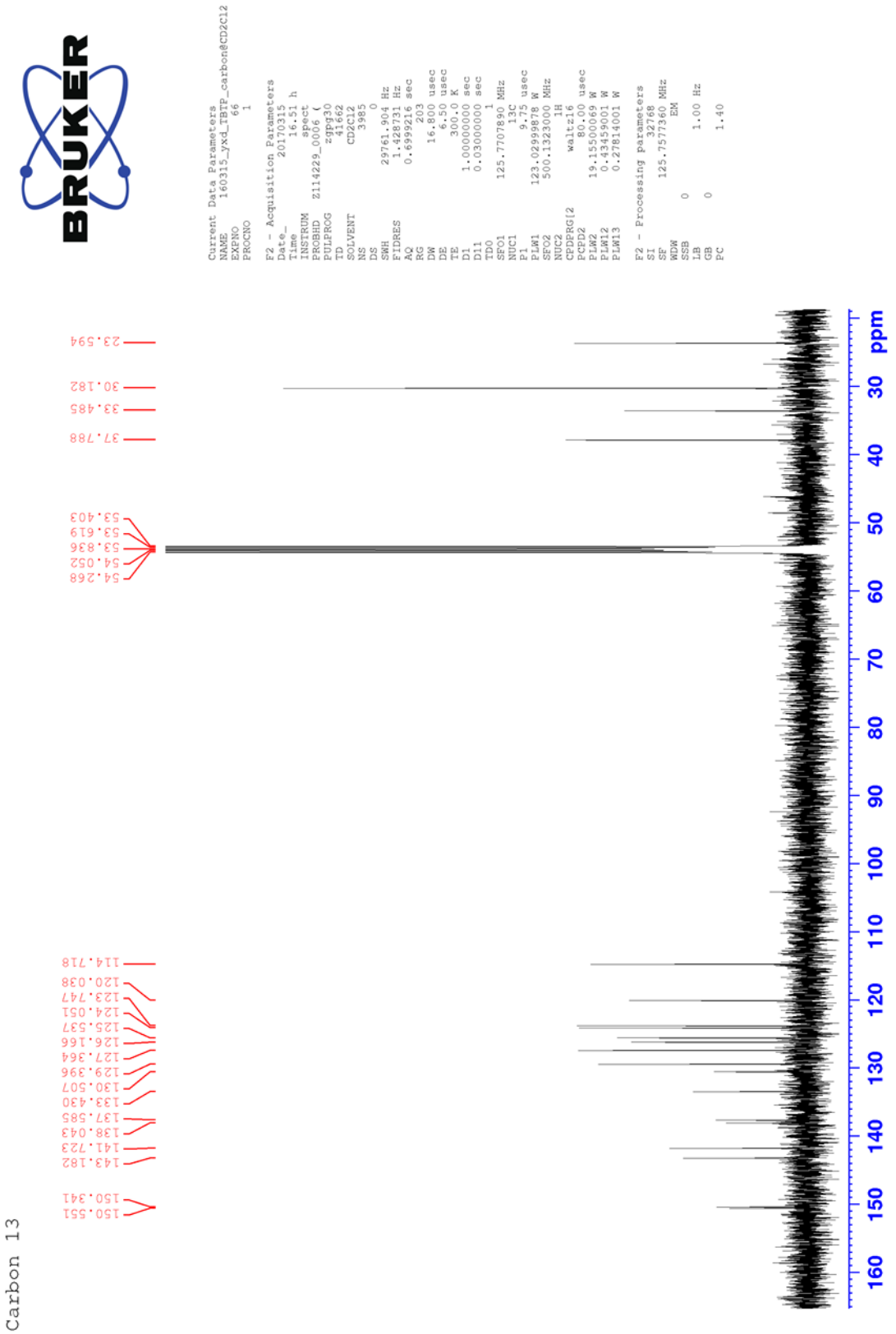
C	7.89501	-1.01556	1.34659	H	-9.00564	-2.43009	3.06697
C	7.34723	-2.26247	0.93513	H	-10.47179	-0.44644	3.46795
C	6.09413	-2.34511	0.39096	H	-10.55691	-1.00148	1.79324
C	7.71195	1.56436	1.56731	H	5.984	2.18302	2.77701
H	-5.98399	-2.18307	2.77697	H	5.95861	2.82668	1.121
H	-5.95861	-2.82671	1.12095	H	7.06673	3.49829	2.30096
H	-7.06673	-3.49834	2.3009	H	9.24451	1.43641	-0.02642
H	-9.24451	-1.4364	-0.02645	H	8.95737	3.07215	0.59251
H	-8.95736	-3.07216	0.59245	H	7.78529	2.30572	-0.48974
H	-7.78529	-2.30572	-0.48978				

NMR and mass spectroscopy data

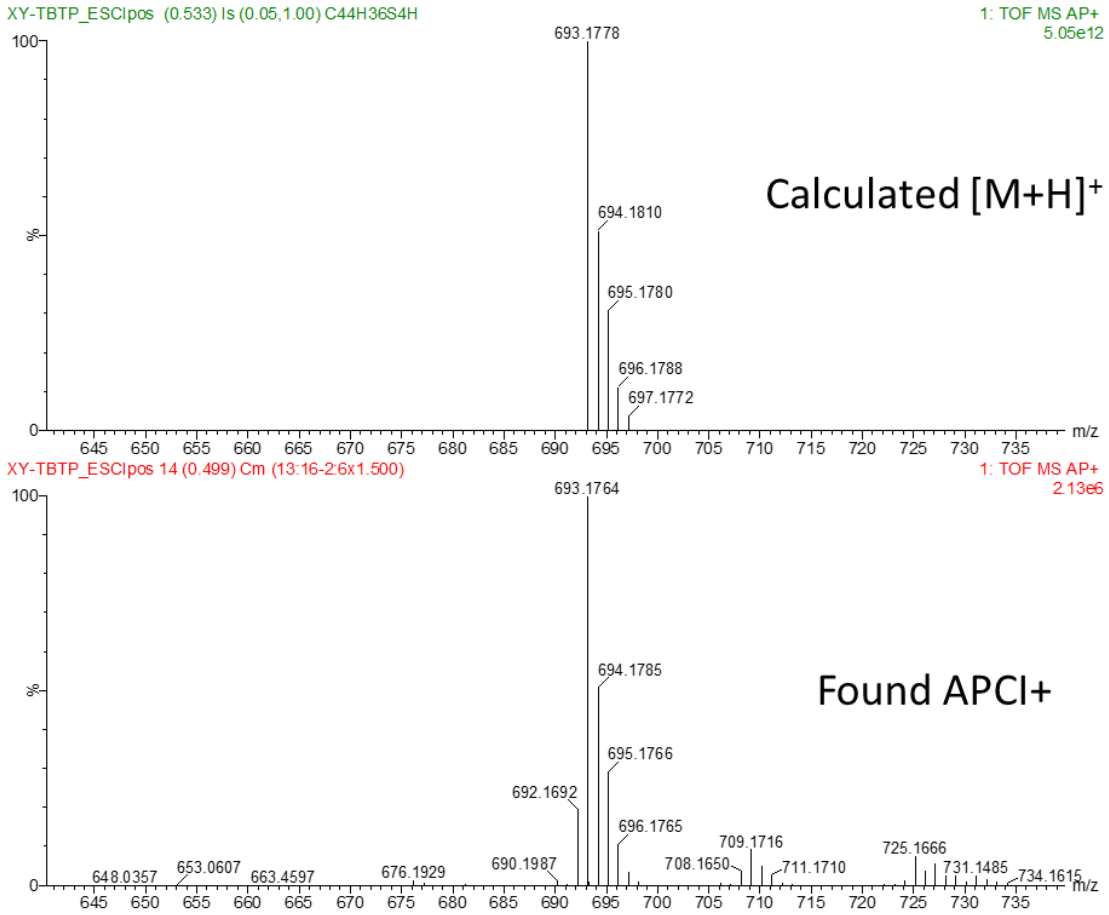
^{1}H NMR of **TBTP** (CD_2Cl_2, 25°C)



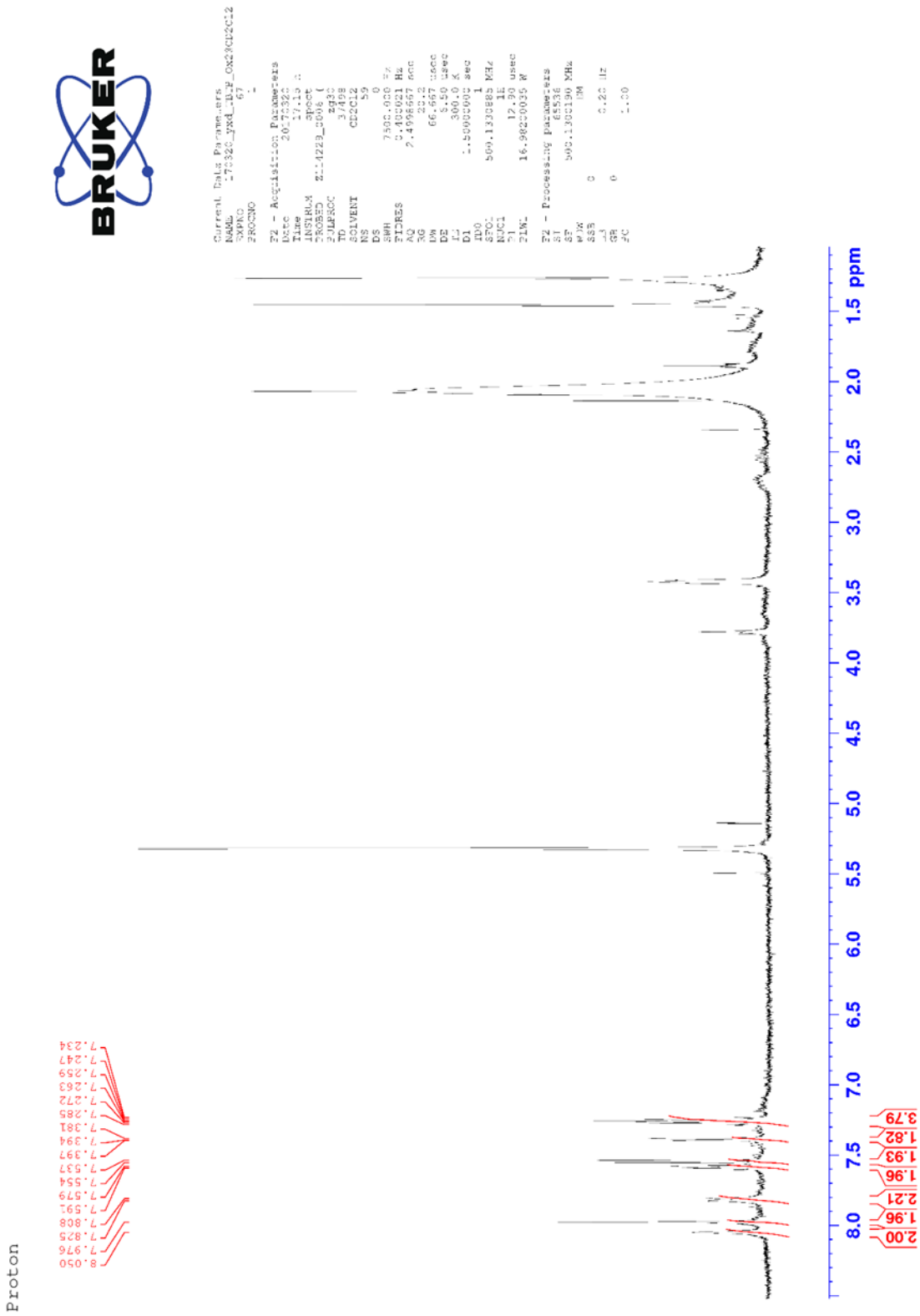
^{13}C NMR of **TBTP** (CD_2Cl_2, 25°C)



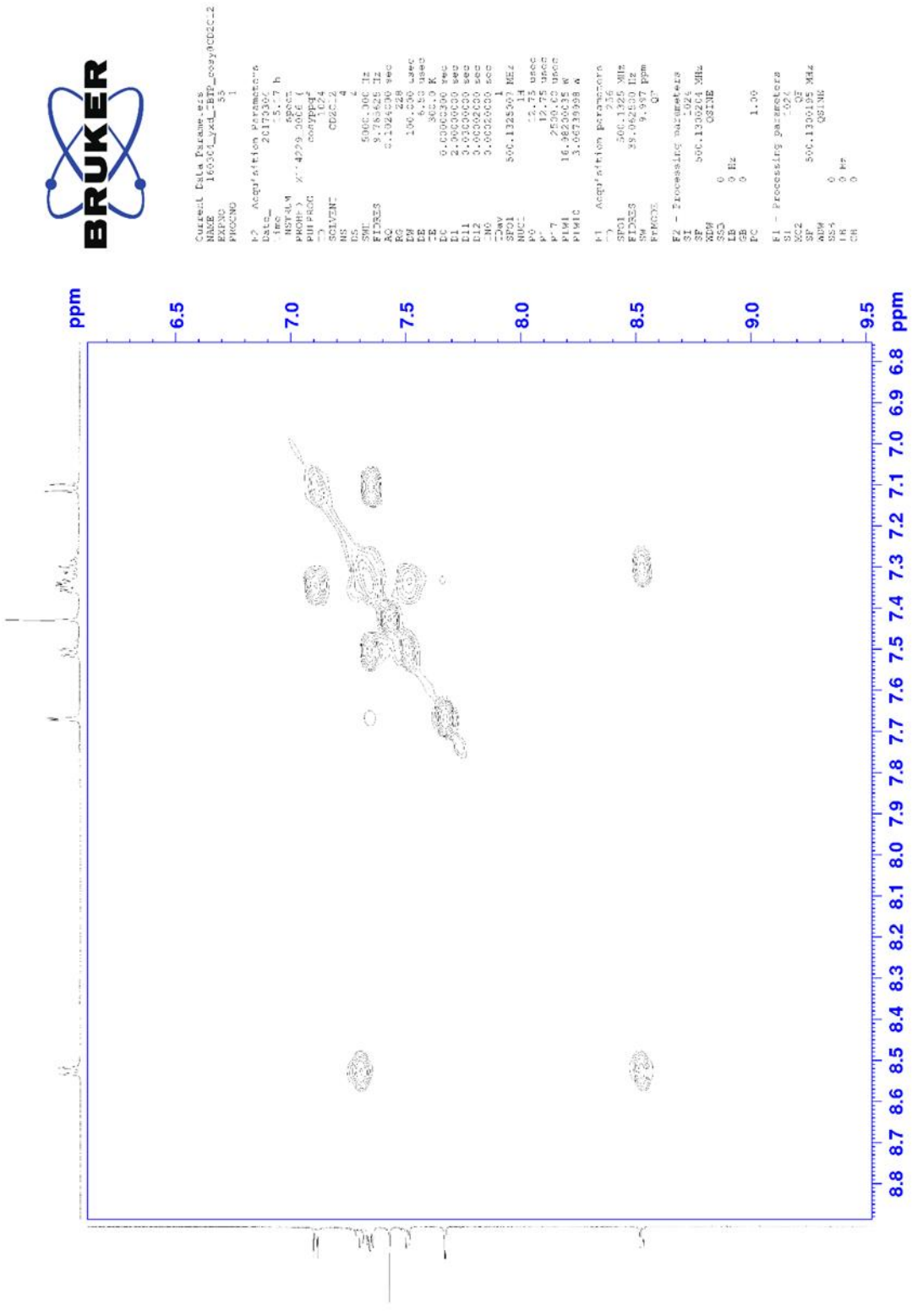
Hi-Res Mass Spectrum of **TBTP**



^{1}H NMR of **TBTP^{2+}** (CD_2Cl_2, 25°C)



COSY Spectrum of **TBTP** (CD_2Cl_2, 25°C)



COSY Spectrum of **TBTP**$^{2+}$ (CD_2Cl_2, 25°C)