Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Synthesis and Characterization of Highly Strained Donor-Acceptor Nanohoop

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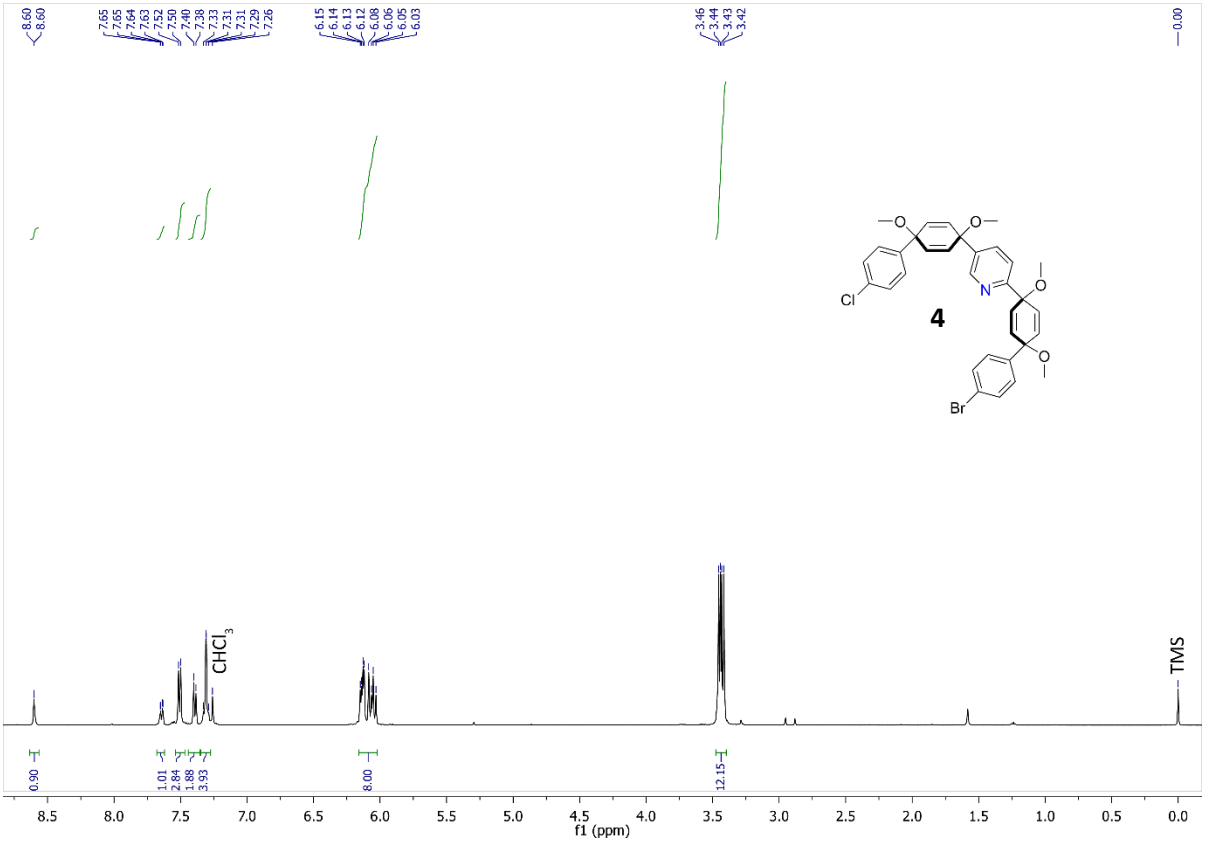
NMR Spectra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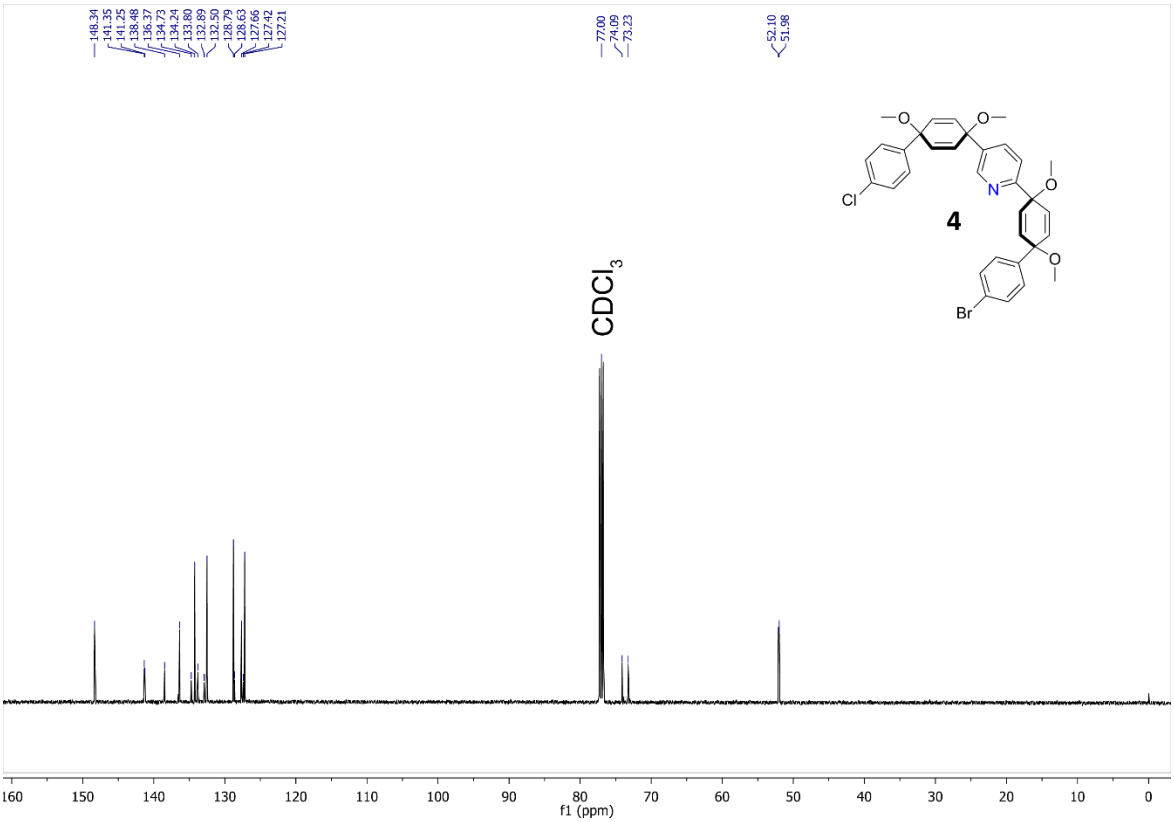
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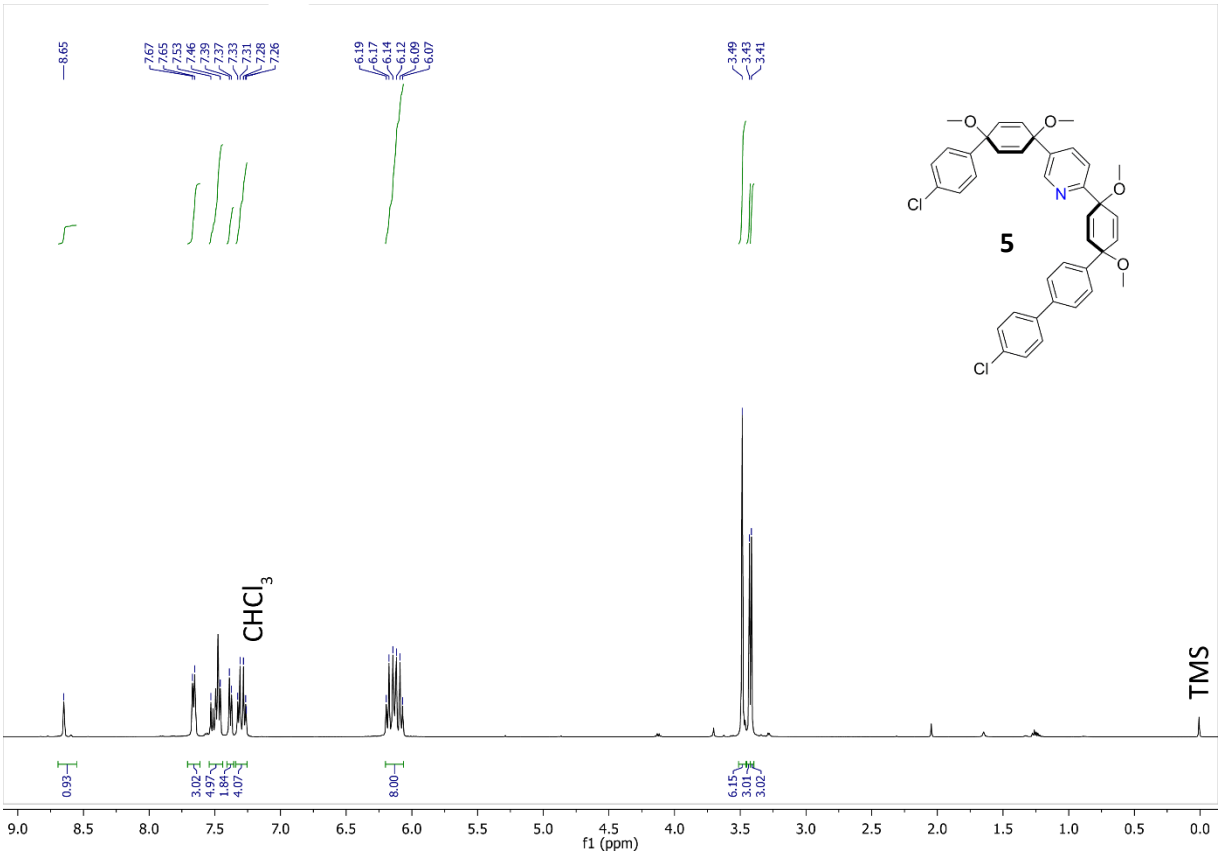
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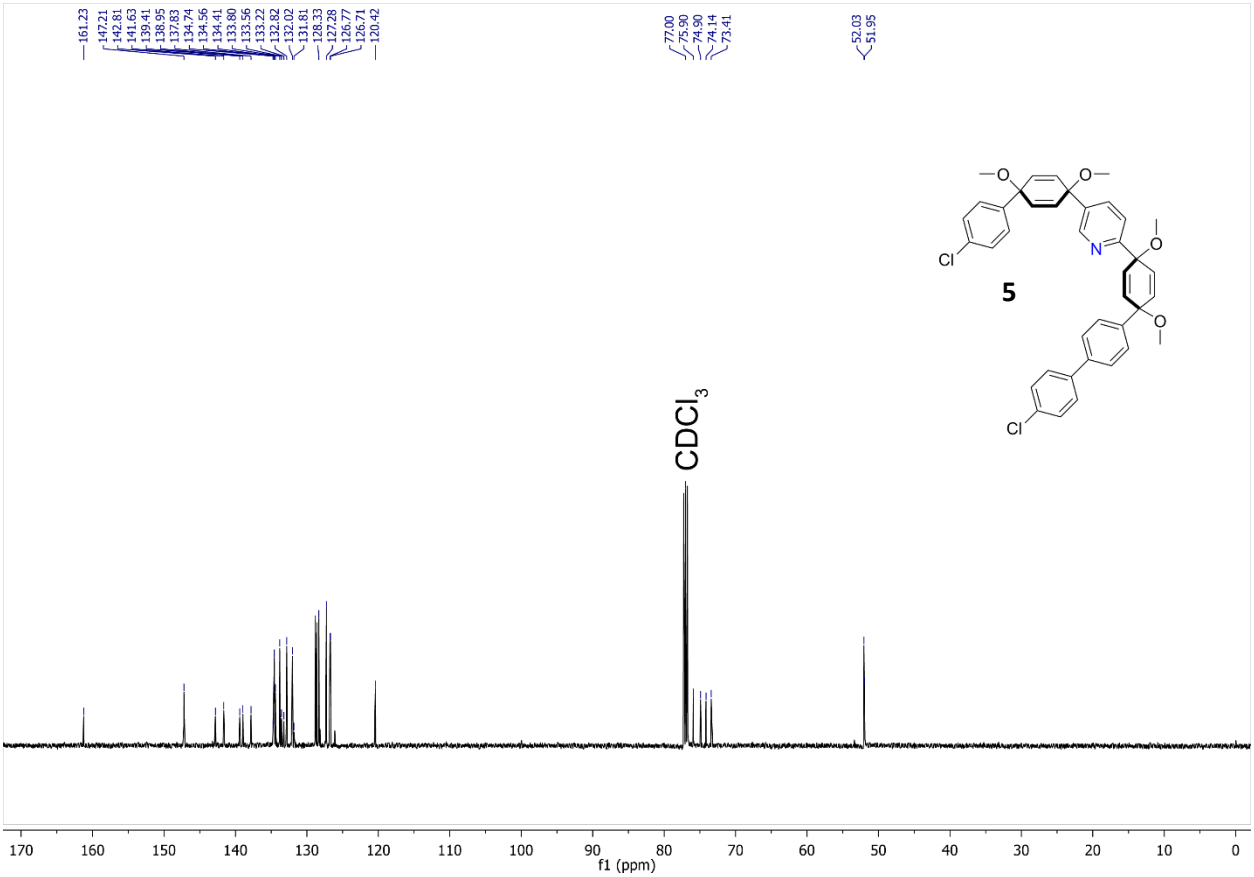
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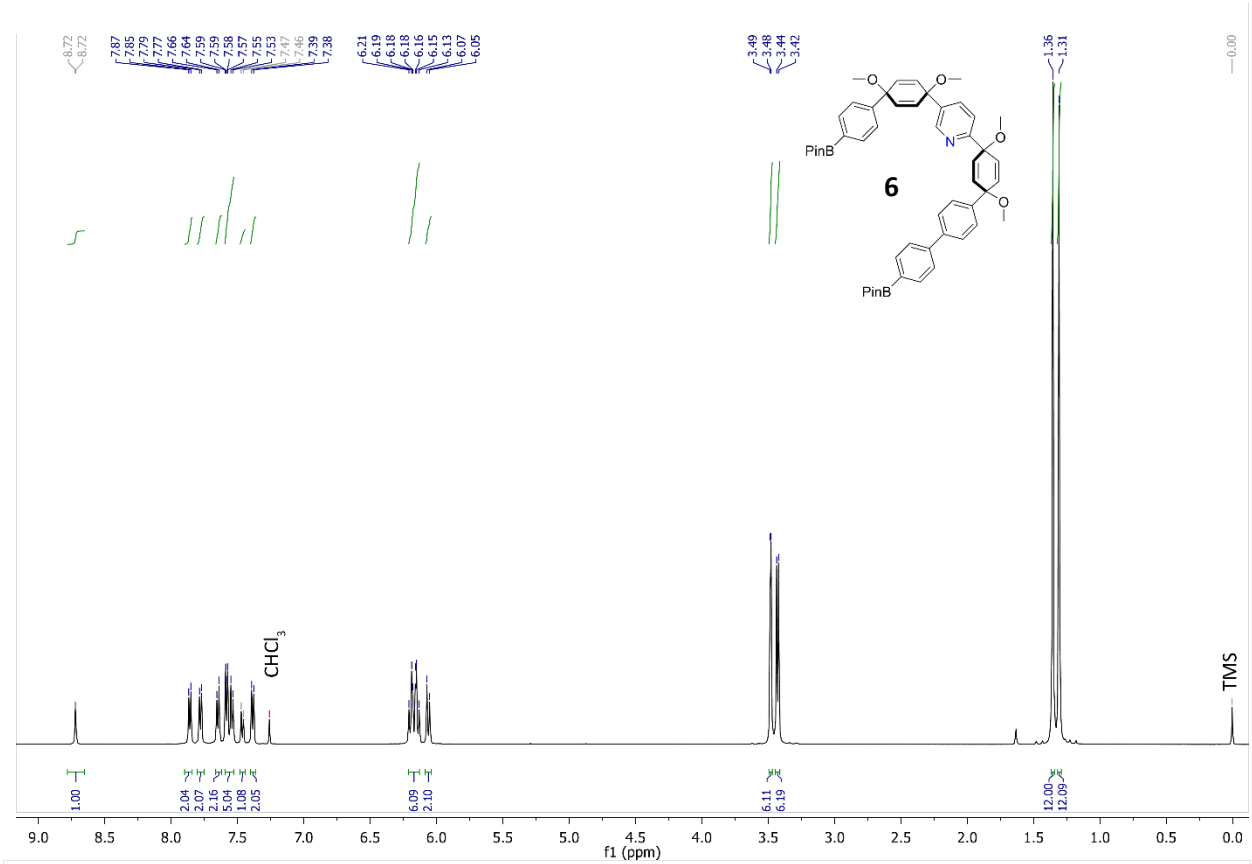
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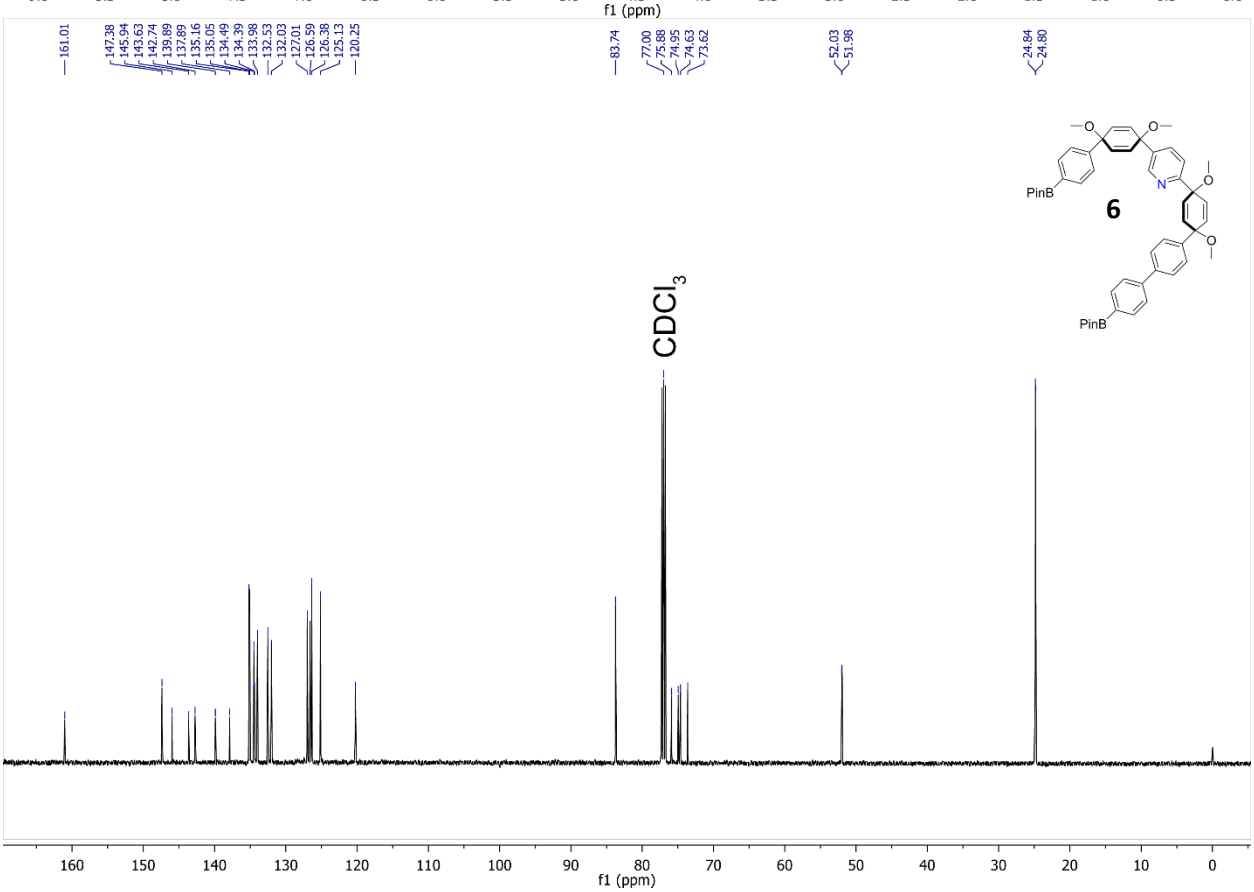
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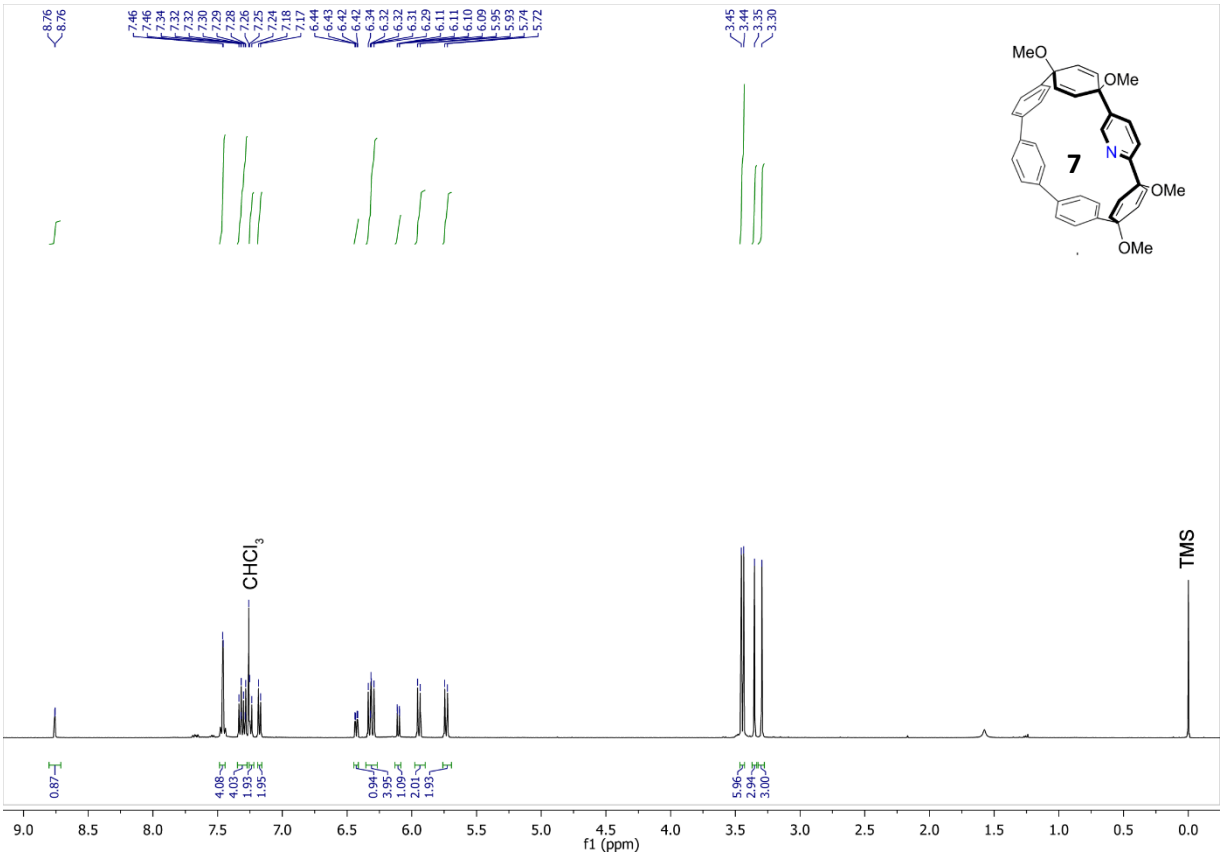
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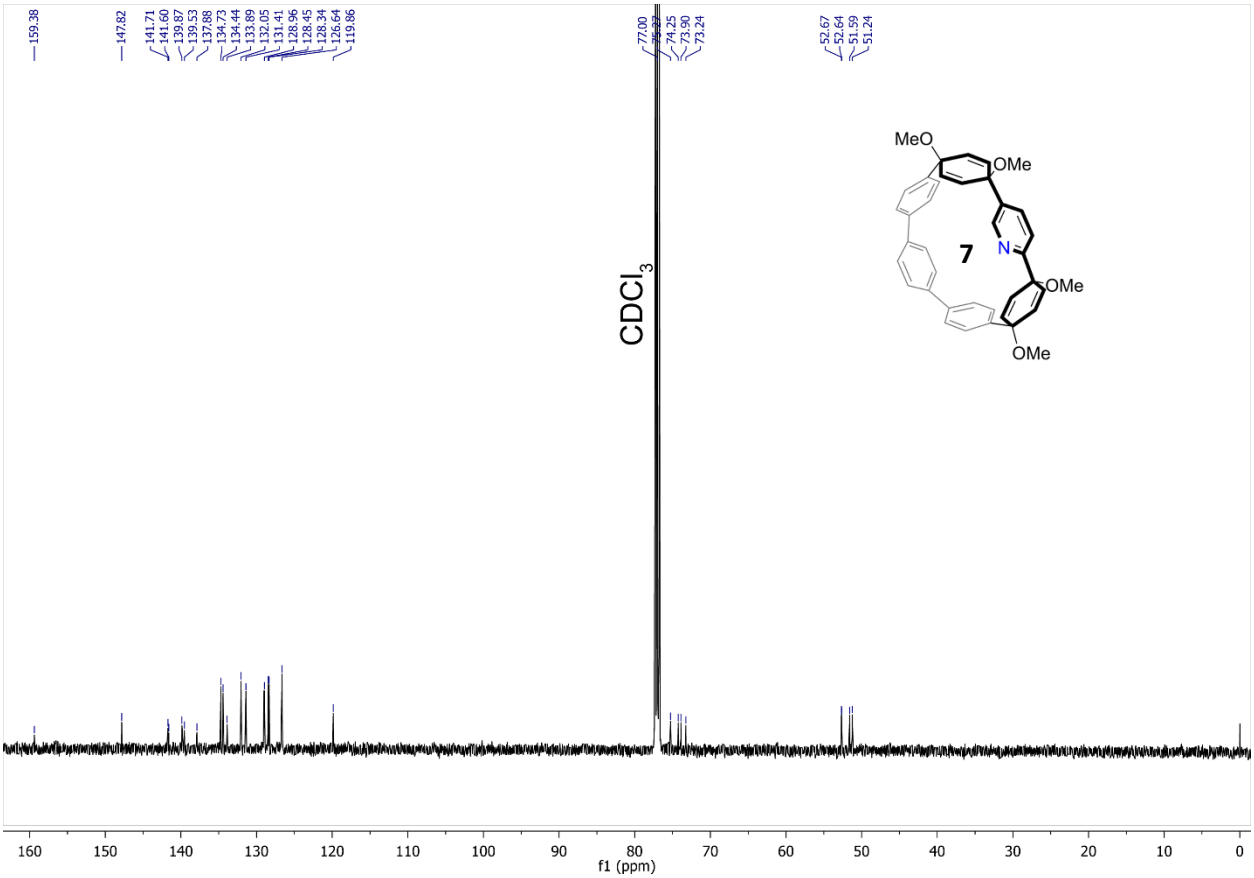
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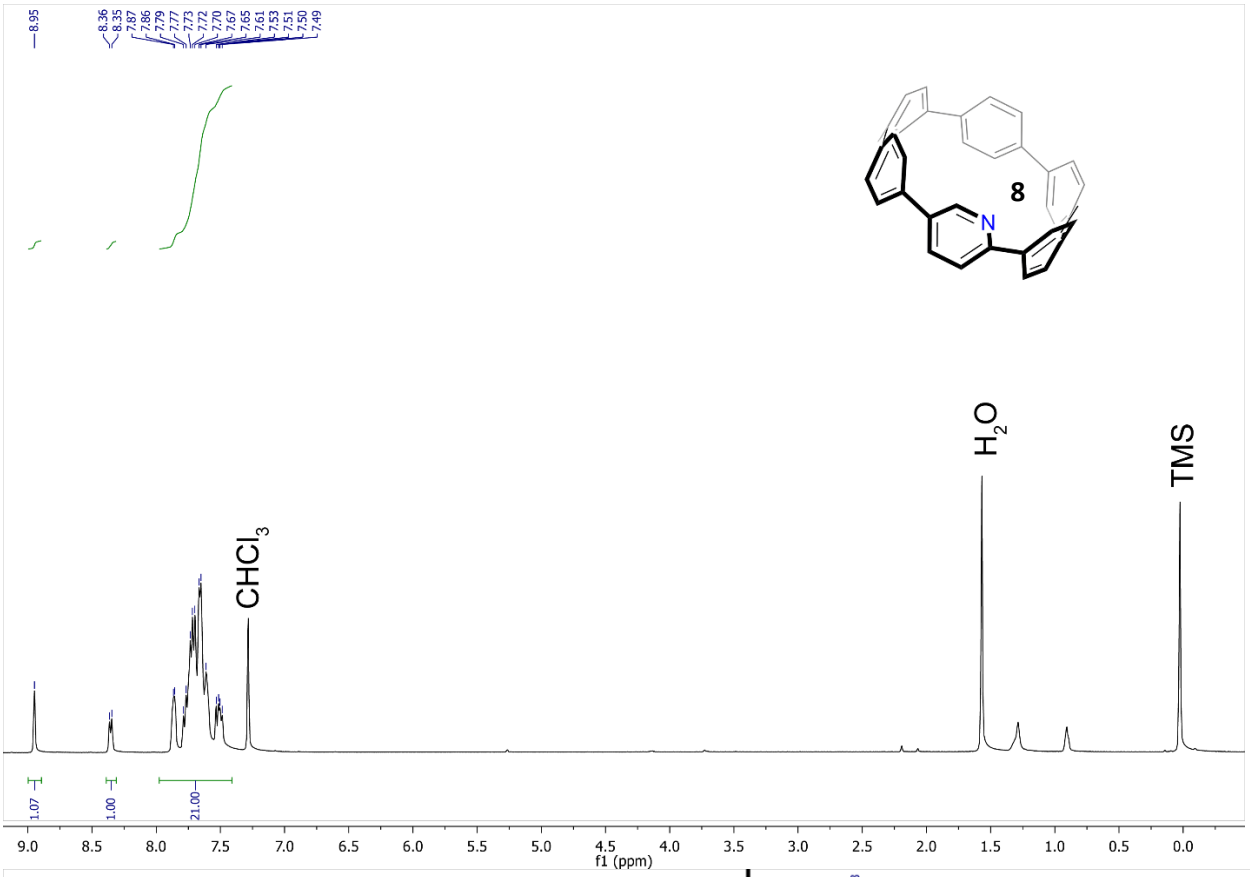
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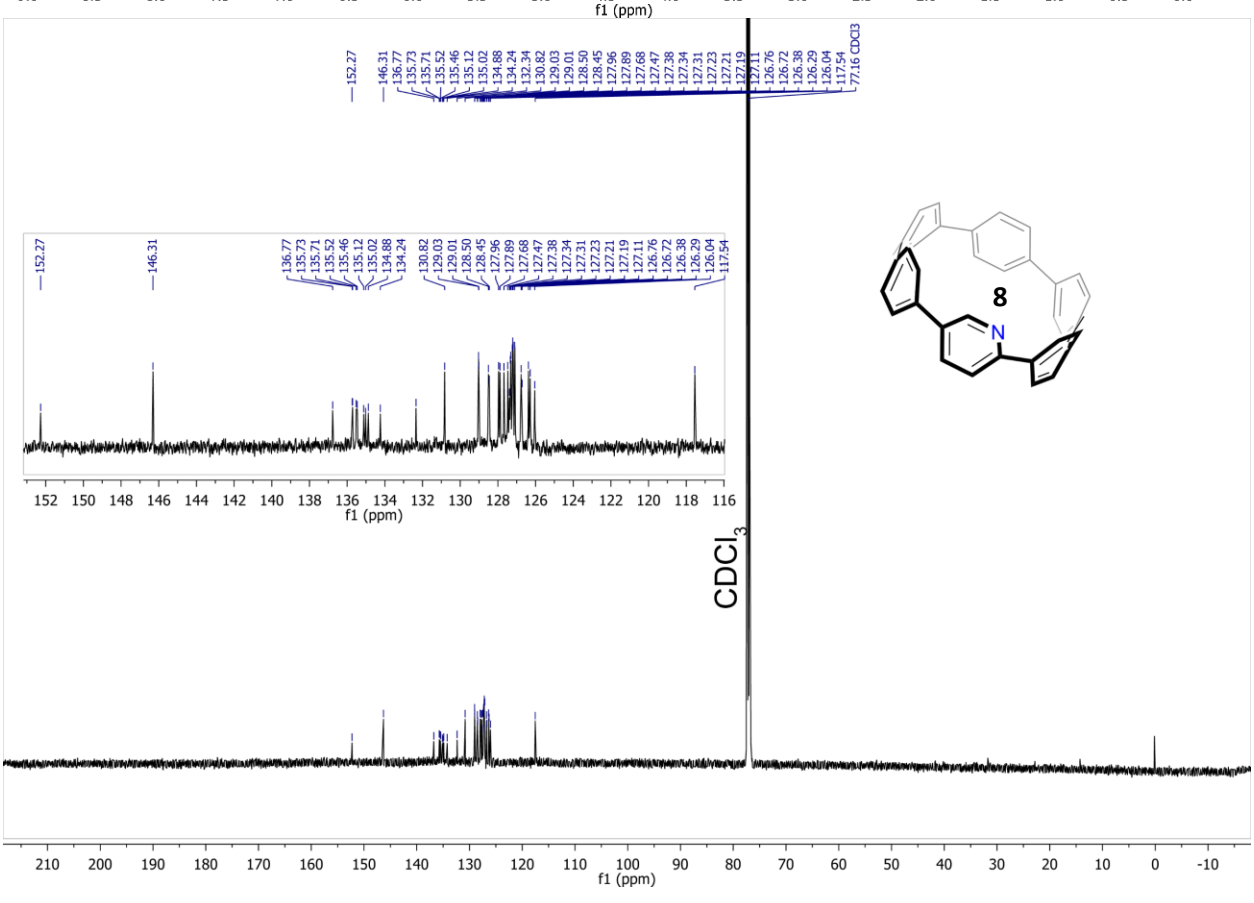
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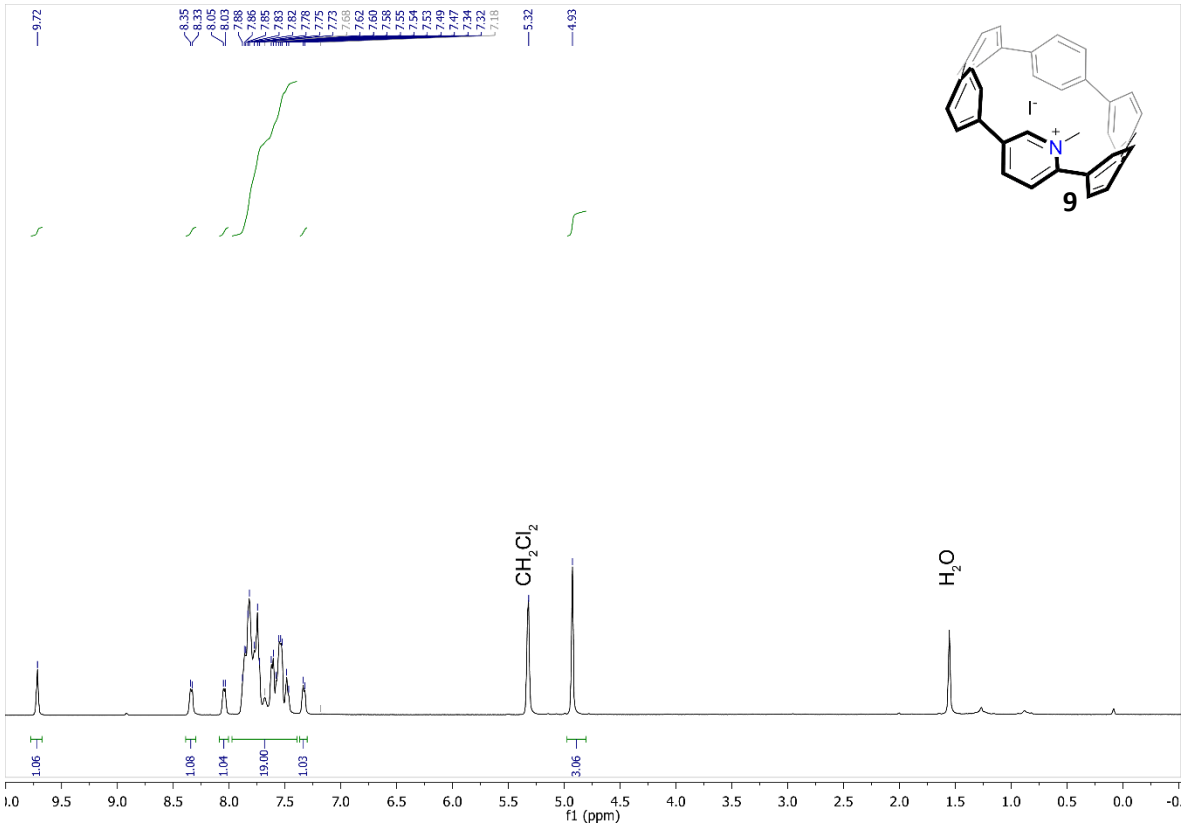
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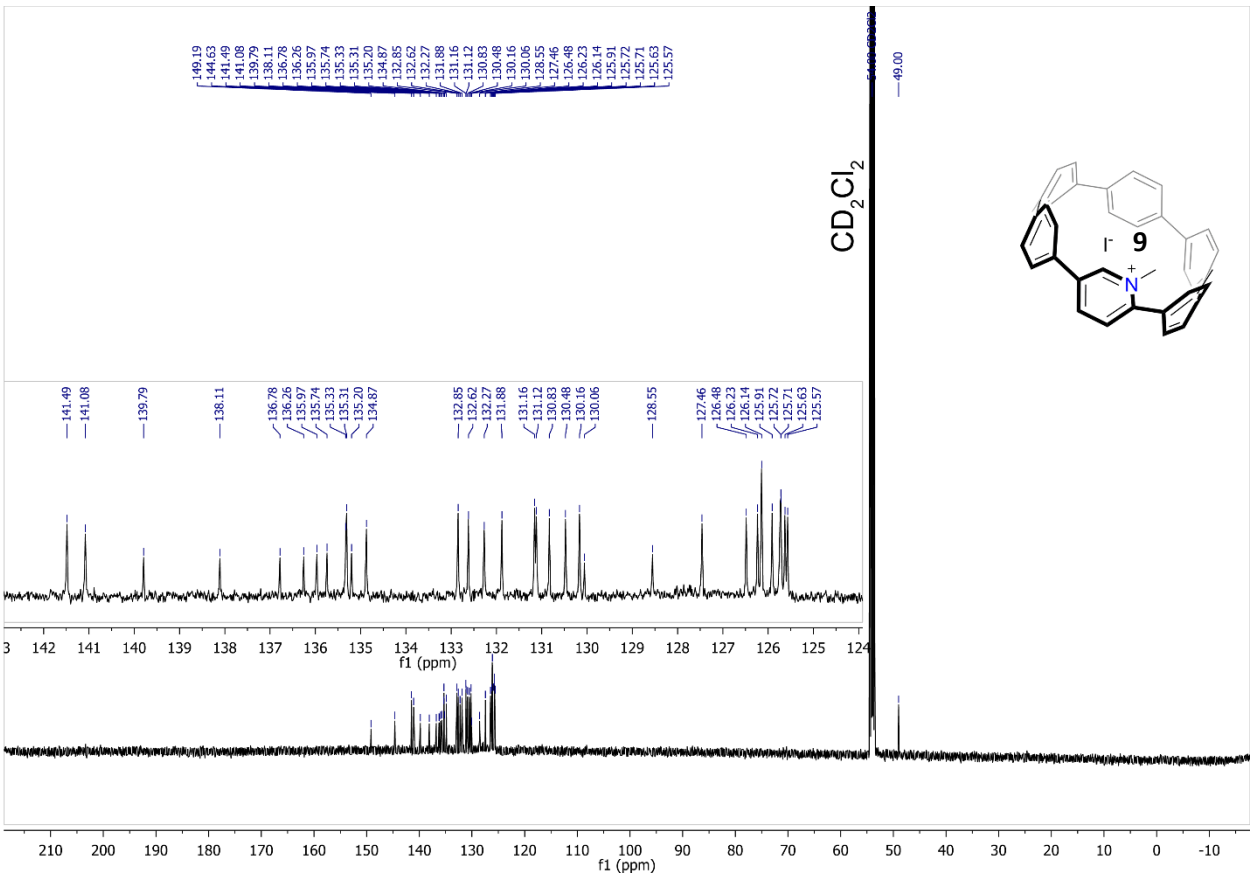
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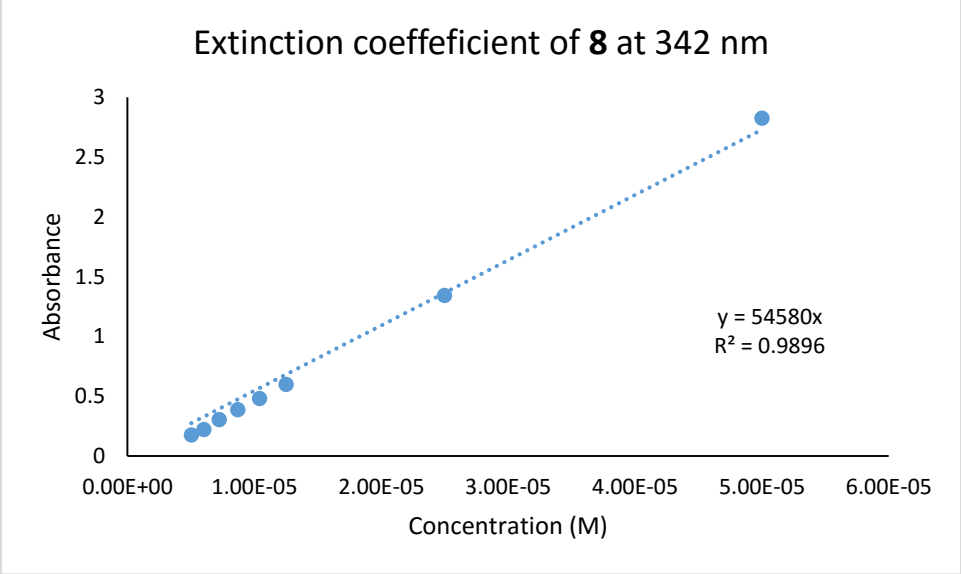
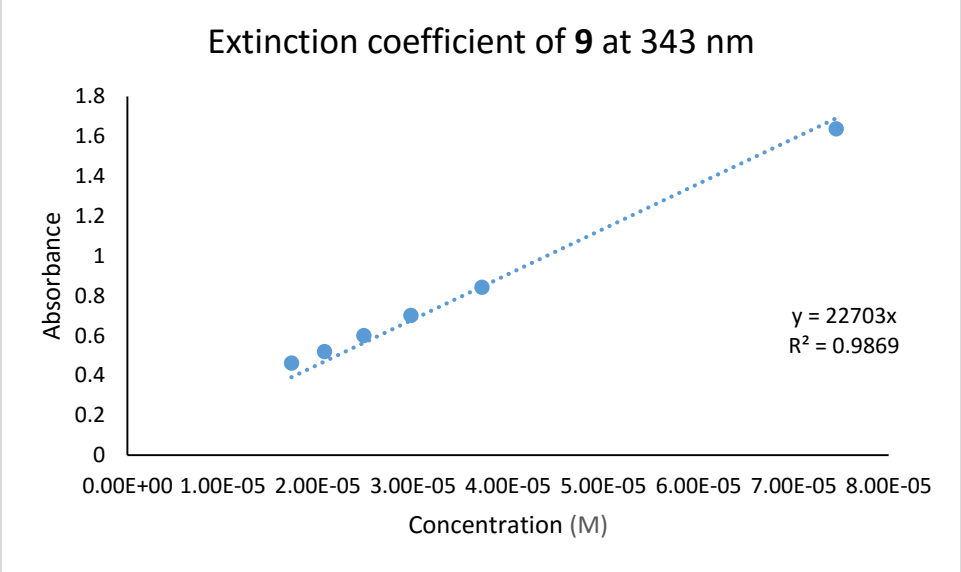
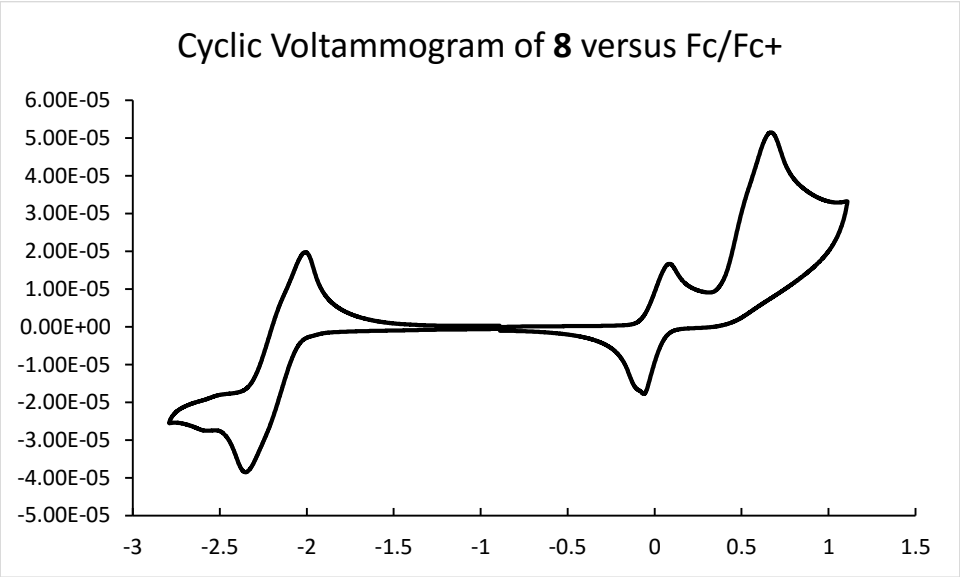


Supplementary Figure S1: Beer-Lambert Plot of **8** at 342 nm ($\varepsilon = 5.5 \times 10^4\ M^{-1}\ cm^{-1}$)

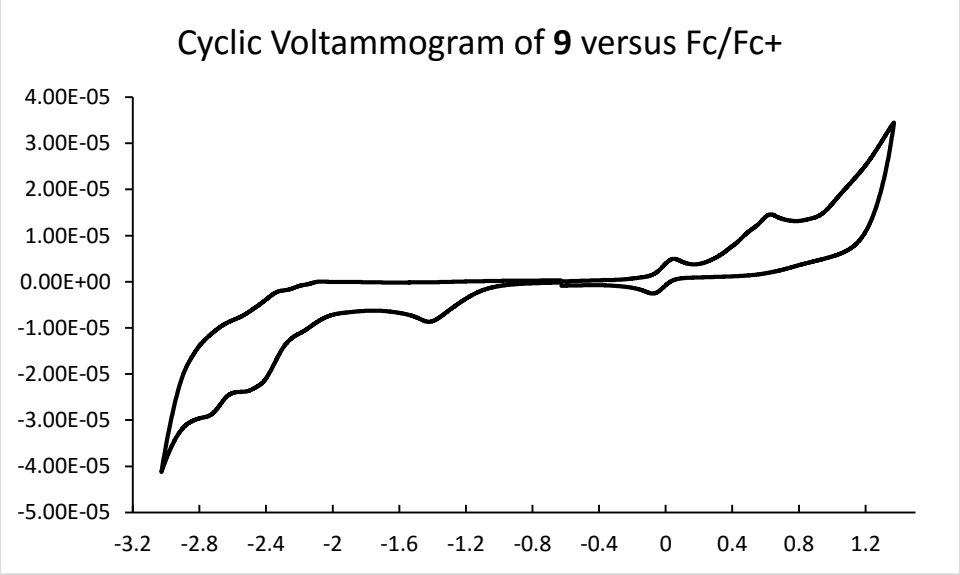


Supplementary Figure S2: Beer-Lambert Plot of **9** at 343 nm ($\varepsilon = 2.3 \times 10^4\ M^{-1}\ cm^{-1}$)

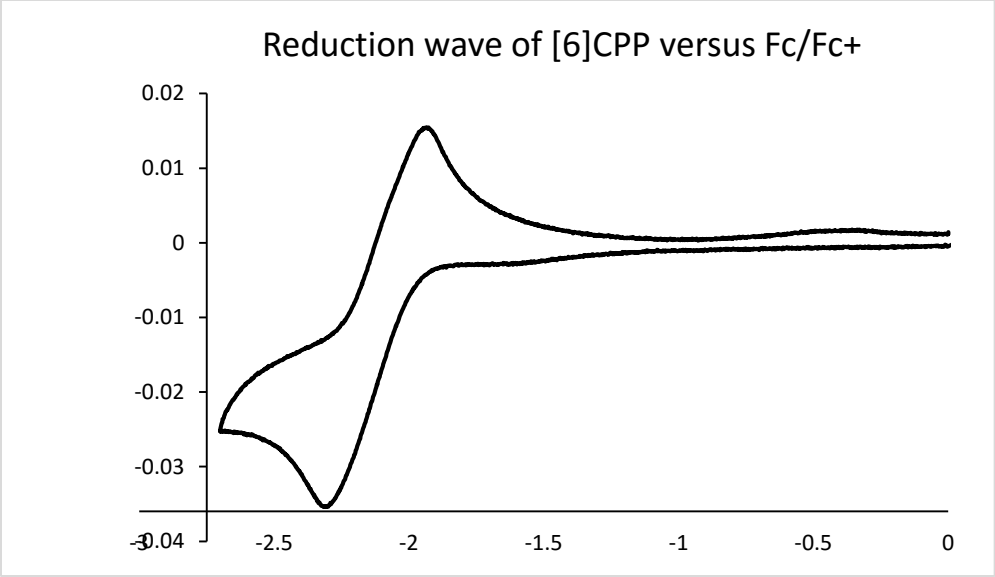
Electrochemical Data



Supplementary Figure S3: Cyclic voltammogram of **8** in THF (0.1 M tetrabutylammonium hexfluorophoshate) with ferrocene/ferrocenium added as internal standard.



Supplementary Figure S4: Cyclic voltammogram of **9** in THF (0.1 M tetrabutylammonium hexfluorophoshate) with ferrocene/ferrocenium added as internal standard.



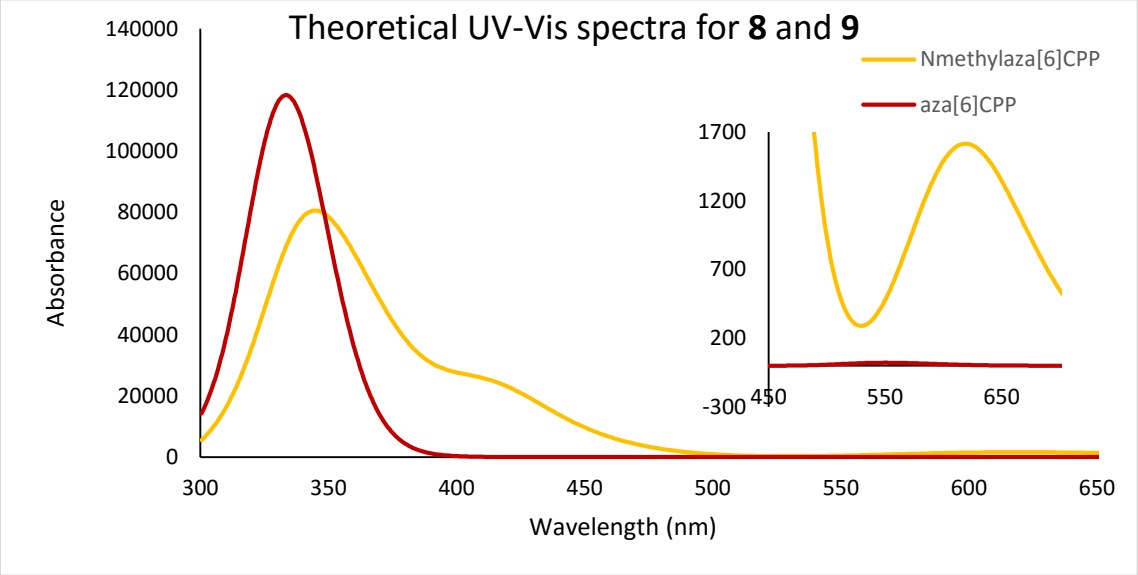
Supplementary Figure S5: Reduction wave of [6]CPP in THF (0.1 M tetrabutylammonium hexfluorophoshate) with ferrocene/ferrocenium added as internal standard.

Supplementary Table 1 (T1). Electrochemical Data for Selected Compounds

Compound	[6]CPP	8	9	aza[8]CPP	*N*-methylaza[8]CPP
Reduction (V)	-2.13	-2.18	-1.42, -2.47, -2.72	-2.39	-1.49
Oxidation (V)	0.440	0.670	0.660	-	-

TD-DFT Data

Optical Transitions using TD-DFT B3LYP/6-31g*



Supplementary Figure S6: TD-DFT (B3LYP/6-31g*) plot for **8** and **9**

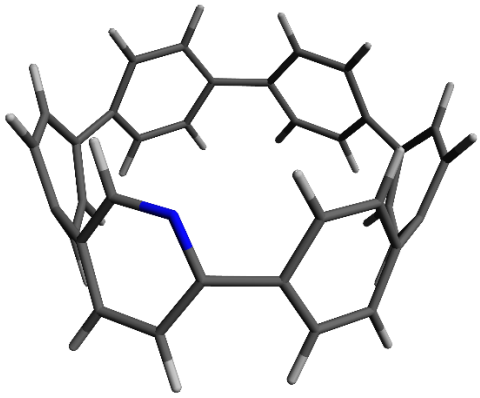
Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs
18166.96	550.4499	0.0003	HOMO->LUMO (99%)
26780.21	373.41	0.0023	H-1->LUMO (45%), HOMO->L+1 (53%)
27754.54	360.3015	0.0093	H-2->LUMO (56%), HOMO->L+2 (41%)
28894.21	346.0902	0.0523	HOMO->L+3 (80%)
29428.95	339.8014	0.7775	H-1->LUMO (40%), HOMO->L+1 (40%)
30469.42	328.1979	0.878	H-2->LUMO (34%), HOMO->L+2 (53%)
30846.89	324.1818	0.061	HOMO->L+4 (73%)
31771.2	314.7504	0.0202	H-4->LUMO (10%), HOMO->L+5 (65%)
32549.54	307.224	0.1062	H-6->LUMO (16%), H-5->LUMO (38%), H-4->LUMO (19%)
33802.93	295.8323	0.0033	H-6->LUMO (20%), H-3->LUMO (57%)
34111.84	293.1533	0.0058	H-2->L+1 (46%), H-1->L+1 (15%), H-1->L+2 (28%)
34239.28	292.0622	0.0061	H-6->LUMO (18%), H-4->LUMO (19%), HOMO->L+4 (11%), HOMO->L+6 (17%)

Supplementary Table 2 (T2): Major transitions for **8** determined by TD-DFT using B3LYP/6-31g*

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs
16154.59	619.0191	0.0223	HOMO->LUMO (97%)
22190.89	450.6355	0.0498	HOMO->L+1 (89%)
24221.8	412.8512	0.278	H-1->LUMO (91%)
26165.61	382.181	0.1353	H-2->LUMO (79%), HOMO->L+2 (16%)
27646.46	361.71	0.4701	H-2->LUMO (14%), H-1->L+1 (11%), HOMO->L+2 (72%)
29062.78	344.0827	0.2255	H-3->LUMO (10%), H-1->L+1 (30%), HOMO->L+3 (47%)
29405.56	340.0717	0.2205	H-3->LUMO (49%), H-1->L+1 (35%)
29635.43	337.4339	0.3963	H-3->LUMO (30%), H-1->L+1 (21%), HOMO->L+3 (43%)
30383.92	329.1214	0.0524	H-4->LUMO (79%)
31036.43	322.202	0.009	H-6->LUMO (19%), H-5->LUMO (57%)
31584.08	316.6152	0.0883	H-6->LUMO (15%), H-5->LUMO (18%), H-2->L+1 (58%)
31765.56	314.8064	0.0599	H-7->LUMO (25%), H-6->LUMO (41%), H-2->L+1 (18%)

Supplementary Table 3 (T3): Major transitions for **9** determined by TD-DFT using B3LYP/6-31g*

Computational Coordinates



aza[6]CPP 8

Dipole Moment (1.5265 D)

C	-2.86394	-1.38272	1.71711
C	-2.1312	-1.31944	0.52431
C	-1.54736	-0.08739	0.20026
C	-2.13223	1.10324	0.65213
C	-2.86512	1.04	1.84486
C	-2.94598	-0.20808	2.47692
H	-3.2999	-2.29966	2.05495
H	-1.98482	-2.18602	-0.08599
H	-1.98655	2.02944	0.1365
H	-3.30204	1.91584	2.2772
C	-0.19383	-0.04822	-0.53304
C	0.45	1.178	-0.74703
C	0.45085	-1.24473	-0.87441
C	1.85089	1.17652	-0.7103
H	-0.10254	2.08393	-0.88452
C	1.85169	-1.24616	-0.83768
H	-0.10107	-2.13163	-1.10616
C	2.48004	-0.05098	-0.46286

H	2.41178	2.08123	-0.81865
H	2.41316	-2.13418	-1.04027
C	3.79305	-0.09291	0.34057
C	4.3565	-1.32615	0.6948
C	4.35579	1.0965	0.82264
C	5.02488	-1.39089	1.92472
H	4.24094	-2.19239	0.07747
C	5.02431	1.0318	2.05249
H	4.2396	2.02288	0.29998
C	5.06882	-0.21641	2.68788
H	5.44049	-2.30866	2.28513
H	5.43964	1.90673	2.50739
C	0.23098	-1.68211	7.41231
C	1.63183	-1.68359	7.44905
C	2.27565	-0.45738	7.23508
C	0.23018	0.74058	7.5397
C	-0.39815	-0.4546	7.16488
H	-0.32993	-2.5868	7.52061
H	2.1844	-2.5895	7.58652
H	-0.33131	1.62859	7.74225
C	3.62915	-0.4182	6.50176
C	4.21303	0.81385	6.17768
C	4.21407	-1.60883	6.04987
C	4.94576	0.87713	4.98485
H	4.06669	1.68045	6.78799
C	4.94694	-1.54559	4.85711
H	4.06843	-2.53503	6.56551
C	5.02782	-0.29751	4.22501
H	5.38174	1.79408	4.64704

H	5.38389	-2.42145	4.4248
C	-1.71114	-0.41266	6.36142
C	-2.27461	0.82057	6.00718
C	-2.2739	-1.60208	5.87934
C	-2.94301	0.8853	4.77723
H	-2.15909	1.68682	6.62449
C	-2.94244	-1.53738	4.64946
H	-2.15774	-2.52849	6.40199
C	-2.98696	-0.28918	4.01405
H	-3.35865	1.80307	4.41685
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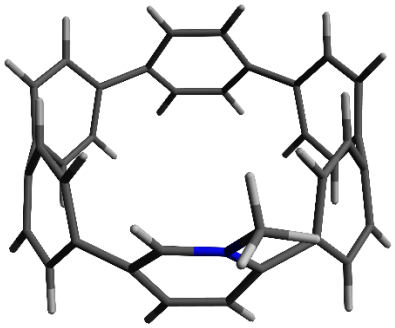


***N*-methylaza[6]CPP 9**

Dipole Moment (10.2669 D)

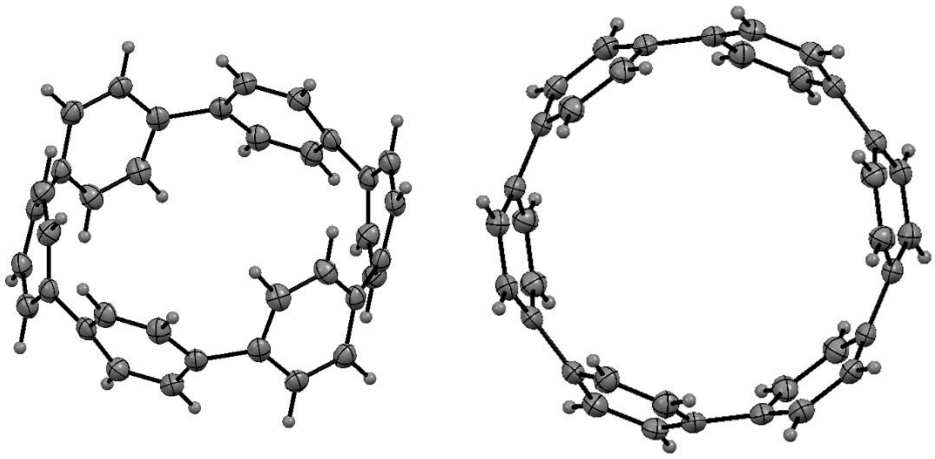
C	-2.86341	-1.39325	1.70971
C	-2.14733	-1.40226	0.50468
C	-1.56979	-0.19161	0.09878
C	-2.14996	1.02374	0.48556
C	-2.86393	1.03272	1.6907
C	-2.93398	-0.17452	2.39845
H	-3.29465	-2.28768	2.10813
H	-2.00843	-2.30411	-0.0542
H	-2.01394	1.9169	-0.08789
H	-3.29494	1.93316	2.0759
C	-0.22639	-0.19189	-0.65335
C	0.40442	1.02261	-0.95353
C	0.42375	-1.40325	-0.92591
C	1.80504	1.03434	-0.93327
H	-0.15725	1.91349	-1.14256
C	1.82528	-1.39142	-0.90525
H	-0.12341	-2.30718	-1.09448
C	2.44691	-0.16938	-0.61415
H	2.35706	1.93432	-1.10654
H	2.39228	-2.28603	-1.0574
C	3.76748	-0.14667	0.17724

C	4.35004	-1.34796	0.60319
C	4.31884	1.07783	0.57765
C	5.02999	-1.32613	1.8285
H	4.24037	-2.25293	0.04305
C	4.99755	1.09974	1.8031
H	4.18674	1.96771	-0.00181
C	5.06404	-0.10507	2.51557
H	5.4614	-2.21369	2.2421
H	5.40451	2.00715	2.19816
C	0.30894	-1.34054	7.39664
C	1.70448	-1.31851	7.41904
C	2.31517	-0.09725	7.10008
C	0.33951	1.07124	7.32066
C	-0.3133	-0.13913	7.05414
H	-0.2464	-2.23563	7.58418
H	2.27681	-2.1996	7.62212
H	-0.20937	1.97935	7.45844
C	3.65954	-0.08416	6.34912
C	4.21533	1.13417	5.93637
C	4.26341	-1.29126	5.97103
C	4.93764	1.13182	4.73614
H	4.05553	2.03704	6.48789
C	4.98398	-1.29344	4.76852
H	4.14067	-2.1838	6.54829
C	5.03629	-0.08835	4.05487
H	5.35358	2.03227	4.33487
H	5.43299	-2.18784	4.38996
C	-1.63821	-0.14029	6.26927
C	-2.19653	1.07166	5.84185

C	-2.21862	-1.35388	5.87625
C	-2.88519	1.06115	4.62217
H	-2.06271	1.97607	6.39777
C	-2.90476	-1.36447	4.65362
H	-2.10307	-2.24448	6.45801
C	-2.95042	-0.15992	3.93836
H	-3.30035	1.9567	4.20945
H	-3.33254	-2.26401	4.26292
N	1.68268	1.06416	7.33758
C	2.43858	2.30689	7.54937
H	2.63009	2.43404	8.59443
H	3.36731	2.25424	7.02048
H	1.86862	3.13698	7.18758

Crystallographic Data

Diffraction intensities for **Jasti29** were collected at 173 K on a Bruker Apex2 CCD diffractometer using CuKα radiation, λ= 1.54178 Å. Space group were determined based on systematic absences. Absorption correction was applied by SADABS[2]. Structure was solved by direct methods and Fourier techniques and refined on F^2 using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. H atoms in the structure were found on the residual density map and refined with isotropic thermal parameters. The molecule has -3 symmetry and the N atom in the structure is disordered over 24 possible positions. Thus the final refinement has been done based on the model where the N atom share four positions (C(2), C(3), C(4) and C(5)) with the C atoms of the CH groups. H atoms in the structure were found on the residual density map and refined with isotropic thermal parameters with occupation factors fixed at value of 0.95833 corresponding the above-mentioned disorder in the molecule. It should be also mentioned that a relatively large isolated peak (around 2.63 eÅ^{-3}) there was on the residual density map. In the crystal structure the molecules form columns and these peak is located at the central line of such the column up and down from the average plane of the molecule. Solvent molecules were found in similar location in some of similar structures, but in this case we could not recognize any possible solvents used in the reactions and crystal grow. It was treated by SQUEEZE[3]; corrections of the X-ray data by SQUEEZE was 111 electron/cell, but a solvent has not been added in the formula of the compound. Another possible reason for the above-mentioned peak on the residual density could be also related to the fact that the disorder of the N atom in the structure could be more complicated. All calculations were performed by the Bruker SHELXL-2013 package[4].



Crystallographic Data for **Aza[6]CPP (9)**: $C_{35}H_{23}N$, M = 457.54, 0.12 x 0.08 x 0.07 mm, T = 173(2) K, Trigonal, space group *R-3*, *a* = 19.3483(6) Å, *b* = 19.3483(6) Å, *c* = 6.2252(3) Å, *V* = 2018.22(13) Å^3, *Z* = 3, D_c = 1.129 Mg/m^3, μ(Cu) = 0.496 mm^{-1}, *F*(000) = 720, $2\vartheta_{max}$ = 132.5°, 5290 reflections, 789 independent reflections [R_{int} = 0.0867], R1 = 0.0422, wR2 = 0.0967 and GOF = 1.075 for 789 reflections (71 parameters) with I>2σ(I), R1 = 0.0562, wR2 = 0.1013 and GOF = 1.075 for all reflections, max/min residual electron density +0.124/-0.196 eÅ^{-3}.

Notes and References

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