Electronic Supplementary Information

Modulating Structure and Properties in Organic Chromophores: Influence of Azulene as a Building Block

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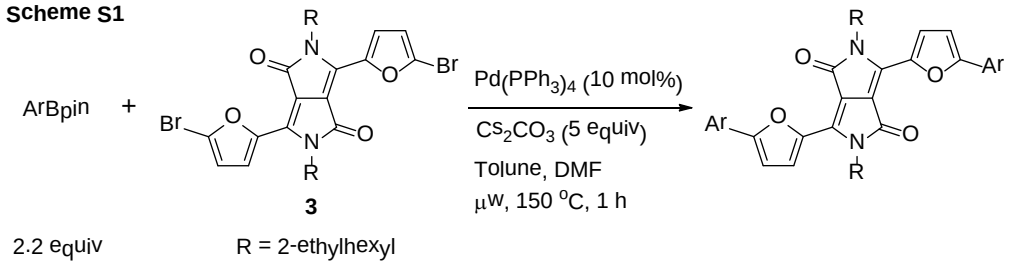
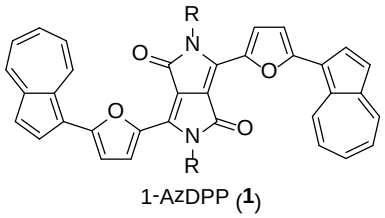
General Methods. Chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. *N*,*N*-dimethylformamide (DMF) and dichloromethane (DCM) were purchased from Fisher Scientific, and purified by passage under N_2 pressure through two packed columns of neutral alumina. 3,6-Bis(5-bromofuran-2-yl)-2,5-di(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **3**[S1], 3,6-di-(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **4**[S1], 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)azulene **8**,[S2] 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)azulene **9**,[S2] 4,4,5,5-tetramethyl-2-(naphthalenyl)-1,3,2-dioxaborolane **10**[S3], were prepared according to the procedure reported previously. Flash chromatography was performed using silica gel (particle size 40-63 μm). All compounds were characterized by ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) on Varian 600 instruments with the solvent signal as internal reference with the spectra being acquired at room temperature. Chemical shifts and coupling constants are reported in ppm and in Hz, respectively. Microwave assisted reactions were conducted on a Biotage Microwave reactor at a frequency of 2.5 GHz. High-resolution mass spectrometry (HRMS) was performed on a Waters GCT Premier Time of Flight Mass Spectrometer equipped with a field ionization source (12000 V extraction voltage), and the values reported represent the most abundant molecular ion. VG70 Magnetic Sector and Waters GCT Premier TOF instruments were used for low and high resolution mass analysis by electron ionization (EI). IR spectra was recorded on JASCO FT/IR 4200 spectrometer. UV-vis and fluorescence spectra were recorded on an Agilent 8453 and Varian Cary Eclipse Fluorescence spectrophotometer using quartz cuvettes and dichloromethane as a solvent, respectively. The excitation wavelength was set at 492 nm (for **4**) or 562 nm (for **5**) and the emission was recorded with the use of excitation and emission slits of 5 nm. Optical microscopy was collected using an Olympus CX equipped with a Motic CMOS camera. High-resolution X-ray diffraction was collected at Stanford Synchrotron Radiation Light source on beamline 2-1 with an incidence energy of 8 keV. The diffracted X-rays was collimated with two 1 mm Soller slits.

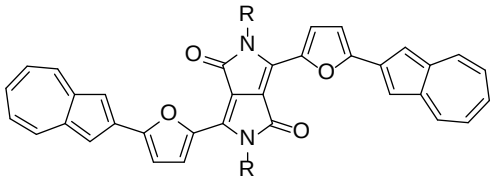
Synthesis of DPP Conjugates 1, 2, and 5 (Scheme S1).



To a solution of 3,6-bis(5-bromofuran-2-yl)-2,5-di(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H, 5H)-dione **3**[S1] (65 mg, 0.10 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)azulene **8**[S2] (for **2**) or 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)azulene **9**[S2] (for **1**) or 4,4,5,5-tetramethyl-2-(naphthalenyl)-1,3,2-dioxaborolane **10**[S3] (for **5**) (56 mg, 0.22 mmol) and Cs_2CO_3 (163 mg, 0.50 mmol) in 2.0 mL of toluene and 0.20 mL of DMF was degassed by the three freeze pump thaw cycles. $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) was added and then the vial was placed into a microwave reactor to heat at 150 °C for 1 h with stirring. The reaction mixture was quenched with water, and the aqueous layer was extracted with $CHCl_3$ (20 mL × 3). The combined organic layer was washed with water and dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on silica gel with hexane/CH_2Cl_2 (*v*/*v* = 1/3) as eluents to afford corresponding conjugates.

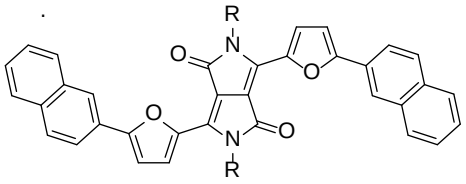


3,6-Bis(5-(1-azulenyl)furan-2-yl)-2,5-di(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1): A blue solid (52 mg, 69% yield). IR (KBr): 1650 cm^{-1} (C=O). ^1H NMR (600 MHz, $CDCl_3$, ppm): δ 0.73 (t, *J* = 7.2 Hz, 6H), 0.87 (t, *J* = 7.2 Hz, 6H), 1.14-1.23 (m, 8H), 1.25-1.46 (m, 8H), 1.95 (q, *J* = 6.0 Hz, 2H), 4.26 (d, *J* = 7.2 Hz, 4H), 6.98 (d, *J* = 4.2 Hz, 2H), 7.23 (t, *J* = 9.6 Hz, 2H), 7.29 (t, *J* = 9.6 Hz, 2H), 7.42 (d, *J* = 3.6 Hz, 2H), 7.66 (t, *J* = 9.6 Hz, 2H), 8.20 (d, *J* = 3.6 Hz, 2H), 8.32 (d, *J* = 9.6 Hz, 2H), 8.55 (d, *J* = 3.6 Hz, 2H), 8.87 (d, *J* = 9.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 10.7, 13.9, 23.1, 23.6, 28.6, 30.4, 39.4, 46.6, 106.5, 109.9, 118.5 119.1, 123.1, 124.9, 125.2, 132.4, 134.7, 135.9, 136.2, 137.8, 139.1, 143.4, 143.7, 155.4, 161.3. HRMS (EI): m/*z* $[M]^+$ calcd for $C_{50}H_{52}N_2O_4$ 744.3927; found, 744.3909.



2-AzDPP (**2**)

3,6-Bis(5-(2-azulenyl)furan-2-yl)-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (2): A blue solid (63 mg, 84% yield). IR (KBr): 1658 cm^{-1} (C=O). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 0.85 (t, *J* = 7.2 Hz, 6H), 0.94 (t, *J* = 7.2 Hz, 6H), 1.25-1.33 (m, 8H), 1.38-1.52 (m, 8H), 2.03(q, *J* = 6.0 Hz, 2H), 4.26 (d, *J* = 7.8 Hz, 4H), 7.16 (d, *J* = 3.6 Hz, 2H), 7.17 (t, *J* = 9.0 Hz, 4H), 7.51 (t, *J* = 9.0 Hz, 2H), 7.59 (s, 4H), 8.25 (d, *J* = 9.0 Hz, 4H), 8.57 (d, *J* = 3.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 10.6, 14.1, 23.3, 23.6, 28.5, 30.4, 39.4, 46.8, 107.7, 113.0, 113.6, 123.4, 124.5, 132.7, 136.6, 137.0, 137.1, 141.3, 145.0, 155.3, 161.2. HRMS (EI): m/*z* $[M]^+$ calcd for $C_{50}H_{52}N_2O_4$ 744.3927; found, 744.3907.

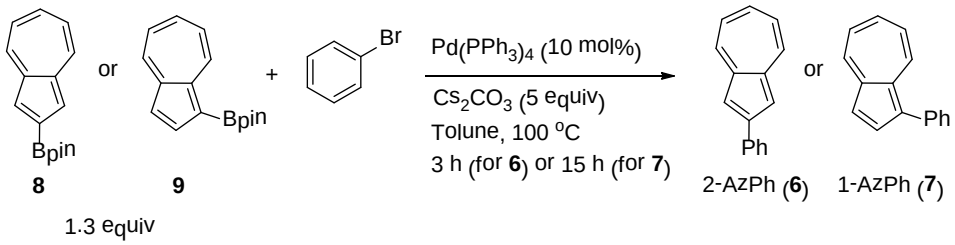


NpDPP (**5**)

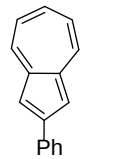
3,6-Bis(5-(2-naphthyl)furan-2-yl)-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (5): A dark red solid (58 mg, 77% yield). IR (KBr): 1656 cm^{-1} (C=O). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 0.82 (t, *J* = 7.2 Hz, 6H), 0.94 (t, *J* = 7.2 Hz, 6H), 1.23-1.30 (m, 8H), 1.34-1.56 (m, 8H), 2.02 (q, *J* = 6.0 Hz, 2H), 4.24 (d, *J* = 7.8 Hz, 4H), 7.07 (d, *J* = 3.6 Hz, 2H), 7.50 (dt, *J* = 1.8, 7.2 Hz, 2H), 7.53 (dt, *J* = 1.8, 7.2 Hz, 2H), 7.81 (dd, *J* = 1.8, 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.88 (t, *J* = 9.0 Hz, 4H), 8.21 (s, 2H), 8.53 (d, *J* = 3.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 10.7, 14.0, 23.2, 23.6, 28.6, 30.4, 39.4, 46.8, 106.8, 109.7, 122.3 122.9, 123.5, 126.7, 126.8, 126.9, 127.9, 128.3, 128.8, 132.9, 133.3, 133.4, 144.3, 156.9, 161.2. HRMS (EI): m/*z* $[M]^+$ calcd for $C_{50}H_{52}N_2O_4$ 744.3927; found, 744.3936.

Synthesis of Phenylazulenes 6 and 7 (Scheme S2).

Scheme S2

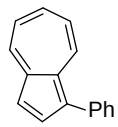


To a solution of bromobenzene (47 mg, 0.30 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)azulene **8**[S2] (for **6**) or 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)azulene **9**[S2] (for **7**) (99 mg, 0.39 mmol) and Cs_2CO_3 (489 mg, 1.5 mmol) in 3.0 mL of toluene was added $Pd(PPh_3)_4$ (36 mg, 0.030 mmol). The reaction mixture was stirred at 100 °C for 3 h (for **6**) or 15 h (for **7**) and then quenched with a saturated aqueous NH_4Cl solution. The aqueous layer was extracted with CH_2Cl_2 (10 mL×3), and the combined organic layer was washed with brine followed by drying over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on silica gel with hexane/CH_2Cl_2 (*v*/*v* = 20/1) as eluents to afford corresponding coupling products.



2-AzPh (**6**)

2-Phenylazulene (6): A purple solid (55 mg, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.19 (t, *J* = 9.6 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 9.6 Hz, 1H), 7.69 (s, 2H), 7.97 (d, *J* = 7.2 Hz, 2H), 8.30 (d, *J* = 9.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 114.4, 123.7, 127.6, 128.2, 128.9, 135.9, 136.4, 136.5, 141.3, 149.9. HRMS (EI): m/*z* $[M]^+$ calcd for $C_{50}H_{52}N_2O_4$ 204.0939; found, 204.0932.



1-AzPh (**7**)

1-Phenylazulene (7): A blue solid (53 mg, 86% yield). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.16 (dt, *J* = 2.4, 9.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 3.6 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 9.6 Hz, 1H), 7.63 (dd, *J* = 2.4, 9.6 Hz, 2H), 8.03 (d, *J* = 3.6 Hz, 1H), 8.36 (d, *J* = 9.6 Hz, 1H), 8.57 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 117.4, 123.0, 123.3, 126.3, 128.6, 129.7, 131.3, 135.2, 135.6, 137.1, 137.3, 137.5, 138.2, 141.7. HRMS (EI): m/*z* $[M]^+$ calcd for $C_{50}H_{52}N_2O_4$ 204.0939; found, 204.0935.

UV-Visible absorption data

Table S1. UV-Vis absorption data for **1**, **2**, and **4-7** in CH_2Cl_2 (1×10^{-6} M) at rt.

compound	λ_{max}/nm (εx10^{-3}/$M^{-1}cm^{-1}$)
1-AzDPP (**1**)	415 (3.9), 633 (15.1)
2-AzDPP (**2**)	309 (14.2), 409 (6.3), 430 (8.8), 619 (18.9), 672 (20.9)
DPP (**4**)	340 (12.1), 353 (14.5), 499 (21.3), 539 (37.6)
NpDPP (**5**)	350 (9.8), 562 (19.5), 610 (31.6)
2-AzPh (**6**)	298 (21.2), 308 (22.2), 372 (3.9), 390 (4.6), 614 (0.1)
1-AzPh (**7**)	297 (17.9), 354 (3.0), 370 (3.2), 601 (0.1)

Theoretical Calculations

Geometry optimizations were carried out using the Gaussian 09 quantum chemistry program package[S4] at the B3LYP functional.[S5] All compounds were fully optimized with the 6-31G* basis set.[S6] Geometry optimizations were performed at the same level of the theory. The time-dependent density functional theory (TDDFT) calculations were conducted at the B3LYP/6-31G* level of theory. Plots of molecular orbitals and spin densities were constructed using the MOLEKEL program 4.1.[S7]

Table S2. TD-DFT calculation for 1-AzDPP **1'**

λ/nm	Oscillator Strength	Transition	Amplitude
702.12	1.9645	LUMO+2 ← HOMO	0.57405
		LUMO ← HOMO	0.42576
561.93	0.0111	LUMO+1 ← HOMO-1	0.55914
475.35	0.0536	LUMO+4 ← HOMO	0.21987
421.49	0.1648	LUMO+2 ← HOMO-2	0.58510

Table S3. TD-DFT calculation for 2-AzDPP **2'**

λ/nm	Oscillator Strength	Transition	Amplitude
677.93	1.7681	LUMO ← HOMO	0.71059
570.05	0.0118	LUMO ← HOMO-2	0.62349
472.22	0.1932	LUMO+2 ← HOMO	0.64512
415.36	0.3183	LUMO ← HOMO-4	0.64116

Table S4. TD-DFT calculation for NpDPP **5'**

λ/nm	Oscillator Strength	Transition	Amplitude
593.87	1.5958	LUMO ← HOMO	0.71138
417.61	0.0706	LUMO+2 ← HOMO	0.53042

Table S5. TD-DFT calculation for 2-AzDPP **2'**$^{2+}$

λ/nm	Oscillator Strength	Transition	Amplitude
819.97	1.5429	LUMO ← HOMO	0.71591
699.81	0.0280	LUMO+2 ← HOMO	0.70286
515.64	0.5336	LUMO ← HOMO-2	0.42728
		LUMO+4 ← HOMO	0.64116

Table S6. TD-DFT calculation for 2-AzDPP **2'**$^{+}$

λ/nm	Oscillator Strength	Transition	Amplitude
975.37	0.0072	LUMO ← HOMO-1	0.69817
855.42	1.4189	LUMO ← HOMO	0.64533
		LUMO+1 ← HOMO	0.31078
807.00	0.5416	LUMO+1 ← HOMO	0.62964
613.08	0.0149	LUMO ← HOMO-2	0.51006
		LUMO+1 ← HOMO-1	0.21652
582.31	0.0129	LUMO+2 ← HOMO-1	0.64012
		LUMO+1 ← HOMO-1	0.15540
543.76	0.2503	LUMO+2 ← HOMO	0.45531
		LUMO ← HOMO-2	0.41483

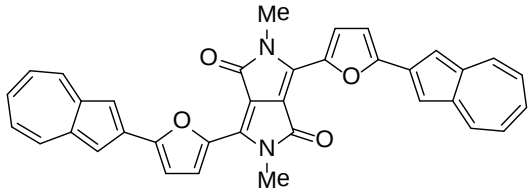
Table S7. TD-DFT calculation for 1-AzDPP **1'**$^{2+}$

λ/nm	Oscillator Strength	Transition	Amplitude
1385.68	0.0161	LUMO+2 ← HOMO	0.70514
574.43	0.9396	LUMO+4 ← HOMO	0.68157
		LUMO ← HOMO-2	0.13278
		LUMO+1 ← HOMO-3	0.11587
544.65	0.0149	LUMO ← HOMO-2	0.43956
		LUMO+1 ← HOMO-3	0.35301
		LUMO+2 ← HOMO-2	0.23467

Table S8. TD-DFT calculation for 1-AzDPP **1'**$^{+}$

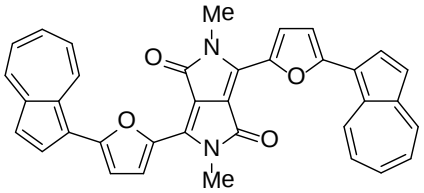
λ/nm	Oscillator Strength	Transition	Amplitude
1162.24	0.0081	LUMO+1 ← HOMO-1	0.68983
688.82	1.4018	LUMO+2 ← HOMO	0.68898
622.82	0.0077	LUMO+3 ← HOMO	0.61719
		LUMO+1 ← HOMO-2	0.27509
		LUMO+3 ← HOMO-1	0.18886
613.92	0.0180	LUMO+1 ← HOMO-2	0.64288
582.67	0.0579	LUMO+1 ← HOMO-4	0.65516
567.36	0.0186	LUMO+1 ← HOMO-3	0.66333
		LUMO+1 ← HOMO-4	0.23484

Cartesian Atomic Coordinates for the Geometry Optimized Structure



2-AzDPP (**2'**)

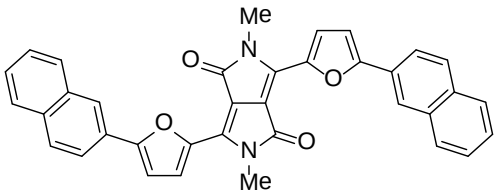
	X	Y	Z
C	7.645471	1.550222	-0.000038
H	7.616522	2.635875	0.000032
C	6.520331	0.687194	-0.000029
C	6.969211	-0.655258	-0.000135
H	6.332722	-1.53414	-0.000156
C	8.368932	-0.659543	-0.000207
C	9.181962	-1.794709	-0.000315
H	8.649903	-2.749154	-0.000338
C	10.576317	-1.876707	-0.000401
H	10.988701	-2.886558	-0.000482
C	11.515349	-0.84001	-0.000402
H	12.559432	-1.159239	-0.000479
C	11.317277	0.546216	-0.000314
H	12.224678	1.151639	-0.000332
C	10.117474	1.258269	-0.000207
H	10.210808	2.347048	-0.00015
C	8.806854	0.772177	-0.000157
O	4.179498	0.14948	0.000099
C	5.150248	1.115932	0.000068
C	4.548933	2.362629	0.000136
H	5.066836	3.314488	0.00013
C	3.154808	2.156593	0.000201
H	2.355338	2.891083	0.000256
C	2.963074	0.783628	0.000185
C	-2.963075	-0.783629	0.000174
O	-4.179497	-0.14948	0.000096
C	-3.154809	-2.156593	0.00015
C	-4.548932	-2.362628	0.000091
C	-5.150249	-1.115932	0.000055
H	-2.35534	-2.891086	0.000179
H	-5.066836	-3.314489	0.000063
C	-6.520332	-0.687194	-0.000033
C	-6.969212	0.655258	-0.000186
C	-7.645472	-1.550222	0.000009
C	-8.806852	-0.772176	-0.000123
C	-8.368931	0.659545	-0.00024
H	-7.616524	-2.635875	0.000128
H	-6.332723	1.53414	-0.000254
C	-10.11747	-1.258268	-0.000129
C	-11.31727	-0.546215	-0.00025
C	-11.51535	0.84001	-0.000399
C	-10.57631	1.876707	-0.000462
C	-9.18196	1.794712	-0.00039
H	-10.2108	-2.347045	-0.000023
H	-10.9887	2.88656	-0.000586
H	-12.55942	1.159241	-0.000477
H	-8.649901	2.749154	-0.000463
H	-12.22467	-1.151637	-0.000226
C	-1.755172	-0.028566	0.000237
C	-0.458159	-0.539421	0.00026
N	-1.655582	1.359729	0.000243
C	-0.282771	1.782152	0.0003
C	0.458157	0.539421	0.000278
C	-2.729709	2.339084	0.000245
C	0.282769	-1.782154	0.000226
C	1.755171	0.028565	0.000225



1-AzDPP (**1'**)

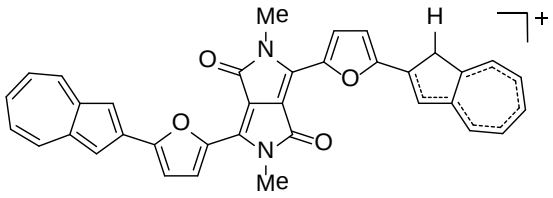
	X	Y	Z
C	6.529671	0.446037	0.262252
C	6.682751	1.839069	0.492209
C	8.028262	2.192359	0.440951
H	8.437779	3.185983	0.59772
C	8.789449	1.036591	0.168333
C	10.176277	0.995825	0.064891
H	10.680736	1.951954	0.224453
C	11.011822	-0.092012	-0.211592
H	12.080937	0.122764	-0.223579
C	10.651042	-1.411028	-0.496268
H	11.48243	-2.087758	-0.703649
C	9.379701	-1.988704	-0.572389
H	9.356444	-3.042834	-0.850977
C	8.130602	-1.402979	-0.337138
H	7.277023	-2.067246	-0.475162
C	7.824763	-0.095641	0.029981
O	4.150276	0.537586	0.110764
C	5.265485	-0.242336	0.286219
C	4.865652	-1.552437	0.49224
H	5.513773	-2.391333	0.712471
C	3.45528	-1.57963	0.430792
H	2.784251	-2.424855	0.549338
C	3.047115	-0.278658	0.198319
C	-3.047088	0.279213	-0.19766
O	-4.150184	-0.537166	-0.110502
C	-3.455353	1.580201	-0.429906
C	-4.865698	1.552864	-0.491654
C	-5.26546	0.242673	-0.28595
H	-2.784396	2.425516	-0.548226
H	-5.513772	2.391766	-0.711942
C	-6.682027	-1.83912	-0.491868
C	-6.52949	-0.445963	-0.262231
C	-8.027413	-2.192874	-0.440903
C	-8.789105	-1.037279	-0.168897
C	-7.824854	0.095322	-0.030489
H	-8.436538	-3.186673	-0.597564
C	-10.17598	-0.99696	-0.066084
C	-11.01202	0.090645	0.209824
C	-10.65181	1.409802	0.494579
C	-9.380685	1.987888	0.571223
C	-8.131304	1.40258	0.336407
H	-10.68004	-1.953293	-0.225674
H	-9.357877	3.042018	0.849831
H	-11.4835	2.086268	0.701568
H	-7.278037	2.067167	0.474751
H	-12.08106	-0.124479	0.221309
C	-1.736266	-0.257611	-0.04766
C	-0.53749	0.451432	-0.098574
N	-1.417435	-1.59413	0.180452
C	0.003482	-1.780676	0.283408
C	0.537503	-0.45069	0.099845
C	-2.3207	-2.724487	0.31052
C	-0.003429	1.781316	-0.282741
C	1.736302	0.258258	0.048442
H	-3.015186	-2.58567	1.147509
H	-2.898846	-2.879553	-0.60903

H	-3.358655	2.238608	-0.892476
H	-3.358882	2.238337	0.89277
H	-2.244776	3.320488	0.000445
O	-0.058145	-2.962617	0.000237
N	1.655581	-1.359729	0.000227
O	0.058143	2.962617	0.000285
C	2.729707	-2.339086	0.000223
H	2.244774	-3.320486	0.000411
H	3.358655	-2.238598	-0.892496
H	3.358878	-2.238348	0.892751



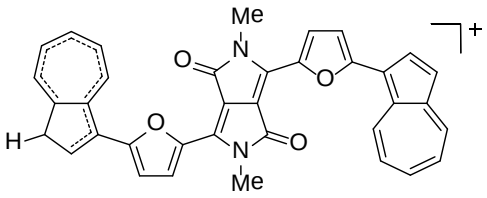
^{N}pDPP (**3'**)

	X	Y	Z
C	7.66813	1.062144	-0.002242
H	7.525369	2.142608	-0.005817
C	6.568472	0.213409	0.000909
C	6.787418	-1.197783	0.005137
H	5.929097	-1.865413	0.007572
C	8.061101	-1.709686	0.006284
C	10.527669	-1.359306	0.004488
C	11.605101	-0.500187	0.001437
C	8.991099	0.560125	-0.001101
C	10.125017	1.419927	-0.00423
C	9.199947	-0.858324	0.003301
O	4.182915	-0.141939	-0.000141
C	5.218813	0.751918	0.000122
C	4.708354	2.035601	-0.000114
H	5.285553	2.95253	0.000298
C	3.300585	1.928568	-0.00062
H	2.556771	2.719343	-0.000831
C	3.01137	0.575575	-0.000616
C	-3.01137	-0.575572	-0.001114
O	-4.182914	0.141941	-0.00038
C	-3.300584	-1.928566	-0.001765
C	-4.708353	-2.035599	-0.001396
C	-5.218812	-0.751917	-0.000561
H	-2.55677	-2.71934	-0.002339
H	-5.285552	-2.952528	-0.001592
C	-6.568472	-0.213408	0.000303
C	-6.787419	1.197786	0.003064
C	-7.66813	-1.062148	-0.001423
C	-8.991099	-0.56013	-0.00038
C	-9.199947	0.858323	0.002487
H	-7.525369	-2.142616	-0.003687
H	-5.929098	1.865421	0.004398
C	-10.12501	-1.419936	-0.002096
C	-11.40062	-0.902462	-0.000981
C	-11.6051	0.500182	0.001892
C	-10.52767	1.359305	0.003575
C	-8.061103	1.70969	0.004119
H	-1.687589	-3.598067	0.496542
O	-0.524374	2.877021	-0.484332
N	1.417497	1.594739	-0.179953
O	0.524454	-2.876383	0.484918
C	2.320729	2.725139	-0.309926
H	1.687595	3.598679	-0.496054
H	2.89877	2.880259	0.609681
H	3.015313	2.586334	-1.146828
H	-5.856486	-2.515236	-0.695523
H	5.857512	2.515434	0.696273
H	7.649521	-2.286136	-0.882291
H	3.308997	2.324706	-0.896885
H	-9.965563	-2.498561	-0.004292
H	-10.68097	2.438839	0.005771
H	-12.61996	0.896183	0.00275
H	-8.213865	2.789262	0.006275
H	-12.2606	-1.57133	-0.002301
C	-1.752438	0.094204	-0.00113
C	-0.495638	-0.506411	-0.001519
N	-1.555414	1.471979	-0.000759
C	-0.155425	1.797225	-0.000997
C	0.495639	0.506414	-0.001233
C	-2.557311	2.524463	-0.00031
C	0.155425	-1.797222	-0.001873
C	1.752438	-0.094201	-0.001044
H	-3.191866	2.469367	-0.893253
H	-3.191327	2.46912	0.893003
H	-2.004657	3.469435	-0.000334
O	-0.265999	-2.951502	-0.002062
N	1.555414	-1.471976	-0.001372
O	0.266	2.951505	-0.000583
C	2.557312	-2.52446	-0.001399
H	2.004658	-3.469432	-0.001884
H	3.191896	-2.468946	-0.894294
H	3.191297	-2.469537	0.891963
C	11.40063	0.902452	-0.002977
H	9.965564	2.498549	-0.007605
H	12.260603	1.571317	-0.005376
H	12.619966	-0.896189	0.002386
H	10.680977	-2.438838	0.007862
H	8.213865	-2.789255	0.009598



2-AzDPP (**2'**$^{+}$)

	X	Y	Z
C	-7.632306	-1.647539	-0.000008
H	-7.624816	-2.306073	-0.882809
C	-6.472504	-0.67694	-0.000001
C	-6.97832	0.623449	-0.000019
C	-8.388396	0.615625	-0.000039
C	-9.194264	1.793348	-0.000061
H	-8.641115	2.733831	-0.000062
C	-10.56356	1.892558	-0.000081
H	-10.9627	2.907516	-0.000097
C	-11.5476	0.859225	-0.000086
H	-12.58199	1.203321	-0.000105
C	-11.36031	-0.502265	-0.000071
H	-12.26413	-1.112372	-0.000078
C	-10.13758	-1.234949	-0.000047
H	-10.24516	-2.32114	-0.000038
C	-8.855197	-0.750527	-0.000033
O	-4.154085	-0.092797	0.000025
C	-5.132099	-1.068885	0.000022
C	-4.507484	-2.324594	0.000042
H	-5.016601	-3.282181	0.000045
C	-3.134305	-2.114174	0.000057
H	-2.332394	-2.845754	0.000072
C	-2.944741	-0.72193	0.000047
C	2.980917	0.738061	0.000027
O	4.201613	0.103482	0.000025
C	3.179376	2.120806	0.000024
C	4.562086	2.323943	0.00001
C	5.165634	1.06666	0.000014
H	2.380308	2.857139	0.000027
H	5.083083	3.273641	-0.000002
C	6.534718	0.651114	-0.000002
C	6.996849	-0.688556	-0.00007
C	7.647686	1.531198	0.00004
C	8.815886	0.762659	0.000003
C	8.395854	-0.671011	-0.000073
H	6.373115	-1.576229	-0.000118
C	10.12044	1.268063	0.000033
C	11.328345	0.571651	-0.000005
C	11.539593	-0.812628	-0.000086
C	10.615263	-1.864322	-0.000145
C	9.22223	-1.7994	-0.000137
H	10.199479	2.35761	0.000094
H	11.042329	-2.867369	-0.000205
H	12.58714	-1.119239	-0.000107
H	8.701411	-2.759714	-0.000188
H	12.228842	1.186115	0.000029
C	1.782956	0.001282	0.000039
C	0.475231	0.539333	0.000056
N	1.662771	-1.379259	0.000056
C	0.287454	-1.774771	0.000052
C	-0.445755	-0.509624	0.000059
C	2.72665	-2.376281	0.000075
C	-0.240665	1.802358	0.00006
C	-1.744501	0.021161	0.000053
H	3.352926	-2.279062	-0.893815
H	3.352909	-2.279046	0.893976
H	2.234196	-3.353162	0.000079
O	0.133295	2.970356	0.000015
N	-1.616007	1.408351	0.00003

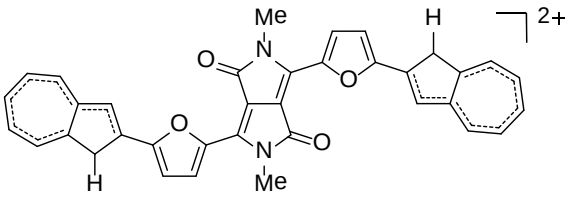


1-AzDPP (**1'**$^{+}$)

	X	Y	Z
C	6.511158	0.448979	-0.236923
C	6.673836	1.749713	-0.633743
C	8.103251	2.169601	-0.59484
H	8.28939	3.02236	0.084347
C	8.804182	0.925903	-0.107386
C	10.1841	0.877929	0.07335
H	10.724697	1.793018	-0.175252
C	10.97156	-0.188182	0.522312
H	12.044698	0.000205	0.562235
C	10.557284	-1.455714	0.941176
H	11.34861	-2.132637	1.263786
C	9.254456	-1.963138	1.019512
H	9.172439	-2.97647	1.414823
C	8.044232	-1.36658	0.664345
H	7.154578	-1.96341	0.848465
C	7.828451	-0.086118	0.123406
O	4.13611	0.549483	-0.166441
C	5.252007	-0.252251	-0.170882
C	4.852773	-1.576514	-0.19858
H	5.490931	-2.449411	-0.263425
C	3.44316	-1.593131	-0.201641
H	2.774823	-2.448231	-0.222199
C	3.035888	-0.267894	-0.179647
C	-3.054683	0.279435	-0.132214
O	-4.161517	-0.538678	-0.133923
C	-3.468562	1.608682	-0.106628
C	-4.868479	1.5935	-0.096058
C	-5.274916	0.257587	-0.108569
H	-2.798076	2.463443	-0.108704
H	-5.515044	2.460544	-0.125317
C	-6.686639	-1.787415	-0.504272
C	-6.533735	-0.41858	-0.140921
C	-8.027111	-2.140667	-0.484821
C	-8.789248	-1.012755	-0.09693
C	-7.835282	0.099348	0.144726
H	-8.439677	-3.113404	-0.734732
C	-10.17792	-0.995385	0.017081
C	-11.02012	0.05221	0.398665
C	-10.66942	1.343681	0.800639
C	-9.401446	1.91933	0.919633
C	-8.14916	1.366295	0.629911
H	-10.67421	-1.936305	-0.230446
H	-9.383178	2.945283	1.288277
H	-11.50367	1.992322	1.072887
H	-7.304741	2.025022	0.828589
H	-12.08684	-0.172871	0.397049
C	-1.751981	-0.259705	-0.150847
C	-0.549474	0.470842	-0.140844
N	-1.416305	-1.608666	-0.180851
C	0.003228	-1.78801	-0.191823
C	0.529034	-0.430758	-0.165612
C	-2.311428	-2.757081	-0.205527
C	-0.034299	1.821399	-0.114619
C	1.724329	0.288328	-0.157237
H	-2.959287	-2.769974	0.678128
H	-2.933257	-2.751247	-1.108609
H	-1.672183	-3.645162	-0.20756
O	-0.570613	2.926034	-0.08894
N	1.391782	1.638559	-0.12525

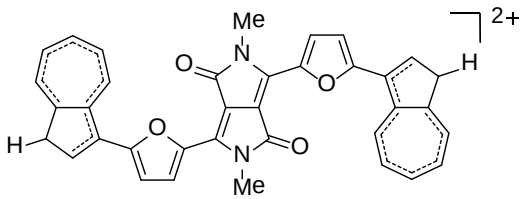
O	-0.082915	-2.938842	0.000083
C	-2.671014	2.410081	-0.000008
H	-2.167635	3.381965	-0.000001
H	-3.298737	2.322996	-0.894992
H	-6.371641	1.524306	-0.00002
H	7.607851	2.616132	0.000102
H	-7.624838	-2.306056	0.882805
H	-3.298786	2.323004	0.894941

O	0.54855	-2.884539	-0.217638
C	2.279241	2.788592	-0.106499
H	1.631845	3.670075	-0.057332
H	2.938917	2.768136	0.769323
H	2.888329	2.836452	-1.018378
H	-5.863299	-2.441292	-0.775703
H	5.866879	2.400977	-0.955896
H	8.476486	2.49596	-1.582837



2-AzDPP ($\mathbf{2'}^{2+}$)

	X	Y	Z
C	7.660026	1.62646	-0.000203
H	7.649376	2.285532	-0.883171
C	6.506959	0.651725	0.000034
C	7.002101	-0.63689	0.000014
C	8.429753	-0.626281	-0.000082
C	9.227811	-1.797447	-0.00012
H	8.679198	-2.740326	-0.000118
C	10.605883	-1.894674	-0.000146
H	11.005418	-2.909407	-0.000165
C	11.578703	-0.865347	-0.00014
H	12.615308	-1.20275	-0.000151
C	11.386792	0.504751	-0.000112
H	12.290739	1.114443	-0.000104
C	10.170462	1.228271	-0.000105
H	10.272089	2.315012	-0.0001
C	8.88318	0.735424	-0.000127
O	4.177875	0.083737	-0.000061
C	5.150735	1.054927	0.000165
C	4.544767	2.308103	0.000605
H	5.056325	3.264181	0.001027
C	3.159646	2.101466	0.000578
H	2.362274	2.838898	0.000686
C	2.970878	0.720558	0.000104
C	-2.970871	-0.720526	-0.000062
O	-4.177876	-0.083721	0.00005
C	-3.15963	-2.101436	-0.00052
C	-4.544746	-2.308087	-0.000525
C	-5.150732	-1.054918	-0.000115
H	-2.36225	-2.83886	-0.000612
H	-5.056294	-3.26417	-0.000914
C	-6.506958	-0.65173	-0.000003
C	-7.002112	0.636877	-0.000096
C	-7.660012	-1.626476	0.000331
C	-8.883183	-0.735457	0.000147
C	-8.429765	0.626253	-0.000006
H	-7.649498	-2.286283	-0.882069
H	-6.400919	1.541314	-0.000262
C	-10.17045	-1.228319	0.000127
C	-11.38679	-0.504813	0.000033
C	-11.57872	0.86528	-0.000039
C	-10.60591	1.894621	-0.000064
C	-9.227839	1.797408	-0.000054
H	-10.27205	-2.31506	0.000201
H	-11.00546	2.909353	-0.000107
H	-12.61533	1.202671	-0.000085
H	-8.679235	2.740296	-0.000097
H	-12.29073	-1.114515	0.000033
C	-1.755787	0.023551	0.000053



1-AzDPP ($\mathbf{1'}^{2+}$)

	X	Y	Z
C	-6.574222	-0.349249	-0.45083
C	-6.852356	-1.473052	-1.182222
C	-8.295352	-1.846807	-1.045484
H	-8.414267	-2.8744	-0.606192
C	-8.855062	-0.789784	-0.121572
C	-10.18112	-0.772368	0.254529
H	-10.82475	-1.578396	-0.165818
C	-10.81478	0.13876	1.100975
H	-11.90471	-0.033541	1.258571
C	-10.26992	1.220286	1.772646
H	-10.98099	1.804648	2.402171
C	-8.953534	1.681736	1.778295
H	-8.764354	2.573512	2.420275
C	-7.850384	1.191014	1.098271
H	-6.887277	1.729088	1.260555
C	-7.7963	0.100204	0.237966
O	-4.179363	-0.524575	-0.340899
C	-5.307415	0.313109	-0.362869
C	-4.913281	1.643416	-0.342214
H	-5.545767	2.527869	-0.384189
C	-3.47509	1.65614	-0.301118
H	-2.828477	2.538591	-0.281131
C	-3.064599	0.328063	-0.302256
C	3.064247	-0.327494	-0.301549
O	4.179042	0.525125	-0.339454
C	3.474718	-1.655577	-0.300592
C	4.912928	-1.642862	-0.341079
C	5.307122	-0.312561	-0.361222
H	2.828104	-2.538041	-0.281124
H	5.545354	-2.527362	-0.382923
C	6.851227	1.475486	-1.177719
C	6.573877	0.349974	-0.448626
C	8.294388	1.848845	-1.041802
C	8.854991	0.789926	-0.120621
C	7.796579	-0.100782	0.238188
H	8.413963	2.875573	-0.600684
C	10.181447	0.771778	0.254106
C	10.815973	-0.140946	1.098182
C	10.27171	-1.22361	1.768512
C	8.95529	-1.684917	1.774754
C	7.851512	-1.193085	1.096546
H	10.824669	1.578513	-0.165488
H	8.766703	-2.577805	2.415355
H	10.983395	-1.809133	2.396286
H	6.888648	-1.731632	1.258642
H	11.906087	0.030972	1.254893
C	1.746016	0.240089	-0.28152
C	0.566662	-0.478869	-0.270706

C	-0.467732	-0.523261	0.000102
N	-1.630996	1.403424	-0.000093
C	-0.248632	1.792014	-0.000062
C	0.467736	0.523301	-0.00002
C	-2.684116	2.411328	-0.000406
C	0.248635	-1.791974	0.000122
C	1.75579	-0.023511	0.000003
H	-3.309114	2.324685	-0.8967
H	-3.309408	2.324892	0.895696
H	-2.179755	3.382334	-0.000479
O	-0.127975	-2.953985	0.000136
N	1.631	-1.403386	0.000103
O	0.127975	2.954025	-0.000079
C	2.684122	-2.411288	0.000498
H	2.179764	-3.382295	0.000435
H	3.309535	-2.324785	-0.895511
H	6.400893	-1.541319	0.000098
H	-7.649364	-2.285422	0.883394
H	7.649524	2.286139	0.882293
H	3.308998	-2.324705	0.896886

N	1.446185	1.61682	-0.277722
C	0.016404	1.822273	-0.271424
C	-0.567012	0.479452	-0.270841
C	2.40605	2.671334	-0.284134
C	-0.016756	-1.821687	-0.27107
C	-1.746366	-0.239508	-0.281734
H	3.071273	2.596245	0.618475
H	3.046131	2.60807	-1.205733
H	1.862855	3.655177	-0.27088
O	0.514027	-2.936355	-0.264114
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O	-0.514374	2.936944	-0.264813
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H	6.150873	2.051748	-1.789938
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H	8.812733	1.840446	-2.039123
H	-8.814838	-1.836554	-2.042183

^{1}H NMR Change of Azulene Derivatives 1, 2, 6 and 7 with TFA and Et_3N.

NMR change with acid and base was monitored in $CDCl_3$ at rt. Each set of ^{1}H NMR shown in Figure S5-S8 contains spectrum in the neutral state (bottom), upon the protonation by excess (>1000 equiv) amount of TFA (middle), and after the subsequent addition of excess amount of triethylamine (upper), respectively. After the neutralization of TFA solutions with triethylamine, starting materials in their neutral states were recovered quantitatively by passing short silica gel pad.

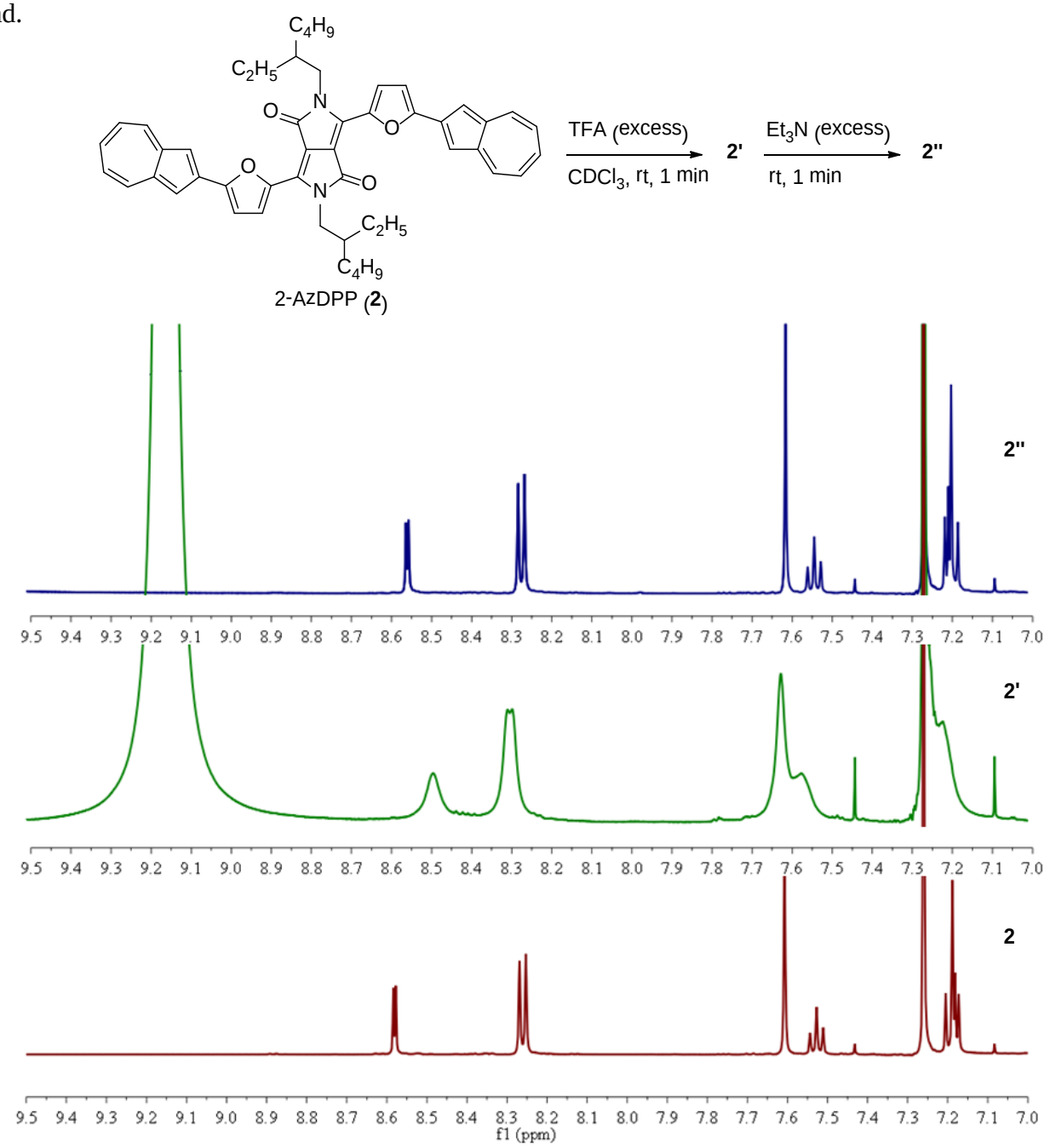

Figure S1. NMR changes of 2-AzDPP **2** in $CDCl_3$ at rt.

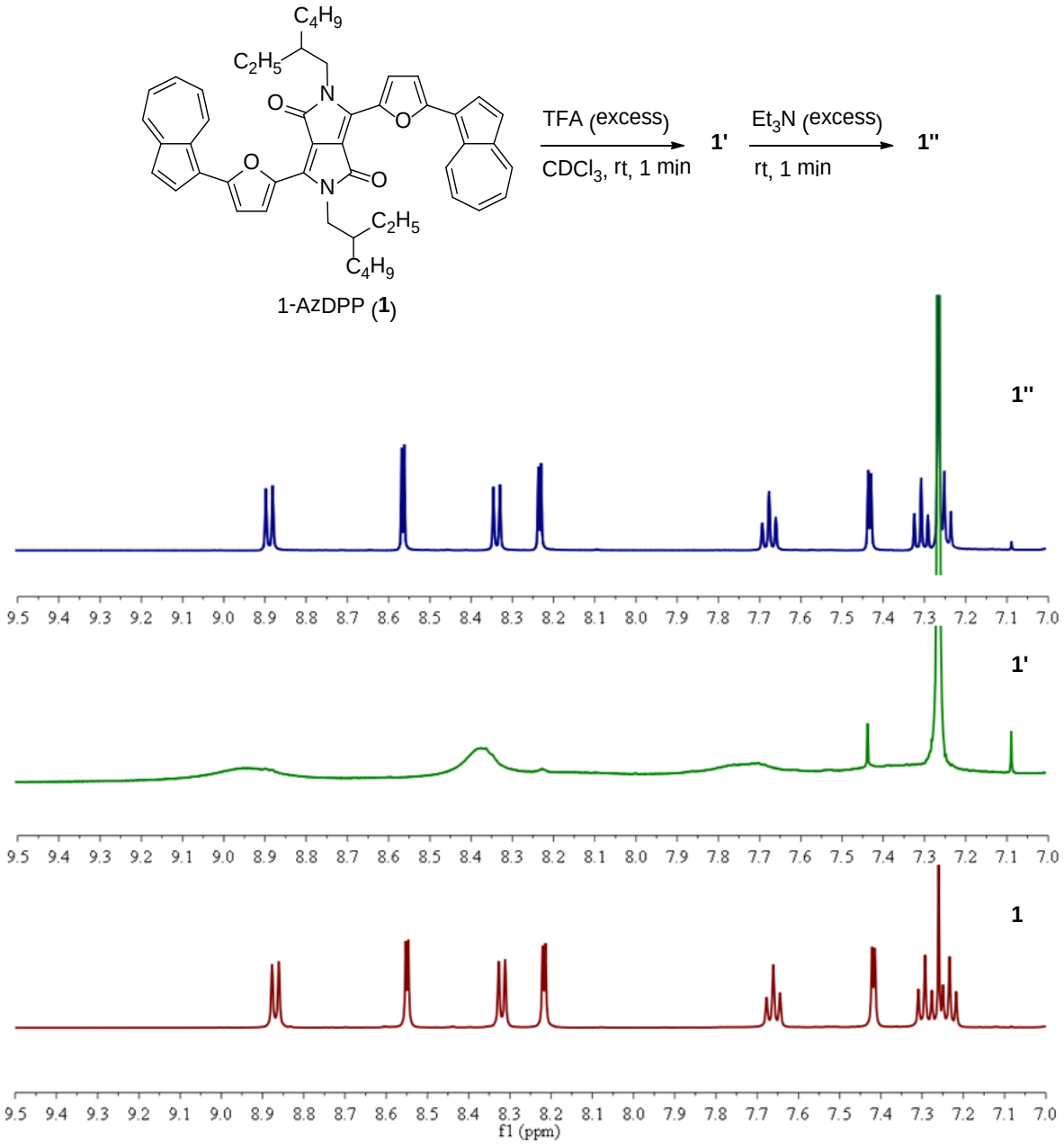

Figure S2. NMR changes of 1-AzDPP **1** in $CDCl_3$ at rt.

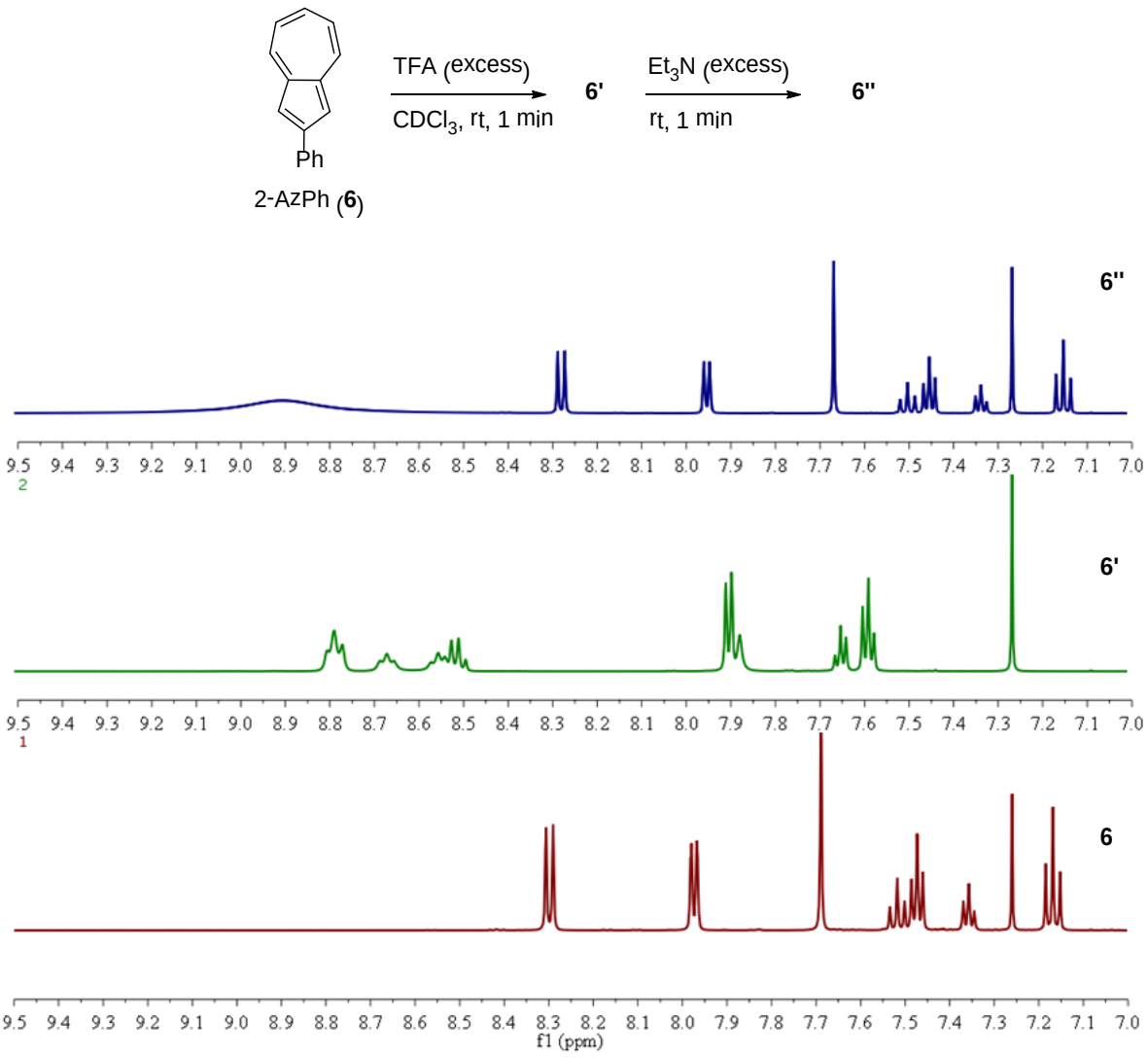

Figure S3. NMR changes of 2-AzPh **6** in $CDCl_3$ at rt.

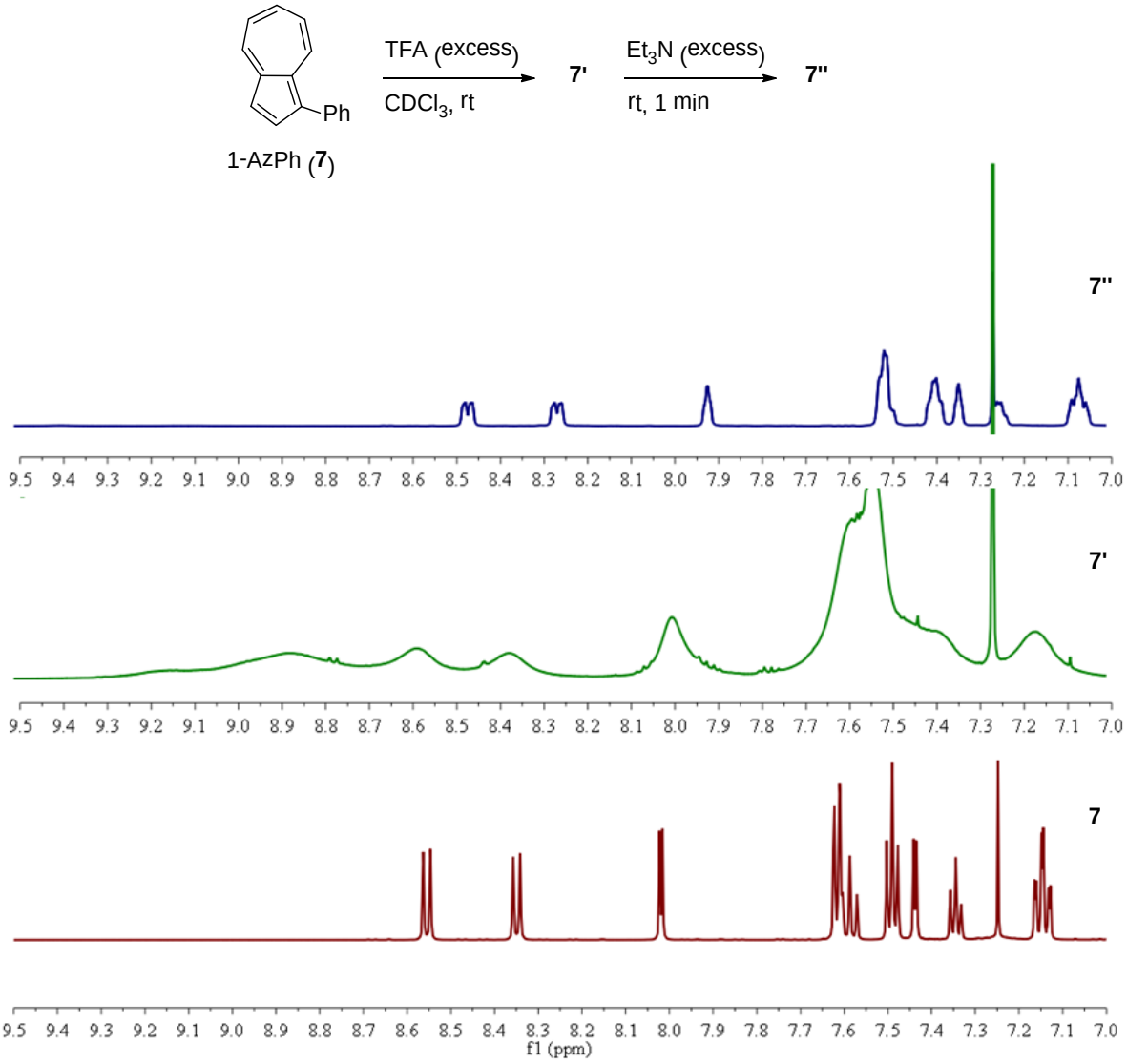

Figure S4. NMR changes of 1-AzPh **7** in $CDCl_3$ at rt.

UV-vis spectra change of AzPh 6 and 7 upon the addition of TFA.

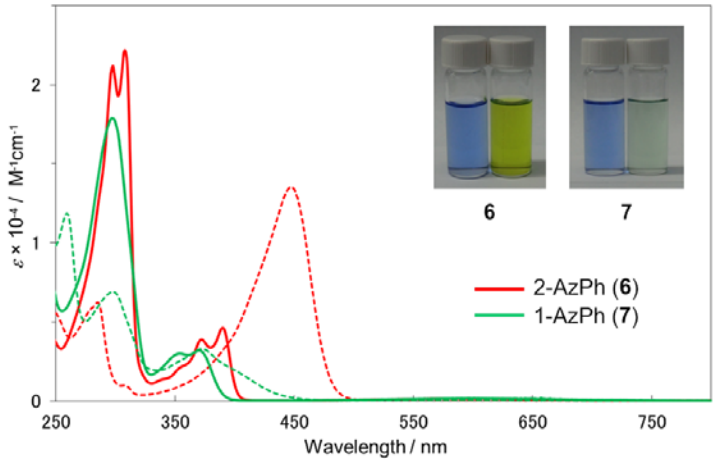

Figure S5. UV-vis spectra in CH_2Cl_2 of AzPh **6** and **7** for neutral state (solid line) and upon the addition of *ca.* 1000 equiv of TFA (dashed line). Inset: photographs in the neutral state (left) and after protonation by TFA (right).

UV-vis spectra of DPP derivatives in thin film.

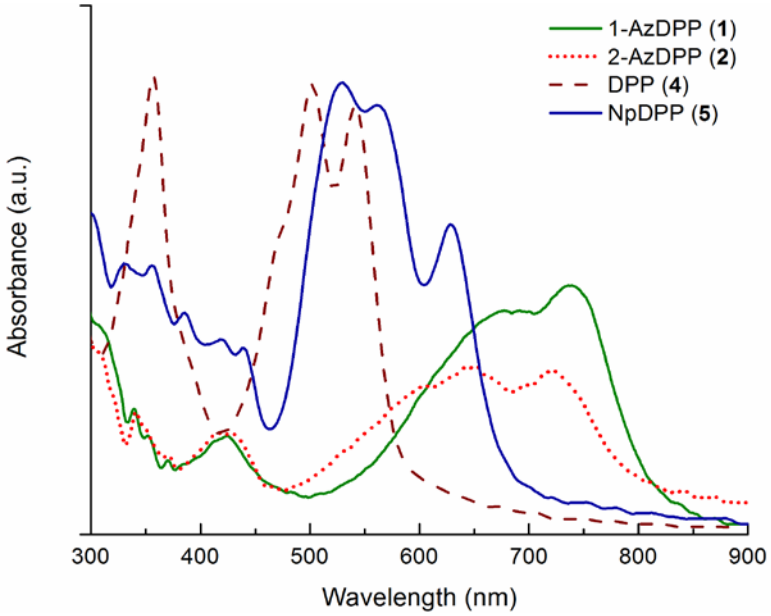

Figure S6. UV-vis spectra in solution-cast thin films of 1-AzDPP **1**, 2-AzDPP **2**, DPP **4**, and NpDPP **5**.

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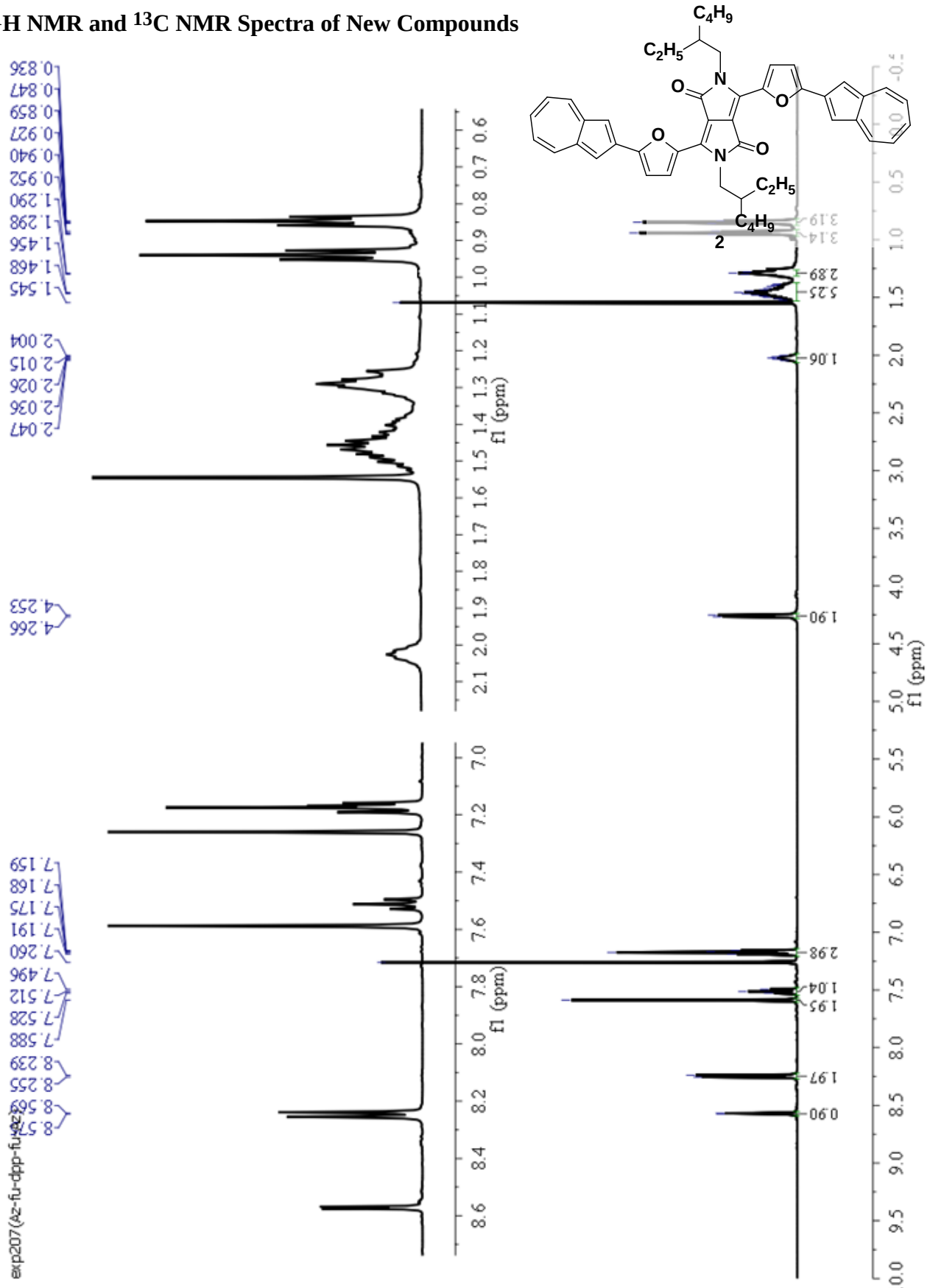
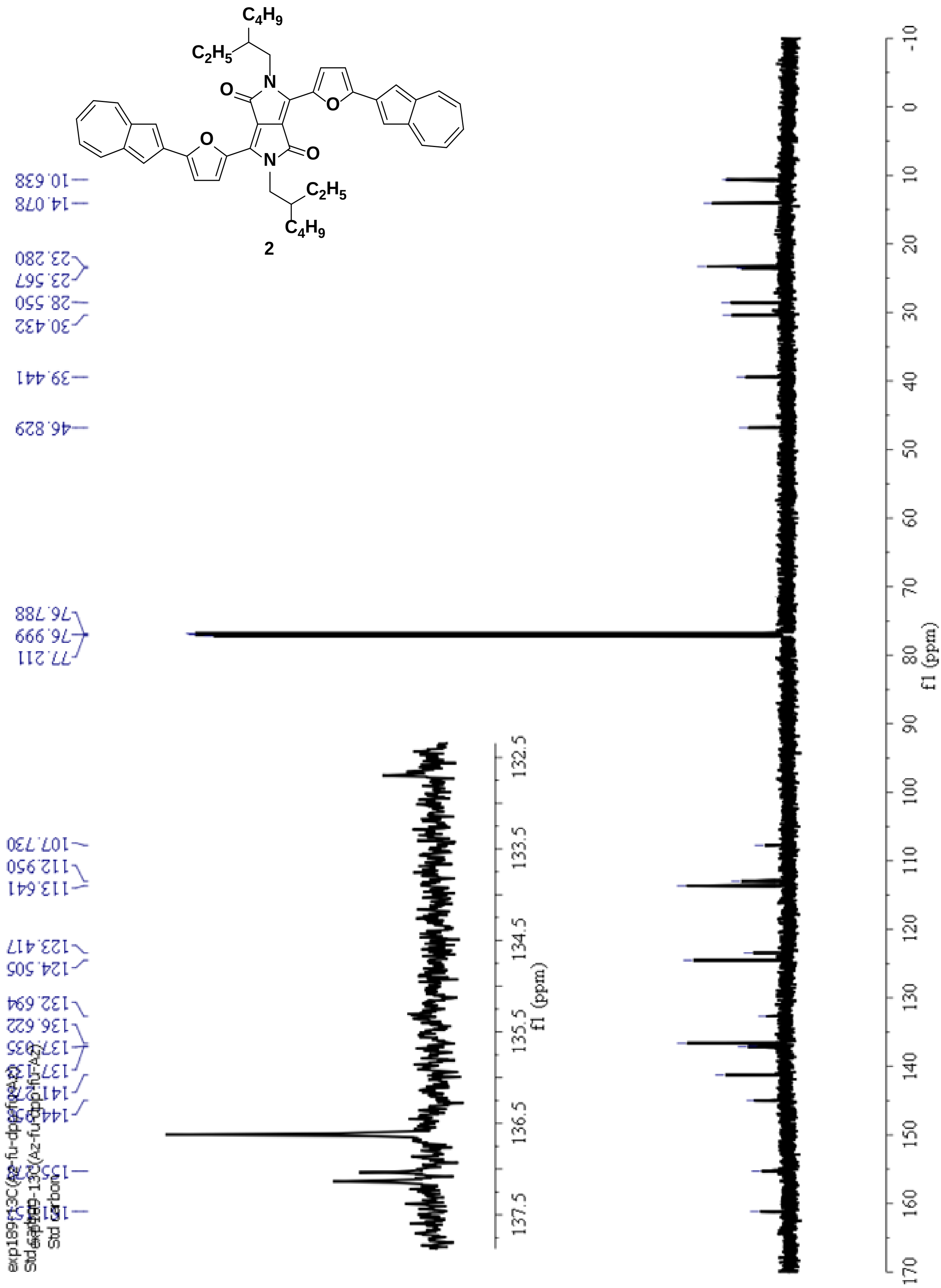
^{1}H NMR and ^{13}C NMR Spectra of New Compounds

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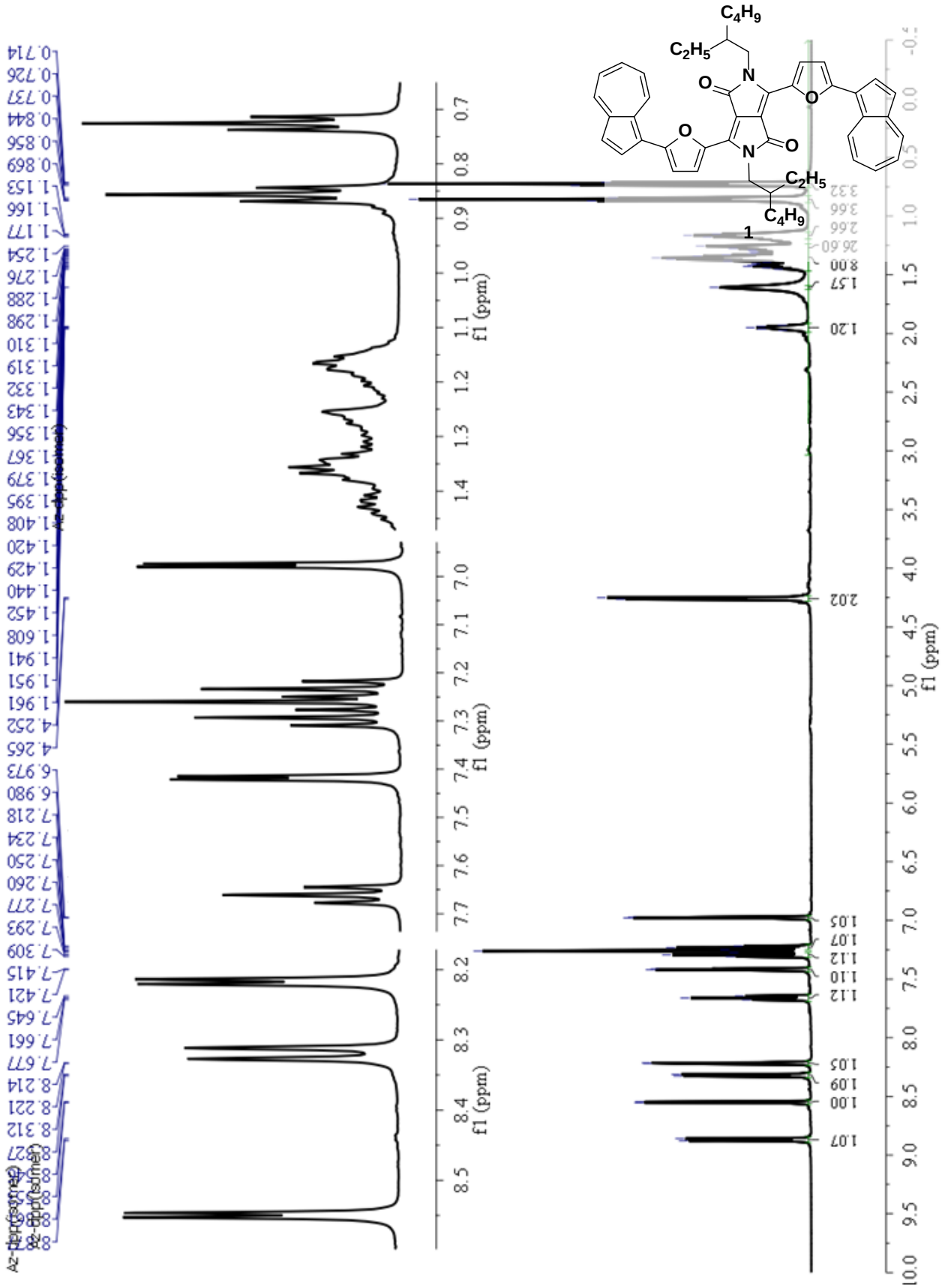
2
f1 (ppm)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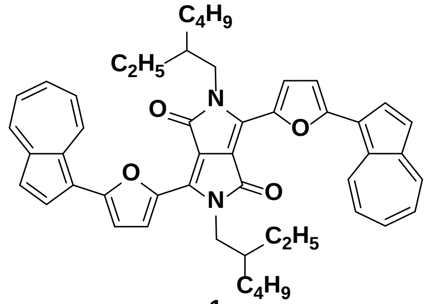
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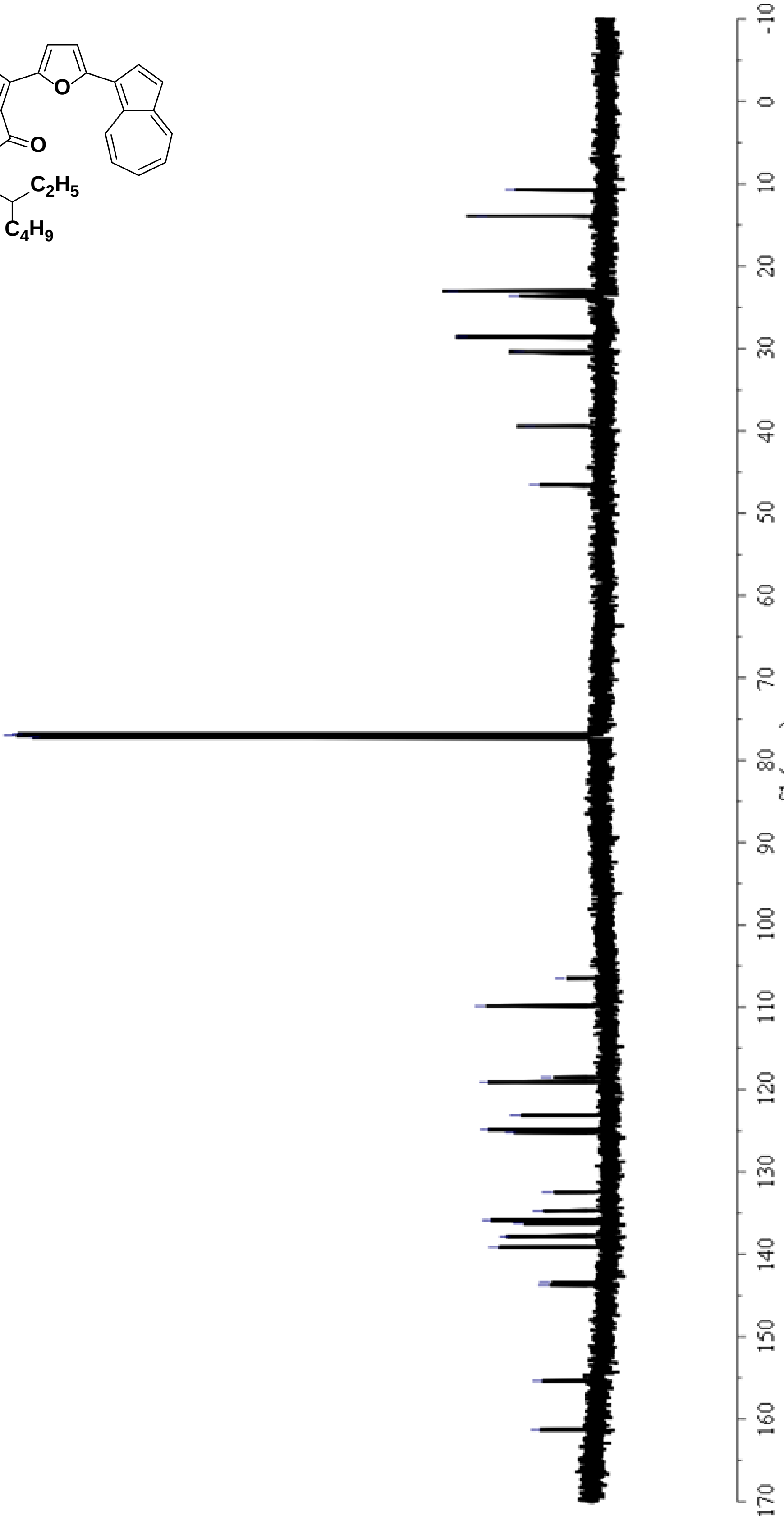
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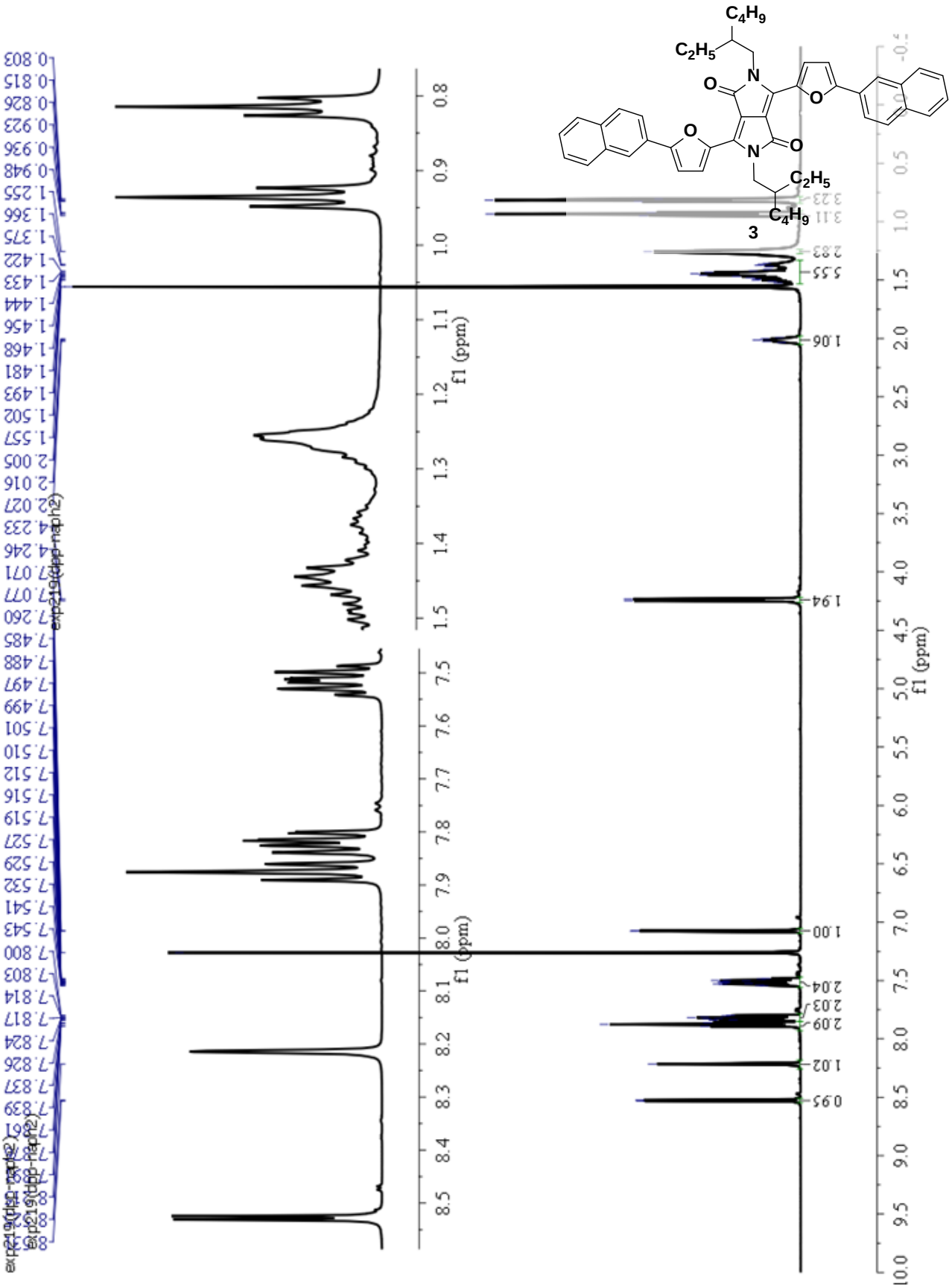
Std carbon
f1 (ppm)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f1 (ppm)
f1 (ppm)
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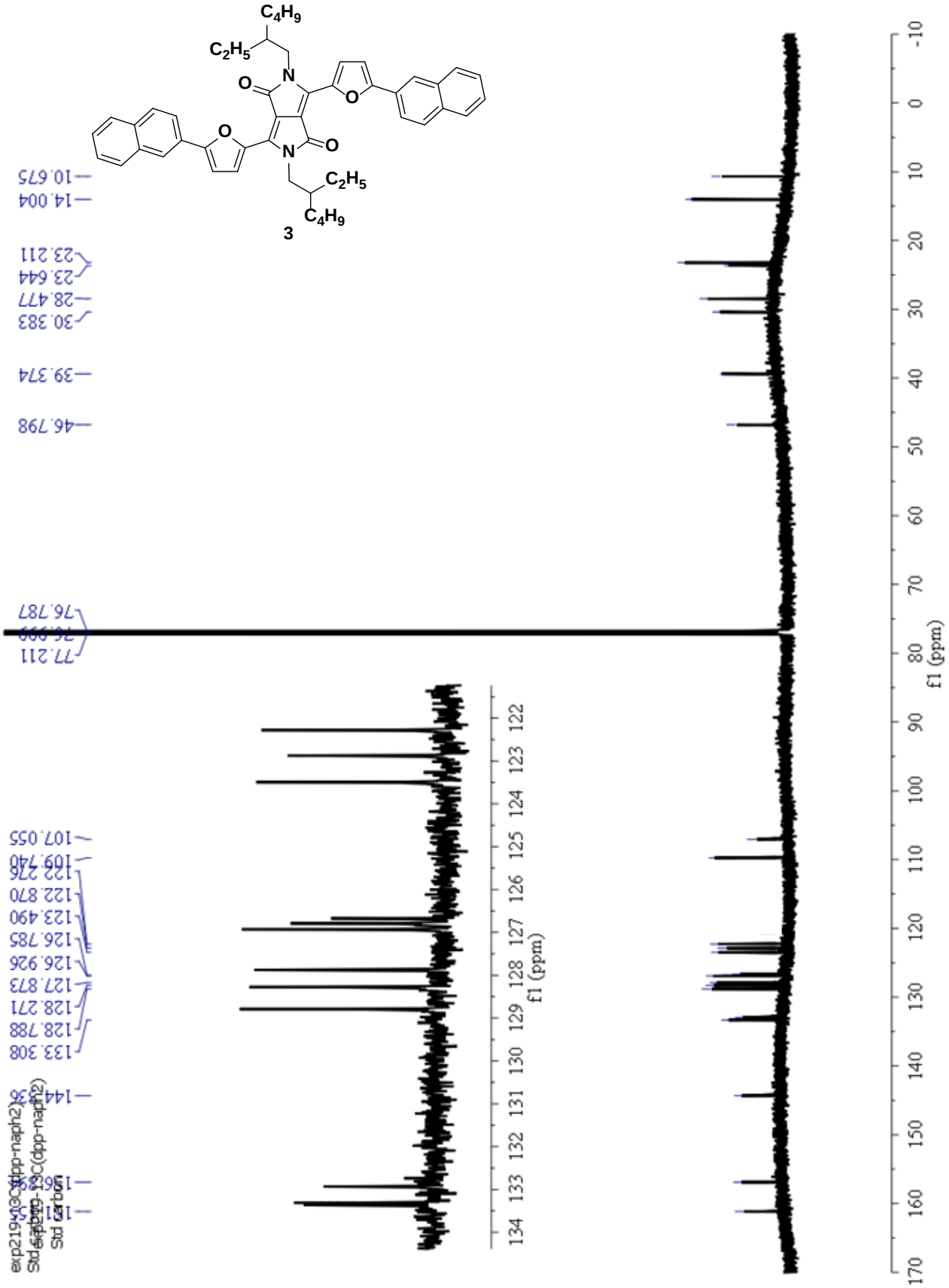
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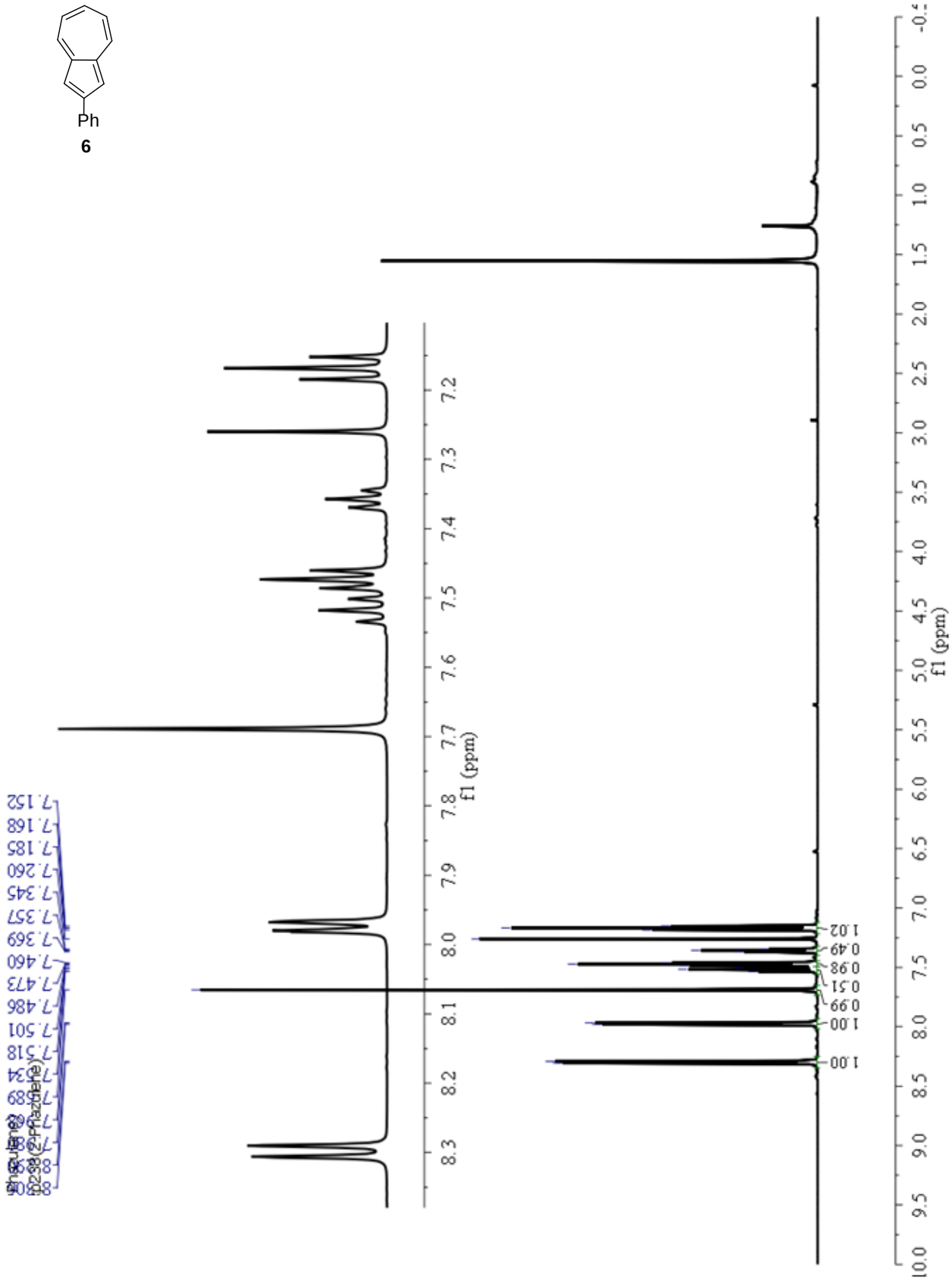
f1 (ppm)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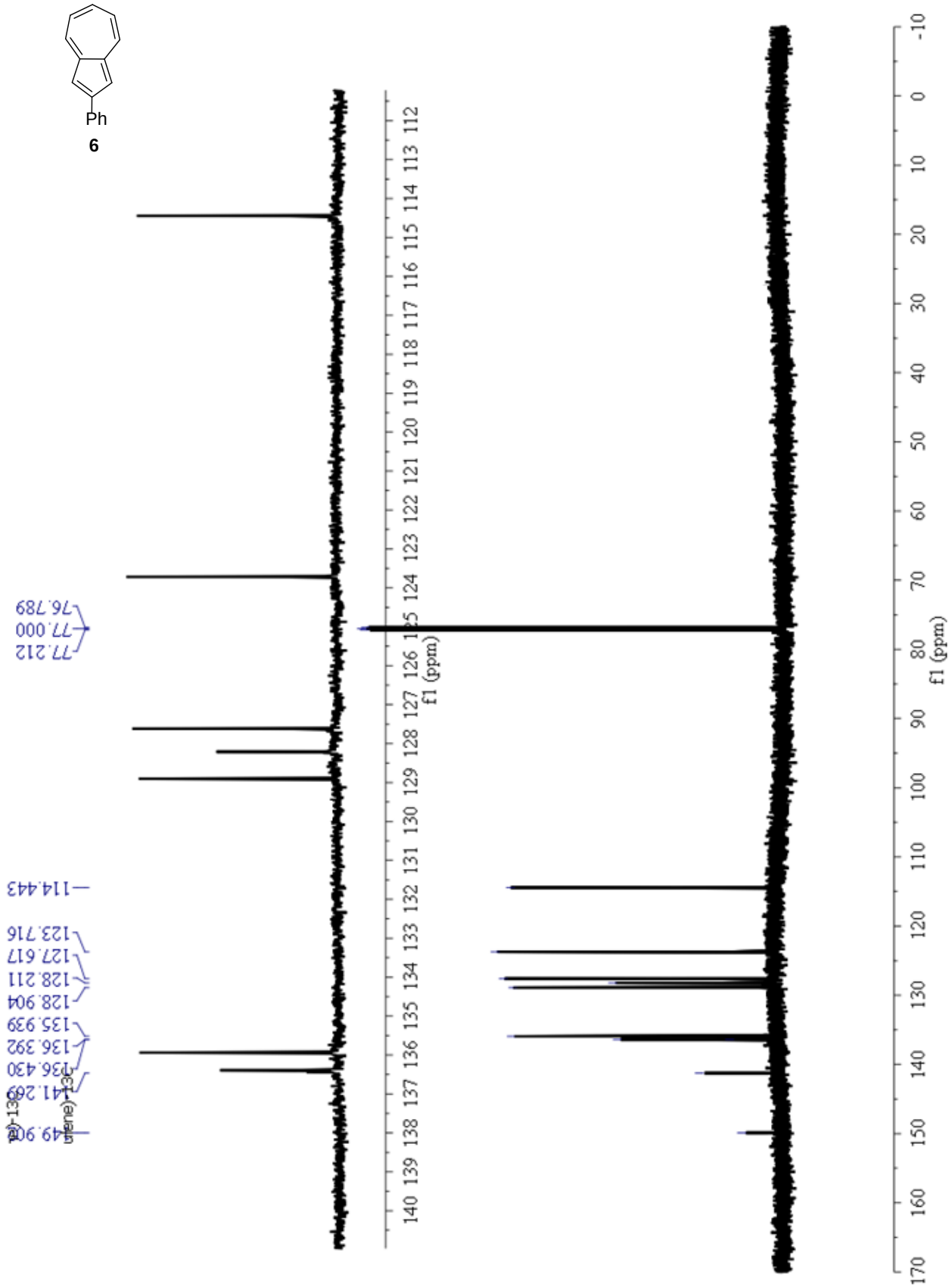
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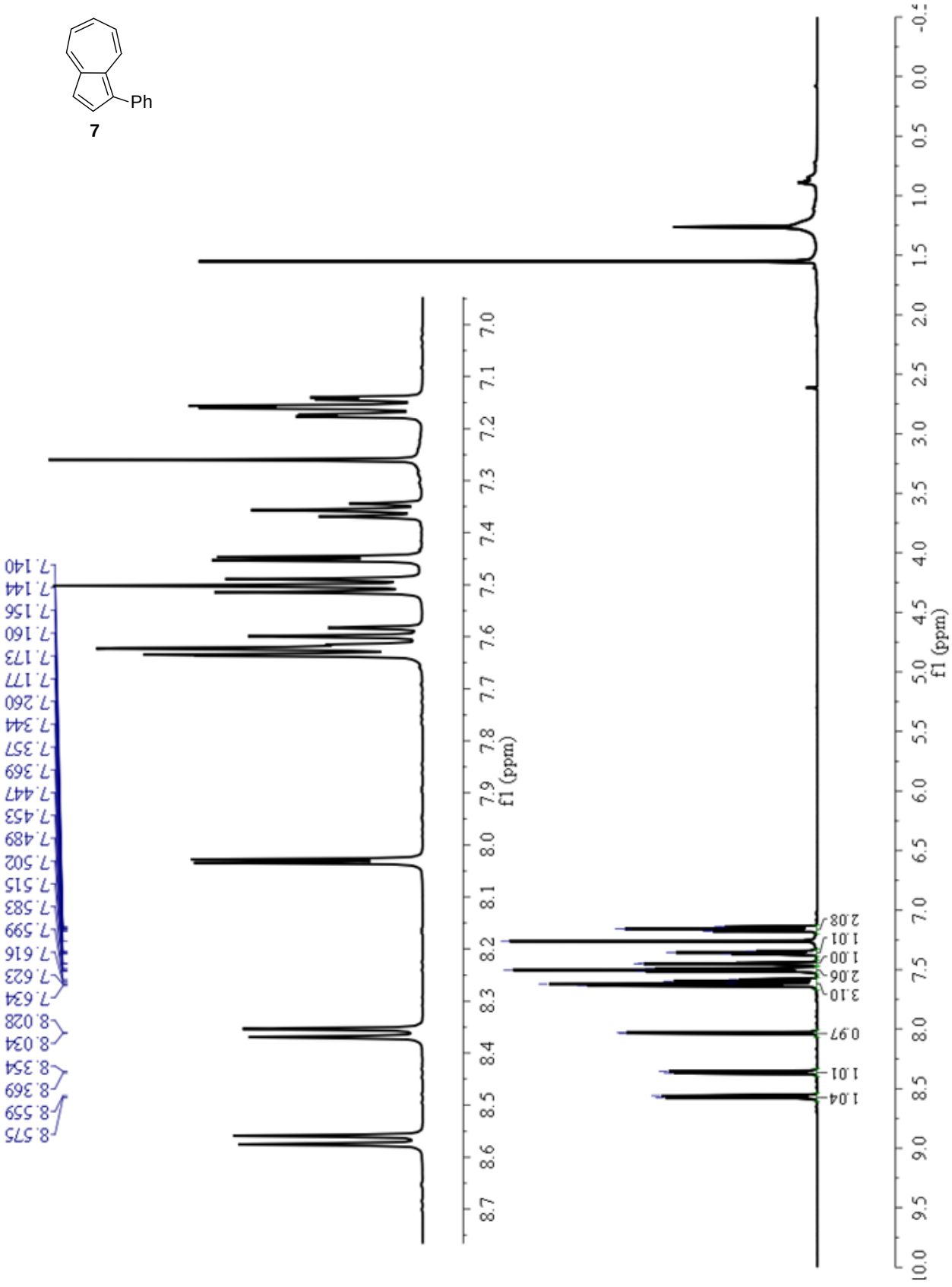
f1 (ppm)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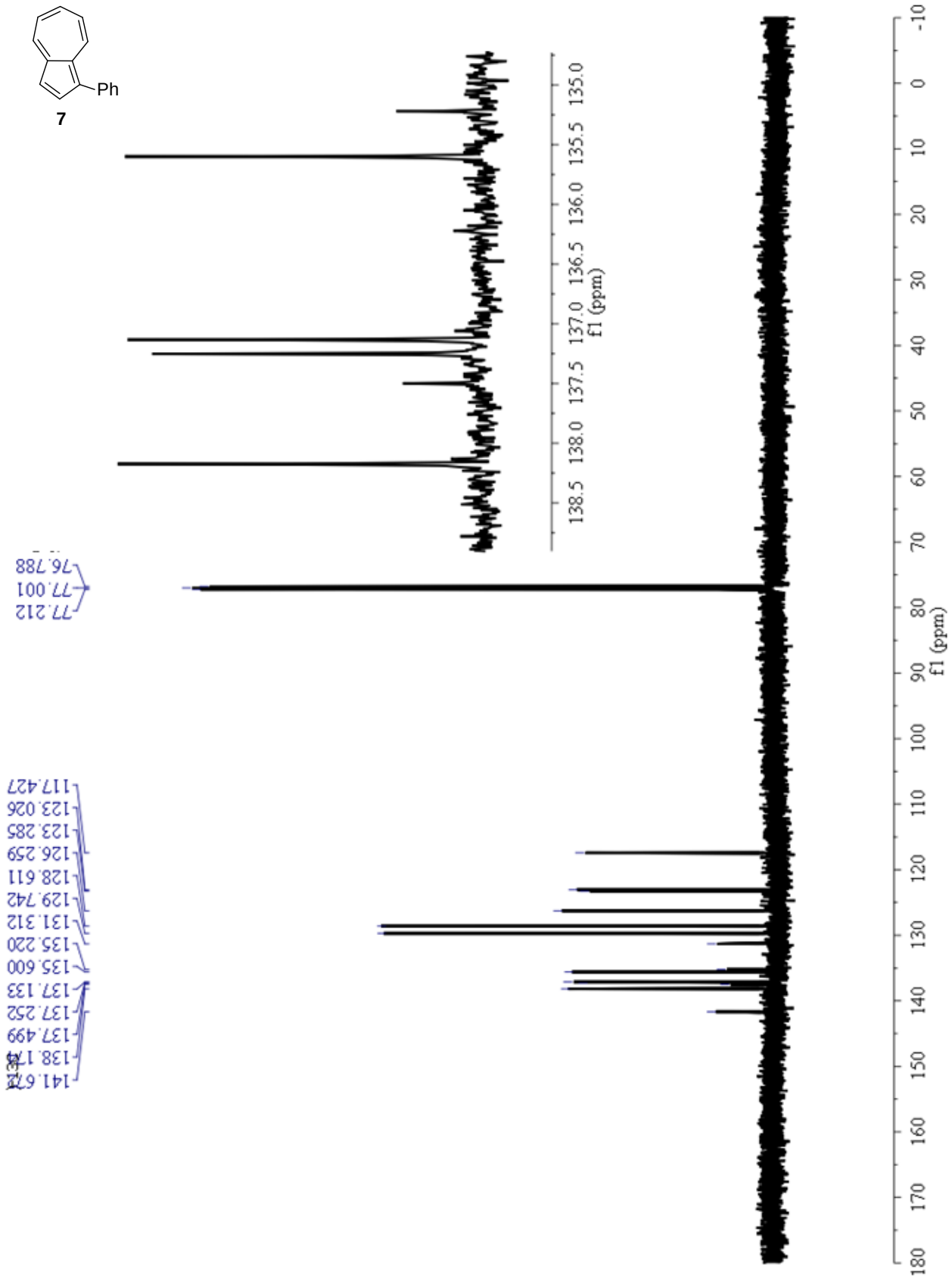
f1 (ppm)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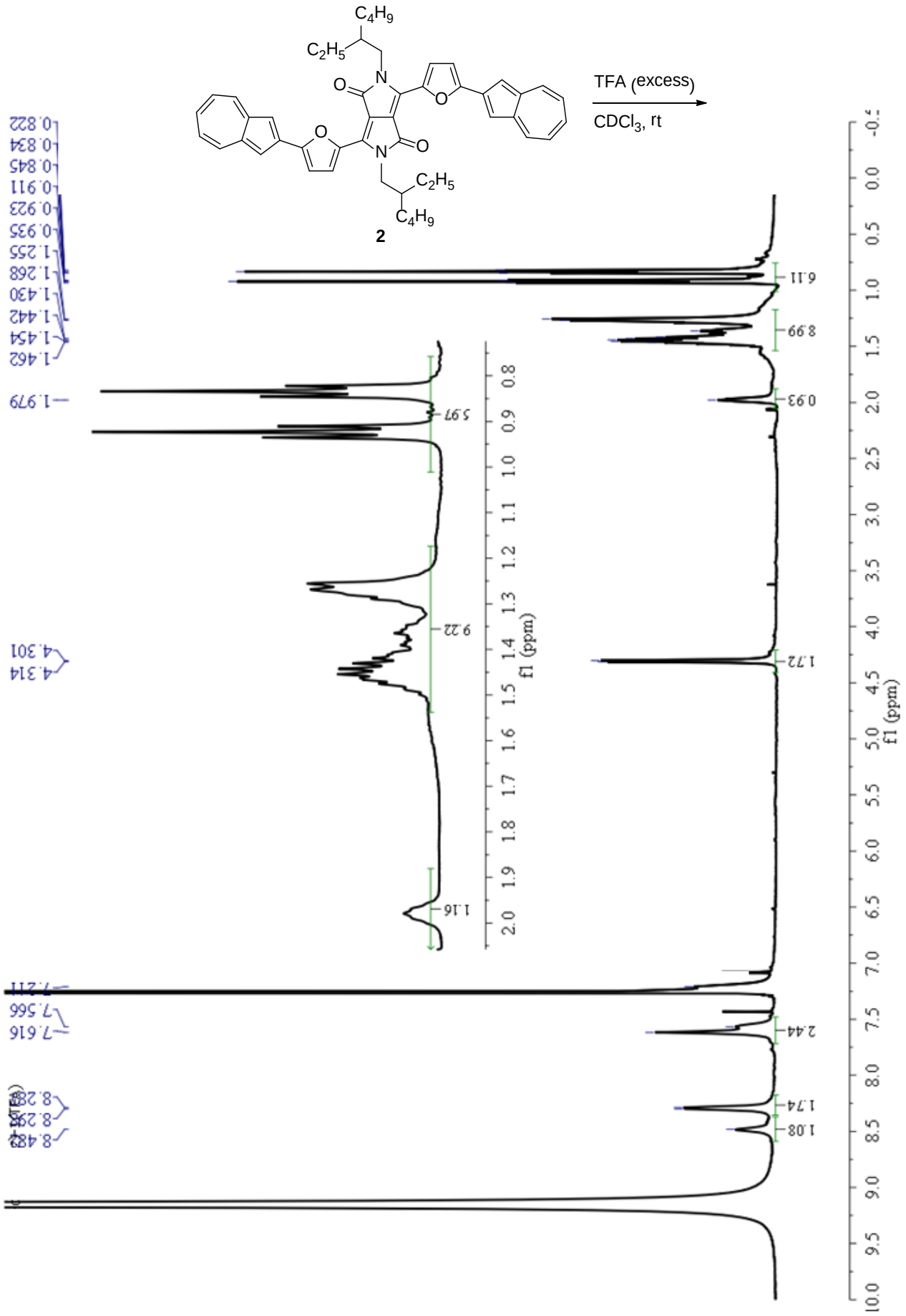
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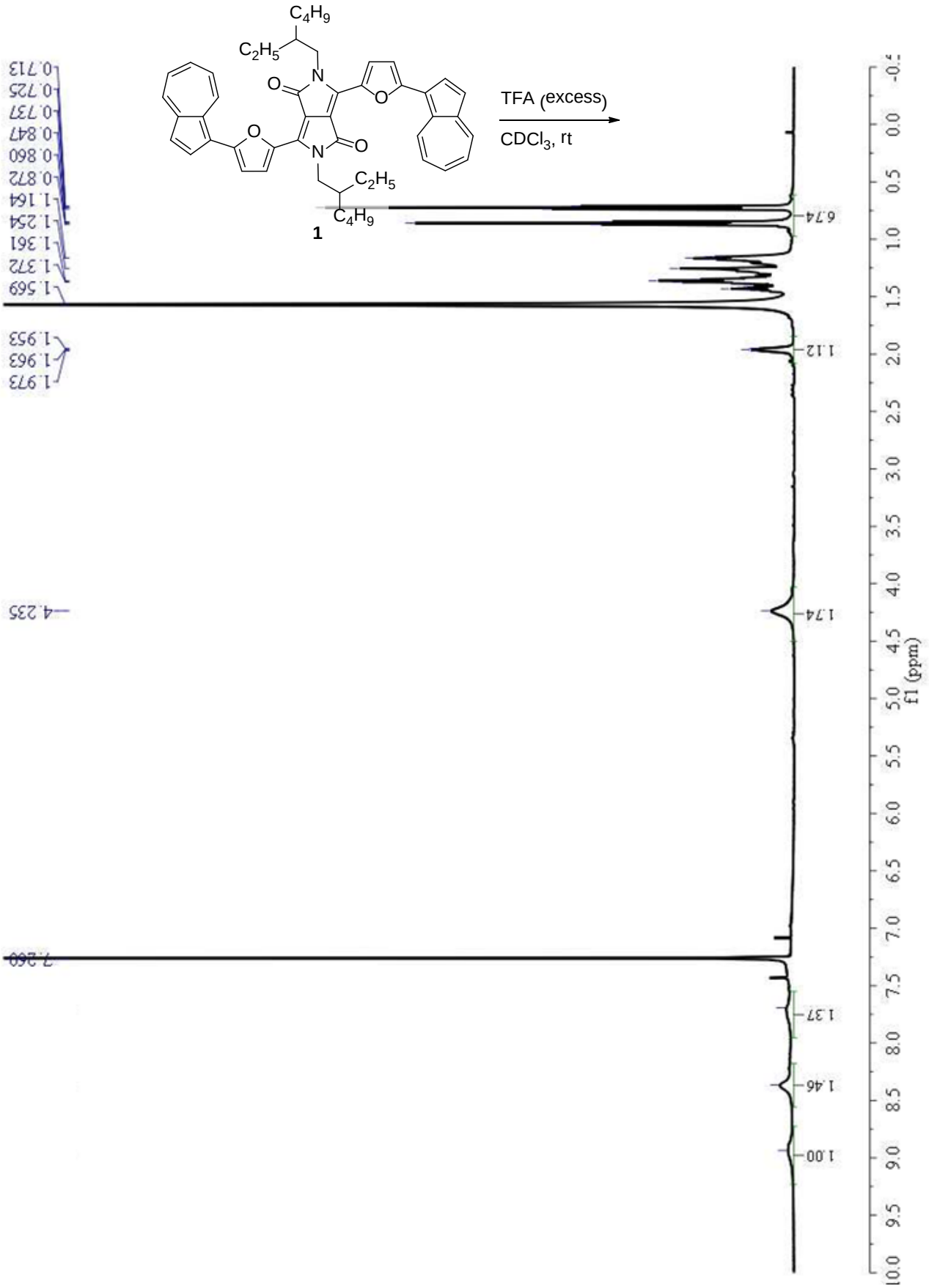
TFA (excess)
CDCl3, rt
f1 (ppm)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