

Supporting Information

Benzodipyrrole-2,6-dione-3,7-diylidenedimalononitrile Derivatives for Air-Stable N-Type Organic Field-Effect Transistors: Critical Role of *N*-Alkyl Substituent on Device Performance

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1. TGA data

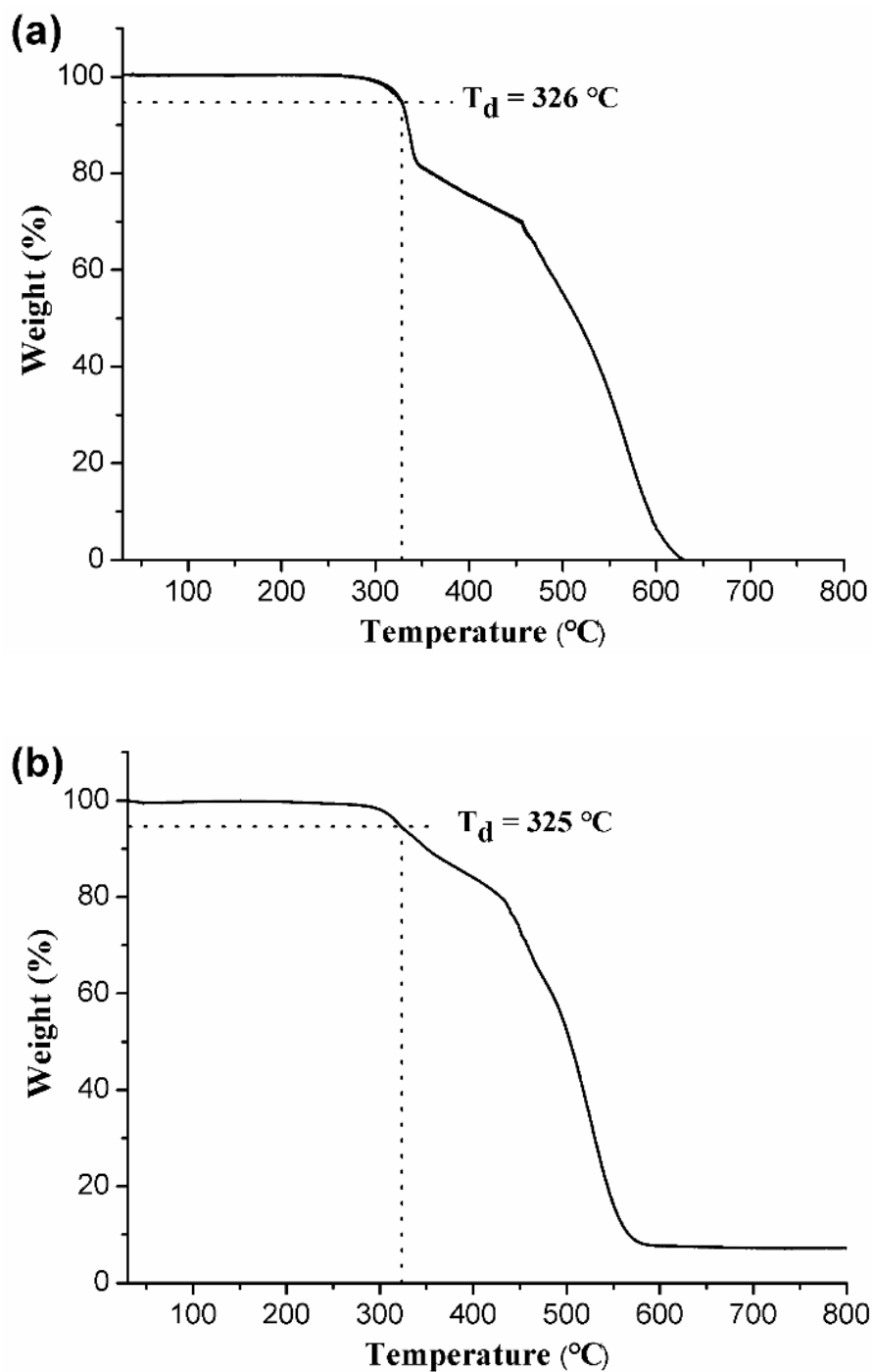


Figure S1. TGA curves of (a) **BDPM-Oct** and (b) **BDPM-But** at the heating rate of 10 °C min⁻¹ under N₂ atmosphere.

2. Computation coordinates

BDPM-Oct (B3LYP/6-31G**)

Number of imaginary frequencies = 0

HF= -1720.07144685 (Hartree)

Cartesian Coordinates (Angstroms)

atom	X	Y	Z
C	1.08764052	-0.74054283	-0.42829292
C	-0.07664540	-1.38393793	0.07514865
C	-1.18457783	-0.64062172	0.51121525
C	-1.08762691	0.74125061	0.42710873
C	0.07664798	1.38464513	-0.07635918
C	1.18458810	0.64132958	-0.51240739
N	2.04165176	-1.69144875	-0.80914164
C	0.17763805	-2.80836373	0.00795231
H	-2.07375347	-1.12384491	0.89363508
N	-2.04162552	1.69215553	0.80798959
C	-0.17764622	2.80907008	-0.00918154
H	2.07377224	1.12455298	-0.89480860
C	-1.57427862	2.97256531	0.56949351
C	1.57429240	-2.97185836	-0.57066911
C	-0.59841190	-3.87688102	0.35816758
O	2.16722213	-4.01056064	-0.78771260
O	-2.16714637	4.01127273	0.78667877
C	0.59838219	3.87758651	-0.35944629
C	1.91214967	3.69381371	-0.89891375

N	2.97760033	3.52159694	-1.33467897
C	0.18598878	5.24317552	-0.22556236
N	-0.03879765	6.38288343	-0.16401390
C	-1.91219746	-3.69310855	0.89759114
N	-2.97766189	-3.52089392	1.33332366
C	-0.18602720	-5.24247075	0.22426392
N	0.03875186	-6.38217888	0.16269248
C	3.37301919	-1.41705267	-1.34501241
C	-3.37281342	1.41774951	1.34429651
C	-4.40392111	1.06030701	0.26587881
C	4.40383383	-1.06013094	-0.26614222
H	3.28456977	-0.61316744	-2.08462781
H	3.67677906	-2.32345969	-1.87484344
H	-3.67654229	2.32429040	1.87391541
H	-3.28404056	0.61412057	2.08415717
H	-4.05169757	0.19595581	-0.31165197
H	-4.47776548	1.89954578	-0.43645952
C	-5.78236155	0.75374324	0.86411608
H	4.47727966	-1.89961506	0.43594471
H	4.05154870	-0.19591105	0.31154971
C	5.78256084	-0.75362211	-0.86374827
C	-6.84317281	0.44374538	-0.19934623
C	6.84302183	-0.444440049	0.20029068
H	-6.11408367	1.60926284	1.46897714
H	-5.69977386	-0.09705807	1.55473544

H	5.70044603	0.09751824	-1.55400432
H	6.11430507	-1.60894634	-1.46887352
H	-6.50754246	-0.40616633	-0.81008028
H	-6.92618066	1.29803006	-0.88573564
C	-8.22363459	0.13009698	0.39030401
H	6.92550723	-1.29903376	0.88630809
H	6.50736074	0.40530666	0.81129287
C	8.22382869	-0.13084300	-0.38860164
C	9.28991119	0.15562928	0.67569644
C	10.67161029	0.47228443	0.09024368
C	11.73214711	0.74840044	1.16005943
C	-9.29011667	-0.15727719	-0.67334985
C	-10.67143645	-0.47405267	-0.08707047
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H	8.55180206	-0.97451570	-1.01246350
H	9.37173220	-0.70944639	1.34929055
H	8.96152723	0.99692937	1.30279292
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H	10.99741181	-0.36600645	-0.54055792
H	11.86162467	-0.11551544	1.82178060
H	11.45114198	1.60322676	1.78568914
H	12.70534302	0.97155372	0.71109736

H	-8.96176139	-0.99881239	-1.30014593
H	-9.37252845	0.70741102	-1.34737077
H	-10.99721024	0.36448168	0.54342228
H	-10.58979112	-1.34156261	0.58178373
H	-11.45140773	-1.60618484	-1.78152010
H	-11.86250559	0.11239453	-1.81834950
H	-12.70529788	-0.97435819	-0.70665733

BDPM-But (B3LYP/6-31G**)

Number of imaginary frequencies = 0

HF= -1405.53912778 (Hartree)

Cartesian Coordinates (Angstroms)

atom	X	Y	Z
C	1.35113768	0.07981108	0.28805338
C	0.60532182	1.24935883	-0.02611916
C	-0.76542946	1.17801311	-0.31966856
C	-1.35115583	-0.07978358	-0.28825565
C	-0.60534509	-1.24932701	0.02593505
C	0.76541160	-1.17798467	0.31946550
N	2.68506602	0.41135015	0.55324504
C	1.53209695	2.36050735	0.04230582
H	-1.33848688	2.06411516	-0.55764713
N	-2.68507390	-0.41132697	-0.55349110
C	-1.53212114	-2.36047356	-0.04245870
H	1.33846316	-2.06408852	0.55745274

C	-2.88378311	-1.77415789	-0.41817078
C	2.88374896	1.77419493	0.41805889
C	1.34664054	3.69856931	-0.16252951
O	3.93062074	2.37157361	0.57502154
O	-3.93067743	-2.37152307	-0.57503490
C	-1.34665717	-3.69853136	0.16239763
C	-0.06033591	-4.22308970	0.51044870
N	0.99411136	-4.62780013	0.79166803
C	-2.38808549	-4.67626728	0.05172355
N	-3.14857307	-5.55450095	-0.00837628
C	0.06032899	4.22314109	-0.51059643
N	-0.99410313	4.62788904	-0.79181841
C	2.38807563	4.67629496	-0.05182895
N	3.14859538	5.55450037	0.00827736
C	3.75960653	-0.52044511	0.88775649
C	-3.75969395	0.52048576	-0.88768937
C	-4.34667933	1.24107952	0.33297220
C	4.34678552	-1.24115996	-0.33274443
H	3.37305685	-1.23960519	1.61892790
H	4.53031070	0.07513583	1.38354114
H	-4.53048037	-0.07505840	-1.38338902
H	-3.37330123	1.23972667	-1.61886402
H	-3.54960839	1.77167141	0.86960013
H	-4.74514262	0.48868553	1.02463164
C	-5.45098695	2.23087321	-0.05818044

H	4.74538149	-0.48881767	-1.02438658
H	3.54976748	-1.77172986	-0.86947645
C	5.45098213	-2.23097202	0.05862110
C	-6.06604353	2.94308282	1.14987973
C	6.06617889	-2.94328422	-1.14930708
H	-6.23657889	1.69691439	-0.60913886
H	-5.04106534	2.97641337	-0.75252404
H	5.04093904	-2.97645629	0.75295458
H	6.23652576	-1.69702150	0.60965876
H	-5.31006578	3.51254128	1.70149803
H	-6.51721989	2.22706565	1.84540255
H	6.51739674	-2.22732403	-1.84486301
H	5.31027835	-3.51283059	-1.70093983
H	-6.84744036	3.64315079	0.83935134
H	6.84757540	-3.64328659	-0.83862948

3. Single crystal structure

The single crystals of BDPM derivatives were grown using the solvent vapor diffusion method in CHCl_3 /isopropanol) as shown in Figure S2. A 2ml bottle containing 0.5 mg/ml BDPMs solution in CHCl_3 (1 ml) was covered by a fine meshed Al foil. This small bottle was put inside a sealed 20 ml bottle containing 1 mL of isopropanol. Sheet-like crystals of BDPM derivatives were obtained after 10 days evaporation under ambient conditions.

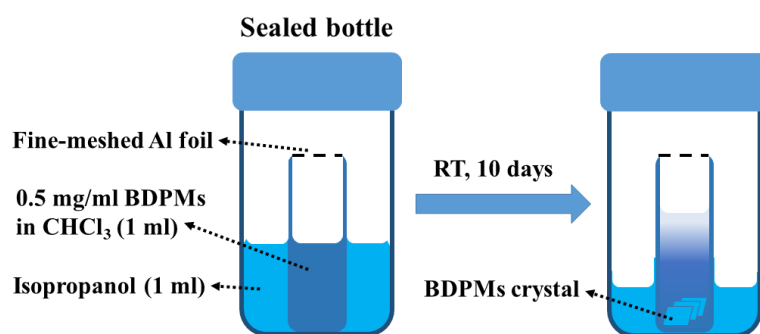


Figure S2. The diagram of single crystals preparation.

Table S1. The crystal structure datum of BDPM derivatives

	BDPM-Oct	BDPM-But
Formula	$\text{C}_{32}\text{H}_{36}\text{N}_6\text{O}_2$	$\text{C}_{24}\text{H}_{20}\text{N}_6\text{O}_2$
M.W.	536.67	424.46
Temp. (K)	100(2)	100(2)
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	$P 2_1/c$	$P 2_1$
Z	4	2
Lattice		
a [Å]	8.6764(7)	9.3720(9)
b [Å]	11.0515(9)	10.1969(10)
c [Å]	31.064(2)	11.3176(11)
α [°]	90	90
β [°]	94.380(3)	96.536(3)
γ [°]	90	90
V (Å ³)	2970.0(4)	1074.54(18)
R-factor (%)	3.68	4.02

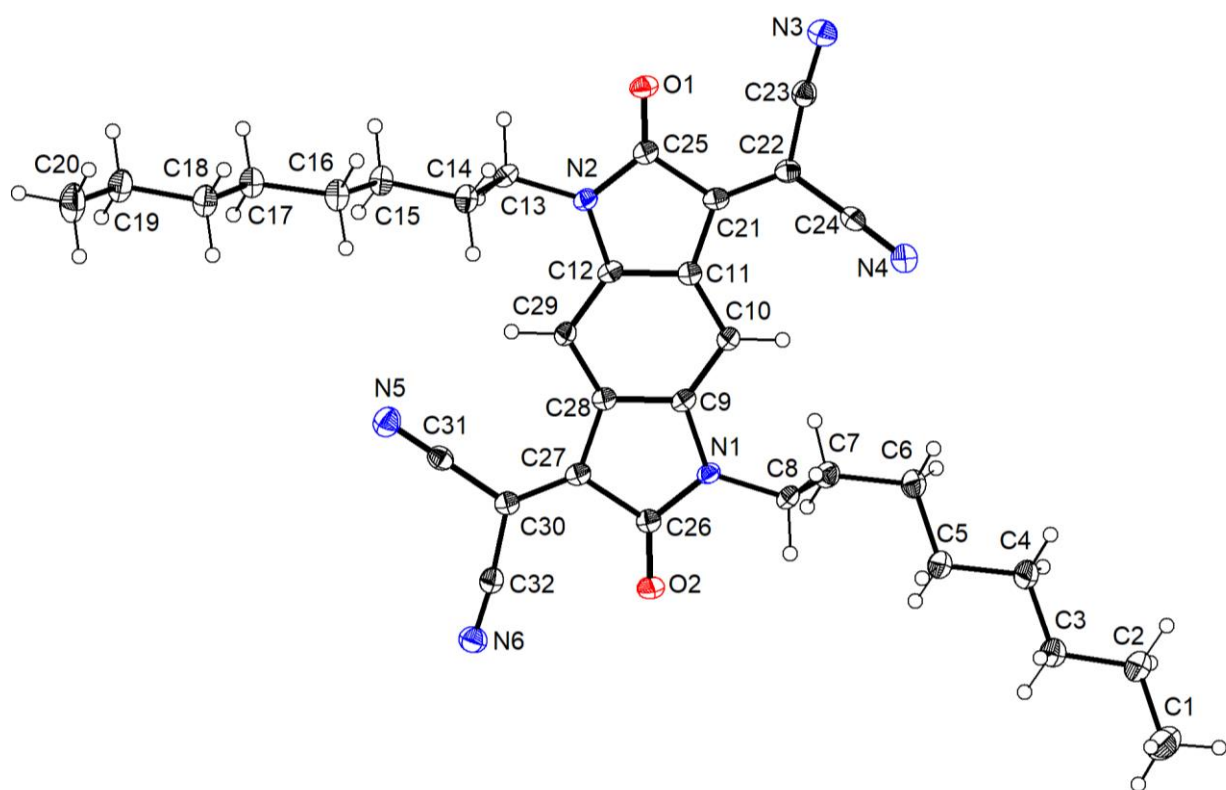


Figure S3. ORTEP plot of **BDPM-Oct** with thermal ellipsoids set at 50% probability level.

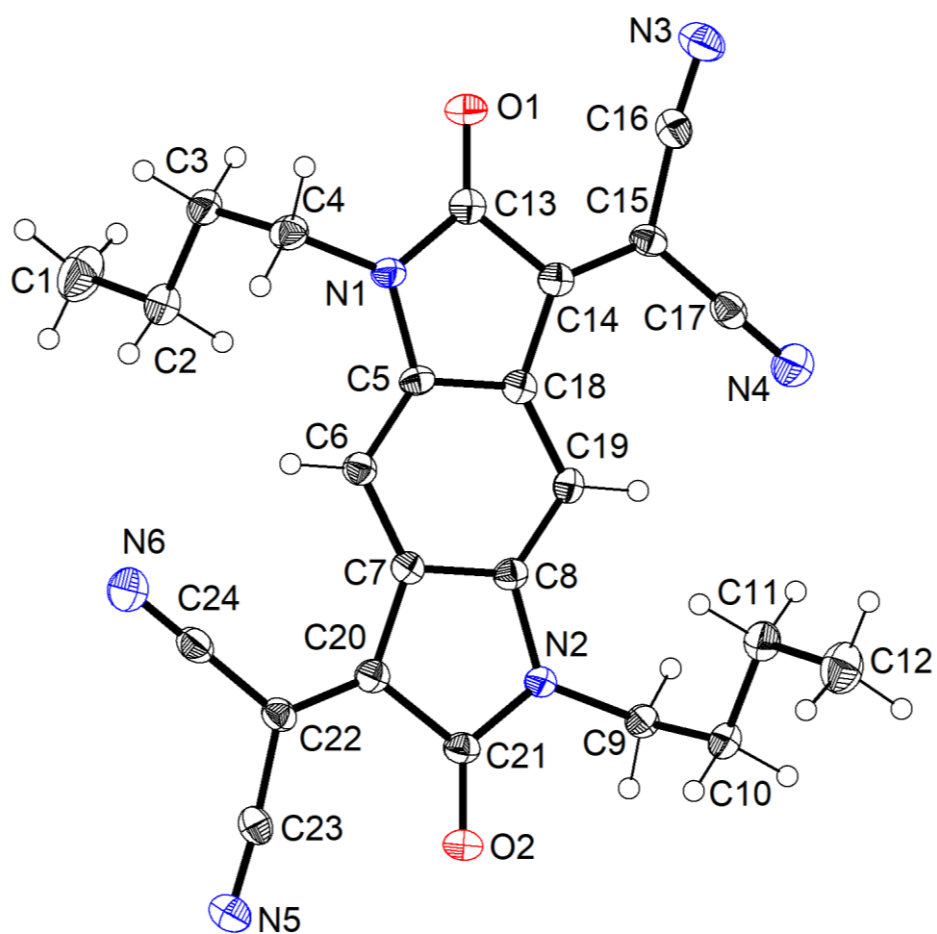


Figure S4. ORTEP plot of **BDPM-But** with thermal ellipsoids set at 50% probability level.

4. Device Characteristics

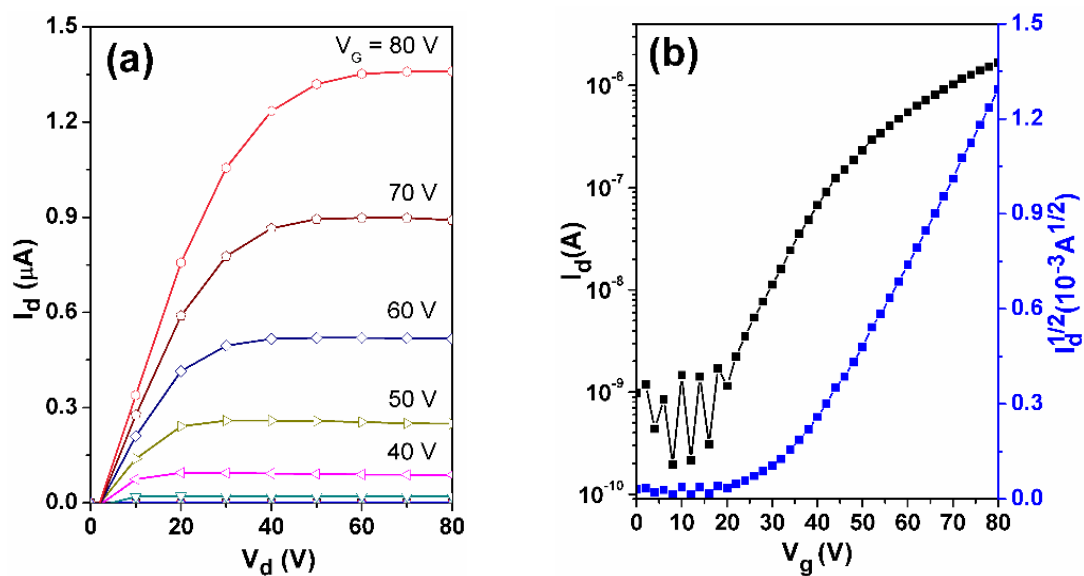


Figure S5. (a) Output and (b) transfer curves characteristics of **BDPM-Oct** based OFETs ($t = 60$ °C) on COC-modified SiO_2 .

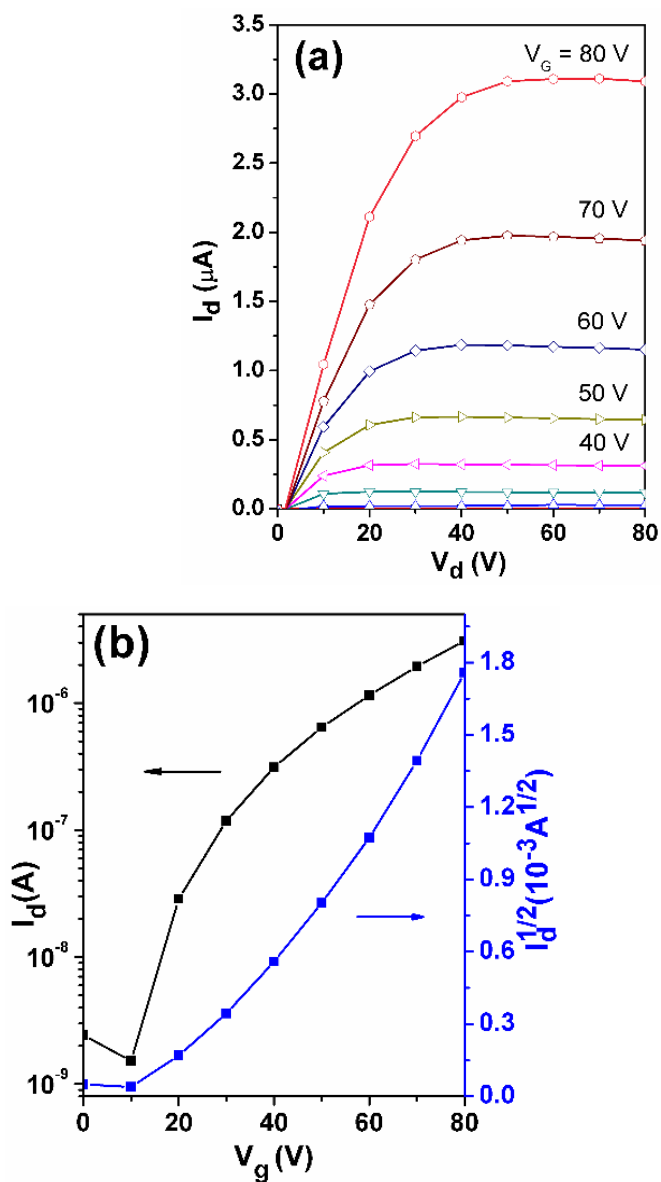
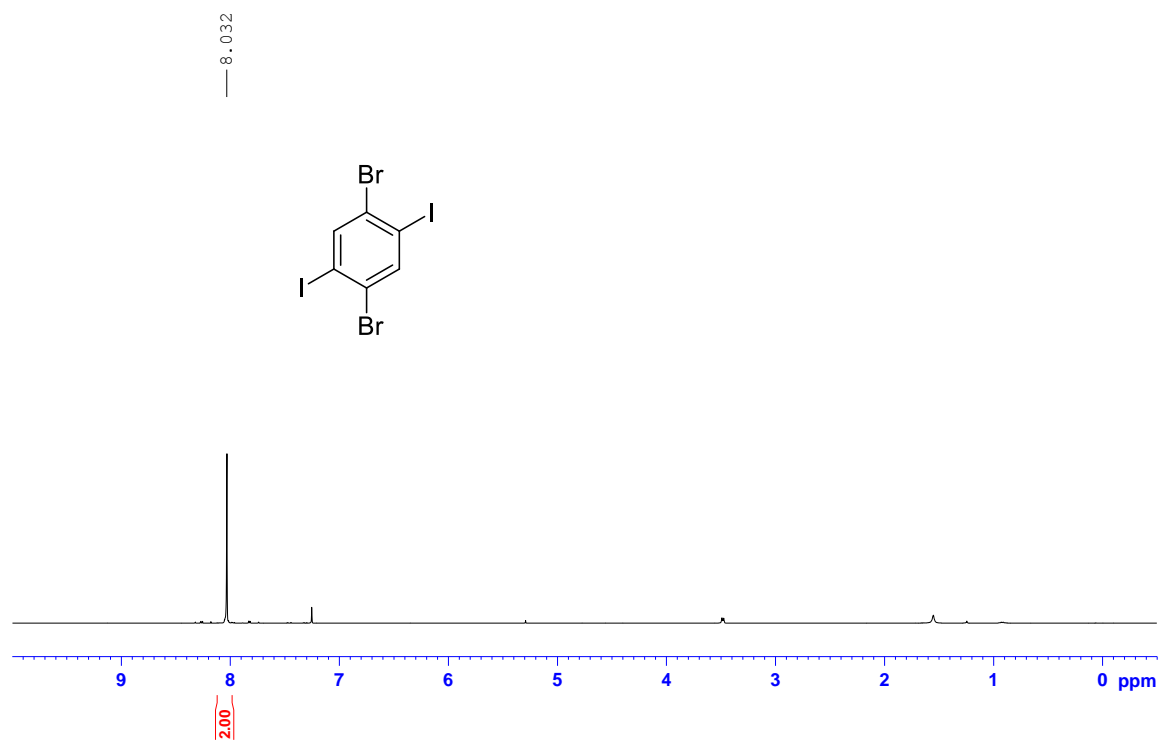


Figure S6. (a) Output and (b) transfer curves characteristics of **BDPM-But** based OFETs ($t = 60$ °C) on COC-modified SiO_2 .

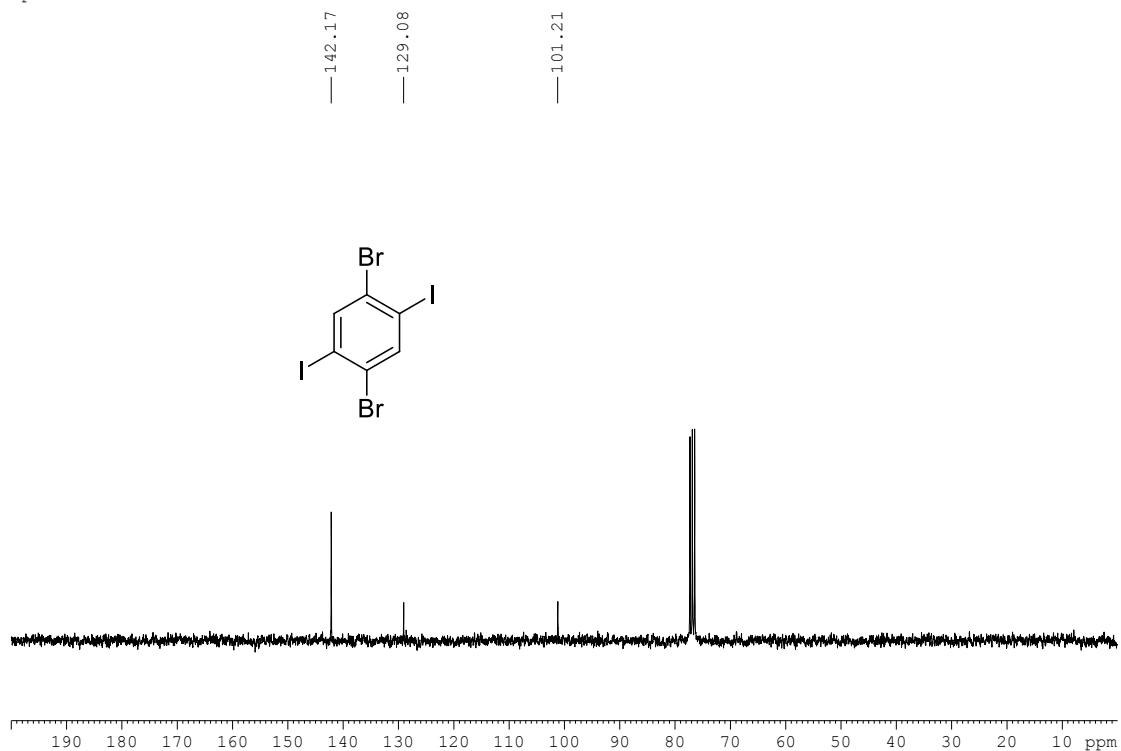
5. NMR spectra

apd 221 H1 dibromodi iodo



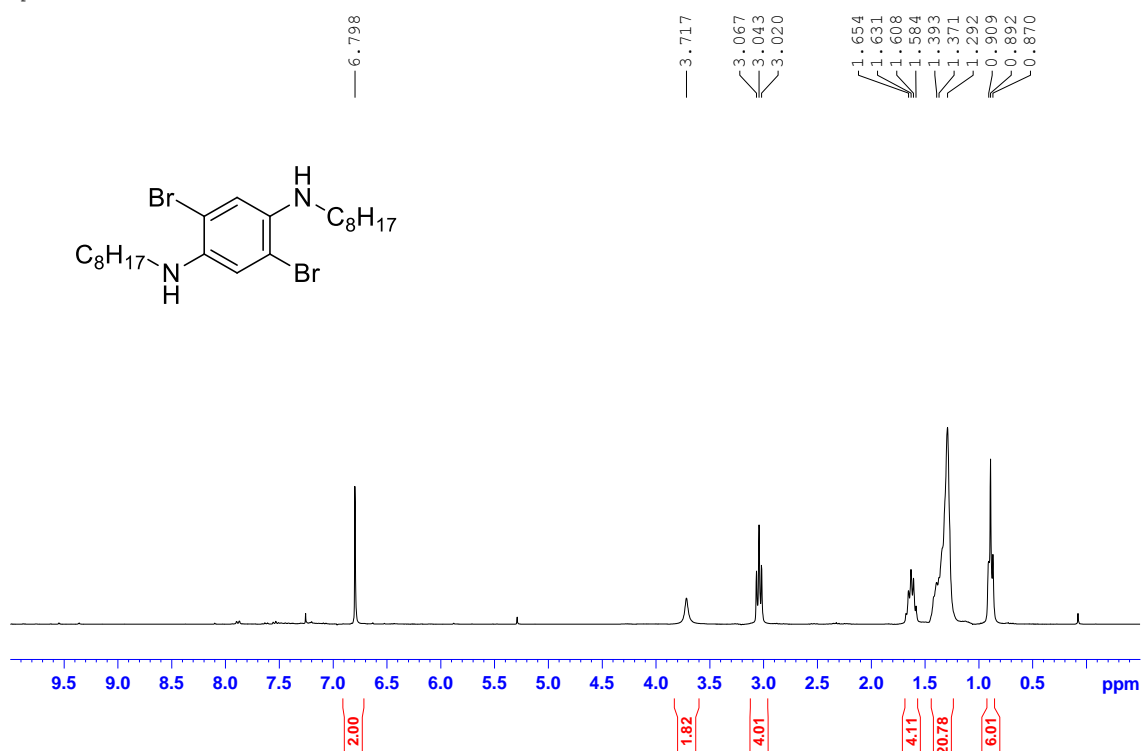
¹H NMR spectra of compound 1

apd 221 c13 dibromodi iodo



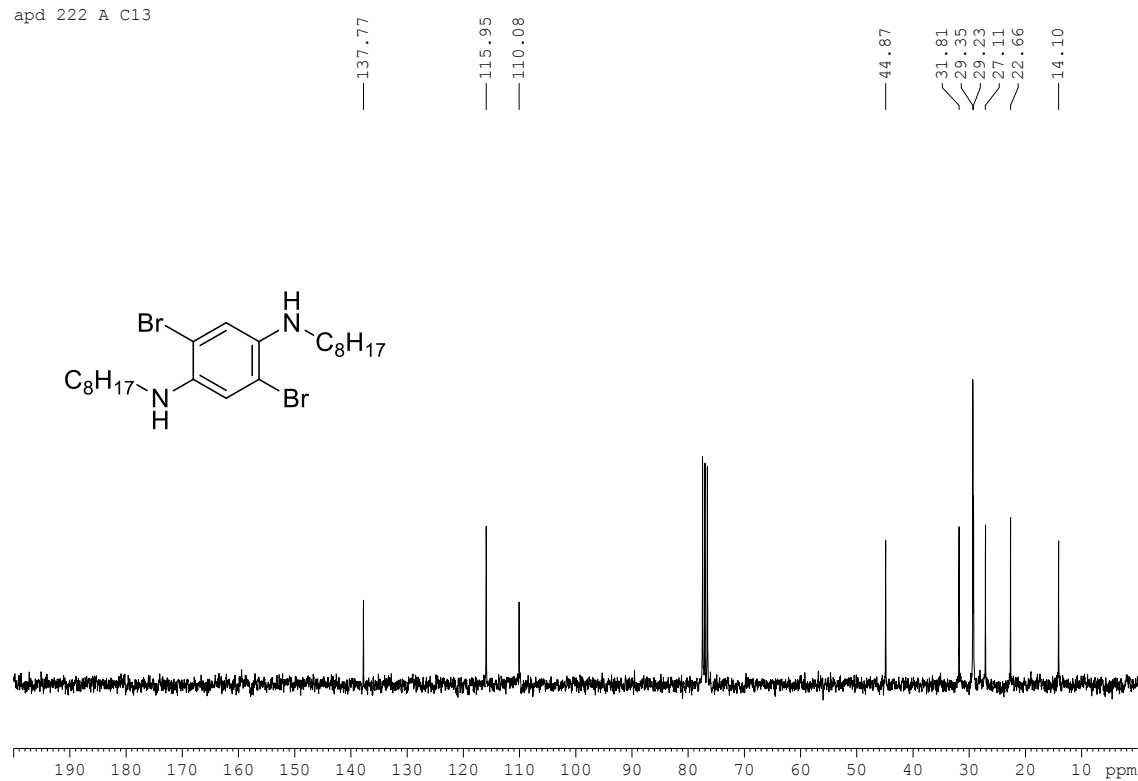
¹³C NMR spectra of compound 1

apd 222 A H1

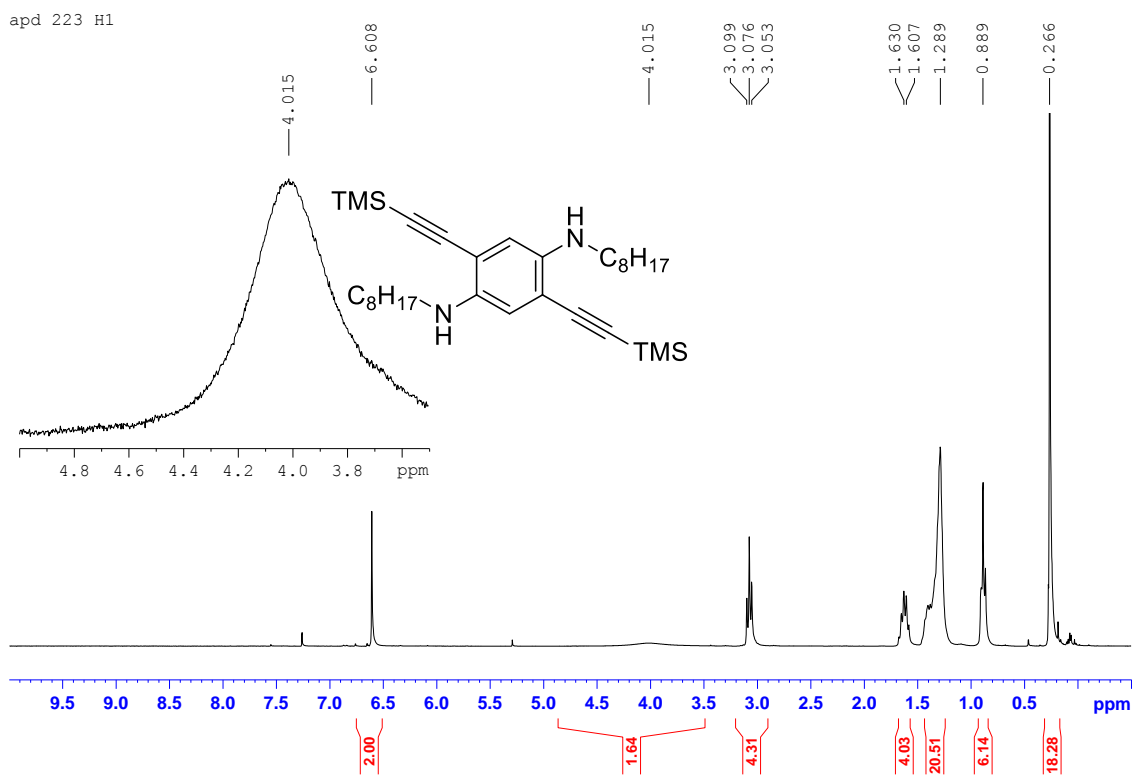


¹H NMR spectra of compound 2

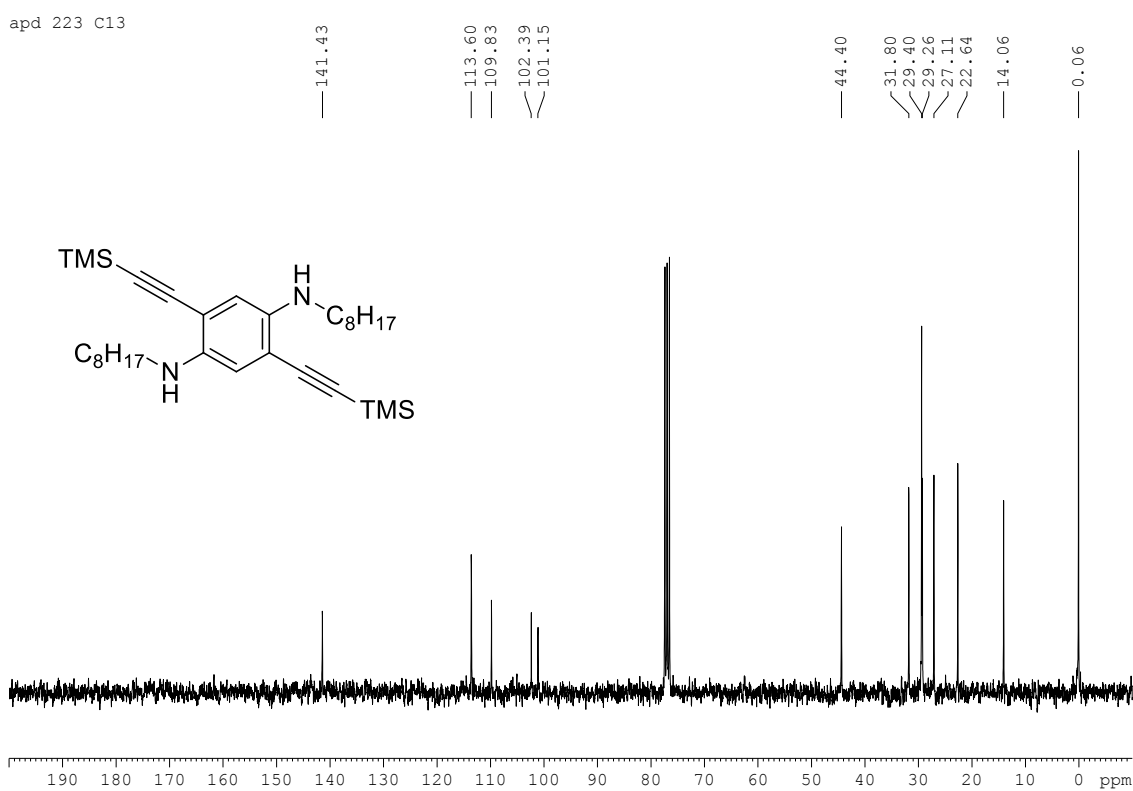
apd 222 A C13



¹³C NMR spectra of compound 2

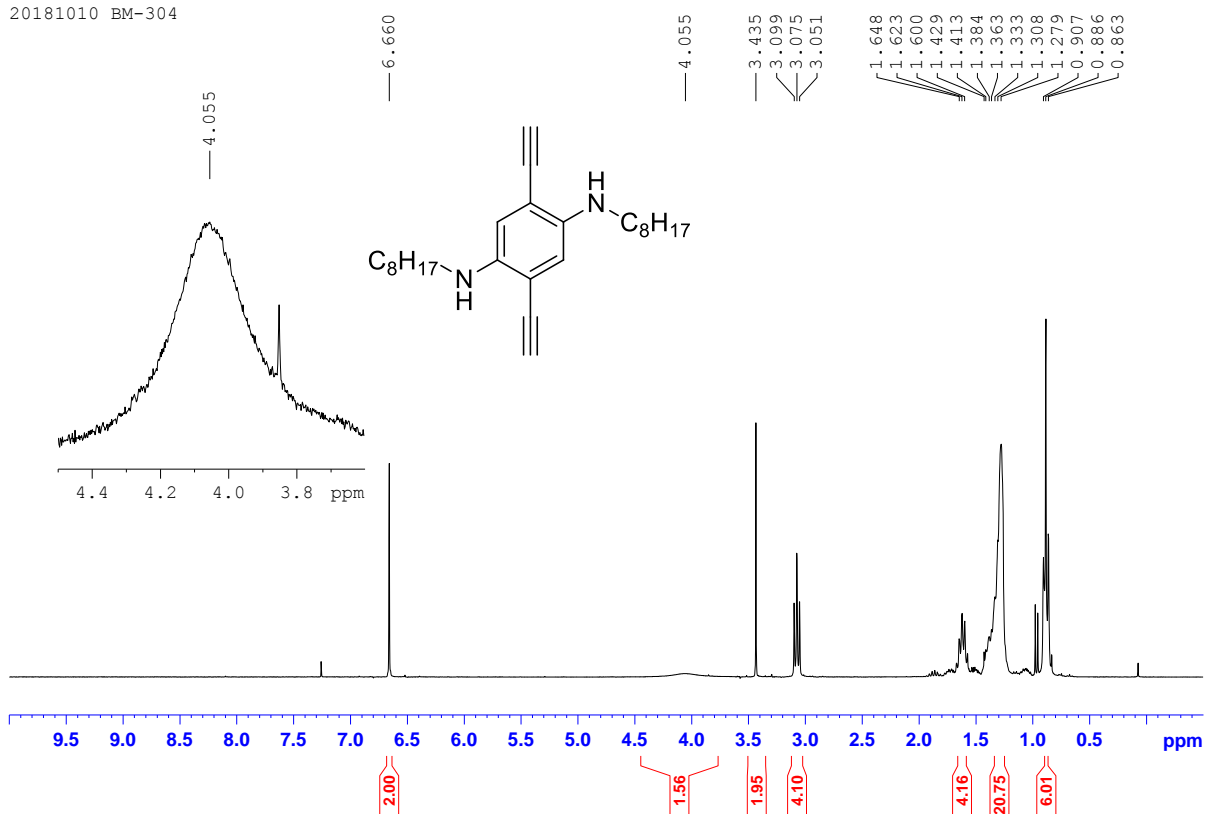


¹H NMR spectra of compound 4



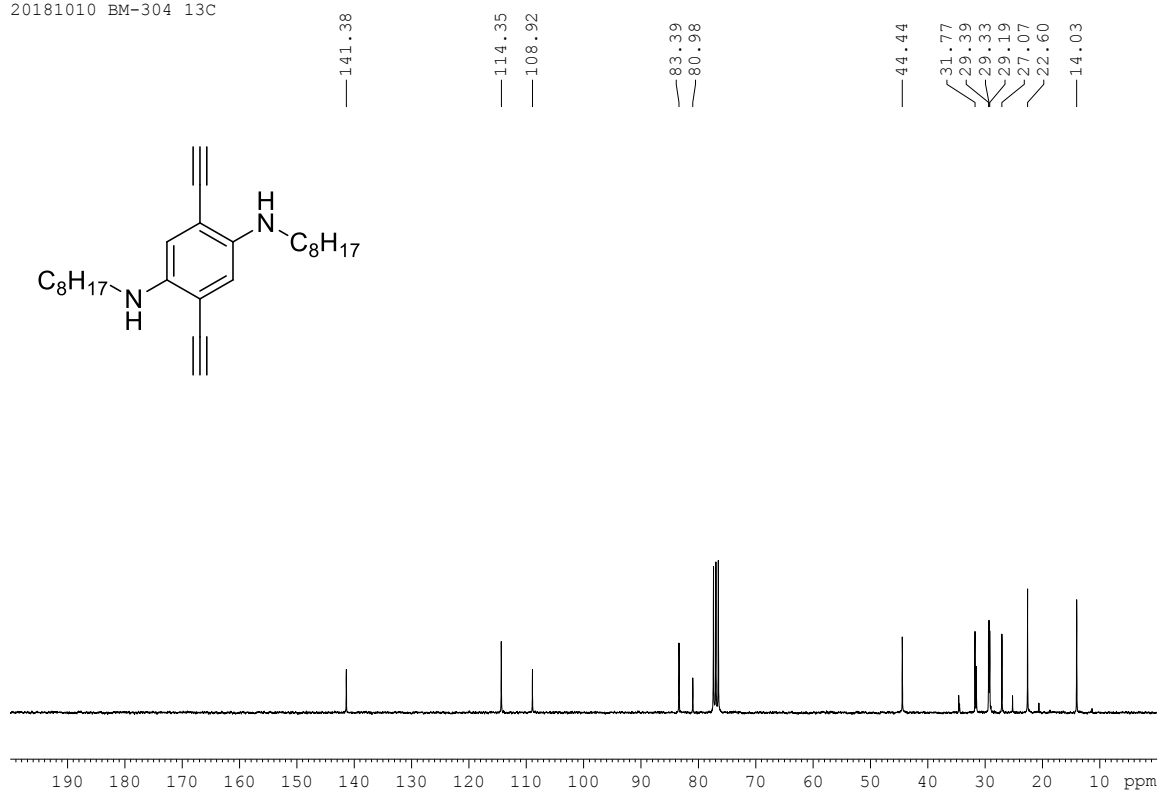
¹³C NMR spectra of compound 4

20181010 BM-304



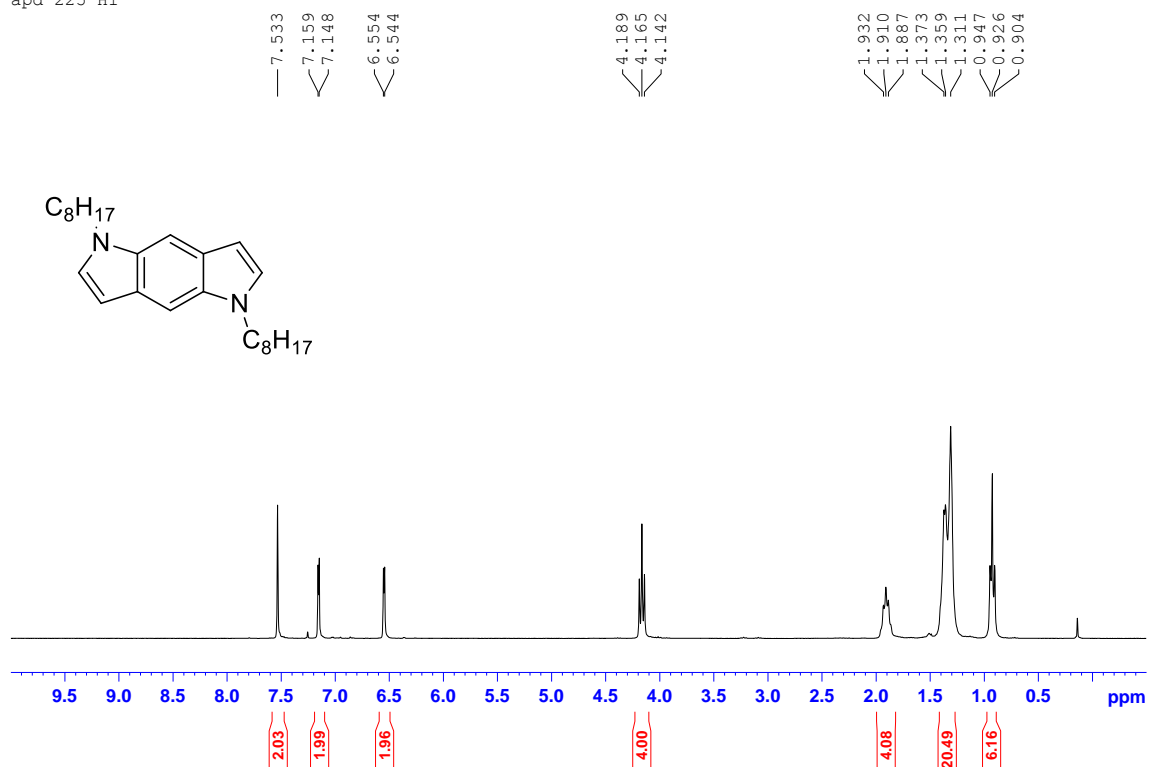
¹H NMR spectra of compound 6

20181010 BM-304 13C



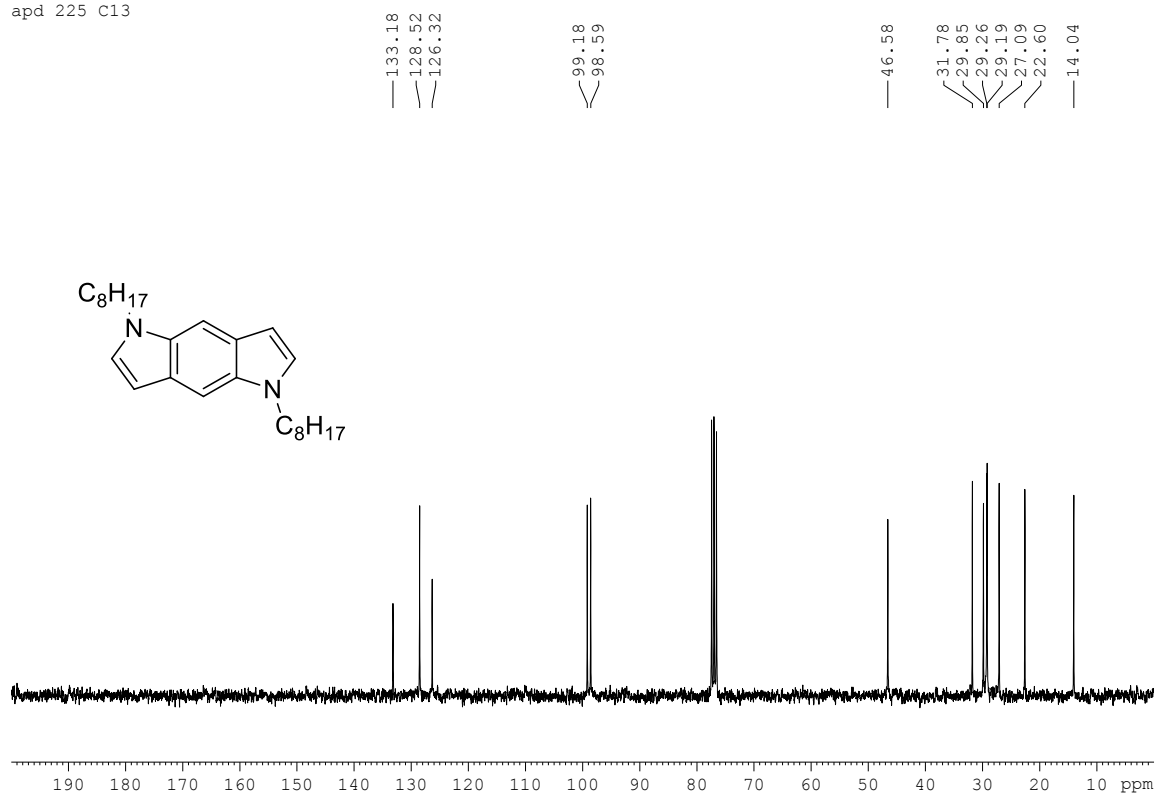
¹³C NMR spectra of compound 6

apd 225 H1



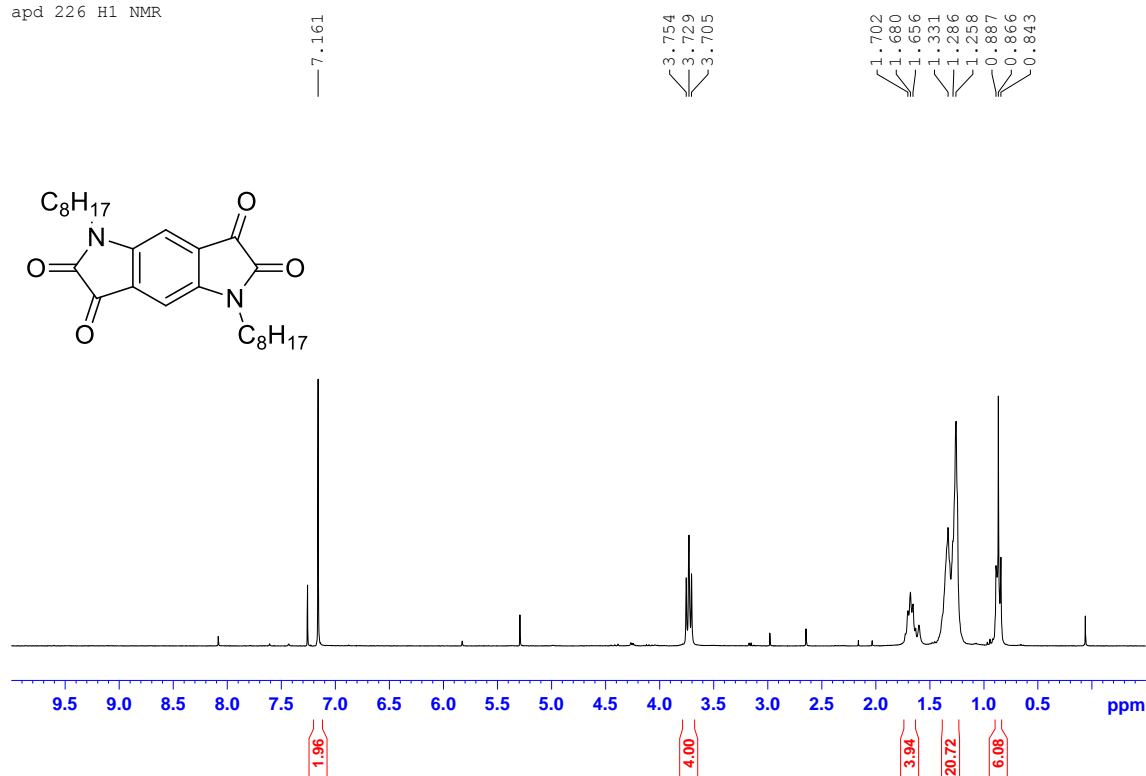
¹H NMR spectra of compound 8

apd 225 C13



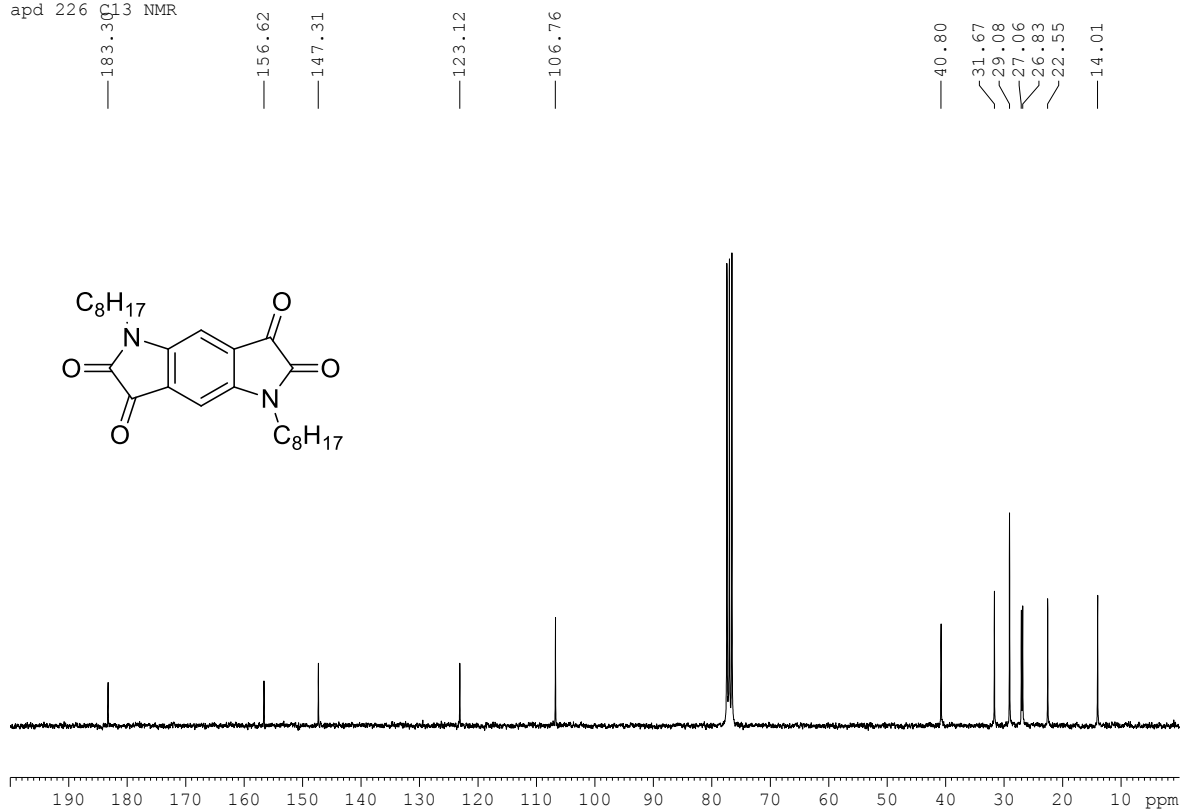
¹³C NMR spectra of compound 8

apd 226 H1 NMR



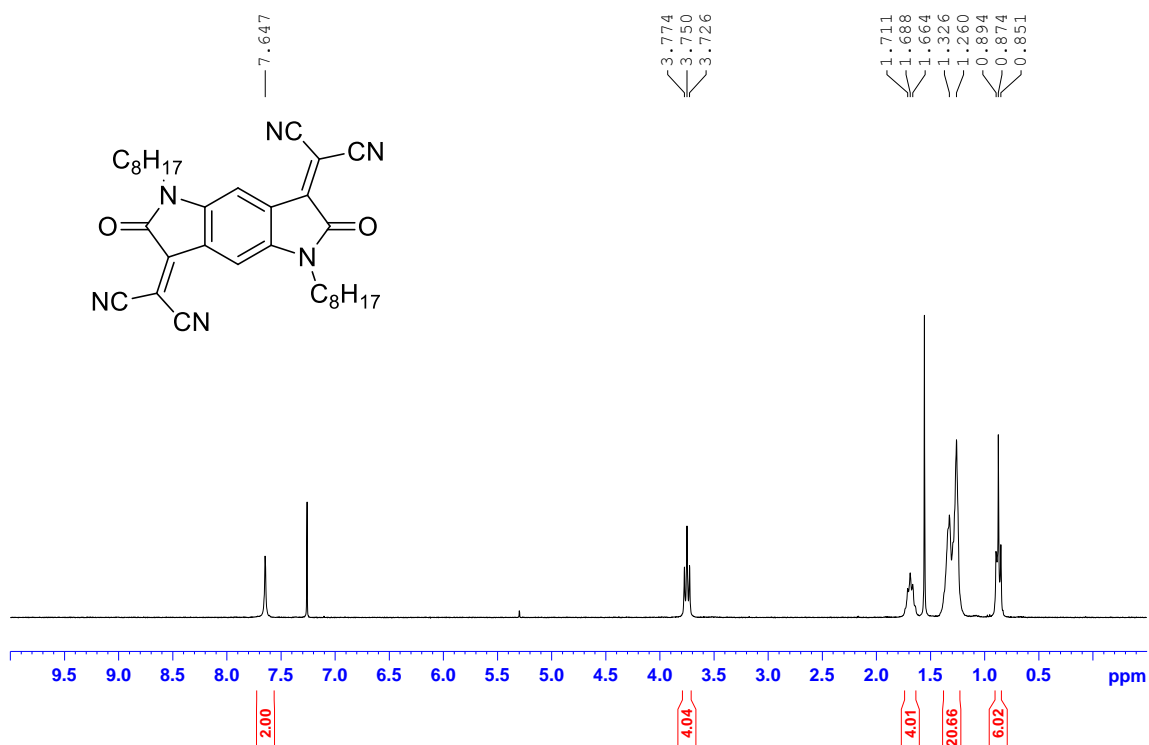
¹H NMR spectra of compound 10

apd 226 Q13 NMR



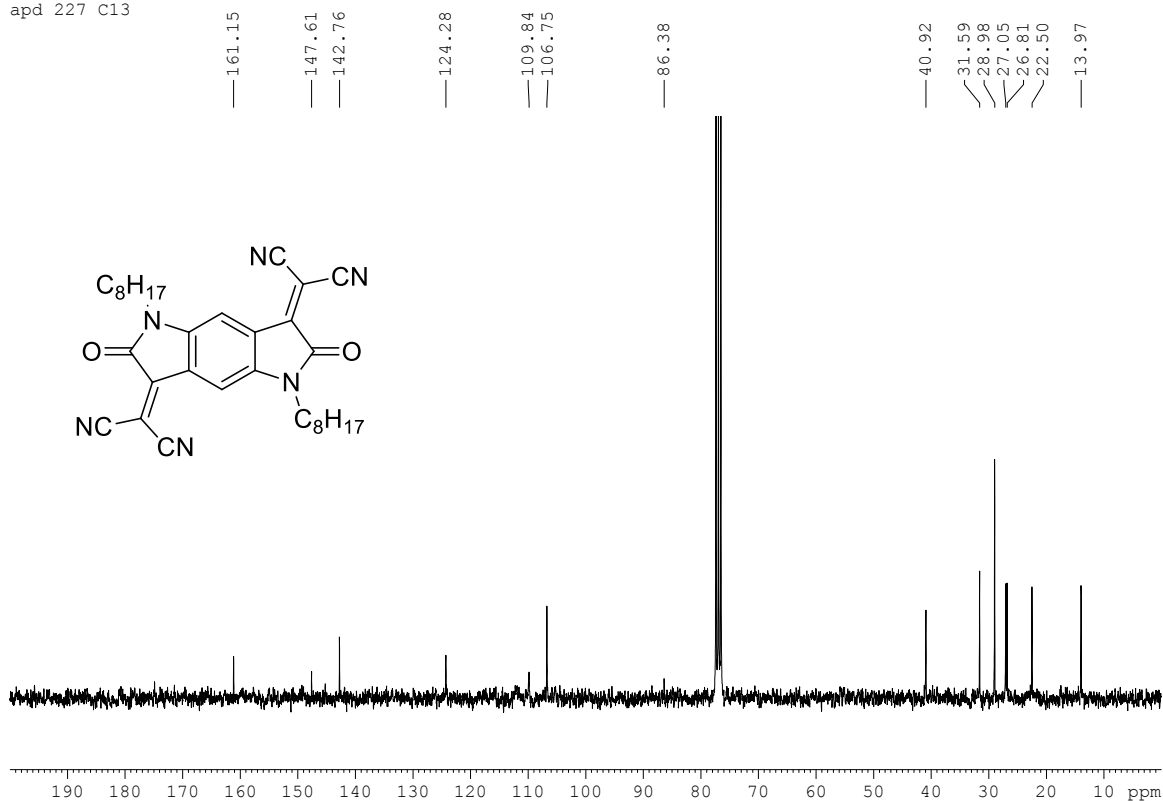
¹³C NMR spectra of compound 10

apd 227 20180306



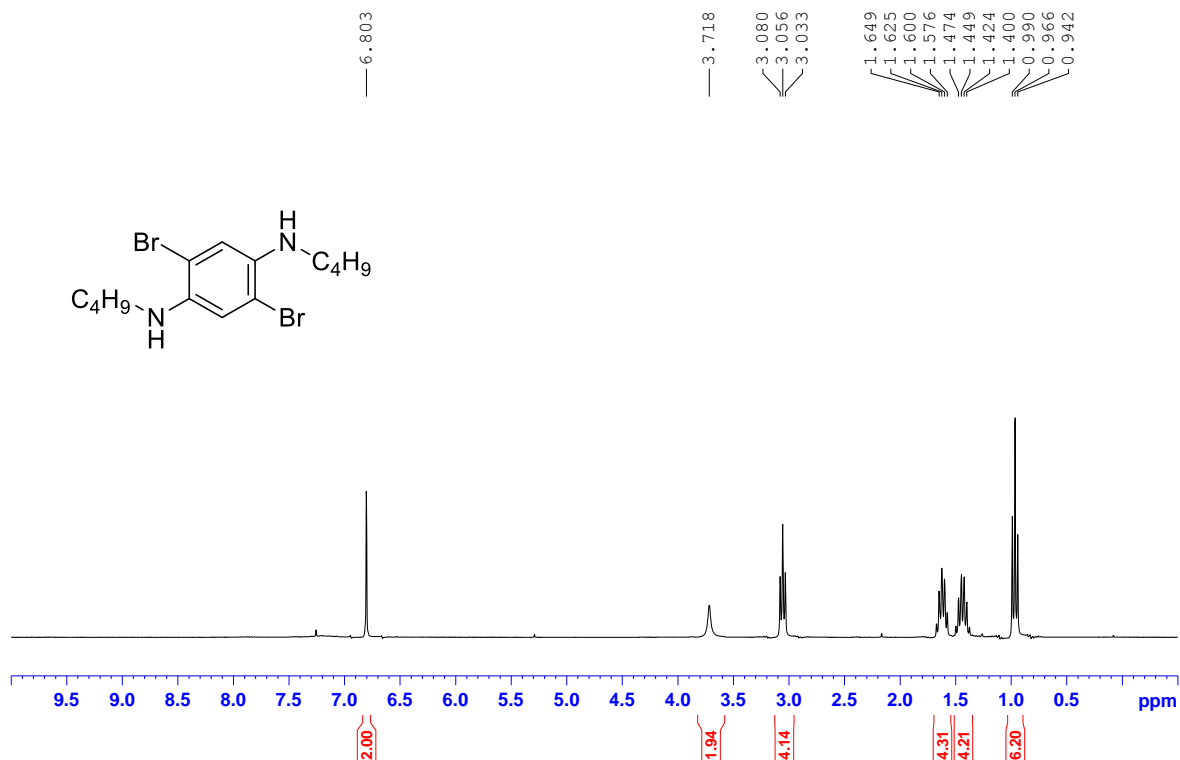
¹H NMR spectra of BDPM-Oct

apd 227 C13



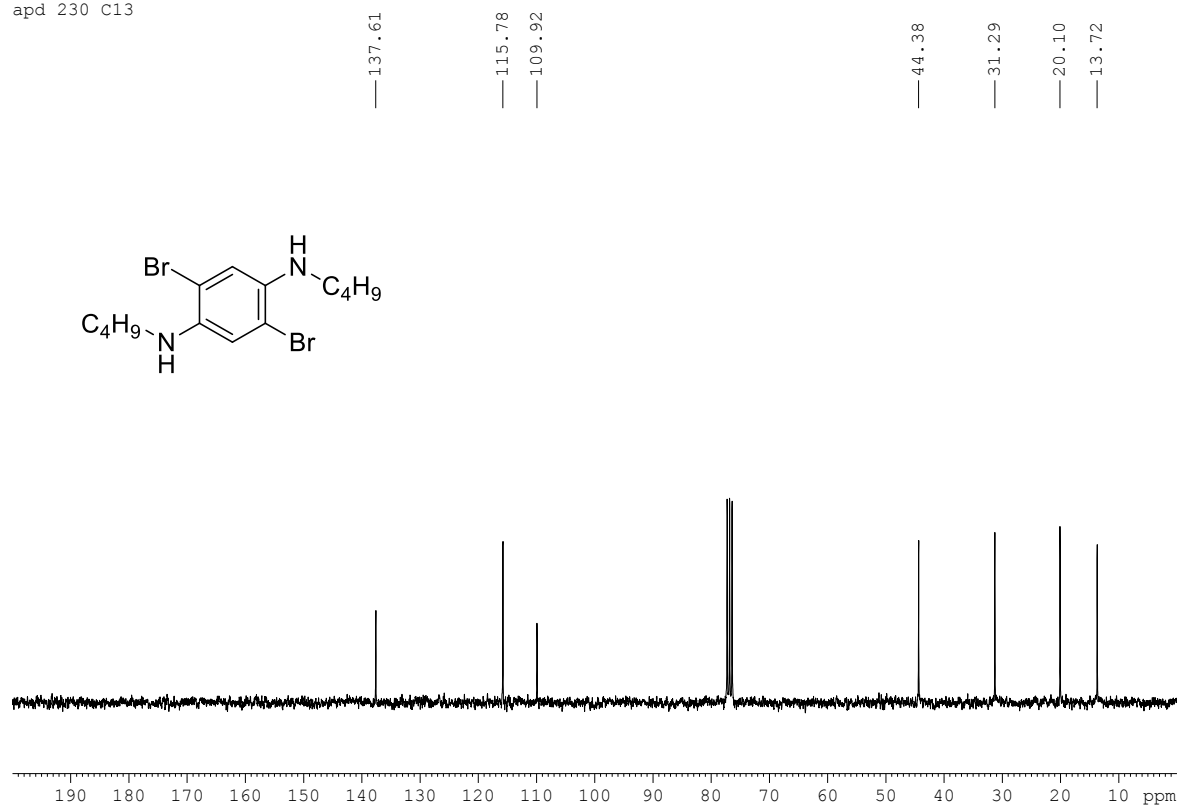
¹³C NMR spectra of BDPM-Oct

apd 230 H1



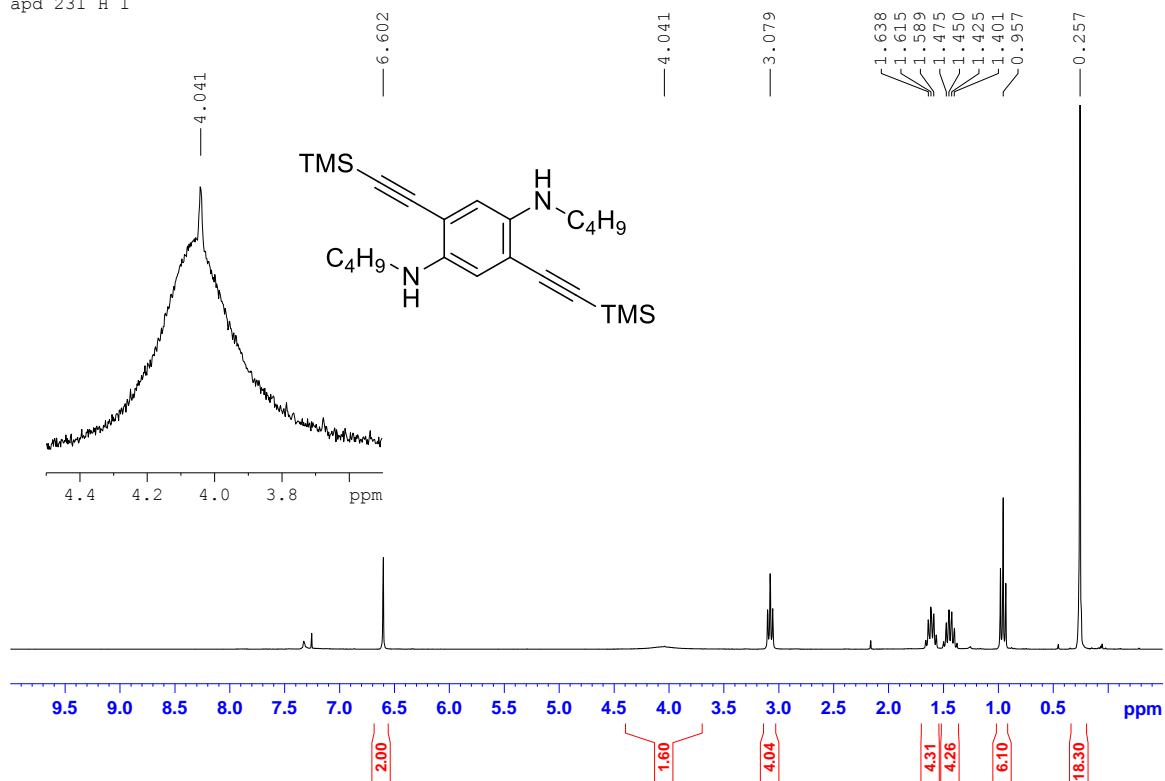
¹H NMR spectra of compound 3

apd 230 C13



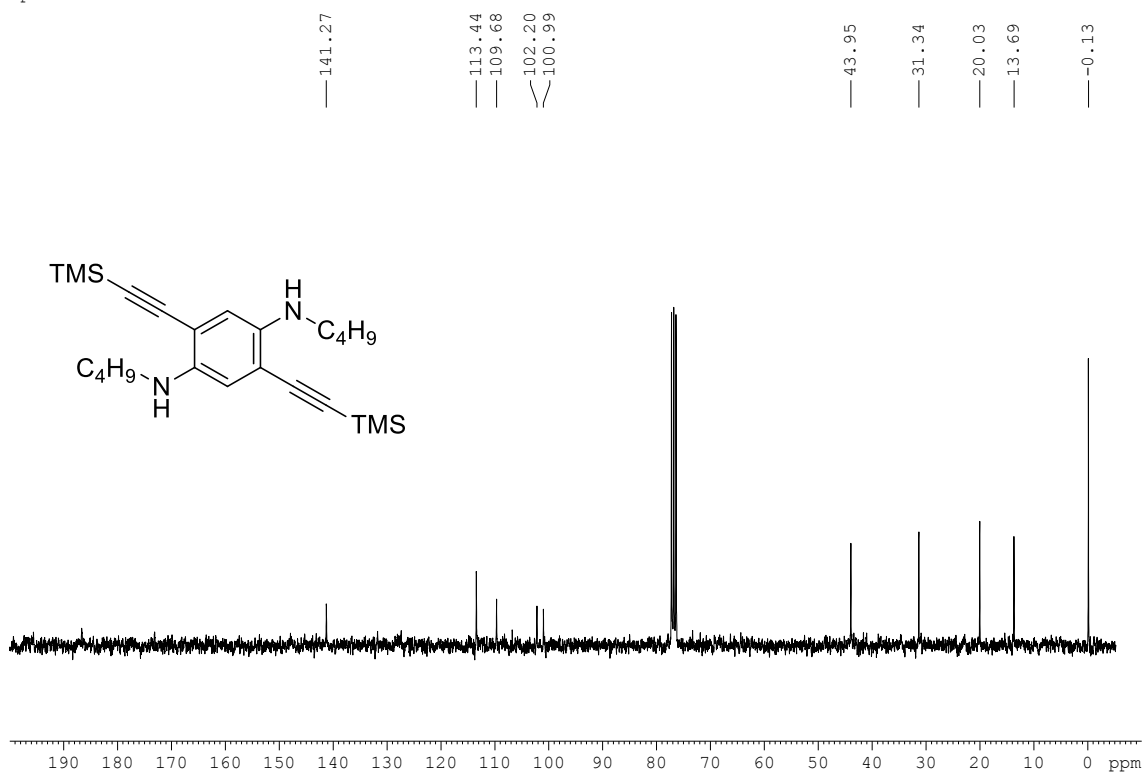
¹³C NMR spectra of compound 3

apd 231 H 1



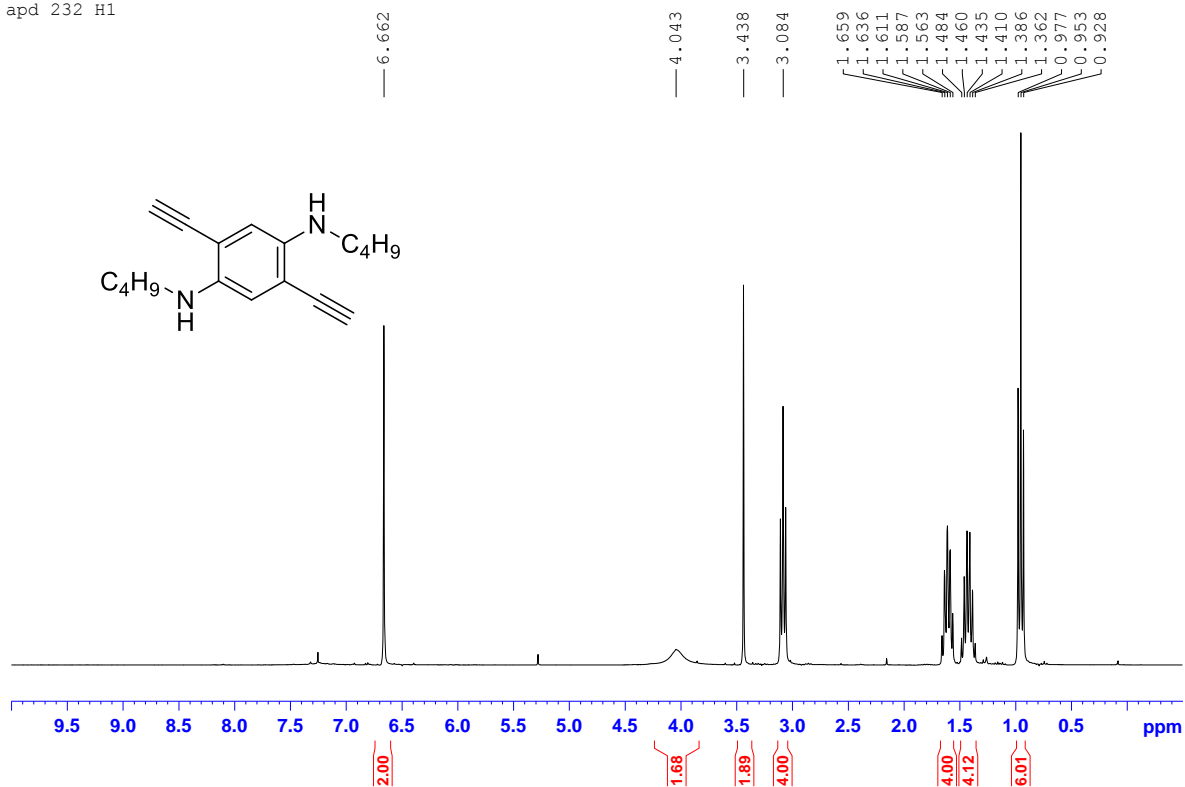
¹H NMR spectra of compound 5

apd 231 C13



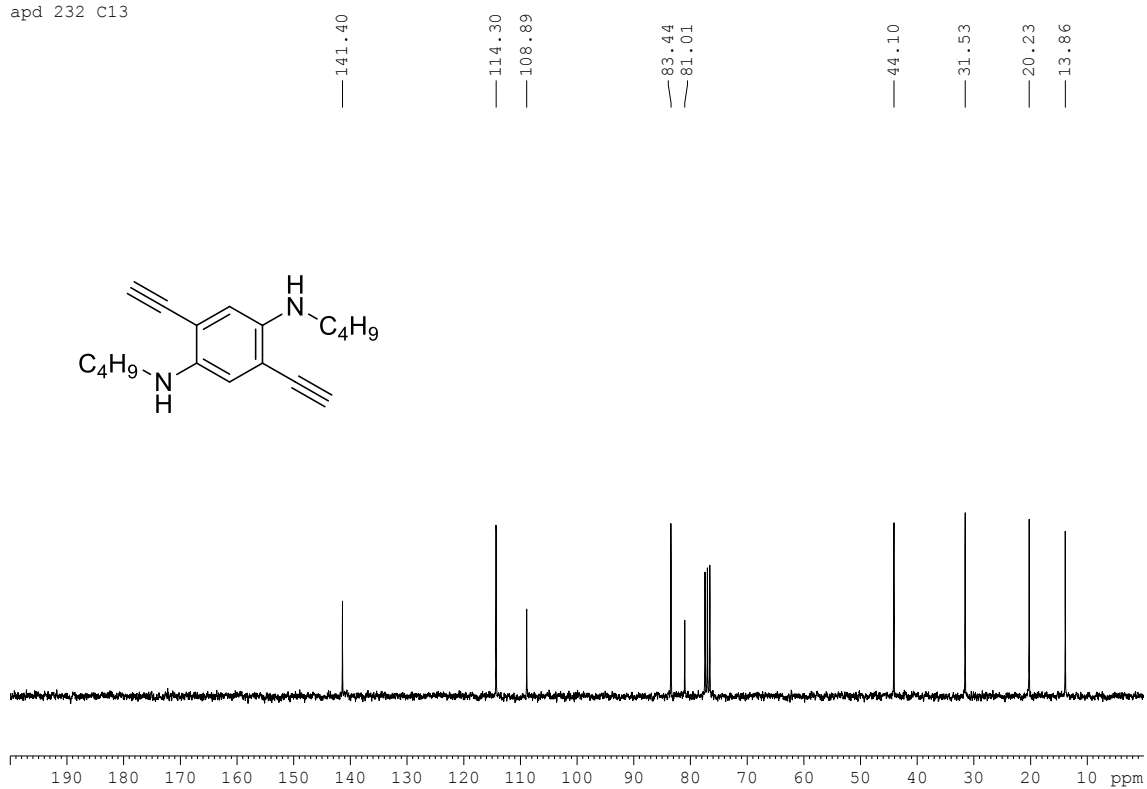
¹³C NMR spectra of compound 5

apd 232 H1



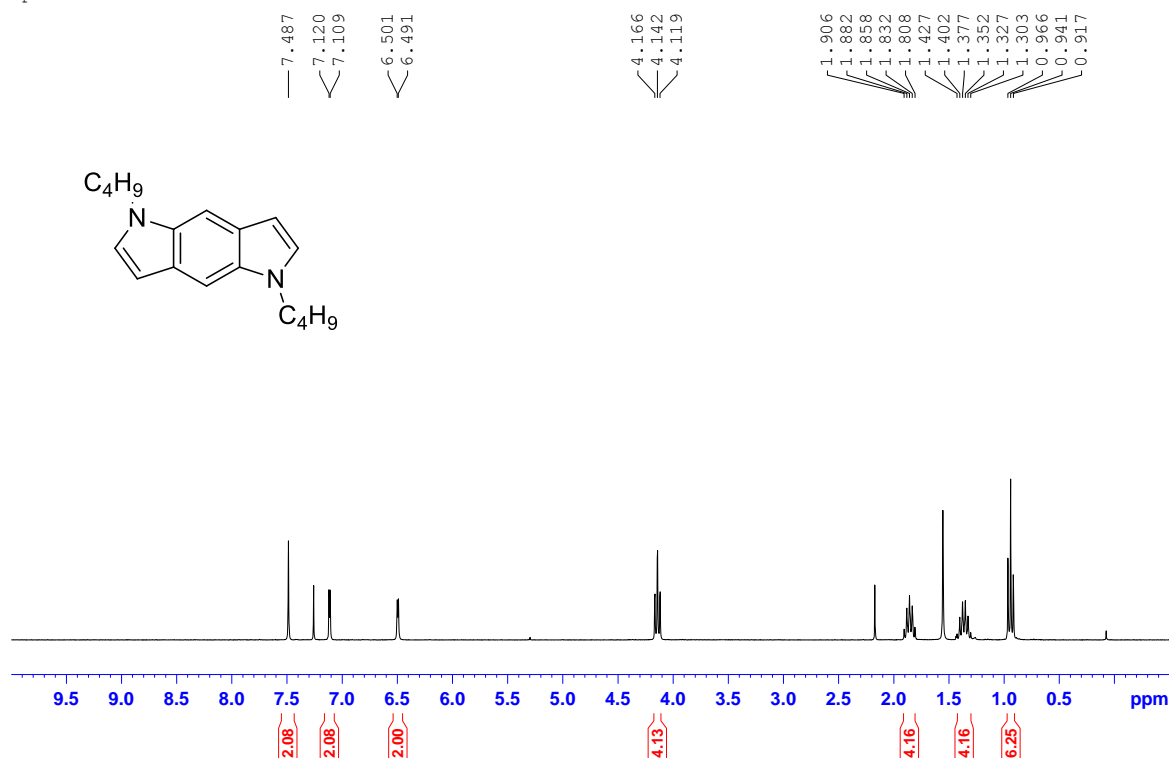
¹H NMR spectra of compound 7

apd 232 C13



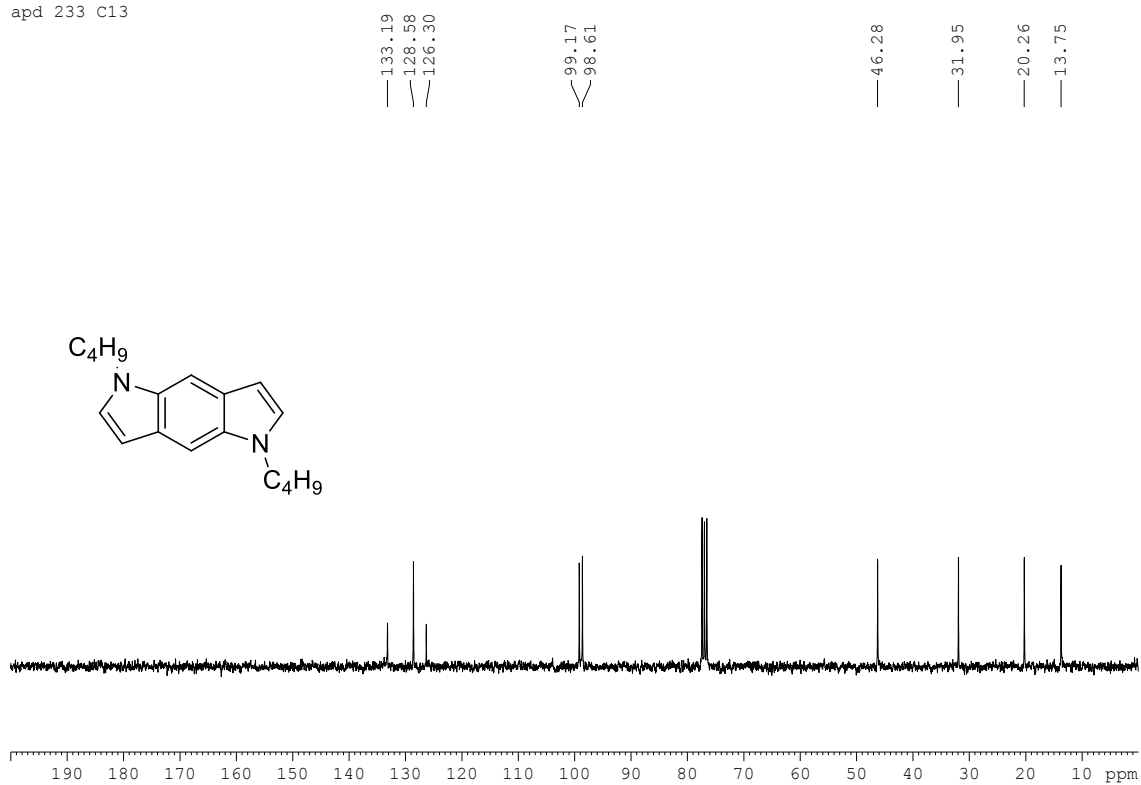
¹³C NMR spectra of compound 7

apd 233 H1NMR



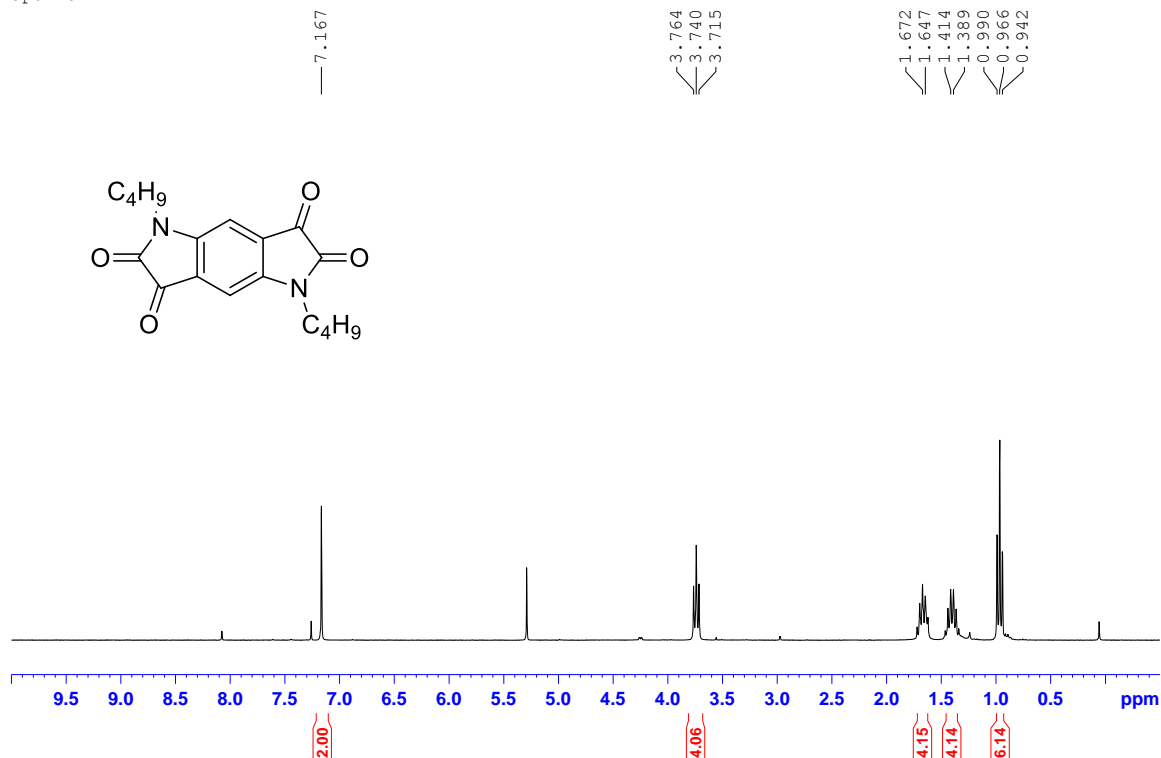
¹H NMR spectra of compound 9

apd 233 C13



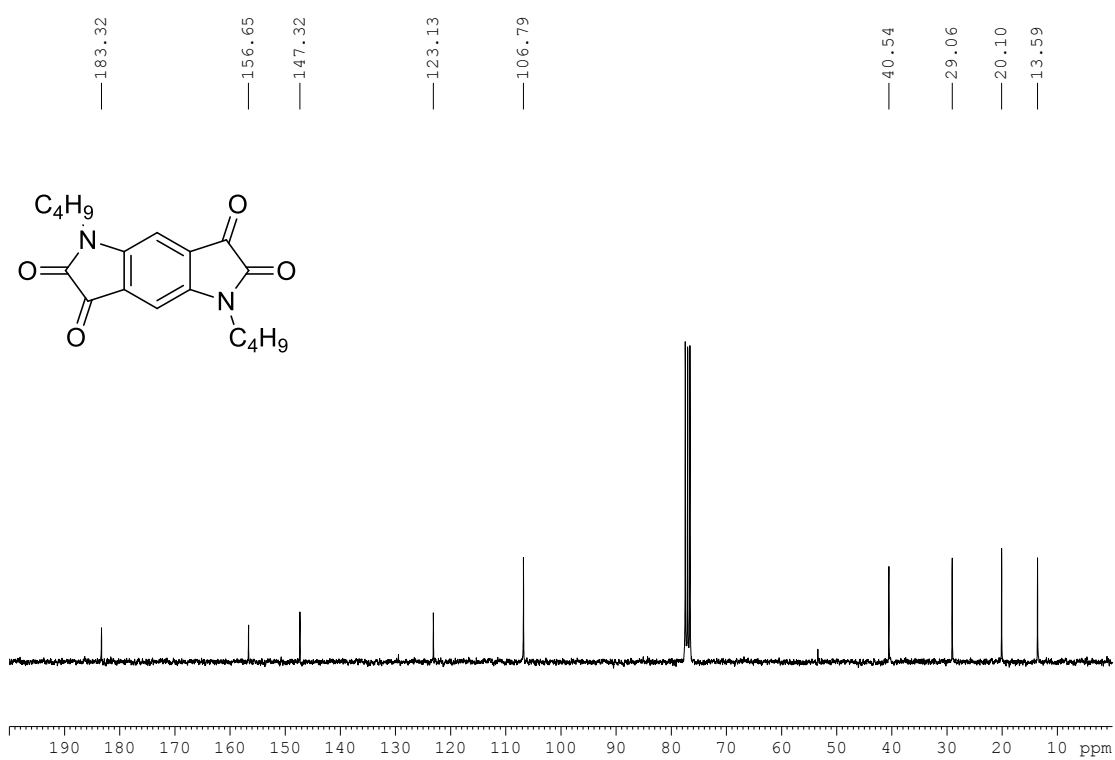
¹³C NMR spectra of compound 9

apd 234 H1 NMR

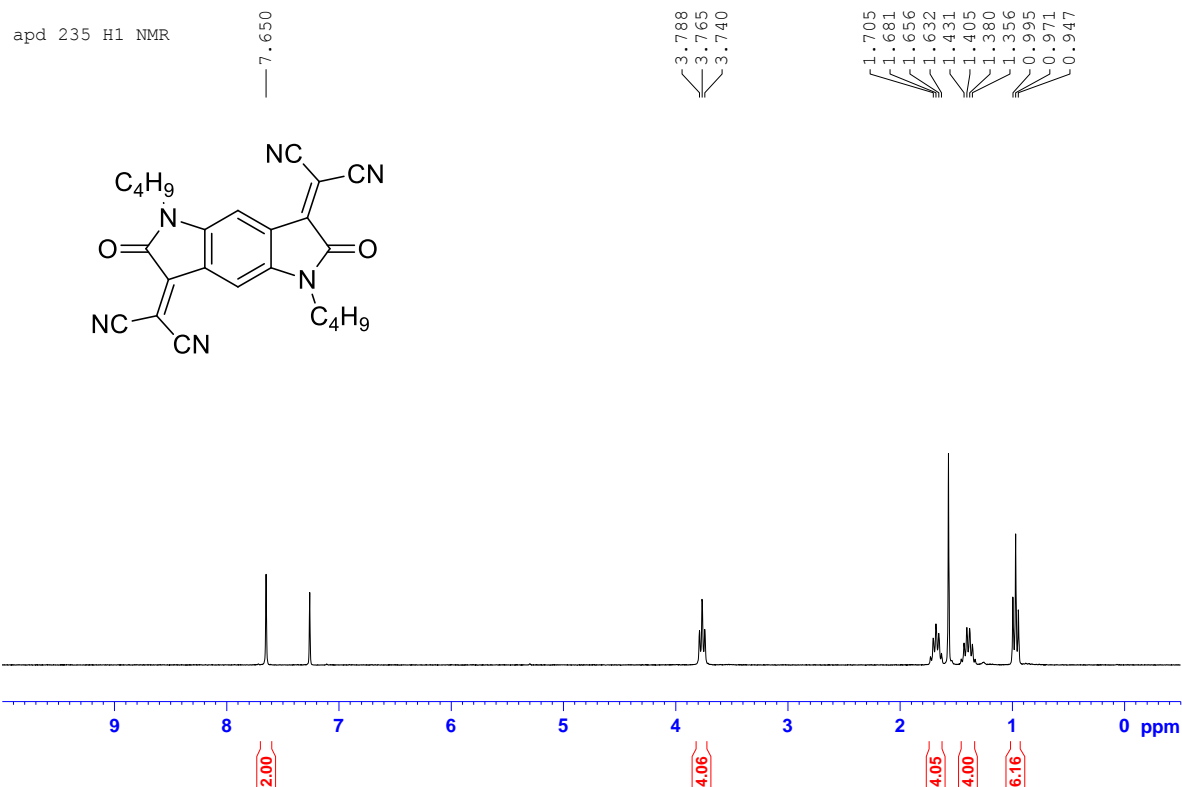


¹H NMR spectra of compound 11

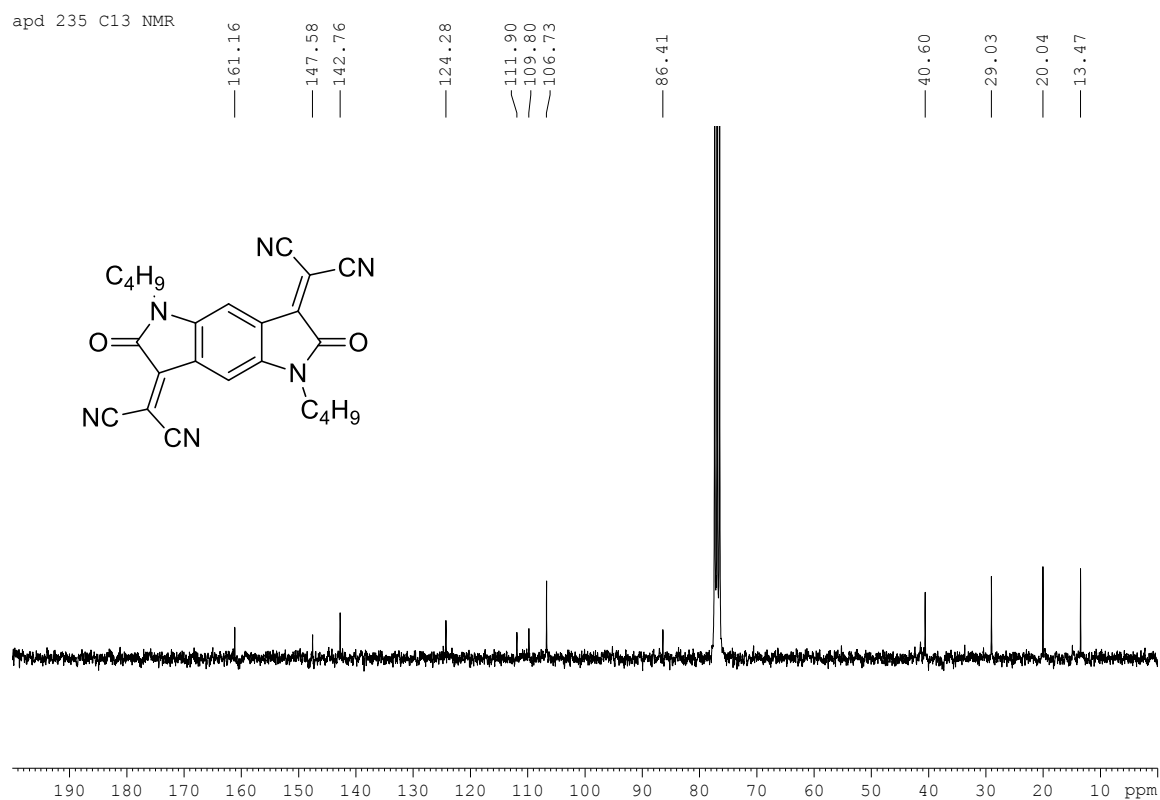
apd 234 C13 NMR



¹³C NMR spectra of compound 11



¹H NMR spectra of BDPM-But



¹³C NMR spectra of BDPM-But