

Comparison of Optical and Electrochemical Properties of Bi(Perylene Diimide)s Linked Through “Ortho” and “Bay” Positions

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1. PDI Numbering Scheme and Torsion-Angle Definitions

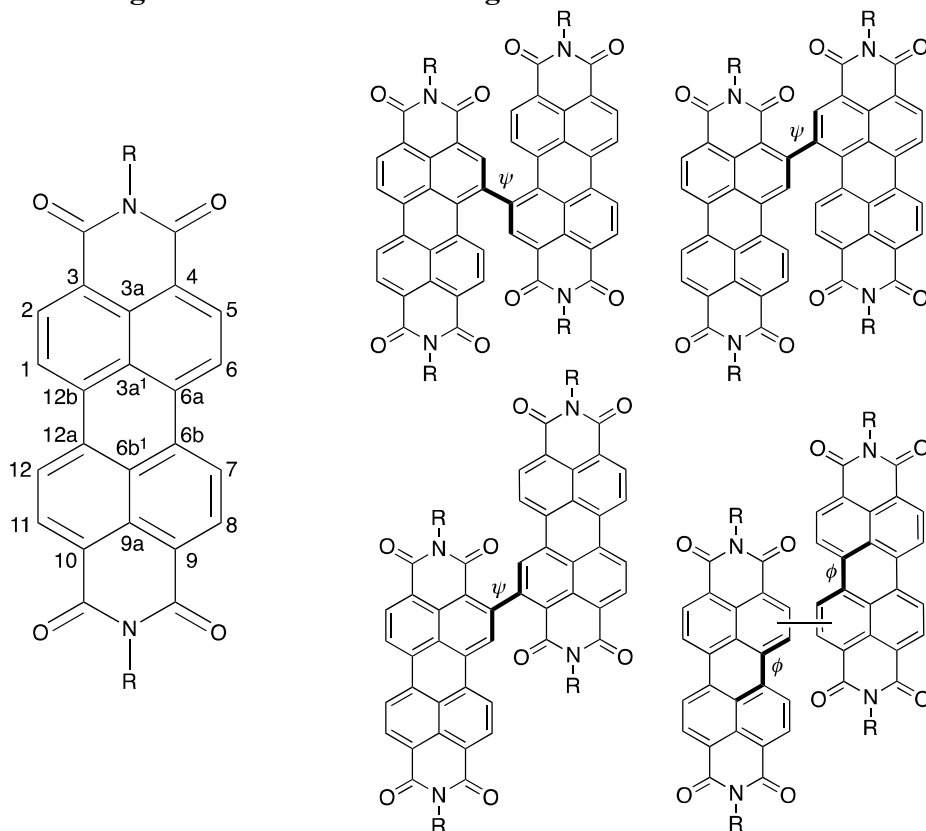


Figure S1. Left: numbering scheme for the perylene core of a PDI. Right: definition of the torsion angles ψ and ϕ used in Table 1.

2. Differential Scanning Calorimetry Data

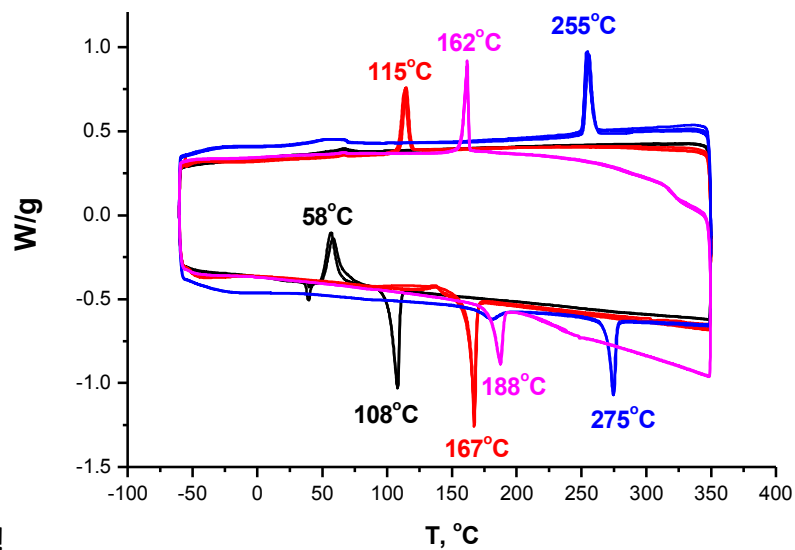


Figure S2. DSC data ($10\text{ }^{\circ}\text{C min}^{-1}$) for **1a** (red), **2a** (magenta), **3a** (blue), and **S1a** (black).

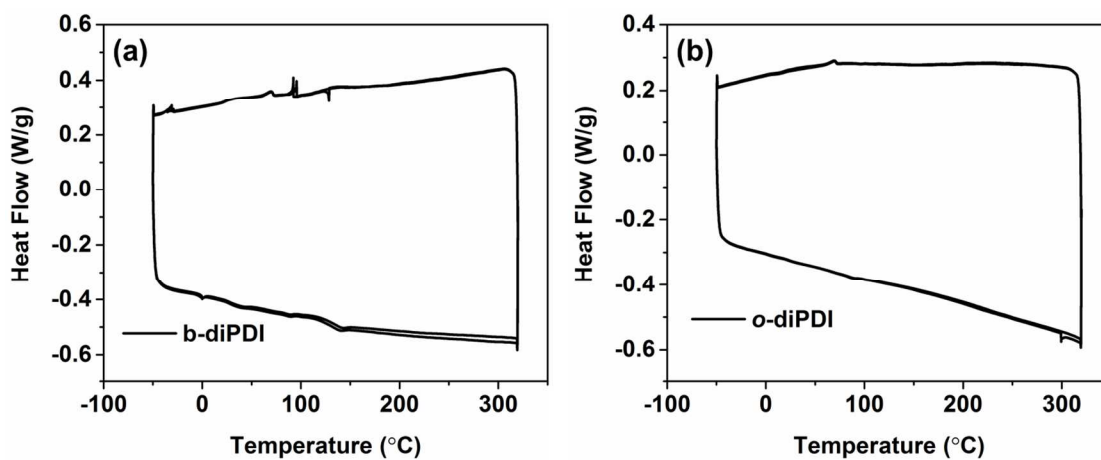


Figure S3. DSC data ($10\text{ }^{\circ}\text{C min}^{-1}$) for (a) **1b** and (b) **3b**.

3. Additional Electrochemical and Optical Data

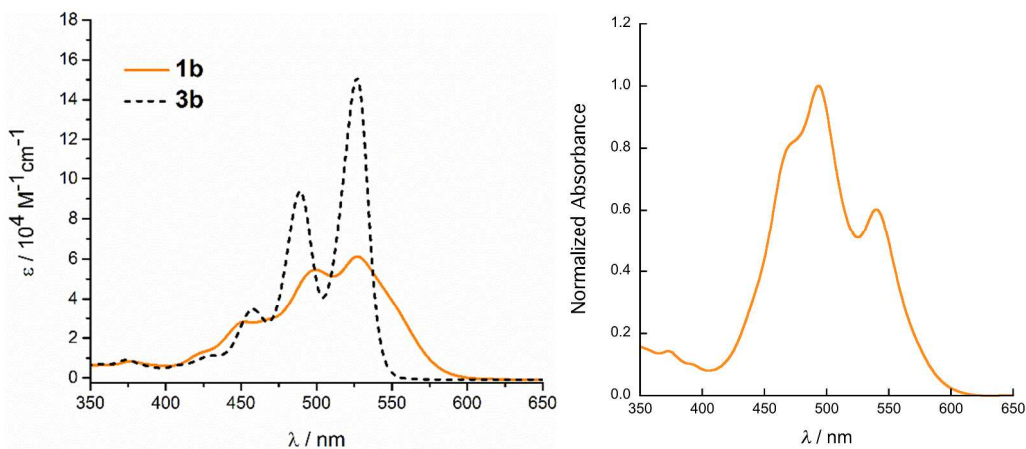


Figure S4. Left: absorption spectra of **1b** and **3b** in THF. Right: Absorption spectrum of a film of **S1a**.

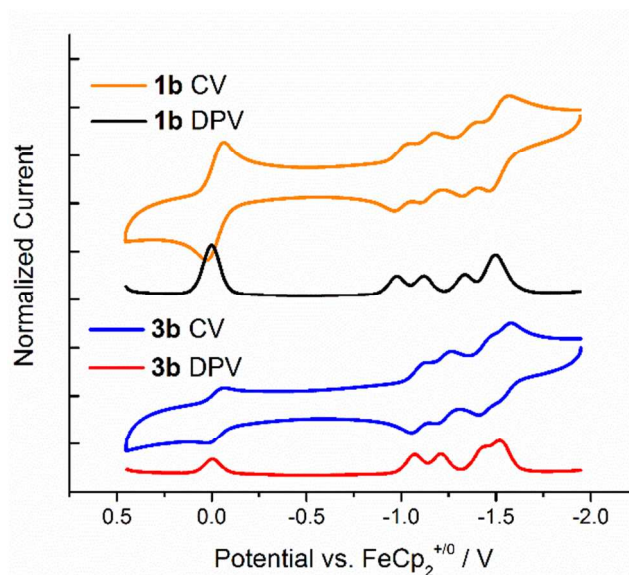


Figure S5. Cyclic voltammograms and reductive differential pulse voltammograms of **1b** and **3b** in THF / 0.1 Bu_4NPF_6 . The feature at 0 V is due to ferrocene used as an internal reference. The first reductions potentials are -0.98 and -1.07 V respectively vs. $\text{FeCp}_2^{+/0}$, i.e., very similar to those for their analogues **1a** and **3a** respectively and yielding estimated solid-state electron affinities of 3.8 and 3.7 eV, respectively.

4. Characterization of OPV Devices and Blends

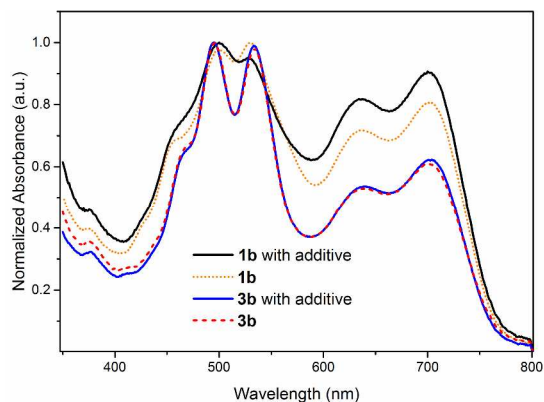


Figure S6. Absorption spectra of films of the blends for which OPV data are shown in Figure 4.

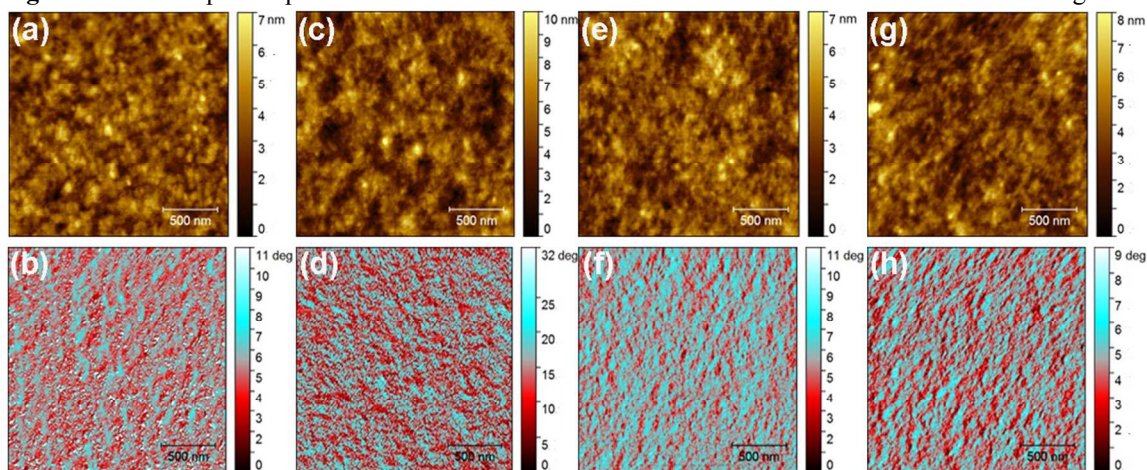


Figure S7. Tapping-mode AFM height (top) and phase (bottom) images ($2 \times 2 \mu\text{m}$) of (a,b) 1:1 PTB7-Th:**1b** without additives, (c,d) 1:1 PTB7-Th:**1b** with 1% DIO and 2% CN, (e,f) 1:1.5 PTB7-Th:**3b** without additives, and (g,h) 1:1.5 PTB7-Th:**3b** with 2% DIO. Images were acquired under atmospheric conditions using an Agilent 5600 LS with an AC-AFM controller. Image acquisition was performed using PicoView 1.10, and image processing was performed using the open source program Gwyddion version 2.20. Root-mean-square roughnesses are 0.87, 0.96, 1.38 and 1.06 nm for (a), (c), (e), and (g), respectively. Feature sizes of 20-30 and 50-70 nm were measured from the phase images (d) and (h).

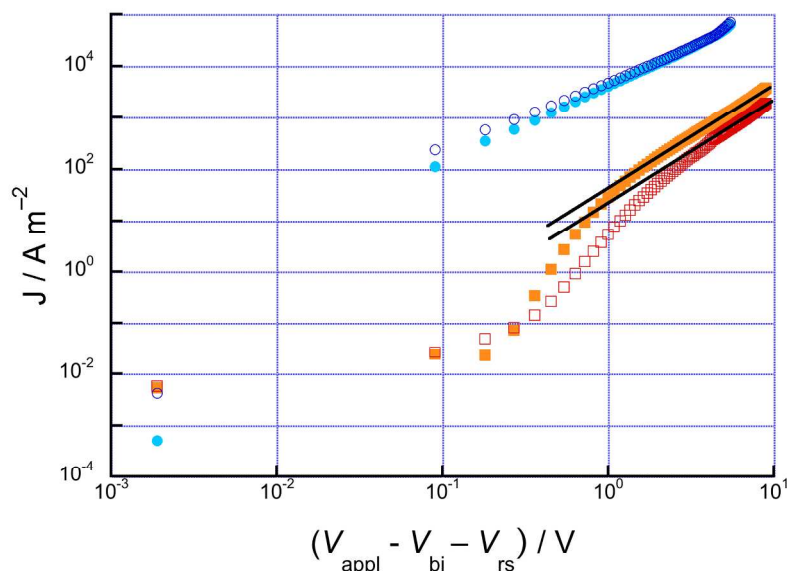


Figure S8. Current J - V characteristics for hole-only (circles) and electron-only devices (squares) with the structures ITO/PEDOT:PSS/PTB7-Th:biPDI/MoO₃/Ag, and ITO/ZnO/PTB7-Th:diPDI/Ca/Al, respectively. Donor:acceptor:additive ratios were the same as for the optimized OPV devices in Table 3. Solid and open symbols denote data for **1b** and **3b**, respectively, as the acceptor. The solid black lines indicate the approximately quadratic portions of the plots, from which SCLC electron mobilities, μ , were estimated using the Mott Gurney law, $J = (9/8)\epsilon_0\epsilon_r\mu V^2 d^{-3}$, where ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the blend, and d is the thickness, as 5.0×10^{-5} and 2.2×10^{-5} cm² V⁻¹ s⁻¹ for the **1b** and **3b** blends, respectively. No clear quadratic régime can be identified for the hole-only devices, precluding determination of hole mobility, but the similarity in J - V curves suggests similar hole-transport properties for the two blends. Thicknesses of the active layers, d , were ca. 80 and 70 nm for **1b** and **3b** blends, respectively.

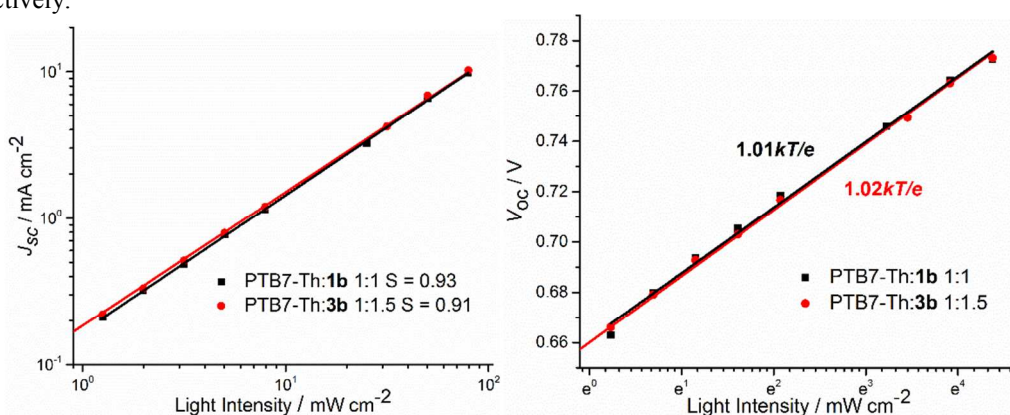


Figure S9. Light-intensity dependence of the short-circuit current of the devices (left) and the open-circuit voltage of the devices (right). The plots of J_{sc} vs. light intensity, P , were fitted as $J_{sc} \propto P^S$.^{S1} $S = 1$ implies that, at short-circuit conditions, all the generated free carriers are swept out before recombination. Values of $S = 0.93$ for PTB7-Th:**1b** based devices and $S = 0.91$ for PTB7-Th:**3b** based devices suggest that some carrier loss through bimolecular recombination or space-charge effects caused by imbalanced electron and hole mobility.^{S2-S3} Consistent with general findings for a wide range of polymer:fullerene BHJ solar cells, the slope of V_{oc} vs. $\ln P$ is close to kT/e , which is consistent with bimolecular recombination kinetics at open circuit (whereas unimolecular recombination processes would afford a gradient of $2kT/e$).^{S2}

- S1. Lu, L.; Xu, T.; Chen, W.; Landry, E. S.; Yu, L. *Nat. Photon.* **2014**, *8*, 716.
 S2. Cowan, S. R.; Roy, A.; Heeger, A. J. *Phys. Rev. B* **2010**, *82*, 245207.
 S3. Koster, L.; Mihailetschi, V.; Xie, H.; Blom, P. *Appl. Phys. Lett.*, 2005, **87**, 203502.

5. NMR Spectra

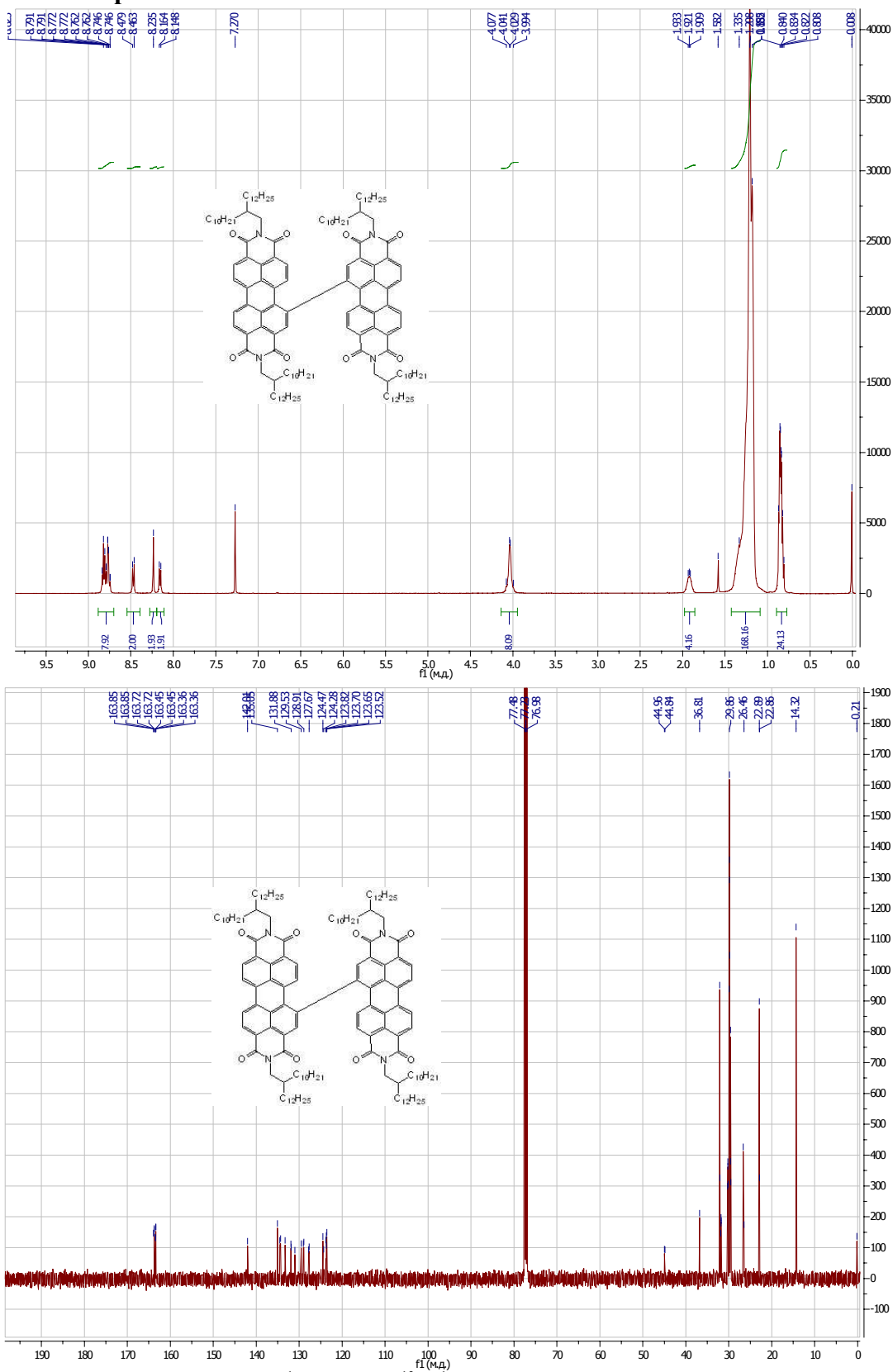


Figure S10. Room-temperature ^1H (top) and $^{13}\text{C}\{^1\text{H}\}$ (bottom) spectra of **1a** in CDCl_3 .

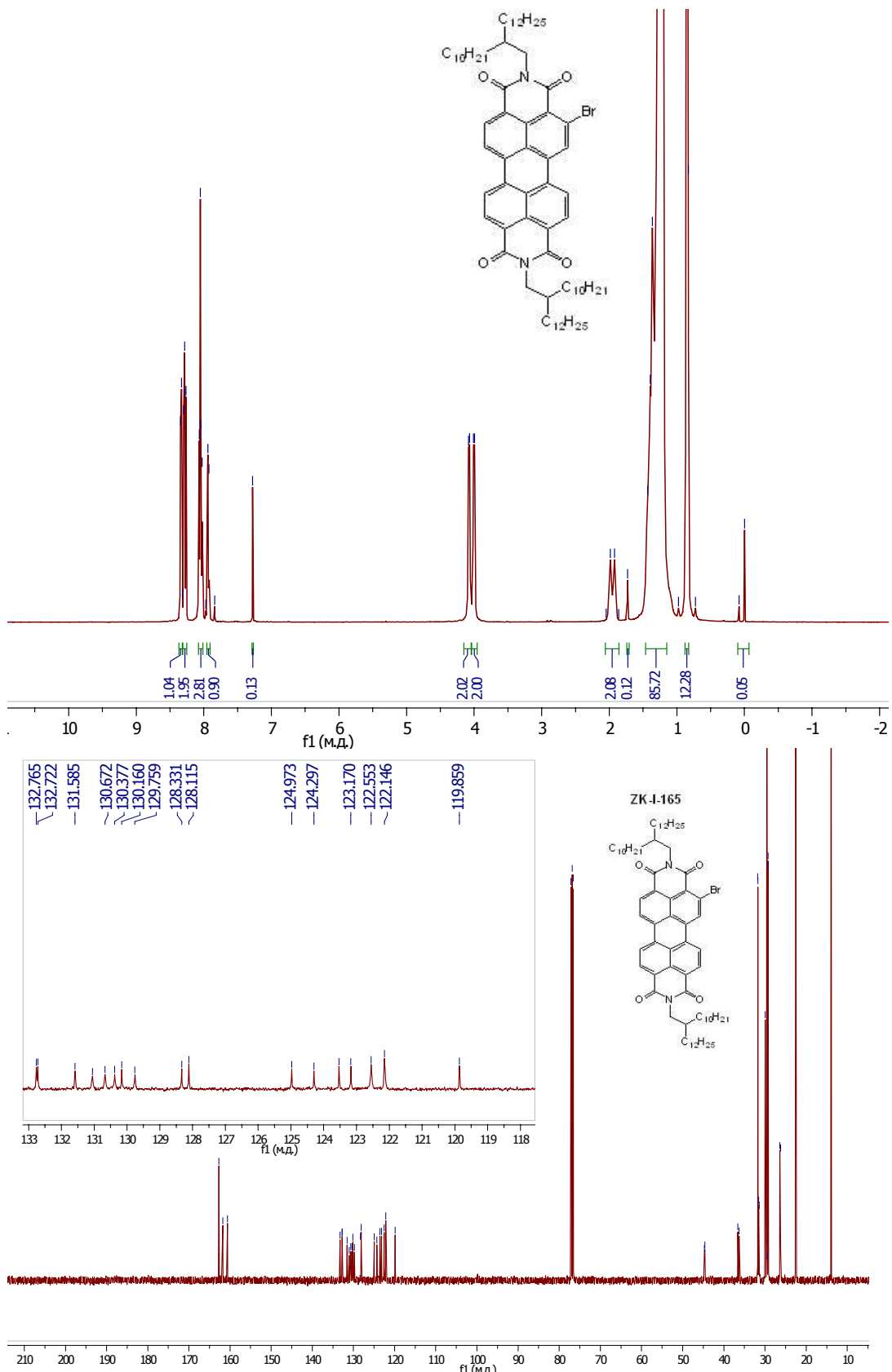


Figure S11. Room-temperature ¹H (top) and ¹³C{¹H} (bottom) spectra of S4a in CDCl₃.

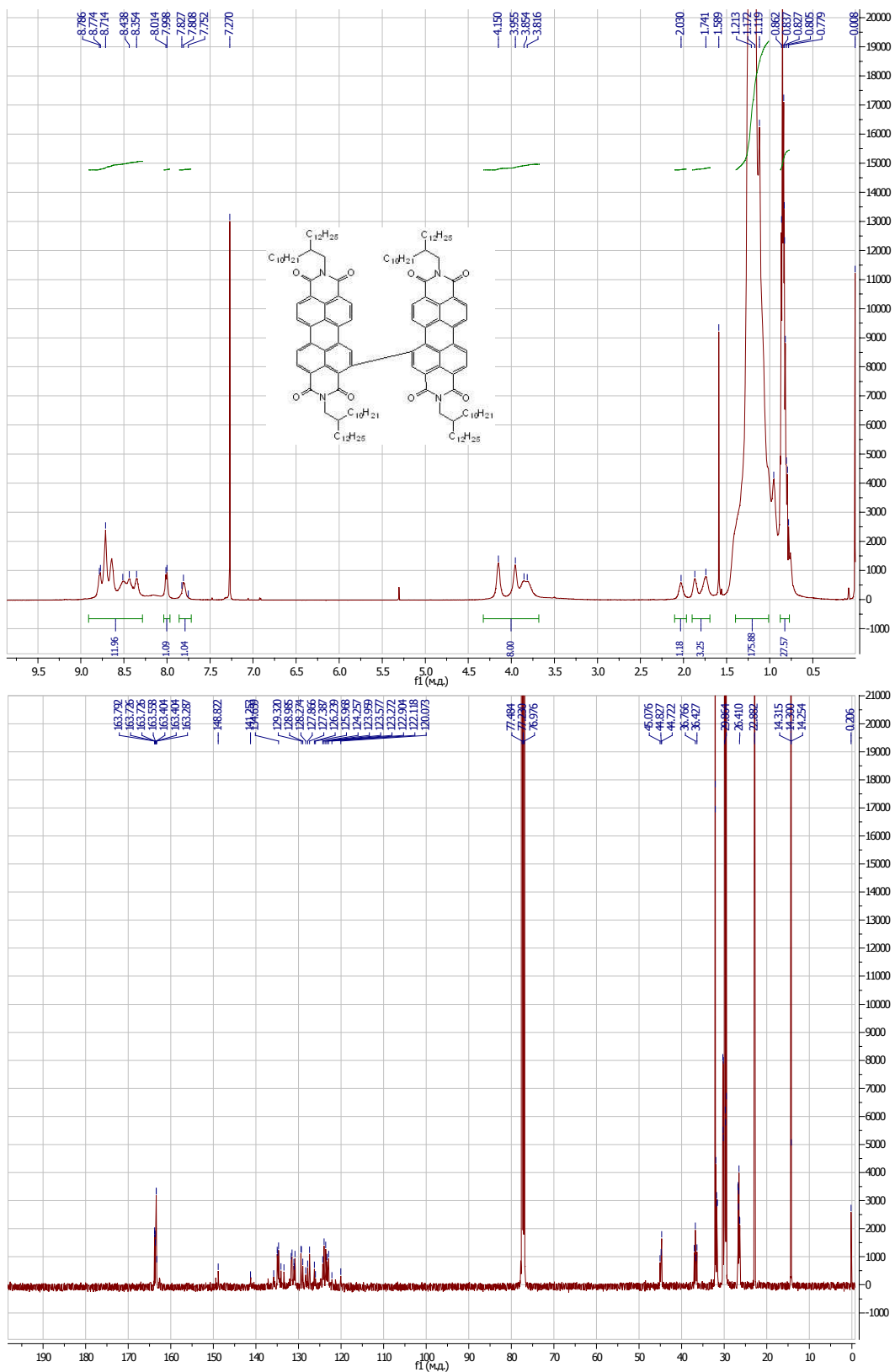


Figure S12. Room-temperature ^1H (top) and $^{13}\text{C}\{^1\text{H}\}$ (bottom) spectra of **2a** in CDCl_3 .

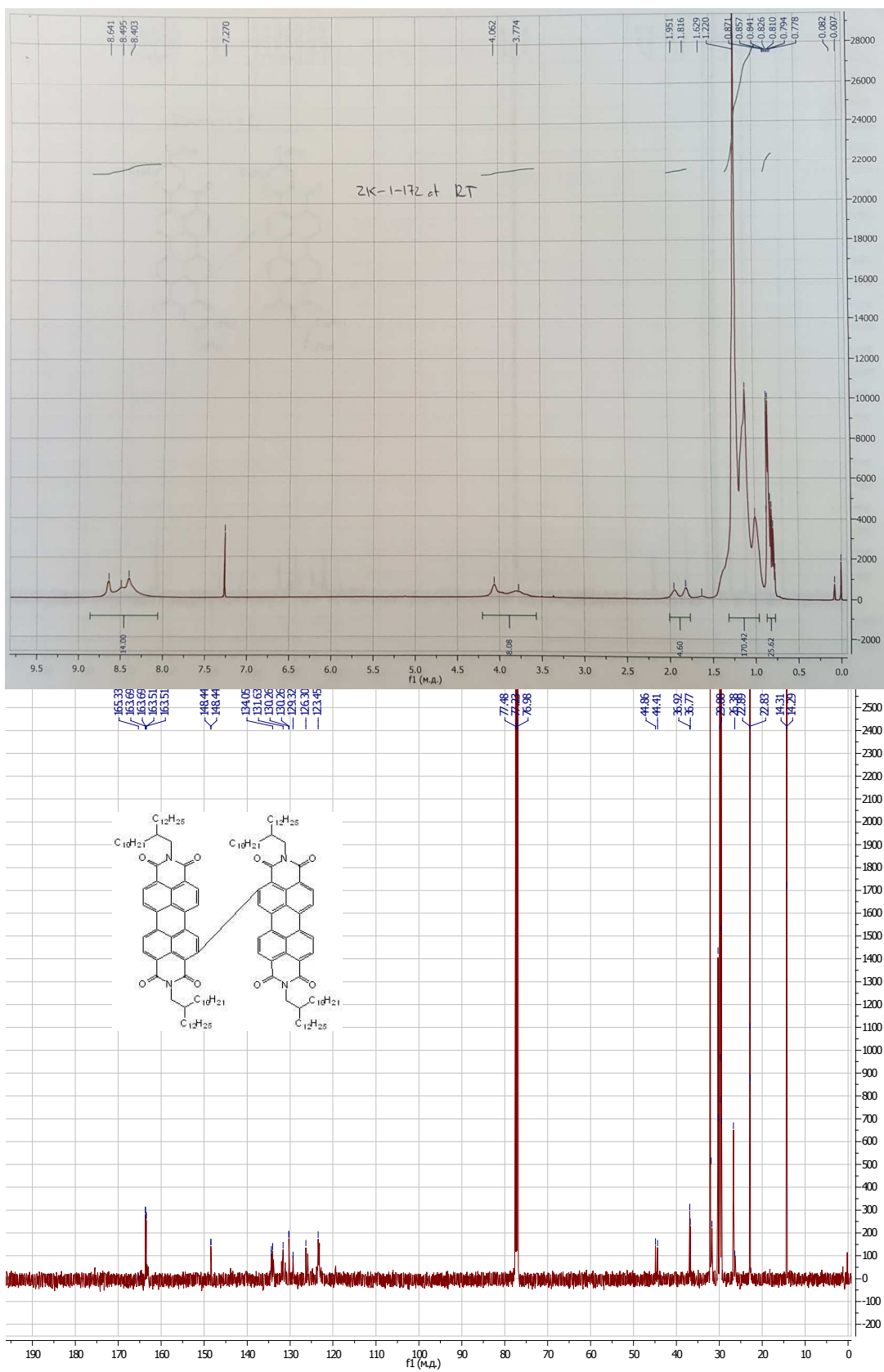


Figure S13. Room-temperature ¹H (top) and ¹³C{¹H} (bottom) spectra of **3a** in CDCl₃.

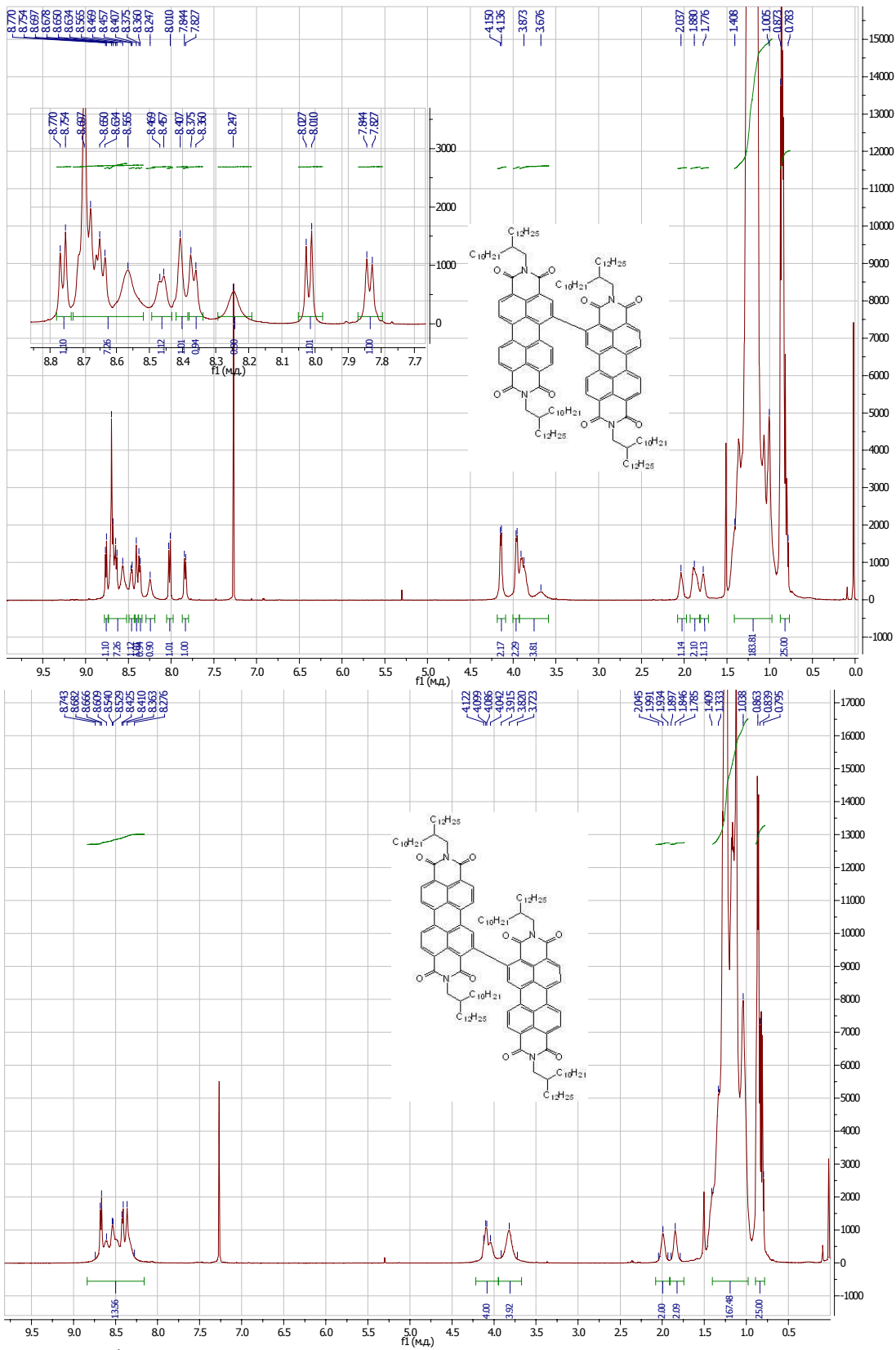


Figure S14. ¹H spectra of 2a (top) and 3a (bottom) in CDCl₃ at 325 K.

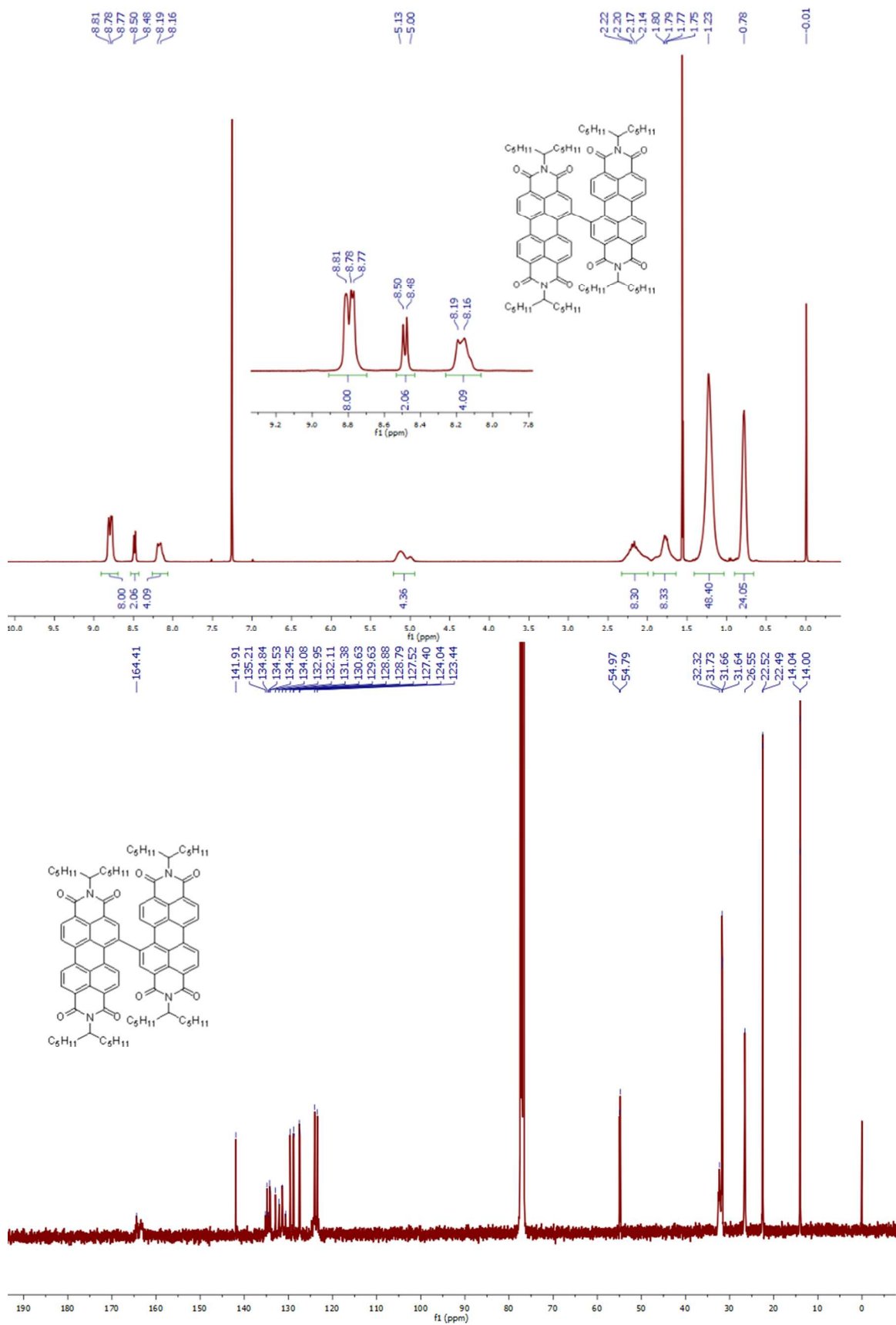


Figure S15. ^1H (top) and $^{13}\text{C}\{^1\text{H}\}$ (bottom) spectra of **1b** in CDCl_3 .

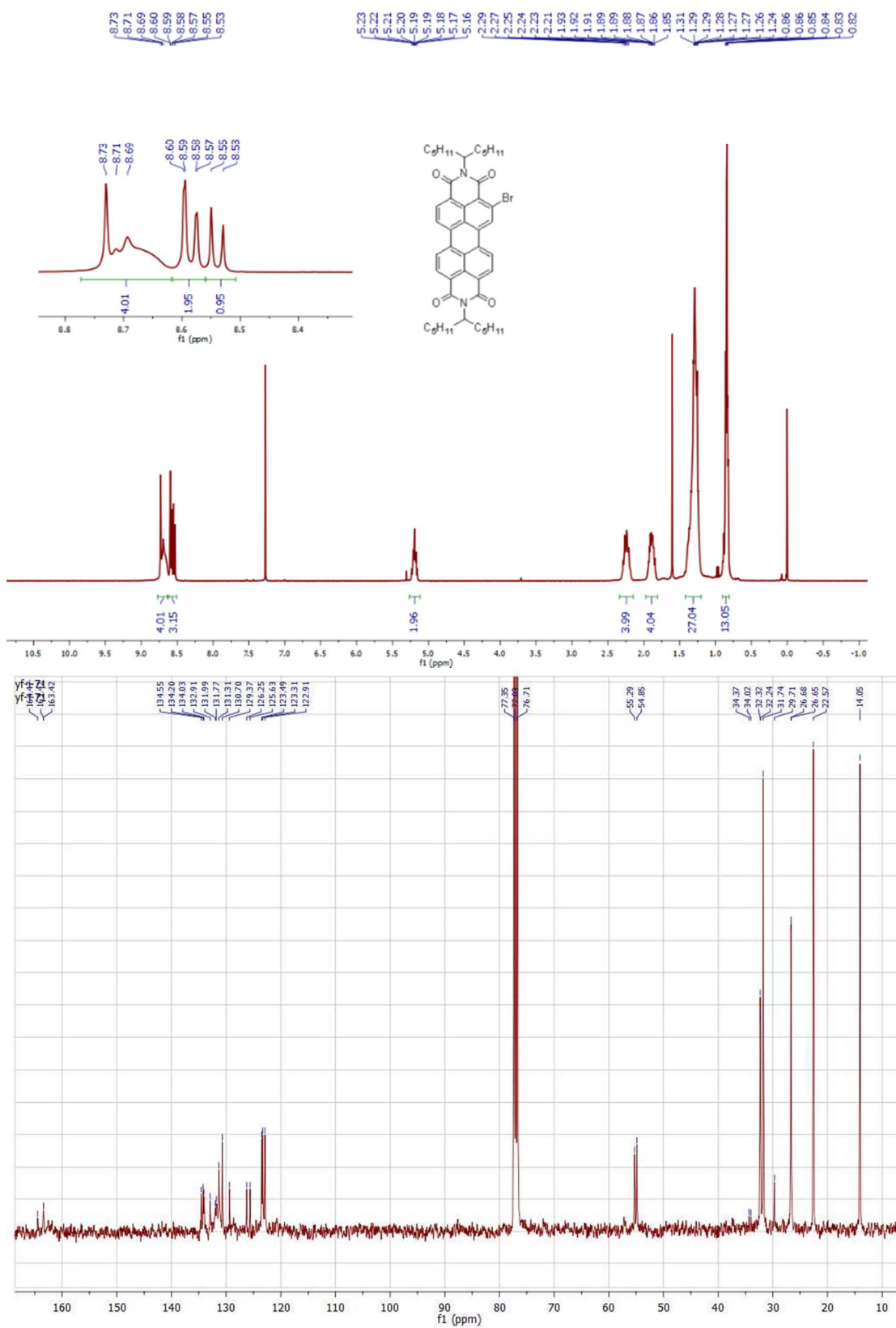


Figure S16. ^1H (top) and $^{13}\text{C}\{^1\text{H}\}$ (bottom) spectra of **S4b** in CDCl_3 .

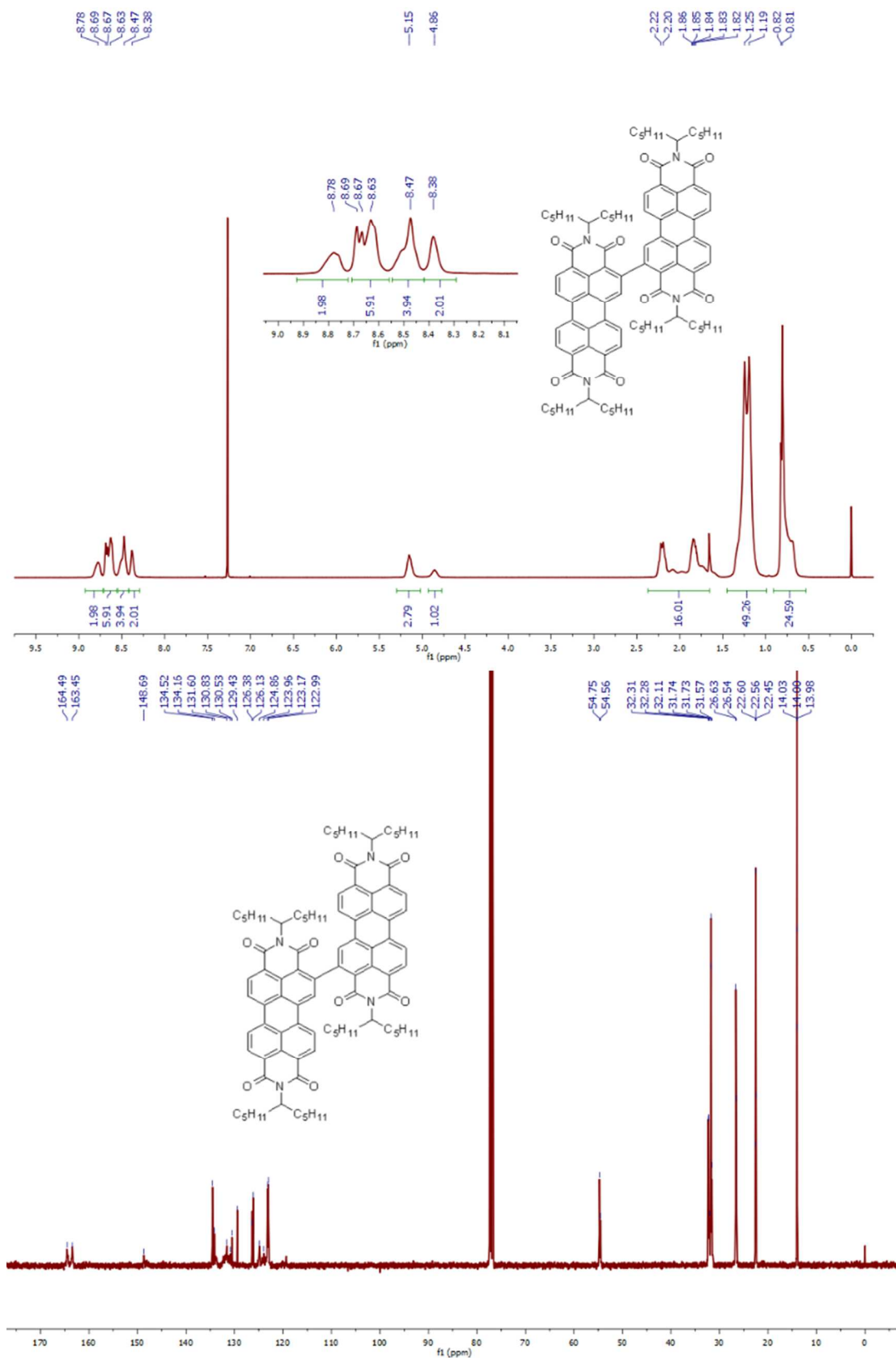


Figure S17. ^1H (top) and $^{13}\text{C}\{^1\text{H}\}$ (bottom) spectra of **3b** in CDCl_3 .

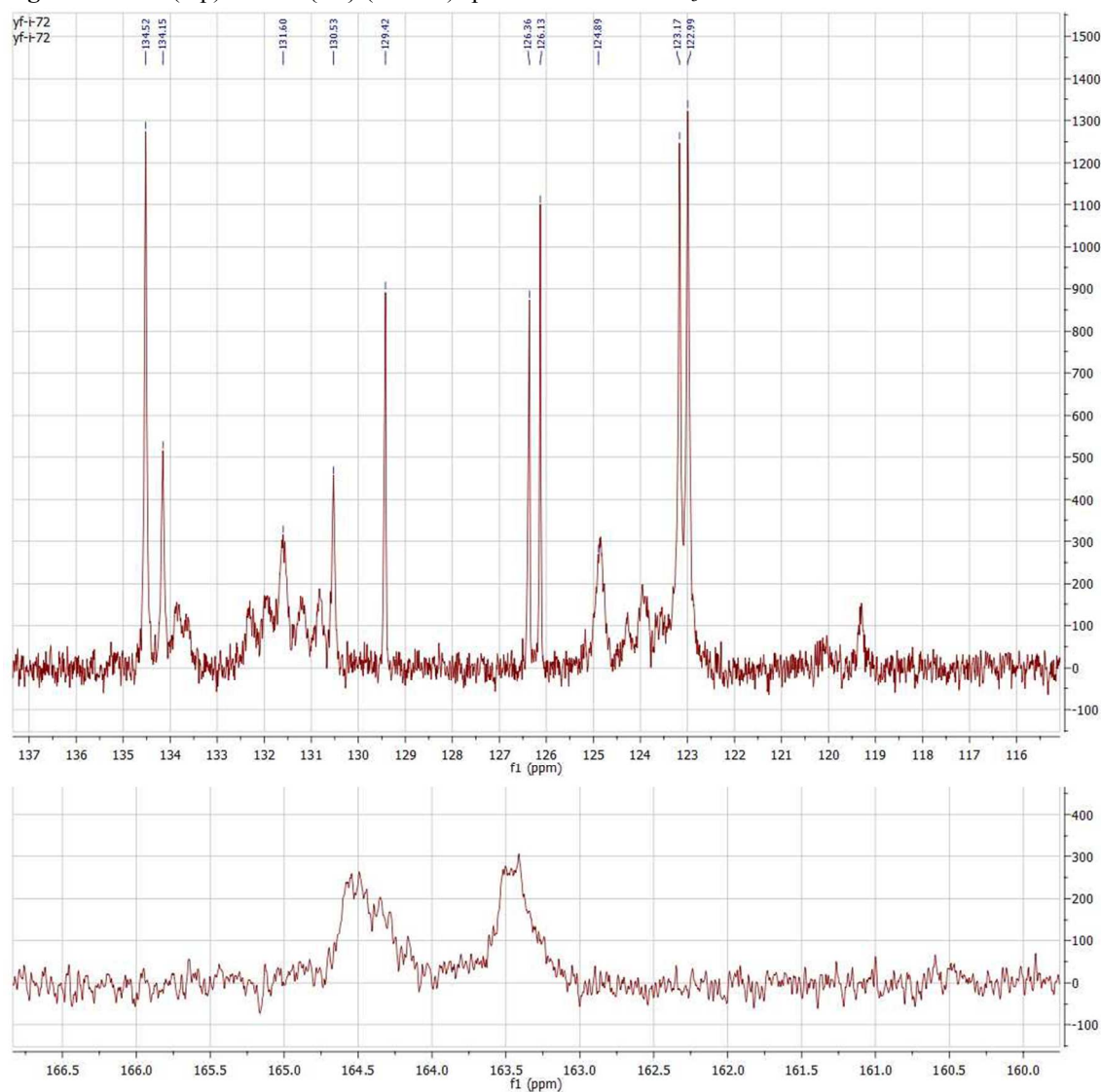
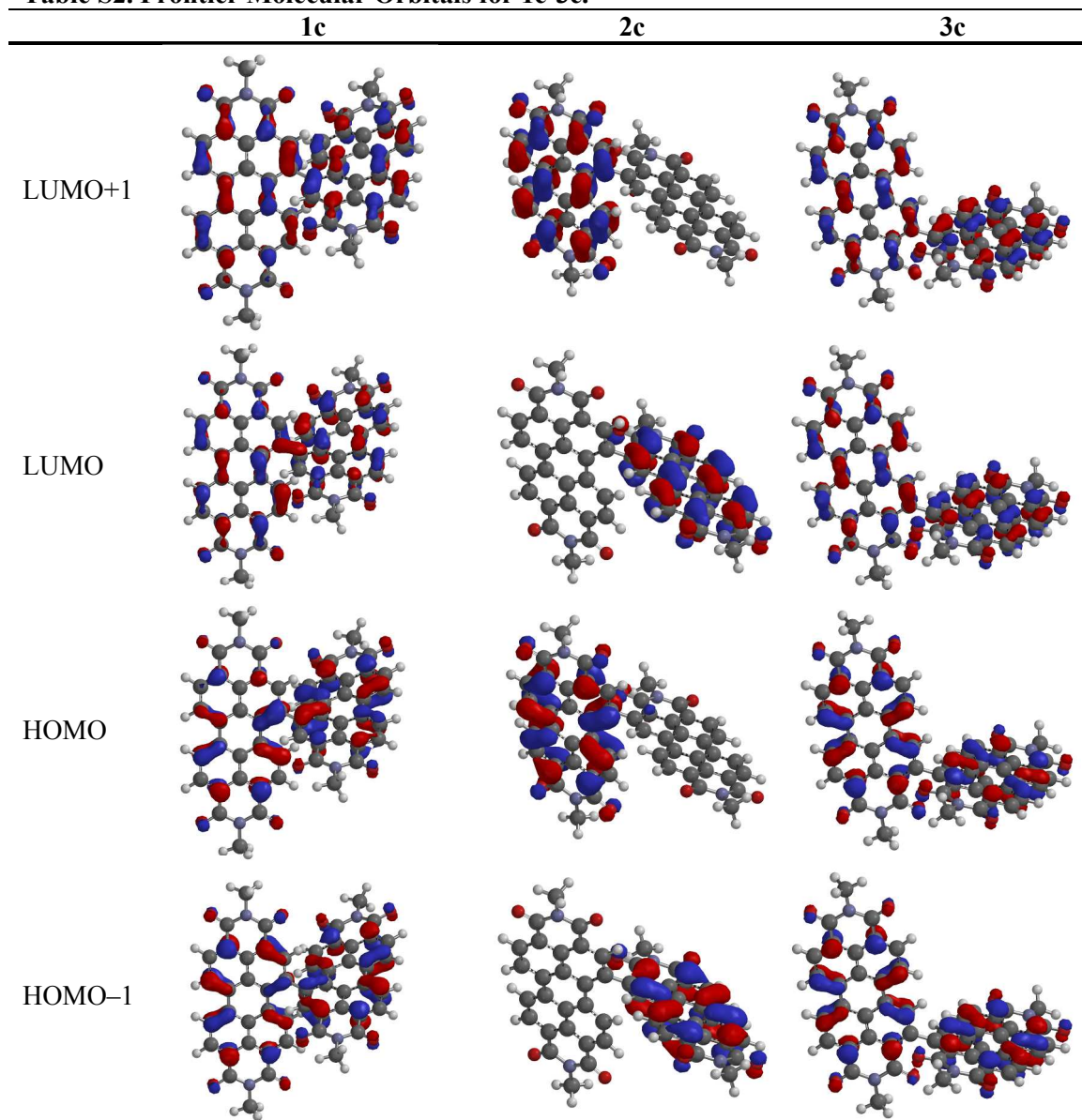


Figure S18. Expansions of selected regions of the $^{13}\text{C}\{^1\text{H}\}$ (bottom) spectrum of **3b** in CDCl_3 showing some broad resonances, presumably due to restricted rotation.

6. Supporting Data for DFT Calculations

Table S1. Total Energies of Minimized Structures.

Compound	Energy (hartree)
1c	-2818.3176765
2c	-2818.3197485
3c	-2818.3265073

Table S2. Frontier Molecular Orbitals for 1c-3c.**Table S3. Cartesian Coordinates (Å) for Minimized Structure of 1c.**

Atom	x	y	z
C	0.191146	-0.720993	0.957987
C	1.406958	-1.231706	0.454112
C	-0.354382	-2.871062	1.976424
C	1.802288	-2.560061	0.838347
C	-0.674087	-1.562296	1.693662
C	0.902102	-3.384658	1.577352
C	3.097325	-3.081943	0.522257
H	-1.616694	-1.173373	2.062175
C	3.401907	-4.397697	0.879419
H	4.363663	-4.819961	0.615523
C	2.493903	-5.208013	1.565573
H	2.743321	-6.229027	1.832369

C	1.254432	-4.708807	1.926260
H	5.772152	-3.517482	0.087827
C	5.401845	-2.596129	-0.344973
C	4.068731	-2.222979	-0.162653
C	5.860053	-0.630807	-1.667840
C	3.621710	-0.975792	-0.694338
C	6.292494	-1.806350	-1.078723
C	4.521491	-0.205249	-1.492513
C	2.290228	-0.494996	-0.471323
H	7.325377	-2.107009	-1.215082
C	1.879817	0.639047	-1.177684
H	0.858628	0.981999	-1.103058
C	2.754300	1.364848	-1.995331
H	2.413818	2.247893	-2.524617
C	4.074585	0.977048	-2.129988
C	0.310715	-5.572757	2.675051
O	0.574122	-6.727580	2.981336
C	-1.321559	-3.700551	2.740717
O	-2.408303	-3.266891	3.098117
N	-0.923833	-5.012739	3.029950
C	4.991251	1.791645	-2.966108
O	4.619889	2.808363	-3.536540
C	6.809111	0.166789	-2.481022
O	7.975925	-0.162868	-2.645844
N	6.314337	1.337458	-3.069485
C	-0.202968	0.725719	0.948684
C	-1.414240	1.233536	0.430854
C	0.340668	2.886302	1.943659
C	-1.808427	2.568070	0.795625
C	0.659297	1.573650	1.680296
C	-0.910827	3.399584	1.530074
C	-3.099567	3.089597	0.464113
H	1.598071	1.187353	2.061364
C	-3.402784	4.410026	0.804668
H	-4.361844	4.831967	0.530578
C	-2.496980	5.226071	1.486824
H	-2.746125	6.250615	1.739569
C	-1.260212	4.729373	1.861084
H	-5.768808	3.529935	-0.000664
C	-5.398128	2.601395	-0.417513
C	-4.068196	2.225731	-0.218472
C	-5.853735	0.620293	-1.718883
C	-3.621779	0.970177	-0.730274
C	-6.285722	1.805215	-1.147858
C	-4.518020	0.192875	-1.525909
C	-2.293628	0.487549	-0.490942
H	-7.316247	2.108193	-1.295723
C	-1.882076	-0.657719	-1.178525
H	-0.862730	-1.003017	-1.091775
C	-2.753418	-1.392318	-1.991755
H	-2.413391	-2.284999	-2.505116
C	-4.070230	-0.999738	-2.142519
C	-0.321878	5.607003	2.604267
O	-0.600856	6.763798	2.887769
C	1.299033	3.726661	2.703607
O	2.383152	3.308224	3.086719
N	0.912109	5.044496	2.967935
C	-4.988282	-1.818536	-2.970451
O	-4.635799	-2.855517	-3.516016
C	-6.805673	-0.181585	-2.527135
O	-7.970794	0.157367	-2.684500

N	-6.301633	-1.354135	-3.110613
C	1.874340	5.873034	3.703681
H	1.493553	6.890935	3.718938
H	2.845035	5.824916	3.208542
H	1.989960	5.497342	4.723322
C	-7.203976	-2.176413	-3.924950
H	-8.128724	-1.621016	-4.058299
H	-7.404251	-3.125414	-3.421218
H	-6.731776	-2.389763	-4.884658
C	7.262118	2.116632	-3.874833
H	6.780034	3.053767	-4.140766
H	7.532264	1.563333	-4.777869
H	8.169357	2.291998	-3.295507
C	-1.845169	-5.880692	3.772515
H	-2.762191	-5.322140	3.940919
H	-1.394050	-6.172611	4.723231
H	-2.042982	-6.785417	3.194788

Table S4. Cartesian Coordinates (Å) for Minimized Structure of 2c.

Atom	x	y	z
H	-1.099608	-1.446549	0.785626
C	-1.173631	-0.812190	-0.088665
C	-2.391987	-0.230994	-0.422685
C	-0.032291	0.177535	-1.977064
C	-2.450628	0.601195	-1.581589
C	0.011444	-0.617052	-0.826452
C	-1.259666	0.796181	-2.350592
C	-3.671687	1.229624	-1.985170
C	-3.664002	2.029367	-3.127642
H	-4.569452	2.521795	-3.459216
C	-2.501439	2.219726	-3.877501
H	-2.504945	2.842276	-4.765244
C	-1.312407	1.615699	-3.506750
H	-6.197096	2.222185	-2.403355
C	-6.115141	1.588644	-1.528994
C	-4.889888	1.011666	-1.190334
C	-7.227482	0.572659	0.358310
C	-4.824958	0.177698	-0.030158
C	-7.269744	1.375422	-0.767666
C	-6.008173	-0.035535	0.741474
C	-3.606780	-0.450026	0.376699
H	-8.212825	1.832957	-1.045631
C	-3.615237	-1.250372	1.520251
H	-2.708274	-1.739617	1.853096
C	-4.778160	-1.452847	2.271235
H	-4.768011	-2.077820	3.157269
C	-5.968550	-0.856968	1.893622
C	-0.116178	1.851797	-4.346735
O	-0.145623	2.565138	-5.340778
C	1.175880	0.371953	-2.824987
O	2.253537	-0.159601	-2.592277
N	1.057227	1.207118	-3.942370
C	-7.186870	-1.093899	2.709052
O	-7.170878	-1.799077	3.708604
C	-8.463656	0.360598	1.149347
O	-9.533687	0.873933	0.851927
N	-8.364461	-0.467956	2.273898
C	1.210430	-1.395247	-0.364288
C	2.353829	-0.879905	0.281636
C	2.107826	-3.661414	-0.280344

C	3.454811	-1.770942	0.518664
C	1.101692	-2.778008	-0.609284
C	3.311657	-3.169725	0.267540
C	4.725470	-1.296099	0.979651
H	0.208537	-3.175497	-1.079301
C	5.735167	-2.219658	1.256769
H	6.686564	-1.877835	1.645041
C	5.560261	-3.591878	1.057174
H	6.353484	-4.296671	1.279800
C	4.365377	-4.071556	0.551396
H	7.072236	0.060792	1.412921
C	6.195708	0.696777	1.388063
C	4.937494	0.146081	1.134391
C	5.275171	2.917511	1.605616
C	3.807946	1.013971	1.049894
C	6.367300	2.066381	1.609607
C	3.983814	2.402305	1.337861
C	2.503771	0.522795	0.712096
H	7.349357	2.482978	1.803804
C	1.426575	1.404316	0.838624
H	0.418217	1.050861	0.692436
C	1.600427	2.755450	1.161681
H	0.747760	3.421159	1.239609
C	2.865448	3.269135	1.374998
C	4.213020	-5.528013	0.313352
O	5.104661	-6.326259	0.569279
C	1.917403	-5.107610	-0.539838
O	0.882567	-5.566983	-1.005948
N	2.986840	-5.952109	-0.223237
C	3.029426	4.711148	1.672482
O	2.085094	5.488655	1.721281
C	5.481363	4.359633	1.886676
O	6.591536	4.829240	2.098991
N	4.333303	5.167361	1.899554
C	-9.596651	-0.676147	3.043693
H	-9.380475	-1.401266	3.823801
H	-10.383335	-1.040125	2.380899
H	-9.927261	0.268115	3.482448
C	2.272689	1.394474	-4.744193
H	3.079903	1.756242	-4.105257
H	2.043228	2.115387	-5.524259
H	2.582138	0.442511	-5.181099
C	2.787428	-7.382462	-0.482359
H	3.702561	-7.899564	-0.206039
H	2.559588	-7.536432	-1.538940
H	1.944680	-7.751074	0.106268
C	4.483699	6.599191	2.182591
H	5.545069	6.803753	2.295730
H	3.944289	6.855493	3.097075
H	4.061763	7.182370	1.362019

Table S5. Cartesian Coordinates (Å) for Minimized Structure of 3c.

Atom	x	y	z
H	1.333629	-0.295060	1.119878
C	1.633919	0.260217	0.240242
C	2.915516	0.110244	-0.274873
C	1.011687	1.872847	-1.448616
C	3.276138	0.862527	-1.435717
C	0.681353	1.136860	-0.311737
C	2.310327	1.743527	-2.012574

C	4.576154	0.755132	-2.021526
C	4.863425	1.516969	-3.155048
H	5.838950	1.459433	-3.621545
C	3.917023	2.375147	-3.718419
H	4.151370	2.964546	-4.597910
C	2.654367	2.496530	-3.162962
H	7.155337	0.252364	-2.812600
C	6.854365	-0.296560	-1.928927
C	5.566459	-0.144888	-1.411866
C	7.467851	-1.874233	-0.205541
C	5.205912	-0.890756	-0.245619
C	7.794034	-1.147400	-1.337153
C	6.171785	-1.757229	0.352622
C	3.904133	-0.789788	0.338365
H	8.790781	-1.250961	-1.751450
C	3.621747	-1.546969	1.476647
H	2.645550	-1.489965	1.942274
C	4.572972	-2.393387	2.056074
H	4.338067	-2.973114	2.942044
C	5.838669	-2.503820	1.508054
C	1.694160	3.431117	-3.792799
O	1.971312	4.081576	-4.792159
C	0.039949	2.823440	-2.042474
O	-1.084111	3.002789	-1.587915
N	0.441026	3.537178	-3.177083
C	6.830578	-3.404865	2.141641
O	6.578482	-4.069052	3.138390
C	8.487779	-2.764302	0.402511
O	9.612970	-2.879229	-0.064927
N	8.097332	-3.473378	1.548922
H	-1.332791	-0.290297	-1.122095
C	-1.632969	0.260885	-0.239824
C	-2.914252	0.108154	0.275234
C	-1.010687	1.866289	1.455924
C	-3.274789	0.855247	1.439472
C	-0.680500	1.135423	0.315667
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C	-2.309017	1.733921	2.019880
C	-4.574704	0.745023	2.025027
C	-4.861515	1.501288	3.162436
H	-5.836777	1.441413	3.629188
C	-3.915035	2.356928	3.729481
H	-4.149081	2.942005	4.611948
C	-2.652723	2.481434	3.173962
H	-7.154533	0.241258	2.812882
C	-6.853688	-0.304214	1.927027
C	-5.565427	-0.151583	1.411012
C	-7.466478	-1.873387	0.196901
C	-5.204651	-0.892617	0.241505
C	-7.793927	-1.151513	1.330957
C	-6.170665	-1.756094	-0.360813
C	-3.902794	-0.789531	-0.341459
H	-8.791445	-1.256035	1.743428
C	-3.620788	-1.542292	-1.482710
H	-2.644492	-1.484130	-1.948003
C	-4.572427	-2.385397	-2.066151
H	-4.336985	-2.960574	-2.954828
C	-5.838943	-2.498508	-1.519750
C	-1.692638	3.413427	3.807676
O	-1.969321	4.058660	4.810563
C	-0.039207	2.814883	2.053471
O	1.084469	2.997034	1.599082

N	-0.440070	3.523298	3.191472
C	-6.827968	-3.397557	-2.164692
O	-6.560498	-4.045716	-3.167827
C	-8.481154	-2.759933	-0.420747
O	-9.612405	-2.884171	0.029739
N	-8.094272	-3.469639	-1.564527
C	-9.109649	-4.340847	-2.166825
H	-8.644127	-4.865777	-2.996824
H	-9.952714	-3.741833	-2.518386
H	-9.478411	-5.044751	-1.418855
C	0.544825	4.449935	3.761175
H	1.419517	3.896453	4.110129
H	0.067856	4.968400	4.588702
H	0.870327	5.155013	2.994602
C	-0.544177	4.465571	-3.743352
H	-0.066468	4.989634	-4.566930
H	-0.872338	5.165516	-2.973264
H	-1.417261	3.912852	-4.097522
C	9.069368	-4.365702	2.190593
H	10.008324	-4.276009	1.650623
H	8.705992	-5.395234	2.158485
H	9.194105	-4.080066	3.236669
