Symmetric and Unsymmetric Donor Functionalization. Comparing Structural and Spectral Benefits of Chromophores for Dye Sensitized Solar Cells.

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Supporting Information

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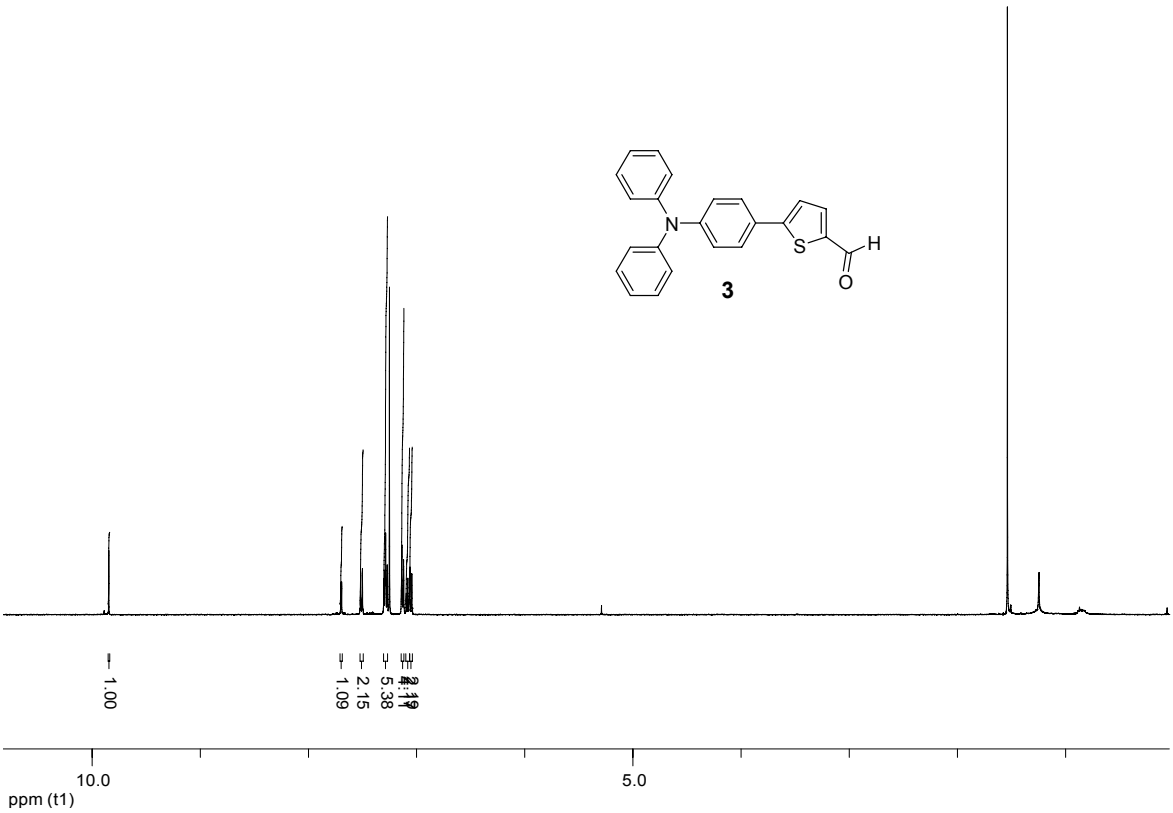
General Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker 500 and 400 MHz instruments by using the residual signals δ = 7.26 ppm and 77.0 ppm from $CDCl_3$, δ = 2.50 and 39.4 ppm from [D_6]DMSO and δ = 2.05, 29.84, and 206.26 ppm from [D_6]acetone, as internal references for ^{1}H and ^{13}C respectively. HRMS were performed using a Q-Tof Micro (Micromass Inc., Manchester, England) mass spectrometer equipped with a Z-spray ionization source.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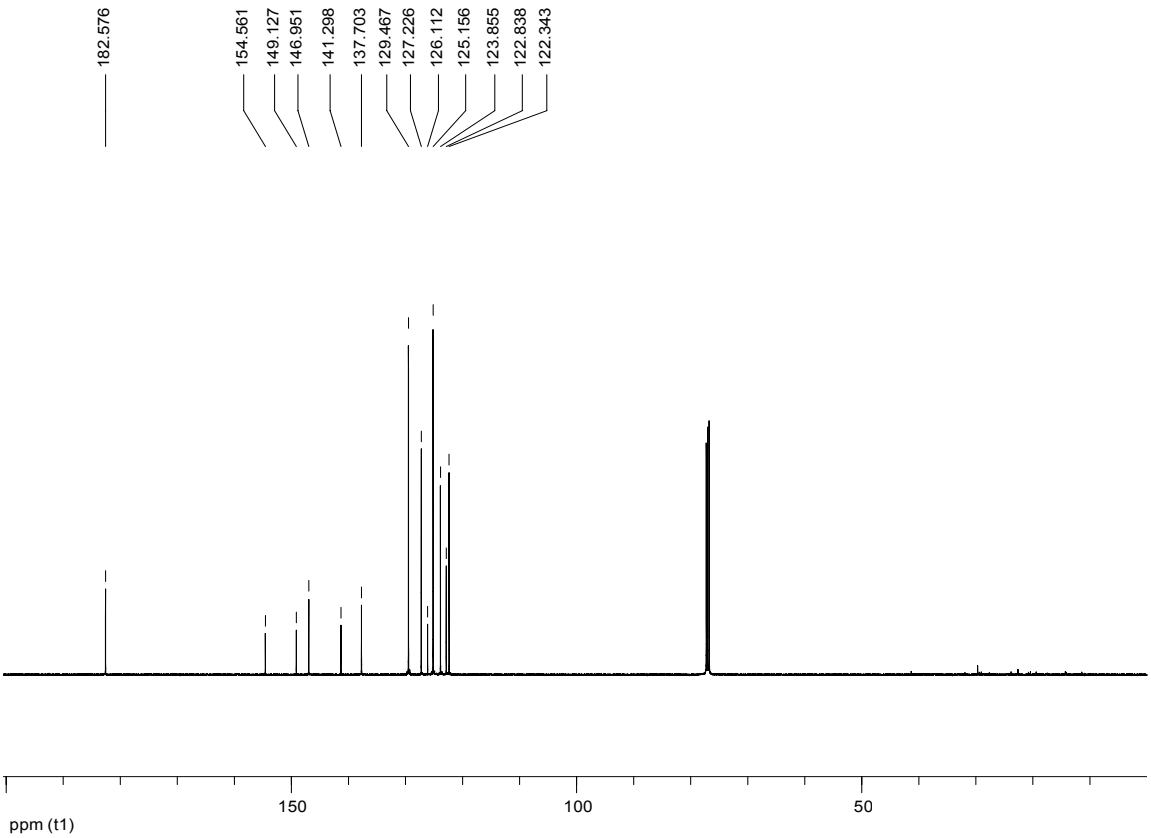
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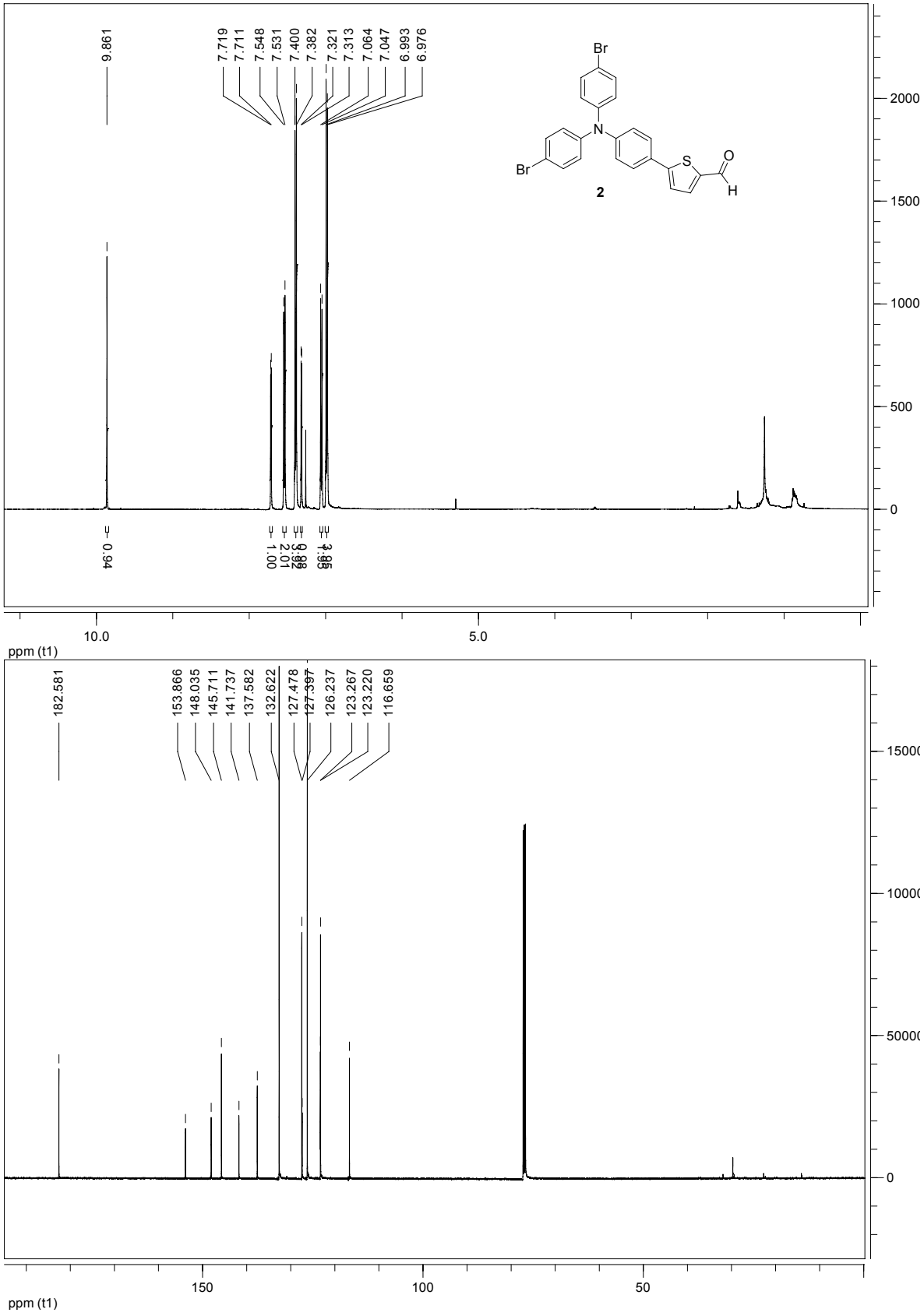
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Br
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O
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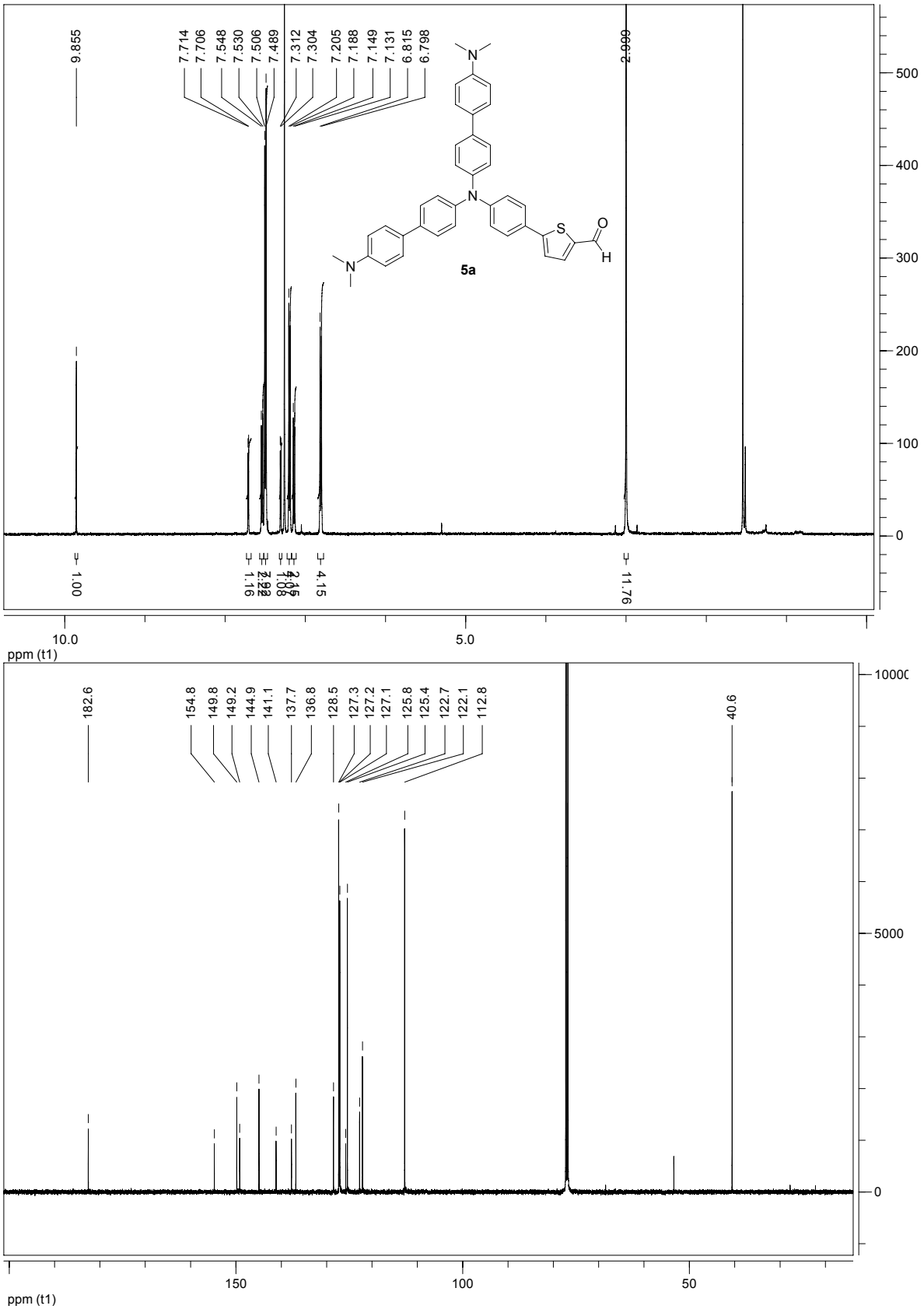
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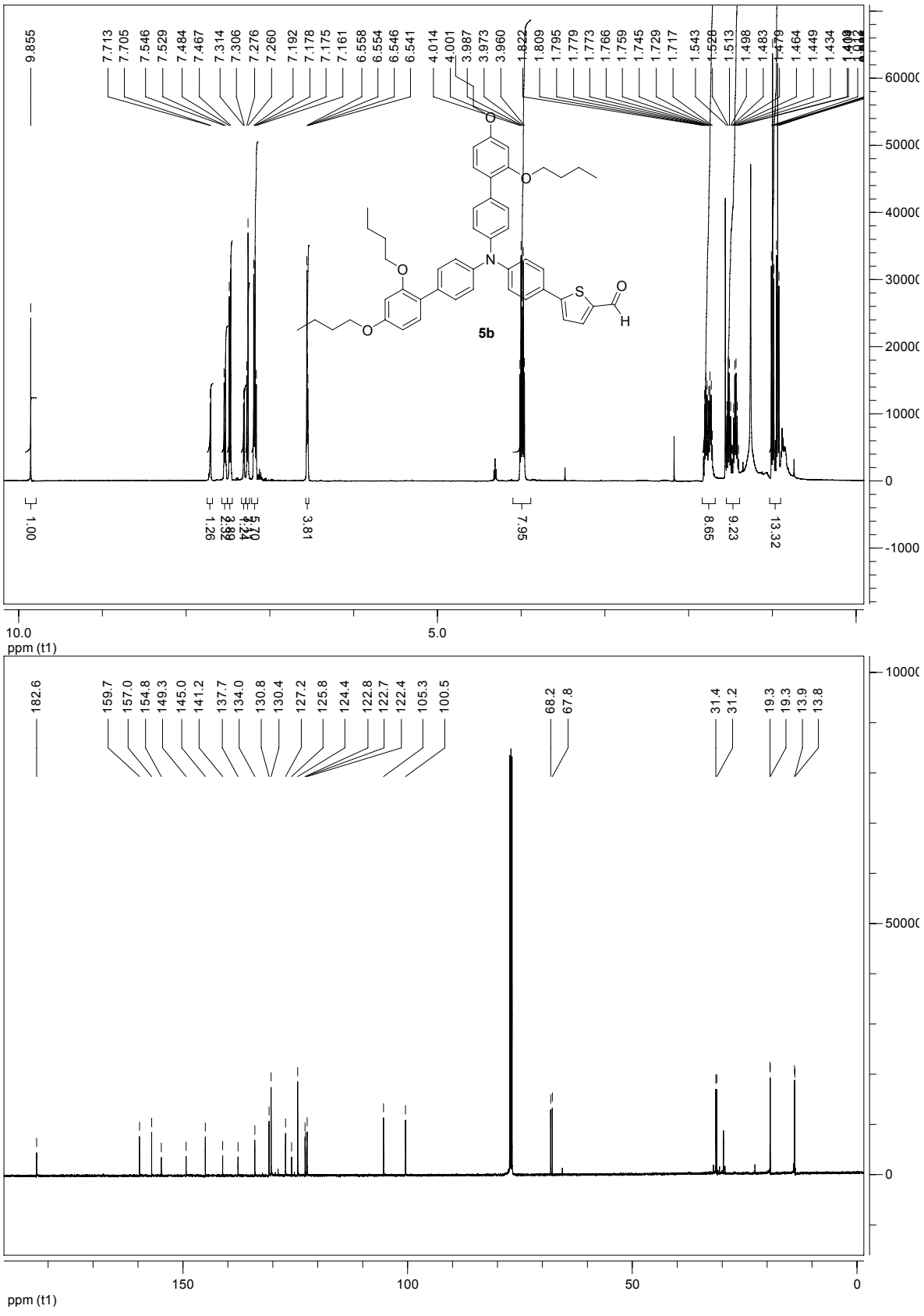
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130.4
127.2
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105.3
100.5
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50
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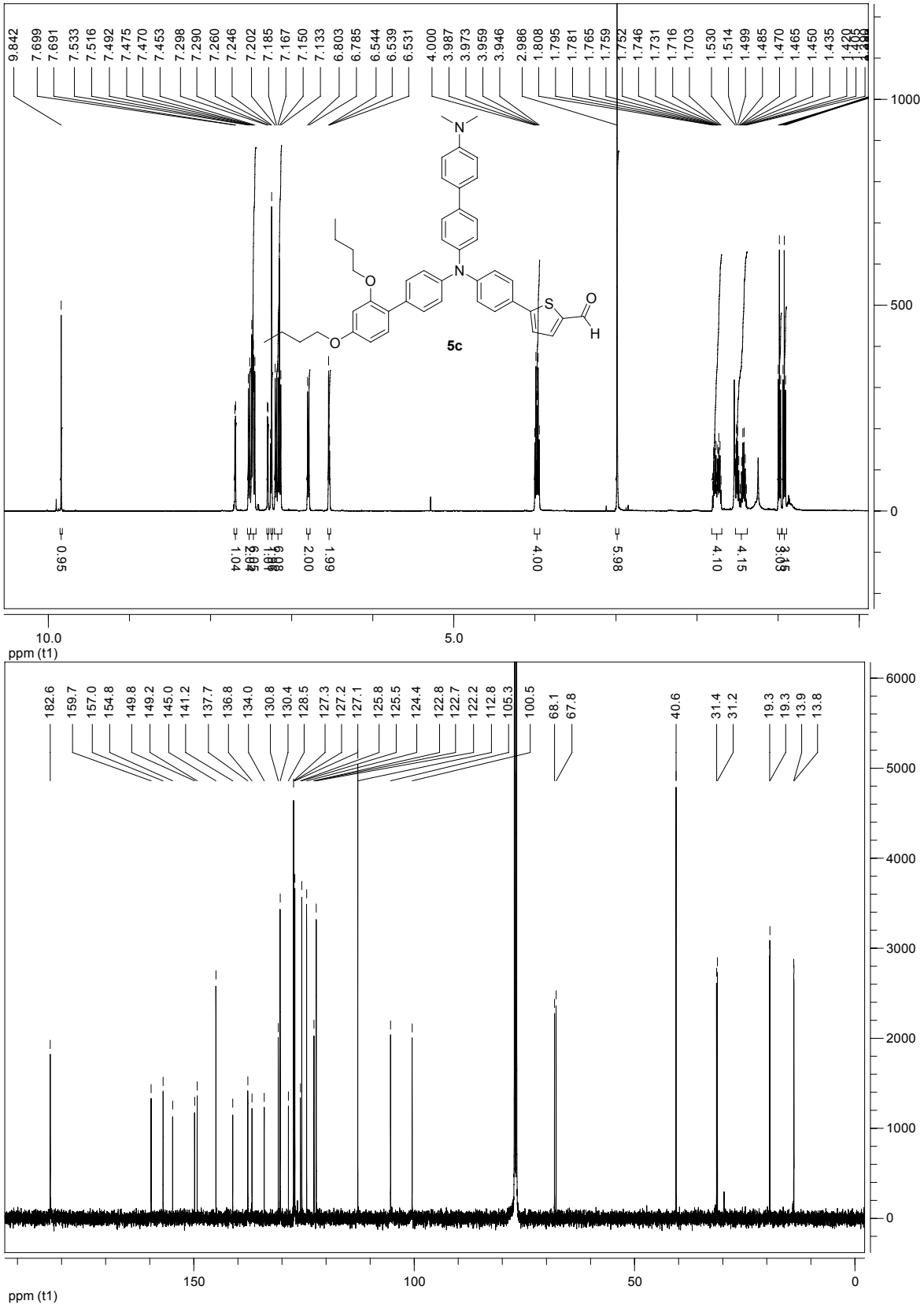
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125.8
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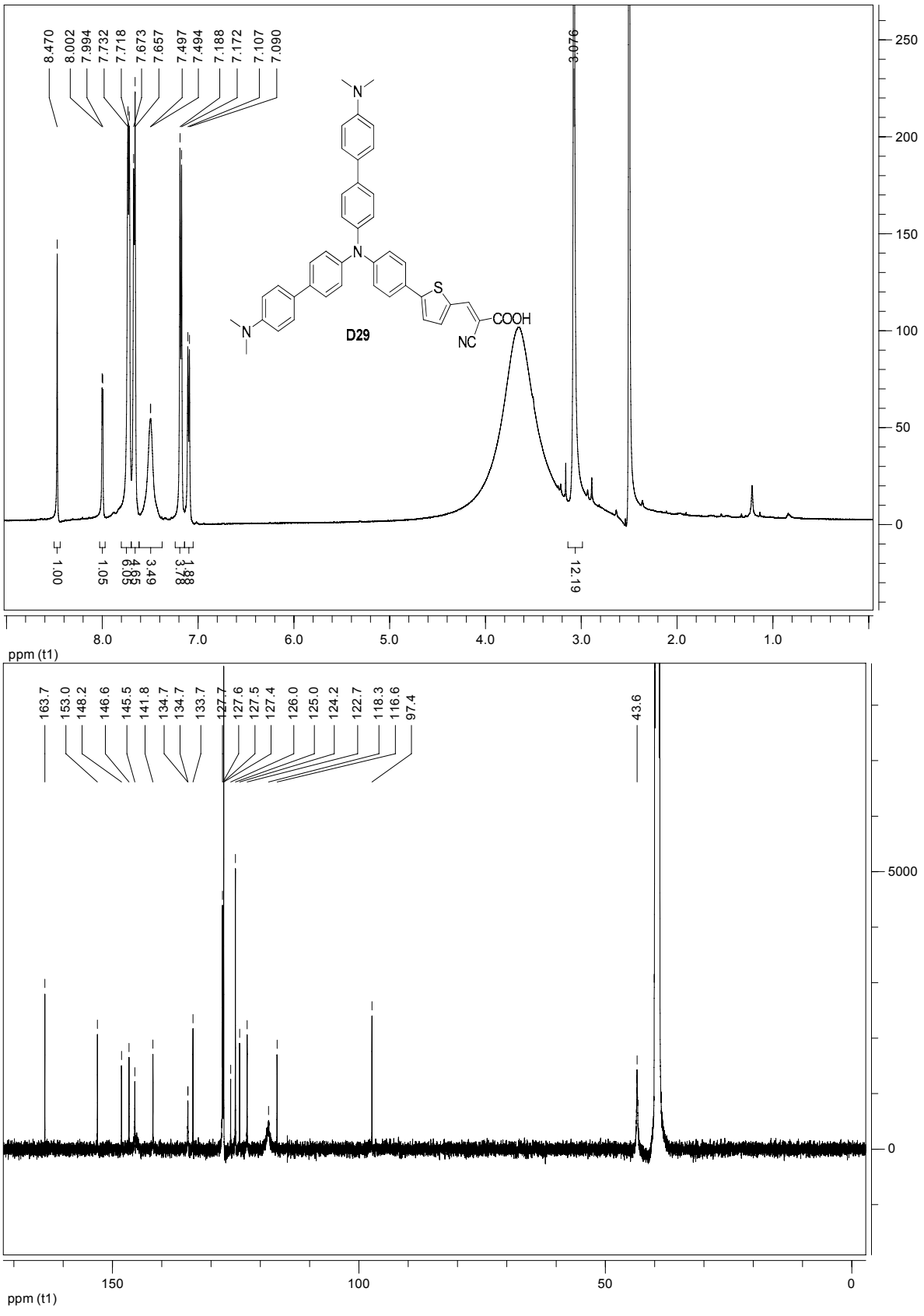
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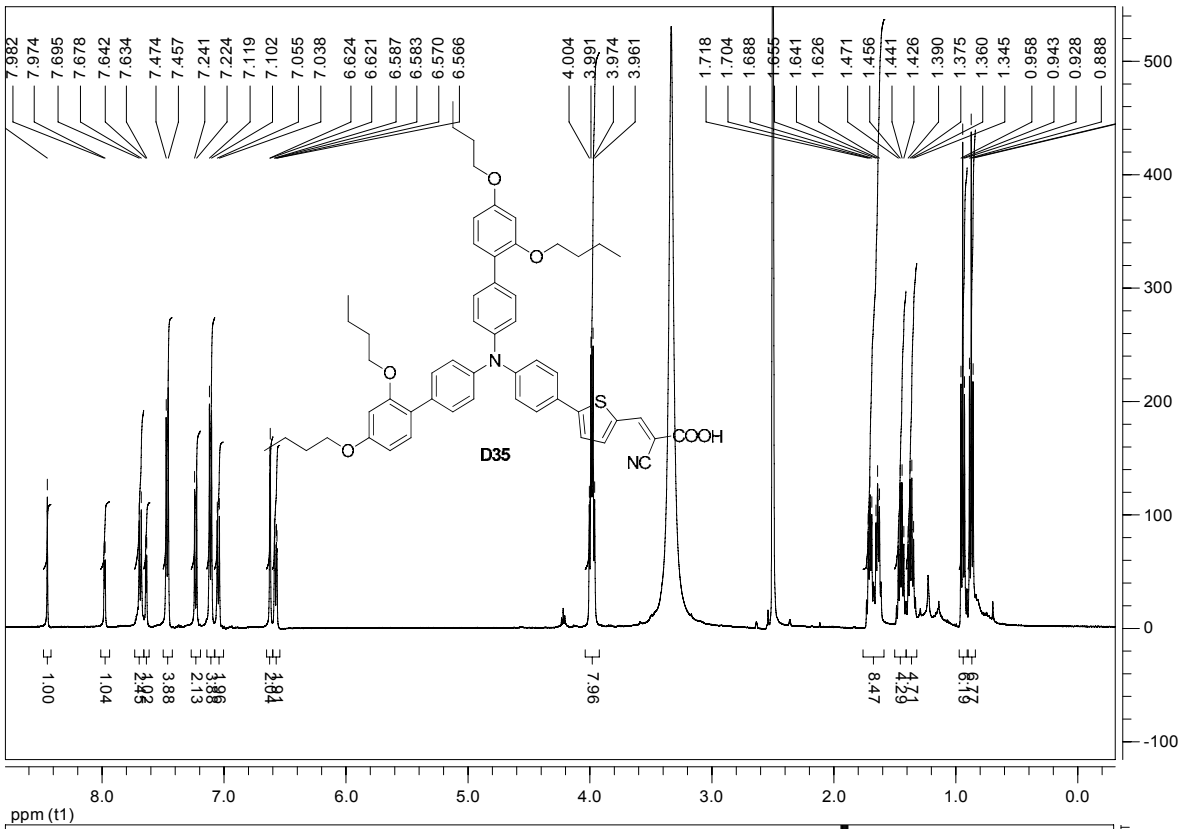
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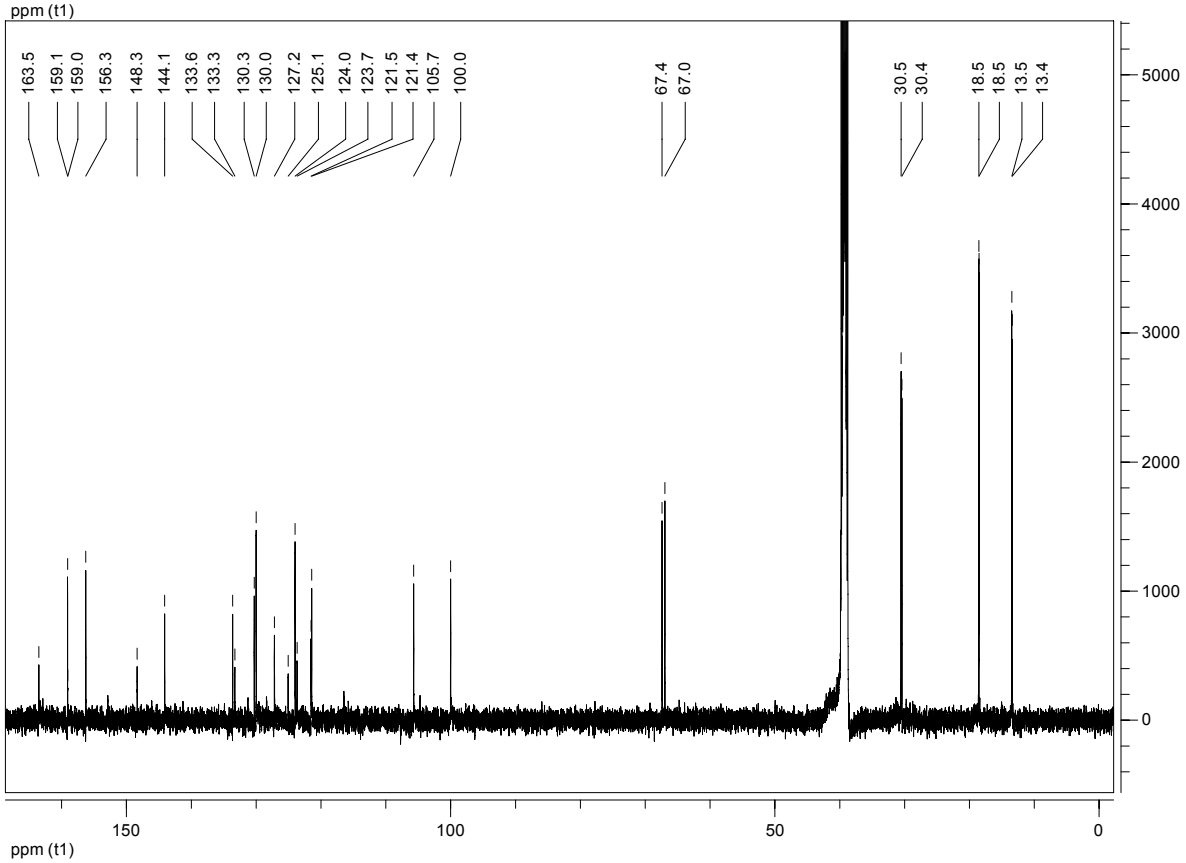
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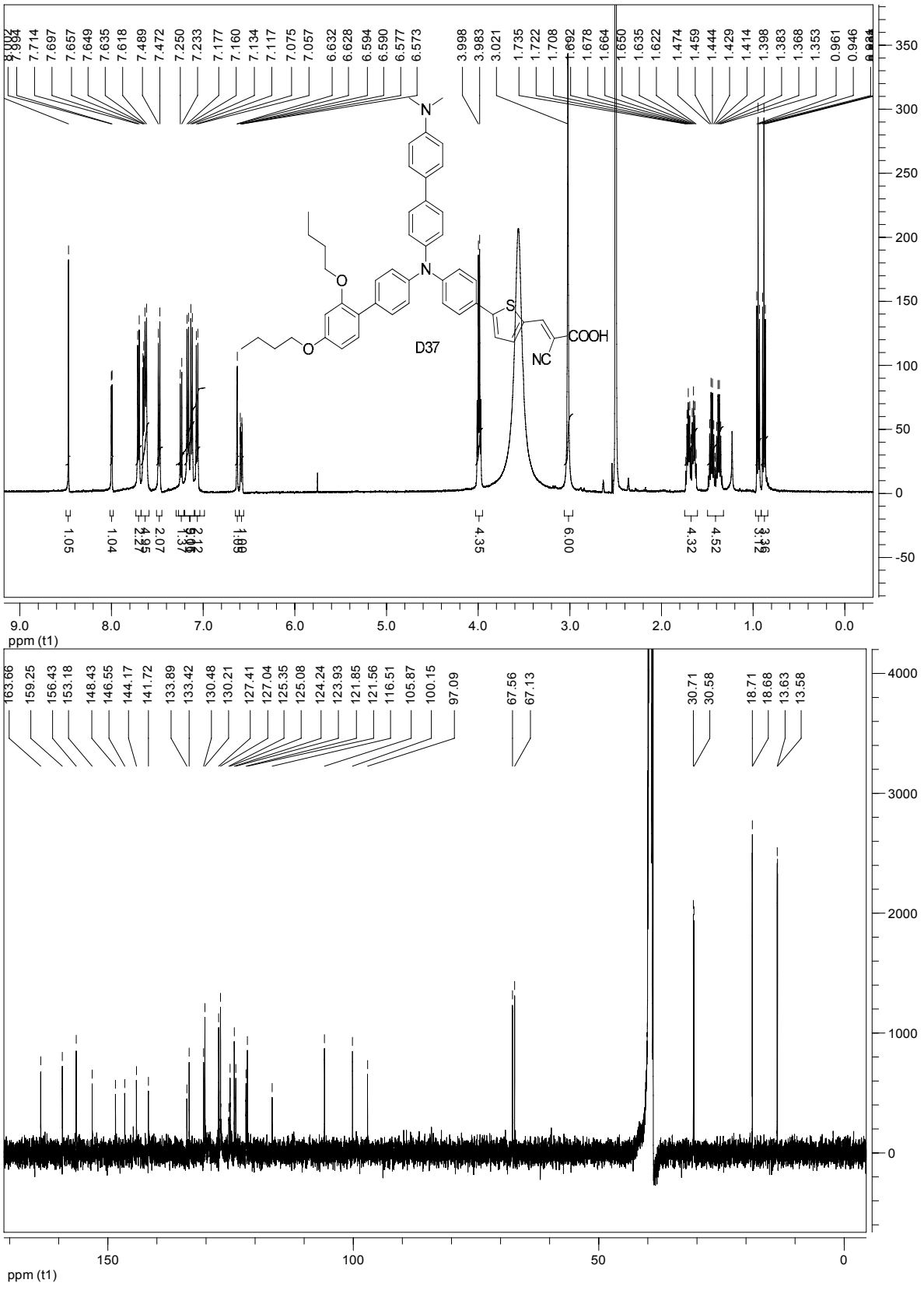
D37
COOH
NC
ppm (t1)
ppm (t1)

Reference 29

M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *GAUSSIAN 03 (Revision C.02), Gaussian, Inc., Pittsburgh PA,* **2003**.

Table S1. Calculated electronic and spectral data for the three dyes.

Dye	E_{HOMO} [eV][a]	E_{LUMO} [eV] [a]	$E_{H\text{-}L}$ [eV] [b]	*Abs* [nm][c]	f [c,d]	Contribution[c,e]
D29	0.23	-2.04	2.28	602; 510	0.52; 0.02	H→L:0.52; H-1→L:0.71
D35	0.35	-2.04	2.39	572; 441	0.67; 0.04	H→L:0.67; H-1→L:0.70
D37	0.34	-2.02	2.36	588; 482	0.55; 0.23	H→L:0.68; H-1→L:0.69

[a]Energy levels with respect to NHE. [b]HOMO-LUMO gap. Note that while the calculations do not reproduce the experimental HOMO and LUMO levels (presented in Table 1), the calculated gaps are quite accurate. [c]First and second transitions are reported. [d]Oscillator strengths, which are proportional to the integrated intensity of the specific absorption band. [e]Orbital coefficients of the most abundant contributions as reported in the Gaussian output.

Molecular coordinates

Presented in .xyz format.

D29

```
N    -0.796748    -0.043612    -0.068258
C    -1.297565     1.292152    -0.058126
C    -2.319490     1.661824     0.827665
C    -0.794432     2.256148    -0.944155
C    -2.819550     2.959592     0.824999
H    -2.711661     0.928440     1.525512
C    -1.294847     3.553839    -0.932446
H    -0.018453     1.979571    -1.651596
C    -2.320526     3.941452    -0.050551
H    -3.588308     3.226918     1.544473
H    -0.909368     4.271609    -1.651029
C     0.585603    -0.290351    -0.075533
C     1.115968    -1.438743    -0.699081
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C     2.849865     0.354653     0.528517
H     1.105438     1.484723     1.042337
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O	1.218103	6.103926	-0.051176
C	2.350221	6.968787	0.012936
H	2.345688	7.658472	-0.843649
H	2.307467	7.570556	0.931893
C	-6.214444	-3.728278	3.212196
H	-7.228832	-3.305478	3.212675
H	-6.305774	-4.823344	3.238643
C	-5.413818	-3.222039	4.399568
H	-4.408258	-3.654360	4.402211
H	-5.320357	-2.132289	4.364754
H	-5.912839	-3.499967	5.334190
C	-10.776512	-6.462136	-1.603272
H	-11.274028	-6.720563	-2.544240
H	-10.536388	-7.388105	-1.071391
H	-11.473036	-5.882494	-0.989422
C	-0.492816	11.102489	-1.299788
H	-0.026500	10.226125	-1.760150
H	-1.363656	11.380343	-1.901872
H	0.225872	11.929810	-1.328933
C	3.593265	6.095637	-0.005007
H	3.593968	5.410347	0.848035
H	3.636733	5.502439	-0.923745
H	4.491719	6.719925	0.047701

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N	-0.422510	0.364572	-0.181329
C	-0.709600	1.761936	-0.165903
C	-1.676012	2.278659	0.708677
C	-0.049490	2.642544	-1.035342
C	-1.969139	3.638255	0.711377
H	-2.187969	1.609249	1.393118
C	-0.343193	4.001964	-1.018170
H	0.684701	2.253760	-1.734499
C	-1.310315	4.537067	-0.147414
H	-2.698906	4.016557	1.421549
H	0.159112	4.656660	-1.724658
C	0.903856	-0.095612	-0.178281
C	1.252271	-1.312478	-0.800565
C	1.929545	0.643247	0.446508
C	2.561406	-1.765835	-0.791520
H	0.487835	-1.891563	-1.306540
C	3.236798	0.183382	0.445405
H	1.688477	1.573817	0.948079
C	3.593353	-1.033690	-0.169059
H	2.796108	-2.689791	-1.311348
H	3.992974	0.765959	0.965317
C	-1.512998	-0.556514	-0.202617
C	-1.544294	-1.654537	0.670161
C	-2.585272	-0.366721	-1.083771
C	-2.611147	-2.546368	0.647714
H	-0.723460	-1.808963	1.364047
C	-3.656665	-1.255324	-1.087354
C	-3.694431	-2.370249	-0.231965
H	-2.610384	-3.388820	1.329588
H	-4.487287	-1.076721	-1.764507
H	-2.581118	0.484605	-1.757431
C	4.963466	-1.529313	-0.169648
C	5.406259	-2.831440	-0.383296
S	6.324210	-0.475738	0.108007
C	6.799556	-2.985542	-0.315079
H	4.727758	-3.659310	-0.553918
C	7.478866	-1.799586	-0.045367
H	7.303877	-3.934968	-0.444400
C	8.864196	-1.510989	0.113059
H	9.127298	-0.478414	0.335506
C	9.951824	-2.343415	0.026942
C	9.854731	-3.735902	-0.254578
C	11.289492	-1.740628	0.242780
N	9.739580	-4.872219	-0.486327
O	11.493449	-0.566949	0.488290
O	12.286488	-2.650295	0.136919
H	13.114084	-2.159341	0.293999
C	-1.622093	5.983636	-0.138959
C	-2.920799	6.458368	0.108359
C	-0.632999	6.953186	-0.373033
C	-3.222529	7.814439	0.117387
H	-3.726992	5.748689	0.274820
C	-0.915512	8.313483	-0.367535
C	-2.226949	8.786620	-0.132839
H	-4.245975	8.114419	0.308727

H	-0.102920	9.010533	-0.534146
C	-4.821953	-3.334126	-0.311217
C	-5.465718	-3.869203	0.836695
C	-5.307383	-3.742044	-1.556939
C	-6.527846	-4.761242	0.705589
C	-6.371042	-4.634826	-1.709470
H	-4.817680	-3.361417	-2.448970
C	-6.982430	-5.148021	-0.564276
H	-7.034609	-5.176988	1.567046
H	-6.694073	-4.920359	-2.703076
H	0.395542	6.639820	-0.531886
N	-2.526272	10.142602	-0.156843
C	-1.445603	11.110108	-0.233747
H	-1.868870	12.115253	-0.284762
H	-0.765795	11.065705	0.632742
H	-0.847977	10.957916	-1.140331
C	-3.823232	10.593907	0.317393
H	-3.879703	11.680163	0.223426
H	-4.634001	10.168587	-0.286500
H	-4.009445	10.328827	1.370622
O	-8.023075	-6.029951	-0.561467
C	-8.544001	-6.477423	-1.812901
H	-7.749089	-6.966708	-2.393492
H	-8.905409	-5.617438	-2.394556
O	-4.998331	-3.447560	2.048070
C	-5.651719	-3.886645	3.238955
H	-5.589468	-4.981289	3.317557
H	-6.714937	-3.611334	3.200770
C	-9.674874	-7.447175	-1.517219
H	-10.108194	-7.816657	-2.452877
H	-9.308199	-8.303106	-0.942034
H	-10.463613	-6.955571	-0.939108
C	-4.958898	-3.218220	4.413804
H	-3.902263	-3.501092	4.453297
H	-5.021027	-2.128955	4.329004
H	-5.434496	-3.522963	5.352274