Supporting Information

Electronic Excited State Redox Properties for BODIPY Dyes Predicted from Hammett Constants: Estimating the Driving Force of Photoinduced Electron Transfer

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- 2,6-Dichloro-1,3,5,7-tetramethyl-Pyrromethene Fluoroborate (**4g**) ^{13}C-NMR spectrum (page S6).
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Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A.

Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

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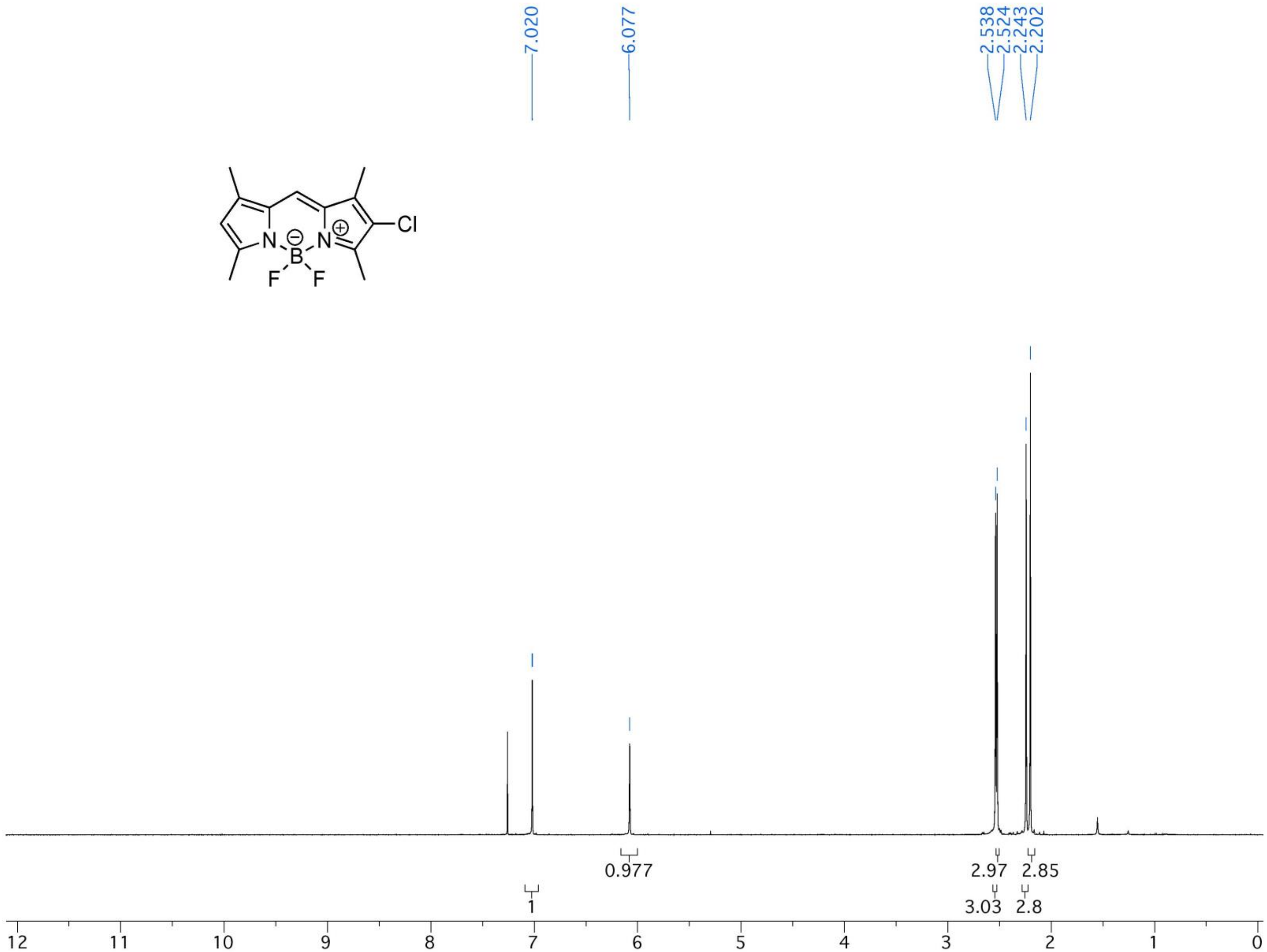
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B
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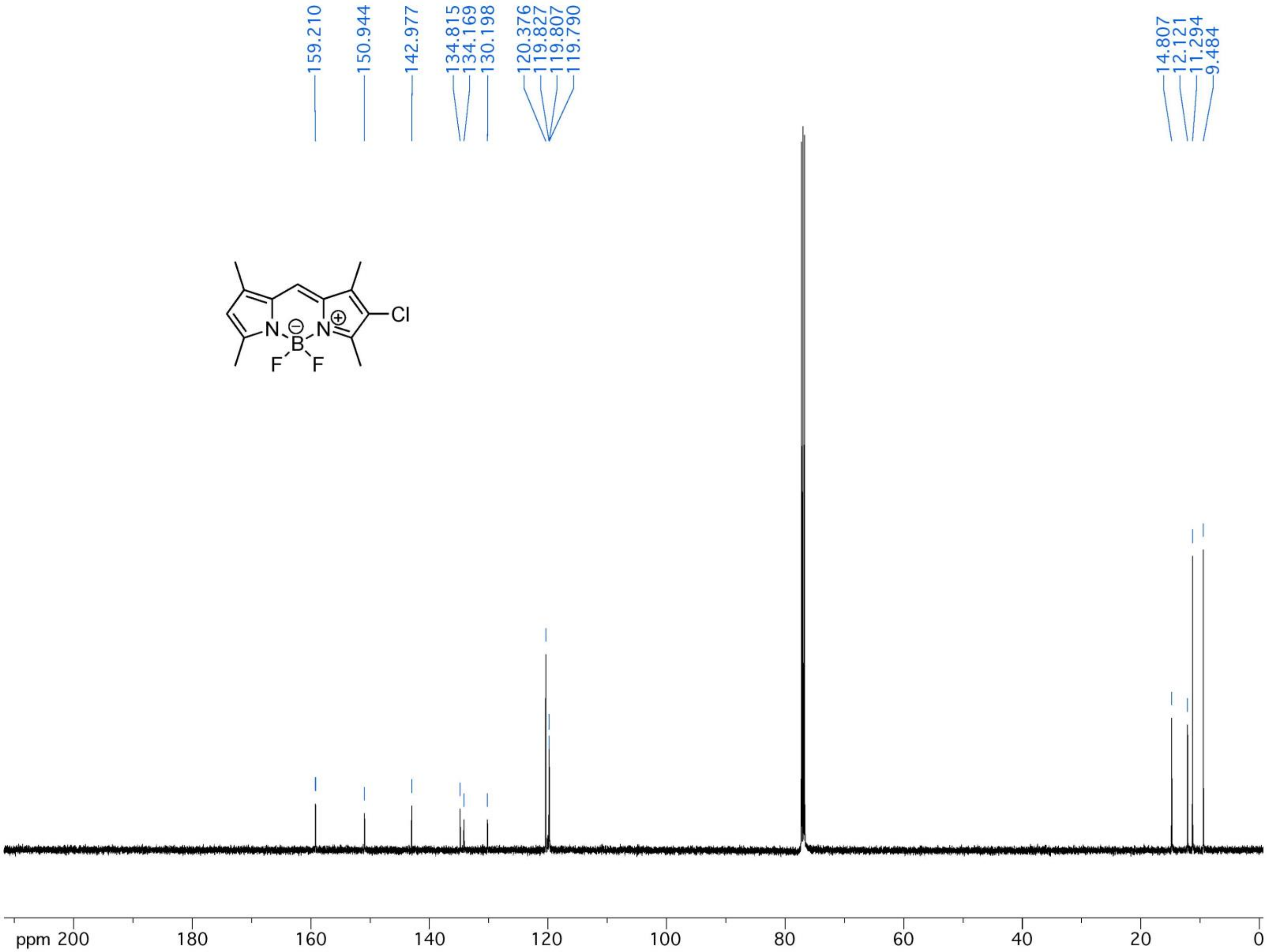
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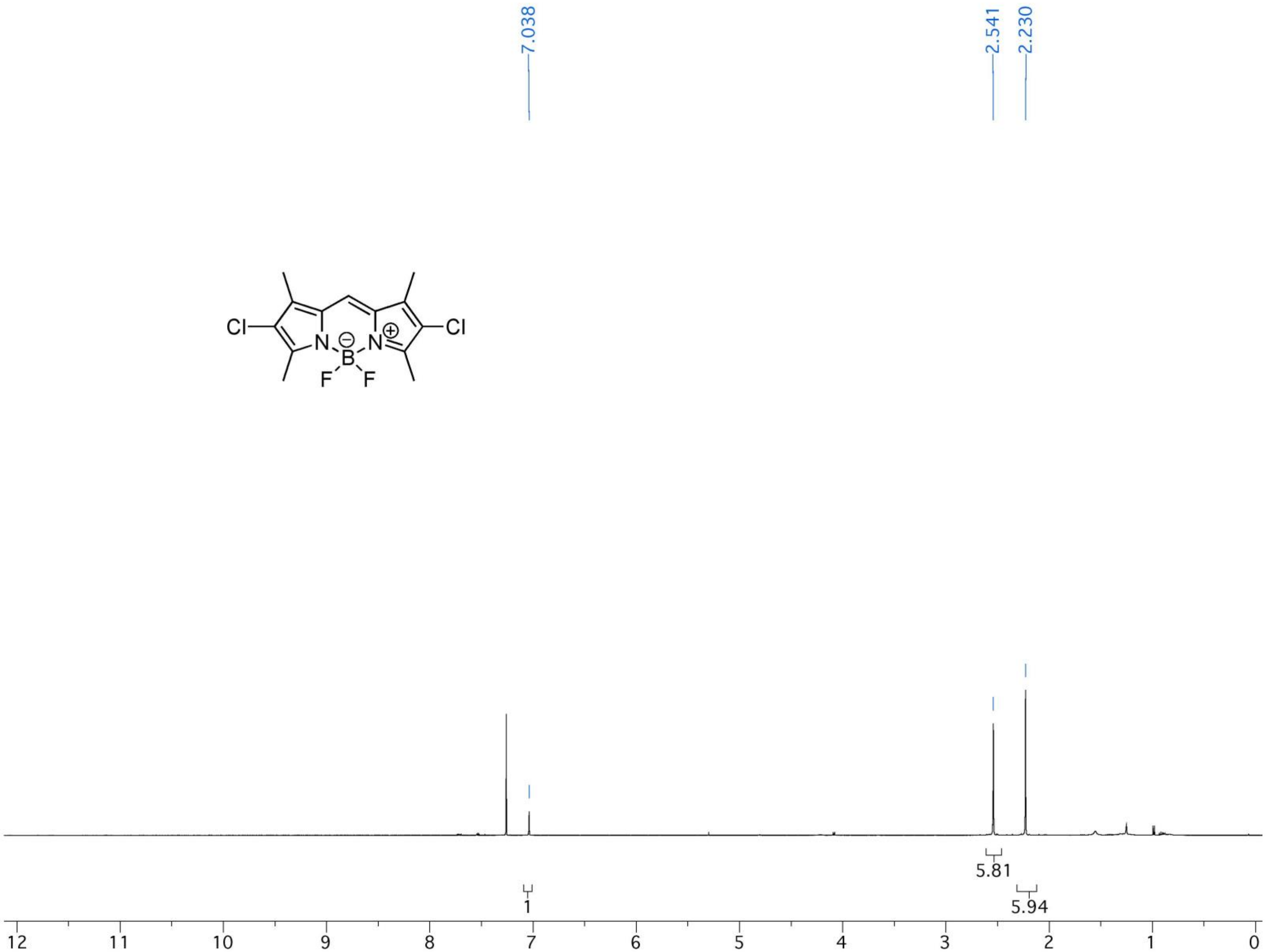
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3
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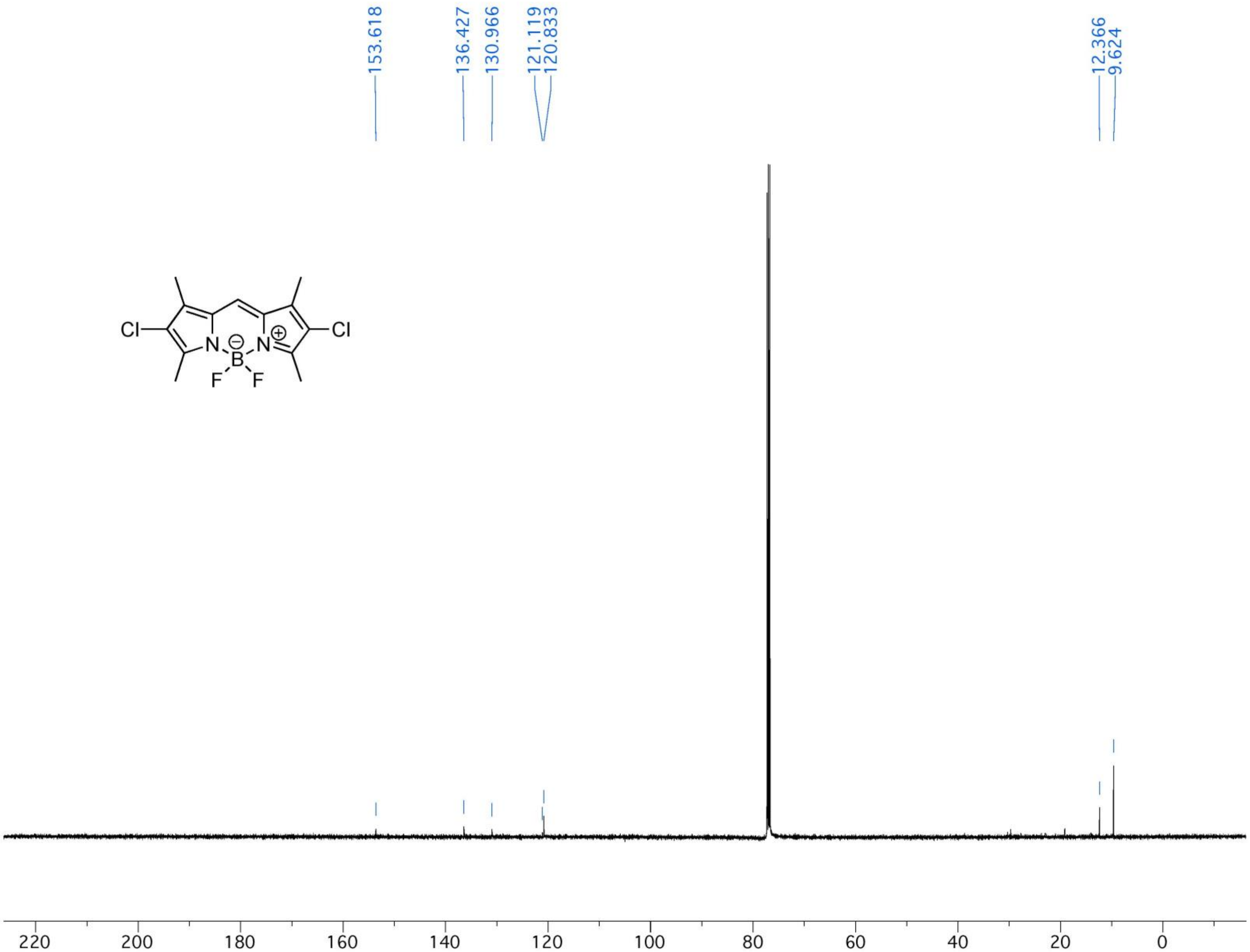
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Cl
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200
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140
120
100
80
60
40
20
0

Table S1. Gaussian09 Output Information

Entry	E(RB3LYP) (a.u.)	RMS Gradient Norm (a.u.)	Imag. Freq	Dipole (Debye)	Point Group	HOMO (a.u.)	LUMO (a.u.)
1a	-1027.99791388	0.00000348	0	5.9025	C1	-0.17951	-0.06317
1b	-949.36806701	0.00000481	0	6.0559	C1	-0.18168	-0.06422
1c	-1051.28171059	0.00000377	0	5.6714	C1	-0.19004	-0.06460
1d	-894.02191951	0.00001131	0	5.9188	C1	-0.19608	-0.06711
1e	-1432.24636164	0.00000723	0	6.3951	C1	-0.19928	-0.07342
1f	-1353.61636374	0.00000910	0	6.3647	C1	-0.20249	-0.07487
1g	-1813.21039833	0.00001031	0	6.0127	C1	-0.20833	-0.08238
1h	-1064.90135000	0.00000168	0	8.7325	C1	-0.21153	-0.08320
1i	-986.27117703	0.00000681	0	8.4911	C1	-0.21518	-0.08501
1j	-1078.51815248	0.00000740	0	6.2657	C1	-0.23281	-0.10302
2a	-1011.95118048	0.00000448	0	3.5090	C1	-0.18253	-0.07991
2b	-933.32137613	0.00000603	0	4.7041	C1	-0.18322	-0.07995
2c	-1035.23366073	0.00000207	0	3.9583	C1	-0.19065	-0.08171
2d	-877.97408932	0.00000153	0	4.1369	C1	-0.19710	-0.08499
2e	-1416.19790692	0.00000514	0	4.8824	C1	-0.20014	-0.09118
2f	-1337.56798145	0.00000416	0	4.7129	C1	-0.20351	-0.09300
2g	-1797.16140337	0.00001045	0	4.1239	C1	-0.20934	-0.10077
2h	-1048.85228599	0.00000163	0	7.8784	C1	-0.21269	-0.10163
2i	-970.22214284	0.00000649	0	7.4572	C1	-0.21641	-0.10382
2j	-1062.46747973	0.00000836	0	4.3897	C1	-0.23353	-0.12237
3a	-1087.15449034	0.00000974	0	2.9879	C1	-0.18524	-0.08898
3b	-1008.52440321	0.00000771	0	3.3475	C1	-0.18785	-0.09024
3c	-1110.43660803	0.00001273	0	2.1413	C1	-0.19553	-0.09179
3d	-953.17644637	0.00000802	0	2.4026	C1	-0.20206	-0.09496
3e	-1491.40038683	0.00000678	0	3.0122	C1	-0.20479	-0.10086
3f	-1412.07700479	0.00000754	0	2.7370	C1	-0.20816	-0.10272
3g	-1872.36325470	0.00001564	0	2.4252	C1	-0.21368	-0.11019
3h	-1124.05420307	0.00000217	0	6.4258	C1	-0.21712	-0.11090
3i	-1045.42360604	0.00000959	0	5.8268	C1	-0.22073	-0.11315
3j	-1137.66822222	0.00000974	0	2.9382	C1	-0.23710	-0.13080
4a	-972.64060868	0.00000145	0	3.9705	C1	-0.18082	-0.08107
4b	-894.01194364	0.00000198	0	4.1106	C1	-0.18302	-0.08293
4c	-995.92539650	0.00000233	0	3.4804	C1	-0.19242	-0.08467
4d	-838.66384493	0.00000889	0	3.6098	C1	-0.19787	-0.08884
4e	-1376.88899519	0.00000200	0	4.4429	C1	-0.20192	-0.09418
4f	-1298.25811494	0.00001595	0	4.1968	C1	-0.20486	-0.09652
4g	-1757.85186039	0.00000691	0	3.4792	C1	-0.21126	-0.10388
4h	-1009.54259577	0.00000373	0	7.5875	C1	-0.21439	-0.10518
4i	-930.91149893	0.00001185	0	7.0622	C1	-0.21767	-0.10792
4j	-1023.15639984	0.00000644	0	3.5139	C1	-0.23504	-0.12660

Table S1 continued.

Entry	E(RB3LYP) (a.u.)	RMS Gradient Norm (a.u.)	Imag. Freq	Dipole (Debye)	Point Group	HOMO (a.u.)	LUMO (a.u.)
5a	-1239.82420888	0.00000478	0	3.5925	C1	-0.18489	-0.08932
5b	-1161.19432222	0.00000196	0	3.8267	C1	-0.18760	-0.09069
5c	-1263.10631407	0.00000150	0	2.5756	C1	-0.19514	-0.09238
5d	-1105.84626574	0.00000608	0	2.6557	C1	-0.20181	-0.09581
5e	-1644.07005340	0.00000443	0	3.7907	C1	-0.20429	-0.10140
5f	-1565.43977854	0.00000194	0	3.5096	C1	-0.20775	-0.10340
5g	-2025.03295693	0.00000562	0	2.7994	C1	-0.21326	-0.11063
5h	-1276.72390605	0.00000335	0	7.1929	C1	-0.21649	-0.11150
5i	-1198.09340772	0.00000515	0	6.6067	C1	-0.22024	-0.11386
5j	-1290.33801041	0.00000835	0	3.7790	C1	-0.23674	-0.13136
6a	-1410.12930781	0.00000241	0	3.2777	C1	-0.18347	-0.08820
6b	-1331.49972594	0.00000505	0	3.5633	C1	-0.18602	-0.08954
6c	-1433.41130090	0.00000419	0	3.0070	C1	-0.19421	-0.09200
6d	-1276.15183854	0.00005088	0	3.2003	C1	-0.20065	-0.09550
6e	-1814.37514480	0.00001014	0	4.0646	C1	-0.20330	-0.10075
6f	-1735.74526027	0.00000176	0	3.8429	C1	-0.20668	-0.10276
6g	-2195.33811507	0.00000310	0	3.3499	C1	-0.21221	-0.11011
6h	-1447.02930397	0.00000455	0	7.3697	C1	-0.21554	-0.11088
6i	-1368.39914478	0.00000979	0	6.8532	C1	-0.21915	-0.11323
6j	-1460.64371864	0.00000251	0	3.9791	C1	-0.23559	-0.13082
7a	-1699.81726378	0.00000115	0	2.4387	C1	-0.18849	-0.09345
7b	-1621.18730211	0.00000343	0	2.7396	C1	-0.19130	-0.09501
7c	-1723.09974761	0.00000416	0	1.6371	C1	-0.19944	-0.09660
7d	-1565.83934157	0.00000420	0	1.8879	C1	-0.20616	-0.10030
7e	-2104.06288244	0.00000188	0	3.3475	C1	-0.20828	-0.10550
7f	-2025.43252664	0.00000212	0	2.9255	C1	-0.21179	-0.10754
7g	-2485.02535648	0.00000195	0	2.0951	C1	-0.21696	-0.11467
7h	-1736.71641473	0.00000431	0	7.0692	C1	-0.22029	-0.11541
7i	-1658.08581010	0.00000215	0	6.4238	C1	-0.22403	-0.11788
7j	-1750.32985509	0.00000188	0	2.6959	C1	-0.24006	-0.13508
8a	-1085.94688450	0.00000220	0	1.2951	C1	-0.18818	-0.10192
8b	-1007.31713589	0.00002022	0	2.9722	C1	-0.19197	-0.10506
8c	-1109.22912895	0.00000265	0	1.9121	C1	-0.19991	-0.10415
8d	-951.96869121	0.00000143	0	2.0257	C1	-0.20694	-0.10964
8e	-1490.19212277	0.00001404	0	3.9889	C1	-0.20900	-0.11322
8f	-1411.56196330	0.00000785	0	2.3268	C1	-0.21292	-0.11643
8g	-1871.15451319	0.00000966	0	2.0618	C1	-0.21816	-0.12259
8h	-1122.84546226	0.00000553	0	7.7472	C1	-0.22110	-0.12322
8i	-1044.21506206	0.00001485	0	5.6422	C1	-0.22566	-0.12655
8j	-1136.45855288	0.00002744	0	2.3258	C1	-0.24187	-0.14287

Table S1 continued.

Entry	E(RB3LYP) (a.u.)	RMS Gradient Norm (a.u.)	Imag. Freq	Dipole (Debye)	Point Group	HOMO (a.u.)	LUMO (a.u.)
9a	-1432.22790934	0.00000526	0	2.9007	C1	-0.18842	-0.08811
9b	-1353.59802563	0.00001704	0	3.1344	C1	-0.19121	-0.08974
9c	-1455.51065269	0.00001092	0	2.1927	C1	-0.19950	-0.09137
9d	-1298.25054422	0.00001243	0	2.3597	C1	-0.20645	-0.09533
9e	-1836.47384551	0.00001790	0	3.5895	C1	-0.20871	-0.10077
9f	-1757.84363719	0.00000713	0	3.2075	C1	-0.21234	-0.10300
9g	-2217.43632438	0.00000832	0	2.4045	C1	-0.21773	-0.11039
9h	-1469.12750704	0.00000194	0	7.1153	C1	-0.22103	-0.11119
9i	-1390.49701351	0.00000800	0	6.4853	C1	-0.22493	-0.11384
9j	-1482.74104282	0.00001087	0	2.7571	C1	-0.24153	-0.13176
10a	-1064.87819462	0.00000452	0	1.8588	C1	-0.19467	-0.10861
10b	-986.24791015	0.00001224	0	2.2755	C1	-0.19767	-0.11044
10c	-1088.16043976	0.00000409	0	0.4320	C1	-0.20599	-0.11203
10d	-930.89944885	0.00001221	0	0.2640	C1	-0.21340	-0.11651
10e	-1469.12283708	0.00000625	0	2.8504	C1	-0.21520	-0.12123
10f	-1390.49215750	0.00000937	0	2.0980	C1	-0.21906	-0.12373
10g	-1850.08447500	0.00001706	0	0.2520	C1	-0.22432	-0.13065
10h	-1101.77567328	0.00001096	0	6.8043	C1	-0.22739	-0.13136
10i	-1023.14467243	0.00002260	0	5.9432	C1	-0.23150	-0.13427
10j	-1115.38746975	0.00001994	0	0.0938	C1	-0.24774	-0.15136

Table S2. Fitting parameters obtained for the correlation of Hammett substituent constants with HOMO and LUMO energy levels calculated via DFT (B3LYP 6-31g(d))

σ_{R^I}	$\sigma_{R^{II}} + \sigma_{R^{III}}$		ρ_{R^I}	$\rho_{R^{II,III}}$	c	R^2
σ_p	σ_p	HOMO	-0.34±0.02	-0.68±0.01	-5.529±0.006	0.98190
		LUMO	-0.96±0.03	-0.55±0.02	-2.64±0.01	0.94881
σ_m	σ_p	HOMO	-0.56±0.02	-0.680±0.008	-5.473±0.006	0.98823
		LUMO	-1.33±0.09	-0.55±0.03	-2.52±0.02	0.84825
σ_m	σ_m	HOMO	-0.56±0.06	-0.94±0.03	-5.29±0.02	0.91559
		LUMO	-1.33±0.09	-0.79±0.04	-2.36±0.03	0.85159
σ_p	σ_m	HOMO	-0.34±0.04	-0.94±0.03	-5.34±0.02	0.90926
		LUMO	-0.96±0.03	-0.79±0.03	-2.48±0.01	0.95215

Table S3. Fitting parameters obtained for the correlation of redox potentials determined by cyclic voltammetry ($E°_{B^{+\cdot}/B}, E°_{B/B^{-\cdot}}$) with orbital energies calculated via DFT ($\varepsilon_{HOMO}, \varepsilon_{LUMO}$).

	intercept	slope	R^2
Including E_{pa} and E_{pc}	-3.50±0.03	-0.774±0.007	0.99537
Excluding E_{pa} and E_{pc}	-3.52±0.04	-0.781±0.008	0.99608

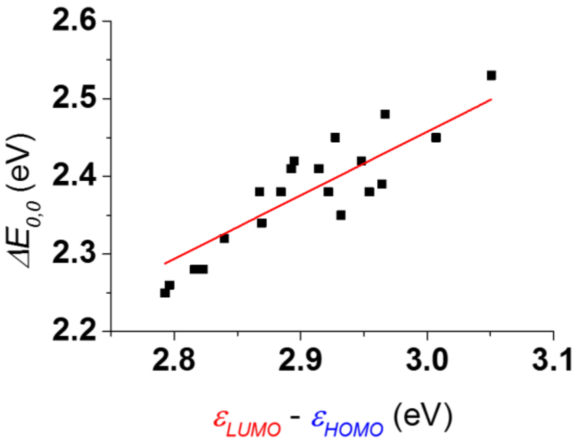

Figure S1. Correlation of $\Delta E_{0,0}$ values with HOMO-LUMO gap energies calculated via DFT (ε_{HOMO} -ε_{LUMO})