Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Colorimetric and Fluorimetric Detection of Fluoride and Cyanide Ions Using Tri and Tetra Coordinated Boron Containing Chromophores

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Contents

1. X-ray crystallographic analysis

Single crystal X-ray structural studies of **3** were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 150(2) K using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on F^2. The crystal refinement data are summarized in Table 1. The CCDC numbers **967476 and 1043936** contain the supplementary crystallographic data for **3** and **4**. These data can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre, 12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement parameters

Compounds	**3**	**4**
Empirical formula	C38 H48 B2 Cl2 N2	C35 H32 B2 F2 N2
Crystal size	0.33 x 0.26 x 0.21 mm	0.13 x 0.09 x 0.05 mm
Crystal system	Monoclinic	Monoclinic
Space group	$P\ 2_1/n$	$P\ 2_1/n$
Formula weight	625.30	540.25
***T*,K**	150(2) K	150(2) K
***θ* range for data collection/°**	3.13 to 24.99 deg.	3.75 to 71.46 deg.
***a* (Å)**	8.9225(3)	13.8290(4)
***b* (Å)**	9.5404(3)	16.4725(3)
***c* (Å)**	42.2003(11)	14.2509(3)
***α*/°**	76.110(10)	90

***β*/°**	87.689(11)	114.352(3)
***γ*/°**	71.391(12)	90
Z	4	4
***F*(000)**	1336	1136
V (A°)^3	3592.25(19)	2957.50(12)
$D_{calc,}$ Mg m^{-3}	1.156	1.213
Collected refins	26185	20171
Unique refins	6330 [R(int) = 0.0428]	5690 [R(int) = 0.0378]
Data/restrains/paramiters	6330 / 0 / 405	5690 / 0 / 376
Goodness-of-fit on F^2	1.024	1.069
Final R indices [I>2σ(l)] [6]	R_1 = 0.0670, wR_2 = 0.1763	R1 = 0.0669, wR2 = 0.2028
R indices (all data)	R_1 = 0.0874, wR_2 = 0.1946	R1 = 0.0831, wR2 = 0.2224

Table S2. Selected bond lengths and angles of pyrazabole 3

pyrazabole 3			
Bond lengths (Å)		**Bond angles °**	
B(2)-N(1)	1.586(4)	N(1)-B(2)-N(2)#1	104.8(2)
B(2)-N(2)#1	1.590(4)	N(1)-B(2)-C(1)	110.4(2)
B(2)-C(1)	1.596(4)	N(2)#1-B(2)-C(1)	110.9(2)
B(2)-C(5)	1.641(4)	N(1)-B(2)-C(5)	105.6(2)
B(1)-C(17)	1.566(4)	N(2)#1-B(2)-C(5)	107.7(2)
B(1)-C(20)	1.573(4)	C(17)-B(1)-C(20)	117.8(2)
B(1)-C(29)	1.575(4)	C(17)-B(1)-C(29)	117.2(2)
N(1)-C(10)	1.335(3)	C(20)-B(1)-C(29)	125.0(2)
N(1)-N(2)	1.366(3)		
N(2)-C(9)	1.337(3)		

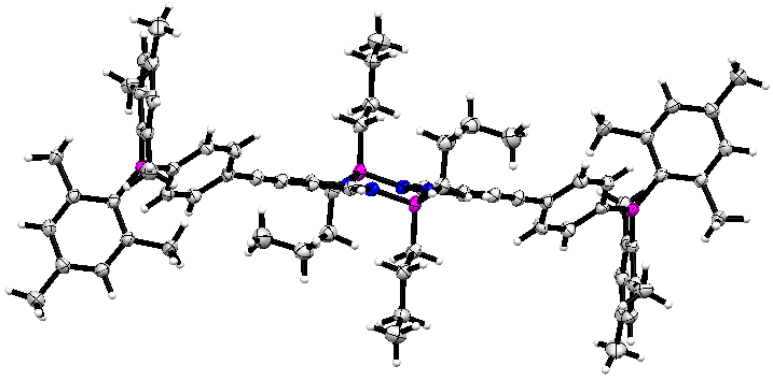

Fig. S1 Crystal structure of **3**.

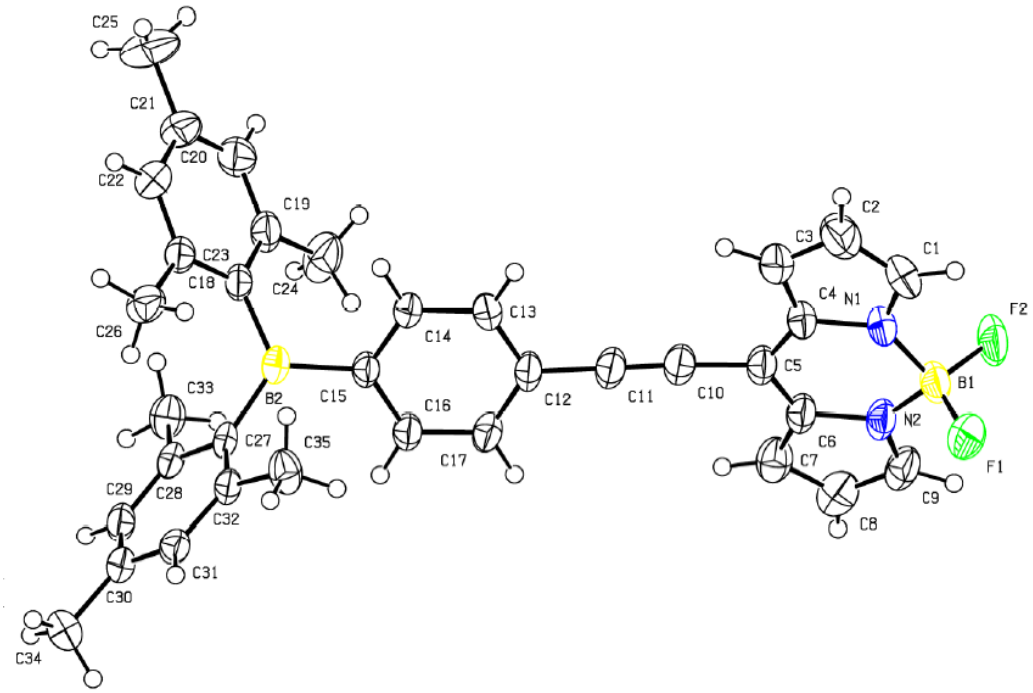

Fig. S2 Crystal structure of **4**.

Table S3. Important distance and angle of intermolecular interactions of **3**.

Interaction	Distance (Å)
C(36)-H(36B)---π (mesityl ring centroid)	3.147
C(26)-H(26c)---Cl(2)	2.869

Table S4. Important distance and angle of intermolecular interactions of **4**.

Interaction	Distance (Å)
C(17)-H(17) --- F(1)	2.653
C(7)-H(7) --- F(1)	2.646
C(3)-H(3) --- F(2)	2.421
C(13)-H(13) --- F(2)	2.466
C(22)-H(22) --- π (C12, C13, C14, C15, C16, C17)	3.021
Two pyrrole ring π--- π (C6, C7, C8, C9, N2)	3.689
B-mesityl C(1)-H(1) --- π (C27, C28, C29, C30, C31, C32)	3.172
C(34A)-H(34A) --- π (C18, C19, C20, C21, C22, C23)	2.892
C(34B)-H(34B) --- π (C1, C2, C3, C4, N1)	3.214

2. Thermogravimetric analysis (TGA)

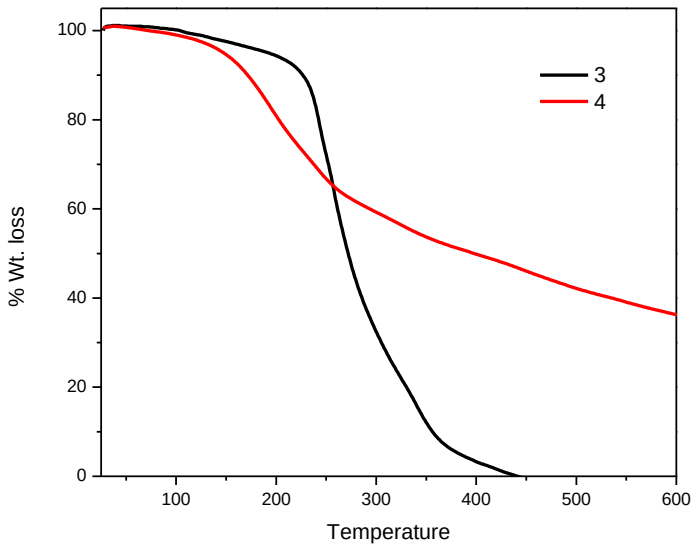

Fig. S3 Thermogravimetric analysis of **3** and **4**, measured at a heating rate of 10° C/ min under nitrogen atmosphere.

3. Anion-sensing properties

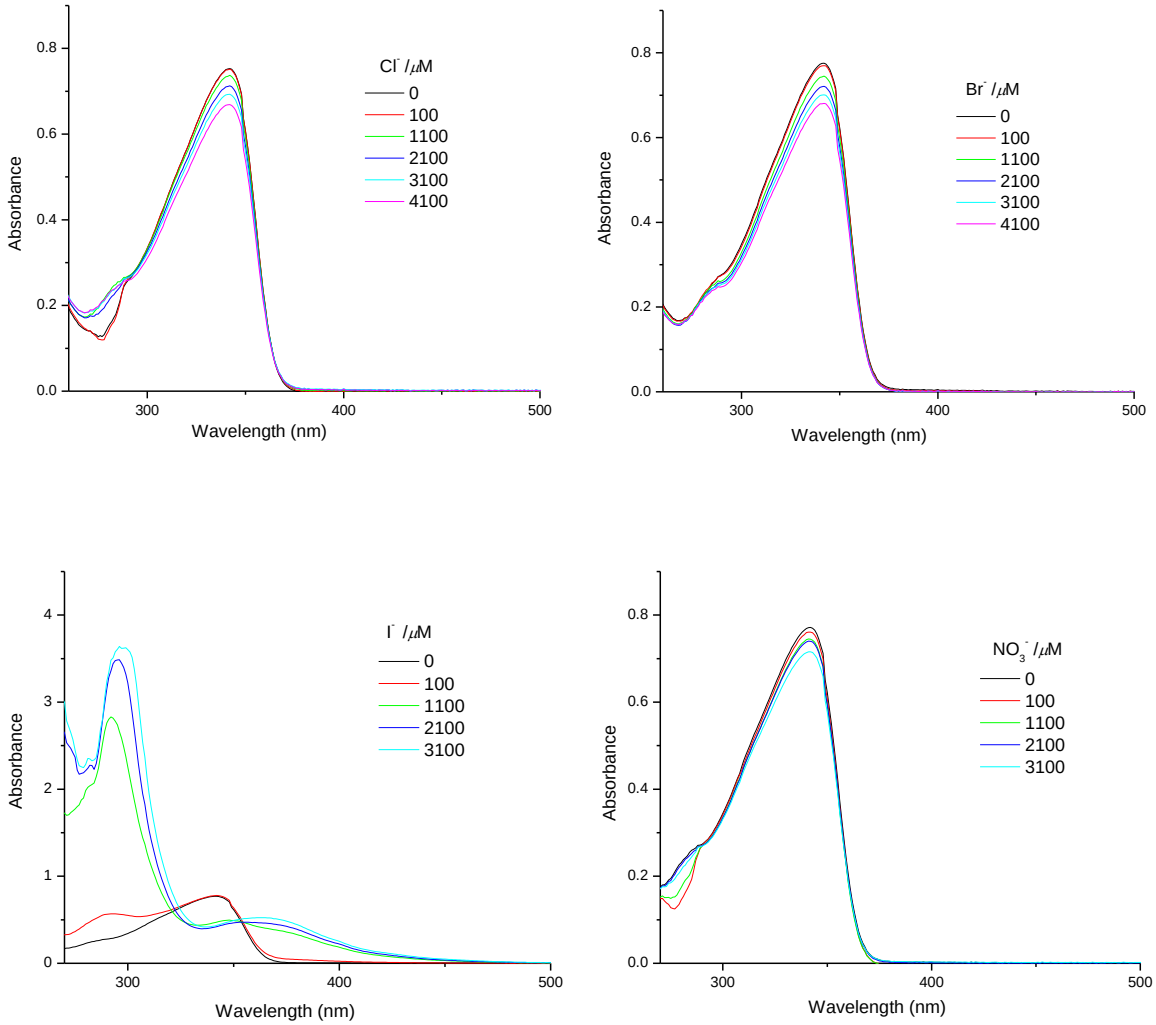

Fig. S4 Spectral changes in UV-vis absorption spectra of **3** (10 μM) at 25 °C in THF upon the addition of various anions with THF solutions of their Bu_4N^+ salts.

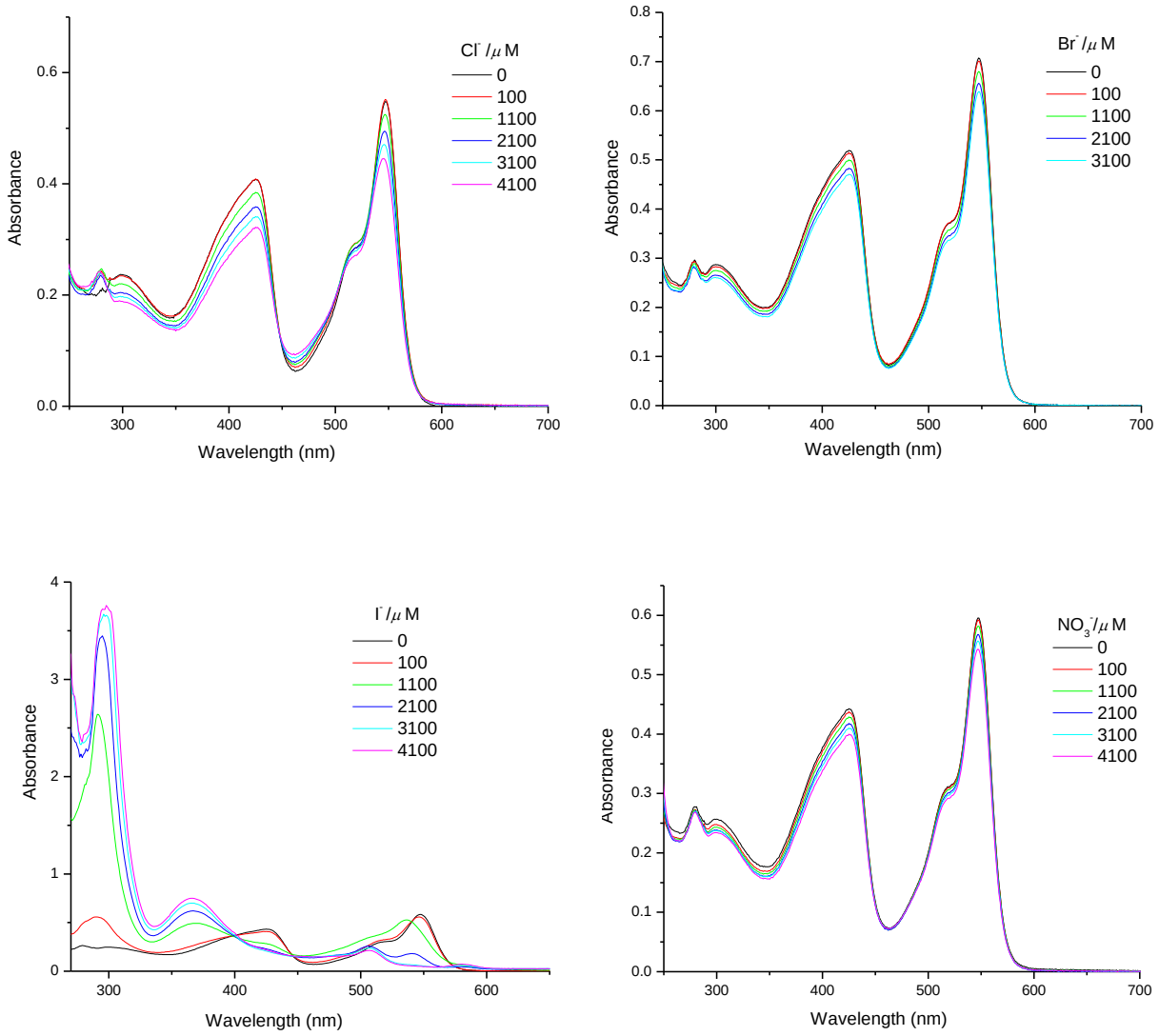

Fig. S5 Spectral changes in UV-vis absorption spectra of **4** (10 μM) at 25 °C in THF upon the addition of various anions with THF solutions of their Bu_4N^+ salts.

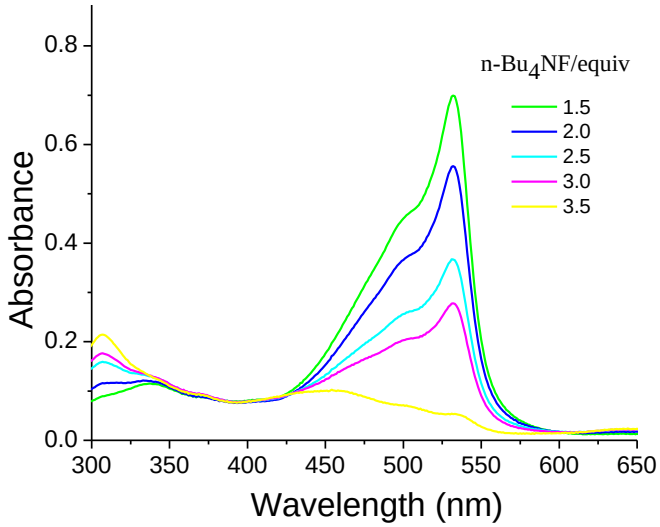

Fig. S6 Spectral changes in UV-vis absorption spectra of **4** upon the addition of 1.5-3.5 equiv of TBAF.

Job's plot:

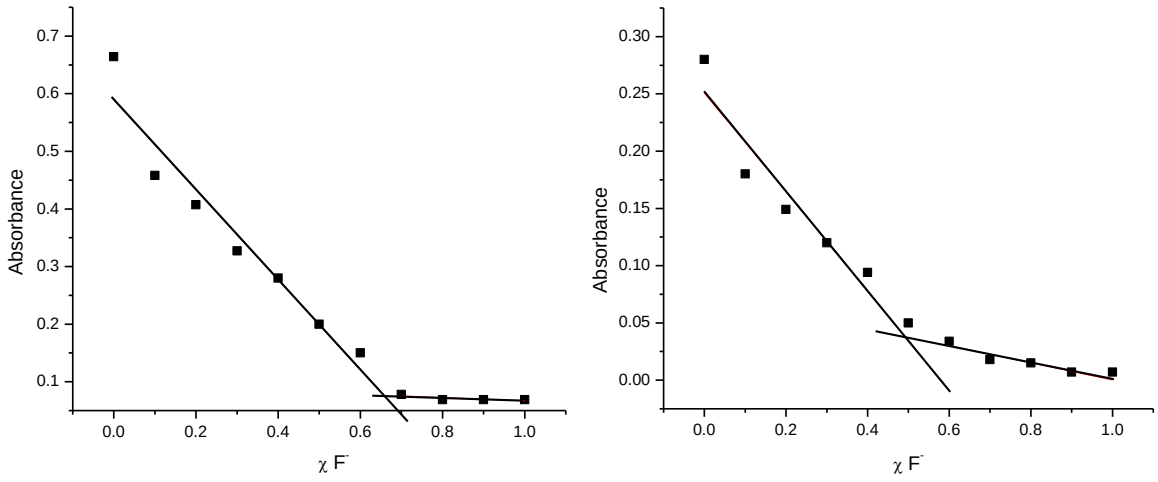

Fig. S7 Job plot of **3** with TBAF ion, equimolar solutions (1.0 x 10^{-5} M) of **1** and TBAF in THF were used, **3** (left, at λ_{ab} = 342 nm) and **4** (right, at λ_{ab} = 427 nm).

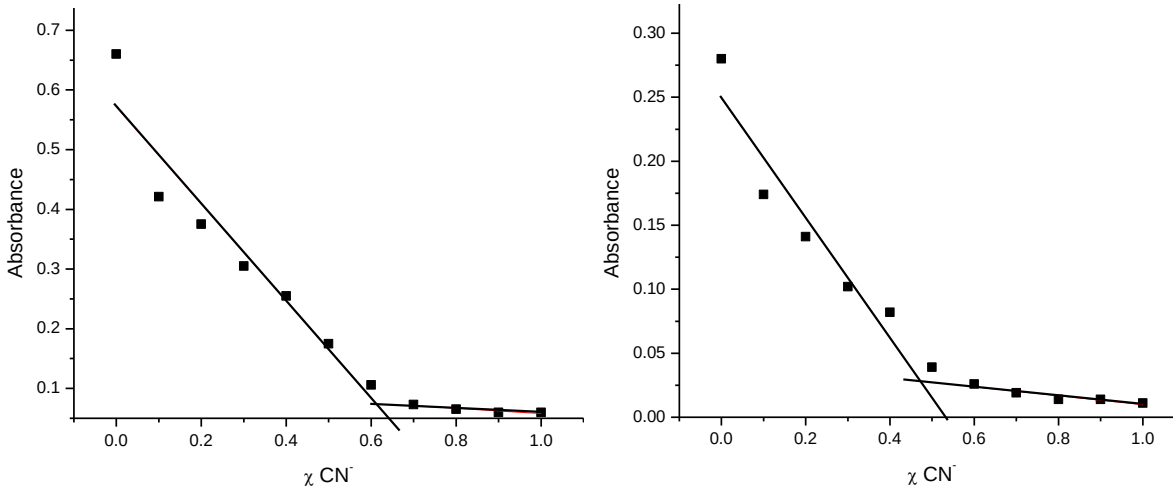

Fig. S8 Job plot of **3** and **4** with TBACN ion, equimolar solutions (1.0 x 10^{-5} M) of **3**/**4** and TBAF in THF were used, **3** (left, at λ_{ab} = 342 nm) and **4** (right, at λ_{ab} = 427 nm).

Binding constant fitting plots:

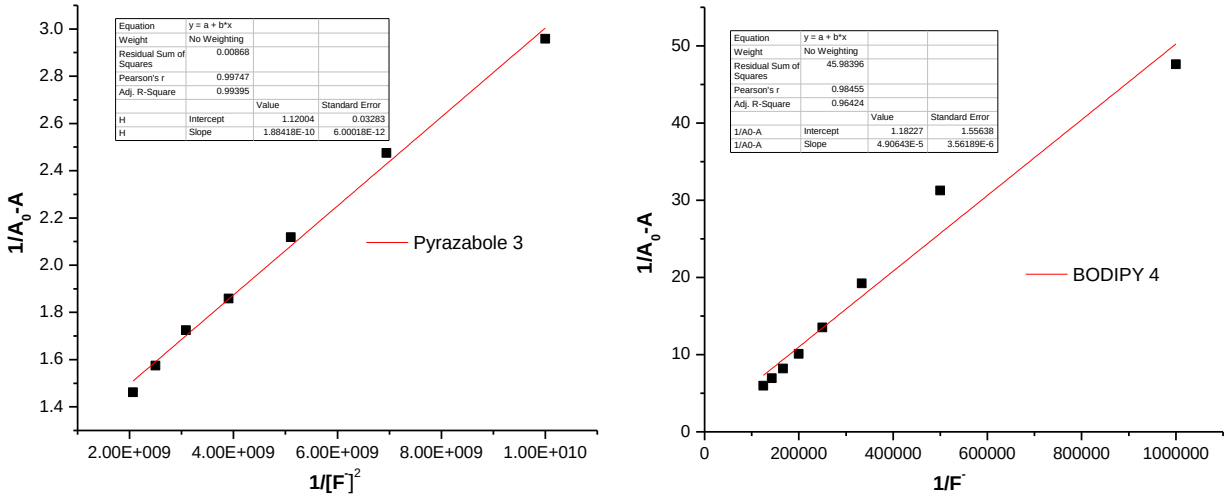

Fig. S9 Fitting of UV-Vis absorption titration of **3** (left, at λ_{ab} = 342 nm) and **4** (right, at λ_{ab} = 427 nm) with fluoride ions.

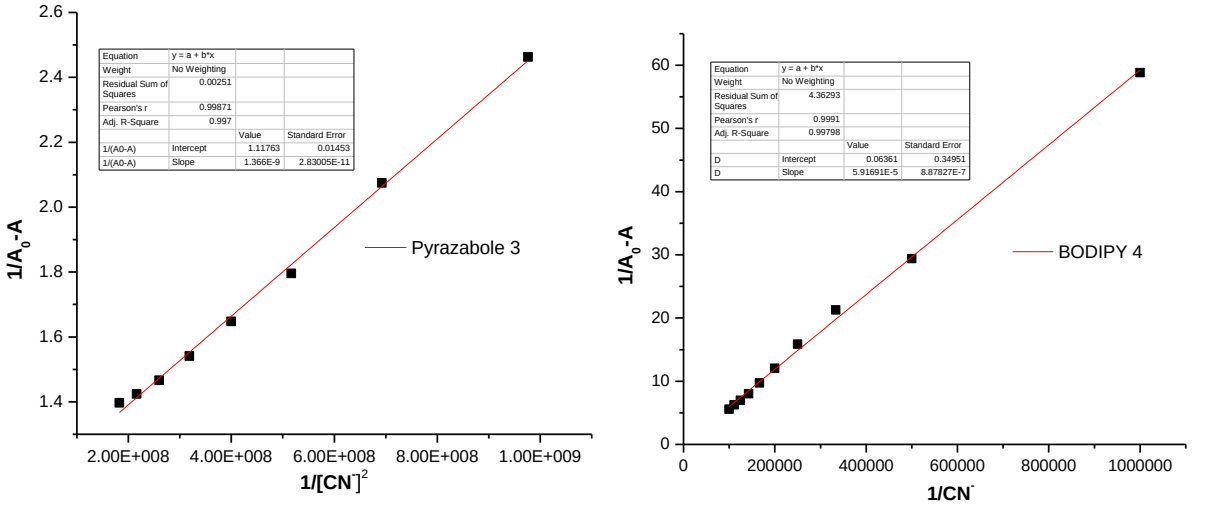

Fig. S10 Fitting of UV-Vis absorption titration of **3** (left, at λ_{ab} = 342 nm) and **4** (right, at λ_{ab} = 427 nm) with cyanide ions.

4. Copies of NMR and Mass spectra of new compounds

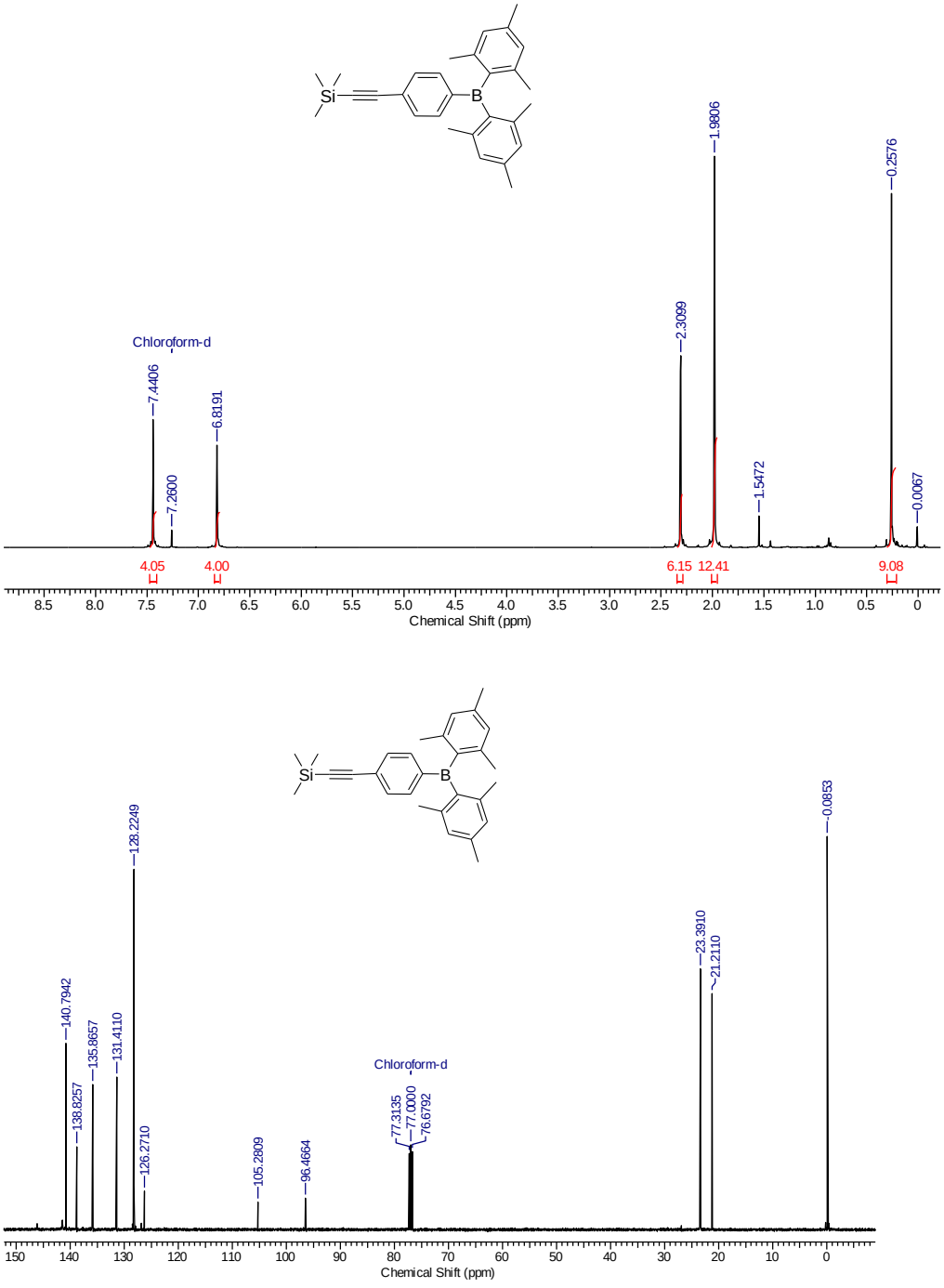

Fig. S11 ^{1}H and ^{13}C-NMR spectrum of (4-trimethylsilanylethynyl-phenyl) dimesitylborane**.**

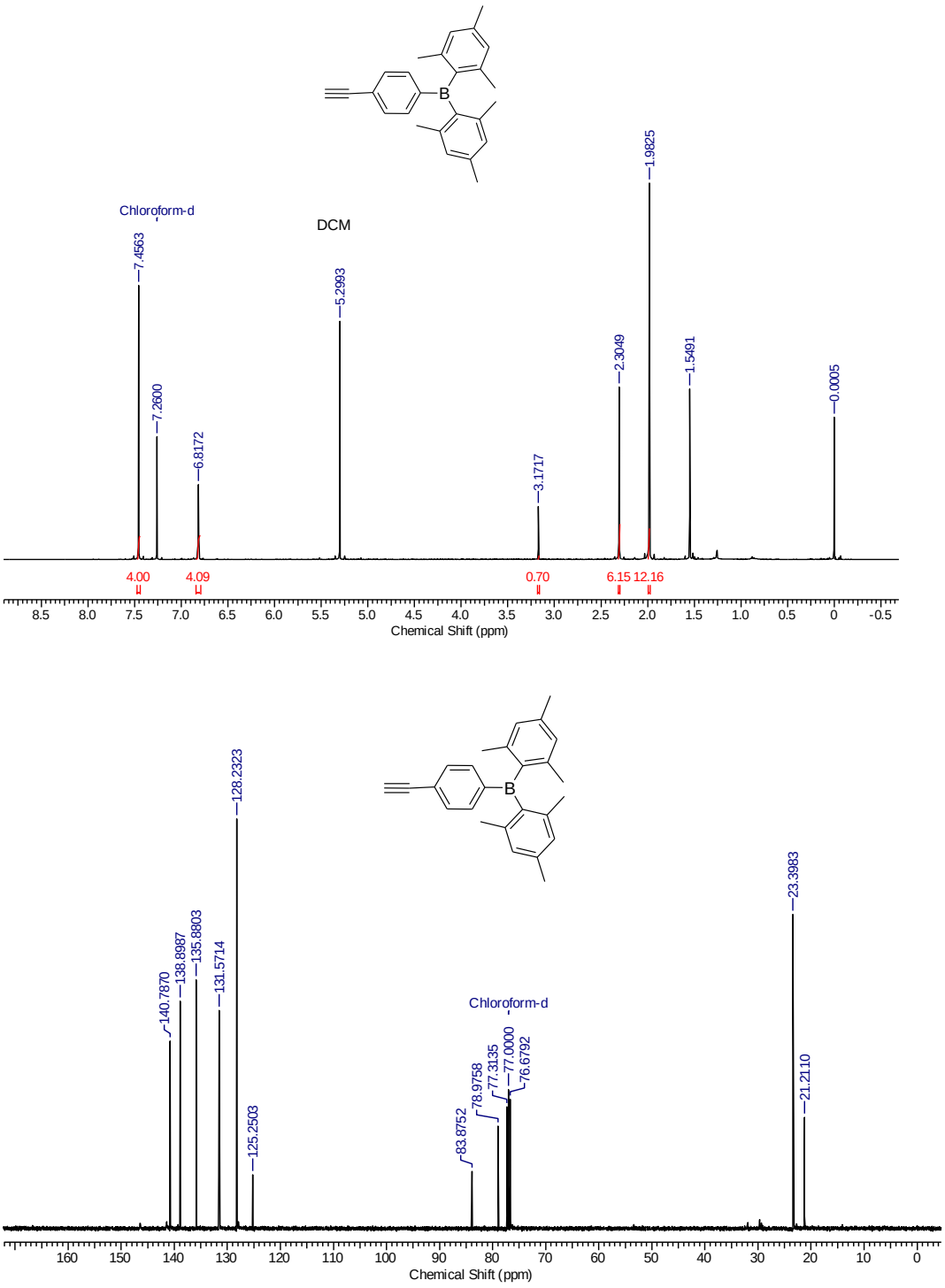

Fig. S12 ^{1}H and ^{13}C-NMR spectrum of (4-Ethynyl-phenyl)-dimesitylborane **2.**

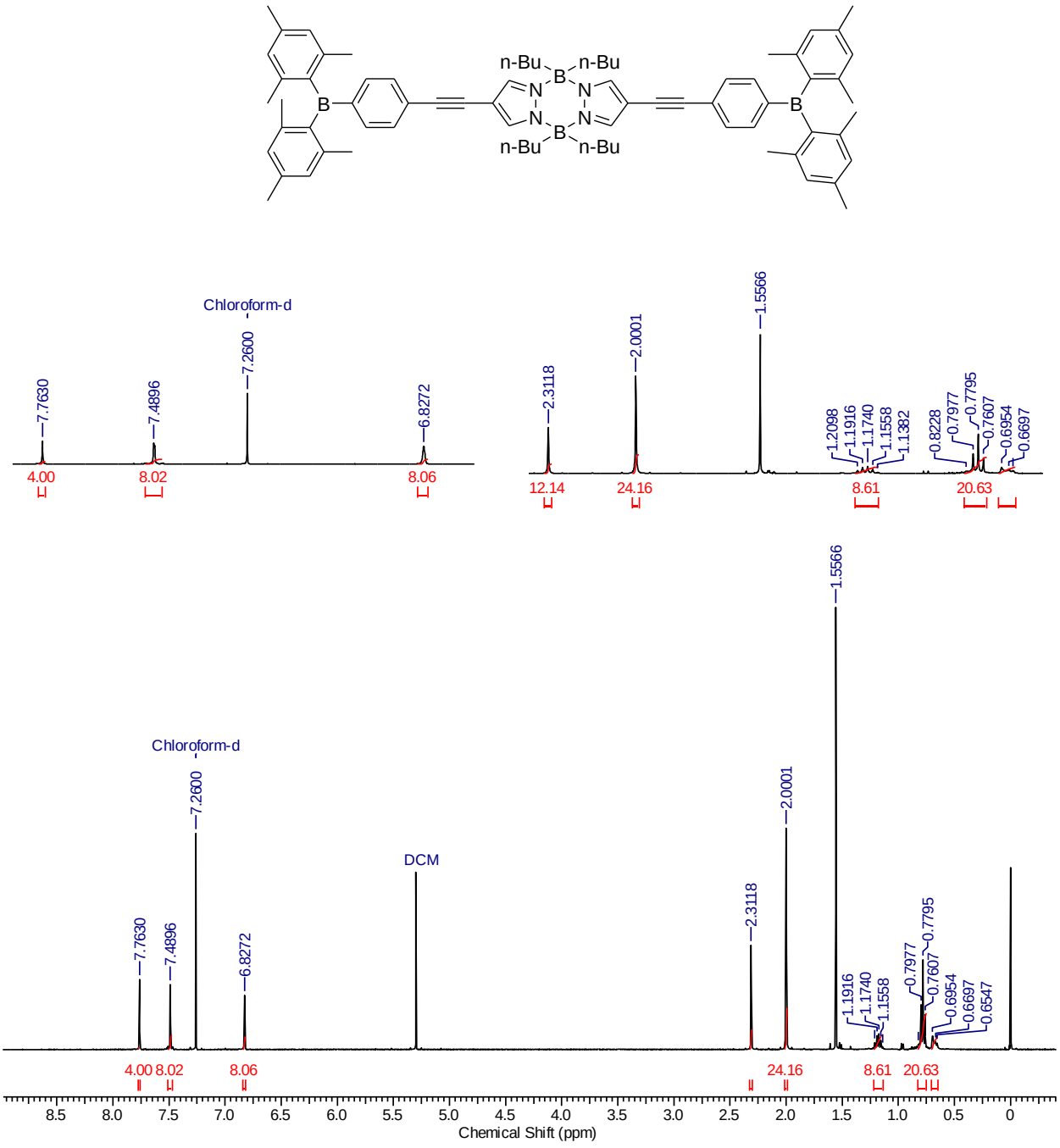

Fig. S13 ^{1}H-NMR spectrum of pyrazabole **3**.

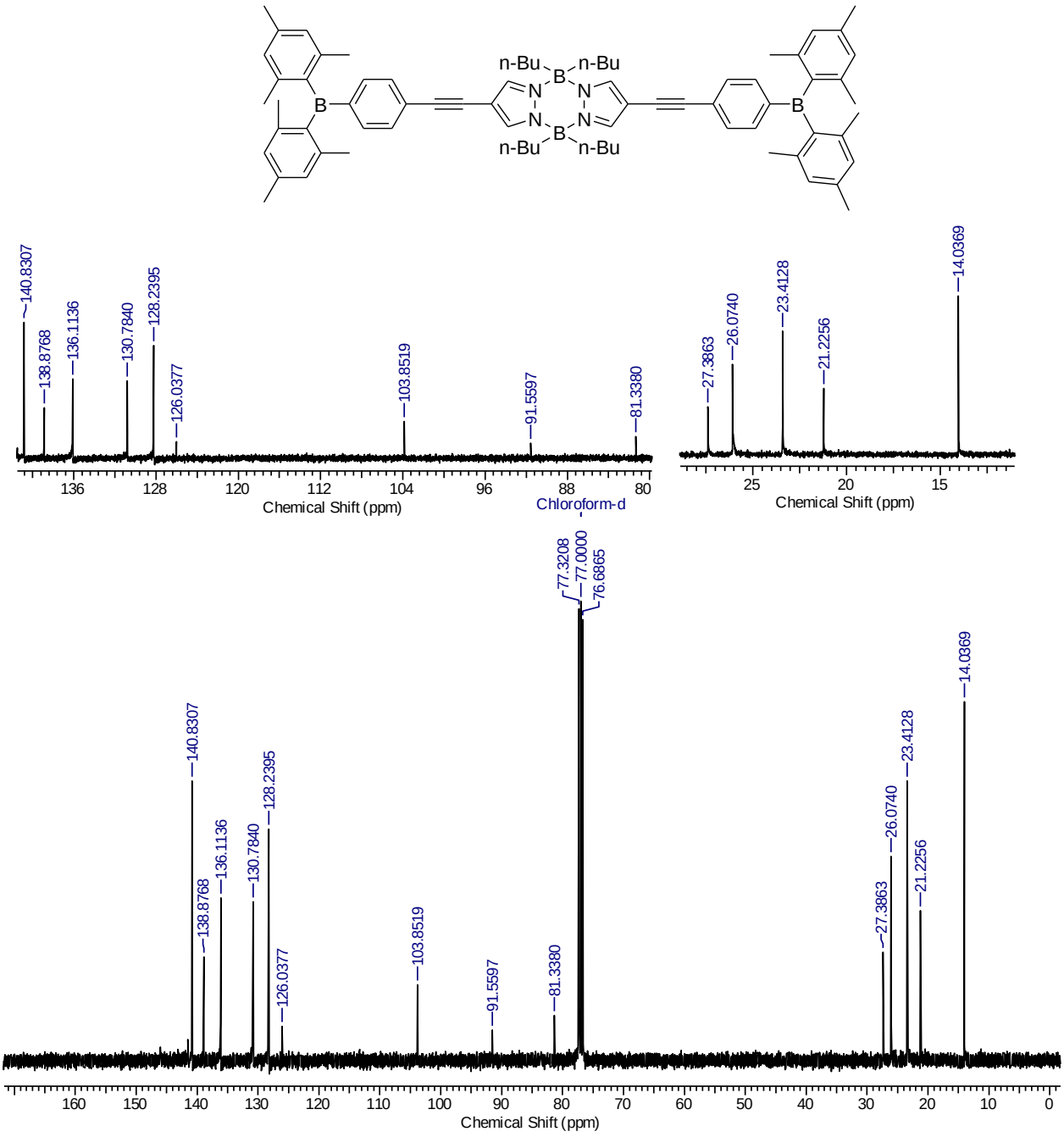

Fig. S14 ^{13}C-NMR spectrum of pyrazabole **3.**

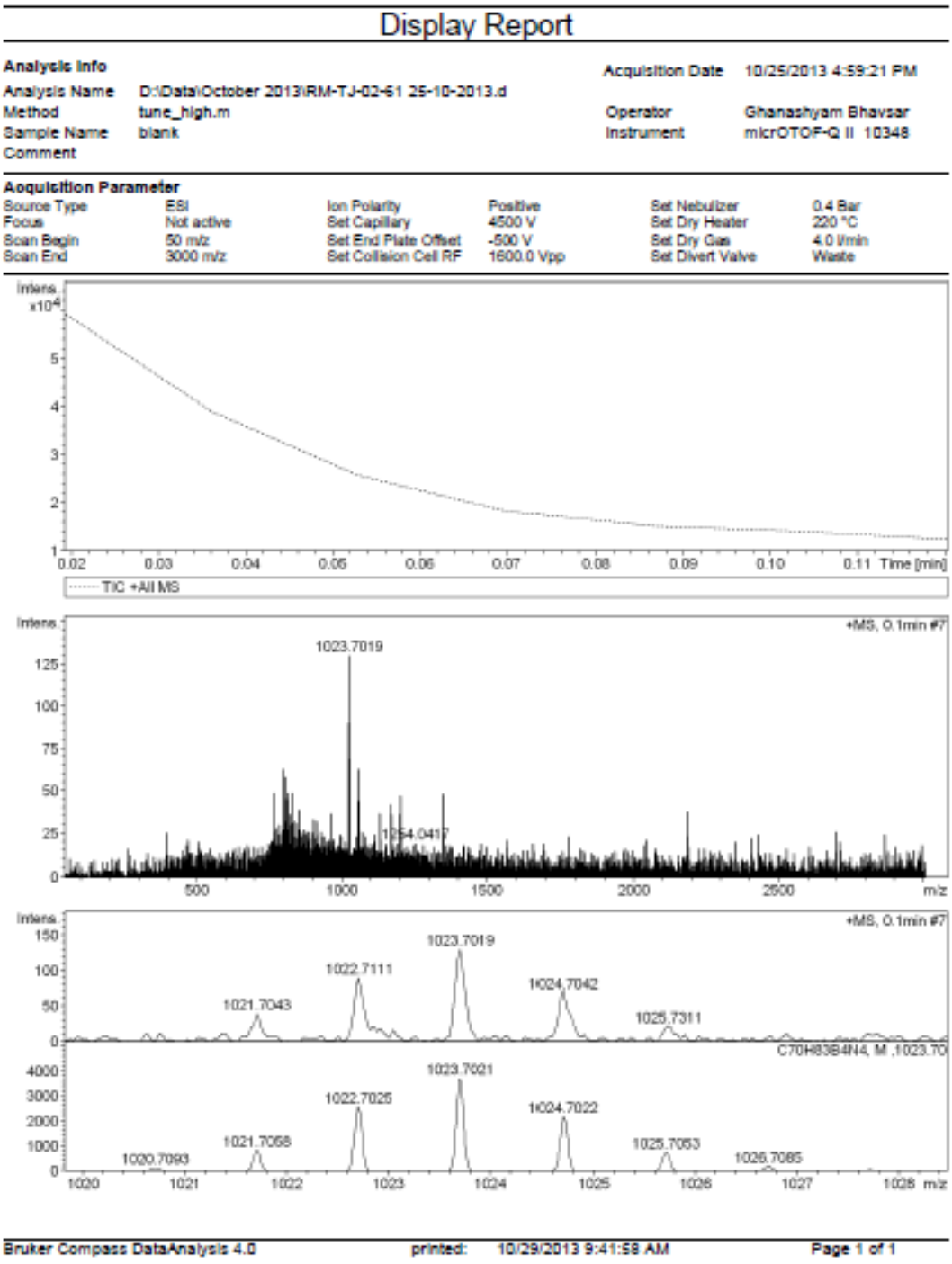

Fig. S15 HRMS spectrum of pyrazabole **3.**

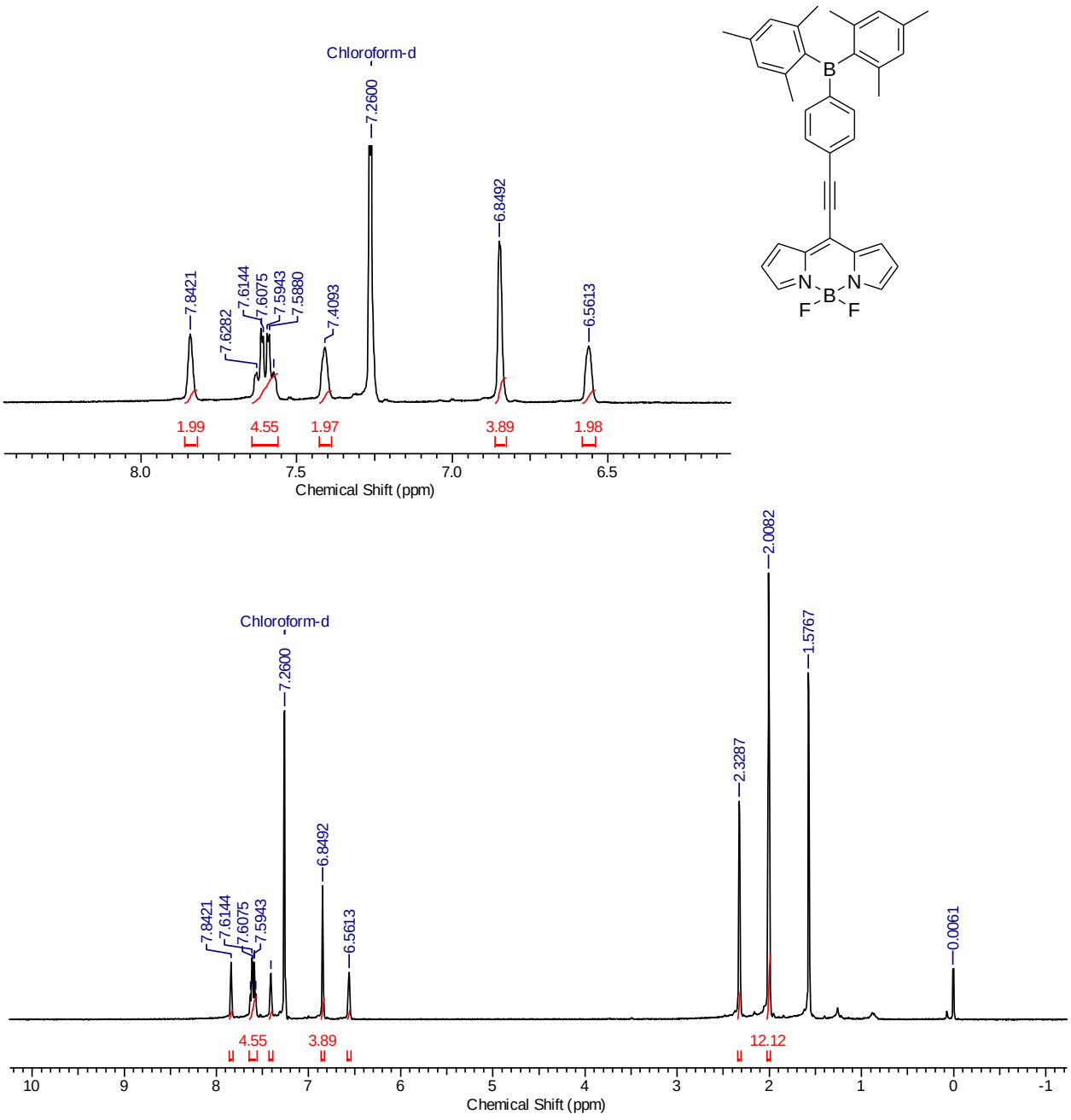

Fig. S16 ^{1}H-NMR spectrum of BODIPY **4**.

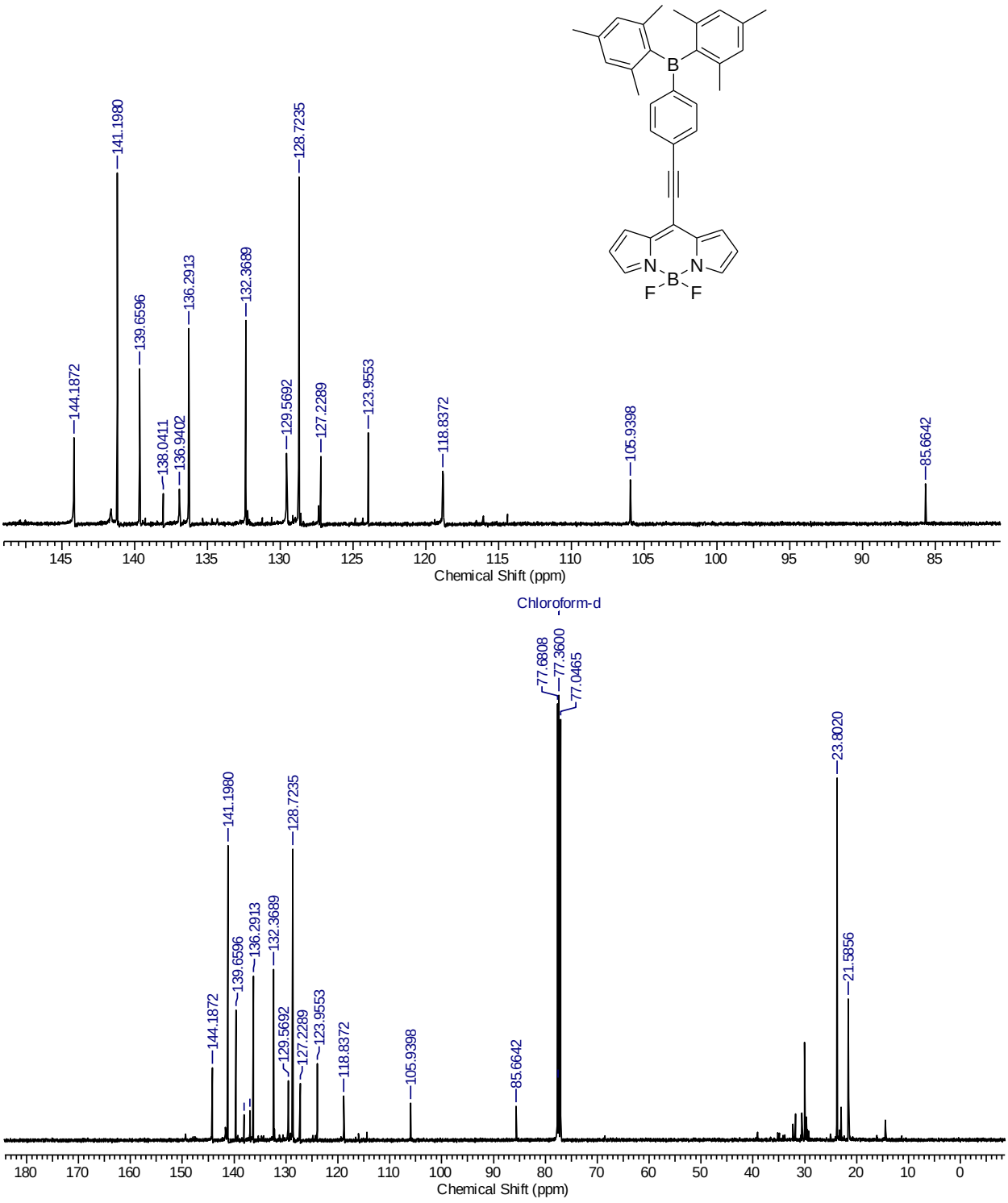

Fig. S17 ^{13}C-NMR spectrum of BODIPY **4.**

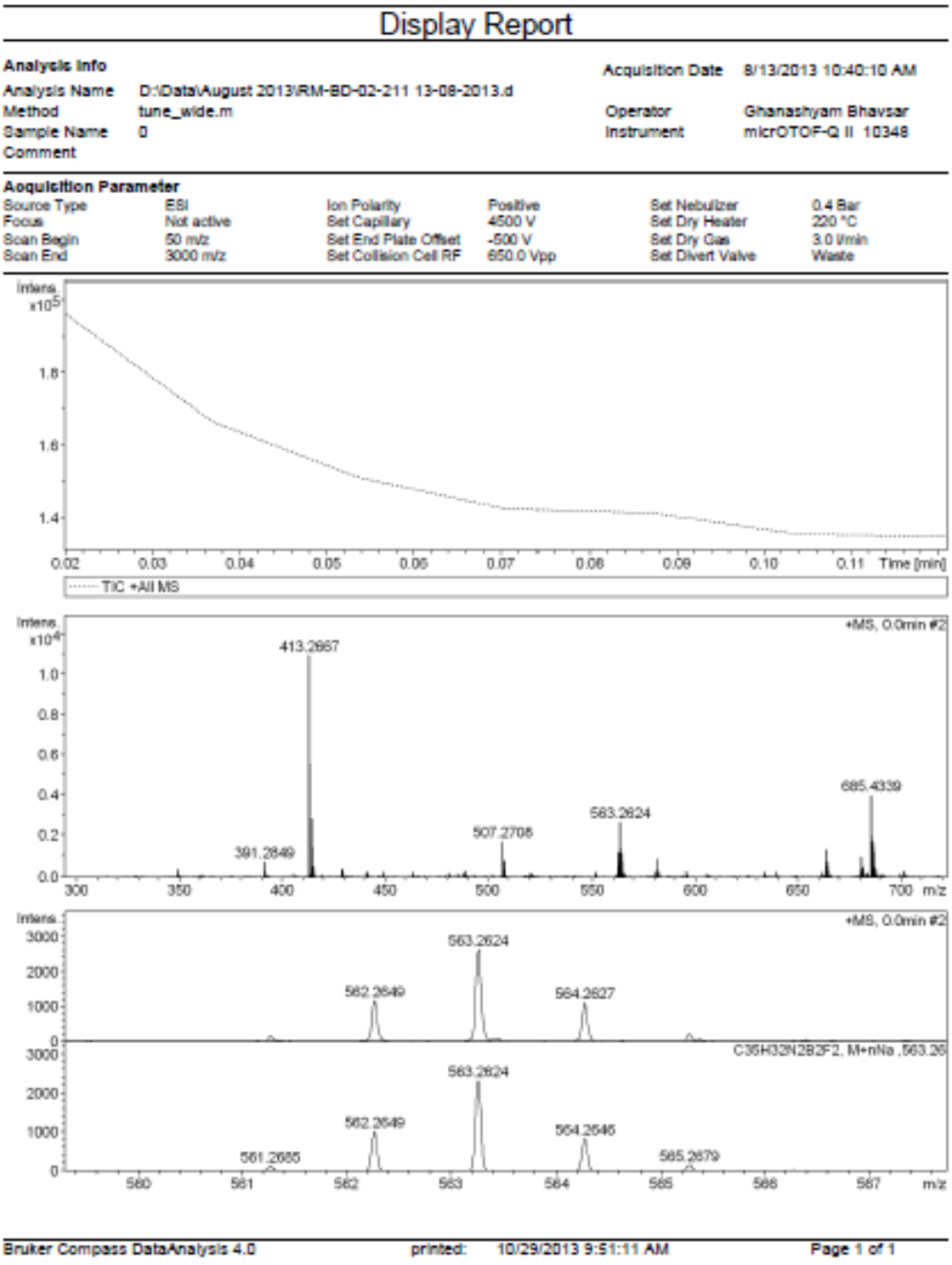

Fig. S18 HRMS spectrum of BODIPY **4.**

5. DFT Calculations

Pyrazabole 3.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	11.877391	0.004276	-0.090516
2	5	0	-0.005174	1.479101	-0.677233
3	7	0	1.265175	0.679537	-0.133677
4	7	0	1.272424	-0.637193	0.210797
5	6	0	-0.022518	2.978562	-0.051952
6	1	0	0.828485	3.536700	-0.471591
7	1	0	-0.904322	3.516367	-0.435813
8	6	0	-0.008686	3.094033	1.483419
9	1	0	0.905385	2.628507	1.880882
10	1	0	-0.842335	2.508909	1.897041
11	6	0	-0.109633	4.529262	2.030356
12	1	0	-1.028677	4.997209	1.647964
13	1	0	-0.224235	4.483538	3.122325
14	6	0	1.090584	5.422989	1.696600
15	1	0	2.024532	4.984127	2.070988
16	1	0	0.984573	6.414136	2.152735
17	1	0	1.202204	5.569667	0.616323
18	6	0	0.071989	1.407103	-2.309740
19	1	0	1.034949	1.850633	-2.611351
20	1	0	0.128030	0.353590	-2.629324
21	6	0	-1.040090	2.102824	-3.111338
22	1	0	-1.109684	3.160588	-2.816494
23	1	0	-2.016015	1.655069	-2.871540
24	6	0	-0.838963	2.030157	-4.632681
25	1	0	0.130101	2.481650	-4.889207
26	1	0	-0.771195	0.975790	-4.936378
27	6	0	-1.951779	2.721243	-5.427481
28	1	0	-2.928839	2.267445	-5.219123
29	1	0	-1.777099	2.651619	-6.507485
30	1	0	-2.021278	3.785697	-5.170115
31	6	0	2.546849	-1.044163	0.301314
32	1	0	2.785510	-2.057338	0.583222
33	6	0	2.534636	1.090752	-0.262629
34	1	0	2.759774	2.102561	-0.562494
35	6	0	3.407048	0.025784	0.008032
36	6	0	4.819768	0.026501	-0.011822
37	6	0	6.035771	0.024070	-0.028173
38	6	0	7.458633	0.019269	-0.045730
39	6	0	8.178108	-1.133360	0.332897
40	1	0	7.632495	-2.019895	0.642208
41	6	0	9.566788	-1.132797	0.301016

42	1	0	10.101213	-2.036509	0.582519
43	6	0	10.306299	0.009128	-0.077079
44	6	0	9.566707	1.155897	-0.439984
45	1	0	10.101272	2.055856	-0.733015
46	6	0	8.177682	1.166484	-0.441171
47	1	0	7.631752	2.056997	-0.738270
48	6	0	12.631855	-1.377196	-0.275987
49	6	0	12.373570	-2.203874	-1.402488
50	6	0	13.047745	-3.420826	-1.552626
51	1	0	12.848998	-4.026159	-2.435736
52	6	0	13.964445	-3.882084	-0.607064
53	6	0	14.205968	-3.075861	0.507712
54	1	0	14.912400	-3.415091	1.263533
55	6	0	13.576299	-1.839706	0.680952
56	6	0	11.392924	-1.816412	-2.495402
57	1	0	11.642799	-2.325958	-3.432112
58	1	0	11.384164	-0.741362	-2.696397
59	1	0	10.365514	-2.095897	-2.233583
60	6	0	14.695814	-5.189831	-0.797263
61	1	0	14.135121	-5.872526	-1.444498
62	1	0	14.870549	-5.694807	0.159257
63	1	0	15.678139	-5.032212	-1.262955
64	6	0	13.905889	-1.051304	1.932819
65	1	0	14.696619	-1.546968	2.504889
66	1	0	13.036982	-0.958541	2.596766
67	1	0	14.241372	-0.036376	1.700804
68	6	0	12.642937	1.381244	0.083453
69	6	0	13.582423	1.834347	-0.882867
70	6	0	14.225603	3.064488	-0.716205
71	1	0	14.933241	3.393747	-1.475316
72	6	0	13.999155	3.875744	0.397936
73	6	0	13.093533	3.419797	1.356751
74	1	0	12.916139	4.022602	2.246104
75	6	0	12.405814	2.209644	1.213532
76	6	0	13.898985	1.038896	-2.133628
77	1	0	13.023436	0.943009	-2.788250
78	1	0	14.236240	0.024981	-1.899744
79	1	0	14.684060	1.531257	-2.716252
80	6	0	14.698757	5.205563	0.550081
81	1	0	14.147606	6.005851	0.037646
82	1	0	15.705759	5.180854	0.119200
83	1	0	14.786265	5.494756	1.602771
84	6	0	11.439602	1.828162	2.321401
85	1	0	11.708874	2.334008	3.254744
86	1	0	11.424184	0.753010	2.520910
87	1	0	10.410791	2.117495	2.076358
88	5	0	-11.879052	-0.025389	0.082941
89	5	0	0.006393	-1.451128	0.728796
90	7	0	-1.264174	-0.651646	0.186023
91	7	0	-1.271699	0.664170	-0.161796
92	6	0	0.022406	-2.951159	0.104723
93	1	0	-0.828269	-3.508653	0.525863

94	1	0	0.904457	-3.489000	0.487975
95	6	0	0.006599	-3.067895	-1.430538
96	1	0	-0.907964	-2.602672	-1.827210
97	1	0	0.839711	-2.483121	-1.845730
98	6	0	0.106785	-4.503566	-1.976461
99	1	0	1.026352	-4.971225	-1.594961
100	1	0	0.219890	-4.458706	-3.068623
101	6	0	-1.092970	-5.397028	-1.640350
102	1	0	-2.027447	-4.958402	-2.013684
103	1	0	-0.987640	-6.388492	-2.095955
104	1	0	-1.203023	-5.542966	-0.559813
105	6	0	-0.068277	-1.377651	2.361304
106	1	0	-1.031154	-1.820028	2.664878
107	1	0	-0.122833	-0.323808	2.680046
108	6	0	1.044581	-2.073712	3.161513
109	1	0	1.112137	-3.131964	2.867963
110	1	0	2.020582	-1.627612	2.918933
111	6	0	0.846854	-1.998710	4.683185
112	1	0	-0.122281	-2.448502	4.942420
113	1	0	0.781217	-0.943842	4.985612
114	6	0	1.960437	-2.690289	5.476483
115	1	0	2.937688	-2.238237	5.265258
116	1	0	1.788292	-2.618855	6.556776
117	1	0	2.027790	-3.755213	5.220497
118	6	0	-2.546307	1.070021	-0.255490
119	1	0	-2.785215	2.082394	-0.540050
120	6	0	-2.533507	-1.063254	0.314491
121	1	0	-2.758461	-2.074607	0.616017
122	6	0	-3.406208	0.000305	0.039372
123	6	0	-4.819023	-0.002697	0.055211
124	6	0	-6.035075	-0.004364	0.066822
125	6	0	-7.458065	-0.007134	0.076893
126	6	0	-8.182900	1.107611	-0.392950
127	1	0	-7.641541	1.972342	-0.765016
128	6	0	-9.571692	1.098619	-0.372458
129	1	0	-10.109332	1.974161	-0.725862
130	6	0	-10.306610	-0.017370	0.085872
131	6	0	-9.560627	-1.125722	0.545284
132	1	0	-10.090081	-2.002905	0.907823
133	6	0	-8.171857	-1.125487	0.556012
134	1	0	-7.621829	-1.985355	0.926684
135	6	0	-12.646763	1.361810	0.071836
136	6	0	-12.454251	2.329965	1.089949
137	6	0	-13.110380	3.567388	1.023956
138	1	0	-12.952019	4.286850	1.826161
139	6	0	-13.957316	3.900494	-0.029527
140	6	0	-14.150995	2.943291	-1.032235
141	1	0	-14.807696	3.178627	-1.868311
142	6	0	-13.529024	1.694766	-0.997110
143	6	0	-11.622387	2.068906	2.331614
144	1	0	-12.272397	1.879899	3.196649
145	1	0	-10.956862	1.210422	2.228983

146	1	0	-11.006205	2.940397	2.581800
147	6	0	-14.638356	5.246703	-0.101027
148	1	0	-14.511477	5.809759	0.829191
149	1	0	-14.229904	5.857787	-0.916645
150	1	0	-15.713886	5.142155	-0.288256
151	6	0	-13.794563	0.741622	-2.145229
152	1	0	-14.529805	1.164900	-2.837069
153	1	0	-12.885880	0.537061	-2.725476
154	1	0	-14.174891	-0.223002	-1.796220
155	6	0	-12.635723	-1.417946	0.071501
156	6	0	-13.583857	-1.742351	1.082354
157	6	0	-14.217592	-2.986715	1.079545
158	1	0	-14.924823	-3.217994	1.874362
159	6	0	-13.978731	-3.939203	0.084186
160	6	0	-13.061522	-3.614585	-0.914106
161	1	0	-12.863993	-4.334875	-1.706618
162	6	0	-12.381332	-2.390210	-0.930528
163	6	0	-13.914850	-0.783209	2.208494
164	1	0	-13.028640	-0.523536	2.800001
165	1	0	-14.334074	0.155280	1.832227
166	1	0	-14.644039	-1.227702	2.893436
167	6	0	-14.709863	-5.260880	0.081700
168	1	0	-14.238551	-5.978234	-0.597994
169	1	0	-14.733595	-5.707714	1.082494
170	1	0	-15.752914	-5.138996	-0.239636
171	6	0	-11.397882	-2.168396	-2.066531
172	1	0	-11.727891	-2.698591	-2.966720
173	1	0	-11.274625	-1.114849	-2.327524
174	1	0	-10.400599	-2.548300	-1.812518

Energy (HF) = -3193.8347488 Hartree.

BODIPY 4.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.156151	-2.350697	-1.026582
2	1	0	4.116269	-2.625583	-1.136094
3	6	0	6.277940	-3.103498	-1.350924
4	1	0	6.304207	-4.098543	-1.773181
5	6	0	7.401393	-2.319782	-1.016234
6	1	0	8.453157	-2.551200	-1.118537
7	7	0	7.012177	-1.139191	-0.508350
8	5	0	7.958864	0.040198	-0.085796

9	6	0	6.269670	3.007348	1.542490
10	6	0	5.149873	2.277297	1.163870
11	1	0	4.109310	2.533579	1.306886
12	6	0	5.619392	1.090927	0.548017
13	6	0	4.919030	-0.012390	0.016559
14	6	0	5.622437	-1.121915	-0.497648
15	7	0	7.009019	1.113069	0.556330
16	9	0	8.878193	-0.398681	0.846432
17	6	0	7.395149	2.254328	1.149361
18	1	0	8.446309	2.481924	1.265433
19	9	0	8.577374	0.568991	-1.203355
20	1	0	6.293341	3.964103	2.045635
21	6	0	3.505142	-0.013820	0.016560
22	6	0	2.286852	-0.012100	0.013556
23	6	0	0.866340	-0.009092	0.010076
24	6	0	0.147789	-1.126511	-0.464814
25	6	0	0.150771	1.111863	0.481167
26	1	0	0.693050	-1.991079	-0.831226
27	6	0	-1.241049	-1.118903	-0.450482
28	6	0	-1.237972	1.111260	0.459277
29	1	0	0.698382	1.973896	0.850045
30	1	0	-1.778109	-1.995621	-0.802532
31	6	0	-1.975904	-0.001926	0.002281
32	1	0	-1.772501	1.990728	0.808298
33	5	0	-3.553451	0.001949	-0.002494
34	6	0	-4.310550	-1.380393	0.129297
35	6	0	-4.303003	1.387809	-0.138889
36	6	0	-4.047403	-2.260013	1.213199
37	6	0	-5.263527	-1.792766	-0.843610
38	6	0	-5.268489	1.800805	0.821920
39	6	0	-4.025709	2.267467	-1.219149
40	6	0	-4.722617	-3.481969	1.308276
41	6	0	-3.062758	-1.926461	2.320204
42	6	0	-5.891996	-3.035436	-0.727086
43	6	0	-5.607071	-0.940325	-2.049475
44	6	0	-5.892889	3.044597	0.698890
45	6	0	-5.635263	0.944619	2.018204
46	6	0	-4.697226	3.491189	-1.321079
47	6	0	-3.034857	1.930316	-2.319600
48	1	0	-4.520848	-4.129181	2.160268
49	6	0	-5.644162	-3.895686	0.345973
50	1	0	-3.329465	-2.454959	3.241548
51	1	0	-3.027879	-0.858100	2.551334
52	1	0	-2.041479	-2.226060	2.055726
53	1	0	-6.603054	-3.337882	-1.493927
54	1	0	-6.364084	-1.434040	-2.666870
55	1	0	-4.733969	-0.762449	-2.689535
56	1	0	-5.995359	0.040560	-1.759446
57	1	0	-6.618607	3.344483	1.452989
58	6	0	-5.625228	3.908376	-0.366851
59	1	0	-4.772480	0.756887	2.669265
60	1	0	-6.026702	-0.031871	1.717854

61	1	0	-6.396956	1.441059	2.627620
62	1	0	-4.488672	4.135773	-2.173422
63	1	0	-3.297256	2.455226	-3.244248
64	1	0	-2.997252	0.861305	-2.546686
65	1	0	-2.015409	2.232481	-2.050950
66	6	0	-6.373723	-5.211929	0.472662
67	6	0	-6.310619	5.249934	-0.471060
68	1	0	-5.843437	-5.902121	1.136934
69	1	0	-6.491732	-5.700382	-0.501125
70	1	0	-7.381596	-5.069527	0.885299
71	1	0	-5.853584	5.982913	0.207252
72	1	0	-7.370696	5.181195	-0.201548
73	1	0	-6.243925	5.656683	-1.485291

Energy (HF) = -1712.0553432 Hartree.