Supporting Information

Donor-Acceptor *meso*-Alkynylated Ferrocenyl BODIPYs: Synthesis, Structure, and Properties

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Single Crystal X-ray Diffraction Studies.

Single crystal X-ray structural studies of **2′**, **3** and **6** were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 293(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 $F^{2.1}$. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions, and refined with isotropic temperature factors, generally 1.2U_{eq} of their parent atoms. The crystal, and refinement data are summarized in Table 1. The CCDC numbers 934137, 934138, and 934139 contain the supplementary crystallographic data for **2′, 3,** and **6** respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (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).

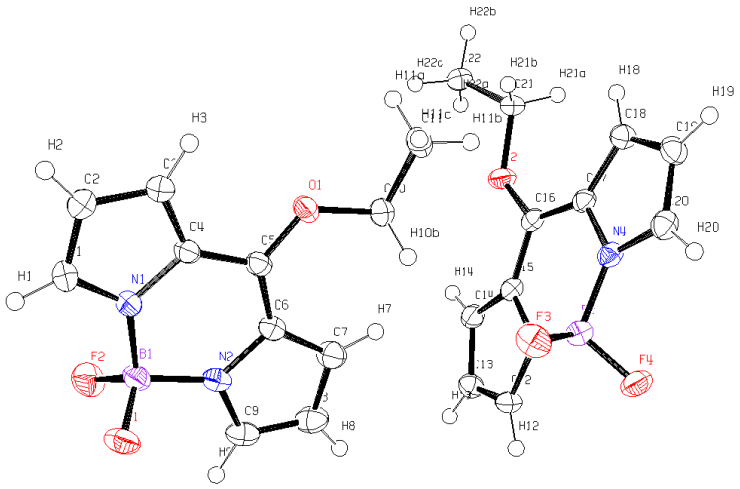


Figure S1. ORTEP view of **2′** showing the atom-labeling scheme. Thermal ellipsoids are plotted at the 50 % level.

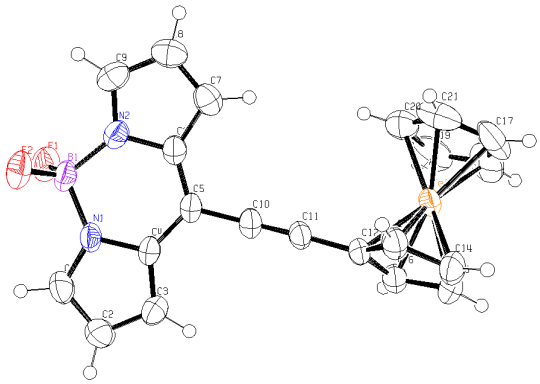


Figure S2. ORTEP view of **3** showing the atom-labeling scheme. Thermal ellipsoids are plotted at the 50 % level.

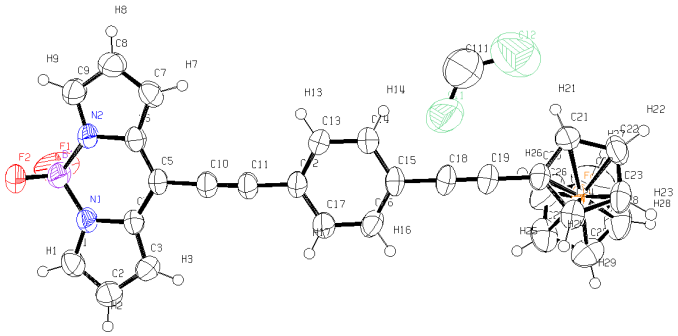


Figure S3. ORTEP view of **6** showing the atom-labeling scheme. Thermal ellipsoids are plotted at the 50 % level.

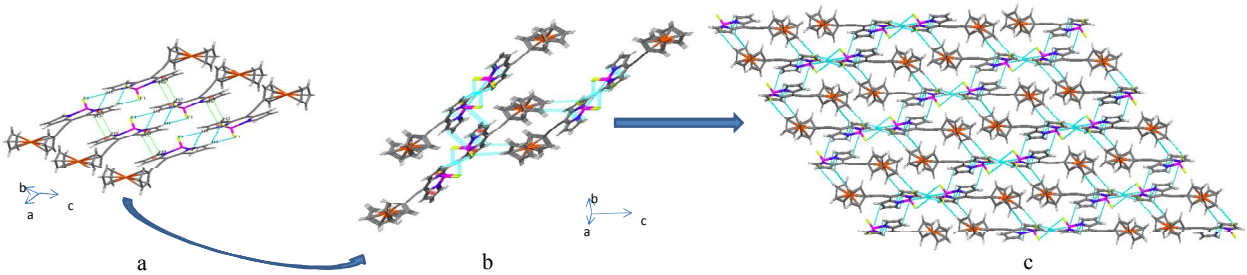


Figure S4. Supramolecular interactions in the crystal structure of **3**

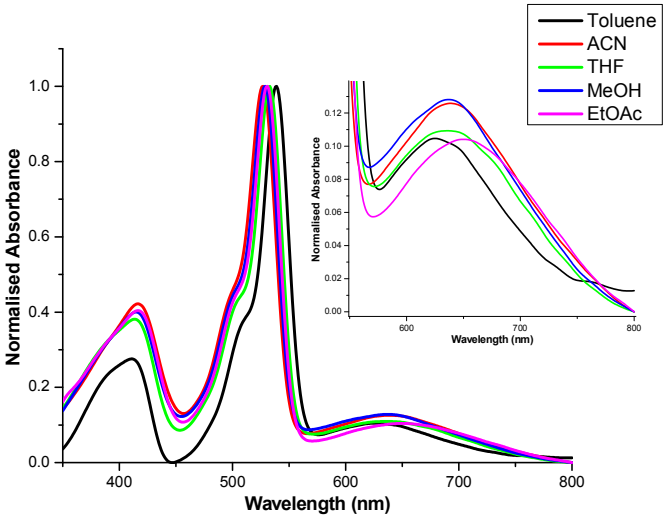


Figure S5- Positive solvatochromism in compound **3**

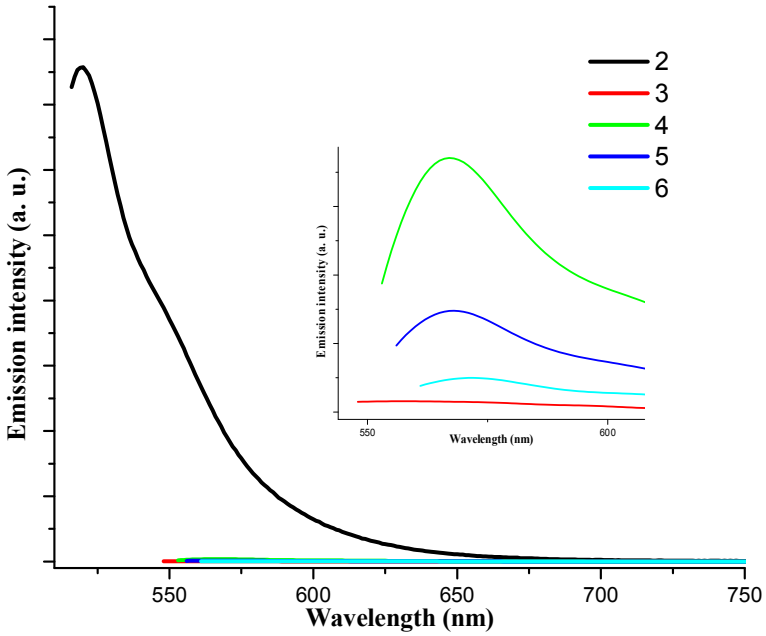


Figure S6. Emission Spectra of **2-6** recorded in toluene, inset shows enlarged view (Excited at respective $\lambda_{S0\rightarrow S1}$ at concentration of 0.1 absorbance)

The fluorescence quantum yields (ϕ_F)

The fluorescence quantum yields (ϕ_F) of compounds **2-6** were calculated by the steady-state comparative method using Rhodamine 6G as a standard (ϕ_{st} = 0.88, ethanol).[i]

$$\phi_F = \phi_{st} \times S_u/S_{st} \times A_{st} / A_u \times n^2_{Du}/n^2_{Dst} \quad \text{..... (Eq. 1)}$$

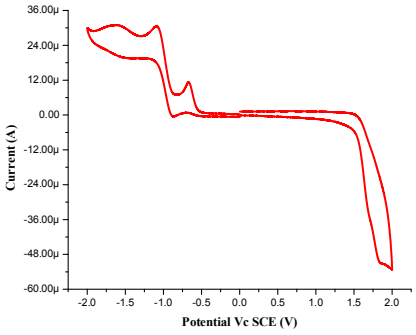
Where ϕ_F is the emission quantum yield of the sample, ϕ_{st} is the emission quantum yield of the standard, A_{st} and A_u represent the absorbance of the standard and sample at the excitation wavelength, respectively, while S_{st} and S_u are the integrated emission band

areas of the standard and sample, respectively, and n_{Dst} and n_{Du} the solvent refractive index of the standard and sample, u and st refer to the unknown and standard, respectively.

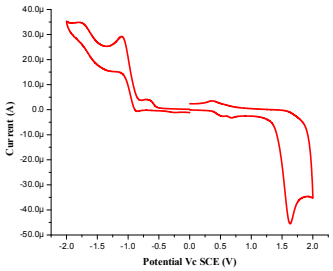
Electrochemical Characterizations

Electrochemical characterization of all compounds was done by cyclic voltametry (CV) and Differential pulse voltametry (DPV). Voltamograms were recorded on a CHI620D electrochemical analyzer using glassy carbon as working electrode, Pt wire as the counter electrode, and saturated calomel electrode as the reference electrode (SCE). The scan speed was 100 mVS^{-1}. A solution of tetrabutylammonium- hexafluorophosphate ($TBAPF_6$) in CH_2Cl_2 (0.1 M) was employed as the supporting electrolyte. CH_2Cl_2 was freshly distilled from CaH_2 prior to use. The half-wave oxidation potential of Ferrocene was measured to be 0.38 V against SCE.

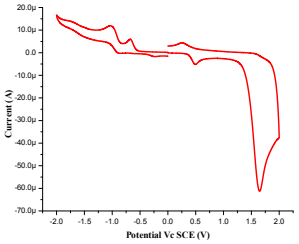
a) Cyclic voltammogram of 2



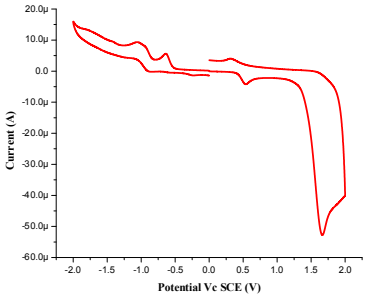
b) Cyclic voltammogram of 4



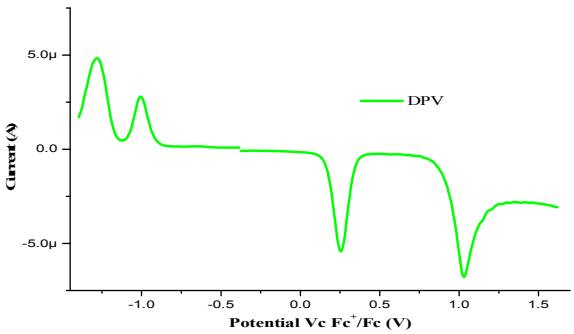
c) Cyclic voltammogram of 5



d) Cyclic voltammogram of 6



e) Representative DPV of the ferrocenyl BODIPY 3



f)

DFT calculations[ii]

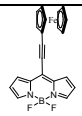
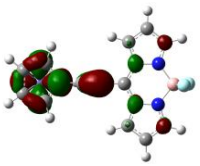
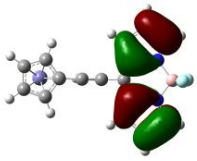
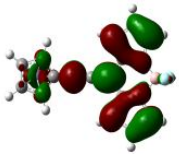
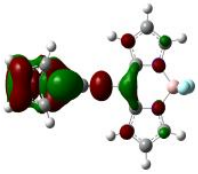
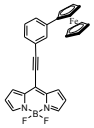
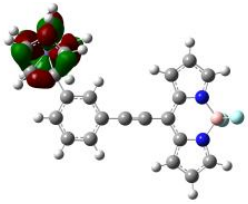
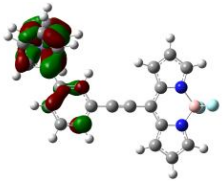
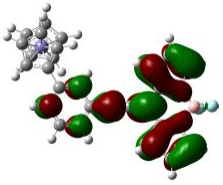
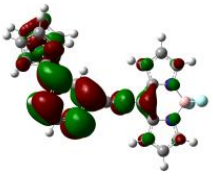
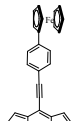
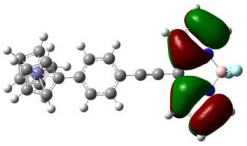
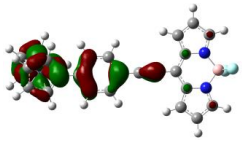
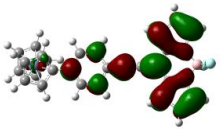
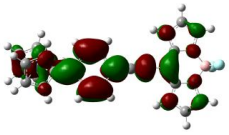
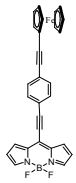
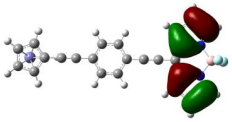
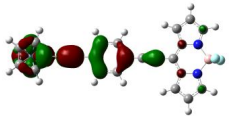
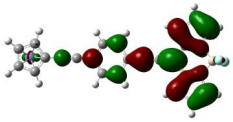
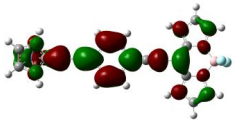
Molecule	HOMO-1	HOMO	LUMO	LUMO+1
 **3**				
 **4**				
 **5**				
 **6**				

Figure S2- HOMO-1, HOMO, and LUMO, and LUMO+1 frontier orbitals of BODIPYs at the B3LYP/6-31+G** for C, N, B, F, H, and Lanl2DZ for Fe level

DFT Calculations.

Calculation method: B3LYP/6-31+G** for C, H, N, S, and Lanl2DZ for Fe with Gaussian 09[iii]

DFT Data for BODIPY **3**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	2.081004	-2.566490	-0.226135
2	1	0	1.066736	-2.867356	-0.446763
3	6	0	3.171650	-3.379297	0.061890
4	1	0	3.192740	-4.458464	0.114941
5	6	0	4.268703	-2.521718	0.280219
6	1	0	5.291992	-2.768931	0.527273
7	7	0	3.892986	-1.239350	0.139127
8	5	0	4.834897	0.011526	0.244903
9	6	0	3.145510	3.382381	-0.040439
10	6	0	2.061350	2.552902	-0.304533
11	1	0	1.044713	2.839104	-0.533699
12	6	0	2.530316	1.219971	-0.213465
13	6	0	1.850523	-0.009079	-0.360629
14	6	0	2.539541	-1.227818	-0.174822
15	7	0	3.883503	1.251375	0.100205
16	9	0	5.458636	0.033188	1.478060
17	6	0	4.249097	2.540226	0.203593
18	1	0	5.270207	2.802539	0.444001
19	9	0	5.752274	-0.001146	-0.789959
20	1	0	3.158173	4.462769	-0.019154
21	6	0	0.474879	-0.020125	-0.677081
22	6	0	-0.711800	-0.032976	-0.955076
23	6	0	-2.082949	-0.053670	-1.291906
24	26	0	-3.671256	-0.001193	0.047472
25	6	0	-2.920990	1.093733	-1.547638
26	6	0	-2.908443	-1.228486	-1.442052

27	6	0	-4.223395	0.623785	-1.866712
28	6	0	-4.215715	-0.803810	-1.801945
29	6	0	-2.931785	0.086268	1.990970
30	6	0	-3.740618	-1.077833	1.825326
31	6	0	-5.053435	-0.653002	1.456667
32	6	0	-5.054019	0.772780	1.392645
33	6	0	-3.741565	1.230229	1.721608
34	1	0	-2.599574	2.124091	-1.495579
35	1	0	-2.575397	-2.246005	-1.296019
36	1	0	-5.082202	1.243028	-2.085546
37	1	0	-5.067692	-1.449550	-1.962811
38	1	0	-1.877058	0.097122	2.229934
39	1	0	-3.409862	-2.101516	1.933546
40	1	0	-5.890812	-1.299071	1.231472
41	1	0	-5.892343	1.395308	1.111389
42	1	0	-3.412193	2.259930	1.737074

Total Energy (HF) = -1266.865121 Hartree

DFT Data for BODIPY **4**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.629051	2.447532	0.518470
2	1	0	3.804939	3.145855	0.547670
3	6	0	5.977139	2.705379	0.735904

4	1	0	6.435923	3.654032	0.975360
5	6	0	6.654301	1.478431	0.578574
6	1	0	7.710217	1.263442	0.668929
7	7	0	5.783842	0.500720	0.277686
8	5	0	6.134279	-1.018300	0.091042
9	6	0	3.277842	-3.250298	-0.987018
10	6	0	2.585300	-2.062039	-0.786981
11	1	0	1.527229	-1.879901	-0.909448
12	6	0	3.537874	-1.090624	-0.392565
13	6	0	3.387553	0.280656	-0.093691
14	6	0	4.514716	1.065009	0.230782
15	7	0	4.789247	-1.693422	-0.355629
16	9	0	7.090476	-1.167559	-0.894831
17	6	0	4.633608	-2.979823	-0.709894
18	1	0	5.485689	-3.644457	-0.749199
19	9	0	6.553092	-1.555228	1.294590
20	1	0	2.874625	-4.203369	-1.298263
21	6	0	2.104419	0.872416	-0.134833
22	6	0	0.996838	1.378500	-0.167744
23	6	0	-0.297316	1.967461	-0.205084
24	6	0	-1.420371	1.182148	-0.523009
25	6	0	-0.467021	3.337199	0.086191
26	6	0	-2.706907	1.735625	-0.563003
27	1	0	-1.280883	0.125297	-0.722825
28	6	0	-1.741547	3.891057	0.049210
29	1	0	0.397567	3.943362	0.334329

30	6	0	-2.848052	3.104740	-0.276264
31	1	0	-1.877481	4.946364	0.266021
32	1	0	-3.832123	3.560039	-0.326182
33	6	0	-3.878718	0.914464	-0.922879
34	26	0	-4.665965	-0.705580	0.134793
35	6	0	-5.245174	1.165739	-0.560028
36	6	0	-3.872924	-0.272898	-1.732382
37	6	0	-6.062656	0.154984	-1.144215
38	6	0	-5.214207	-0.733321	-1.870344
39	6	0	-3.509104	-1.028671	1.831223
40	6	0	-3.530533	-2.204633	1.021765
41	6	0	-4.888200	-2.628682	0.895098
42	6	0	-5.705357	-1.714947	1.626649
43	6	0	-4.852988	-0.726080	2.205508
44	1	0	-5.592057	1.961897	0.084116
45	1	0	-2.998358	-0.735012	-2.169008
46	1	0	-7.132695	0.057250	-1.024209
47	1	0	-5.527931	-1.617218	-2.408193
48	1	0	-2.633377	-0.444986	2.080299
49	1	0	-2.672777	-2.676298	0.562078
50	1	0	-5.238582	-3.474234	0.319270
51	1	0	-6.783565	-1.747769	1.702389
52	1	0	-5.171796	0.120334	2.798156

Total Energy (HF) = -1497.9228397 Hartree

DFT Data of BODIPY **5**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.427746	-2.554191	0.248189
2	1	0	-3.411453	-2.907499	0.147927
3	6	0	-5.576038	-3.304721	0.473246
4	1	0	-5.649618	-4.376527	0.590040
5	6	0	-6.652126	-2.394988	0.515173
6	1	0	-7.704821	-2.586242	0.671722
7	7	0	-6.209356	-1.140716	0.326100
8	5	0	-7.080348	0.163209	0.389693
9	6	0	-5.317087	3.369589	-0.562869
10	6	0	-4.231473	2.501676	-0.535664
11	1	0	-3.192820	2.729483	-0.728076
12	6	0	-4.737746	1.217894	-0.217279
13	6	0	-4.085270	-0.029454	-0.103605
14	6	0	-4.831812	-1.199966	0.155170
15	7	0	-6.113781	1.317612	-0.052692
16	9	0	-8.142846	0.069255	-0.488520
17	6	0	-6.458286	2.599670	-0.259278
18	1	0	-7.491720	2.908394	-0.181871
19	9	0	-7.507452	0.379466	1.687644
20	1	0	-5.308219	4.428412	-0.778853

21	6	0	-2.685617	-0.109942	-0.270554
22	6	0	-1.476551	-0.180381	-0.410324
23	6	0	-0.070406	-0.263620	-0.574872
24	6	0	0.705137	0.899640	-0.771805
25	6	0	0.587115	-1.510992	-0.550265
26	6	0	2.079340	0.812633	-0.932402
27	1	0	0.213755	1.867051	-0.790506
28	6	0	1.962330	-1.587523	-0.720314
29	1	0	0.004295	-2.415307	-0.408434
30	6	0	2.741925	-0.430802	-0.909914
31	1	0	2.655416	1.722820	-1.063928
32	1	0	2.440808	-2.561405	-0.725523
33	6	0	4.196157	-0.526884	-1.108479
34	26	0	5.698692	0.084256	0.211057
35	6	0	5.039591	-1.634928	-0.751196
36	6	0	5.044890	0.460853	-1.720093
37	6	0	6.373801	-1.337324	-1.150782
38	6	0	6.376331	-0.042993	-1.751908
39	6	0	4.823120	0.867649	1.927439
40	6	0	5.647004	1.852568	1.302981
41	6	0	6.981210	1.345236	1.254911
42	6	0	6.980697	0.046594	1.847700
43	6	0	5.646738	-0.248730	2.263362
44	1	0	4.724589	-2.528103	-0.230287
45	1	0	4.726988	1.420689	-2.101907
46	1	0	7.238423	-1.966183	-0.990261

47	1	0	7.241615	0.478527	-2.136824
48	1	0	3.754555	0.936635	2.078983
49	1	0	5.315495	2.804936	0.912571
50	1	0	7.835044	1.842169	0.815165
51	1	0	7.833563	-0.612517	1.934413
52	1	0	5.313136	-1.168167	2.724317

Total Energy (HF) = -1497.9241301 Hartree

DFT Data for BODIPY **6**

Standard orientation:

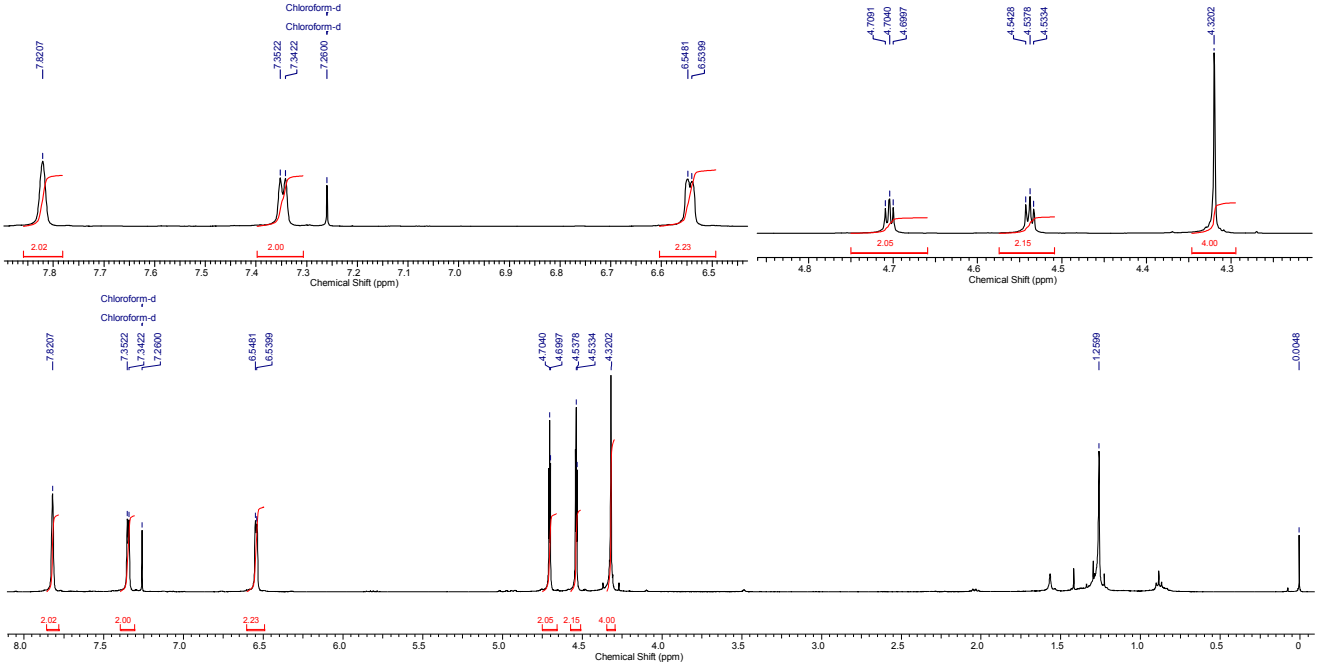
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.460810	2.564138	0.012557
2	1	0	-4.424584	2.852398	-0.091464
3	6	0	-6.568799	3.391410	0.154553
4	1	0	-6.584648	4.471587	0.182101
5	6	0	-7.692448	2.547205	0.266633
6	1	0	-8.734874	2.807402	0.388840
7	7	0	-7.315803	1.259349	0.200152
8	5	0	-8.275061	0.017267	0.192965
9	6	0	-6.591546	-3.365236	0.341806
10	6	0	-5.477963	-2.554476	0.155297
11	1	0	-4.443738	-2.855148	0.067723

12	6	0	-5.943692	-1.217452	0.112883
13	6	0	-5.241802	0.001392	-0.012869
14	6	0	-5.935559	1.229992	0.043805
15	7	0	-7.324124	-1.228884	0.269901
16	9	0	-9.106461	0.050893	1.295762
17	6	0	-7.709480	-2.508600	0.406583
18	1	0	-8.753713	-2.754646	0.541960
19	9	0	-8.993533	-0.013373	-0.988765
20	1	0	-6.614696	-4.442150	0.428501
21	6	0	-3.838729	-0.008005	-0.171956
22	6	0	-2.627591	-0.017033	-0.311107
23	6	0	-1.218891	-0.028959	-0.471204
24	6	0	-0.508114	-1.248994	-0.499769
25	6	0	-0.498438	1.178385	-0.604139
26	6	0	0.868757	-1.260738	-0.653632
27	1	0	-1.052993	-2.181938	-0.399693
28	6	0	0.878455	1.165983	-0.758553
29	1	0	-1.035921	2.120739	-0.584586
30	6	0	1.590962	-0.053656	-0.785630
31	1	0	1.406716	-2.202587	-0.675155
32	1	0	1.423696	2.098287	-0.860877
33	6	0	3.002012	-0.067037	-0.941838
34	6	0	4.211175	-0.081869	-1.083039
35	6	0	5.615299	-0.103267	-1.263501
36	26	0	7.064067	0.014448	0.227283
37	6	0	6.457017	-1.273881	-1.283669

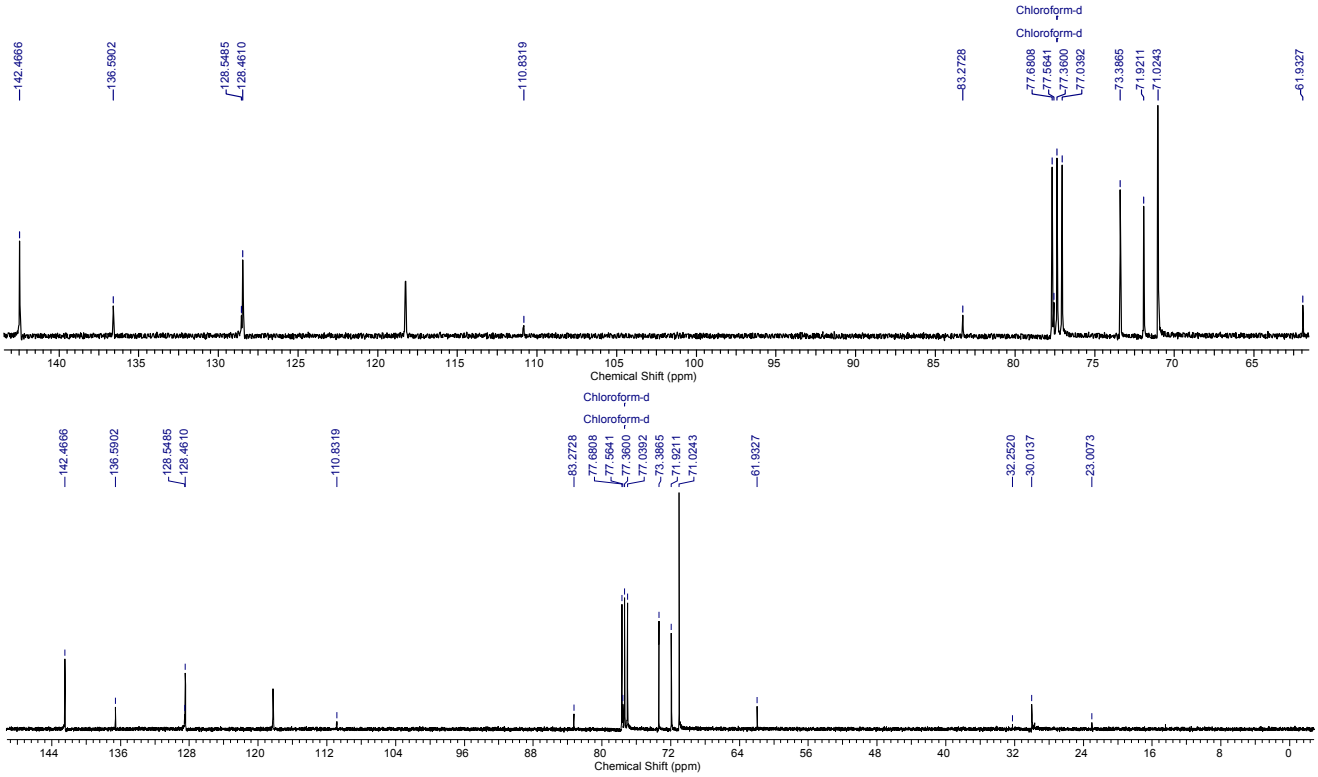
38	6	0	6.469173	1.039106	-1.476858
39	6	0	7.794601	-0.852984	-1.521516
40	6	0	7.802275	0.570679	-1.640590
41	6	0	6.116493	0.202199	2.067201
42	6	0	6.977920	1.318118	1.843790
43	6	0	8.308291	0.823188	1.684506
44	6	0	8.267871	-0.598338	1.808167
45	1	0	6.116166	-2.287946	-1.130830
46	1	0	6.138243	2.067652	-1.495510
47	1	0	8.661065	-1.497878	-1.568709
48	1	0	8.675555	1.189569	-1.792618
49	6	0	6.912557	-0.982493	2.044252
50	1	0	5.041510	0.242502	2.177856
51	1	0	6.671884	2.352976	1.776646
52	1	0	9.186686	1.417395	1.473090
53	1	0	9.109884	-1.269150	1.706586
54	1	0	6.548814	-1.994643	2.155634

Total energy (HF) = -1574.0776342 Hartree

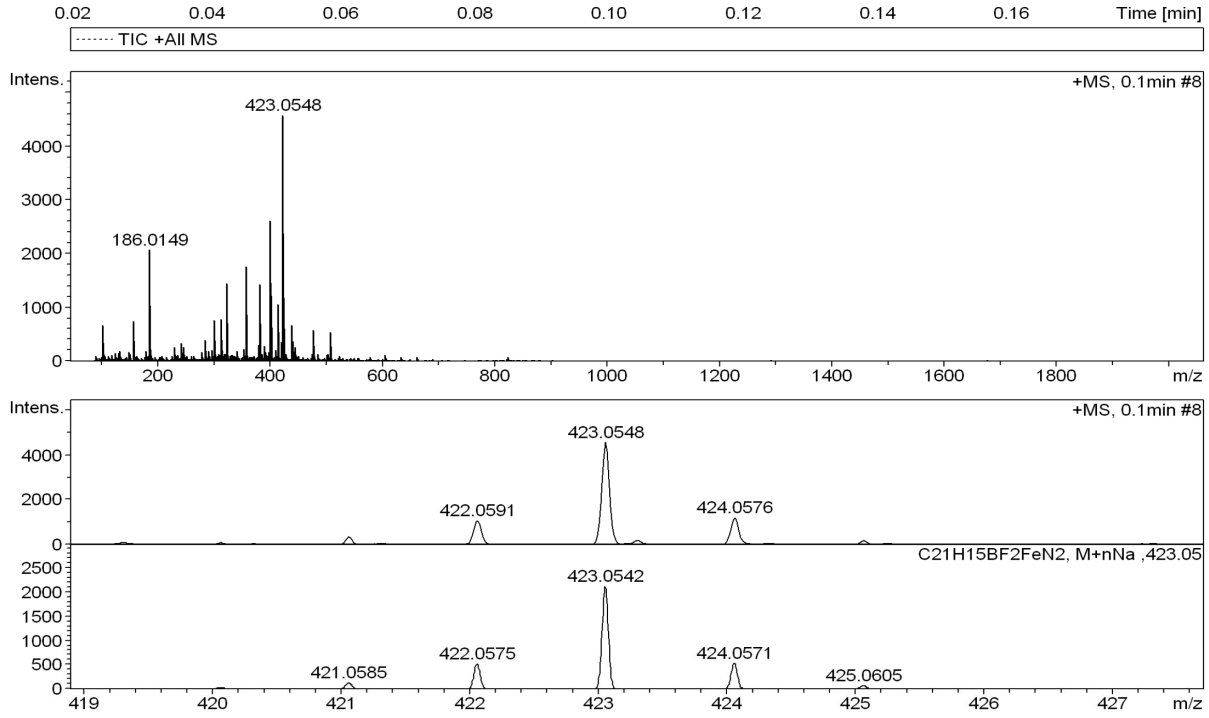
^{1}H NMR of **3**



^{13}C NMR of **3**

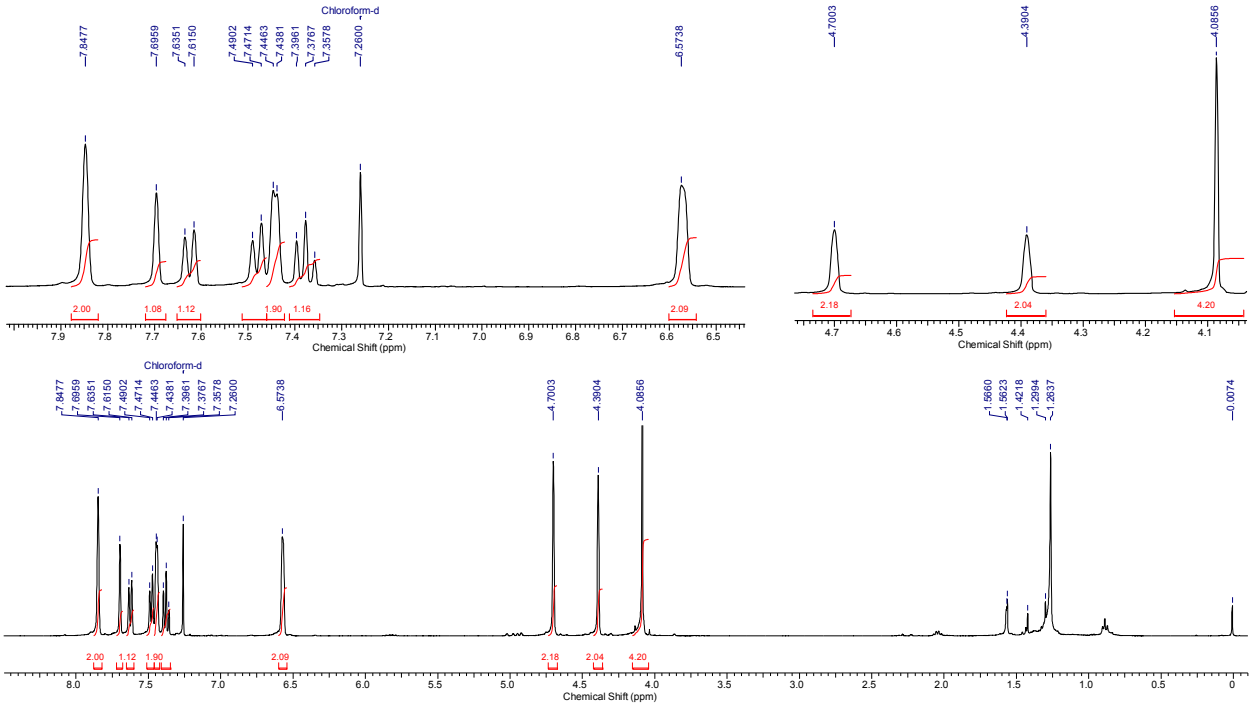


HRMS of **3**



Bruker Compass DataAnalysis 4.0 printed: 2/14/2013 6:09:22 PM Page 1 of 1

^{1}H NMR of **4**



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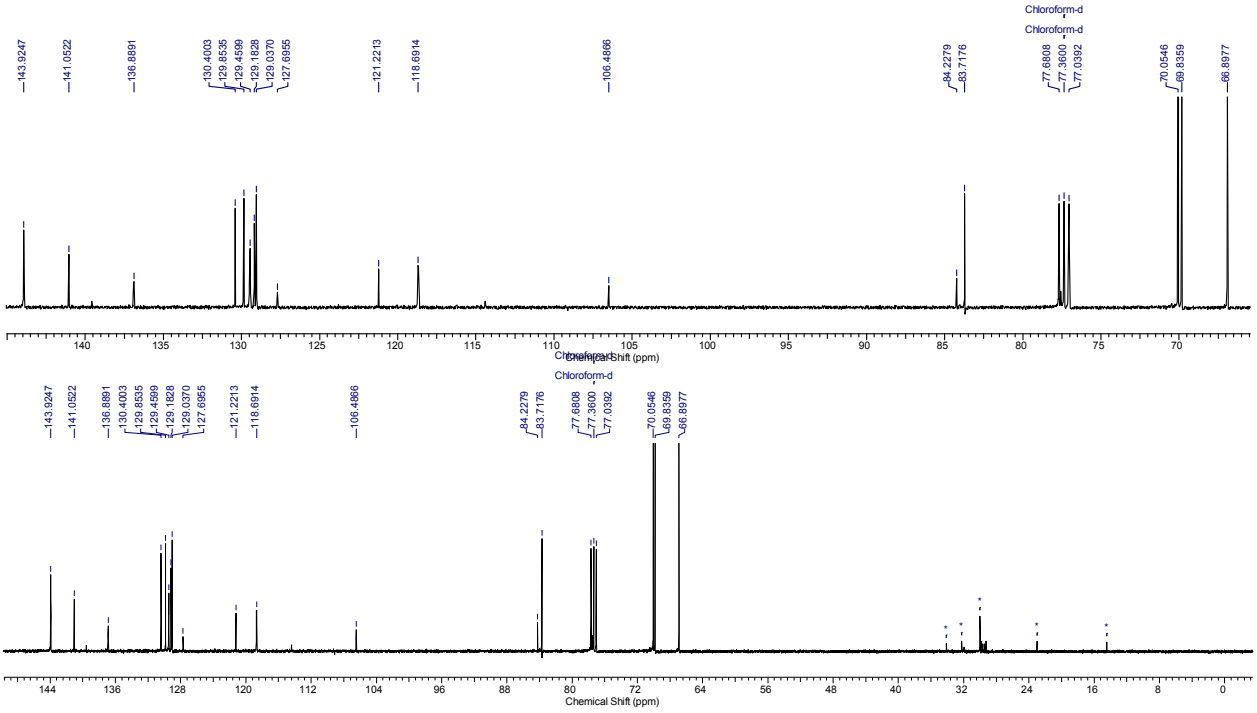

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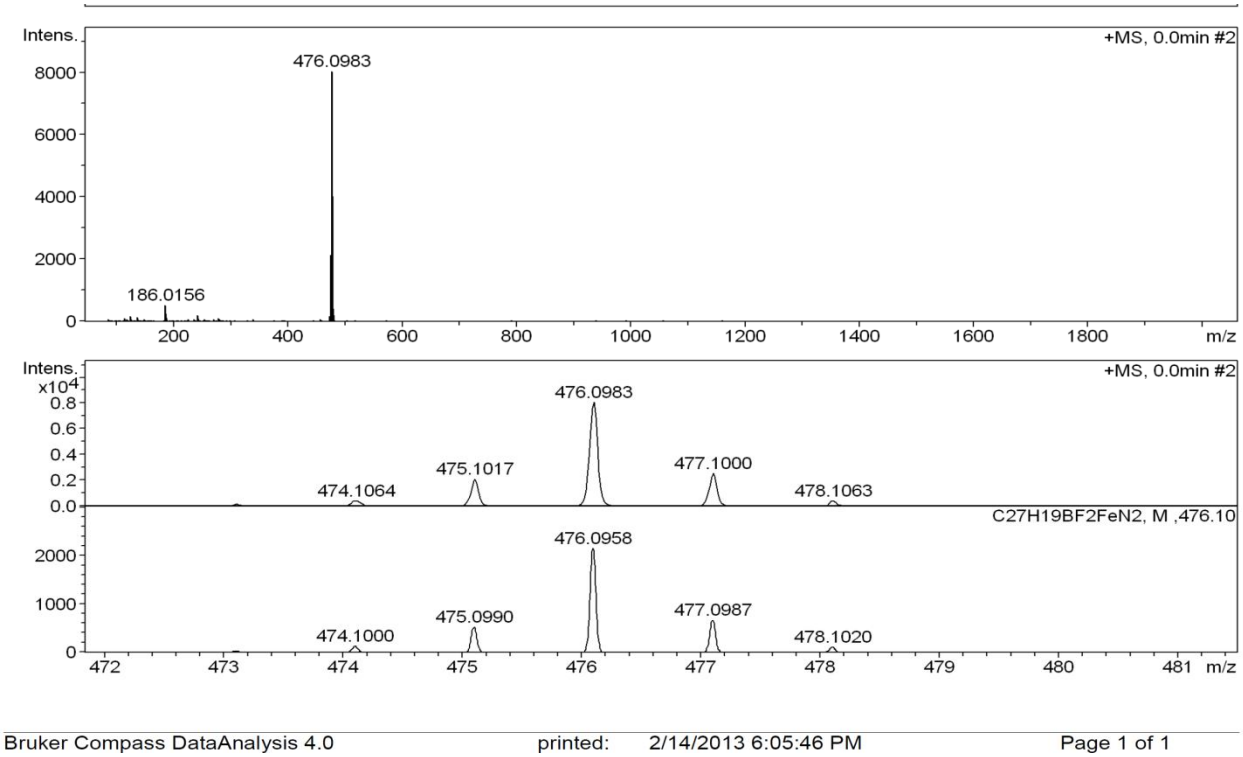
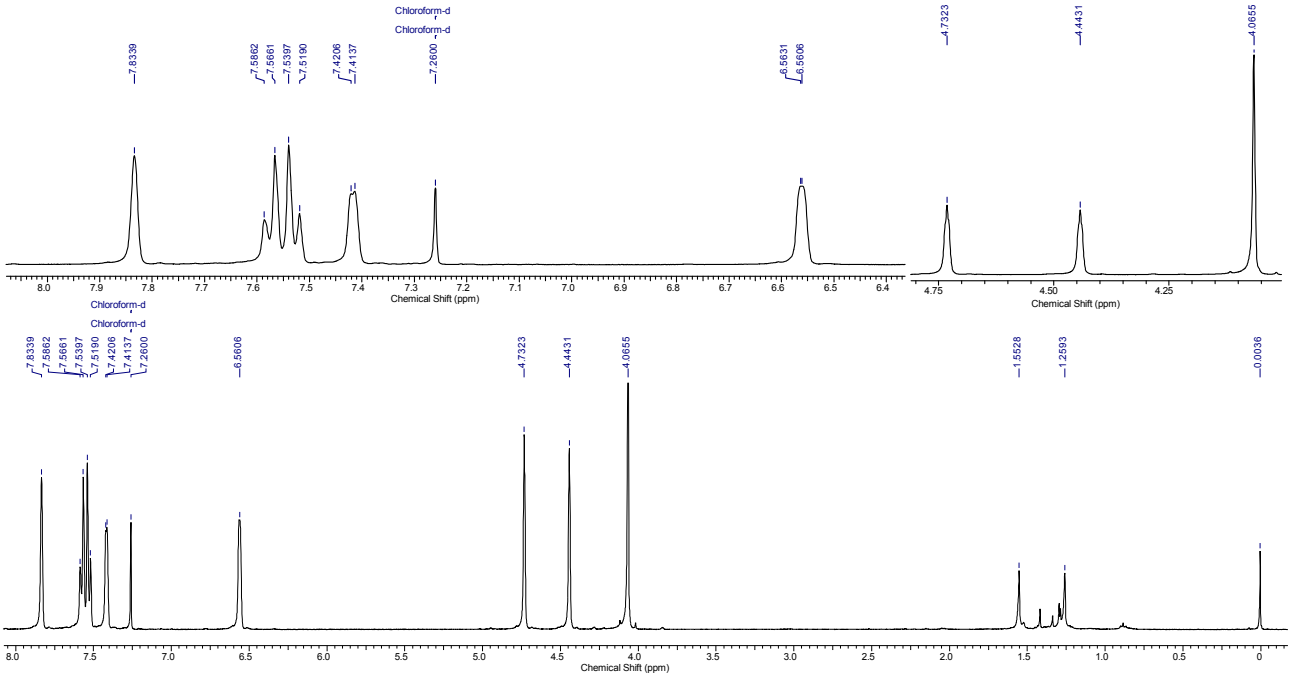


^{1}H NMR of **5**



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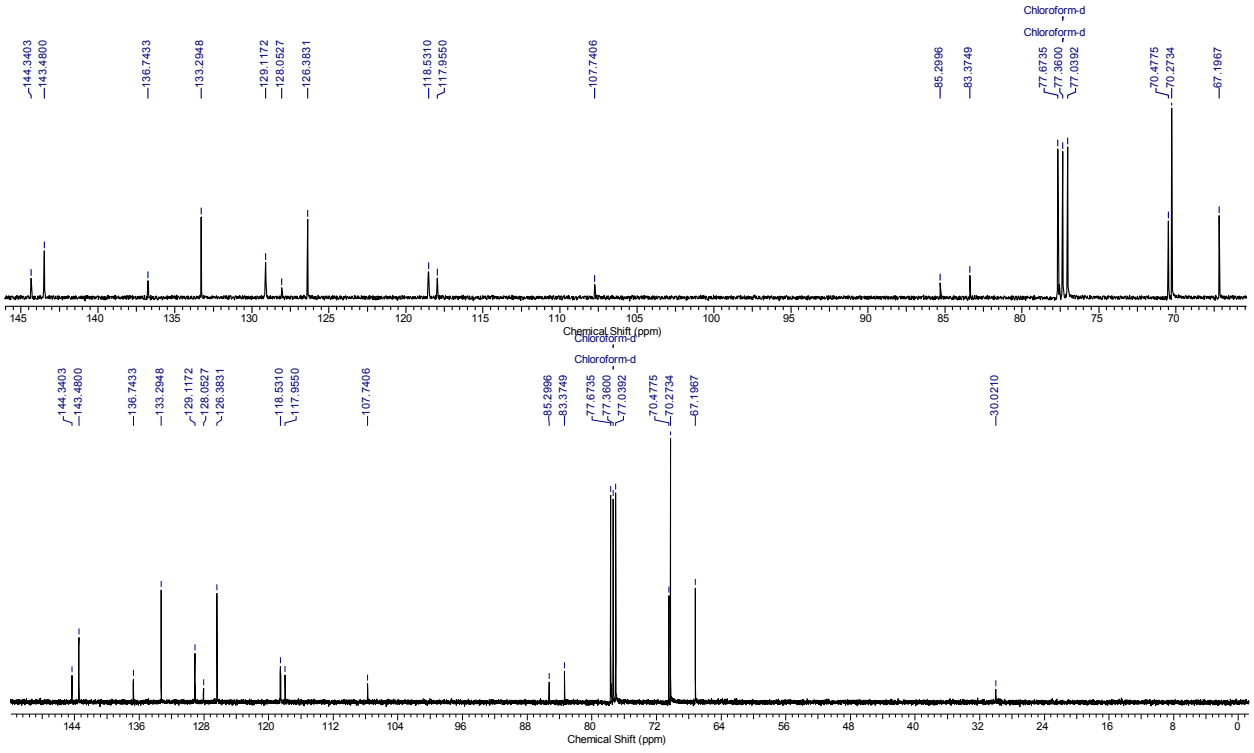

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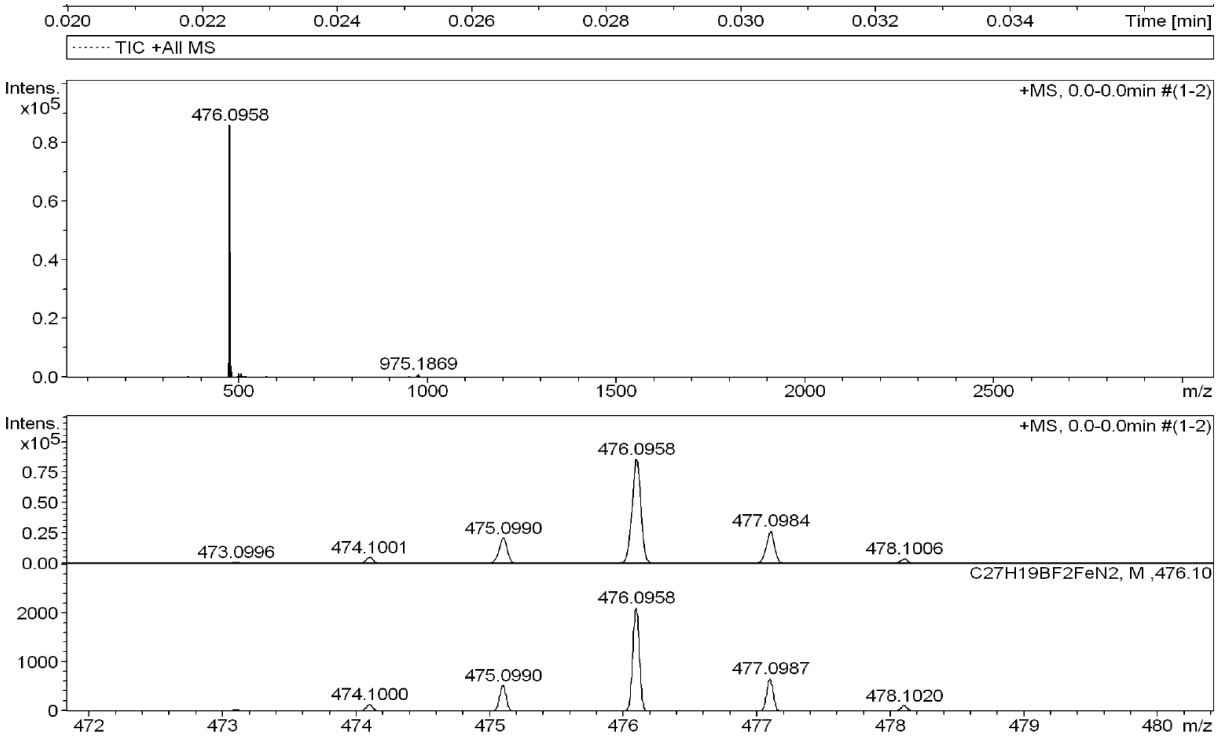

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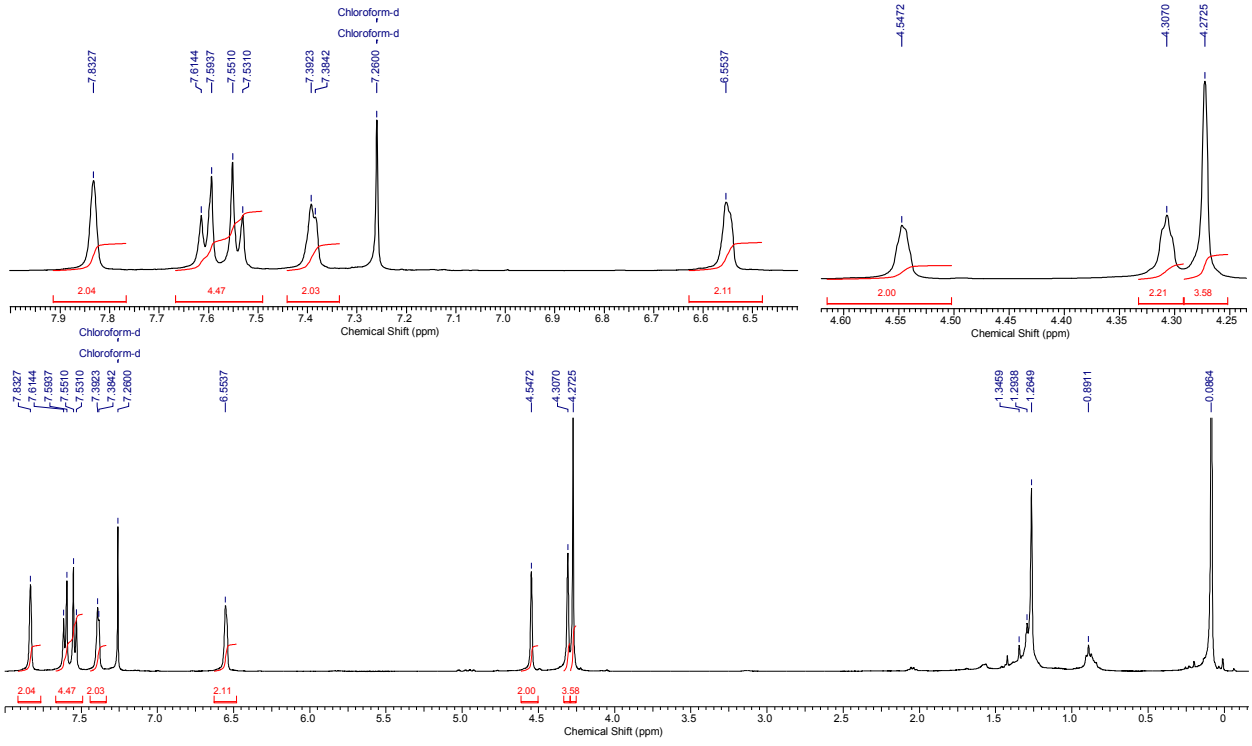

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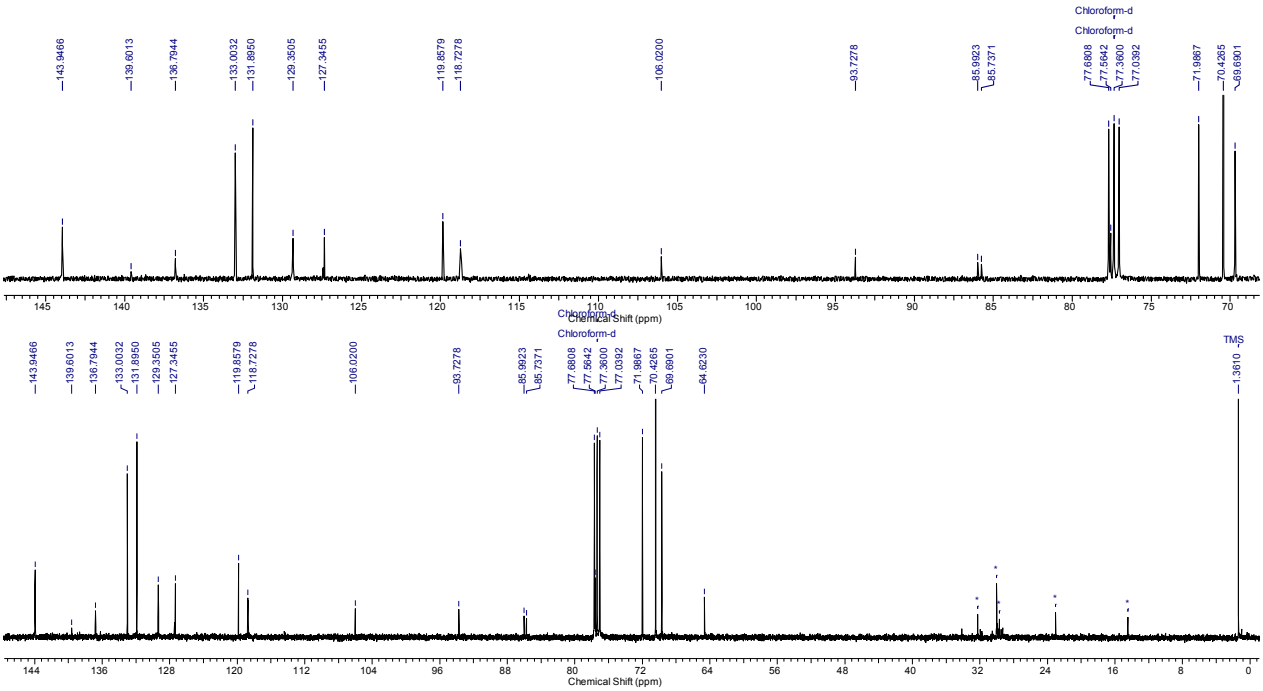

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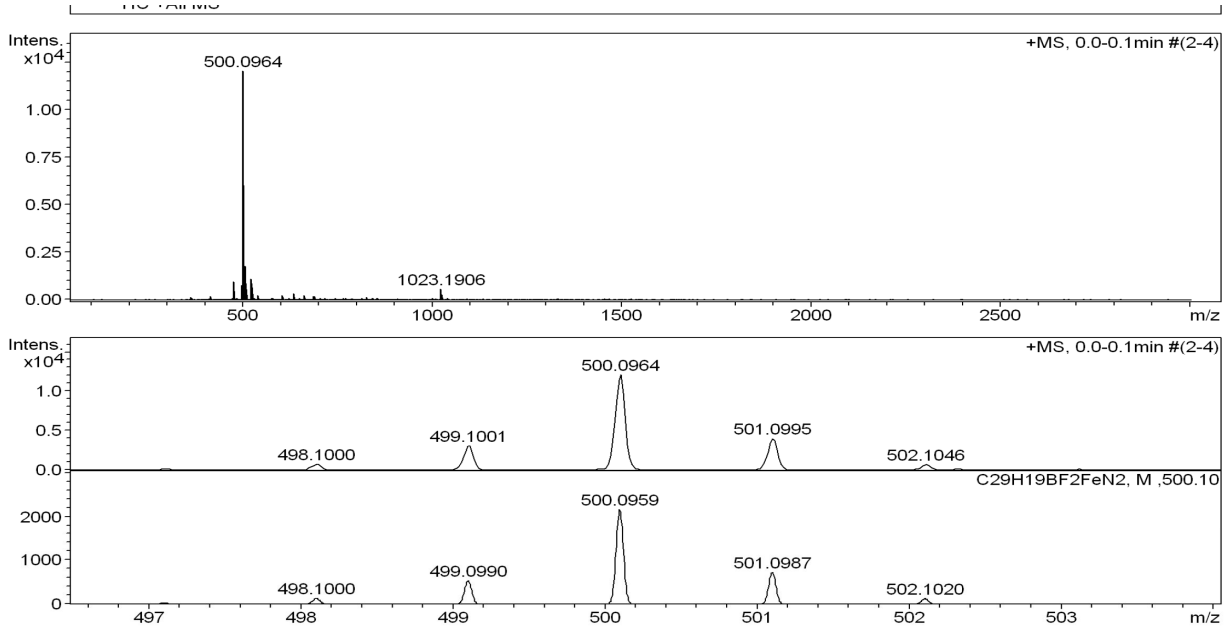

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