Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synergistic effect of donors on the tetracyanobutadine (TCBD) substituted ferrocenyl pyrenes

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Photophysical Data

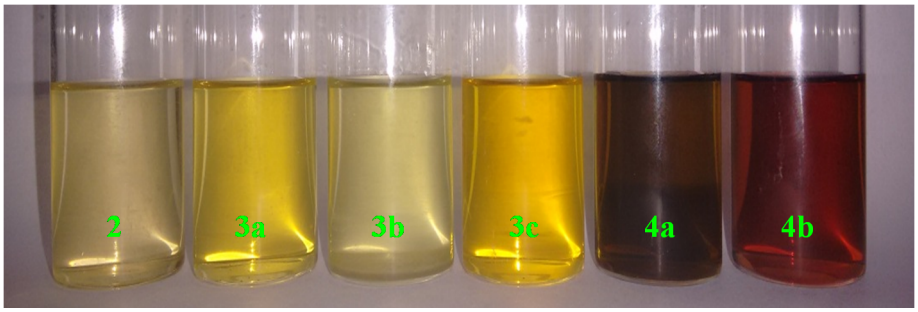


Figure S1 Photographs of ferrocenyl substituted pyrenes **2, 3a – 3c, 4a** and **4b** in 10^{-4} M dichloromethane solution in day light.

Electrochemical Data

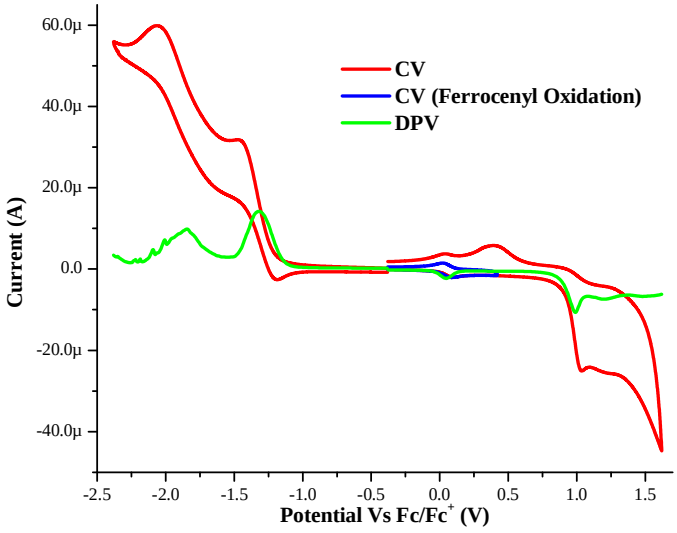


Figure S2 Overlaid CV and DPV plots of ferrocenyl pyrene **2.**

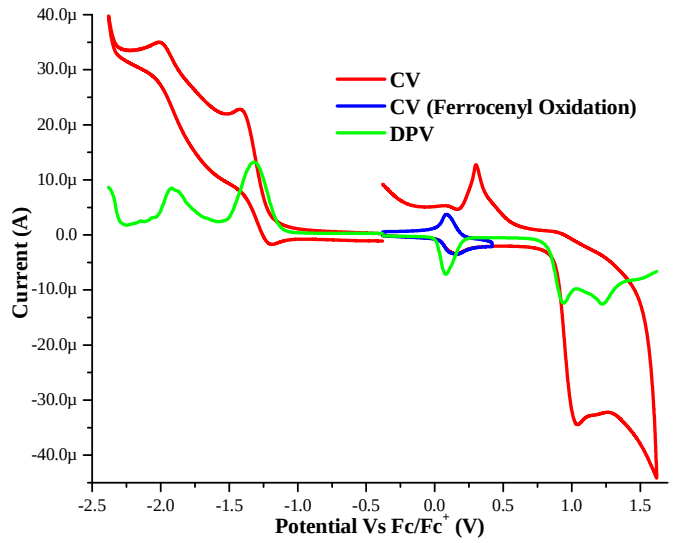


Figure S3 Overlaid CV and DPV plots of ferrocenyl pyrene **3a**.

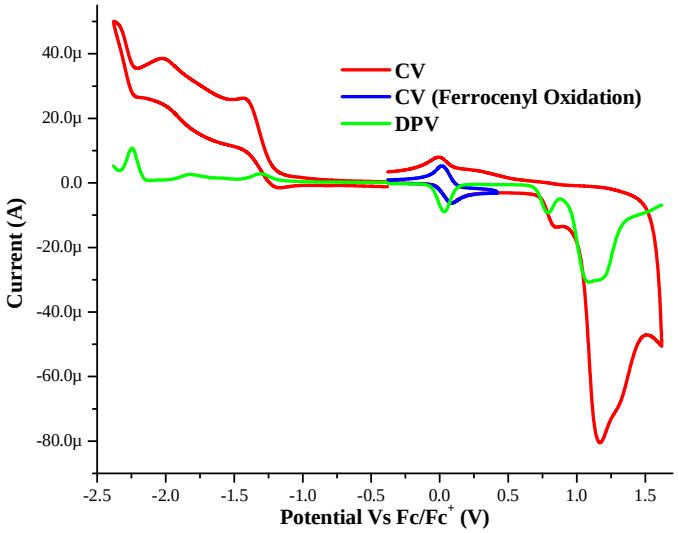


Figure S4 Overlaid CV and DPV plots of ferrocenyl pyrene **3b**.

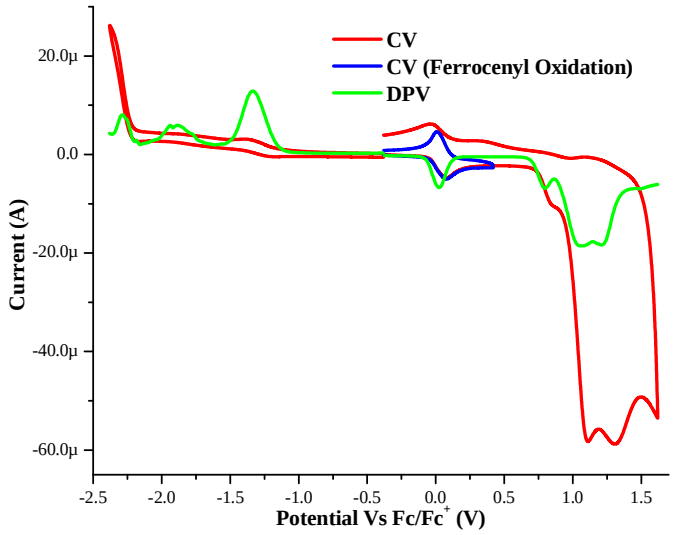


Figure S5 Overlaid CV and DPV plots of ferrocenyl pyrene **3c**.

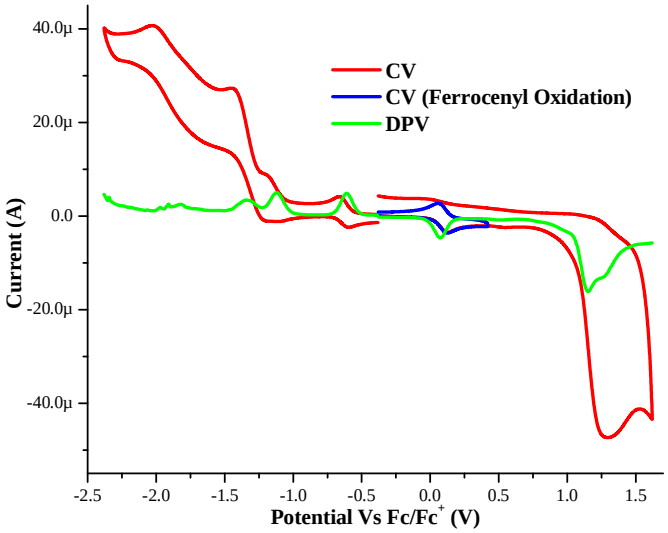


Figure S6 Overlaid CV and DPV plots of ferrocenyl pyrene **4b**.

Single Crystal X-ray Diffraction Studies.

Single crystal X-ray structural studies of ferrocenyl substituted pyrene **3b** 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 1054932 for **3b** contains the supplementary crystallographic data. 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).

Table S1. Crystal data and structure refinement parameters

BODIPY	**3b**
Empirical formula	C_{34} H_{22} Fe
Formula weight	486.37
Temperature/K	150(2)
Crystal system	Monoclinic
Space group	*P 21/n*
Unit cell dimensions	
a/Å	a = 7.7281(2)
α/°	90
b/ Å	b = 10.2249(3)
β/°	90.696(3)
c/ Å	c = 29.6634(12)
γ/°	90
Volume/ $Å^3$	2343.80(13)
Z	4
Calculated density/ Mg/m^3	1.378
Absorption coefficient/mm^{-1}	0.665
F(000)	1008
Crystal size/mm	0.26 x 0.21 x 0.18
θ range from data collection/°	3.30 to 24.99
Reflections collected/unique	16811 / 4114 [R(int) = 0.0372]
Absorption correction	Semi-empirical from equivalents
Data/restraints/parameters	4114 / 0 / 316
Goodness-of-fit on F^2	1.069
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0353, wR_2 = 0.0817
R indices (all data)	R_1 = 0.0493, wR_2 = 0.0895
Largest diff. peak and hole/e $Å^{-3}$	0.256 and -0.259
CCDC number	1054932

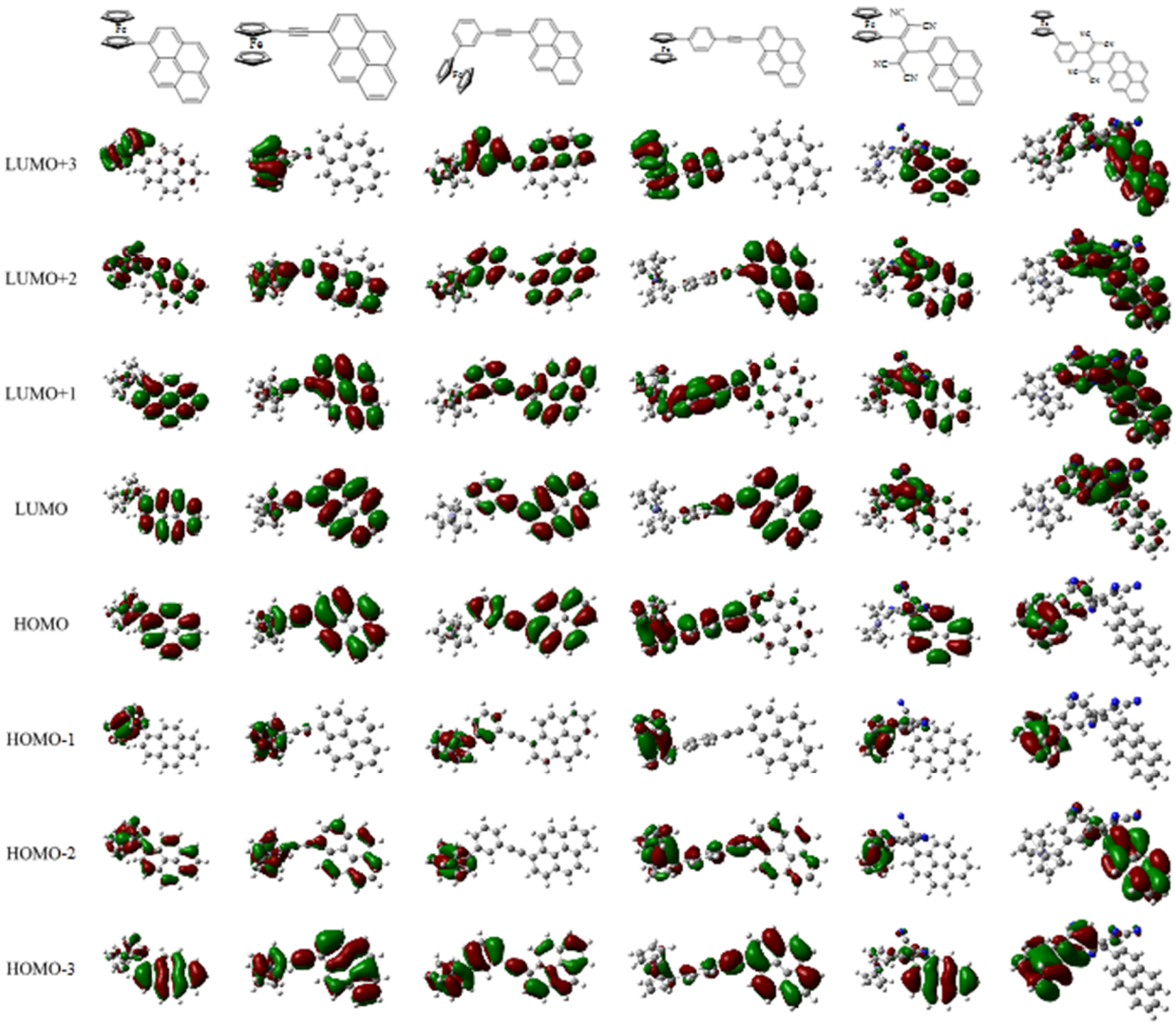


Figure S7 Frontier molecular orbital plots of ferrocenyl substituted pyrenes **2**, **3a – 3c**, **4a**, and **4b c**alculated at B3LYP/6-31G* level for C, N, H and Lanl2DZ level for Fe[i]

Ferrocenyl substituted pyrene **2**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.882346	-0.020568	1.370280
2	26	0	-3.265234	-0.190156	0.073917
3	6	0	-5.102465	0.777197	0.207120
4	6	0	-3.692767	0.446463	2.007511
5	6	0	-4.048621	1.737499	0.125437
6	6	0	-3.178025	1.532973	1.238992
7	6	0	-3.024154	-2.205621	-0.340623

8	6	0	-1.810359	-1.666562	0.181398
9	6	0	-1.355236	-0.624627	-0.696554
10	6	0	-2.325689	-0.519423	-1.751407
11	1	0	-5.906575	0.653149	-0.505194
12	1	0	-3.242324	0.029636	2.897773
13	1	0	-3.921637	2.473074	-0.657254
14	1	0	-2.263380	2.073443	1.439444
15	6	0	-3.342653	-1.495022	-1.536610
16	1	0	-3.618909	-2.985862	0.114085
17	1	0	-1.329804	-1.963618	1.103056
18	1	0	-2.278505	0.183744	-2.571795
19	1	0	-4.215718	-1.648779	-2.155841
20	1	0	-5.490107	-0.855034	1.692184
21	6	0	-0.121865	0.188633	-0.586470
22	6	0	1.149309	-0.393284	-0.333549
23	6	0	-0.201567	1.577647	-0.779298
24	6	0	2.299609	0.455008	-0.216609
25	6	0	1.352830	-1.814378	-0.217140
26	6	0	0.912344	2.400078	-0.686545
27	1	0	-1.174314	2.014037	-0.981548
28	6	0	3.584849	-0.104544	0.065021
29	6	0	2.175529	1.867229	-0.387488
30	6	0	2.579453	-2.345677	0.042547
31	1	0	0.505651	-2.473790	-0.360249
32	1	0	0.808419	3.472659	-0.829434
33	6	0	3.738325	-1.516541	0.210181
34	6	0	4.727801	0.744565	0.198598
35	6	0	3.340419	2.695753	-0.251463
36	1	0	2.700749	-3.423422	0.117241
37	6	0	5.008499	-2.045902	0.491033
38	6	0	5.977907	0.170315	0.482761
39	6	0	4.559674	2.161508	0.032867
40	1	0	3.225534	3.768940	-0.380685
41	6	0	6.114223	-1.208948	0.628181
42	1	0	5.120529	-3.121590	0.598975
43	1	0	6.844472	0.818080	0.586433
44	1	0	5.432372	2.801266	0.135316
45	1	0	7.089473	-1.634524	0.846638

Total energy (Sum of electronic and zero-point energies):

-1125.1046585 Hartree

Ferrocenyl substituted pyrene **3a**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.766782	0.094399	1.533783
2	26	0	4.287638	-0.183476	0.098395

3	6	0	5.381088	-1.279355	1.486795
4	6	0	4.610710	0.866239	1.862633
5	6	0	3.986625	-1.356603	1.786767
6	6	0	3.511427	-0.030693	2.019853
7	6	0	5.031866	0.447245	-1.739571
8	6	0	3.857340	1.179514	-1.407763
9	6	0	2.768770	0.245528	-1.266507
10	6	0	3.306627	-1.070684	-1.501984
11	1	0	6.024168	-2.111285	1.234414
12	1	0	4.568106	1.943469	1.946252
13	1	0	3.388248	-2.257100	1.802489
14	1	0	2.486963	0.249655	2.223110
15	6	0	4.692522	-0.939109	-1.797915
16	1	0	6.017737	0.865832	-1.887622
17	1	0	3.780599	2.248552	-1.269140
18	1	0	2.743215	-1.991212	-1.446616
19	1	0	5.376608	-1.752185	-1.997623
20	6	0	1.419904	0.562724	-0.969670
21	6	0	0.258956	0.837304	-0.725070
22	6	0	-1.089925	1.184588	-0.440152
23	6	0	-2.106839	0.192059	-0.355039
24	6	0	-1.426988	2.537868	-0.232446
25	6	0	-3.444735	0.590875	-0.055985
26	6	0	-1.834913	-1.201933	-0.559542
27	6	0	-2.727706	2.920368	0.055964
28	1	0	-0.642587	3.284479	-0.302606
29	6	0	-4.478030	-0.391193	0.037406
30	6	0	-3.758389	1.969091	0.152337
31	6	0	-2.821543	-2.137575	-0.471498
32	1	0	-0.815756	-1.494462	-0.790016
33	1	0	-2.960001	3.970537	0.211643
34	6	0	-4.176648	-1.771529	-0.169847
35	6	0	-5.818203	0.003578	0.339083
36	6	0	-5.112827	2.335709	0.452587
37	1	0	-2.594002	-3.188476	-0.630893
38	6	0	-5.208835	-2.719778	-0.072391
39	6	0	-6.816526	-0.980761	0.426800
40	6	0	-6.097274	1.398134	0.542477
41	1	0	-5.338955	3.387378	0.608452
42	6	0	-6.512547	-2.325802	0.222921
43	1	0	-4.978315	-3.770081	-0.230367
44	1	0	-7.835545	-0.680712	0.656614
45	1	0	-7.118272	1.692504	0.771025
46	1	0	-7.298092	-3.072539	0.294848
47	1	0	6.753170	0.484767	1.323606

Total energy (Sum of electronic and zero-point energies):

-1201.2639259 Hartree

Ferrocenyl substituted pyrene **3b**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.864643	2.416220	-0.315537
2	6	0	0.707433	1.021853	-0.439119
3	6	0	2.131842	2.981854	-0.430907
4	6	0	1.843164	0.223824	-0.680209
5	6	0	3.249082	2.181462	-0.662212
6	1	0	2.251364	4.057203	-0.333757
7	6	0	3.120423	0.786248	-0.789591
8	1	0	1.711435	-0.845984	-0.801649
9	1	0	4.232697	2.635691	-0.730336
10	6	0	4.291645	-0.069114	-1.065366
11	26	0	5.959828	-0.391390	0.155089
12	6	0	4.427985	-1.463563	-0.752297
13	6	0	5.499059	0.327243	-1.735413
14	6	0	5.692167	-1.916062	-1.231205
15	6	0	6.354075	-0.808309	-1.840659
16	6	0	5.725479	0.706775	1.903326
17	6	0	6.918739	1.106979	1.228739
18	6	0	7.768570	-0.035667	1.118739
19	6	0	7.100206	-1.141780	1.725353
20	1	0	3.710331	-2.059891	-0.206061
21	1	0	5.720471	1.320333	-2.100701
22	1	0	6.094065	-2.913183	-1.115874
23	1	0	7.342107	-0.818968	-2.279864
24	6	0	5.837504	-0.683077	2.209863
25	1	0	4.868292	1.334487	2.104937
26	1	0	7.130563	2.094682	0.842801
27	1	0	8.733782	-0.065976	0.632053
28	1	0	7.471112	-2.156203	1.778926
29	1	0	5.084454	-1.288840	2.694926
30	1	0	-0.005516	3.037904	-0.132764
31	6	0	-0.580617	0.422713	-0.334815
32	6	0	-1.679459	-0.096056	-0.251047
33	6	0	-2.948685	-0.728951	-0.159139
34	6	0	-4.147979	0.029942	-0.047378
35	6	0	-3.021076	-2.136972	-0.182901
36	6	0	-5.398067	-0.654653	0.036389
37	6	0	-4.146995	1.464389	-0.018417
38	6	0	-4.236845	-2.797056	-0.099513
39	1	0	-2.098791	-2.702176	-0.268767
40	6	0	-6.612880	0.088899	0.144997
41	6	0	-5.442790	-2.082472	0.010324
42	6	0	-5.306412	2.172489	0.085915
43	1	0	-3.192236	1.975488	-0.083446
44	1	0	-4.264786	-3.883200	-0.119785
45	6	0	-6.580352	1.516102	0.170892

46	6	0	-7.866499	-0.592386	0.227129
47	6	0	-6.715804	-2.739171	0.095808
48	1	0	-5.283213	3.259037	0.105608
49	6	0	-7.787758	2.226685	0.276944
50	6	0	-9.047481	0.160929	0.331853
51	6	0	-7.873784	-2.028717	0.199153
52	1	0	-6.736937	-3.825672	0.075539
53	6	0	-9.005670	1.554044	0.356184
54	1	0	-7.761678	3.313012	0.296241
55	1	0	-10.000841	-0.357149	0.394208
56	1	0	-8.829877	-2.541761	0.262621
57	1	0	-9.929507	2.119457	0.437542

Total energy (Sum of electronic and zero-point energies):

-1432.3228567 Hartree

Ferrocenyl substituted pyrene **3c**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	7.770067	0.656254	-1.493562
2	26	0	6.359847	-0.067205	-0.146766
3	6	0	7.865368	1.362391	-0.256371
4	6	0	6.452647	0.848762	-2.010601
5	6	0	6.607406	1.991834	-0.009208
6	6	0	5.734629	1.674828	-1.093548
7	6	0	6.710631	-2.094908	0.140665
8	6	0	5.385676	-1.887983	-0.340844
9	6	0	4.676743	-1.064264	0.600611
10	6	0	5.600981	-0.758400	1.657787
11	1	0	8.727595	1.388052	0.395846
12	1	0	6.060330	0.421521	-2.923273
13	1	0	6.350489	2.578946	0.861834
14	1	0	4.697755	1.969450	-1.181177
15	6	0	6.844018	-1.395836	1.377258
16	1	0	7.486023	-2.657909	-0.360232
17	1	0	4.984210	-2.288244	-1.260987
18	1	0	5.402327	-0.121497	2.508177
19	1	0	7.740258	-1.329468	1.978503
20	1	0	8.547671	0.053669	-1.942518
21	6	0	3.267645	-0.641706	0.514522
22	6	0	2.545083	-0.736604	-0.689442
23	6	0	2.587394	-0.159457	1.646789
24	6	0	1.206682	-0.373173	-0.760001
25	1	0	3.041726	-1.092961	-1.586506

26	6	0	1.251046	0.216794	1.583120
27	1	0	3.106653	-0.096108	2.597740
28	6	0	0.530901	0.112667	0.377574
29	1	0	0.668540	-0.456899	-1.698864
30	1	0	0.745552	0.581386	2.471632
31	6	0	-0.847029	0.476908	0.313280
32	6	0	-2.025387	0.779561	0.264902
33	6	0	-3.401827	1.146807	0.212066
34	6	0	-4.417767	0.163628	0.055115
35	6	0	-3.763061	2.503991	0.319569
36	6	0	-5.783690	0.576687	0.008610
37	6	0	-4.118640	-1.236283	-0.052431
38	6	0	-5.091052	2.901684	0.270826
39	1	0	-2.977143	3.242562	0.439268
40	6	0	-6.818576	-0.396174	-0.142455
41	6	0	-6.123044	1.960367	0.115700
42	6	0	-5.106984	-2.162868	-0.195708
43	1	0	-3.077892	-1.540595	-0.013780
44	1	0	-5.342956	3.955555	0.353450
45	6	0	-6.490474	-1.782031	-0.245766
46	6	0	-8.186980	0.012899	-0.188712
47	6	0	-7.506030	2.341842	0.063533
48	1	0	-4.858933	-3.218288	-0.273734
49	6	0	-7.525083	-2.721333	-0.390453
50	6	0	-9.186854	-0.962662	-0.335147
51	6	0	-8.491815	1.413034	-0.081991
52	1	0	-7.752290	3.397390	0.144380
53	6	0	-8.856921	-2.313439	-0.434173
54	1	0	-7.274316	-3.775974	-0.467995
55	1	0	-10.227641	-0.651540	-0.369919
56	1	0	-9.534168	1.718924	-0.119012
57	1	0	-9.644048	-3.053530	-0.546008

Total energy (Sum of electronic and zero-point energies):

-1432.322145 Hartree

Ferrocenyl substituted pyrene **4a**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.395987	-0.207466	0.210456
2	6	0	-6.539892	0.881439	0.360814
3	6	0	-5.148636	0.722168	0.248437
4	6	0	-4.612522	-0.570844	-0.021973
5	6	0	-5.497250	-1.683816	-0.160658
6	6	0	-6.882031	-1.477283	-0.045980

7	6	0	-4.236185	1.811718	0.424302
8	6	0	-3.201000	-0.752531	-0.145690
9	6	0	-2.317496	0.370526	-0.035290
10	6	0	-2.890501	1.645130	0.293736
11	6	0	-0.915151	0.151692	-0.181651
12	6	0	-0.433765	-1.166275	-0.332656
13	6	0	-1.291743	-2.245488	-0.442871
14	6	0	-2.684394	-2.065188	-0.372020
15	6	0	-3.594013	-3.165820	-0.503224
16	6	0	-4.940702	-2.982663	-0.408400
17	1	0	-5.618882	-3.825426	-0.512382
18	1	0	-3.182757	-4.155682	-0.680425
19	1	0	-4.636865	2.788411	0.680104
20	1	0	-8.469113	-0.066817	0.297454
21	1	0	-6.943160	1.868552	0.569245
22	1	0	-7.553068	-2.324568	-0.158364
23	1	0	-2.236721	2.488830	0.471731
24	1	0	0.636263	-1.328353	-0.410791
25	1	0	-0.891950	-3.244355	-0.593075
26	6	0	0.090906	1.227331	-0.211149
27	6	0	-0.012413	2.362687	-0.981315
28	6	0	1.243884	1.002203	1.956892
29	6	0	2.337217	0.720085	2.835434
30	6	0	0.001590	1.268721	2.617900
31	6	0	-1.056628	2.572091	-1.939032
32	6	0	0.958566	3.415947	-0.913425
33	7	0	3.201567	0.470061	3.574083
34	7	0	-0.987016	1.503263	3.186044
35	7	0	-1.866499	2.768112	-2.751066
36	7	0	1.726653	4.288920	-0.866170
37	6	0	1.354792	1.029725	0.584650
38	6	0	2.602809	0.917628	-0.161072
39	26	0	3.840913	-0.752007	-0.388932
40	6	0	2.701690	0.551394	-1.556249
41	6	0	3.947395	1.198957	0.293462
42	6	0	4.061759	0.634006	-1.944625
43	6	0	4.824916	1.042912	-0.809081
44	6	0	3.137242	-2.387044	0.698436
45	6	0	4.431969	-2.007751	1.162013
46	6	0	5.337338	-2.118338	0.063480
47	6	0	4.601498	-2.559555	-1.077243
48	1	0	1.877604	0.260103	-2.191733
49	1	0	4.233158	1.498161	1.289464
50	1	0	4.455016	0.395943	-2.922898
51	1	0	5.897195	1.177147	-0.779557
52	6	0	3.238734	-2.726465	-0.684960
53	1	0	2.230470	-2.379581	1.288161
54	1	0	4.667698	-1.655216	2.156337
55	1	0	6.389461	-1.869475	0.081271
56	1	0	4.998901	-2.709184	-2.071694
57	1	0	2.428080	-3.037793	-1.329539

Total energy (Sum of electronic and zero-point energies):

-1648.8337766 Hartree

Ferrocenyl substituted pyrene **4b**

Standard orientation:

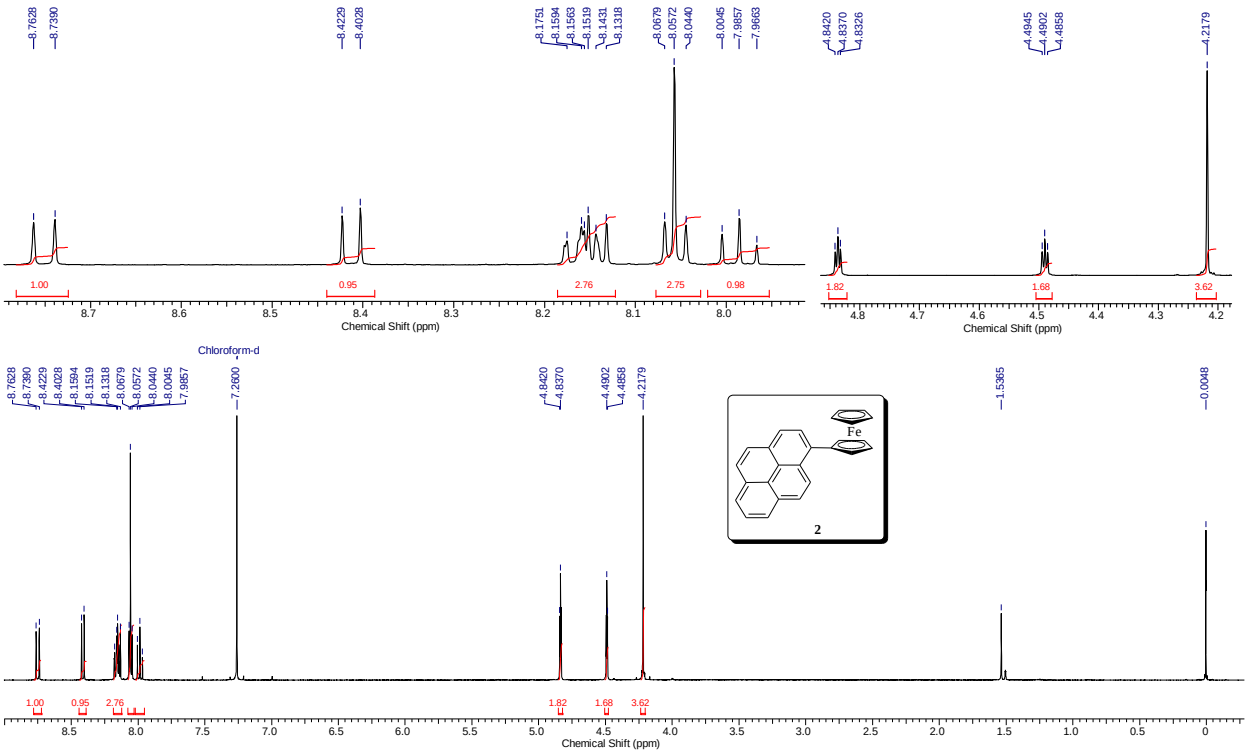
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.044450	-3.447049	-1.905875
2	6	0	-4.781466	-2.965539	-2.240959
3	6	0	-4.134568	-2.021131	-1.425500
4	6	0	-4.780597	-1.554817	-0.243228
5	6	0	-6.074448	-2.058647	0.094103
6	6	0	-6.684823	-2.999669	-0.751022
7	6	0	-2.834114	-1.507871	-1.732629
8	6	0	-4.140131	-0.593090	0.597553
9	6	0	-2.847908	-0.078706	0.254469
10	6	0	-2.220260	-0.590998	-0.931893
11	6	0	-2.235296	0.873706	1.124021
12	6	0	-2.909222	1.266304	2.298277
13	6	0	-4.161063	0.775727	2.619049
14	6	0	-4.802308	-0.155997	1.786225
15	6	0	-6.101598	-0.675657	2.099514
16	6	0	-6.711441	-1.585166	1.289693
17	1	0	-7.696209	-1.971012	1.539014
18	1	0	-6.590662	-0.325596	3.004019
19	1	0	-2.330678	-1.868740	-2.625441
20	1	0	-6.532960	-4.175082	-2.546342
21	1	0	-4.282857	-3.316818	-3.140184
22	1	0	-7.670299	-3.378208	-0.493488
23	1	0	-1.230826	-0.248310	-1.203688
24	1	0	-2.459295	2.016991	2.937705
25	1	0	-4.664744	1.126381	3.514677
26	6	0	-0.926838	1.500083	0.841771
27	6	0	-0.639460	2.087943	-0.501174
28	6	0	0.029891	1.587642	1.834440
29	6	0	-1.612080	2.836340	-1.128926
30	6	0	0.683394	1.841859	-1.116822
31	6	0	1.338812	2.841367	-1.858203
32	6	0	1.325703	0.602894	-0.928451
33	6	0	2.593841	2.584960	-2.401290
34	1	0	0.894555	3.821947	-1.974357
35	6	0	2.591830	0.335733	-1.463149
36	1	0	0.828595	-0.169130	-0.353069
37	6	0	3.212835	1.352151	-2.211902
38	1	0	3.103463	3.363102	-2.960767
39	1	0	4.200358	1.185059	-2.628592

40	6	0	3.247314	-0.965402	-1.240068
41	26	0	4.747351	-1.355656	0.153905
42	6	0	2.833007	-1.992457	-0.322078
43	6	0	4.433145	-1.448172	-1.894935
44	6	0	3.741793	-3.084499	-0.423470
45	6	0	4.730316	-2.748020	-1.395102
46	6	0	5.114755	0.375248	1.257415
47	6	0	6.289987	-0.017415	0.547878
48	6	0	6.652742	-1.328977	0.982705
49	6	0	5.699825	-1.747401	1.959925
50	1	0	1.998688	-1.940205	0.363003
51	1	0	5.011390	-0.917862	-2.638150
52	1	0	3.708344	-3.991644	0.163762
53	1	0	5.576924	-3.357051	-1.680189
54	6	0	4.750534	-0.694152	2.128997
55	1	0	4.571853	1.303049	1.135750
56	1	0	6.802481	0.565991	-0.204787
57	1	0	7.483390	-1.914611	0.613185
58	1	0	5.681405	-2.706257	2.459579
59	1	0	3.890421	-0.713195	2.784176
60	6	0	-1.509901	3.281921	-2.488453
61	6	0	-2.826320	3.260821	-0.494031
62	6	0	-0.083059	0.893130	3.084223
63	6	0	1.230713	2.364800	1.729527
64	7	0	-1.505253	3.648745	-3.592967
65	7	0	-3.811718	3.677197	-0.035716
66	7	0	-0.093875	0.326037	4.100766
67	7	0	2.216706	2.983372	1.720619

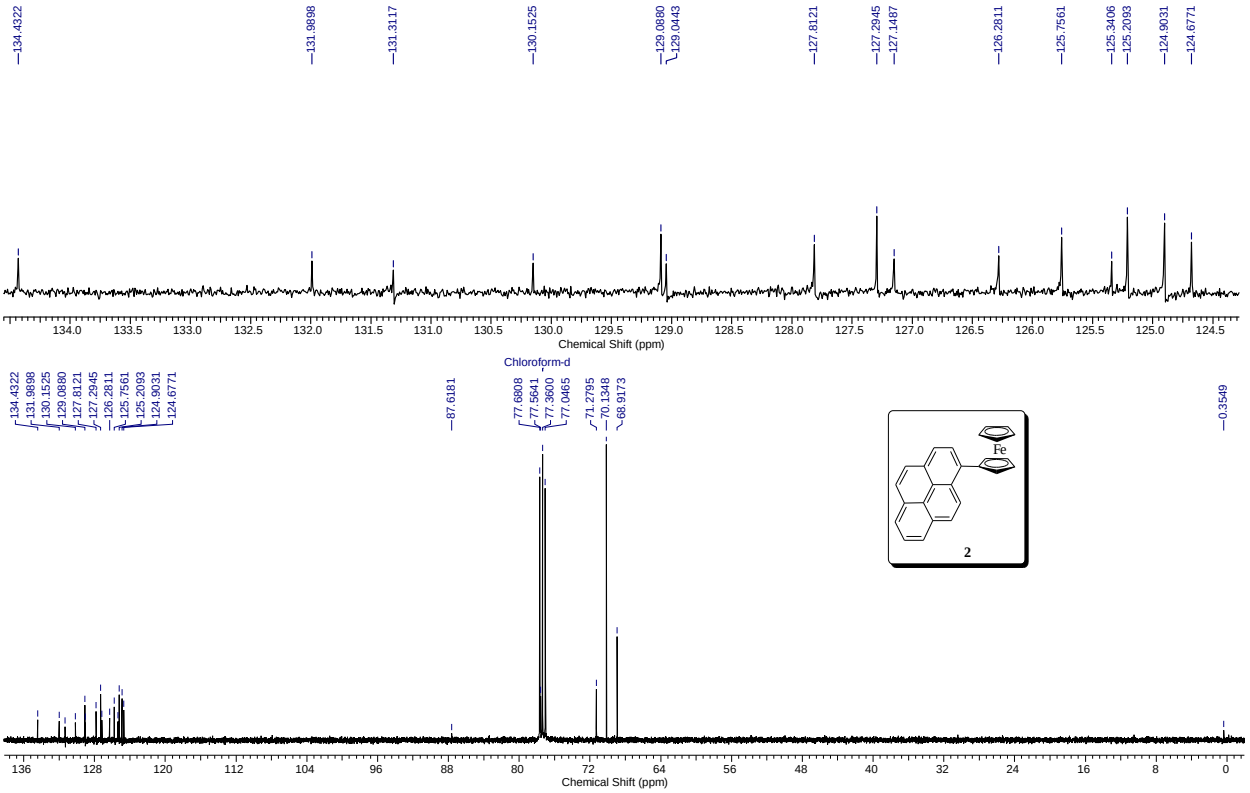
Total energy (Sum of electronic and zero-point energies):

-1879.8878569 Hartree

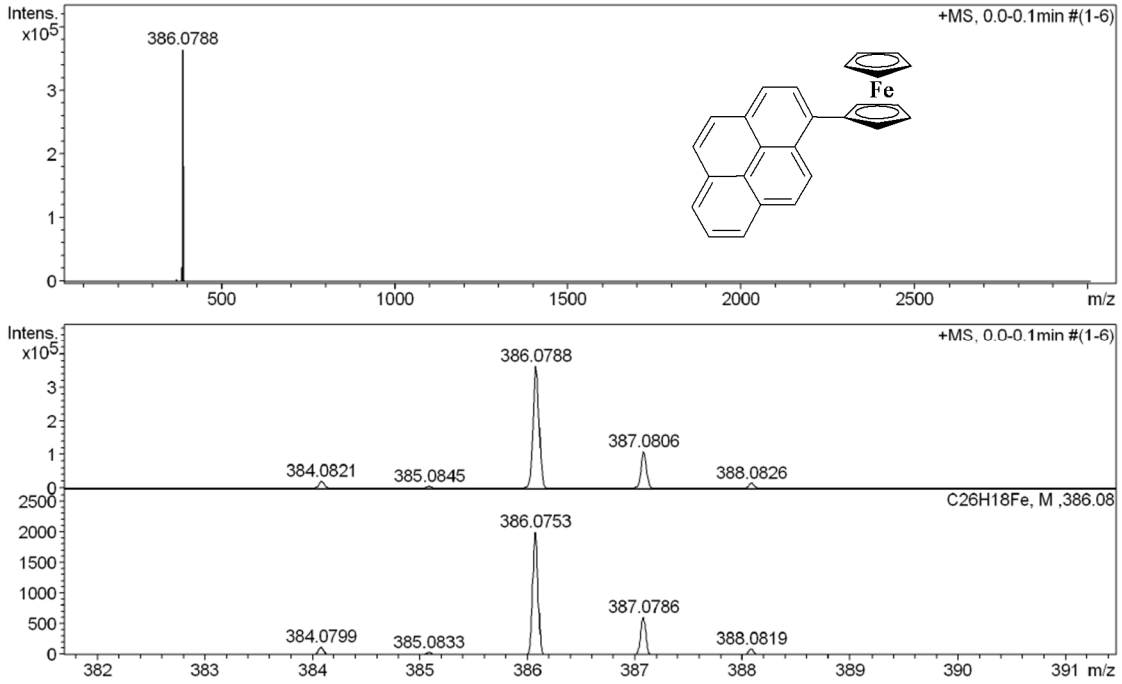
^{1}H NMR Spectra of **2**



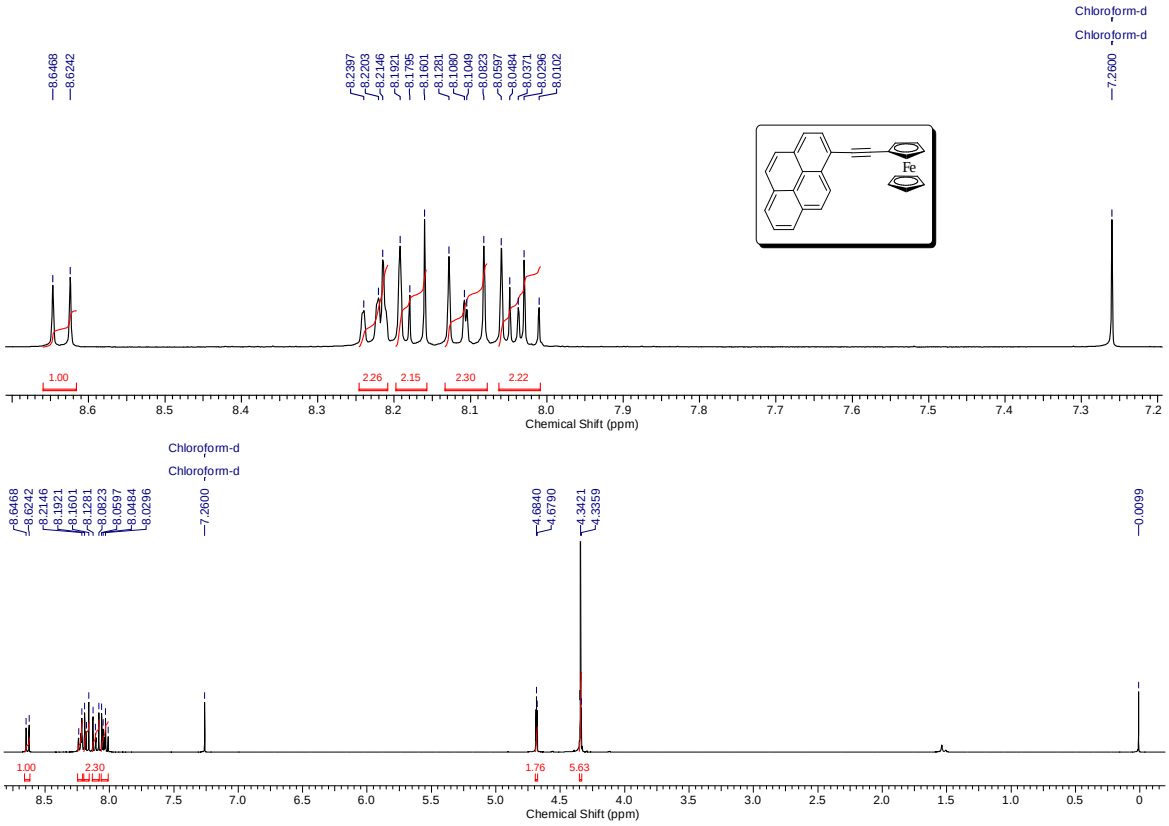
^{13}C NMR Spectra of **2**



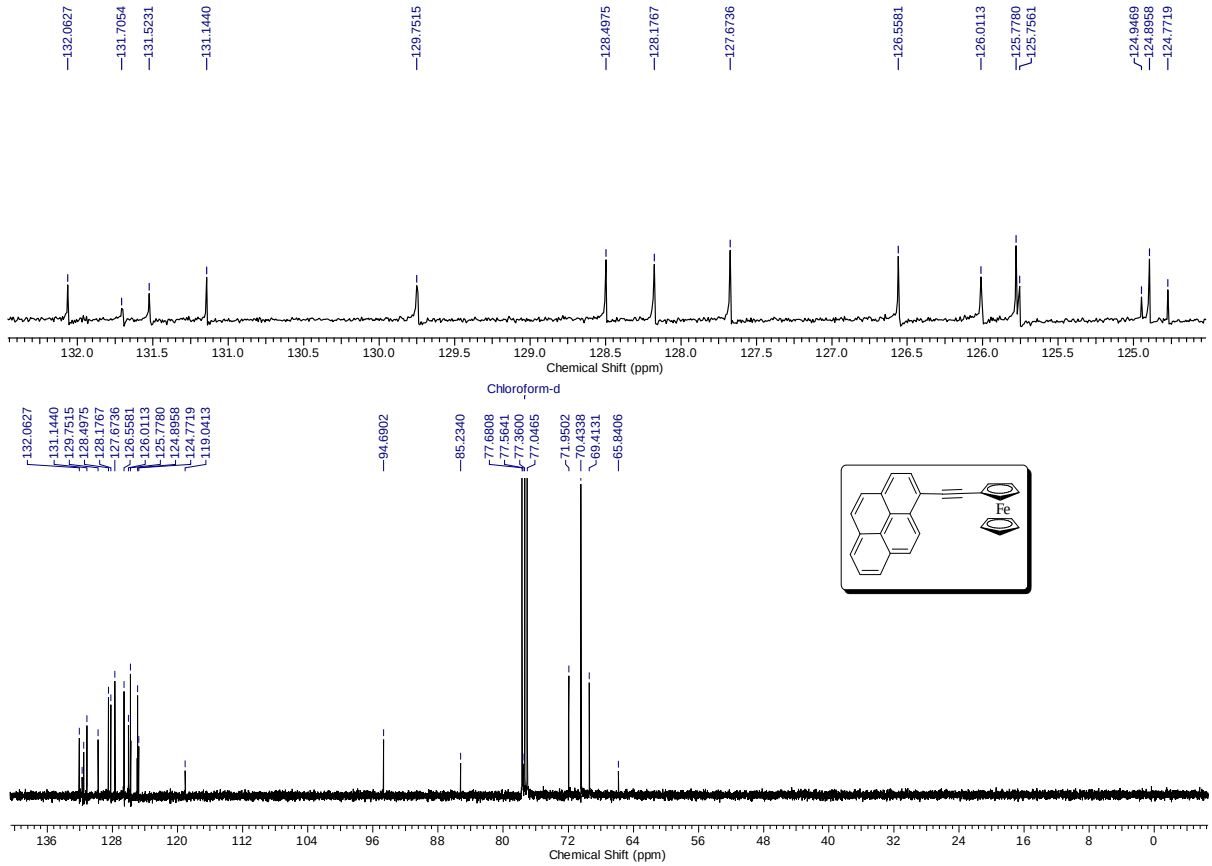
HRMS spectra of **2**



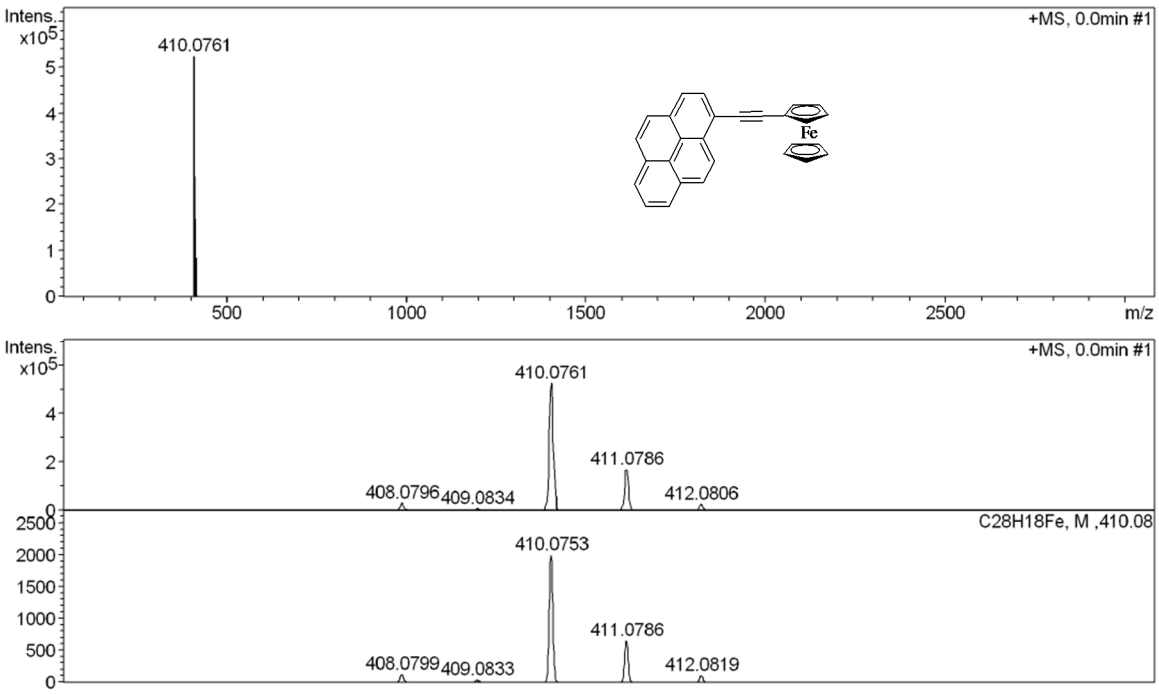
^{1}H NMR Spectra of **3a**



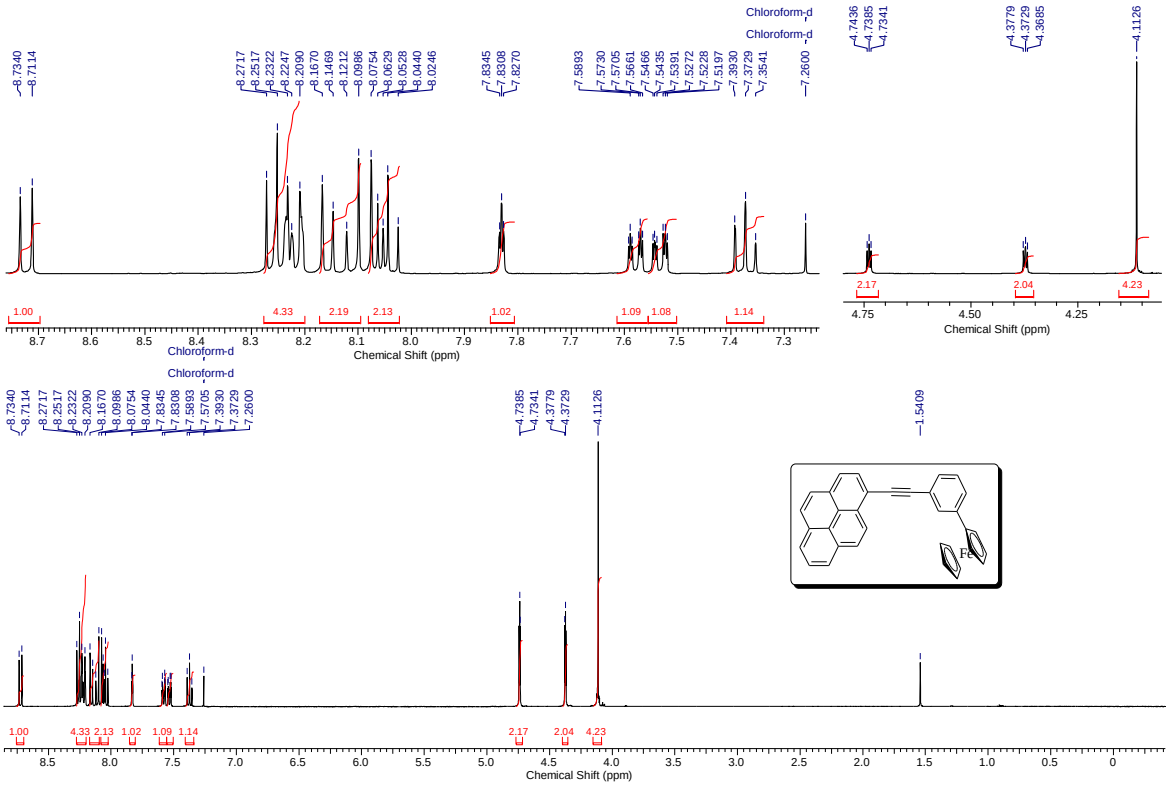
^{13}C NMR Spectra of **3a**



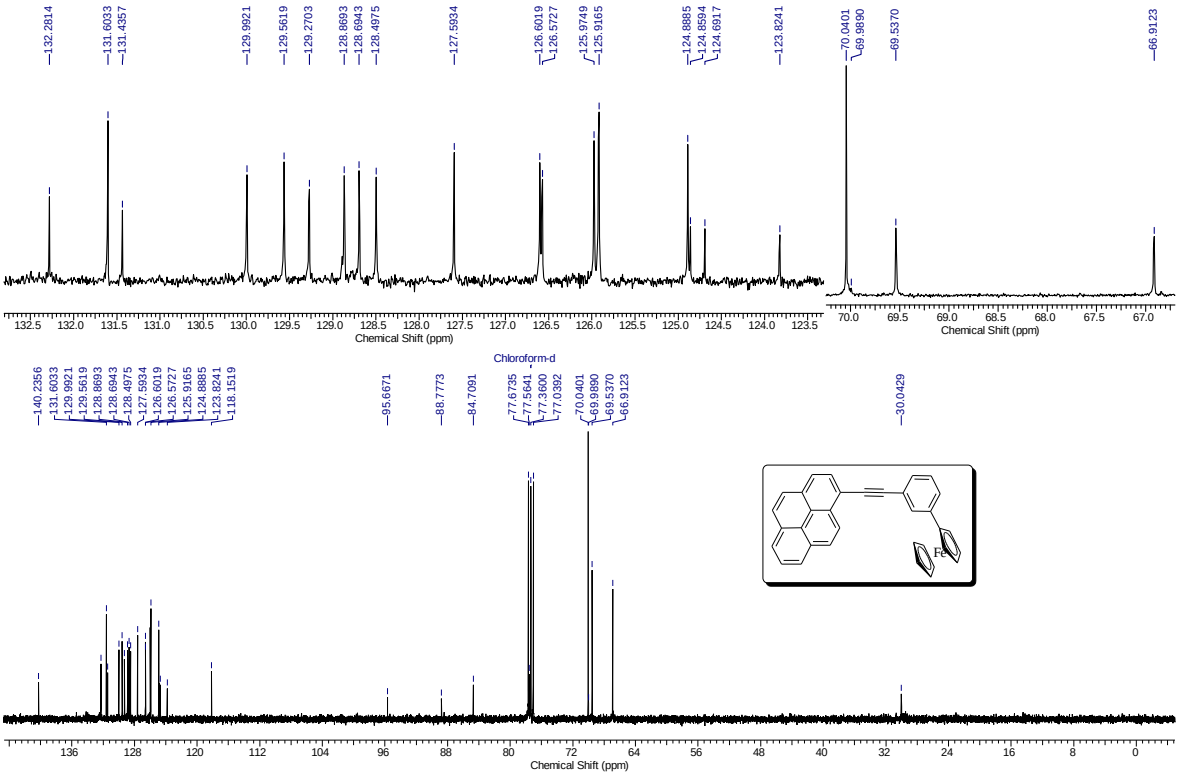
HRMS of **3a**



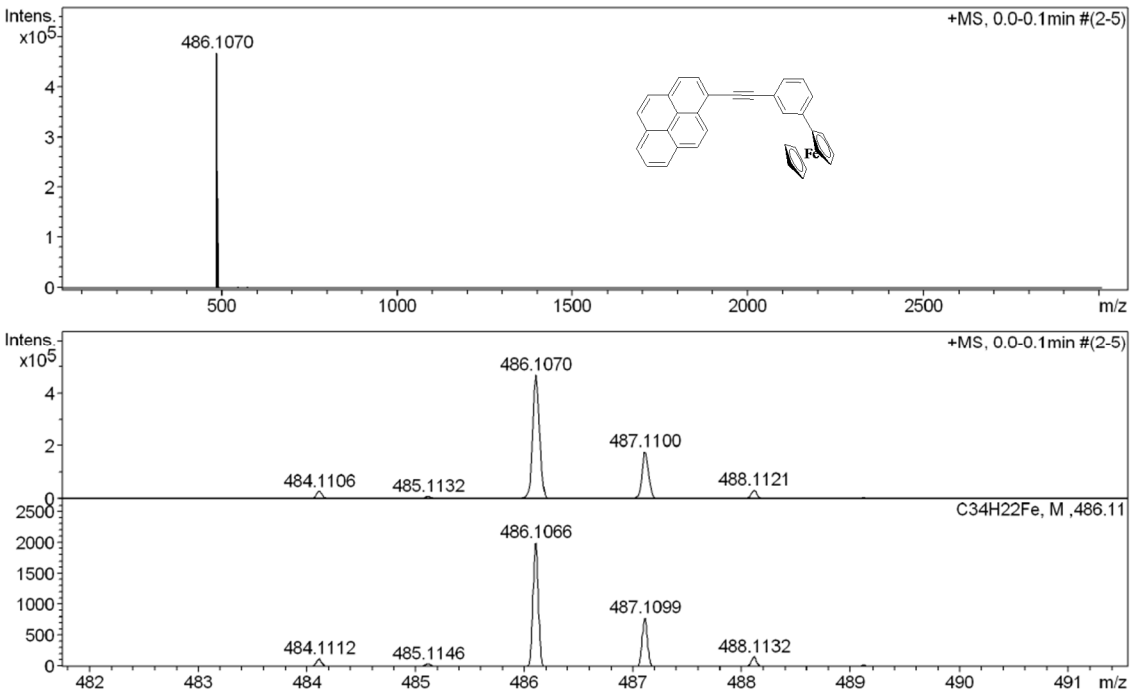
^{1}H NMR Spectra of **3b**



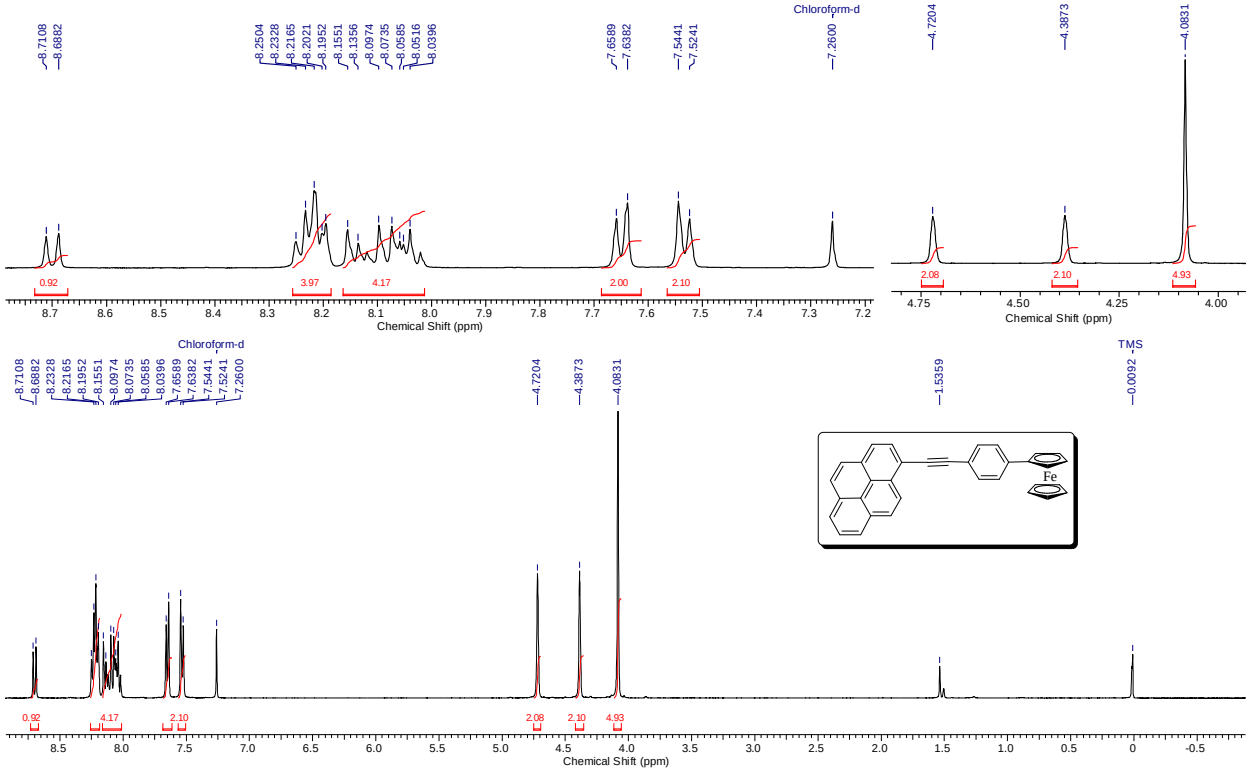
^{13}C NMR Spectra of **3b**



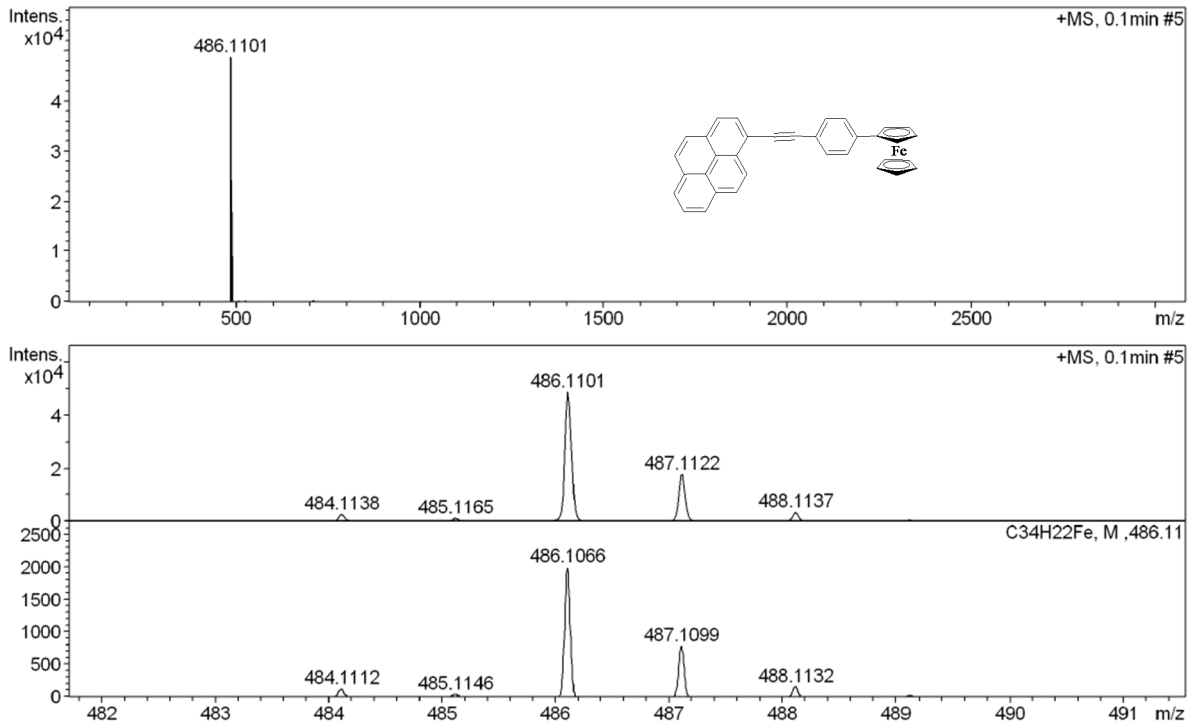
HRMS of **3b**



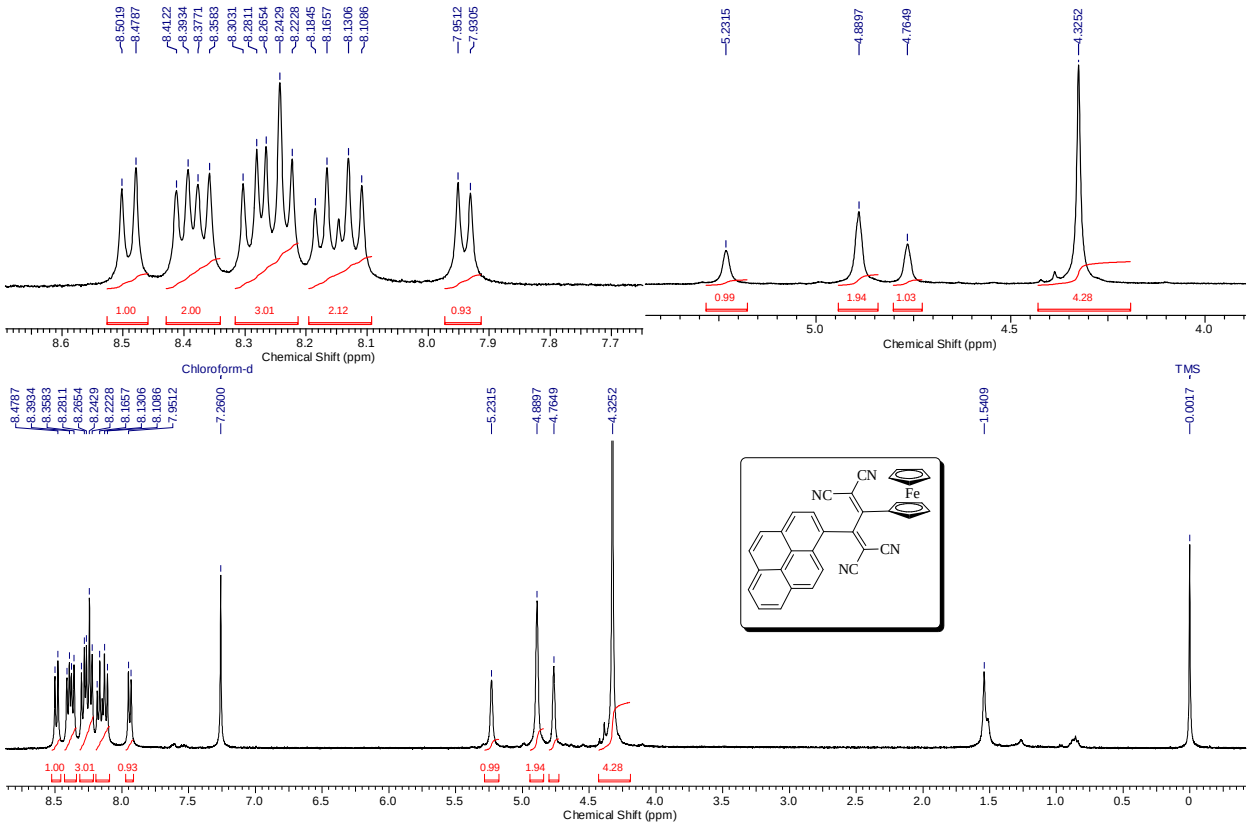
^{1}H NMR Spectra of **3c**



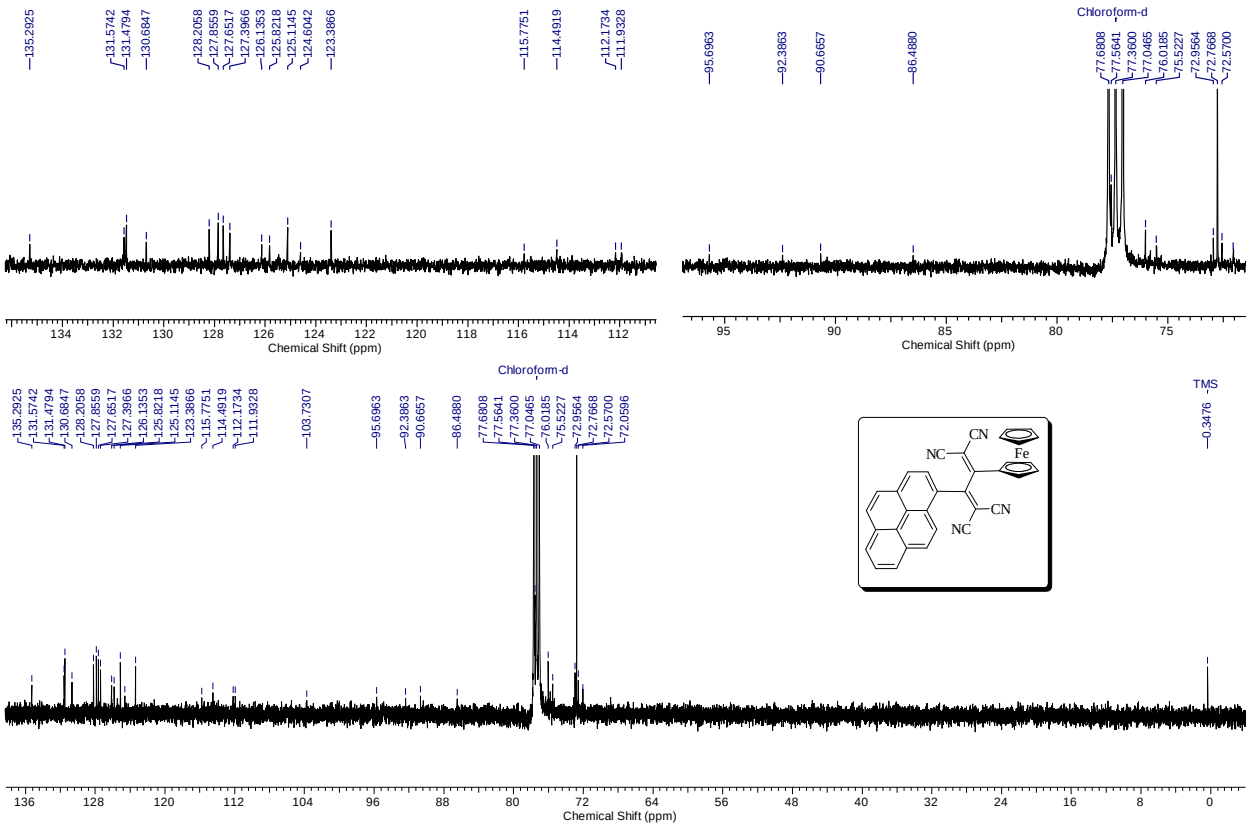
HRMS of **3c**



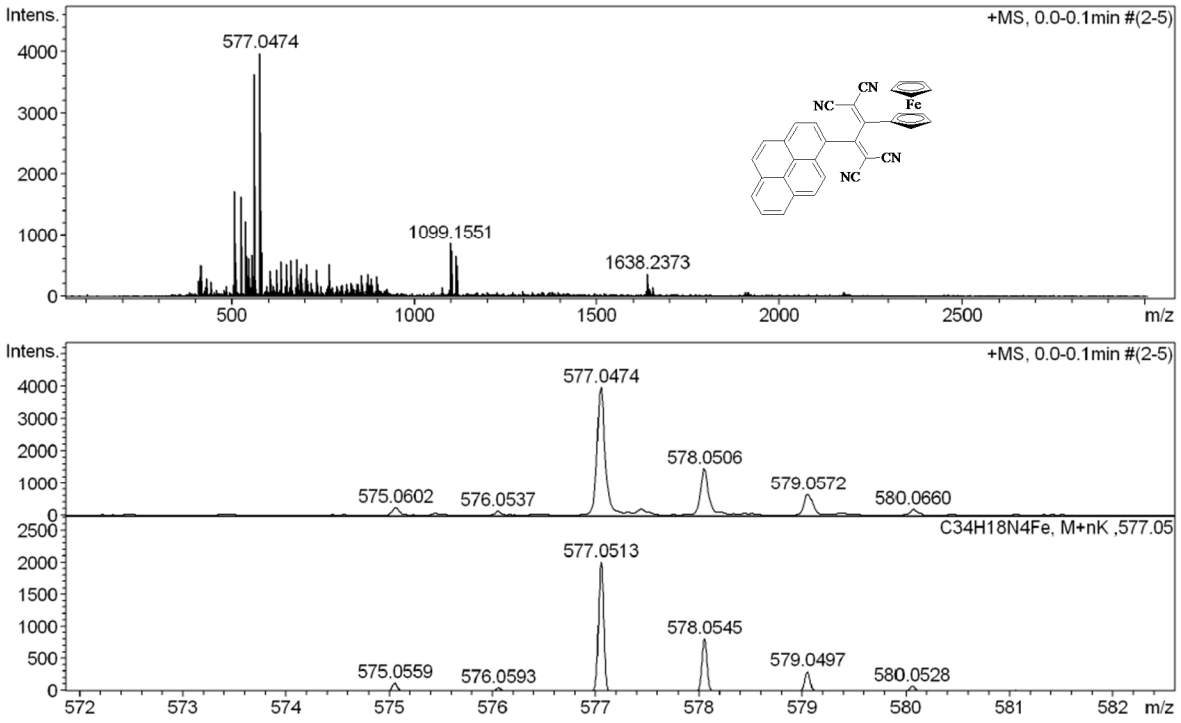
^{1}H NMR Spectra of **4a**



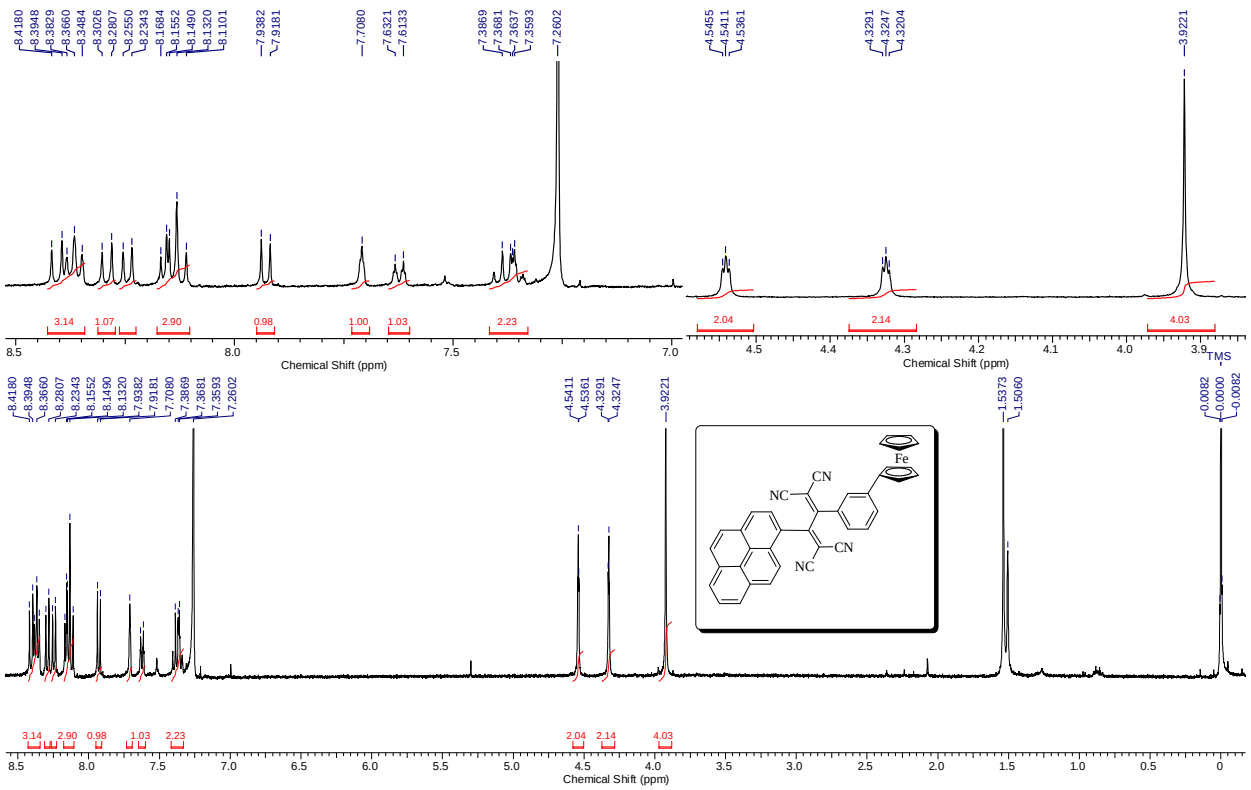
^{13}C NMR Spectra of **4a**



HRMS of **4a**



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



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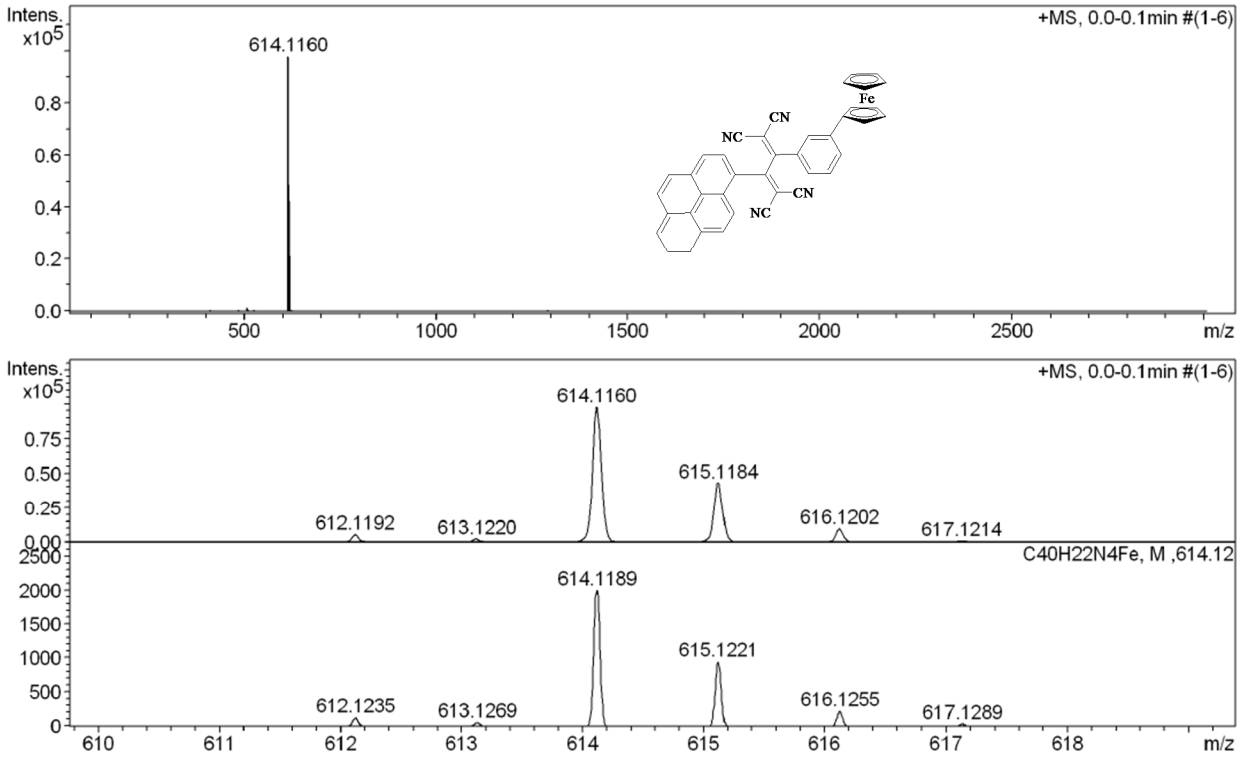

[i] (a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. 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 09, revision A.02; Gaussian, Inc.: Wallingford, CT, **2009**; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785− 789; (c) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372−1377; (c) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270-283; (d) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654-3665.