Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis, optical and electrochemical properties of new ferrocenyl substituted triphenylamine based donor-acceptor dyes for dye sensitized solar cells

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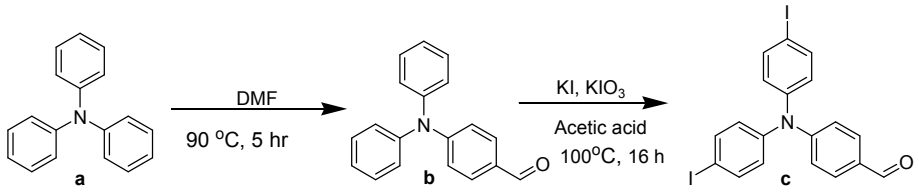
I. General Experimental.

All reagents were obtained from commercial sources, and used as received unless otherwise stated. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance (III) 400 MHz instrument by using $CDCl_3$ as solvent. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak ($CDCl_3$, 7.26 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplet), and the coupling constants, J, are given in Hz. ^{13}C NMR chemical shifts are reported relative to the solvent residual peak ($CDCl_3$, 77.36ppm). UV−visible absorption spectra were recorded on a Cary-100 Bio UV−visible spectrophotometer. Cyclic voltamograms (CVs) were recorded on a CHI620D electrochemical analyzer using glassy carbon as the working electrode, Pt wire as the counter electrode, and the saturated calomel electrode (SCE) as the reference electrode. The scan rate was 100 mV s−1. A solution of tetrabutylammonium hexafluorophosphate (TBAPF6) in CH_2Cl_2 (0.1 M) was employed as the supporting electrolyte. DCM was freshly distilled from CaH2 prior to use. All potentials were experimentally referenced against the saturated calomel electrode couple but were then manipulated to be referenced against Fc/Fc+ as recommended by IUPAC. Under our conditions, the Fc/Fc+ couple exhibited E° = 0.38 V versus SCE. HRMS was recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer. FTIR spectra of pristine dyes in KBr pellet and adsorbed onto TiO2 films were recorded on a Perkin-Elmer 16PC FTIR spectrometer.

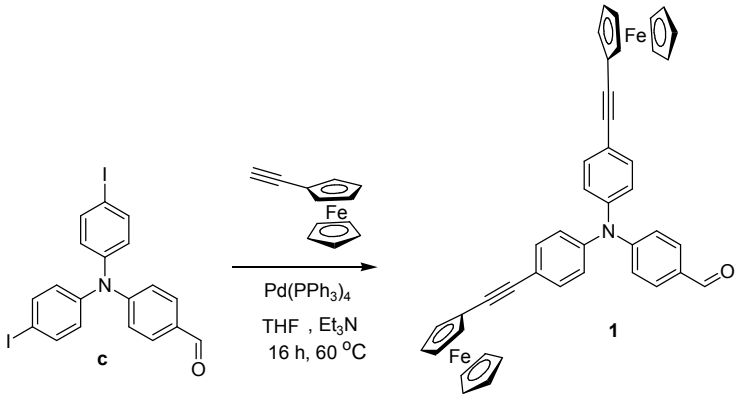
II. The synthesis of compound D1

The triphenylamine based intermediate **b** was synthesized by the Vilsmeier–Haack formylation reaction of triphenylamine **a**.[1] The monoformylation reaction selectively occurred at the para position of the phenyl ring which resulted 4-(diphenylamino)-benzaldehyde **b** in 80 % yield. The iodination reaction of **b** in the presence of potassium iodide (KI), potassium iodate (KIO_3), and acetic acid as a solvent resulted 4-(bis(4-iodophenyl)amino)-benzaldehyde **c** in 85 % yield (Scheme S1).



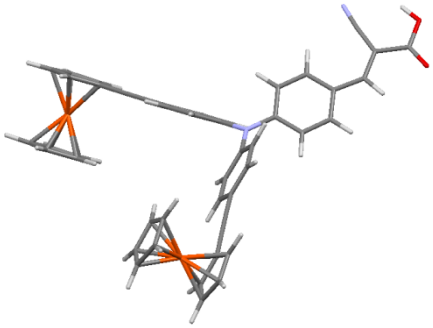
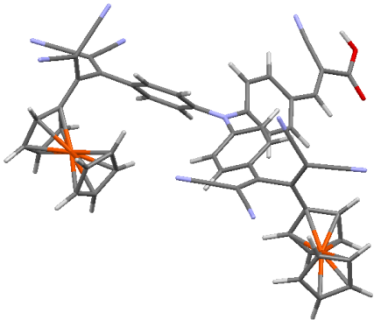
Scheme S1. Synthesis of compounds b and c

The Pd-catalyzed Sonogashira cross-coupling reaction of **c** (4-(Bis-(4-iodo-phenyl)-amino]-benzaldehyde) with ethynyl ferrocene resulted di-substituted ferrocenyl triphenylamine aldehyde **1** in 65% yield respectively (Scheme S2).



Scheme S2. Synthesis of aldehyde 1

Table S1. Optimized structures of ferrocenyl substituted triphenylamine donor–acceptor compounds D1-D2 with dihedral angles

Optimized structure D1	Two Ferrocenyl groups planarity with respected to the phenyl rings (Dihedral angle°)	Optimized structure D2	After TCNE the ferrocenyl groups planarity (Dihedral angle°)
 **D1**	2.58°, 3.55°	 **D2**	68.63°, 87.46°

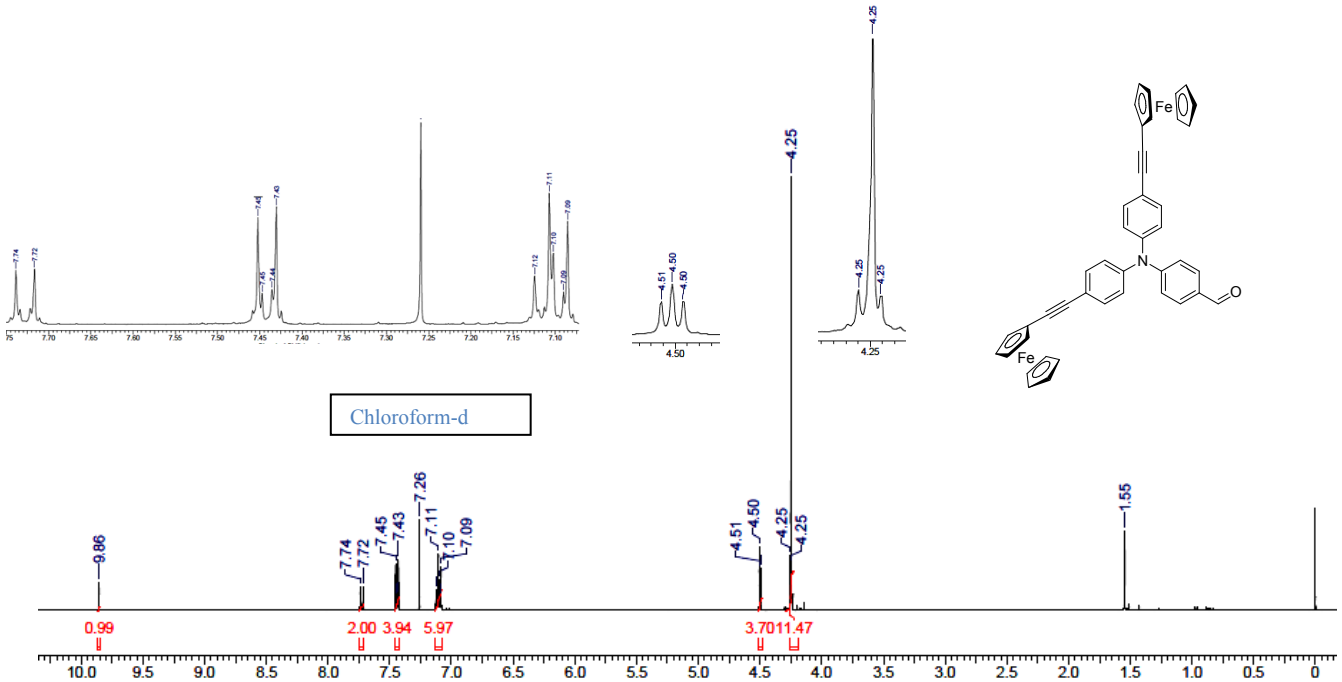


Figure S1. [1]H NMR Spectra of compound **1.**

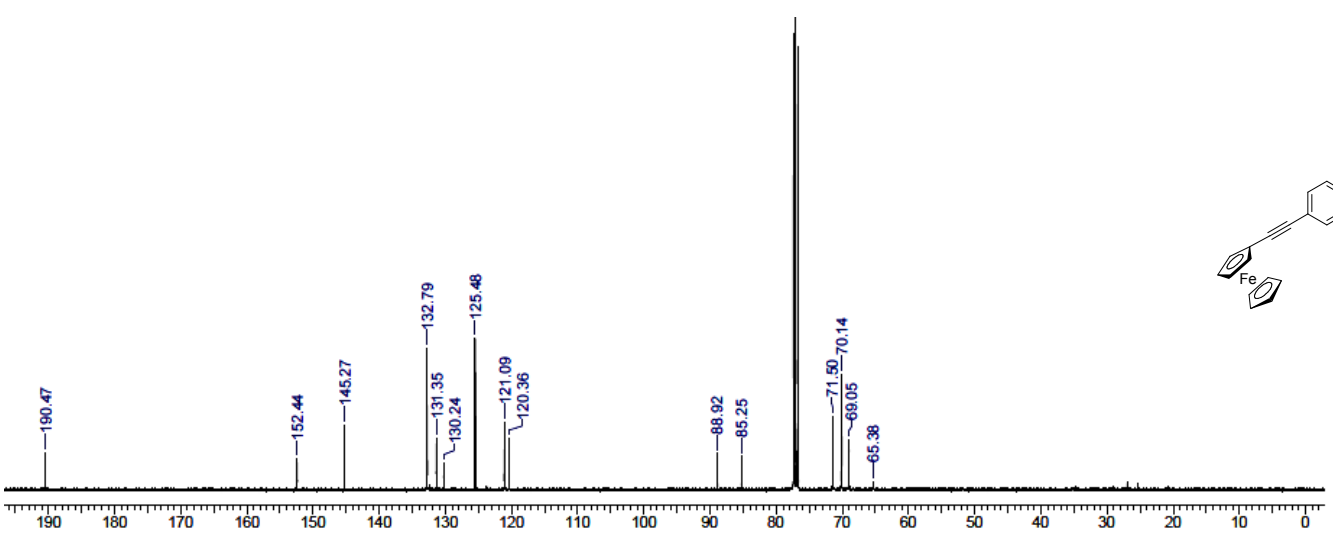


Figure S2. [13]C NMR Spectra of compound **1**.

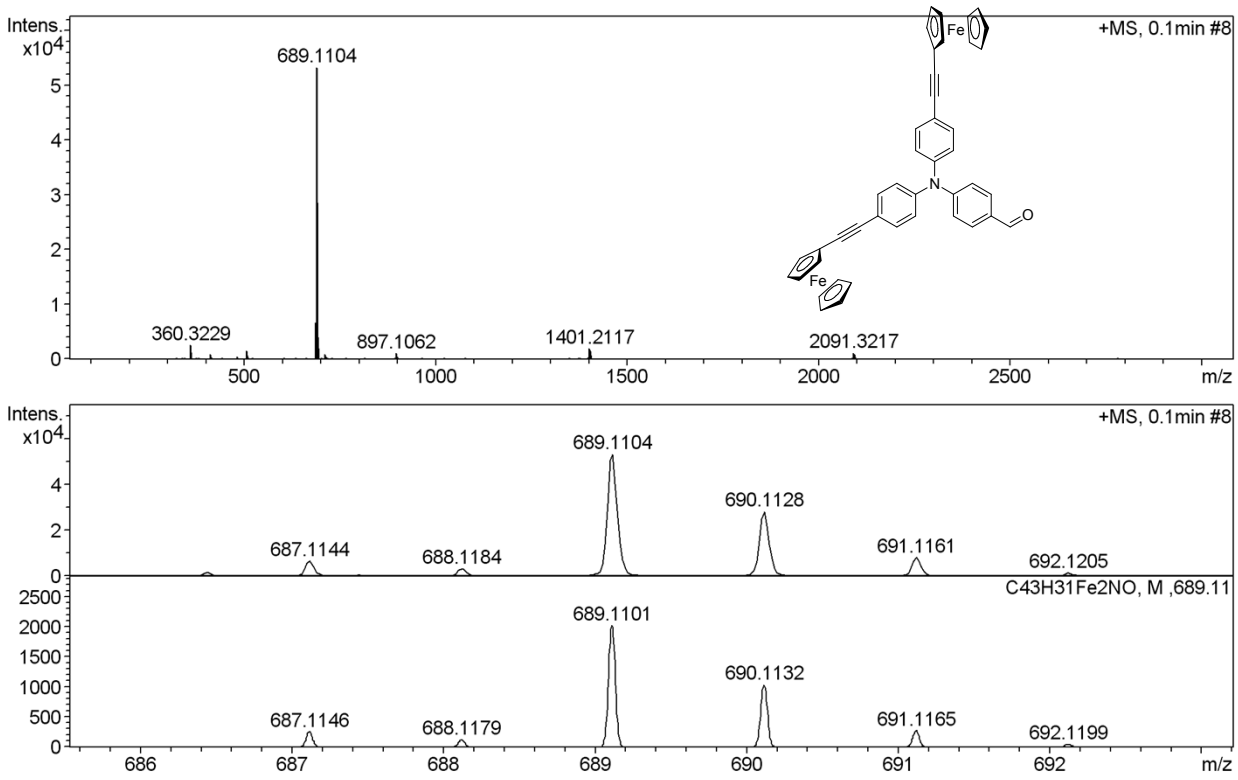


Figure S3. HRMS Spectra of **1**.

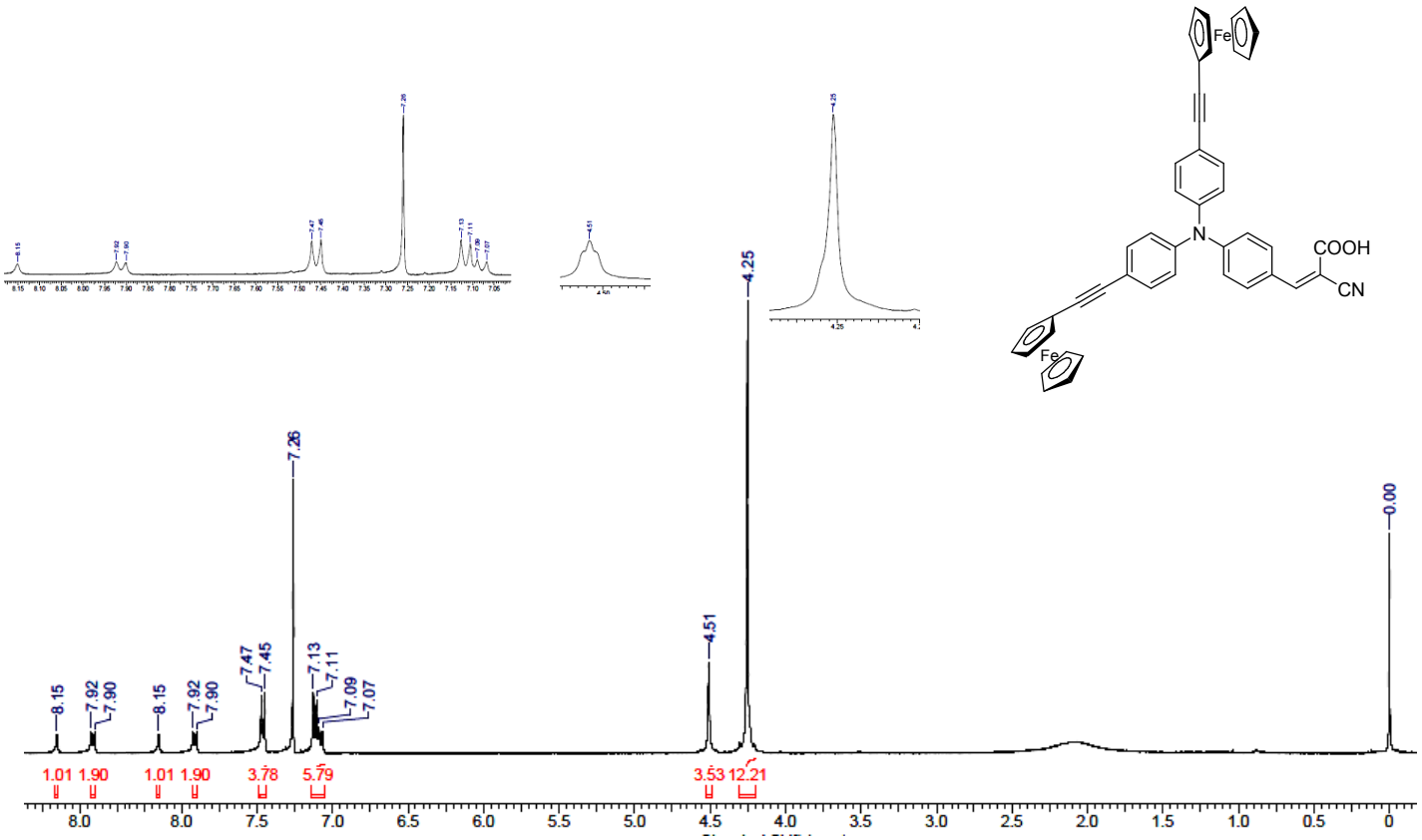


Figure S3. ^{1}H NMR Spectra of compound **D1.**

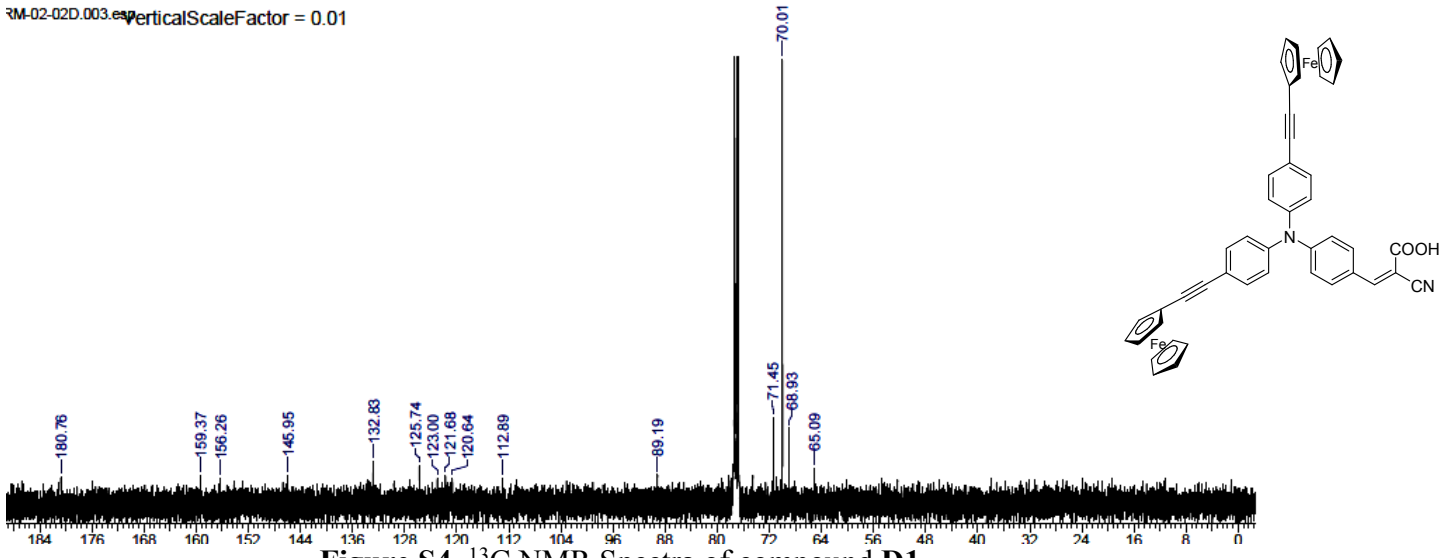


Figure S4. ^{13}C NMR Spectra of compound **D1.**

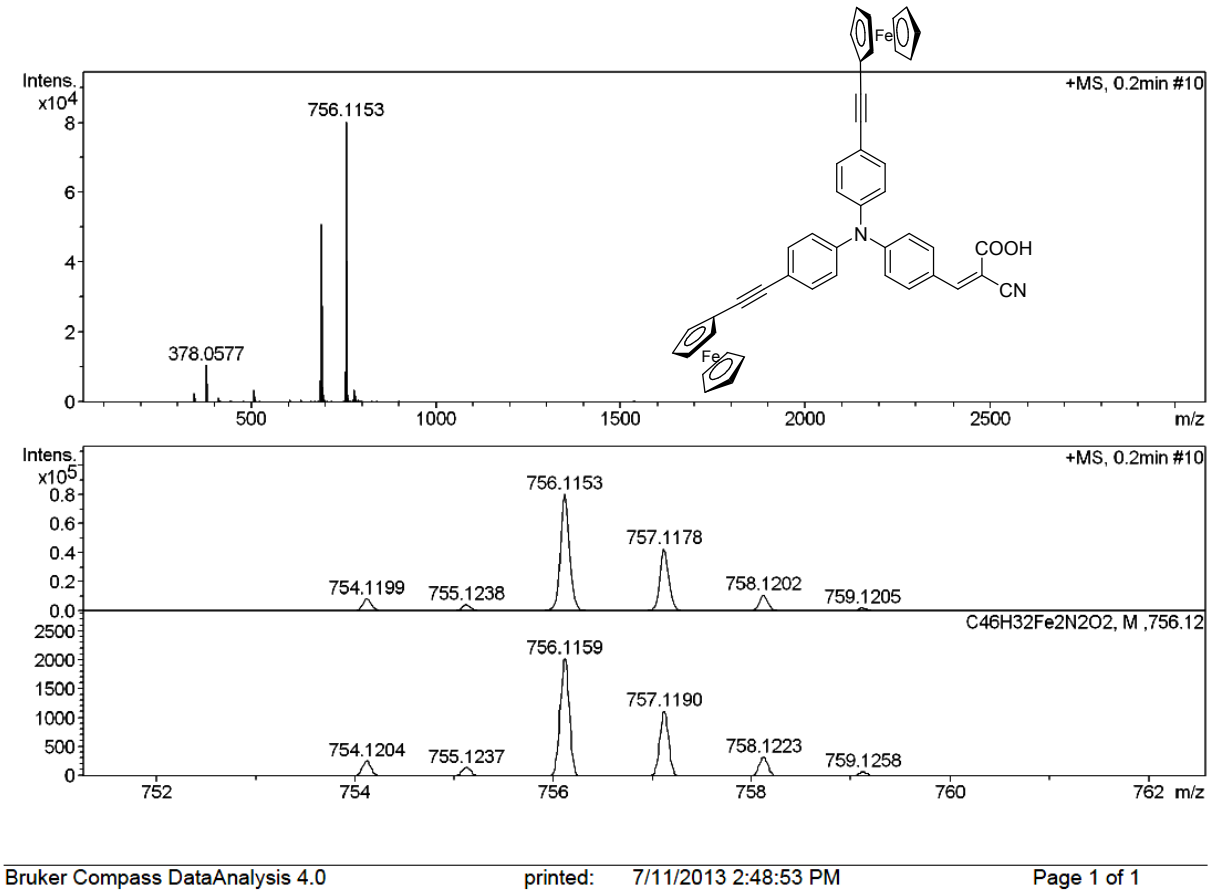
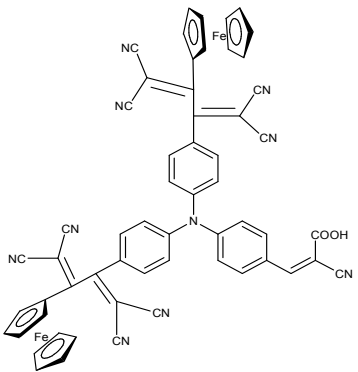


Figure S5. HRMS Spectra of **D1**.



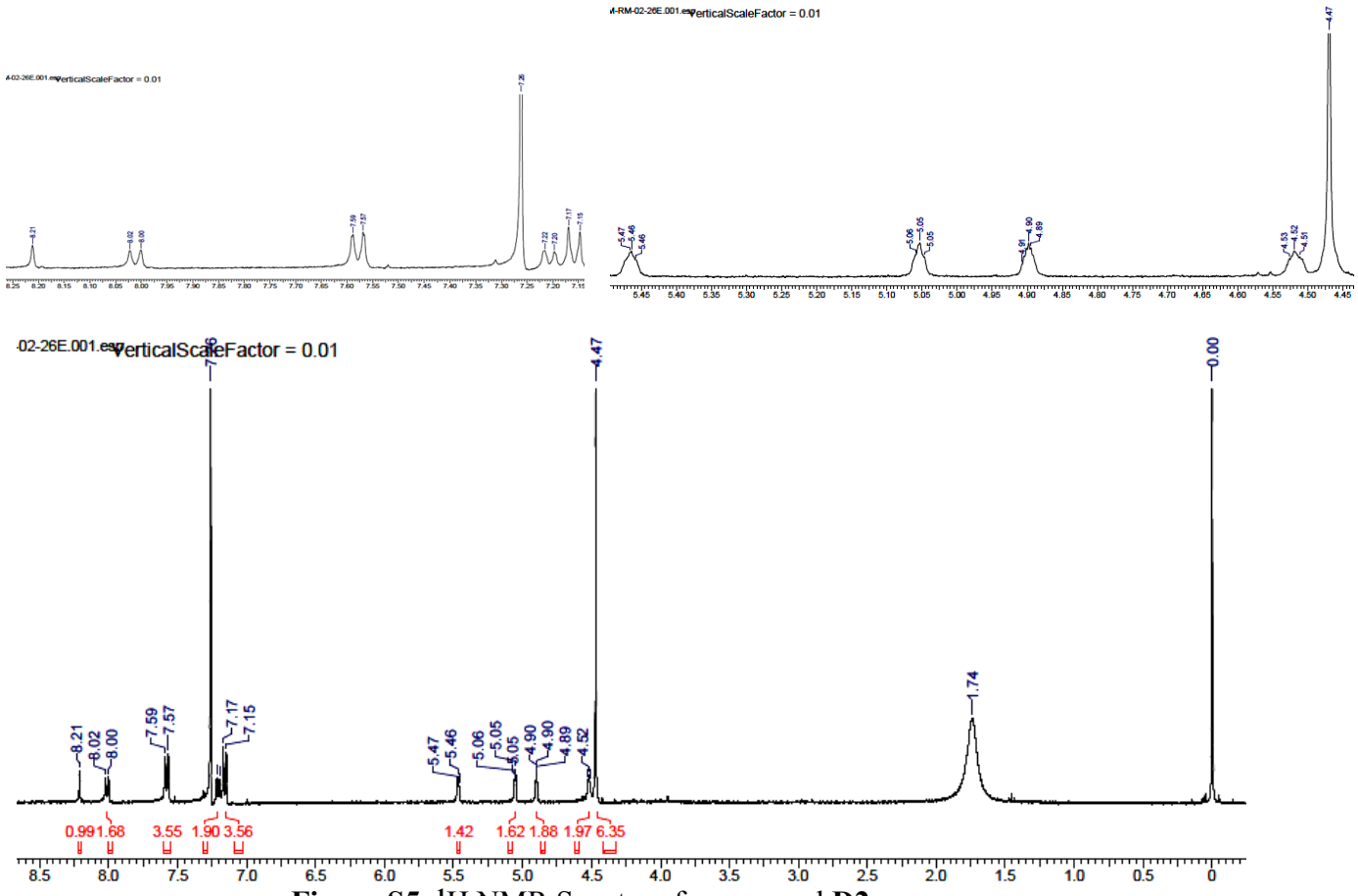


Figure S5. [1]H NMR Spectra of compound **D2**

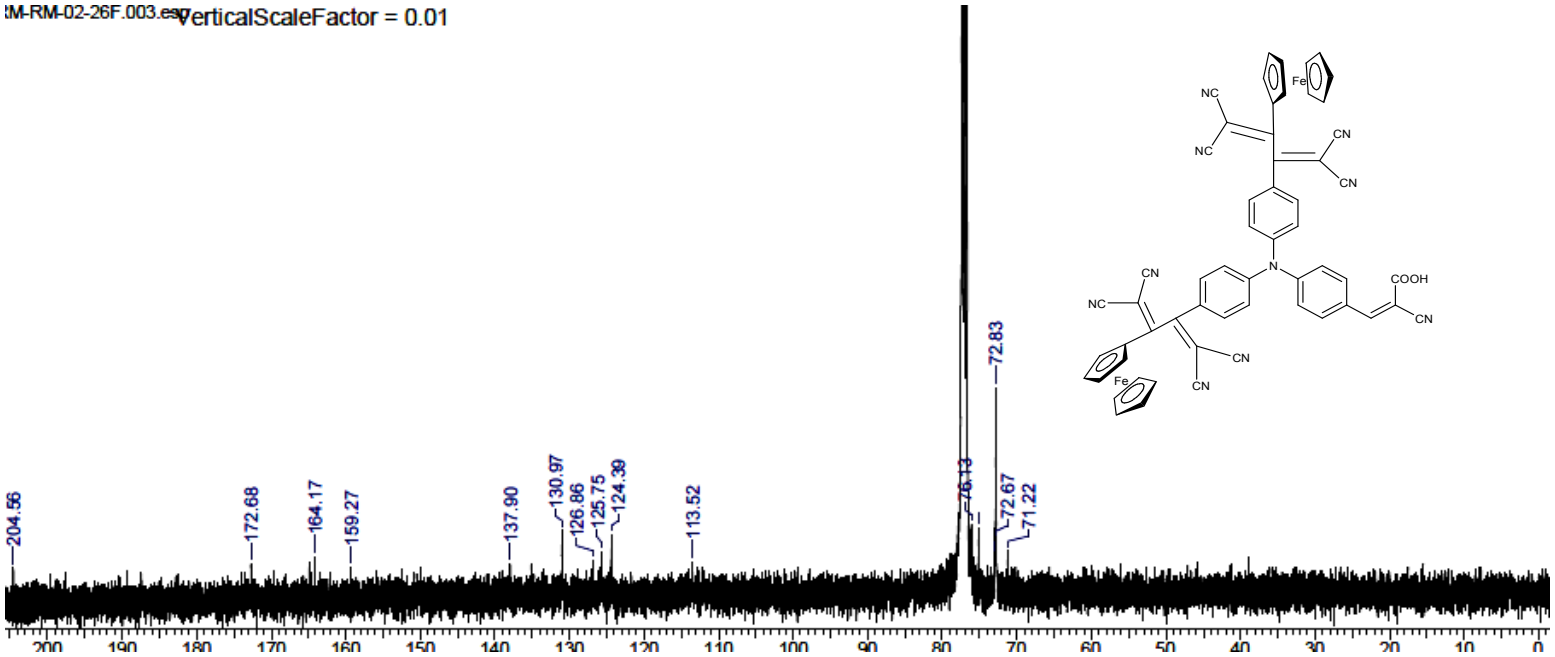


Figure S6. ^{13}C NMR Spectra of compound **D2**

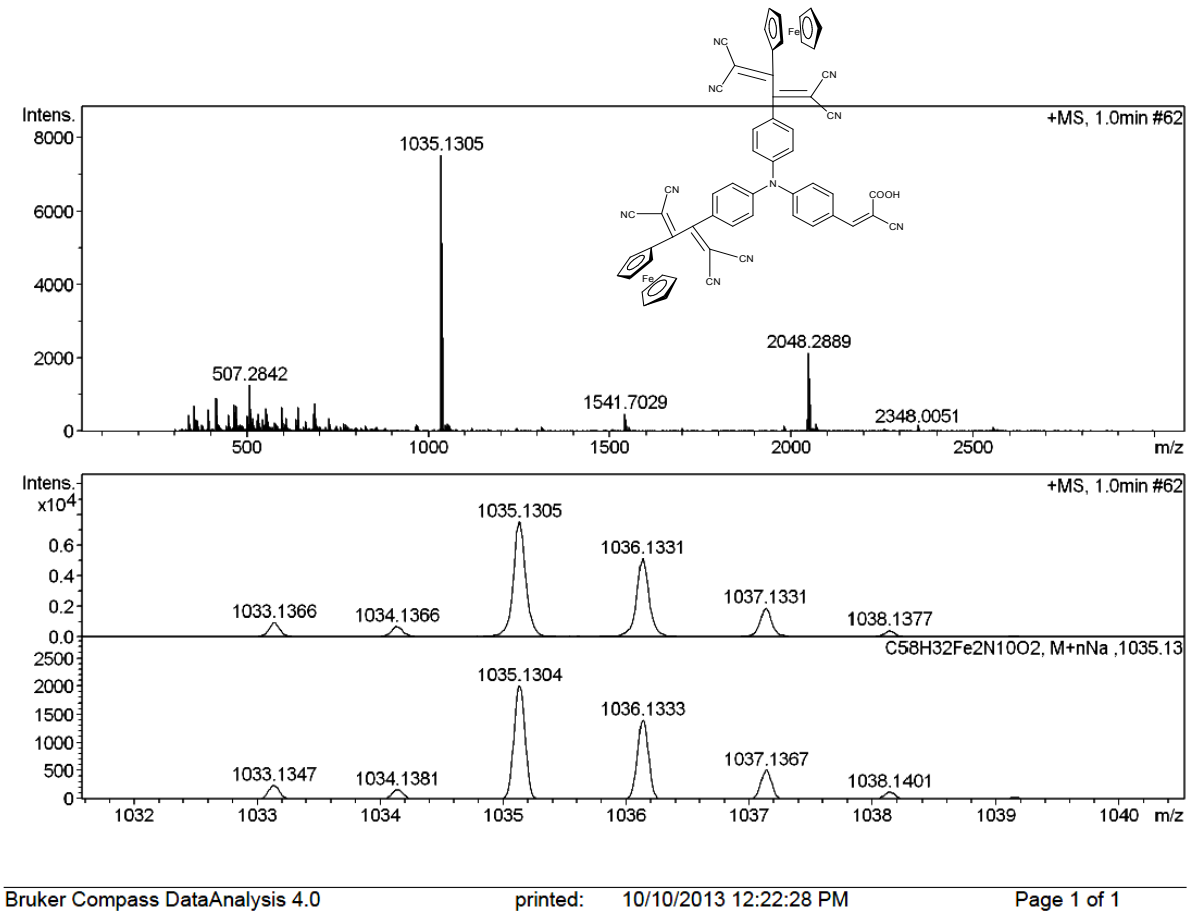


Figure S7. HRMS Spectra of **D2**

IV. DFT Calculations.

IV. DFT calculation data of the ferrocenyl substituted triphenylamine donor-acceptor compounds **D1,** and **D2** Calculation method: B3LYP/6-31+G** for C, H, N, O, and Lanl2DZ for Fe with Gaussian 09[1].

Data for compound **D1**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	8.132703	-2.981136	0.202504
2	26	0	-7.188119	-4.465702	-0.120168
3	7	0	-0.102638	2.197695	-0.126786
4	6	0	-1.243647	1.358328	0.054498
5	6	0	-1.214242	0.320852	0.998410
6	1	0	-0.324497	0.173551	1.601728
7	6	0	-2.313883	-0.511687	1.163822
8	1	0	-2.283240	-1.308588	1.899574
9	6	0	-3.483862	-0.327047	0.397813
10	6	0	-3.502856	0.720192	-0.547202
11	1	0	-4.390807	0.870806	-1.152307
12	6	0	-2.398047	1.543564	-0.722091
13	1	0	-2.423230	2.335257	-1.463797
14	6	0	-4.614449	-1.173332	0.569175
15	6	0	-5.589143	-1.886596	0.716587

16	6	0	-0.239511	3.590570	-0.178566
17	6	0	-1.290065	4.239414	0.511266
18	1	0	-1.986011	3.650487	1.097098
19	6	0	-1.432462	5.613578	0.463156
20	1	0	-2.244189	6.067468	1.018957
21	6	0	-0.533092	6.420193	-0.274507
22	6	0	-0.598365	7.855457	-0.384508
23	1	0	0.181822	8.316638	-0.988093
24	6	0	0.514659	5.758672	-0.956863
25	1	0	1.215007	6.348620	-1.542059
26	6	0	0.664394	4.384281	-0.917228
27	1	0	1.471140	3.912060	-1.465290
28	6	0	1.175501	1.578831	-0.267780
29	6	0	1.335085	0.474600	-1.118840
30	1	0	0.483706	0.107409	-1.682339
31	6	0	2.571428	-0.146112	-1.242841
32	1	0	2.685253	-0.996663	-1.906902
33	6	0	3.693337	0.323589	-0.528601
34	6	0	3.521996	1.434610	0.323661
35	1	0	4.371014	1.803002	0.890114
36	6	0	2.282287	2.046232	0.458631
37	1	0	2.164062	2.890024	1.130521
38	6	0	4.962057	-0.305750	-0.662902
39	6	0	6.049918	-0.836403	-0.787559
40	6	0	7.320760	-1.443529	-0.945906

41	6	0	8.554170	-1.019545	-0.332616
42	1	0	8.652452	-0.197010	0.361462
43	6	0	9.594478	-1.877246	-0.787707
44	1	0	10.631586	-1.828184	-0.486069
45	6	0	9.023573	-2.841381	-1.673694
46	1	0	9.553356	-3.649214	-2.159137
47	6	0	7.627291	-2.584403	-1.771592
48	1	0	6.906202	-3.146025	-2.348235
49	6	0	7.938928	-3.072245	2.268680
50	1	0	8.021120	-2.217563	2.925891
51	6	0	9.013967	-3.910024	1.841217
52	1	0	10.053849	-3.799730	2.116645
53	6	0	8.481816	-4.890604	0.950813
54	1	0	9.047738	-5.654062	0.434763
55	6	0	7.077749	-4.659137	0.827592
56	1	0	6.394251	-5.217054	0.202440
57	6	0	6.742586	-3.536602	1.643303
58	1	0	5.764694	-3.082910	1.729069
59	6	0	-6.733677	-2.703334	0.894693
60	6	0	-7.988711	-2.576396	0.197497
61	1	0	-8.197416	-1.855463	-0.580092
62	6	0	-8.878199	-3.566775	0.700050
63	1	0	-9.888948	-3.741109	0.358053
64	6	0	-8.190043	-4.319519	1.700135
65	1	0	-8.589413	-5.162200	2.247300

66	6	0	-6.871211	-3.798893	1.820921
67	1	0	-6.092430	-4.158782	2.478166
68	6	0	-7.167679	-6.462775	-0.700380
69	1	0	-7.636304	-7.263104	-0.144274
70	6	0	-7.789485	-5.665928	-1.708511
71	1	0	-8.811665	-5.757136	-2.049407
72	6	0	-6.838944	-4.697615	-2.154594
73	1	0	-7.014220	-3.928468	-2.894158
74	6	0	-5.629425	-4.897758	-1.423043
75	1	0	-4.736004	-4.292912	-1.495986
76	6	0	-5.832192	-5.987637	-0.523756
77	1	0	-5.111738	-6.366348	0.188170
78	6	0	-1.467659	8.775685	0.131151
79	6	0	-2.588365	8.478280	0.956574
80	6	0	-1.224673	10.224731	-0.198387
81	8	0	-0.303629	10.594152	-0.890853
82	1	0	-2.777399	10.676413	0.852358
83	8	0	-2.095556	11.118113	0.320945
84	7	0	-3.527072	8.335180	1.636004

Total energy (Sum of electronic and zero-point energies): -2278.8929149

Data for compound **D2**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	-4.605857	-3.537002	-1.576459
2	26	0	7.432169	-1.211237	-1.067112
3	7	0	-0.661189	1.843569	0.100933
4	6	0	0.461652	0.995414	0.267934
5	6	0	0.487514	-0.275234	-0.333531
6	1	0	-0.335666	-0.590328	-0.964889
7	6	0	1.559498	-1.130077	-0.132352
8	1	0	1.552477	-2.091824	-0.629489
9	6	0	2.656574	-0.747525	0.667203
10	6	0	2.644540	0.550767	1.219563
11	1	0	3.469951	0.881098	1.840107
12	6	0	1.564701	1.402229	1.037861
13	1	0	1.562058	2.378051	1.510386
14	6	0	3.786291	-1.648229	0.938861
15	6	0	5.134383	-1.009485	1.135028
16	6	0	-0.479140	3.236219	-0.096940
17	6	0	0.553763	3.706809	-0.925461
18	1	0	1.208086	3.001486	-1.425928
19	6	0	0.726703	5.069644	-1.111254
20	1	0	1.523696	5.419041	-1.761489

21	6	0	-0.118170	6.016432	-0.491535
22	6	0	0.147114	7.416211	-0.758076
23	6	0	-1.153546	5.527326	0.336272
24	1	0	-1.821662	6.212019	0.844256
25	6	0	-1.327983	4.166325	0.532234
26	1	0	-2.120356	3.815612	1.184139
27	6	0	-1.967661	1.297652	0.173037
28	6	0	-2.267894	0.283467	1.098596
29	1	0	-1.502072	-0.070179	1.779566
30	6	0	-3.543027	-0.258847	1.159016
31	1	0	-3.745181	-1.026441	1.895851
32	6	0	-4.580569	0.215242	0.330430
33	6	0	-4.267285	1.231290	-0.595581
34	1	0	-5.022860	1.596703	-1.280559
35	6	0	-2.984807	1.755097	-0.682646
36	1	0	-2.766301	2.519327	-1.420153
37	6	0	-5.938223	-0.346002	0.437012
38	6	0	-6.083294	-1.822850	0.708548
39	6	0	-6.158903	-2.684990	-0.459391
40	6	0	-6.165964	-2.197110	-1.824375
41	1	0	-6.057800	-1.166314	-2.127374
42	6	0	-6.358850	-3.298538	-2.693356
43	1	0	-6.394415	-3.252334	-3.772735
44	6	0	-6.445252	-4.481408	-1.899396
45	1	0	-6.555272	-5.490013	-2.272806

46	6	0	-6.305599	-4.123920	-0.534749
47	1	0	-6.318132	-4.811111	0.295158
48	6	0	-2.788092	-2.585605	-1.887393
49	1	0	-2.686901	-1.514871	-1.999508
50	6	0	-3.038462	-3.521192	-2.936739
51	1	0	-3.159863	-3.284791	-3.985041
52	6	0	-3.162091	-4.817322	-2.351631
53	1	0	-3.389096	-5.732895	-2.880254
54	6	0	-2.979662	-4.686963	-0.941515
55	1	0	-3.037368	-5.484589	-0.214339
56	6	0	-2.746462	-3.311519	-0.656544
57	1	0	-2.595263	-2.887614	0.325522
58	6	0	5.760678	-0.470679	-0.061925
59	6	0	6.794053	0.539813	-0.172904
60	1	0	7.293824	1.034757	0.644545
61	6	0	7.025588	0.779889	-1.551756
62	1	0	7.752211	1.472804	-1.952614
63	6	0	6.182455	-0.085257	-2.313969
64	1	0	6.164563	-0.167294	-3.391678
65	6	0	5.409624	-0.857750	-1.411248
66	1	0	4.688294	-1.615789	-1.680849
67	6	0	8.563062	-2.438081	-2.302411
68	1	0	8.444469	-2.488150	-3.376200
69	6	0	9.412436	-1.534079	-1.595171
70	1	0	10.046388	-0.779228	-2.040046

71	6	0	9.240436	-1.767998	-0.196272
72	1	0	9.714262	-1.221765	0.607473
73	6	0	8.289682	-2.818873	-0.042587
74	1	0	7.914188	-3.214499	0.890143
75	6	0	7.865394	-3.230581	-1.341126
76	1	0	7.131092	-3.995546	-1.550443
77	6	0	5.618572	-0.915587	2.420936
78	6	0	3.686594	-3.015672	1.026029
79	6	0	-7.088662	0.384228	0.285283
80	6	0	-6.193970	-2.213653	2.024192
81	6	0	-7.118086	1.806216	0.100243
82	6	0	-8.379379	-0.242282	0.324329
83	6	0	6.898719	-0.362773	2.742267
84	6	0	4.857621	-1.368379	3.547897
85	6	0	4.838100	-3.848154	1.221349
86	6	0	2.450570	-3.740058	0.958302
87	7	0	7.939474	0.074639	3.025400
88	7	0	4.249324	-1.708116	4.480067
89	7	0	5.749253	-4.557385	1.363938
90	7	0	1.472393	-4.368439	0.912178
91	7	0	-7.184988	2.957450	-0.053067
92	7	0	-9.433939	-0.732980	0.338391
93	6	0	-6.166484	-1.252414	3.087394
94	6	0	-6.319419	-3.572919	2.452263
95	7	0	-6.404456	-4.670256	2.830494

96	7	0	-6.127419	-0.485684	3.962272
97	1	0	0.974227	7.617576	-1.436783
98	6	0	-0.451108	8.555120	-0.312734
99	6	0	0.099629	9.871853	-0.812507
100	6	0	-1.551834	8.612240	0.589901
101	7	0	-2.447254	8.761023	1.322921
102	8	0	1.032041	9.933384	-1.579321
103	8	0	-0.501835	10.989801	-0.360720
104	1	0	-1.232118	10.784253	0.245116

Total energy (Sum of electronic and zero-point energies): -3174.0415687

[1] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652; b) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B.* **1988**, *37*, 785-789.