Electronic Supplementary Material (ESI) for RSC Advances.

Heteroatom–Connected Ferrocenyl Substituted Naphthalimides

T. Sheshashena Reddy, Ramesh Maragani, Bhausaheb Dhokale, Shaikh M. Mobin, Rajneesh Misra*

Department of Chemistry,
Indian Institute of Technology Indore,
Indore 452017, India.

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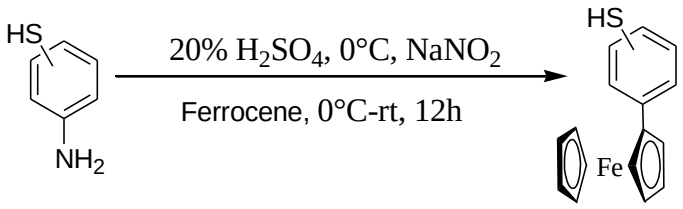
Experimental section:

All the chemicals were purchased from commercial sources and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were performed on 400 MHz and 100 MHz Bruker Ultra shield (Avance–III) Nano Bay spectrometer. All the spectra were recorded at 298K.^{1}H NMR data are reported as follows: s: singlet, d: doublet, t: triplet, bs: broad singlet and coupling constants, *J*, are given in Hz. Chemical shifts in ^{1}H NMR and ^{13}C NMR spectra were reported in parts per million (ppm) with TMS (0 ppm) and CDCl3 (77.00) as standards. TLC analysis was carried out using silica gel 60 F_{254} plates. UV–vis absorption spectra of all compounds were recorded in DCM. Cyclic voltamograms (CVs) were recorded on electrochemical analyzer using Glassy carbon as working electrode, Pt wire as the counter electrode and saturated Calomel electrode (SCE) as the reference electrode. The scan rate was 100 mVs^{-1} for CV. A solution of tetrabutylammoniumhexafluorophosphate (TBAPF6) in DCM (0.1 M) was employed as the supporting electrolyte. DCM was freshly distilled from CaH_2 prior to use. All potentials were experimentally referenced against the saturated calomel electrode couple. HRMS was recorded on TOF–Q mass spectrometer.

Scheme S1: Synthesis of ferrocenylthiophenols **c**, **d**.



Copies of ^{1}H, ^{13}C and HRMS spectra of the new compounds:

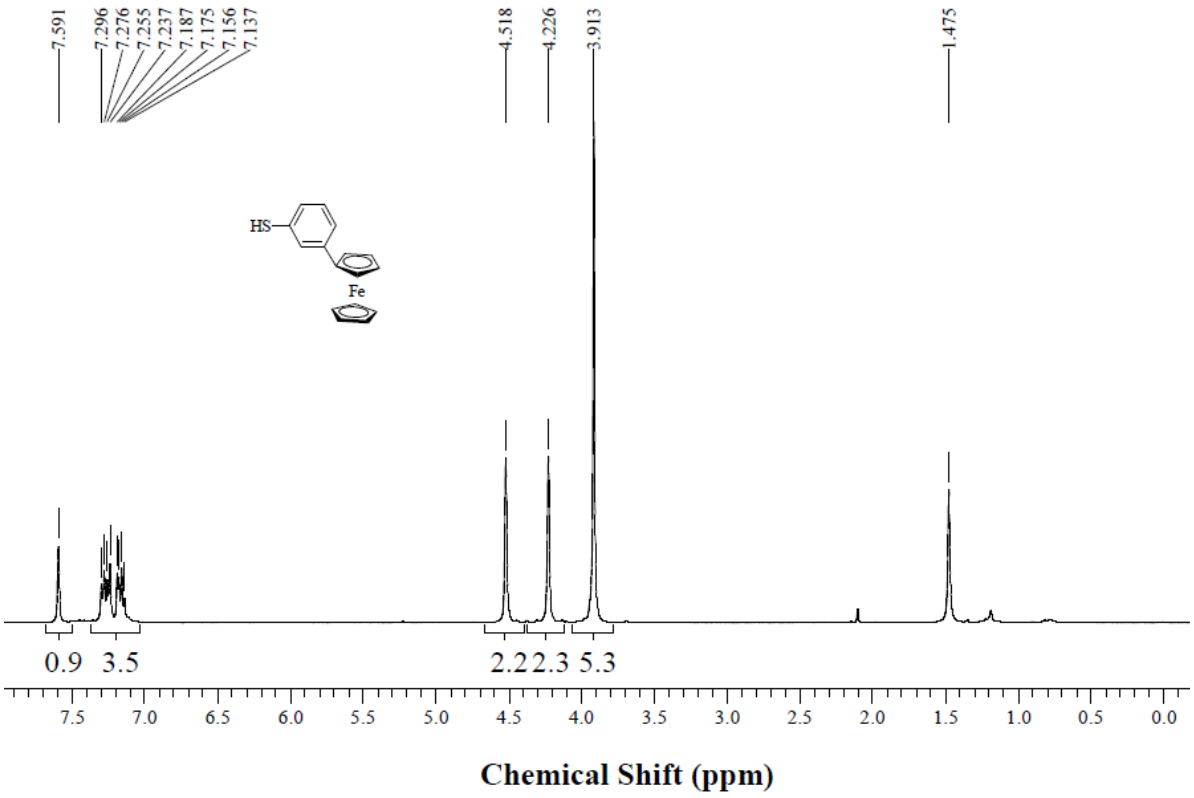


Figure S1: ^{1}H–NMR spectrum of **c**.

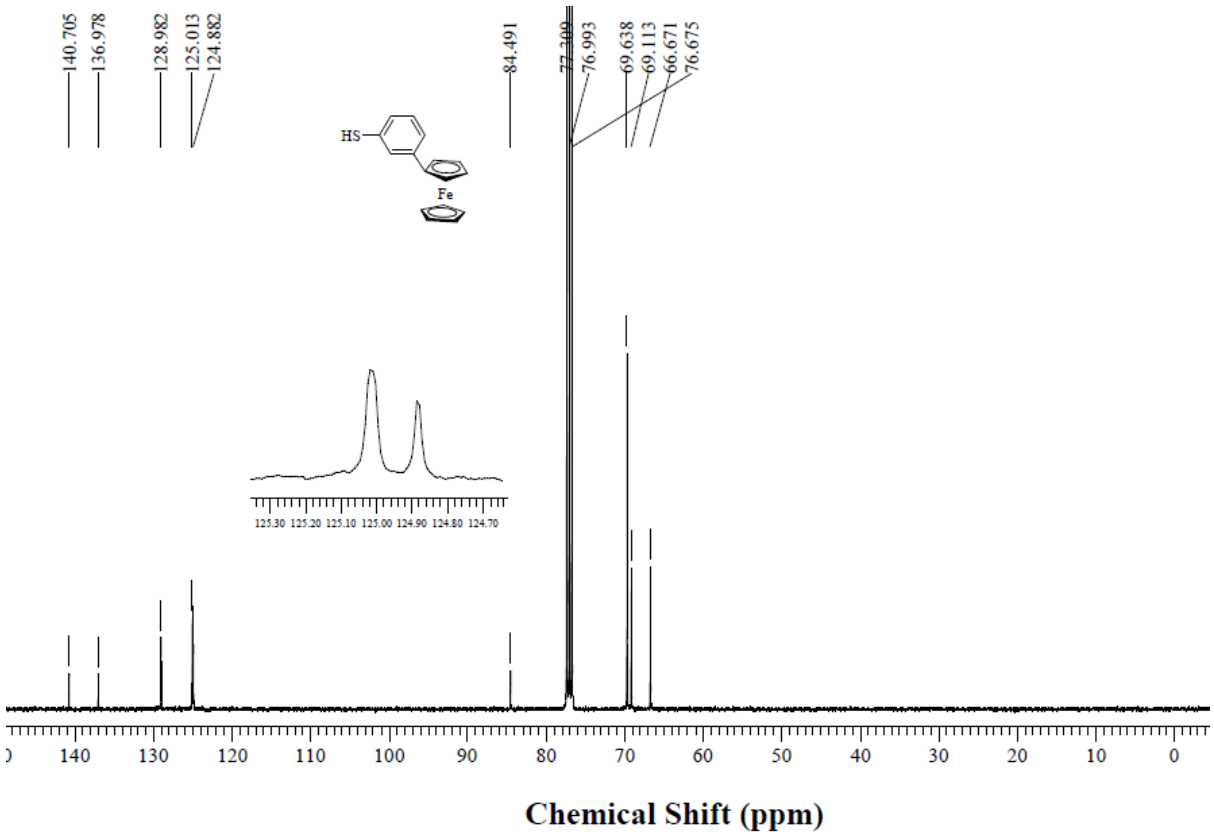


Figure S2: ^{13}C–NMR spectrum of **c**.

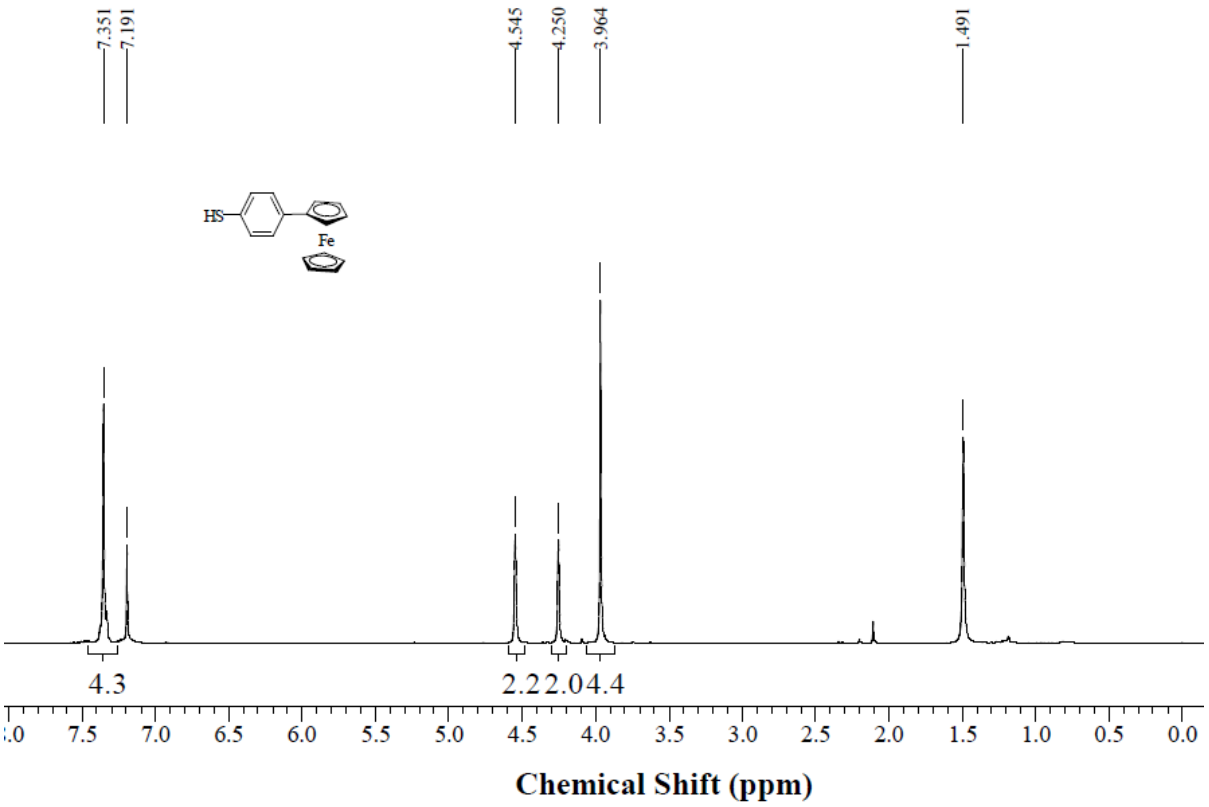


Figure S3: ^{1}H–NMR spectrum of **d**.

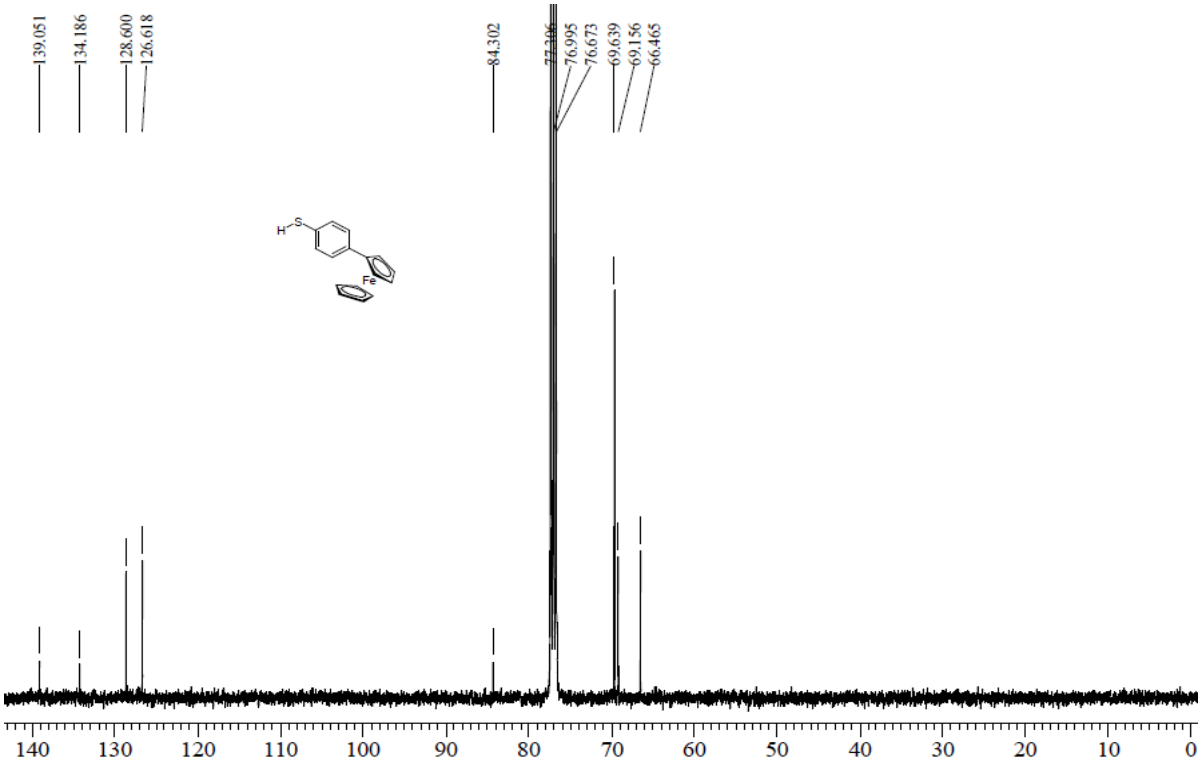


Figure S4: ^{13}C–NMR spectrum of **d**.

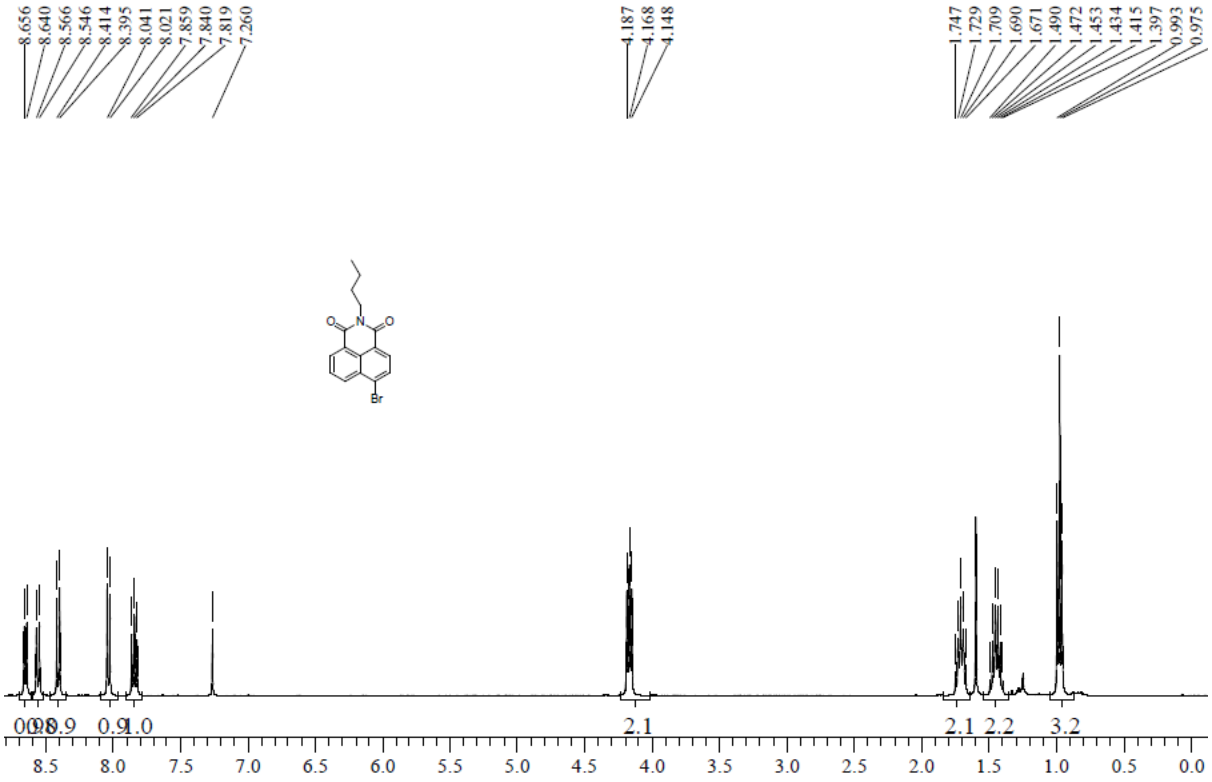


Figure S5: ^{1}H–NMR spectrum of **2**.

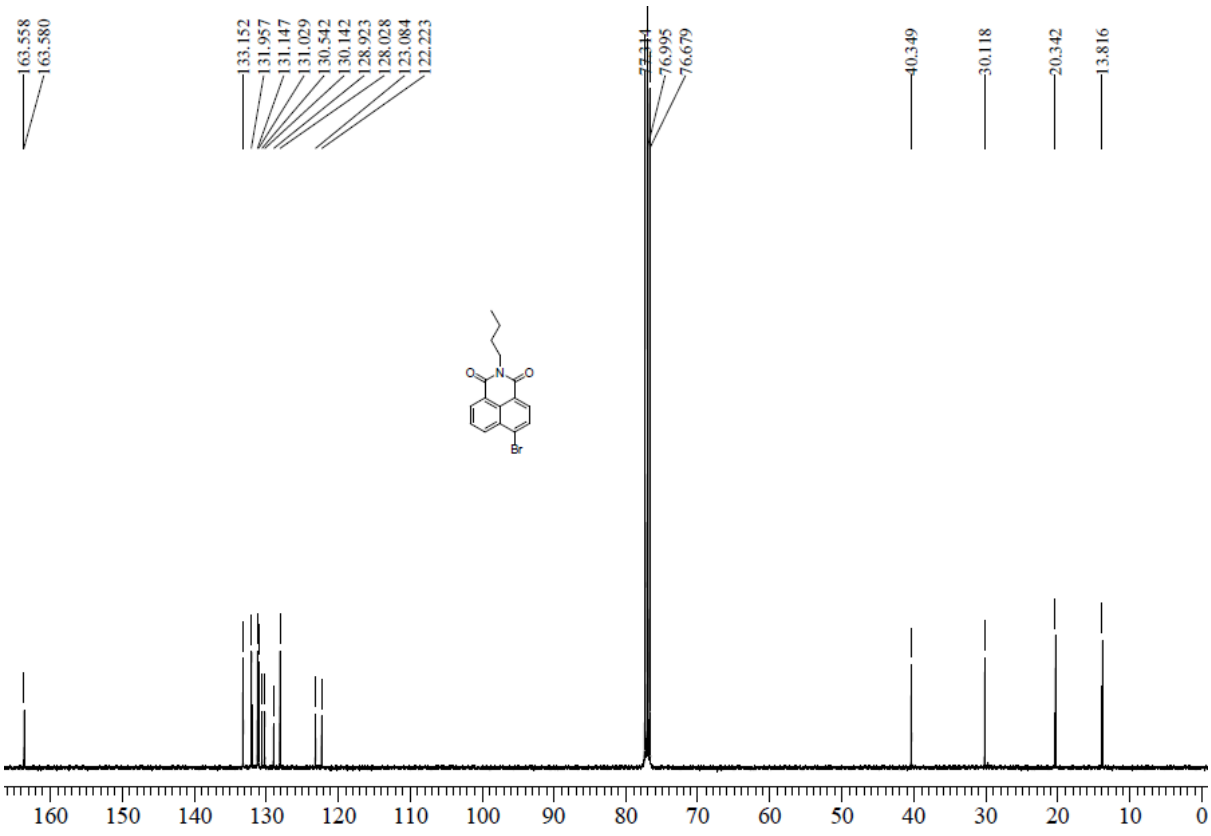


Figure S6: ^{13}C–NMR spectrum of **2**.

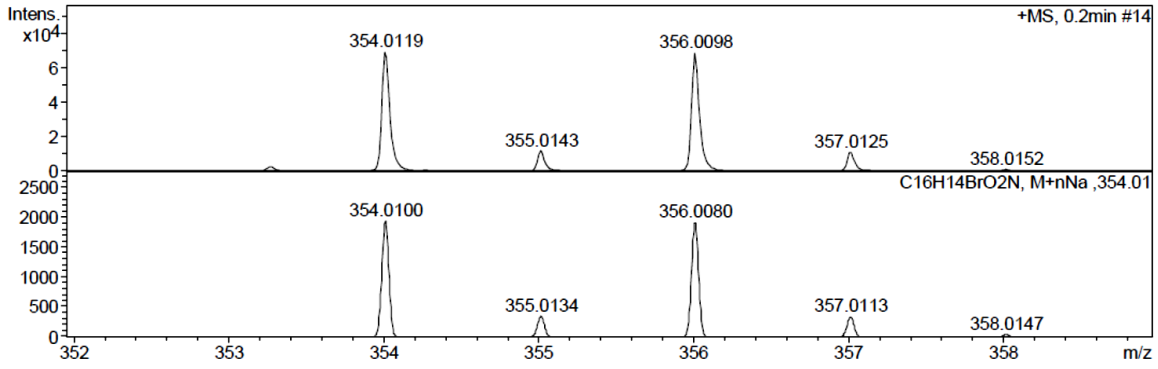
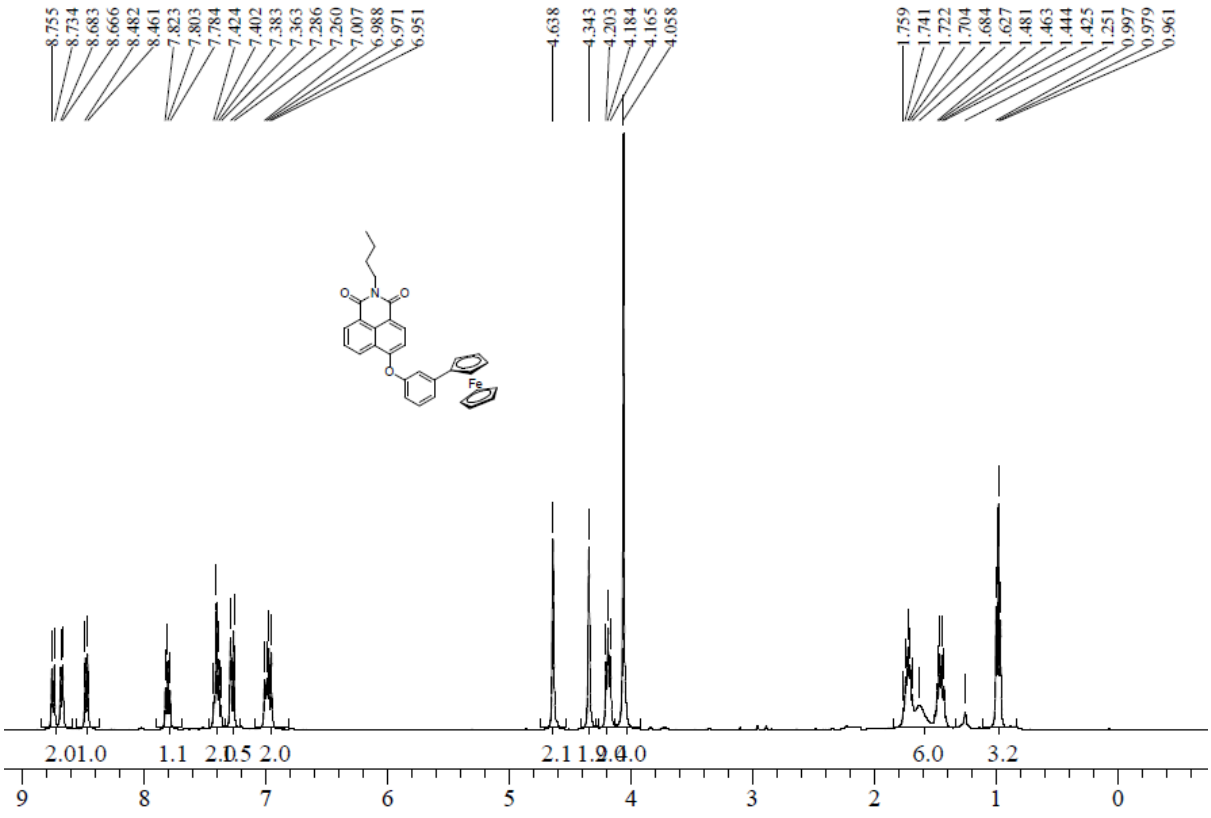


Figure S7: HRMS of **2**.



Chemical Shift (ppm)

Figure S8: ^{1}H–NMR spectrum of **3a**.

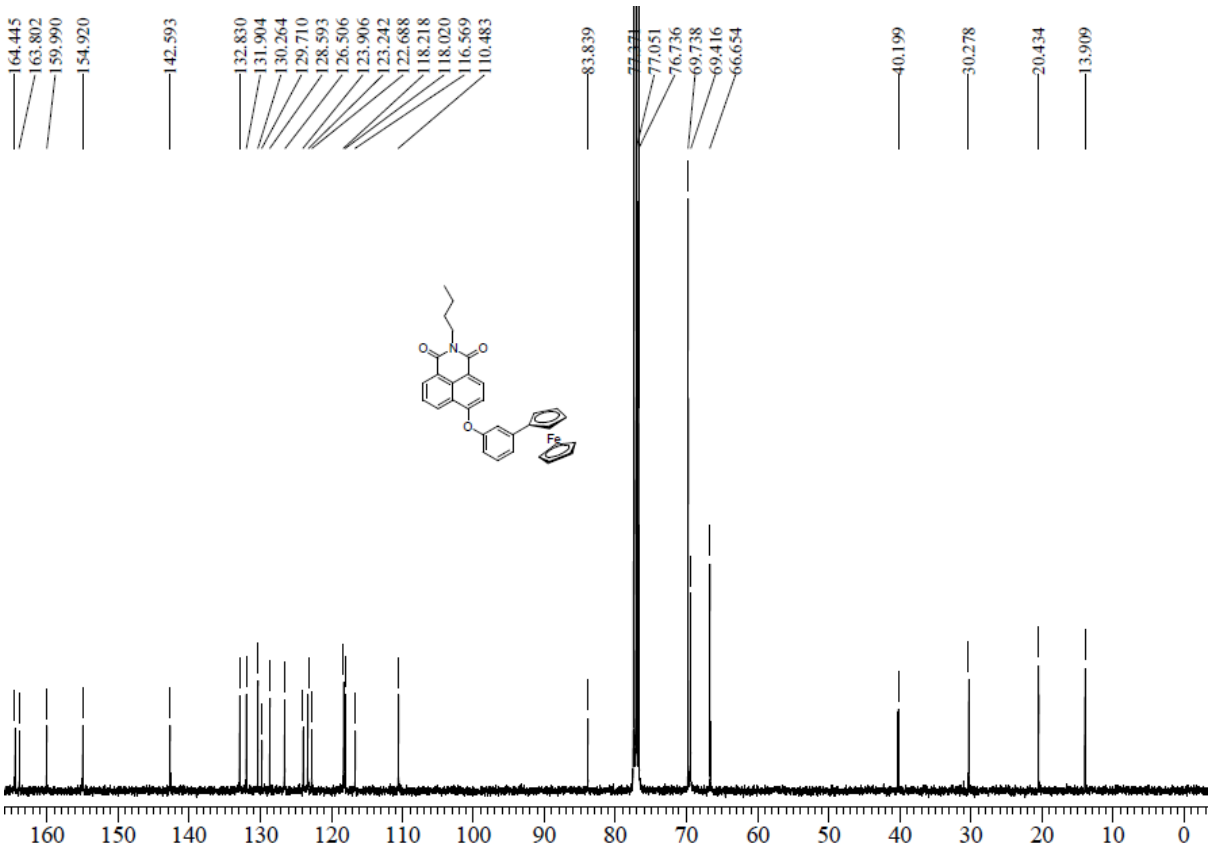


Figure S9: ^{13}C–NMR spectrum of **3a**.

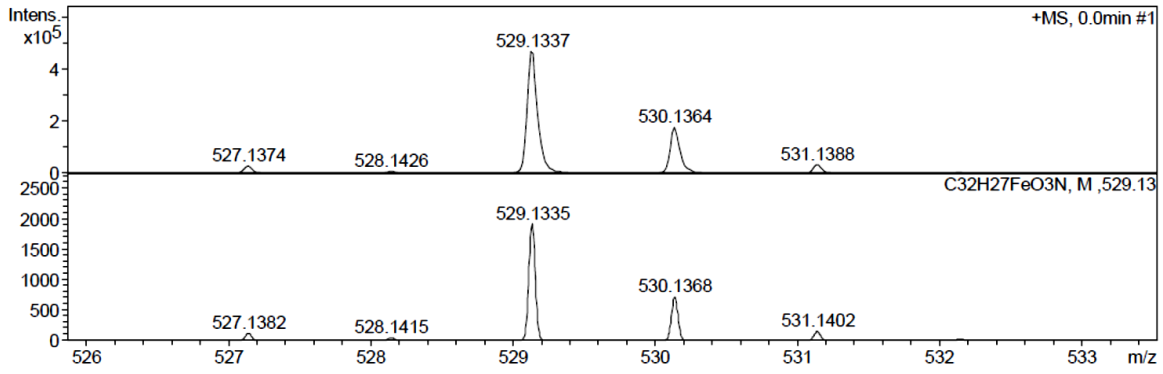


Figure S10: HRMS of **3a**.

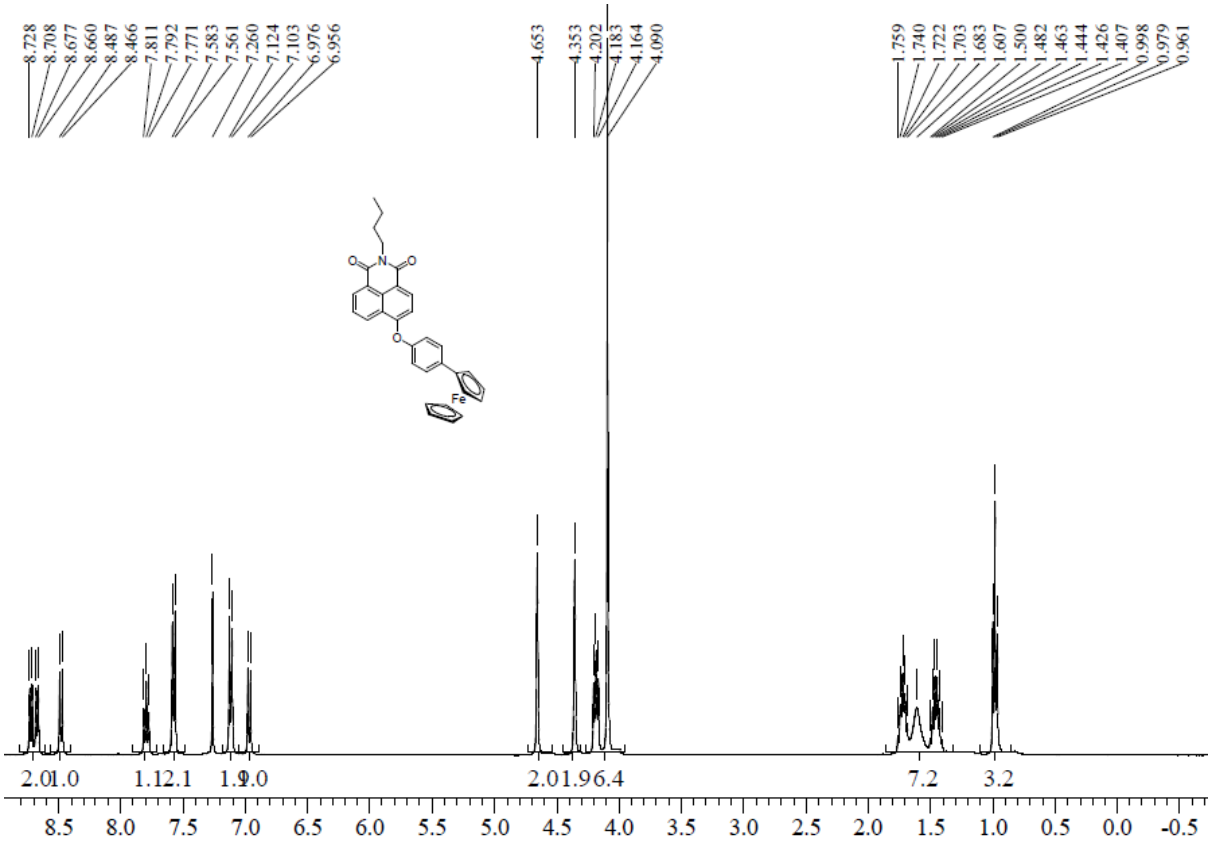


Figure S11: ^{1}H–NMR spectrum of **3b**.

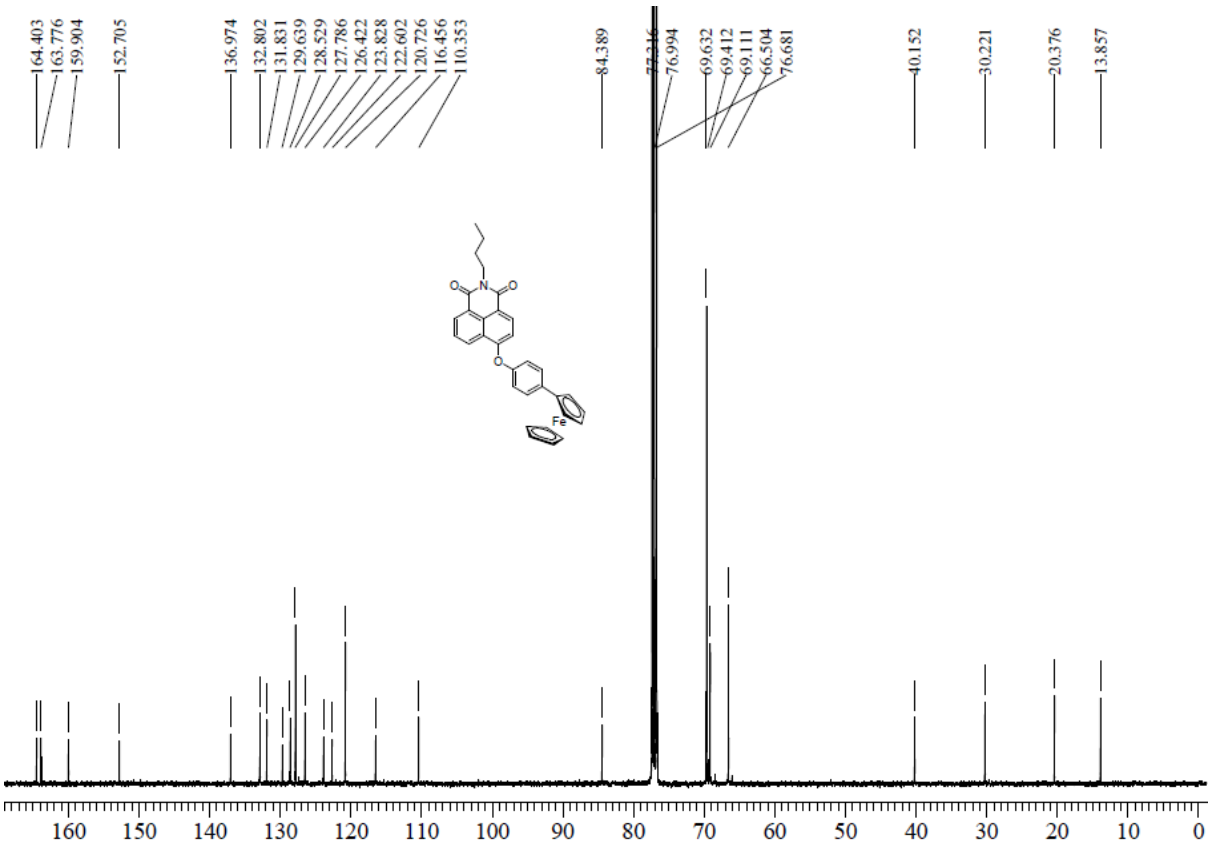


Figure S12: ^{13}C–NMR spectrum of **3b**.

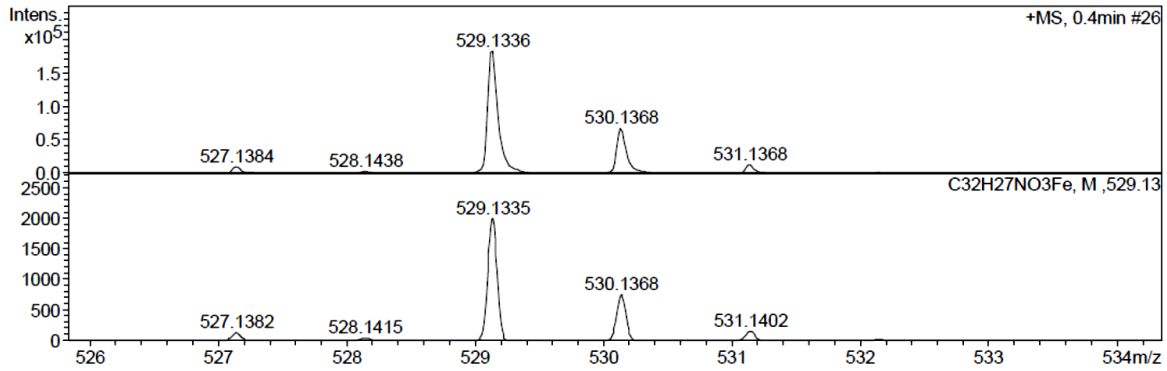


Figure S13: HRMS Spectrum of **3b**.

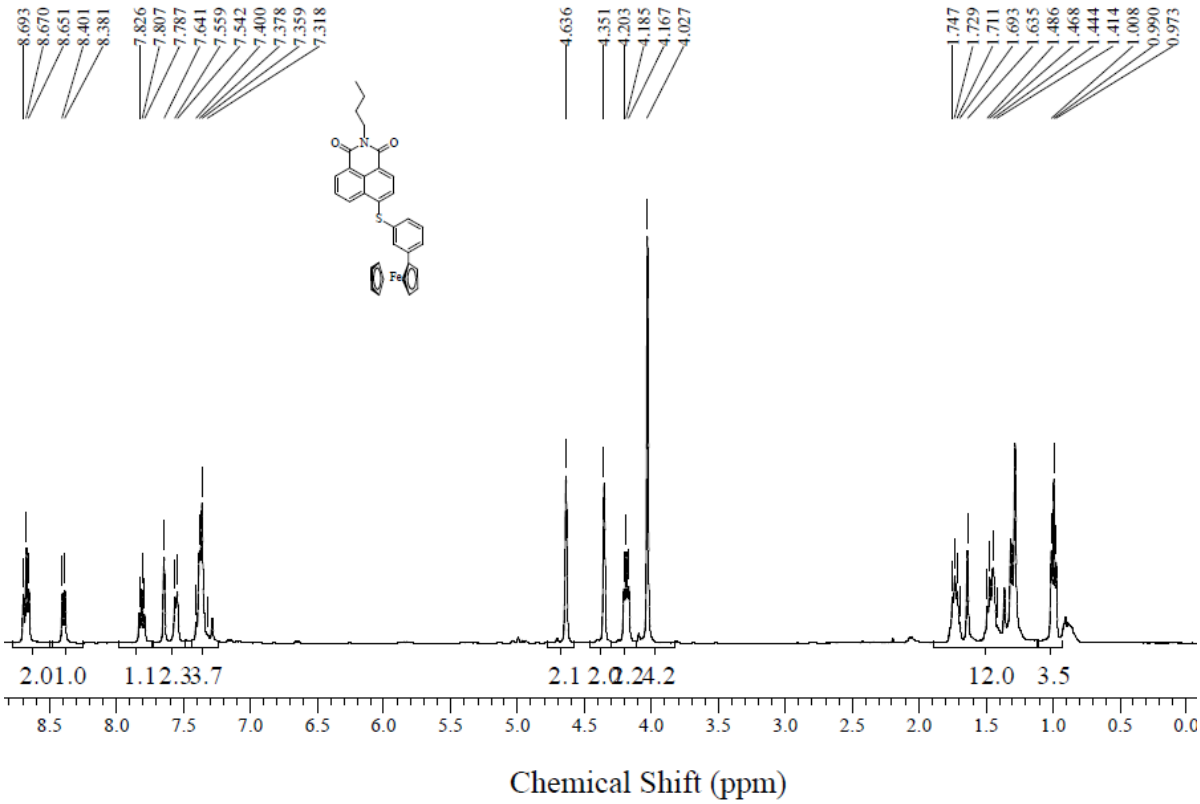


Figure S14: ^{1}H–NMR Spectrum of **3c**.

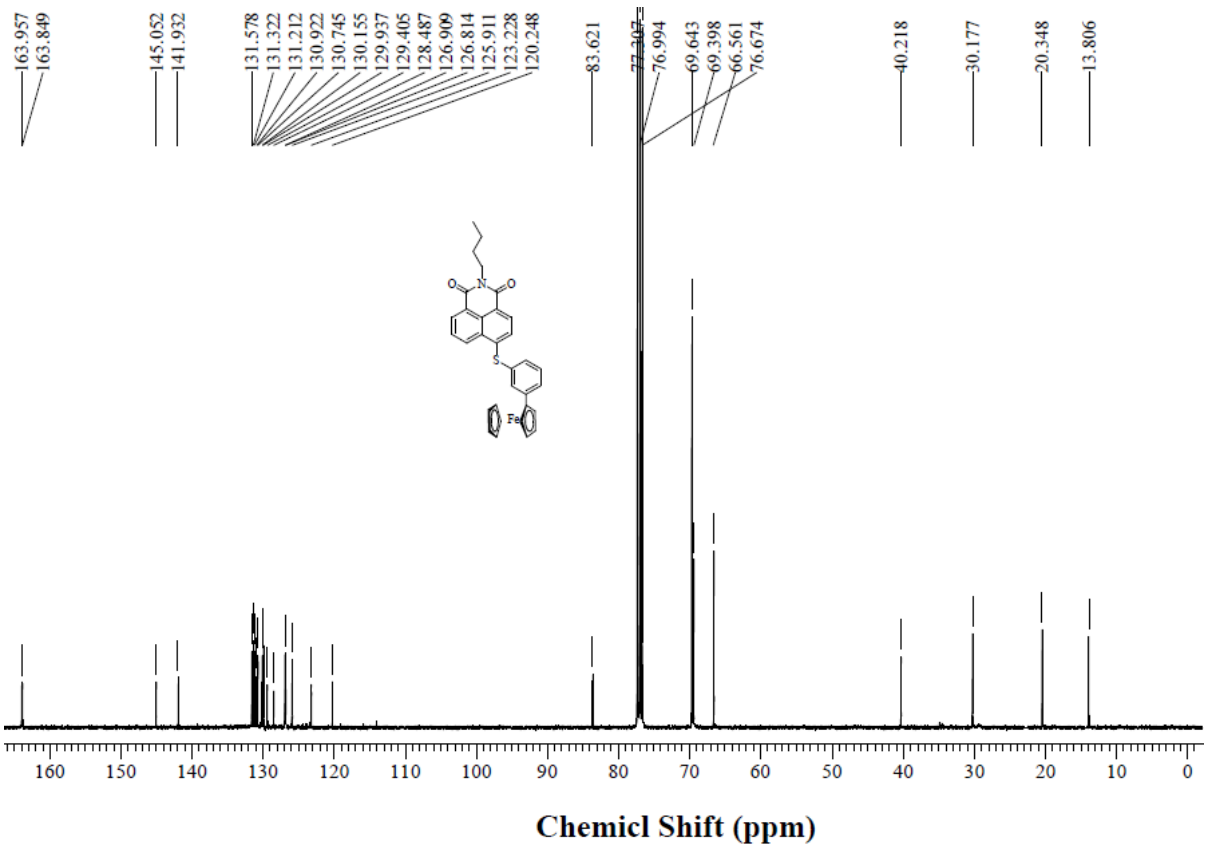


Figure S15: ^{13}C–NMR Spectrum of **3c**.

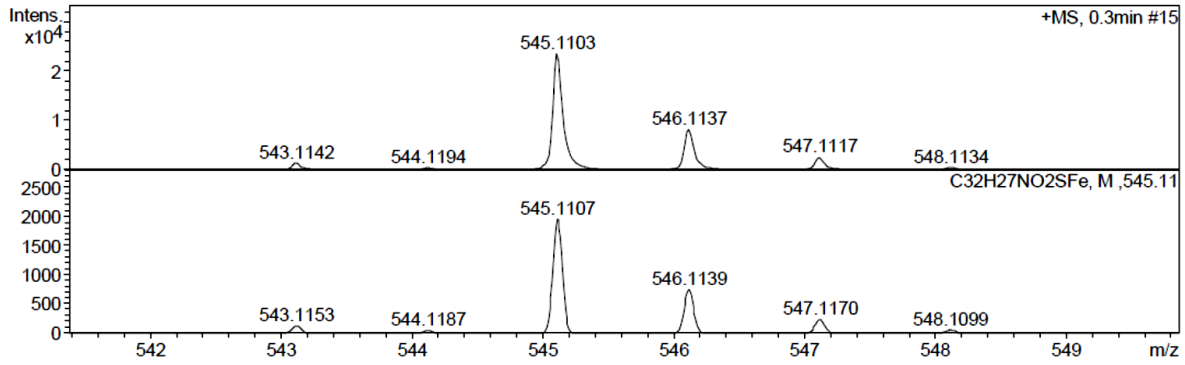


Figure S16: HRMS spectrum of **3c**.

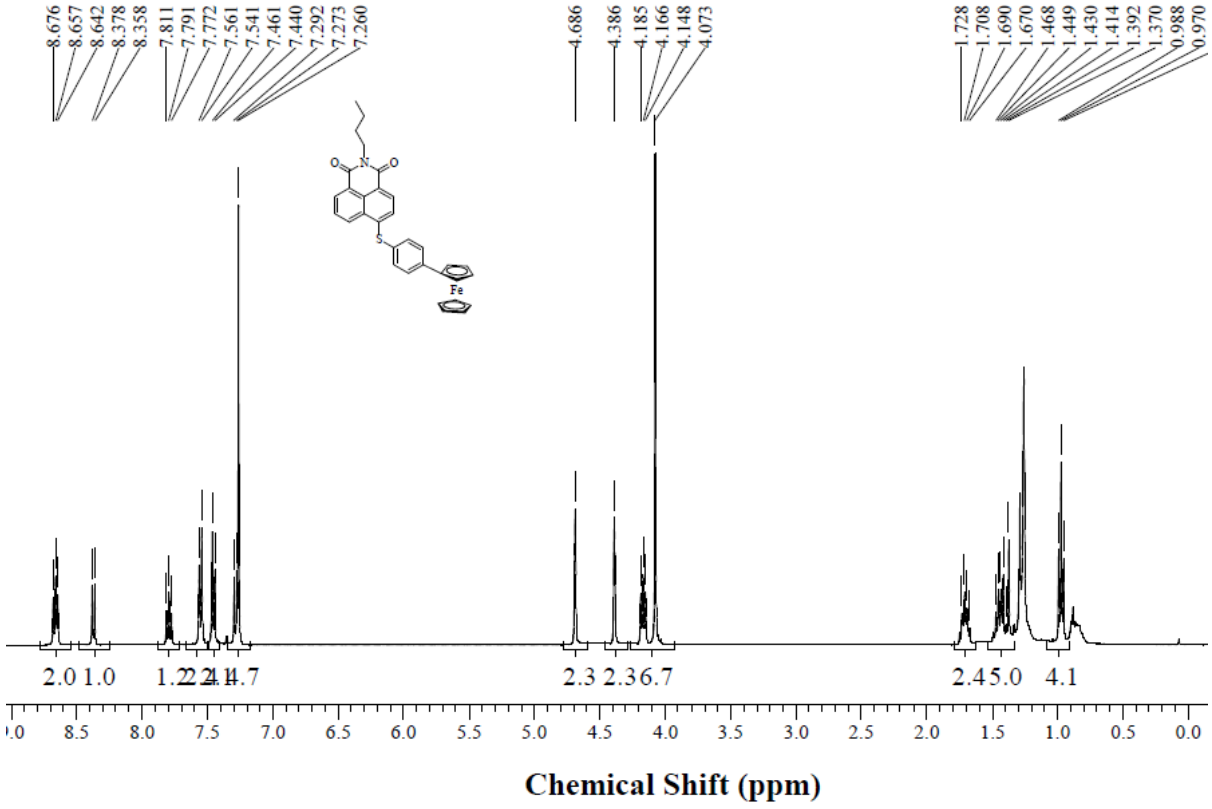
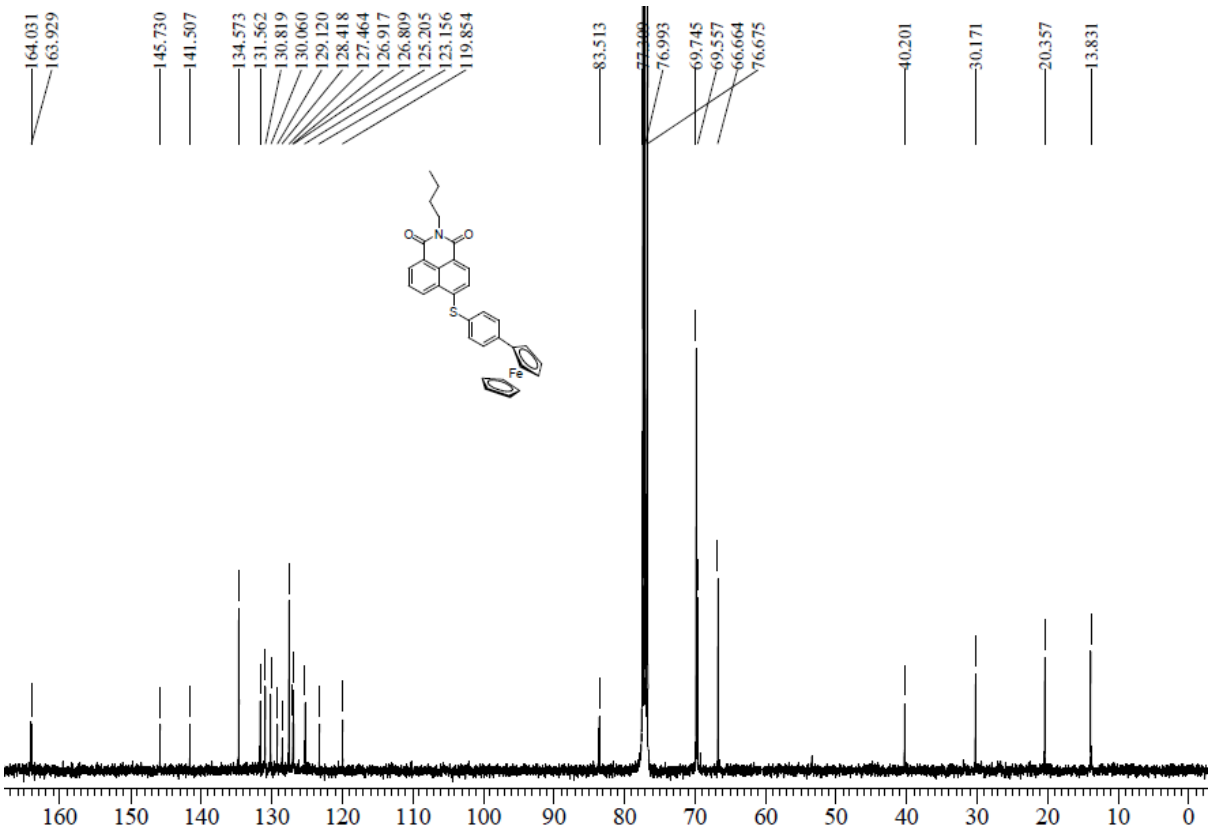


Figure S17: ^{1}H–NMR Spectrum of **3d**.



Chemical Shift (ppm)

Figure S18: ^{1}H–NMR Spectrum of **3d**.

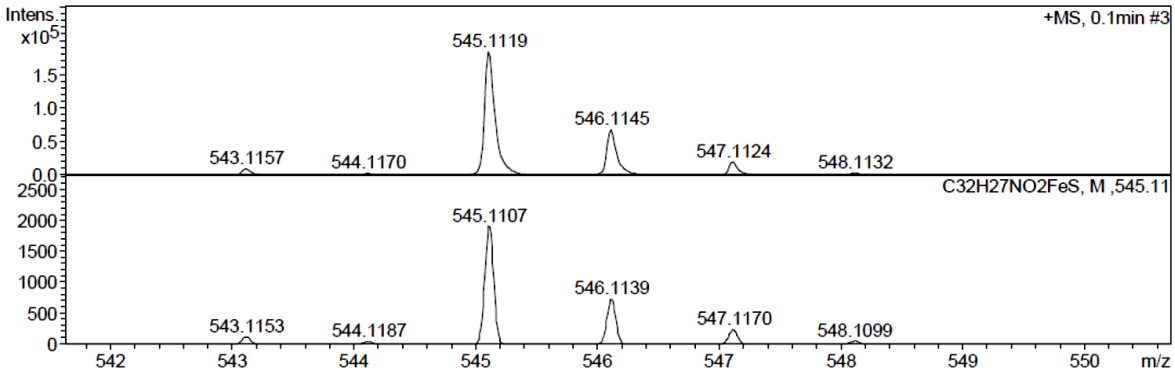


Figure S19: HRMS spectrum of **3d**.

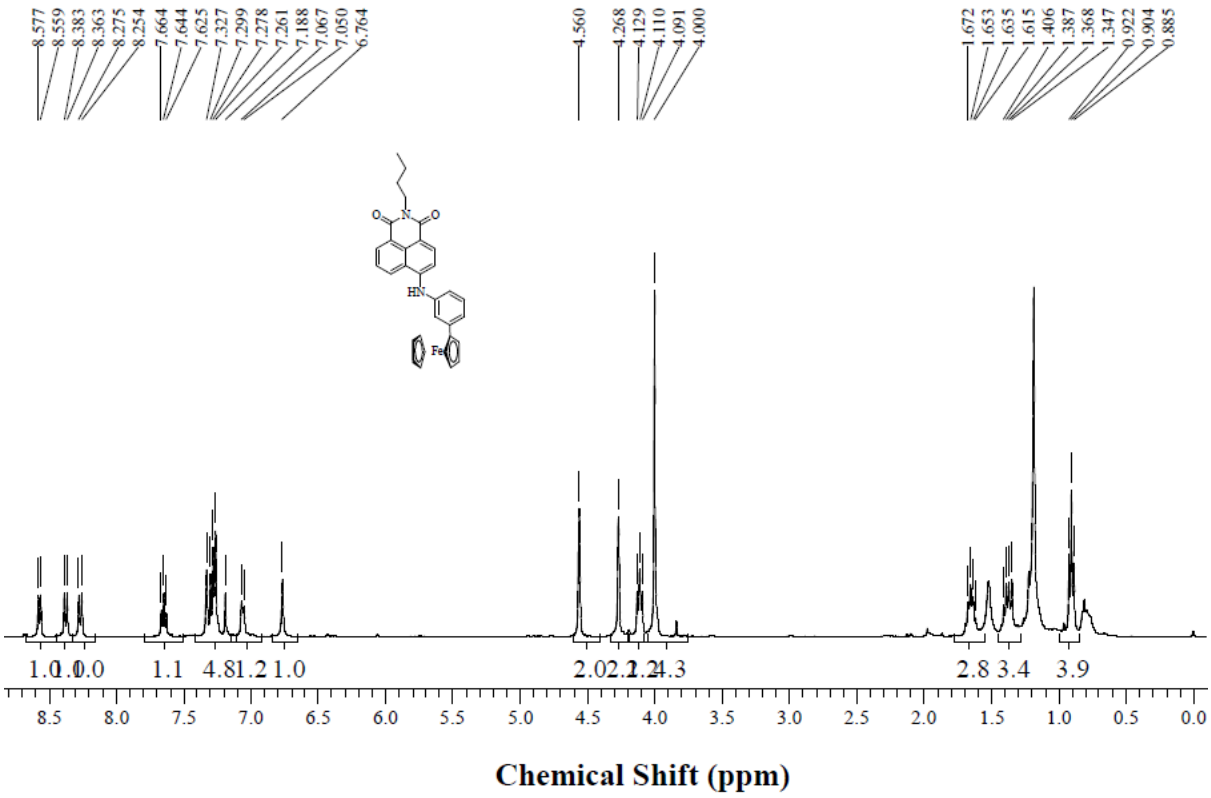


Figure S20: ^{1}H–NMR Spectrum of **3e**.

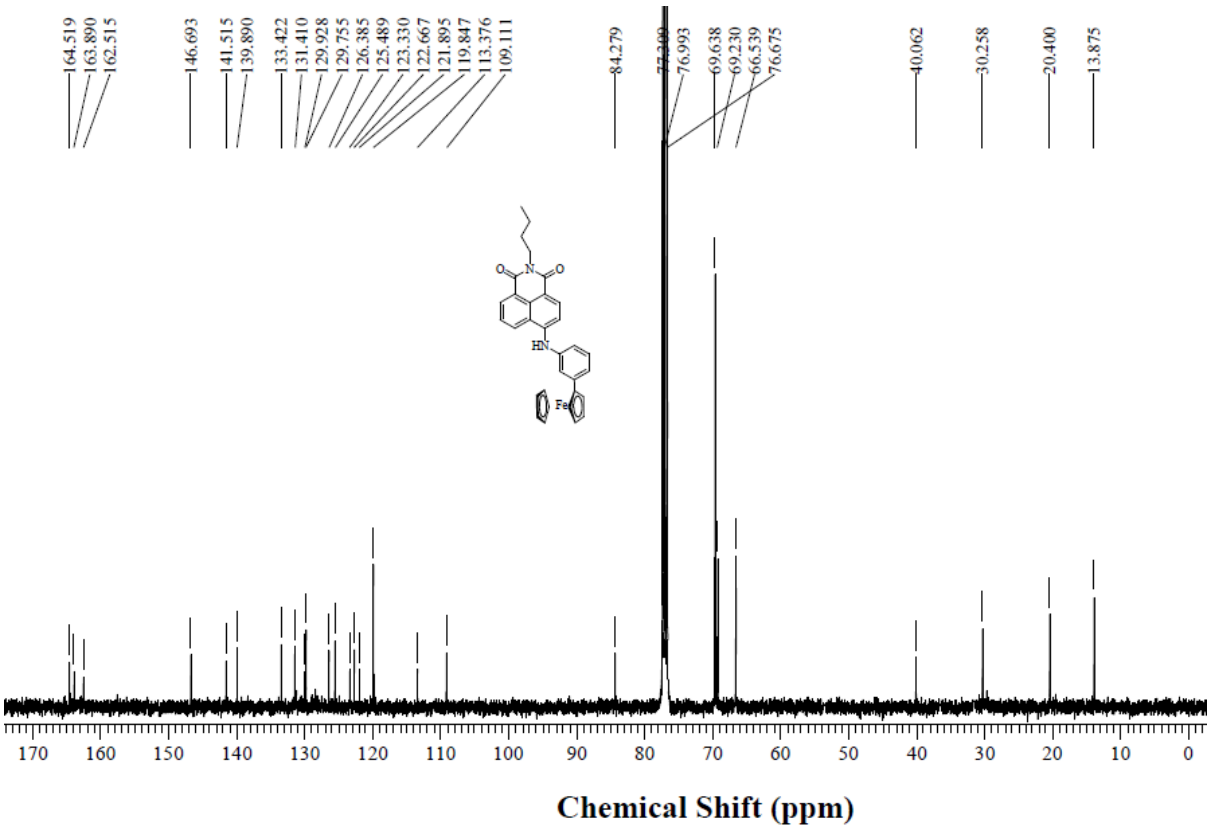


Figure S21: ^{13}C–NMR Spectrum of **3e**.

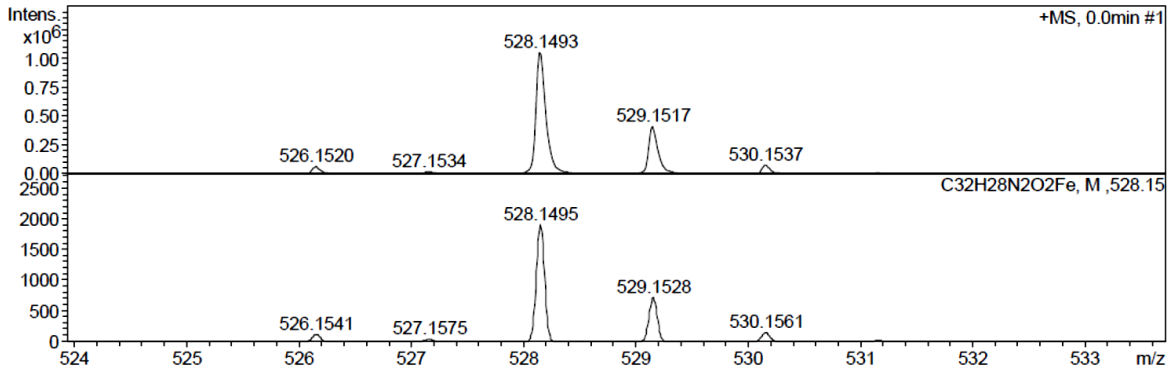
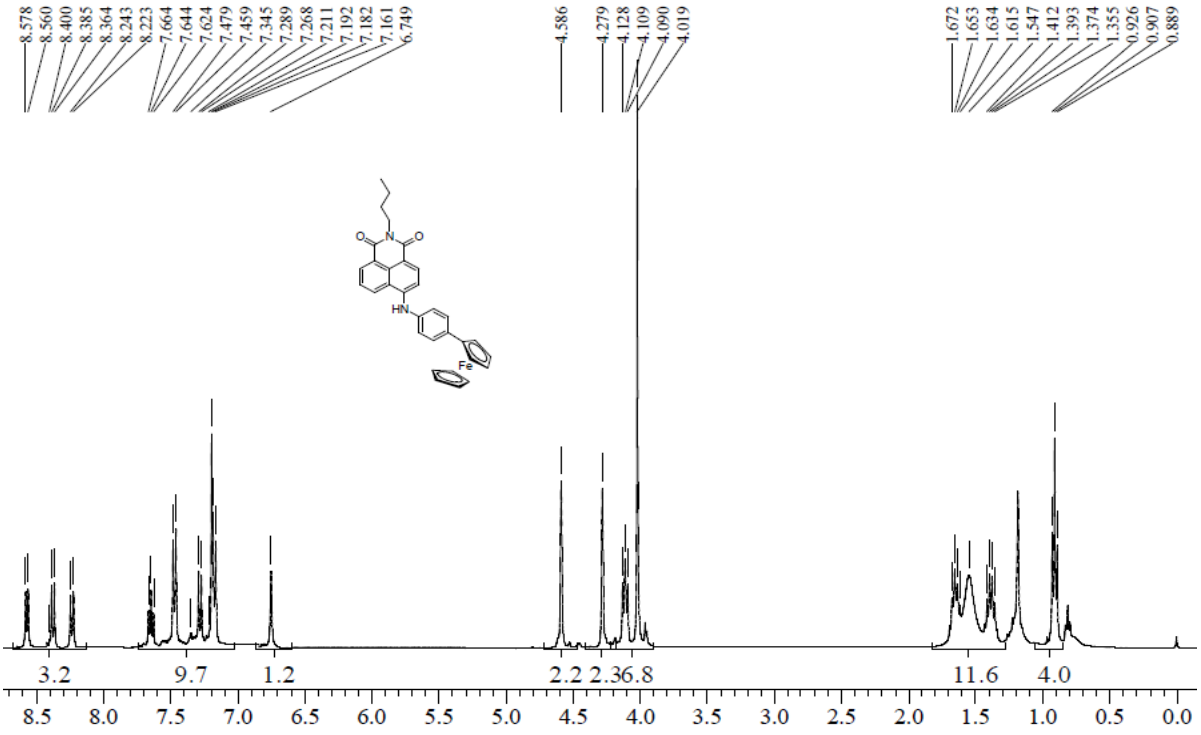


Figure S22: HRMS of **3e**.



Chemical Shift (ppm)

Figure S23: ^{1}H–NMR Spectrum of **3f**.

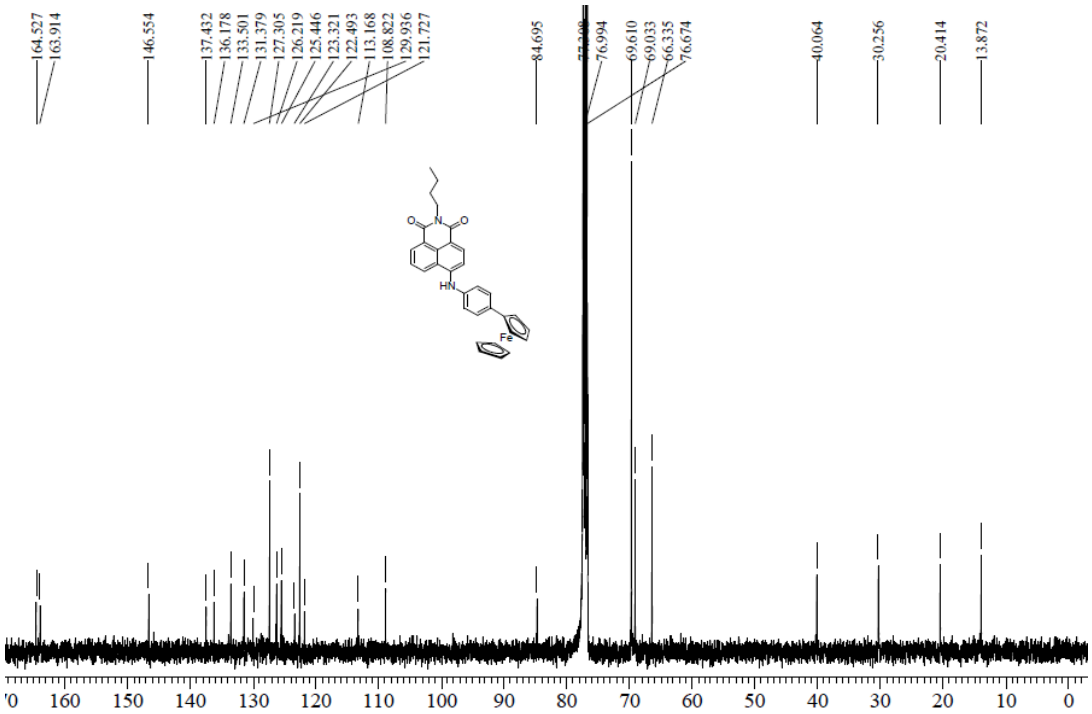


Figure S24: ^{13}C–NMR spectrum of **3f**.

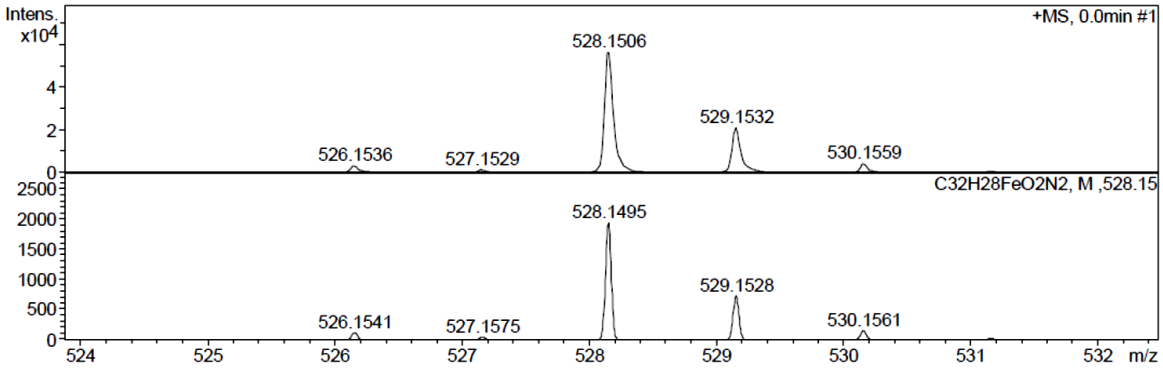


Figure S25: HRMS Spectrum of **3f**.

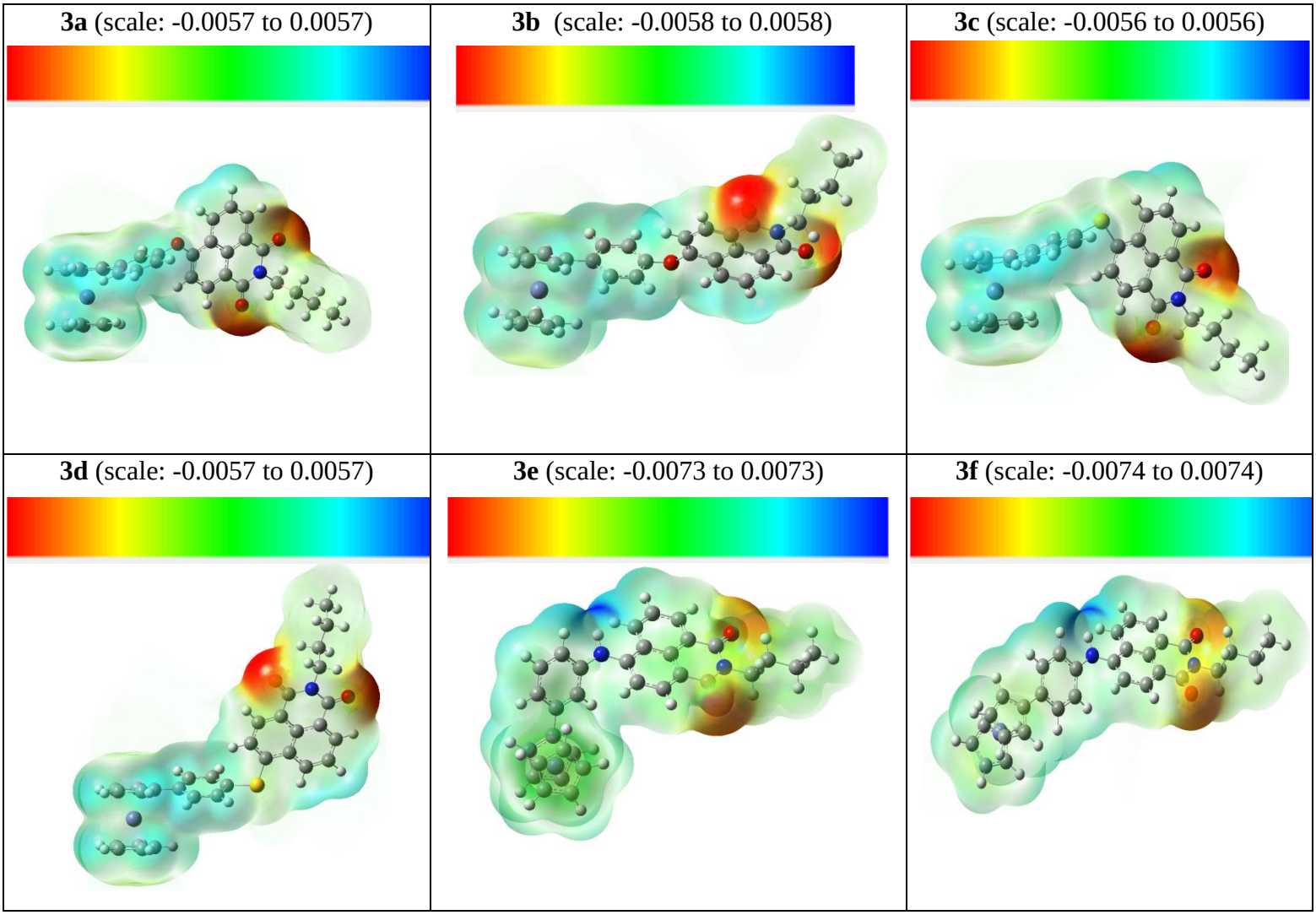


Figure 26: Molecular Electrostatic Potential (MEP) surface of FcNMIs **3a**–**3f** by B3LYP/6–31G (d,p) method.

Electrochemical Properties:

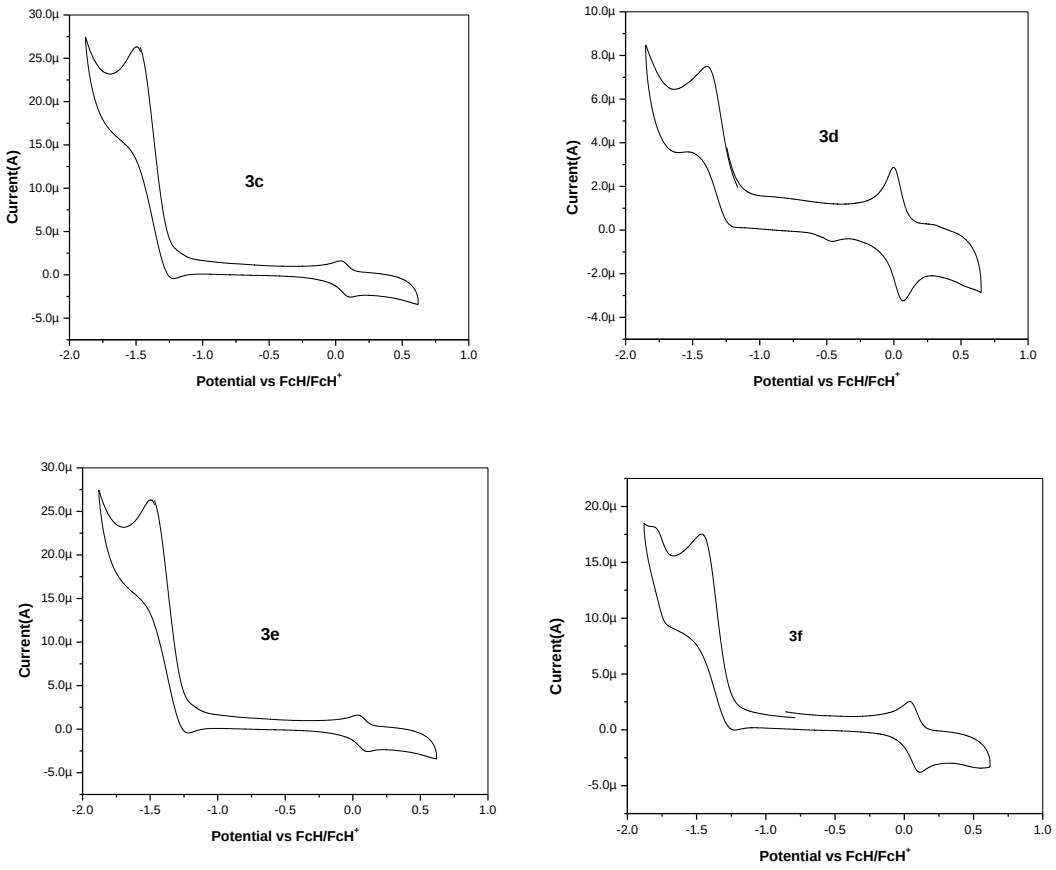


Figure S27: Cyclic voltammograms of the FcNMIs **3c**–**3f** (1.0×10^{-4} M) concentration in dichloromethane recorded at a scan rate of 100 mVs^{-1}.

Theoretical Calculations:

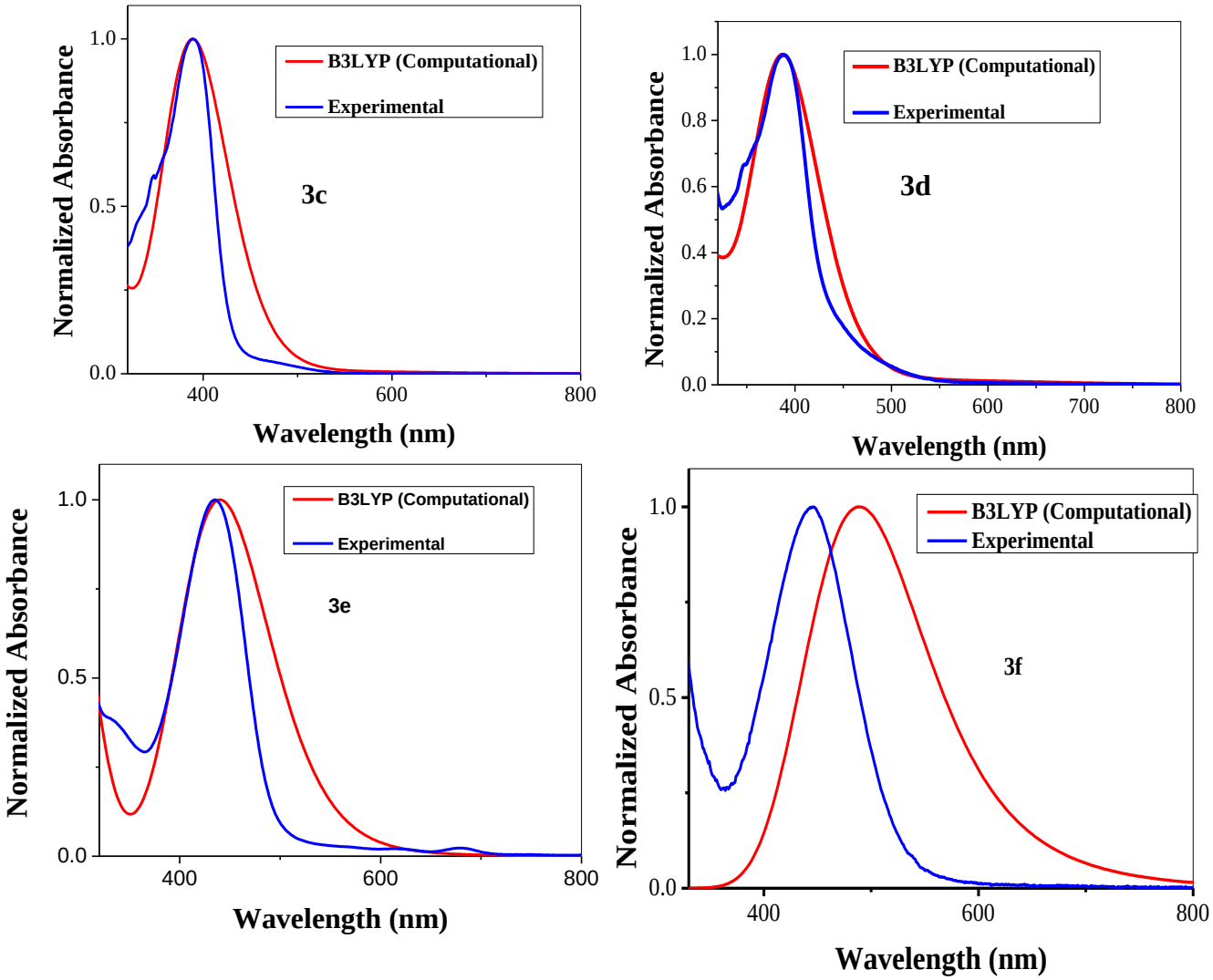


Figure S28: Comparison of experimental UV–vis spectra with theoretical TD–DFT UV–vis spectra of FcNMIs.

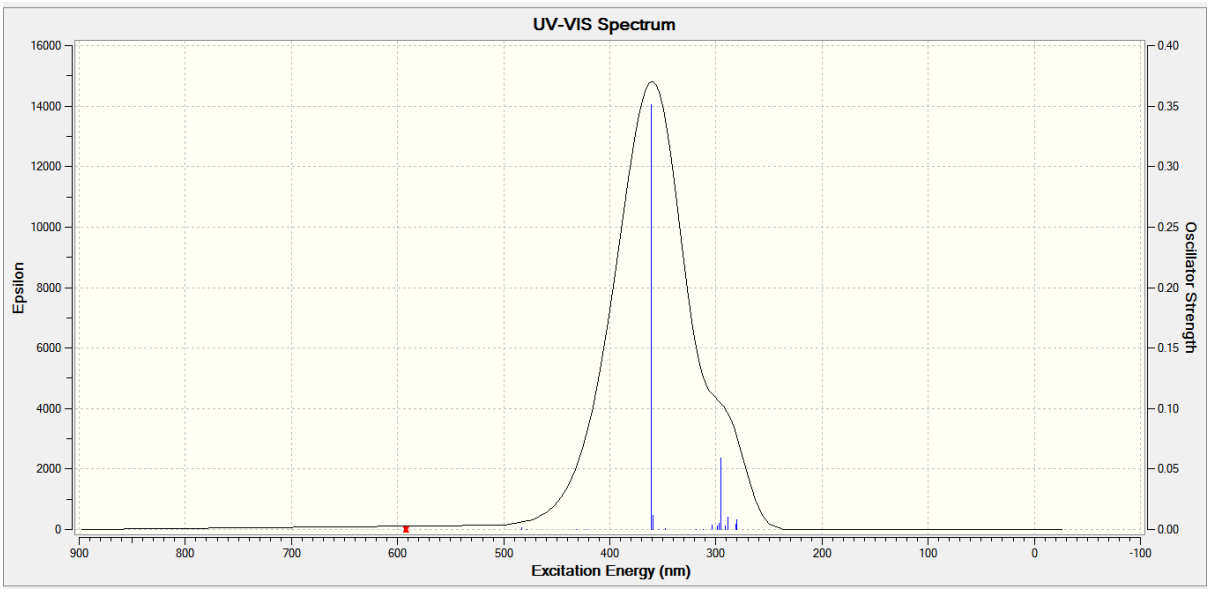


Figure S29: Theoretical TD–DFT UV–vis spectra of 3a.

```
Excited State   7:      Singlet-A      3.4365 eV  360.62 nm  f=0.3509
<S**2>=0.000
     131 ->134         0.68366
```

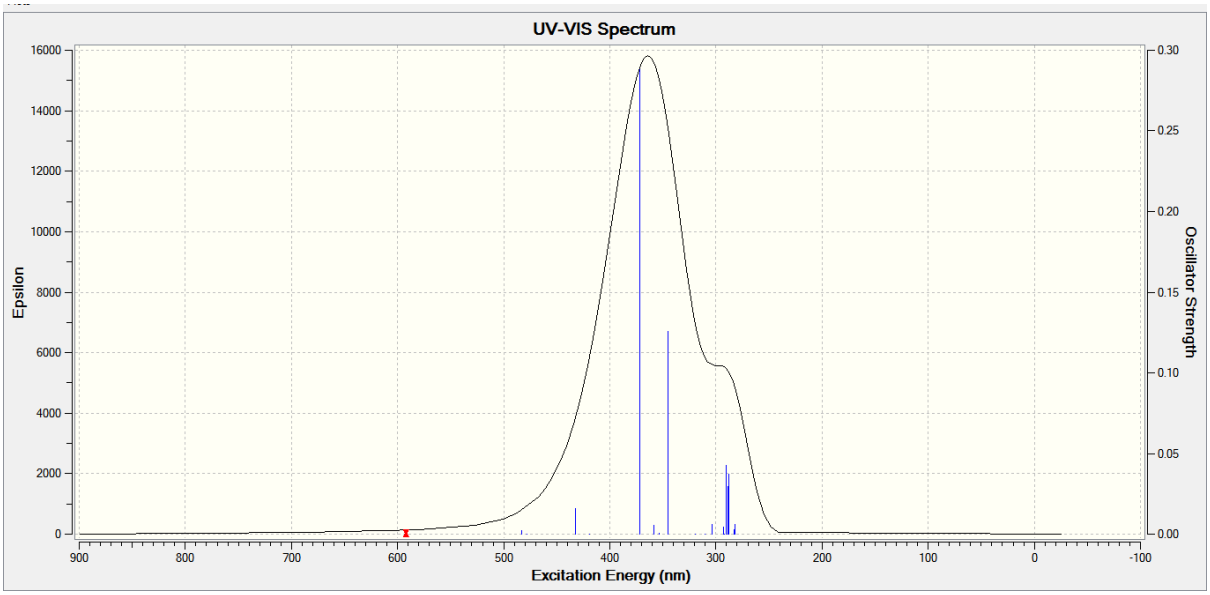


Figure S30: Theoretical TD–DFT UV–vis spectra of 3b.

```
Excited State   7:      Singlet-A      3.3372 eV  363.47 nm  f=0.2886
<S**2>=0.000
     131 ->134         0.69672
```

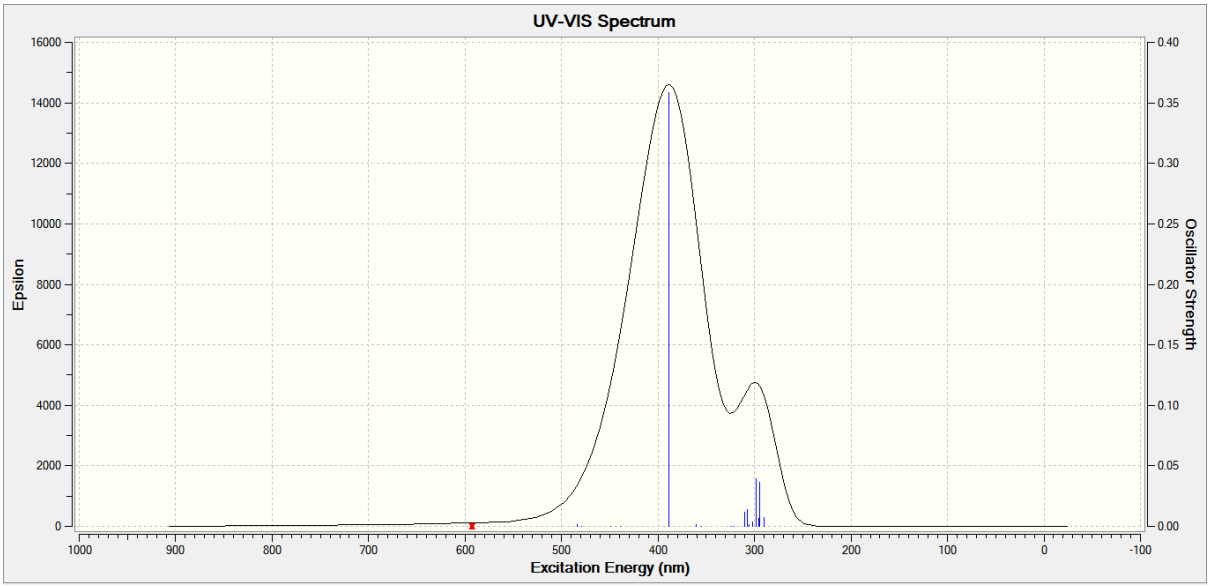


Figure S31: Theoretical TD–DFT UV–vis spectra of 3c.

```
Excited State   7:      Singlet-A      3.1865 eV  386.10 nm  f=0.3586
<S**2>=0.000
     135 ->138         0.69740
```

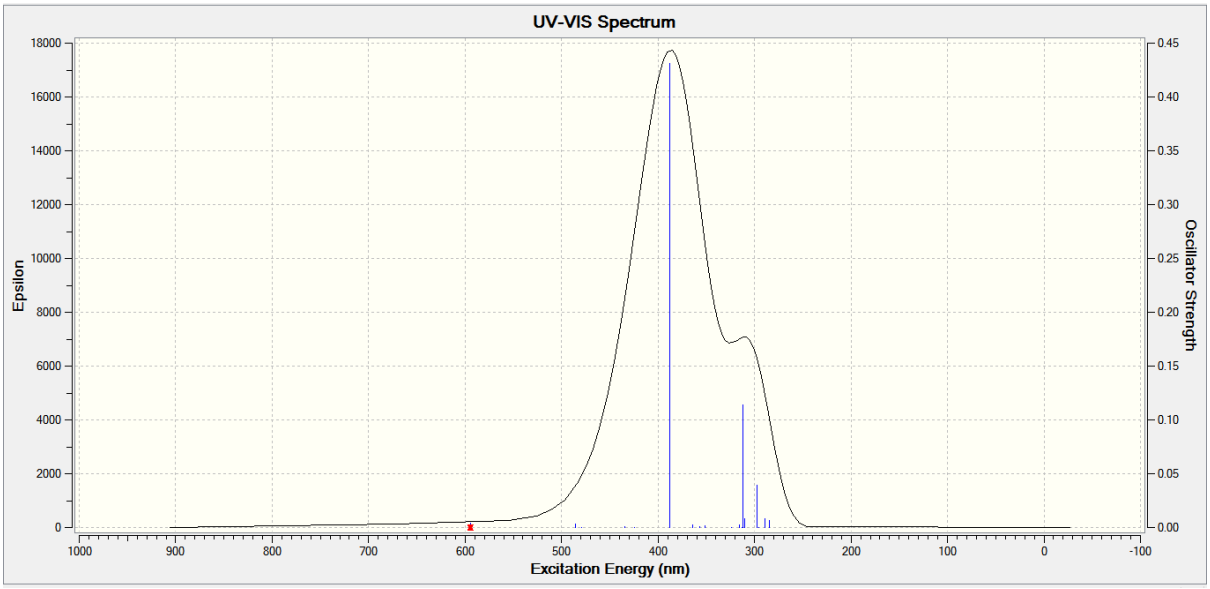


Figure S32: Theoretical TD–DFT UV–vis spectra of 3d.

```
Excited State   7:      Singlet-A      3.1969 eV  389.05 nm  f=0.4315
<S**2>=0.000
     135 ->138         0.69622
```

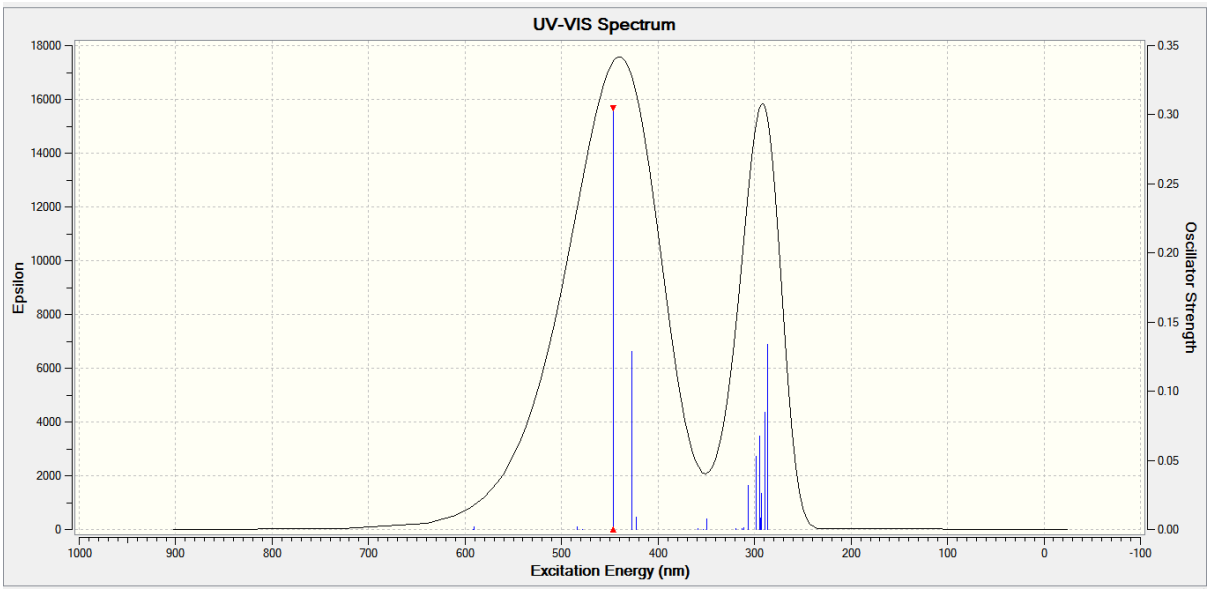


Figure S33: Theoretical TD–DFT UV–vis spectra of 3e.

```
Excited State   5:      Singlet-A      2.7788 eV  439.18 nm  f=0.3045
<S**2>=0.000
     131 ->134        -0.21962
     133 ->134         0.66577
```

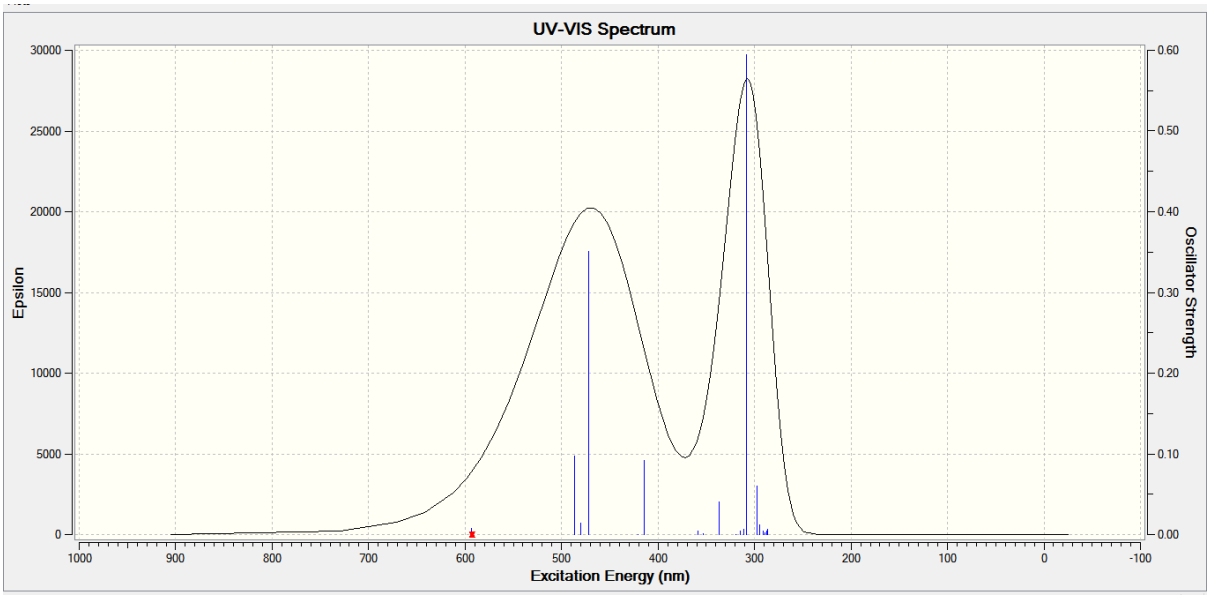
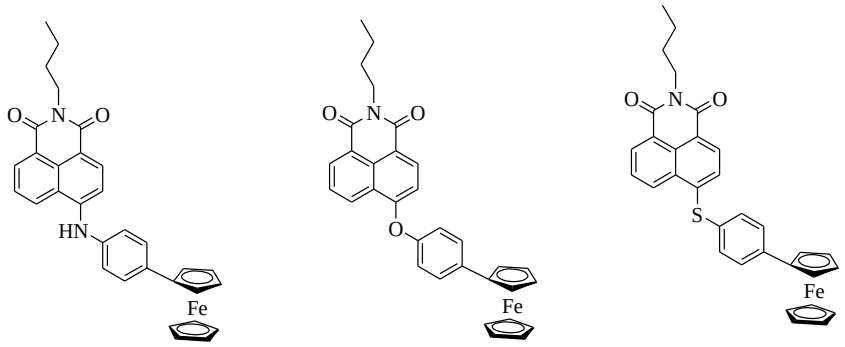


Figure S34: Theoretical TD–DFT UV–vis spectra of **3f**.

```
Excited State   5:      Singlet-A      2.6278 eV  469.64 nm  f=0.3507
<S**2>=0.000
     129 ->135        -0.11643
     129 ->137        -0.10582
     129 ->139         0.10192
     129 ->140        -0.11776
     131 ->134        -0.14525
     132 ->139        -0.14033
     133 ->134         0.59719
```



3f **3b** **3d**

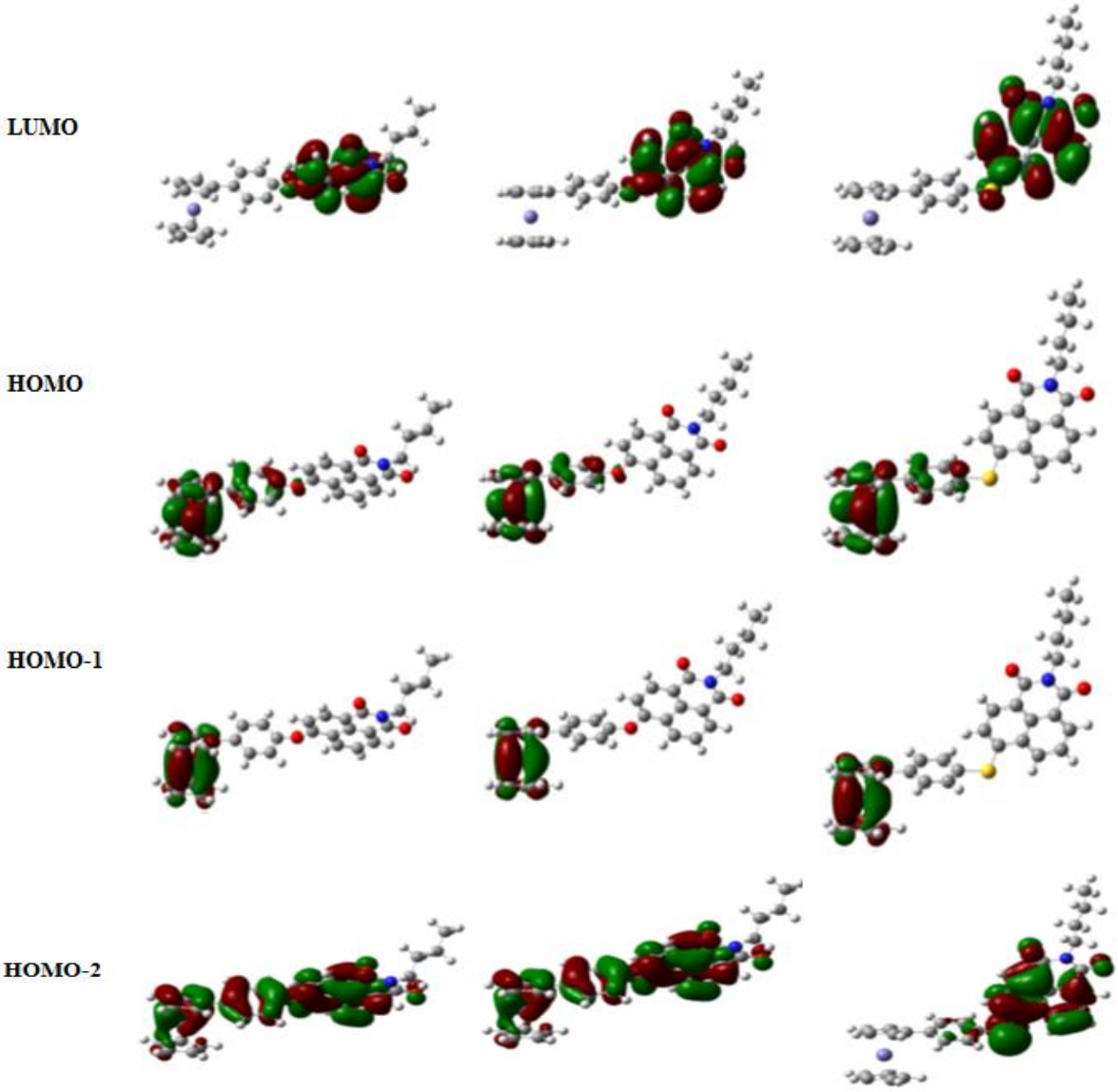


Figure S35: The energy level diagram of the frontier molecular orbitals (HOMO-2 to LUMO) of the FcNMIs **3f**, **3b** and **3d** calculated using B3LYP level of TD-DFT theory.

DFT data of FcNMI 3a:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.937557	1.601800	0.459973
2	6	0	2.177687	2.063947	-0.083510
3	6	0	2.396281	3.411010	-0.464307
4	6	0	0.769773	0.275701	0.824974
5	6	0	3.232246	1.117406	-0.244385
6	6	0	3.042418	-0.237818	0.128193
7	6	0	1.826527	-0.636528	0.655844
8	6	0	4.129628	-1.224697	-0.038349
9	6	0	5.586365	0.579261	-0.954672
10	6	0	4.473353	1.546246	-0.778436
11	6	0	4.659644	2.870223	-1.138534
12	6	0	3.616305	3.803393	-0.981651
13	1	0	3.774080	4.837940	-1.270152
14	1	0	5.622891	3.163887	-1.542033
15	1	0	-0.172638	-0.056266	1.243163
16	1	0	1.704825	-1.676344	0.940690
17	8	0	4.012612	-2.402152	0.281918
18	8	0	6.680321	0.911069	-1.396067
19	7	0	5.331546	-0.752472	-0.596308
20	8	0	-0.025582	2.560853	0.598111
21	6	0	-1.313711	2.209427	1.000250
22	6	0	-1.709308	2.507100	2.300836
23	6	0	-2.196285	1.658799	0.073424
24	6	0	-3.029104	2.235539	2.670517
25	1	0	-0.999451	2.947380	2.992612
26	6	0	-3.518544	1.371461	0.445925
27	1	0	-1.853797	1.478967	-0.939879
28	6	0	-3.919918	1.671648	1.760993
29	1	0	-3.360074	2.460859	3.680019
30	1	0	-4.935007	1.447019	2.072335
31	6	0	-4.460345	0.799530	-0.534755
32	6	0	-5.890338	0.942364	-0.530160
33	26	0	-5.392141	-1.068985	-0.456943
34	6	0	-4.122522	0.018962	-1.691887
35	6	0	-6.416127	0.270459	-1.671607
36	6	0	-5.323386	-0.302267	-2.388848
37	6	0	-4.796917	-2.043391	1.279121
38	6	0	-4.409279	-2.803682	0.134831
39	6	0	-5.590944	-3.135478	-0.595228
40	6	0	-6.217913	-1.905175	1.256756
41	6	0	-6.708721	-2.580564	0.097970
42	1	0	-3.128884	-0.309043	-1.964354
43	1	0	-7.462404	0.186447	-1.931165
44	1	0	-5.395540	-0.908004	-3.281495
45	1	0	-4.128510	-1.609202	2.010129
46	1	0	-3.396585	-3.058773	-0.145763
47	1	0	-5.629422	-3.682665	-1.527102
48	1	0	-7.741868	-2.633666	-0.216843
49	1	0	-6.468626	1.476009	0.211148
50	1	0	-6.816059	-1.362340	1.975769
51	6	0	6.423403	-1.726135	-0.779401
52	1	0	5.954423	-2.688977	-0.986738

53	1	0	6.994275	-1.400399	-1.650233
54	1	0	1.590936	4.126435	-0.342177
55	6	0	7.335802	-1.831410	0.447519
56	1	0	7.767081	-0.844704	0.655500
57	1	0	6.729766	-2.114578	1.316734
58	6	0	8.458592	-2.855597	0.243270
59	1	0	8.018402	-3.836450	0.018141
60	1	0	9.049999	-2.575578	-0.639058
61	6	0	9.383271	-2.978146	1.458690
62	1	0	8.826764	-3.292025	2.349058
63	1	0	10.175833	-3.713493	1.285321
64	1	0	9.862665	-2.020007	1.689188

Total energy = -1639.54607908 HF.

DFT data of **FcNMI 3b:**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.404835	0.718901	0.480374
2	6	0	2.557256	1.554890	0.342577
3	6	0	2.516808	2.958593	0.531491
4	6	0	1.491952	-0.651211	0.293420
5	6	0	3.795176	0.936660	-0.003387
6	6	0	3.865818	-0.466081	-0.199671
7	6	0	2.725255	-1.235127	-0.046035
8	6	0	5.144071	-1.112744	-0.563318
9	6	0	6.254147	1.118934	-0.510695
10	6	0	4.954562	1.739394	-0.148307
11	6	0	4.885967	3.108433	0.046990
12	6	0	3.662277	3.718004	0.386529
13	1	0	3.621259	4.792700	0.534119
14	1	0	5.793207	3.691671	-0.069703
15	1	0	0.612128	-1.271864	0.411725
16	1	0	2.802918	-2.307311	-0.192622
17	8	0	5.252804	-2.322298	-0.729233
18	8	0	7.283083	1.773680	-0.630010
19	7	0	6.257455	-0.267601	-0.721081
20	6	0	-0.973149	0.717603	0.769128
21	6	0	-1.540095	0.382409	-0.462211
22	6	0	-1.662320	0.486278	1.955907
23	6	0	-2.804301	-0.197595	-0.494527
24	1	0	-0.996467	0.585667	-1.379229
25	6	0	-2.928488	-0.096783	1.909386
26	1	0	-1.202665	0.757624	2.900564
27	6	0	-3.524158	-0.449855	0.687825
28	1	0	-3.252683	-0.439779	-1.452914
29	1	0	-3.452511	-0.299797	2.838037
30	6	0	-4.849503	-1.096253	0.654290
31	6	0	-5.324092	-2.014550	-0.343839
32	26	0	-6.606389	-0.388177	-0.232950
33	6	0	-5.892807	-0.967232	1.632061
34	6	0	-6.630501	-2.449073	0.024182
35	1	0	-4.777806	-2.328689	-1.222388
36	6	0	-6.983360	-1.799980	1.245239

37	6	0	-6.239680	1.488916	-1.047972
38	6	0	-7.298050	1.567546	-0.093281
39	6	0	-8.350425	0.705957	-0.528771
40	6	0	-6.637124	0.577447	-2.072941
41	6	0	-7.942375	0.094272	-1.752342
42	1	0	-5.871896	-0.312754	2.492569
43	1	0	-7.254257	-3.129233	-0.539168
44	1	0	-7.927080	-1.891042	1.764912
45	1	0	-5.286158	1.994658	-0.981722
46	1	0	-7.291301	2.153365	0.815610
47	1	0	-9.279607	0.523520	-0.006544
48	1	0	-6.045160	0.285099	-2.929390
49	1	0	-8.507848	-0.632855	-2.318726
50	1	0	1.572770	3.423914	0.791451
51	6	0	7.537579	-0.895285	-1.097036
52	1	0	7.294618	-1.754582	-1.723736
53	1	0	8.090130	-0.158528	-1.681922
54	6	0	8.360010	-1.337206	0.118183
55	1	0	8.557795	-0.462737	0.750029
56	1	0	7.765874	-2.043041	0.711221
57	6	0	9.685216	-1.991797	-0.290768
58	1	0	10.266604	-1.285877	-0.899291
59	1	0	9.479041	-2.855756	-0.937103
60	6	0	10.523953	-2.441979	0.909523
61	1	0	11.462126	-2.906872	0.589226
62	1	0	10.776249	-1.594201	1.556521
63	1	0	9.981113	-3.173085	1.519243
64	8	0	0.254966	1.370704	0.830679

Total Energy = -1639.54575336.

DFT data of FcNMI 3c:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.012605	1.991694	0.367455
2	6	0	2.278738	2.255145	-0.258718
3	6	0	2.637838	3.512988	-0.810328
4	6	0	0.745831	0.730719	0.880451
5	6	0	3.232483	1.191196	-0.333992
6	6	0	2.924308	-0.087926	0.193694
7	6	0	1.695367	-0.301104	0.791276
8	6	0	3.898816	-1.198425	0.115189
9	6	0	5.495630	0.325385	-1.033533
10	6	0	4.494043	1.418940	-0.941894
11	6	0	4.809659	2.662311	-1.460040
12	6	0	3.873631	3.711308	-1.394415
13	1	0	4.124607	4.682613	-1.809031
14	1	0	5.784226	2.800929	-1.915595
15	1	0	-0.204650	0.533377	1.361435
16	1	0	1.480204	-1.284736	1.195626
17	8	0	3.669745	-2.312902	0.570938
18	8	0	6.600525	0.489834	-1.536940
19	7	0	5.120578	-0.924326	-0.521776
20	6	0	-1.664679	2.561066	1.039159
21	6	0	-2.039347	2.674418	2.381989

22	6	0	-2.501418	1.913882	0.122451
23	6	0	-3.255400	2.125067	2.796042
24	1	0	-1.390441	3.184849	3.085632
25	6	0	-3.715072	1.342452	0.534182
26	1	0	-2.210148	1.870465	-0.921390
27	6	0	-4.078041	1.463795	1.888387
28	1	0	-3.556526	2.207034	3.836384
29	1	0	-5.009408	1.023963	2.231049
30	6	0	-4.591827	0.668109	-0.441657
31	6	0	-6.016060	0.503663	-0.342499
32	26	0	-5.111099	-1.355468	-0.503110
33	6	0	-4.189782	0.081314	-1.689295
34	6	0	-6.477857	-0.160479	-1.515535
35	6	0	-5.348551	-0.423206	-2.347472
36	6	0	-4.212035	-2.334974	1.095375
37	6	0	-3.748228	-2.884164	-0.137803
38	6	0	-4.878645	-3.393569	-0.845997
39	6	0	-5.628653	-2.504996	1.149942
40	6	0	-6.040676	-3.159675	-0.050378
41	1	0	-3.173783	-0.003191	-2.048959
42	1	0	-7.501132	-0.441716	-1.722769
43	1	0	-5.362450	-0.948309	-3.292482
44	1	0	-3.602818	-1.839961	1.839393
45	1	0	-2.724943	-2.887842	-0.487232
46	1	0	-4.861537	-3.846909	-1.827569
47	1	0	-7.057831	-3.405295	-0.323219
48	1	0	-6.634598	0.833876	0.480337
49	1	0	-6.279593	-2.173674	1.947359
50	6	0	6.095414	-2.025047	-0.629543
51	1	0	5.519314	-2.947388	-0.716574
52	1	0	6.660090	-1.856871	-1.547822
53	1	0	1.928184	4.333221	-0.777408
54	6	0	7.043556	-2.100758	0.572161
55	1	0	7.579135	-1.148059	0.663393
56	1	0	6.450459	-2.232883	1.485203
57	6	0	8.049822	-3.250105	0.436374
58	1	0	7.505711	-4.198063	0.327621
59	1	0	8.626479	-3.119915	-0.489375
60	6	0	9.010226	-3.346393	1.626146
61	1	0	8.464860	-3.510403	2.562426
62	1	0	9.716948	-4.173661	1.503414
63	1	0	9.592494	-2.424986	1.739757
64	16	0	-0.153166	3.343421	0.471168

Total Energy = -1962.51414692 HF.

DFT data of FcNMI 3d:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.600371	1.332998	0.059473
2	6	0	2.901076	1.942732	0.093016
3	6	0	3.117888	3.320634	0.356728
4	6	0	1.480771	-0.023660	-0.201818
5	6	0	4.043657	1.117155	-0.151048
6	6	0	3.886005	-0.266641	-0.415918

7	6	0	2.617148	-0.816503	-0.436324
8	6	0	5.059486	-1.131446	-0.668080
9	6	0	6.541201	0.845632	-0.370614
10	6	0	5.342381	1.687544	-0.122866
11	6	0	5.512200	3.035459	0.138831
12	6	0	4.392146	3.853151	0.378379
13	1	0	4.531810	4.909976	0.583231
14	1	0	6.519793	3.436762	0.154095
15	1	0	0.500861	-0.485046	-0.227387
16	1	0	2.515831	-1.877505	-0.639451
17	8	0	4.961352	-2.333757	-0.884730
18	8	0	7.678767	1.299872	-0.336650
19	7	0	6.319179	-0.508932	-0.653026
20	6	0	-1.210281	1.277561	0.317644
21	6	0	-1.918128	1.074822	-0.875330
22	6	0	-1.658568	0.662484	1.493015
23	6	0	-3.051864	0.268110	-0.888229
24	1	0	-1.581527	1.556942	-1.787626
25	6	0	-2.789039	-0.150720	1.470516
26	1	0	-1.116300	0.816056	2.420531
27	6	0	-3.512298	-0.360216	0.283483
28	1	0	-3.599325	0.138021	-1.816448
29	1	0	-3.106590	-0.641113	2.385221
30	6	0	-4.700710	-1.231607	0.270991
31	6	0	-5.251536	-1.913011	-0.869112
32	26	0	-6.685982	-0.662319	-0.046534
33	6	0	-5.515087	-1.585686	1.400538
34	6	0	-6.372680	-2.680100	-0.440368
35	1	0	-4.875056	-1.859674	-1.880972
36	6	0	-6.537389	-2.475902	0.962279
37	6	0	-6.755129	1.391587	-0.359072
38	6	0	-7.534613	1.043699	0.784916
39	6	0	-8.559056	0.142509	0.363165
40	6	0	-7.296502	0.705247	-1.487979
41	6	0	-8.412462	-0.066169	-1.041480
42	1	0	-5.399683	-1.207250	2.406603
43	1	0	-7.004970	-3.286028	-1.074429
44	1	0	-7.322306	-2.892532	1.578206
45	1	0	-5.881386	2.028881	-0.361878
46	1	0	-7.360622	1.379254	1.798017
47	1	0	-9.296387	-0.325154	1.001108
48	1	0	-6.914440	0.742656	-2.498879
49	1	0	-9.018901	-0.719909	-1.653185
50	1	0	2.269072	3.969212	0.547529
51	6	0	7.500412	-1.353864	-0.907195
52	1	0	7.183439	-2.139764	-1.594175
53	1	0	8.243657	-0.719414	-1.392334
54	6	0	8.076184	-1.964924	0.374830
55	1	0	8.342255	-1.155548	1.065501
56	1	0	7.299745	-2.568603	0.860346
57	6	0	9.309512	-2.833139	0.096637
58	1	0	10.075027	-2.225754	-0.405015
59	1	0	9.040839	-3.631208	-0.608633
60	6	0	9.900868	-3.452136	1.367096
61	1	0	10.780487	-4.063953	1.141662
62	1	0	10.207564	-2.676915	2.078442
63	1	0	9.169506	-4.093361	1.871924
64	16	0	0.190134	2.391955	0.358969

Total Energy = -1962.51502539 HF.

DFT data of FcNMI 3e:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.918220	1.706995	-0.374782
2	6	0	-2.228475	2.155157	0.031732
3	6	0	-2.541087	3.513616	0.288553
4	6	0	-0.687020	0.340307	-0.536696
5	6	0	-3.261693	1.182234	0.203206
6	6	0	-2.990410	-0.196664	0.019655
7	6	0	-1.710932	-0.593051	-0.337382
8	6	0	-4.046618	-1.209474	0.198361
9	6	0	-5.657532	0.610036	0.742223
10	6	0	-4.565876	1.603760	0.569788
11	6	0	-4.840926	2.944260	0.777931
12	6	0	-3.818687	3.901202	0.648507
13	1	0	-4.030812	4.947424	0.845236
14	1	0	-5.850294	3.227689	1.056140
15	1	0	0.289230	-0.000203	-0.859451
16	1	0	-1.524119	-1.651715	-0.485023
17	8	0	-3.853251	-2.410175	0.039923
18	8	0	-6.802894	0.940526	1.028780
19	7	0	-5.320341	-0.737244	0.569842
20	6	0	1.446329	2.467919	-0.772715
21	6	0	2.135087	3.225701	-1.730060
22	6	0	2.160739	1.598955	0.064480
23	6	0	3.518400	3.096892	-1.846301
24	1	0	1.587932	3.902583	-2.381109
25	6	0	3.548086	1.446375	-0.066154
26	1	0	1.633760	1.065917	0.847249
27	6	0	4.222200	2.210118	-1.036446
28	1	0	4.048231	3.684458	-2.590585
29	1	0	5.294275	2.099669	-1.160485
30	6	0	4.281162	0.535922	0.834751
31	6	0	5.677683	0.604554	1.166805
32	26	0	5.254665	-1.242011	0.322888
33	6	0	3.733719	-0.570695	1.568883
34	6	0	5.975405	-0.433409	2.096424
35	6	0	4.773165	-1.160917	2.344813
36	6	0	4.995073	-1.582387	-1.710990
37	6	0	4.468066	-2.676193	-0.959971
38	6	0	5.532951	-3.237782	-0.191764
39	6	0	6.385364	-1.467411	-1.406819
40	6	0	6.717909	-2.491071	-0.468031
41	1	0	2.713328	-0.923884	1.514387
42	1	0	6.948590	-0.647853	2.516016
43	1	0	4.674799	-2.031380	2.978537
44	1	0	4.430824	-0.926453	-2.359688
45	1	0	3.437311	-3.002894	-0.950547
46	1	0	5.449197	-4.062287	0.502776
47	1	0	7.688836	-2.650996	-0.019470
48	1	0	6.384527	1.324873	0.779532

49	1	0	7.062286	-0.720446	-1.798314
50	6	0	-6.387277	-1.736568	0.757643
51	1	0	-5.906825	-2.643116	1.128290
52	1	0	-7.061332	-1.340165	1.518435
53	1	0	-1.762029	4.268185	0.240544
54	6	0	-7.156577	-2.032323	-0.534498
55	1	0	-7.598281	-1.100038	-0.906998
56	1	0	-6.449964	-2.387321	-1.294491
57	6	0	-8.257416	-3.078655	-0.321377
58	1	0	-7.808953	-4.003056	0.067028
59	1	0	-8.949698	-2.724646	0.454568
60	6	0	-9.041012	-3.389650	-1.600564
61	1	0	-8.381003	-3.778810	-2.384058
62	1	0	-9.820300	-4.137410	-1.420203
63	1	0	-9.527404	-2.490186	-1.994740
64	7	0	0.058361	2.661662	-0.620738
65	1	0	-0.279851	3.554109	-0.947233

Total Energy = -1619.69044521 HF.

DFT data of **FcNMI 3f:**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.448259	0.680244	-0.522526
2	6	0	-2.592813	1.519075	-0.258282
3	6	0	-2.543438	2.935350	-0.287103
4	6	0	-1.578429	-0.704275	-0.406892
5	6	0	-3.837560	0.895432	0.065840
6	6	0	-3.931094	-0.514994	0.169774
7	6	0	-2.803080	-1.287151	-0.060206
8	6	0	-5.207597	-1.168957	0.511408
9	6	0	-6.291121	1.070382	0.620703
10	6	0	-4.984309	1.698892	0.294532
11	6	0	-4.904137	3.078838	0.222167
12	6	0	-3.673406	3.698707	-0.057637
13	1	0	-3.607603	4.781955	-0.080575
14	1	0	-5.802951	3.658859	0.401666
15	1	0	-0.730530	-1.340621	-0.628092
16	1	0	-2.896038	-2.365904	0.010385
17	8	0	-5.329496	-2.385618	0.605461
18	8	0	-7.308980	1.731848	0.792808
19	7	0	-6.312421	-0.324366	0.733416
20	6	0	1.033143	0.744175	-0.949684
21	6	0	1.507778	-0.138852	0.034886
22	6	0	1.914378	1.155173	-1.960741
23	6	0	2.816983	-0.603159	-0.013663
24	1	0	0.859559	-0.438670	0.850730
25	6	0	3.225768	0.691745	-1.992614
26	1	0	1.562073	1.830196	-2.737133
27	6	0	3.709162	-0.201798	-1.023602
28	1	0	3.165954	-1.269165	0.769599
29	1	0	3.876841	1.008354	-2.801650
30	6	0	5.089795	-0.713786	-1.082454

31	6	0	5.561670	-1.963909	-0.553767
32	26	0	6.630982	-0.405685	0.301480
33	6	0	6.214635	-0.076989	-1.707997
34	6	0	6.946866	-2.095451	-0.863679
35	1	0	4.963884	-2.686541	-0.015868
36	6	0	7.351360	-0.927740	-1.577069
37	6	0	5.909985	0.784333	1.846659
38	6	0	7.010242	1.428555	1.204685
39	6	0	8.151074	0.577692	1.324262
40	6	0	6.370472	-0.464704	2.363030
41	6	0	7.756015	-0.592402	2.040526
42	1	0	6.211156	0.903046	-2.164751
43	1	0	7.583437	-2.923104	-0.582617
44	1	0	8.351986	-0.706557	-1.921792
45	1	0	4.895438	1.155976	1.893743
46	1	0	6.977497	2.379694	0.691322
47	1	0	9.133475	0.771208	0.916016
48	1	0	5.770027	-1.197886	2.883975
49	1	0	8.386092	-1.441015	2.268845
50	1	0	-1.598487	3.442602	-0.456495
51	7	0	-0.264002	1.287598	-0.915071
52	1	0	-0.368137	2.158144	-1.413776
53	6	0	-7.597012	-0.961786	1.074458
54	1	0	-7.360343	-1.862275	1.642943
55	1	0	-8.140030	-0.258941	1.707991
56	6	0	-8.428039	-1.316699	-0.163473
57	1	0	-8.618671	-0.401849	-0.737729
58	1	0	-7.842713	-1.989190	-0.802186
59	6	0	-9.758504	-1.982848	0.207617
60	1	0	-10.332051	-1.310674	0.860155
61	1	0	-9.559025	-2.886956	0.798728
62	6	0	-10.603812	-2.350057	-1.016310
63	1	0	-11.545420	-2.825965	-0.723364
64	1	0	-10.850023	-1.461381	-1.608391
65	1	0	-10.068469	-3.046225	-1.671812

Total Energy = -1619.69082360 HF.

Single Crystal X–ray Diffraction Studies:

Single crystal X–ray structural studies of **3a**, **3c** were performed on a SUPER NOVA diffractometer. Data were collected at 293(2) K using graphite–monochromated Mo Kα radiation (λα=0.71073 Å). The strategy for the data collection was evaluvated 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 nonhydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained 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 CCDC numbers 1407605 and 1407604 contain the supplementary crystallographic data for **3a** and **3c** 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).

Table S1: Crystal structure and data refinement parameters of **3c** and **3a**.

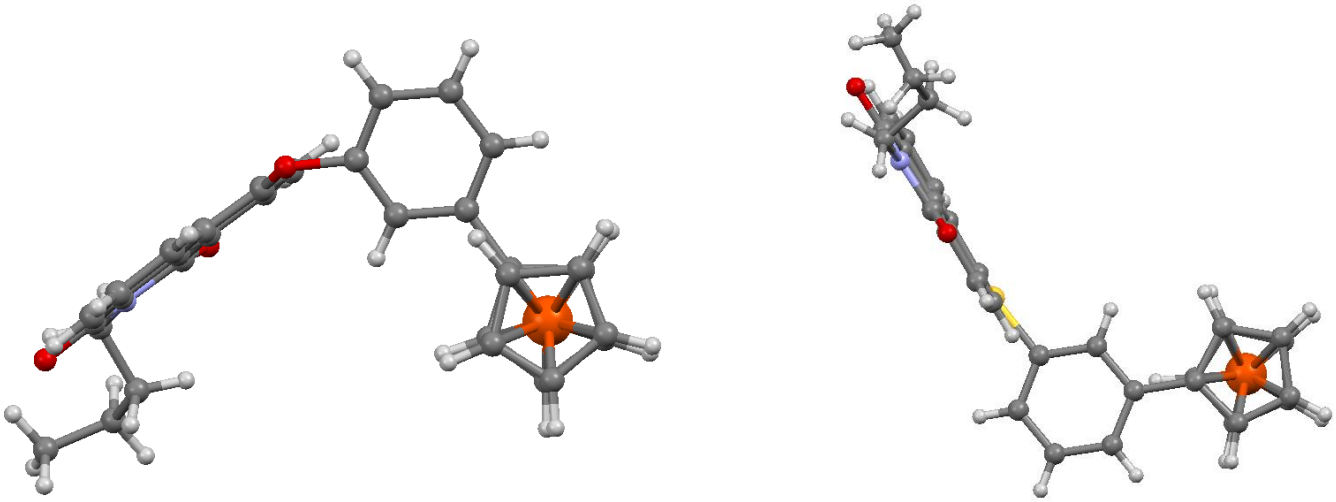
Parameters	**3c**	**3a**
Empirical formula	$C_{64}H_{54}Fe_2N_2O_4S_2$	$C_{64}H_{54}Fe_2N_2O_6$
Formula Weight	1090.91	1058.79
Temperature	150(2) K	150(2) K
Crystal system	Triclinic	Triclinic
Space group	P–1	P–1
Unit Cell Dimensions		
α/A°βγ	12.1041(7)	11.582(5)
α/°	84.266 (5)	86.196(5)
β/A°	14.5758	14.738
β/°	84.771	78.480
γ/A°	16.2867	16.567
γ/°	67.853	67.167
Volume/A^3	2643.6 (3)	2553.6(16)
Z	2	2
Calculated density/Mg/mA^3	1.370	1.377
Absorption coefficient/mm^{-3}	5.545	0.625
F(000)	1136	1104
Crystal size/mm	0.33 x 0.26 x 0.21	0.33 x 0.26 x 0.21
θ range from data collection	3.28 to 71.36	1.499 to 25.893
Reflections collected/unique	18442/10021 [R(int)=0.0361]	17586/9663 [R(int)=0.0292]
Absorption correction	Semi empirical from equivalents	Semi empirical from equivalents
Data/restraints/parameters	10021/0/669	9663/30/734
Goodness of fit on F^2	1.028	1.104
Final R indices [I>2 σ(I)]	R_1=0.0571 WR_2=0.1383	R_1=0.0600 WR_2=0.1596
R indices (all data)	R_1=0.0824 WR_2=0.1592	R_1=0.0711 WR_2=0.1678
Largest diff. Peak and hole/e A^-3	0.265 and –0.408	0.361 and –0.779
CCDC number	1407604	1407605

Table S2: Distances of intermolecular interactions in the Crystal Structure of FcNMI **3a**.

Interaction	Distance (Å)
C(4)-H(4)----C(58)	2.709
C(32)-H(32)----C(56)	2.852
C(27)-H(27)----C(55)	3.264
C(53)-H(53B)----C(30)	2.895
C(14)-H(14)----C(64)	2.851
C(15)-H(15)----C(64)	2.788
C(9)----C(43)	3.319
C(51)-H(51B)----C(8)	2.830

Table S3: Distances of intermolecular interactions in the Crystal Structure of FcNMI **3c**.

Interaction	Bond distance (Å)
C(56)−H(56)----C(24)	2.662
C(61)−H(61)----C(27)	2.777
C(41)−H(41)----C(29)	2.753
C(32)-----C(32)	3.385



(a) **(b)**

Figure S36: The ferrocenyl cyclopentadienyl groups conformations of FcNMIs (a) **3a** **(**skew–eclipsed) (b) **3c (**skew–eclipsed).

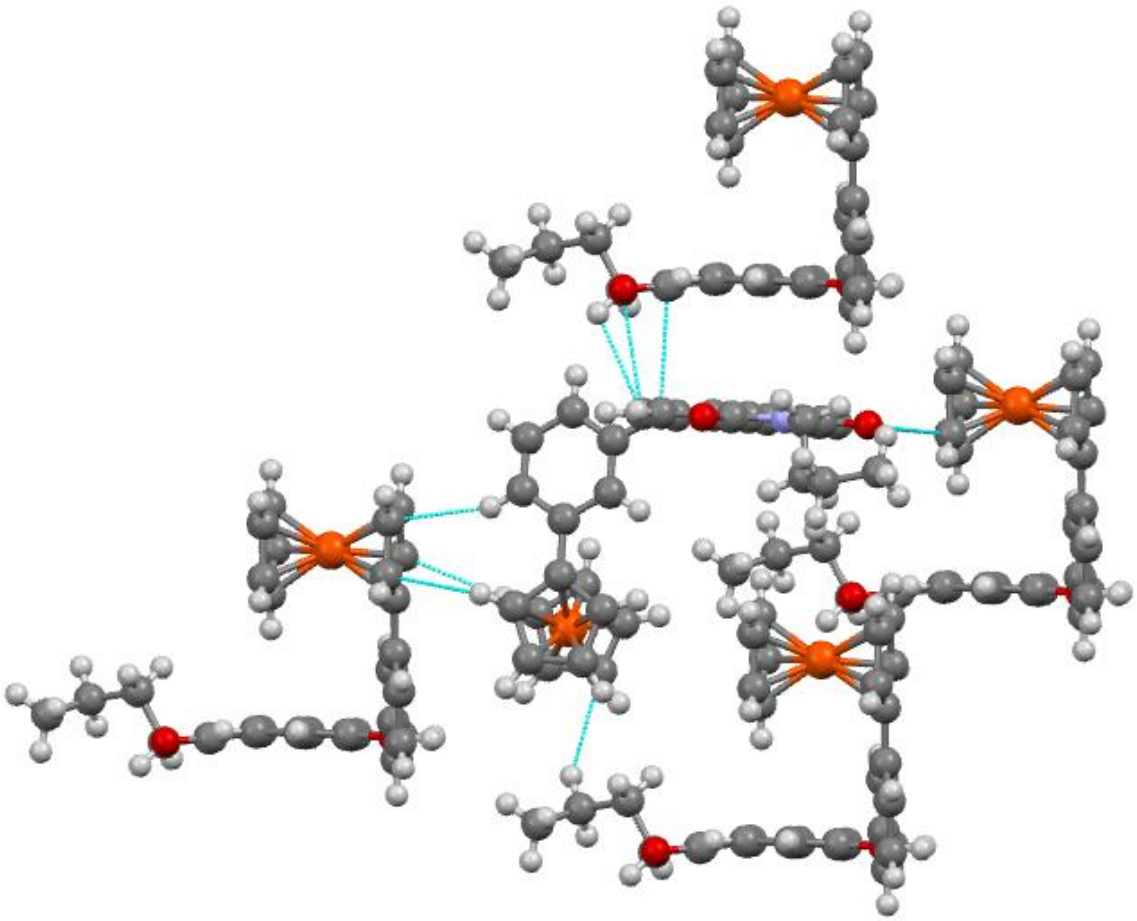


Figure 37: Packing diagram of FcNMI **3a**, forming 2–D network through *b*-axis.

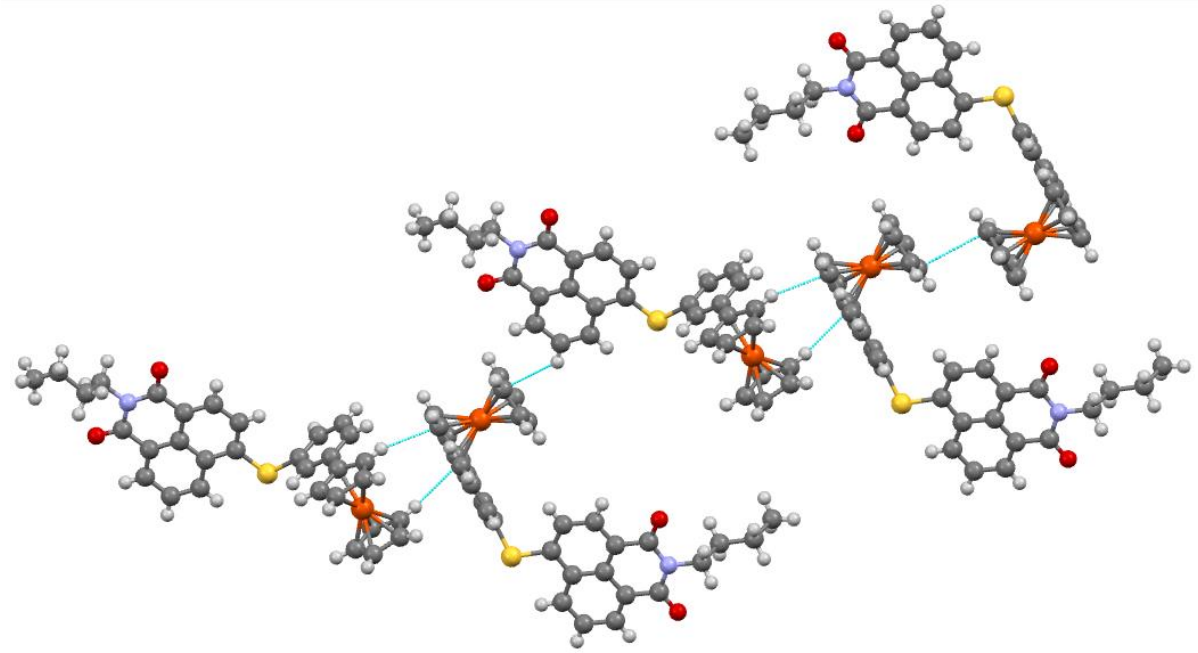


Figure 38: Packing diagram of FcNMI **3c**, forming 2–D network through *b*–axis.