Supplementary Information

Ferrocene catalysed heteroarylation of BODIPy and reaction mechanism studies by EPR and DFT methods

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Contents:

NMR spectra:

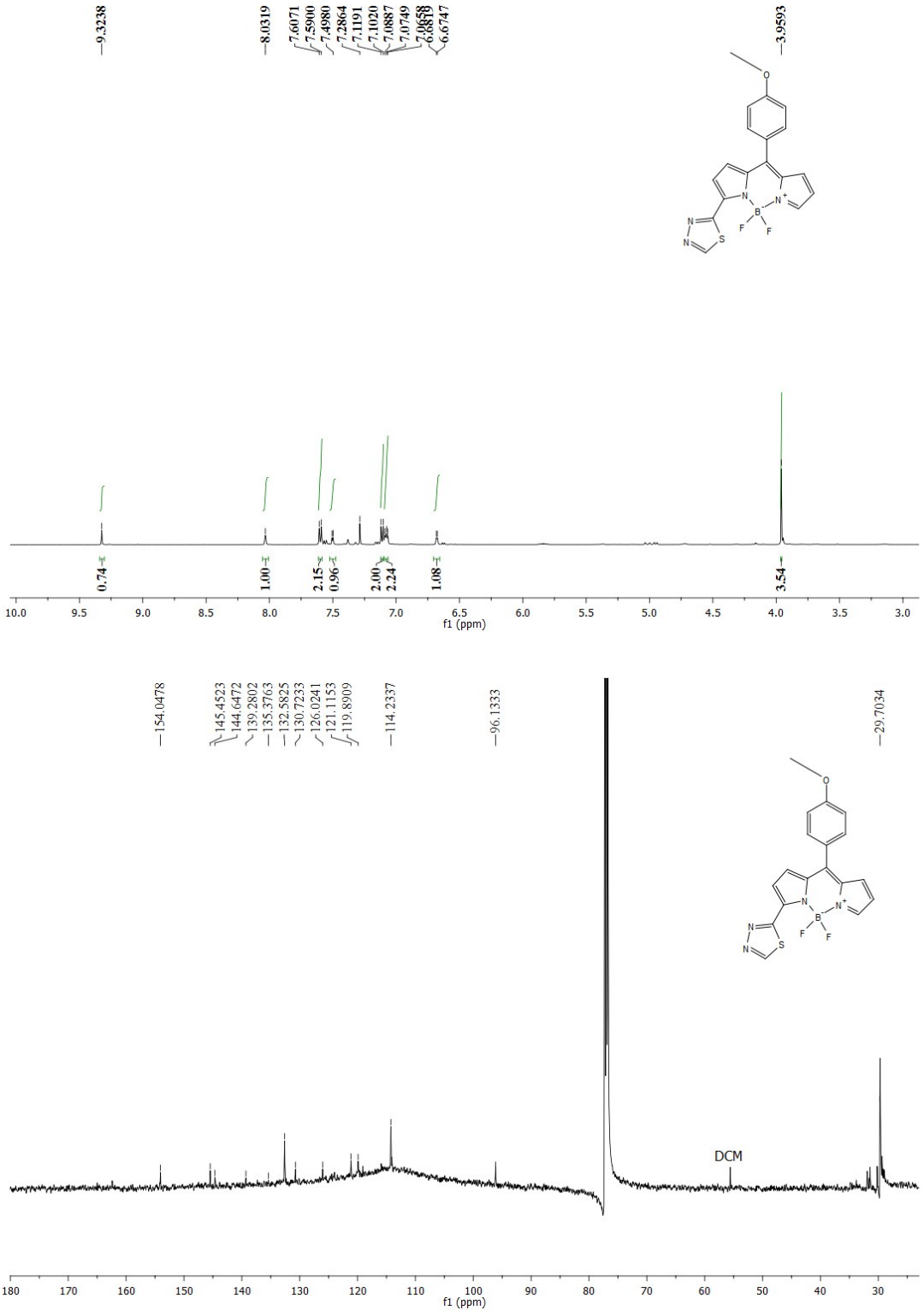

Figure SI 1: ^{1}H NMR (above) and ^{13}C NMR (below) spectra of **1** in $CDCl_3$

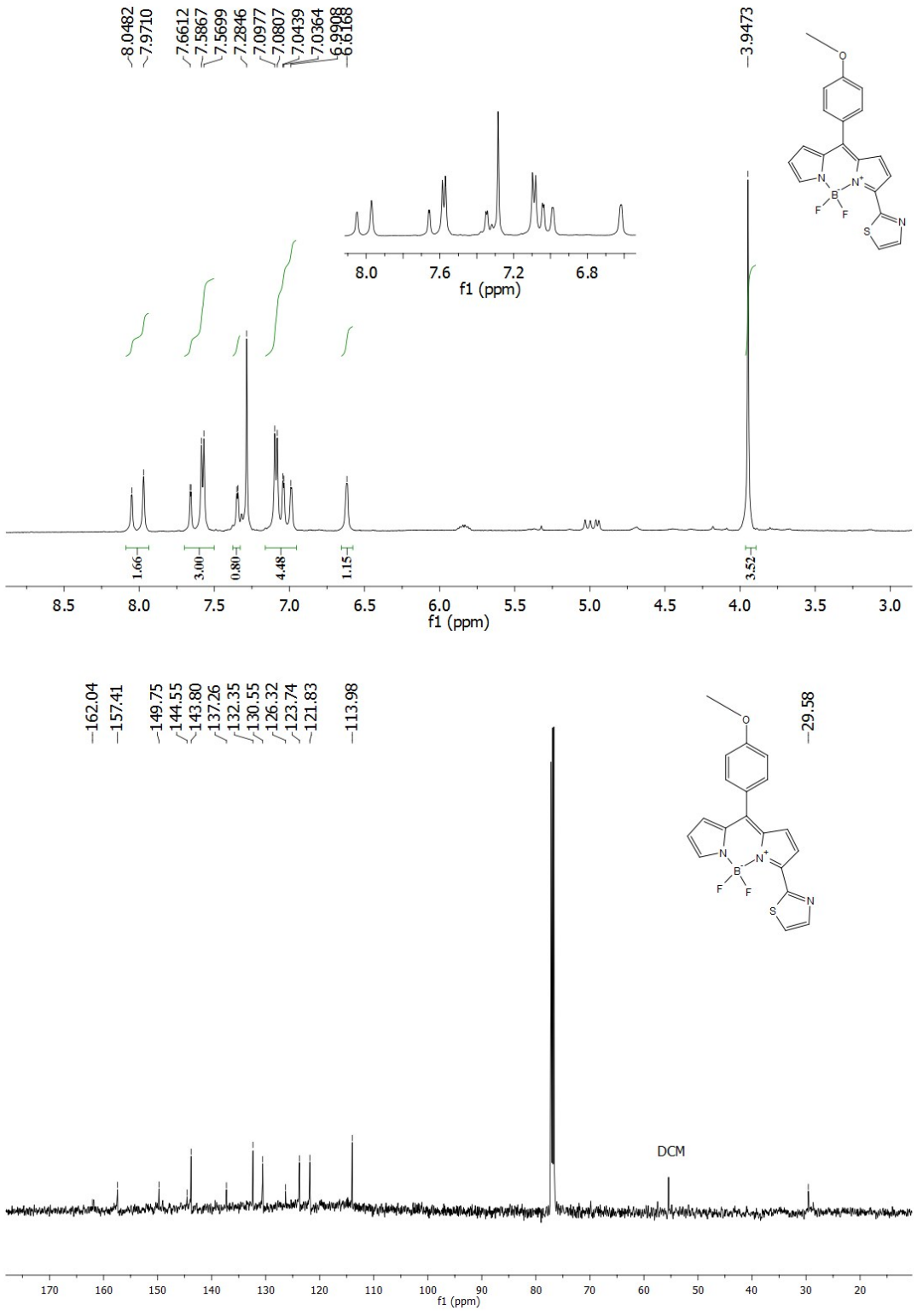

Figure SI 2: ^{1}H NMR (above) and ^{13}C NMR (below) spectra of **3** in $CDCl_3$

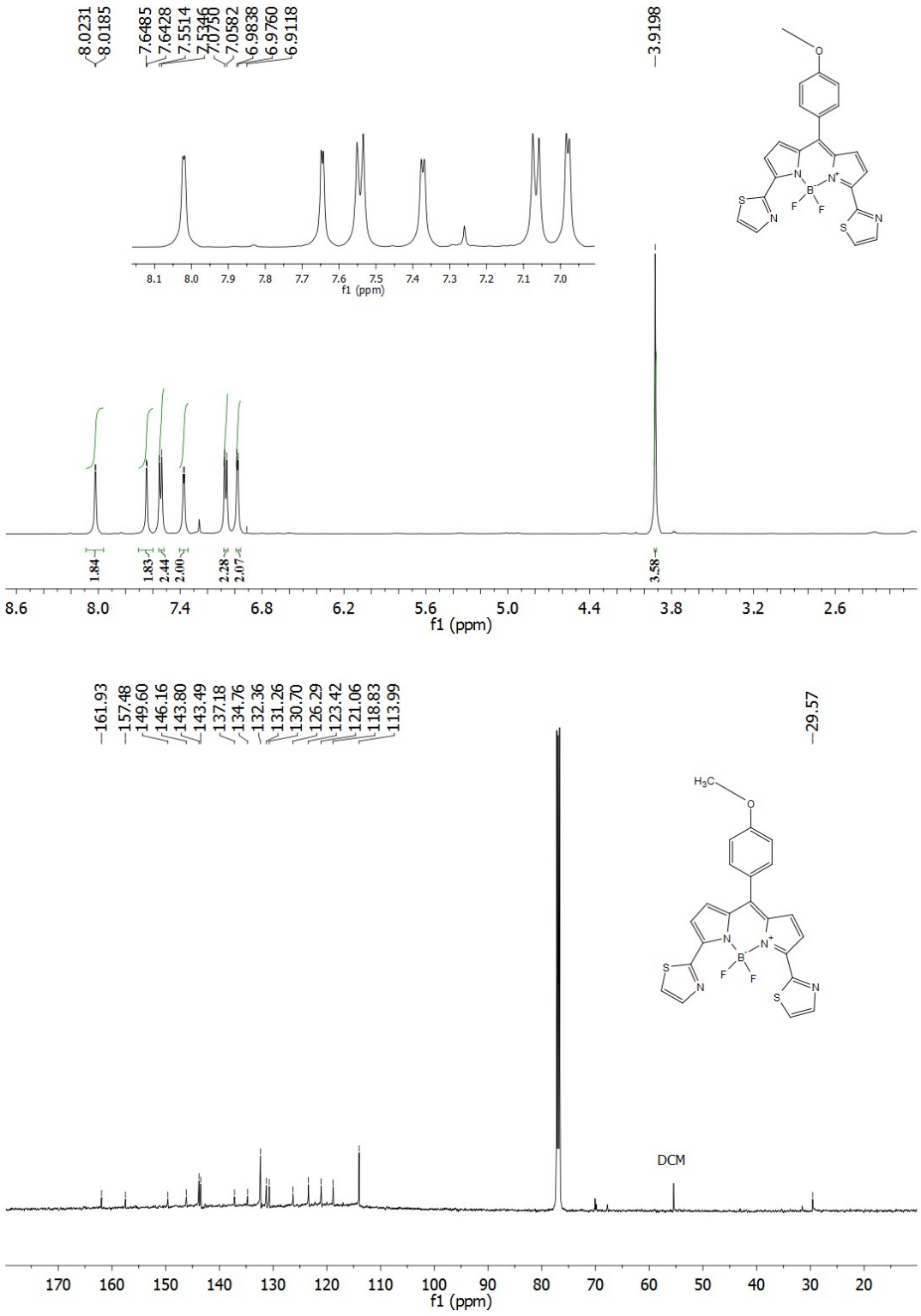

Figure SI 3: ^{1}H NMR (above) and ^{13}C NMR (below) spectra of **4** in $CDCl_3$

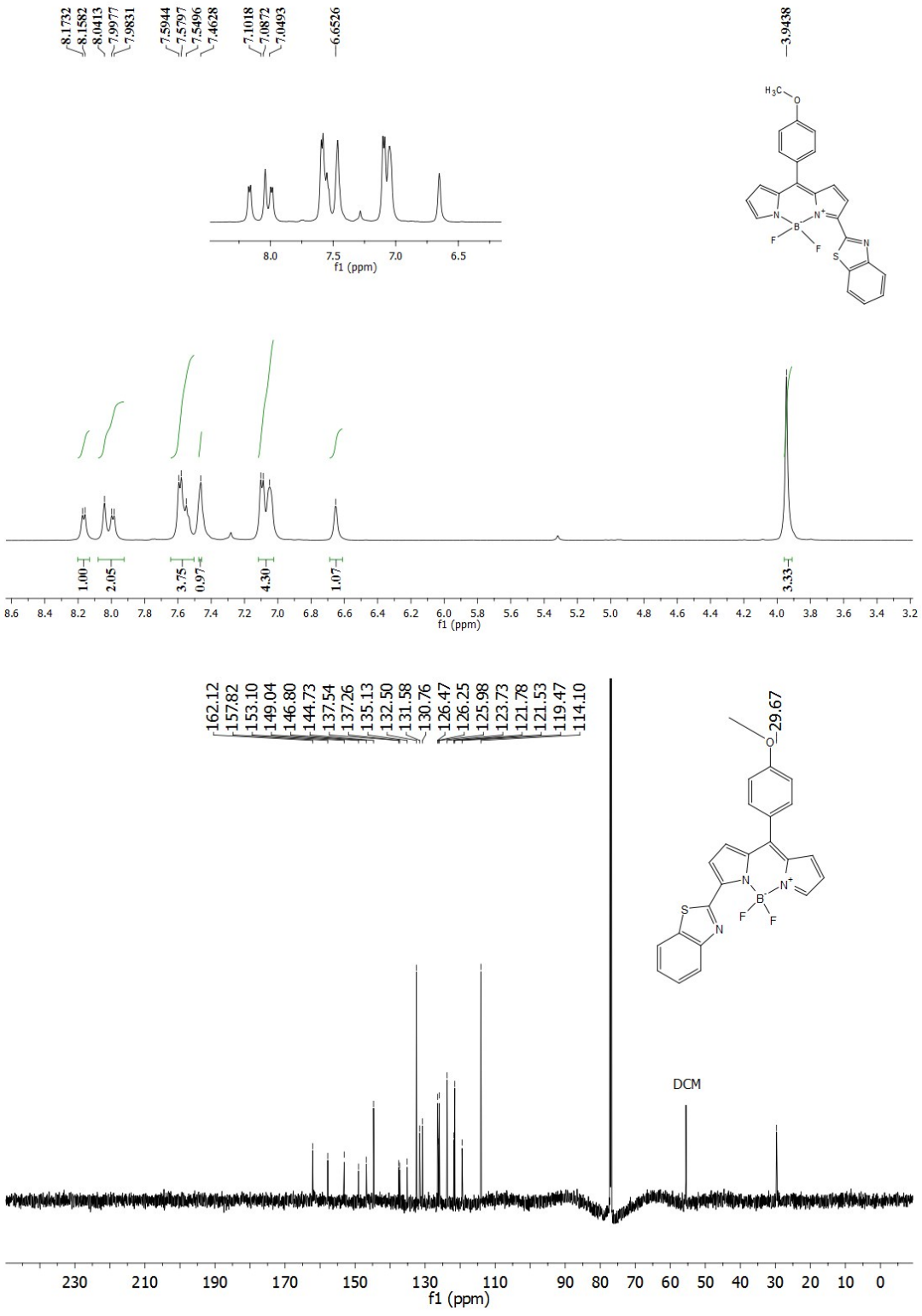

Figure SI 4: ^{1}H NMR (above) and ^{13}C NMR (below) spectra of **5** in $CDCl_3$

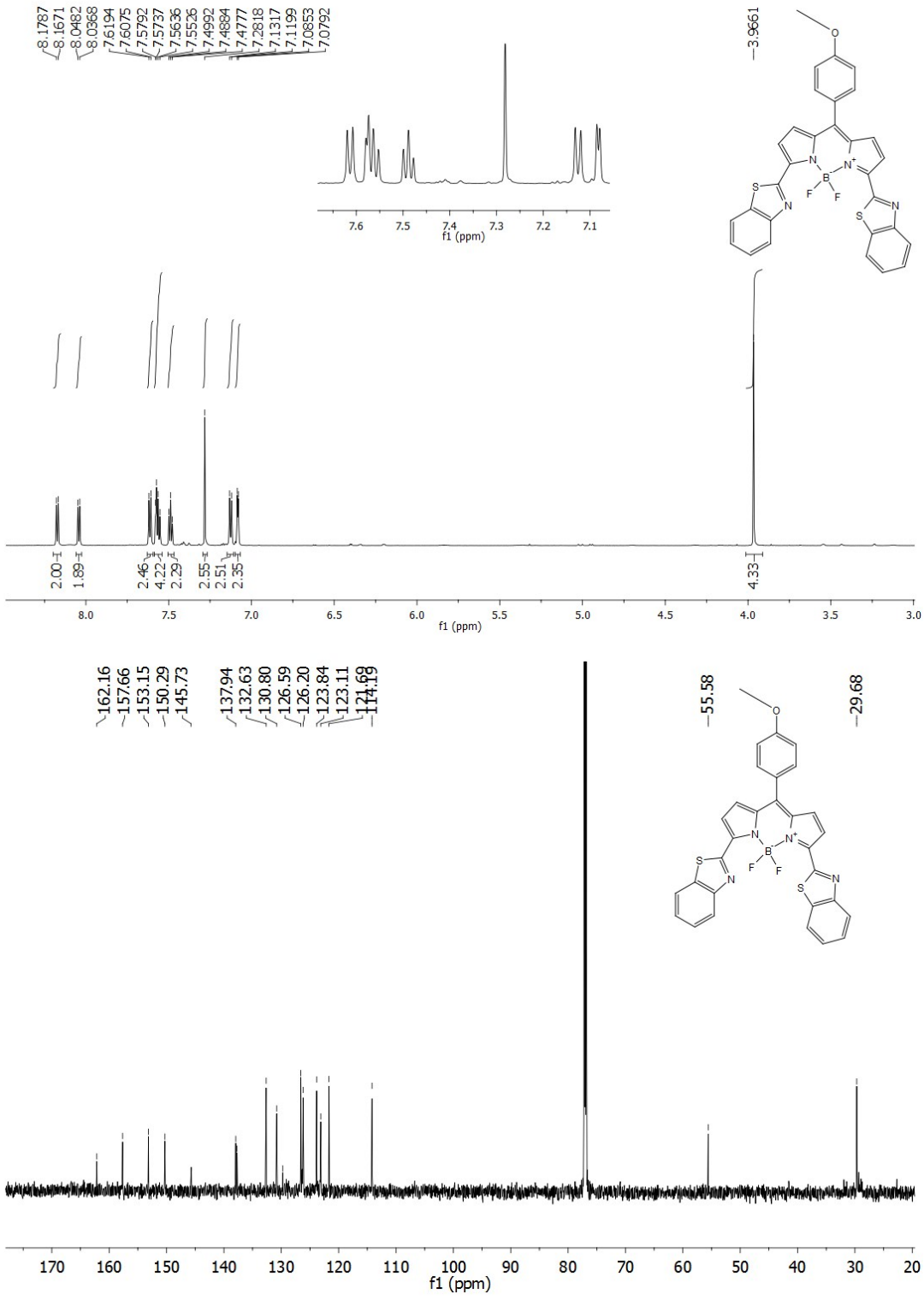

Figure SI 5: ^{1}H NMR (above) and ^{13}C NMR (below) spectra of **6** in $CDCl_3$

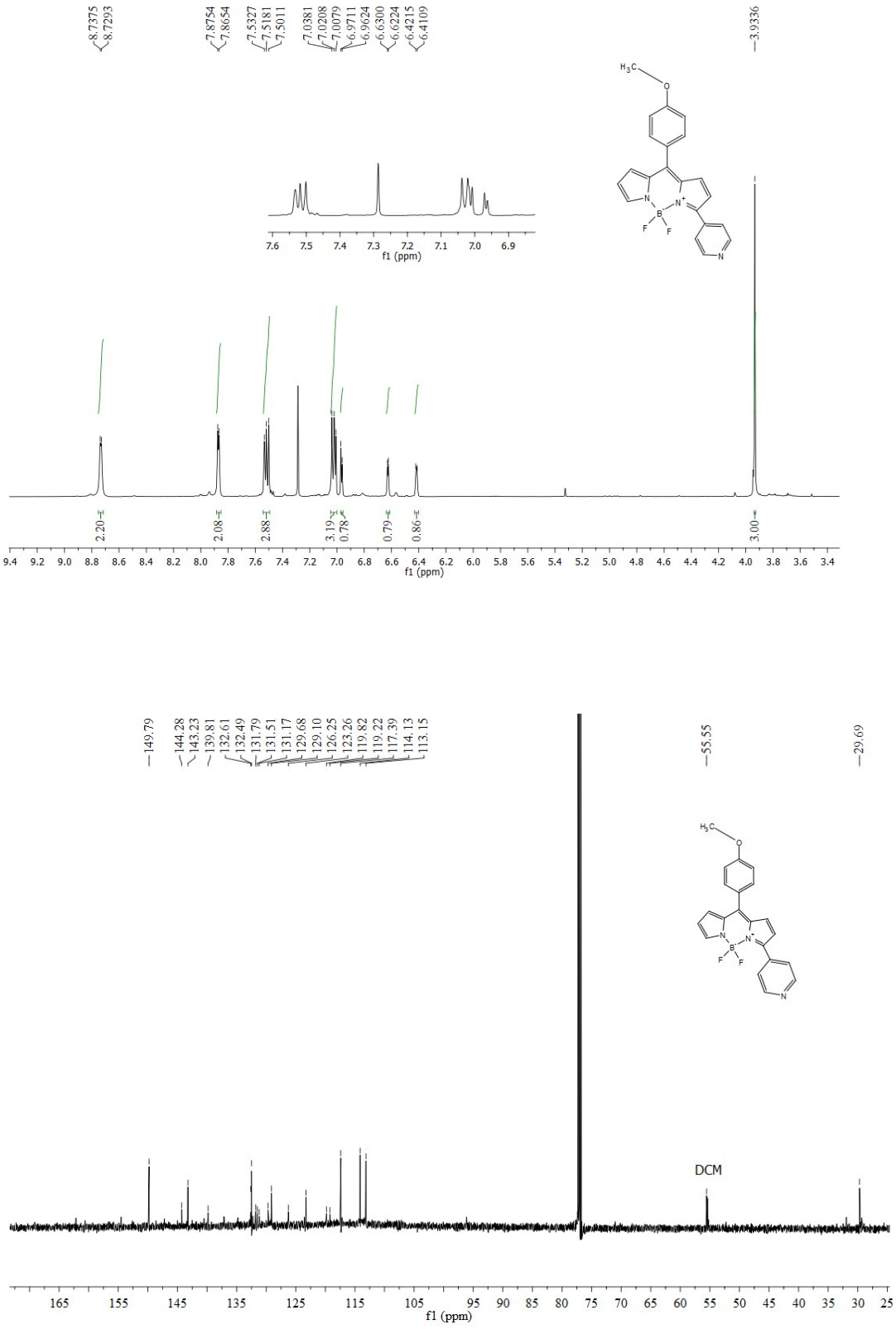

Figure SI 6: ^{1}H NMR (above) and ^{13}C NMR (below) spectra of **7** in $CDCl_3$

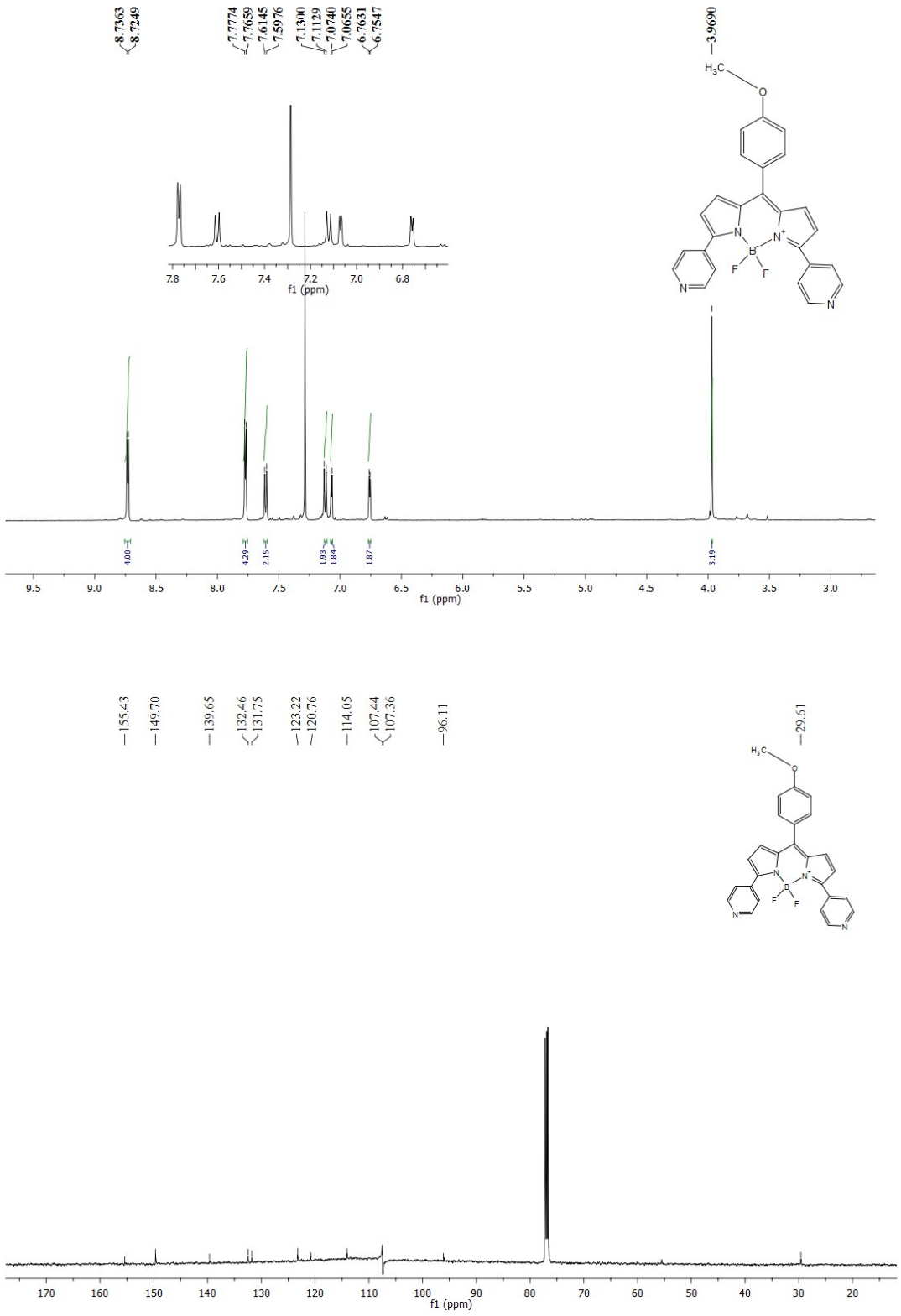

Figure SI 7: ^{1}H NMR (above) and ^{13}C NMR (below) spectra of **8** in $CDCl_3$

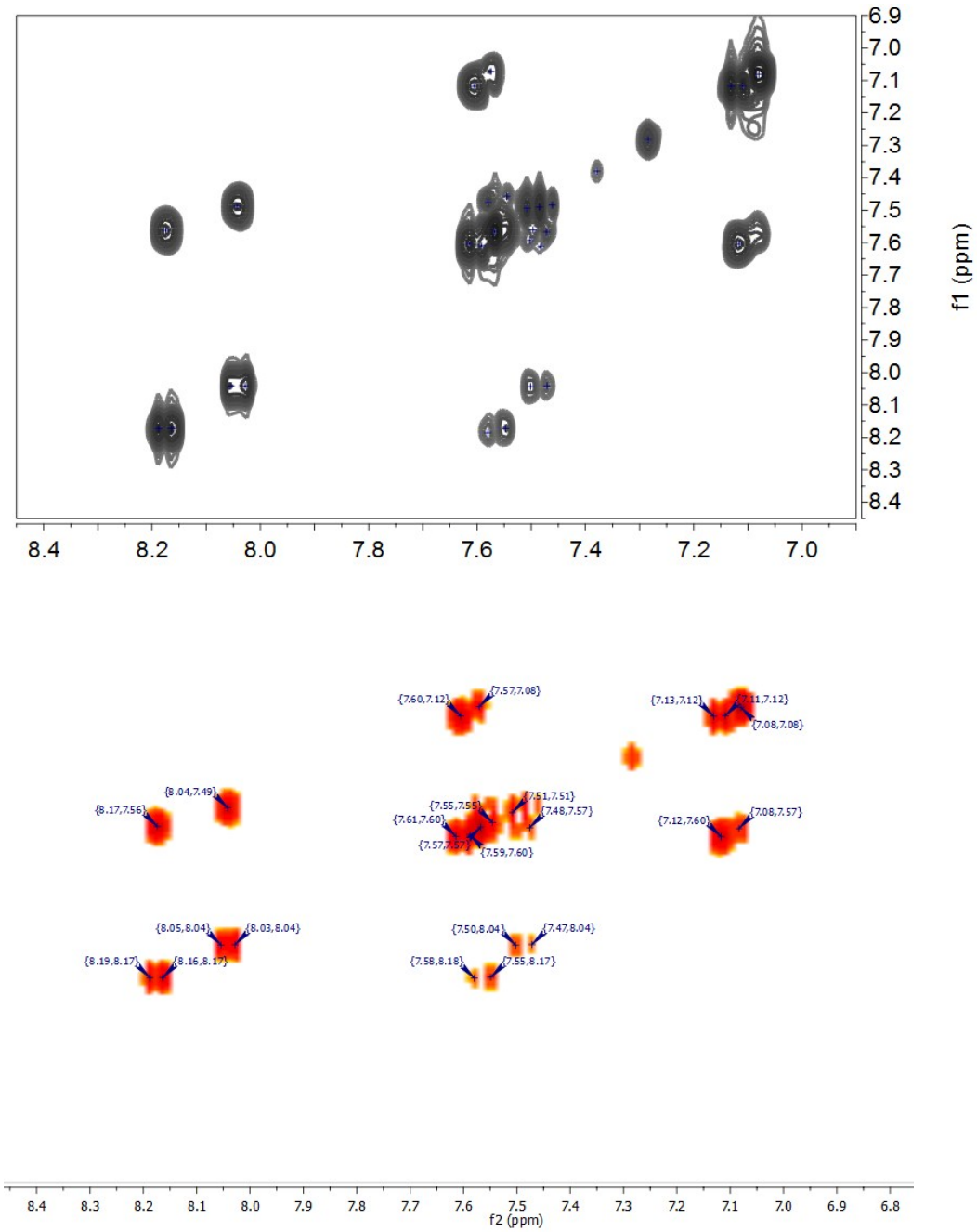

Figure SI 8: COSY of compound **6** in $CDCl_3$

Mass spectra:

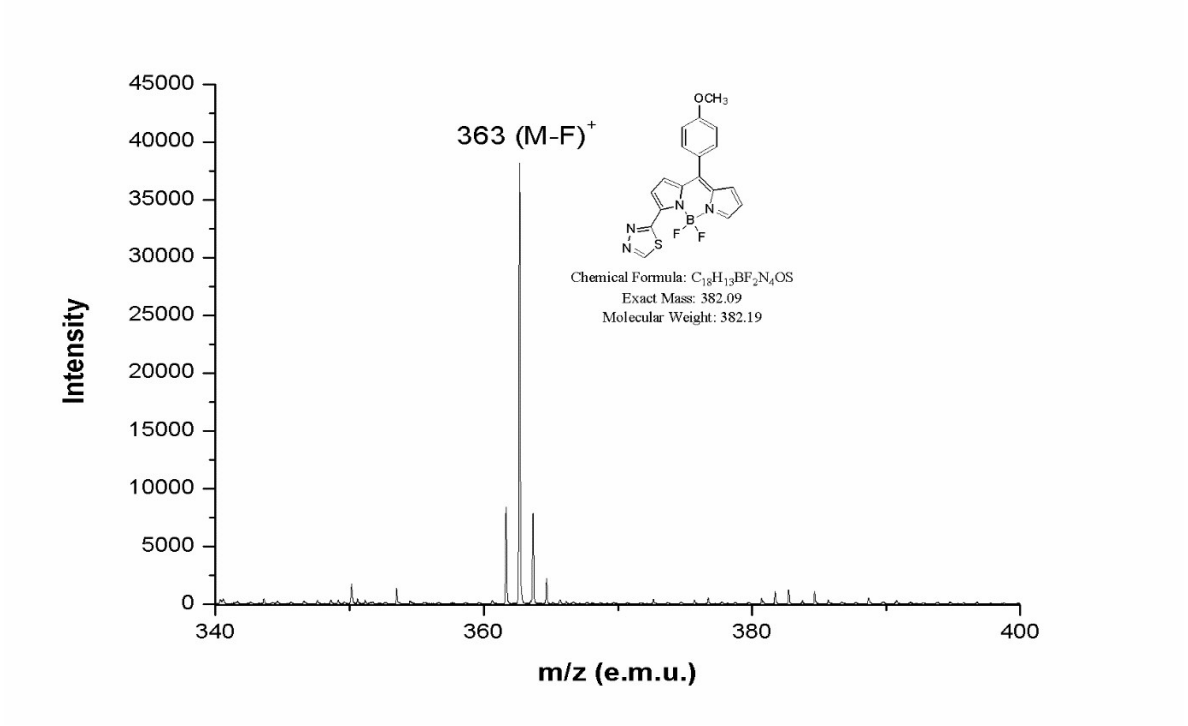

Figure SI 9: MALDI-TOF spectrum of compound **1**

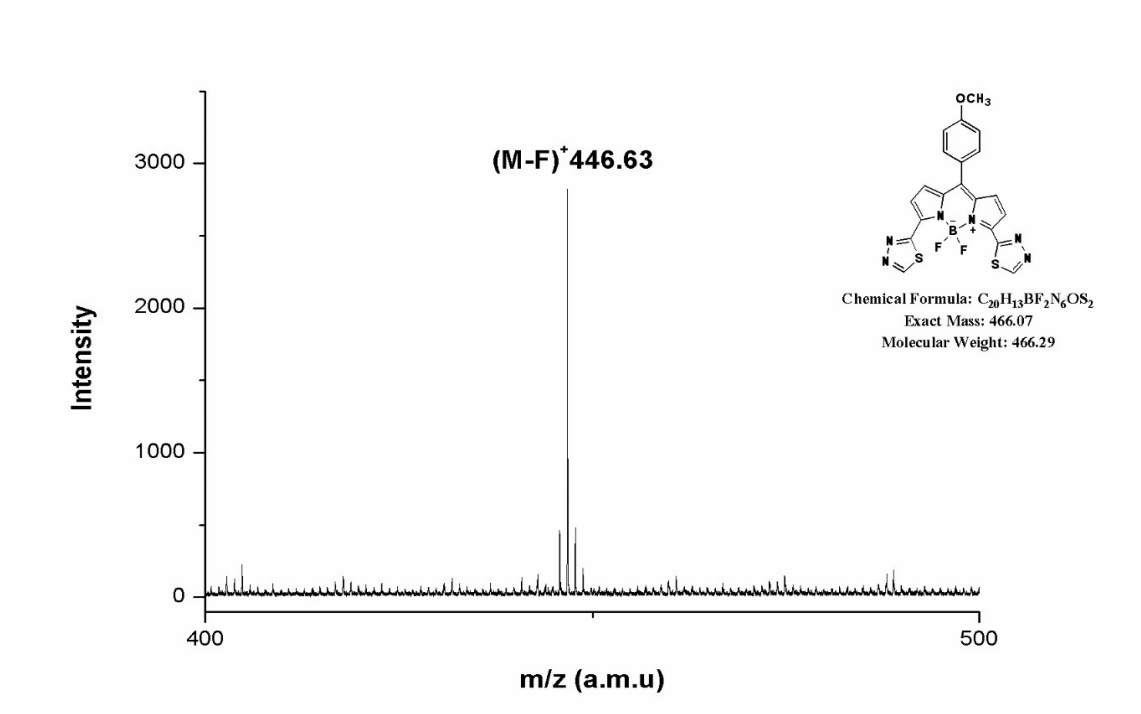

Figure SI 10: MALDI-TOF spectrum of compound **2**

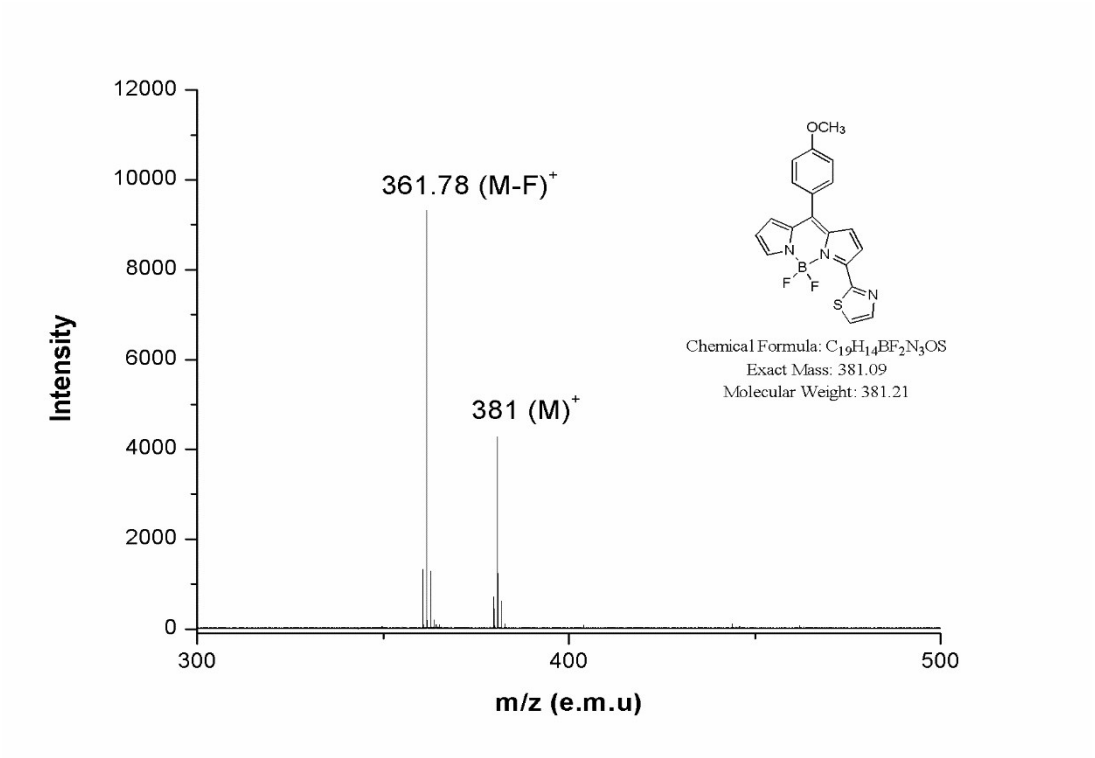

Figure SI 11: MALDI-TOF spectrum of compound **3**

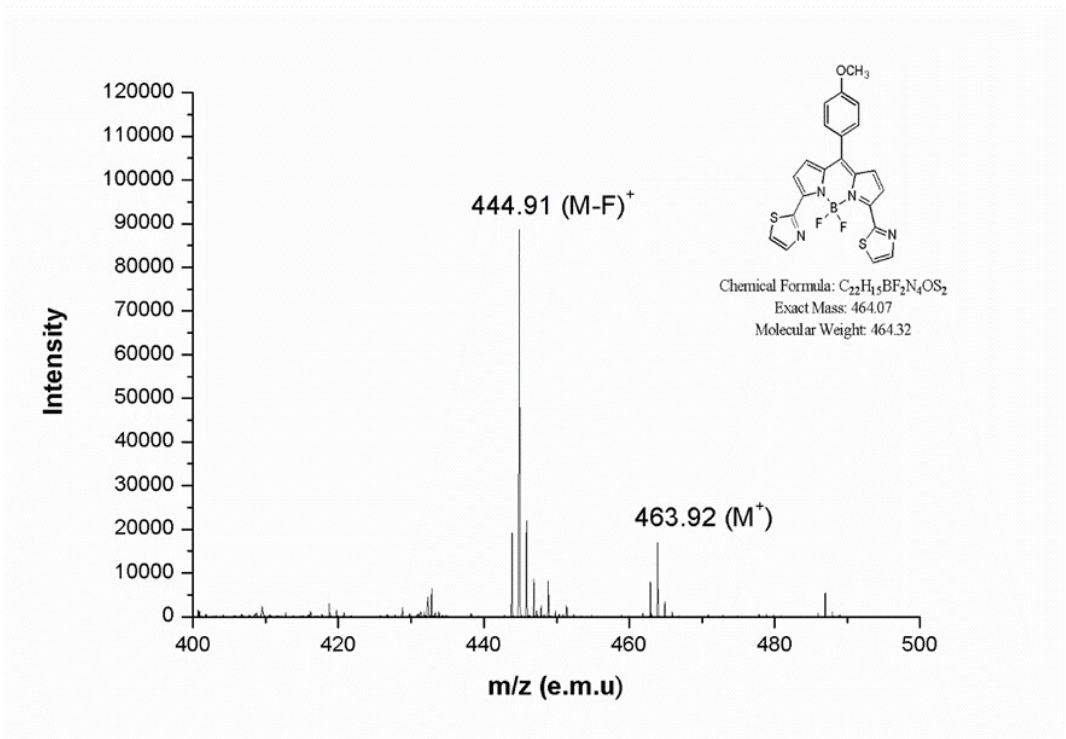

Figure SI 12: MALDI-TOF spectrum of compound **4**

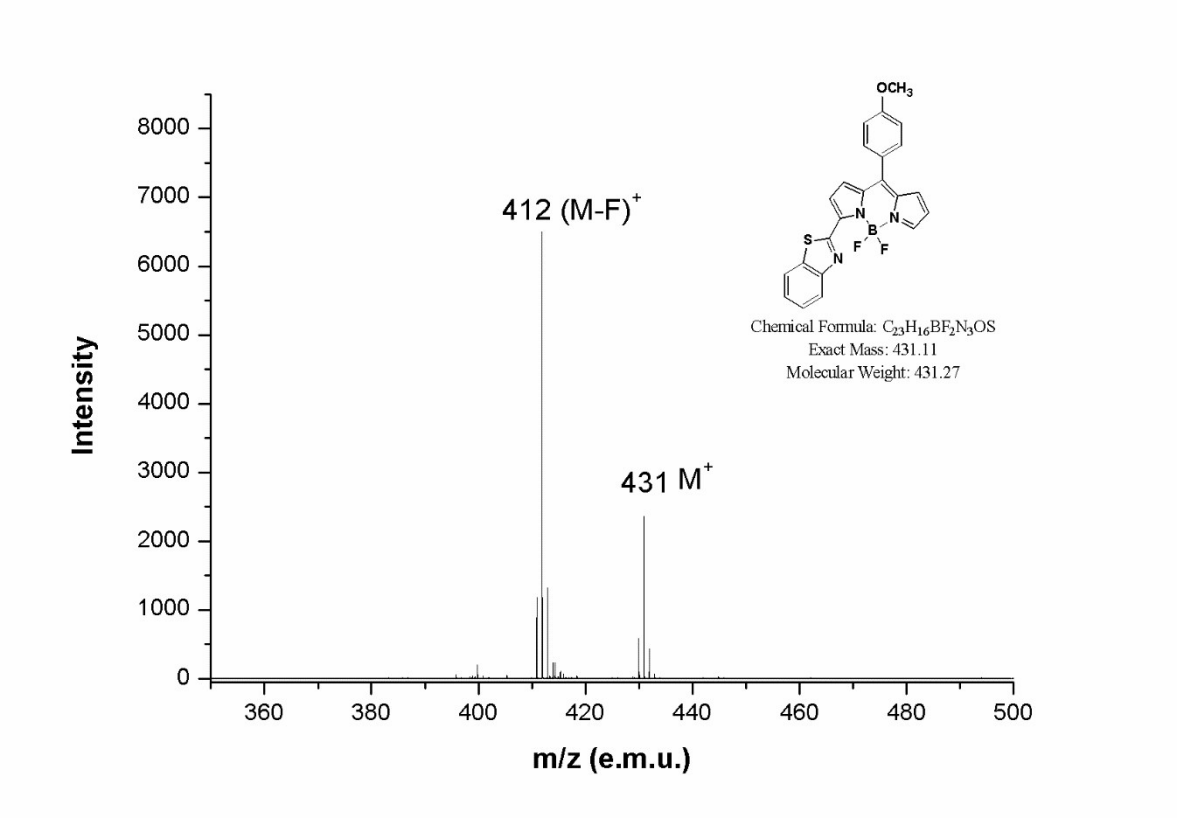

Figure SI 13: MALDI-TOF spectrum of compound **5**

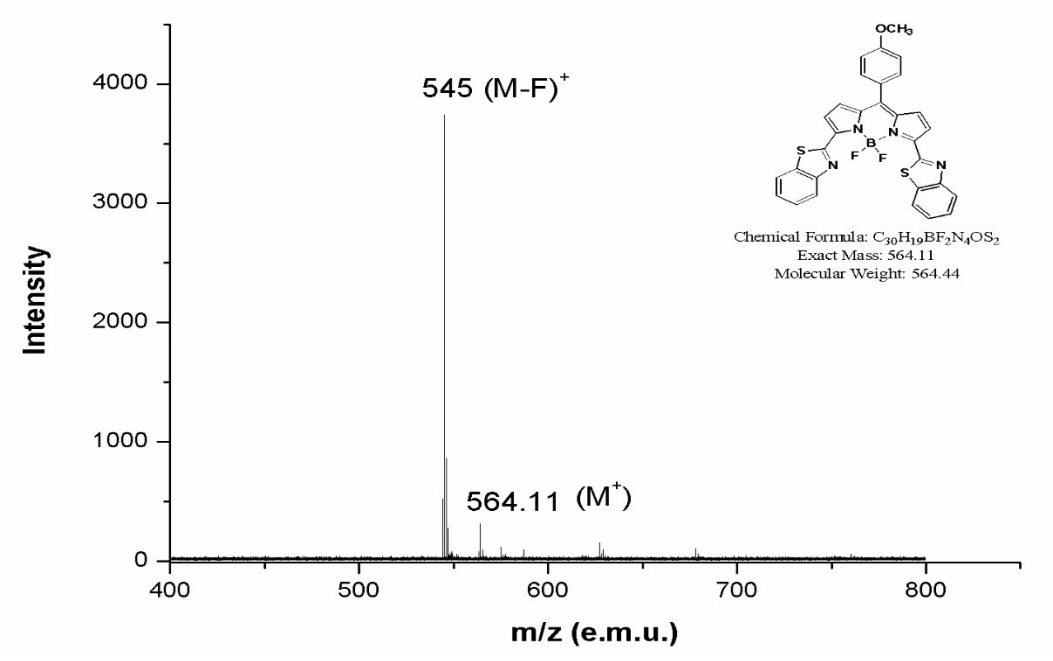

Figure SI 14: MALDI-TOF spectrum of compound **6**

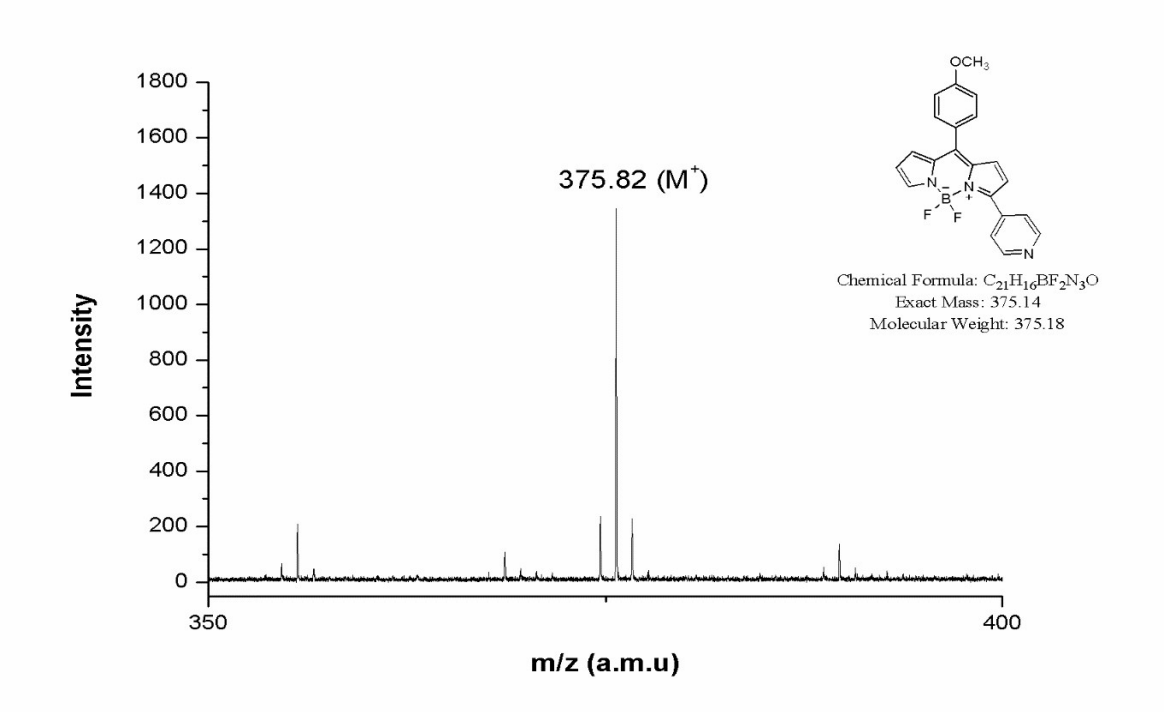

Figure SI 15: MALDI-TOF spectrum of compound **7**

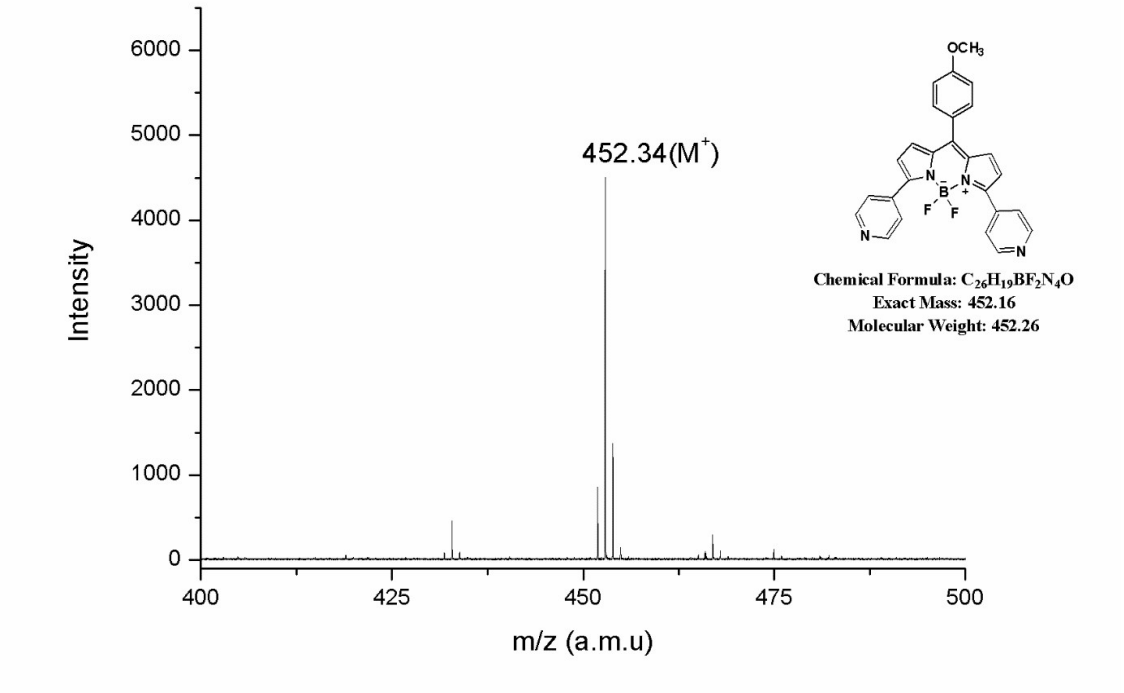

Figure SI 16: MALDI-TOF spectrum of compound **8**

FT-IR Spectra of compound

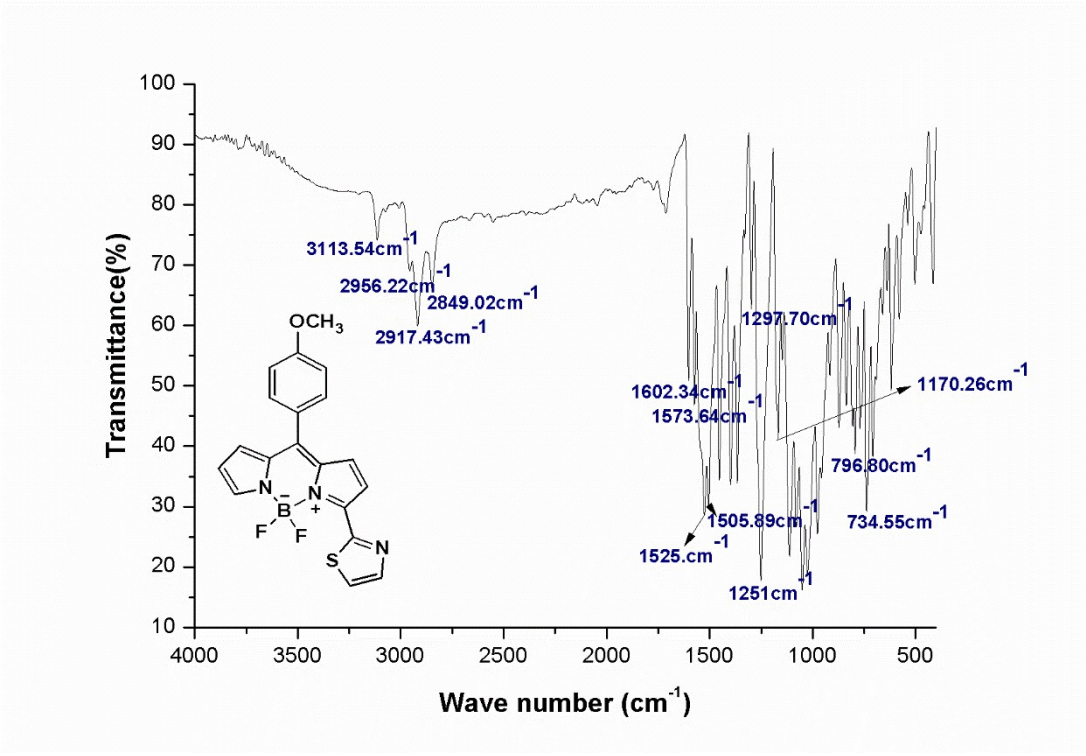

Figure SI 17: FT-IR spectrum of compound **3**

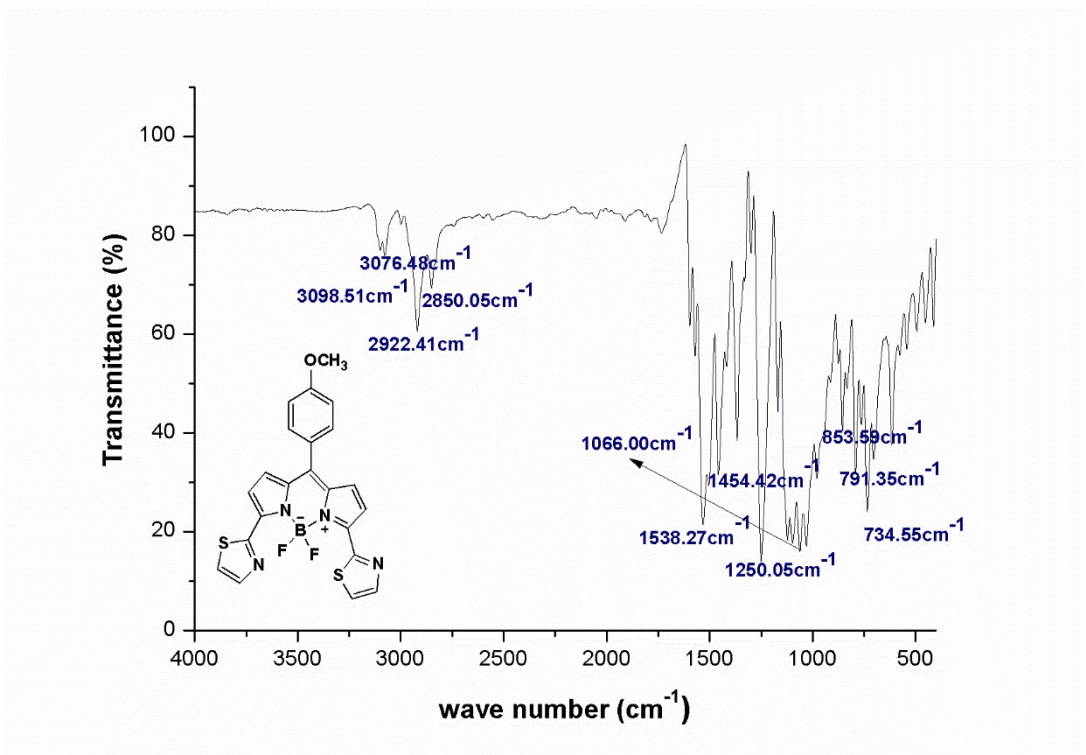

Figure SI 18: FT-IR spectrum of compound **4**

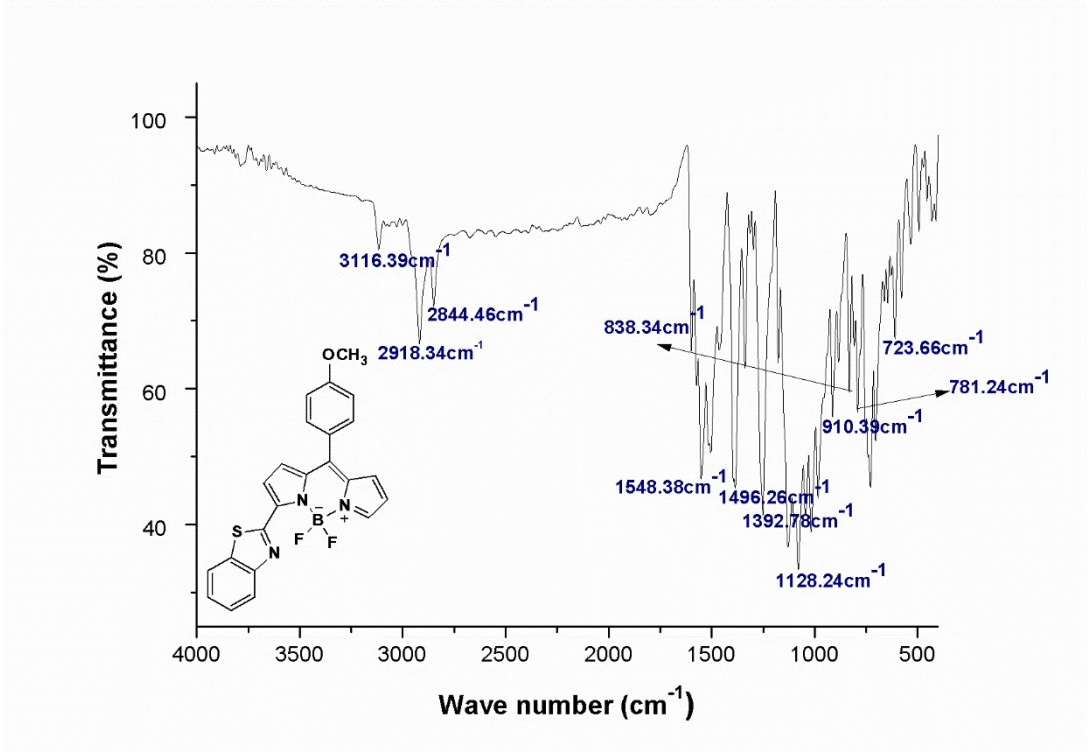

Figure SI 19: FT-IR spectrum of compound **5**

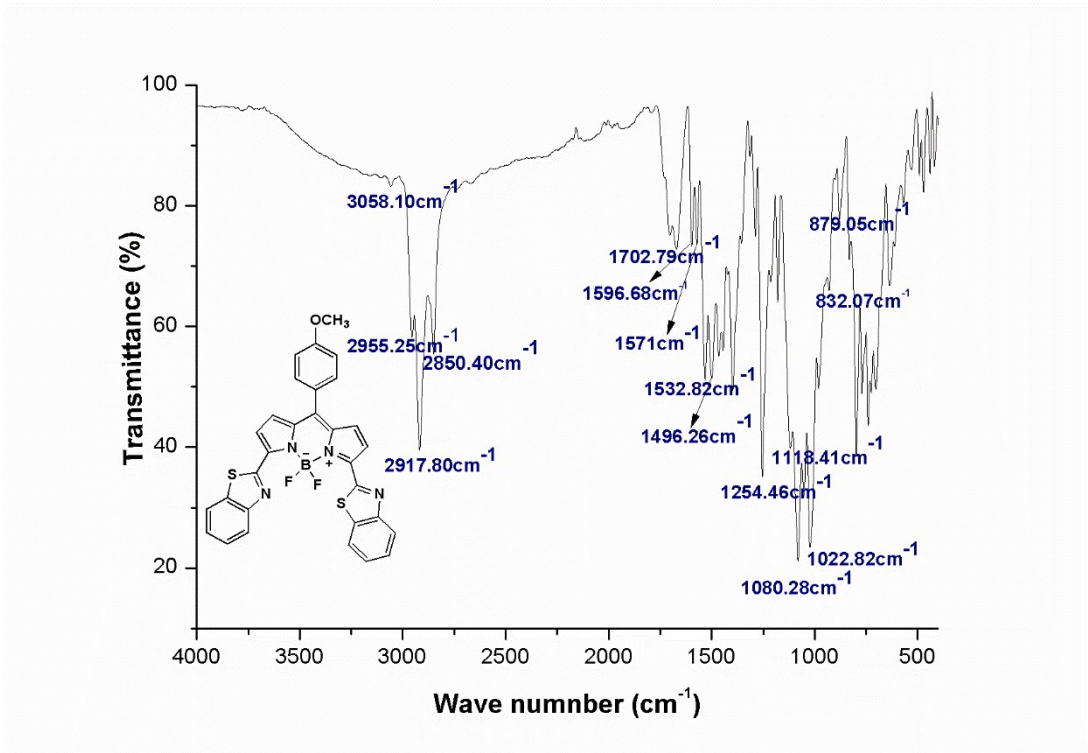

Figure SI 20: FT-IR spectrum of compound **6**

Density Functional Theory (DFT) calculations data

Table S1. Optimized geometries (M06-2X, Cartesian coordinates in Å) and energies of reactants and intermediates (in a.u.). Notation: E = total electronic energy, Tc = thermal correction at 298K to obtain the Gibbs free energy, Nimag = number of imaginary frequencies ⟨S2⟩= expectation value.

ArN_2^+				Ferrocene ($FeCp_2$)			
E = -677.649637				E = -1650.6172541			
Nimag = 0				Nimag = 0			
Tc = 0.024781				Tc = 0.135911			
6	-0.426157	0.188148	-0.000127	6	-1.743603	0.062580	1.205755
7	0.139287	1.361369	-0.000439	6	-1.744254	1.166041	0.312652
16	0.579080	-1.204018	-0.000109	6	-1.743511	0.657498	-1.012675
6	1.475265	1.183546	0.000201	6	-1.742322	-0.760220	-0.938612
6	1.891188	-0.132633	0.000183	6	-1.742432	-1.127882	0.432421
1	2.133358	2.039179	0.000626	1	-1.708354	0.119162	2.283007
1	2.900715	-0.516001	0.000665	1	-1.709191	2.208018	0.591864
7	-1.804959	0.096277	-0.000035	1	-1.708114	1.245469	-1.917133
7	-2.897347	0.014746	0.000318	1	-1.705255	-1.438634	-1.777249
				1	-1.705440	-2.134962	0.818830
				26	-0.000019	0.000598	0.000293
				6	1.742754	-1.166169	-0.314192
				6	1.742797	-0.061674	-1.206053
				6	1.743329	-0.659086	1.011766
				1	1.706045	-2.207717	-0.594723
				6	1.743568	1.127867	-0.431363
				1	1.706475	-0.116768	-2.283363
				6	1.743800	0.758736	0.939224
				1	1.707699	-1.248076	1.915544
				1	1.707795	2.135496	-0.816532

	1 1.708067 1.436307 1.778614
Ar radical E = -568.3295967 Nimag = 0 Tc = 0.015199 ⟨S2⟩ = 0.759031	$FeCp_2^{+}$• E = -1650.4111418 Nimag = 0 Tc = 0.135243 ⟨S2⟩ = 0.867605
6 -0.051901 -1.229014 -0.000058 7 -1.241357 -0.822950 0.000054 16 1.193948 -0.036772 0.000015 6 -1.278854 0.570351 -0.000045 6 -0.061965 1.167067 -0.000025 1 -2.231438 1.078887 0.000093 1 0.174098 2.219690 0.000053	6 1.718464 -1.062107 0.577868 6 1.718360 -0.878207 -0.831378 6 1.719161 0.519201 -1.091572 6 1.719840 1.198268 0.156655 6 1.719400 0.221057 1.187944 1 1.660161 -2.008698 1.093186 1 1.660112 -1.660527 -1.572606 1 1.662482 0.982447 -2.064766 1 1.662671 2.266948 0.296559 1 1.662450 0.418741 2.247587 26 0.000000 0.000275 -0.000008 6 -1.718782 0.877216 0.832218 6 -1.718983 1.062449 -0.576865 6 -1.718899 -0.520444 1.091086 1 -1.660967 1.658862 1.574184 6 -1.719308 -0.220148 -1.188147 1 -1.661198 2.009558 -1.091285 6 -1.719241 -1.198328 -0.157777 1 -1.661986 -0.984571 2.063849 1 -1.662285 -0.416791 -2.247980 1 -1.661513 -2.266849 -0.298697
BODPy E = -912.329743 Nimag = 0	Ar•−BODPy E = -1480.7403376 Nimag = 0

Tc = 0.190406			Tc = 0.230487 ⟨S2⟩ = 0.765938		
6	-2.053872	-2.509280 -0.175499	6	1.737544	-1.032752 -1.007564
6	-0.934851	-3.354289 -0.271214	6	0.949903	-2.310697 -1.031719
6	-0.274473	-1.210292 -0.061136	6	-0.455106	-0.619637 -0.481054
6	0.184623	-2.540299 -0.207764	6	-0.324087	-2.060334 -0.717549
7	-1.662421	-1.238593 -0.051100	7	0.734151	-0.039106 -0.629394
5	-2.600920	-0.003570 0.020464	5	1.071679	1.447661 -0.379376
9	-3.439501	0.025902 -1.088110	9	1.902997	1.586815 0.734323
6	-0.945035	3.358320 0.210120	6	-1.839333	3.717581 0.263611
6	-2.061185	2.508548 0.123993	6	-0.480568	3.461627 0.025103
6	0.176921	2.546000 0.173516	6	-2.488643	2.492837 0.252437
6	-0.277726	1.211993 0.051049	6	-1.502656	1.497472 0.010262
7	-1.665754	1.236440 0.029754	7	-0.283709	2.138579 -0.128544
6	0.425556	0.001584 -0.000612	6	-1.619978	0.108483 -0.144859
6	1.902666	0.002001 0.003435	6	-2.921150	-0.567582 0.043313
6	2.604383	-0.781940 0.925497	6	-3.450904	-1.405366 -0.944484
6	2.610304	0.784628 -0.915217	6	-3.650109	-0.363210 1.220155
6	3.993339	-0.774721 0.931716	6	-4.679129	-2.028220 -0.755159
1	2.057662	-1.372513 1.651033	1	-2.908866	-1.550312 -1.872543
6	3.999247	0.776146 -0.913539	6	-4.878391	-0.986015 1.406261
1	2.068504	1.374446 -1.644987	1	-3.238913	0.273820 1.994899
6	4.692287	0.000539 0.011164	6	-5.395411	-1.820517 0.419862
1	4.529692	-1.372591 1.658197	1	-5.080374	-2.669705 -1.530411
1	4.540253	1.373022 -1.637388	1	-5.427997	-0.823564 2.325545
1	5.775445	0.000024 0.014181	1	-6.352875	-2.306028 0.565514
9	-3.360177	-0.036679 1.185884	9	1.715208	1.981627 -1.497472
1	-3.111964	2.760234 0.135191	1	0.345207	4.153909 -0.046090
1	-0.975800	4.432229 0.296919	1	-2.278347	4.690947 0.413783
1	1.209569	2.851209 0.238556	1	-3.542841	2.303911 0.380733

1 1.218605 -2.840752 -0.274112 1 -0.962251 -4.425871 -0.383911 1 -3.103889 -2.763141 -0.199578	1 -1.133277 -2.768868 -0.635063 1 1.399792 -3.265635 -1.260673 1 2.124457 -0.787424 -2.004256 6 2.878983 -1.069472 -0.018948 7 2.752075 -1.505341 1.195050 16 4.447580 -0.462993 -0.416992 6 3.930182 -1.365327 1.883601 6 4.961330 -0.822749 1.181098 1 3.987330 -1.686399 2.914085 1 5.970684 -0.626688 1.505585
Ar−BODPy E = -1480.1656083 Nimag = 0 Tc = 0.220929	BF_4^- E = -424.6105985 Nimag = 0 Tc = -0.010895
6 1.632786 -1.153675 0.100456 6 0.962474 -2.393105 0.198979 6 -0.533130 -0.724249 0.028172 6 -0.388196 -2.125320 0.154920 7 0.734845 -0.153781 0.005234 5 1.002093 1.383059 0.002185 9 1.764948 1.741005 1.106512 6 -1.961564 3.670324 -0.029609 6 -0.584881 3.395247 0.030215 6 -2.612361 2.447185 -0.048222 6 -1.615422 1.445658 0.015352 7 -0.381317 2.074752 0.057591 6 -1.701479 0.050162 0.008162 6 -3.021612 -0.612137 -0.018271 6 -3.301598 -1.573862 -0.995256	5 0.000000 0.000000 0.000000 9 0.810622 0.810622 0.810622 9 -0.810622 -0.810622 0.810622 9 -0.810622 0.810622 -0.810622 9 0.810622 -0.810622 -0.810622

6 -4.000840 -0.280679 0.923679 6 -4.546471 -2.188320 -1.031803 1 -2.550040 -1.815729 -1.737586 6 -5.238937 -0.909941 0.890936 1 -3.778822 0.448738 1.693755 6 -5.514878 -1.860353 -0.087884 1 -4.759483 -2.921888 -1.799630 1 -5.987674 -0.659668 1.632452 1 -6.483326 -2.344951 -0.114785 9 1.654472 1.752307 -1.173312 1 0.248666 4.082316 0.043941 1 -2.405973 4.651619 -0.063402 1 -3.674362 2.268961 -0.111077 1 -1.199658 -2.832893 0.220086 1 1.454974 -3.346802 0.290088 6 3.088466 -1.036410 0.118857 7 3.809278 -2.034880 0.562430 16 4.024305 0.292641 -0.496396 6 5.141060 -1.772967 0.446460 6 5.452452 -0.565204 -0.103889 1 5.860965 -2.504358 0.785561 1 6.425746 -0.139478 -0.291092	
HBF_4 E = -425.0057614 Nimag = 0 Tc = -0.006141	
5 -0.492523 0.037064 -0.001775 9 -0.387715 1.348214 -0.108970 9 -0.643946 -0.510183 1.186631 9 -0.652205 -0.695258 -1.084795	

9 1.712167 -0.225072 0.008165 1 2.207905 0.555366 -0.000395	
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29 0.000000 0.000000 0.812516 17 0.000000 0.000000 -1.386057	29 0.000000 0.000000 0.785272 17 0.000000 0.000000 -1.339581
L-Ascorbic acid E = -684.7212139 Nimag = 0 Tc = 0.114898	L-Ascorbic acid radical cation E = -684.4779961 Nimag = 0 Tc = 0.115528 ⟨S2⟩ = 0.756504
6 -0.172174 -0.292196 0.685854 6 0.662469 0.915294 0.356777 6 1.841711 0.519496 -0.125855 6 1.884609 -0.949073 -0.082905 8 0.707148 -1.393747 0.431129 1 -0.456933 -0.325792 1.742388 8 2.770408 -1.688446 -0.402107 8 2.908978 1.211100 -0.566759 8 0.263489 2.197133 0.476584 1 2.728547 2.154403 -0.474968 1 -0.360619 2.298623 1.204980 6 -1.419262 -0.469288 -0.171655 1 -1.096055 -0.605801 -1.213057 6 -2.369040 0.718470 -0.100012 1 -1.925752 1.598569 -0.573511 1 -2.598465 0.939430 0.950038 8 -3.535492 0.296901 -0.789972	6 -0.187929 -0.237880 0.676466 6 0.647392 0.962103 0.334720 6 1.886359 0.509230 -0.143784 6 1.881729 -0.986153 -0.060267 8 0.690581 -1.350001 0.447659 1 -0.462089 -0.230436 1.735911 8 2.758071 -1.723963 -0.363231 8 2.908016 1.157222 -0.562389 8 0.381127 2.212169 0.444193 1 2.786051 2.124878 -0.550318 1 -0.474766 2.425394 0.855381 6 -1.440663 -0.428582 -0.185873 1 -1.128552 -0.504743 -1.235797 6 -2.446128 0.707555 -0.041900 1 -2.058055 1.635999 -0.477757 1 -2.683197 0.857858 1.017582 8 -3.579526 0.261247 -0.758552

1	-4.253537	0.901433	-0.587050	1	-4.346210	0.774357	-0.489235
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