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Supporting Information

C_2-Symmetric ferrocenyl bisthiazoles: synthesis, photophysical, elecrtrochemical and DFT studies

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Table of Contents

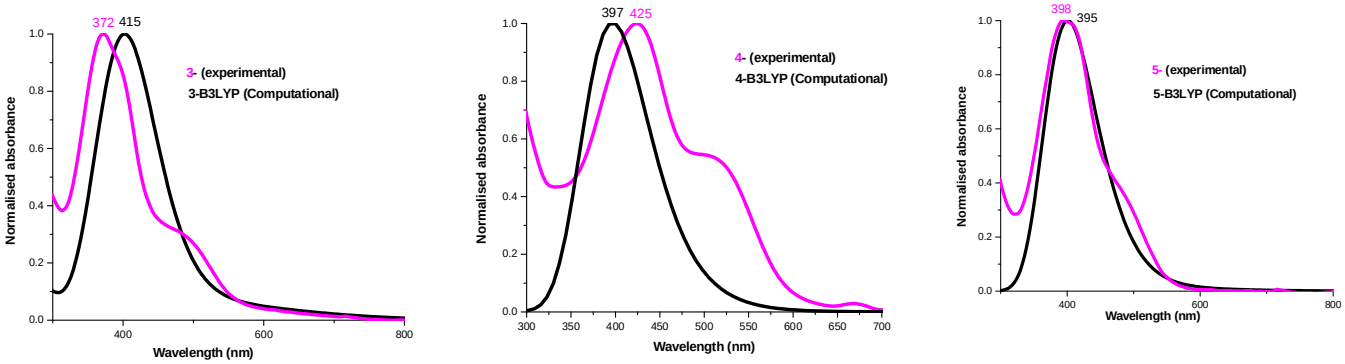


Figure S1. The comparison of experimental and calculated (TD-DFT at B3LYP level) absorption spectrum of Fc-bisthiazole **3**, **4** and **5** in DCM solution.

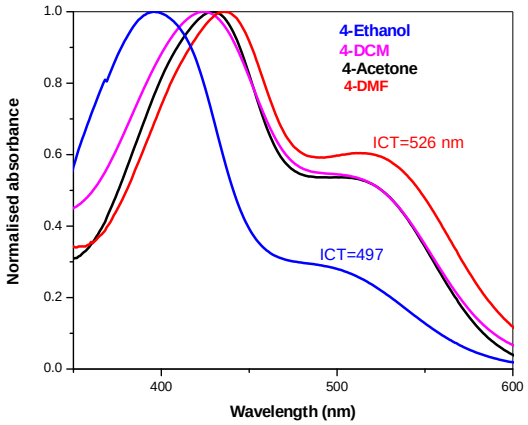
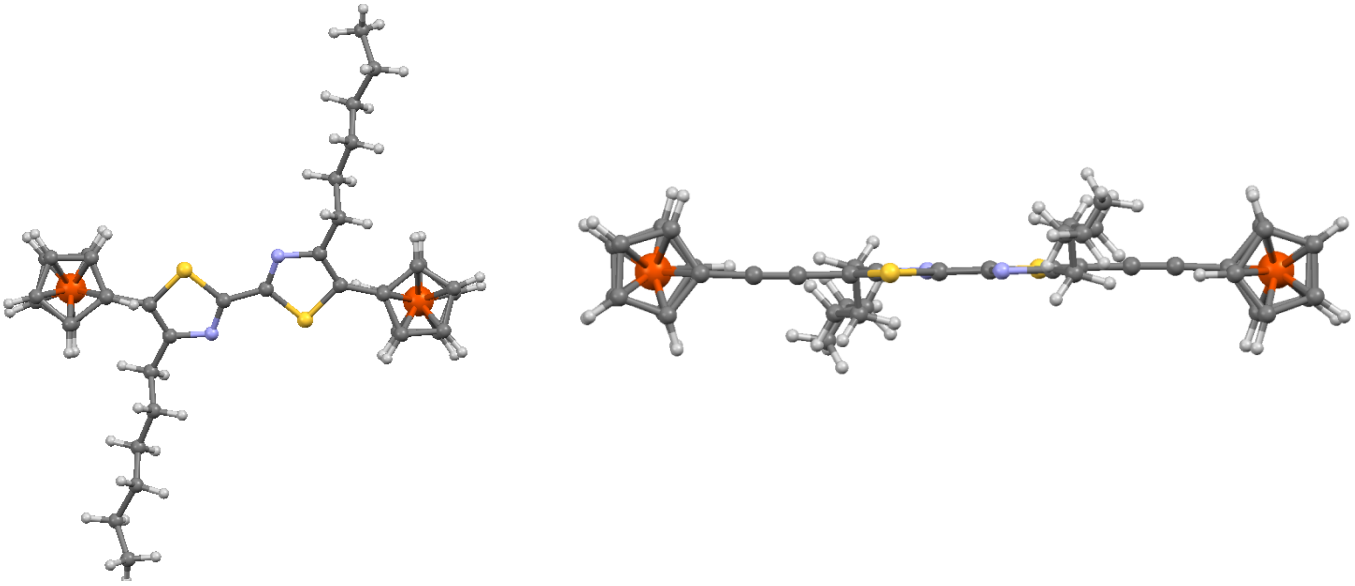


Figure S2. Normalized electronic absorption spectra of the ferrocenyl substituted bisthiazole **4** in different solvents with varying polarities.

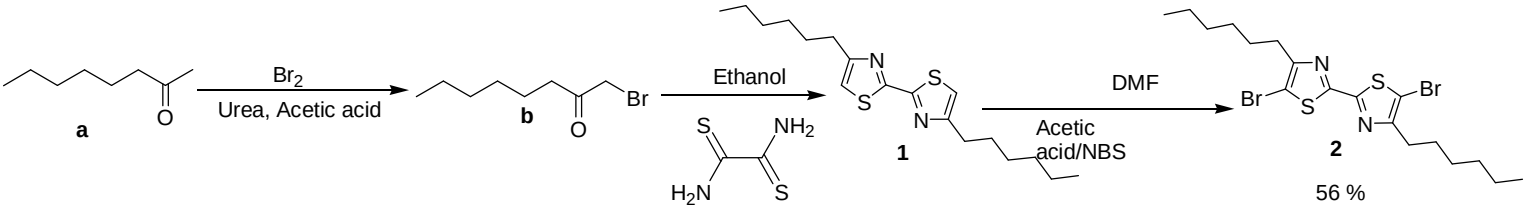


(a) (b)

Figure S3. Single crystal X-ray structures Skew-eclipsed conformations through b-axis (a) Fc-bisthiazole **3** and (b) Fc-bisthiazole **5**.

Table S1. The comparison of experimental and calculated (TD-DFT at B3LYP and CAM-B3LYP level) absorption spectrum of Fc-bisthiazole **3** -**5** in DCM solution.

Fc-bisthiazoles	**$\lambda_{max[nm]}$**		**HOMO−LUMO gap (eV)**	**Optical HOMO−LUMO gap (eV)**
	TD-DFT (B3LYP)	**exp**		
3	415	372	3.36	3.85
4	397	425	3.08	3.25
5	395	400	3.17	3.56



Scheme 1. Synthesis of bisthiazole **2**.

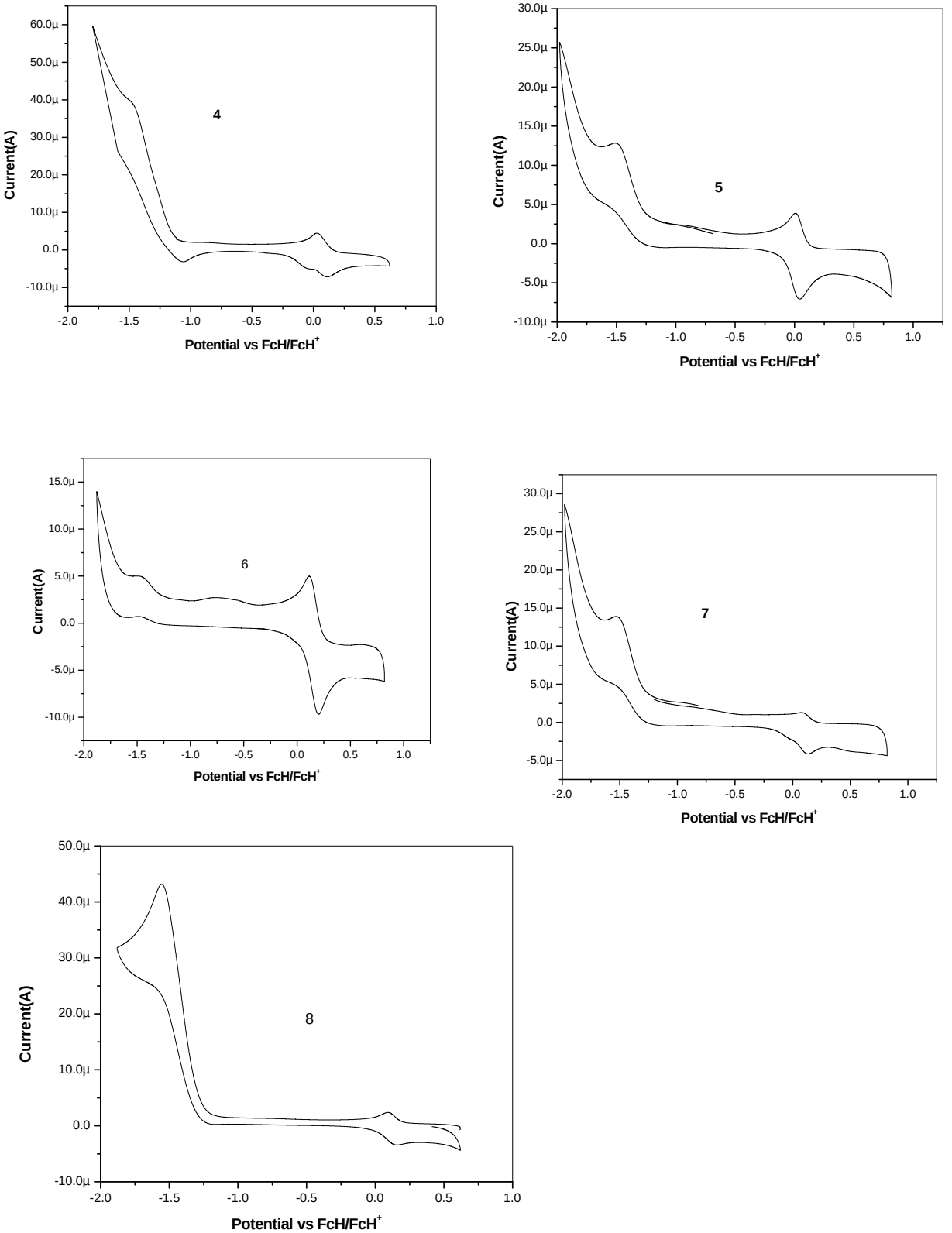
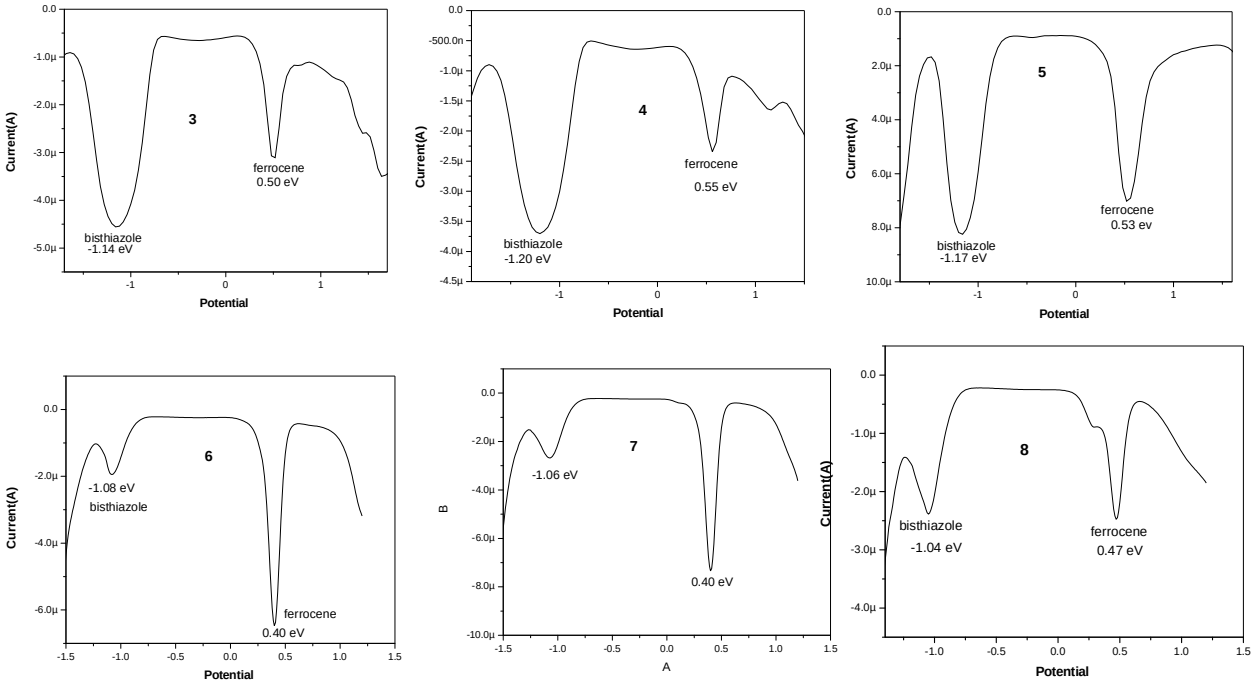


Figure S4. The Cyclic voltammograms of the Fc-bisthiazoles **4**-**8**.



Fiugre S5. The differential pulse voltammograms of the Fc-bisthiazoles **3-8.**

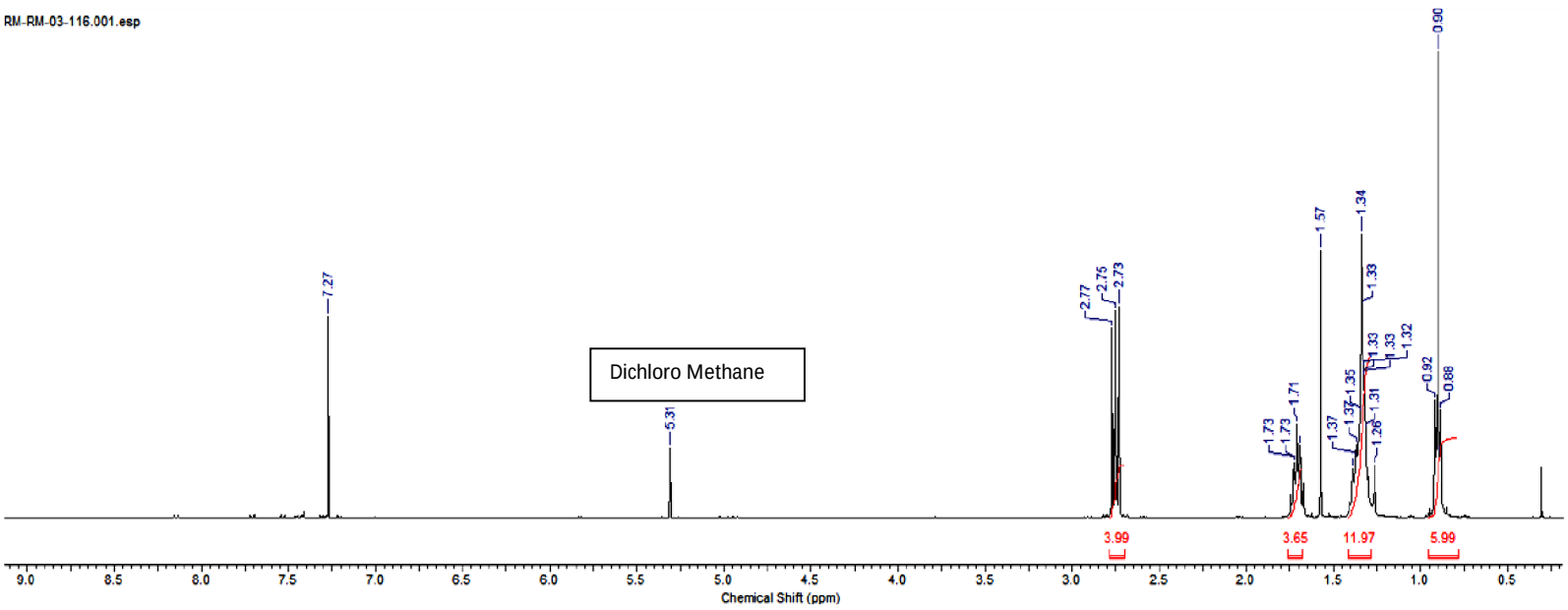


Figure S6. ^{1}H NMR Spectra of bisthiazole **2**.

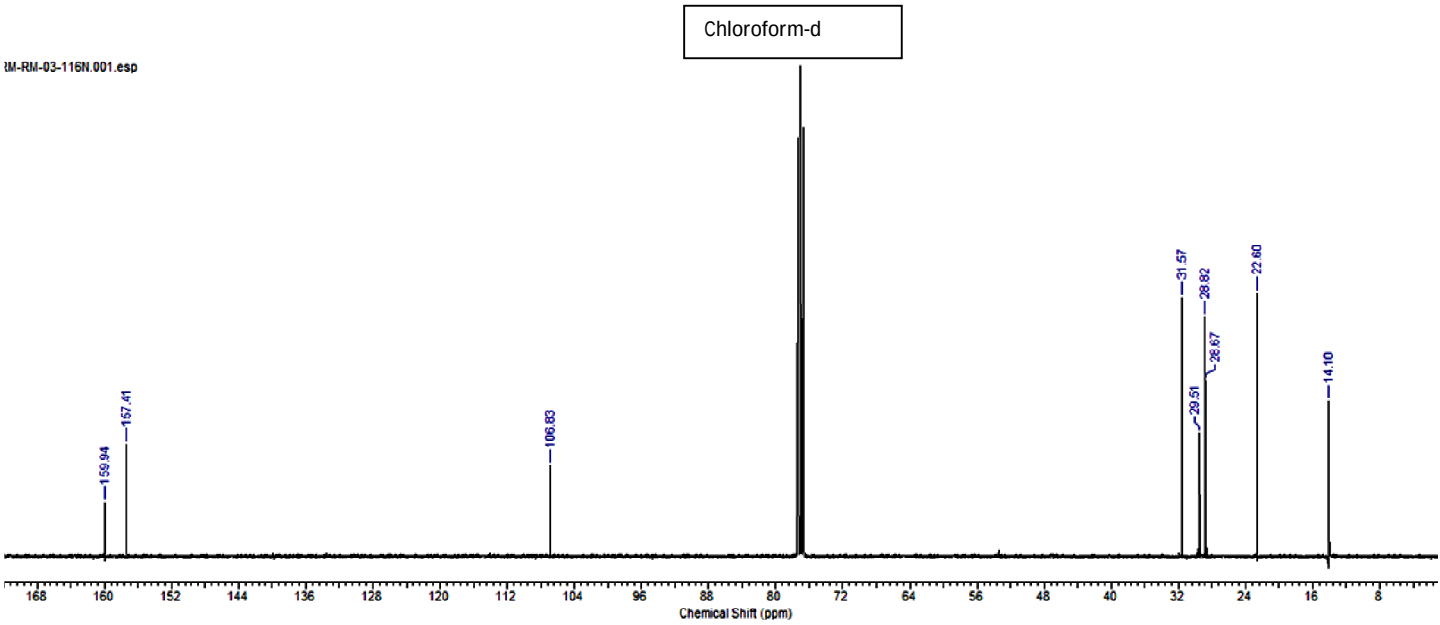


Figure S7. ^{13}C NMR Spectra of bisthiazole **2**.

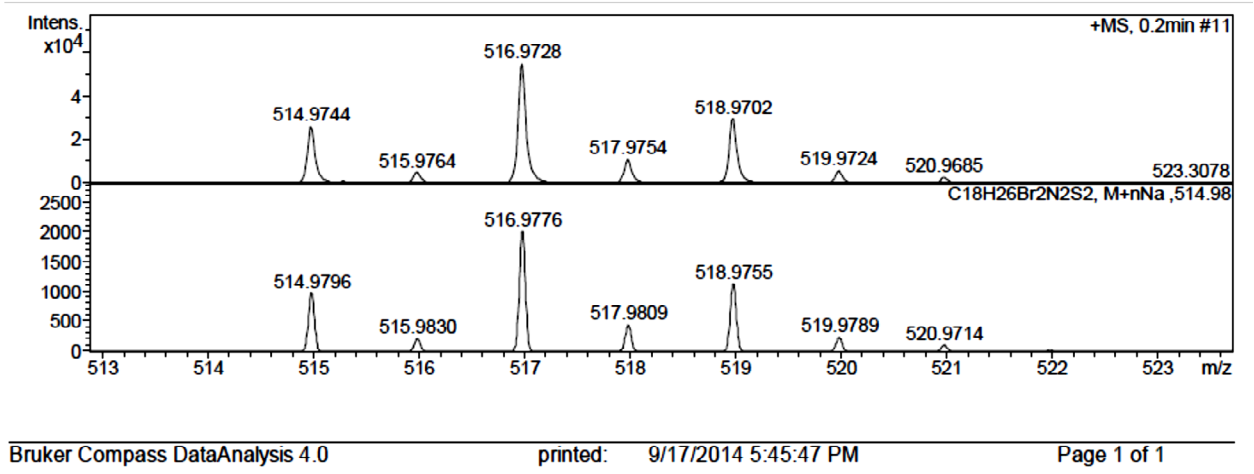


Figure S6. HRMS Spectra of bisthiazole **2**.

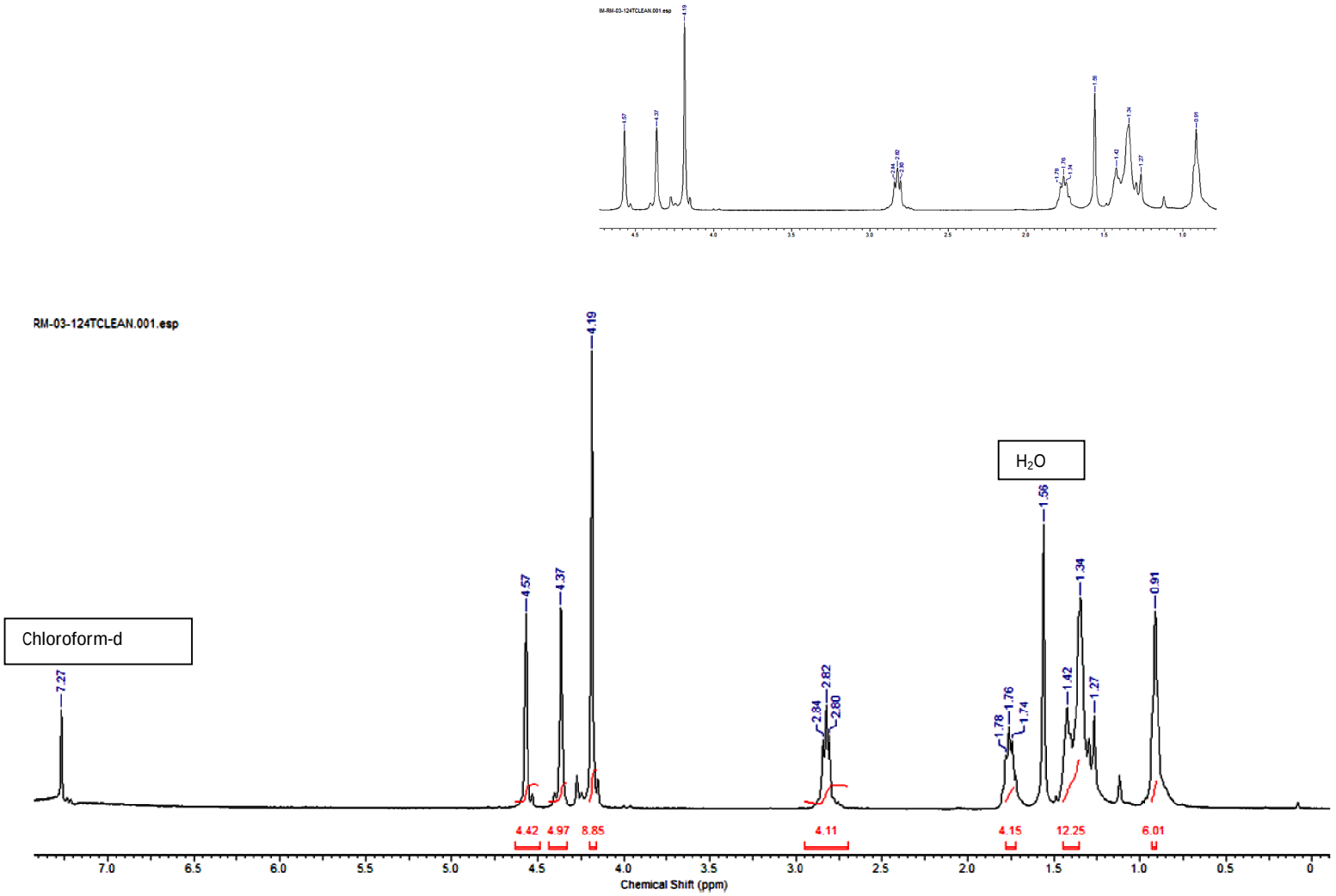


Figure S8. ^{1}H NMR Spectra of Fc-bisthiazole **3**.

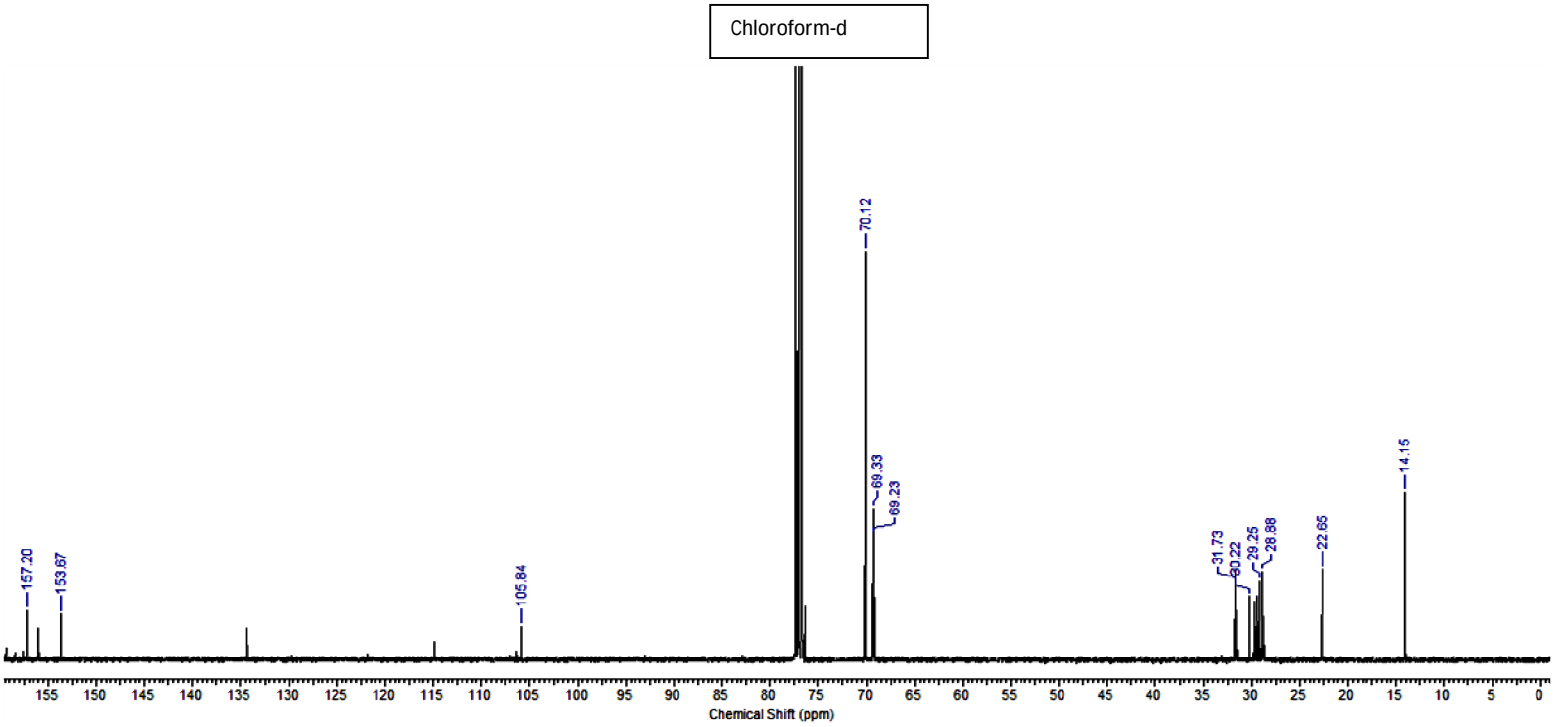


Figure S9. ^{13}C NMR Spectra of Fc-bisthiazole **3**.

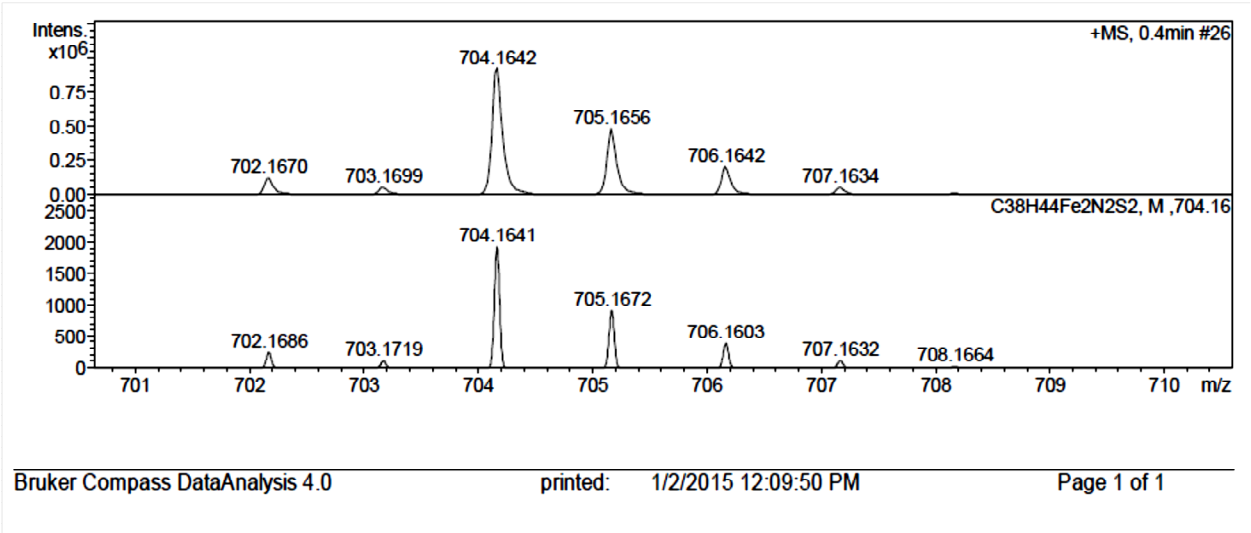


Figure S10. HRMS Spectra of Fc-bisthiazole **3**.

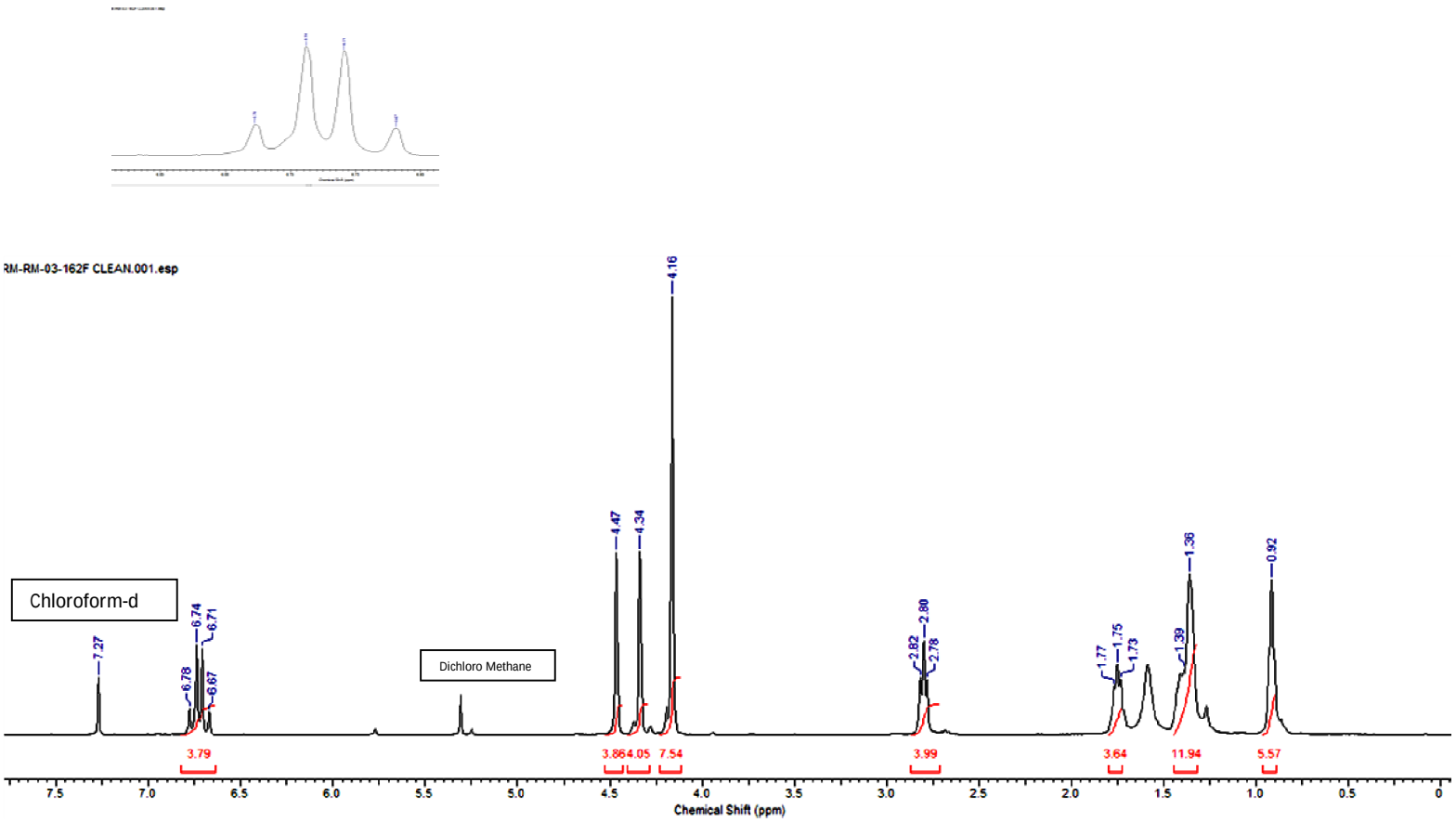


Figure S11. ^{1}H NMR Spectra of Fc-bisthiazole **4**.

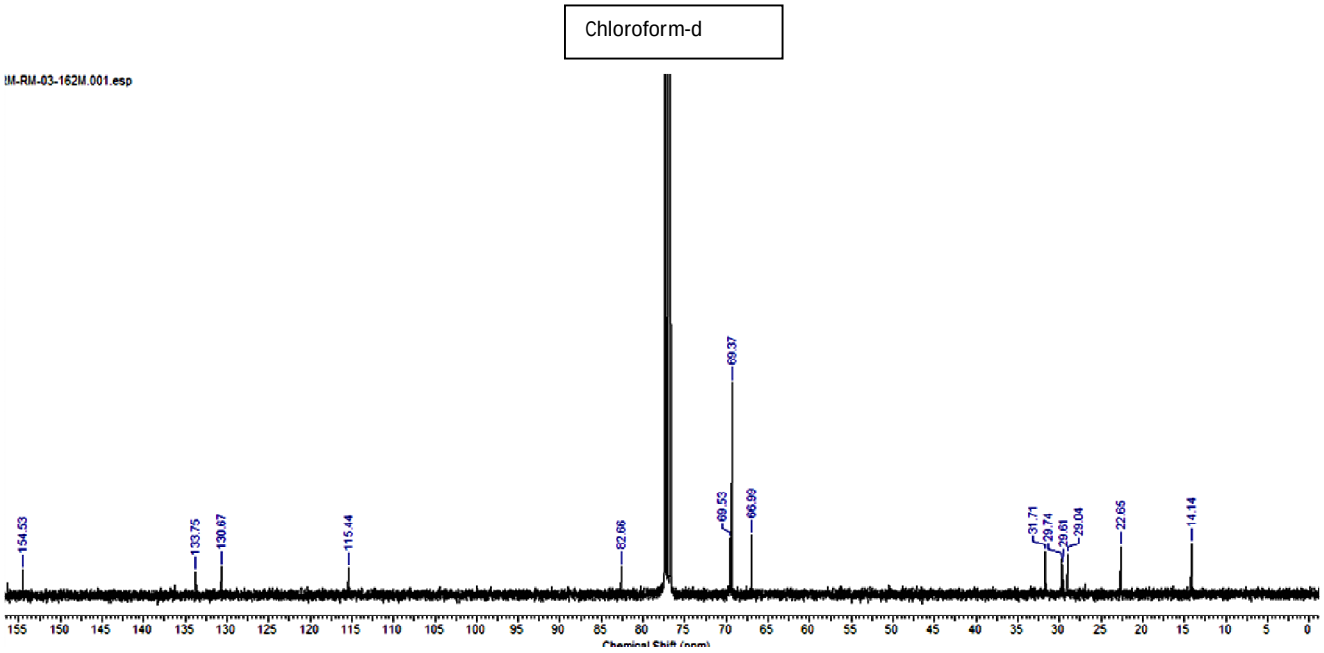


Figure S12. ^{13}C NMR Spectra of Fc-bisthiazole **4**.

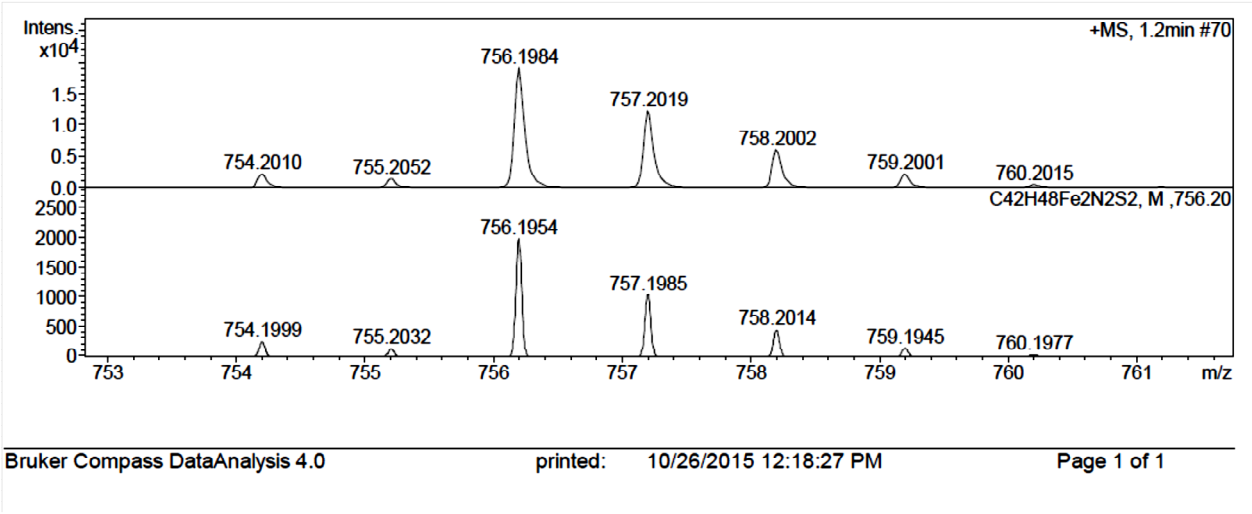


Figure S13. HRMS Spectra of Fc-bisthiazole **4**.

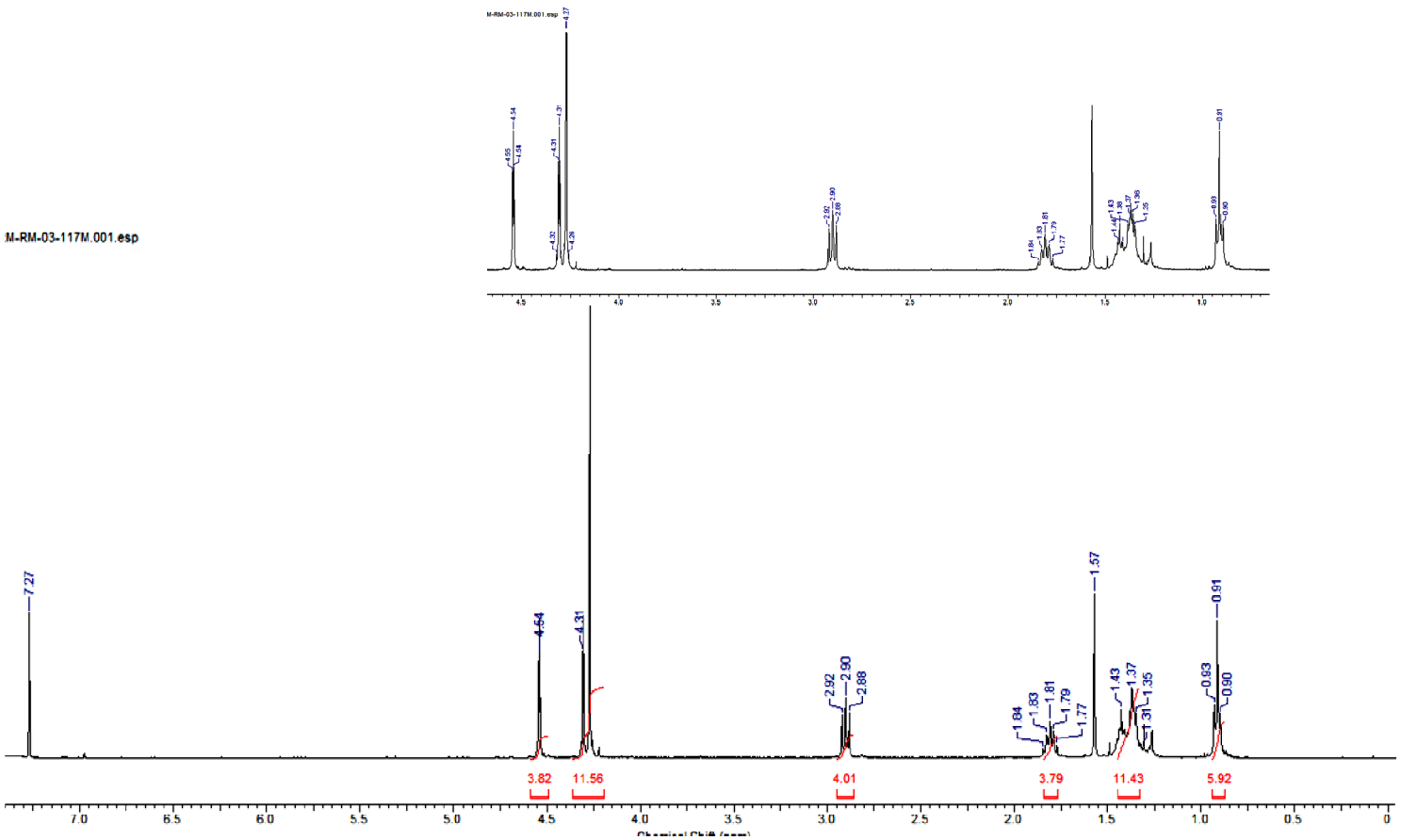


Figure S14. ^{1}H NMR Spectra of Fc-bisthiazole **5**.

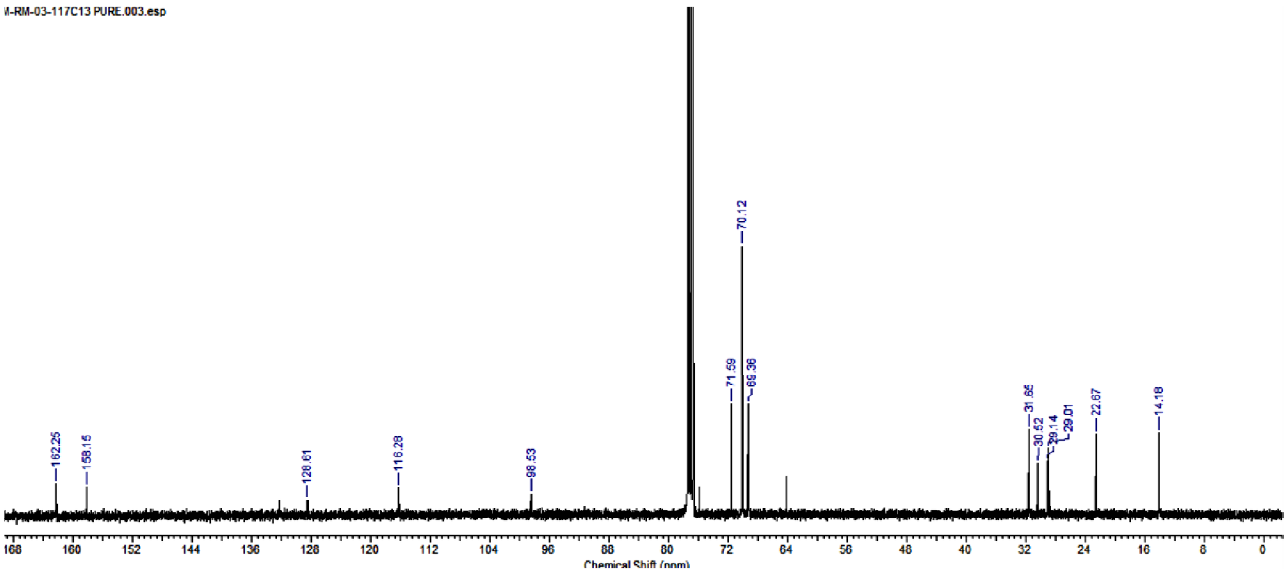


Figure S15. ^{13}C NMR Spectra of Fc-bisthiazole **5**.

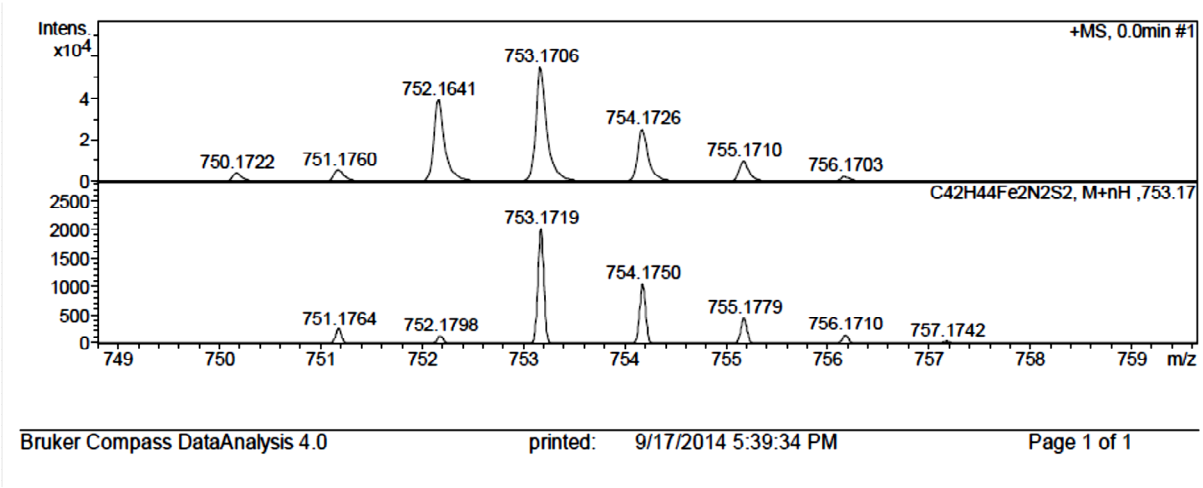


Figure S16. HRMS Spectra of Fc-bisthiazole **5**.

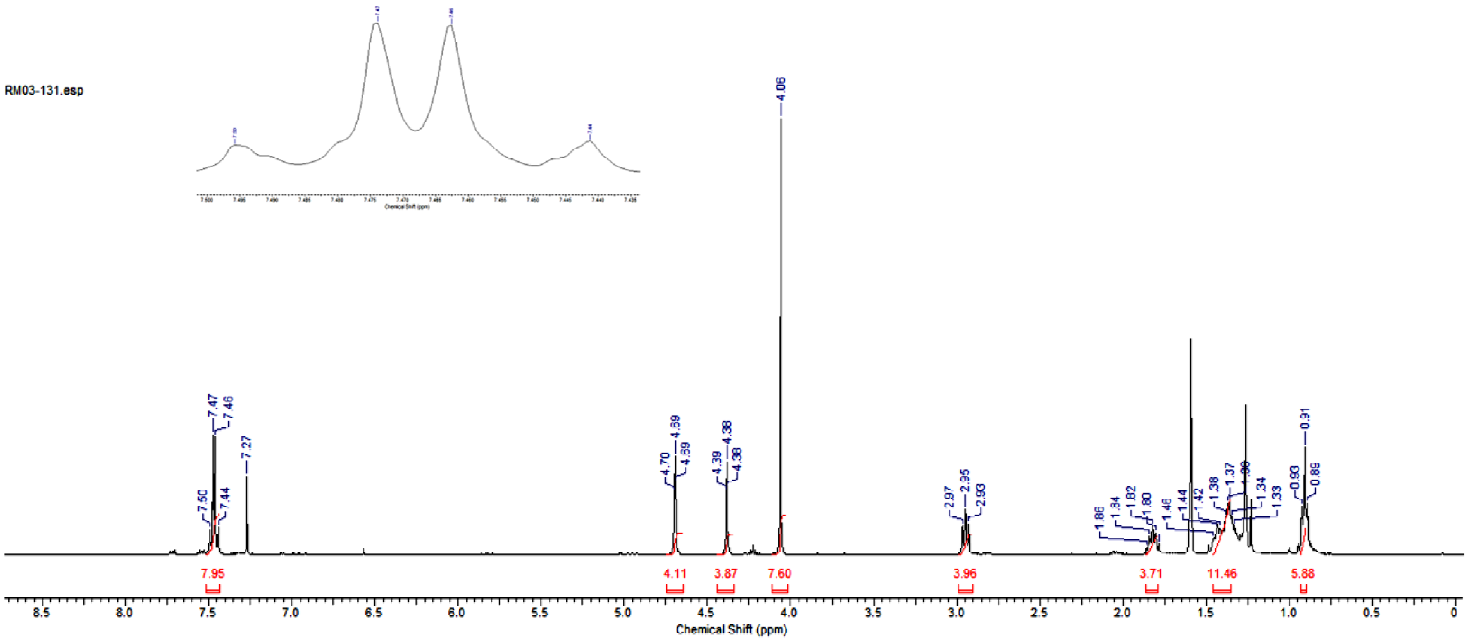


Figure S17. ^{1}H NMR Spectra of Fc-bisthiazole **6**.

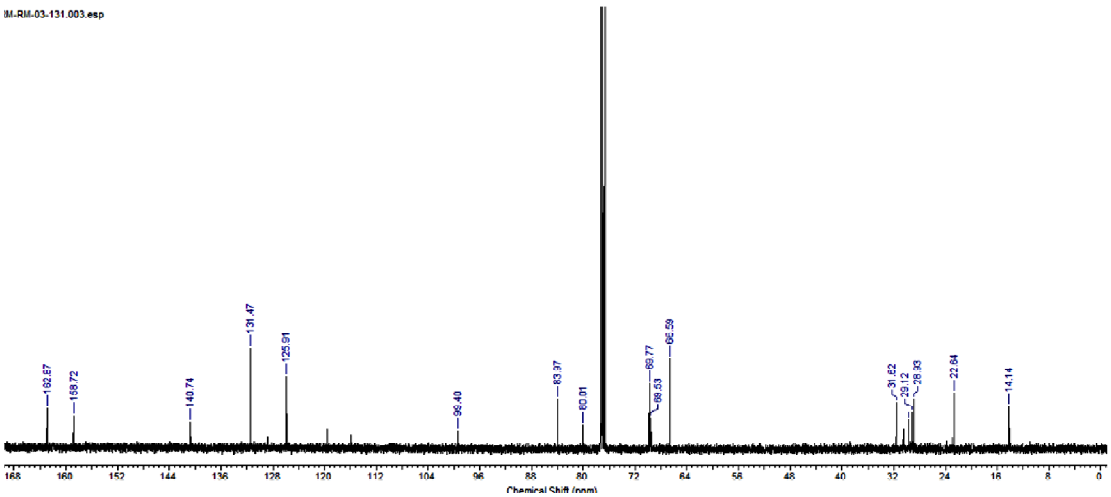


Figure S18. ^{13}C NMR Spectra of Fc-bisthiazole **6**.

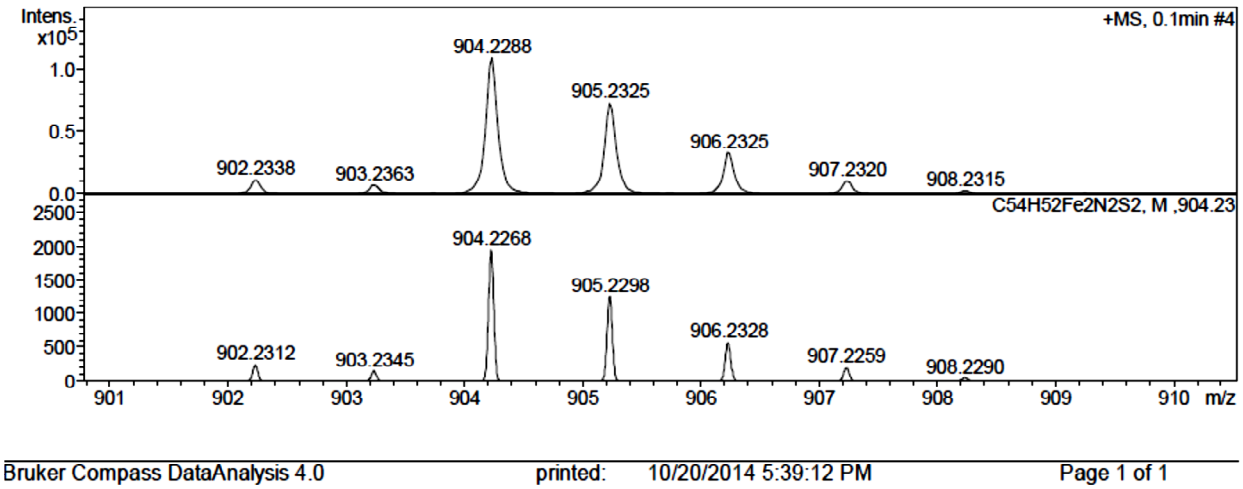


Figure S19. HRMS Spectra of Fc-bisthiazole **6**.

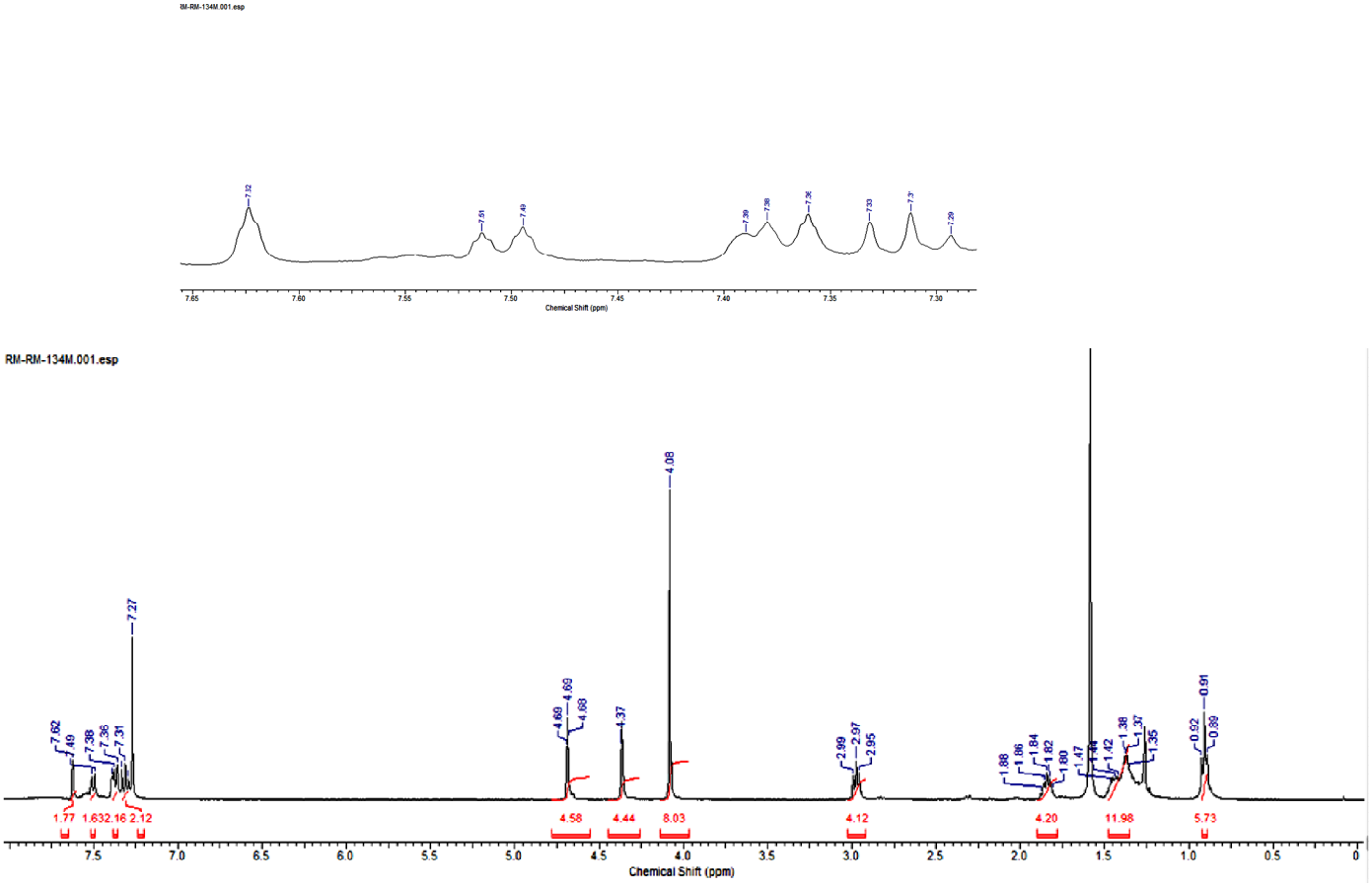


Figure S20. ^{1}H NMR Spectra of Fc-bisthiazole **7**.

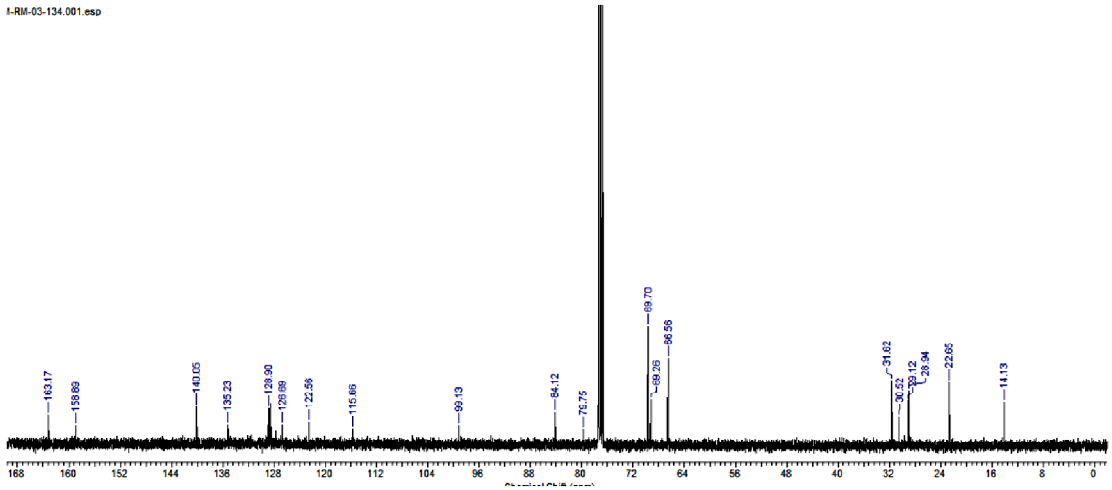
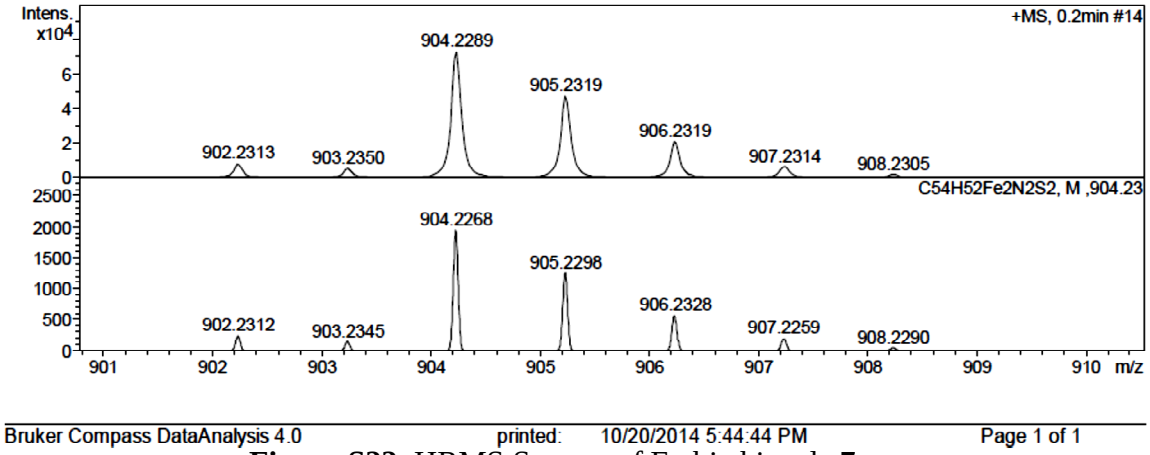


Figure S21. ^{13}C NMR Spectra of Fc-bisthiazole **7**.



Bruker Compass DataAnalysis 4.0 printed: 10/20/2014 5:44:44 PM Page 1 of 1

Figure S22. HRMS Spectra of Fc-bisthiazole **7**.

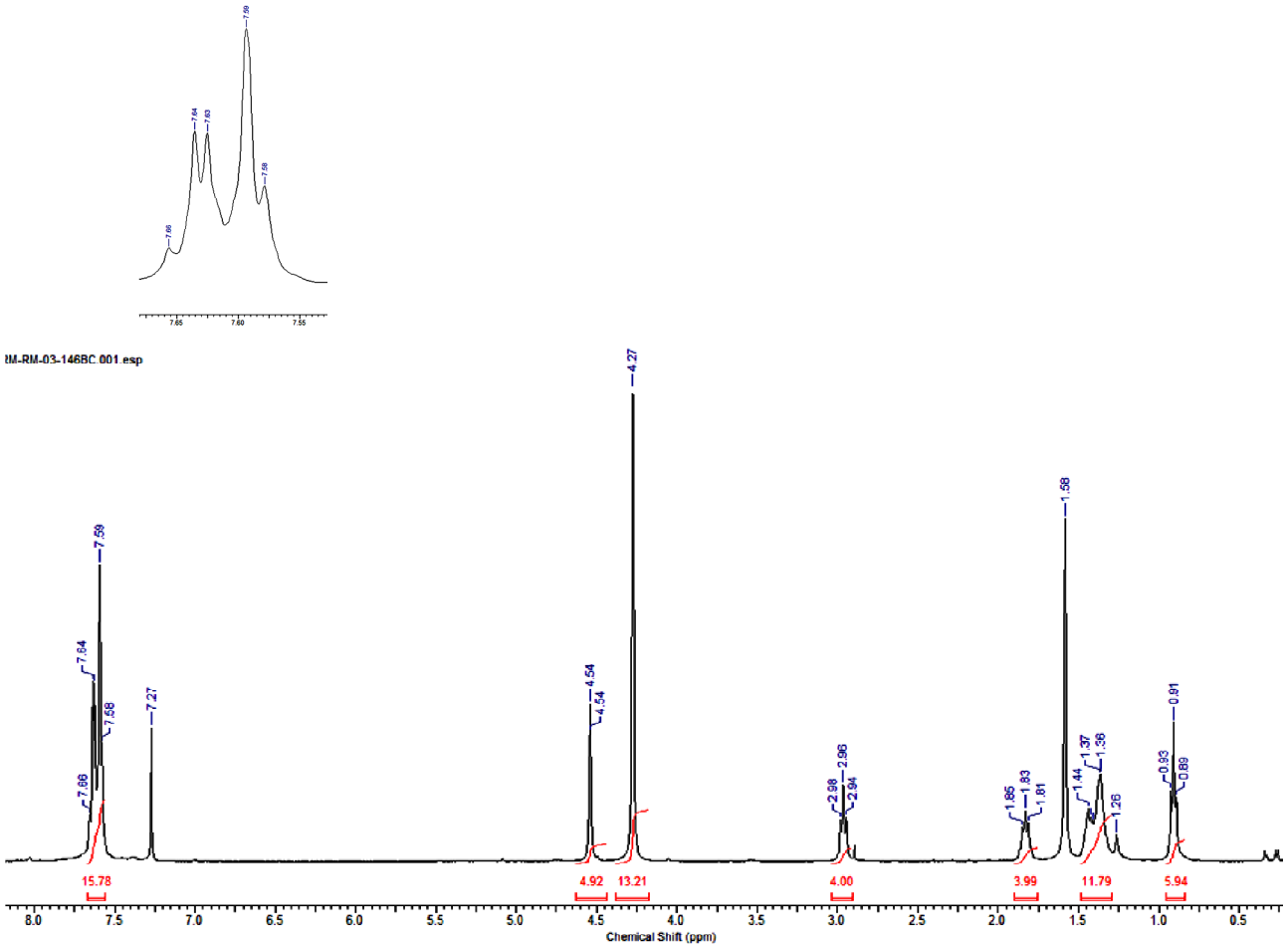


Figure S23. ^{1}H NMR Spectra of Fc-bisthiazole **8**.

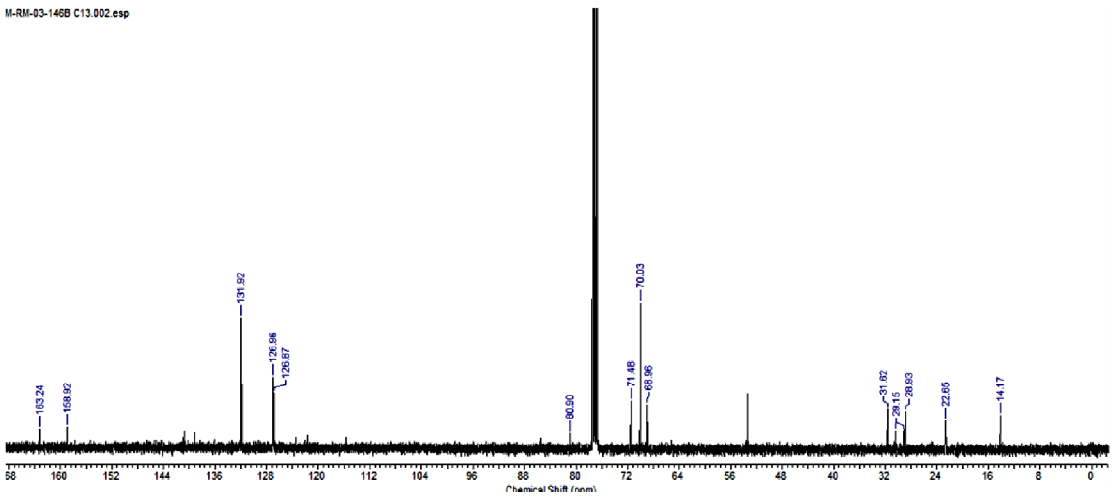


Figure S24. ^{13}C NMR Spectra of Fc-bisthiazole **8**.

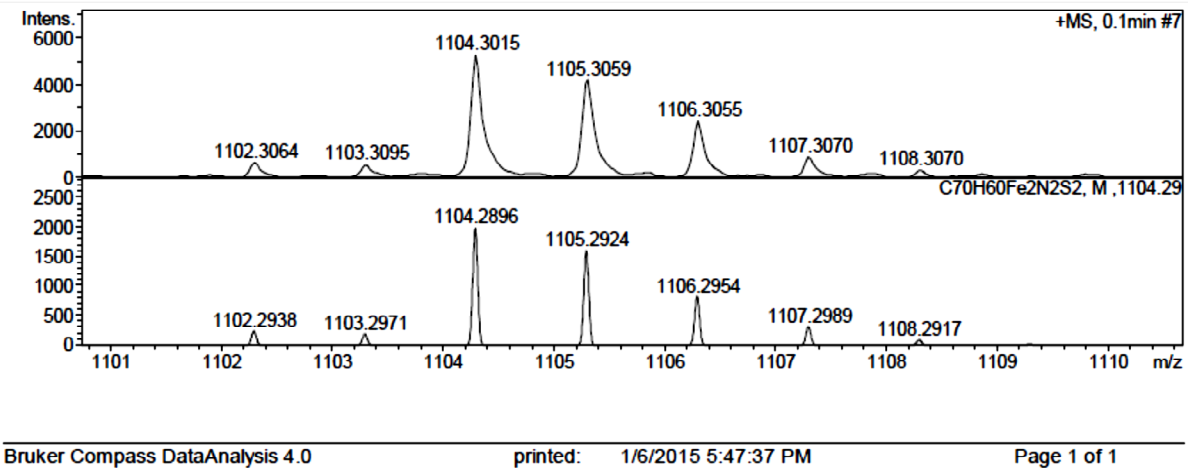


Figure S25. HRMS Spectra of Fc-bisthiazole **8**.

Table S2. Crystal data and structure refinement for 3.

Identification code	shelx
Empirical formula	C38 H44 Fe2 N2 S2
Formula weight	704.57
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 7.4367(9) A alpha = 104.092(12) deg. b = 9.4600(14) A beta = 103.546(12) deg. c = 13.6597(17) A gamma = 100.411(12) deg.
Volume	876.9(2) A^3
Z, Calculated density	1, 1.334 Mg/m^3
Absorption coefficient	7.952 mm^-1
F(000)	370
Crystal size	0.330 x 0.290 x 0.210 mm
Theta range for data collection	4.981 to 71.123 deg.
Limiting indices	-8<=h<=7, -11<=k<=11, -12<=l<=16
Reflections collected / unique	5509 / 3281 [R(int) = 0.0437]
Completeness to theta = 67.684	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.60378
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3281 / 42 / 201
Goodness-of-fit on F^2	1.060

Final R indices [I>2sigma(I)]	R1 = 0.0785, wR2 = 0.2237
R indices (all data)	R1 = 0.0940, wR2 = 0.2517
Extinction coefficient	n/a
Largest diff. peak and hole	0.648 and -0.473 e.A^-3

Table S3. Crystal data and structure refinement for 5.

Identification code	shelx
Empirical formula	C21 H22 Fe N S
Formula weight	376.30
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 7.3744(5) A alpha = 71.880(6) deg. b = 11.4485(8) A beta = 85.210(5) deg. c = 11.5972(7) A gamma = 87.105(6) deg.
Volume	926.99(11) A^3
Z, Calculated density	2, 1.348 Mg/m^3
Absorption coefficient	0.927 mm^-1
F(000)	394
Crystal size	0.330 x 0.260 x 0.210 mm
Theta range for data collection	3.223 to 24.991 deg.
Limiting indices	-8<=h<=8, -13<=k<=13, -10<=l<=13
Reflections collected / unique	7008 / 3254 [R(int) = 0.0364]
Completeness to theta = 24.991	99.7 %

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.76968
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3254 / 7 / 256
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.1181
R indices (all data)	R1 = 0.0537, wR2 = 0.1279
Extinction coefficient	n/a
Largest diff. peak and hole	0.452 and -0.342 e.A^-3

IV. DFT Calculations.

IV. DFT calculation data of the ferrocenyl substituted triphenylamine donor-acceptor compounds **3-6** Calculation method: B3LYP/6-31+G** for C, H, N with Gaussian 09[1].

Data for compound **3**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	5.893819	0.974427	0.477598
2	16	0	2.164233	-0.595481	-0.961742
3	7	0	0.813763	1.595890	-1.252765
4	6	0	5.363542	-0.243576	-1.127851
5	1	0	5.023521	-1.266760	-1.046229
6	6	0	6.712199	0.193539	-1.263560
7	1	0	7.585915	-0.443202	-1.282577
8	6	0	6.712199	1.620701	-1.317882
9	1	0	7.585915	2.254153	-1.385246
10	6	0	5.363542	2.066867	-1.215793
11	1	0	5.023521	3.093295	-1.212185
12	6	0	4.514650	0.914599	-1.094216
13	6	0	3.043879	0.913443	-1.124591
14	6	0	2.138509	1.935612	-1.266053
15	6	0	0.664783	0.303770	-1.100777

16	6	0	4.952098	1.045441	2.343301
17	1	0	3.886058	1.052104	2.518357
18	6	0	5.778049	2.195127	2.163341
19	1	0	5.443643	3.223318	2.153959
20	6	0	7.118570	1.745467	1.966411
21	1	0	7.977507	2.373403	1.773269
22	6	0	7.118570	0.318790	2.020715
23	1	0	7.977507	-0.322010	1.875864
24	6	0	5.778049	-0.114598	2.251255
25	1	0	5.443643	-1.140528	2.320059
26	16	0	-2.164233	0.595481	-0.961742
27	7	0	-0.813763	-1.595890	-1.252765
28	6	0	-5.363542	-2.066867	-1.215793
29	1	0	-5.023521	-3.093295	-1.212185
30	6	0	-6.712199	-1.620701	-1.317882
31	1	0	-7.585915	-2.254153	-1.385246
32	6	0	-6.712199	-0.193539	-1.263560
33	1	0	-7.585915	0.443202	-1.282577
34	6	0	-5.363542	0.243576	-1.127851
35	1	0	-5.023521	1.266760	-1.046229
36	6	0	-4.514650	-0.914599	-1.094216
37	6	0	-3.043879	-0.913443	-1.124591
38	6	0	-2.138509	-1.935612	-1.266053
39	6	0	-0.664783	-0.303770	-1.100777
40	26	0	-5.893819	-0.974427	0.477598
41	6	0	-4.952098	-1.045441	2.343301
42	1	0	-3.886058	-1.052104	2.518357
43	6	0	-5.778049	0.114598	2.251255
44	1	0	-5.443643	1.140528	2.320059
45	6	0	-7.118570	-0.318790	2.020715
46	1	0	-7.977507	0.322010	1.875864
47	6	0	-7.118570	-1.745467	1.966411
48	1	0	-7.977507	-2.373403	1.773269
49	6	0	-5.778049	-2.195127	2.163341
50	1	0	-5.443643	-3.223318	2.153959
51	1	0	-2.454673	-2.951307	-1.381396
52	1	0	2.454673	2.951307	-1.381396

Total Energy, E(TD-HF/TD-KS) = -2155.50582408

Data for compound **4**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	-0.205411	8.606465	0.000000
2	16	0	1.727813	1.662155	0.000000
3	7	0	-0.783762	1.118070	0.000000
4	6	0	1.172179	7.593538	1.149955
5	1	0	1.017225	7.290612	2.175959
6	6	0	1.713685	8.832005	0.710701
7	1	0	2.037622	9.643228	1.347197
8	6	0	1.713685	8.832005	-0.710701
9	1	0	2.037622	9.643228	-1.347197
10	6	0	1.172179	7.593538	-1.149955
11	1	0	1.017225	7.290612	-2.175959
12	6	0	0.833672	6.818267	0.000000
13	6	0	0.283523	5.445104	0.000000
14	6	0	1.070958	4.364484	0.000000
15	6	0	0.601908	2.983569	0.000000
16	6	0	-0.672861	2.477006	0.000000
17	6	0	0.392937	0.554925	0.000000
18	6	0	-2.222736	8.191690	0.000000
19	1	0	-2.648197	7.197714	0.000000
20	6	0	-1.879768	8.953738	-1.150952
21	1	0	-1.993203	8.638554	-2.178594
22	6	0	-1.323694	10.186694	-0.711107
23	1	0	-0.936411	10.970857	-1.346170
24	6	0	-1.323694	10.186694	0.711107
25	1	0	-0.936411	10.970857	1.346170
26	6	0	-1.879768	8.953738	1.150952
27	1	0	-1.993203	8.638554	2.178594
28	16	0	-0.739404	-1.985731	0.000000
29	7	0	1.779566	-1.441085	0.000000
30	6	0	-1.863028	-7.428722	-1.146412
31	1	0	-1.753226	-7.106925	-2.173210
32	6	0	-2.312432	-8.699505	-0.709001
33	1	0	-2.589733	-9.528224	-1.346045
34	6	0	-2.312432	-8.699505	0.709001
35	1	0	-2.589733	-9.528224	1.346045
36	6	0	-1.863028	-7.428722	1.146412
37	1	0	-1.753226	-7.106925	2.173210
38	6	0	-1.579262	-6.633453	0.000000
39	6	0	-1.222027	-5.200199	0.000000
40	6	0	0.021514	-4.712321	0.000000

41	6	0	0.390553	-3.306745	0.000000
42	6	0	1.663312	-2.801380	0.000000
43	6	0	0.603749	-0.880373	0.000000
44	26	0	-0.237267	-8.427890	0.000000
45	6	0	1.961434	-8.064661	0.000000
46	1	0	2.415320	-7.083482	0.000000
47	6	0	1.624907	-8.826447	1.148356
48	1	0	1.756754	-8.519005	2.176806
49	6	0	1.080910	-10.060344	0.709274
50	1	0	0.717489	-10.856574	1.344537
51	6	0	1.080910	-10.060344	-0.709274
52	1	0	0.717489	-10.856574	-1.344537
53	6	0	1.624907	-8.826447	-1.148356
54	1	0	1.756754	-8.519005	-2.176806
55	1	0	2.557130	-3.413892	0.000000
56	1	0	-1.573403	3.078251	0.000000
57	1	0	-0.797541	5.329097	0.000000
58	1	0	2.149009	4.505966	0.000000
59	1	0	0.861065	-5.402140	0.000000
60	1	0	-2.065099	-4.508118	0.000000

Total Energy, E(TD-HF/TD-KS) = -2310.32434205

Data for compound **5**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.004626	8.719425	0.000000
2	16	0	1.224453	1.847137	0.000000
3	7	0	-1.307127	1.265186	0.000000
4	6	0	1.485990	7.843041	1.160445
5	1	0	1.359337	7.523913	2.185125
6	6	0	1.920996	9.121885	0.714281
7	1	0	2.173915	9.960238	1.348543
8	6	0	1.920996	9.121885	-0.714281
9	1	0	2.173915	9.960238	-1.348543
10	6	0	1.485990	7.843041	-1.160445
11	1	0	1.359337	7.523913	-2.185125
12	6	0	1.214842	7.031881	0.000000
13	6	0	0.793587	5.677402	0.000000
14	6	0	0.436917	4.513026	0.000000
15	6	0	0.055635	3.160085	0.000000
16	6	0	-1.219333	2.621218	0.000000

17	6	0	-0.114627	0.714025	0.000000
18	6	0	-1.978946	8.105432	0.000000
19	1	0	-2.274456	7.065293	0.000000
20	6	0	-1.712626	8.900541	-1.155265
21	1	0	-1.792683	8.574067	-2.182960
22	6	0	-1.281946	10.188826	-0.713751
23	1	0	-0.977209	11.009236	-1.348934
24	6	0	-1.281946	10.188826	0.713751
25	1	0	-0.977209	11.009236	1.348934
26	6	0	-1.712626	8.900541	1.155265
27	1	0	-1.792683	8.574067	2.182960
28	16	0	-1.224453	-1.847137	0.000000
29	7	0	1.307127	-1.265186	0.000000
30	6	0	-1.485990	-7.843041	-1.160445
31	1	0	-1.359337	-7.523913	-2.185125
32	6	0	-1.920996	-9.121885	-0.714281
33	1	0	-2.173915	-9.960238	-1.348543
34	6	0	-1.920996	-9.121885	0.714281
35	1	0	-2.173915	-9.960238	1.348543
36	6	0	-1.485990	-7.843041	1.160445
37	1	0	-1.359337	-7.523913	2.185125
38	6	0	-1.214842	-7.031881	0.000000
39	6	0	-0.793587	-5.677402	0.000000
40	6	0	-0.436917	-4.513026	0.000000
41	6	0	-0.055635	-3.160085	0.000000
42	6	0	1.219333	-2.621218	0.000000
43	6	0	0.114627	-0.714025	0.000000
44	26	0	-0.004626	-8.719425	0.000000
45	6	0	1.978946	-8.105432	0.000000
46	1	0	2.274456	-7.065293	0.000000
47	6	0	1.712626	-8.900541	1.155265
48	1	0	1.792683	-8.574067	2.182960
49	6	0	1.281946	-10.188826	0.713751
50	1	0	0.977209	-11.009236	1.348934
51	6	0	1.281946	-10.188826	-0.713751
52	1	0	0.977209	-11.009236	-1.348934
53	6	0	1.712626	-8.900541	-1.155265
54	1	0	1.792683	-8.574067	-2.182960
55	1	0	2.122934	-3.219174	0.000000
56	1	0	-2.122934	3.219174	0.000000

Total Energy, E(TD-HF/TD-KS) = -2307.81491822

1) a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652.