Supporting Information

Fluorescence Probing of the Ferric Fenton Reaction via Novel Chelation

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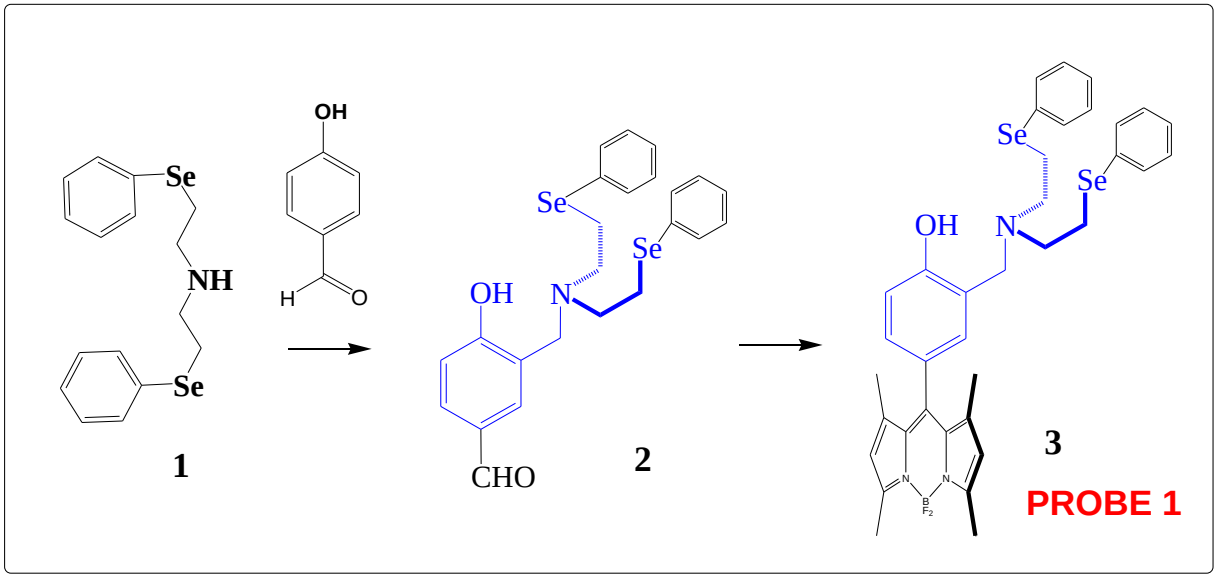
Experimental Section:

General Remarks. All reagents used herein were used as received from commercial suppliers (Aldrich, Acros, and Junsei companies). ^{1}H and ^{13}C NMR spectra were acquired using a Bruker Avance 400 MHz spectrometer. TMS was used as an internal standard. ^{1}H and ^{13}C NMR spectral signals were calibrated internally by the respective protio impurity or carbon resonance of the NMR spectroscopic solvent, *e.g.*, DMSO-d_6. ESI-mass spectrometry was performed on a VG AUTOSPEC ULTIMA by the research support staff at KAIST. This instrument possesses a trisector double focusing magnetic sector analyzer and was operated at a resolution of 80,000. Absorption spectra were measured using a JASCO V–530 UV/Vis spectrophotometer. Fluorescence measurements were carried out with a Shimadzu RF–5301pc spectrofluorophotometer.

Synthesis of probe:



Synthesis of amine precursor (1):

The amine precursor has been synthesized herein according to previous published reports.

Synthesis of aldehyde (2):

4-hydroxy benzaldehyde (1 mmol), the amine (**1**)(1mmol) and paraformaldehyde (1.1 mmol) were taken into a small round bottom flask. The reaction mixture was stirred at 50° C for 16 h under an inert atmosphere (argon). The oily residue was then dissolved in dichloromethane and purified by flash column chromatography using a hexane : ethylacetate eluent system to obtain product as a yellowish white solid.

Compound 2: Eluent: Hexane /ethyl acetate 8/2. (Yield: 70%).

^{1}H NMR spectroscopy: 9.80 (s, 1H), 7.72 (d, $^{4}J_{(H,H)}$ = 8 Hz, 1H), 7.49 (s, 1H), 7.48-7.40 (m, 4H), 7.24-7.20 (m, 6H), 6.95 (d, $^{4}J_{(H,H)}$ = 8 Hz, 1H), 3.82 (s, 2H), 2.93 (t, $^{4}J_{(H,H)}$ = 8 Hz, 1H 2H), 2.83 (t, $^{4}J_{(H,H)}$ = 8 Hz, 1H 2H).

^{13}C NMR spectroscopy: 190.69, 163.76, 132.92, 132.41, 130.17, 129.25, 128.87, 128.75, 127.40, 121.94, 116.91, 57.26, 53.11, 23.66.

ES-MS: $[M+H]^{+}$ = 520.0294(cal.), 520.029 (exp.).

Synthesis of BODIPY dye (3): Compound **2** (1.0 mmol) and 2,4-dimethyl pyrrole (2.0 mmol) were dissolved in 100 mL of CH_2Cl_2 under an argon atmosphere, followed by the addition of trifluoroacetic acid (1-3 drops); the solution was stirred at room temperature overnight. A solution of 2,3-dichloro-5,6-dicyanobenzoquinone (1.0 mmol) in CH_2Cl_2 was added; stirring was continued for 30 min more before the reaction mixture was washed with H_2O, dried over Na_2SO_4, filtered, and evaporated to a residue. This crude compound and TEA (10 mmol) were dissolved in 60 mL of CH_2Cl_2 under an argon atmosphere and stirred at room temperature for 15 min. BF_3-OEt_2 (10.0 mmol) was then added; stirring continued for 1 hour. The reaction mixture was washed with H_2O and NaOH (2 N). The aqueous solution was extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4, filtered, and evaporated. The crude compound was purified first by column chromatography over silica gel (eluent : CH_2Cl_2) to afford a purple powder, followed by purification with PTLC afford the pure compound.

Compound 3: yield (23%):

^{1}H NMR spectroscopy: 7.44-7.39 (m, 4H), 7.23-7.19 (m, 6H), 7.02(d, $^{3}J_{(H,H)}$ = 8.4 Hz, 1H), 6.95 (d, $^{3}J_{(H,H)}$ = 8.2 Hz, 1H), 6.78 ((d, $^{3}J_{(H,H)}$ = 2.08 Hz, 1H) 5.93 (s, 2H), 3.77 (s, 2H), 2.92 (t, $^{3}J_{(H,H)}$ = 7.36 Hz, 4H), 2.79 (t, $^{3}J_{(H,H)}$ = 7.36 Hz, 4H), 2.51 (s, 6H), 1.33 (s, 6H).

^{13}C NMR spectroscopy: 158.20, 155.22, 143.02, 141.79, 132.64, 131.83, 129.28, 128.98, 128.83, 128.26, 127.29, 125.82, 122.44, 121.09, 117.28, 57.49, 53.16, 23.77, 14.69, 14.57.

^{11}B NMR spectroscopy: (CDCl3, BF3·OEt_2, d 0.00): 0.64 (t, 29.85 Hz).

^{19}F NMR spectroscopy: (CDCl3, CFCl3, d 0.00): -146.19 (m).

^{77}Se NMR spectroscopy: 278.78(S)

ES-MS: $[M+H]^+$ = 738.1485 (cal.), 738.1531 (exp.).

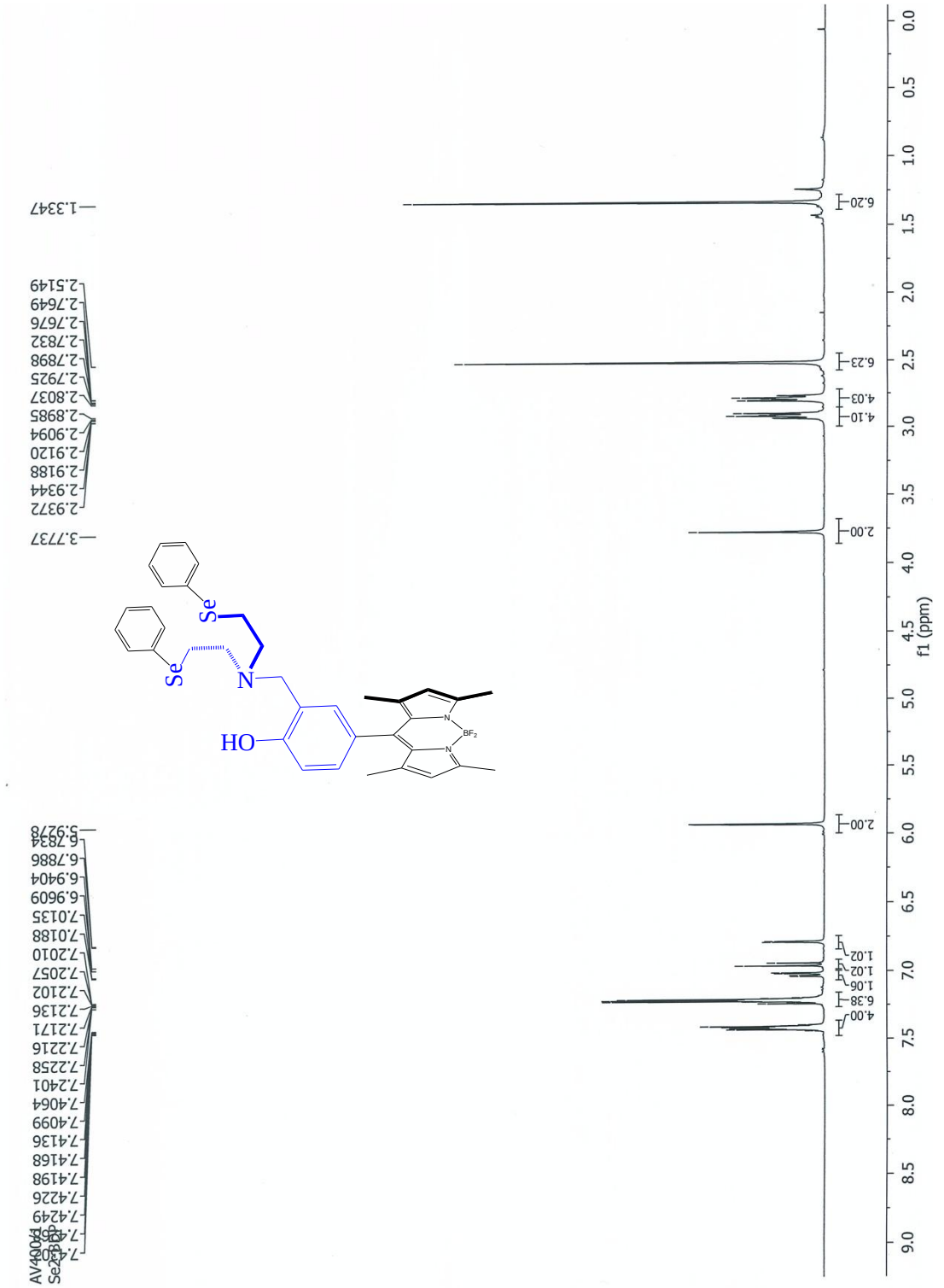


Fig. S1. ^{1}H NMR spectrum of probe **1.**

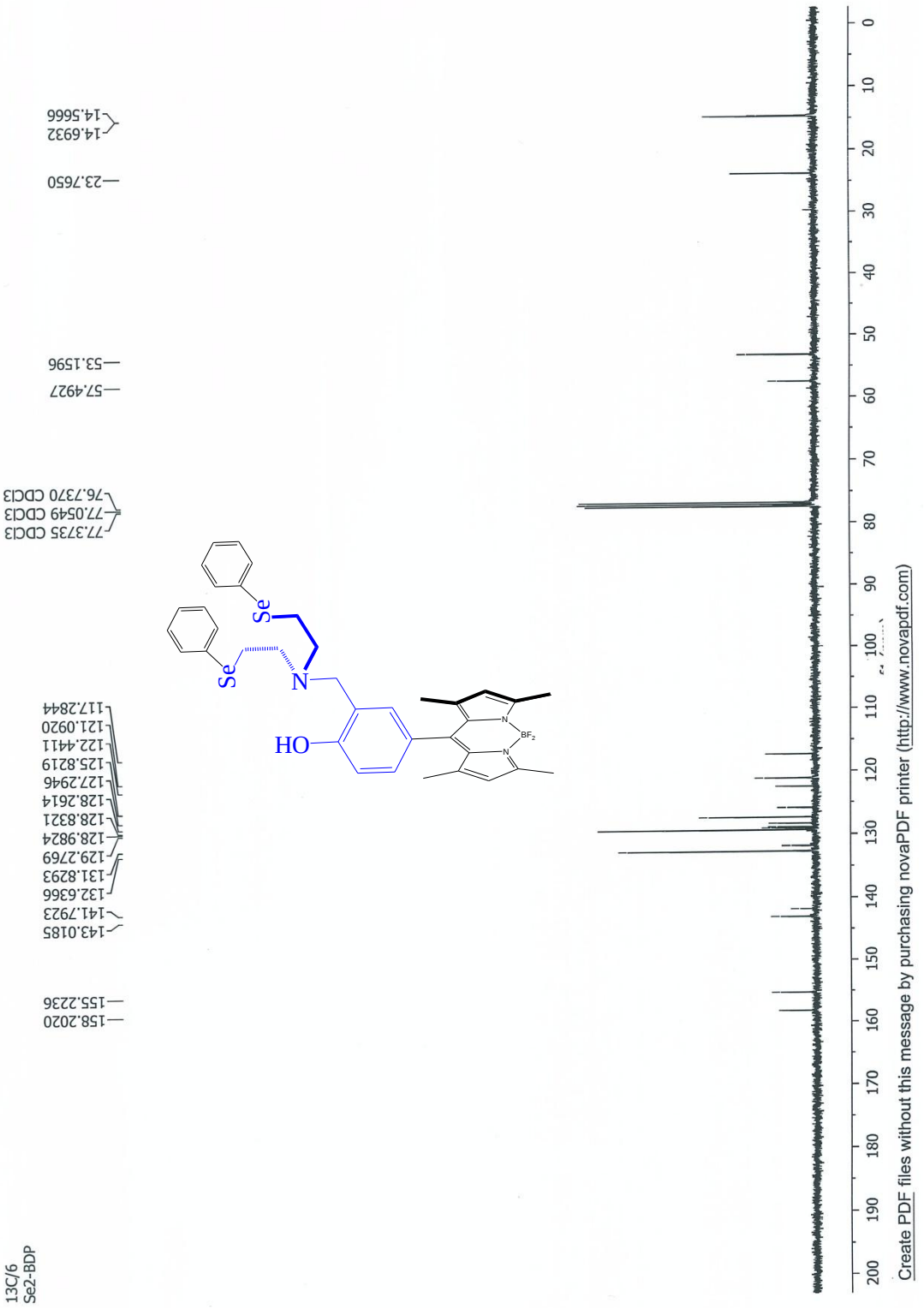


Fig. S2a. ^{13}C NMR spectrum of probe **1.**

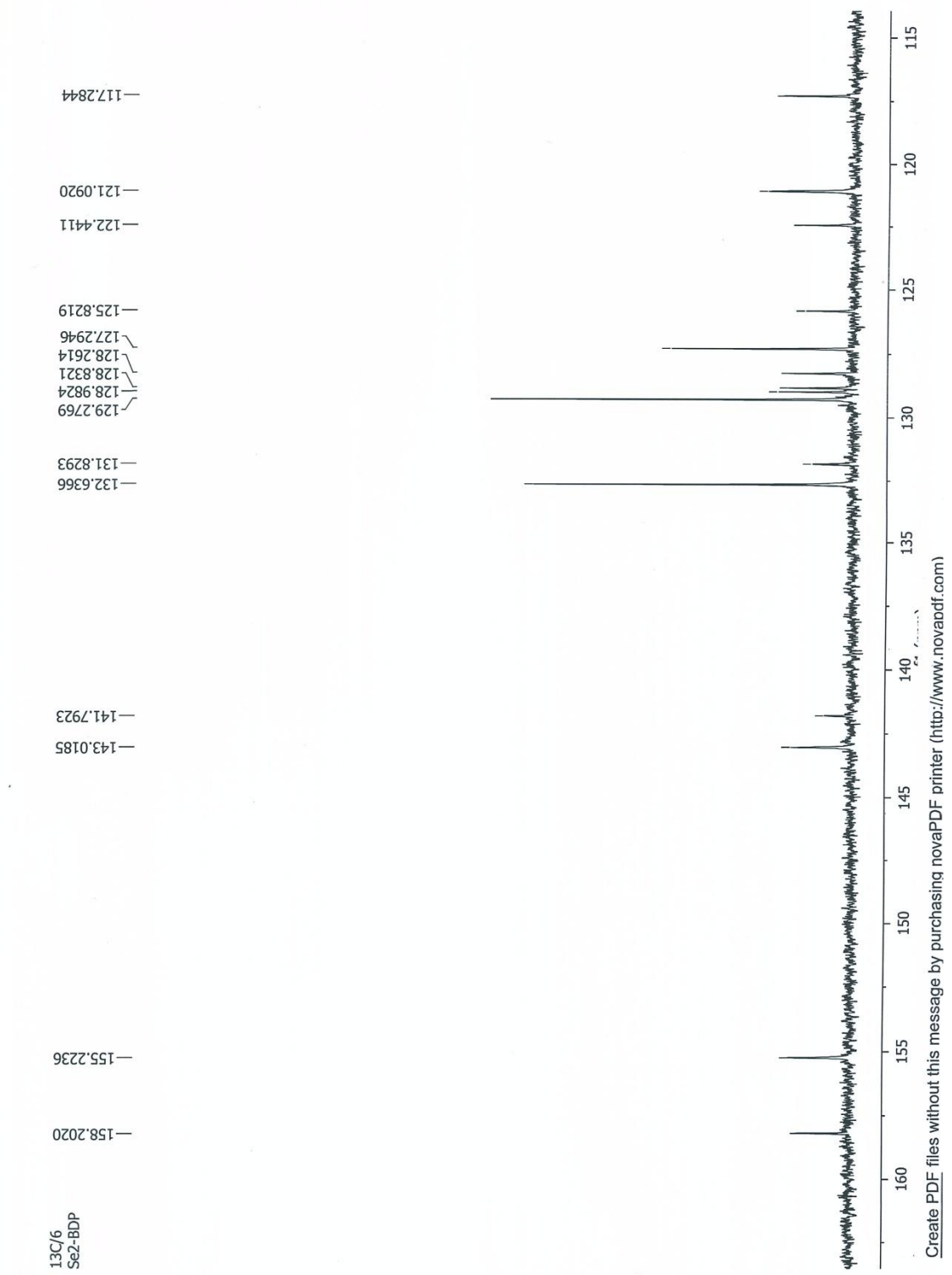


Fig. S2b. ^{13}C NMR spectrum of probe **1** (EXPANDED VIEW).

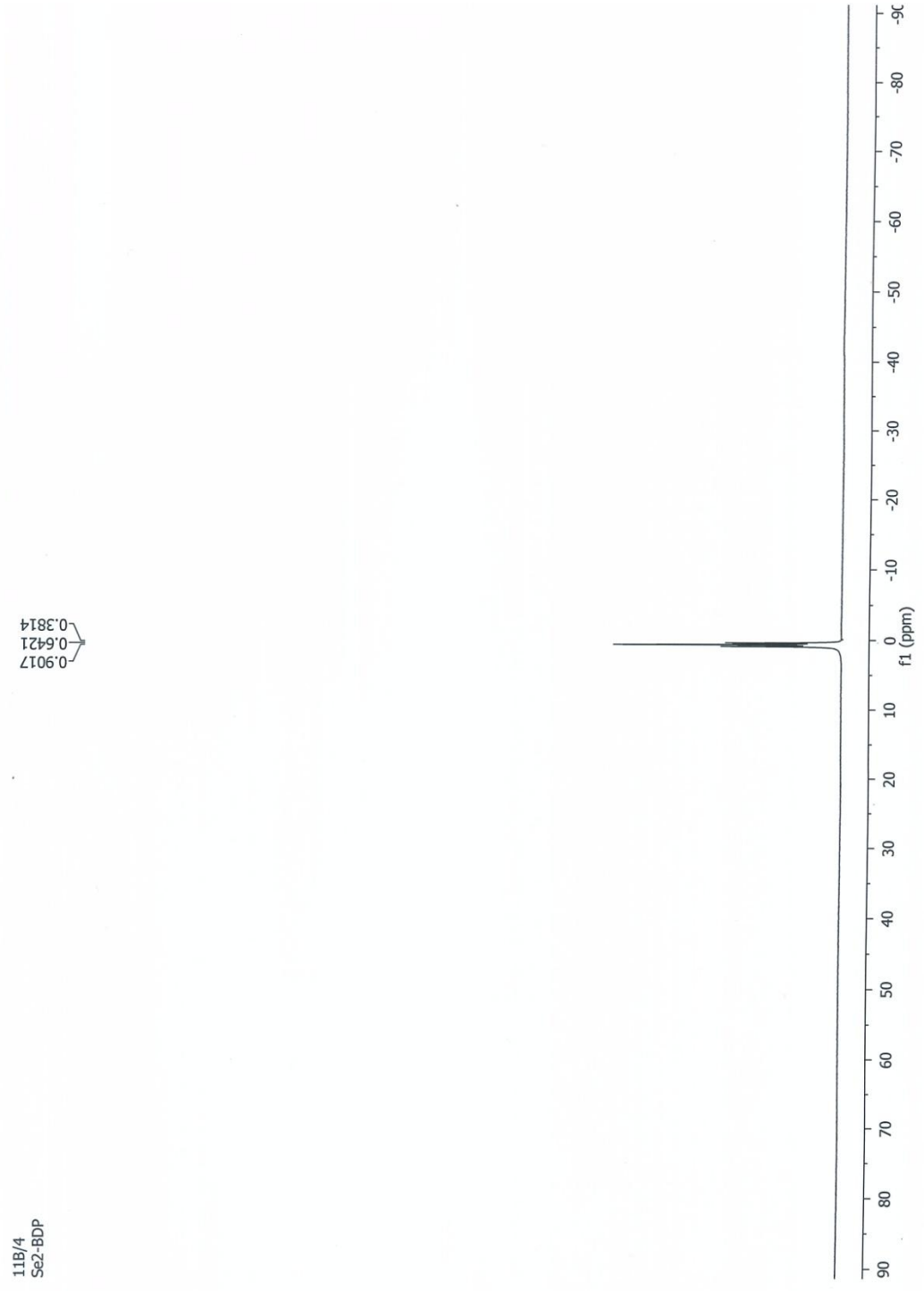


Fig. S3. ^{11}B NMR spectrum of probe **1.**

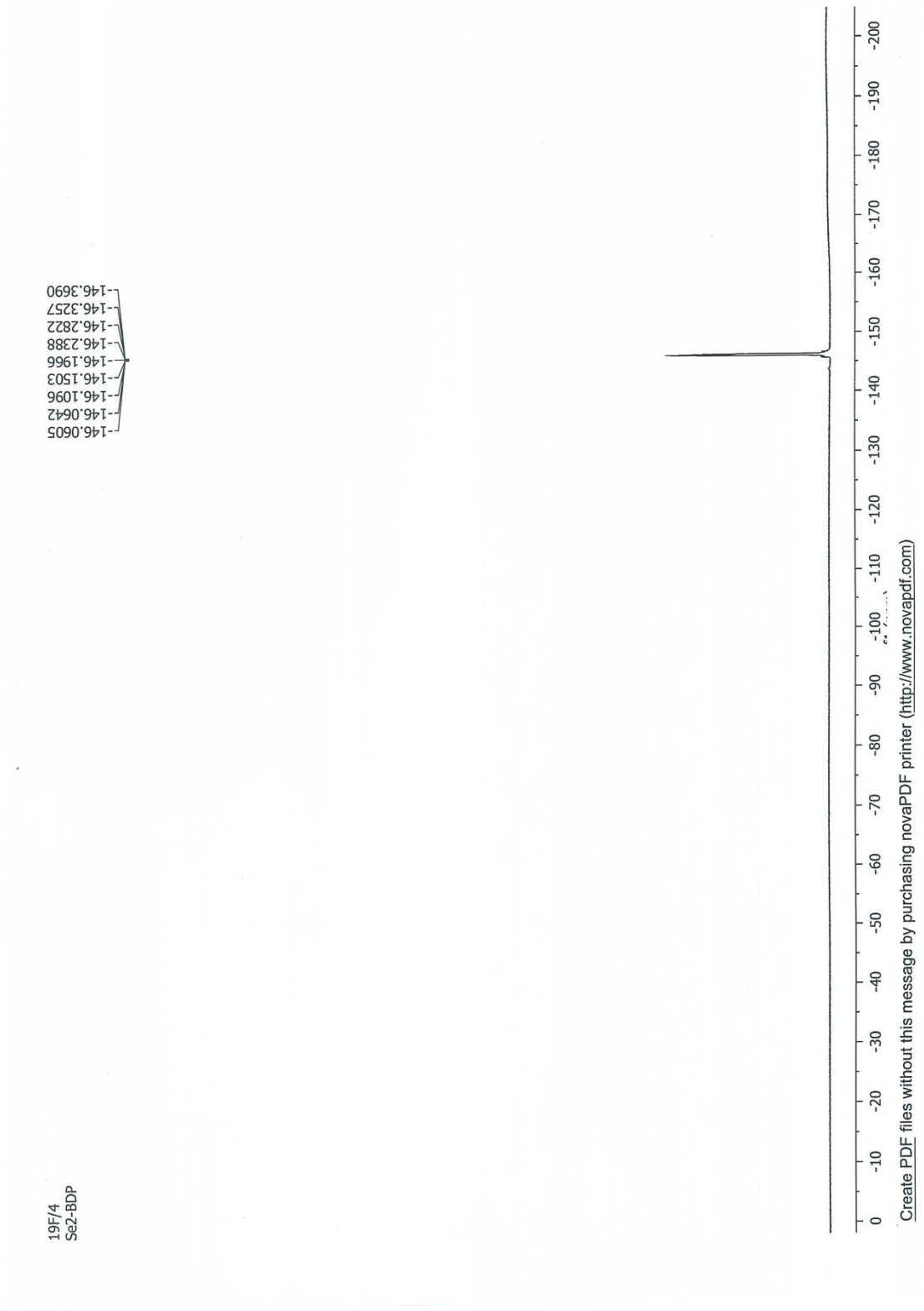


Fig. S4. ^{19}F NMR spectrum of probe **1.**

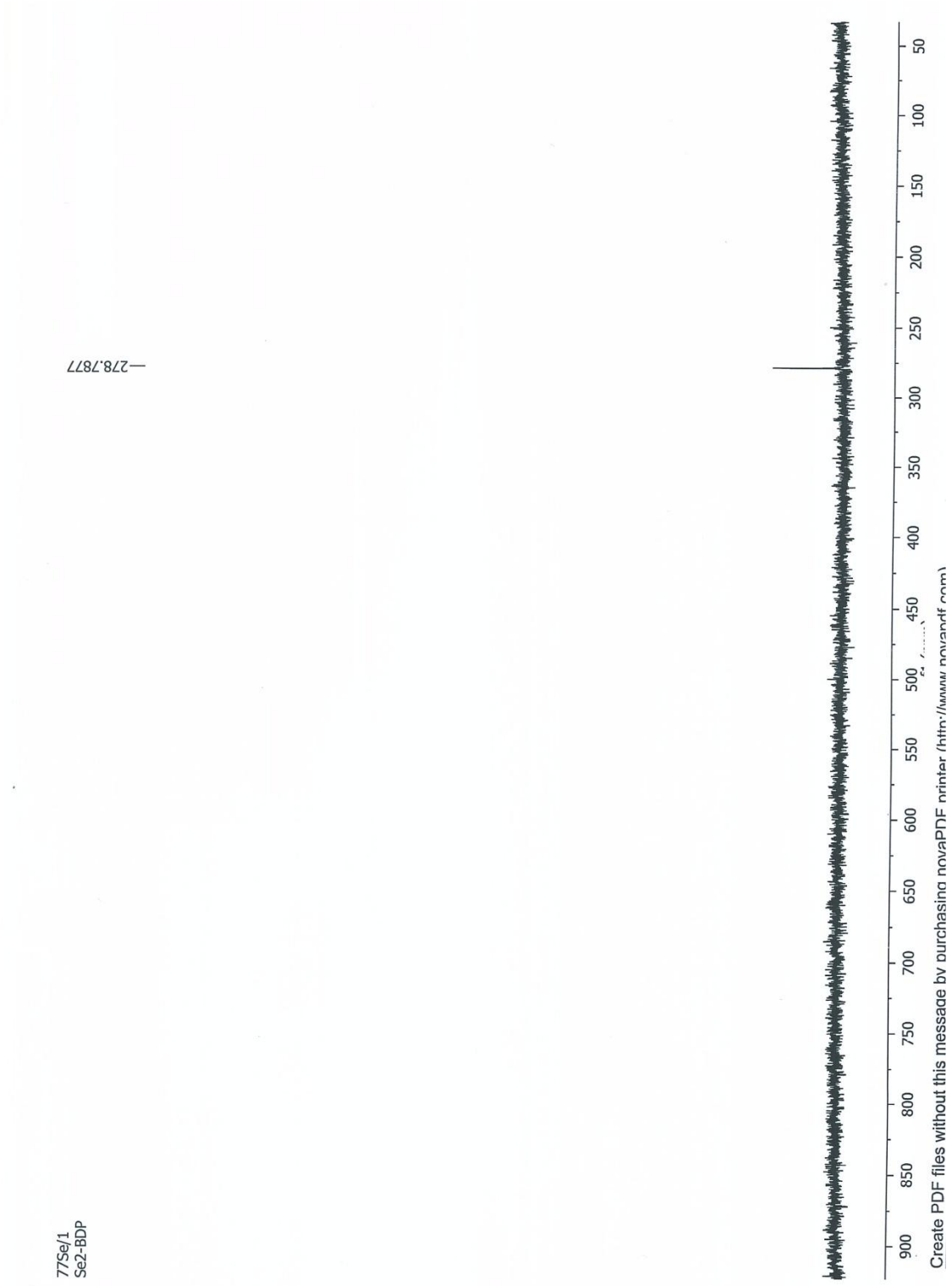


Fig. S5. ^{77}Se NMR spectrum of probe **1.**

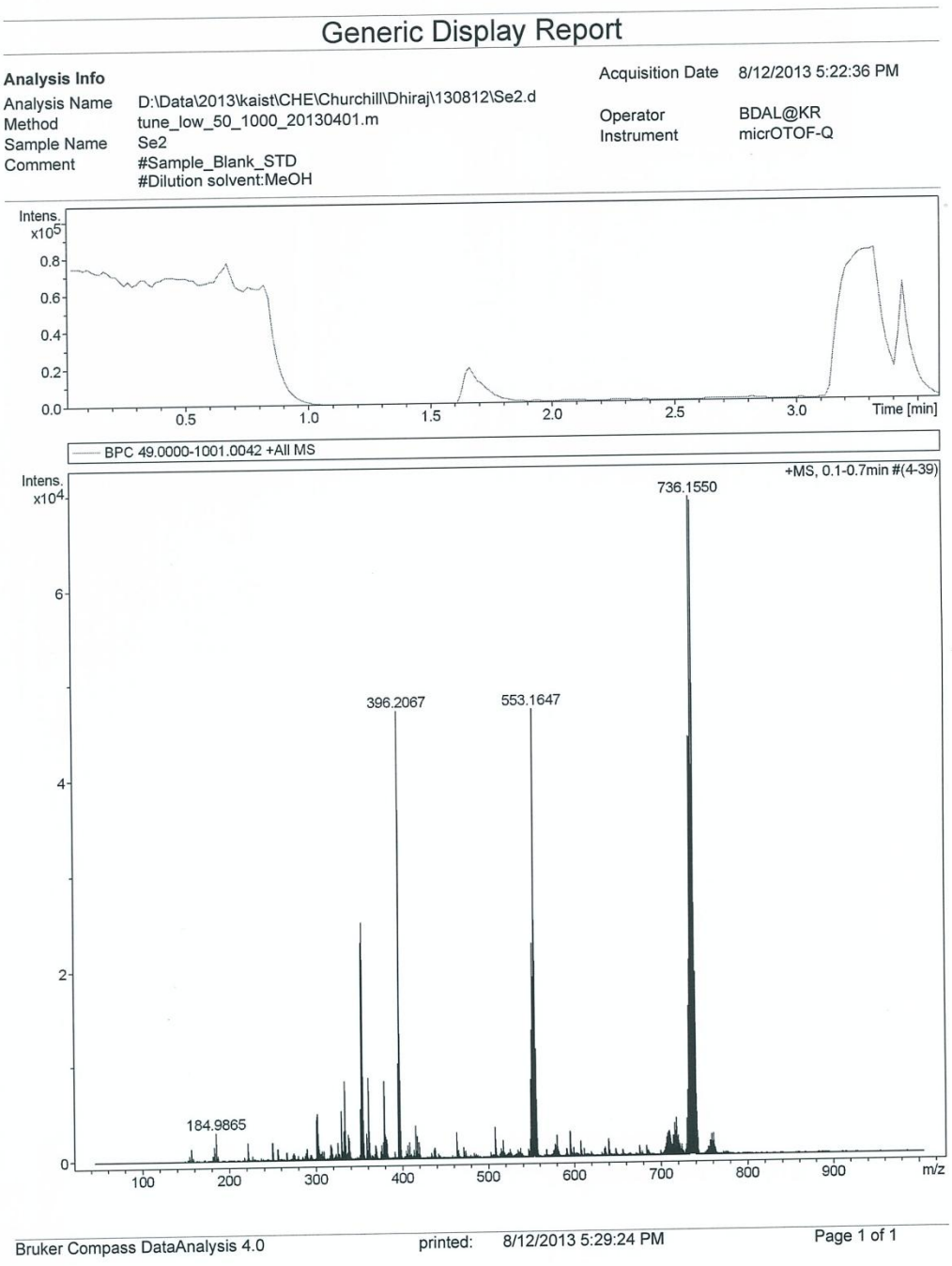


Fig. S6a. ESI–mass spectrum of Probe **1.**

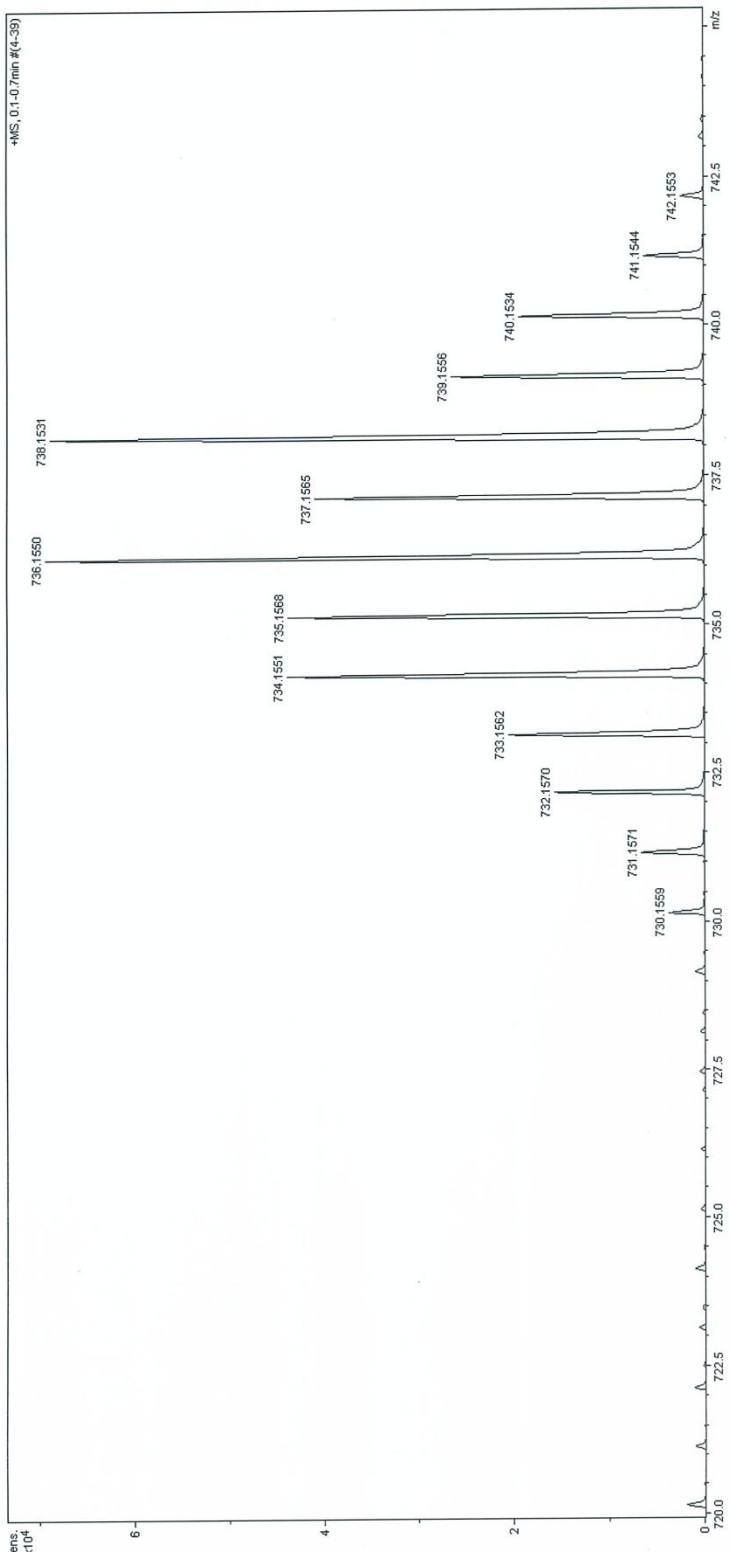


Fig. S6b. ESI–mass spectrum of Probe **1**(Expanded view)**.**

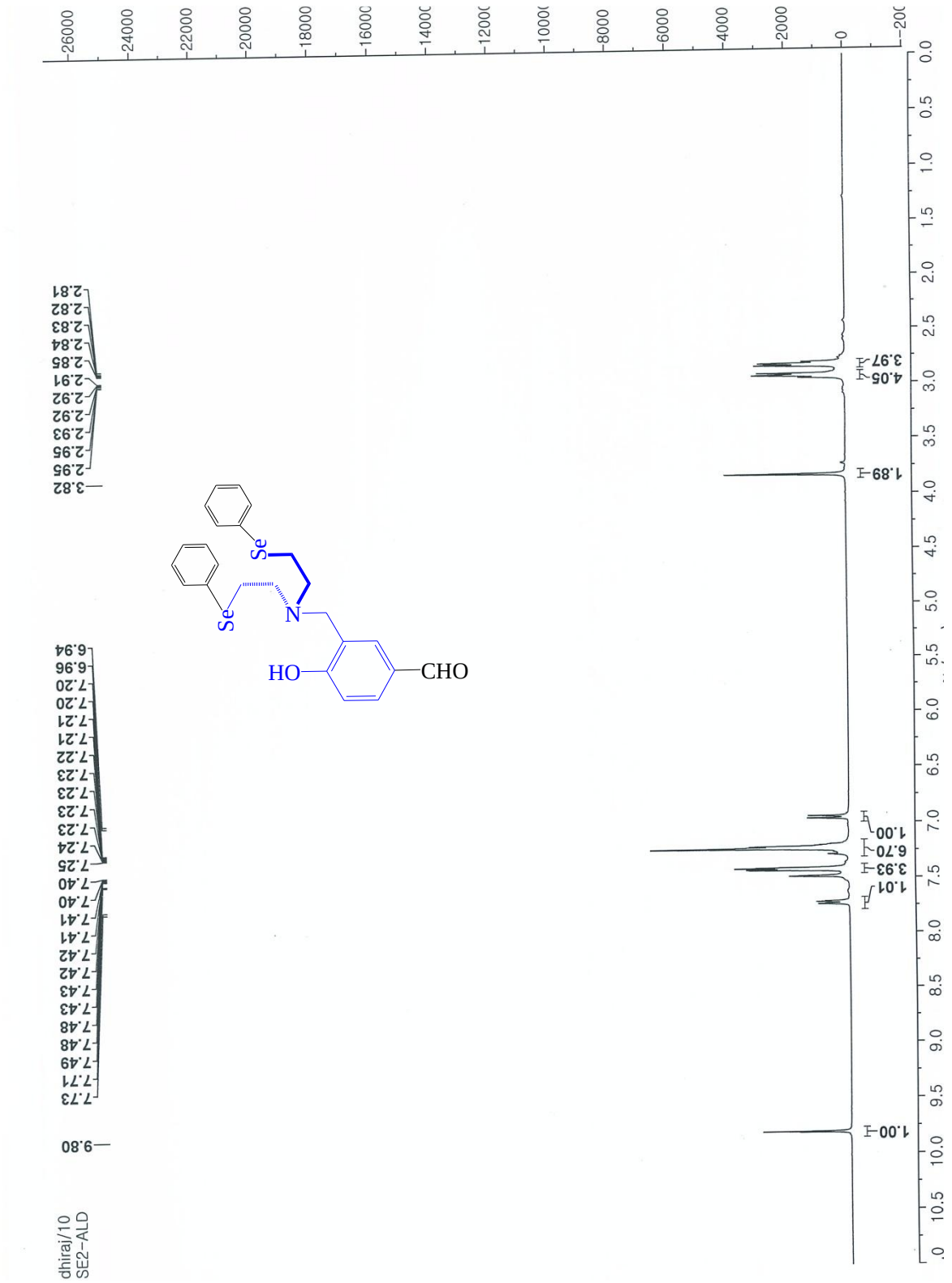


Fig. S7. ^{1}H NMR spectrum of compound **2.**

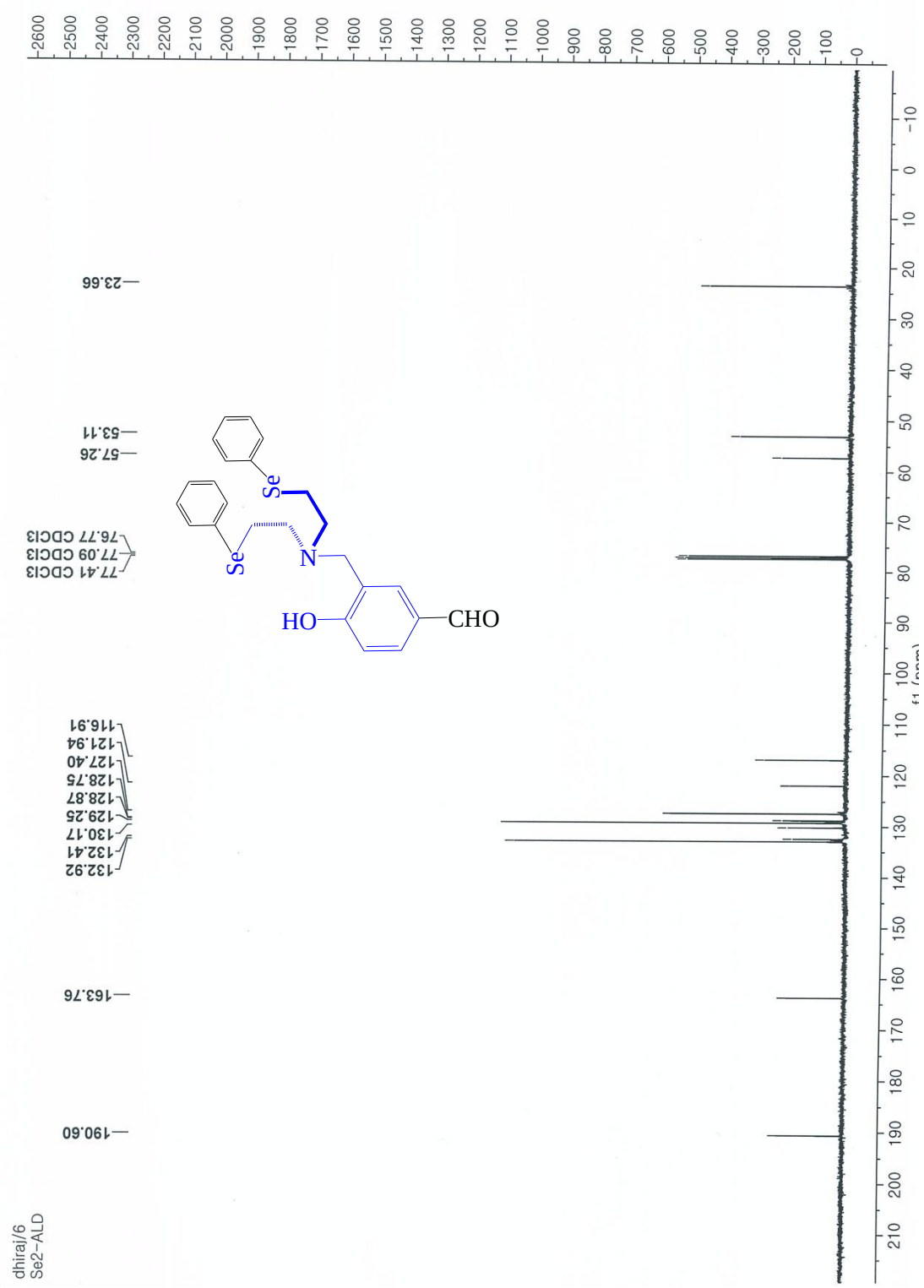


Fig. S8. ^{13}C NMR spectrum of compound **2.**

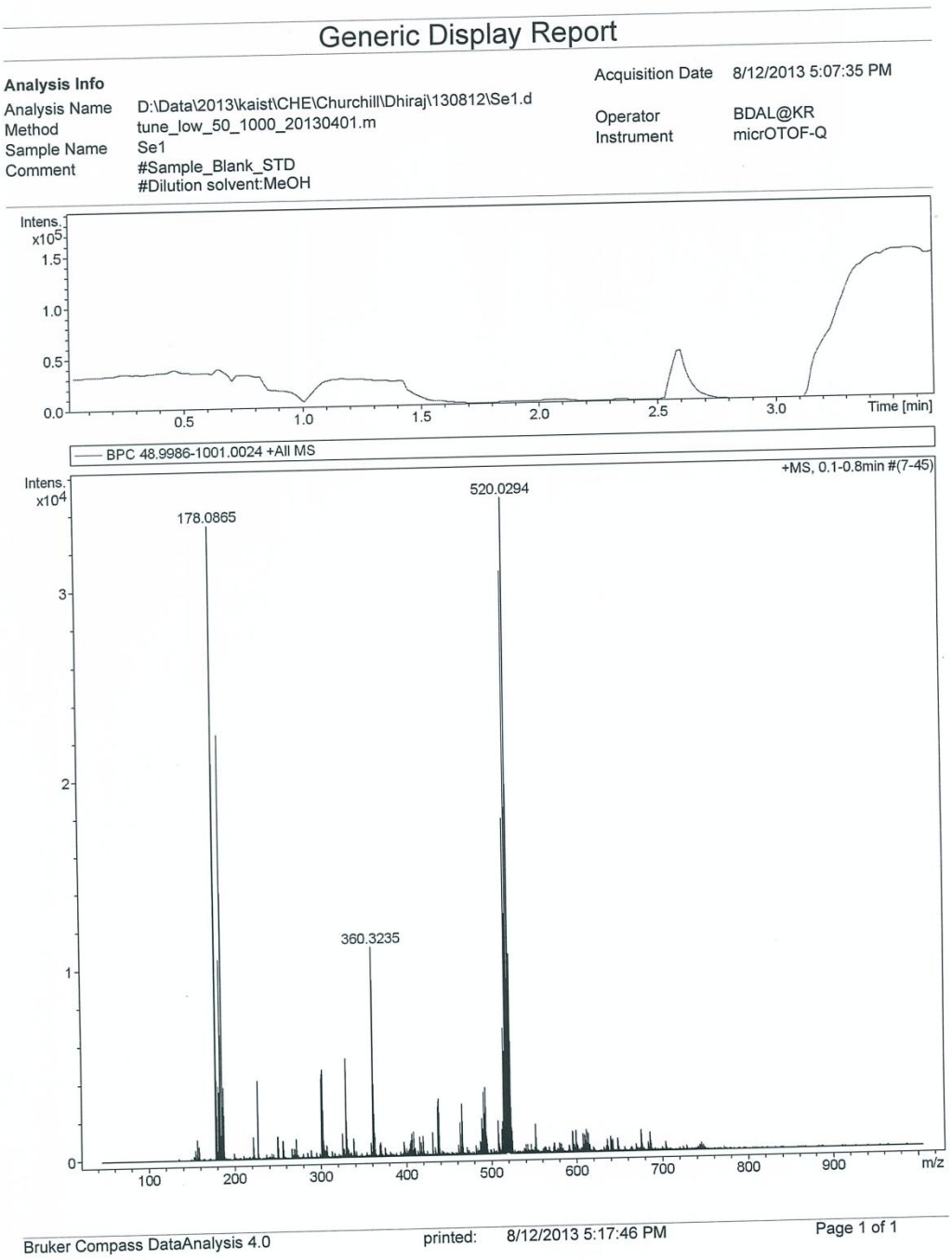


Fig. S9a. ESI–mass spectrum of compound **2.**

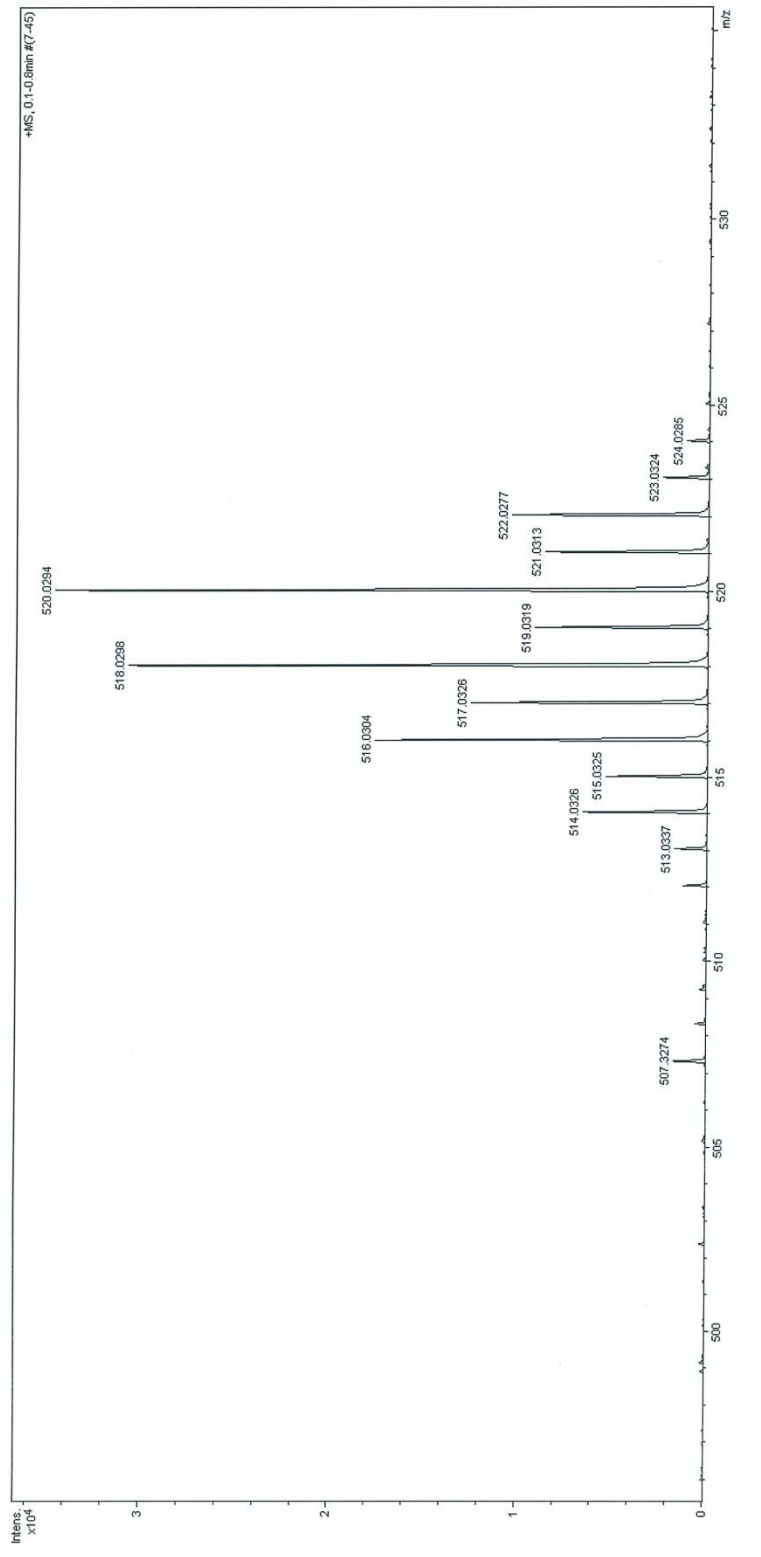


Fig. S9b. ESI–mass spectrum of compound **2**(Expanded view)**.**

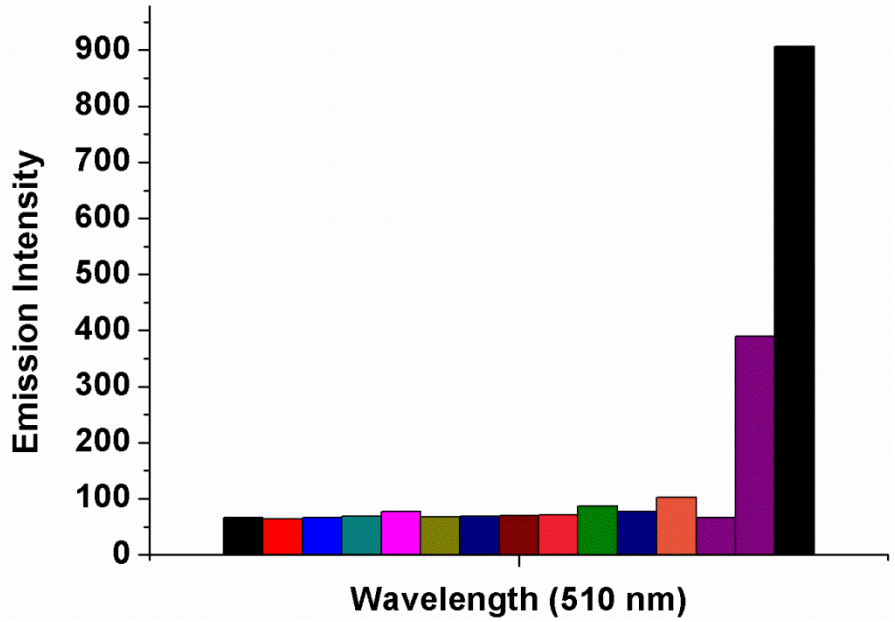


Fig. S10. Relative fluorescence intensity of probe **1** (1.0×10^{-6}, in 50:50, water:DMSO) with from left to right Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Hg^{2+}, Na^{+}, K^{+}, Ag^{+}, and Fe^{3+} metal ions (66.7 μM in water).

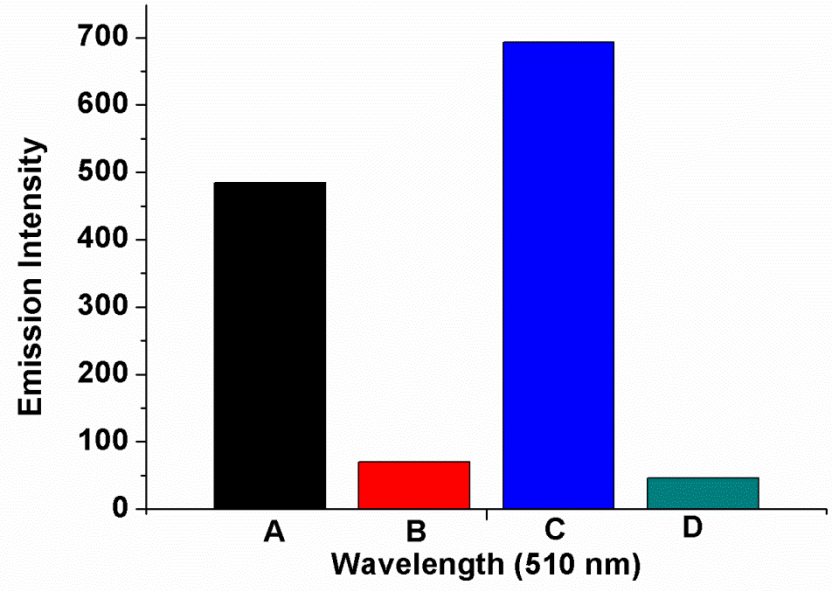


Fig. S11: Relative fluorescence intensity of probe **1** (1.0×10^{-6}, in 50:50, water:DMSO) with from left to right Fe^{2+} + H_2O_2, Fe^{2+}, Fe^{3+} and probe.

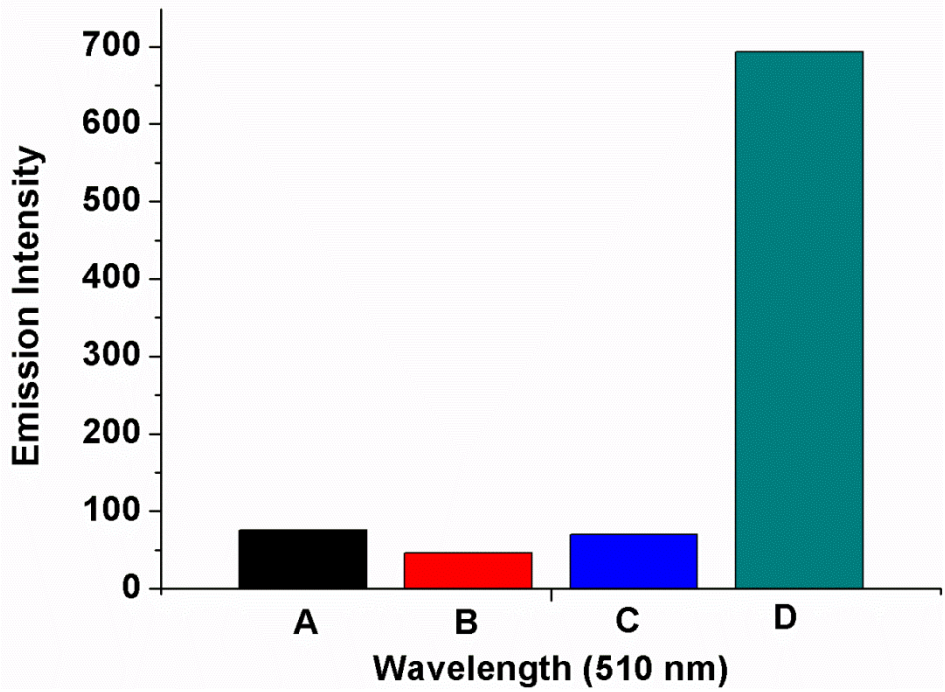
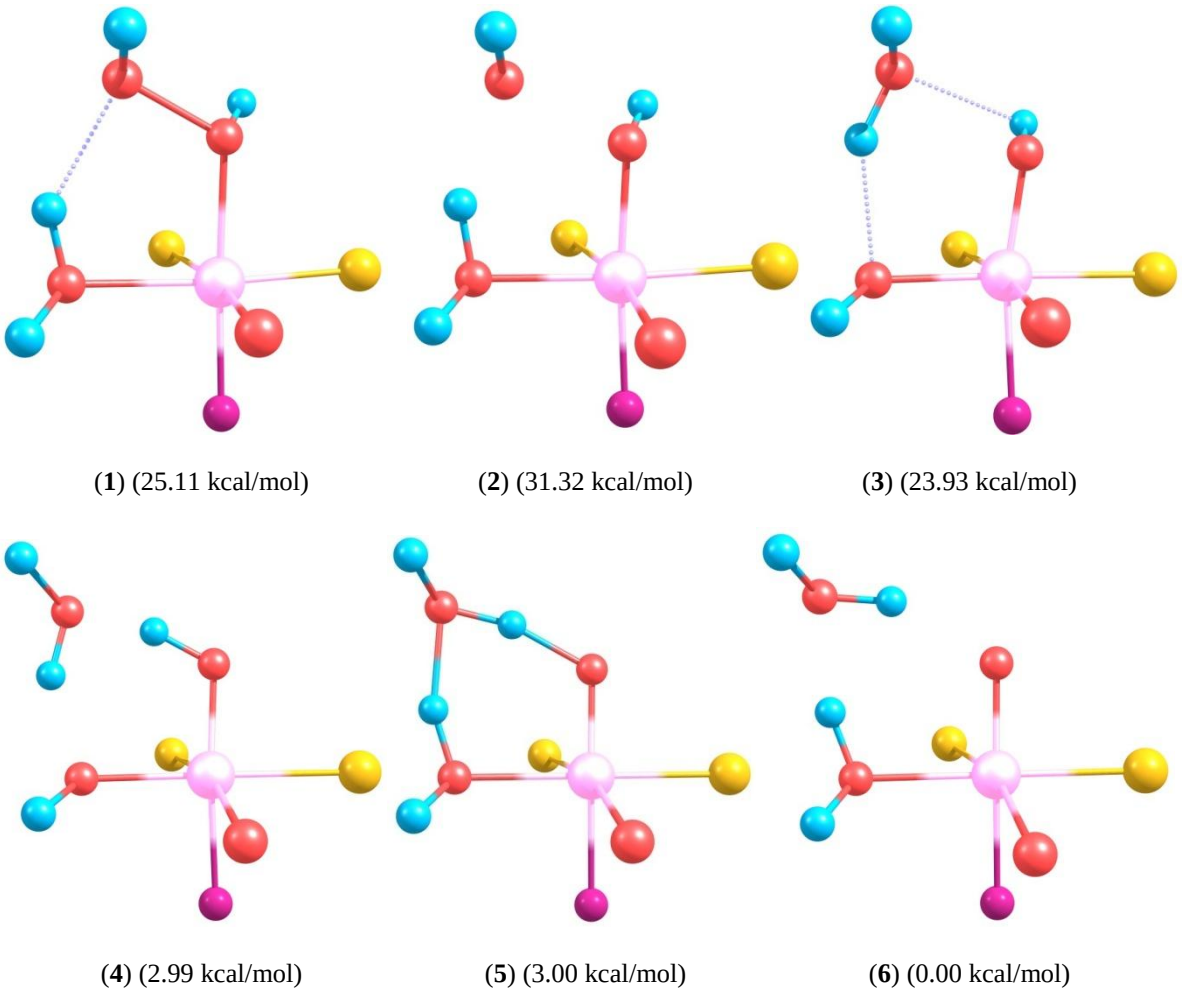


Fig. S12: Relative fluorescence intensity of probe **1** (1.0×10^{-6}, in 50:50, water:DMSO) with from left to right Fe^{3+} + H_2O_2, Fe^{2+}, probe and Fe^{3+}.

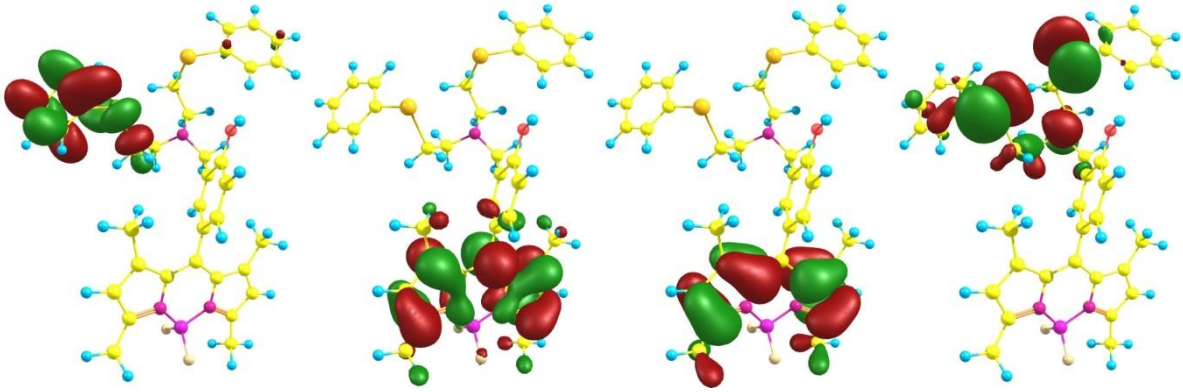


(**1**) (25.11 kcal/mol) (**2**) (31.32 kcal/mol) (**3**) (23.93 kcal/mol)

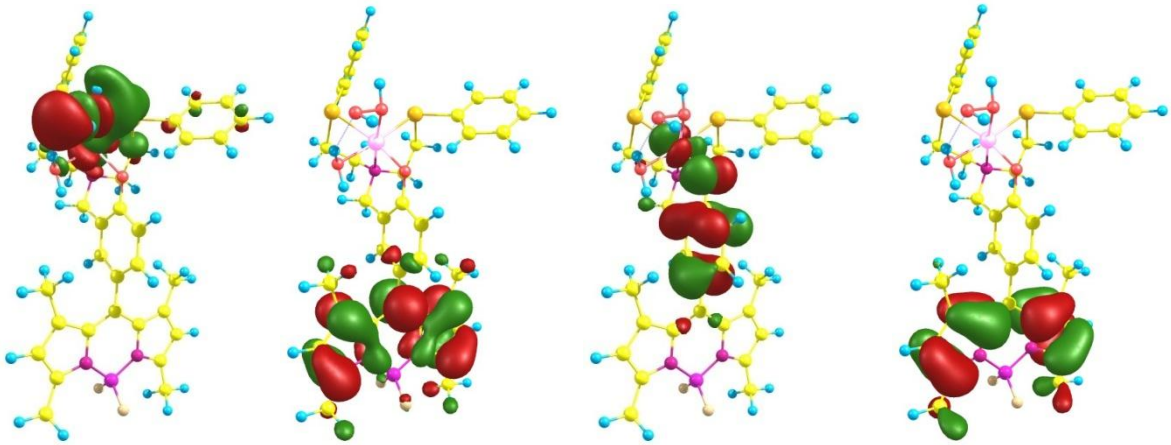
(**4**) (2.99 kcal/mol) (**5**) (3.00 kcal/mol) (**6**) (0.00 kcal/mol)

Fig. S13: Fe-Core structures of the Optimized geometries.

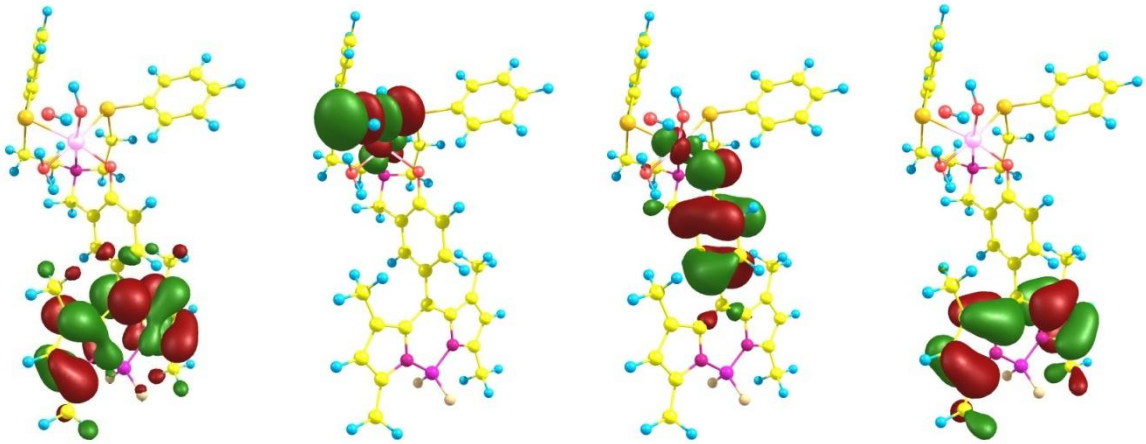
Probe 1 LUMO+1 LUMO HOMO HOMO-1



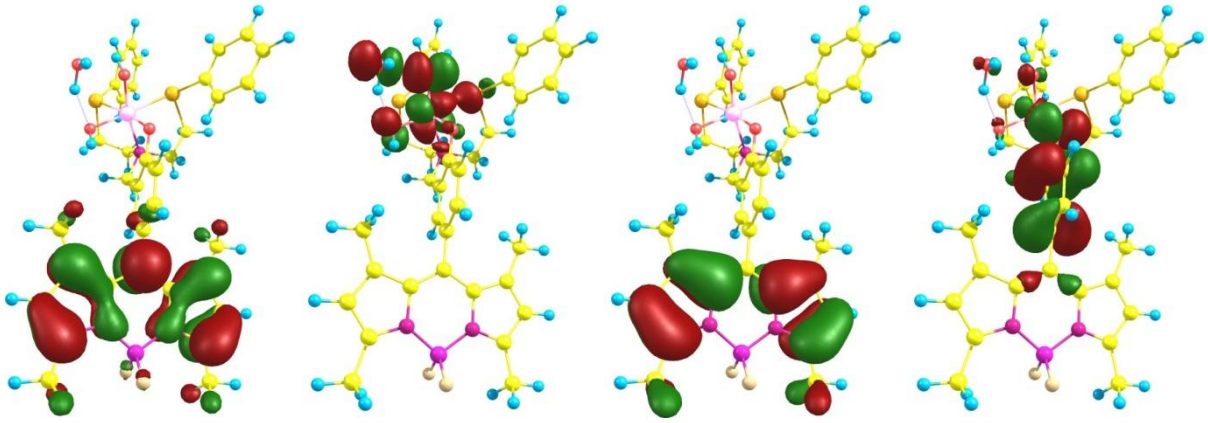
Optimized complex 1.



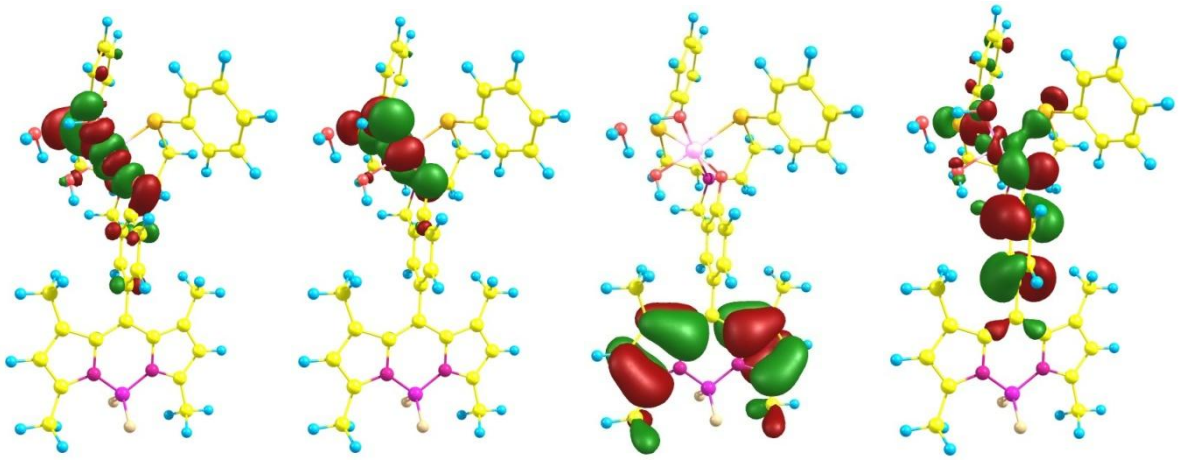
Optimized complex 2.



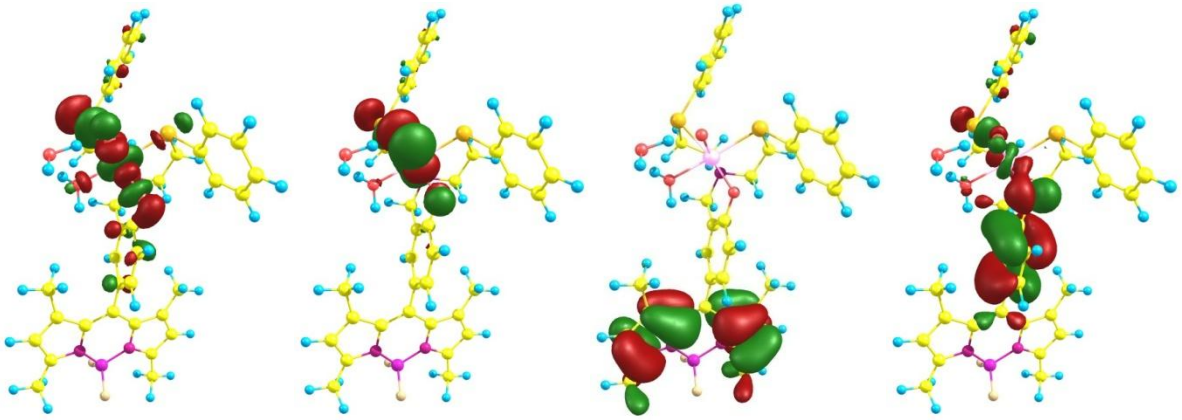
Optimized complex 3.



Optimized complex 4.



Optimized complex 5.



Optimized complex 6.

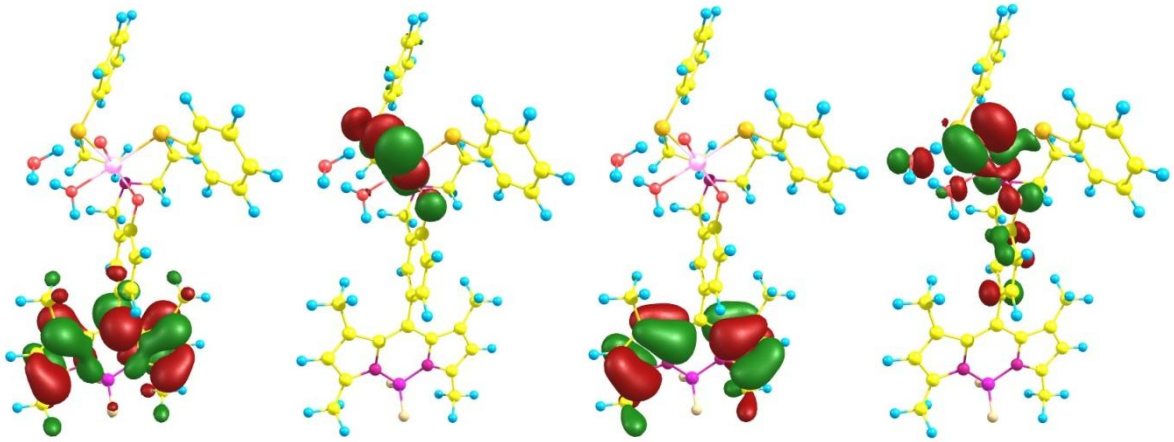
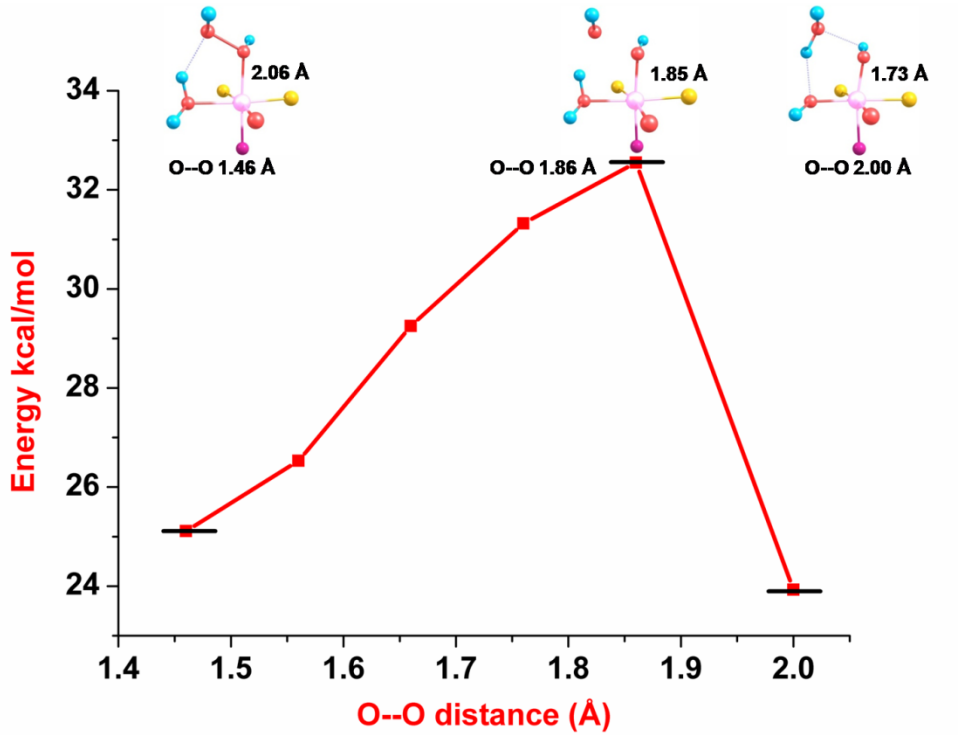


Fig. S14: HOMO-1, HOMO, LUMO and LUMO+1 drawings of Probe complex in various stages of hydrogen peroxide substrate reactivity.



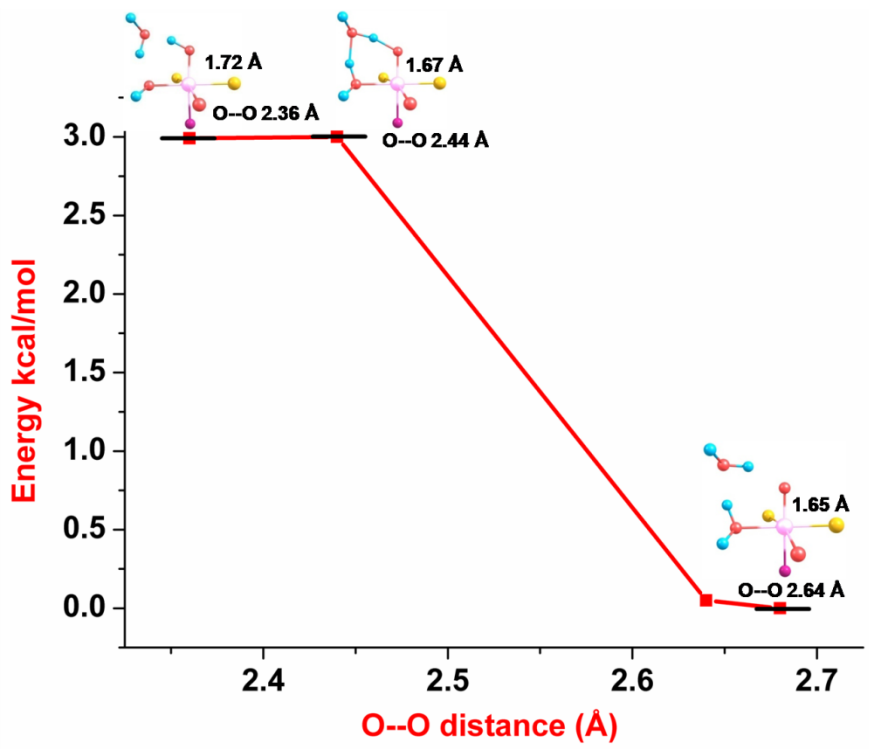


Fig. S15: The computed energies for the transformation of $[Fe^{II}H_2O•H_2O_2•probe]^{2+}$ to $[Fe^{IV}(OH)_2•probe]^{2+}$ (top) and $[Fe^{IV}(OH)_2•probe]^{2+}$ to $[Fe^{IV}H_2O•O•probe]^{2+}$ (bottom) as a function of O-O bond length. The zero energy corresponds to $[Fe^{IV}H_2O•O•probe]^{2+}$.

Tables S1. Coordinates of optimized complex 1.

6	**3.170865000**	**0.197981000**	**0.363513000**
6	**2.213202000**	**-0.450499000**	**-0.419157000**
6	**0.838286000**	**-0.352939000**	**-0.164198000**
6	**0.383978000**	**0.431032000**	**0.935799000**
6	**1.369700000**	**1.098191000**	**1.712918000**
6	**2.722242000**	**0.989877000**	**1.435524000**
8	**-0.883857000**	**0.592856000**	**1.259222000**
7	**-1.495147000**	**-0.662608000**	**-1.194365000**
34	**-3.915499000**	**-2.395944000**	**0.111146000**
6	**-5.550185000**	**-1.869780000**	**-0.815999000**
6	**-5.766308000**	**-2.090059000**	**-2.179428000**
6	**-6.989221000**	**-1.723828000**	**-2.750955000**
6	**-7.993100000**	**-1.149789000**	**-1.969942000**
6	**-7.774931000**	**-0.944417000**	**-0.605095000**
6	**-6.557523000**	**-1.303176000**	**-0.024323000**
6	**4.626753000**	**0.045033000**	**0.079668000**
6	**5.317654000**	**1.057518000**	**-0.610005000**
7	**6.693386000**	**0.940328000**	**-0.859239000**
7	**6.667344000**	**-1.282794000**	**0.254751000**
6	**5.299325000**	**-1.111920000**	**0.515534000**
6	**7.066091000**	**-2.457743000**	**0.790811000**
6	**5.965333000**	**-3.073524000**	**1.415019000**
6	**4.851252000**	**-2.251258000**	**1.262296000**
6	**4.871698000**	**2.290384000**	**-1.190759000**
6	**5.998959000**	**2.877074000**	**-1.761093000**
6	**7.102421000**	**2.030109000**	**-1.545966000**
6	**3.490708000**	**-2.559946000**	**1.815650000**
6	**3.493796000**	**2.883257000**	**-1.233316000**
6	**8.517288000**	**2.231825000**	**-1.984008000**
6	**8.472052000**	**-2.957698000**	**0.702594000**
5	**7.586428000**	**-0.261241000**	**-0.460709000**
9	**8.158319000**	**-0.839490000**	**-1.603572000**
9	**8.607761000**	**0.160064000**	**0.405008000**
1	**2.544746000**	**-1.054001000**	**-1.261964000**
1	**1.024672000**	**1.700563000**	**2.548671000**
1	**3.443589000**	**1.512847000**	**2.058360000**
1	**-5.010019000**	**-2.546456000**	**-2.807740000**
1	**-7.150429000**	**-1.894154000**	**-3.811519000**
1	**-8.940457000**	**-0.868026000**	**-2.419731000**
1	**-8.551567000**	**-0.504401000**	**0.013749000**
1	**-6.405095000**	**-1.144067000**	**1.039243000**
1	**5.994189000**	**-4.024535000**	**1.931567000**
1	**6.032326000**	**3.821331000**	**-2.289567000**
1	**3.087050000**	**-1.727380000**	**2.400578000**
1	**2.762497000**	**-2.770517000**	**1.024319000**
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1	**2.757774000**	**2.179882000**	**-1.636203000**
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1	**8.630854000**	**3.204492000**	**-2.468456000**

1	8.562293000	-3.927680000	1.197170000
1	8.784173000	-3.060655000	-0.342419000
1	9.165590000	-2.252550000	1.173461000
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6	-3.399080000	3.050075000	0.527712000
6	-4.289351000	4.063608000	0.149296000
6	-2.342255000	3.312610000	1.404381000
6	-4.104807000	5.358532000	0.638467000
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6	-2.175177000	4.612228000	1.893402000
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6	-3.048735000	5.633180000	1.511787000
1	-4.790908000	6.147137000	0.342789000
1	-1.354910000	4.824500000	2.573822000
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26	-2.324687000	-0.528605000	0.679494000
8	-1.269567000	-2.117265000	1.451013000
1	-1.570487000	-2.148073000	2.387206000
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6	-2.715638000	-2.865328000	-1.384931000
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6	-2.220654000	-1.618016000	-2.099880000
1	-3.073309000	-1.098458000	-2.536678000
1	-1.559680000	-1.903979000	-2.928983000
6	-1.457593000	0.695702000	-1.837909000
1	-1.031337000	0.602981000	-2.846966000
1	-0.782302000	1.309078000	-1.242580000
6	-2.815650000	1.373388000	-1.922073000
1	-2.704826000	2.431847000	-2.161267000
1	-3.489216000	0.927333000	-2.655338000

Tables S2. Coordinates of optimized complex 2.

6	3.188058000	0.232470000	0.377128000
6	2.238620000	-0.411522000	-0.418082000
6	0.861715000	-0.310075000	-0.176410000
6	0.398538000	0.473590000	0.916411000
6	1.374276000	1.132588000	1.710000000
6	2.730327000	1.020427000	1.447619000
8	-0.877272000	0.651068000	1.219966000
7	-1.465916000	-0.606745000	-1.208601000
34	-3.863536000	-2.425183000	0.079080000
6	-5.510416000	-1.893329000	-0.820096000
6	-5.732225000	-2.074787000	-2.188105000
6	-6.965685000	-1.711153000	-2.738034000
6	-7.972406000	-1.179027000	-1.931400000
6	-7.747577000	-1.013295000	-0.562326000
6	-6.520107000	-1.370086000	-0.002235000
6	4.645974000	0.076554000	0.100980000
6	5.334851000	1.072860000	-0.613069000
7	6.708917000	0.946929000	-0.867107000
7	6.685182000	-1.248491000	0.300802000
6	5.317815000	-1.071110000	0.560215000
6	7.082362000	-2.415023000	0.855649000
6	5.981182000	-3.018381000	1.491692000
6	4.868168000	-2.197675000	1.325508000
6	4.889172000	2.295945000	-1.214712000
6	6.014541000	2.867437000	-1.803389000
6	7.116874000	2.021355000	-1.578023000
6	3.506184000	-2.496895000	1.880457000
6	3.513495000	2.893939000	-1.256977000
6	8.529509000	2.209952000	-2.028689000
6	8.486207000	-2.921267000	0.770133000
5	7.602003000	-0.247057000	-0.445709000
9	8.163652000	-0.854882000	-1.578081000
9	8.630293000	0.192645000	0.402053000
1	2.577053000	-1.013874000	-1.258744000
1	1.021433000	1.734000000	2.542931000
1	3.445669000	1.538627000	2.081032000
1	-4.974211000	-2.499481000	-2.836104000
1	-7.132799000	-1.850780000	-3.802043000
1	-8.927773000	-0.899210000	-2.365024000
1	-8.526405000	-0.606489000	0.075976000
1	-6.362356000	-1.243015000	1.064748000
1	6.008990000	-3.960906000	2.023572000
1	6.047775000	3.801127000	-2.350275000
1	3.108036000	-1.661563000	2.465288000
1	2.776296000	-2.703584000	1.089631000
1	3.558400000	-3.377126000	2.528788000
1	3.518571000	3.785675000	-1.891459000
1	2.773834000	2.192464000	-1.656654000
1	3.161118000	3.188508000	-0.262529000
1	9.217062000	2.178878000	-1.176787000
1	8.830631000	1.406303000	-2.709833000
1	8.640837000	3.168148000	-2.541617000

1	8.579752000	-3.873227000	1.297949000
1	8.786115000	-3.063132000	-0.274052000
1	9.186468000	-2.201251000	1.207016000
34	-3.775965000	1.241636000	-0.217392000
6	-3.504023000	3.004805000	0.568157000
6	-4.480728000	3.963239000	0.268477000
6	-2.432236000	3.304783000	1.413743000
6	-4.370308000	5.245577000	0.810396000
1	-5.317417000	3.715356000	-0.377681000
6	-2.340065000	4.591314000	1.953750000
1	-1.687962000	2.548309000	1.636767000
6	-3.301169000	5.559569000	1.653554000
1	-5.123306000	5.992898000	0.577551000
1	-1.509828000	4.834434000	2.611128000
1	-3.219902000	6.556188000	2.078039000
26	-2.299297000	-0.510189000	0.679095000
8	-1.245363000	-2.062001000	1.416900000
1	-1.645788000	-2.109293000	2.334817000
1	-0.304852000	-1.840458000	1.552384000
8	-3.004359000	-0.238314000	2.374256000
1	-3.967460000	-0.340145000	2.501241000
8	-2.720925000	-1.547832000	3.515496000
1	-2.210145000	-0.985498000	4.131330000
6	-0.052684000	-1.102237000	-1.090792000
1	0.381970000	-1.117723000	-2.098511000
1	-0.109318000	-2.144738000	-0.765256000
6	-2.662824000	-2.822536000	-1.435731000
1	-3.175986000	-3.485033000	-2.133771000
1	-1.851486000	-3.389074000	-0.976508000
6	-2.197916000	-1.548943000	-2.124183000
1	-3.063789000	-1.028187000	-2.532716000
1	-1.547626000	-1.804237000	-2.971162000
6	-1.420645000	0.760167000	-1.836093000
1	-0.981933000	0.677243000	-2.839898000
1	-0.754644000	1.366699000	-1.224824000
6	-2.778930000	1.434883000	-1.930182000
1	-2.668241000	2.504095000	-2.114514000
1	-3.429021000	1.020115000	-2.701917000

Tables S3. Coordinates of optimized complex 3.

6	3.182959000	0.203671000	0.372402000
6	2.238533000	-0.409363000	-0.452481000
6	0.860531000	-0.312600000	-0.213689000
6	0.399441000	0.439919000	0.898368000
6	1.365853000	1.070033000	1.720949000
6	2.723758000	0.955332000	1.467181000
8	-0.882185000	0.639146000	1.195249000
7	-1.469958000	-0.573516000	-1.238352000
34	-3.906910000	-2.413757000	0.051027000
6	-5.542965000	-1.850901000	-0.846842000
6	-5.758971000	-2.004742000	-2.219740000
6	-6.986892000	-1.623198000	-2.769410000
6	-7.994619000	-1.099878000	-1.958268000
6	-7.776964000	-0.962146000	-0.584974000
6	-6.555227000	-1.337727000	-0.024721000
6	4.644140000	0.054953000	0.100757000
6	5.301372000	0.991388000	-0.715584000
7	6.674512000	0.869254000	-0.975979000
7	6.720236000	-1.180879000	0.431676000
6	5.347387000	-1.020277000	0.671443000
6	7.148500000	-2.277962000	1.093925000
6	6.061424000	-2.853502000	1.779290000
6	4.925296000	-2.087449000	1.532162000
6	4.827360000	2.157569000	-1.402796000
6	5.934417000	2.697427000	-2.052120000
6	7.054415000	1.889953000	-1.775697000
6	3.564815000	-2.382546000	2.092249000
6	3.443800000	2.735821000	-1.459563000
6	8.459867000	2.071816000	-2.250787000
6	8.567322000	-2.747170000	1.061570000
5	7.598980000	-0.258389000	-0.450963000
9	8.135502000	-0.984028000	-1.525422000
9	8.643709000	0.285851000	0.308787000
1	2.580392000	-0.986142000	-1.309136000
1	1.006628000	1.649314000	2.566200000
1	3.437345000	1.447265000	2.122687000
1	-5.001049000	-2.422656000	-2.872044000
1	-7.149062000	-1.741923000	-3.836662000
1	-8.945625000	-0.805576000	-2.391832000
1	-8.557130000	-0.563258000	0.056570000
1	-6.405270000	-1.233457000	1.046029000
1	6.113293000	-3.743481000	2.393427000
1	5.945505000	3.587119000	-2.668739000
1	3.180428000	-1.554495000	2.697153000
1	2.826996000	-2.564411000	1.303339000
1	3.612276000	-3.273898000	2.725313000
1	3.447144000	3.640295000	-2.075596000
1	2.723147000	2.032987000	-1.891407000
1	3.066978000	3.001786000	-0.466360000
1	9.141574000	2.212333000	-1.404665000
1	8.804427000	1.184728000	-2.792991000
1	8.529542000	2.940707000	-2.909335000

1	8.676082000	-3.668330000	1.638800000
1	8.893159000	-2.930953000	0.032123000
1	9.238375000	-1.987120000	1.476745000
34	-3.765063000	1.269280000	-0.271787000
6	-3.444774000	2.958198000	0.630899000
6	-4.594057000	3.665720000	1.002572000
6	-2.167363000	3.463939000	0.891951000
6	-4.458880000	4.901150000	1.640664000
1	-5.581247000	3.265943000	0.792642000
6	-2.048786000	4.704564000	1.522016000
1	-1.286248000	2.889557000	0.638434000
6	-3.188679000	5.421866000	1.896504000
1	-5.347479000	5.454402000	1.929662000
1	-1.060355000	5.105767000	1.726287000
1	-3.085999000	6.384470000	2.388850000
26	-2.282208000	-0.525578000	0.694223000
8	-1.383690000	-2.011770000	1.197484000
1	-2.081038000	-1.968890000	2.922866000
1	-0.446909000	-1.808114000	1.375761000
8	-3.026553000	-0.163828000	2.221288000
1	-3.929056000	-0.500643000	2.371323000
8	-2.671656000	-1.564591000	3.604008000
1	-2.098317000	-0.958723000	4.102133000
6	-0.055573000	-1.083929000	-1.140692000
1	0.369581000	-1.078394000	-2.151714000
1	-0.121422000	-2.127275000	-0.825390000
6	-2.701226000	-2.782145000	-1.468794000
1	-3.216426000	-3.430936000	-2.177932000
1	-1.893096000	-3.353416000	-1.012847000
6	-2.230944000	-1.503849000	-2.145796000
1	-3.094152000	-0.967213000	-2.540260000
1	-1.593561000	-1.758520000	-3.002374000
6	-1.402046000	0.790252000	-1.870354000
1	-0.981385000	0.689724000	-2.879337000
1	-0.705141000	1.378792000	-1.276820000
6	-2.743314000	1.502063000	-1.952381000
1	-2.604166000	2.573569000	-2.101401000
1	-3.392368000	1.128690000	-2.745864000

Tables S4. Coordinates of optimized complex 4.

6	3.062532000	0.199279000	0.292456000
6	2.157638000	-0.390273000	-0.595553000
6	0.774666000	-0.251951000	-0.435180000
6	0.294692000	0.514344000	0.646146000
6	1.197695000	1.116757000	1.539885000
6	2.566742000	0.956020000	1.365728000
8	-1.020561000	0.778169000	0.776970000
7	-1.562131000	-0.497585000	-1.458959000
34	-3.731339000	-2.358144000	-0.104591000
6	-5.453747000	-1.751927000	-0.763231000
6	-5.888023000	-1.936962000	-2.079478000
6	-7.183034000	-1.545918000	-2.430154000
6	-8.033946000	-0.980983000	-1.478122000
6	-7.592255000	-0.804544000	-0.163687000
6	-6.302006000	-1.188922000	0.201078000
6	4.533489000	0.025181000	0.092670000
6	5.235223000	0.933636000	-0.717475000
7	6.614361000	0.781603000	-0.922965000
7	6.572652000	-1.231246000	0.537977000
6	5.193670000	-1.047011000	0.716108000
6	6.956034000	-2.321462000	1.237650000
6	5.832164000	-2.869027000	1.886265000
6	4.719150000	-2.092766000	1.576535000
6	4.809228000	2.095392000	-1.444132000
6	5.949471000	2.600702000	-2.061943000
6	7.042902000	1.778100000	-1.728176000
6	3.331257000	-2.360884000	2.080688000
6	3.441426000	2.701268000	-1.561762000
6	8.467851000	1.923998000	-2.154460000
6	8.367803000	-2.810541000	1.273862000
5	7.499132000	-0.348372000	-0.336891000
9	8.056860000	-1.112041000	-1.372993000
9	8.526901000	0.196881000	0.443889000
1	2.536014000	-0.972464000	-1.432051000
1	0.802222000	1.712141000	2.356311000
1	3.256050000	1.423571000	2.062539000
1	-5.250964000	-2.388106000	-2.831305000
1	-7.522272000	-1.689195000	-3.451611000
1	-9.038788000	-0.680067000	-1.758565000
1	-8.249653000	-0.366208000	0.581048000
1	-5.957048000	-1.041454000	1.220363000
1	5.844676000	-3.748056000	2.517827000
1	6.000602000	3.477626000	-2.694493000
1	2.940433000	-1.527954000	2.674853000
1	2.621595000	-2.527140000	1.262905000
1	3.335270000	-3.254439000	2.712101000
1	3.490563000	3.604536000	-2.177327000
1	2.726025000	2.014000000	-2.026392000
1	3.027140000	2.977101000	-0.586347000
1	9.119672000	2.076960000	-1.287218000
1	8.816925000	1.016530000	-2.658663000
1	8.576956000	2.772912000	-2.833354000

1	8.438668000	-3.724385000	1.868285000
1	8.734805000	-3.013560000	0.262119000
1	9.030779000	-2.053327000	1.706823000
34	-3.810301000	1.435412000	-0.212582000
6	-3.203785000	3.008117000	0.746227000
6	-3.990210000	3.376569000	1.844257000
6	-2.073841000	3.752334000	0.396812000
6	-3.634933000	4.495126000	2.600912000
1	-4.876278000	2.805344000	2.105754000
6	-1.738261000	4.879129000	1.151999000
1	-1.452814000	3.475419000	-0.446795000
6	-2.511722000	5.249822000	2.254468000
1	-4.245098000	4.779391000	3.453243000
1	-0.863867000	5.461803000	0.876855000
1	-2.241945000	6.124617000	2.838709000
26	-2.322593000	-0.424762000	0.601763000
8	-1.276784000	-1.942705000	1.124061000
1	-1.884125000	-2.430217000	2.525333000
1	-0.354541000	-1.688921000	1.291109000
8	-3.253271000	-0.469165000	2.031983000
1	-3.023136000	-1.223611000	2.694121000
8	-2.577135000	-2.364036000	3.265643000
1	-2.089193000	-2.237210000	4.096841000
6	-0.143065000	-0.983174000	-1.391895000
1	0.279781000	-0.934945000	-2.403120000
1	-0.184398000	-2.033859000	-1.099402000
6	-2.723589000	-2.714000000	-1.749992000
1	-3.331651000	-3.319282000	-2.423929000
1	-1.885891000	-3.323980000	-1.410051000
6	-2.302391000	-1.407283000	-2.396258000
1	-3.185182000	-0.881110000	-2.759478000
1	-1.670898000	-1.613997000	-3.269936000
6	-1.572108000	0.890963000	-2.040245000
1	-1.257361000	0.831755000	-3.090888000
1	-0.822756000	1.470275000	-1.505679000
6	-2.924334000	1.595969000	-1.974809000
1	-2.809758000	2.657189000	-2.202925000
1	-3.653331000	1.189357000	-2.677959000

Tables S5. Coordinates of optimized complex 5.

6	3.063935000	0.196638000	0.287923000
6	2.158125000	-0.383529000	-0.603851000
6	0.773752000	-0.231541000	-0.453539000
6	0.288470000	0.538122000	0.626043000
6	1.198487000	1.118949000	1.530774000
6	2.566790000	0.951351000	1.362717000
8	-1.020249000	0.817846000	0.758270000
7	-1.555615000	-0.477938000	-1.497965000
34	-3.715738000	-2.352424000	-0.127096000
6	-5.455232000	-1.756198000	-0.752091000
6	-5.898292000	-1.923734000	-2.066878000
6	-7.202293000	-1.543757000	-2.396975000
6	-8.050853000	-1.008755000	-1.425972000
6	-7.598124000	-0.850555000	-0.113029000
6	-6.298916000	-1.223420000	0.232119000
6	4.535731000	0.025820000	0.089442000
6	5.233359000	0.936687000	-0.722140000
7	6.614085000	0.793784000	-0.924262000
7	6.584676000	-1.211099000	0.547113000
6	5.203026000	-1.039275000	0.717819000
6	6.975057000	-2.295480000	1.251966000
6	5.853197000	-2.852368000	1.895921000
6	4.734430000	-2.087987000	1.577579000
6	4.801228000	2.093509000	-1.453246000
6	5.939362000	2.604586000	-2.070337000
6	7.037635000	1.790750000	-1.731543000
6	3.344986000	-2.373778000	2.066685000
6	3.430076000	2.690648000	-1.576495000
6	8.462700000	1.945777000	-2.154340000
6	8.391271000	-2.770827000	1.296927000
5	7.506773000	-0.324141000	-0.327860000
9	8.076974000	-1.088218000	-1.356958000
9	8.525641000	0.235270000	0.454773000
1	2.535561000	-0.965676000	-1.441018000
1	0.803751000	1.712148000	2.349370000
1	3.255665000	1.410928000	2.065425000
1	-5.262208000	-2.351455000	-2.833085000
1	-7.549694000	-1.672123000	-3.417651000
1	-9.062619000	-0.716815000	-1.690510000
1	-8.253718000	-0.435299000	0.646384000
1	-5.944167000	-1.089684000	1.249940000
1	5.870629000	-3.730018000	2.529289000
1	5.985789000	3.479868000	-2.705529000
1	2.927766000	-1.539436000	2.640198000
1	2.654220000	-2.568384000	1.238913000
1	3.355907000	-3.257246000	2.712040000
1	3.477224000	3.597822000	-2.186491000
1	2.722785000	2.001210000	-2.050269000
1	3.006954000	2.957429000	-0.602441000
1	9.110605000	2.109034000	-1.286020000
1	8.820749000	1.038370000	-2.652268000
1	8.566995000	2.791749000	-2.837659000

1	8.468637000	-3.679251000	1.898804000
1	8.763654000	-2.978477000	0.288069000
1	9.045587000	-2.003953000	1.725963000
34	-3.809607000	1.375438000	-0.207686000
6	-3.255085000	2.958437000	0.766295000
6	-4.070948000	3.307229000	1.848812000
6	-2.138046000	3.729198000	0.433673000
6	-3.757000000	4.435925000	2.609030000
1	-4.946301000	2.713732000	2.095753000
6	-1.844516000	4.864921000	1.192053000
1	-1.495269000	3.464341000	-0.396991000
6	-2.647099000	5.217310000	2.279984000
1	-4.388640000	4.706636000	3.449918000
1	-0.980434000	5.469204000	0.931697000
1	-2.409747000	6.099687000	2.866862000
26	-2.341523000	-0.398620000	0.574072000
8	-1.163255000	-1.949992000	1.187724000
1	-1.505811000	-2.252156000	2.117134000
1	-0.227609000	-1.705448000	1.302597000
8	-3.224290000	-0.494755000	1.984586000
1	-2.844300000	-1.486621000	2.896622000
8	-2.393121000	-2.323309000	3.369388000
1	-1.889495000	-1.966816000	4.119939000
6	-0.133577000	-0.946762000	-1.436506000
1	0.297552000	-0.866940000	-2.442999000
1	-0.159095000	-2.011285000	-1.189180000
6	-2.718650000	-2.693537000	-1.786887000
1	-3.332380000	-3.296401000	-2.458028000
1	-1.880648000	-3.310543000	-1.457551000
6	-2.292644000	-1.388246000	-2.435557000
1	-3.173918000	-0.862667000	-2.803222000
1	-1.660658000	-1.600364000	-3.308048000
6	-1.582867000	0.914594000	-2.064109000
1	-1.277356000	0.874859000	-3.118477000
1	-0.837523000	1.496046000	-1.526395000
6	-2.943686000	1.599700000	-1.976158000
1	-2.848786000	2.668860000	-2.173303000
1	-3.673163000	1.200082000	-2.682702000

Tables S6. Coordinates of optimized complex 6.

6	3.061852000	0.201472000	0.282875000
6	2.153346000	-0.367054000	-0.613299000
6	0.768887000	-0.214960000	-0.460189000
6	0.283580000	0.542931000	0.629149000
6	1.198938000	1.111825000	1.537731000
6	2.566723000	0.945565000	1.366076000
8	-1.022275000	0.820922000	0.773905000
7	-1.557906000	-0.454374000	-1.511165000
34	-3.714277000	-2.345238000	-0.146942000
6	-5.456495000	-1.751542000	-0.770139000
6	-5.906704000	-1.938253000	-2.079689000
6	-7.212030000	-1.561620000	-2.408905000
6	-8.055323000	-1.011957000	-1.441529000
6	-7.595416000	-0.834629000	-0.133586000
6	-6.294358000	-1.203045000	0.210057000
6	4.533149000	0.029142000	0.082704000
6	5.233812000	0.946721000	-0.718674000
7	6.614606000	0.803517000	-0.920359000
7	6.579936000	-1.215256000	0.531578000
6	5.198082000	-1.043428000	0.701104000
6	6.967755000	-2.306561000	1.227160000
6	5.843976000	-2.868352000	1.863300000
6	4.726618000	-2.099833000	1.549691000
6	4.804619000	2.111261000	-1.439031000
6	5.944403000	2.626382000	-2.049817000
6	7.040865000	1.807534000	-1.717433000
6	3.335616000	-2.390177000	2.031634000
6	3.434498000	2.711601000	-1.558057000
6	8.466756000	1.964034000	-2.136949000
6	8.383530000	-2.783398000	1.271437000
5	7.504734000	-0.321197000	-0.333134000
9	8.075889000	-1.076100000	-1.368545000
9	8.523077000	0.229316000	0.456602000
1	2.528631000	-0.940924000	-1.457265000
1	0.806310000	1.695772000	2.364103000
1	3.257034000	1.396492000	2.073100000
1	-5.273990000	-2.376932000	-2.842578000
1	-7.564628000	-1.704198000	-3.425955000
1	-9.068273000	-0.723144000	-1.705077000
1	-8.246555000	-0.407163000	0.622942000
1	-5.932625000	-1.053182000	1.223232000
1	5.859115000	-3.752000000	2.488349000
1	5.993097000	3.507598000	-2.676589000
1	2.913610000	-1.558889000	2.605950000
1	2.649506000	-2.583390000	1.199580000
1	3.345426000	-3.276195000	2.673542000
1	3.483465000	3.624274000	-2.159688000
1	2.726606000	2.027404000	-2.038449000
1	3.010926000	2.969860000	-0.581901000
1	9.114184000	2.115167000	-1.266091000
1	8.823027000	1.061736000	-2.645366000
1	8.573914000	2.817834000	-2.810020000

1	8.458245000	-3.698462000	1.863536000
1	8.759221000	-2.980176000	0.261640000
1	9.036969000	-2.021853000	1.711203000
34	-3.814044000	1.378152000	-0.196912000
6	-3.262955000	2.956104000	0.787866000
6	-4.081333000	3.298804000	1.870395000
6	-2.145826000	3.729637000	0.462118000
6	-3.770130000	4.423800000	2.637309000
1	-4.956833000	2.703381000	2.112224000
6	-1.854908000	4.861703000	1.226923000
1	-1.500717000	3.469104000	-0.368044000
6	-2.660201000	5.207866000	2.314872000
1	-4.403925000	4.689583000	3.478174000
1	-0.990643000	5.467968000	0.971747000
1	-2.424903000	6.087388000	2.906871000
26	-2.353182000	-0.396043000	0.571608000
8	-1.154142000	-1.957115000	1.173788000
1	-1.457160000	-2.282534000	2.085079000
1	-0.216603000	-1.711406000	1.271466000
8	-3.220724000	-0.506620000	1.974028000
1	-2.784150000	-1.718400000	3.160371000
8	-2.256083000	-2.499000000	3.485417000
1	-1.707719000	-2.147801000	4.207095000
6	-0.136245000	-0.920105000	-1.453447000
1	0.297849000	-0.828857000	-2.458094000
1	-0.159432000	-1.987898000	-1.219432000
6	-2.716530000	-2.669468000	-1.811311000
1	-3.327759000	-3.270495000	-2.486290000
1	-1.875823000	-3.285414000	-1.486692000
6	-2.295434000	-1.358454000	-2.452613000
1	-3.180427000	-0.833427000	-2.812511000
1	-1.667274000	-1.563674000	-3.329927000
6	-1.588954000	0.942860000	-2.060955000
1	-1.282936000	0.918600000	-3.115924000
1	-0.845994000	1.520130000	-1.515202000
6	-2.951822000	1.622761000	-1.964878000
1	-2.861360000	2.694239000	-2.151329000
1	-3.680823000	1.227267000	-2.674275000

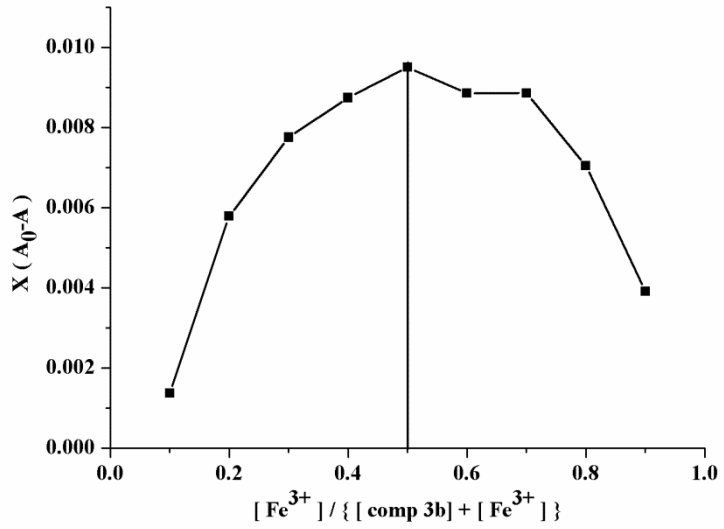
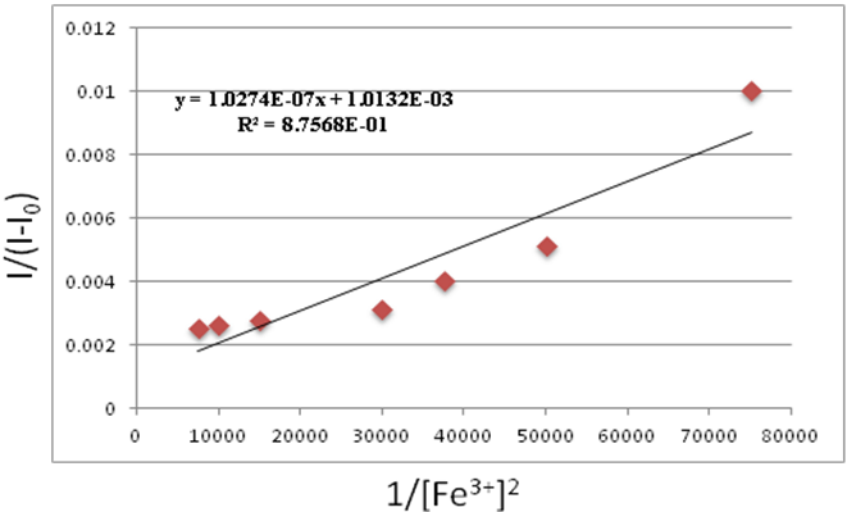


Figure S16: Job Plot for probe with Fe^{3+}.



$$\frac{I}{I_0} = \frac{1 + aK_a[analyte]^n}{1 + K_a[analyte]^n} \quad (2)$$

$$\frac{1}{(I - I_0)} = \frac{1}{(a - 1)} + \frac{1}{K_a(a - 1)[analyte]^n} \quad (3)$$

K_a = y-intercept / slope, (in plotting $1/[I-I_0]$ vs. $1/[analyte]^n$)

By using this equation the Kd value found to be **1.014×10^{-4}**.

Figure S17: From plotting data (y-intercept and slope), binding constants were calculated by following equation 2. K_a: binding constant, I_0 : Fluorescence intensity in the absence of analyte, I: Fluorescence intensity in the presence of analyte, a: the ratio of the fluorescence intensities of the complexed and uncomplexed chromophore, n: binding ratio of the analyte to the probe.

END