Supporting Information

Twisting (conformational changes) based selective 2D chalcogeno podand fluorescent probes for Cr(III) and Fe(II)

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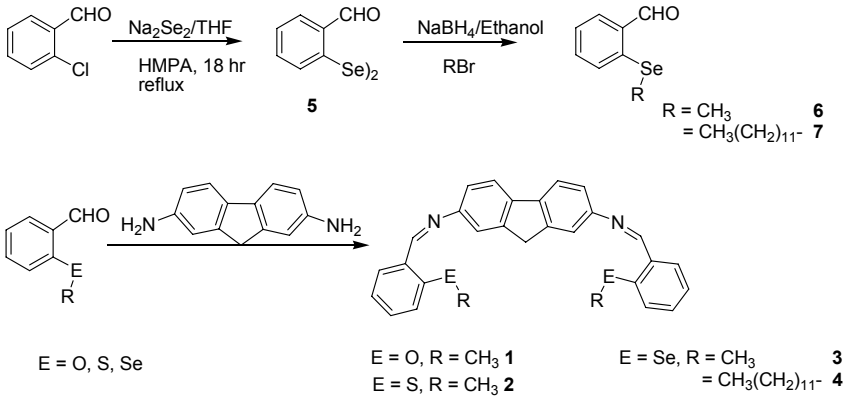
Table of Contents

Sr. No.	Title	Page No.
1	Experimental Section	S4
2	**Figure S1.** ^{1}H NMR spectrum of podand **1**.	S7
3	**Figure S2.** ^{13}C NMR spectrum of podand **1**.	S8
4	**Figure S3.** ^{1}H NMR spectrum of podand **2**.	S9
5	**Figure S4.** ^{13}C NMR spectrum of podand **2**.	S10
6	**Figure S5.** ^{1}H NMR spectrum of podand **3**.	S11
7	**Figure S6.** ^{13}C NMR spectrum of podand **3**.	S12
8	**Figure S7.** ^{1}H NMR spectrum of podand **4**.	S13
9	**Figure S8.** ^{13}C NMR spectrum of podand **4**.	S14
10	**Figure S9.** HOMO and LUMO of podand **1** and **3** calculated at B3LYP/6-31G(d).	S15
11	**Figure S10.** Fluorescence response following excitation at 270 nm from podand **1** solution upon addition of perchlorate salts of Cr(III) in THF.	S15
12	**Figure S11.** Change in absorption spectra upon addition of Fe(II)-perchlorate salt solution in THF to the solution of podand **1** (33 μM).	S16
13	**Figure S12.** Fluorescence response following excitation at 270 nm from podand **1** solution upon addition of perchlorate salts of Fe(II) in THF.	S16
14	**Figure S13.** Change in absorption spectra upon addition of Cu(II)-perchlorate salt solution in THF to the solution of podand **1** (33 μM).	S17
15	**Figure S14.** Fluorescence response following excitation at 270 nm from podand **1** solution upon addition of perchlorate salts of Cu(II) in THF.	S17
16	**Figure S15.** Change in absorption spectra upon addition of Cr(III)-perchlorate salt solution in THF to the solution of podand **2** (33 μM).	S18
17	**Figure S16.** Change in absorption spectra upon addition of Cr(III)-perchlorate salt solution in THF to the solution of podand **3** (33 μM).	S18
18	**Figure S17.** Fluorescence response following excitation at 270 nm from podand **3** solution upon addition of perchlorate salts of Cr(III) in THF.	S19

19	**Figure S18.** Change in absorption spectra upon addition of Fe(II)-perchlorate salt solution in THF to the solution of podand **3** (33 μM).	S19
20	**Figure S19.** Fluorescence response following excitation at 270 nm from podand **3** solution upon addition of perchlorate salts of Fe(II) in THF.	S20
21	**Figure S20.** Change in absorption spectra upon addition of Cr(III)-perchlorate salt solution in THF to the solution of podand **4** (33 μM).	S20
22	**Figure S21.** Fluorescence response following excitation at 270 nm from podand **4** solution upon addition of perchlorate salts of Cr(III) in THF.	S21
23	**Figure S22.** Change in absorption spectra upon addition of Fe(II)-perchlorate salt solution in THF to the solution of podand **4** (33 μM).	S21
24	**Figure S23.** Fluorescence response following excitation at 270 nm from podand **4** solution upon addition of perchlorate salts of Cr(III) in THF.	S22
25	**Figure S24.** The optimized structures (at B3LYP/6-31G(d)) of (a) podand **2** (optimized without any constrain, dihedral angle between atoms 14, 15, 22 and 23 (or 4, 3, 25 and 26) is 34° and (b) twisted podand **2** (dihedral angle between atoms 14, 15, 22 and 23 (or 4, 3, 25 and 26) is freezed at 90°).	S22
26	**FigureS25.** HOMO and LUMO+2 orbitals of twisted podand **2** at B3LYP/6-31G(d).	S23
27	**Figure S26.** The absorption energy vs oscillator strength (*f*) calculated using TD-DFT at B3LYP/6-31G(d) for podand **2** and twisted podand **2** (as shown in Figure S26).	S23
28	**Figure S27.** The optimized structure (at B3LYP/6-31G(d)/sdd) of quintet Fe complex **5**, where only one substitution at 2-position of fluorene was considered in the form of (*o*-methylthio)phenylazomethine.	S24
29	**Figure S28.** The absorption energy vs oscillator strength (*f*) calculated using TD-DFT at B3LYP/6-31G(d)/sdd for Fe complx **5**.	S24
30	**Figure S29.** Frontier molecular orbitals of the Fe complx **5** calculated at B3LYP/6-31G(d)/sdd.	S25-S27
31	**Table S1.** Absorption and emission data for the podands **1**-**4**.	S28
32	**Table S2.** TDDFT calculated electronic excitations of **5** (at B3LYP/6-31G(d)/sdd).	S29
33	**Table S3.** Calculated absolute energies	S30
34	Coordinates of the optimized geometries.	S30-S36

Experimental Section

General. All the reagents were purchased from Aldrich / Merck and used without further purification. AR grade THF was passed through alumina to remove hydrogen peroxide and partial drying and kept over the molecular sieves. AR grade acetonitrile was distilled from P_2O_5 and kept over molecular sieves. UV-vis spectra were recorded on a Hitachi U4100 spectrophotometer, with a quartz cuvette (path length, 1 cm). The fluorescence spectra were recorded with a Fluoromax-3 spectrofluorimeter. ^1H and ^{13}C NMR spectra were recorded on a JEOL-FT NMR-AL 400 MHz spectrophotometer using $CDCl_3$/DMSO-d_6 as solvent and tetramethylsilane $SiMe_4$ as internal standards. UV-vis studies were performed in THF AR grade. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s=singlet, d=doublet, br=broad singlet, m= multiplet), coupling constants J (Hz), integration, and interpretation. Silica gel 60 (60-120 mesh) was used for column chromatography. Solutions of compounds **1**, **2**, **3** and **4** and perchlorate salts were prepared in THF.



Scheme

Syntheses

Comound **5** was synthesized using the literature procedure.[1]

Synthesis of compound 6: Sodium borohydride (0.1 gm, 2.7 mmole) was added portion-wise to bis (*o*-formyl)pheny diselenide (0.5 gm, 1.3 mmole) in MeOH:THF mixture (25% THF in MeOH) at 0 deg C under inert atmosphere. Immediately the yellow color of the reaction mixture changed to dark orange-red color indicating the formation of selenol. To this reaction mixture

methyl iodide (0.4 gm, 2.6 mmole) was added. After 6 hour stirring at room temperature, the solvent was evaporated and the residue washed with saturated brine solution and was extracted with DCM. The compound was purified by column chromatography using 4% ethyl acetate in hexane. Yield: 0.35 gm, 74%. Oily liquid. ^{1}HNMR(500 MHz): δ 2.29(m, 3H, CH_3), 7.81-7.33 (m, 4H, ArH), 10.14 (s, 1H, CHO). ^{13}C NMR: 5.79, 124.81, 127.84, 133.77, 134.22, 135.47, 138.67. ^{77}Se NMR: 258 (s). IR ν_{max} ($CHCl_3$, cm^{-1}): 1700 (C=O).

Compounds **7** was analogously prepared starting from the appropriate alkyl bromide.

Compound 7: Yield: 0.7 gm, 68%.^{1}HNMR (500 MHz): δ 0.9(t, 3H, CH_3), 1.25(m, 14H), 1.42(m,2H), 1.74(m, 2H), 2.7(m, 2H), 2.9 (t, 2H), 7.28-7.83 (m, 4H, ArH), 10.23 (s, 1H, CHO). ^{13}C NMR: 14.08, 22.64, 25.82, 26.07, 26.33, 28.98, 29.1, 29.3, 29.45, 29.55, 29.58, 30.05, 31.87, 125.42, 130, 133.65, 133.98, 134.94, 137.8, 192.53. ^{77}Se NMR: 309 (s). IR ν_{max} ($CHCl_3$, cm^{-1}): 1694 (C=O).

Compound 1: A solution of 2,7-diamminofluorene (0.2 g, 1 mmol) in acetonitrile (10 ml) was added to a stirred solution of 2-methoxybenzaldehyde (0.27 g, 2 mmol) in acetonitrile (10 ml) over a period of 1 h. The mixture was stirred overnight and the precipitated dark yellow powder was filtered off, washed with acetonitrile. Yield: 72% Mp: 204.3º C ^{1}H NMR (400 MHz): 3.92 (s, 6H), 3.96 (s, 2H), 6.96-8.2 (m, 12H, Ar-H), 9.02 (s, 2H) ^{13}C NMR: 36.95, 55.54, 111.07, 117.67, 120.03, 120.53, 120.88, 124.83, 127.48, 132.57, 139.42, 144.48, 151.3, 155.54, 159.44. Anal. Calcd for $C_{29}H_{24}N_2O_2$ (432.51): C, 80.53; H, 5.59; N, 6.48 Found C, 79.88; H, 5.03; N, 6.48.

Compounds **2**, **3** and **4** were analogously prepared starting from the appropriate unsymmetrical monosulfide and monoselenides.

Compound 2: Orange crystalline solid. Yield: 72%, Mp: 107.4º C ^{1}H NMR (400 MHz): 2.52 (s, 6H), 3.98 (s, 2H), 7.26-8.09 (m, 12H, Ar-H), 9.04 (s, 2H) ^{13}C NMR: 16.92, 36.99, 117.73, 120.21, 120.57, 125.56, 127.34, 128.7, 131.24, 134.31, 139.7, 140.3, 144.6, 150.69, 157.3. Anal. Calcd for $C_{29}H_{24}N_2S_2$ (464.64): C, 74.96; H, 5.21; N, 6.03 Found C, 74.73; H, 4.64; N, 6.54.

Compound 3: Yellow crystalline solid. Yield: 80%, Mp: 190º C. ^{1}HNMR(500 MHz): 2.29 (s, 6H) 3.98 (s, 2H), 7.26-7.80 (m, 12H, Ar-H), 8.85 (s, 2H) ^{13}C NMR: 16.52, 36, 117.75, 120.25, 120.34, 126, 129.85, 130.25, 131.84, 134.31, 139.7, 141, 144.6, 150.59, 157.3 ^{77}Se NMR: 268 Anal. Calcd for $C_{29}H_{24}N_2Se_2$ (558.43): C, 62.37; H, 4.33; N, 5.02 Found C, 61.92; H, 4.3; N, 5.02

Compound 4: Orange amorphous solid. Yield: 70% Mp: 98º C. ^{1}HNMR(500 MHz): δ 0.8 (t, 6H,-CH_3), 1.24 (m, 28 H), 1.42 (m, 4H), 1.70 (m, 4H), 2.9 (m, 4H), 3.8 (m, 4H) 4.43 (s, 1H), 7.3-8.0 (m, 12 H, Ar-H) 9.0 (s, 2H, N=CH), ^{13}C NMR: 14.12, 22.67, 28.07, 29.12, 29.32, 29.5, 29.52, 29.55, 29.57, 29.60, 30.02, 31.85, 36.96, 117.79, 120.18, 120.46, 126.50, 130.1, 130.86, 132.28, 134.77, 136.4, 139.69, 144.56, 150.19,159.52. ^{77}Se NMR: 268 Anal. Calcd for $C_{51}H_{68}N_2Se_2$ (867.02): C, 70.65; H, 7.91; N, 3.23 Found C, 69.85; H, 7.11; N, 3.03

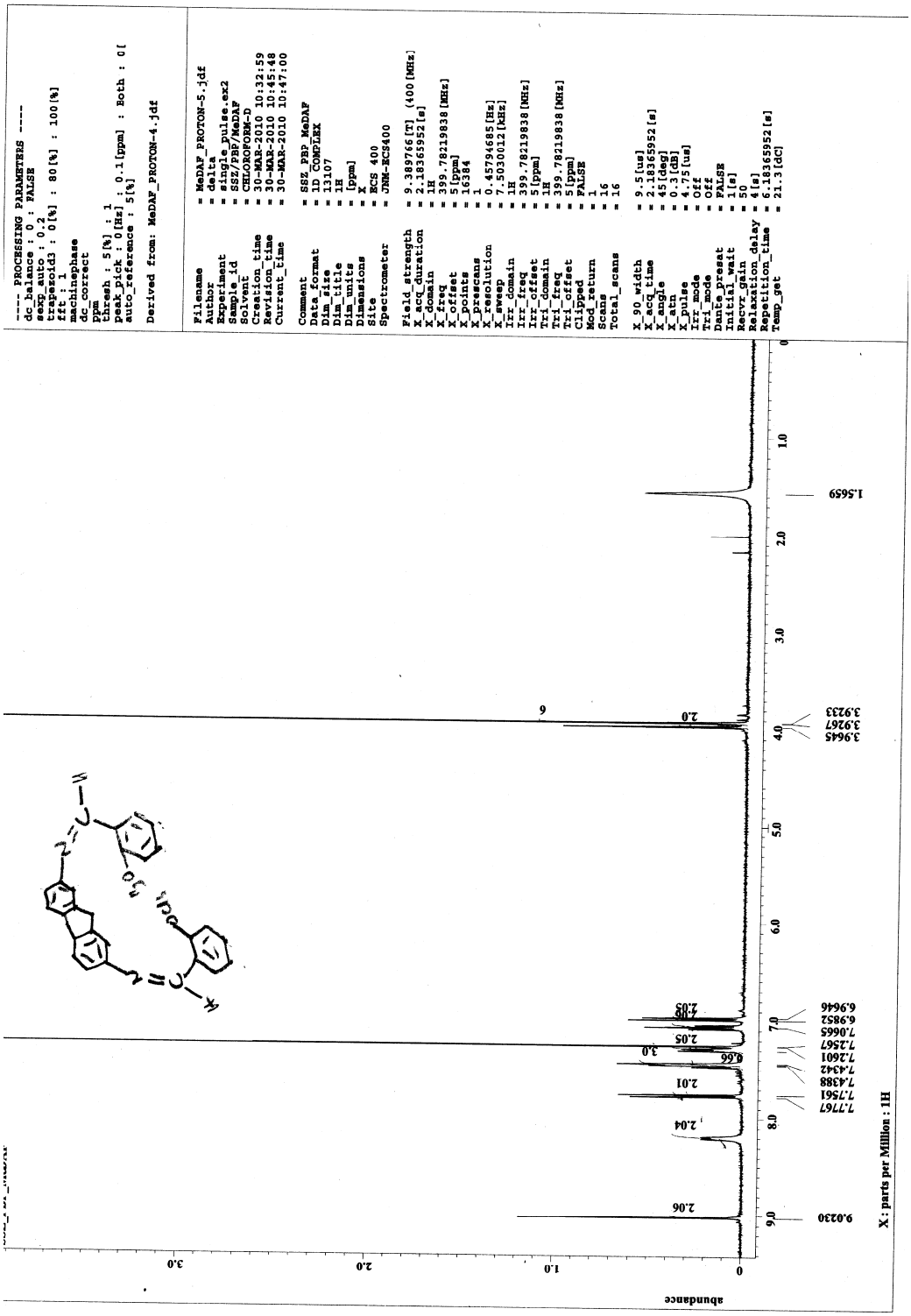


Figure S1. ^{1}H NMR spectrum of podand **1**.

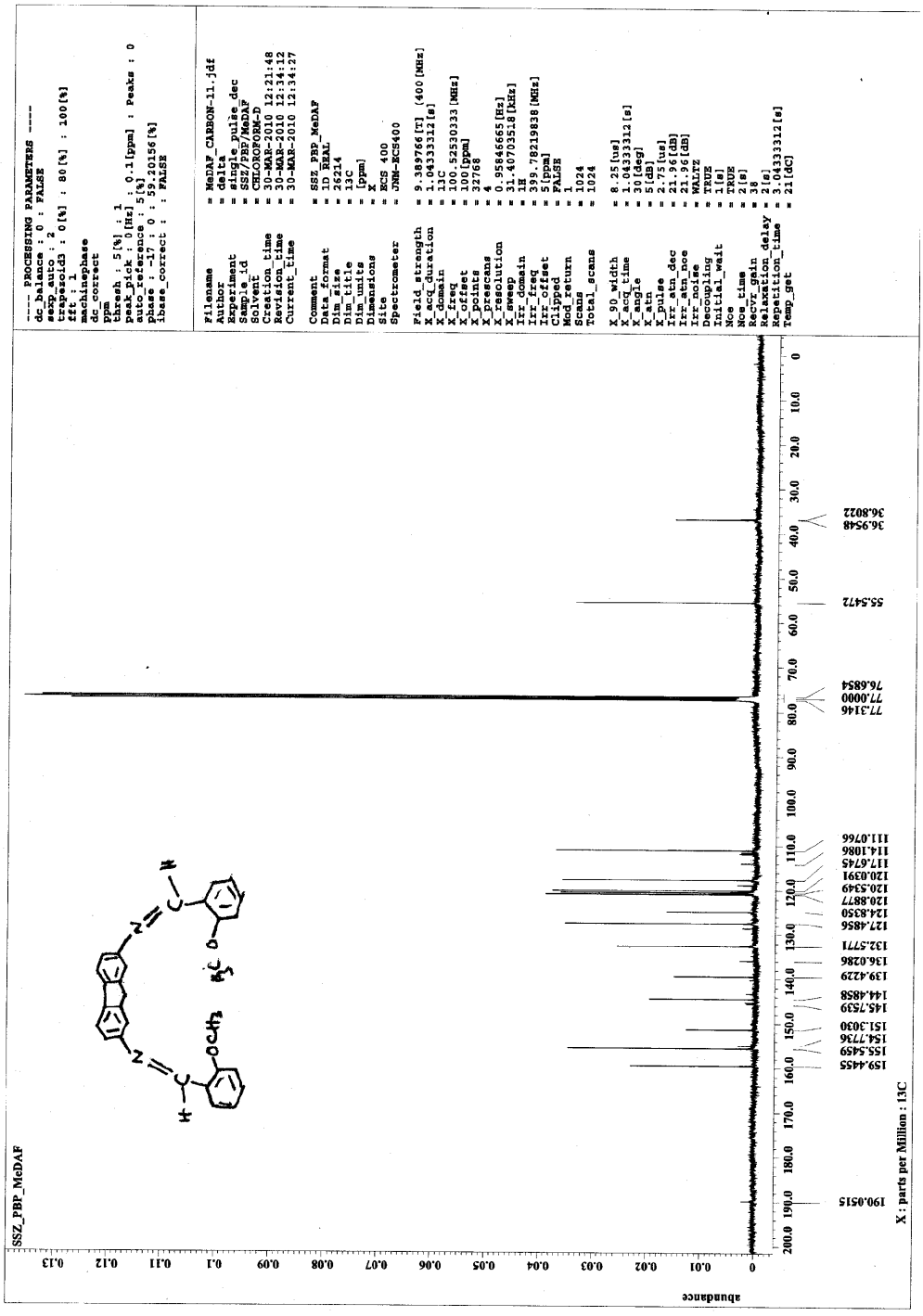


Figure S2. ^{13}C NMR spectrum of podand **1**.

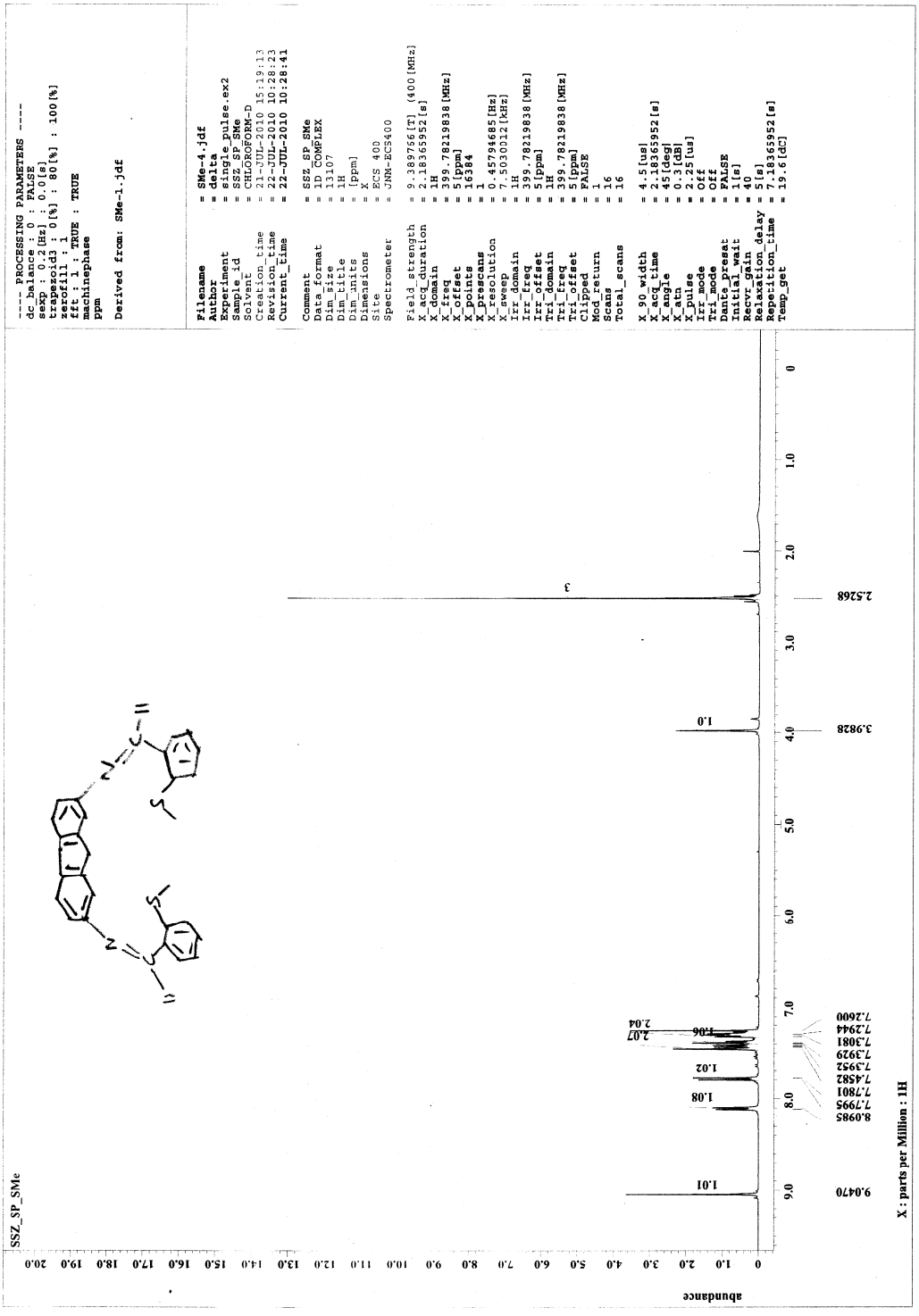


Figure S3. ^{1}H NMR spectrum of podand **2**.

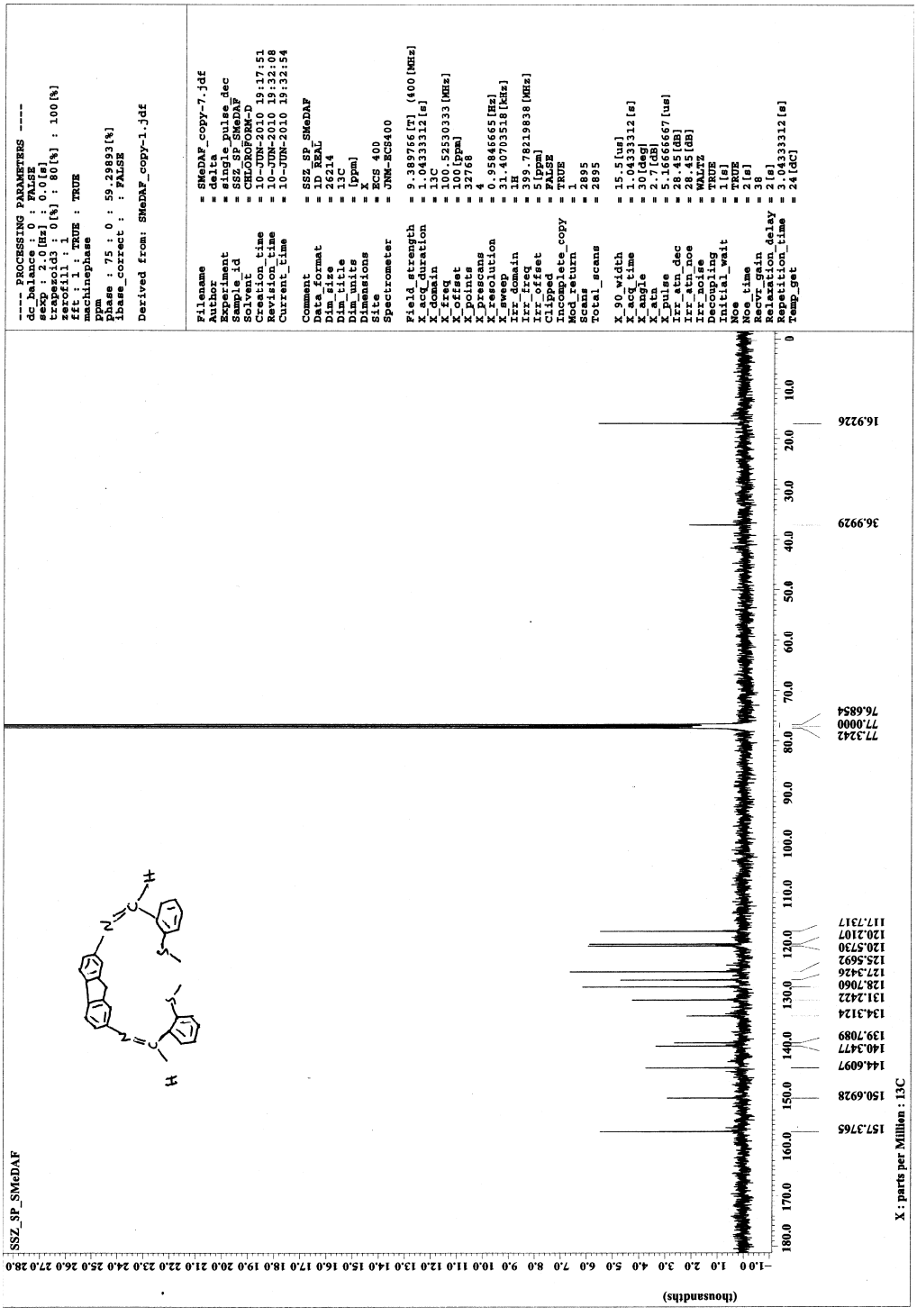


Figure S4. ^{13}C NMR spectrum of podand **2**.

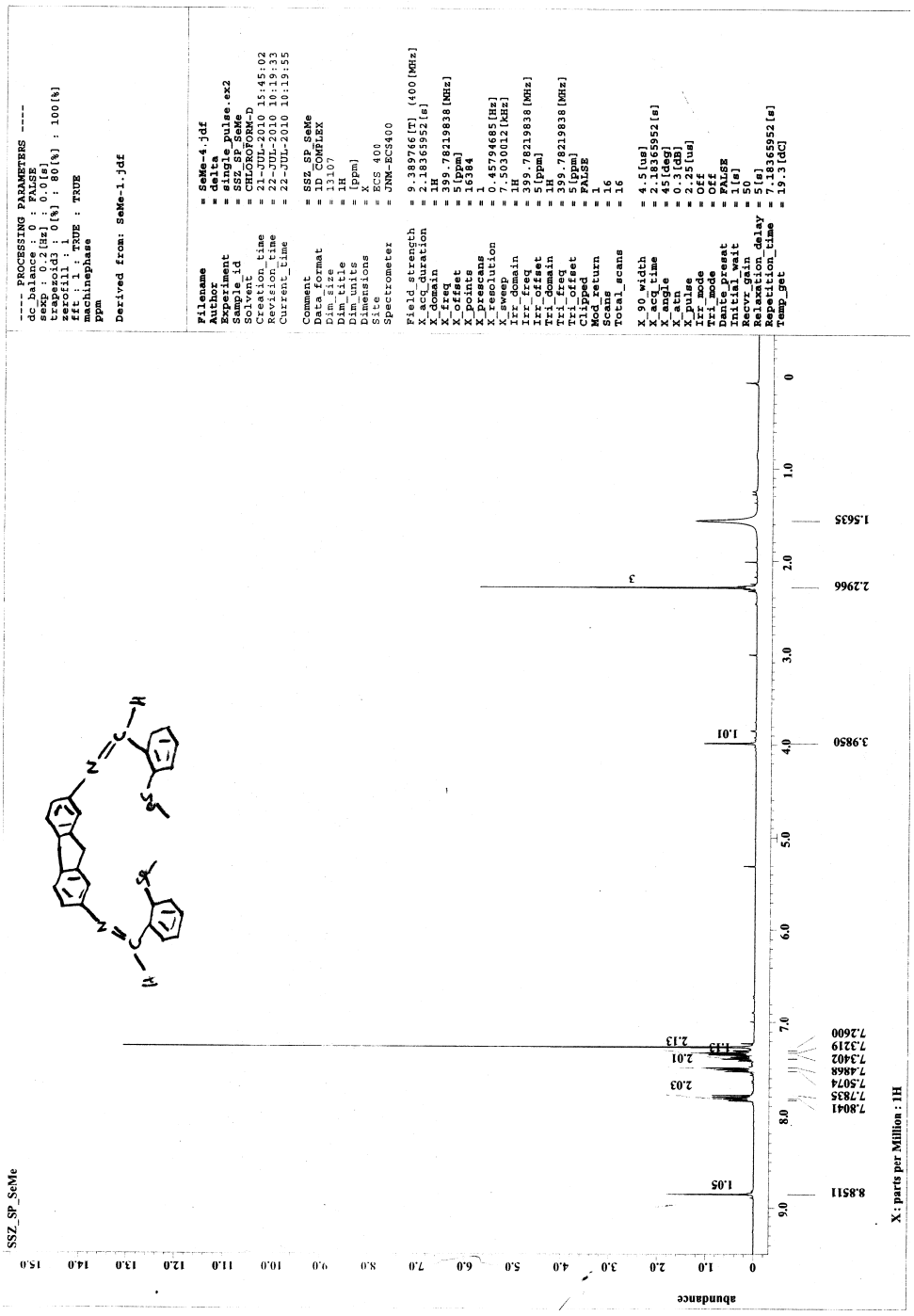


Figure S5. ^{1}H NMR spectrum of podand **3**.

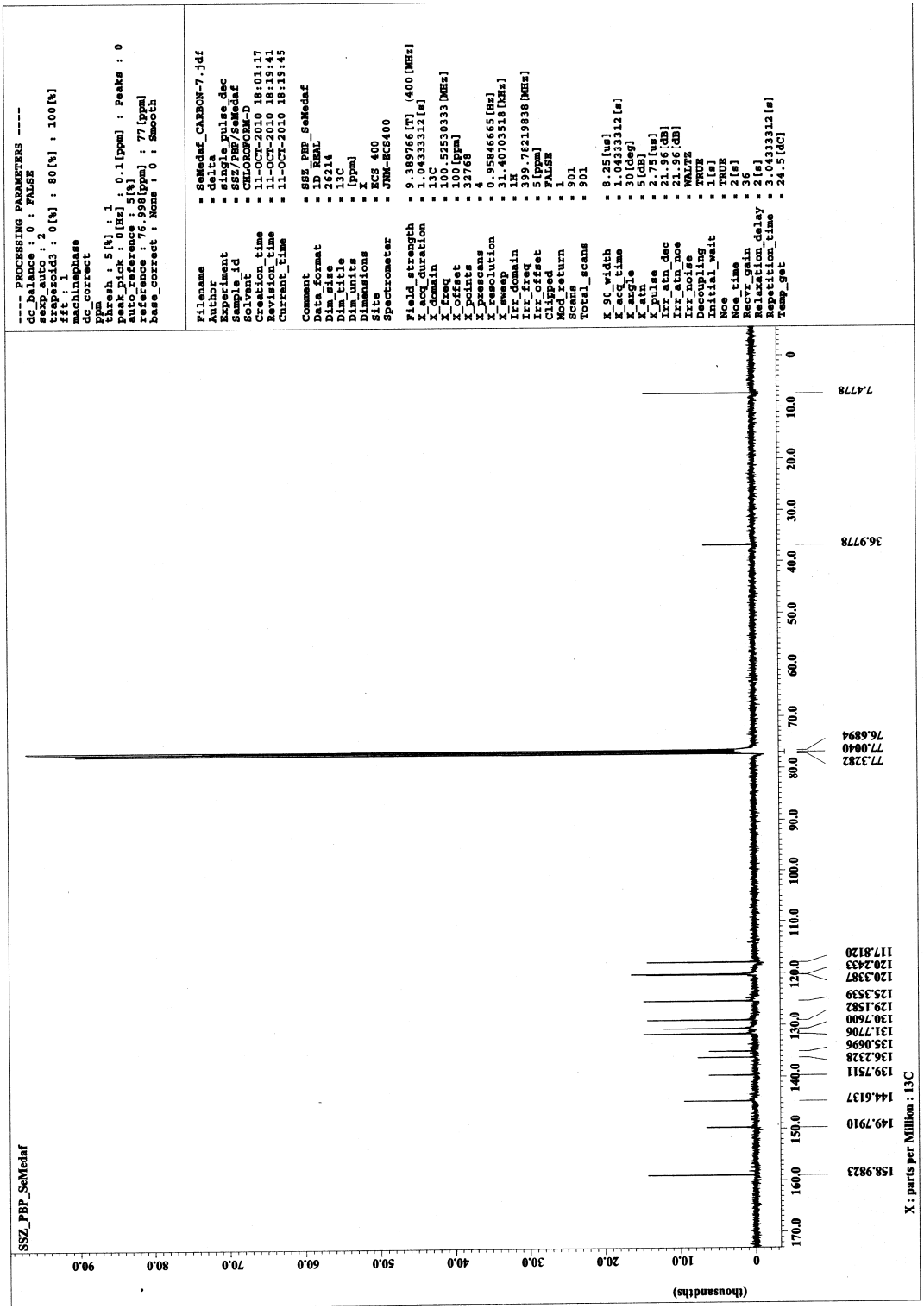


Figure S6. ^{13}C NMR spectrum of podand **3**

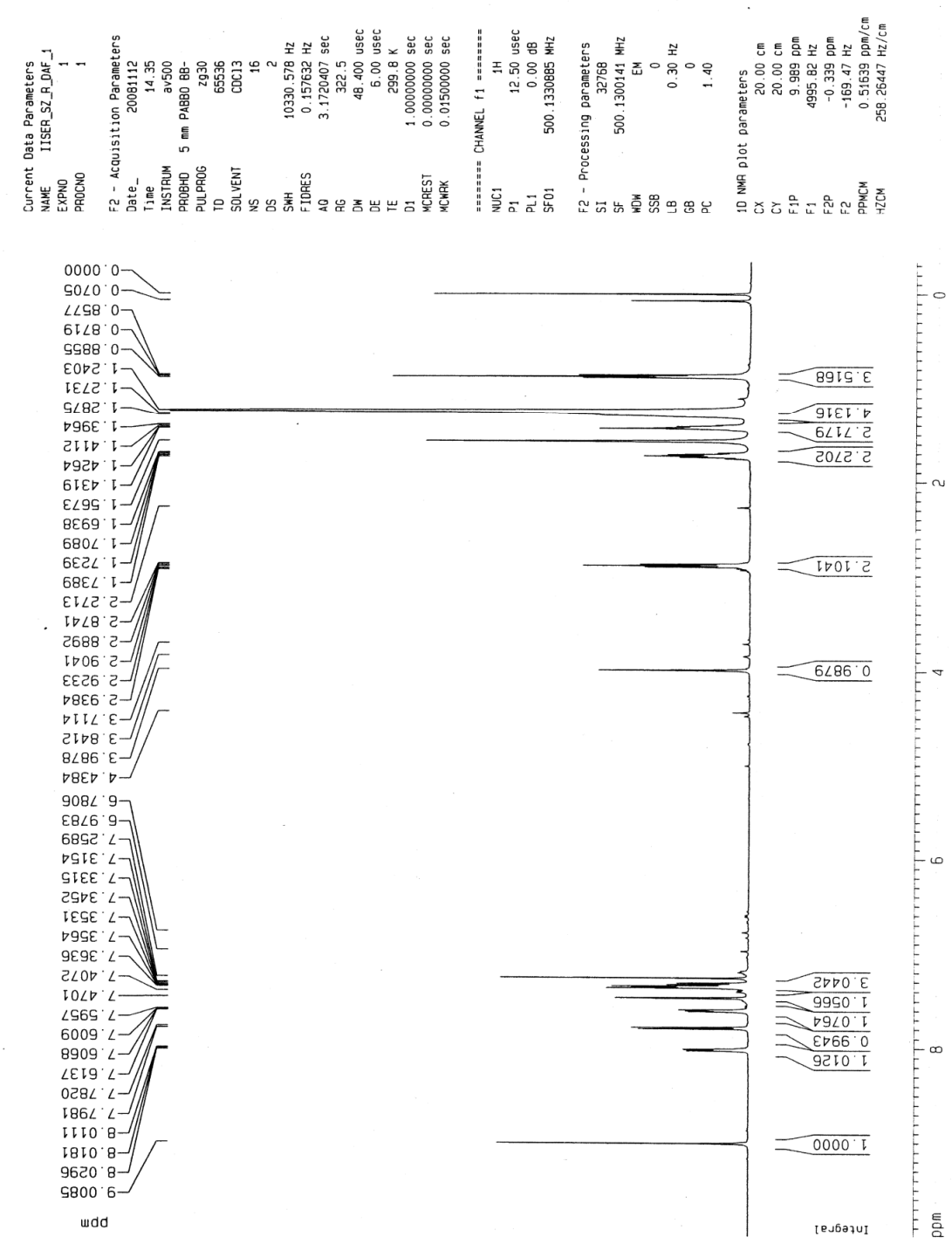


Figure S7. ^{1}H NMR spectrum of podand **4**.

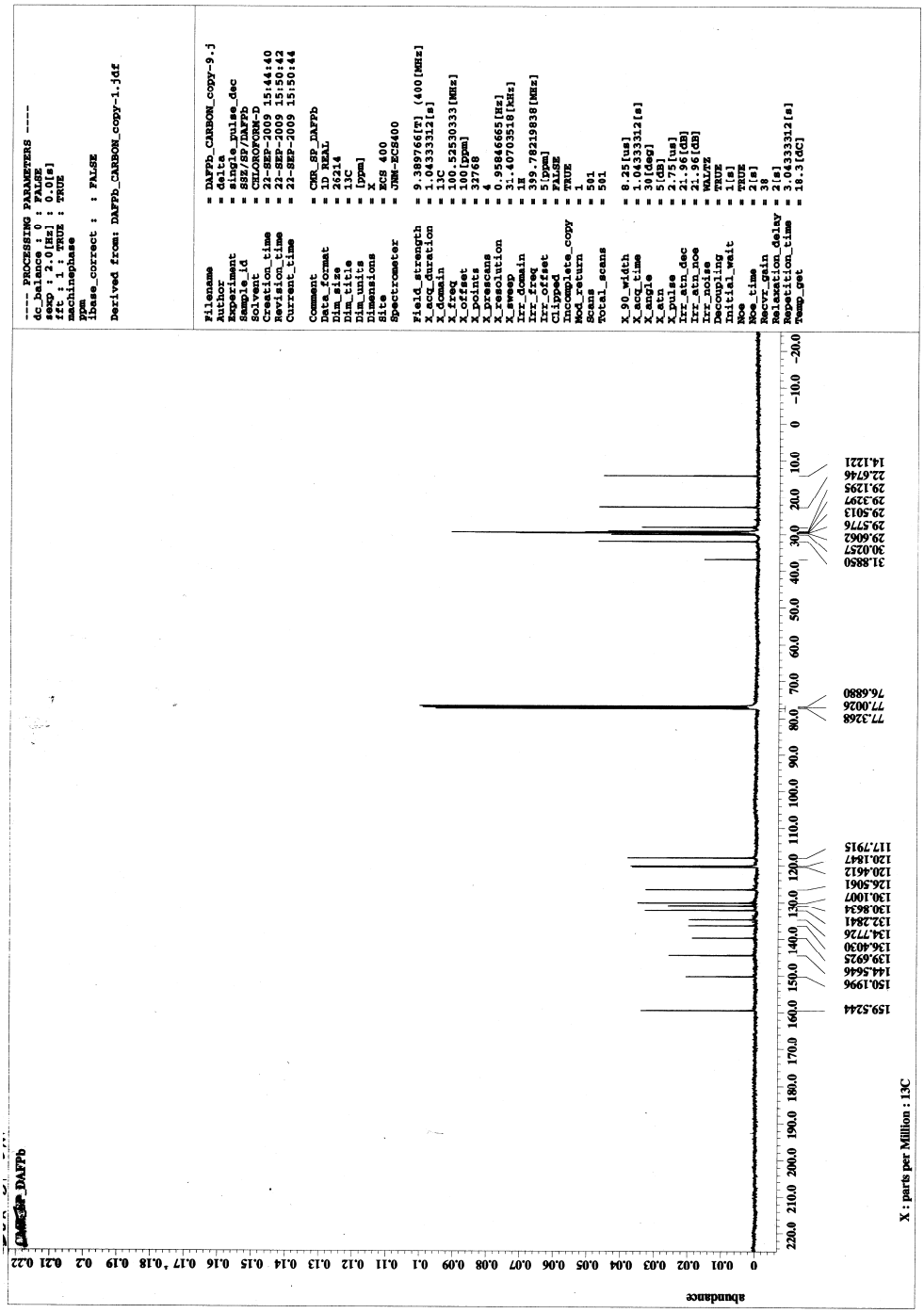


Figure S8. ^{13}C NMR spectrum of podand **4**.

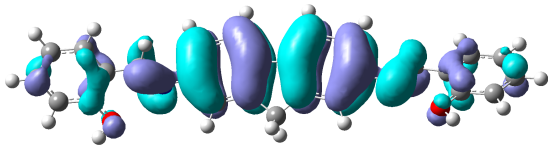
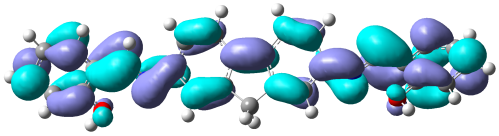
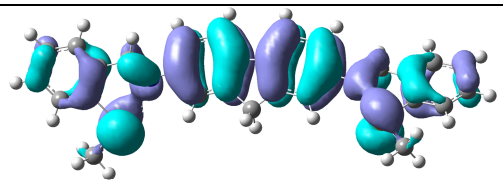
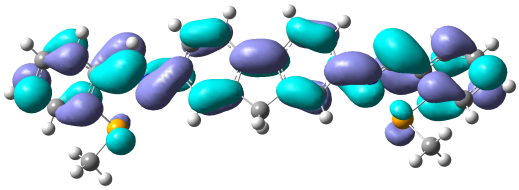
	HOMO	**LUMO**
1		
3		

Figure S9. HOMO and LUMO of podand **1** and **3** calculated at B3LYP/6-31G(d).

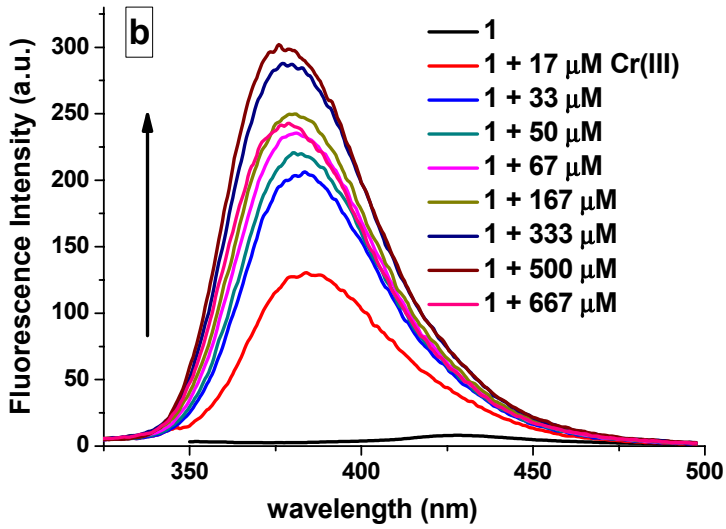


Figure S10. Fluorescence response following excitation at 270 nm from podand **1** solution upon addition of perchlorate salts of Cr(III) in THF.

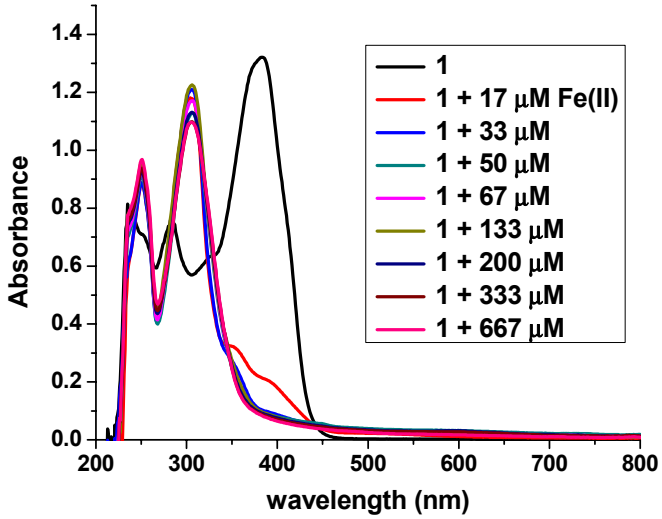


Figure S11. Change in absorption spectra upon addition of Fe(II)-perchlorate salt solution in THF to the solution of podand **1** (33 μM).

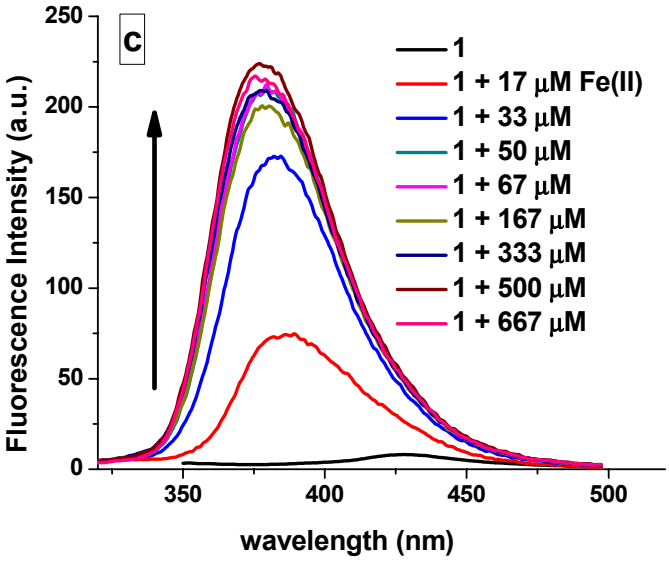


Figure S12. Fluorescence response following excitation at 270 nm from podand **1** solution upon addition of perchlorate salts of Fe(II) in THF.

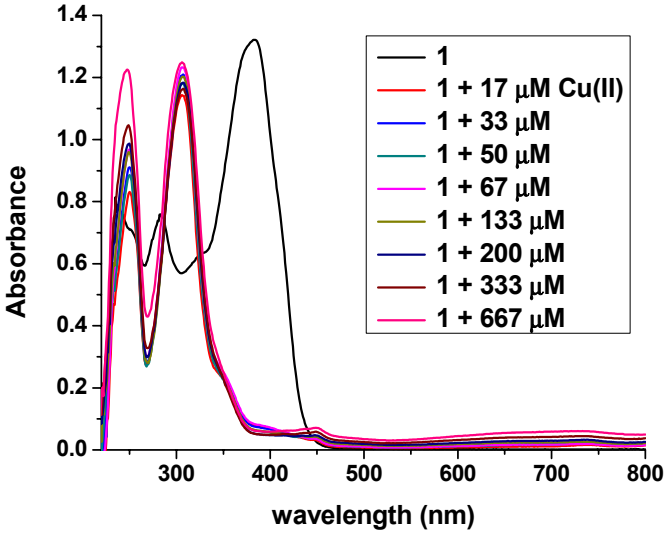


Figure S13. Change in absorption spectra upon addition of Cu(II)-perchlorate salt solution in THF to the solution of podand **1** (33 μM).

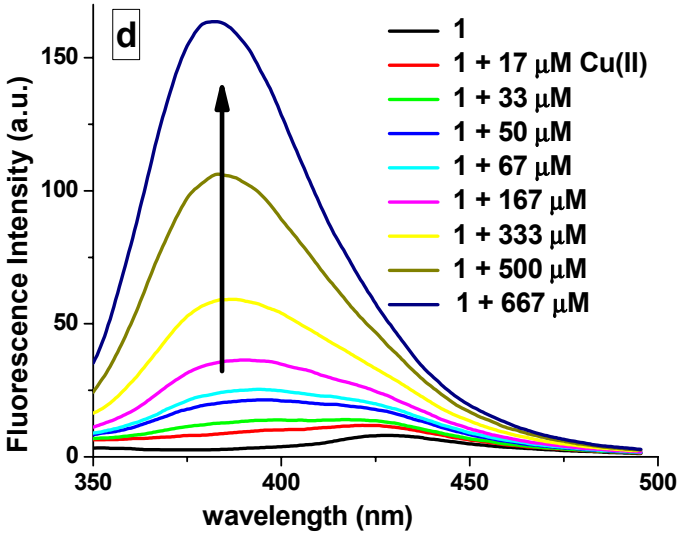


Figure S14. Fluorescence response following excitation at 270 nm from podand **1** solution upon addition of perchlorate salts of Cu(II) in THF.

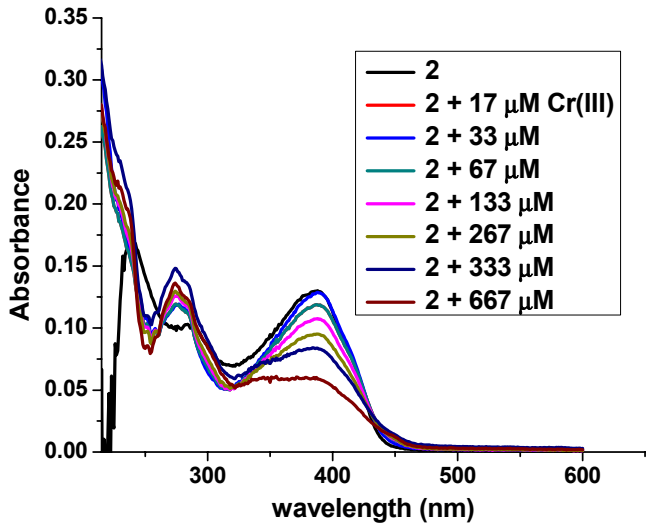


Figure S15. Change in absorption spectra upon addition of Cr(III)-perchlorate salt solution in THF to the solution of podand **2** (33 μM).

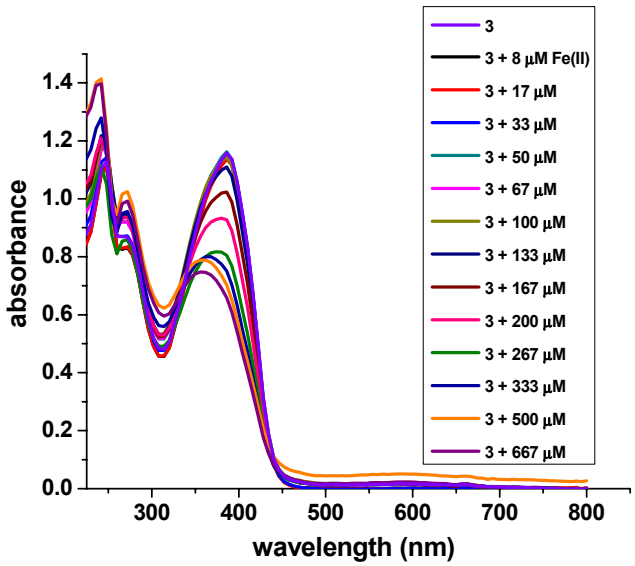


Figure S16. Change in absorption spectra upon addition of Cr(III)-perchlorate salt solution in THF to the solution of podand **3** (33 μM).

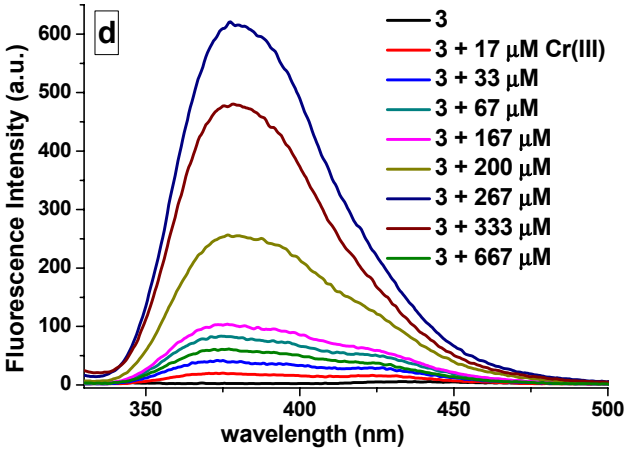


Figure S17. Fluorescence response following excitation at 270 nm from podand **3** solution upon addition of perchlorate salts of Cr(III) in THF.

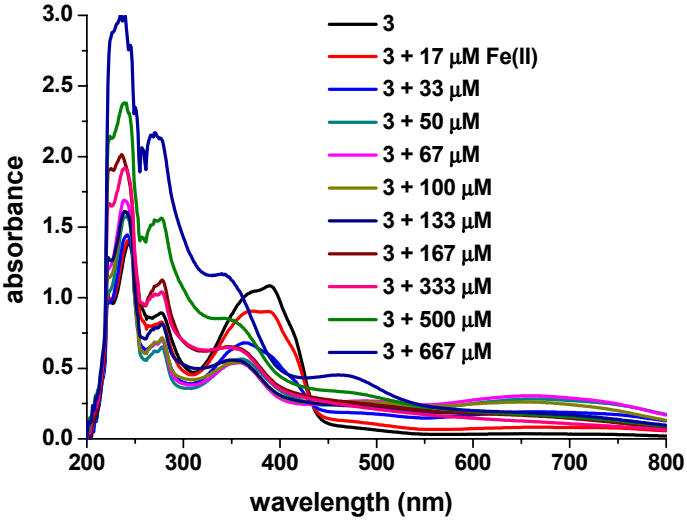


Figure S18. Change in absorption spectra upon addition of Fe(II)-perchlorate salt solution in THF to the solution of podand **3** (33 μM).

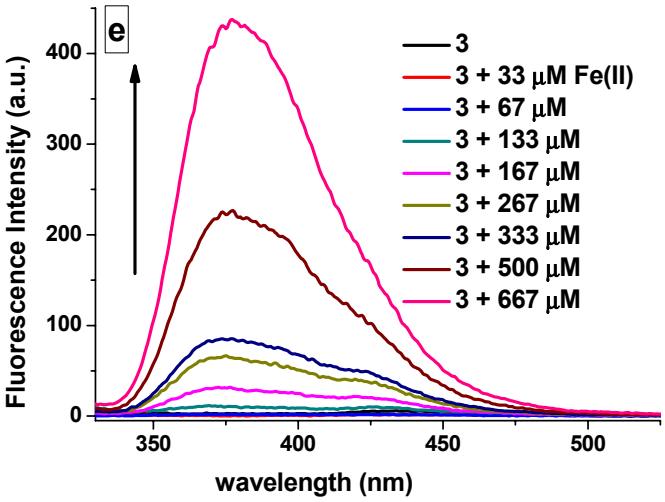


Figure S19. Fluorescence response following excitation at 270 nm from podand **3** solution upon addition of perchlorate salts of Fe(II) in THF.

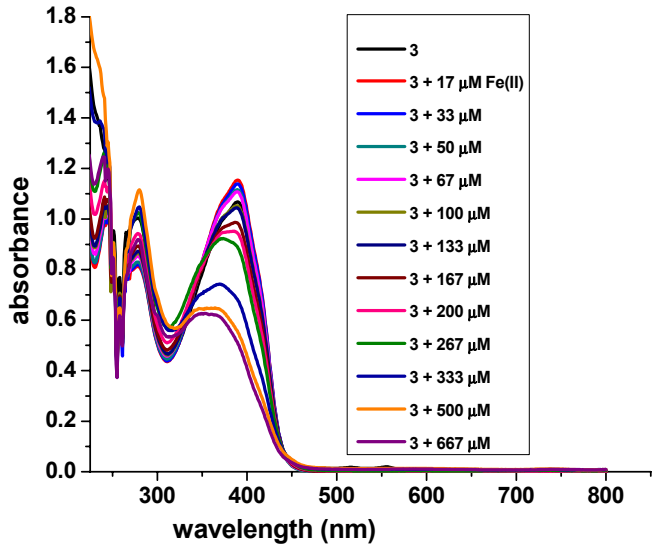


Figure S20. Change in absorption spectra upon addition of Cr(III)-perchlorate salt solution in THF to the solution of podand **4** (33 μM).

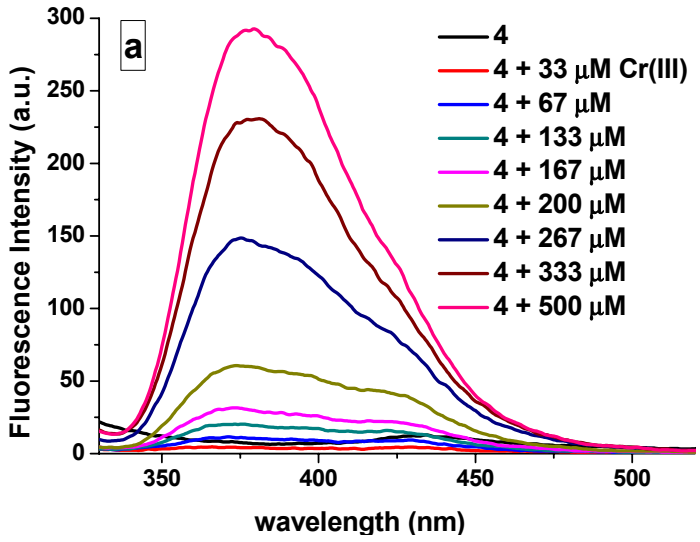


Figure S21. Fluorescence response following excitation at 270 nm from podand **4** solution upon addition of perchlorate salts of Cr(III) in THF.

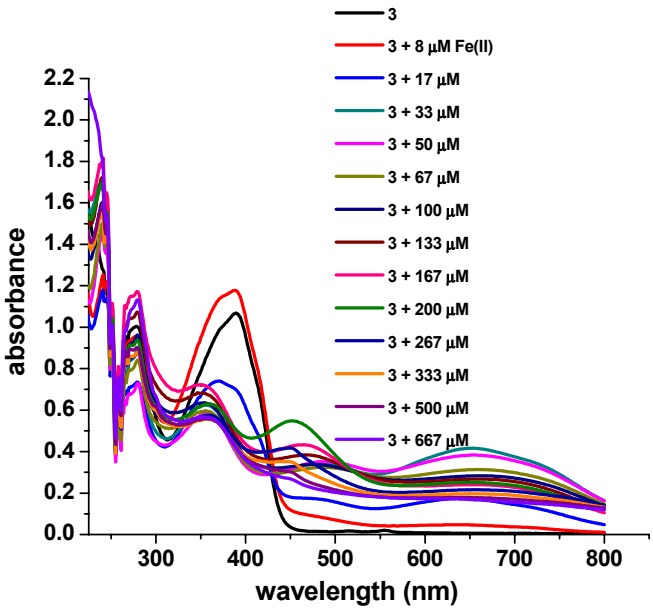


Figure S22. Change in absorption spectra upon addition of Fe(II)-perchlorate salt solution in THF to the solution of podand **4** (33 μM).

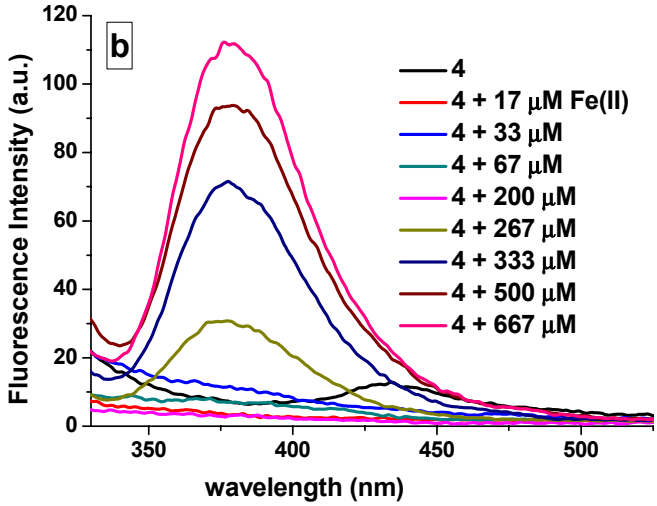
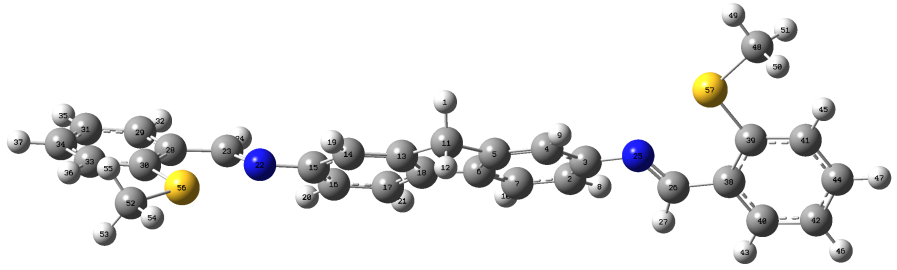


Figure S23. Fluorescence response following excitation at 270 nm from podand **4** solution upon addition of perchlorate salts of Cr(III) in THF.

(a)



(b)

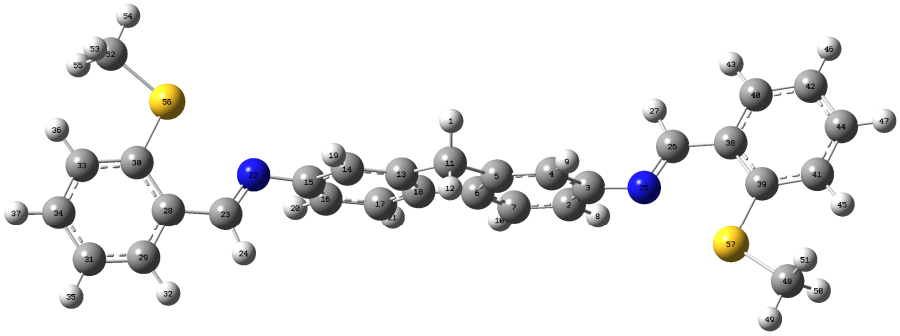
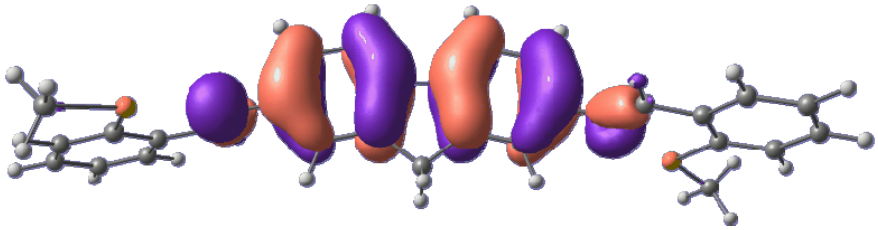
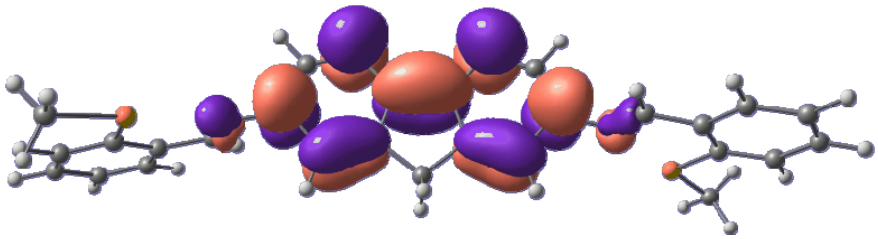


Figure S24. The optimized structures (at B3LYP/6-31G(d)) of (a) podand **2** (optimized without any constrain, dihedral angle between atoms 14, 15, 22 and 23 (or 4, 3, 25 and 26) is 34° and (b) twisted podand **2** (dihedral angle between atoms 14, 15, 22 and 23 (or 4, 3, 25 and 26) is freezed at 90°).

HOMO	
LUMO+2	

FigureS25. HOMO and LUMO+2 orbitals of twisted podand **2** at B3LYP/6-31G(d).

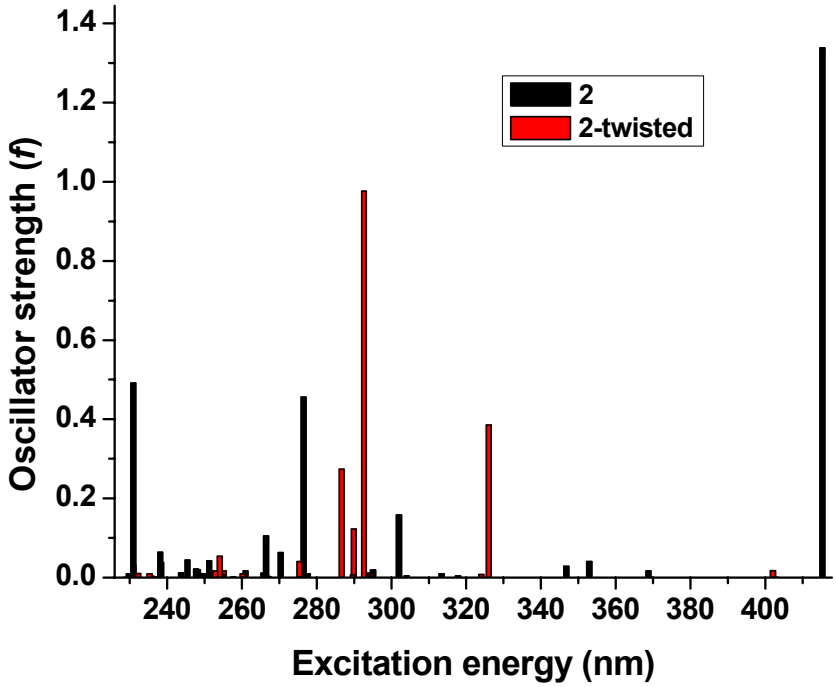


Figure S26. The absorption energy vs oscillator strength (*f*) calculated using TD-DFT at B3LYP/6-31G(d) for podand **2** and twisted podand **2** (as shown in Figure S24).

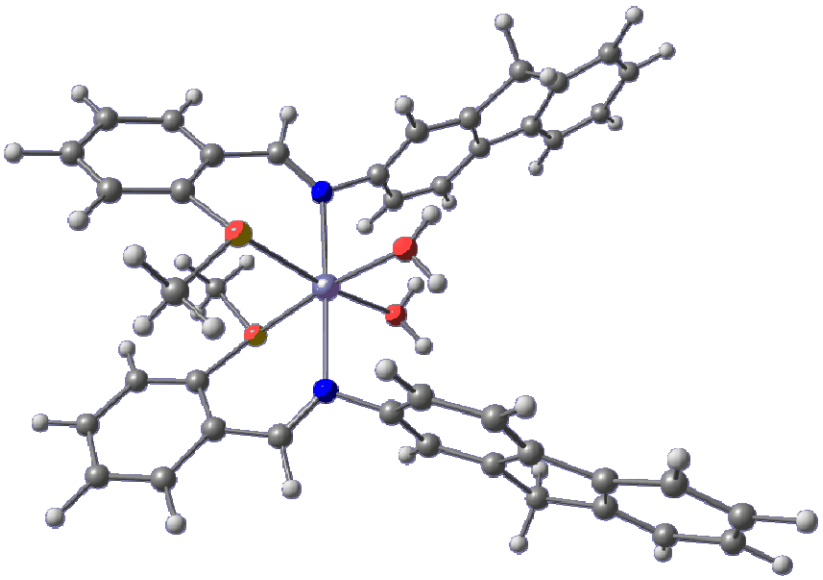


Figure S27. The optimized structure (at B3LYP/6-31G(d)/sdd) of quintet Fe complex **5**, where only one substitution at 2-position of fluorene was considered in the form of (*o*-methylthio)phenylazomethine.

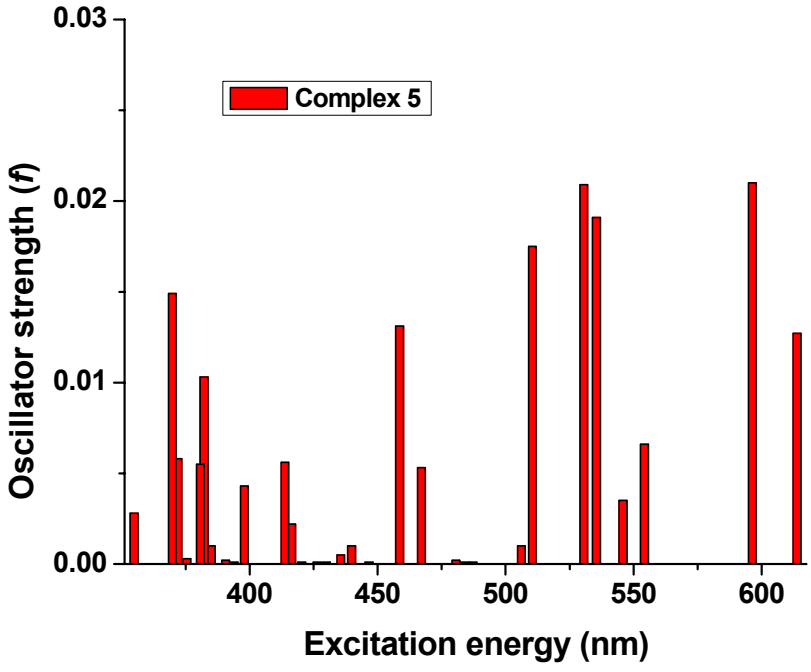
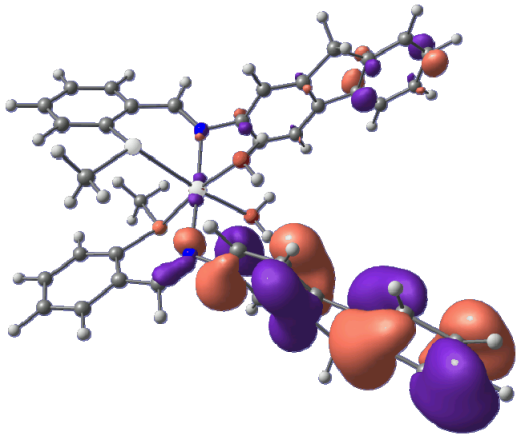
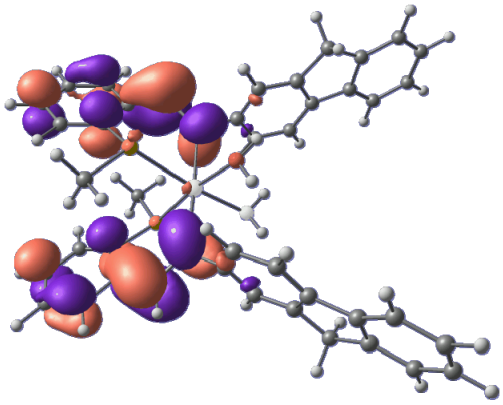
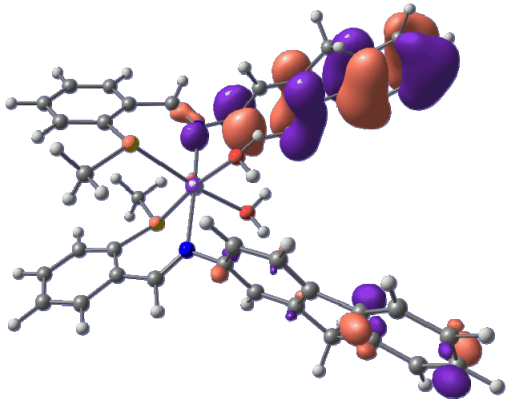
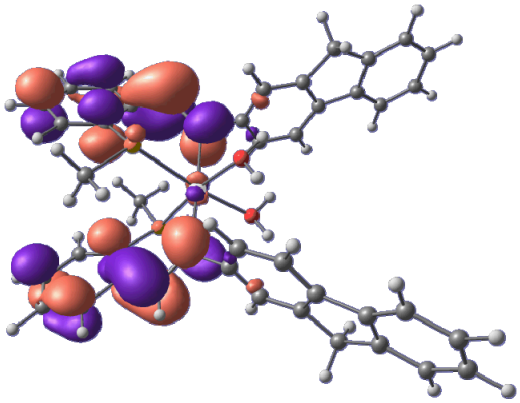
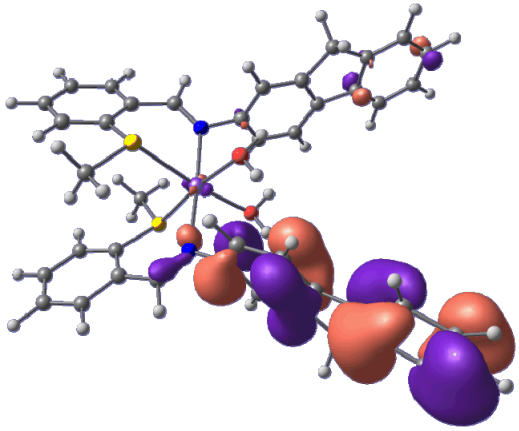
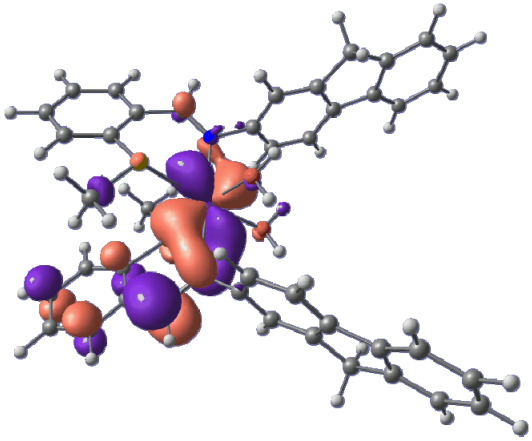
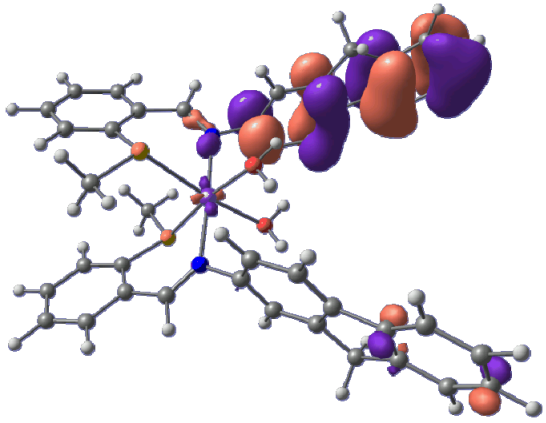
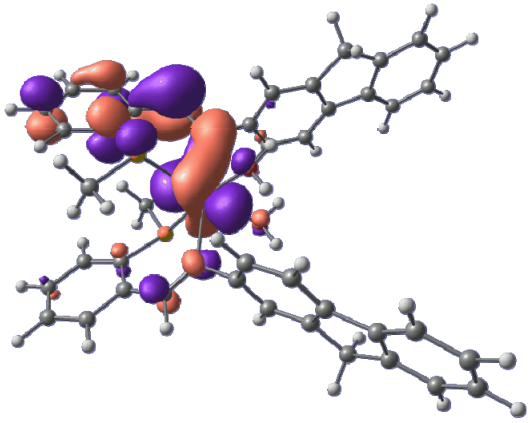
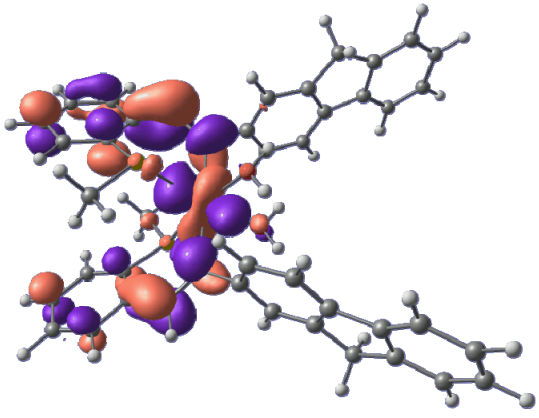


Figure S28. The absorption energy vs oscillator strength (*f*) calculated using TD-DFT at B3LYP/6-31G(d)/sdd for Fe complx **5**.

HOMO α	LUMO α
	
HOMO-1 α	LUMO+1 α
	
HOMO β	LUMO β

	
HOMO-1 β	LUMO+1 β
	
	LUMO+2 β
	
	LUMO+3 β

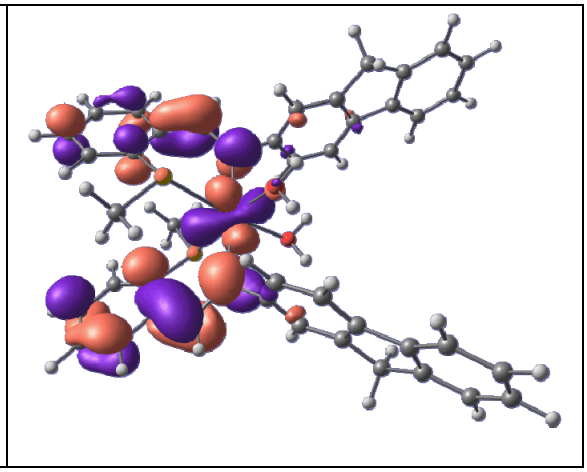


Figure S29. Frontier molecular orbitals of the Fe complx **5** calculated at B3LYP/6-31G(d)/sdd.

TD-TFT calculations at the same level of the theory indicate that the higher wavelength excitations are mostly from the HOMO and HOMO-1 to LUMO, LUMO+1, LUMO+2, LUMO+3 for β set of orbitals as well as HOMO, HOMO-1 to LUMO and LUMO+1 for α set of orbitals. β-Occupied orbitals are spaced mostly on the fluorene moiety whereas β-unoccupied orbitals are spaced mostly on metal extended over the *o*-methylthiophenylazomethine. Whereas, α-Occupied orbitals are spaced mostly on the fluorene moiety whereas the α-unoccupied orbitals are spaced mostly on the *o*-methylthiophenylazomethine moiety.

Table S1. Absorption and emission data for the podands **1**-**4**.

Compound	Absorbance λ_{max} (nm, THF)	ε $M^{-1}cm^{-1}$	Emission λ_{max} (nm)	Quantum yield (Φ)
2,7-Diamino fluorene	347	5.9×10^3	385	0.23[a]
	299	3.4×10^4		
	233	5.8×10^3		
1	384	4.1×10^4	428	0.097[b]
	283	1.9×10^4		
	234	1.9×10^4		
2	388	4.5×10^4	440	0.0010[b]
	285	2.6×10^4		
	243	4.2×10^4		
3	384	6.8×10^4	430	0.0012[b]
	274	6.8×10^4		
	236	9.6×10^4		
4	380	4.2×10^4	437	0.016[b]
	278	3.0×10^4		
	240	4.1×10^4		

[a] ref., rhodamine-6G (excitation wavelength 350 nm); [b] ref., phenol (excitation wavelength 270 nm)

Table S2. TDDFT calculated electronic excitations of **5** (at B3LYP/6-31G(d)/sdd).

E (eV)	λ (nm)	Oscillator Strength (*f*)	Most important configurations		
2.02	613.9	0.0127	H β→L β	H-1 β→L β	
2.08	596.3	0.0210	H-1 β→L β	H β→L+1 β	H-1 α→L α
2.24	554.3	0.0066	H-1 β→ L+1 β	H β→ L+1 β	H-1 α→L α
2.27	545.8	0.0035	H β→ L+1 β	H α→ L α	H-1 β→ L+1 β
2.32	535.5	0.0191	H α→ L α	H β→L+1 β	H α→ L+1 α
2.34	530.5	0.0209	H-1 α→L α	H-1 α→ L+1 α	H α→ L+1 α
2.43	510.5	0.0175	H-1 β→ L+2 β	H β→ L+2 β	H-1 α→L α
2.45	506.2	0.0010	H β→ L+2 β	H-1 β→ L+2 β	H β→ L+3 β
2.65	467.1	0.0053	H β→ L+3 β	H β→ L+2 β	H β→ L+1 β
2.70	458.6	0.0131	H-1 β→ L+3 β	H-1 β→ L+2 β	

Table S3. Calculated absolute energies.

Compound	E
Podand **2**[a]	-2025.425506
Twisted (90°) podand **2**[a]	-2025.4180745
Complex **5**-singlet[b]	-2803.1897932
Complex **5**-quintet[b]	-2803.214919

[a] calculated at B3LYP/6-31G(d), [b] calculated at B3LYP with sdd basis set for Fe and 6-31G(d) basis set for all other atoms.

Coordinates of the optimized geometries.

Podand **2** at B3LYP/6-31G(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.001511	1.899324	-0.879426
2	6	0	3.017932	-1.802460	-0.005395
3	6	0	3.475015	-0.468284	0.009804
4	6	0	2.539153	0.584593	-0.012490
5	6	0	1.185053	0.294400	0.001056
6	6	0	0.732235	-1.044151	0.002634
7	6	0	1.655593	-2.093033	-0.010580
8	1	0	3.741319	-2.611455	-0.051428
9	1	0	2.909729	1.605705	-0.025582
10	1	0	1.322871	-3.127800	-0.035658
11	6	0	-0.000005	1.240689	0.000005
12	1	0	-0.001525	1.899329	0.879432
13	6	0	-1.185058	0.294393	-0.001042
14	6	0	-2.539160	0.584579	0.012498
15	6	0	-3.475017	-0.468302	-0.009793
16	6	0	-3.017926	-1.802476	0.005420
17	6	0	-1.655585	-2.093042	0.010610
18	6	0	-0.732232	-1.044155	-0.002611
19	1	0	-2.909742	1.605689	0.025584
20	1	0	-3.741307	-2.611476	0.051463
21	1	0	-1.322857	-3.127806	0.035699
22	7	0	-4.834479	-0.122270	0.006007
23	6	0	-5.701329	-0.826288	-0.623682
24	1	0	-5.402040	-1.682568	-1.246694
25	7	0	4.834476	-0.122247	-0.005997
26	6	0	5.701327	-0.826271	0.623684
27	1	0	5.402040	-1.682575	1.246663
28	6	0	-7.135497	-0.557151	-0.597768
29	6	0	-7.943981	-1.405954	-1.376556

30	6	0	-7.750726	0.489033	0.151288
31	6	0	-9.322815	-1.259622	-1.442157
32	1	0	-7.457534	-2.198297	-1.940988
33	6	0	-9.146609	0.623057	0.070852
34	6	0	-9.920472	-0.234018	-0.709541
35	1	0	-9.920739	-1.930220	-2.051895
36	1	0	-9.650252	1.405912	0.623266
37	1	0	-10.997837	-0.093506	-0.740693
38	6	0	7.135498	-0.557154	0.597745
39	6	0	7.750728	0.489048	-0.151286
40	6	0	7.943987	-1.406002	1.376479
41	6	0	9.146616	0.623034	-0.070891
42	6	0	9.322825	-1.259701	1.442048
43	1	0	7.457539	-2.198358	1.940894
44	6	0	9.920483	-0.234086	0.709449
45	1	0	9.650262	1.405893	-0.623297
46	1	0	9.920753	-1.930337	2.051742
47	1	0	10.997852	-0.093601	0.740572
48	6	0	8.021235	2.670948	-1.908939
49	1	0	7.449623	3.352167	-2.545329
50	1	0	8.563300	3.262774	-1.165693
51	1	0	8.726666	2.118191	-2.536106
52	6	0	-8.021249	2.670866	1.909009
53	1	0	-8.726504	2.118136	2.536398
54	1	0	-7.449618	3.352276	2.545177
55	1	0	-8.563516	3.262484	1.165743
56	16	0	-6.759467	1.581743	1.151803
57	16	0	6.759462	1.581807	-1.151742

Podand **2**-twisted (90°) at B3LYP/6-31G(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.007148	-0.811717	-1.877176
2	6	0	3.023957	-0.032187	1.846754
3	6	0	3.471507	0.009269	0.515585
4	6	0	2.539704	0.050009	-0.536503
5	6	0	1.184667	0.020656	-0.240153
6	6	0	0.733903	-0.034701	1.095932
7	6	0	1.660293	-0.058737	2.140114
8	1	0	3.759313	-0.037184	2.645943
9	1	0	2.898289	0.105373	-1.560907
10	1	0	1.332758	-0.097380	3.176146
11	6	0	-0.001175	0.042395	-1.185815
12	1	0	-0.010278	0.945938	-1.811224
13	6	0	-1.185843	-0.006890	-0.239731
14	6	0	-2.541475	-0.013335	-0.535808
15	6	0	-3.471881	-0.054335	0.517349
16	6	0	-3.022885	-0.111296	1.847475
17	6	0	-1.659057	-0.105223	2.140283

18	6	0	-0.733681	-0.051600	1.096039
19	1	0	-2.901015	0.008683	-1.561165
20	1	0	-3.757510	-0.165378	2.645474
21	1	0	-1.330278	-0.142550	3.175971
22	7	0	-4.853770	-0.120971	0.231885
23	6	0	-5.545204	0.950921	0.173027
24	1	0	-5.085241	1.935372	0.346950
25	7	0	4.852279	0.100441	0.231828
26	6	0	5.556039	-0.961216	0.140673
27	1	0	5.107361	-1.955672	0.284637
28	6	0	-6.978431	0.980204	-0.122203
29	6	0	-7.587990	2.246965	-0.125343
30	6	0	-7.767509	-0.172567	-0.402563
31	6	0	-8.940600	2.414651	-0.391401
32	1	0	-6.967533	3.114024	0.089711
33	6	0	-9.133933	0.015934	-0.669387
34	6	0	-9.711065	1.284481	-0.664137
35	1	0	-9.385929	3.404852	-0.386753
36	1	0	-9.768308	-0.833846	-0.886521
37	1	0	-10.772606	1.383221	-0.876025
38	6	0	6.989542	-0.965057	-0.154402
39	6	0	7.765738	0.204772	-0.397761
40	6	0	7.613281	-2.224151	-0.197434
41	6	0	9.134088	0.040172	-0.670395
42	6	0	8.967644	-2.368151	-0.468344
43	1	0	7.002655	-3.104499	-0.010088
44	6	0	9.725376	-1.221378	-0.705196
45	1	0	9.758747	0.903547	-0.860429
46	1	0	9.424059	-3.352945	-0.494971
47	1	0	10.787890	-1.301510	-0.920040
48	6	0	8.402008	2.922658	-0.752729
49	1	0	7.967702	3.926147	-0.747830
50	1	0	9.193573	2.882909	0.001195
51	1	0	8.818134	2.728054	-1.745409
52	6	0	-8.432635	-2.869548	-0.851108
53	1	0	-8.844484	-2.635364	-1.836997
54	1	0	-8.009035	-3.877170	-0.881096
55	1	0	-9.225327	-2.848139	-0.097630
56	16	0	-7.020324	-1.790405	-0.412052
57	16	0	7.000578	1.813695	-0.355115

Complex **5**-singlet at B3LYP/6-31G(d)/sdd (at Fe).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	4.968617	3.237919	-2.168681
2	6	0	6.509803	5.039263	2.075063
3	6	0	6.541357	5.795367	0.894970
4	6	0	5.866921	5.366498	-0.253080
5	6	0	5.159476	4.170357	-0.204052
6	6	0	5.128222	3.408853	0.983319
7	6	0	5.803135	3.838804	2.130266

8	1	0	7.042709	5.391953	2.952751
9	1	0	5.901088	5.960945	-1.161969
10	1	0	5.784693	3.255477	3.046936
11	6	0	4.355763	3.483897	-1.290548
12	1	0	3.528406	4.107744	-1.656069
13	6	0	3.854729	2.236072	-0.593944
14	6	0	3.061701	1.208927	-1.089511
15	6	0	2.722063	0.136443	-0.246631
16	6	0	3.190346	0.102561	1.079271
17	6	0	3.992275	1.136690	1.573817
18	6	0	4.322735	2.211136	0.741364
19	1	0	2.706515	1.227739	-2.117869
20	1	0	2.969777	-0.755646	1.708800
21	1	0	4.364678	1.084113	2.592658
22	7	0	1.891545	-0.943022	-0.749955
23	6	0	2.460371	-1.630844	-1.696159
24	1	0	3.484563	-1.346135	-1.944918
25	6	0	1.991599	-2.774090	-2.472153
26	6	0	2.996501	-3.388484	-3.255353
27	6	0	0.688854	-3.330833	-2.511095
28	6	0	2.745035	-4.519748	-4.020917
29	1	0	3.997194	-2.965293	-3.243817
30	6	0	0.435875	-4.455942	-3.299562
31	6	0	1.457986	-5.057304	-4.038037
32	1	0	3.540642	-4.971803	-4.603748
33	1	0	-0.564069	-4.869647	-3.363228
34	1	0	1.236159	-5.934010	-4.638701
35	6	0	-1.711363	-3.907950	-1.099308
36	1	0	-1.123180	-4.608633	-0.504963
37	1	0	-2.496149	-3.463592	-0.486432
38	1	0	-2.173607	-4.415329	-1.946676
39	16	0	-0.683714	-2.514122	-1.697503
40	26	0	-0.032187	-1.052426	-0.015455
41	8	0	0.259690	0.459474	1.366507
42	1	0	1.213164	0.651950	1.504766
43	8	0	-0.395405	0.555531	-1.292593
44	1	0	-1.342690	0.662412	-1.536080
45	1	0	-0.108336	1.263316	0.954647
46	1	0	0.122649	0.564852	-2.114889
47	1	0	7.098654	6.727054	0.871702
48	1	0	0.590739	-4.770314	3.433561
49	6	0	-0.415900	-4.373121	3.368065
50	6	0	-0.696350	-3.286553	2.535720
51	6	0	-1.417348	-4.953009	4.150235
52	6	0	-2.003633	-2.744188	2.499962
53	16	0	0.658701	-2.506272	1.658153
54	6	0	-2.710637	-4.430804	4.132651
55	1	0	-1.174447	-5.799249	4.785436
56	6	0	-2.491262	-1.626632	1.699707
57	6	0	-2.987654	-3.334577	3.325951
58	6	0	1.614381	-3.940181	1.035013
59	1	0	-3.490580	-4.865580	4.748864
60	7	0	-1.950214	-0.977488	0.714383
61	1	0	-3.502894	-1.322395	1.975182
62	1	0	-3.991657	-2.919264	3.318043
63	1	0	0.984004	-4.630529	0.472666

64	1	0	2.394248	-3.534319	0.389777
65	1	0	2.089102	-4.453783	1.871682
66	6	0	-2.769578	0.112375	0.223099
67	6	0	-3.021277	1.219581	1.052968
68	6	0	-3.295806	0.067110	-1.081194
69	6	0	-3.795438	2.266043	0.566095
70	1	0	-2.612171	1.241658	2.060465
71	6	0	-4.076424	1.123117	-1.565774
72	1	0	-3.141311	-0.816193	-1.695888
73	6	0	-4.216123	3.547978	1.253561
74	6	0	-4.325616	2.228989	-0.745614
75	1	0	-4.499355	1.062594	-2.564395
76	1	0	-4.796044	3.345013	2.164414
77	6	0	-5.043029	4.240178	0.188628
78	1	0	-3.350266	4.147377	1.567169
79	6	0	-5.096311	3.451028	-0.979840
80	6	0	-5.702798	5.463219	0.241190
81	6	0	-5.809461	3.879725	-2.103897
82	6	0	-6.415185	5.890853	-0.884082
83	1	0	-5.671877	6.078799	1.136000
84	6	0	-6.468179	5.106991	-2.045173
85	1	0	-5.857619	3.274850	-3.005436
86	1	0	-6.936516	6.843043	-0.857618
87	1	0	-7.029892	5.459035	-2.904985

Complex **5**-quintet at B3LYP/6-31G(d)/sdd (at Fe).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	2.870229	5.254878	2.079342
2	6	0	6.111979	5.350333	-1.534727
3	6	0	6.470478	5.658770	-0.215064
4	6	0	5.606983	5.379027	0.849316
5	6	0	4.379736	4.785487	0.574965
6	6	0	4.018884	4.474173	-0.753019
7	6	0	4.882846	4.755407	-1.816176
8	1	0	6.797553	5.579933	-2.344658
9	1	0	5.894868	5.626827	1.867302
10	1	0	4.609226	4.522810	-2.841896
11	6	0	3.268763	4.392005	1.528123
12	1	0	3.601271	3.670181	2.286832
13	6	0	2.226879	3.804538	0.598862
14	6	0	0.973281	3.278369	0.898795
15	6	0	0.159347	2.814649	-0.152396
16	6	0	0.602771	2.891440	-1.483004
17	6	0	1.863493	3.422197	-1.779369
18	6	0	2.684633	3.871717	-0.738783
19	1	0	0.602006	3.251503	1.921860
20	1	0	-0.062350	2.588630	-2.288690
21	1	0	2.180509	3.506298	-2.815000
22	7	0	-1.121829	2.216964	0.147954
23	6	0	-2.074914	3.039257	0.448663
24	1	0	-1.863044	4.109800	0.371435

25	6	0	-3.445703	2.720790	0.840012
26	6	0	-4.390265	3.738996	0.597074
27	6	0	-3.890890	1.508761	1.433067
28	6	0	-5.742804	3.559893	0.865965
29	1	0	-4.046136	4.679942	0.175869
30	6	0	-5.249289	1.339784	1.710191
31	6	0	-6.169145	2.351832	1.416669
32	1	0	-6.451247	4.355840	0.662246
33	1	0	-5.609728	0.431432	2.176854
34	1	0	-7.218931	2.195192	1.645720
35	6	0	-3.652203	-1.137563	2.508478
36	1	0	-4.319688	-1.496779	1.723512
37	1	0	-2.917733	-1.909982	2.747674
38	1	0	-4.206715	-0.888805	3.415434
39	16	0	-2.674324	0.304114	1.961524
40	26	0	-1.028994	0.008253	-0.022612
41	8	0	0.539865	-0.108651	-1.524604
42	1	0	1.087756	0.694088	-1.631394
43	8	0	0.552640	0.133374	1.471137
44	1	0	1.100738	-0.660006	1.628672
45	1	0	1.132227	-0.881123	-1.448597
46	1	0	1.133882	0.915870	1.440742
47	1	0	7.431381	6.124029	-0.016825
48	1	0	-5.598647	-0.620391	-2.184809
49	6	0	-5.198973	-1.509394	-1.712851
50	6	0	-3.836013	-1.611609	-1.425275
51	6	0	-6.072066	-2.562751	-1.422629
52	6	0	-3.337058	-2.799950	-0.825278
53	16	0	-2.679096	-0.348012	-1.942335
54	6	0	-5.593084	-3.747217	-0.864028
55	1	0	-7.126404	-2.456591	-1.659630
56	6	0	-1.956621	-3.062396	-0.426568
57	6	0	-4.235737	-3.860537	-0.585394
58	6	0	-3.721167	1.036783	-2.515981
59	1	0	-6.264274	-4.575222	-0.662053
60	7	0	-1.024131	-2.211894	-0.134276
61	1	0	-1.713929	-4.125164	-0.333511
62	1	0	-3.850910	-4.783239	-0.159104
63	1	0	-4.415484	1.369366	-1.742488
64	1	0	-3.023046	1.842839	-2.752929
65	1	0	-4.251621	0.753242	-3.427129
66	6	0	0.269225	-2.784344	0.166761
67	6	0	1.090103	-3.229194	-0.887048
68	6	0	0.715429	-2.859688	1.496437
69	6	0	2.353310	-3.735104	-0.591030
70	1	0	0.716217	-3.207852	-1.909515
71	6	0	1.984814	-3.371409	1.788818
72	1	0	0.046413	-2.571633	2.304413
73	6	0	3.404017	-4.299659	-1.524347
74	6	0	2.812832	-3.801725	0.745522
75	1	0	2.304583	-3.454348	2.823693
76	1	0	3.019553	-5.165646	-2.080678
77	6	0	4.522048	-4.680190	-0.574179
78	1	0	3.723793	-3.567549	-2.278666
79	6	0	4.157209	-4.382038	0.755678
80	6	0	5.758612	-5.252017	-0.852765

81	6	0	5.026614	-4.654741	1.816488
82	6	0	6.627609	-5.523250	0.209327
83	1	0	6.049545	-5.489491	-1.872357
84	6	0	6.265219	-5.227819	1.530826
85	1	0	4.750200	-4.432164	2.843684
86	1	0	7.595874	-5.971516	0.007771
87	1	0	6.955188	-5.450365	2.338998

[1] S. Panda, S. S. Zade, H. B. Singh and R. J. Butcher, *J.Organomet. Chem.*, **2006**, 2793.