Electronic Supplementary Information (ESI)

NLO-active Y-shaped ferrocene conjugated imidazole chromophores as precursors for SHG polymeric films

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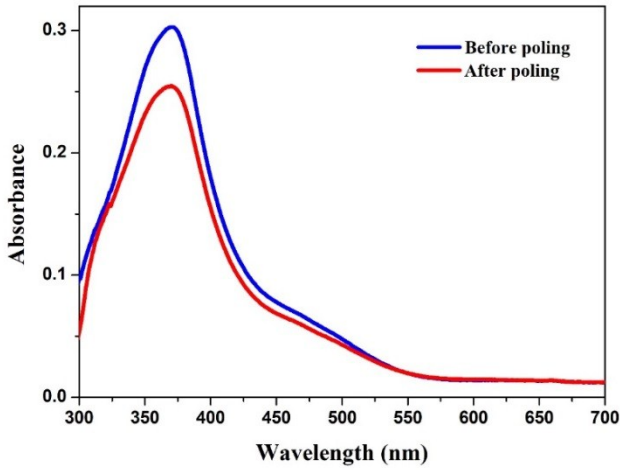


Figure S1. Absorption spectra of a PMMA film containing compound 3 before and after poling

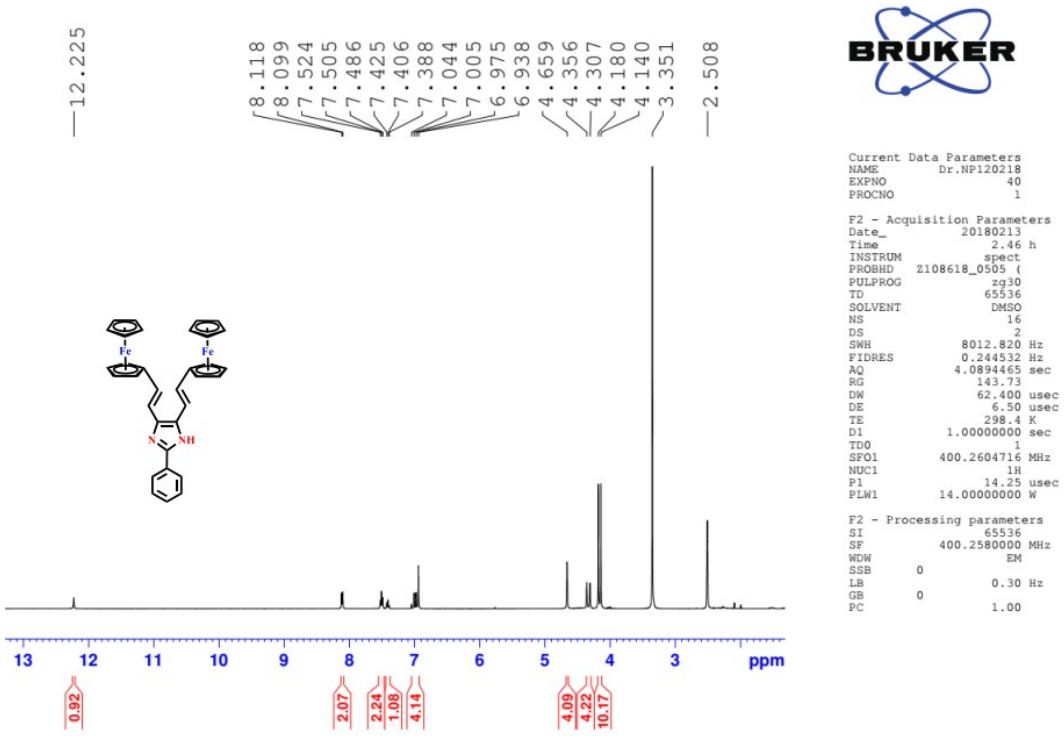


Figure S2. ^{1}H NMR spectrum of compound 1(H) in DMSO-d_6 at 25 ^{o}C

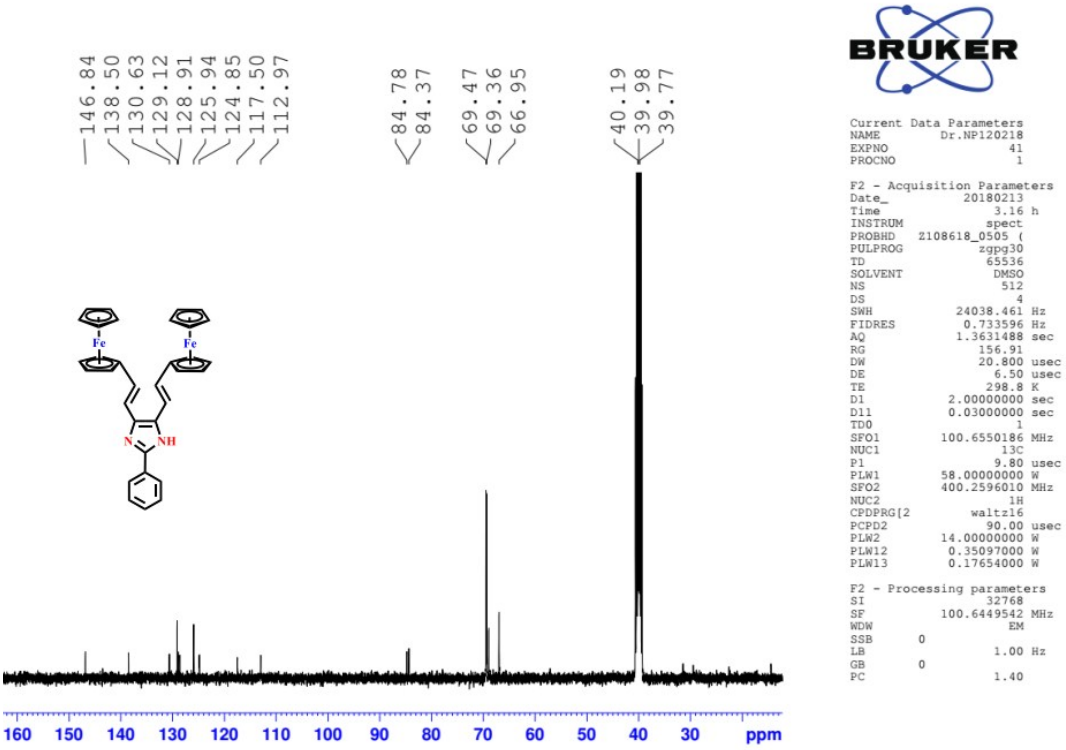


Figure S3. ^{13}C NMR spectrum of compound 1(H) in DMSO-d_6 at 25 ^{o}C

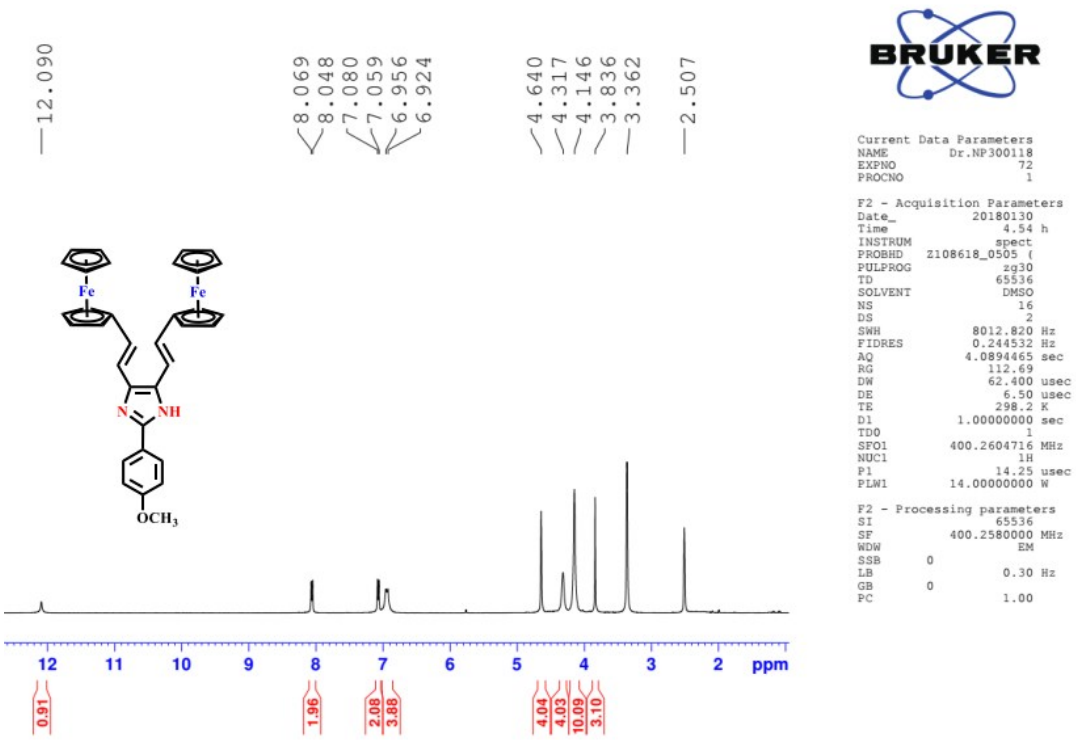


Figure S4. ^{1}H NMR spectrum of compound 2(OCH_3) in DMSO-d_6 at 25 ^{o}C

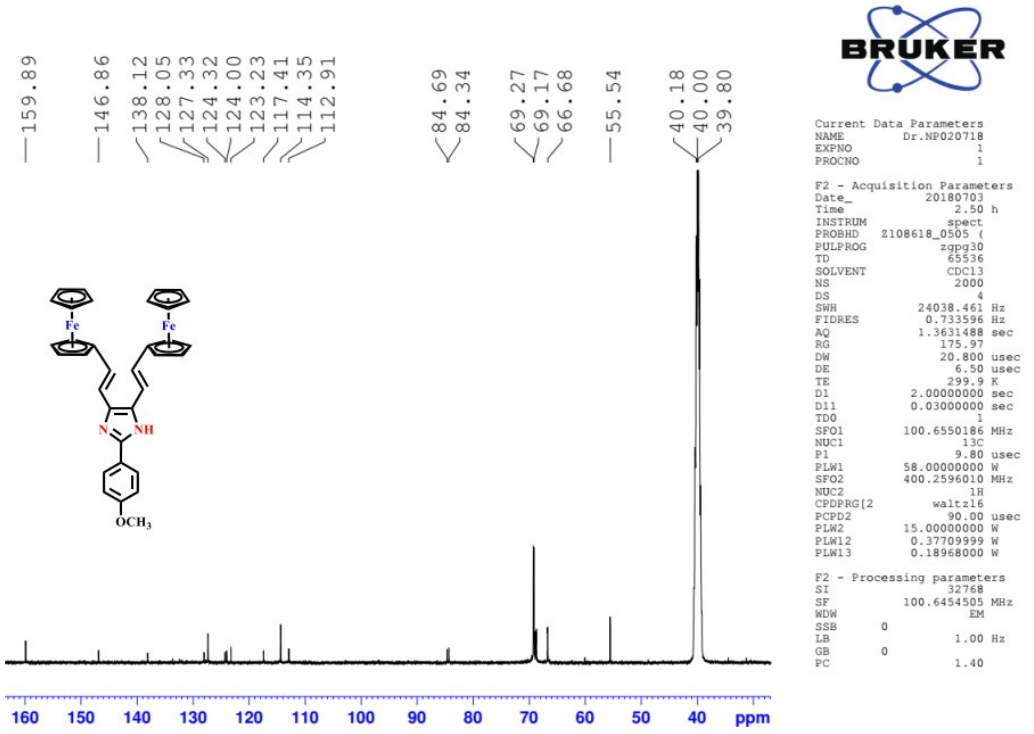


Figure S5. ^{13}C NMR spectrum of compound 2(OCH_3) in DMSO-d_6 at 25 °C

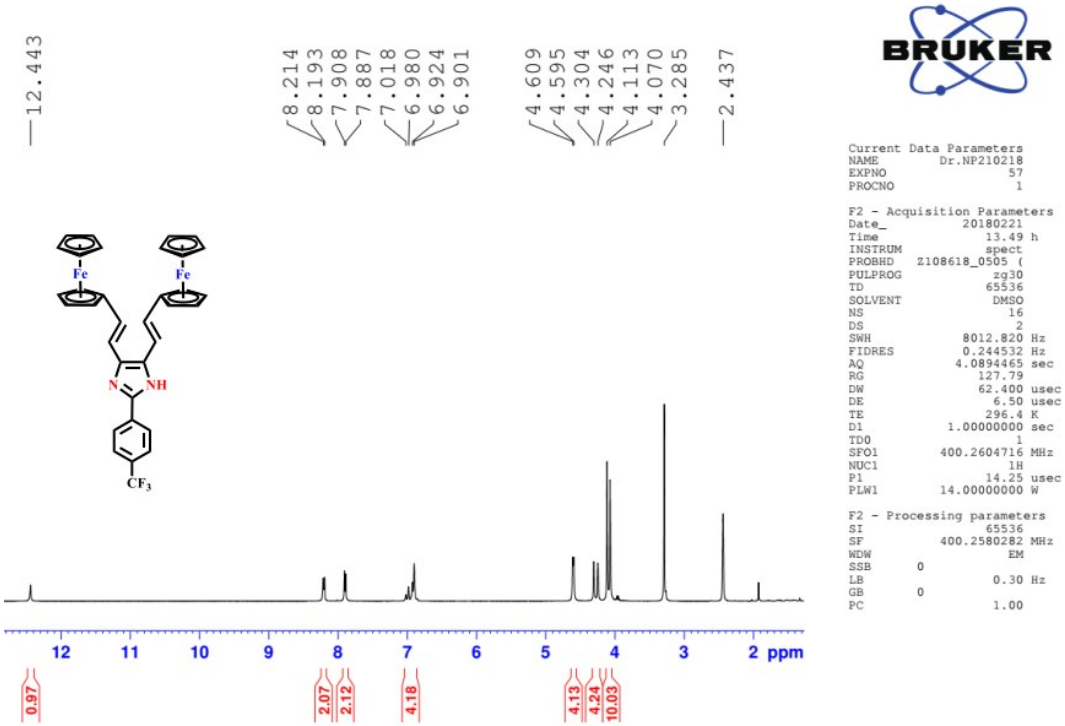


Figure S6. ^{1}H NMR spectrum of compound 3(CF_3) in DMSO-d_6 at 25 °C

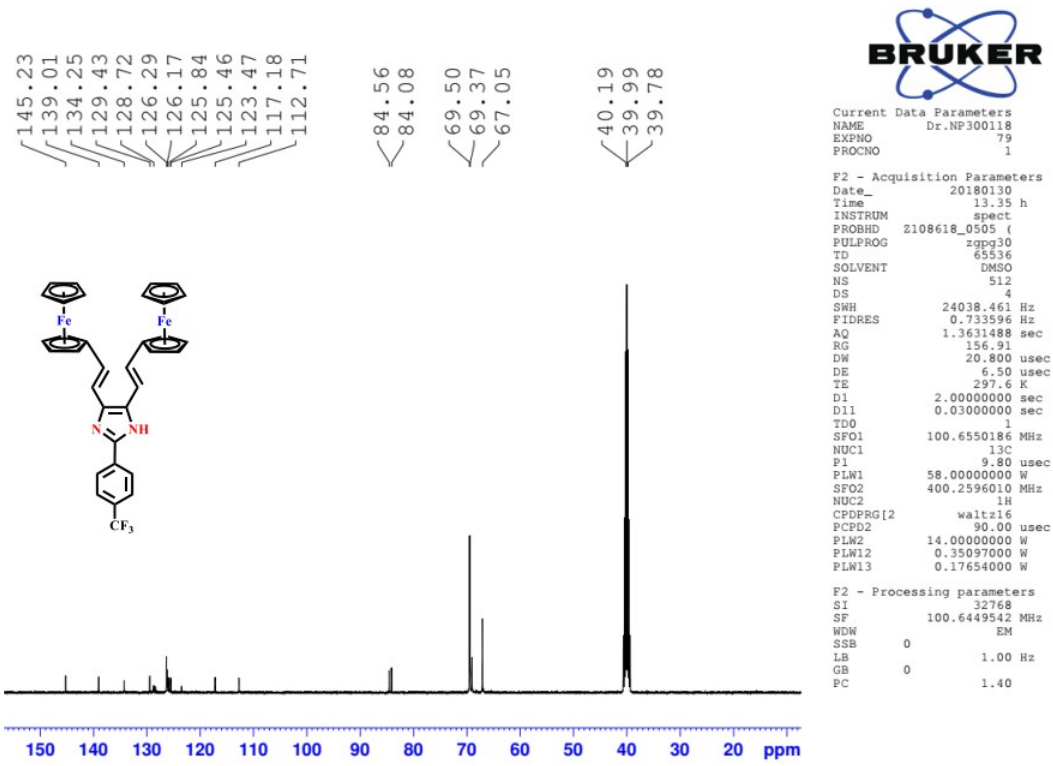


Figure S7. ^{13}C NMR spectrum of compound 3(CF_3) in DMSO-d_6 at 25 °C

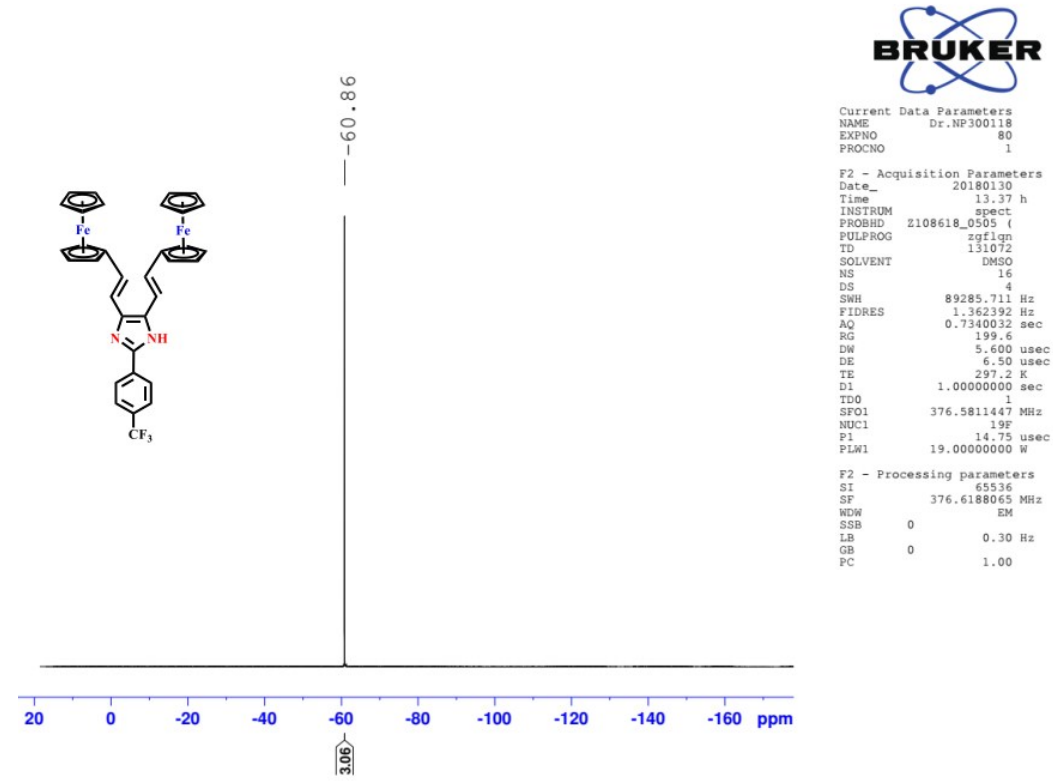


Figure S8. ^{19}F NMR spectrum of compound 3(CF_3) in DMSO-d_6 at 25 °C

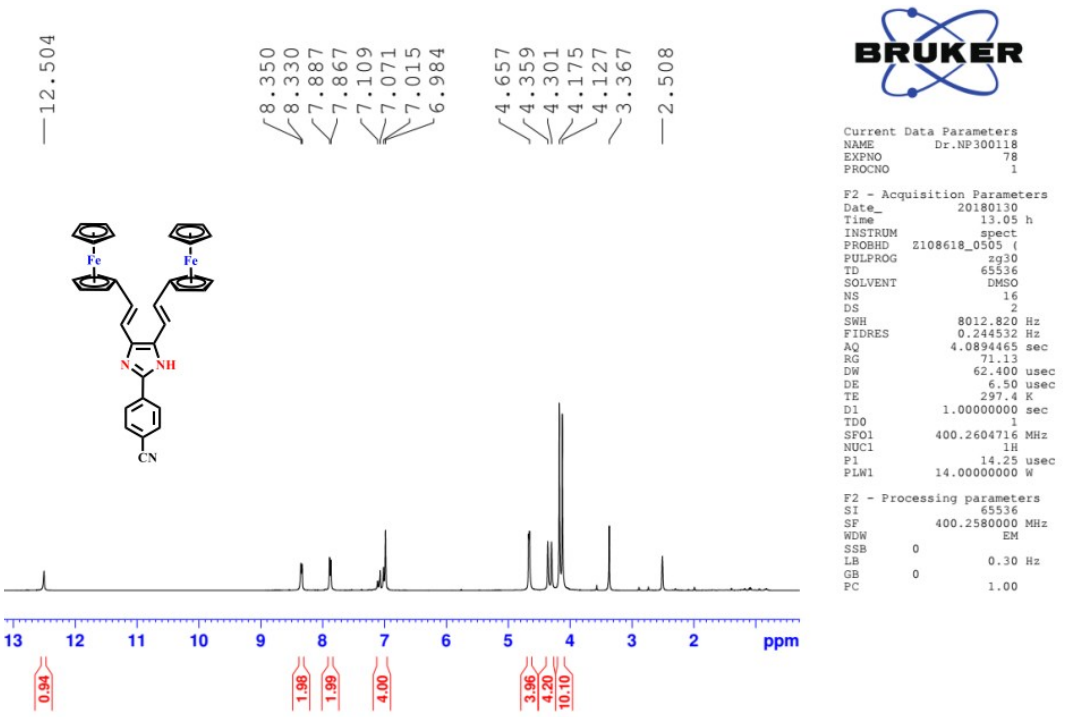


Figure S9. ^{1}H NMR spectrum of compound 4(CN) in DMSO-d_6 at 25 ^{o}C

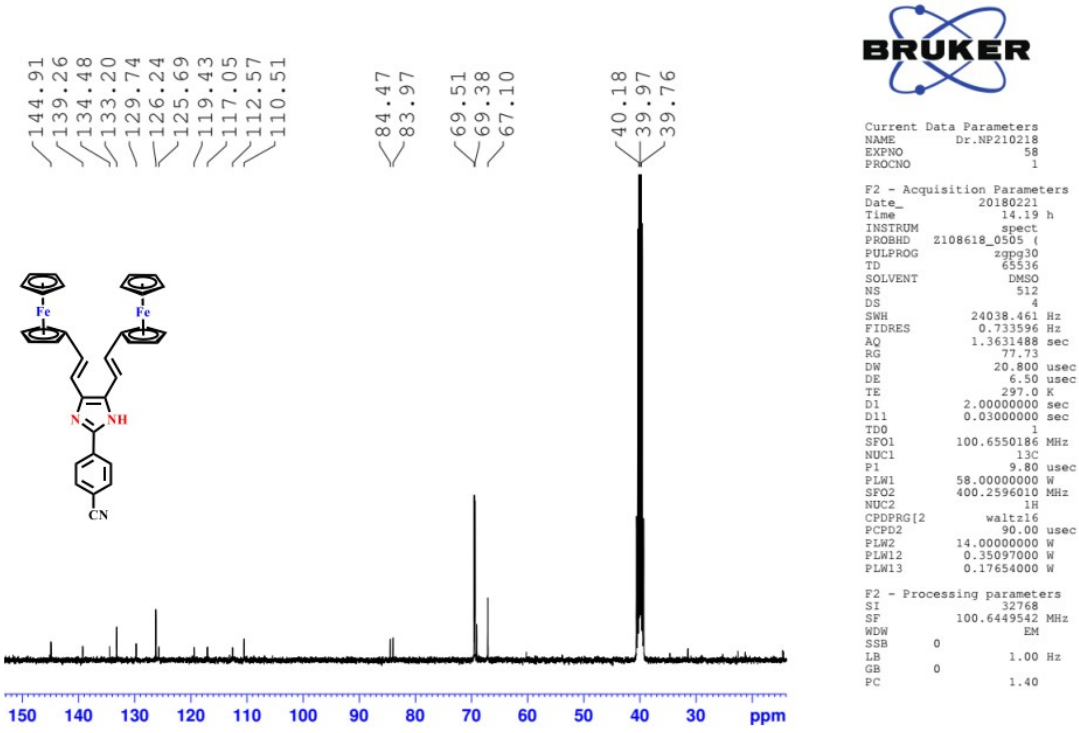


Figure S10. ^{13}C NMR spectrum of compound 4(CN) in DMSO-d_6 at 25 ^{o}C

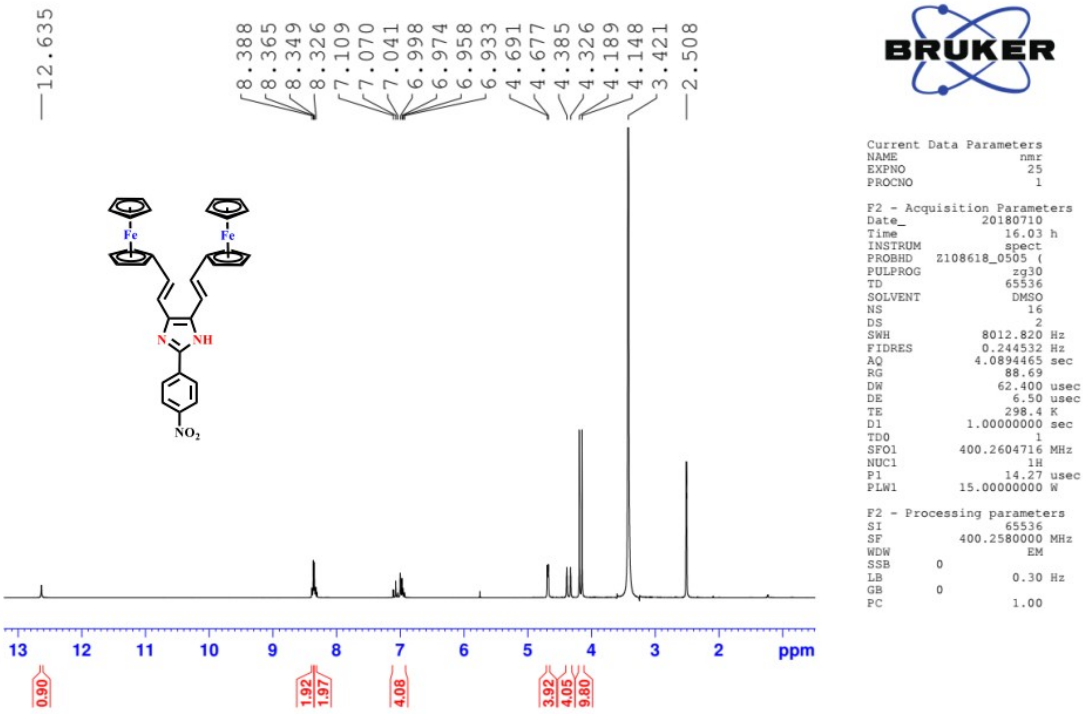


Figure S11. ^{1}H NMR spectrum of compound 5(NO_2) in DMSO-d_6 at 25 °C

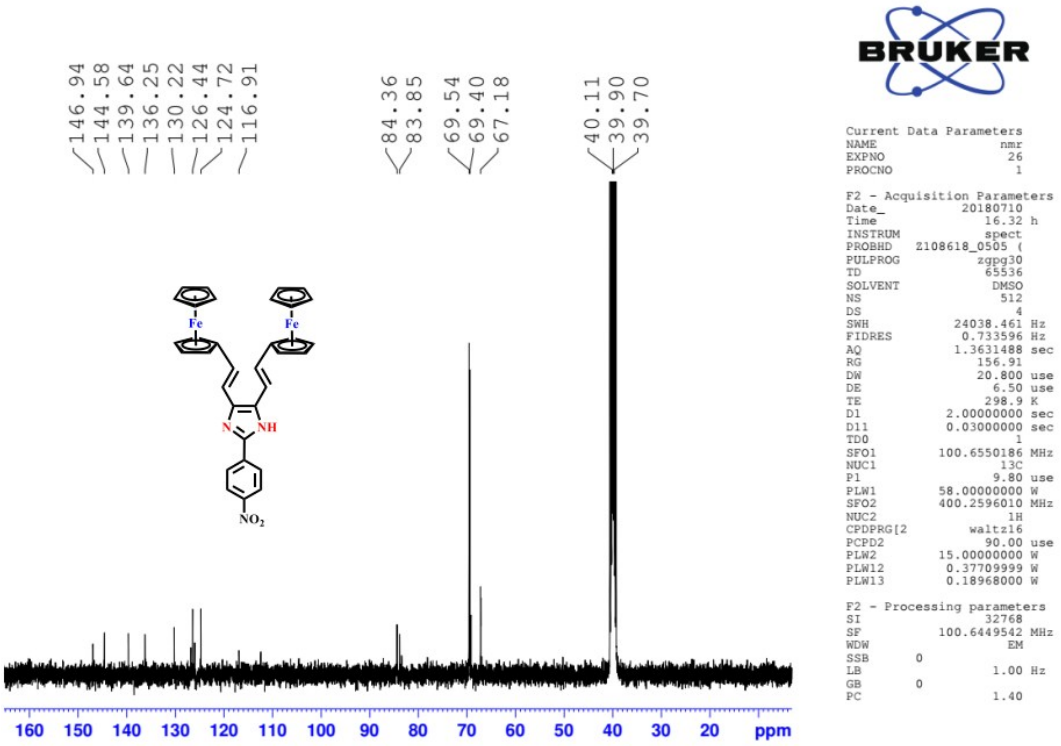


Figure S12. ^{13}C NMR spectrum of compound 5(NO_2) in DMSO-d_6 at 25 °C

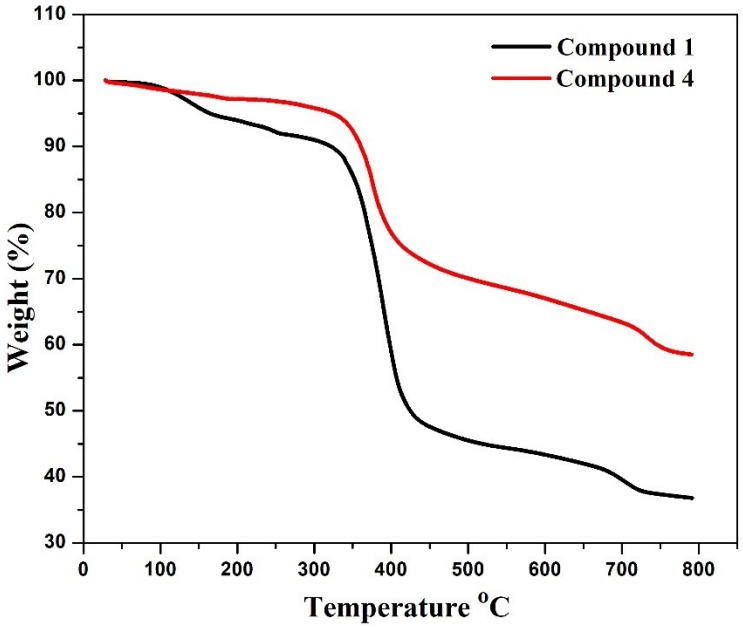


Figure S13. TGA curve of compounds 1(H) and 4(CN)

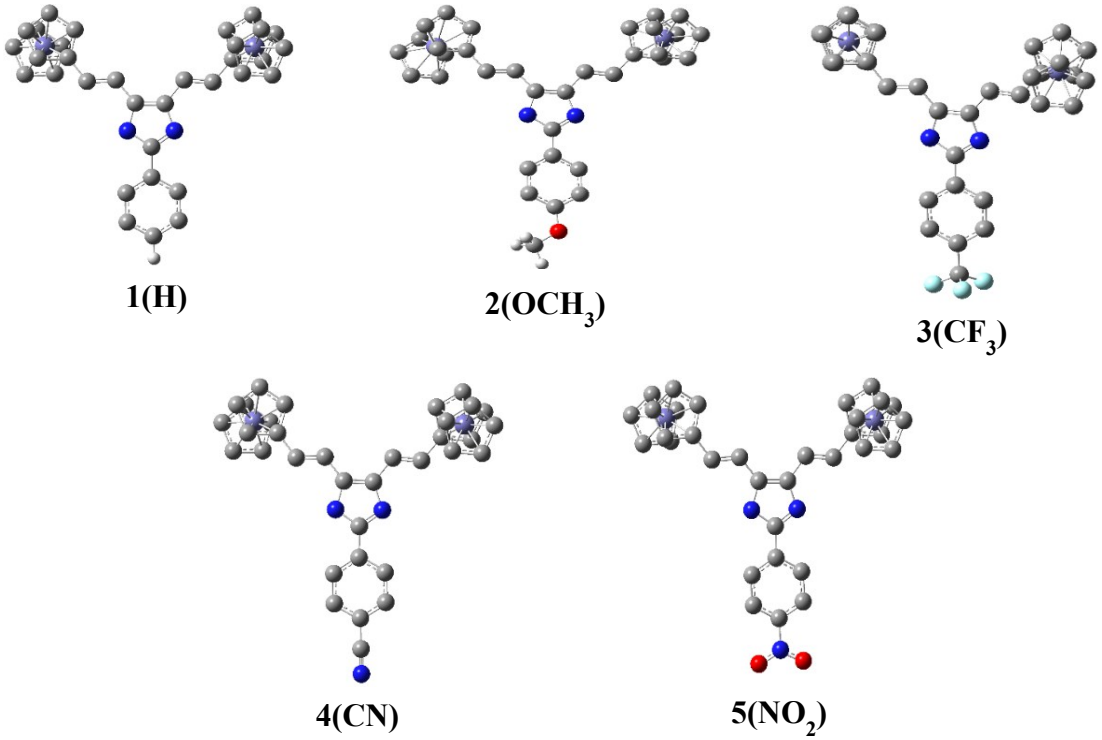


Figure S14. The optimized geometries of chromophores 1-5 obtained at B3LYP/6-31+G level of theory**

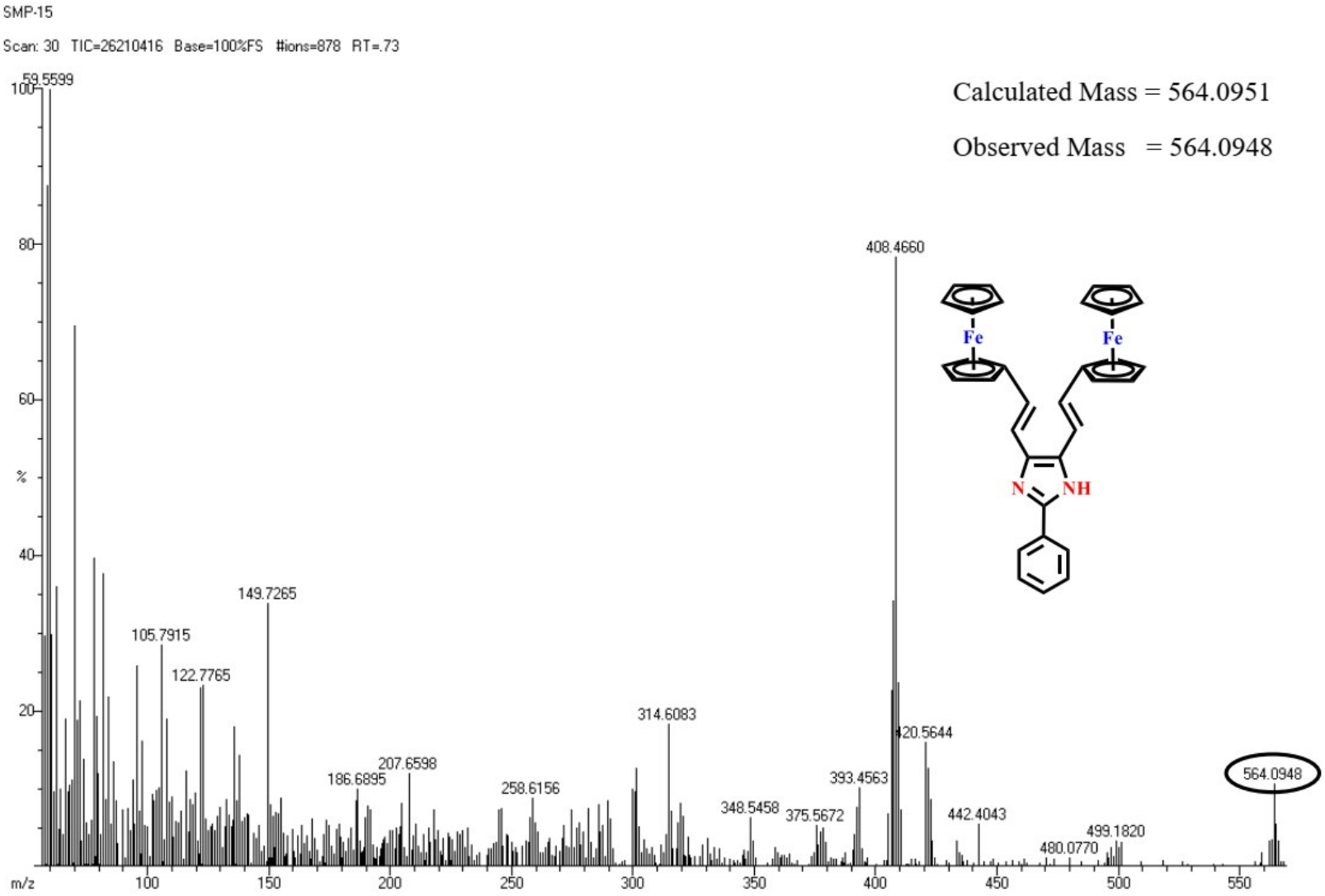


Figure S15. HRMS (EI) spectrum of compound 1(H)

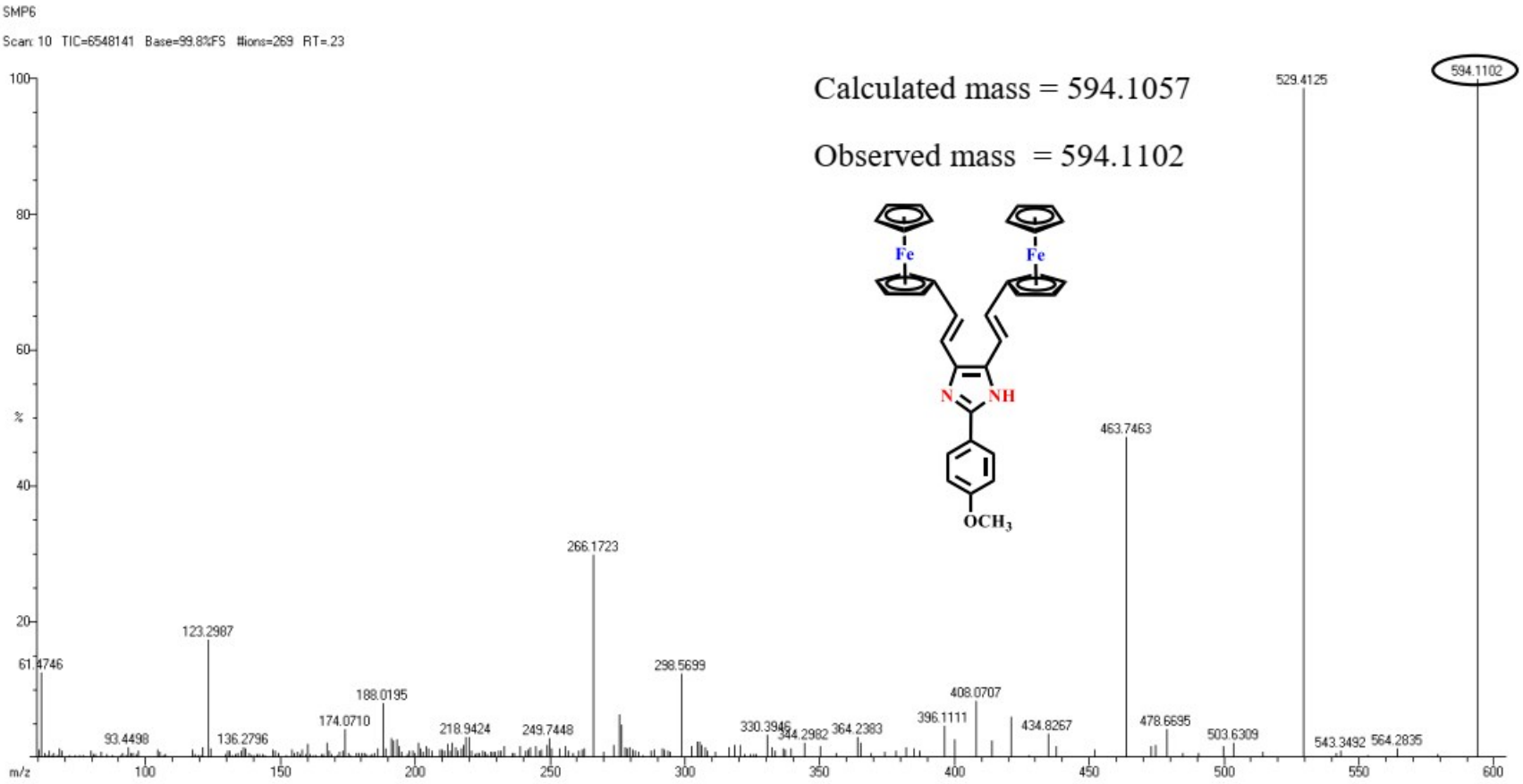


Figure S16. HRMS (EI) spectrum of compound 2(OCH_3)

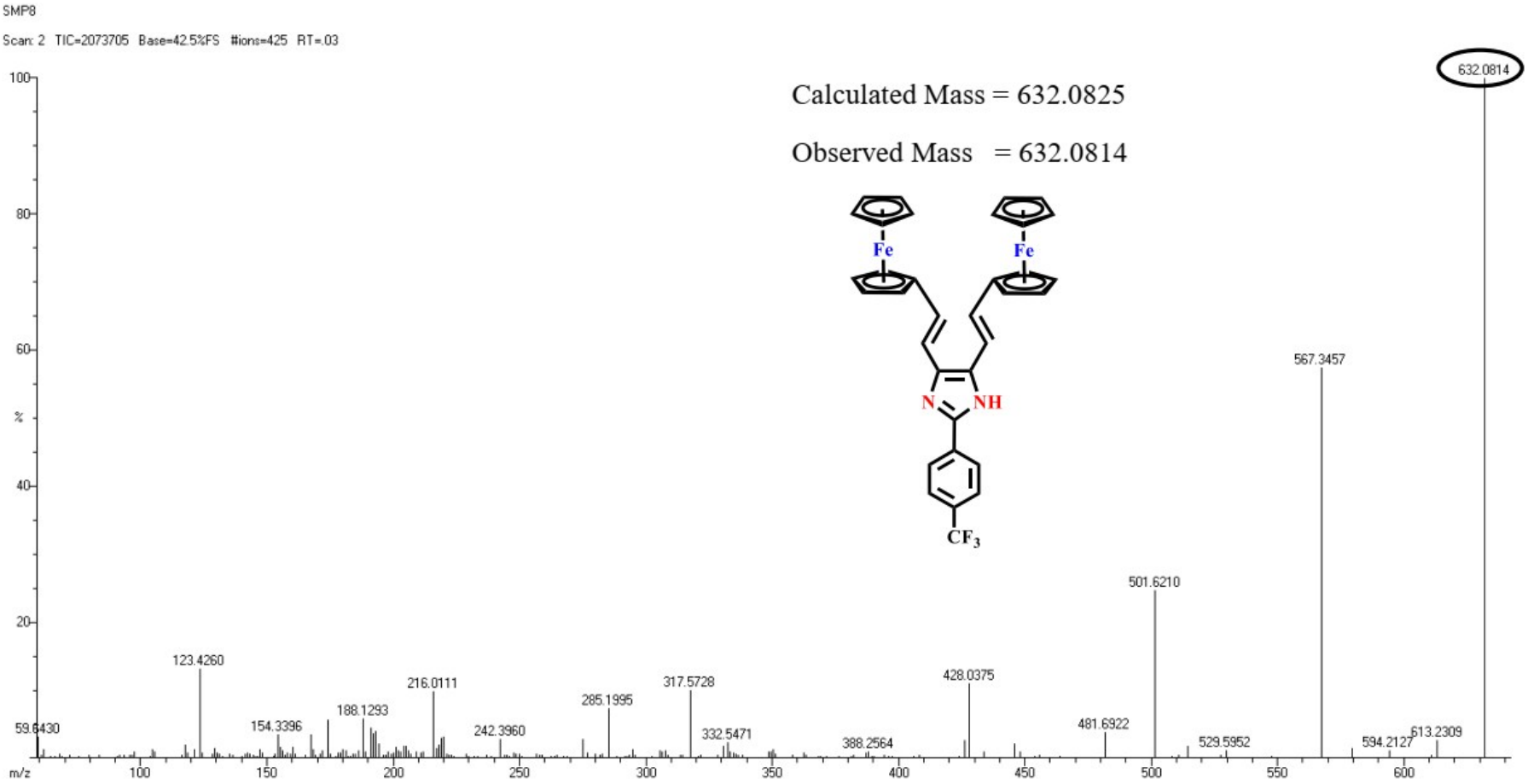


Figure S17. HRMS (EI) spectrum of compound 3(CF_3)

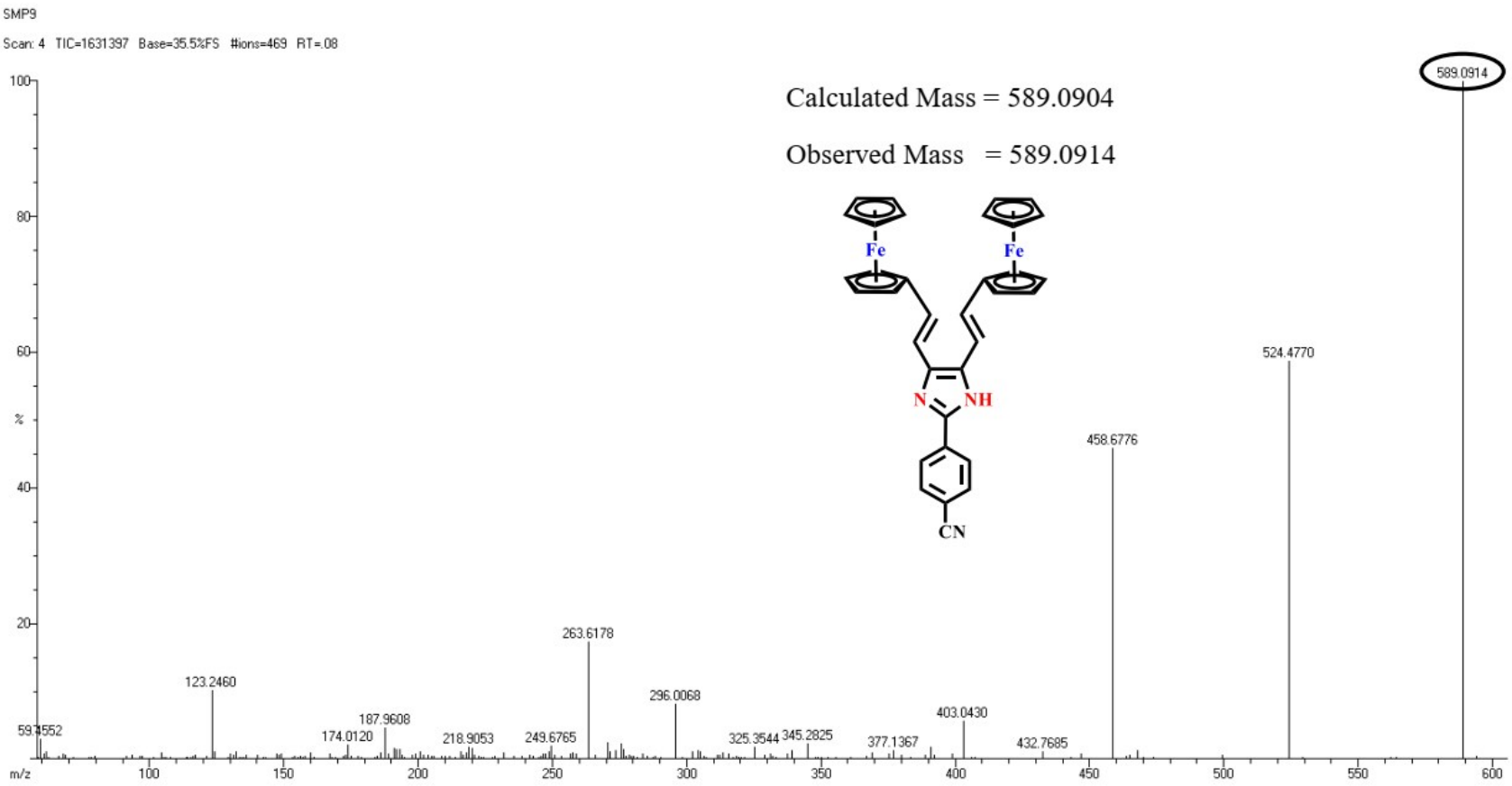


Figure S18. HRMS (EI) spectrum of compound 4(CN)

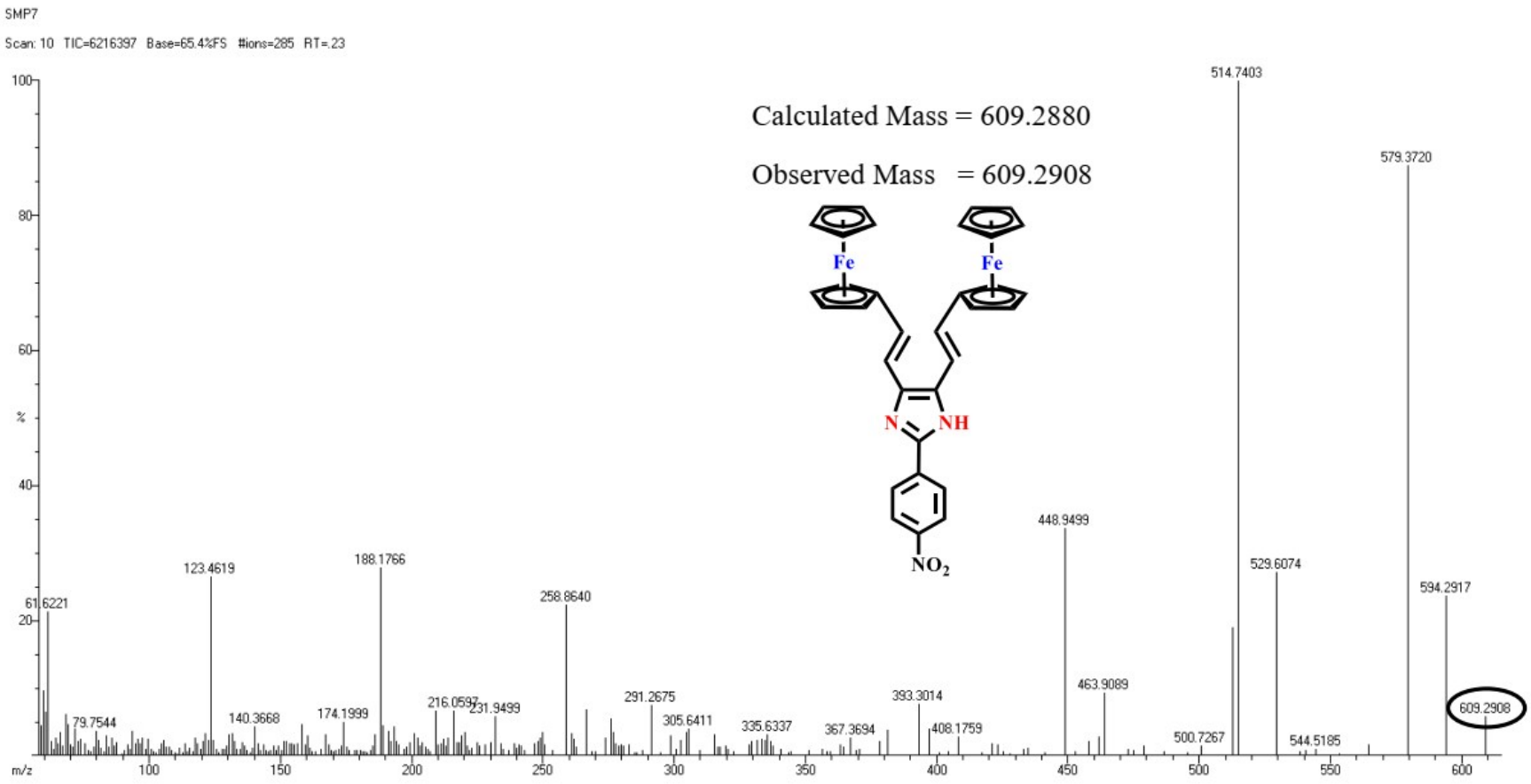


Figure S19. HRMS (EI) spectrum of compound 5(NO_2)

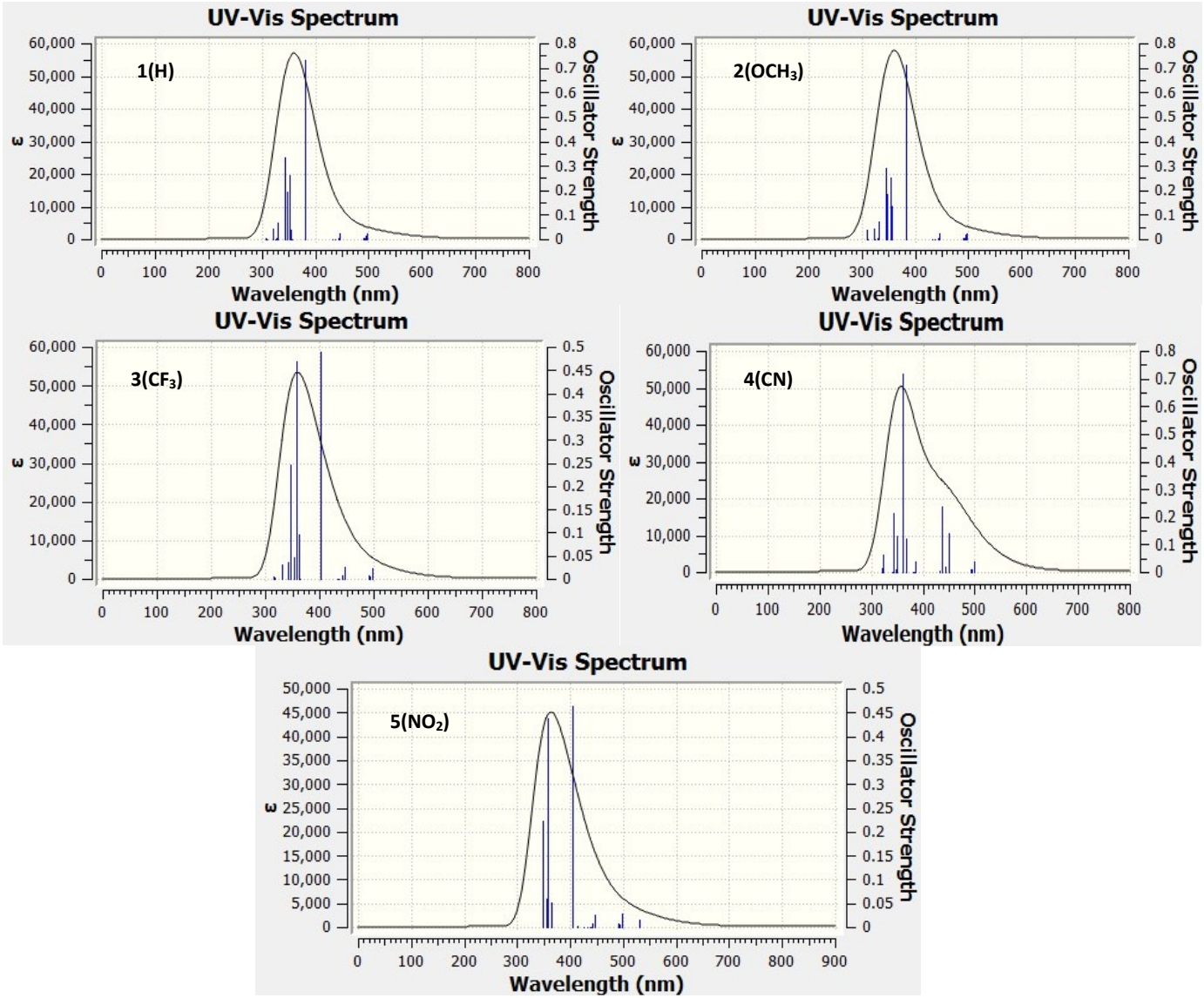


Figure S20. **Theoretically calculated absorption spectra of chromophores 1-5. The absorption spectra were obtained by TD-DFT calculation with B3LYP/6-31+G** level of theory. The spectra were visualized in GaussView 5.0**

Table S1. Crystallographic data and structure refinement parameters of compound **4**

Identification code	**Compound 4.** Methanol
CCDC	1885673
Empirical formula	$C_{35}\ H_{32}\ Fe_2\ N_3\ O_1$
Formula weight	621.33
Temperature, K	298
Wavelength, Å	0.71073
Crystal System	Orthorhombic
Space group	Pbca
Unit cell dimensions	a =21.827(2)Å b = 11.6814(10)Å c = 22.747(2)Å $\alpha = 90^o$ $\beta = 90^o$ $\gamma = 90^o$
Volume	5799.8(9) A^3
Z	8
Calculated density (Mg/m^3)	1.425
Absorption coefficient (mm^{-1})	1.034
F (000)	2576.0
Crystal size **(**mm^3)	0.32 x 0.25 x 0.16
Theta range for data collection (^{o})	1.79 to 28.51
Reflections collected	45309
Completeness to theta = 25.242	99.0 %
Max. and min. transmission	0.741 and 0.848
Goodness-of-fit on F^2	0.863
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma\ (I)$]	$R_1 = 0.0550$, $wR_2 = 0.1634$
R indices (all data)	$R_1 = 0.1330$, $wR_2 = 0.1884$

Table S2. Cyclic voltammetry data and experimental HOMO, LUMO and optical band gap

Chromophores	E_{pa} (mV)[a]	E_{pc} (mV)[a]	i_{pc}/i_{pa}	$E_{1/2}$ (mV)[a]	ΔE (mV)[a]	E_{HOMO} (eV)[a]	E_{LUMO} (eV)[a]	λ^{onset} (nm)[b]	E_g optical (eV)[c]
Compound 1	578	439	1.3	797	139	-5.07	-1.81	380	3.26
Compound 2	615	490	1.5	860	125	-5.09	-1.81	378	3.28
Compound 3	570	420	1.2	780	150	-5.05	-1.85	387	3.20
Compound 4	517	403	1.2	718	114	-5.00	-1.80	387	3.20
Compound 5	491	408	0.8	685	083	-4.97	-1.89	402	3.08

[a]Calculated as HOMO and LUMO level obtained from cyclic voltammetry using E_{HOMO} = -e ($E_{ox}^{onset} + 4.4$). $E^{optical}$ onset values obtained from oxidation peak in cyclic voltagram. $E_{LUMO} = E_{g}^{optical} + E_{HOMO}$

[b]Calculated as λ^{onset} values from absorption spectra in CH_2Cl_2 solvent.

[c]Calculated as optical band gap calculated from absorption onset/edge using the equation e ($E_{g}^{optical}$) = 1240/λonset.

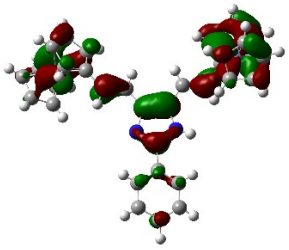
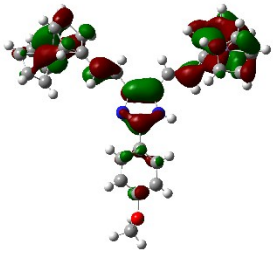
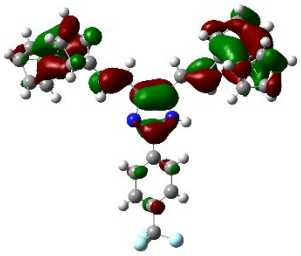
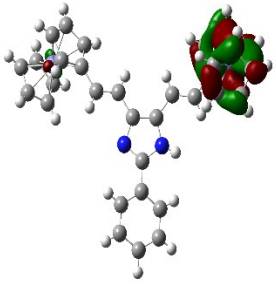
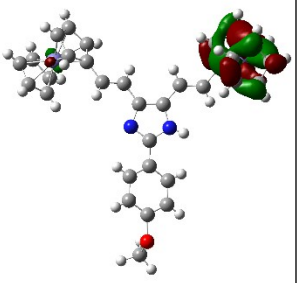
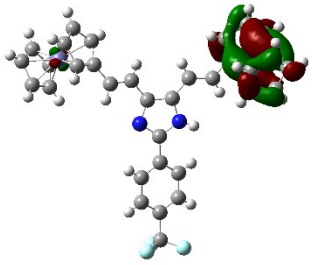
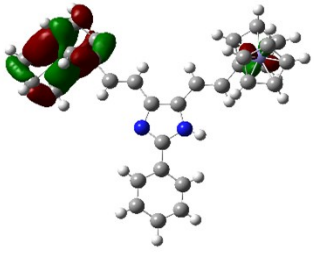
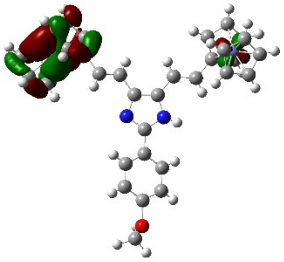
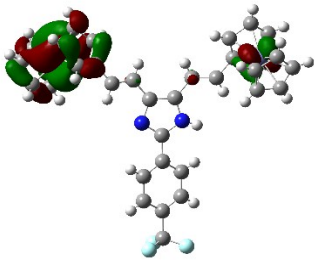
Table S3. Selected transitions obtained from TD-DFT calculation with B3LYP/6-31+G** level theory

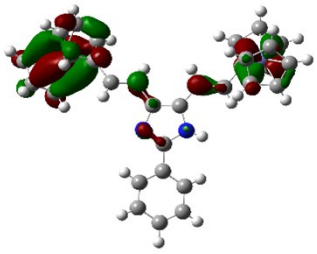
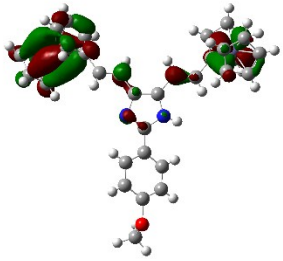
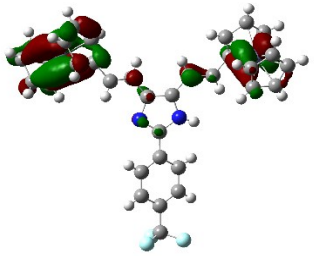
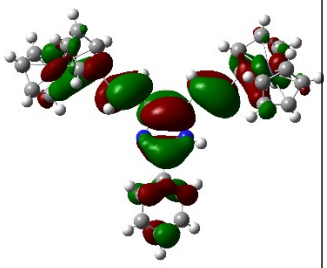
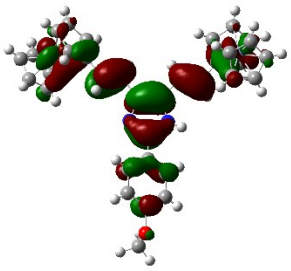
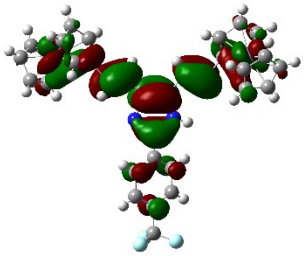
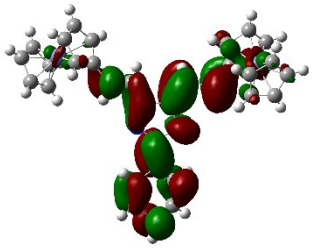
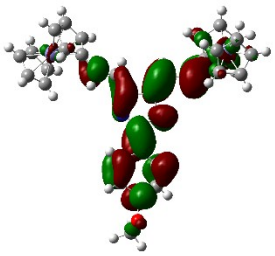
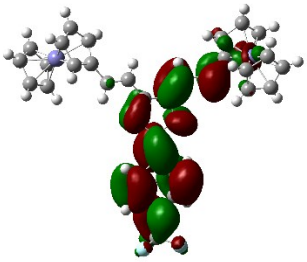
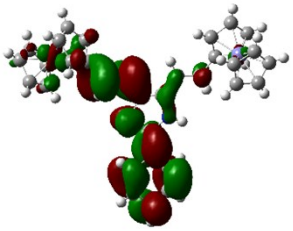
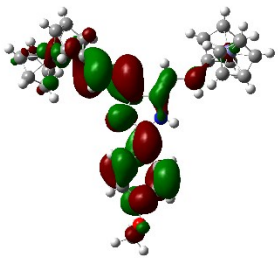
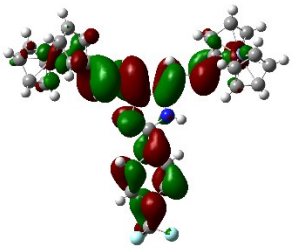
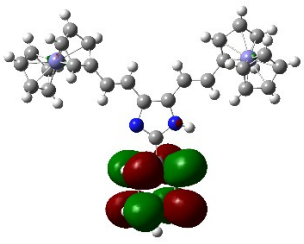
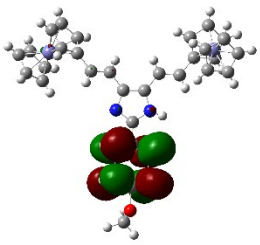
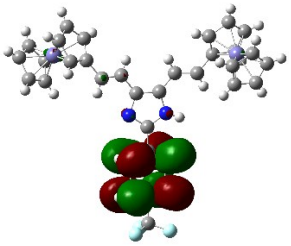
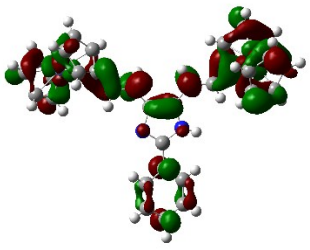
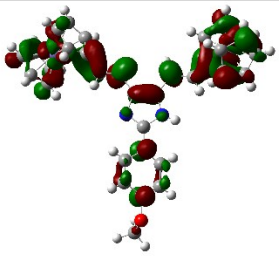
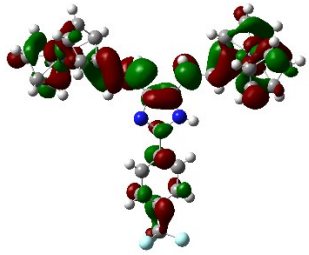
Entry	λ (nm)	Oscillator strength, *f*	Energy (eV)	Selected Major Transitions[a]
1 (H)	380	0.7314	3.25	H → L (85%)
	352	0.2626	3.51	H → L+1 (38%)
	347	0.1952	3.56	H-2 → L (24%), H → L+1 (18%), H-5 → L+6 (17%)
	330	0.0679	3.74	H-1 → L (53%)
	321	0.0420	3.85	H-4 → L (53%)
	445	0.0222	2.71	H-3 → L+5 (29%), H-6 → L+4 (14%)
2 (OCH_3)	382	0.7112	3.23	H → L (85%)
	344	0.2913	3.59	H → L+2 (18%)
	353	0.2518	3.50	H → L+2 (30%)
	347	0.1853	3.56	H-2 → L (24%), H-5→ L+6 (16%), H → L+1 (15%)
	332	0.0745	3.72	H-1 → L (53%)
	322	0.0450	3.84	H-4 → L (52%)
	310	0.0377	3.99	H → L+2 (91%)
3 (CF_3)	401	0.4888	3.08	H → L (89%)
	357	0.4683	3.46	H → L+1 (51%), H-1 → L (14%)
	346	0.2454	3.57	H-4 → L (32%), H-2 → L (25%)
	362	0.0963	3.42	H-1 → L (28%), H-3 → L+5 (13%)
	352	0.0464	3.51	H-2 → L (62%)
	342	0.0375	3.61	H-3 → L+1 (31%), H-5 → L+6 (15%)
	331	0.0300	3.74	H-4 → L (31%)
	445	0.0260	2.78	H-3 → L+5 (30%)
4 (CN)	360	0.7159	3.44	H → L+1 (65%)
	436	0.2386	2.84	H → L (50%)
	449	0.1413	2.76	H-3 → L+5 (30%), H → L+1 (26%), H-6 → L+8 (12%)
	350	0.1308	3.54	H-1 → L+1 (31%), H-2 → L+6 (11%)

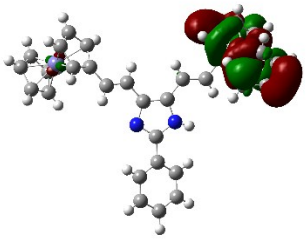
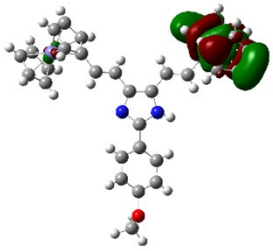
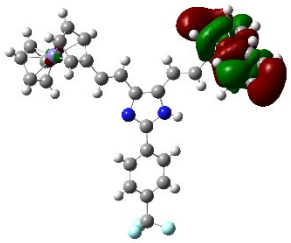
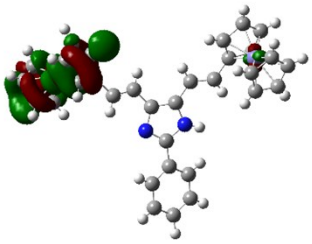
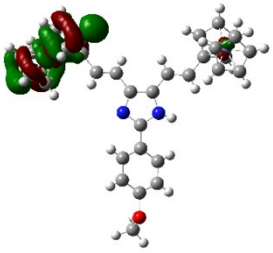
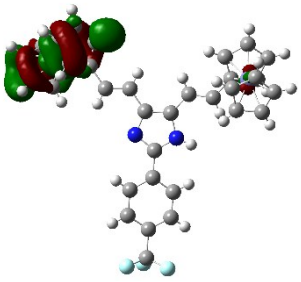
	368	0.1228	3.36	H-4 → L (74%)
	322	0.0619	3.84	H → L+2 (93%)
	498	0.0222	2.48	H-3 → L+3 (40%)
	321	0.0152	3.85	H-1 → L+1 (40%)
5 (NO_2)	404	0.4633	3.06	H → L+1 (89%)
	358	0.4372	3.45	H → L+2 (51%)
	347	0.2233	3.56	H-5 → L (32%)
	349	0.1743	3.55	H-4 → L+1 (31%)
	355	0.0584	3.48	H-2 → L+1 (64%)
	497	0.0290	2.49	H-3 → L+6 (30%)
	446	0.0260	2.77	H-3 → L+7 (30%), H-5 → L+10 (14%)

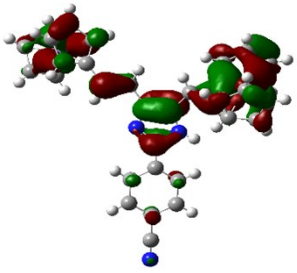
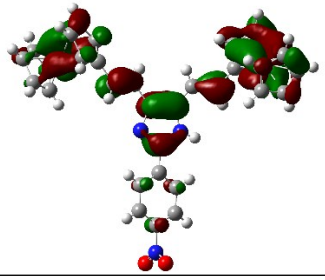
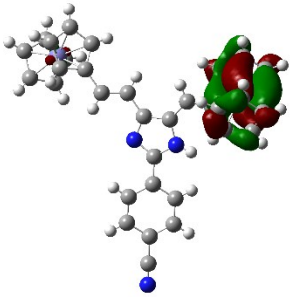
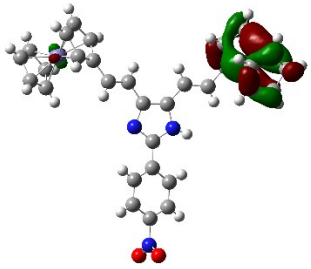
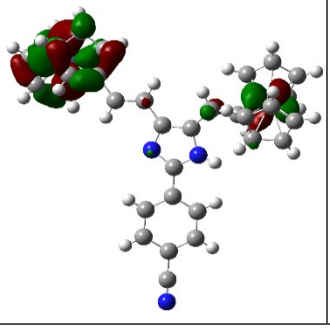
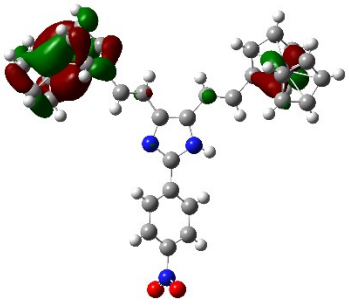
[a] H = HOMO; L = LUMO; only contributions above 10% are included.

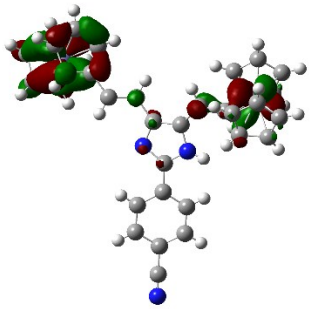
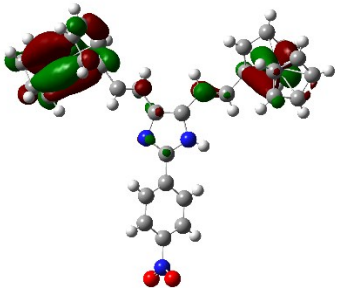
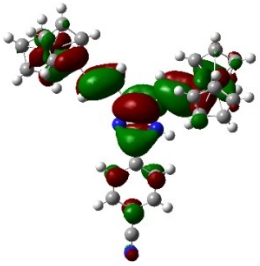
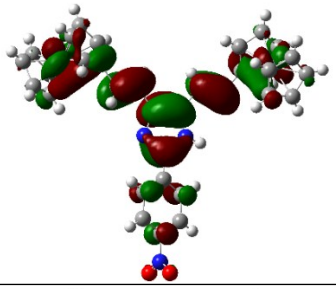
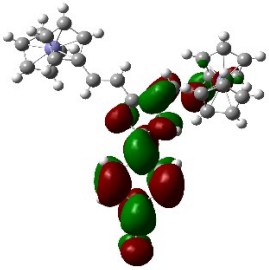
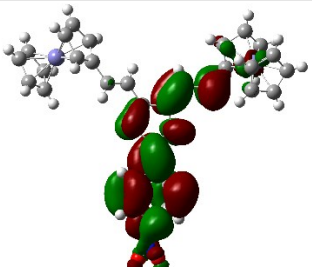
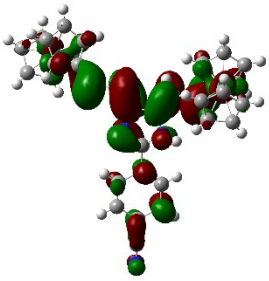
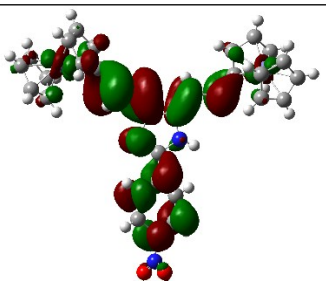
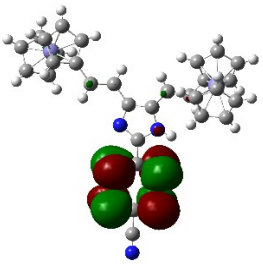
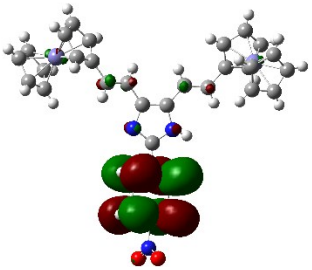
Table S4. Density surfaces of the frontier orbitals involved in electronic transitions of chromophores **1-5** which is derived from B3LYP/6-31+G** level of theory using isosurface value of 0.02 au.

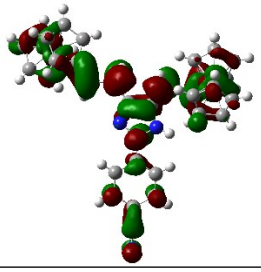
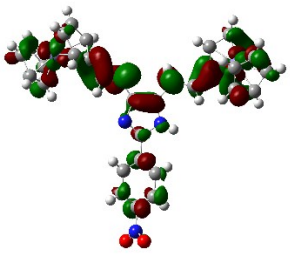
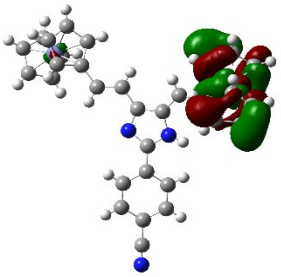
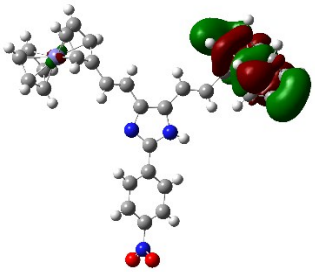
Orbitals	Compound 1	Compound 2	Compound 3
HOMO-4			
HOMO-3			
HOMO-2			

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

LUMO+4			
LUMO+5			

Orbitals	Compound 4	Compound 5
HOMO-4		
HOMO-3		
HOMO-2		

HOMO-1		
HOMO		
LUMO		
LUMO+1		
LUMO+2		

LUMO+3		
LUMO+4		
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