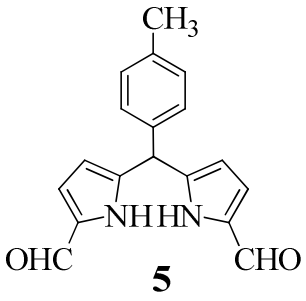
3, 5-Diformyl-Borondipyrromethenes as Fluorescent pH sensors

Sheri Madhu[a], Malakalapalli Rajeswara Rao[a], Mushtaque S. Shaikh[b] and Mangalampalli Ravikanth[a*]

[a]Department of Chemistry, Indian Institute of Technology, Bombay, Powai, Mumbai 400 076, India. E-mail: ravikanth@chem.iitb.ac.in

[b]Department of Pharmaceutical Chemistry, Bombay College of Pharmacy, Santacruz (E), Mumbai-400 098, India.



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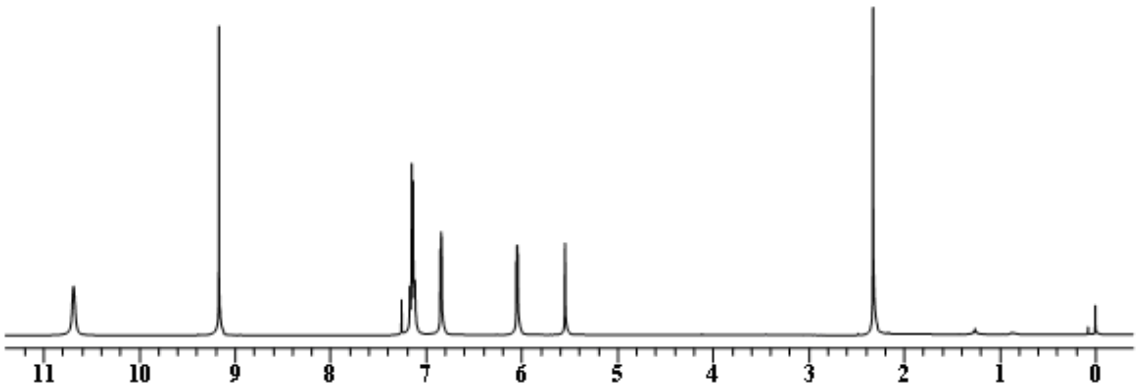
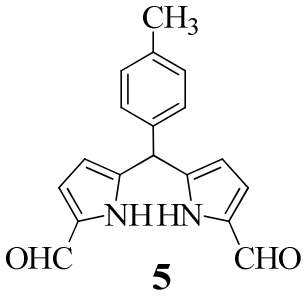


Figure S1: ^{1}H NMR spectrum of compound **5** recorded in $CDCl_3$



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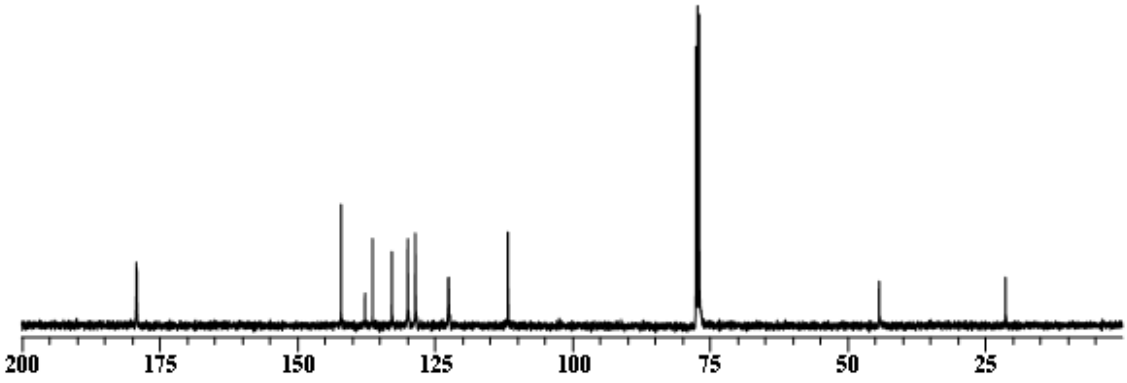
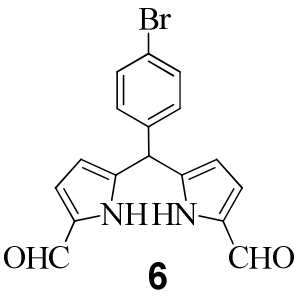


Figure S2: ^{13}C NMR spectrum of compound **5** recorded in $CDCl_3$



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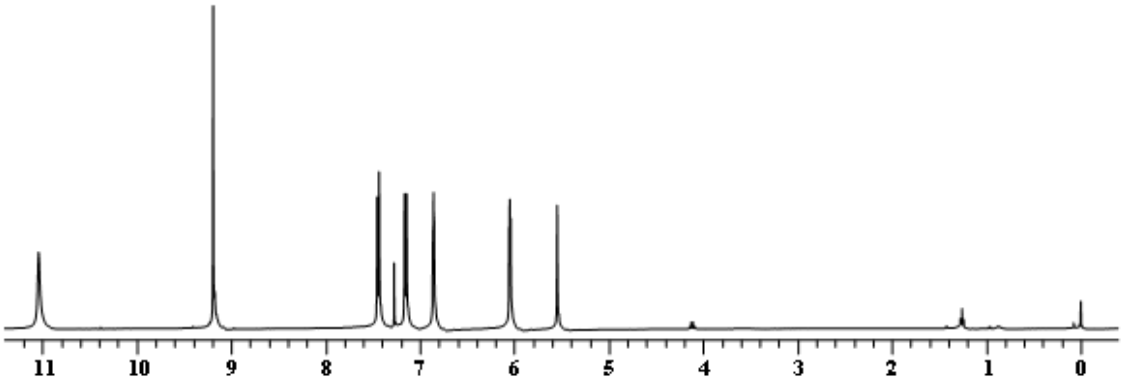


Figure S3: ^{1}H NMR spectrum of compound **6** recorded in $CDCl_3$

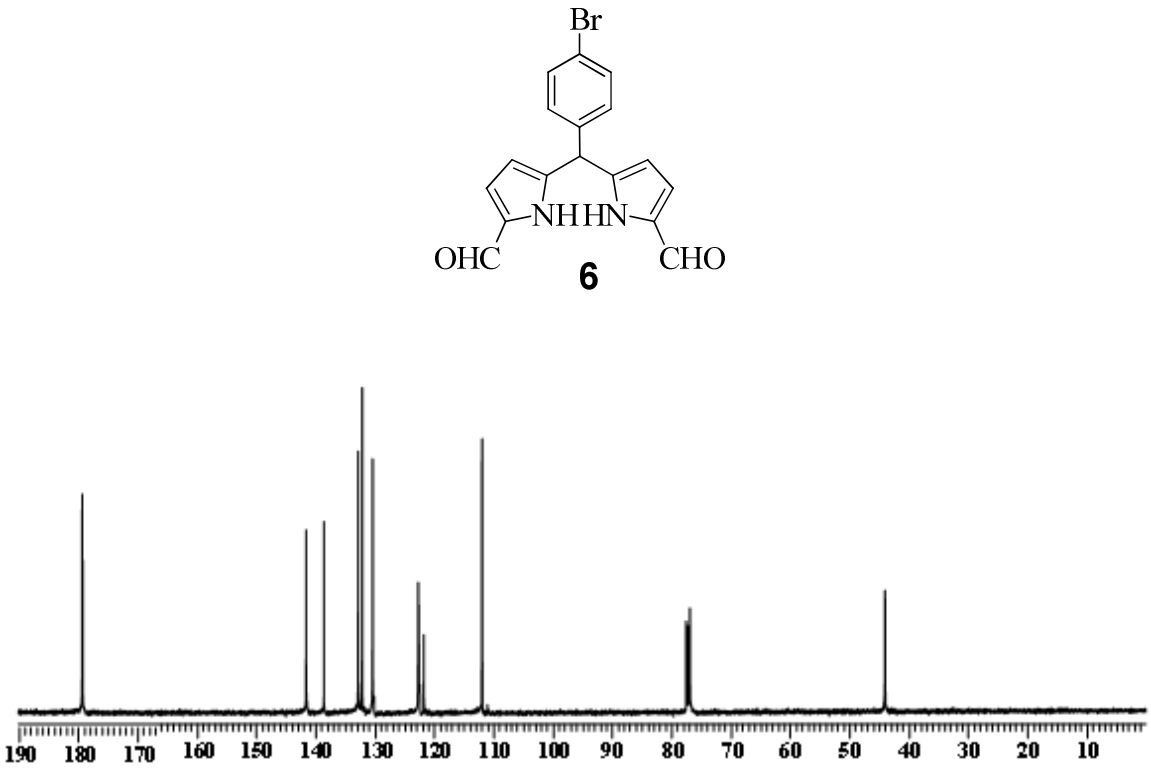


Figure S4: ^{13}C NMR spectrum of compound **6** recorded in $CDCl_3$

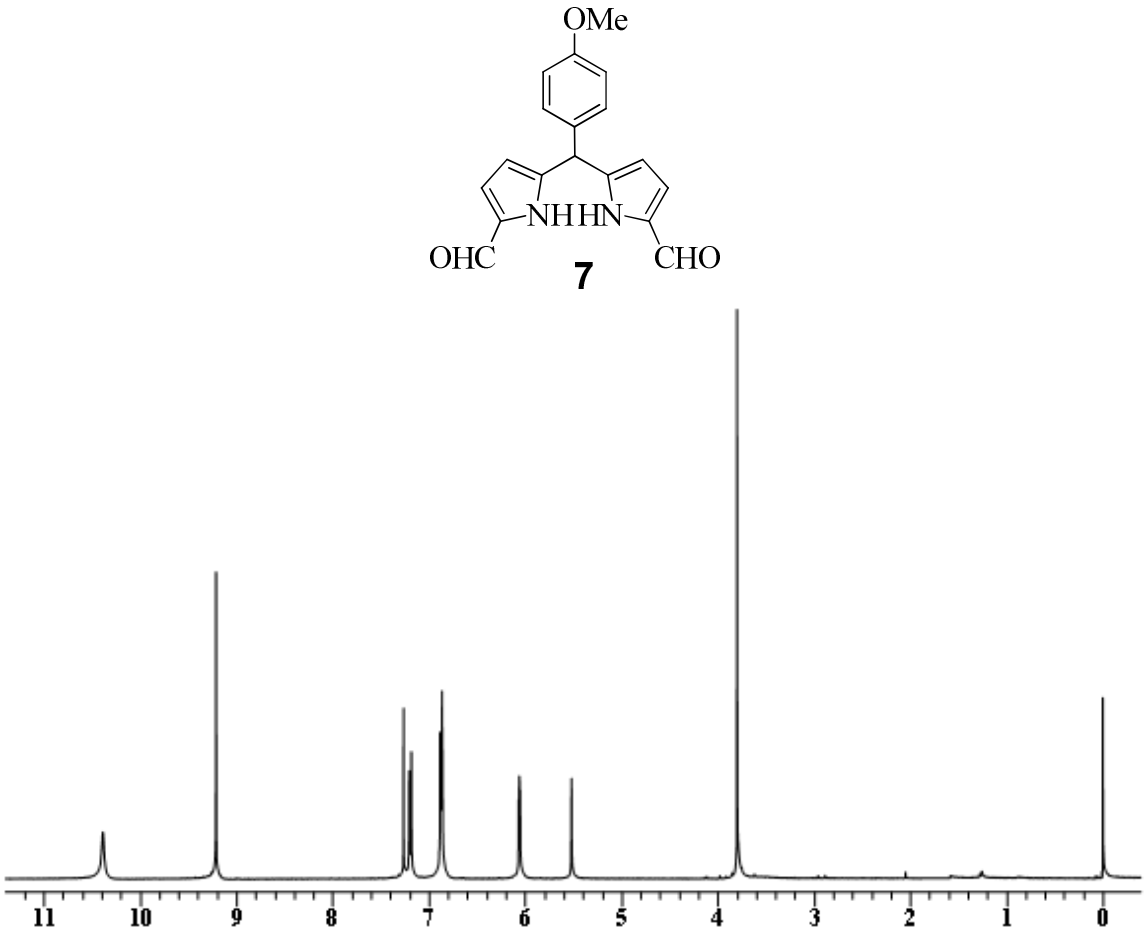
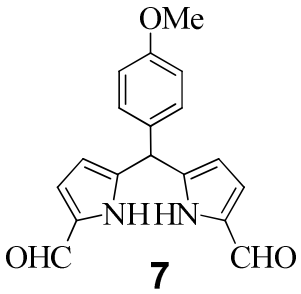


Figure S5: ^{1}H NMR spectrum of compound **7** recorded in $CDCl_3$



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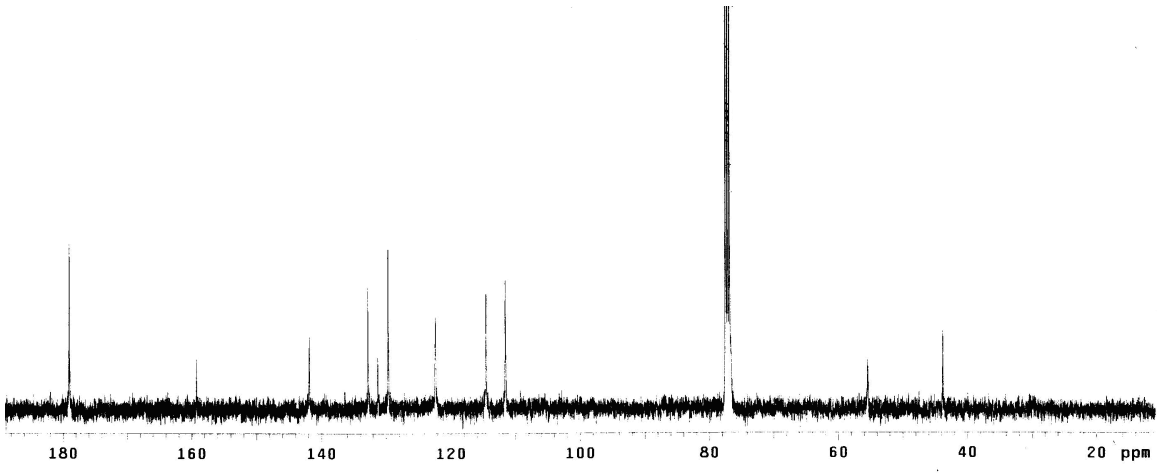


Figure S6: ^{13}C NMR spectrum of compound **7** recorded in $CDCl_3$

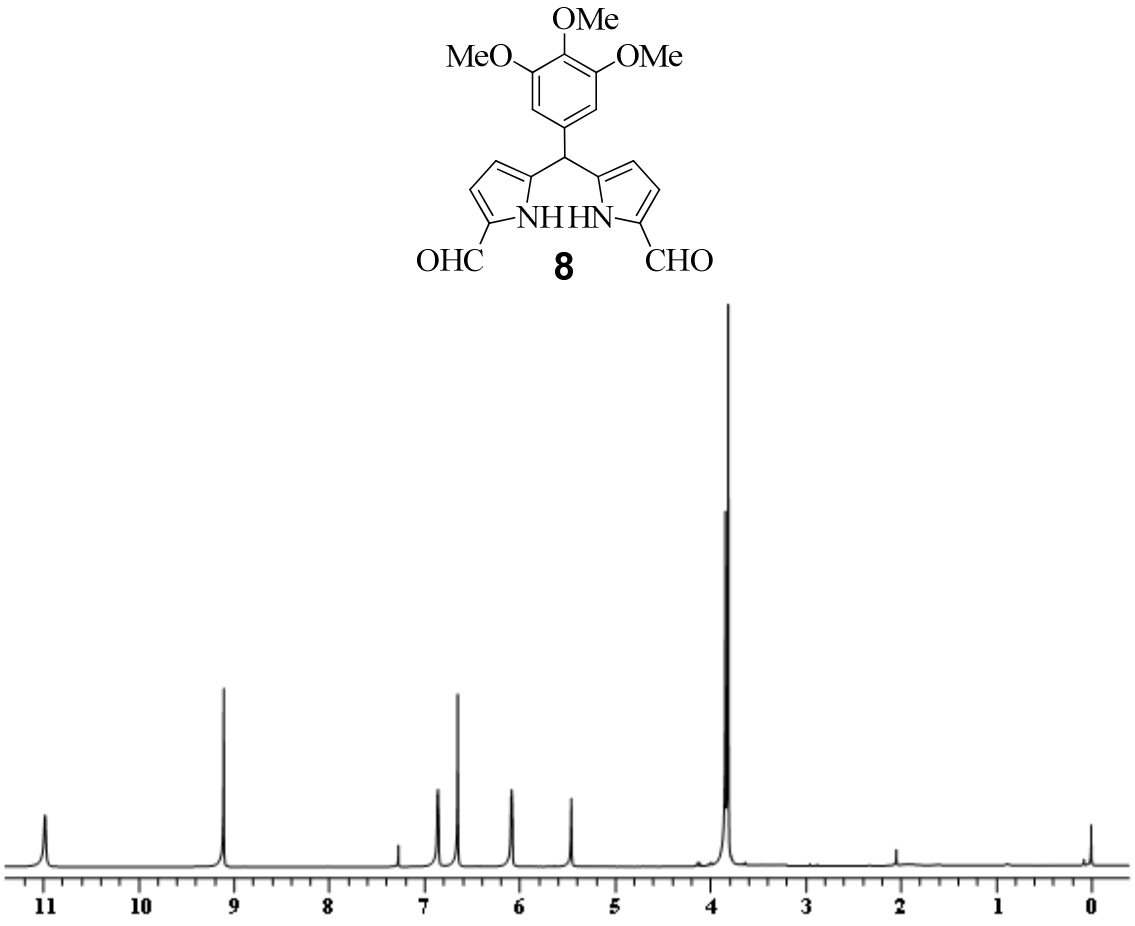


Figure S7: ^{1}H NMR spectrum of compound **8** recorded in $CDCl_3$

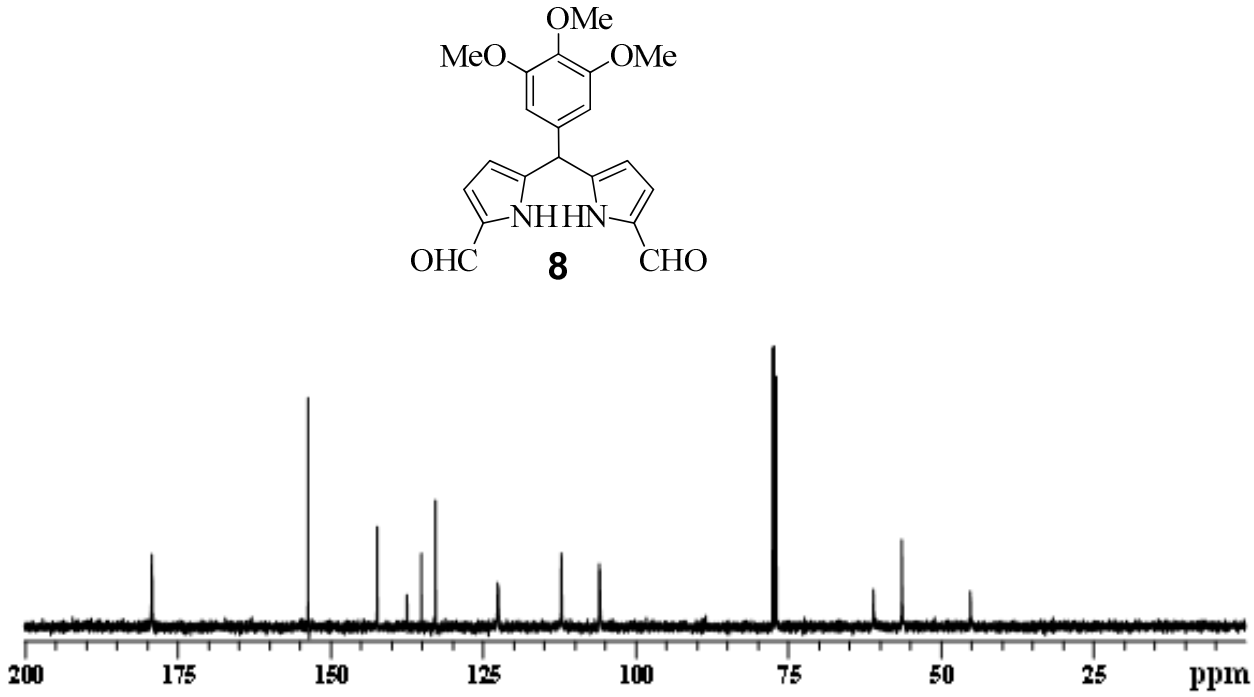
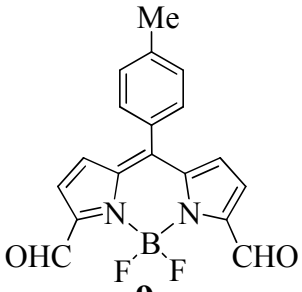


Figure S8: ^{13}C NMR spectrum of compound **8** recorded in $CDCl_3$



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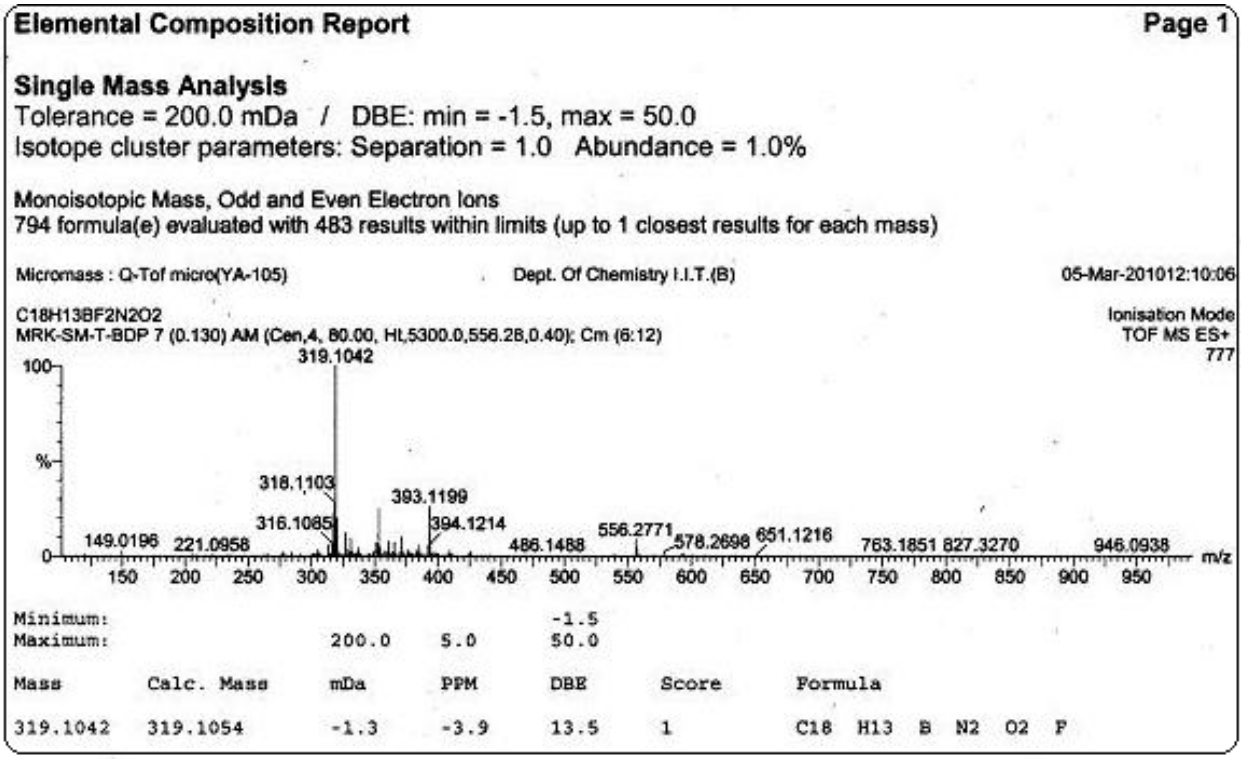
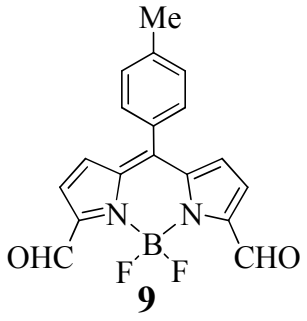


Figure S9: HRMS spectrum of compound **9**



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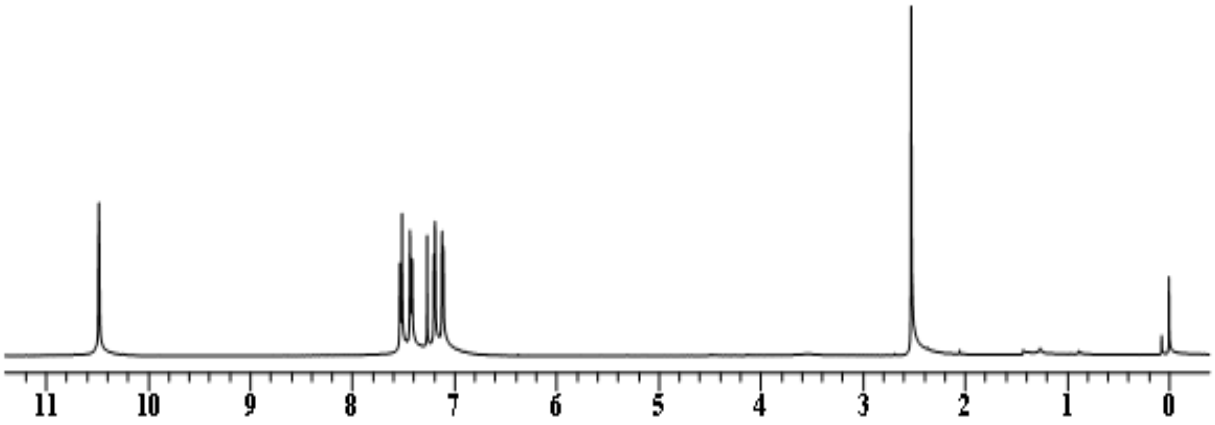
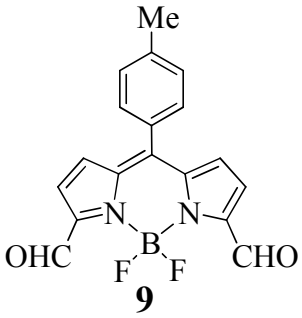


Figure S10: ^{1}H NMR spectrum of compound **9** recorded in $CDCl_3$



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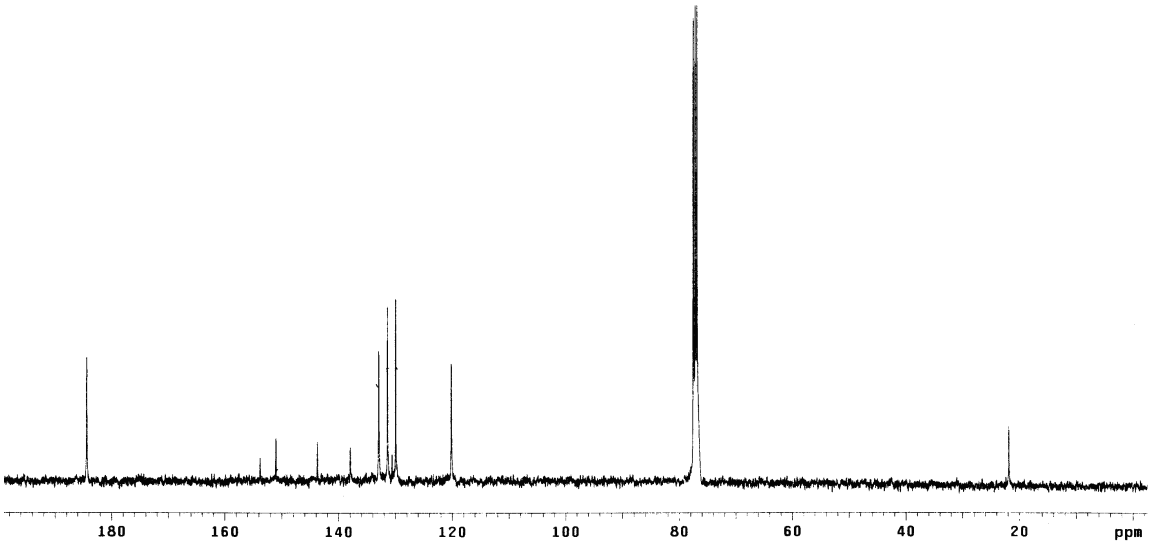
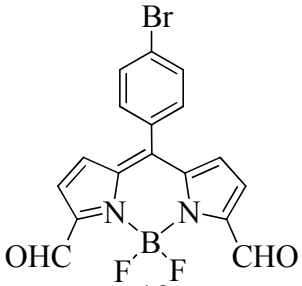


Figure S11: ^{13}C NMR spectrum of compound **9** recorded in $CDCl_3$



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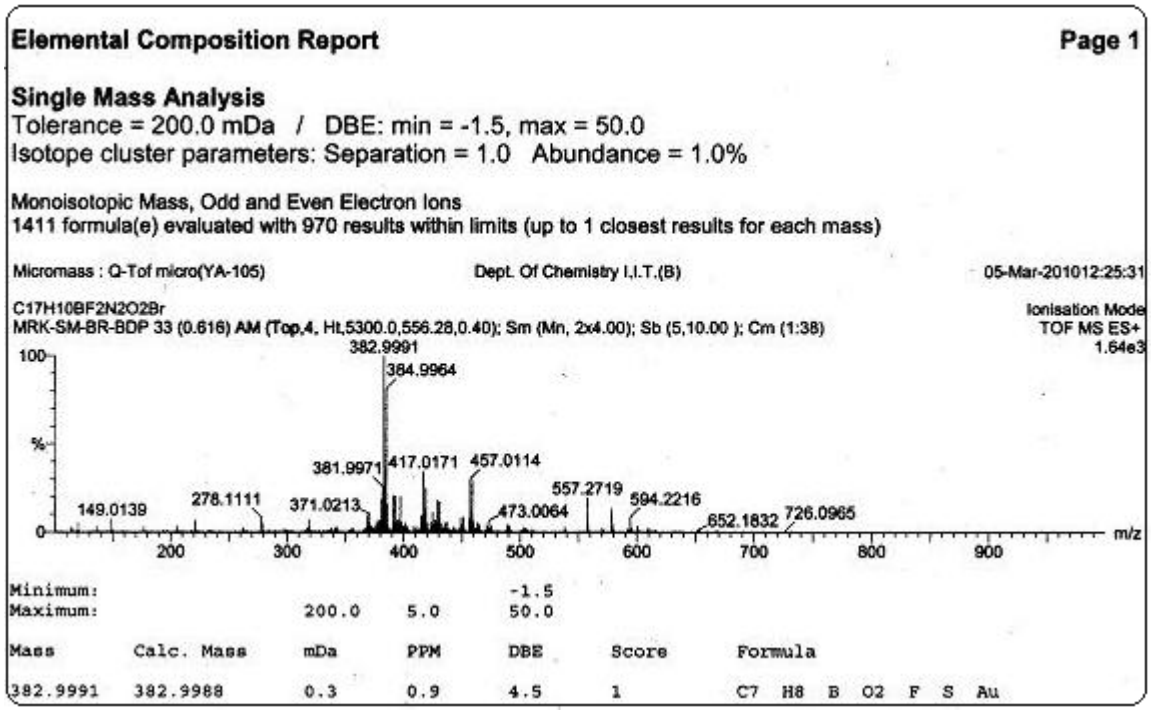
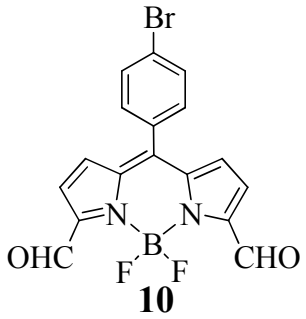


Figure S12: HRMS spectrum of compound **10**



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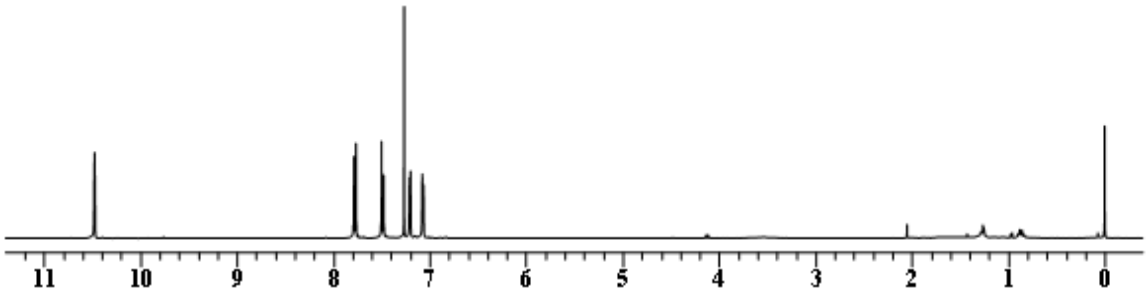
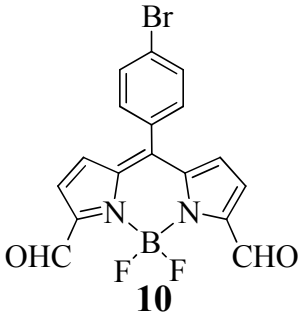


Figure S13: ^{1}H NMR spectrum of compound **10** recorded in $CDCl_3$



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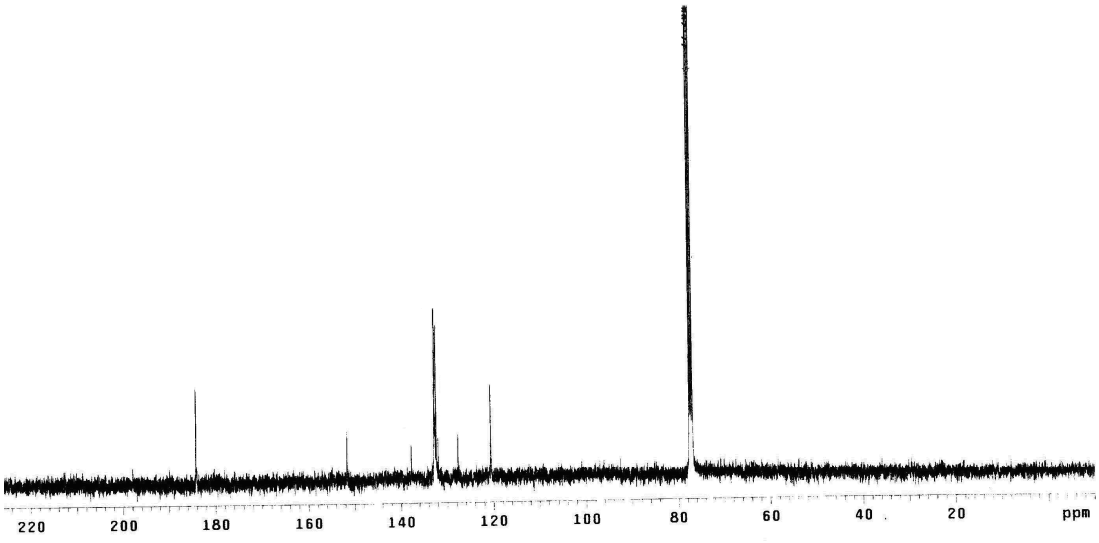


Figure S14: ^{13}C NMR spectrum of compound **10** recorded in $CDCl_3$

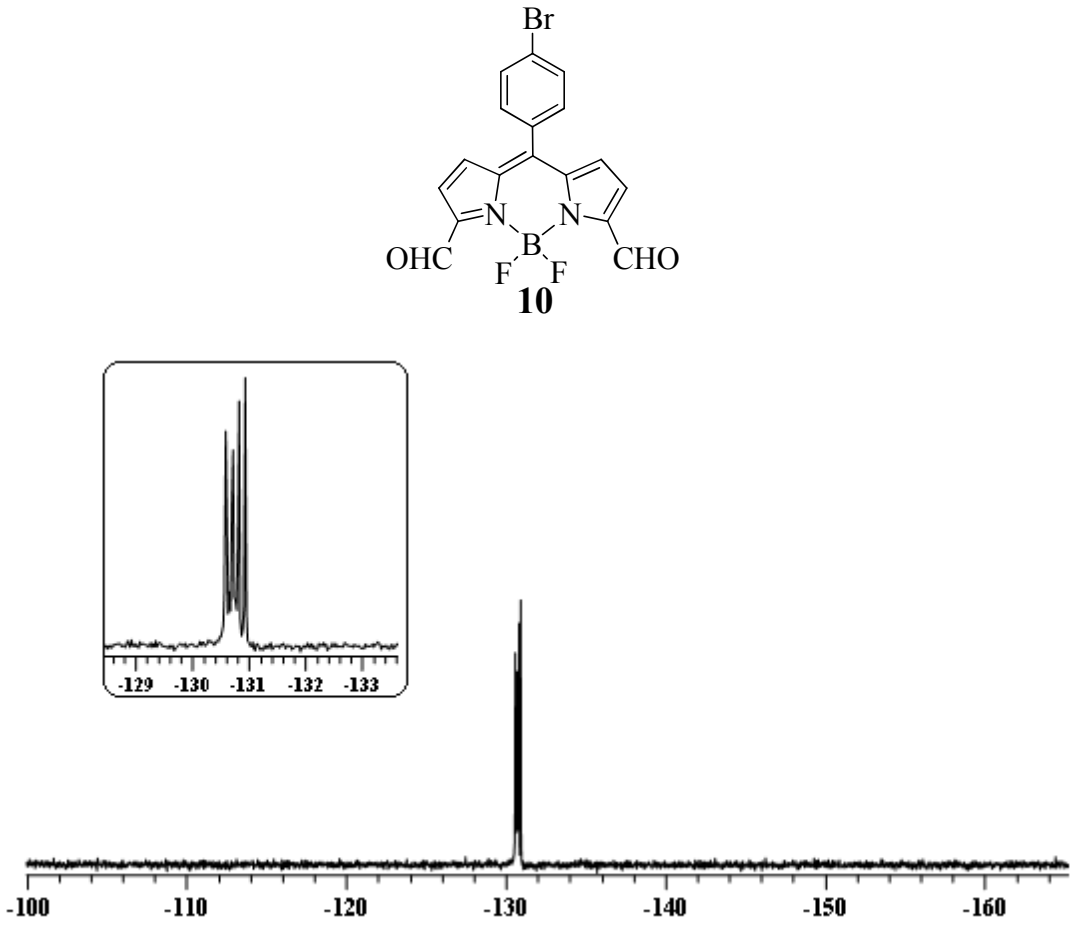
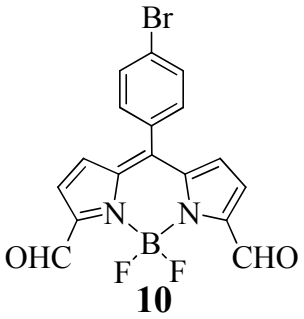


Figure S15: ^{19}F NMR spectrum of compound **10** recorded in $CDCl_3$**.** Inset shows the expansion



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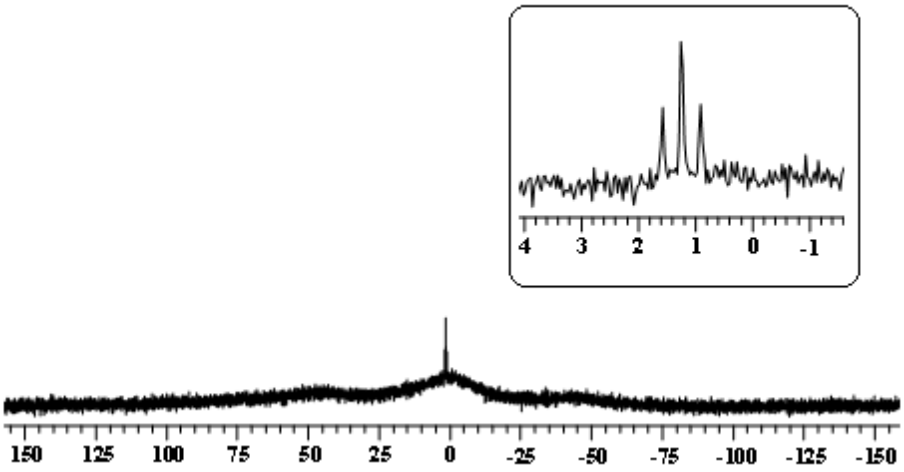
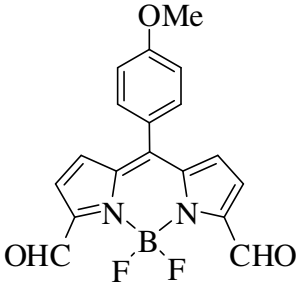


Figure S16: ^{11}B NMR spectrum of compound **10** recorded in $CDCl_3$**.** Inset shows the expansion.



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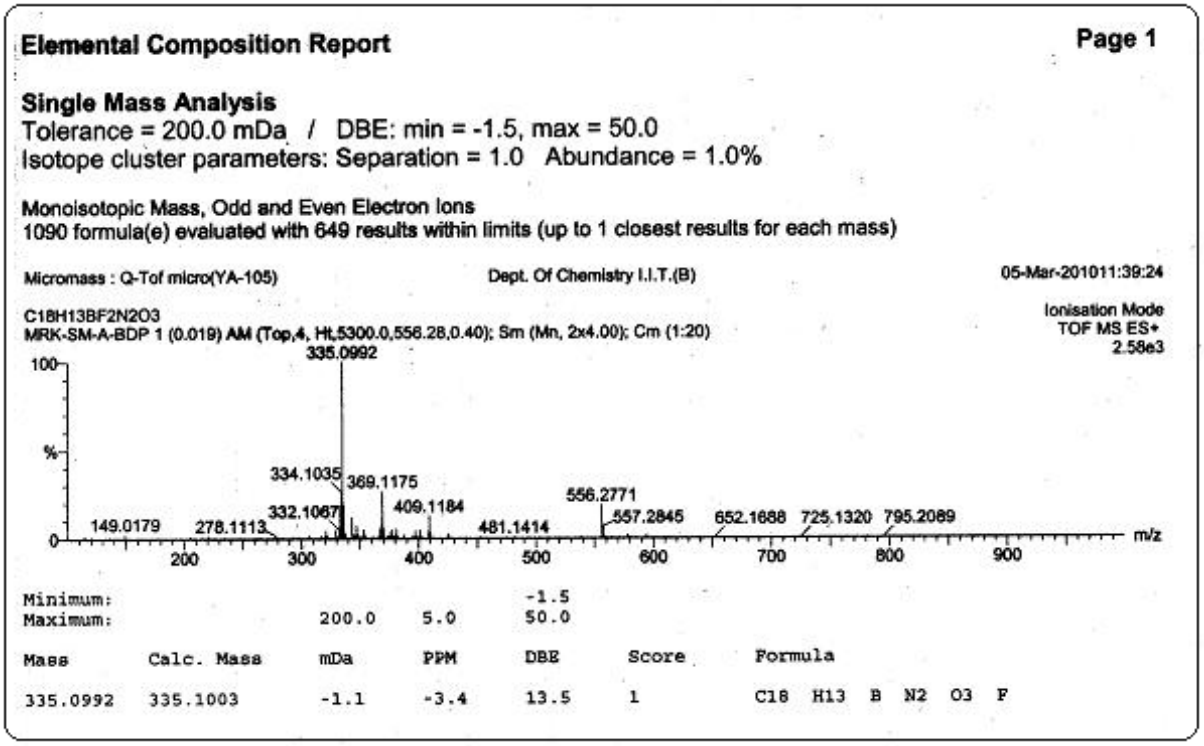
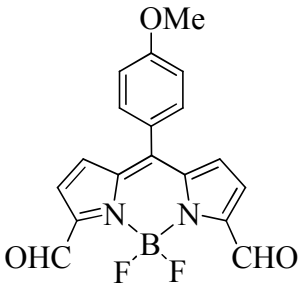


Figure S17: HRMS spectrum of compound **11**



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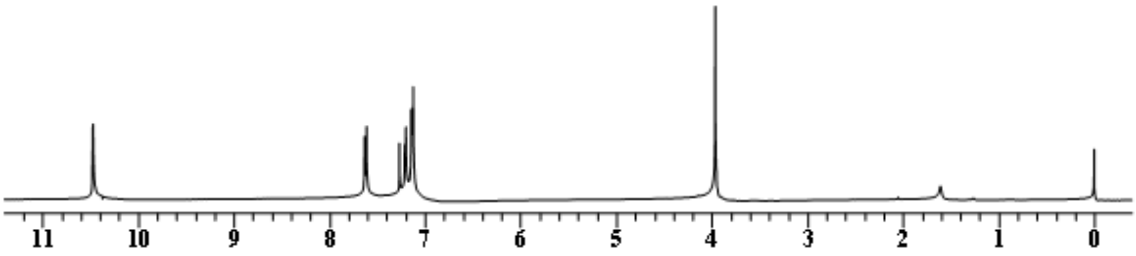
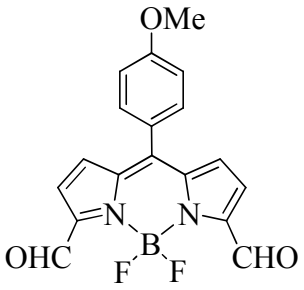


Figure S18: ^{1}H NMR spectrum of compound **11** recorded in $CDCl_3$



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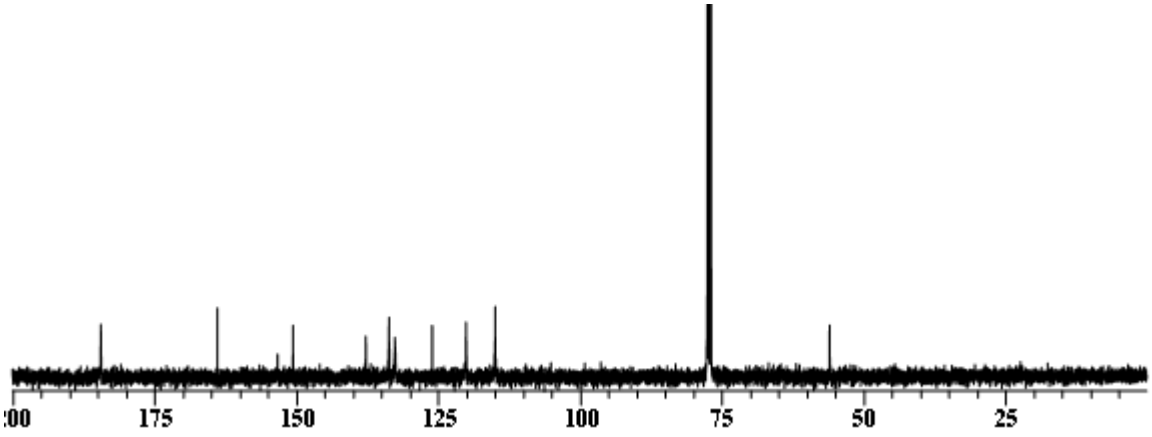
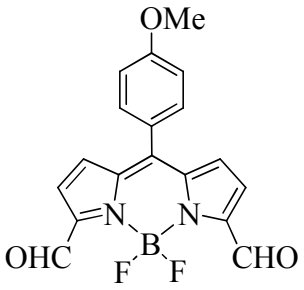


Figure S19: ^{13}C NMR spectrum of compound **11** recorded in $CDCl_3$



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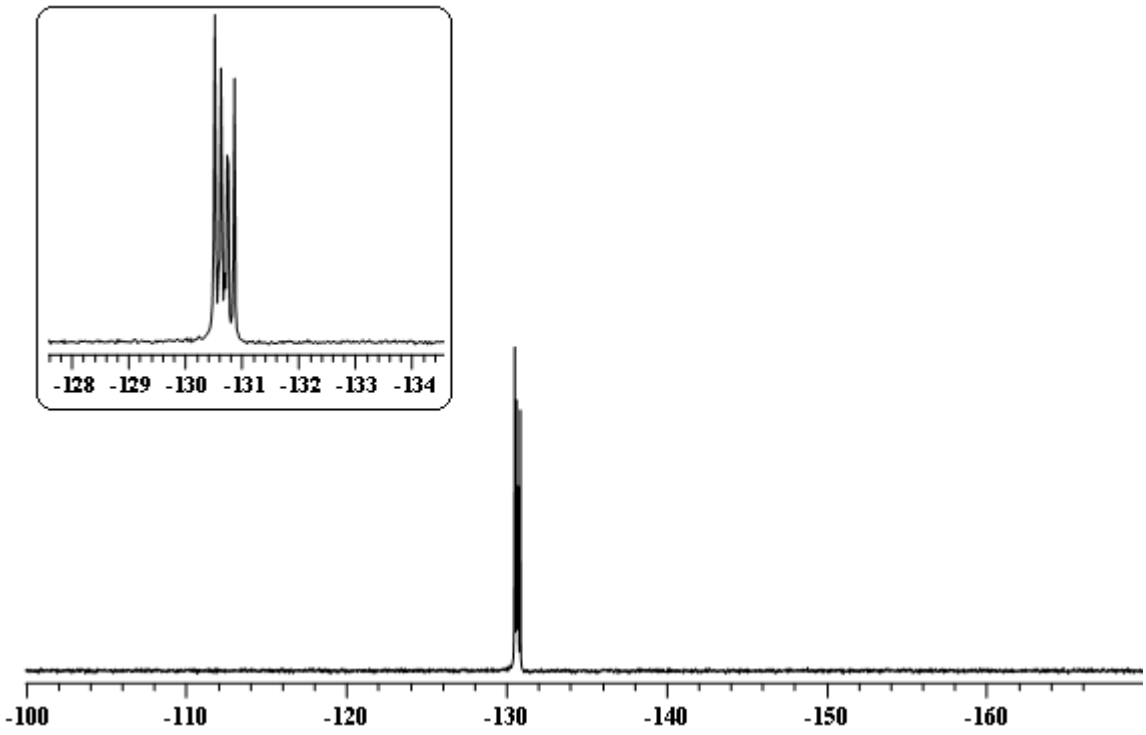
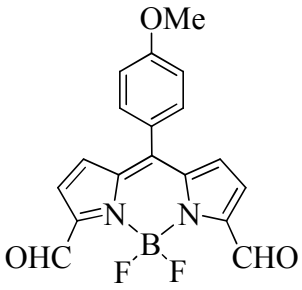


Figure S20: ^{19}F NMR spectrum of compound **11** recorded in $CDCl_3$. Inset shows the expansion



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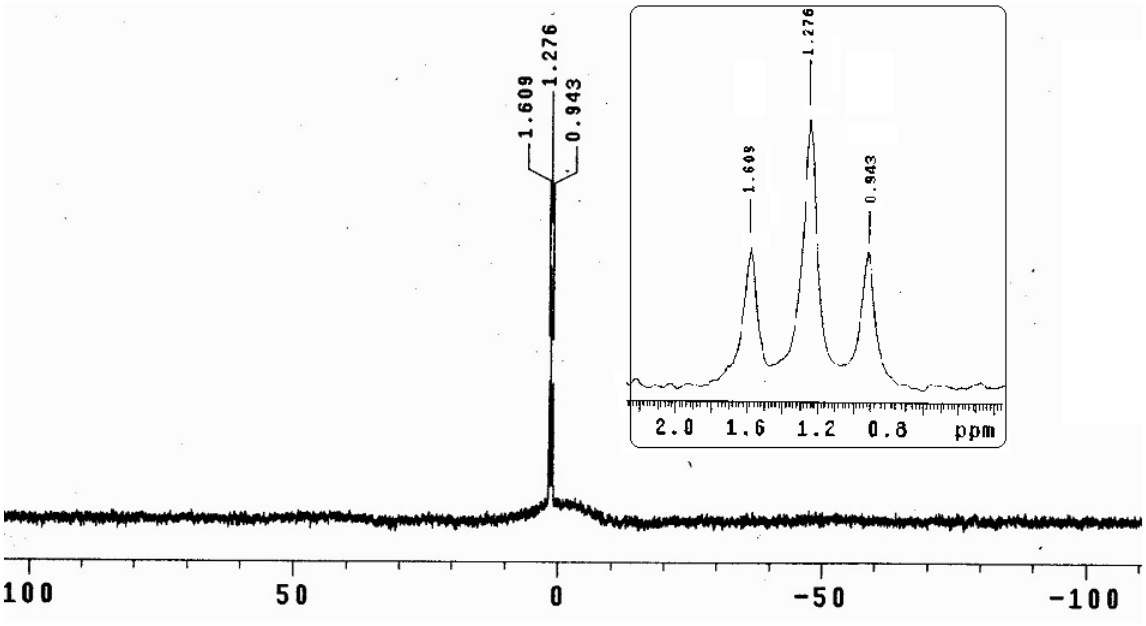
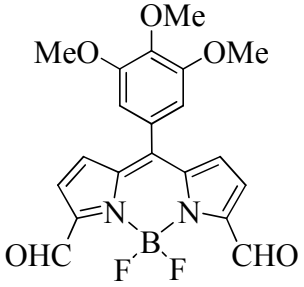


Figure S21: ^{11}B NMR spectrum of compound **11** recorded in $CDCl_3$. Inset shows the expansion



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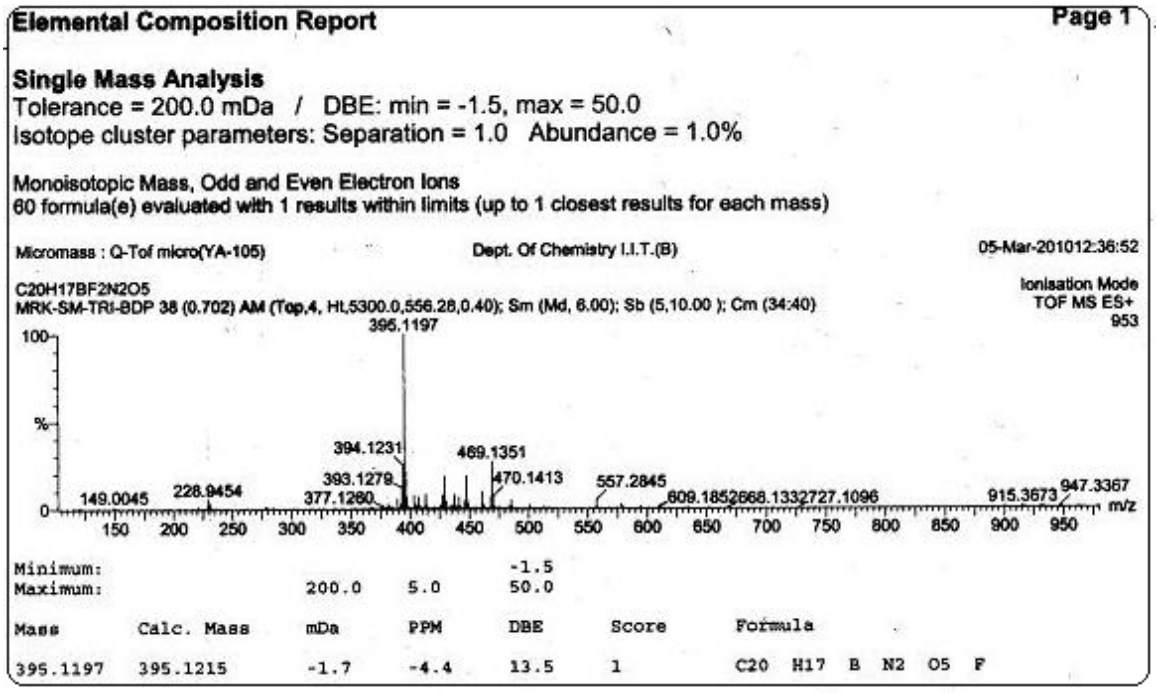
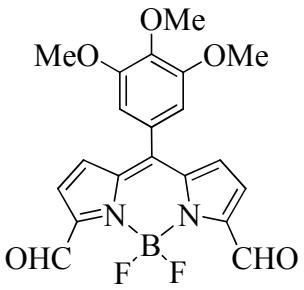


Figure S22: HRMS spectrum of compound **12**



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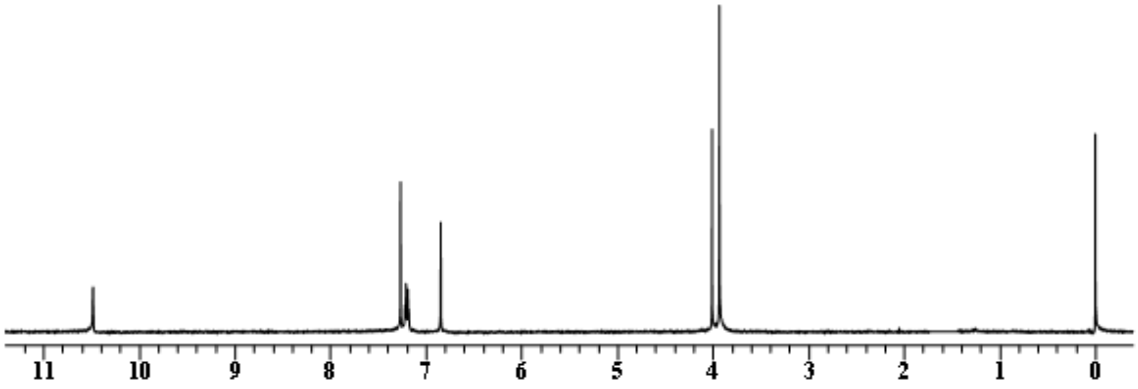
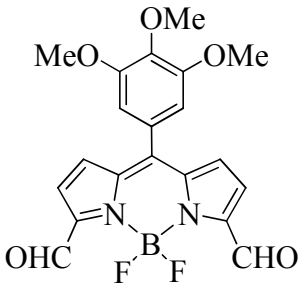


Figure S23: ^{1}H NMR spectrum of compound **12** recorded in $CDCl_3$



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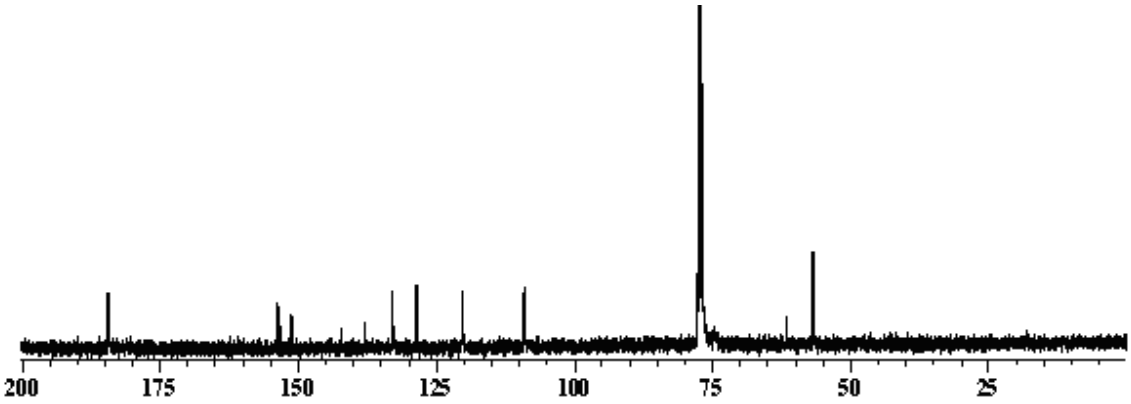
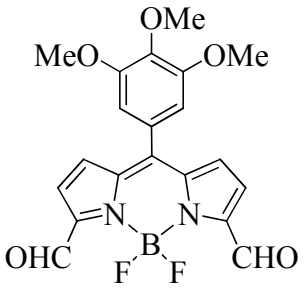


Figure S24: ^{13}C NMR spectrum of compound **12** recorded in $CDCl_3$



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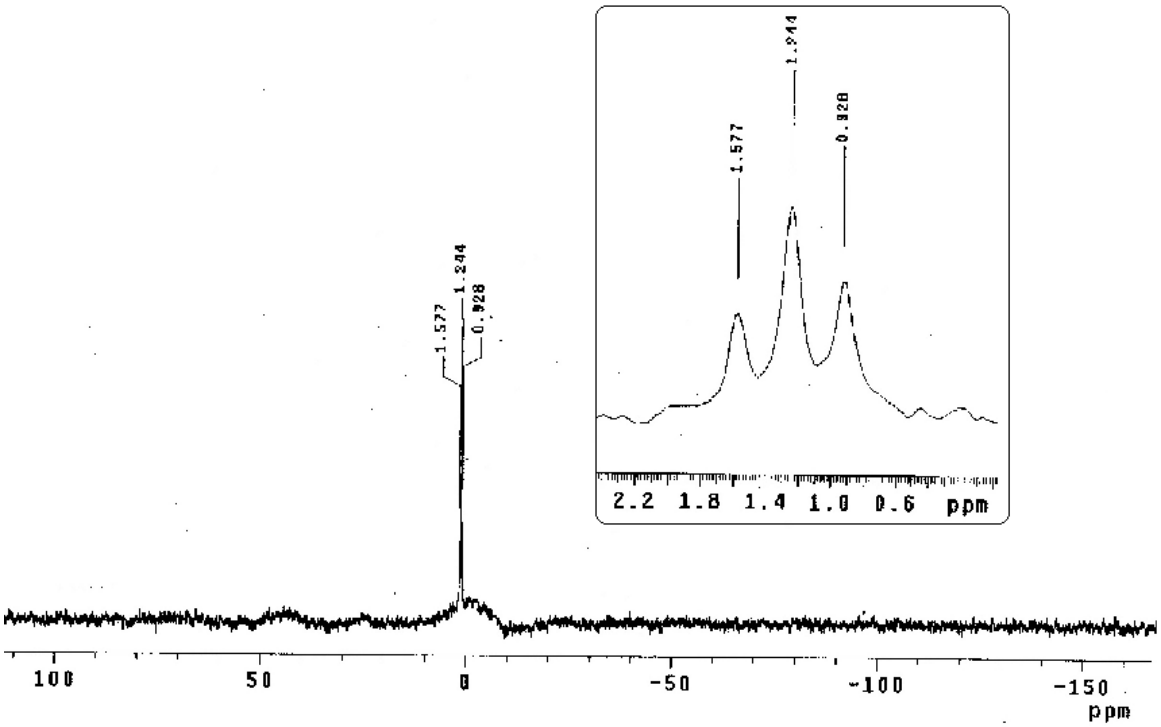


Figure S25: ^{11}B NMR spectrum of compound **12** recorded in $CDCl_3$. Inset shows the expansion

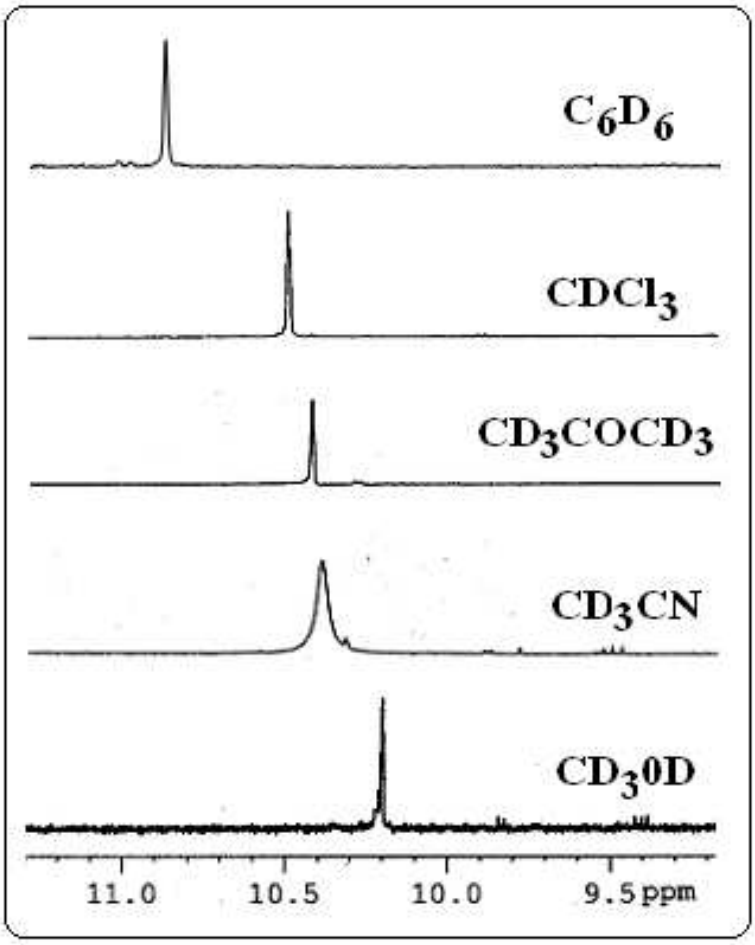


Figure S26: Comparison of ^{1}H NMR spectra of compound **9** in five different solvents

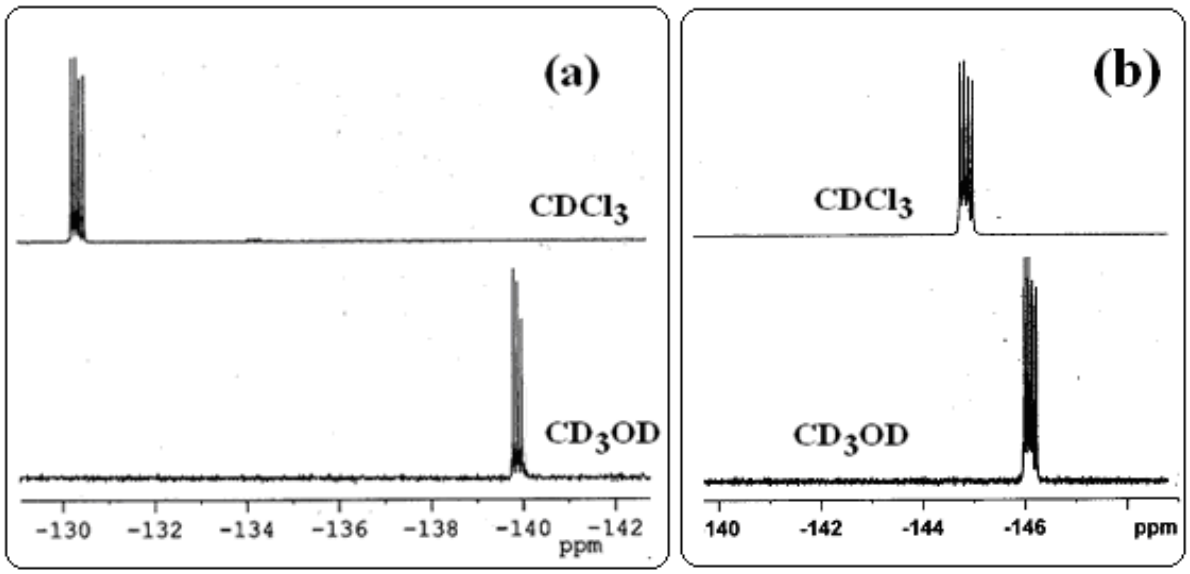
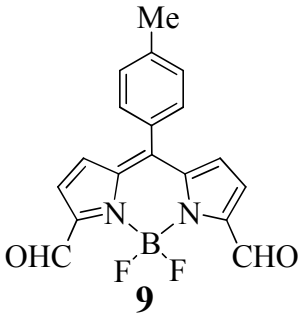


Figure S27: Comparison of ^{19}F NMR spectra of compounds **9** (a) and **13** (b) in two different solvents



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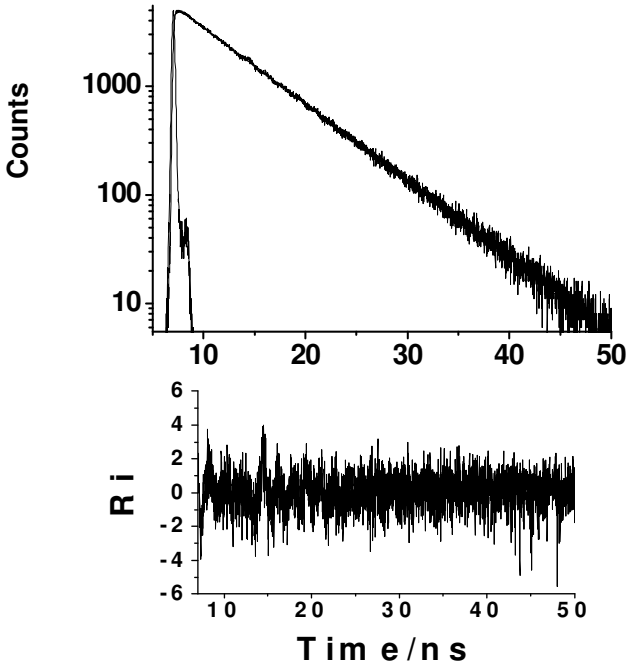


Figure S28: Fluorescence decay profile and weighted, residual, distribution fit of **9** in chloroform. The excitation wavelength used was 406 nm and emission was detected at 556 nm.

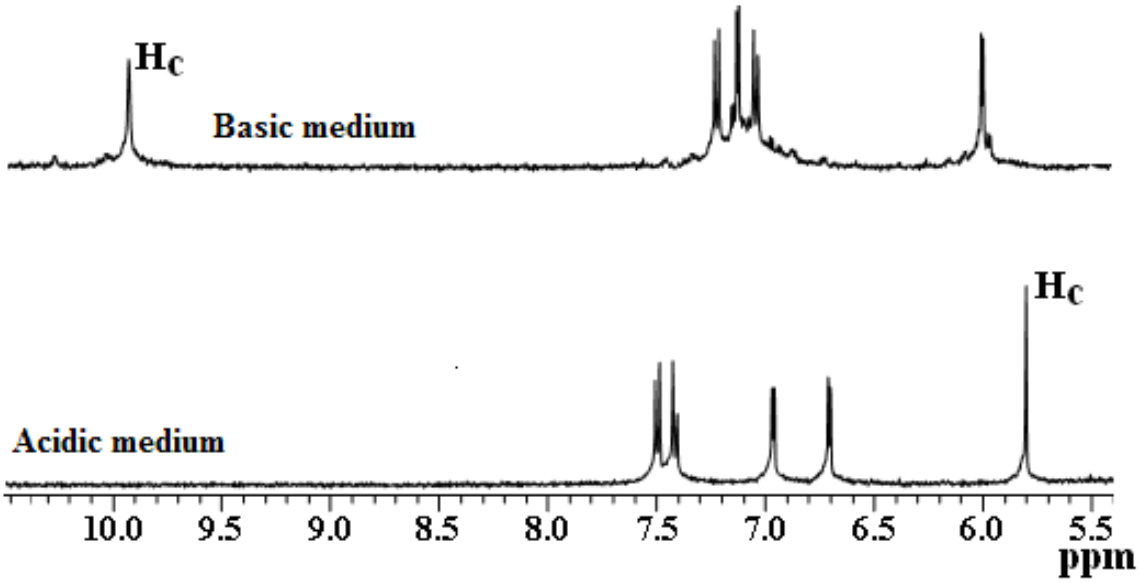


Figure S29: Comparison of ^{1}H NMR spectra of compound **9** at basic and acidic media.

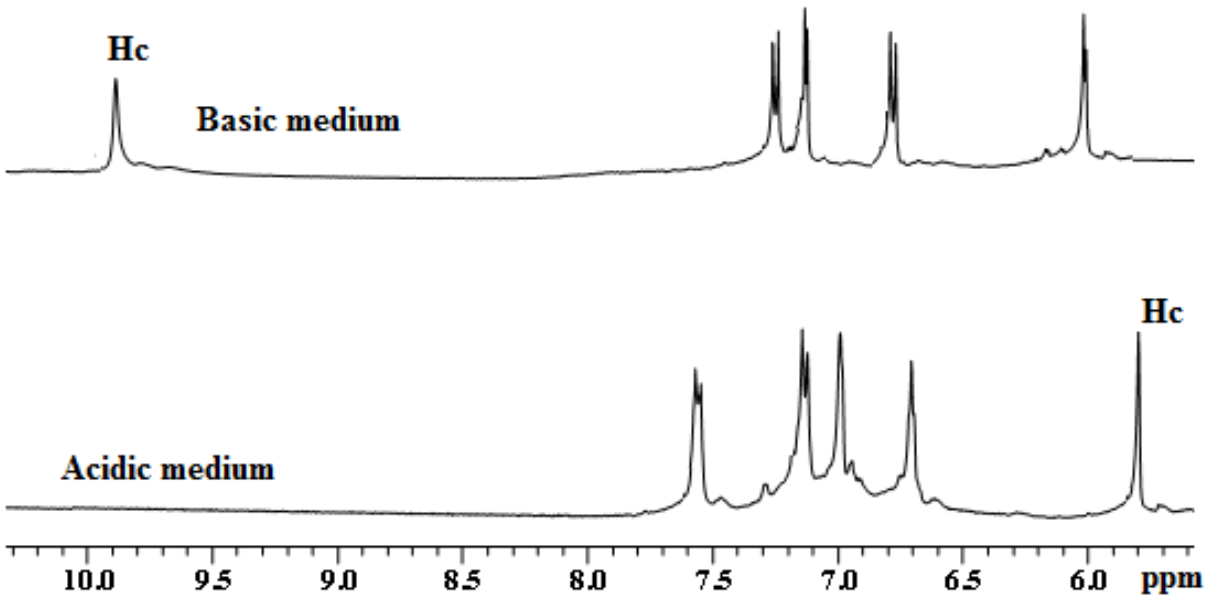


Figure S30: Comparison of ^{1}H NMR spectra of compound **11** at basic and acidic media.

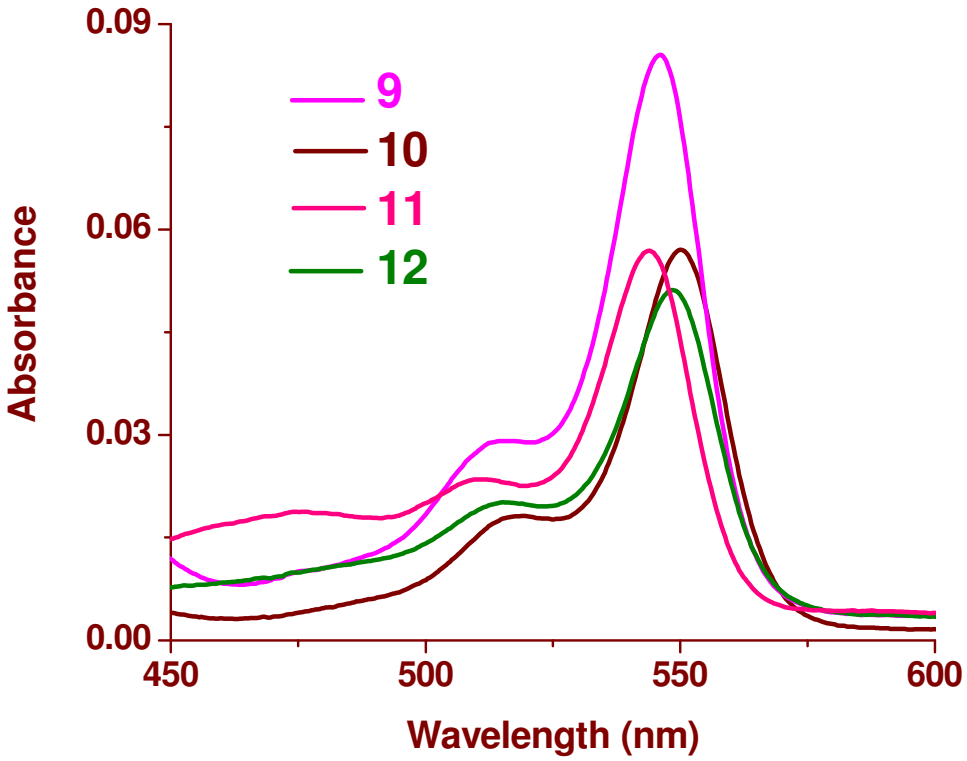


Figure S31: Absorption spectra of compounds **9**-**12** (5 µM) recorded in $CHCl_3$

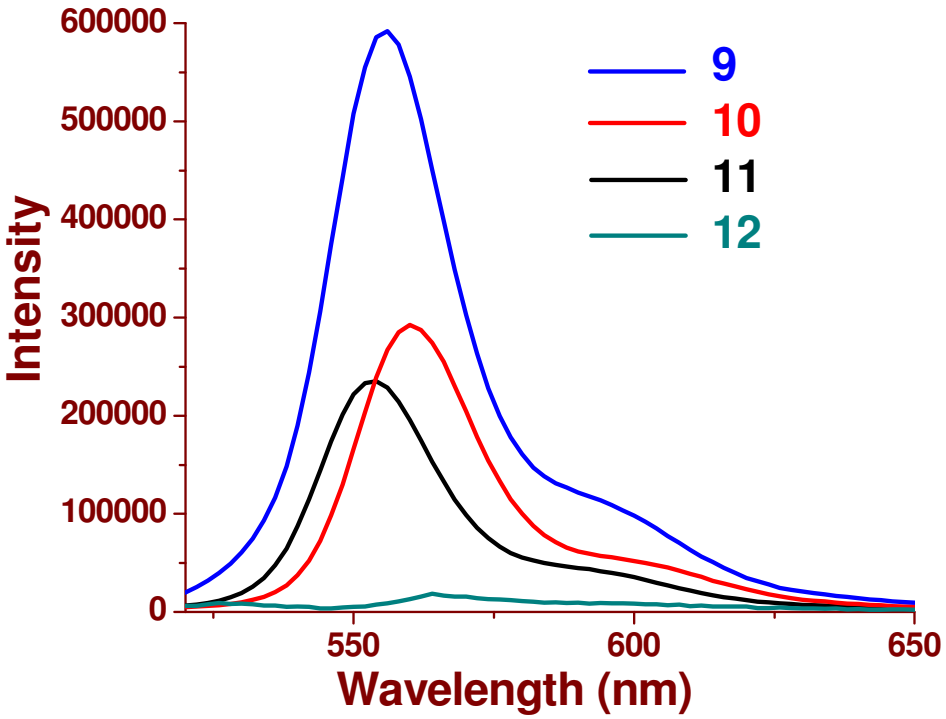


Figure S32: Emission spectra of compounds **9-12** (5 μM) recorded in $CHCl_3$

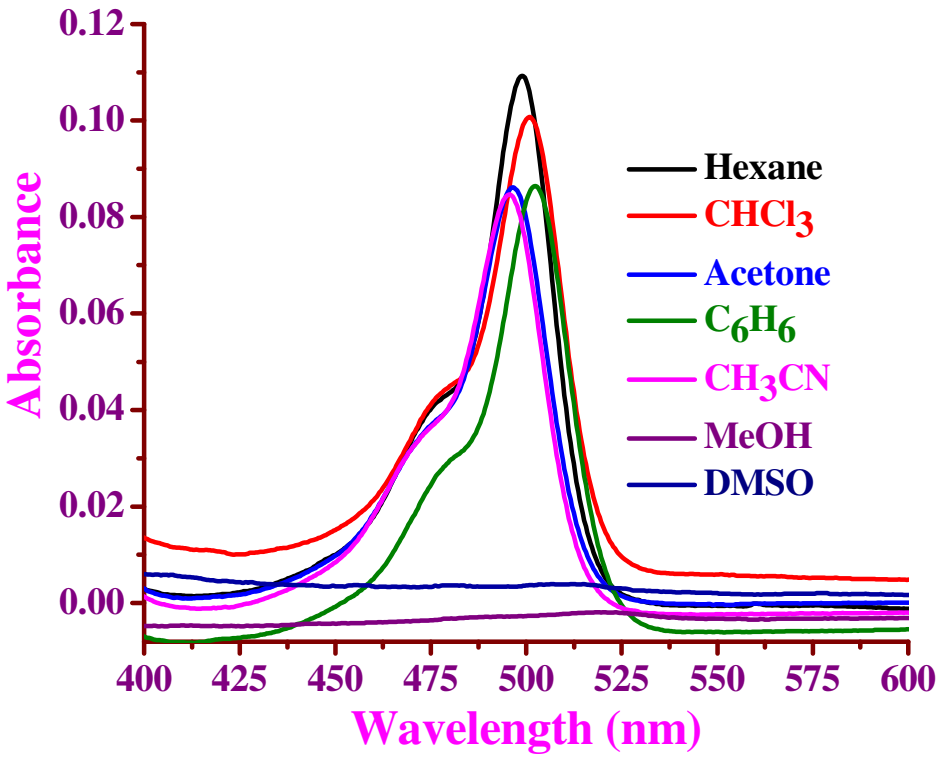


Figure S33: Absorption spectra of compound **9** (5 µM) recorded in different solvents

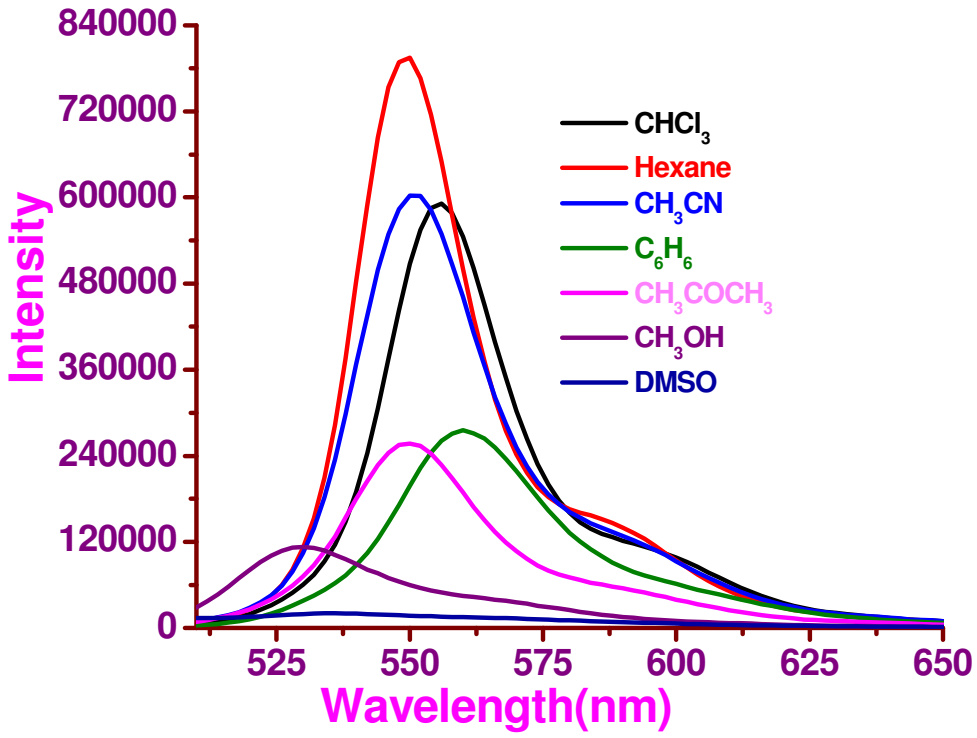


Figure S34: Emission spectra of compound **9** (5 μM) recorded in different solvents

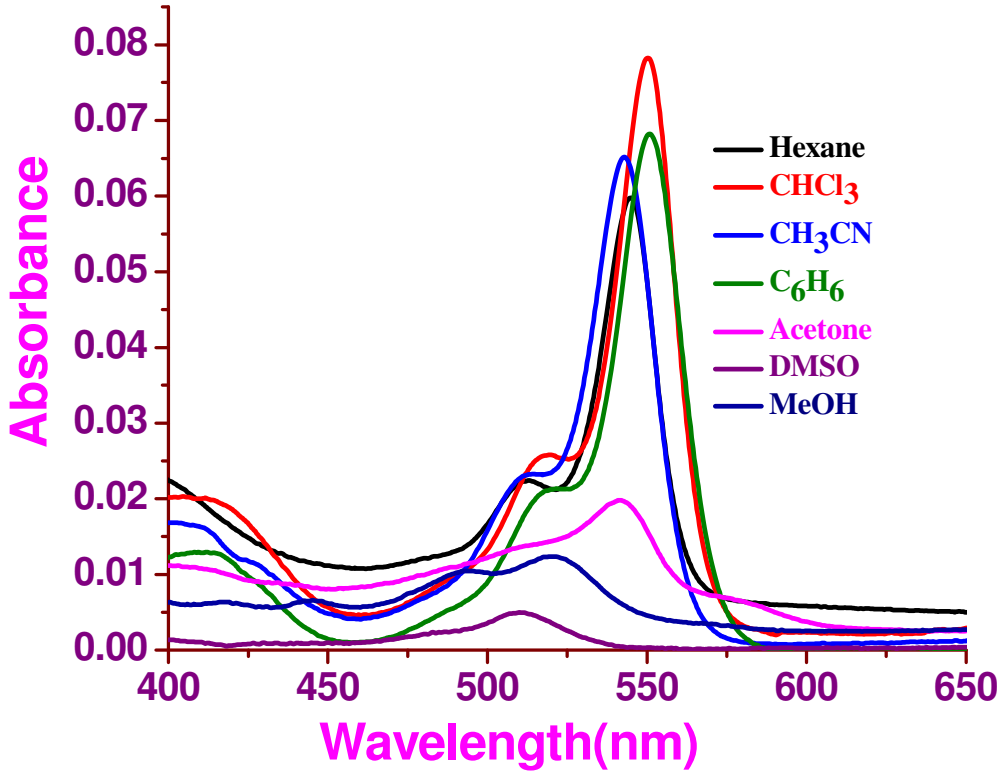


Figure S35: Absorption spectra of compound **10** (5 µM) recorded in different solvents

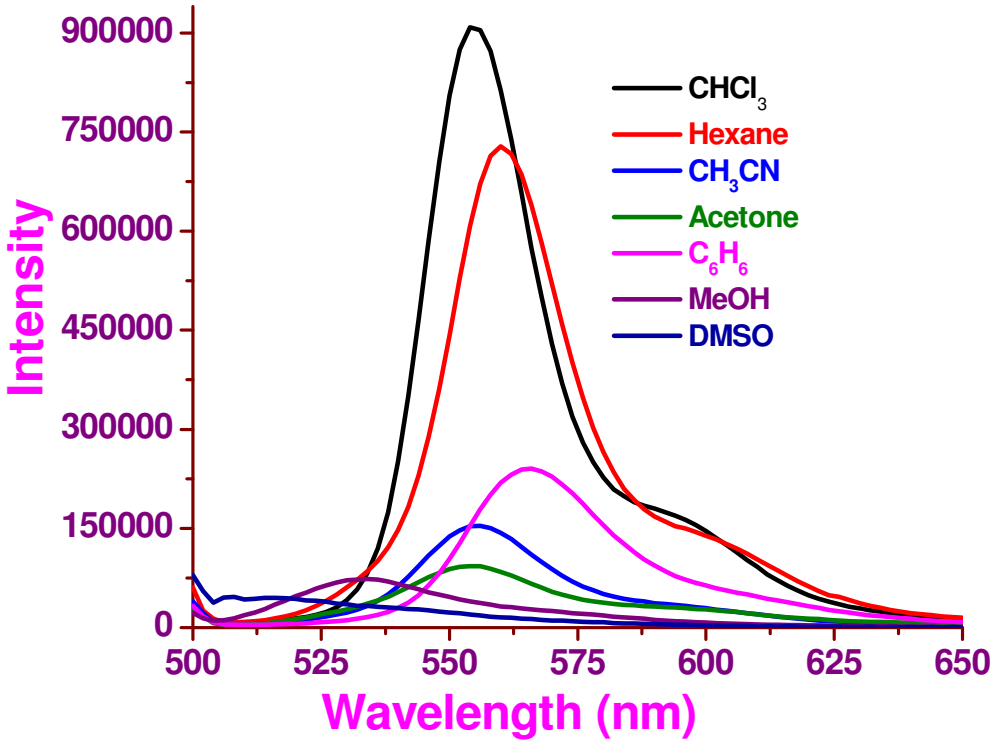


Figure S36: Emission spectra of compound **10** (5 μM) recorded in different solvents

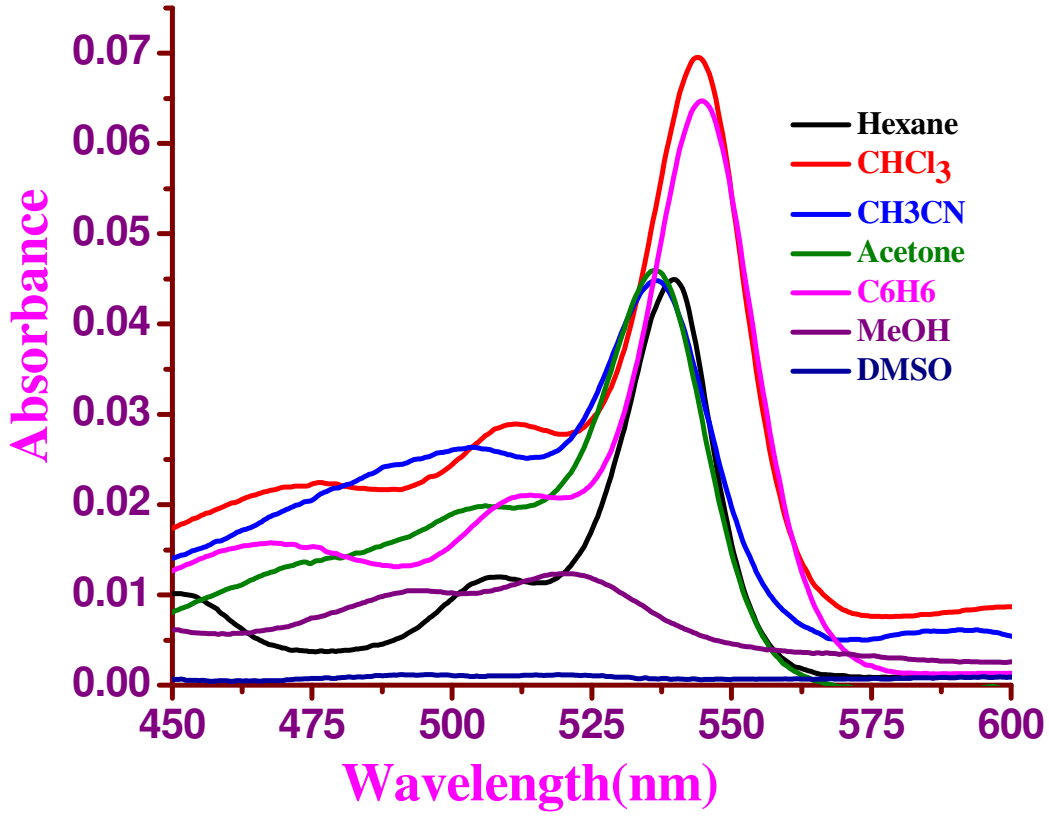


Figure S37: Absorption spectra of compound **11** (5 µM) recorded in different solvents.

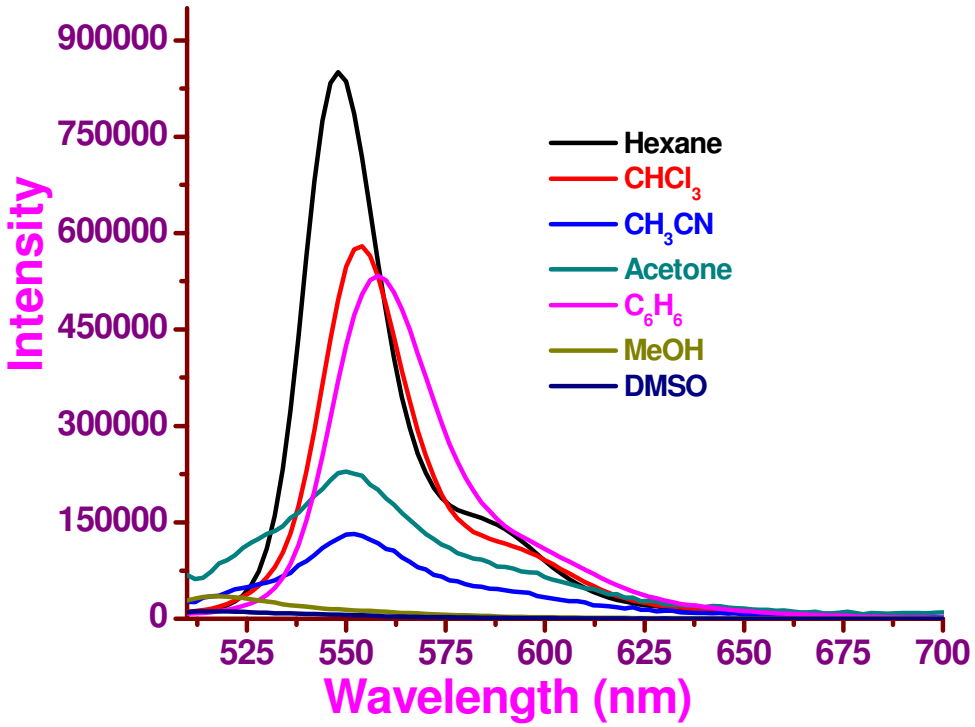


Figure S38: Emission spectra of compound **11** (5 μM) recorded in different solvents.

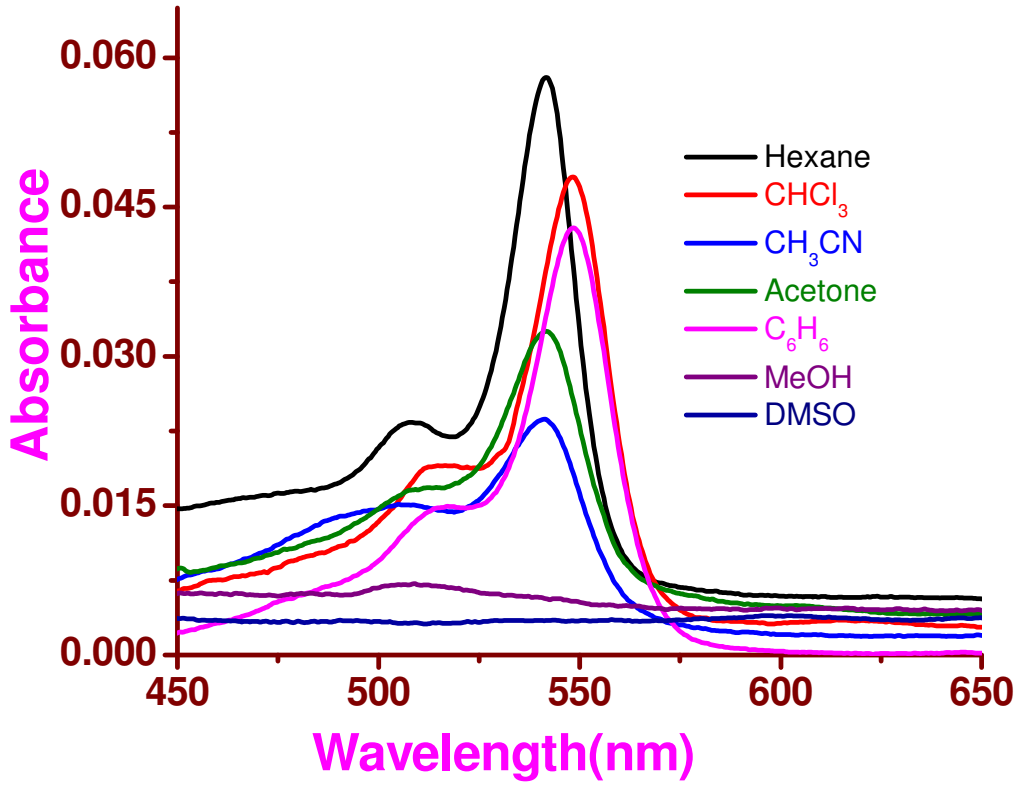


Figure S39: Absorption spectra of compound **12** (5 µM) recorded in different solvents.

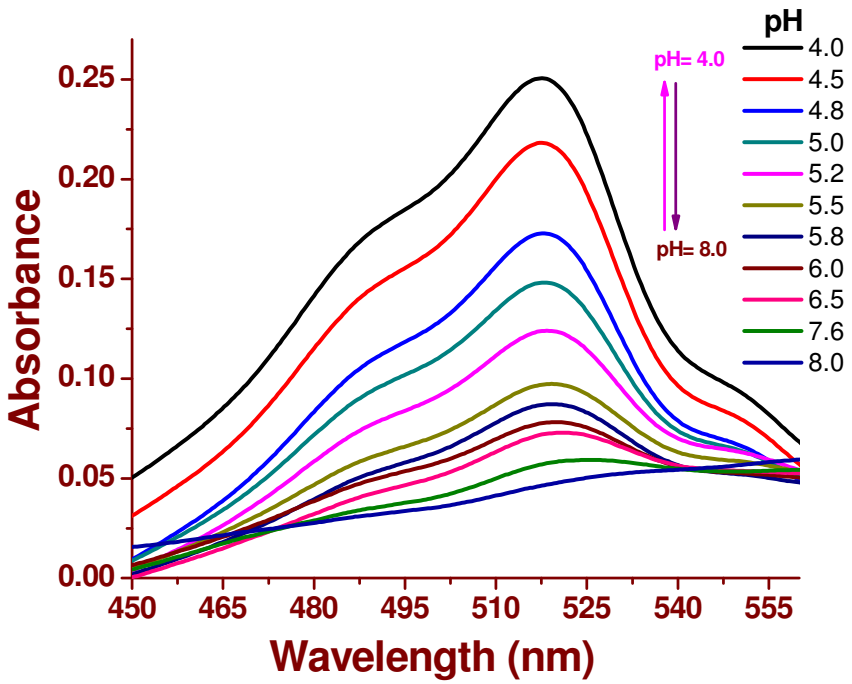


Figure S40: Absorption spectra of compound **10** (5 μM) in aqueous acetate buffer solution (0.1 M) as a function of pH.

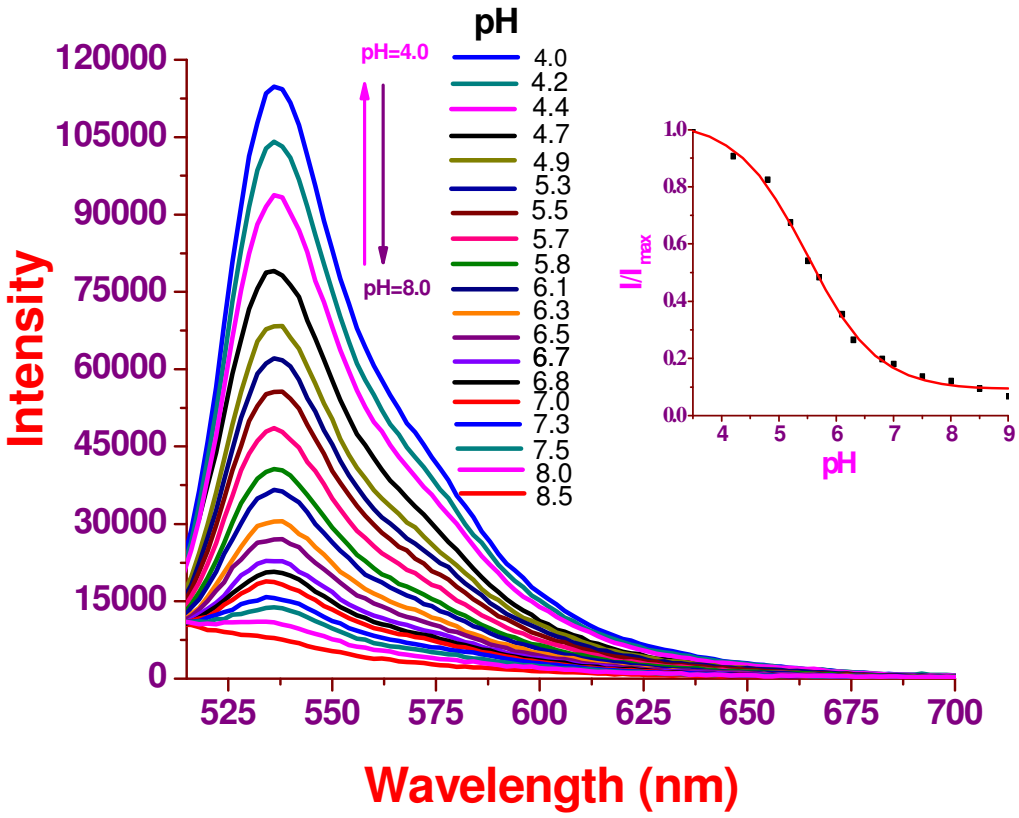


Figure S41: Fluorescence spectra of compound **10** (5 μM) in aqueous acetate buffer solution (0.1 M) as a function of pH. Excitation wavelength used was 488 nm. The inset shows the plot of emission intensity verses pH.

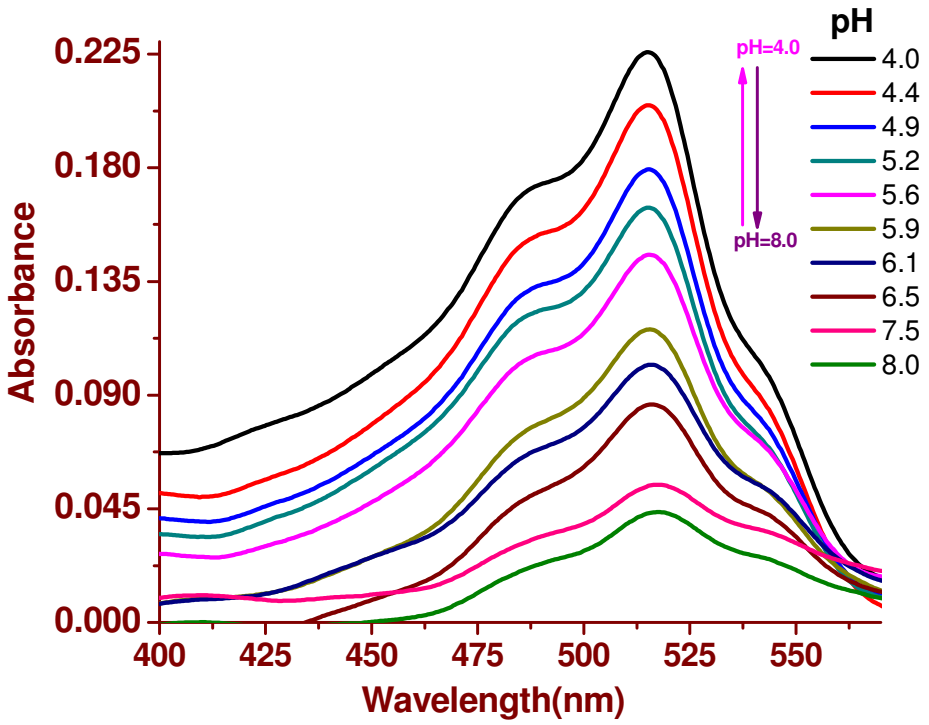


Figure S42: Absorption spectra of compound **11** (10^{-5}M) in aqueous acetate buffer solution (0.1 M) as a function of pH.

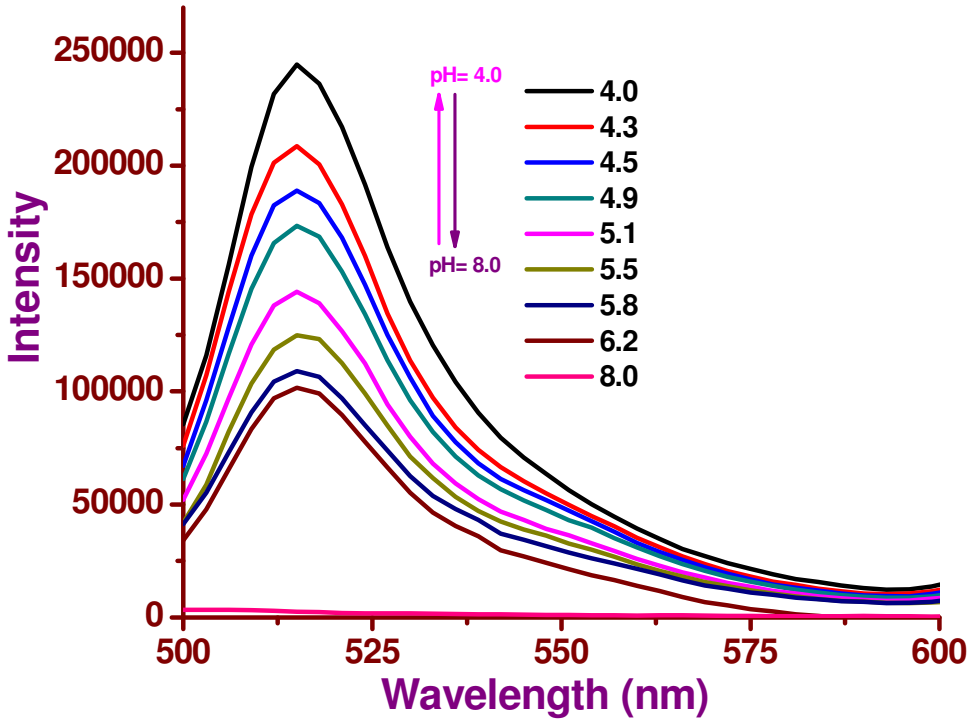


Figure S43: Fluorescence spectra of compound **11** (10^{-5}M) in aqueous acetate buffer solution (0.1 M) as a function of pH. Excitation wavelength used was 488 nm. The inset shows the plot of emission intensity verses pH.

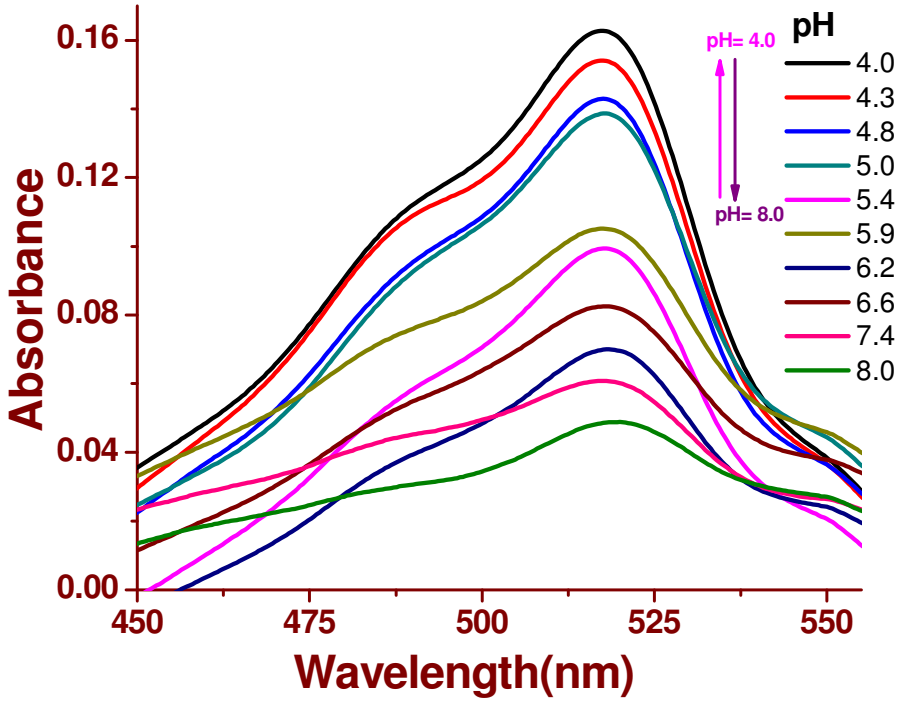


Figure S44: Absorption spectra of compound **12** (5×10^{-5}M) in aqueous acetate buffer solution (0.1 M) as a function of pH.

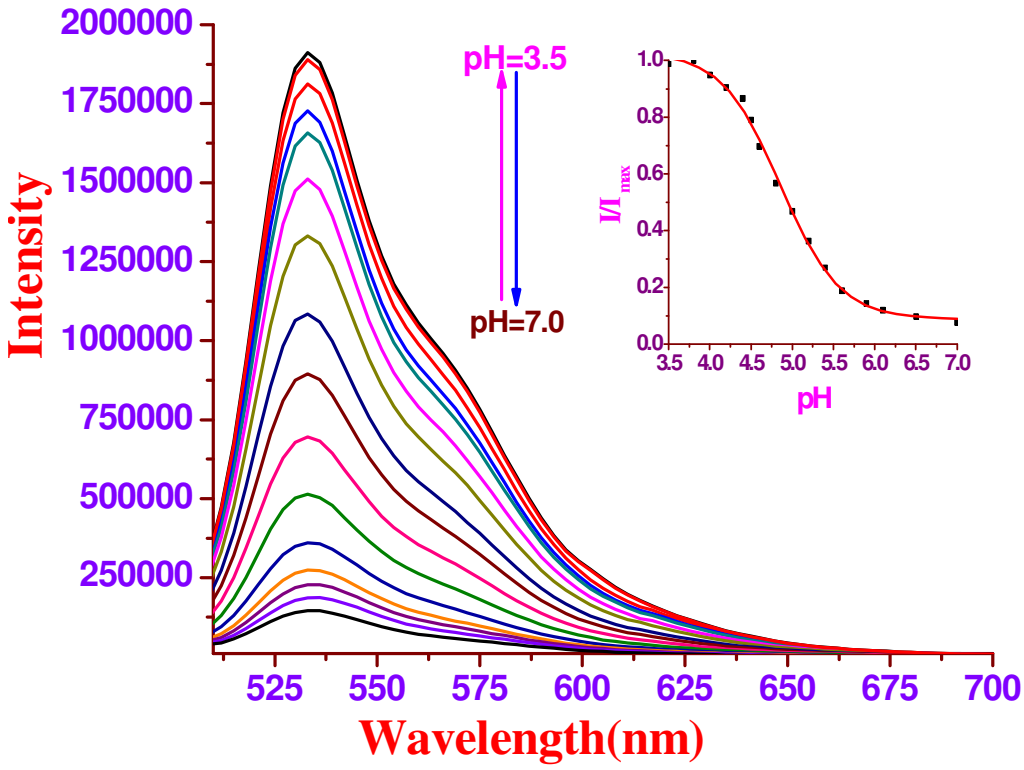


Figure S45: Fluorescence spectra of compound **9** (5×10^{-5}M) in aqueous acetate buffer solution (0.1 M) as a function of pH in acidic medium.

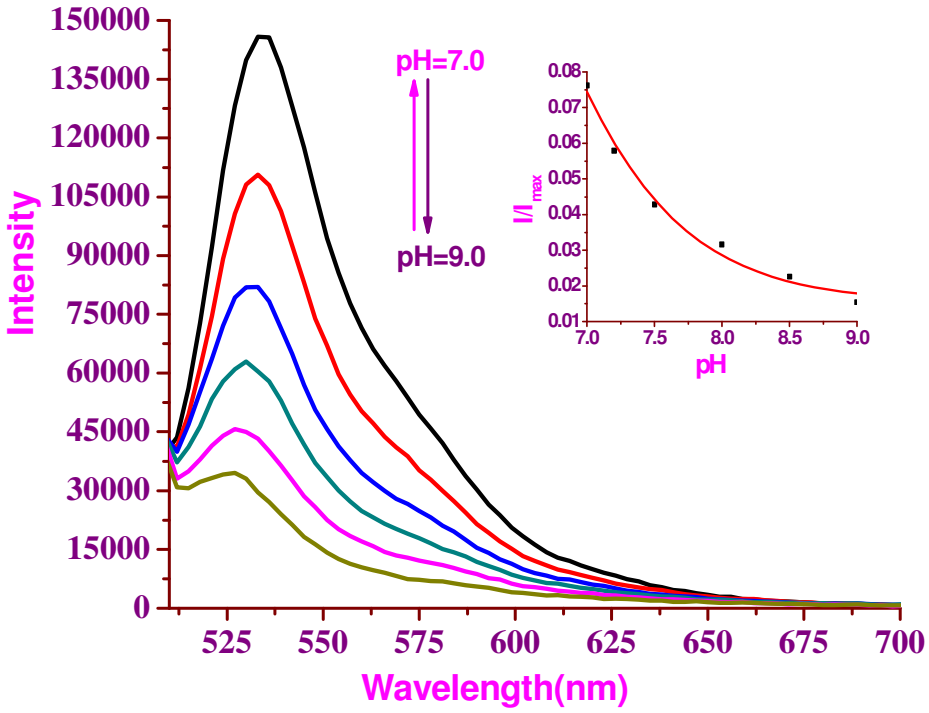
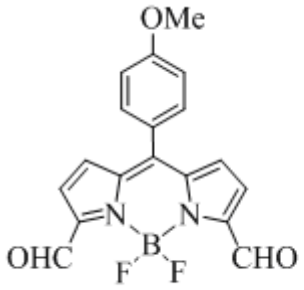


Figure S46: Fluorescence spectra of compound **9** (5×10^{-5}M) in aqueous acetate buffer solution (0.1 M) as a function of pH in basic medium.

(a)

(b)

Figure S47: (a) Photograph of compound **9** in different solvents, Hexane (1), $CHCl_3$ (2), Acetone (3), Acetonitrile (4), Benzene (5), Methanol (6), DMSO (7) under UV lamp. (b) Photograph of compound **9** at basic (left) and acidic (right) pH under UV lamp.



11

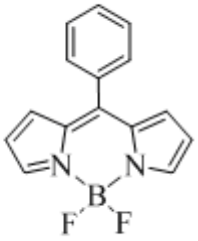


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Table S1: Selected bond lengths [Å] and bond angles [º]

	11	**14**
B–F1	1.391(1)	1.381
B–F2	1.384(1)	1.381
B–N1	1.549(1)	1.547
B–N2	1.546(1)	1.547
N1–C2	1.355(1)	1.345
N1–C5	1.389(1)	1.389
C6–C12	1.468(1)	1.481
C1–C2	1.469(1)	---
H1–F1	2.502	---
H11–F2	2.911	---
C1–O1	1.210(1)	---
C1–H1	0.950(1)	---
N1–B–N2	106.00	106.38
N1–B–F1	110.11	109.75
N1–B–F2	110.21	109.75
N2–B–F1	110.03	109.75
N2–B–F2	110.40	109.75
F1–B–F2	109.50	110.28

Table S2: Electrochemical data of compounds **9-13** in dichloromethane containing 0.1 M TBAP as supporting electrolyte

Compd	E_{ox}(V) I	E_{ox}(V) II	E_{red}(V) I	E_{red}(V) II
13	----	1.680	-0.800	-1.820
9	----	----	-0.132	-1.040
10	----	----	-0.067	-0.979
11	----	----	-0.148	-1.055
12	0.807	1.320	-0.107	----

Table S3: Photophysical data of compound **9**-**13** in seven different solvents.

Compound	Solvent	λ_{abs}(nm)	λ_{em}(nm)	$\Delta\nu_{st}$ (cm^{-1})	log ε	ϕ	τ(ns)	k_r ($10^9 s^{-1}$)	k_{nr} ($10^9 s^{-1}$)
13	Hexane	499	512	509	4.79	0.02	0.34	0.059	2.9
	$CHCl_3$	501	517	618	4.74	0.03	0.51	0.059	1.9
	CH_3CN	496	512	630	4.81	0.01	0.19	0.053	5.2
	C_6H_6	502	518	615	4.58	0.04	0.48	0.083	2.0
	Acetone	496	512	630	4.79	0.01	0.22	0.045	4.5
	MeOH	496	512	630	4.89	0.01	0.21	0.048	4.7
	DMSO	501	518	655	4.73	0.02	0.29	0.069	3.4
9	Hexane	542	550	268	4.17	0.31	6.2	0.050	0.112
	$CHCl_3$	546	556	329	4.09	0.31	5.9	0.053	0.117
	CH_3CN	538	551	439	4.25	0.23	4.6	0.050	0.168
	C_6H_6	547	560	424	4.21	0.13	3.6	0.036	0.240
	Acetone	538	550	406	4.24	0.21	4.4	0.048	0.181
	MeOH	509	530	778	4.07	0.09	1.9	0.047	0.474
	DMSO	519	535	576	3.94	0.02	----	-----	----
10	Hexane	544	554	268	4.17	0.34	5.1	0.050	0.112
	$CHCl_3$	549	560	329	4.09	0.30	5.5	0.053	0.117
	CH_3CN	543	555	439	4.25	0.24	3.9	0.050	0.168
	C_6H_6	551	566	424	4.21	0.17	2.8	0.036	0.240
	Acetone	541	555	406	4.24	0.22	3.8	0.048	0.181
	MeOH	510	533	778	4.07	0.07	1.4	0.047	0.474
	DMSO	512	524	576	3.94	0.02	----	-----	----
11	Hexane	540	548	509	4.79	0.18	3.6	0.059	2.9
	$CHCl_3$	544	554	618	4.74	0.09	1.4	0.059	1.9
	CH_3CN	536	552	630	4.81	0.06	1.1	0.053	5.2
	C_6H_6	545	558	615	4.58	0.13	2.1	0.083	2.0
	Acetone	536	551	630	4.79	0.04	0.8	0.045	4.5
	MeOH	508	517	630	4.89	0.01	0.6	0.048	4.7
	DMSO	---	525	655	4.73	-----	----	0.069	3.4
12	Hexane	542	536	---	---	---	---	----	----
	$CHCl_3$	548	---	---	---	---	---	----	----
	CH_3CN	541	---	---	---	---	---	----	----
	C_6H_6	548	---	---	---	---	---	----	----
	Acetone	542	---	---	---	---	---	----	----
	MeOH	509	519	---	---	---	---	----	----
	DMSO	----	523	---	---	---	---	----	----

[log(ε/$mol^{-1}dm^3cm^{-1}$)]-(Molar extinction coefficient), λ_{abs}(absorption maxima), λ_{em}(emission maxima), Δν(Stokes shift),Φ(quantum yield), τ(lifetime), k_r(radiative decay), k_{nr}(nonradiative decay)

Table S4: Photophysical data of compounds **9-12** recorded in acetate buffer solution at pH 4.0 and 8.0.

Compound	pH	λ_{abs}(nm)	λ_{em}(nm)	$\Delta\nu_{st}$ (cm^{-1})	log ε	ϕ	τ(ns)	k_r ($10^9 s^{-1}$)	k_{nr} ($10^9 s^{-1}$)
9	4.0	515	533	656	4.73	0.51	6.1	0.084	0.080
	8.0	517	534	616	4.14	0.03	1.4	0.021	0.693
10	4.0	517	536	686	4.70	0.43	5.2	0.083	0.110
	8.0	517	536	686	4.20	0.01	1.2	0.008	0.825
11	4.0	515	515	----	4.66	0.24	2.5	0.096	0.304
	8.0	517	515	75.1	3.95	< 0.01	0.6	0.006	1.600
12	4.0	517	----	----	----	-----	----	----	----
	8.0	517	----	----	----	-----	----	----	----

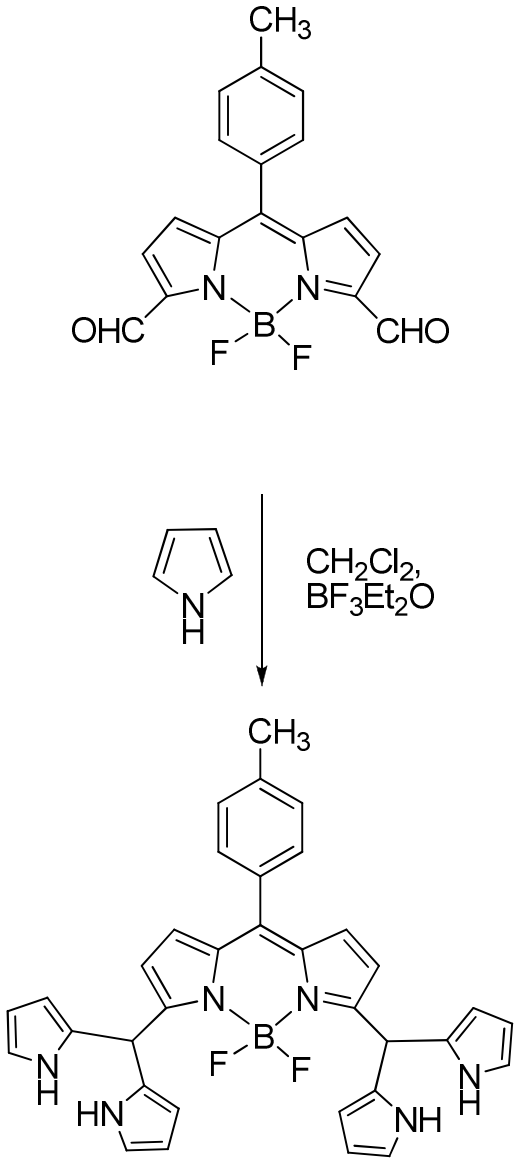
[log(ε/$mol^{-1}dm^3cm^{-1}$)]-(Molar extinction coefficient), λ_{abs}(absorption maxima), λ_{em}(emission maxima), Δν(Stokes shift), Φ(quantum yield), τ(lifetime), k_r(radiative decay), k_{nr}(nonradiative decay).

Table S5: Cartesian coordinate data of compound **13**

Compound **13**									
Atoms	**Neutral**			**Anion**			**Cation**		
	X	**Y**	**Z**	**X**	**Y**	**Z**	**X**	**Y**	**Z**
F(1)	-3.76	-0.029	-1.16	-3.779	-0.022	-1.154	3.653	-0.028	1.282
F(2)	-3.779	0.037	1.133	-3.792	0.036	1.133	3.875	0.013	-1.007
N(3)	-2.029	1.245	-0.04	-2.024	1.24	-0.035	2.046	1.242	0.006
N(4)	-2.033	-1.242	0.042	-2.031	-1.234	0.035	2.042	-1.244	-0.054
C(5)	-0.638	-1.217	0.062	-0.64	-1.232	0.056	0.642	-1.209	-0.089
C(6)	2.274	0.731	0.96	2.311	0.876	0.818	-2.284	0.799	-0.911
C(7)	1.552	-0.003	0.003	1.565	-0.006	0.003	-1.554	0.001	-0.007
C(8)	0.07	-0.001	0.003	0.095	-0.003	0.002	-0.082	0.003	-0.017
C(9)	-0.181	-2.556	0.194	-0.216	-2.573	0.194	0.168	-2.562	-0.265
C(10)	-0.635	1.216	-0.056	-0.633	1.231	-0.052	0.645	1.214	0.037
C(11)	-2.42	2.526	-0.14	-2.453	2.533	-0.146	2.43	2.512	0.077
C(12)	-2.428	-2.521	0.146	-2.467	-2.525	0.148	2.422	-2.51	-0.186
C(13)	-1.297	3.374	-0.227	-1.356	3.382	-0.238	1.282	3.382	0.159
C(14)	3.668	0.718	0.962	3.705	0.87	0.818	-3.675	0.78	-0.901
C(15)	-0.174	2.555	-0.183	-0.201	2.57	-0.185	0.176	2.576	0.15
C(16)	2.272	-0.742	-0.952	2.309	-0.893	-0.807	-2.263	-0.805	0.907
C(17)	-1.307	-3.372	0.239	-1.375	-3.38	0.246	1.272	-3.37	-0.315
B(18)	-2.975	0.003	-0.007	-2.945	0.005	-0.005	3.013	-0.005	0.064
C(19)	4.391	-0.008	0.004	4.436	-0.01	0.006	-4.389	-0.008	0.019
C(20)	3.666	-0.736	-0.952	3.704	-0.893	-0.803	-3.654	-0.796	0.921
C(21)	5.901	0.012	-0.016	5.947	0.015	-0.021	-5.895	0.009	0.053
H(22)	1.738	1.288	1.723	1.78	1.553	1.48	-1.763	1.392	-1.657
H(23)	0.852	-2.862	0.263	0.809	-2.907	0.275	-0.868	-2.849	-0.364
H(24)	-3.472	2.78	-0.156	-3.511	2.756	-0.161	3.481	2.777	0.089
H(25)	-3.48	-2.772	0.161	-3.526	-2.742	0.16	3.472	-2.779	-0.204
H(26)	-1.323	4.451	-0.319	-1.39	4.46	-0.336	1.321	4.46	0.234
H(27)	4.203	1.278	1.724	4.237	1.557	1.475	-4.218	1.379	-1.626
H(28)	0.861	2.858	-0.248	0.825	2.898	-0.26	-0.859	2.873	0.228
H(29)	1.735	-1.302	-1.711	1.777	-1.575	-1.462	-1.724	-1.401	1.638
H(30)	-1.336	-4.448	0.336	-1.415	-4.457	0.347	1.307	-4.443	-0.448
H(31)	4.199	-1.305	-1.709	4.234	-1.589	-1.451	-4.18	-1.407	1.649
H(32)	6.273	0.748	-0.74	6.329	0.744	-0.75	-6.252	0.746	0.783
H(33)	6.311	0.278	0.963	6.361	0.29	0.956	-6.316	0.279	-0.918
H(34)	6.31	-0.962	-0.304	6.359	-0.963	-0.296	-6.3	-0.963	0.349

Table S6: Cartesian coordinate data of compound **9**

Compound **9**									
Atoms	**Neutral**			**Anion**			**Cation**		
	X	**Y**	**Z**	**X**	**Y**	**Z**	**X**	**Y**	**Z**
F(1)	-3.101	0.005	-1.152	-3.109	-0.001	-1.152	-3.101	0.005	-1.152
F(2)	-3.105	0.003	1.145	-3.115	0.014	1.142	-3.105	0.003	1.145
N(3)	-1.373	1.254	-0.003	-1.367	1.252	-0.009	-1.373	1.254	-0.003
N(4)	-1.377	-1.252	0.002	-1.374	-1.248	0.01	-1.377	-1.252	0.002
C(5)	0.009	-1.221	0.028	0.004	-1.227	0.031	0.009	-1.221	0.028
C(6)	2.919	0.725	0.965	2.947	0.762	0.926	2.919	0.725	0.965
C(7)	2.198	-0.004	0.003	2.21	-0.007	0.004	2.198	-0.004	0.003
C(8)	0.718	-0.002	0.002	0.732	-0.004	0.003	0.718	-0.002	0.002
C(9)	0.484	-2.562	0.127	0.469	-2.571	0.124	0.484	-2.562	0.127
C(10)	0.013	1.219	-0.025	0.011	1.224	-0.026	0.013	1.219	-0.025
C(11)	-1.756	2.555	-0.069	-1.776	2.575	-0.075	-1.756	2.555	-0.069
C(12)	-1.764	-2.552	0.069	-1.789	-2.569	0.076	-1.764	-2.552	0.069
C(13)	-0.613	3.389	-0.139	-0.632	3.395	-0.14	-0.613	3.389	-0.139
C(14)	4.313	0.71	0.968	4.343	0.758	0.924	4.313	0.71	0.968
C(15)	0.493	2.558	-0.121	0.482	2.565	-0.115	0.493	2.558	-0.121
C(16)	2.918	-0.738	-0.958	2.945	-0.781	-0.916	2.918	-0.738	-0.958
C(17)	-0.624	-3.388	0.143	-0.65	-3.395	0.145	-0.624	-3.388	0.143
B(18)	-2.312	0.003	-0.002	-2.289	0.004	-0.003	-2.312	0.003	-0.002
C(19)	5.036	-0.009	0.005	5.069	-0.012	0.004	5.036	-0.009	0.005
C(20)	4.311	-0.73	-0.957	4.34	-0.784	-0.912	4.311	-0.73	-0.957
C(21)	6.545	0.01	-0.014	6.581	0.012	-0.019	6.545	0.01	-0.014
C(22)	-3.177	-2.982	0.065	-3.176	-2.983	0.071	-3.177	-2.982	0.065
O(23)	-3.482	-4.163	0.121	-3.536	-4.166	0.122	-3.482	-4.163	0.121
C(24)	-3.167	2.991	-0.068	-3.161	2.996	-0.076	-3.167	2.991	-0.068
O(25)	-3.469	4.172	-0.124	-3.515	4.181	-0.127	-3.469	4.172	-0.124
H(26)	2.384	1.275	1.734	2.414	1.351	1.666	2.384	1.275	1.734
H(27)	1.522	-2.853	0.194	1.505	-2.871	0.185	1.522	-2.853	0.194
H(28)	-0.644	4.466	-0.204	-0.659	4.474	-0.201	-0.644	4.466	-0.204
H(29)	4.847	1.263	1.736	4.876	1.356	1.66	4.847	1.263	1.736
H(30)	1.531	2.846	-0.186	1.52	2.86	-0.171	1.531	2.846	-0.186
H(31)	2.383	-1.291	-1.723	2.41	-1.375	-1.651	2.383	-1.291	-1.723
H(32)	-0.659	-4.466	0.209	-0.683	-4.474	0.208	-0.659	-4.466	0.209
H(33)	4.845	-1.292	-1.719	4.871	-1.392	-1.642	4.845	-1.292	-1.719
H(34)	6.916	0.744	-0.74	6.958	0.75	-0.739	6.916	0.744	-0.74
H(35)	6.954	0.278	0.964	6.991	0.275	0.962	6.954	0.278	0.964
H(36)	6.953	-0.965	-0.3	6.993	-0.962	-0.307	6.953	-0.965	-0.3
H(37)	-3.94	-2.189	0.006	-3.925	-2.176	0.016	-3.94	-2.189	0.006
H(38)	-3.933	2.2	-0.012	-3.914	2.192	-0.025	-3.933	2.2	-0.012



Scheme S1: Synthesis of 3,5-bisdipyrromethane-BODIPY