Supporting Information

Singlet and Triplet Excited State Dynamics of 3,7-Bis(ArylEthynyl)Phenothiazines: Intramolecular Charge Transfer and Reverse Intersystem Crossing

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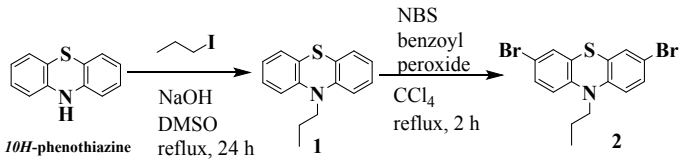
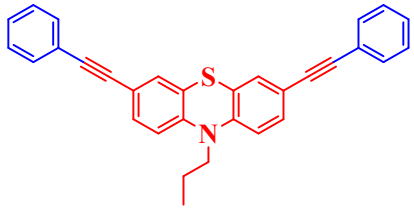


Scheme S1. Synthesis of 3,7-dibromophenothiazine **2**.

^{1}H NMR



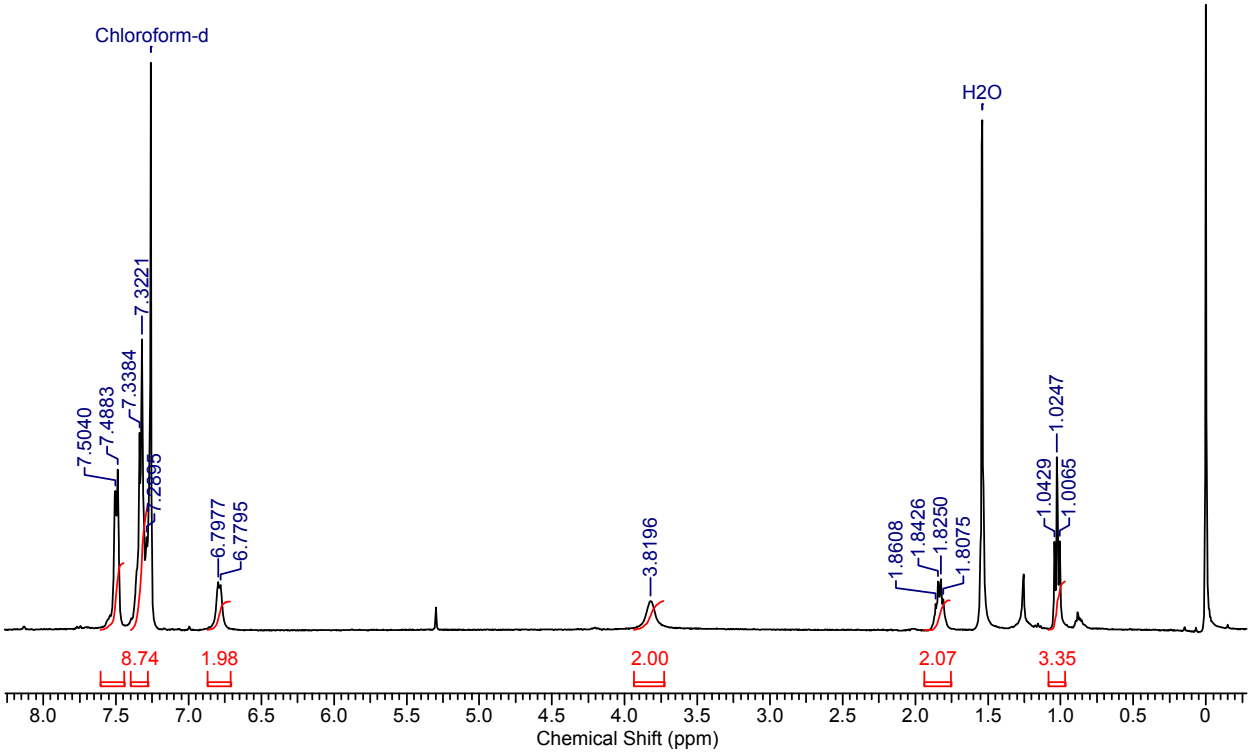


Figure S1. ^{1}HNMR of phenothiazine **4a**.

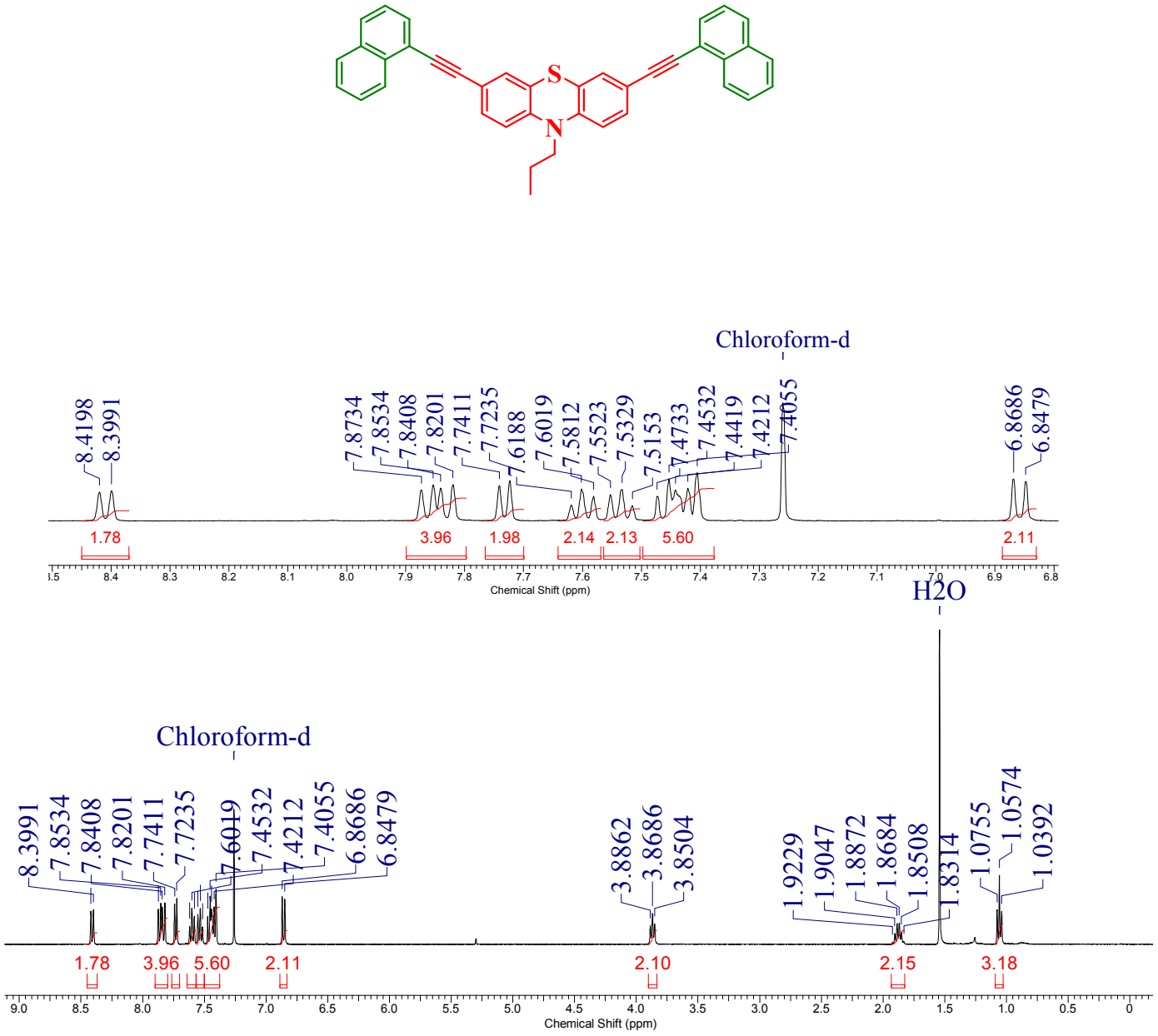


Figure S2. [1]HNMR of phenothiazine **4b**.

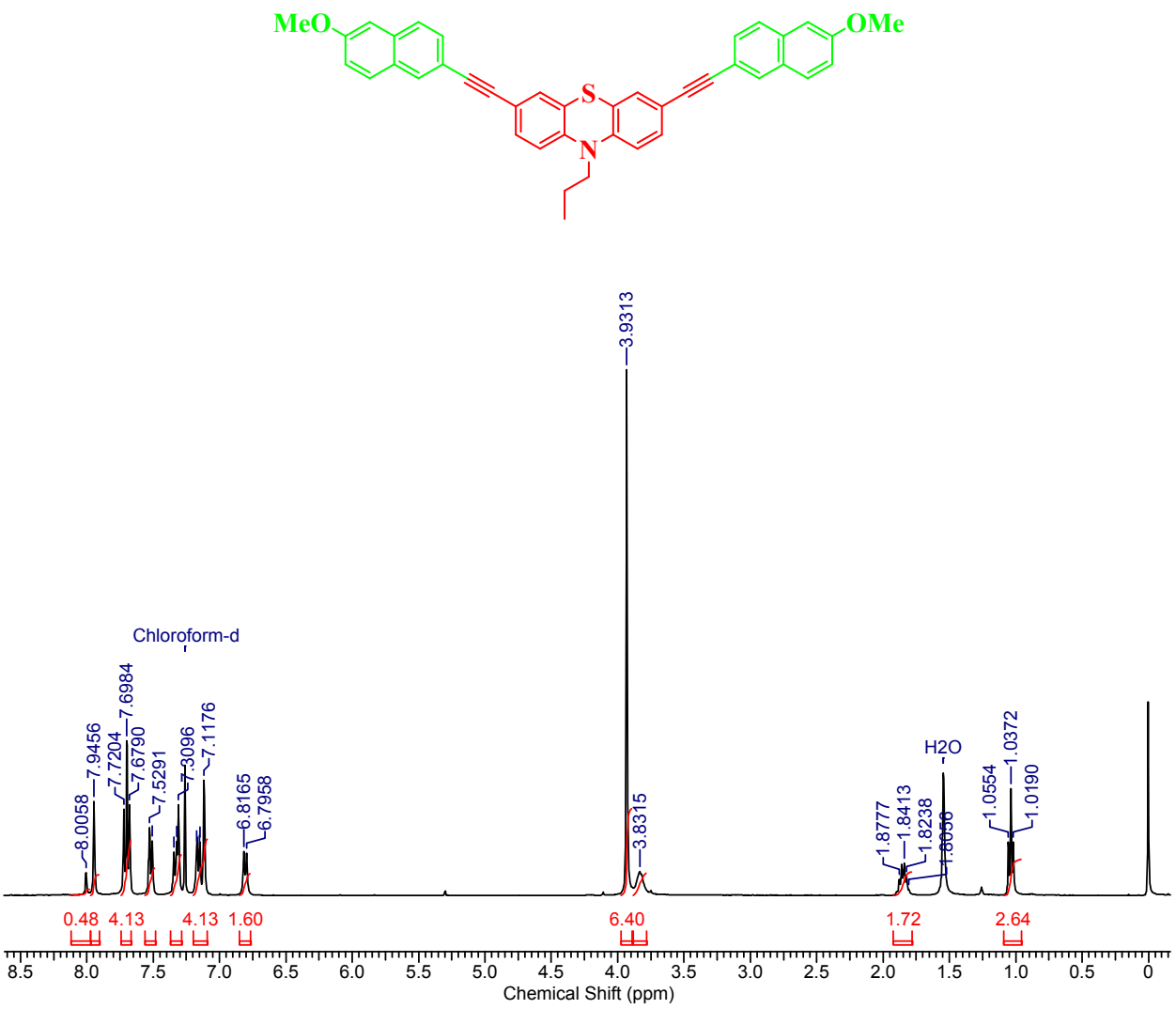


Figure S3. [1]HNMR of phenothiazine **4c**.

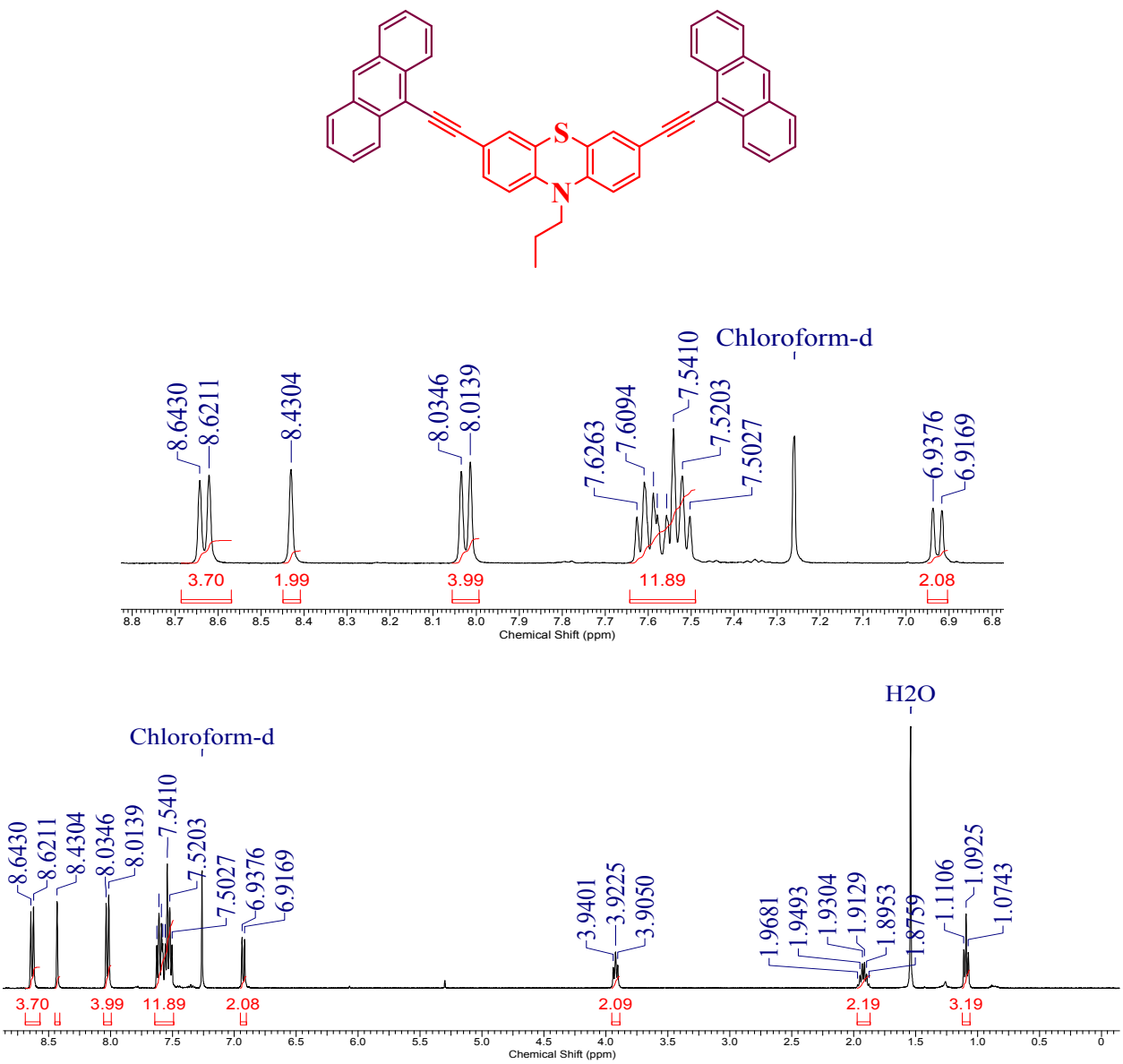


Figure S4. [1]HNMR of phenothiazine **4d**.

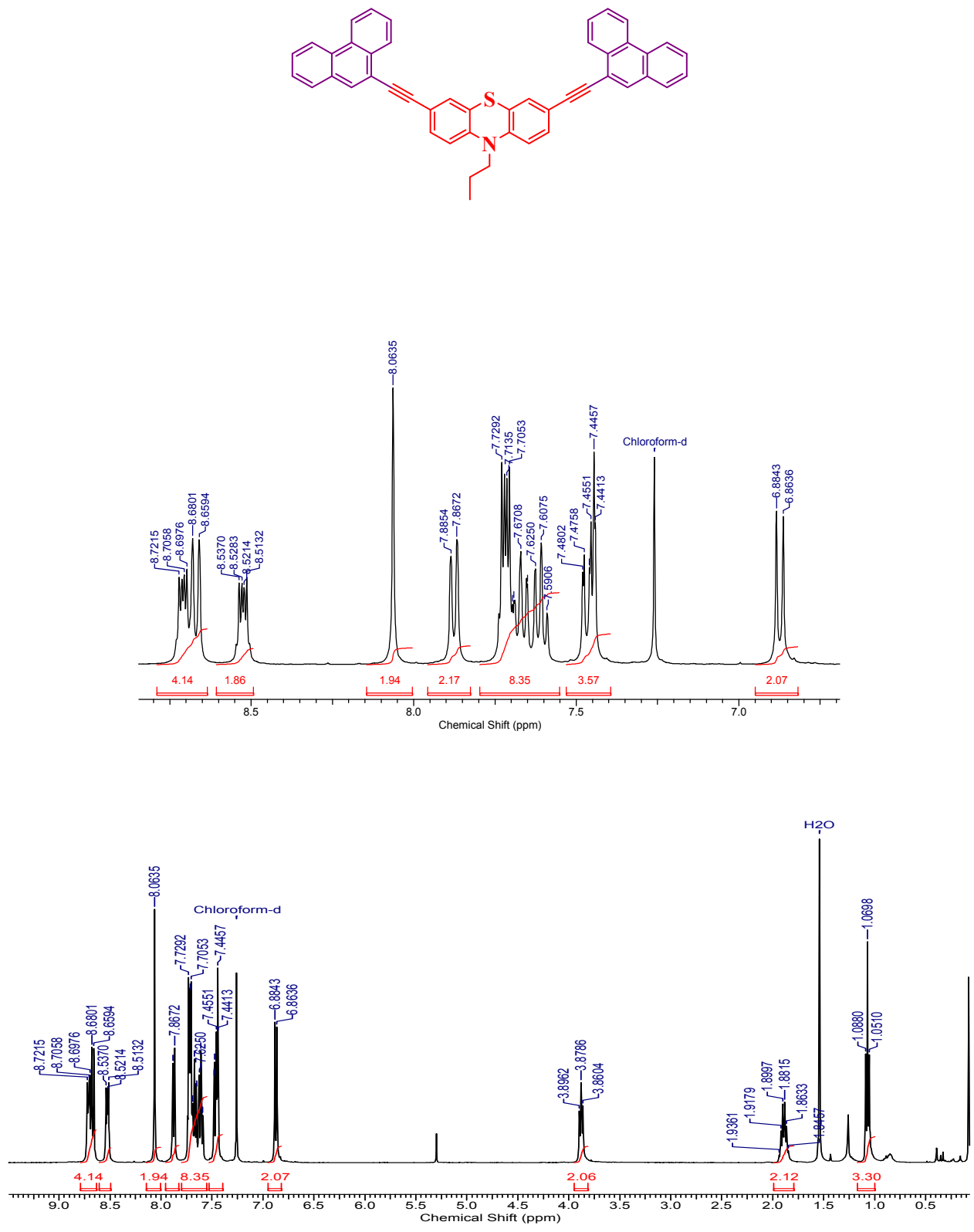


Figure S5. [1]HNMR of phenothiazine **4e**.

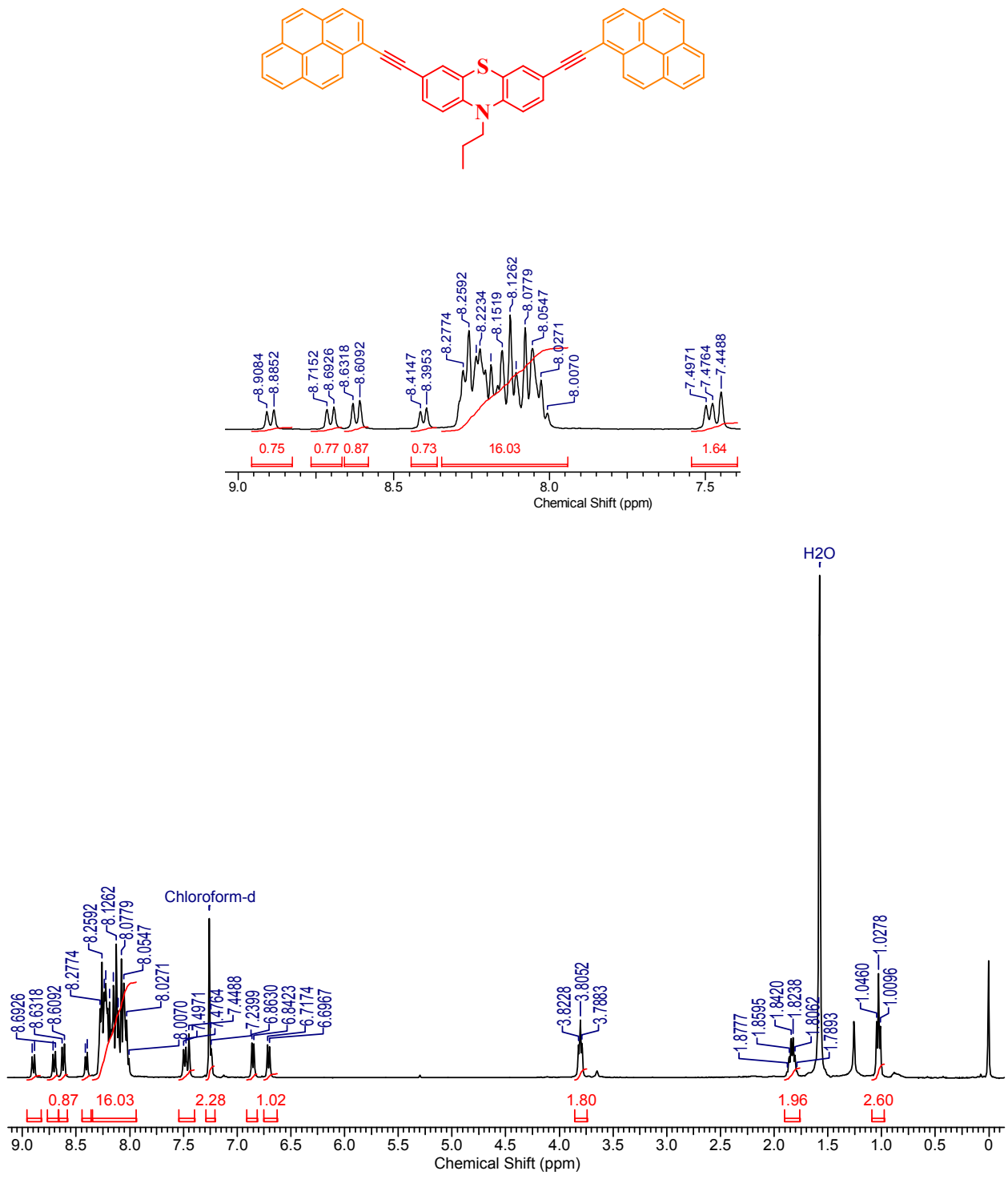


Figure S6. [1]HNMR of phenothiazine **4f**.

^{13}C NMR

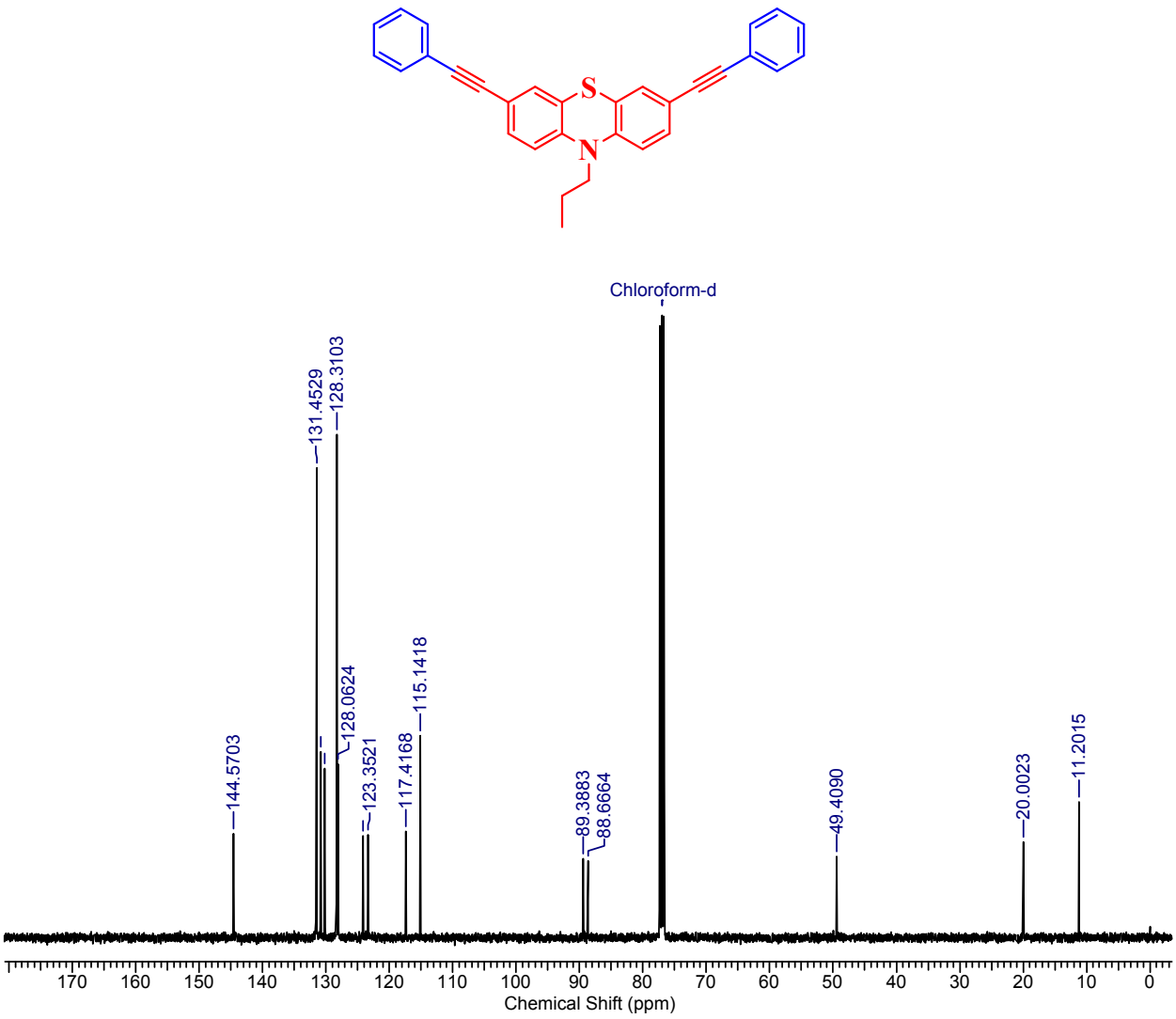


Figure S7. ^{13}C NMR of phenothiazine **4a**.

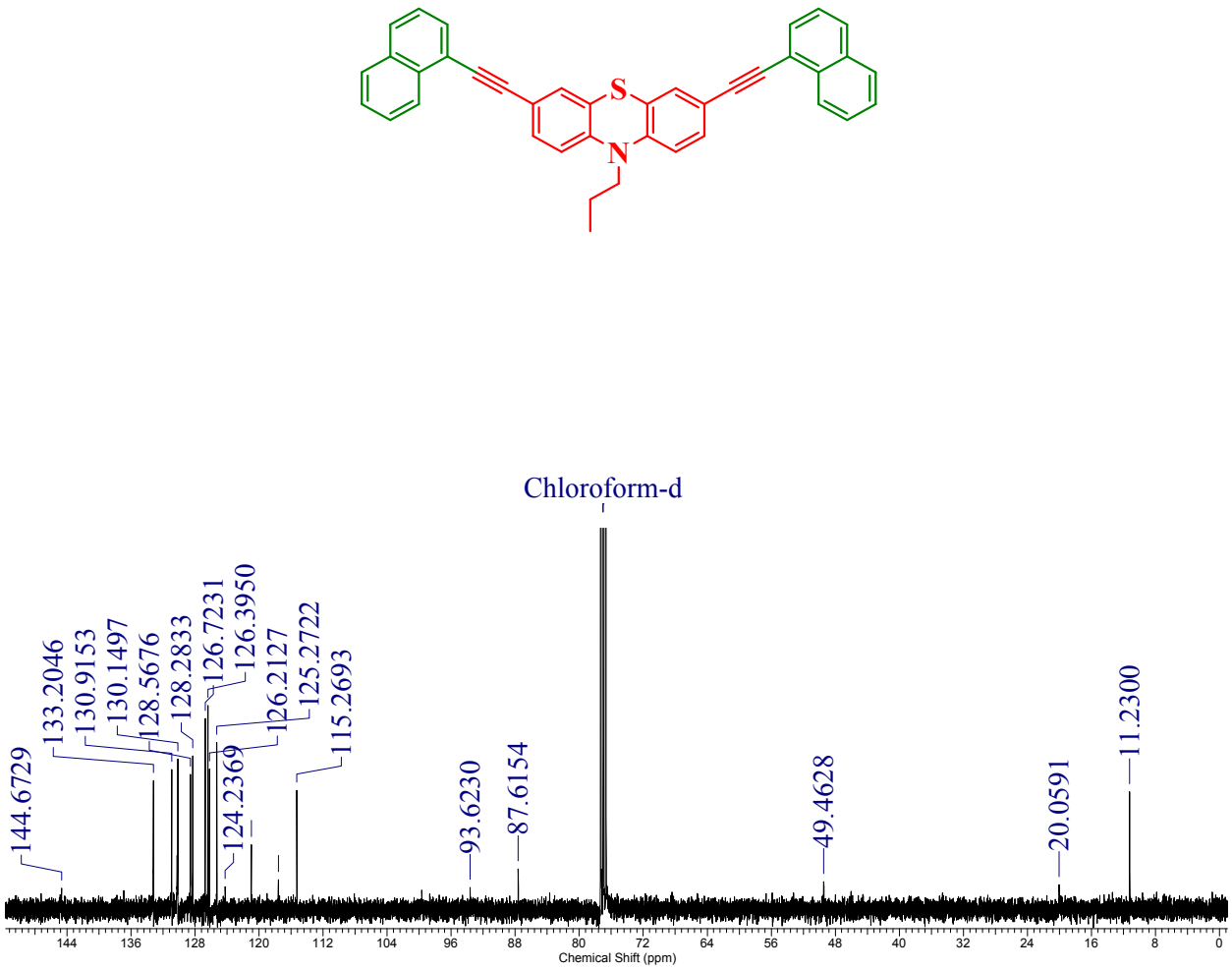


Figure S8. ^{13}C NMR of phenothiazine **4b**.

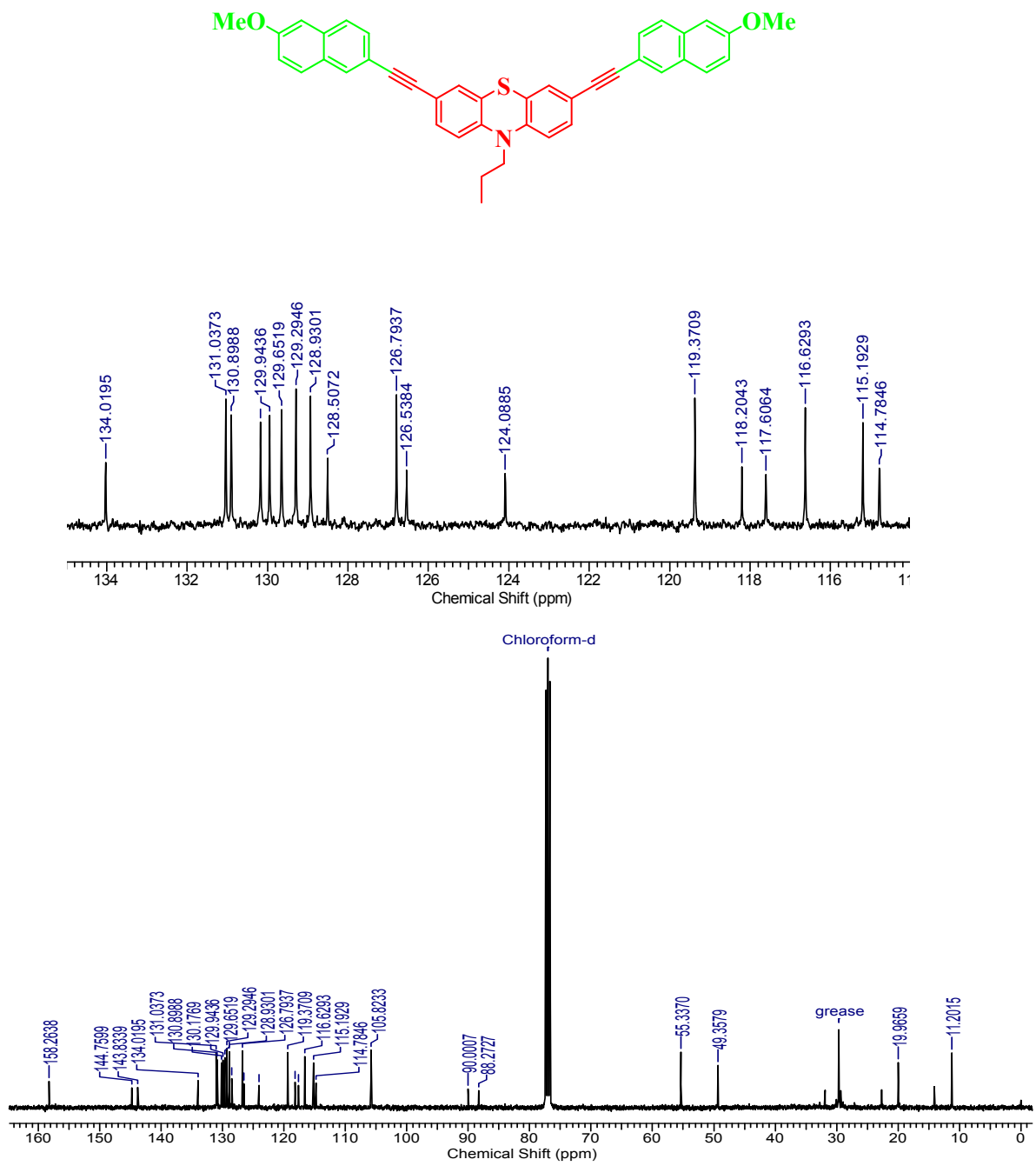


Figure S9. ^{13}C NMR of phenothiazine **4c**.

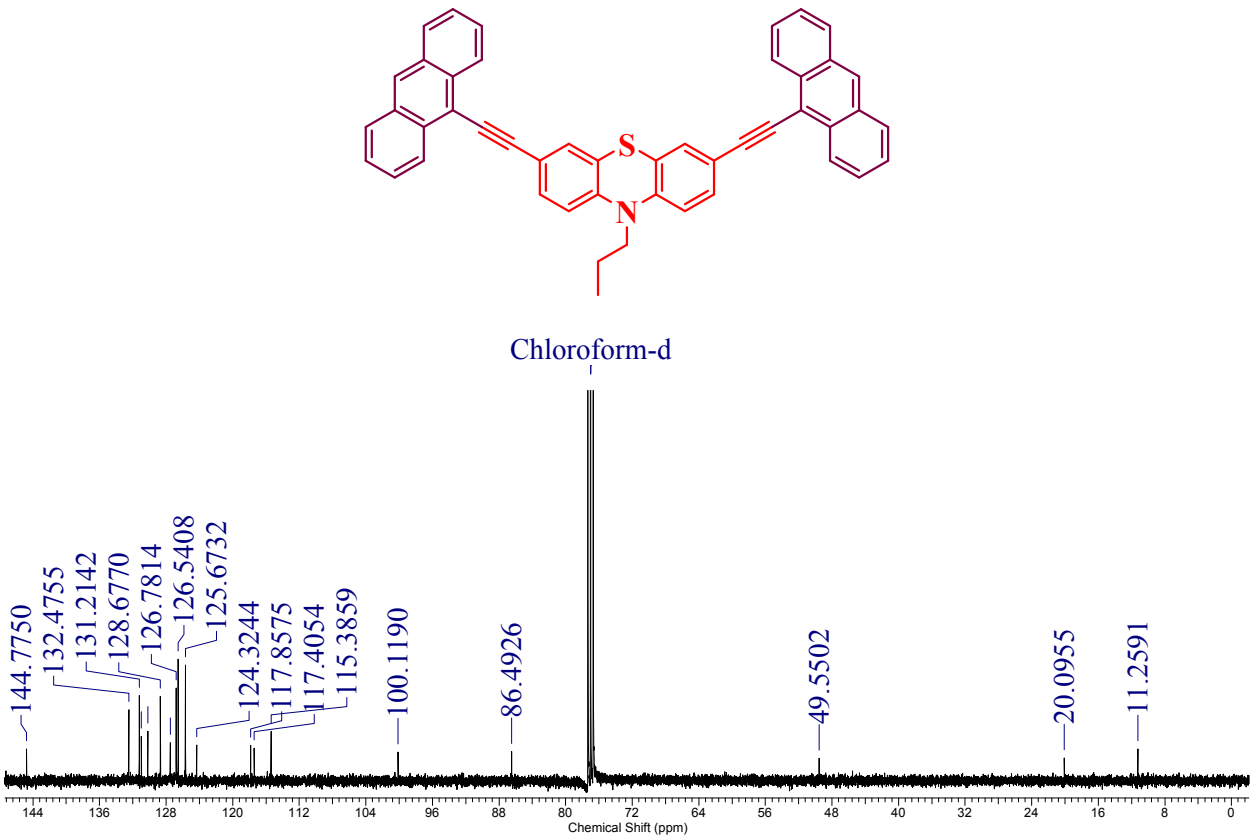


Figure S10. ^{13}C NMR of phenothiazine **4d**.

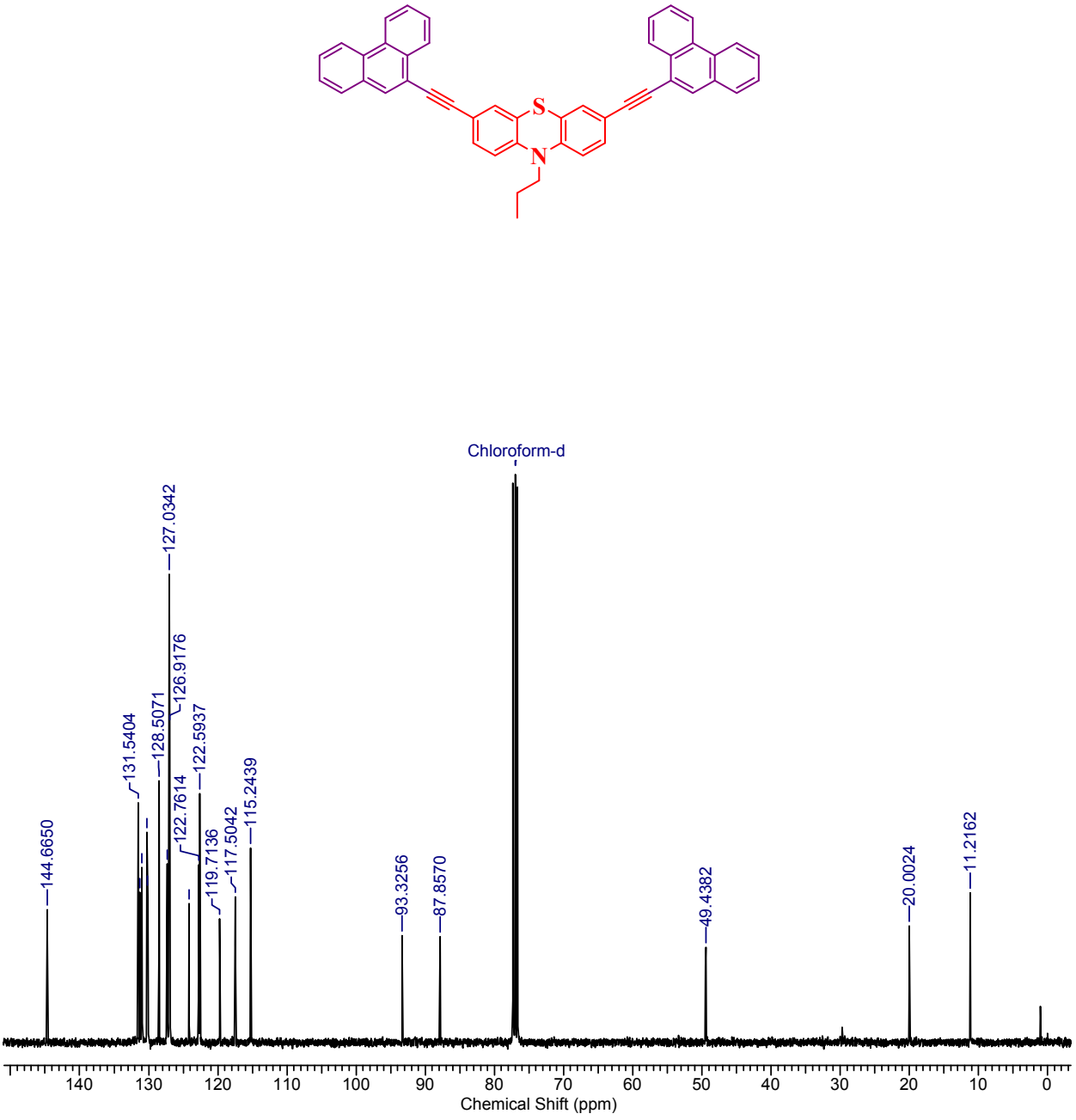


Figure S11. ^{13}C NMR of phenothiazine **4e**.

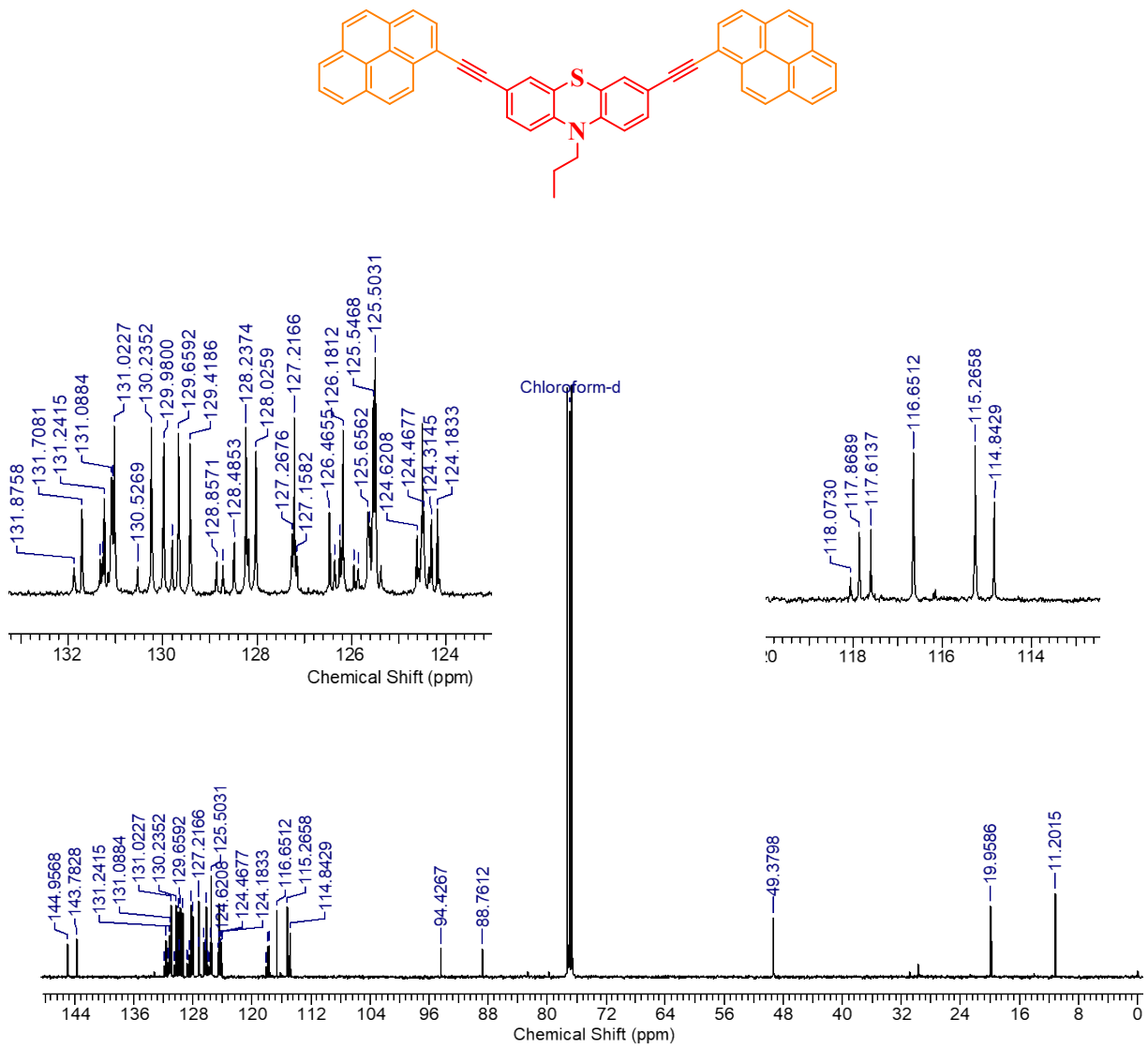


Figure S12. ^{13}C NMR of phenothiazine **4f**.

HRMS

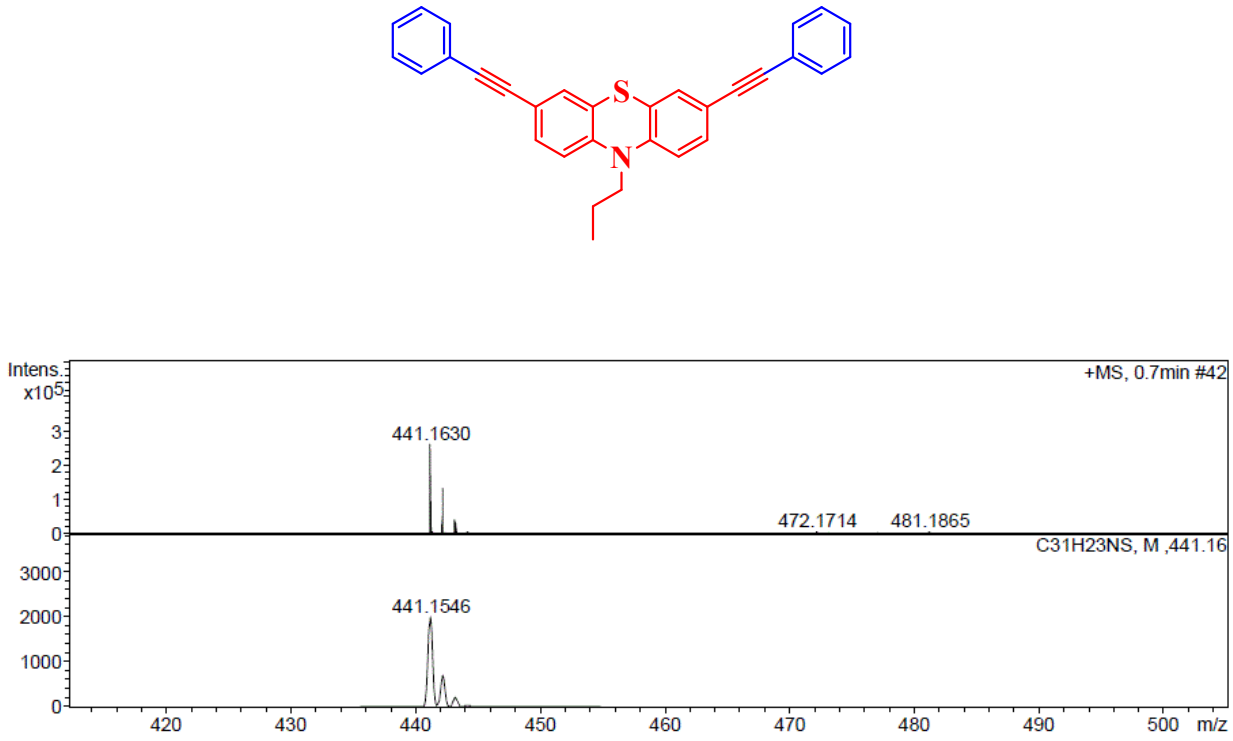
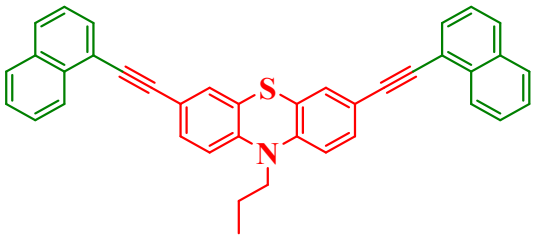


Figure S13. HRMS of **4a**.



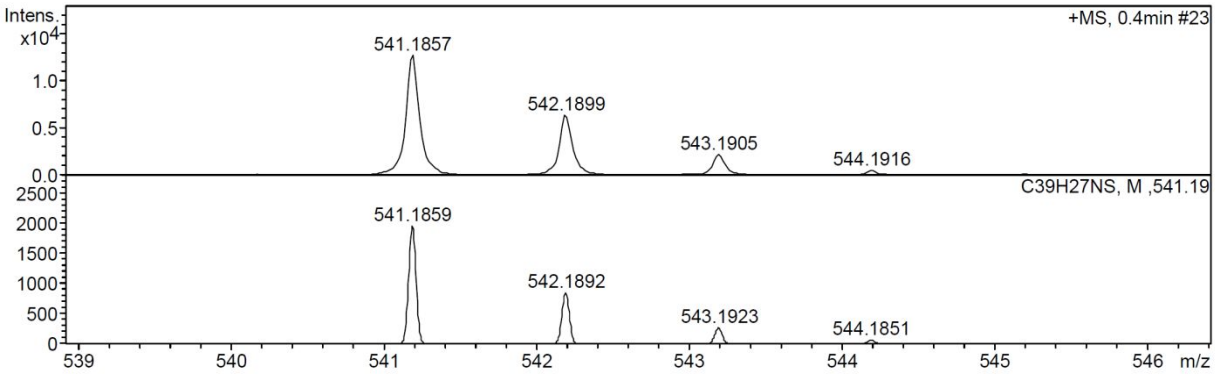
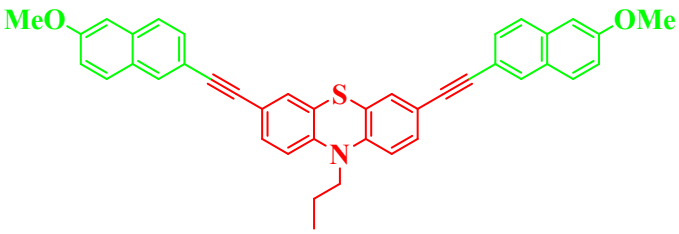


Figure S14. HRMS of **4b.**



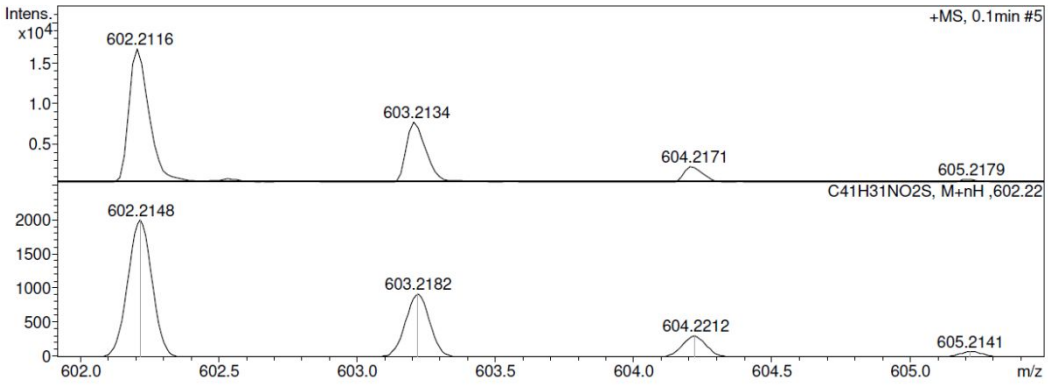


Figure S15. HRMS of **4c**.

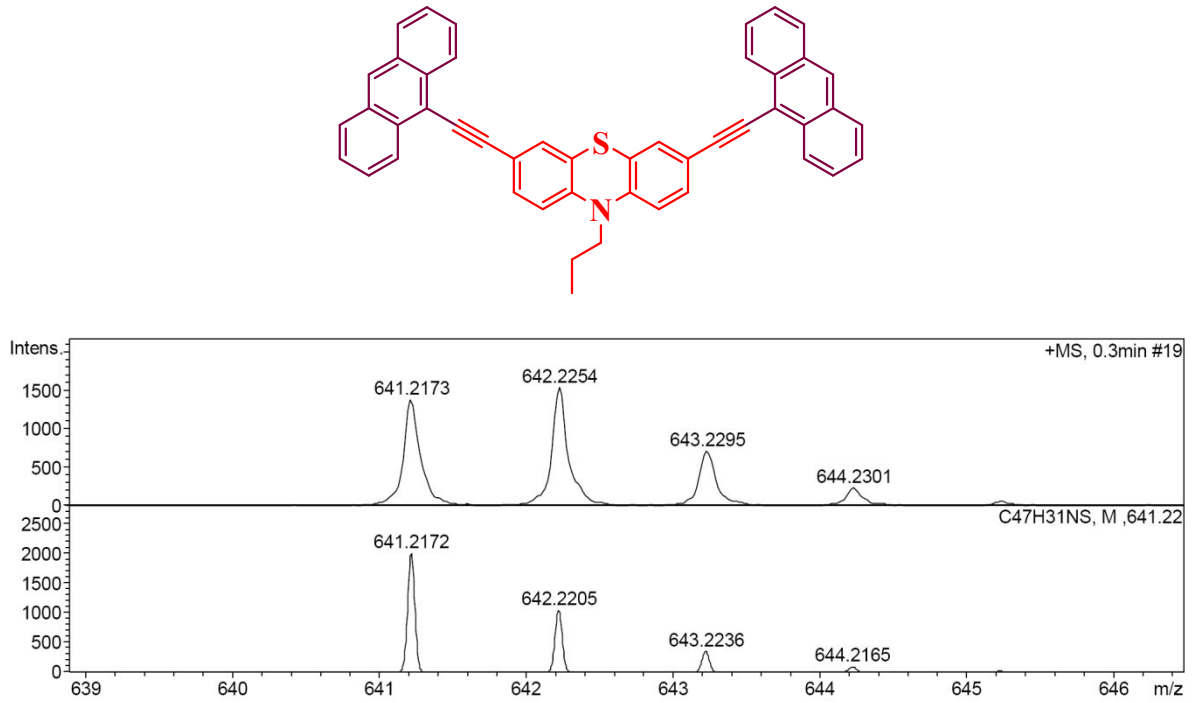


Figure S16. HRMS of **4d**.

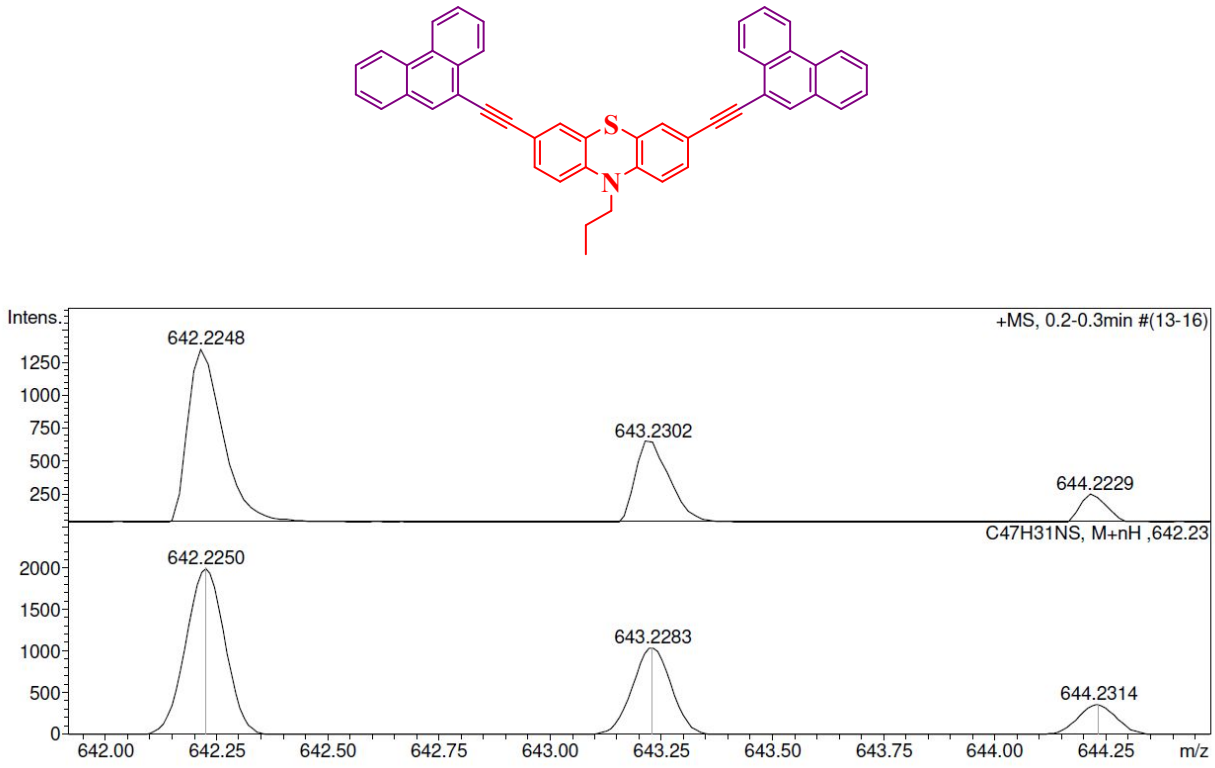


Figure S17. HRMS of **4e**.

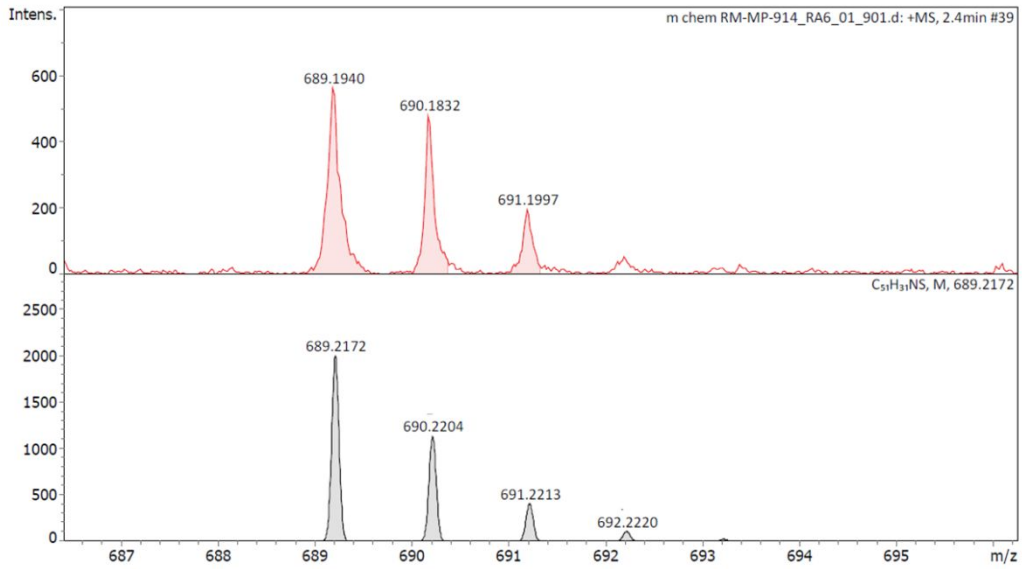


Figure S18. HRMS of **4f**.

Table S1. Solvent dependent studies of phenothiazines **4a–4f** in different solvents.

Phenothiazine	Solvent	f (ε,n²)	λ_{abs} (nm)	λ_{em} (nm)	Stokes Shift Δυ (cm^{-1})
4a	Toluene	0.0242	380	479	5440
	THF	0.441	371	480	6120
	DCM	0.474	374	483	6035
	DMF	0.664	377	489	6075
4b	Toluene	0.0242	381	490	5840
	THF	0.441	383	495	5910
	DCM	0.474	385	497	5850
	DMF	0.664	389	512	6180
4c	Toluene	0.0242	369	482	6355
	THF	0.441	367	484	6590
	DCM	0.474	368	487	6640
	DMF	0.664	369	493	6820

4d	Toluene	0.0242	439	528	3840
	$CHCl_3$	0.293	439	547	4498
	EtAc	0.400	436	564	5205
	THF	0.441	439	568	5173
	DCM	0.474	440	589	5750
	Acetone	0.651	437	627	6934
	DMF	0.664	443	657	7350
4e	Toluene	0.0242	382	492	5850
	THF	0.441	383	501	6150
	DCM	0.474	388	502	5853
	DMF	0.664	393	520	6215
4f	Toluene	0.0242	406	446 476	2210
	THF	0.441	403	443 473	2240
	DCM	0.474	404	446 474	2330
	DMF	0.664	405	450 474	2450

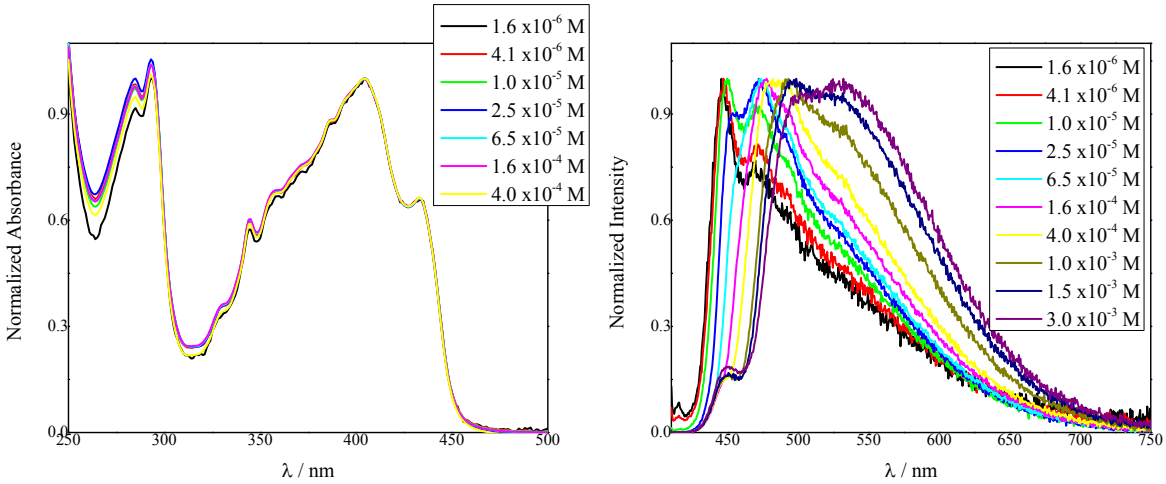


Figure S19. Normalized absorption and emission spectra of **4f** in DCM solution at different concentrations.

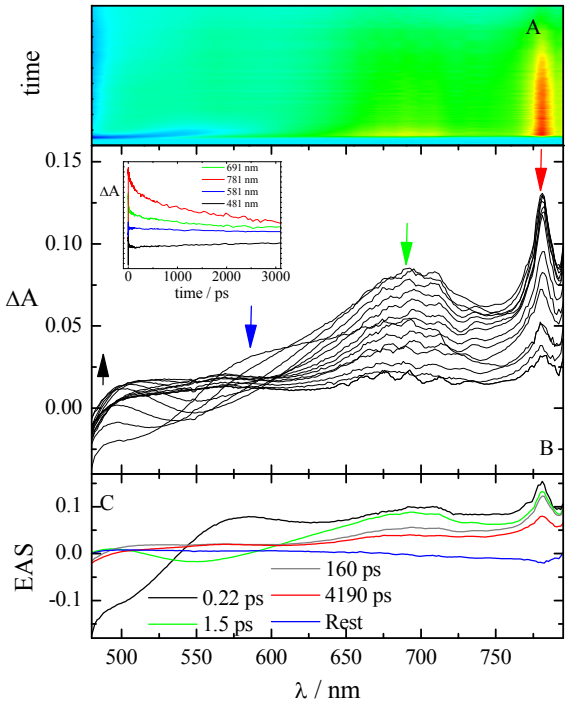


Figure S20. Femtosecond transient absorption spectroscopy of **4d** in DCM: A) contour plot of the experimental data, B) time resolved absorption spectra recorded at different delays after the laser pulse. Insets: decay kinetics recorded at meaningful wavelengths and C) evolution associated spectra obtained by SVD and Global Analysis.

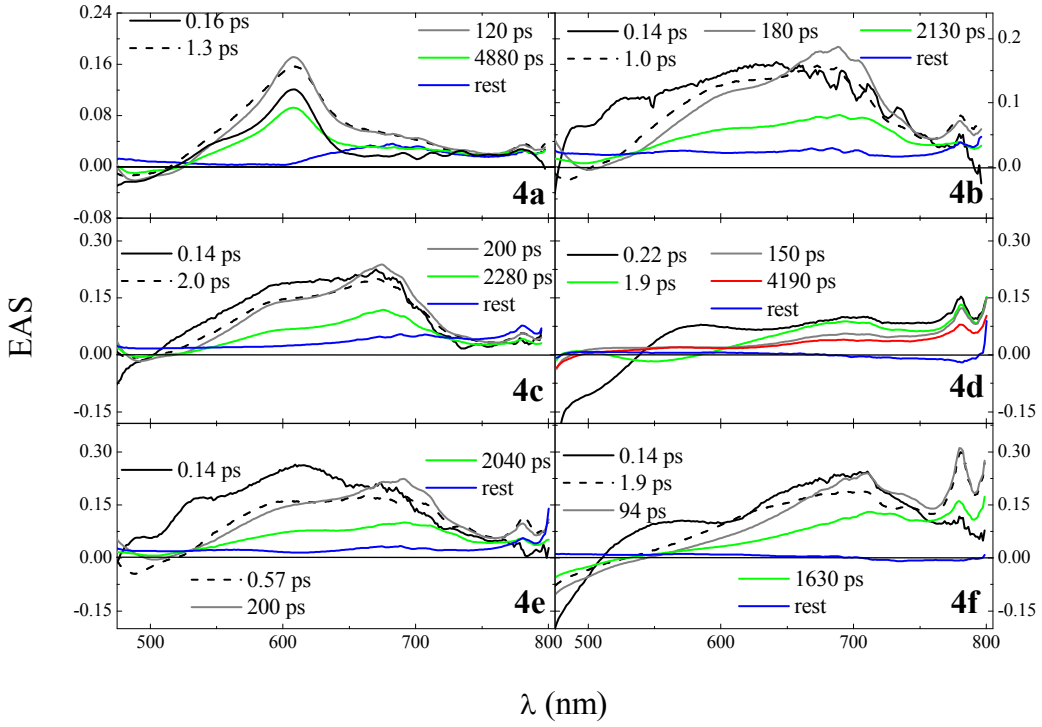


Figure S21. Evolution associated spectra obtained by SVD and Global Analysis of the femtosecond transient absorption data in DCM.

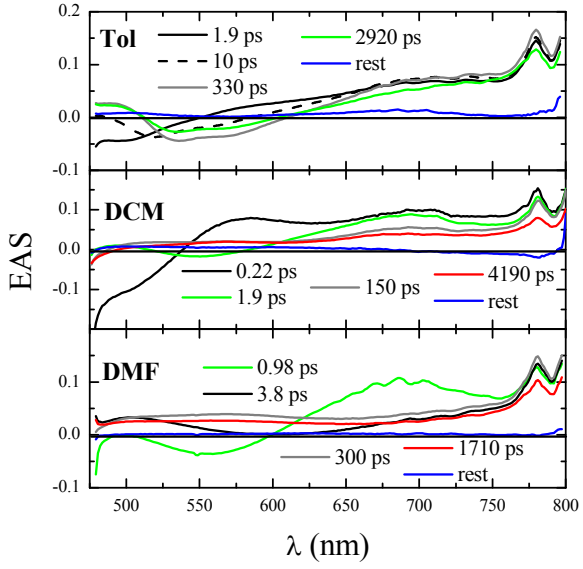


Figure S22. Evolution associated spectra obtained by SVD and Global Analysis of the femtosecond transient absorption data for **4d**.

Table S2. Lifetimes and assignment of the exponential components revealed by Global Fitting of the femtosecond transient absorption data of **4a–4f** in DCM.

Compound	τ / ps	Assignment
4a	0.16 1.3 120 4880 Rest	Solvation Solvation Structural Relaxation S_1 T_1
4b	0.14 1.0 180 2130 Rest	Solvation Solvation Structural Relaxation S_1 T_1
4c	0.14 2.0 200 2280 Rest	Solvation Solvation Structural Relaxation S_1 T_1
4d	0.22 1.9 150 4190 Rest	Solvation Solvation+ S_1 (LE) Structural Relaxation S_1 (ICT) T_1
4e	0.14 0.57 200 2040 Rest	Solvation Solvation Structural Relaxation S_1 T_1
4f	0.14 1.9 94 1630 Rest	Solvation Solvation Structural Relaxation S_1 T_1

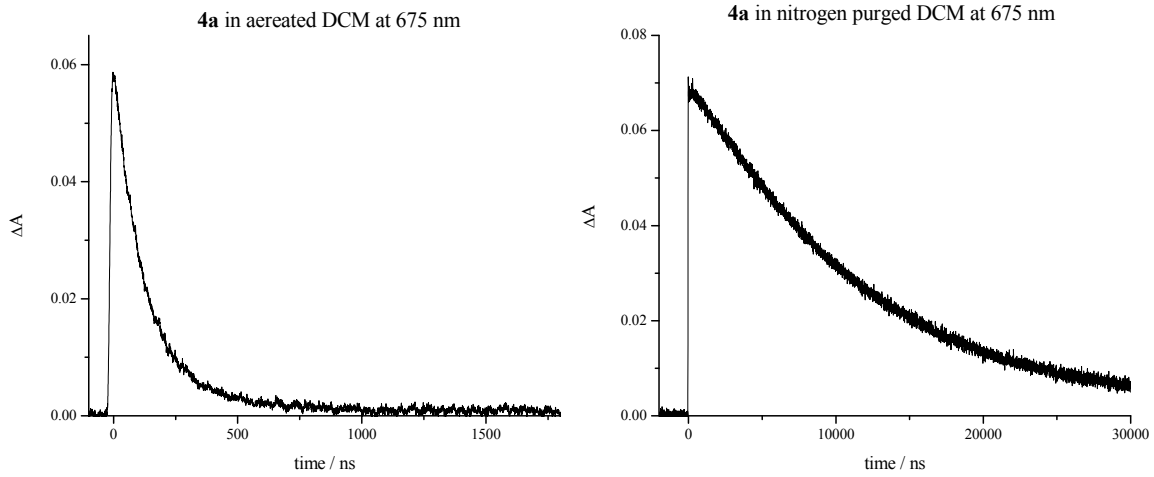


Figure S23. Nanosecond transient absorption decay kinetics of **4a** in air–equilibrated and nitrogen–purged DCM.

Evaluation of reverse intersystem crossing rate constants

Adachi Method:

4d *in toluene*

$$\phi_{prompt} = \frac{\phi_{prompt,air} \times \tau_{prompt,N2}}{\tau_{prompt,air}} = \frac{0.75 \times 3.27ns}{2.92ns} = 0.84$$

$$\phi_{delayed} = \phi_{N2} - \phi_{prompt} = 0.88 - 0.84 = 0.04$$

$$k_{prompt} = \frac{1}{\tau_{prompt,N2}} = \frac{1}{3.27\ ns} = 3.06 \times 10^{8} s^{-1}$$

$$k_{delayed} = \frac{1}{\tau_{delayed,N2}} = \frac{1}{6\ \mu s} = 1.67 \times 10^{5} s^{-1}$$

$$k_{ISC} = (1 - \phi_{prompt}) \times k_{prompt} = 4.90 \times 10^{7} s^{-1}$$

$$k_{rISC} = \frac{k_{prompt} \times k_{delayed} \times \phi_{delayed}}{k_{ISC} \times \phi_{prompt}} = 4.97 \times 10^{4} s^{-1}$$

Goodson Method:

4d *in toluene*

$$\phi_{TADF} = \phi_{N2} - \phi_{air} = 0.88 - 0.75 = 0.13$$

$$k_{T} = \frac{1}{\tau_{T,N2}} = \frac{1}{6\ \mu s} = 1.67 \times 10^{5} s^{-1}$$

$k_{rISC} = k_T \times \phi_{TADF} = 2.17 \times 10^4 s^{-1}$

Goodson Method:

4a *in DCM*

$\phi_{TADF} = \phi_{N2} - \phi_{air} = 0.89 - 0.82 = 0.07$

$k_T = \frac{1}{\tau_{T,N2}} = \frac{1}{12\ \mu s} = 8.33 \times 10^4 s^{-1}$

$k_{rISC} = k_T \times \phi_{TADF} = 5.83 \times 10^3\ s^{-1}$

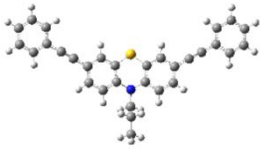
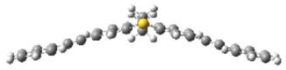
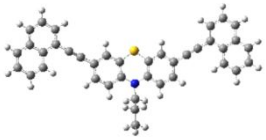
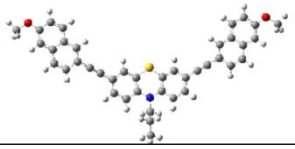
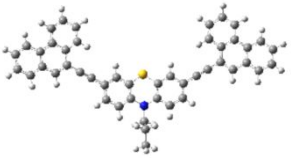
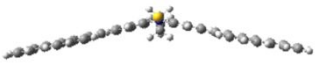
Phenothiazines	Front View	Top View
4a		
4b		
4c		
4d		
4e		
4f		

Figure S24. Front view and top view of the optimized geometry of **4a-4f.**

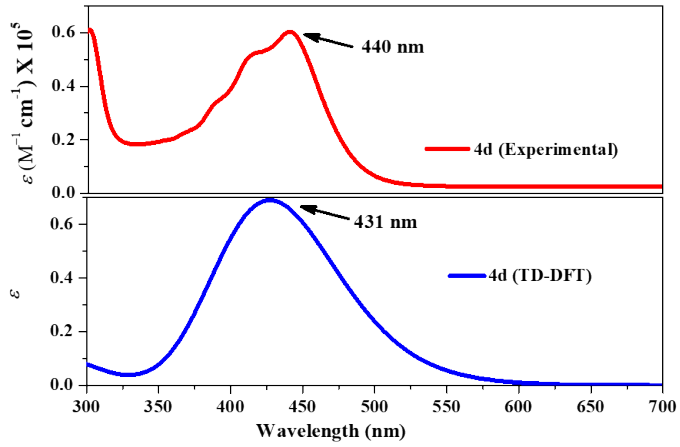


Figure S25. Theoretical absorption spectra of **4d**.

DFT Calculations

Phenothiazine **4a**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.403757	2.354307	-0.033080
2	6	0	-1.234372	1.685949	0.375985
3	6	0	-3.622105	1.694651	-0.147864
4	6	0	-1.354867	0.310726	0.677376
5	6	0	-3.727899	0.319106	0.113303
6	6	0	1.234377	1.685943	0.375979
7	6	0	-2.562075	-0.358941	0.519943
8	6	0	2.403770	2.354297	-0.033071
9	6	0	1.354865	0.310719	0.677371

10	1	0	-2.612759	-1.419765	0.741416
11	6	0	3.622114	1.694635	-0.147853
12	1	0	2.375247	3.408784	-0.269492
13	6	0	2.562070	-0.358954	0.519940
14	6	0	3.727899	0.319087	0.113306
15	1	0	2.612748	-1.419779	0.741411
16	7	0	0.000004	2.359741	0.498357
17	16	0	-0.000002	-0.571575	1.416860
18	6	0	0.000003	3.828104	0.507852
19	1	0	0.873710	4.148359	1.084314
20	1	0	-0.873645	4.148351	1.084407
21	6	0	-0.000085	4.533719	-0.862575
22	1	0	0.871232	4.220406	-1.446291
23	1	0	-0.871480	4.220406	-1.446175
24	6	0	-0.000074	6.057427	-0.702847
25	1	0	-0.883714	6.402370	-0.153912
26	1	0	0.883638	6.402370	-0.154030
27	1	0	-0.000139	6.555220	-1.676756
28	1	0	-4.501458	2.247941	-0.459345
29	1	0	4.501472	2.247922	-0.459325
30	1	0	-2.375225	3.408791	-0.269513
31	6	0	-4.964554	-0.369647	-0.021189
32	6	0	-6.021832	-0.961238	-0.135765
33	6	0	4.964551	-0.369672	-0.021182
34	6	0	6.021829	-0.961263	-0.135755

35	6	0	7.258585	-1.655198	-0.269098
36	6	0	7.337934	-3.037129	-0.001782
37	6	0	8.548414	-3.711181	-0.132888
38	1	0	6.442993	-3.567198	0.307242
39	6	0	9.698658	-3.025661	-0.531072
40	6	0	-7.258571	-1.655203	-0.269101
41	6	0	-7.337891	-3.037131	-0.001763
42	6	0	-8.425371	-0.973345	-0.670324
43	6	0	-8.548356	-3.711212	-0.132861
44	1	0	-6.442939	-3.567175	0.307272
45	6	0	-9.631187	-1.656305	-0.798620
46	6	0	-9.698613	-3.025724	-0.531060
47	6	0	9.631202	-1.656240	-0.798611
48	1	0	10.522266	-1.118151	-1.108626
49	6	0	8.425370	-0.973308	-0.670308
50	1	0	8.370264	0.090430	-0.877396
51	1	0	-8.370288	0.090391	-0.877427
52	1	0	-10.522263	-1.118241	-1.108644
53	1	0	-8.594861	-4.775943	0.076360
54	1	0	-10.641197	-3.555288	-0.632190
55	1	0	8.594943	-4.775914	0.076316
56	1	0	10.641253	-3.555203	-0.632209

E (HF) = –1648.0364362

Phenothiazine **4b**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.403321	2.342749	-0.253648
2	6	0	1.234155	1.669043	-0.654373
3	6	0	3.621369	1.684694	-0.129188
4	6	0	1.354855	0.289962	-0.937919
5	6	0	3.727787	0.305686	-0.372204
6	6	0	-1.234158	1.669016	-0.654340
7	6	0	2.561922	-0.377519	-0.771286
8	6	0	-2.403309	2.342684	-0.253486
9	6	0	-1.354858	0.289951	-0.937929
10	1	0	2.612670	-1.441153	-0.978760
11	6	0	-3.621349	1.684623	-0.129027
12	1	0	-2.374645	3.400154	-0.030884
13	6	0	-2.561922	-0.377544	-0.771297
14	6	0	-3.727776	0.305633	-0.372145
15	1	0	-2.612671	-1.441166	-0.978833
16	7	0	-0.000007	2.341145	-0.785317
17	16	0	0.000006	-0.601813	-1.666061
18	6	0	-0.000017	3.809393	-0.815579
19	1	0	-0.873711	4.121263	-1.396639

20	1	0	0.873639	4.121270	-1.396696
21	6	0	0.000025	4.534615	0.544564
22	1	0	-0.871253	4.229783	1.132821
23	1	0	0.871391	4.229864	1.132731
24	6	0	-0.000051	6.055868	0.363010
25	1	0	0.883580	6.393070	-0.190683
26	1	0	-0.883785	6.392998	-0.190562
27	1	0	-0.000005	6.567281	1.329820
28	1	0	4.499793	2.243190	0.175632
29	1	0	-4.499760	2.243088	0.175888
30	1	0	2.374668	3.400241	-0.031145
31	6	0	4.962799	-0.382970	-0.226949
32	6	0	6.014764	-0.984234	-0.104634
33	6	0	-4.962786	-0.383030	-0.226897
34	6	0	-6.014748	-0.984300	-0.104584
35	6	0	-7.234928	-1.702963	0.033501
36	6	0	-8.433637	-1.041486	0.482049
37	6	0	-7.274204	-3.061406	-0.266518
38	6	0	-8.464655	0.339089	0.804989
39	6	0	-9.638228	-1.806207	0.607315
40	6	0	-8.466775	-3.800838	-0.139097
41	1	0	-6.366835	-3.551453	-0.603538
42	6	0	-9.628486	0.939343	1.232005
43	1	0	-7.549804	0.914322	0.708991
44	6	0	-10.821449	-1.155433	1.050703

45	6	0	-9.624621	-3.189870	0.288155
46	1	0	-8.464238	-4.859294	-0.381304
47	6	0	-10.819682	0.185925	1.356693
48	1	0	-9.634095	1.997788	1.475351
49	1	0	-11.732362	-1.740983	1.143917
50	1	0	-10.545071	-3.758901	0.387065
51	1	0	-11.731271	0.669982	1.694519
52	6	0	7.234912	-1.702935	0.033533
53	6	0	8.433655	-1.041477	0.482027
54	6	0	7.274119	-3.061407	-0.266364
55	6	0	8.464751	0.339127	0.804854
56	6	0	9.638202	-1.806256	0.607380
57	6	0	8.466647	-3.800889	-0.138867
58	1	0	6.366729	-3.551435	-0.603356
59	6	0	9.628615	0.939352	1.231813
60	1	0	7.549930	0.914401	0.708820
61	6	0	10.821461	-1.155509	1.050707
62	6	0	9.624521	-3.189947	0.288347
63	1	0	8.464057	-4.859368	-0.380973
64	6	0	10.819771	0.185877	1.356568
65	1	0	9.634288	1.997820	1.475058
66	1	0	11.732338	-1.741104	1.143983
67	1	0	10.544929	-3.759029	0.387342
68	1	0	11.731386	0.669915	1.694351

E (HF) = –1955.3308079

Phenothiazine **4c**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.404200	3.739460	0.074898
2	6	0	1.234520	3.092930	-0.367240
3	6	0	3.621885	3.073842	0.159216
4	6	0	1.354821	1.734017	-0.735278
5	6	0	3.727350	1.712200	-0.167619
6	6	0	-1.234484	3.092905	-0.367169
7	6	0	2.561119	1.056306	-0.608755
8	6	0	-2.404123	3.739421	0.075088
9	6	0	-1.354788	1.734003	-0.735223
10	1	0	2.611018	0.007414	-0.881316
11	6	0	-3.621804	3.073801	0.159467
12	1	0	-2.376622	4.781282	0.362352
13	6	0	-2.561084	1.056291	-0.608639
14	6	0	-3.727279	1.712173	-0.167407
15	1	0	-2.611002	0.007402	-0.881208
16	7	0	0.000019	3.772077	-0.457606
17	16	0	0.000003	0.889821	-1.518307

18	6	0	0.000020	5.238414	-0.387779
19	1	0	-0.873610	5.589804	-0.945854
20	1	0	0.873632	5.589798	-0.945890
21	6	0	0.000057	5.867215	1.019701
22	1	0	-0.871389	5.521531	1.584548
23	1	0	0.871382	5.521307	1.584593
24	6	0	0.000248	7.397419	0.944746
25	1	0	0.883947	7.771704	0.415400
26	1	0	-0.883287	7.771927	0.415285
27	1	0	0.000237	7.841220	1.944438
28	1	0	4.501131	3.610826	0.498390
29	1	0	-4.501026	3.610768	0.498729
30	1	0	2.376732	4.781341	0.362102
31	6	0	4.961935	1.015234	-0.063466
32	6	0	6.013987	0.408974	0.023945
33	6	0	-4.961835	1.015148	-0.063144
34	6	0	-6.013854	0.408845	0.024347
35	6	0	-7.247997	-0.291400	0.131095
36	6	0	-7.336763	-1.642995	-0.187072
37	6	0	-8.558767	-2.344465	-0.082144
38	1	0	-6.449910	-2.172129	-0.522816
39	6	0	-9.733051	-1.654854	0.360520
40	6	0	7.248072	-0.291346	0.130659
41	6	0	7.336521	-1.643259	-0.186216
42	6	0	8.425175	0.389291	0.569453

43	6	0	8.558522	-2.344745	-0.081322
44	1	0	6.449418	-2.172652	-0.520893
45	6	0	9.622513	-0.273586	0.678495
46	6	0	9.733145	-1.654815	0.359949
47	6	0	8.668014	-3.728835	-0.401000
48	6	0	10.963397	-2.356764	0.467972
49	6	0	9.863184	-4.389203	-0.290892
50	6	0	11.027635	-3.699430	0.148792
51	6	0	-9.622088	-0.273959	0.680376
52	1	0	-10.507721	0.258549	1.017187
53	6	0	-8.424751	0.388915	0.571265
54	1	0	-8.354795	1.442999	0.819001
55	6	0	-8.668586	-3.728232	-0.403128
56	6	0	-10.963322	-2.356784	0.468553
57	6	0	-11.027891	-3.699120	0.148063
58	1	0	-11.839208	-1.814981	0.806443
59	1	0	-7.783080	-4.260168	-0.740177
60	1	0	8.355450	1.443616	0.816224
61	1	0	10.508392	0.259150	1.014299
62	1	0	11.839546	-1.814708	0.804781
63	1	0	7.782252	-4.261031	-0.736962
64	1	0	9.956488	-5.442900	-0.531773
65	6	0	-9.863751	-4.388590	-0.292942
66	1	0	-9.957313	-5.442043	-0.534789
67	6	0	-13.355012	-3.860502	0.649684

68	1	0	-14.114162	-4.643491	0.630670
69	1	0	-13.262230	-3.469663	1.670903
70	1	0	-13.657907	-3.045213	-0.019534
71	6	0	13.355064	-3.860451	0.648958
72	1	0	13.263000	-3.468616	1.669859
73	1	0	14.114151	-4.643507	0.630196
74	1	0	13.657556	-3.045836	-0.021261
75	8	0	12.149478	-4.471165	0.215378
76	8	0	-12.149754	-4.470858	0.214672

E (HF) = –2184.3837787

Phenothiazine **4d**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.403779	-3.065162	-0.375284
2	6	0	-1.234073	-2.363043	-0.722697
3	6	0	-3.621407	-2.418412	-0.200456
4	6	0	-1.354742	-0.966199	-0.899514
5	6	0	-3.728266	-1.024181	-0.336483
6	6	0	1.234073	-2.363049	-0.722667
7	6	0	-2.561395	-0.313246	-0.681995

8	6	0	2.403759	-3.065187	-0.375225
9	6	0	1.354767	-0.966212	-0.899497
10	1	0	-2.609896	0.763298	-0.807154
11	6	0	3.621396	-2.418459	-0.200389
12	1	0	2.375689	-4.136722	-0.234828
13	6	0	2.561430	-0.313279	-0.681970
14	6	0	3.728281	-1.024230	-0.336432
15	1	0	2.609953	0.763264	-0.807141
16	7	0	0.000000	-3.023128	-0.903772
17	16	0	0.000020	-0.021437	-1.557611
18	6	0	0.000012	-4.485006	-1.046138
19	1	0	0.873762	-4.751556	-1.649185
20	1	0	-0.873684	-4.751568	-1.649258
21	6	0	-0.000030	-5.310666	0.255401
22	1	0	0.871302	-5.050486	0.864526
23	1	0	-0.871428	-5.050525	0.864449
24	6	0	0.000014	-6.814074	-0.039485
25	1	0	-0.883607	-7.108981	-0.616761
26	1	0	0.883713	-7.108950	-0.616658
27	1	0	-0.000030	-7.396230	0.886425
28	1	0	-4.499758	-2.998875	0.060290
29	1	0	4.499735	-2.998934	0.060373
30	1	0	-2.375735	-4.136699	-0.234900
31	6	0	-4.963510	-0.350886	-0.138838
32	6	0	-6.022614	0.228711	0.030950

33	6	0	4.963545	-0.350964	-0.138803
34	6	0	6.022659	0.228621	0.030957
35	6	0	7.256013	0.904095	0.227352
36	6	0	8.412070	0.170982	0.618911
37	6	0	7.332086	2.312360	0.031204
38	6	0	8.386389	-1.239606	0.829429
39	6	0	9.659058	0.867364	0.813536
40	6	0	8.589706	2.987605	0.232045
41	6	0	9.515422	-1.920703	1.206689
42	1	0	7.448904	-1.765109	0.684242
43	6	0	10.813204	0.120436	1.206604
44	6	0	9.716227	2.251563	0.616023
45	6	0	10.746955	-1.233652	1.398402
46	1	0	9.472929	-2.994824	1.361614
47	1	0	11.748144	0.655413	1.350555
48	1	0	10.660878	2.769061	0.765381
49	1	0	11.631253	-1.788632	1.697203
50	6	0	-7.255990	0.904134	0.227376
51	6	0	-8.412026	0.170958	0.618879
52	6	0	-7.332115	2.312406	0.031285
53	6	0	-8.386294	-1.239638	0.829330
54	6	0	-9.659044	0.867283	0.813518
55	6	0	-8.589767	2.987591	0.232132
56	6	0	-9.515306	-1.920797	1.206544
57	1	0	-7.448787	-1.765097	0.684131

58	6	0	-10.813167	0.120291	1.206533
59	6	0	-9.716265	2.251488	0.616065
60	6	0	-10.746869	-1.233803	1.398272
61	1	0	-9.472772	-2.994923	1.361425
62	1	0	-11.748131	0.655225	1.350493
63	1	0	-10.660940	2.768942	0.765422
64	1	0	-11.631150	-1.788831	1.697033
65	6	0	-6.202624	3.090576	-0.360270
66	6	0	-8.653908	4.401965	0.032294
67	6	0	-7.545908	5.113207	-0.343456
68	1	0	-7.608510	6.187167	-0.491571
69	6	0	-6.304496	4.446117	-0.541890
70	1	0	-5.431371	5.018962	-0.840067
71	6	0	8.653789	4.401976	0.032156
72	6	0	6.202565	3.090467	-0.360393
73	6	0	6.304382	4.446005	-0.542059
74	1	0	5.431238	5.018804	-0.840267
75	6	0	7.545764	5.113156	-0.343635
76	1	0	7.608323	6.187113	-0.491785
77	1	0	-5.255676	2.584483	-0.512336
78	1	0	-9.606838	4.901143	0.186622
79	1	0	9.606695	4.901199	0.186482
80	1	0	5.255641	2.584328	-0.512455

E (HF) = –2262.6131034

Phenothiazine **4e**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.404129	3.455951	0.130137
2	6	0	-1.234213	2.782534	0.529603
3	6	0	-3.622119	2.797446	0.006056
4	6	0	-1.354323	1.403235	0.812073
5	6	0	-3.727419	1.417920	0.247580
6	6	0	1.234246	2.782556	0.529629
7	6	0	-2.560866	0.735280	0.644888
8	6	0	2.404134	3.455987	0.130105
9	6	0	1.354403	1.403271	0.812157
10	1	0	-2.609413	-0.328529	0.852089
11	6	0	3.622156	2.797528	0.006074
12	1	0	2.376019	4.513668	-0.091722
13	6	0	2.560978	0.735366	0.645042
14	6	0	3.727514	1.418027	0.247710
15	1	0	2.609569	-0.328429	0.852304
16	7	0	0.000002	3.454576	0.660692
17	16	0	0.000027	0.511714	1.540852
18	6	0	-0.000029	4.922802	0.694226

19	1	0	0.873687	5.233320	1.275990
20	1	0	-0.873732	5.233273	1.276043
21	6	0	-0.000089	5.651095	-0.664188
22	1	0	0.871289	5.347748	-1.253085
23	1	0	-0.871438	5.347646	-1.253072
24	6	0	-0.000168	7.171909	-0.478960
25	1	0	-0.883876	7.507686	0.075463
26	1	0	0.883500	7.507769	0.075477
27	1	0	-0.000186	7.685621	-1.444539
28	1	0	-4.501628	3.354714	-0.297731
29	1	0	4.501639	3.354815	-0.297753
30	1	0	-2.376060	4.513660	-0.091564
31	6	0	-4.963579	0.731122	0.103033
32	6	0	-6.025121	0.147551	-0.022061
33	6	0	4.963681	0.731249	0.103170
34	6	0	6.025208	0.147657	-0.021963
35	6	0	7.271769	-0.522428	-0.169967
36	6	0	7.369082	-1.957858	0.051930
37	6	0	8.393446	0.188604	-0.523780
38	6	0	8.627563	-2.611117	-0.099679
39	6	0	9.667674	-0.433532	-0.684251
40	1	0	8.314636	1.259014	-0.687426
41	6	0	9.804654	-1.837895	-0.475616
42	6	0	-7.271705	-0.522490	-0.170114
43	6	0	-7.369117	-1.957868	0.052072

44	6	0	-8.393287	0.188522	-0.524260
45	6	0	-8.627606	-2.611096	-0.099582
46	6	0	-9.667561	-0.433559	-0.684616
47	1	0	-8.314387	1.258880	-0.688199
48	6	0	-9.804659	-1.837851	-0.475586
49	6	0	6.232370	-2.713082	0.415724
50	6	0	8.679342	-4.007016	0.125717
51	6	0	7.554015	-4.726294	0.481439
52	6	0	6.317235	-4.074903	0.628299
53	6	0	10.799853	0.334793	-1.049417
54	6	0	11.086148	-2.409494	-0.646117
55	6	0	12.178456	-1.639295	-1.003347
56	6	0	12.037656	-0.253829	-1.207656
57	6	0	-6.232479	-2.713080	0.416121
58	6	0	-8.679439	-4.006989	0.125840
59	6	0	-7.554177	-4.726264	0.481778
60	6	0	-6.317419	-4.074879	0.628827
61	6	0	-10.799681	0.334759	-1.049982
62	6	0	-11.086252	-2.409352	-0.645694
63	6	0	-12.178516	-1.639149	-1.003049
64	1	0	-13.150098	-2.108496	-1.125729
65	6	0	-12.037547	-0.253790	-1.207981
66	1	0	-12.898113	0.346063	-1.488429
67	1	0	-10.674443	1.403181	-1.204553
68	1	0	-11.229588	-3.473214	-0.495510

69	1	0	-9.620034	-4.534848	0.019124
70	1	0	-7.628676	-5.796988	0.647321
71	1	0	-5.432647	-4.638996	0.908202
72	1	0	-5.284444	-2.197798	0.525930
73	1	0	10.674717	1.403277	-1.203635
74	1	0	12.898276	0.346037	-1.487911
75	1	0	13.149948	-2.108732	-1.126401
76	1	0	11.229339	-3.473451	-0.496476
77	1	0	9.619984	-4.534848	0.019276
78	1	0	7.628487	-5.797017	0.647003
79	1	0	5.432398	-4.639032	0.907442
80	1	0	5.284337	-2.197774	0.525447

E (HF) = –2262.6280617

Phenothiazine **4f**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	2.403389	2.719946	-0.458095
2	6	0	1.234073	2.065236	-0.889302
3	6	0	3.620436	2.056033	-0.360265
4	6	0	1.354588	0.699941	-1.233890

5	6	0	3.726380	0.688418	-0.662662
6	6	0	-1.234061	2.065228	-0.889255
7	6	0	2.560657	0.024662	-1.094539
8	6	0	-2.403355	2.719929	-0.457975
9	6	0	-1.354589	0.699939	-1.233863
10	1	0	2.610749	-1.028898	-1.348351
11	6	0	-3.620400	2.056016	-0.360118
12	1	0	-2.375587	3.766661	-0.189379
13	6	0	-2.560656	0.024664	-1.094490
14	6	0	-3.726363	0.688413	-0.662557
15	1	0	-2.610763	-1.028889	-1.348330
16	7	0	0.000002	2.742589	-0.990264
17	16	0	-0.000008	-0.157255	-2.002940
18	6	0	-0.000006	4.210485	-0.944130
19	1	0	-0.873465	4.552505	-1.508099
20	1	0	0.873429	4.552520	-1.508126
21	6	0	0.000004	4.861679	0.452996
22	1	0	-0.871302	4.525220	1.023625
23	1	0	0.871324	4.525226	1.023608
24	6	0	-0.000001	6.390510	0.353393
25	1	0	0.883634	6.756576	-0.181710
26	1	0	-0.883641	6.756568	-0.181708
27	1	0	-0.000002	6.849859	1.345997
28	1	0	4.498667	2.599832	-0.029451
29	1	0	-4.498613	2.599807	-0.029240

30	1	0	2.375637	3.766686	-0.189530
31	6	0	4.959650	-0.006335	-0.541286
32	6	0	6.013964	-0.607828	-0.434424
33	6	0	-4.959632	-0.006338	-0.541168
34	6	0	-6.013944	-0.607835	-0.434312
35	6	0	-7.229415	-1.333090	-0.314709
36	6	0	-8.416412	-0.713093	0.168492
37	6	0	-7.260415	-2.695067	-0.678468
38	6	0	-9.610672	-1.487438	0.275581
39	6	0	-8.456313	0.667541	0.555136
40	6	0	-8.422620	-3.441872	-0.573980
41	1	0	-6.348811	-3.154799	-1.045445
42	6	0	-10.810871	-0.884268	0.761314
43	6	0	-9.614029	-2.865903	-0.099352
44	6	0	-9.601649	1.242053	1.017488
45	1	0	-7.543763	1.247761	0.469976
46	1	0	-8.418738	-4.489778	-0.861153
47	6	0	-10.819457	0.492435	1.139179
48	6	0	-12.008113	-1.656398	0.871887
49	6	0	-10.831046	-3.615549	0.021543
50	1	0	-9.609851	2.290064	1.305246
51	6	0	-12.011153	1.064054	1.614943
52	6	0	-13.175160	-1.041026	1.353267
53	6	0	-11.974840	-3.039283	0.485422
54	1	0	-10.820957	-4.663193	-0.267139

55	6	0	-13.173681	0.303508	1.719704
56	1	0	-12.016699	2.111992	1.902454
57	1	0	-14.085641	-1.628229	1.437548
58	1	0	-12.888387	-3.621521	0.571186
59	1	0	-14.086012	0.761870	2.089878
60	6	0	7.229436	-1.333080	-0.314801
61	6	0	8.416413	-0.713092	0.168461
62	6	0	7.260451	-2.695048	-0.678590
63	6	0	9.610671	-1.487435	0.275569
64	6	0	8.456293	0.667530	0.555147
65	6	0	8.422653	-3.441855	-0.574075
66	1	0	6.348863	-3.154772	-1.045614
67	6	0	10.810855	-0.884271	0.761346
68	6	0	9.614044	-2.865893	-0.099393
69	6	0	9.601615	1.242038	1.017540
70	1	0	7.543739	1.247744	0.469990
71	1	0	8.418783	-4.489755	-0.861270
72	6	0	10.819426	0.492426	1.139237
73	6	0	12.008098	-1.656397	0.871934
74	6	0	10.831060	-3.615538	0.021526
75	1	0	9.609804	2.290041	1.305329
76	6	0	12.011109	1.064043	1.615036
77	6	0	13.175131	-1.041028	1.353351
78	6	0	11.974840	-3.039277	0.485446
79	1	0	10.820979	-4.663178	-0.267172

80	6	0	13.173639	0.303501	1.719810
81	1	0	12.016645	2.111975	1.902566
82	1	0	14.085612	-1.628228	1.437645
83	1	0	12.888386	-3.621513	0.571228
84	1	0	14.085958	0.761860	2.090014

E (HF) = –2415.0994039

TD-DFT Calculations

Phenothiazine 4a

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.4080 eV 363.81 nm f=1.0118 <S**2>=0.000
115 ->118 0.14772
116 ->117 0.64671
116 ->119 -0.13196
116 ->123 0.13942

Excited State 2: Singlet-A 4.1724 eV 297.15 nm f=0.4024 <S**2>=0.000
115 ->117 0.29045
116 ->118 0.56700
116 ->120 0.20297

Excited State 3: Singlet-A 4.2835 eV 289.44 nm f=0.7546 <S**2>=0.000
113 ->117 -0.12769
114 ->119 0.10851
115 ->118 0.17454
115 ->120 0.10509
116 ->119 0.61417

Excited State 4: Singlet-A 4.4236 eV 280.28 nm f=0.2369 <S**2>=0.000
110 ->117 0.14829
114 ->118 0.21765
115 ->117 -0.26936
116 ->120 0.54917

Excited State 5: Singlet-A 4.4732 eV 277.17 nm f=0.8906 <S**2>=0.000
114 ->117 0.53820

114 ->119 -0.11794
115 ->118 -0.26279
115 ->120 0.10499
116 ->123 0.21328
116 ->125 0.10253

Excited State 6: Singlet-A 4.9414 eV 250.91 nm f=0.0106 <S**2>=0.000
113 ->118 -0.14025
114 ->118 -0.21915
115 ->117 0.44907
116 ->118 -0.34447
116 ->120 0.24389
116 ->124 0.14496

Excited State 7: Singlet-A 5.1198 eV 242.16 nm f=0.0000 <S**2>=0.000
111 ->117 -0.29879
111 ->123 0.16472
112 ->118 -0.30673
112 ->124 -0.12343
113 ->121 -0.18008
114 ->121 -0.18013
115 ->122 0.31086
116 ->121 0.28040

Excited State 8: Singlet-A 5.1199 eV 242.16 nm f=0.0001 <S**2>=0.000
111 ->118 -0.30672
111 ->124 -0.12343
112 ->117 -0.29879
112 ->123 0.16473
113 ->122 -0.18012
114 ->122 -0.18017
115 ->121 0.31087
116 ->122 0.28047

Phenothiazine 4b

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.2891 eV 376.95 nm f=1.4353 <S**2>=0.000
140 ->145 0.11710
141 ->144 -0.20133
142 ->143 0.60968
142 ->145 0.23079

Excited State 2: Singlet-A 3.8023 eV 326.08 nm f=0.3639 <S**2>=0.000
140 ->144 -0.17449

141 ->143 -0.40901
142 ->144 0.51003

Excited State 3: Singlet-A 4.0458 eV 306.45 nm f=0.8099 <S**2>=0.000
140 ->143 0.37279
141 ->144 0.36463
142 ->145 0.34927
142 ->147 0.17020
142 ->149 -0.11189
142 ->151 0.10305

Excited State 4: Singlet-A 4.3275 eV 286.50 nm f=0.0016 <S**2>=0.000
139 ->143 -0.17516
139 ->145 -0.14847
140 ->143 -0.28278
140 ->147 0.10785
141 ->144 -0.11708
141 ->146 0.10437
142 ->145 0.10691
142 ->147 0.41902
142 ->149 -0.29606

Excited State 5: Singlet-A 4.3326 eV 286.17 nm f=0.0215 <S**2>=0.000
135 ->143 0.12691
140 ->144 0.24277
140 ->146 0.14706
141 ->143 0.22576
142 ->144 0.17572
142 ->146 0.49497
142 ->150 -0.14380

Excited State 6: Singlet-A 4.5037 eV 275.30 nm f=0.0003 <S**2>=0.000
136 ->144 0.31698
137 ->143 0.31862
137 ->145 -0.16622
138 ->144 -0.11373
140 ->147 -0.14300
140 ->149 -0.19660
141 ->148 -0.31667
142 ->147 0.13826
142 ->149 0.18769

Excited State 7: Singlet-A 4.5037 eV 275.30 nm f=0.0027 <S**2>=0.000
136 ->143 0.30010
136 ->145 -0.15627
137 ->144 0.33643

138 ->143 -0.10745
140 ->148 -0.24261
141 ->147 -0.18798
141 ->149 -0.25575
142 ->148 0.23289

Excited State 8: Singlet-A 4.6257 eV 268.03 nm f=0.0399 <S**2>=0.000
138 ->143 0.11365
139 ->144 -0.14342
140 ->144 0.26465
141 ->143 0.30043
142 ->144 0.35267
142 ->146 -0.22924
142 ->150 0.28502

Phenothiazine 4c

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.3426 eV 370.92 nm f=1.4217 <S**2>=0.000
157 ->160 0.17398
158 ->159 0.61794
158 ->161 0.15590
158 ->163 0.10037
158 ->165 -0.10607

Excited State 2: Singlet-A 3.9283 eV 315.62 nm f=1.0315 <S**2>=0.000
156 ->160 -0.15102
157 ->159 0.39777
158 ->160 0.49949

Excited State 3: Singlet-A 4.1053 eV 302.01 nm f=0.6249 <S**2>=0.000
155 ->159 -0.10349
156 ->159 -0.30856
156 ->163 -0.14694
157 ->160 0.35325
158 ->161 -0.27302
158 ->163 -0.30804

Excited State 4: Singlet-A 4.2593 eV 291.09 nm f=0.0166 <S**2>=0.000
153 ->160 -0.15035
154 ->159 0.18426
154 ->165 0.10910
155 ->160 0.16633
156 ->162 -0.23576
157 ->161 0.35440

157 ->163 -0.11543
157 ->165 0.10130
158 ->162 0.35852

Excited State 5: Singlet-A 4.2692 eV 290.42 nm f=0.4060 <S**2>=0.000
153 ->161 -0.10101
154 ->160 -0.17564
155 ->159 -0.15309
156 ->161 0.22585
156 ->165 0.13017
157 ->162 -0.34807
158 ->161 -0.21486
158 ->163 0.35462

Excited State 6: Singlet-A 4.3540 eV 284.76 nm f=0.0399 <S**2>=0.000
153 ->159 0.18916
154 ->160 -0.10077
155 ->159 0.11504
155 ->161 0.11350
156 ->159 0.33827
156 ->163 -0.10807
157 ->160 -0.14070
157 ->162 -0.11606
157 ->164 -0.11922
158 ->163 -0.33537
158 ->165 -0.26039

Excited State 7: Singlet-A 4.3541 eV 284.75 nm f=0.1172 <S**2>=0.000
151 ->159 0.13490
156 ->160 -0.20323
156 ->162 -0.12548
156 ->164 0.14066
157 ->159 0.22218
158 ->160 -0.11926
158 ->164 0.51116

Excited State 8: Singlet-A 4.6817 eV 264.83 nm f=0.0279 <S**2>=0.000
154 ->159 -0.15653
154 ->161 0.13791
155 ->160 -0.16337
156 ->160 0.30387
156 ->164 0.10123
157 ->159 -0.26279
158 ->160 0.30281
158 ->162 0.14178
158 ->164 0.27710

158 ->166 0.15998

Phenothiazine 4d

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.8744 eV 431.34 nm f=1.4530 <S**2>=0.000
166 ->171 -0.12073
167 ->170 -0.36935
168 ->169 0.56389
168 ->171 -0.12080

Excited State 2: Singlet-A 3.0515 eV 406.30 nm f=0.2956 <S**2>=0.000
166 ->170 -0.18569
167 ->169 -0.46761
168 ->170 0.48305

Excited State 3: Singlet-A 3.5477 eV 349.48 nm f=0.0196 <S**2>=0.000
166 ->169 0.41641
166 ->171 -0.16586
167 ->170 0.31625
168 ->169 0.13668
168 ->171 -0.37345

Excited State 4: Singlet-A 3.9604 eV 313.06 nm f=0.0023 <S**2>=0.000
163 ->169 0.35823
164 ->170 -0.35807
166 ->173 0.19042
167 ->172 -0.10602
167 ->174 -0.30059
168 ->173 -0.27398

Excited State 5: Singlet-A 3.9604 eV 313.06 nm f=0.0110 <S**2>=0.000
163 ->170 -0.35738
164 ->169 0.35755
166 ->174 0.18166
167 ->173 -0.31871
168 ->174 -0.25543

Excited State 6: Singlet-A 3.9696 eV 312.33 nm f=0.0225 <S**2>=0.000
162 ->169 0.14408
166 ->170 0.39270
166 ->172 0.10005
167 ->169 0.29891
168 ->170 0.42150
168 ->172 0.14533

Excited State	7:	Singlet-A	4.1950 eV	295.55 nm	f=0.0621	<S**2>=0.000
162 ->170	0.12308					
166 ->169	0.25091					
166 ->171	0.10894					
166 ->175	0.24413					
167 ->170	0.11094					
168 ->169	0.18654					
168 ->171	0.30906					
168 ->175	0.39402					

Excited State	8:	Singlet-A	4.3741 eV	283.45 nm	f=0.0082	<S**2>=0.000
159 ->169	-0.10863					
159 ->171	0.12574					
162 ->175	0.10475					
165 ->170	0.12331					
166 ->172	0.17745					
166 ->176	-0.18895					
167 ->169	-0.14053					
167 ->175	-0.12136					
168 ->170	-0.15075					
168 ->172	0.39740					
168 ->174	-0.13896					
168 ->176	-0.32506					

Phenothiazine 4e

Excitation energies and oscillator strengths:

Excited State	1:	Singlet-A	3.2748 eV	378.60 nm	f=1.7054	<S**2>=0.000
166 ->173	0.11704					
167 ->170	0.20018					
168 ->169	0.60593					
168 ->173	0.23200					

Excited State	2:	Singlet-A	3.7784 eV	328.14 nm	f=0.2653	<S**2>=0.000
166 ->170	-0.16527					
167 ->169	0.40789					
168 ->170	0.50754					

Excited State	3:	Singlet-A	4.0262 eV	307.94 nm	f=1.0322	<S**2>=0.000
166 ->169	0.37696					
166 ->175	-0.10264					
167 ->170	-0.36629					
168 ->173	0.33825					
168 ->175	-0.18202					

Excited State 4: Singlet-A 4.1337 eV 299.93 nm f=0.0004 <S**2>=0.000

164 ->170	0.32266
165 ->169	-0.31547
165 ->173	0.14955
166 ->172	0.24138
167 ->171	-0.31972
168 ->172	-0.24590

Excited State 5: Singlet-A 4.1338 eV 299.93 nm f=0.0025 <S**2>=0.000

164 ->169	-0.31138
164 ->173	0.14792
165 ->170	0.32704
166 ->171	-0.23948
167 ->172	0.32028
168 ->171	0.24708

Excited State 6: Singlet-A 4.3196 eV 287.03 nm f=0.0001 <S**2>=0.000

160 ->169	-0.11907
166 ->170	-0.25818
166 ->174	0.14567
167 ->169	0.23449
168 ->170	-0.20280
168 ->174	0.47168
168 ->176	-0.13755

Excited State 7: Singlet-A 4.3205 eV 286.97 nm f=0.0040 <S**2>=0.000

163 ->169	0.16796
163 ->173	0.14284
166 ->169	0.26163
166 ->175	0.14844
167 ->170	-0.10727
167 ->174	-0.10237
168 ->173	-0.12823
168 ->175	0.51437

Excited State 8: Singlet-A 4.5923 eV 269.98 nm f=0.1934 <S**2>=0.000

162 ->169	0.11995
163 ->170	-0.14280
165 ->171	0.10131
166 ->170	0.24793
166 ->174	0.10264
167 ->169	-0.26258
168 ->170	0.33078
168 ->174	0.26060
168 ->176	-0.27737

Phenothiazine 4f

Excitation energies and oscillator strengths:

Excited State	1:	Singlet-A	3.0561 eV	405.69 nm	f=2.6756	<S**2>=0.000
178 ->183	0.12533					
179 ->182	0.30005					
180 ->181	0.57341					
180 ->183	0.17982					
Excited State	2:	Singlet-A	3.3408 eV	371.12 nm	f=0.1508	<S**2>=0.000
178 ->182	-0.16816					
179 ->181	0.45073					
180 ->182	0.48805					
Excited State	3:	Singlet-A	3.7088 eV	334.30 nm	f=0.2999	<S**2>=0.000
176 ->183	0.10175					
178 ->181	0.41655					
178 ->183	0.12277					
179 ->182	-0.35542					
180 ->183	0.28009					
180 ->185	0.19523					
Excited State	4:	Singlet-A	3.8368 eV	323.15 nm	f=0.0028	<S**2>=0.000
174 ->181	-0.11558					
175 ->182	0.18220					
176 ->182	-0.25908					
177 ->181	0.30923					
178 ->182	0.12373					
178 ->184	-0.20762					
179 ->183	-0.21143					
179 ->185	0.25668					
180 ->184	0.26055					
Excited State	5:	Singlet-A	3.8418 eV	322.73 nm	f=0.0021	<S**2>=0.000
174 ->182	-0.12960					
175 ->181	0.18332					
176 ->181	-0.26338					
177 ->182	0.30318					
178 ->185	-0.19610					
179 ->184	0.32709					
180 ->183	-0.24355					
180 ->185	0.17640					
Excited State	6:	Singlet-A	4.1333 eV	299.96 nm	f=0.1500	<S**2>=0.000
174 ->181	0.10827					
178 ->182	0.36229					

178 ->186 0.13900
179 ->181 -0.29082
180 ->182 0.35535
180 ->184 -0.16334
180 ->186 0.19839
180 ->188 -0.10315

Excited State 7: Singlet-A 4.2578 eV 291.20 nm f=0.0823 <S**2>=0.000
178 ->181 -0.21513
178 ->187 0.25580
180 ->181 -0.12397
180 ->183 0.11353
180 ->185 0.17752
180 ->187 0.47364

Excited State 8: Singlet-A 4.4202 eV 280.50 nm f=0.1566 <S**2>=0.000
170 ->181 -0.11080
170 ->183 -0.10386
174 ->181 0.10087
175 ->182 -0.11544
178 ->182 0.10800
178 ->186 -0.15506
178 ->188 0.19456
179 ->181 -0.11578
180 ->182 0.16678
180 ->186 -0.31699
180 ->188 0.39879