

SUPPLEMENTARY MATERIALS

Near-infrared emitting *meso*-substituted heptamethine cyanine dyes: From the synthesis and photophysics to their use in bioimaging

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Summary

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Spectroscopic characterization

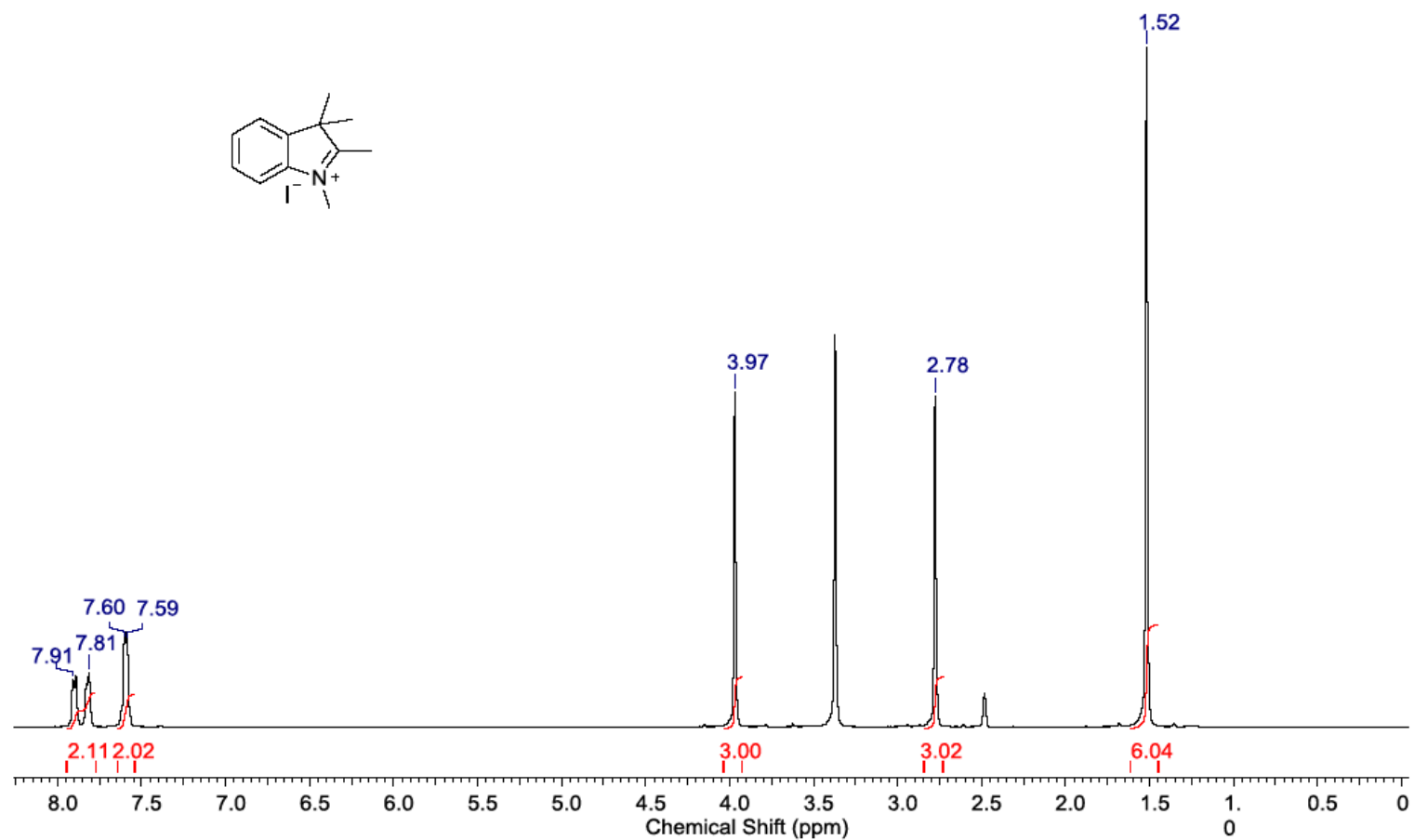


Figure S1. ^1H NMR spectrum of indole **3a** in $\text{DMSO-}d_6$ (300MHz).

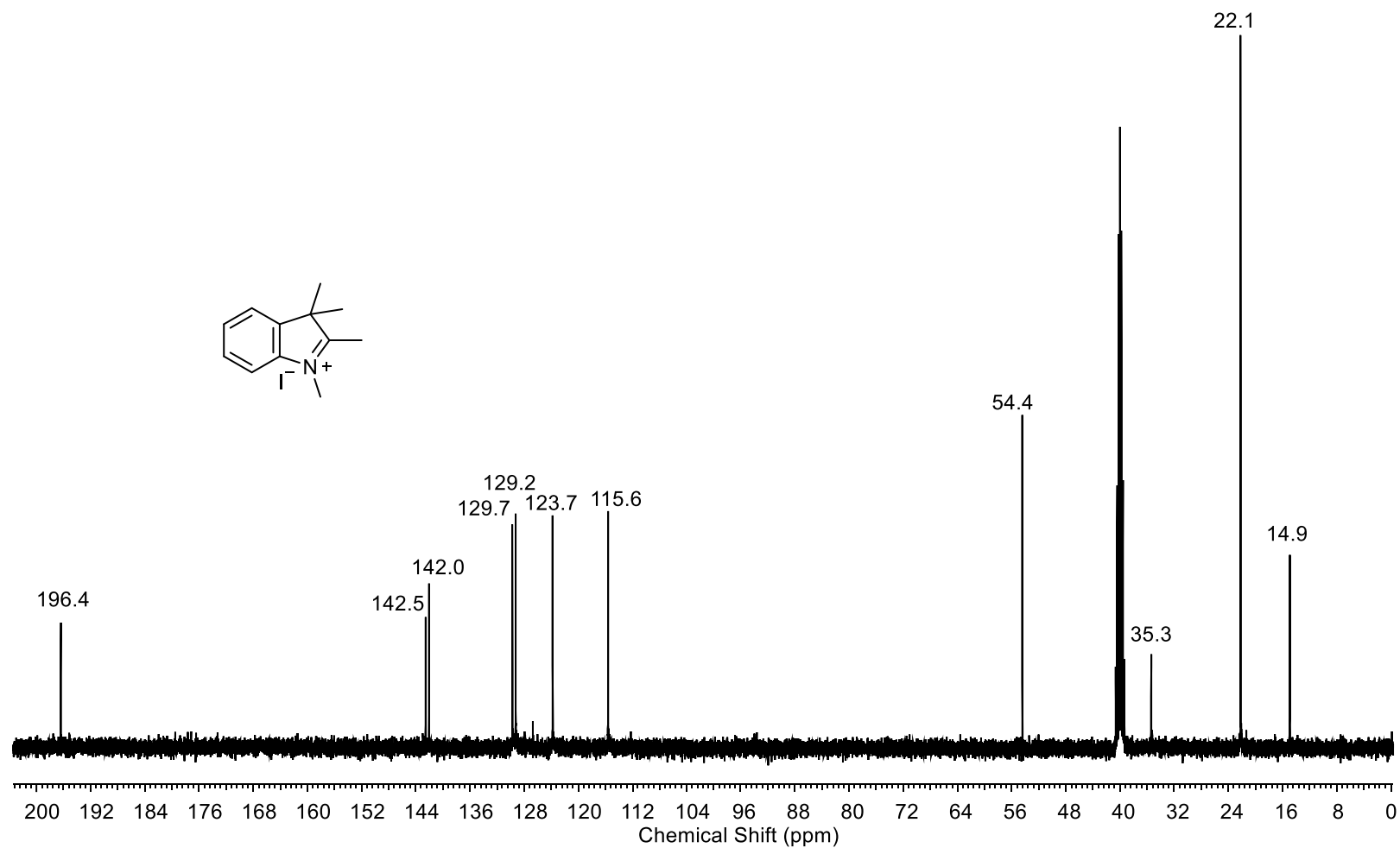


Figure S2. ¹³C NMR spectrum of indole **3a** in DMSO-*d*₆ (75 MHz).

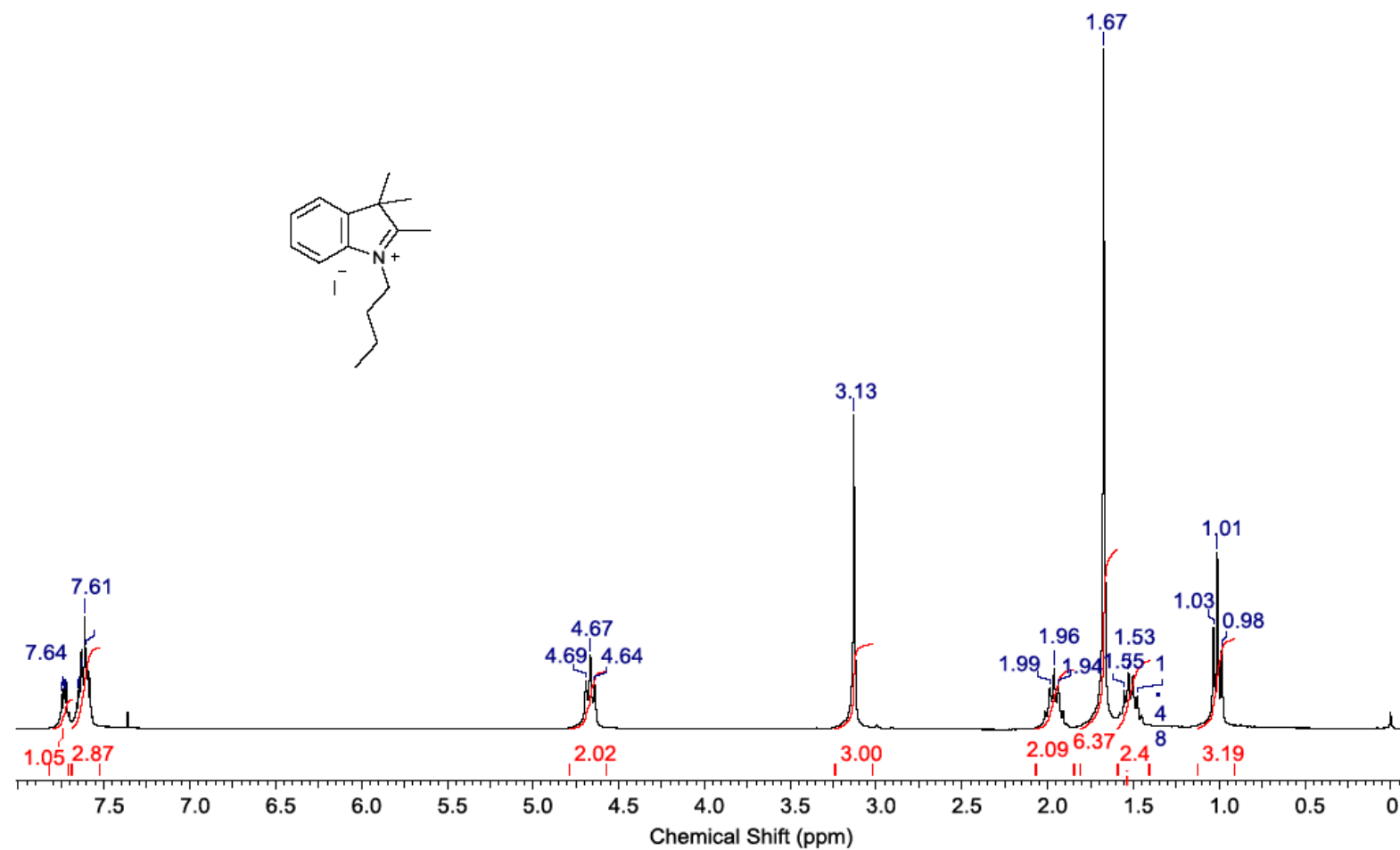


Figure S3. ^1H NMR spectrum of indole **3b** in CDCl_3 (400 MHz).

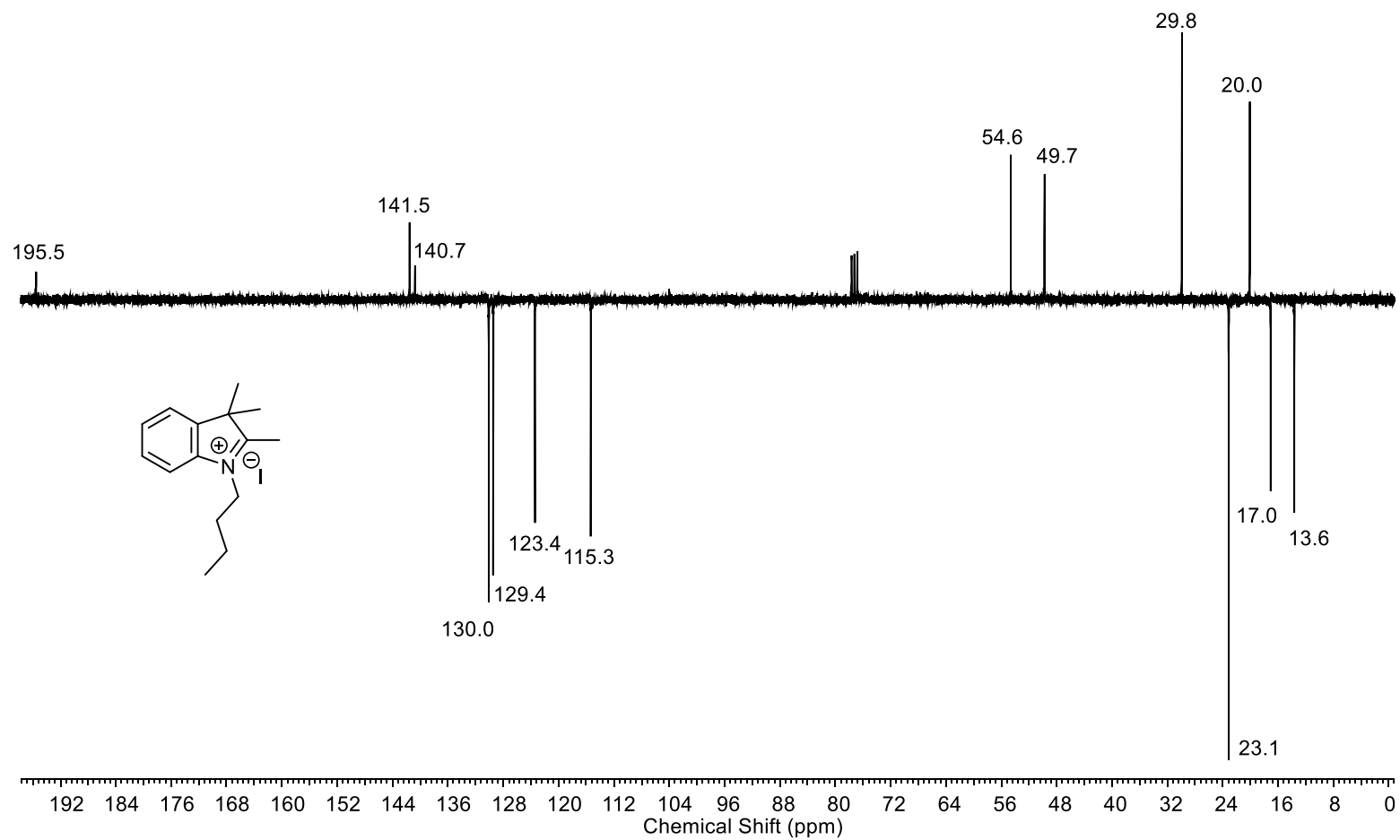


Figure S4. ^{13}C APT NMR spectrum of indole **3b** in $\text{DMSO-}d_6$ (75 MHz).

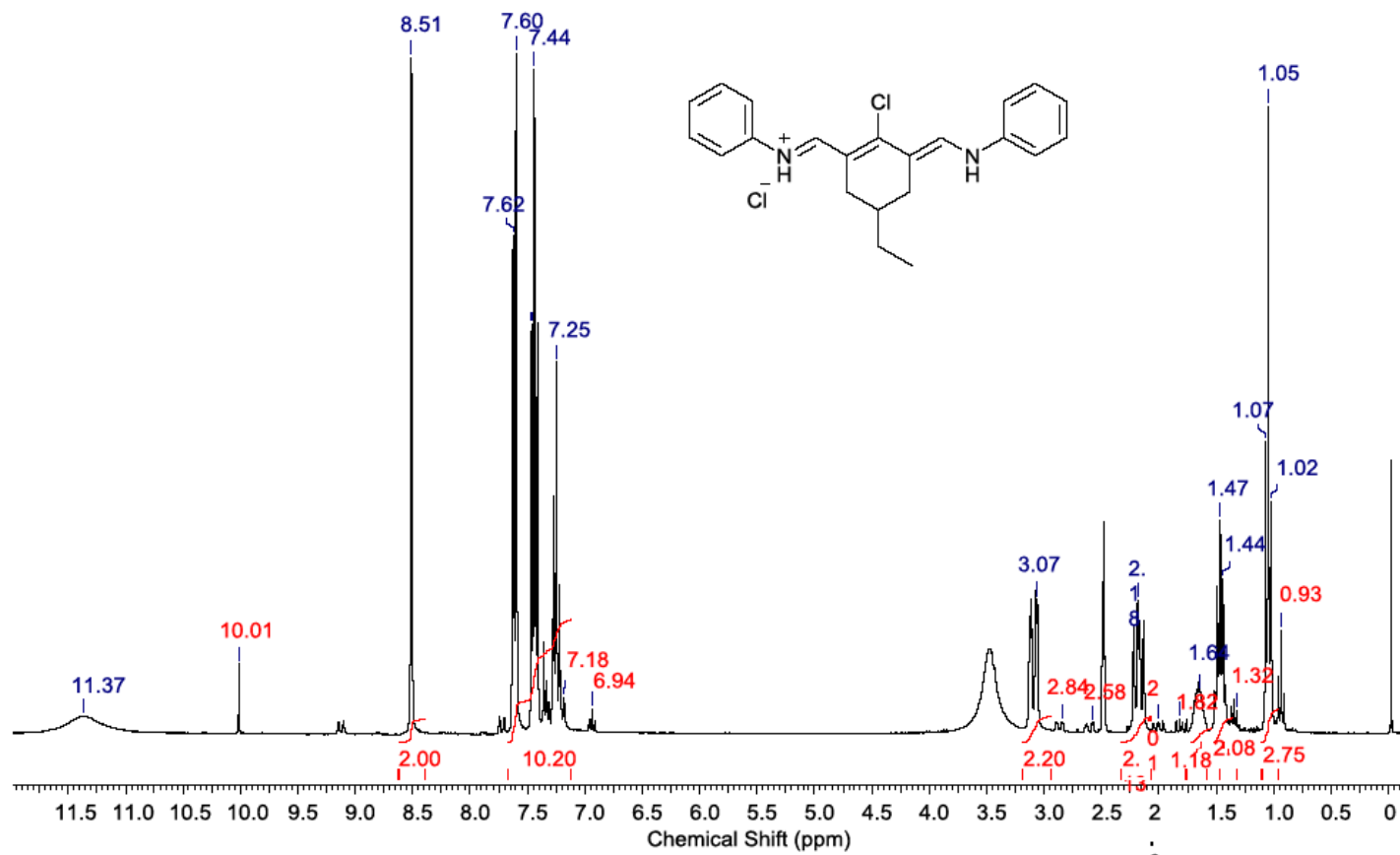


Figure S5. ¹H NMR spectrum of compound **5** in DMSO-*d*₆ (300 MHz).

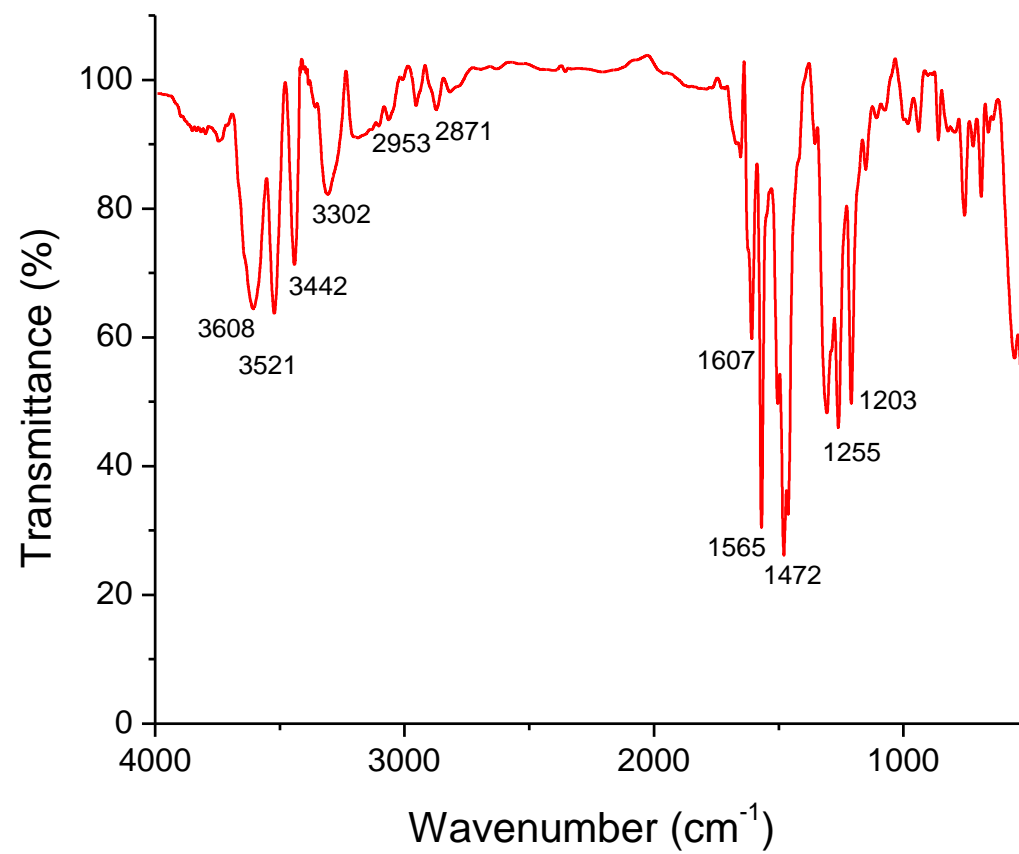


Figure S6. FTIR spectrum of compound **5** in KBr.

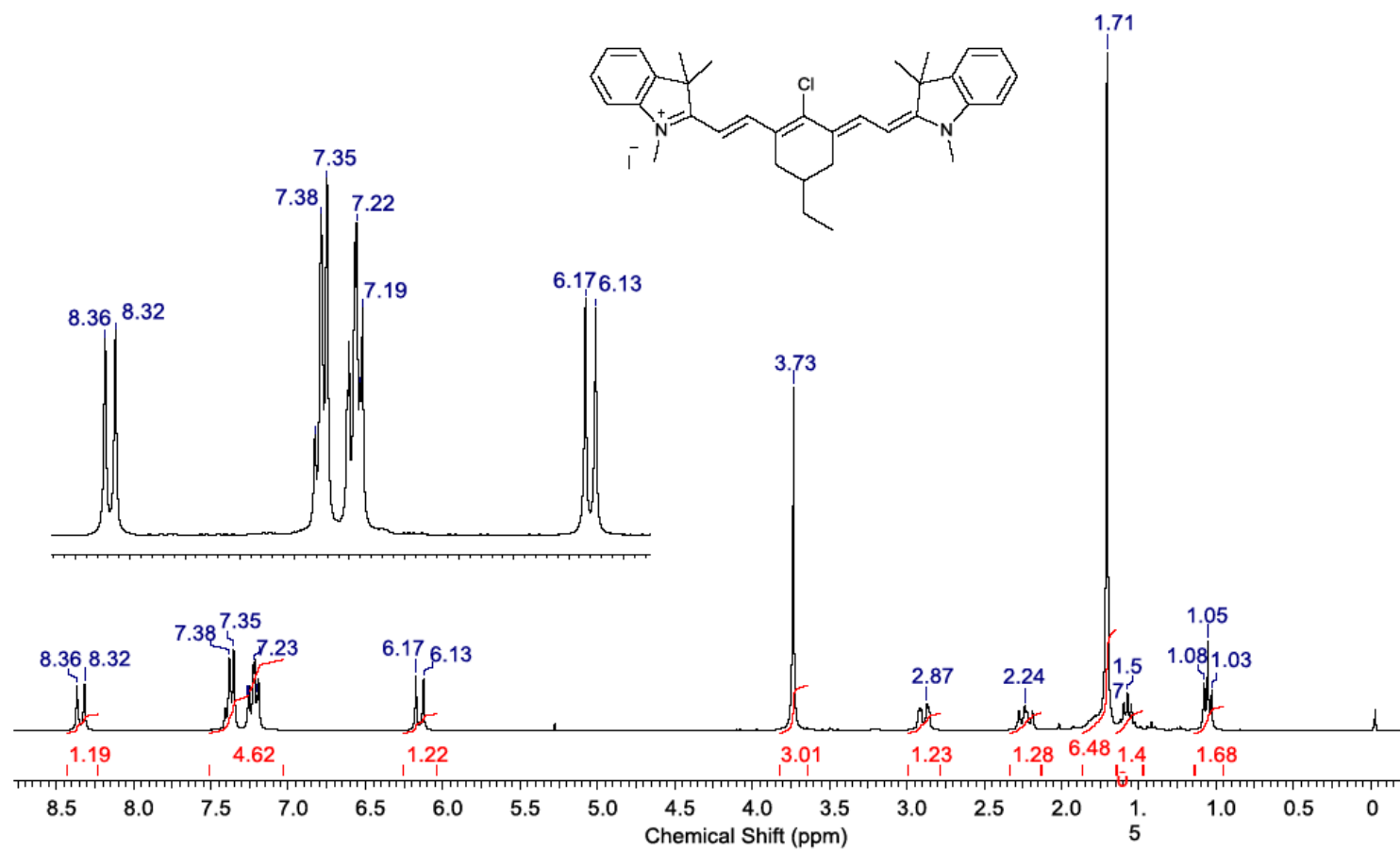


Figure S7. ^1H NMR spectrum of heptamethine cyanine dye **6a** in CDCl_3 (300 MHz).

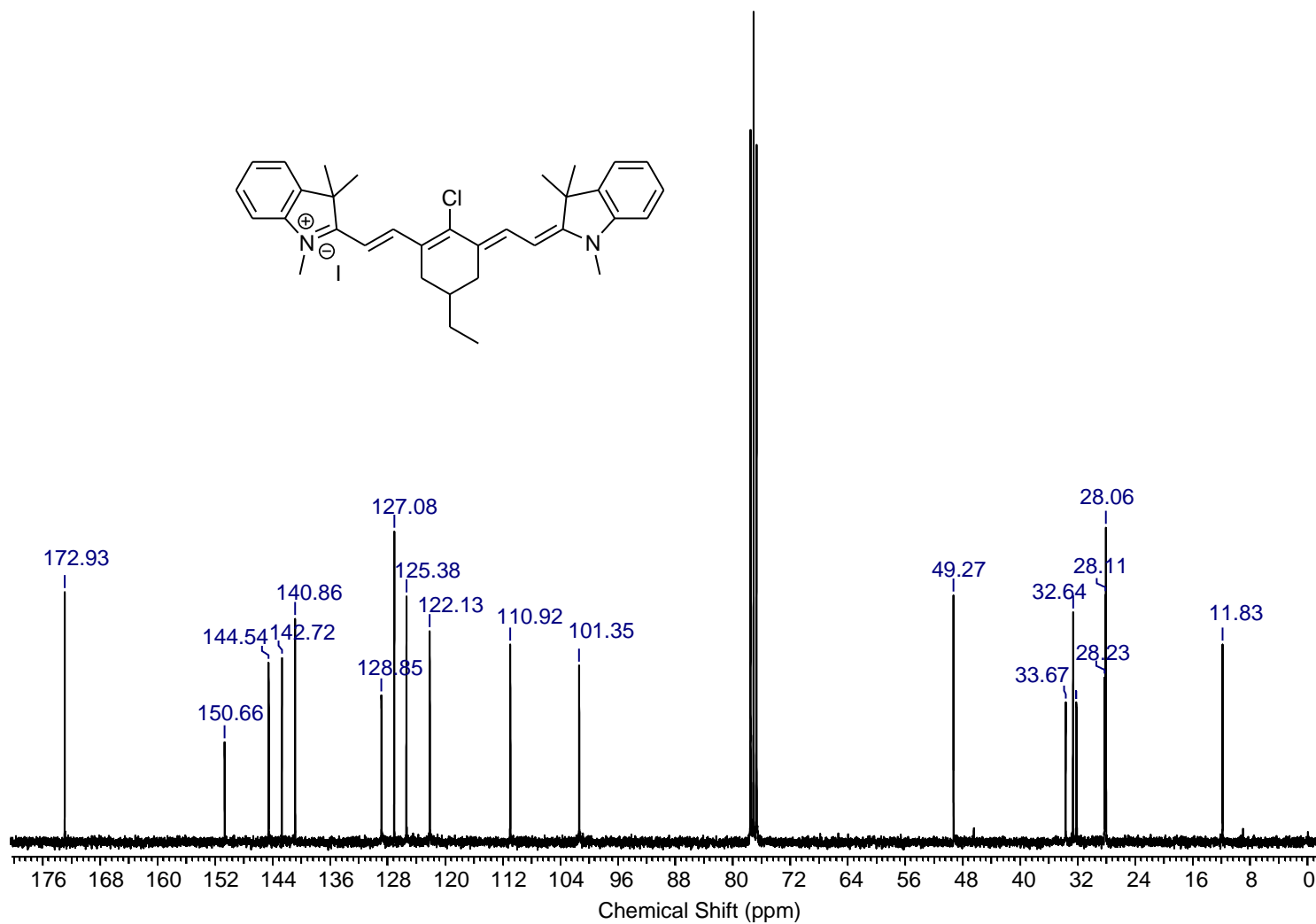


Figure S8. ^{13}C NMR spectrum of heptamethine cyanine dye **6a** in CDCl_3 (75 MHz).

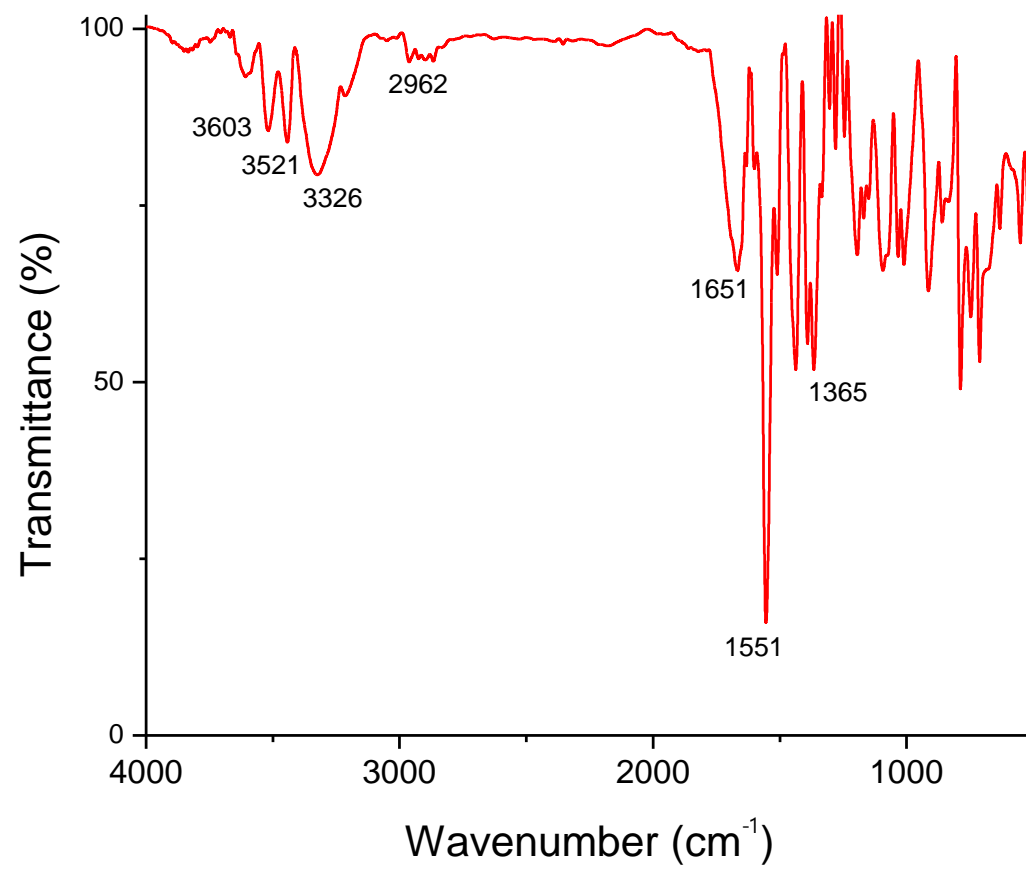


Figure S9. FTIR spectrum of heptamethine cyanine dye **6a** in KBr.

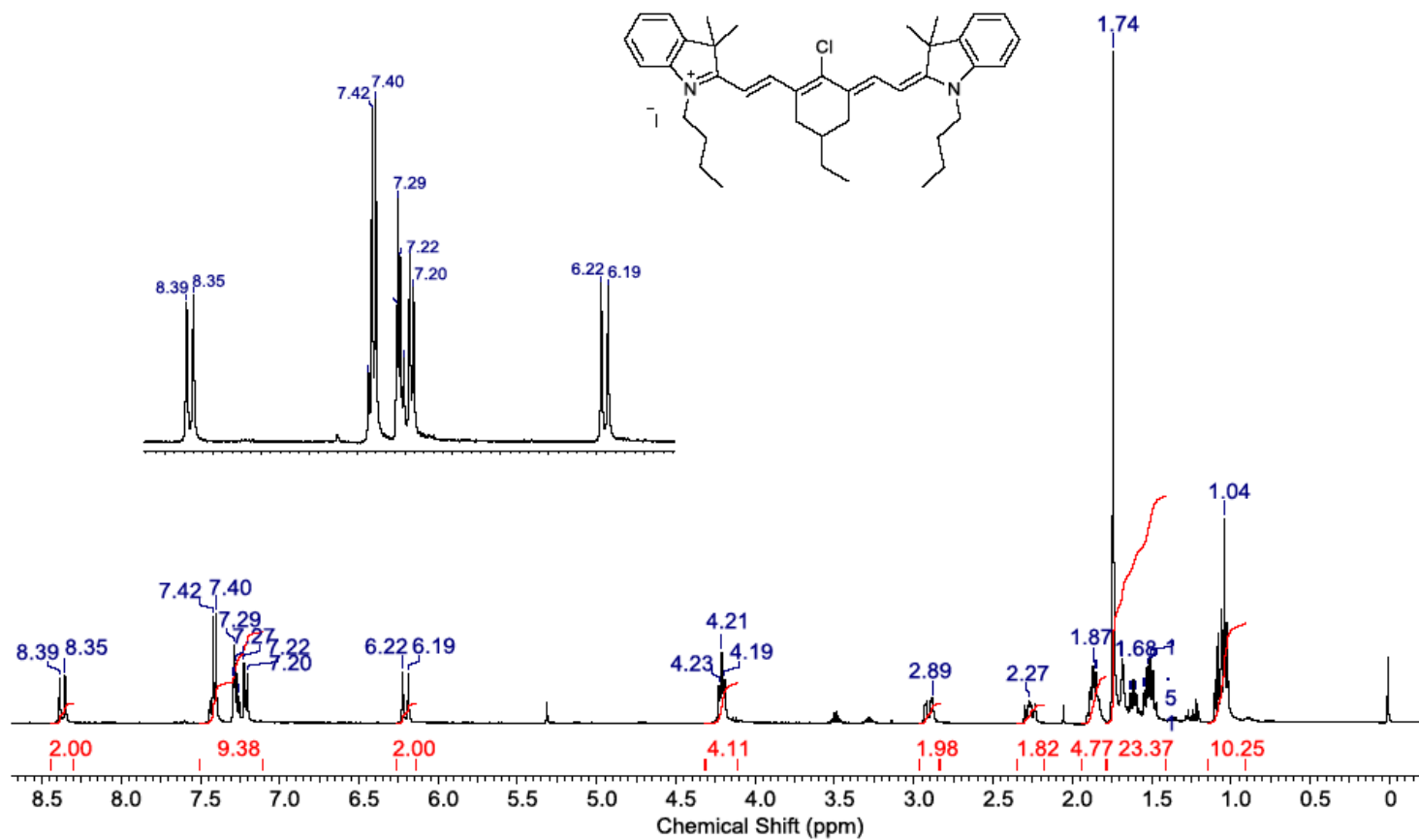


Figure S10. ^1H NMR spectrum of heptamethine cyanine dye **6b** in CDCl_3 (400 MHz).

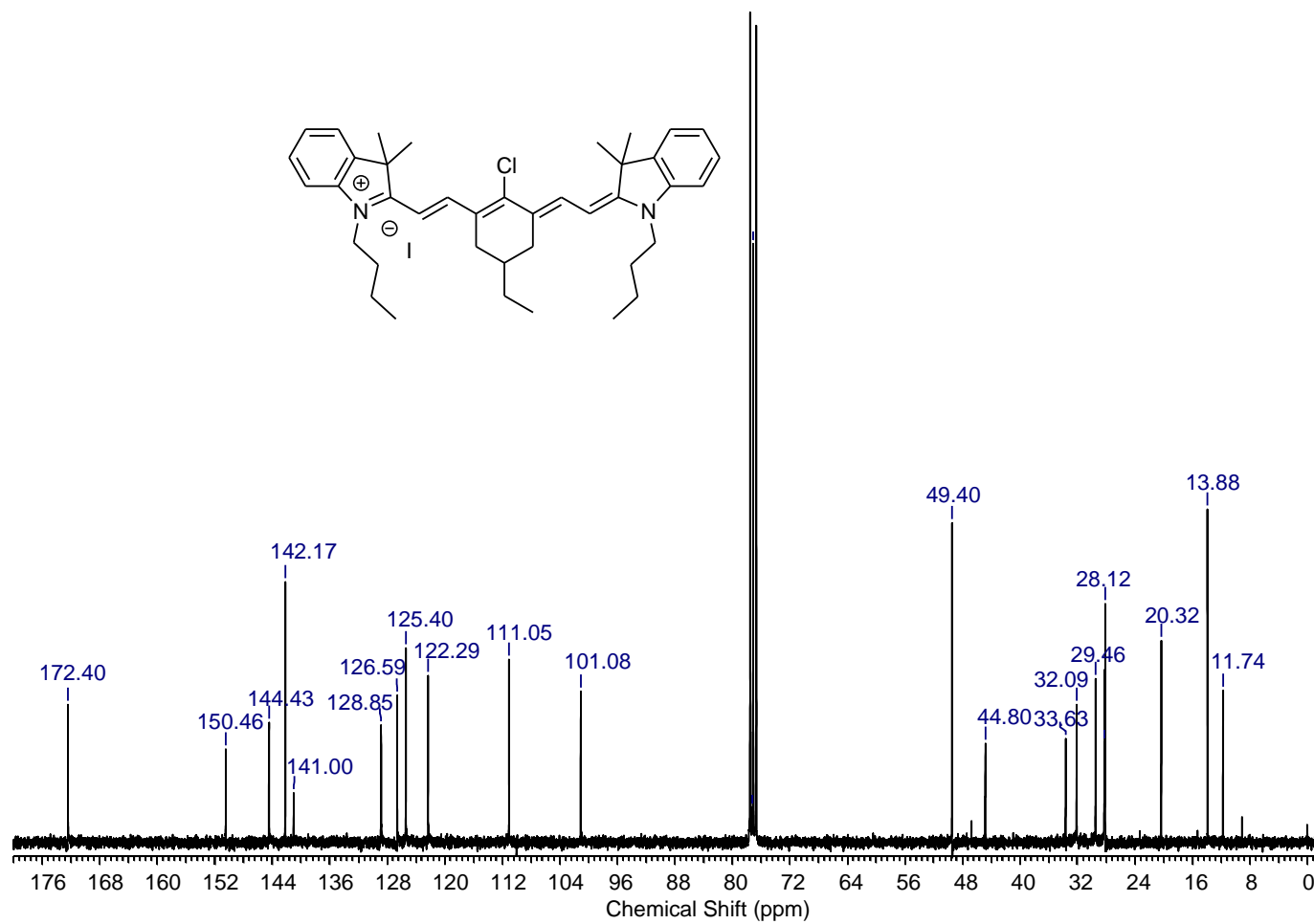


Figure S11. ^{13}C NMR spectrum of heptamethine cyanine dye **6b** in CDCl_3 (100 MHz).

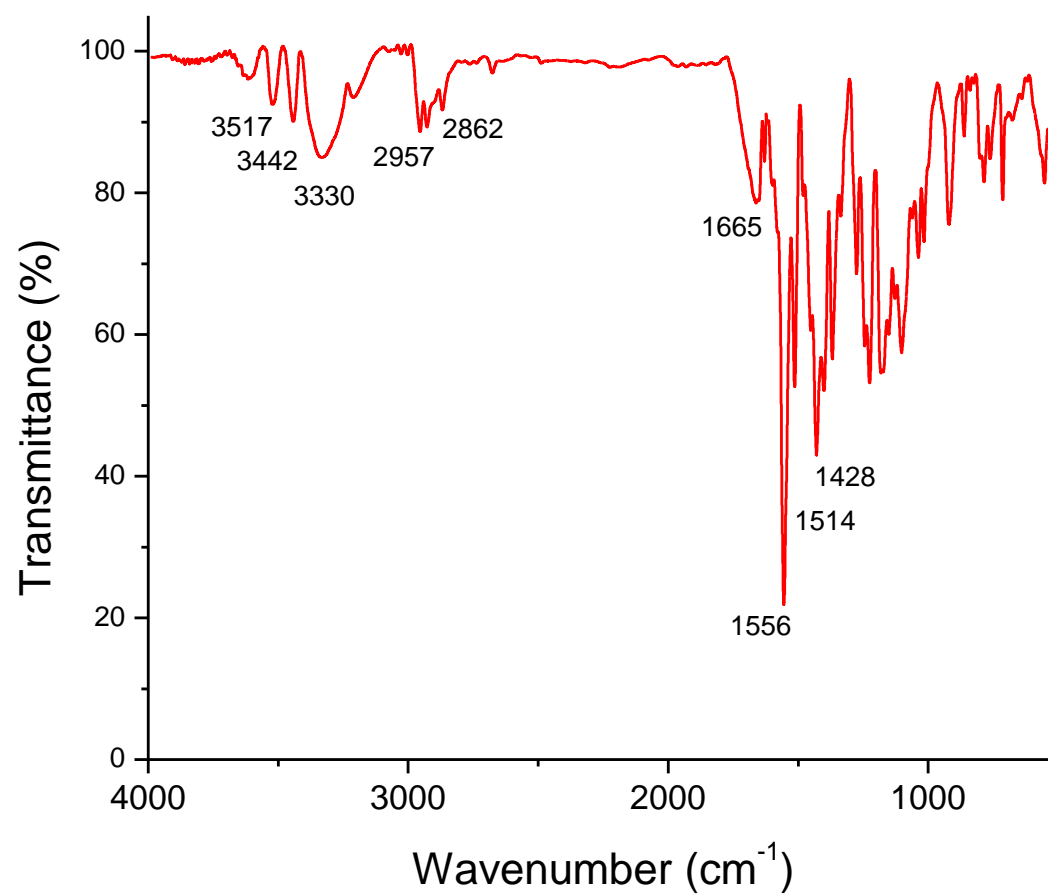


Figure S12. FTIR spectrum of heptamethine cyanine dye **6b** in KBr.

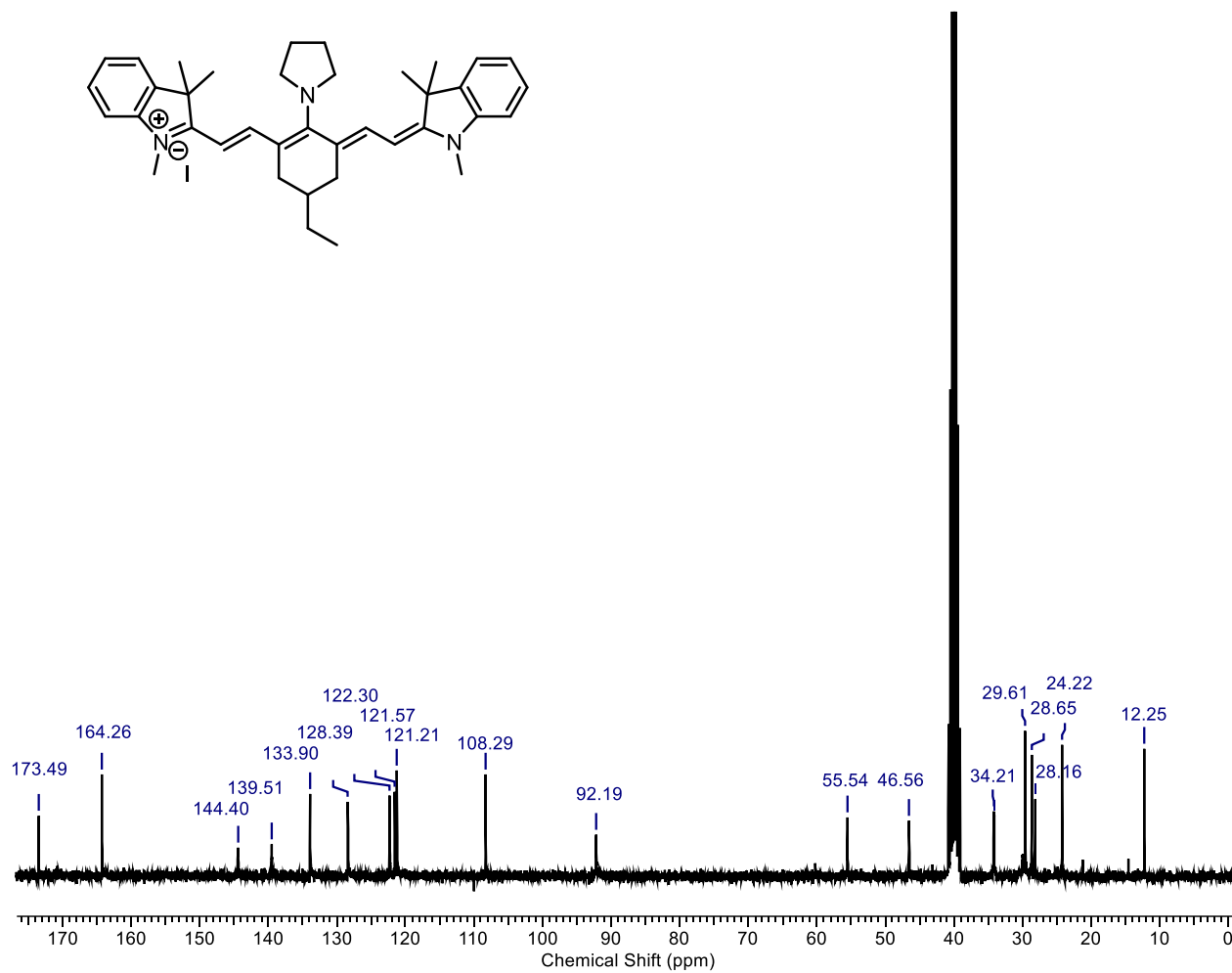


Figure S14. ^{13}C NMR spectrum of *meso*-substituted cyanine dye **8a** in $\text{DMSO}-d_6$ (75 MHz).

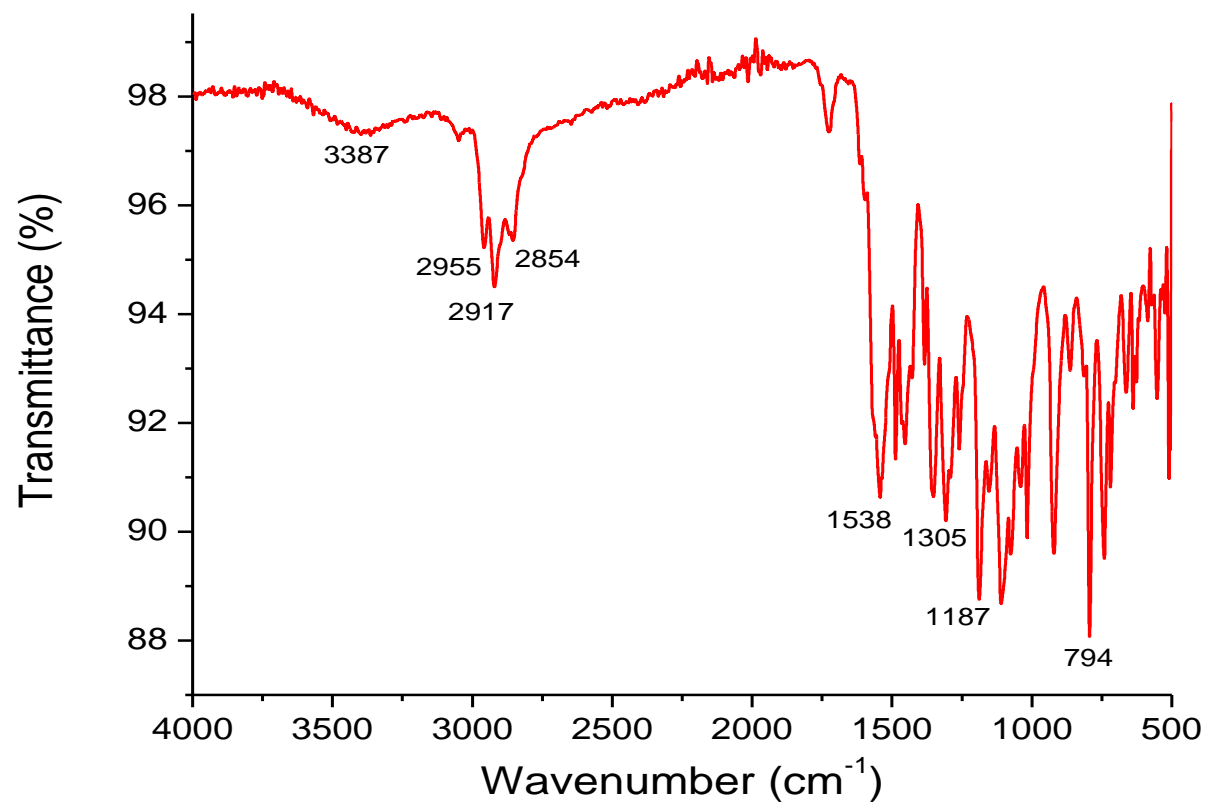
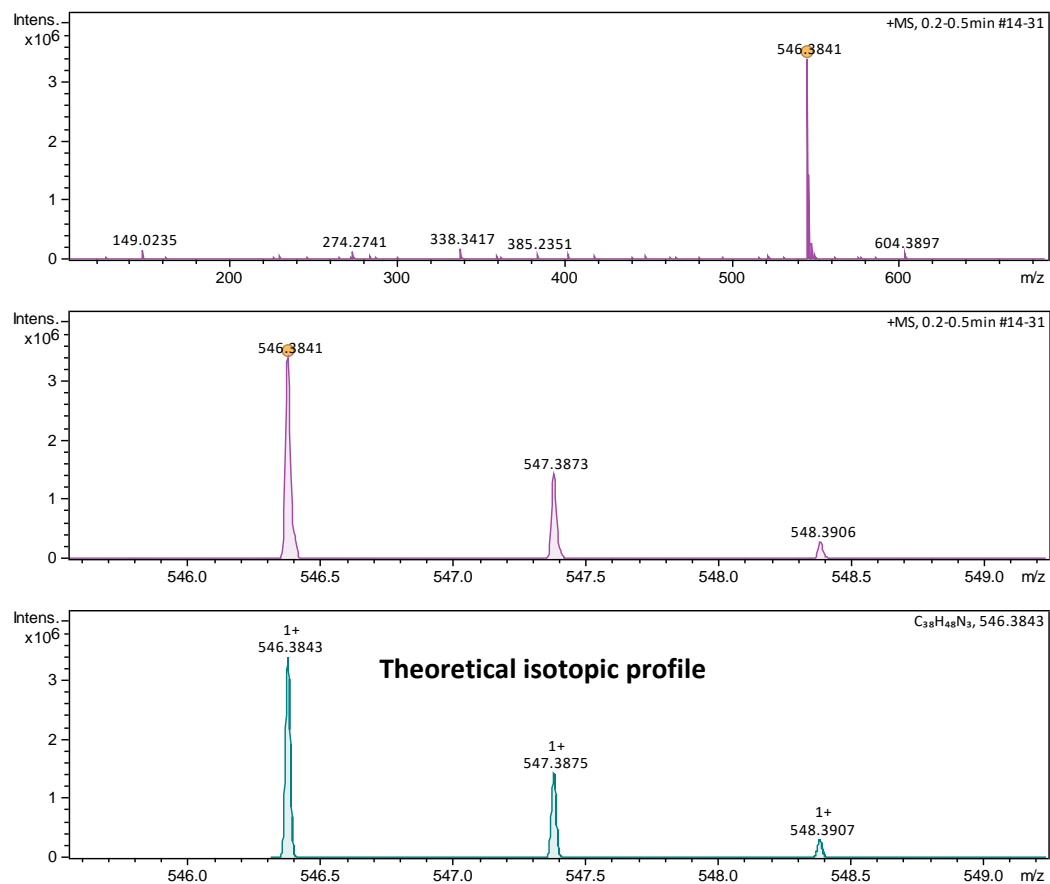


Figure S15. FTIR (ATR mode) spectrum of *meso*-substituted cyanine dye **8a**.



Meas. m/z	Ion Formula	m/z	err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
546,3841	C38H48N3	546,3843	0.3	2.2	16.5	even	ok

Figure S16. HRMS spectrum of *meso*-substituted cyanine dye **8a**.

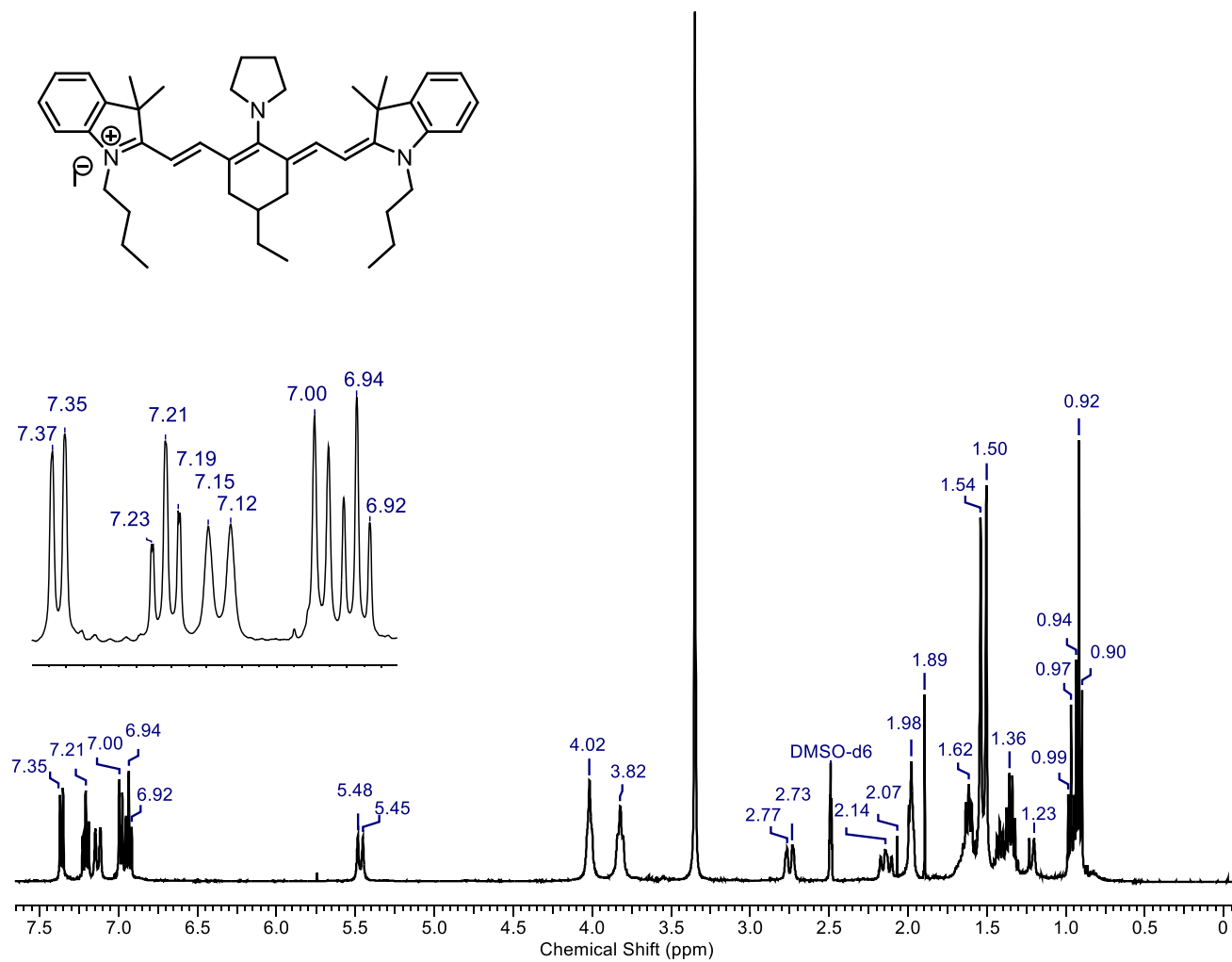


Figure S17. ¹H NMR spectrum of *meso*-substituted cyanine dye **8b** in DMSO-*d*₆ (400 MHz).

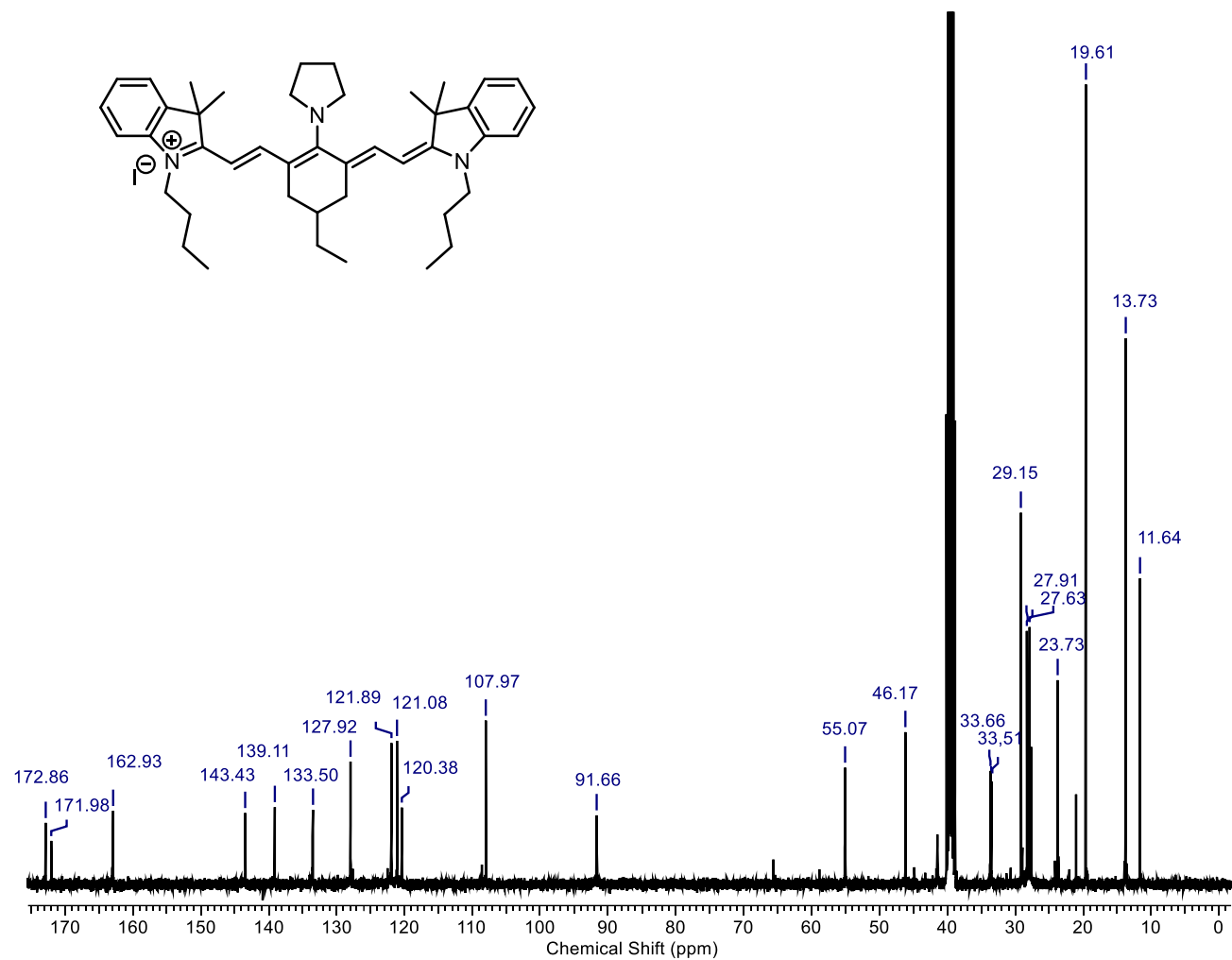


Figure S18. ^{13}C NMR spectrum of meso-substituted cyanine dye **8b** in $\text{DMSO}-d_6$ (100 MHz).

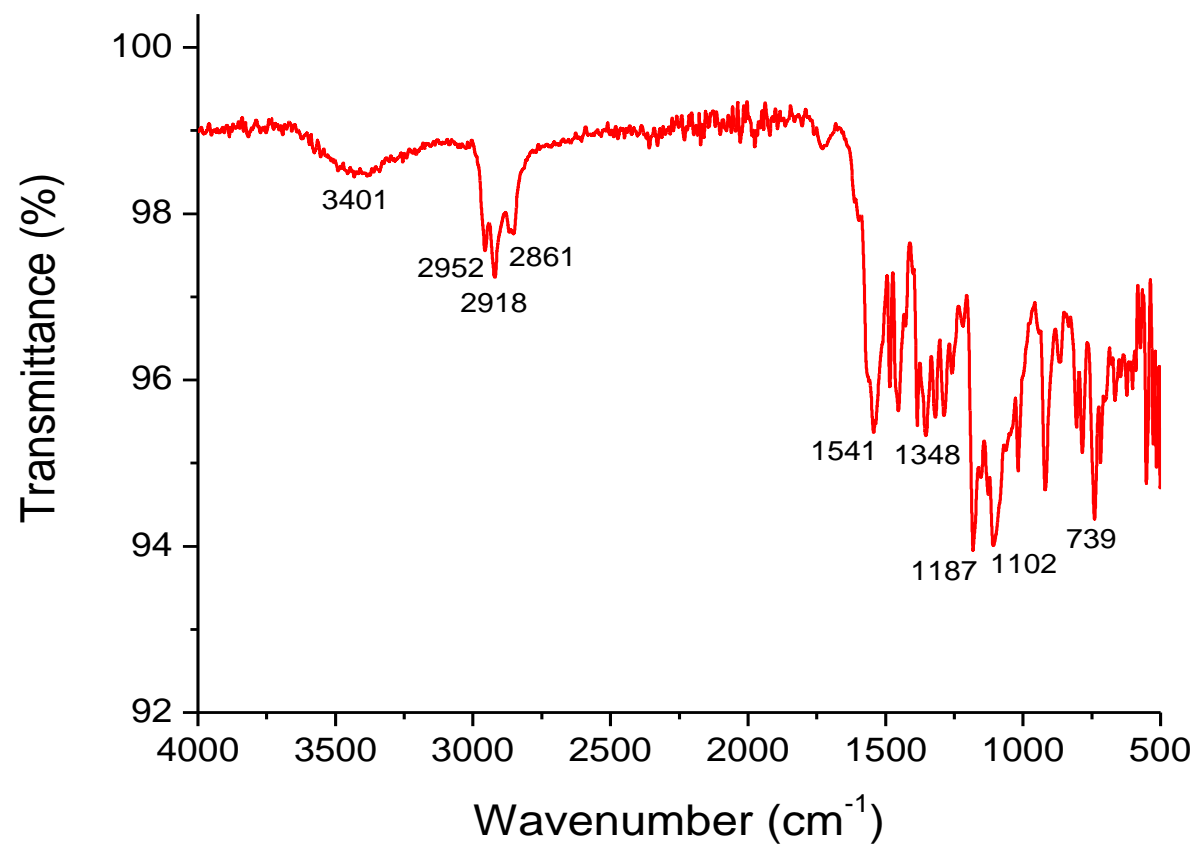
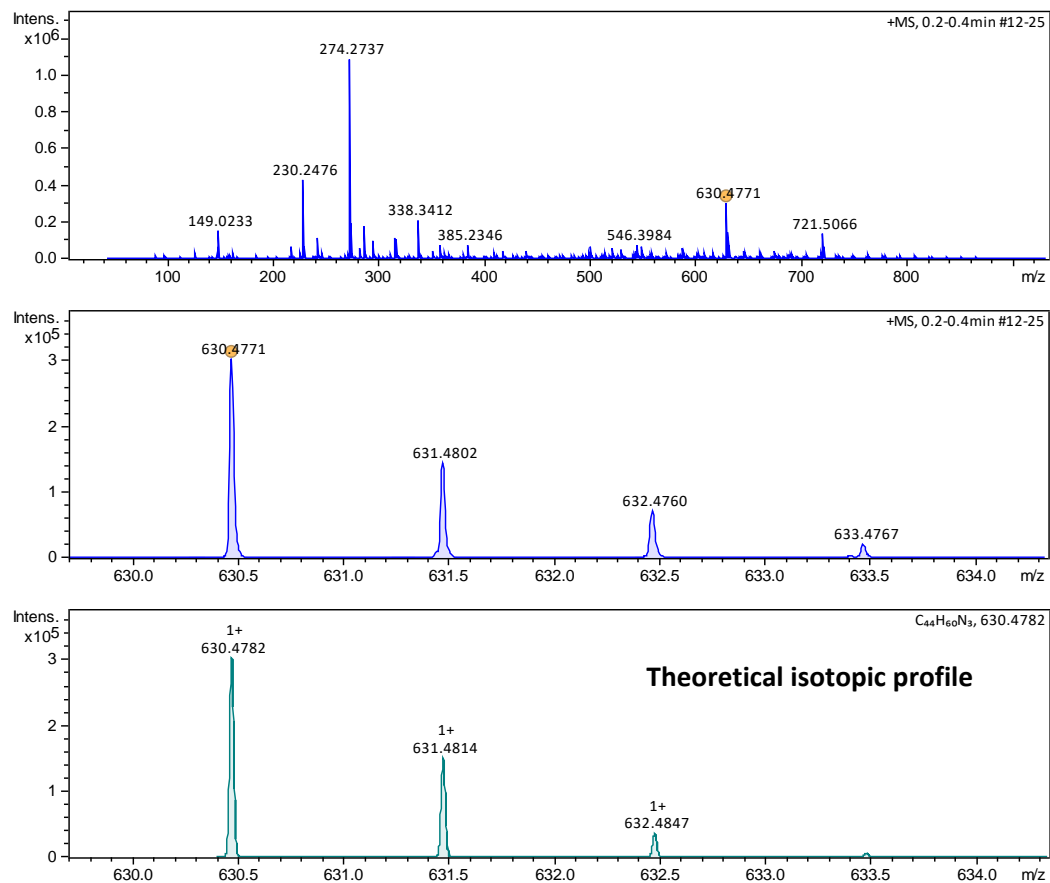


Figure S19. FTIR (ATR mode) spectrum of *meso*-substituted cyanine dye **8b**.



Meas. m/z	Ion Formula	m/z	err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
630,4771	C ₄₄ H ₆₀ N ₃	630,4782	1.8	60.5	16.5	even	ok

Figure S20. HRMS spectrum of *meso*-substituted cyanine dye **8b**.

Additional photophysics data

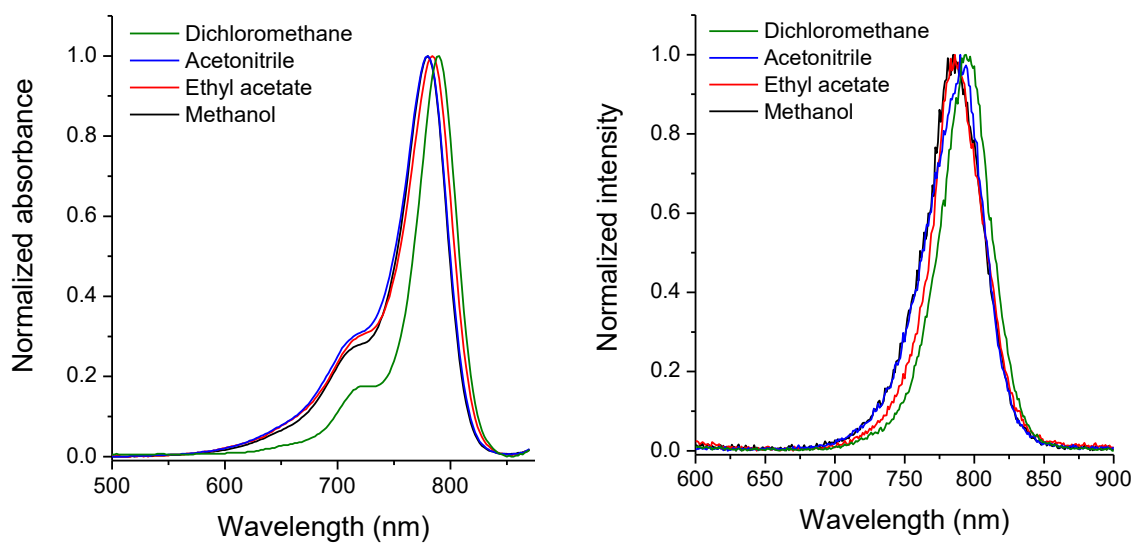


Figure S21. UV-Vis absorption (left) and steady-state fluorescence emission (right) spectra in solution of different organic solvents [$\sim 10^{-6}$ M] of the heptamethine cyanine dye **6b**.

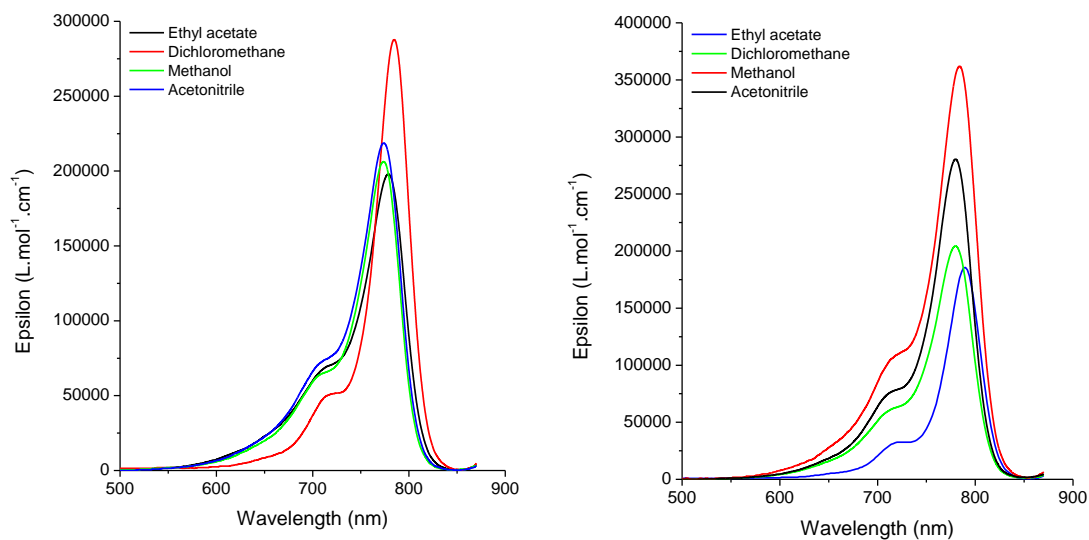


Figure S22. UV-Vis absorption spectra of cyanines **6a** (top) and **6b** (bottom) in solution of different organic solvents [$\sim 10^{-6}$ M].

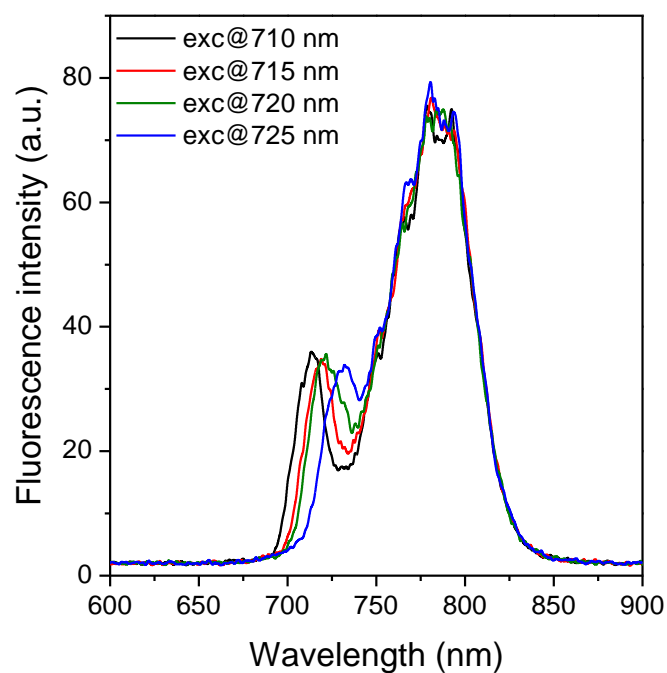


Figure S23. Steady-state fluorescence emission spectra in acetonitrile solution [$\sim 10^{-6}$ M] at different excitation wavelengths of the heptamethine cyanine dye **6a** (Slits Em./Exc. 10.0 nm/10.0 nm).

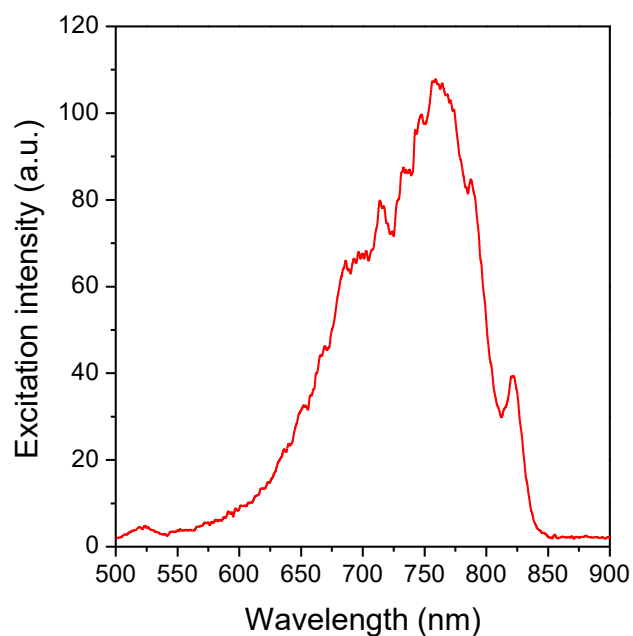


Figure S24. Excitation spectra in acetonitrile solution [$\sim 10^{-6}$ M] of the heptamethine cyanine dye **6a** ($\lambda_{\text{obs}}=787$ nm and slits Em./Exc. 10.0 nm/10.0 nm).

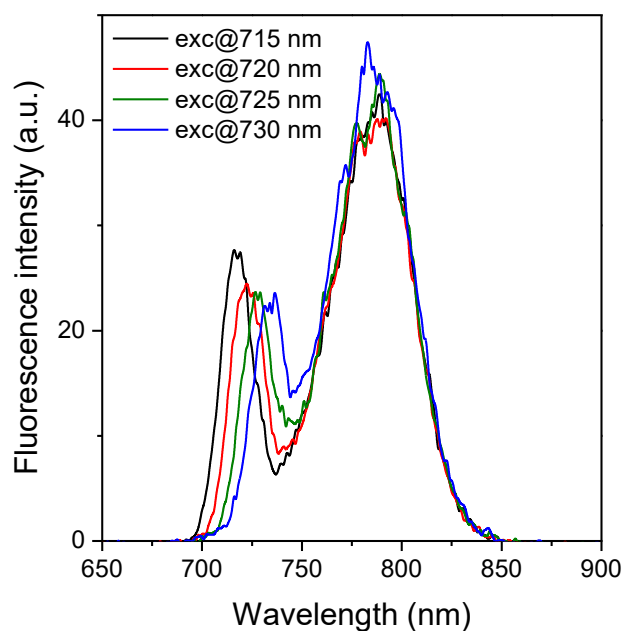


Figure S25. Steady-state fluorescence emission spectra in acetonitrile solution at different dye concentrations of the heptamethine cyanine dye **6b** (Slits Em./Exc. 10.0 nm/10.0 nm).

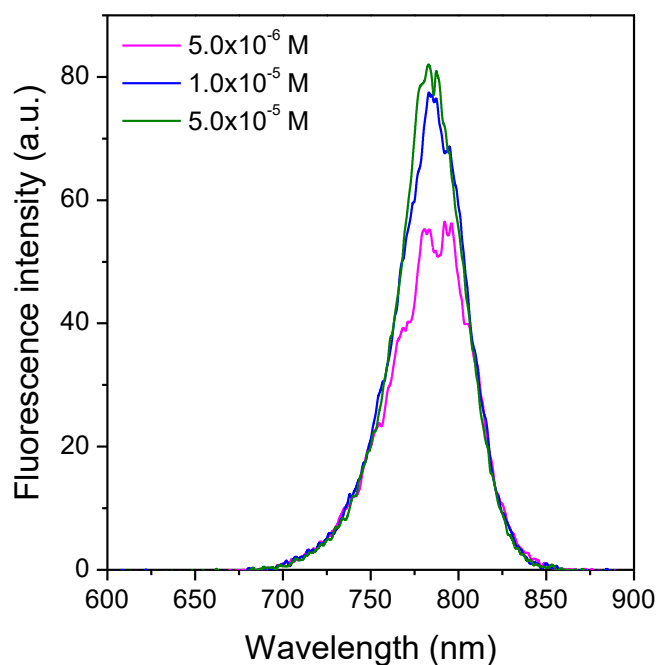


Figure S26. Steady-state fluorescence emission spectra in acetonitrile solution [$\sim 10^{-6}$ M] at different excitation wavelengths of the heptamethine cyanine dye **6b** ($\lambda_{\text{exc}}=780$ nm and slits Em./Exc. 10.0 nm/10.0 nm).

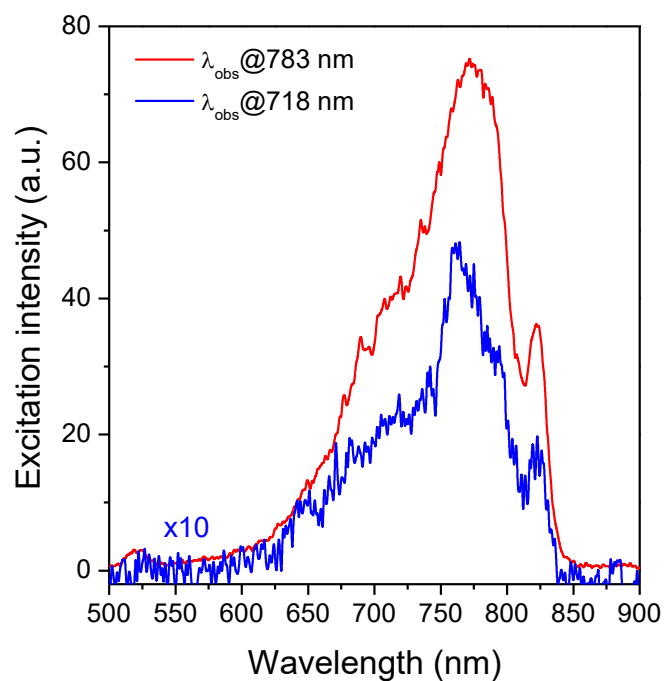


Figure S27. Excitation spectra in acetonitrile solution [$\sim 10^{-6}$ M] of the heptamethine cyanine dye **6b** (Slits Em./Exc. 10.0 nm/10.0 nm).

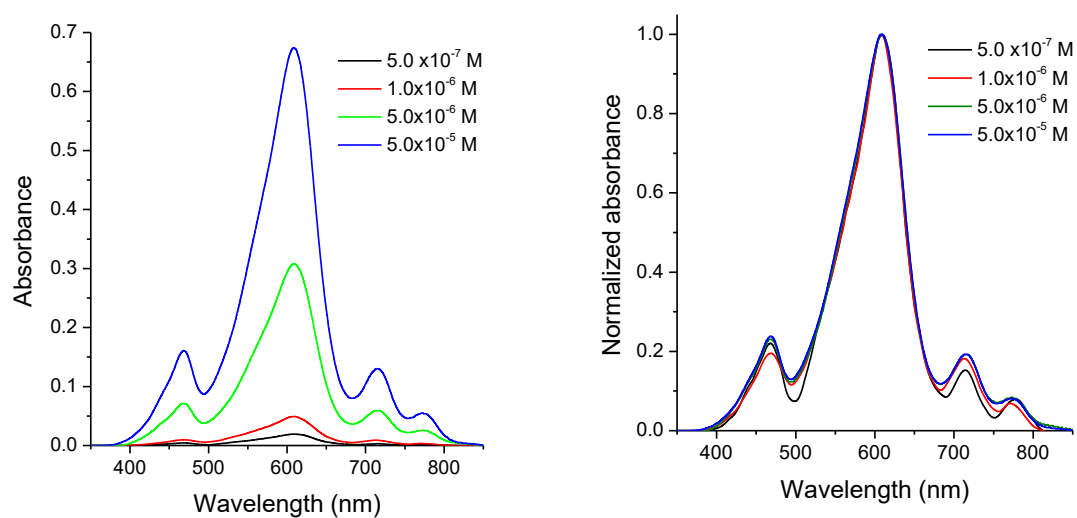


Figure S28. UV-Vis absorption spectra of *meso*-substituted cyanine dye **8b** in dichloromethane at different solution concentrations (left) and the respective normalized spectra (right).

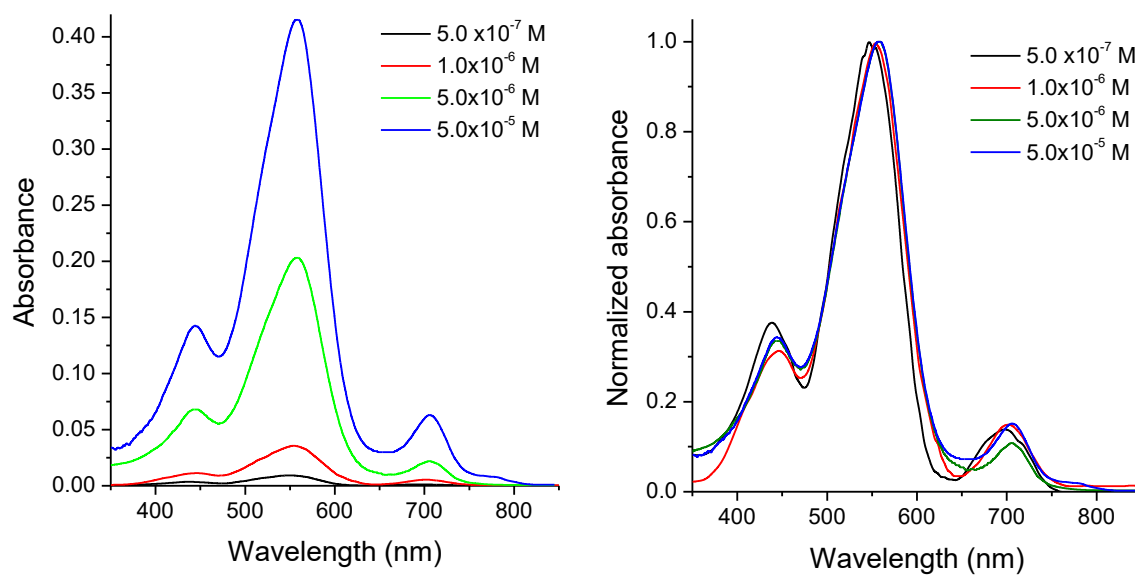


Figure S29. UV-Vis absorption spectra of *meso*-substituted cyanine dye **8b** in 1,4-dioxane at different solution concentrations (left) and the respective normalized spectra (right).

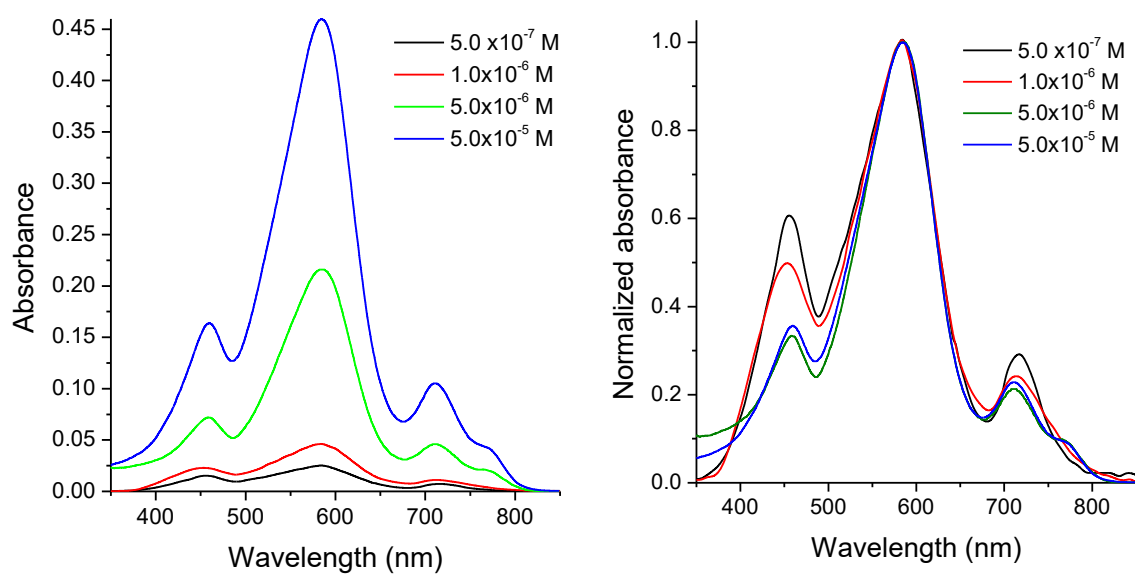


Figure S30. UV-Vis absorption spectra of *meso*-substituted cyanine dye **8b** in ethanol at different solution concentrations (left) and the respective normalized spectra (right).

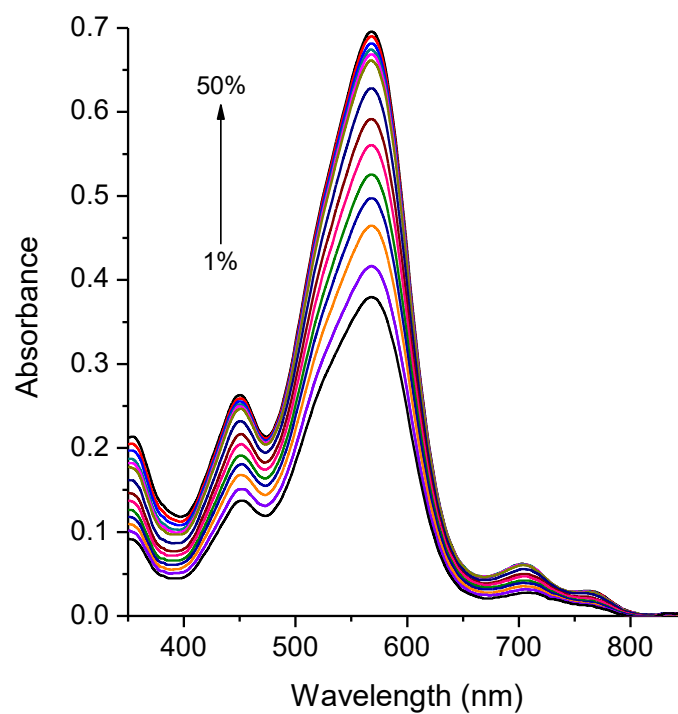


Figure S31. UV-Vis absorption spectra of *meso*-substituted cyanine dye **8b** in acetonitrile ($\sim 10^{-5}$ M) (black line) at different water content (1%-50%).

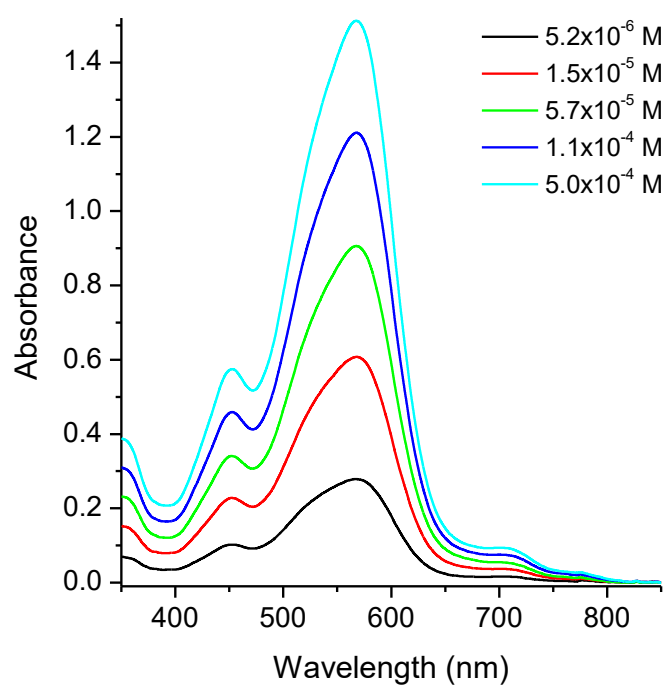


Figure S32. UV-Vis absorption spectra of *meso*-substituted cyanine dye **8b** in acetonitrile:water (1:1) ($\sim 10^{-5}$ M) solution at different dye concentrations.

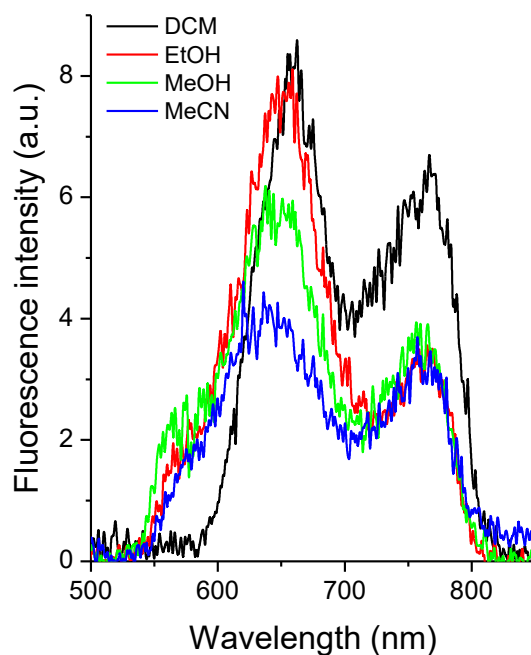


Figure S33. Steady-state fluorescence emission spectra of *meso*-substituted cyanine dye **8a** in solution of different organic solvents [$\sim 10^{-6}$ M] at excitation wavelength between 559-602 nm (Table 2). (DCM=dichloromethane and MeCN=acetonitrile).

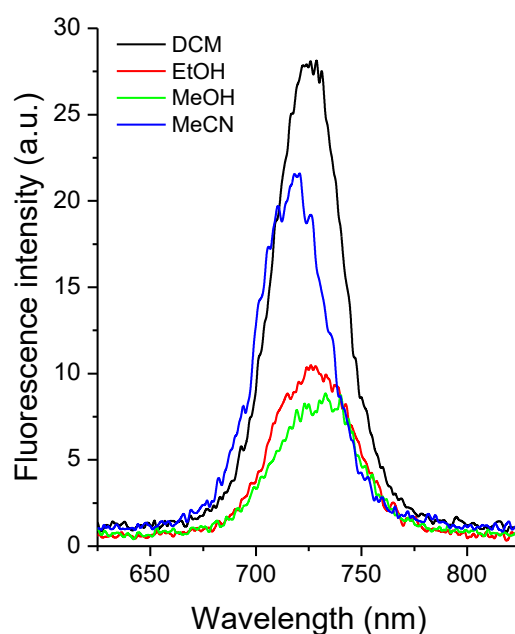


Figure S34. Steady-state fluorescence emission spectra of *meso*-substituted cyanine dye **8a** in solution of different organic solvents [$\sim 10^{-6}$ M] at excitation wavelength between 703-712 nm (Table S2). (DCM=dichloromethane and MeCN=acetonitrile).

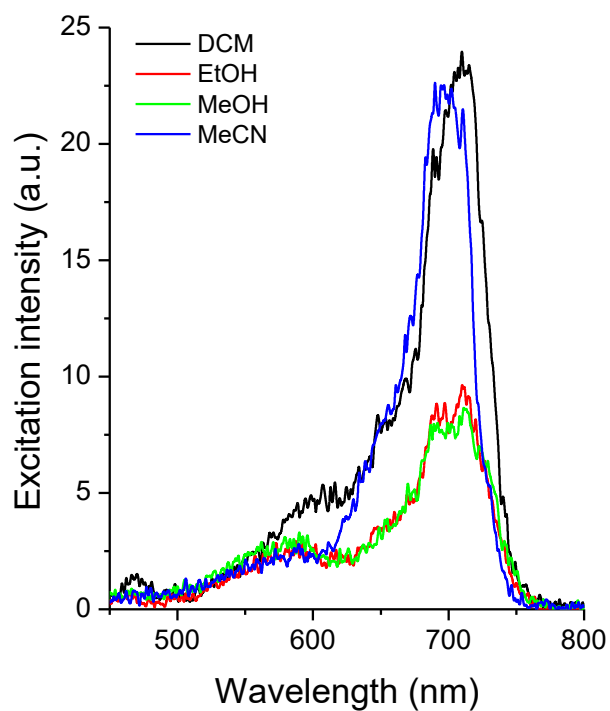


Figure S35. Excitation spectra of the *meso*-substituted cyanine dye **8a** in different organic solvents under the observation wavelength around 700 nm.

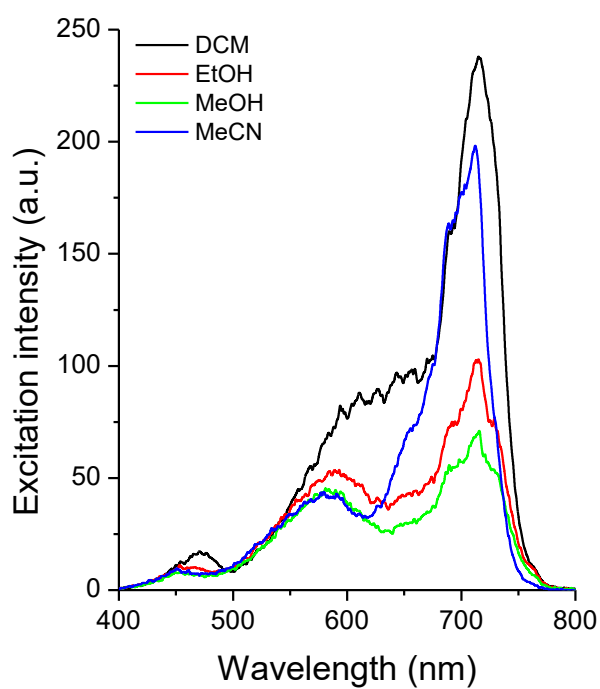


Figure S36. Excitation spectra of the *meso*-substituted cyanine dye **8b** in different organic solvents under the observation wavelength around 700 nm.

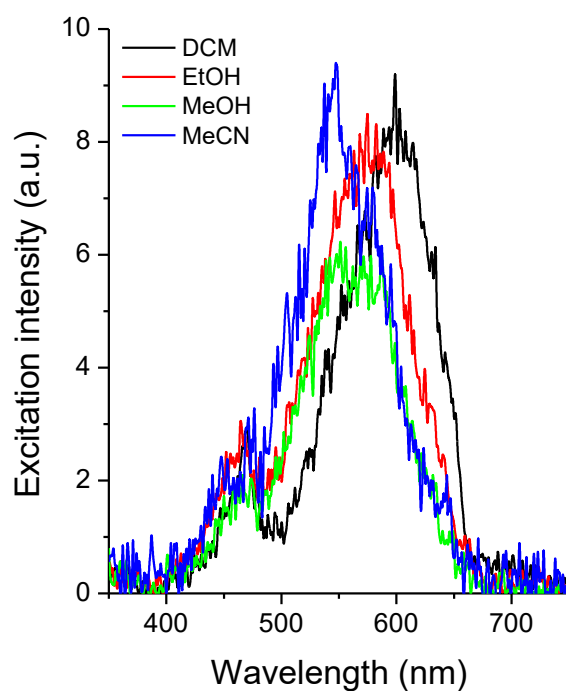


Figure S37. Excitation spectra of the *meso*-substituted cyanine dye **8a** in different organic solvents under the observation wavelength around 650 nm.

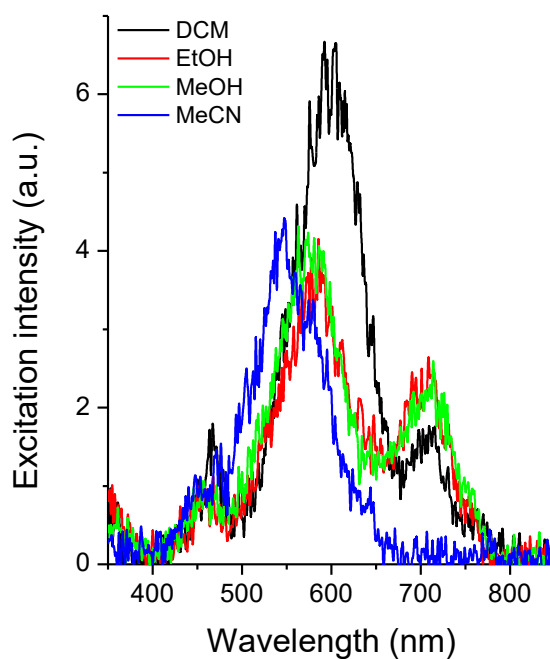


Figure S38. Excitation spectra of the *meso*-substituted cyanine dye **8a** in different organic solvents under the observation wavelength around 750 nm.

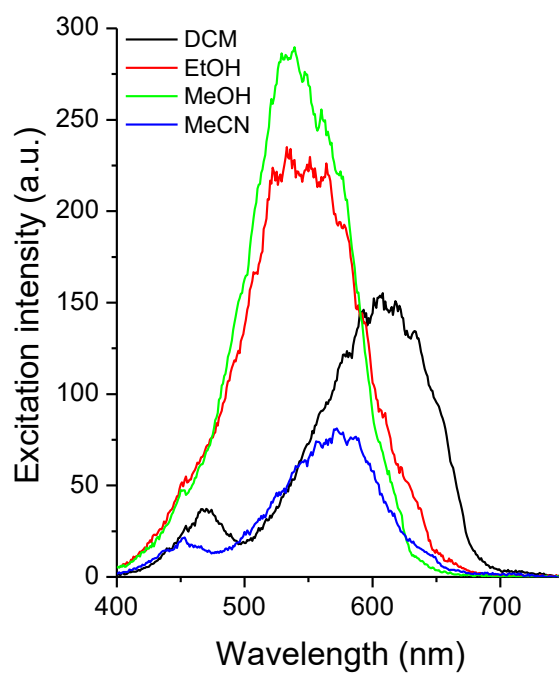


Figure S39. Excitation spectra of the *meso*-substituted cyanine dye **8b** in different organic solvents under the observation wavelength around 650 nm.

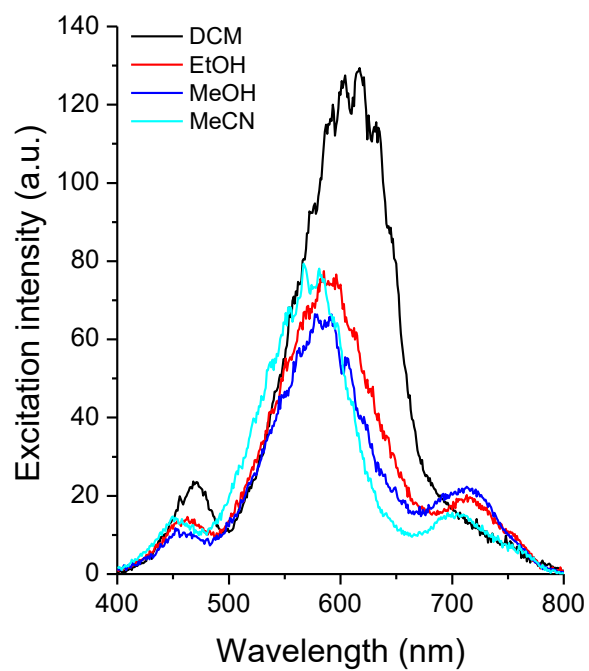


Figure S40. Excitation spectra of the *meso*-substituted cyanine dye **8b** in different organic solvents under the observation wavelength around 750 nm.

Table S1 Lippert-Mataga data of the meso-substituted cyanine dye **8b** in 1,4-dioxane/acetonitrile mixtures, where Δf is the solvent polarity function, λ_{abs} and λ_{em} (in cm^{-1}) are the absorption and emission maxima and $\Delta\lambda_{\text{ST}}$ is the Stokes shift (in cm^{-1}).

Mixture	Solvent volume (mL)		Δf	λ_{abs}	$\lambda_{\text{em}}^{\text{a)}$	$\lambda_{\text{em}}^{\text{b)}$	Stokes shift	
	Acetonitrile	1,4-Dioxane					$\Delta\lambda_{\text{ST}}^{\text{a)}$	$\Delta\lambda_{\text{ST}}^{\text{b)}$
1	1.0	0.5	0.298	17422	15267	13038	2155	4384
2	1.0	1.0	0.274	17331	15198	13038	2133	4293
3	1.0	1.5	0.254	17271	15221	13004	2050	4267
4	1.0	2.0	0.226	17182	15198	12970	1984	4212
5	1.0	2.5	0.205	17153	15198	12987	1955	4166

^{a)} emission at shorter wavelength

^{b)} emission at longer wavelength

Theoretical calculations

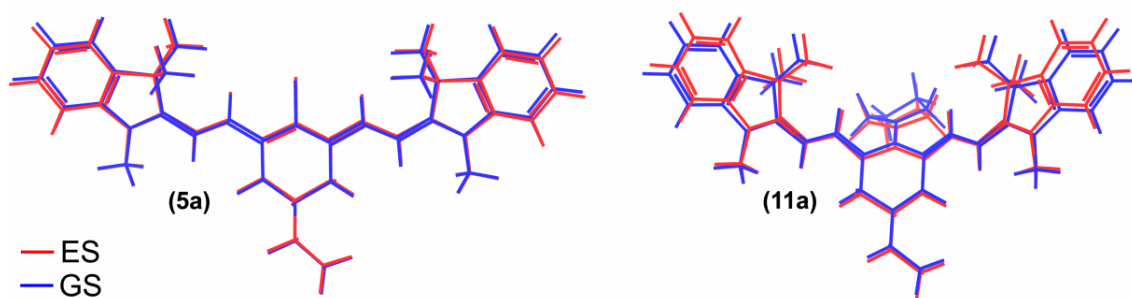


Figure S41. Optimized geometries for cyanines **8a** and **6a** to the ground (GS blue) and excited (ES red) states.

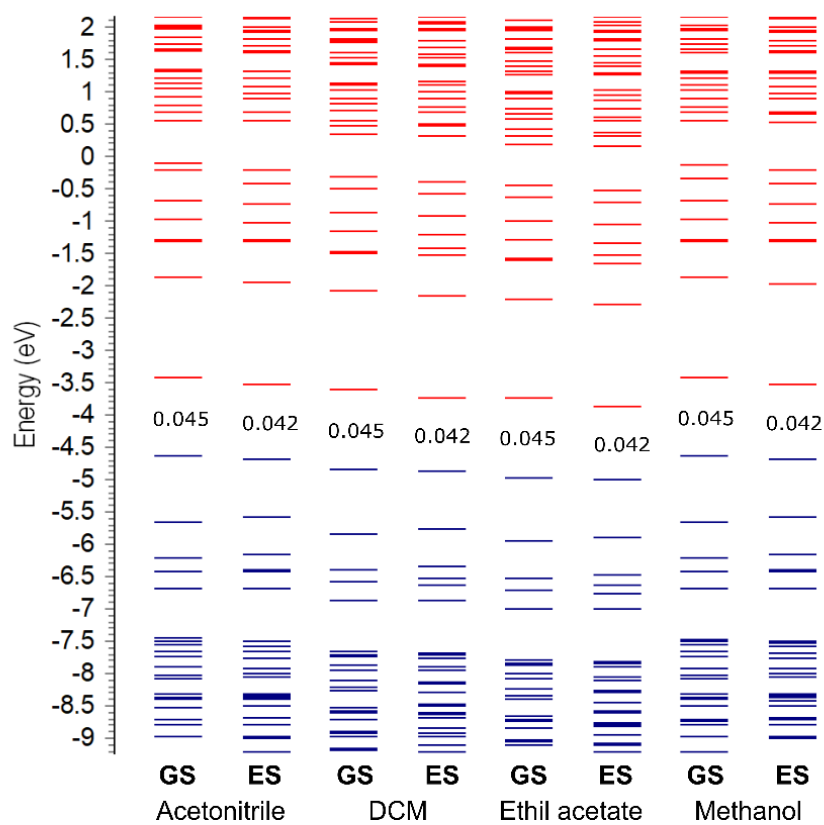


Figure S42. HOMO-LUMO gap in Hartree for cyanines **8a** in the ground (GS) and excited (ES) states under different solvation conditions using the B97-3c scheme.

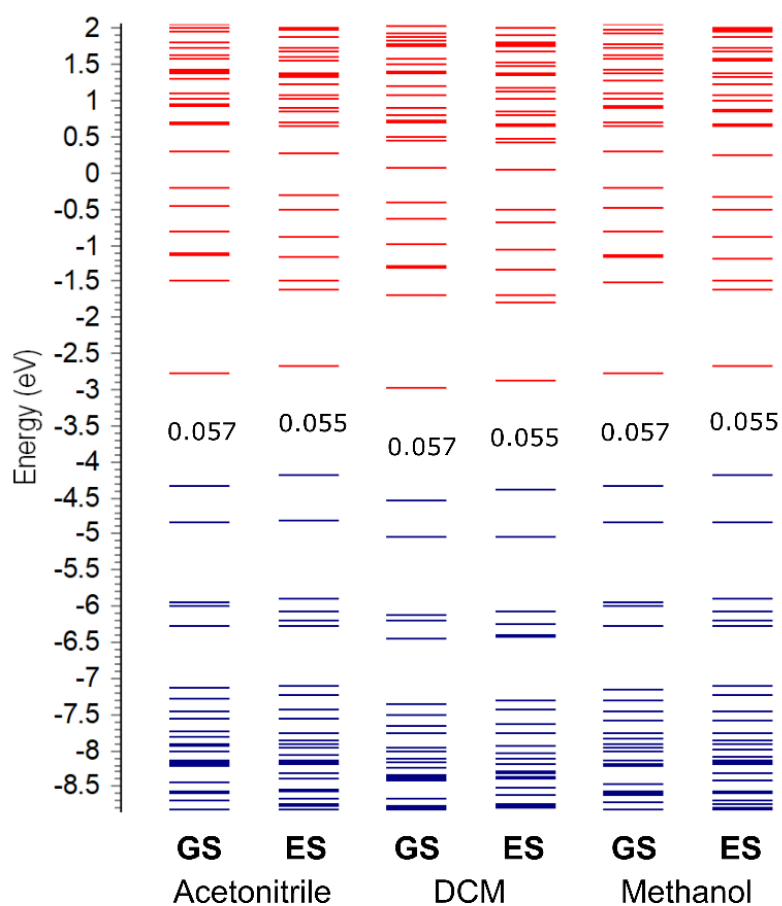


Figure S43. HOMO-LUMO gap in Hartree for cyanines **6a** in the ground (GS) and excited (ES) states under different solvation conditions using the B97-3c scheme.

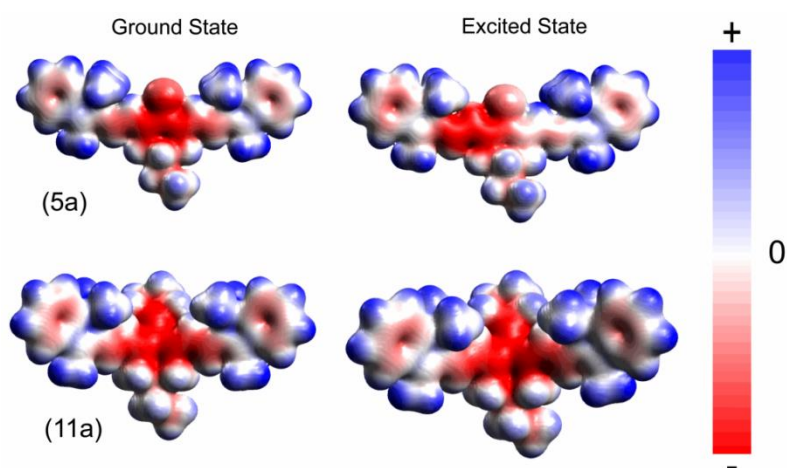


Figure S44. Molecular Electrostatic Potential Surfaces for cyanines **8a** and **6a**, where the red color indicates increased negative charge, blue positive charge and white a neutral environment.

Table S2 Atomic charge distribution of the *meso*-substituted cyanine dye **8a** using CHELPG.

GS	Acetonitrile	DCM	Ethyl acetate	MeOH
0 C	-0.2922	-0.2871	-0.2912	-0.2860
1 C	0.4660	0.4575	0.4595	0.4565
2 C	-0.4143	-0.4148	-0.4094	-0.4197
3 C	-0.1158	-0.1191	-0.1215	-0.1165
4 C	-0.0906	-0.0821	-0.0801	-0.0843
5 N	0.1243	0.1163	0.1165	0.1134
6 C	0.1228	0.1193	0.1173	0.1258
7 C	-0.0791	-0.0766	-0.0757	-0.0828
8 C	-0.2087	-0.2125	-0.2102	-0.2134
9 C	-0.1600	-0.1575	-0.1554	-0.1604
10 C	-0.1465	-0.1456	-0.1433	-0.1485
11 C	-0.2569	-0.2521	-0.2508	-0.2565
12 H	0.1931	0.1899	0.1884	0.1928
13 H	0.1614	0.1603	0.1599	0.1609
14 H	0.1567	0.1571	0.1568	0.1572
15 H	0.1747	0.1760	0.1745	0.1773
16 C	0.6308	0.6343	0.6288	0.6465
17 C	-0.5557	-0.5550	-0.5526	-0.5612
18 H	0.1465	0.1465	0.1461	0.1477
19 H	0.1339	0.1338	0.1339	0.1345
20 H	0.1532	0.1496	0.1489	0.1509
21 C	-0.5636	-0.5525	-0.5508	-0.5579
22 H	0.1513	0.1476	0.1473	0.1487
23 H	0.1475	0.1425	0.1425	0.1433
24 H	0.1365	0.1340	0.1342	0.1344
25 C	-0.4139	-0.4081	-0.4066	-0.4065
26 H	0.1787	0.1796	0.1789	0.1796
27 H	0.1684	0.1654	0.1641	0.1663
28 H	0.1706	0.1680	0.1668	0.1688
29 H	0.1707	0.1727	0.1711	0.1752
30 H	0.2129	0.2135	0.2100	0.2157
31 C	-0.6094	-0.5955	-0.5970	-0.5964
32 H	0.1561	0.1505	0.1503	0.1514
33 H	0.1601	0.1559	0.1557	0.1568
34 C	0.3639	0.3709	0.3679	0.3748
35 H	-0.0205	-0.0216	-0.0209	-0.0231
36 C	0.0879	0.0717	0.0724	0.0733
37 H	0.0052	0.0067	0.0070	0.0067
38 H	-0.0041	-0.0013	-0.0009	-0.0019
39 C	-0.3703	-0.3571	-0.3623	-0.3598
40 H	0.0817	0.0786	0.0805	0.0787
41 H	0.0861	0.0810	0.0818	0.0825
42 H	0.0963	0.0958	0.0982	0.0945
43 C	-0.3301	-0.3101	-0.3046	-0.3137
44 C	0.2512	0.2395	0.2422	0.2383

45	C	-0.2847	-0.2753	-0.2736	-0.2789
46	C	-0.2208	-0.2332	-0.2304	-0.2325
47	C	-0.0136	-0.0094	-0.0132	-0.0087
48	N	0.1086	0.1049	0.1076	0.1032
49	C	0.1004	0.1074	0.1042	0.1115
50	C	-0.0468	-0.0592	-0.0572	-0.0611
51	C	-0.2212	-0.2202	-0.2189	-0.2215
52	C	-0.1576	-0.1496	-0.1476	-0.1548
53	C	-0.1478	-0.1533	-0.1503	-0.1544
54	C	-0.2444	-0.2448	-0.2435	-0.2487
55	H	0.1903	0.1896	0.1881	0.1923
56	H	0.1602	0.1620	0.1613	0.1621
57	H	0.1565	0.1555	0.1553	0.1565
58	H	0.1782	0.1773	0.1761	0.1787
59	C	0.5693	0.5830	0.5795	0.5901
60	C	-0.5441	-0.5292	-0.5288	-0.5354
61	H	0.1319	0.1277	0.1283	0.1283
62	H	0.1418	0.1340	0.1344	0.1356
63	H	0.1498	0.1469	0.1466	0.1482
64	C	-0.5378	-0.5482	-0.5452	-0.5514
65	H	0.1463	0.1443	0.1436	0.1456
66	H	0.1461	0.1489	0.1481	0.1495
67	H	0.1299	0.1339	0.1339	0.1337
68	C	-0.3919	-0.3982	-0.3971	-0.3993
69	H	0.1732	0.1761	0.1754	0.1770
70	H	0.1679	0.1689	0.1678	0.1703
71	H	0.1639	0.1645	0.1634	0.1660
72	H	0.1805	0.1848	0.1821	0.1874
73	H	0.2084	0.2086	0.2058	0.2102
74	H	0.1230	0.1169	0.1144	0.1190
75	H	0.1129	0.1073	0.1051	0.1095
76	Cl	-0.0853	-0.0880	-0.0834	-0.0919
Total		1.0000	1.0000	1.0000	1.0000

Table S3. Atomic charge distribution of cyanine dye **6a** using CHELPG.

GS	Acetonitrile	DCM	MeOH
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0	N	0.0462	0.0422	0.0461
1	N	0.1017	0.1048	0.1002
2	N	0.1091	0.1058	0.1091
3	C	-0.0010	-0.0002	-0.0018
4	C	-0.1319	-0.1301	-0.1305
5	C	-0.1173	-0.1151	-0.1184
6	C	0.0129	0.0111	0.0140
7	C	-0.3699	-0.3690	-0.3697
8	C	0.0448	0.0457	0.0448
9	C	-0.4007	-0.3996	-0.4002
10	C	-0.6069	-0.6032	-0.6083
11	C	-0.5915	-0.5851	-0.5901
12	C	0.7250	0.6977	0.7195
13	C	-0.2671	-0.2661	-0.2693
14	C	-0.1567	-0.1518	-0.1554
15	C	-0.1841	-0.1803	-0.1847
16	C	-0.2085	-0.2092	-0.2082
17	C	-0.1020	-0.0876	-0.1009
18	C	0.1254	0.1192	0.1274
19	C	-0.1480	-0.1360	-0.1447
20	C	-0.1694	-0.1756	-0.1703
21	C	-0.3780	-0.3692	-0.3779
22	C	0.3798	0.3796	0.3801
23	C	-0.5346	-0.5342	-0.5347
24	C	0.2711	0.2677	0.2709
25	C	-0.1628	-0.1636	-0.1627
26	C	-0.3930	-0.3896	-0.3936
27	C	-0.5631	-0.5557	-0.5593
28	C	-0.5874	-0.5841	-0.5856
29	C	0.7055	0.6997	0.7065
30	C	-0.2783	-0.2788	-0.2797
31	C	-0.1464	-0.1387	-0.1454
32	C	-0.1860	-0.1837	-0.1860
33	C	-0.2114	-0.2069	-0.2106
34	C	-0.0903	-0.0927	-0.0926
35	C	0.1224	0.1261	0.1241
36	C	-0.1625	-0.1593	-0.1635
37	C	-0.1530	-0.1515	-0.1526
38	C	-0.3489	-0.3478	-0.3493
39	C	0.0560	0.0579	0.0560
40	C	-0.1633	-0.1639	-0.1633
41	H	0.0651	0.0640	0.0651
42	H	0.0932	0.0903	0.0931
43	H	0.0779	0.0775	0.0775
44	H	0.0723	0.0720	0.0721
45	H	0.0684	0.0684	0.0686

46	H	0.0707	0.0698	0.0708
47	H	0.0954	0.0951	0.0952
48	H	0.0553	0.0527	0.0549
49	H	0.0796	0.0800	0.0795
50	H	0.0835	0.0831	0.0834
51	H	0.1014	0.1027	0.1014
52	H	0.0183	0.0189	0.0184
53	H	0.0103	0.0100	0.0104
54	H	0.1394	0.1384	0.1394
55	H	0.1304	0.1304	0.1305
56	H	0.1601	0.1545	0.1602
57	H	0.1778	0.1765	0.1778
58	H	0.1754	0.1744	0.1752
59	H	0.1550	0.1540	0.1549
60	H	0.1546	0.1536	0.1545
61	H	0.1484	0.1487	0.1491
62	H	0.1624	0.1620	0.1631
63	H	0.1387	0.1400	0.1395
64	H	0.1459	0.1455	0.1457
65	H	0.1330	0.1335	0.1329
66	H	0.1556	0.1537	0.1557
67	H	0.1701	0.1696	0.1702
68	H	0.1555	0.1555	0.1556
69	H	0.1607	0.1601	0.1604
70	H	0.1857	0.1850	0.1864
71	H	0.0139	0.0135	0.0140
72	H	0.0883	0.0886	0.0883
73	H	0.0890	0.0883	0.0889
74	H	0.2355	0.2340	0.2355
75	H	0.1569	0.1541	0.1568
76	H	0.1688	0.1675	0.1689
77	H	0.1595	0.1580	0.1596
78	H	0.1540	0.1529	0.1542
79	H	0.1389	0.1371	0.1378
80	H	0.1261	0.1260	0.1250
81	H	0.1474	0.1435	0.1462
82	H	0.1403	0.1374	0.1395
83	H	0.1468	0.1461	0.1462
84	H	0.1339	0.1347	0.1335
85	H	0.1699	0.1680	0.1697
86	H	0.1562	0.1561	0.1561
87	H	0.1568	0.1550	0.1566
88	H	0.1915	0.1905	0.1919
Total		1.0000	1.0000	1.0000