Electronic Supplementary Information (ESI) for Phys. Chem. Chem. Phys.

Deeply coloured and fluorescent highly dipolar merocyanines based on tricyanofuran

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Content

Table S1. Some characteristics of the solvents used in the study

Solvent	ε_D	n_D	E_T^N	η (cP)
n-Hexane	1.90	1.375	0.010	0.31
Toluene	2.38	1.497	0.099	0.59
DCM (CH_2Cl_2)	8.93	1.424	0.309	0.44
DMF	36.7	1.431	0.386	0.92
EtOH	24.6	1.361	0.654	1.10

ε_D, relative permittivity (dielectric constant); n_D, refractive index; E_T^N, normalized Dimroth–Reichardt solvent polarity parameter; η, viscosity. The parameters are given for 20 °C or 25 °C (in case if the parameter at 20 °C was not found). They were taken from: C. Reichardt and T. Welton, *Solvents and Solvent Effects in Organic Chemistry (4th edn)*, Wiley-VCH, Weinheim, 2010.

UV-Vis absorption spectra

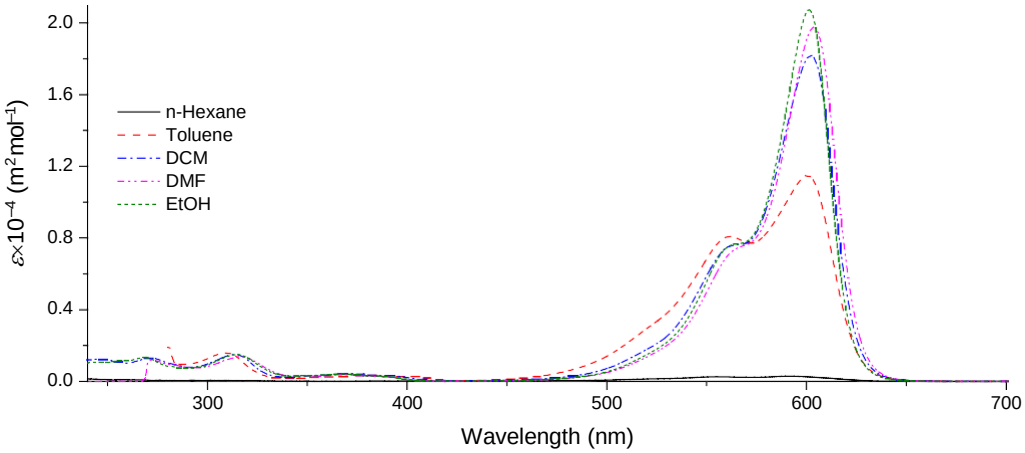


Fig. S1. Absorption spectra of dye **7** in solvents of different polarities.

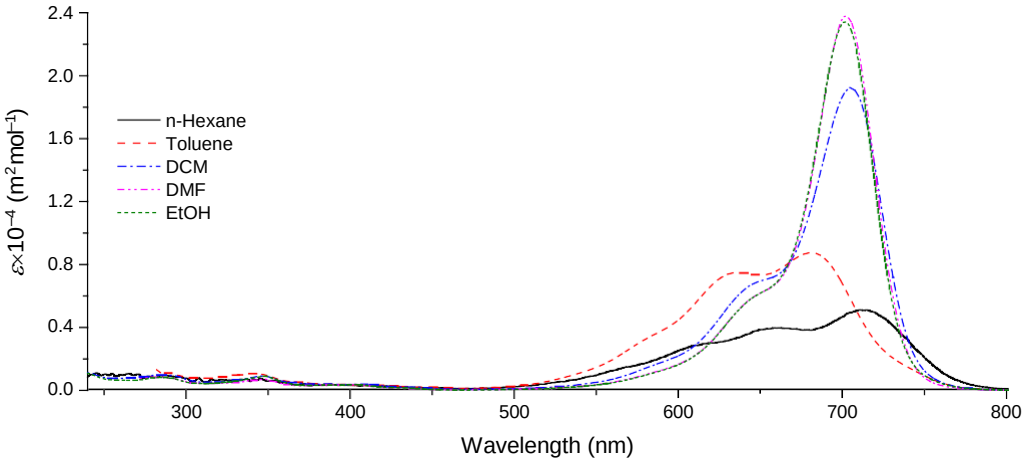


Fig. S2. Absorption spectra of dye **8** in solvents of different polarities (spectrum in *n*-hexane is the actual absorbance spectrum multiplied 10 times, not quantitative).

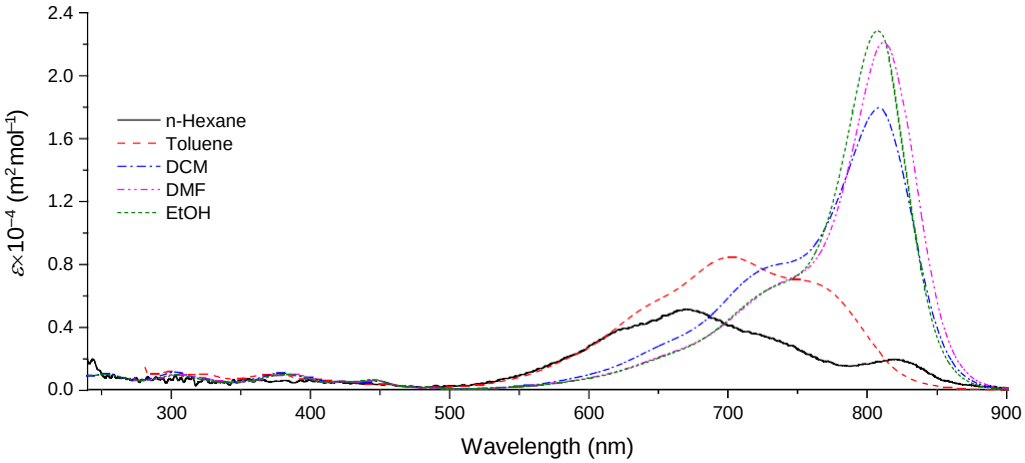


Fig. S3. Absorption spectra of dye **9** in solvents of different polarities (spectrum in *n*-hexane is the actual absorbance spectrum multiplied 20 times, not quantitative).

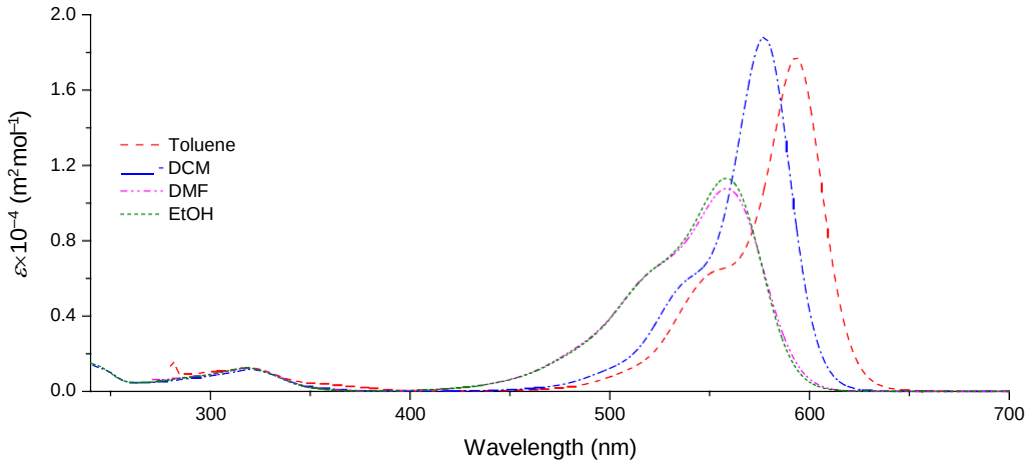


Fig. S4. Absorption spectra of dye **10** in solvents of different polarities.

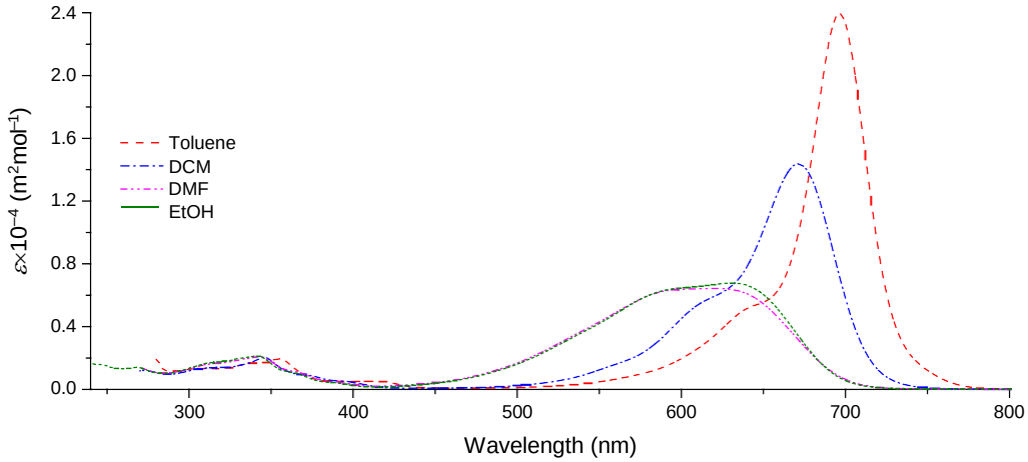


Fig. S5. Absorption spectra of dye **11** in solvents of different polarities (the same spectra are shown in Fig. 2 in the paper).

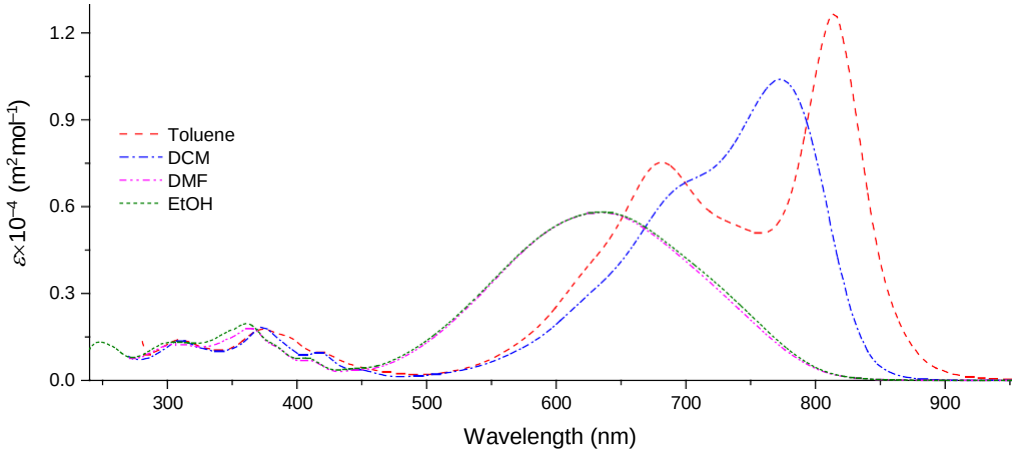


Fig. S6. Absorption spectra of dye **12** in solvents of different polarities (spectrum in toluene was measured at dye's concentration $C = 1\times10^{-5}$ mol L^{-1}).

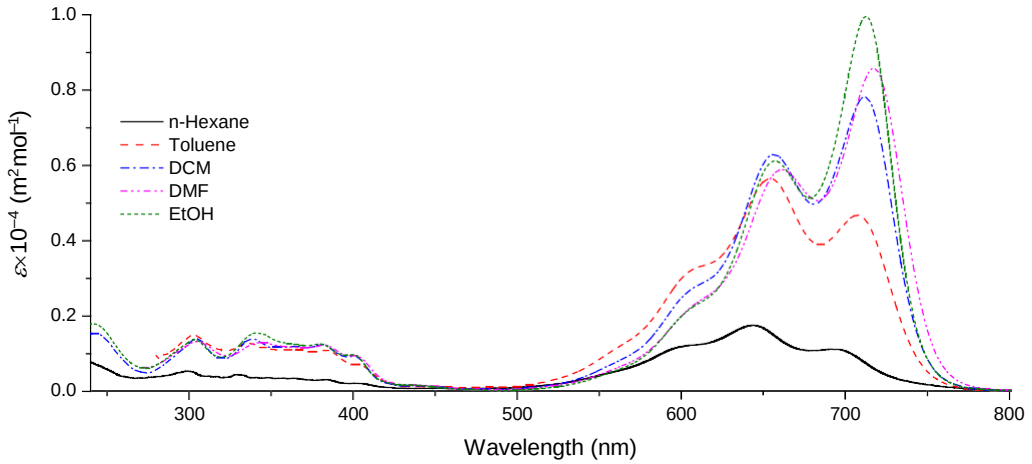


Fig. S7. Absorption spectra of dye **13** in solvents of different polarities (spectrum in *n*-hexane not quantitative).

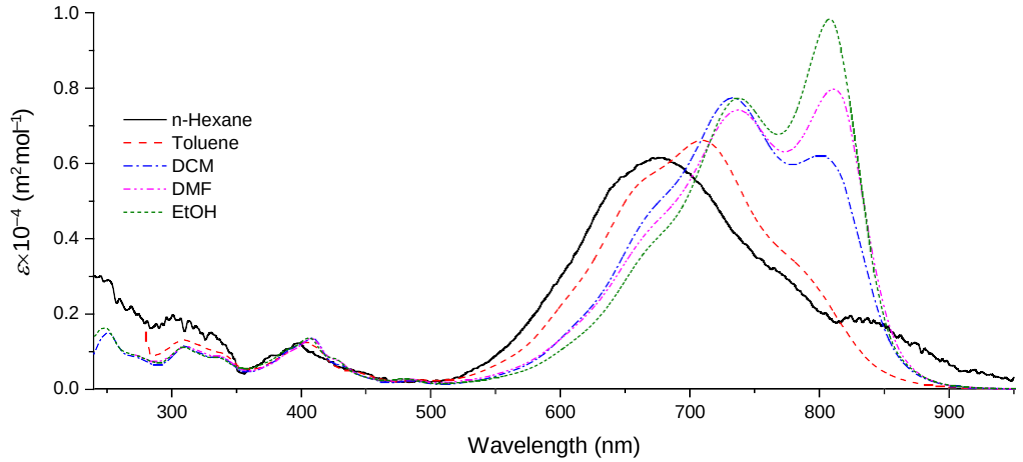


Fig. S8. Absorption spectra of dye **14** in solvents of different polarities (spectrum in *n*-hexane is the actual absorbance spectrum multiplied 10 times, not quantitative).

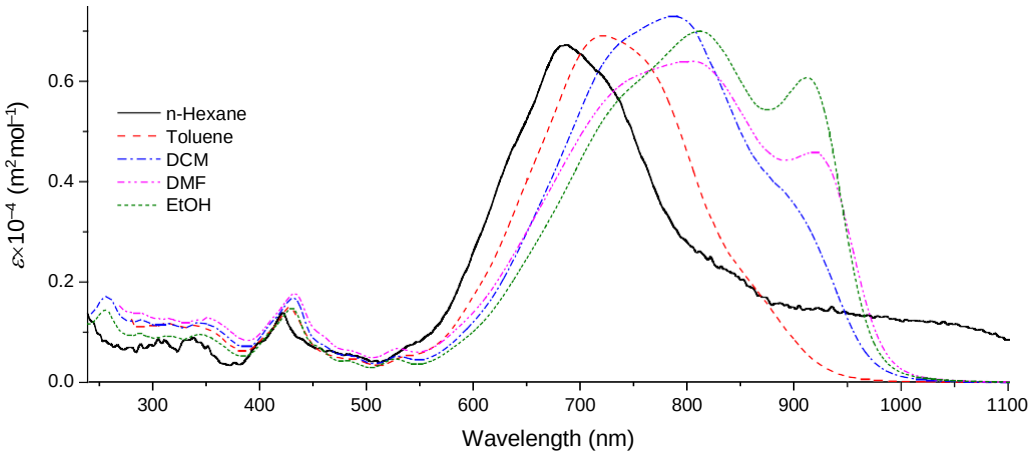


Fig. S9. Absorption spectra of dye **15** in solvents of different polarities (spectrum in *n*-hexane is the actual absorbance spectrum multiplied 8 times, not quantitative).

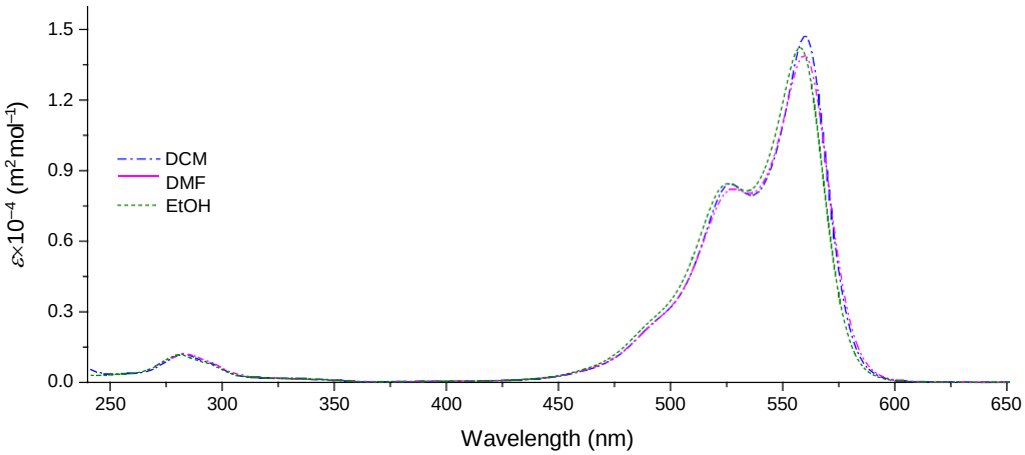


Fig. S10. Absorption spectra of cationic dye **16** in solvents of different polarities.

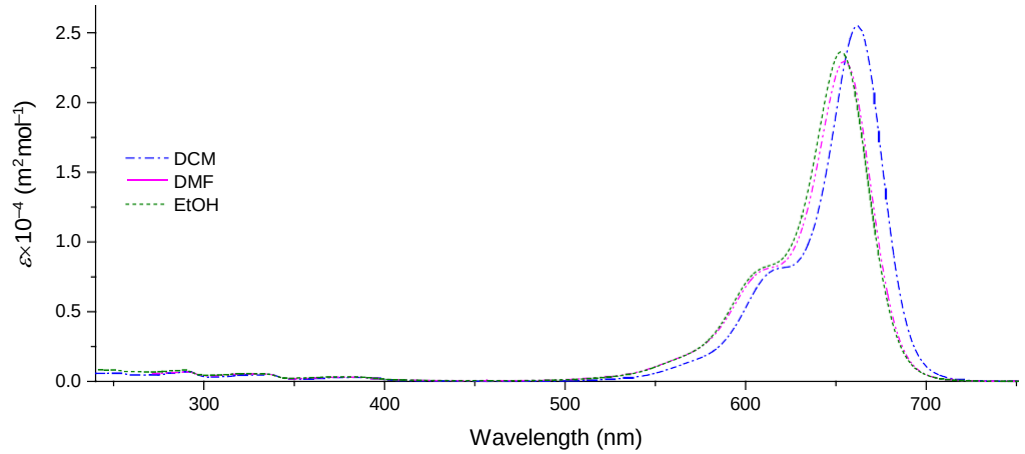


Fig. S11. Absorption spectra of cationic dye **17** in solvents of different polarities.

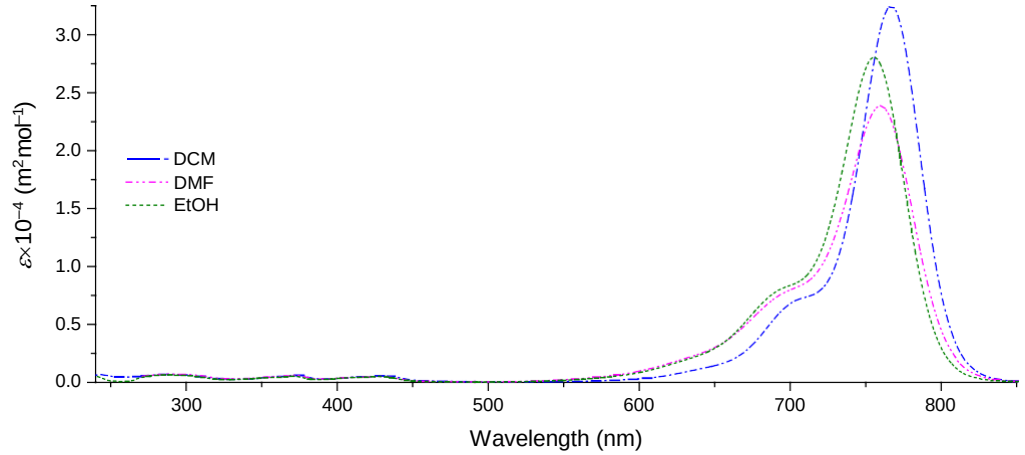


Fig. S12. Absorption spectra of cationic dye **18** in solvents of different polarities.

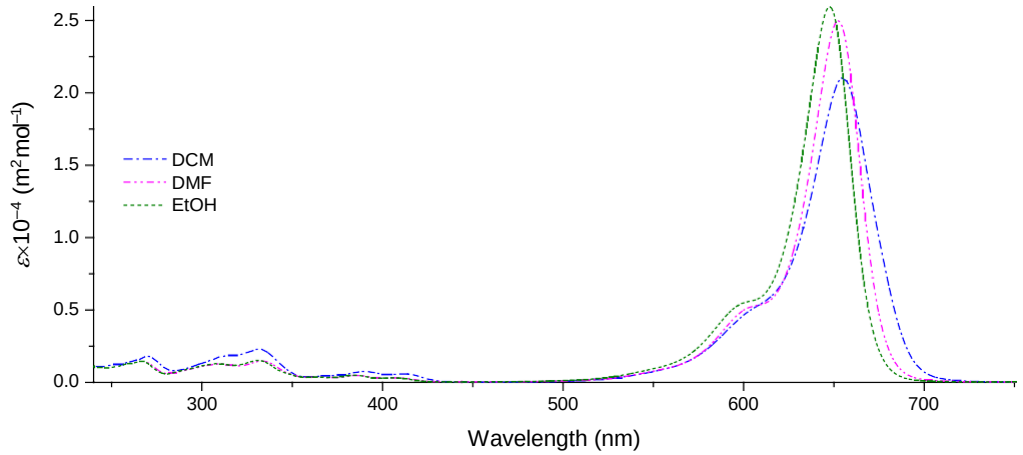


Fig. S13. Absorption spectra of anionic dye **19** in solvents of different polarities.

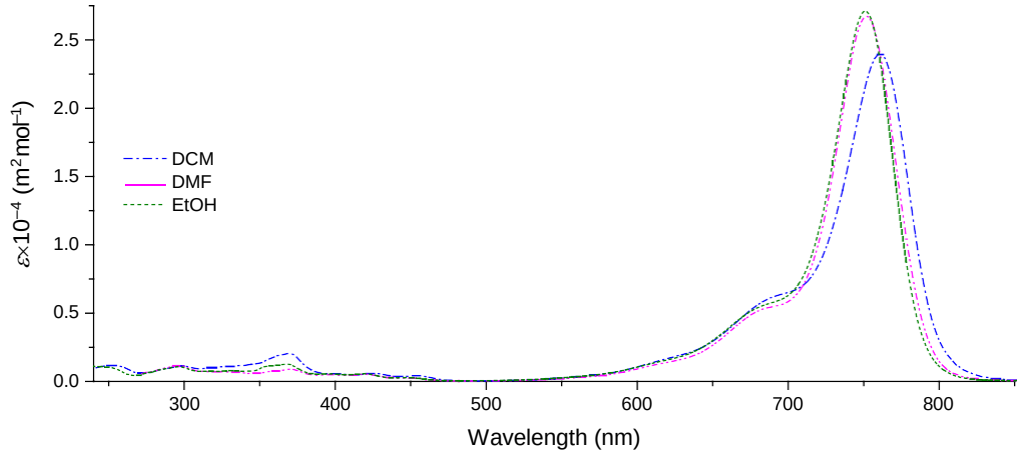


Fig. S14. Absorption spectra of anionic dye **20** in solvents of different polarities.

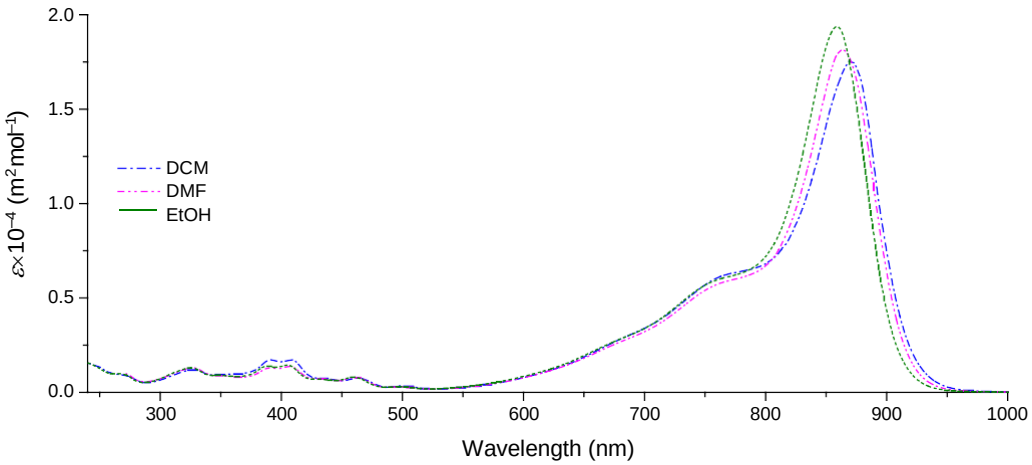


Fig. S15. Absorption spectra of anionic dye **21** in solvents of different polarities.

Fluorescence spectra

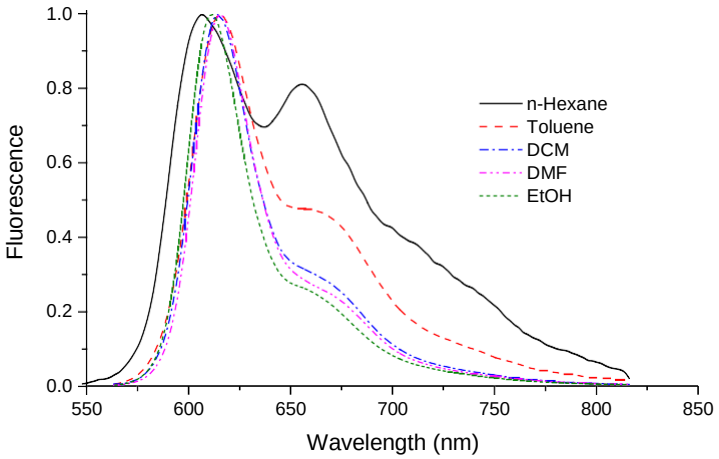


Fig. S16. Normalized fluorescence spectra of dye **7** in solvents of different polarities. Excitation wavelengths (λ_{exc}) were equal to 560 nm in all solvents.

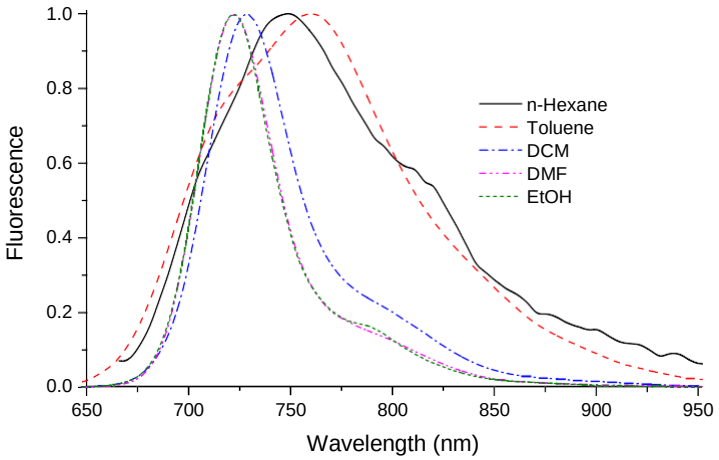


Fig. S17. Normalized fluorescence spectra of dye **8** in solvents of different polarities. Excitation wavelengths (λ_{exc}) were equal to 620 nm in *n*-hexane, 630 nm in toluene, 700 nm in DCM, DMF and ethanol.

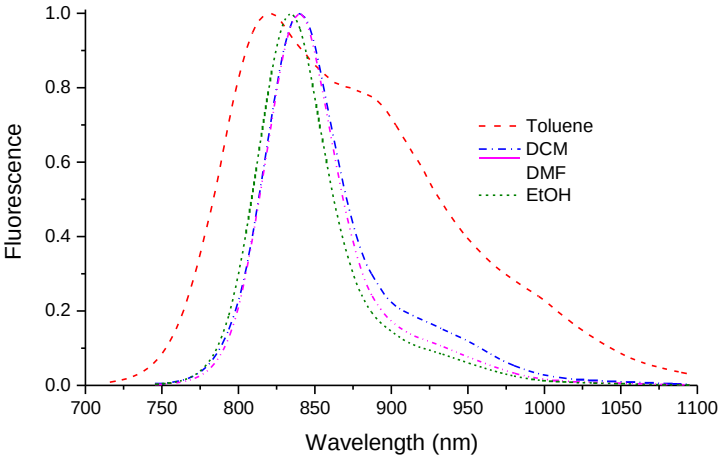


Fig. S18. Normalized fluorescence spectra of dye **9** in solvents of different polarities. Excitation wavelengths (λ_{exc}) were equal to 700 nm in toluene, 800 nm in DCM, DMF and ethanol.

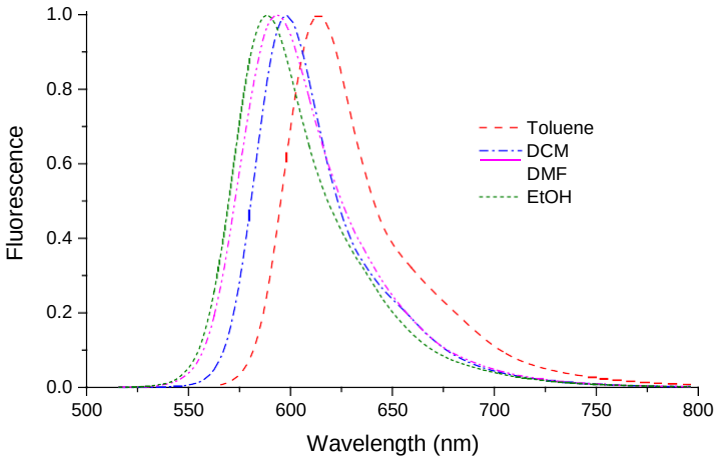


Fig. S19. Normalized fluorescence spectra of dye **10** in solvents of different polarities. Excitation wavelengths (λ_{exc}) were equal to 560 nm in all solvents.

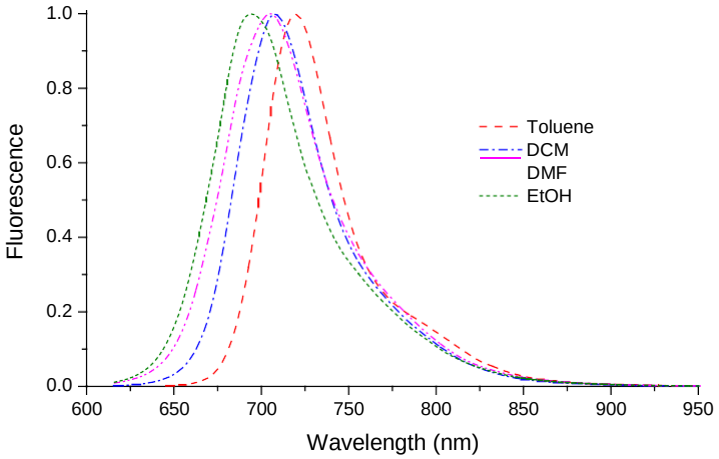


Fig. S20. Normalized fluorescence spectra of dye **11** in solvents of different polarities. Excitation wavelengths (λ_{exc}) were equal to 690 nm in toluene, 650 nm in DCM, 600 nm in DMF and ethanol.

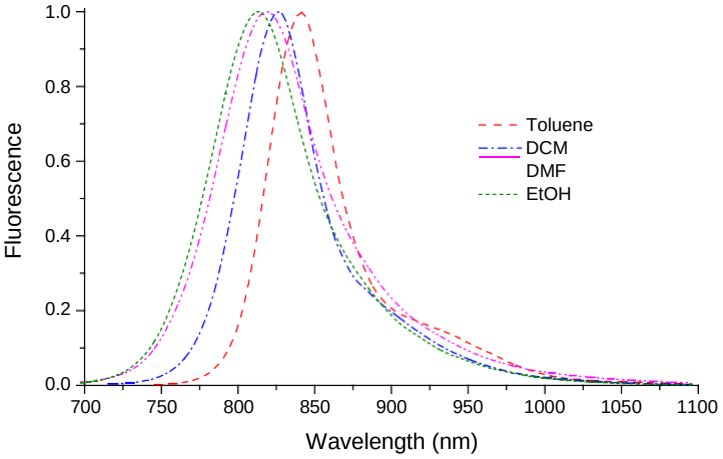


Fig. S21. Normalized fluorescence spectra of dye **12** in solvents of different polarities. Excitation wavelengths (λ_{exc}) were equal to 810 nm in toluene, 700 nm in DCM, 650 nm in DMF and ethanol.

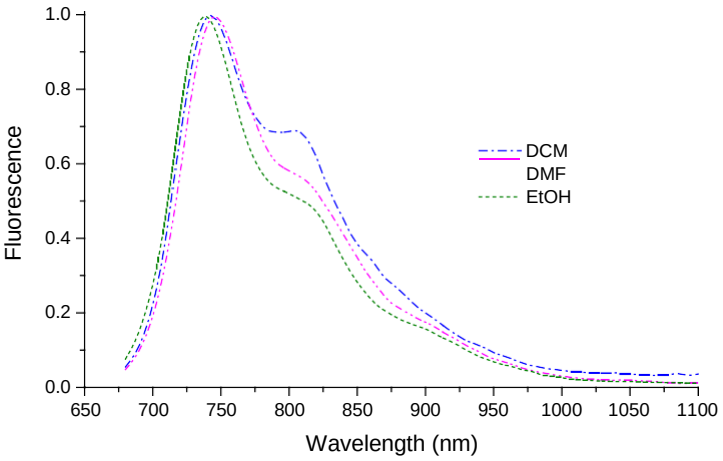


Fig. S22. Normalized fluorescence spectra of dye **13** in solvents of different polarities. Excitation wavelengths (λ_{exc}) were equal to 660 nm in all solvents.

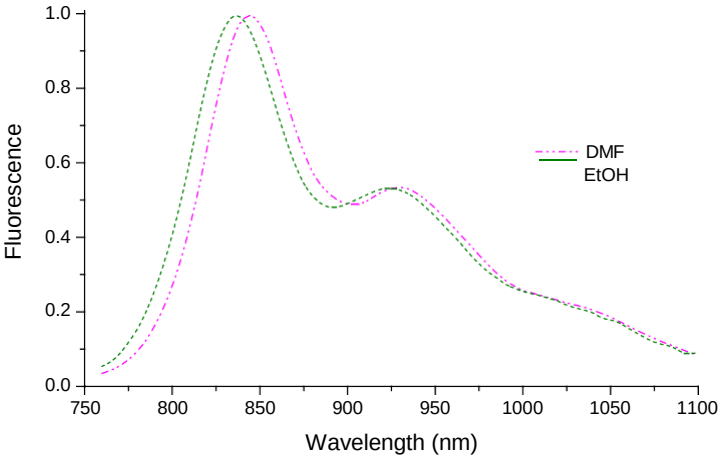


Fig. S23. Normalized fluorescence spectra of dye **14** in DMF and ethanol. Excitation wavelengths (λ_{exc}) were equal to 740 nm both solvents.

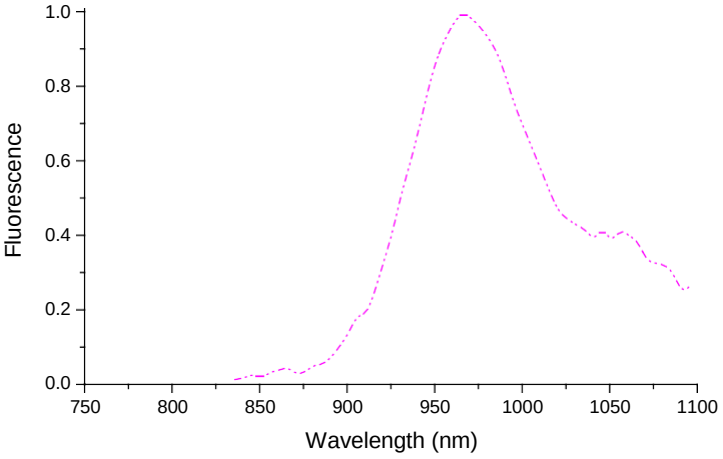


Fig. S24. Normalized fluorescence spectrum of dye **15** in DMF. Excitation wavelength (λ_{exc}) was equal to 810 nm.

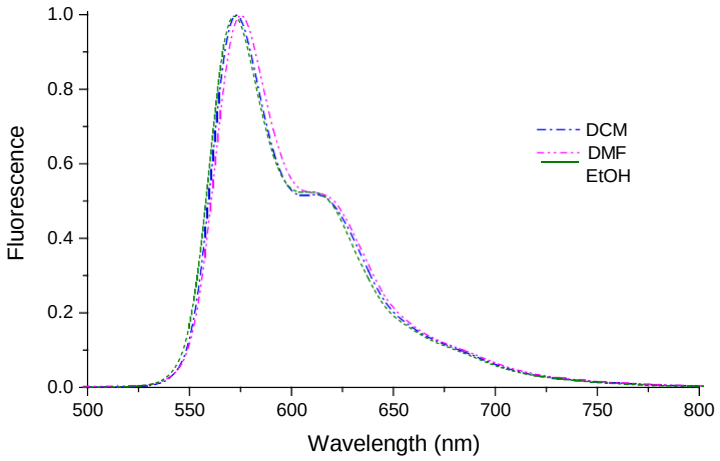


Fig. S25. Normalized fluorescence spectra of dye **16** in solvents of different polarities. Excitation wavelengths (λ_{exc}) were equal to 530 nm in all solvents.

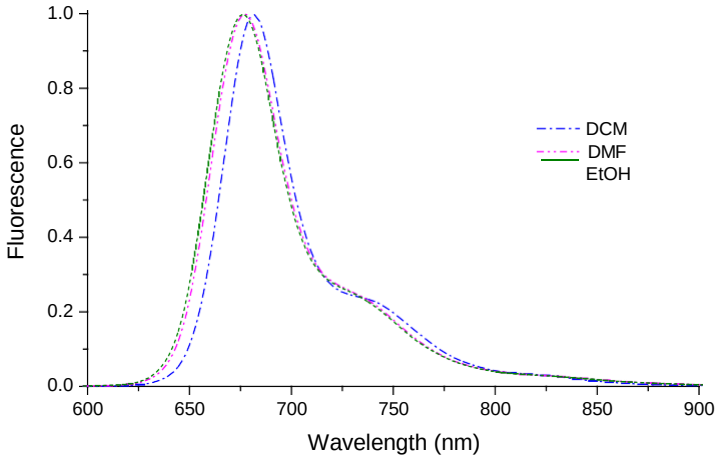


Fig. S26. Normalized fluorescence spectra of dye **17** in solvents of different polarities. Excitation wavelengths (λ_{exc}) were equal to 620 nm in all solvents.

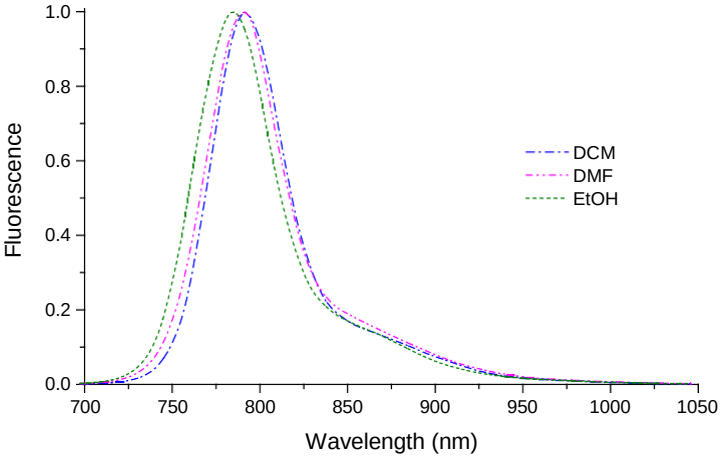


Fig. S27. Normalized fluorescence spectra of dye **18** in solvents of different polarities. Excitation wavelengths (λ_{exc}) were equal to 750 nm in all solvents.

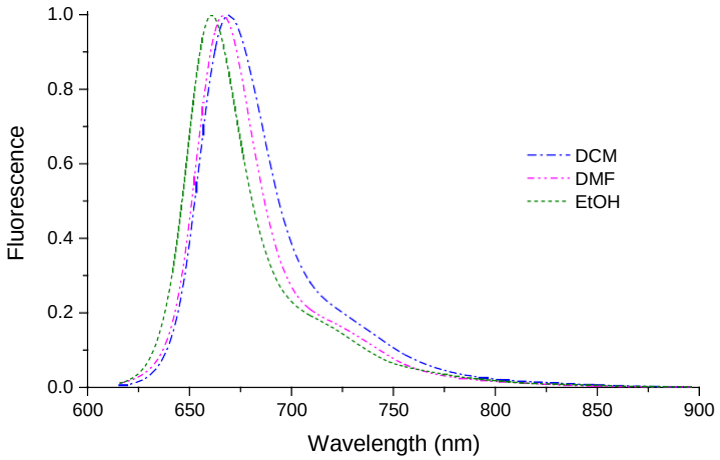


Fig. S28. Normalized fluorescence spectra of dye **19** in solvents of different polarities. Excitation wavelengths (λ_{exc}) were equal to 610 nm in all solvents.

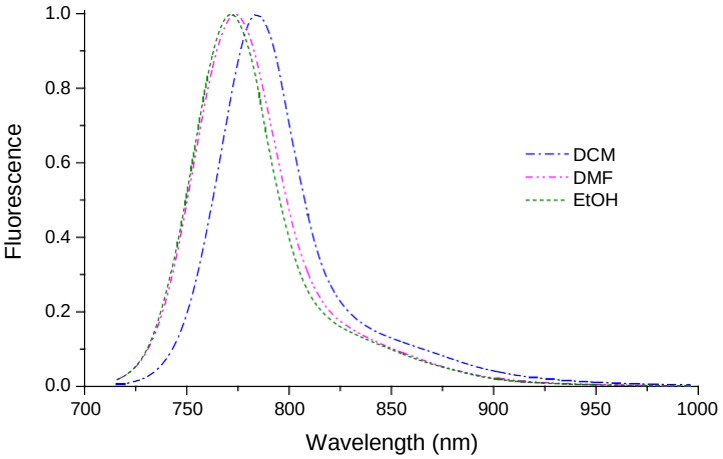


Fig. S29. Normalized fluorescence spectra of dye **20** in solvents of different polarities. Excitation wavelengths (λ_{exc}) were equal to 750 nm in all solvents.

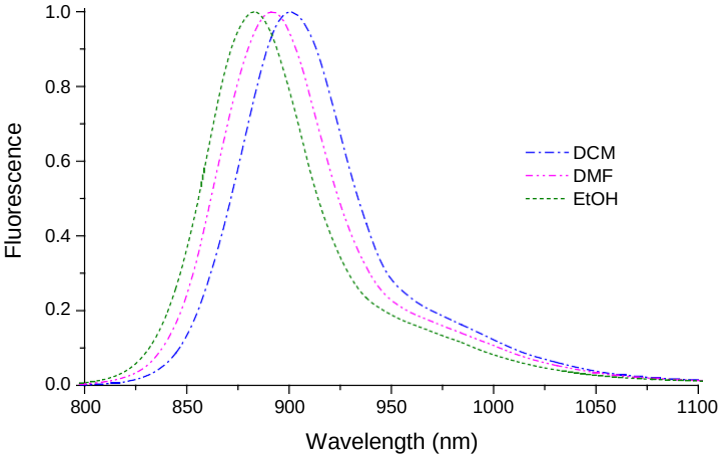


Fig. S30. Normalized fluorescence spectra of dye **21** in solvents of different polarities. Excitation wavelengths (λ_{exc}) were equal to 860 nm in all solvents.

Comparison of the absorption and fluorescence excitation spectra

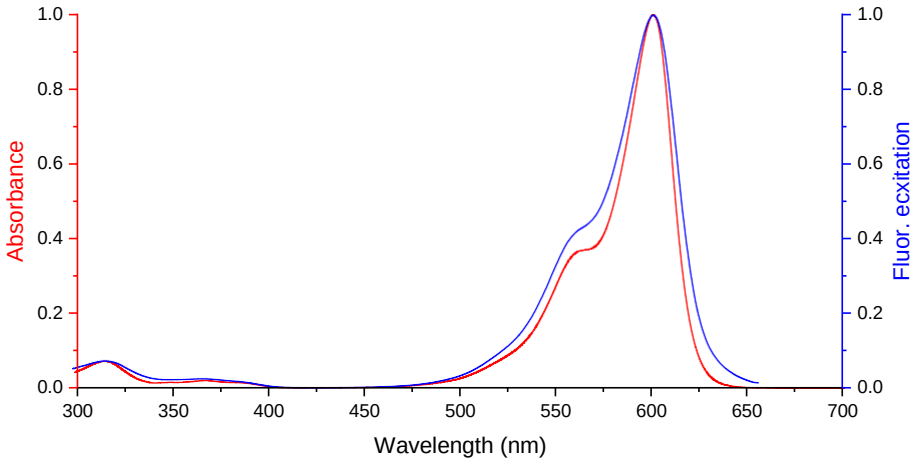


Fig. S31. Normalized absorption and fluorescence excitation spectra of dye **7** in ethanol. The fluorescence excitation spectrum was measured with λ_{reg} = 680 nm and both slit width set to 5 nm.

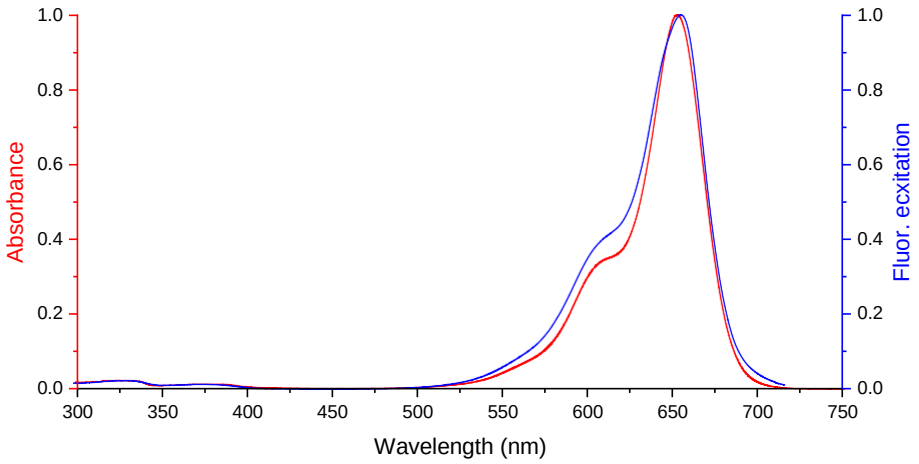


Fig. S32. Normalized absorption and fluorescence excitation spectra of dye **17** in ethanol. The fluorescence excitation spectrum was measured with λ_{reg} = 750 nm and both slit width set to 5 nm.

Absorption and fluorescence spectra of dye 9 in polyvinyl butyral (PVB)

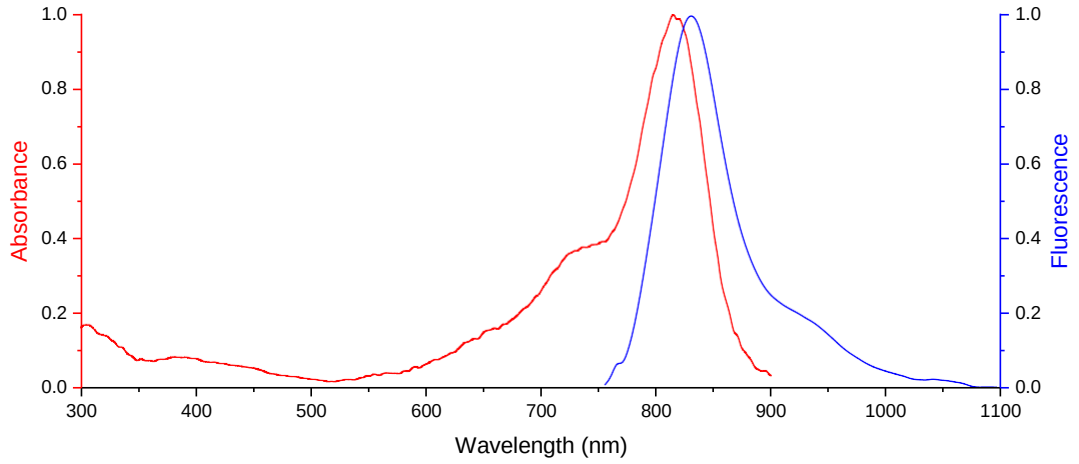


Fig. S33. Normalized absorption and fluorescence spectra of dye **9** (0.02 wt.%) in PVB. Excitation wavelength (λ_{exc}) was equal to 770 nm.

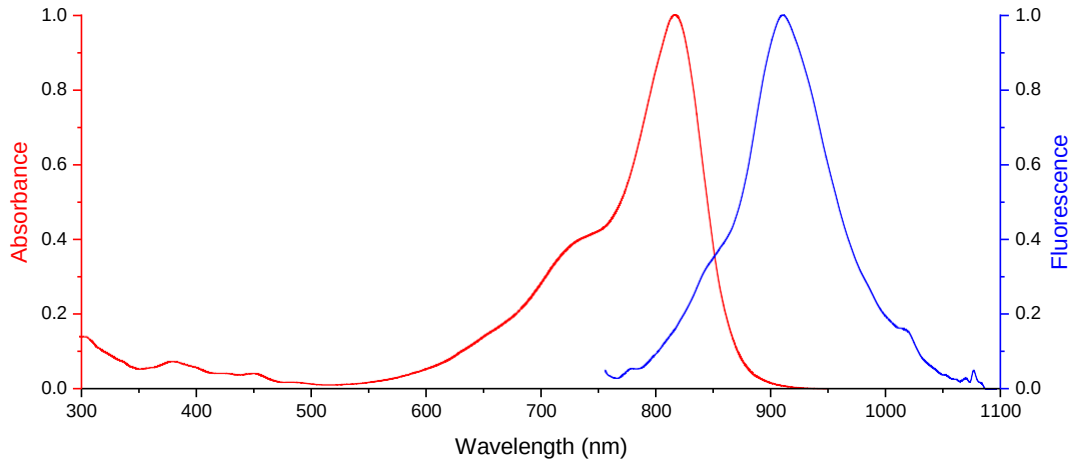


Fig. S34. Normalized absorption and fluorescence spectra of dye **9** (0.25 wt.%) in PVB. Excitation wavelength (λ_{exc}) was equal to 770 nm.

Additional data from quantum chemical calculations

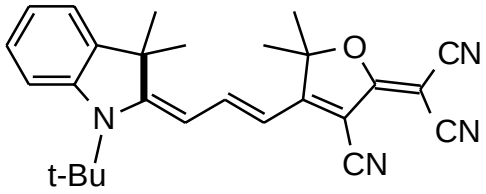
Cartesian atomic coordinates (in Å) for the optimized (the convergence criterion on the residual forces has been set to 1×10^{-5} Hartree Bohr^{-1} or Hartree Rad^{-1}) ground (S_0) and fluorescent (S_1) states geometries of molecules **7a–9a**, **10–15** from the PCM_{DCM}/(TD)DFT-functional/6-31G(d,p) calculations are given as XYZ-files in a separate ZIP-archive.

Table S2. Polarizability and hyperpolarizability characteristics[a] of merocyanines **7a–9a** and **10–15** from the PCM_{DCM}/DFT-CAM-B3LYP/6-31G(d,p) and PCM_{DCM}/DFT-M062X/6-31G(d,p) calculations.

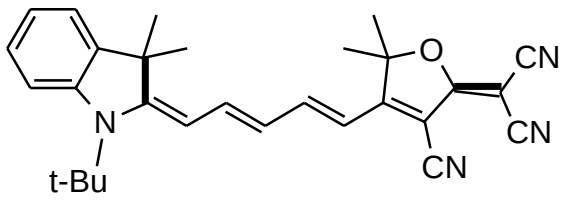
Dye	CAM-B3LYP				M062X			
	α	α' (Å3)	β	β_μ	α	α' (Å3)	β	β_μ
7a-t	536.4	79.5	19842	15239	544.8	80.7	21947	18222
7a-c	498.2	73.8	15321	13094	503.6	74.6	15629	13434
8a-t	715.6	106.0	67190	61500	731.2	108.4	75451	70571
8a-c	669.5	99.2	50908	46934	683.1	101.2	54737	50474
9a-t	925.0	137.1	196325	189129	950.1	140.8	217659	211299
9a-c	880.0	130.4	150618	140327	905.4	134.2	165054	153915
10-t	631.8	93.6	25492	−24854	640.9	95.0	26263	−25684
10-c	584.5	86.6	14282	−13847	591.8	87.7	14594	−13967
11-t	800.3	118.6	79379	−79007	815.9	120.9	79169	−78724
11-c	738.8	109.5	49100	−46587	748.5	110.9	54923	−52017
12-t	996.4	147.7	211254	−211196	1021.5	151.4	226953	−226915
12-c	913.7	135.4	147747	−141911	933.7	138.4	165094	−158830
13-t	692.6	102.6	30461	25432	695.3	130.0	33536	29563
13-c	644.8	95.5	22051	19236	651.3	96.5	24938	21782
14-t	879.4	130.3	115647	110137	888.2	131.6	125237	120572
14-c	830.7	123.1	92063	82320	841.6	124.7	100389	89384
15-t	1055.9	156.5	278407	272155	1073.4	159.1	301925	296434
15-c	1018.3	150.9	244122	214738	1035.4	153.4	262203	229591

[a] α, isotropic average polarizability; α', polarizability volume; β, magnitude of the first hyperpolarizability; β_μ, projection of β on dipole moment. Polarizabilities and hyperpolarizabilities are given in atomic units.

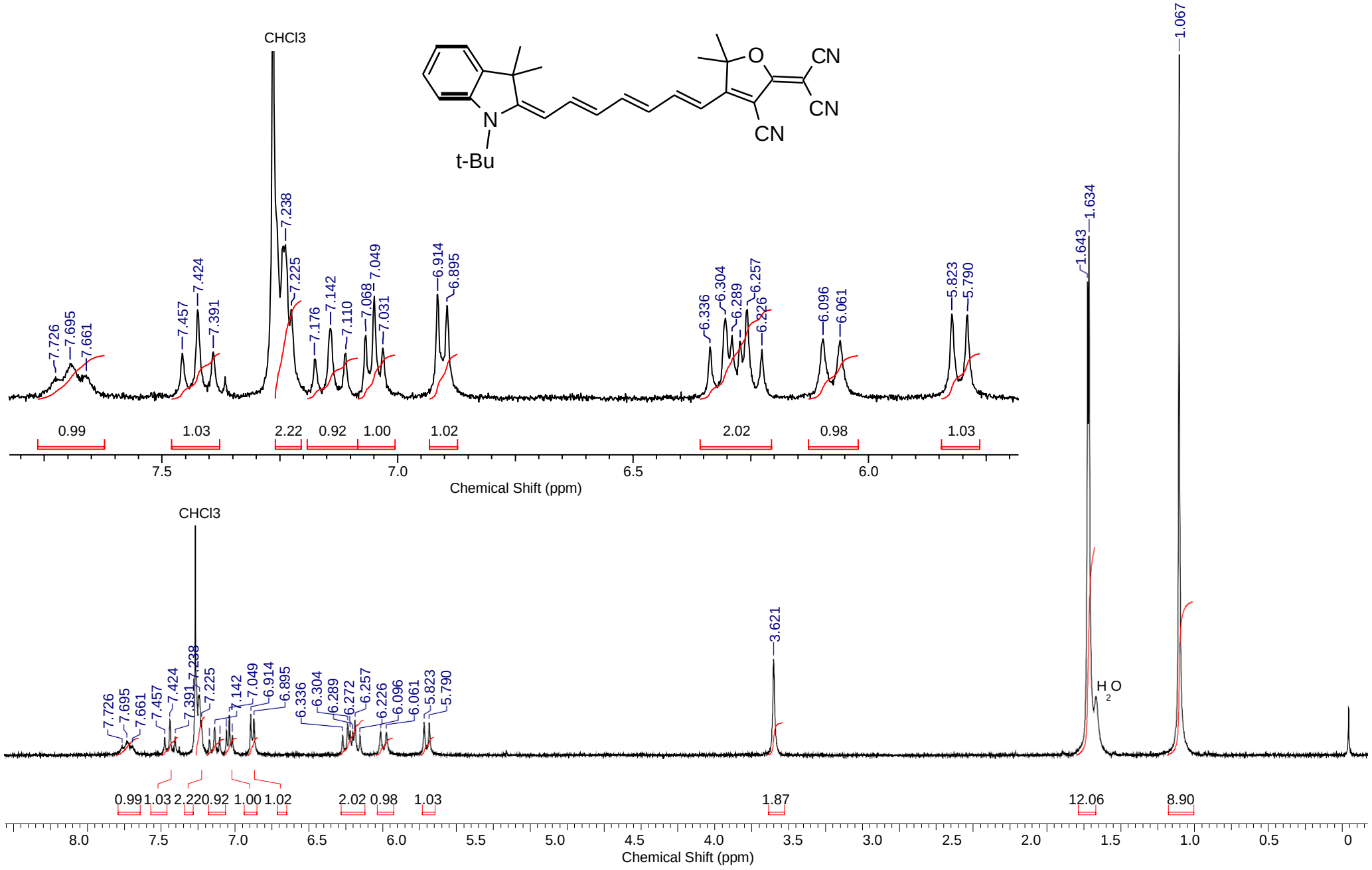
Frequency (MHz)	399.98	***Nucleus***	1H
Solvent	dmso-D6		
Temperature (degree C)	AMBIENT TEMPERATURE		



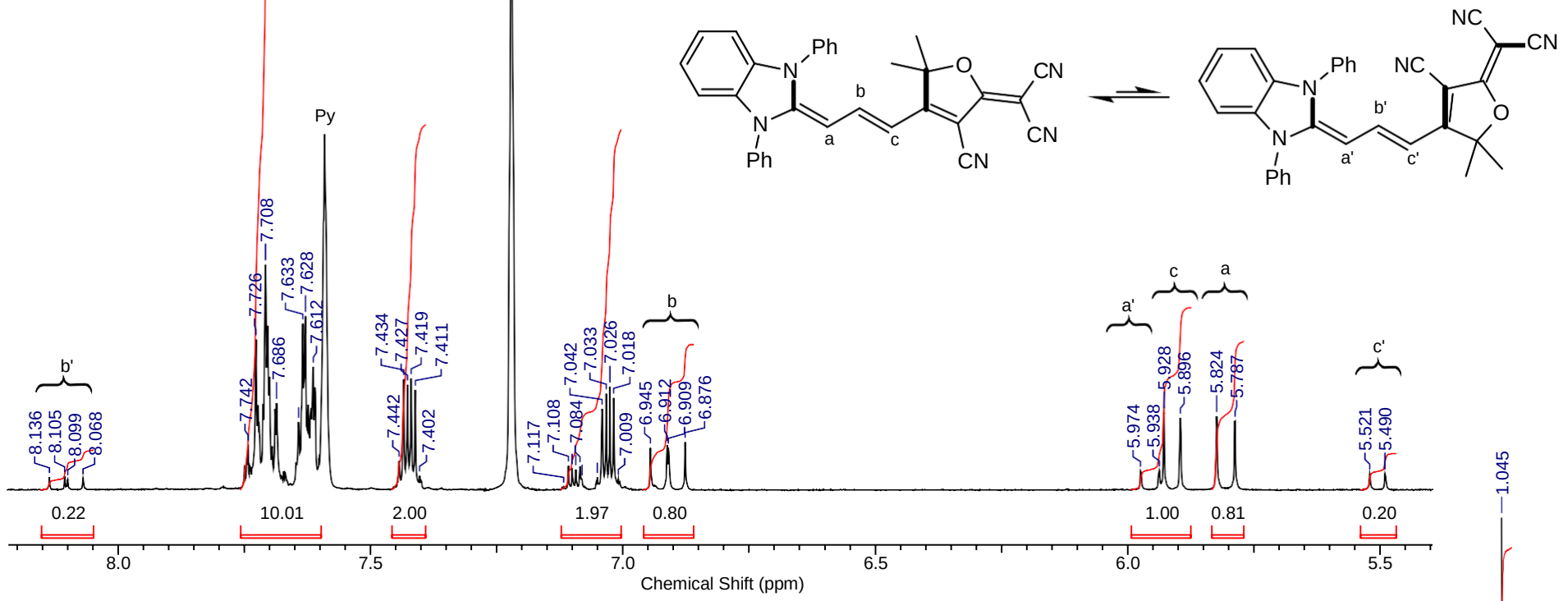
Frequency (MHz)	399.98	***Nucleus***	1H
Solvent	CHLOROFORM-d		
Temperature (degree C)	AMBIENT TEMPERATURE		

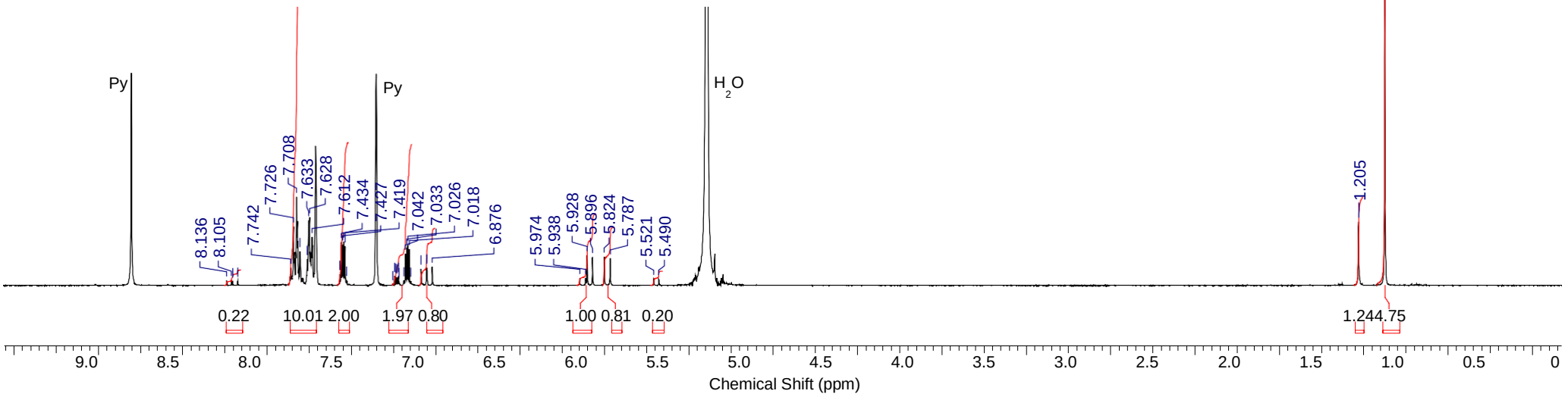


Frequency (MHz)	399.98	***Nucleus***	1H
Solvent	CHLOROFORM-d		
Temperature (degree C)	AMBIENT TEMPERATURE		

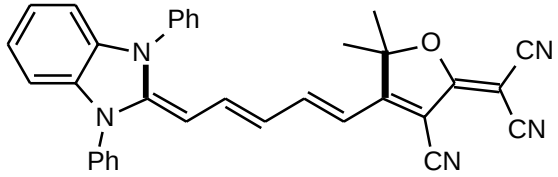


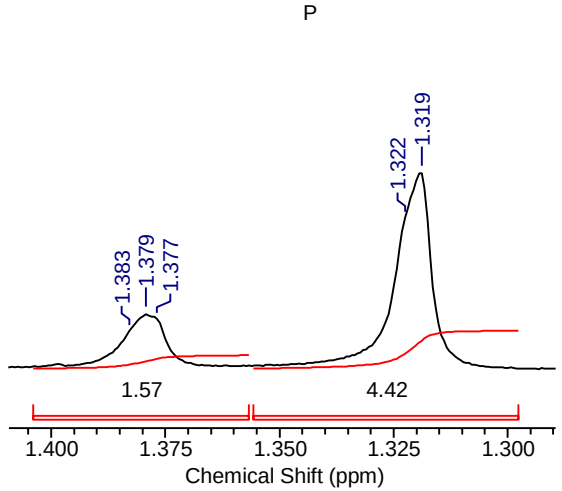
Frequency (MHz)	400.07	***Nucleus***	1H
Solvent	pyridine		
Temperature (degree C)	AMBIENT TEMPERA URE		

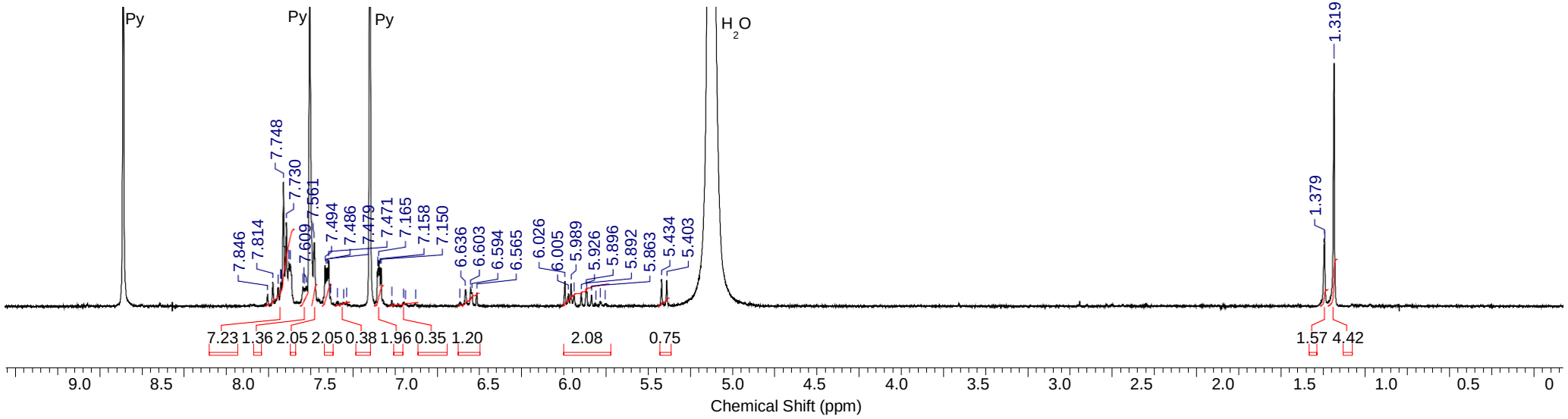




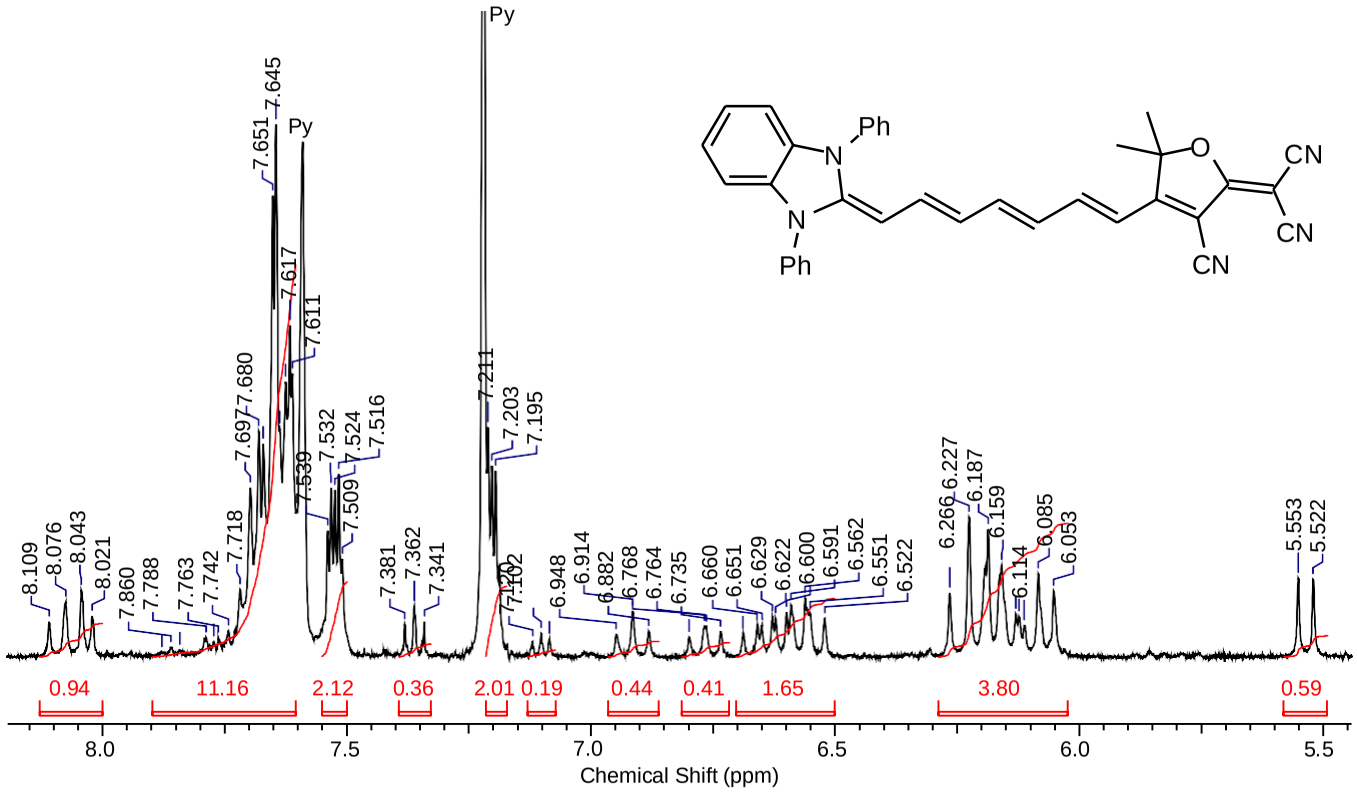
Frequency (MHz)	400.07	***Nucleus***	1H
Solvent	pyridine		
Temperature (degree C)	AMBIENT TEMPERATURE		

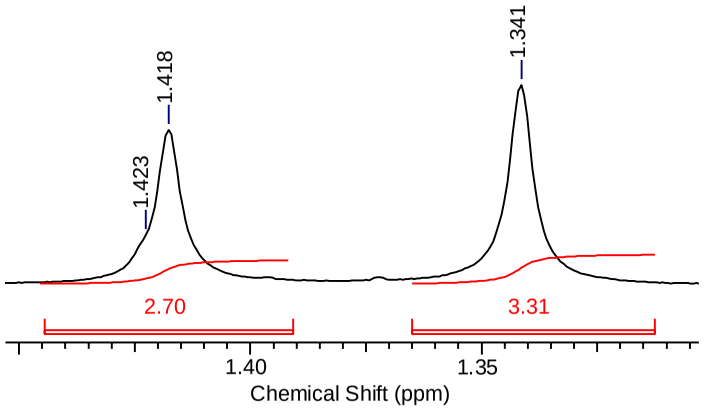


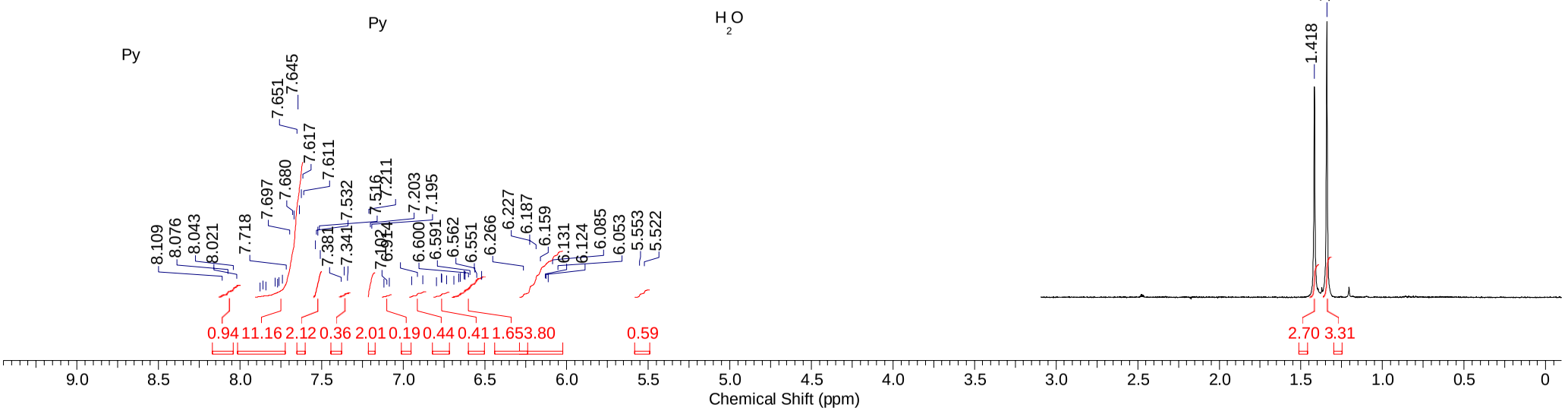




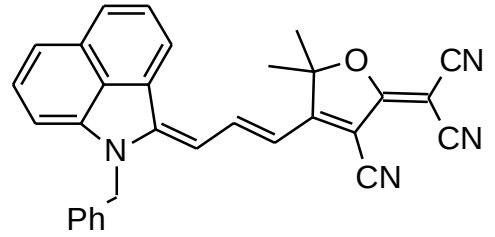
Frequency (MHz)	400.07	***Nucleus***	1H
Solvent	pyridine		
Temperature (degree C)	AMBIENT TEMPERATURE		



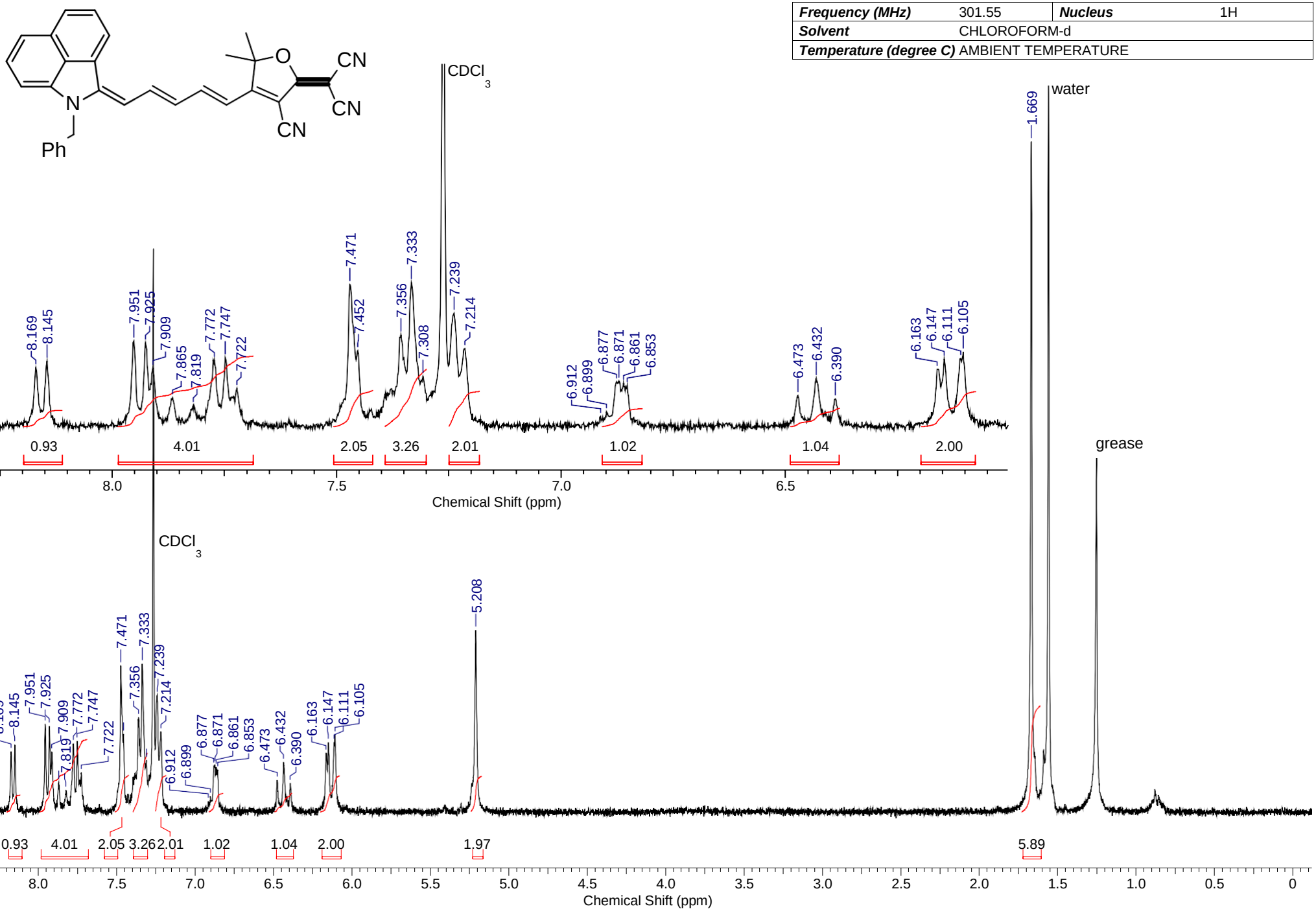


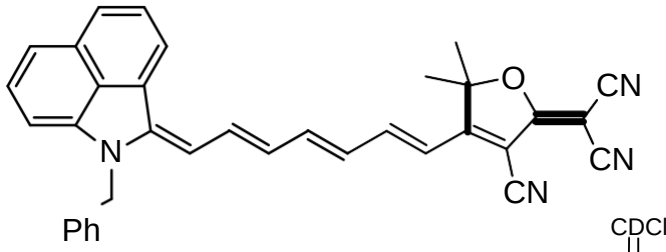


Frequency (MHz)	301.55	***Nucleus***	1H
Solvent	CHLOROFORM-d		
Temperature (degree C)	AMBIENT TEMPERATURE		

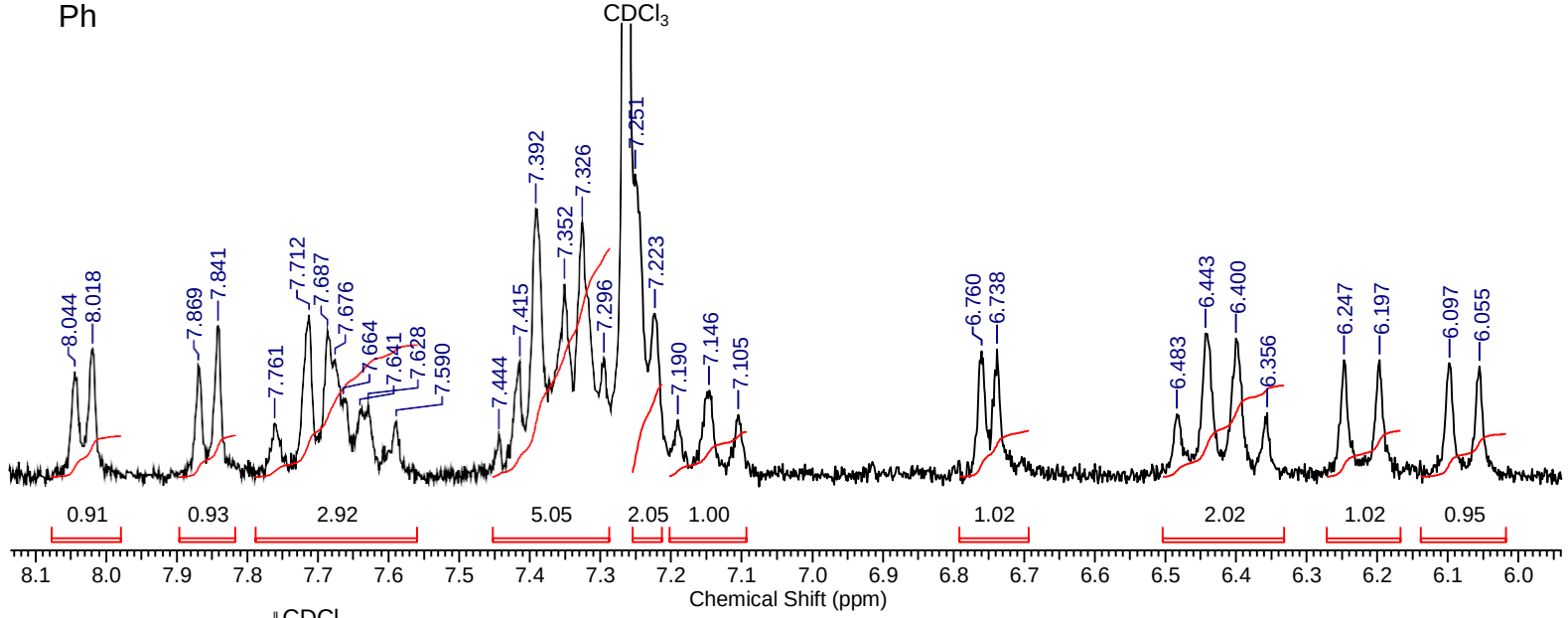


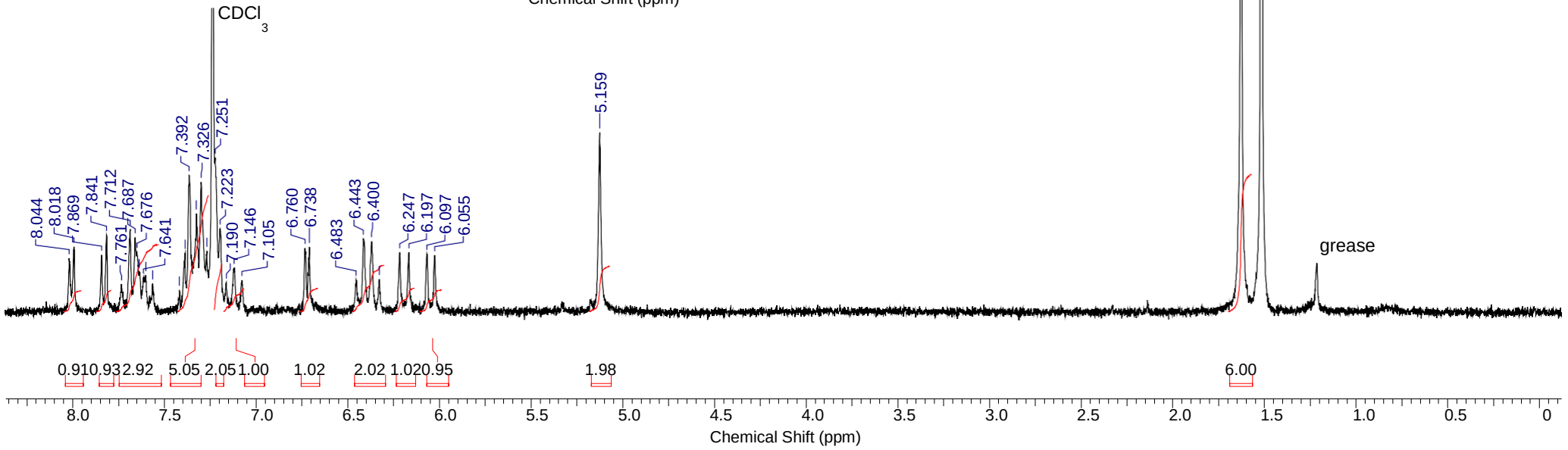
Frequency (MHz)	301.55	***Nucleus***	1H
Solvent	CHLOROFORM-d		
Temperature (degree C)	AMBIENT TEMPERATURE		


Frequency (MHz) 301.55
Nucleus 1H
Solvent CHLOROFORM-d
Temperature (degree C) AMBIENT TEMPERATURE
N
Ph
O
CN
CN
CN
CDCl3
water
grease
8.169
8.145
7.951
7.925
7.909
7.865
7.819
7.772
7.747
7.722
7.471
7.452
7.356
7.333
7.308
7.239
7.214
6.912
6.899
6.877
6.871
6.861
6.853
6.473
6.432
6.390
6.163
6.147
6.111
6.105
5.208
1.669
0.93
4.01
2.05
3.26
2.01
1.02
1.04
2.00
1.97
5.89
Chemical Shift (ppm)

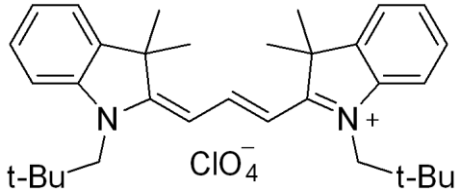


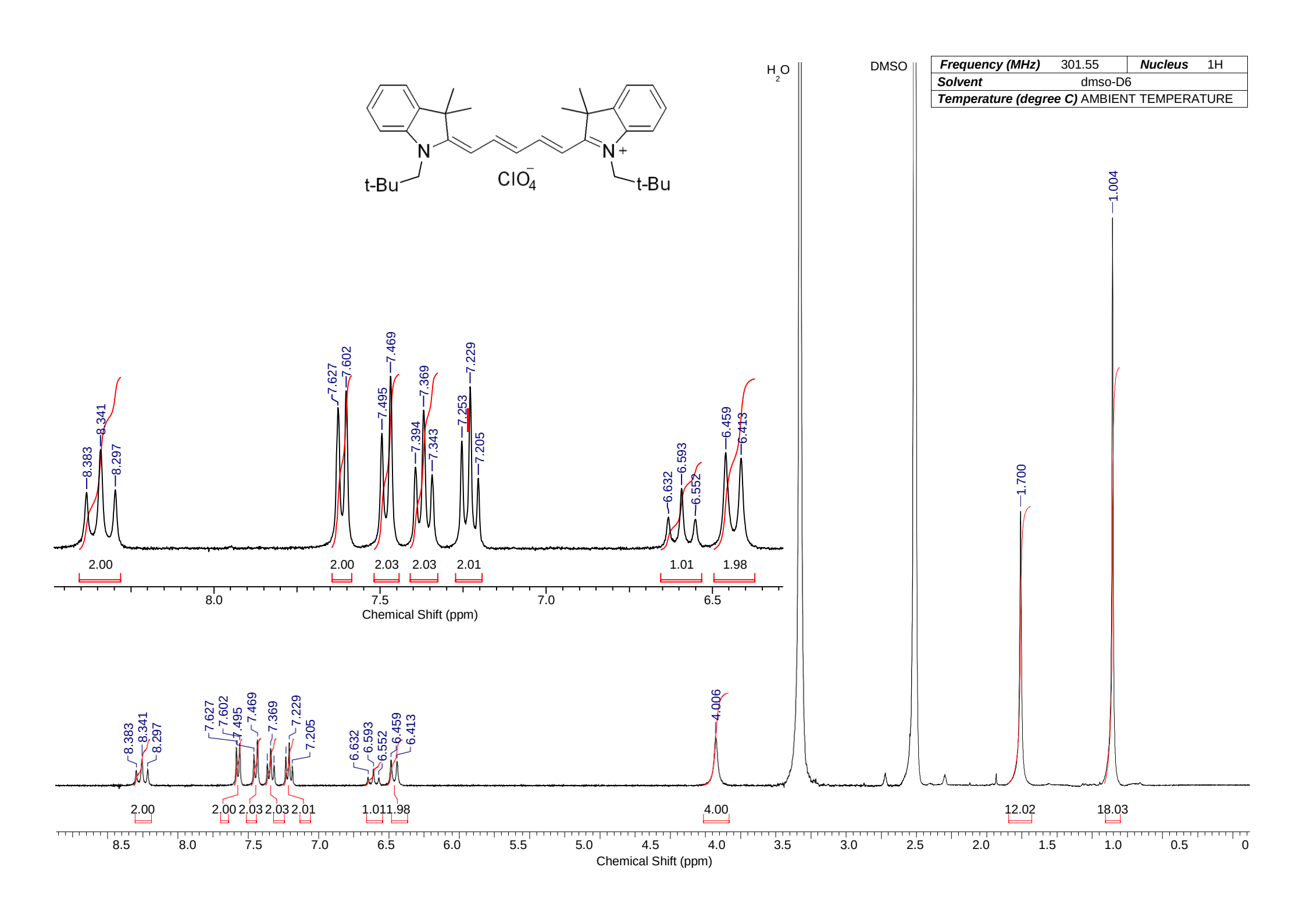
Frequency (MHz)	301.55	***Nucleus***	1H
Solvent	CHLOROFORM-d		
Temperature (degree C)	AMBIENT TEMPERATURE		



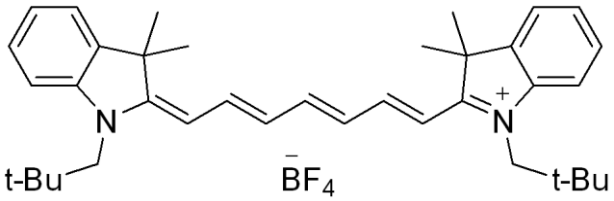


Frequency (MHz)	301.55	***Nucleus***	1H
Solvent	CHLOROFORM-d		
Temperature (degree C)	AMBIENT TEMPERATURE		

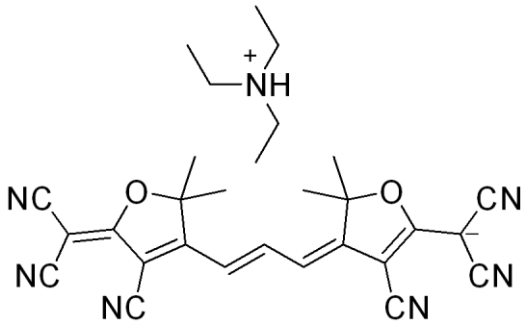


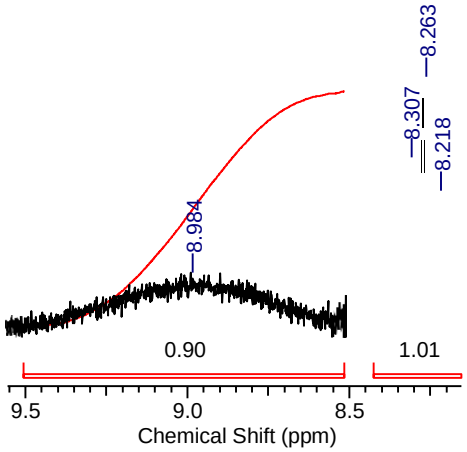

Frequency (MHz) 301.55
Nucleus 1H
Solvent dmso-D6
Temperature (degree C) AMBIENT TEMPERATURE
H2O
DMSO
t-Bu
t-Bu
ClO4
8.383
8.341
8.297
7.627
7.602
7.495
7.469
7.394
7.369
7.343
7.253
7.229
7.205
6.632
6.593
6.552
6.459
6.413
4.006
1.700
1.004
2.00
2.00
2.03
2.03
2.01
1.01
1.98
4.00
12.02
18.03
Chemical Shift (ppm)
Chemical Shift (ppm)

Frequency (MHz)	399.98	***Nucleus***	1H
Solvent	dmso-D6		
Temperature (degree C)	AMBIENT TEMPERATURE		

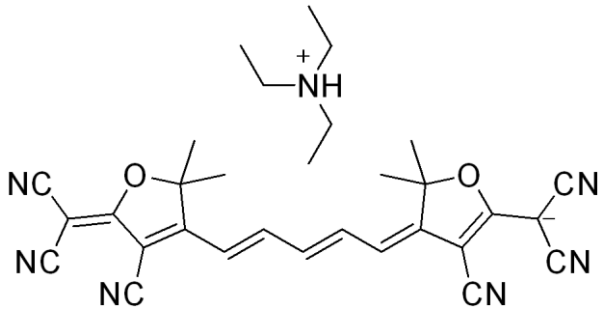


Frequency (MHz)	301.55	***Nucleus***	1H
Solvent	dmso-D6		
Temperature (degree C)	AMBIENT TEMPERATURE		

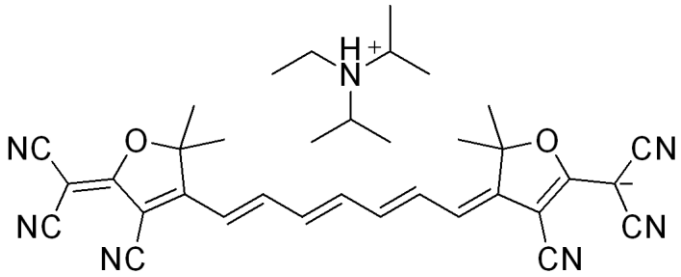




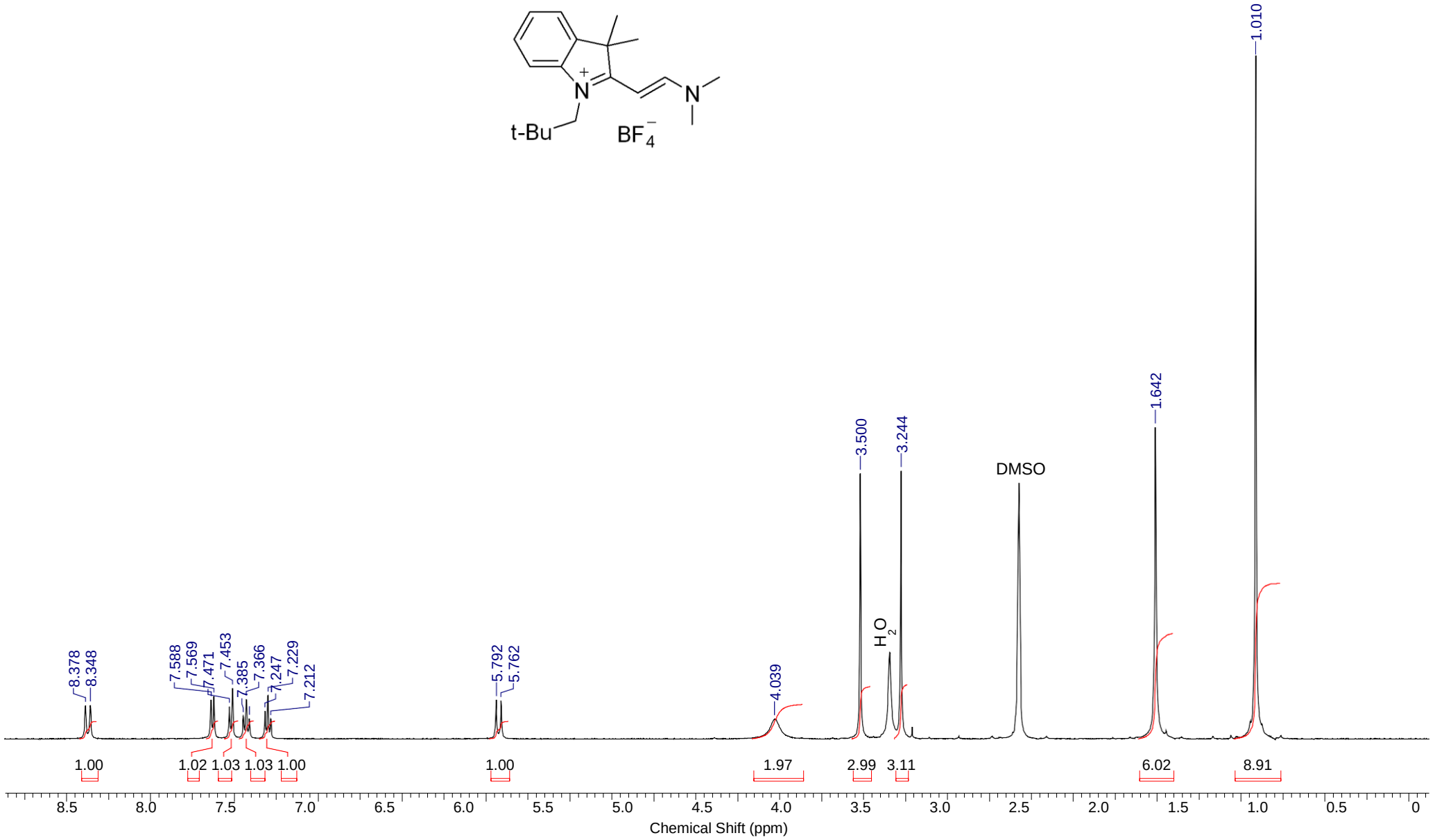
Frequency (MHz)	301.55	***Nucleus***	1H
Solvent	dmso-D6		
Temperature (degree C)	AMBIENT TEMPERATURE		



Frequency (MHz)	301.55	***Nucleus***	1H
Solvent	dmso-D6		
Temperature (degree C)	AMBIENT TEMPERATURE		



Frequency (MHz)	399.98	***Nucleus***	1H
Solvent	dmso_d6		
Temperature (degree C) AMBIENT TEMPERATURE			



Frequency (MHz)	399.98	***Nucleus***	1H
	Solvent	dmso_d6	
Temperature (degree C) AMBIENT TEMPERATURE