

Supporting information

'Hybrid' mero-anionic polymethines with a 1,3,2-dioxaborine core

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Photostability Check

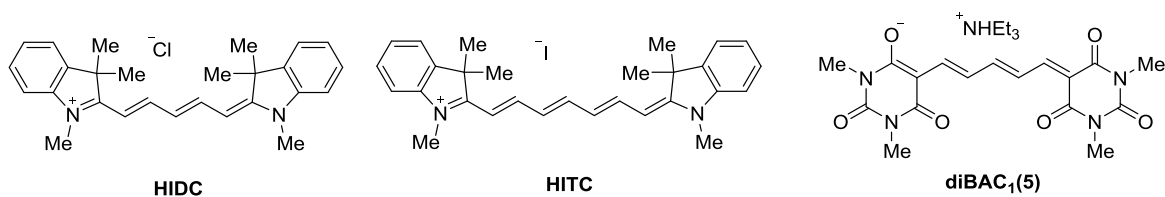


Figure S1. Structure formulae of indodicarbocyanine (**HIDC**), indotricarbocyanine (**HITC**) and bis(1,3-dimethyl barbituric acid) pentamethine oxonol (**diBAC₁(5)**).

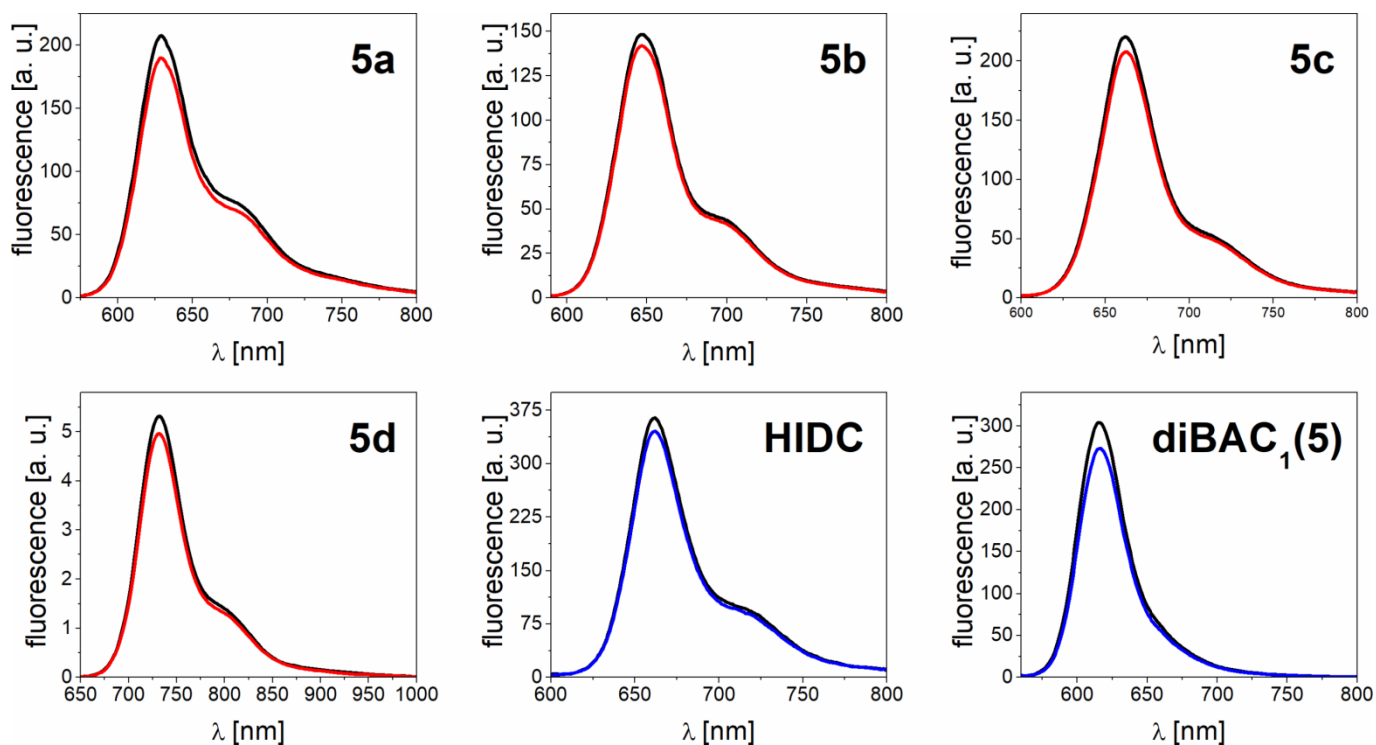


Figure S2. Fluorescence spectra of the dyes **5a-d**, **HIDC**, and **diBAC₁(5)** in acetonitrile before (black lines) and after (colored lines) irradiation.

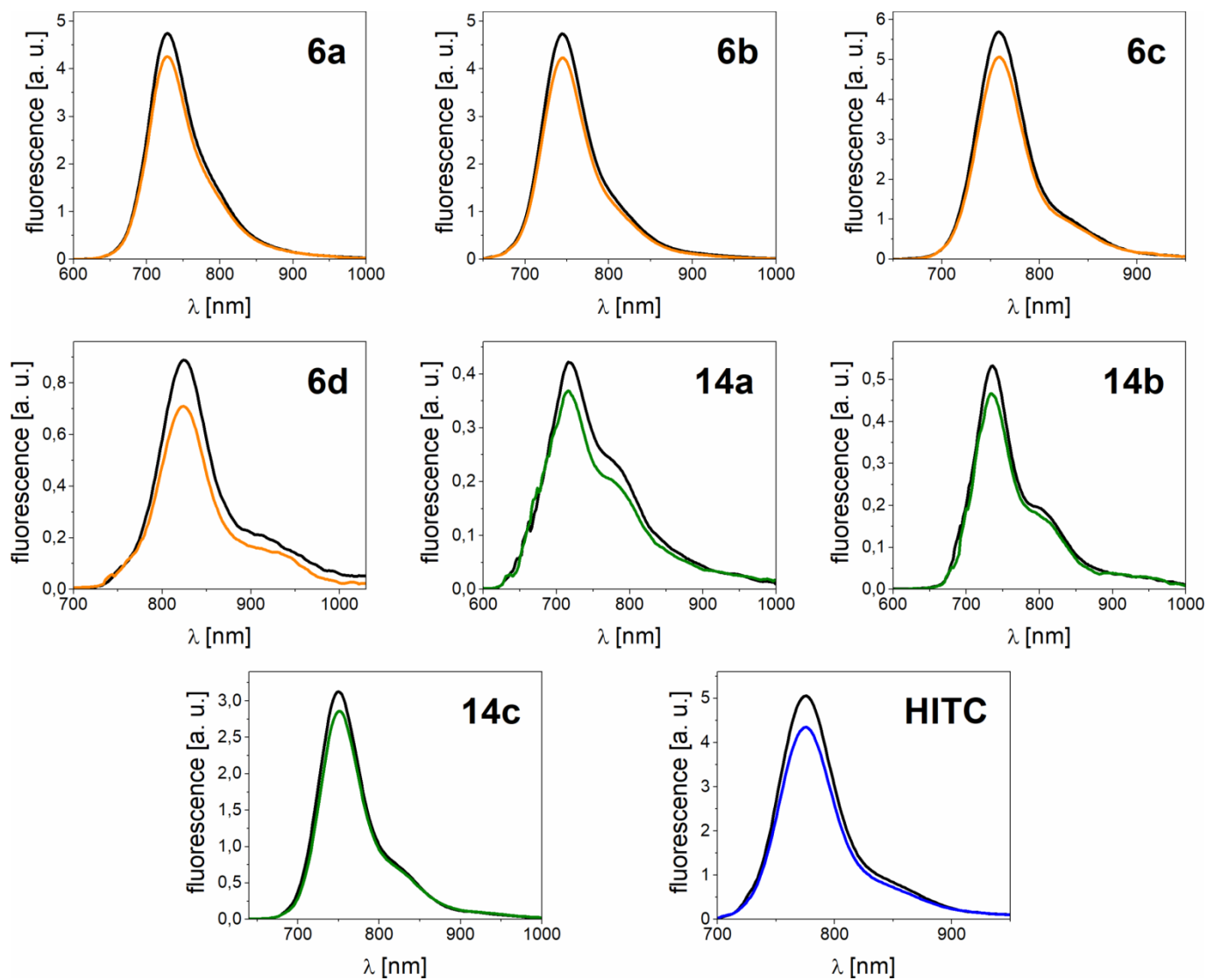


Figure S3. Fluorescence spectra of the longer-chained dyes **6a-d**, **14a-c** and **HITC** in acetonitrile before (black lines) and after (colored lines) irradiation.

X-Ray Crystal Data

All crystallographic measurements were performed at 173 K on a Bruker Smart Apex II diffractometer operating in the ω scans mode. The intensity data were collected within the $\theta_{\max} \leq 25.4^\circ$ using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The intensities of 27044 reflections were collected (7767 unique reflections, $R_{\text{merge}} = 0.0596$). The structure was solved by direct method and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using the Bruker SHELXTL program package.¹ All CH hydrogen atoms were placed at calculated positions and refined using the 'riding' model. Convergence was obtained at $R_1 = 0.0622$ and $wR_2 = 0.1608$ for 5347 observed reflections with $I \geq 2\sigma(I)$, $R_1 = 0.0923$ and $wR_2 = 0.1873$, GOF = 0.994 for 7667 independent reflections, 526 parameters, the largest and minimal peaks in the final difference map 0.48 and -0.43 e/\AA^3 .

Crystal data for **5b'**: triclinic, space group P-1, $a = 12.5711(7)$, $b = 13.4042(8)$, $c = 14.1491(8) \text{ \AA}$, $\alpha = 92.556(4)$, $\beta = 105.136(4)$, $\gamma = 111.373(4)^\circ$, $V = 2117.2(2) \text{ \AA}^3$, $Z = 2$, $d_c = 1.226 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.087 \text{ mm}^{-1}$, $F(000) = 840$, crystal size ca. $0.2 \times 0.50 \times 0.50 \text{ mm}$.

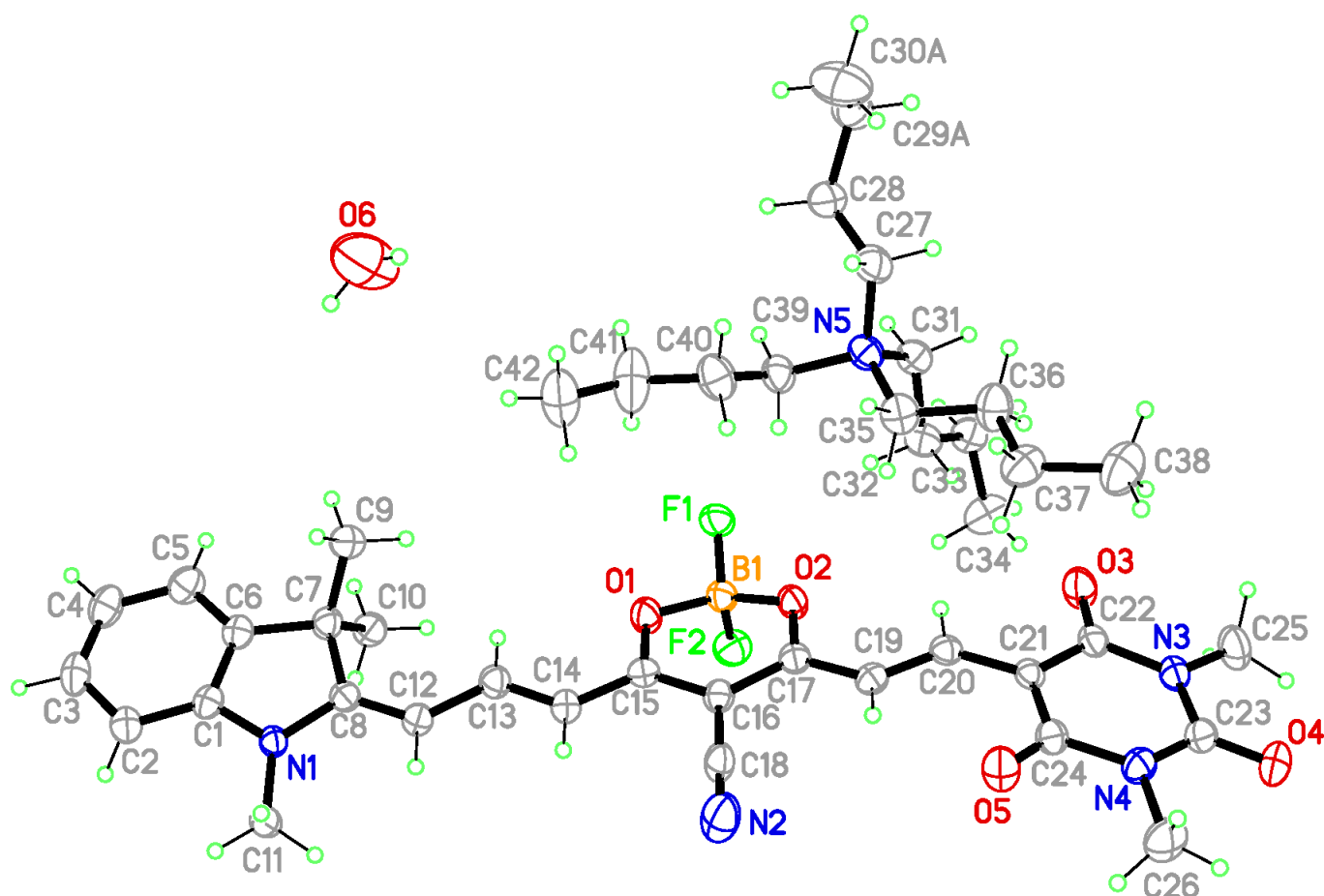


Figure S4. Molecular structure of dye **5b'** (ellipsoid contour probability level set at 50 %).

Additional Computation Details

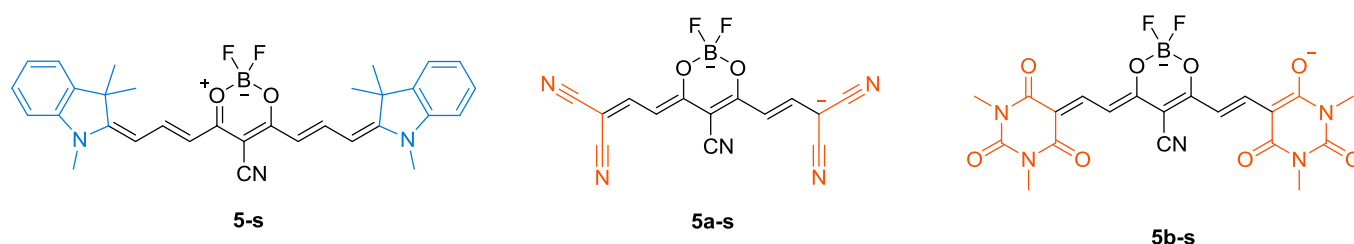


Figure S5. Structures of symmetrical dioxaborine dyes, parent to mero-anionic polymethines **5a** and **5b** (dianionic chromophores **5a-s** and **5b-s** are presented without counterions, since the latter were omitted in the (TD-)DFT calculations).

The computed total energies of the DFT-B3LYP/6-31G(d,p)/IEFPCM_{CH₂Cl₂} optimized structures of molecules **5a**, **6a**, **14a**, **5b**, **6b**, **14b**, **5-s**, **5a-s**, **5b-s** in the ground state S_0 are listed below (in Hartree). In all cases, there were no negative (imaginary) frequencies, indicating that the found geometries were true minima. It should be repeated here that the indole 1-alkyl groups in molecules **6a**, **6b** were truncated into 1-methyl for uniformity.

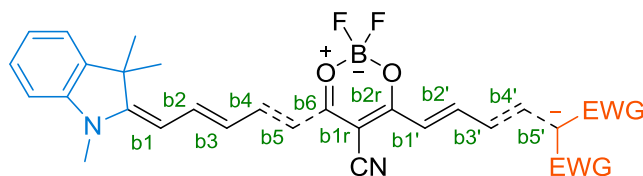
5a	-1481.606418
6a	-1825.317729
14a	-1559.016431
5b	-1902.727740
6b	-1559.016513
14b	-1902.728189
5-s	-1778.169158
5a-s	-1185.037599
5b-s	-1872.459775

Table S1. The (TD-)DFT-B3LYP/6-31G(d,p)/IEFPCM_{CH₂Cl₂} calculated NBO² charges of the constituent parts of molecules **5a**, **6a**, **14a**, **5b**, **6b**, **14b**, **5-s**, **5a-s**, **5b-s** in the ground state S_0 and their dipole moments (in Debye) in the ground state S_0 and first excited Frank-Condon state S_1^{FC}

Dye	Charge at the fragment* in the ground state S_0						Dipole moment (D)	
	D	$\pi 1$	A	$\pi 2$	A'	Total	S_0	S_1^{FC}
5a	0.368	-0.117	-0.673	0.018	-0.596	-1.000	35.42	39.34
5b	0.365	-0.117	-0.663	0.043	-0.628	-1.000	27.34	27.49
6a	0.345	-0.104	-0.669	0.020	-0.592	-1.000	43.50	49.96
6b	0.342	-0.105	-0.658	0.044	-0.623	-1.000	34.68	37.37
14a	0.369	-0.117	-0.680	0.024	-0.596	-1.000	36.92	38.24
14b	0.368	-0.116	-0.676	0.052	-0.628	-1.000	28.77	25.89
5-s	0.417	-0.104	-0.626	—	—	0.000	3.74	4.30
5a-s	—	—	-0.722	0.001	-0.640	-2.000	3.55	2.39
5b-s	—	—	-0.698	0.027	-0.678	-2.000	2.46	4.18

* D — the donor end-group (see the main text), A — the central dioxaborine ring (with the CN-group), A' — the acceptor end-group, $\pi 1$ — the tri- or pentamethine chain between the D and A, $\pi 2$ — the di- or tetramethine chain between the A and A'. Note that for symmetric dyes there are two D or two A groups together with the corresponding linker.

Table S2. The (TD-)DFT-B3LYP/6-31G(d,p)/IEFPCM_{CH₂Cl₂} calculated length (Å) of the chromophore CC-bonds in molecules **5a**, **6a**, **14a**, **5b**, **6b**, **14b**, **5-s**, **5a-s**, **5b-s** and the bond length alternations (Å) in the mero (BLA1) and anionic (BLA2) parts of the chromophore, estimated as a mean absolute deviation from the average bond length.



bond/ BLA	5a	5b	6a	6b	14a	14b	5-s	5a-s	5b-s
b1	1.3786	1.3784	1.3772	1.377	1.3788	1.3787	1.3833		
b2	1.417	1.4173	1.4191	1.4195	1.4168	1.4169	1.4109		
b3	1.3729	1.3726	1.3757	1.3754	1.3731	1.3731	1.378		
b4	1.4287	1.4291	1.4178	1.4182	1.4284	1.4284	1.4212		
b5			1.3718	1.3715					
b6			1.4301	1.4306					
b1r	1.4162	1.4164	1.4154	1.4155	1.4165	1.4166	1.4253		
b2r	1.437	1.437	1.4377	1.4378	1.4366	1.4364		1.4281	1.4283
b1'	1.4064	1.4107	1.4059	1.4101	1.4072	1.408		1.4138	1.4191
b2'	1.3892	1.3874	1.3896	1.3879	1.3904	1.3896		1.3839	1.3814
b3'	1.402	1.4057	1.4016	1.4051	1.3975	1.4009		1.4082	1.4127
b4'					1.3924	1.3915			
b5'					1.404	1.4061			
BLA1	0.024	0.024	0.024	0.024	0.022	0.023	0.018	—	—
BLA2	0.007	0.010	0.006	0.009	0.006	0.007	—	0.012	0.015

* Note that for symmetric dyes b1r = b2r and the two parts of the chromophore are identical.

Table S3. The (TD-)DFT-B3LYP/6-31G(d,p)/IEFPCM_{CH₂Cl₂} calculated energies (eV) of selected MOs of mero-anionic polymethines **5a**, **5b** and the corresponding symmetric dyes **5-s**, **5a-s**, **5b-s**.

Dye	HOMO-1	HOMO	LUMO	LUMO+1
5a	-5.35	-4.76	-2.04	-0.86
5b	-5.32	-4.74	-2.04	-0.90
5-s	-5.54	-5.04	-2.53	-1.52
5a-s	-5.11	-4.40	-1.41	-0.22
5b-s	-5.07	-4.39	-1.45	-0.33

Table S4. The data from the TD-DFT computations of the three lowest singlet–singlet transitions* in molecules **5a**, **6a**, **14a**, **5b**, **6b**, **14b**

Dye	Transition to	Major components	E , eV	E , nm	f
Dye 5a	Excited State 1	HOMO→LUMO (100%)	2.541	488	1.985
	Excited State 2	HOMO-1→LUMO (95.9%) HOMO→LUMO+1 (3.2%)	3.019	411	0.015
	Excited State 3	HOMO-2→LUMO (3%) HOMO-1→LUMO (3.3%) HOMO→LUMO+1 (93%)	3.565	348	0.051
Dye 5b	Excited State 1	HOMO→LUMO (98.8%)	2.488	498	2.113
	Excited State 2	HOMO-1→LUMO (97.2%) HOMO→LUMO+1 (2.2%)	2.975	417	0.018
	Excited State 3	HOMO-1→LUMO (2.3%) HOMO→LUMO+1 (94.4%)	3.476	357	0.043
Dye 6a	Excited State 1	HOMO→LUMO (100%)	2.237	554	2.424
	Excited State 2	HOMO-1→LUMO (97.2%) HOMO→LUMO+1 (2.4%)	2.760	449	0.006
	Excited State 3	HOMO-2→LUMO (2.3%) HOMO-1→LUMO (2.5%) HOMO→LUMO+1 (94.3%)	3.330	372	0.039
Dye 6b	Excited State 1	HOMO→LUMO (99.1%)	2.208	562	2.559
	Excited State 2	HOMO-1→LUMO (97.9%)	2.719	456	0.005
	Excited State 3	HOMO→LUMO+1 (94.8%)	3.252	381	0.035
Dye 14a	Excited State 1	HOMO→LUMO (99.3%)	2.410	514	2.336
	Excited State 2	HOMO-1→LUMO (90.4%) HOMO→LUMO+1 (7.8%)	2.765	448	0.043
	Excited State 3	HOMO-1→LUMO (7.8%) HOMO→LUMO+1 (90.2%)	3.152	393	0.062
Dye 14b	Excited State 1	HOMO→LUMO (99.6%)	2.345	529	2.491
	Excited State 2	HOMO-1→LUMO (92.2%) HOMO→LUMO+1 (6.3%)	2.739	453	0.053
	Excited State 3	HOMO-1→LUMO (6.5%) HOMO→LUMO+1 (92.9%)	3.087	402	0.058

* Note that the TD-B3LYP/6-31G(d,p) vertical excitation energies of the long-wavelength $S_1^{FC} \leftarrow S_0$ transitions were calculated within the nonequilibrium solvation state-specific PCM approach, while for the higher transitions the linear-response TD-DFT vertical transition energies are given. For comparison, the linear-response $S_1^{FC} \leftarrow S_0$ transition energy for dye **5a** is equal to 2.300 eV (539 nm), a 0.241 eV difference from the value given in the table.

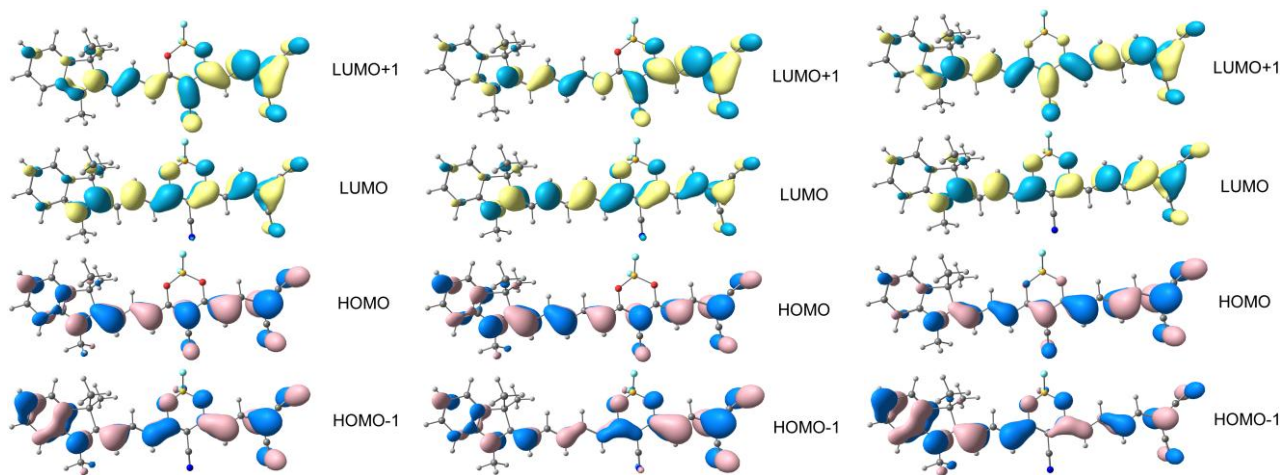


Figure S6. Selected MOs of dyes **5a**, **6a**, **14a**.

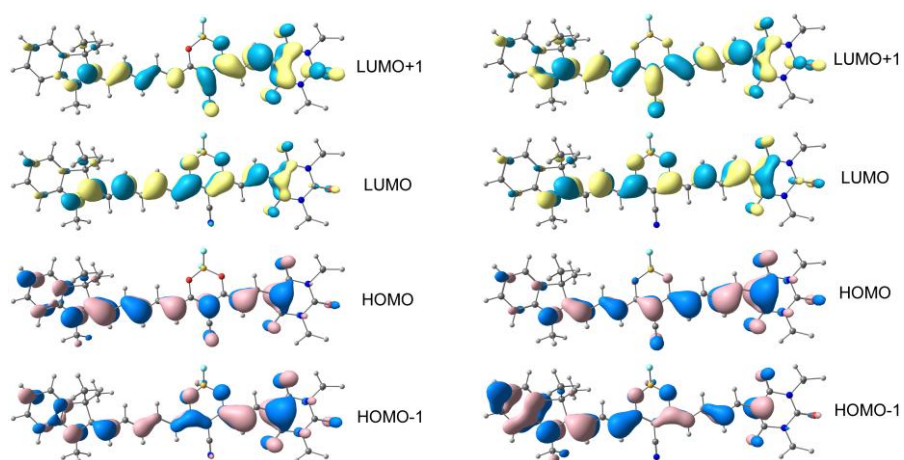


Figure S7. Selected MOs of dyes **6b**, **14b** (the MOs of dye **5b** are shown in the main paper).

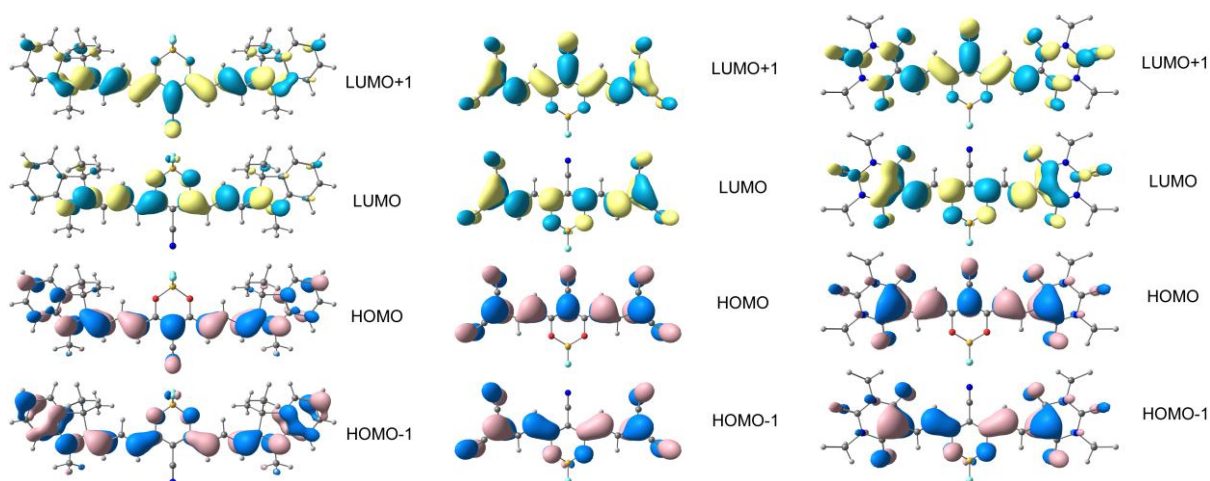


Figure S8. Selected MOs of dyes **5-s**, **5a-s**, **5b-s**.

The Cartesian atomic coordinates (in Å) from the DFT-B3LYP/6-31G(d,p)/IEFPCM_{CH₂Cl₂} optimization of the ground-state geometries of molecules 5a, 6a, 14a, 5b, 6b, 14b, 5-s, 5a-s, 5b-s

Dye 5a

N	-5.457518424539	2.096760876417	-0.109588311349
C	-6.661562668917	1.373047243718	-0.177392139403
C	-7.971711925986	1.845569855671	-0.223863540829
C	-9.000315338199	0.897652786834	-0.287873948545
C	-8.724850798289	-0.471453687140	-0.304645618190
C	-7.398322923269	-0.924867383188	-0.257588562544
C	-6.370124702075	0.003943551872	-0.194332008566
C	-4.862490057043	-0.195007402781	-0.134629122178
C	-4.366564184369	1.263084973391	-0.082912746053
C	-3.076532129598	1.745483011789	-0.022224233806
C	-1.892168193490	0.968419438088	0.012605352916
C	-0.625513617923	1.494539693622	0.071912803666
C	0.545726097981	0.676819204334	0.096664853055
C	1.853078647997	1.214764094834	0.181449981147
C	3.000807875995	0.356974731298	0.072516073139
C	4.317011460553	0.850258174842	0.025933929573
C	5.415970072834	0.004749651042	-0.060155524498
C	6.764662536928	0.382418860389	-0.123991333884
C	7.790049980246	-0.595710402886	-0.203868339817
C	7.166685160627	1.744886475568	-0.113355055333
C	-5.365754856145	3.547188666776	-0.071916804246
C	-4.475684676571	-0.979538261731	1.141875024761
C	-4.367357034766	-0.924875484892	-1.406084192131
C	2.031613055651	2.616027990237	0.301975386616
N	2.178021006683	3.769899860115	0.407231666734
O	0.383469268232	-0.628547967895	0.013099141066
O	2.802684406104	-0.946178774492	-0.018560025587
B	1.496486780142	-1.578564192919	0.294911216953
F	1.338574536884	-2.680260477239	-0.523115242090
F	1.462180097379	-1.930962563913	1.639054624173
N	8.634536593462	-1.401007239145	-0.271069219610
N	7.484342537214	2.869204436394	-0.104192920662
H	-8.204637653134	2.904361893296	-0.212058735723
H	-10.029920535862	1.240434604894	-0.324992950677
H	-9.539057095551	-1.187307939649	-0.354504748333
H	-7.183848548439	-1.989807709015	-0.270741110665
H	-2.944028125572	2.823361340346	0.001190317720
H	-1.965556187748	-0.113226568980	-0.007928763530
H	-0.483044134185	2.569813575804	0.098764436817
H	4.456860614132	1.924895493836	0.056986744984
H	5.218804535475	-1.063657208584	-0.079986598011
H	-4.808876241806	3.920994501204	-0.936966655854
H	-4.861247421859	3.876487731170	0.841799387644
H	-6.365251138365	3.976299196504	-0.090162101294
H	-4.819262054415	-0.459365848407	2.040144393050
H	-3.395377858366	-1.119992592996	1.219228017144
H	-4.943963461616	-1.968133233325	1.120195442511
H	-4.832870937478	-1.913159697147	-1.466309362705
H	-3.283973442450	-1.062599229802	-1.397786883371
H	-4.635378484998	-0.366537168979	-2.307150013468

Dye 6a

N	-6.827230391059	1.480991369603	-0.139815311107
C	-7.998736002656	0.707676127694	-0.201167397442
C	-9.328439946606	1.124014869265	-0.239206717657
C	-10.316648031422	0.133775131171	-0.298561407003
C	-9.984368534926	-1.222568273900	-0.319009322327
C	-8.639418253584	-1.619510769549	-0.280379795908
C	-7.650755288005	-0.648614496180	-0.221657472846
C	-6.135596467464	-0.784841934208	-0.170612745948
C	-5.699722269312	0.692319414511	-0.119945400217
C	-4.431881643485	1.227358661530	-0.065010759625
C	-3.207754455744	0.509882982413	-0.038655952155
C	-1.964259968077	1.096180823315	0.011487628170
C	-0.763707833158	0.342323188076	0.036997431597
C	0.500351377774	0.873059676361	0.085266583607
C	1.679607630515	0.064190278767	0.100332463620
C	2.981950115550	0.613998599274	0.170755393084
C	4.136603178050	-0.234450632884	0.053059457088

C	5.447369492834	0.270399297088	-0.006729230575
C	6.553049793908	-0.565959534061	-0.102076905417
C	7.897206626884	-0.176429317803	-0.179650214397
C	8.930655185989	-1.145538471230	-0.267593917349
C	8.287325302531	1.189684702220	-0.175614412357
C	-6.795590248329	2.933173017411	-0.101818670624
C	-5.709550995864	-1.554140689047	1.102549418589
C	-5.617875905905	-1.492871039003	-1.445261242374
C	3.150266253404	2.017142841363	0.286533630417
N	3.289793550797	3.172115447546	0.387934713514
O	1.526692127555	-1.242134676766	0.021587565894
O	3.948471876397	-1.539168153256	-0.033735432325
B	2.650460680687	-2.182788692609	0.291987056502
F	2.494374358234	-3.285352446610	-0.525047276693
F	2.632365141859	-2.535682241214	1.636160072247
N	9.781707671756	-1.943208164672	-0.341403907180
N	8.595401237094	2.316628879773	-0.171849550127
H	-9.605672256035	2.172093496522	-0.224468388837
H	-11.359946960429	0.433177670174	-0.329064225056
H	-10.768026011698	-1.971970572730	-0.365144938563
H	-8.380413031155	-2.674530773533	-0.296437140297
H	-4.346604803894	2.310173070797	-0.039455820341
H	-3.236010679304	-0.576059485121	-0.059444203910
H	-1.891060128081	2.182922050568	0.031946342361
H	-0.853335261168	-0.742420873968	0.016251928367
H	0.636171681644	1.949243780454	0.110215800205
H	5.578164063842	1.346226259984	0.021214143713
H	6.364934849123	-1.636056591636	-0.118212001290
H	-6.255065586990	3.330418165404	-0.967044429216
H	-6.304619649624	3.283933029183	0.811586245450
H	-7.811972259058	3.320854128021	-0.119718478958
H	-6.071762450930	-1.050972893426	2.003158681670
H	-4.623635719044	-1.646487717693	1.175602411898
H	-6.133491559121	-2.562652198926	1.081601455636
H	-6.040604177002	-2.500363745092	-1.503539368761
H	-4.529367194890	-1.583561880445	-1.444085870911
H	-5.915001787326	-0.946262717879	-2.344372552833

Dye 14a

N	-6.485091793237	2.012861702167	-0.145684438730
C	-7.661571882645	1.244753987730	-0.209156631379
C	-8.987559573530	1.668556827316	-0.272830536340
C	-9.980605925933	0.682954009100	-0.328119142007
C	-9.655575946077	-0.675324929494	-0.319800715899
C	-8.313931382091	-1.079429209488	-0.255344634046
C	-7.320580805688	-0.112922504792	-0.200166273992
C	-5.807261828606	-0.255768585457	-0.125585615816
C	-5.365046076137	1.220052200125	-0.094225844951
C	-4.093971701060	1.750125817176	-0.028031585542
C	-2.882541698067	1.017600197924	0.027990570760
C	-1.636399710164	1.590414789321	0.094789595467
C	-0.436745365195	0.816374193573	0.138699523415
C	0.849782915463	1.402009606690	0.230136593151
C	2.028541504519	0.585383911046	0.144091392956
C	3.327911764990	1.124197260788	0.106489109647
C	4.468905408001	0.332967853436	0.034172283913
C	5.783540188395	0.804273439211	-0.017458296970
C	6.869665273409	-0.064291023532	-0.085880918176
C	8.229073629714	0.281970792179	-0.143096459822
C	9.232500852211	-0.718558170976	-0.212926856291
C	8.660683347170	1.634834710784	-0.135645727237
C	-6.446430897191	3.466144509620	-0.135199610178
C	-5.402584798909	-1.004520253980	1.166732231723
C	-5.275748738312	-0.987799067845	-1.381027882229
C	0.976375014765	2.810192563417	0.335926340558
N	1.081308122103	3.969667086836	0.428807288410
O	-0.550575277203	-0.494857214036	0.066232718265
O	1.879979595704	-0.725697343577	0.065945754439
B	0.593298841618	-1.404421924681	0.358207852404
F	0.485603218427	-2.507712498341	-0.466753678751
F	0.553064431731	-1.765156991098	1.700238769757
N	10.057247989849	-1.545035723510	-0.271182980018
N	9.002970485046	2.752121646965	-0.128935296161
H	-9.258650040135	2.718278438803	-0.280231528910
H	-11.021651194871	0.987361713432	-0.378264364950
H	-10.442907500489	-1.421027273917	-0.363324686303
H	-8.061037468959	-2.135966369937	-0.248802585053
H	-4.001257582157	2.832362073840	-0.017725872588
H	-2.915912260985	-0.066180417032	0.018283547620
H	-1.533701731106	2.670435550180	0.112427276909

H	3.424516574949	2.204425575547	0.131642250519
H	4.320465950802	-0.745750197921	0.016745677411
H	5.961690249321	1.877723226248	-0.004815399156
H	6.657072176618	-1.131798029411	-0.097740557158
H	-5.884530491303	3.842344812890	-0.995872518753
H	-5.974340231459	3.832068370635	0.781968972714
H	-7.460097434867	3.858011444020	-0.184145396795
H	-5.772717772804	-0.482744133548	2.053455190569
H	-4.318515006579	-1.103437208676	1.254853324943
H	-5.833768846186	-2.010044854628	1.157986011319
H	-5.704224773935	-1.993399838266	-1.427830979892
H	-4.188159917275	-1.085391867602	-1.362739394793
H	-5.557180915894	-0.454722729747	-2.293239541707

Dye 5b

N	-6.578331078226	1.541519642322	-0.063822597947
C	-7.776735457320	0.808062316563	-0.123055202926
C	-9.090912176595	1.269919964325	-0.163424380501
C	-10.112262897104	0.313678696585	-0.219391196663
C	-9.825993404453	-1.053220150450	-0.234308541914
C	-8.495602270927	-1.495869447256	-0.193419326510
C	-7.474509259738	-0.558776863091	-0.138078949317
C	-5.965014276211	-0.745602435758	-0.085836030716
C	-5.480382162595	0.716480562887	-0.040409676938
C	-4.194226945019	1.209257566341	0.013215727175
C	-3.002770933085	0.442393226877	0.044812388628
C	-1.741217642074	0.980438185852	0.100461866507
C	-0.561436322733	0.174314446640	0.125174873728
C	0.740600662984	0.725346562562	0.210385144409
C	1.898304760415	-0.119592722101	0.106896453888
C	3.209391285644	0.399343135757	0.064896749445
C	4.315805539687	-0.433695743697	-0.016613544974
C	5.682569517962	-0.109990274916	-0.071593171083
C	6.609354094449	-1.229582020908	-0.152420505799
N	7.981883823984	-0.903620276337	-0.208040045687
C	8.485569440710	0.387799875447	-0.180286279100
N	7.568902839060	1.424046373000	-0.106866075410
C	6.163664452093	1.256147232110	-0.049133030112
C	-6.497894231340	2.992644300909	-0.030400266042
C	-5.565279762019	-1.523657745833	1.190638713548
C	-5.470628367541	-1.474812346787	-1.357928866676
C	0.900533119767	2.129714685792	0.327193467062
N	1.021615367343	3.286694635909	0.429464662552
O	-0.711087574665	-1.132180100676	0.042134243896
O	1.712238588851	-1.423643790824	0.018762447579
B	0.412470643739	-2.071797934548	0.320560448796
F	0.268265225257	-3.169146419214	-0.506247981338
F	0.374914381917	-2.434959151649	1.661949583686
O	6.270651074080	-2.417745714253	-0.175788591048
O	9.695616724718	0.603753410227	-0.221187273989
O	5.445310411240	2.260198508045	0.016519892613
C	8.970231929100	-1.980854389802	-0.292494928016
C	8.128203397124	2.777375181228	-0.086003428001
H	-9.332190119935	2.326860458381	-0.152899824496
H	-11.144766821902	0.648167897041	-0.251611629873
H	-10.634707423965	-1.775685554562	-0.277869049361
H	-8.272665187695	-2.559092719912	-0.205082697355
H	-4.070480284702	2.288240859328	0.034308301040
H	-3.066475105398	-0.639920902453	0.025452478291
H	-1.609273264156	2.057016034861	0.126628572844
H	3.337235709365	1.471628393115	0.097033045060
H	4.118594276122	-1.502348354819	-0.041865827521
H	-5.946318073580	3.368360232367	-0.898022856359
H	-5.993463744718	3.328665562106	0.880951328426
H	-7.500789207360	3.413860702022	-0.047215813583
H	-5.908474650548	-1.003928258100	2.089319030305
H	-4.483469434831	-1.654994104384	1.262764101474
H	-6.025510348494	-2.516137412904	1.173990024696
H	-5.928229578101	-2.467086195658	-1.413090435407
H	-4.386110669004	-1.603530045263	-1.354977729827
H	-5.747984398610	-0.921111759334	-2.259038662642
H	9.612914152523	-1.979060732933	0.591186588295
H	9.596611471506	-1.847749251004	-1.176803406124
H	8.421516133123	-2.916676699856	-0.354025683641
H	7.293890375273	3.470908226717	-0.026103120557
H	8.708422173087	2.961121259812	-0.993061624459
H	8.786015115602	2.902096157403	0.776948107225

Dye 6b

N	-8.044842740101	1.472172133322	-0.059135258591
C	-9.212171079412	0.692437775587	-0.114926385790
C	-10.544393272055	1.101354367024	-0.145899791116
C	-11.527420182426	0.105699772987	-0.200710530147
C	-11.187792371898	-1.248768289298	-0.223667845791
C	-9.840441319212	-1.638235071492	-0.192246128907
C	-8.856841997811	-0.661967252163	-0.138057170498
C	-7.340677158402	-0.789891862112	-0.094825523427
C	-6.912605784621	0.689602761393	-0.046020023604
C	-5.647718010179	1.231585777021	0.002129406255
C	-4.418721645607	0.521613522255	0.022456328143
C	-3.179416072125	1.116507140586	0.067702576338
C	-1.972419627251	0.372265558738	0.089655382857
C	-0.713562700704	0.914658506284	0.136495643580
C	0.474329421523	0.117644271362	0.152119599740
C	1.770883710244	0.680772893941	0.225454337600
C	2.936001877273	-0.154314071861	0.114614200847
C	4.241253731197	0.376669613109	0.062247089637
C	5.355000598584	-0.446825005373	-0.025016170591
C	6.717834795481	-0.110975103940	-0.089538776004
C	7.654583620813	-1.222646851429	-0.171552376884
N	9.023495365496	-0.884314927190	-0.235815702749
C	9.515400808729	0.411887418972	-0.216449642156
N	8.589809897363	1.440189628787	-0.141881548235
C	7.186766008448	1.259877354912	-0.075254456392
C	-8.021012248129	2.924383192801	-0.019887856455
C	-6.903862559360	-1.556935835027	1.176042973125
C	-6.825429865469	-1.494914324655	-1.372089284727
C	1.919941966152	2.086781514269	0.339350233248
N	2.033513283526	3.244617937763	0.439405453499
O	0.334424913358	-1.189659931433	0.072267443442
O	2.760442461779	-1.459844483630	0.029631678317
B	1.468399073078	-2.119810657318	0.340289042373
F	1.327756587550	-3.216987752056	-0.487203220766
F	1.444538989514	-2.485019652786	1.681276570890
O	7.326226280251	-2.413686506704	-0.188503149215
O	10.723067271376	0.638594826601	-0.265288981593
O	6.459470353784	2.257261600772	-0.009508042599
C	10.021649760049	-1.952511127169	-0.320915383852
C	9.137059607771	2.798629500765	-0.129959637791
H	-10.827323603348	2.147894342636	-0.129270849042
H	-12.572504978813	0.399367064094	-0.225665925948
H	-11.967514833728	-2.002479937764	-0.266201328680
H	-9.575683834251	-2.691795948589	-0.210317802899
H	-5.568548648639	2.314883759042	0.027499149778
H	-4.439897504034	-0.564505513734	0.001480889566
H	-3.114201246936	2.203783064407	0.088429899366
H	-2.052802762647	-0.713207987902	0.068581253464
H	-0.588372143221	1.992056707031	0.162374753194
H	4.359425498612	1.450145299669	0.091540415407
H	5.167173610891	-1.517250949253	-0.046424098589
H	-7.489666589516	3.325783858604	-0.888914625799
H	-7.524686428583	3.276904872678	0.889953268444
H	-9.039674589460	3.306383411014	-0.029036013492
H	-7.264655766482	-1.056090931734	2.078521433128
H	-5.817057216992	-1.642693839616	1.243735543780
H	-7.321820667982	-2.567991756122	1.156984268203
H	-7.242384654027	-2.504943652471	-1.428176331548
H	-5.736402772421	-1.579068689342	-1.376539178548
H	-7.130448848901	-0.950106624374	-2.269656302513
H	10.671866197472	-1.937267959548	0.557039452472
H	10.638997569758	-1.820140020716	-1.211691617641
H	9.481754131706	-2.894133585003	-0.370629683474
H	9.801405765673	2.931521000124	0.726682137146
H	8.297173449888	3.484895863105	-0.064515904812
H	9.707402719161	2.985035636961	-1.042752500579

Dye 14b

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C	-8.794827874753	0.692135229078	-0.177034225608
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C	-11.108590360122	0.109605776315	-0.299205665487
C	-10.770974534412	-1.245620679520	-0.299579644574
C	-9.425613452771	-1.637666332952	-0.237947909230
C	-8.441238304605	-0.662366997948	-0.176807746742
C	-6.926637660227	-0.791601554427	-0.103168703917
C	-6.498116697455	0.688007223194	-0.063106499948
C	-5.232040914797	1.229545423010	0.004873282960

C	-4.013440798210	0.508611038748	0.057170247778
C	-2.773292255954	1.094009206888	0.125631961160
C	-1.565395156694	0.332740175454	0.168115163214
C	-0.285241271093	0.932307641768	0.260143363097
C	0.902303699216	0.128594071558	0.175780892049
C	2.195948447066	0.683279162060	0.138658428568
C	3.348882609568	-0.089482474190	0.070715896277
C	4.656796727772	0.410204176523	0.022548084303
C	5.744641638846	-0.455408083077	-0.036788145752
C	7.123052644327	-0.182375510038	-0.088577290576
C	8.007976919119	-1.336819711042	-0.142709172986
N	9.391804847509	-1.064977516404	-0.191183107595
C	9.943370633396	0.207186378537	-0.190537996607
N	9.065762234070	1.278119555215	-0.140555465504
C	7.654793810016	1.165225621761	-0.088365291587
C	-7.600474029995	2.924180602583	-0.088291638051
C	-6.514948820309	-1.544153775540	1.184737254782
C	-6.388243836916	-1.511104169207	-1.362871424516
C	-0.174851162019	2.341973861157	0.365717323134
N	-0.085019226052	3.502702545239	0.458440266068
O	-1.664918977151	-0.979363664989	0.094161697027
O	0.768637066315	-1.183718265780	0.099713003969
B	-0.511496662395	-1.877546380504	0.385364177876
F	-0.605395537191	-2.978460969483	-0.444352996718
F	-0.551772456061	-2.2438754443121	1.725749642916
O	7.622710110915	-2.511507466524	-0.148106292495
O	11.160626951985	0.377092262215	-0.233253895360
O	6.974903176260	2.197207761916	-0.046995909903
C	10.339084035508	-2.180494307060	-0.246810992080
C	9.675797025869	2.609566175098	-0.143748772913
H	-10.405497632377	2.151212765538	-0.238661943967
H	-12.152427991568	0.404653773945	-0.347273837565
H	-11.551364765013	-1.998301739418	-0.347761574414
H	-9.162970348427	-2.691845595998	-0.238224825039
H	-5.149583214082	2.312548891433	0.020295053109
H	-4.035923221723	-0.575426615590	0.043467564238
H	-2.682020663647	2.174991530434	0.146510556913
H	2.277869842515	1.764852523676	0.162294201833
H	3.219351962543	-1.170987218980	0.055191122221
H	4.825047655114	1.480363659550	0.031897892903
H	5.517754035780	-1.520609023407	-0.044633432418
H	-7.045678516605	3.311881769011	-0.948493057106
H	-7.128077129388	3.287938980335	0.829568074670
H	-8.617987315847	3.306794221896	-0.130165998397
H	-6.890510623602	-1.031452687734	2.074465130761
H	-5.429987237312	-1.632810247966	1.272673014255
H	-6.936105805401	-2.553849234846	1.169739075062
H	-6.807285277202	-2.520362184140	-1.415802913317
H	-5.299791483278	-1.598601351867	-1.344935760719
H	-6.674505074402	-0.975190091652	-2.271919022095
H	11.008304286297	-2.152664393984	0.615957941540
H	10.942016210270	-2.120430392669	-1.155610021346
H	9.756700342500	-3.097818803033	-0.241705295773
H	8.867928472848	3.334855681770	-0.100309855580
H	10.265171467842	2.753752809376	-1.051983045169
H	10.335352436301	2.725865025476	0.719038272327

Dye 5-s

O	0.669080659123	0.124382848847	1.221406788047
O	0.669080659123	0.124382848847	-1.221406788047
C	-0.646617666998	0.158462759580	1.235864910635
C	-0.646617666998	0.158462759580	-1.235864910635
C	-1.353387202937	0.225554888685	0.000000000000
B	1.466594028314	0.428134184474	0.000000000000
F	2.582460943806	-0.382479494047	0.000000000000
F	1.804915369008	1.773507053539	0.000000000000
C	-2.770650026323	0.285515978645	0.000000000000
N	-3.936806349155	0.340092408574	0.000000000000
C	-1.306731237716	0.097532679401	2.492985193871
C	-1.306731237716	0.097532679401	-2.492985193871
C	-0.620137764460	0.049372740526	3.686796055146
C	-0.620137764460	0.049372740526	-3.686796055146
C	-1.237440070218	-0.020022610595	4.953542728721
C	-1.237440070218	-0.020022610595	-4.953542728721
C	-0.589684587467	-0.070043286064	6.174819085160
C	-0.589684587467	-0.070043286064	-6.174819085160
C	0.920304721696	-0.073541351413	6.478743994629
C	0.920304721696	-0.073541351413	-6.478743994629
C	0.918352967832	-0.152980765861	7.998004891368
C	0.918352967832	-0.152980765861	-7.998004891368

C	-0.401282664568	-0.183073371002	8.461579560550
C	-0.401282664568	-0.183073371002	-8.461579560550
N	-1.274555303021	-0.129517264661	7.357158489658
N	-1.274555303021	-0.129517264661	-7.357158489658
C	1.971935477694	-0.195018058294	8.899678314022
C	1.971935477694	-0.195018058294	-8.899678314022
C	1.690453028273	-0.267637390318	10.271478996062
C	1.690453028273	-0.267637390318	-10.271478996062
C	0.367421995144	-0.297151270287	10.718735849758
C	0.367421995144	-0.297151270287	-10.718735849758
C	-0.704463376196	-0.255554794673	9.819227132476
C	-0.704463376196	-0.255554794673	-9.819227132476
C	-2.726749688125	-0.138168398793	7.454156573564
C	-2.726749688125	-0.138168398793	-7.454156573564
C	1.600777053542	1.235796064675	6.011403700143
C	1.624955453097	-1.313248002620	-5.877589590834
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C	1.600777053542	1.235796064675	-6.011403700143
H	-2.391470656229	0.086990606571	2.488795798134
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Dye 5a-s

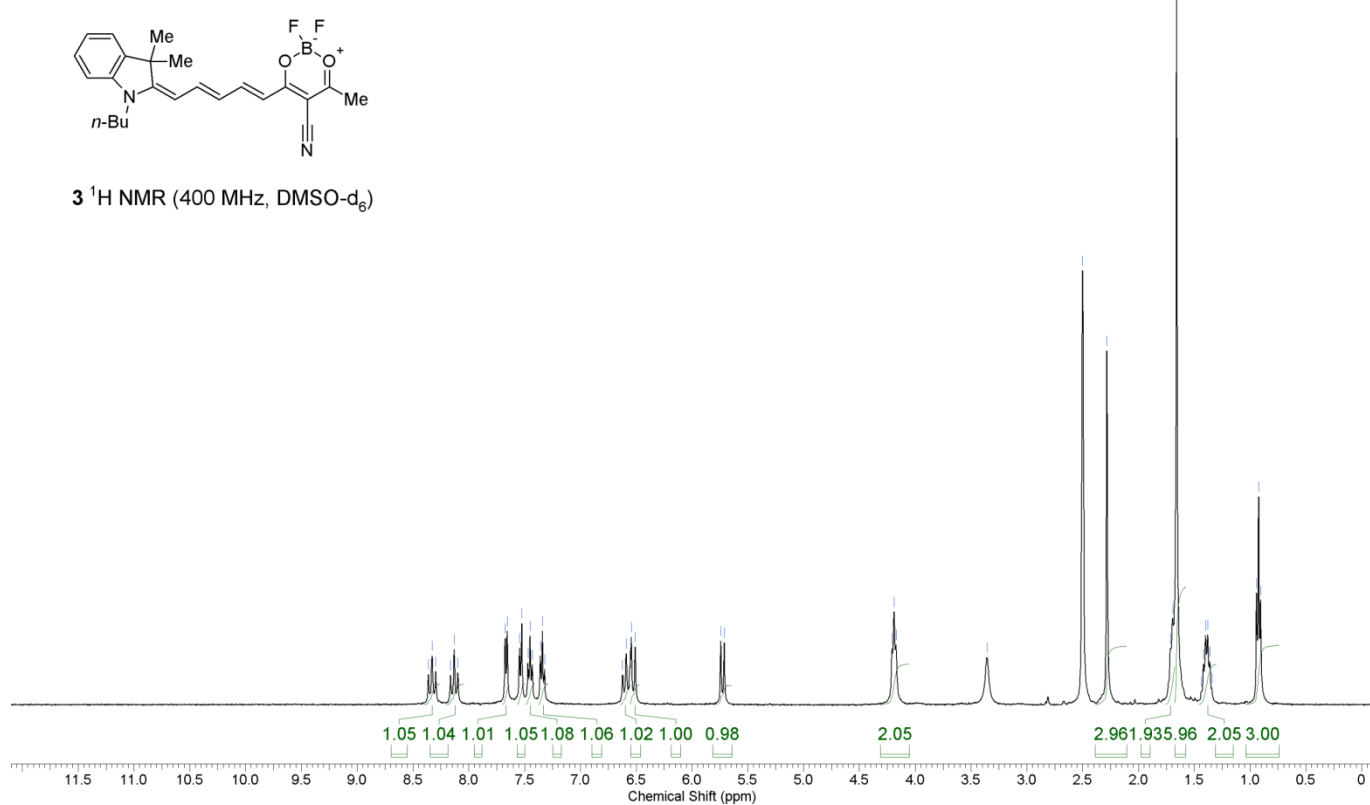
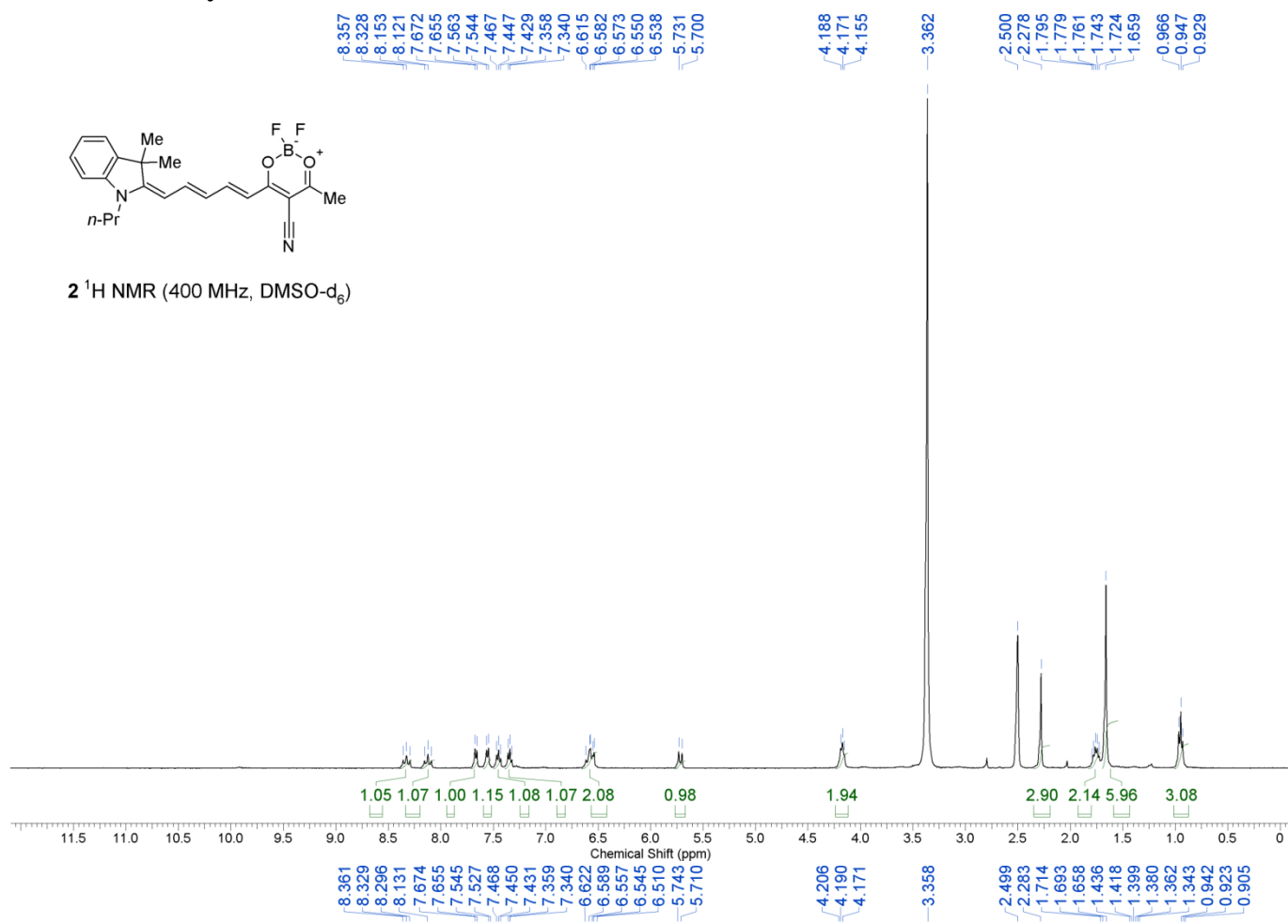
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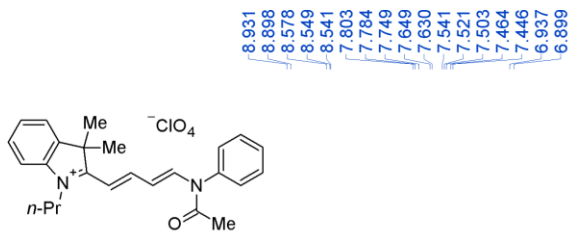
Dye 5b-s

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O	-2.396882562538	0.415780736863	4.514741529493
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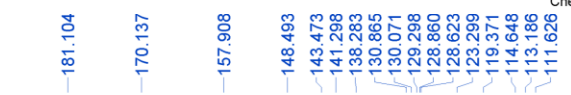
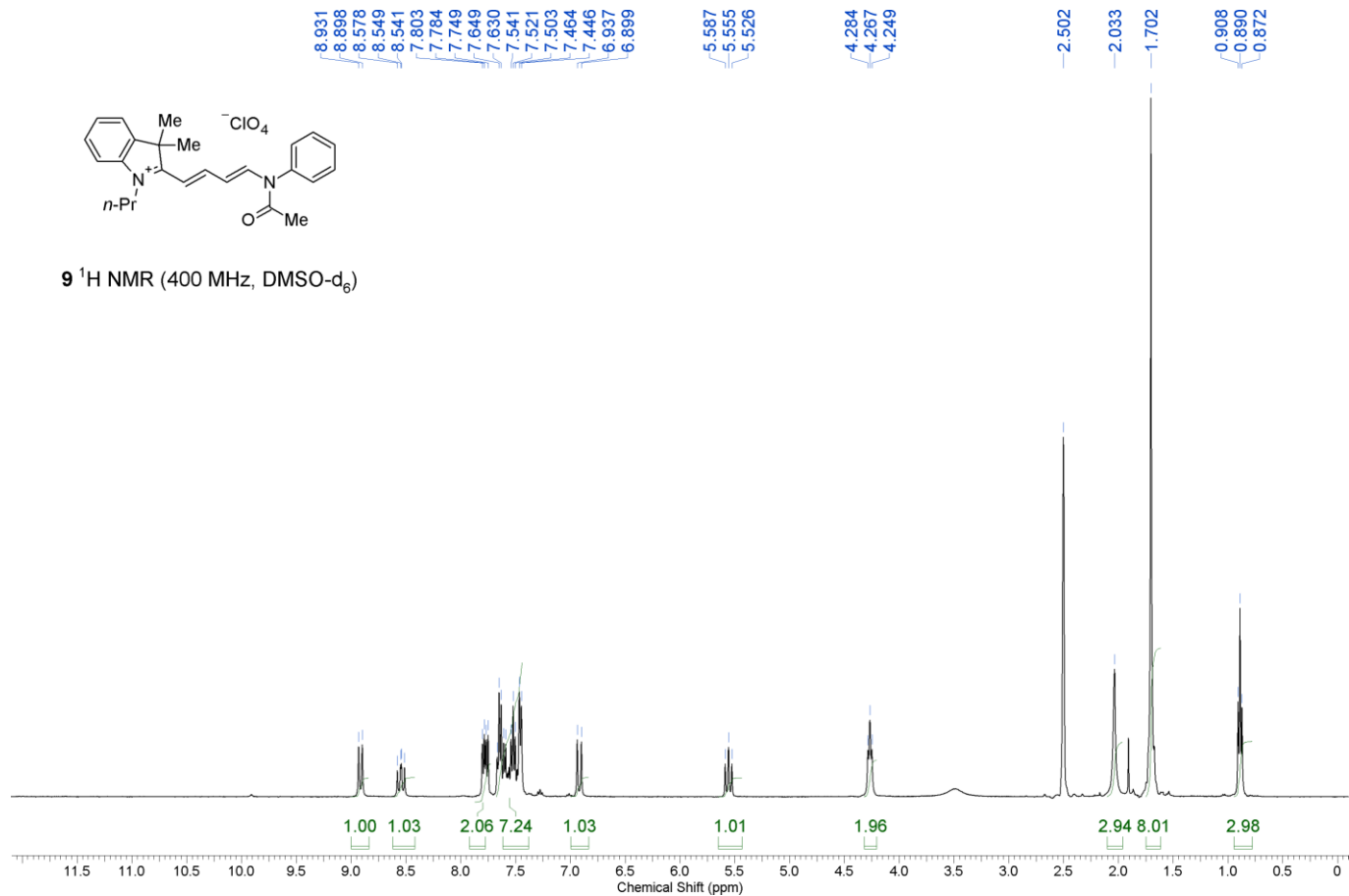
NMR Spectra of the Synthesized Compounds

Intermediate Dyes

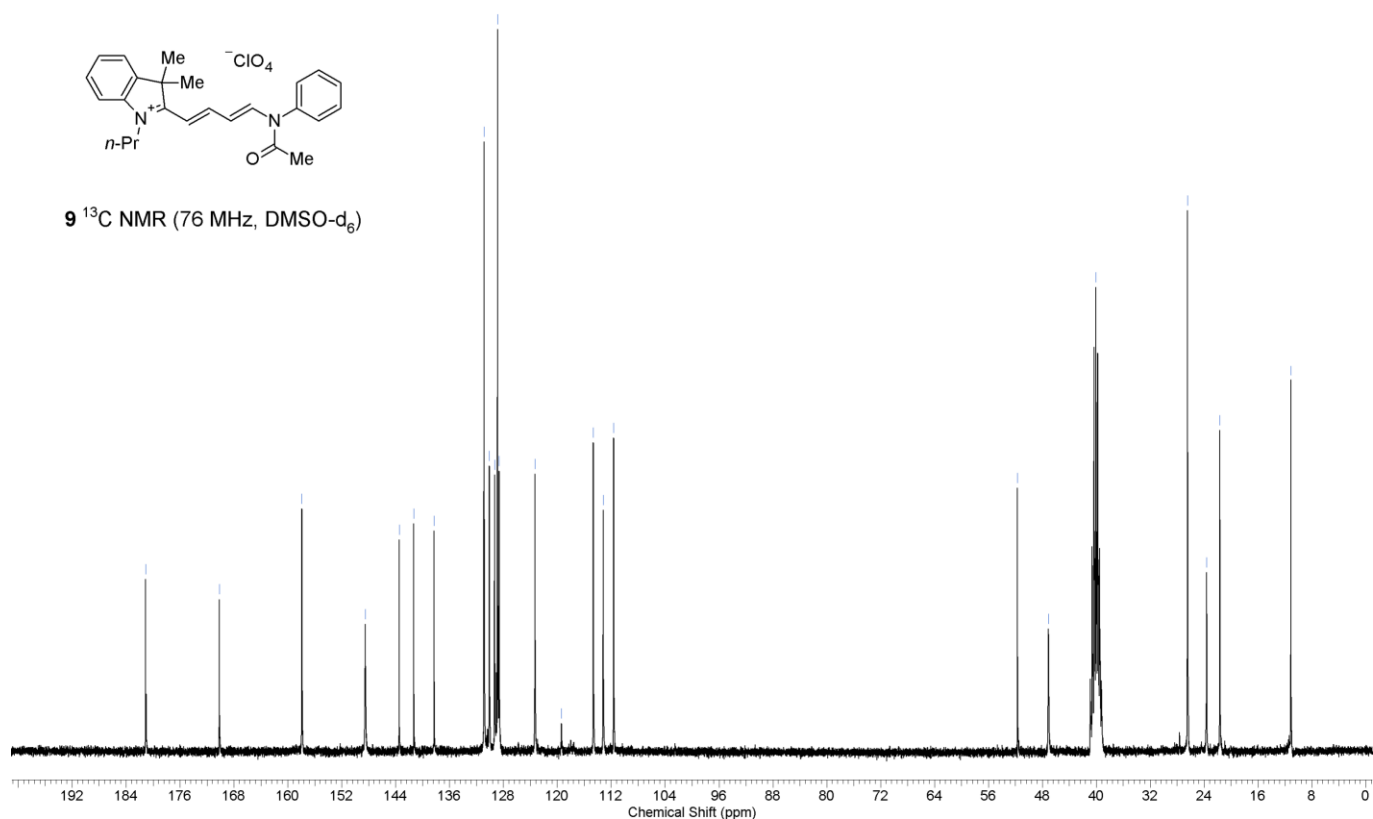


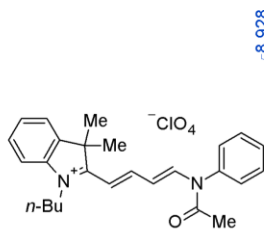


9 ^1H NMR (400 MHz, DMSO-d_6)

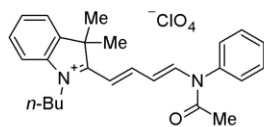
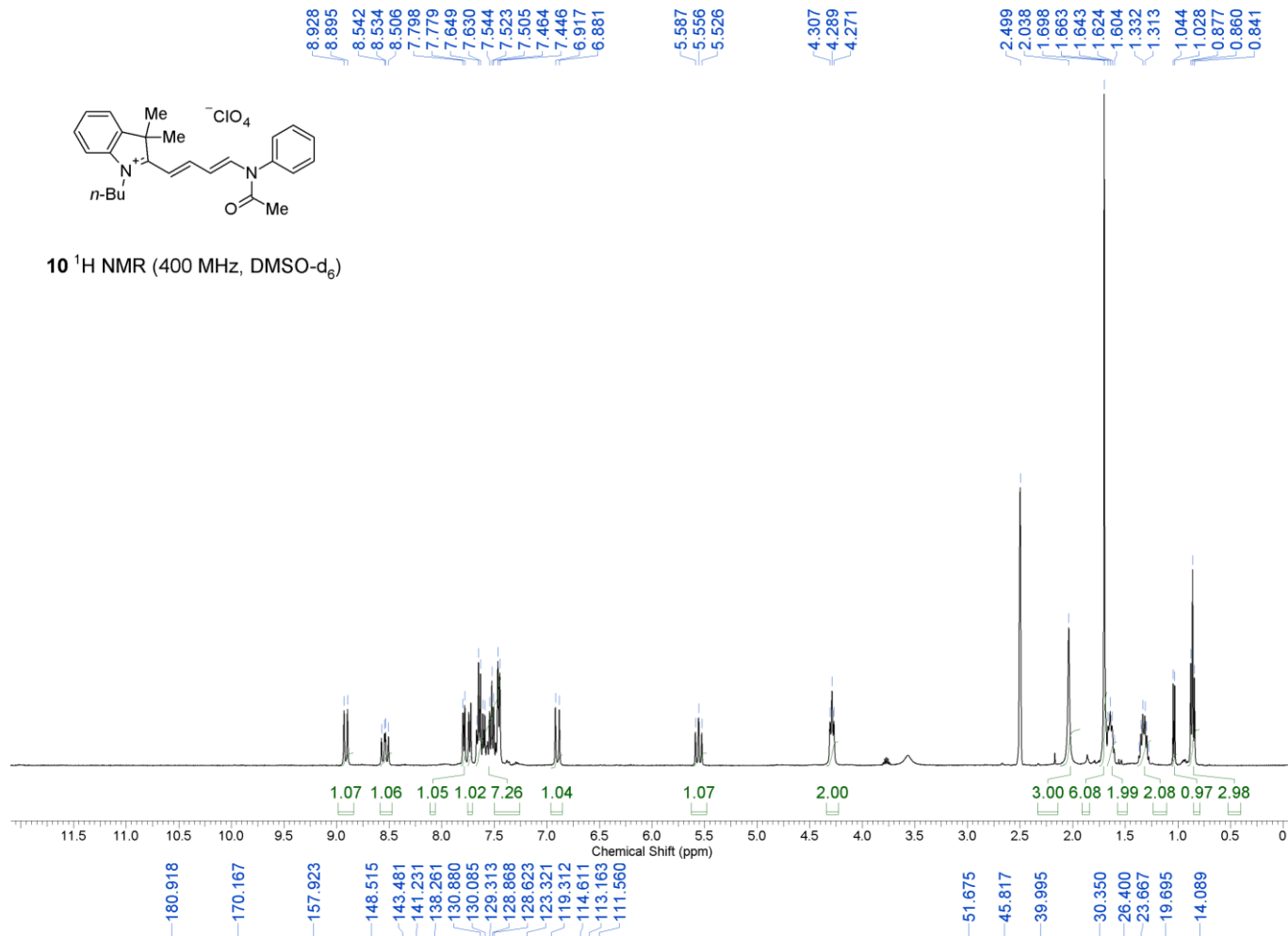


9 ^{13}C NMR (76 MHz, DMSO-d_6)

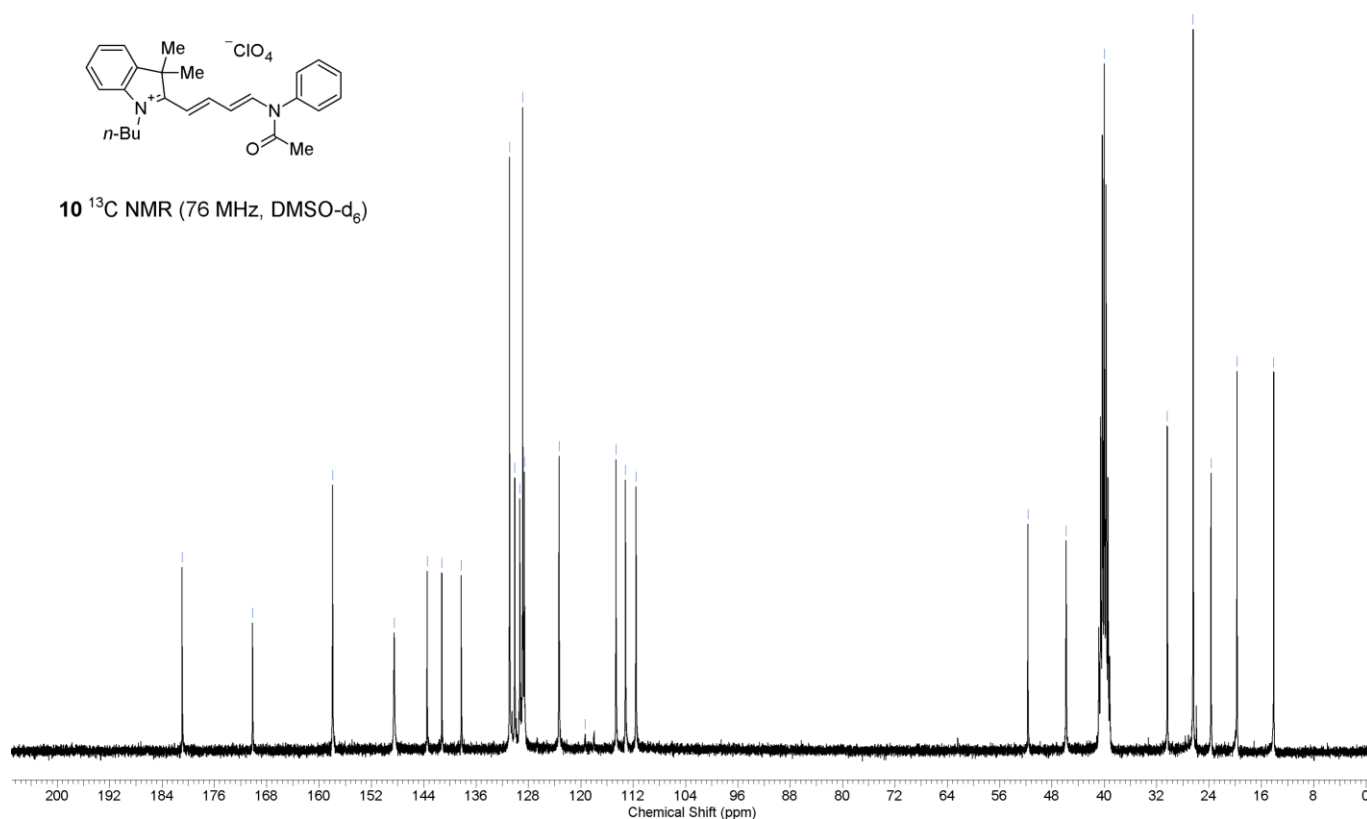


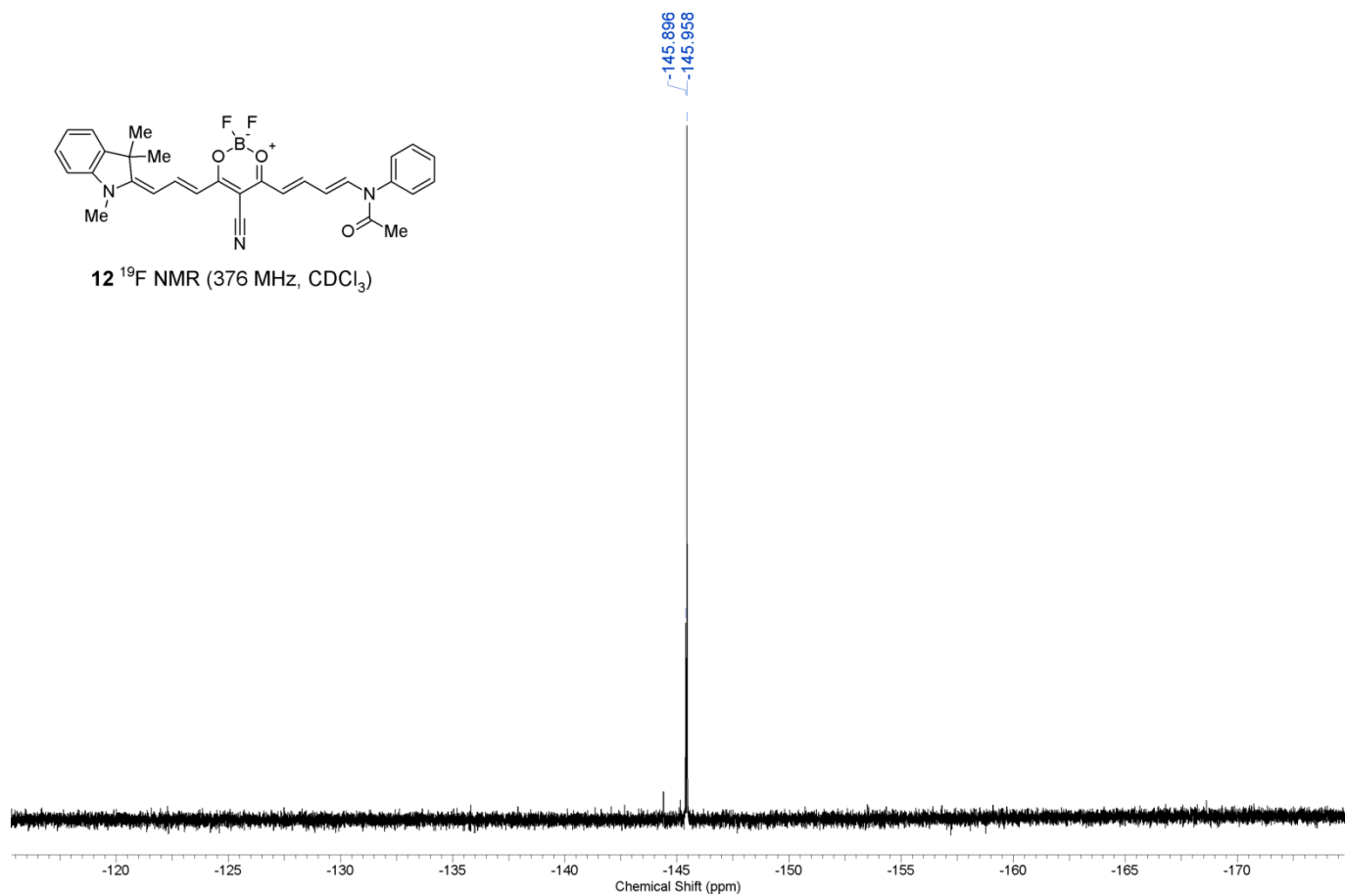
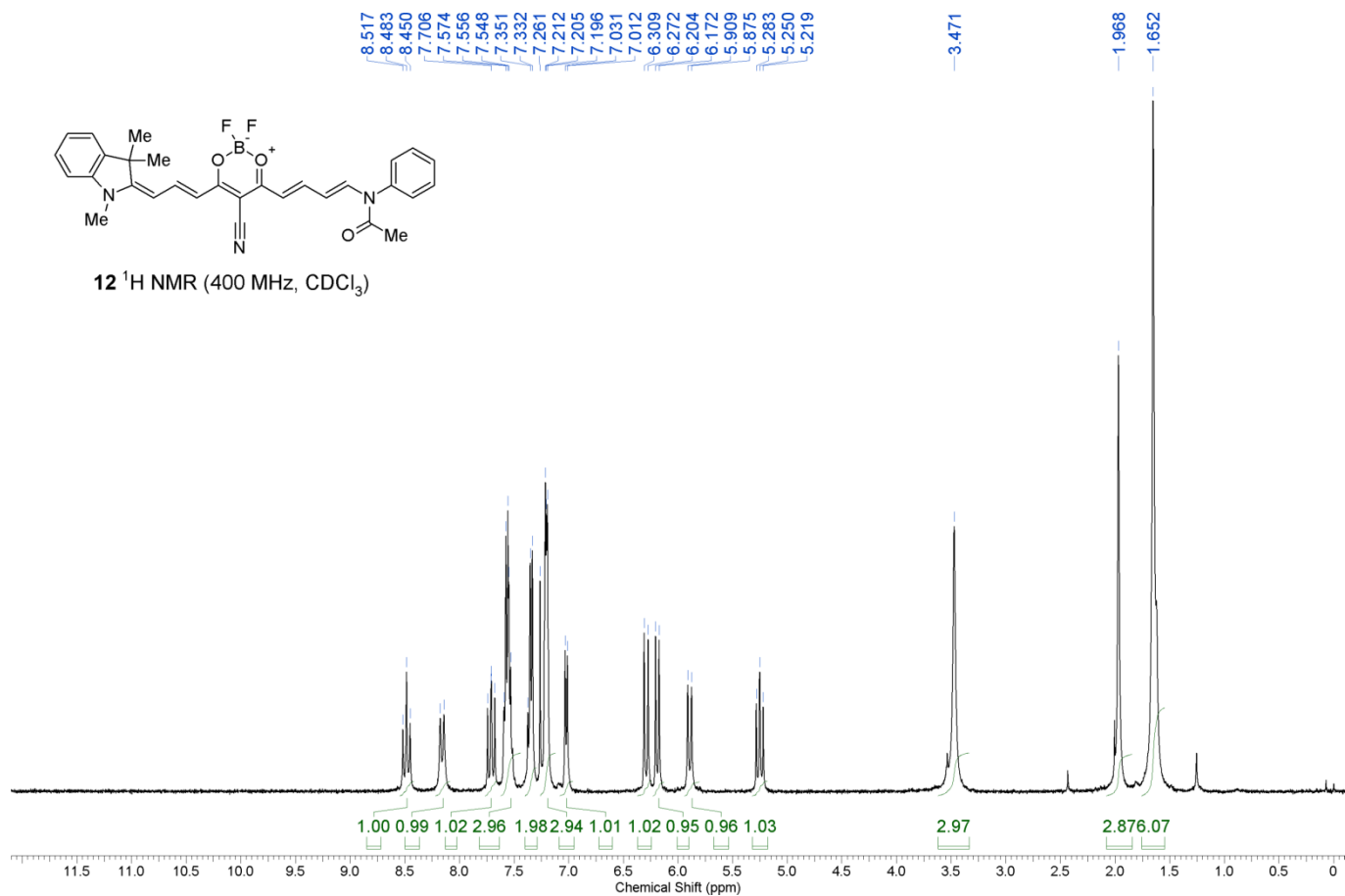


10 ^1H NMR (400 MHz, DMSO-d_6)

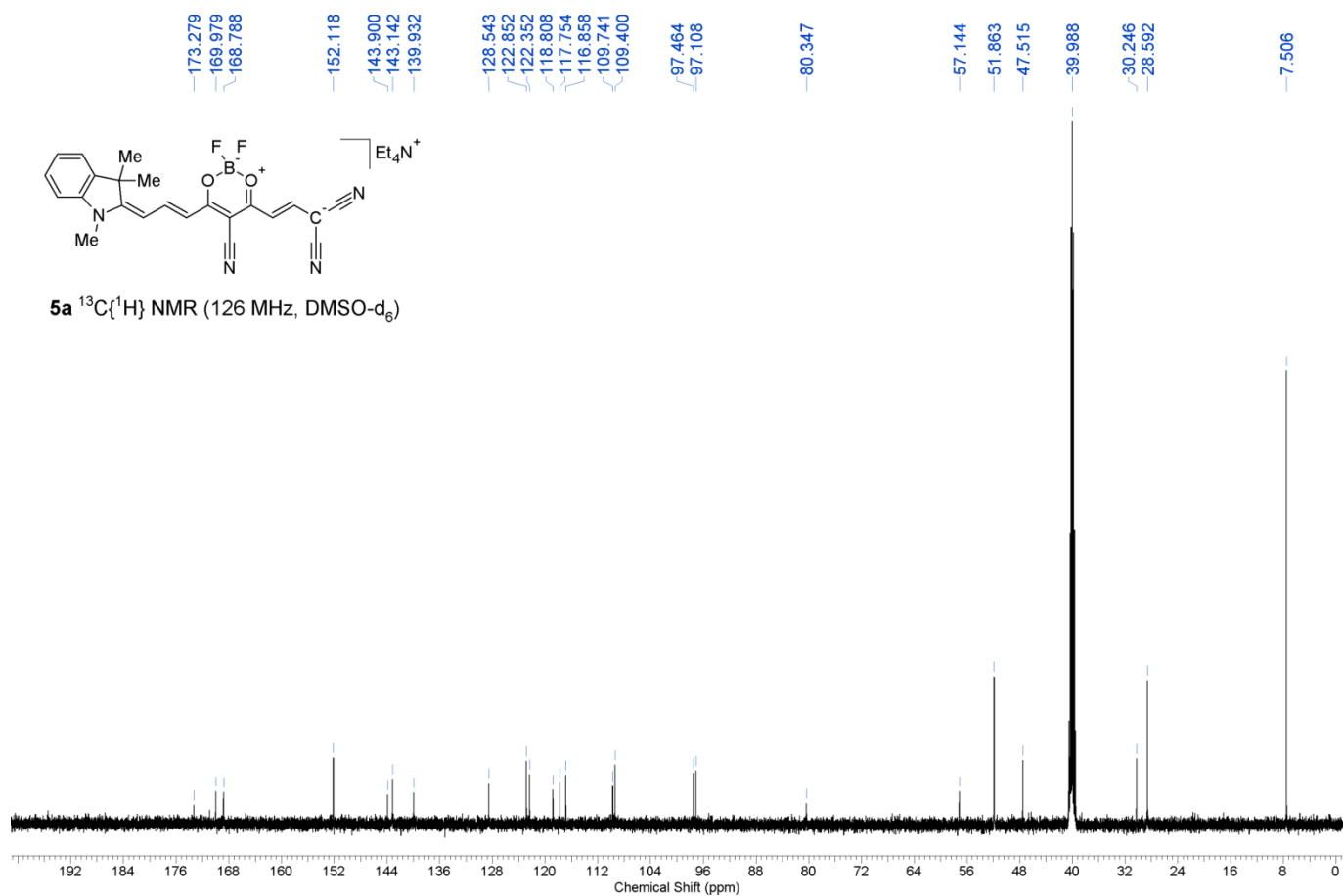
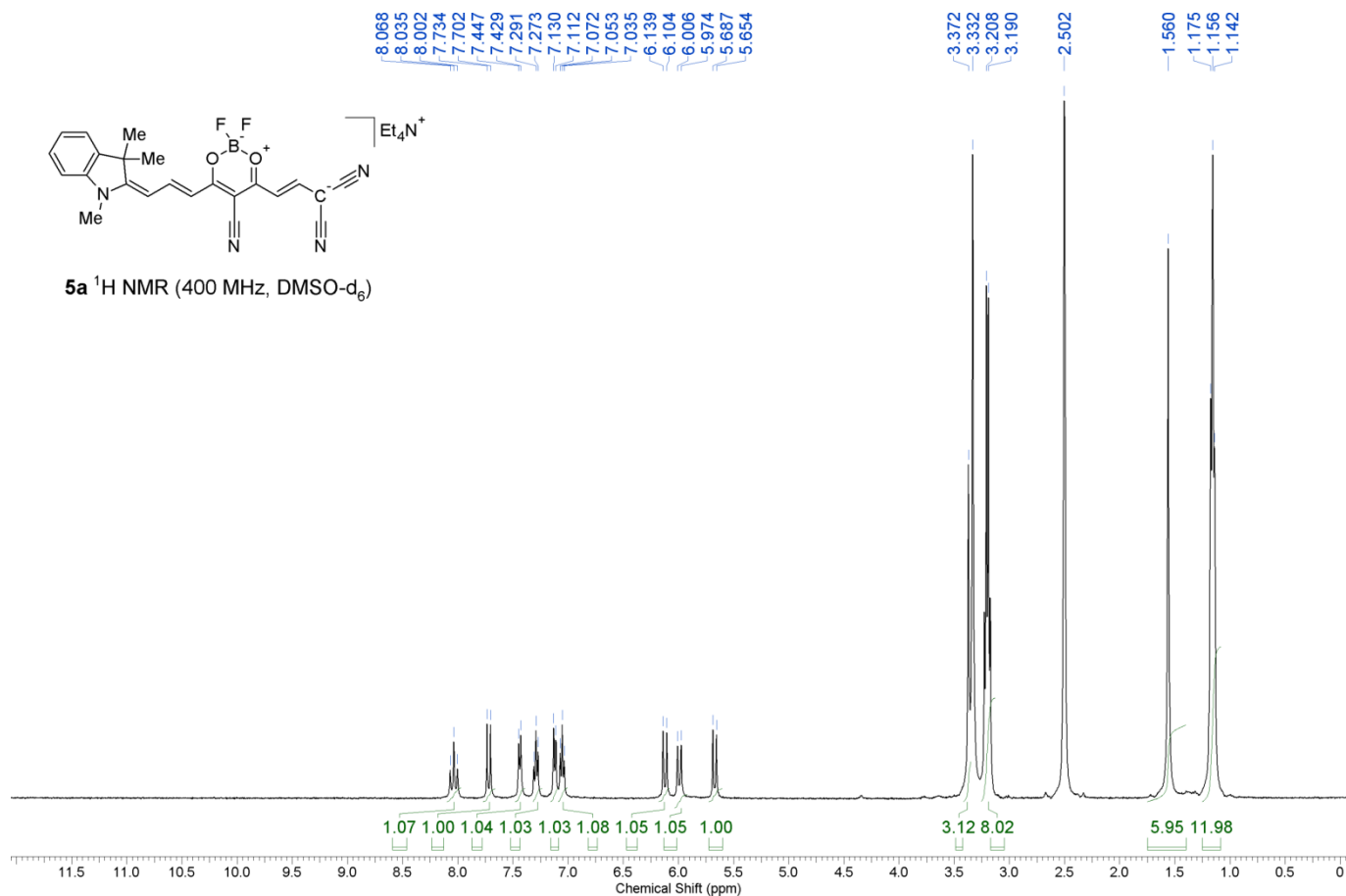


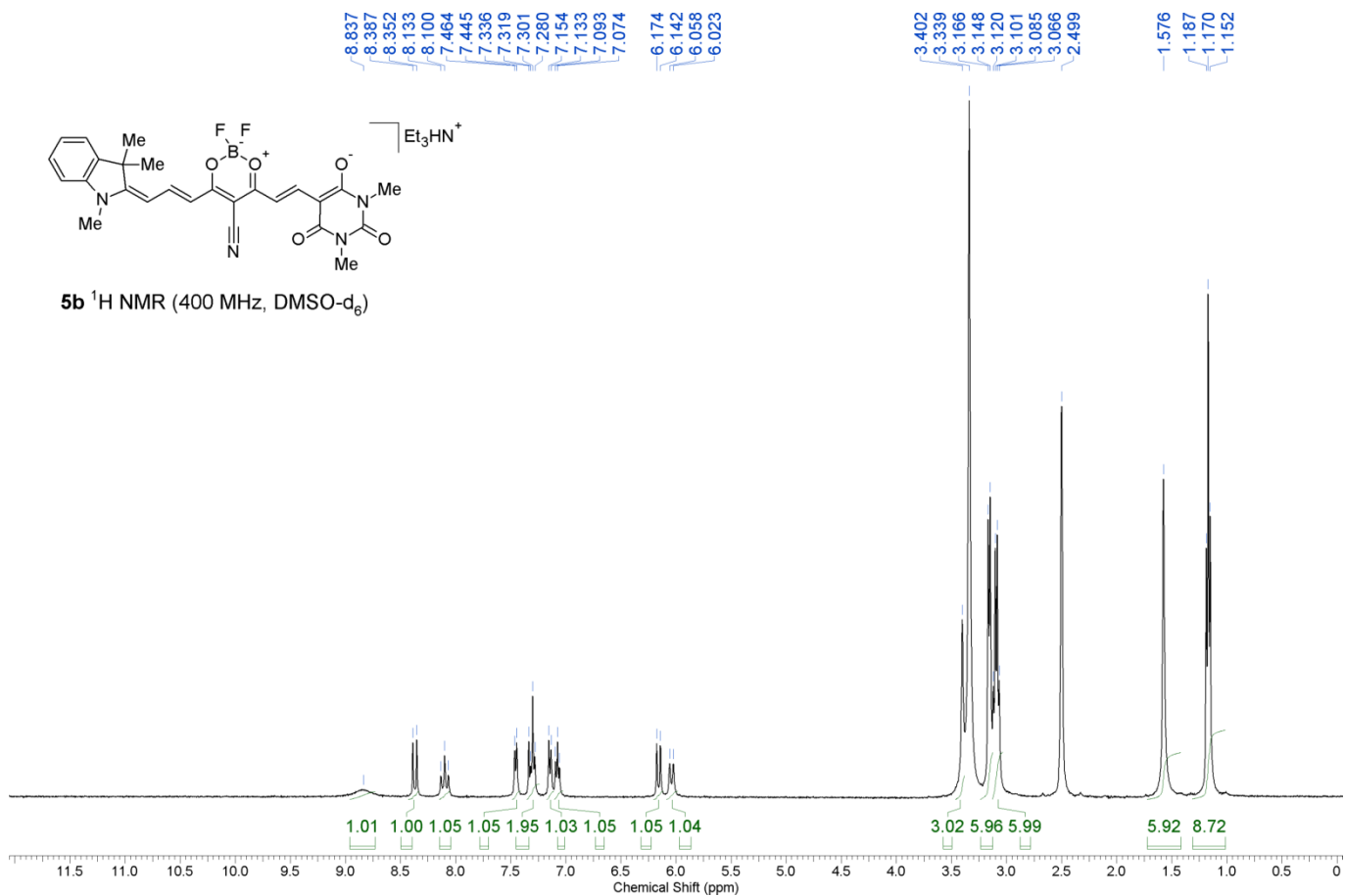
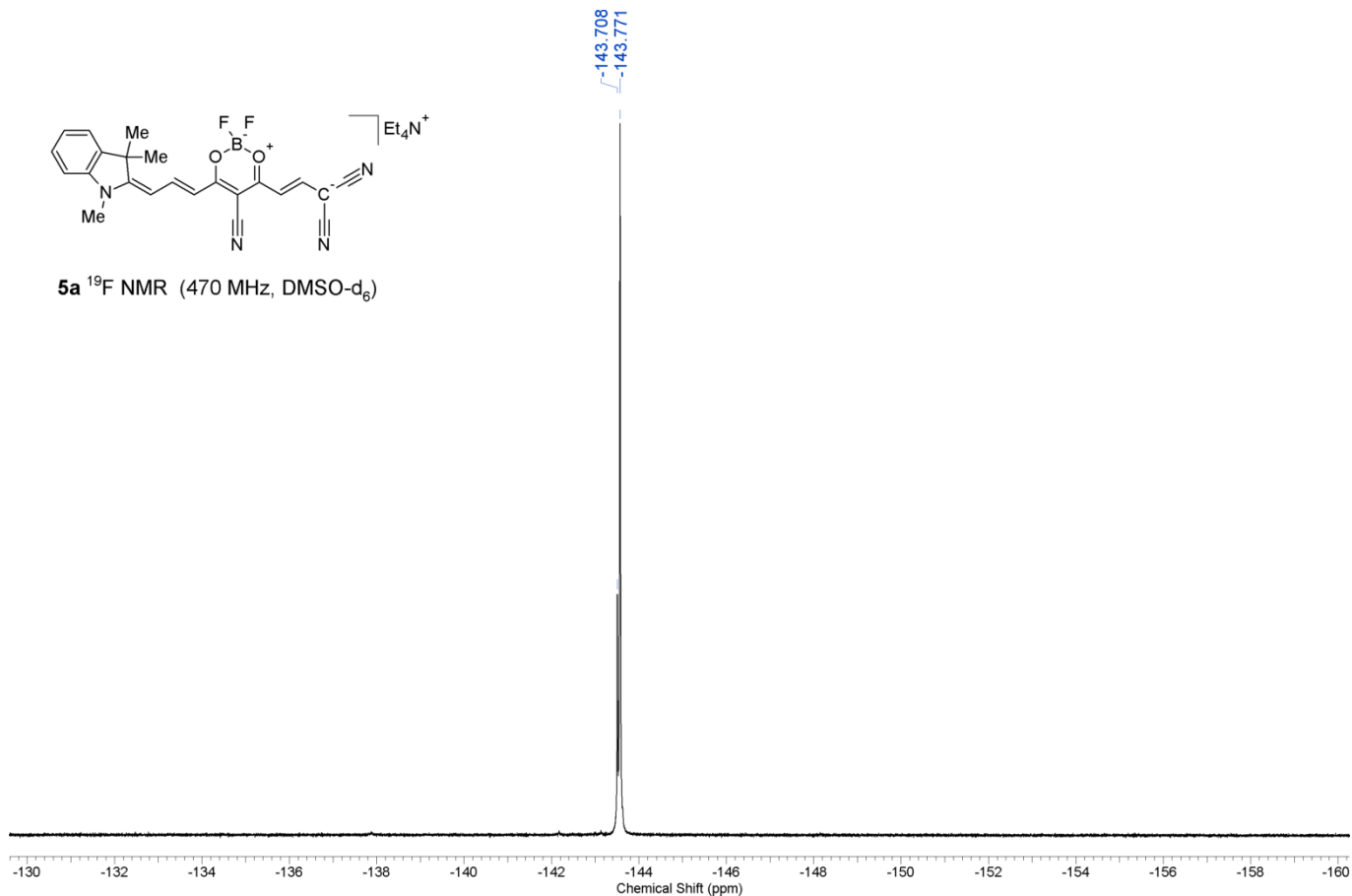
10 ^{13}C NMR (76 MHz, DMSO-d_6)

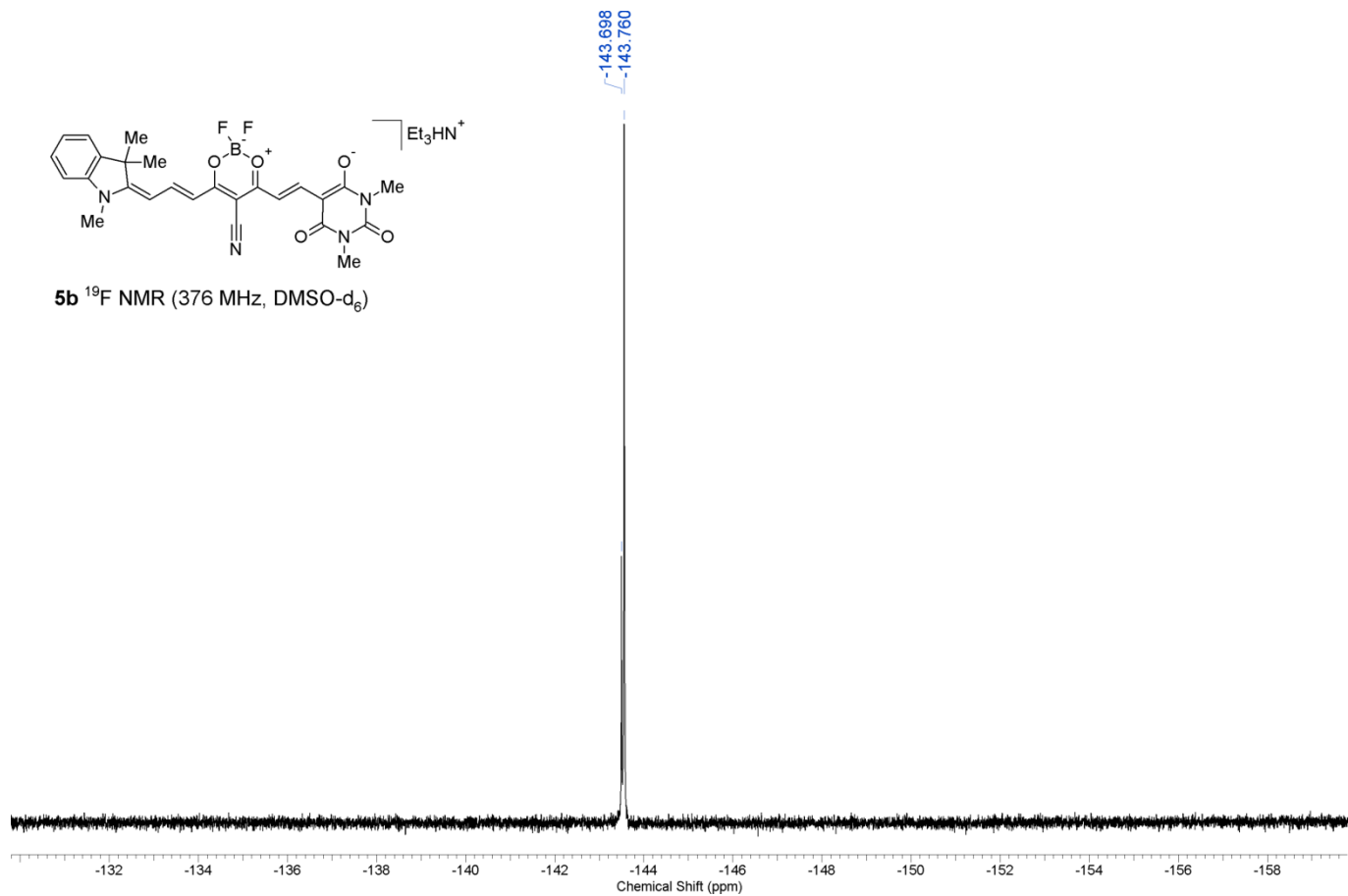
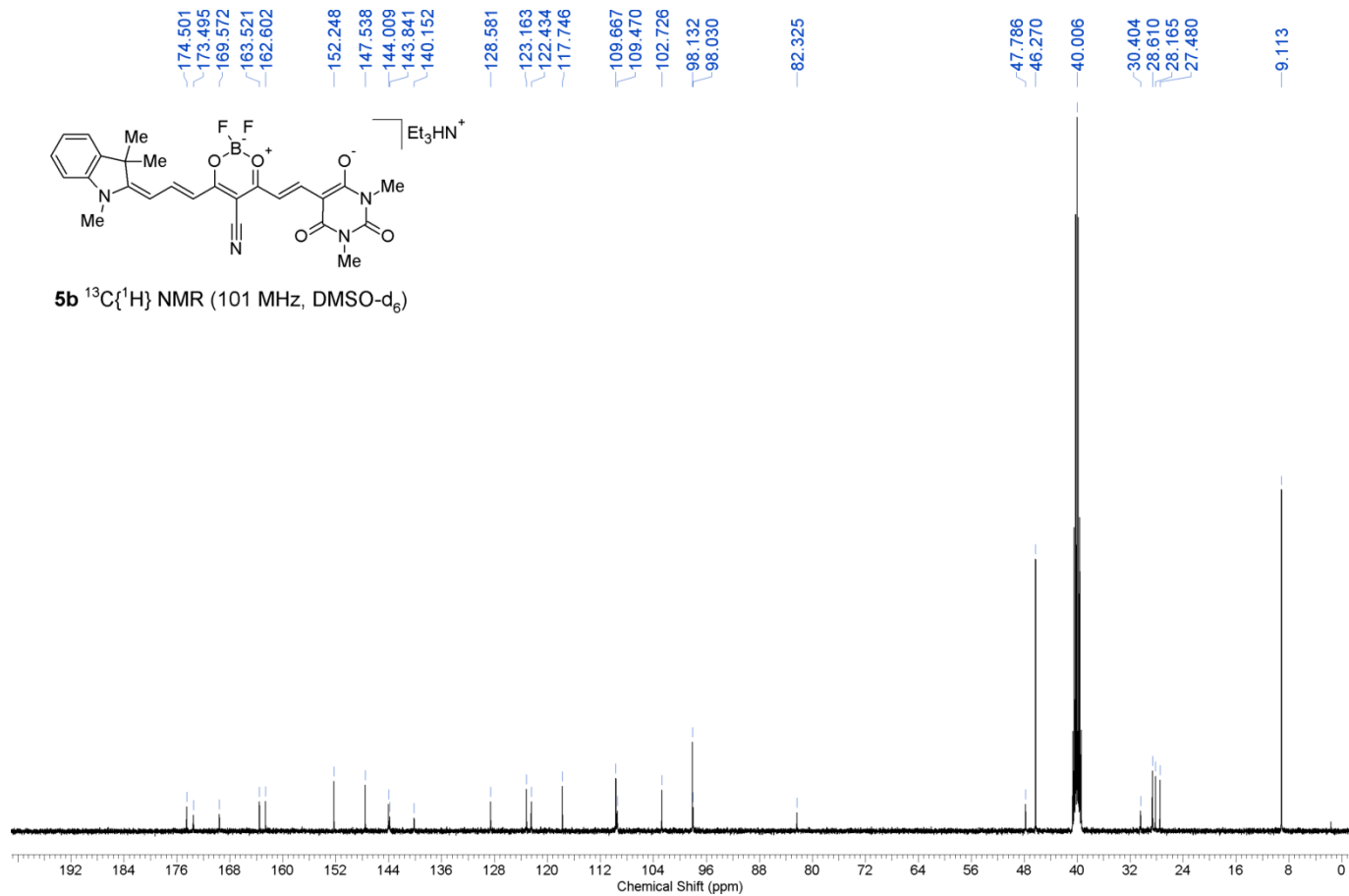


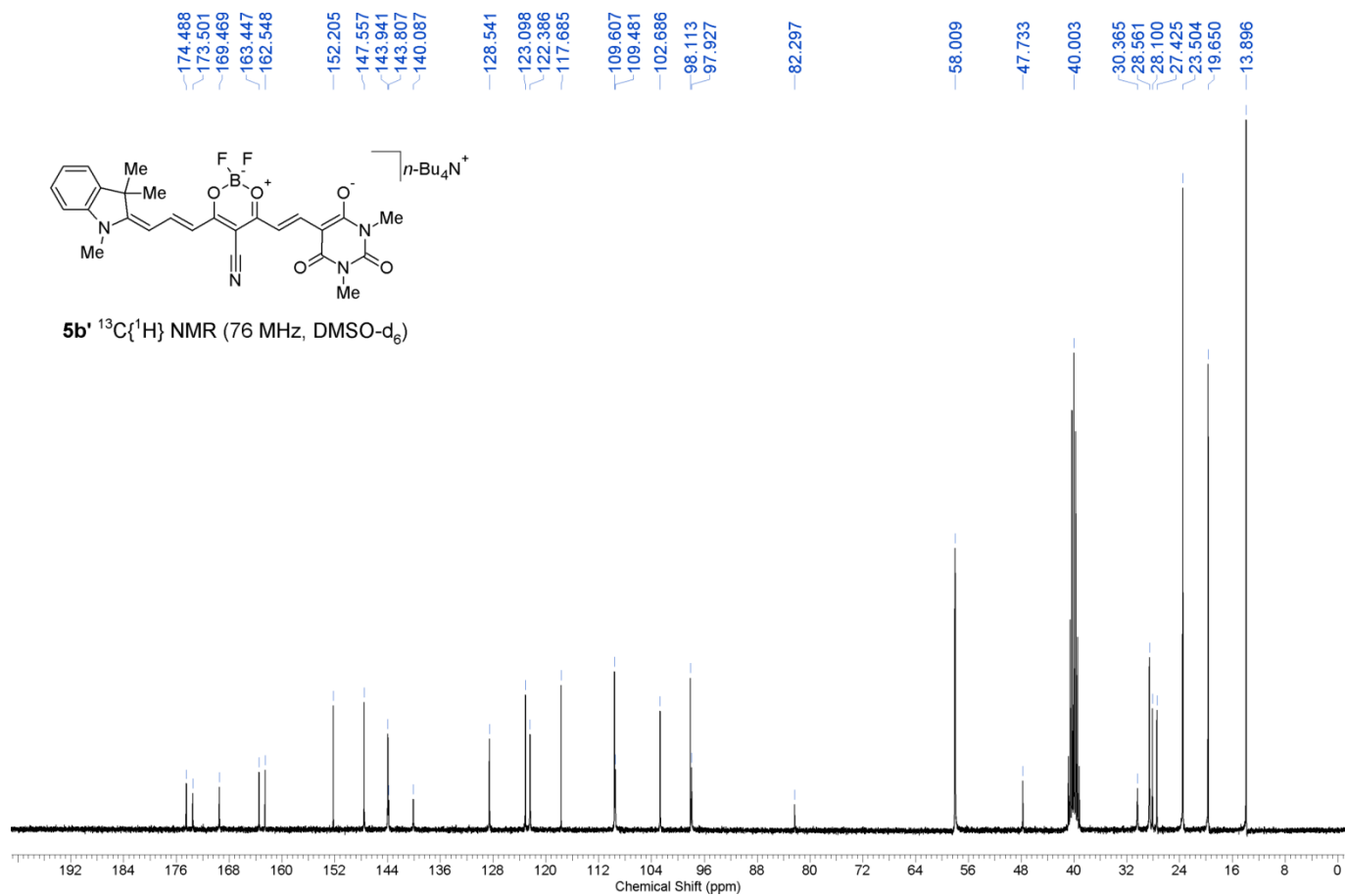
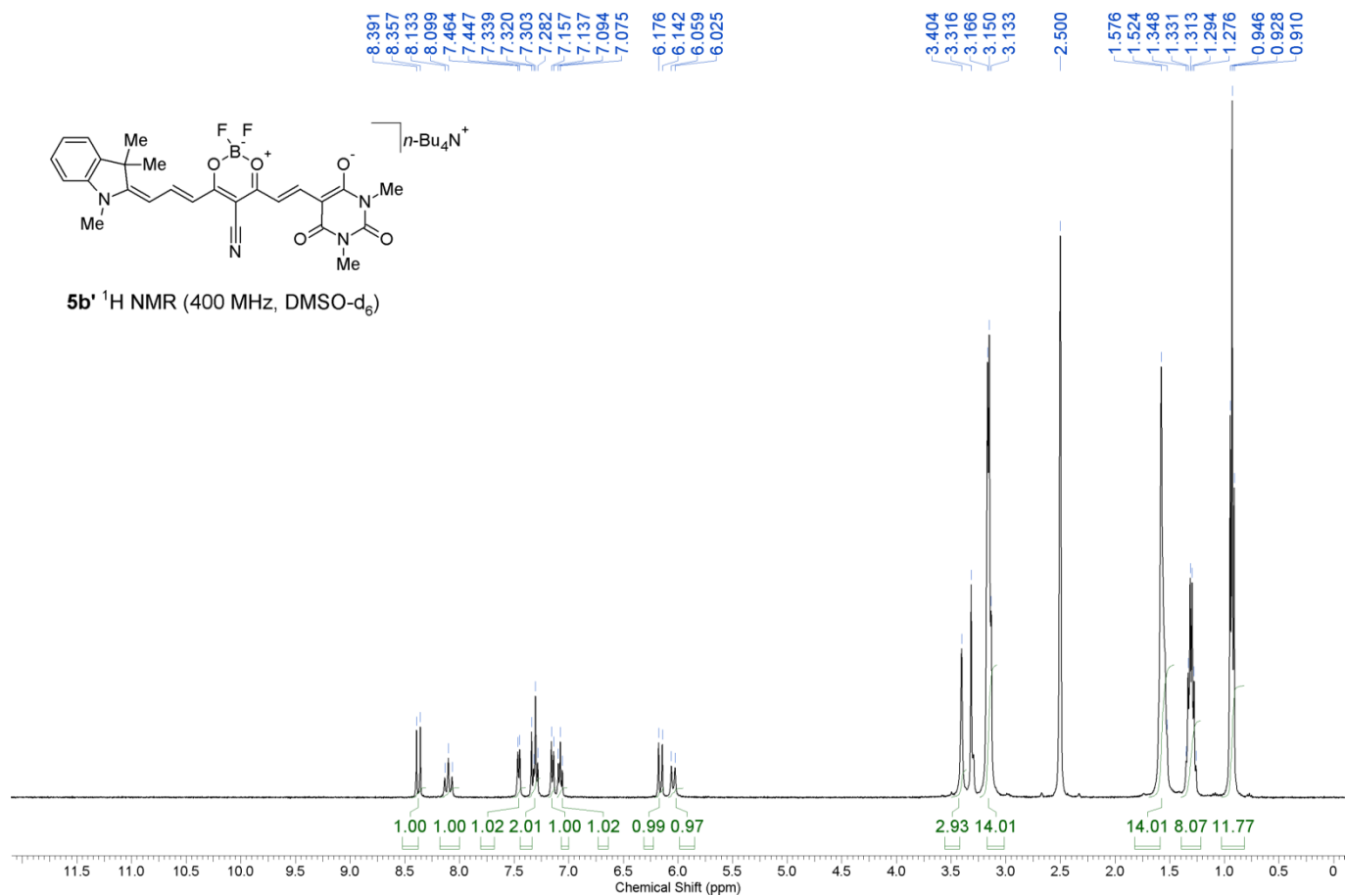


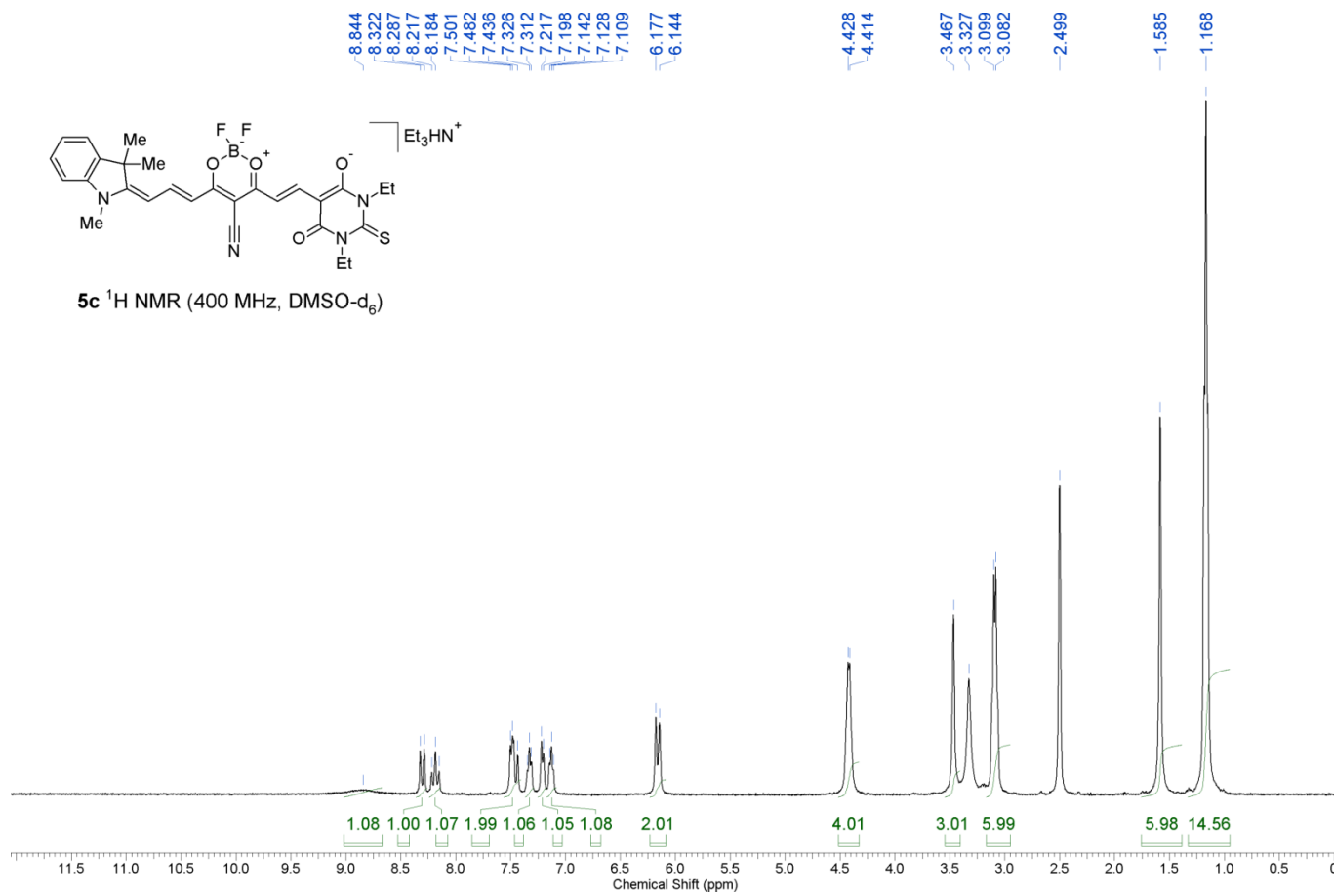
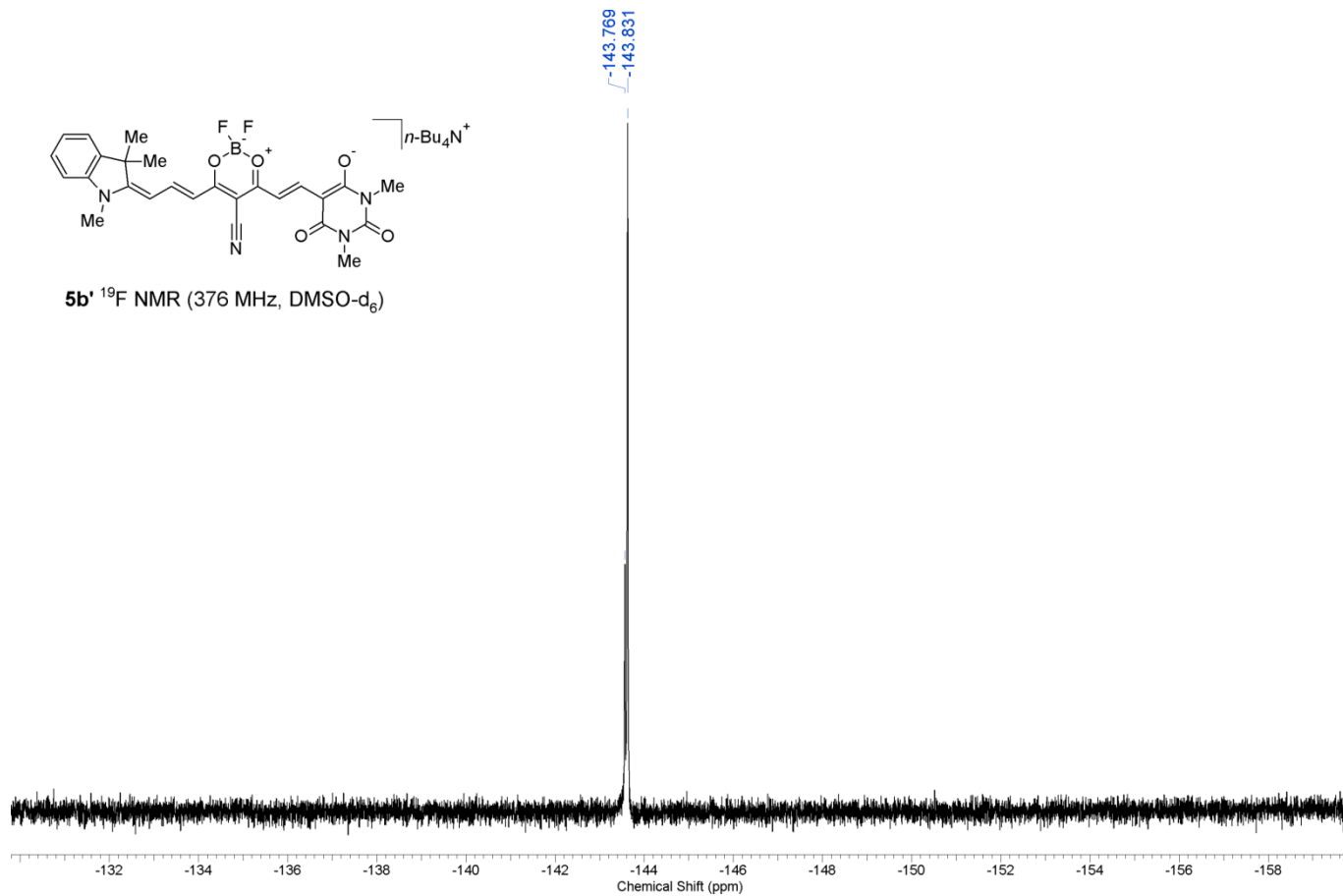
Mero-Anionic Dyes 5a-d

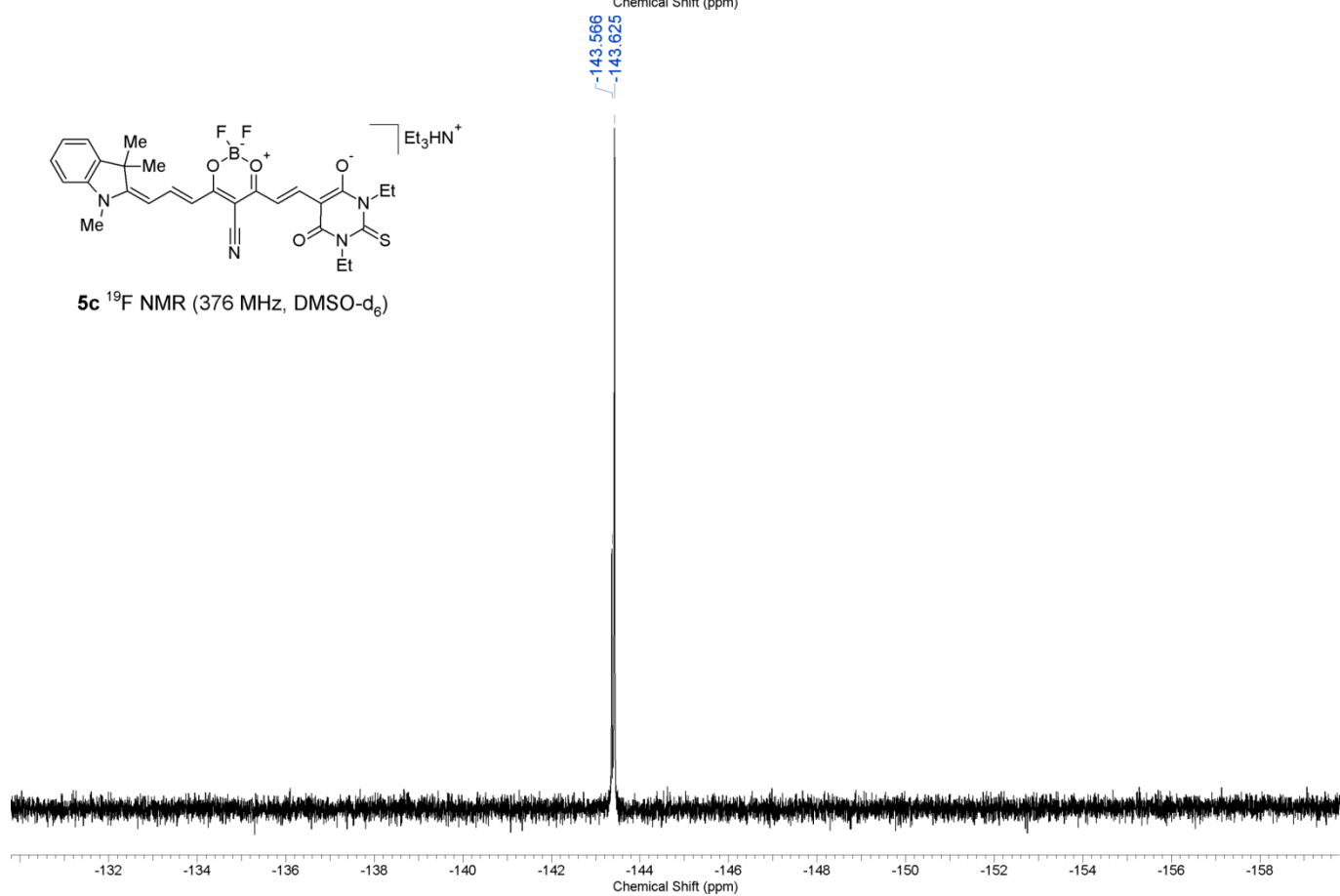
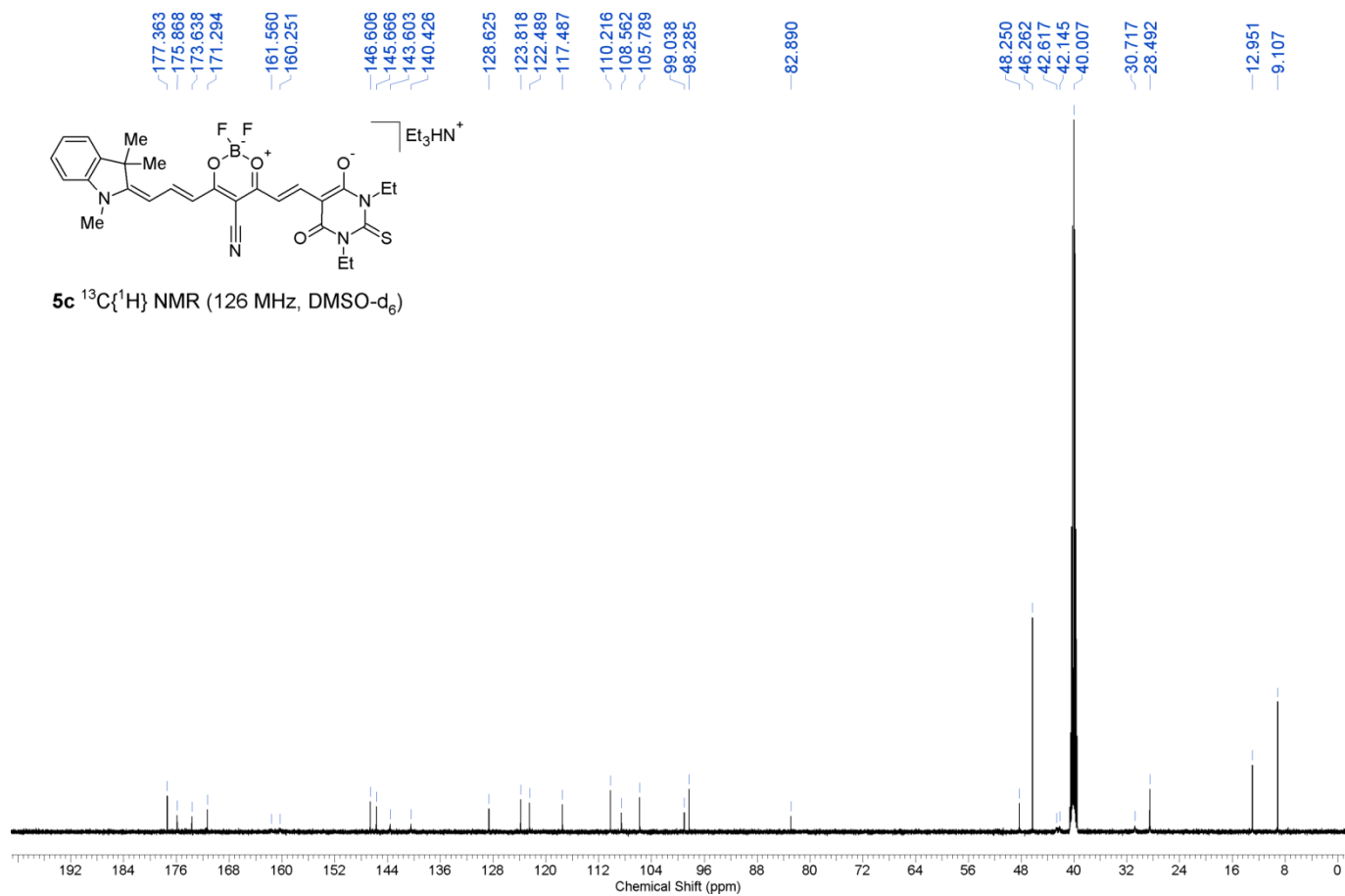


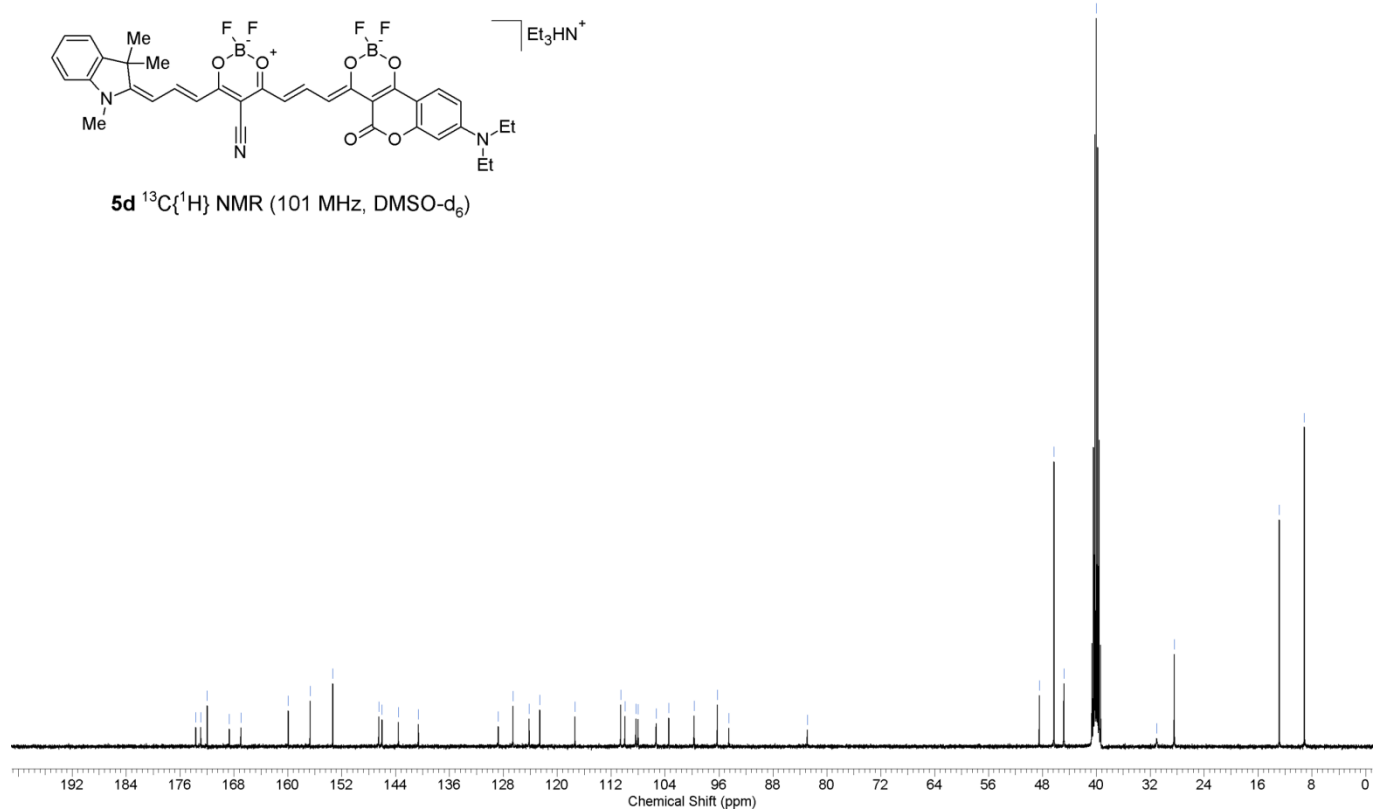
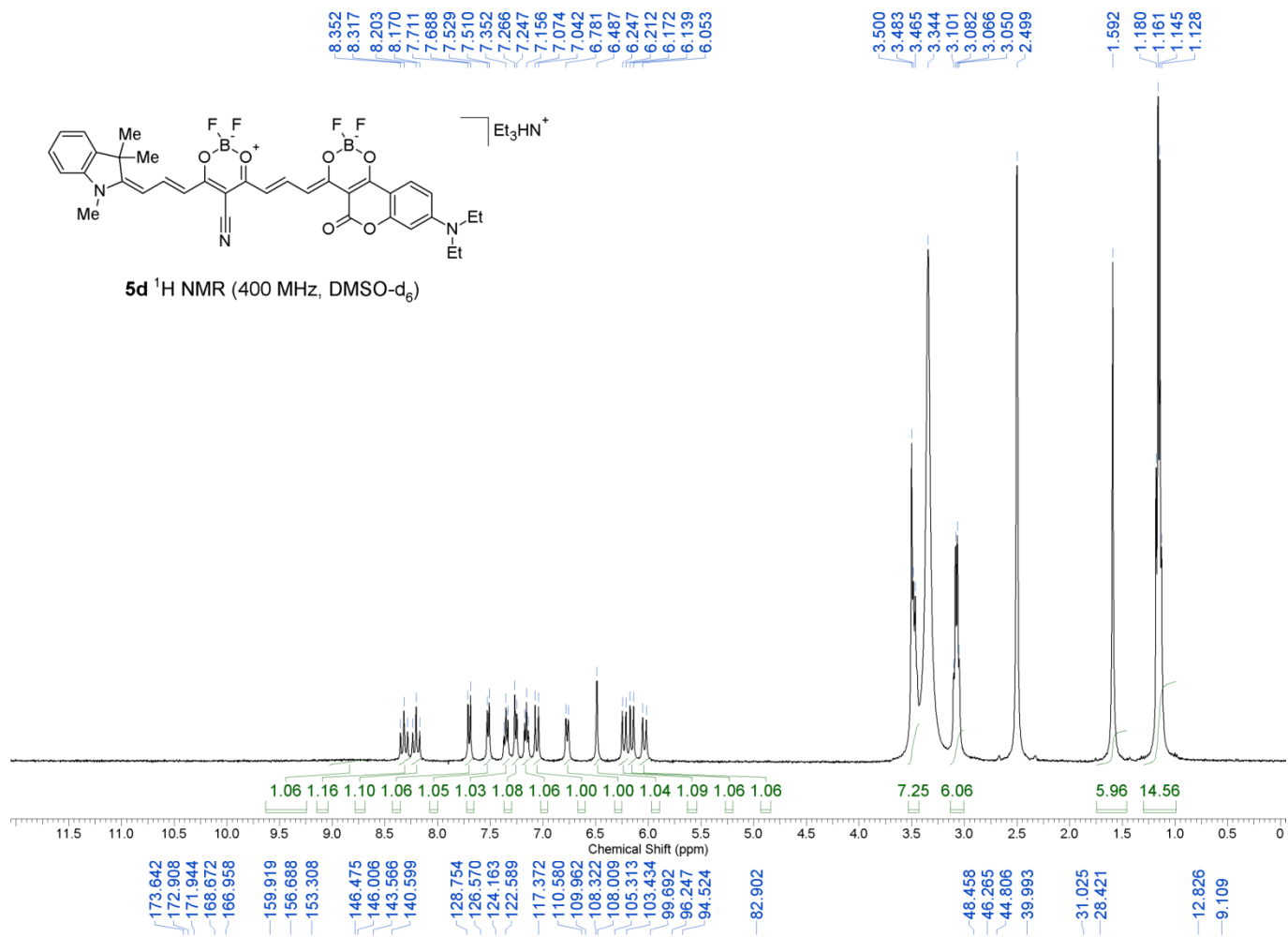


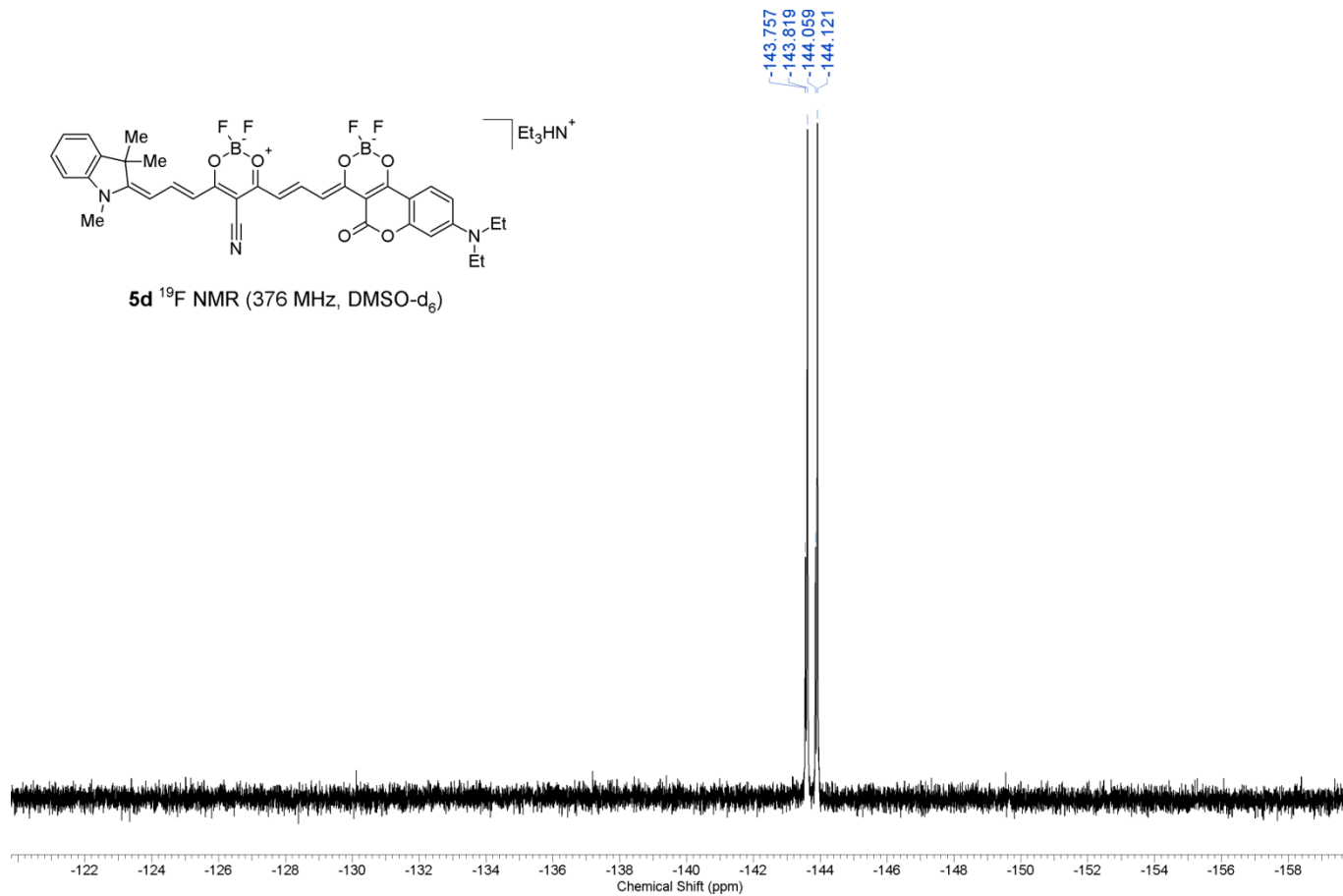




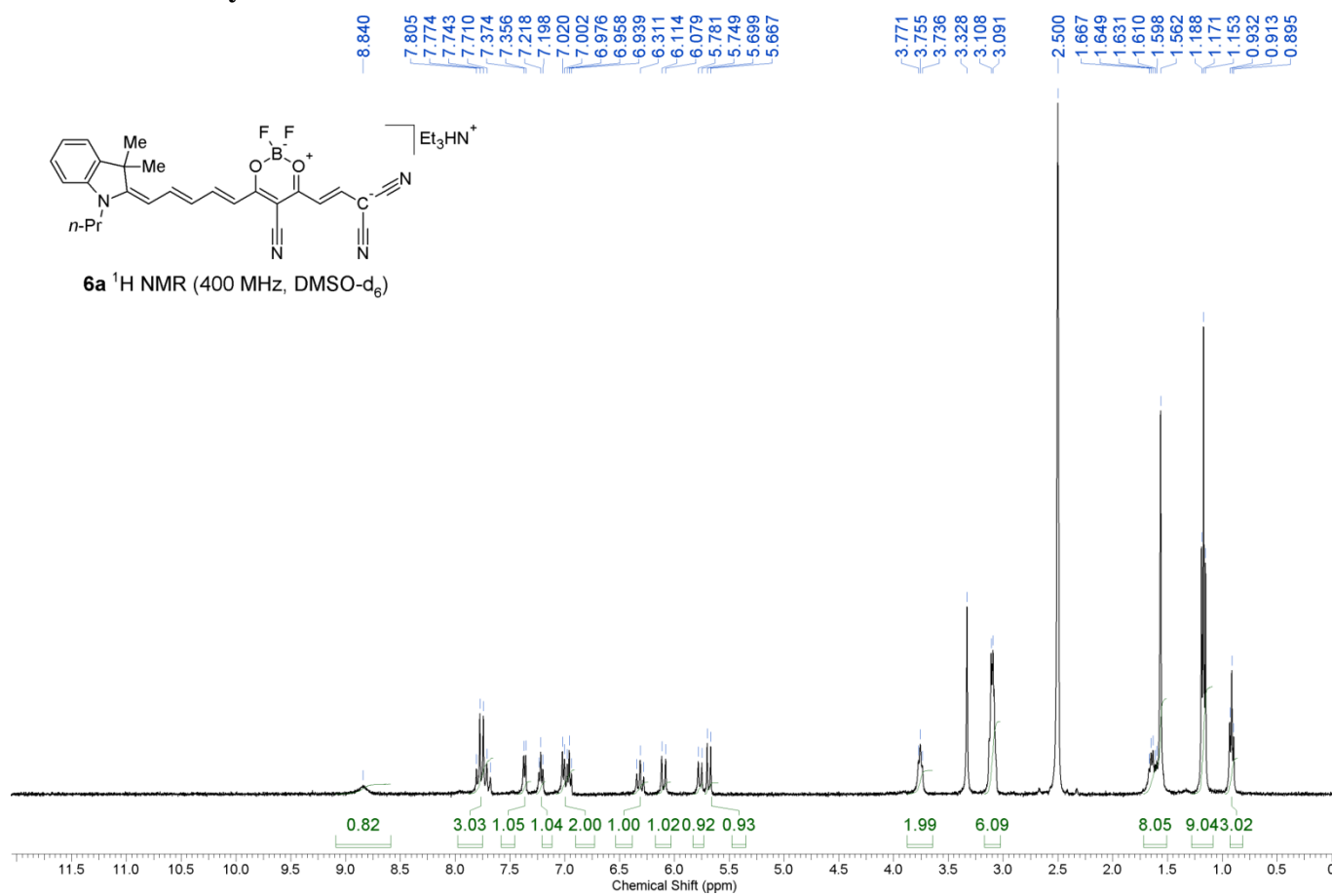


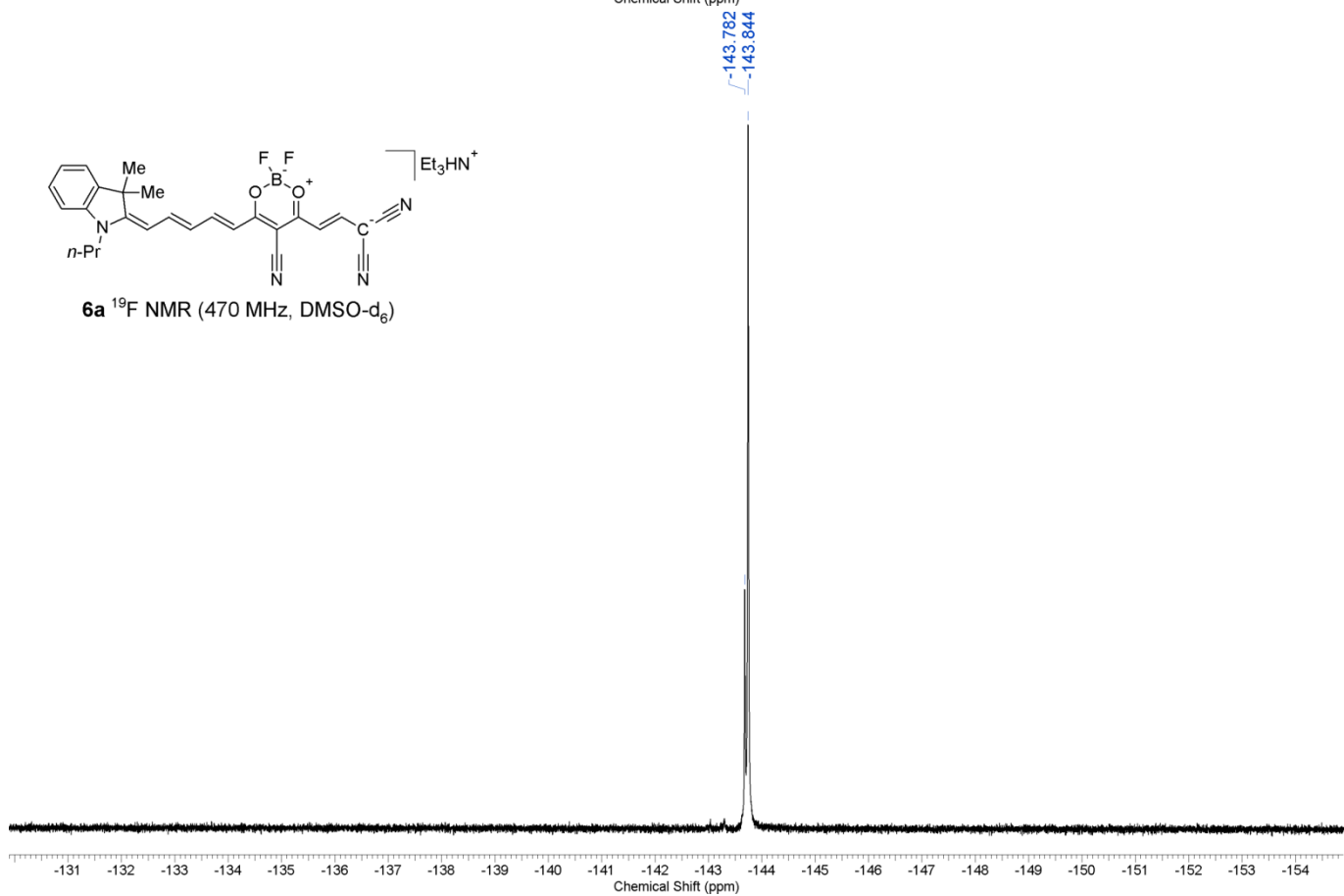
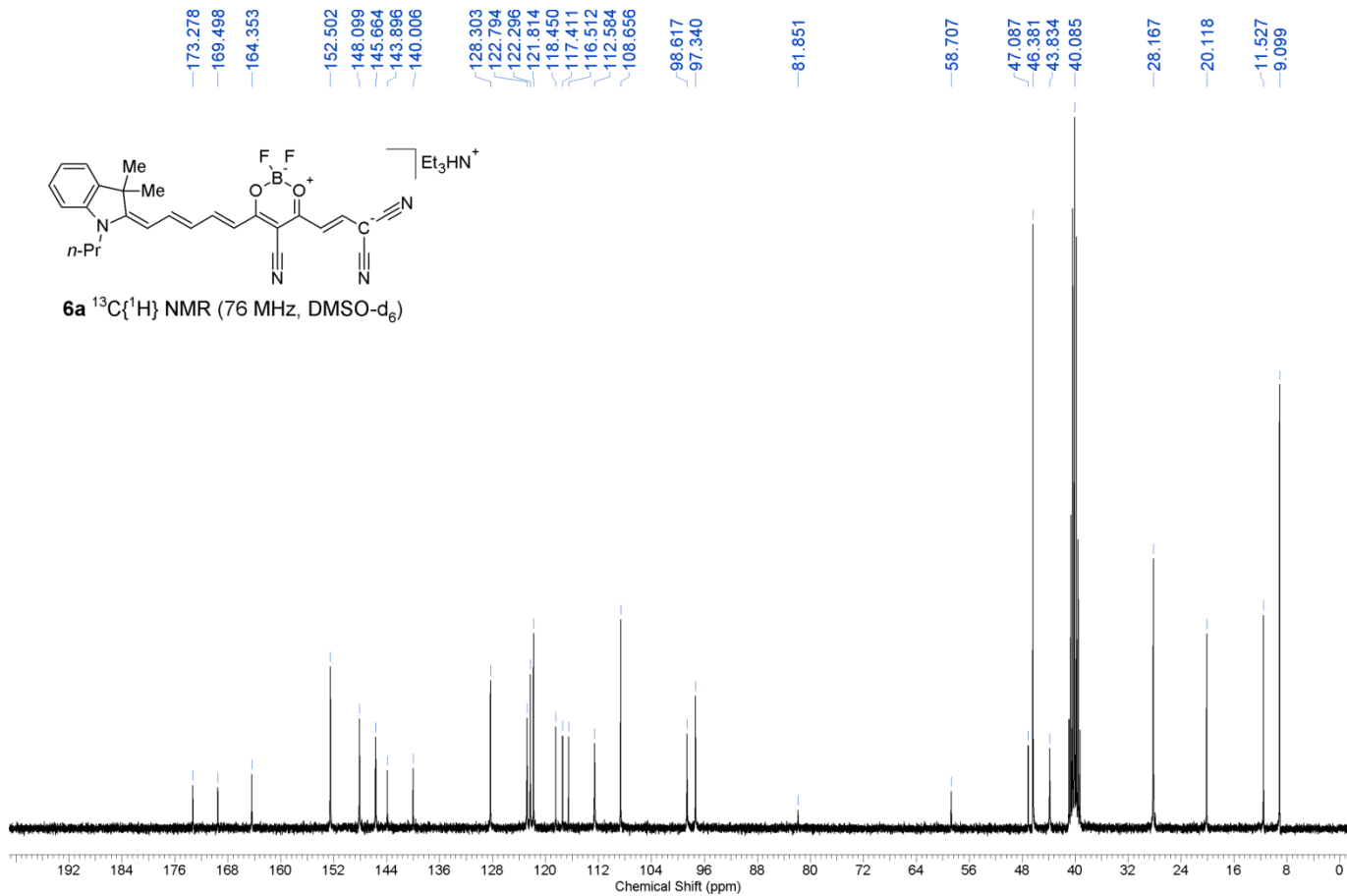


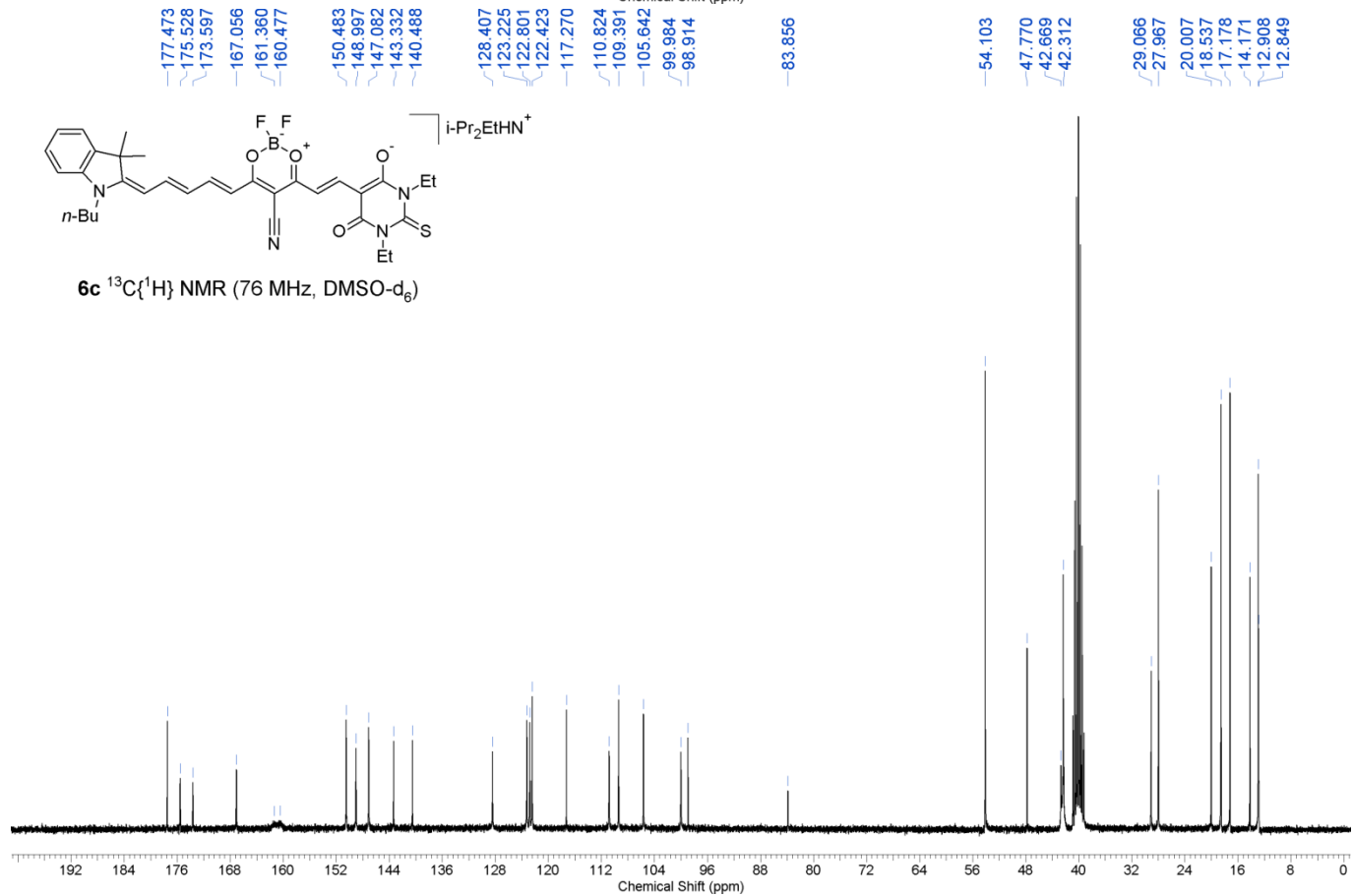
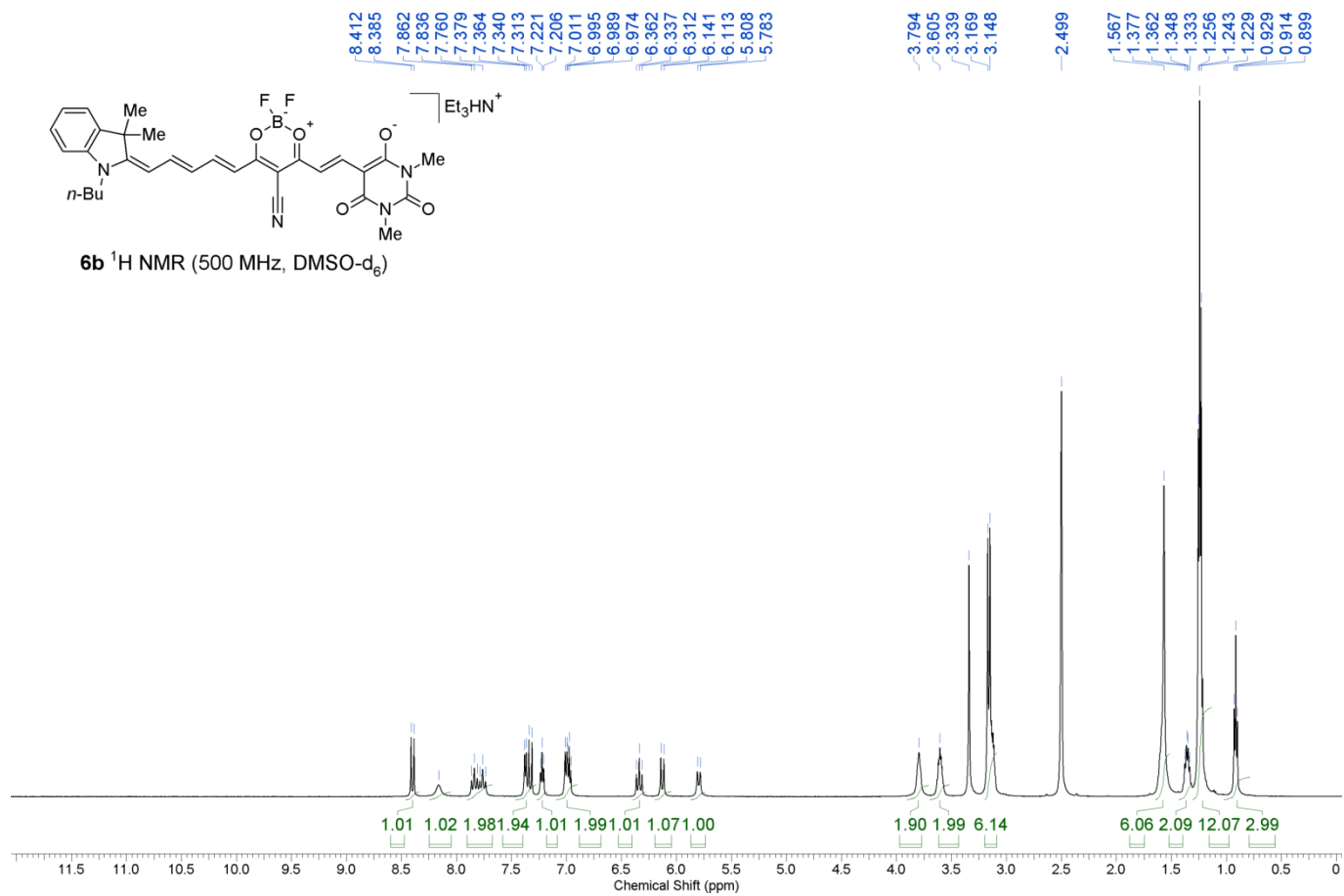


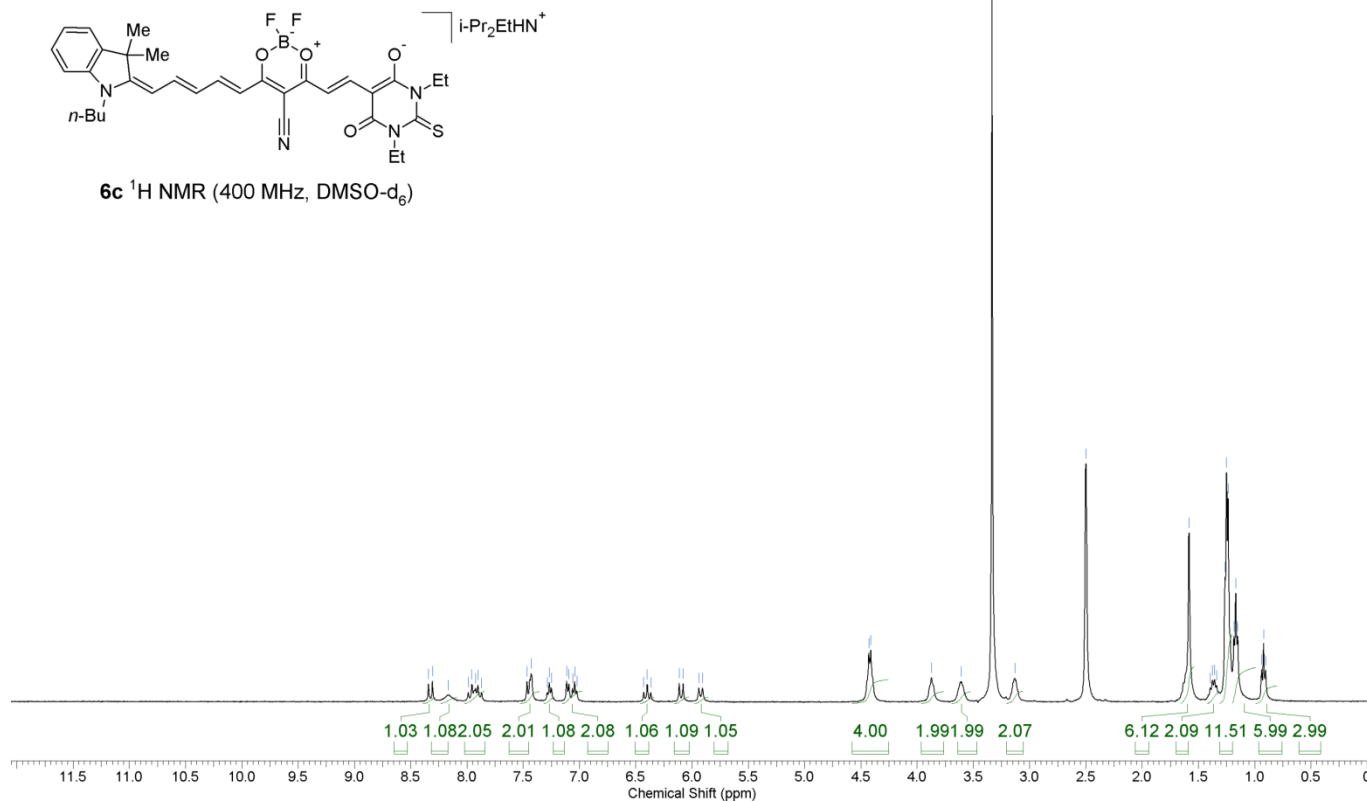
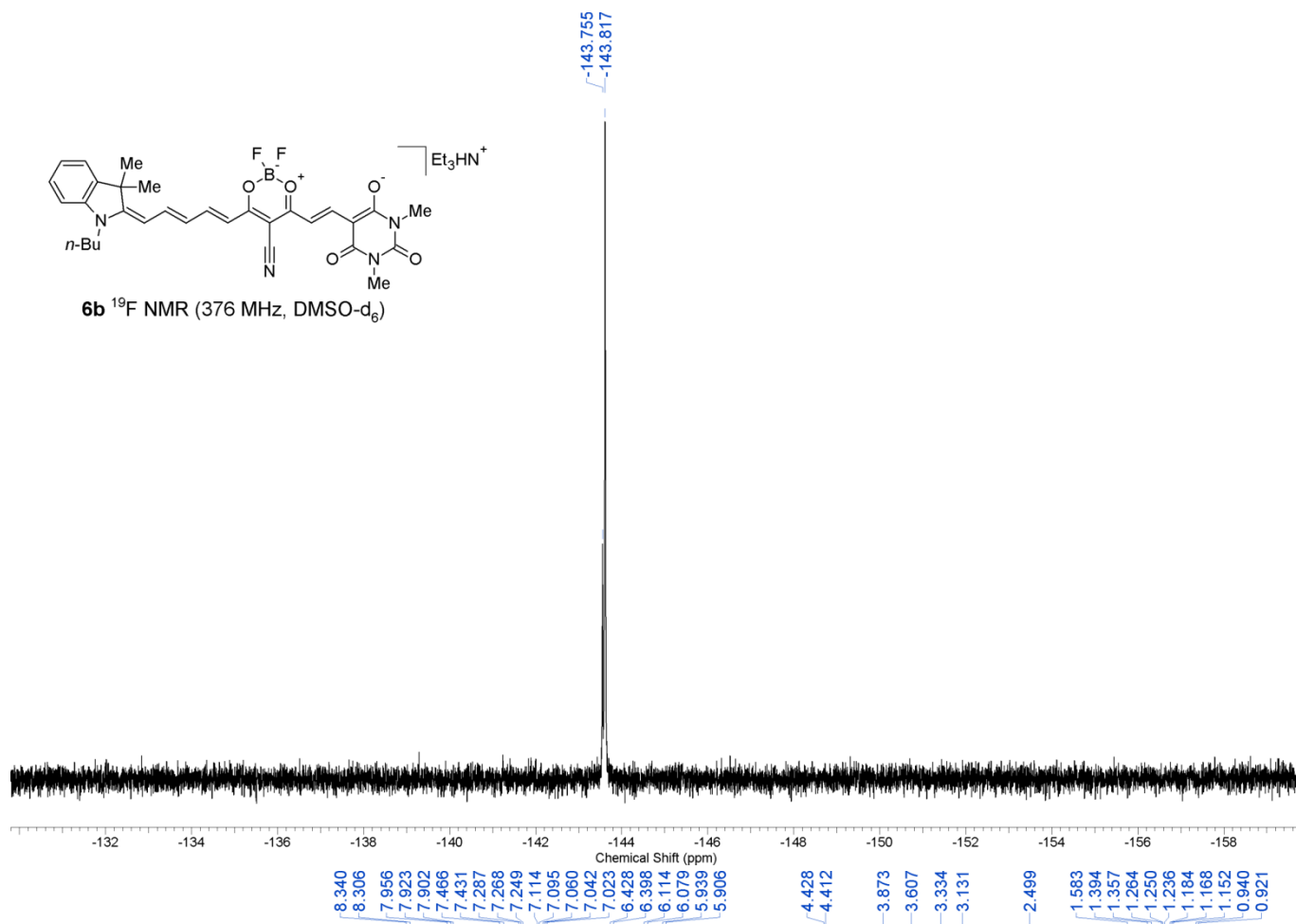


Mero-Anionic Dyes 6a-d









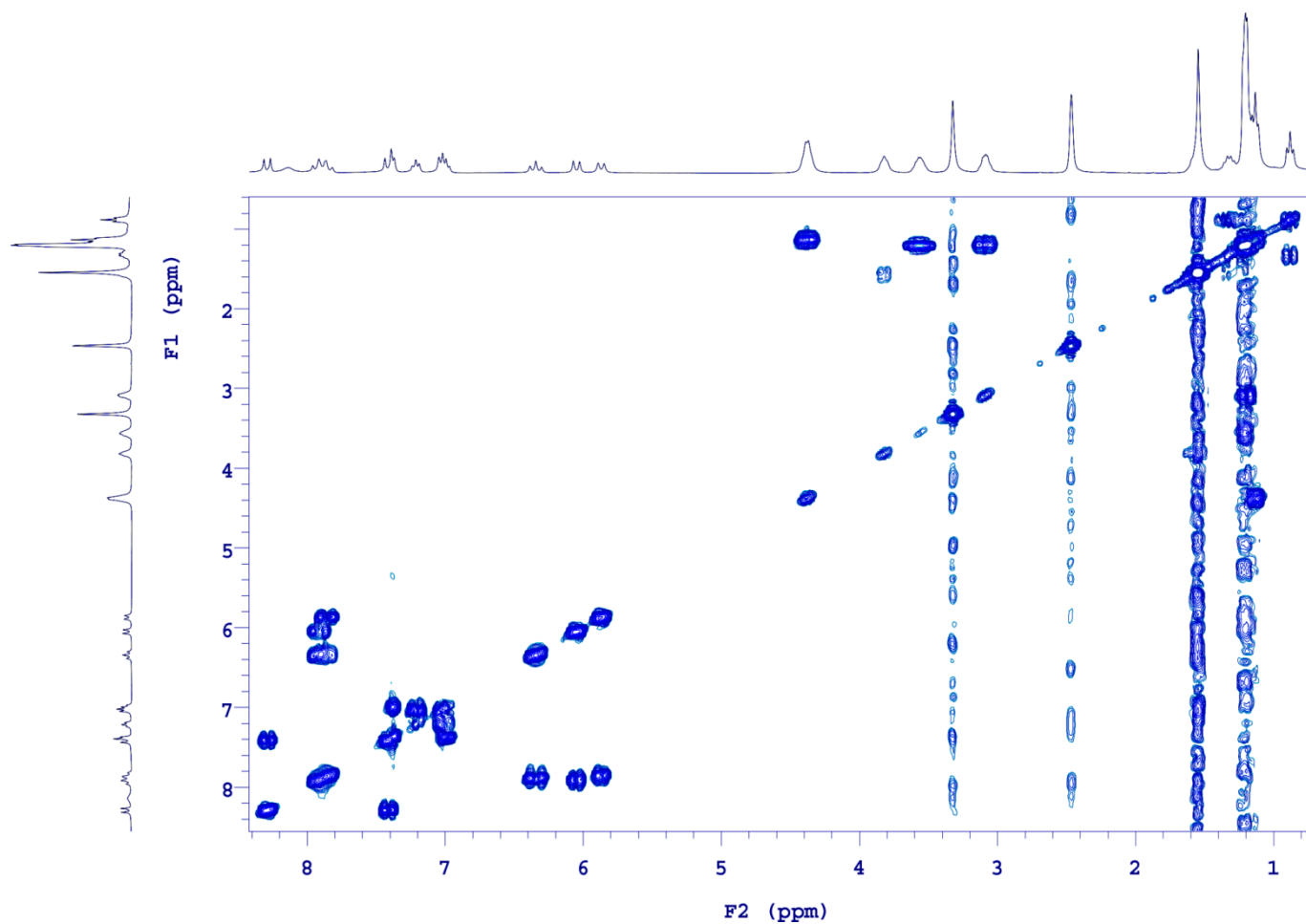
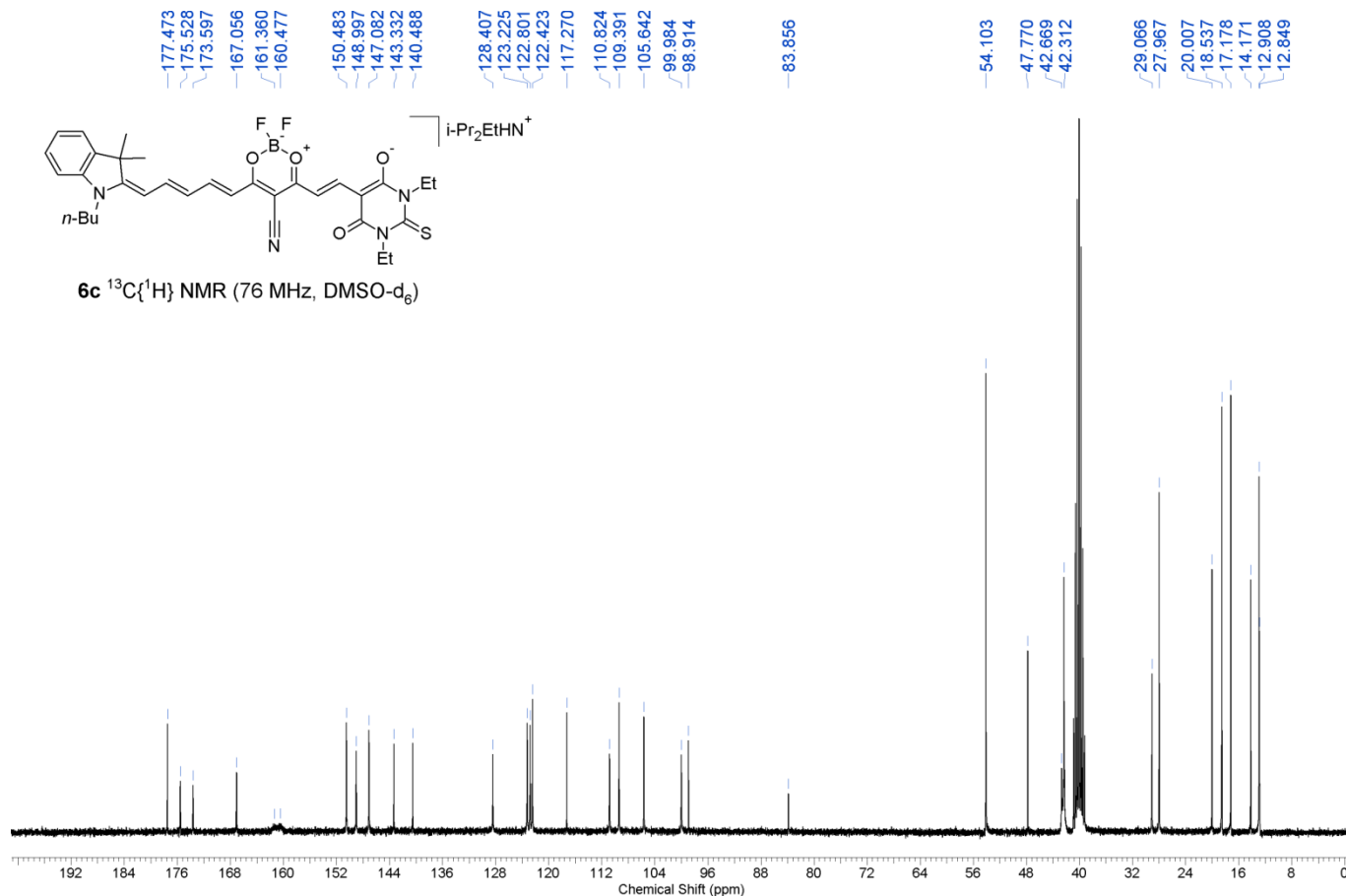
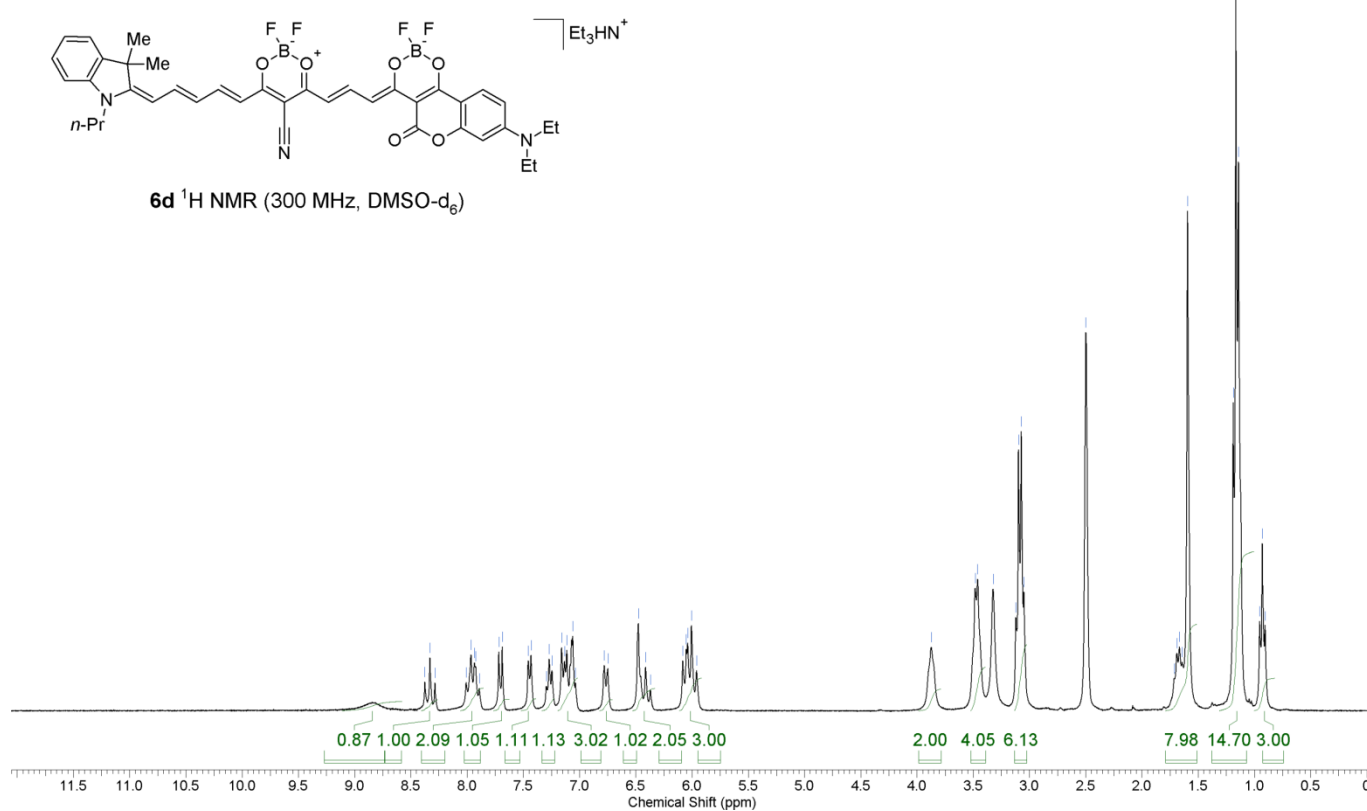
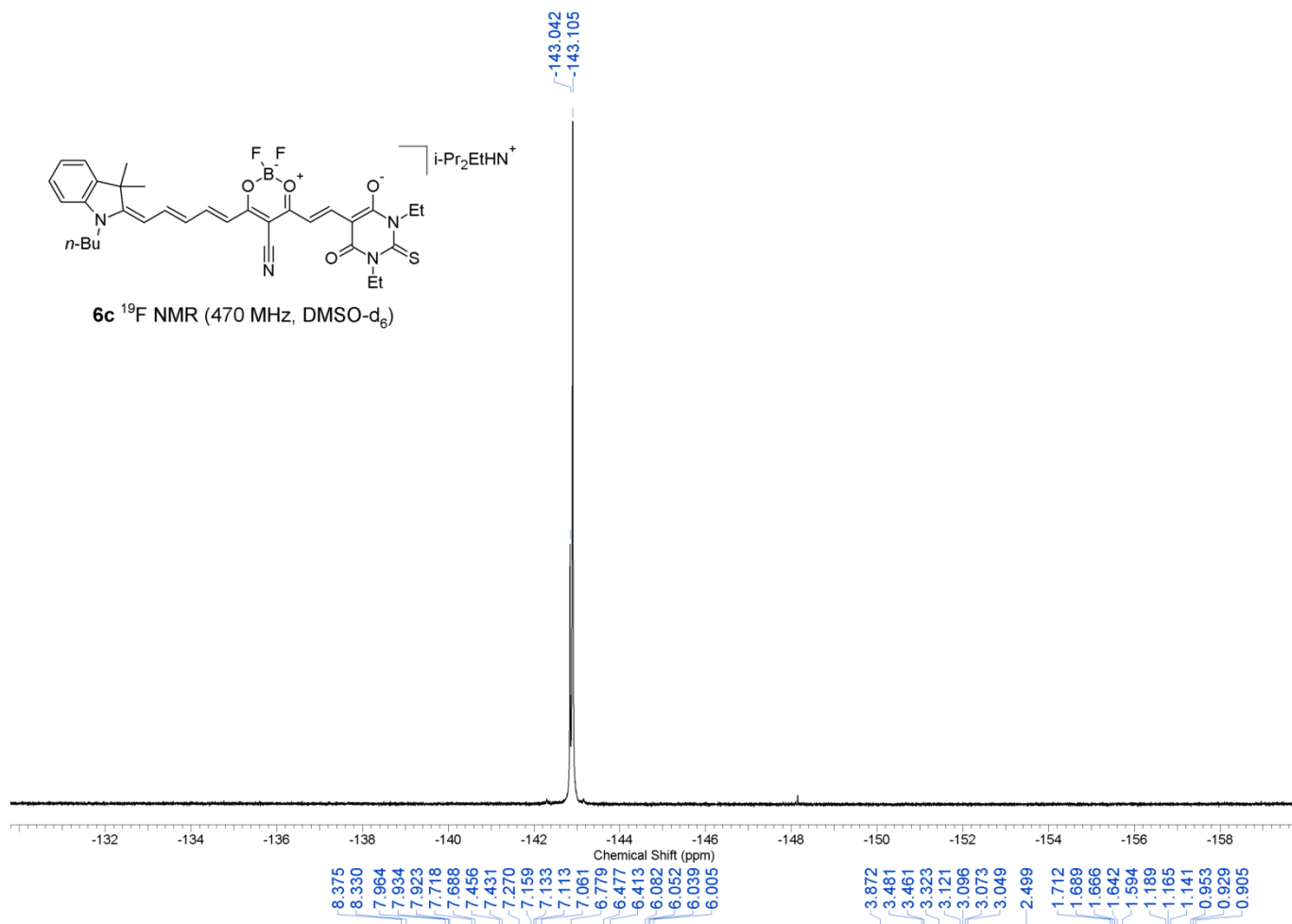


Figure S9. COSY NMR spectrum of **6c** (DMSO- d_6 , 300 MHz)





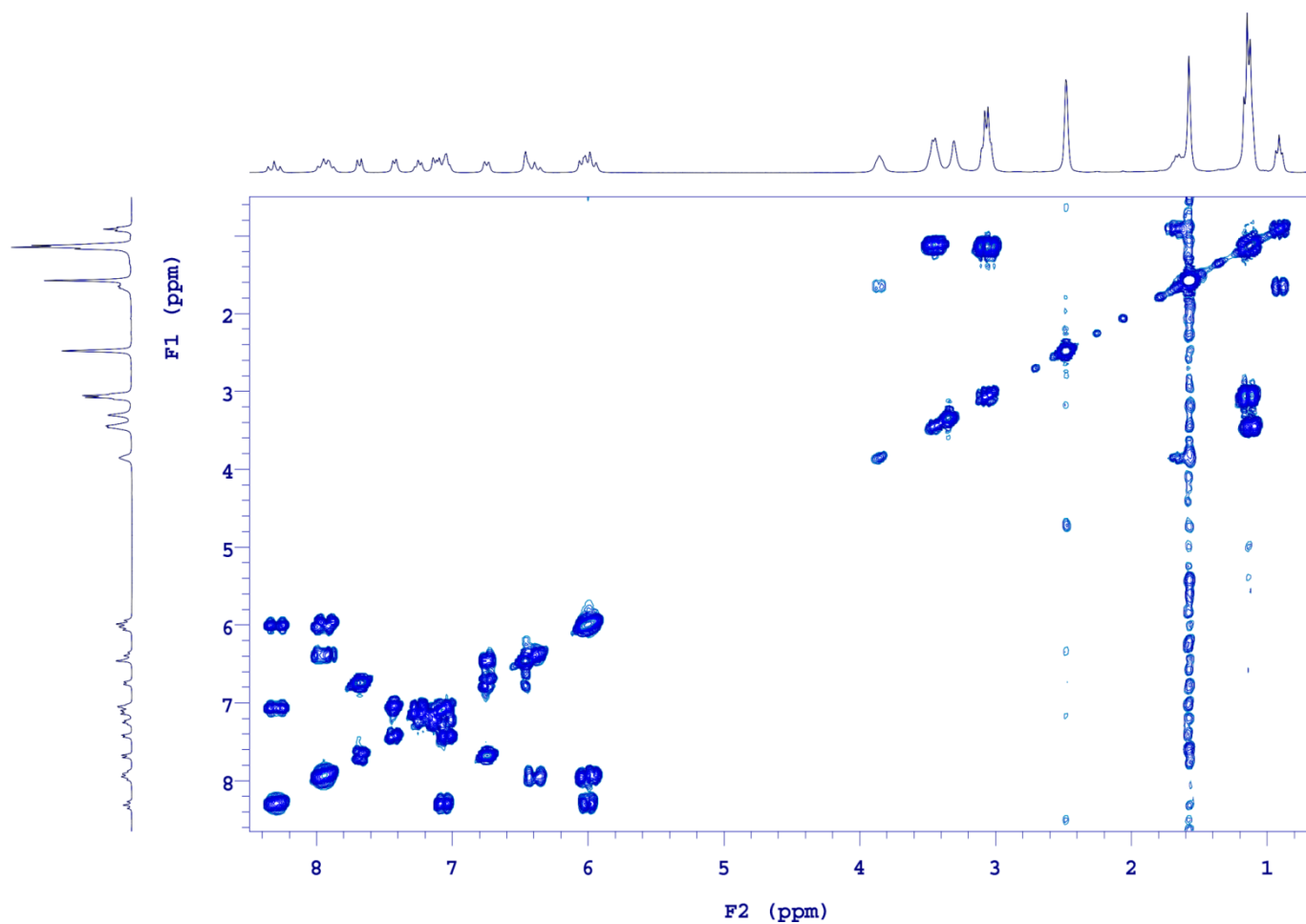
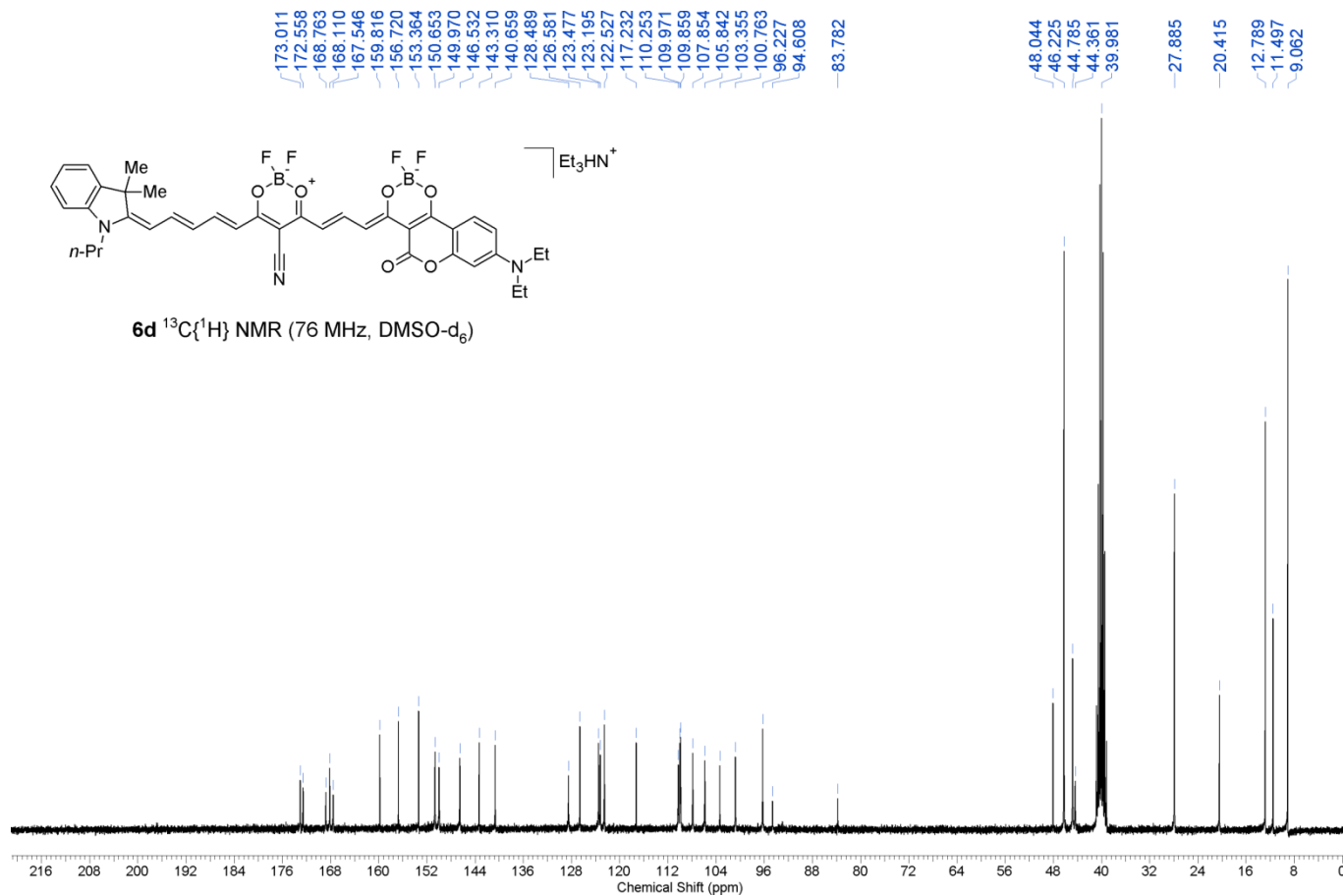
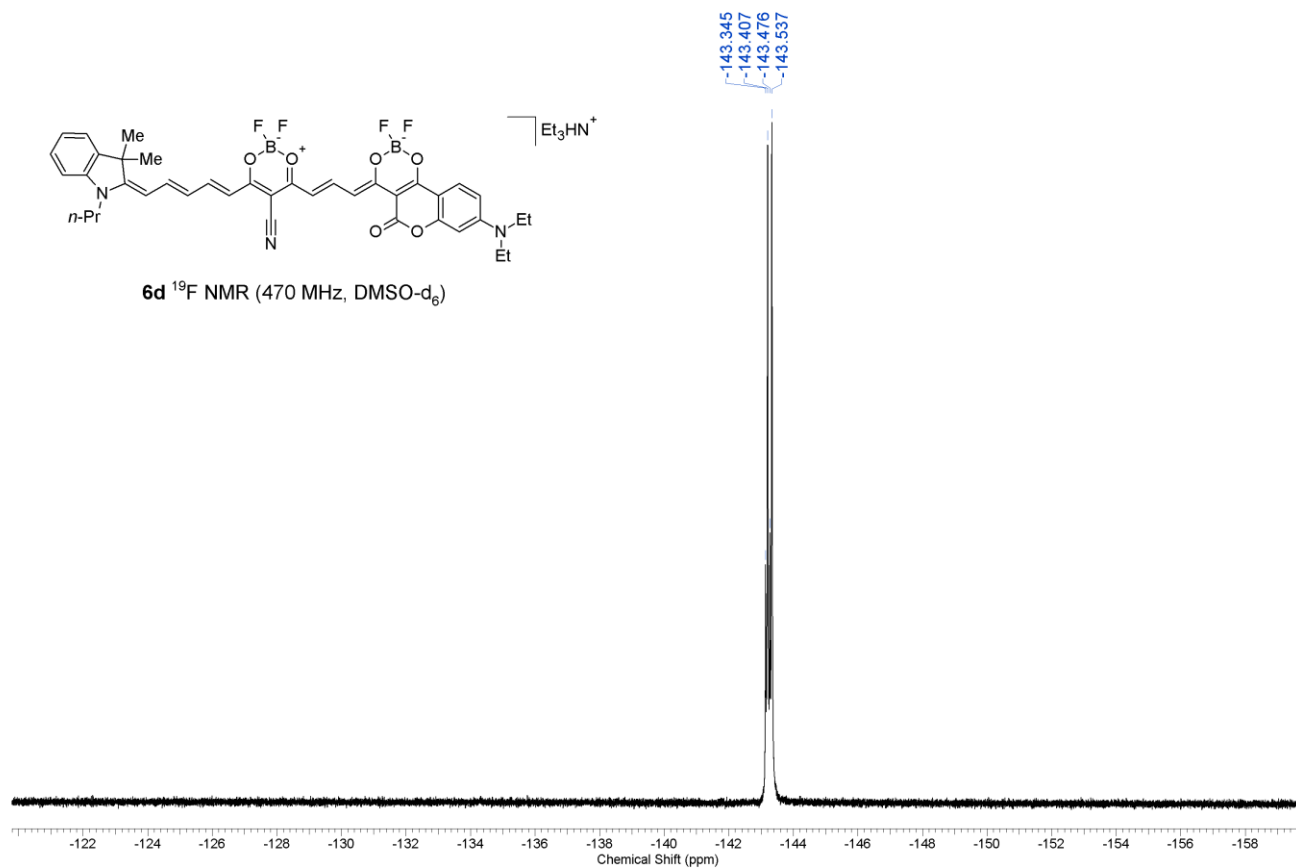
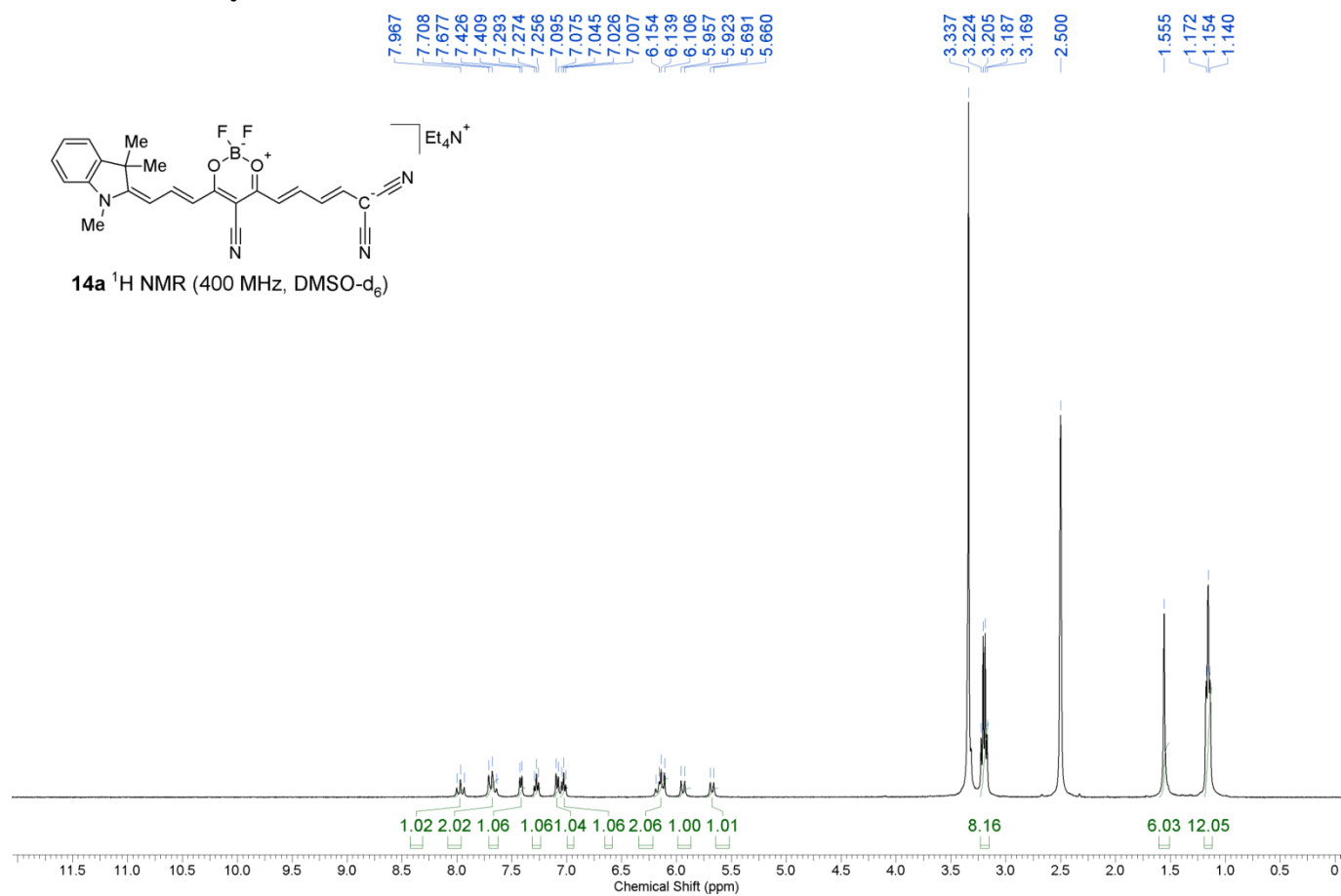


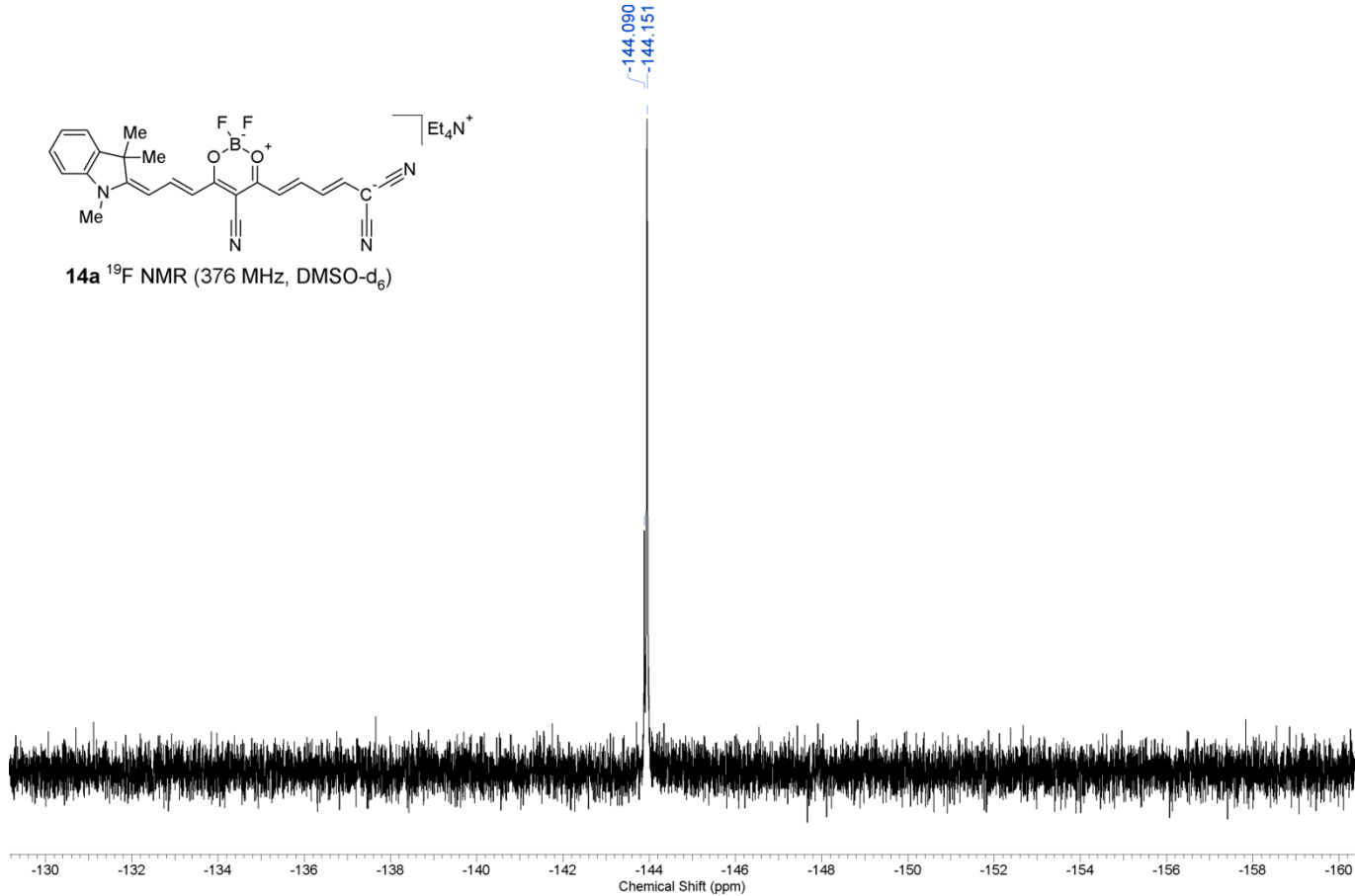
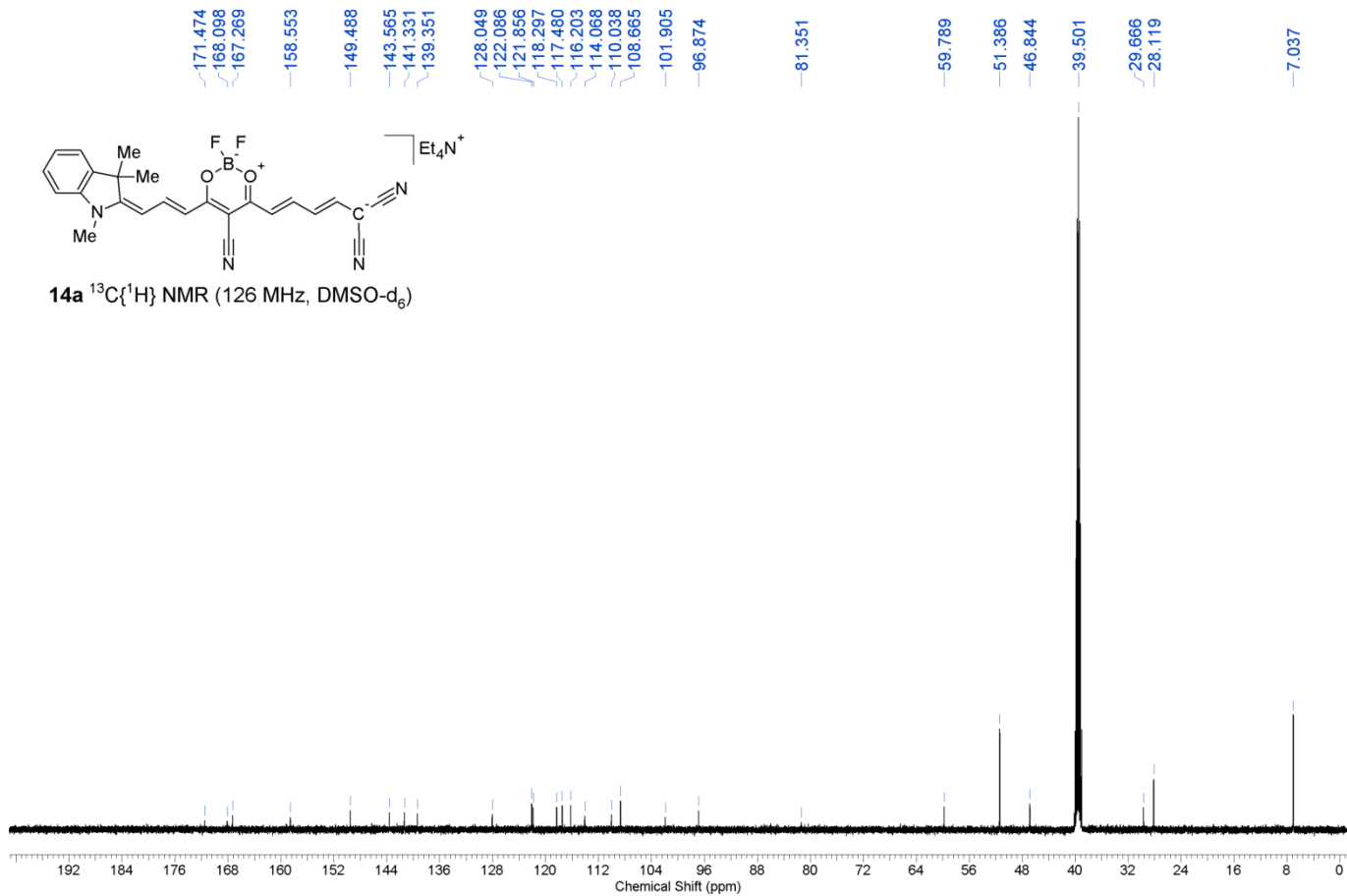
Figure S10. COSY NMR spectrum of **6d** (DMSO- d_6 , 300 MHz)

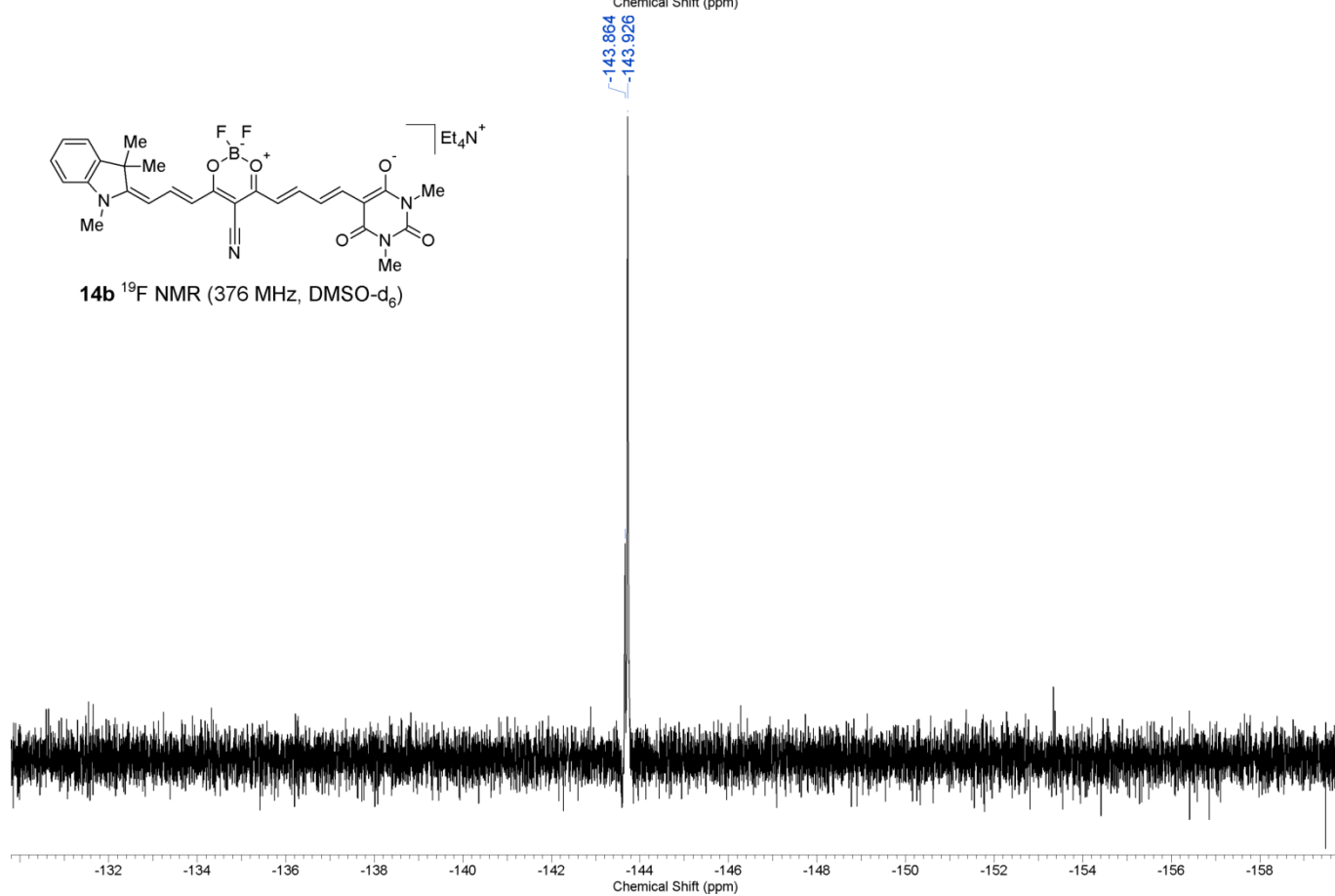
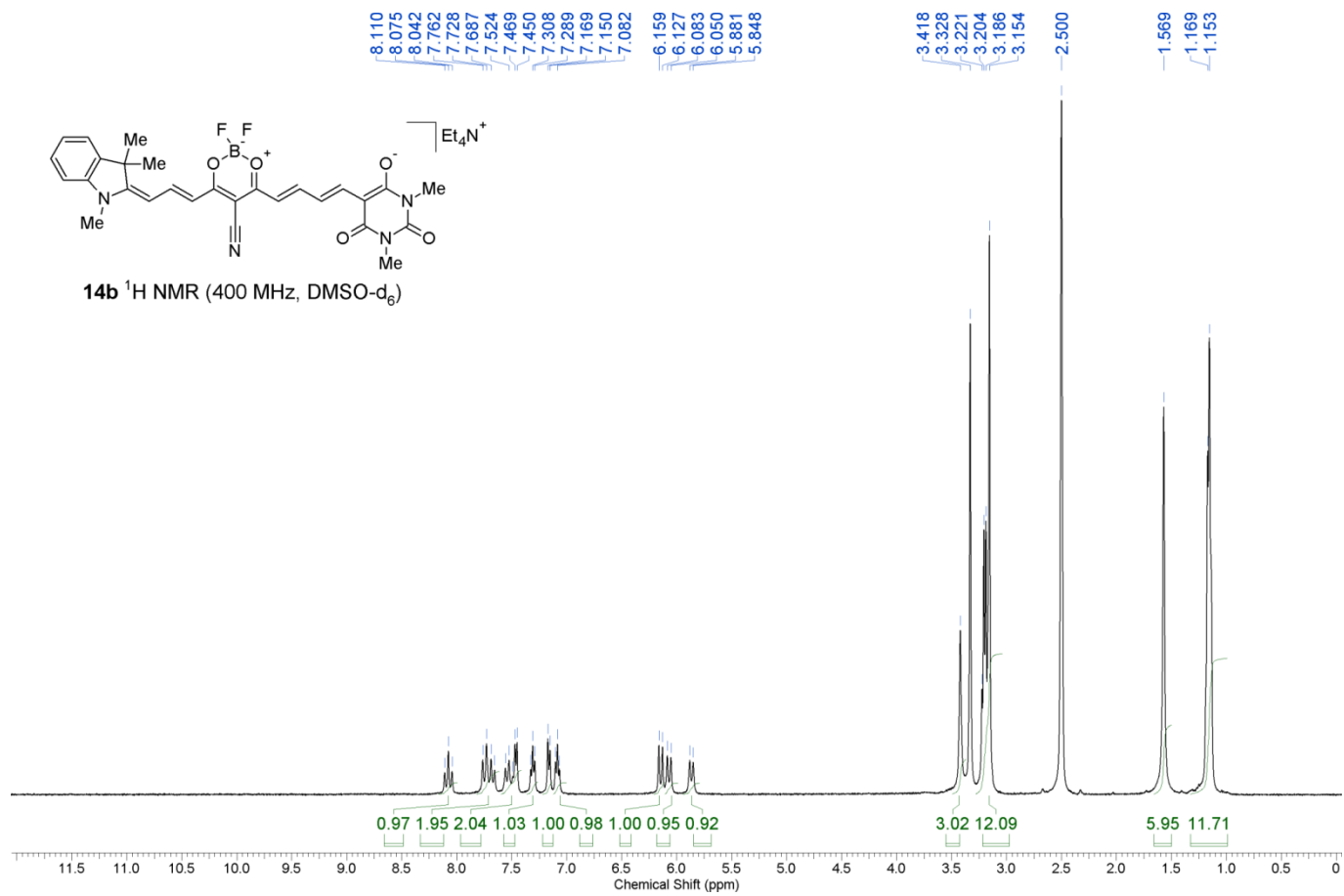


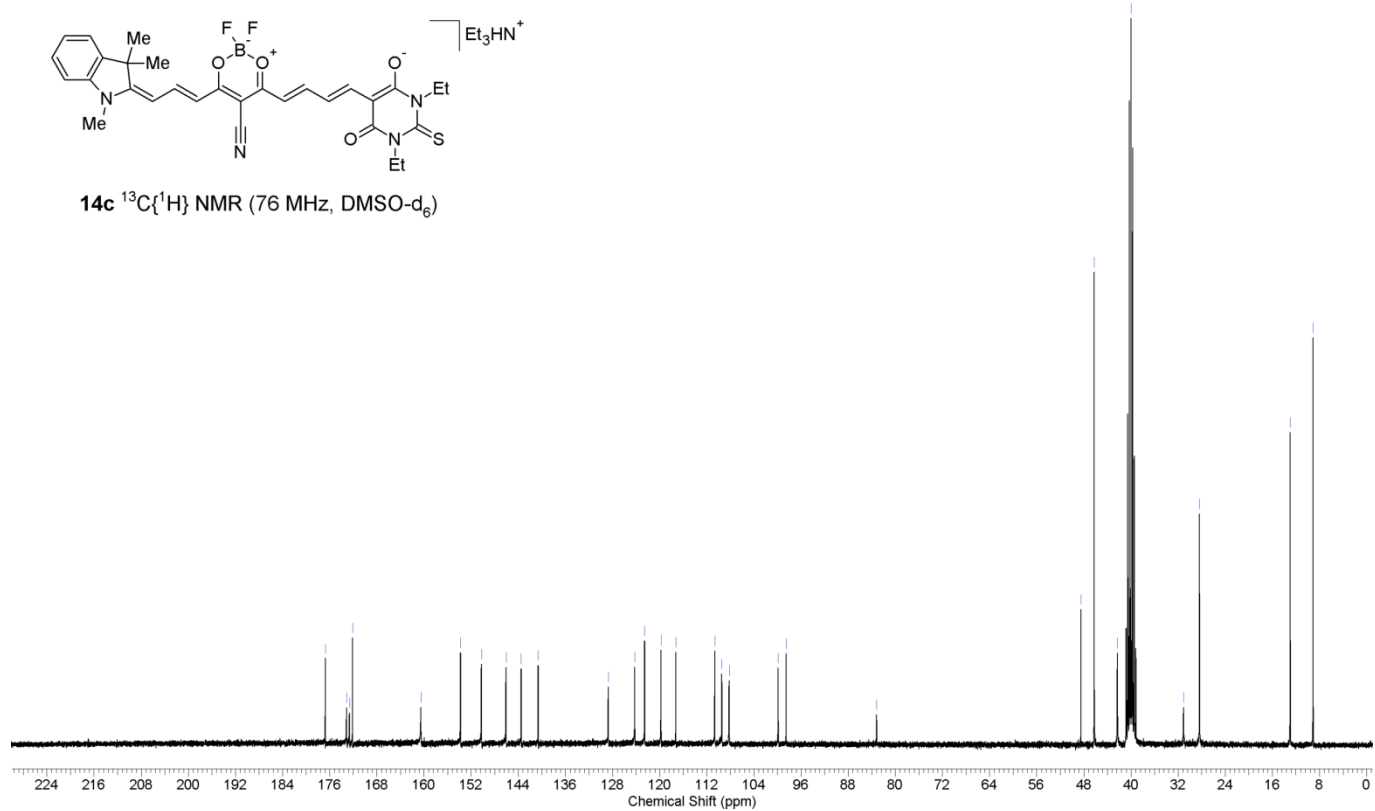
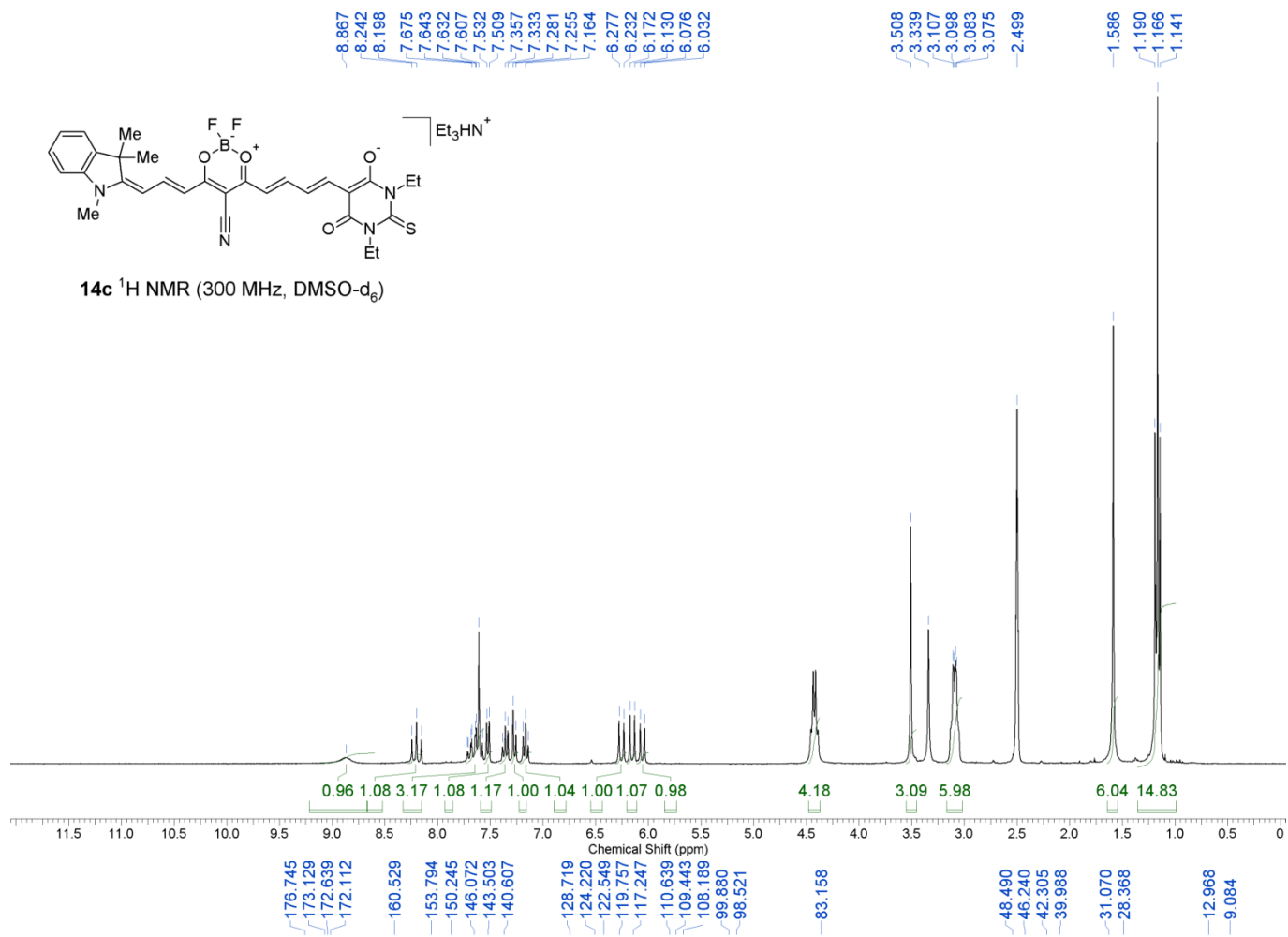


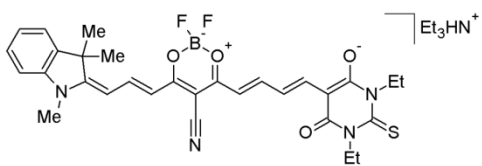
Mero-Anionic Dyes 14a-c



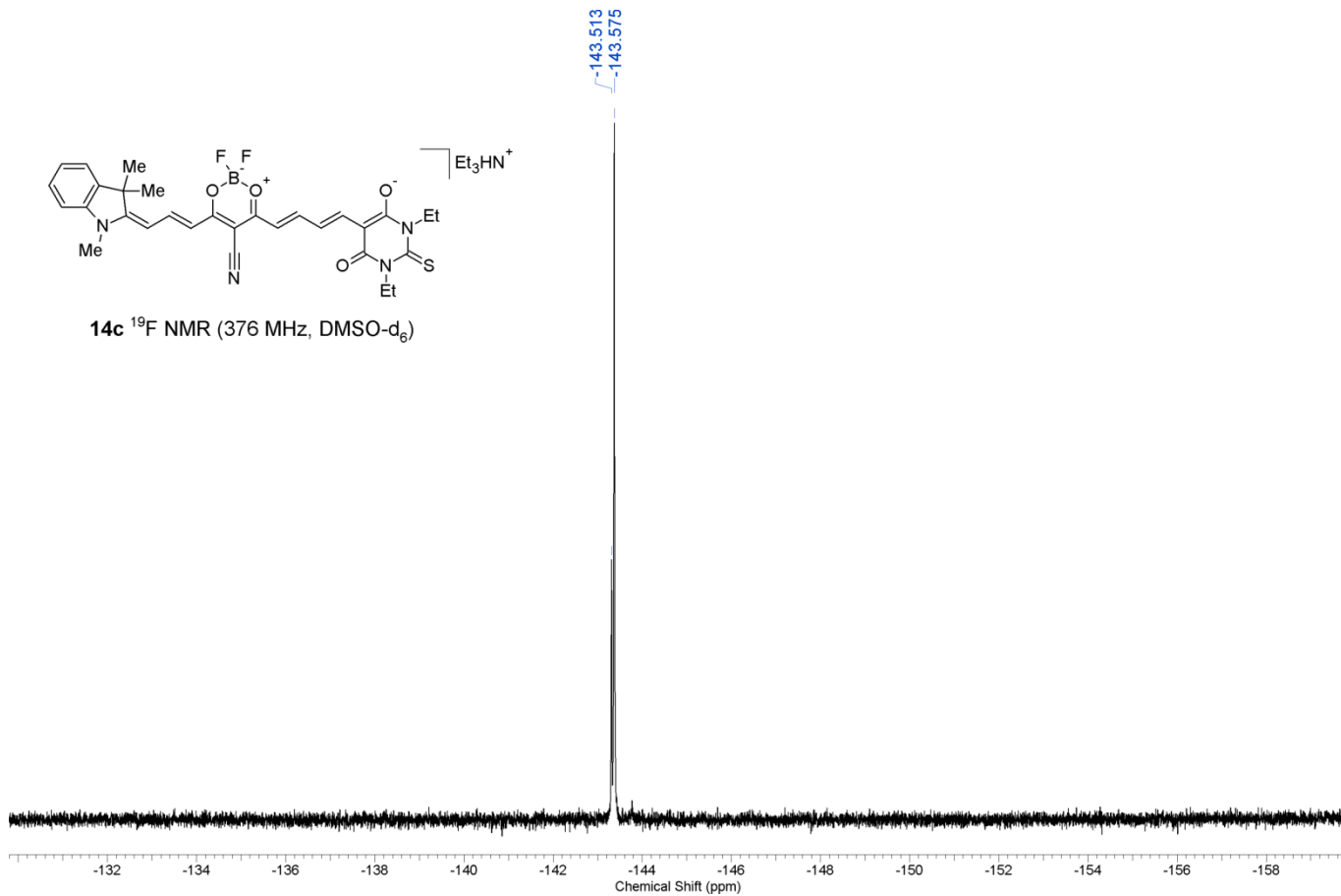








14c ^{19}F NMR (376 MHz, DMSO-d_6)



References

- 1 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.
- 2 A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735–746.