Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Domino synthesis of protochromic “ON-OFF-ON” luminescent 2-styryl quinolines

Rahime Cinar, Jan Nordmann, Elena Dirksen, Thomas J. J. Müller*

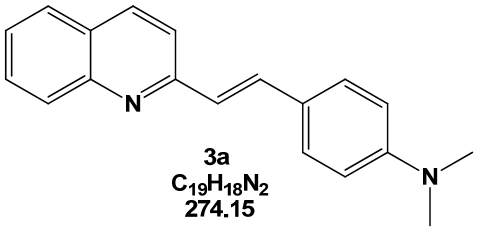
Institut für Organische Chemie und Makromolekulare Chemie, Heinrich-Heine-Universität Düsseldorf Universitätsstraße 1, 40225 Düsseldorf, Germany

Email: ThomasJJ.Mueller@uni-duesseldorf.de

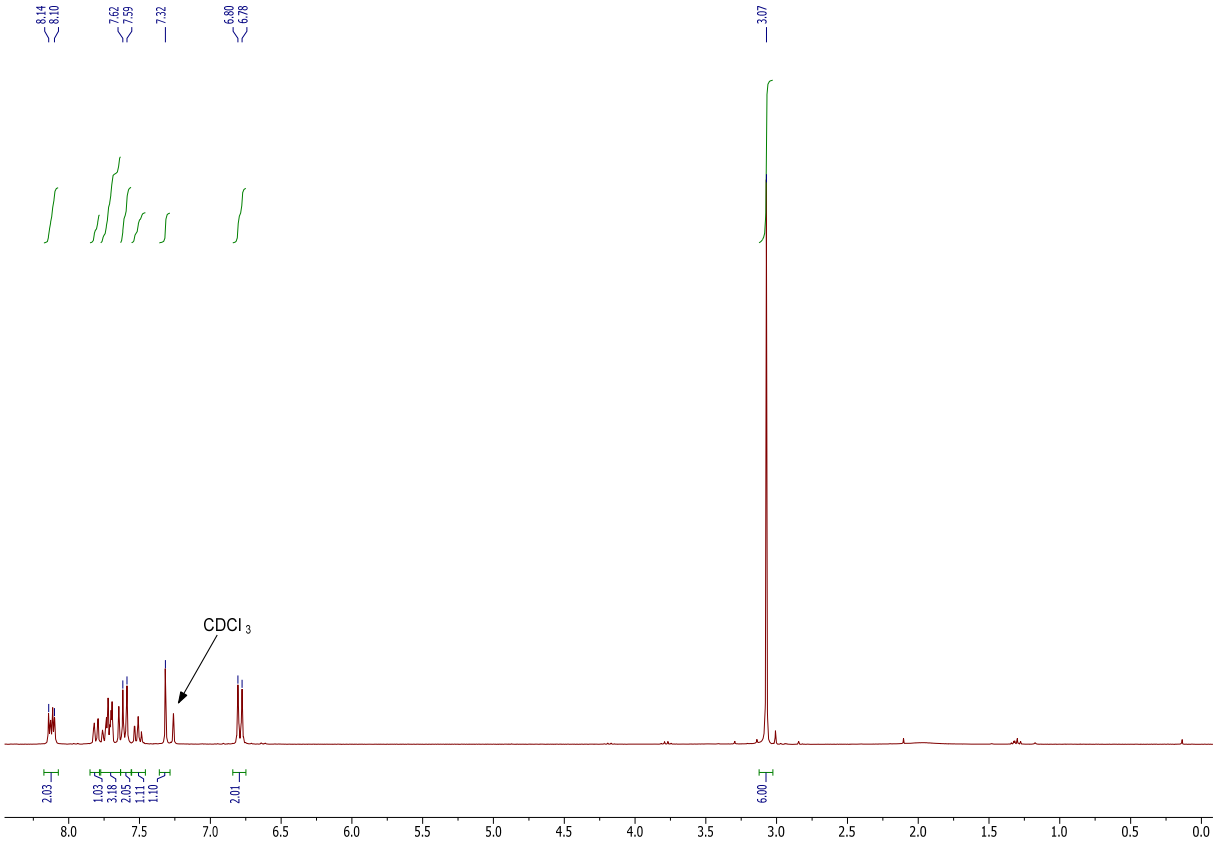
Table of contents

1 ^{1}H and ^{13}C NMR spectra of 2-styrylquinoline 3a-3c

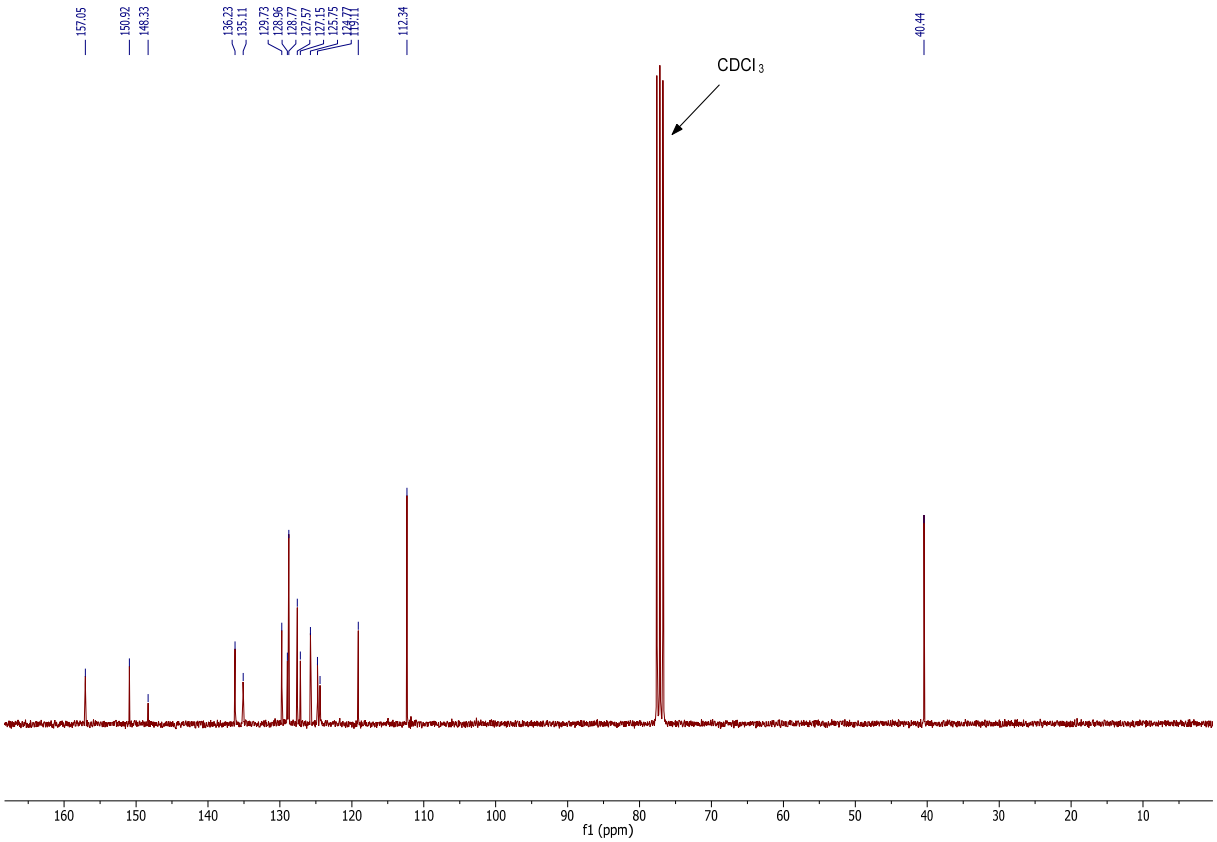
1.1 (*E*)-2-(4-Dimethylamino)styryl)-quinoline (3a)



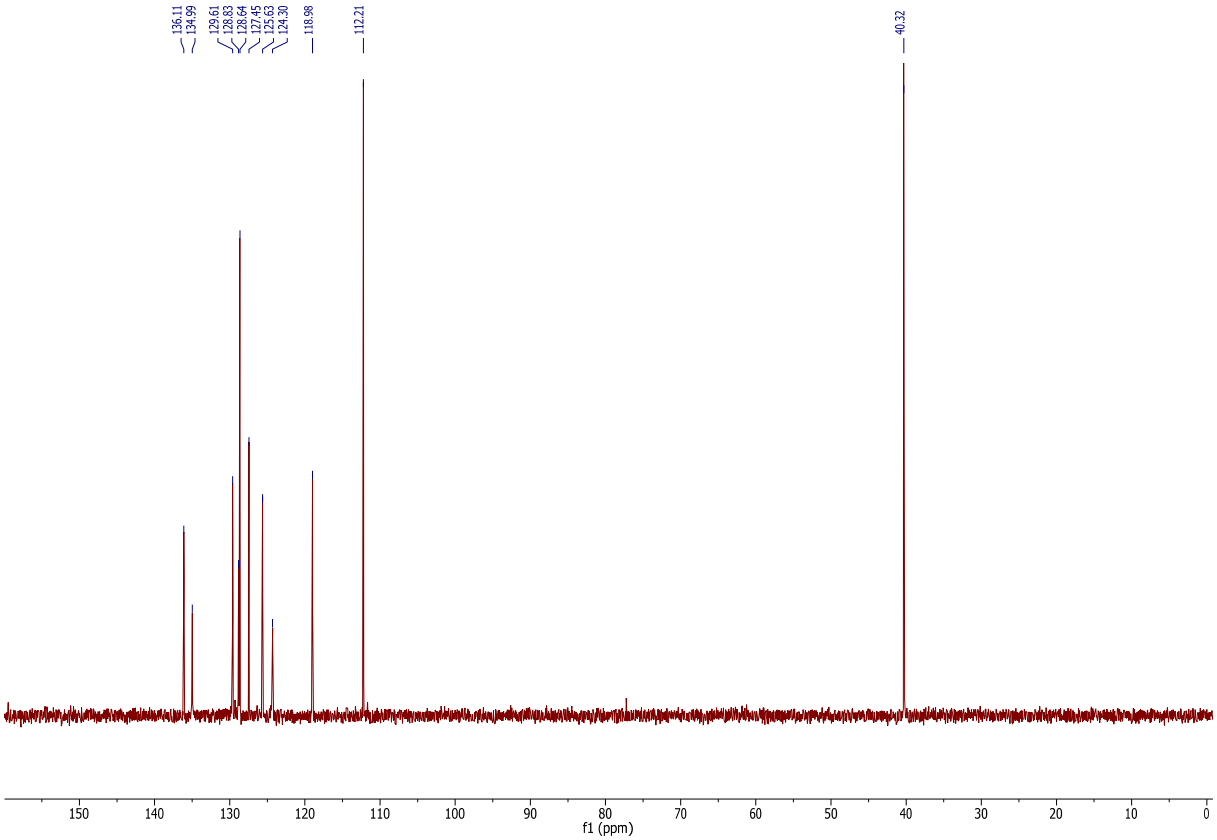
3a
$C_{19}H_{18}N_2$
274.15



^{1}H NMR (300 MHz) of **3a** (20 mg) in $CDCl_3$ at 298 K.

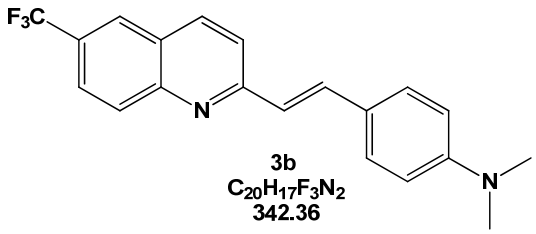


^{13}C NMR (75 MHz) of **3a** (20 mg) in $CDCl_3$ at 298 K.

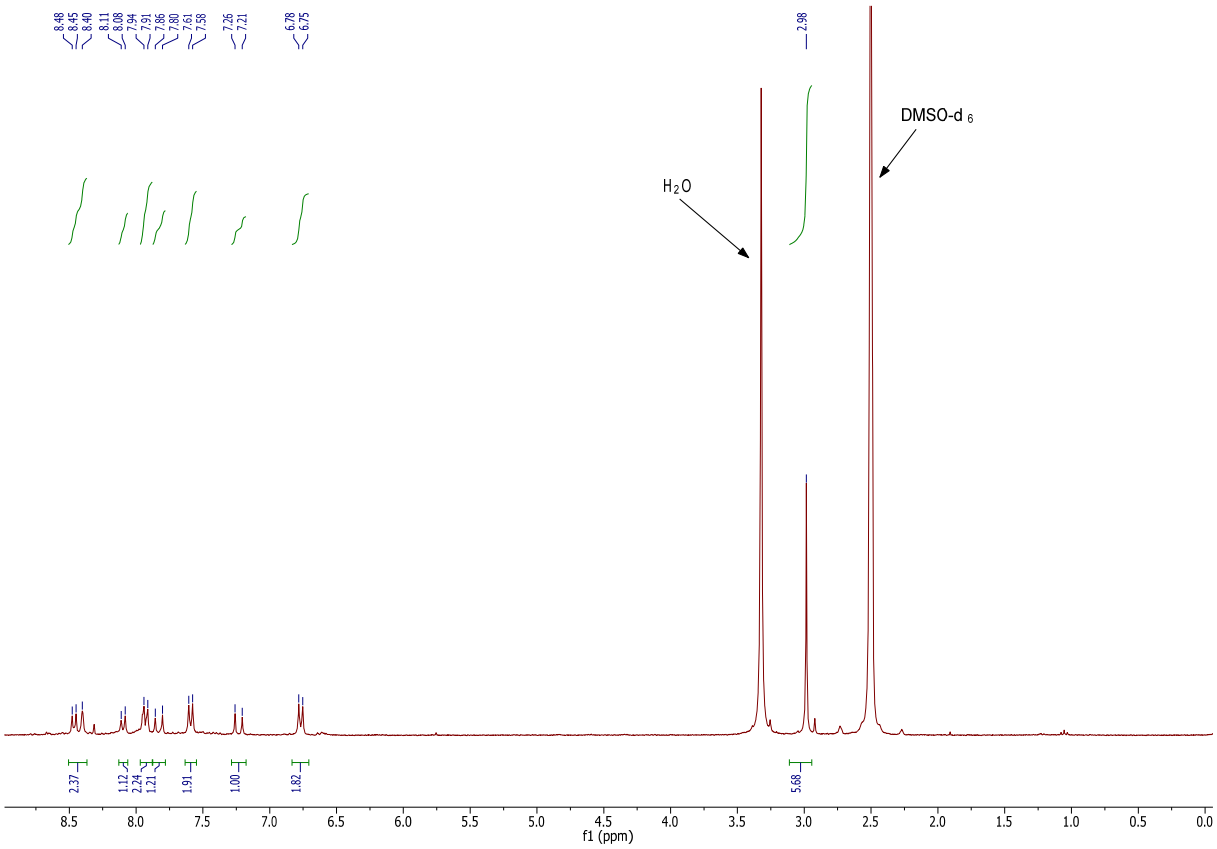


^{13}C-DEPT 135 NMR (75 MHz) of **3a** (20 mg) in $CDCl_3$ at 298 K.

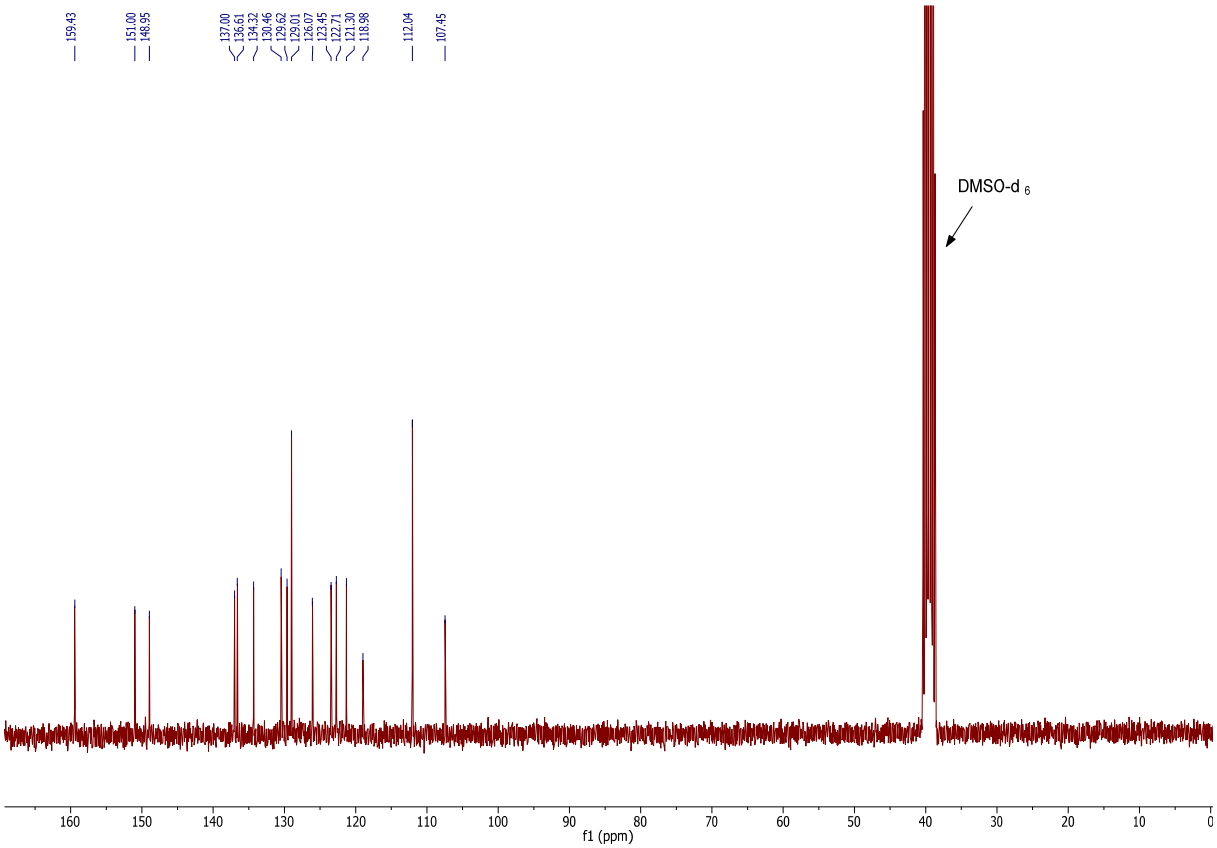
1.2 (*E*)-2-(4-Dimethylamino)styryl)-quinoline-6-trifluoromethane (3b)



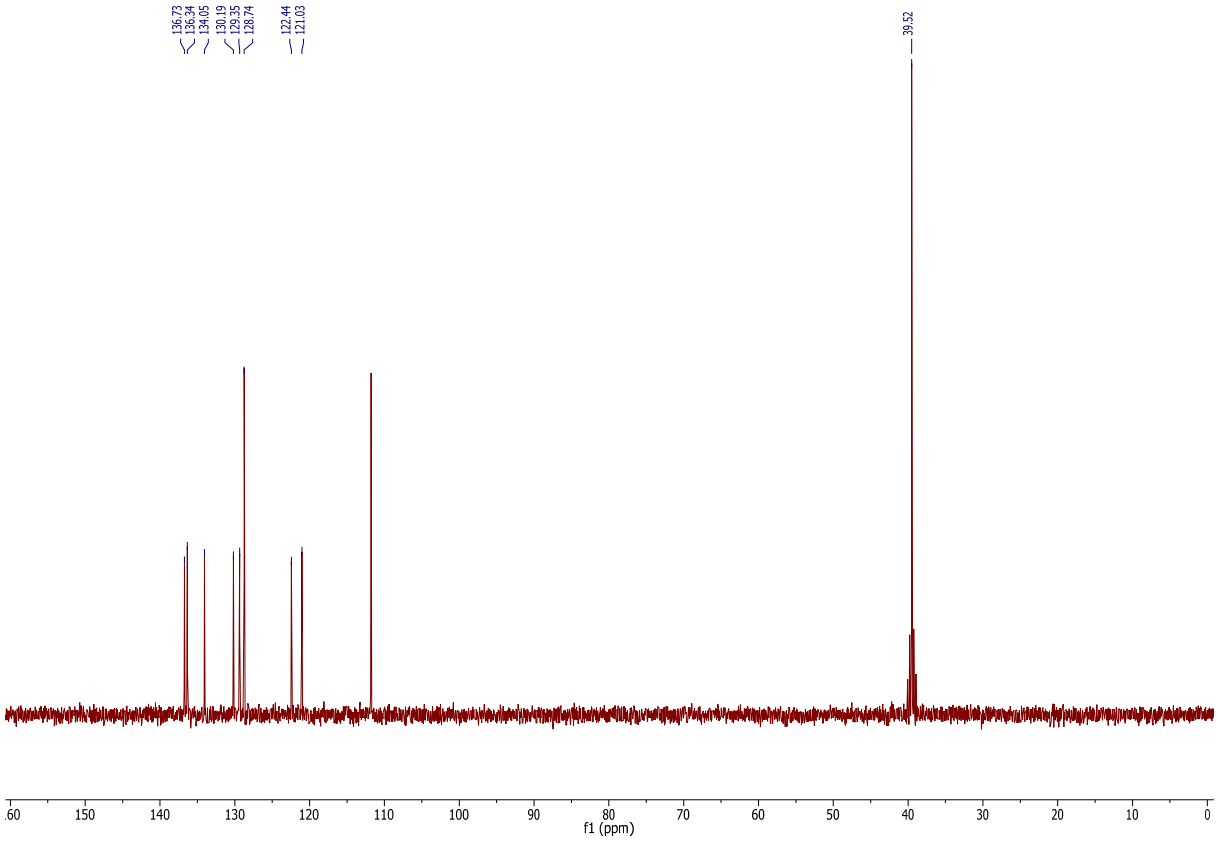
3b
$C_{20}H_{17}F_3N_2$
342.36



^{1}H NMR (300 MHz) of **3b** (20 mg) in DMSO-d_6 at 298 K.

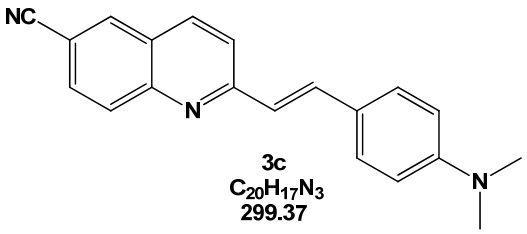


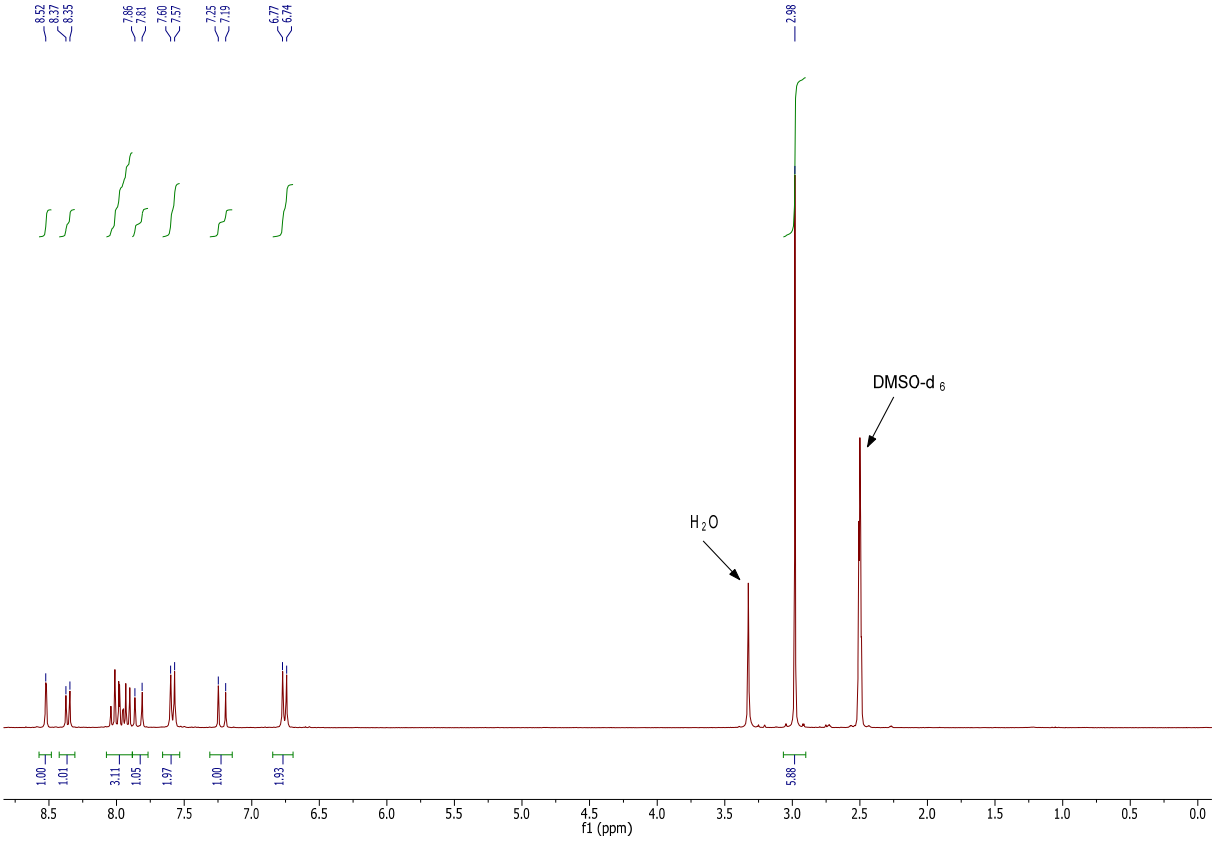
^{13}C NMR (75 MHz) of **3c** (20 mg) in DMSO-d_6 at 298 K.



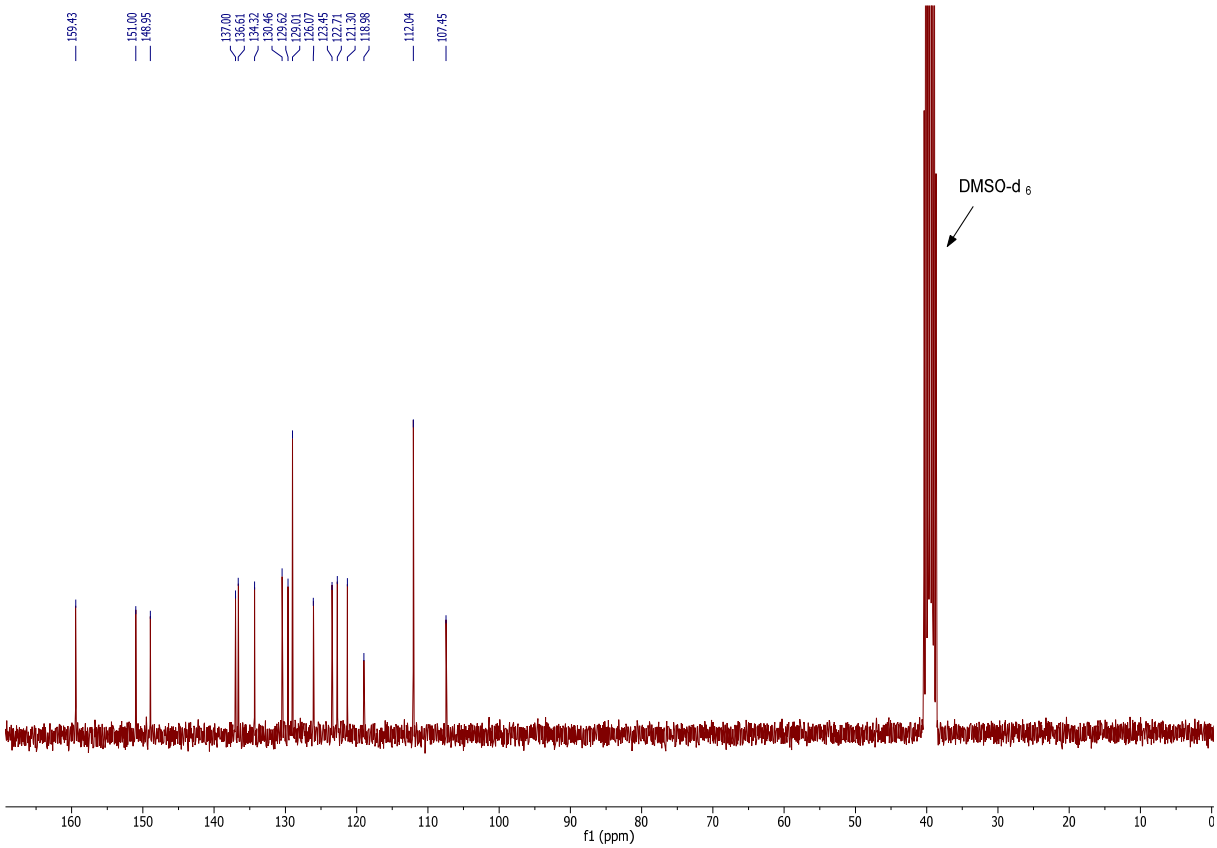
^{13}C- DEPT 135 NMR (75 MHz) of **3c** (20 mg) in DMSO-d_6 at 298 K.

1.3 (*E*)-2-(4-Dimethylamino)styryl)-quinoline-6-carbonitril (3c)

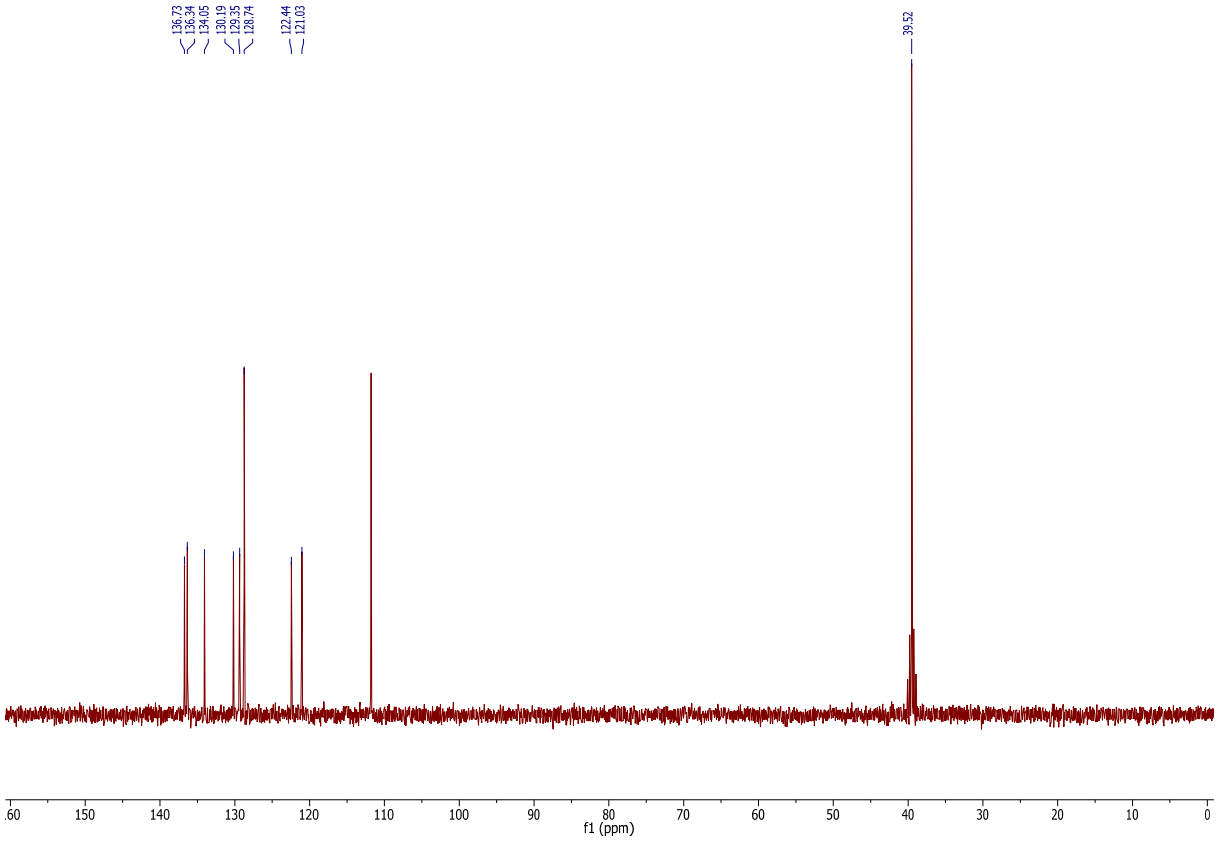




^{1}H NMR (300 MHz) of **3c** (20 mg) in DMSO-d_6 at 298 K.



^{13}C NMR (75 MHz) of **3c** (20 mg) in DMSO-d_6 at 298 K.



^{13}C- DEPT 135 NMR (75 MHz) of **3c** (20 mg) in DMSO-d_6 at 298 K.

2 Selected UV/Vis and emission spectra of 2-styryl quinoline 3c

Absorption and Emission Solvochromicity of Compound 3c

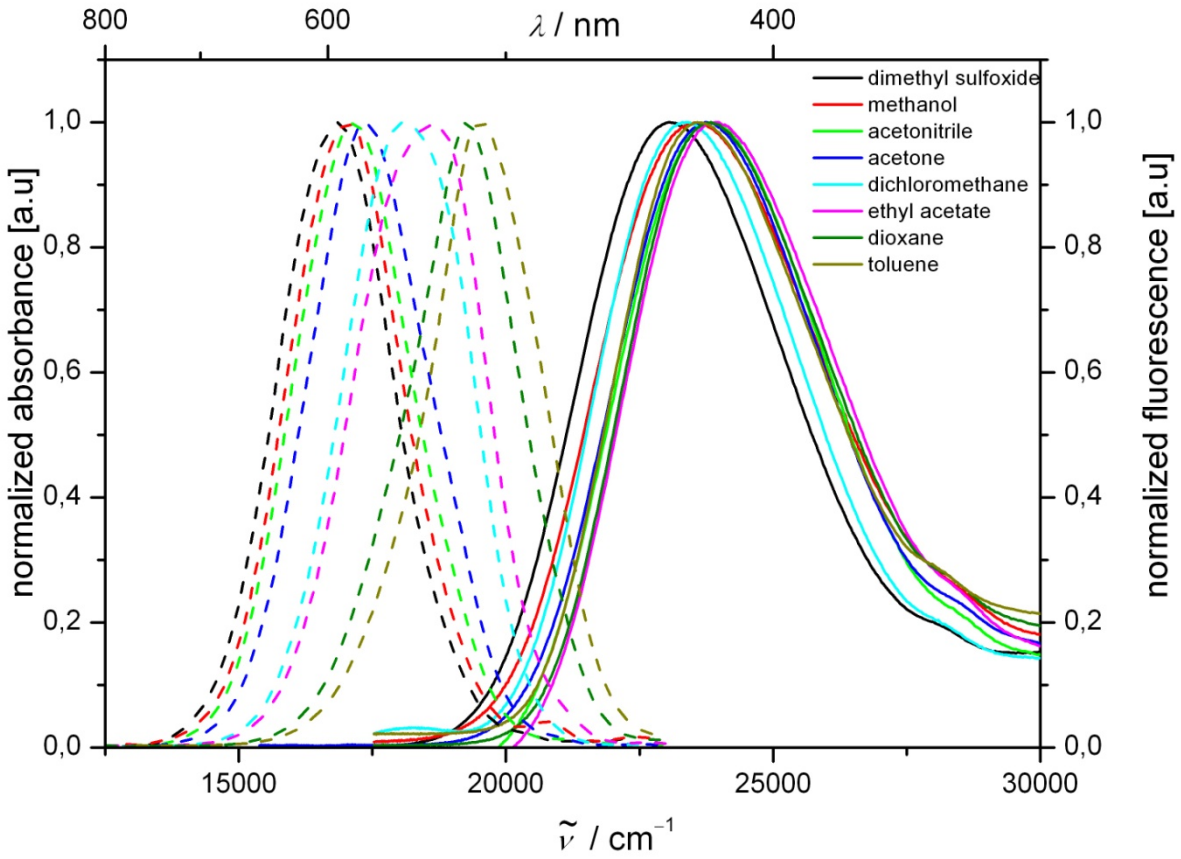


Figure 1: Normalized solvent dependent absorption and emission spectra of 2-styryl quinoline **3c** (recorded in DMSO, methanol, acetonitrile, acetone, CH_2Cl_2, ethyl acetate, dioxane and toluene: T = 293 K, λ_{exc} = longest-wavelength λ_{max}).

Titration of 3c with Trifluoroacetic Acid in Dichloromethane

Solutions of **3c** were prepared using spectroscopic grade dichloromethane purchased from OmniSolv. All absorption spectra were collected using a Shimadzu UV-2401PC spectraphotometer; emission spectra were acquired using a Shimadzu RF-5301PC spectrofluorophotometer. Increasing equivalents of trifluoroacetic acid (purchased from Acros) were added to solutions of **3c** using Eppendorf Reference variable volume pipettors.

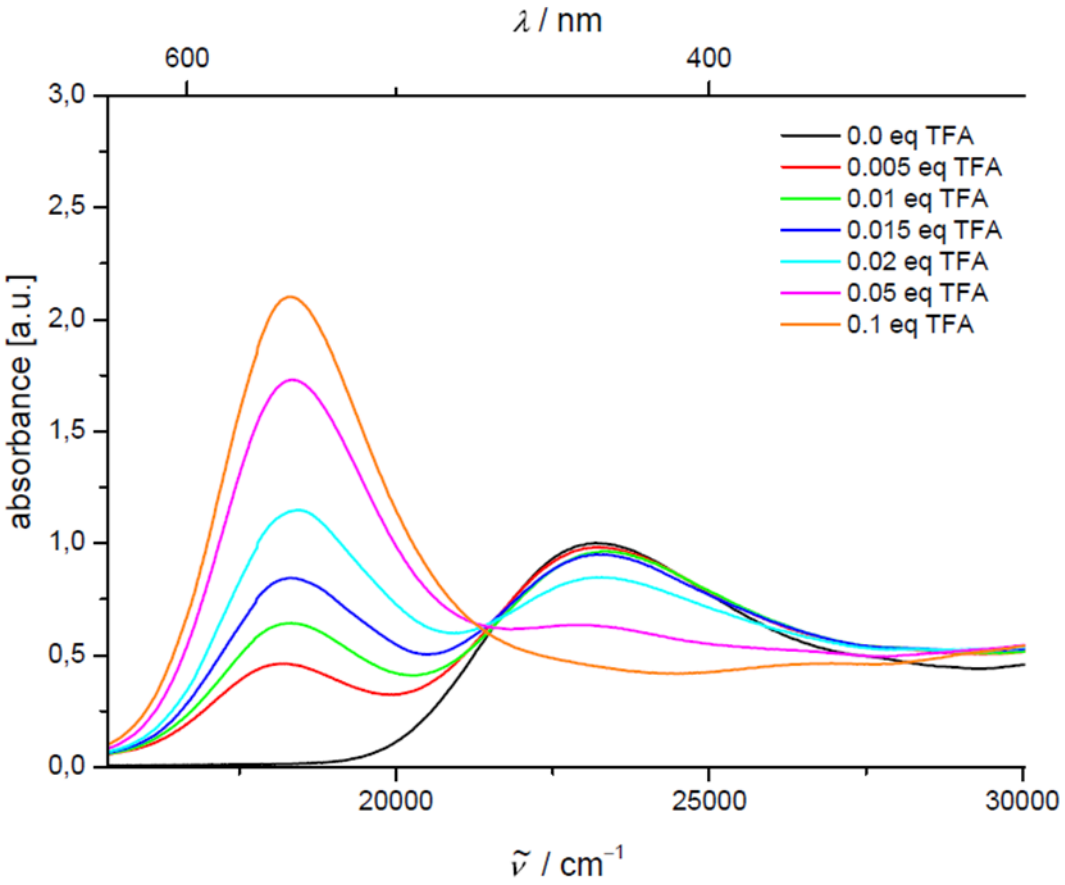


Figure 2: UV/Vis spectra of the titration of compound **3c** to the monoprotonated species **3c-H**$^+$ with trifluoroacetic acid (TFA) in CH_2Cl_2 (recorded at room temperature).

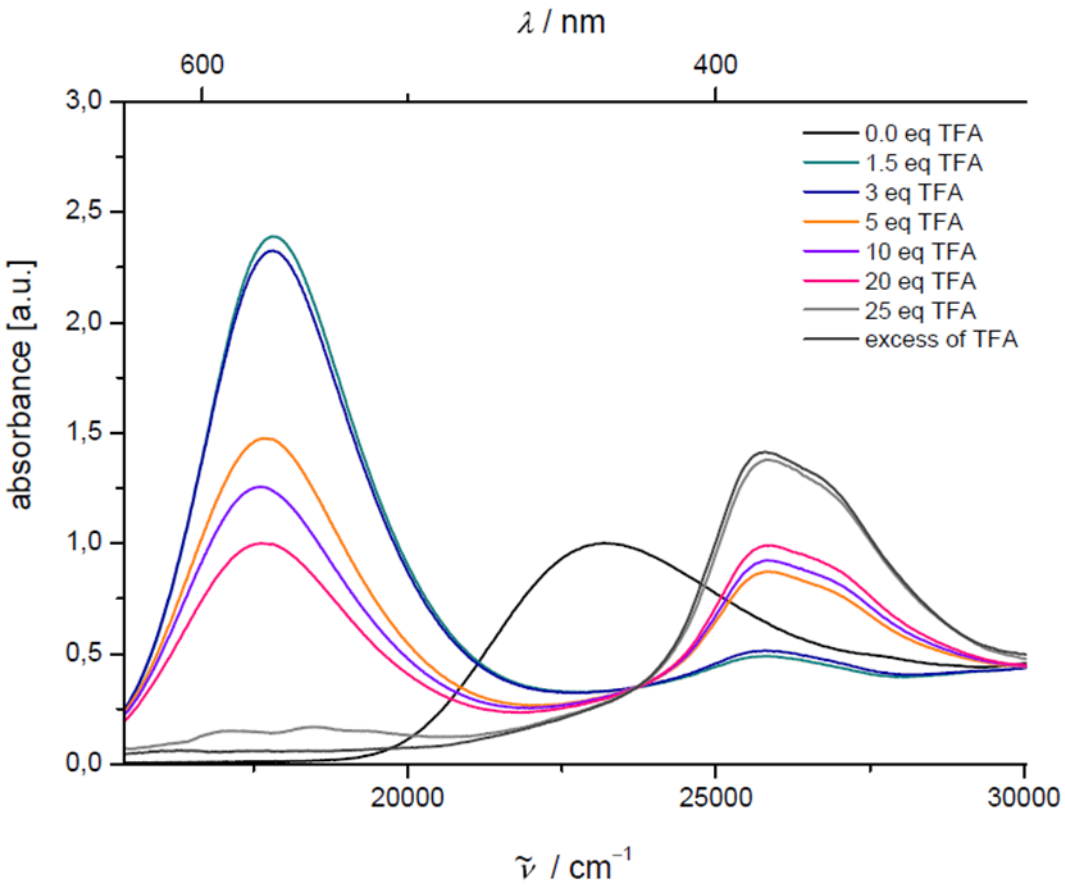


Figure 3: UV/Vis spectra of the titration of compound **3c-H**$^+$ to the diprotonated species **3c-2 H**$^+$ with trifluoroacetic acid (TFA) in CH_2Cl_2 (recorded at room temperature). The black curve represents the free base **3c**.

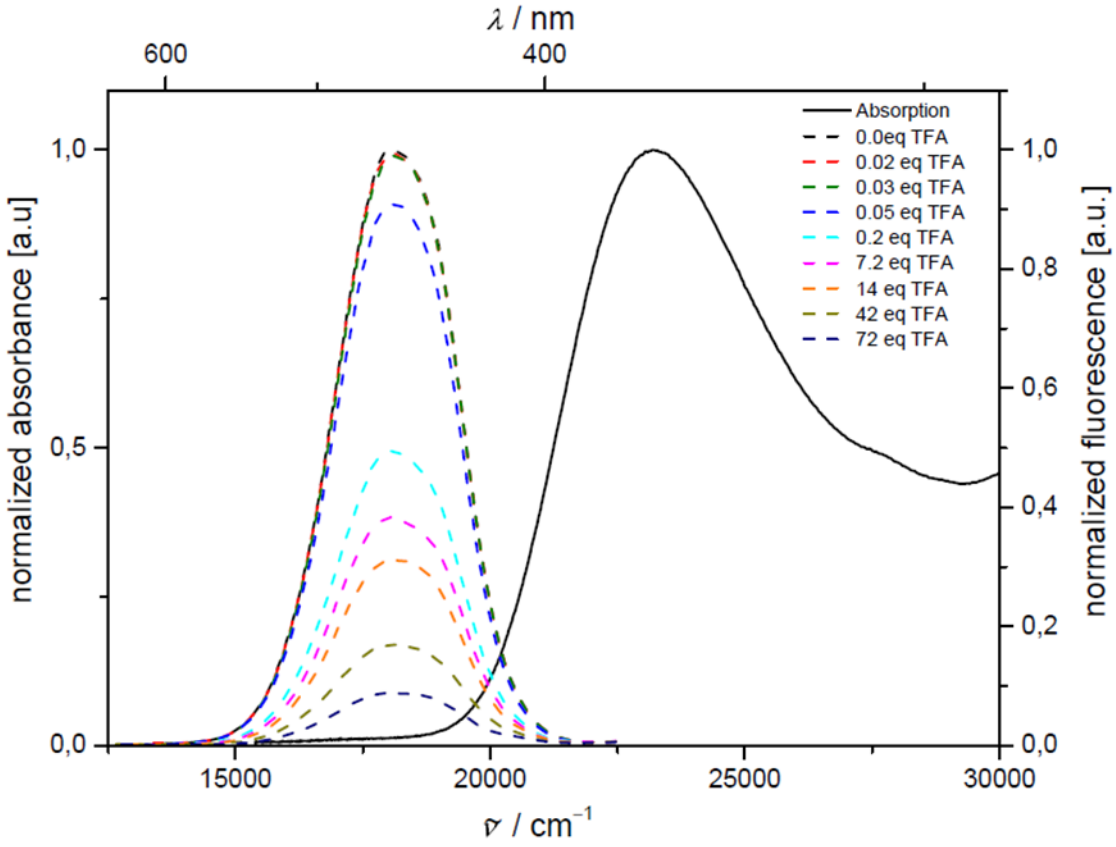


Figure 4: Absorption (solid line) and emission (dashed line) spectra of compound **3c** in CH_2Cl_2, *T* = 293 K. Dependence of fluorescence emission spectra of gradually added TFA concentration.

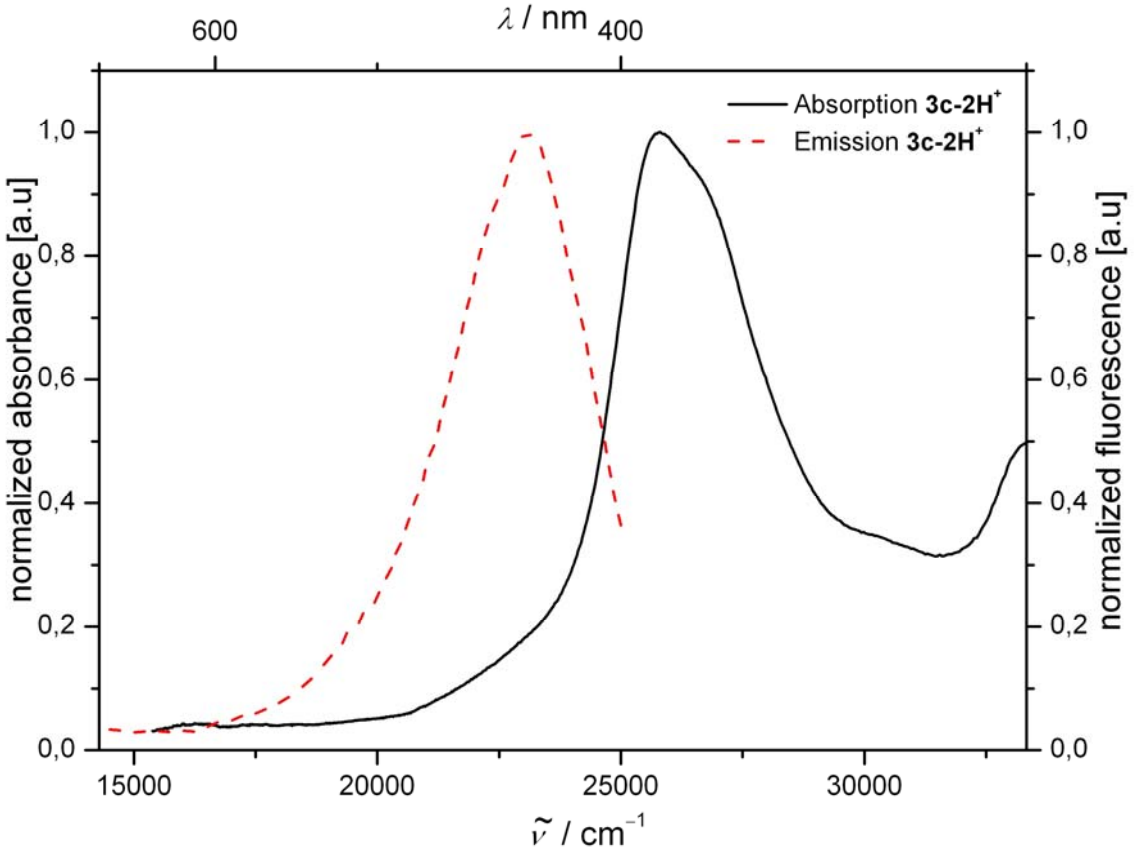
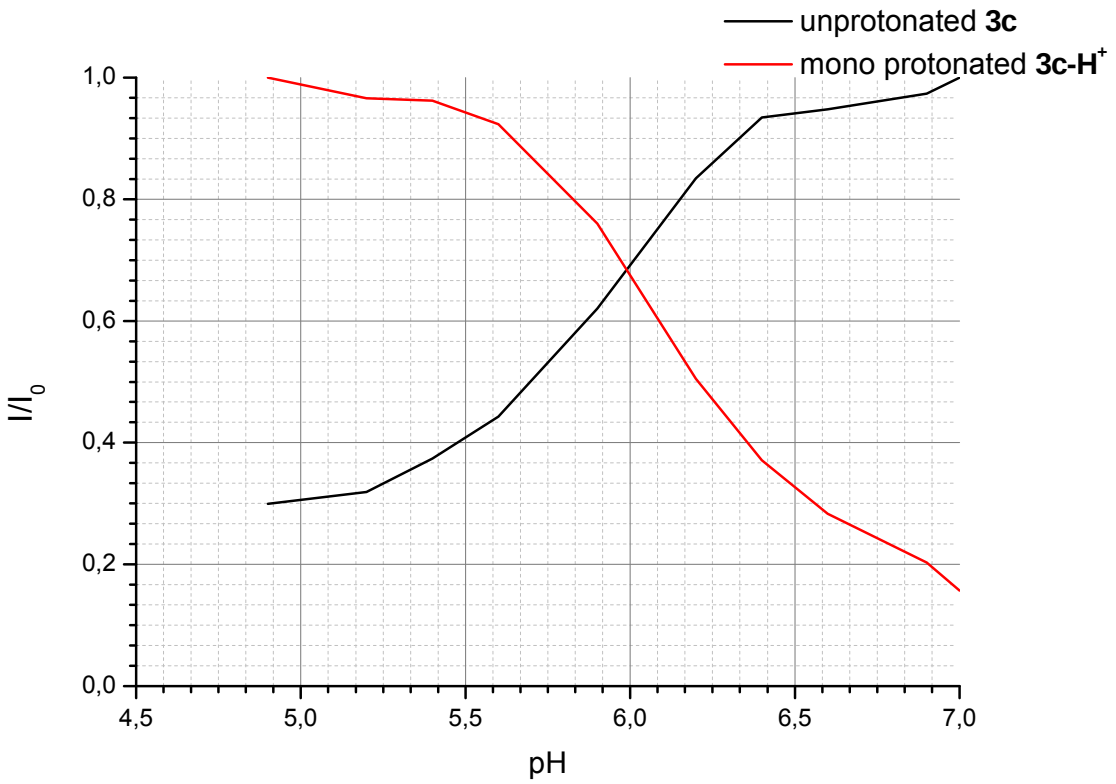
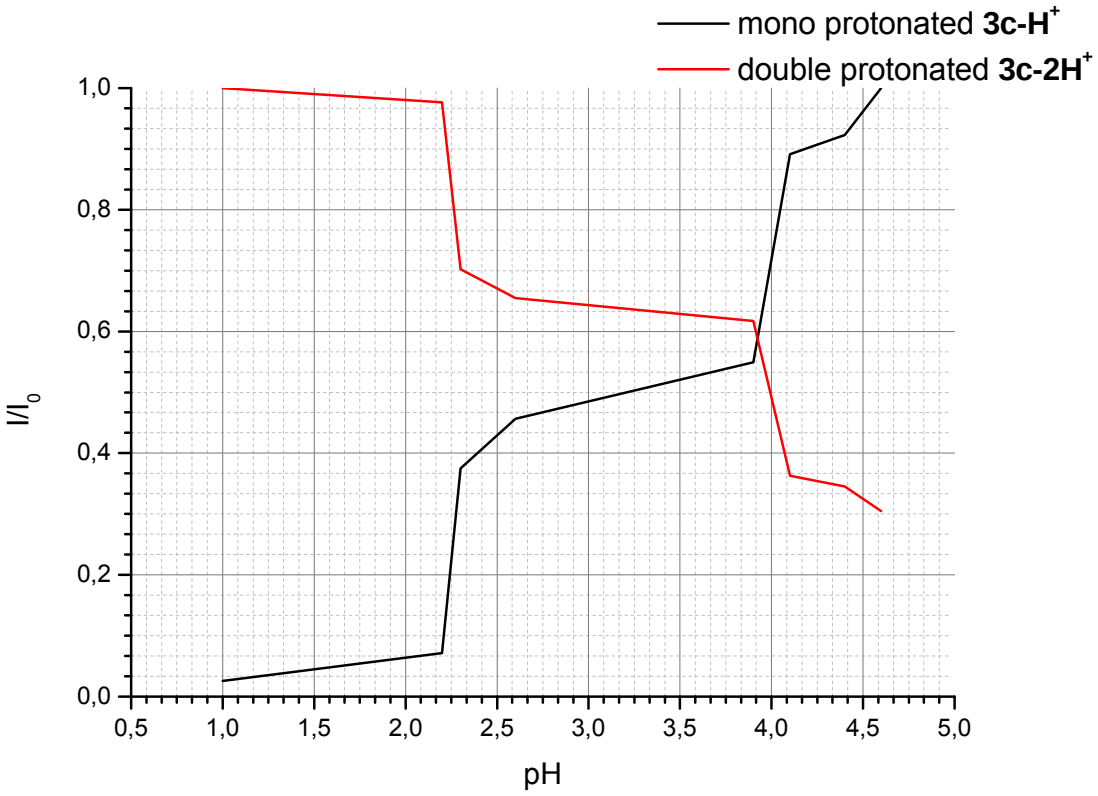


Figure 5: Absorption (solid line) and emission (dashed line) spectra of compound **3c-2H$^+$** in CH_2Cl_2, *T* = 293 K.

3 Determination of the p*K*a-Value of 3c

Since trifluoroacetic acid is completely dissociated in dichloromethane the p*H*-Value of a solution could be easily calculated as p*H* = - log (cH^+). This allows calculating the p*H*-Value in the UV-cuvette at any point of the titration if the concentration of the TFA is known. Drawing the intensity of the longest absorption maximum of **3c** and **3c-H$^+$** and **3c-2H$^+$** against the p*H* value the p*K*a-value could be determined at the point of intersection of these two lines.




mono protonated 3c-H+
double protonated 3c-2H+
I/I0
pH
1,0
0,8
0,6
0,4
0,2
0,0
0,5
1,0
1,5
2,0
2,5
3,0
3,5
4,0
4,5
5,0

4 Computational details

Computed xyz-Coordinates for the quinolines (3), their monoprotonated (3-H^+), and diprotonated species (3-$2H^+$)

The ground state geometries of the unprotonated **3**, the monoprotonated **3-H^+** and double protonated quinolines **3-$2H^+$** were optimized in by DFT calculation with the B3LYP functional and the 6-311G(d,p) basis set as implemented in the program package Gaussian09. The minima structures were confirmed by analytical frequency analysis.

XYZ-coordinates for **3a**:

C	-6.683638	0.807221	0.012172
C	-5.831931	1.937894	0.020221
C	-4.465458	1.787144	0.017571
C	-3.879715	0.492424	0.006709
C	-4.744350	-0.647782	-0.001304
C	-6.148276	-0.459998	0.001630
N	-2.525566	0.386275	0.004624
C	-1.970186	-0.821212	-0.005346
C	-2.761106	-2.012395	-0.013650
C	-4.125729	-1.923863	-0.011750
C	-0.512691	-0.947113	-0.008334
C	0.340074	0.099821	-0.007737
C	1.792755	0.071756	-0.011030
C	2.506549	1.284407	-0.026882
C	3.890324	1.332308	-0.033125
C	4.658818	0.142982	-0.029450
C	3.943858	-1.083492	-0.000573
C	2.562222	-1.108891	0.005111
N	6.031667	0.171602	-0.056429
C	6.794942	-1.063341	0.062726
C	6.737014	1.443216	0.023305
H	-7.758634	0.945392	0.014373
H	-6.265770	2.931562	0.028560
H	-3.800624	2.642978	0.023712
H	-6.793809	-1.332295	-0.004526
H	-2.266403	-2.976635	-0.021643
H	-4.742046	-2.816958	-0.018197
H	-0.135187	-1.964918	-0.012991
H	-0.108341	1.090105	-0.006630
H	1.952754	2.218073	-0.032140
H	4.377348	2.297282	-0.040120
H	4.479435	-2.022336	0.018920
H	2.069538	-2.074611	0.027121

H	6.628894	-1.564331	1.025193
H	6.540649	-1.767154	-0.735802
H	7.855165	-0.834195	-0.022393
H	6.451005	2.108625	-0.797242
H	6.545611	1.966554	0.969095
H	7.806854	1.261205	-0.054226

SCF Done: E(RB3LYP) = -844.576185892 Hartrees A.U. after 13 cycles
Sum of electronic and zero-point Energies= -844.255087 Hartrees
Sum of electronic and thermal Energies= -844.236788 Hartrees
Sum of electronic and thermal Enthalpies= -844.235844 Hartrees
Sum of electronic and thermal Free Energies= -844.303999 Hartrees

XYZ-coordinates for **3a-H**$^+$:

C	6.715286	-0.720995	0.011675
C	5.907059	-1.873576	0.062121
C	4.529376	-1.777103	0.071498
C	3.934389	-0.505954	0.029280
C	4.730846	0.665337	-0.021053
C	6.135722	0.529208	-0.029029
N	2.561988	-0.365558	0.037842
C	1.899384	0.816062	-0.006596
C	2.697328	1.994103	-0.050455
C	4.060426	1.921672	-0.057974
C	0.475315	0.900103	-0.008559
C	-0.397008	-0.153414	-0.036976
C	-1.825836	-0.104536	-0.027150
C	-2.557715	-1.314611	-0.083622
C	-3.932975	-1.343224	-0.072590
C	-4.684750	-0.136991	-0.001705
C	-3.951804	1.086381	0.053911
C	-2.578462	1.094260	0.041312
N	-6.042026	-0.147174	0.013959
C	-6.773800	-1.411411	-0.037571
C	-6.796746	1.102778	0.087667
H	7.793281	-0.821865	0.005028
H	6.370966	-2.851860	0.093755
H	3.911078	-2.666577	0.109627
H	6.747124	1.422901	-0.067834
H	2.020874	-1.219275	0.091821
H	2.189452	2.948146	-0.081909
H	4.651180	2.829740	-0.094157
H	0.095050	1.913625	0.004744
H	0.002271	-1.164996	-0.079281
H	-2.014992	-2.252371	-0.138415
H	-4.437711	-2.297112	-0.118462
H	-4.477607	2.028421	0.109888

H	-2.071637	2.050642	0.089258
H	-6.561095	-1.958857	-0.961130
H	-6.521907	-2.052596	0.812758
H	-7.840146	-1.204575	-0.003203
H	-6.579273	1.751308	-0.766318
H	-7.859280	0.874507	0.078097
H	-6.573570	1.651390	1.008010

SCF Done: E(RB3LYP) = -845.029471412 Hartrees A.U. after 13 cycles
Sum of electronic and zero-point Energies= -844.693841 Hartrees
Sum of electronic and thermal Energies= -844.675526 Hartrees
Sum of electronic and thermal Enthalpies= -844.674582 Hartrees
Sum of electronic and thermal Free Energies= -844.741887 Hartrees

XYZ-coordinates for **3a-2H$^+$**:

C	6.733309	-0.792140	0.034415
C	5.902589	-1.934166	-0.019624
C	4.530211	-1.817069	-0.049822
C	3.960046	-0.532380	-0.024569
C	4.777222	0.629560	0.028765
C	6.183023	0.467339	0.057850
N	2.595680	-0.364740	-0.052380
C	1.965319	0.825228	-0.027187
C	2.764863	1.986757	0.018140
C	4.134627	1.890085	0.046148
C	0.518645	0.925822	-0.044863
C	-0.354228	-0.100144	0.014626
C	-1.812293	-0.004401	-0.001050
C	-2.557806	-1.191120	0.106794
C	-3.946420	-1.176213	0.100717
C	-4.597603	0.044962	-0.015693
C	-3.892347	1.238213	-0.129418
C	-2.505671	1.211907	-0.121276
N	-6.080910	0.100677	-0.024953
C	-6.684067	-0.634074	-1.199190
C	-6.695674	-0.336673	1.284968
H	7.808426	-0.916454	0.057206
H	6.352142	-2.919196	-0.037297
H	3.895816	-2.694712	-0.090636
H	6.810313	1.349344	0.098918
H	2.037529	-1.208981	-0.105598
H	2.273861	2.949556	0.033945
H	4.739007	2.788779	0.082924
H	0.160136	1.946227	-0.096360
H	0.011513	-1.120489	0.090776
H	-2.043058	-2.139921	0.197535
H	-4.490515	-2.107940	0.183555
H	-4.414273	2.183275	-0.226368

H	-1.971746	2.148070	-0.213207
H	-6.330697	1.085526	-0.141661
H	-7.755940	-0.450772	-1.196073
H	-6.230798	-0.253205	-2.110731
H	-6.481993	-1.695392	-1.085518
H	-7.769913	-0.179014	1.220299
H	-6.267030	0.264829	2.082315
H	-6.478628	-1.390053	1.438915

SCF Done: E(RB3LYP) = -845.446092208 Hartrees A.U. after 12 cycles
Sum of electronic and zero-point Energies= -845.093934 Hartrees
Sum of electronic and thermal Energies= -845.076180 Hartrees
Sum of electronic and thermal Enthalpies= -845.075236 Hartrees
Sum of electronic and thermal Free Energies= -845.140363 Hartrees

XYZ-coordinates for **3b**:

C	-5.150602	-0.339111	-0.002791
C	-4.361148	-1.517872	0.006946
C	-2.993164	-1.433580	0.009497
C	-2.340270	-0.169476	0.002895
C	-3.145051	1.012060	-0.006139
C	-4.554320	0.900699	-0.008910
N	-0.985762	-0.134876	0.005201
C	-0.368359	1.044550	-0.000889
C	-1.098825	2.274755	-0.009267
C	-2.465218	2.257192	-0.012133
C	1.090119	1.096352	0.000398
C	1.886075	0.003455	0.001895
C	3.335555	-0.047188	0.002612
C	-6.642130	-0.480227	0.000276
F	-7.083849	-1.214465	-1.052412
F	-7.284501	0.705728	-0.052865
F	-7.088961	-1.118383	1.112280
C	3.982848	-1.297587	-0.007776
C	5.361138	-1.419819	-0.009714
C	6.192310	-0.272315	-0.000959
C	5.544547	0.992307	0.011581
C	4.167158	1.091481	0.012986
N	7.558801	-0.374751	-0.004292
C	8.388683	0.822523	0.010934
C	8.196392	-1.684302	-0.011523
H	-4.846521	-2.486472	0.010751
H	-2.375892	-2.323485	0.016084
H	-5.156501	1.800841	-0.016523
H	-0.555403	3.212118	-0.013704
H	-3.035560	3.179923	-0.018880
H	1.520450	2.092766	-0.001627
H	1.383872	-0.960686	0.001339
H	3.379273	-2.199794	-0.015002

H	5.796602	-2.409068	-0.018060
H	6.130340	1.900896	0.020561
H	3.726374	2.081993	0.023516
H	8.213796	1.427246	0.908102
H	9.435855	0.528611	0.002286
H	8.206981	1.453240	-0.866539
H	7.928766	-2.271743	0.874409
H	7.921422	-2.264322	-0.899880
H	9.276255	-1.553971	-0.015732

SCF Done: E(RB3LYP) = -1181.71659528 Hartrees A.U. after 13 cycles
Sum of electronic and zero-point Energies= -1181.391320 Hartrees
Sum of electronic and thermal Energies= -1181.369210 Hartrees
Sum of electronic and thermal Enthalpies= -1181.368266 Hartrees
Sum of electronic and thermal Free Energies= -1181.447615 Hartrees

XYZ-coordinates for **3b-H$^+$**:

C	-5.180269	-0.321266	-0.021353
C	-4.427550	-1.512907	-0.074593
C	-3.050909	-1.473060	-0.081574
C	-2.398360	-0.228931	-0.033647
C	-3.141591	0.974044	0.018499
C	-4.548763	0.903287	0.024246
N	-1.023691	-0.151791	-0.040152
C	-0.307700	1.002146	0.007263
C	-1.055936	2.214779	0.053085
C	-2.418922	2.203637	0.059157
C	1.113419	1.024485	0.010356
C	1.939415	-0.070226	0.037218
C	3.364679	-0.086078	0.026781
C	-6.680524	-0.417818	-0.000191
F	-7.146278	-1.155969	-1.033934
F	-7.277147	0.788137	-0.068792
F	-7.124448	-1.018014	1.129158
C	4.041502	-1.329493	0.090133
C	5.412539	-1.419802	0.079819
C	6.218403	-0.247715	0.003147
C	5.541545	1.008621	-0.060243
C	4.171395	1.078568	-0.048850
N	7.571545	-0.319403	-0.011062
C	8.383711	0.894992	-0.086364
C	8.246347	-1.616061	0.036981
H	-4.934192	-2.468922	-0.114356
H	-2.475973	-2.390152	-0.124653
H	-5.123230	1.819223	0.063049
H	-0.520411	-1.028297	-0.094728
H	-0.506396	3.145175	0.088431
H	-2.970153	3.135858	0.097275
H	1.539327	2.019599	0.000029
H	1.493951	-1.062048	0.080077

H	3.456649	-2.241342	0.150698
H	5.873970	-2.394927	0.131702
H	6.109651	1.925334	-0.122414
H	3.708052	2.056257	-0.104790
H	8.189179	1.556338	0.762810
H	9.434343	0.618174	-0.067184
H	8.191740	1.447000	-1.011415
H	8.007334	-2.155647	0.958316
H	7.966764	-2.241342	-0.816263
H	9.320688	-1.456534	0.004804

SCF Done: E(RB3LYP) = -1182.16532240 Hartrees A.U. after 13 cycles
Sum of electronic and zero-point Energies= -1181.825489 Hartrees
Sum of electronic and thermal Energies= -1181.803489 Hartrees
Sum of electronic and thermal Enthalpies= -1181.802545 Hartrees
Sum of electronic and thermal Free Energies= -1181.879664 Hartrees

XYZ-coordinates for **3b-2H**$^+$:

C	-5.223084	-0.280779	0.007920
C	-4.493256	-1.489849	0.101493
C	-3.119680	-1.480703	0.131658
C	-2.444104	-0.247924	0.067109
C	-3.161261	0.972457	-0.023179
C	-4.574504	0.928301	-0.053194
N	-1.072015	-0.193517	0.095812
C	-0.347089	0.941436	0.040933
C	-1.049502	2.163812	-0.034123
C	-2.421068	2.179279	-0.069661
C	1.100911	0.922202	0.059522
C	1.881414	-0.168950	-0.083520
C	3.341147	-0.201669	-0.069973
C	-6.728078	-0.352835	-0.013337
F	-7.210133	-0.868299	1.139040
F	-7.165451	-1.152518	-1.010315
F	-7.298023	0.853727	-0.183222
C	3.981027	-1.416898	-0.360610
C	5.367545	-1.512968	-0.370524
C	6.120098	-0.384111	-0.080509
C	5.519098	0.836057	0.219839
C	4.136107	0.921903	0.222421
N	7.599521	-0.502521	-0.076780
C	8.272164	0.447821	-1.039690
C	8.184586	-0.402550	1.314119
H	-5.021696	-2.433663	0.147139
H	-2.564049	-2.407583	0.203607
H	-5.130684	1.853173	-0.124648
H	-0.582363	-1.076829	0.185442
H	-0.480156	3.081777	-0.072265
H	-2.950555	3.122439	-0.134175
H	1.544530	1.903355	0.171712
H	1.425817	-1.141191	-0.252104

H	3.389075	-2.296035	-0.583860
H	5.842969	-2.460092	-0.598858
H	6.105957	1.715364	0.451497
H	3.681460	1.873805	0.462315
H	7.813827	-1.445159	-0.409712
H	9.333770	0.212376	-1.055953
H	7.831630	0.307392	-2.023231
H	8.119109	1.465697	-0.692952
H	9.250113	-0.610596	1.246922
H	7.689721	-1.135423	1.946592
H	8.016625	0.603086	1.689619

SCF Done: E(RB3LYP) = -1182.57956883 Hartrees A.U. after 12 cycles
Sum of electronic and zero-point Energies= -1182.223857 Hartrees
Sum of electronic and thermal Energies= -1182.202252 Hartrees
Sum of electronic and thermal Enthalpies= -1182.201308 Hartrees
Sum of electronic and thermal Free Energies= -1182.276539 Hartrees

XYZ-coordinates for **3c**:

C	-6.023045	-0.553202	-0.005658
C	-5.200086	-1.715448	-0.005515
C	-3.835729	-1.593364	-0.002872
C	-3.214152	-0.313460	-0.000230
C	-4.047600	0.850634	-0.000388
C	-5.449027	0.708549	-0.003123
N	-1.862574	-0.246586	0.002331
C	-1.272365	0.947903	0.004820
C	-2.032198	2.161787	0.004855
C	-3.396466	2.113117	0.002293
C	0.181986	1.034702	0.007590
C	1.003631	-0.040461	0.007751
C	2.452257	-0.058098	0.010391
C	3.127040	-1.294465	0.009818
C	4.507090	-1.386120	0.012186
C	5.312719	-0.220051	0.015320
C	4.637288	1.030504	0.016003
C	3.258502	1.099361	0.013596
N	6.680262	-0.292768	0.017583
C	7.346189	-1.588545	0.017389
C	7.484736	0.922232	0.021315
C	-7.444030	-0.693264	-0.008426
N	-8.594179	-0.814116	-0.010675
H	-5.665310	-2.693213	-0.007515
H	-3.195995	-2.467231	-0.002725
H	-6.075246	1.593036	-0.003231
H	-1.510280	3.111224	0.006931
H	-3.988668	3.021772	0.002275
H	0.588938	2.040619	0.009566
H	0.523397	-1.015588	0.005621
H	2.543273	-2.209587	0.007431
H	4.964664	-2.365307	0.011611
H	5.203352	1.951493	0.018462

H	2.795842	2.079937	0.014269
H	7.088715	-2.176692	-0.870832
H	8.422906	-1.434933	0.019224
H	7.085905	-2.178503	0.903608
H	7.294539	1.537535	-0.865247
H	7.291858	1.533981	0.909778
H	8.537906	0.650545	0.022331

SCF Done: E(RB3LYP) = -936.845636114 Hartrees A.U. after 6 cycles
Sum of electronic and zero-point Energies= -936.525941 Hartrees
Sum of electronic and thermal Energies= -936.505744 Hartrees
Sum of electronic and thermal Enthalpies= -936.504800 Hartrees
Sum of electronic and thermal Free Energies= -936.578083 Hartrees

XYZ-coordinates for **3c-H$^+$**:

C	1.386141	5.423241	4.175402
C	2.303936	5.069621	3.157213
C	2.053117	3.996932	2.331690
C	0.874309	3.251095	2.504883
C	-0.053941	3.590594	3.519766
C	0.221097	4.688327	4.351801
N	0.595979	2.174495	1.695012
C	-0.518793	1.399641	1.782145
C	-1.450046	1.736603	2.809514
C	-1.230001	2.788889	3.645193
C	-0.765060	0.307932	0.910203
C	0.017640	-0.072788	-0.152204
C	-0.191132	-1.168297	-1.036702
C	0.723505	-1.380851	-2.099121
C	0.588424	-2.420448	-2.986116
C	-0.493624	-3.340419	-2.869432
C	-1.420169	-3.130004	-1.801950
C	-1.268781	-2.085776	-0.926050
N	-0.638588	-4.373428	-3.732733
C	-1.757999	-5.306814	-3.601810
C	0.329008	-4.581982	-4.810061
C	1.662982	6.541146	5.022241
N	1.890587	7.445410	5.704045
H	3.208650	5.649305	3.029133
H	2.758537	3.730604	1.553939
H	-0.482607	4.954870	5.129823
H	1.286043	1.946385	0.990455
H	-2.341024	1.130877	2.899732
H	-1.950685	3.031143	4.417225
H	-1.670467	-0.241201	1.134450
H	0.907025	0.509952	-0.383257
H	1.557325	-0.696753	-2.215647
H	1.314896	-2.532774	-3.777314

H	-2.255381	-3.802603	-1.672236
H	-1.996069	-1.974323	-0.130935
H	-1.726029	-5.835861	-2.644672
H	-2.717865	-4.789278	-3.684670
H	-1.698756	-6.042371	-4.399418
H	1.336483	-4.737909	-4.413299
H	0.044342	-5.465826	-5.374200
H	0.351078	-3.729672	-5.495667

SCF Done: E(RB3LYP) = -937.292695466 Hartrees A.U. after 5 cycles
Sum of electronic and zero-point Energies= -936.958463 Hartrees
Sum of electronic and thermal Energies= -936.938353 Hartrees
Sum of electronic and thermal Enthalpies= -936.937409 Hartrees
Sum of electronic and thermal Free Energies= -937.008912 Hartrees

XYZ-coordinates for **3c-2H$^+$**:

C	6.082057	-0.548793	0.014105
C	5.281926	-1.720885	-0.050716
C	3.911709	-1.632845	-0.080634
C	3.304752	-0.363701	-0.044674
C	4.087524	0.818511	0.018723
C	5.492849	0.702043	0.047344
N	1.937837	-0.235651	-0.070969
C	1.274436	0.937692	-0.033741
C	2.043409	2.122019	0.021420
C	3.412711	2.065495	0.047739
C	-0.170925	1.002553	-0.048039
C	-1.016971	-0.047898	0.005065
C	-2.475368	0.008908	-0.004653
C	-3.186093	-1.198805	0.107210
C	-4.574228	-1.222610	0.106757
C	-5.259210	-0.019946	-0.008009
C	-4.588984	1.193355	-0.124766
C	-3.202222	1.206223	-0.122541
N	-6.743264	-0.008398	-0.012769
C	-7.327589	-0.749357	-1.193137
C	-7.339351	-0.482041	1.293250
C	7.507379	-0.669586	0.046013
N	8.656822	-0.773216	0.072051
H	5.761171	-2.690596	-0.076174
H	3.306218	-2.529581	-0.129425
H	6.099312	1.596795	0.095638
H	1.401761	-1.094114	-0.131171
H	1.524586	3.069732	0.047121
H	3.992105	2.979912	0.092647
H	-0.555688	2.013635	-0.089079
H	-0.623862	-1.058722	0.072133
H	-2.643693	-2.131878	0.197832
H	-5.092703	-2.168498	0.192645

H	-5.137820	2.122970	-0.220464
H	-2.694886	2.156834	-0.217974
H	-7.023386	0.969381	-0.118462
H	-8.404784	-0.600682	-1.182863
H	-6.891242	-0.344066	-2.102306
H	-7.090658	-1.804818	-1.092129
H	-8.417001	-0.345930	1.238842
H	-6.917251	0.111782	2.099274
H	-7.098814	-1.533291	1.425415

SCF Done: E(RB3LYP) = -937.705878009 Hartrees A.U. after 13 cycles
Sum of electronic and zero-point Energies= -937.355129 Hartrees
Sum of electronic and thermal Energies= -937.335570 Hartrees
Sum of electronic and thermal Enthalpies= -937.334626 Hartrees
Sum of electronic and thermal Free Energies= -937.403993 Hartrees

Computed UV/vis Spectrums of calculated Compounds by TD-DFT

The optimized structures **3** were used in TD-DFT calculations applying the hybrid exchange-correlation functional CAM-B3LYP.

First three computed transitions of the first excited state for **3a**:

1) 387 nm, oscillator strength: 1.5168, orbitals involved: HOMO-2 → LUMO, HOMO-1 → LUMO, HOMO → LUMO, HOMO → LUMO+1
2) 291 nm, oscillator strength: 0.0930, orbitals involved: HOMO-5 → LUMO, HOMO-2 → LUMO, HOMO-1 → LUMO+1, HOMO → LUMO+1, HOMO → LUMO+2
3) 281 nm, oscillator strength: 0.0020, orbitals involved: HOMO-4 → LUMO, HOMO-4 → LUMO+4

First three computed transitions of the first excited state for **3a-H$^+$**:

1) 509 nm, oscillator strength: 1.7179, orbitals involved: HOMO-1 → LUMO, HOMO → LUMO
2) 304 nm, oscillator strength: 0.0122, orbitals involved: HOMO-2 → LUMO, HOMO-1 → LUMO, HOMO-1 → LUMO+1, HOMO → LUMO+1
3) 298 nm, oscillator strength: 0.1322, orbitals involved: HOMO-2 → LUMO, HOMO-2 → LUMO+1, HOMO-1 → LUMO, HOMO → LUMO+1

First three computed transitions of the first excited state for **3a-2H$^+$**:

1) 372 nm, oscillator strength: 1.3871, orbitals involved: HOMO → LUMO
2) 320 nm, oscillator strength: 0.0436, orbitals involved: HOMO-1 → LUMO, HOMO-1 → LUMO+1
3) 267 nm, oscillator strength: 0.2934, orbitals involved: HOMO-3 → LUMO, HOMO-1 → LUMO+1, HOMO-1 → LUMO+2, HOMO-1 → LUMO+3, HOMO → LUMO+1

First three computed transitions of the first excited state for **3b**:

1) 402 nm, oscillator strength: 1.5644, orbitals involved: HOMO-1 → LUMO, HOMO → LUMO, HOMO → LUMO+1, HOMO → LUMO+2
2) 294 nm, oscillator strength: 0.0889, orbitals involved: HOMO-5 → LUMO, HOMO-2 → LUMO, HOMO-1 → LUMO, HOMO-1 → LUMO+1, HOMO → LUMO+1
3) 283 nm, oscillator strength: 0.0019, orbitals involved: HOMO-4 → LUMO, HOMO-4 → LUMO+4

First three computed transitions of the first excited state for **3b-H$^+$**:

1) 525 nm, oscillator strength: 1.7880, orbitals involved: HOMO-1 → LUMO, HOMO → LUMO
2) 307 nm, oscillator strength: 0.0720, orbitals involved: HOMO-3 → LUMO, HOMO-1 → LUMO, HOMO-1 → LUMO+1, HOMO → LUMO+1
3) 287 nm, oscillator strength: 0.0222, orbitals involved: HOMO-3 → LUMO, HOMO-3 → LUMO+1, HOMO-1 → LUMO, HOMO → LUMO, HOMO → LUMO+1

First three computed transitions of the first excited state for **3b-2H$^+$**:

1) 373 nm, oscillator strength: 1.4302, orbitals involved: HOMO → LUMO
2) 305 nm, oscillator strength: 0.0250, orbitals involved: HOMO-1 → LUMO, HOMO-1 → LUMO+1, HOMO → LUMO+1
3) 268 nm, oscillator strength: 0.0429, orbitals involved: HOMO-3 → LUMO+3, HOMO-2 → LUMO, HOMO-2 → LUMO+1, HOMO-2 → LUMO+2, HOMO → LUMO+3

First three computed transitions of the first excited state for **3c**:

1) 418 nm, oscillator strength: 1.6842, orbitals involved: HOMO-1 → LUMO, HOMO → LUMO, HOMO → LUMO+2
2) 298 nm, oscillator strength: 0.0696, orbitals involved: HOMO-5 → LUMO, HOMO-2 → LUMO, HOMO-1 → LUMO+1, HOMO → LUMO+1, HOMO → LUMO+2
3) 286 nm, oscillator strength: 0.0016, orbitals involved: HOMO-4 → LUMO, HOMO-4 → LUMO+4,

First three computed transitions of the first excited state for **3b-H$^+$**:

1) 536 nm, oscillator strength: 1.8978, orbitals involved: HOMO-1 → LUMO, HOMO → LUMO
2) 310 nm, oscillator strength: 0.0788, orbitals involved: HOMO-3 → LUMO, HOMO-1 → LUMO, HOMO-1 → LUMO+1, HOMO → LUMO+1, HOMO → LUMO+2
3) 294 nm, oscillator strength: 0.0396, orbitals involved: HOMO-3 → LUMO, HOMO-3 → LUMO+1, HOMO-1 → LUMO, HOMO → LUMO+1

First three computed transitions of the first excited state for **3b-2H$^+$**:

1) 382 nm, oscillator strength: 1.5331, orbitals involved: HOMO → LUMO
2) 309 nm, oscillator strength: 0.0416, orbitals involved: HOMO-1 → LUMO, HOMO-1 → LUMO+1
3) 271 nm, oscillator strength: 0.2015, orbitals involved: HOMO-3 → LUMO, HOMO-1 → LUMO+1, HOMO-1 → LUMO+2, HOMO → LUMO+1, HOMO → LUMO+2