Supporting Information for

Fluorinated 2,3-diaminophenazines: synthesis, mechanism of formation, properties

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1. General methods

All NMR spectra were recorded in DMSO-d6 solution at room temperature (293 K), unless otherwise noted, on a Bruker AV-300 spectrometer operating at 300.13 MHz for ^{1}H, 282.40 MHz for ^{19}F, or Bruker AV-400 (400.13 MHz for ^{1}H, 376.50 for ^{19}F, 100.61 for ^{13}C and 40.54 MHz for ^{15}N), or Bruker DRX-500 (500.13 MHz for ^{1}H, 125.76 MHz for ^{13}C), or Bruker AV-600 (600.30 MHz for ^{1}H, 150.95 MHz for ^{13}C and 60.83 MHz for ^{15}N). ^{1}H, ^{19}F and ^{13}C spectra were referenced internally in ppm, δ 2.50 for ^{1}H (to DMSO-d_5), δ 0.00 for ^{19}F (to C_6F_6) and δ 39.50 for ^{13}C (to DMSO-d_6). ^{15}N chemical shifts for **DAPs 9**, **10**, **12**, **13**, and **15** were obtained indirectly from ^{1}H–^{15}N HMBC experiment and referred to ammonia (0 ppm). 2D NMR experiments were performed on the Bruker AV600 spectrometer or on the Bruker AV400 spectrometer, equipped with a 5 mm zaxis field-gradient probehead. Bruker programs for pulse sequence were used. Typical parameters for 2D NMR experiments were as follow. Spectral width was optimized to cover all signals. FID data was processed with zero-filling and sine-bell function weighting applied prior to Fourier transformation, in order for the resolution to be optimized appropriately. Delay times for relaxation are set to 2-3 s in all 2D NMR experiments. COSY: cosygpqf - pulse program, gradient pulses for selection was used, 4 K x 256 (^{1}H–^{1}H COSY) or 8 K x 512 (^{19}F–^{19}F COSY) time-domain data matrix, 1 scan for each FID. ^{1}H–^{13}C HSQC: hsqcetgp - pulse program, echo/antiecho acqution mode, 1 K x 512 time-domain data matrix, GARP composite pulse decoupling during acquisition, 1-8 scans for each FID. ^{1}H–^{13}C HMBC: hmbcgpndqf - pulse program, delay for evolution was specified for 7 Hz long-range coupling, 4 K x 512 time-domain data matrix, 8-16 scans for each FID. ^{1}H–^{15}N HMBC: hmbcgpndqf - pulse program, delay for evolution was specified for 3 or 6 Hz long-range coupling, 4 K x 512 or 4 K x 640 time-domain data matrix, 16-32 scans for each FID.

Fluorescence measurements were made using a Cary Eclipse Fluorescence Spectrophotometer by Varian. Emission spectra were recorded within the range of 440 – 740 nm in quartz cuvettes with a light-absorbing layer thickness of 1×1 cm by varying the excitation wavelengths for determination of the Stokes shift values. Excitation and emission slit sizes were set at 5 nm. The scan rate was set at 600 nm/min with a data interval of 1.000 nm and an averaging time of 0.1 second. The excitation filter was set to auto, the emission filter set to open. To compare the fluorescence intensities of all samples excitation was set at 430 nm and the PMT detector voltage set to 650 V.

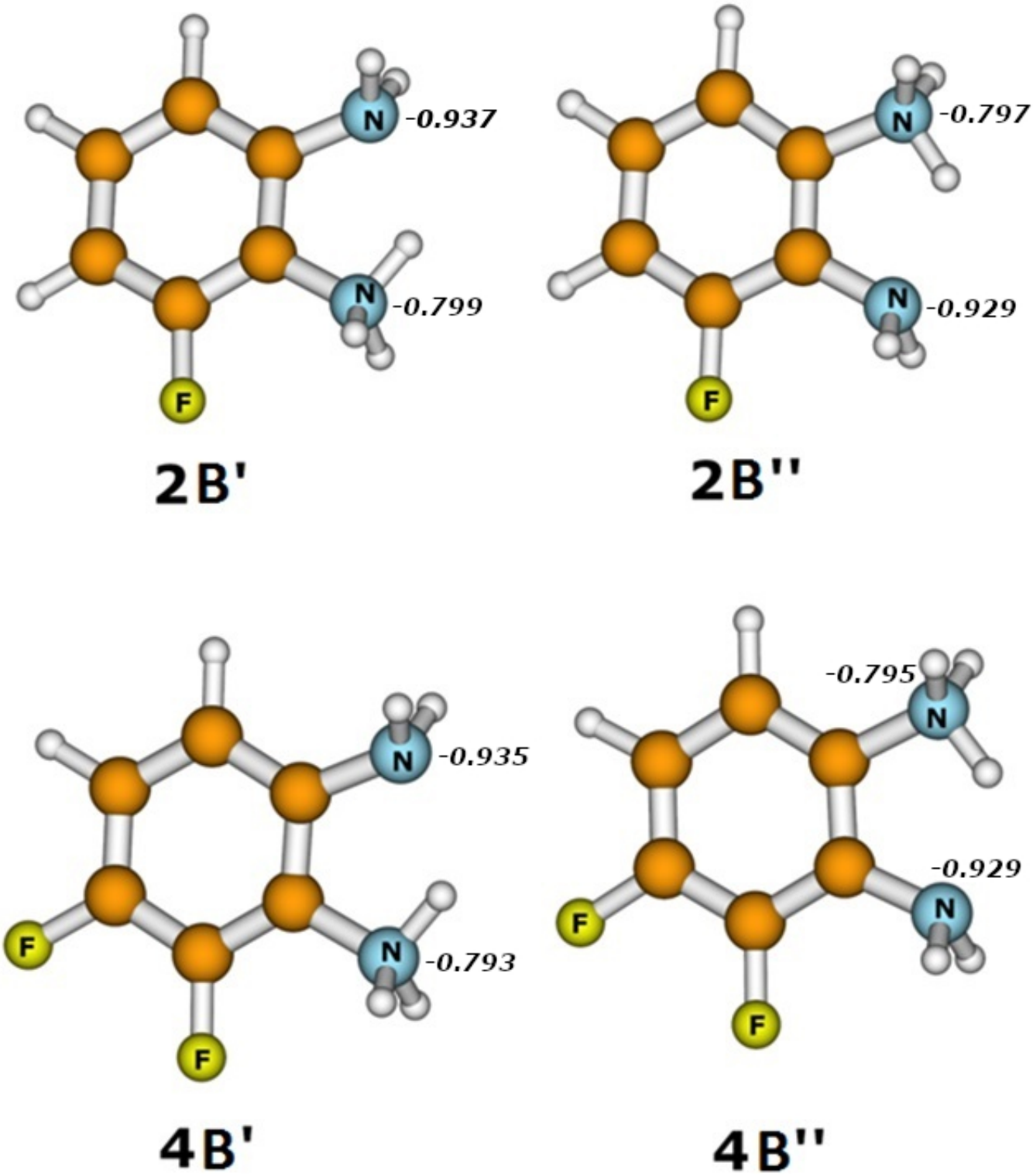
Gas phase calculations of the structures for the fluoro-phenylenediamines and fluoro-phenylenediimines were performed at the DFT level using the functional B3LYP with the basis set 6-31G(d). Atom charges were obtained from NBO-analysis.[1] All calculations were performed with default parameters using the GAMESS program.[2]

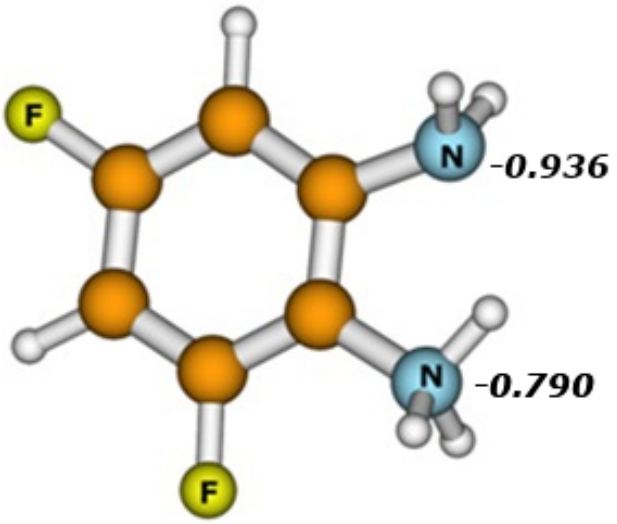
Images of calculated structures were built by the MOLDEN program.[3] Cartesian coordinates, total energies of the stationary structures and other results of these calculations are shown in Supp. Inf. (Fig. S1 and Table S1).

The quantum chemical calculation of the chemical shifts of the ^{1}H, ^{19}F, ^{13}C and ^{15}N nuclei was performed at PBE0/6-311+G(2d,p) level using ORCA program, v. 5.03.[4.]

2. Numbering of the optimized structures protonated fluorinated **o-PDAs B** and phenylenediimines **C**

Fig. S1. Structures and numbering of the optimized structures protonated fluorinated **o-PDA**s **B** and fluorinated phenylenediimines **C** (B3LYP with the basis set 6-31G(d)) and charges on N,C-atoms obtained from NBO-analysis.

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N
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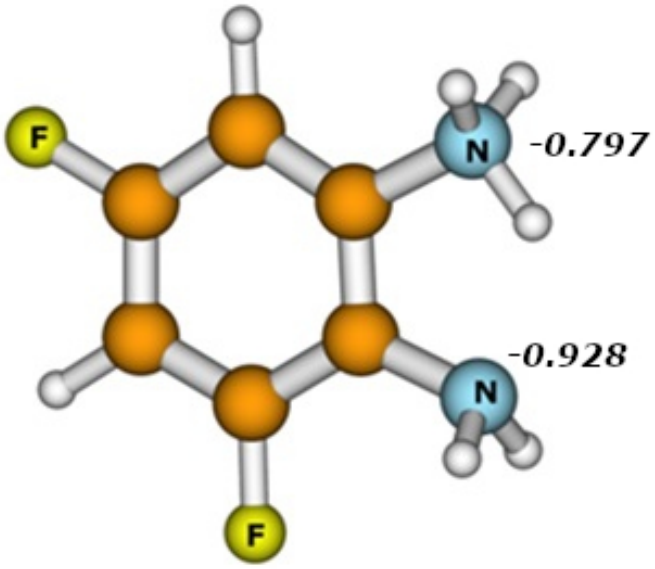
N
-0.790
F

5B'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N
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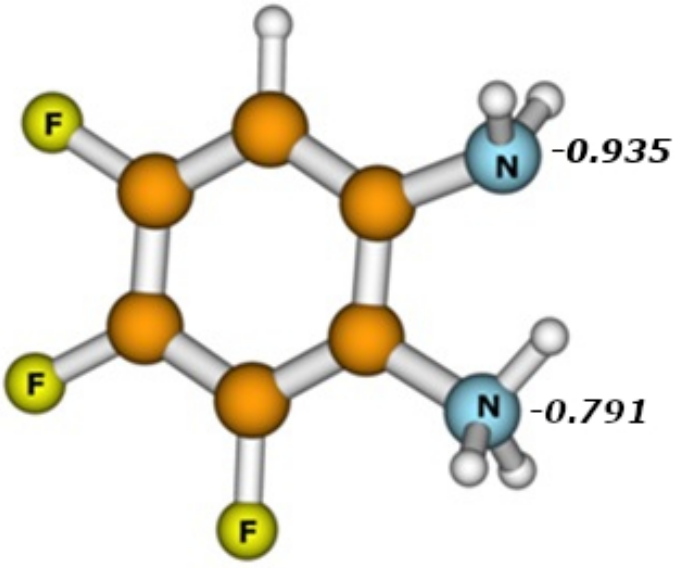
5B''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F
N
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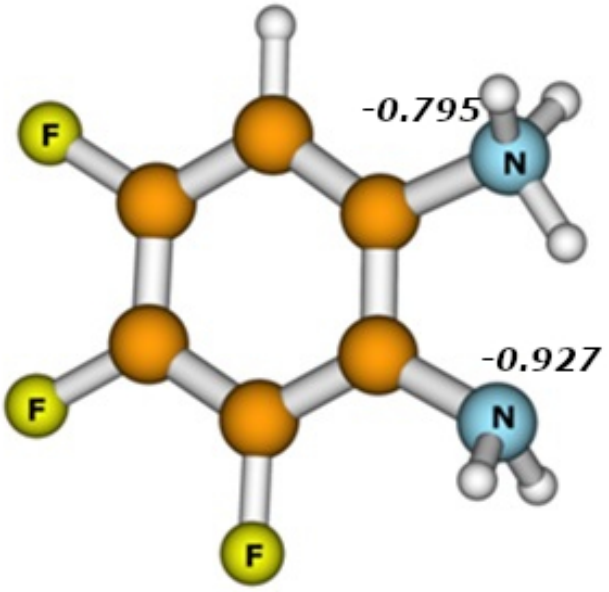
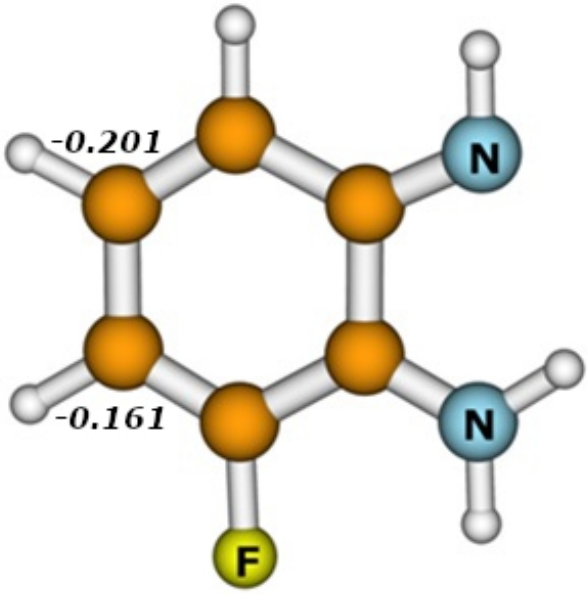
F

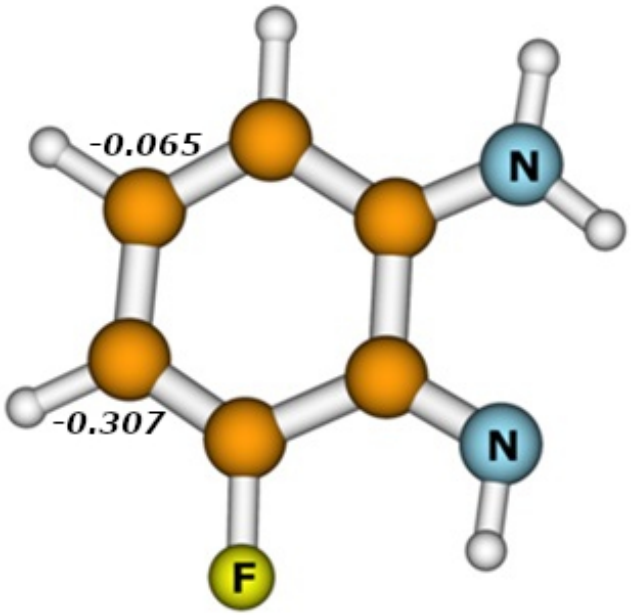
7B'


-0.795
F
N
-0.927
F
N
F

7B''



2C'



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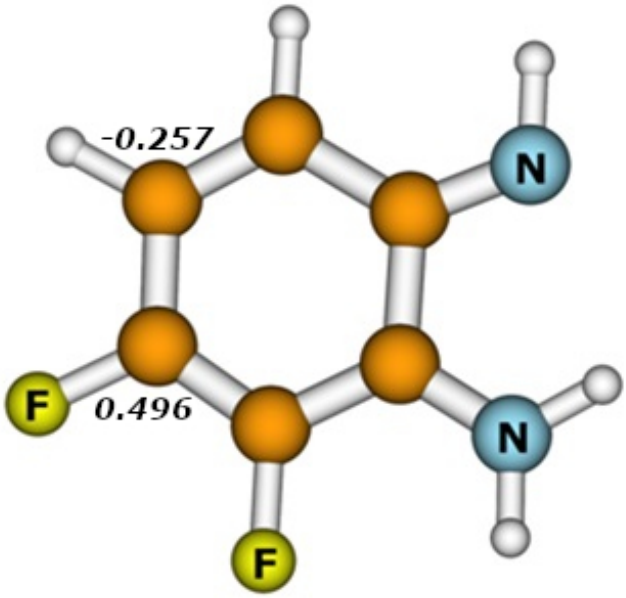
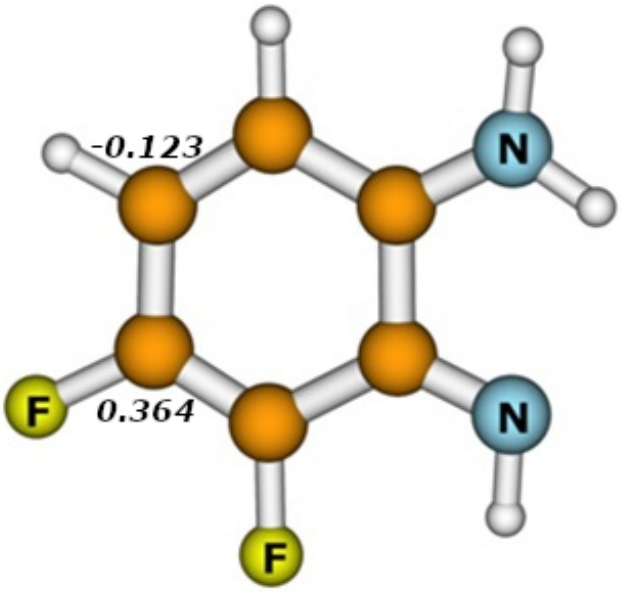


4C'



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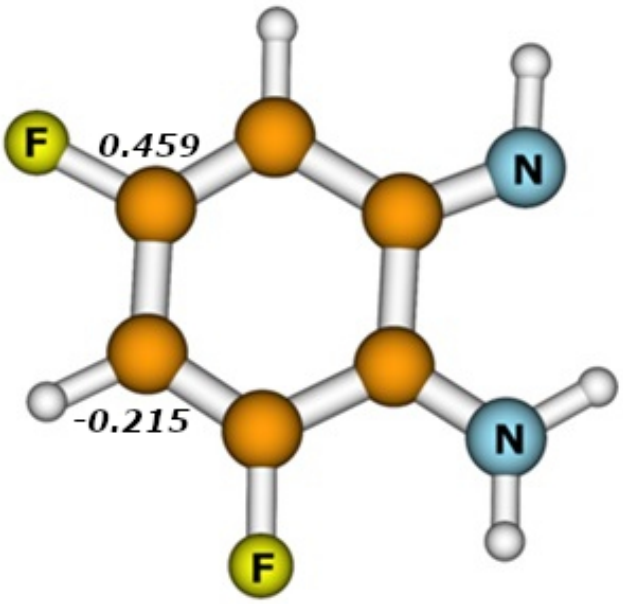
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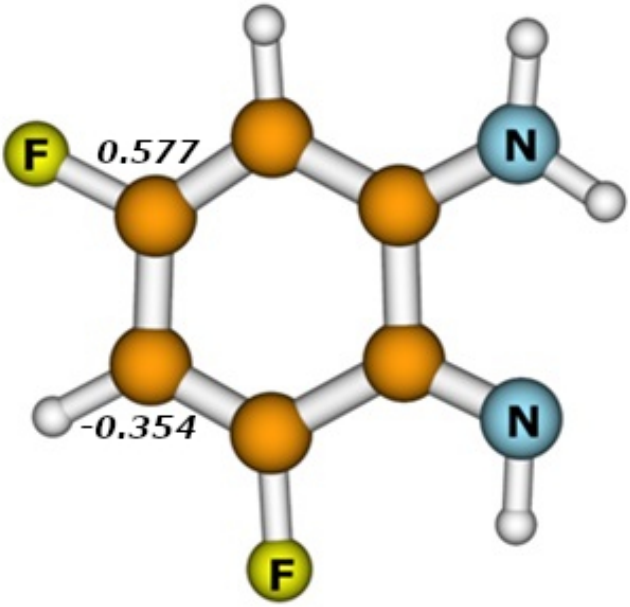
N
F

5C'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N
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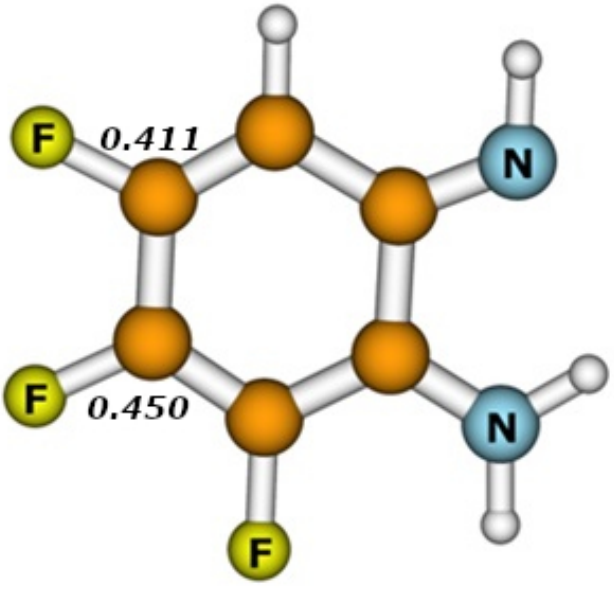
5C''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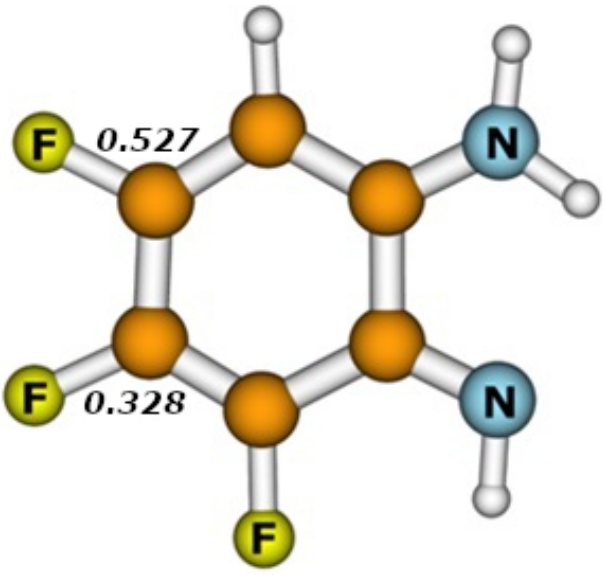
F
0.450
N
F

7C'


F
0.527
N
F
0.328
N
F

7C''

Table S1. Cartesian coordinates of the optimized structures protonated fluorinated **o-PDA**s **B** and phenylenediimines **C** by B3LYP/6-31G(d), GAMESS.

2B'	**X**	**Y**	**Z**
E = - 442.303933 a.u.			
C	-1.2699748770	-1.3835938367	0.1166913974
C	-0.0760000650	-2.1120572570	0.0598383778
C	1.1683719123	-1.4798031206	-0.0219590917
C	1.2036856032	-0.0926128986	-0.0479645571
C	0.0210113034	0.6321012625	0.0079313851
C	-1.2309516018	0.0110421571	0.0912931018
F	2.3556927688	0.5901635425	-0.1289252658
N	0.0089854605	2.1019230491	-0.0235050142
N	-2.3518666018	0.9141364903	0.1402382967
H	2.0960139341	-2.0403916181	-0.0659200199
H	-0.1136250584	-3.1967128718	0.0800220805
H	-2.2242366213	-1.8973172486	0.1807238741
H	-1.0259961841	2.3139188803	0.0254144545
H	0.4976032402	2.5315901671	0.7725259713
H	0.4130408174	2.4938673836	-0.8836790710
H	-3.0014563121	0.7571254674	-0.6308934161
H	-2.8857309045	0.8109887534	1.0037348050

2B''	**X**	**Y**	**Z**
E = -442,304229 a.u.			
C	-1.2866355770	-1.4835557888	0.0530482138
C	-0.0491163395	-2.1350447587	0.0836699768
C	1.1451790171	-1.4117281002	0.0895013633
C	1.1016793374	-0.0210213855	0.0655277416
C	-0.1090433596	0.6744742147	0.0349787364
C	-1.2772938072	-0.0961890991	0.0291602181
F	2.2321589556	0.6909870783	0.0699081631
N	-0.2600002303	2.1008628317	0.0045263214
N	-2.5107908225	0.7233799803	-0.0120329429
H	2.1089149033	-1.9097996671	0.1121675413
H	-0.0176493581	-3.2195045375	0.1025615738
H	-2.2132371113	-2.0498312134	0.0474277335
H	-3.0823800369	0.5574824081	-0.8491808297
H	-3.1106268719	0.6026602235	0.8132830519
H	-2.1257369297	1.7102131681	-0.0310230665
H	0.1534786735	2.5410592739	0.8278575937

H	0.2059809232	2.5108938156	-0.8061420823

4B'

	X	Y	Z

E = -541.493249 a.u.

C	1.4211231172	0.5604983251	-0.0576390885
C	0.6947806411	1.7520870362	-0.0220632922
C	-0.7023616773	1.7237504726	0.0279159412
C	-1.3878959813	0.5121287198	0.0436150123
C	-0.6816974693	-0.6916815345	0.0088967384
C	0.7029585585	-0.6427647114	-0.0410254169
F	-2.7146526800	0.4736765758	0.0913279876
F	-1.3023593322	-1.8748276046	0.0210459541
N	1.5098368353	-1.8699004294	-0.0898823707
N	2.8510975120	0.4114099107	-0.1154821111
H	-1.2800794380	2.6420503348	0.0558102173
H	1.2137645904	2.7054605164	-0.0333261717
H	3.3127062784	0.8148725195	0.7000742438
H	3.2511054929	0.8602967793	-0.9397187954
H	2.4940721368	-1.4812133897	-0.1368637739
H	1.4039089788	-2.4637021180	0.7431068457
H	1.3156959350	-2.4521904744	-0.9147951313

4B''

	X	Y	Z

E = -541.494728 a.u.

C	1.4587519604	0.6058673241	0.0482000434
C	0.7950405550	1.8232110560	-0.0013138592
C	-0.6015314465	1.8080103511	-0.0427060884
C	-1.2835881490	0.5952727190	-0.0335998098
C	-0.5911909881	-0.6202394582	0.0163545371
C	0.8011027752	-0.6327353179	0.0585514911
F	-2.6102856126	0.5678754670	-0.0723037104
F	-1.2624729808	-1.7697981767	0.0253178932
N	1.6172676156	-1.8100966712	0.1184549714
N	2.9320566969	0.4837597140	0.0990123997
H	-1.1731599175	2.7290123289	-0.0822658415
H	1.3299617683	2.7680633217	-0.0082061410
H	3.0731386124	-0.5649713284	0.1342007227
H	3.4044749670	0.8664217919	-0.7294184234
H	3.3510921662	0.9150925914	0.9321792189
H	1.4745306038	-2.4126964844	-0.6936185361

H	1.4030707299	-2.3747480186	0.9415726923

5B' **X** **Y** **Z**

E = -541.500282 a.u.

C	-1.1014567957	0.0610616780	-0.0129279491
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C	0.8947670415	-1.2734607797	-0.1029818302
C	1.6238958593	-0.0810905393	-0.1200663077
C	1.0292279786	1.1816773496	-0.0850654834
C	-0.3540177606	1.2329864208	-0.0305375101
N	-1.4116781743	-2.3114778251	-0.0237385035
F	2.9505929976	-0.1476003342	-0.1728619893
F	-1.0121642043	2.3984336296	0.0073693237
N	-2.5686771866	0.0740524732	0.0459608326
H	1.6271181636	2.0858995993	-0.0998994027
H	1.4171282335	-2.2236456637	-0.1321233809
H	-1.3242273804	-2.8954282133	-0.8561465427
H	-1.2542185293	-2.9167846638	0.7826880000
H	-2.9404187962	0.5194447321	0.8950109035
H	-3.0068957371	0.5337114848	-0.7628834836
H	-2.7989686899	-0.9574850284	0.0459616806

5B'' **X** **Y** **Z**

E = -541.499783 a.u.

C	1.0753828428	0.0929783614	-0.0847269612
C	0.2717678864	1.2353842100	-0.0086084730
C	-1.1136268061	1.2137479690	0.0424746426
C	-1.7124803699	-0.0478202668	0.0150381240
C	-0.9761299438	-1.2287194907	-0.0589670998
C	0.4095045819	-1.1379736958	-0.1081418508
N	1.0516007822	2.4920957853	0.0149511866
F	-3.0398498734	-0.1165168672	0.0619765650
F	1.1473229906	-2.2462376368	-0.1805373429
N	2.4947530074	0.2887540171	-0.1300472668
H	-1.4723763274	-2.1927811805	-0.0780872126
H	-1.7274233705	2.1064434359	0.1014406592
H	2.0498197975	2.1377661280	-0.0346105623
H	0.8599684278	3.1063957651	-0.7861395256
H	0.9185354405	3.0378437977	0.8753125561
H	2.9671665526	-0.1710146637	0.6494910576
H	2.9046162026	-0.0908878253	-0.9846198012

7B'	**X**	**Y**	**Z**
E = -640.682927 a.u.			
C	-1.2473492266	0.3823871360	-0.0122683399
C	-1.2471017513	-1.0174463370	-0.0497863778
C	-0.0195424720	-1.6786202011	-0.1029442220
C	1.1580640955	-0.9324508863	-0.1168211627
C	1.1490272540	0.4683104895	-0.0792756808
C	-0.0752686610	1.1284218394	-0.0262508822
N	-2.5503549663	-1.6246684756	-0.0294113682
F	2.3332312720	-1.5442063662	-0.1668529478
F	2.2802049768	1.1562701946	-0.0938887159
F	-0.1392305639	2.4611690024	0.0112756846
N	-2.5649593581	1.0270709446	0.0433724214
H	0.0447914536	-2.7613076443	-0.1341890210
H	-2.7201091541	-2.1945014437	-0.8586717940
H	-2.6781362226	-2.2299165137	0.7822335167
H	-2.7127188349	1.5835305959	0.8958323090
H	-2.7579465259	1.6358087651	-0.7631199612
H	-3.2187155030	0.1956156208	0.0359452097

7B''	**X**	**Y**	**Z**
E = -640.683479 a.u.			
C	0.0251069516	1.0594210630	-0.0439421224
C	-1.2277547796	0.4403001352	-0.0334811905
C	-1.2509991031	-0.9585440993	-0.0407534196
C	-0.1115928999	-1.7515368951	-0.0576966817
C	1.1167927351	-1.0950898045	-0.0678003037
C	1.1977848677	0.3028201616	-0.0606833397
N	-2.4885678381	1.1204555681	-0.0142386043
N	-2.6179350062	-1.5195335913	-0.0264706934
F	2.2439112424	-1.7941980953	-0.0843790630
F	2.3782189709	0.9010847807	-0.0697778105
F	0.0969222617	2.3868422160	-0.0371822107
H	-0.1353240420	-2.8364053222	-0.0629699383
H	-2.8162567530	-2.0948012537	0.8018455940
H	-3.2200460809	-0.6479526417	-0.0076715308
H	-2.8421130581	-2.0750541592	-0.8615425673
H	-2.5861930782	1.7199792849	0.8063699634
H	-2.6113185077	1.7195475844	-0.8319134320

2C’ **X** **Y** **Z**

E = -441.064374 a.u.

C	0.2098173047	2.0995666818	-0.0407519947
C	-1.0713615981	1.4165418049	0.0260007031
C	-1.1475279814	0.0611045916	0.0784070936
C	0.0344532204	-0.7376273034	0.0686780000
C	1.3745702864	-0.0479174253	-0.0004428682
C	1.3763009713	1.4154985768	-0.0536543892
H	-1.9914859745	1.9940220741	0.0350489053
F	-2.3072030393	-0.6012854682	0.1420293723
N	-0.0111703638	-2.0425748107	0.1176860619
N	2.3787929889	-0.8430948891	-0.0048485624
H	0.2026229542	3.1838631782	-0.0801079211
H	2.3361762438	1.9204122133	-0.1029852487
H	3.2798811998	-0.3553511012	-0.0523125925
H	0.8676505785	-2.5625677841	0.1074958398
H	-0.8957470012	-2.5411859295	0.1639069587

2C’’ **X** **Y** **Z**

E = -441.068991 a.u.

C	1.2340997856	1.4969556566	0.0093480633
C	-0.0015223781	2.0918248156	-0.0501710003
C	-1.2531879241	1.3707500316	-0.0520413828
C	-1.2215875564	0.0239904684	0.0075702850
C	0.0426325712	-0.7306444791	0.0740450264
C	1.3143434310	0.0826713072	0.0733725653
F	-2.3139527817	-0.7254355994	0.0116649150
N	0.1598813664	-1.9999268127	0.1315570057
N	2.4380469977	-0.5934260664	0.1336487776
H	-2.1961964989	1.9041347636	-0.1003781782
H	-0.0522346271	3.1762339642	-0.0993943457
H	2.1402191080	2.0941655685	0.0077079698
H	3.3456860308	-0.1387118895	0.1379060306
H	2.3967045720	-1.6121802002	0.1766828501
H	-0.7468160962	-2.4815635284	0.1274644182

4C’ **X** **Y** **Z**

E = -540.258772 a.u.

C	1.3765303199	1.4178950863	0.0000000000
C	0.2175084885	2.1084293483	0.0000000000
C	-1.0507236526	1.4063031124	0.0000000000
C	-1.1513150040	0.0384072105	0.0000000000
C	0.0257856869	-0.7427242900	0.0000000000
C	1.3682404815	-0.0510320421	0.0000000000
F	-2.3306394614	-0.5841549481	0.0000000000
N	-0.0096037121	-2.0535692988	0.0000000000
N	2.3764181035	-0.8374791057	0.0000000000
F	-2.1442841941	2.1288432728	0.0000000000
H	0.1795614986	3.1932762815	0.0000000000
H	2.3380843200	1.9220305454	0.0000000000
H	3.2763281654	-0.3454874359	0.0000000000
H	0.8727234835	-2.5652556647	0.0000000000
H	-0.8886145238	-2.5624820720	0.0000000000

4C'' **X** **Y** **Z**

E = -540.255757 a.u.

C	-1.5484964113	-0.4825456510	0.0000000000
C	-0.9007568857	-1.7494831023	0.0000000000
C	0.4667399088	-1.7914979375	0.0000000000
C	1.2985931451	-0.6117503962	0.0000000000
C	0.7391877429	0.6214830089	0.0000000000
C	-0.7164798198	0.7794472101	0.0000000000
F	2.6108657915	-0.7830553257	0.0000000000
F	1.4513946571	1.7371477375	0.0000000000
N	-1.3537154952	1.8869270095	0.0000000000
N	-2.8487340154	-0.3229793326	0.0000000000
H	0.9863406812	-2.7463809388	0.0000000000
H	-1.4853532019	-2.6635069847	0.0000000000
H	-3.4947967757	-1.1066347026	0.0000000000
H	-3.2238868515	0.6275402710	0.0000000000
H	-0.7329024702	2.7042891345	0.0000000000

5C' **X** **Y** **Z**

E = -540.258692 a.u.

C	0.2920306945	1.3947956233	0.0000000000
C	-1.1518445097	1.2128099230	0.0000000000
C	-1.6520647317	-0.0423350998	0.0000000000
C	-0.8237084401	-1.2371146618	0.0000000000

C	0.5265673013	-1.1309841157	0.0000000000
C	1.1569110998	0.1557742632	0.0000000000
H	-1.3057930639	-2.2105371180	0.0000000000
F	1.3381336502	-2.1891054333	0.0000000000
N	2.4541695881	0.2825898965	0.0000000000
N	0.9618317672	2.4887493494	0.0000000000
F	-2.9560104801	-0.2703510818	0.0000000000
H	-1.8058481076	2.0779856603	0.0000000000
H	0.3726732093	3.3276955214	0.0000000000
H	2.8484248456	1.2262880177	0.0000000000
H	3.0698101453	-0.5271215122	0.0000000000

5C'' **X** **Y** **Z**

E = -540.270304 a.u.

C	-1.1486941610	-0.1641149901	0.0000000000
C	-0.2188573936	-1.3546588929	0.0000000000
C	1.1743788479	-1.1514460401	0.0000000000
C	1.6358515146	0.1446855190	0.0000000000
C	0.8197031896	1.3352099677	0.0000000000
C	-0.5162069218	1.1710198588	0.0000000000
N	-0.7975211583	-2.5361257959	0.0000000000
F	2.9317257156	0.3537543918	0.0000000000
F	-1.3624229203	2.1860807857	0.0000000000
N	-2.4016043392	-0.3957876468	0.0000000000
H	1.2931383856	2.3109532231	0.0000000000
H	1.8784007067	-1.9763214669	0.0000000000
H	-0.2684231584	-3.4018133439	0.0000000000
H	-1.8161990327	-2.5818404227	0.0000000000
H	-2.9662692748	0.4614048533	0.0000000000

7C' **X** **Y** **Z**

E = -639.447284 a.u.

C	1.2158586420	1.2111753097	0.0000000000
C	-0.1293968391	1.7794970898	0.0000000000
C	-1.1953422160	0.9557198460	0.0000000000
C	-1.0477626006	-0.5001439558	0.0000000000
C	0.1817718483	-1.0988093785	0.0000000000
C	1.3499676628	-0.2948672006	0.0000000000
F	-2.1395866409	-1.2154344123	0.0000000000
F	0.3180125898	-2.4233346909	0.0000000000

N	2.5475091227	-0.8211028570	0.0000000000
N	2.3335060653	1.8351373956	0.0000000000
F	-2.4422547713	1.3845783356	0.0000000000
H	-0.2604445049	2.8564544165	0.0000000000
H	2.2331917343	2.8553329231	0.0000000000
H	3.3518050223	-0.1915263670	0.0000000000
H	2.6904665711	-1.8272844648	0.0000000000

7C''	**X**	**Y**	**Z**

E = -639.451483 a.u.

C	-0.1457374931	-1.1214024374	0.0000000000
C	1.2314207039	-0.6133110489	0.0000000000
C	1.4170800222	0.8881767481	0.0000000000
C	0.2883531766	1.7369186583	0.0000000000
C	-0.9541344832	1.1571524011	0.0000000000
C	-1.2004043614	-0.2771982854	0.0000000000
N	2.2886967406	-1.3268749510	0.0000000000
N	2.6585396828	1.3144089004	0.0000000000
F	-2.0286804219	1.9019577509	0.0000000000
F	-2.4549128212	-0.6813934620	0.0000000000
F	-0.2897880227	-2.4353916639	0.0000000000
H	0.3767872389	2.8179272399	0.0000000000
H	2.8984290884	2.3007950946	0.0000000000
H	3.4092914949	0.6227050224	0.0000000000
H	2.0940594552	-2.3344699672	0.0000000000

3. References

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3. G. Schaftenaar, J. H. Noordik, *J. Comput. Aided Mol. Des.*, 2000, **14**, 123–134.
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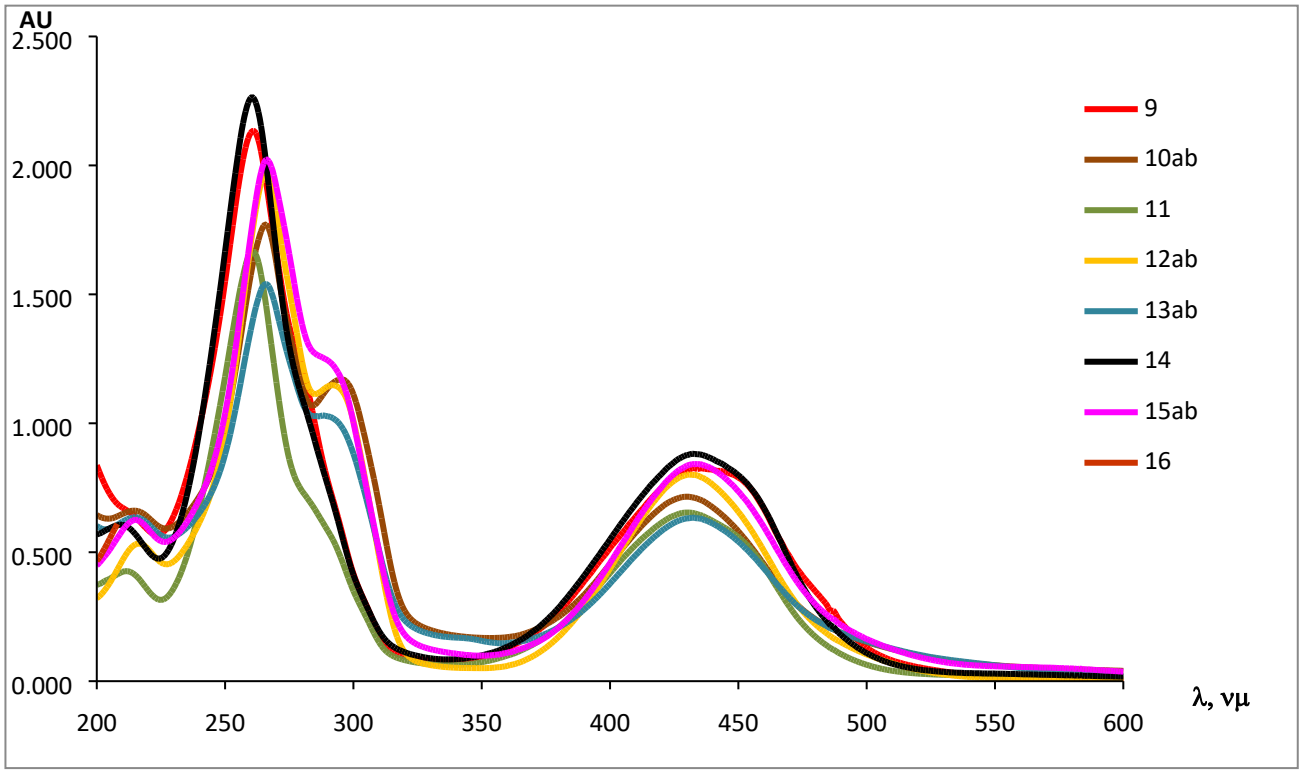
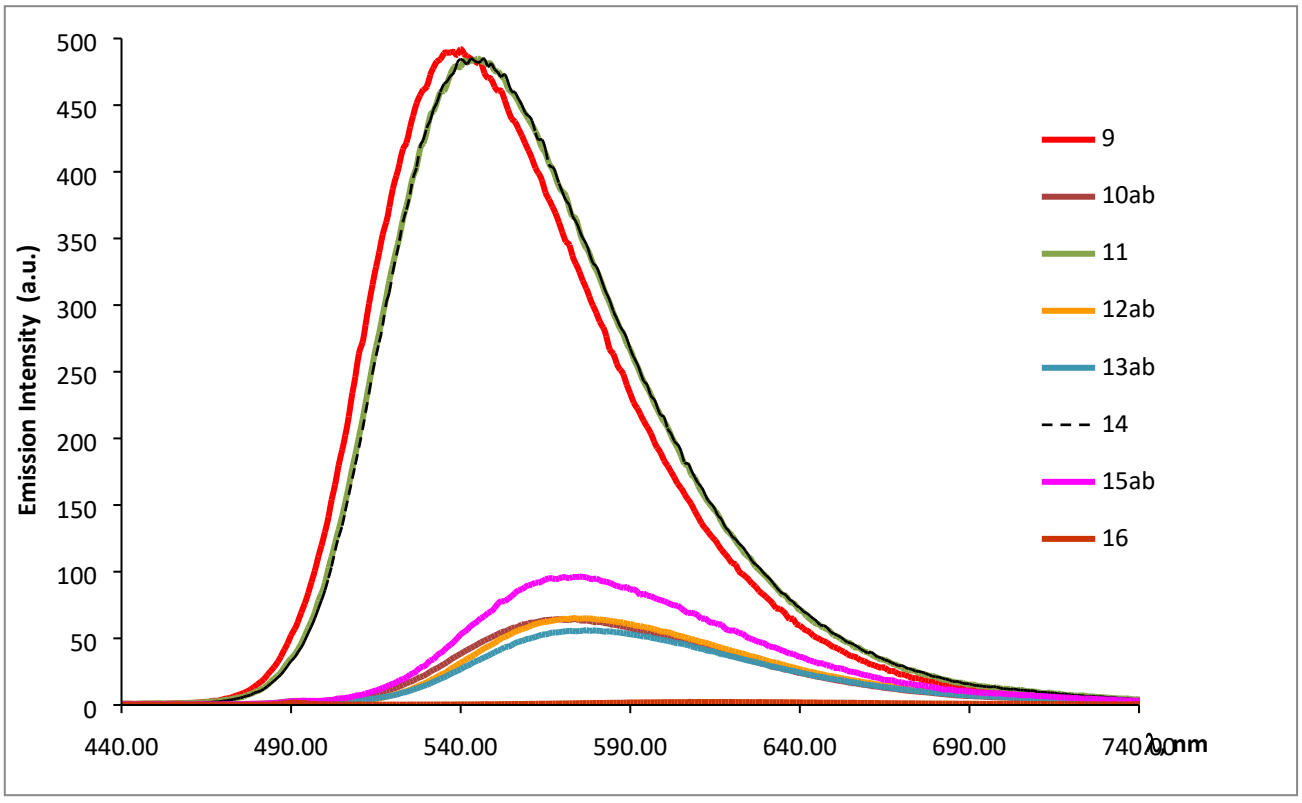
4. **Fig. S2**. Absorption (1) and emission (2) spectra of 2,3-diaminophenazines.

1.



2.



5. Quantum chemical calculations of relative values of chemical shifts of signals in ^{1}H, ^{19}F, ^{13}C, ^{15}N spectra

Table S2. Calculated and experimental ^{1}H, ^{13}C, ^{15}N and ^{19}F chemical shifts (δ, ppm). Difference (Δ) in chemical shift for **a** and **b** isomers.

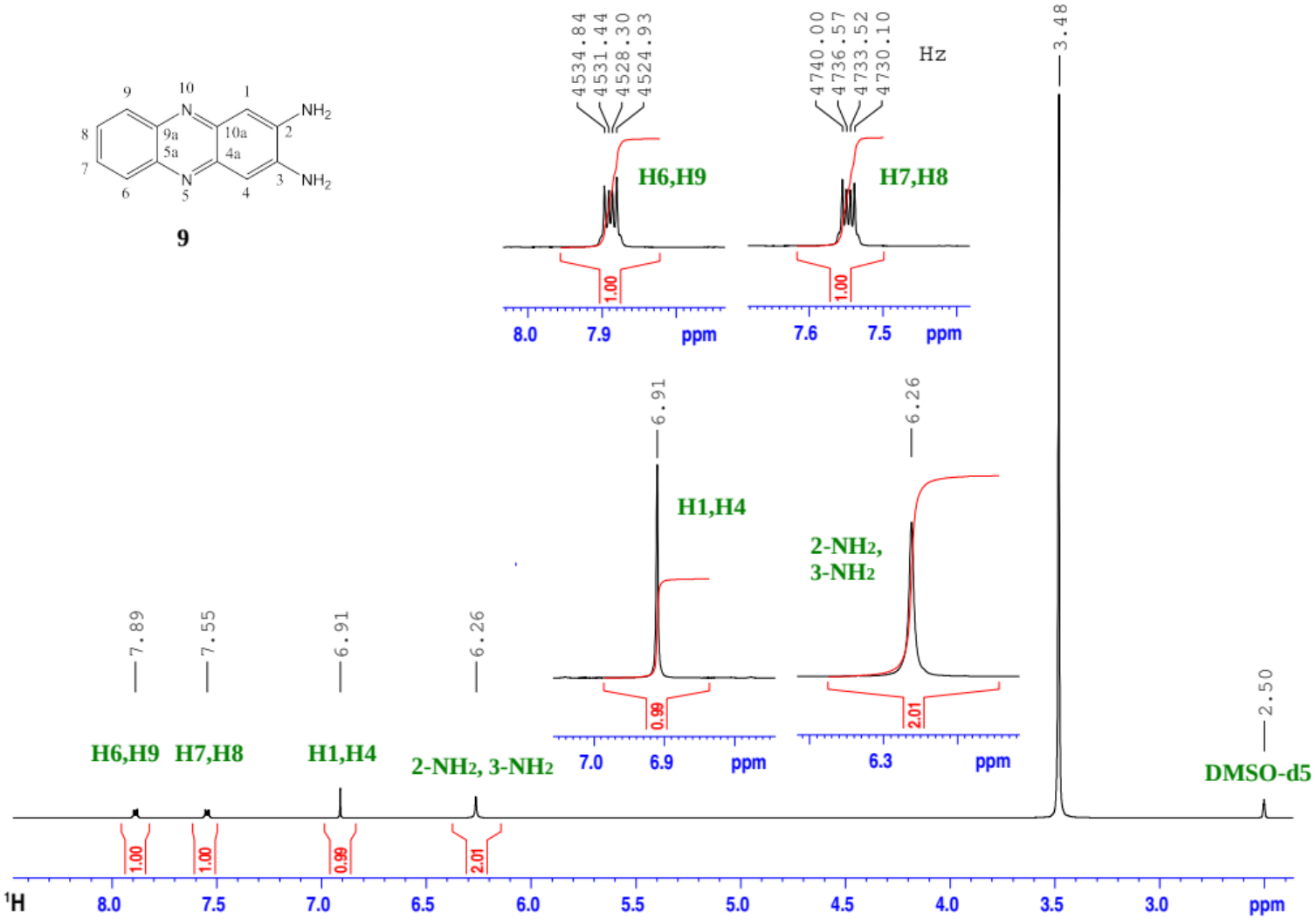
		Nuclear and position											
		C1	C2	C3	C4	C6	C7	C8	C9	C4a	C5a	C9a	C10a
		Δ											
		aC1-bC1	aC2-bC2	aC3-bC3	aC4-bC4	aC6-bC9	aC7-bC8	aC8-bC7	aC9-bC6	aC4a-bC4a	aC5a-bC9a	aC9a-bC5a	aC10a-bC10a
10a	calc	142.42	132.16	145.21	102.98	156.93	112.34	126.57	124.3	137.64	131.98	139.72	130.63
10b	calc	142.86	131.81	145.56	102.48	123.87	127.3	111.82	157.36	138.77	141.06	130.63	129.54
10a	exp	138.34	130.45	144.69	98.11	156.28	110.67	125.75	124.27	139.48	131.13	140.42	131.93
10b	exp	138.62	130.34	144.86	97.81	123.97	126.28	110.3	156.6	140.22	141.51	130.07	131.21
Δ **10a-10b**	calc	-0.44	0.35	-0.35	0.5	-0.43	0.52	-0.73	0.43	-1.13	1.35	-1.34	1.09
Δ **10a-10b**	exp	-0.28	0.11	-0.17	0.3	-0.32	0.37	-0.53	0.3	-0.74	1.06	-1.09	0.72
12a	calc	142.61	131.85	146.04	102.37	143.66	149.12	117.89	124.74	137.93	132.45	136.33	130.19
12b	calc	142.39	132.73	145.19	102.83	124.25	118.56	148.72	144.05	138.2	137.67	131.02	129.76
12a	exp	138.34	130.29	145.56	97.63	142.31	147.02	116.91	124.68	139.72	131.63	136.76	131.63
12b	exp	138.32	131.24	144.65	97.89	124.35	117.45	146.75	142.67	139.82	137.82	130.54	131.4
Δ **12a-12b**	calc	0.22	-0.88	0.85	-0.46	-0.39	0.4	-0.67	0.49	-0.27	1.43	-1.34	0.43
Δ **12a-12b**	exp	0.02	-0.95	0.91	-0.26	-0.36	0.27	-0.54	0.33	-0.1	1.09	-1.06	0.23
13a	calc	141.94	133.01	144.8	103.31	157.33	104.85	160.48	107.7	137.17	129.68	139.19	131.13
13b	calc	143.04	131.46	146.33	101.92	107.4	160.95	104.24	157.8	139.34	140.62	128.33	129.17
13a	exp	138.15	131.46	144.59	98.41	156.94	103.26	159.34	107.3	139.24	128.7	139.91	132.52
13b	exp	138.78	130.27	145.85	97.5	106.9	159.68	102.86	157.3	140.91	141.02	127.63	131.09
Δ **13a-13b**	calc	-1.1	1.55	-1.53	1.39	-0.47	0.61	-0.47	0.3	-2.17	1.35	-1.43	1.96
Δ **13a-13b**	exp	-0.63	1.19	-1.26	0.91	-0.36	0.4	-0.34	0.4	-1.67	1.07	-1.11	1.43
15a	calc	142.16	132.64	145.61	102.75	145.02	141.56	151.36	108.92	137.53	129.86	134.63	130.81
15b	calc	142.62	132.31	145.94	102.32	108.6	151.78	141.11	145.44	138.92	136.03	128.47	129.49
15a	exp	138.01	130.86	145.07	97.73	143.5		149.36	108.37	139.26	128.7	134.91	132.02
15b	exp	138.28	130.77	145.2	97.46	107.98	149.68		143.87	140.36	136.02	127.57	130.97
Δ **15a-15b**	calc	-0.46	0.33	-0.33	0.43	-0.42	0.45	-0.42	0.32	-1.39	1.39	-1.4	1.32
Δ **15a-15b**	exp	-0.27	0.09	-0.13	0.27	-0.37		-0.32	0.39	-1.1	1.13	-1.11	1.05

Continuation of **Table S2**

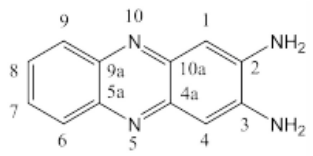
		Nuclear and position											
		N2 ($2\text{-}NH_2$)	N3 ($3\text{-}NH_2$)	N5	N10	H2 ($2\text{-}NH_2$)	H3 ($3\text{-}NH_2$)	H4	H6 or F6	H7 or F7	H8 or F8	H9 or F9	F1
		Δ											
		aN2-bN2	aN3-bN3	aN5-bN5	aN10-bN10	aH2-bH2	aH3-bH3	aH4-bH4	aH6-bH9 or aF6-bF9	aH7-bH8 or aF7-bF8	aH8-bH7 or aF8-bF7	aH9-bH6 or aF9-bF6	aF1-bF1
10a	calc	58.33	72.52	289.31	290.31	4.69 and 3.77	4.33 and 4.55	7.28	32.83	7.45	7.73	7.96	4.25
10b	calc	57.70	73.05	298.92	281	3.71 and 4.68	4.56 and 4.39	7.22	7.89	7.74	7.45	33.26	4.98
10a	exp	58.8	71	289.3	290.4	6.39	6.67	6.85	35.84	7.42	7.55	7.83	6.94
10b	exp	58.5	71.3	300.2		6.38	6.68	6.82	7.75	7.56	7.41	36.22	7.12
Δ 10a-10b	calc	0.63	-0.53	-9.61	9.31	0.04	-0.04	0.06	-0.43	0	-0.01	0.07	-0.73
Δ 10a-10b	exp	0.3	-0.3	-10.9		0.01	-0.01	0.03	-0.38	0.01	-0.01	0.08	-0.18
12a	calc	57.93	72.82	285.63	292.26	4.67 and 3.73	4.41 and 4.60	7.25	7.45	26.42	7.62	7.98	4.9
12b	calc	59.13	72.73	300.93	277.39	3.81 and 4.72	4.55 and 4.33	7.22	7.91	7.63	25.36	7.91	4.35
12a	exp	58.8	73.2	284.9	291.6	6.38	6.79	6.84	8.53	23.45	7.68	7.87	7.08
12b	exp	60.7	71.3	301.4		6.50	6.67	6.82	7.8	7.69	22.95	9.38	6.63
Δ 12a-12b	calc	-1.2	1.09	-15.3	14.87	-0.07	0.07	0.03	-0.46	1.06	-0.01	0.07	0.55
Δ 12a-12b	exp	-1.9	1.9	-16.5		-0.12	0.06	0.02	-0.85	0.50	-0.01	0.07	0.45
13a	calc	59.7	72.12	291.25	286.84	4.73 and 3.85	4.27 and 4.53	7.27	39.27	7.28	53.47	7.57	3.71
13b	calc	57.21	74.34	295.33	282.81	3.66 and 4.65	4.61 and 4.47	7.16	7.48	54.28	7.26	39.74	5.69
13a	exp	61	70.8	290.5		6.52	6.66	6.84	40.41	7.58	51.81	7.62	6.63
13b	exp	58.5	73.5	296.8		6.37	6.80	6.79	7.52	52.43	7.56	40.8	7.36
Δ 13a-13b	calc	2.49	-2.22	-4.08	4.03	0.14	-0.14	0.11	-0.47	0.02	-0.81	0.09	-1.98
Δ 13a-13b	exp	2.5	-2.7	-6.3		0.15	-0.14	0.05	-0.39	0.02	-0.62	0.1	-0.73
15a	calc	59.23	73.37	287.75	288.79	4.71 and 3.81	4.36 and 4.58	7.25	12.97	6.19	30.97	7.71	4.44
15b	calc	58.56	73.93	297.32	279.52	3.75 and 4.70	4.59 and 4.41	7.18	7.62	31.78	5.14	13.49	5.13
15a	exp	60.4	72.5	286.3		6.49	6.76	6.82	13.03	2.71	27.52	7.87	6.76
15b	exp	60.2	72.9	297.9		6.48	6.78	6.78	7.76	28.19	2.17	13.53	6.76
Δ 15a-15b	calc	0.67	-0.56	-9.57	9.27	0.04	-0.03	0.07	-0.52	1.05	-0.81	0.09	-0.69
Δ 15a-15b	exp	0.2	-0.4	-11.6		0.01	-0.02	0.04	-0.5	0.54	-0.67	0.11	0

6. ^{1}H, ^{19}F and ^{13}C NMR spectra of the synthesized **DAPs 9–16**

^{1}H NMR spectrum of **9** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30 MHz)

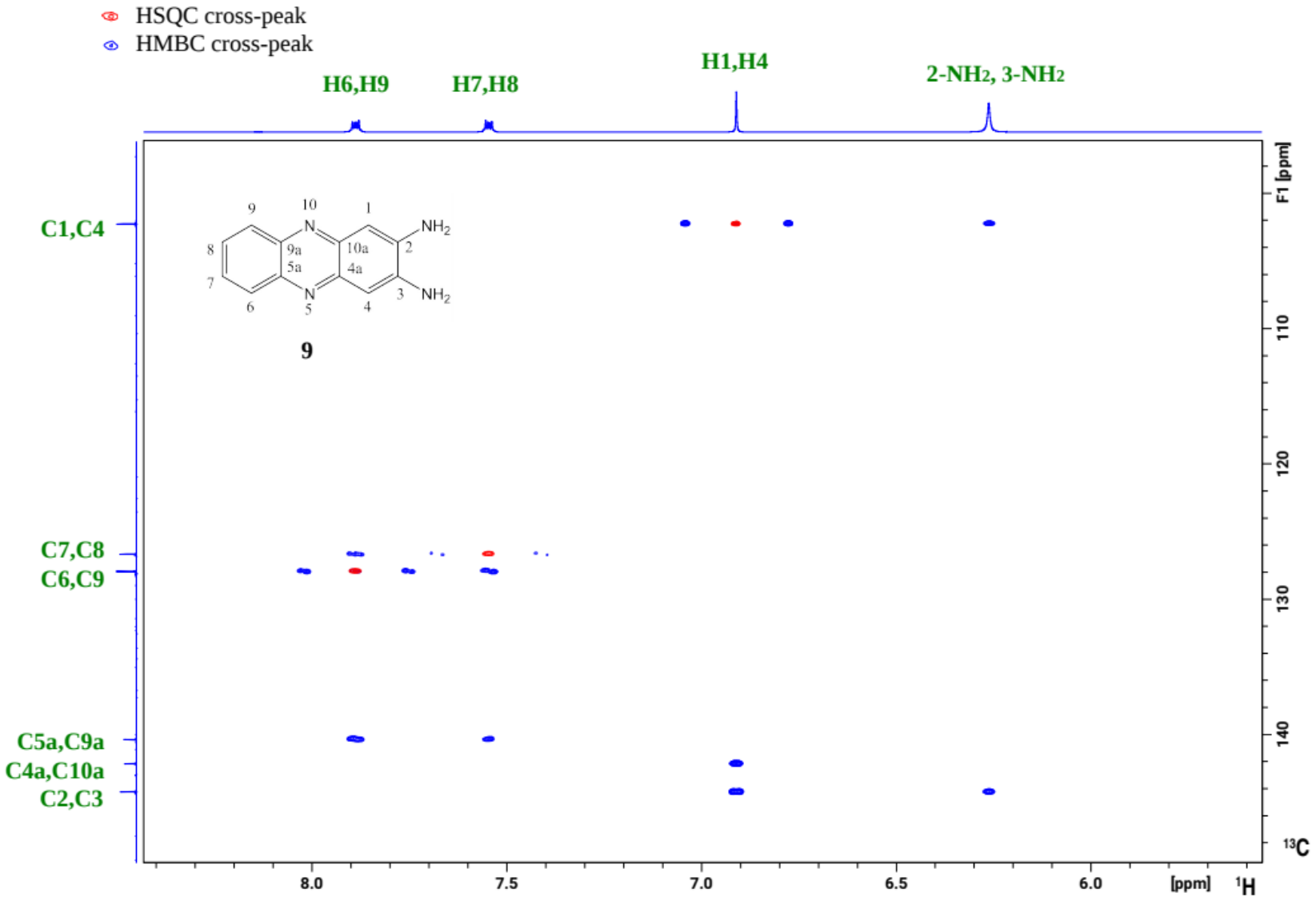


$^{13}C\{^{1}H\}$ NMR spectrum of **9** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{13}C – 150.95 MHz)

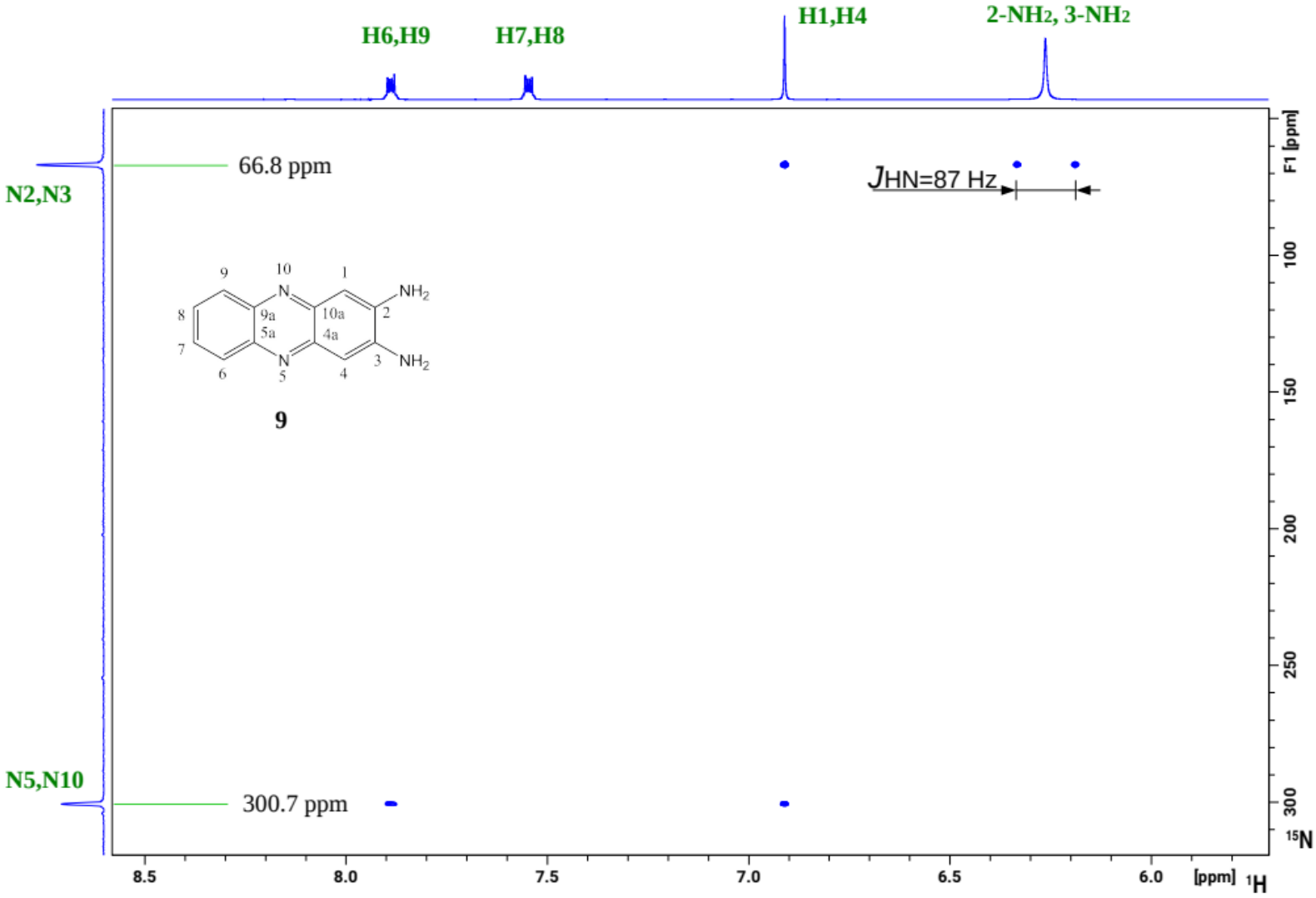


9

^{1}H-^{13}C correlation NMR spectra of **9** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{13}C – 150.95 MHz)

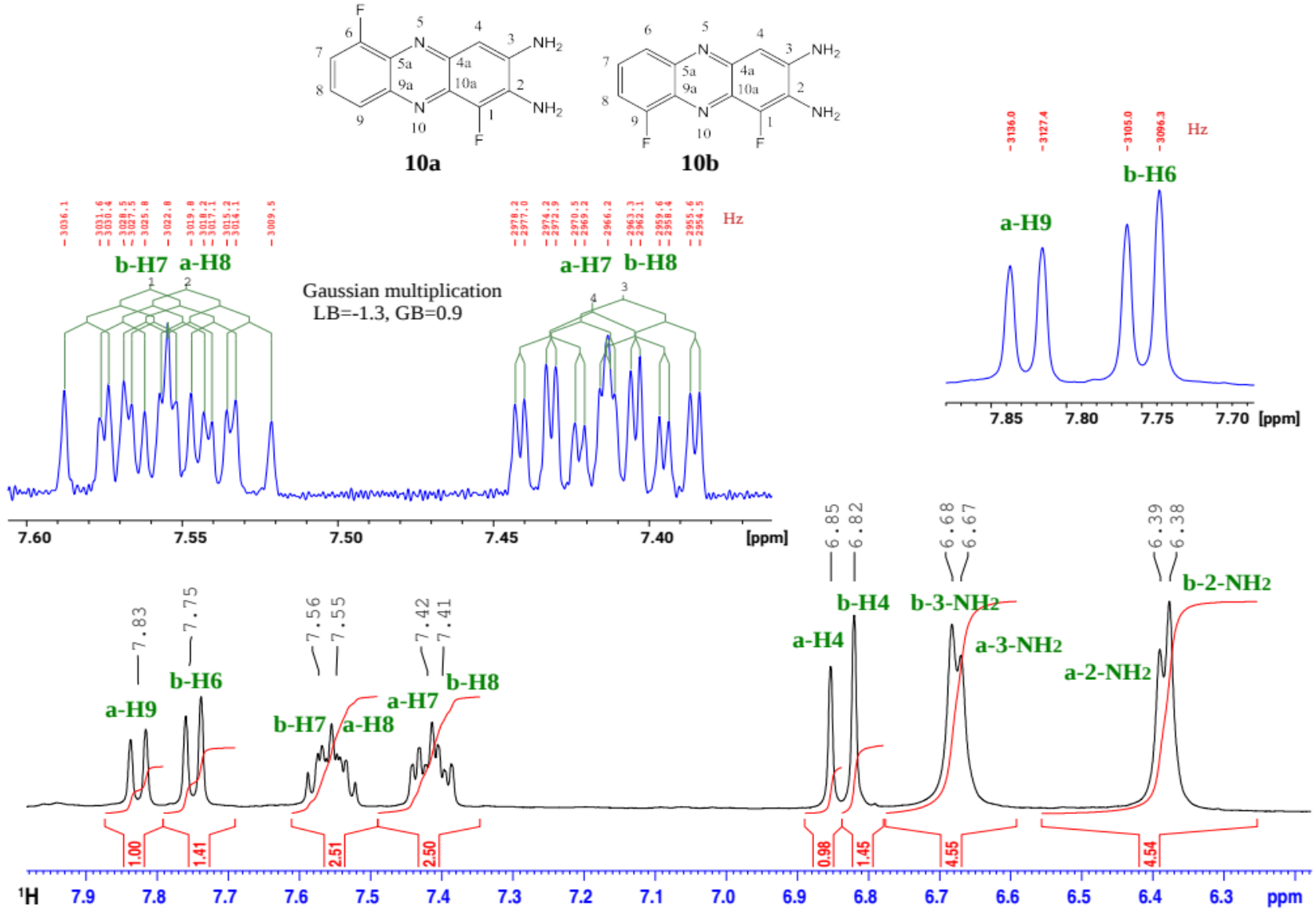


^{1}H-^{15}N HMBC spectrum of **9** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{15}N – 60.83 MHz)

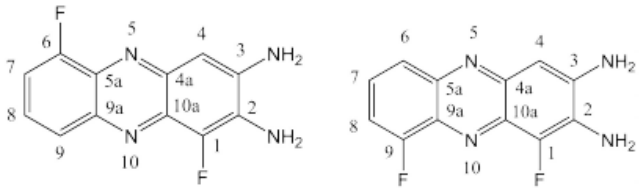


9

^{1}H NMR spectrum of **10a** and **10b** (DMSO-d6), Bruker AV-400 (^{1}H – 400.13 MHz)

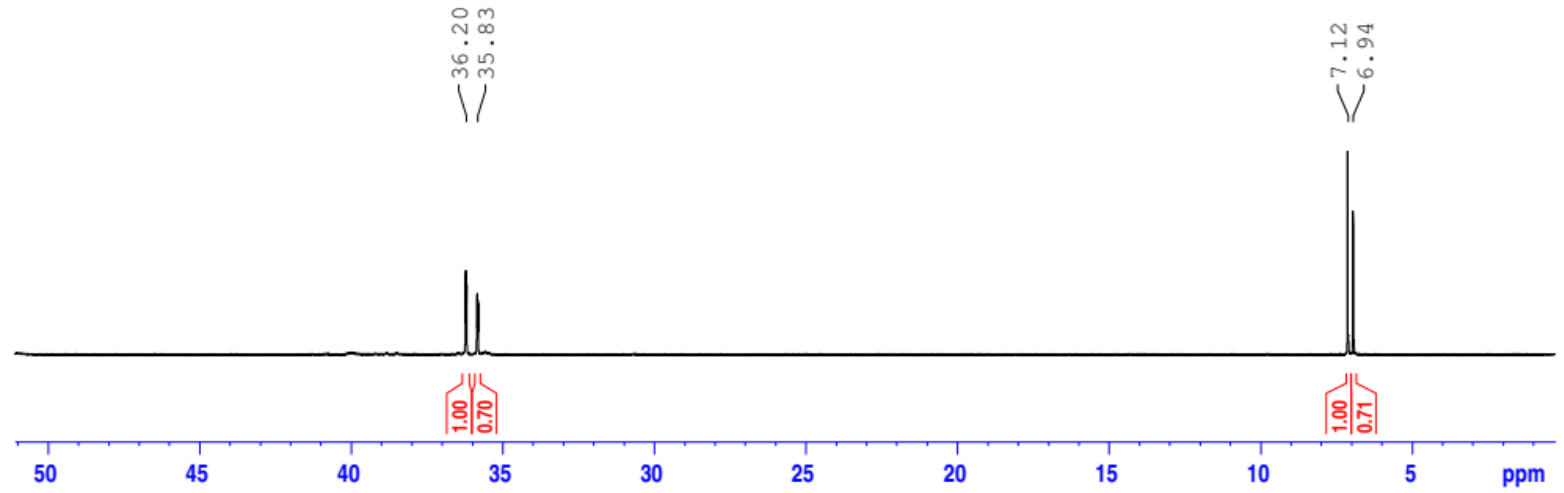


^{19}F NMR spectrum of **10a** and **10b** (DMSO-d6), Bruker AV-400 (^{19}F – 376.50, ^{1}H – 400.13 MHz)

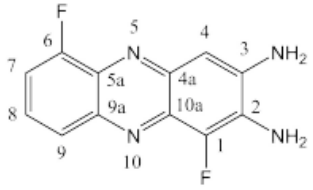


10a

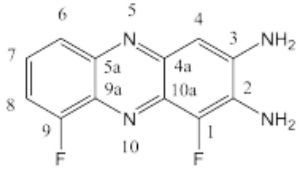
10b



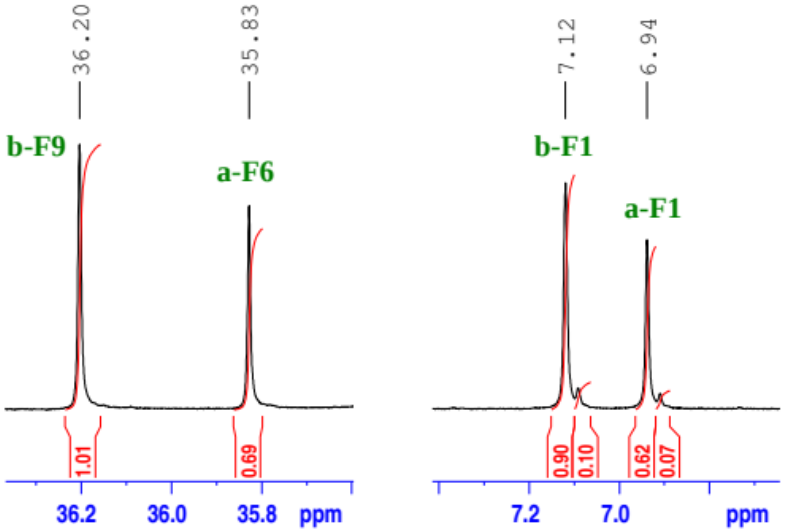
$^{19}F\{^{1}H\}$ NMR spectrum of **10a** and **10b** (DMSO-d6), Bruker AV-400 (^{19}F – 376.50, ^{1}H – 400.13 MHz)

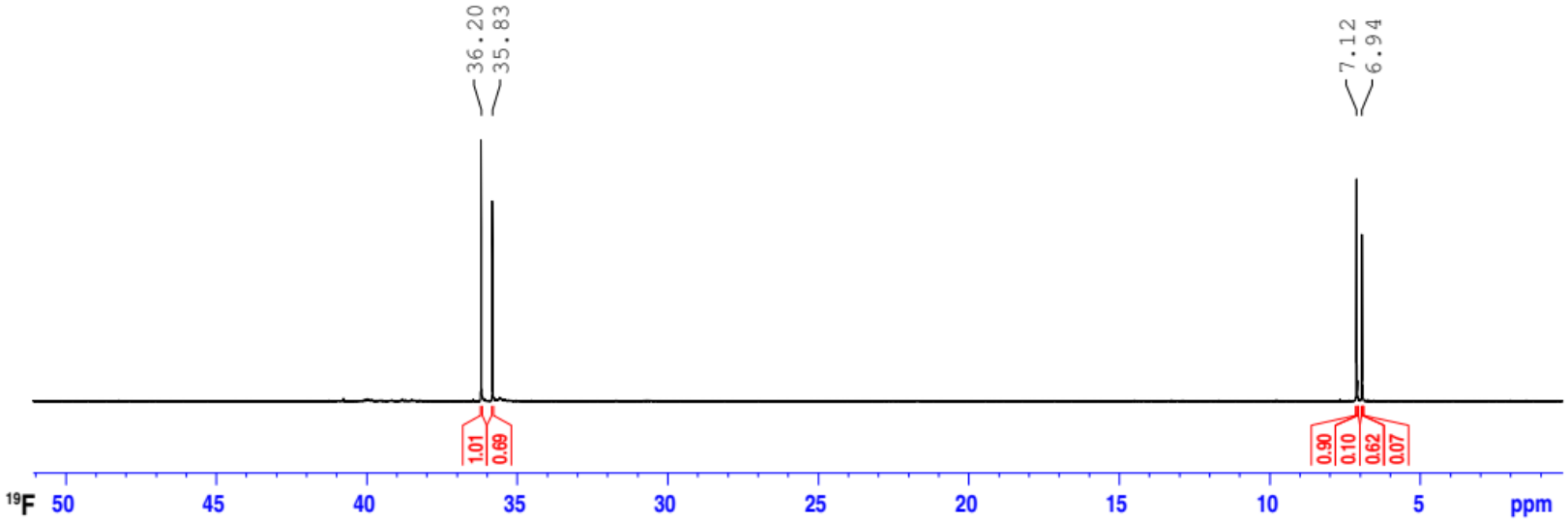


10a

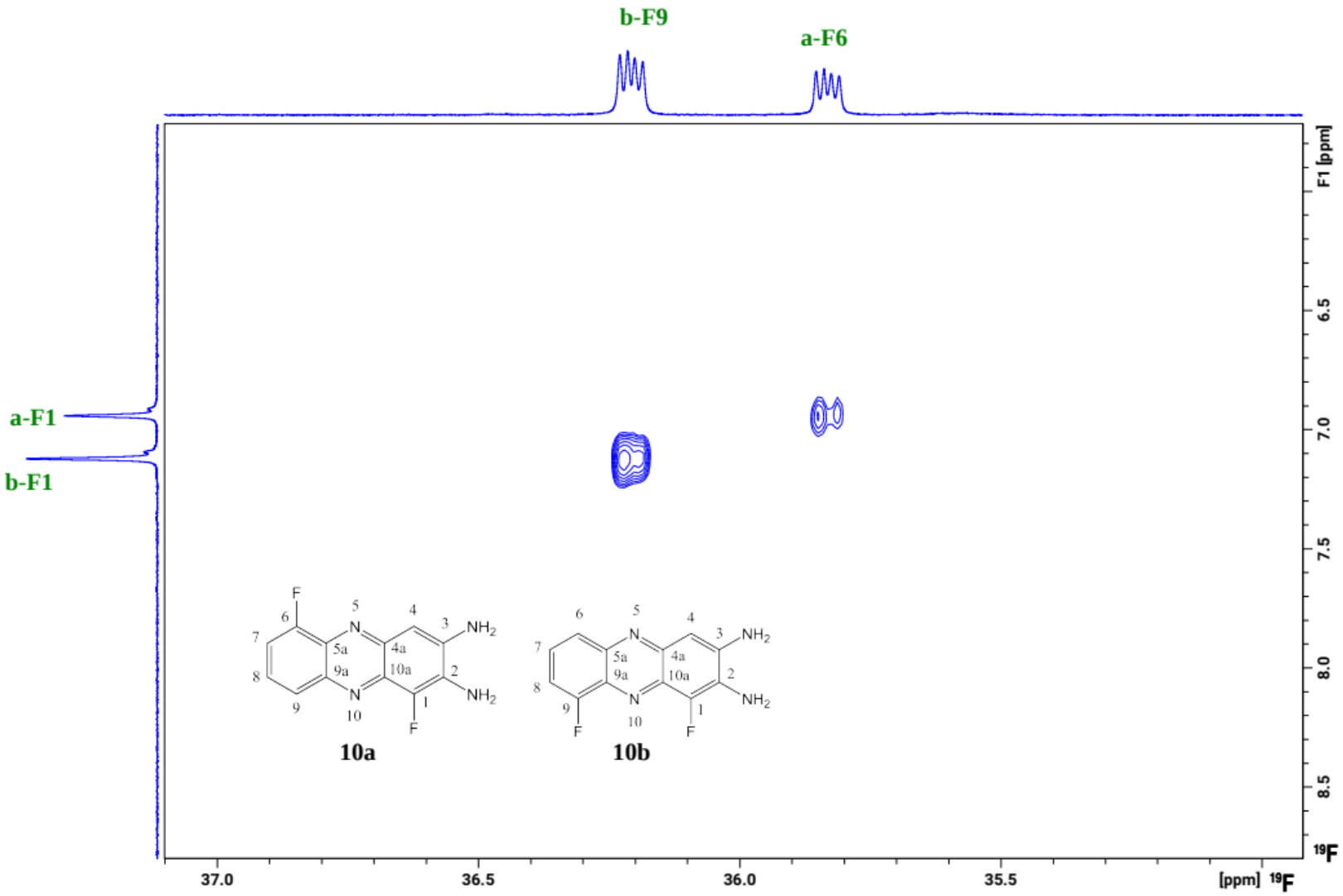


10b

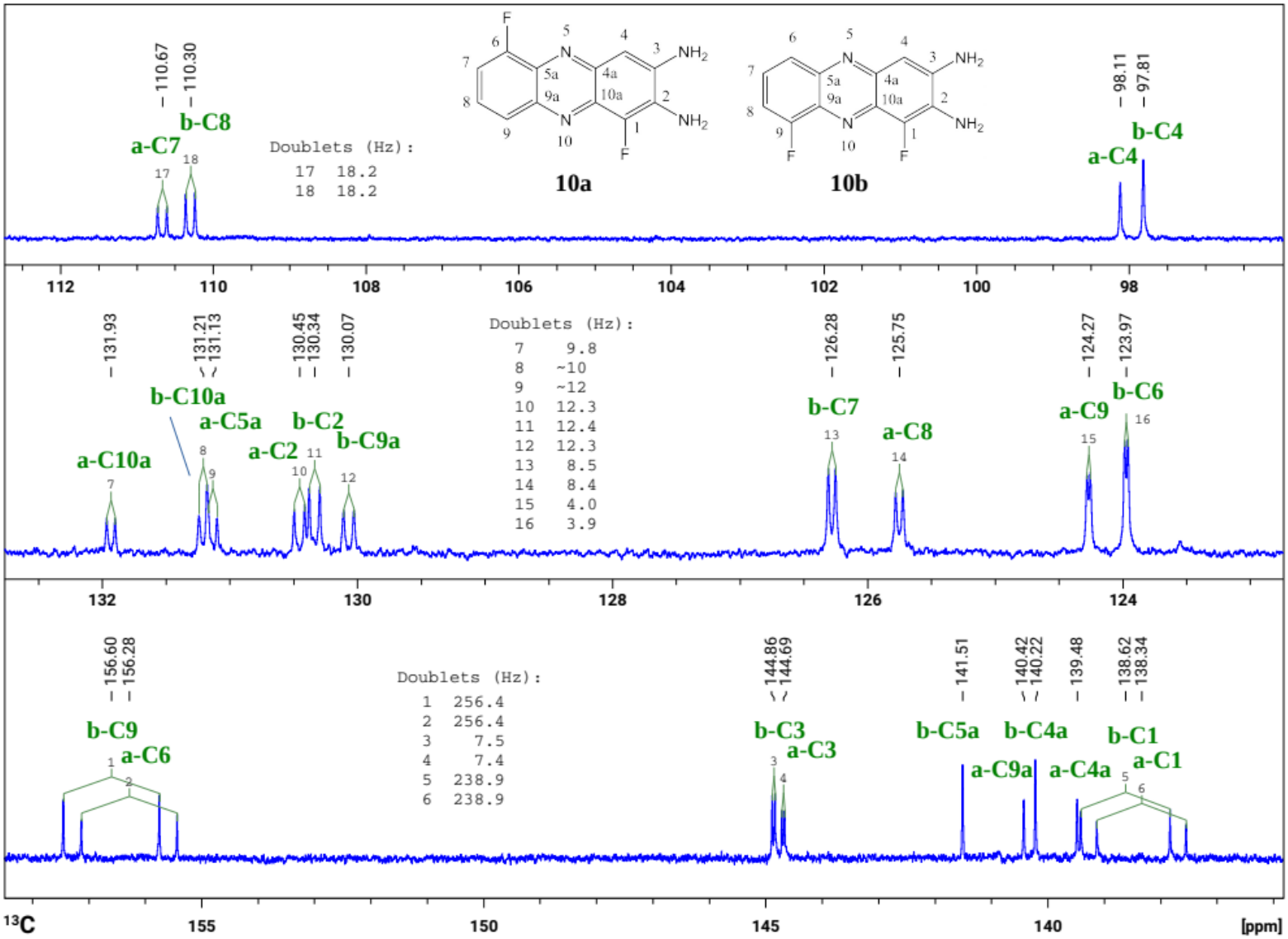




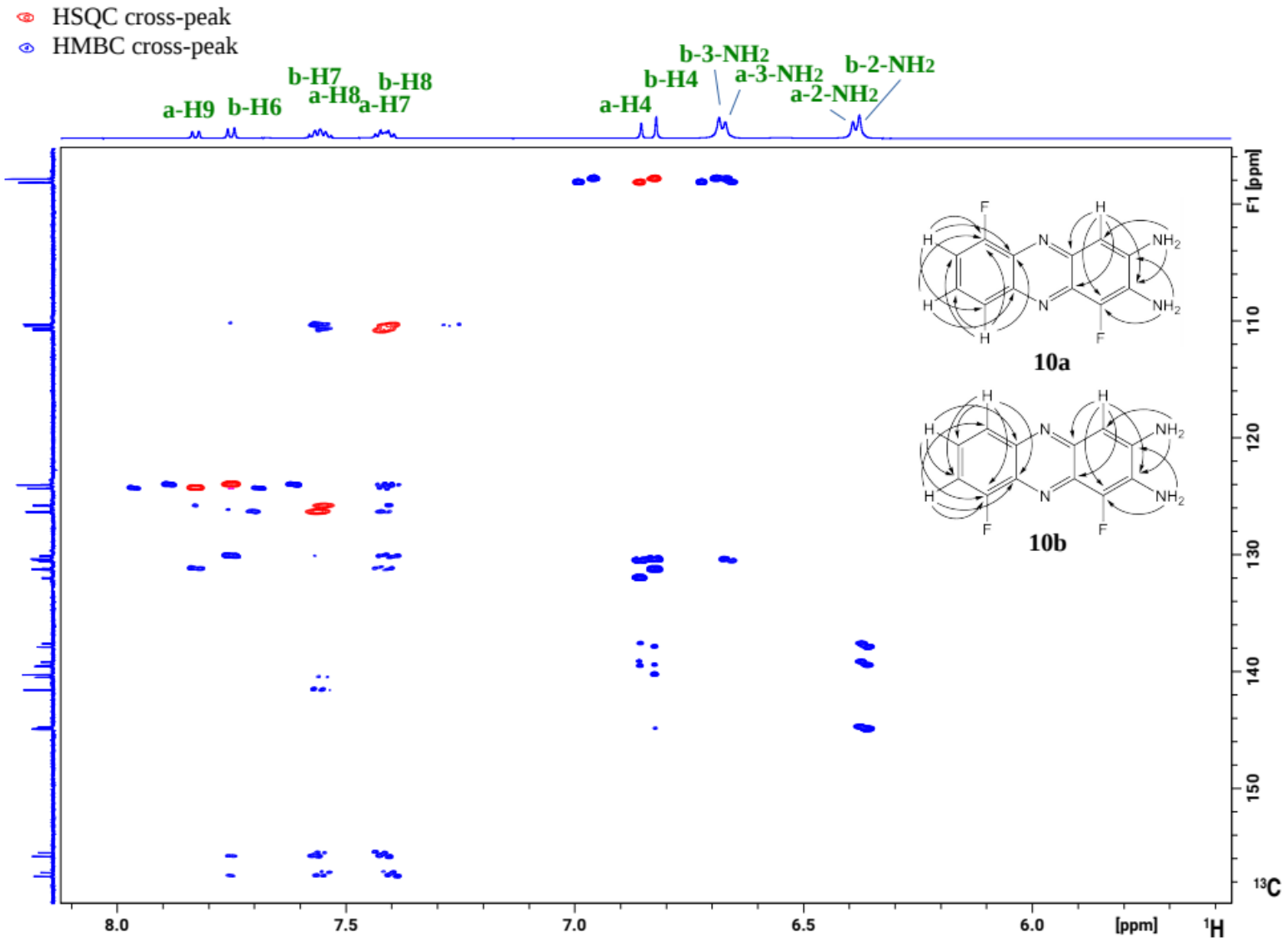
Cross-peaks in ^{19}F-^{19}F COSY spectrum of **10a** and **10b** (DMSO-d6), Bruker AV-400 (^{19}F – 376.50)



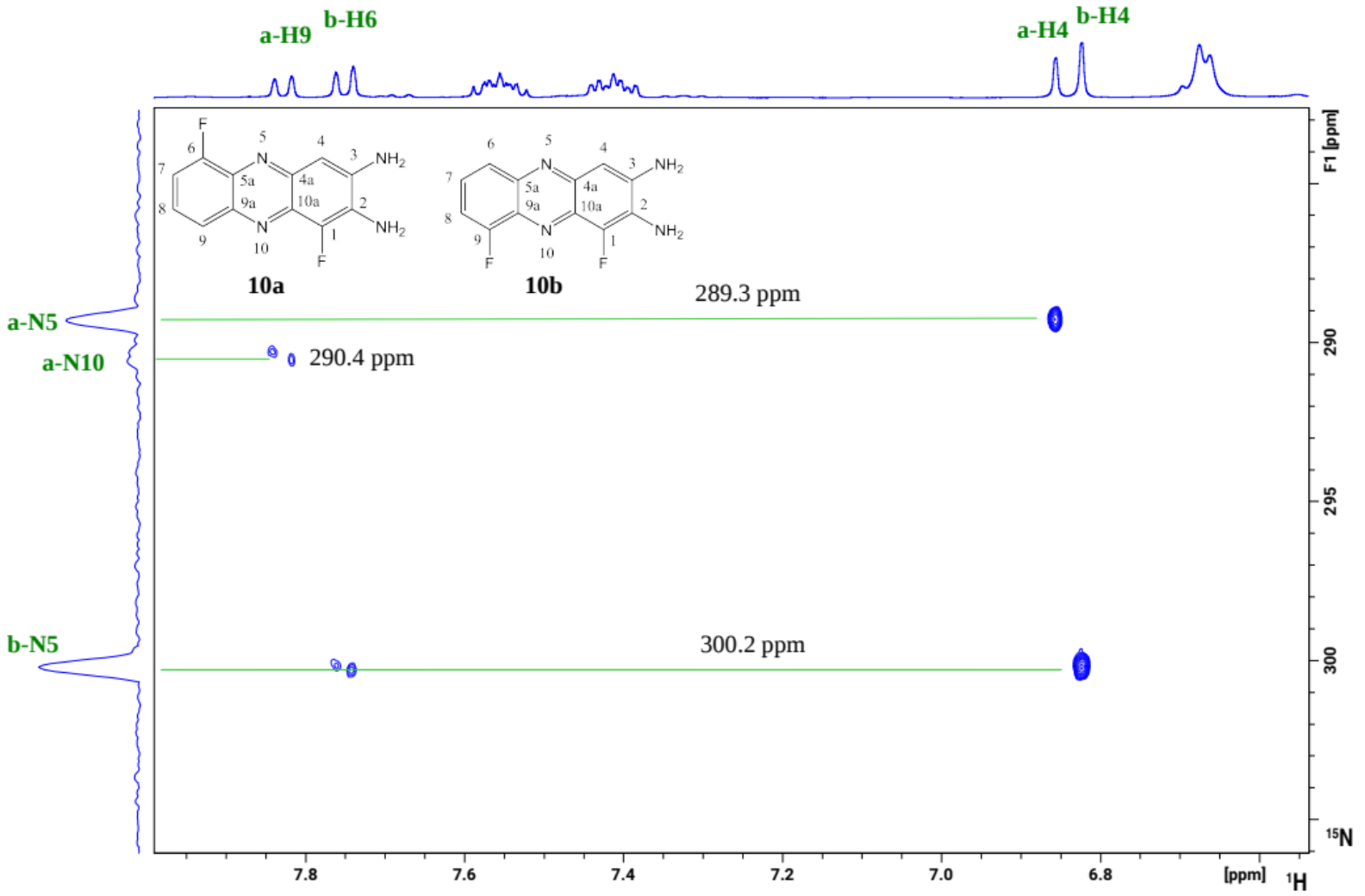
$^{13}C\{^{1}H\}$ NMR spectrum of **10a** and **10b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{13}C – 150.95 MHz)



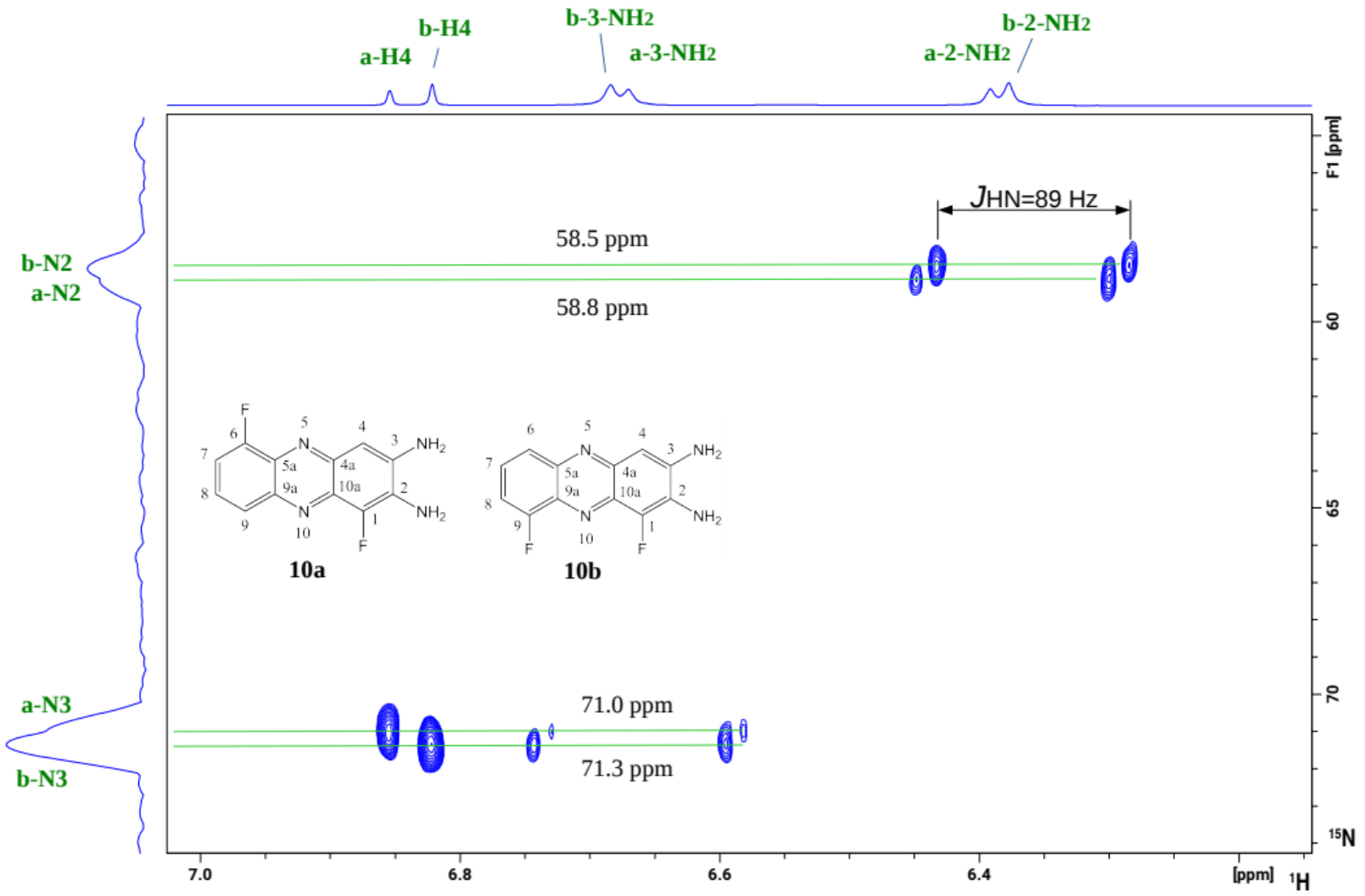
^{1}H-^{13}C correlation NMR spectra of **10a** and **10b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{13}C – 150.95 MHz)



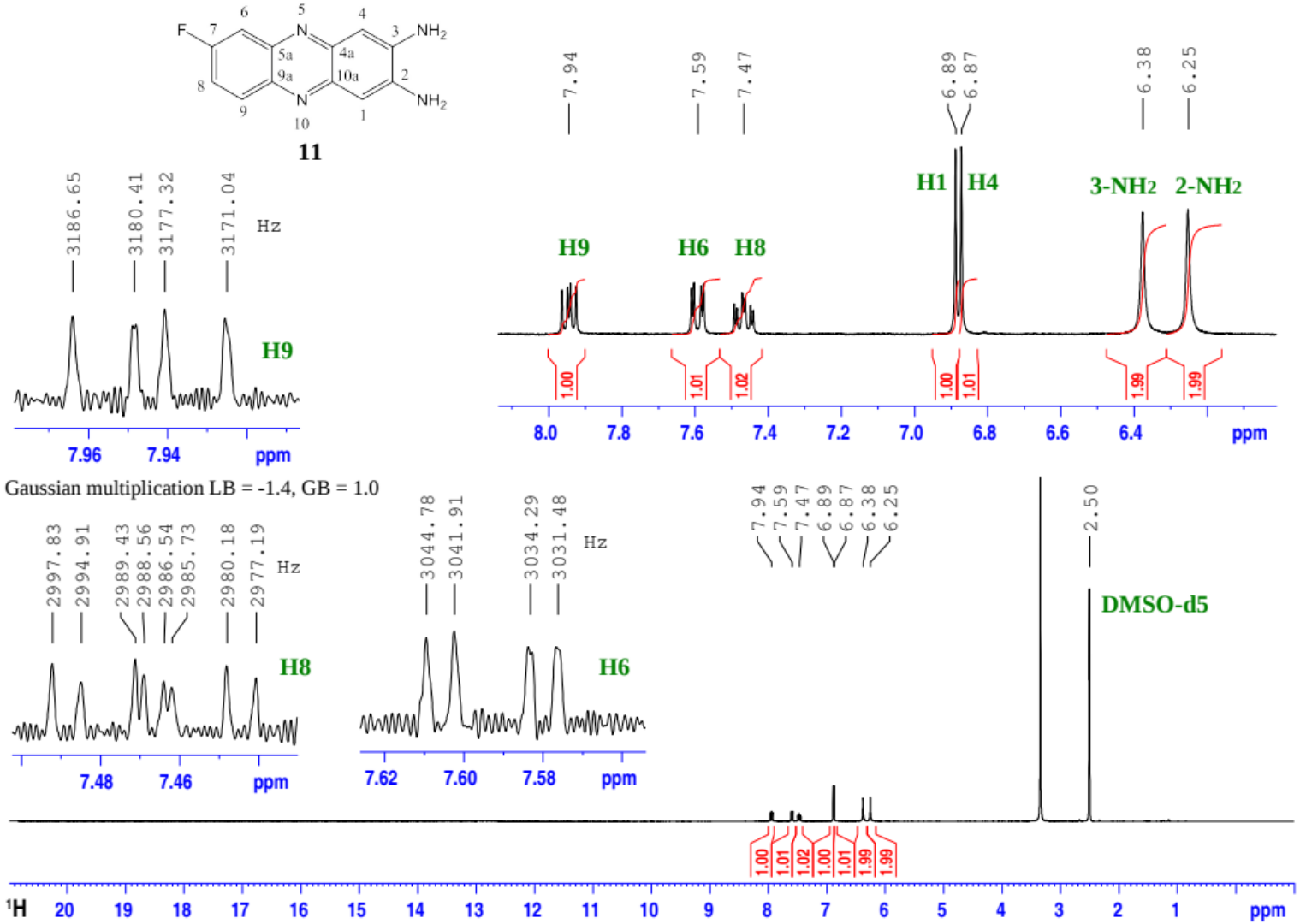
The part of the ^{1}H-^{15}N HMBC spectrum of **10a** and **10b** (DMSO-d6), Bruker AV-400 (^{1}H – 400.13, ^{15}N – 40.54 MHz)



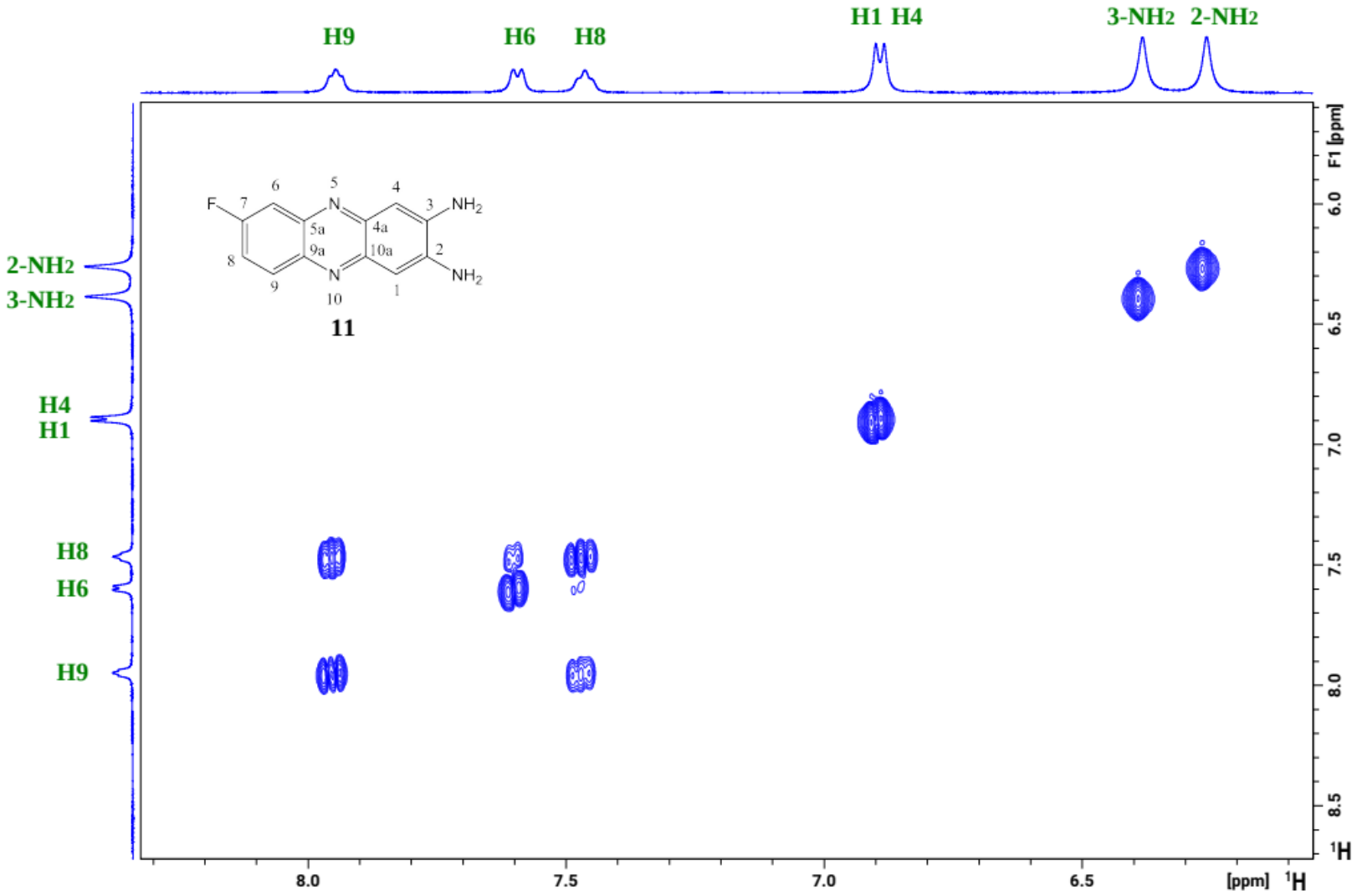
The part of the ^{1}H-^{15}N HMBC spectrum of **10a** and **10b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{15}N – 60.83 MHz)



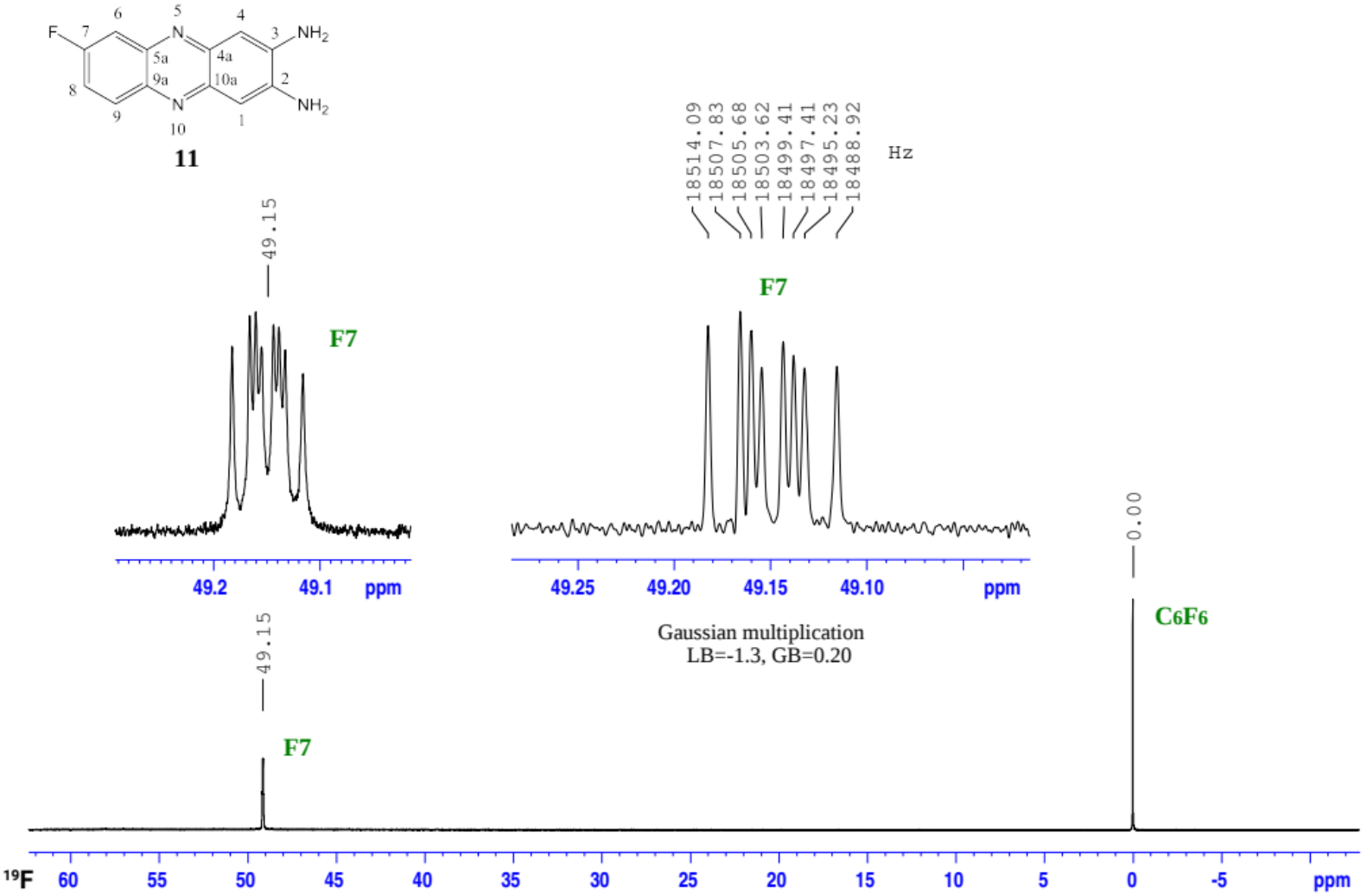
^{1}H NMR spectrum of **11** (DMSO-d6), Bruker AV-400 (^{1}H – 400.13 MHz)



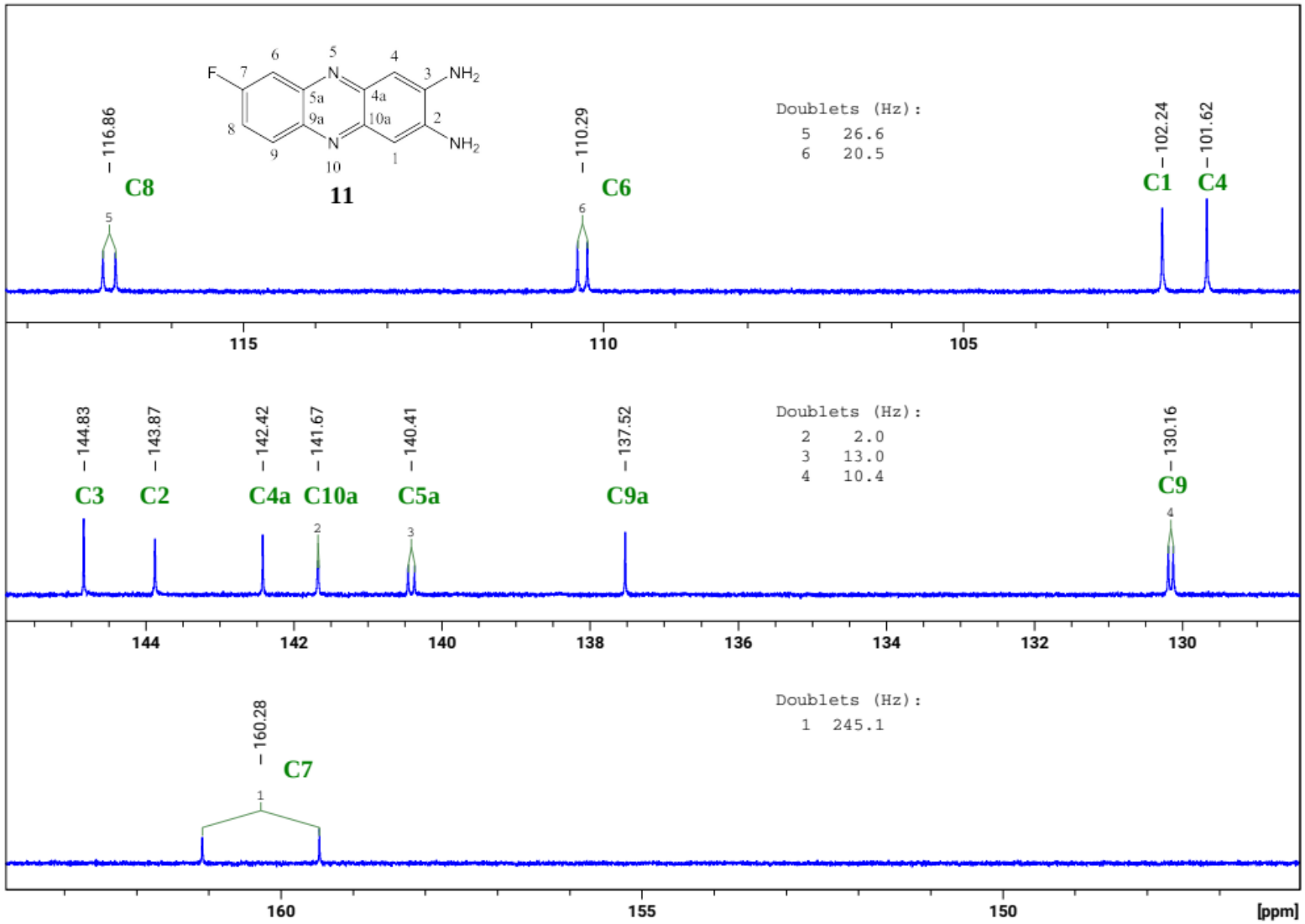
^{1}H-^{1}H COSY spectrum of **11** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30 MHz)



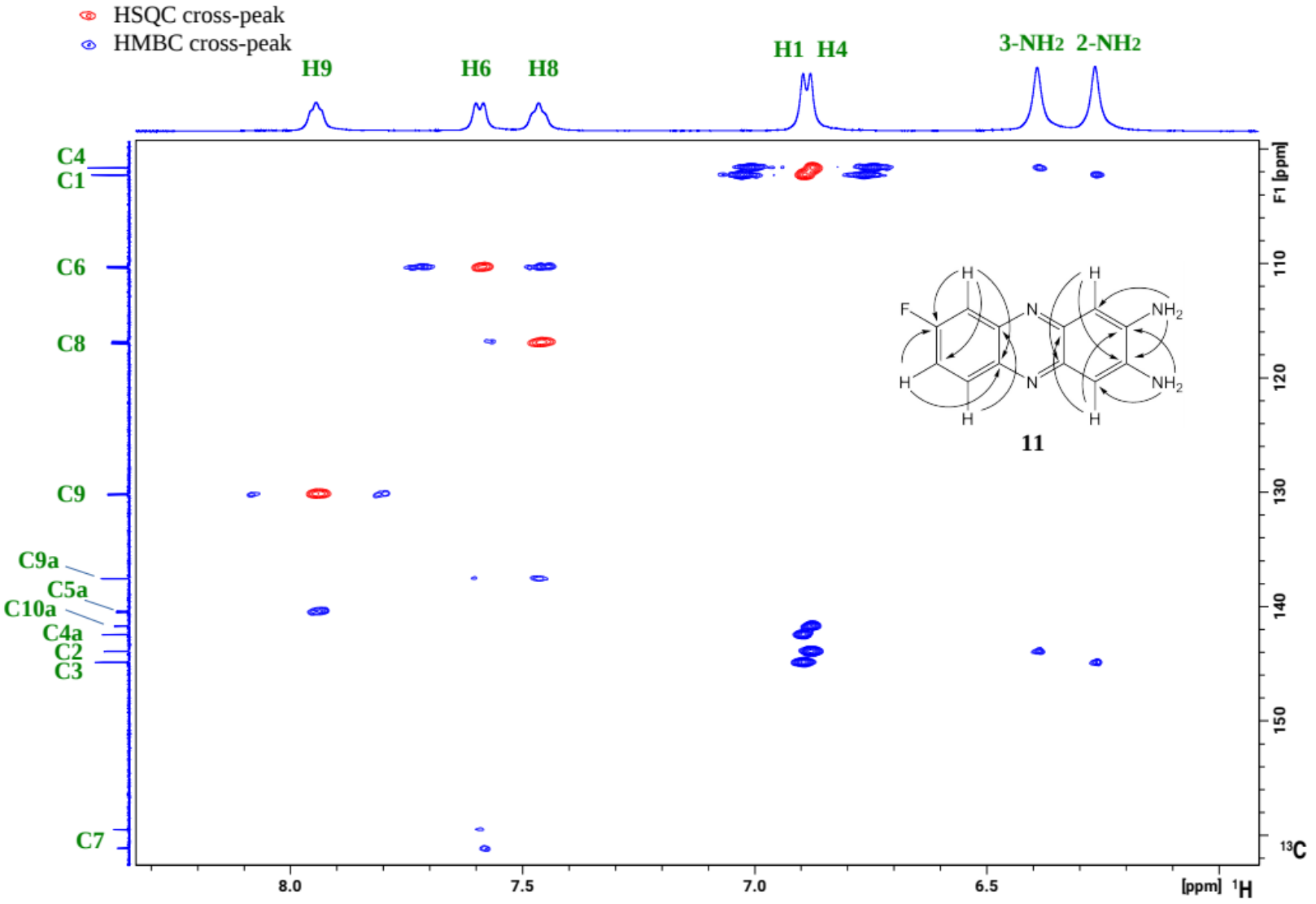
^{19}F NMR spectrum of **11** (DMSO-d6), Bruker AV-400 (^{19}F – 376.50 MHz)



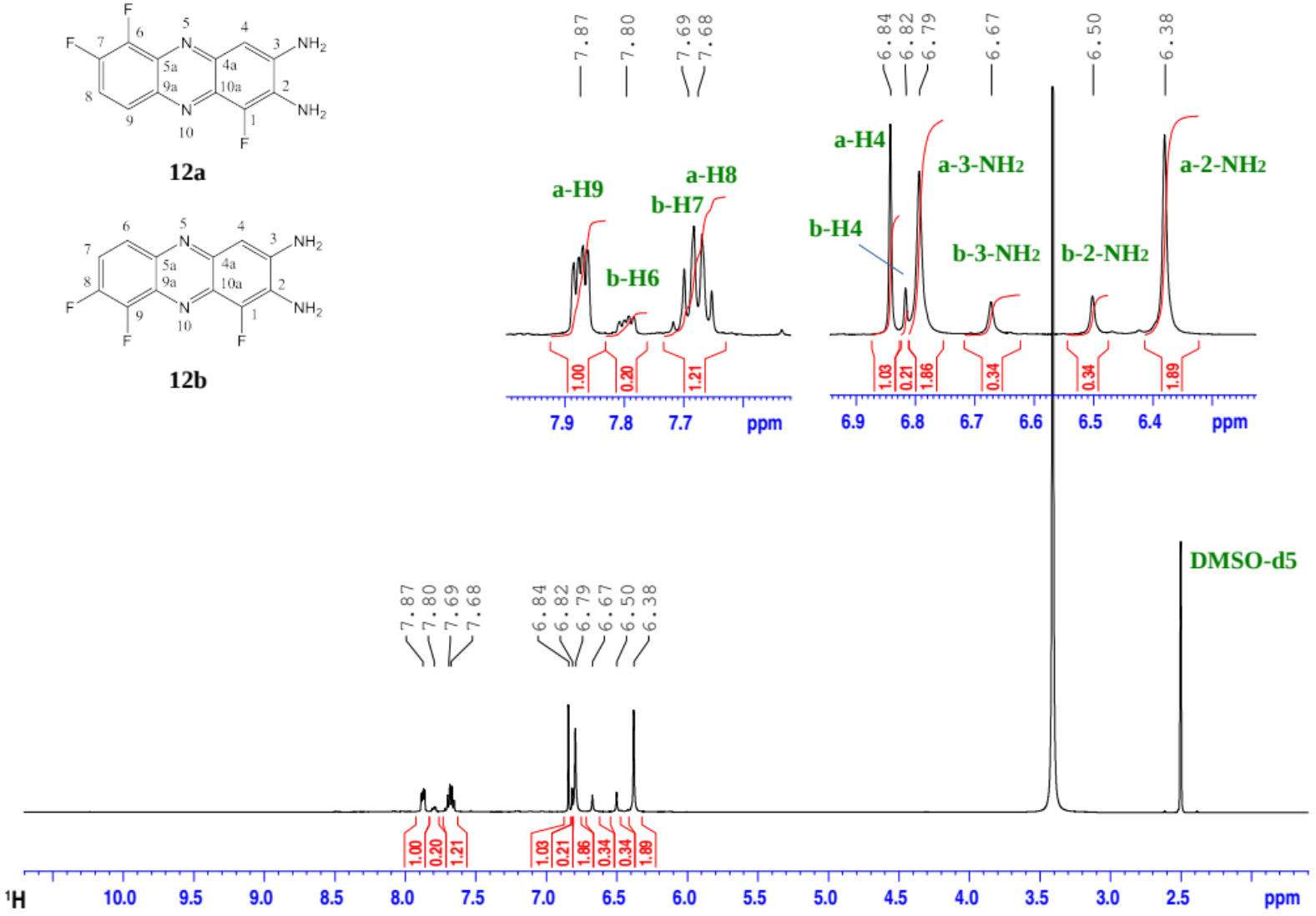
$^{13}C\{^{1}H\}$ NMR spectrum of **11** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{13}C – 150.95 MHz)



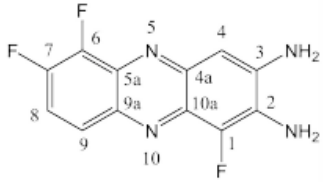
^{1}H-^{13}C correlation NMR spectra of **11** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{13}C – 150.95 MHz)



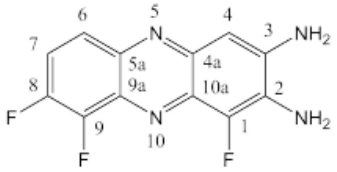
^{1}H NMR spectrum of **12a** and **12b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30 MHz)



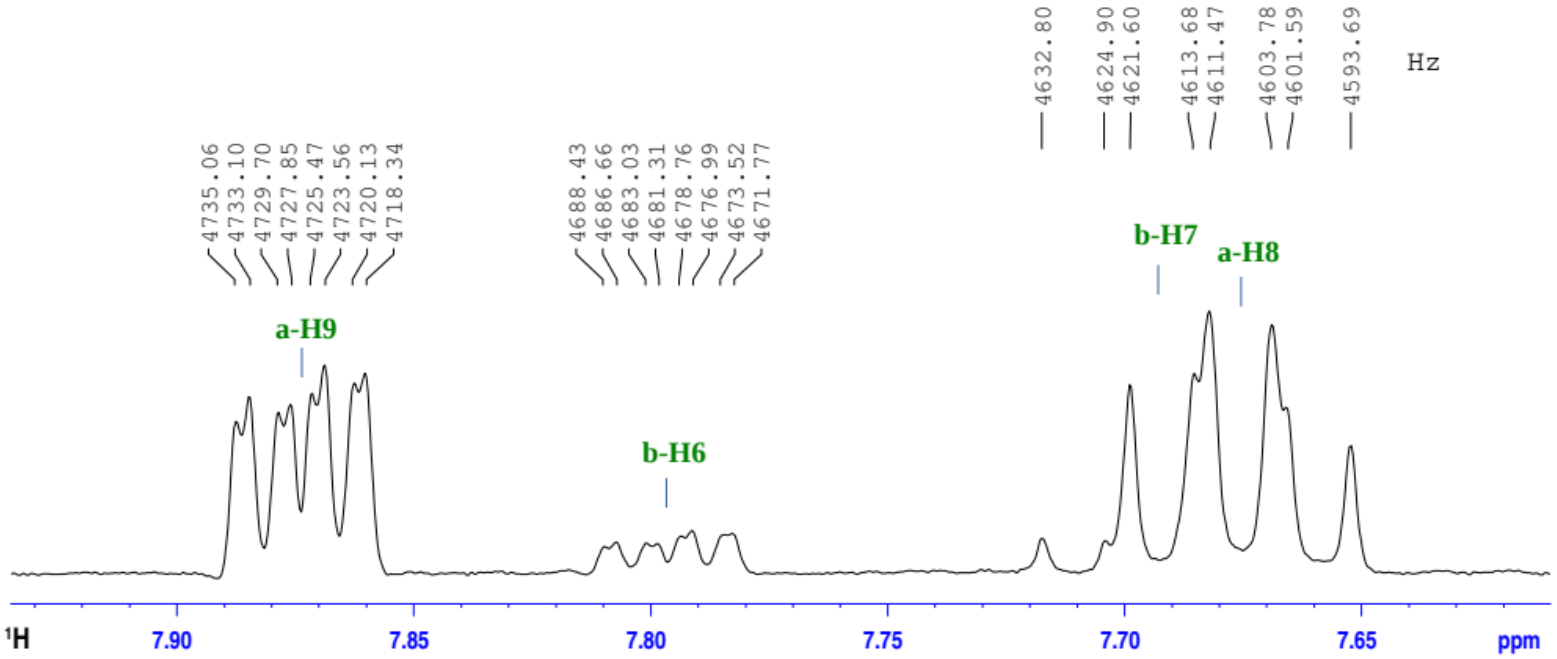
Multiplets in ^{1}H NMR spectrum of **12a** and **12b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30 MHz)



12a

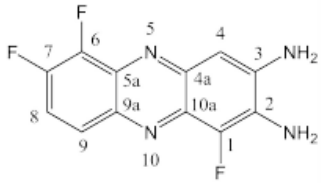


12b

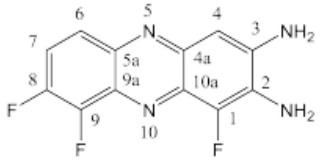


Gaussian multiplication LB=-1.5, GB=0.3

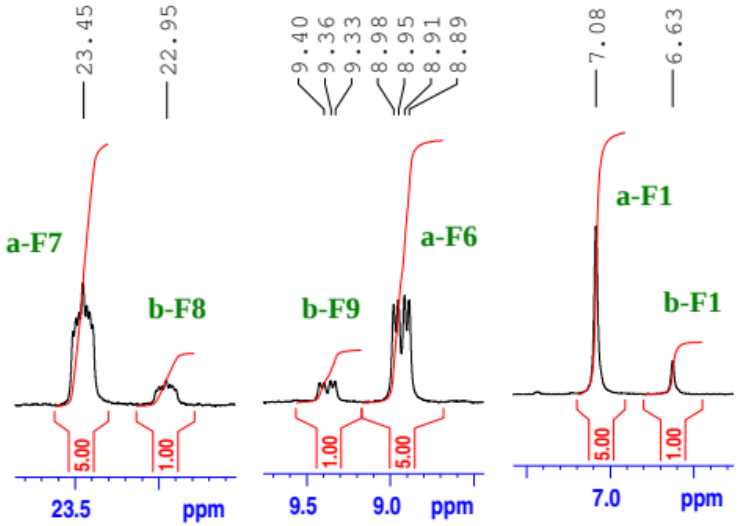
^{19}F NMR spectrum of **12a** and **12b** (DMSO-d6), Bruker AV-300 (^{19}F – 282.40 MHz)

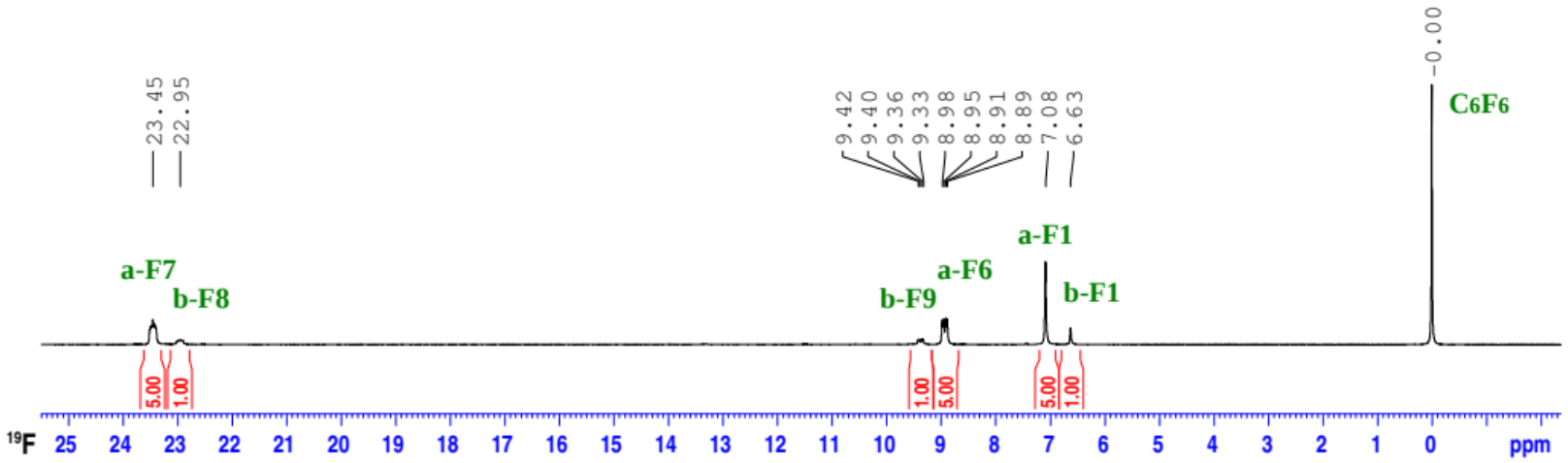


12a

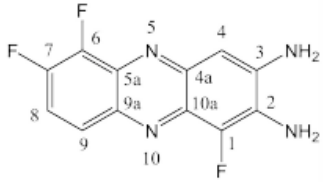


12b

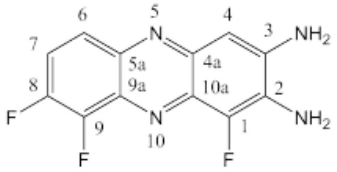




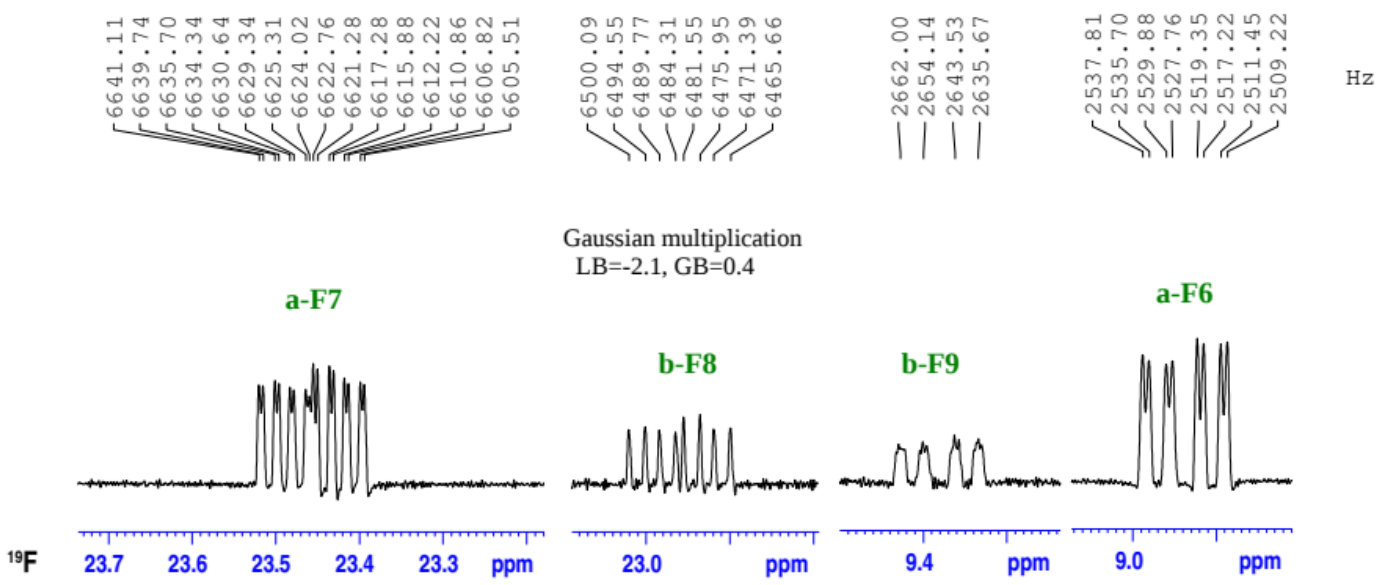
Multiplets in ^{19}F NMR spectrum of **12a** and **12b** (DMSO-d6), Bruker AV-300 (^{19}F – 282.40 MHz)



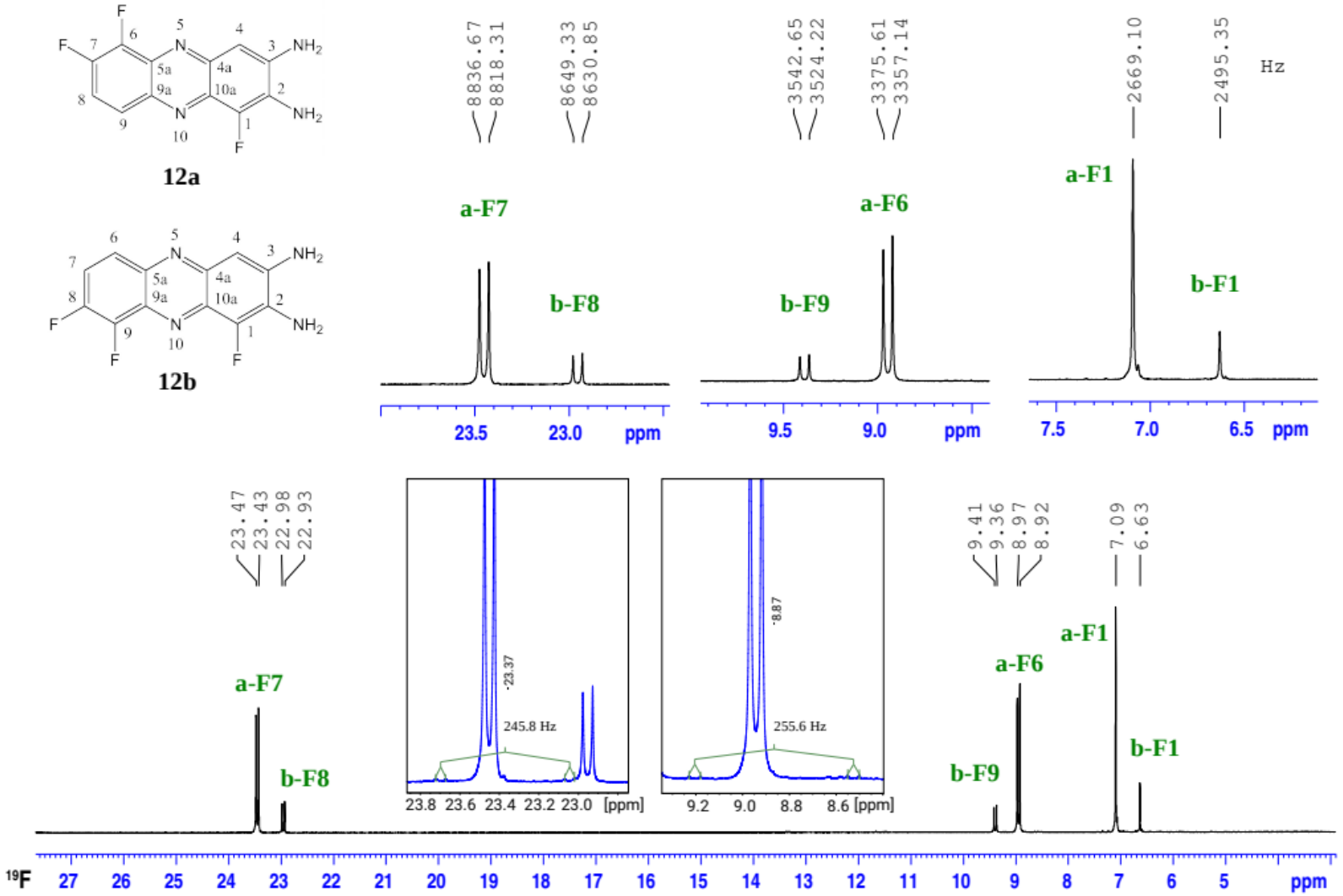
12a



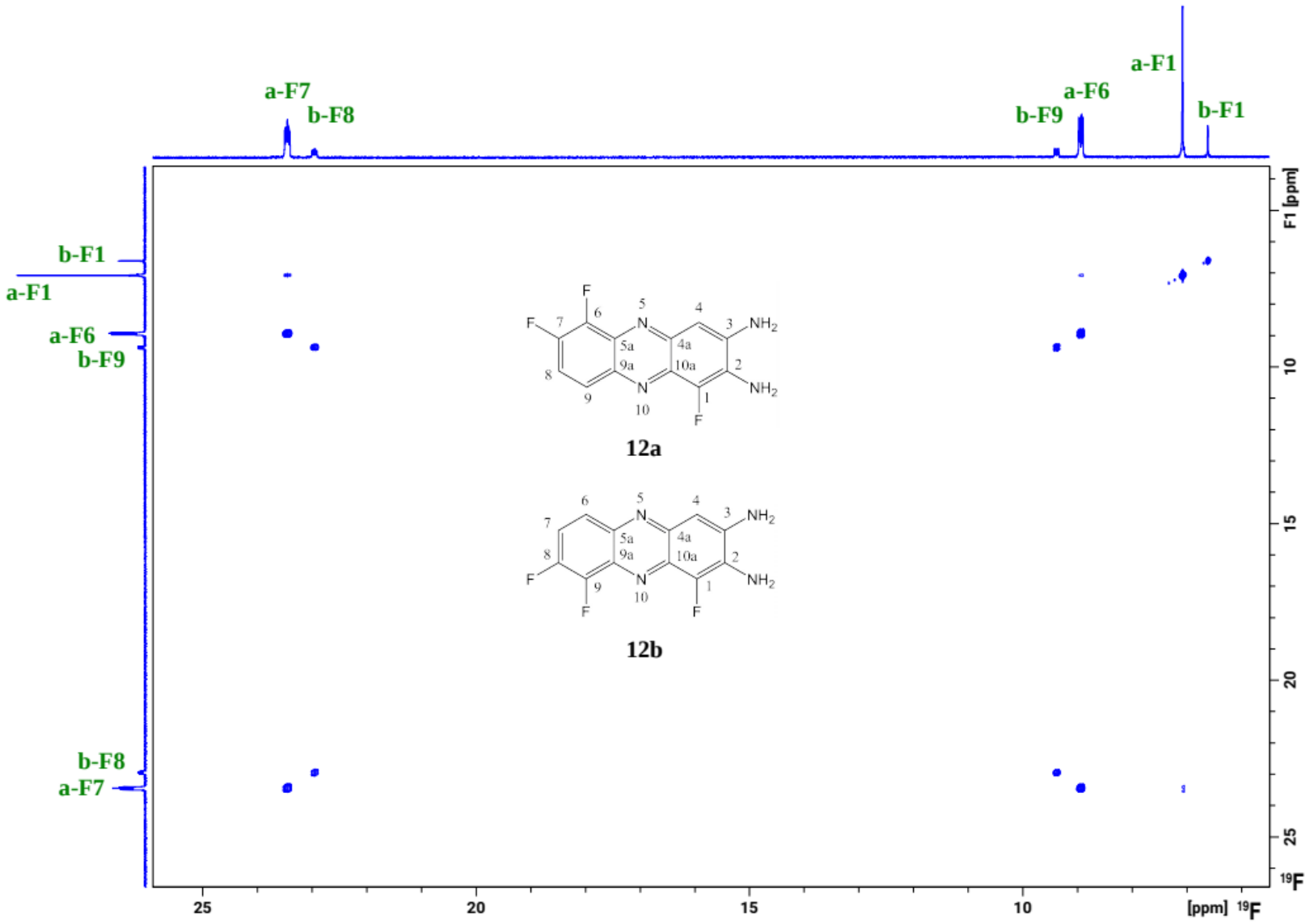
12b



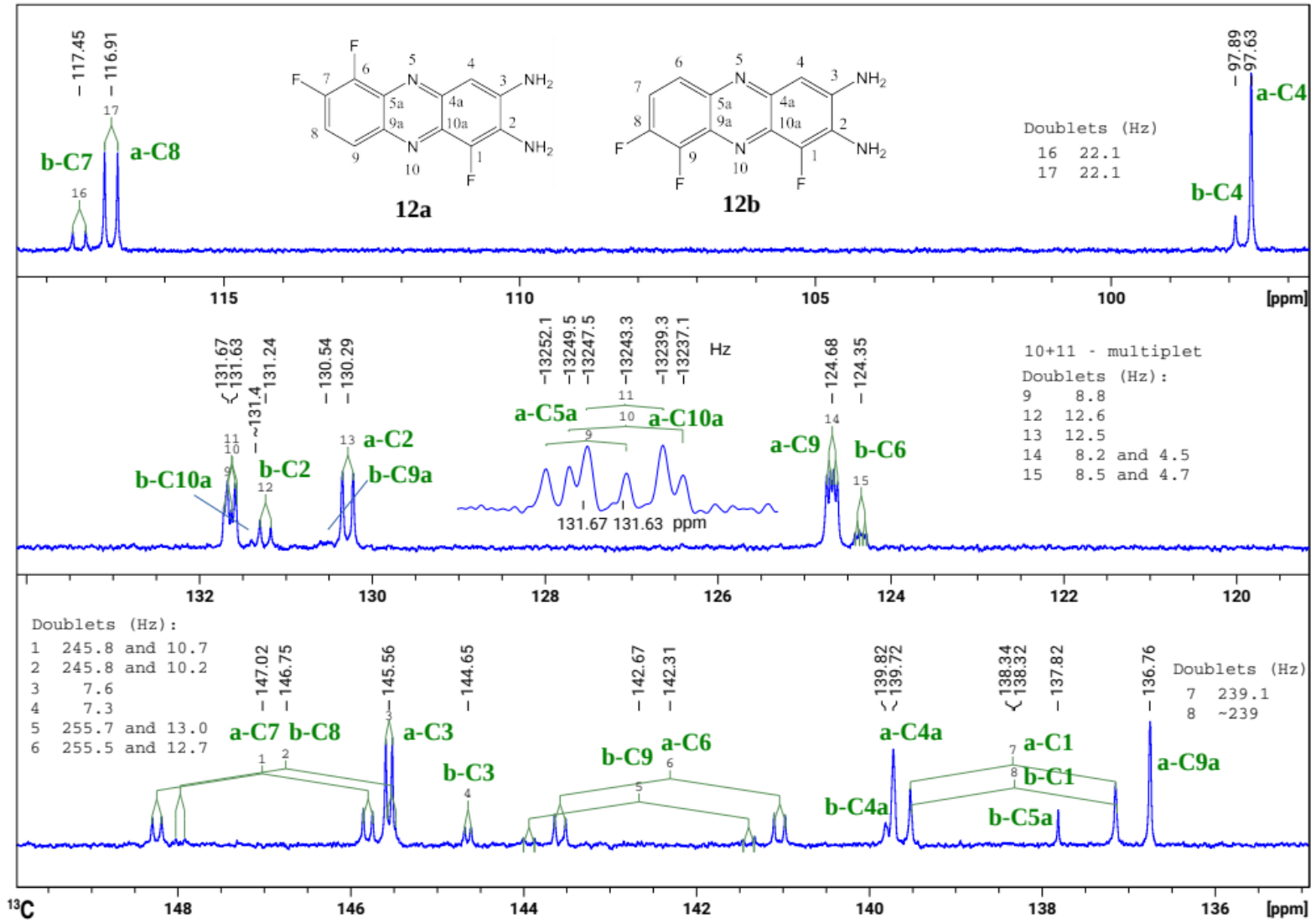
$^{19}F\{^{1}H\}$ NMR spectrum of **12a** and **12b** (DMSO-d6), Bruker AV-400 (^{19}F – 376.50 MHz, ^{1}H – 400.13 MHz)



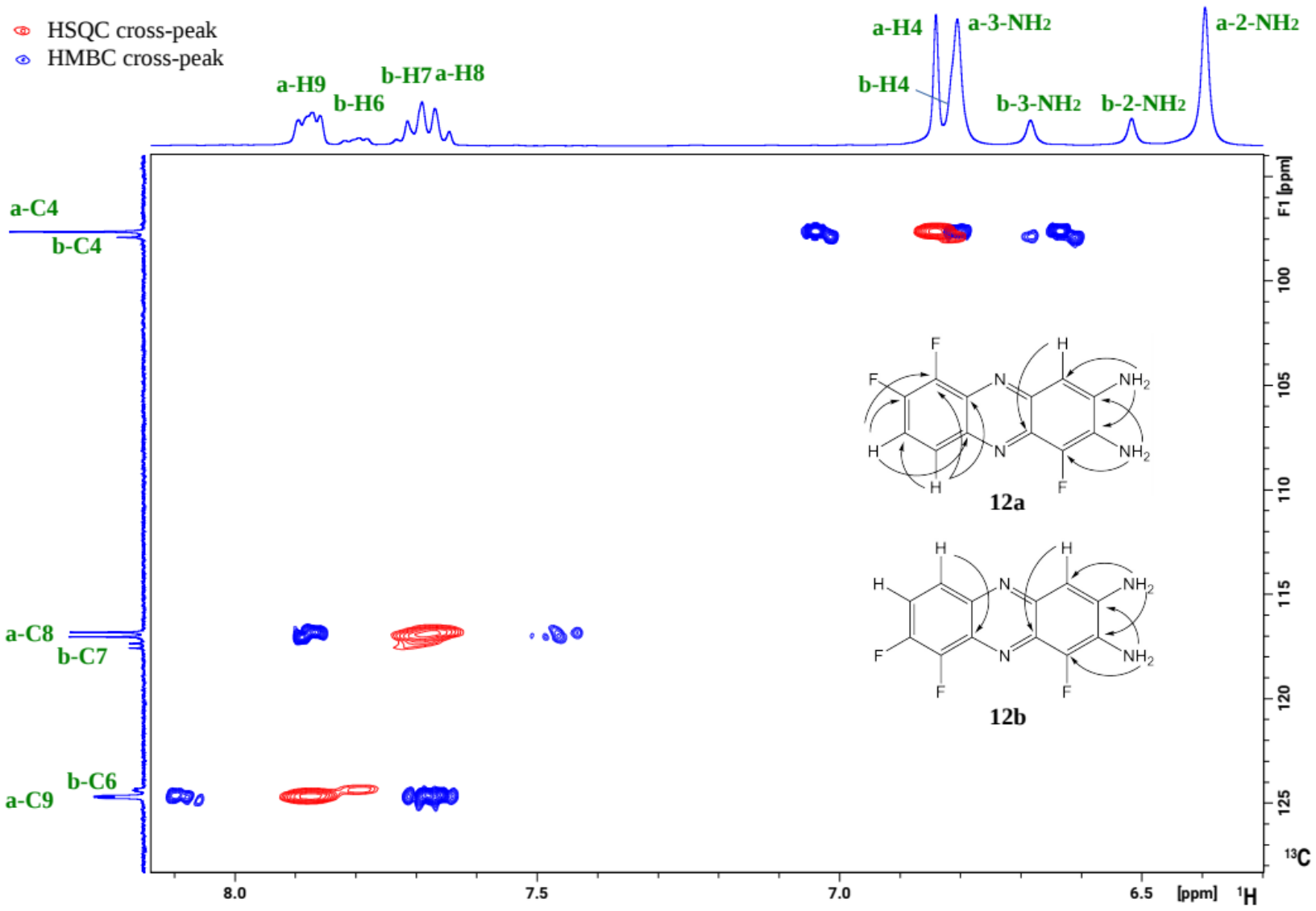
^{19}F-^{19}F COSY spectrum of **12a** and **12b** (DMSO-d6), Bruker AV-400 (^{19}F – 376.50)



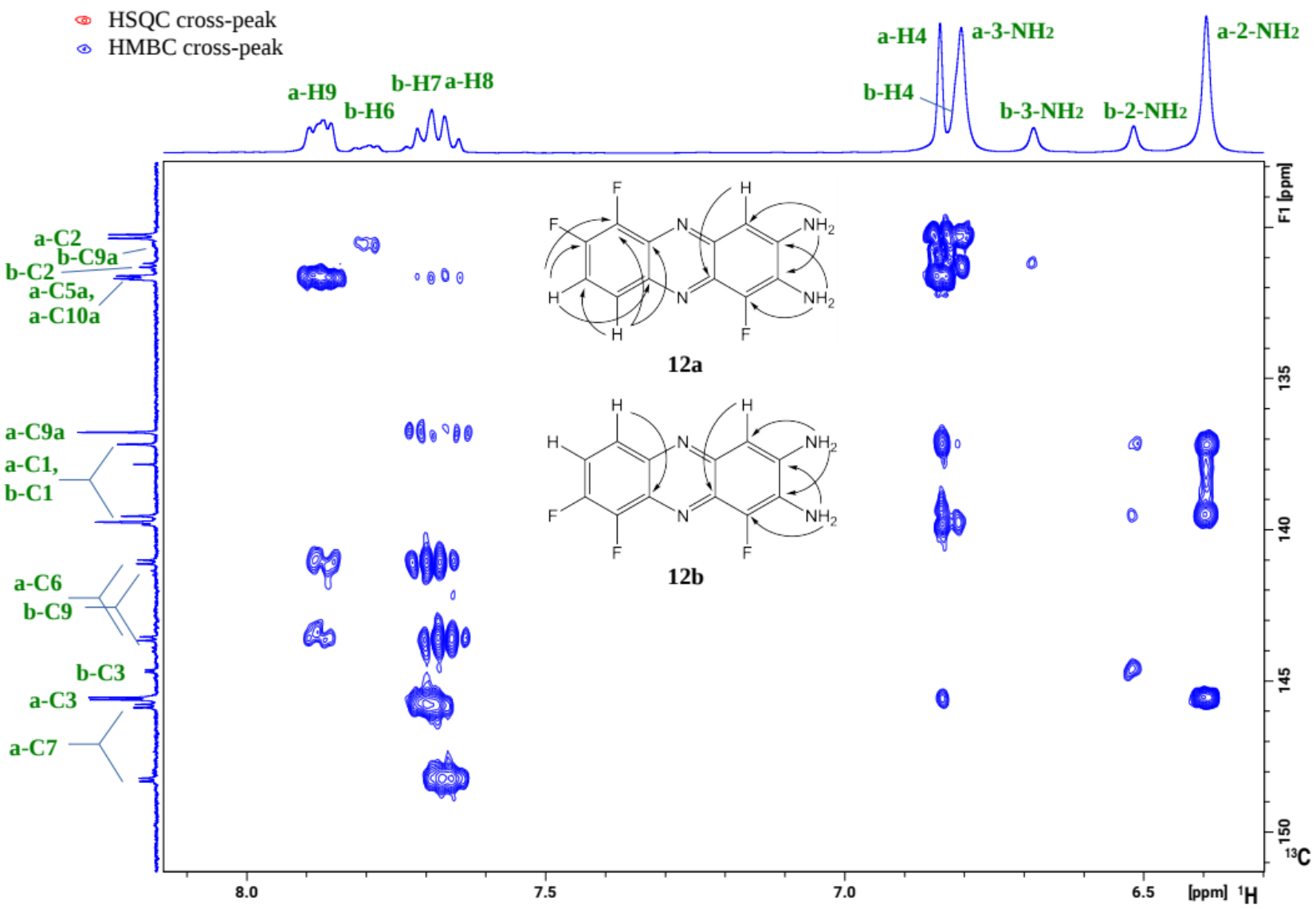
$^{13}C\{^{1}H\}$ NMR spectrum of **12a** and **12b** (DMSO-d6), Bruker AV-400 (^{13}C – 100.61 MHz, ^{1}H – 400.13 MHz)



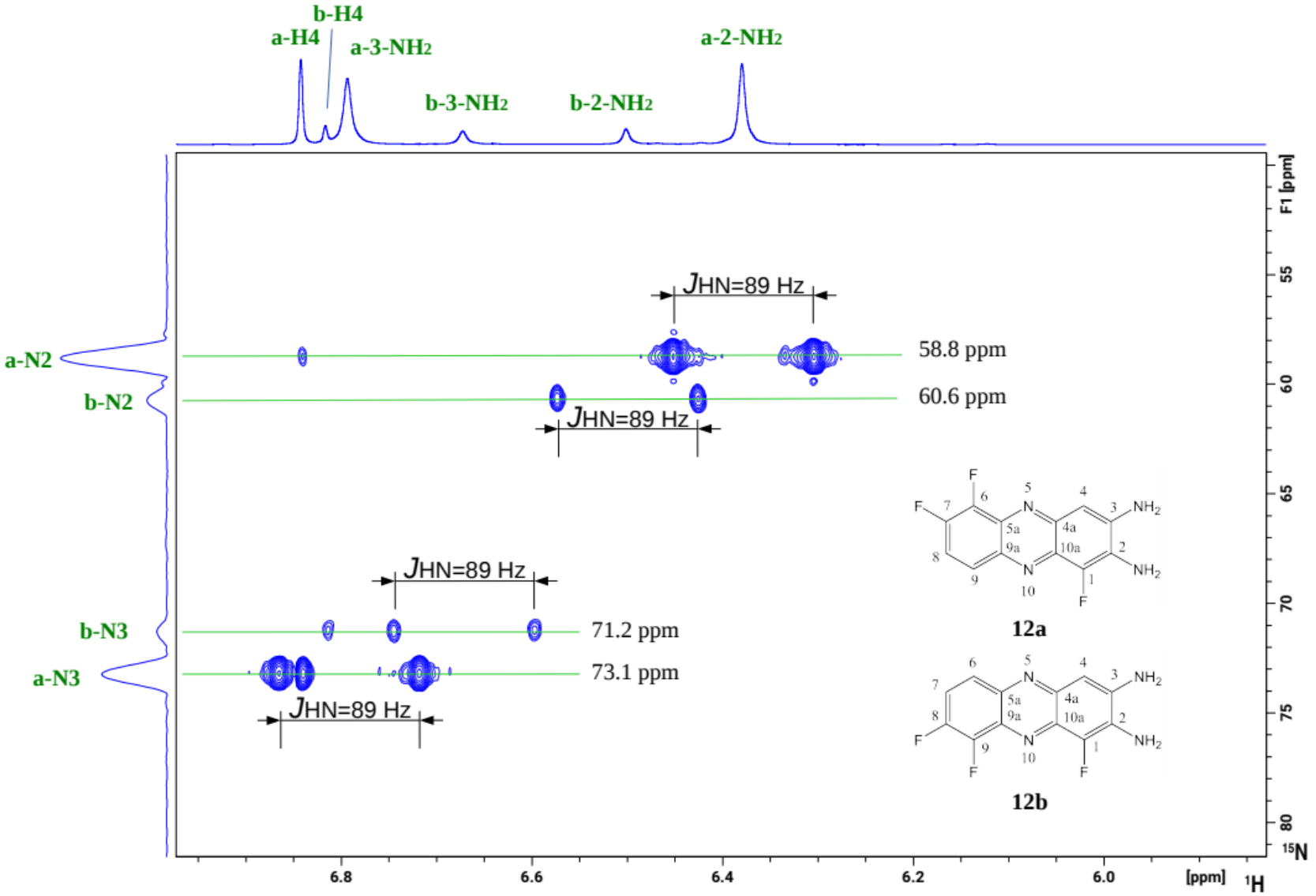
The part of the ^{1}H-^{13}C correlation NMR spectra of **12a and 12b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{13}C – 150.95 MHz)



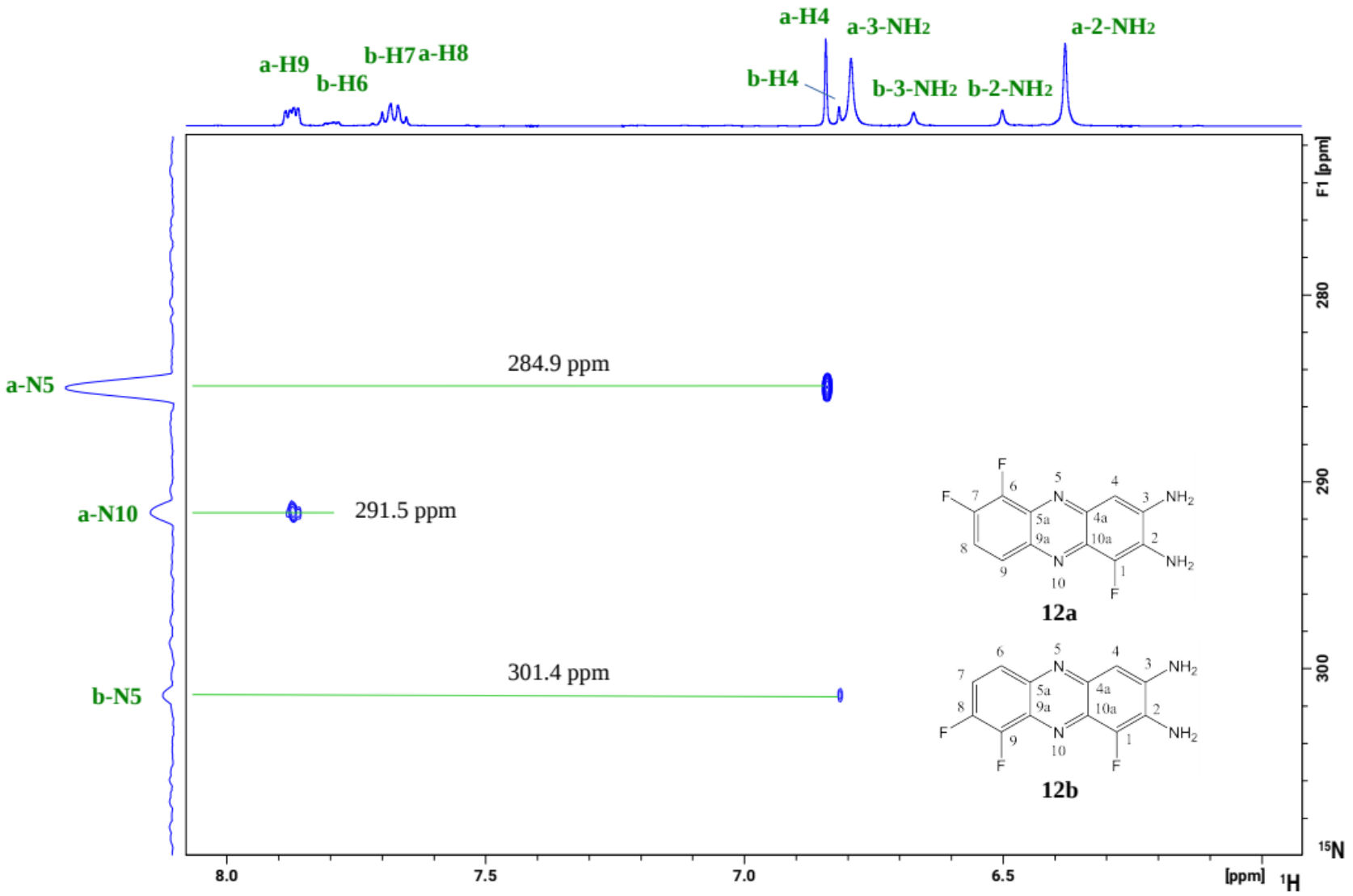
The part of the ^{1}H-^{13}C correlation NMR spectra of **12a and 12b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{13}C – 150.95 MHz)



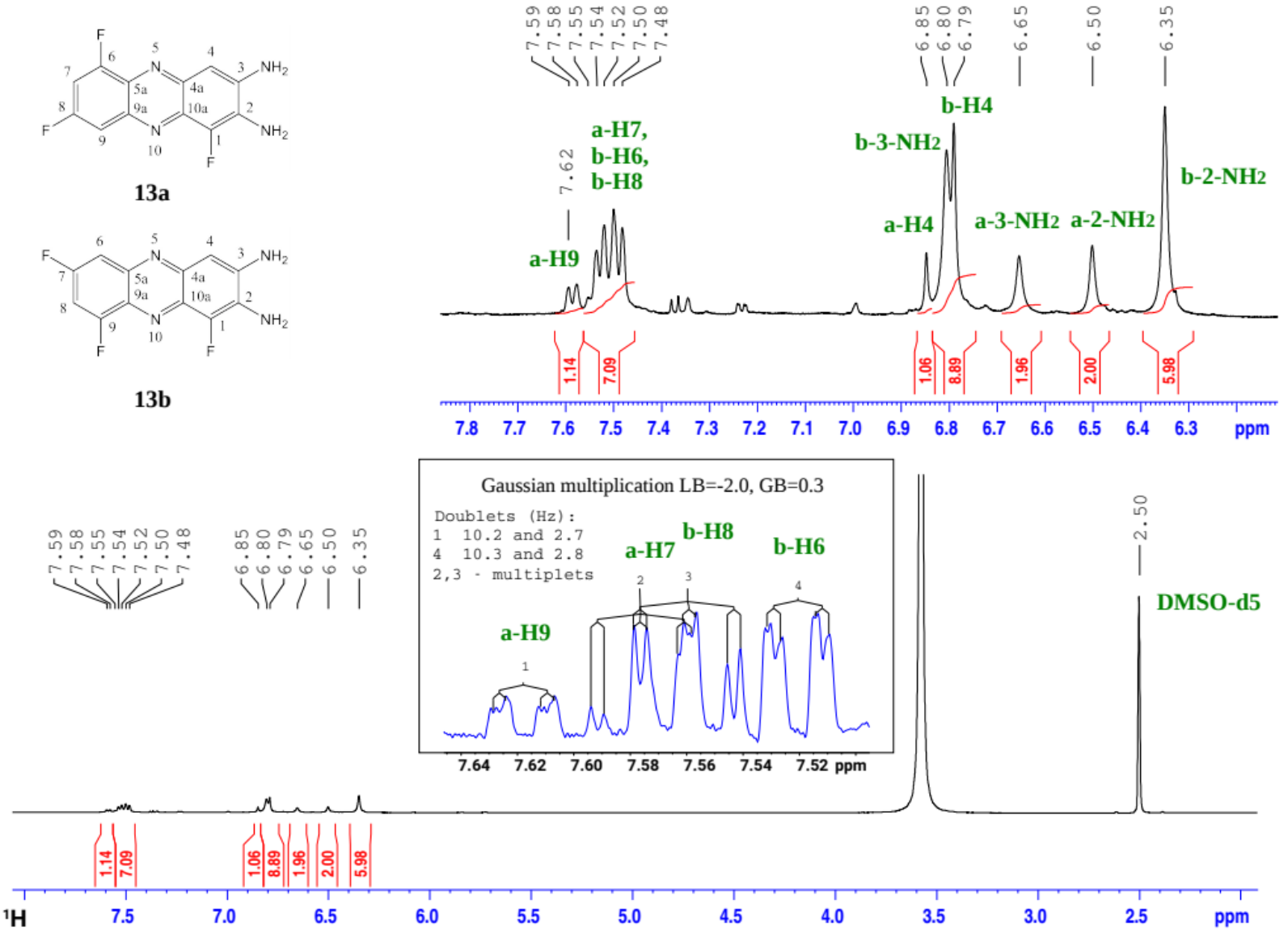
The part of the ^{1}H-^{15}N HMBC spectrum of **12a and 12b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{15}N – 60.83 MHz)



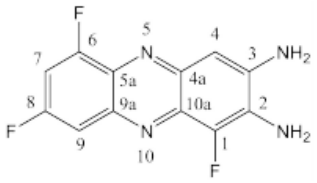
The part of the ^{1}H-^{15}N HMBC spectrum of **12a and 12b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{15}N – 60.83 MHz)



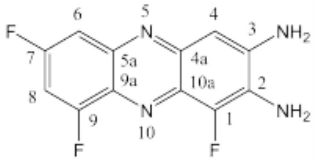
^{1}H NMR spectrum of **13a** and **13b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30 MHz)



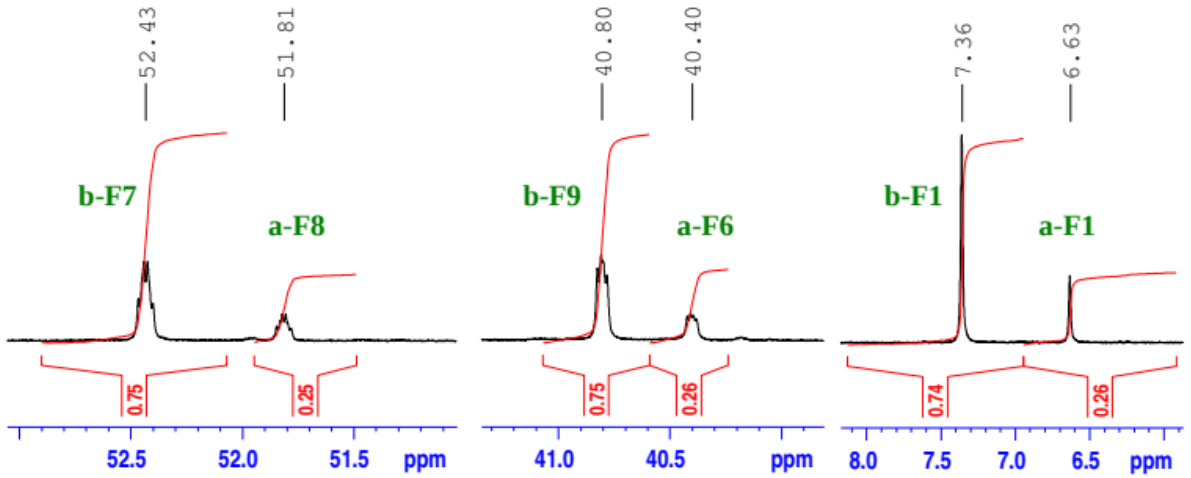
^{19}F NMR spectrum of **13a** and **13b** (DMSO-d6), Bruker AV-400 (^{19}F – 376.50 MHz)

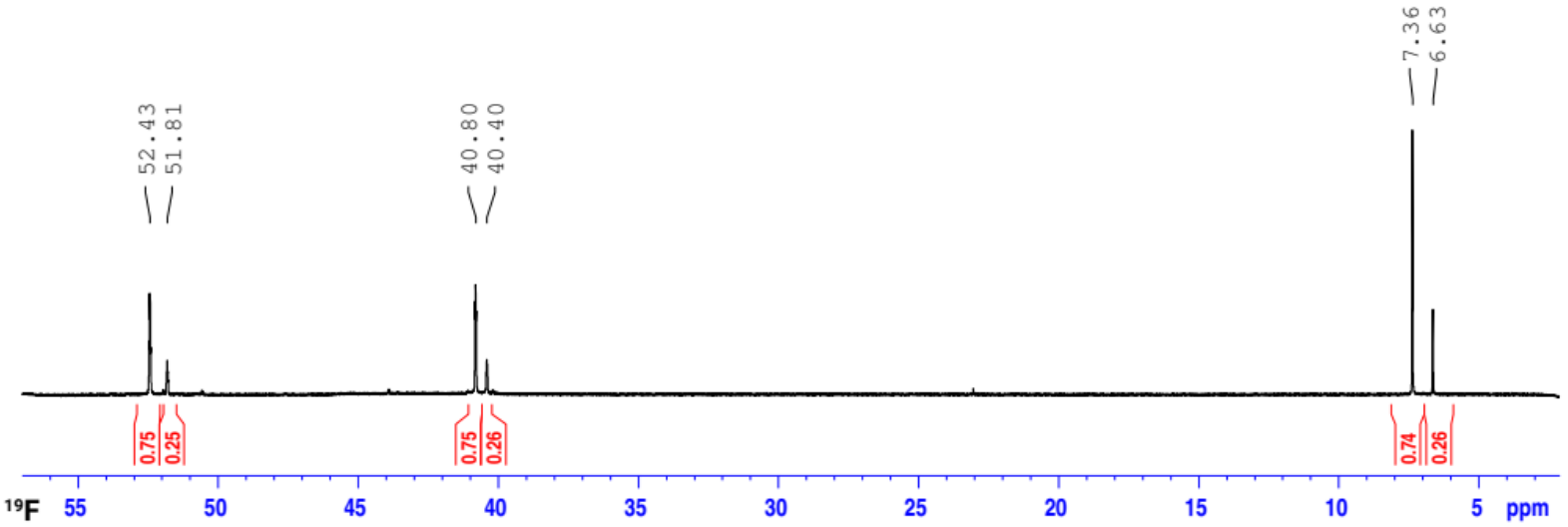


13a

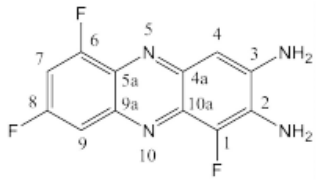


13b

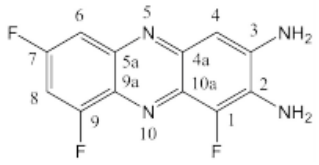




Multiplets in ^{19}F NMR spectrum of **13a** and **13b** (DMSO-d6), Bruker AV-400 (^{19}F – 376.50 MHz)

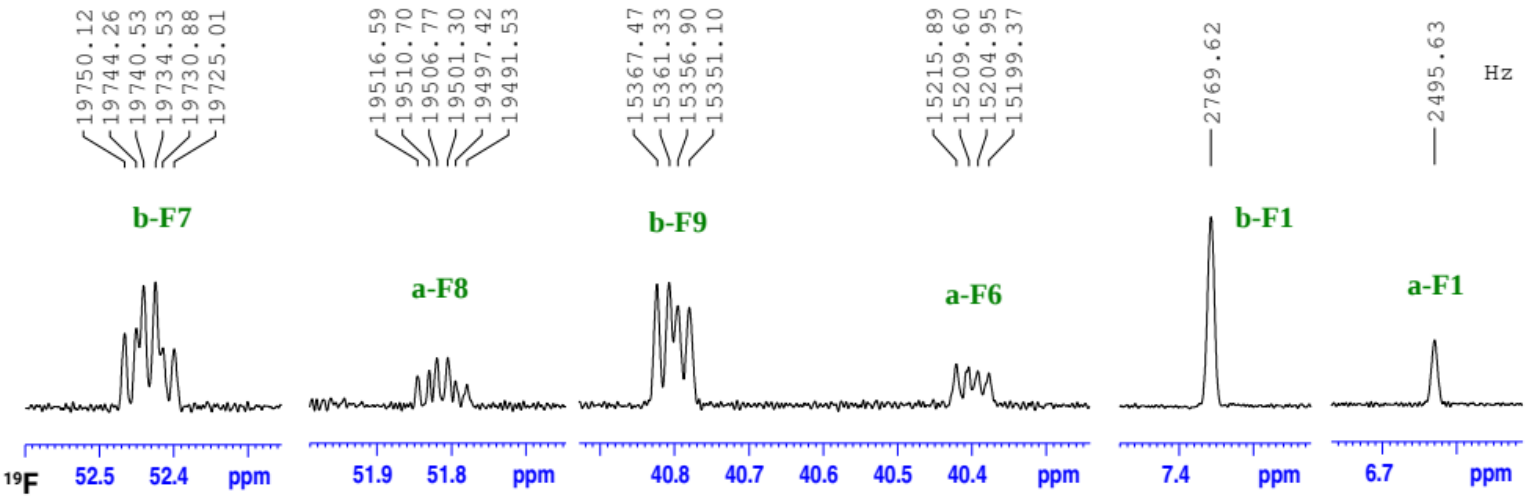


13a



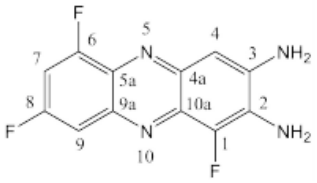
13b

Gaussian multiplication LB=-4.0, GB=0.22



Simulated and experimental ^{19}F signals of **13a** and **13b** (DMSO-d6), Bruker AV-400 (^{19}F – 376.50 MHz), DAISY Spectrum Simulation Module 3.5.2, TopSpin

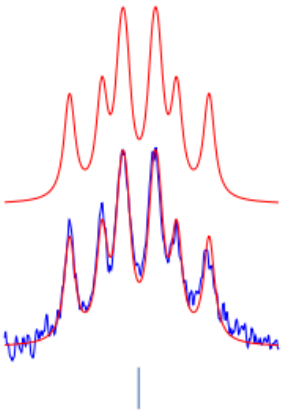
Red lines – simulated signals
Blue lines – real signals



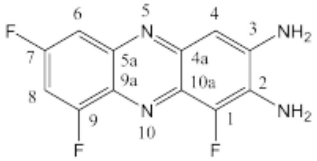
13a

13a-F8

Simulation parameters:
$J_{F8\text{-}H7}$ = 9.23 Hz
$J_{F8\text{-}H9}$ = 10.21 Hz
$J_{F8\text{-}F6}$ = 5.87 Hz
$J_{F8\text{-}F1}$ = 0
Linewidth = 2.20 Hz



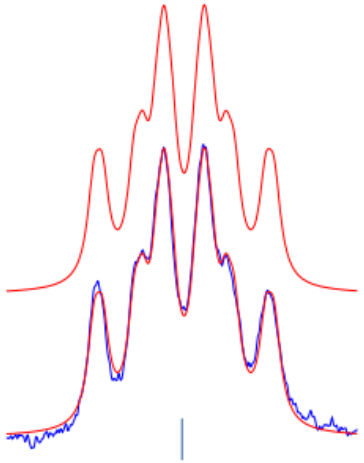
51.81 ppm



13b

13b-F7

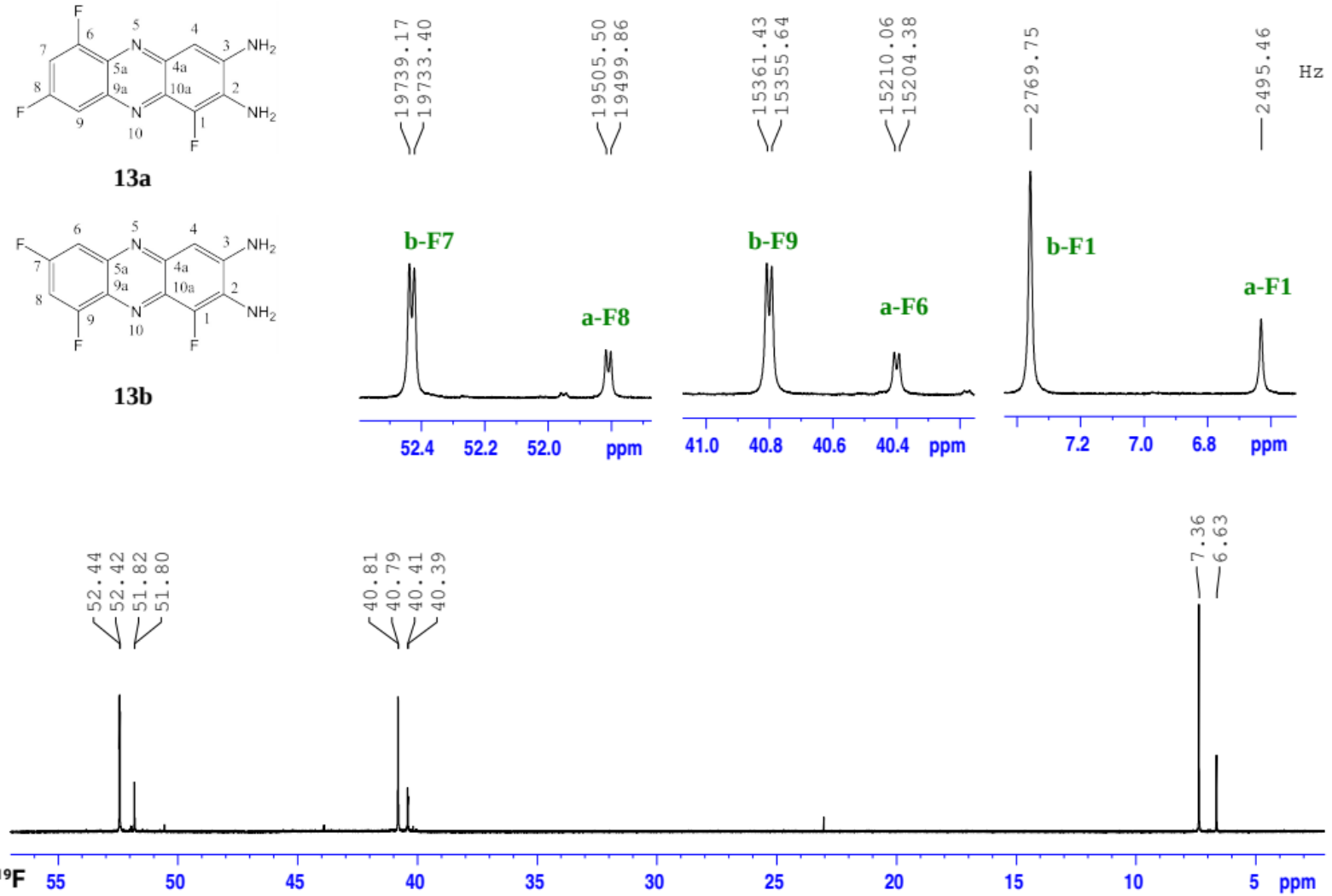
Simulation parameters:
$J_{F7\text{-}H8}$ = 9.26 Hz
$J_{F7\text{-}H6}$ = 10.25 Hz
$J_{F7\text{-}F9}$ = 5.94 Hz
$J_{F7\text{-}F1}$ = 1.26 Hz
Linewidth = 2.37 Hz



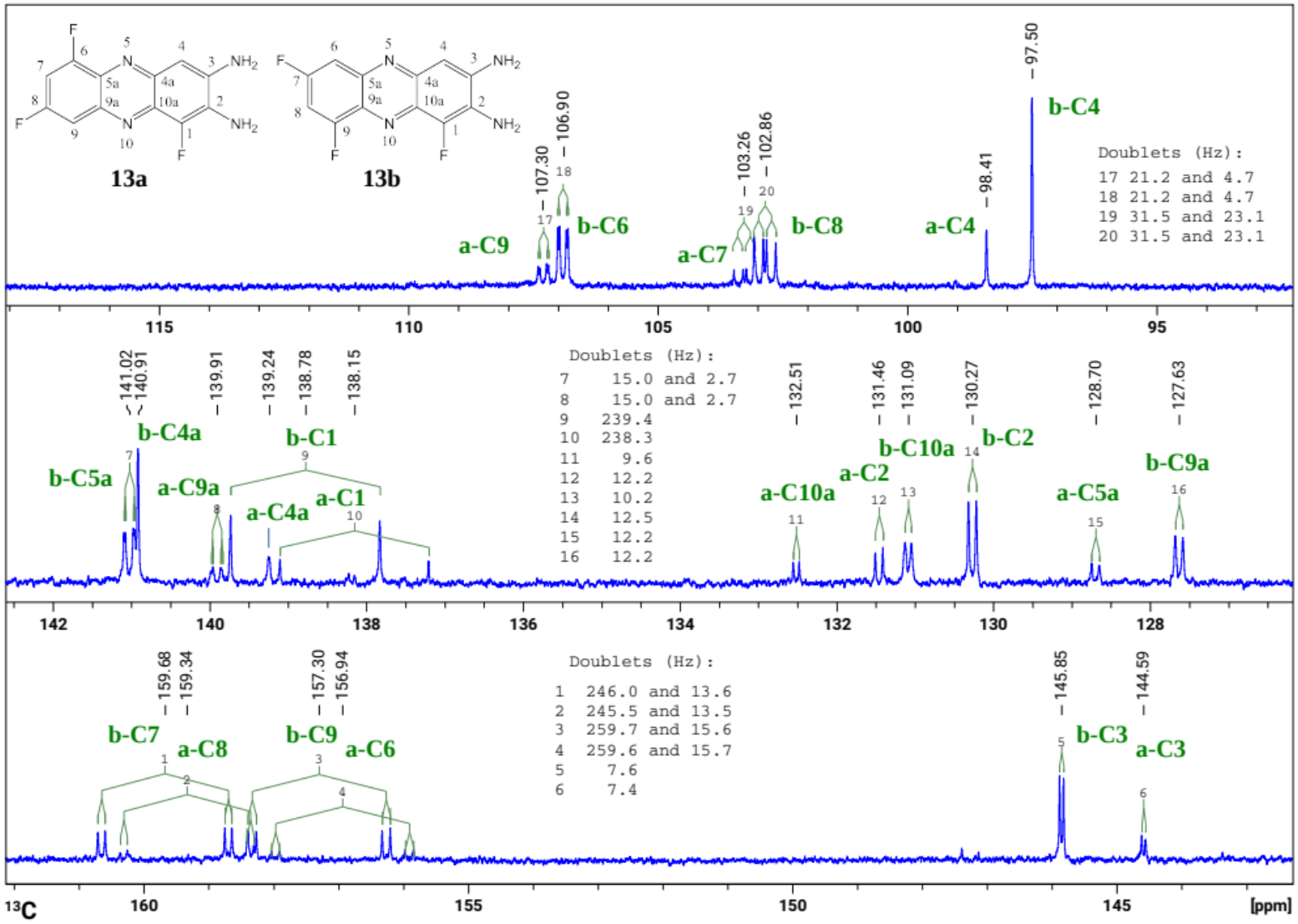
52.43 ppm

4.0.9

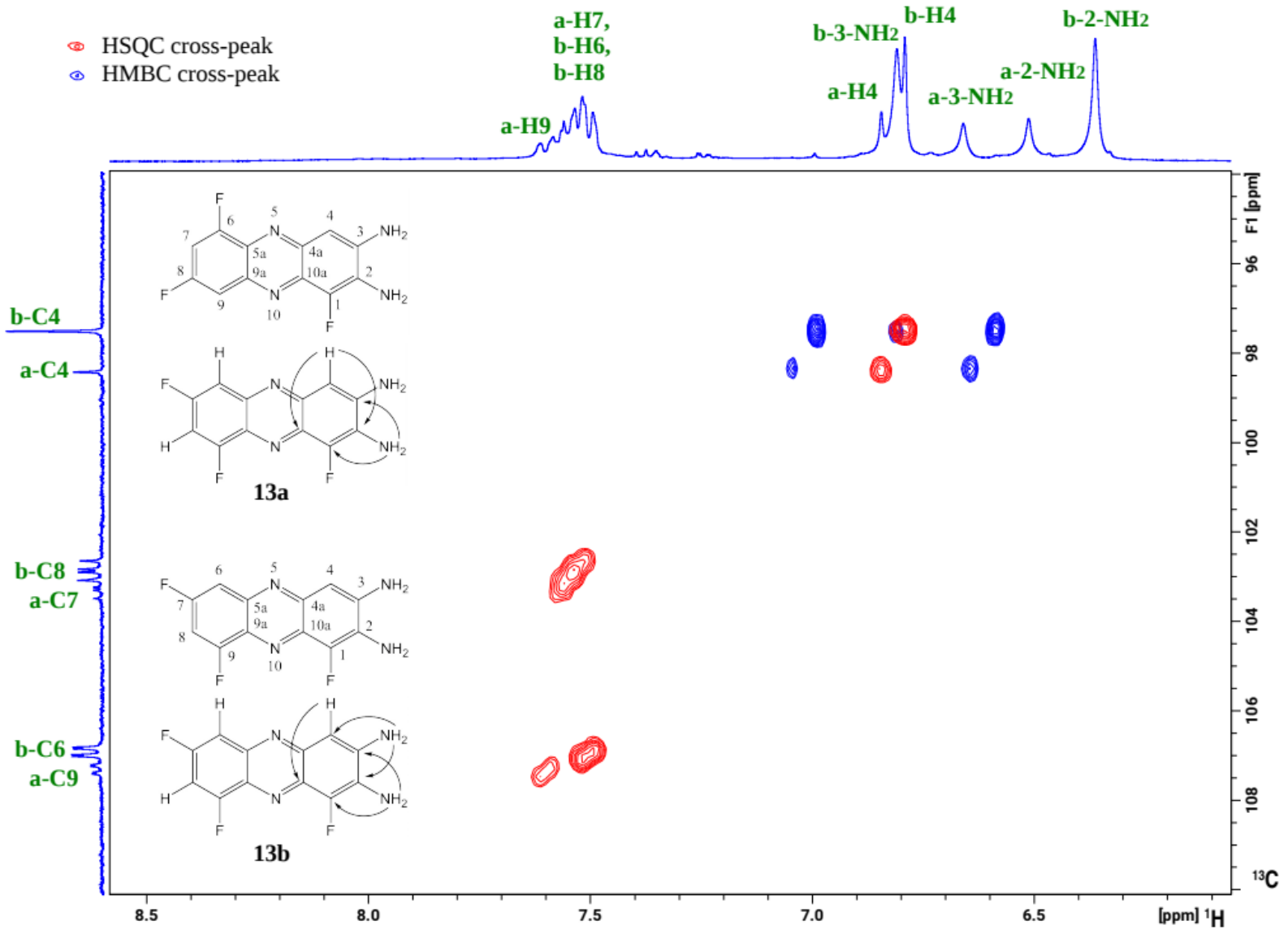
$^{19}F\{^{1}H\}$ NMR spectrum of **13a** and **13b** (DMSO-d6), Bruker AV-400 (^{19}F – 376.50 MHz, ^{1}H – 400.13 MHz)



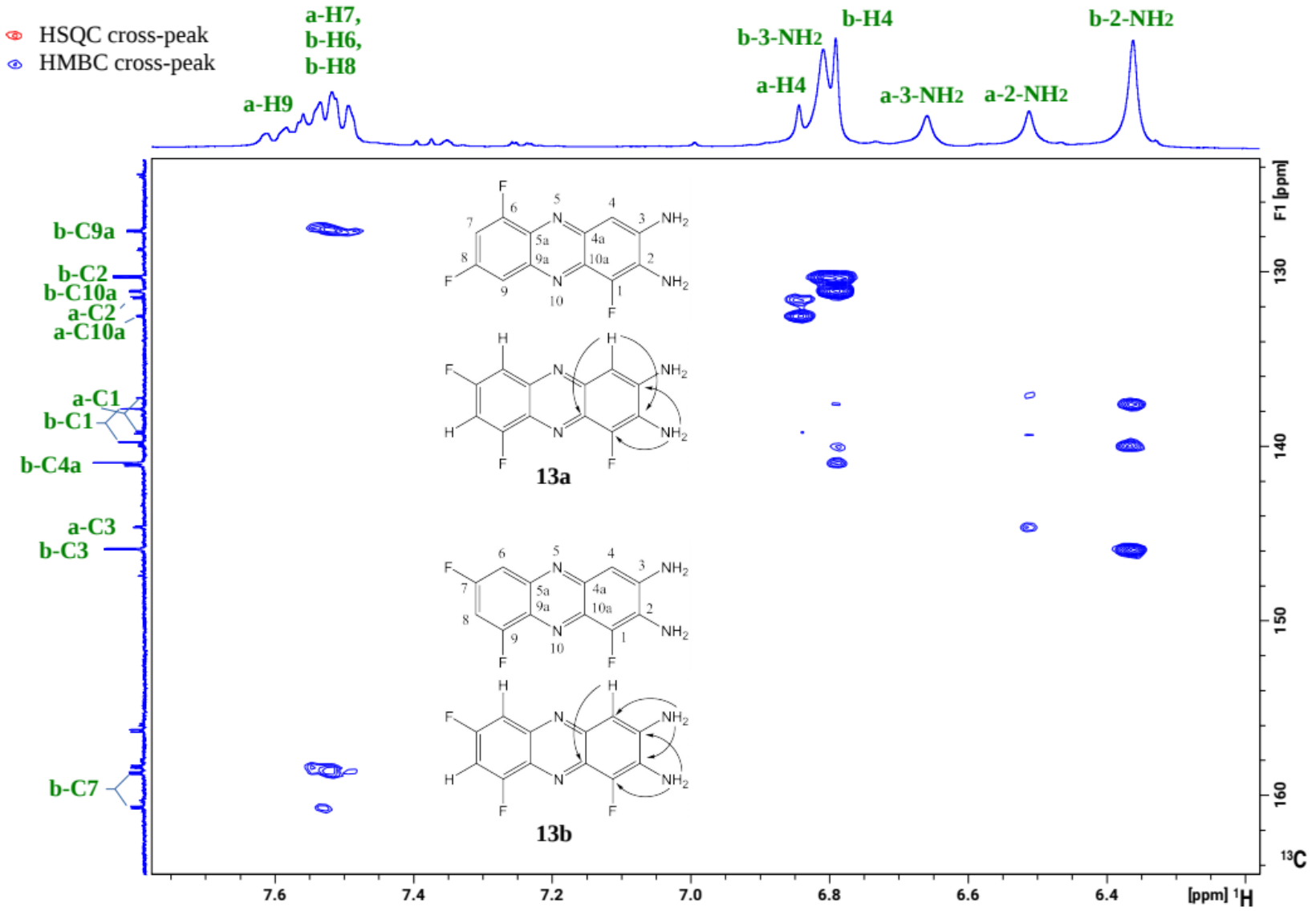
$^{13}C\{^{1}H\}$ NMR spectrum of **13a** and **13b** (DMSO-d6), Bruker DRX-500 (^{1}H – 500.13, ^{13}C – 125.76 MHz)



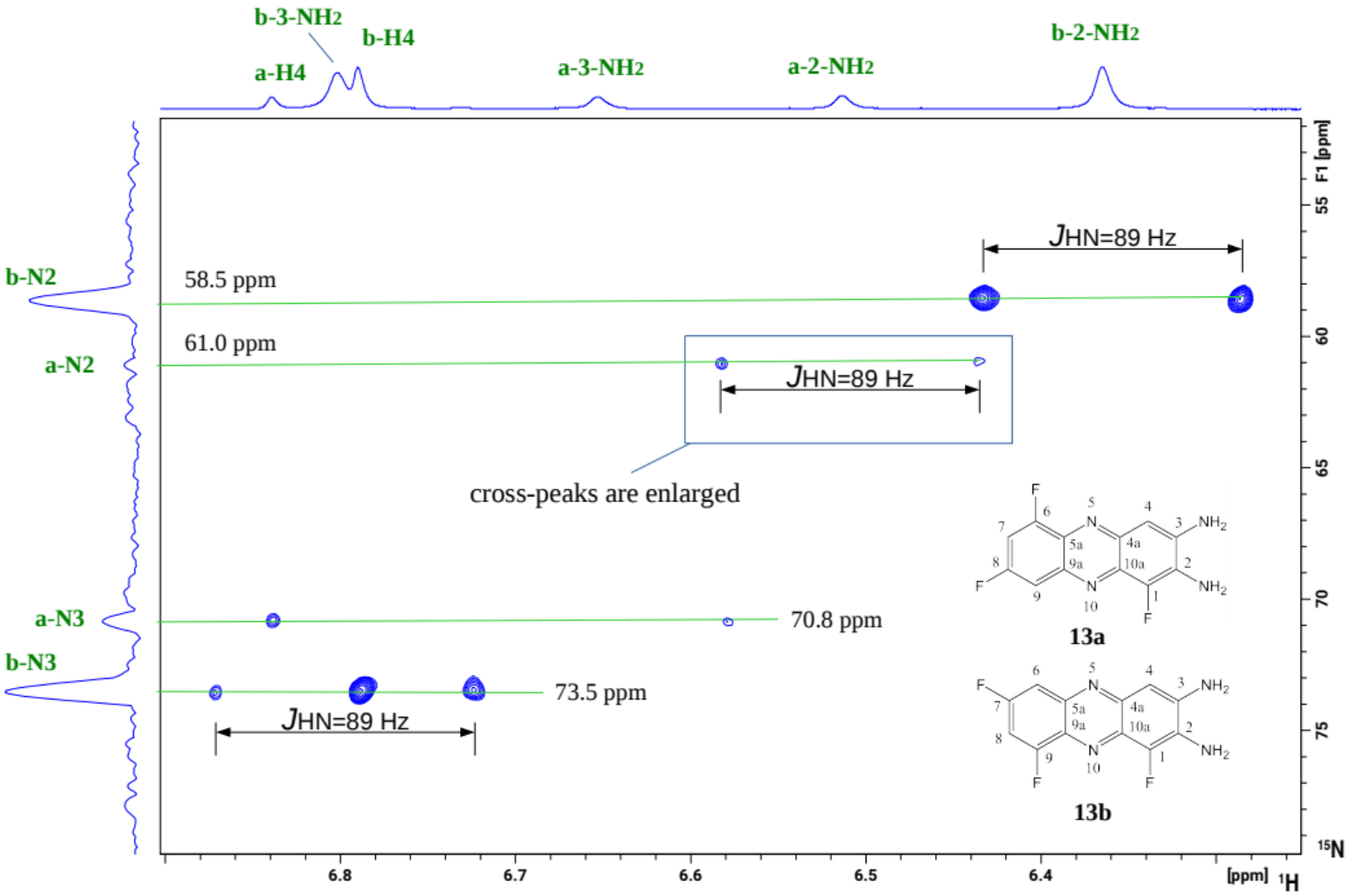
The part of the ^{1}H-^{13}C correlation NMR spectra of **13a and 13b** (DMSO-d6), Bruker AV-400 (^{1}H – 400.13, ^{13}C – 100.61 MHz)



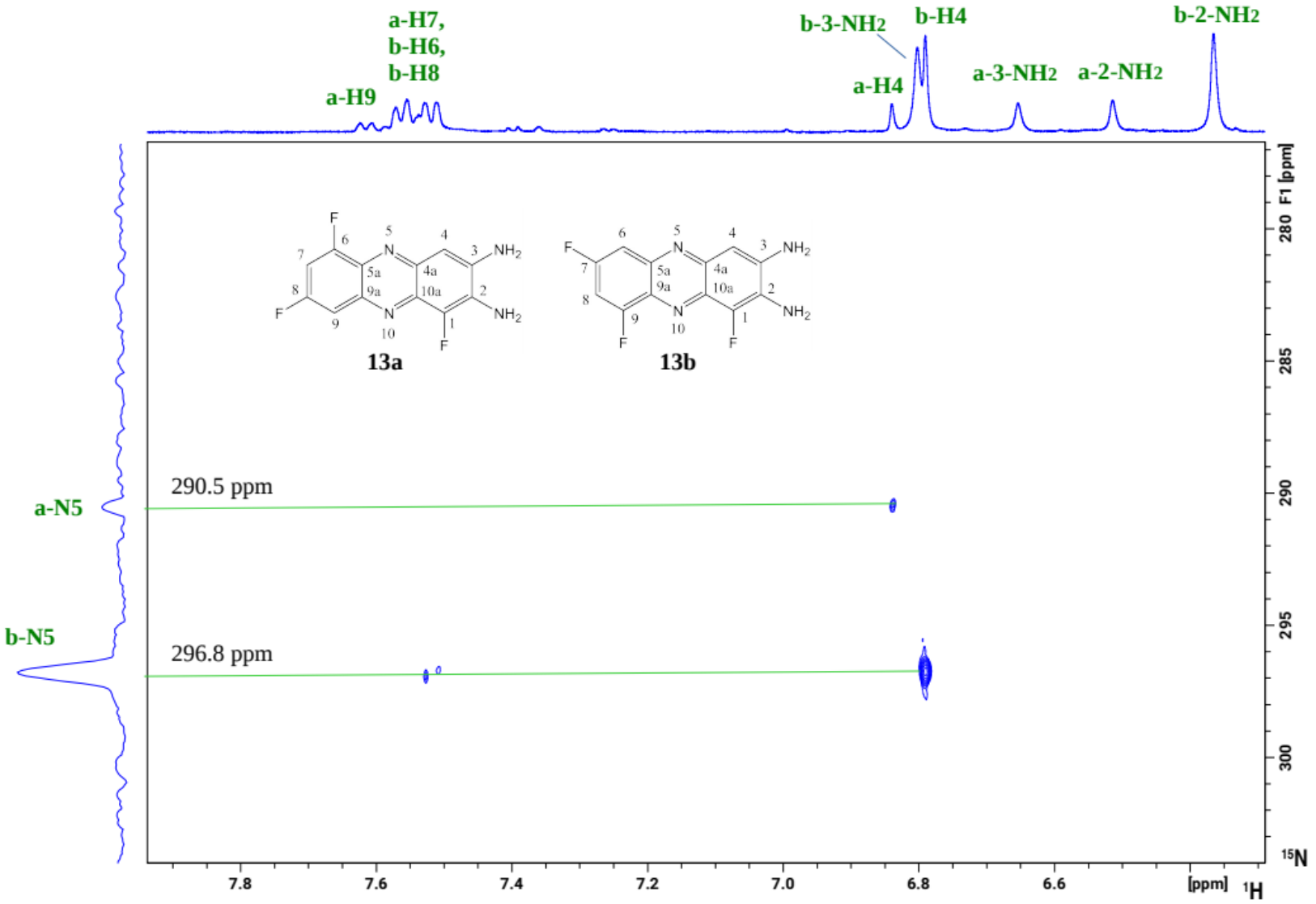
The part of the ^{1}H-^{13}C correlation NMR spectra of **13a and 13b** (DMSO-d6), Bruker AV-400 (^{1}H – 400.13, ^{13}C – 100.61 MHz)



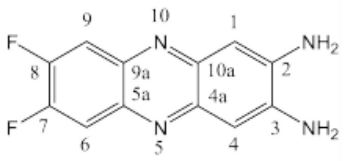
The part of the ^{1}H-^{15}N HMBC spectrum of **13a and 13b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{15}N – 60.83 MHz)



The part of the ^{1}H-^{15}N HMBC spectrum of **13a and 13b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{15}N – 60.83 MHz)

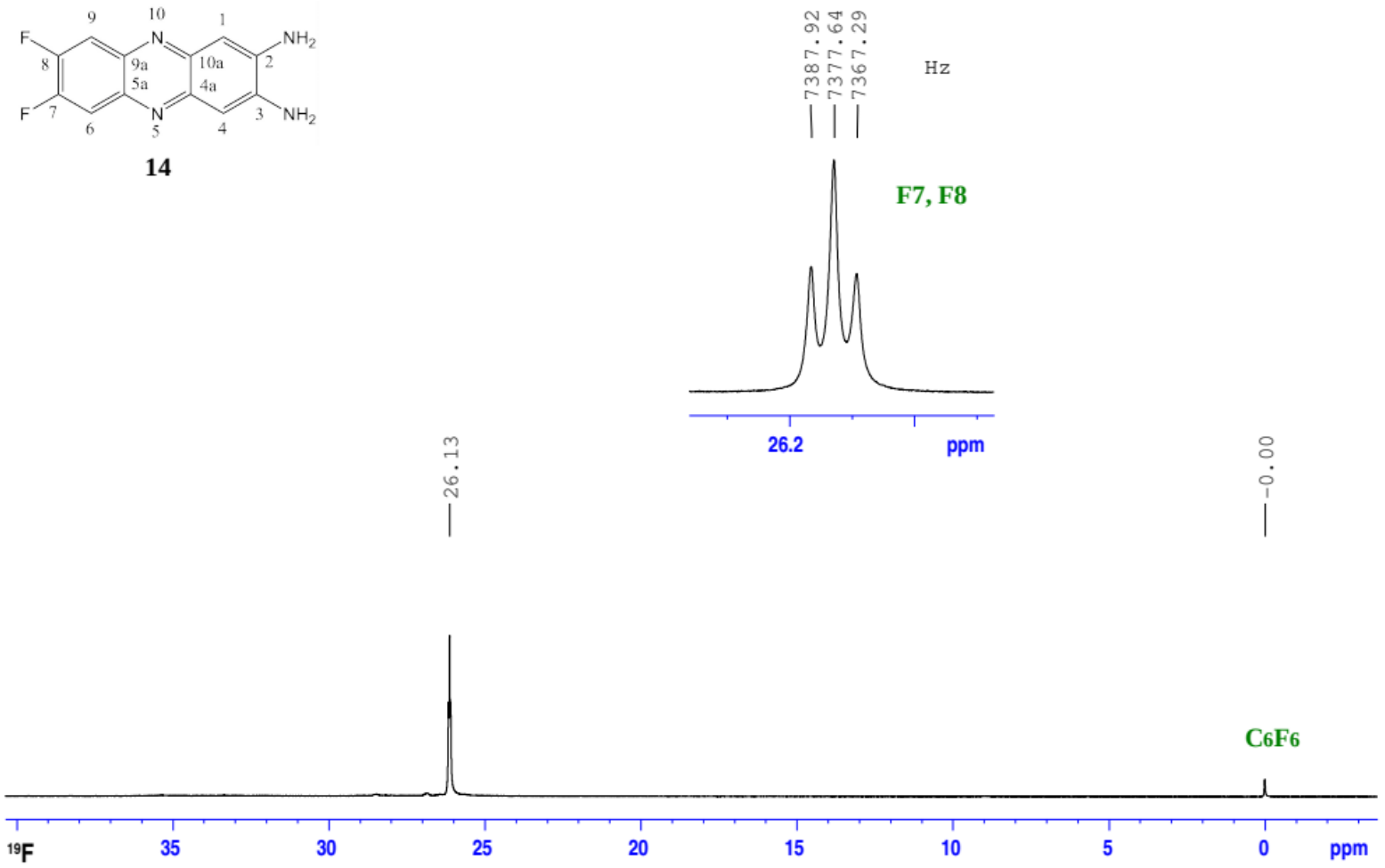


^{1}H NMR spectrum of **14** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30 MHz)

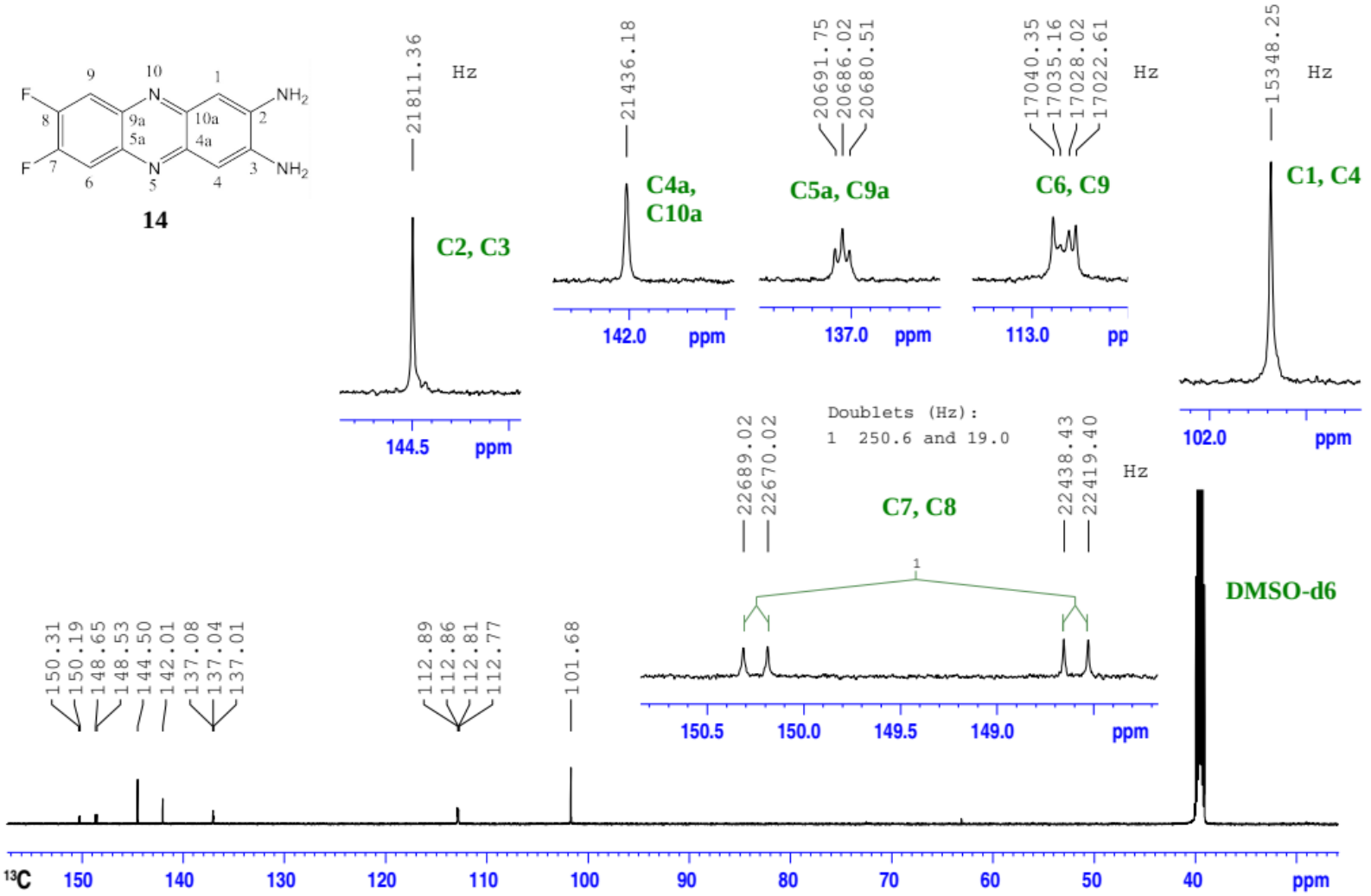


14

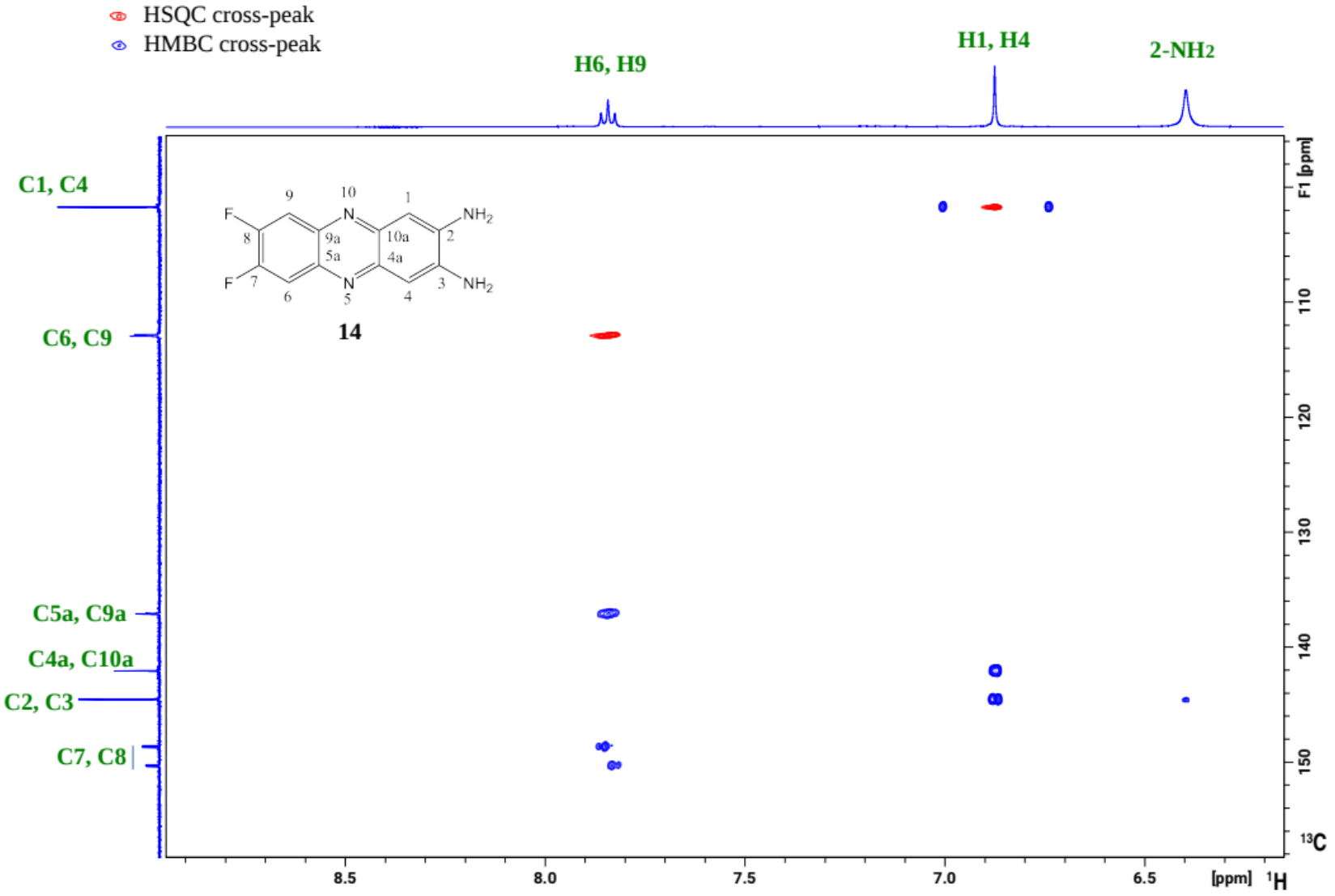
^{19}F NMR spectrum of **14** (DMSO-d6), Bruker AV-300 (^{19}F – 282.40 MHz)



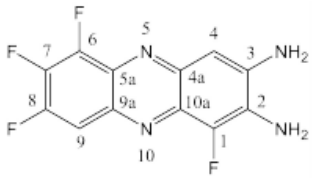
$^{13}C\{^{1}H\}$ NMR spectrum of **14** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{13}C – 150.95 MHz)



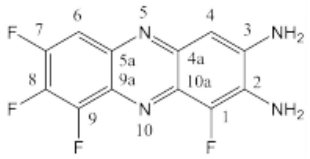
^{1}H-^{13}C correlation NMR spectra of **14** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{13}C – 150.95 MHz)



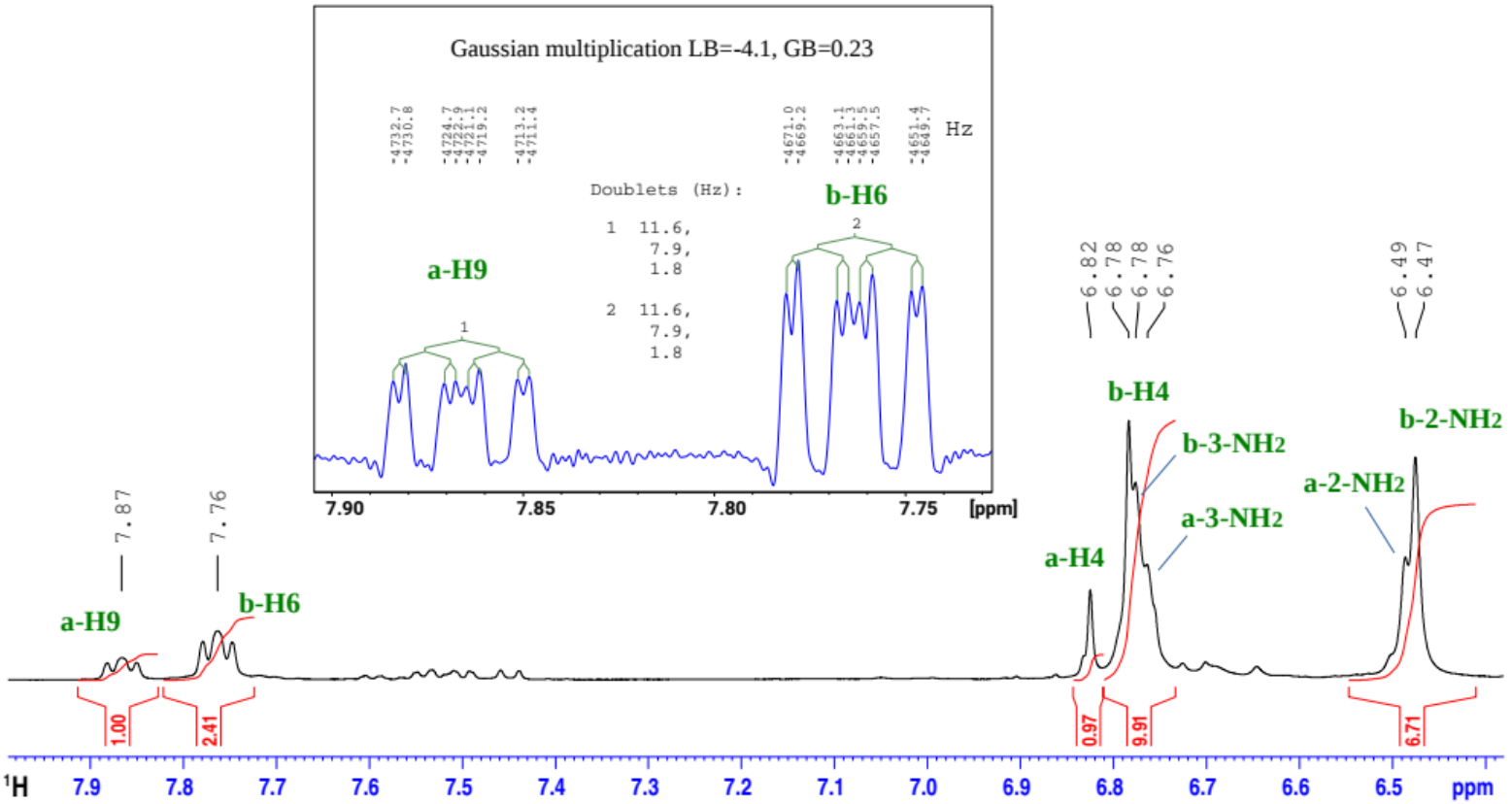
^{1}H NMR spectrum of **15a** and **15b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30 MHz)



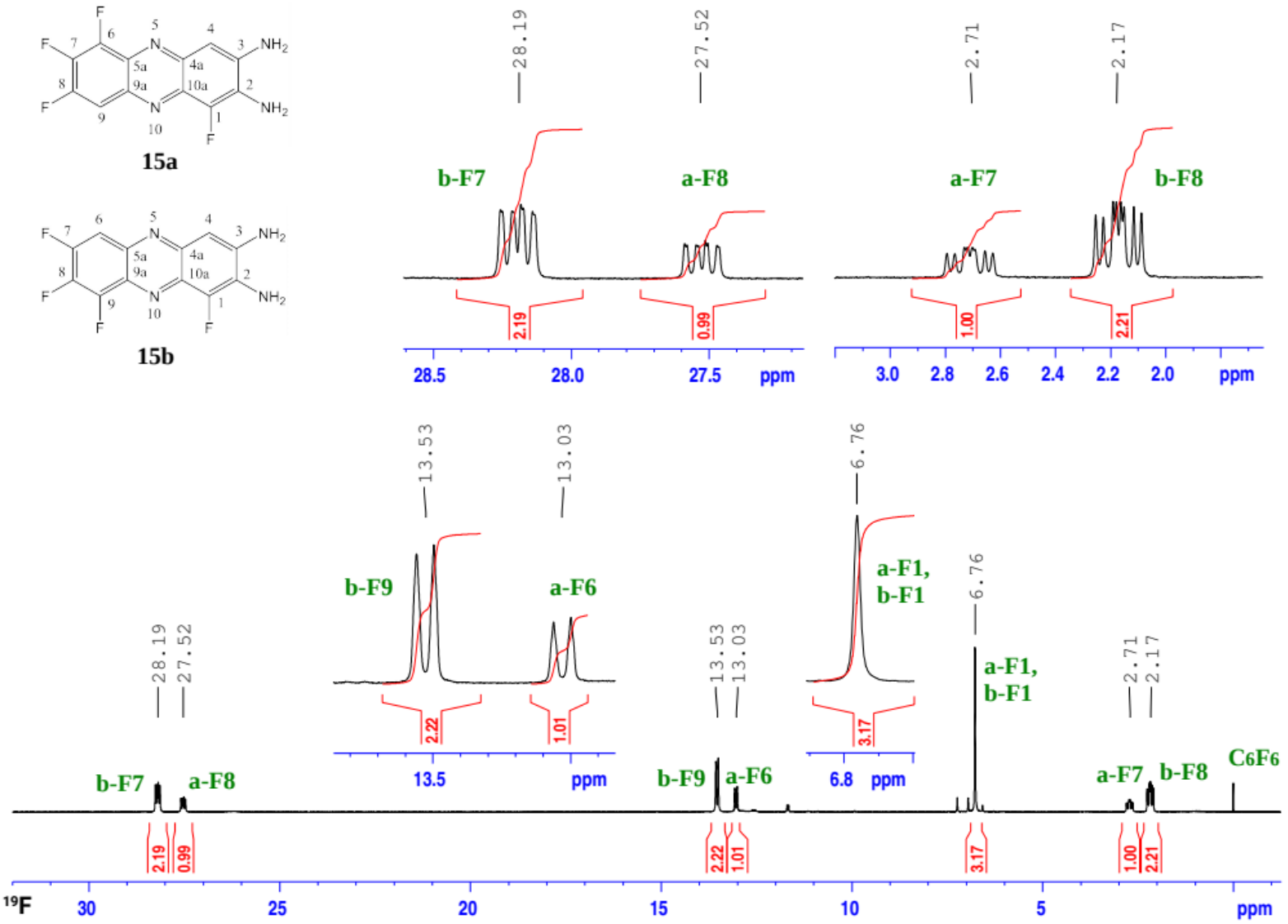
15a



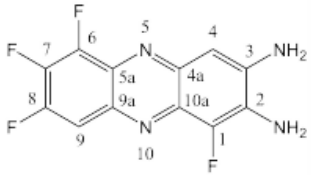
15b



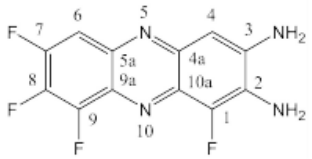
^{19}F NMR spectrum of **15a** and **15b** (DMSO-d6), Bruker AV-300 (^{19}F – 282.40 MHz)



Multiplets in ^{19}F NMR spectrum of **15a** and **15b** (DMSO-d6), Bruker AV-300 (^{19}F – 282.40 MHz)

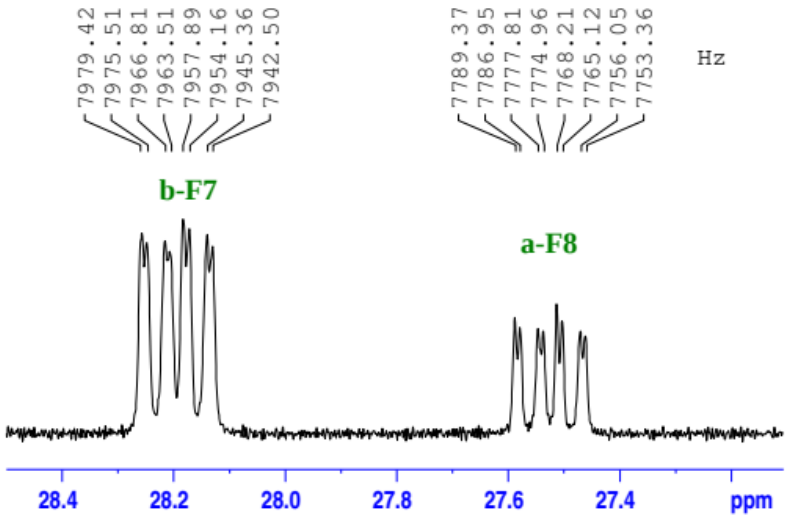


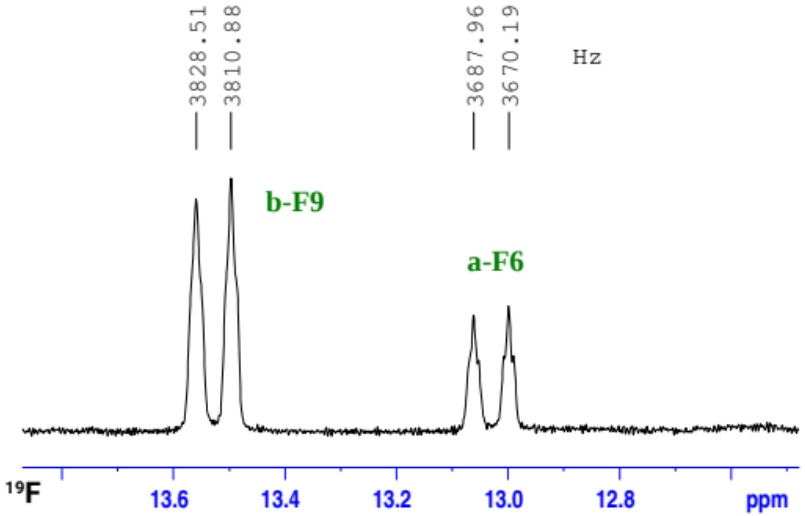
15a

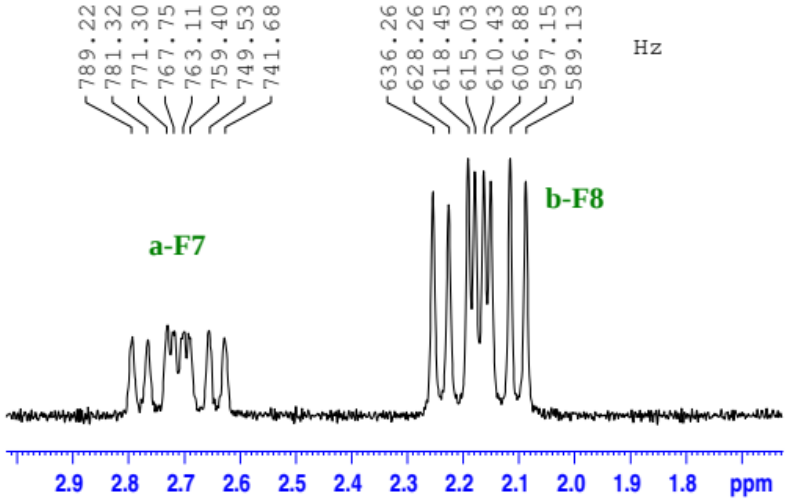


15b

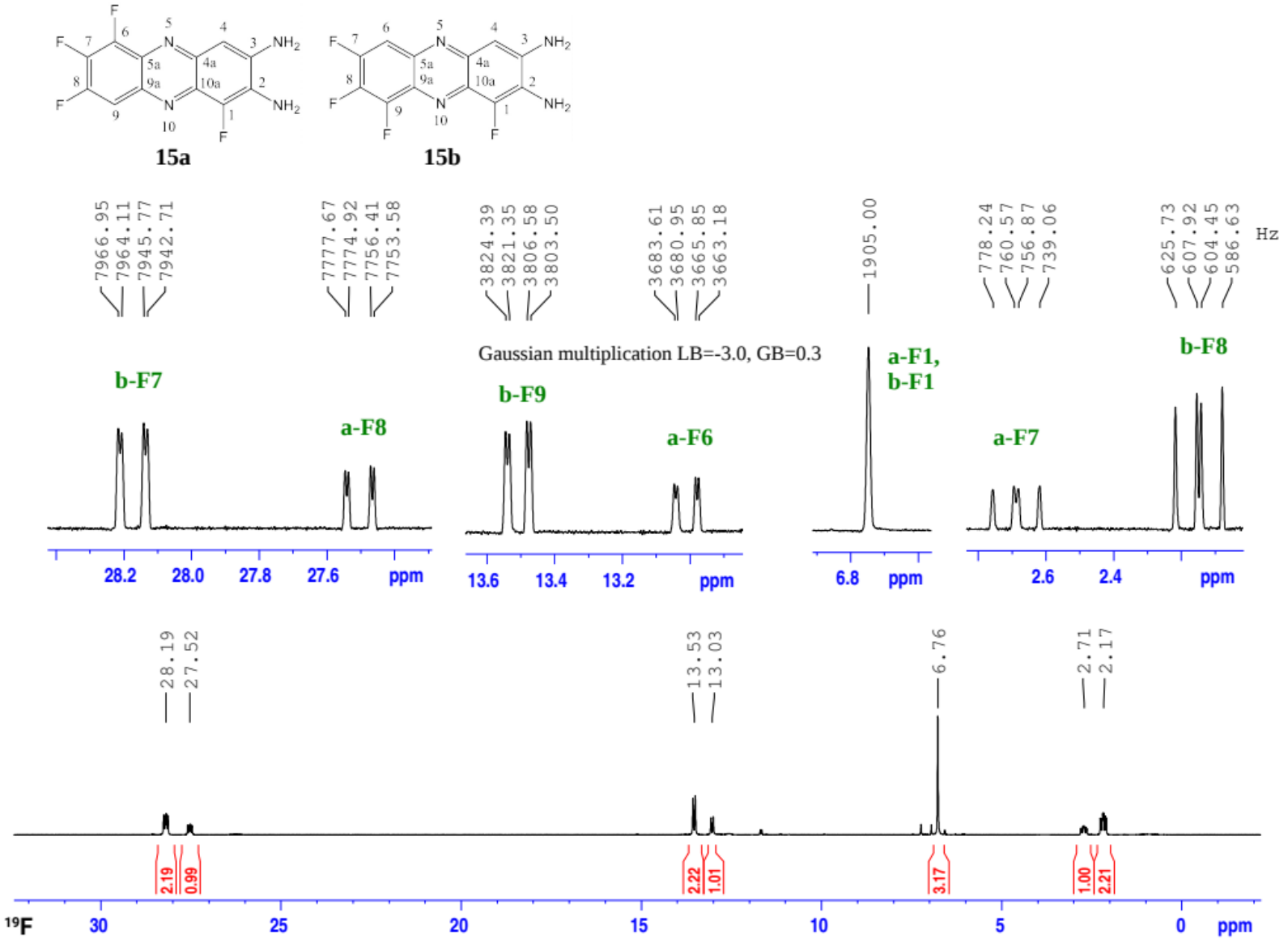
Gaussian multiplication LB= -2.0, GB=0.5



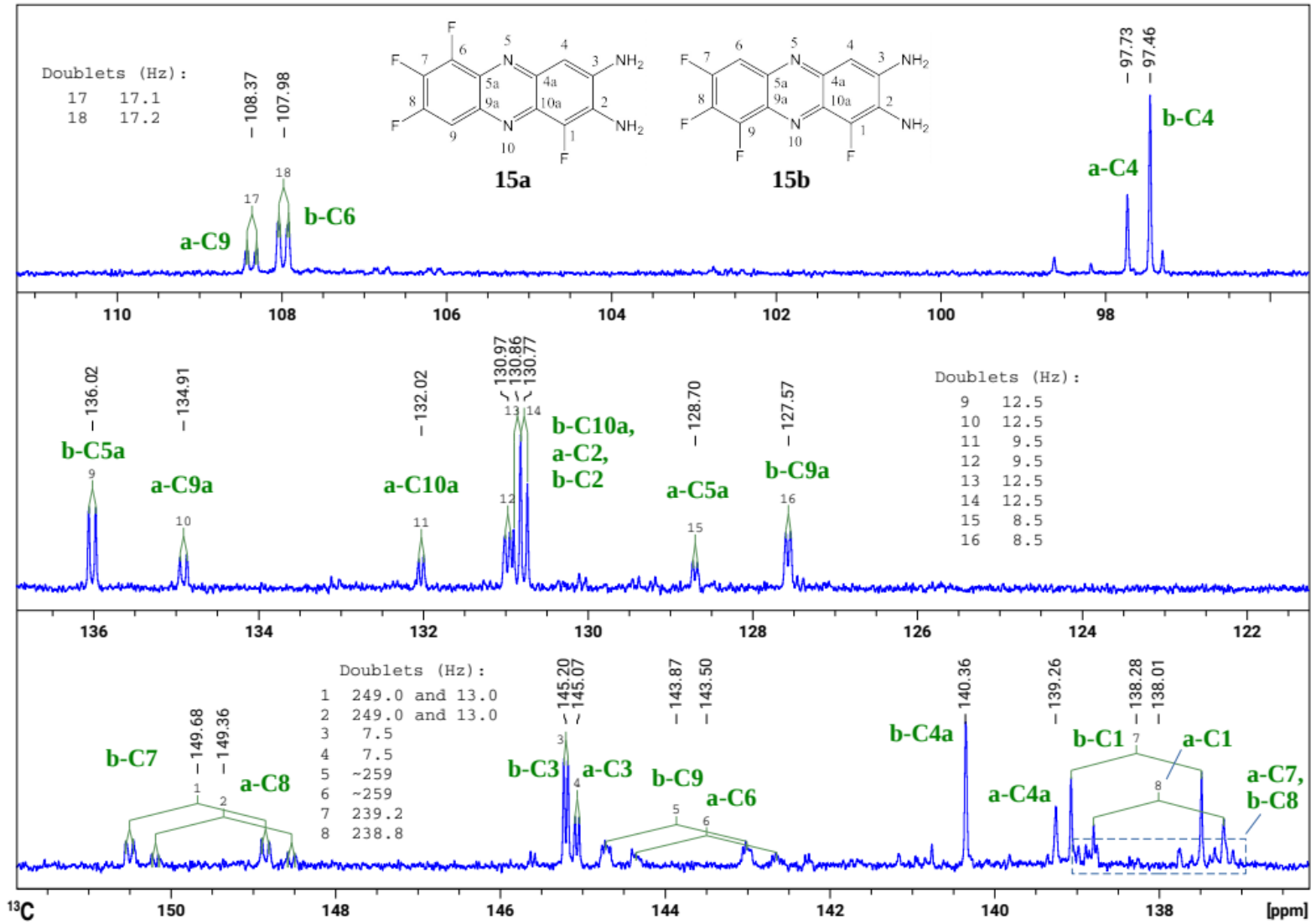




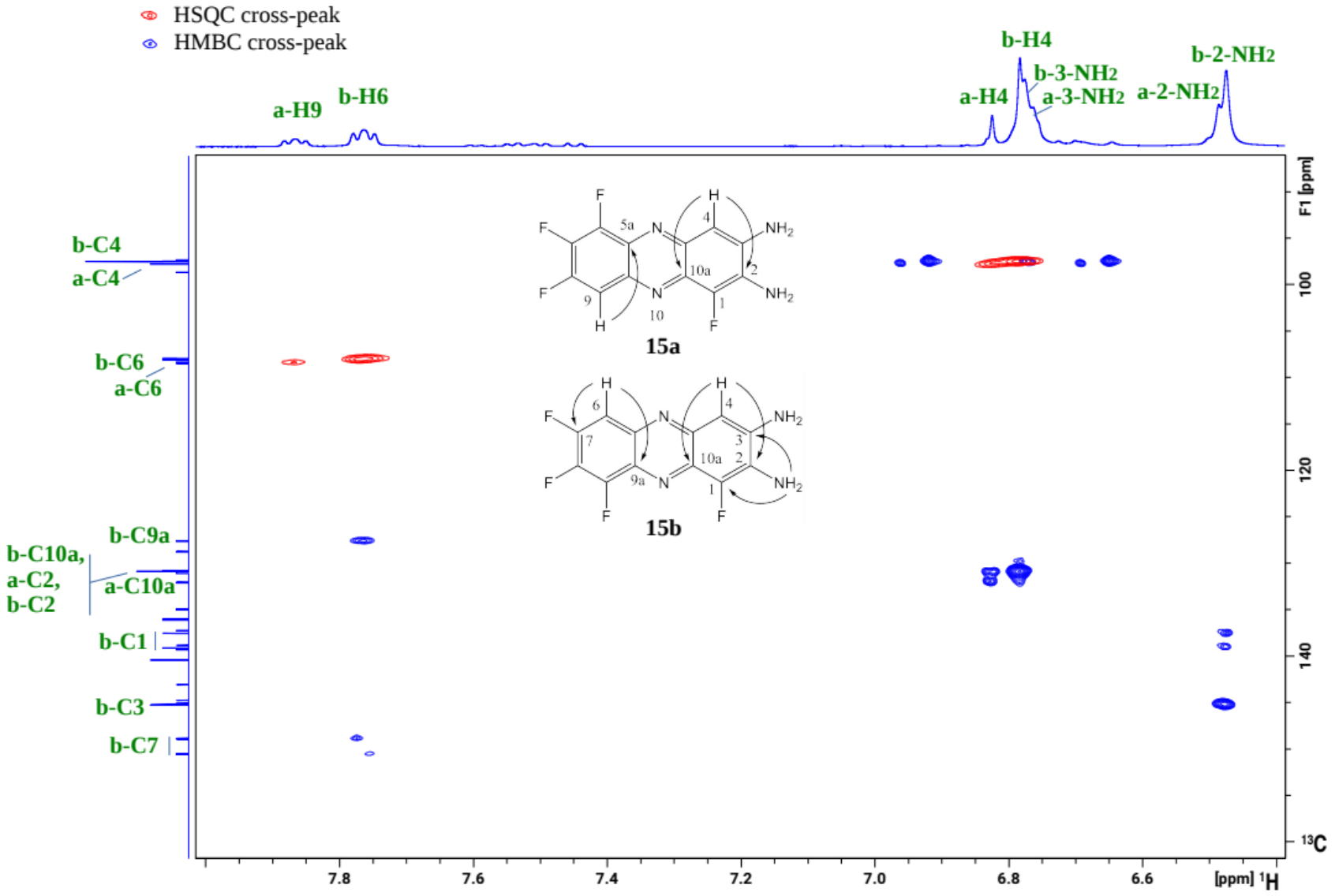
$^{19}F\{^{1}H\}$ NMR spectrum of **15a** and **15b** (DMSO-d6), Bruker AV-300 (^{19}F – 282.40 MHz, ^{1}H – 300.13 MHz)



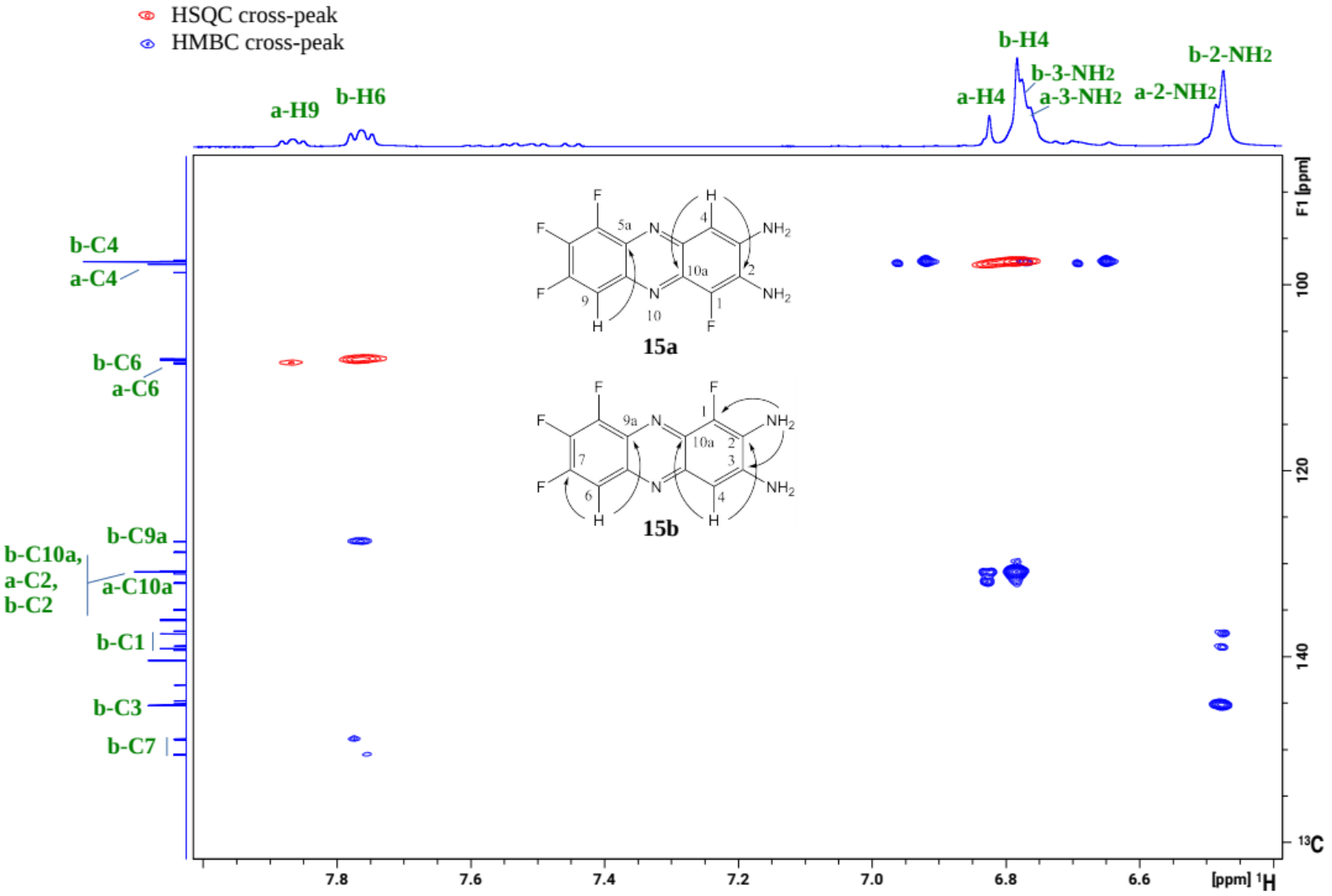
$^{13}C\{^{1}H\}$ NMR spectrum of **15a** and **15b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{13}C – 150.95 MHz)



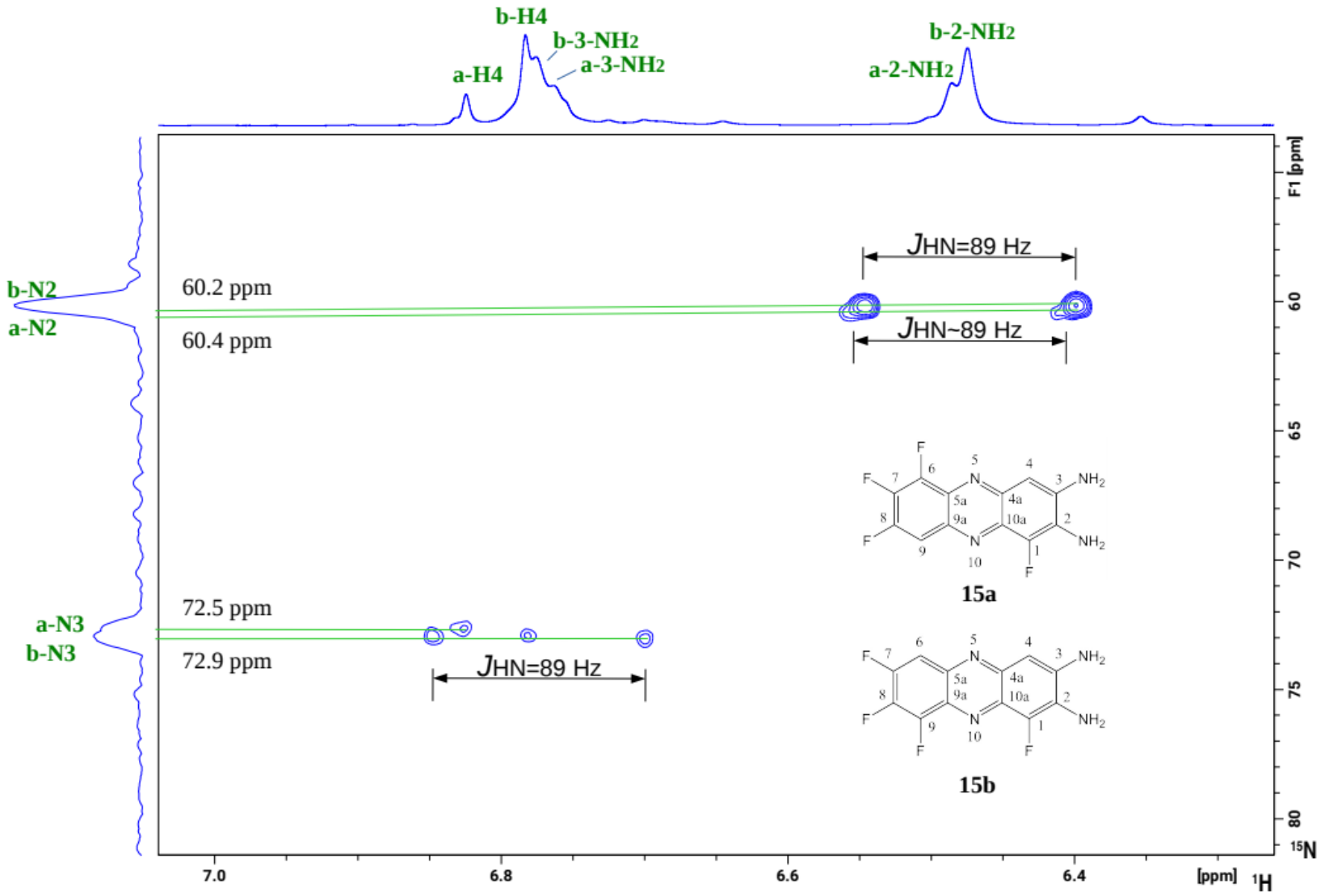
^{1}H-^{13}C correlation NMR spectra of **15a and 15b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{13}C – 150.95 MHz)



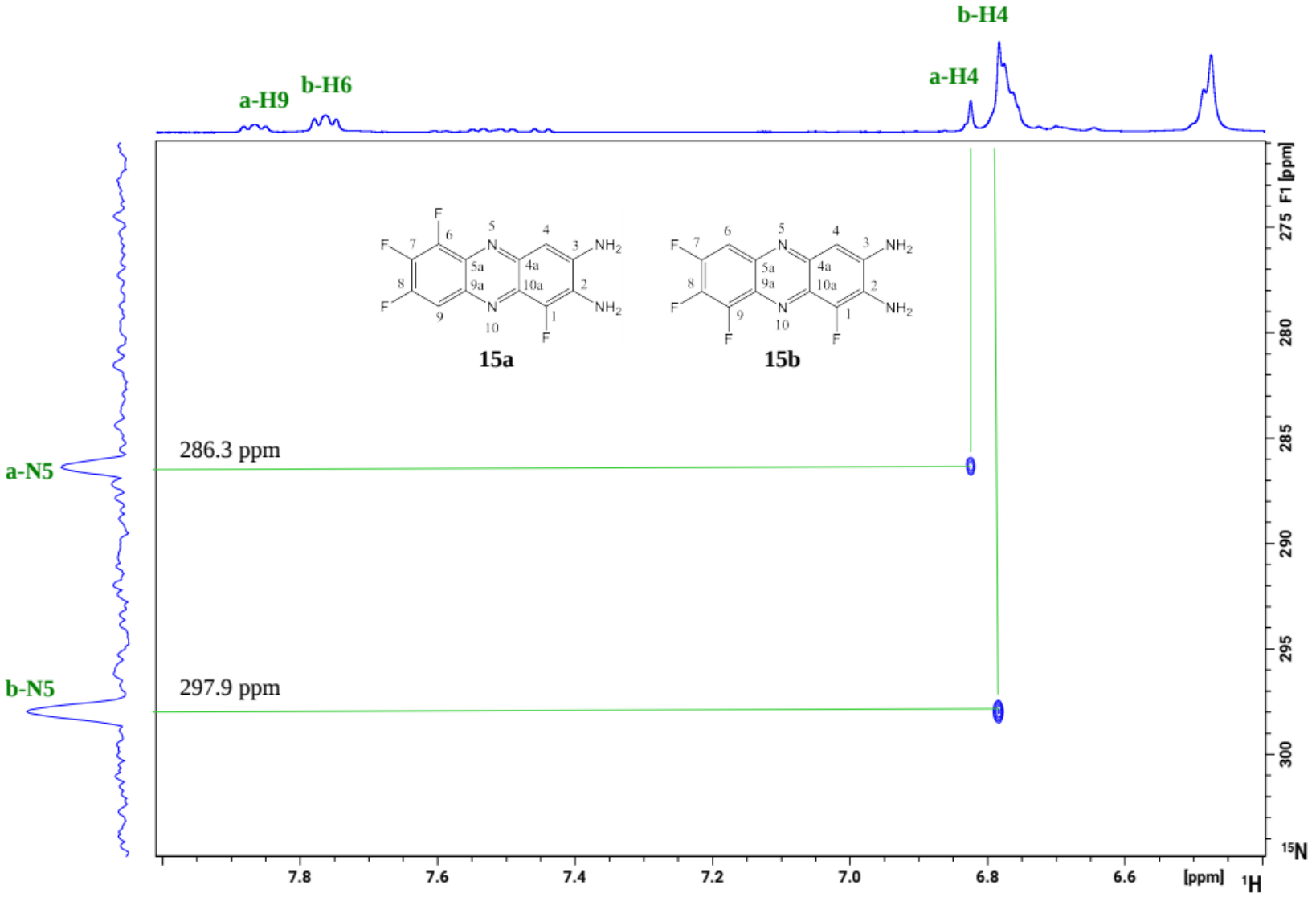
The part of the ^{1}H-^{15}N HMBC spectrum of **15a and 15b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{15}N – 60.83 MHz)



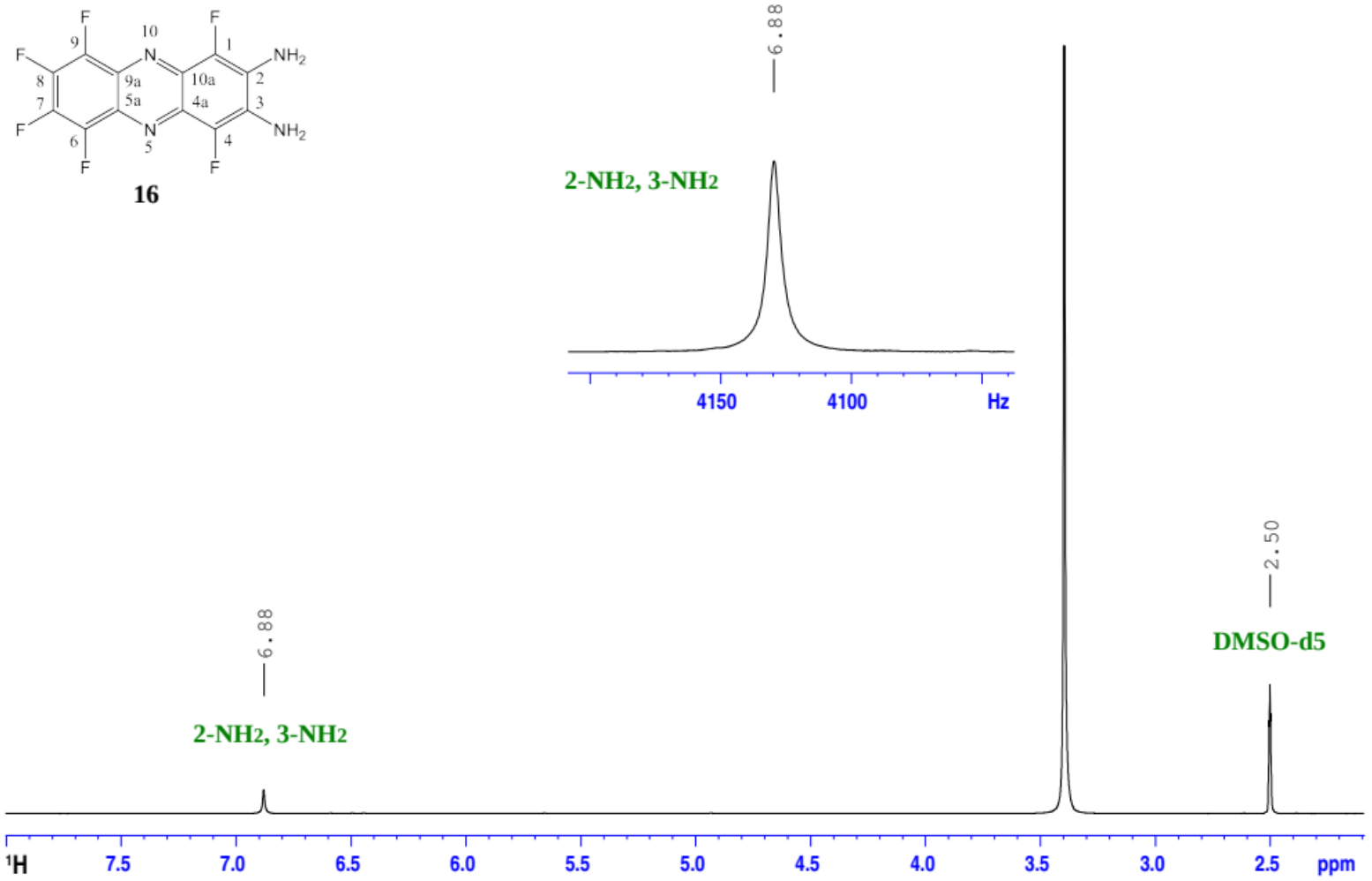
The part of the ^{1}H-^{15}N HMBC spectrum of **15a and 15b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{15}N – 60.83 MHz)



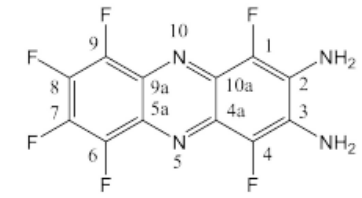
The part of the ^{1}H-^{15}N HMBC spectrum of **15a and 15b** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{15}N – 60.83 MHz)



^{1}H NMR spectrum of **16** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30 MHz)



^{19}F NMR spectrum of **16** (DMSO-d6), Bruker AV-300 (^{19}F – 282.40 MHz)



16

$^{13}C\{^{1}H\}$ NMR spectrum of **16** (DMSO-d6), Bruker AV-600 (^{1}H – 600.30, ^{13}C – 150.95 MHz)