

## Supporting Information

### Spin-Vibronic Control of Intersystem Crossing in Iodine-Substituted Heptamethine Cyanines

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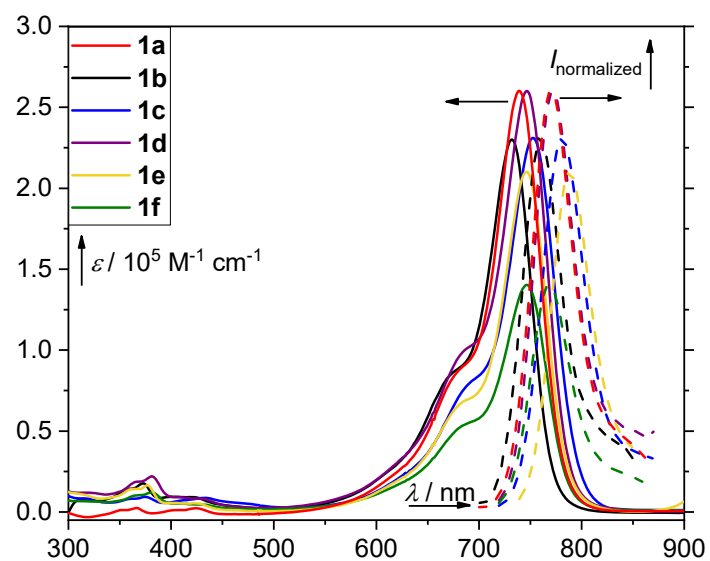
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<sup>¶</sup> These authors contributed equally to this work.

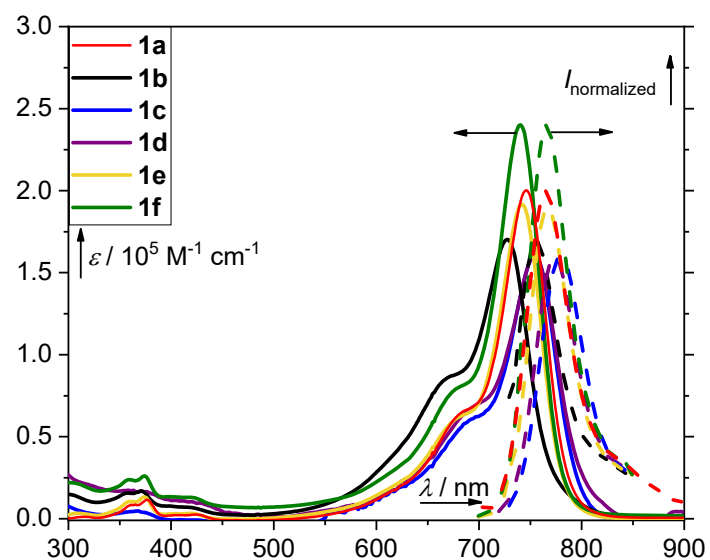
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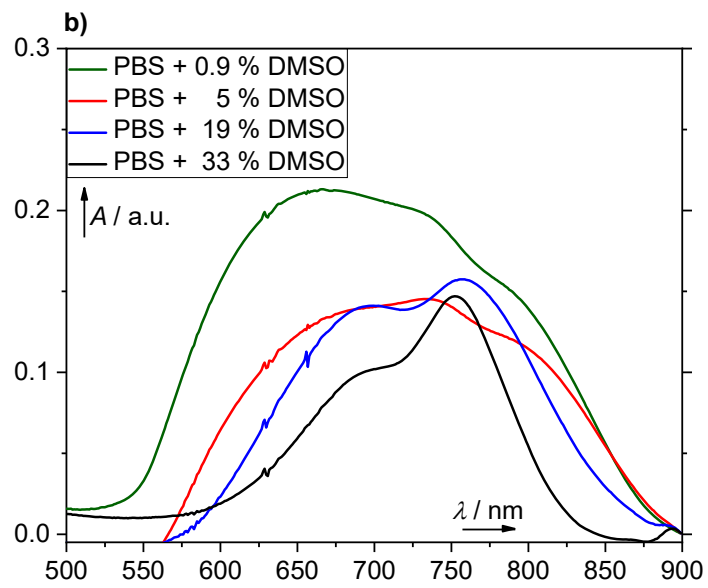
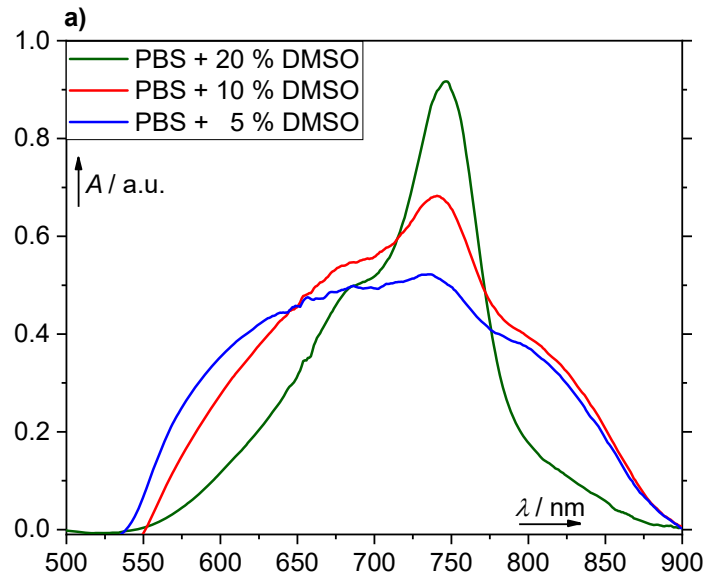
## UV-VIS Absorption and Emission Spectra

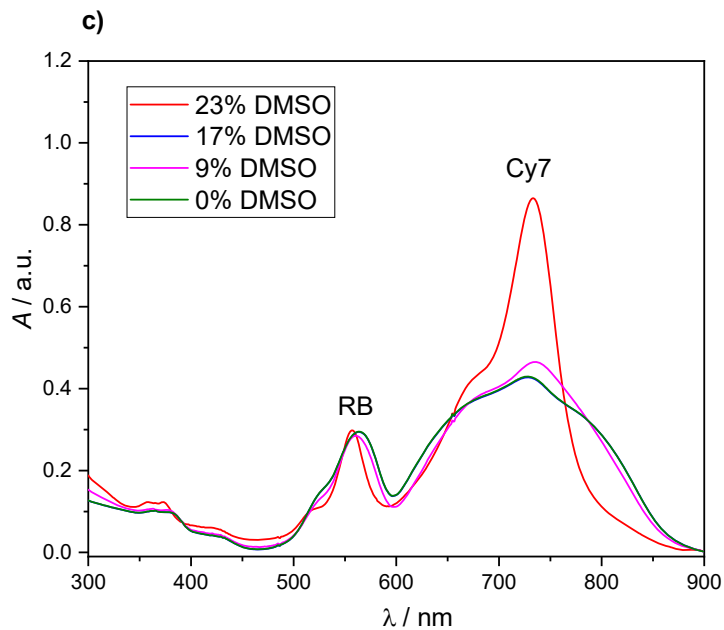


**Figure S1:** Absorption (—, right y-axis) and normalized emission (---, left y-axis) spectra of **1a–f** in methanol.

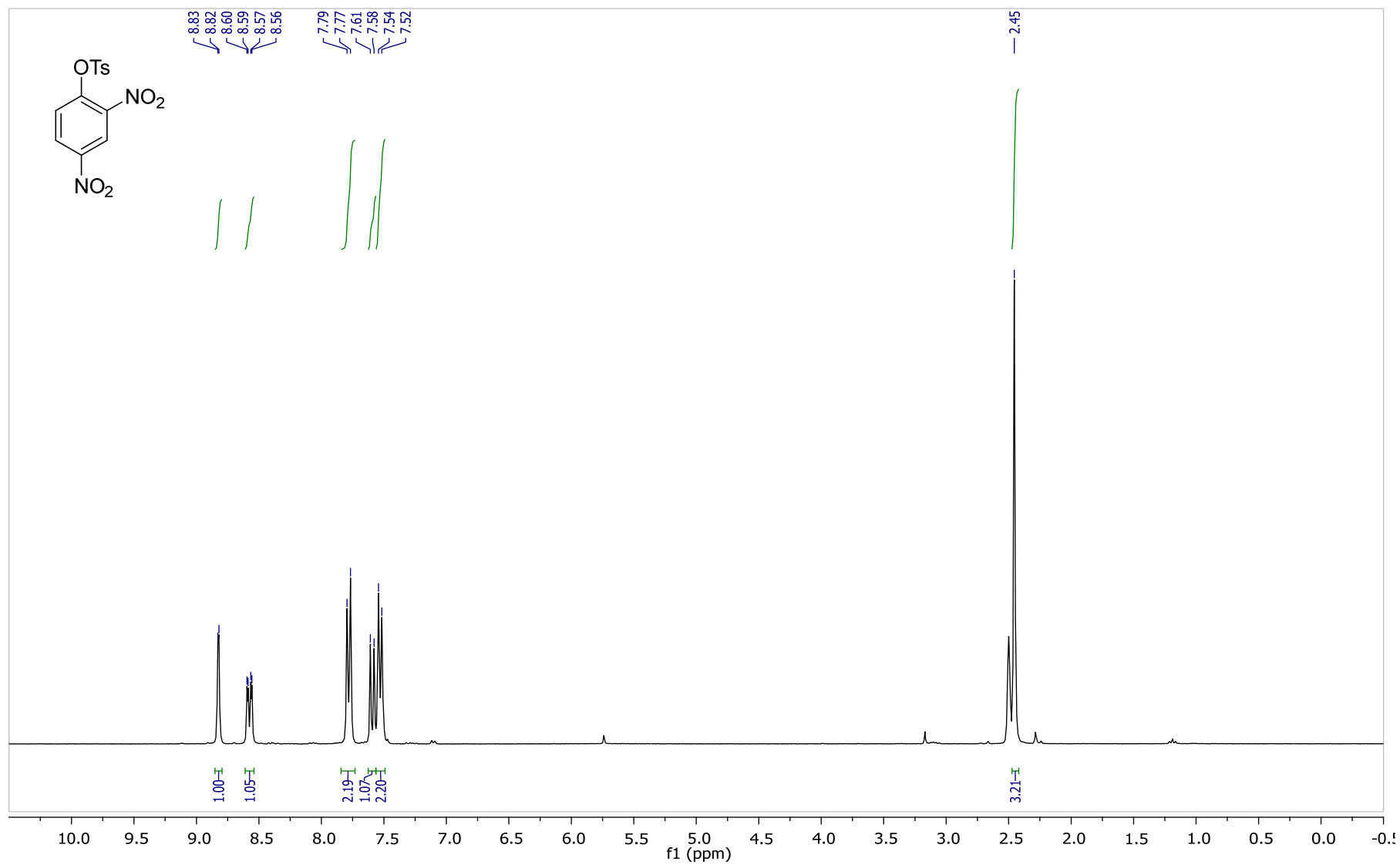


**Fig. S2:** Absorption (—, right y-axis) and normalized emission (---, left y-axis) spectra of **1a–f** in PBS.

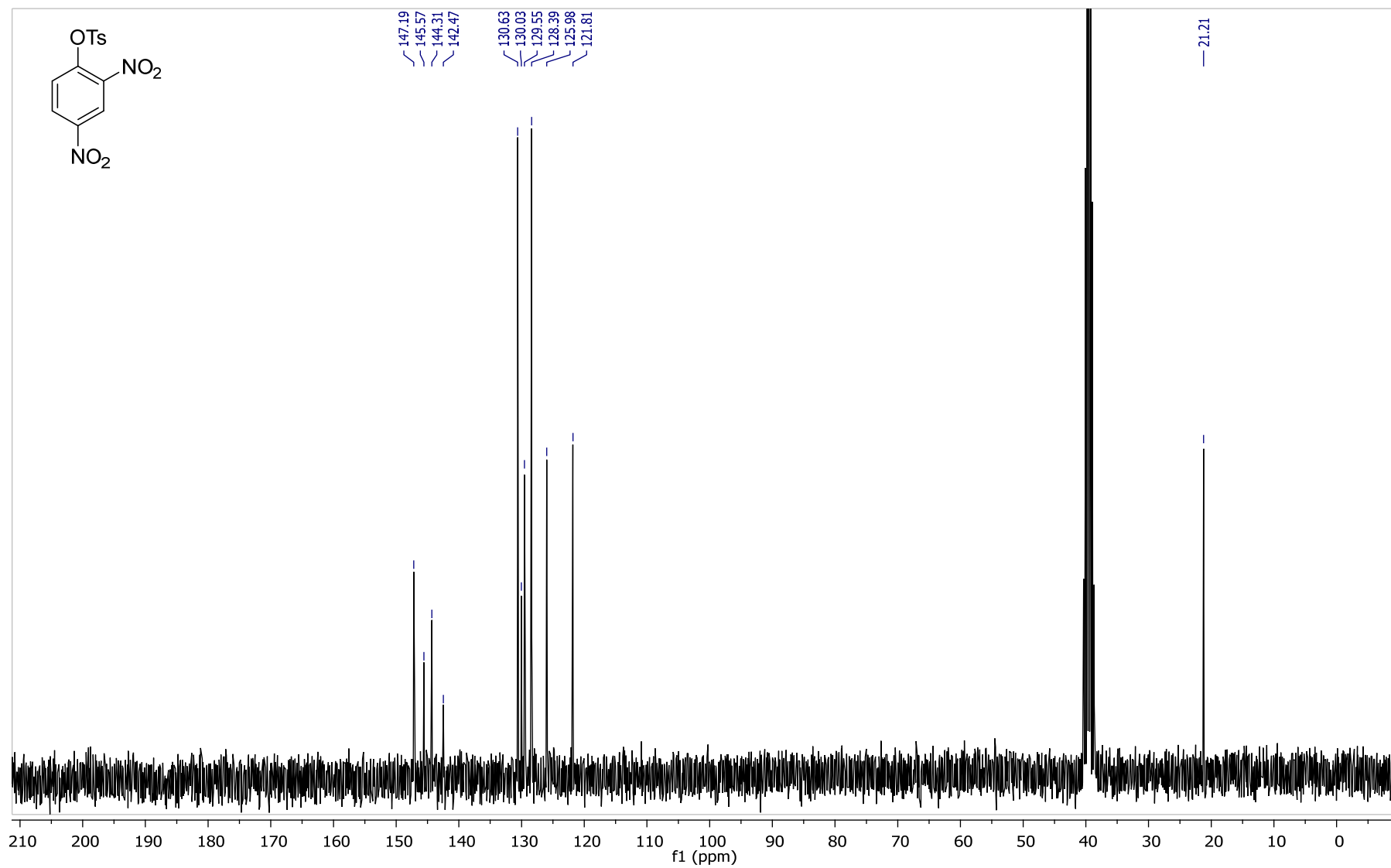




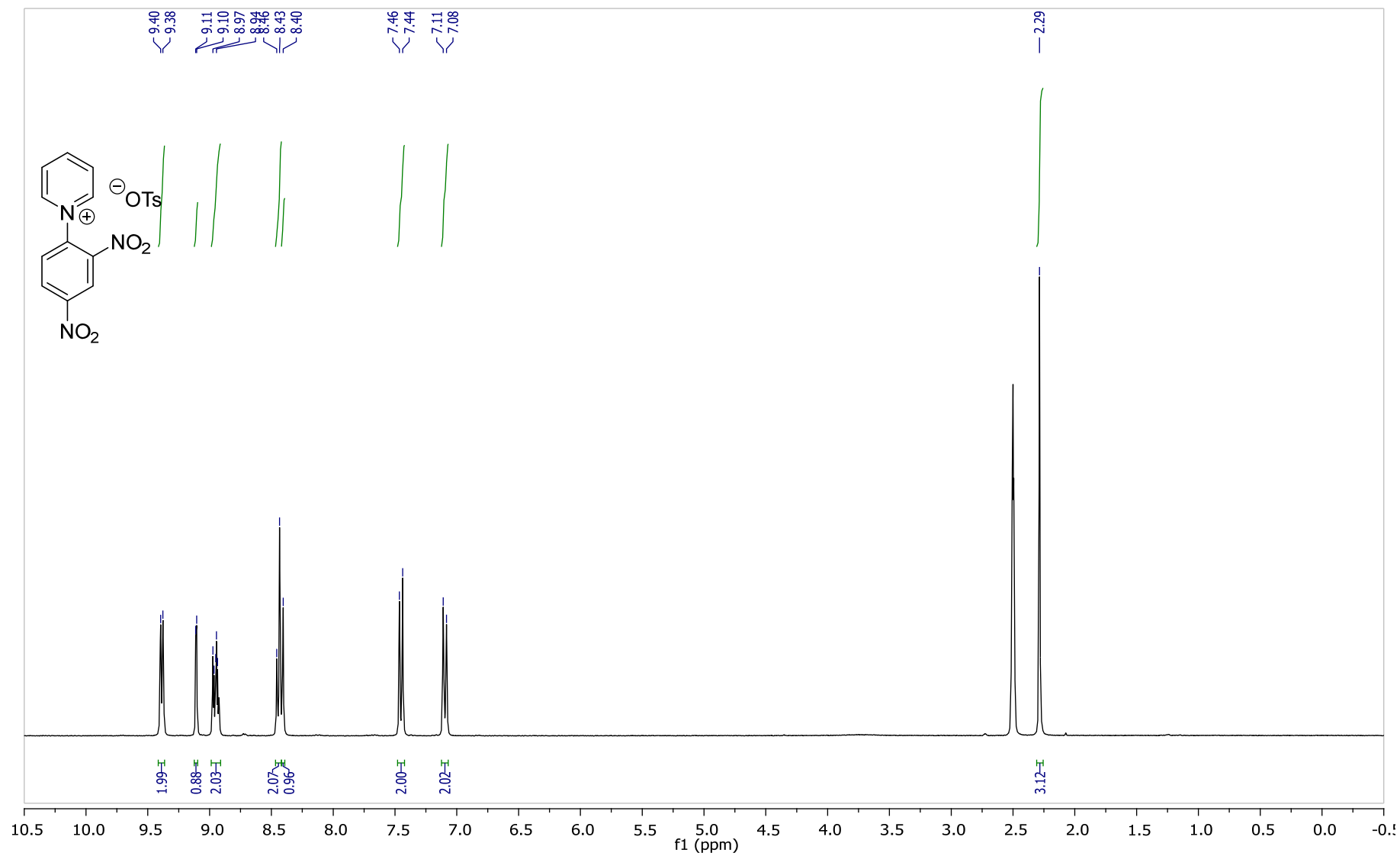
**Figure S3.** Aggregation of a) **1c** ( $c = 1.4 \times 10^{-5}$  M) b) **1d** ( $c = 4.8 \times 10^{-6}$  M) in PBS (pH= 7.4,  $I = 0.1$  mM) with different amounts of DMSO (the spikes at 629 and 658 nm are artifacts of a spectrometer) determined by absorption spectroscopy (dye aggregation, a 500–600 nm band, disappears with an increasing amount of DMSO). c) Aggregation of **1b** ( $c = 5.8 \times 10^{-6}$  M) in PBS (pH= 7.4,  $I = 0.1$  mM) with different amounts of DMSO in the presence of rose bengal (RB;  $c = 4 \times 10^{-6}$  M).



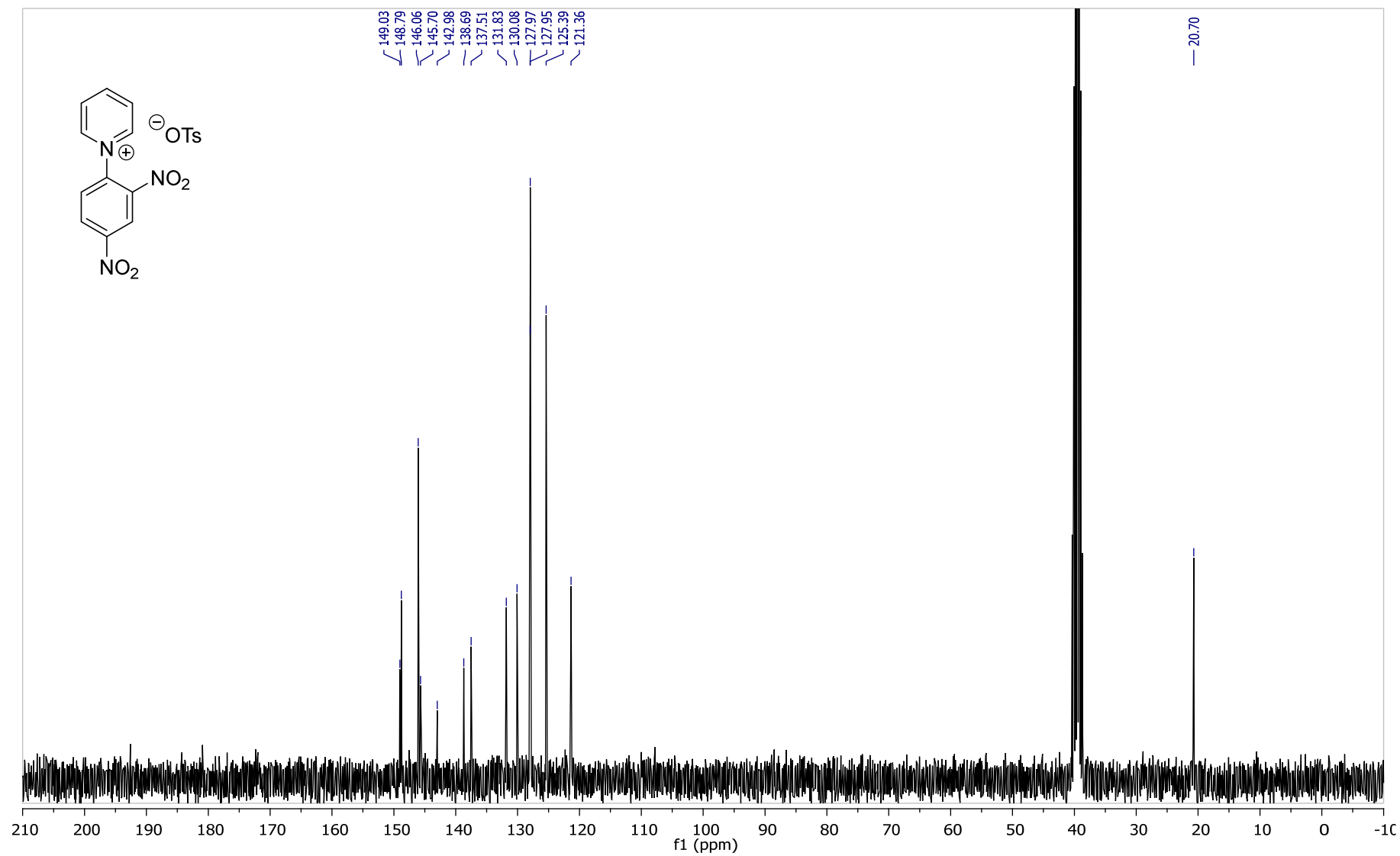
**Figure S4.**  $^1\text{H}$  NMR (300 MHz,  $d_6$ -DMSO): **4**.



**Figure S5.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $d_6$ -DMSO): **4**.

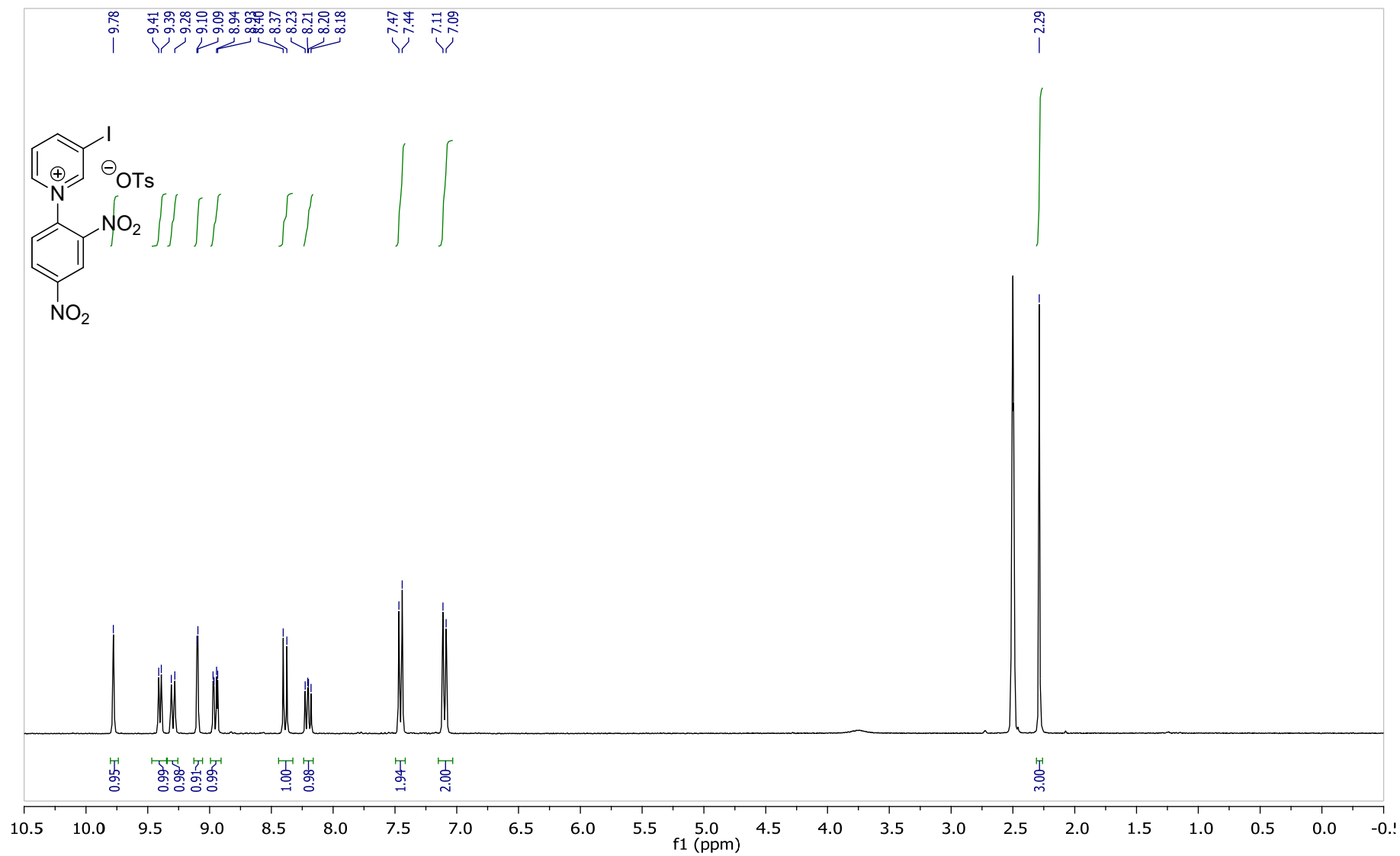


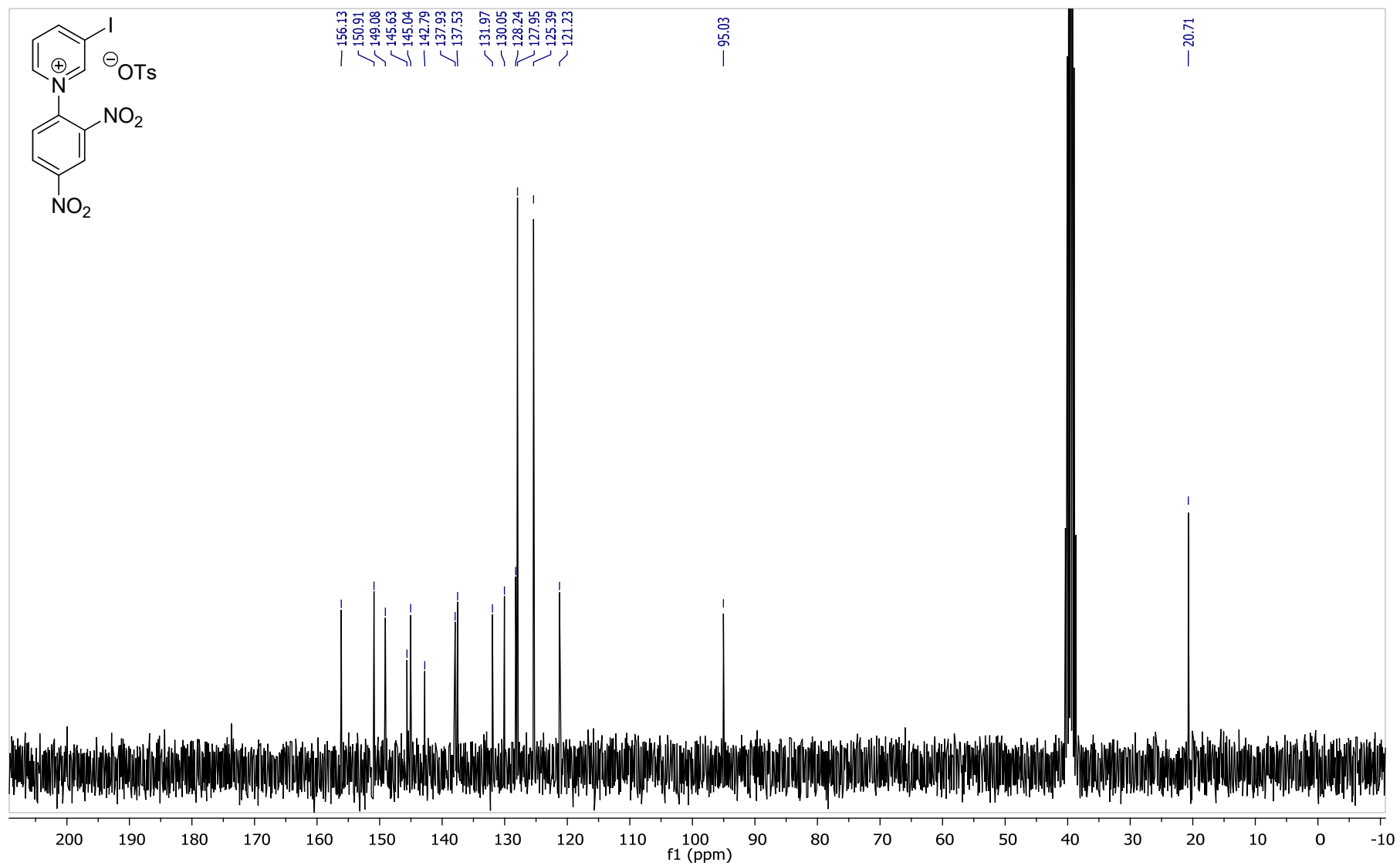
**Figure S6.** <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO): **5a**.



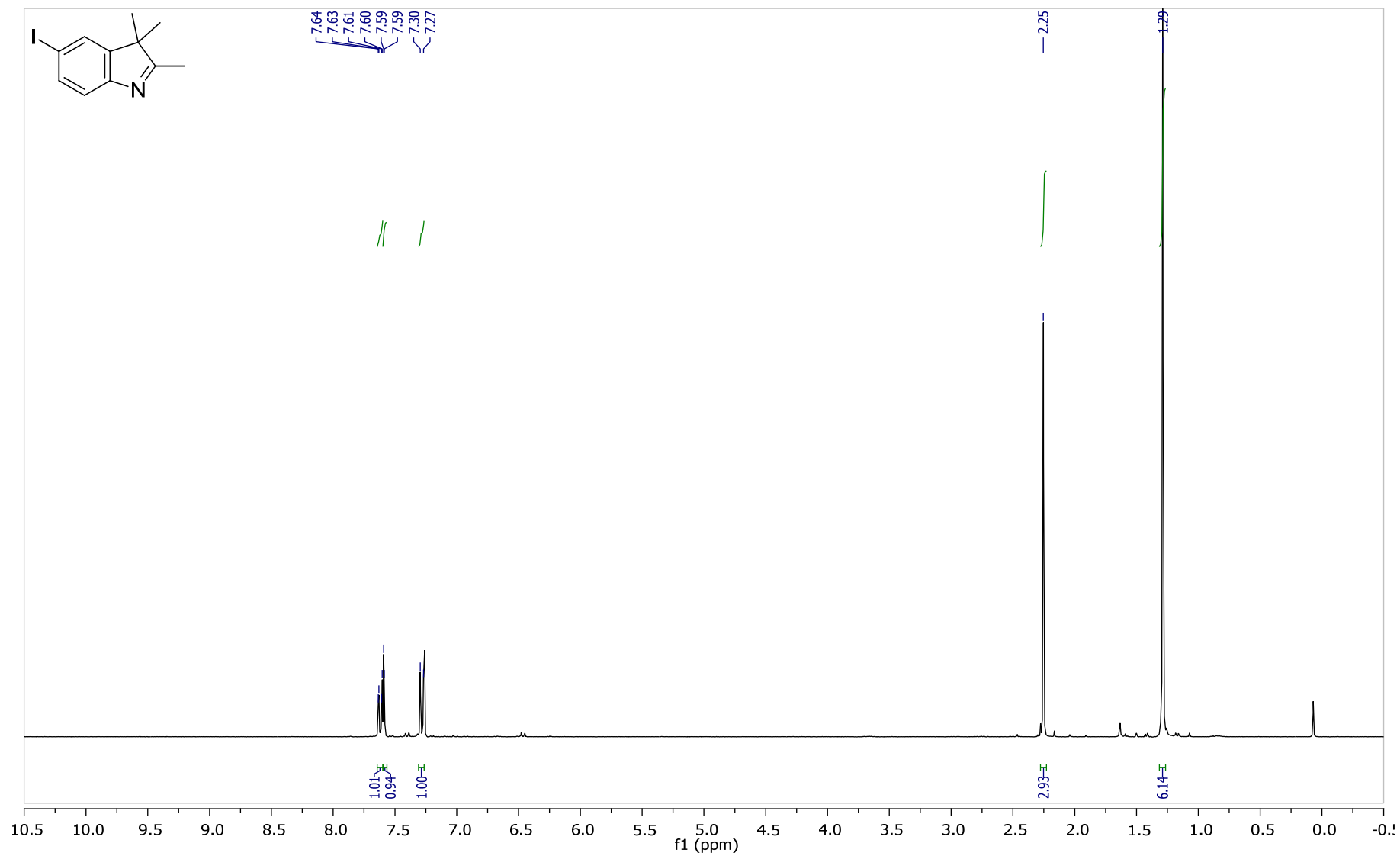
**Figure S7.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $d_6$ -DMSO): **5a**.



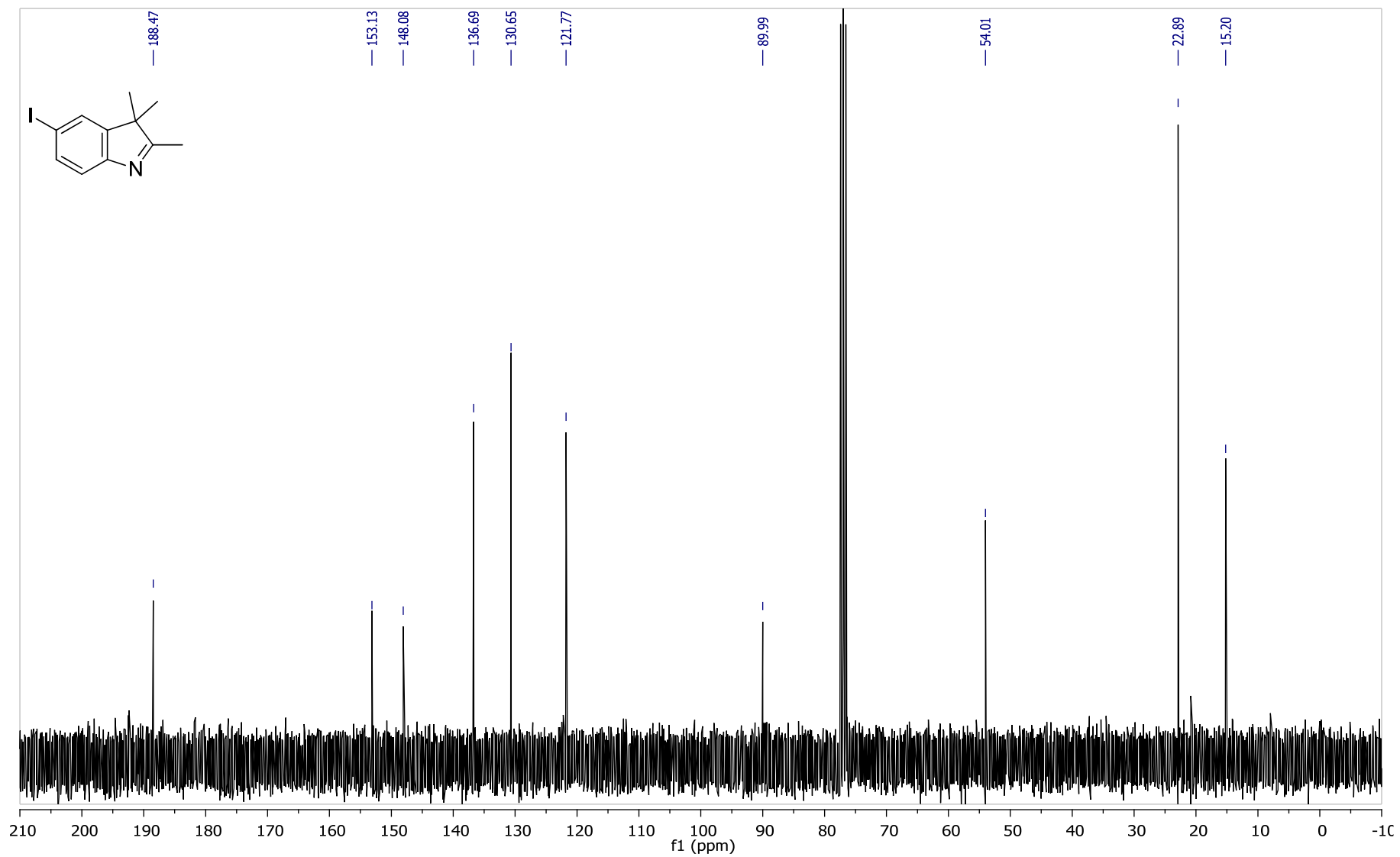




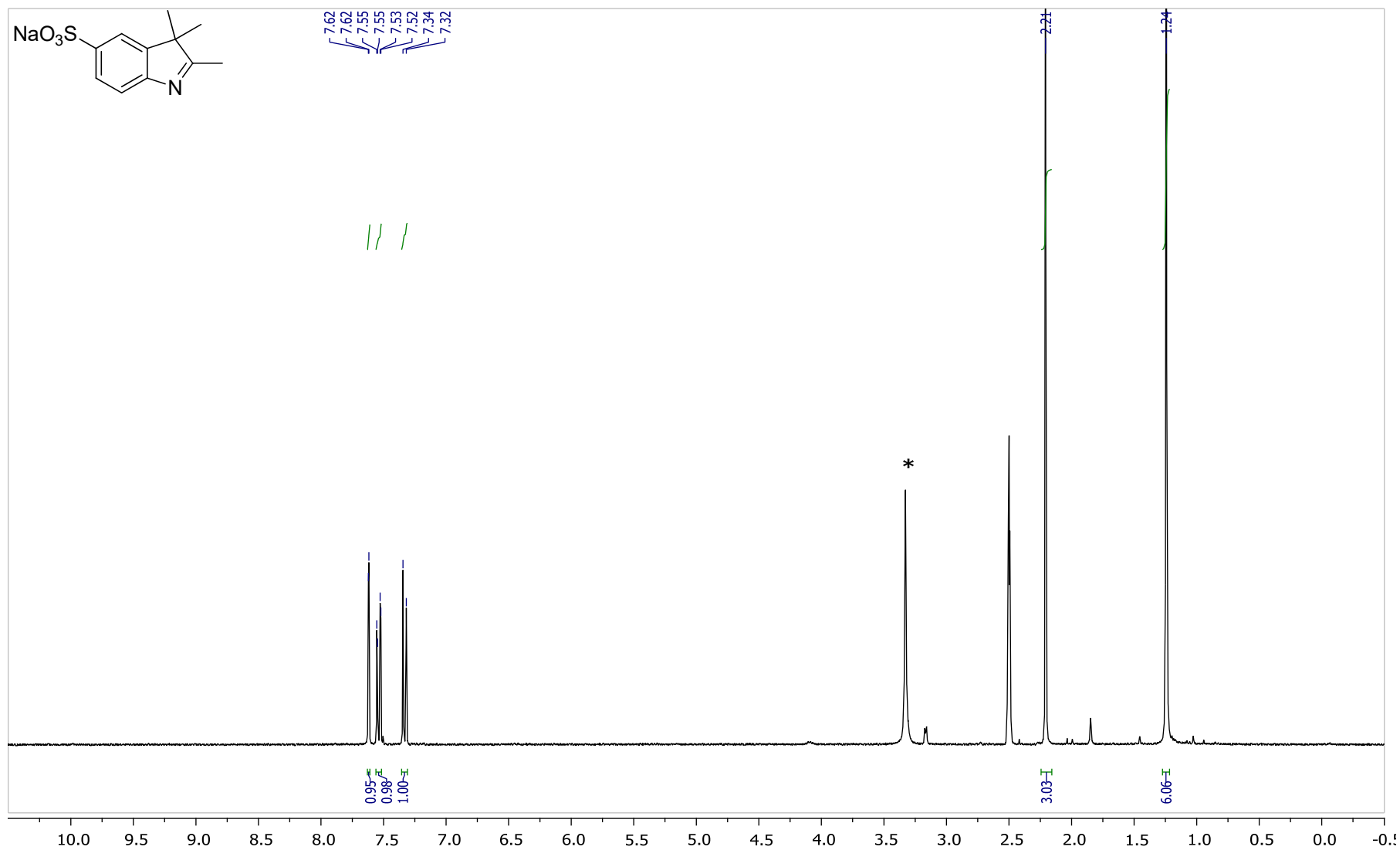
**Figure S9.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $d_6$ -DMSO): **5b**.



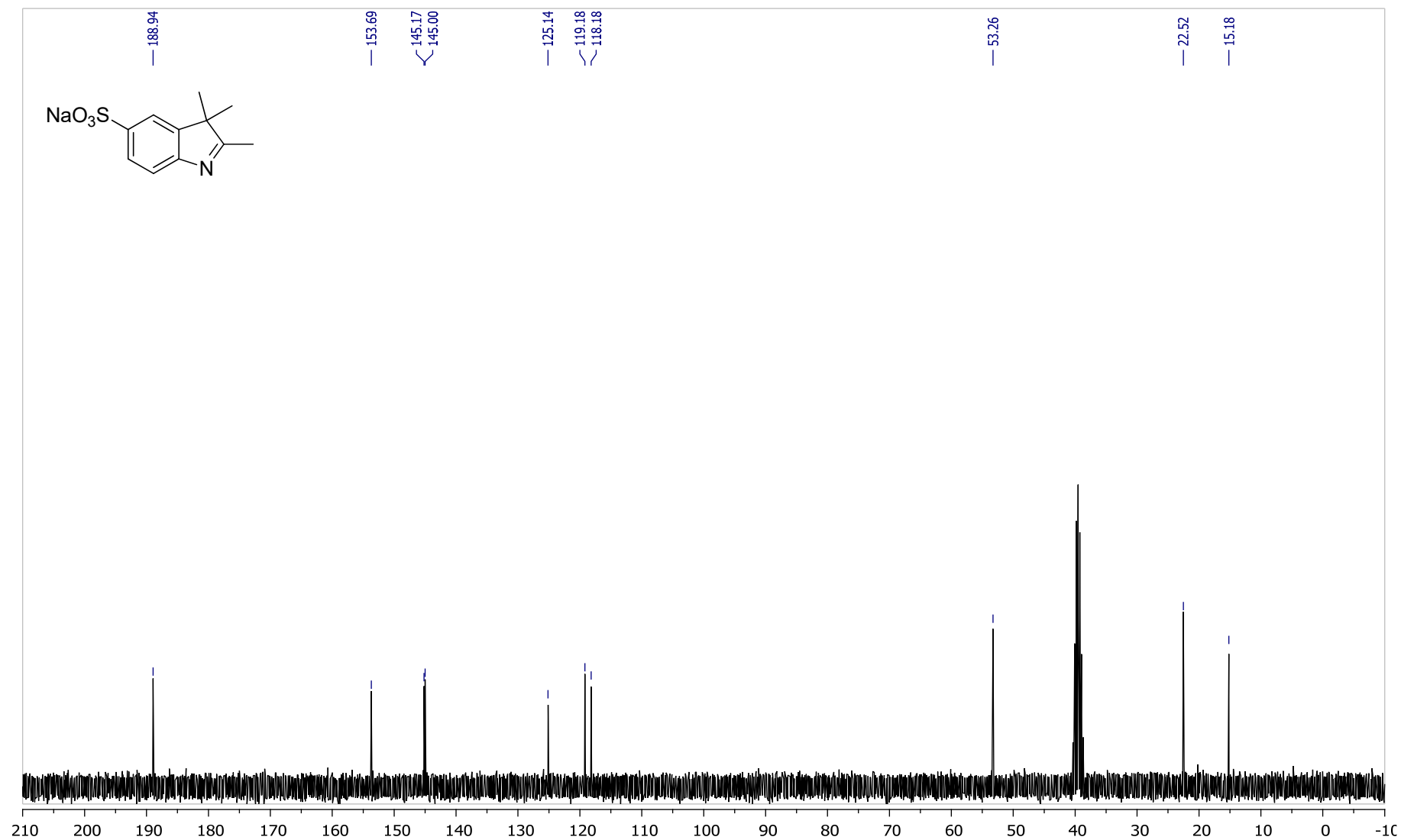
**Figure S10.** <sup>1</sup>H NMR (300 MHz, CCl<sub>3</sub>D): **2b**.



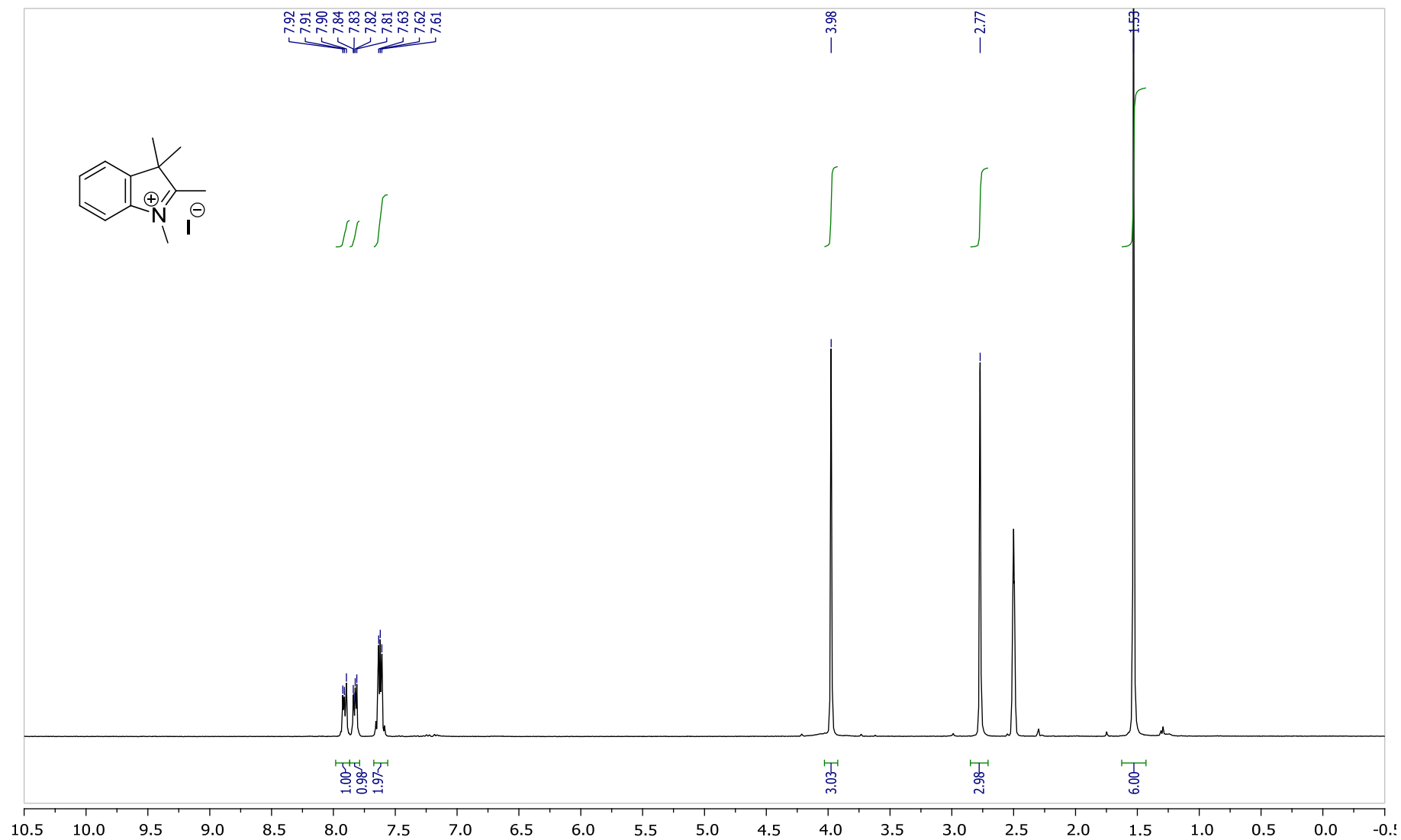
**Figure S11.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CCl}_3\text{D}$ ): **2b**.



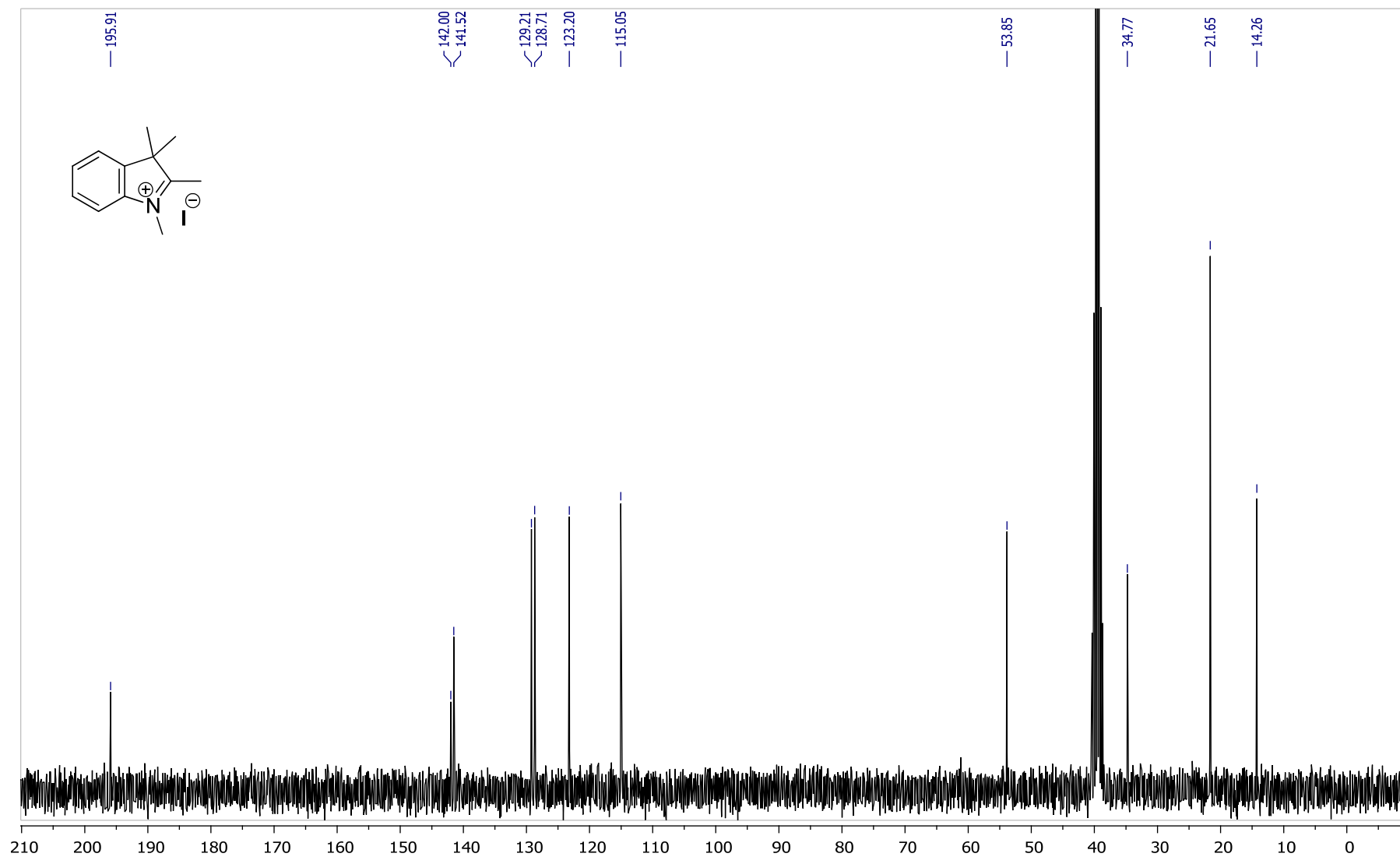
**Figure S12.** <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO): **2c** (black asterisk denotes water).



**Figure S13.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $d_6$ -DMSO): **2c**.

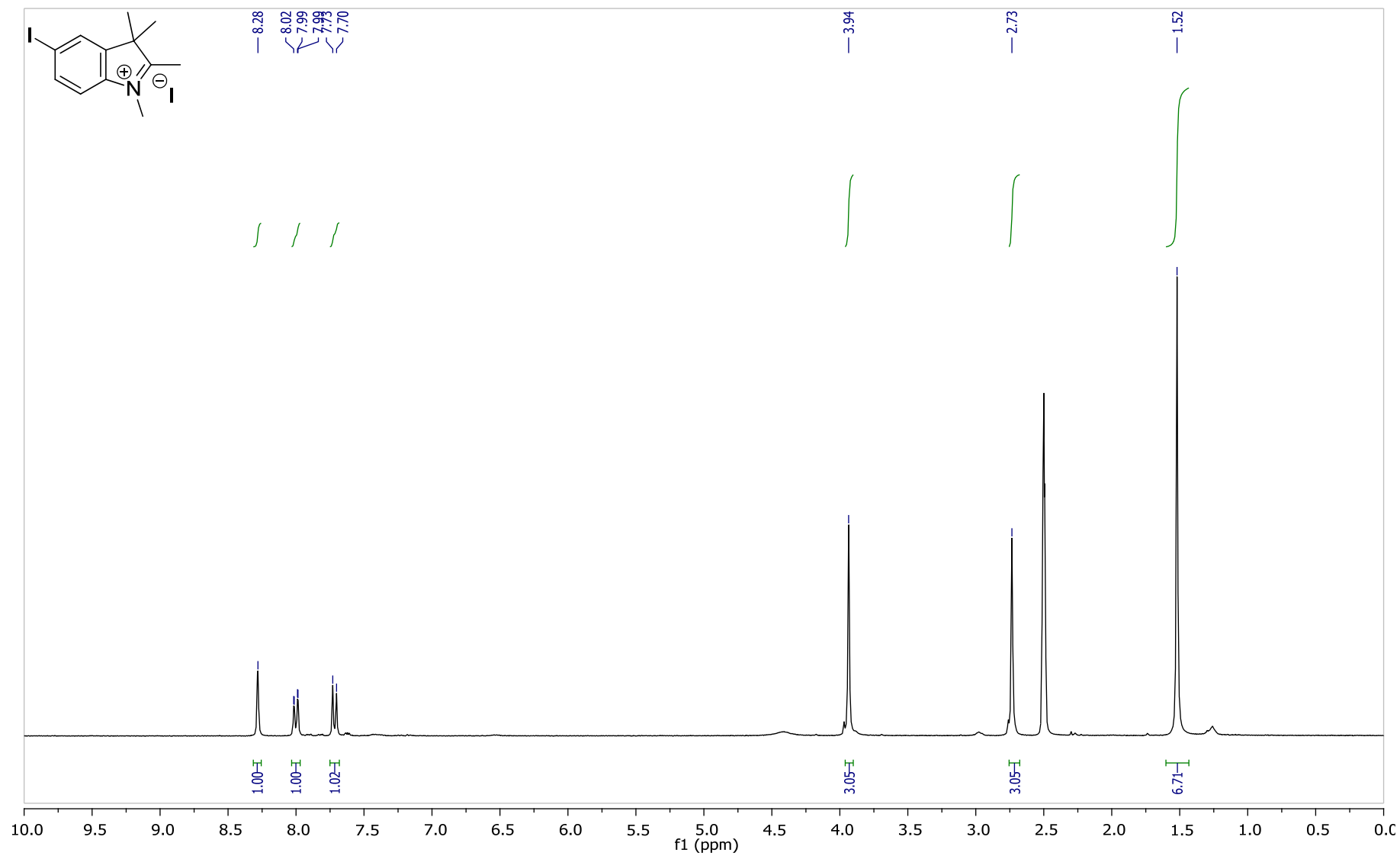


**Figure S14.** <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO): **3a**.

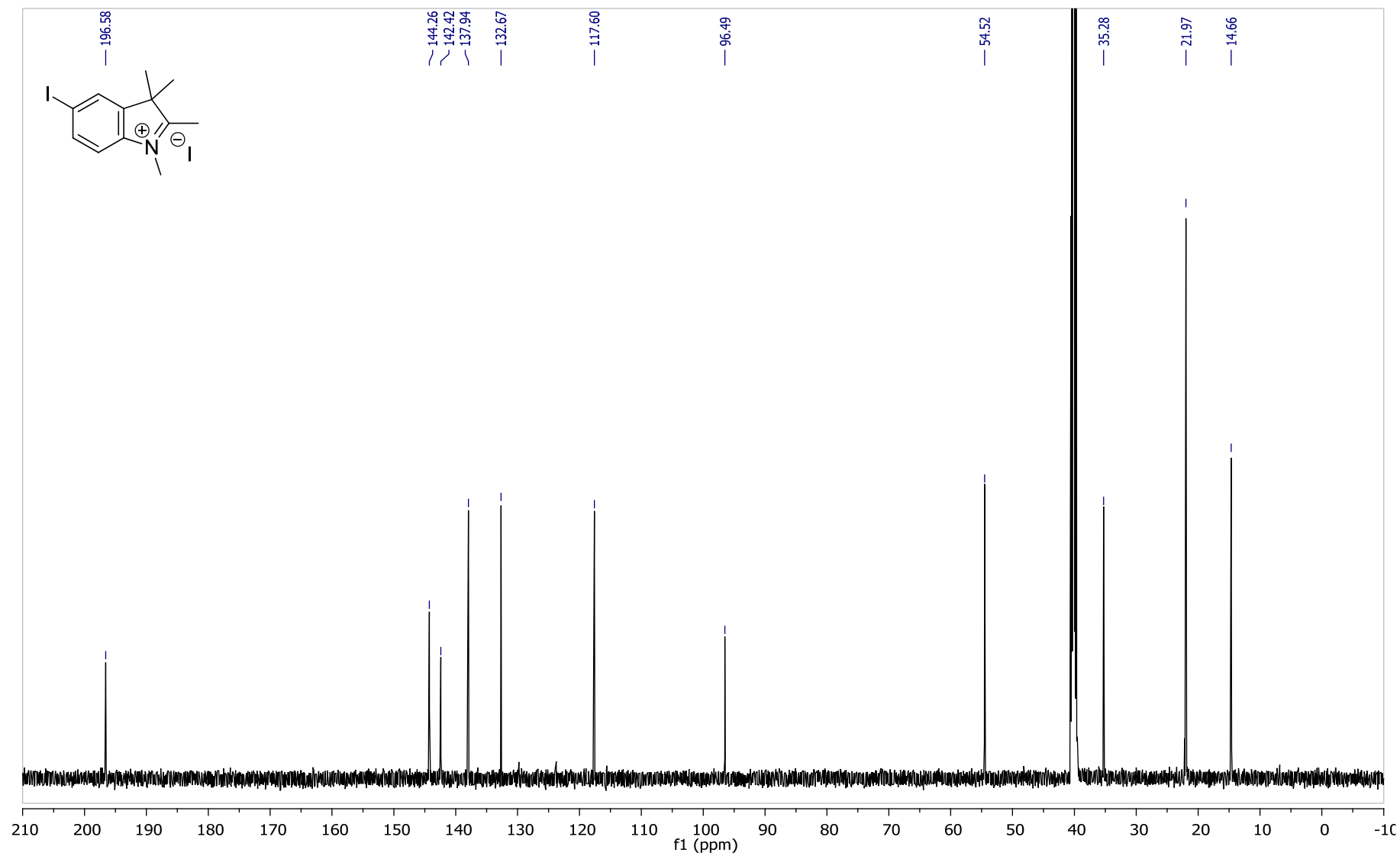


**Figure S15.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $d_6$ -DMSO): **3a**.

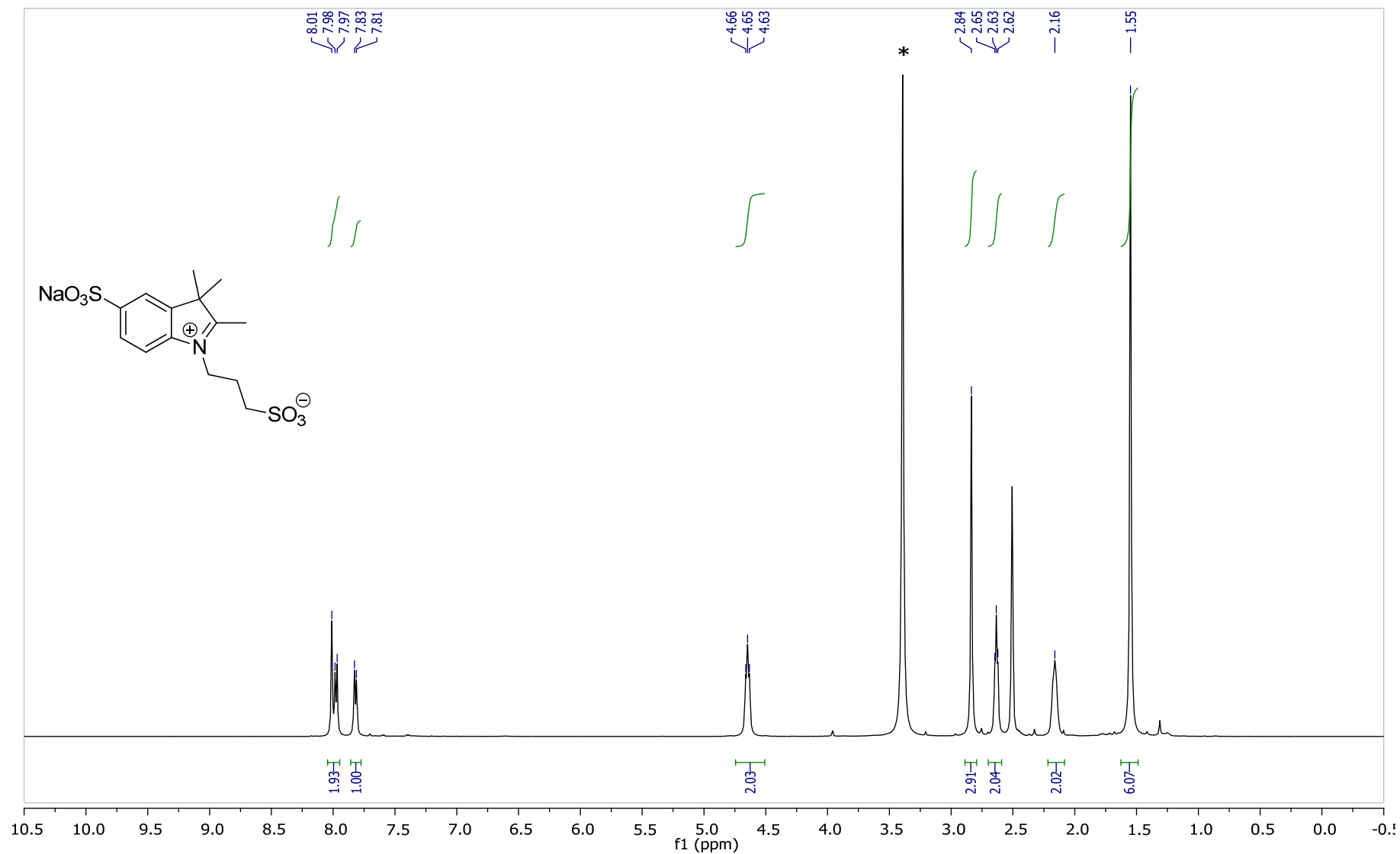




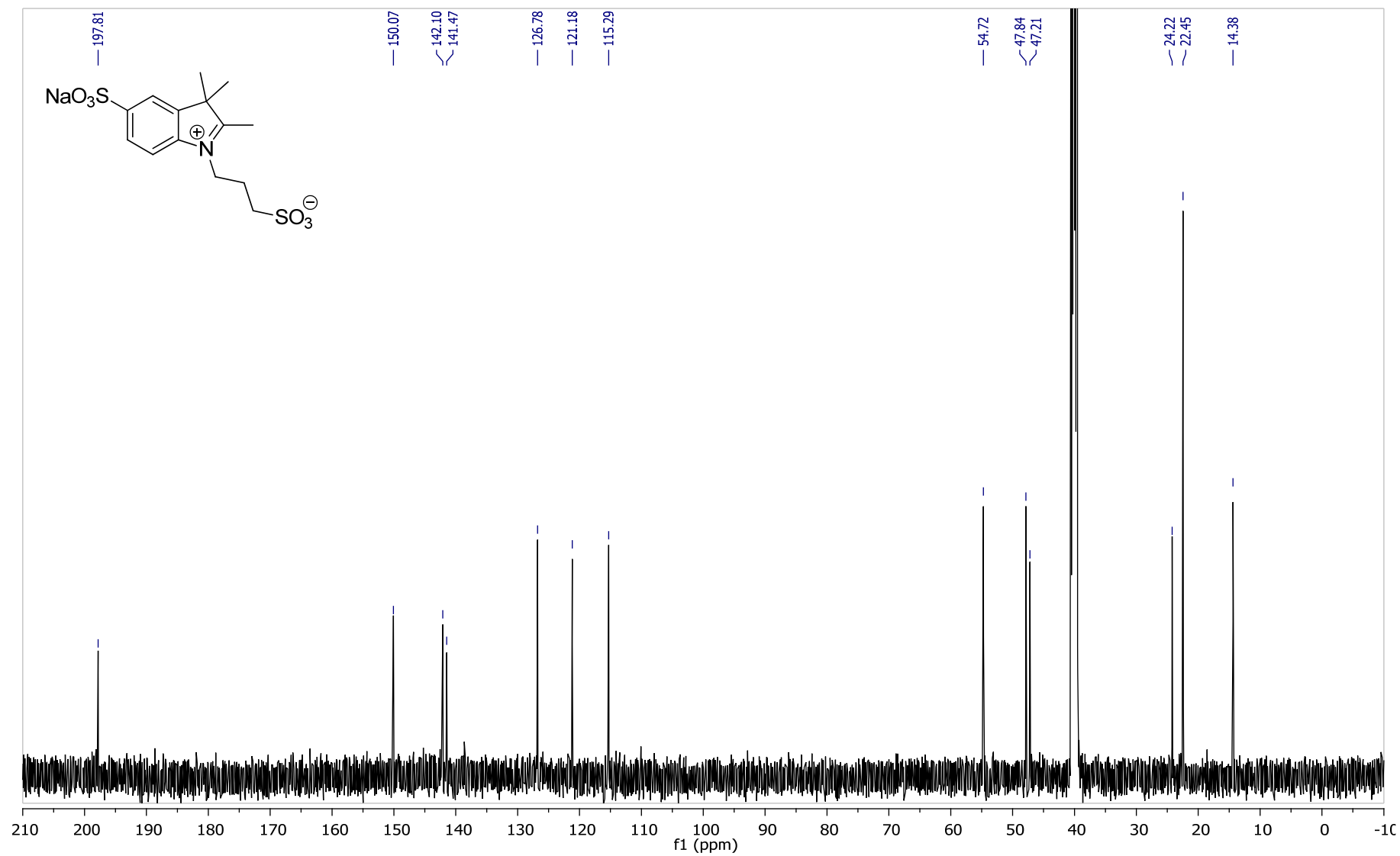
**Figure S16.** <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO): **3b**.



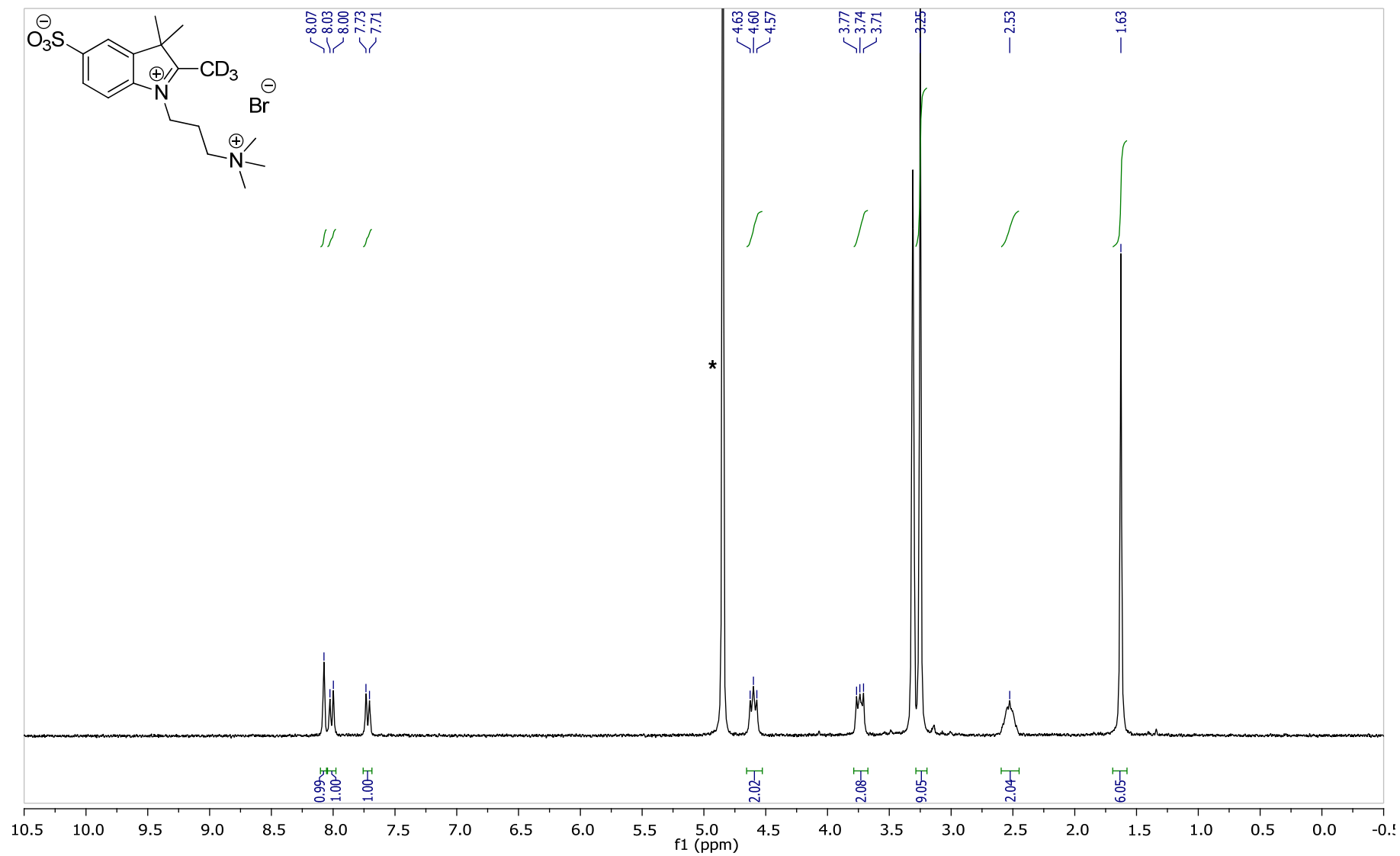
**Figure S17.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $d_6$ -DMSO): **3b**.



**Figure S18.** <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO): **3c** (black asterisk denotes water).



**Figure S19.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $d_6$ -DMSO): **3c**.



**Figure S20.** <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): **3d** (black asterisk denotes water).

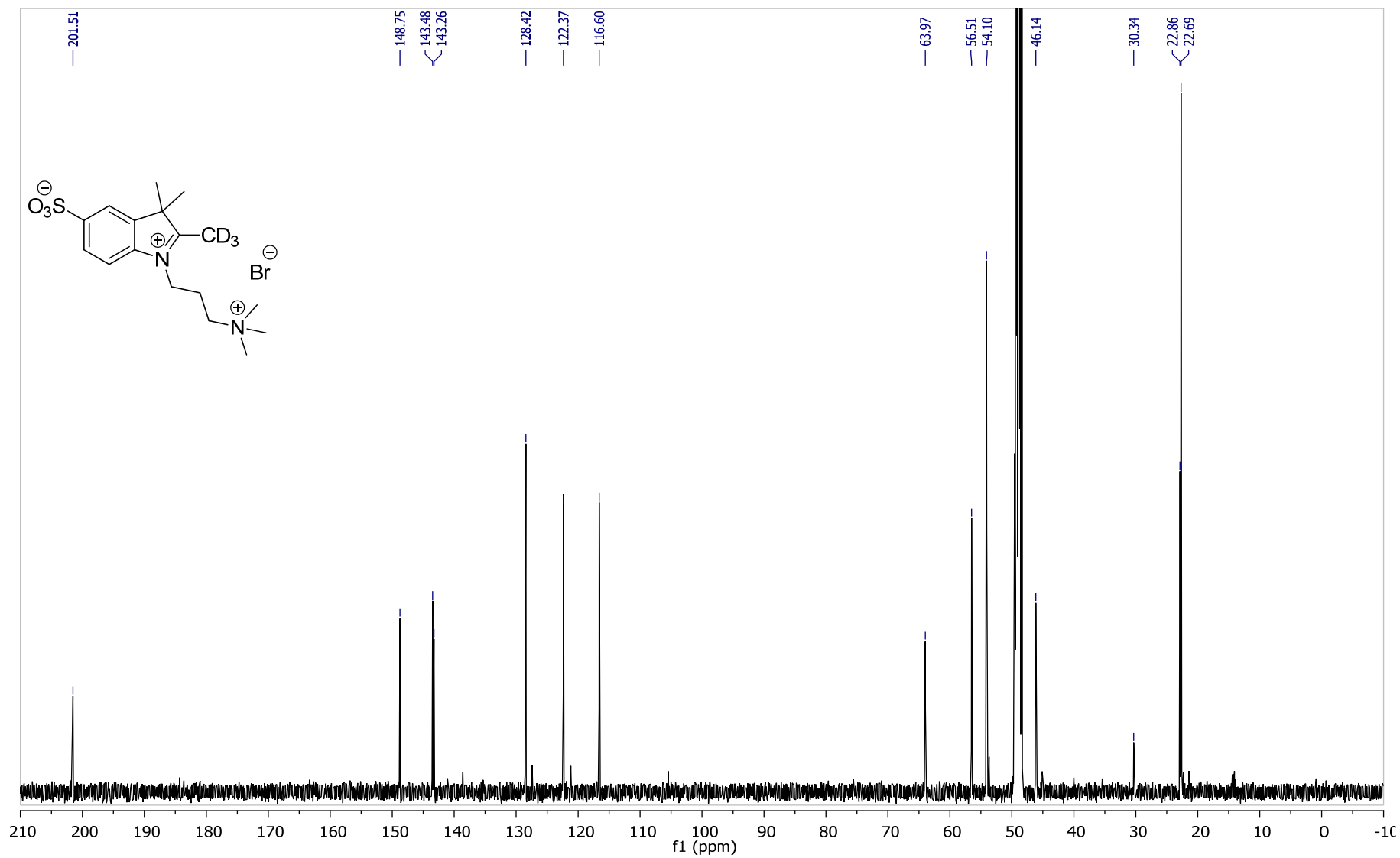
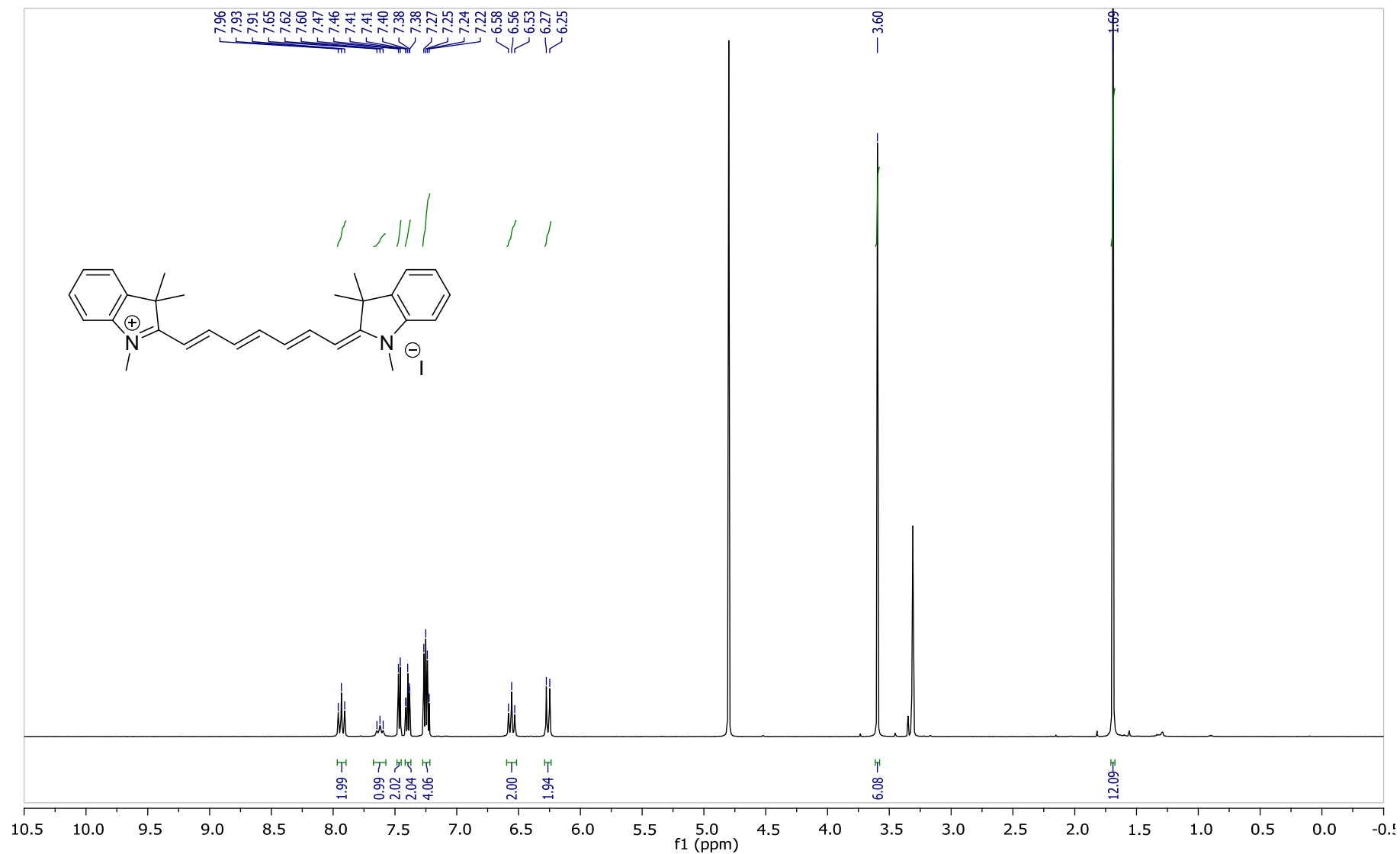


Figure S21.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_3\text{OD}$ ): 3d.



**Figure S22.**  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{OD}$ ): **1a** (black asterisk denotes water).

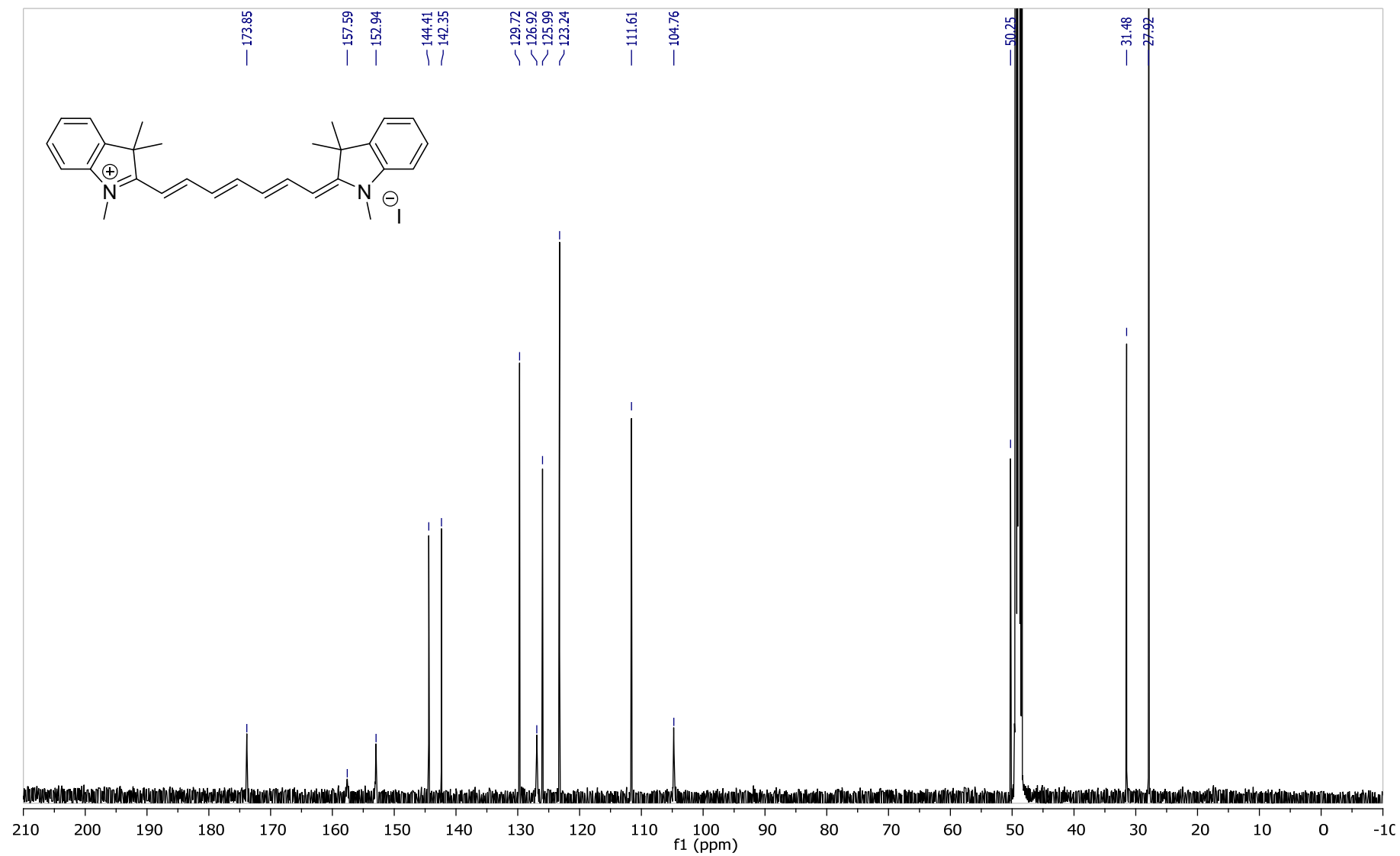
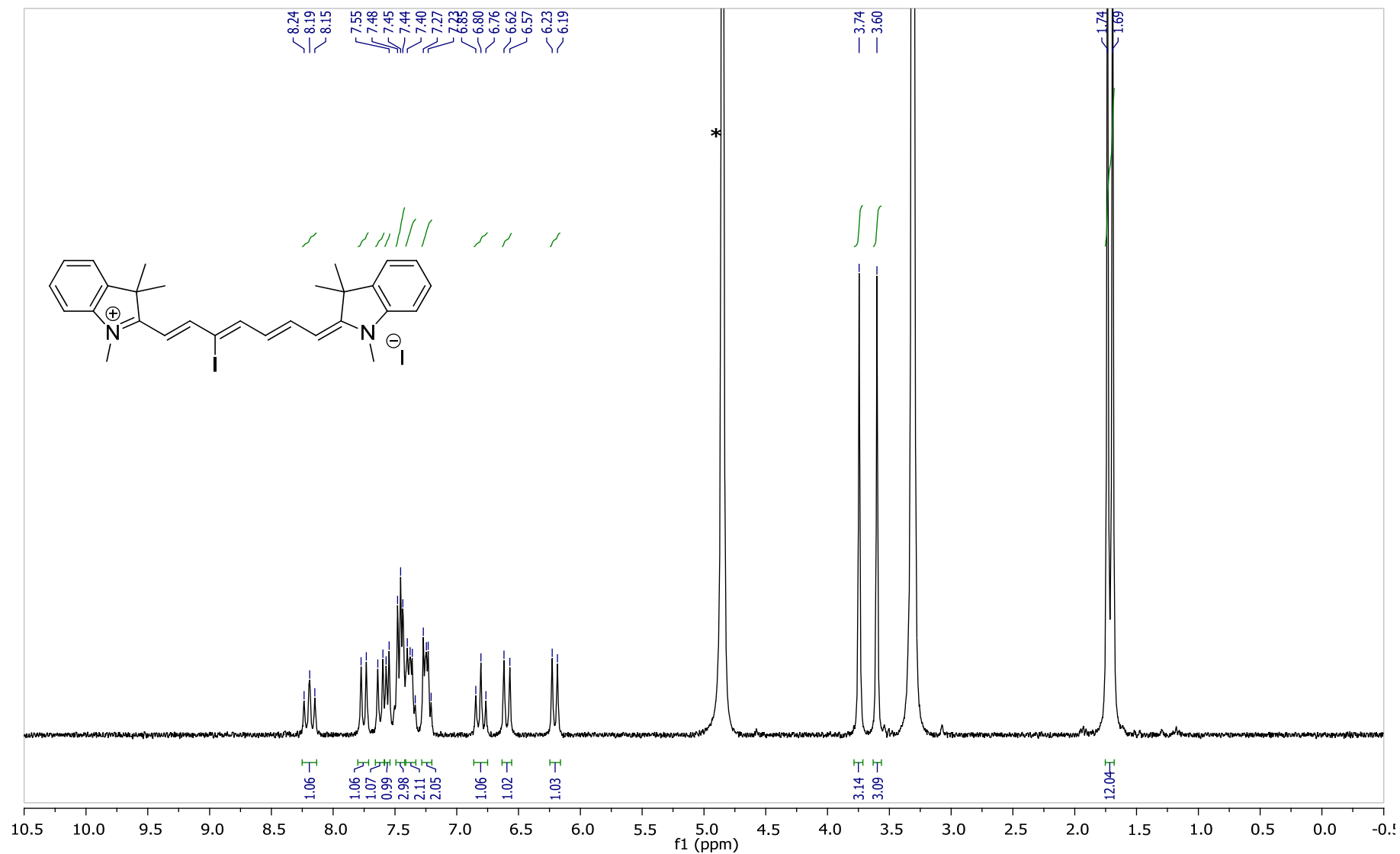


Figure S23.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_3\text{OD}$ ): **1a**.





**Figure S24.** <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): **1b** (black asterisk denotes water).

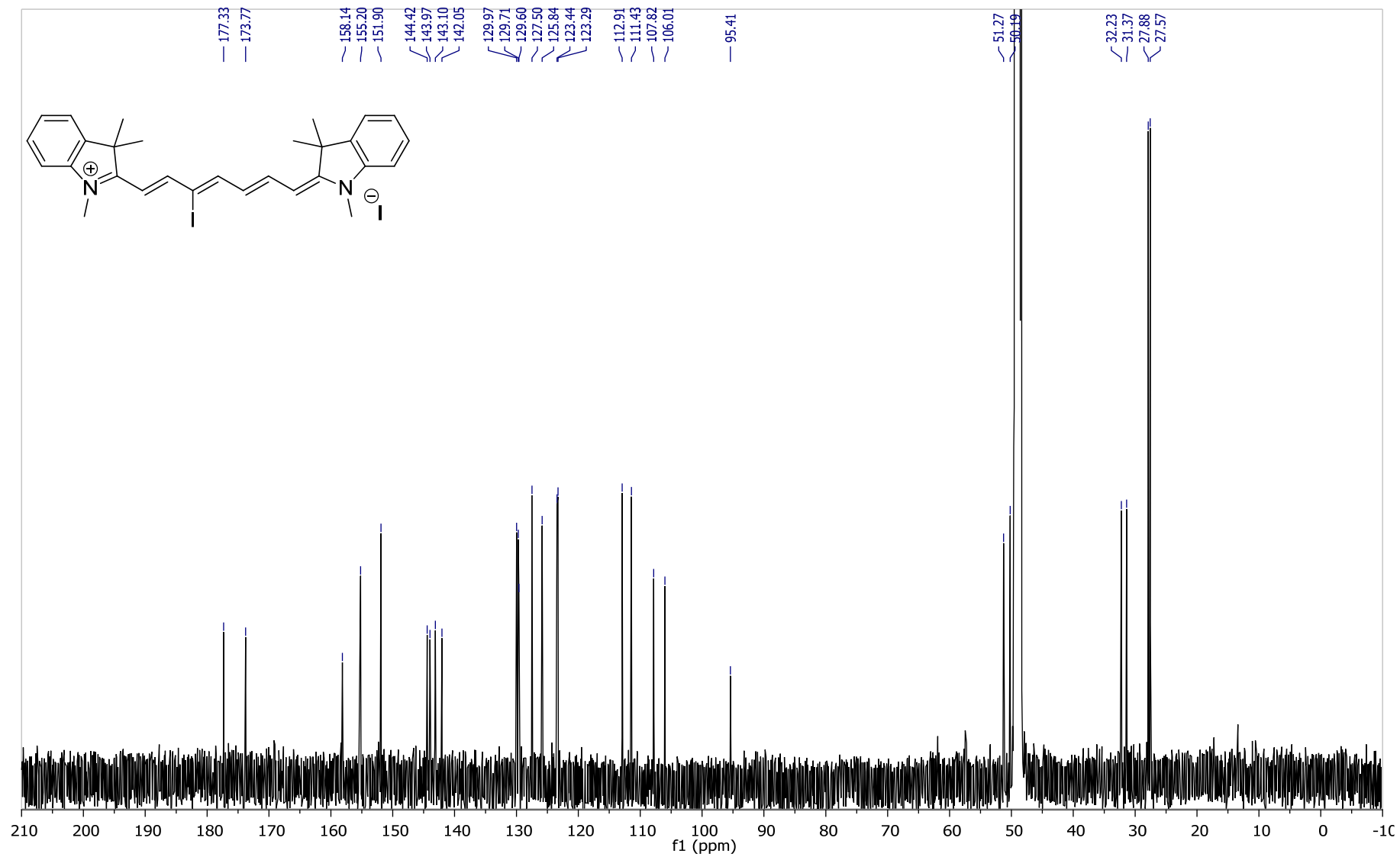
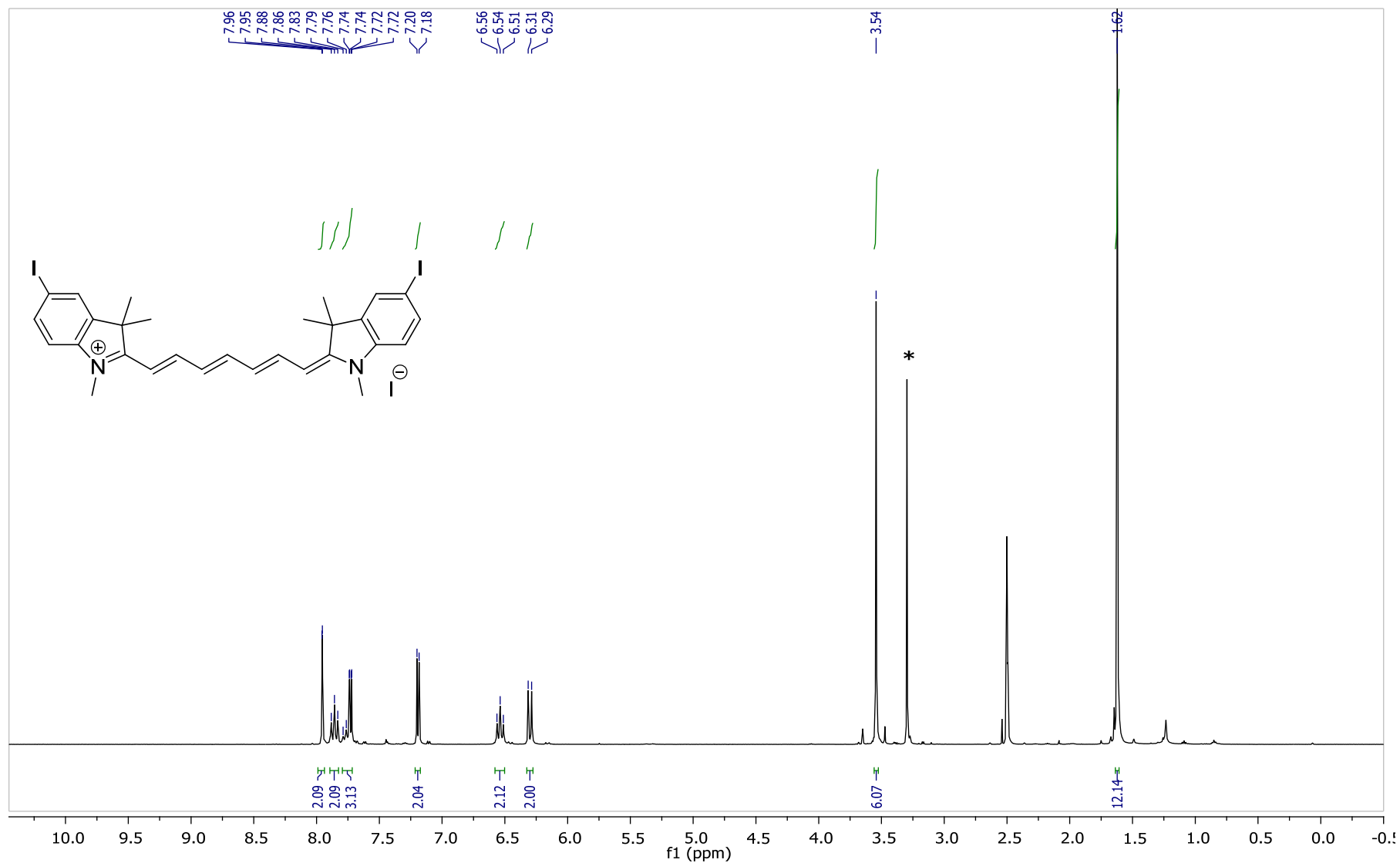
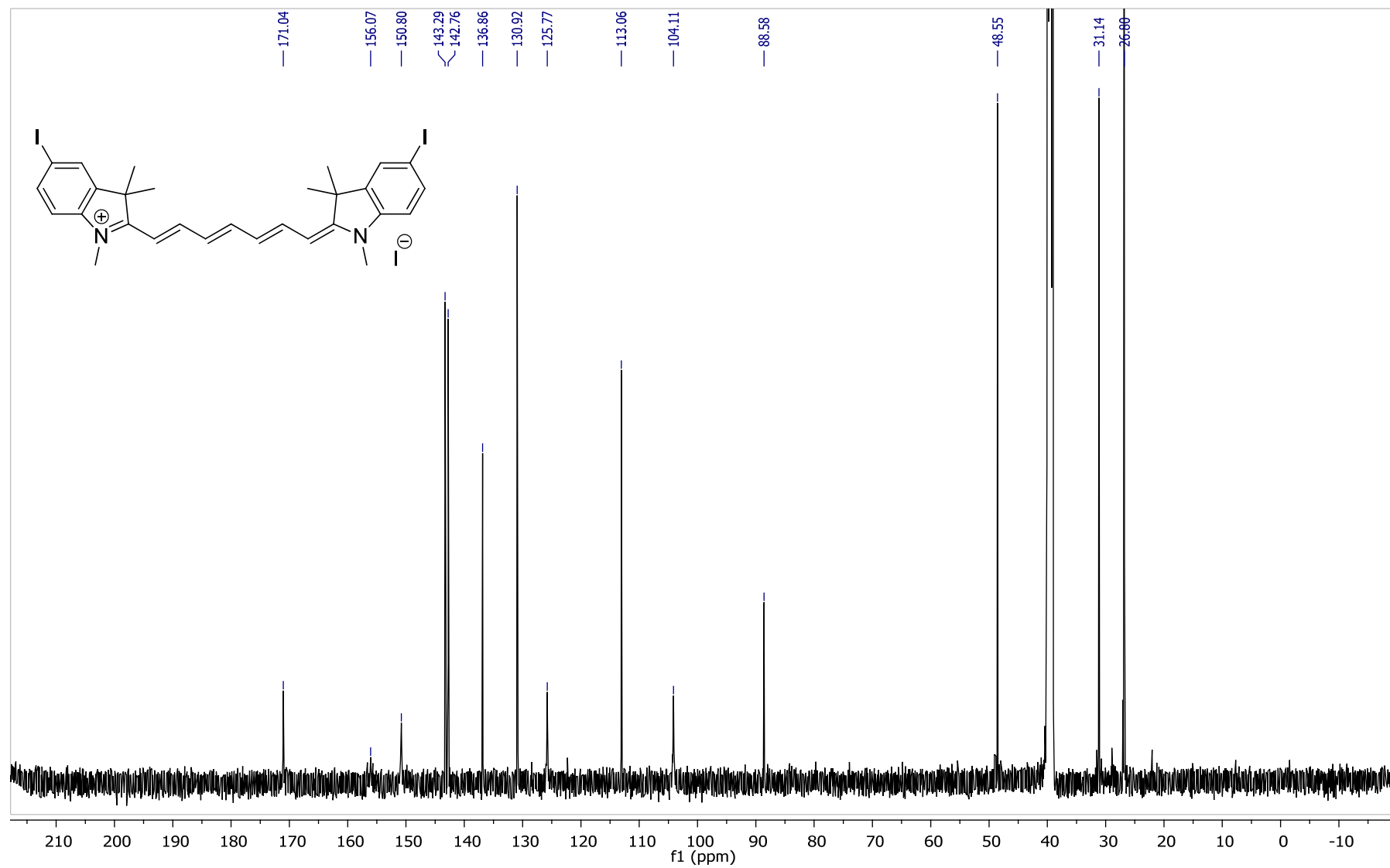


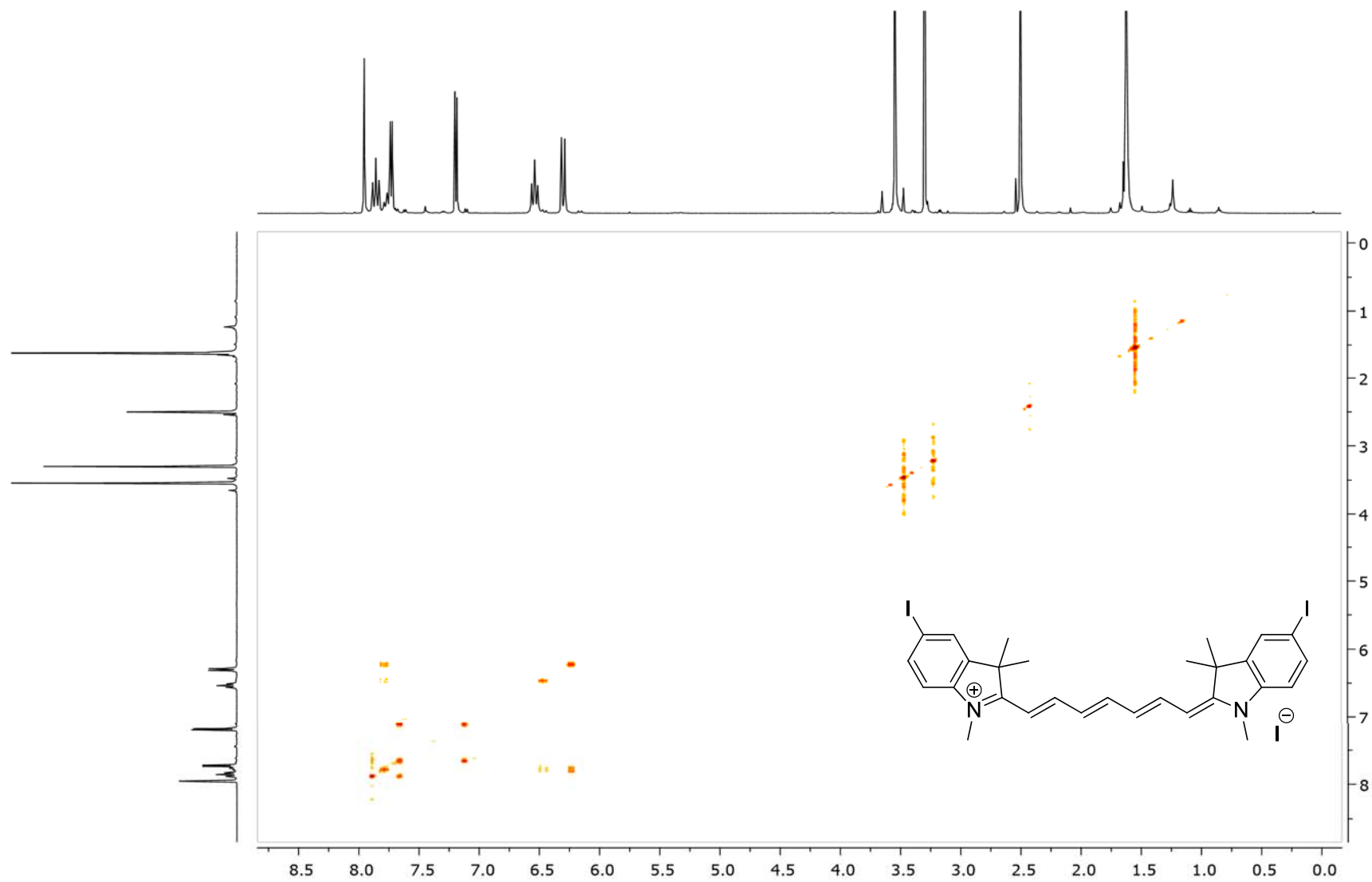
Figure S25.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_3\text{OD}$ ): **1b**.



**Figure S26.**  $^1\text{H NMR}$  (300 MHz,  $d_6$ -DMSO): **1c** (black asterisk denotes water).



**Figure S27.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $d_6$ -DMSO): **1c**.



**Figure S28.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR (500 MHz,  $d_6$ -DMSO): **1c**.

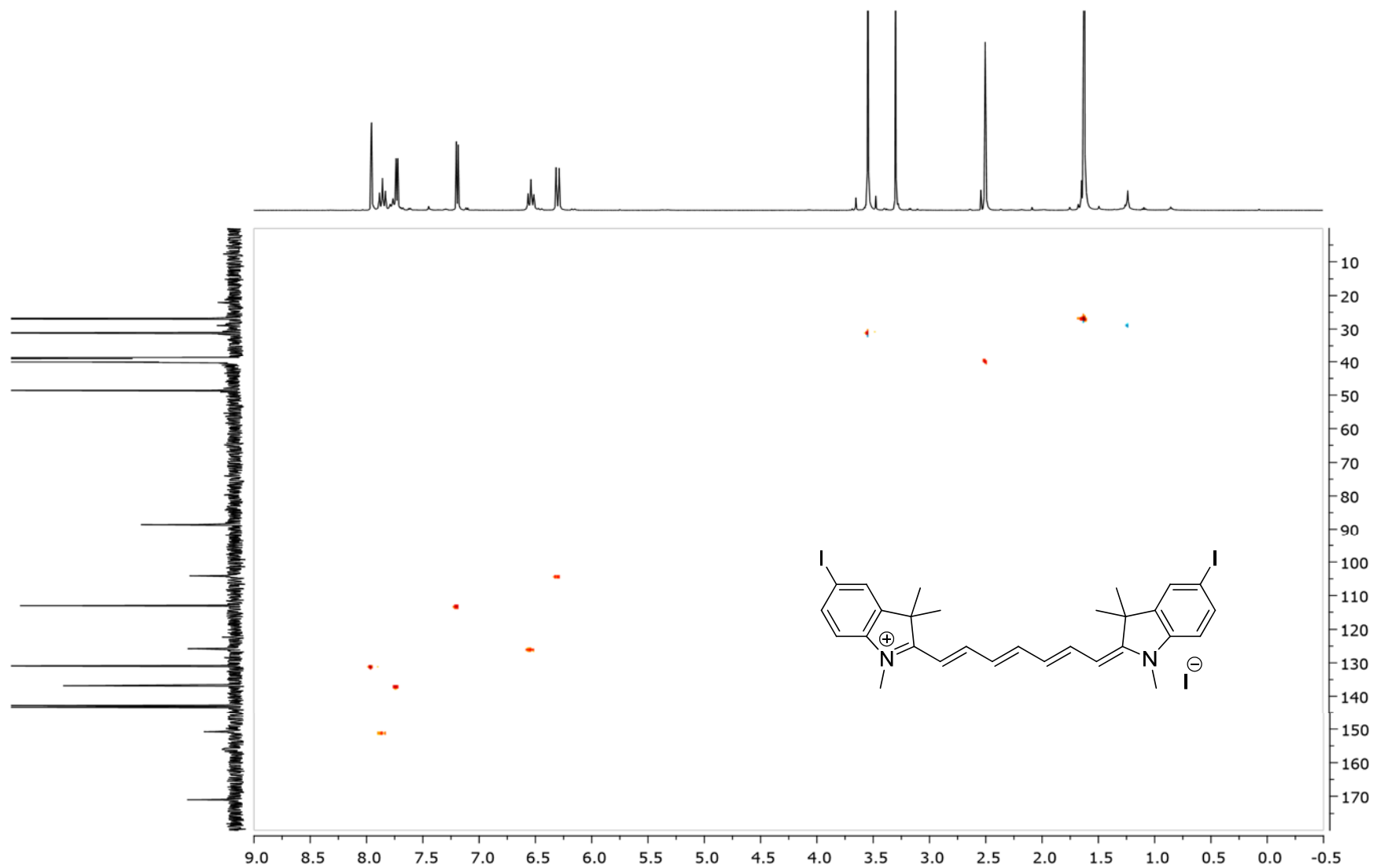


Figure S29.  $^1\text{H}$ - $^{13}\text{C}$  gHSQC (500 MHz,  $d_6$ -DMSO): **1c**.

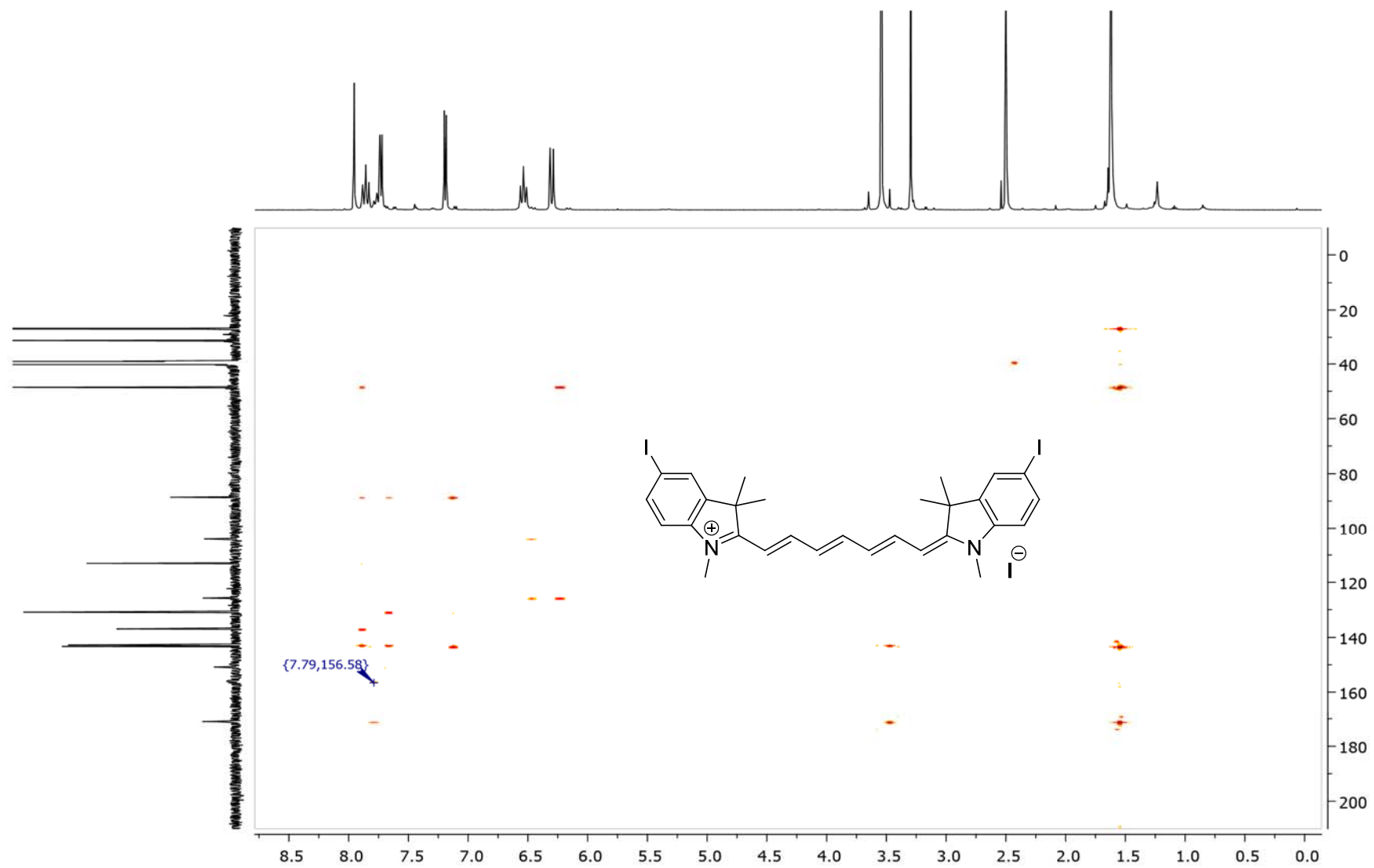
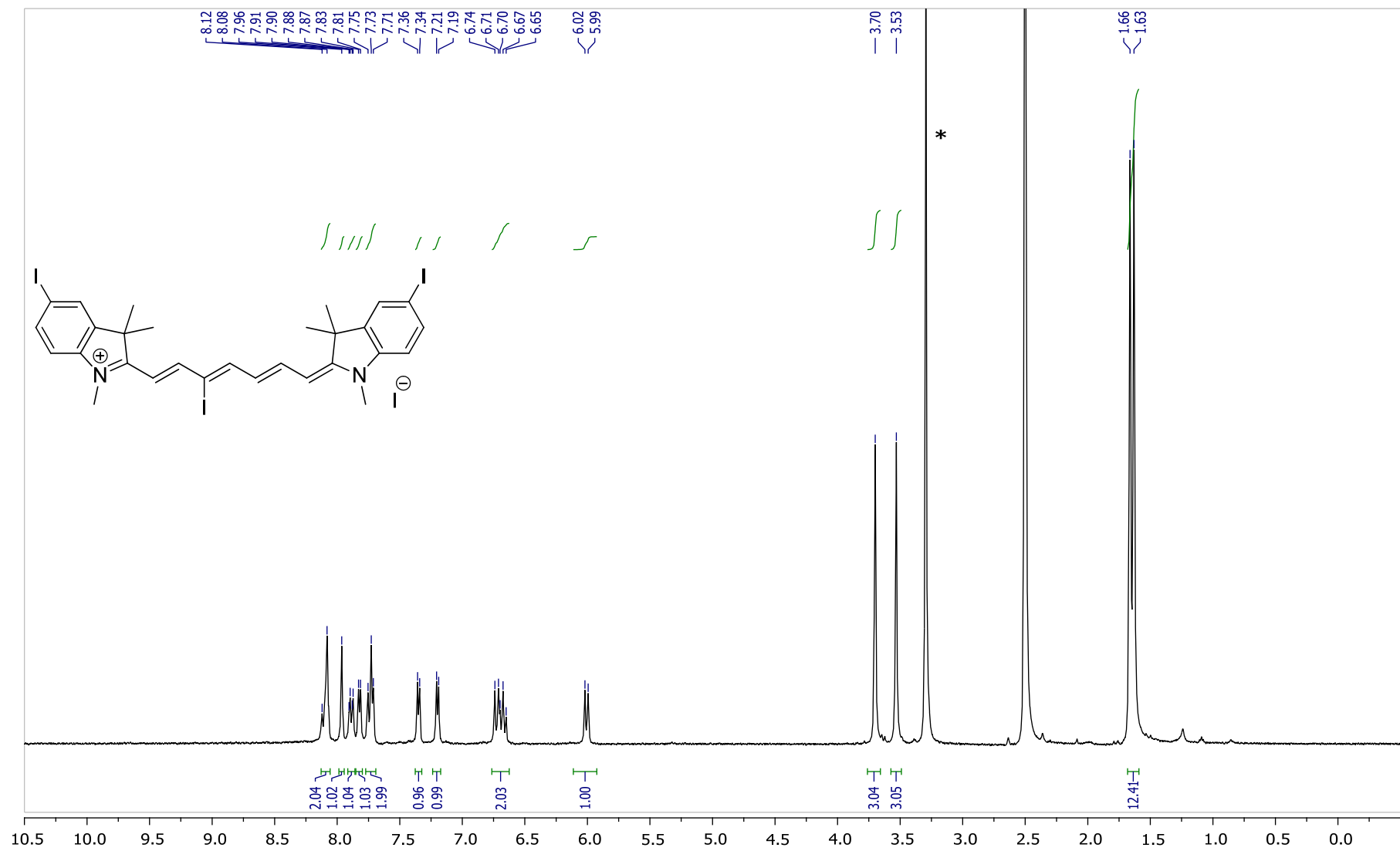
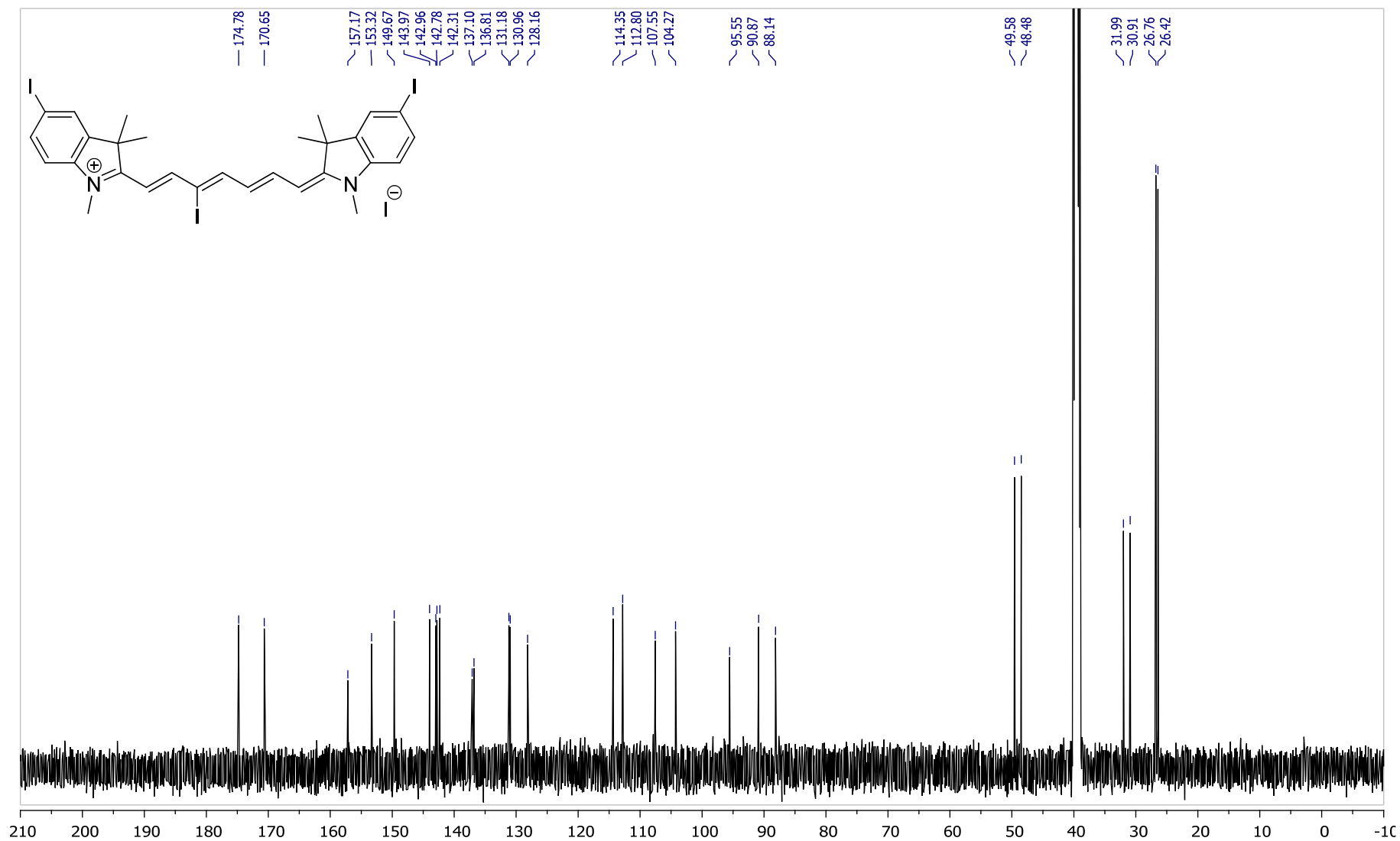


Figure S30.  $^1\text{H}$ - $^{13}\text{C}$  gHMBC (500 MHz,  $d_6$ -DMSO): **1c**.

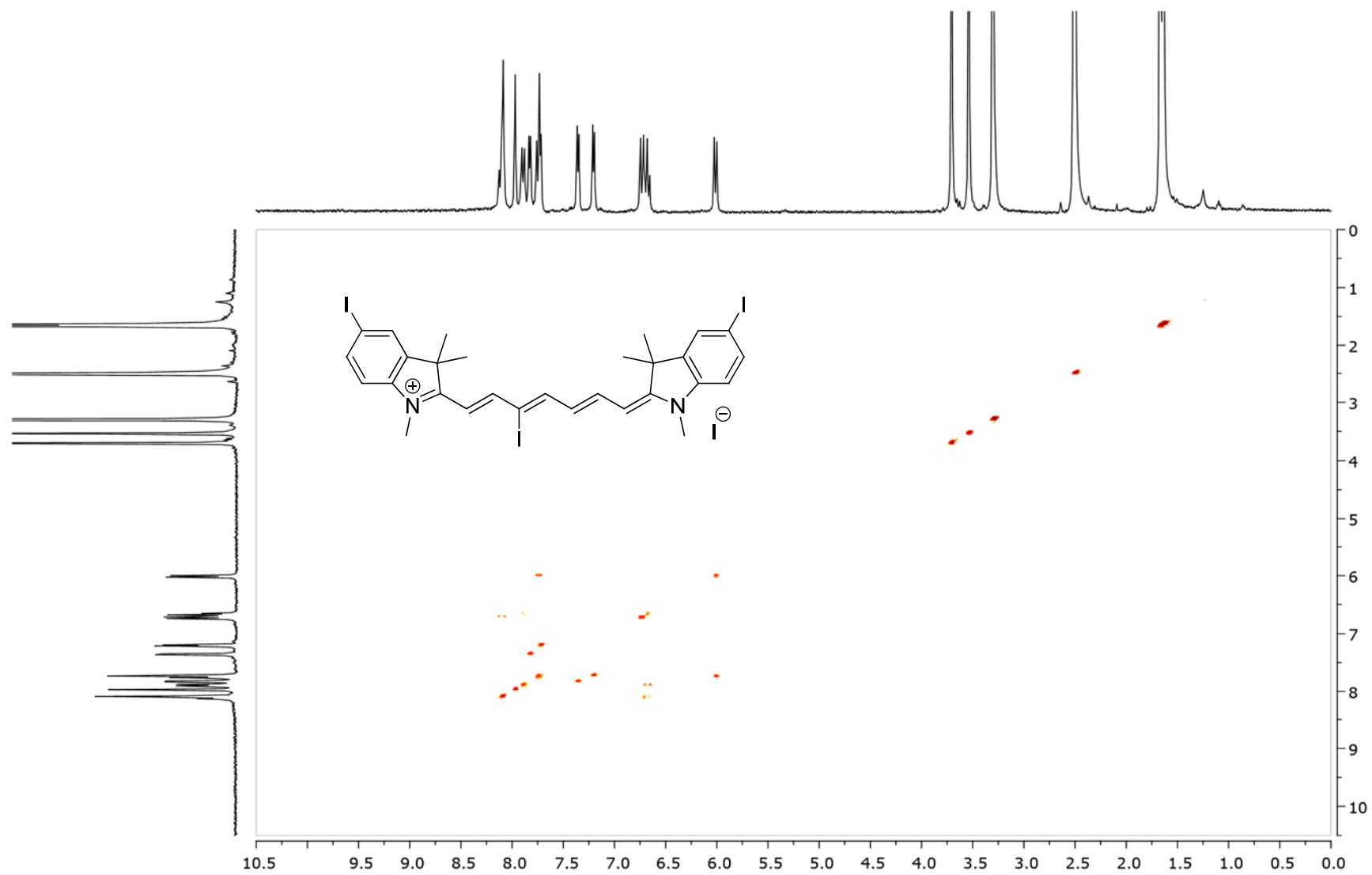


**Figure S31.**  $^1\text{H NMR}$  (300 MHz,  $d_6$ -DMSO): **1d** (black asterisk denotes water).





**Figure S32.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $d_6$ -DMSO): **1d**.



**Figure S33.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR (500 MHz,  $d_6$ -DMSO): **1d**.

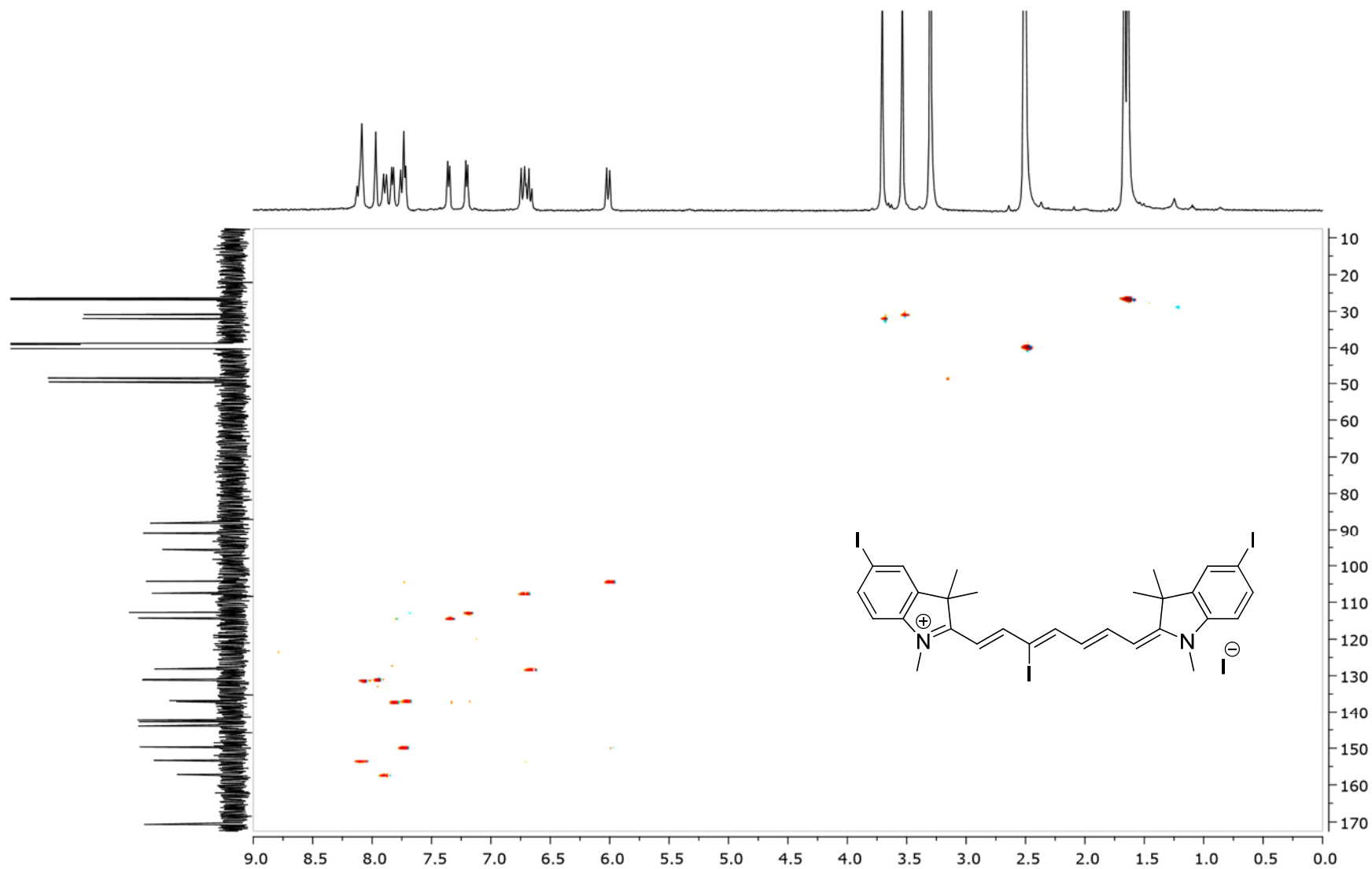


Figure S34.  $^1\text{H}$ - $^{13}\text{C}$  gHSQC (500 MHz,  $d_6$ -DMSO): **1d**.

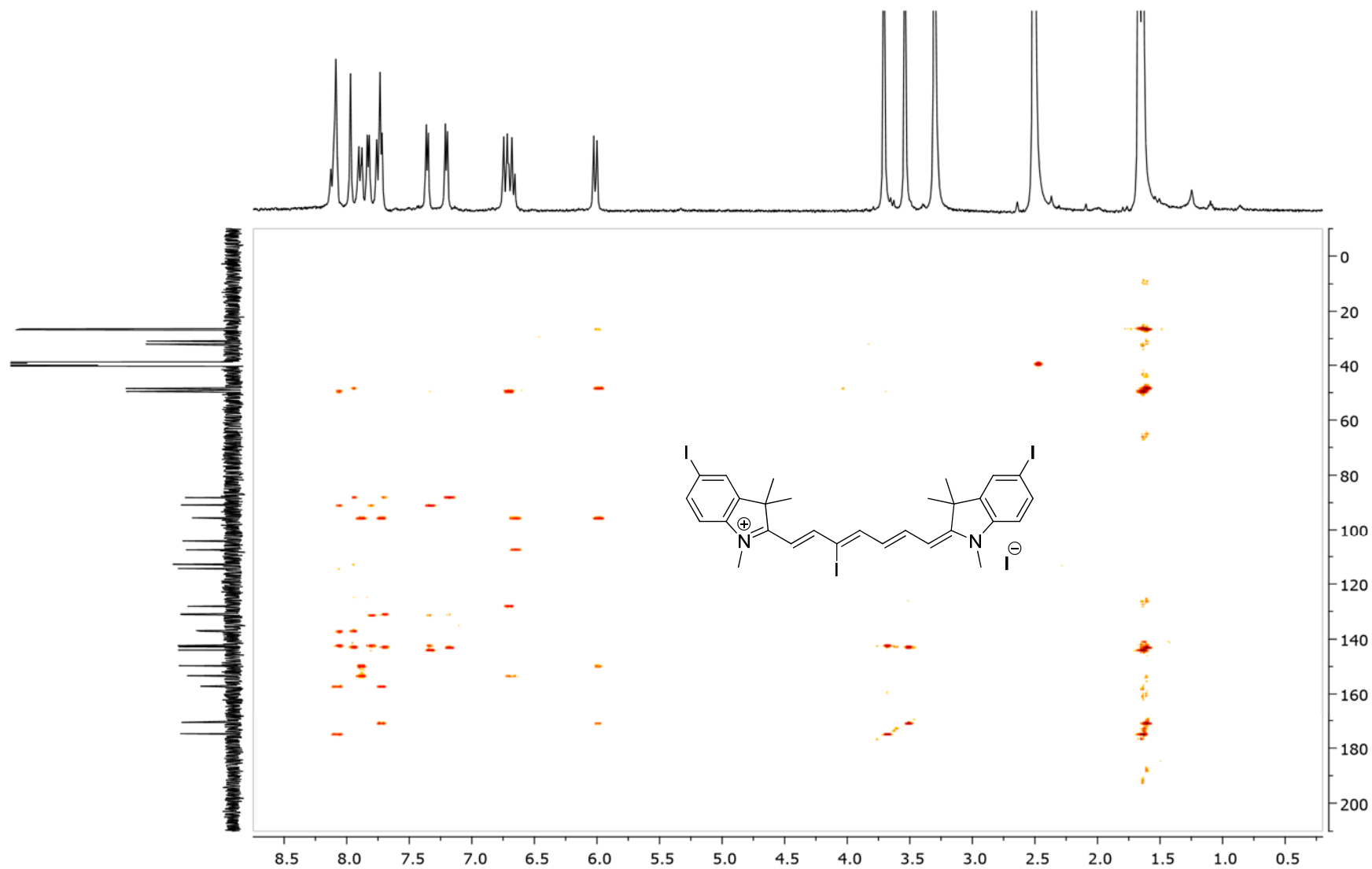


Figure S35.  $^1\text{H}$ - $^{13}\text{C}$  gHMBC (500 MHz,  $d_6$ -DMSO): **1d**.

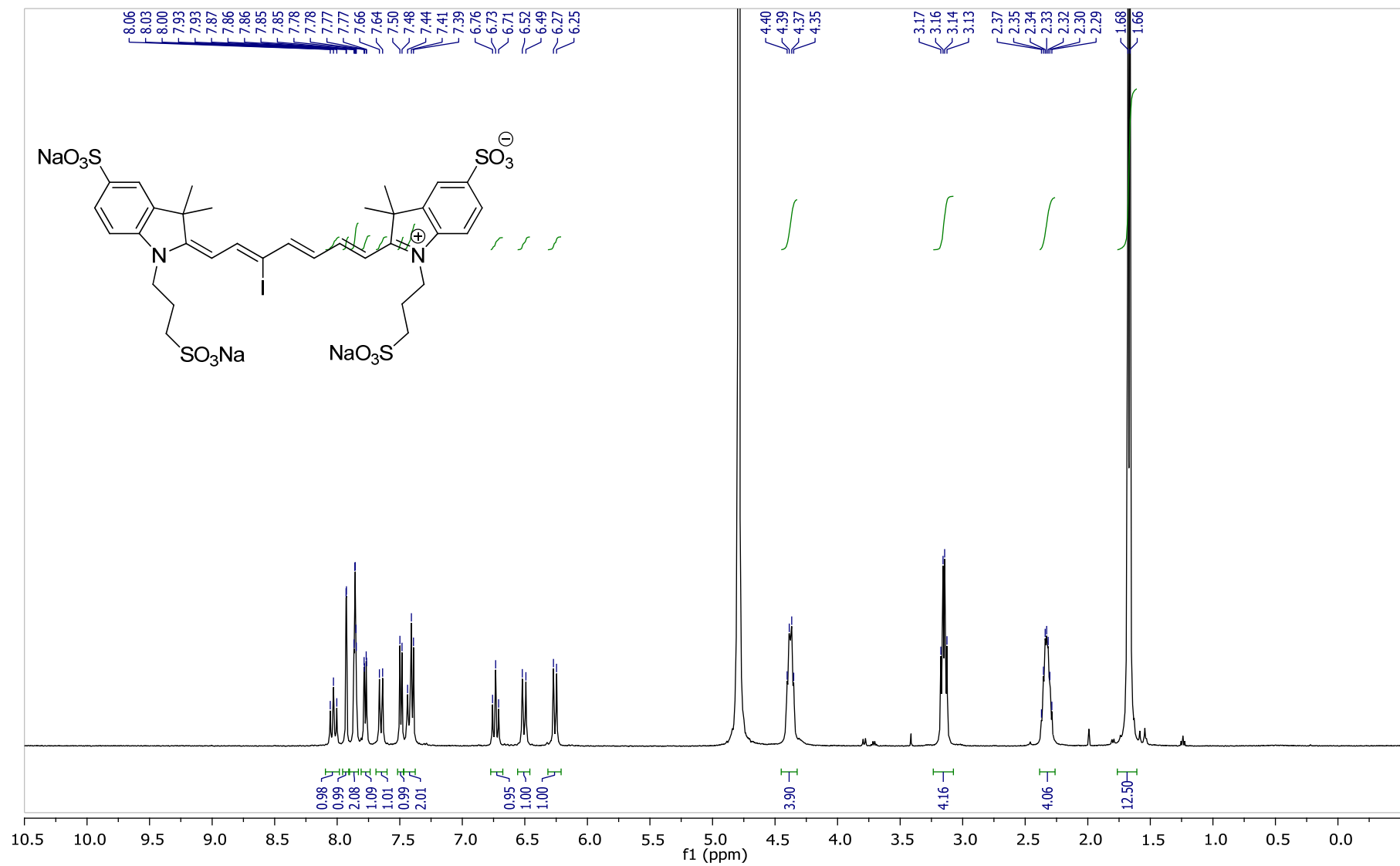


Figure S36.  $^1\text{H}$  NMR (500 MHz,  $\text{D}_2\text{O}$ ): **1e**.

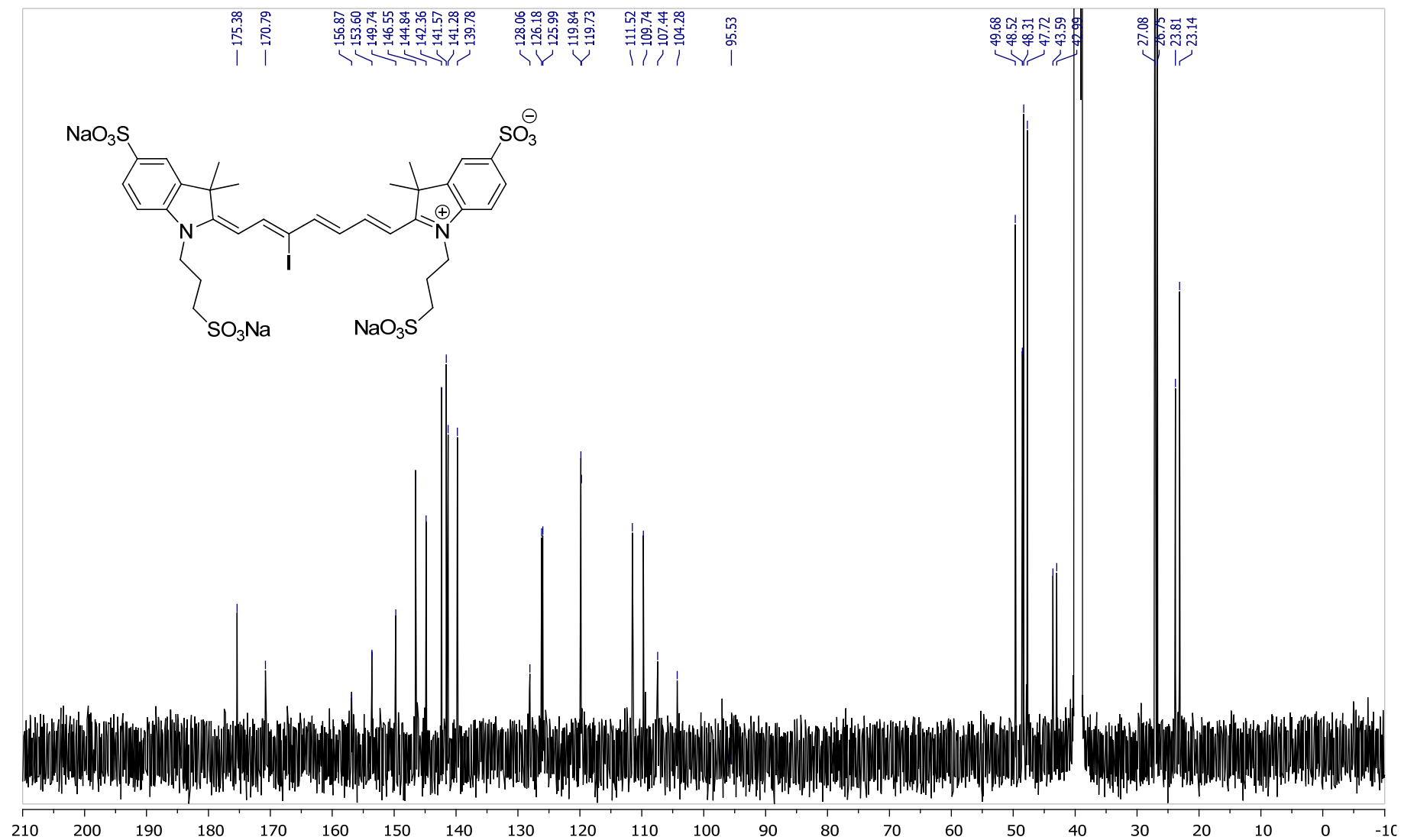


Figure S37. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, *d*<sub>6</sub>-DMSO): **1e**.

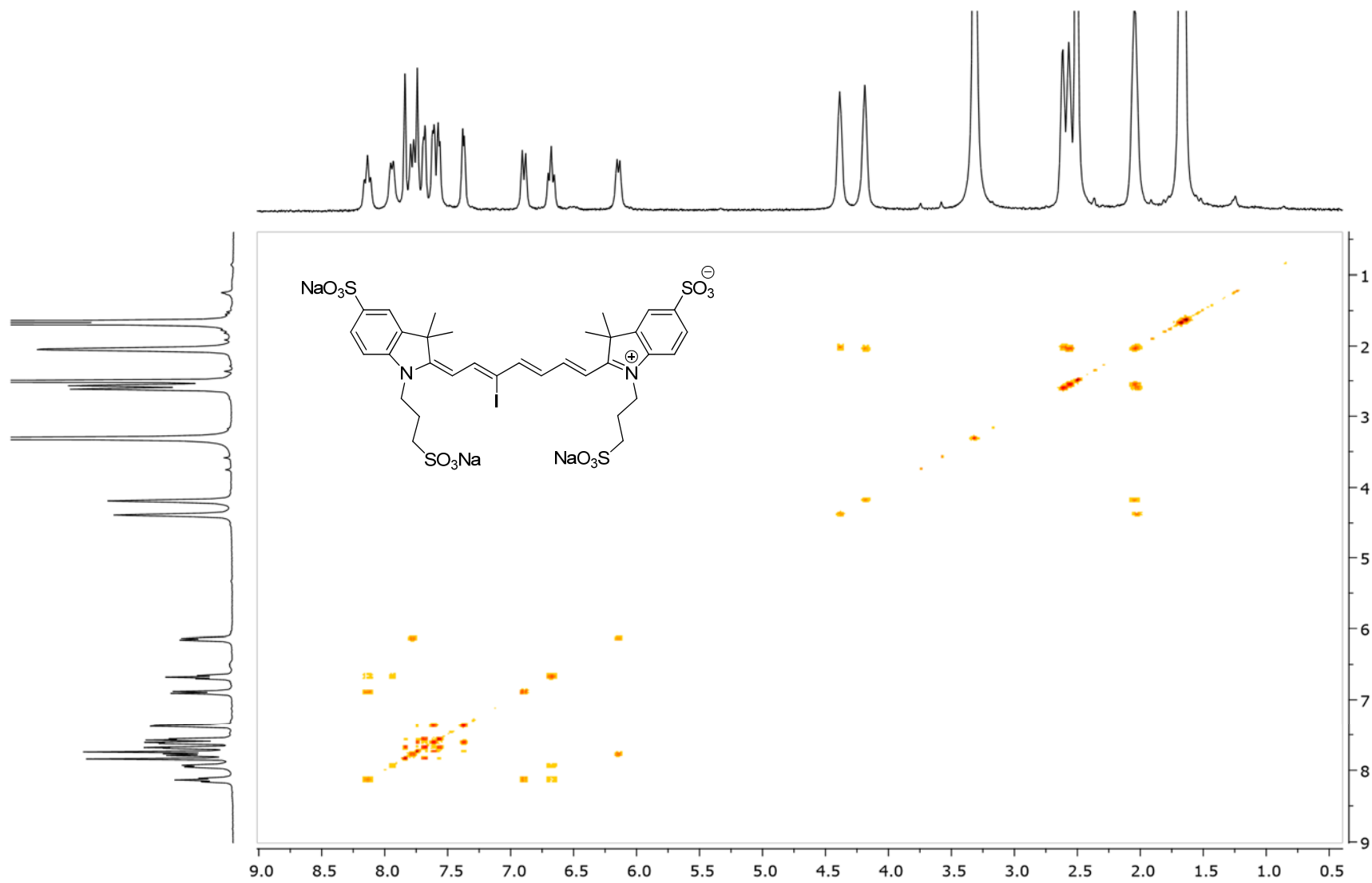


Figure S38.  $^1\text{H}$ - $^1\text{H}$  COSY NMR (500 MHz,  $d_6$ -DMSO): **1e**.

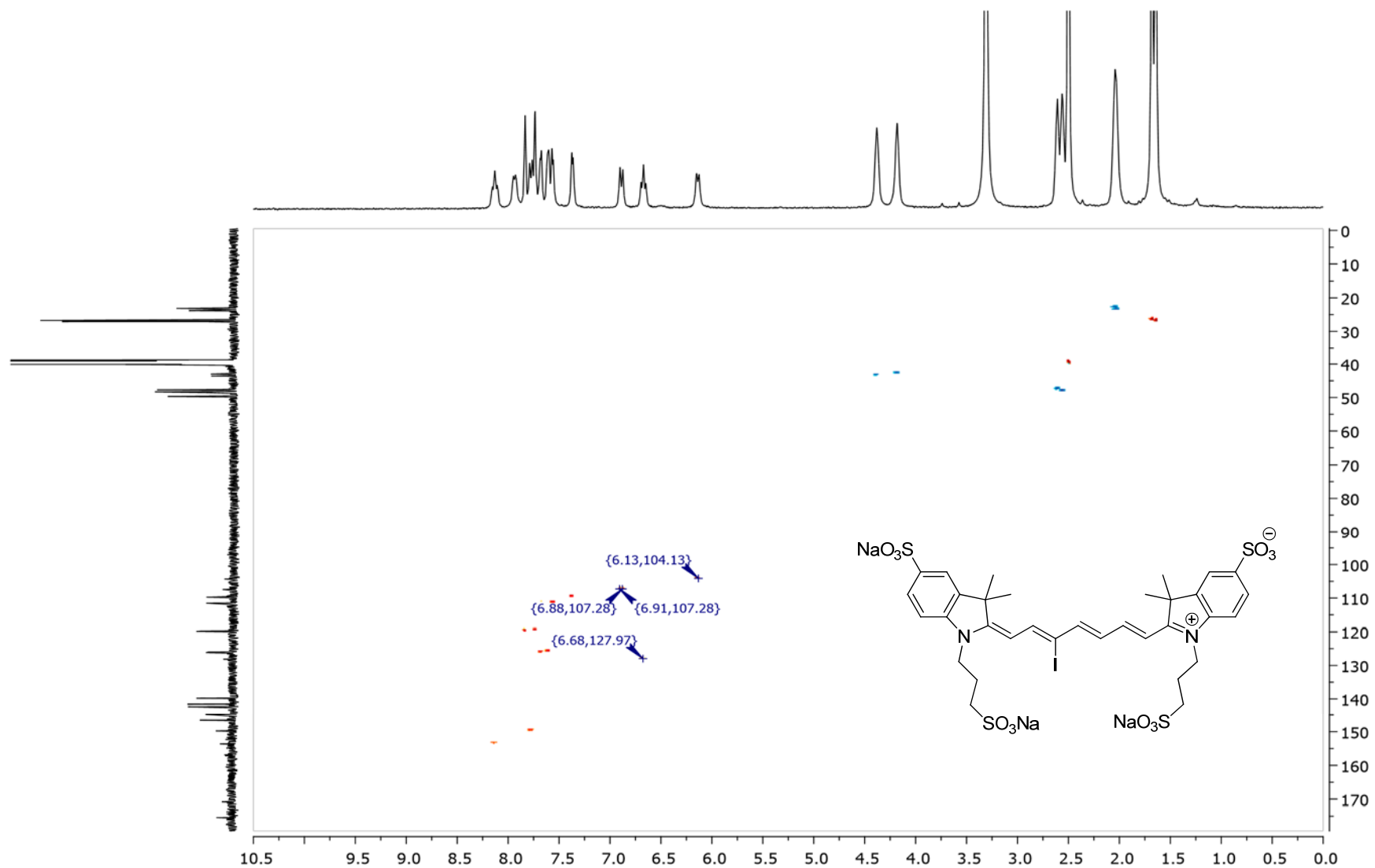


Figure S39.  $^1\text{H}$ - $^{13}\text{C}$  gHSQC (500 MHz,  $d_6$ -DMSO): **1e**.



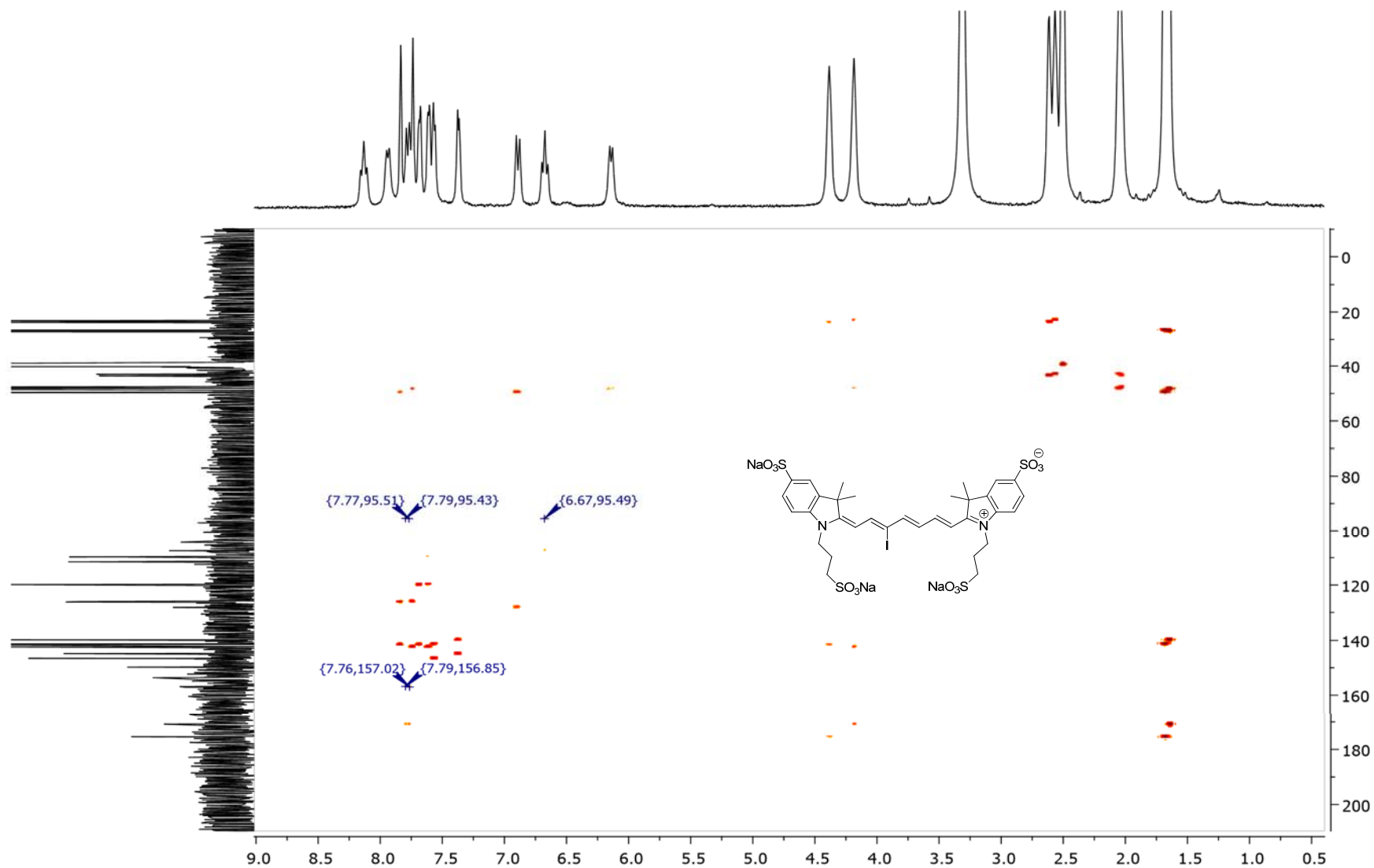
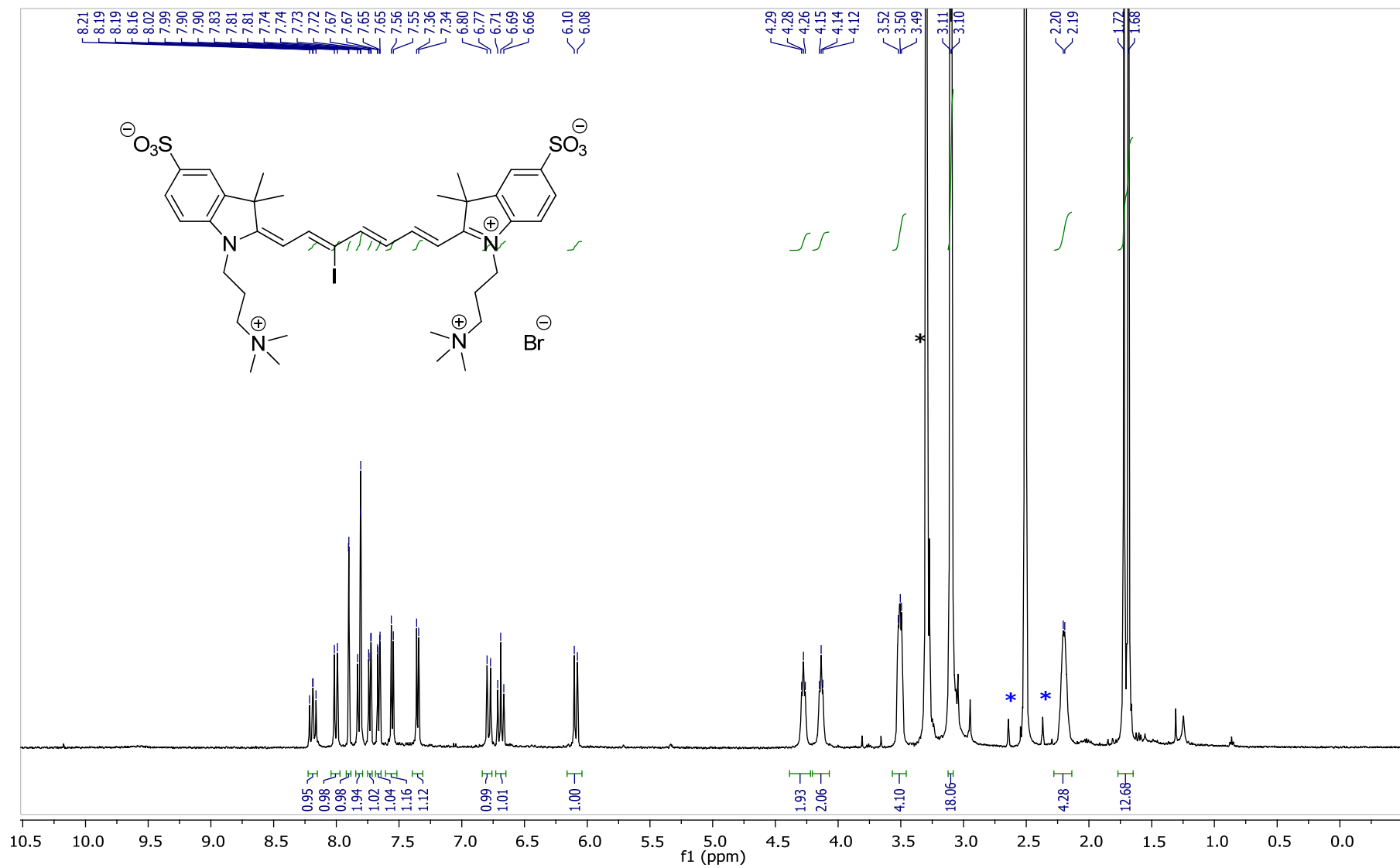


Figure S40.  $^1\text{H}$ - $^{13}\text{C}$  gHMBC (500 MHz,  $d_6$ -DMSO):**1e**.



**Figure S41.** <sup>1</sup>H NMR (500 MHz, *d*<sub>6</sub>-DMSO): **1f** (black and blue asterisks denote water and *d*<sub>6</sub>-DMSO satellites, respectively).

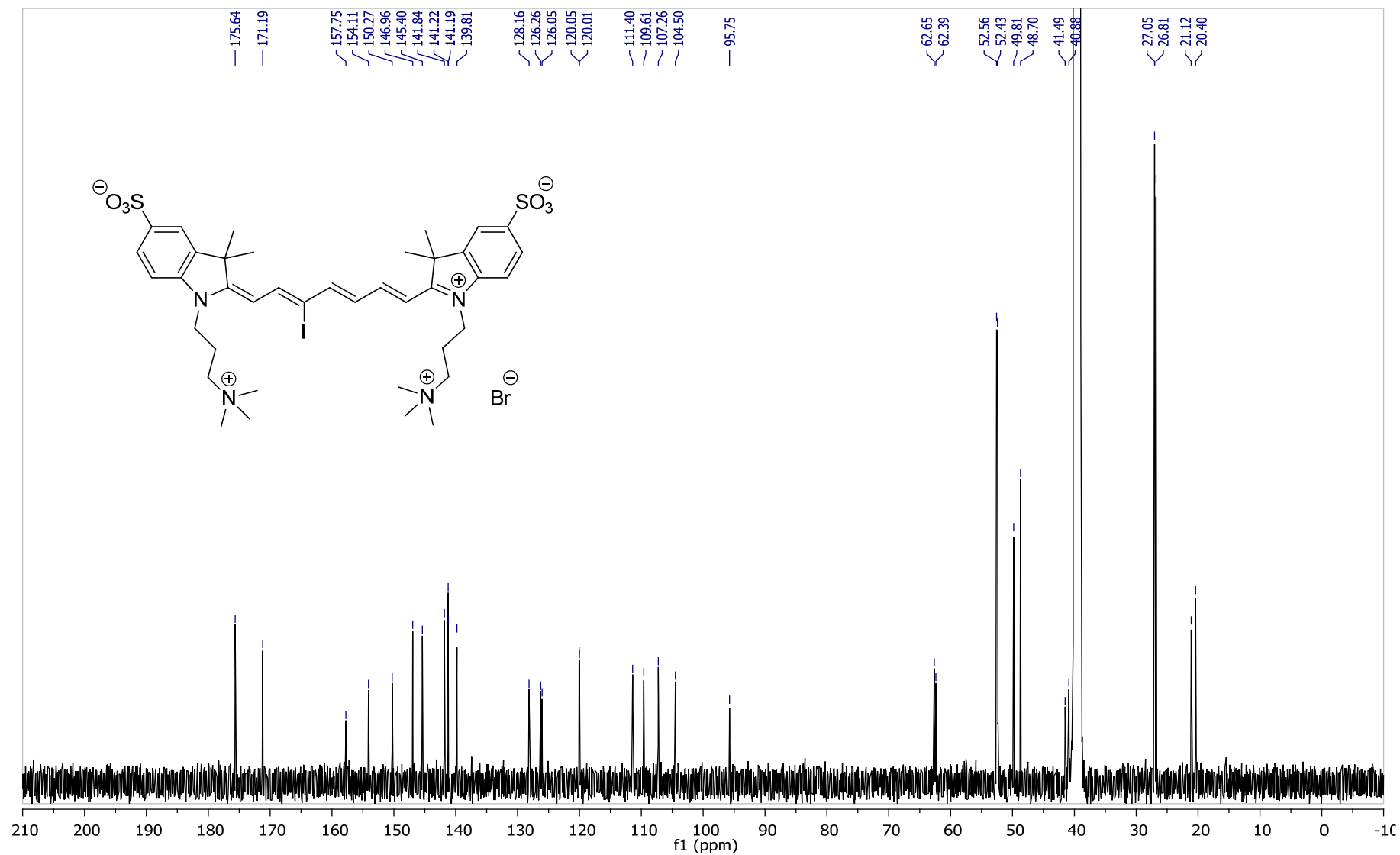
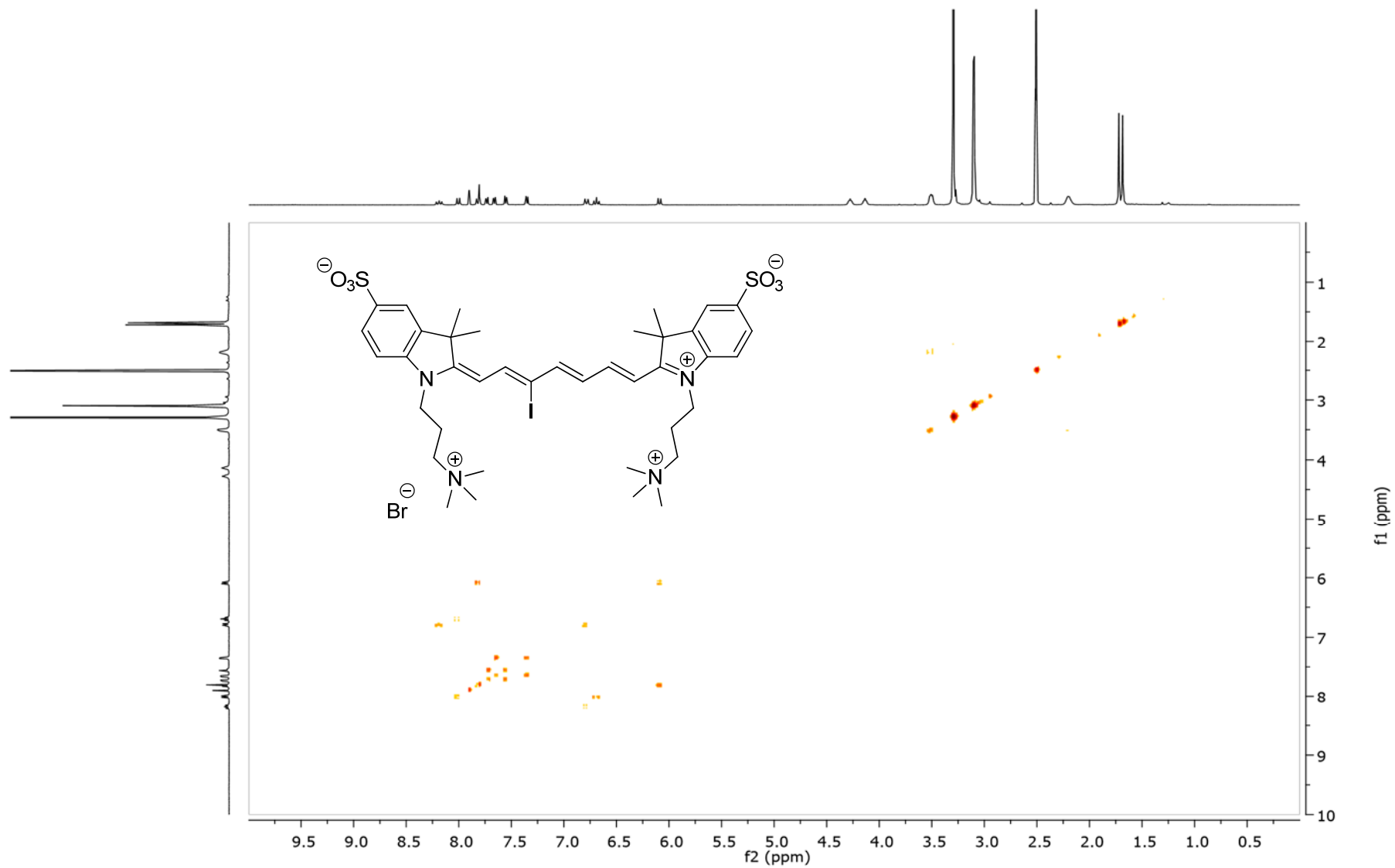


Figure S42. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, *d*<sub>6</sub>-DMSO): 1f.



**Figure S43.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR (500 MHz,  $d_6$ -DMSO): **1f**.

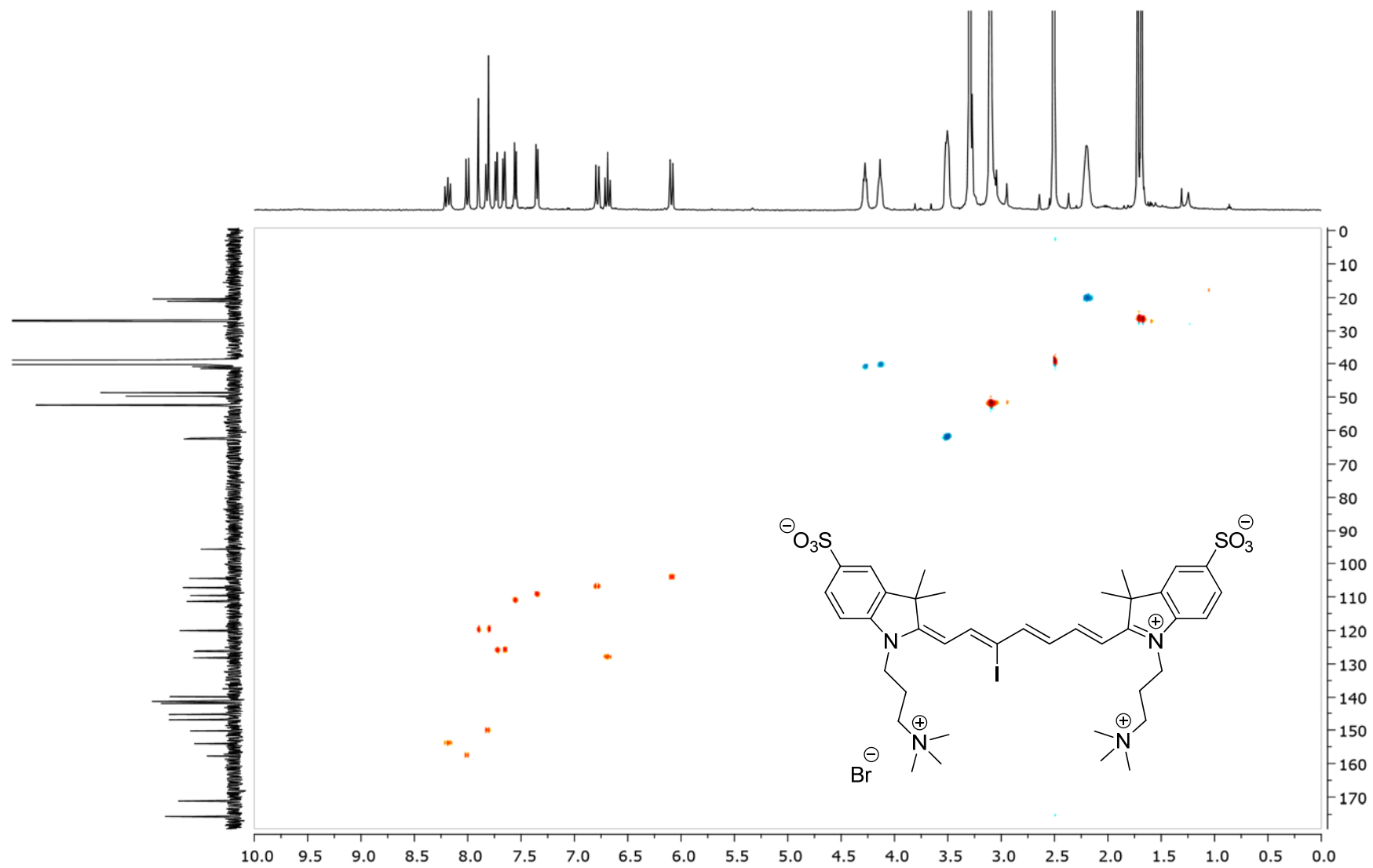
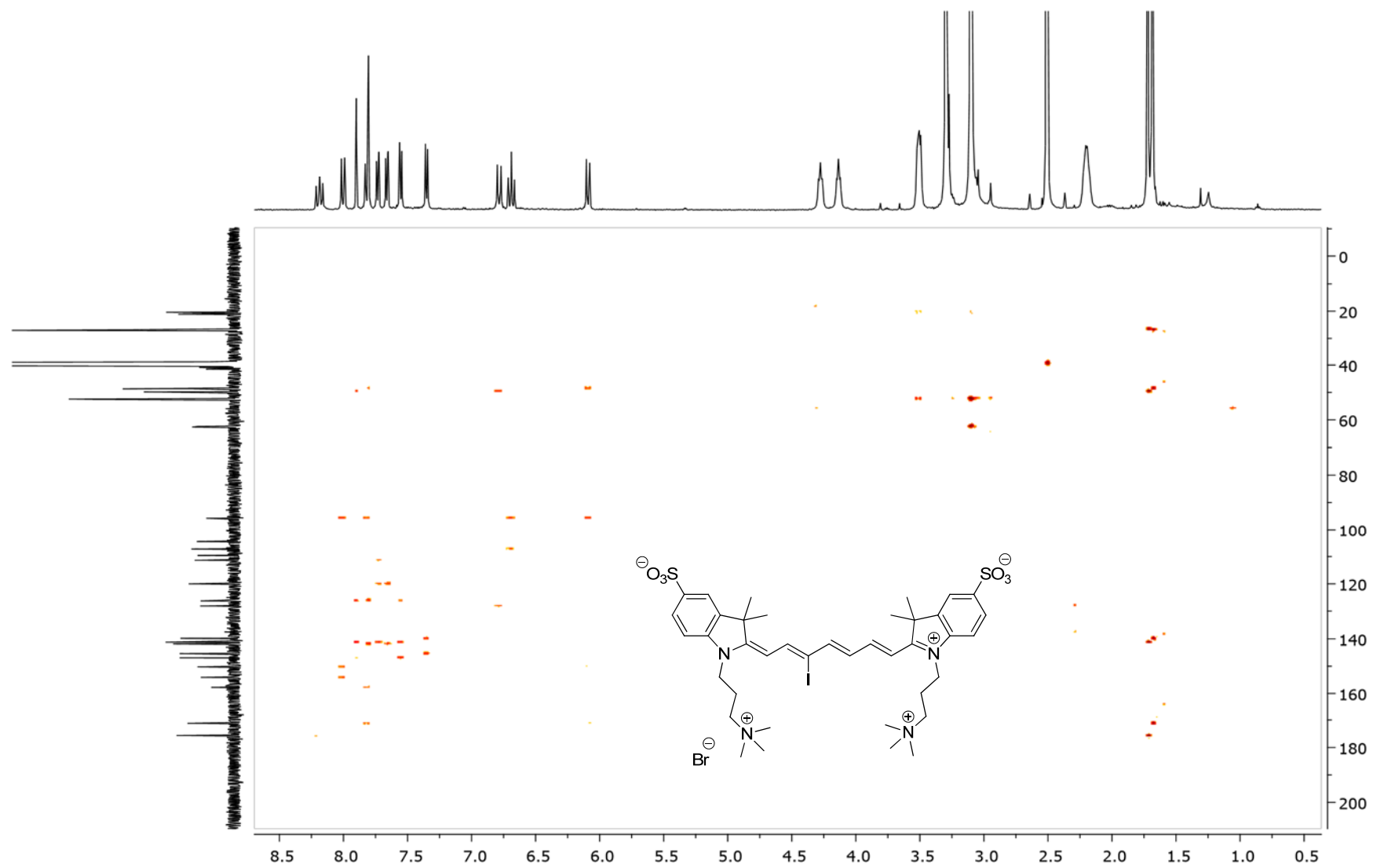


Figure S44.  $^1\text{H}$ - $^{13}\text{C}$  gHSQC (500 MHz,  $d_6$ -DMSO): **1f**.



**Figure S45.**  $^1\text{H}$ - $^{13}\text{C}$  gHMBC (500 MHz,  $d_6$ -DMSO): **1f**.

**Table S1.** Optimized ground state geometries of **1a**, **1b**, **1c**, and **1d** calculated at CAM-B3LYP/def2-TZVP level in water modeled as polarizable continuum. The first number (64) is the number of atoms in the molecule. There are no imaginary frequencies.

64

molecule <b>1a</b>			
C	0.59943332665212	0.01394968503640	16.23561045254111
C	-0.33159214422440	0.01004924048556	15.23414227740518
C	-1.67038851871755	0.00627455307113	15.55147022279222
C	-2.11711832776628	0.00635638724516	16.84816392073910
C	-1.16847411190619	0.01038890974235	17.85647500500204
C	0.17995477320525	0.01413522964546	17.55709851777701
C	-0.16976231229775	0.00884089505955	13.74625803062630
C	-1.61172575400120	0.00397438150207	13.29010005577955
N	-2.41375885621942	0.00272981176175	14.36332947141416
C	-2.11836206271711	0.00074081924759	12.01513095715962
C	-1.38800049209932	0.00200898920003	10.84038554714480
C	-1.95499449675501	-0.00159407310225	9.5858883973155
C	-1.19582790509703	0.00001986764946	8.43279369367202
C	-1.70044240237172	-0.00377589183147	7.14805769468462
C	-0.88358066824814	-0.00206394983376	6.03949955112465
C	-1.34794838994196	-0.00580887816881	4.73651538487045
C	-0.57976042116477	-0.00470628511415	3.59902317558408
C	0.92607085410769	0.00053484541185	3.46027067210596
C	1.08438819034428	-0.00083513241841	1.97163380778510
C	-0.15609577220140	-0.00628585620069	1.37696330267273
N	-1.13516574646318	-0.00855299101111	2.38046015776136
C	2.20690448189599	0.00230241121576	1.18994080004157
C	2.07622274099029	-0.00001621914612	-0.19041131118536
C	0.82202367303250	-0.00551301115535	-0.76881332434674
C	-0.31883189017085	-0.00876038935954	0.01548763207523
C	1.54426887340899	1.26996120249840	4.05809780656051
C	1.55306452486444	-1.26303078377126	4.06138633626978
C	-2.55836522643786	-0.01402435731423	2.12711017396560
C	-3.85818362804859	-0.00179797991572	14.30760840126921
C	0.57069576243235	-1.25613708186152	13.29514624821458
C	0.56341911247294	1.27704294667025	13.29236112522091
H	-2.77697017031283	-0.00833926007644	7.00595201995372
H	-0.30586652576875	0.00612272822007	10.88177090812989
H	-3.03761091094967	-0.00596749978057	9.50087410302152
H	-0.11384316059331	0.00444419858668	8.54555202014799
H	0.18308691597491	0.00245311113185	6.22874336910199
H	-2.42245942467901	-0.01005319988105	4.60783380421564
H	-2.73086410559839	-0.01793191318518	1.05733822461373
H	-3.01749811886289	-0.90230267943097	2.56021597378499
H	-3.02342524122081	0.87381716278700	2.55482636705116
H	1.08654057703299	2.16066938344703	3.62838376715050
H	1.42450960561091	1.30665382019849	5.13876874441080
H	2.61058743788565	1.29014603381786	3.83412997724863
H	1.43256555790129	-1.29824361733304	5.14202290902807
H	1.10217988302981	-2.15798631074463	3.63326253954943
H	2.61969812261079	-1.27587450130964	3.83833295469223
H	-1.29334082864312	-0.01308497324420	-0.44880233092309
H	0.72493307022685	-0.00734403353510	-1.84628936399062
H	2.95774516272713	0.00249587572044	-0.81623799007709
H	3.19408832574280	0.00661329208032	1.63232358606884
H	-4.21453364691040	-0.89184553846168	13.78966694576400
H	-4.25587224960136	-0.00111548797394	15.31570057151118
H	-4.21991704938865	0.88412831191169	13.78635457598969
H	1.65819198603845	0.01692822163936	16.01190031636332
H	0.90888747436780	0.01724768793703	18.35556480678848
H	-1.49152462878031	0.01052451794479	18.88869910711890
H	-3.16775573693788	0.00341542516878	17.09570115140080
H	0.03874975932366	-2.15034864843258	13.61960298855762
H	0.68404640681914	-1.29404478215982	12.21394078559974
H	1.56476384685433	-1.26797885685408	13.74084031827080

H	0.67706238355929	1.31302483939496	12.21113318653832
H	0.02611395907603	2.16886855391519	13.61450647011419
H	1.55726108319959	1.29573143192878	13.73835357498708
H	-3.19585494629108	-0.00312958866576	11.91121899135812

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molecule **1b**

C	6.39946562689748	1.17128543851428	0.10623678044562
C	7.35829460696578	0.19762612851055	0.04862178962763
C	6.97972343541128	-1.12167312412509	-0.03027266553482
C	5.66602669752582	-1.51232186329694	-0.05490186322988
C	4.70121943366651	-0.52159004146863	0.00264818341261
C	5.06154420157367	0.80994509589421	0.08260008387090
N	8.13703465899709	-1.91680287047398	-0.07599287120673
C	9.23691323530520	-1.16749038834738	-0.03413305731906
C	8.85076258097039	0.28998949844816	0.05343990132676
C	10.49526242086675	-1.73312044167966	-0.07241562421493
C	11.68588283410666	-1.05347079613659	-0.02961367150325
C	12.92813906154933	-1.66952740768916	-0.07293914003063
C	14.08003560175110	-0.93459696055819	-0.02776820270855
C	15.40470762058313	-1.34933953268655	-0.06063327318512
I	15.85323520252056	-3.36361746630684	-0.18687281733503
C	9.33869333982000	0.92684125782397	1.36086058550589
C	9.33748286488809	1.07755367728483	-1.16962566307782
C	8.12444420209338	-3.36203114389503	-0.15936936490004
C	16.40988372391194	-0.41412064859192	-0.00625640001102
C	17.77289263247264	-0.61126403304200	-0.02392026853384
C	18.72464265356698	0.37782919552127	0.02775645261328
N	20.02939262715599	0.08680289204251	0.00662017454516
C	20.80935128064007	1.25089577196620	0.07131702080625
C	19.97105110157754	2.33919220701705	0.13371498320531
C	18.54737865521852	1.87638268821709	0.11015470958346
C	20.50314290963394	3.59744976495732	0.20304435268477
C	21.88088488559662	3.75380671385625	0.20907438506063
C	22.70653573300493	2.64830444439314	0.14585640942367
C	22.17485040626324	1.37173591608345	0.07587088038451
C	20.56907733204324	-1.25188447834098	-0.07411718611295
C	17.83218559010546	2.43166879143243	-1.12761778095372
C	17.83433089845424	2.29629749343175	1.40099692569188
H	11.68778545677319	0.02665024473287	0.04277176503557
H	12.97009006059630	-2.74968551544986	-0.14522254277318
H	13.96201436945963	0.14395767490385	0.04362912727549
H	16.03434928693376	0.59806023820307	0.05840115581220
H	18.12325045791144	-1.63015447865412	-0.08384919965346
H	21.65138563100370	-1.20067881391930	-0.10324681468424
H	20.26704329155409	-1.83655084740474	0.79479059447786
H	20.21687752589101	-1.74644179291604	-0.97875215682319
H	18.33933108085152	2.11623259824939	-2.03915803480287
H	16.79594116883278	2.10551876072722	-1.17630922099335
H	17.84242035292786	3.52044149884237	-1.08640141079909
H	16.79688919215685	1.97107845372421	1.41394266707599
H	18.34049885258905	1.88234339268142	2.27275585368926
H	17.84848024368040	3.38301942257780	1.47856732790493
H	22.82880869291128	0.51461383248048	0.02711958823333
H	23.78068052514914	2.77679670748884	0.15073224934905
H	22.31159535446736	4.74394592887992	0.26318939816837
H	19.86548729049554	4.46956028982385	0.25249784822953
H	8.64904561117987	-3.79175496373432	0.69266974672711
H	7.09851340146521	-3.71019836739450	-0.15225438173873
H	8.60368746179966	-3.69055421138626	-1.08068882274986
H	6.66969212217956	2.21697732531426	0.16851852480184
H	4.29594018636515	1.57206171068397	0.12720585447174
H	3.65548385133006	-0.79692119889420	-0.01544568989518
H	5.37396884210038	-2.54926832368982	-0.11754264845548
H	8.99327890429764	0.35323177164396	2.22061578733233
H	10.42382669863737	0.99047454418617	1.39907564706950
H	8.93676750308502	1.93653468255328	1.43760818371086



H	10.42269953053912	1.14573962278717	-1.20008083901186
H	8.99253726934466	0.60906700028190	-2.09115119318744
H	8.93452066805060	2.08868948334844	-1.12629073516004
H	10.55107806030269	-2.81149144942675	-0.14318539696794

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Molecule 1c

C	-0.41311350999597	-0.10502999155960	0.00351623840882
C	-0.21817956210229	-0.04830722895538	1.35729310281887
C	1.04033362291680	-0.06917733110212	1.90509502224098
C	2.13152630591339	-0.14756215611145	1.09043154944602
C	1.97768291175059	-0.20737999223921	-0.28196493682218
C	0.70472121759300	-0.18477910781097	-0.80564132578273
C	0.94300712928326	0.00152127781353	3.39591125869034
C	-0.55604939746581	0.05460550242264	3.58944132793761
N	-1.15787621572296	0.03163167317242	2.38844410355524
C	-1.28084864403136	0.10925095751062	4.75001216771967
C	-0.77866392536822	0.13076958700676	6.04131903678387
C	-1.57570746794656	0.14909325220978	7.16255475225254
H	-2.65407770392445	0.14773758237830	7.03531340267546
C	-2.58862220749337	0.07330419480614	2.18576043557006
C	1.62561695582343	1.27480509786523	3.90995706535494
C	1.55275201303270	-1.25601668650043	4.02576522926559
C	-1.06017588979958	0.14885339646971	8.44447024243349
C	-1.82314859434695	0.12514844419001	9.59458958000904
C	-1.27272892048169	0.10666661993717	10.85677299933899
C	-2.03417715678676	0.04562913198511	12.01136863673830
C	-1.57430444981041	0.01561635356194	13.30181580020061
N	-2.42162448388825	-0.06994242921681	14.33985360488698
C	-1.72972829375983	-0.08525891296579	15.55404953703003
C	-0.38344176167378	-0.00329643047753	15.29798315428620
C	-0.15454009318529	0.06707684111675	13.82114963046191
C	-2.21447427999279	-0.16556214838598	16.83144652888991
C	-1.30150333155732	-0.16047902902244	17.86872957074896
C	0.05350791622952	-0.07753754760198	17.64048451670257
C	0.50265241001177	0.00102427942974	16.33510435668774
C	-3.86086945746087	-0.13981069412414	14.22269986195108
C	0.66540690852285	-1.14209925125023	13.35516469551796
C	0.53406494692574	1.38587461917101	13.45115958109869
H	-0.19170669834969	0.13433297565823	10.91988124409328
H	-2.90480839913453	0.10678386676809	9.50055214465212
H	0.02179137033783	0.15759217800877	8.55478249438438
H	0.29167548803434	0.12595153216799	6.20614104375856
H	-2.35893537845503	0.12833455690485	4.65731780013930
H	-2.80097506213501	0.06046601372271	1.12278213303522
H	-3.06369135697768	-0.79053307438440	2.65056331157670
H	-3.00491425873576	0.98407284065228	2.61545432017558
H	1.17971494882046	2.15944805860450	3.45554850288813
H	1.54776427018223	1.36263368499808	4.99139329275218
H	2.68210918350681	1.24563052343925	3.64456988907203
H	1.48100924941567	-1.23660773165757	5.11069306999636
H	1.04962585641768	-2.15081037203703	3.65930298986848
H	2.60643242454373	-1.31671756843278	3.75449452766118
H	-1.39559430734450	-0.09089760285082	-0.44110387510885
H	0.55748679703479	-0.23058564816634	-1.87366158463758
I	3.59660141203445	-0.32733371283230	-1.50871057837191
H	3.12331927338069	-0.16451556721587	1.51502450465627
H	-4.15147282232624	-1.01766319776460	13.64637931271919
H	-4.29697108026760	-0.21060866667365	15.21249992005309
H	-4.24493976790674	0.75370640251258	13.73134450498999
H	1.56207349892365	0.06544691517570	16.13998120682247
I	1.36274048763297	-0.07256669861007	19.19773815215214
H	-1.67848730148182	-0.22387945827076	18.87789416517500
H	-3.26948769804292	-0.23133367619961	17.04628168812522
H	0.15778793663065	-2.07229851162918	13.61004320384156
H	0.83639371475376	-1.12166499482536	12.28125839851297
H	1.63410707070289	-1.12955401969764	13.85400053812119

H	0.68975918978600	1.46868273106892	12.37778038027415
H	-0.06102750524060	2.23614680055949	13.78423554190386
H	1.50613411046876	1.43081563890735	13.94155606630482
H	-3.10655363741771	0.01013290837641	11.87153696331420

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molecule **1d**

C	0.86160755424622	0.01327054307691	15.90312575869585
C	-0.16551323721873	0.00970067322803	15.00500053734879
C	-1.46026041051437	0.00564036924061	15.45752051220711
C	-1.75976160794064	0.00552412422719	16.79208320509163
C	-0.70633091068382	0.00933277026257	17.68593859940280
C	0.60361721046758	0.01315454471929	17.26034328696691
C	-0.15360574475544	0.00898245080176	13.51034311588844
C	-1.63409696201098	0.00447968649532	13.20851254970455
N	-2.32186228272454	0.00224967412398	14.35258463329662
C	-2.27608537119613	0.00278424394426	11.98843451047199
C	-1.67211086002580	0.00356187083269	10.75419673517062
C	-2.37388314668052	0.00246519044679	9.55739112069086
C	-1.72069437597908	0.00177350514167	8.35487701208976
C	-2.23429180509614	0.00216062055622	7.06378668819683
I	-4.28026618446904	0.00404968888044	6.76836397277811
C	-3.76630172483657	-0.00283596973886	14.44978756750229
C	0.53744256109452	-1.25749108951174	12.98886492956368
C	0.53009676191693	1.27895333734352	12.98765078151052
I	2.12586939460201	0.01887310498653	18.60958772140084
C	-1.37388167687250	0.00047849929504	5.99221545463083
C	-1.67208912304015	0.00175569522838	4.64592024218835
C	-0.74841911243779	-0.00144860162563	3.63062955334936
C	0.76092051825853	-0.00921976011148	3.71060848670882
C	1.12670605870181	-0.01001090776492	2.26123820746833
C	-0.01285955845800	-0.00343534647533	1.49578410019605
N	-1.12519162815468	0.00160377924256	2.34467487847667
C	2.34809800588767	-0.01609027650004	1.65448178706010
C	2.44507579966368	-0.01558209933834	0.27581835300279
C	1.28695376264083	-0.00887824125156	-0.46808898122715
C	0.04050040203473	-0.00268361607791	0.12855485396809
I	4.26110602904484	-0.02548892112325	-0.64114042461571
C	1.30293902345954	1.25511883677959	4.38833379910039
C	1.28953111962459	-1.27991494806309	4.38678201576088
C	-2.49889143654328	0.00943820014579	1.89227624453318
H	-0.59189394564555	0.00439217462237	10.67889345746504
H	-3.45665080542582	0.00196601521246	9.59216218004033
H	-0.63396817001406	0.00078070674587	8.39396962001401
H	-0.33518099887444	-0.00226399045264	6.29308825007402
H	-2.71466391733699	0.00516856950488	4.36660379398324
H	-2.51959605152518	0.01279901121176	0.80851578410902
H	-3.01965060031802	-0.87724000349977	2.25274258250194
H	-3.01109353435811	0.89893263862551	2.25794738299697
H	0.90671119218318	2.14902567676602	3.90686067949754
H	1.04880892323611	1.28694111923952	5.44521092263960
H	2.38893584418355	1.26741639103140	4.29948743107001
H	1.03381239882442	-1.31079285969782	5.44334494976106
H	0.88481500428050	-2.16903742861130	3.90351059158620
H	2.37545044624191	-1.30299395539765	4.29905253139852
H	-0.84655453751288	0.00239374112257	-0.48474696971416
H	1.33538603951029	-0.00863402018908	-1.54615451171864
H	3.24761039343119	-0.02165853876365	2.25058668279242
H	-4.17265647688753	-0.89104362121520	13.96778495667013
H	-4.05306060298706	-0.00726601716617	15.49481034602051
H	-4.17875935643297	0.88559978032082	13.97336993222202
H	1.88320745844000	0.01641497437368	15.55599213684114
H	-0.93395724075427	0.00900491942387	18.74076405076631
H	-2.77415258237057	0.00243767604603	17.15827132612218
H	0.03348841337800	-2.15020005304342	13.35901517557144
H	0.55145466358152	-1.29042224248242	11.90197760271405
H	1.56759980564438	-1.27044777039038	13.34333719496094

H	0.54452200890425	1.31061091826691	11.90072442189650
H	0.02055633593603	2.16909204646662	13.35638451096815
H	1.55996926294732	1.29861270691085	13.34266029716409
H	-3.35806541228442	0.00064180360133	11.99987388100535

**Table S2.** Optimized ground state geometries of **1a**, **1b**, **1c**, and **1d** calculated at CAM-B3LYP/def2-SVP level in the gas phase. The first number (64) is the number of atoms in the molecule. There are no imaginary frequencies.

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molecule **1a**

C	0.659528	0.011337	16.271733
C	-0.308412	0.008132	15.281145
C	-1.657597	0.004786	15.626070
C	-2.082599	0.004862	16.947555
C	-1.099339	0.008122	17.938508
C	0.255308	0.011270	17.609782
C	-0.175261	0.007610	13.771199
C	-1.646611	0.003735	13.341586
N	-2.426599	0.001617	14.440871
C	-2.182219	0.002379	12.056670
C	-1.460012	0.003228	10.859726
C	-2.032402	0.001670	9.592886
C	-1.268177	0.002498	8.427024
C	-1.769720	0.000789	7.126409
C	-0.942346	0.001584	6.009017
C	-1.394785	-0.000129	4.686058
C	-0.599728	-0.000015	3.543139
C	0.929223	-0.001023	3.433314
C	1.117633	-0.004281	1.929241
C	-0.128374	-0.004090	1.307586
N	-1.130211	-0.000173	2.304162
C	2.272558	-0.007271	1.164530
C	2.159218	-0.010372	-0.228498
C	0.904470	-0.010627	-0.835399
C	-0.265550	-0.007582	-0.073717
C	1.542561	1.273376	4.043008
C	1.541422	-1.273345	4.048329
C	-2.551504	0.001481	2.025589
C	-3.874572	-0.002810	14.412938
C	0.556121	-1.264355	13.302724
C	0.550161	1.282475	13.301398
H	-2.850955	-0.001363	6.981748
H	-0.371769	0.005130	10.901467
H	-3.119846	-0.000398	9.505717
H	-0.180504	0.004596	8.542963
H	0.129987	0.003754	6.200866
H	-2.473445	-0.002404	4.544435
H	-2.711412	0.017453	0.947710
H	-3.028999	-0.897419	2.433151
H	-3.030635	0.887362	2.458462
H	1.093390	2.173561	3.611060
H	1.412361	1.313274	5.128666
H	2.616910	1.299058	3.830976
H	1.411275	-1.308552	5.134164
H	1.091398	-2.174937	3.620222
H	2.615729	-1.300925	3.836334
H	-1.236155	-0.008486	-0.562627
H	0.830451	-0.013456	-1.920909
H	3.056092	-0.012833	-0.843575
H	3.255678	-0.007341	1.632884
H	-4.249575	-0.892845	13.894326
H	-4.258910	-0.011836	15.432539
H	-4.255929	0.891945	13.907071
H	1.719400	0.013933	16.020524

H	1.002272	0.013793	18.400251
H	-1.400319	0.008278	18.983890
H	-3.134435	0.002684	17.221097
H	0.028596	-2.166443	13.629614
H	0.658251	-1.302464	12.214077
H	1.561400	-1.287520	13.736374
H	0.652328	1.319859	12.212752
H	0.018345	2.182424	13.627212
H	1.555272	1.310879	13.735146
H	-3.266690	0.000465	11.966202

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molecule **1b**

C	6.25012159018823	1.13888034921594	0.10486871077870
C	7.23255680277237	0.16418387182300	0.04605016724122
C	6.87564325048820	-1.17865019535301	-0.04485487469294
C	5.55109073107706	-1.59213886439162	-0.08124872759610
C	4.56847681819347	-0.60224490111128	-0.02172925979922
C	4.90892888470028	0.74668504679291	0.07048456205476
N	8.05502373362847	-1.95673723774847	-0.08882929882114
C	9.15852593486228	-1.18917482398269	-0.03476823231345
C	8.74336992452691	0.28273305277171	0.06216074790851
C	10.44078072223734	-1.73715915042546	-0.06915175302178
C	11.64149626888333	-1.02997150387859	-0.01905233164108
C	12.90319488562759	-1.62214364690884	-0.05873717165983
C	14.06736737215463	-0.86637875580377	-0.01111922691914
C	15.40205047654519	-1.28877483731707	-0.04079894619765
I	15.84674919890055	-3.34248587552047	-0.16412891623199
C	9.21329498948182	0.91712849382231	1.38448516937848
C	9.22655727993195	1.09001425841909	-1.15698691045253
C	8.06893364130651	-3.40279221047673	-0.18344509473148
C	16.43382151471792	-0.35034679488436	0.00936435805970
C	17.80747752244055	-0.57907007808441	-0.01085340843924
C	18.79888679750480	0.40140139234597	0.03386318689964
N	20.10551572395957	0.08318892133489	0.00773610133574
C	20.92435342988601	1.23387796976863	0.06292908192784
C	20.10611194482869	2.35879292545814	0.12537057744597
C	18.65381232188501	1.92480568627641	0.11340176558409
C	20.67062117232721	3.62237093275454	0.18631227273288
C	22.06343215080645	3.73866618942504	0.18390625151635
C	22.86857299768630	2.60218183384706	0.12183245541636
C	22.30944945642876	1.32436260186585	0.06017929505331
C	20.61339324551561	-1.27228492828975	-0.06762219252285
C	17.93938447980459	2.49226479205301	-1.127207366601087
C	17.95948887793429	2.36112832637683	1.41700618187295
H	11.61110720427827	0.05606201922033	0.05588756016882
H	12.97364582892820	-2.70628096957567	-0.13151139333039
H	13.94076957401114	0.21781462176824	0.05861634268886
H	16.08511579281732	0.67938333847350	0.07030015653098
H	18.13119842960907	-1.61377457323285	-0.06868077212444
H	21.70265741480610	-1.25208879277839	-0.10198523748453
H	20.30315191089392	-1.85269519343762	0.80919251577642
H	20.24738223416694	-1.77154590058901	-0.97188310980300
H	18.43102523380058	2.16652838033060	-2.04971821929914
H	16.89008458335435	2.18671930424030	-1.174374440441246
H	17.97090058811105	3.58675592327003	-1.09734938178891
H	16.91134440456213	2.04997842246512	1.44955815913000
H	18.46656905044017	1.94461033623217	2.29344838236536
H	17.98977015085552	3.45297973269999	1.49860583094490
H	22.95028242627177	0.44811679018426	0.01298296113266
H	23.95138790514117	2.70848714733957	0.12128574317021
H	22.52353051770299	4.72302138172035	0.23122532959427
H	20.04758560477580	4.51391218970944	0.23533293643016
H	8.59117734606214	-3.84142146580392	0.67438903936791
H	7.04570504570269	-3.77715551656480	-0.19090781124216
H	8.56327495591832	-3.72667084386680	-1.10663444755598
H	6.50958143795877	2.19422742123899	0.17700560582524

H	4.12453380877122	1.49871858307509	0.11560754242325
H	3.52053145725609	-0.89292791336228	-0.04849377492399
H	5.26846758732200	-2.63896012595750	-0.15403489728972
H	8.87549826970000	0.33137381213551	2.24568226494219
H	10.30276976228474	1.00303013859652	1.43485883479264
H	8.79131899697114	1.92349248134616	1.47722179307231
H	10.31612157950950	1.18754160142764	-1.18037340854510
H	8.90401538313930	0.62277172408336	-2.09331046649665
H	8.79896831216672	2.09746193840378	-1.12016968716358
H	10.52048006147777	-2.81972783296693	-0.14431516105137

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molecule 1c

C	-0.26273194153685	-0.00556224349950	-0.07133512355458
C	-0.13296664198141	-0.00299933704716	1.31013011119050
C	1.11317478319991	-0.00964943539983	1.93060712603453
C	2.27155694712111	-0.01771178351731	1.17347742425323
C	2.15953322139238	-0.01947638399849	-0.22135767199411
C	0.90606666704207	-0.01368912363667	-0.83394883745101
C	0.92643439300565	-0.00649205138559	3.43508107647760
C	-0.60297057790874	0.00084145639989	3.54408892061566
N	-1.13386998797795	0.00567481112549	2.30392946247628
C	-1.39779170841735	0.00150919378018	4.68594223173437
C	-0.94513614728490	0.00068520008884	6.00954051382912
C	-1.77270967956347	0.00162430003855	7.12624755187338
H	-2.85398163788891	0.00289110925010	6.98173382332235
C	-2.55511276189541	0.01519954526524	2.02386054710847
C	1.54478068216321	1.26581902576572	4.04384610532021
C	1.53443775166236	-1.28132266558816	4.04836522150032
C	-1.27083277787133	0.00112793868997	8.42693585659803
C	-2.03569665796333	0.00251446120237	9.59255407335421
C	-1.46313528048677	0.00224073557154	10.85891550434104
C	-2.18577932729610	0.00355720952312	12.05633329233380
C	-1.65020624693298	0.00364495800687	13.34022335270808
N	-2.43086593161097	0.00304497346466	14.44053013859382
C	-1.66217189811263	0.00641770930927	15.62288248355734
C	-0.31311878180554	0.00708227816879	15.27910517842431
C	-0.17821119088442	0.00511945059086	13.76910549488698
C	-2.07985329352135	0.00905628142035	16.94611647616781
C	-1.09789237406614	0.01171171881055	17.93766175338315
C	0.25675269645304	0.01188364833203	17.60308887552218
C	0.65983333627972	0.00965243199507	16.26300413228181
C	-3.87914518309169	0.00064281188672	14.41389853886995
C	0.55119281251389	-1.26857492202998	13.30293559693234
C	0.54938399499240	1.27873600416448	13.29989366925018
H	-0.37489974500195	0.00075381981879	10.90098498842426
H	-3.12313657637279	0.00381415313877	9.50514805992659
H	-0.18322064092085	-0.00038735800251	8.54299802573521
H	0.12727528439931	-0.00053225140175	6.20093273294928
H	-2.47646794360293	0.00223841494584	4.54423806451400
H	-2.71423640098956	0.05055346332800	0.94625256844203
H	-3.03545540748598	-0.88922594606259	2.41556435275272
H	-3.03195960706244	0.89501310011598	2.47092301220403
H	1.10097545908483	2.16779505251563	3.61001855935926
H	1.41177617070404	1.30739254128487	5.12902723934830
H	2.61989325160481	1.28636449819209	3.83505448599124
H	1.40424942930042	-1.31641244264682	5.13408048421443
H	1.08123896239960	-2.18132861858772	3.62018858105948
H	2.60873984733251	-1.31297301394441	3.83689426170626
H	-1.22896231222369	-0.00237714720657	-0.56866748195445
H	0.83247885352797	-0.01586433579589	-1.91850934189946
I	3.89303804842238	-0.03153204499786	-1.39842647361733
H	3.25195577712838	-0.02283046694835	1.64507610508348
H	-4.25517447685467	-0.88496117317953	13.88876336601348
H	-4.26305150910604	-0.01653279745764	15.43363152821893
H	-4.26003334484442	0.89986272817080	13.91572275583099
H	1.71765144268224	0.00999887217750	16.00804436069950

I	1.70320917476584	0.01598619972329	19.11877299397651
H	-1.39828797190310	0.01387986693362	18.98222586530622
H	-3.12915597043444	0.00959305674659	17.22894666002790
H	0.02239750756372	-2.16965499887379	13.63064739251933
H	0.65298928278596	-1.30791835453736	12.21440286677681
H	1.55676299935290	-1.29313973491223	13.73585759239207
H	0.64839087087266	1.31697850495030	12.21106924816326
H	0.02074860661394	2.17978964104675	13.62792898434771
H	1.55595389252144	1.30444208025318	13.73043842701700
H	-3.27027221198752	0.00499238446509	11.96598283452878

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molecule **1d**

C	0.85878105009636	0.00719773452001	16.02638642440253
C	-0.18538102350547	0.00671501774456	15.11821175271941
C	-1.50419107325895	0.00741627885180	15.56327054386876
C	-1.82209403247385	0.00893014530816	16.91373261090742
C	-0.76854641645175	0.00947369135858	17.82856119334684
C	0.55733284910177	0.00855741477618	17.39291416966408
C	-0.16615303665730	0.00566870560248	13.60254124747082
C	-1.66584648268081	0.00608569398226	13.28757055886606
N	-2.36032852213628	0.00634111239595	14.44101511277956
C	-2.29960411253526	0.00618964659328	12.04599114571540
C	-1.67329474833533	0.00411502724272	10.79961340277820
C	-2.35034060914823	0.00439623075144	9.58109762321311
C	-1.67236850704054	0.00227493458029	8.36900292662939
C	-2.18410378756734	0.00201598775317	7.06542599594218
I	-4.26611232886447	0.00503297799043	6.75903293066438
C	-3.80732941751950	0.00607633702330	14.52533289624003
C	0.52289873343101	-1.26873073190906	13.07993689360059
C	0.52435424994098	1.27859109746014	13.07829979196163
I	2.11331943357778	0.00950345842694	18.79534658891885
C	-1.31381435135507	-0.00017899371466	5.97492671188032
C	-1.63235066960827	-0.00091924762798	4.61839114563151
C	-0.71787119299569	-0.00300005553557	3.56601744728311
C	0.81423418171243	-0.00537324476122	3.61143114558814
C	1.15073497675264	-0.00765640818328	2.13325426758199
C	-0.02707140466532	-0.00638188509714	1.39159567069488
N	-1.12204477499787	-0.00325808513715	2.28161860406753
C	2.37893168734528	-0.01056429219134	1.49543669219743
C	2.40612273444038	-0.01224169245480	0.09649206981906
C	1.21959507989397	-0.01106107746062	-0.63800138112076
C	-0.01923389901558	-0.00812172710878	0.00414554377110
I	4.24762902140223	-0.01669623153676	-0.90225280157842
C	1.36507342322295	1.26891294382113	4.27838274139420
C	1.36138830037777	-1.27957255487908	4.28150307127564
C	-2.50995383636517	-0.00112278677616	1.86254608213597
H	-0.58494153979612	0.00201175697591	10.75468057878277
H	-3.43918981188483	0.00634258634202	9.58394091093843
H	-0.57977323040802	0.00052473193272	8.42321414724413
H	-0.26166727912197	-0.00136433796821	6.25595867834879
H	-2.68758671051308	0.00012608173924	4.36225488283383
H	-2.56233052490782	0.00248736932100	0.77372937768405
H	-3.02726373641085	-0.89398377995945	2.23209786121685
H	-3.02581043759030	0.89022742680045	2.23757781746559
H	0.96250735464255	2.16967055795118	3.80374838689432
H	1.12739016818338	1.31073301323864	5.34540524987216
H	2.45533384001812	1.29321370119573	4.17520630920400
H	1.12449564779474	-1.31761654941497	5.34883868866216
H	0.95556640990980	-2.18035022668976	3.80969012784867
H	2.45148184004444	-1.30771997298281	4.17755532688805
H	-0.93150470399204	-0.00738447585968	-0.58606727650472
H	1.25478609391057	-0.01249811758148	-1.72450286645434
H	3.30732455170307	-0.01157885144552	2.06234568910330
H	-4.22325536934552	-0.88298129092867	14.03774202118456
H	-4.11093082998407	-0.00209692459152	15.57173989590511
H	-4.22348136929251	0.90231874548401	14.05105822450013

H	1.89454633518647	0.00665793568730	15.69326587830998
H	-0.98941562556876	0.01072630143793	18.89281494907914
H	-2.84734161735297	0.00992833208206	17.27376839091465
H	0.01839389666121	-2.16971618957990	13.44402098173963
H	0.54210048323391	-1.30499162655390	11.98658364262869
H	1.55816458928614	-1.29681330661420	13.43599349806039
H	0.54389606840974	1.31331801161735	11.98493995498849
H	0.02071774542526	2.18061727715025	13.44100576594215
H	1.55956968076957	1.30609850028643	13.43455696419693
H	-3.38765241312756	0.00797989911853	12.04058812221031

**Table S3.** Optimized  $S_1$  excited state geometries of **1a**, **1b**, **1c**, and **1d** calculated at CAM-B3LYP/def2-SVP level in the gas phase. The first number (64) is the number of atoms in the molecule. There are no imaginary frequencies.

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molecule **1a**

C	0.47859745058542	0.01284002313141	16.46469576639716
C	-0.41219381685982	0.00859075466165	15.40902768013209
C	-1.80360747646188	0.00444291973116	15.65542345854620
C	-2.31138959505313	0.00476925820244	16.96251461808498
C	-1.40121609406400	0.00904271431382	18.00909167505751
C	-0.01660329584268	0.01303418970308	17.77289532694815
C	-0.15876719139195	0.00733980485082	13.91538250599641
C	-1.59283114166278	0.00286018386555	13.37523375016180
N	-2.48213457000552	0.00043450566770	14.46082574570119
C	-2.03152921437416	0.00146037909545	12.08467336693820
C	-1.22659403802343	0.00306388410323	10.90067982869806
C	-1.74816829369283	0.00157311060643	9.62527525220862
C	-0.96613359998189	0.00289447155911	8.46000515889782
C	-1.48192893786770	0.00126440521742	7.15515408097701
C	-0.70114610882078	0.00229789634005	6.01951012982608
C	-1.23720209960163	0.00092871399351	4.69200803938431
C	-0.53680842456601	0.00044780531333	3.52254126077656
C	0.97839330535459	-0.00149241952253	3.29503541824549
C	1.04376545136610	-0.00518681430616	1.78136896794235
C	-0.26501294069718	-0.00376151088406	1.24880621503797
N	-1.17876266860844	0.00114795413747	2.27475606311809
C	2.13597311797677	-0.00937366993022	0.93568236794684
C	1.92570998771663	-0.01231910119235	-0.44714860943517
C	0.62128563952565	-0.01123547716144	-0.96829931943370
C	-0.48791817190419	-0.00709591555426	-0.13554757137949
C	1.64973432812979	1.26878192208520	3.85367596011415
C	1.64798735190728	-1.26999663106012	3.85962853444344
C	-2.61077840806575	0.00436999498429	2.12146490367369
C	-3.91462767124967	-0.00468474468846	14.31034778807834
C	0.61741919072928	-1.26070579831936	13.50839970063059
C	0.61101974453514	1.27820256476085	13.50516427765522
H	-2.56820515630702	-0.00105492676191	7.03823669138380
H	-0.14265497742215	0.00541899604713	11.00014281922537
H	-2.83435486035935	-0.00084440772426	9.50761406248278
H	0.12054745894807	0.00532971122032	8.57741933838123
H	0.37939840264845	0.00472531491958	6.15377186632926
H	-2.32447798854086	0.00036592048805	4.62851041559263
H	-2.87158873388636	0.01571501080595	1.06297011617174
H	-3.05592937311870	-0.89027818753463	2.57727592693179
H	-3.05229889283637	0.89166608642003	2.59447348775653
H	1.17536117367500	2.17251407536150	3.45762457402482
H	1.59713284767018	1.30741995215578	4.94599501975362
H	2.70730542465044	1.28776222067975	3.56766538433392
H	1.59600531061358	-1.30329558785815	4.95211771394345
H	1.17204987425434	-2.17491682696348	3.46819595425651
H	2.70537831603901	-1.29199581335135	3.57318103954380
H	-1.48994627806540	-0.00687472622340	-0.55508625587058
H	0.47717655720725	-0.01394013325579	-2.04676768650900

H	2.77566947573407	-0.01565324660989	-1.12545261332969
H	3.14969152658784	-0.01044274373541	1.33278949605895
H	-4.24668286994340	-0.89487532852315	13.75949940789113
H	-4.39178265478765	-0.01123879470471	15.29061026845777
H	-4.25456033020687	0.88728205134945	13.76711477832924
H	1.55326196419676	0.01603950140557	16.28857154088777
H	0.67220088017920	0.01636211281392	18.61436365139432
H	-1.76791059849358	0.00940331815912	19.03327990954923
H	-3.37915751982935	0.00197512989045	17.16344741100368
H	0.07234478971009	-2.16596822651828	13.79530213954106
H	0.79485028447429	-1.29780832302186	12.42962462029874
H	1.59141211252162	-1.27797395903214	14.00940350129354
H	0.78849718539509	1.31340135701364	12.42634122274105
H	0.06134003301831	2.18144761766362	13.78961108476260
H	1.58483882327388	1.30168963000986	14.00626520063790
H	-3.10770201603161	-0.00119114829036	11.91698557138061

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molecule **1b**

C	6.09139556445440	1.00480390651170	0.09805902255164
C	7.12090128975457	0.08599266677059	0.04286082720646
C	6.83451352618227	-1.29647746825743	-0.05195165160684
C	5.51227322573904	-1.76472515785386	-0.09389072487232
C	4.49344547579821	-0.82676178694562	-0.03769547612117
C	4.76975855758453	0.54867379410476	0.05796674097567
N	8.00666140444060	-2.00768732944610	-0.09063921802400
C	9.11912263499830	-1.14940094526896	-0.03063362264262
C	8.62085388051335	0.29632817861424	0.06623011331787
C	10.39543950719993	-1.62574446309103	-0.06291334376968
C	11.60258297920219	-0.85961558460219	-0.00805203633526
C	12.86018023487146	-1.42578900906764	-0.05451196989413
C	14.03815916749610	-0.67166341496178	-0.00403368145248
C	15.37661180892997	-1.11041420120861	-0.04119826486314
I	15.76278428107545	-3.18051101351546	-0.18060964979554
C	9.04410126882013	0.96848250920098	1.38750952786999
C	9.05820746200735	1.14339513658882	-1.14517143036015
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H	12.93964771828445	-2.50972372066073	-0.13617924003389
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H	17.01565661837378	2.31587023498980	-1.16700590260189
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H	17.03136283546339	2.17296031446016	1.44700030136531
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H	22.75661561164654	4.57440102984282	0.23524518696342
H	20.27240912133142	4.47033394306451	0.24000016934392
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H	8.58335582885772	2.12960166296159	-1.10109354582744
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molecule 1c

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C	-1.21480191508562	0.00567727868424	10.90371340092267
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C	-1.80951551369823	-0.00132529663614	15.65412572827412
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C	-3.91648416830421	-0.02582604485231	14.30296334189975
C	0.62542748880293	-1.24931425165672	13.51765021140060
C	0.60291730343375	1.29003034109911	13.51604698257225
H	-0.13116754119216	0.01415313905300	11.00518737301466
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H	0.39379168614409	0.01792196353672	6.15299775412144
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H	2.71418504553121	1.28606167880563	3.55432077238298
H	1.59806262184756	-1.29687683273981	4.94945627952535
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H	2.70947698353542	-1.29193387982043	3.57234314530364
H	-1.49558988455982	-0.01724094717771	-0.55435486339840
H	0.45492552427690	-0.04100858122287	-2.05276050109687

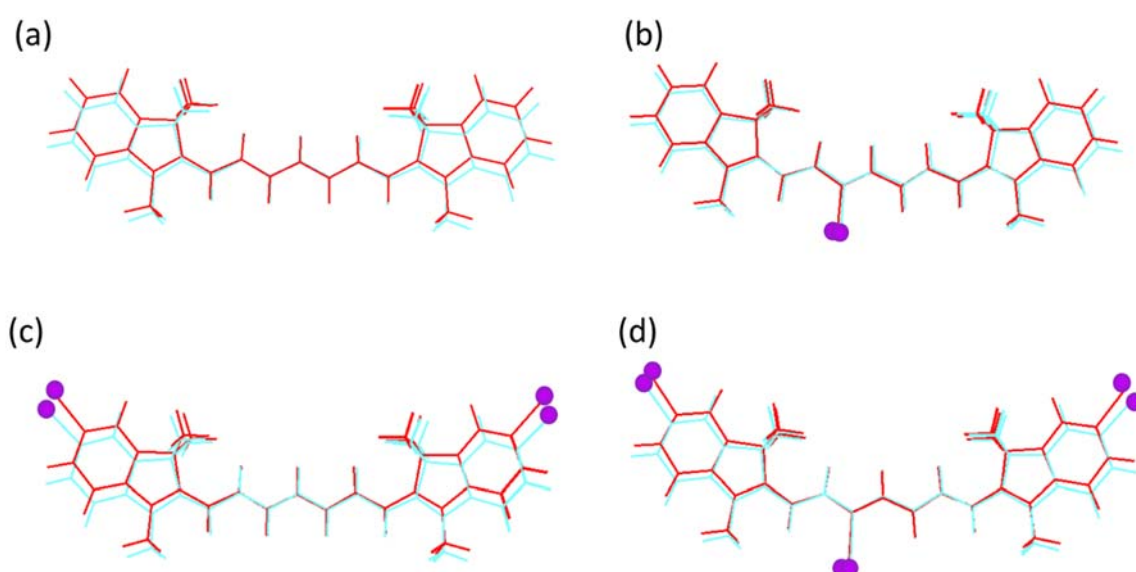
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H	-4.26316024547575	0.86741049215064	13.76645064046635
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H	0.80045717611533	-1.28726856896938	12.43867134868111
H	1.60081415127443	-1.26016577639883	14.01643207952061
H	0.77565306932577	1.33068390372067	12.43682065773150
H	0.04858890710062	2.18886977019916	13.80545574283677
H	1.57874736441232	1.31776812939254	14.01335038458523
H	-3.09812375479794	-0.01070404638637	11.91233133901308

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molecule **1d**

C	0.71964969712745	0.00901060131061	16.21771161181683
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C	-2.01192886295699	0.00658919970587	16.96447604343626
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C	0.34010117759607	0.00936546097699	17.57095408442296
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C	-2.16555113338598	0.00562198174403	12.08221617001230
C	-1.47454336245723	0.00512369916465	10.83336451565149
C	-2.12023250052120	0.00554500706832	9.61236280825544
C	-1.44493837632246	0.00424948234777	8.38875292200515
C	-1.97408133392728	0.00420096554880	7.08316626020122
I	-4.07247094959574	0.00727053003990	6.83335366489120
C	-3.84715894066244	0.00179330102822	14.46452484789708
C	0.59425797403911	-1.26284183002880	13.26712071778502
C	0.59279644814381	1.27653239159387	13.26589575092423
I	1.79261757521910	0.01178393605404	19.05070775035027
C	-1.14740444490401	0.00202728114286	5.97451353361764
C	-1.52234777417125	0.00143352892658	4.60130206403395
C	-0.67882374979685	-0.00152543916458	3.52695695212715
C	0.85313269026435	-0.00540781971388	3.48397218097584
C	1.10018131000360	-0.00890226837035	1.98746015451687
C	-0.13288573689902	-0.00656071979713	1.30602354314016
N	-1.16392403290026	-0.00172754055147	2.21690041923050
C	2.28643766768499	-0.01367278980899	1.28746778149509
C	2.24363439392169	-0.01623110481638	-0.11640016449405
C	1.01307762349959	-0.01401015060155	-0.79306404350481
C	-0.18484626295813	-0.00920535629017	-0.09310063373461
I	4.01261726485352	-0.02342945627290	-1.20394711755894
C	1.45181756036059	1.26464690710934	4.11843510415118
C	1.44573647768514	-1.27582697989214	4.12333676838608
C	-2.56927546017014	0.00174514601355	1.89205469334551
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H	-3.21019950558114	0.00676611750233	9.60344724643099
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H	-0.08548362045932	0.00055063689470	6.21539398014537
H	-2.58997070509552	0.00334866126659	4.39924664972780
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H	2.53122659682644	-1.29816993426343	3.97364492559468

H	-1.12643296694850	-0.00773582355869	-0.63467827506158
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H	3.24289621609198	-0.01548319395104	1.80568283761324
H	-4.22813246322836	-0.88716223231492	13.94488328025123
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H	-4.23193195878851	0.89502449631936	13.95496607234554
H	1.77297271650900	0.01004301250835	15.94520097332850
H	-1.29705654587807	0.00869869700102	18.98233878623105
H	-3.05623673007666	0.00598820454127	17.26334325661974
H	0.07710718702114	-2.16687124469488	13.60483744534875
H	0.66877952609502	-1.30174917351815	12.17641977751787
H	1.61158809966171	-1.28147035184721	13.67358243745344
H	0.66751816922572	1.31443722214750	12.17520115241865
H	0.07449493467811	2.18028341421970	13.60258851140318
H	1.61003079227355	1.29681528692096	13.67252380804962
H	-3.25251964375520	0.00576012987255	12.01219387196099



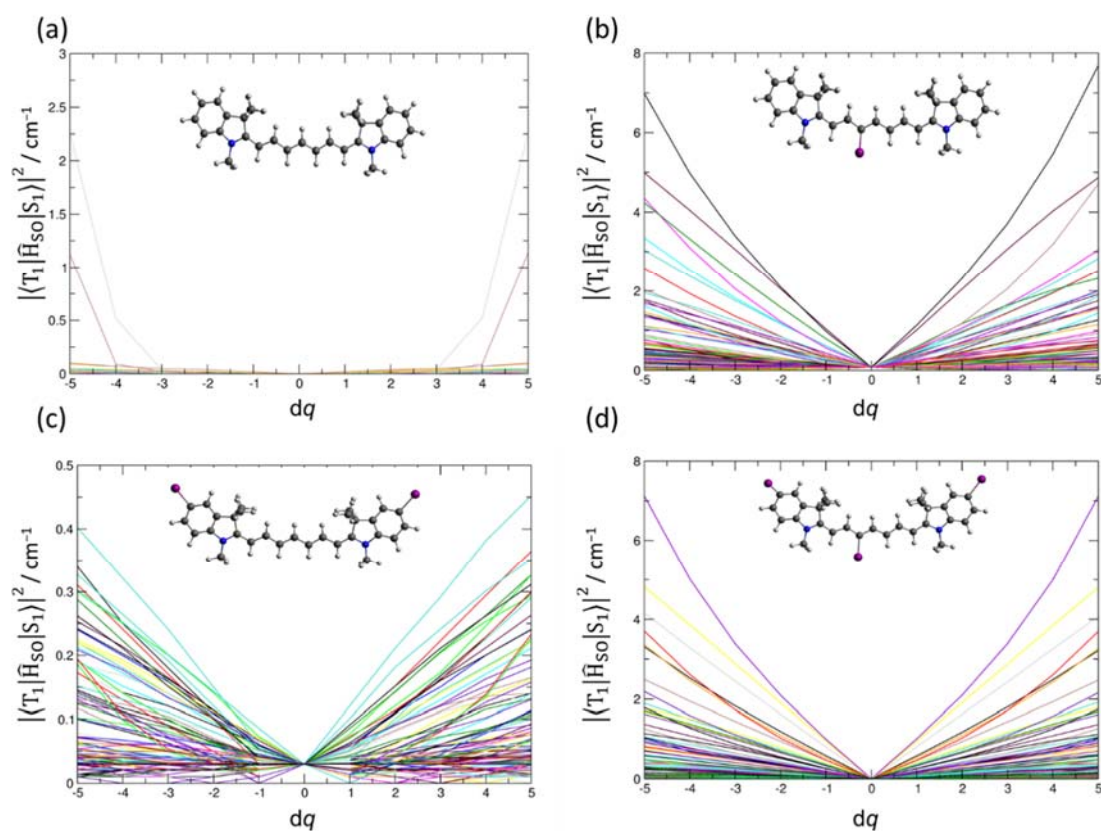
**Figure S46.** Overlap between the  $S_1$  excited (turquoise) and ground state (red) optimized geometries of **1a** (a), **1b** (b), **1c** (c), and **1d** (d) calculated at CAM-B3LYP/def2-SVP level in the gas phase. The cyan circle shows the iodine atom.

**Table S4.** Excitation energies in eV (nm) for molecules **1a–d** calculated for  $S_1$  minimized structures at the TDDFT DKH CAM-B3LYP/def2-TZVP level in water as a polarizable continuum with or without Tamm-Dancoff approximation.

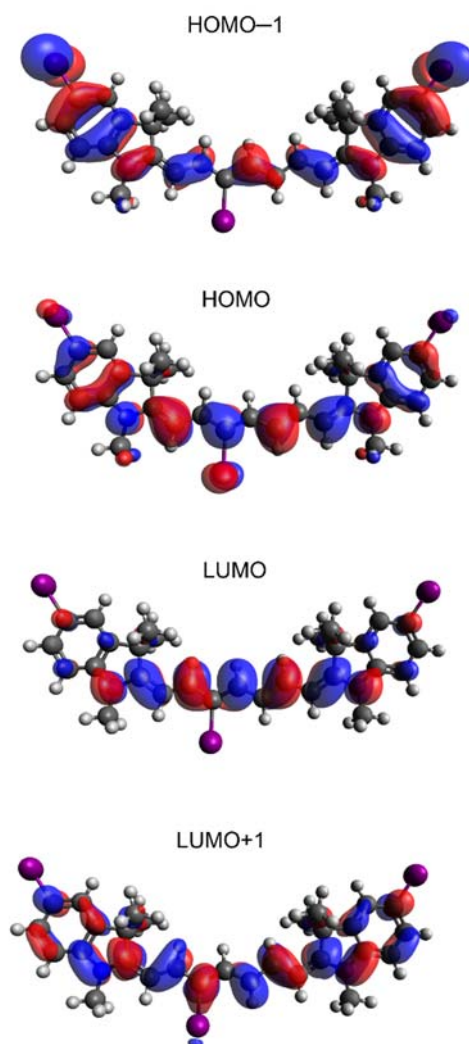
	TDDFT	TDA	TDDFT	TDA	TDDFT	TDA
Cy7	$S_1$	$S_1$	$T_1$	$T_1$	$T_2$	$T_2$
<b>1a</b>	2.176 (570)	2.354 (527)	0.718 (1727)	1.100 (1127)	2.010 (617)	2.140 (579)
<b>1b</b>	2.173 (571)	2.345 (529)	0.808 (1534)	1.144 (1084)	1.984 (625)	2.128 (583)
<b>1c</b>	2.141 (579)	2.308 (537)	0.727 (1705)	1.107 (1120)	2.017 (615)	2.139 (580)
<b>1d</b>	2.135 (581)	2.295 (540)	0.815 (1521)	1.148 (1080)	1.983 (625)	2.120 (585)

**Table S5.** SOCMEs in  $\text{cm}^{-1}$  for **1a–1d** calculated for the  $S_1$  optimal structures at the DKH CAM-B3LYP/def2-TZVP and def2-SVP levels in water as a polarizable continuum.

Cy7	SOCME $T_2-S_1$		SOCME $T_1-S_1$	
	def2-TZVP	def2-SVP	def2-TZVP	def2-SVP
<b>1a</b>	0.010	0.010	0.000	0.000
<b>1b</b>	0.432	0.425	0.054	0.054
<b>1c</b>	0.037	0.030	0.010	0.010
<b>1d</b>	0.000	0.000	0.000	0.000



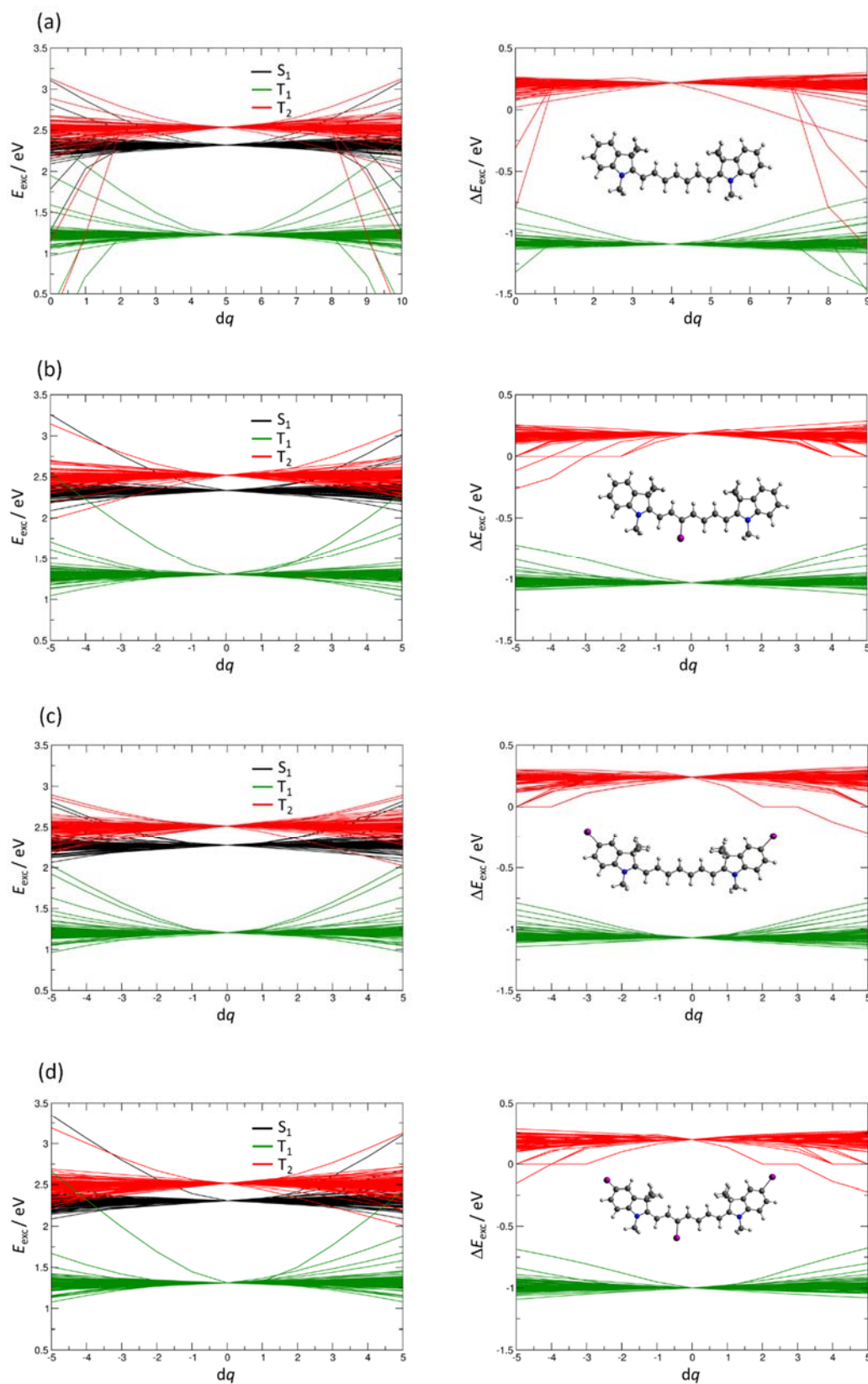
**Figure S47.** Spin-orbit coupling matrix elements (SOCMEs) at the DKH CAM-B3LYP/def2-SVP level in water as a polarizable continuum between the  $T_1$  and  $S_1$  states for **1a** (a), **1b** (b), **1c** (c), and **1d** (d) along all normal modes  $q_i$ . The  $dq$  values are given in units of a dimensionless normal-mode coordinate displacement.



**Figure S48.** Frontier molecular orbitals for **1d** for  $dq = 5$  (the values are given in units of a dimensionless normal-mode coordinate displacement) along an out-of-plane normal mode  $\omega_{80}$  ( $941.93 \text{ cm}^{-1}$ ) at CAM-B3LYP/def2-SVP level. The contour threshold is set to 0.02 a.u. to better illustrate the contribution of orbitals on the iodine atom (C3' position).

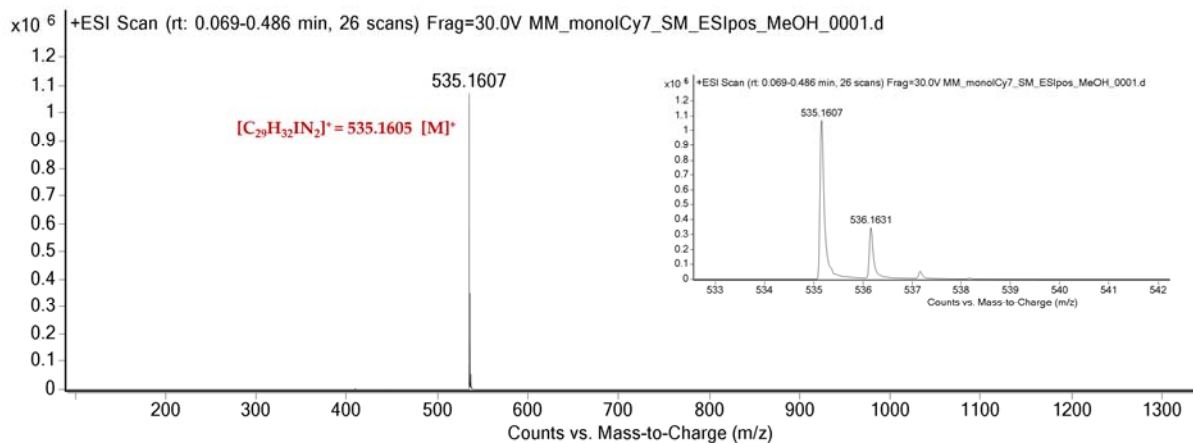
**Table S6.** SOCMEs in  $\text{cm}^{-1}$  for **1b** calculated for the optimal structures at the DKH CAM-B3LYP/ def2-TZVPP, def2-TZVP, and def2-SVP levels in water as a polarizable continuum.

Cy7	SOCME T <sub>2</sub> -S <sub>1</sub>			SOCME T <sub>1</sub> -S <sub>1</sub>		
	def2-TZVPP	def2-TZVP	def2-SVP	def2-TZVPP	def2-TZVP	def2-SVP
<b>1b</b>	0.071	0.244	0.472	0.020	0.037	0.079

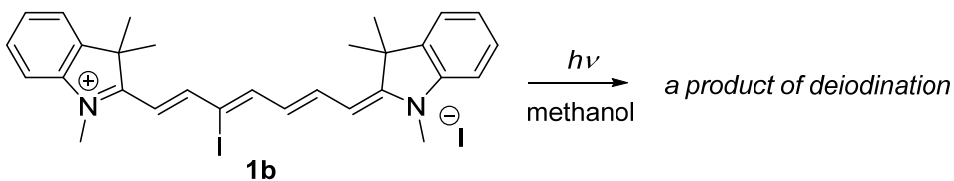
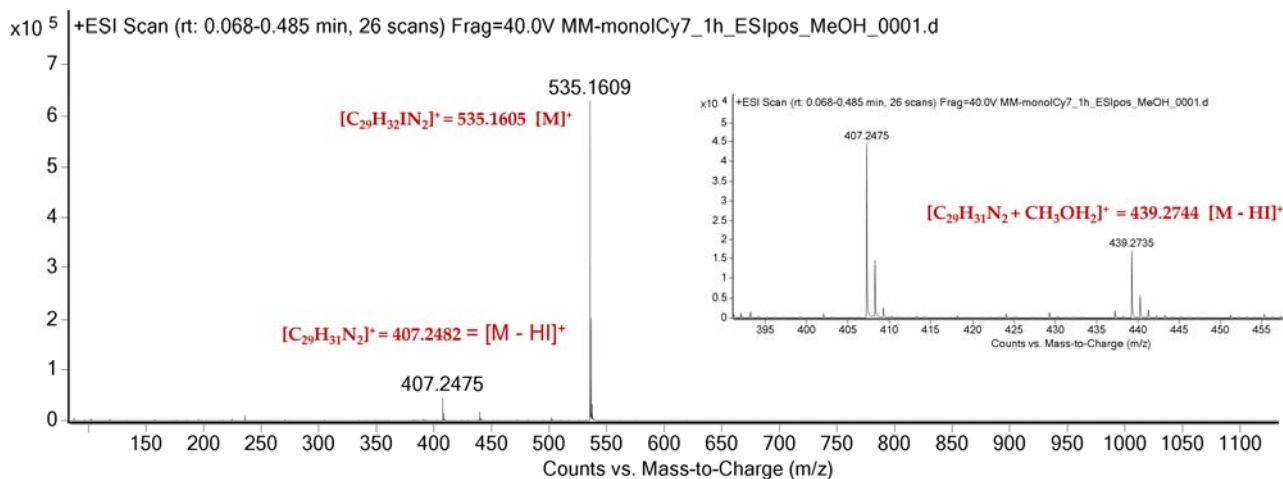


**Figure S49.** TDDFT energies at the DKH CAM-B3LYP/def2-SVP level in water as a polarizable continuum of the  $S_1$ ,  $T_1$ , and  $T_2$  states and energy differences between the  $S_1$  and  $T_1$  and  $S_1$  and  $T_2$  states along all vibrational modes for **1a** (a), **1b** (b), **1c** (c), and **1d** (d).

(a) Starting material (**1b**)



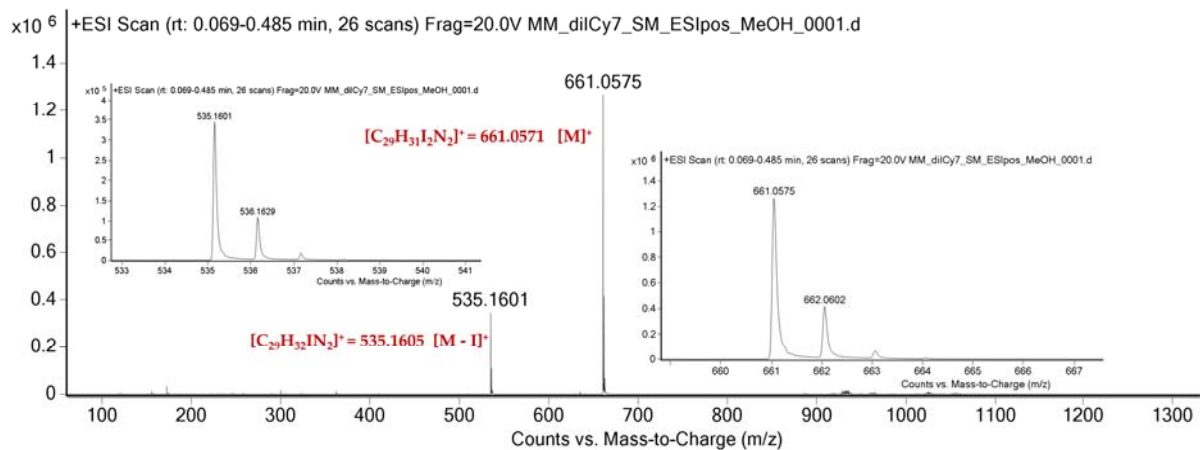
(b) Irradiated mixture



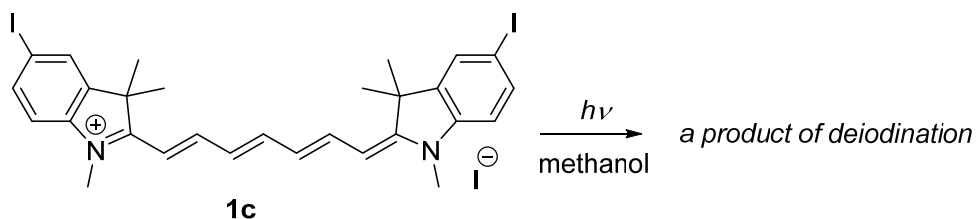
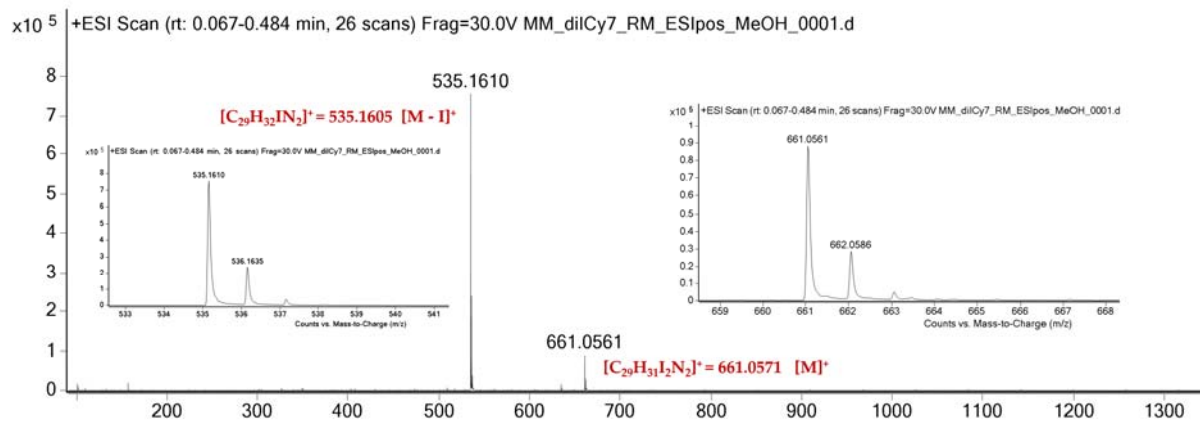
**Figure S50.** Irradiation of **1b** in methanol ( $c(\text{init}) = 5 \times 10^{-6}$  M) using 700 nm LEDs: (a) **1b** before irradiation; (b) the formation of a product of deiodination (accompanied by the loss 2 H atoms) as a major detectable photoproduct (at  $\sim 50\%$  reaction conversion).



(a) Starting material (**1c**)



(b) Irradiated mixture



**Figure S51.** Irradiation of **1c** in methanol ( $c(\text{init}) = 5 \times 10^{-6}$  M) using 700 nm LEDs: (a) **1c** before irradiation (partial deiodination detected during the MS analysis); (b) the formation of a monodeiodinated Cy7 as a major detectable photoproduct (at a complete reaction conversion).