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Supporting Information

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Designing Excited States: Theory-Guided Access to Efficient Photosensitizers for Photodynamic Action**

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Computational Details

Geometries were fully optimized with the *ab initio* Complete Active Space Self Consistent Field (CASSCF)[1] methodology and B3LYP Density Functional[2,3,4] employing CEP-31G (SBKJC) and cc-pVDZ basis sets.[5,6] Harmonic vibrational frequencies were computed to assure that the species did not possess any imaginary frequencies and hence correspond to true minima. After a number of trial and error the active space in the CASSCF calculations were established as 6 electrons distributed over 6 valence orbitals (6,6) for the 8,2' dimer **3** and 4 electrons distributed over 4 valence orbitals (4,4) for the 8,8' dimer **6** and. Enlarged active spaces up to 12,12 also reproduced the key features presented in the main text. For the sake of consistency a 6 electrons in 6 orbitals CAS is used for both dimers. Geometries of excited states T_1 and S_1 were also fully optimized. Natural orbitals of the CASSCF wavefunction and configuration state function coefficients were analyzed to understand the nature of the electronic state as being a single electron HOMO → LUMO type or multiply substituted type. Whereas Bodipy core S_1 is a clean HOMO → LUMO dominated $\pi\pi^*$ state, S_1 states of **3** and **6** are drastically different and showed a large degree of multi-reference character. Gaussian 03[7] suite was mainly used for the DFT calculations, CASSCF calculations were mainly performed with MOLCAS[8], and GAMESS-US[9] programs.

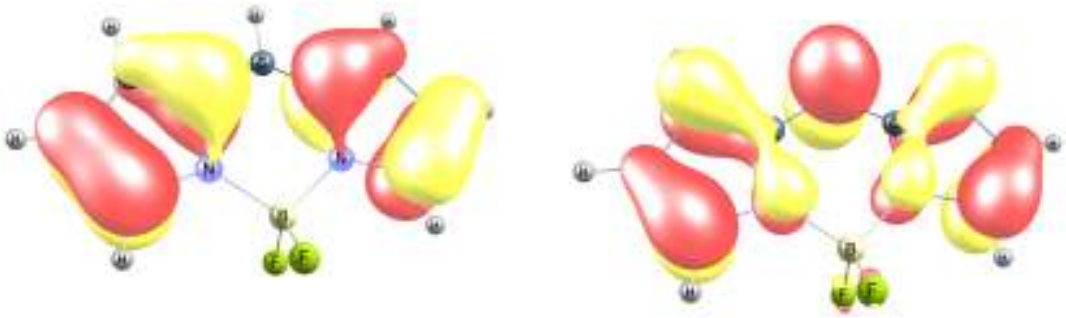


Figure S1. Frontier molecular orbitals. HOMO (left) LUMO (right), of the parent Bodipy core at B3LYP/6-31G(d,p) level of theory. Surfaces are plotted at 0.2 a.u.

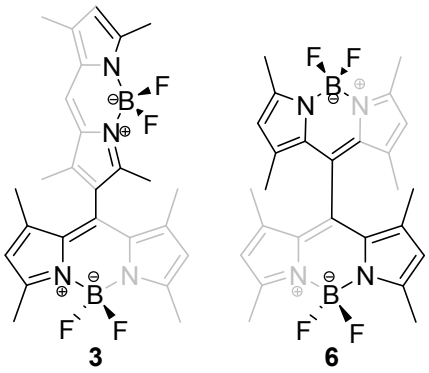


Figure S2. Orthogonal Bodipy Dimers, **3** and **6**, Investigated in the Computational Work

Table S1. CASSCF and B3LYP Total Energies (Hartree) of Dimers for S_0, S_1, and T_1 States

Description	Species	S_0 (AU) CAS(6,6)/CEP-31G	S_1 (AU) CAS(6,6)CEP-31G	T_1 (AU) CAS(6,6)/CEP-31G	S_0 (AU) B3LYP/CEP-31G
8,2' dimer	**3**	-298.348771	-298.219017	-298.273883	-305.669947
8,8' dimer	**6**	-298.319915	-298.184341	-298.253988	-305.665073

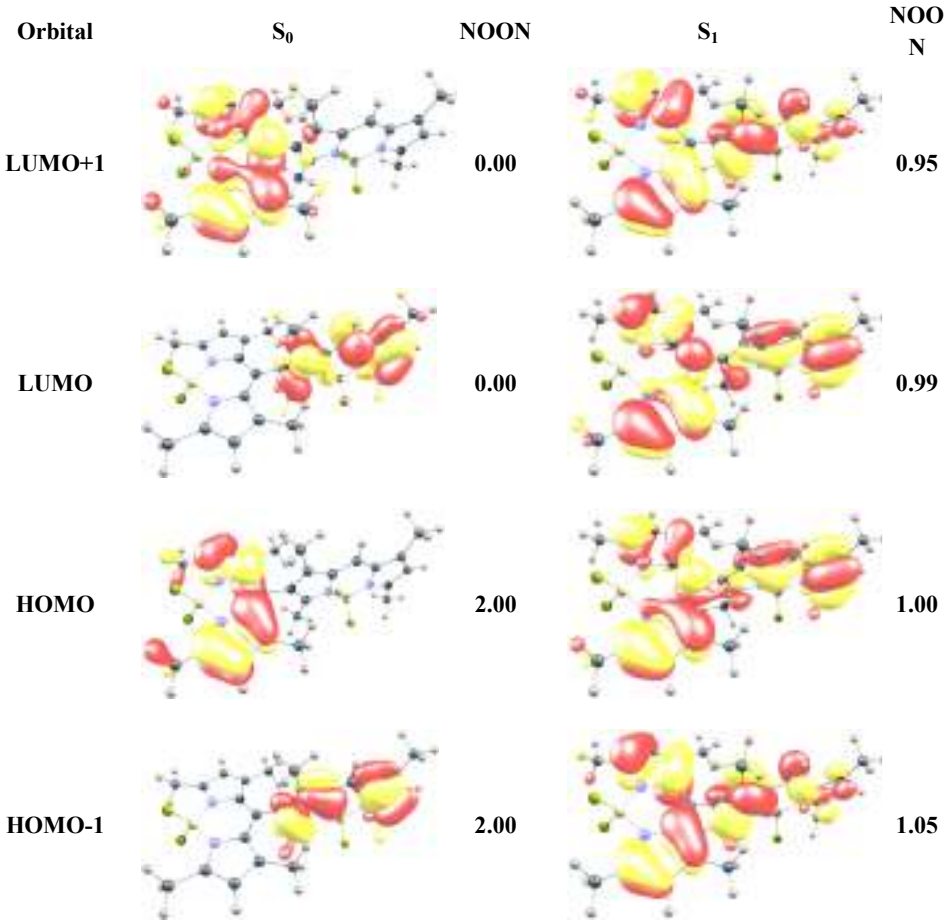


Figure S3. Frontier orbital plots and natural orbital occupation numbers (NOON) for the dimer **3**. a, S_0 state. b, S_1 state. a, b, Calculations were done at CAS(6e in 6o)/cc-pVDZ level. Surfaces are plotted at 0.2 a.u. All four orbitals in both states retain characteristics of Bodipy frontier orbitals and NOONs prove tetraradicalic character of S_1.

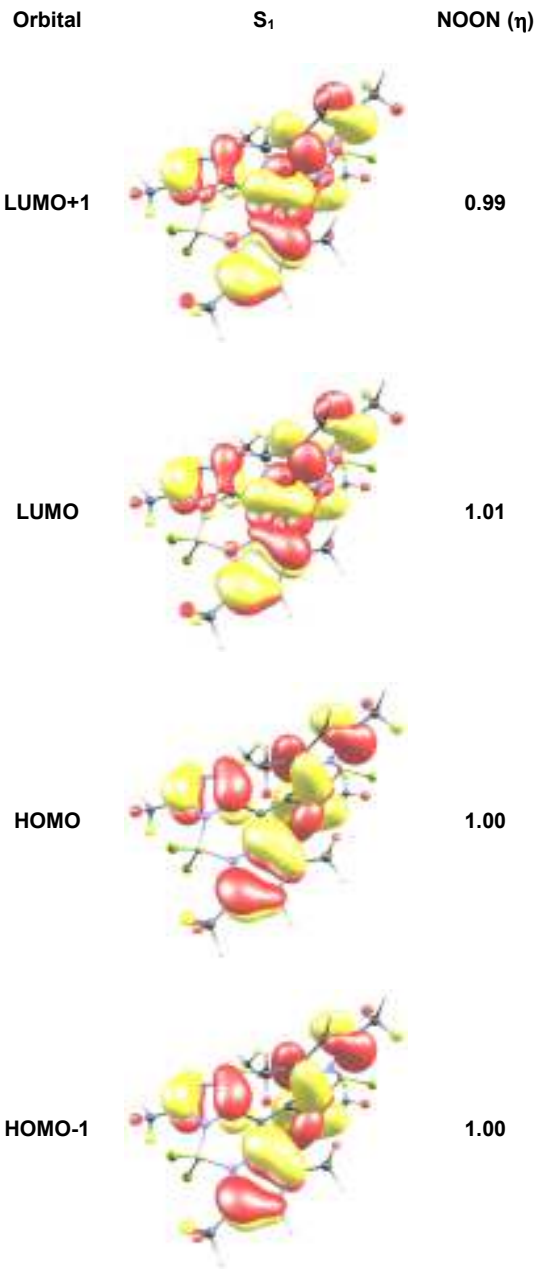


Figure S4. Frontier orbital plots and natural orbital occupation numbers (NOON) of S_1 of **6** at CAS(6e in 6o)/cc-pVDZ level. Surfaces are plotted at 0.2 a.u. It is clear that all the four orbitals in both states retain characteristics of BODIPY frontier orbitals and S_1 is a tetra-radical.

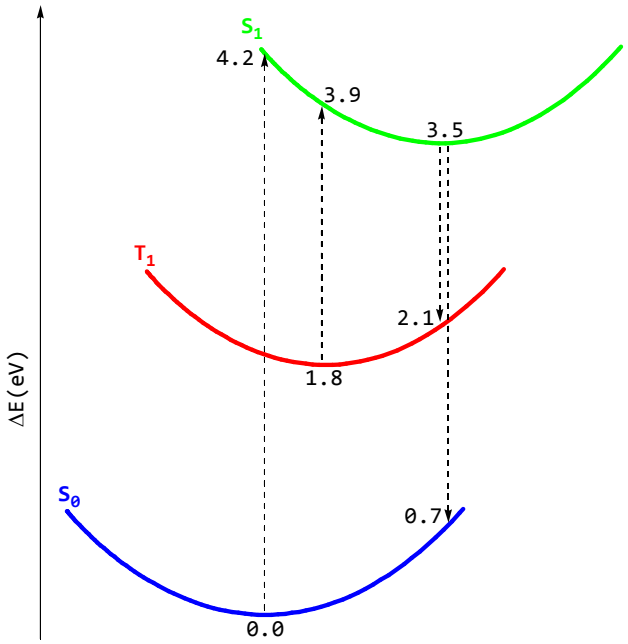


Figure S5. Relative energies (eV) of equilibrium structures of S_0, S_1, and T_1 states of **3.** Vertical transitions computed at CAS(6e in 6o)/cc-pVDZ level.

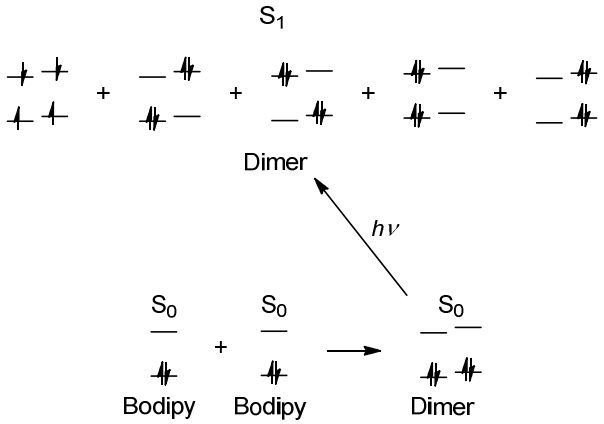


Figure S6. Conceptual frontier MO diagram describing the building up of S_1 states of the dimers **3** and **6** and dominance of doubly substituted configurations. Only the leading configurations are shown and minus signs to restrain antisymmetry in the S_1 states are intentionally excluded for clarity.As a result of spatial orthogonal arrangement HOMO and LUMO of both Bodipy cores are essentially kept in their original form (only slightly modified) in the dimers. Thus upon irradiation all the five configurations are almost equally probable and this picture is verified by CASSCF calculations. Each of the five configurations making up S_1 are termed as doubly substituted with respect to the closed shell reference S_0 state of the dimer.

CAS(6,6)/CEP-31G Cartesian Coordinates

Species 3, 8-2’ dimer, Electronic state S_0

	x(Å)	y(Å)	z (Å)
C	5.044983000	-3.636003000	-0.031147000
N	5.454190000	-2.270498000	-0.008230000
B	4.458420000	-1.061767000	0.013721000
N	3.031794000	-1.608684000	0.009672000
C	2.691955000	-2.970544000	-0.010428000
C	3.708297000	-3.965988000	-0.031769000
C	1.882888000	-0.878314000	0.024812000
C	0.785603000	-1.757875000	0.017690000
C	1.288545000	-3.086505000	-0.006018000
C	6.247167000	-4.451683000	-0.048930000
C	7.316042000	-3.575794000	-0.035801000
C	6.787903000	-2.218849000	-0.010087000
C	6.282912000	-5.965539000	-0.077031000
C	0.464835000	-4.358500000	-0.022347000
F	4.705407000	-0.244677000	-1.127358000
F	4.713604000	-0.281198000	1.178916000
C	-0.658400000	-1.377313000	0.024620000
C	-1.323176000	-1.216693000	1.233207000
N	-2.711879000	-0.887791000	1.254993000
B	-3.596589000	-0.708936000	-0.020393000
N	-2.719619000	-0.889470000	-1.244573000
C	-1.345869000	-1.209892000	-1.223163000
C	-3.128369000	-0.779285000	-2.537039000
C	-2.028820000	-1.023234000	-3.380544000
C	-0.897544000	-1.294670000	-2.568432000
C	-0.890065000	-1.306613000	2.634979000
C	-2.014683000	-1.033160000	3.407345000
C	-3.134212000	-0.777208000	2.516526000
C	0.483703000	-1.596060000	-3.124769000
C	0.491257000	-1.618030000	3.182190000
F	-4.650957000	-1.673106000	0.023948000
F	-4.193502000	0.586950000	0.019655000
H	3.423031000	-5.002808000	-0.048709000
H	8.358032000	-3.822940000	-0.043239000
H	7.310053000	-6.319338000	-0.084870000
H	5.787025000	-6.385888000	0.797247000
H	5.784899000	-6.353030000	-0.965144000
H	-0.219440000	-4.363441000	-0.868967000
H	1.092010000	-5.244003000	-0.089237000
H	-0.138965000	-4.439982000	0.880495000
H	-2.048634000	-1.002342000	-4.451534000
H	-2.068887000	-1.007422000	4.477239000
H	0.441320000	-1.586411000	-4.211437000
H	1.217977000	-0.857999000	-2.812265000
H	0.847908000	-2.571122000	-2.810452000
H	0.455320000	-1.628435000	4.269459000
H	0.851197000	-2.586654000	2.845023000
H	1.222413000	-0.874229000	2.876835000
C	7.585984000	-0.935779000	0.018045000
H	7.400241000	-0.394625000	0.942044000
H	8.645651000	-1.159678000	-0.055506000
H	7.298886000	-0.287705000	-0.804448000
C	1.867806000	0.633141000	0.041954000
H	2.375676000	1.030117000	-0.833095000
H	0.845547000	0.996601000	0.051382000
H	2.387317000	1.012037000	0.918306000
C	-4.553076000	-0.439569000	2.917166000
H	-5.252970000	-1.151899000	2.490767000
H	-4.640402000	-0.457673000	3.999633000
H	-4.828160000	0.546685000	2.554566000
C	-4.548236000	-0.447741000	-2.934623000
H	-4.629301000	-0.432235000	-4.017780000
H	-5.242577000	-1.184433000	-2.538665000
H	-4.841913000	0.523032000	-2.543976000

Species 3, 8-2’ dimer, Electronic state T_1

	x (Å)	y(Å)	z(Å)
C	5.069889000	-3.592887000	-0.020313000
N	5.445741000	-2.268316000	0.017653000
B	4.474705000	-1.083481000	0.061733000
N	3.048624000	-1.641845000	0.024432000
C	2.728943000	-2.983829000	-0.004063000
C	3.711096000	-3.992720000	-0.027222000
C	1.874104000	-0.898903000	0.036959000
C	0.772060000	-1.806377000	0.028530000
C	1.270912000	-3.105467000	-0.002616000
C	6.282125000	-4.416733000	-0.048918000
C	7.351989000	-3.527670000	-0.025838000
C	6.837131000	-2.194397000	0.016023000
C	6.293961000	-5.927510000	-0.095841000
C	0.522786000	-4.418351000	-0.043657000
F	4.703628000	-0.201359000	-1.042108000
F	4.676033000	-0.311981000	1.255543000
C	-0.667122000	-1.409375000	0.032157000
C	-1.340892000	-1.219074000	1.229239000
N	-2.719469000	-0.852491000	1.244200000
B	-3.593716000	-0.653936000	-0.034253000
N	-2.728745000	-0.880592000	-1.246431000
C	-1.362900000	-1.235199000	-1.233493000
C	-3.140919000	-0.778398000	-2.558488000
C	-2.066284000	-1.058493000	-3.392736000
C	-0.919137000	-1.352086000	-2.569869000
C	-0.915610000	-1.310914000	2.639495000
C	-2.024993000	-1.003257000	3.398078000
C	-3.129505000	-0.723919000	2.498450000
C	0.449738000	-1.707627000	-3.130261000
C	0.449676000	-1.667329000	3.189105000
F	-4.696488000	-1.569707000	0.036561000
F	-4.151482000	0.665905000	0.008782000
H	3.441440000	-5.028928000	-0.054361000
H	8.394033000	-3.776568000	-0.037361000
H	7.315525000	-6.299010000	-0.110431000
H	5.791167000	-6.353761000	0.773003000
H	5.786050000	-6.298722000	-0.986603000
H	-0.550637000	-4.252619000	-0.038572000
H	0.771654000	-4.980710000	-0.944081000
H	0.776414000	-5.043749000	0.813333000
H	-2.086666000	-1.053866000	-4.464275000
H	-2.085672000	-0.969147000	4.466317000
H	0.422848000	-1.625576000	-4.214596000
H	1.232671000	-1.044488000	-2.770002000
H	0.740683000	-2.727139000	-2.883375000
H	0.421747000	-1.644031000	4.274871000
H	0.754936000	-2.661169000	2.873098000
H	1.210813000	-0.968829000	2.852526000
C	7.588389000	-0.889764000	0.053338000
H	7.322613000	-0.321902000	0.941824000
H	8.657965000	-1.077661000	0.055135000
H	7.333082000	-0.278083000	-0.808629000
C	1.860622000	0.607707000	0.044828000
H	2.365707000	0.993614000	-0.837271000
H	0.840064000	0.975900000	0.058782000
H	2.395569000	0.990609000	0.910846000
C	-4.533163000	-0.345470000	2.897967000
H	-5.243634000	-1.053119000	2.481354000
H	-4.622071000	-0.330855000	3.979157000
H	-4.782365000	0.632908000	2.497610000
C	-4.556823000	-0.413661000	-2.943382000
H	-4.647224000	-0.401750000	-4.026251000
H	-5.266286000	-1.131135000	-2.538534000
H	-4.823779000	0.566596000	-2.556669000

Species 3, 8-2' dimer, Electronic state S_1

	x(Å)	y(Å)	z(Å)
C	5.089998000	-3.618033000	-0.017514000
N	5.475475000	-2.293504000	-0.004957000
B	4.504272000	-1.104033000	0.006369000
N	3.082223000	-1.659245000	0.001069000
C	2.761633000	-2.977575000	-0.010136000
C	3.729255000	-4.000763000	-0.019949000
C	1.879325000	-0.878429000	0.007943000
C	0.773816000	-1.767534000	0.001181000
C	1.279401000	-3.094935000	-0.009992000
C	6.293865000	-4.447424000	-0.026573000
C	7.371638000	-3.562437000	-0.018537000
C	6.861576000	-2.229429000	-0.005074000
C	6.302556000	-5.959217000	-0.041623000
C	0.490403000	-4.386574000	-0.020249000
F	4.729712000	-0.265984000	-1.136362000
F	4.729532000	-0.287885000	1.164912000
C	-0.668188000	-1.384714000	0.004556000
C	-1.383483000	-1.211519000	1.223683000
N	-2.728047000	-0.894071000	1.242299000
B	-3.606545000	-0.699394000	0.010584000
N	-2.729024000	-0.876547000	-1.224476000
C	-1.384892000	-1.196172000	-1.211434000
C	-3.164733000	-0.750923000	-2.538934000
C	-2.056411000	-0.998174000	-3.394926000
C	-0.935256000	-1.276727000	-2.616064000
C	-0.931941000	-1.308623000	2.626662000
C	-2.052518000	-1.041317000	3.410271000
C	-3.162325000	-0.785429000	2.558751000
C	0.452290000	-1.582828000	-3.144079000
C	0.456343000	-1.620889000	3.149108000
F	-4.685289000	-1.647837000	0.004198000
F	-4.210139000	0.601774000	0.020174000
H	3.448749000	-5.033951000	-0.029237000
H	8.412281000	-3.817001000	-0.021701000
H	7.323413000	-6.332963000	-0.045755000
H	5.796890000	-6.365823000	0.834829000
H	5.796229000	-6.348245000	-0.925643000
H	-0.154559000	-4.440681000	-0.896464000
H	1.143279000	-5.254706000	-0.028050000
H	-0.153173000	-4.455382000	0.855953000
H	-2.092478000	-0.967476000	-4.465175000
H	-2.087403000	-1.024280000	4.480868000
H	0.436283000	-1.547450000	-4.230926000
H	1.190021000	-0.863763000	-2.796754000
H	0.793914000	-2.572324000	-2.846658000
H	0.441068000	-1.601711000	4.236371000
H	0.798719000	-2.605489000	2.836701000
H	1.193121000	-0.896000000	2.812054000
C	7.621225000	-0.928801000	0.007771000
H	7.363409000	-0.346497000	0.889000000
H	8.689693000	-1.123000000	0.005705000
H	7.363193000	-0.328989000	-0.861566000
C	1.905944000	0.628984000	0.020369000
H	2.429306000	1.014466000	-0.851467000
H	0.889305000	1.011413000	0.023780000
H	2.429707000	1.000018000	0.898243000
C	-4.582525000	-0.451049000	2.932714000
H	-5.270327000	-1.181338000	2.513739000
H	-4.685575000	-0.439819000	4.013789000
H	-4.863158000	0.521088000	2.535116000
C	-4.584564000	-0.408570000	-2.906993000
H	-4.688268000	-0.381067000	-3.987721000
H	-5.273400000	-1.143879000	-2.498595000
H	-4.863288000	0.557979000	-2.494750000

Species 6, 8-8' dimer, Electronic state S_0

	x(Å)	y(Å)	z(Å)
C	0.390650000	0.429207000	0.002169000
C	0.515964000	1.518121000	-0.854859000
C	1.435397000	0.047727000	0.883447000
N	2.642916000	0.780963000	0.905929000
N	1.719800000	2.281946000	-0.861817000
B	2.950310000	1.999915000	0.044304000
C	1.548958000	-1.009600000	1.837643000
C	2.831882000	-0.882119000	2.412458000
C	3.477049000	0.226964000	1.818513000
C	-0.372793000	2.115693000	-1.841676000
C	0.315494000	3.187945000	-2.389010000
C	1.613780000	3.267240000	-1.760279000
C	-0.883331000	-0.368045000	-0.003794000
C	-0.997223000	-1.474224000	-0.885263000
N	-2.184443000	-2.239847000	-0.907414000
B	-3.414474000	-1.984282000	-0.044590000
N	-3.130158000	-0.754171000	0.861321000
C	-1.917104000	-0.005040000	0.853822000
C	-2.051157000	-3.231908000	-1.820376000
C	-0.771913000	-3.136134000	-2.414931000
C	-0.096283000	-2.038131000	-1.840086000
C	-3.969580000	-0.228549000	1.760399000
C	-3.330716000	0.904586000	2.388921000
C	-2.065879000	1.055424000	1.840784000
F	-3.712949000	-3.111373000	0.778129000
F	-4.563020000	-1.715260000	-0.848782000
F	3.209323000	3.149928000	0.849663000
F	4.094904000	1.777244000	-0.778268000
H	3.252364000	-1.513445000	3.168510000
H	-0.038410000	3.854051000	-3.149087000
H	-0.388217000	-3.790013000	-3.171373000
H	-3.774872000	1.513861000	3.149303000
C	2.700071000	4.279719000	-2.042573000
H	2.955980000	4.828673000	-1.140974000
H	3.602110000	3.785511000	-2.391962000
H	2.359735000	4.978030000	-2.800956000
C	-1.777401000	1.695785000	-2.234216000
H	-2.139184000	2.346552000	-3.025464000
H	-1.805317000	0.671846000	-2.596717000
H	-2.465620000	1.767346000	-1.395769000
C	0.550828000	-2.088338000	2.220842000
H	0.250045000	-2.686492000	1.365064000
H	1.003282000	-2.750884000	2.953642000
H	-0.349416000	-1.665806000	2.660615000
C	4.862247000	0.754348000	2.110486000
H	5.330430000	0.146550000	2.878850000
H	5.478026000	0.732320000	1.215411000
H	4.816816000	1.785214000	2.451321000
C	-1.074356000	2.135489000	2.232790000
H	-1.501075000	2.744993000	3.024557000
H	-0.140758000	1.713305000	2.594379000
H	-0.838863000	2.786052000	1.394287000
C	-5.354793000	-0.763351000	2.043267000
H	-5.963582000	-0.744928000	1.143877000
H	-5.305035000	-1.793613000	2.383723000
H	-5.830502000	-0.157579000	2.808366000
C	1.310031000	-1.611630000	-2.223715000
H	1.979653000	-1.602030000	-1.368078000
H	1.708263000	-2.308275000	-2.956372000
H	1.323064000	-0.617385000	-2.663814000
C	-3.130999000	-4.247243000	-2.112248000
H	-2.789729000	-4.932874000	-2.881924000
H	-3.378984000	-4.811976000	-1.217565000
H	-4.038936000	-3.755669000	-2.451218000

Species 6, 8-8' dimer, Electronic state T_1

	x(Å)	y(Å)	z(Å)
C	0.399017000	0.427821000	-0.004831000
C	0.533893000	1.525088000	-0.854675000
C	1.453884000	0.054914000	0.873595000
N	2.660827000	0.789950000	0.901912000
N	1.734440000	2.296020000	-0.857336000
B	2.966530000	2.009598000	0.042757000
C	1.569088000	-1.002623000	1.825125000
C	2.851420000	-0.875140000	2.404540000
C	3.495203000	0.236009000	1.814754000
C	-0.354808000	2.126628000	-1.836621000
C	0.327297000	3.207573000	-2.377322000
C	1.624616000	3.287780000	-1.748426000
C	-0.872143000	-0.369563000	-0.013639000
C	-1.023634000	-1.487232000	-0.875527000
N	-2.187531000	-2.231267000	-0.891548000
B	-3.418505000	-1.968177000	-0.028838000
N	-3.124579000	-0.755235000	0.849382000
C	-1.949501000	-0.028986000	0.845788000
C	-2.067744000	-3.259785000	-1.819999000
C	-0.780303000	-3.165760000	-2.415870000
C	-0.099853000	-2.082782000	-1.861982000
C	-4.004179000	-0.209708000	1.778400000
C	-3.364099000	0.903989000	2.387816000
C	-2.090782000	1.053100000	1.841003000
F	-3.723368000	-3.113335000	0.778160000
F	-4.568489000	-1.727670000	-0.851729000
F	3.233786000	3.158202000	0.849589000
F	4.109508000	1.787246000	-0.785350000
H	3.271217000	-1.506878000	3.160905000
H	-0.030139000	3.878036000	-3.132143000
H	-0.405948000	-3.828925000	-3.169173000
H	-3.802443000	1.520909000	3.145878000
C	2.706940000	4.306697000	-2.023619000
H	2.953208000	4.857701000	-1.120507000
H	3.614637000	3.818184000	-2.366295000
H	2.367725000	5.002849000	-2.784751000
C	-1.756564000	1.705088000	-2.236532000
H	-2.128769000	2.376801000	-3.005912000
H	-1.776035000	0.693204000	-2.632916000
H	-2.444152000	1.740723000	-1.395411000
C	0.575857000	-2.086924000	2.205756000
H	0.318586000	-2.718756000	1.359342000
H	1.012896000	-2.718968000	2.974814000
H	-0.349026000	-1.672235000	2.598661000
C	4.878936000	0.765731000	2.110391000
H	5.348121000	0.155452000	2.876417000
H	5.495908000	0.749579000	1.215904000
H	4.830919000	1.794923000	2.455969000
C	-1.086557000	2.124494000	2.220957000
H	-1.504678000	2.737314000	3.015765000
H	-0.152309000	1.699994000	2.579138000
H	-0.850914000	2.776567000	1.383162000
C	-5.380830000	-0.764759000	2.033968000
H	-5.973365000	-0.751774000	1.122602000
H	-5.320589000	-1.798609000	2.364652000
H	-5.880397000	-0.173119000	2.795186000
C	1.304075000	-1.640676000	-2.228280000
H	1.970576000	-1.644817000	-1.369719000
H	1.708611000	-2.322792000	-2.972031000
H	1.317844000	-0.638215000	-2.649587000
C	-3.162191000	-4.259372000	-2.087637000
H	-2.840612000	-4.961159000	-2.851272000
H	-3.411729000	-4.804617000	-1.180857000
H	-4.066499000	-3.755975000	-2.420329000

Species 6, 8-8' dimer, Electronic state S_1

	x(Å)	y(Å)	z(Å)
C	0.394338000	0.415849000	0.004987000
C	0.572487000	1.540228000	-0.847994000
C	1.472927000	0.078198000	0.868797000
N	2.651833000	0.801007000	0.891351000
N	1.738074000	2.284673000	-0.850752000
B	2.955768000	2.018934000	0.026694000
C	1.605184000	-1.010519000	1.858644000
C	2.873619000	-0.869150000	2.420013000
C	3.521115000	0.247446000	1.825165000
C	-0.336833000	2.142636000	-1.844419000
C	0.351438000	3.225902000	-2.389192000
C	1.631454000	3.315598000	-1.778081000
C	-0.872893000	-0.377245000	-0.005828000
C	-1.040763000	-1.494547000	-0.870104000
N	-2.206232000	-2.238836000	-0.892969000
B	-3.434436000	-1.980114000	-0.028186000
N	-3.141045000	-0.769198000	0.849864000
C	-1.961951000	-0.046362000	0.847436000
C	-2.088387000	-3.262249000	-1.827260000
C	-0.801104000	-3.167716000	-2.422095000
C	-0.119407000	-2.089022000	-1.860196000
C	-4.021687000	-0.222938000	1.777317000
C	-3.381412000	0.888744000	2.388980000
C	-2.106254000	1.034454000	1.844252000
F	-3.736790000	-3.129007000	0.778459000
F	-4.589720000	-1.743410000	-0.847437000
F	3.248272000	3.161292000	0.846153000
F	4.120887000	1.788775000	-0.780398000
H	3.303947000	-1.492836000	3.177366000
H	-0.012226000	3.891323000	-3.145971000
H	-0.428259000	-3.827086000	-3.179699000
H	-3.820936000	1.506429000	3.145971000
C	2.731018000	4.313721000	-2.030600000
H	2.973492000	4.854200000	-1.119016000
H	3.637357000	3.809667000	-2.356802000
H	2.418627000	5.019986000	-2.794185000
C	-1.737284000	1.707422000	-2.228847000
H	-2.119675000	2.375829000	-2.997210000
H	-1.756970000	0.694957000	-2.625099000
H	-2.422205000	1.740005000	-1.384876000
C	0.597064000	-2.082711000	2.222746000
H	0.337629000	-2.706874000	1.370938000
H	1.021569000	-2.724311000	2.991848000
H	-0.327099000	-1.660785000	2.610542000
C	4.896324000	0.798027000	2.098511000
H	5.385704000	0.202531000	2.863581000
H	5.499390000	0.786652000	1.194021000
H	4.835258000	1.831059000	2.431717000
C	-1.102602000	2.103593000	2.229101000
H	-1.536466000	2.739267000	2.997906000
H	-0.183314000	1.678491000	2.624943000
H	-0.832657000	2.734332000	1.385451000
C	-5.400238000	-0.775337000	2.029302000
H	-5.992308000	-0.756025000	1.117710000
H	-5.343500000	-1.811171000	2.354467000
H	-5.898704000	-0.186186000	2.793430000
C	1.285716000	-1.651081000	-2.223958000
H	1.960400000	-1.691237000	-1.372099000
H	1.677133000	-2.313013000	-2.993382000
H	1.310506000	-0.635242000	-2.611170000
C	-3.184698000	-4.258341000	-2.101012000
H	-2.863011000	-4.958495000	-2.866366000
H	-3.438066000	-4.806106000	-1.196759000
H	-4.087101000	-3.751746000	-2.434077000

B3LYP/CEP-31G Cartesian Coordinates

Species 3, 8-2' dimer, Electronic state S_0

	x(Å)	y(Å)	z(Å)
C	4.515288000	-0.021710000	1.052163000
N	4.613167000	0.006135000	-0.369238000
B	3.395771000	0.025599000	-1.337848000
N	2.095828000	0.007257000	-0.485608000
C	2.056046000	-0.020401000	0.933921000
C	3.257277000	-0.034422000	1.685329000
C	0.802540000	0.016789000	-0.958459000
C	-0.100822000	-0.004908000	0.160225000
C	0.675482000	-0.028117000	1.353250000
C	5.859535000	-0.031691000	1.603525000
C	6.737643000	-0.009589000	0.493397000
C	5.943314000	0.013664000	-0.712347000
C	6.222814000	-0.060123000	3.079873000
C	0.155360000	-0.053417000	2.780553000
F	3.435788000	-1.126168000	-2.211902000
F	3.434565000	1.213700000	-2.162416000
C	-1.595429000	-0.002498000	0.084502000
C	-2.303408000	1.234799000	0.074778000
N	-3.729225000	1.253978000	0.031812000
B	-4.638518000	0.001675000	0.009066000
N	-3.732051000	-1.252873000	0.005945000
C	-2.306160000	-1.237750000	0.046871000
C	-4.163100000	-2.557873000	-0.029052000
C	-3.015965000	-3.422582000	-0.013567000
C	-1.847007000	-2.621114000	0.032756000
C	-1.841329000	2.617183000	0.095150000
C	-3.008488000	3.421985000	0.064509000
C	-4.157398000	2.560325000	0.026056000
C	-0.422426000	-3.157912000	0.052555000
C	-0.415833000	3.150504000	0.134347000
F	-5.507065000	-0.009453000	1.170865000
F	-5.483590000	0.014950000	-1.167873000
H	3.208287000	-0.055114000	2.774717000
H	7.823035000	-0.009497000	0.520565000
H	7.316585000	-0.059583000	3.206828000
H	5.819996000	0.819147000	3.613927000
H	5.825092000	-0.962297000	3.578390000
H	-0.481658000	-0.938306000	2.955744000
H	0.976062000	-0.073809000	3.514780000
H	-0.469056000	0.832810000	2.991293000
H	-3.052476000	-4.507537000	-0.037167000
H	-3.042700000	4.507267000	0.066488000
H	-0.441771000	-4.259388000	0.038794000
H	0.160672000	-2.817731000	-0.819171000
H	0.130429000	-2.835477000	0.950625000
H	-0.433312000	4.251869000	0.156693000
H	0.134967000	2.797705000	1.022188000
H	0.168221000	2.838403000	-0.747196000
C	6.423827000	0.042256000	-2.147478000
H	6.042331000	0.937224000	-2.665890000
H	7.523097000	0.043277000	-2.182085000
H	6.042851000	-0.831659000	-2.700989000
C	0.463058000	0.044790000	-2.433384000
H	0.878049000	-0.839856000	-2.944125000
H	-0.626743000	0.067425000	-2.575020000
H	0.912737000	0.926571000	-2.918514000
C	-5.619568000	2.952075000	-0.014032000
H	-6.161367000	2.522417000	0.844344000
H	-5.718547000	4.047630000	0.005068000
H	-6.102566000	2.558925000	-0.923520000
C	-5.626300000	-2.945341000	-0.073452000
H	-5.727308000	-4.040549000	-0.099003000
H	-6.160009000	-2.551243000	0.806952000
H	-6.116188000	-2.513265000	-0.961188000

Species 6, 8-8' dimer, Electronic state S_0

	x(Å)	y(Å)	z(Å)
C	0.399432000	0.419545000	0.010293000
C	0.530906000	1.534712000	-0.860257000
C	1.453501000	0.046408000	0.886779000
N	2.670155000	0.791622000	0.902814000
N	1.733665000	2.302176000	-0.864143000
B	2.970481000	2.032158000	0.026848000
C	1.576464000	-1.030650000	1.862394000
C	2.867801000	-0.895729000	2.431834000
C	3.521544000	0.231620000	1.826109000
C	-0.375195000	2.119487000	-1.842141000
C	0.317238000	3.221750000	-2.403985000
C	1.612022000	3.313845000	-1.787561000
C	-0.877629000	-0.381283000	-0.000087000
C	-0.999475000	-1.489251000	-0.881224000
N	-2.202481000	-2.255926000	-0.905470000
B	-3.449435000	-1.992504000	-0.026826000
N	-3.158869000	-0.759266000	0.862644000
C	-1.941602000	-0.014878000	0.867261000
C	-2.070690000	-3.260080000	-1.835703000
C	-0.768770000	-3.163778000	-2.436159000
C	-0.082295000	-2.066605000	-1.857268000
C	-4.020706000	-0.206630000	1.780649000
C	-3.373264000	0.914779000	2.403917000
C	-2.075255000	1.053711000	1.850813000
F	-3.735769000	-3.149152000	0.797909000
F	-4.608077000	-1.748478000	-0.861388000
F	3.246700000	3.182256000	0.864055000
F	4.138832000	1.795285000	-0.796262000
H	3.301884000	-1.529929000	3.198706000
H	-0.056671000	3.891531000	-3.172323000
H	-0.386269000	-3.827360000	-3.205639000
H	-3.815705000	1.542577000	3.171285000
C	2.707503000	4.323671000	-2.056921000
H	2.968115000	4.870092000	-1.135843000
H	3.626476000	3.818418000	-2.396458000
H	2.381715000	5.040145000	-2.825279000
C	-1.781344000	1.682593000	-2.228903000
H	-2.181961000	2.363119000	-2.996487000
H	-1.798184000	0.659175000	-2.638827000
H	-2.470230000	1.694894000	-1.368513000
C	0.561976000	-2.102076000	2.237113000
H	0.271816000	-2.719759000	1.371456000
H	0.991186000	-2.767453000	3.002535000
H	-0.365156000	-1.666555000	2.645106000
C	4.909035000	0.769792000	2.104956000
H	5.394945000	0.174684000	2.892122000
H	5.527868000	0.740949000	1.193100000
H	4.860882000	1.824247000	2.422028000
C	-1.064661000	2.120980000	2.247368000
H	-1.502210000	2.778596000	3.014760000
H	-0.142156000	1.681072000	2.661078000
H	-0.764927000	2.747428000	1.391299000
C	-5.412185000	-0.745475000	2.037442000
H	-6.022907000	-0.697142000	1.120858000
H	-5.370160000	-1.805815000	2.334797000
H	-5.903258000	-0.163464000	2.831175000
C	1.328574000	-1.627817000	-2.224325000
H	2.007152000	-1.645727000	-1.355898000
H	1.738121000	-2.303737000	-2.991268000
H	1.350756000	-0.601916000	-2.627811000
C	-3.163694000	-4.266764000	-2.126016000
H	-2.829767000	-4.977051000	-2.896641000
H	-3.435079000	-4.820810000	-1.212634000
H	-4.078408000	-3.757926000	-2.471620000

Experimental Details

General: ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DPX-400 (operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) in $CDCl_3$ solvent with tetramethylsilane as internal standard. All spectra were recorded at 25^{o}C and coupling constants (*J* values) are given in Hz. Chemical shifts are given in parts per million (ppm). Absorption spectra were performed by using a Varian Cary-100 and Varian Cary 5000 UV-VIS-NIR absorption spectrophotometer. Fluorescence measurements were conducted on a Varian Eclipse spectrofluometer. The Fluorescence decay measurements were carried out with the Horiba Jobin-Yvon Time-Resolved Fluorometer, Fluorolog FL-1057. The instrument response function was measured with an aqueous Ludox solution. Singlet oxygen phosphorescence around 1270 nm was determined by using Horiba Jobin-Yvon Fluoremeter with Hamamatsu NIR PMT module, model H-10330-75. The decays were analyzed with a multiexponential fitting function by iterative reconvolution and chi-square minimization. Mass spectra were recorded with Agilent Technologies 6224 TOF LC/MS and 6530 Accurate Mass Q-TOF LC/MS. Irradiation of photosensitizers **3**, **6**, **7** and Methylene Blue (MB) was accomplished by monochromatic light system composed of Spectral Products CM 110 1/8m monochromator, ASB-XE-175 Xenon light source, Newport Multi Function Optical Meter model 1835-C. Electrophoretic Light Scattering was performed with Malvern NanoZS zeta potential. Reactions were monitored by thin layer chromatography using Merck TLC Silica gel 60 F254. Silica gel column chromatography was performed over Merck Silica gel 60 (particle size: 0.040-0.063 mm, 230-400 mesh ASTM). 4,4-Difluoro-8-formyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (**4**)[10] and 4,4-Difluoro-8-formyl-2,6-diethyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (**5**)[10] were synthesized according to literature. All other reagents and solvents were purchased from suppliers and used without further purification. Micelle has been prepared with compound **3** according to the literature.[11] In singlet oxygen measurements 1,3-Diphenylisobenzofuran was used as a singlet oxygen trap in organic solvent measurements and was purchased from supplier. 2,2'-(Anthracene-9,10-diylbis(methylene))dimalonic acid was used a singlet oxygen trap in aqueous solvent and was synthesized according to the literature.[12]

Synthetic Details

Compound 1

Compound **1** was synthesized by modifying a literature procedure.[13] 250 mL 1,2-dichloroethane was deaerated by bubbling N_2. 2,4-dimethyl pyrrole (1 mL, 11.37 mmol), triethylorthoformate (0.95 mL, 5.69 mmol) and $POCl_3$ (0.58 mL, 6.25 mmol) were added to the deaerated solvent. Reaction was allowed to stir for 2 hours at room temperature. Then 11.5 mL NEt_3 and 11.5 mL $BF_3.OEt_2$ were added. After 1 hour the reaction was washed with water (3x250 mL), the organic layer separated, dried on $NaSO_4$ and evaporated *in vacuo*. Column chromatography with $CHCl_3$ yielded the pure product as reddish solid (400 mg, 28 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.09 (1H, s, Ar*H*), 6.10 (2H, s, Ar*H*), 2.60 (6H, s, C*H*$_3$), 2.29 (6H, s, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 156.8, 141.3, 133.5, 120.2, 119.1, 14.8, 11.2 ppm.

Compound 2

Compound **2** was synthesized by modifying a literature procedure.[14] 4 mL of DMF and 4 mL of $POCl_3$ was stirred in an ice bath for 5 min under argon. Then, warmed to room temperature and stirred for another 30 minutes. To this mixture, compound **1** (100 mg, 0.328 mmol) was added in dichloroethane (40 mL). The temperature was raised to 50 °C and the reaction mixture was stirred for 2 additional hours. The reaction mixture was cooled and poured into cold 150 mL saturated $NaHCO_3$ solution. The resulting mixture was stirred for further 30 min, the organic layer was washed with water (50 mL) 3 times. The organic layers was combined and dried over $NaSO_4$ and evaporated to dryness. The compound was purified by column chromatography by using chloroform as an eluant and the compound was obtained as reddish solid (95 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.02 (1H, s, C*H*O), 7.20 (1H, s, Ar*H*), 6.20 (1H, s, Ar*H*), 2.77 (3H, s, C*H*$_3$), 2.58 (3H, s, C*H*$_3$), 2.48 (3H, s, C*H*$_3$), 2.28 ppm (3H, s, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 185.5, 163.5, 157.2, 145.4, 140.6, 136.4, 131.1, 125.8, 122.0, 121.5, 15.2, 12.9, 11.5, 10.4 ppm; MS HRMS (TOF- ESI): *m*/z calcd for $C_{14}H_{15}BF_2N_2O^+$: 275.1246 $[M+H]^+$; found: 275.1212$[M+H]^+$, Δ = 12.3 ppm.

Compound 3

In N_2 bubbled 250 mL dichloromethane, 2,4-Dimethylpyrrole (50 µL, 0.478 mmol) and **2** (60 mg, 0.217 mmol) were mixed. 1 drop of trifluoroacetic acid was also added. The reaction mixture stirred at room temperature overnight. Then p-chloranil (49.2 mg, 0.217 mmol) was added to the reaction medium. After stirring 1 hour at room temperature, NEt_3 (2 mL) and $BF_3.OEt_2$ (2 mL) was added and stirred again for another 1 hour. The reaction was stopped by extracting with water (3x250 mL). Column chromatography with $CHCl_3$ yielded the pure product (20 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.18 (1H, s, Ar*H*), 6.15 (1H, s, Ar*H*), 6.02 (2H, s, Ar*H*), 2.61 (3H, s, C*H*$_3$), 2.59 (3H, s, C*H*$_3$), 2.57 (3H, s, C*H*$_3$), 2.54 (3H, s, C*H*$_3$), 2.40 (3H, s, C*H*$_3$), 2.30 (3H, s, C*H*$_3$), 2.12 (3H, s, C*H*$_3$), 1.72 ppm (3H, s, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 160.3, 155.8, 151.5, 143.7, 142.5, 136.6, 134.7, 133.4, 132.3, 131.7, 124.2, 121.3,

120.7, 120.5, 14.9, 14.7, 13.9, 12.7, 9.8, 8.7 ppm; MS HRMS (TOF-ESI): *m*/z calcd for $C_{26}H_{28}B_2F_4N_4^+$: 493.2436 $[M+H]^+$; found: 493.2417 $[M+H]^+$, Δ = 3.9 ppm. Extinction coefficient (ε); 119,400 $cm^{-1}mol^{-1}L$ in $CHCl_3$.

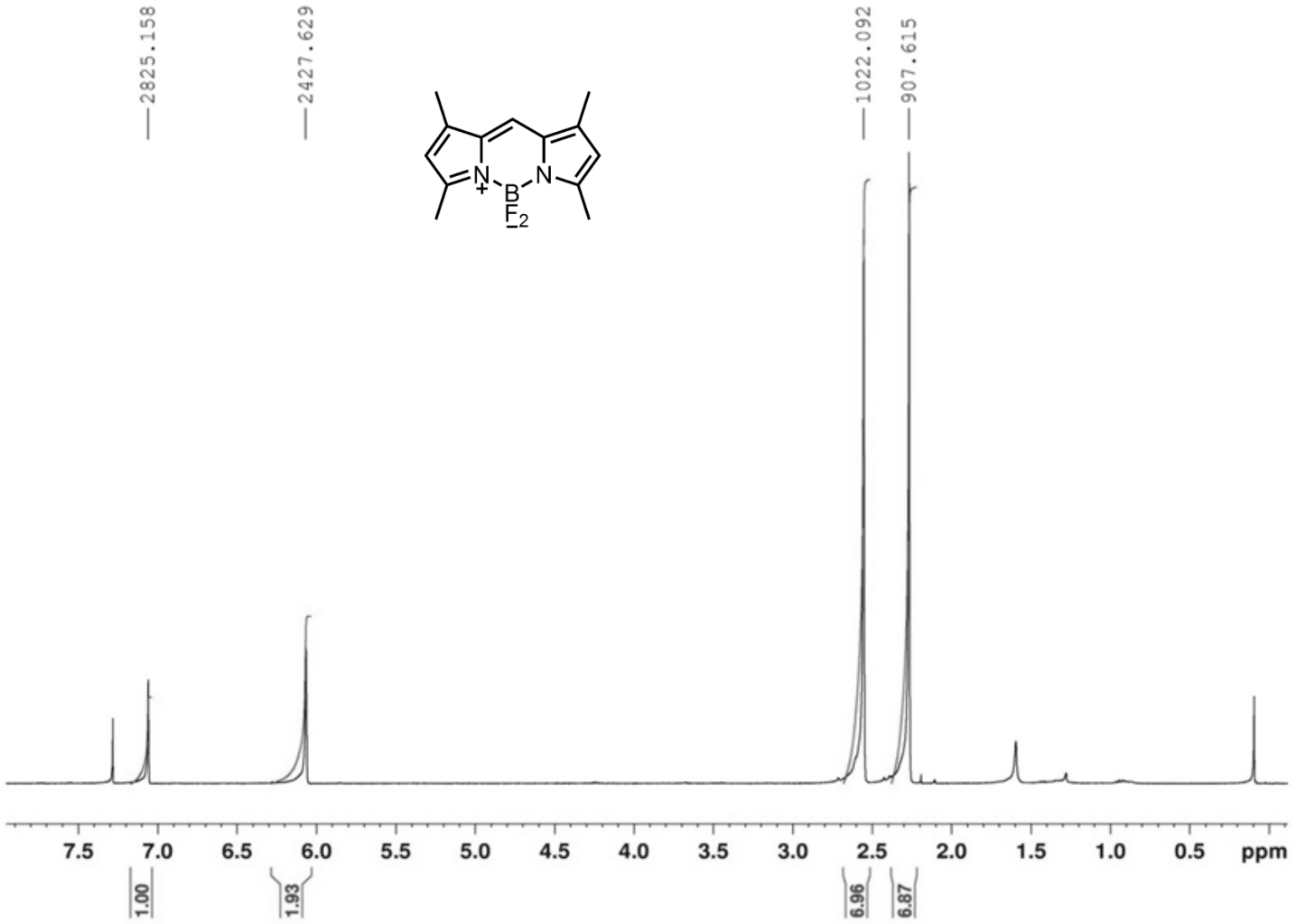
Compound 6

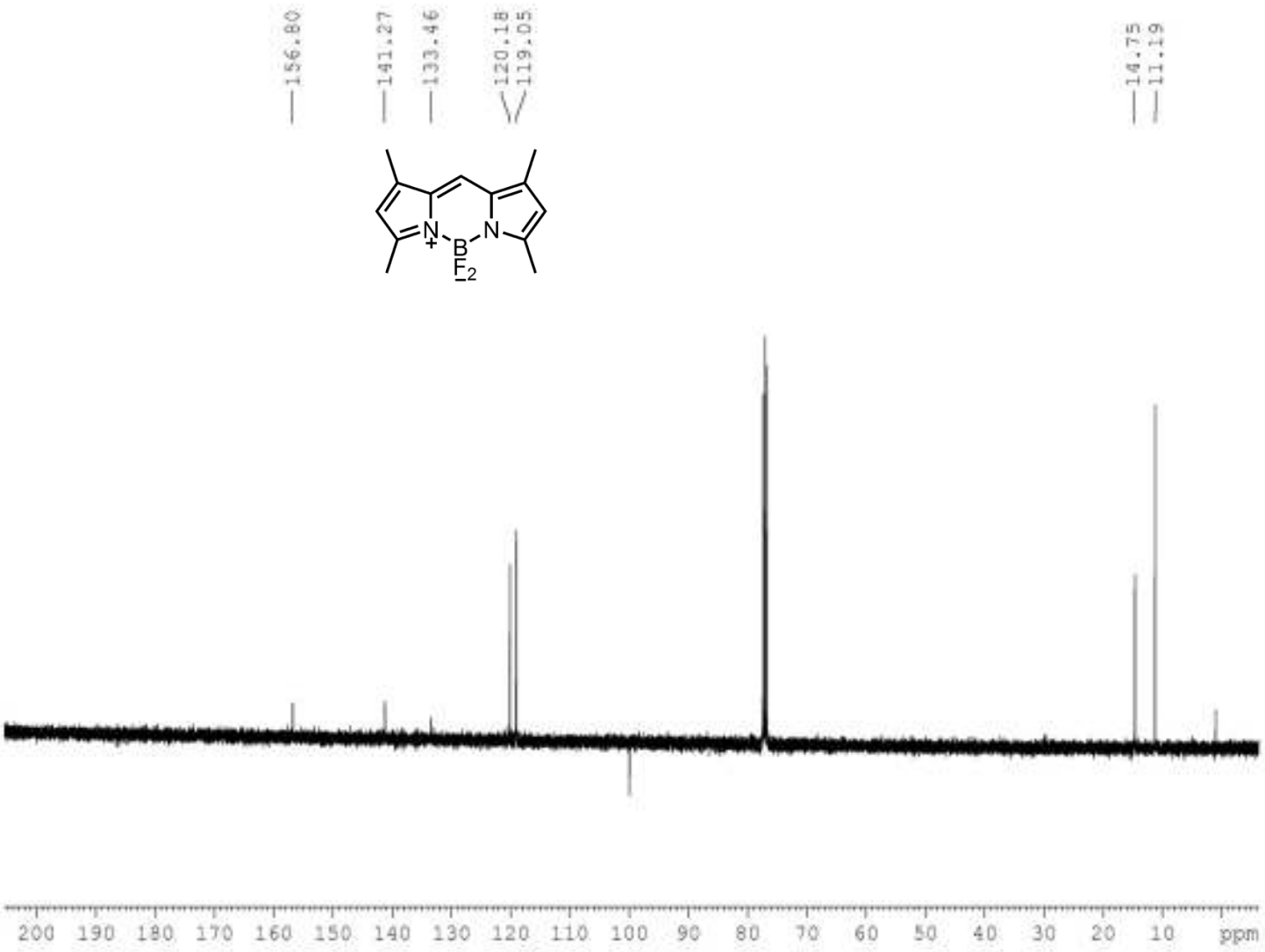
In N_2 bubbled 100 mL dichloromethane 2,4-Dimethylpyrrole (16.2 µL, 0.12 mmol) and **4** (20 mg, 0.06 mmol) were mixed. 1 drop of trifluoroacetic acid has been added. The reaction mixture was stirred at room temperature overnight. Then p-chloranil (14.8 mg, 0.06 mmol) was added to the reaction medium. After stirring 1 hour at room temperature, NEt_3 (1 mL) and $BF_3.OEt_2$ (1 mL) was added and stirred again for 1 hour. The reaction was stopped by extracting with water (3x100 mL). Column chromatography with $CHCl_3$ yielded the pure product (16 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.05 (4H, s, Ar*H*), 2.61 (12H, s, CH_3), 1.60 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 157.2, 142.6, 121.6, 14.8, 14.3 ppm; MS HRMS (TOF-APCI): *m*/z calcd for $C_{26}H_{28}B_2F_4N_4$: 493.2358 $[M-H]^-$; 493.2385 found: $[M-H]^-$, Δ = 5.5 ppm.

Compound 7

In N_2 bubbled 100 mL dichloromethane 2,4-Dimethylpyrrole (14.8 µL, 0.143 mmol) and **5** (18 mg, 0.065 mmol) were stirred together. 1 drop of trifluoroacetic acid was also added. The resulting reaction mixture was stirred at room temperature overnight. Then p-chloranil (16 mg, 0.065 mmol) was added to the reaction medium. After stirring 1 hour at room temperature, NEt_3 (1 mL) and $BF_3.OEt_2$ (1 mL) was added and stirring was continued for another hour. The reaction was stopped by extracting with water (3x100 mL). Column chromatography with $CHCl_3$ yielded the pure product (9 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.54 (12H, s, CH_3), 2.36 (8H, q, J = 11.3 Hz, CH_2,), 1.82 (12H, s, CH_3), 1.10 (12H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 155.1, 137.8, 134.8, 133.2, 129.9, 17.1, 14.7, 12.8, 11.6 ppm; MS HRMS (TOF-APCI): *m*/z calcd for $C_{34}H_{43}B_2F_4N_4$: 605.3610 $[M-H]^-$; found: 605.3618 $[M-H]^-$, Δ = 1.3 ppm.

^{1}H , ^{13}C NMR and Mass Spectra

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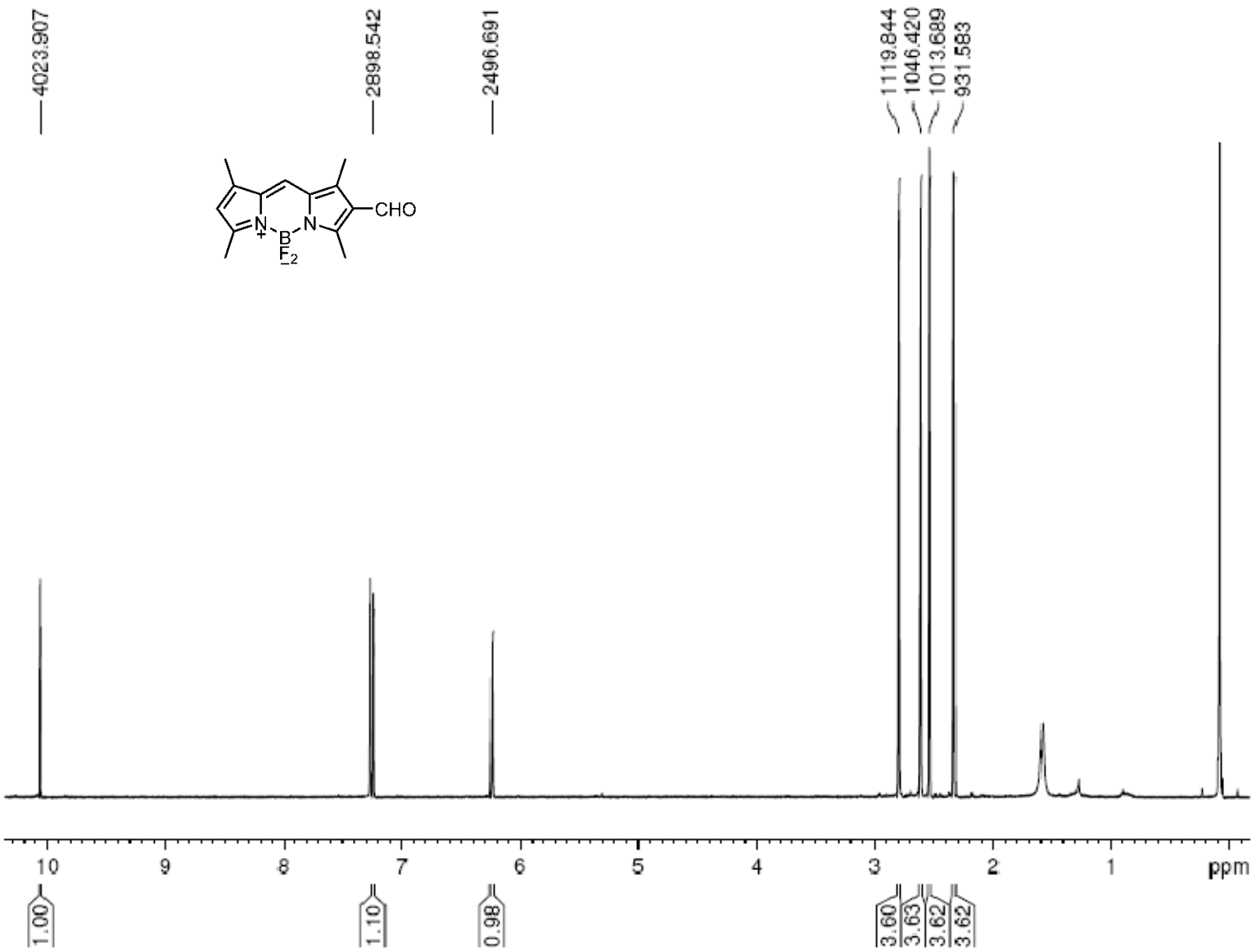
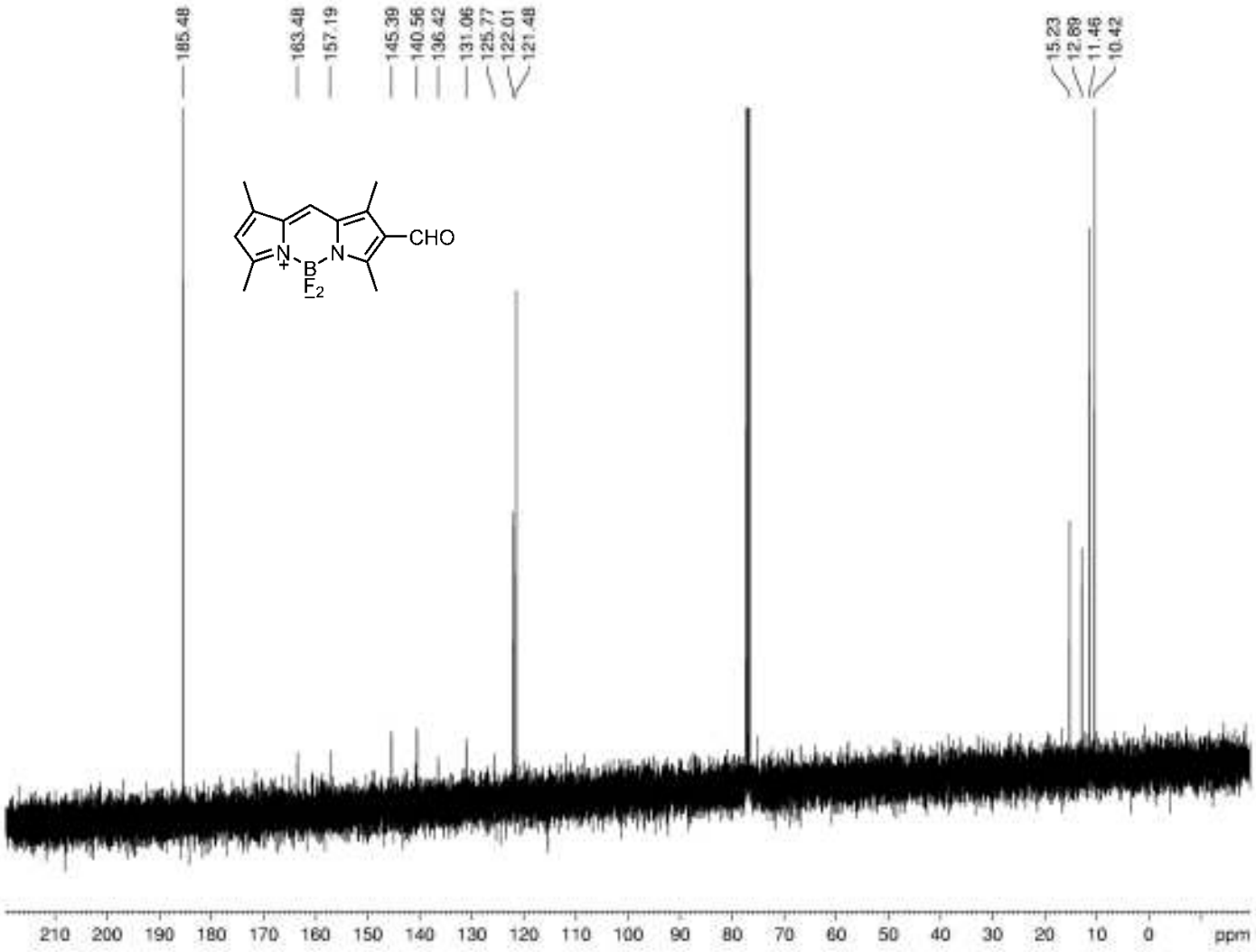
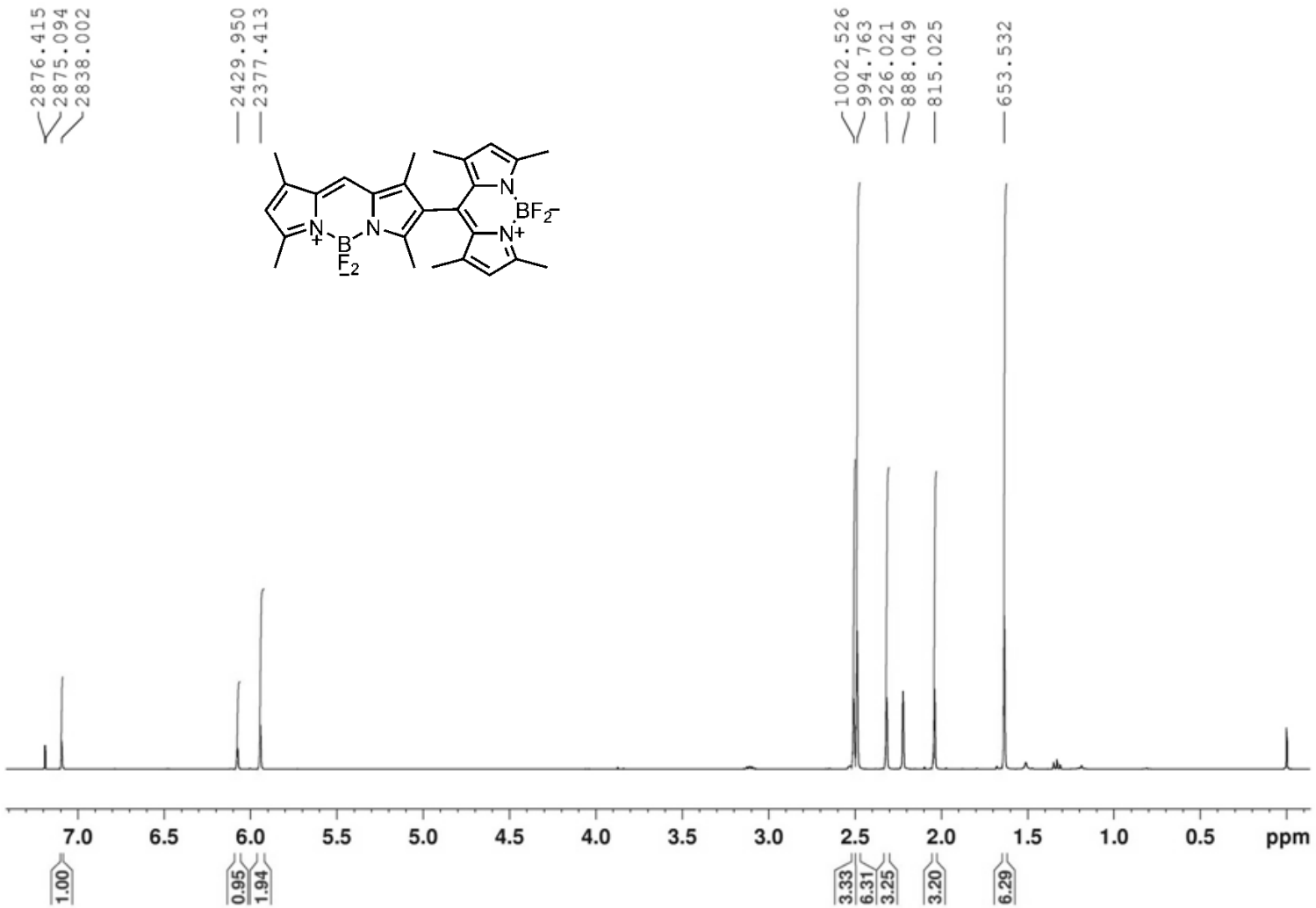
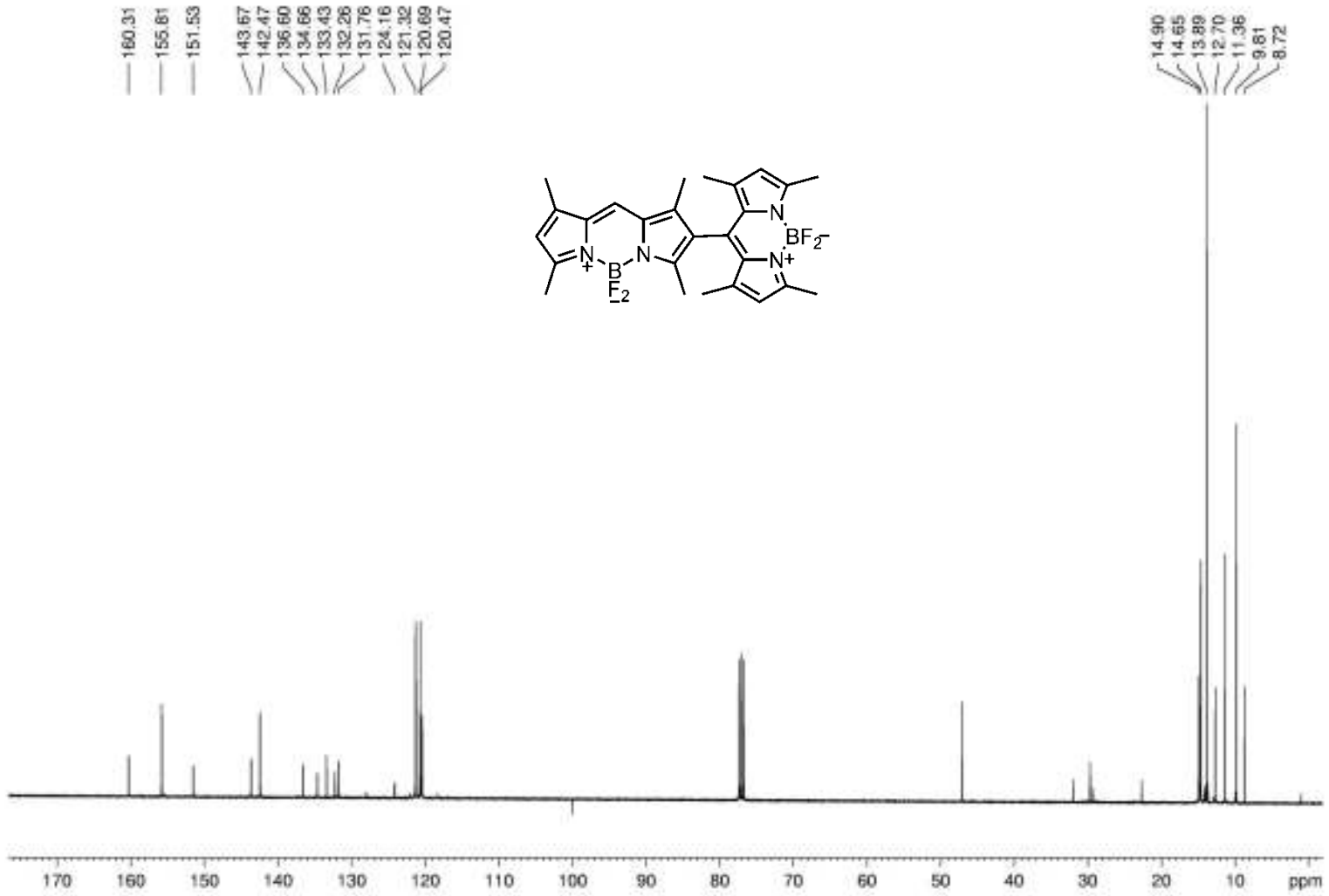
141.27
133.46
120.18
119.05
14.75
11.19
N
B
N
F2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


4023.907
2898.542
2496.691
1119.844
1046.420
1013.689
931.583
CHO
N
B
F2
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.10
0.98
3.60
3.63
3.62
3.62


185.48
163.48
157.19
145.39
140.56
136.42
131.06
125.77
122.01
121.48
15.23
12.89
11.46
10.42
CHO
N
B
N
F2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


2876.415
2875.094
2838.002
2429.950
2377.413
1002.526
994.763
926.021
888.049
815.025
653.532
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.95
1.94
3.33
6.31
3.25
3.20
6.29


160.31
155.61
151.53
143.67
142.47
136.60
134.66
133.43
132.26
131.76
124.16
121.32
120.69
120.47
14.90
14.65
13.89
12.70
11.36
9.81
8.72
N
BF2
N+
N
B
F2
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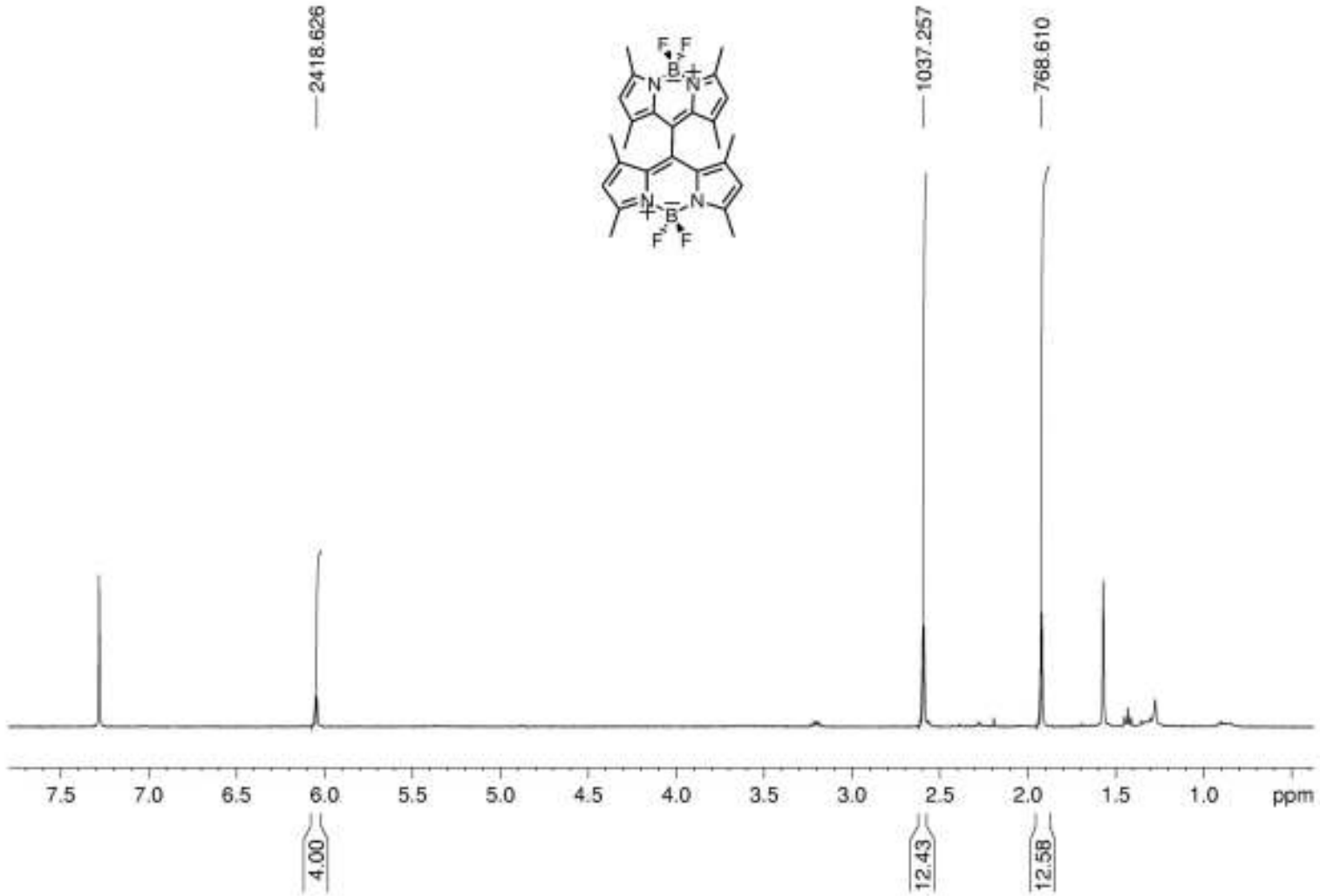
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


2418.626
1037.257
768.610
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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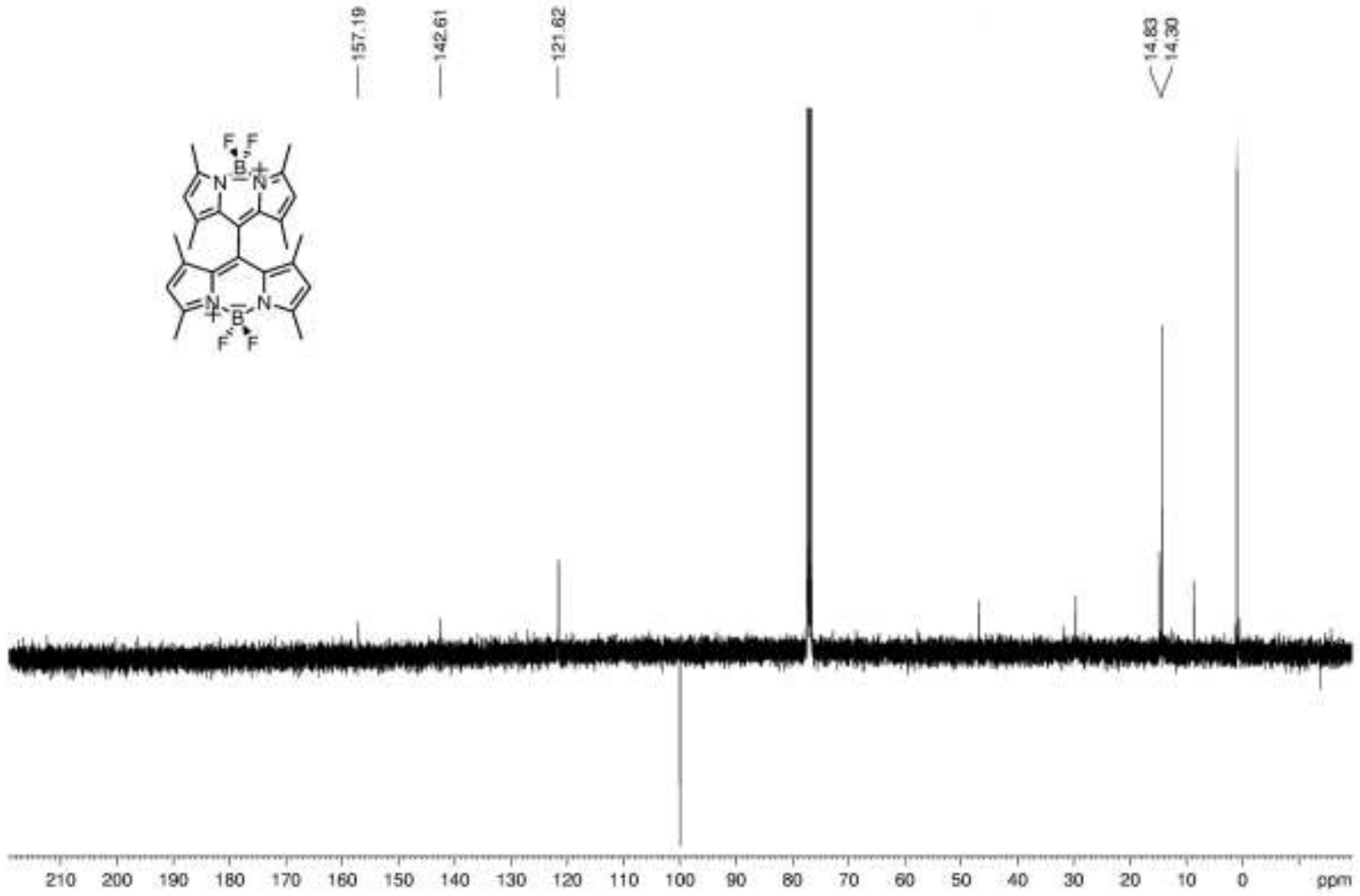
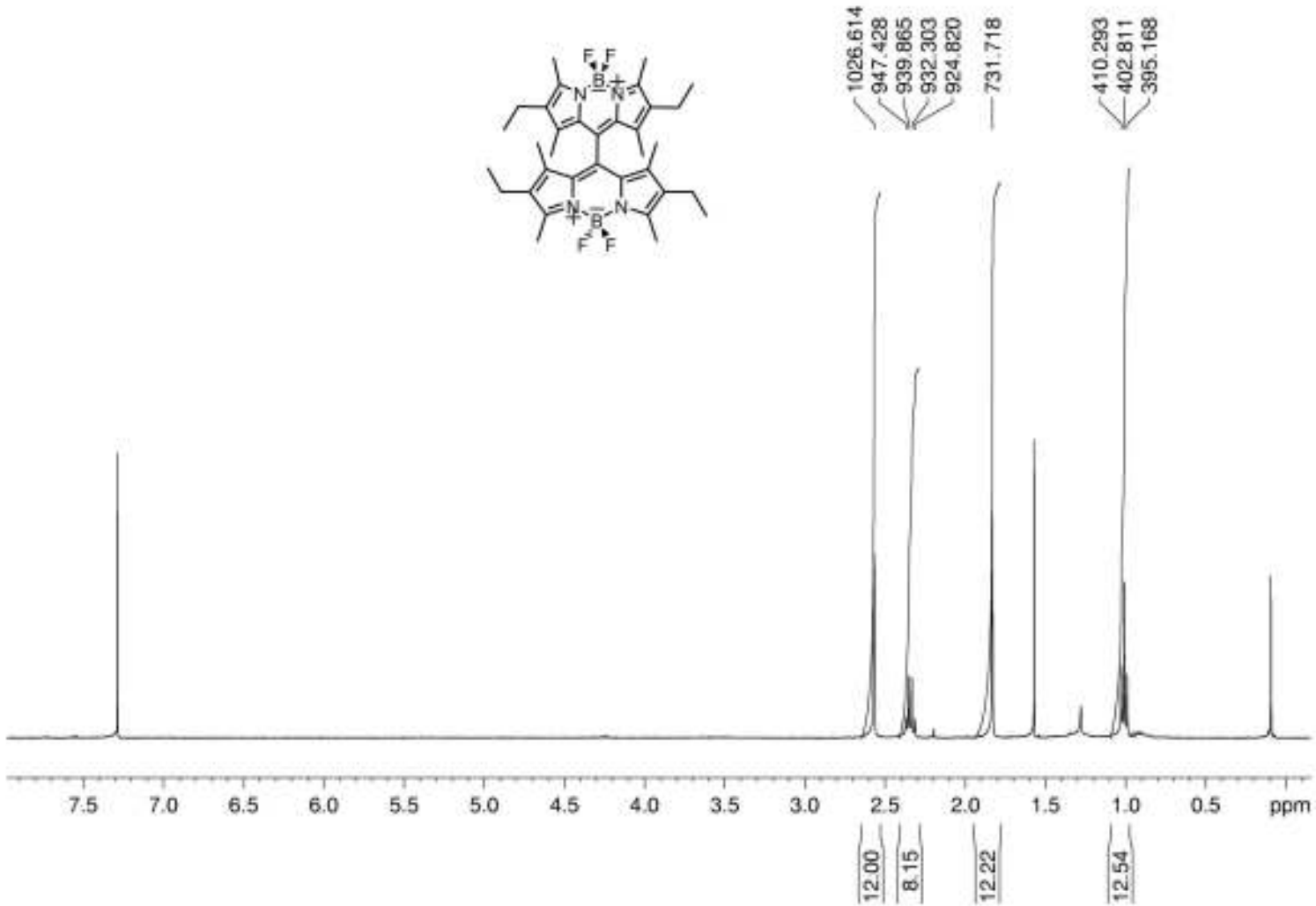
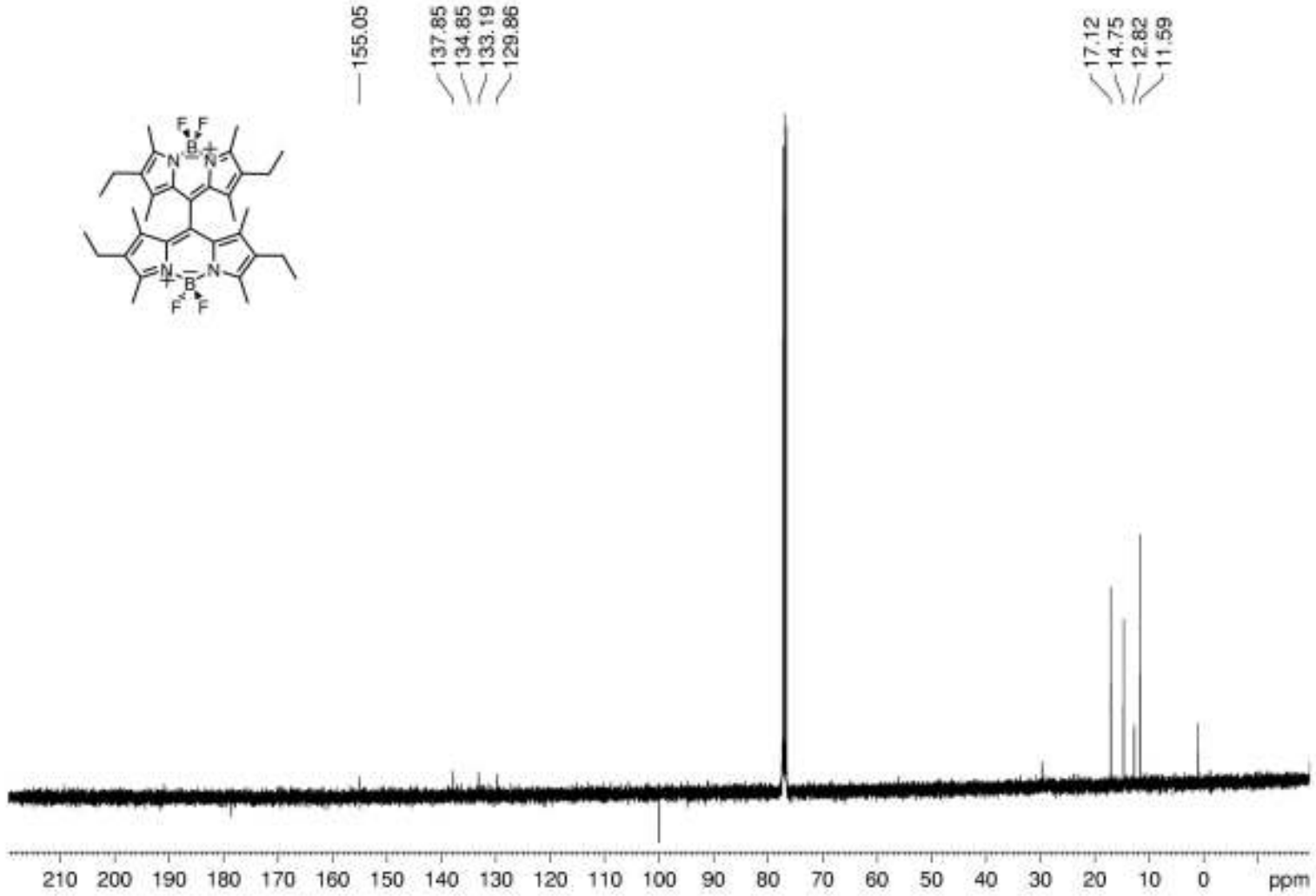
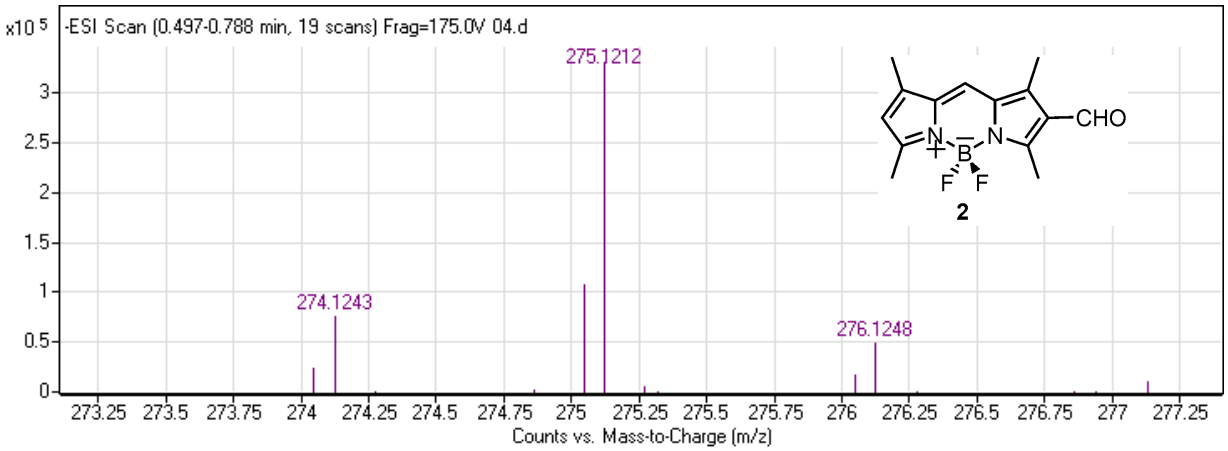
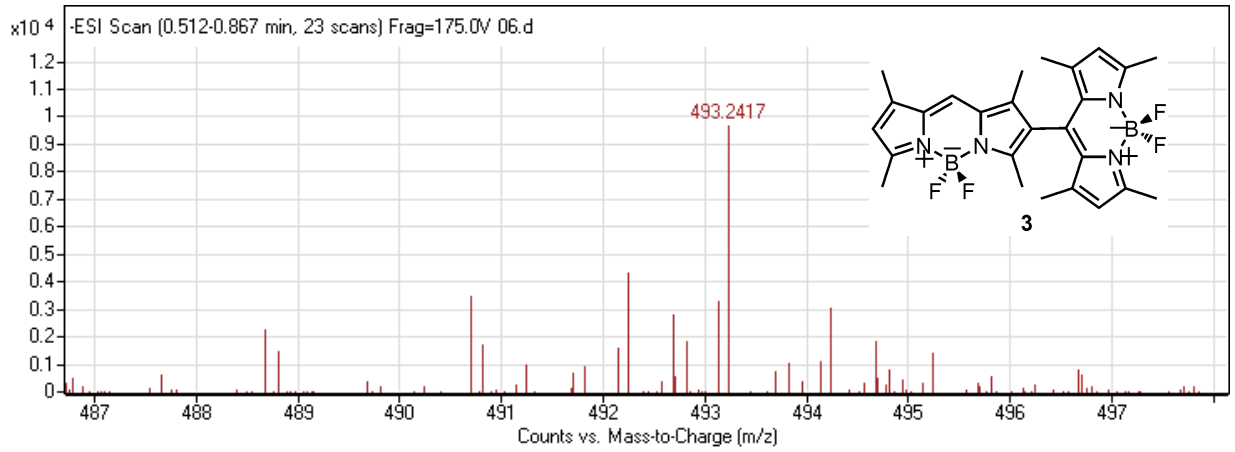
1.5
1.0
ppm
4.00
12.43
12.58

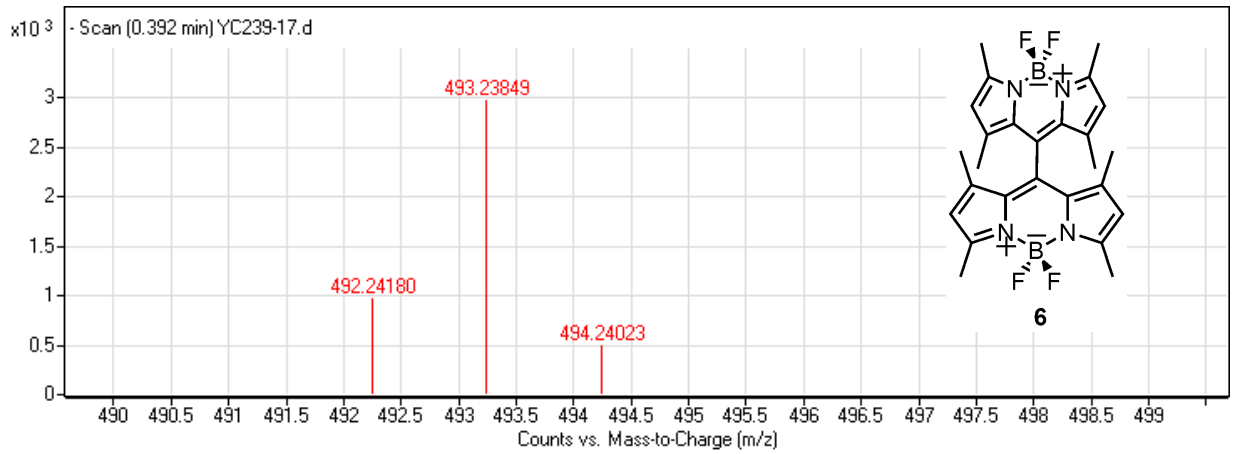

157.19
142.61
121.62
14.83
14.30
F
F
B
N
N
N
N
B
F
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

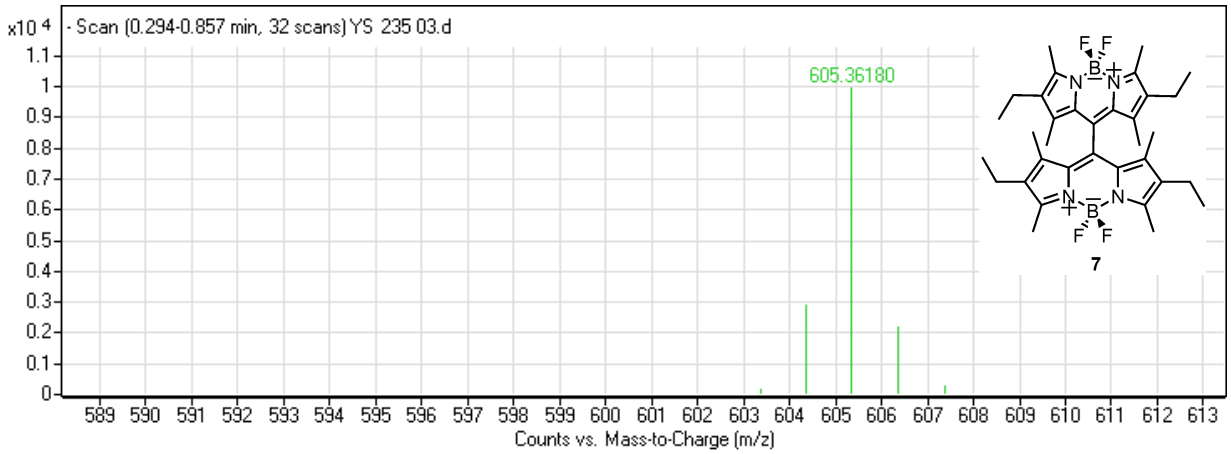

1026.614
947.428
939.865
932.303
924.820
731.718
410.293
402.811
395.168
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
12.00
8.15
12.22
12.54


155.05
137.85
134.85
133.19
129.86
17.12
14.75
12.82
11.59
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


x10 5
-ESI Scan (0.497-0.788 min, 19 scans) Frag=175.0V 04.d
275.1212
274.1243
276.1248
CHO
2
Counts vs. Mass-to-Charge (m/z)


x10 4
-ESI Scan (0.512-0.867 min, 23 scans) Frag=175.0V 06.d
493.2417
3
Counts vs. Mass-to-Charge (m/z)


x10 3
- Scan (0.392 min) YC239-17.d
493.23849
492.24180
494.24023
6
Counts vs. Mass-to-Charge (m/z)



Size distribution analysis

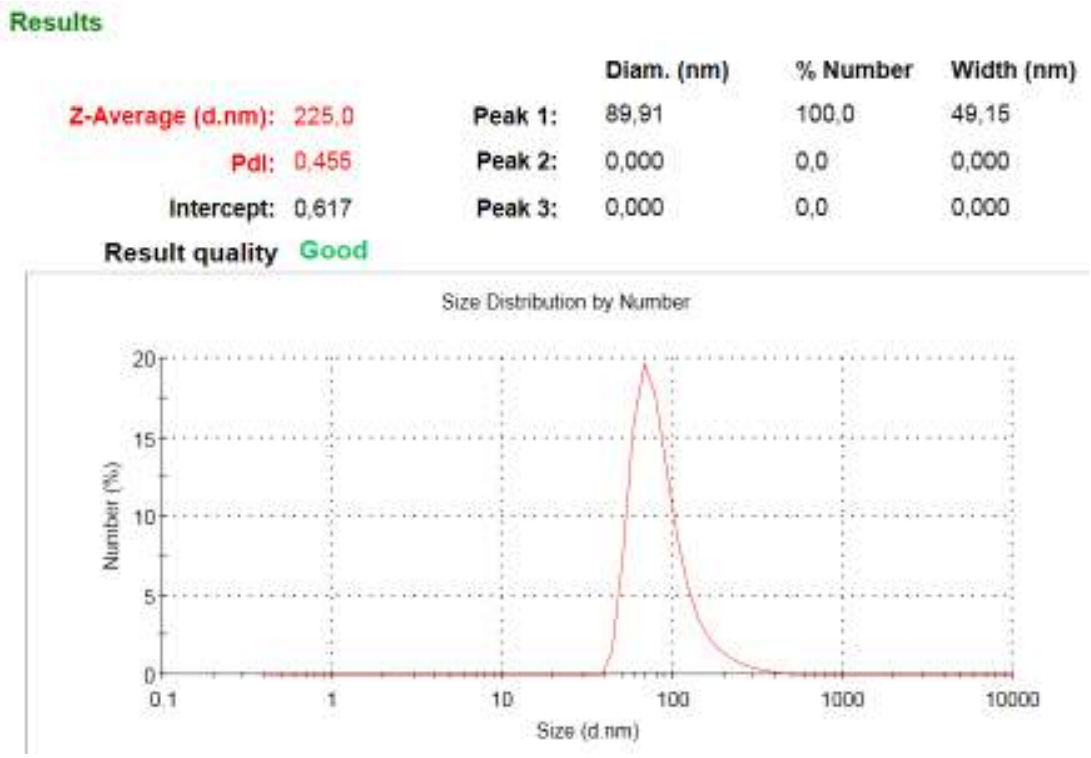


Figure S7. Size distribution of compound micellar compound **3.** Cremophor EL was used for micelle formation. Other information related with instrument is given in the Experimental Details.

Singlet oxygen measurements:

Singlet oxygen quantum yields were calculated according to the literature.[15] The relative quantum yields were calculated with reference to Methylene Blue (MB) in dichloromethane as 0.57.[15b] Air satutared DCM was obtained by bubbling air for 15 minutes. The absorbance of DPBF was adjusted around 1.0 in air saturated dichloromethane. Then, the photosensitizer was added to cuvette and photosentizer's absorbance was adjusted around 0.2-0.3. After, taking some measurements in dark, we exposed the cuvette to monochromatic light at the peak absorption wavelength for 20 seconds. Absorbance was measured for several times after each irradiation. The graphics recorded are shown below; Figures S9 to S12. Then, slope of absorbance maxima of DPBF at 414 nm versus time graph for each photosensitizer were calculated. Singlet oxygen quantum yield were calculated according to the equation:

$$\phi_{\Delta}\,(\mathrm{bod}) = \phi_{\Delta}(\mathrm{ref}) \times \frac{\mathrm{m\ (bod)}}{\mathrm{m\ (ref)}} \times \frac{\mathrm{F\ (ref)}}{\mathrm{F\ (bod)}} \times \frac{\mathrm{PF\ (ref)}}{\mathrm{PF}\ (bod)}$$

where *bod* and *ref* designate the "orthogonal bodipy photosensitizer" and "MB" respectively. *m* is the slope of difference in change in absorbance of DPBF (414 nm) with the irradiation time, *F* is the absorption correction factor, which is given by $\mathrm{F} = 1 - 10^{-\mathrm{OD}}$ (OD at the irradiation wavelength), and *PF* is absorbed photonic flux (μEinstein dm^{-3} s^{-1}).

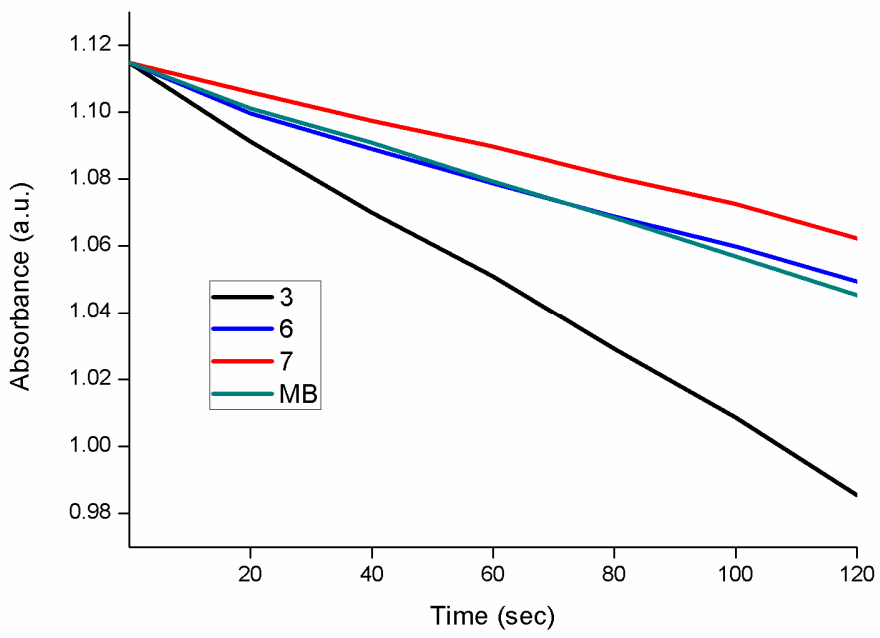


Figure S8. Comparative singlet oxygen generation experiment. Absorbance decrease of DPBF at 414 nm with time in dichloromethane in the presence of Bodipy photosensitizers: **3** (black), **6** (blue), **7** (red) and reference photosensitizer methylene blue (green).

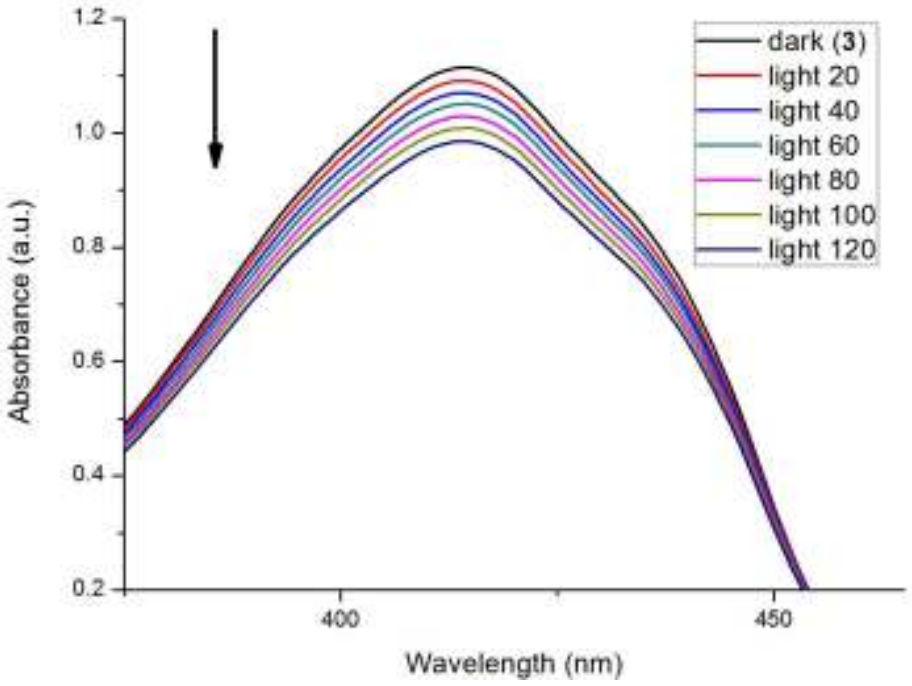


Figure S9. Decrease in absorbance of DPBF in dichloromethane in the presence of compound **3** in medium. Details are given in singlet oxygen measurements part.

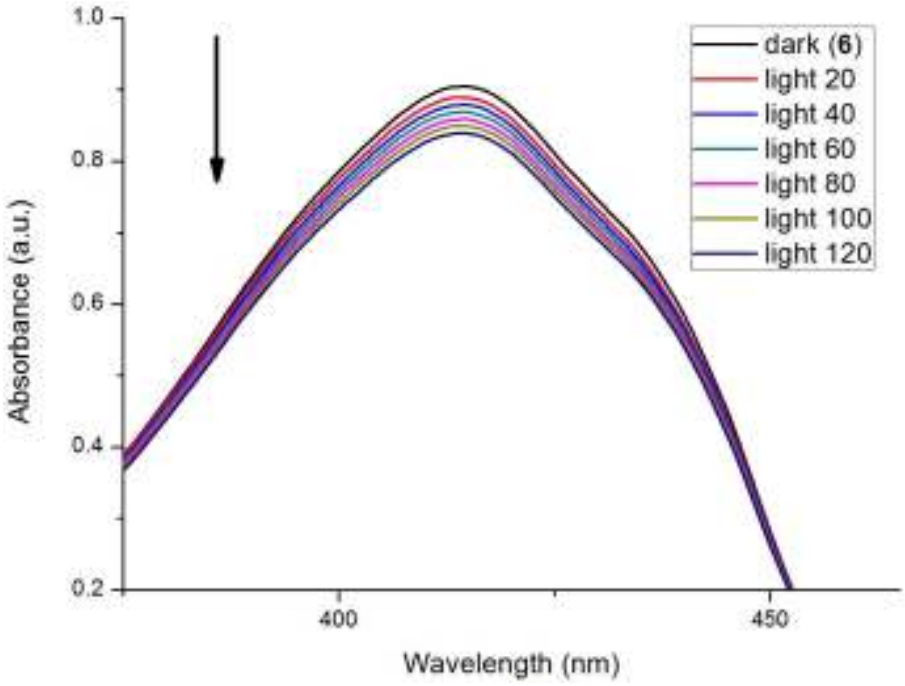


Figure S10. Decrease in absorbance of DPBF in dichloromethane in the presence of compound **6** in medium. Details are given in singlet oxygen measurements part.

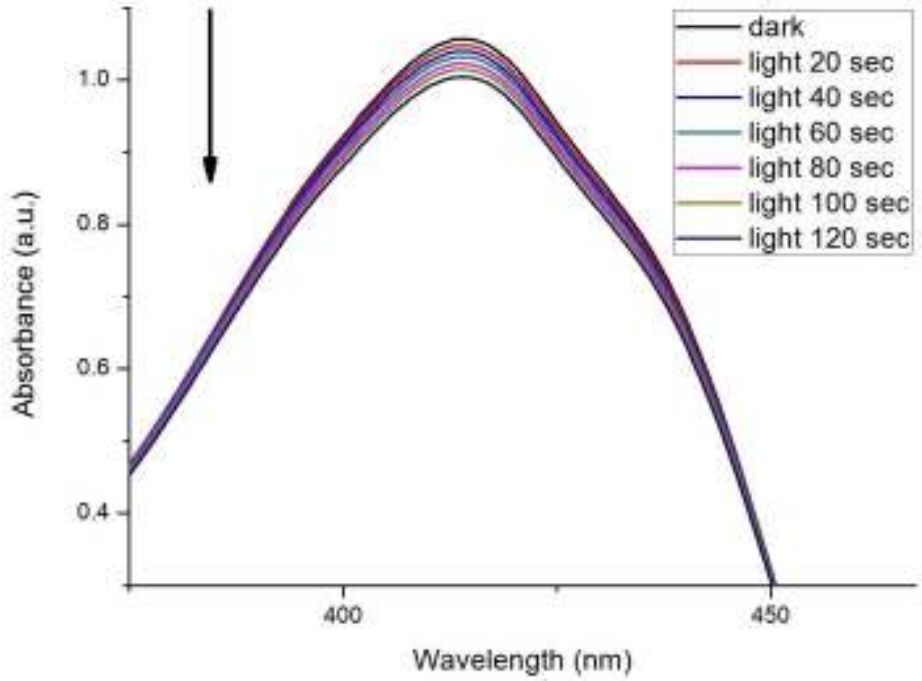


Figure S11. Decrease in absorbance of DPBF in dichloromethane in the presence of compound **7** in medium. Details are given in singlet oxygen measurements part.

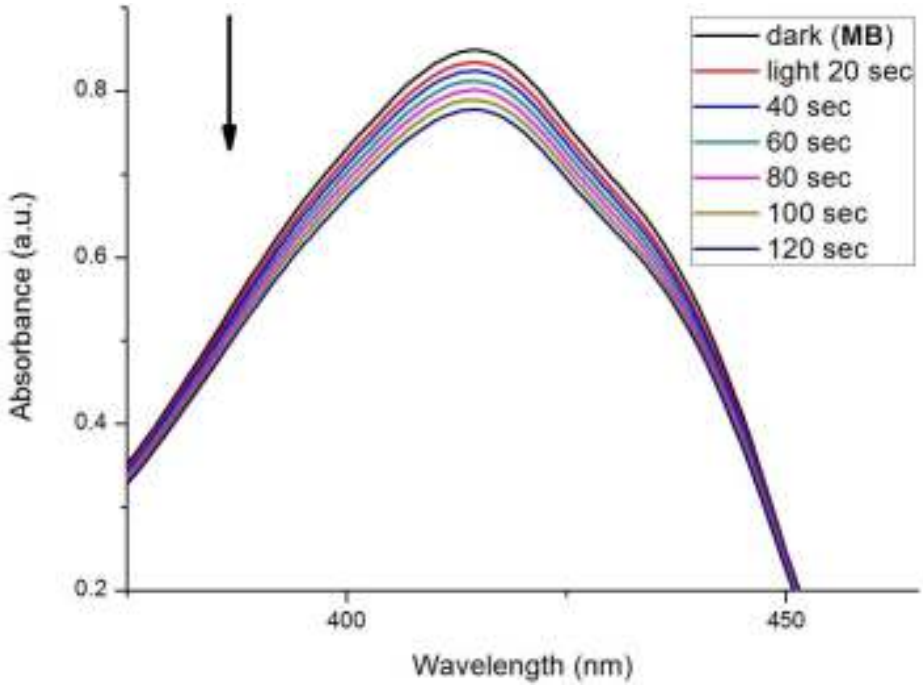


Figure S12. Decrease in absorbance of DPBF in dichloromethane in the presence of **MB** in medium. Details are given in singlet oxygen measurements part.

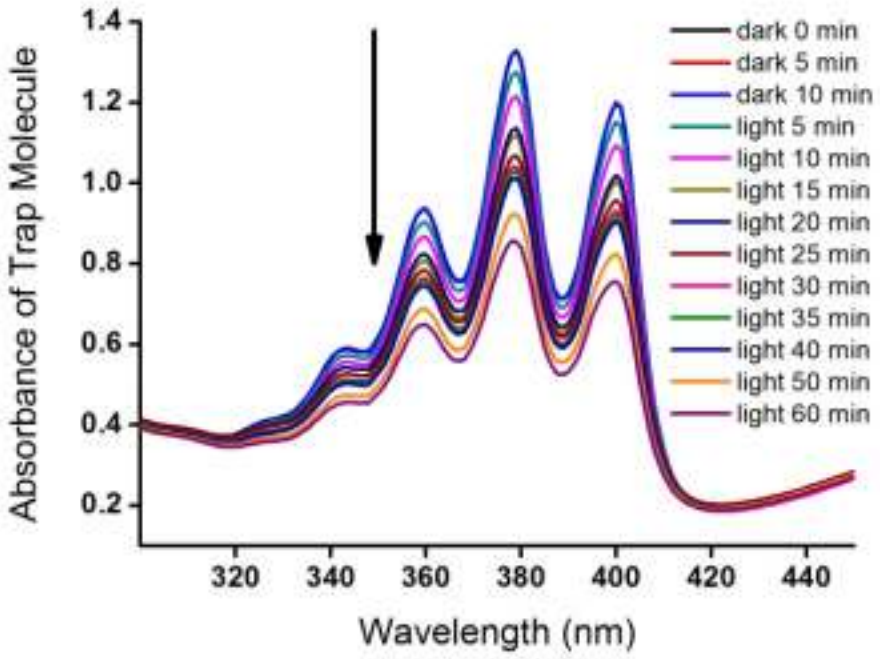


Figure S13. Singlet oxygen generation experiment in aqueous solution. Decrease in Absorbance spectrum of trap molecule (2,2'-(Anthracene-9,10-diyl)bis(methylene)dimalonic acid) in the presence of 1.69 μM compound **3** in phosphate buffer saline (PBS). Details are given in singlet oxygen measurements part.

Photophysical Measurements

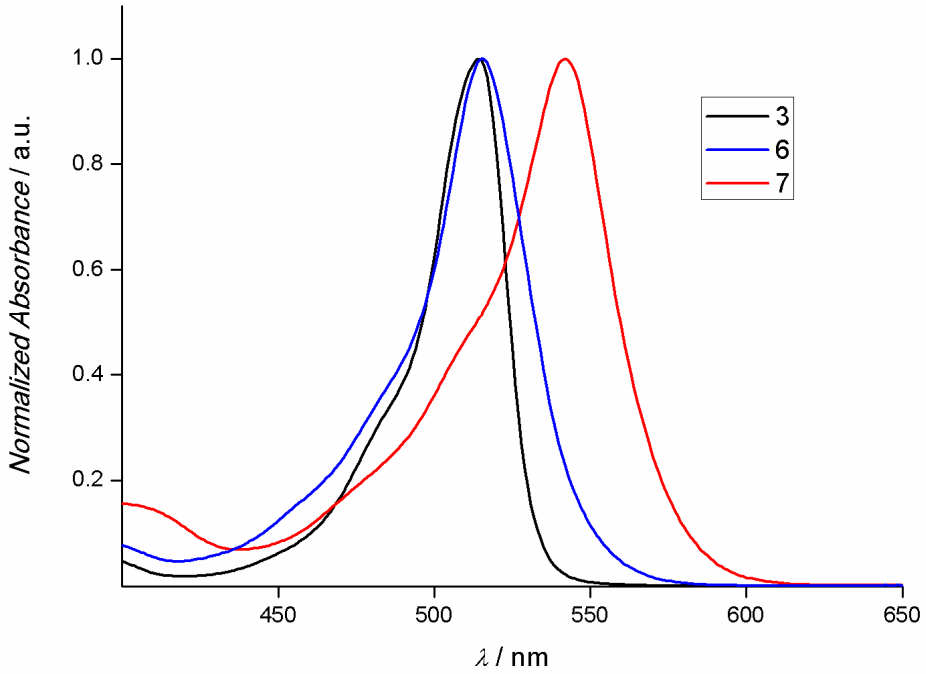


Figure S14. Absorbance spectra of the synthesized molecules **3**, **6** and **7** in $CHCl_3$.

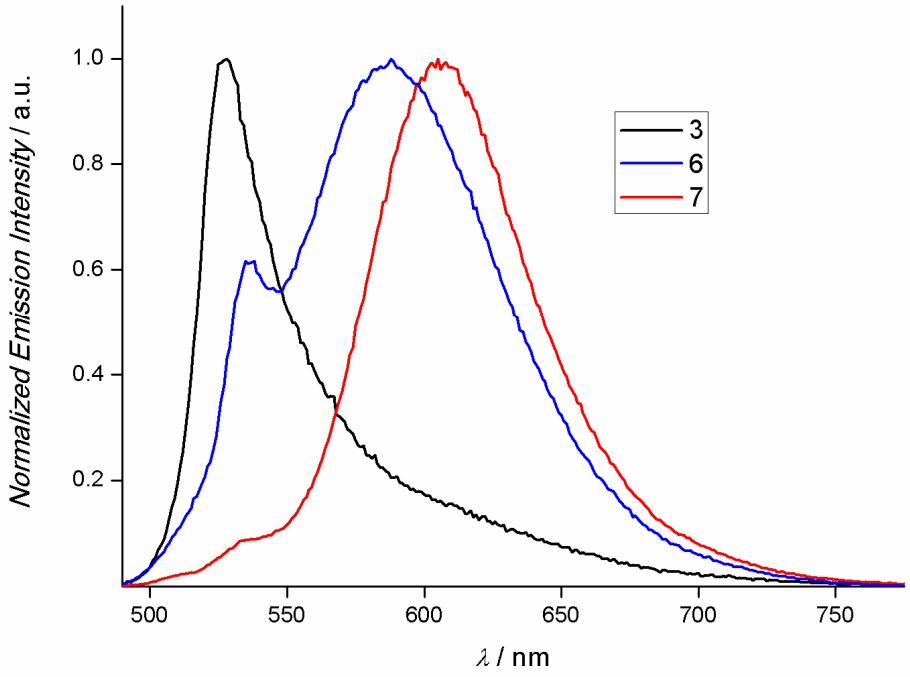


Figure S15. Fluorescence Spectra of the synthesized molecules in $CHCl_3$. Compounds **3**, **6** and **7** were excited at maximum absorbances of compounds in Table 1. λ_{abs} (**3**) = 514 nm, λ_{abs} (**6**) = 515 nm, λ_{abs} (**7**) = 542 nm.

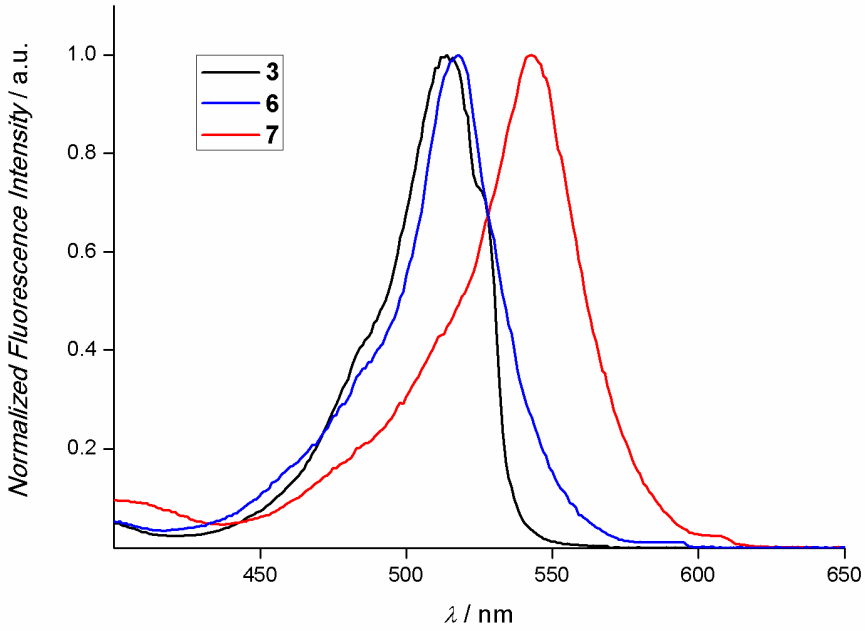


Figure S16. Excitation Spectra of compounds **3**, **6** and **7** in $CHCl_3$. Emission data were collected at 527 nm for **3**, at 588 nm for **6** and 605 nm for **7**.

X-ray Crystal Structure Determinations

X-ray diffraction data were obtained on an Enraf-Nonius CAD4 (κ-geometry) diffractometer operating in ω/2θ scan mode using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at room temperature. The lattice parameters and their estimated standard deviations were determined by using CAD4 Express[16]. Data reduction was carried out using XCAD4[17]. The structures were solved by direct methods and refined by the full-matrix least-squares refinement on F^2 using the programs SHELXS97 and SHELXL97[18], respectively, in the WinGX package[19]. Atomic scattering factors were taken from the International Tables for X-ray Crystallography[20]. Hydrogen atoms bonded to carbon were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model. The data collection details, crystals data and refinement parameters are summarized in Table S2. Positional parameters of non-hydrogen atoms are given in Table S3. Perspective view of molecule is given in Figure 3a. Selected bond lengths and angles are given in Table S4. The molecules are held together by weak van der Waals interactions. Hydrogen bond and molecular packing geometry of the title molecule was calculated with PLATON[21]. The compound has one intermolecular and four intramolecular hydrogen bonds. Hydrogen bonding geometry is summarized in Table S5. Packing Figure (Fig. S17) are prepared by MERCURY[22] program.

Table S2. Crystal data and experimental details of compound **3.** Details are given in X-Ray Crystal Structure Determinations part.

Empirical formula	$C_{26}H_{28}B_2F_4N_4$
Formula weight	494.14
Crystal system	Monoclinic
Space group	P 2/c
Crystal shape /color	Needle / red
Cell parameters from 15 reflections	θ = 6.84 – 11.06 °
Unit cell dimensions	
a (Å)	10.319(2)
b (Å)	10.956(2)
c (Å)	22.732(4)
β (º)	92.196(15)
Volume ($Å^3$)	2567.9(8)
Z	4
D_{calc} (Mg/m^3)	1.278
Absorbtion coefficient (mm^{-1})	0.096
F(000)	1032
h, k, l ranges	-12→ 12, -13 → 0, 0 → 27
θ-range for data collection (°)	2.58 – 25.32
Refinement on F^2	$w = 1/\left[\sigma^2 F_0^2 + (0.0588P)^2\right]$, $P = (F_0^2 + 2F_c^2)/3$
Reflections collected / refined	4601 / 4483 [R_{int} = 0.1293]
Parameters	332
Goodness of fit on F^2	0.664
R indices [I>2σ(I)]	R_1= 0.0846, wR_2= 0.1457
$(\Delta/\sigma)_{max}$	0.000
Largest difference peak and hole ($e/Å^3$)	0.233 and -0.186

Additional material available from Cambridge Crystallographic Data Center as deposition numbers: CCDC 832689.

Table S3. Atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms of compound **3.** Details are given in X-Ray Crystal Structure Determinations part.

$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

Atom	X	y	z	U_{eq} (Å^2)	Atom	x	y	z	U_{eq} (Å^2)
B1	-0.1028(12)	-0.0247(12)	0.4194(6)	0.079(4)	C9	0.0961(11)	-0.1363(8)	0.3855(4)	0.082(3)
B2	0.4033(9)	0.5239(10)	0.3845(5)	0.069(3)	C10	0.1448(8)	0.2867(7)	0.3652(4)	0.067(3)
F1	-0.1901(5)	-0.0555(4)	0.3718(2)	0.1088(17)	C11	0.1377(9)	0.3468(8)	0.3131(4)	0.071(3)
F2	-0.1226(5)	-0.0945(4)	0.4666(2)	0.124(2)	C12	0.2290(8)	0.4401(7)	0.3140(4)	0.060(3)
F3	0.5166(4)	0.4588(4)	0.3998(2)	0.1064(17)	C13	0.2416(9)	0.3398(7)	0.3998(4)	0.077(3)
F4	0.3721(5)	0.5890(4)	0.4344(2)	0.1112(19)	C14	0.2530(8)	0.5236(7)	0.2696(4)	0.086(3)
N1	-0.1287(8)	0.1121(7)	0.4339(3)	0.073(2)	C15	0.3497(8)	0.6043(8)	0.2813(4)	0.057(2)
N2	0.0322(7)	-0.0350(7)	0.3970(3)	0.068(2)	C16	0.3969(9)	0.7015(10)	0.2460(4)	0.080(3)
N3	0.2958(6)	0.4332(6)	0.3694(3)	0.066(2)	C17	0.5004(11)	0.7570(8)	0.2761(5)	0.092(3)
N4	0.4286(7)	0.6102(6)	0.3337(3)	0.071(2)	C18	0.5208(9)	0.7019(9)	0.3311(6)	0.094(3)
C1	-0.2356(9)	0.1648(12)	0.4578(4)	0.087(3)	C19	-0.3383(7)	0.0859(7)	0.4808(3)	0.119(4)
C2	-0.2191(10)	0.2910(10)	0.4572(4)	0.097(3)	C20	-0.0667(8)	0.4491(6)	0.4183(3)	0.112(4)
C3	-0.1093(9)	0.3193(9)	0.4285(4)	0.074(3)	C21	0.3338(8)	0.0834(8)	0.3294(4)	0.149(4)
C4	-0.0493(9)	0.2066(9)	0.4138(4)	0.073(3)	C22	0.0496(8)	-0.2610(7)	0.3975(3)	0.110(3)
C5	0.0668(10)	0.1841(8)	0.3862(4)	0.073(3)	C23	0.0443(8)	0.3176(7)	0.2632(4)	0.118(4)
C6	0.1064(9)	0.0653(8)	0.3789(3)	0.064(3)	C24	0.2942(8)	0.3144(7)	0.4609(3)	0.096(3)
C7	0.2239(9)	0.0147(10)	0.3538(4)	0.086(3)	C25	0.3454(8)	0.7379(7)	0.1869(4)	0.112(3)
C8	0.2140(10)	-0.1127(9)	0.3607(4)	0.097(3)	C26	0.6126(9)	0.7238(8)	0.3816(4)	0.139(5)

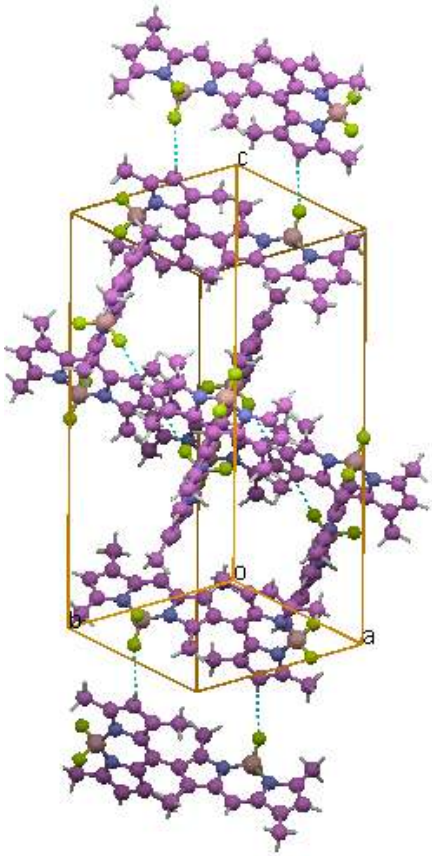
Table S4. Selected bond lengths (Å) and bond angles (°). Details are given in X-Ray Crystal Structure Determinations part.

B1 – F1	1.422(11)	F1 – B1 – F2	111.3(9)
B1 – F2	1.340(11)	F3 – B2 – F4	106.0(9)
B2 – F3	1.402(9)	F1 – B1 – N1	106.3(9)
B2 – F4	1.389(10)	F1 – B1 – N2	106.9(9)
B1 – N1	1.560(11)	F2 – B1 – N1	110.3(9)
B1 – N2	1.506(12)	F2 – B1 – N2	113.5(10)
B2 – N3	1.519(11)	F3 – B2 – N3	108.6(8)
B2 – N4	1.524(11)	F3 – B2 – N4	109.8(7)
		F4 – B2 – N3	109.3(7)
		F4 – B2 – N4	110.7(8)

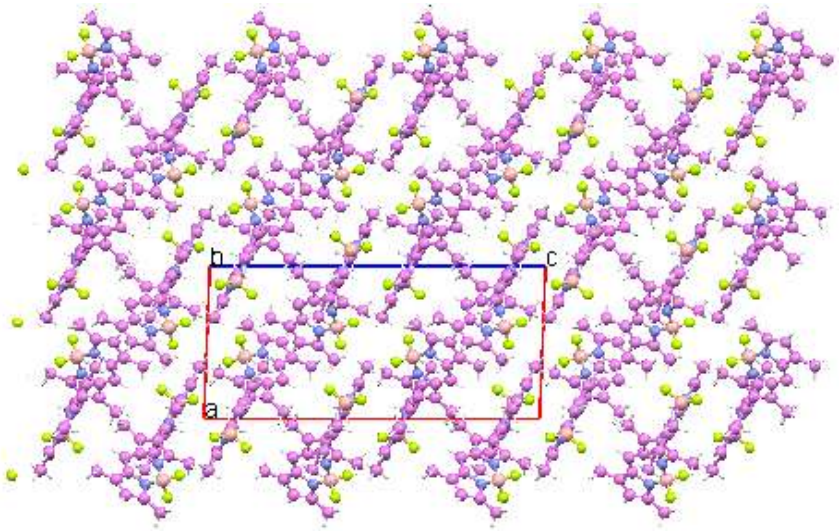
Table S5. Structural parameters of hydrogen bonds between donor (D), acceptor (A) and hydrogen (H). Details are given in X-Ray Crystal Structure Determinations part**.**

Molecule	D – H ··· A	D–H (Å)	A···H (Å)	D···A (Å)	D–H···H (°)
1	C2 – H2···F4^{i}	0.93	2.45	3.254(11)	144
2	C19 – H19C···F2	0.96	2.45	3.004(9)	116
2	C24 – H24C···F4	0.96	2.46	3.178(9)	131
2	C26 – H26A···F3	0.96	2.43	3.101(10)	127
2	C26 – H26A···F4	0.96	2.53	3.164(10)	123

Symmetry codes [i: -x, 1-y, 1-z]

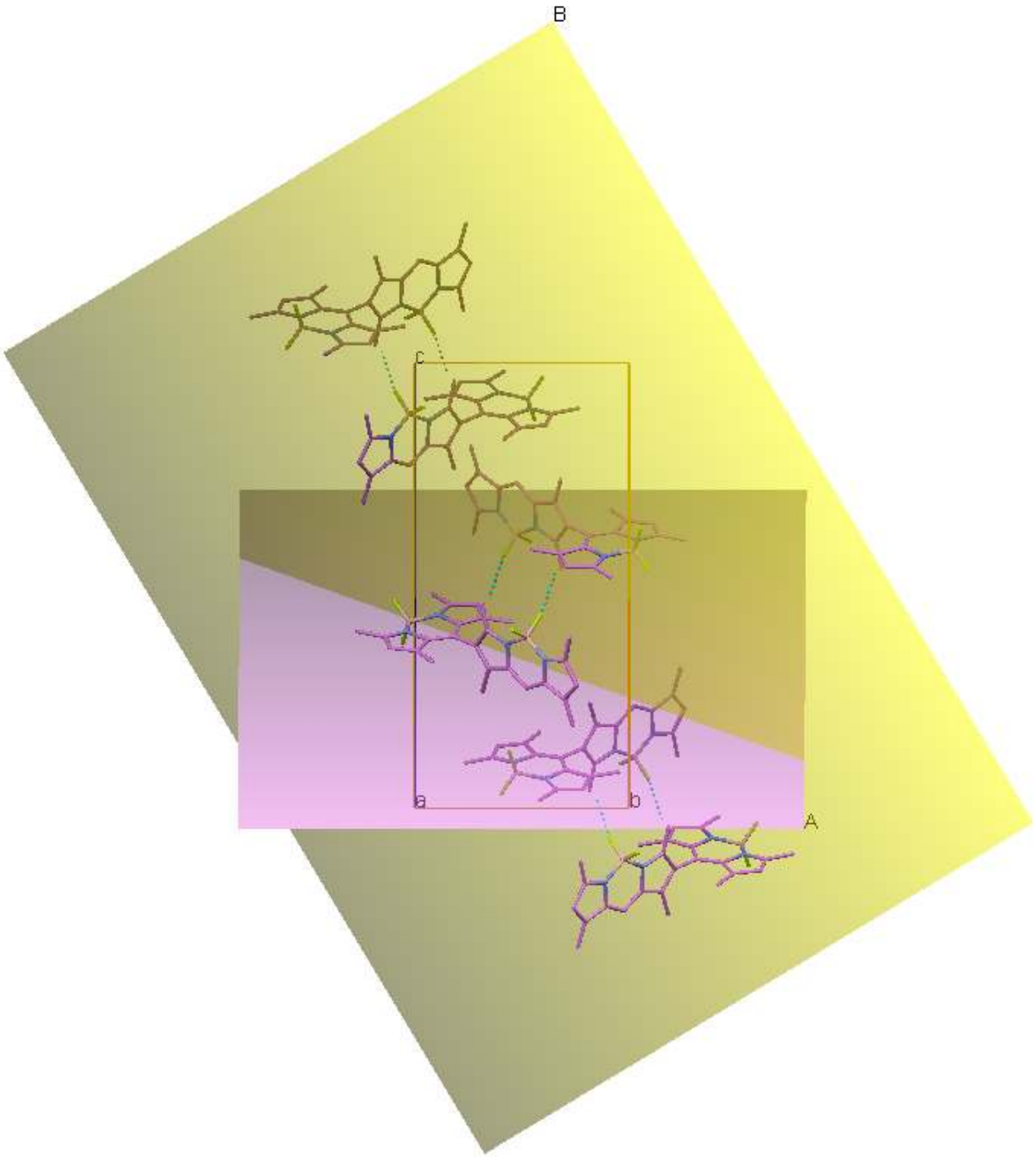


(a)

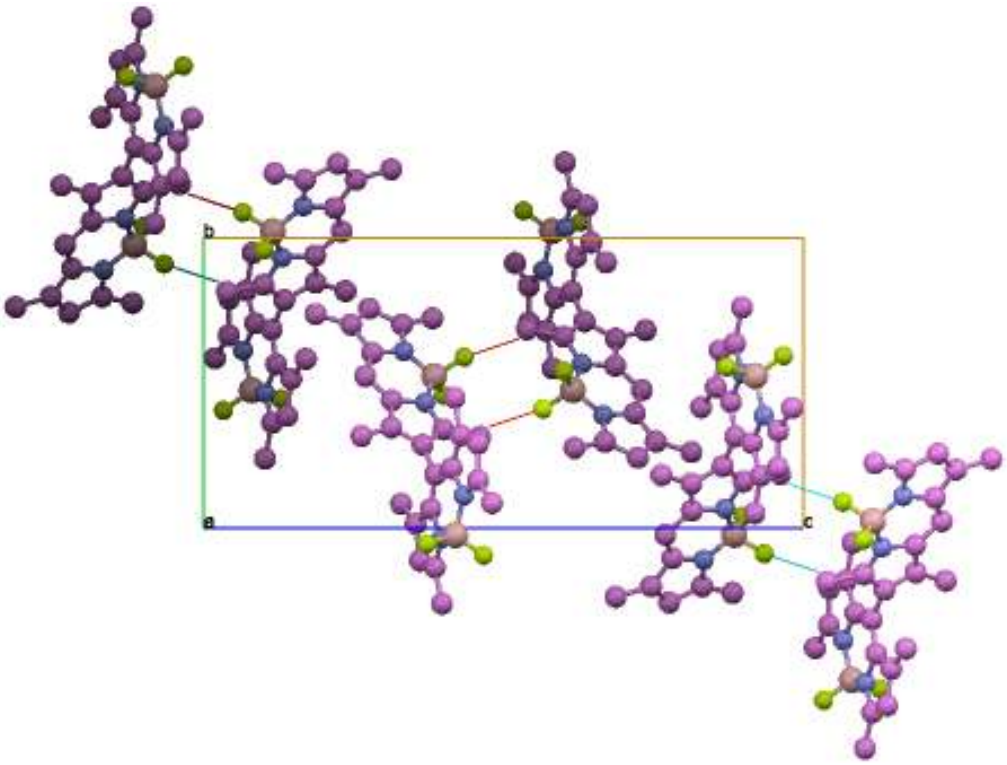


(b) View along b-axis

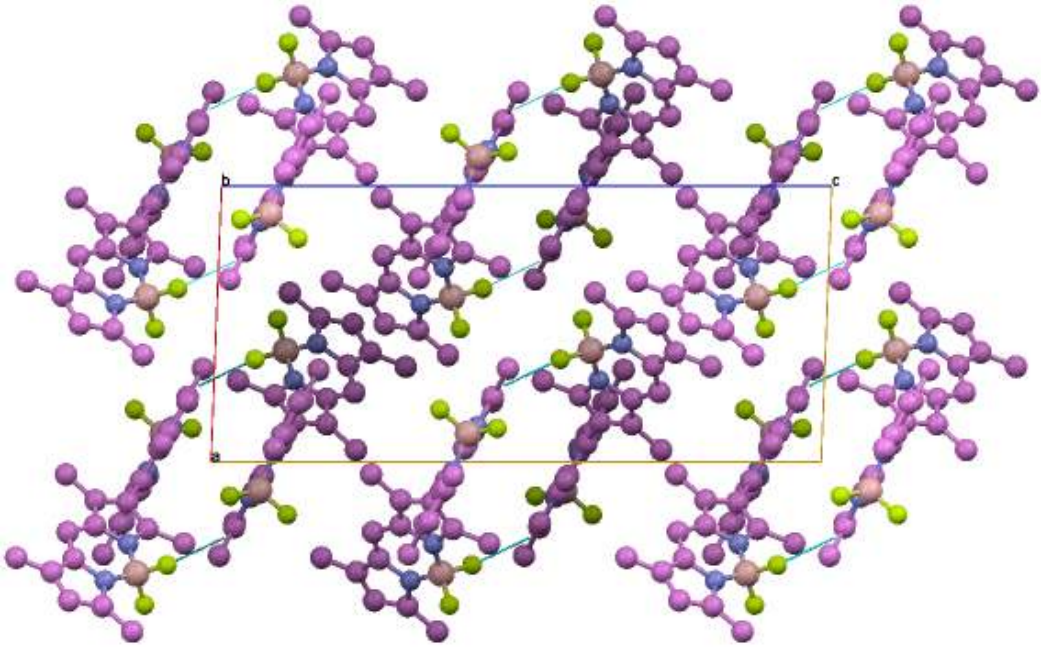
Figure S17. Packing diagrams of compound **3.** Dashed lines indicate inter H-bond between C2 and F4 atoms. Details are given in X-Ray Crystal Structure Determinations part.



View along a-axis



View along a-axis



View along b-axis

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