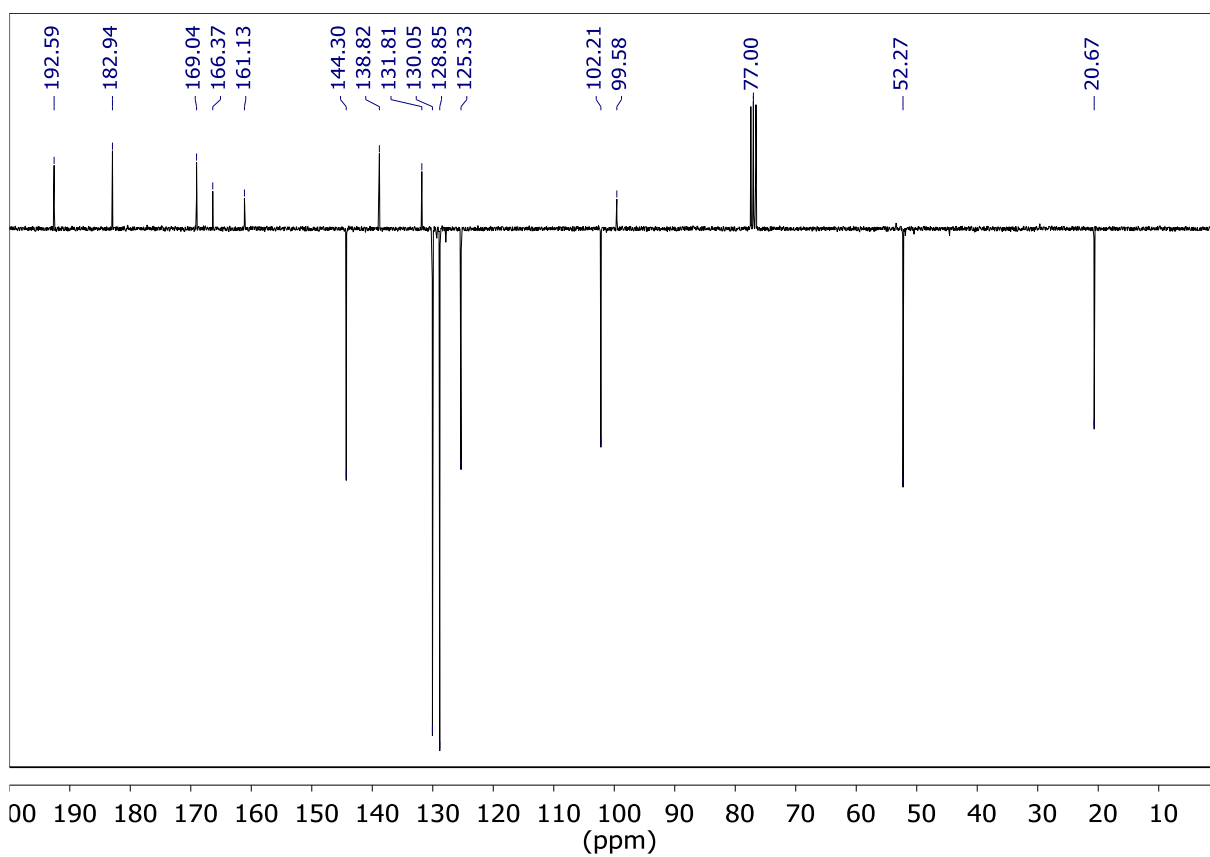
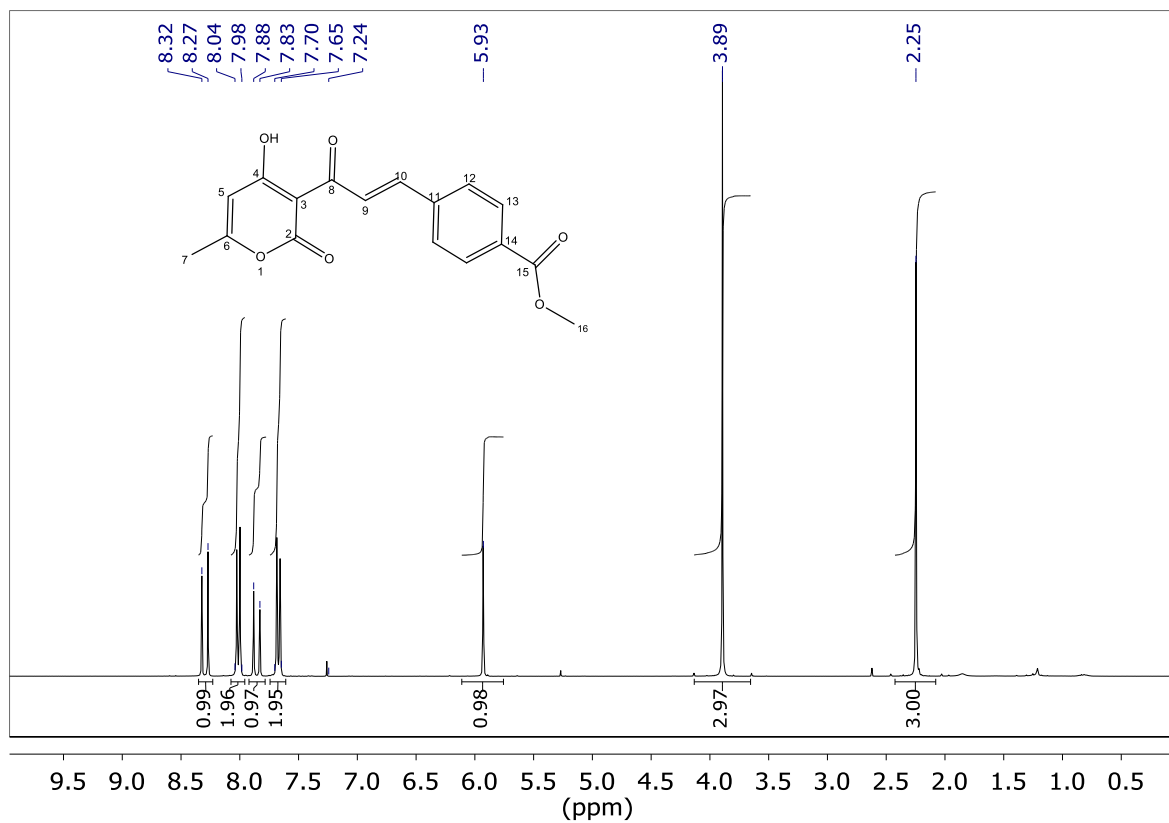


## Supplementary Materials

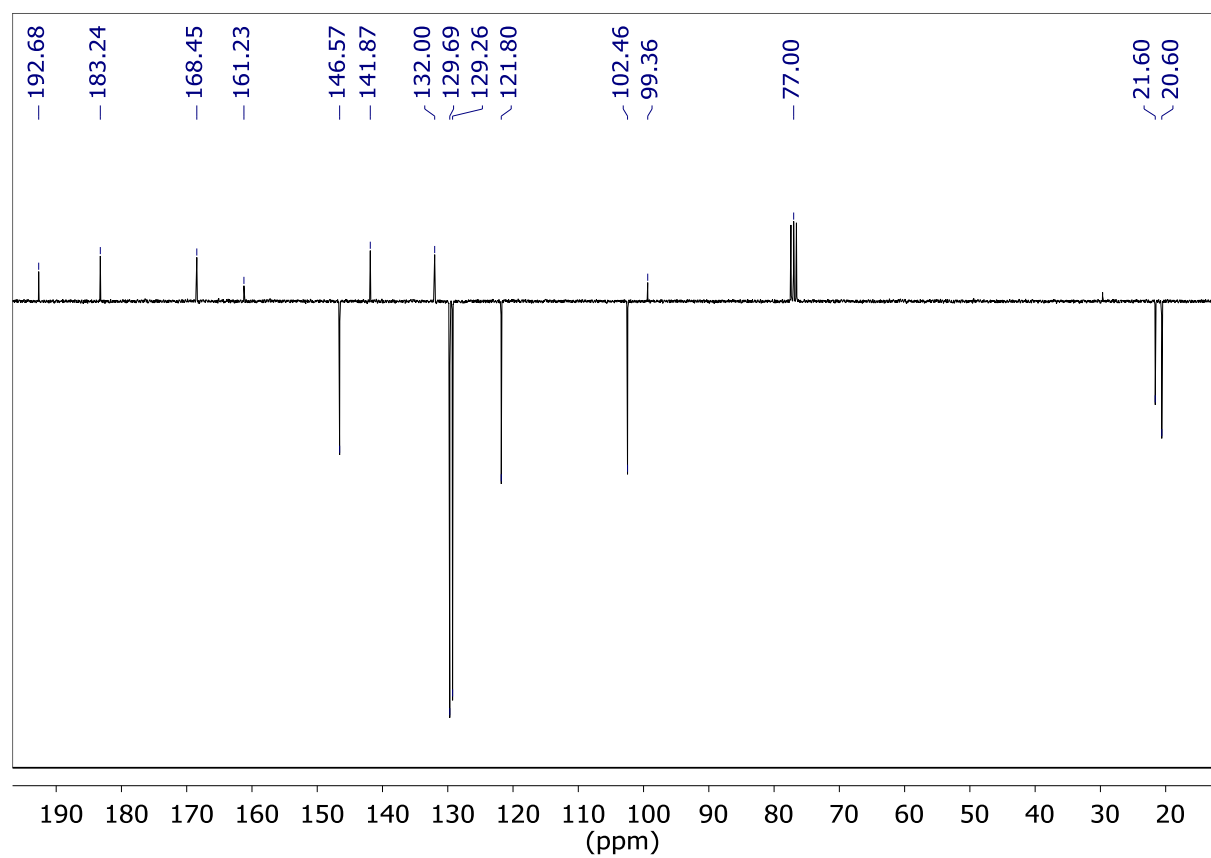
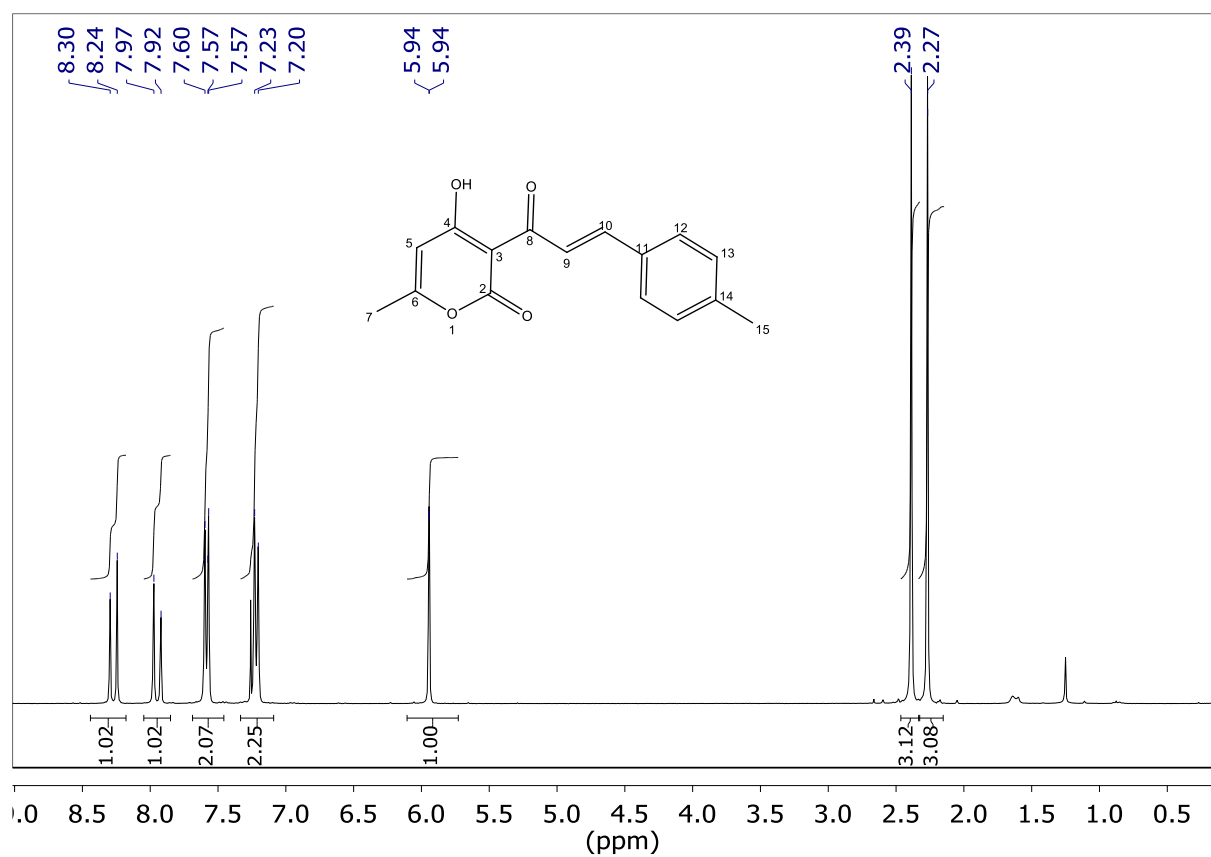
### ESIPT-Active cinnamoyl pyrones are bright solid-state emitters: Revisited theoretical approach and experimental study

Emma Bremond, Martial Boggio-Pasqua, Nadine Leygue, Mokhtar Fodili, Pascal Hoffmann, Nathalie Saffon-Merceron, Rémi Métivier, Suzanne Fery-Forgues \*

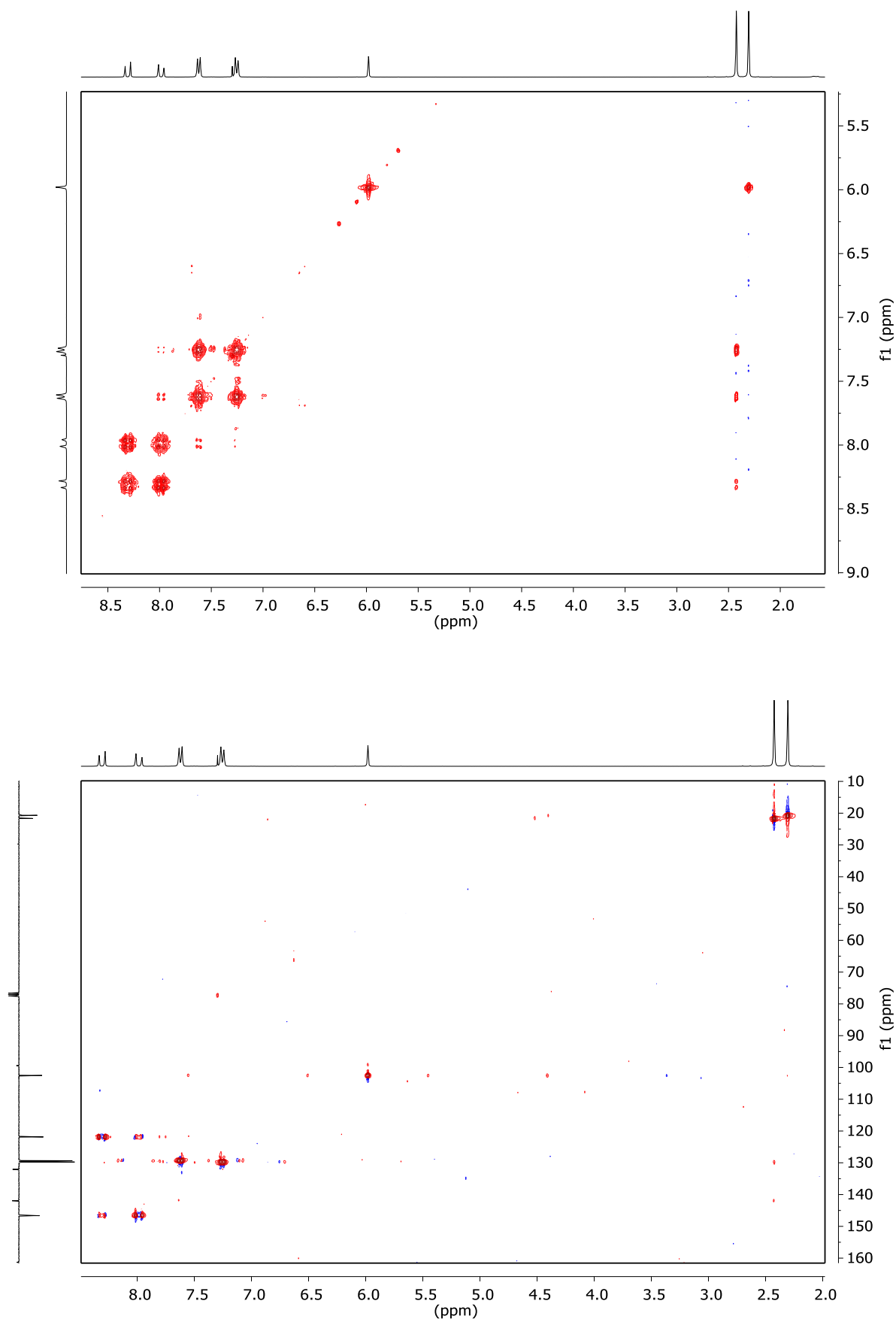
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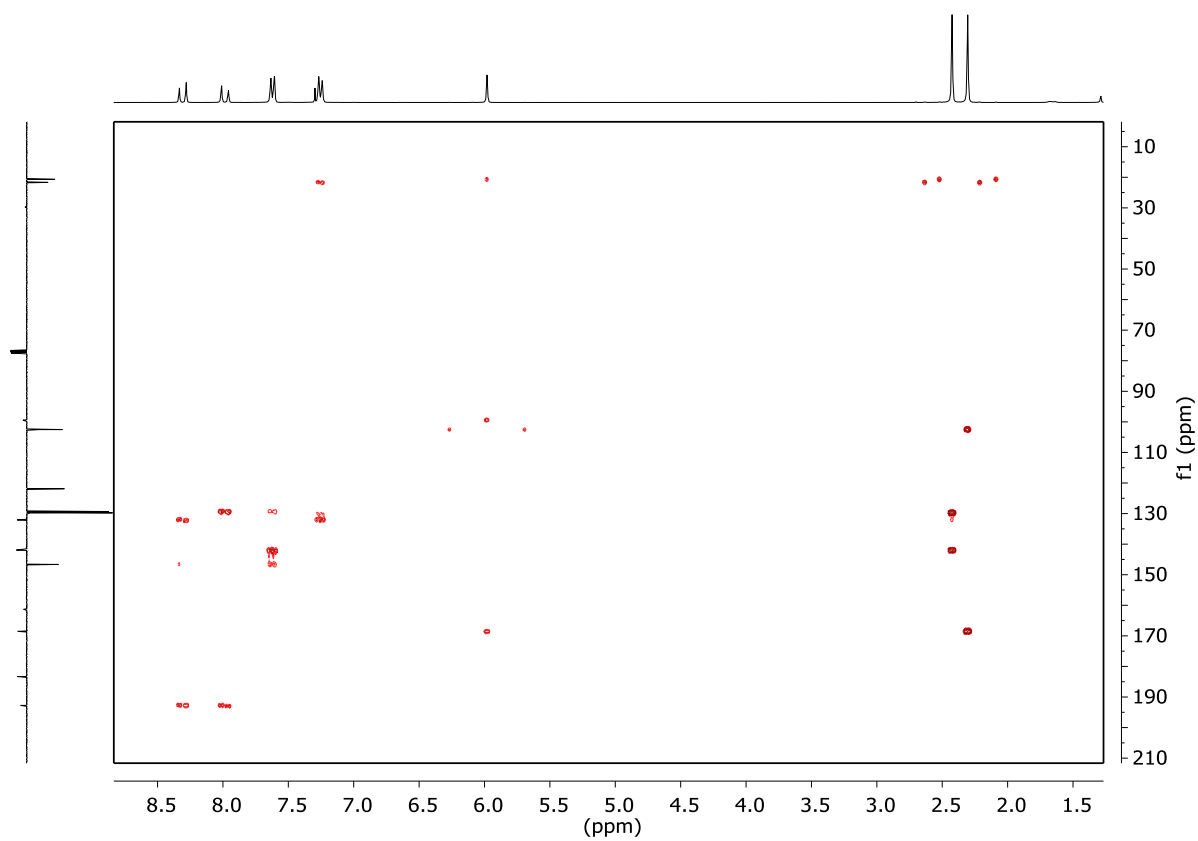
**Figure S1.**  $^1\text{H}$  NMR (top) and  $^{13}\text{C}$  NMR (bottom) spectra of compound **4** in  $\text{CDCl}_3$ .



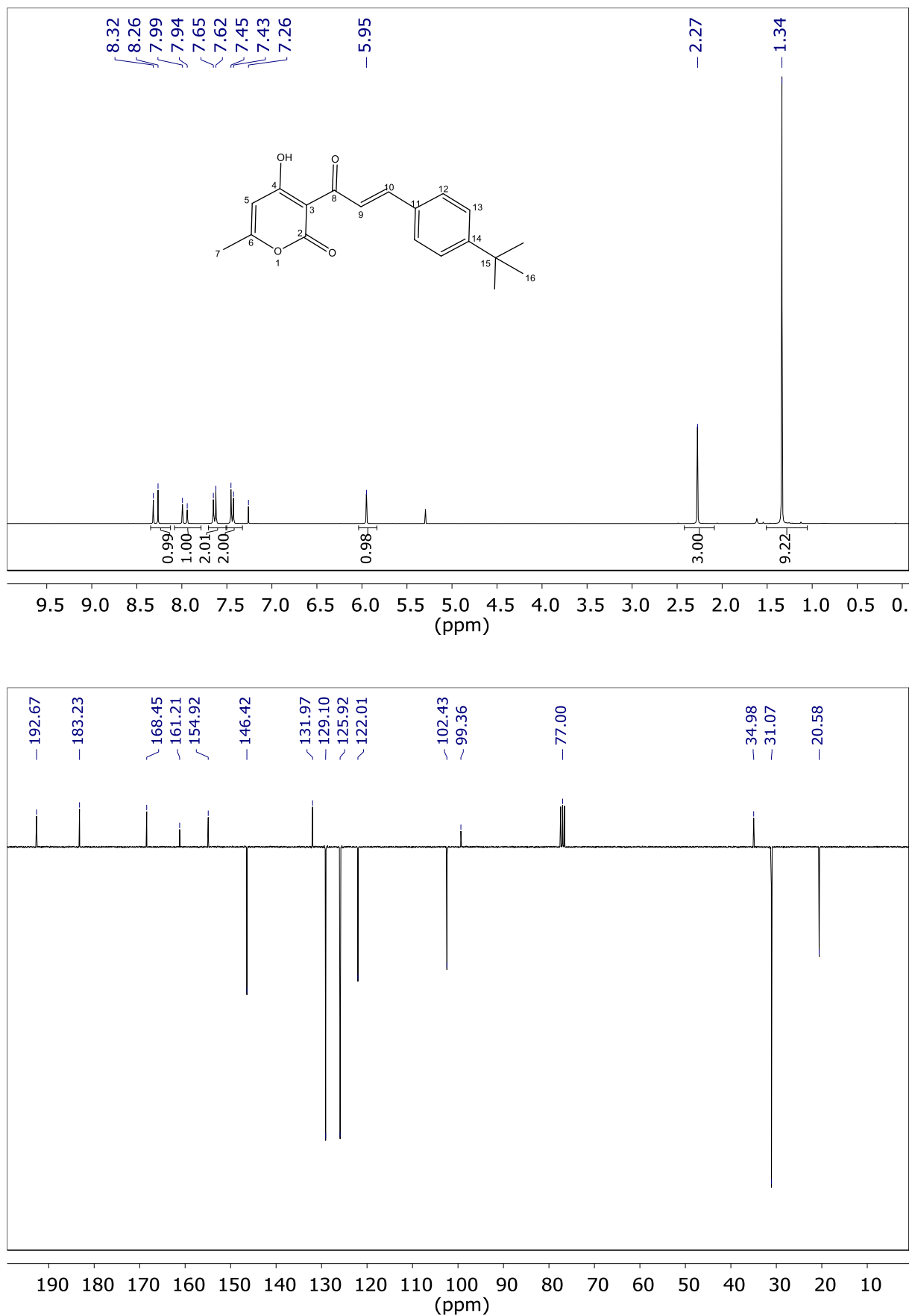
**Figure S2.** <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of compound **5** in CDCl<sub>3</sub>



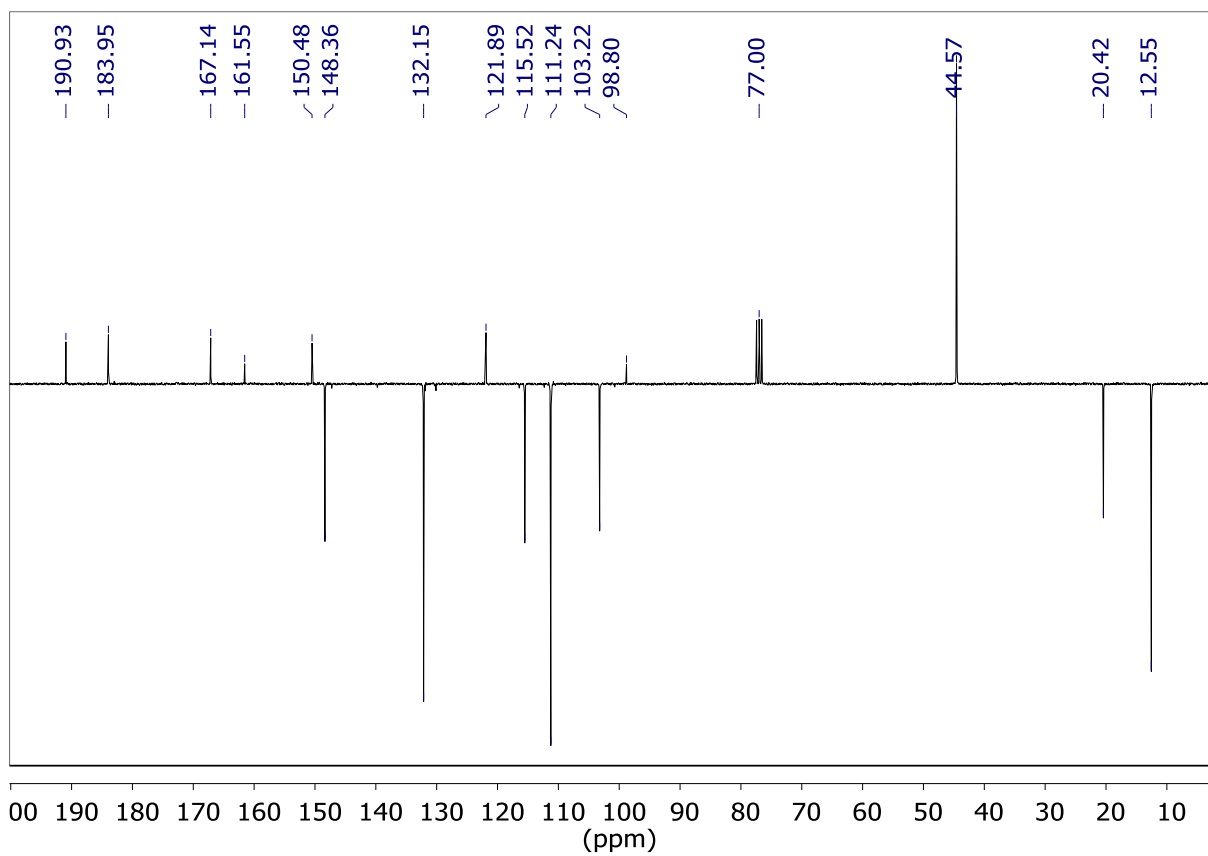
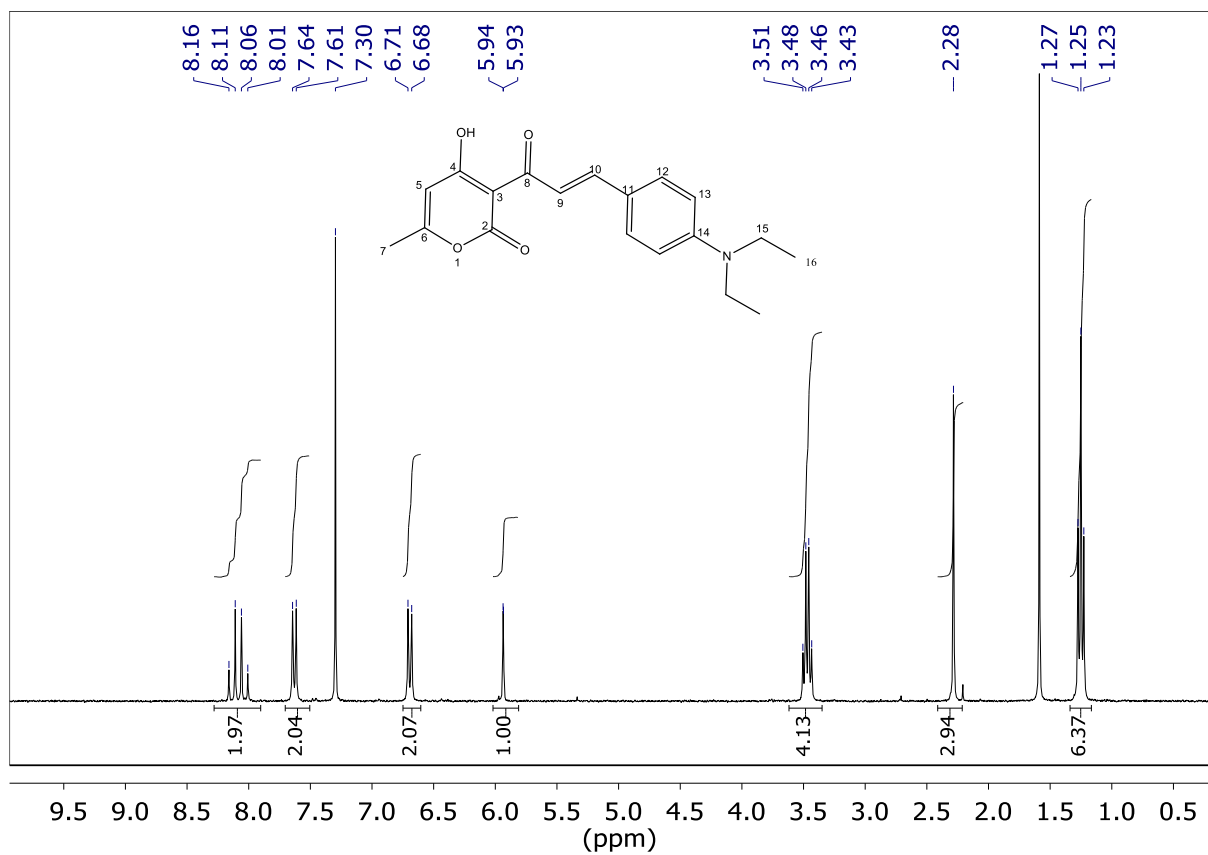
**Figure S3.** COSY (top) and HSQC (bottom) spectra of compound **5** in CDCl<sub>3</sub>.



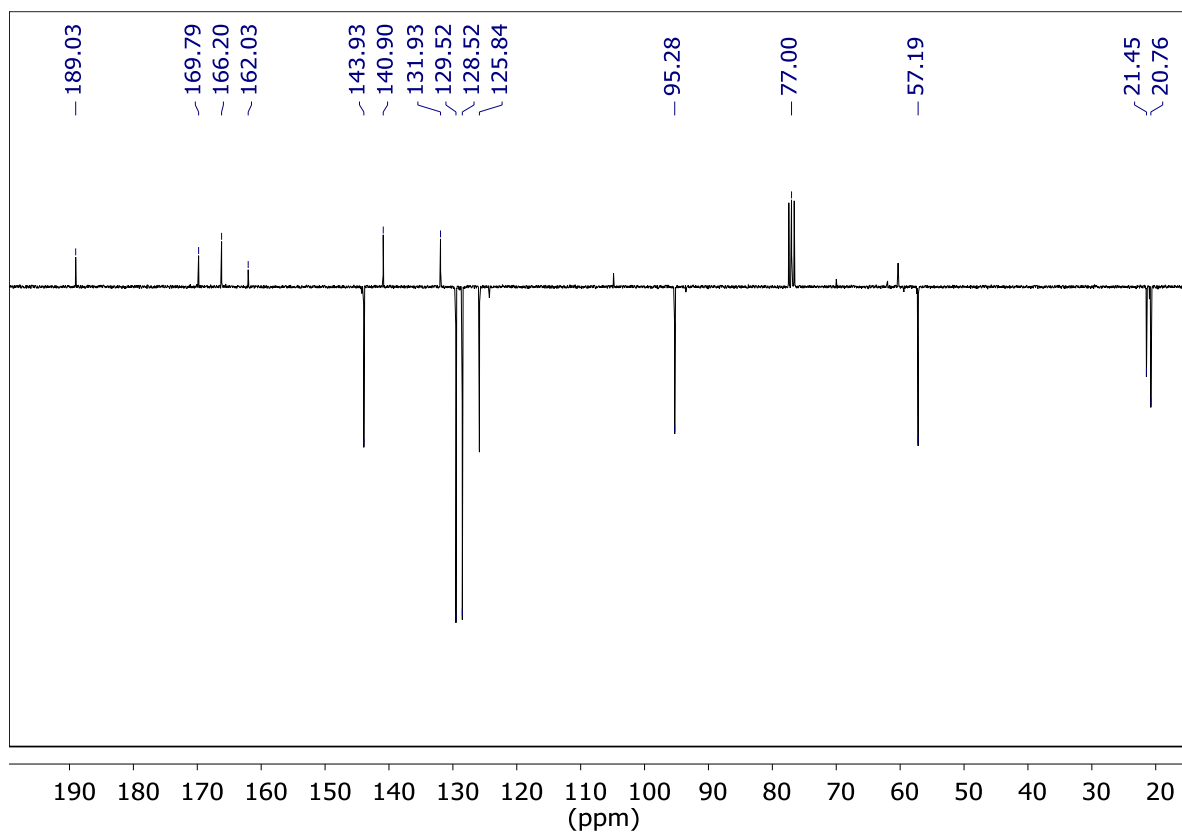
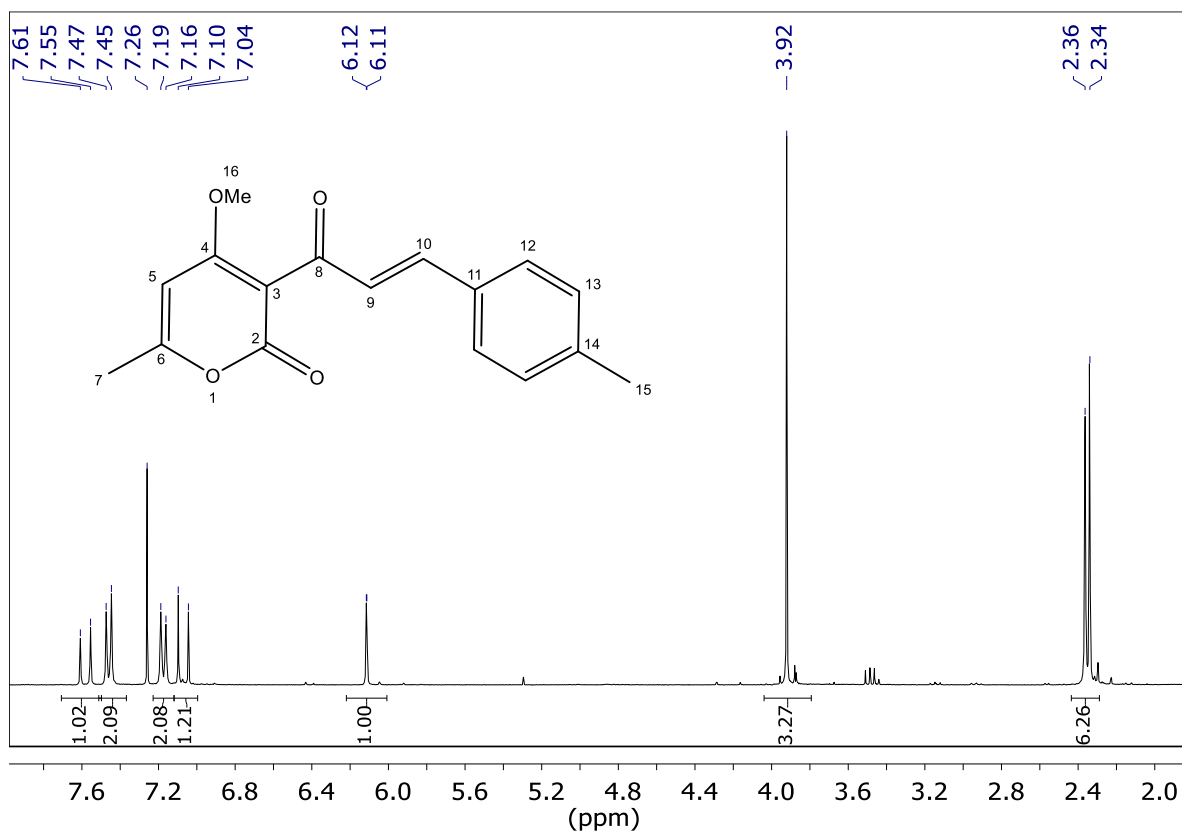
**Figure S4.** HMBC NMR spectrum of compound **5** in CDCl<sub>3</sub>.



**Figure S5.** <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of compound **6** in CDCl<sub>3</sub>

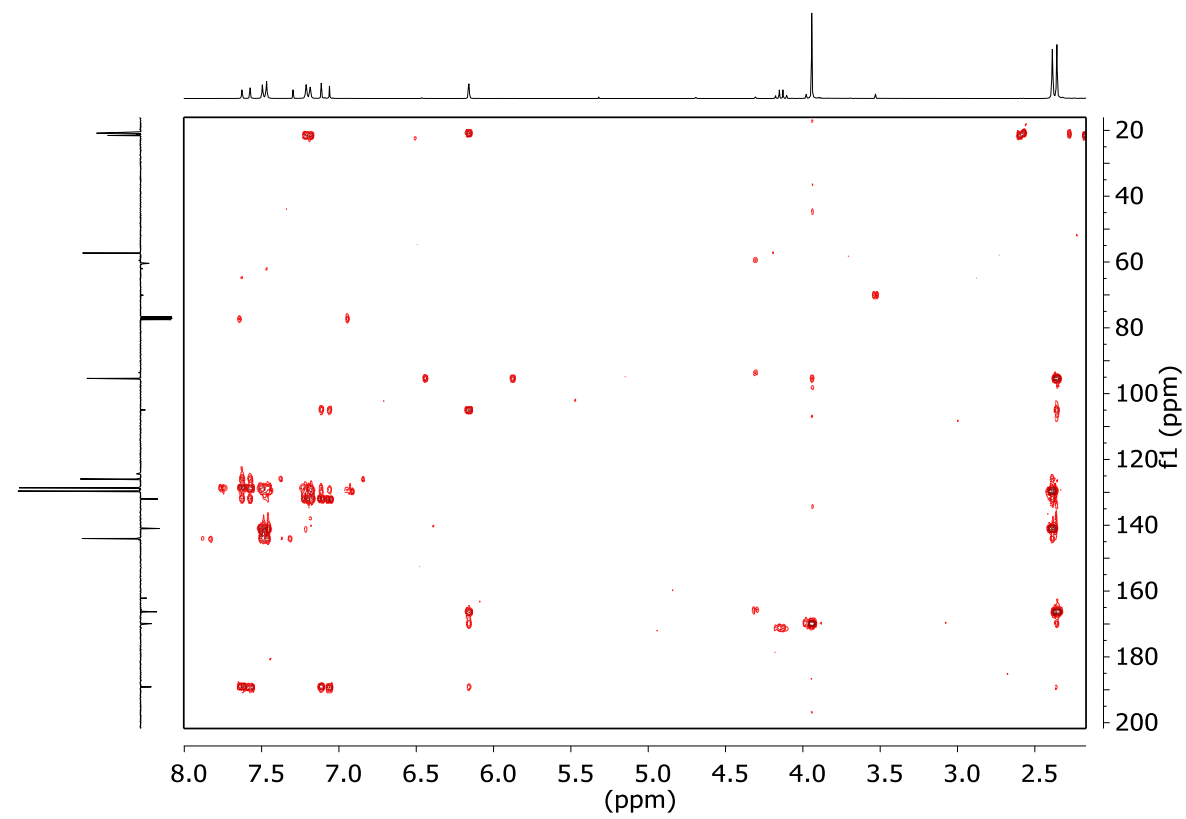
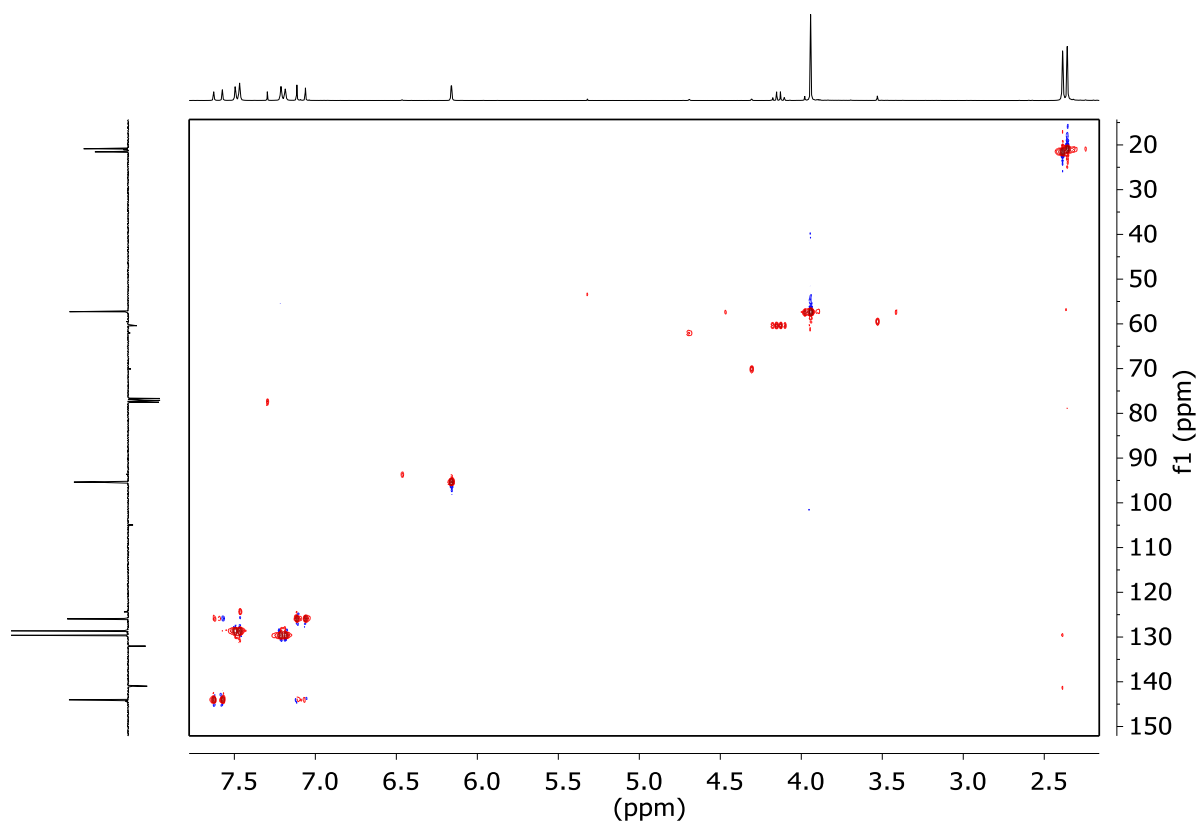


**Figure S6.** <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of compound **7** in CDCl<sub>3</sub>

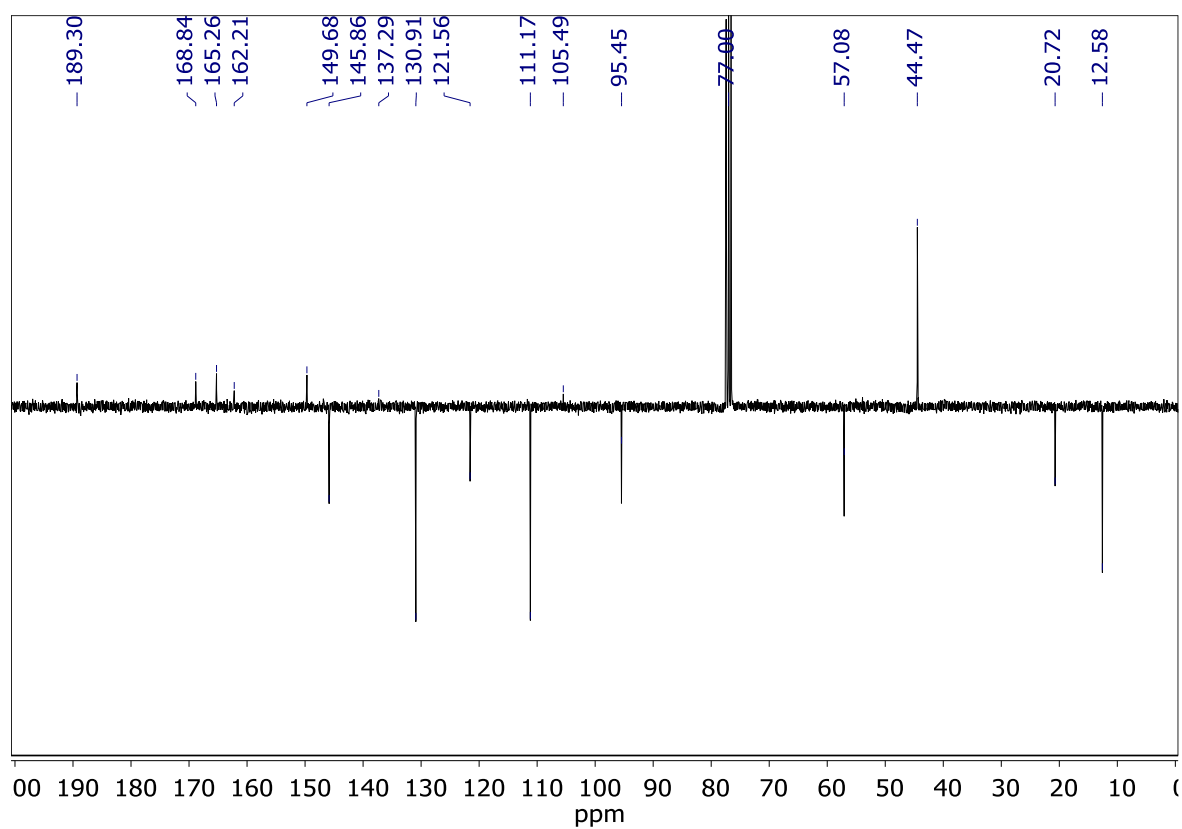
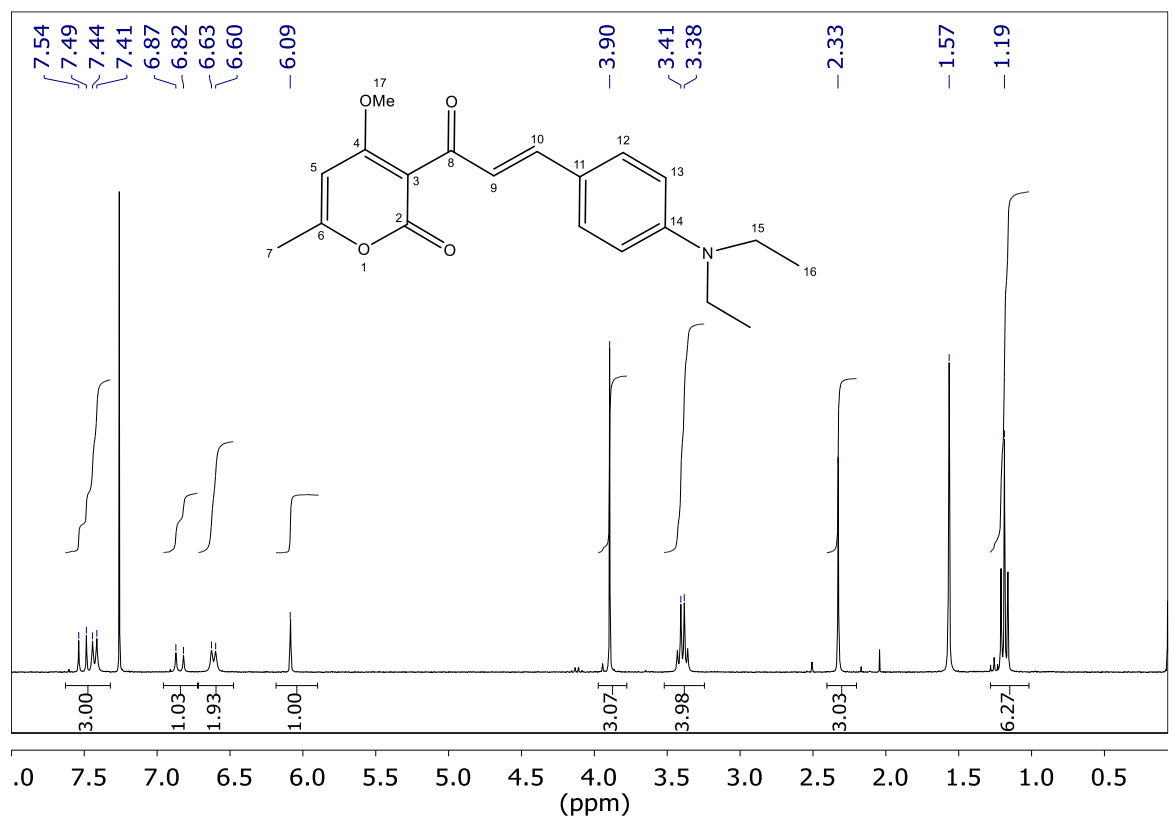


**Figure S7.** <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of compound **8** in CDCl<sub>3</sub>

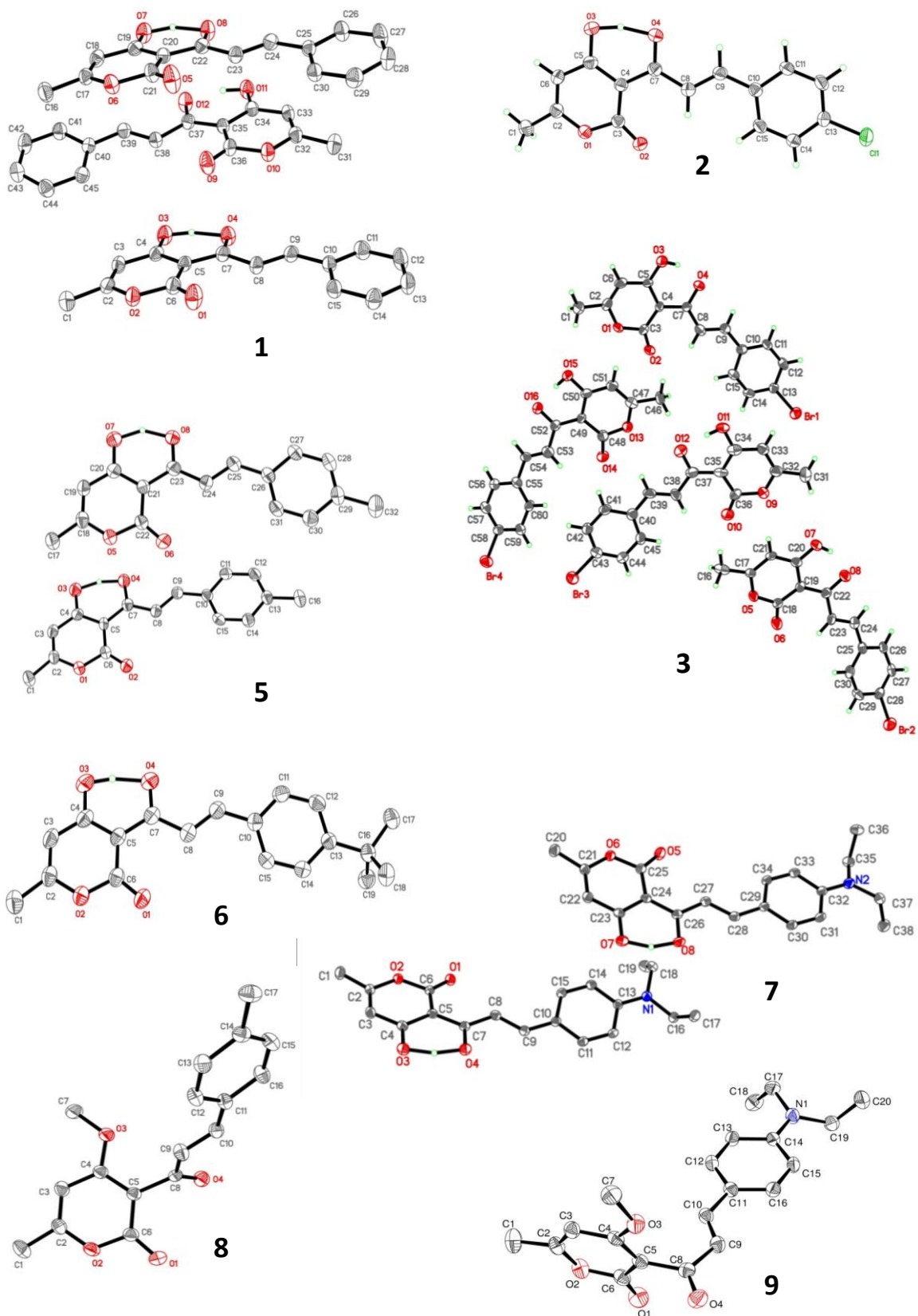




**Figure S8.** HSQC (top) and HMBC (bottom) spectra of compound **8** in CDCl<sub>3</sub>.



**Figure S9.** <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of compound **9** in CDCl<sub>3</sub>.



**Figure S10.** Molecular structure of compounds 2, 6, 8 and 9, and molecular views of the asymmetric unit of compounds 1, 3, 5 and 7. Displacement ellipsoids are drawn at 50% probability.

**Table S1.** SF-TD-BH&HLYP/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>0</sub>-trans of isolated molecule **1**.

C	-0.3157792380	1.7526766119	0.0000000000	E(S <sub>0</sub> ) = -879.455974 a.u.
C	1.1194305289	1.9180966522	0.0000000000	E(S <sub>1</sub> ) = -879.300310 a.u.
C	0.7965452417	4.3033269269	0.0000000000	
C	-0.5371668683	4.1939963475	0.0000000000	
C	-1.1156677595	2.8952032803	0.0000000000	
H	-1.1754510648	5.0553406825	0.0000000000	
C	1.5680616053	5.5695794426	0.0000000000	
H	2.2084133970	5.6099309898	-0.8757908043	
H	2.2084133970	5.6099309898	0.8757908043	
H	0.9051782116	6.4246510853	0.0000000000	
O	1.5829675723	3.2284652628	0.0000000000	
O	1.9686052186	1.0823500662	0.0000000000	
O	-2.4143964022	2.8438043611	0.0000000000	
C	-0.9720614370	0.4423249751	0.0000000000	
O	-2.2076581538	0.3991853038	0.0000000000	
C	-0.1978861584	-0.7954636686	0.0000000000	
H	0.8685097153	-0.7119388123	0.0000000000	
C	-0.8276213356	-1.9761462257	0.0000000000	
H	-1.9058883467	-1.9630282020	0.0000000000	
C	-0.2031383133	-3.2902412793	0.0000000000	
C	-1.0204692376	-4.4205369118	0.0000000000	
C	1.1823270978	-3.4734869106	0.0000000000	
C	-0.4778531686	-5.6925168115	0.0000000000	
H	-2.0899416599	-4.2940135671	0.0000000000	
C	1.7226000226	-4.7411842140	0.0000000000	
H	1.8371580397	-2.6205224856	0.0000000000	
C	0.8952928613	-5.8564259577	0.0000000000	
H	-1.1254190098	-6.5519750349	0.0000000000	
H	2.7915761321	-4.8653423964	0.0000000000	
H	1.3226507914	-6.8441921003	0.0000000000	
H	-2.6591641017	1.8799152106	0.0000000000	

**Table S1 (continued).** SF-TD-BH&HLYP/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>1</sub>-trans of isolated molecule **1**.

C	-0.3120480941	1.7266162211	0.0000000000	E(S <sub>0</sub> ) = -879.445474 a.u.
C	1.1242736970	1.8887938775	0.0000000000	E(S <sub>1</sub> ) = -879.311191 a.u.
C	0.8210307336	4.2724073533	0.0000000000	
C	-0.5151130538	4.1689840302	0.0000000000	
C	-1.1070882456	2.8797538720	0.0000000000	
H	-1.1441626202	5.0377155114	0.0000000000	
C	1.6052432759	5.5304805653	0.0000000000	
H	2.2464237012	5.5697818524	-0.8758321005	
H	2.2464237012	5.5697818524	0.8758321005	
H	0.9486413292	6.3906783486	0.0000000000	
O	1.5992317137	3.1858433736	0.0000000000	
O	1.9634997209	1.0357289541	0.0000000000	
O	-2.4066618495	2.8124014678	0.0000000000	
C	-0.9753014077	0.4351021068	0.0000000000	
O	-2.2478083893	0.3878632449	0.0000000000	
C	-0.2367759007	-0.7808529076	0.0000000000	
H	0.8308952071	-0.7223538052	0.0000000000	
C	-0.9152639224	-2.0121401504	0.0000000000	
H	-1.9906473947	-1.9771217453	0.0000000000	
C	-0.2783068021	-3.2557765747	0.0000000000	
C	-1.0557944481	-4.4530569495	0.0000000000	
C	1.1493342689	-3.3899238678	0.0000000000	
C	-0.4568444178	-5.6778588343	0.0000000000	
H	-2.1282988278	-4.3675059820	0.0000000000	
C	1.7302300249	-4.6323287620	0.0000000000	
H	1.7663533215	-2.5120857144	0.0000000000	
C	0.9433120326	-5.7792248378	0.0000000000	
H	-1.0550221350	-6.5718818083	0.0000000000	
H	2.8022496958	-4.7202906934	0.0000000000	
H	1.4079159640	-6.7493414834	0.0000000000	
H	-2.6277533013	1.8215750949	0.0000000000	

**Table S1 (continued).** SF-TD-BH&HLYP/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>1</sub>-trans-ESIPT of isolated molecule **1**.

C	-0.3266420838	1.7752521567	0.0000000000	E(S <sub>0</sub> ) = -879.438217 a.u.
C	1.1057022443	1.9414070901	0.0000000000	E(S <sub>1</sub> ) = -879.324587 a.u.
C	0.8330300130	4.3119707018	0.0000000000	
C	-0.5010808171	4.2282071200	0.0000000000	
C	-1.1689930165	2.9548201562	0.0000000000	
H	-1.1086299688	5.1126705697	0.0000000000	
C	1.6346239718	5.5586524785	0.0000000000	
H	2.2763254944	5.5863768030	-0.8758085750	
H	2.2763254944	5.5863768030	0.8758085750	
H	0.9909924255	6.4281497937	0.0000000000	
O	1.6070931797	3.2173787818	0.0000000000	
O	1.9224767960	1.0608470952	0.0000000000	
O	-2.4046312068	2.8813018920	0.0000000000	
C	-0.9488279849	0.4142402689	0.0000000000	
O	-2.2754990099	0.3786417471	0.0000000000	
C	-0.2553106076	-0.7582890768	0.0000000000	
H	0.8101426438	-0.7040415353	0.0000000000	
C	-0.9089402496	-2.0052345001	0.0000000000	
H	-1.9852488330	-2.0027061208	0.0000000000	
C	-0.2680841694	-3.2533907829	0.0000000000	
C	-1.0485371931	-4.4393793894	0.0000000000	
C	1.1455560139	-3.3998264111	0.0000000000	
C	-0.4597076685	-5.6759065873	0.0000000000	
H	-2.1214028469	-4.3505445002	0.0000000000	
C	1.7206071029	-4.6464592047	0.0000000000	
H	1.7729273881	-2.5280150486	0.0000000000	
C	0.9307005683	-5.7916927785	0.0000000000	
H	-1.0708039155	-6.5616529165	0.0000000000	
H	2.7928551474	-4.7375125867	0.0000000000	
H	1.3905489838	-6.7641996338	0.0000000000	
H	-2.6254003116	1.2943212579	0.0000000000	

**Table S1 (continued).** SF-TD-BH&HLYP/6-311+G\*\* optimized Cartesian coordinates for  $S_0/S_1$ -trans/cis-ESIPT-MECI of isolated molecule **1**.

C	-0.3087913992	1.7778607899	-0.0519212099	E( $S_0$ ) = -879.356647 a.u.
C	1.1185439717	1.9330570630	-0.0472935323	E( $S_1$ ) = -879.356647 a.u.
C	0.8195938926	4.3107510626	0.0278785013	
C	-0.5098281829	4.2242735658	0.0168055946	
C	-1.1613069819	2.9351181688	-0.0271816202	
H	-1.1246885712	5.1032861158	0.0431243107	
C	1.6154062818	5.5630608885	0.0766088775	
H	2.2558964757	5.6300647323	-0.7978891813	
H	2.2575203634	5.5591851577	0.9522976570	
H	0.9668549705	6.4286407725	0.1120060293	
O	1.6071580940	3.2233543334	-0.0057276071	
O	1.9522398907	1.0704640629	-0.0778180655	
O	-2.3998876279	2.8604203966	-0.0406367254	
C	-0.9022167325	0.4704975592	-0.0737060628	
O	-2.2318047944	0.3804809795	-0.0934697265	
C	-0.2155684984	-0.7109160285	-0.0736734228	
H	0.8599834772	-0.6913157658	-0.0307133999	
C	-0.9053301929	-1.9715563781	-0.0483091699	
H	-1.1548896133	-2.4040271734	0.9145135735	
C	-1.2760168519	-2.7301524792	-1.1597495039	
C	-1.9415348136	-3.9655628583	-0.9754062545	
C	-1.0150522104	-2.2889322820	-2.4775102065	
C	-2.3258367866	-4.7176168335	-2.0548091773	
H	-2.1454779542	-4.3032159449	0.0260900343	
C	-1.4026023797	-3.0527328985	-3.5500694305	
H	-0.5132057895	-1.3492666563	-2.6168985179	
C	-2.0568451893	-4.2625114363	-3.3431842079	
H	-2.8340796512	-5.6543610431	-1.9109607901	
H	-1.2038710582	-2.7155381627	-4.5517390314	
H	-2.3601301623	-4.8544701738	-4.1893091897	
H	-2.5966462460	1.2986867959	-0.0787515146	

**Table S1 (continued).** SF-TD-BH&HLYP/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>0</sub>-IPT-trans of isolated molecule **1**.

C	-0.3595486986	1.7238946801	0.0000000000	E(S <sub>0</sub> ) = -879.454732 a.u.
C	1.0784716249	1.9125532758	0.0000000000	
C	0.7113184027	4.2882539554	0.0000000000	
C	-0.6173496615	4.1778027508	0.0000000000	
C	-1.2373946859	2.8781697429	0.0000000000	
H	-1.2484171552	5.0451924600	0.0000000000	
C	1.4811373282	5.5561817001	0.0000000000	
H	2.1217673428	5.5979895497	-0.8756555815	
H	2.1217673428	5.5979895497	0.8756555815	
H	0.8165215589	6.4098210605	0.0000000000	
O	1.5233523571	3.2181320096	0.0000000000	
O	1.9336910747	1.0817190044	0.0000000000	
O	-2.4696074262	2.7664941243	0.0000000000	
C	-0.9393568442	0.4470952409	0.0000000000	
O	-2.2345917555	0.3389104975	0.0000000000	
C	-0.2045284590	-0.7936669530	0.0000000000	
H	0.8617539621	-0.7151011016	0.0000000000	
C	-0.8397956624	-1.9752242332	0.0000000000	
H	-1.9173477674	-1.9707771326	0.0000000000	
C	-0.2140659847	-3.2854784076	0.0000000000	
C	-1.0314507205	-4.4166865817	0.0000000000	
C	1.1723274893	-3.4667860058	0.0000000000	
C	-0.4878112050	-5.6875579809	0.0000000000	
H	-2.1010758216	-4.2913262988	0.0000000000	
C	1.7130314893	-4.7338722311	0.0000000000	
H	1.8271752001	-2.6138920219	0.0000000000	
C	0.8859357703	-5.8495246124	0.0000000000	
H	-1.1342055419	-6.5477745085	0.0000000000	
H	2.7819659760	-4.8576138772	0.0000000000	
H	1.3141062107	-6.8369044510	0.0000000000	
H	-2.6201679400	1.2642432158	0.0000000000	



**Table S1 (continued).** SF-TD-BH&HLYP/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>0</sub>-IPT-cis of isolated molecule **1**.

C	-0.1871440548	1.6756040128	-0.1416889016	E(S <sub>0</sub> ) = -879.441220 a.u.
C	1.1277871858	1.9217185686	0.4206095850	
C	0.7592739650	4.2768648954	0.1068148649	
C	-0.4501193117	4.1119586688	-0.4306209096	
C	-0.9983991058	2.7910786083	-0.5923440222	
H	-1.0352281867	4.9507975148	-0.7542216881	
C	1.4442882051	5.5734911441	0.3290683293	
H	2.3893675183	5.5860843698	-0.2054015448	
H	1.6647275515	5.6968194019	1.3850490510	
H	0.8292641475	6.3968177948	-0.0085864418	
O	1.5128218385	3.2435903387	0.5168772120	
O	1.9218591385	1.1248608093	0.8114195709	
O	-2.1154489805	2.6281185636	-1.0987629399	
C	-0.7009198517	0.3801052311	-0.2821609737	
O	-1.8730544768	0.2186989419	-0.8120118823	
C	-0.0368927451	-0.8192792693	0.1851725427	
H	0.7237425814	-0.6513644813	0.9207668298	
C	-0.2898028530	-2.0922744004	-0.1578160222	
H	0.2434968965	-2.8213404605	0.4341321725	
C	-1.1145728032	-2.6981908687	-1.1989837659	
C	-1.6335409936	-3.9718868019	-0.9602969595	
C	-1.3414573874	-2.1144713484	-2.4457133701	
C	-2.3992121545	-4.6190435941	-1.9106668445	
H	-1.4411220594	-4.4494488828	-0.0141044283	
C	-2.0861035574	-2.7702520887	-3.4030437874	
H	-0.9199388304	-1.1535294967	-2.6701943116	
C	-2.6284845979	-4.0184452444	-3.1367244552	
H	-2.8056789955	-5.5928110371	-1.6999175265	
H	-2.2438500472	-2.3086585638	-4.3623145286	
H	-3.2146987746	-4.5231457452	-3.8849918319	
H	-2.2333735319	1.1245597517	-1.0467459915	

**Table S1 (continued).** SF-TD-BH&HLYP/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>0</sub>-cis of isolated molecule **1**.

C	0.0267904508	-1.6103326751	0.0000000000	E(S <sub>0</sub> ) = -879.444429 a.u.
C	-1.2088689466	-2.3656239522	0.0000000000	
C	0.0789920006	-4.4005499283	0.0000000000	
C	1.2439323732	-3.7434472274	0.0000000000	
C	1.2280275454	-2.3216941859	0.0000000000	
H	2.1849208302	-4.2570673527	0.0000000000	
C	-0.0934005955	-5.8732759960	0.0000000000	
H	-0.6582019987	-6.1775540286	-0.8759104513	
H	-0.6582019987	-6.1775540286	0.8759104513	
H	0.8661966692	-6.3730411525	0.0000000000	
O	-1.0820931271	-3.7503952185	0.0000000000	
O	-2.3315469334	-1.9686831556	0.0000000000	
O	2.3939640898	-1.7451057960	0.0000000000	
C	0.0864763469	-0.1398513111	0.0000000000	
O	1.2029960112	0.3927327579	0.0000000000	
C	-1.1383284401	0.6428461793	0.0000000000	
H	-2.0325906414	0.0544225982	0.0000000000	
C	-1.3364944939	1.9784527258	0.0000000000	
H	-2.3892500413	2.2193156159	0.0000000000	
C	-0.5356652625	3.1967693091	0.0000000000	
C	-1.2653972087	4.3940421254	0.0000000000	
C	0.8603750849	3.2853918616	0.0000000000	
C	-0.6398653442	5.6230323657	0.0000000000	
H	-2.3415092489	4.3512958939	0.0000000000	
C	1.4836316927	4.5183945170	0.0000000000	
H	1.4407826236	2.3870652136	0.0000000000	
C	0.7434007564	5.6891160695	0.0000000000	
H	-1.2274407003	6.5245619288	0.0000000000	
H	2.5590525646	4.5640573809	0.0000000000	
H	1.2395714282	6.6443566697	0.0000000000	
H	2.2245044836	-0.7677756336	0.0000000000	

**Table S1 (continued).** SF-TD-BH&HLYP/6-311+G\*\* optimized Cartesian coordinates for  $S_0/S_1$ -trans/cis-MECI of isolated molecule **1**.

C	-0.2619276082	1.7732010935	-0.0734710610	E( $S_0$ ) = -879.350904 a.u.
C	1.1603579537	1.9523371119	-0.0389423082	E( $S_1$ ) = -879.350902 a.u.
C	0.8124082007	4.3288155423	0.0501889147	
C	-0.5170607890	4.2009971663	0.0142273758	
C	-1.0804450374	2.8905931157	-0.0490981038	
H	-1.1664235085	5.0541762753	0.0356506063	
C	1.5678977366	5.6043755792	0.1229305666	
H	2.2242880473	5.6975761119	-0.7369902789	
H	2.1900388275	5.6162054241	1.0127156196	
H	0.8916753610	6.4490469253	0.1488425908	
O	1.6162683847	3.2629390779	0.0227078190	
O	2.0145885915	1.1136574888	-0.0584547270	
O	-2.3785253151	2.8044819729	-0.0803209913	
C	-0.8925183355	0.4390660620	-0.1208575329	
O	-2.1720923008	0.3942761547	-0.1643973584	
C	-0.1571584306	-0.7242933798	-0.1150232600	
H	0.9152790295	-0.7154557578	-0.0348860623	
C	-0.8719531173	-1.9616451051	-0.0778873544	
H	-1.1465274416	-2.3831050457	0.8856722114	
C	-1.2691920838	-2.7313914114	-1.1743331275	
C	-1.9723779503	-3.9389486157	-0.9614515337	
C	-1.0017085901	-2.3160703700	-2.4970290594	
C	-2.3853185200	-4.6982541968	-2.0251693323	
H	-2.1811503296	-4.2494999097	0.0476544058	
C	-1.4188211670	-3.0847965266	-3.5549474442	
H	-0.4740206536	-1.3928258459	-2.6451624709	
C	-2.1078085823	-4.2698326321	-3.3207340940	
H	-2.9223152235	-5.6157160767	-1.8650203054	
H	-1.2192340543	-2.7716466496	-4.5639413388	
H	-2.4339603086	-4.8661645266	-4.1553591441	
H	-2.5714923952	1.8026388976	-0.1216797515	

**Table S1 (continued).** TD-MN15/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>1</sub>-trans-ESIPT of molecule **1** in dichloromethane.

C	0.900658004715	-1.529456477380	0.015408101773	E(S <sub>0</sub> ) = -878.944339 a.u.
C	-0.404578168610	-2.164192219242	0.053164325358	E(S <sub>1</sub> ) = -878.840452 a.u.
C	0.654847603651	-4.319826848022	-0.114945508113	
C	1.893036934405	-3.787371437299	-0.118889041368	
C	2.086949169085	-2.364105340603	-0.046532254060	
H	2.763928185947	-4.425675975962	-0.179165789572	
C	0.313500554603	-5.762954095470	-0.190273584748	
H	-0.255084981600	-6.059992233470	0.694500979551	
H	-0.314493264544	-5.953473686278	-1.064180581439	
H	1.216741653396	-6.366585380274	-0.257385909242	
O	-0.446112566102	-3.536995585215	-0.033047079138	
O	-1.486610684208	-1.615172926455	0.154870261199	
O	3.248618908298	-1.869581738755	-0.044263554350	
C	1.047972327883	-0.091855685652	0.046345547432	
O	2.282525480569	0.418488452762	0.097629886145	
C	-0.010168259785	0.829917434910	-0.006897198211	
H	-1.010990497183	0.429653738281	-0.041883770674	
C	0.213614438580	2.221511016340	-0.025712358422	
H	1.240460234648	2.572716781123	-0.031992601823	
C	-0.810137875071	3.193922046758	-0.035043094003	
C	-0.450562912880	4.578720799942	-0.071786015127	
C	-2.205580850507	2.867452941797	-0.006606136882	
C	-1.413173845236	5.561960550396	-0.084785671201	
H	0.602875480699	4.836259229480	-0.091562310939	
C	-3.157776823430	3.864198868883	-0.019635627963	
H	-2.517445144388	1.830919454793	0.028222158108	
C	-2.774905995870	5.213033014438	-0.059250537102	
H	-1.124989008558	6.605751747959	-0.114464716445	
H	-4.209635983221	3.605711789702	0.001977943547	
H	-3.531555860071	5.988972827486	-0.069445870868	
H	2.925575084198	-0.356490981347	0.058482240834	

**Table S1 (continued).** TD-MN15/6-311+G\*\* optimized Cartesian coordinates for TS\* of molecule **1** in dichloromethane.

C	0.939374937179	-1.575682829036	-0.269132113516	E(S <sub>0</sub> ) = -878.908215 a.u.
C	-0.368983703834	-2.184575220762	-0.326287953169	E(S <sub>1</sub> ) = -878.835162 a.u.
C	0.652715280042	-4.342576375506	-0.021311973283	
C	1.898834187002	-3.833576376183	-0.025785990565	
C	2.114987656037	-2.414286831604	-0.162613423203	
H	2.757773733234	-4.482668014553	0.075243456533	
C	0.288311234752	-5.776047418205	0.119407077568	
H	-0.270463043155	-6.107227889503	-0.759126595893	
H	1.180704538674	-6.389010618169	0.231373075222	
H	-0.356273141165	-5.912387718766	0.991041970590	
O	-0.437736224719	-3.551756911763	-0.160122820709	
O	-1.435608375049	-1.623823279529	-0.504721694620	
O	3.280495651820	-1.937853995958	-0.186957523361	
C	1.092870386959	-0.144754228228	-0.322239303931	
O	2.327167723802	0.360858144405	-0.434240155571	
C	0.057185213897	0.774550337293	-0.188805351589	
H	-0.951765594237	0.390730157235	-0.075042901395	
C	0.319986847815	2.187941334880	-0.131551141100	
H	1.088649933416	2.539081101224	0.557243041172	
C	-0.312960938008	3.138091839604	-0.942972091616	
C	0.028147362671	4.520945311151	-0.831007322328	
C	-1.296125953978	2.756374377919	-1.908154611678	
C	-0.583616404614	5.459227395454	-1.632570709369	
H	0.777619276232	4.814940430363	-0.103999613610	
C	-1.893747168974	3.708881447793	-2.708146759023	
H	-1.568969473867	1.709771010791	-1.994399998494	
C	-1.545094180329	5.059384725115	-2.575132722203	
H	-0.323550357322	6.506732630484	-1.539960275489	
H	-2.640870818606	3.414803169824	-3.435477980339	
H	-2.026449030484	5.802869307304	-3.199908631520	
H	2.968424574812	-0.412478863075	-0.385839543511	

**Table S1 (continued).** SF-TD-BH&HLYP/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>1</sub>-TICT of isolated molecule **1**.

C	0.6755208989	-1.6329397503	-0.2904975959	E(S <sub>0</sub> ) = -879.381697 a.u.
C	-0.2619641867	-2.3706454423	-1.1209230665	E(S <sub>1</sub> ) = -879.307546 a.u.
C	0.4483218325	-4.3730298556	-0.0082408923	
C	1.3935960635	-3.7292692574	0.7138380960	
C	1.5803509573	-2.3510091386	0.5122037735	
H	2.0332199227	-4.2642424622	1.3878751134	
C	0.1792728908	-5.8283002798	0.0444427696	
H	-0.8558800854	-5.9975657921	0.3256542949	
H	0.3231885223	-6.2607835260	-0.9411126502	
H	0.8314237964	-6.3190950206	0.7537708154	
O	-0.3277070293	-3.7425985886	-0.8789436945	
O	-0.9898441959	-1.9312026373	-1.9410127883	
O	2.5836216040	-1.7666993336	1.0964476908	
C	0.8320991055	-0.1682381744	-0.4115020719	
O	2.0451048363	-0.1186115517	-0.8460179829	
C	-0.0771023443	0.8121951956	-0.1668704471	
H	-1.0435682673	0.4913092262	0.1793104176	
C	0.2135000684	2.1644056581	-0.3508735026	
H	1.1868028560	2.4028563006	-0.7454899377	
C	-0.6485528537	3.2707657435	-0.0570450885	
C	-0.2041772997	4.5736670843	-0.3310139050	
C	-1.9275634626	3.1321997961	0.5045917998	
C	-0.9901893126	5.6737073162	-0.0614517131	
H	0.7734213168	4.7084752504	-0.7629116949	
C	-2.7094263205	4.2357030383	0.7740561078	
H	-2.3094899513	2.1534821084	0.7353202403	
C	-2.2503973700	5.5146564899	0.4946744987	
H	-0.6205440730	6.6600799903	-0.2848419533	
H	-3.6860165004	4.1002924123	1.2073647068	
H	-2.8645278184	6.3720341265	0.7080291000	
H	2.7296903995	-0.9166479262	0.6411695603	

**Table S1 (continued).** SF-TD-BH&HLYP/6-311+G\*\* optimized Cartesian coordinates for  $S_0/S_1$ -TICT-MECI of isolated molecule **1**.

C	0.6031311889	-1.6555037738	-0.2934588701	E( $S_0$ ) = -879.298616 a.u.
C	0.1064132393	-2.5004543851	-1.3920938003	E( $S_1$ ) = -879.298615 a.u.
C	0.5458383115	-4.4109915887	-0.0010809962	
C	1.0043657664	-3.6635713319	1.0294457505	
C	1.0345996639	-2.2715882180	0.8979972881	
H	1.3206883987	-4.1256473425	1.9442594013	
C	0.4132705550	-5.8853907268	-0.0014945973	
H	-0.6308534451	-6.1539326893	-0.1365928571	
H	0.9682785575	-6.3089953401	-0.8326376501	
H	0.7736889703	-6.3067778208	0.9271401114	
O	0.1323469314	-3.8621684982	-1.1441225154	
O	-0.3267713543	-2.1342960760	-2.4237136401	
O	1.4704734325	-1.5497033304	1.9036184056	
C	0.6572707471	-0.2164388619	-0.4470060127	
O	1.8246075930	-0.4955034369	-0.9793607769	
C	-0.1324221732	0.8332803407	-0.2186025760	
H	-1.0804816839	0.5894387378	0.2270760659	
C	0.2035886270	2.1922601137	-0.4708906804	
H	1.1565849982	2.3971885568	-0.9273370170	
C	-0.6153162587	3.3085370860	-0.1192696537	
C	-0.1440561220	4.6144553283	-0.3388082510	
C	-1.8934173243	3.1785674173	0.4515181130	
C	-0.8981366566	5.7175599887	-0.0016097554	
H	0.8308019696	4.7480497754	-0.7772519632	
C	-2.6434874344	4.2862567550	0.7856001594	
H	-2.3077507459	2.2024917440	0.6296811327	
C	-2.1549940210	5.5649208557	0.5659693262	
H	-0.5058710176	6.7043735896	-0.1798637700	
H	-3.6201944456	4.1516931359	1.2191838019	
H	-2.7437309451	6.4256737053	0.8306323603	
H	1.4218707075	-0.6142986897	1.6834975668	

**Table S1 (continued).** TD-MN15/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>1</sub>-TICT of molecule **1** in dichloromethane.

C	0.780958913186	-1.615874549051	-0.265934897575	E(S <sub>0</sub> ) = -878.925295 a.u.
C	-0.364612965720	-2.262589433652	-0.875338538156	E(S <sub>1</sub> ) = -878.828851 a.u.
C	0.401517584359	-4.347760627722	0.042280941881	
C	1.518647014058	-3.781523639870	0.576721717582	
C	1.751758320569	-2.403205864335	0.379260512617	
H	2.234864442475	-4.381524864804	1.118943464572	
C	0.040440986178	-5.782964898994	0.121746230045	
H	-0.932427445358	-5.891386782559	0.607171244513	
H	-0.047717669988	-6.195923656240	-0.886011286036	
H	0.789849951602	-6.340035551227	0.679469427683	
O	-0.489725933443	-3.624562871238	-0.652315392300	
O	-1.232157005534	-1.726450491256	-1.520610795832	
O	2.870407694789	-1.892909062049	0.858149283819	
C	0.971472972426	-0.162941242969	-0.407815312749	
O	2.161829561531	0.001937489263	-0.903094325954	
C	0.024331255424	0.832550836392	-0.138902362082	
H	-0.940103374731	0.477789299543	0.209136119572	
C	0.282765590379	2.172428092552	-0.308032395519	
H	1.277424386291	2.455657707491	-0.643746933145	
C	-0.639509217502	3.261253766736	-0.057166249503	
C	-0.173403272057	4.587247307411	-0.158044627715	
C	-1.994237009475	3.067255916224	0.283316622567	
C	-1.013585000543	5.667744260934	0.078131067485	
H	0.865175739474	4.756426465159	-0.424921681069	
C	-2.830583577130	4.148680343743	0.521251706639	
H	-2.396753784131	2.062956789283	0.353193170304	
C	-2.348799784212	5.456242513937	0.422118049455	
H	-0.627755067139	6.677469761043	-0.006257520862	
H	-3.868831533074	3.974217043776	0.780804542168	
H	-3.007356729875	6.296942063990	0.606108804922	
H	2.998298957171	-0.992195121512	0.490389412674	



**Table S2.** TD-MN15/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>1</sub>-trans-ESIPT of molecule **2** in dichloromethane.

C	0.896258527843	-1.527338235278	-0.064120792522	E(S <sub>0</sub> ) = -1338.479399 a.u.
C	-0.409212997517	-2.161415151904	-0.077481030898	E(S <sub>1</sub> ) = -1338.377300 a.u.
C	0.656502572902	-4.321386170275	-0.086592589187	
C	1.893561840466	-3.787700237376	-0.074451820274	
C	2.083853458437	-2.361678972763	-0.062624259205	
H	2.766499321353	-4.426075109882	-0.073394920406	
C	0.318499538053	-5.767286497353	-0.099709065127	
H	-0.284972973813	-6.018202566404	0.776175838037	
H	-0.274109477205	-6.004670524437	-0.986711866097	
H	1.223666484324	-6.371663979856	-0.098763280447	
O	-0.446678390647	-3.537674400151	-0.088022753399	
O	-1.495749721663	-1.611898233906	-0.080639246282	
O	3.245455014595	-1.867211533767	-0.051409887539	
C	1.044038130255	-0.090257495085	-0.051992773858	
O	2.278897301710	0.419515310830	-0.041428392782	
C	-0.014803965982	0.832615269905	-0.049210860676	
H	-1.016137649789	0.432402973324	-0.057888410906	
C	0.211041421352	2.223347198609	-0.034792752179	
H	1.237591153944	2.574567110287	-0.027356323257	
C	-0.810600596654	3.195163974564	-0.027826985276	
C	-0.452499390587	4.581589934692	-0.011377459531	
C	-2.207560892616	2.871048154214	-0.035381648914	
C	-1.406612723296	5.568522272047	-0.002824178693	
H	0.599346573894	4.844225499923	-0.005231767583	
C	-3.162640378569	3.860410139551	-0.026873669427	
H	-2.524963622238	1.836102952961	-0.047570664455	
C	-2.764875347595	5.205298294718	-0.010556150644	
H	-1.131324444901	6.615491812963	0.009869099190	
H	-4.217334142048	3.615481243114	-0.032493286133	
H	2.921473783434	-0.358072987509	-0.043346660940	
Cl	-3.961149457443	6.436286574242	0.000520359413	

**Table S2 (continued).** TD-MN15/6-311+G\*\* optimized Cartesian coordinates for TS\* of molecule **2** in dichloromethane.

C	0.940929895295	-1.578274504068	-0.310223701748	E(S <sub>0</sub> ) = -1338.441405 a.u.
C	-0.374632909072	-2.167018840979	-0.220495735747	E(S <sub>1</sub> ) = -1338.371269 a.u.
C	0.642704314219	-4.338590610817	-0.009686817061	
C	1.888550754835	-3.848631241832	-0.148934563670	
C	2.109067860941	-2.433573093521	-0.320125591876	
H	2.744217765501	-4.509645609477	-0.133625910509	
C	0.274202504204	-5.765560247092	0.178557198789	
H	1.164326984163	-6.391408783745	0.202570112461	
H	-0.279289392751	-5.886908935038	1.112729918609	
H	-0.376722743113	-6.093208784718	-0.635503637508	
O	-0.444835722691	-3.532294571289	-0.038853813452	
O	-1.446085466386	-1.591330250069	-0.286072813868	
O	3.272368307216	-1.975483152281	-0.470822831138	
C	1.109001765527	-0.150223375978	-0.392961844054	
O	2.332543651442	0.334549704009	-0.636350683586	
C	0.107107677962	0.786846269528	-0.167207819435	
H	-0.891355735534	0.423854324051	0.054946099699	
C	0.400019006438	2.196782214932	-0.156204197106	
H	1.225683559858	2.545372146032	0.464371504052	
C	-0.277307436502	3.143145440354	-0.931111845277	
C	0.093588238494	4.522256666669	-0.875794591997	
C	-1.340796667527	2.764567719011	-1.808926445184	
C	-0.557815654343	5.460124495483	-1.640562674187	
H	0.902506675400	4.820778631237	-0.218360132699	
C	-1.987447745364	3.705621606937	-2.578520441297	
H	-1.639220396231	1.722911112274	-1.856979354635	
C	-1.595857531717	5.046848927032	-2.490261178162	
H	-0.283069103686	6.506558093698	-1.599738632976	
H	-2.796359454965	3.425552733469	-3.241512440626	
H	2.963921500196	-0.448703449460	-0.647784964210	
Cl	-2.419170641808	6.225333475649	-3.437476401601	

**Table S3.** SF-TD-BH&HLYP/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>1</sub>-trans of isolated model molecule **7'** (with dimethylamino group).

C	0.3361888539	-2.9196013893	0.0000000000	E(S <sub>0</sub> ) = -1013.369383 a.u.
C	-1.1096632038	-2.9326704178	0.0000000000	E(S <sub>1</sub> ) = -1013.247588 a.u.
C	-1.0574143479	-5.3376053489	0.0000000000	
C	0.2814325147	-5.3711420924	0.0000000000	
C	1.0036466501	-4.1496804177	0.0000000000	
H	0.8180172827	-6.3000792455	0.0000000000	
C	-1.9720639737	-6.5048885229	0.0000000000	
H	-2.6143503289	-6.4771566119	-0.8757891969	
H	-2.6143503289	-6.4771566119	0.8757891969	
H	-1.4111367420	-7.4305364150	0.0000000000	
O	-1.7173741494	-4.1725759036	0.0000000000	
O	-1.8594860495	-1.9982290338	0.0000000000	
O	2.3074332841	-4.2223786840	0.0000000000	
C	1.1278631018	-1.7061943175	0.0000000000	
O	2.3966153798	-1.7906087400	0.0000000000	
C	0.5199147051	-0.4081330745	0.0000000000	
H	-0.5492296686	-0.3642574802	0.0000000000	
C	1.3033907705	0.7334377347	0.0000000000	
H	2.3715180136	0.6079349155	0.0000000000	
C	0.7753242612	2.0519613497	0.0000000000	
C	1.6488404757	3.1678928787	0.0000000000	
C	-0.6181201514	2.3383710759	0.0000000000	
C	1.1906504017	4.4499462473	0.0000000000	
H	2.7097625282	2.9868684535	0.0000000000	
C	-1.0869839153	3.6213649152	0.0000000000	
H	-1.3254648897	1.5306194069	0.0000000000	
C	-0.2042829965	4.7254287542	0.0000000000	
H	1.8991146254	5.2557142580	0.0000000000	
H	-2.1478267998	3.7816857283	0.0000000000	
H	2.6284541835	-3.2608691671	0.0000000000	
N	-0.6639272758	5.9970403829	0.0000000000	
C	0.2549864102	7.1158404602	0.0000000000	
H	0.8896959790	7.1064763622	0.8825037469	
H	0.8896959790	7.1064763622	-0.8825037469	
H	-0.3093508841	8.0361109339	0.0000000000	
C	-2.0877117896	6.2605623388	0.0000000000	
H	-2.5651627352	5.8411842508	-0.8820175193	
H	-2.5651627352	5.8411842508	0.8820175193	
H	-2.2514929951	7.3277154225	0.0000000000	

**Table S3 (continued).** SF-TD-BH&HLYP/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>1</sub>-trans-ESIPT of isolated model molecule 7' (with dimethylamino group).

C	2.9229793739	0.3644830803	0.0000000000	E(S <sub>0</sub> ) = -1013.369269 a.u.
C	2.9183982104	-1.0808520552	0.0000000000	E(S <sub>1</sub> ) = -1013.255788 a.u.
C	5.3158477792	-1.0688836207	0.0000000000	
C	5.3847934893	0.2629356481	0.0000000000	
C	4.1875265322	1.0654563658	0.0000000000	
H	6.3316422442	0.7679607376	0.0000000000	
C	6.4625747360	-2.0108616843	0.0000000000	
H	6.4171445674	-2.6517940046	-0.8757762845	
H	6.4171445674	-2.6517940046	0.8757762845	
H	7.4012839248	-1.4725496947	0.0000000000	
O	4.1397521108	-1.7161072197	0.0000000000	
O	1.9647317733	-1.8115222157	0.0000000000	
O	4.2615139270	2.3048102161	0.0000000000	
C	1.7044938068	1.1186690328	0.0000000000	
O	1.7671001705	2.4513157843	0.0000000000	
C	0.4242181307	0.5628285380	0.0000000000	
H	0.3721651131	-0.5045177033	0.0000000000	
C	-0.7316294661	1.3423055498	0.0000000000	
H	-0.6307196567	2.4126611576	0.0000000000	
C	-2.0444648034	0.7986641698	0.0000000000	
C	-3.1677824829	1.6580707306	0.0000000000	
C	-2.3149548709	-0.5939451158	0.0000000000	
C	-4.4469521693	1.1852187887	0.0000000000	
H	-3.0007459950	2.7215123943	0.0000000000	
C	-3.5937786525	-1.0786411785	0.0000000000	
H	-1.5011325677	-1.2946303411	0.0000000000	
C	-4.7068206504	-0.2098398865	0.0000000000	
H	-5.2597812091	1.8855444608	0.0000000000	
H	-3.7407951170	-2.1413423976	0.0000000000	
H	2.7160207036	2.7070545625	0.0000000000	
N	-5.9742894133	-0.6853075653	0.0000000000	
C	-7.1021027187	0.2211881933	0.0000000000	
H	-7.1002797045	0.8566982542	0.8823316645	
H	-7.1002797045	0.8566982542	-0.8823316645	
H	-8.0167705864	-0.3525099789	0.0000000000	
C	-6.2190997905	-2.1115806176	0.0000000000	
H	-5.7941112546	-2.5849570985	-0.8818593007	
H	-5.7941112546	-2.5849570985	0.8818593007	
H	-7.2841656125	-2.2896223979	0.0000000000	

**Table S3 (continued).** TD-MN15/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>1</sub>-trans of model molecule **7'** (with dimethylamino group) in dichloromethane.

C	2.046378389116	2.135999219447	-0.007750638105	E(S <sub>0</sub> ) = -1012.791892 a.u. E(S <sub>1</sub> ) = -1012.696617 a.u.
C	3.009543873864	1.057652029455	-0.065064354478	
C	4.800347115090	2.685885941115	-0.021471617798	
C	3.936609343278	3.723866264287	0.025500487224	
C	2.537990756622	3.463644972493	0.033272806815	
H	4.292664399820	4.743986604279	0.058531464548	
C	6.283359755081	2.768272580463	-0.033525727461	
H	6.696958417672	2.233153828487	0.824975276961	
H	6.679283438910	2.297903752593	-0.937061714823	
H	6.607674676260	3.806922147933	0.001555399978	
O	4.347844074609	1.415653000297	-0.063887353459	
O	2.798703562320	-0.139386608613	-0.115125454734	
O	1.712745237784	4.479541621571	0.080912546506	
C	0.607743263570	1.937205181604	0.009830818182	
O	-0.153707013511	2.987523606472	0.053423783882	
C	0.000064637999	0.641849652830	-0.012055777749	
H	0.654913124102	-0.216263797657	-0.049046368031	
C	-1.384757971455	0.494597619181	0.017399264202	
H	-1.990762980695	1.394069748819	0.056678594260	
C	-2.063474272362	-0.755758138555	0.003611587613	
C	-3.490920235713	-0.786920302471	0.046864614395	
C	-1.397351919780	-2.021274478244	-0.050813558163	
C	-4.196192185303	-1.959088077611	0.039754763715	
H	-4.024515558897	0.156645243903	0.087425174318	
C	-2.092730136054	-3.202069949232	-0.058983823972	
H	-0.315448669028	-2.055936143235	-0.086690800675	
C	-3.519168825182	-3.218431144043	-0.012906315723	
H	-5.276762823829	-1.926246146190	0.074189386283	
H	-1.543614469423	-4.133207243610	-0.100413041852	
H	0.744226285727	4.012347836055	0.076526885441	
N	-4.210041192648	-4.382697892517	-0.018697960159	
C	-5.664969915335	-4.381486972927	0.035100111608	
H	-6.090132378837	-3.856745144972	-0.825384637331	
H	-6.019918662599	-5.408244828160	0.022351151976	
H	-6.024333019454	-3.901250543496	0.949929160785	
C	-3.508119673123	-5.656370392959	-0.076036828007	
H	-2.850183639055	-5.781369487988	0.789146953758	
H	-4.236066405600	-6.462968926312	-0.076101167395	
H	-2.905436403941	-5.731483632493	-0.985963092536	

**Table S3 (continued).** TD-MN15/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>1</sub>-trans-ESIPT of model molecule **7'** (with dimethylamino group) in dichloromethane.

C	2.038885820127	2.158695827929	0.001260820277	E(S <sub>0</sub> ) = -1012.793054 a.u.
C	2.995102193257	1.073192084880	-0.058631913291	E(S <sub>1</sub> ) = -1012.702543 a.u.
C	4.797177897520	2.678198427573	-0.012254618356	
C	3.952122236039	3.724430941906	0.036689943248	
C	2.525597708648	3.521880682893	0.045273348153	
H	4.330928039065	4.736919528362	0.071814624791	
C	6.282263977477	2.739648587500	-0.023976268508	
H	6.687436858358	2.196413959993	0.833373102702	
H	6.670973897212	2.265231877626	-0.928464483629	
H	6.621905996978	3.773341834359	0.013344619317	
O	4.336016007064	1.406910326768	-0.057963005260	
O	2.765128513362	-0.122976624438	-0.110759464785	
O	1.743705513889	4.515635537451	0.091626997546	
C	0.625515157903	1.917319338127	0.017889949534	
O	-0.201015126029	2.971855186743	0.066386404983	
C	0.000753392105	0.648532428976	-0.006351870967	
H	0.651159505396	-0.211557954576	-0.044771038078	
C	-1.386549120642	0.499941141320	0.021731616763	
H	-2.002745352802	1.391848602332	0.061544456100	
C	-2.058585766002	-0.754391179724	0.006480877065	
C	-3.484939498213	-0.790544507187	0.049054756713	
C	-1.388354071657	-2.016228266127	-0.048012102971	
C	-4.186455192672	-1.965873374600	0.041887271792	
H	-4.022590576156	0.150800699352	0.089388735000	
C	-2.079280611275	-3.199920061308	-0.056240848031	
H	-0.306309059319	-2.048634475679	-0.083789995877	
C	-3.505491891847	-3.222027304815	-0.010140575950	
H	-5.267161882077	-1.936382055418	0.075963514109	
H	-1.526163323506	-4.128686101431	-0.097655940695	
H	0.379487865000	3.796636744495	0.084673707216	
N	-4.191416503330	-4.389374236432	-0.015353553209	
C	-5.646157973998	-4.393520829900	0.038570095525	
H	-6.073663361178	-3.871152610392	-0.822329080287	
H	-5.997426752440	-5.421620711265	0.026736111861	
H	-6.007519288958	-3.913828007110	0.953007673140	
C	-3.483986897198	-5.660014991777	-0.071519081208	
H	-2.825847798842	-5.782107564705	0.794005599757	
H	-4.208611807643	-6.469675555905	-0.071293621856	
H	-2.880672723616	-5.733704345793	-0.981196762633	

**Table S3 (continued).** TD-MN15/6-311+G\*\* optimized Cartesian coordinates for TS\* of model molecule 7' (with dimethylamino group) in dichloromethane.

C	0.904515494908	-1.557243643923	-0.231850408762	E(S <sub>0</sub> ) = -1012.757125 a.u.
C	-0.394762765190	-2.185697140824	-0.179022446541	E(S <sub>1</sub> ) = -1012.690794 a.u.
C	0.682049378048	-4.340697984385	-0.067762772767	
C	1.912904887913	-3.810437324563	-0.179599654797	
C	2.092396261210	-2.381665636984	-0.281074463162	
H	2.788114185920	-4.445493922466	-0.191407139998	
C	0.352074566420	-5.784840187894	0.055396175872	
H	-0.291008813265	-6.093330785669	-0.772226921617	
H	1.258891213763	-6.386941258670	0.050678924161	
H	-0.195841312464	-5.963966890070	0.983572408543	
O	-0.425807456874	-3.563329359532	-0.064051563959	
O	-1.485601306807	-1.646454180577	-0.224245476616	
O	3.247773020992	-1.892403270204	-0.403660142595	
C	1.036016898492	-0.125467756428	-0.256435573681	
O	2.257134469122	0.396928617225	-0.436695357410	
C	0.006021510224	0.786684430489	-0.034144297305	
H	-0.984920563909	0.391389215873	0.156953479298	
C	0.263814449828	2.210214500238	0.015932846281	
H	1.039972764361	2.576727853828	0.685707246078	
C	-0.367902138539	3.128143124427	-0.822370163620	
C	-0.019141036354	4.516795578434	-0.796742607439	
C	-1.369738174895	2.734287779668	-1.767682887744	
C	-0.609305918937	5.425107010401	-1.630033294892	
H	0.738983521854	4.846130755276	-0.093635600925	
C	-1.961670379908	3.639104555936	-2.609634883531	
H	-1.668344758479	1.691749077425	-1.806552215614	
C	-1.602837068106	5.018646922206	-2.575795858608	
H	-0.314173543566	6.464188583536	-1.571378464934	
H	-2.723982519023	3.296778245372	-3.296759967707	
H	2.902986033219	-0.372976524285	-0.485429952585	
N	-2.192707375426	5.918627539163	-3.397670178946	
C	-1.845192036201	7.330066789060	-3.320370796322	
H	-2.445532943538	7.881186370493	-4.039733313359	
H	-2.046774210697	7.733695291619	-2.323691291760	
H	-0.789294766836	7.493878358070	-3.555746017966	
C	-3.189887720830	5.486898842806	-4.365738897262	
H	-2.777619256699	4.740674561126	-5.050960403189	
H	-4.066178688099	5.057417555323	-3.870059692547	
H	-3.512072041632	6.345876668482	-4.948744492073	

**Table S4.** TD-MN15/6-311+G\*\* optimized Cartesian coordinates for Min-S<sub>1</sub>-trans-ESIPT of molecule **7** (with diethylamino group) in dichloromethane.

C	0.293260783929	-3.022339497766	0.125553158913	E(S <sub>0</sub> ) = -1091.338207 a.u.
C	-0.855548923814	-2.972326512130	-0.754046660954	E(S <sub>1</sub> ) = -1091.248166 a.u.
C	-0.773544812028	-5.374850037569	-0.973034701230	
C	0.296948599102	-5.478083828209	-0.163970560275	
C	0.889959164396	-4.306380267297	0.429109267094	
H	0.730688950410	-6.444561673857	0.054602689813	
C	-1.483507105084	-6.492108797734	-1.649172956209	
H	-2.531364291077	-6.513673717199	-1.339597306931	
H	-1.462715829114	-6.349795718994	-2.732502320557	
H	-1.017295836952	-7.444798776215	-1.403554993568	
O	-1.324923767675	-4.171617479033	-1.254734488204	
O	-1.475353510464	-1.987627335900	-1.118390471505	
O	1.897276887738	-4.419150073893	1.186654135109	
C	0.854631052021	-1.834555042350	0.699047203393	
O	1.923891782414	-1.956291752483	1.498777847726	
C	0.383039641850	-0.514922447430	0.502832748647	
H	-0.478966334493	-0.397861975142	-0.135659181849	
C	0.992899340381	0.589730021577	1.097186253258	
H	1.861434797574	0.426291214910	1.726323783119	
C	0.551650984816	1.933520660398	0.933370151290	
C	1.253866615731	2.991944512067	1.583265605748	
C	-0.577485497366	2.310757370466	0.142743859840	
C	0.879821651010	4.302861971214	1.459217435767	
H	2.109726930686	2.739626458595	2.200388215924	
C	-0.965101474975	3.619181273273	0.014965024123	
H	-1.145916987754	1.550893572260	-0.379569962362	
C	-0.251737721999	4.671985318178	0.664872967595	
H	1.440799357207	5.059634420238	1.990989291681	
H	-1.816729627475	3.848954217013	-0.611405526472	
H	2.141359586567	-2.940275902584	1.546561079417	
N	-0.628929271251	5.967185941008	0.536558297748	
C	-1.853600261493	6.358090508068	-0.158107853601	
H	-2.633092618940	5.619061023522	0.033444450334	
H	-2.191627148001	7.292360465480	0.297793920420	
C	0.163710085422	7.070481576938	1.075520927243	
H	1.225233317601	6.837031837677	0.981389647467	
H	-0.021832932886	7.935651890947	0.433584120694	
C	-0.211699271003	7.394348217700	2.518803585375	
H	-1.269841498203	7.656956441564	2.589625187401	
H	-0.027585456759	6.537824049155	3.171120777043	
H	0.376195128675	8.239688599280	2.880791604829	
C	-1.624454500394	6.553252358984	-1.654347188612	
H	-0.865816949233	7.319848388952	-1.828826470184	
H	-1.286596720669	5.625178630103	-2.120806871319	
H	-2.549550608430	6.869525366215	-2.139473153181	

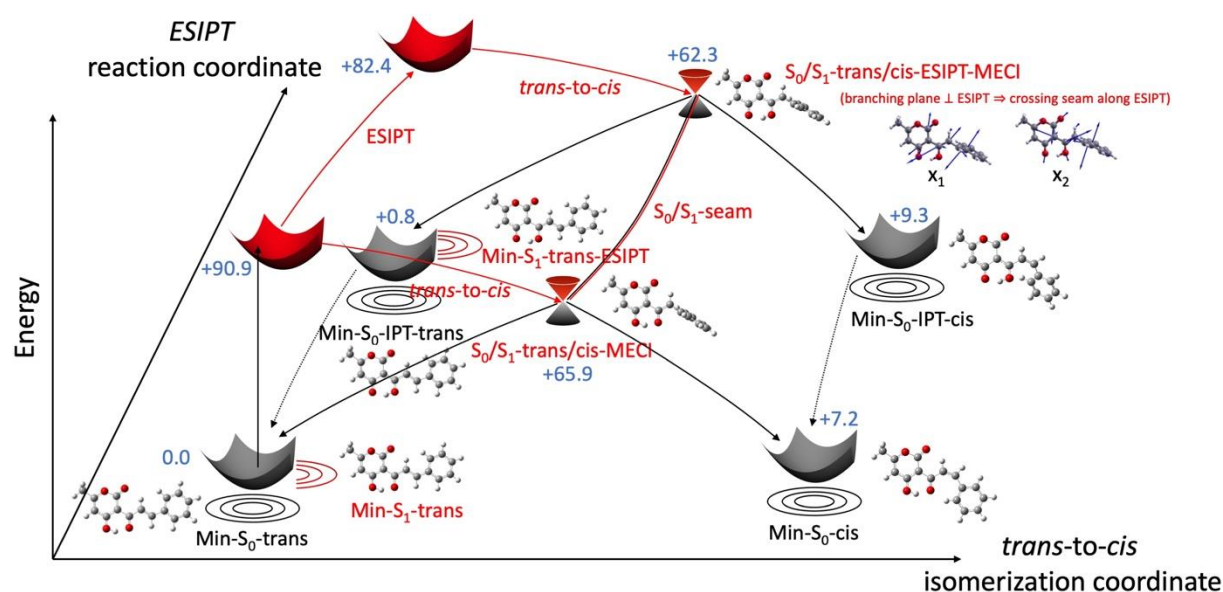


**Table S4 (continued).** TD-MN15/6-311+G\*\* optimized Cartesian coordinates for TS\* of molecule 7 (with diethylamino group) in dichloromethane.

C	0.911881860981	-1.566304128049	-0.213014050502	E(S <sub>0</sub> ) = -1091.302455 a.u.
C	-0.377298176999	-2.217390590798	-0.218746848140	E(S <sub>1</sub> ) = -1091.236010 a.u.
C	0.732572043469	-4.355839208663	-0.113103971949	
C	1.957025337672	-3.802916842266	-0.173300038392	
C	2.114883501414	-2.369513111443	-0.240276225955	
H	2.843021793539	-4.422942521258	-0.168464022683	
C	0.424046124995	-5.807493637941	-0.028654924670	
H	-0.151715413109	-6.013847048726	0.876742591826	
H	-0.185079303896	-6.110818637838	-0.883427574891	
H	1.341010928769	-6.393858977497	-0.013614859339	
O	-0.388200692356	-3.597452353696	-0.131853284203	
O	-1.475144960521	-1.695825811327	-0.292475650329	
O	3.264922259258	-1.858529123126	-0.315107009019	
C	1.018914914162	-0.132479322199	-0.203998514425	
O	2.235638680929	0.414234630563	-0.335081490126	
C	-0.033881847490	0.756988929129	0.004406321236	
H	-1.022358396211	0.339708445145	0.158002575341	
C	0.195301081043	2.184218825829	0.085075865170	
H	0.943692631730	2.554943873069	0.783499162545	
C	-0.424617326305	3.101801986909	-0.762117361067	
C	-0.098186018967	4.495102040099	-0.713236092674	
C	-1.391006474445	2.706729564733	-1.742716668796	
C	-0.672089067285	5.403032074067	-1.557585770939	
H	0.624754846133	4.830715436283	0.023250267876	
C	-1.968805631049	3.612398997596	-2.593171539179	
H	-1.668359988839	1.659818270613	-1.809567512661	
C	-1.631402346160	4.997662528744	-2.540843891592	
H	-0.405609496986	6.447027169353	-1.459939028307	
H	-2.687331509197	3.257416506241	-3.320017510370	
H	2.896086633384	-0.343456443421	-0.378547304462	
N	-2.206921440598	5.898598419739	-3.373778933277	
C	-3.279107381465	5.532912553896	-4.296623061117	
H	-3.933802967996	4.798340177814	-3.824053111026	
H	-3.885290233565	6.429840138497	-4.450232379875	
C	-1.797935944518	7.300982935873	-3.414076552763	
H	-0.720021710552	7.373403333965	-3.260290669186	
H	-1.985427220757	7.656545636596	-4.430971346707	
C	-2.564081566029	8.152200882032	-2.407042052481	
H	-3.638537084805	8.093243666840	-2.597853265413	
H	-2.380449288985	7.807351137233	-1.386738893871	
H	-2.259928497164	9.198070509179	-2.479703743430	
C	-2.741641217728	5.023185270453	-5.629751983550	
H	-2.117460077253	5.784004193423	-6.104945169154	
H	-2.135054254280	4.125881522765	-5.487002720914	
H	-3.563502611967	4.782246151569	-6.306599686558	

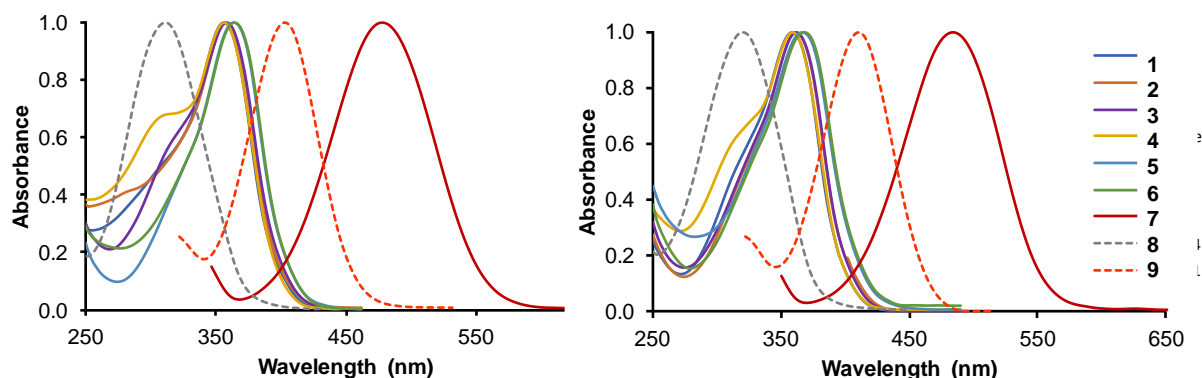
**Table S5.** Value of the dihedral angle  $\alpha$  between the planes of the pyrone and phenyl rings for the CP derivatives. Mean value  $\langle\alpha\rangle$  and H-bond distance between the carbonyl oxygen atom O(4) and the hydrogen atom H(3) of the hydroxyl group.

Compound	$\alpha$ ( $^\circ$ )	$\langle\alpha\rangle$ ( $^\circ$ )	$d_{(\text{CO-H})}$ ( $\text{\AA}$ )
<b>1</b>	6.03	9.65	1.48(3)
	10.17		1.53(3)
	12.76		1.40(3)
<b>2</b>	6.51	6.51	1.34(3)
	28.78		1.70
<b>3</b>	7.19	18.83	1.58(3)
	30.79		1.53(12)
	8.58		1.62
<b>4</b>			
<b>5</b>	7.38	5.34	1.23(4)
	3.31		1.28(4)
<b>6</b>	15.14	---	1.42(6)
<b>7</b>	6.06	12.37	1.22(3)
	18.68		1.23(3)
<b>8</b>	67.44	---	---
<b>9</b>	83.75	---	---

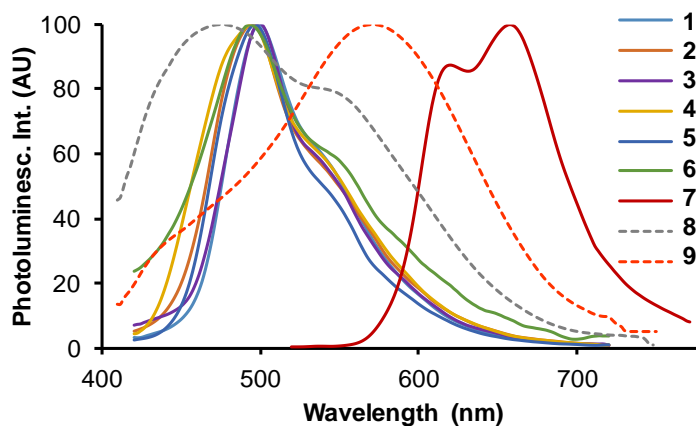


**Figure S11.** Schematic energy diagram of the critical structures for the isolated molecule **1** along the main  $S_1$  excited-state relaxation pathways (i.e., ESIPT and *trans-to-cis* isomerization). Calculations performed at the SF-TD-BH&HLYP/6-311+G\*\* level in the gas phase. Energies in kcal/mol with respect to the ground-state minimum (Min- $S_0$ -trans). The two first-order degeneracy-lifting coordinates ( $x_1$  and  $x_2$ ) that constitute the branching plane do not involve the ESIPT coordinate. Thus, a crossing seam connects the two minimum energy conical intersections,  $S_0/S_1$ -*trans/cis*-ESIPT-MECI and  $S_0/S_1$ -*trans/cis*-MECI. These two MECIs show a *peaked* pattern [1] meaning that ground-state relaxation pathways arising from these funnels can either lead to the *trans* or the *cis* isomer.

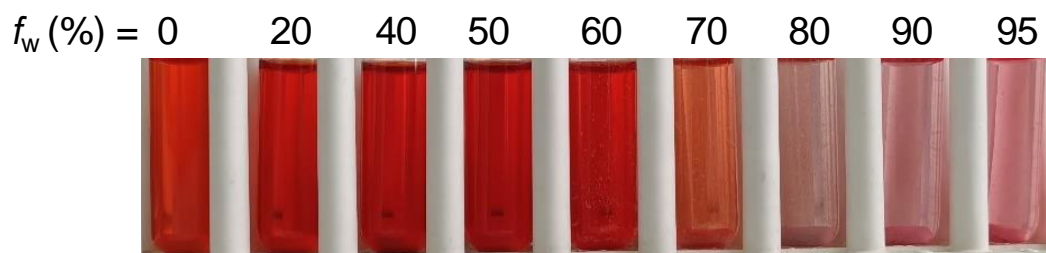
[1] Atchity, GJ, Xantheas, SS, Ruedenberg, K. Potential Energy Surfaces Near Intersections. *J Chem Phys* 1991;95:1862–1876. DOI: 10.1063/1.46103



**Figure S12.** UV-vis absorption spectra of compounds **1–9** in  $\text{CH}_3\text{CN}$  (Top) and  $\text{CH}_2\text{Cl}_2$  (Bottom) at  $2.3\text{--}4.3 \times 10^{-5}$  M. The spectra have been normalized for the sake of clarity, but the maximum absorbance of the original spectra is close to 1.



**Figure S13.** Normalized photoluminescence spectra of compounds **1–9** in the microcrystalline state ( $\lambda_{\text{ex}} = 380$  nm).

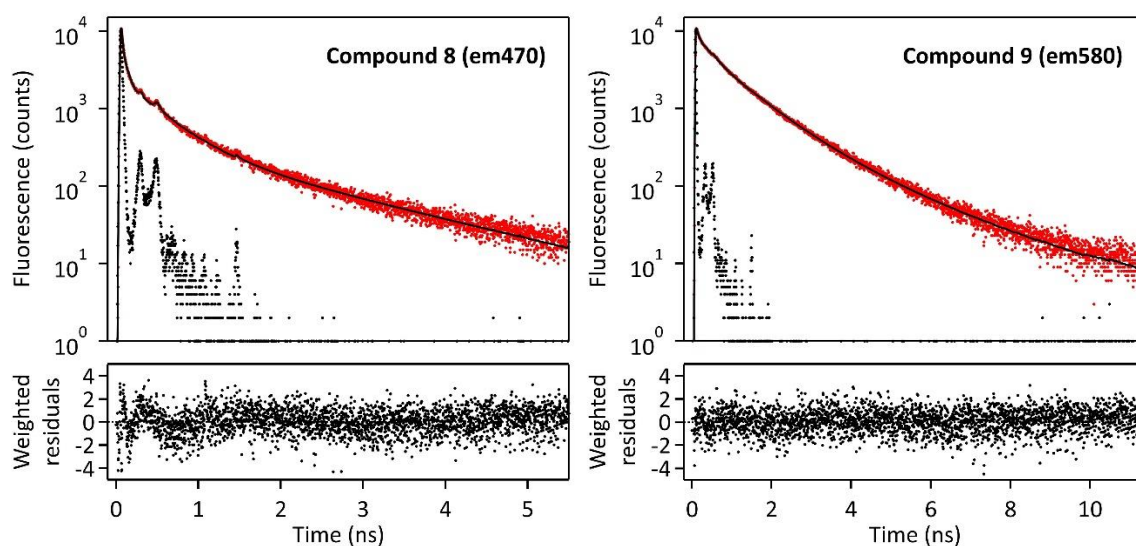


**Figure S14.** Samples of compound **7** at  $\sim 2.4 \times 10^{-4}$  M in pure acetonitrile and various water/acetonitrile mixtures containing from 20 to 95% water, observed in daylight. The decrease in colour intensity is due to the formation of aggregates, and then microparticles that may precipitate in the suspensions.

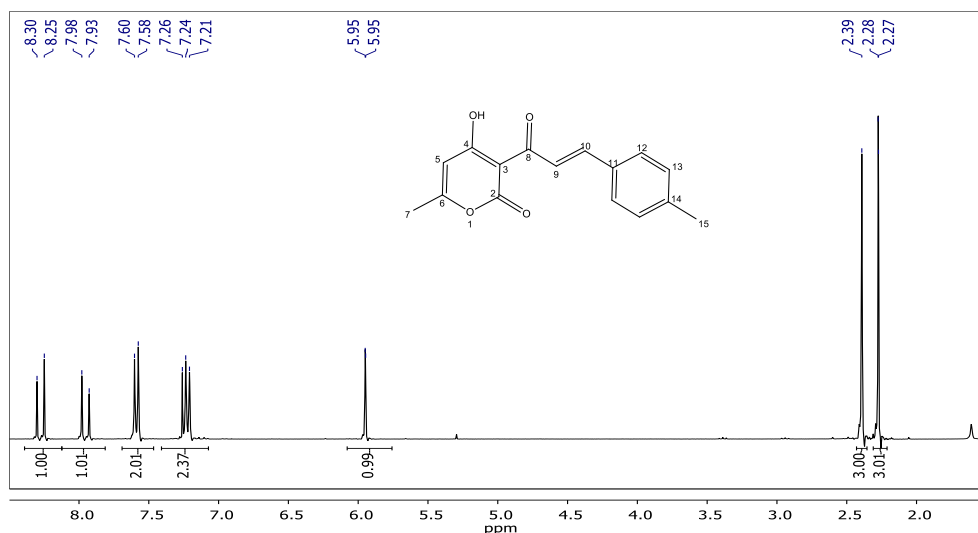
**Table S6.** Analysis of the fluorescence decays of the microcrystalline powders of CP derivatives.  $a_i$ : normalized pre-exponential factors,  $f_i$ : intensity fraction,  $\tau_i$ : photoluminescence lifetime;  $\langle\tau_{\text{PL}}\rangle$  and  $\langle\tau'_{\text{PL}}\rangle$  are respectively the amplitude-weighted and intensity-weighted mean PL lifetimes,  $\chi_{\text{R}}^2$  is the goodness-of-fit indicator.  $\lambda_{\text{ex}} = 380$  nm.

	1 <sup>a</sup>	2 <sup>a</sup>	3 <sup>a</sup>	4 <sup>a</sup>	5 <sup>a</sup>	5 <sup>b</sup>	6 <sup>a</sup>	7 <sup>c</sup>	8 <sup>d</sup>	9 <sup>e</sup>
$\tau_1$	<b>0.012</b>	<b>0.013</b>	<b>0.016</b>	<b>0.012</b>	<b>0.016</b>	<b>0.020</b>	<b>0.013</b>	<b>0.021</b>	<b>0.0005</b>	<b>0.029</b>
$a_1$	<b>-6.93</b>	<b>-5.54</b>	<b>-9.56</b>	<b>-5.29</b>	<b>-8.11</b>	<b>-11.62</b>	<b>0.86</b>	<b>-13.19</b>	<b>0.95</b>	<b>0.27</b>
$f_1$	-0.01	-0.01	-0.03	-0.01	-0.02	-0.02	0.32	-0.01	0.04	0.02
$\tau_2$	<b>0.16</b>	<b>0.20</b>	<b>0.21</b>	<b>1.32</b>	<b>0.17</b>	<b>0.16</b>	<b>0.09</b>	<b>0.75</b>	<b>0.074</b>	<b>0.23</b>
$a_2$	<b>2.02</b>	<b>3.58</b>	<b>4.08</b>	<b>1.89</b>	<b>3.52</b>	<b>1.54</b>	<b>0.12</b>	<b>-19.64</b>	<b>0.03</b>	<b>0.35</b>
$f_2$	0.06	0.15	0.18	0.25	0.10	0.02	0.30	-0.64	0.21	0.16
$\tau_3$	<b>0.56</b>	<b>0.75</b>	<b>0.56</b>	<b>1.72</b>	<b>0.80</b>	<b>1.12</b>	<b>0.48</b>	<b>1.58</b>	<b>0.41</b>	<b>0.94</b>
$a_3$	<b>3.24</b>	<b>2.16</b>	<b>5.82</b>	<b>4.40</b>	<b>3.87</b>	<b>10.56</b>	<b>0.02</b>	<b>12.94</b>	<b>0.01</b>	<b>0.33</b>
$f_3$	0.32	0.34	0.71	0.76	0.53	0.85	0.27	0.88	0.40	0.61
$\tau_4$	<b>1.35</b>	<b>3.17</b>	<b>0.99</b>	–	<b>1.31</b>	<b>4.06</b>	<b>1.75</b>	<b>0.84</b>	<b>1.71</b>	<b>2.23</b>
$a_4$	<b>2.67</b>	<b>0.80</b>	<b>0.66</b>	–	<b>1.72</b>	<b>0.53</b>	<b>0.00</b>	<b>20.88</b>	<b>0.00</b>	<b>0.05</b>
$f_4$	0.64	0.53	0.14	–	0.39	0.15	0.11	0.76	0.35	0.22
$\chi_{\text{R}}^2$	1.08	1.14	1.25 <sup>d</sup>	1.14	1.18	1.12	1.62 <sup>f</sup>	1.22	1.27 <sup>f</sup>	1.04
$\langle\tau_{\text{PL}}\rangle$	<b>5.67</b>	<b>4.80</b>	<b>4.62</b>	<b>9.98</b>	<b>5.80</b>	<b>13.97</b>	<b>0.04</b>	<b>23.06</b>	<b>0.01</b>	<b>0.51</b>
$\langle\tau'_{\text{PL}}\rangle$	<b>1.05</b>	<b>1.95</b>	<b>0.58</b>	<b>1.63</b>	<b>0.95</b>	<b>1.57</b>	<b>0.36</b>	<b>1.56</b>	<b>0.78</b>	<b>1.09</b>

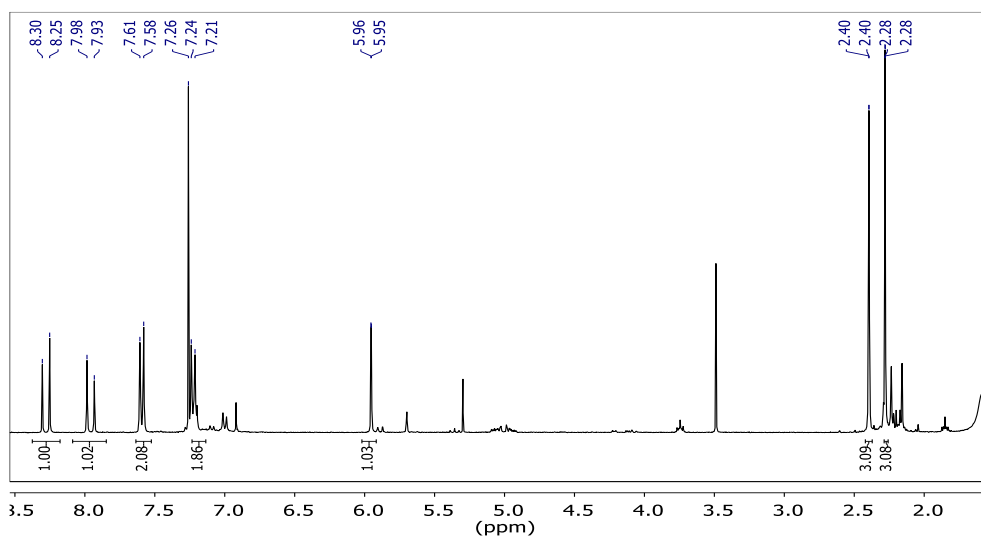
<sup>a</sup>  $\lambda_{\text{em}} = 500$  nm; <sup>b</sup>  $\lambda_{\text{em}} = 600$  nm; <sup>c</sup>  $\lambda_{\text{em}} = 670$  nm; <sup>d</sup>  $\lambda_{\text{em}} = 470$  nm; <sup>e</sup>  $\lambda_{\text{em}} = 580$  nm; <sup>f</sup> The measurement was repeated three times, leading to the same results. The  $\chi_{\text{R}}^2$  value higher than 1.2 can be explained by the very short decay, close to the instrument function, with artefacts difficult to correct by deconvolution.



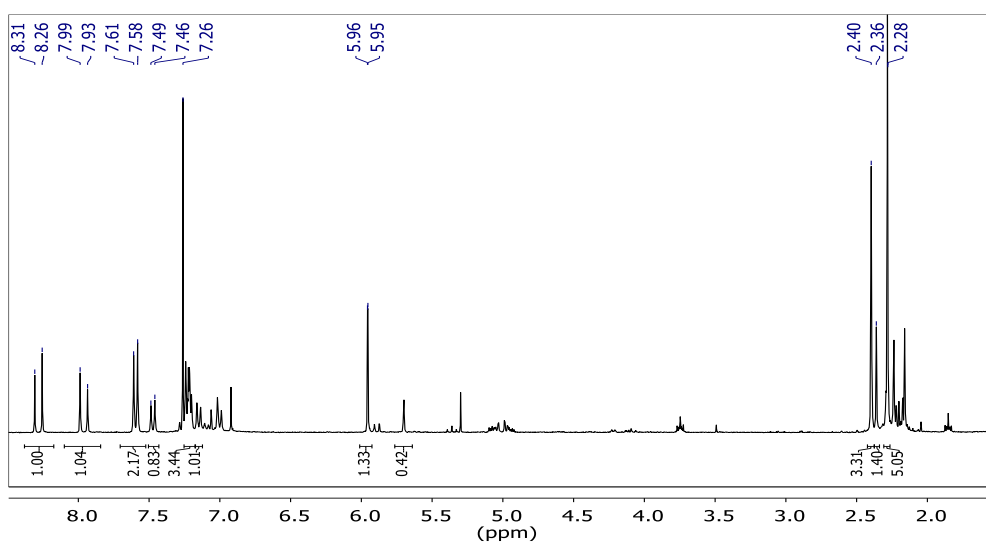
**Figure S15.** Examples of decays for compounds 8 and 9.



Before irradiation

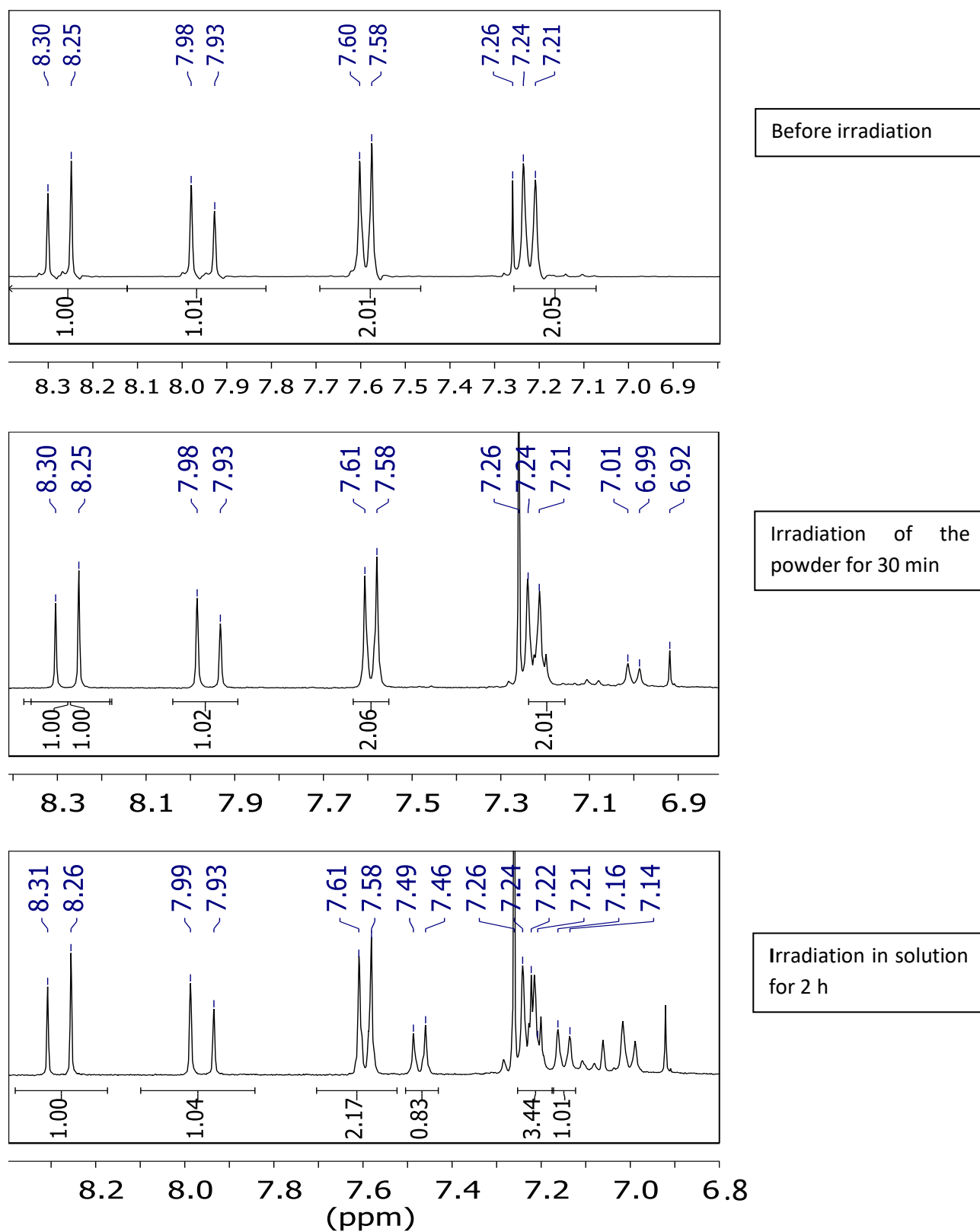


Irradiation of the powder for 30 min

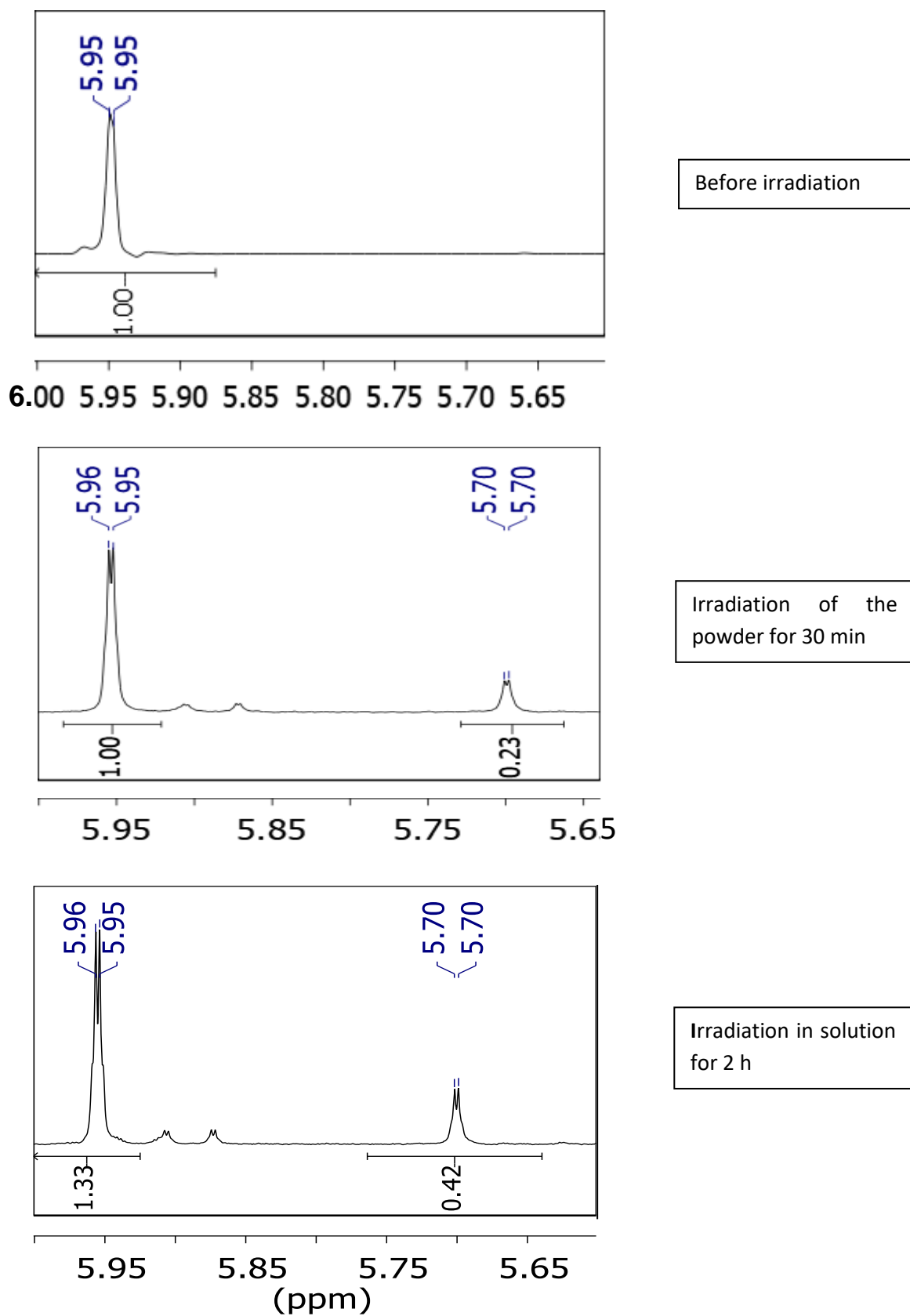


Irradiation in solution for 2 h

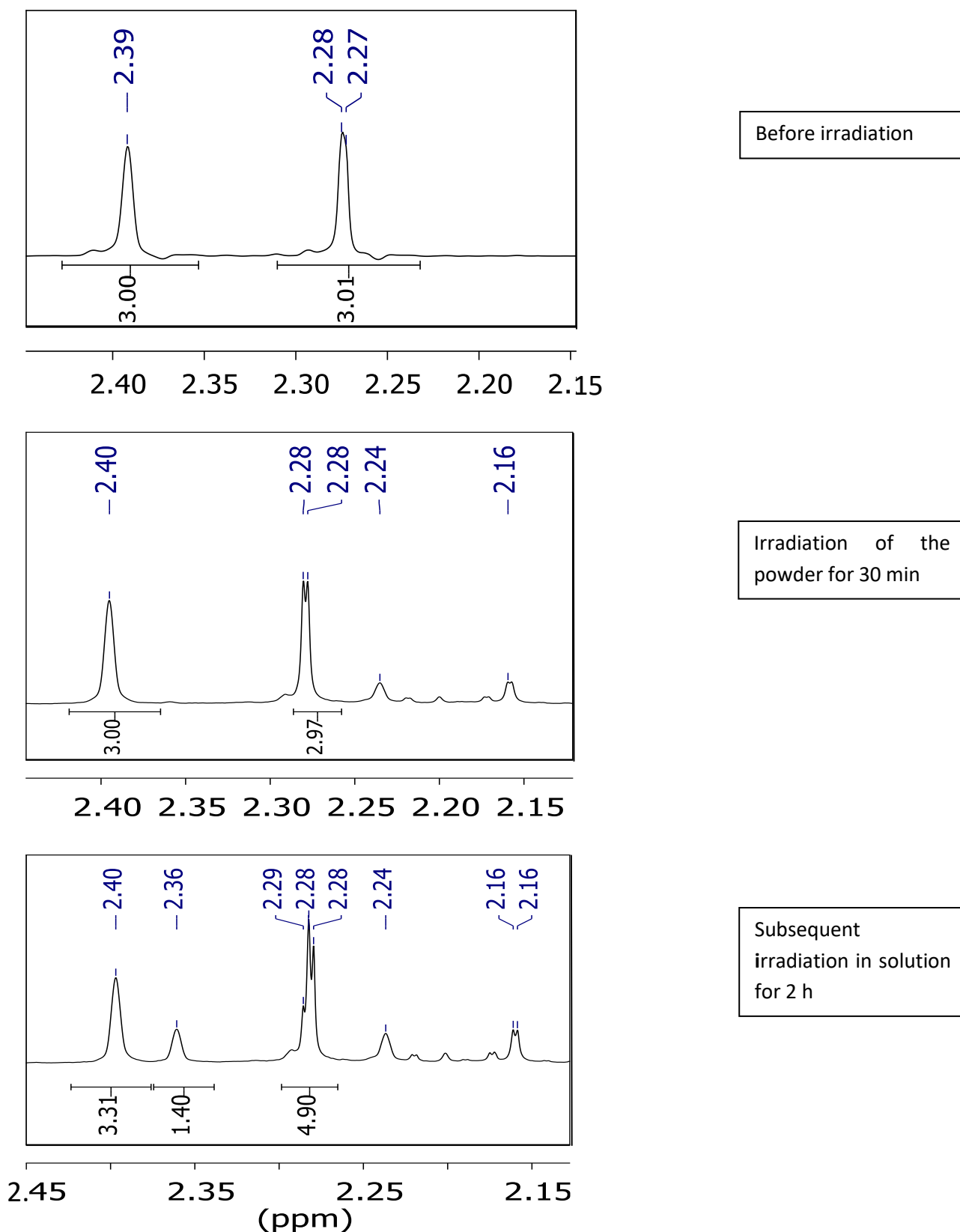
**Figure S16.**  $^1\text{H}$  NMR spectra of compound **5** in  $\text{CDCl}_3$  before irradiation (top); after irradiation of the powder by the visible-light lamp (no filter) of the microscope for 30 min (middle); and after irradiation of a solution at  $6 \times 10^{-3}$  M in  $\text{CDCl}_3$  for 2 h (bottom).



**Figure S17.** Enlarged region (8.4–6.9 ppm) of the  $^1\text{H}$  NMR spectra of compound **5** in  $\text{CDCl}_3$  before irradiation (top); after irradiation of the powder by the visible-light lamp (no filter) of the microscope for 30 min (middle); and after irradiation of a solution at  $6 \times 10^{-3}$  M in  $\text{CDCl}_3$  for 2h (bottom).



**Figure S18.** Enlarged region (6.00–5.65 ppm) of the  $^1\text{H}$  NMR spectra of compound **5** in  $\text{CDCl}_3$  before irradiation (top); after irradiation of the powder by the visible-light lamp (no filter) of the microscope for 30 min (middle); and after irradiation of a solution at  $6 \times 10^{-3}$  M in  $\text{CDCl}_3$  for 2h (bottom).



**Figure S19.** Enlarged region (2.45–2.15 ppm) of the  $^1\text{H}$  NMR spectra of compound **5** in  $\text{CDCl}_3$  before irradiation (top); after irradiation of the powder by the visible-light lamp (no filter) of the microscope for 30 min (middle); and after irradiation of a solution at  $6 \times 10^{-3}$  M in  $\text{CDCl}_3$  for 2h (bottom).