Off-on fluorometric detection of cyanide anion in aqueous mixture by indane-based receptor

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Electronic Supplementary Information (ESI†)

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Table S1 Calculated excitation energy (*E*), wavelength (λ), and oscillator strength (*f*) for low-laying singlet state (S_n) of **1′**.

	main orbital transition (CIC[a])	*E* (eV) [λ (nm)]	*f*
$S_0 \rightarrow S_1$	HOMO–2 → LUMO (–0.10532) HOMO–1 → LUMO (–0.10560) HOMO → LUMO (0.63475)	2.3937 [517.97]	0.3161
$S_0 \rightarrow S_2$	HOMO → LUMO+1 (0.68631)	2.5567 [484.93]	0.0168
$S_0 \rightarrow S_3$	HOMO–2 → LUMO (0.10030) HOMO–1 → LUMO (0.62943) HOMO–1 → LUMO+2 (–0.12951) HOMO → LUMO (0.10896) HOMO → LUMO+2 (0.13600)	2.8788 [430.68]	0.0369
$S_0 \rightarrow S_4$	HOMO–4 → LUMO+1 (0.13751) HOMO–3 → LUMO (0.57462) HOMO–3 → LUMO+1 (–0.15872) HOMO–2 → LUMO (–0.29719)	3.1014 [399.77]	0.0173
$S_0 \rightarrow S_5$	HOMO–4 → LUMO (0.18076) HOMO–3 → LUMO (0.17857) HOMO–3 → LUMO+1 (0.53677) HOMO–2 → LUMO+1 (–0.17763) HOMO–1 → LUMO+1 (0.26800)	3.1632 [391.96]	0.0045
$S_0 \rightarrow S_6$	HOMO–3 → LUMO+1 (0.11952) HOMO–2 → LUMO (–0.10266) HOMO–1 → LUMO (–0.12880) HOMO → LUMO+2 (0.60116)	3.3032 [375.34]	0.1579

[a] CI expansion coefficients for the main orbital transitions.

Table S2 Calculated excitation energy (*E*), wavelength (λ), and oscillator strength (*f*) for low-laying singlet state (S_n) of **1′**–CN^-.

	Main orbital transition (CIC[a])	*E* (eV) [λ (nm)]	*f*
$S_0 \rightarrow S_1$	HOMO–1 → LUMO+1 (–0.11672) HOMO → LUMO (0.15723) HOMO → LUMO+1 (0.64660) HOMO → LUMO+2 (–0.15422)	2.5798 [480.59]	0.005
$S_0 \rightarrow S_2$	HOMO → LUMO+1 (0.16799) HOMO → LUMO+2 (0.63442)	2.6214 [472.97]	0.0104
$S_0 \rightarrow S_3$	HOMO–1 → LUMO (0.51780) HOMO–1 → LUMO+1 (–0.10778) HOMO → LUMO (0.45136) HOMO → LUMO+1 (–0.11641)	2.7175 [456.24]	0.0014
$S_0 \rightarrow S_4$	HOMO–1 → LUMO (–0.45304) HOMO–1 → LUMO+1 (0.10956) HOMO → LUMO (0.51415) HOMO → LUMO+1 (–0.12682)	2.8117 [440.96]	0.0003
$S_0 \rightarrow S_5$	HOMO → LUMO+3 (0.70130)	2.8645 [432.83]	0.0005
$S_0 \rightarrow S_6$	HOMO–1 → LUMO+1 (–0.18181) HOMO–1 → LUMO+2 (0.67092)	2.886 [429.60]	0.0047
$S_0 \rightarrow S_7$	HOMO–2 → LUMO+1 (–0.14029) HOMO–2 → LUMO+2 (0.66980)	3.0436 [407.36]	0.0002
$S_0 \rightarrow S_8$	HOMO–1 → LUMO (0.12438) HOMO–1 → LUMO+1 (0.56699) HOMO–1 → LUMO+2 (0.18396)	3.0748 [403.22]	0.2832

[a] CI expansion coefficients for the main orbital transitions.

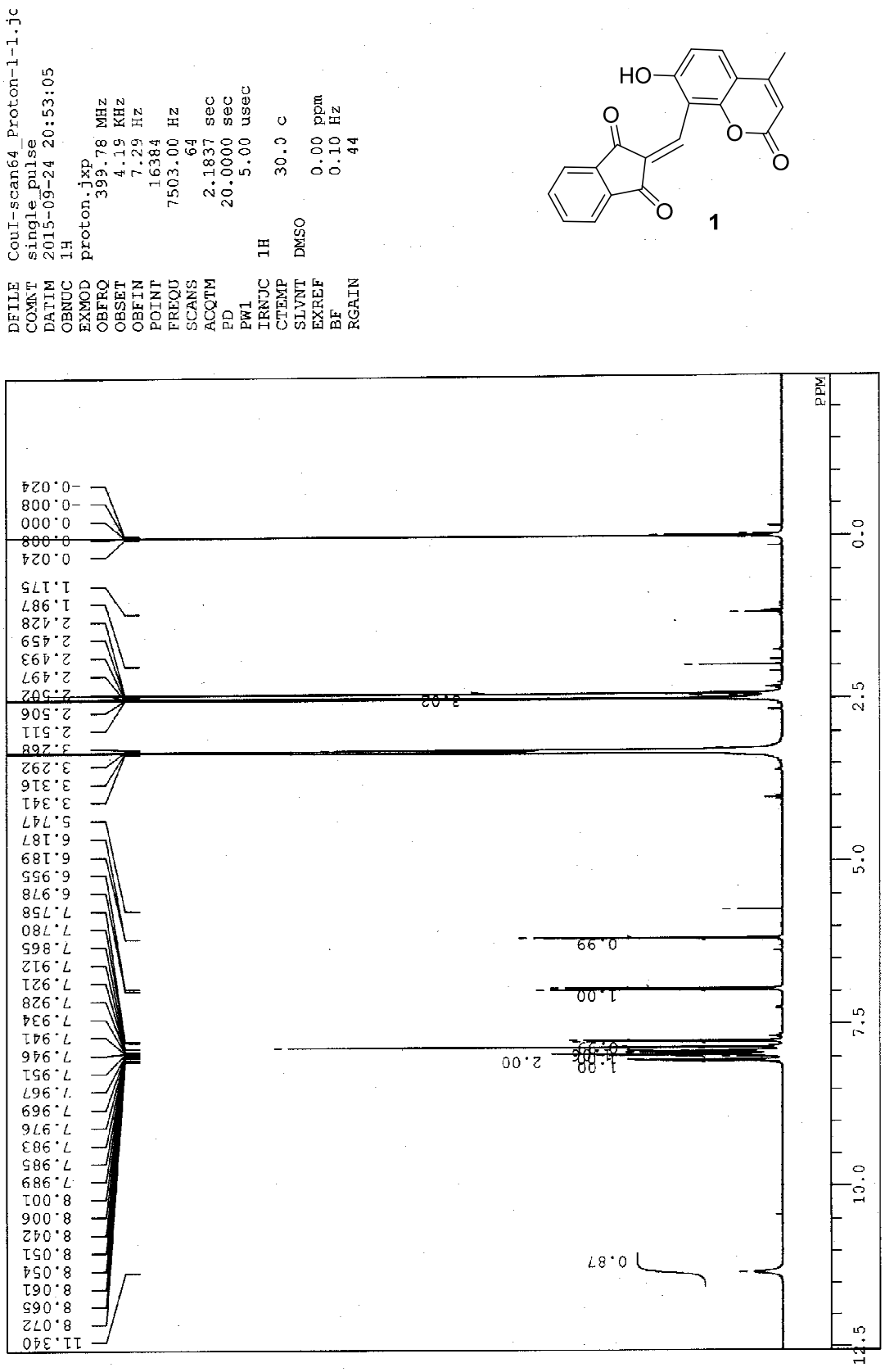


Fig. S1 ^{1}H NMR chart of **1** (DMSO-d_6, 400 MHz).

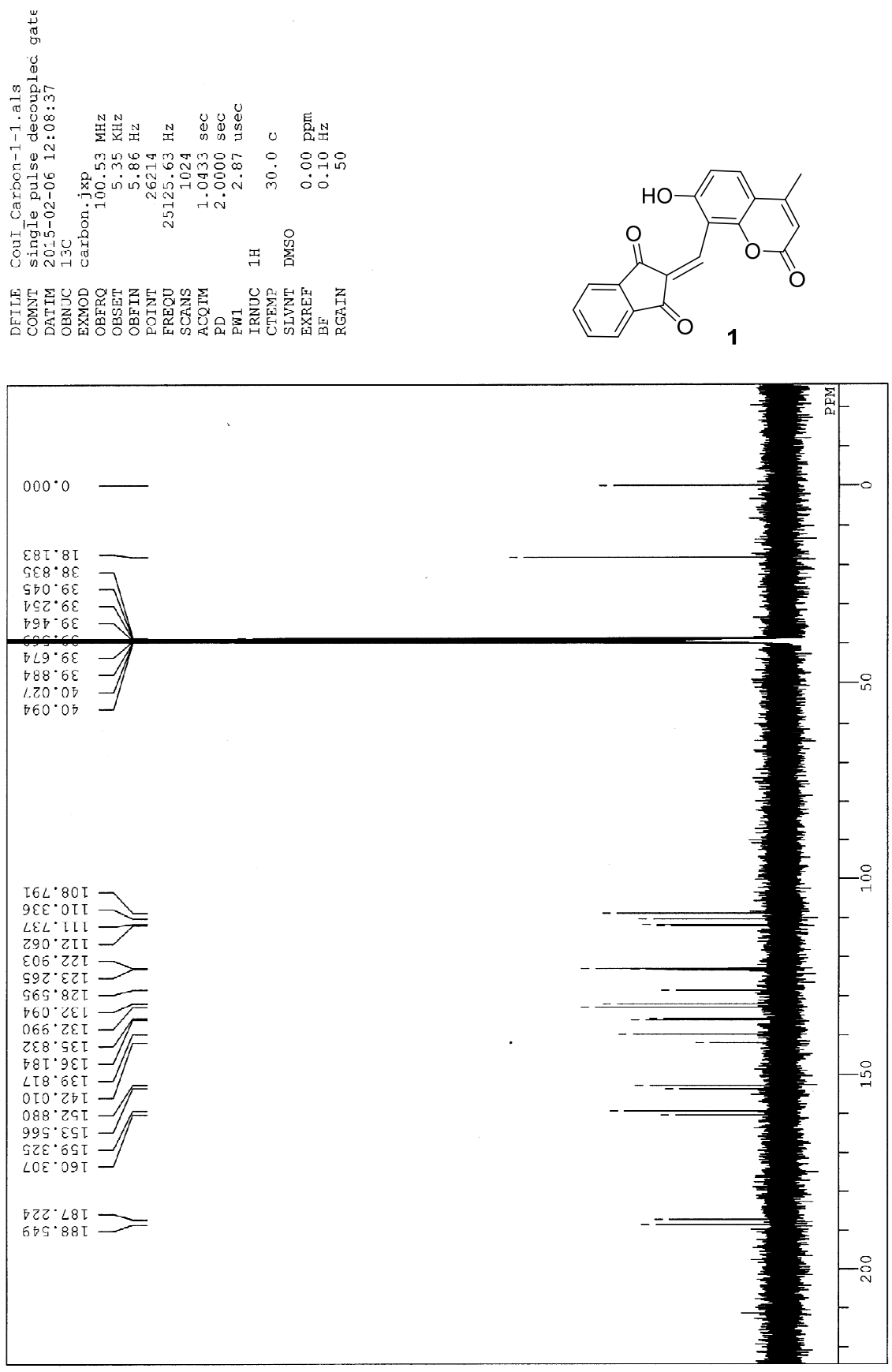


Fig. S2 ^{13}C NMR chart of **1** (DMSO-d_6, 100 MHz).

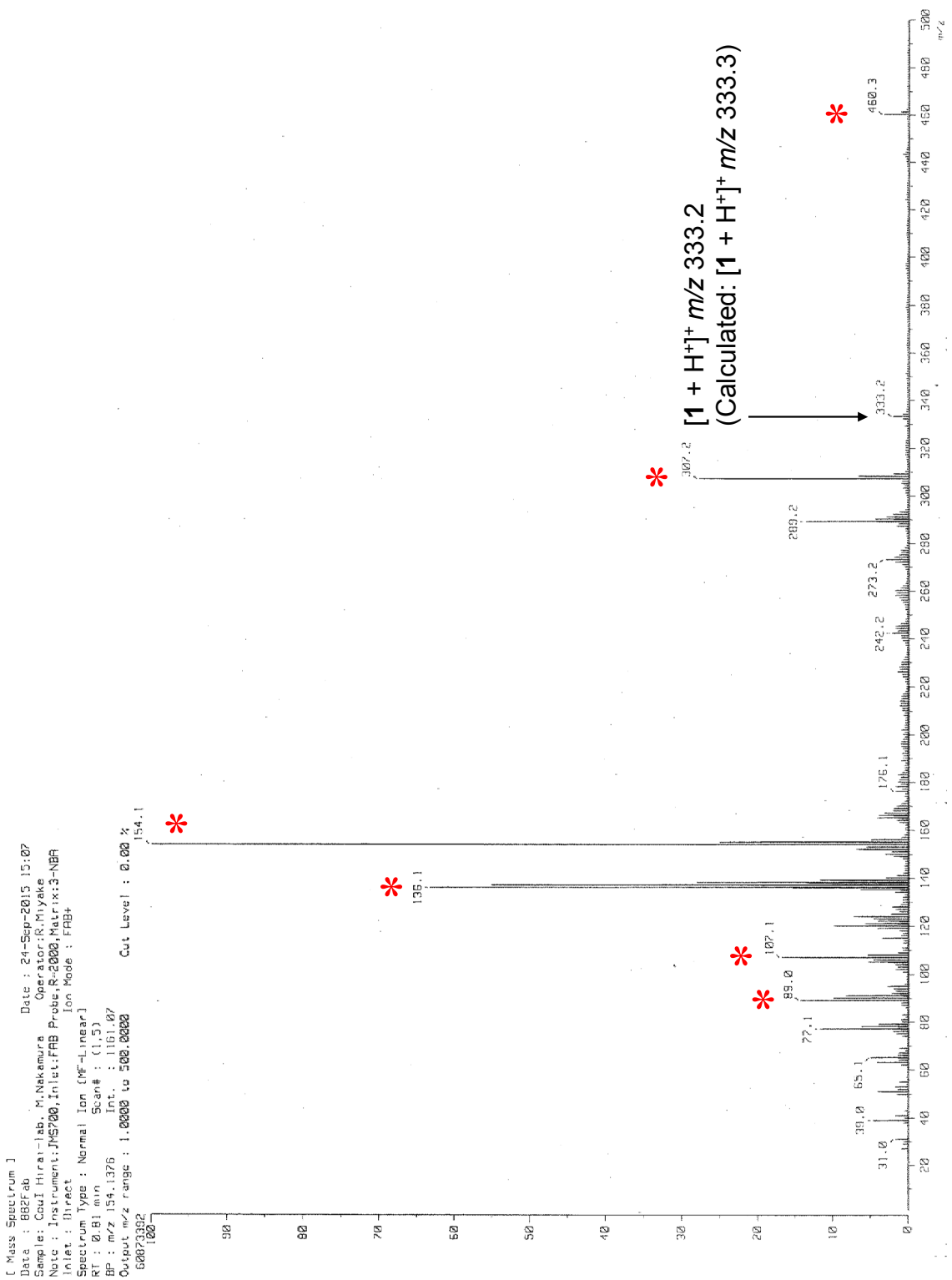


Fig. S3 FAB-MS chart of **1**. The peaks marked with asterisks are assigned to the multimers or the fragment peaks for 3-nitrobenzyl alcohol used as a matrix.

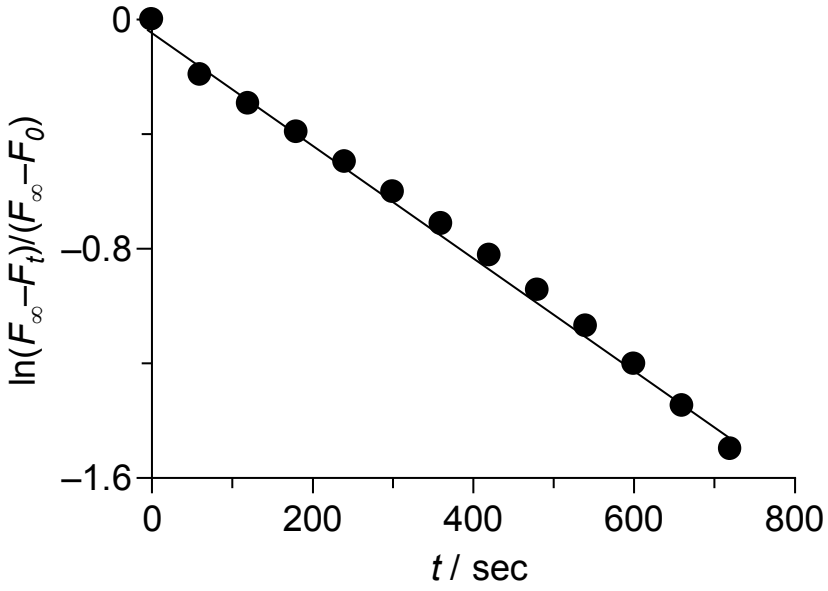


Fig. S4 Kinetic fluorescence data for **1** obtained after addition of 10 equiv of CN^-.

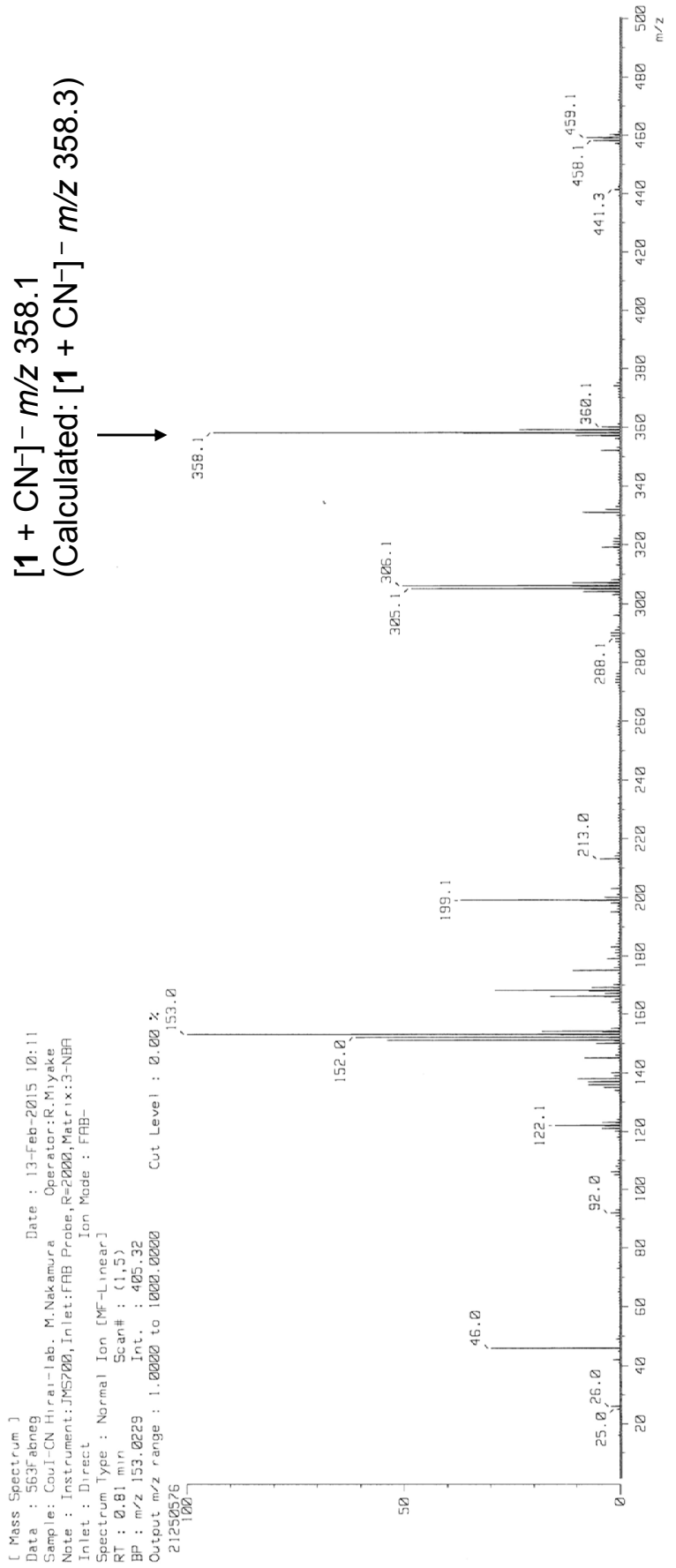


Fig. S5 FAB-MS chart for the solution containing **1** and CN^-.

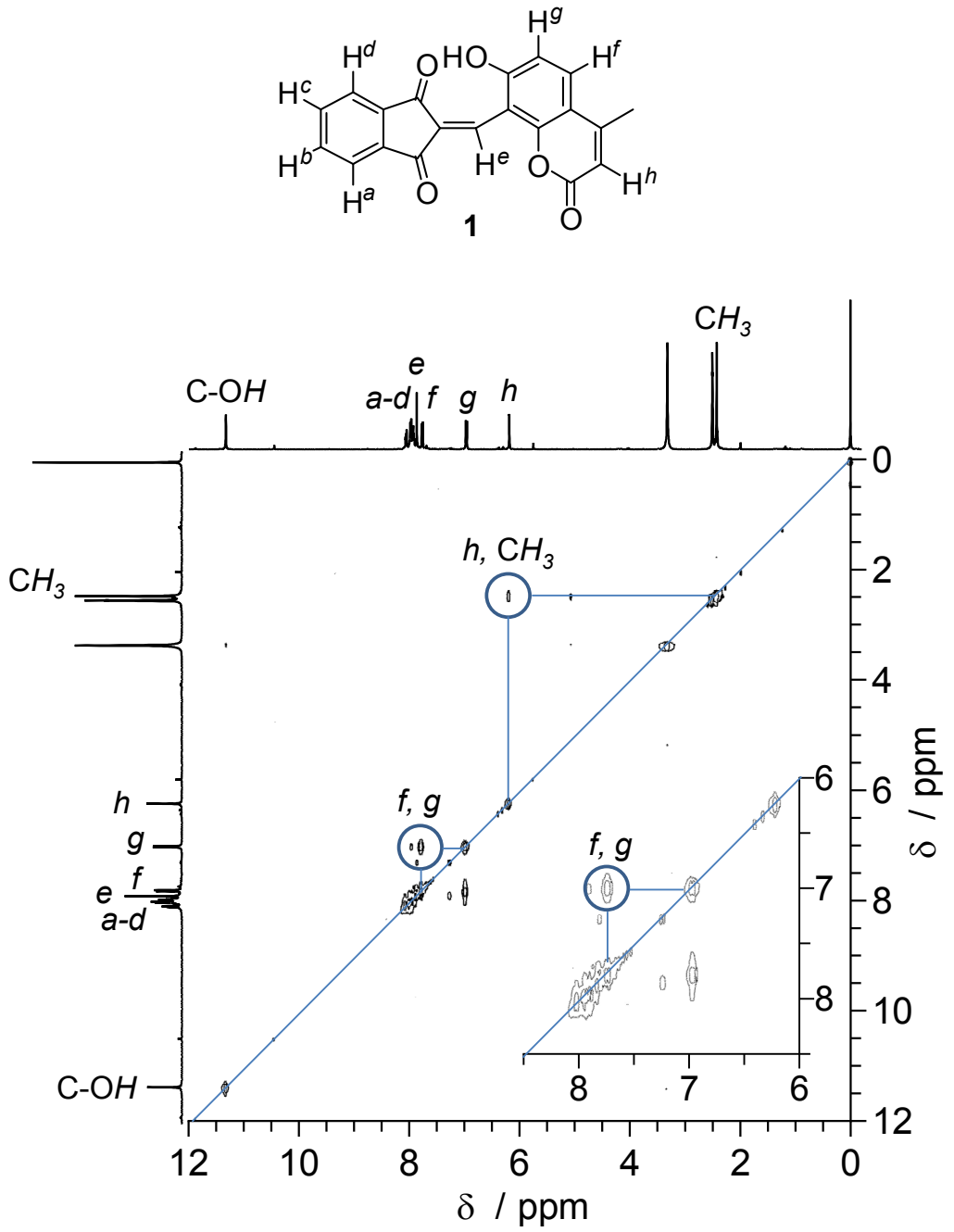


Fig. S6 ^{1}H–^{1}H COSY chart of **1** (DMSO-d_6, 400 MHz). Blue circles indicate the observed cross peaks. The texts above the circle indicate the coupling protons.

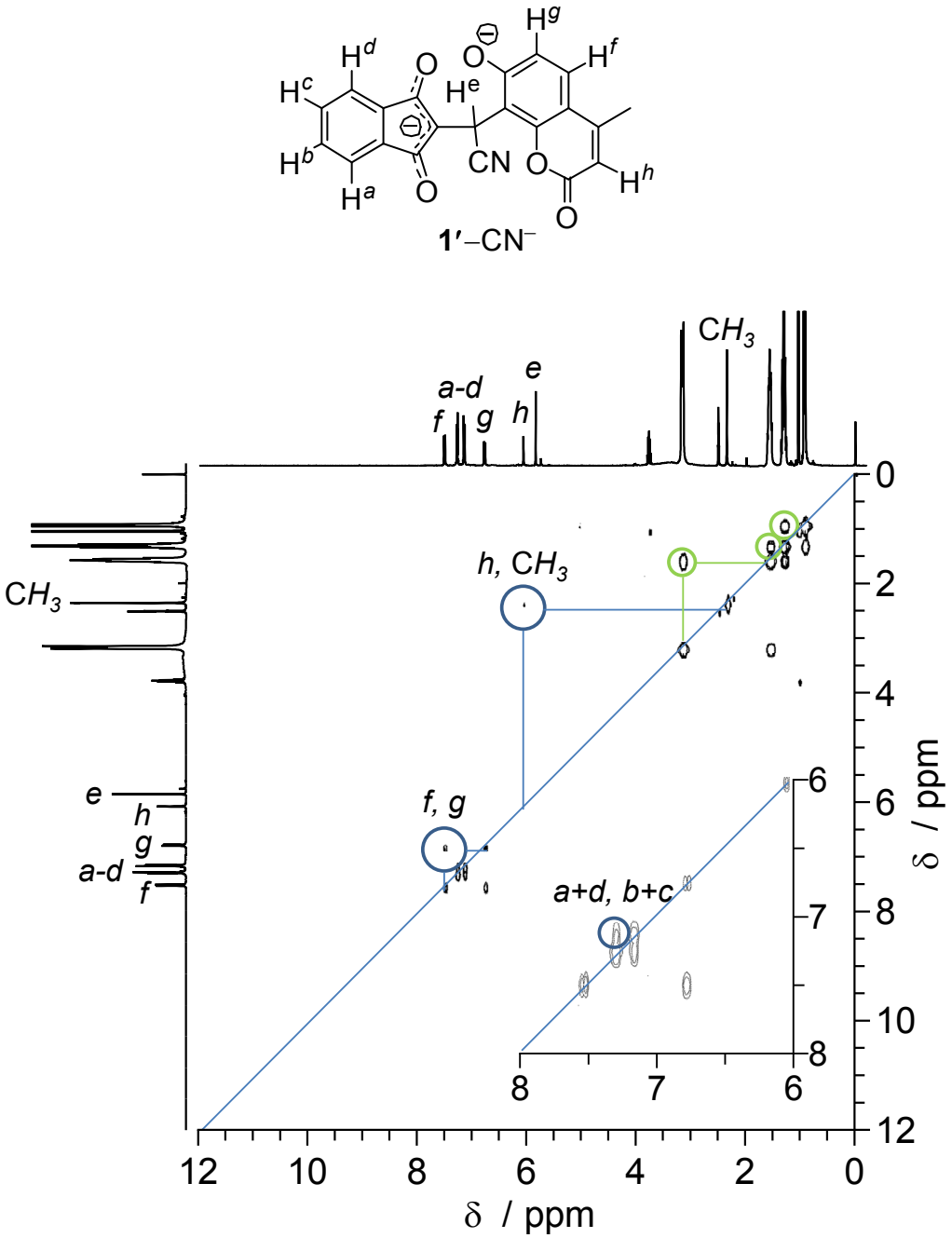


Fig. S7 ^{1}H–^{1}H COSY chart of 1:1 association species for **1** and CN^{-} (DMSO-d_6, 400 MHz). Blue and yellow green circles indicate the observed cross peaks of **1** and n-Bu_4N^{+}, respectively. The texts above the circle indicate the coupling protons.

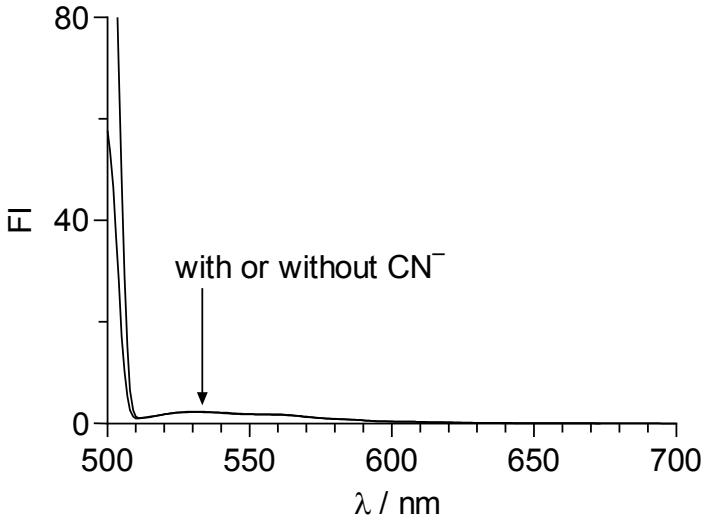


Fig. S8 Fluorescence spectra (λ_{ex} = 500 nm) of **1** (20 μM) measured without or with 10 equiv of CN^- in a buffered water/MeCN mixture (1/9 v/v; CHES 100 mM, pH 9.0) at 25 °C.

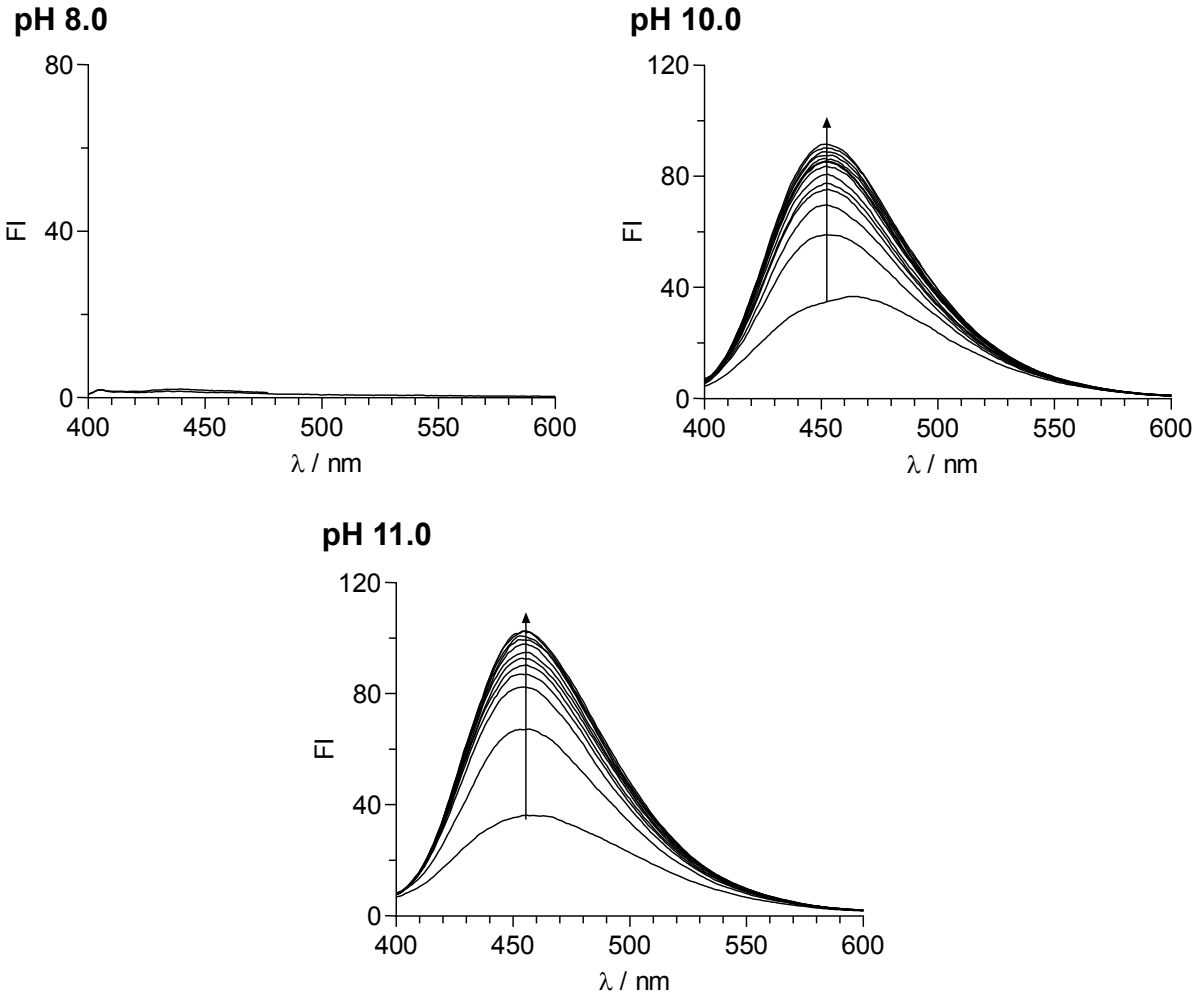
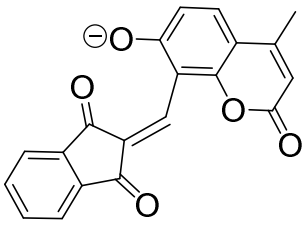
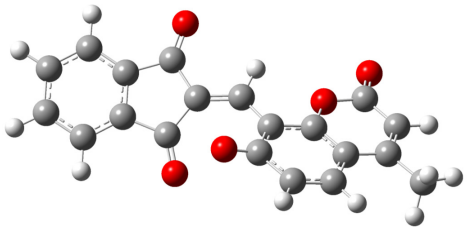


Fig. S9 Fluorescence spectra (λ_{ex} = 360 nm) of **1** (20 μM) measured with 10 equiv of CN^- in a buffered water/MeCN mixture (1/9 v/v) at different pH.

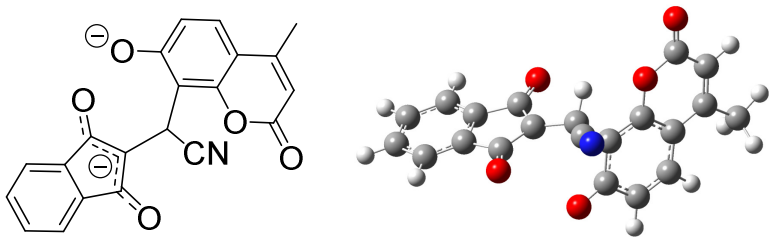
Cartesian Coordinates (in Å) of **1′** (DFT/B3LYP/ 6-31G*, PCM: MeCN)





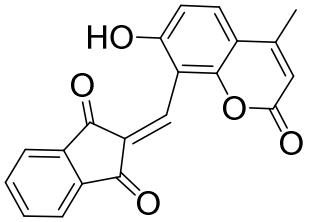
C	5.991217	-0.645498	0.701584	O	0.22898	-2.309321	-1.083378
C	6.168228	0.588236	0.05531	C	-4.708075	-0.075919	0.226742
C	5.06499	1.319723	-0.405721	C	-4.775797	1.279357	0.44311
C	3.79592	0.782864	-0.209823	C	-3.60891	2.117084	0.401527
C	3.619187	-0.446981	0.433317	O	-2.400047	1.462709	0.145229
C	4.708408	-1.173233	0.904237	C	-5.967403	-0.907589	0.287862
C	2.449011	1.33417	-0.587428	O	-3.561042	3.325451	0.572215
C	1.447871	0.324217	-0.192333	H	6.863037	-1.196302	1.049121
C	2.144793	-0.757716	0.531082	H	7.173952	0.97892	-0.085915
O	1.686872	-1.673563	1.203807	H	5.184885	2.279751	-0.90144
O	2.269278	2.419218	-1.140927	H	4.555872	-2.123837	1.40878
C	0.098913	0.536955	-0.387796	H	-0.158293	1.565827	-0.642268
C	-0.988426	-0.380058	-0.326604	H	-1.924539	-3.688756	-0.774806
C	-0.835169	-1.813043	-0.672366	H	-4.139232	-2.745363	-0.250478
C	-2.048635	-2.626842	-0.579794	H	-5.714077	1.779033	0.659653
C	-3.268714	-2.094516	-0.295373	H	-5.899219	-1.677677	1.06702
C	-3.448414	-0.690216	-0.057084	H	-6.837332	-0.2798	0.505035
C	-2.296995	0.118786	-0.095143	H	-6.149368	-1.426442	-0.662117

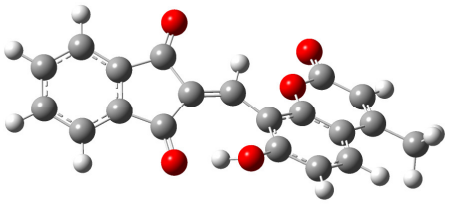
Cartesian Coordinates (in Å) of **1′**–CN^- (DFT/B3LYP /6-31G*, PCM: MeCN)



C	5.33012	-2.05753	-0.848418	C	-4.572204	-1.262529	0.558248
C	5.912889	-0.806082	-0.625792	C	-3.575728	-1.191662	1.586943
C	5.133241	0.276373	-0.162841	O	-2.41616	-0.499195	1.276064
C	3.781039	0.066226	0.056122	C	-5.487664	-0.759	-1.710412
C	3.198009	-1.18597	-0.166533	O	-3.656242	-1.675998	2.71501
C	3.952315	-2.259376	-0.615163	H	5.946097	-2.883309	-1.205622
C	2.701644	1.018719	0.554869	H	6.978049	-0.666465	-0.812499
C	1.482724	0.265583	0.570149	H	5.570209	1.256488	0.018677
C	1.72336	-1.086275	0.179315	H	3.483527	-3.227749	-0.779727
O	0.948206	-2.066265	0.119174	H	-1.552978	1.933857	-3.301935
O	2.960915	2.187224	0.893909	H	-3.67003	0.700121	-2.970435
C	-0.966845	0.763137	-0.111081	H	-5.476696	-1.812135	0.799837
C	-0.714671	1.501679	-1.345931	H	-5.125427	-1.246293	-2.625512
C	-1.755151	1.410555	-2.369136	H	-6.332098	-1.342308	-1.325721
C	-2.92537	0.728373	-2.175564	H	-5.862088	0.23179	-2.001169
C	-3.199367	0.055679	-0.950067	C	0.097832	0.712579	0.998308
C	-2.179821	0.115102	0.056372	H	-0.264572	-0.046069	1.704713
O	0.317382	2.187833	-1.540012	N	-0.084328	2.901344	2.463017
C	-4.39268	-0.654549	-0.670289	C	0.066911	1.969613	1.781756

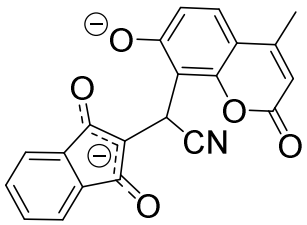
Cartesian Coordinates (in Å) of **1** (DFT/B3LYP/6-311+G(2d,p), PCM: DMSO)

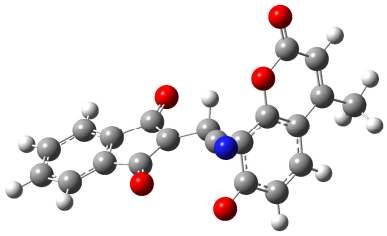




C	-6.036222	-0.326239	-0.741024	C	4.706593	0.249667	-0.235768
C	-6.071789	0.951434	-0.16869	C	4.568204	1.588128	-0.411615
C	-4.915773	1.548563	0.331609	C	3.287919	2.235225	-0.377613
C	-3.730276	0.834859	0.242263	O	2.183459	1.419001	-0.164935
C	-3.695235	-0.443028	-0.32708	C	6.060564	-0.393047	-0.277666
C	-4.844182	-1.041781	-0.827013	O	3.063745	3.420619	-0.52192
C	-2.359744	1.211775	0.671421	H	-6.954951	-0.764014	-1.121907
C	-1.462926	0.064283	0.323079	H	-7.017967	1.483301	-0.11548
C	-2.317279	-0.972872	-0.274726	H	-4.942661	2.539915	0.775244
O	-1.977229	-2.087814	-0.680838	H	-4.814878	-2.033896	-1.268497
O	-2.024698	2.258342	1.196741	H	0.139907	1.216992	0.774329
C	-0.117123	0.212622	0.44543	H	2.414981	-3.730948	0.550911
C	1.052962	-0.610186	0.240953	H	4.495073	-2.478021	0.199005
C	1.140874	-2.020034	0.398215	H	-0.727384	-2.504681	0.123704
C	2.393257	-2.656211	0.400111	H	5.422299	2.233755	-0.58829
C	3.550559	-1.946338	0.203924	H	6.108641	-1.149721	-1.065828
C	3.526141	-0.552295	-0.003039	H	6.836159	0.348958	-0.462273
C	2.282195	0.078021	0.027338	H	6.281839	-0.8984	0.666694
O	0.085551	-2.802461	0.632419				

Cartesian Coordinates (in Å) of **1′**–CN^- (DFT/B3LYP/6-311+G(2d,p), PCM: $CHCl_3$)





C	5.203936	-2.118573	-0.95405	C	-4.463588	-1.385772	0.495567
C	5.823542	-0.896873	-0.716206	C	-3.461834	-1.349217	1.508263
C	5.089418	0.193451	-0.216399	O	-2.335182	-0.59561	1.248469
C	3.74284	0.017089	0.024435	C	-5.426108	-0.755032	-1.710091
C	3.121892	-1.208234	-0.213248	O	-3.498542	-1.918002	2.59532
C	3.831439	-2.287066	-0.698948	H	5.786275	-2.950152	-1.3402
C	2.699637	0.98424	0.553165	H	6.884489	-0.78398	-0.919721
C	1.465188	0.274549	0.580005	H	5.566953	1.150219	-0.026704
C	1.662215	-1.070167	0.161852	H	3.341637	-3.239475	-0.879274
O	0.848378	-2.012886	0.102615	H	-1.646653	2.214053	-3.113513
O	2.978946	2.142933	0.904437	H	-3.683952	0.868373	-2.862041
C	-0.971832	0.830001	-0.04776	H	-5.339567	-1.987555	0.704008
C	-0.76952	1.664212	-1.211978	H	-5.052381	-1.151636	-2.657971
C	-1.804505	1.611325	-2.223979	H	-6.239122	-1.395767	-1.368234
C	-2.936477	0.864117	-2.076091	H	-5.835832	0.237432	-1.916506
C	-3.166019	0.090267	-0.911271	C	0.106985	0.759272	1.037866
C	-2.148767	0.115254	0.080823	H	-0.255833	0.033842	1.774291
O	0.239257	2.4088	-1.344855	N	0.028831	2.967376	2.447316
C	-4.329519	-0.687551	-0.679643	C	0.132632	2.026564	1.788814