Pyrylium–coumarin dyad as a colorimetric receptor for ratiometric detection of cyanide anion by two absorption bands in visible region

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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI†)

CONTENTS

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

compound		Main orbital transition (CIC[a])	*E* (eV) [λ (nm)]	*f*
1	$S_0 \rightarrow S_1$	HOMO → LUMO (0.63574)	2.1389 [517.65]	1.6574
	$S_0 \rightarrow S_2$	HOMO–1 → LUMO (0.67037)	2.9968 [413.72]	0.3438
	$S_0 \rightarrow S_3$	HOMO–3 → LUMO (0.18301) HOMO–2 → LUMO (0.57594) HOMO → LUMO+1 (–0.34251)	3.1441 [394.34]	0.2277
	$S_0 \rightarrow S_4$	HOMO–3 → LUMO (0.58965) HOMO → LUMO+1 (0.31551) HOMO → LUMO+2 (0.16884)	3.2941 [376.39]	0.2496
1–CN$^-$	$S_0 \rightarrow S_1$	HOMO → LUMO (0.65670)	2.1460 [577.75]	0.6537
	$S_0 \rightarrow S_2$	HOMO–7 → LUMO (0.24260) HOMO–6 → LUMO (–0.12127) HOMO–4 → LUMO (0.22493) HOMO–3 → LUMO (–0.17634) HOMO–2 → LUMO (0.48357) HOMO–1 → LUMO (0.23696)	2.8659 [432.62]	0.1001
	$S_0 \rightarrow S_3$	HOMO–7 → LUMO (–0.15776) HOMO–2 → LUMO (–0.15381) HOMO–1 → LUMO (0.54466) HOMO → LUMO+1 (–0.30720)	3.0772 [402.92]	0.3863
	$S_0 \rightarrow S_4$	HOMO–7 → LUMO (–0.11002) HOMO–4 → LUMO (–0.11068) HOMO–1 → LUMO (0.25740) HOMO → LUMO+1 (0.56501)	3.1392 [394.95]	0.8202

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

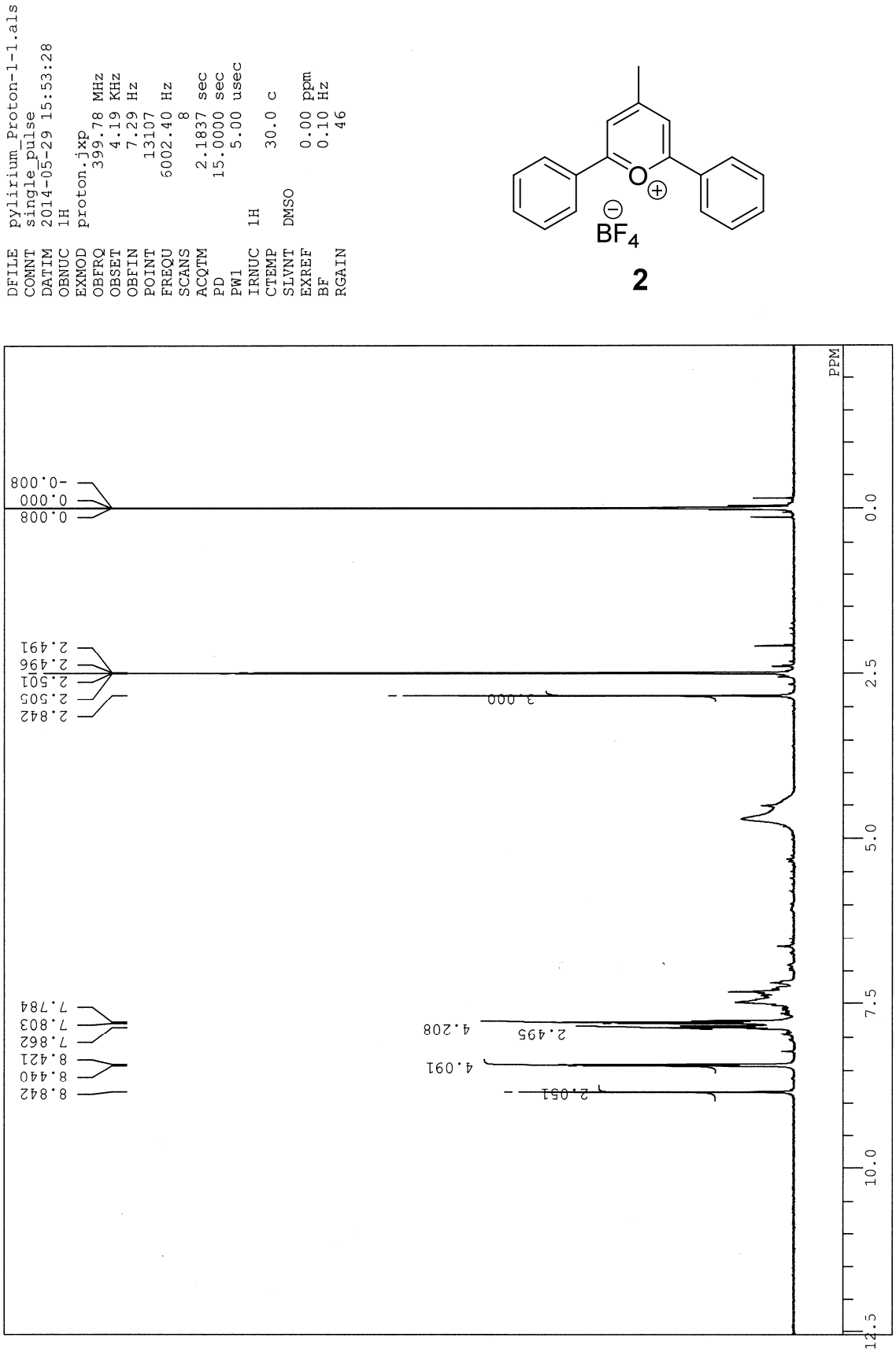


Fig. S1 ^{1}H NMR chart of **2** (DMSO-d_6, 400 MHz).

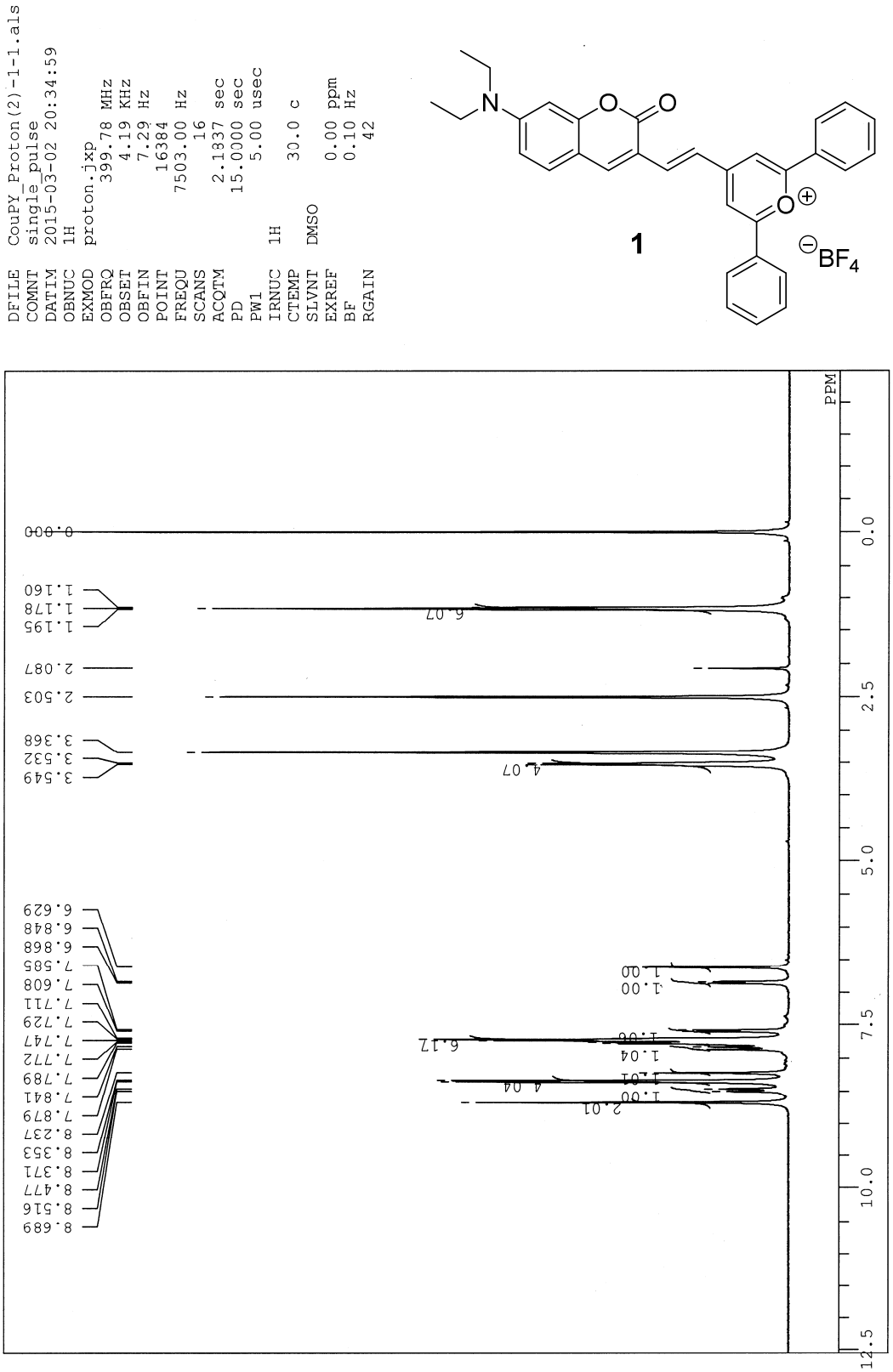


Fig. S2 ^{1}H NMR chart of **1** (DMSO-d_6, 400 MHz).

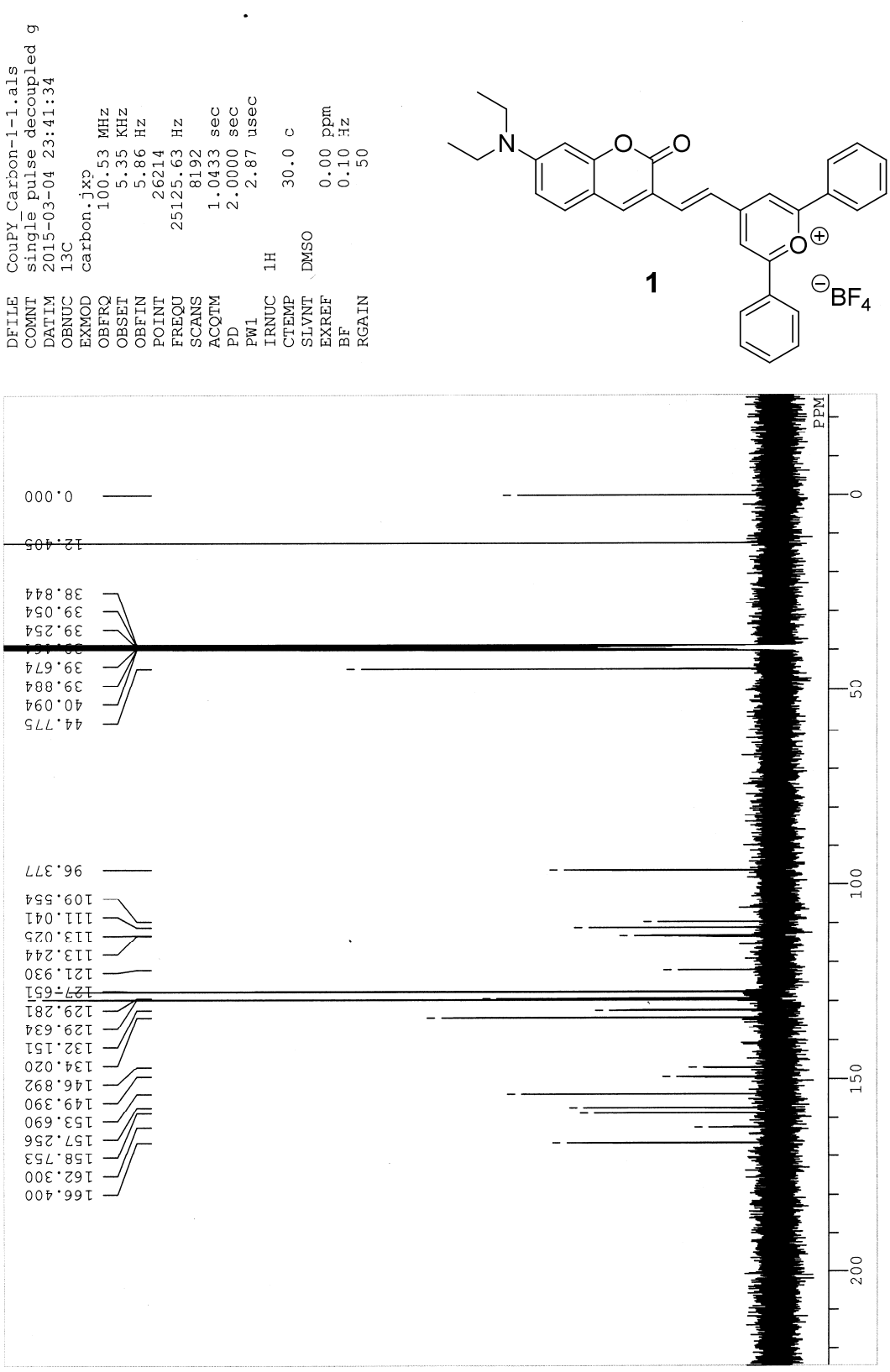


Fig. S3 ^{13}C NMR chart of **1** (DMSO-d_6, 100 MHz).

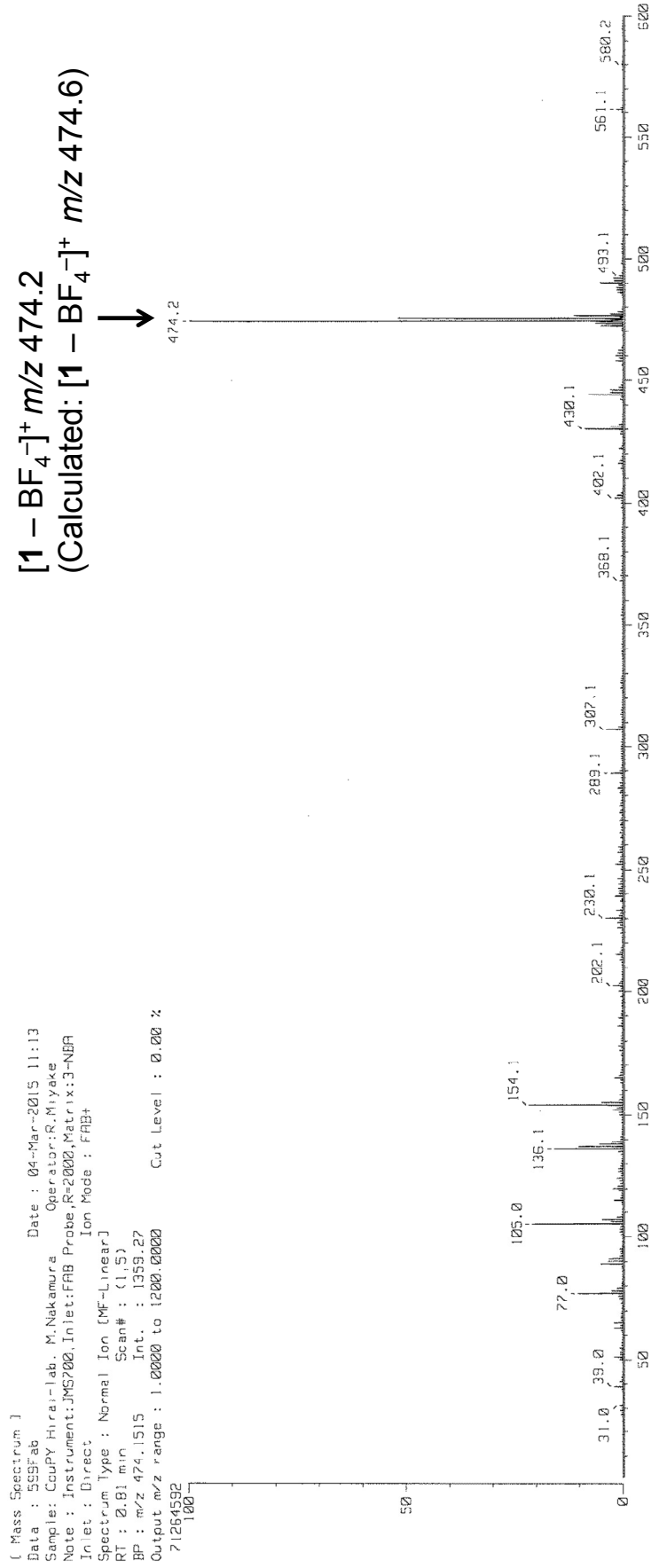


Fig. S4 FAB-MS chart of **1**.

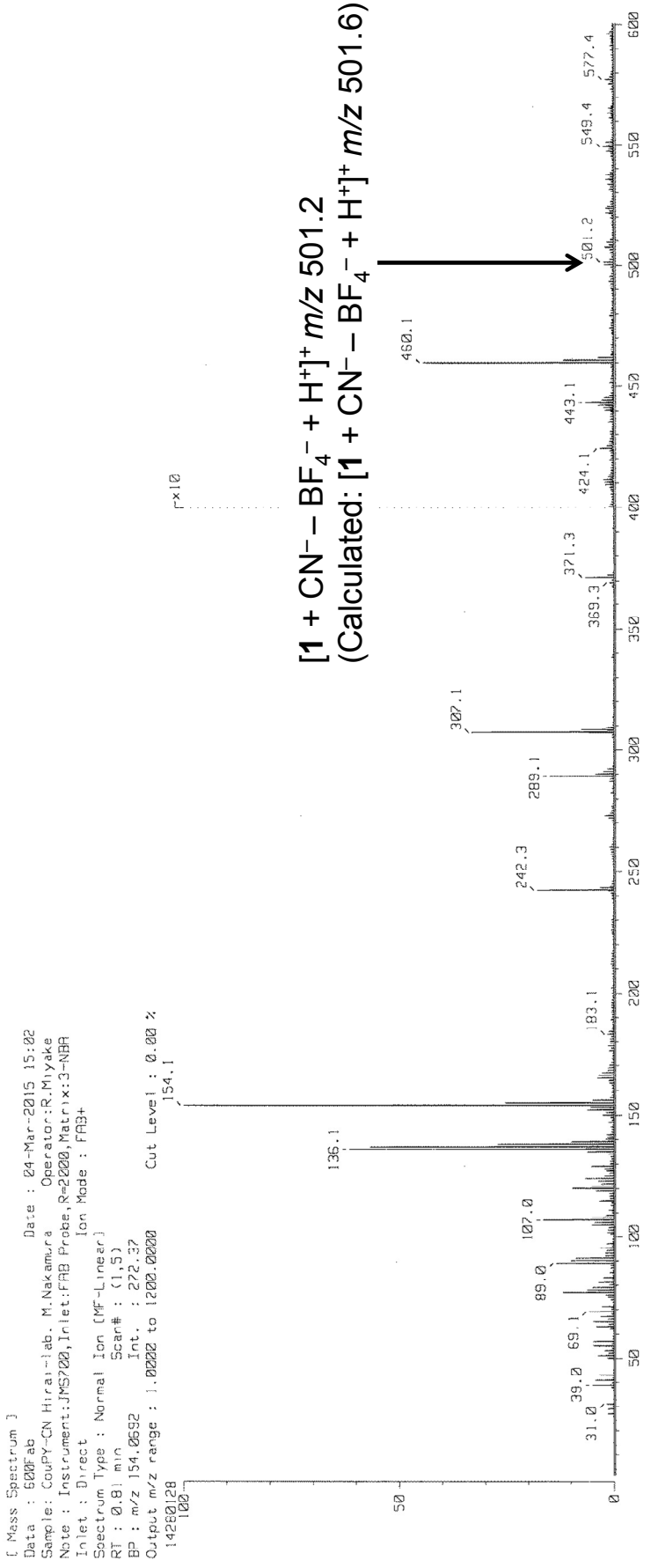


Fig. S5 FAB-MS chart for the product obtained by the reaction of **1** with CN^-.

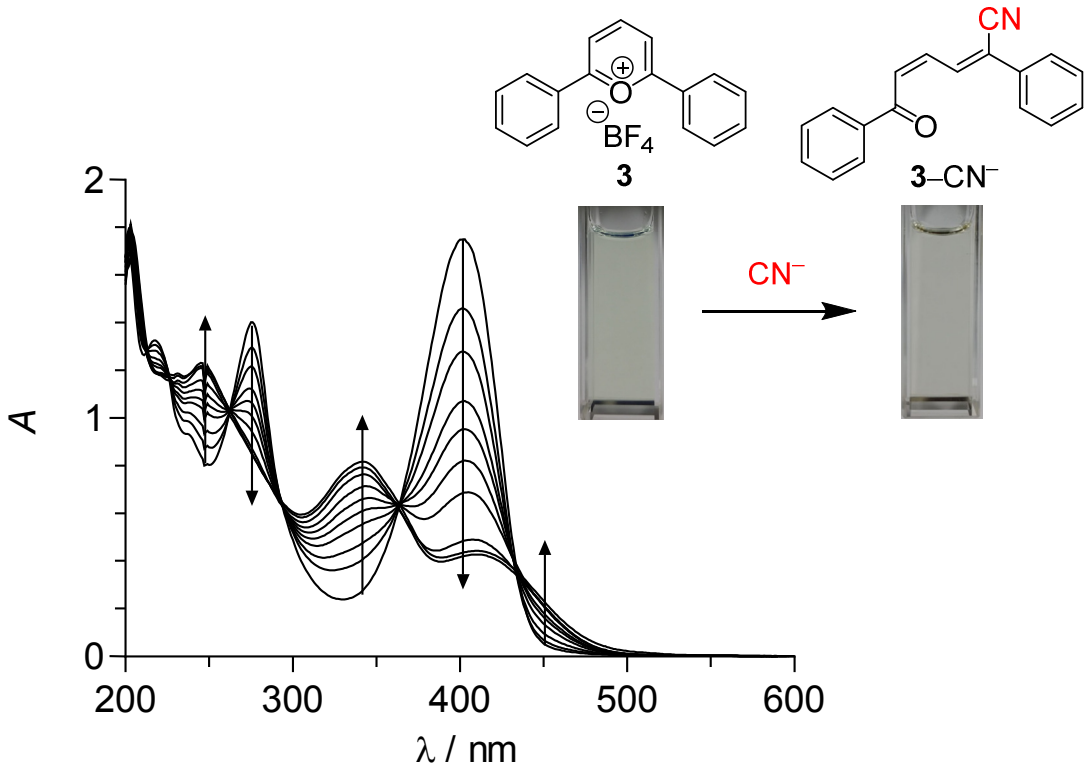


Fig S6 Result of absorption titration of **3** (100 μM) with 0–1 equiv of CN^- in MeCN at 25 °C.

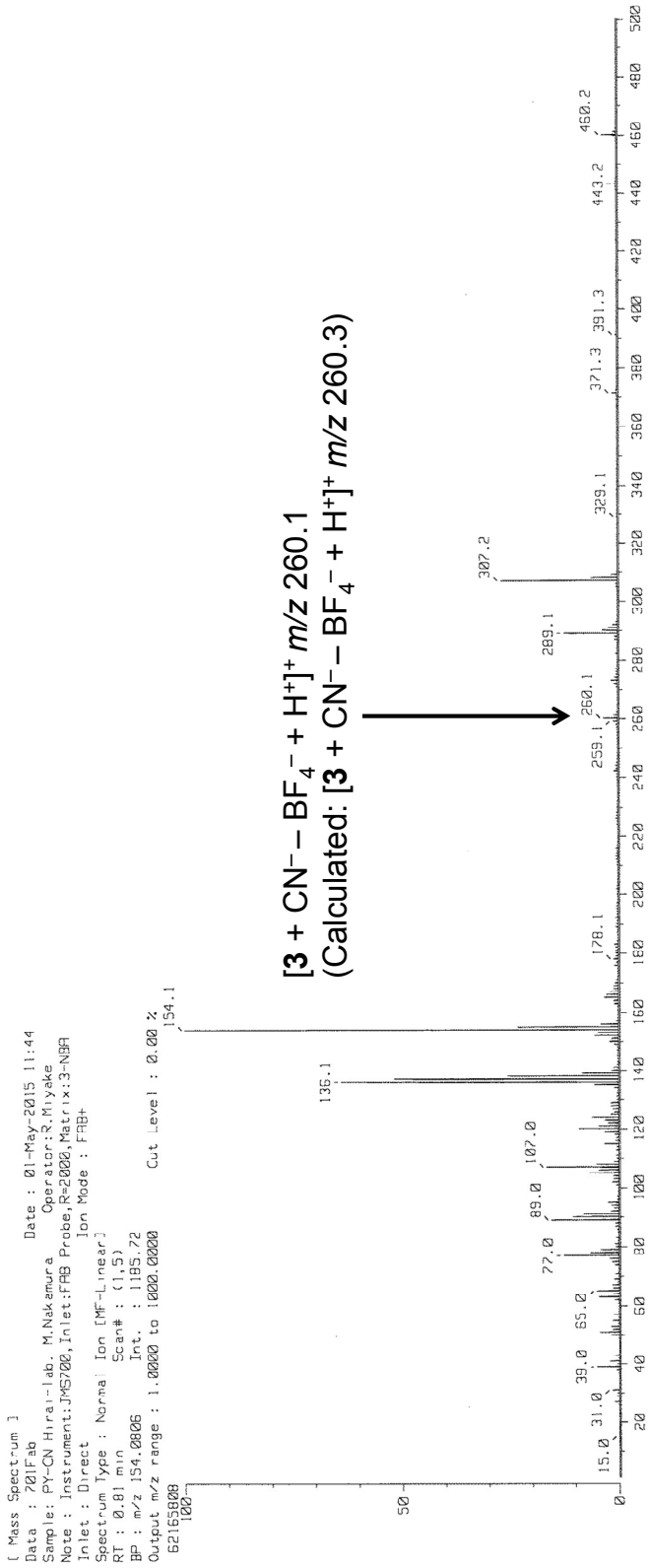


Fig S7 FAB-MS chart of the product obtained by the reaction of **3** with CN^-. An MeCN solution containing **3** and 1 equiv of CN^- was stirred for 5 min at 298 K. The resultant was concentrated by evaporation and purified by silica gel column chromatography with a mixture of toluene/CH_2Cl_2/*n*-hexane (1/1/3 v/v/v, 600 mL), (3/2/3 v/v/v, 600 mL), and then (0/1/0 v/v/v, 600 mL) as an eluent. The concentration of the final eluent was subjected to analysis.

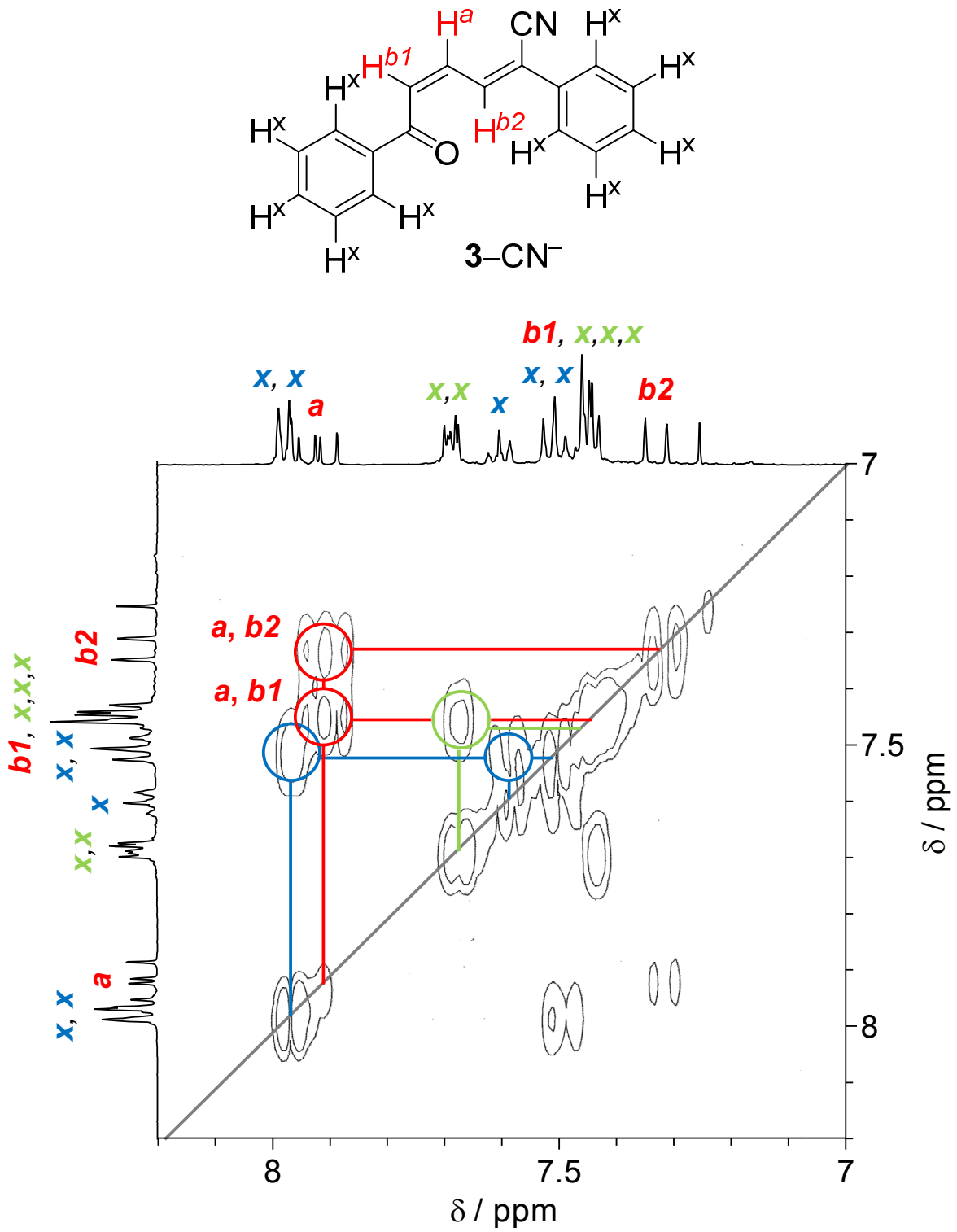


Fig S8 ^{1}H-^{1}H COSY chart of the product obtained by the reaction of **3** with CN^- ($CDCl_3$, 400 MHz). Red, blue, and yellow green circles indicate the observed cross peaks of olefinic protons, phenyl group, and another phenyl group, respectively. The texts next to the circle mean the coupling protons.

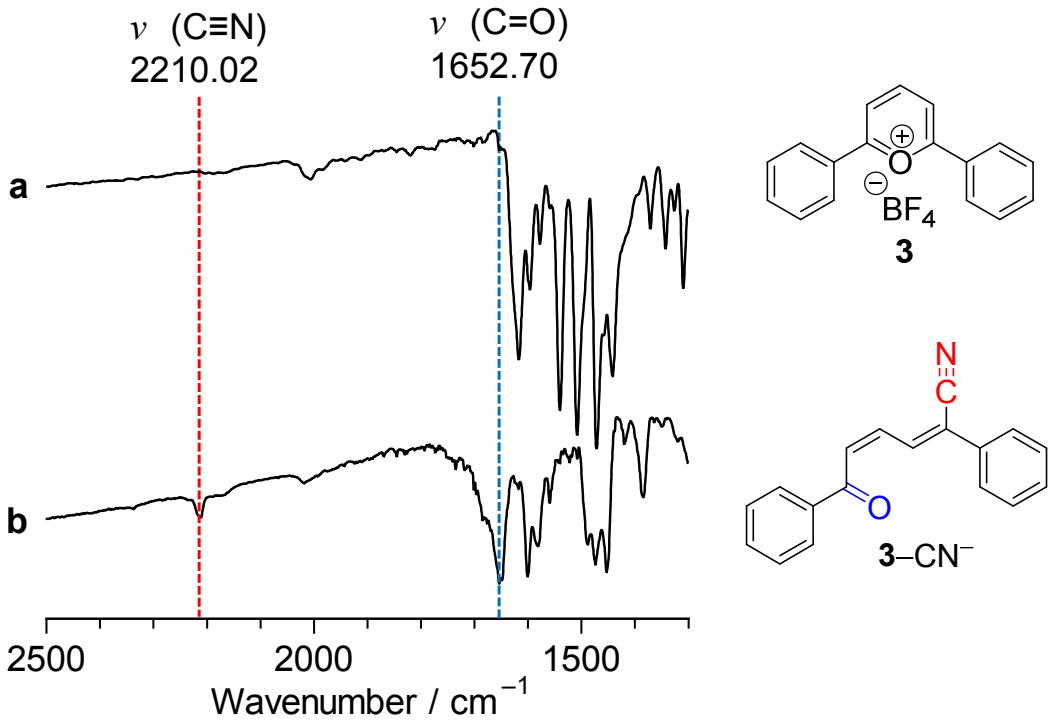


Fig. S9 IR chart of (a) **3** and (b) **3**–CN^- measured on KBr disk.

The sample (b) was measured as follows: an MeCN solution containing **3** and 1 equiv of CN^- was stirred for 5 min at 298 K. The resultant was concentrated by evaporation and subjected to IR analysis.

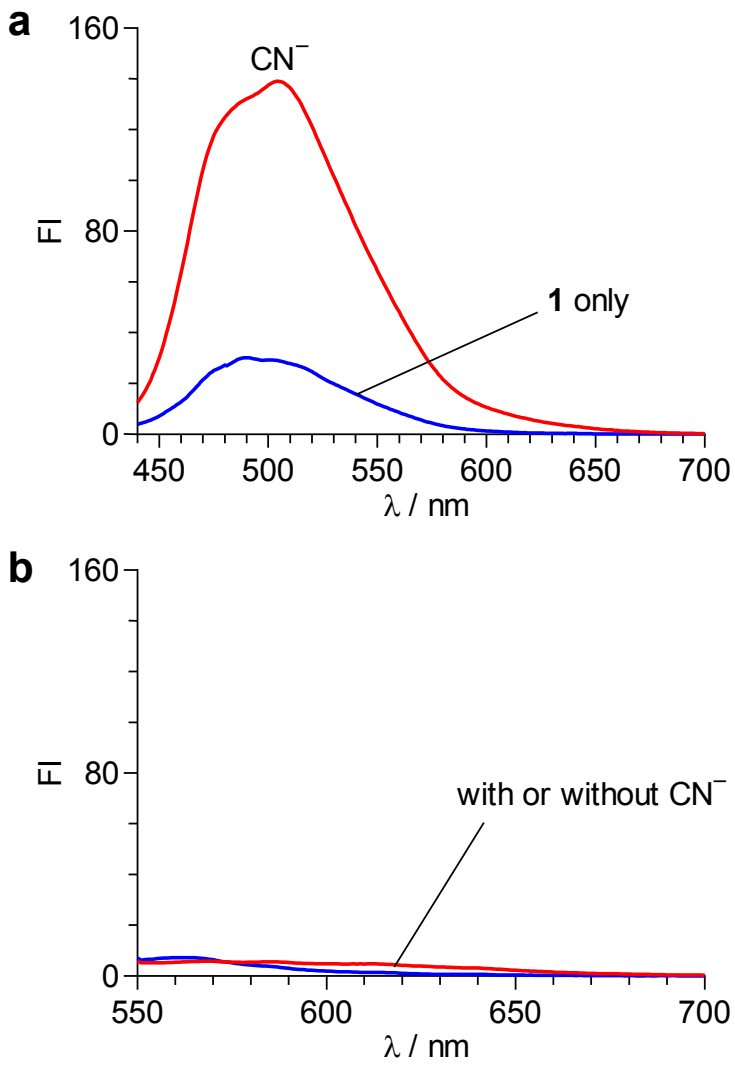
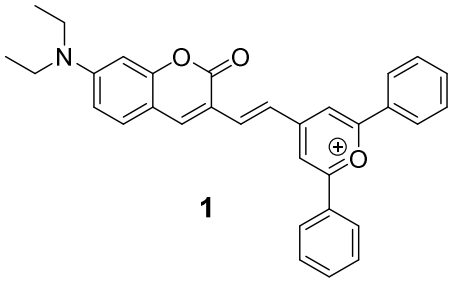
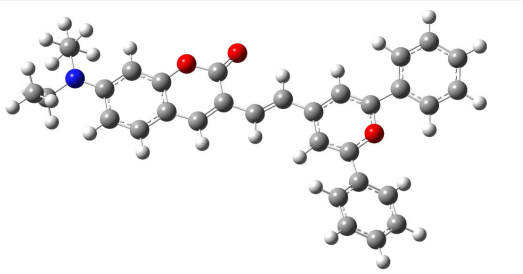


Fig. S10 Fluorescence spectra of **1** (10 μM) measured at (a) λ_{ex} = 427 nm and (b) λ_{ex} = 540 nm without or with 50 equiv of CN^- in a buffered water/MeCN mixture (1/9 v/v; Tris-HCl 10 mM, pH 9.0) at 25 °C.

Cartesian Coordinates (in Å) of **1**

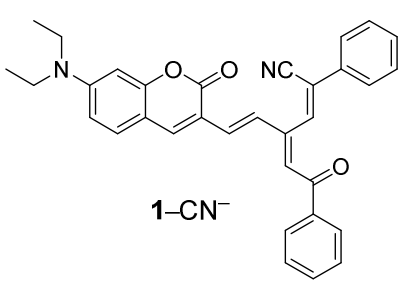


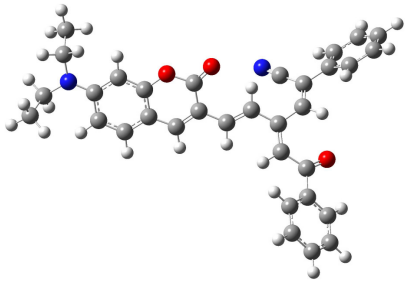
1



C	3.194408	-1.407424	-0.076478	C	-9.436433	1.59037	-1.207551
C	4.540247	-1.138617	-0.06519	C	-9.033509	1.00649	0.150581
O	4.960186	0.149896	-0.022756	C	-8.682856	-2.110117	1.327469
C	4.092182	1.192791	0.009834	C	-8.552344	-1.427112	-0.038403
C	2.740878	0.966022	-0.000091	H	2.852775	-2.438213	-0.090429
C	2.234177	-0.362592	-0.047681	H	2.074266	1.81873	0.064688
C	4.76022	2.497204	0.064235	H	0.618083	-1.772494	-0.070419
C	5.635562	-2.110925	-0.096683	H	0.038096	1.250338	-0.004169
C	0.845551	-0.713667	-0.048106	H	3.138608	3.564258	-0.905329
C	-0.19054	0.183186	-0.023967	H	4.25182	5.760961	-0.786367
C	-1.598134	-0.090892	-0.022567	H	6.521389	5.965007	0.219616
C	4.119731	3.643213	-0.441306	H	7.663875	3.943029	1.120085
C	4.752806	4.882431	-0.383829	H	6.545737	1.744388	1.031014
C	6.02871	4.994943	0.176379	H	7.174464	-0.667619	0.390805
C	6.672456	3.860014	0.678383	H	9.012944	-2.307248	0.353472
C	6.047145	2.61697	0.620742	H	8.546727	-4.700006	-0.161844
C	6.95847	-1.705791	0.165006	H	6.214171	-5.428416	-0.648739
C	7.996055	-2.633902	0.143502	H	4.374867	-3.803493	-0.624877
C	7.733515	-3.976148	-0.144268	H	-2.107407	1.990749	0.018514
C	6.424335	-4.386437	-0.414452	H	-6.013127	-1.890994	0.000333
C	5.381812	-3.464782	-0.393194	H	-6.888152	2.388242	0.060533
C	-2.128209	-1.456513	-0.043895	H	-4.506598	2.85586	0.050221
O	-3.509278	-1.599003	-0.035756	H	-10.213791	2.350506	-1.071439
C	-4.382866	-0.546875	-0.009392	H	-8.582657	2.058198	-1.708851
C	-3.887432	0.780682	0.010875	H	-9.834078	0.811722	-1.867732
C	-2.498721	0.971734	0.002679	H	-9.907557	0.567328	0.642096
C	-5.728815	-0.846237	0.003187	H	-8.670878	1.789901	0.821888
C	-6.688676	0.203522	0.033688	H	-9.107935	-3.112419	1.204333
C	-6.196768	1.554818	0.049765	H	-7.709376	-2.208313	1.818828
C	-4.852161	1.822774	0.040027	H	-9.342933	-1.539564	1.989939
O	-1.491326	-2.49372	-0.074086	H	-9.534363	-1.360356	-0.517381
N	-8.023607	-0.05788	0.04706	H	-7.925151	-2.017099	-0.71322

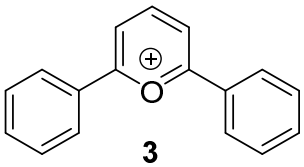
Cartesian Coordinates (in Å) of **1**–CN^-





C	-2.573706	0.162579	0.202867	H	-0.324609	1.36954	-0.681665
C	-3.591397	-0.896052	0.208617	C	1.293993	0.211808	0.08181
N	-5.194943	1.23074	-0.58094	C	2.217925	0.988763	-0.592975
C	-4.288801	1.97735	-0.178363	C	1.782655	-0.863589	0.943847
C	-2.939643	1.484825	0.116443	C	3.610438	0.775378	-0.491658
C	-4.565021	3.441685	-0.001613	H	1.859488	1.797601	-1.23227
C	-4.540202	-3.191285	-0.108169	C	4.602228	1.529658	-1.163992
C	-4.675682	-4.231222	-1.045046	C	4.064753	-0.271549	0.339435
C	-5.69886	-5.170842	-0.921242	C	5.941256	1.254199	-1.013808
C	-6.599947	-5.094334	0.143322	H	4.290227	2.349807	-1.809688
C	-6.465905	-4.072751	1.088392	C	5.403863	-0.574307	0.507716
C	-5.443956	-3.132814	0.968649	C	6.392496	0.186542	-0.169208
C	-5.695167	3.981131	-0.640757	H	6.655599	1.87456	-1.54142
C	-6.011937	5.330149	-0.504948	H	5.654923	-1.406374	1.154162
C	-5.210868	6.160533	0.286771	C	-1.176917	-0.225982	0.398348
C	-4.09361	5.633126	0.939126	H	-0.992686	-1.145545	0.941157
C	-3.768353	4.283711	0.793134	O	1.114782	-1.629519	1.617835
H	-4.559386	-0.617757	0.608728	O	3.15929	-1.043464	1.017405
H	-2.165547	2.228826	0.265339	N	7.724727	-0.081908	-0.019031
H	-3.986232	-4.300718	-1.88386	C	8.756895	0.611088	-0.800358
H	-5.791274	-5.963842	-1.661581	C	9.260358	1.899695	-0.140259
H	-7.396028	-5.83054	0.241879	H	8.378648	0.812576	-1.806967
H	-7.152073	-4.013873	1.931756	H	9.589032	-0.08977	-0.926124
H	-5.335014	-2.364116	1.730897	H	10.045756	2.354232	-0.754881
H	-6.314141	3.32553	-1.24791	H	8.452202	2.628983	-0.021563
H	-6.883848	5.737094	-1.014797	H	9.680494	1.694338	0.850637
H	-5.458754	7.215378	0.396235	C	8.210494	-1.104069	0.915074
H	-3.473636	6.272327	1.565636	C	8.28264	-2.507562	0.302566
H	-2.904433	3.89099	1.32421	H	7.582357	-1.103652	1.811243
C	-3.46564	-2.171895	-0.249454	H	9.206967	-0.791403	1.24479
C	-2.300365	-2.593633	-0.978448	H	8.675236	-3.218307	1.038703
N	-1.405211	-3.000149	-1.602668	H	7.294382	-2.85484	-0.016213
C	-0.121145	0.486747	-0.072334	H	8.945488	-2.521193	-0.569842

Cartesian Coordinates (in Å) of **3**



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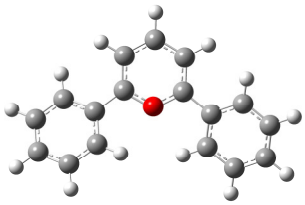
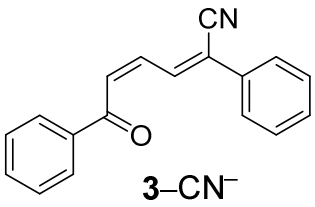
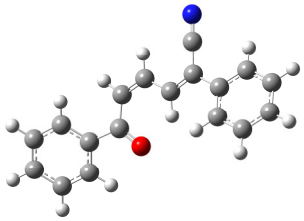


C	0.000019	3.00211	0.00007	C	4.691912	-0.34327	0.358302
C	-1.206753	2.313224	0.004491	C	3.593504	0.502591	0.391072
C	-1.186997	0.933626	0.004836	H	-2.150735	2.845259	0.031318
O	-0.000026	0.302088	0.000218	H	2.150712	2.845181	-0.031133
C	1.186986	0.933539	-0.004548	H	-1.249783	-1.638718	0.852714
C	1.206735	2.313136	-0.004353	H	-3.206782	-3.128642	0.904346
C	2.337599	0.041851	-0.034411	H	-5.4191	-2.309357	0.132155
C	-2.337624	0.041954	0.034549	H	-5.657431	0.0169	-0.701526
C	-2.207234	-1.277098	0.497743	H	-3.711556	1.512001	-0.772933
C	-3.312941	-2.11295	0.534418	H	1.249454	-1.639178	-0.851589
C	-4.555477	-1.650406	0.104567	H	3.206534	-3.128958	-0.903677
C	-4.691733	-0.343398	-0.359113	H	5.419164	-2.309321	-0.132779
C	-3.593348	0.50251	-0.391624	H	5.657752	0.017177	0.700157
C	2.20705	-1.277374	-0.497124	H	3.71186	1.512183	0.772037
C	3.312799	-2.113157	-0.534076	H	0.000068	4.089957	0.000068
C	4.555513	-1.650418	-0.10495				

Cartesian Coordinates (in Å) of **3**–CN^-



3–CN^-



C	-0.12127	1.524439	-0.09873	H	0.680208	-0.47448	-0.07473
C	0.952761	0.570076	-0.049	H	-2.11371	2.108029	-0.18807
O	-1.41429	-1.08885	-0.54764	H	4.873237	1.274066	-0.67747
C	-2.07034	-0.08141	-0.29195	H	6.697868	-0.36645	-0.59867
C	-1.44474	1.255805	-0.18515	H	6.271429	-2.67576	0.210762
C	-3.55139	-0.1835	-0.1035	H	3.990283	-3.3124	0.959093
C	3.37342	-0.08264	0.081475	H	2.166912	-1.67945	0.903521
C	4.670149	0.270822	-0.31813	H	-3.61068	-2.10597	-1.05426
C	5.703009	-0.65754	-0.27693	H	-6.05691	-2.39066	-0.76516
C	5.463735	-1.95161	0.174082	H	-7.37822	-0.63141	0.383787
C	4.182506	-2.31	0.589818	H	-6.24854	1.407801	1.229368
C	3.147938	-1.38707	0.547662	H	-3.83417	1.702482	0.922018
C	-4.19781	-1.33917	-0.56206	C	2.27176	0.898602	0.005906
C	-5.56552	-1.49633	-0.39498	C	2.645881	2.284111	-0.03056
C	-6.30801	-0.50713	0.249203	N	2.957858	3.394419	-0.05607
C	-5.67566	0.639677	0.719658	H	0.154597	2.575445	-0.0461
C	-4.30691	0.805969	0.538087				