<p style="text-align:center">**SUPPLEMENTARY INFORMATION (SI)**</p>

Chemodosimeter for CN⁻ -Interplay between experiment and theory

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S1. Experimental

1. General

Mass spectra were recorded on UPLC-Q-TOF mass spectrometer. ^{1}H NMR and ^{13}C NMR spectra have been recorded on JEOL-FT NMR-AL at 300 and 75 MHz, respectively, with TMS as internal standard using both $CDCl_3$ and CD_3CN as deuterated solvents. Data are reported as follows: chemical shift in ppm (δ), integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet), coupling constant J (Hz) and assignment. The purity of the solid products was checked by elemental analysis performed on Thermoelectron FLASH EA1112, CHNS analyser. UV-visible spectral studies were conducted on Shimadzu 1601 PC spectrophotometer with a quartz cuvette (path length, 1cm). The absorption spectra have been recorded between 1100 and 200 nm. The cell holder of the spectrophotometer was thermostatted at 25°C for consistency in the recordings. The pH titrations have been performed with the Equip-Tronics Digital pH meter model-EQ 610. The electrochemical behaviour was determined by cyclic voltammetry on a CHI 660C Electrochemical Workstation with a conventional three-electrode configuration consisting of a platinum working (2 mm diameter) and counter electrodes and Ag/AgCl as the reference electrode. The experiments were carried out in 10^{-3} M solutions of samples in acetonitrile containing 0.1 M sodium perchlorate as supporting electrolyte at room temperature. Deoxygenation of the solutions was achieved by bubbling nitrogen for 10 min and the working electrode was cleaned after each run. The voltammograms were recorded with a scan rate of 100 mVs^{-1}.

2. Computational Methods

All theoretical calculations were carried out by using the Gaussian 09 suite of programs. The molecular geometries of **1** and **1**+CN⁻ were optimized by

DFT/B3LYP[1]/6-311G* method. Energy values and properties of the systems were computed at the same level and considering solvent (acetonitrile) effects by using the Cossi and Barone's CPCM (conductor-like polarizable continuum model) modification[2] of the Tomasi's PCM formalism.[3] The first 20 excited states were calculated by using time-dependent density functional theory (TD-DFT) calculations. The molecular orbital contours were plotted using Gauss view 5.0.9.

3. Chemicals

Anions used in the spectrophotometric studies were added as sodium salts of analytical grade. The solvents used were also of analytical grade purchased from Thomas Baker.

4. Synthetic Procedure for 1[4]
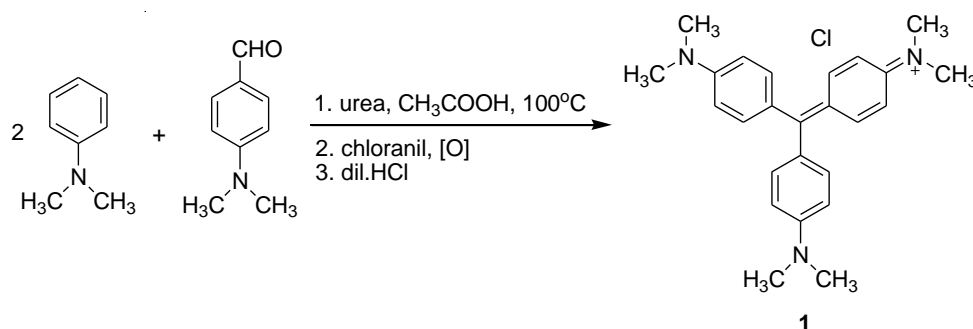
Scheme S1. Preparation of compound **1**.

N,N-dimethylaniline (72.6g, 0.60 mol), urea (10g, 0.17 mol) and 4-dimethylamino- benzaldehyde (44.76g, 0.30 mol) in 600ml of glacial acetic acid were heated to 100°C under nitrogen for 8 hours. Thereafter, the reaction mixture was cooled. 6g of chloranil was added and the mixture was subjected to vigorous gassing with air at 50°C for 12 hours along with uniform addition of 2.5g of sodium nitrite. Afterwards, some of the glacial acetic acid was evaporated off in vacuo and the residue was taken up in hot water. The aqueous mixture was then acidified with dilute hydrochloric acid whereupon precipitation occurred. The solution was filtered hot to obtain the dye. The dye obtained was purified by column chromatography with silica

[1] L. J. Bartolottiand and K. Fluchick, in *Reviews in Computational Chemistry*, ed. K. B. Lipkowitz and B. D. Boyd, VCH, New York, 1996, **7**, 187-216.

[2] (a) V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995-2001; (b) M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comp. Chem.*, 2003, **24**, 669-681.

[3] (a) S. Miertus, E. Scrocco and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117-129; (b) R. Cammi, B. Mennucci and J. Tomasi, *J. Phys. Chem. A*, 2000, **104**, 5631-5637.

[4] K. H. Hermann, *US Pat.*, 4 330 476, 1982.

gel G (100-200 mesh) using 50% methanol/ ethyl acetate as eluent. Yield: 80%. Found: C, 73.70; H, 7.41; N, 10.39. Calc. for $C_{25}H_{30}N_3Cl$: C, 73.62; H, 7.36; N, 10.31%. ^{1}H NMR (300 MHz; CDCl$_3$; Me$_4$Si; ppm) δ_H: 3.28 (18H, s, -CH_3), 6.86 (6H, d, J=9 Hz, aromatic H), 7.32 (6H, d, J=9 Hz, aromatic H). ^{13}C NMR (75 MHz; CDCl$_3$; Me$_4$Si; ppm) δ_C: 40.56, 112.36, 126.65, 139.74, 155.58. m/z (EI): 372.6 (M$^+$-Cl$^-$+1).
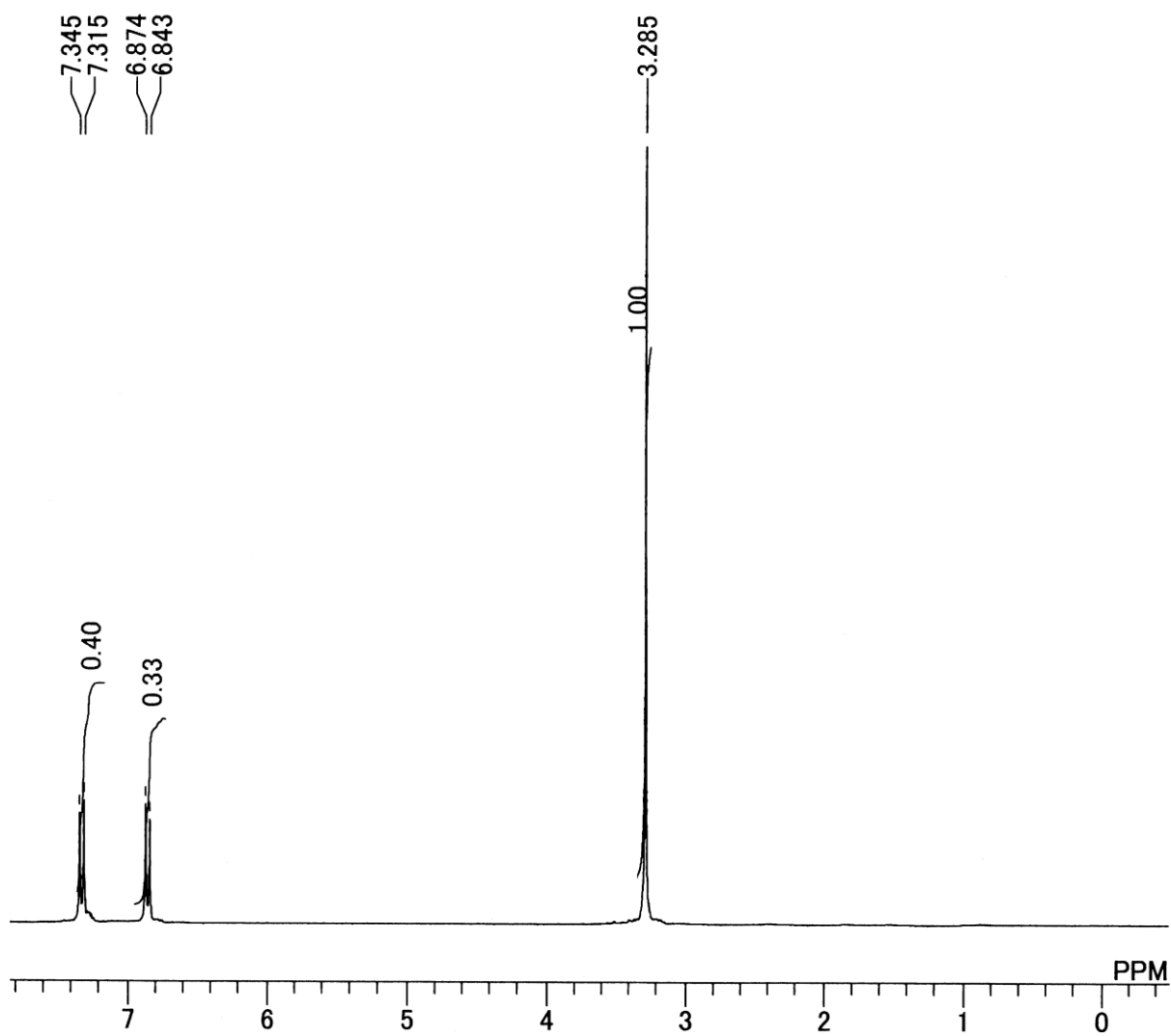
## 5. Synthetic Procedure for 2
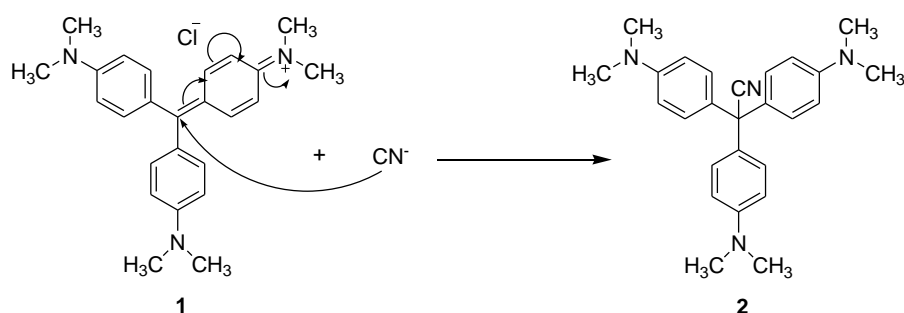
Scheme S2. Preparation of compound **2** from **1**.

The cyanide adduct was obtained by taking **1** (1.0g, 2.45mmol) in acetonitrile and adding NaCN (0.150g, 3.0mmol) dissolved in minimum amount of water, to it. The reaction mixture was stirred at room temperature for 24 hours. White precipitates of adduct were formed which were obtained upon filtration. The precipitates were given charcoal treatment and recrystallized from dichloromethane to give the product. Yield: 85%. Found: C, 78.48; H, 7.61; N, 14.16. Calc. for $C_{26}H_{30}N_4$: C, 78.39; H, 7.54; N, 14.07%. ^{1}H NMR (300 MHz; CDCl$_3$; Me$_4$Si; ppm) δ_H: 2.94 (18H, s, -CH_3), 6.64 (6H, d, J=9 Hz, aromatic H), 7.06 (6H, d, J=9 Hz, aromatic H). ^{13}C NMR (75 MHz; CDCl$_3$; Me$_4$Si; ppm) δ_C: 40.41, 55.08, 111.98, 129.17, 129.42, 149.69. m/z (EI): 399.7 (M$^+$+1).

6. Spectral data for 1 and 2

(a) ^{1}H NMR spectrum of **1** (in CDCl$_3$)

7.406
7.376
6.935
6.904
3.346
3.343
1.970
1.965
1.963

1.35
1.37

PPM

8   6   4   2   0
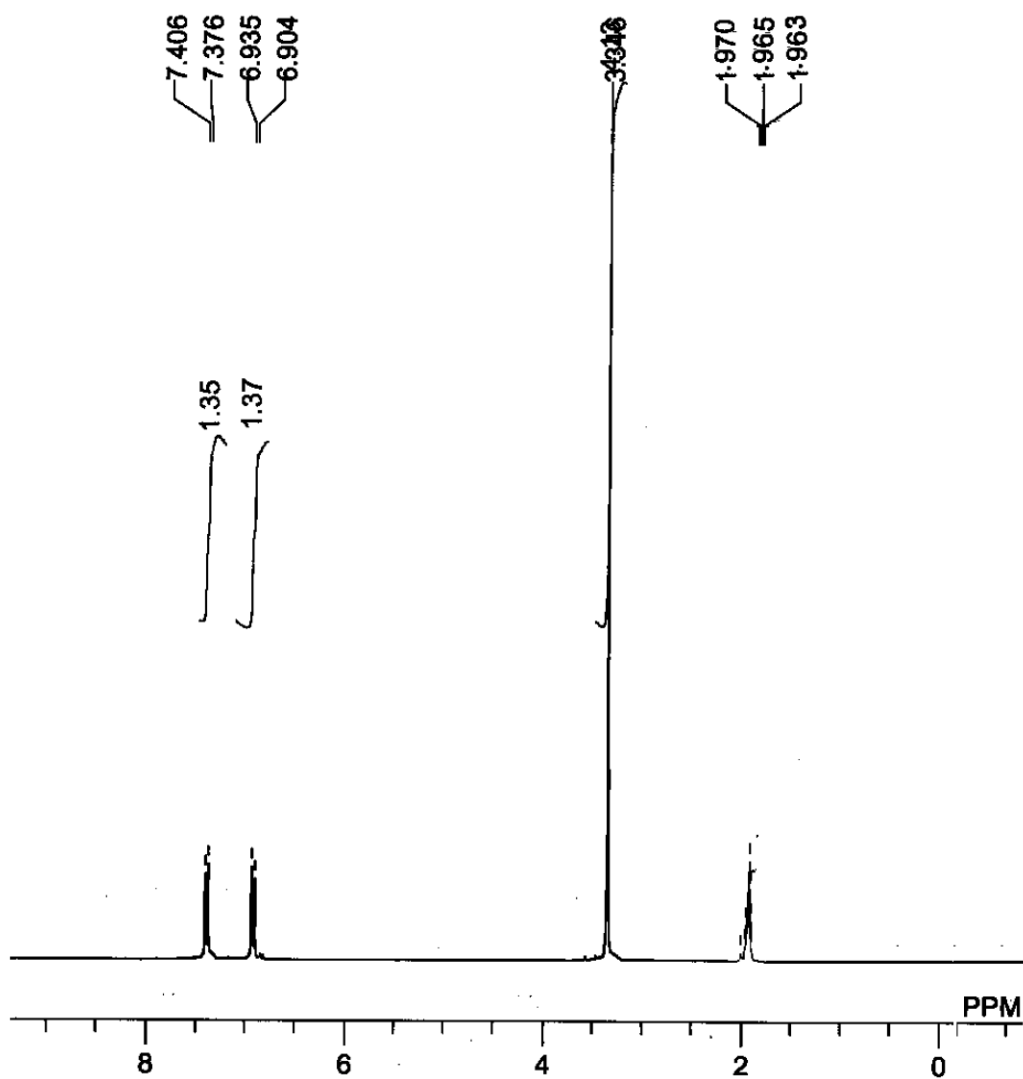
(b) ^{1}H NMR spectrum of **1** (in CD$_3$CN)
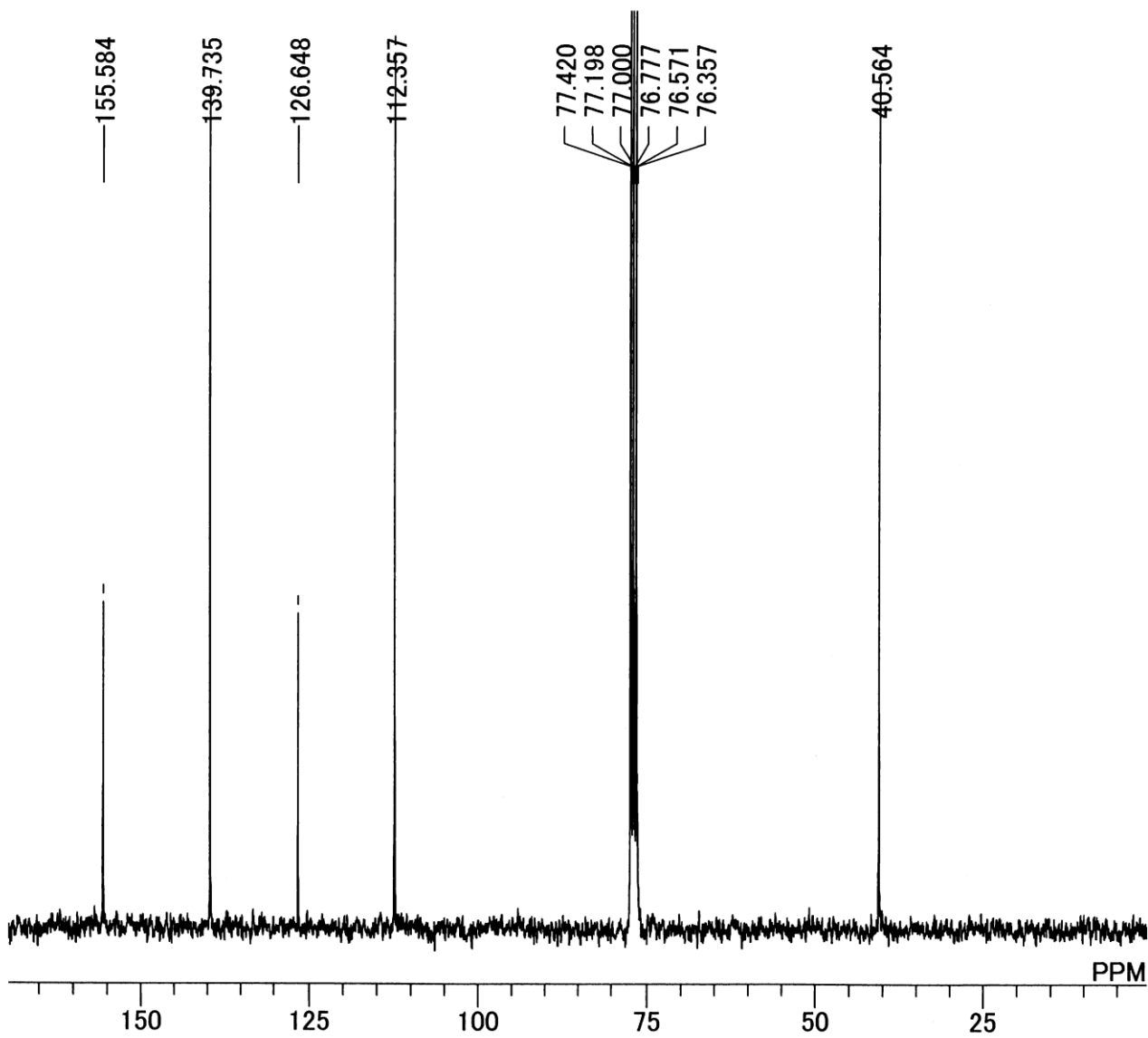
(c) ^{13}C NMR spectrum of **1** (in CDCl$_3$)
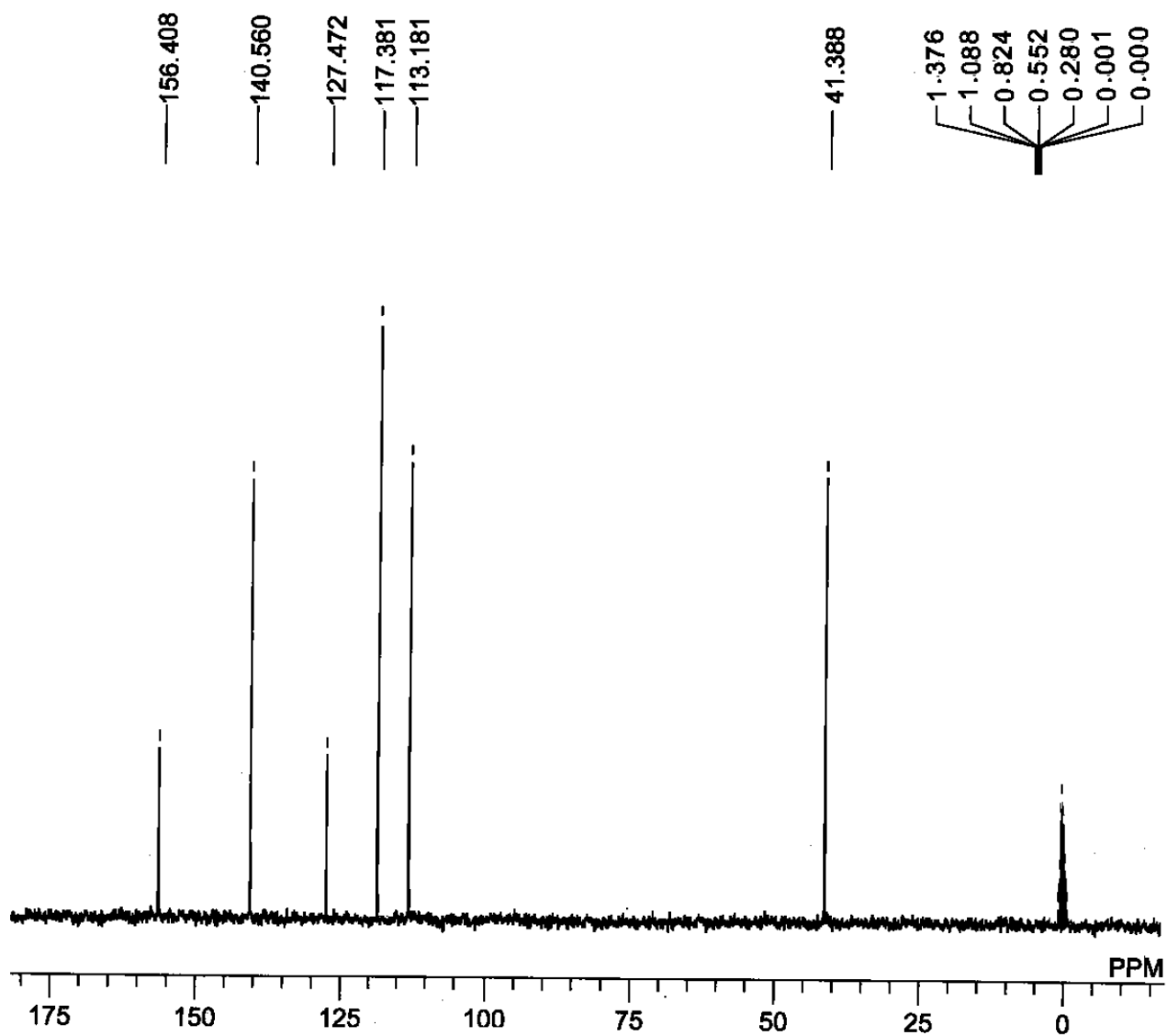
(d) ^{13}C NMR spectrum of **1** (in CD$_3$CN)

(e) Mass spectrum of **1**

7.087
7.057
6.660
6.630
3.87
2.90
2.935
13.32

PPM

7   6   5   4   3   2   1   0

(f) ^{1}H NMR spectrum of **2** (in CDCl$_3$)

7.162
7.132
6.745
6.715
3.020
1.970
1.965
1.963

1.00
1.10

3.02

PPM
7   6   5   4   3   2   1
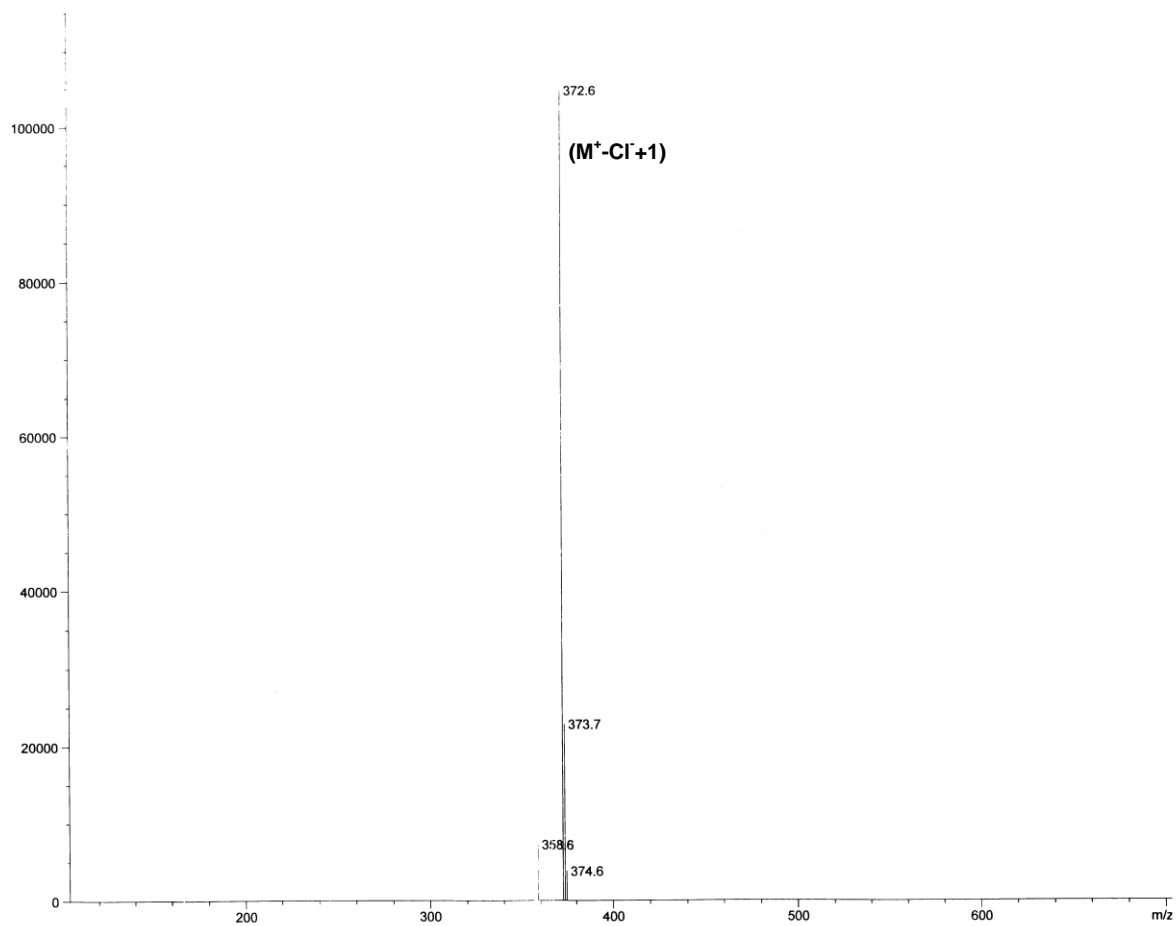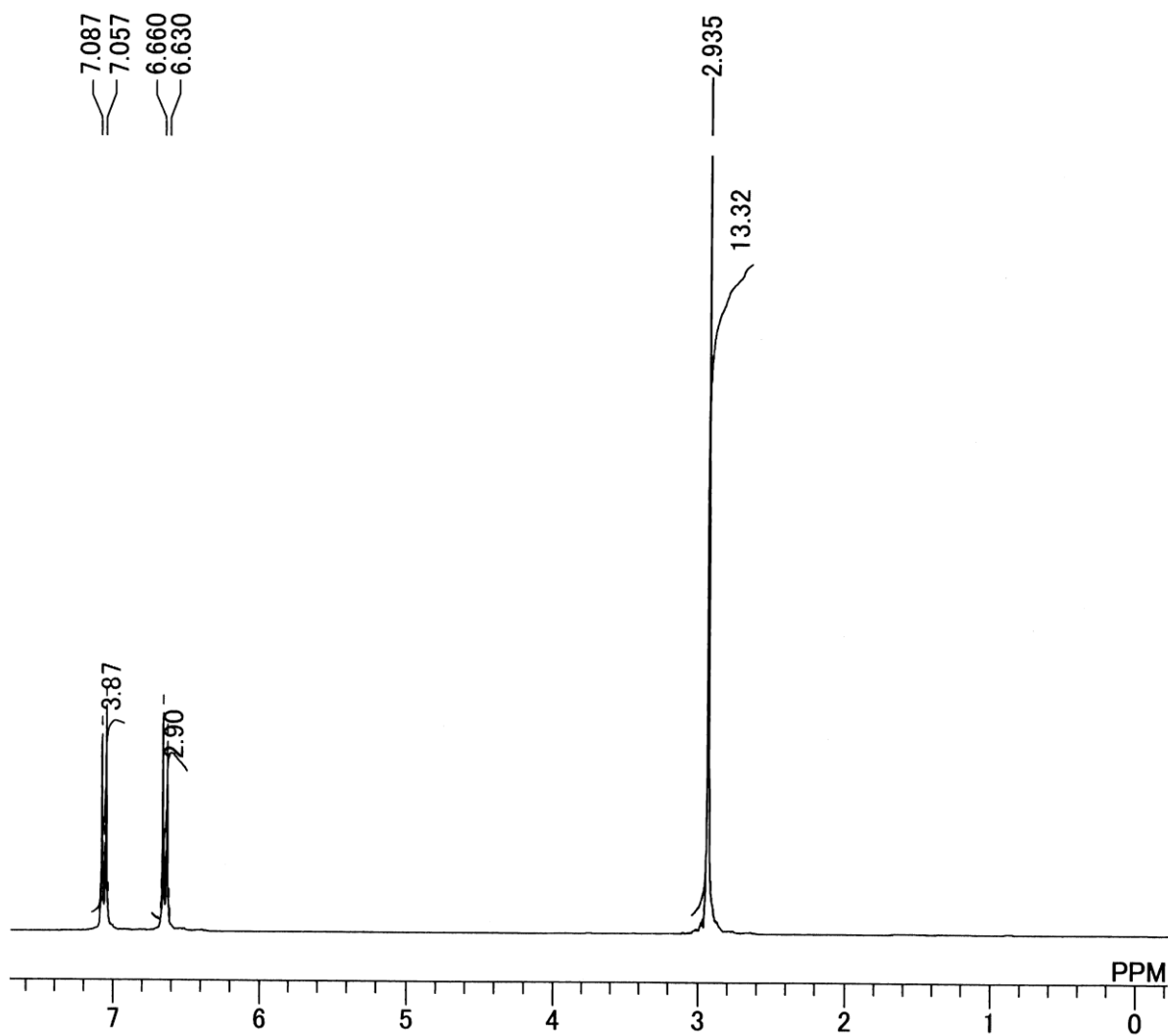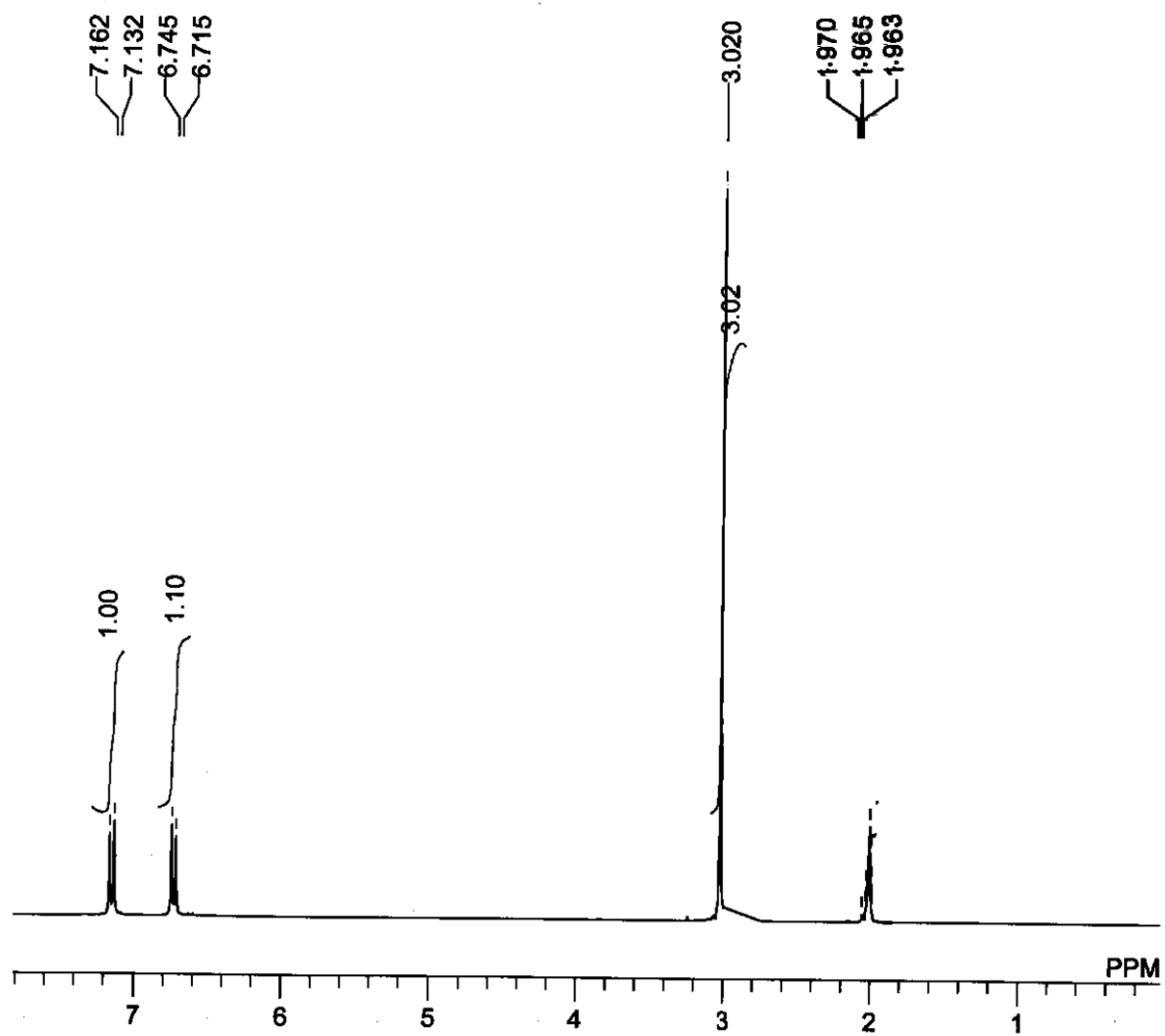
(g) ^{1}H NMR spectrum of **2** (in CD$_3$CN)

(h) ^{13}C NMR spectrum of **2** (in CDCl$_3$)

Peaks: 149.691, 129.417, 129.170, 111.977, 77.429, 77.371, 77.198, 77.000, 76.885, 76.868, 76.580, 55.077, 40.448, 40.415, 40.374

150.515

130.241
129.994

117.381
112.802

55.901

41.272
41.240
41.198

1.376
1.088
0.824
0.552
0.280
0.001
0.000

PPM

150   125   100   75   50   25   0
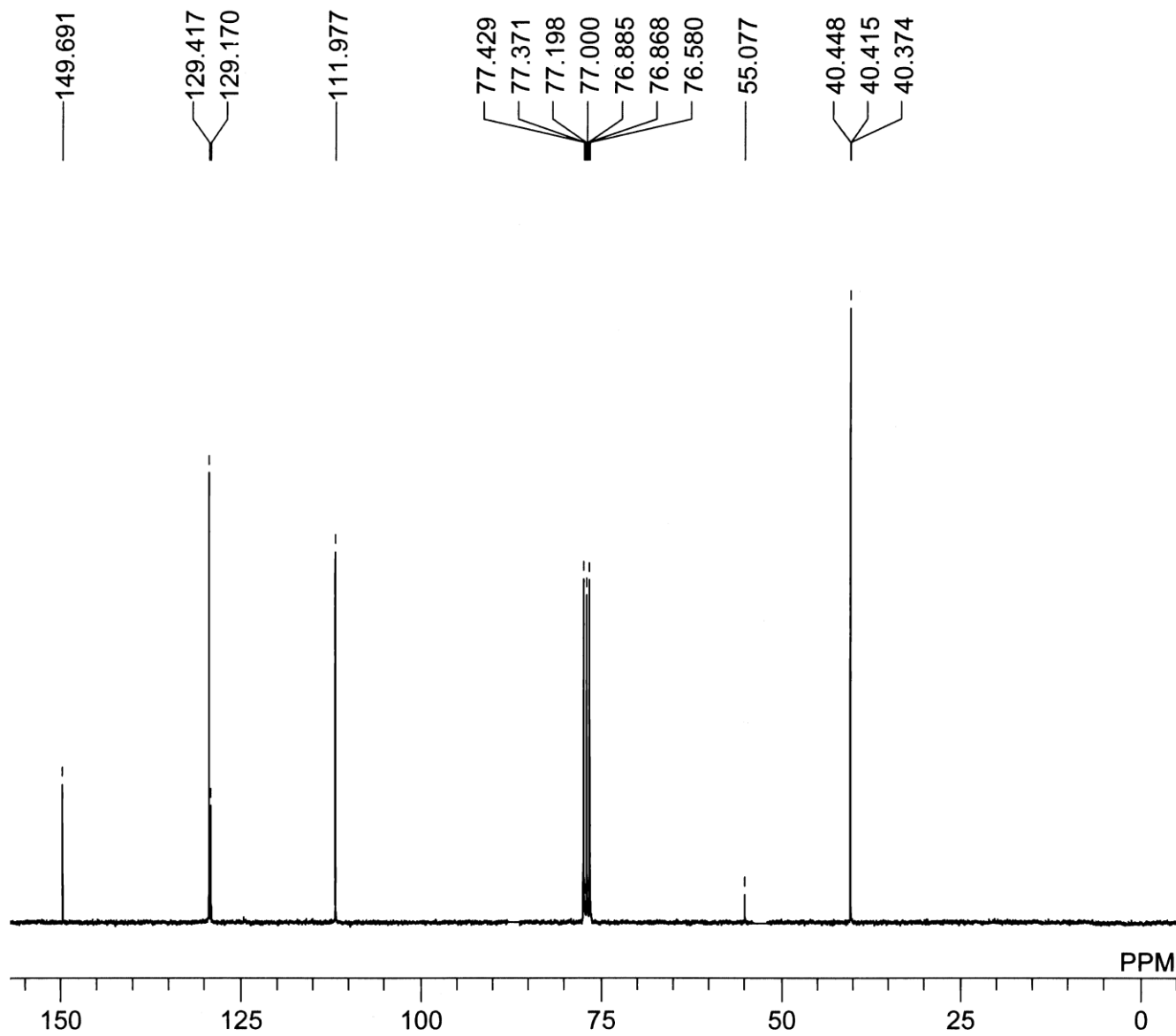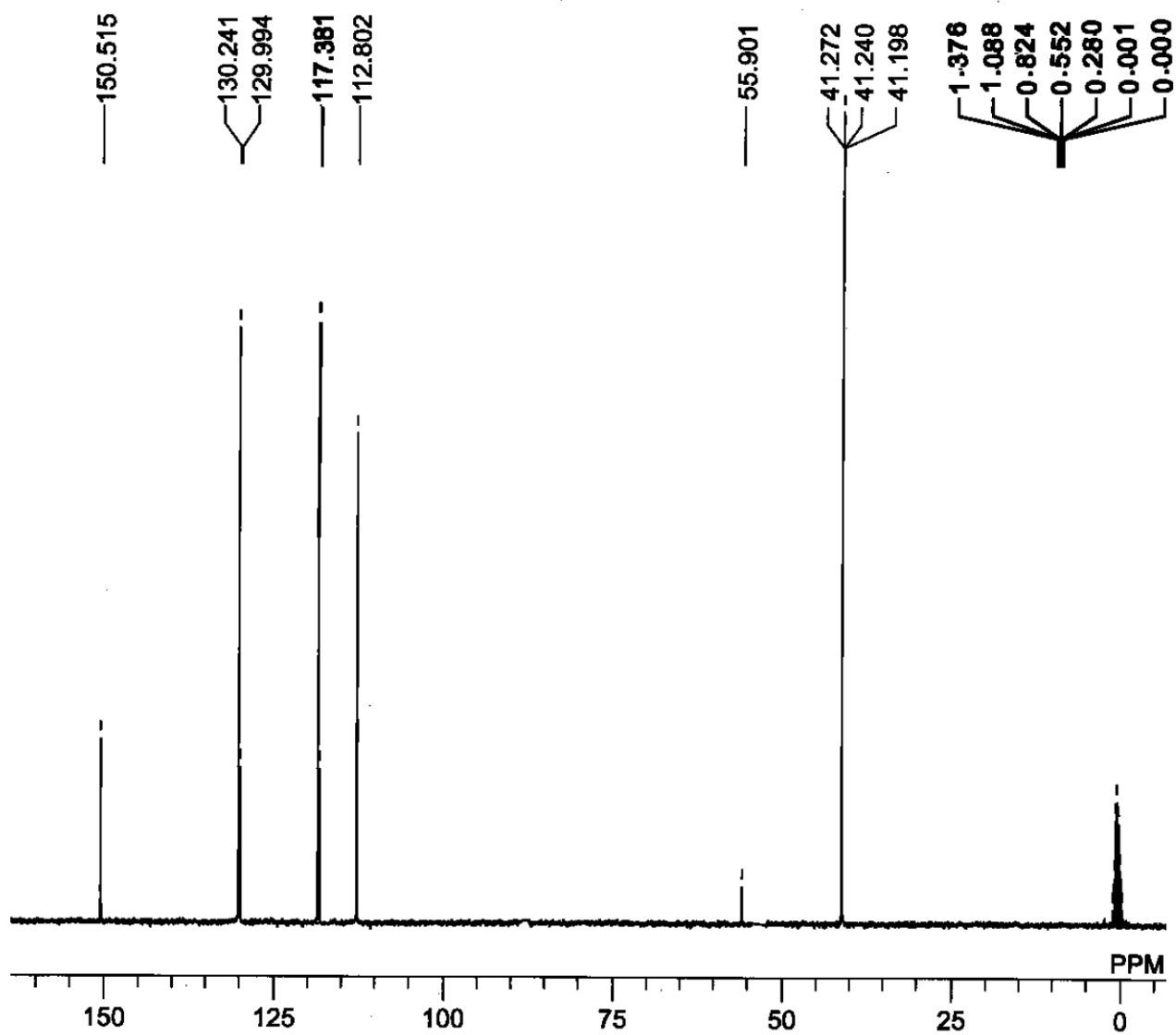
(i) ^{13}C NMR spectrum of **2** (in CD_3CN)
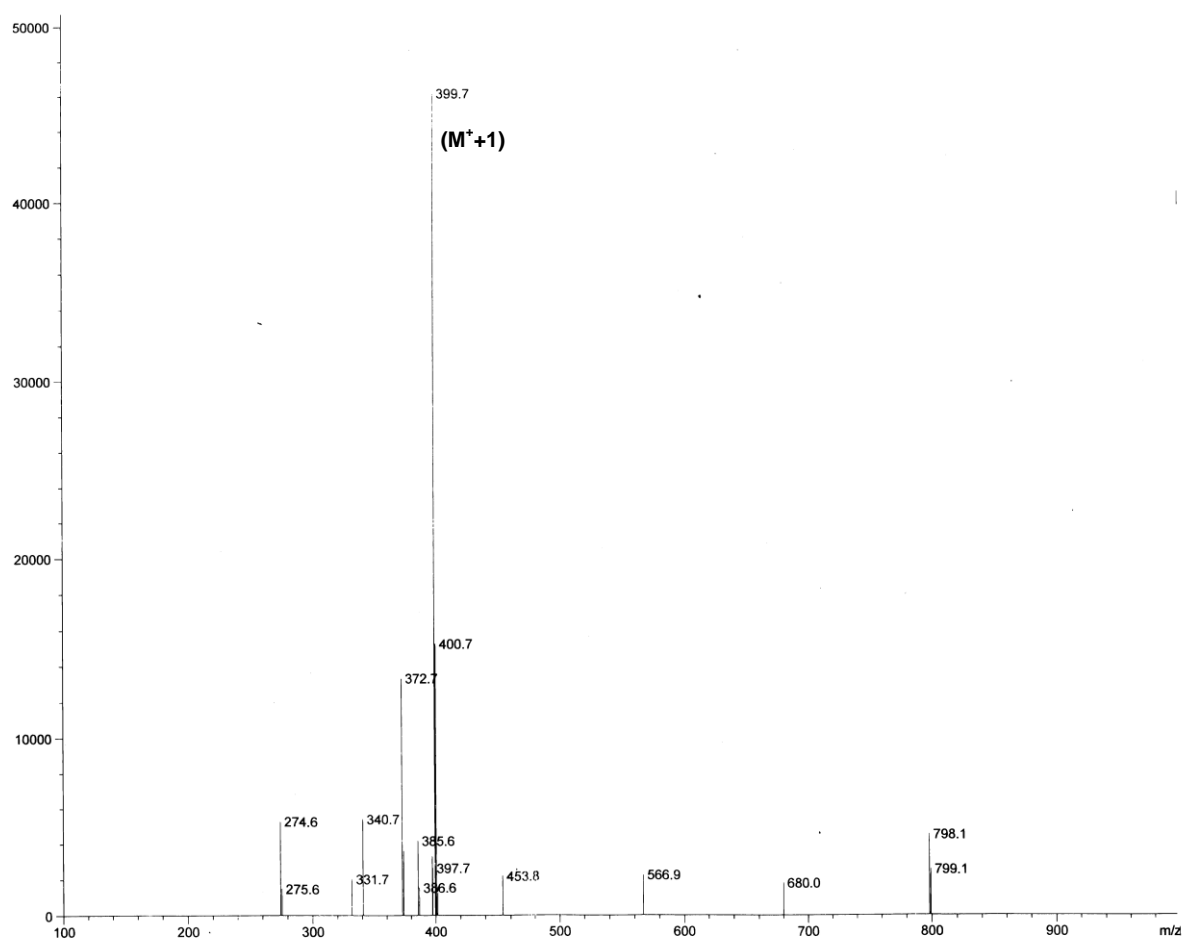
(j) Mass spectrum of **2**
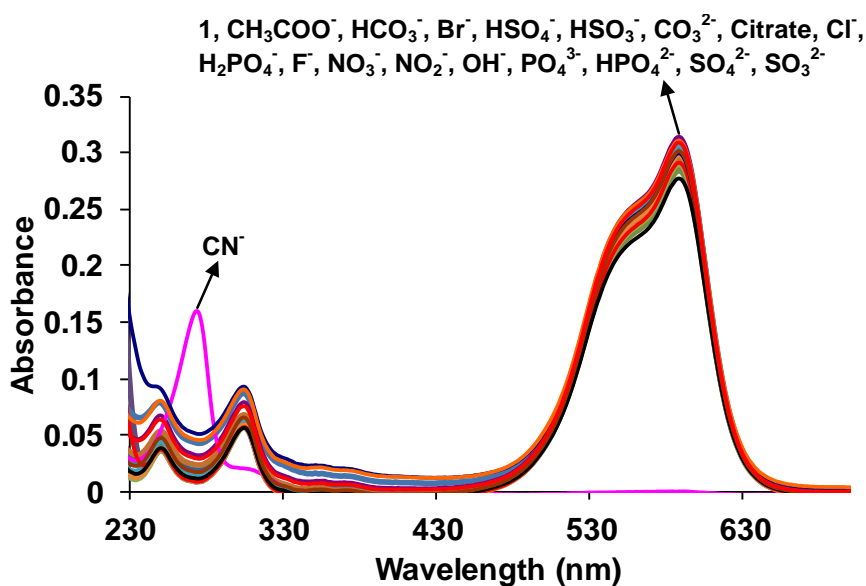
Fig. S2. Changes in the UV-vis spectrum of **1** (3×10^{-6} M, in CH_3CN) upon addition of different anions (3×10^{-5} M, in HEPES buffered H_2O).

Table S3. (a) Selected data of electronic transitions in **1** by TD-DFT method at the B3LYP/6-311G* level.[a][b]

State	λ [nm (eV)]	f	Composition of band and CI coefficiencies
1	522.11 (2.37)	0.7273	H→L, 0.70
2	503.24 (2.46)	0.7506	H-1→L, 0.70
14	270.49 (4.58)	0.1733	H-1→L+2, 0.63; H→L+3, 0.17; H-1→L+3, 0.12; H-10→L, 0.11; H→L+2, -0.10; H-1→L+4, -0.13;
15	263.53 (4.70)	0.0909	H→L+4, 0.58; H-1→L+4, 0.12; H→L+3, -0.10; H-9→L, -0.21; H-1→L+3, -0.25

[a] Calculations were carried out for the lowest 20 excited states, and only energies above 250 nm with f > 0.09 are shown. [b] f = oscillator strength; CI = configuration interaction; H = HOMO; L = LUMO.

(b) Cartesian coordinates from the optimized structure of **1** at B3LYP/6-311G*.

E= -1595.4109 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.560181	-1.124209	-1.119839
2	6	0	0.300841	-1.205580	-0.462150
3	6	0	-0.007526	-2.447669	0.161970
4	6	0	0.920518	-3.454783	0.258834
5	6	0	2.237939	-3.287125	-0.265771
6	6	0	2.490340	-2.118522	-1.037871

14

7	1	0	1.804615	-0.233775	-1.684382
8	1	0	-0.957527	-2.562548	0.670911
9	1	0	0.671112	-4.336988	0.833804
10	1	0	3.449391	-1.974994	-1.511066
11	6	0	-0.520540	-0.049976	-0.286434
12	6	0	-1.966368	-0.184500	-0.149265
13	6	0	-2.687617	-1.146423	-0.887325
14	6	0	-2.714967	0.628359	0.727740
15	6	0	-4.057476	-1.283165	-0.774552
16	1	0	-2.154806	-1.773879	-1.593061
17	6	0	-4.081953	0.490765	0.868130
18	1	0	-2.197376	1.356147	1.342095
19	6	0	-4.803674	-0.467252	0.112295
20	1	0	-4.555233	-2.021375	-1.389508
21	1	0	-4.593413	1.122858	1.582093
22	6	0	0.104611	1.247437	-0.198218
23	6	0	-0.555032	2.435815	-0.605290
24	6	0	1.431117	1.393374	0.294966
25	6	0	0.064207	3.664374	-0.558695
26	6	0	2.054055	2.616090	0.357110
27	1	0	2.000186	0.544024	0.661013
28	6	0	1.398746	3.795896	-0.077543
29	7	0	3.225571	-4.181977	-0.031349
30	6	0	4.627082	-3.813888	-0.275513
31	1	0	4.809409	-2.778244	0.032064
32	1	0	4.894625	-3.940853	-1.330819
33	6	0	2.956840	-5.430769	0.665981
34	1	0	3.808642	-6.096625	0.539431
35	1	0	2.080082	-5.932126	0.250304
36	7	0	-6.163961	-0.598034	0.232793
37	6	0	-6.904979	0.254666	1.148629
38	1	0	-6.604100	0.098214	2.191387
39	1	0	-7.966543	0.029709	1.069558
40	6	0	-6.870214	-1.627750	-0.512873
41	1	0	-6.507704	-2.631924	-0.265068
42	1	0	-6.770733	-1.487028	-1.595053
43	1	0	-0.472661	4.529732	-0.925124
44	1	0	3.063717	2.630180	0.746505
45	1	0	-1.555586	2.372814	-1.018315
46	1	0	-7.929614	-1.585567	-0.268733
47	1	0	-6.770002	1.315090	0.910453
48	1	0	2.796641	-5.276999	1.740384
49	1	0	5.265544	-4.465241	0.319568
50	7	0	2.025124	5.007806	-0.037898
51	6	0	1.324261	6.217849	-0.438310
52	6	0	3.414754	5.099741	0.401485
53	1	0	0.416097	6.373264	0.153781
54	1	0	1.973570	7.076601	-0.282644
55	1	0	1.042519	6.196323	-1.497529
56	1	0	3.758833	6.125055	0.282553

57	1	0	3.525928	4.819775	1.453971
58	1	0	4.064514	4.450544	-0.191159
59	17	0	4.571286	-0.279603	0.796637

(c) Selected data of electronic transitions in **1**+CN⁻ by TD-DFT method at the B3LYP/6-311G* level.[a][b]

State	λ [nm (eV)]	f	Composition of band and CI coefficiencies
4	275.70 (4.50)	0.1616	H→L+1, 0.64; H→L+2, 0.17; H-1→L, 0.12
5	275.03 (4.51)	0.1847	H→L+2, 0.64; H→L+3, -0.11; H-2→L, 0.12; H→L+1, -0.17

[a] Calculations were carried out for the lowest 15 excited states, and only energies above 250 nm with f > 0.15 are shown. [b] f = oscillator strength; CI = configuration interaction; H = HOMO; L = LUMO.

(d) Cartesian coordinates from the optimized structure of **1**+CN⁻ at B3LYP/6-311G*.

E= -1228.0491 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.747507	2.417645	1.269256
2	6	0	-0.039998	1.455584	0.629385
3	6	0	-0.806702	1.879023	-0.455914
4	6	0	-0.795240	3.201389	-0.887717
5	6	0	-0.018392	4.179053	-0.233426
6	6	0	0.766772	3.741550	0.855970
7	1	0	1.364009	2.132436	2.115680
8	1	0	-1.431831	1.169426	-0.984964
9	1	0	-1.409431	3.465150	-1.738808
10	1	0	1.396792	4.436884	1.394951
11	6	0	0.002799	-0.025801	1.077234
12	6	0	-1.265882	-0.788705	0.623579
13	6	0	-2.484462	-0.600364	1.282586
14	6	0	-1.264581	-1.632888	-0.486306
15	6	0	-3.647920	-1.228425	0.863613
16	1	0	-2.532932	0.052334	2.148378
17	6	0	-2.423527	-2.265494	-0.924774
18	1	0	-0.343739	-1.807204	-1.030273
19	6	0	-3.650677	-2.094159	-0.252311
20	1	0	-4.558168	-1.041717	1.418113
21	1	0	-2.357667	-2.903567	-1.796436
22	6	0	1.291098	-0.733457	0.589002
23	6	0	1.703361	-1.933809	1.176719
24	6	0	2.058588	-0.243458	-0.466579
25	6	0	2.823213	-2.619807	0.732482
26	6	0	3.183694	-0.920592	-0.927746
27	1	0	1.786371	0.690782	-0.943052
28	6	0	3.594482	-2.138204	-0.348816

|					
29	7	0	-0.035549	5.509503	-0.628879
30	6	0	0.943842	6.429255	-0.078228
31	1	0	1.980111	6.145927	-0.315050
32	1	0	0.853484	6.497565	1.009458
33	6	0	-0.679708	5.870705	-1.878482
34	1	0	-0.618982	6.949743	-2.014379
35	1	0	-1.740539	5.604494	-1.866609
36	7	0	-4.803281	-2.754921	-0.656207
37	6	0	-4.812357	-3.447650	-1.931810
38	1	0	-4.634716	-2.777302	-2.786118
39	1	0	-5.780057	-3.927669	-2.072200
40	6	0	-6.081887	-2.364789	-0.088828
41	1	0	-6.342323	-1.316557	-0.297606
42	1	0	-6.091898	-2.505097	0.995545
43	1	0	3.098381	-3.534768	1.240280
44	1	0	3.744270	-0.483067	-1.743448
45	1	0	1.143115	-2.344063	2.010830
46	1	0	-6.865290	-2.998168	-0.503149
47	1	0	-4.053438	-4.234570	-1.957942
48	1	0	-0.219591	5.388931	-2.754091
49	1	0	0.764409	7.425626	-0.480125
50	7	0	4.699054	-2.835688	-0.820270
51	6	0	5.218058	-3.950072	-0.046902
52	6	0	5.595788	-2.189361	-1.761588
53	1	0	4.464495	-4.733994	0.068534
54	1	0	6.062462	-4.390332	-0.575867
55	1	0	5.558074	-3.655789	0.956945
56	1	0	6.390485	-2.882974	-2.033494
57	1	0	5.072053	-1.919289	-2.682998
58	1	0	6.059791	-1.278153	-1.355893
59	6	0	0.025887	-0.042180	2.558062
60	7	0	0.045457	-0.055318	3.711501
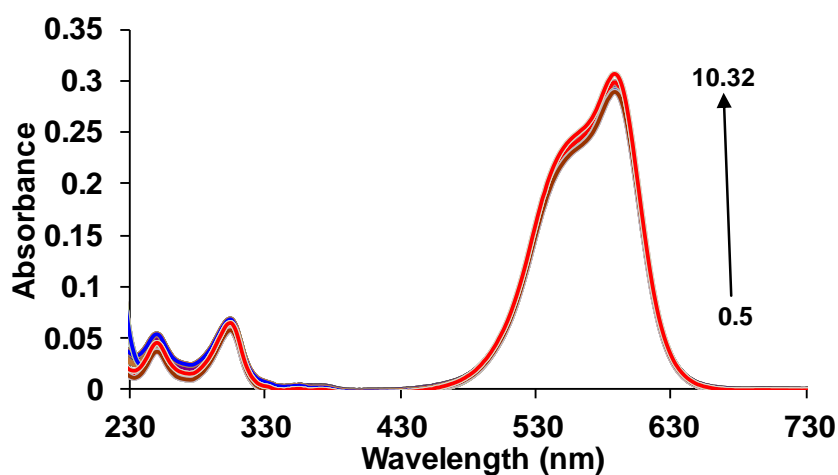
Fig. S4. Changes in the UV-vis spectrum of **1** upon pH titrations with HCl (0.01 and 0.1 M) and NaHCO$_3$ (0.1 and 1 M).

Complete Reference for Gaussian (Reference 16 in manuscript)

Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.