Supporting information

A highly selective and sensitive fluorescent chemosensor for distinguishing cadmium(II) from zinc(II) based on amide tautomerization

Yuanyuan Zhang, Xiangzhu Chen, Jingjing Liu, Gui Gao, Xueyan Zhang, Shicong Hou*, Hongmei Wang*

Department of Applied Chemistry, China Agricultural University, Beijing, 100193, P.R. China.

*Corresponding authors

E-mail addresses: houshc@cau.edu.cn (S. C. Hou); Fax number: +86-10-62731881.
whmd@cau.edu.cn (H. M. Wang).

Contents

1. Additional data

Reference	analyte	Solvent (v:v)	$\lambda_{ex}/\lambda_{em}$ (nm)	Detection limit
Ref. [19]	Cd^{2+}	DMSO:H_2O=1:1	341/473	0.3 μM
Ref. [42]	Cd^{2+}	10 mM Tris–HCl buffer	312/410	1.18 μM
Ref. [43]	Cd^{2+}	CH_3OH: HEPES buffer =1:4	505/550	0.71 μM
Ref. [44]	Cd^{2+}	Tris-HCl (0.02 M) solution (containing 0.1 mM sodium phosphate, pH =7.4)	370/502	0.04μM
Ref. [48]	Cd^{2+}	CH_3CN: HEPES buffer =3:7	387/495	58.4 nM
Ref. [57]	Cd^{2+}	CH_3CN	341/455	2.81 ppb
This work	Cd^{2+}	EtOH:H_2O=1:1	360/506	0.24 nM

Table S1. A comparison table about the detection limits of **L2** and other probes for Cd^{2+}.

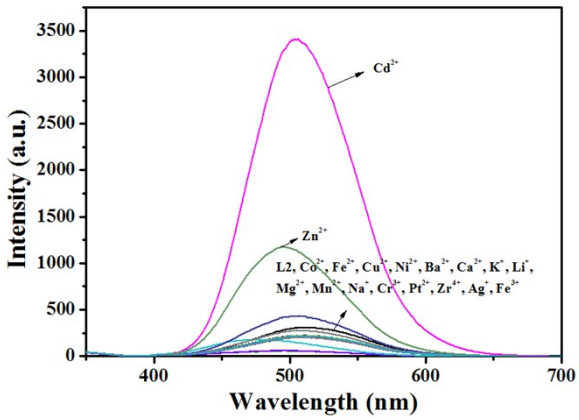

Fig. S1 The fluorescent spectra of **L2** in the presence of various metal ions (1.0 equiv.) in EtOH-H_2O (1/1, v/v) solution.

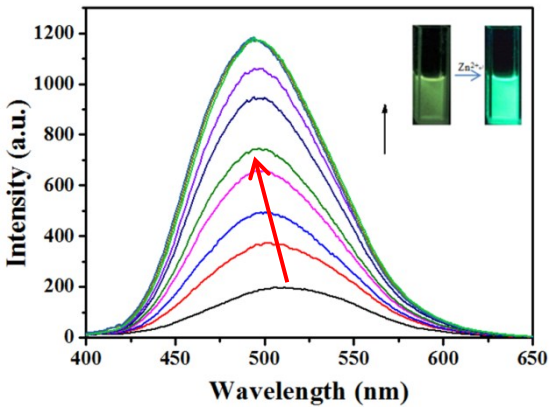

Fig. S2 Fluorescence spectra changes of **L2** (10 μM) upon addition of Zn^{2+}, λ_{em}= 490

nm. Insert: The color change of **L2** upon addition of Zn^{2+} under 365 nm UV light.

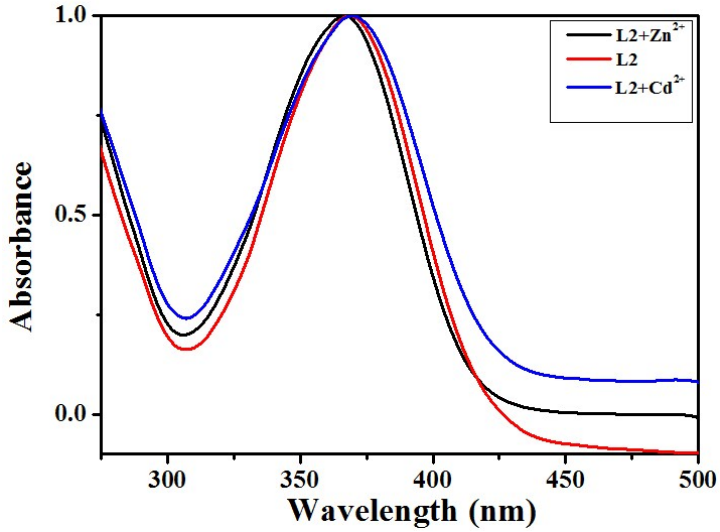

Fig. S3 Absorption spectra of **L2** (10 μM) before and after coordinated with 1.0 equiv. of Cd^{2+} and 1.0 equiv. of Zn^{2+}.

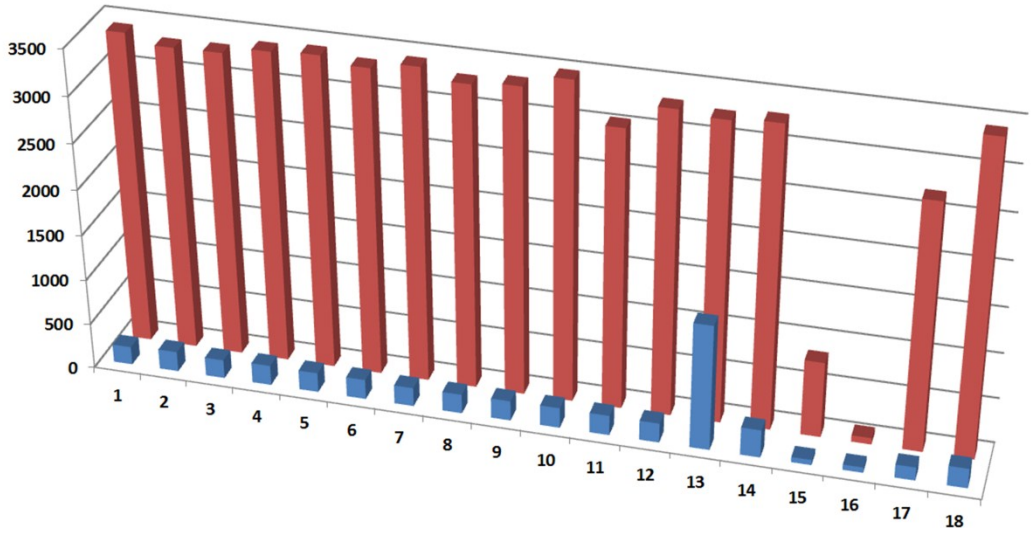

Fig. S4 The fluorescent spectra of **L2** (10 μM) at 506 nm in the presence of various metal ions (1.0 equiv.) (blue bars) and further addition of 1.0 equiv. of Cd^{2+} (red bars). (1)**L2**; (2)Li^{+}; (3)Mg^{2+}; (4)Mn^{2+}; (5)Na^{+}; (6)K^{+}; (7)Ca^{2+}; (8)Ba^{2+}; (9)Fe^{2+}; (10)Fe^{3+}; (11)Pt^{2+}; (12)Zr^{4+}; (13)Zn^{2+}; (14)Ag^{+}; (15)Co^{2+}; (16)Cu^{2+}; (17)Ni^{2+}; (18)Cr^{3+}.

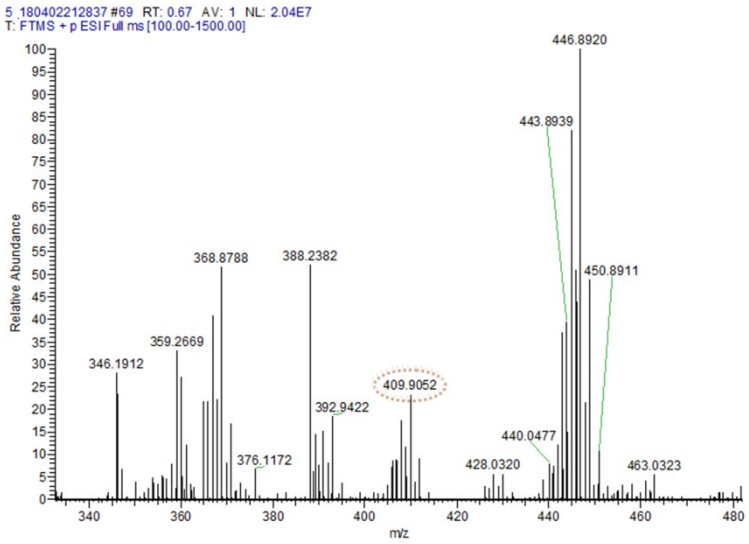

Fig. S5 Isotopic distribution pattern for the molecular ion peak at m/z= 409.9052 (z=2) for [**L2** + Cd^{2+} + Na^{+} + ClO_4^{-}] $^{2+}$ obtained from HRMS-ESI.

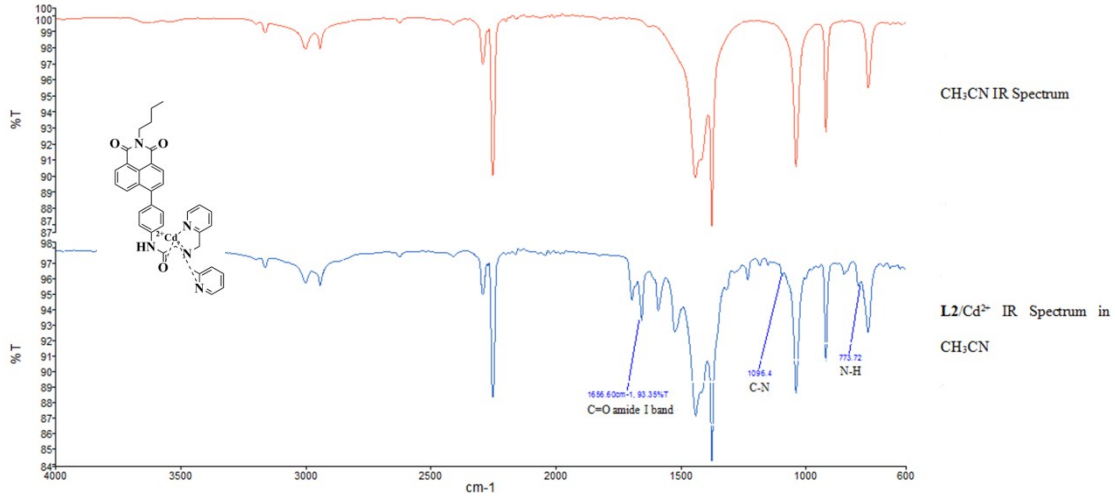

Fig. S6 IR spectrum of **L2**/Cd^{2+} complex in CH_3CN**.**

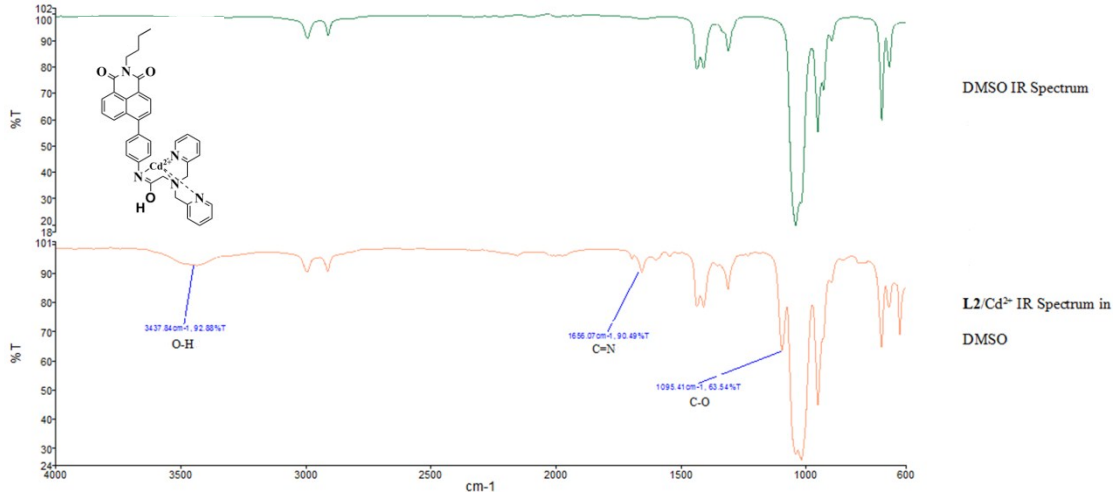

Fig. S7 IR spectrum of **L2**/Cd^{2+} complex in DMSO**.**

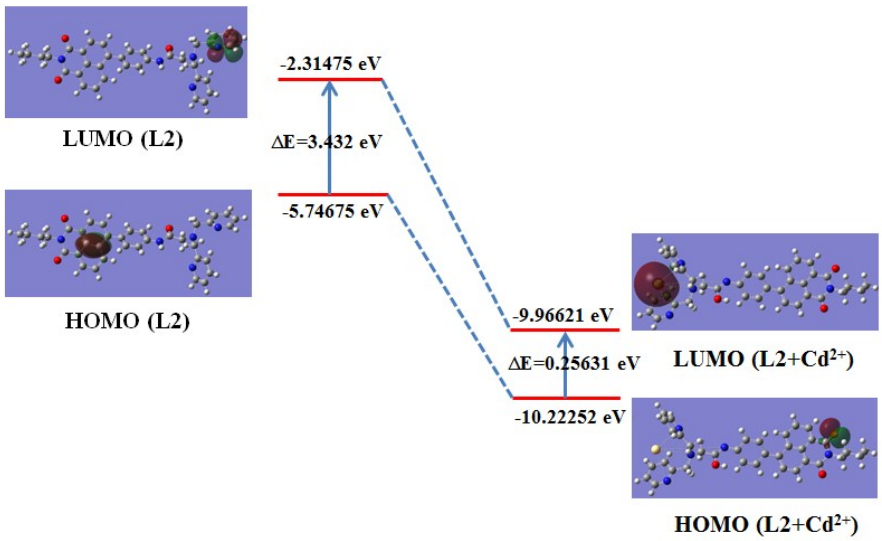

Fig. S8 The HOMO and LUMO orbitals of **L2** and **L2**/Cd^{2+} complex calculated at the DFT level.

Center Number	Coordinates (Angstroms)		
	X	Y	Z
1C	5.1868889155	2.7839572507	2.0385183961
2C	4.2392940577	1.787688718	2.3391175808
3C	3.2215493153	1.4959844331	1.452961495
4C	3.1022477901	2.1828214306	0.214346938
5C	4.0466044695	3.2225209645	-0.0643995577
6C	5.0886342654	3.4986349106	0.8585552159
7C	2.0645304186	1.9144336694	-0.7435895115
8C	1.9846138889	2.7069858262	-1.8829617746
9C	2.9075916336	3.734365406	-2.1397916856
10C	3.9372499712	3.987421909	-1.2526044451
11C	4.9115685512	5.0621337191	-1.5581402962
12N	5.9163635204	5.295175893	-0.6067080896
13C	6.0857864092	4.5624660732	0.5768958995
14O	7.0172719155	4.8058102313	1.3341791453
15O	4.8567950526	5.7281004597	-2.5847879693
16C	6.8934546376	6.3616240866	-0.8942902946
17C	8.1069965589	5.8537967525	-1.6795355609
18C	9.1147030069	6.9721063292	-1.9710384539
19C	10.3358078389	6.4843117767	-2.7562558634
20C	1.0783242665	0.8175492231	-0.5618511217
21C	1.4788715082	-0.5092240947	-0.3297075292
22C	0.5429357593	-1.5294873828	-0.2166042147
23C	-0.8304047906	-1.2592795784	-0.3269012277
24C	-1.2486953064	0.0601735309	-0.5594886704
25C	-0.2977491956	1.0698292523	-0.6781615106
26N	-1.7207806002	-2.3425332587	-0.1993600037

27C	-3.0969567097	-2.3559468592	-0.2858081856
28C	-3.7029941294	-3.7739049442	-0.1802210526
29O	-3.7839908145	-1.3594292758	-0.4611502606
30N	-5.1061085177	-3.8320306804	0.1447113505
31C	-6.0239299108	-3.393650982	-0.9042214383
32C	-5.4252630129	-3.381867293	1.4985354228
33C	-7.3972536043	-4.0331269477	-0.7776927248
34C	-5.0221124511	-4.3996404789	2.5531326996
35N	-7.4458086038	-5.3745994429	-0.6984924883
36C	-8.647537903	-5.9542639475	-0.6224728814
37C	-9.8538452967	-5.2503918454	-0.6233433963
38C	-9.8007574333	-3.861533101	-0.7035851967
39C	-8.5528837509	-3.2437070611	-0.7797903946
40N	-4.5190816208	-3.9092026866	3.6962830884
41C	-4.1972760364	-4.7813652625	4.6614176953
42C	-4.347684193	-6.1615652116	4.5392457925
43C	-4.8651675445	-6.6633956597	3.3437686518
44C	-5.2086751896	-5.7718085379	2.3318074168
45H	5.9949909758	3.021222071	2.7217977016
46H	4.305334772	1.2508426632	3.2802659364
47H	2.4880391091	0.7403128322	1.7082647216
48H	1.2056809666	2.5010039207	-2.6101478455
49H	2.8410203445	4.3330195995	-3.0417933257
50H	6.3649566261	7.1272788802	-1.46369172
51H	7.2063531447	6.7698959075	0.0675831285
52H	8.5940037481	5 .0573633299	-1.1039907289
53H	7.7605732341	5.4127311736	-2.6220025128
54H	8.6155009876	7.7736815163	-2.5319409243
55H	9.4439857465	7.4202012593	-1.0238730591
56H	11.0380427199	7.3013704363	-2.9506832062
57H	10.8750989061	5.7056493807	-2.205300109
58H	10.0410690239	6.0612745294	-3.7231359935
59H	2.5353034935	-0.7495637306	-0.2638492734
60H	0.8806990966	-2.549913743	0.0501959945
61H	-2.3042624985	0.2766580748	-0.6373194978
62H	-0.6355914608	2.0880097352	-0.8469437122
63H	-1.2820761803	-3.2344231152	-0.0154744122
64H	-3.5376353915	-4.2731396549	-1.1449478546
65H	-3.1427754951	-4.3511737579	0.5682140325
66H	-6.1280141585	-2.300800389	-0.9527006218
67H	-5.5941179286	-3.7113189332	-1.8622312241
68H	-4.9750584446	-2.4128469868	1.7563778633
69H	-6.5117806776	-3.2455826954	1.5529993818
70H	-8.6497256491	-7.0415191115	-0.5612632928

71H	-10.7992228158	-5.7796461492	-0.5608304265
72H	-10.7107276045	-3.2684341774	-0.7019129973
73H	-8.4690299707	-2.162790619	-0.8387531663
74H	-3.7931175546	-4.3511091986	5.5764398649
75H	-4.0653785937	-6.8197389461	5.3549618642
76H	-5.0001973893	-7.7326727034	3.2052006401
77H	-5.6147682174	-6.1009787121	1.3806557748

Table S2. XYZ Coordinates for Calculated Optimized Geometry of **L2** at DFT/B3LYP/6-31G (d,p).

Center Number	Coordinates (Angstroms)		
	X	Y	Z
1C	7.4188340901	2.3822645612	-1.5928904893
2C	6.0904856886	2.6336775417	-1.9569083631
3C	5.0848572994	1.7099340032	-1.6764251531
4C	5.3676425159	0.5039395683	-0.9939156082
5C	6.7381071737	0.22927446	-0.6815937275
6C	7.7455846916	1.1804362716	-0.9725745035
7C	4.375680795	-0.4938121364	-0.6712564846
8C	4.8145549607	-1.7427749481	-0.1747631808
9C	6.1513677418	-1.9968727479	0.1102619985
10C	7.1140895872	-1.0119728215	-0.1217114811
11C	8.5386487522	-1.3100912035	0.2212462669
12N	9.4837255325	-0.3336974981	-0.0793878402
13C	9.1764141354	0.9119215596	-0.6341184878
14O	10.0368010604	1.7519022568	-0.8401325912
15O	8.8407991548	-2.3733204664	0.7415313585
16C	10.9028068125	-0.6137043336	0.2575681847
17C	11.2672504677	-0.1767807147	1.679892116
18C	12.7369107117	-0.4762052185	2.0062268731
19C	13.1257387742	-0.0467780633	3.4242433243
20C	2.9367474463	-0.2600790722	-0.776206063
21C	2.3432251976	0.9751751351	-0.4003353854
22C	0.9789539137	1.1710977762	-0.4832346027
23C	0.1279996074	0.1361819189	-0.9414089463
24C	0.7094947711	-1.1013268298	-1.3234967538
25C	2.0748710387	-1.2950721204	-1.2231759477
26N	-1.2200860884	0.3985605295	-1.0846302704
27C	-2.1941082263	-0.3320264054	-0.7008550254
28C	-3.612219025	-0.0491322675	-1.1948386344
29O	-2.132715028	-1.3888397823	0.1334678641
30N	-4.6918854843	-0.3318016644	-0.2675383071
31C	-4.7667183255	0.5304116074	0.9037272998
32C	-5.1180825657	-1.7113081341	-0.0924320703

33C	-5.8090118643	1.6425165727	0.8008040164
34C	-6.6048309614	-1.948538124	-0.3372645209
35N	-5.9212024374	2.2632582293	-0.3844348626
36C	-6.7399350394	3.3193869699	-0.4771023366
37C	-7.4941416284	3.8199168602	0.5953493467
38C	-7.4093067013	3.1681426431	1.8198838383
39C	-6.5678500219	2.0408715533	1.9279932036
40N	-7.1250114255	-3.0367556942	0.2519186859
41C	-8.3779731352	-3.3980451056	-0.0561402941
42C	-9.1901518471	-2.6974266425	-0.9593656403
43C	-8.6785688903	-1.5388985003	-1.5389595073
44C	-7.3649708261	-1.1321568201	-1.2097622938
45H	8.2117345833	3.091463806	-1.8040397903
46H	5.8411280395	3.5516268814	-2.4790274052
47H	4.0782487677	1.9098774526	-2.024076453
48H	4.0769068539	-2.5010145693	0.0645469324
49H	6.4704713535	-2.9420699804	0.535557869
50H	11.0440631407	-1.688103902	0.1331622235
51H	11.5063996372	-0.0818953601	-0.478621254
52H	11.076567617	0.8983390776	1.7846328631
53H	10.6166350477	-0.6965388979	2.3939853948
54H	12.9239790465	-1.5510354368	1.883417046
55H	13.3810135967	0.0340072865	1.2782036707
56H	14.1763972104	-0.2718515043	3.6287388391
57H	12.9826131308	1.0300084665	3.5664149343
58H	12.5218341561	-0.5663951308	4.1763125856
59H	2.9668905158	1.7655048129	0.002091958
60H	0.535049687	2.1149319468	-0.1857173236
61H	0.0817148898	-1.8852279194	-1.7366857936
62H	2.4980554556	-2.239659624	-1.5488041438
63H	-3.6497049733	0.9982412434	-1.5008154467
64H	-3.7598318889	-0.6446643807	-2.1038503251
65H	-3.7994737794	1.023956736	1.0790451794
66H	-4.5818118727	-2.346629639	-0.8066368905
67H	-4.8681631381	-2.1176961665	0.8963271536
68H	-6.7881382486	3.8006558614	-1.4512902626
69H	-8.1204879311	4.695494692	0.4631508622
70H	-7.9707165965	3.5168937216	2.6814598009
71H	-6.4123851359	1.5588048295	2.8908734882
72H	-8.7492651903	-4.2941779619	0.4355429377
73H	-10.1876186817	-3.0535238039	-1.1929218743
74H	-9.2668191759	-0.9631996221	-2.2482431513
75H	-6.8909061845	-0.2797424445	-1.6894971873
76H	-1.2184418243	-1.54389055	0.424047049

77H	-4.9542825339	-0.0659385627	1.8052100482
78Cd	-8.2738479729	0.150465939	0.9251714614

Table S3. XYZ Coordinates for Calculated Optimized Geometry of **L2**/Cd^{2+} complex at DFT/B3LYP/GEN.

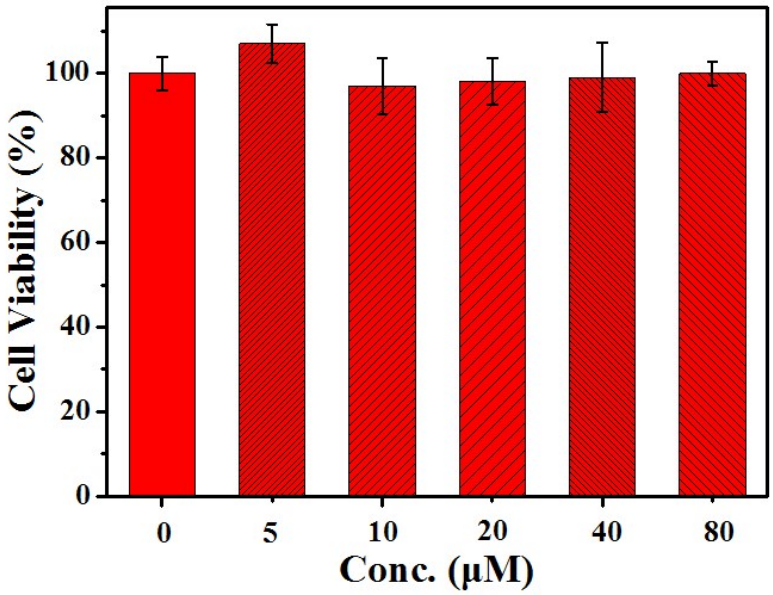

Fig. S9 Cytotoxicity of **L2** at different concentrations for HeLa cells.

2. ^{1}H NMR, ^{13}C NMR and HRMS analyses

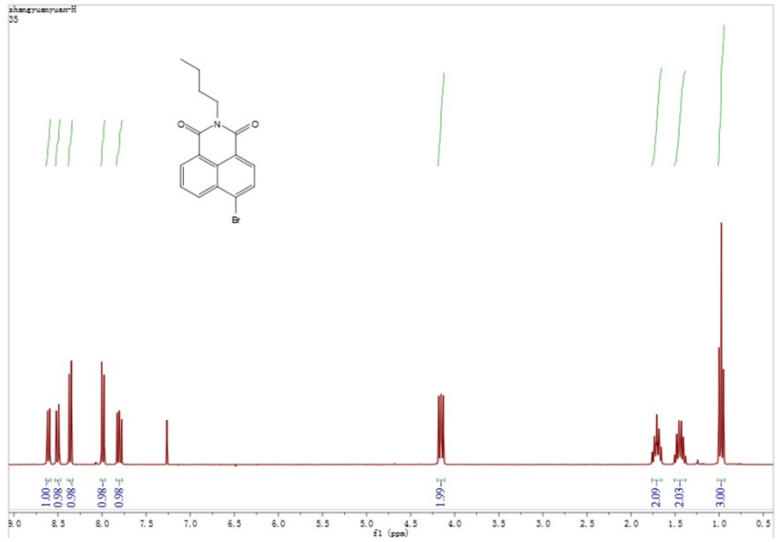

Fig. S10 ^{1}H NMR spectrum of **1** in $CDCl_3$.

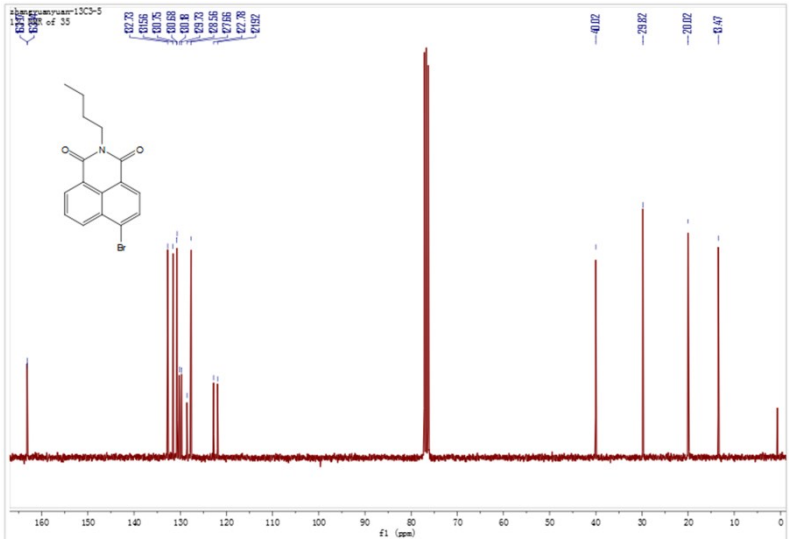

Fig. S11 ^{13}C NMR spectrum of **1** in $CDCl_3$.

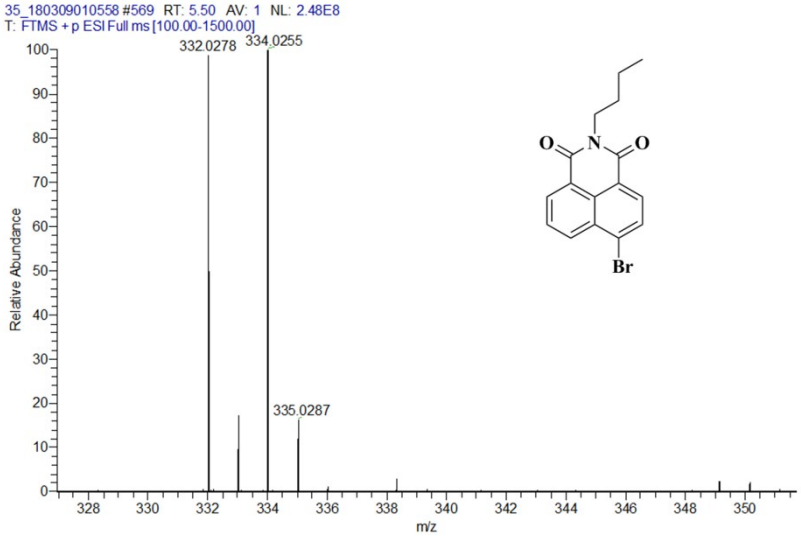

Fig. S12 High resolution mass spectra of **1**.

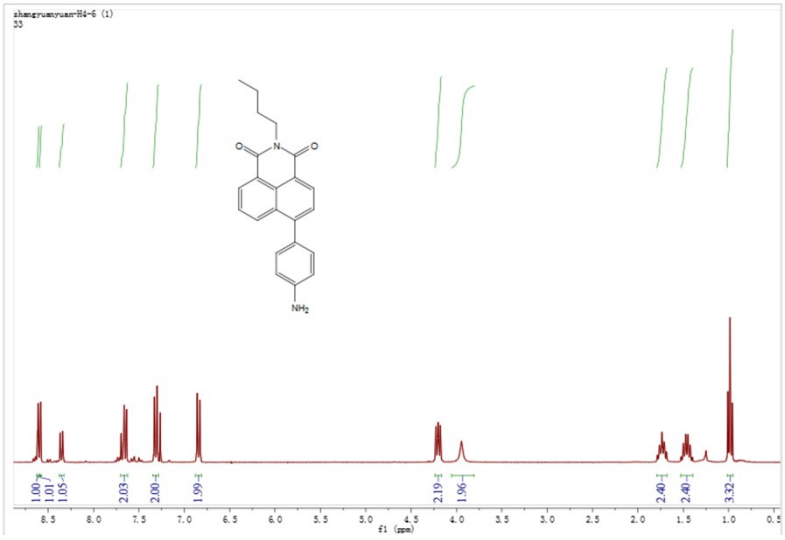

Fig. S13 ^{1}H NMR spectrum of **3** in $CDCl_3$.

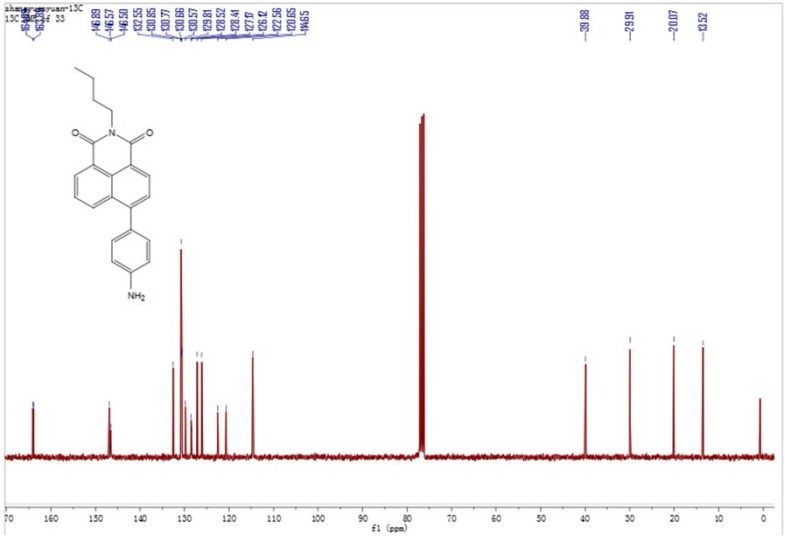

Fig. S14 ^{13}C NMR spectrum of **3** in $CDCl_3$.

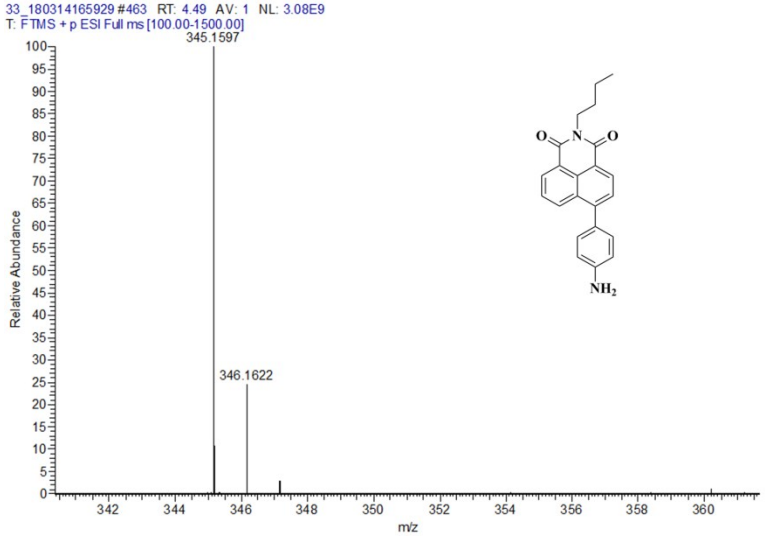

Fig. S15 High resolution mass spectra of **3**.

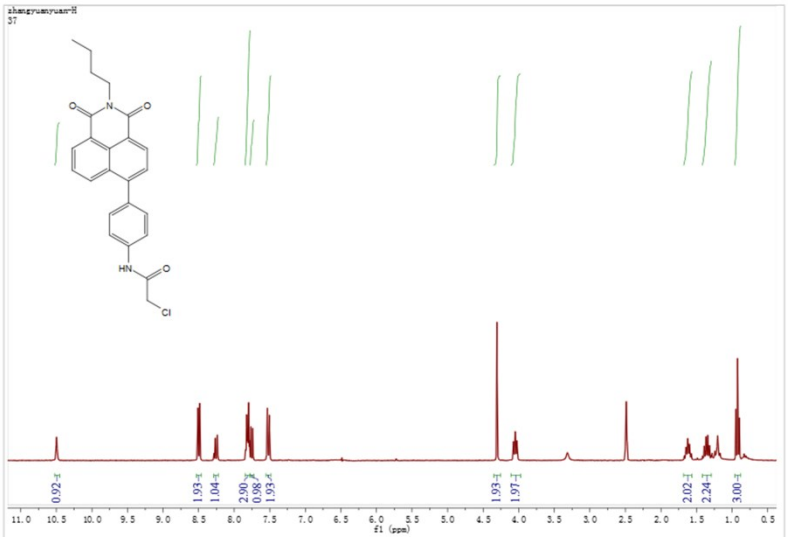

Fig. S16 ^{1}H NMR spectrum of **4** in DMSO-d6.

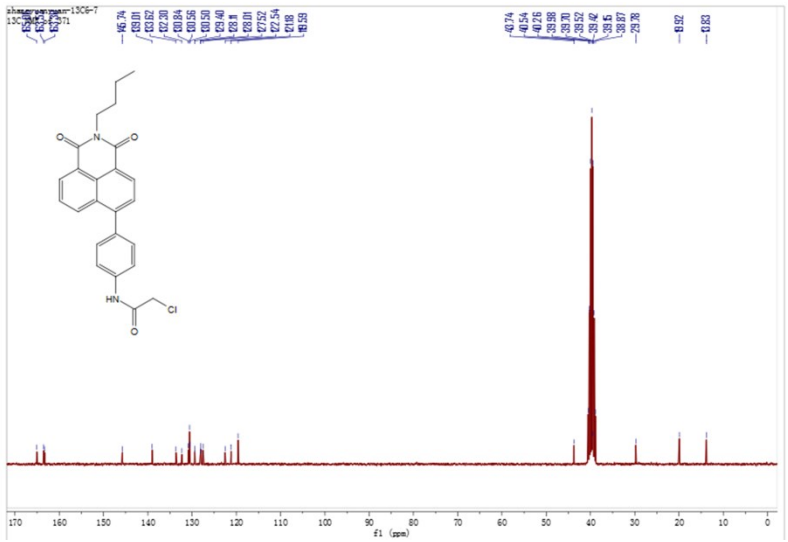

Fig. S17 ^{13}C NMR spectrum of **4** in DMSO-d6.

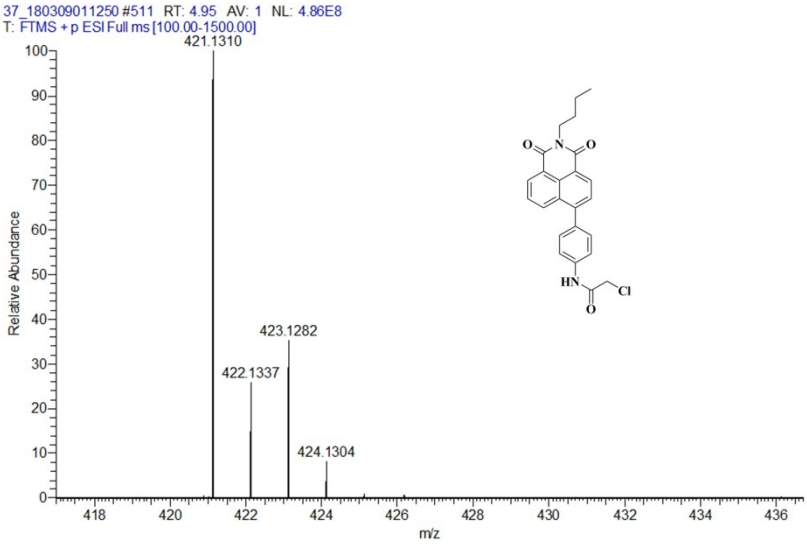

Fig. S18 High resolution mass spectra of **4**.

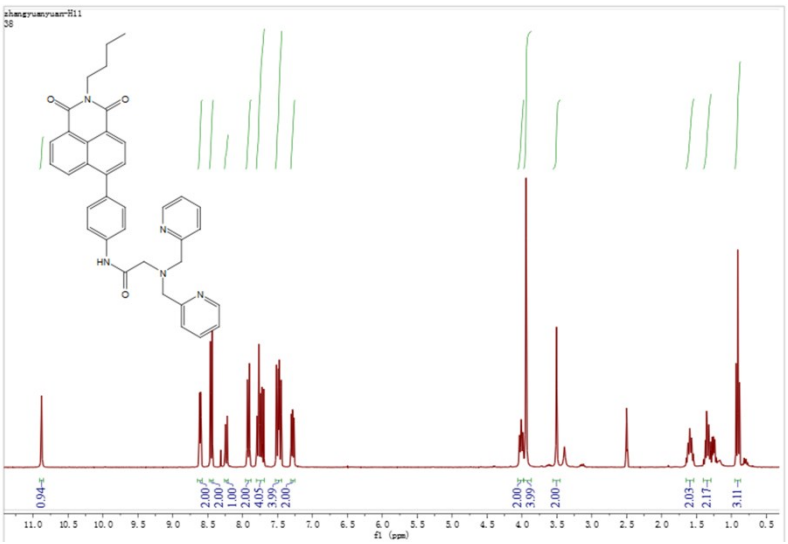

Fig. S19 ^{1}H NMR spectrum of **L2** in DMSO-d6.

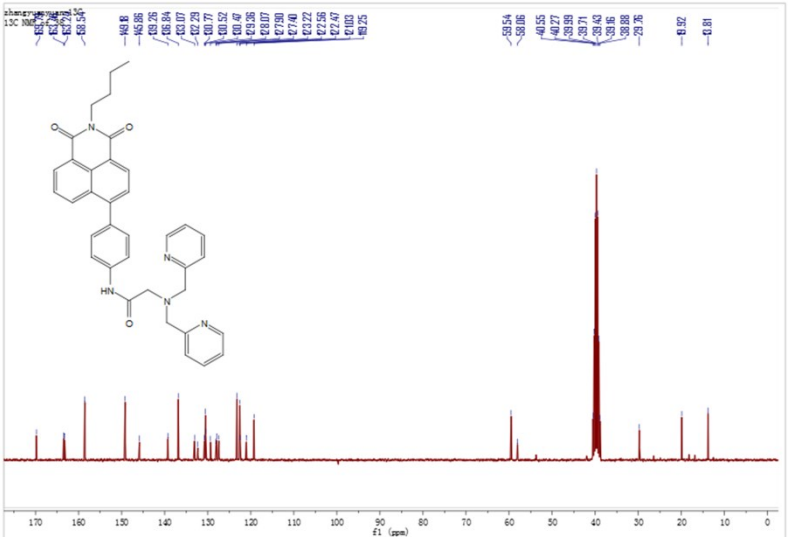

Fig. S20 ^{13}C NMR spectrum of **L2** in DMSO-d6.

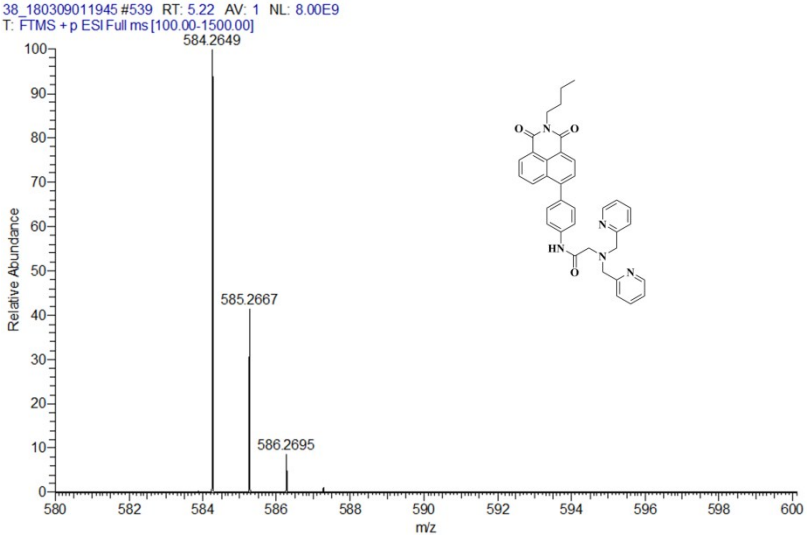

Fig. S21 High resolution mass spectra of **L2**.