Photoactive platinum(II) β-diketonates as dual action anticancer agents†

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ELECTRONIC SUPPLEMENTARY INFORMATION

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UV-visible absorption based DNA binding methods

The calf thymus ct-DNA was first tested for purity. The ratio of absorbance at 260 and 280 nm was approximately 1.9:1 confirming that the DNA was apparently free from protein. The concentration of DNA was determined by from the ratio of its absorption intensity at 260 nm and its known molar absorption coefficient value of 6600 dm^3 mol^{-1} cm^{-1}. Absorption titration experiments were performed in Tris-HCl buffer (5 mM, pH 7.2) by varying the concentration of the ct-DNA while keeping the complex concentration as constant (**1-4**, 50μM in 5% DMSO Tris buffer). The spectra were recorded with increasing concentration of ct-DNA and after equilibration for 5 min with due correction made for the absorbance of only DNA. The regression analysis equation used is (1)

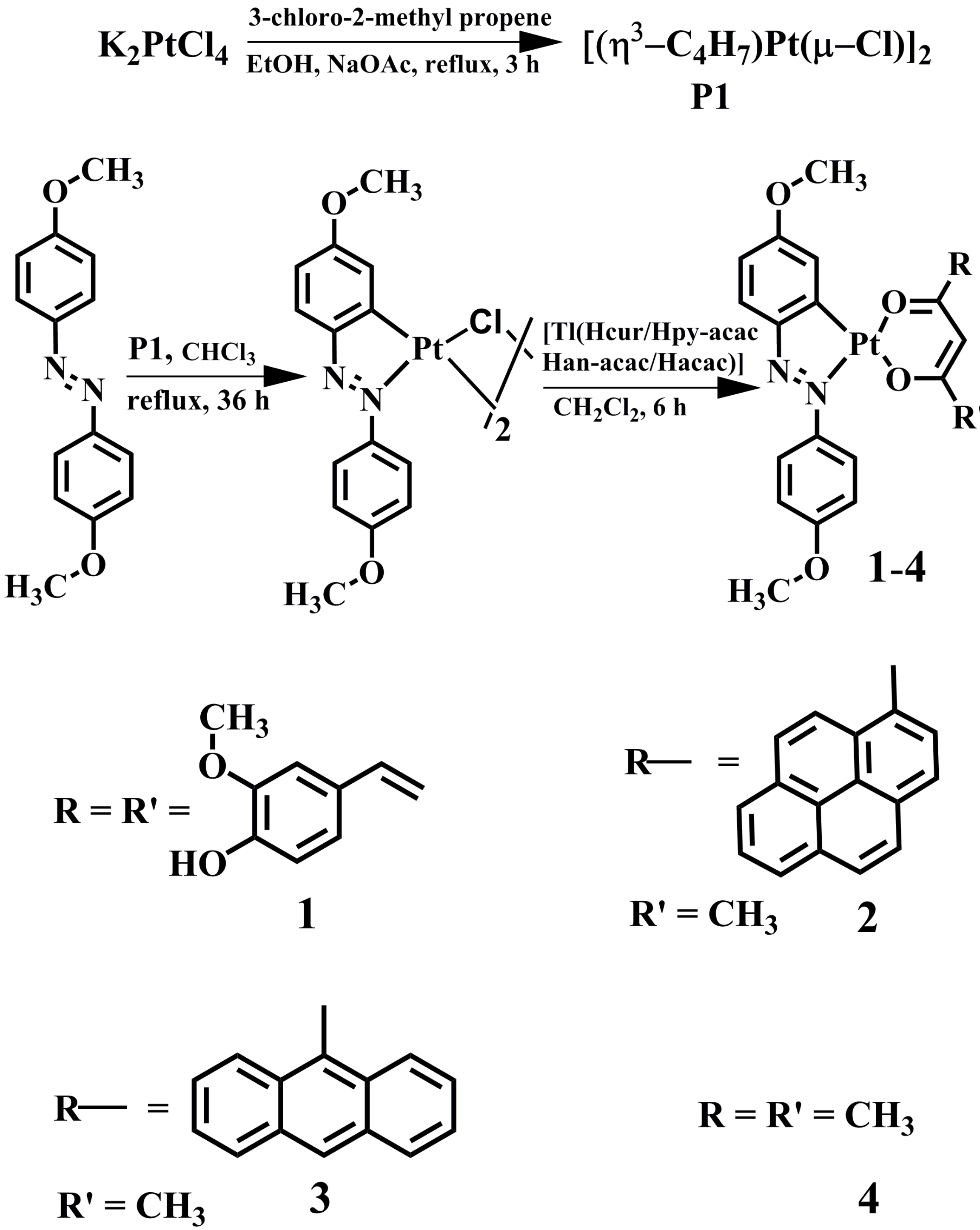
$$(\varepsilon_a - \varepsilon_f)/(\varepsilon_b - \varepsilon_f) = (b - (b^2 - 2K_b^2C_t[DNA]_t/s)^{1/2})/2K_bC_t, \text{ ---(1)}$$

$$b = 1 + K_bC_t + K_b[DNA]_t/2s,$$

where C_t is the total metal complex concentration, ε_a is the extinction coefficient observed for the charge transfer absorption band at a given DNA concentration, ε_f is the extinction coefficient of the DNA unbound complex, ε_b is the extinction coefficient of the complex when fully bound to DNA, $[DNA]_t$ is the DNA concentration, K_b is the equilibrium binding constant, and s is the MvH fitting parameter in base pairs. The graphs were plotted and non-linear least-squares analysis was done using Origin Lab, version 6.1.

Reference for DFT studies

S1. 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, 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, Ö.Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, GAUSSIAN 09 (RevisionA.1), Gaussian, Inc., Wallingford, CT, 2009.



Scheme S1. Synthesis of the complexes **1-4**.

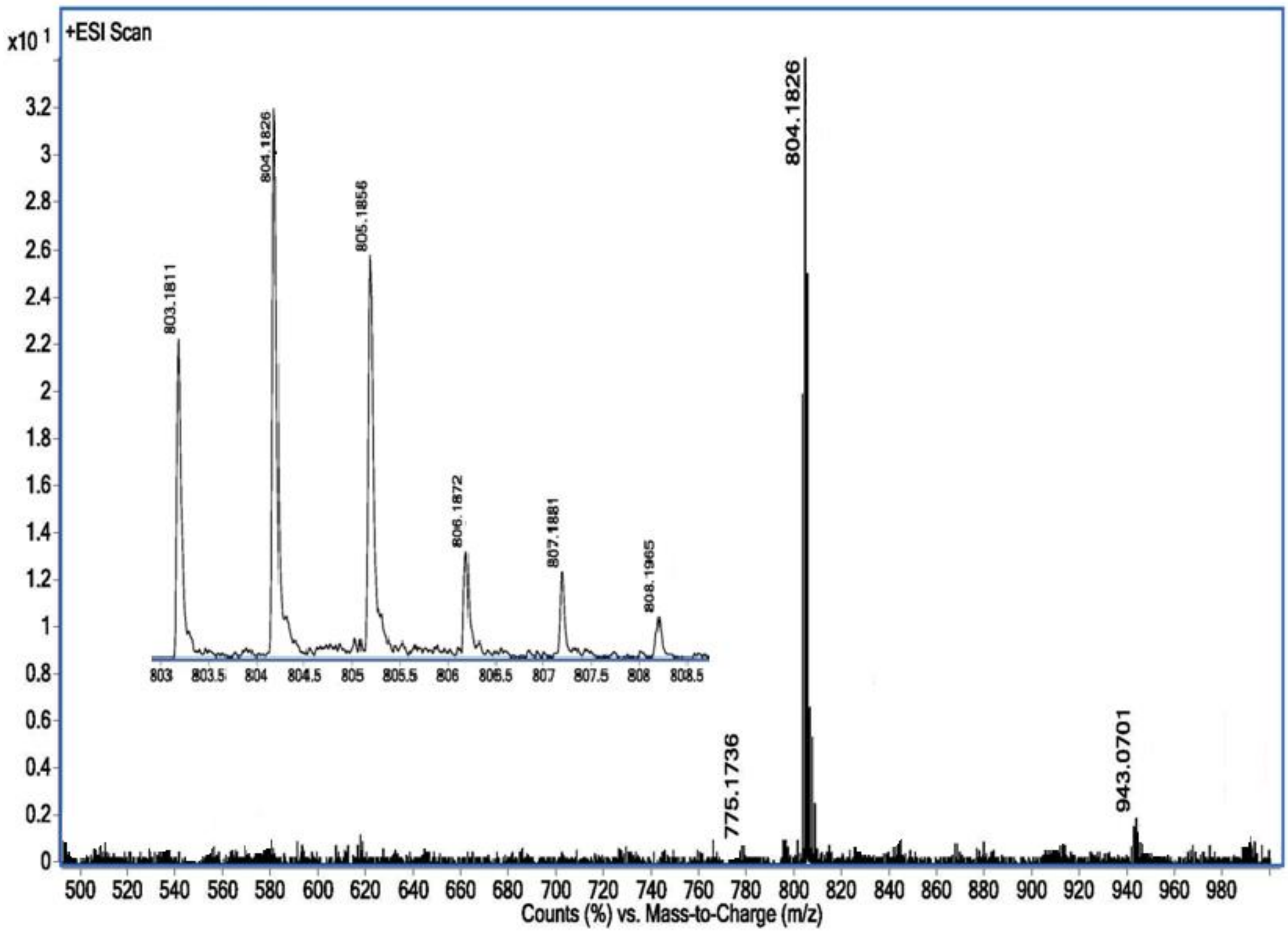


Figure S1. Mass spectrum of complex **1** [Pt(L)(cur)] in MeOH showing prominent parent ion peak at 804.18 (m/z) which corresponds to $[M+H]^+$. Inset shows the isotopic distribution pattern for platinum of the molecular ion peak.

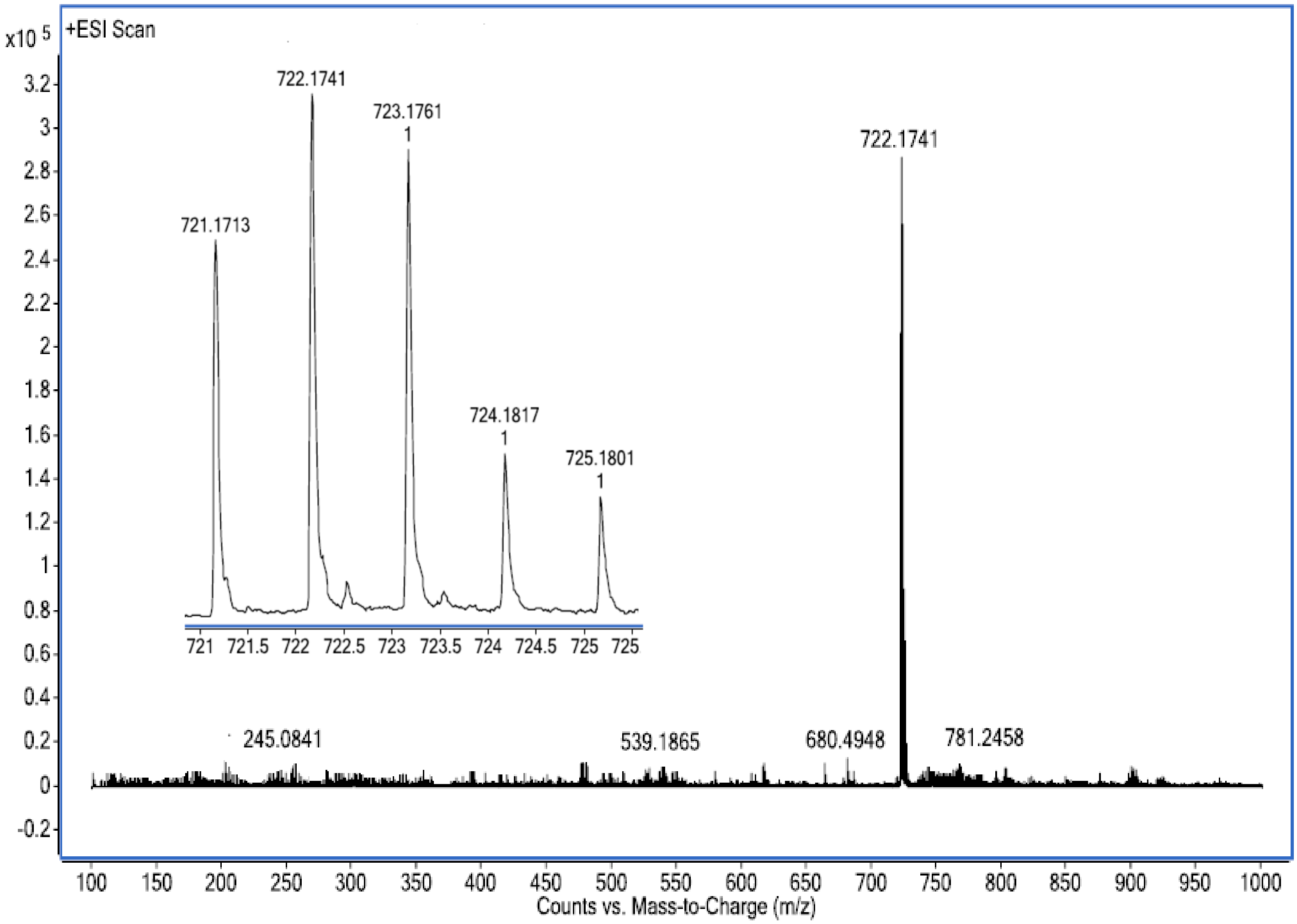


Figure S2. Mass spectrum of complex **2** [Pt(L)(py-acac)] in MeOH showing prominent parent ion peak at 722.17 (m/z) which corresponds to $[M+H]^+$. Inset shows the isotopic distribution pattern for platinum of the molecular ion peak.

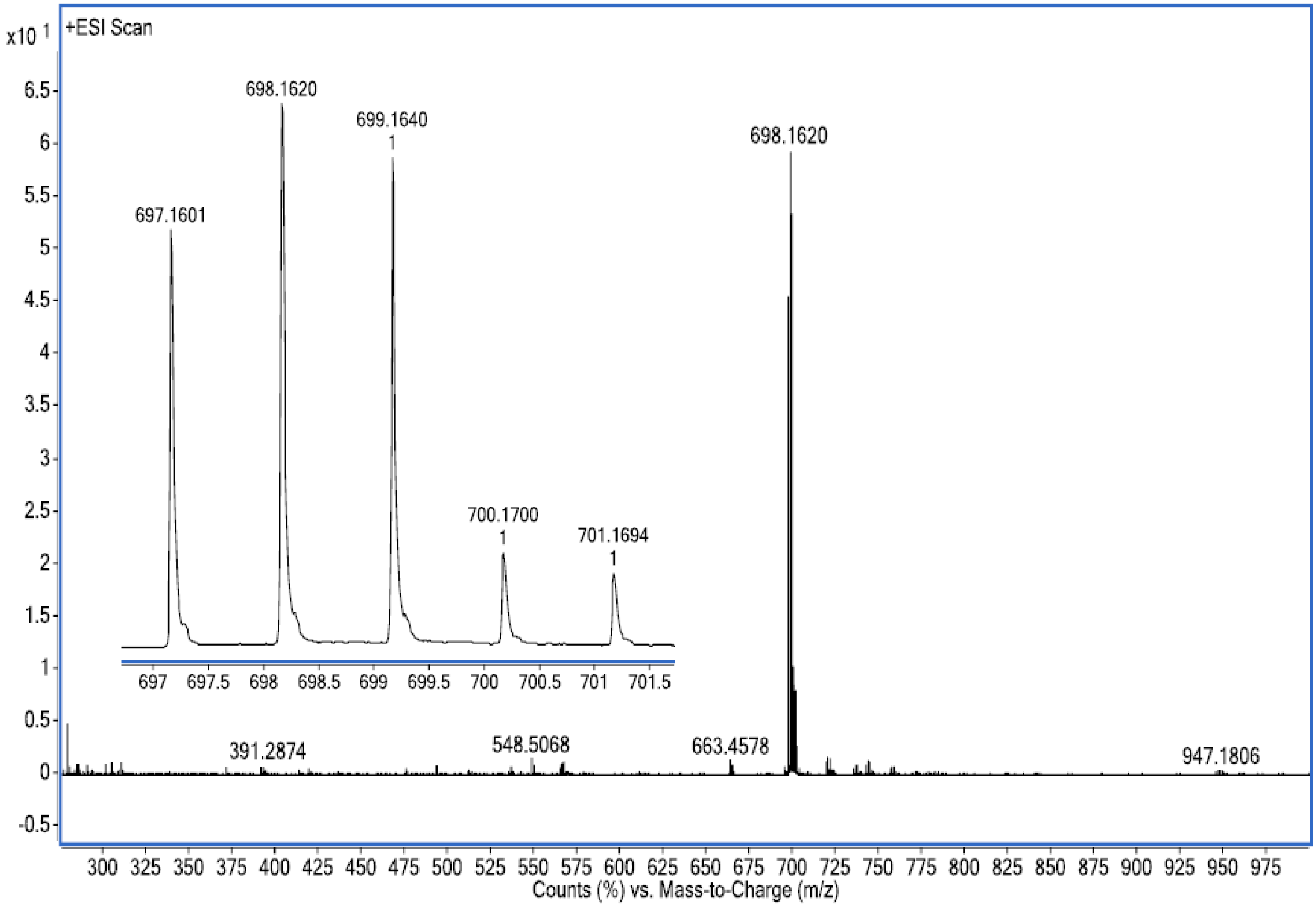


Figure S3. Mass spectrum of complex **3** [Pt(L)(an-acac)] in MeOH showing prominent parent ion peak at 698.16 (m/z) which corresponds to $[M+H]^+$. Inset shows the isotopic distribution pattern for platinum of the molecular ion peak.

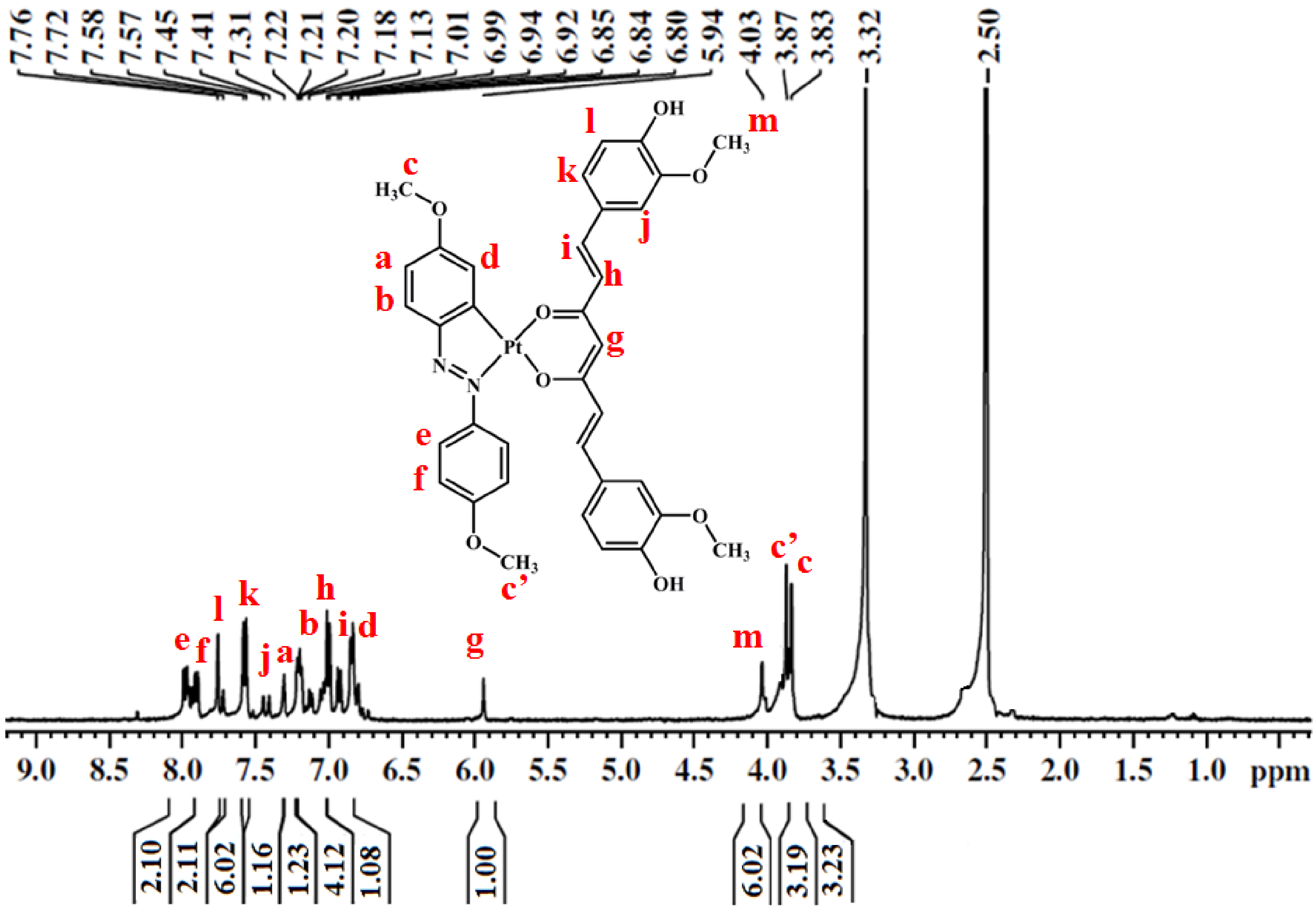


Figure S4.^{1}H NMR spectrum of complex **1** [Pt(L)(cur)] in DMSO-d_6.

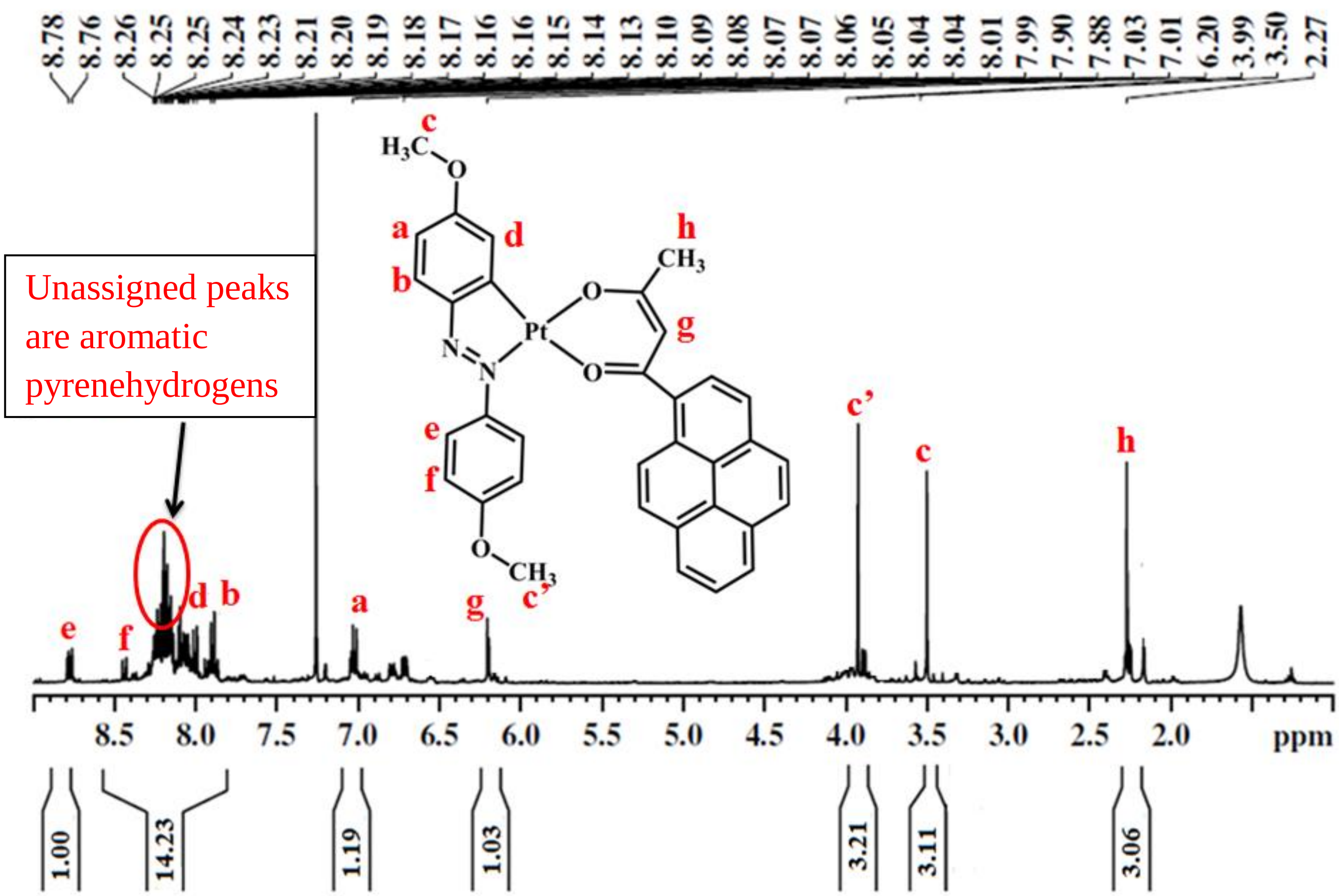


Figure S5.^{1}H NMR spectrum of complex **2** [Pt(L)(py-acac)] in $CDCl_3$.

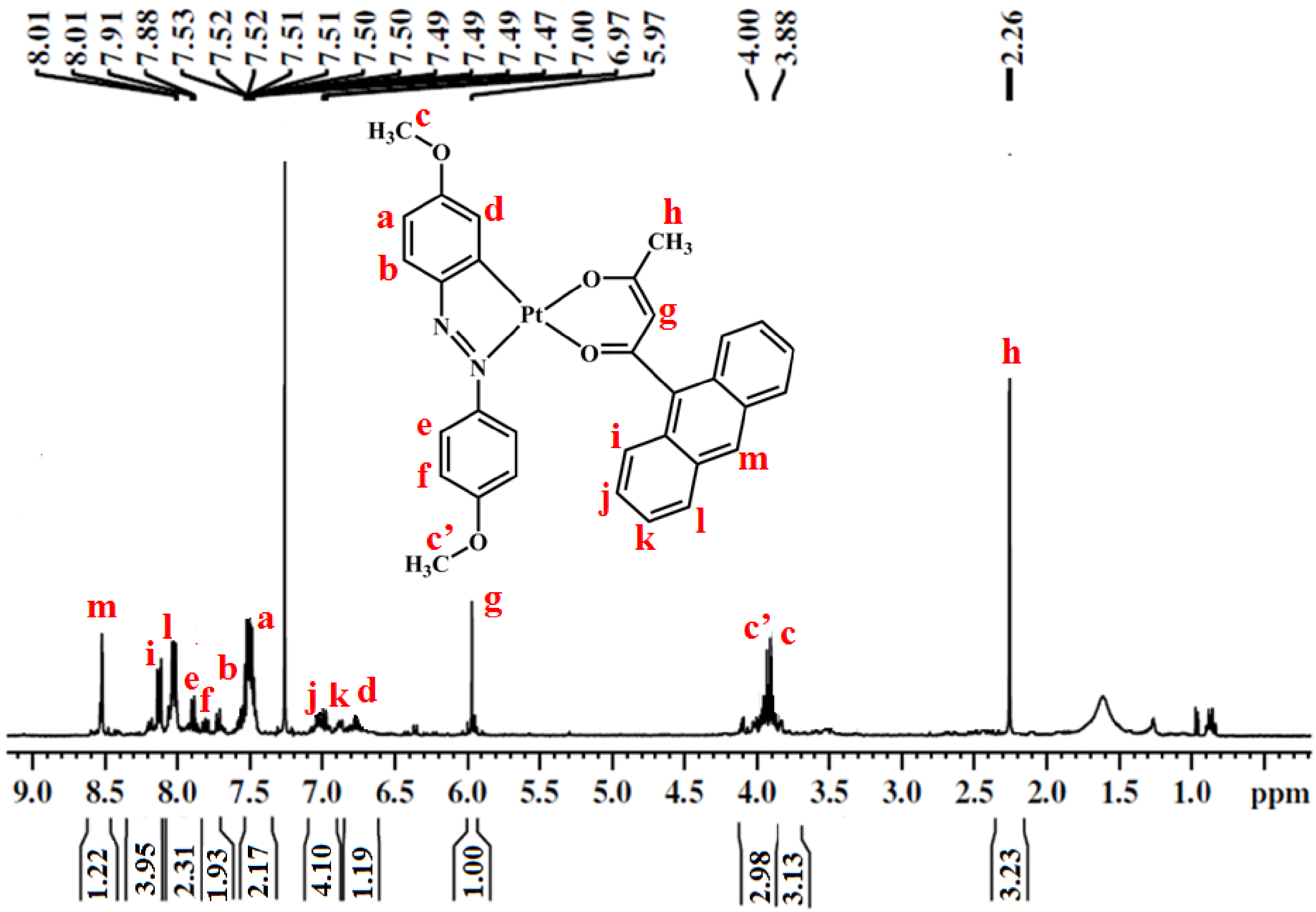


Figure S6: ^{1}H NMR spectrum of complex **3** [Pt(L)(an-acac)] in $CDCl_3$.

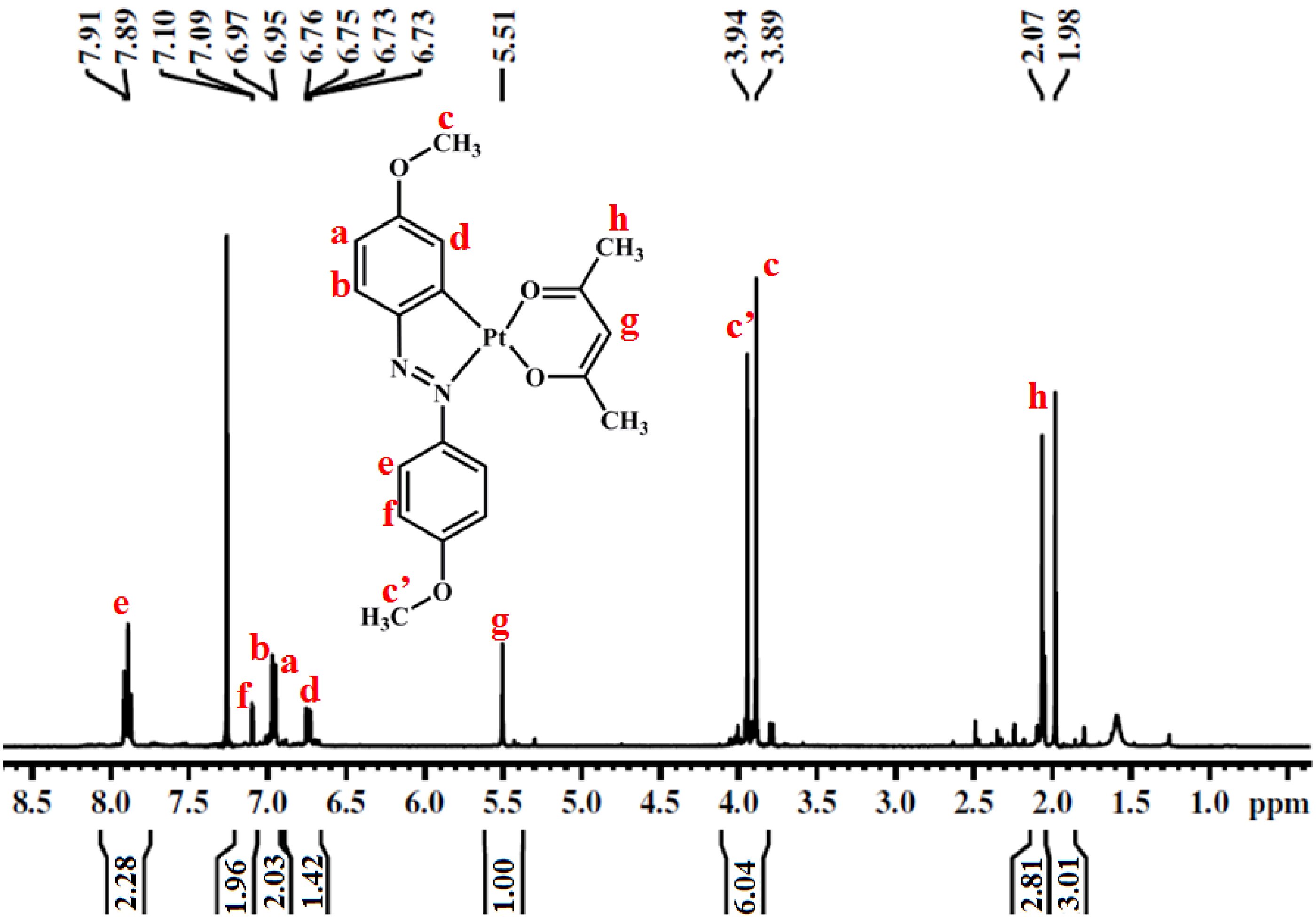


Figure S7: ^{1}H NMR spectrum of complex **4** [Pt(L)(acac)] in $CDCl_3$.

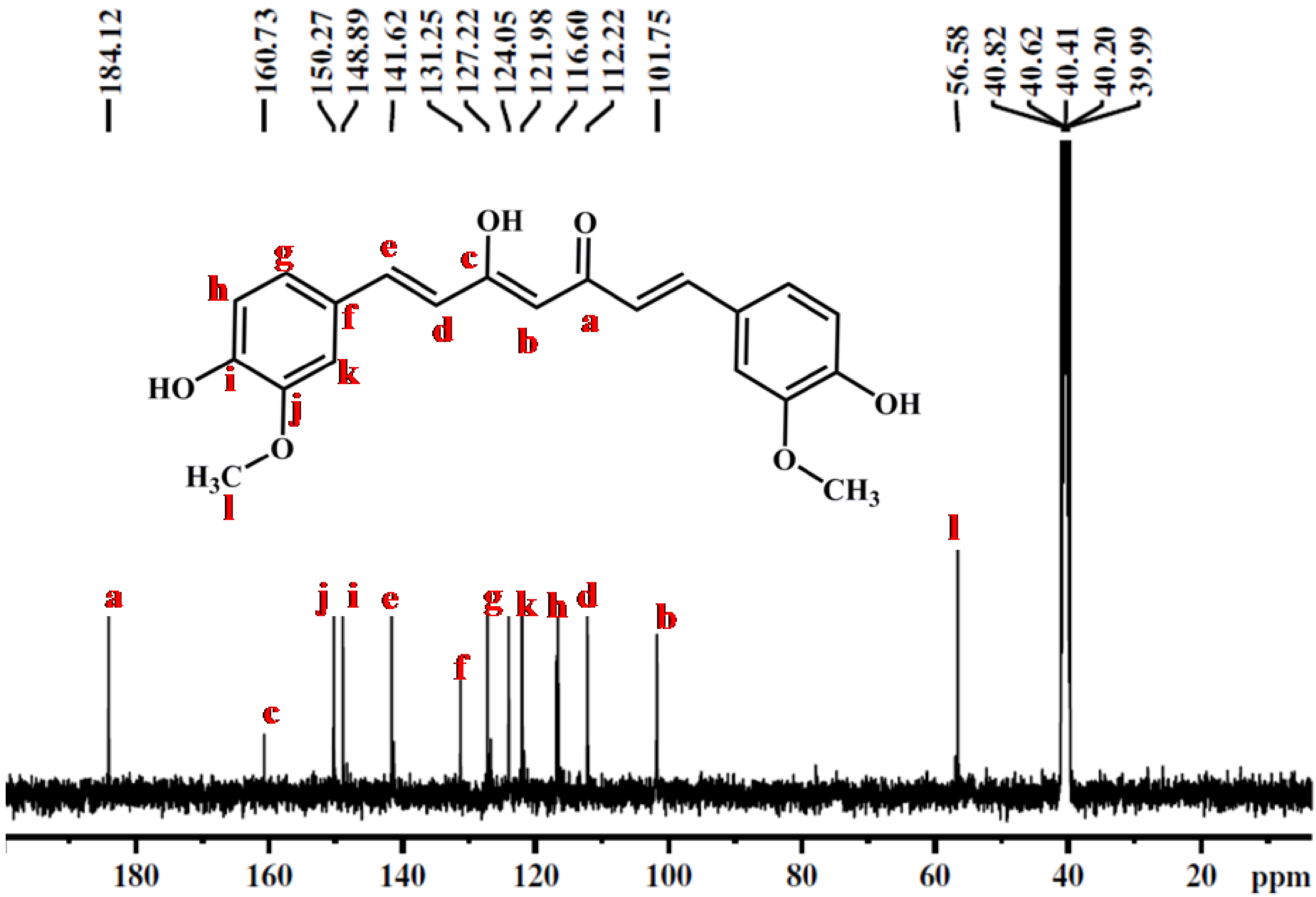


Figure S8: ^{13}C NMR spectrum of ligand Hcur in DMSO-d_6.

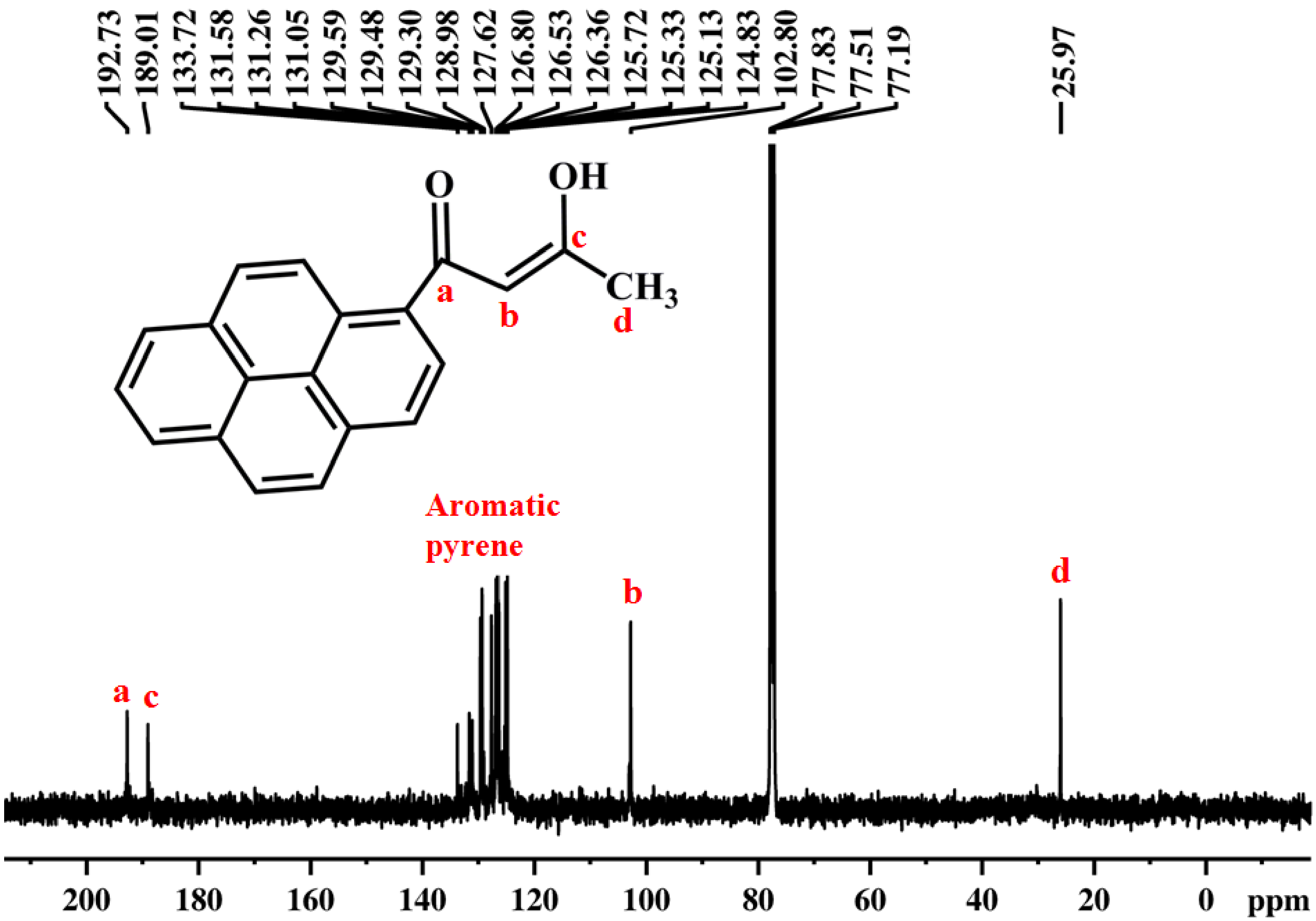


Figure S9: ^{13}C NMR spectrum of ligand [Hpy-acac] in $CDCl_3$.

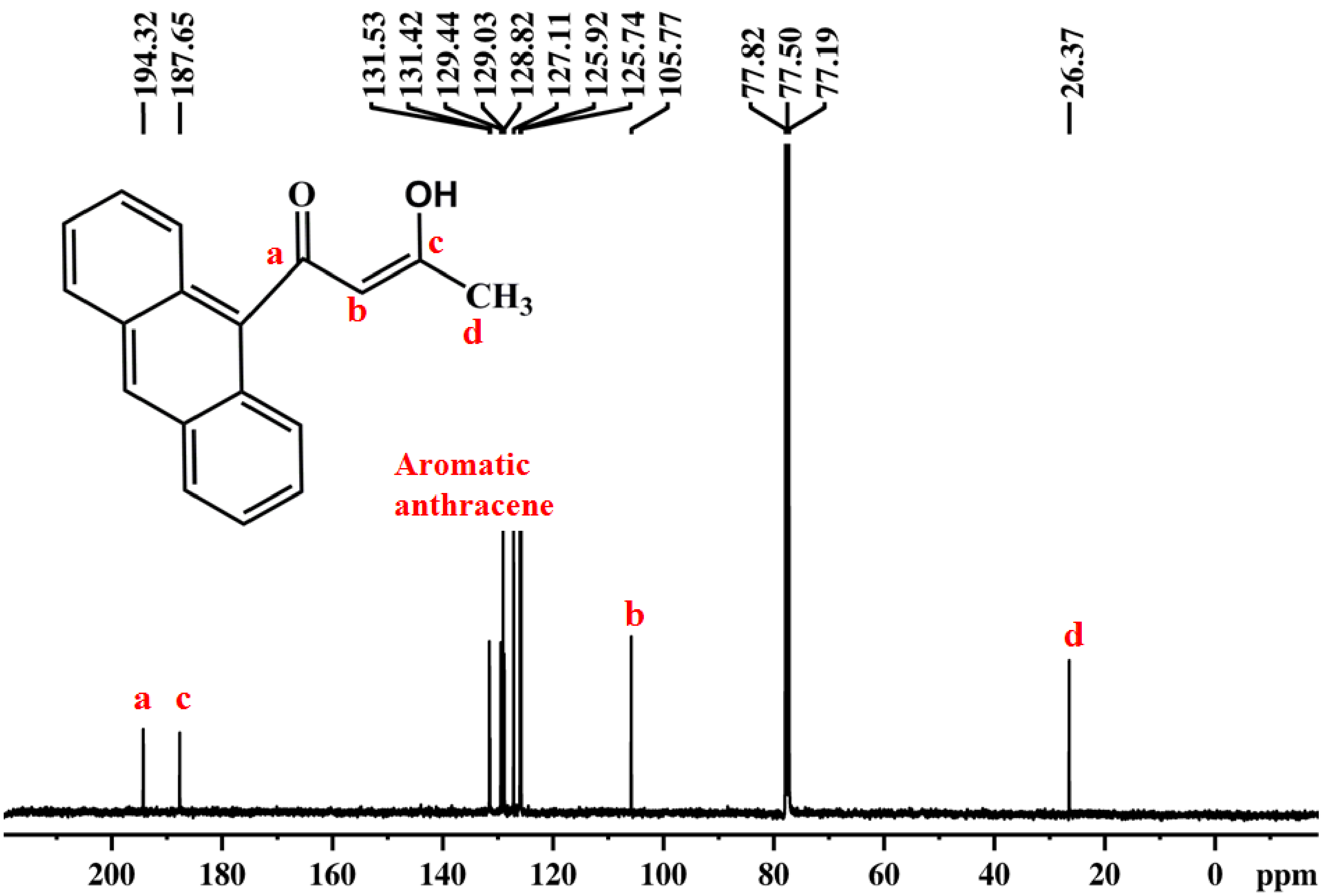


Figure S10: ^{13}C NMR spectrum of ligand [Han-acac] in $CDCl_3$.

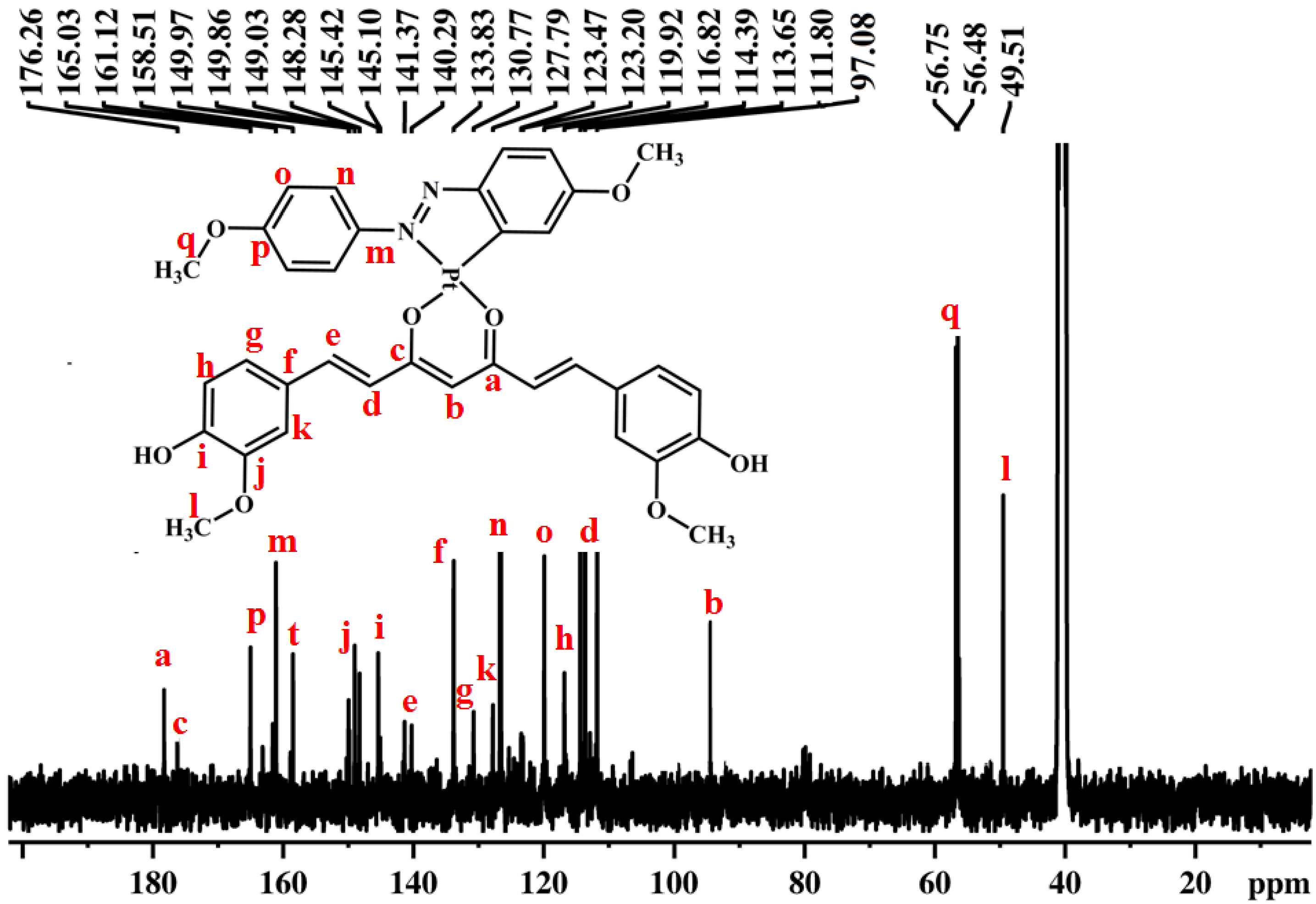


Figure S11: ^{13}C NMR spectrum of complex **1** [Pt(L)(cur)] in DMSO-d_6.

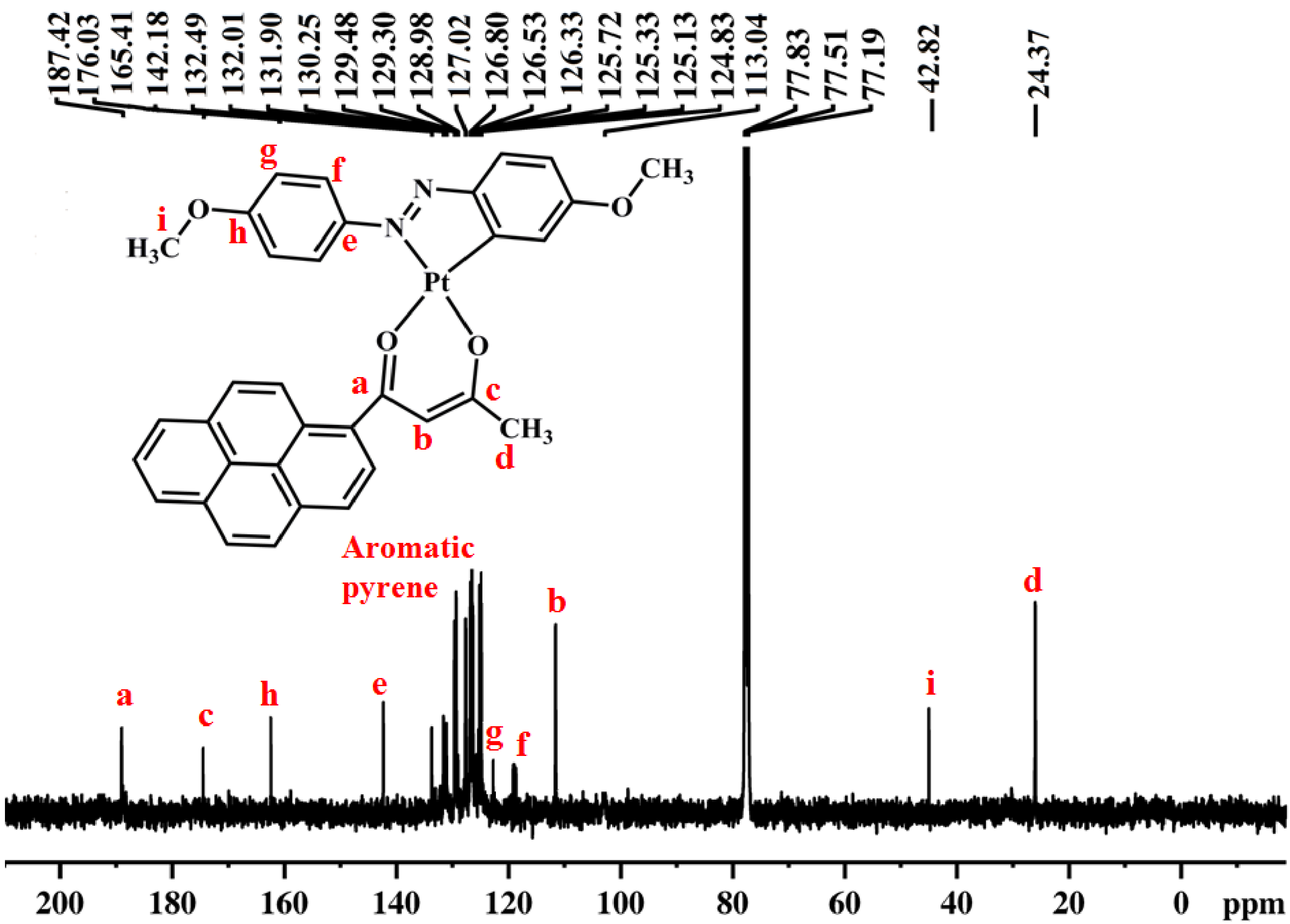


Figure S12: ^{13}C NMR spectrum of complex **2** [Pt(L)(py-acac)] in $CDCl_3$.

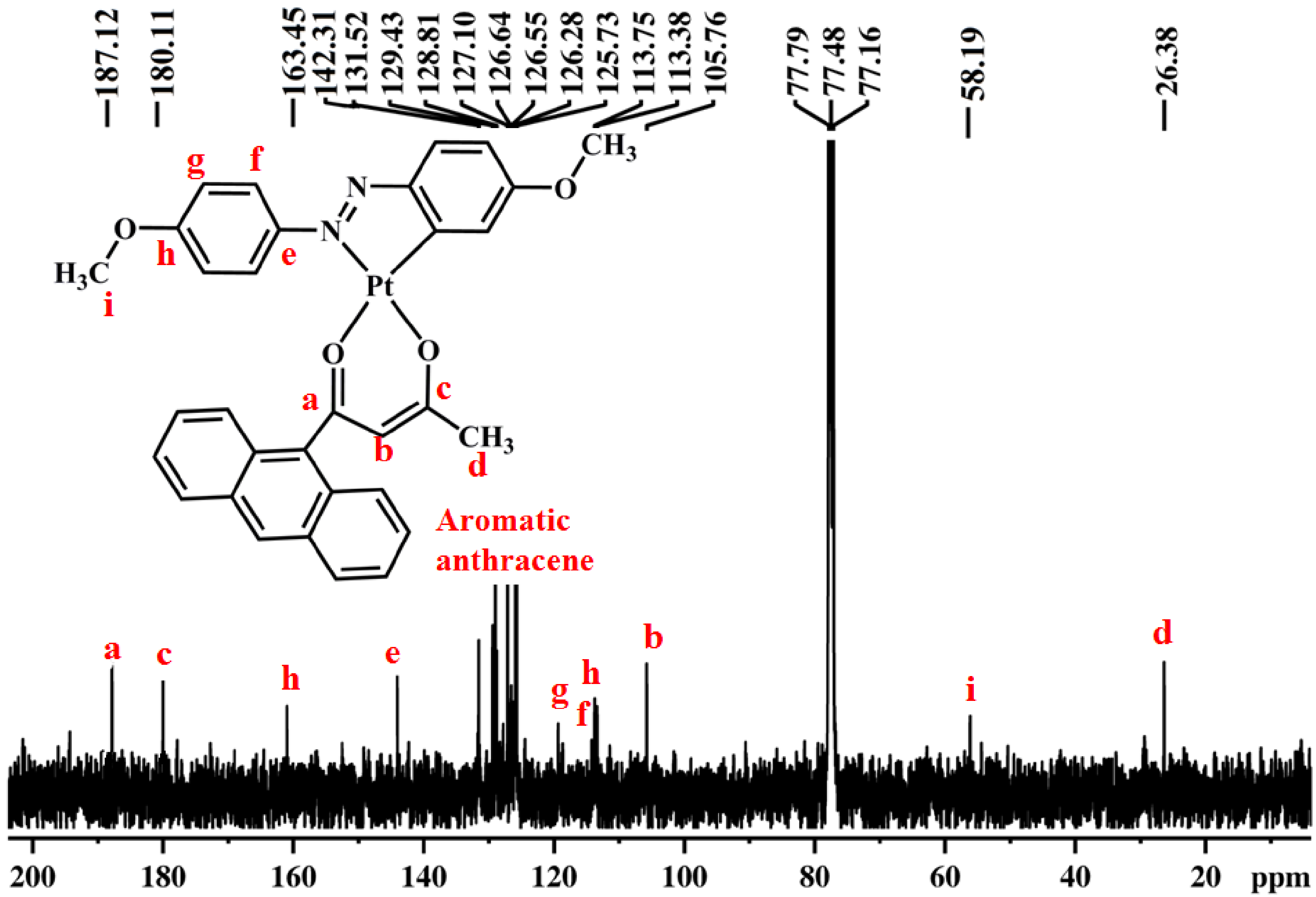


Figure S13: ^{13}C NMR spectrum of complex **3** [Pt(L)(an-acac)] in $CDCl_3$.

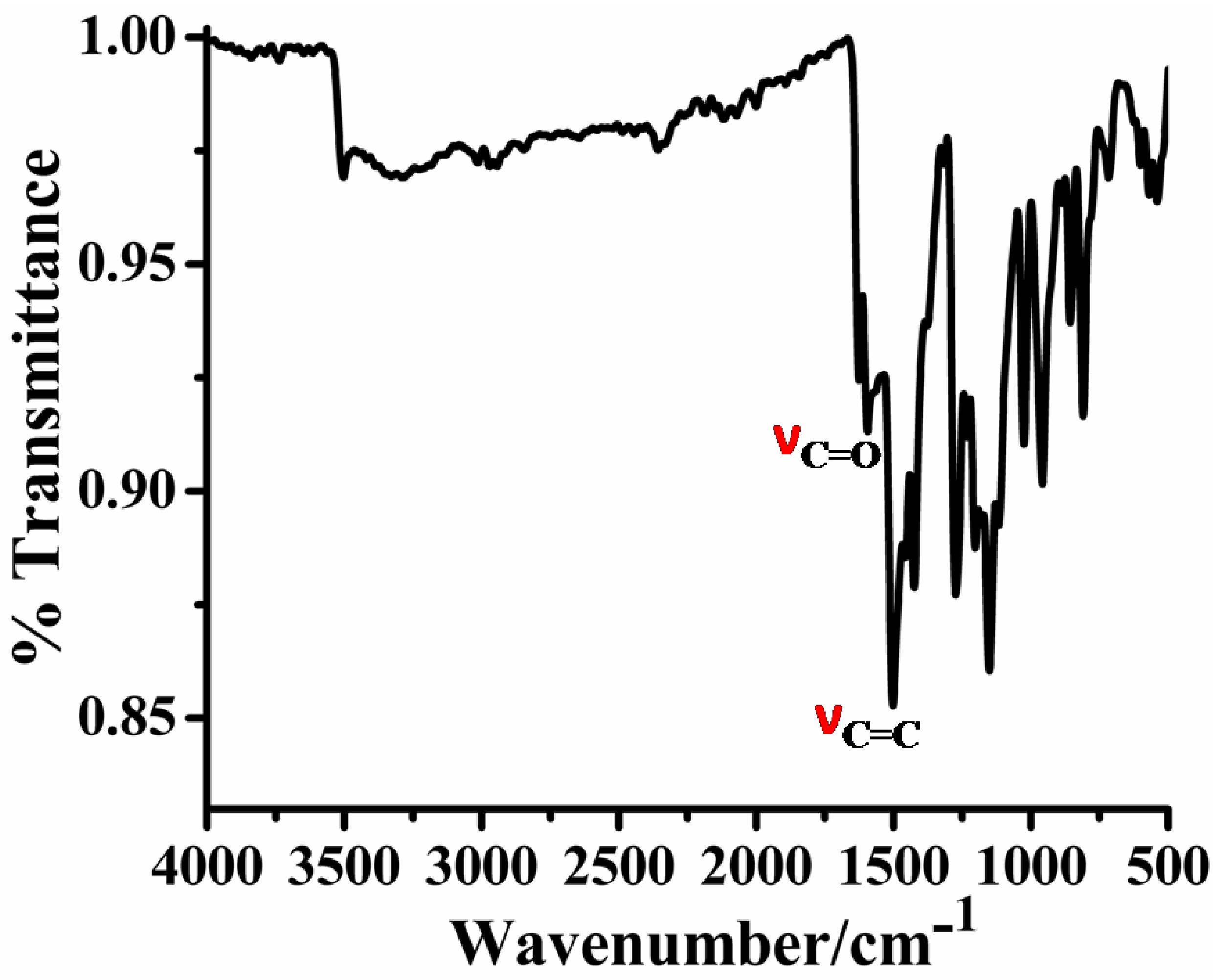


Figure S14: The IR spectrum of ligand Hcur in solid phase.

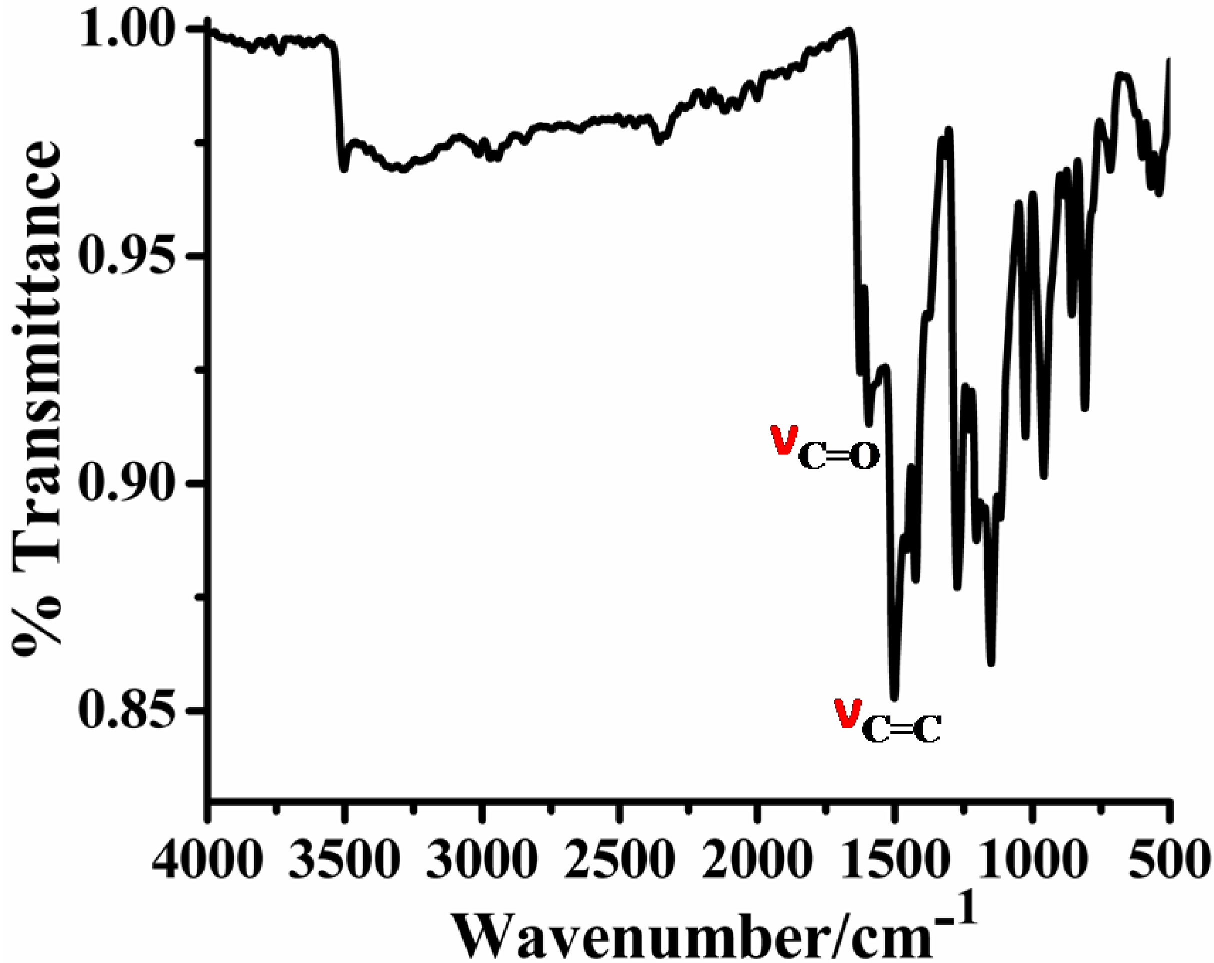


Figure S15: The IR spectrum of ligand Hpy-acac in solid phase.

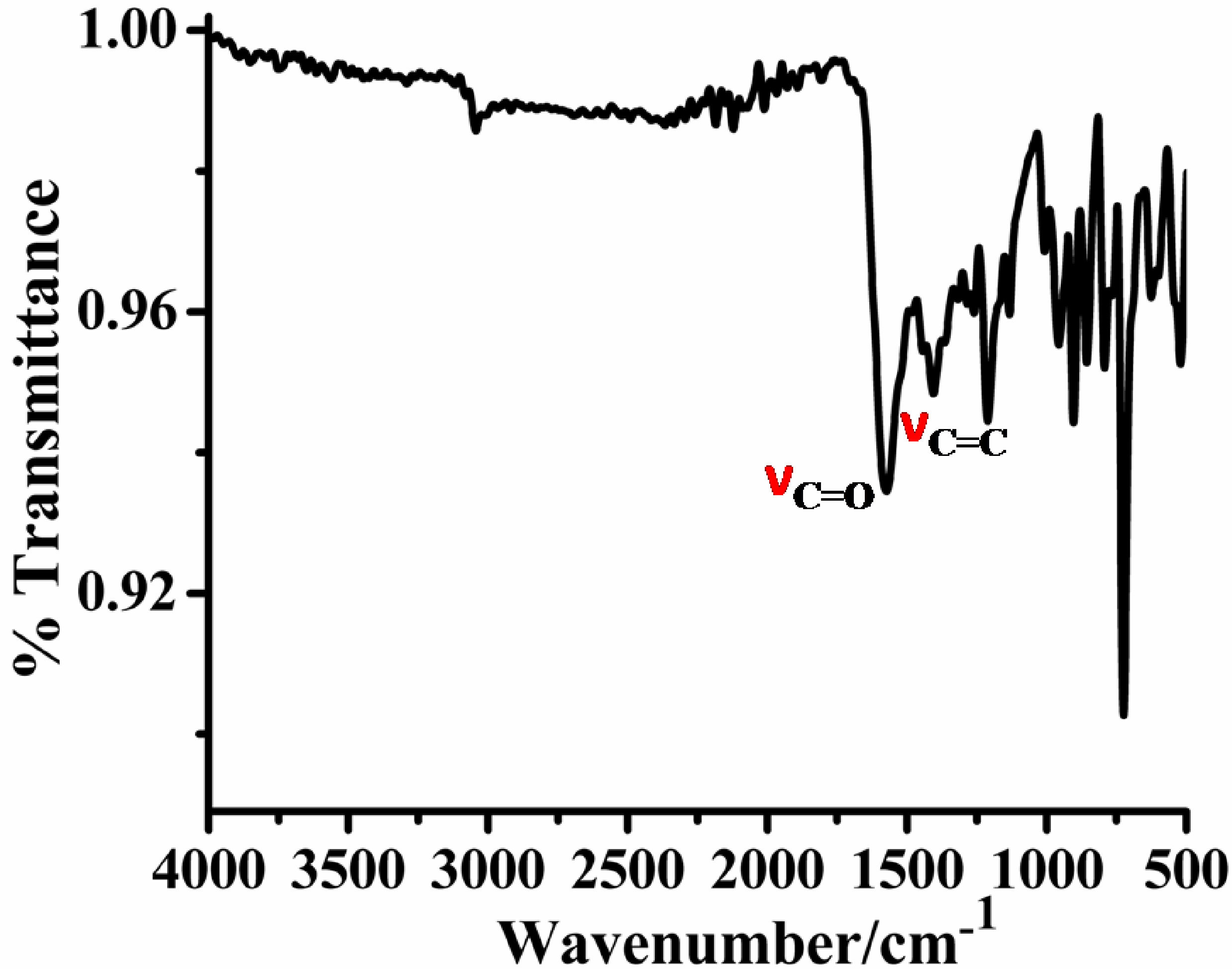


Figure S16: The IR spectrum of ligand Hn-acac in solid phase.

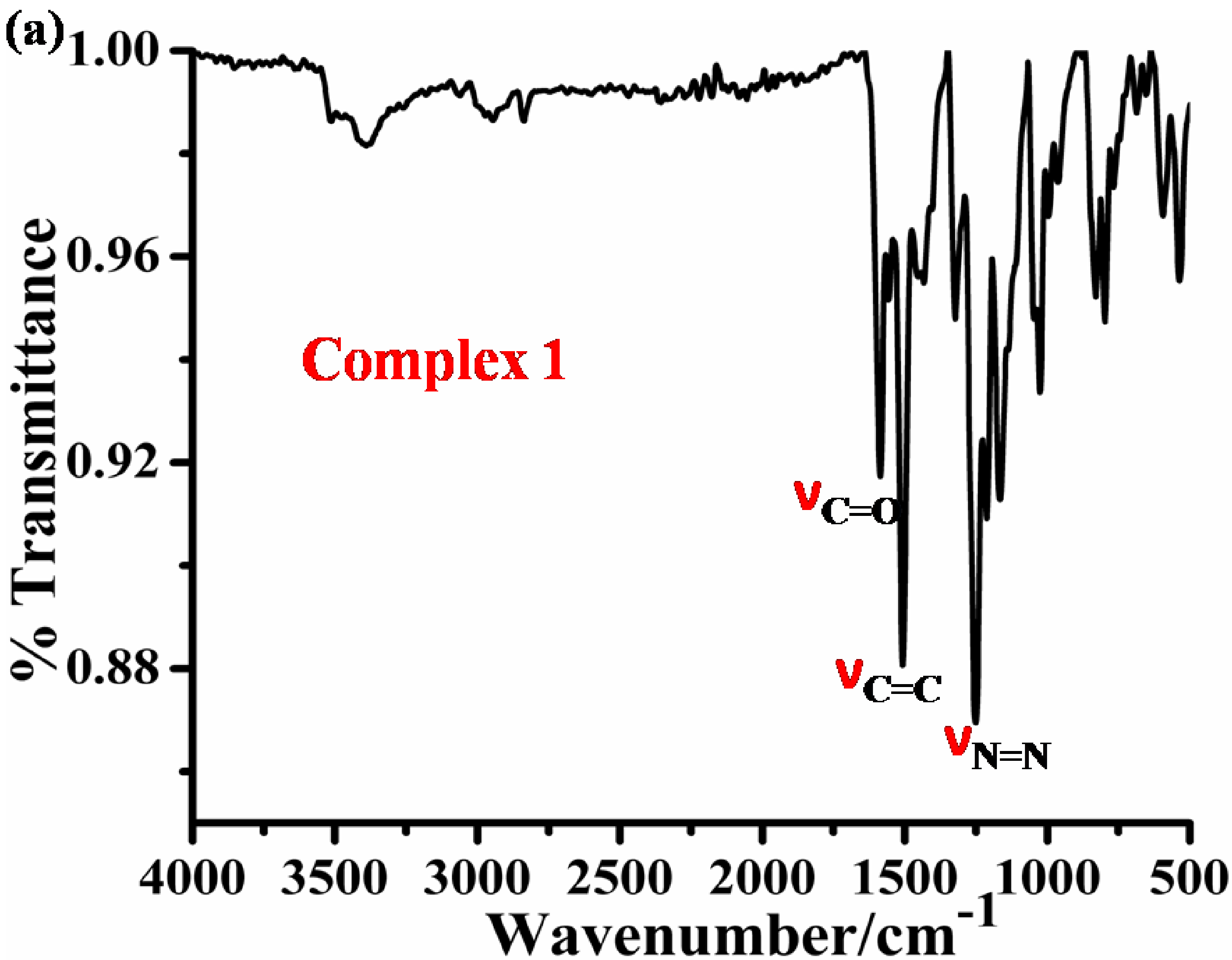


Figure S17: The IR spectrum of complex **1** [Pt(L)(cur)] in solid phase.

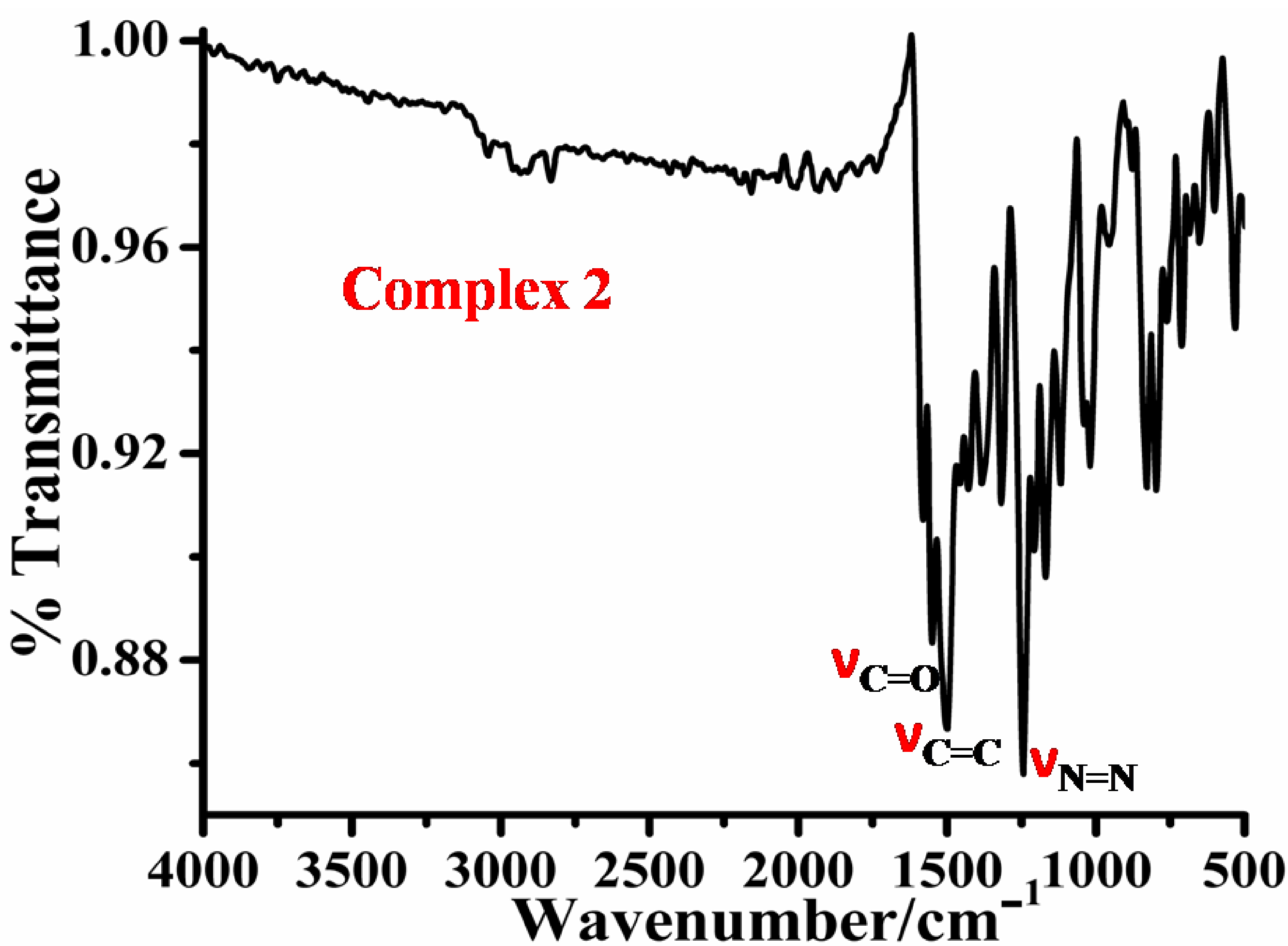


Figure S18: The IR spectrum of complex **2** [Pt(L)(py-acac)] in solid phase.

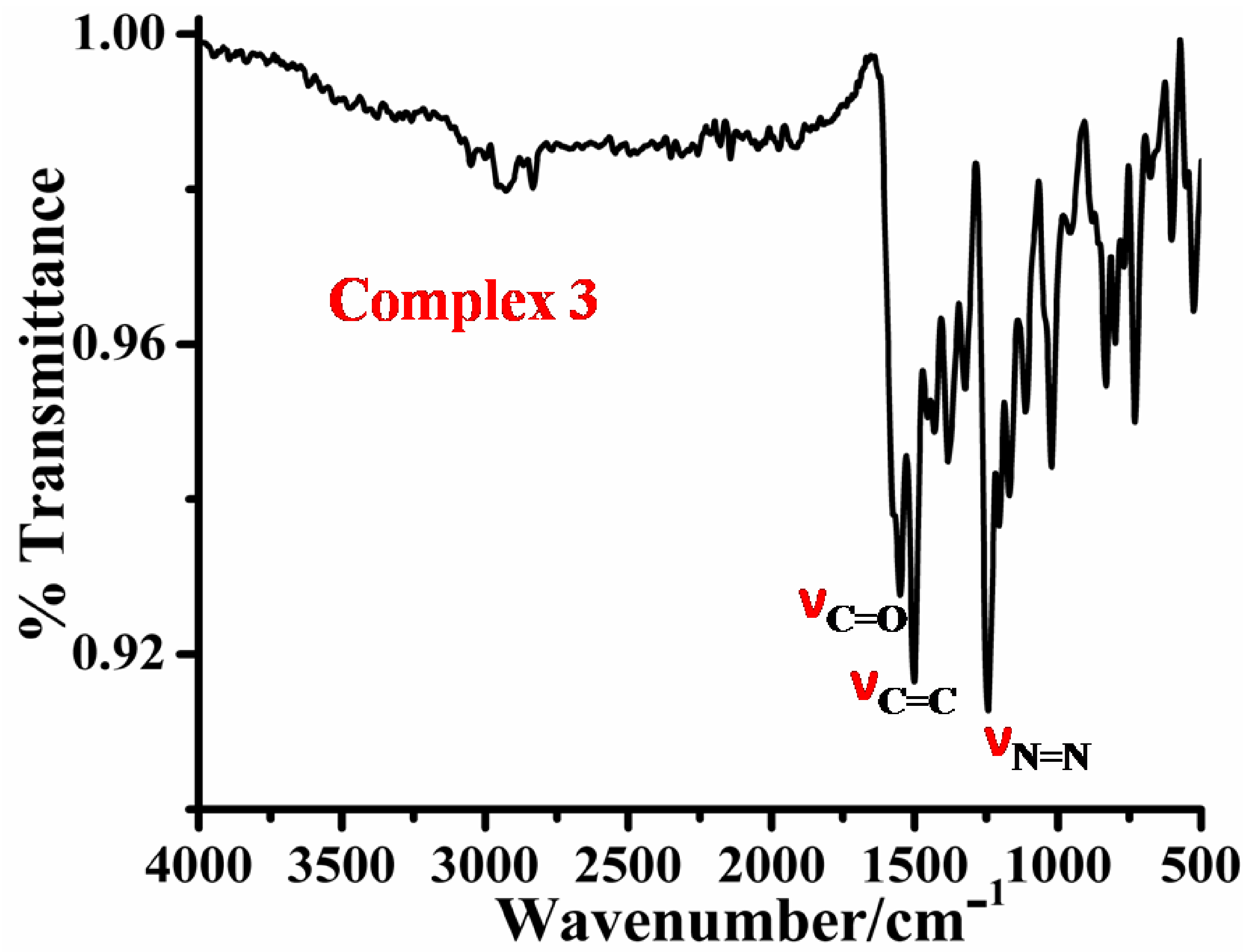


Figure S19: The IR spectrum of complex **3** [Pt(L)(an-acac)] in solid phase.

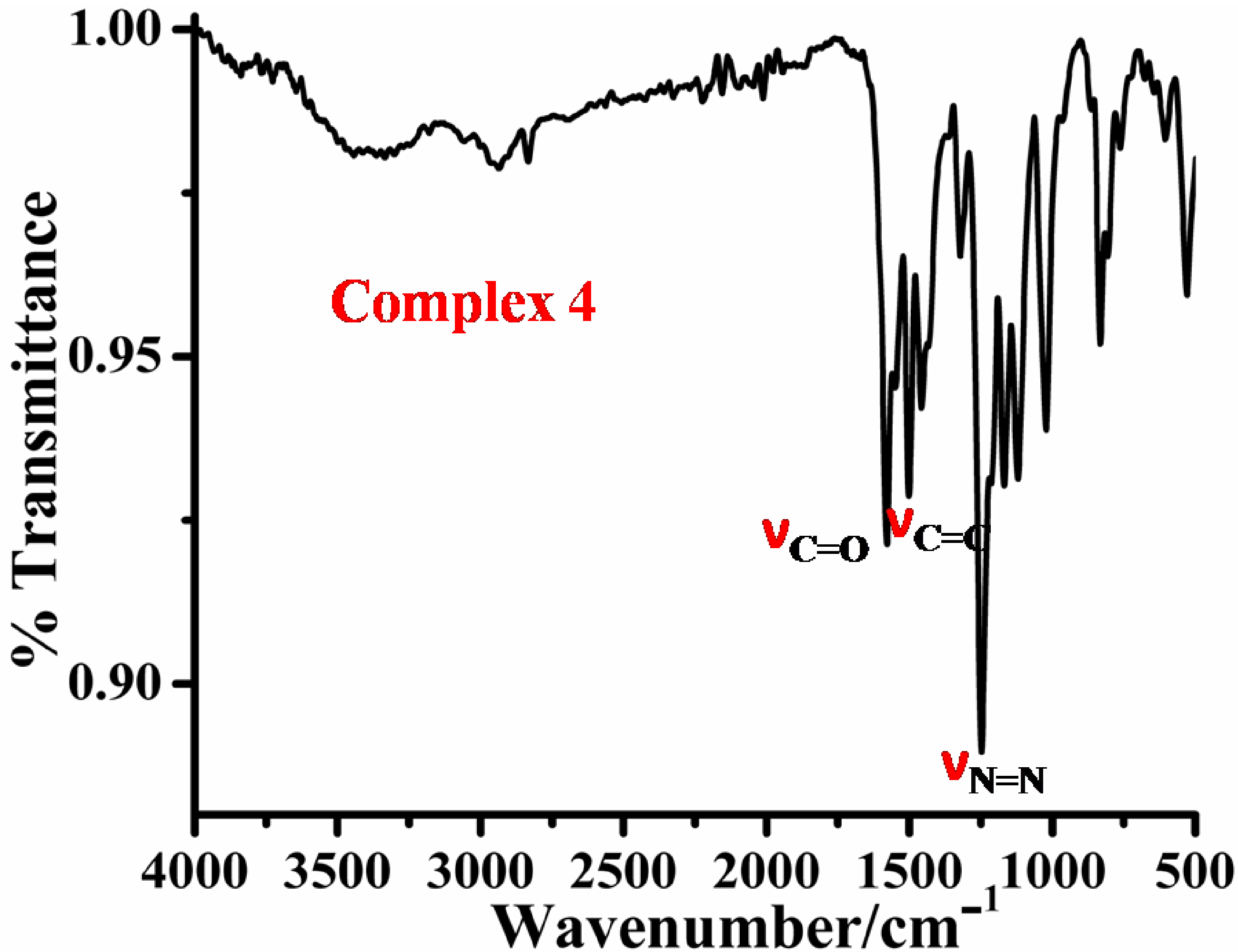


Figure S20: The IR spectrum of complex **4** [Pt(L)(acac)] in solid phase.

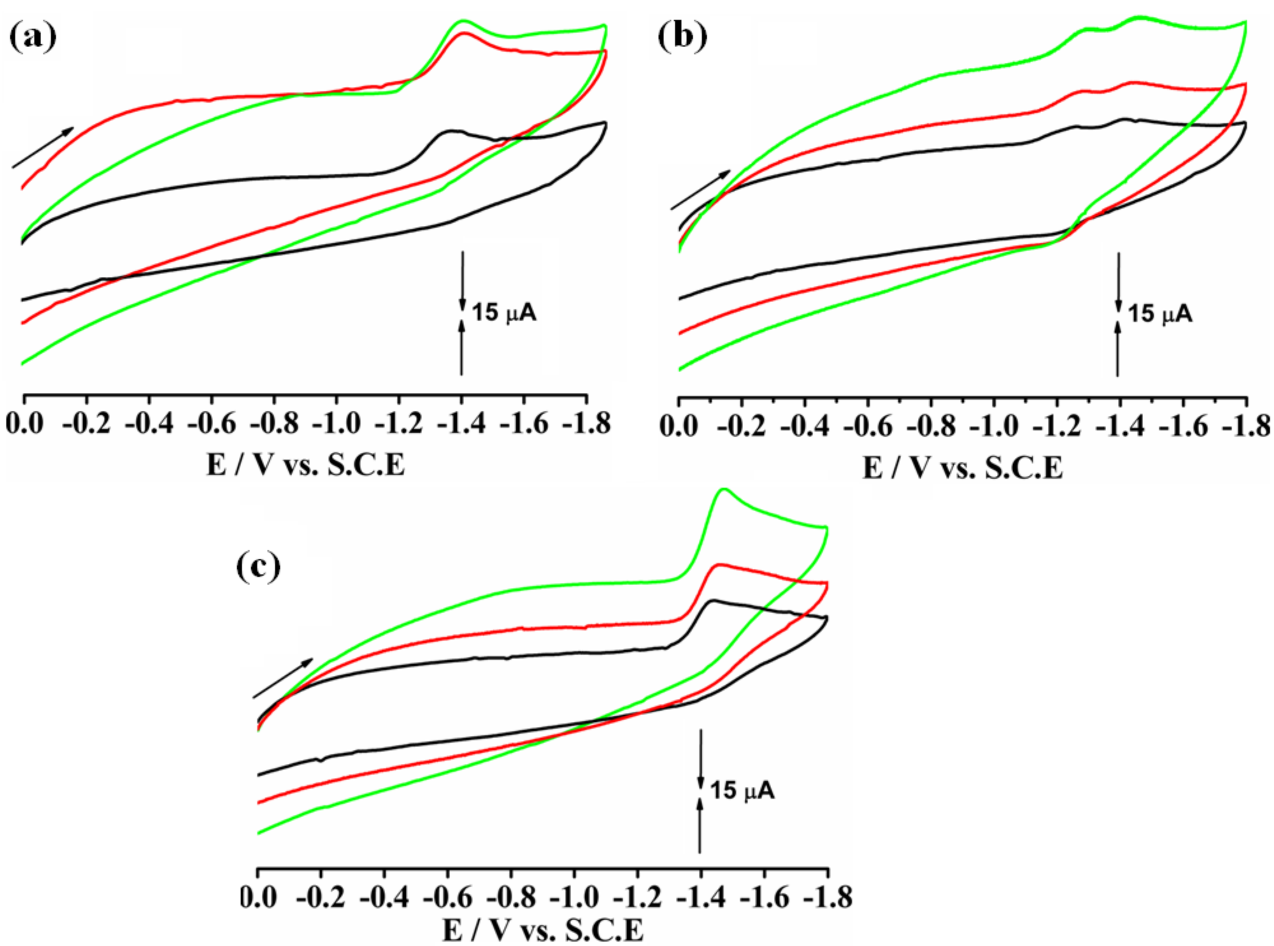


Figure S21. Cyclic voltammograms of 2mM of ligands Hcur (a), Hpy-acac (b) and Han-acac (c) in DMF-0.1M TBAP at various scan rates of 50 mV sec^{-1}(black), 100 mV sec^{-1} (red) and 200 mV sec^{-1} (green).

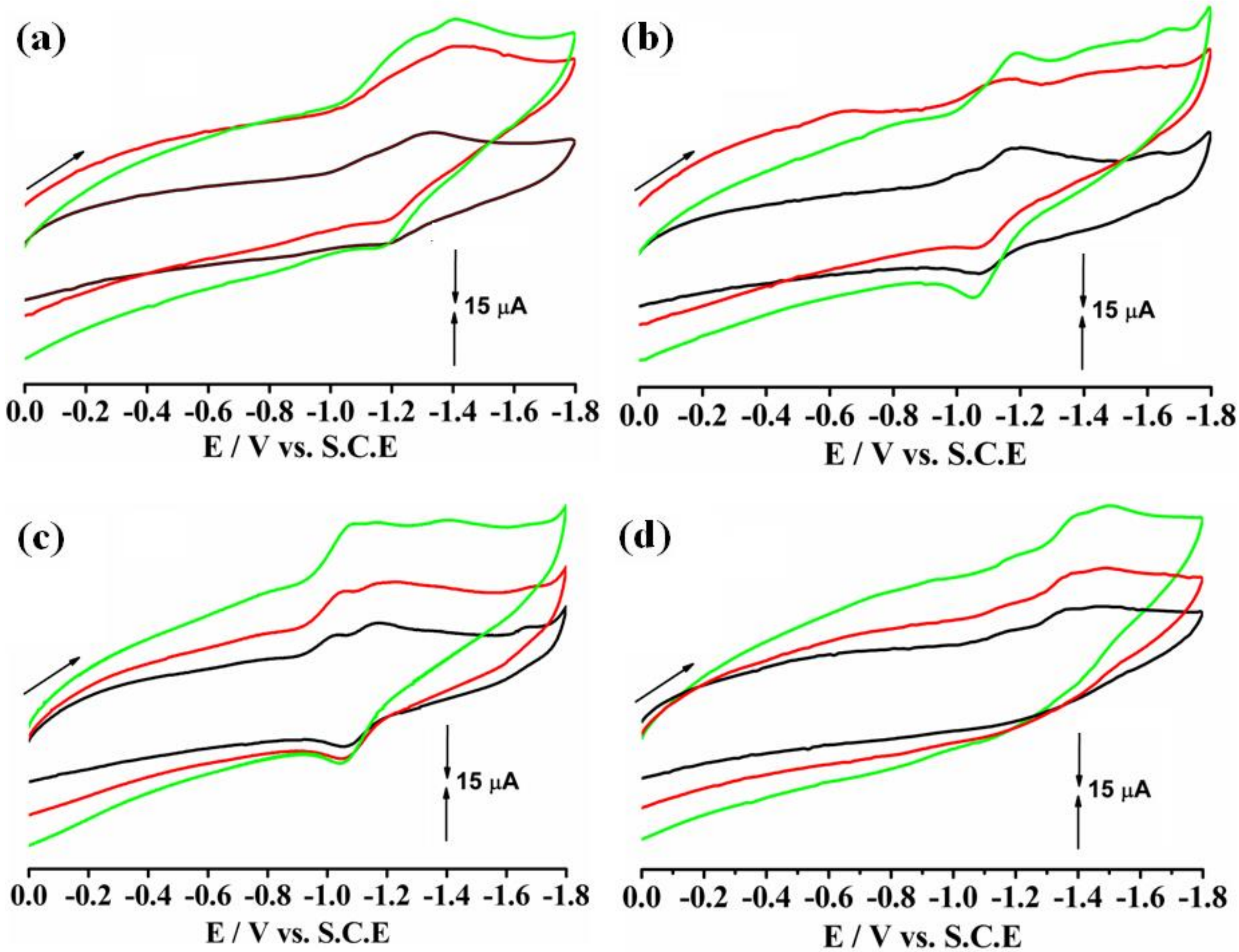


Figure S22. Cyclic voltammograms of 2mM of complex **1** (a), complex **2** (b), complex **3** (c) and complex **4** (d) in DMF-0.1M TBAP at various scan rates of 50 mV sec^{-1} (black), 100 mV sec^{-1} (red) and 200 mV sec^{-1} (green). The redox responses are ligand based.

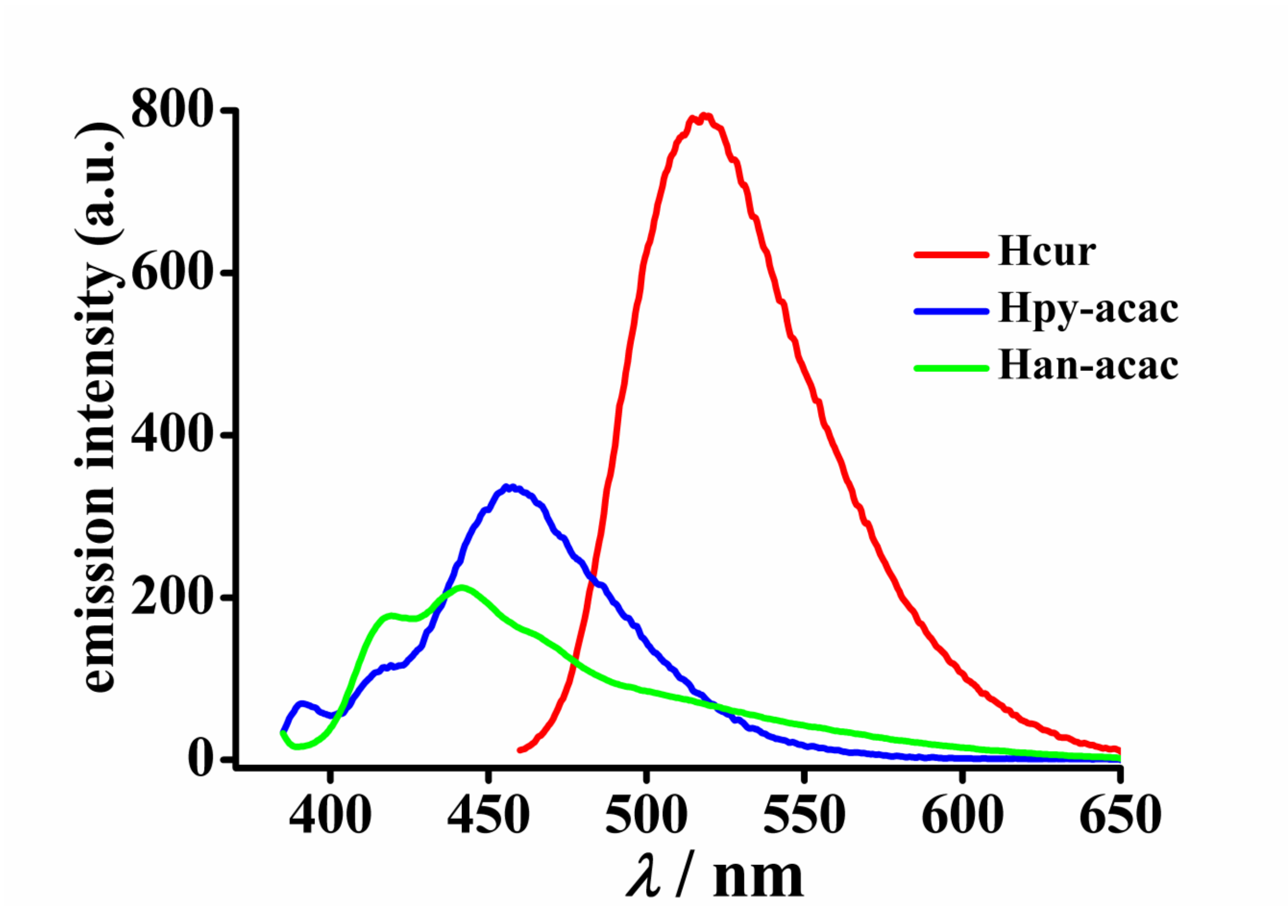


Figure S23. Emission spectra of ligands Hcur, Hpy-acac and Han-acacin aqueous DMSO (1:3 v/v) (λex = 460 nm for Hcur, 390 nm for Hpy-acac and 385 nm for Han-acac. The reduced intensity for Hpy-acac and Han-acac is possibly due to association of the planar pyrenyl/anthracenyl rings.

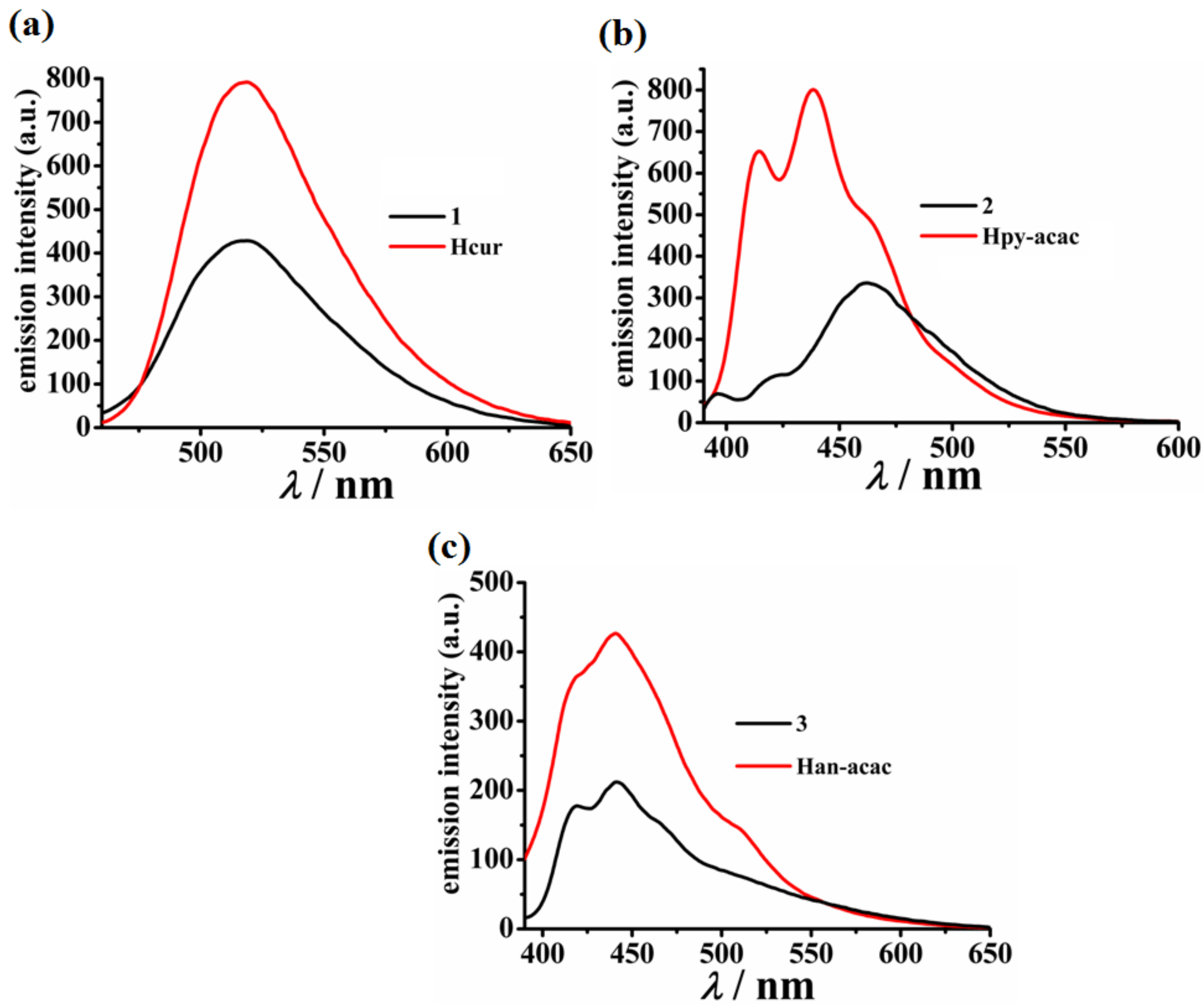


Figure S24. Emission spectra of complexes **1**(a), **2** (b) and **3**(c) and the corresponding free ligands, viz. Hcur, Hpy-acac and Han-acac in aqueous DMSO (1:3 v/v).

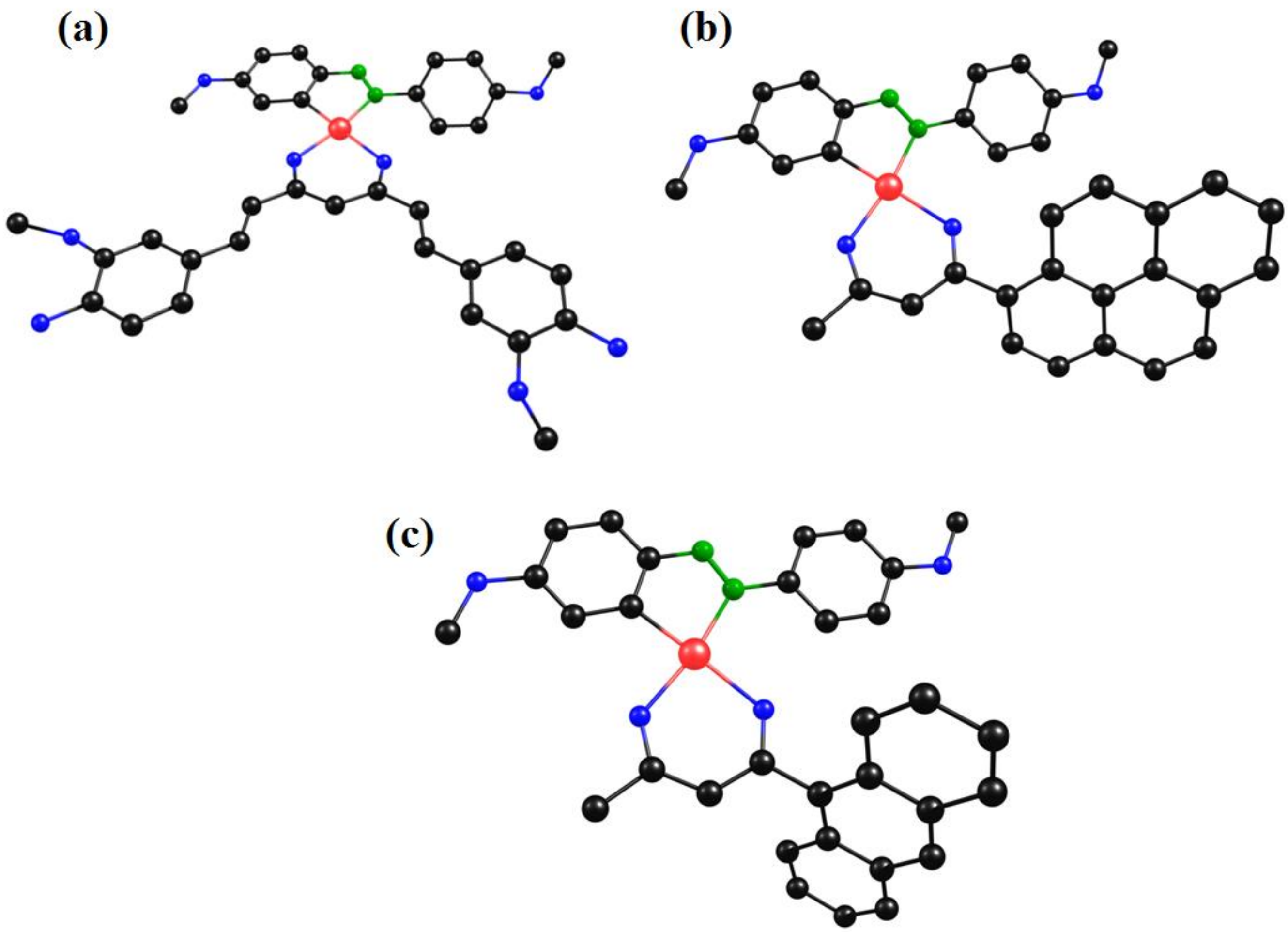


Figure S25. Energy-minimized structures of complexes **1** (a), **2** (b) and **3** (c) as obtained by DFT calculations using B3LYP/LanL2DZ level of theory. Color codes: Pt, red; N, green; O, blue and C, black. Hydrogen atoms are omitted for clarity.

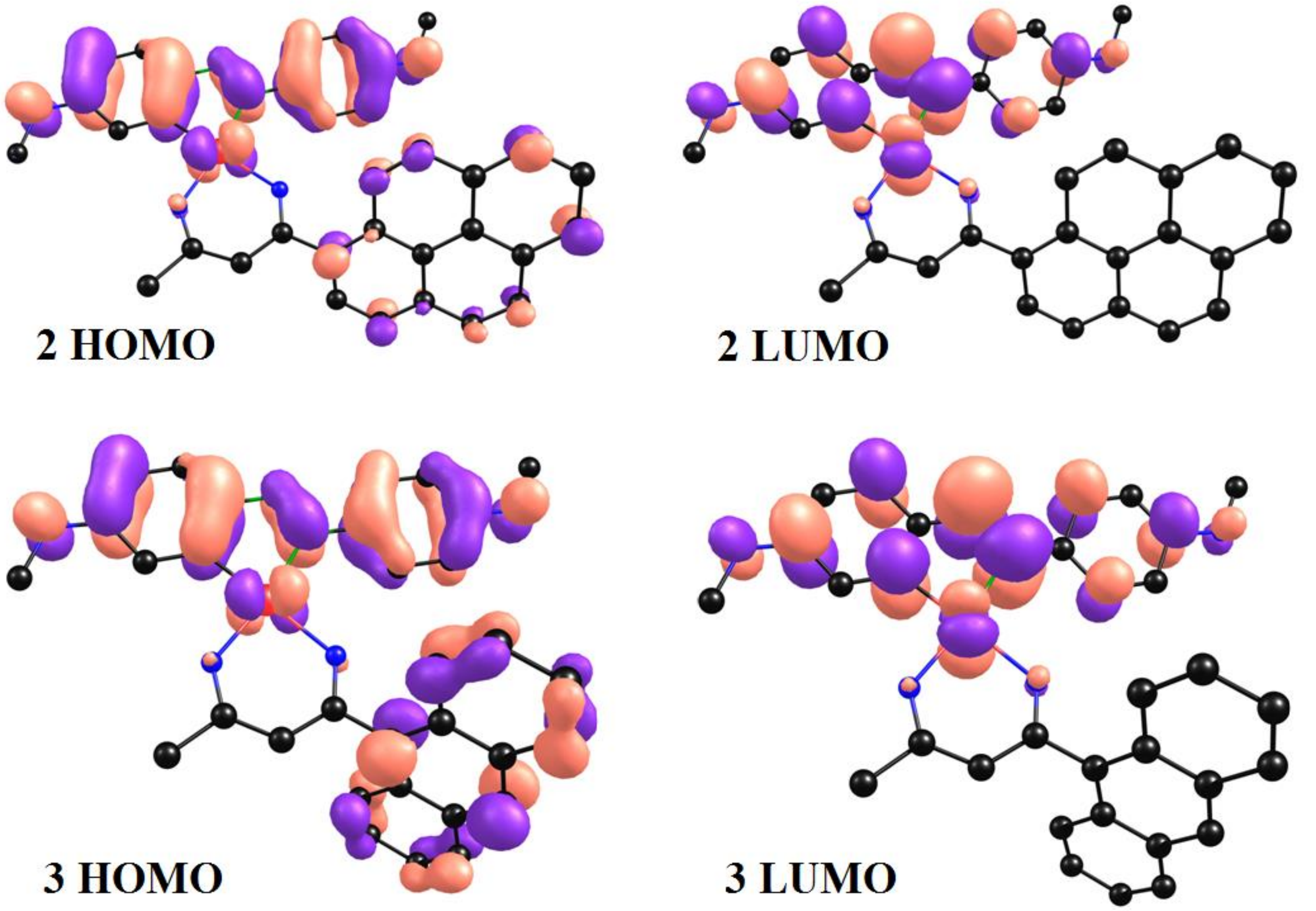


Figure S26. Frontier molecular orbitals of complexes **2** and **3** as obtained by DFT calculations using B3LYP/LanL2DZ level of theory. Color codes: Pt, red; N, green; O, blue and C, black. Hydrogen atoms are omitted for clarity. Orbitals are represented at a contour value of 0.03.

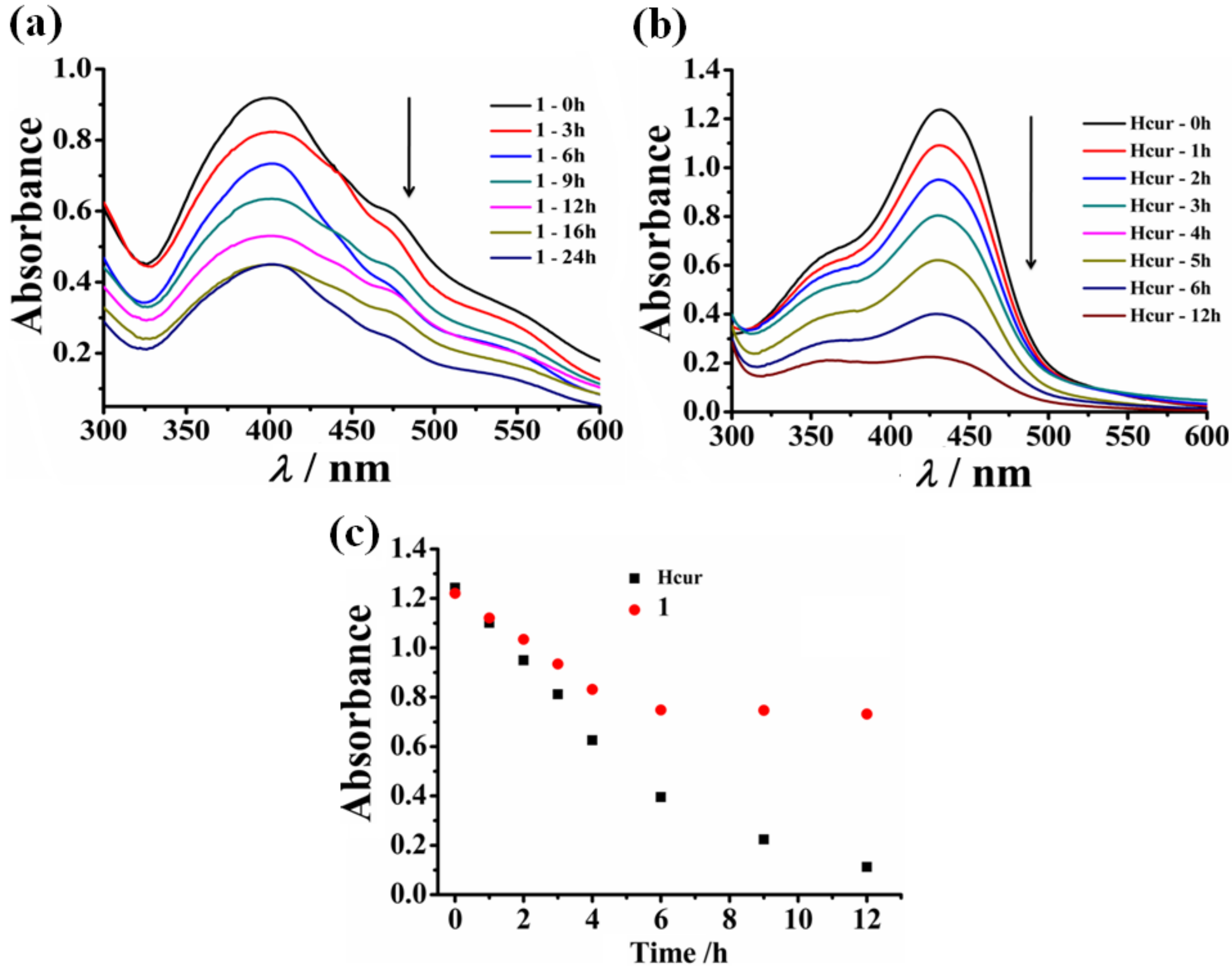


Figure S27. Stability studies of complex **1** (a) and free ligand Hcur (b) in 10% DMF tris buffer (pH, 7.2; 37 °C) as monitored by time dependent UV-visible spectra. (c) Absorbance (at 435 nm) vs time plot for complex **1** and Hcur in 10% DMSO-DPBS (pH, 7.2; 37 °C). Curcumin is more stable in its complex than in the free form.

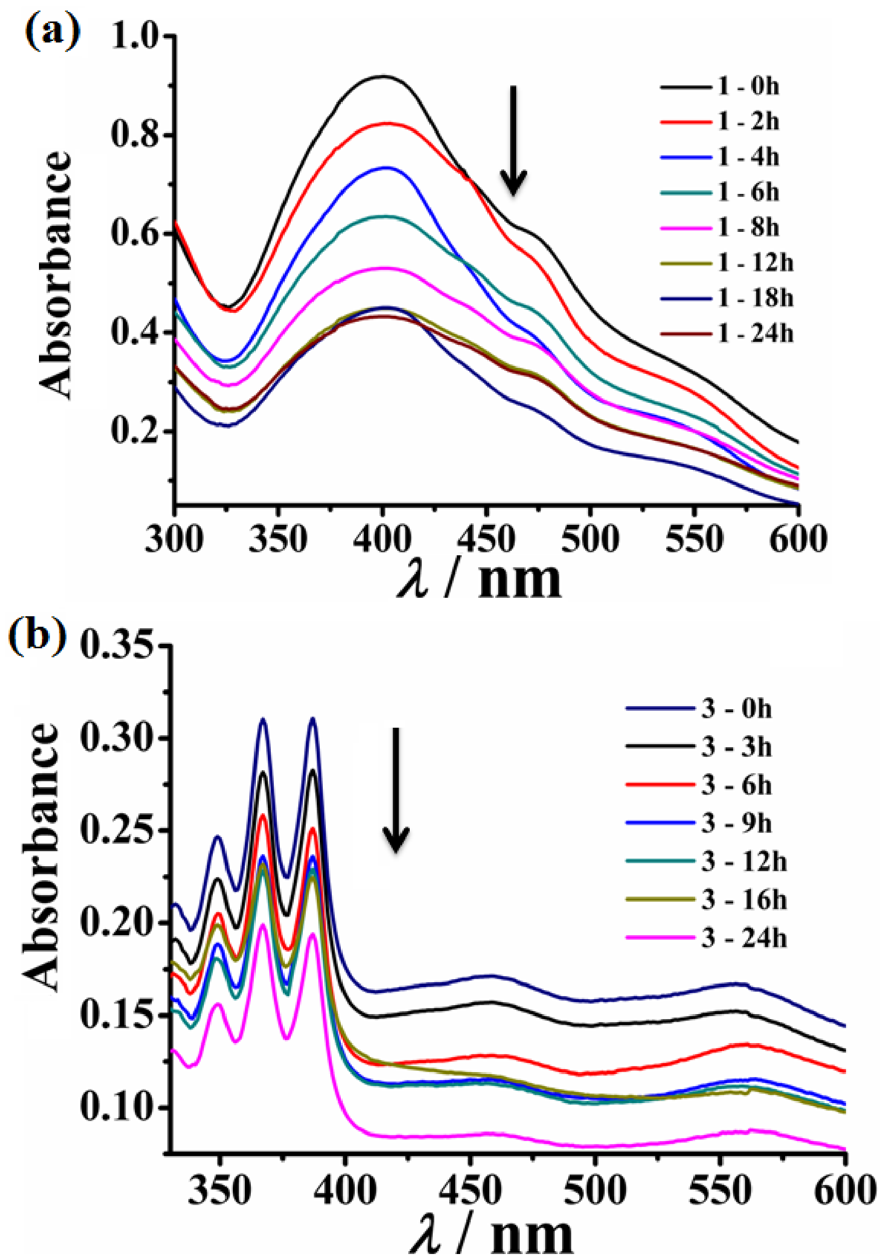


Figure S28. Stability studies of complexes **1** (a) and **3** (b) in 10% DMF Tris buffer (pH, 7.2; 37 °C) as monitored by time dependent UV-visible spectra. The complexes retain the spectral features over 24 h.

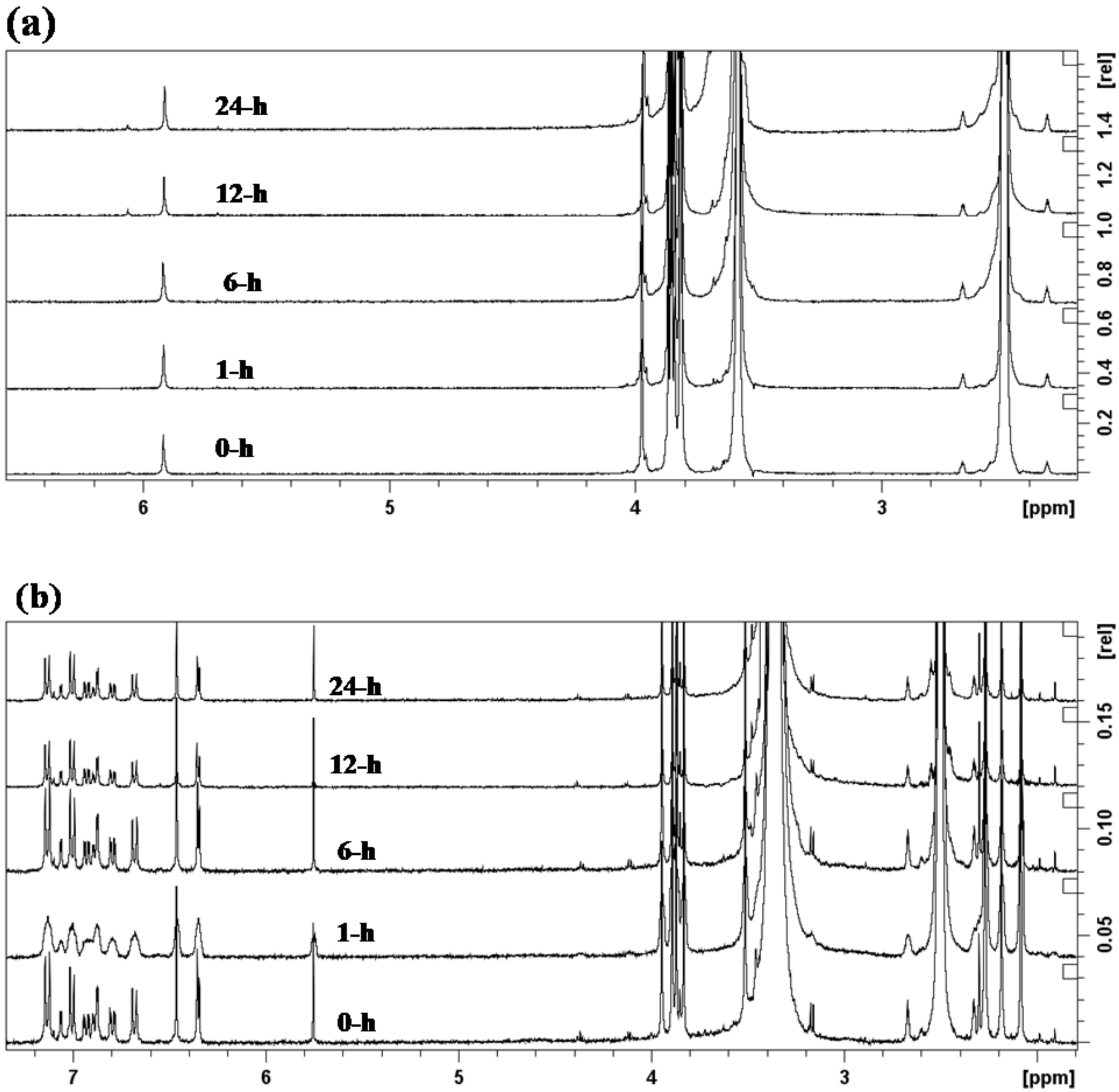


Figure S29. Stability studies of complexes **1** (a) and **2** (b) at 37 °C as monitored by time dependent ^{1}H NMR spectra. The complexes retain the spectral features over 24 h.

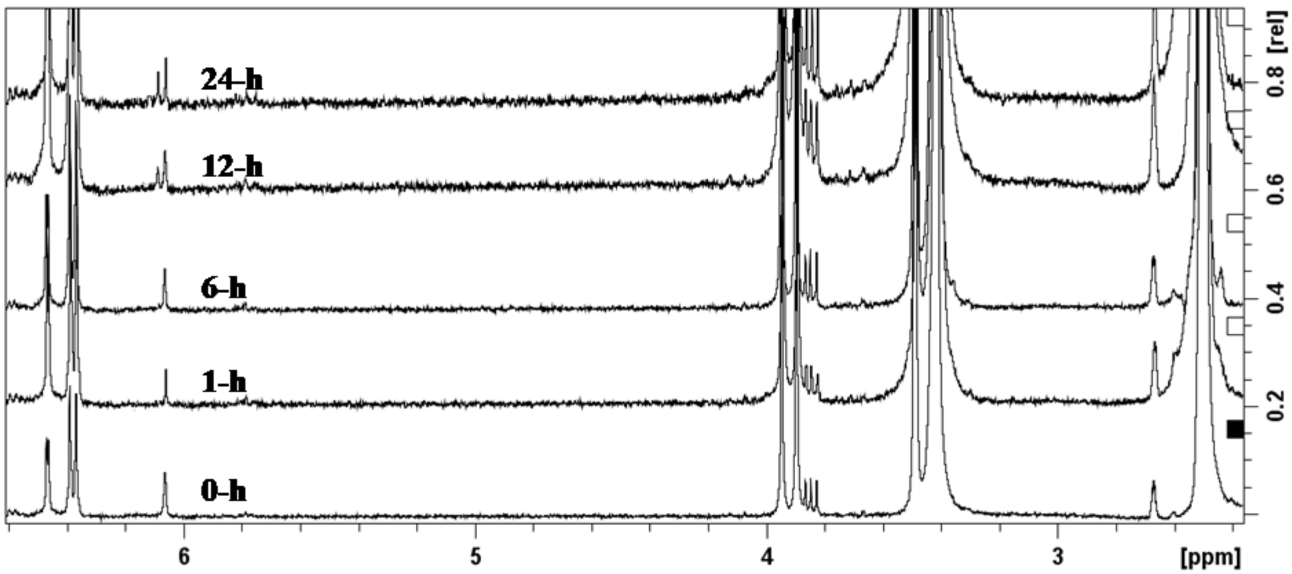


Figure S30. Stability studies of complex **3** at 37 °C as monitored by time dependent ^{1}H NMR spectra. The complexes retain the spectral features over 24 h.

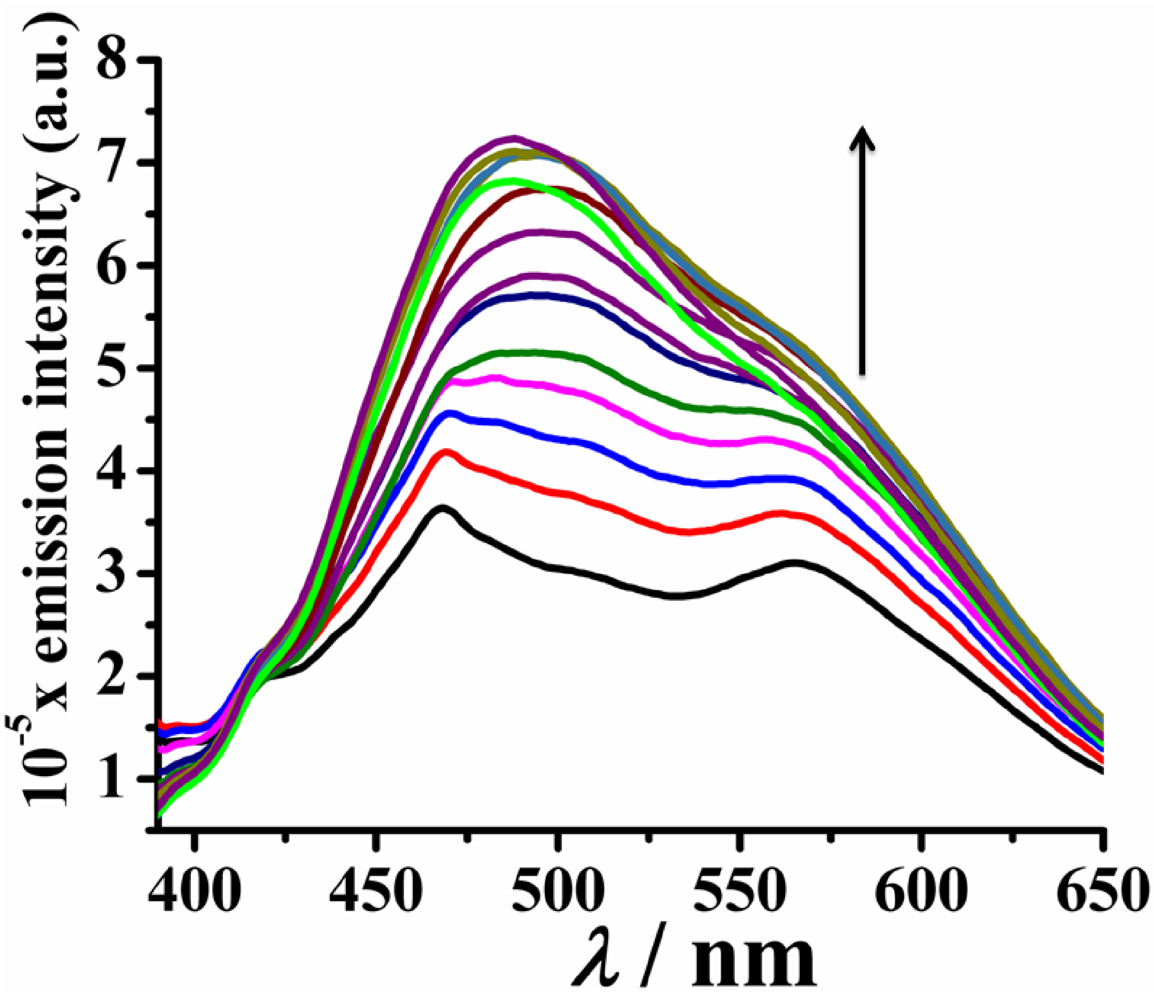


Figure S31. Increase in the emission spectra of complex **3** recorded in DMSO-DPBS buffer (3:2 v/v) solution on gradual addition of GSH (50-650 μM).

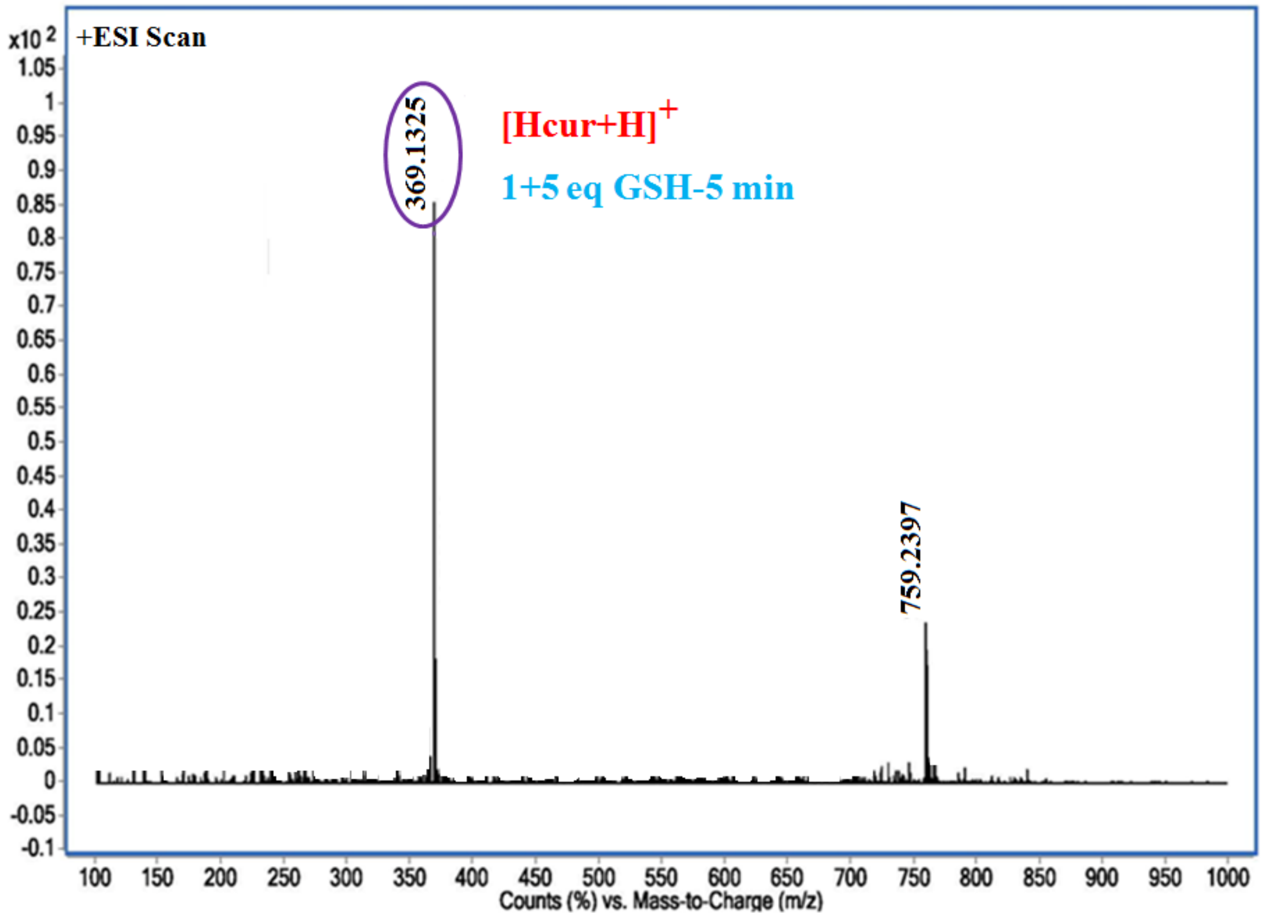


Figure S32. Mass spectrum of complex **1** treated with 5 equivalents of GSH for 5 min and diluted with methanol showing m/z peak corresponding to free curcumin (369.13). Another m/z peak at 759.23 was probably due to the Pt-GSH adduct having the azo ligand. Observation of free curcumin indicates release of this ligand.

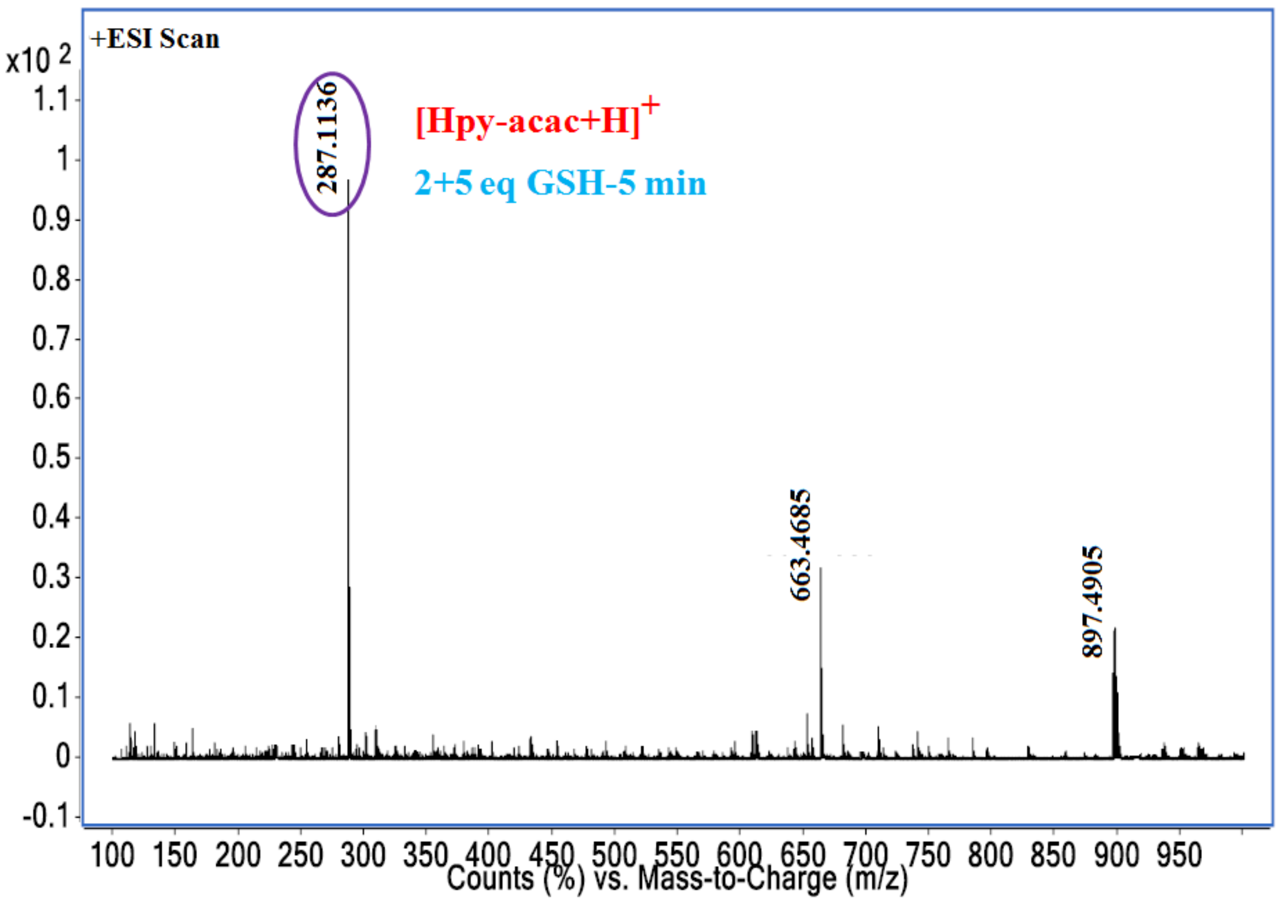


Figure S33. Mass spectrum of complex **2**treated with 5 equivalents of GSH for 5 min and diluted with methanol showing m/z peak corresponding to free ligand Hpy-acac (287.11).

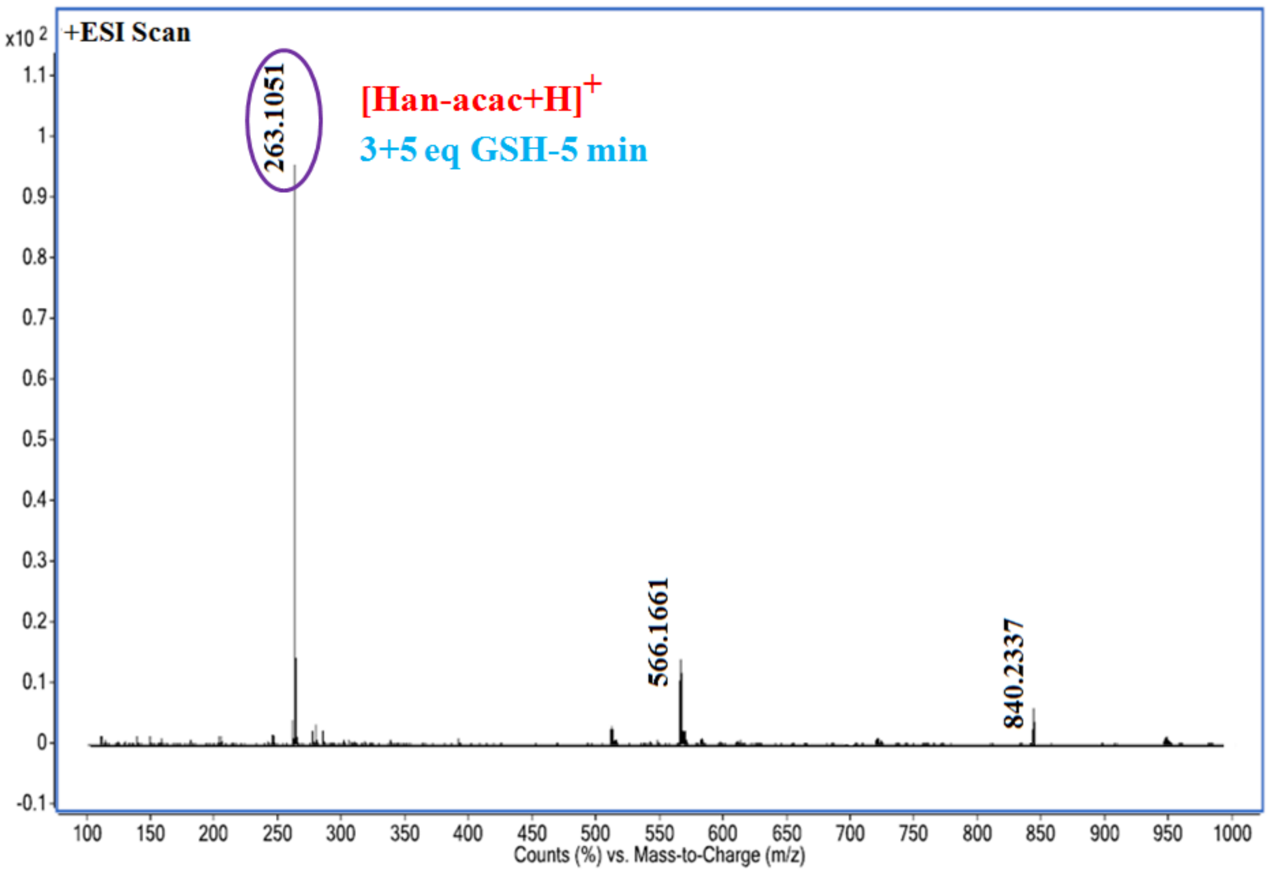


Figure S34. Mass spectrum of complex **3**treated with 5 equivalents of GSH for 5 min and diluted with methanol showing m/z peak corresponding to free ligand Han-acac (263.10).

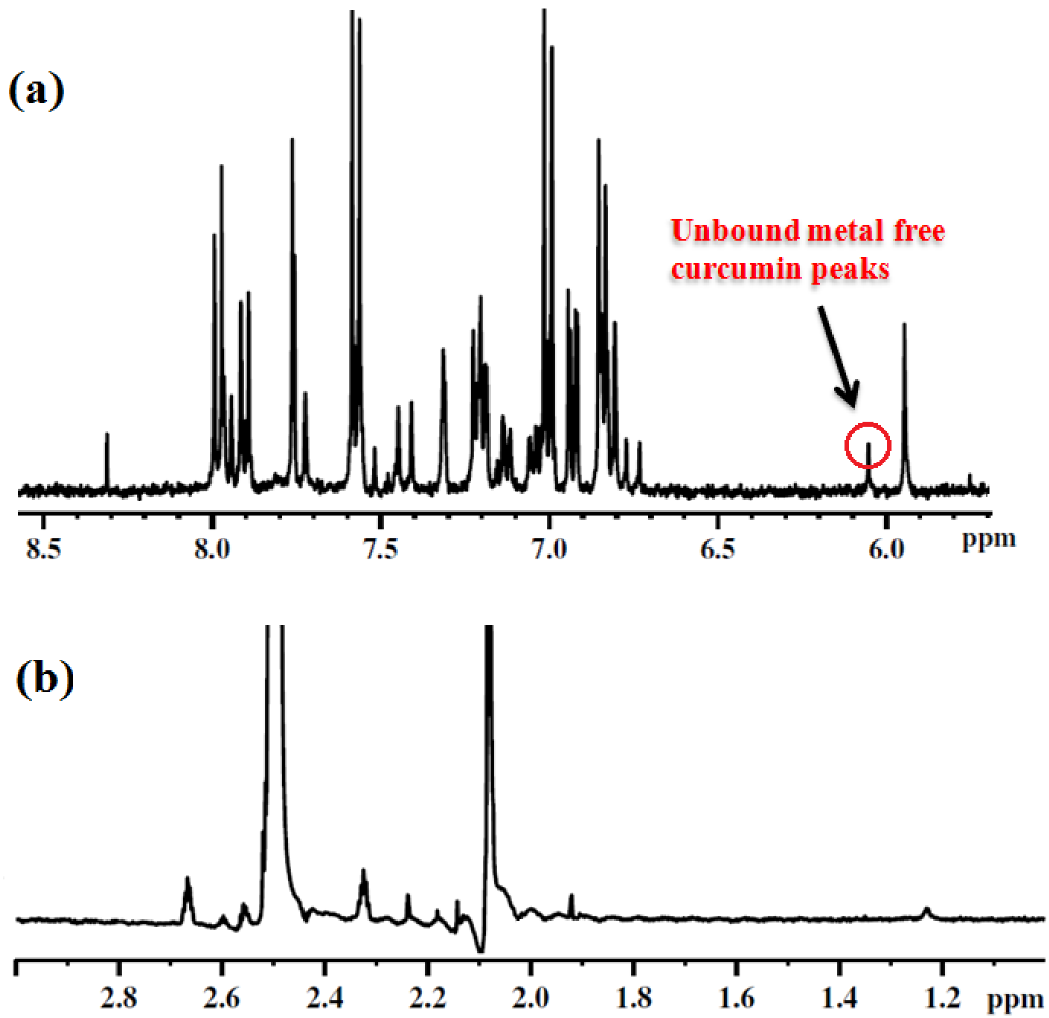


Figure S35.[1]H NMR spectra of complex **1** in presence of excess GSH recorded in DMSO-d_6: (a) expanded region showing peak for released curcuminat 6.10 ppm and (b) expanded region of the spectra from 1.8-2.8 ppm showing no splitting of peaks of GSH in presence of the complex.

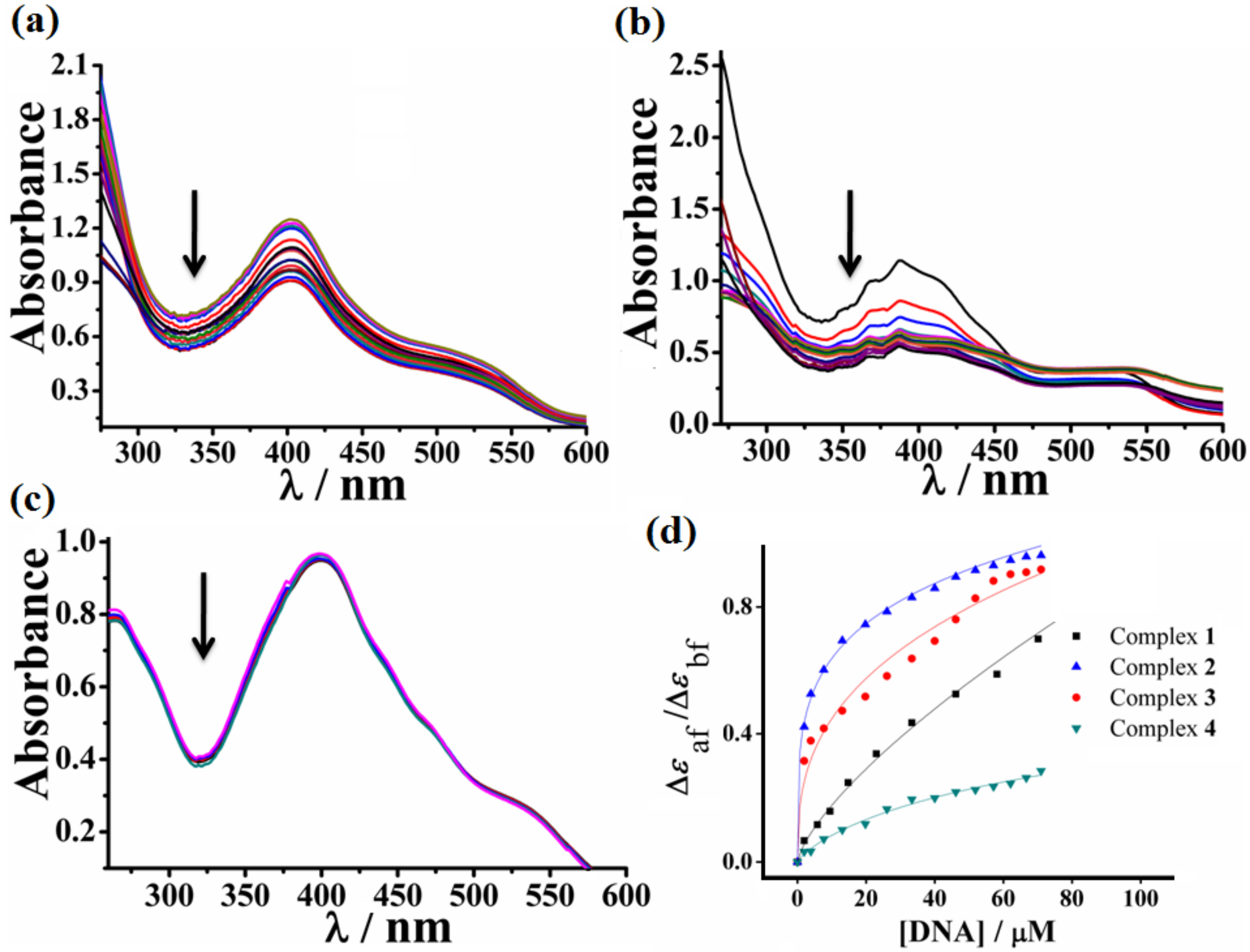


Figure S36. UV- visible spectral changes observed for **1** (a), **2** (b) and **3** (c) on gradual addition of ct-DNA (200 μM) to the complexes (25 μM) in 5% DMSO-tris buffer. (d) The McGhee-von Hippel plot of the complexes **1**-**3**. The DNA binding propensity varies as: py-acac complex >an-acac complex >curcumin complex >acac complex based on the planarity of the β-diketonate ligands.

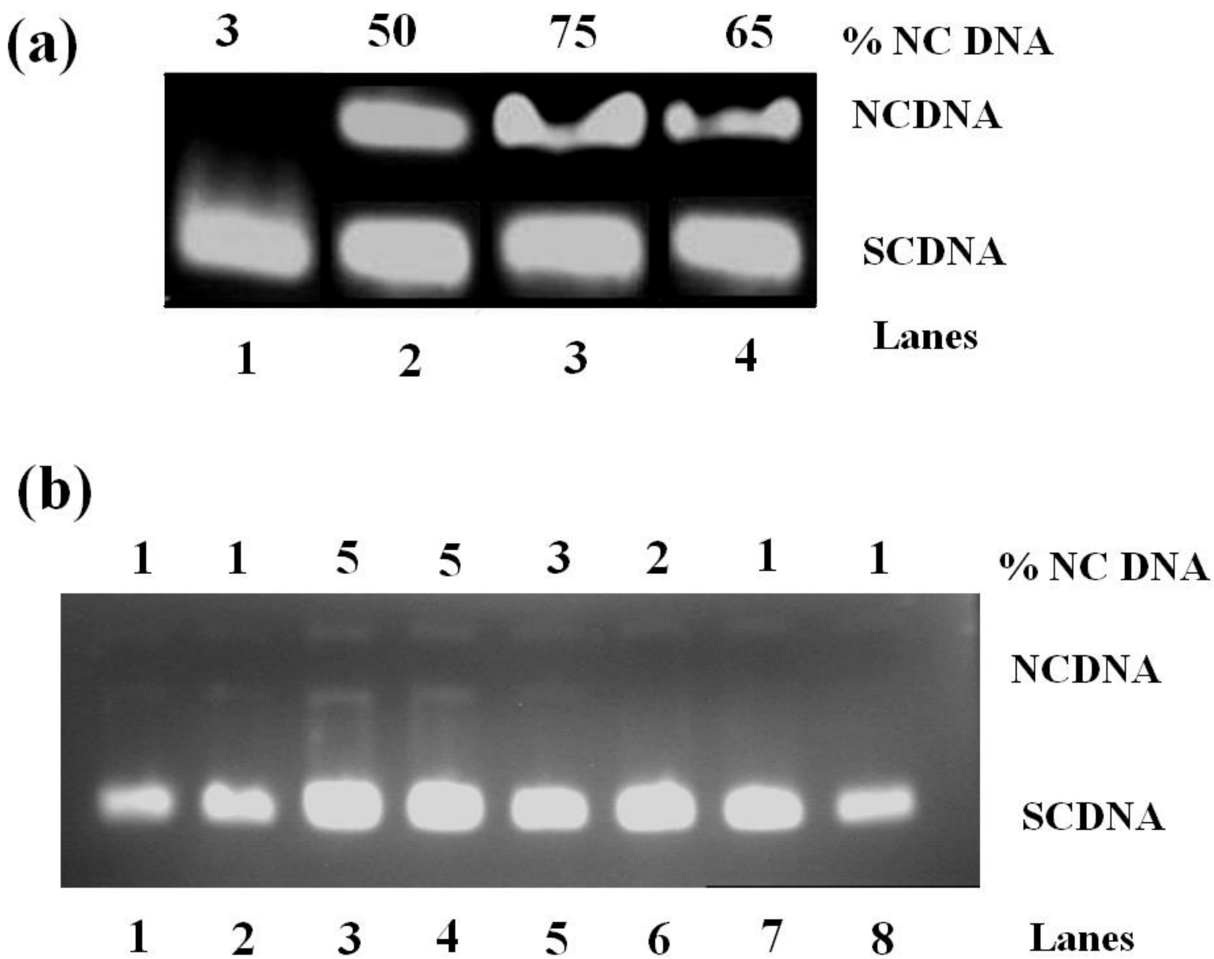


Figure S37. (a) Gel diagram showing photocleavage (% nicked circular DNA) of pUC19 DNA (0.2 μg, 30 μM, b.p.) in presence of complexes **1**-**3** (15 μM) and irradiated with blue light of 457 nm for 30 min. Lane 1: DNA + light; Lane 2: DNA + complex **1** + light; Lane 3: DNA + complex **2** + light; Lane 4: DNA + complex **3** + light. (b) Gel diagram showing chemical nuclease activity of complexes **1**-**3** using pUC19 DNA (0.2 μg, 30 μM, b.p.) in presence of GSH (5 mM) as the reducing agent. Lane 1: DNA in dark; Lane 2: DNA + GSH in dark; Lane 3: DNA + complex **1** in dark; Lane 4: DNA + complex **2** in dark; Lane 5: DNA + complex **3** in dark; Lane 6: DNA + GSH + complex **1** in dark; Lane 7: DNA + GSH + complex **2** in dark; Lane 8: DNA + GSH + complex **3** in dark. NC is nicked circular DNA. SC is super coiled DNA.

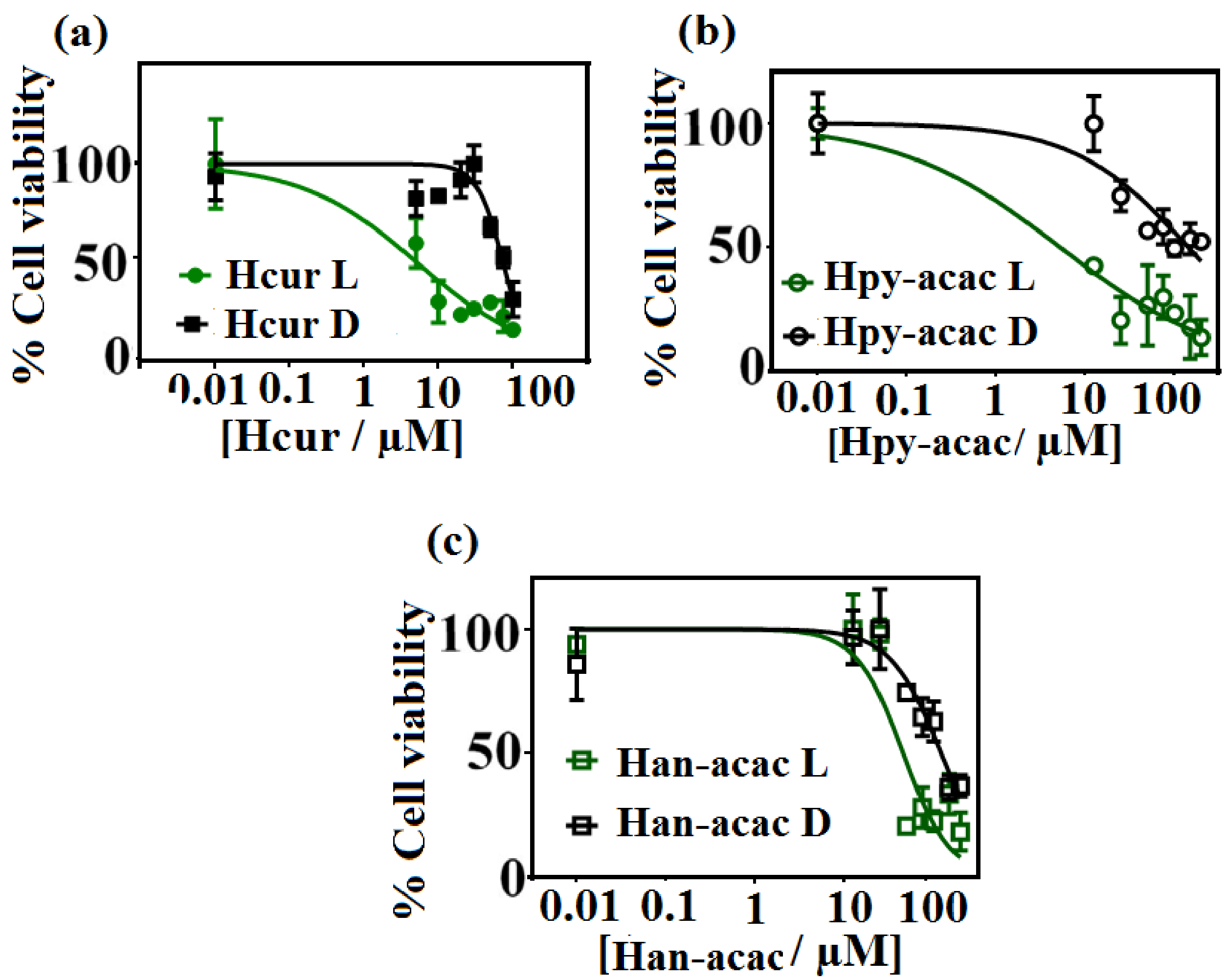


Figure S38. Cell viability plots for the ligands Hcur (a), Hpy-acac (b) and Han-acac (c) as obtained from MTT assay in HaCaT cells with 4h pre-incubation with the compounds in dark. D denotes samples kept in the dark while L is for samples exposed to light (400-700 nm) for 1 h.

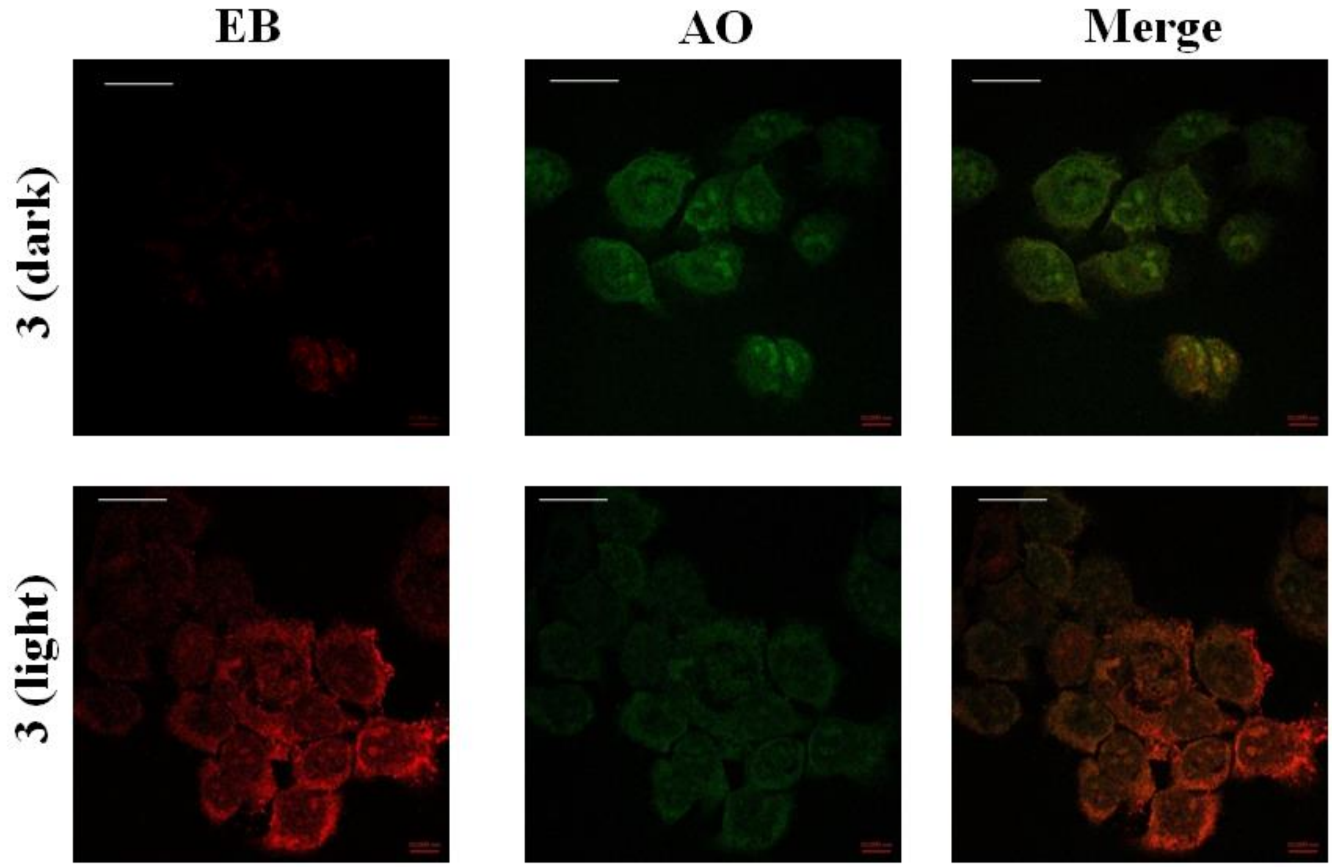


Figure S39. Confocal microscopic images of HaCaT cells treated with complex **3** either kept in the dark or irradiated with visible light (400-700 nm) and stained with ethidium bromide (EB)/ acridine orange (AO). First column is for fluorescence of EB, second column is for fluorescence of AO and third column is the merged images of one and two. Scale bar = 10 μm.

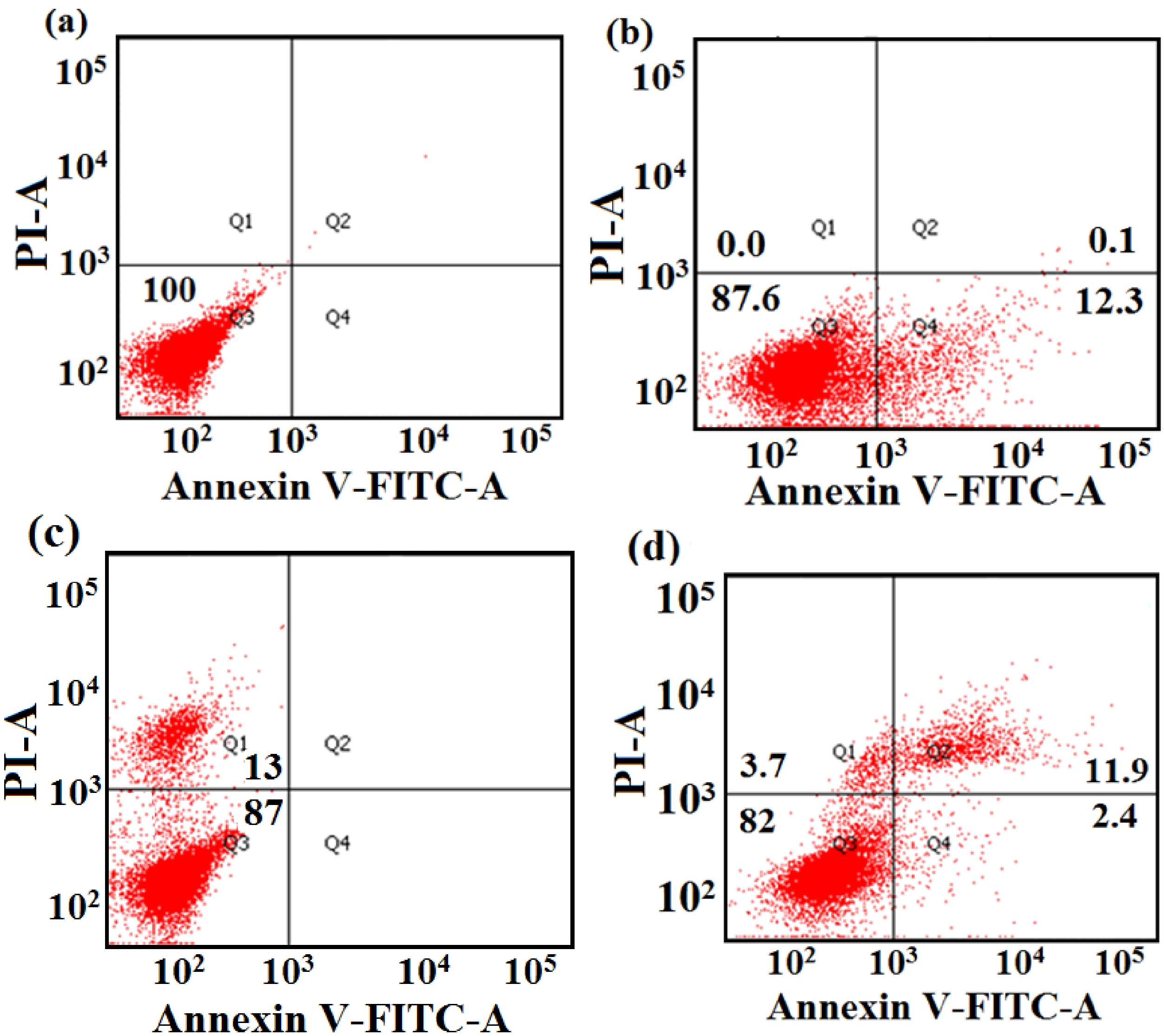


Figure S40.AnnexinV-FITC/PI assay in HaCaT cells showing early apoptotic populations (lower right quadrant) in (a) cells alone; (b) cells + annexinV-FITC; (c) cells + PI and (d) cells + PI + annexinV. Percentage population is depicted each of the quadrants.

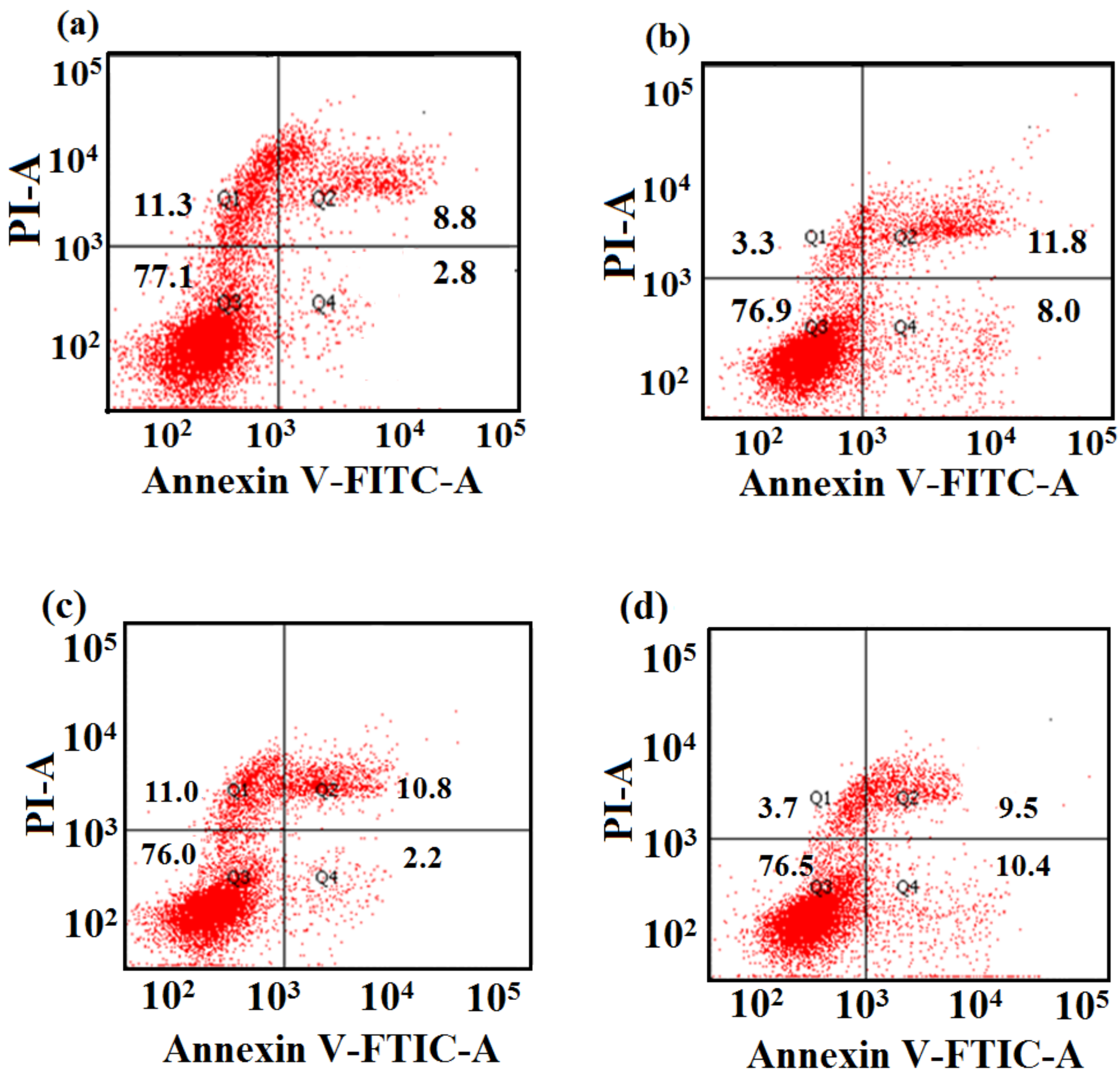


Figure S41. AnnexinV-FITC/PI assay in HaCaT cells showing early apoptotic populations (lower right quadrant) in (a) cells + complex **2** in dark; (b) cells + complex **2** in light; (c) cells + complex **3** in dark and (d) cells + complex **3** in light. Percentage population is depicted each of the quadrants.

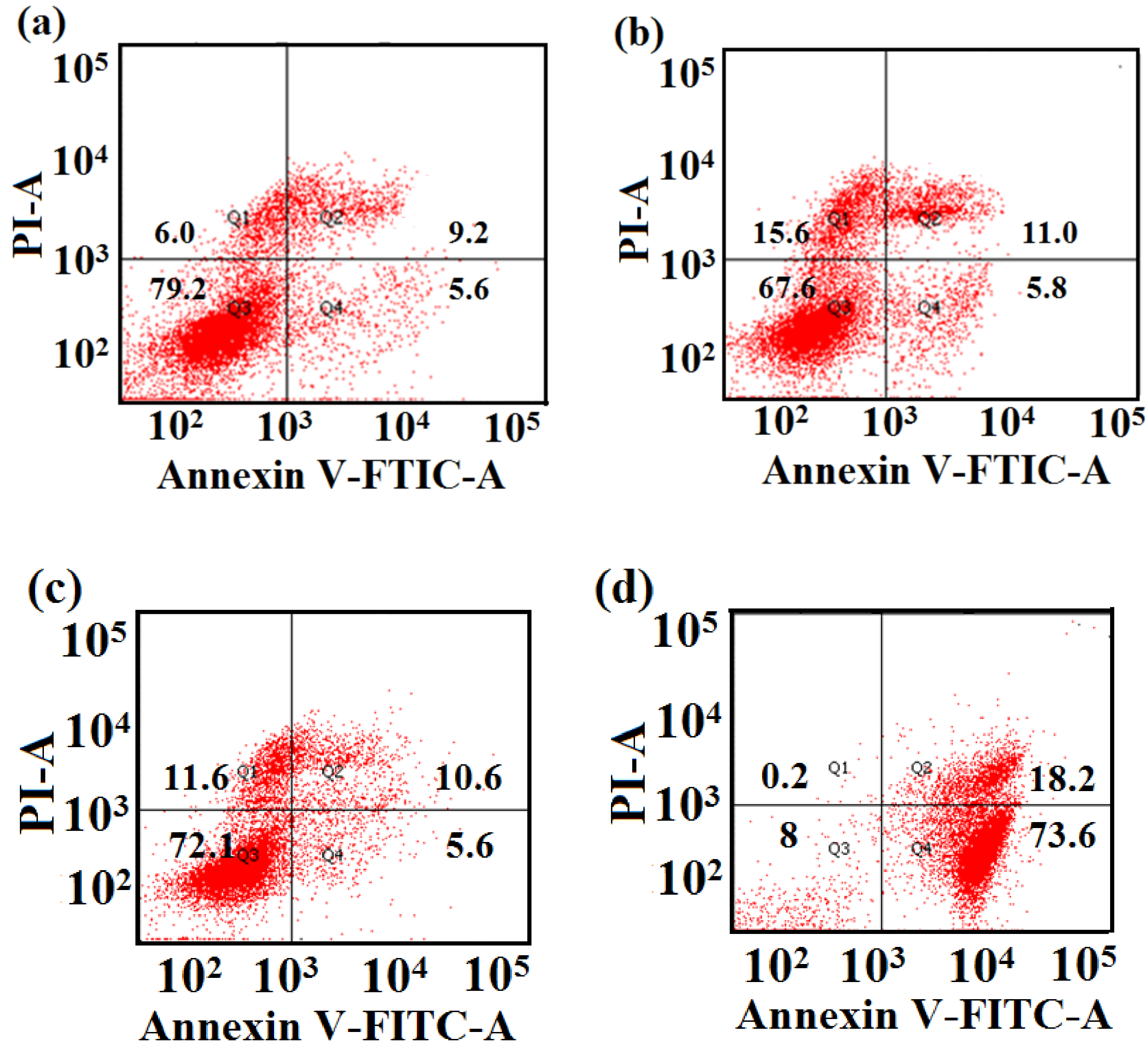


Figure S42.AnnexinV-FITC/PI assay in HaCaT cells showing early apoptotic populations (lower right quadrant) in (a) cells + complex **4** in dark; (b) cells + complex **4** in light; (c) cells + Hcur in dark and (d) cells + Hcur in light. Percentage population is depicted each of the quadrants.

Table S1. Coordinates of optimized structures of complexes **1-3** as obtained from DFT calculations using B3LYP/LanL2DZ level of theory

<u>Complex 1</u>

78	-0.226174674	-2.049609019	-0.09923048
7	-1.690416250	-3.477127388	-0.051651807
6	0.868572920	-3.698421492	-0.093672664
6	0.074323820	-4.885705836	-0.022146321
6	-3.112295764	-3.281422374	-0.008523511
6	-3.682789882	-2.105355768	-0.544062455
1	-3.040601513	-1.333590714	-0.946882612
6	-5.070780482	-1.935053818	-0.538058325
1	-5.527190272	-1.043460609	-0.956713984
6	2.266118350	-3.822898459	-0.134815616
1	2.869668578	-2.923398727	-0.186184516
6	-3.953691268	-4.274025477	0.540913395
1	-3.507758950	-5.174277493	0.947768841
6	2.049852499	-6.288082120	-0.036473607
1	2.550454796	-7.250548219	-0.018361872
6	-5.344746572	-4.101446213	0.558620814
1	-5.968706558	-4.874439043	0.995695541
6	2.847544772	-5.111556167	-0.108589422
7	-1.303107728	-4.733177521	0.002596244
6	0.663754861	-6.175649629	0.006717938
1	0.026845420	-7.054144135	0.060295132
6	-5.909013353	-2.926606833	0.012971355
8	4.216959691	-5.344678097	-0.150500352
8	-7.276367200	-2.652149672	-0.023226775
6	5.126260113	-4.206273062	-0.234388543
1	5.024848802	-3.556337348	0.644791942
1	6.127393268	-4.640444008	-0.261934916
1	4.945834595	-3.624966006	-1.148085571
6	-8.203037792	-3.641188718	0.511329888
1	-8.122557023	-4.594164356	-0.029530371
1	-8.030917441	-3.808778735	1.583582762
1	-9.197125988	-3.215622252	0.360736067
8	-1.402008284	-0.272457932	-0.057161711
8	1.433744001	-0.864594179	-0.104598637
6	-0.963924199	0.966024022	0.000863241
6	1.504033149	0.459005157	-0.042175572
6	0.403834590	1.336377710	0.014467399
1	0.626250444	2.392953395	0.085525951
6	-2.048714609	1.968639333	0.058473612
1	-3.033252257	1.510077825	0.121461779
6	2.901139066	0.936998322	-0.030573935
1	3.619791468	0.120450341	-0.037026307
6	-1.915089162	3.322607499	0.031118829
1	-0.915477641	3.750542705	-0.042375877
6	3.326365012	2.229512758	-0.022579353
1	2.585036873	3.028438485	-0.029634528
6	4.720654658	2.692481170	-0.009438746
6	5.830192296	1.811219532	0.032043952
6	4.980402999	4.083772429	-0.034525769
1	5.696473386	0.734694532	0.057354613
1	4.150223830	4.785824445	-0.058680646
6	7.148390656	2.282200084	0.036148350
6	6.295541243	4.571009899	-0.033466686
1	6.477966369	5.644631954	-0.062392946
6	7.384678935	3.682404815	-0.010473909
6	-3.000898789	4.311537879	0.085000833
6	-2.669250262	5.686964176	0.037952080
6	-4.371731097	3.962265897	0.178767313
1	-1.631981133	6.004113225	-0.034731562
1	-4.674476751	2.920506239	0.212721729
6	-3.643764266	6.695140606	0.091352636
6	-5.354368443	4.956978095	0.233599377
1	-6.404415864	4.676861198	0.313413520
6	-5.005639657	6.322305018	0.202928963
8	-5.965605949	7.338888698	0.294751407
1	-6.863938358	6.978460464	0.441656931

8	8.713464650	4.123276690	-0.045917446
1	8.772557979	5.094900799	-0.150965100
8	-3.189881574	8.015687085	0.118630809
8	8.165314227	1.325546563	-0.002714307
6	-3.799429628	8.995780818	-0.793477869
1	-3.233210781	9.916334544	-0.634530666
1	-3.689547253	8.665557546	-1.835934363
1	-4.855267915	9.145149035	-0.555636826
6	9.266612041	1.421259218	0.968445659
1	9.884537606	0.540588882	0.779453529
1	9.842207237	2.337123020	0.814776745
1	8.873030694	1.387657351	1.99399020

Complex 2

78	-2.033376819	-0.278592584	-0.09717684
7	-1.919580718	1.768110382	-0.207790049
6	-3.938636779	0.206790046	0.118950426
6	-4.152169980	1.619570831	0.111036859
6	-0.754357059	2.589379920	-0.385458562
6	0.430387036	2.038445559	-0.923243000
1	0.477065964	0.984552973	-1.163386704
6	1.550398797	2.850081320	-1.129506184
1	2.466984879	2.440234282	-1.541373976
6	-5.042468632	-0.643960499	0.284542517
1	-4.880947267	-1.716227209	0.292899751
6	-0.790448858	3.962421576	-0.048786098
1	-1.702281510	4.378531803	0.362835618
6	-6.536340440	1.326243622	0.426933472
1	-7.547182865	1.701530798	0.547479776
6	0.332152420	4.776304371	-0.247945899
1	0.280618936	5.825331591	0.025724354
6	-6.331289918	-0.081613894	0.436453320
7	-3.045344216	2.432808078	-0.067437480
6	-5.447295091	2.176962128	0.264144503
1	-5.570344623	3.256221213	0.251045099
6	1.510417101	4.219697278	-0.796661658
8	-7.488856737	-0.831950833	0.604698743
8	2.680555271	4.936568120	-1.038635327
6	-7.392163988	-2.287463614	0.631579762
1	-6.763063099	-2.624697432	1.465936261
1	-8.415804776	-2.639822445	0.771672993
1	-6.990260059	-2.673069239	-0.314693577
6	2.709057414	6.360538021	-0.731461153
1	1.957337859	6.908712575	-1.315991369
1	2.547035496	6.539834121	0.340516335
1	3.709474481	6.694904646	-1.012781356
8	0.036135309	-0.848969358	-0.282181083
8	-2.469935461	-2.270689008	0.070319505
6	0.527185185	-2.061432834	-0.281870708
6	-1.644532783	-3.295728607	0.050011638
6	-0.250669091	-3.239798789	-0.121165007
1	0.281056161	-4.182407353	-0.085083129
6	-2.335393680	-4.631741741	0.242073175
1	-2.840863529	-4.648071341	1.216104914
1	-3.105079480	-4.762094565	-0.528910028
1	-1.632012101	-5.467364349	0.191753069
6	6.208082585	-2.769789748	-1.223646086
6	4.794993483	-2.590021834	-0.979541050
6	7.142924626	-1.982052119	-0.598587555
6	4.361122570	-1.562073527	-0.074538834
6	6.743918101	-0.946129254	0.327018572
6	5.344156593	-0.745099114	0.582299723
1	6.515652732	-3.549688738	-1.916705550
6	3.826071279	-3.403984810	-1.608271944
6	2.956579945	-1.354731027	0.174620302
6	4.934220091	0.276231363	1.501954075
6	2.007031883	-2.204250503	-0.473795867
6	2.465016504	-3.217378756	-1.348768480
1	4.145883412	-4.177623548	-2.302332807
6	2.578864396	-0.317681179	1.113999798
1	1.736684752	-3.842916785	-1.856579478
6	7.693436502	-0.129846082	0.984861526
6	5.914385772	1.071421213	2.140938509
6	7.280382173	0.869008518	1.882994012

1	8.204410213	-2.126310383	-0.788513398
6	3.522938246	0.453746593	1.745803487
1	1.526371086	-0.147079154	1.301254116
1	5.599224048	1.846255320	2.836143416
1	8.022273225	1.488353797	2.380660692
1	3.212200513	1.227151256	2.444639037
1	8.752506871	-0.282507439	0.788652360

Complex 3

78	-1.446891606	-0.266721234	0.00742339
7	-1.712702810	1.763057173	-0.241446747
6	-3.421417152	-0.155490213	-0.007173790
6	-3.898329035	1.181144760	-0.164788939
6	-0.721060682	2.797077905	-0.370899288
6	0.653853160	2.470866500	-0.382562782
1	0.970013325	1.440493339	-0.286274918
6	1.614365706	3.478885574	-0.516201696
1	2.672909247	3.239136492	-0.525689885
6	-4.352696116	-1.197725217	0.118087804
1	-3.990114692	-2.212551770	0.238624231
6	-1.110018983	4.153143745	-0.492004687
1	-2.164333848	4.399992555	-0.481874347
6	-6.202610363	0.437477475	-0.072267201
1	-7.273640879	0.609857793	-0.090772830
6	-0.150014067	5.163440027	-0.624665654
1	-0.477358564	6.194418964	-0.714948658
6	-5.734293366	-0.896604423	0.084804605
7	-2.956145607	2.186376123	-0.288375715
6	-5.285281692	1.476311564	-0.197122288
1	-5.610513039	2.505623815	-0.318781491
6	1.223802919	4.827454464	-0.638678442
8	-6.738149487	-1.850799497	0.199792093
8	2.258670488	5.751267097	-0.766998358
6	-6.367982698	-3.252386927	0.363900490
1	-5.785803003	-3.400846847	1.282937973
1	-7.314220836	-3.792383416	0.431976392
1	-5.793846021	-3.611624887	-0.500387746
6	1.927976316	7.163699754	-0.904330850
1	1.326181068	7.345278196	-1.805479144
1	1.391662376	7.534406674	-0.019893708
1	2.887825528	7.676035620	-0.993706755
8	0.700395220	-0.462376192	0.046347185
8	-1.529655573	-2.299381173	0.261247126
6	1.392322192	-1.562267523	0.170534086
6	-0.540080041	-3.158155921	0.375555575
6	0.833525818	-2.854155567	0.326220395
1	1.527715334	-3.677583317	0.443312126
6	2.750807366	-0.075097291	2.316168411
6	3.503489019	-0.685873787	1.248508786
6	2.891773296	-1.411198315	0.185733891
6	4.952043257	-0.574612016	1.290245477
6	5.723302725	-1.171504315	0.275339971
6	5.127522614	-1.871575271	-0.789998311
6	3.680048892	-1.996657438	-0.844887095
6	3.385402232	0.596260694	3.344412533
6	5.574435111	0.136581871	2.375759712
1	6.808173342	-1.086837458	0.313928937
6	5.926956113	-2.460684342	-1.831806590
6	3.109709448	-2.686548325	-1.976257369
6	3.910464260	-3.232912373	-2.961812487
6	5.340065259	-3.128001697	-2.888462646
1	7.008996585	-2.362925396	-1.771826053
1	2.030390492	-2.763514283	-2.059101253
1	3.456608445	-3.741704391	-3.808741364
1	5.951091940	-3.567407656	-3.672859643
6	4.815907372	0.708012584	3.377815296
1	1.668060380	-0.131932691	2.301267563
1	6.659768546	0.212581594	2.390698031
1	5.292795919	1.243716938	4.194750539
6	-0.995217937	-4.589426458	0.581128871
1	-1.584253187	-4.659650041	1.504494412
1	-1.647515200	-4.891888229	-0.247659440
1	-0.150817541	-5.281029223	0.644047120
1	2.796998068	1.052002021	4.136813246