

Supplementary information

Half-sandwich RuCl₂(η^6 -*p*-cymene) core complexes containing sulfur donor aroylthiourea ligand: DNA and protein binding, DNA cleavage and cytotoxic studies

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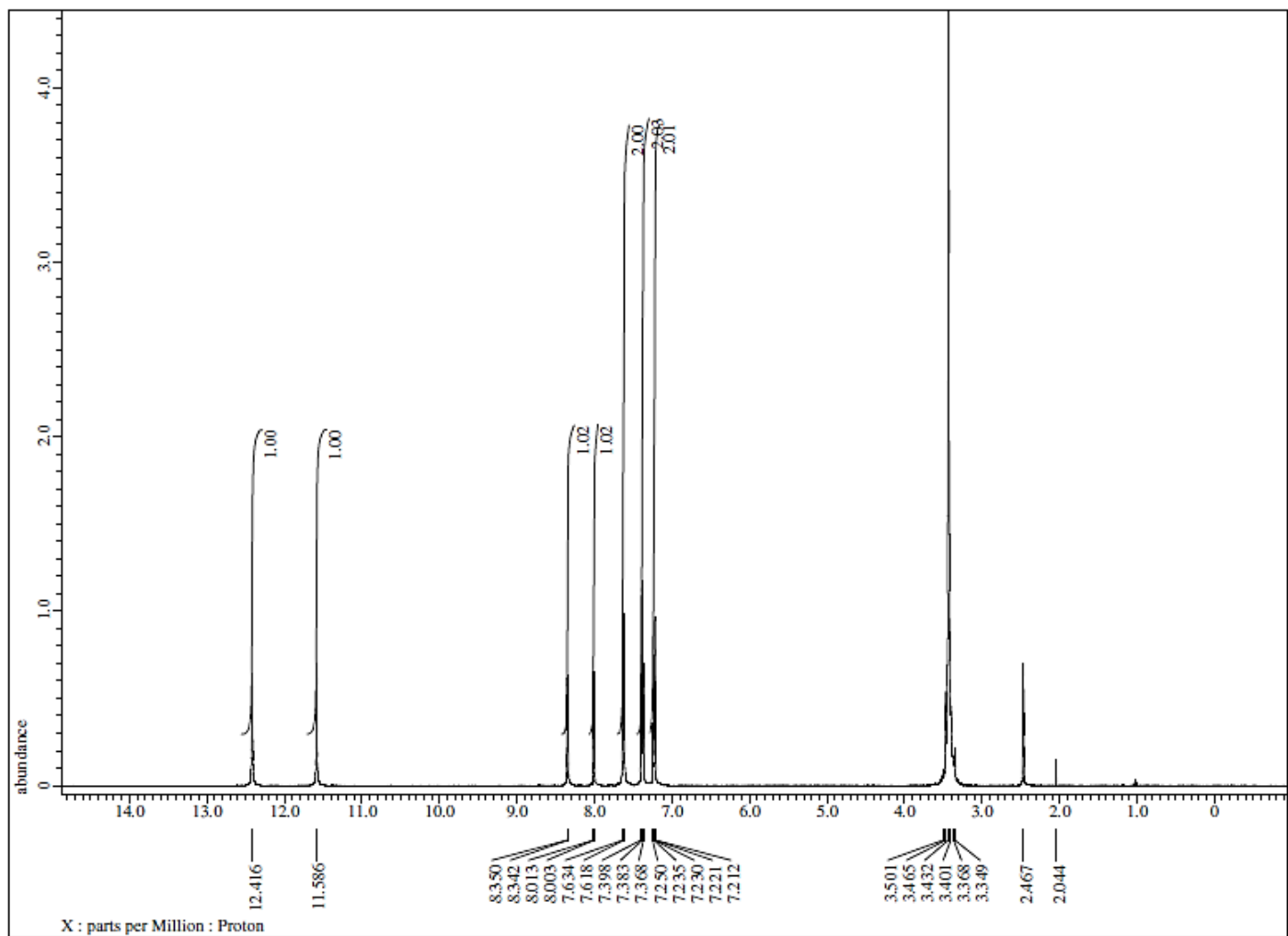


Fig. S1 ^1H NMR spectrum of the L1.

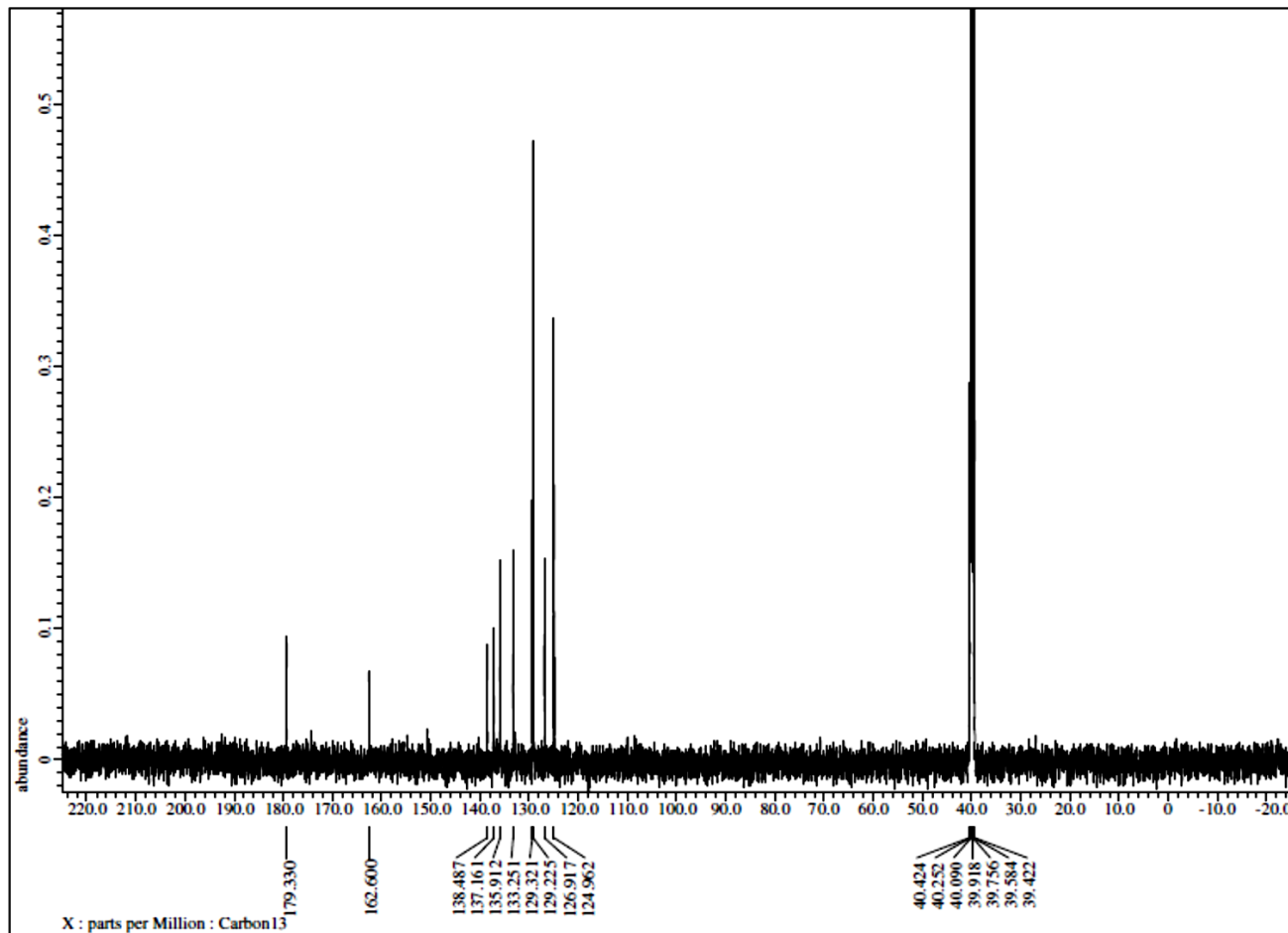


Fig. S2 ^{13}C NMR spectrum of L1.

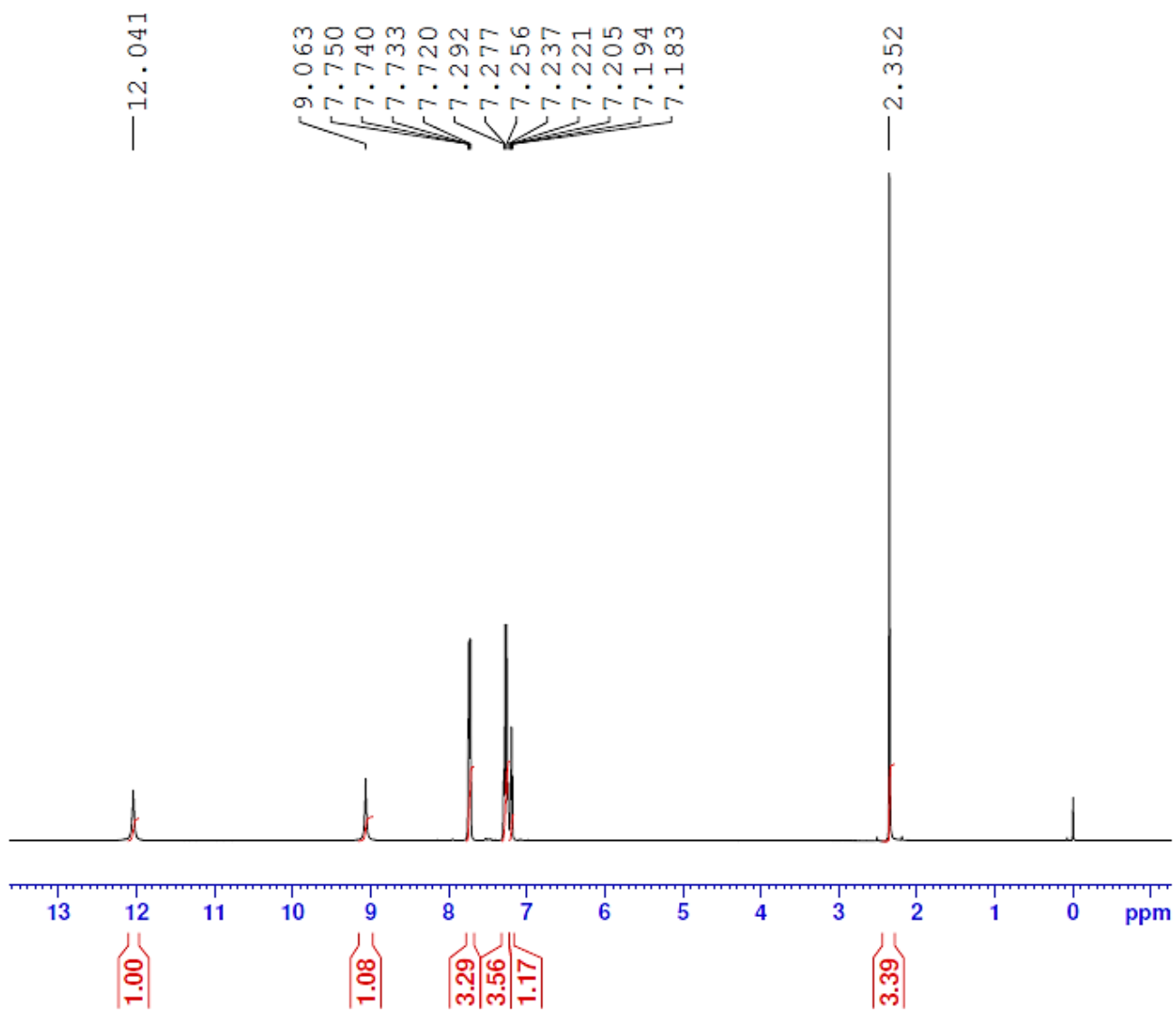


Fig. S3 ^1H NMR spectrum of L2.

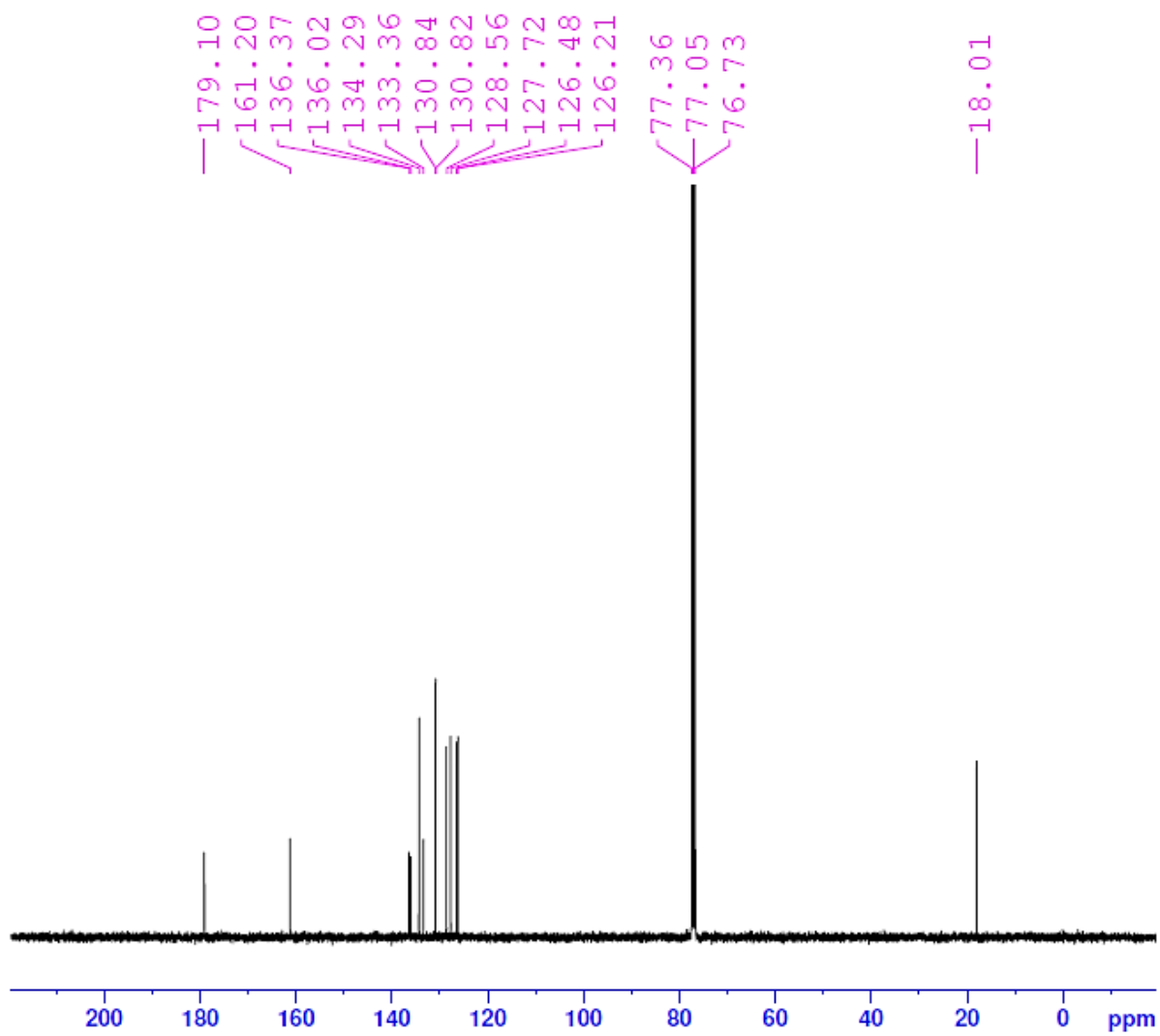


Fig. S4 ^{13}C NMR spectrum of L2.

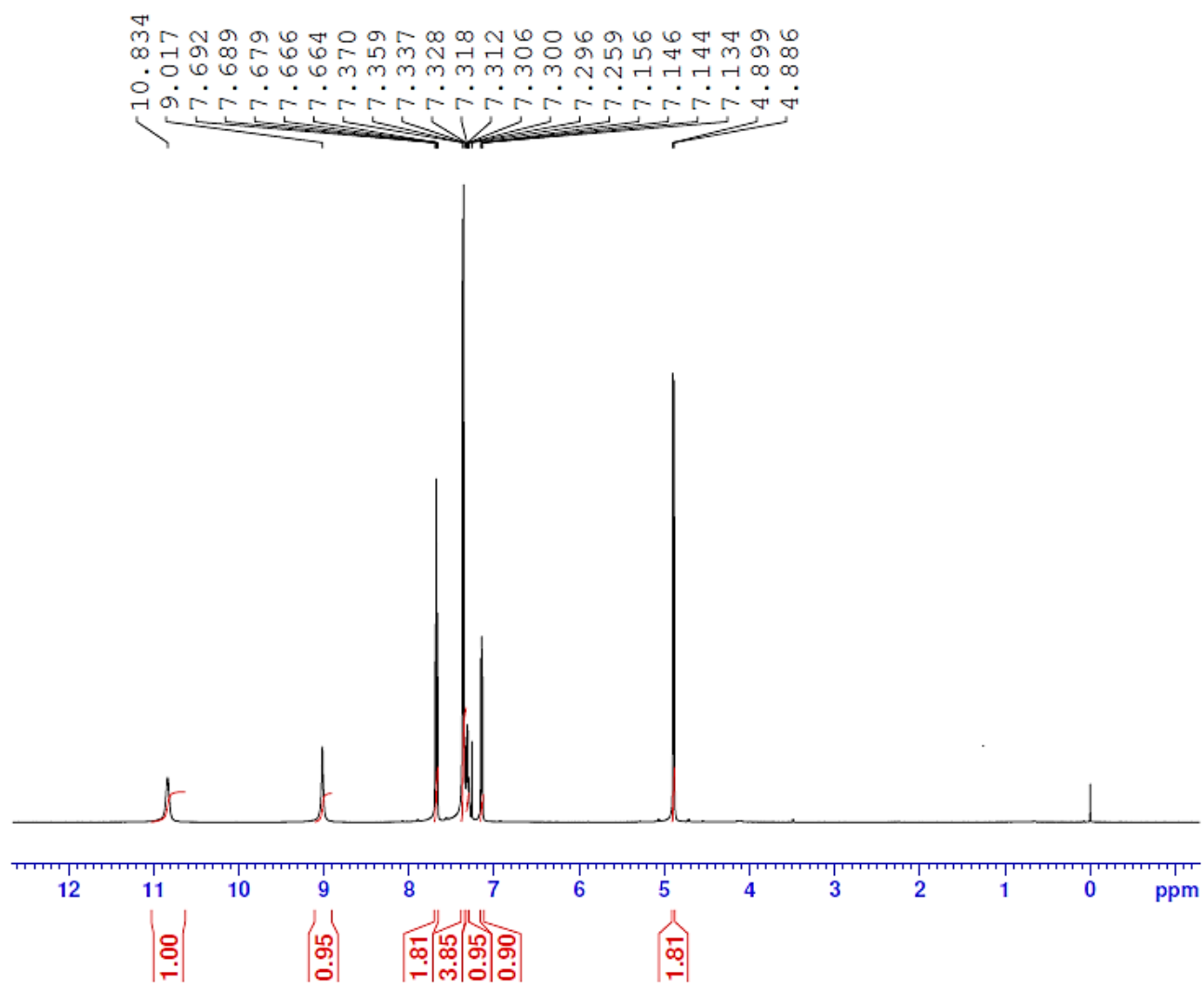


Fig. S5 ¹H NMR spectrum of L3.

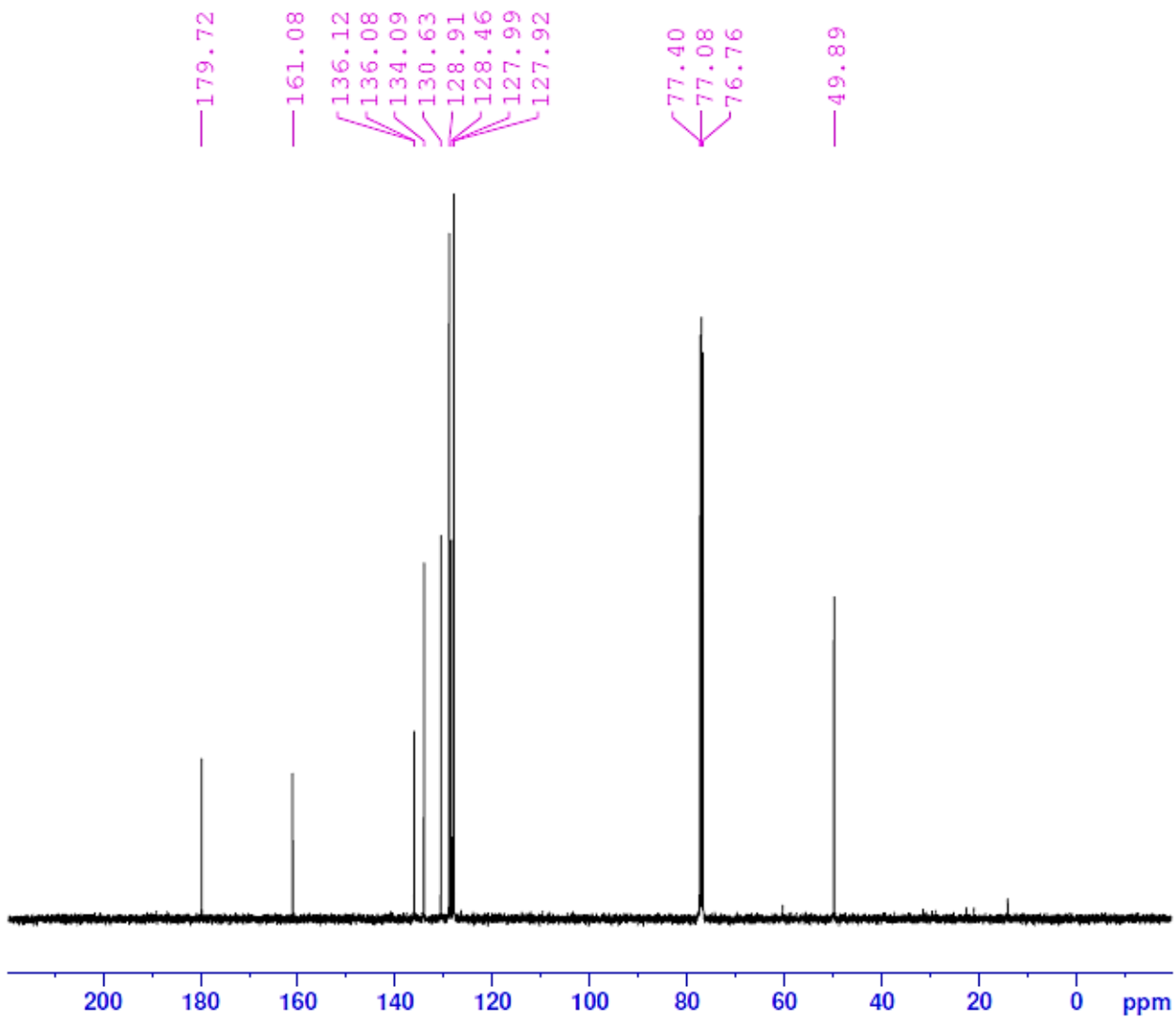


Fig. S6 ¹³C NMR spectrum of L3.

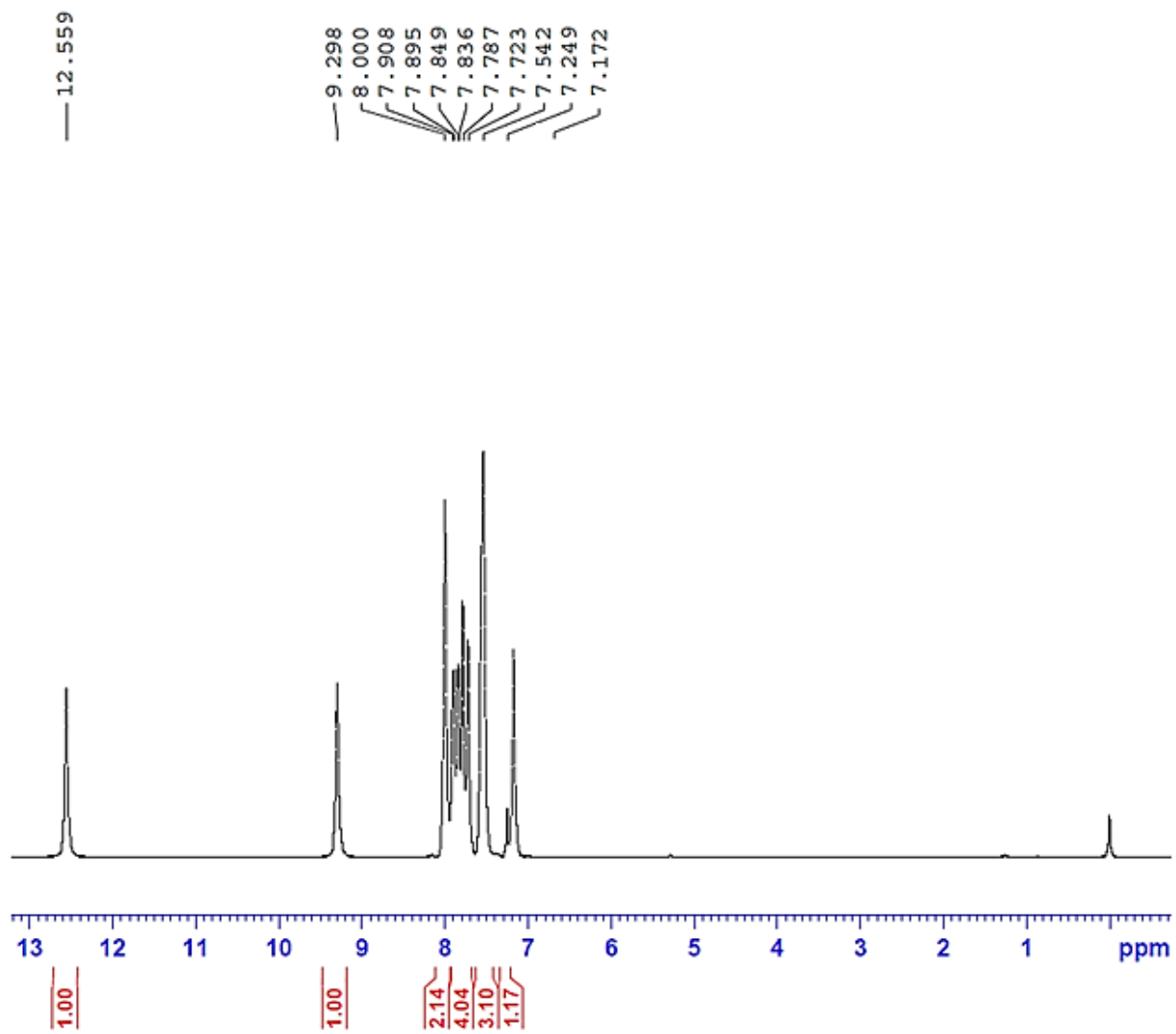


Fig. S7 ^1H NMR spectrum of L4.

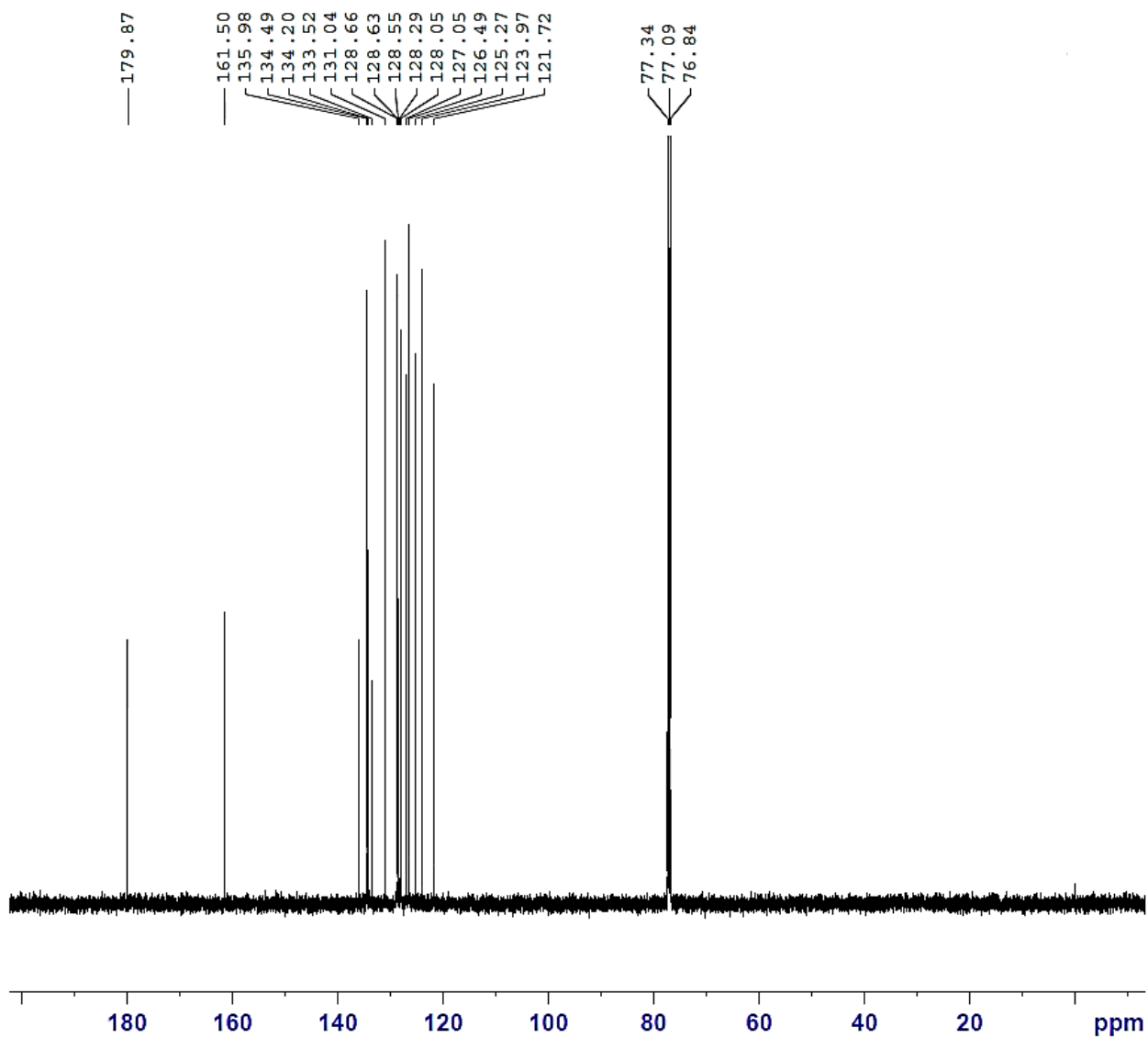


Fig. S8 ^{13}C NMR spectrum of L4.

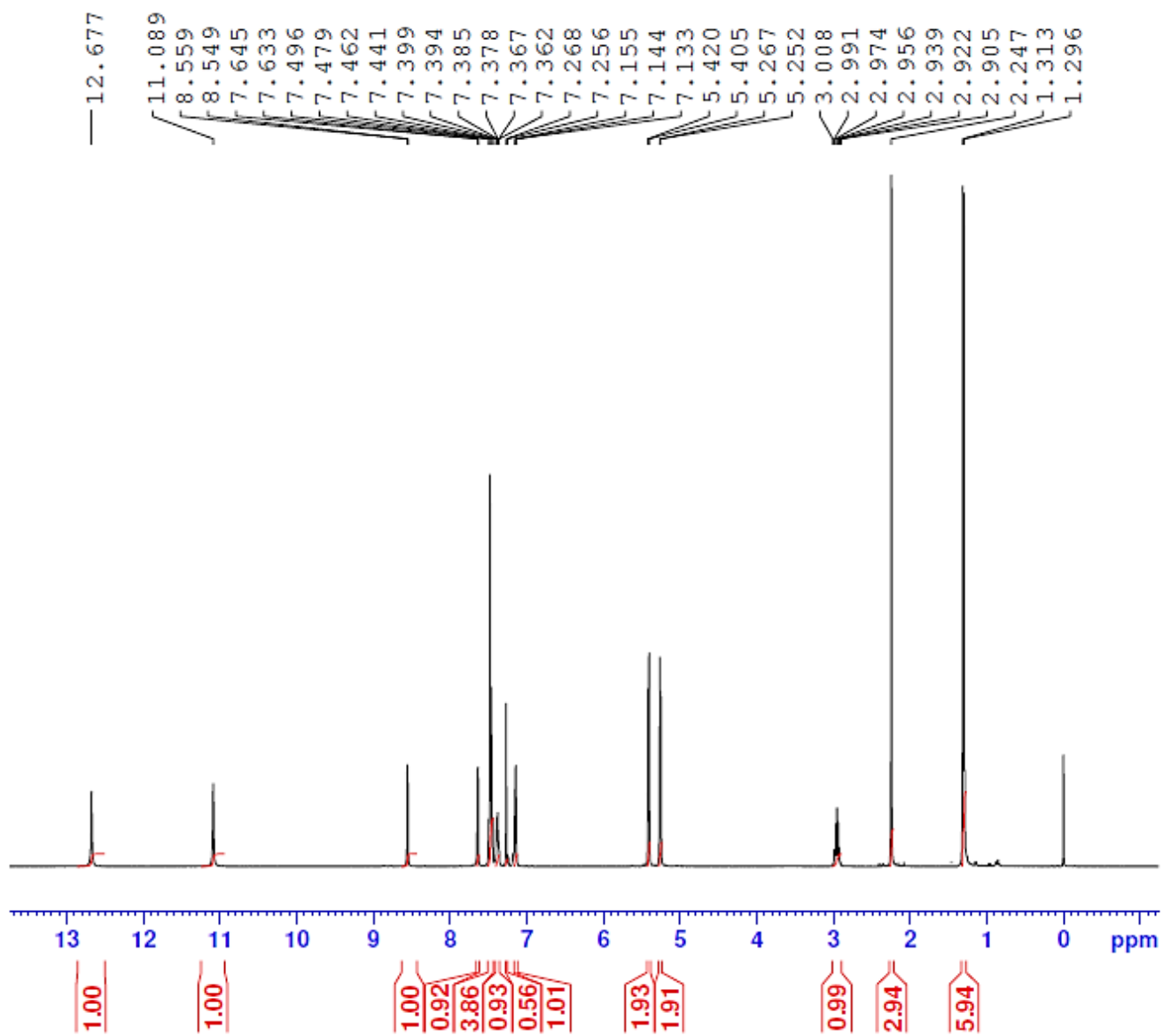


Fig. S9 ^1H NMR spectrum of **1**.

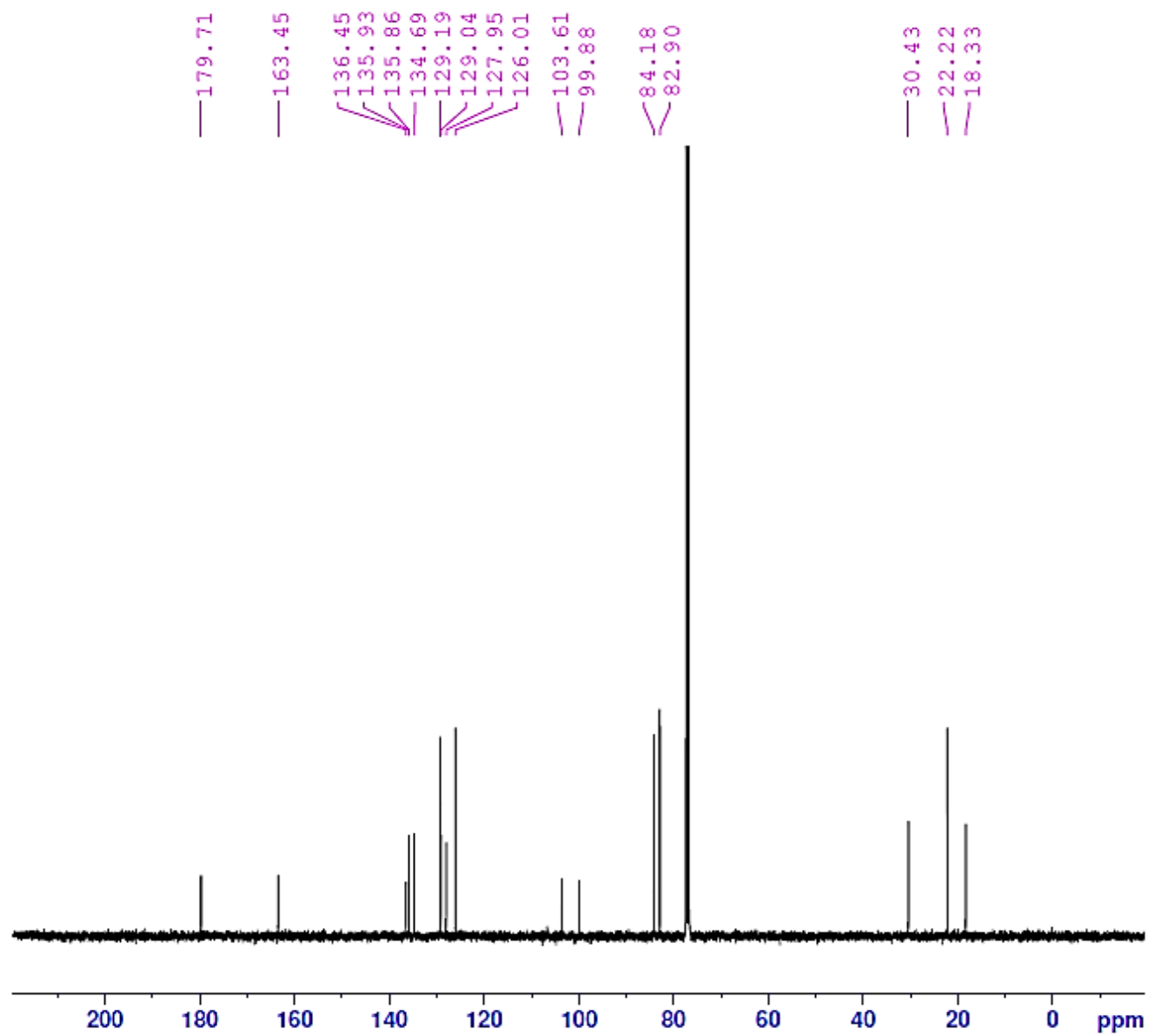


Fig. S10 ^{13}C NMR spectrum of **1**.

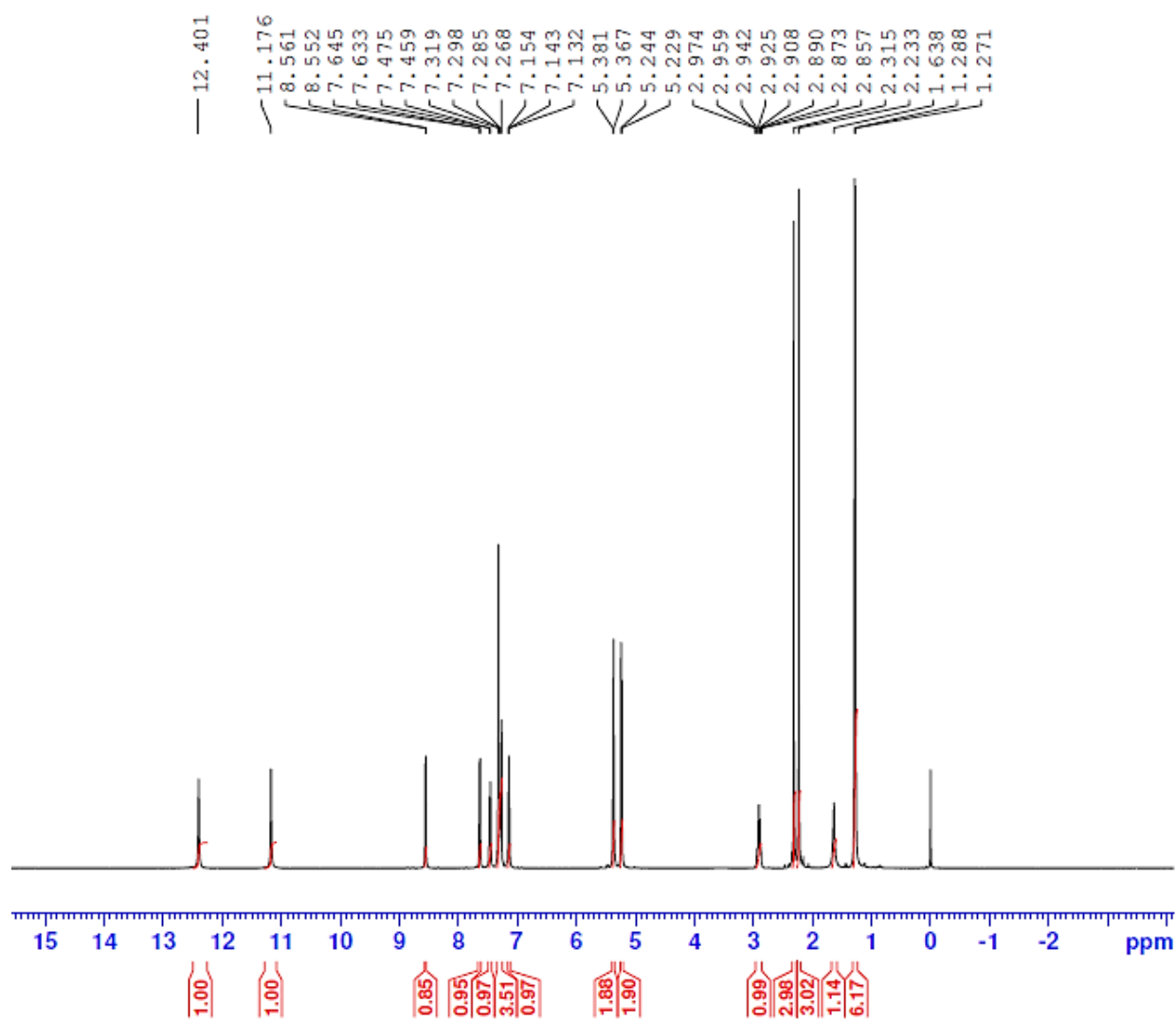


Fig. S11 ^1H NMR spectrum of **2**.

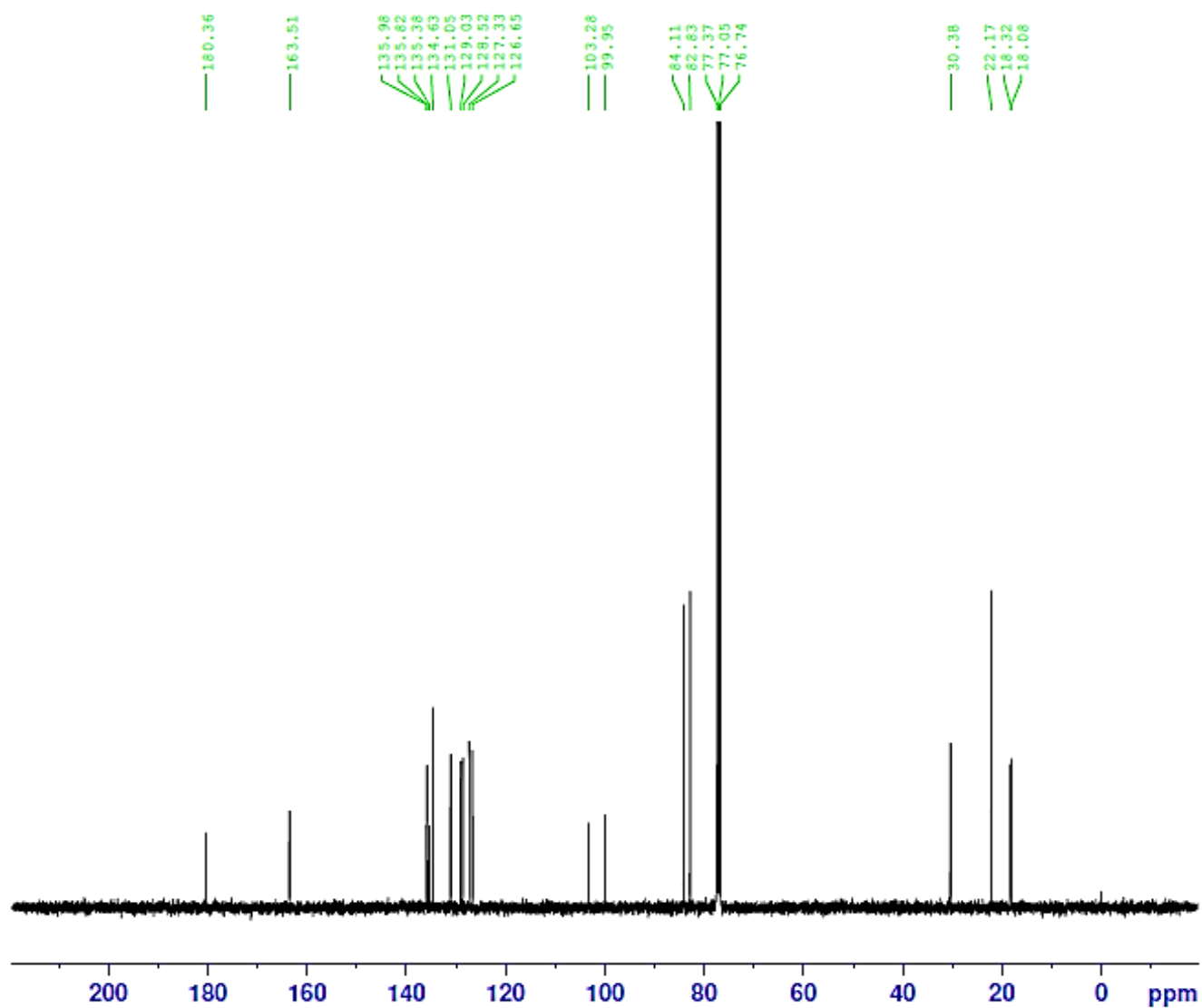


Fig. S12 ^{13}C NMR spectrum of **2**.

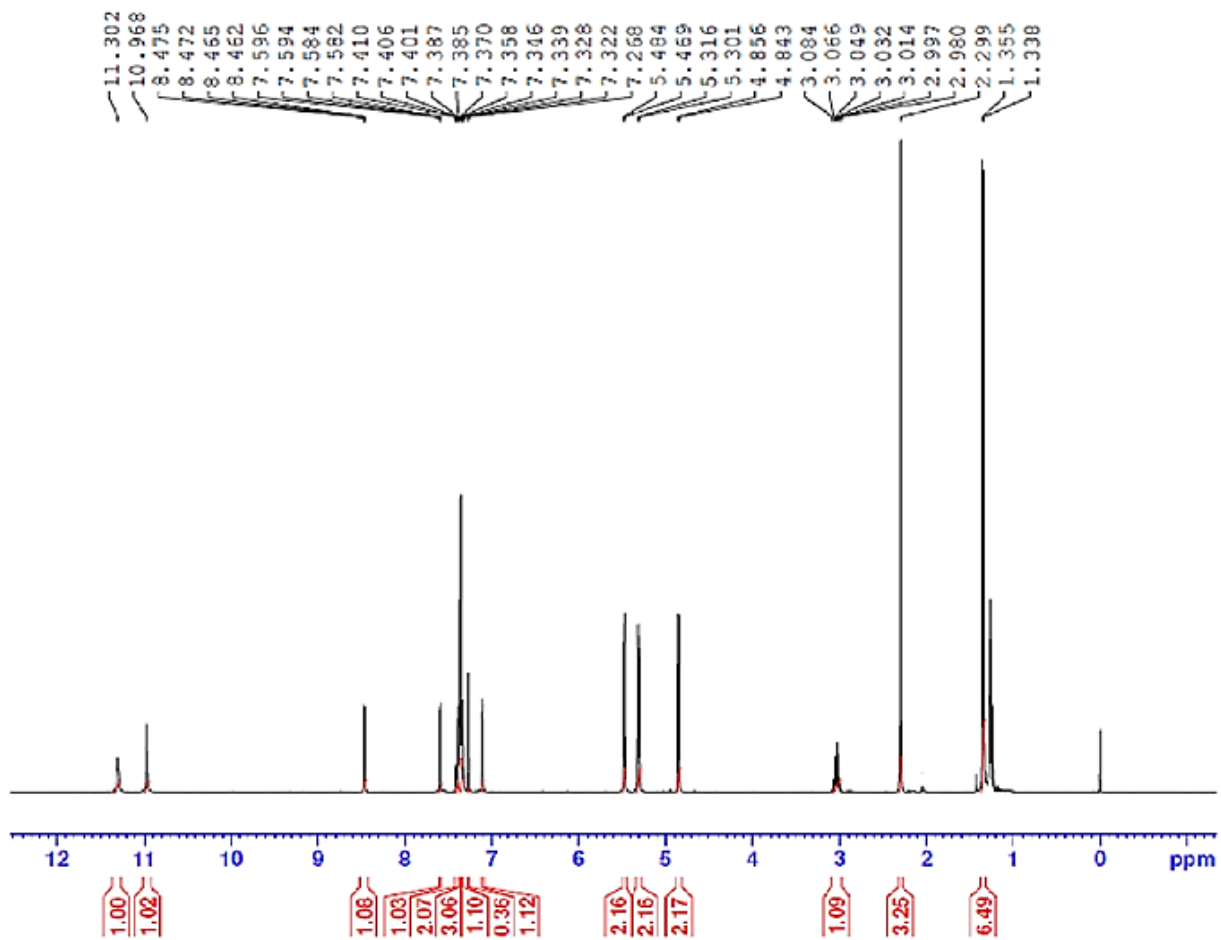


Fig. S13 ^1H NMR spectrum of **3**.

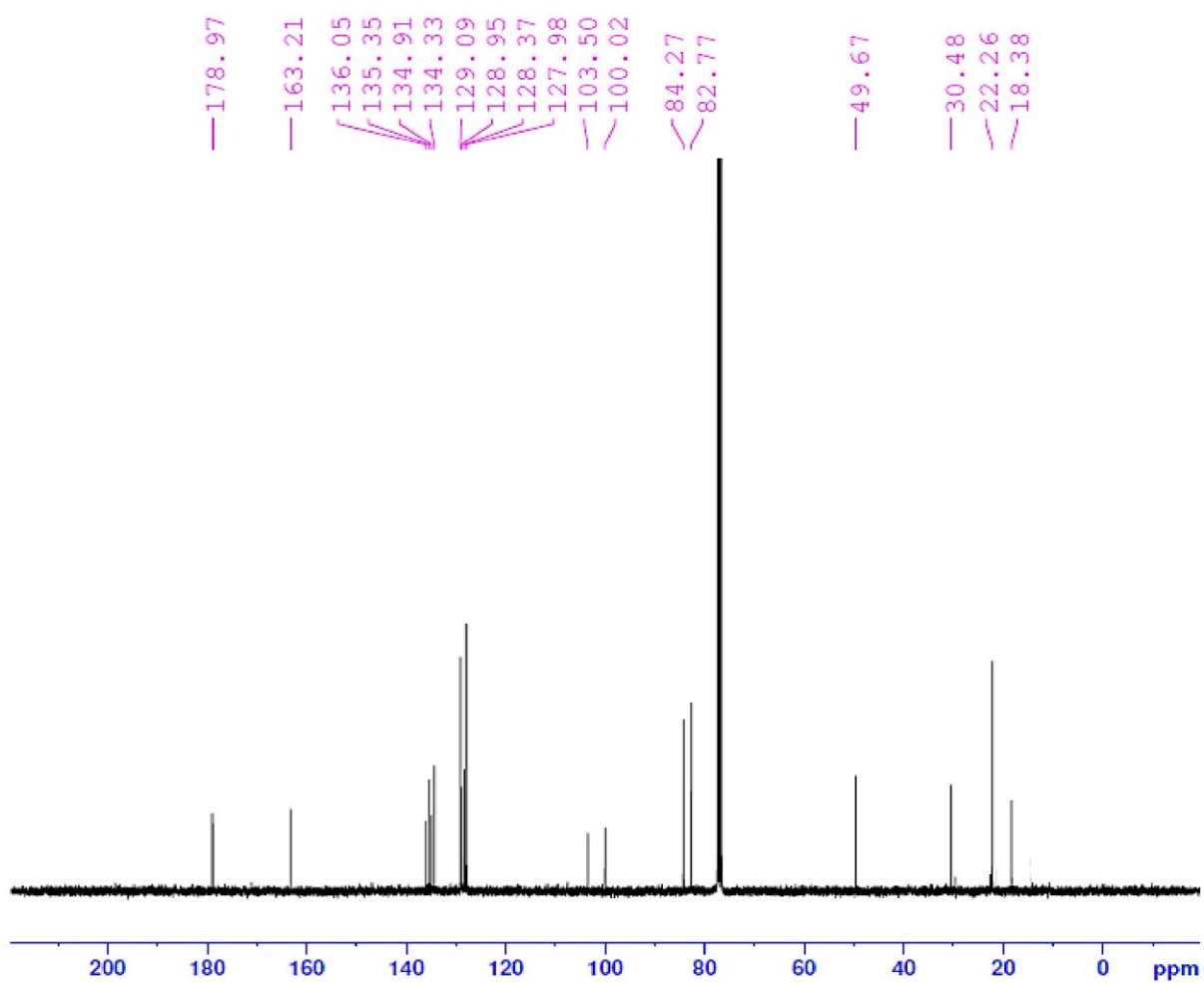


Fig. S14 ^{13}C NMR spectrum of **3**.

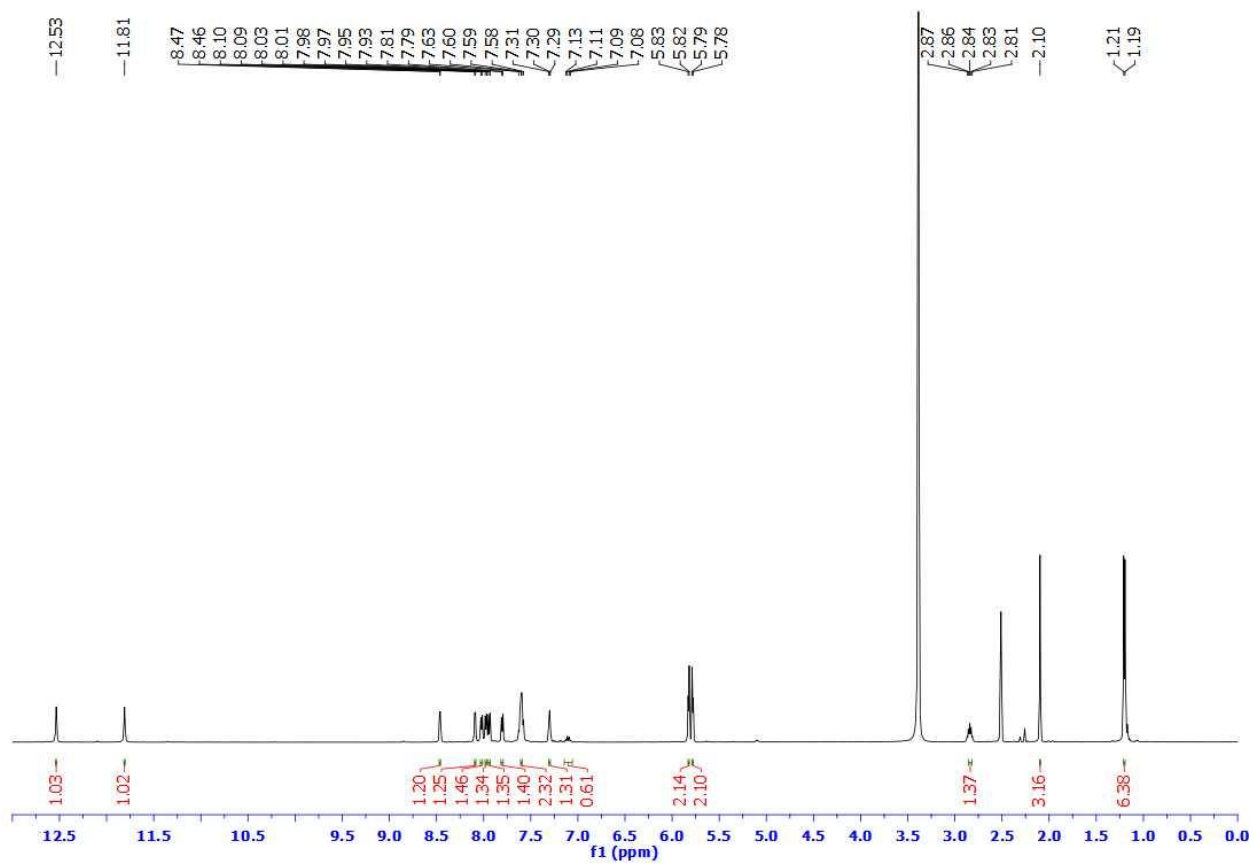


Fig. S15 ^1H NMR spectrum of 4.

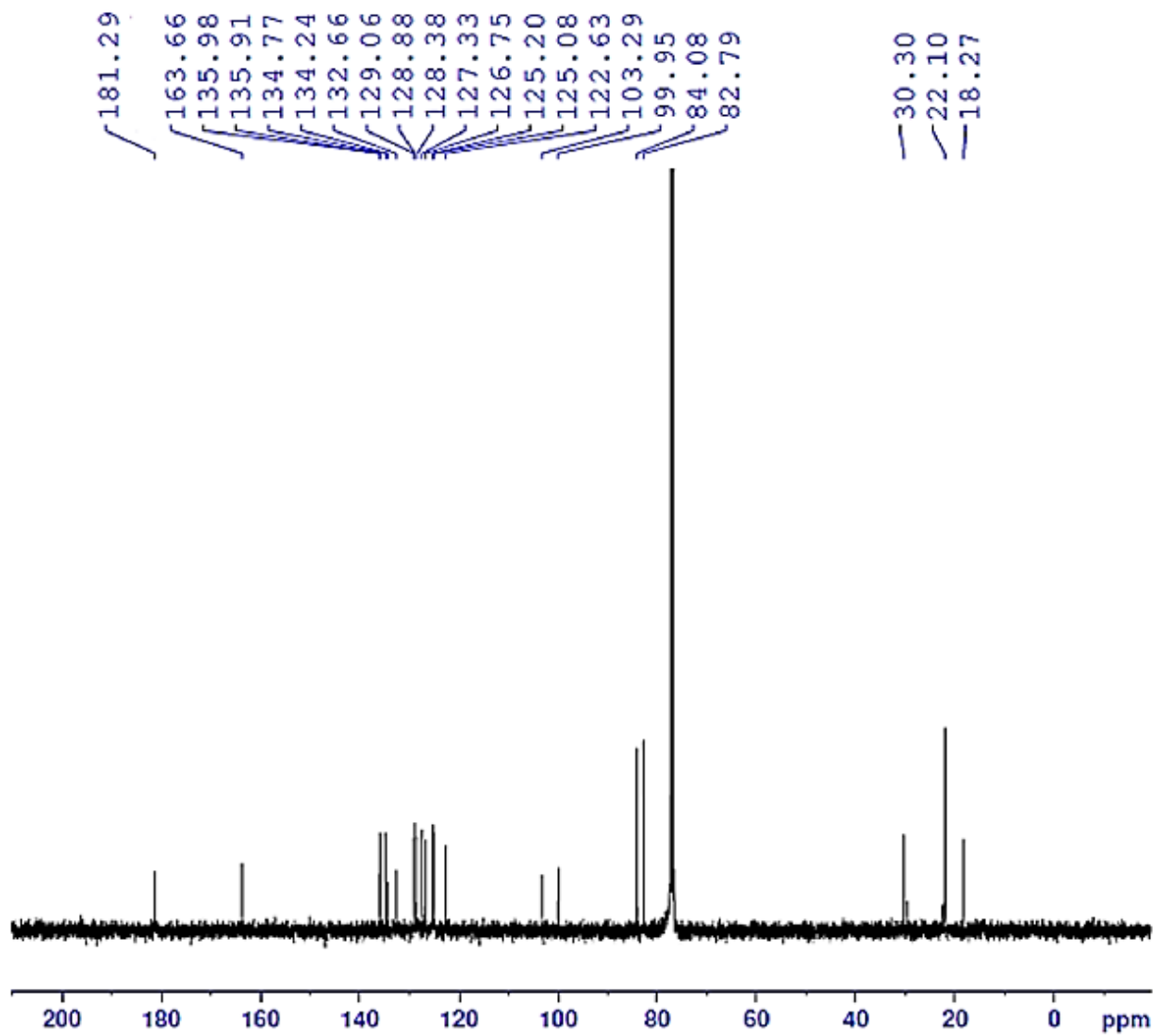


Fig. S16 ^{13}C NMR spectrum of **4**.

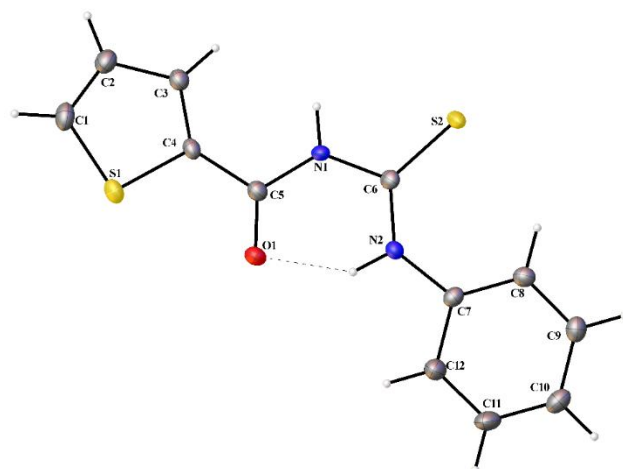


Fig. S17 Molecular structure of L1.

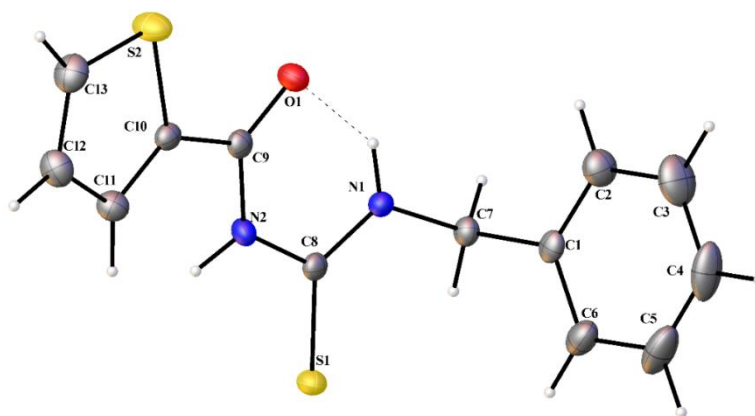


Fig. S18 Molecular structure of L3.

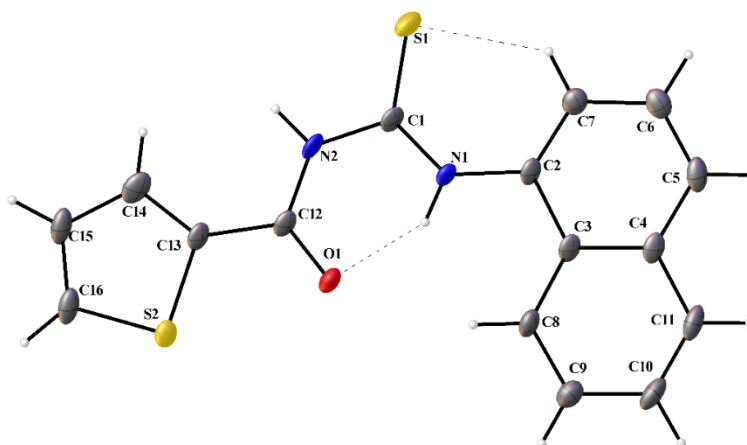


Fig. S19 Molecular structure of L4.

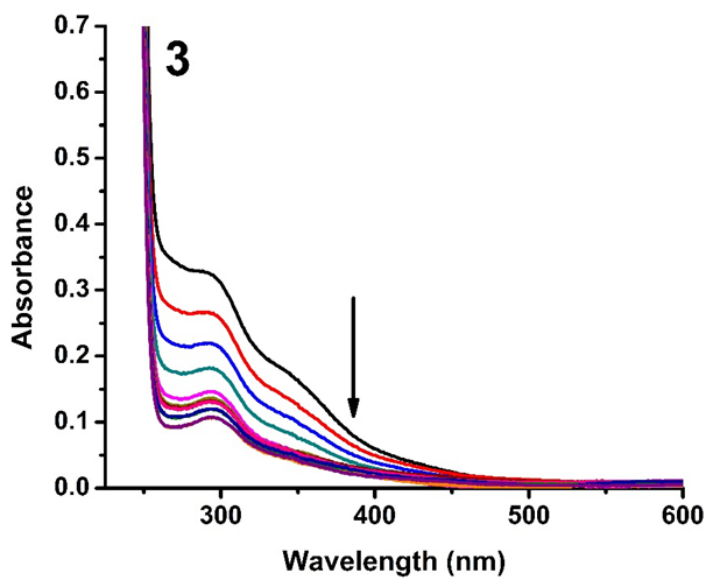
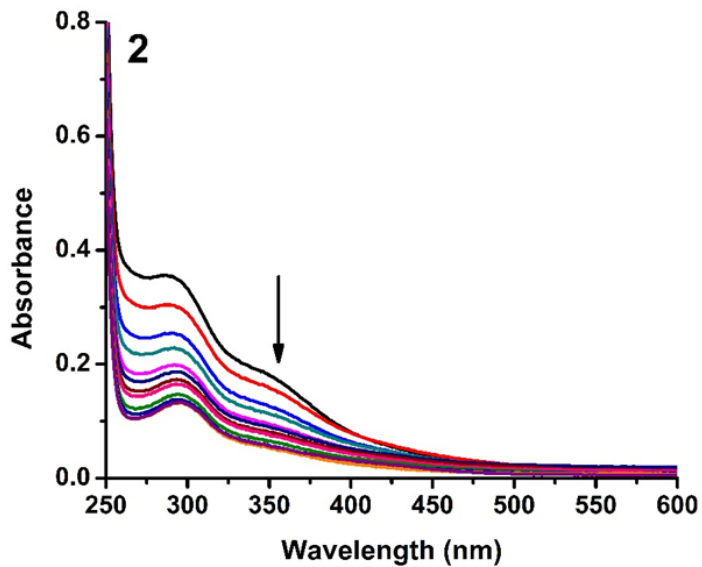
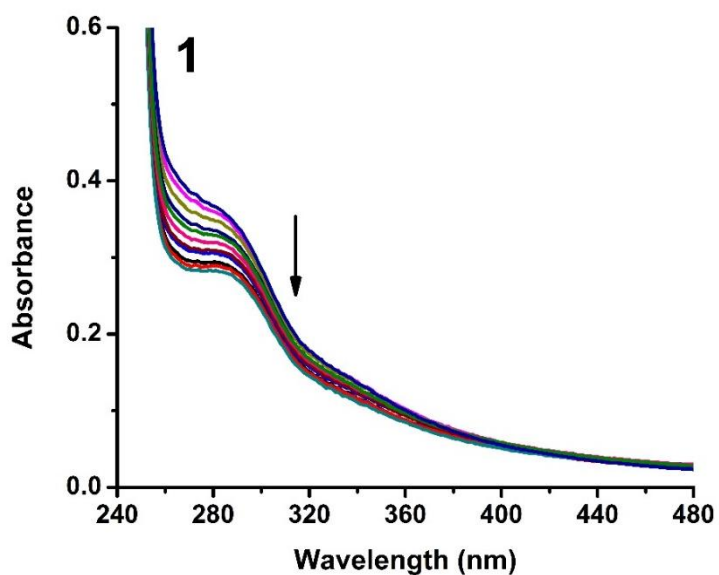


Fig. S20 Absorption spectra of complexes (1-3) in Tris-HCl buffer upon addition of CT DNA. [complex] = 2.5×10^{-5} M, [DNA] = 0-60 μ M. The arrow shows that the absorption intensity decreases upon increasing the DNA concentration.

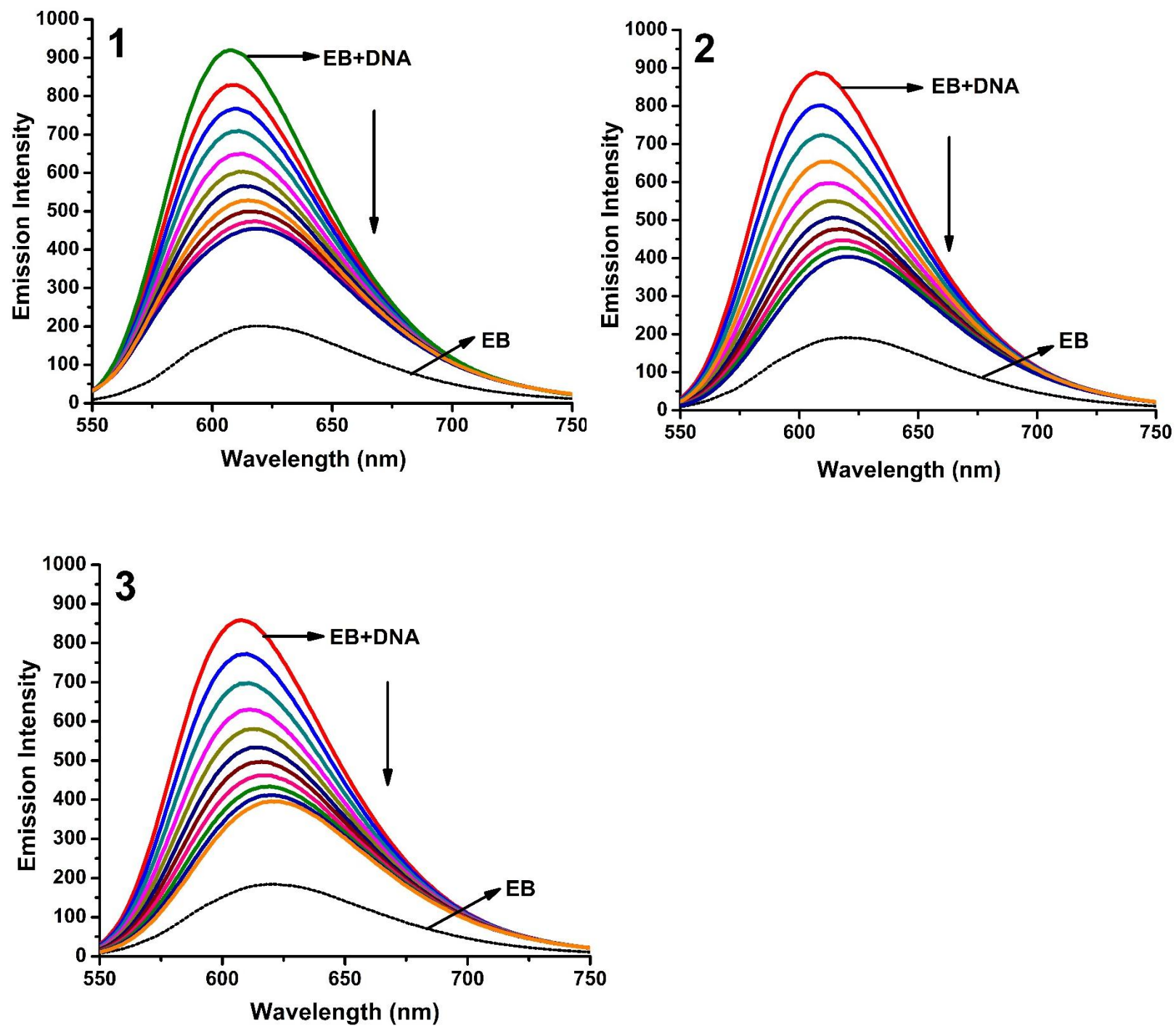


Fig. S21 Fluorescence quenching curves of EB bound to DNA in the presence of **1-3**. [DNA] = 5 μ M, [EB] = 5 μ M and [complex] = 0-50 μ M.

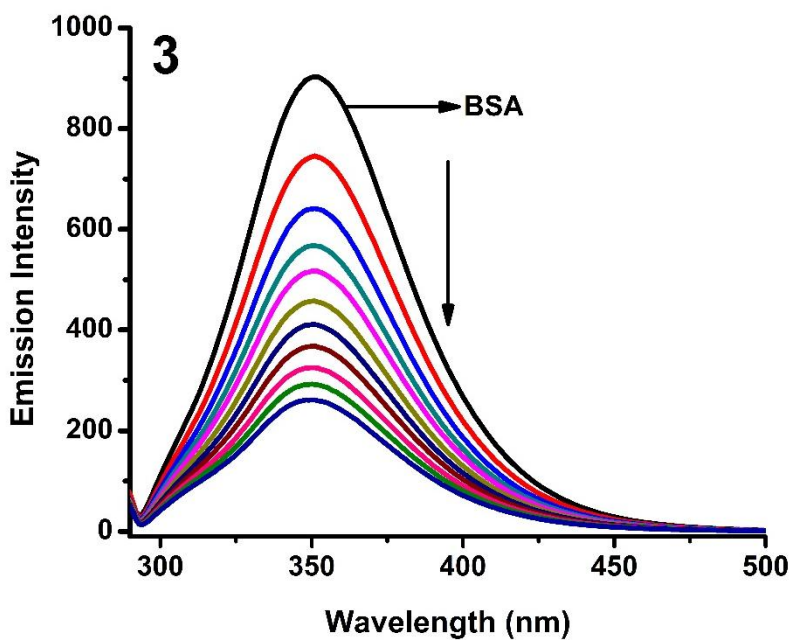
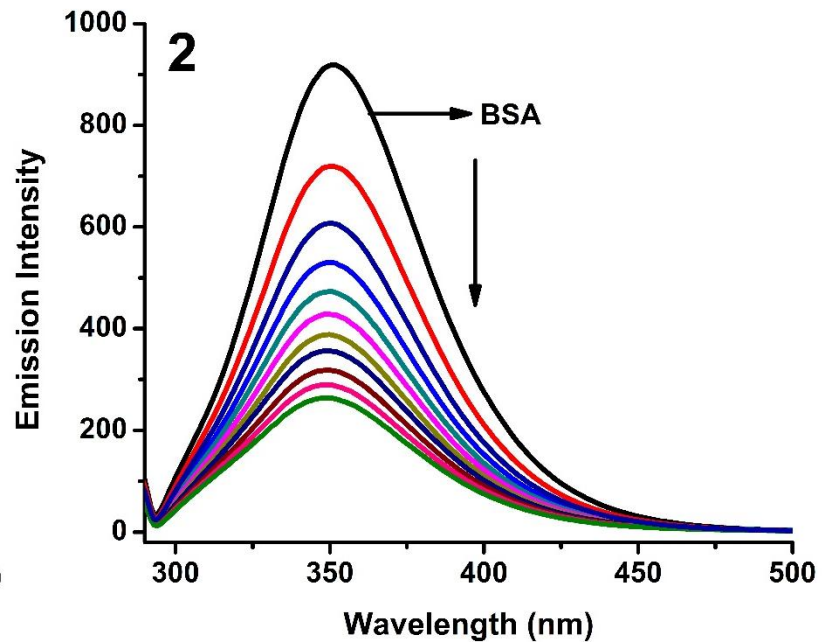
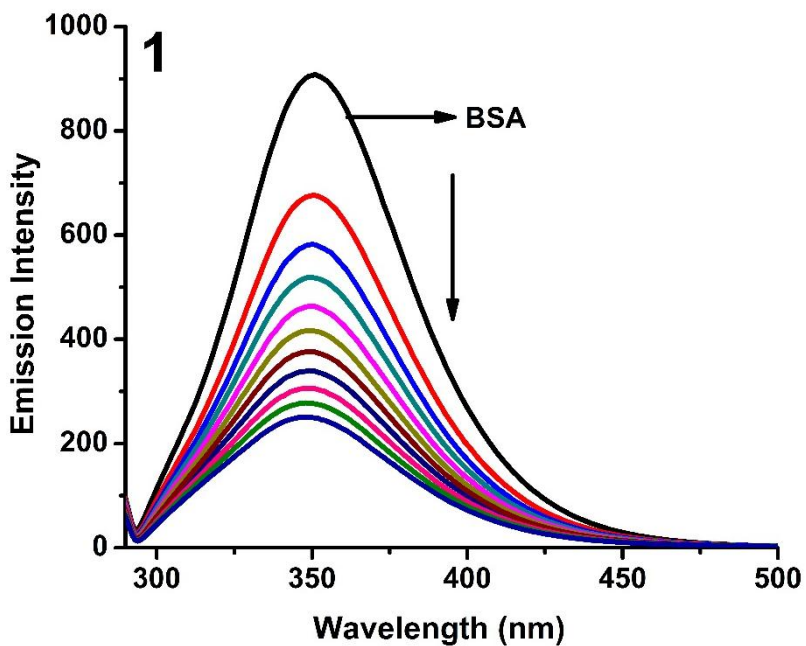


Fig. S22 Fluorescence quenching curves of BSA in the absence and presence of **1-3**. [BSA] = 1 μ M and [complex] = 0-20 μ M.

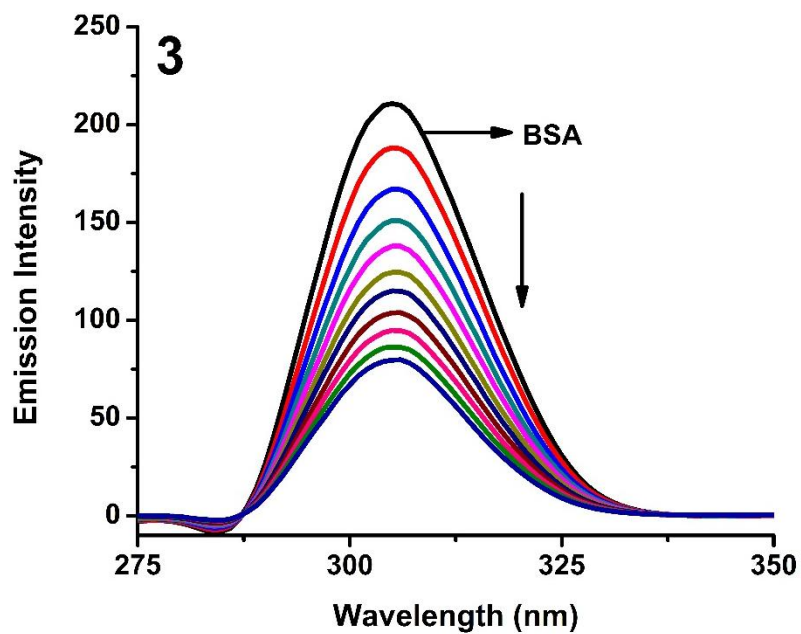
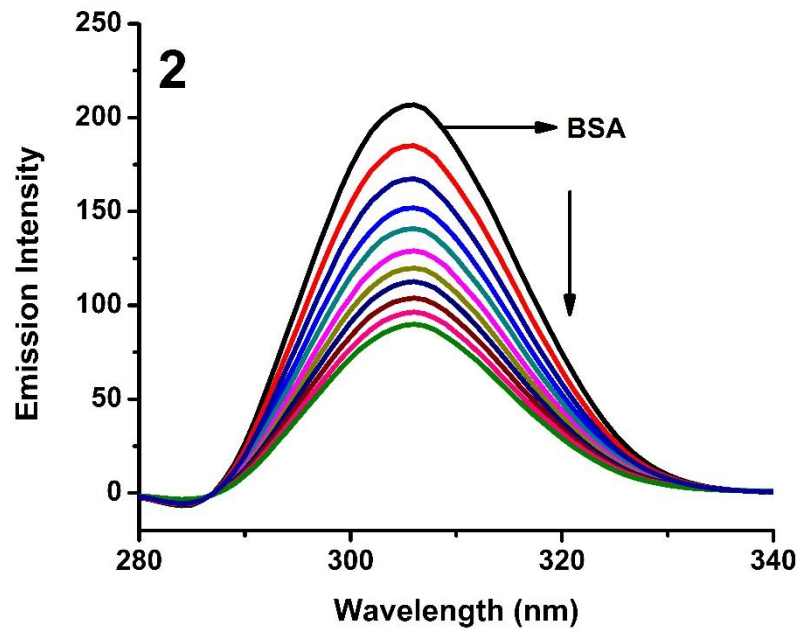
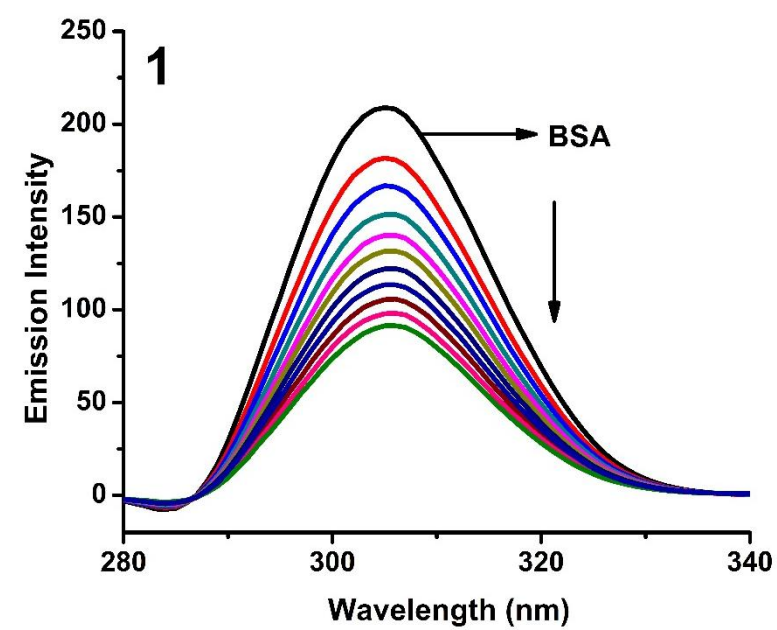


Fig. S23 Synchronous spectra of BSA (1 μM) as a function of concentration of 1-3 (0-20 μM) with $\Delta\lambda = 15$ nm.

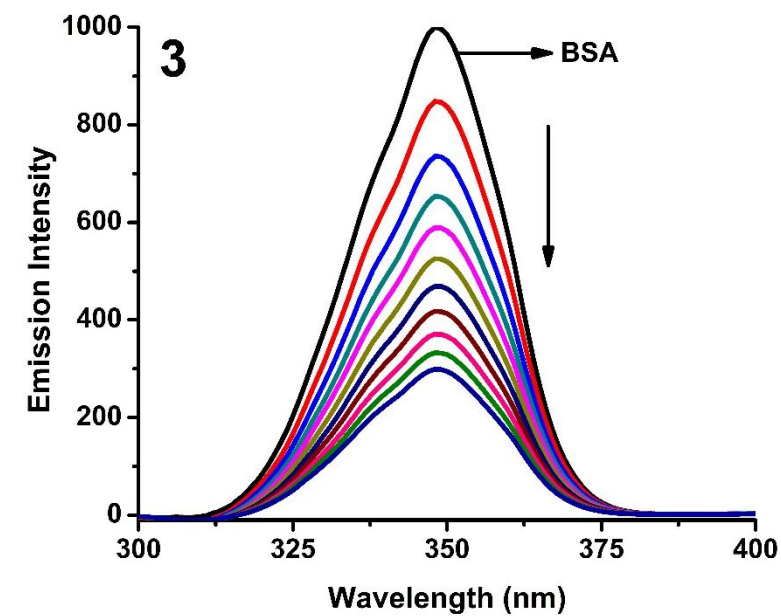
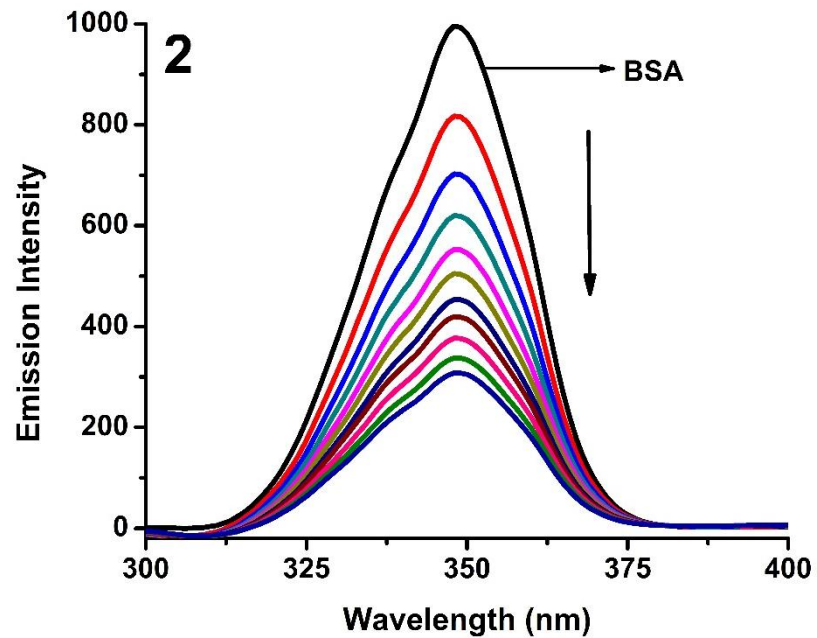
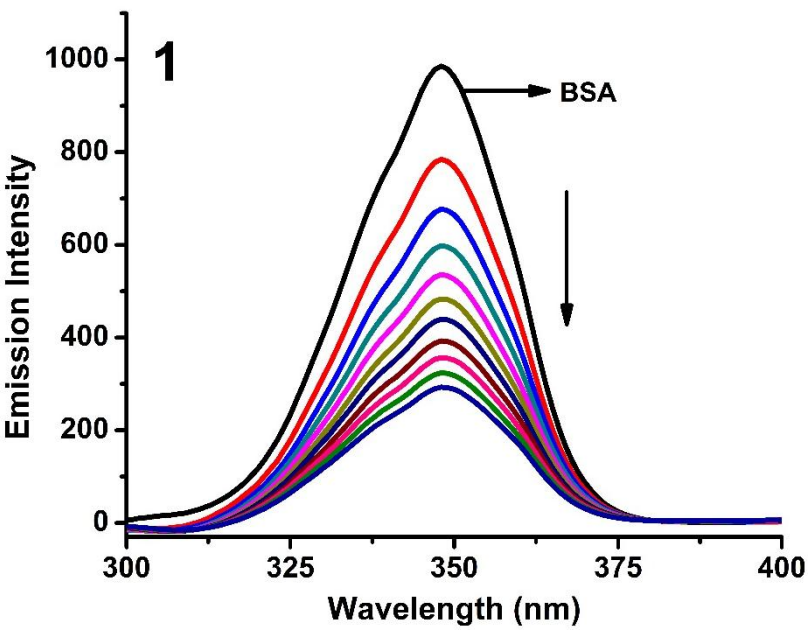


Fig. S24 Synchronous spectra of BSA (1 μM) as a function of concentration of **1-3** (0-20 μM) with $\Delta\lambda = 60$ nm.

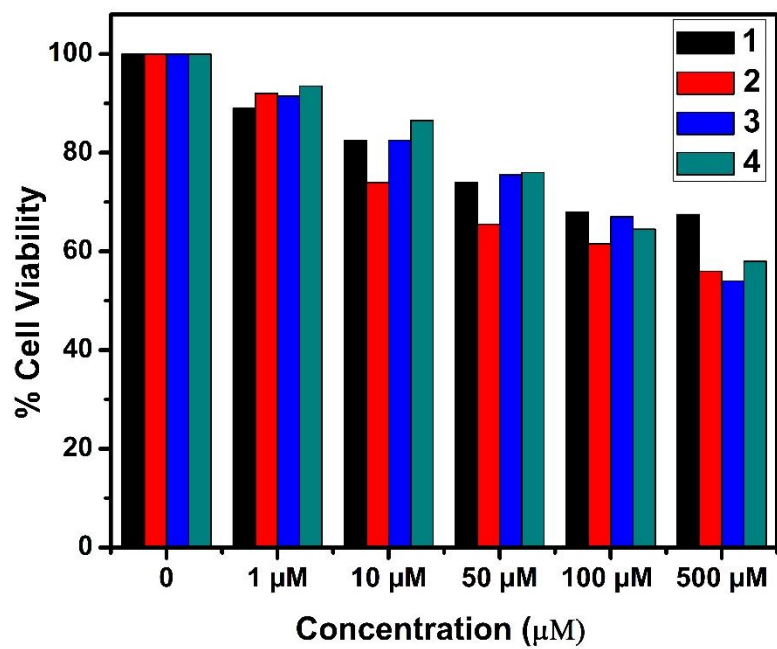


Fig. S25 Cytotoxicity of complexes **1-4** after 24 h incubation on L929 cell lines.

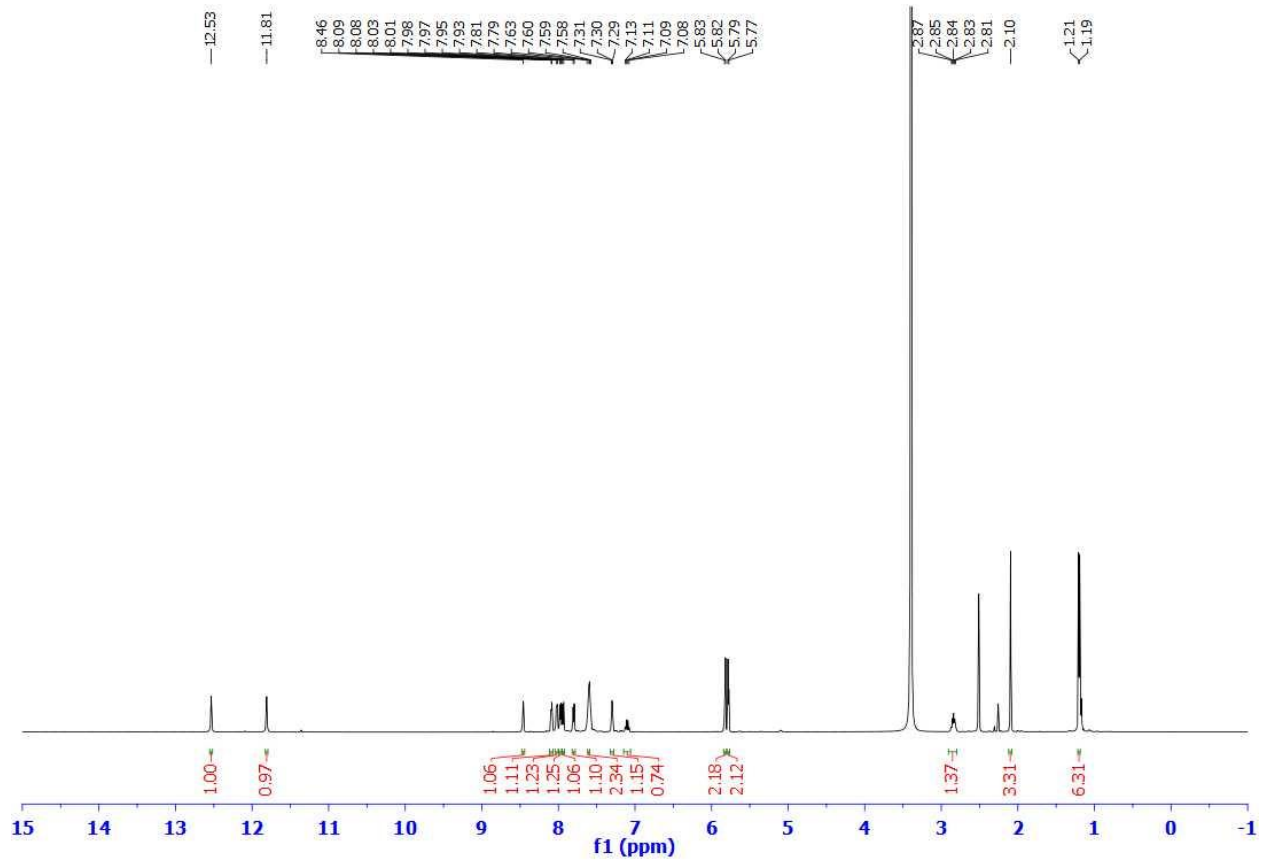


Fig. S26 ^1H NMR spectrum of **4** in DMSO-d_6 after 72 h

Table S1. Crystal data and structure refinement for ligands

	L1	L3	L4
Empirical formula	C ₁₂ H ₁₀ N ₂ OS ₂	C ₁₃ H ₁₂ N ₂ OS ₂	C ₁₆ H ₁₂ N ₂ OS ₂
Formula weight	262.34	276.37	312.40
Temperature (K)	110.15	150.15	150.15
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P 1 21/n 1</i>	<i>P-1</i>	<i>P 1 21/c 1</i>
<i>a</i> (Å)	9.669(2)	6.0928(13)	14.808(3)
<i>b</i> (Å)	4.7975(12)	8.8375(19)	5.9200(13)
<i>c</i> (Å)	25.794(6)	12.646(3)	16.679(4)
α (°)	90	89.795(2)	90
β (°)	98.061(2)	84.279(2)	103.112(3)
γ (°)	90	71.621(2)	90
Volume (Å ³)	1184.6(5)	642.7(2)	1424.0(5)
<i>Z</i>	4	2	4
Density (calculated) Mg/m ³	1.471	1.428	1.457
Absorption coefficient (mm ⁻¹)	0.432	0.402	0.373
<i>F</i> (000)	544	288	648
Crystal size (mm ³)	0.58x0.4x 0.35	0.57x0.54x0.48	0.54x0.54x 0.12
Theta range for data collection (°)	2.165 to 27.483	2.430 to 27.485	1.412 to 27.421
Index ranges	-12<= <i>h</i> <=12, -6<= <i>k</i> <=6, -33<= <i>l</i> <=33	-7<= <i>h</i> <=7, -11<= <i>k</i> <=11, -16<= <i>l</i> <=16	19<= <i>h</i> <=19, -7<= <i>k</i> <=7, -21<= <i>l</i> <=21

Reflections collected	12786	7387	24391
Independent reflections [R(int)]	2679 [R(int) = 0.0431]	2887[R(int) = 0.0310]	3221 [R(int) = 0.0633]
Completeness to theta = 25.242	99.8	99.0	99.8
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5881	0.7456 and 0.5125	0.7456 and 0.3326
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameter	2679 / 0 / 154	2887 / 0 / 163	3221 / 13 / 201
Goodness-of-fit on F^2	1.130	1.066	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0362 wR2 = 0.0821	R1 = 0.0334 wR2 = 0.0863	R1 = 0.0445 wR2 = 0.1189
R indices (all data)	R1 = 0.0417 wR2 = 0.0846	R1 = 0.0353 wR2 = 0.0873	R1 = 0.0497 wR2 = 0.1264
Largest diff. peak and hole (e.Å ⁻³)	0.333 and -0.271	0.287 and -0.419	0.499 and -0.515
