

Supplementary Material

A Fluorecent Chemosensor for Zn²⁺ ion Based on a C₃-Symmetrical and Pre-organized 2,2',2''-Nitrilotribenzoic Acid Material

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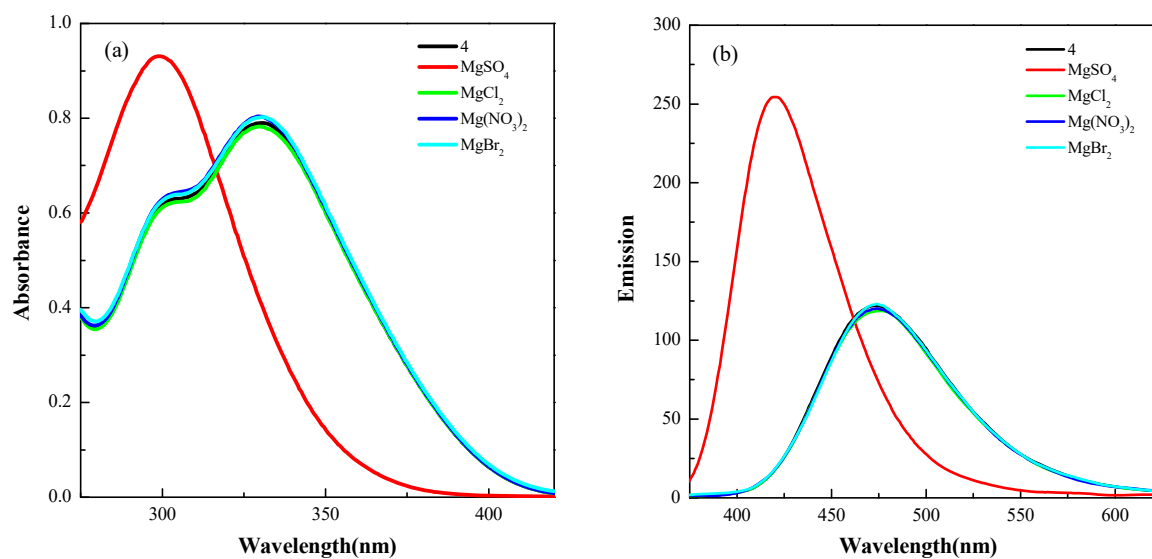


Fig. S1 Absorption and emission spectrum of **4** (3.5×10^{-5} M, $\lambda_{\text{ex}} = 325$ nm) in DMSO after addition of salt with the ratio of [salt]/[**4**](30:1).



Fig. S2 Absorption and emission spectrum of **4** (4×10^{-5} M, $\lambda_{\text{ex}} = 325$ nm) in THF after addition of salt sulfate with the ratio of $[\text{salt}]/[\mathbf{4}](30:1)$.

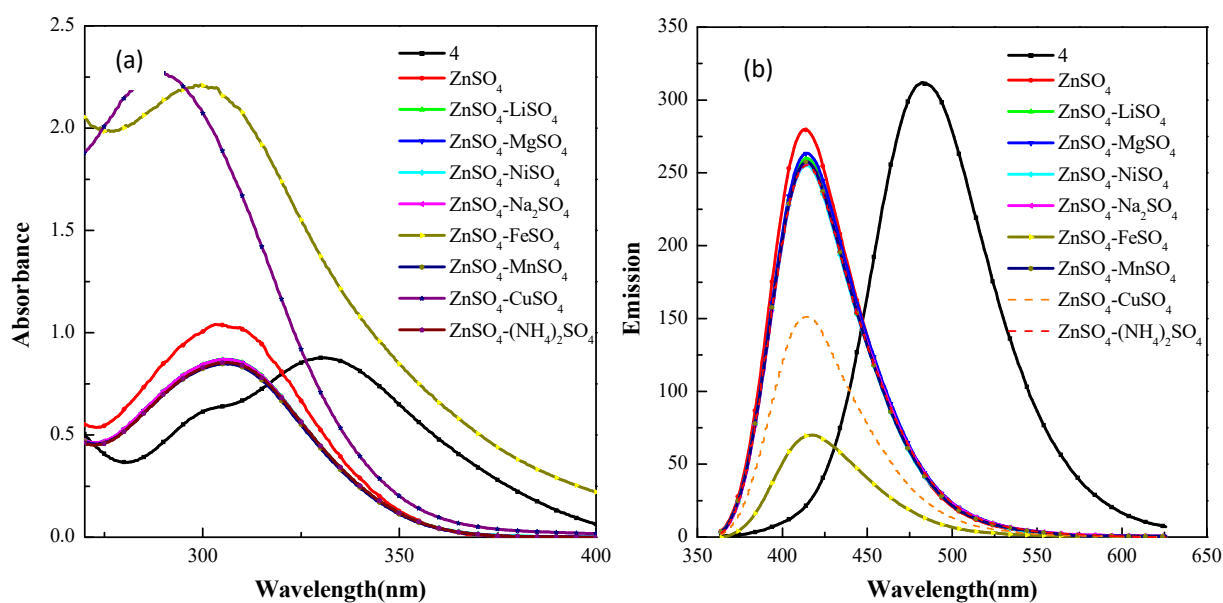


Fig. S3 Absorbance and fluorescence of **4** containing 12 equiv. of ZnSO_4 (a and b in DMSO, 3.5×10^{-5} M, $\lambda_{\text{ex}} = 325$ nm) exposed to 12 equiv. of various metal ions.

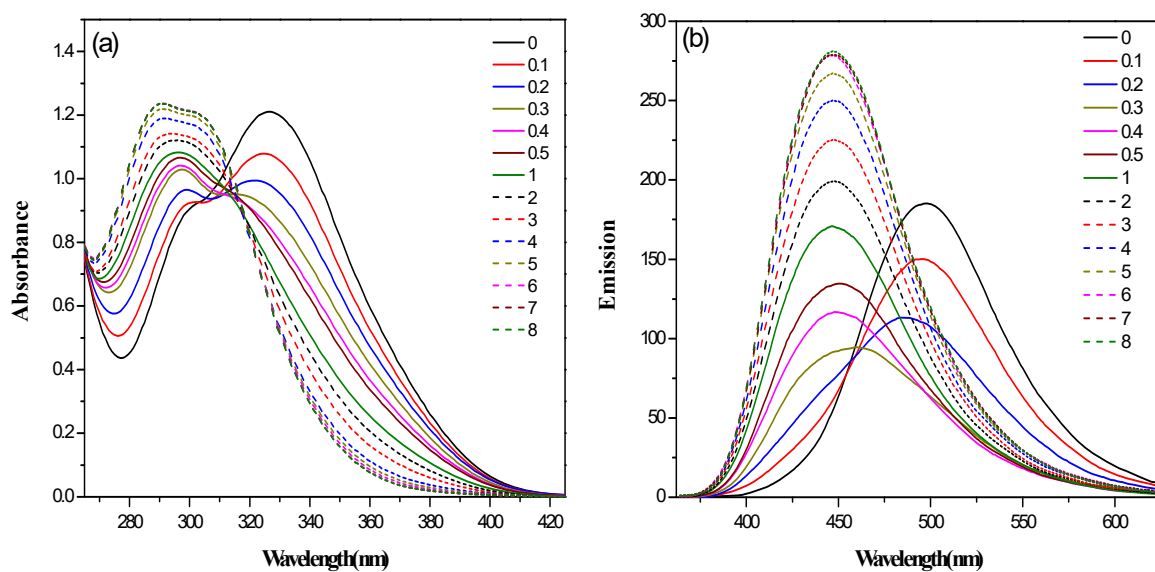


Fig. S4 Absorption and emission spectrum change of **4** (5×10^{-5} M, $\lambda_{\text{ex}} = 325$ nm) in MeOH after addition of Znic sulfate with the different equiv (0, 0.1, 0.2, 0.3, 0.4, 0.5, 1, 2, 3, 4, 5, 6, 7 and 8 equiv).

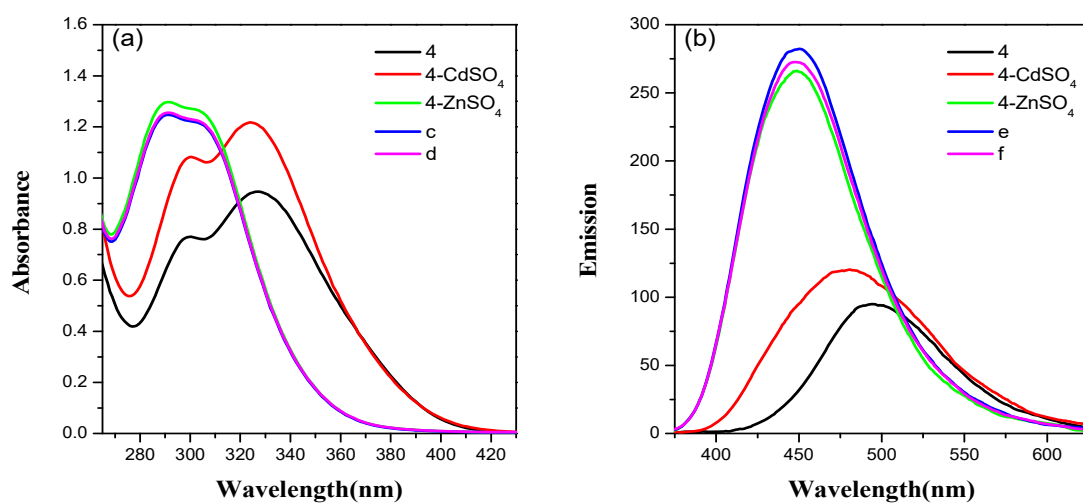


Fig. S5. Absorbance and fluorescence spectrum of **4** containing 12 equiv. of ZnSO_4 or CdSO_4 (in MeOH, 5×10^{-5} M), the spectrum change of **4** containing 12 equiv. of CdSO_4 with subsequent addition of 12 equiv. of ZnSO_4 (c and e), and the spectrum change of **4** containing 12 equiv. of ZnSO_4 with subsequent addition of 12 equiv. of CdSO_4 (d and f).

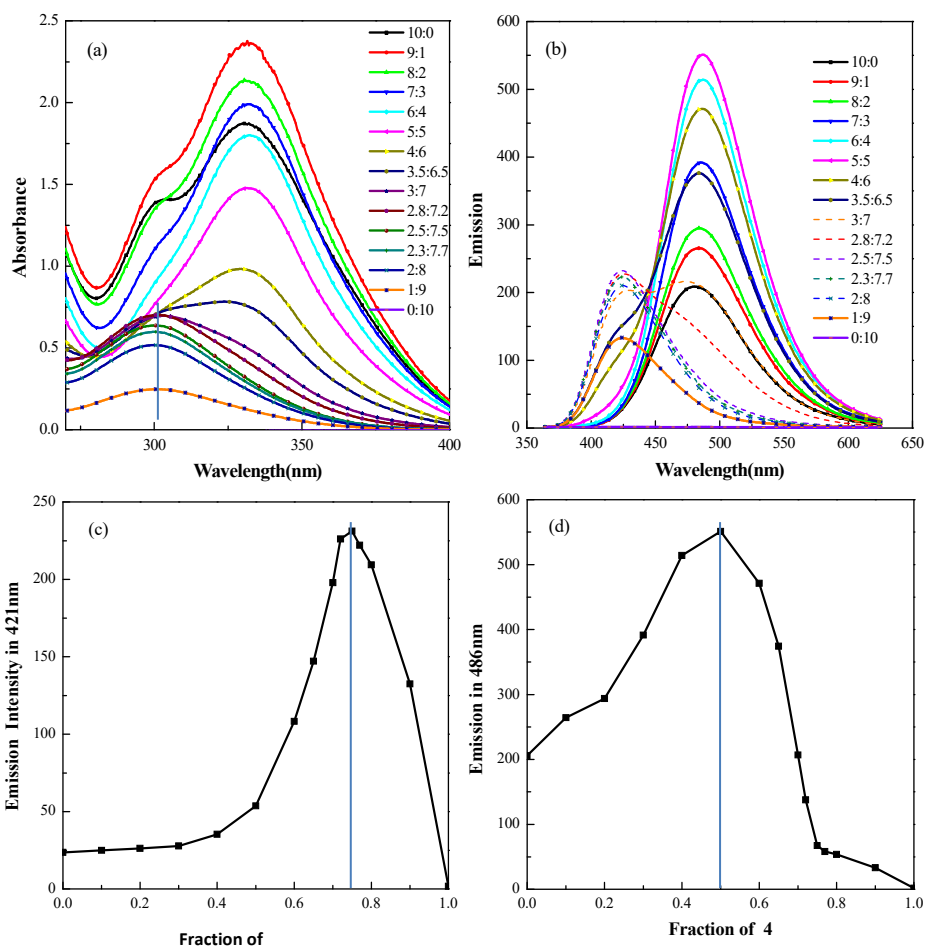


Fig. S6 Absorption and Emission spectrum of **4** in DMSO after addition of MgSO_4 with the different ratio of $[\text{salt}]/[\mathbf{4}]$ (a and b), under the condition of an invariant total concentration ($5 \times 10^{-5} \text{ M}$, $\lambda_{\text{ex}} = 325 \text{ nm}$). A Job plot analysis between **4** and MgSO_4 (c and d).

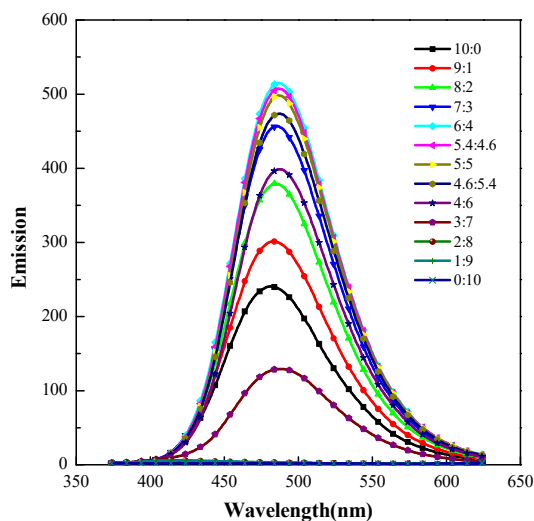


Fig. S7 Emission spectrum (a) of **4** in DMSO after addition of NiSO_4 with the different ratio of

[salt]/[4], under the condition of an invariant total concentration (5×10^{-5} M, $\lambda_{\text{ex}}= 325$ nm).

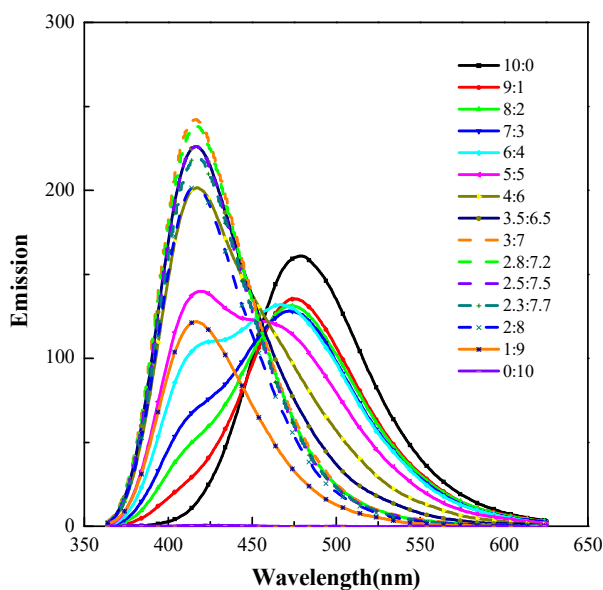


Fig. S8 Emission spectrum of **4** in DMSO after addition of ZnSO_4 with the different ratio of [salt]/[4], under the condition of an invariant total concentration (5×10^{-5} M, $\lambda_{\text{ex}}= 325$ nm).

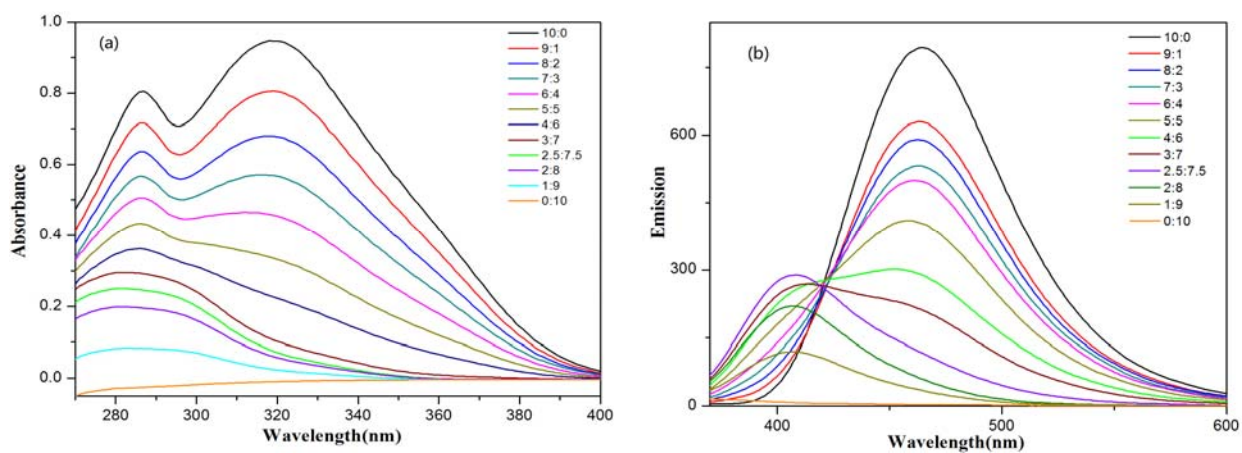


Fig. S9 Absorbance and emission spectrum of **1** in DMSO after addition of Zn^{2+} with the different ratio of [1]/[salt], under the condition of an invariant total concentration (3.5×10^{-4} M, $\lambda_{\text{ex}}= 325$ nm).

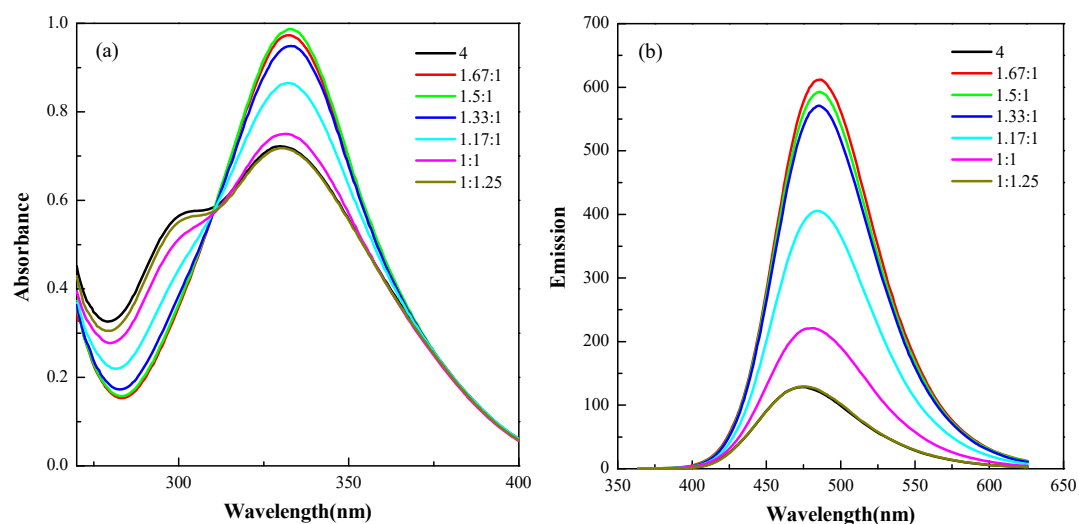


Fig. S10 Absorption and emission spectrum of **4** (3.5×10^{-5} M, a and b, $\lambda_{\text{ex}} = 325$ nm) in DMSO after addition of sodium sulfate with the different ratio of $[\text{SO}_4^{2-}]/[\text{COOH}]$

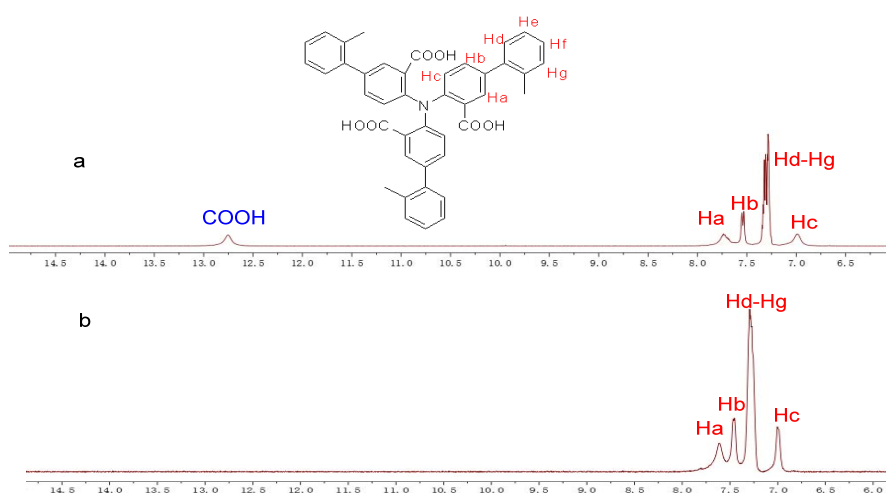
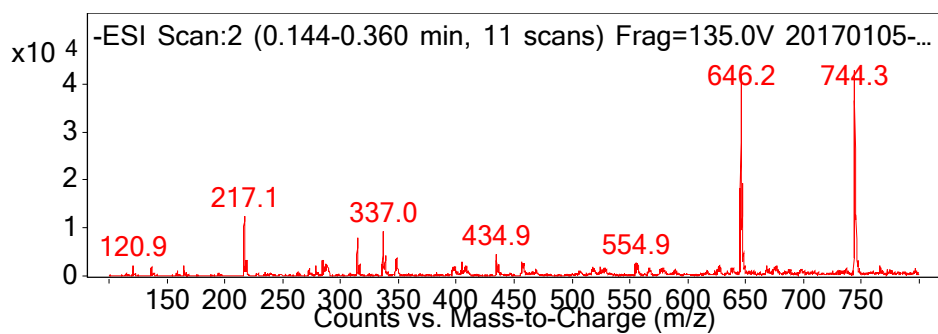
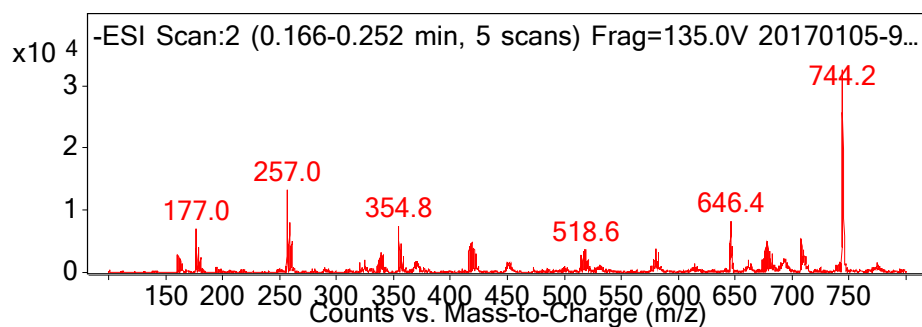


Fig. S11 The ^1H -NMR spectrum of **4** (300 MHz, d_6 -DMSO) with the addition of 3 equiv. of Na_2SO_4 in different ratio.

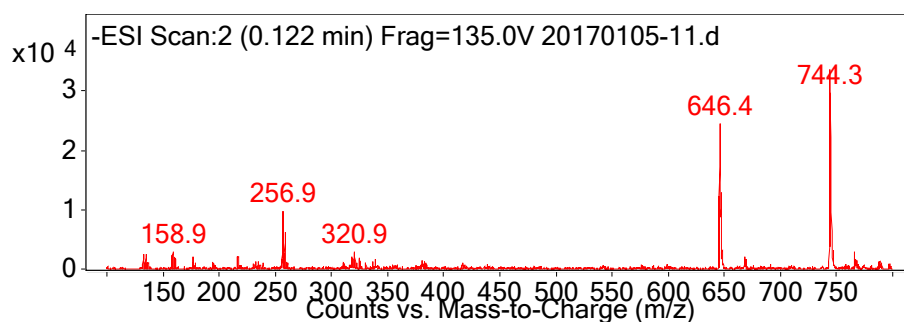
MgSO₄



ZnSO₄



CuSO₄



FeSO₄

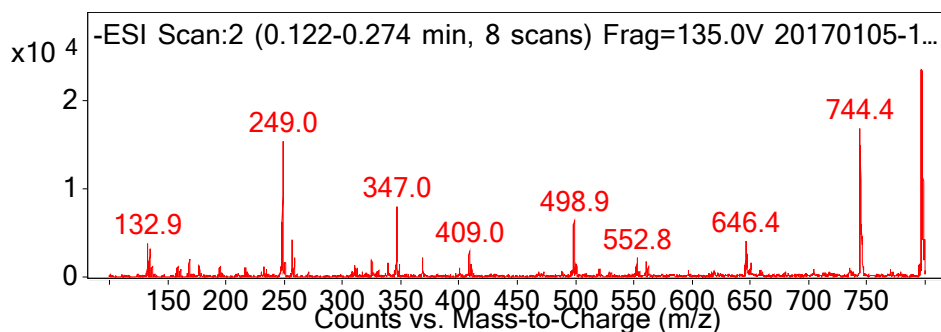
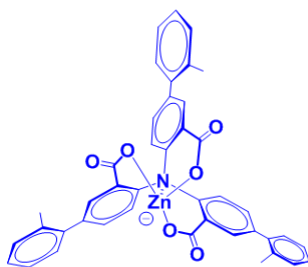
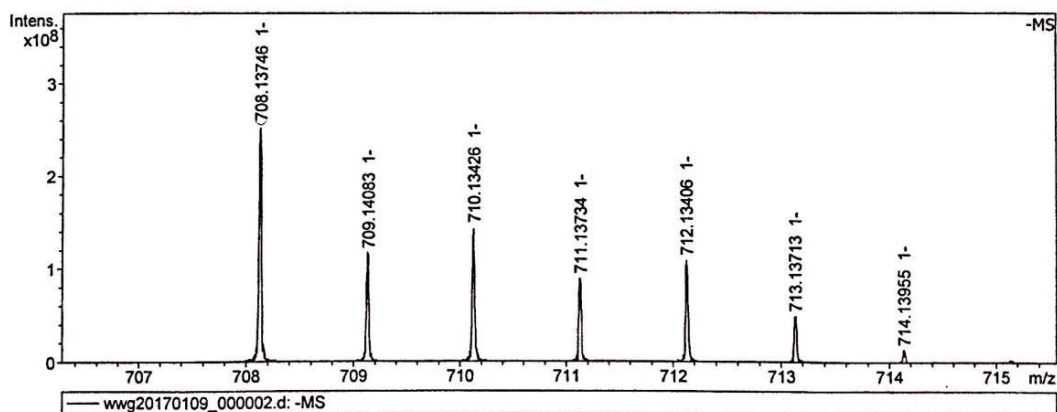
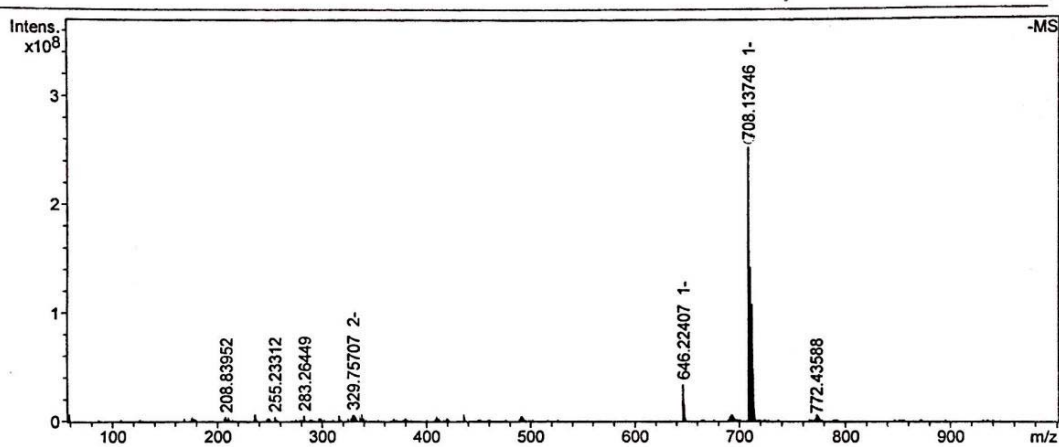


Fig. S12 The ESI (negative) spectrum of **4** in the presence of Mg²⁺, Cu²⁺, Fe²⁺, Zn²⁺ (as sulfate salt) in DMSO



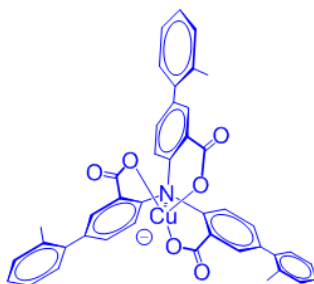
Acquisition Parameter

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Broadband Low Mass	57.7 m/z	Source Accumulation	0.001 sec	Data Processing Size	2097152
Broadband High Mass	1000.0 m/z	Ion Accumulation Time	0.100 sec	Apodization	Sine-Bell Multiplication



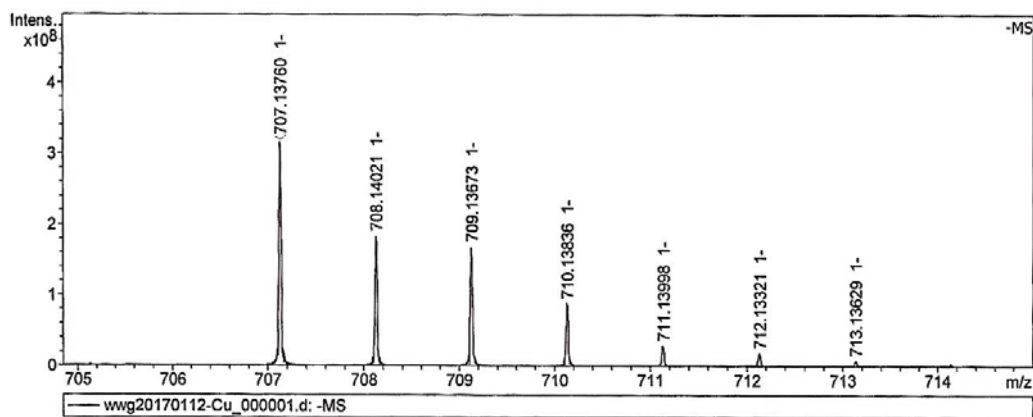
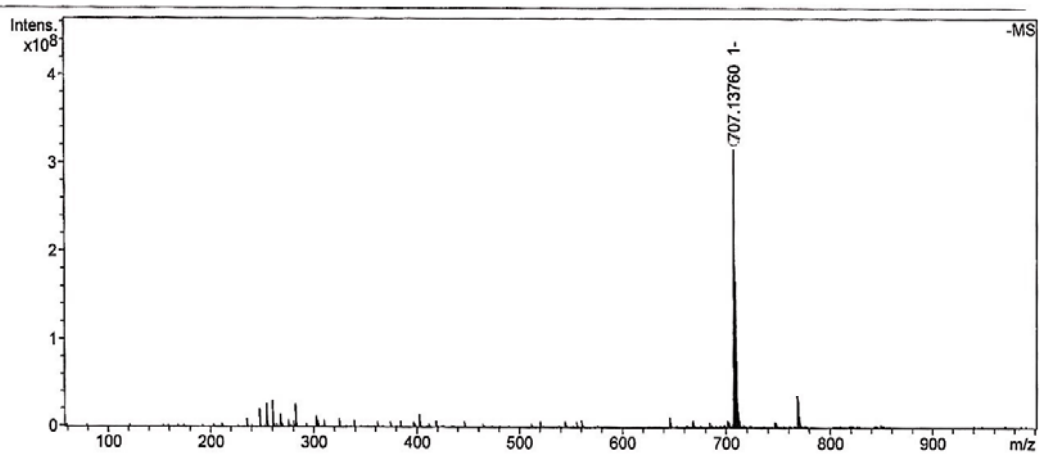
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
708.137456	1	C42H30NO6Zn	100.00	708.137003	-0.6	-0.0	56.0	28.5	even	ok

Fig. S13 The HRMS (ESI-TOF) spectrum of $[4+Zn-3H]^-$ complex



Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	10	Calibration Date	Wed Dec 28 12:57:30
Polarity	Negative	No. of Cell Fills	1	Data Acquisition Size	2046576
Broadband Low Mass	57.7 m/z	Source Accumulation	0.001 sec	Data Processing Size	2097152
Broadband High Mass	1000.0 m/z	Ion Accumulation Time	0.100 sec	Apodization	Sine-Bell Multiplication



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
707.137598	1	C ₄₂ H ₃₀ CuNO ₆	100.00	707.137459	0.2		1.0	55.8	28.0	odd ok

Fig. S14 The HRMS (ESI-TOF) spectrum of [4+Cu-3H]⁻ complex

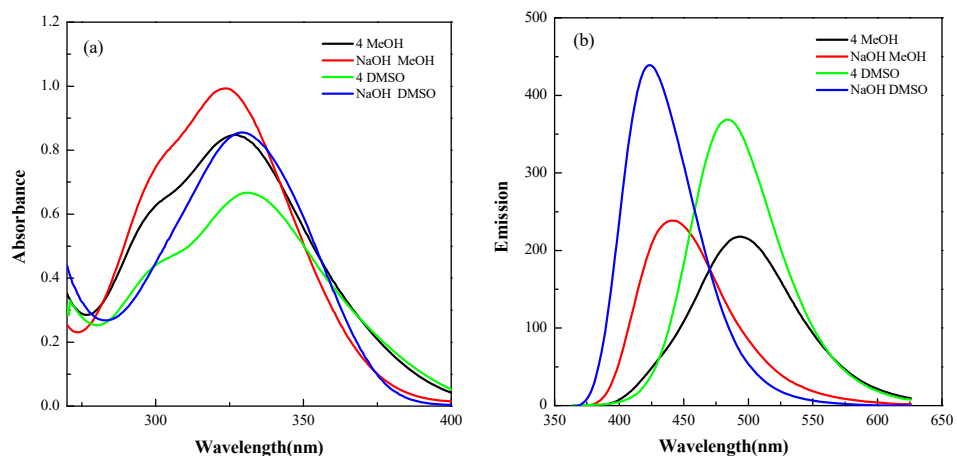


Fig. S15 Absorption and emission spectrum of **4** in DMSO (3.5×10^{-5} M, $\lambda_{ex} = 325$ nm) and MeOH (4×10^{-5} M) after addition of OH^- anion with the ratio of $[\text{OH}^-]/[\mathbf{4}]$ (30:1)

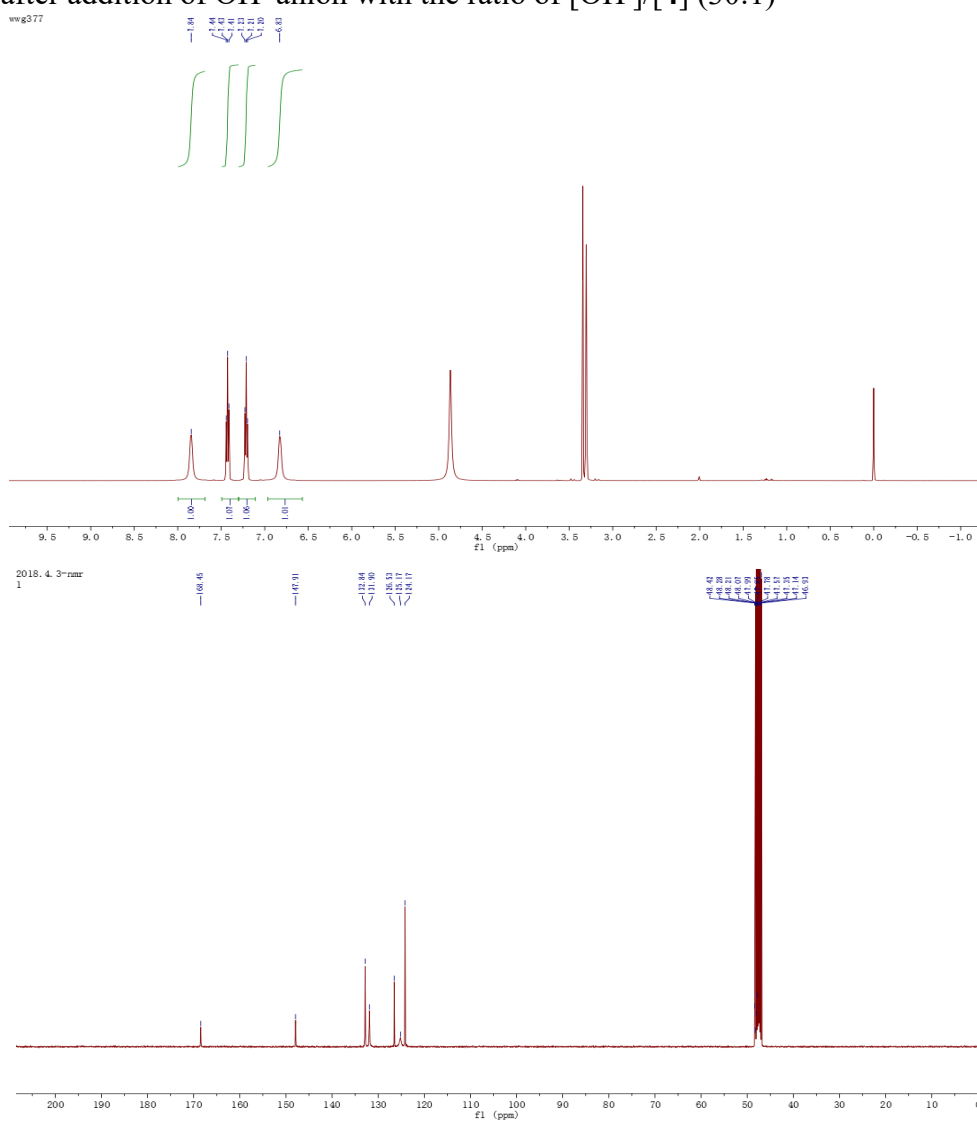


Fig. S16 The ^1H and ^{13}C NMR spectra of **1** in Methanol- D_4

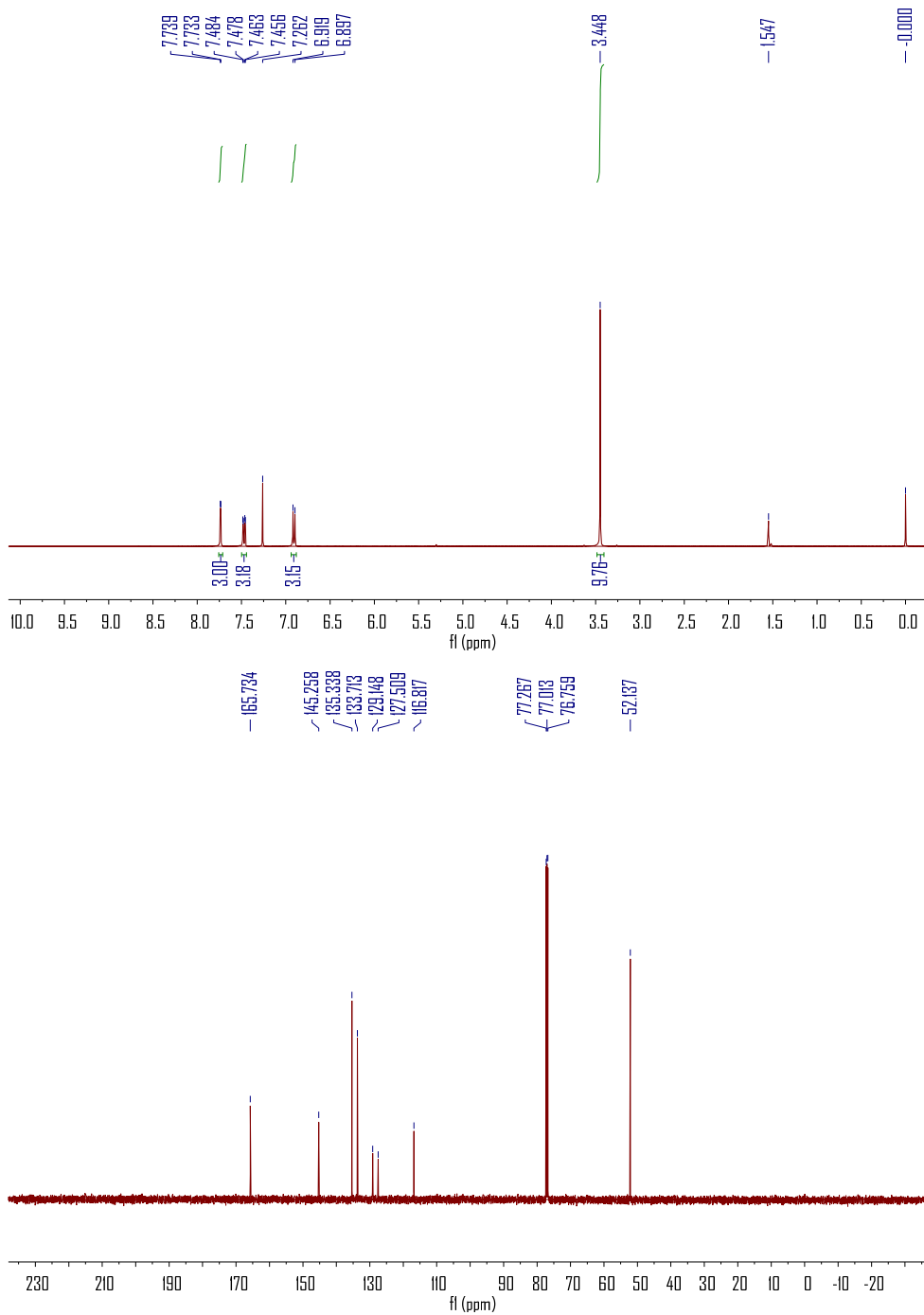
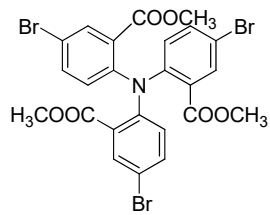


Fig. S17 The ¹H and ¹³C NMR spectra of **2** in CDCl₃

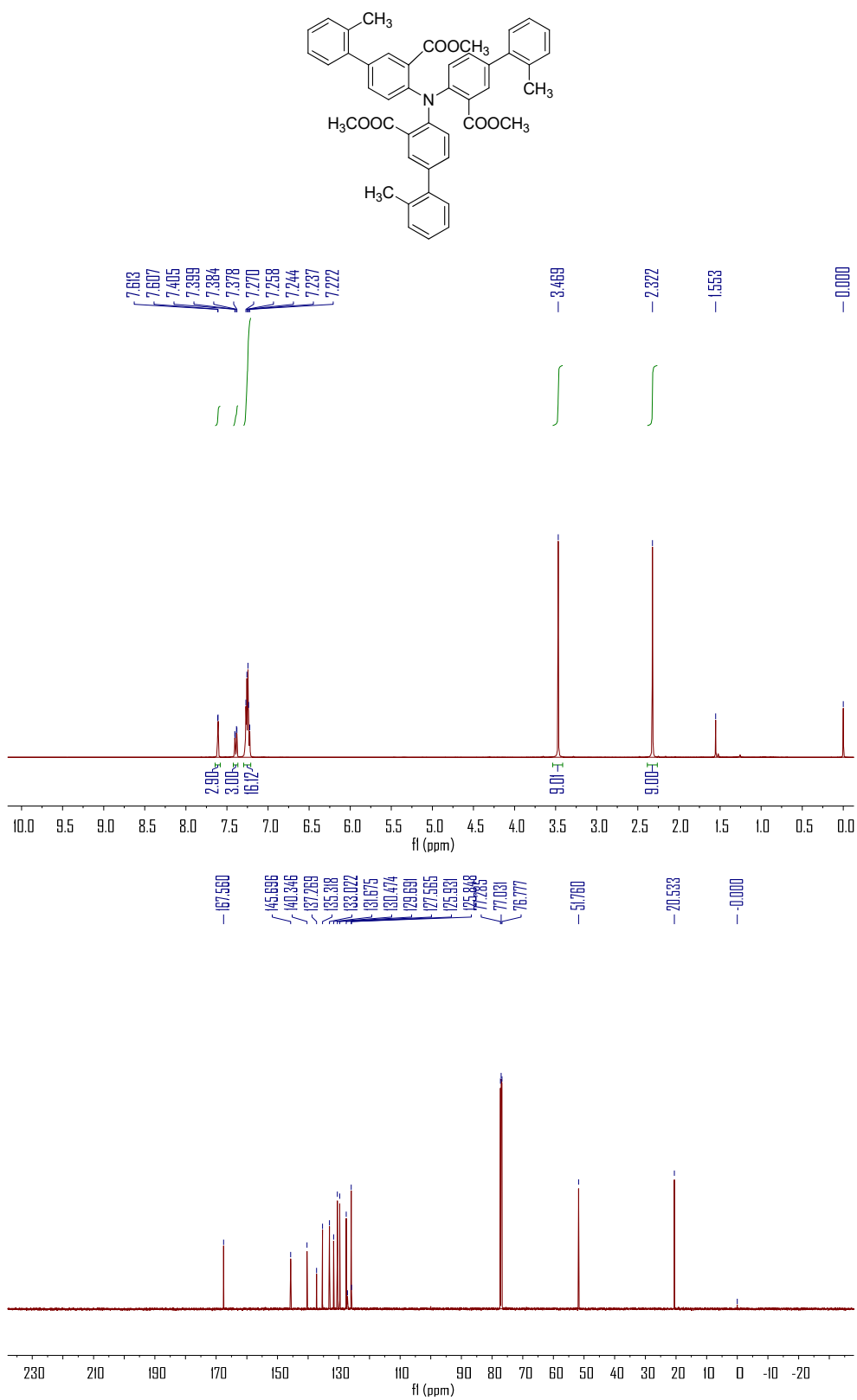


Fig. S18 The ¹H and ¹³C NMR spectra of **3** in CDCl₃

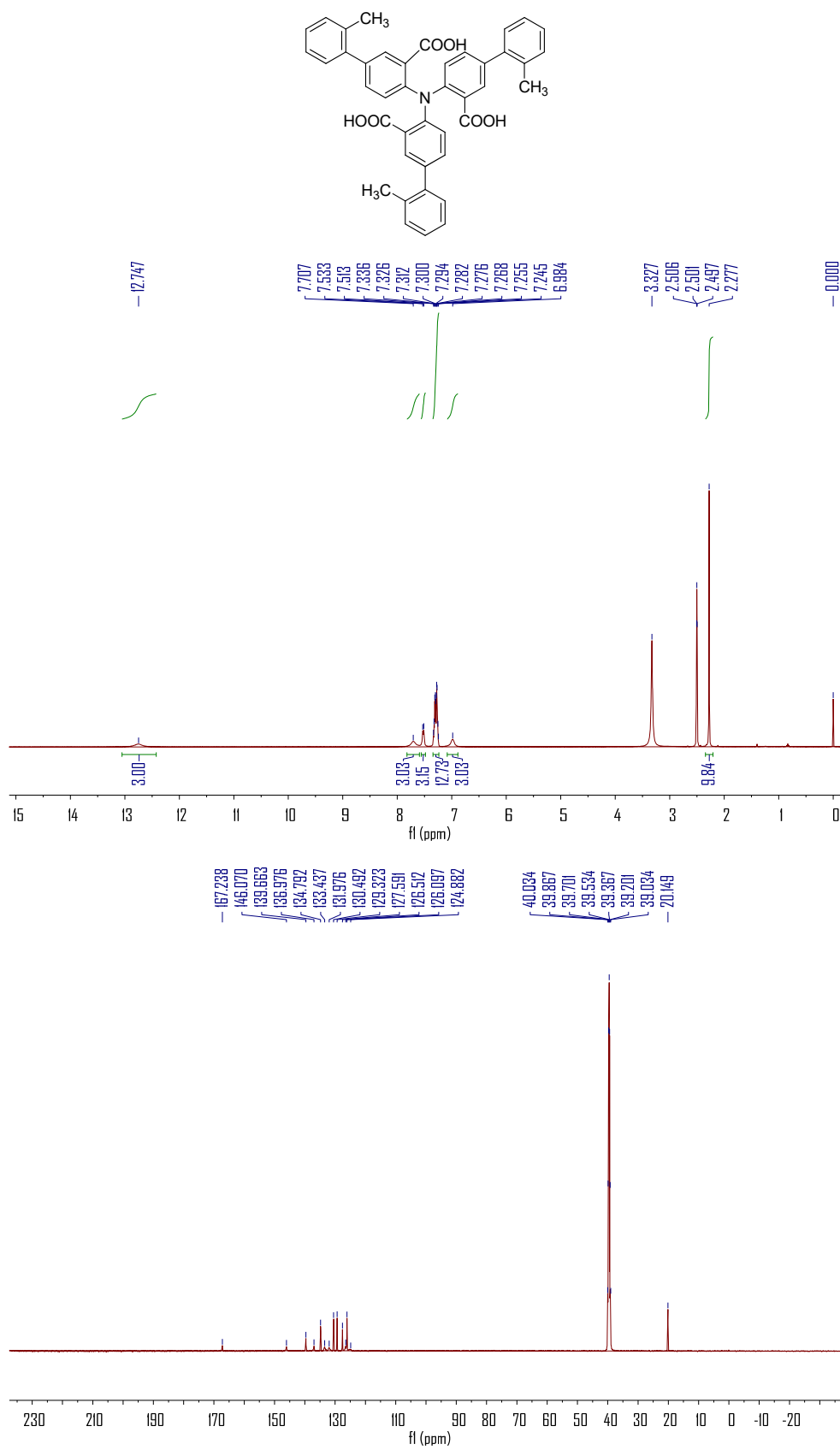


Fig. S19 The ^1H and ^{13}C NMR spectra of **4** in d_6 -DMSO