Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Quantifying factors that influence metal ion release in photocaged complexes using ZinCast derivatives

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Data Fitting Protocols.

Binding data was fitted with XLfit program using the Levenberg–Marquardt algorithm. Several equilibrium models were selected in order to achieve the best fit and parameter approximation for changes in absorption by the ligand (y) as a function of metal concentration (x). Affinity for binding of the metal (K_D) was assigned to $\frac{1}{2}ML_{max}$ where ML_{max} is the upper limit of the curve defined as maximum binding capacity. The following fitting models were selected for all K_D determinations:

1. $y = A + Bx + [\frac{(C-B)(1-\exp(-D)x)}{D}]$

2. $y = \frac{A+Bx}{1+Cx+Dx^2}$

3. $y = \frac{A}{[1+Bexp(-Cx)]^{\frac{1}{D}}}$

4. $y = Aexp[-\exp(B - Cx)]$

5. $y = \frac{A}{1+Bexp(-Cx)}$

All parameters were tabulated below

				Parameter			
			Equation	**A**	**B**	**C**	**D**
ZinCast-1	**Cu^{2+}**	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	2	0.006337	10787.91	-41939.9	2.27E+09
		Buffer	2	-0.00031	115445.3	222756.6	36007317
	Zn^{2+}	MeCN	3	0.370947	-0.55448	174771.8	0.143991
		EtOH	3	0.351268	-1.50518	134524.6	0.055722
		Buffer	2	-0.0012	3875.063	10109.89	2589954
	Cd^{2+}	MeCN	3	0.359653	-3.94818	185815.2	0.006361
		EtOH	1	-0.0056	4.34229	13653.63	41715.65
		Buffer	2	-0.00146	734.7071	2356.68	3534.758
ZinUnc-1	**Cu^{2+}**	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	3	0.317422	1.348434	302076.4	0.519484
		Buffer	2	-0.00808	10014.95	1808.931	3.2E+08
	Zn^{2+}	MeCN	3	0.615161	-3.89187	152027.2	0.006888
		EtOH	2	-0.00226	8935.359	18956.95	6881535
		Buffer	2	0.000568	97.46232	147.7034	230.9362
	Cd^{2+}	MeCN	2	0.001	19970.95	31783.55	-127412
		EtOH	2	-0.00197	494.3082	968.9761	4147.366
		Buffer	2	0.000417	26.53198	46.48144	-9.30404

				Parameter			
			Equation	**A**	**B**	**C**	**D**
ZinCast-2	**Cu^{2+}**	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	2	0.002698	11581.46	-41109.6	2.26E+09
		Buffer	N/A	N/A	N/A	N/A	N/A
	Zn^{2+}	MeCN	4	0.384744	1.096614	174088	N/A
		EtOH	2	0.006634	1360.419	4295.127	-97083.3
		Buffer	N/A	N/A	N/A	N/A	N/A
	Cd^{2+}	MeCN	3	0.363537	-3.84506	105226.5	0.007992
		EtOH	2	-0.00023	413.5244	1239.445	5557.656
		Buffer	N/A	N/A	N/A	N/A	N/A
ZinUnc-2	**Cu^{2+}**	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	4	0.352159	1.325151	162444.6	
		Buffer	N/A	N/A	N/A	N/A	N/A
	Zn^{2+}	MeCN	2	0.00231	12046.11	19779.92	-158071
		EtOH	N/A	N/A	N/A	N/A	N/A
		Buffer	N/A	N/A	N/A	N/A	N/A
	Cd^{2+}	MeCN	2	0.011498	2506.327	3578.055	6076.577
		EtOH	N/A	N/A	N/A	N/A	N/A
		Buffer	N/A	N/A	N/A	N/A	N/A

				Parameter			
			Equation	A	B	C	D
ZinCast-3	Cu^{2+}	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	3	0.253117	-3.82371	56104.84	0.006915
		Buffer	N/A	N/A	N/A	N/A	N/A
	Zn^{2+}	MeCN	2	0.004463	16249.56	47002.98	-3309568
		EtOH	2	0.00178	37.02968	216.0619	-1947.49
		Buffer	N/A	N/A	N/A	N/A	N/A
	Cd^{2+}	MeCN	2	0.008552	996.2301	1832.451	802014.9
		EtOH	N/A	N/A	N/A	N/A	N/A
		Buffer	N/A	N/A	N/A	N/A	N/A
ZinUnc-3	Cu^{2+}	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	N/A	N/A	N/A	N/A	N/A
		Buffer	N/A	N/A	N/A	N/A	N/A
	Zn^{2+}	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	1	0.019111	0.641237	60.32722	204.5505
		Buffer	N/A	N/A	N/A	N/A	N/A
	Cd^{2+}	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	N/A	N/A	N/A	N/A	N/A
		Buffer	N/A	N/A	N/A	N/A	N/A

				Parameter			
			Equation	A	B	C	D
ZinCast-4	Cu^{2+}	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	5	0.091073	12.03822	327762.8	N/A
		Buffer	N/A	N/A	N/A	N/A	N/A
	Zn^{2+}	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	5	0.136268	13.97318	227696.1	N/A
		Buffer	3	0.09706	-3.51397	131530	0.009581
	Cd^{2+}	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	3	0.107343	1.268591	326996.5	0.451497
		Buffer	2	0.000447	4208.884	-4975.91	6.09E+08
ZinUnc-4	Cu^{2+}	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	2	0.004372	10677.93	-45408.2	2E+09
		Buffer	N/A	N/A	N/A	N/A	N/A
	Zn^{2+}	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	3	0.412474	-1.49224	142599.4	0.061138
		Buffer	2	-0.00408	6635.591	15904.89	425031.6
	Cd^{2+}	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	1	-0.00879	-2.46832	23546.69	63045.78
		Buffer	2	-0.00329	7805.349	18651.11	314529.2

				Parameter			
			Equation	A	B	C	D
ZinCast-5	Cu^{2+}	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	5	0.056872	17.96121	211296.2	N/A
		Buffer	N/A	N/A	N/A	N/A	N/A
	Zn^{2+}	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	3	0.105775	1.808159	153244.6	0.66402
		Buffer	3	0.071566	-3.94866	99973.54	0.006775
	Cd^{2+}	MeCN	N/A	N/A	N/A	N/A	N/A
		EtOH	3	0.080784	1.977601	257394.3	0.648377
		Buffer	1	-0.00142	16.95323	3763.374	61727.2

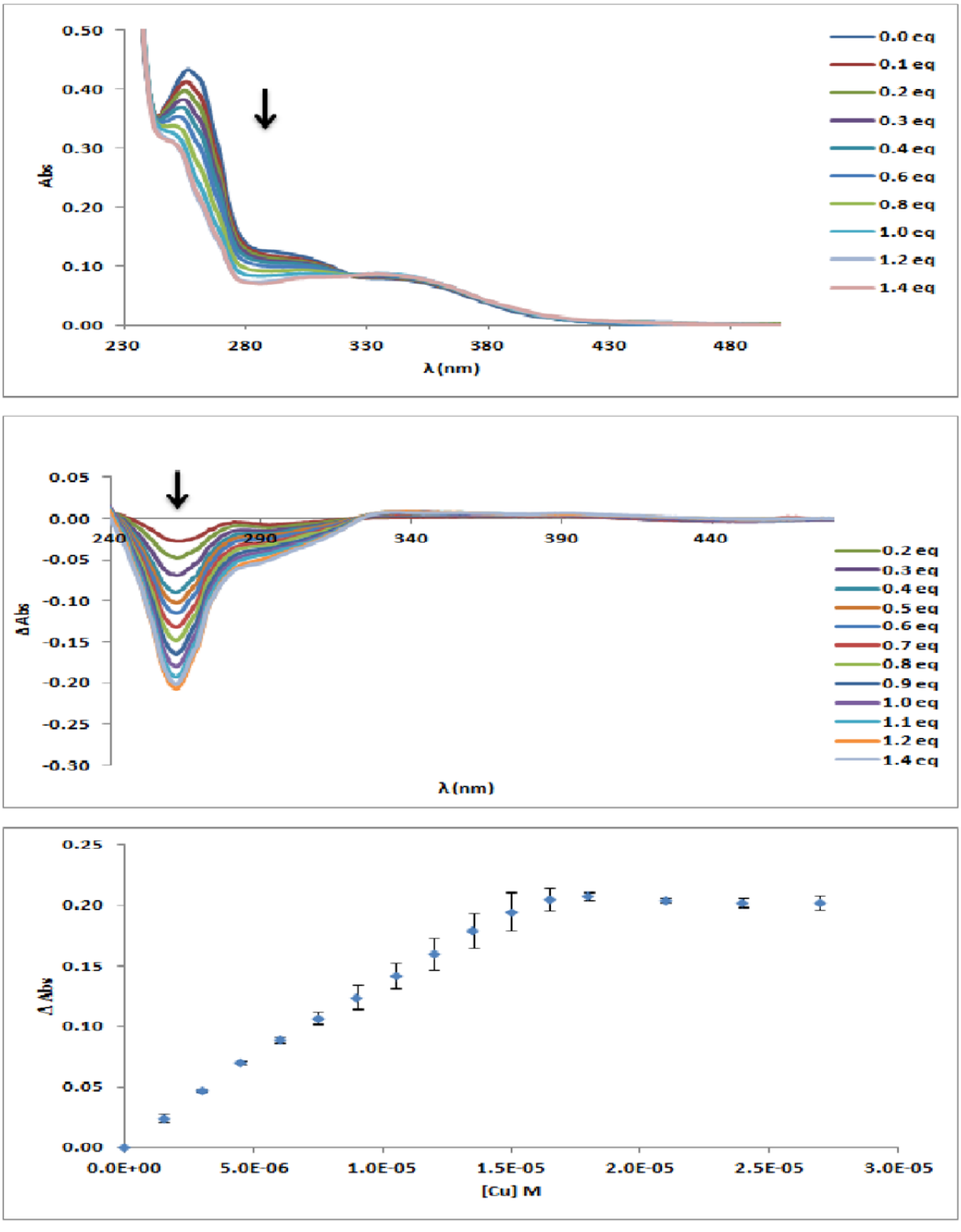
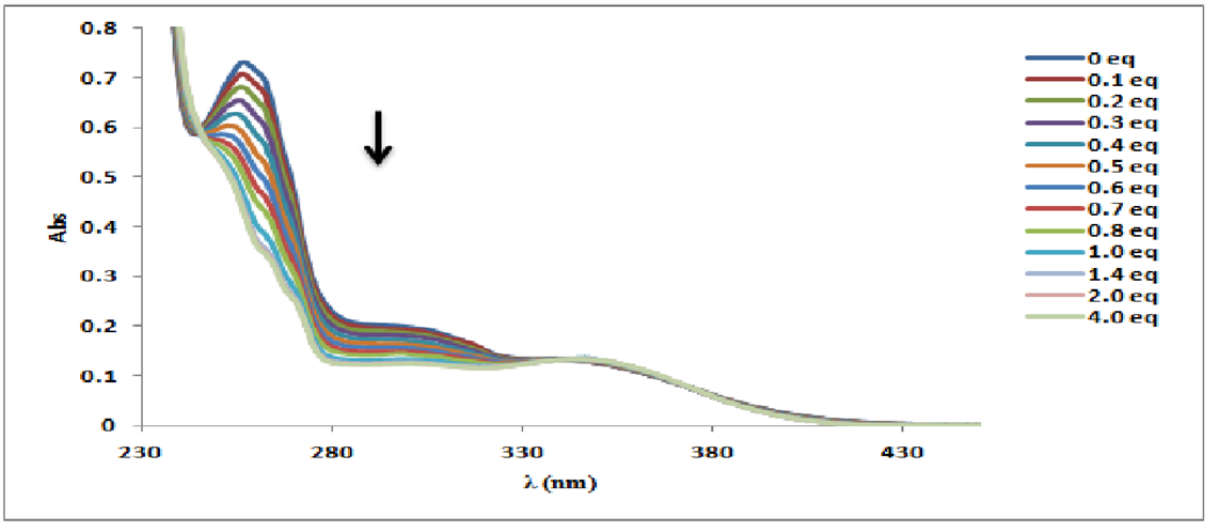
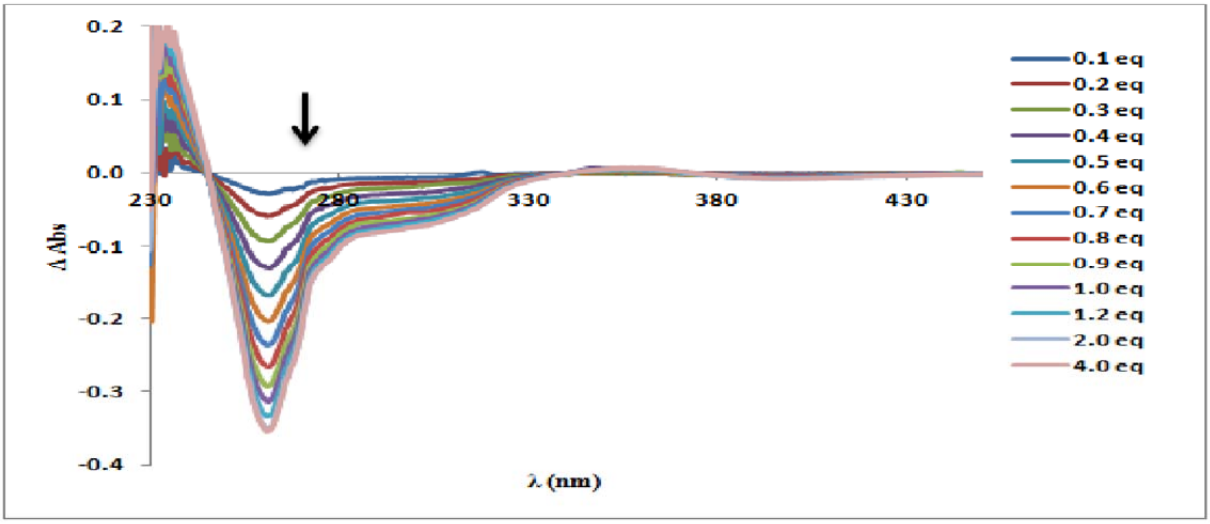


Figure S1 Titration of ZinCast-1 with $Cu(ClO_4)_2$ in EtOH.





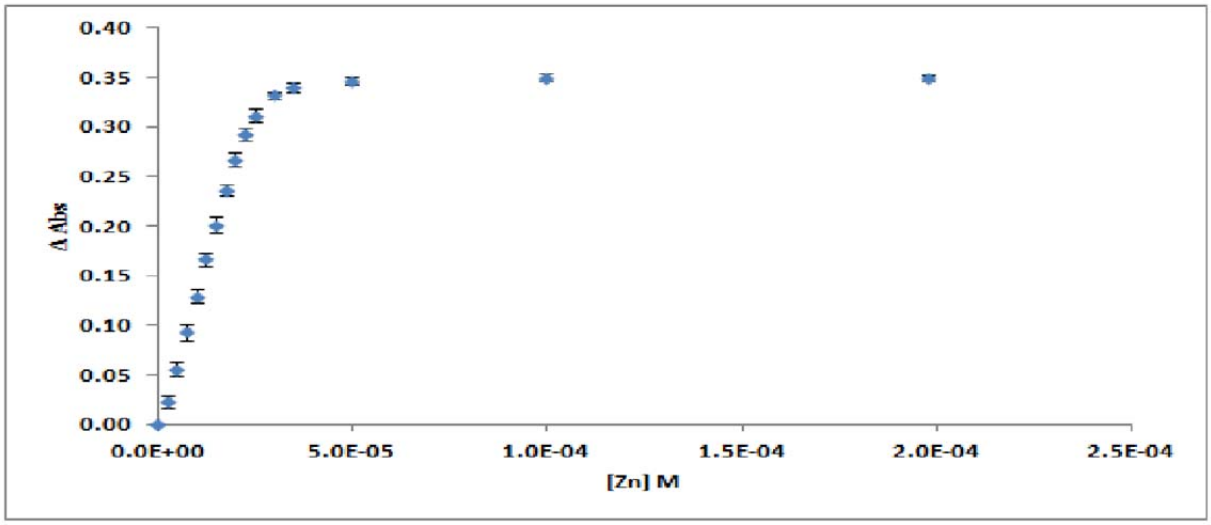


Figure S2 Titration of ZinCast-1 with $Zn(ClO_4)_2$ in EtOH.

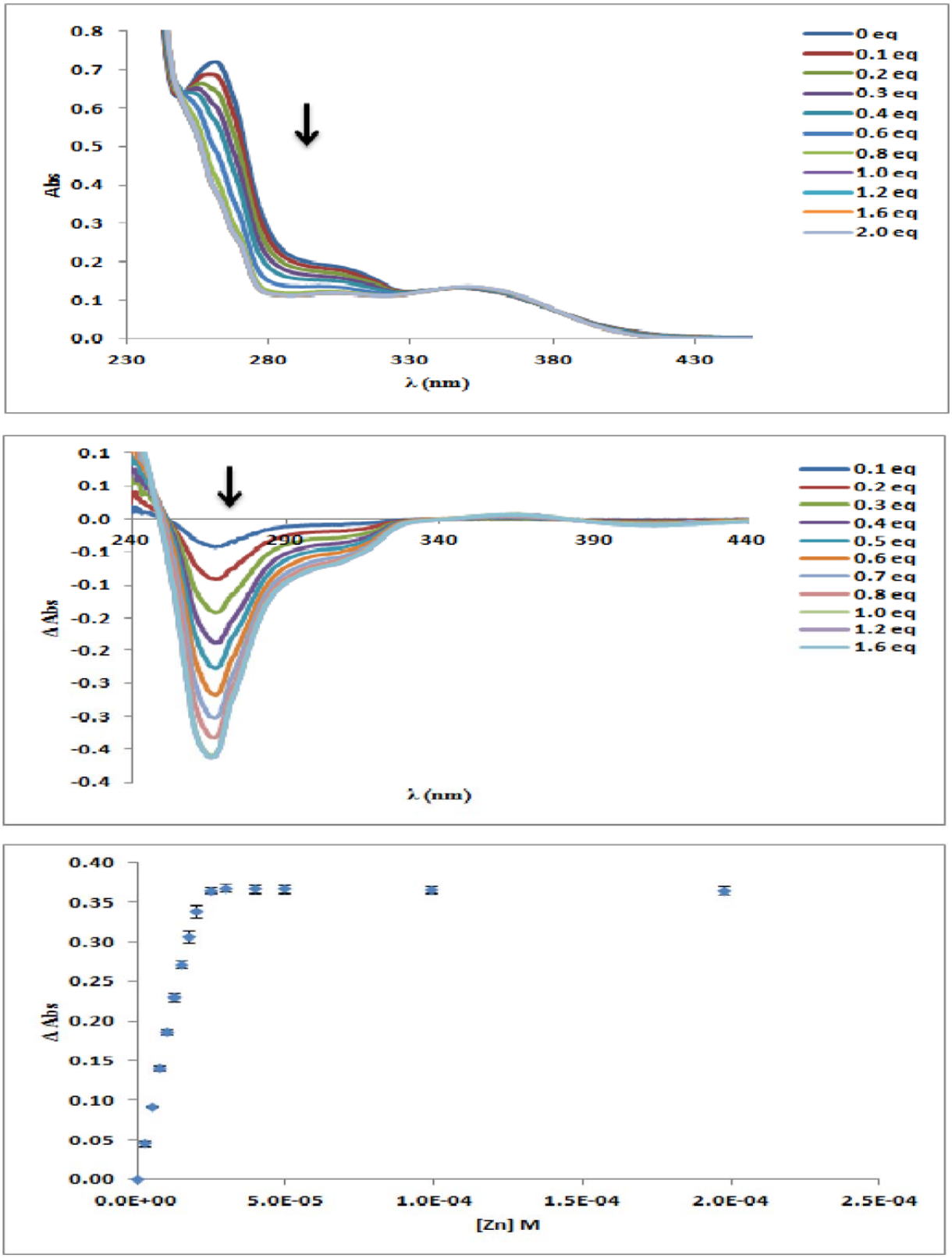
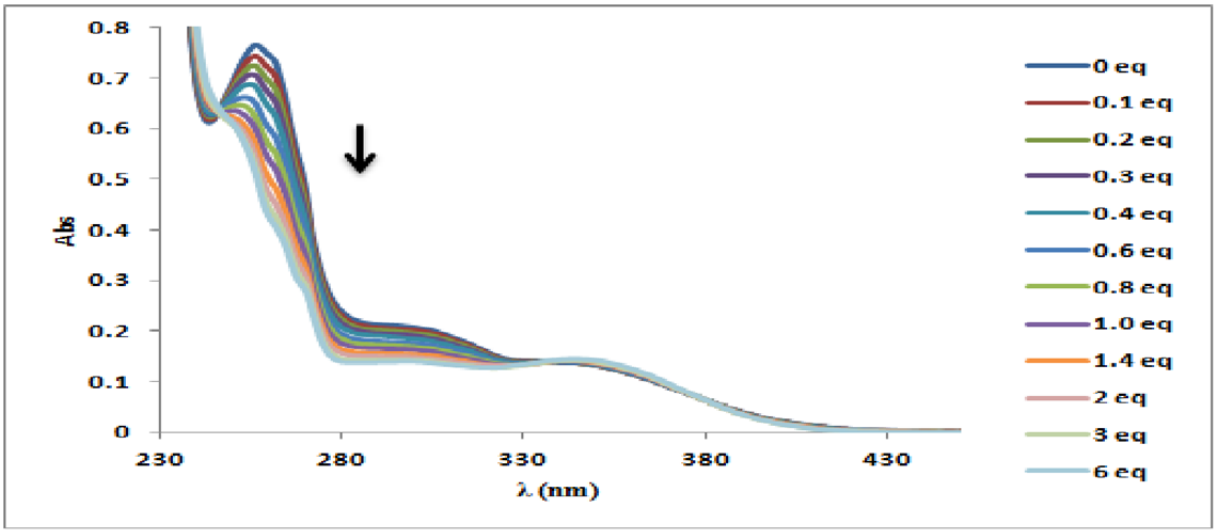
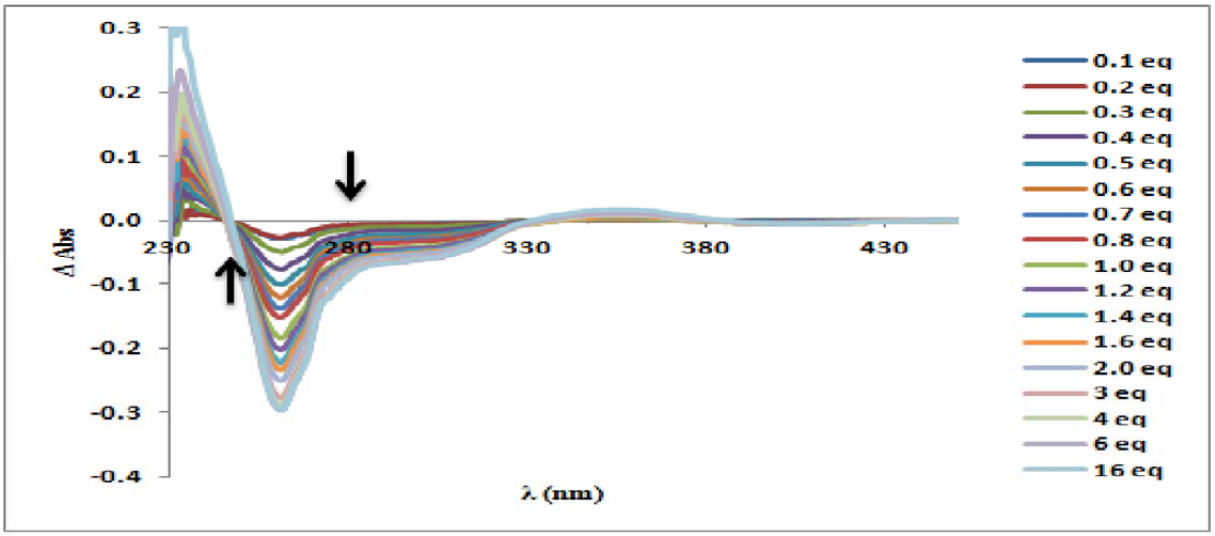


Figure S3 Titration of ZinCast-1 with $Zn(ClO_4)_2$ in CH_3CN.





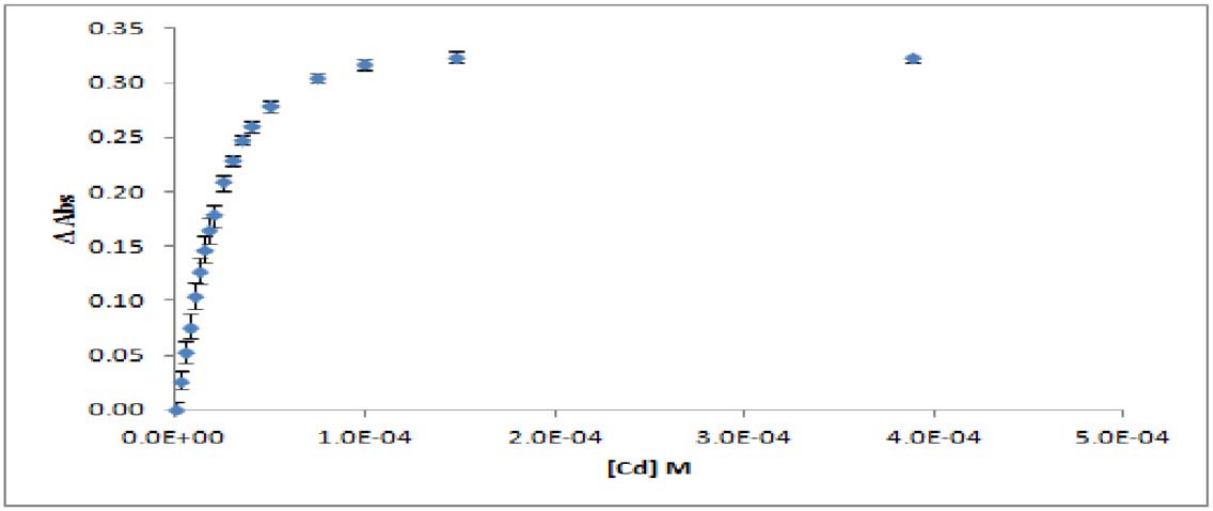
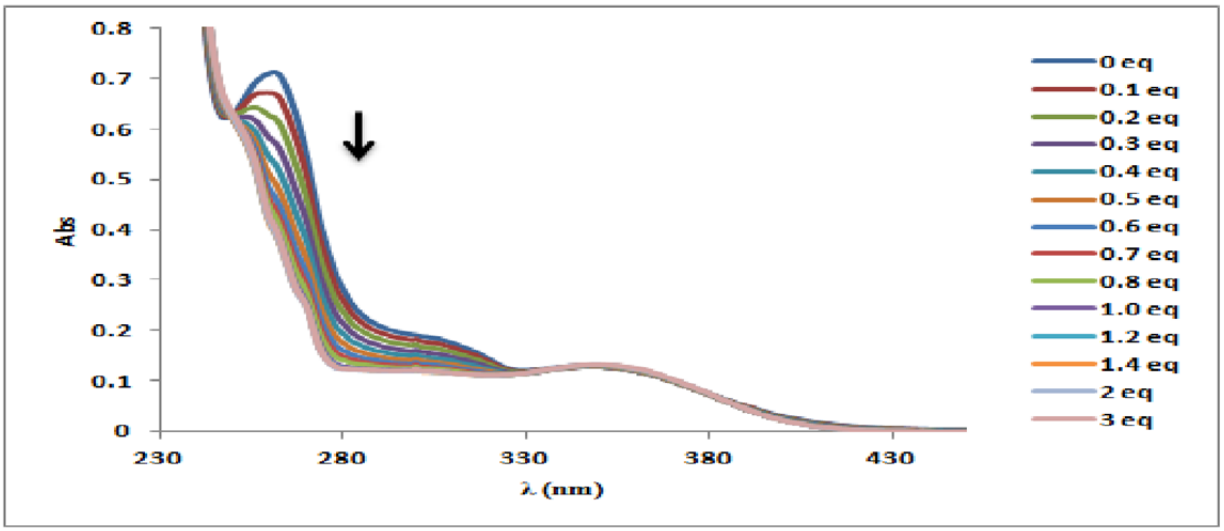
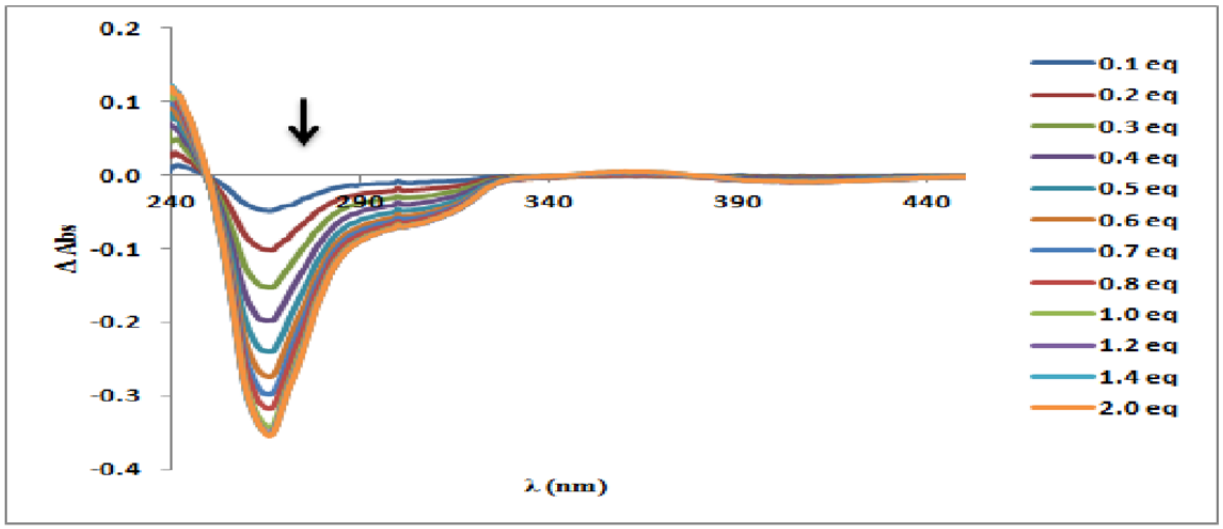


Figure S4 Titration of ZinCast-1 with $Cd(ClO_4)_2$ in EtOH.





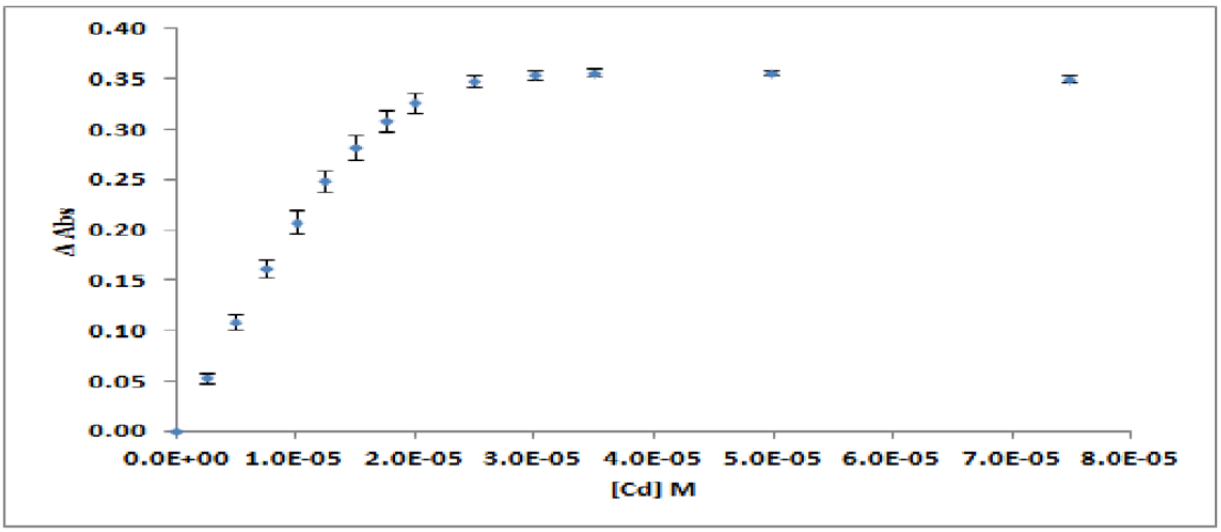


Figure S5 Titration of ZinCast-1 with $Cd(ClO_4)_2$ in CH_3CN.

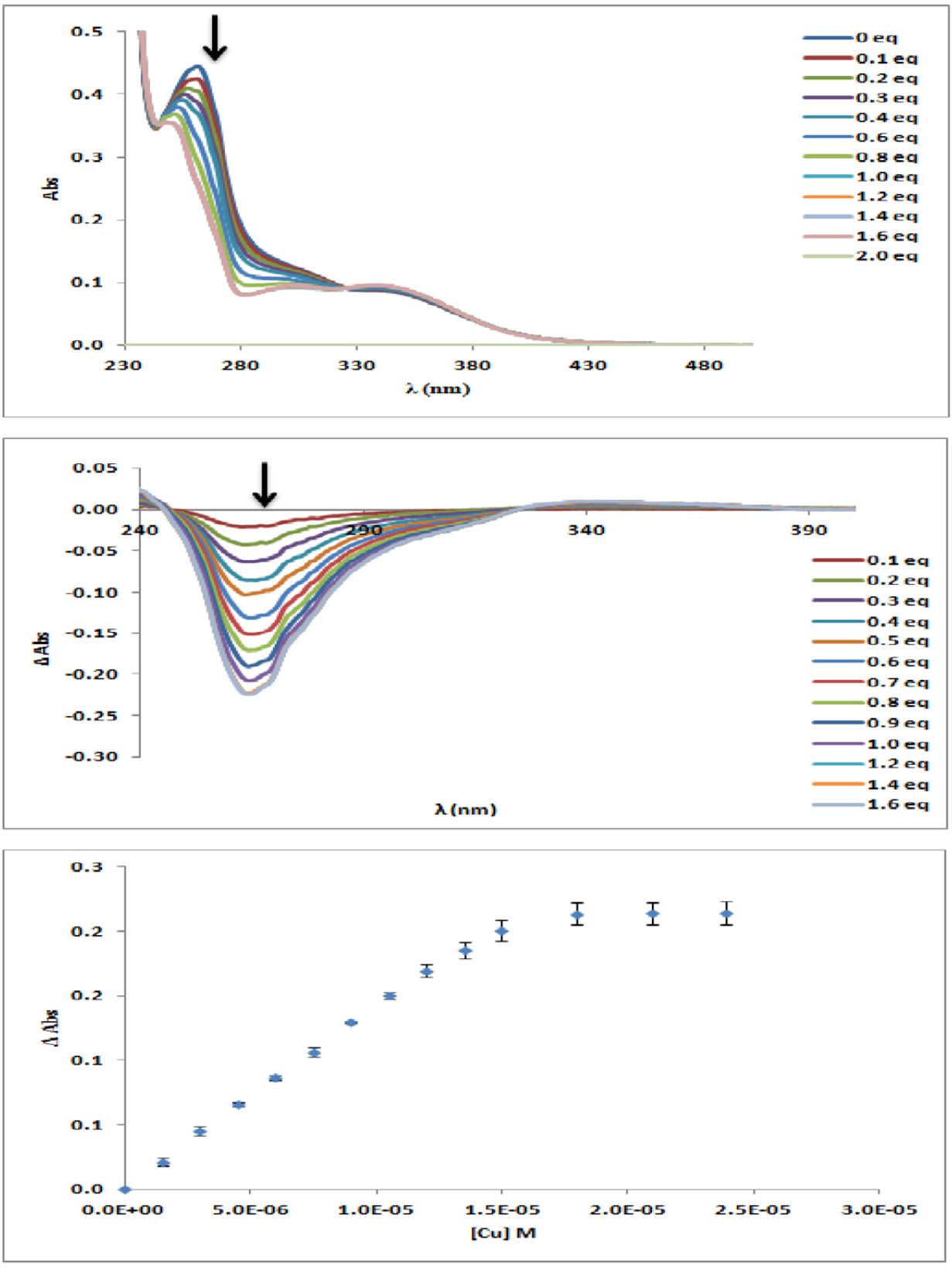


Figure S6 Titration of ZinCast-2 with $Cu(ClO_4)_2$ in EtOH.

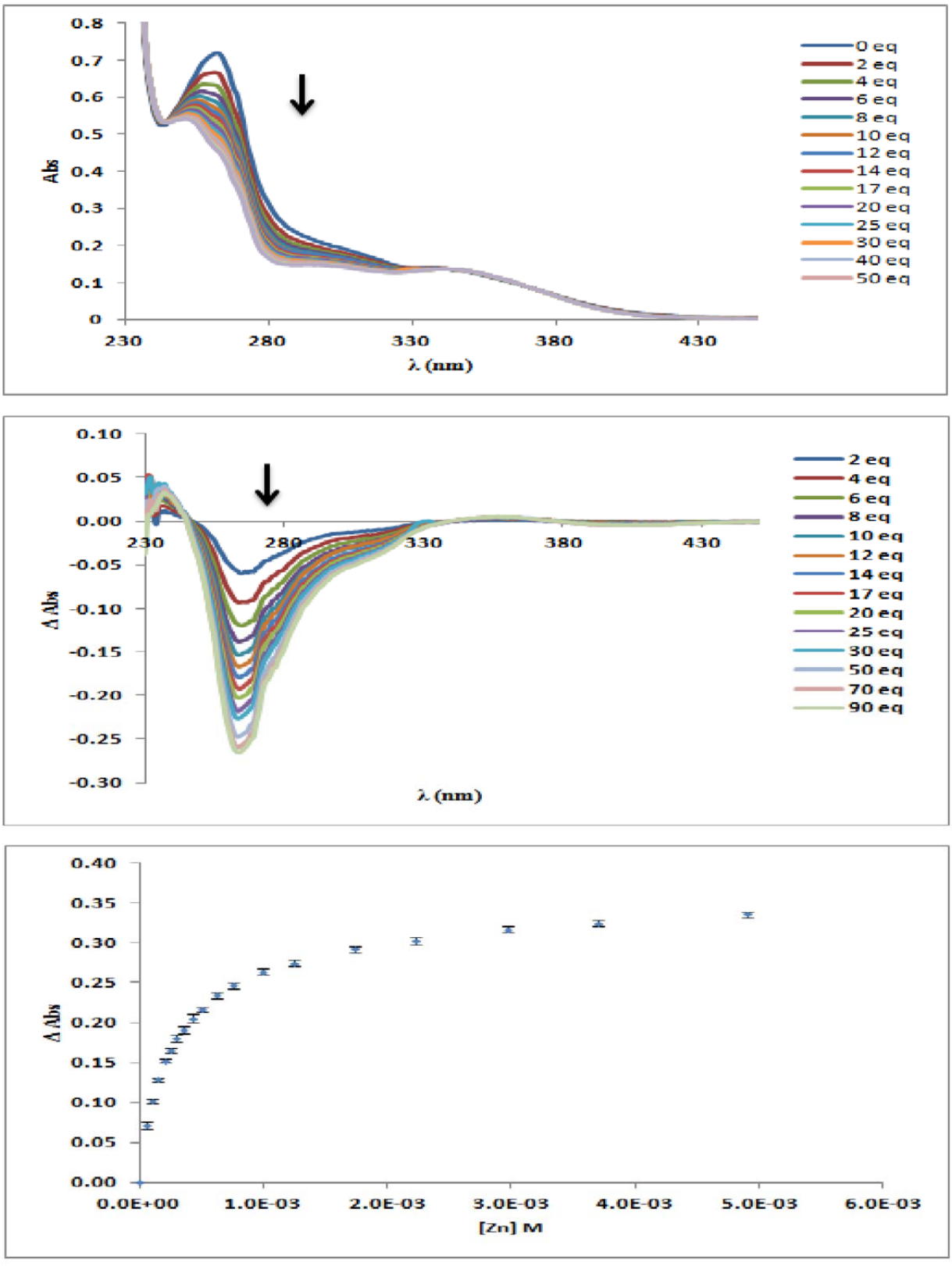


Figure S7 Titration of ZinCast-2 with $Zn(ClO_4)_2$ in EtOH.

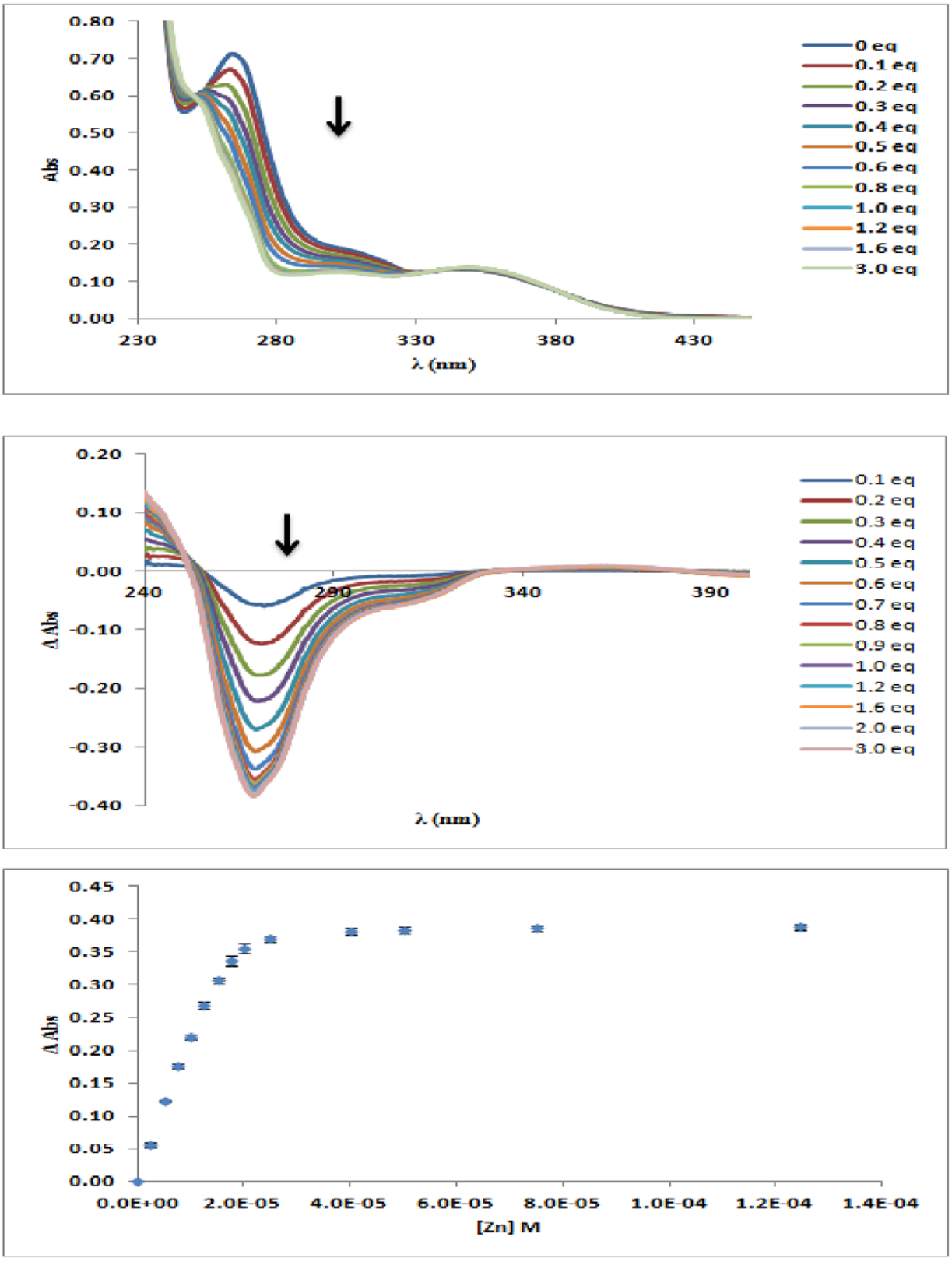


Figure S8 Titration of ZinCast-2 with $Zn(ClO_4)_2$ in CH_3CN.

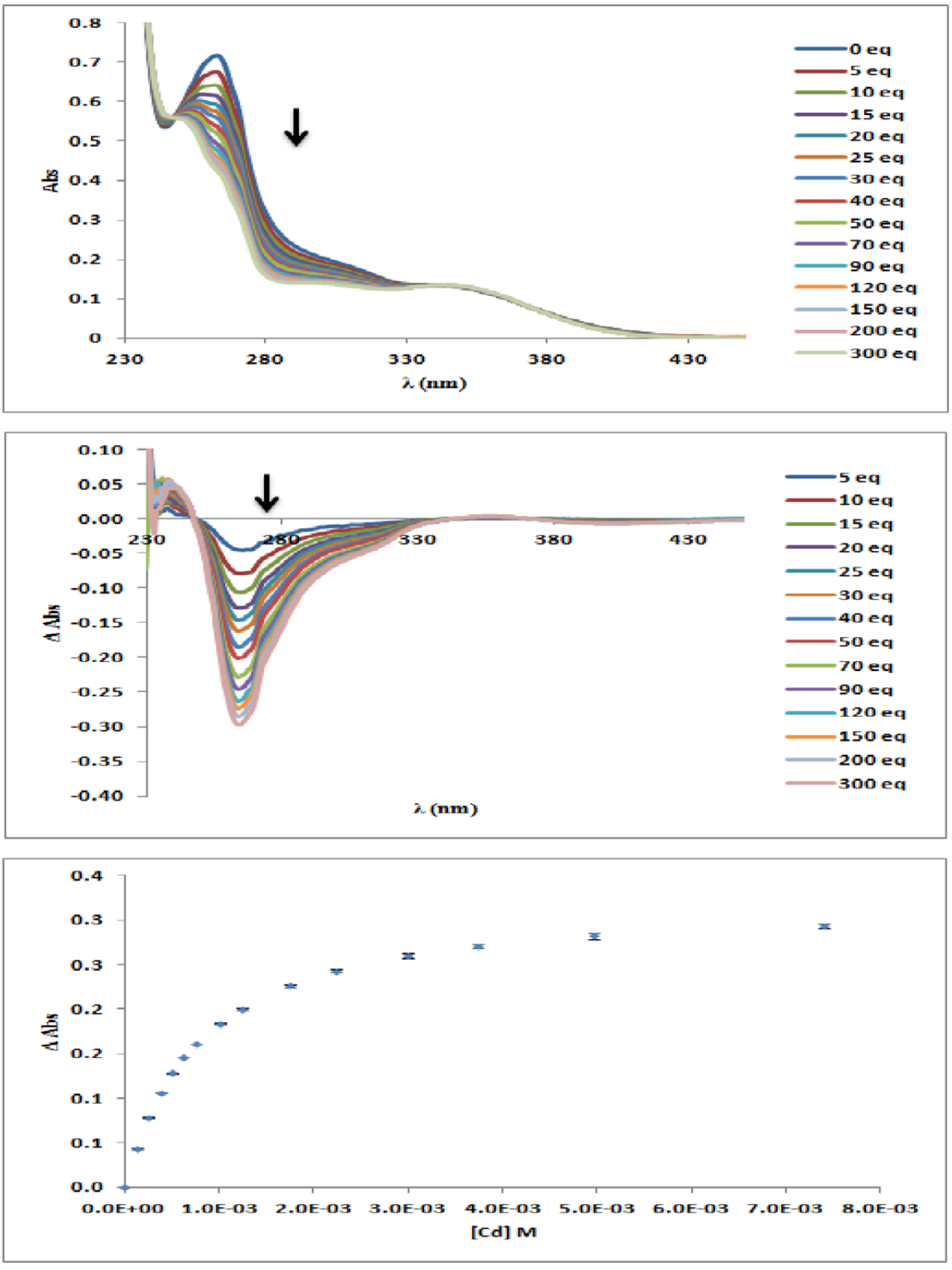


Figure S9 Titration of ZinCast-2 with $Cd(ClO_4)_2$ in EtOH.

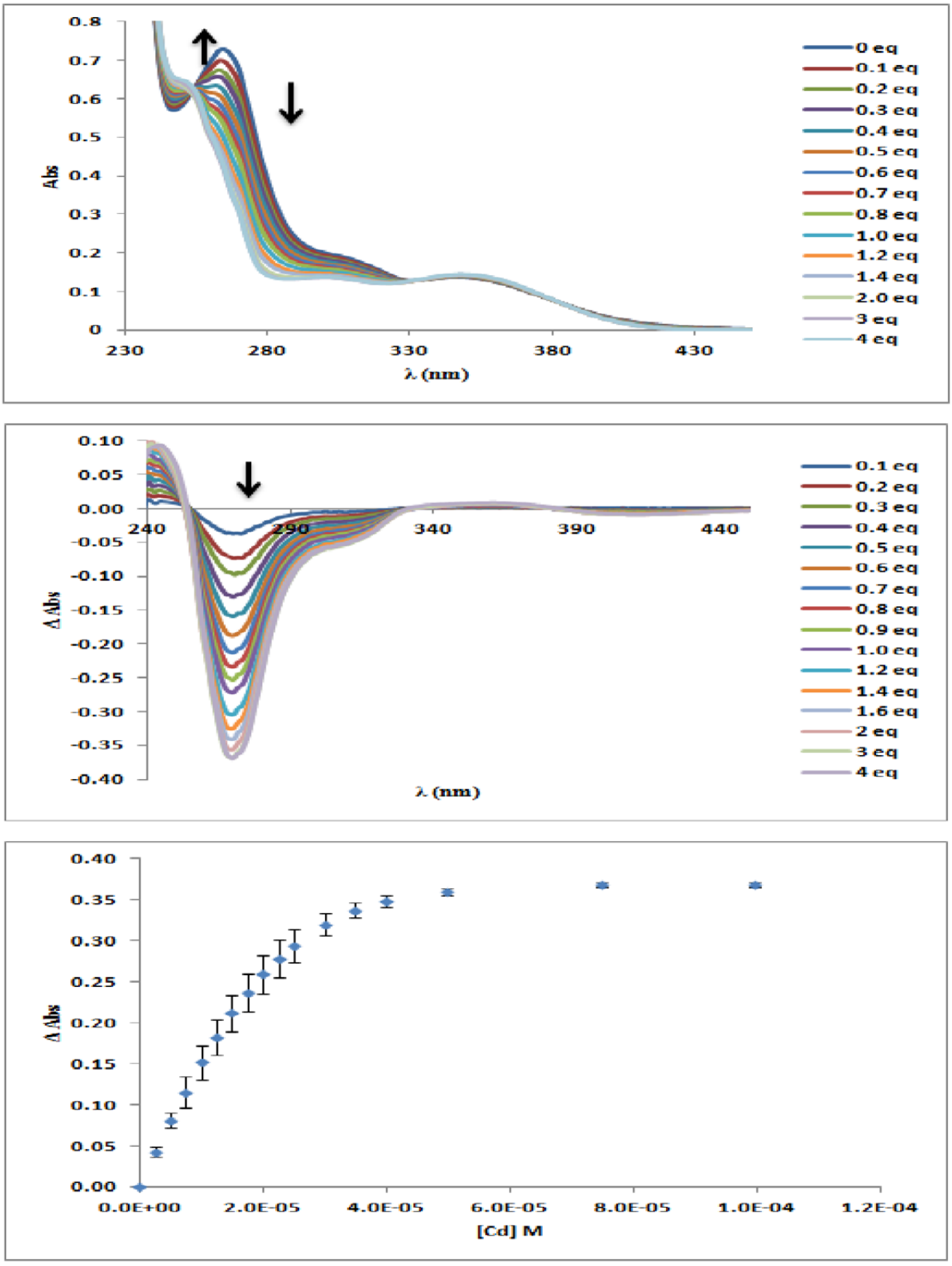
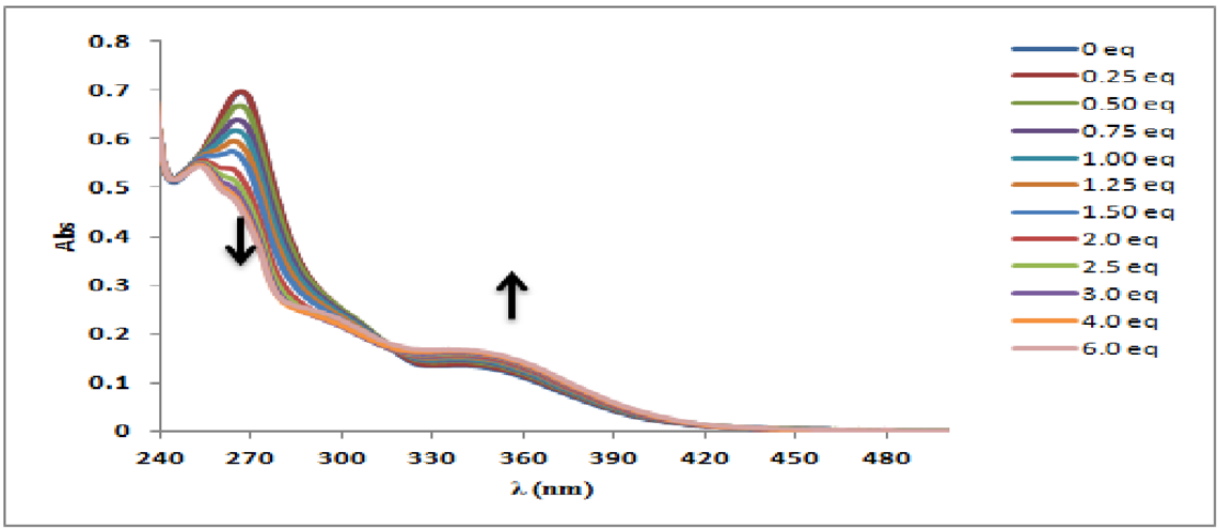
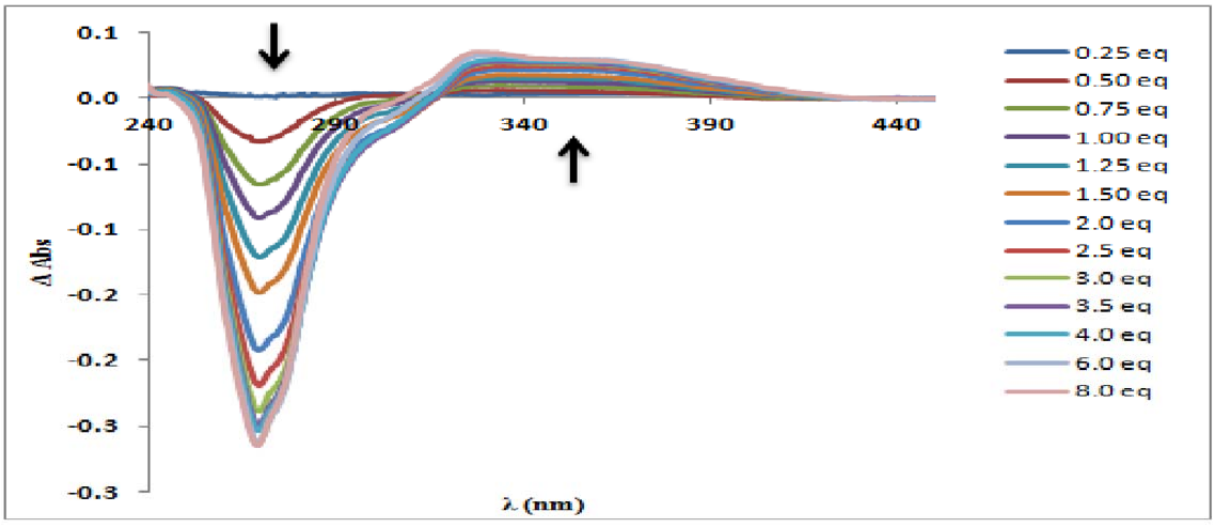


Figure S10 Titration of ZinCast-2 with $Cd(ClO_4)_2$ in CH_3CN.





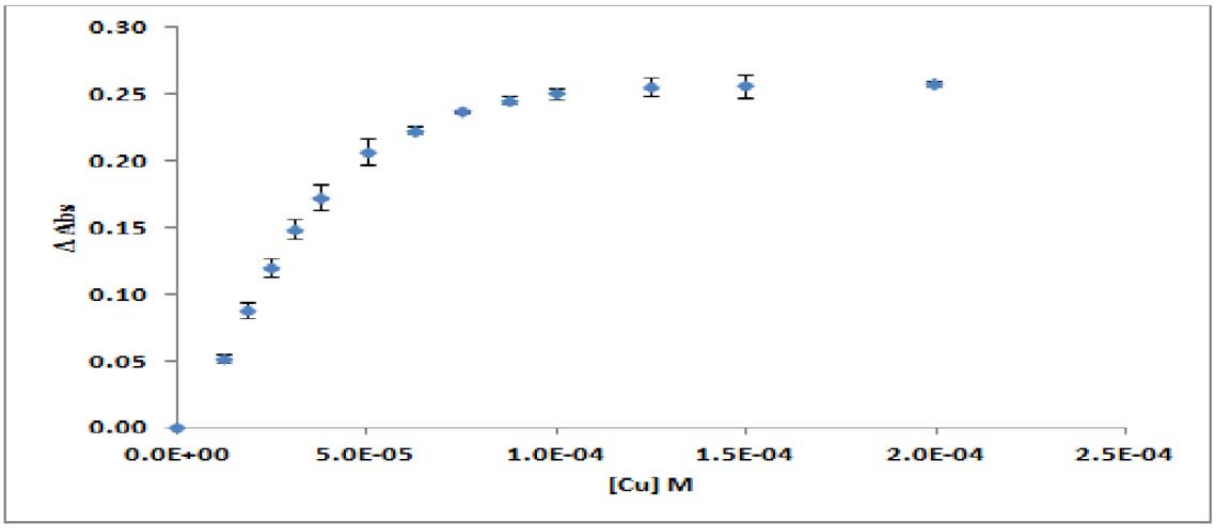


Figure S11 Titration of ZinCast-3 with $Cu(ClO_4)_2$ in EtOH.

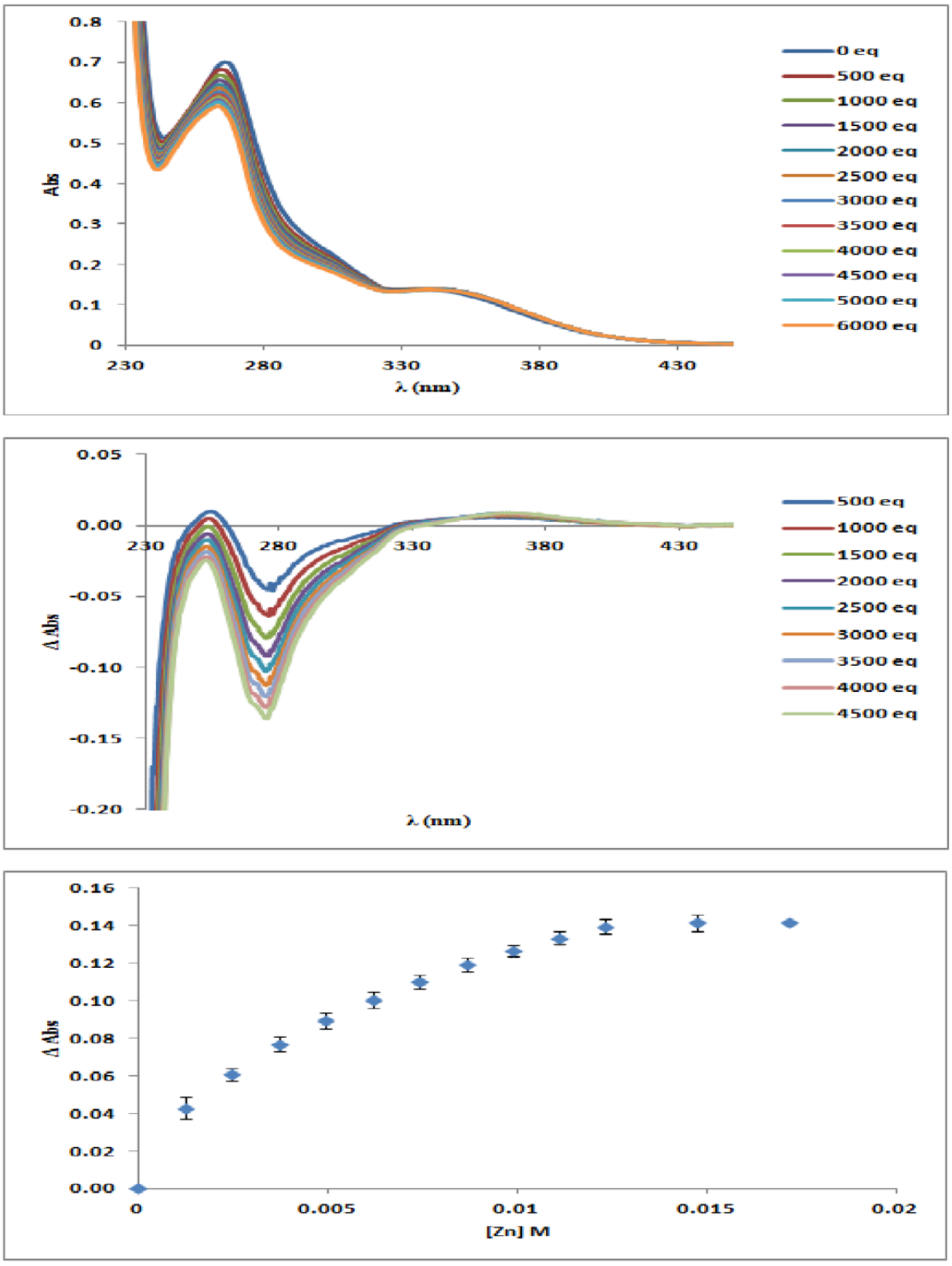


Figure S12 Titration of ZinCast-3 with $Zn(ClO_4)_2$ in EtOH.

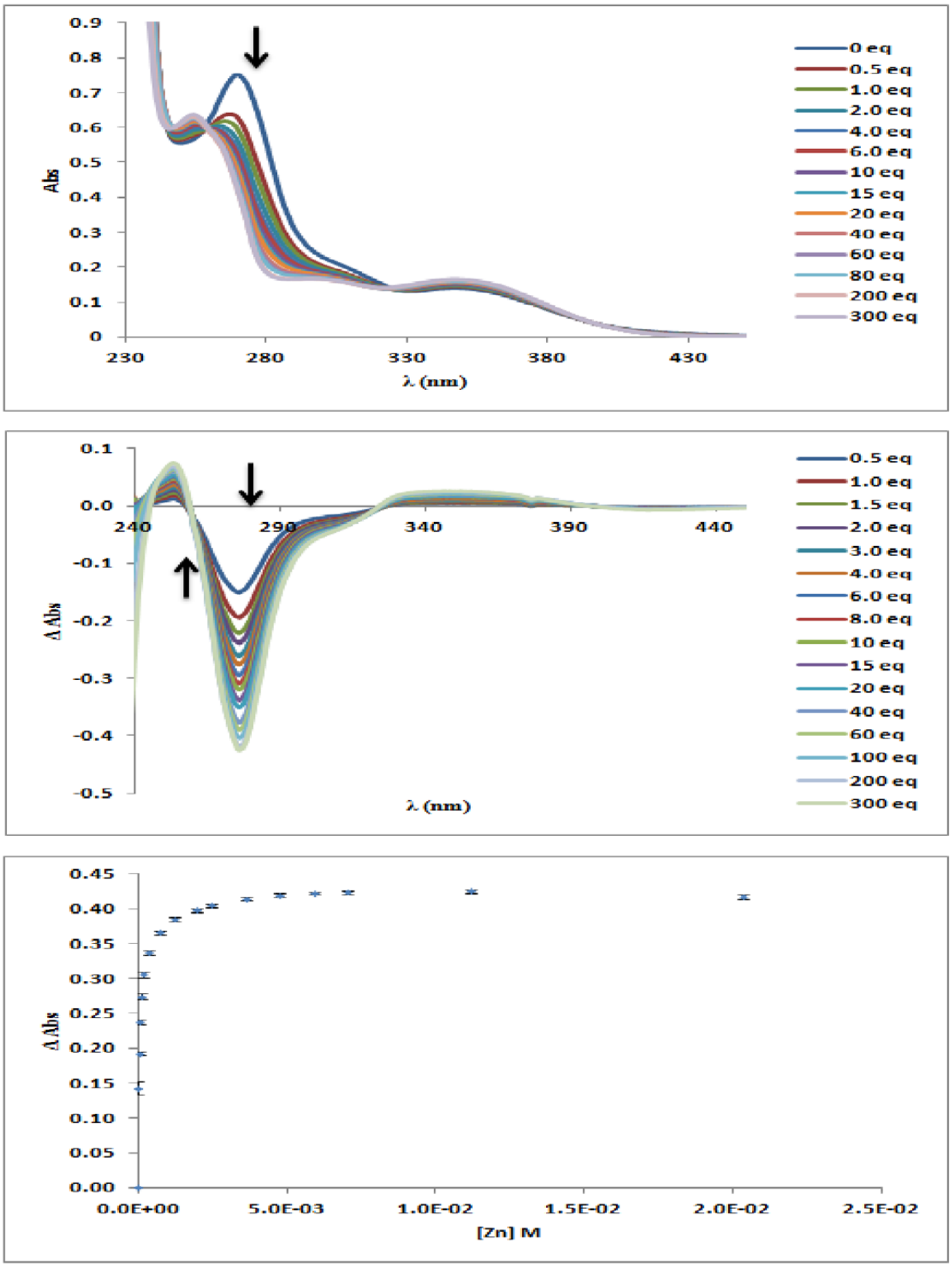


Figure S13 Titration of ZinCast-3 with $Zn(ClO_4)_2$ in CH_3CN.

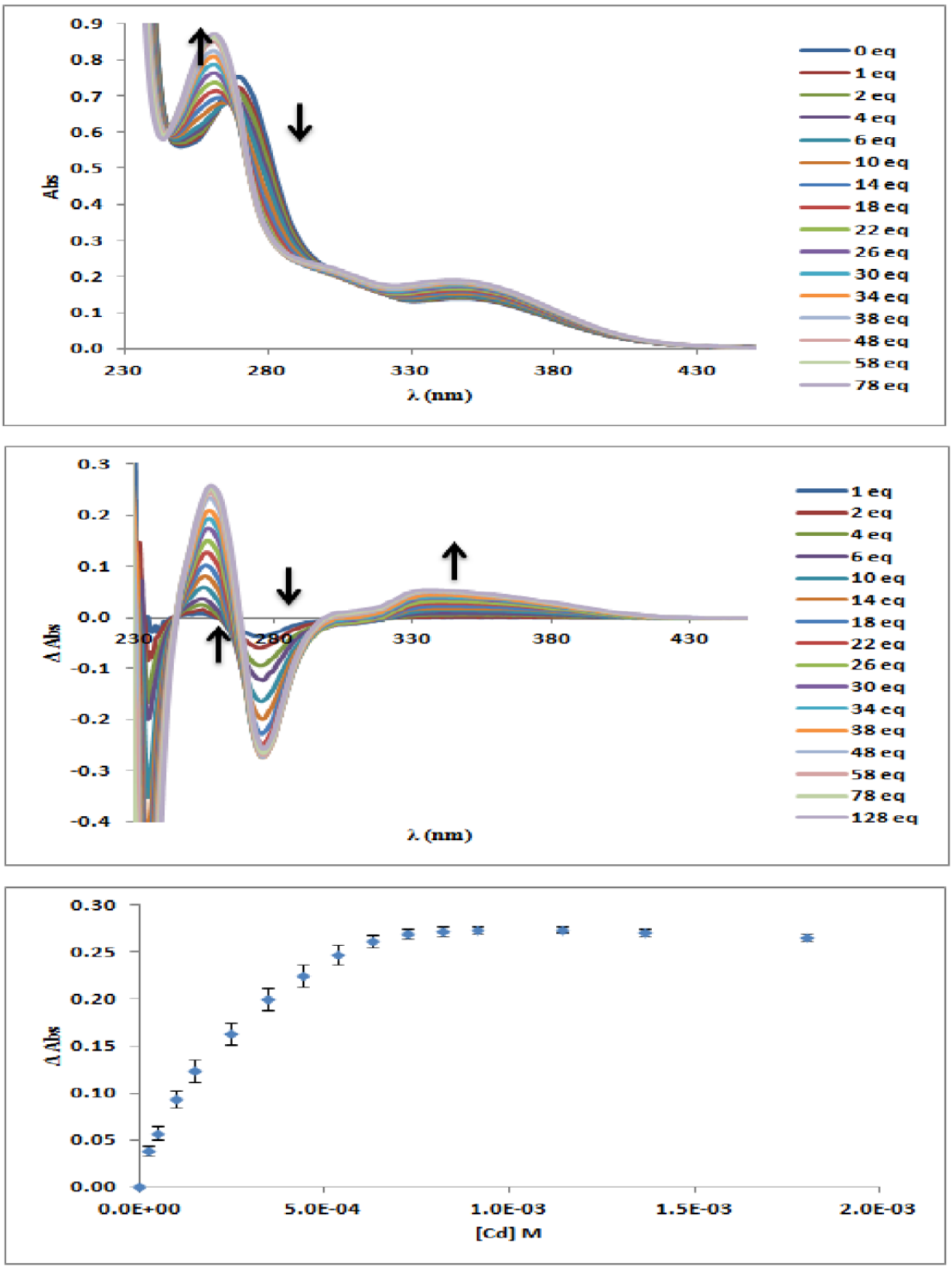


Figure S14 Titration of ZinCast-3 with $Cd(ClO_4)_2$ in CH_3CN.

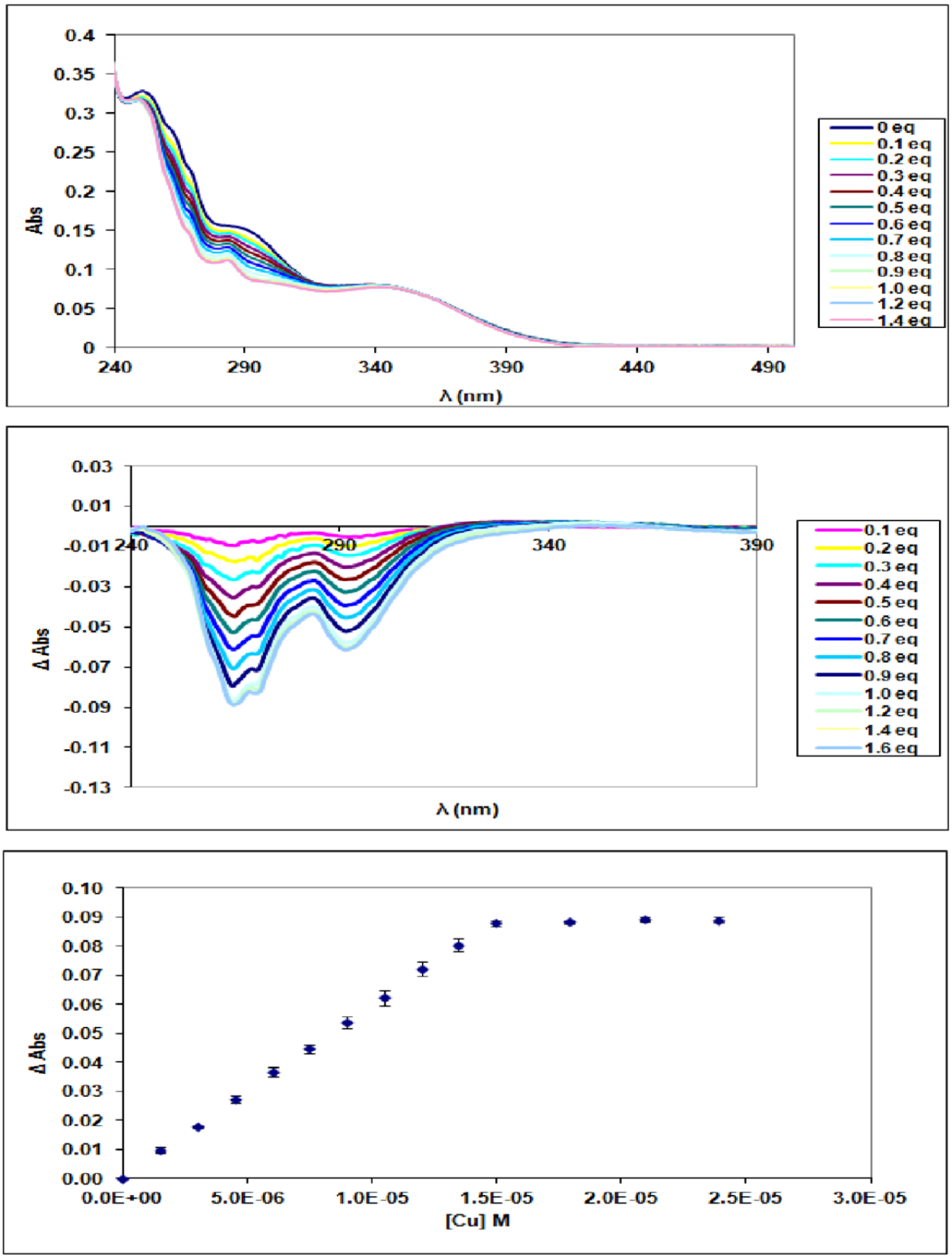


Figure S15 Titration of ZinCast-4 with $Cu(ClO_4)_2$ in EtOH.

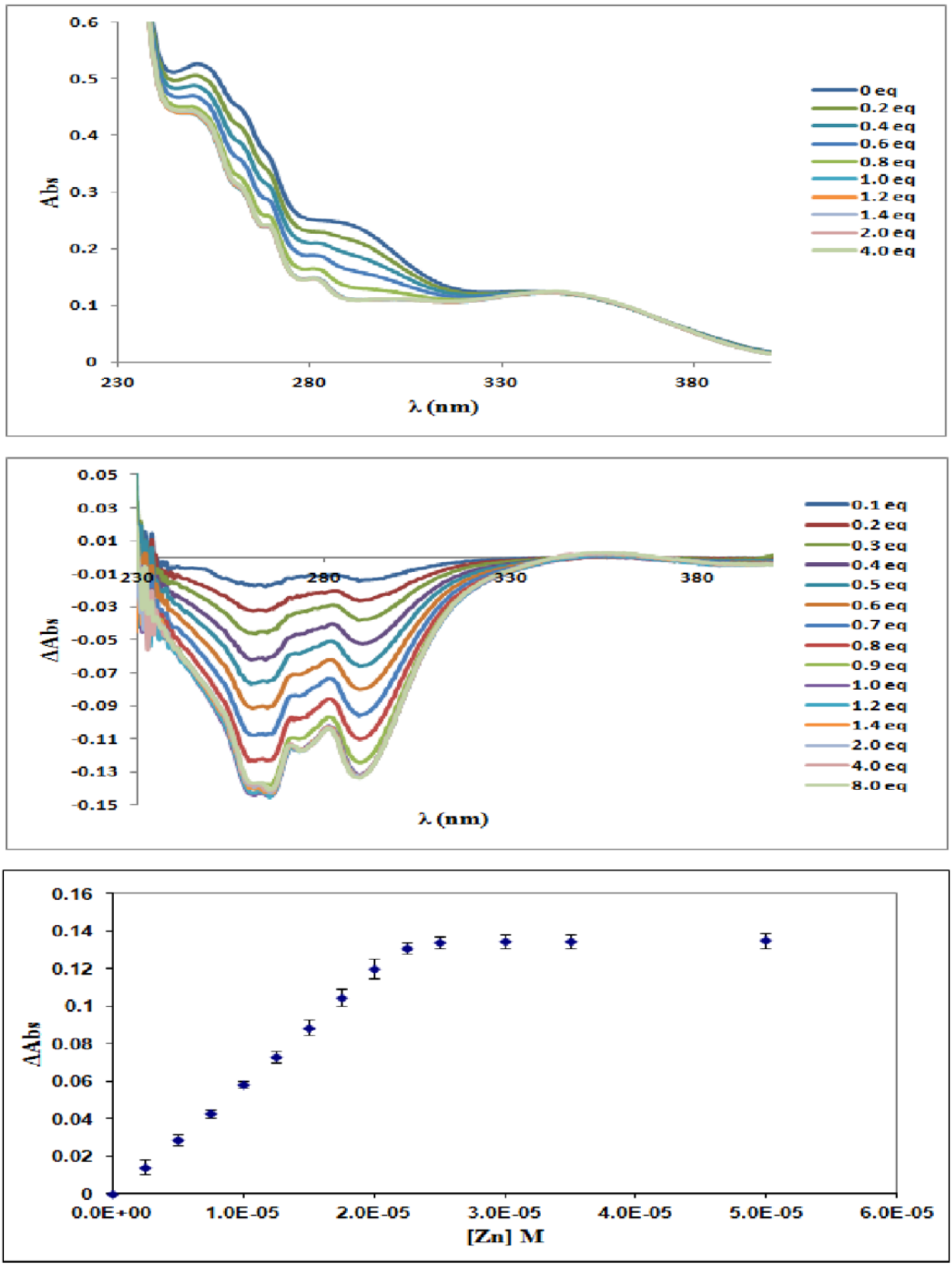


Figure S16 Titration of ZinCast-4 with $Zn(ClO_4)_2$ in EtOH.

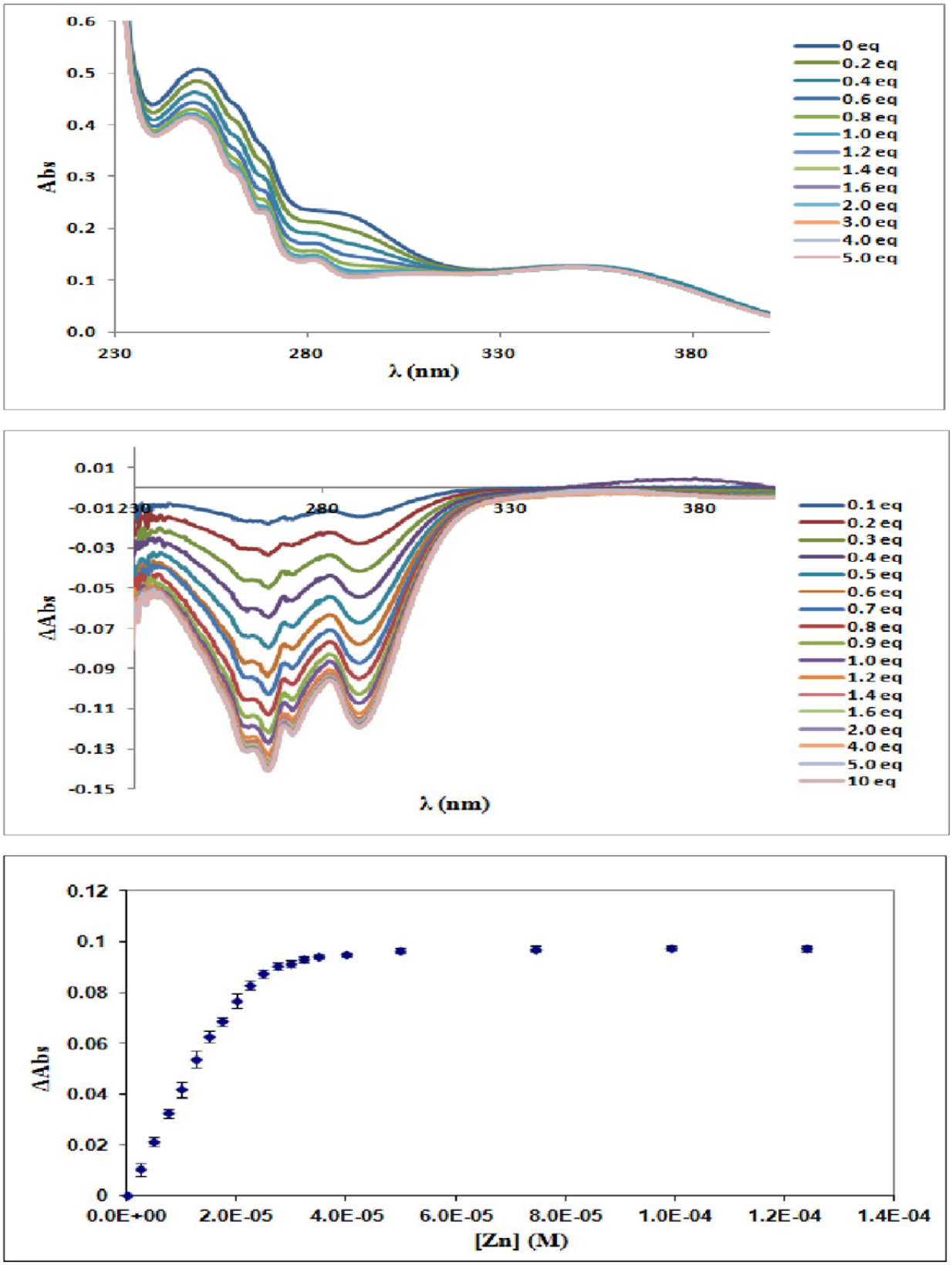


Figure S17 Titration of ZinCast-4 with $Zn(ClO_4)_2$ in water.

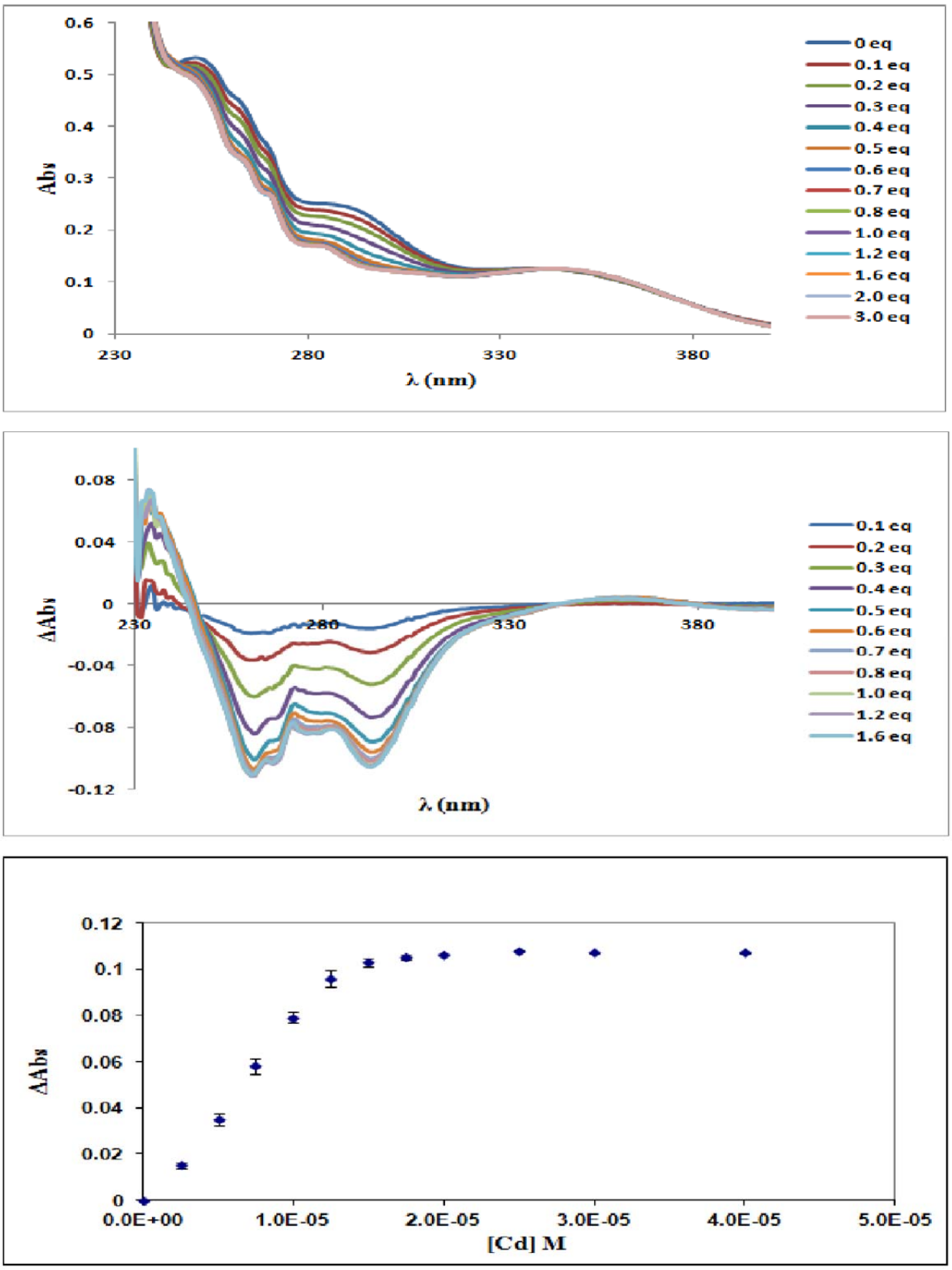


Figure S18 Titration of ZinCast-4 with $Cd(ClO_4)_2$ in EtOH

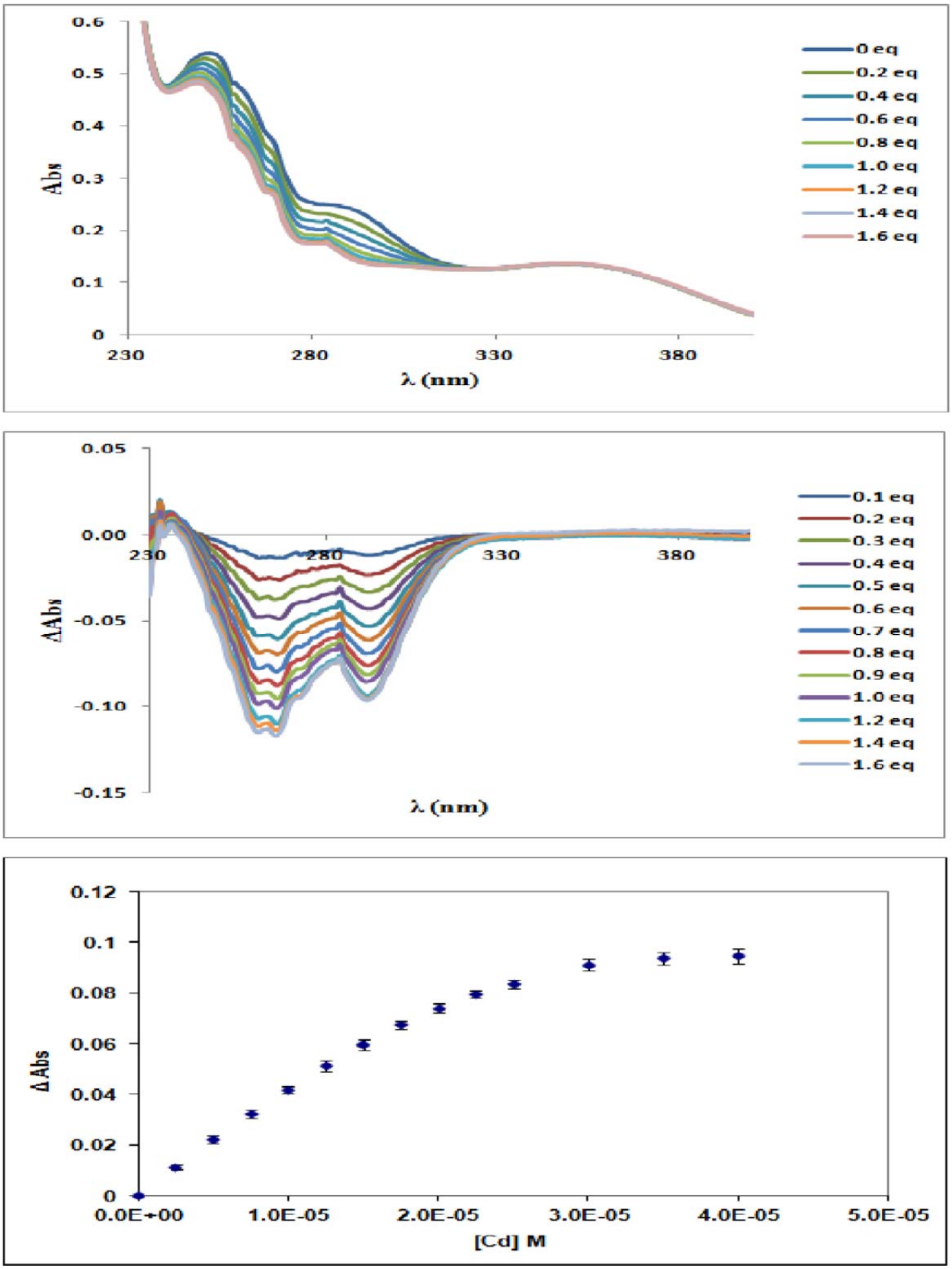


Figure S19 Titration of ZinCast-4 with $Cd(ClO_4)_2$ in water.

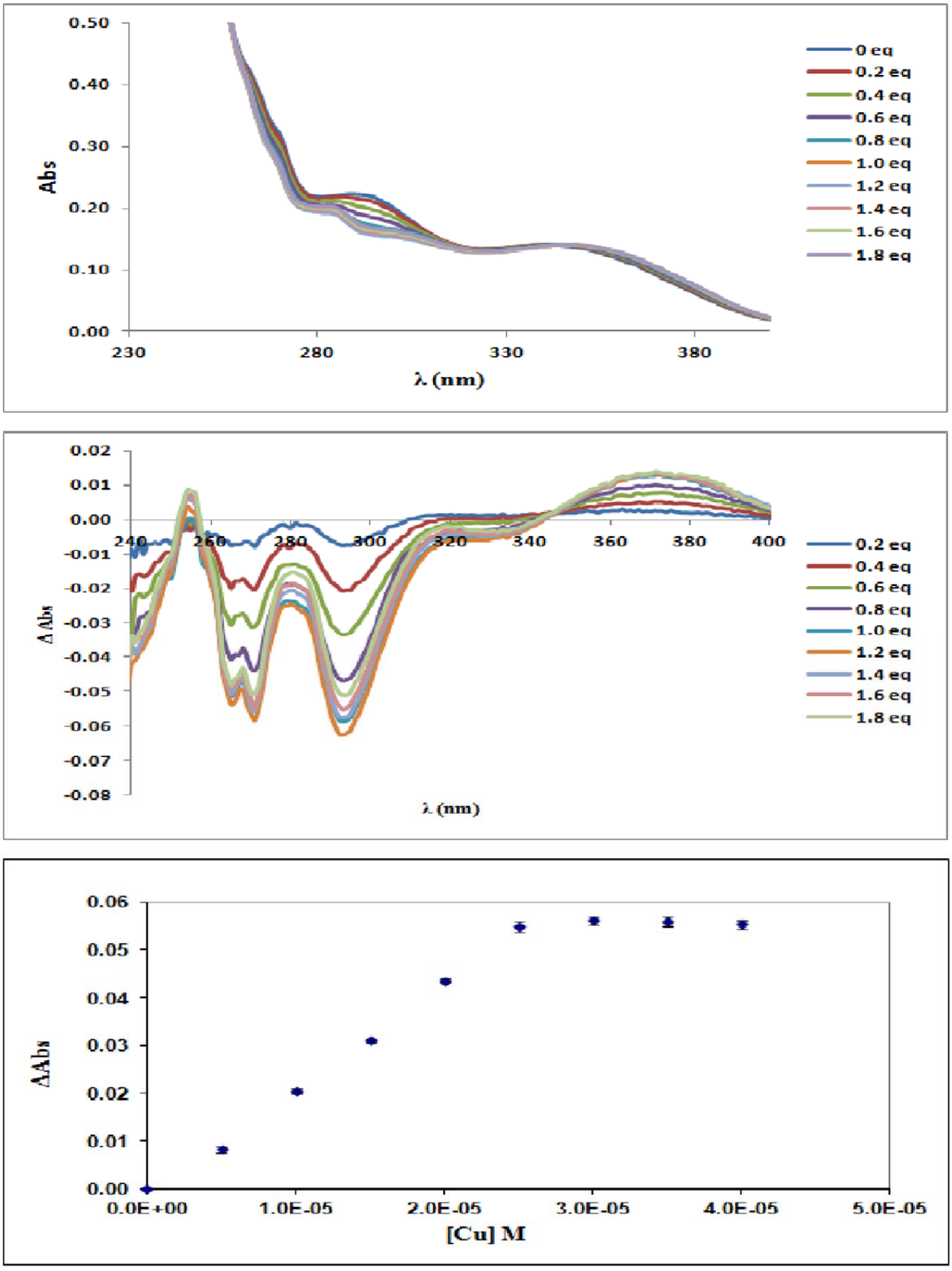


Figure S20 Titration of ZinCast-5 with $Cu(ClO_4)_2$ in EtOH.

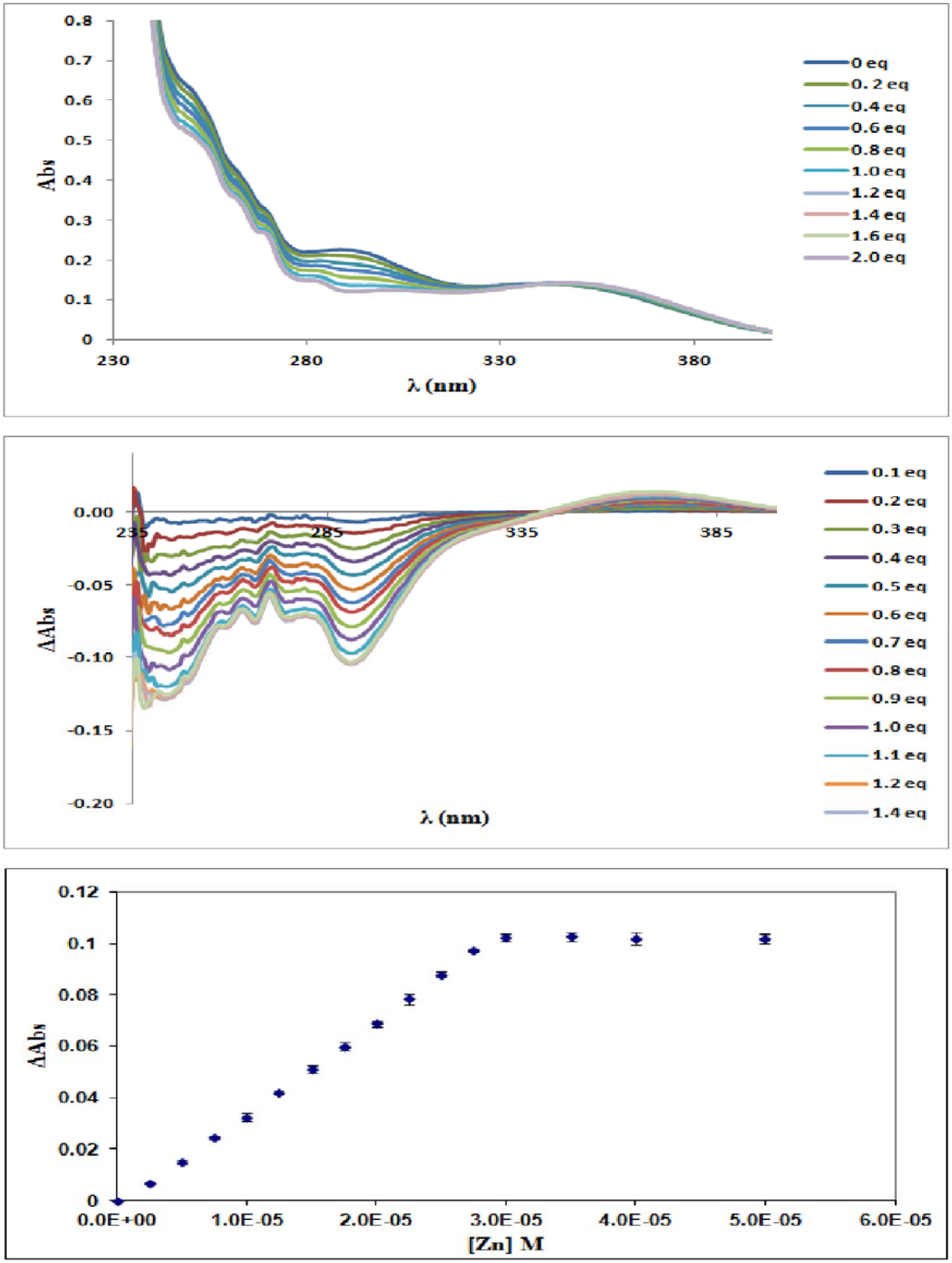


Figure S21 Titration of ZinCast-5 with $Zn(ClO_4)_2$ in EtOH.

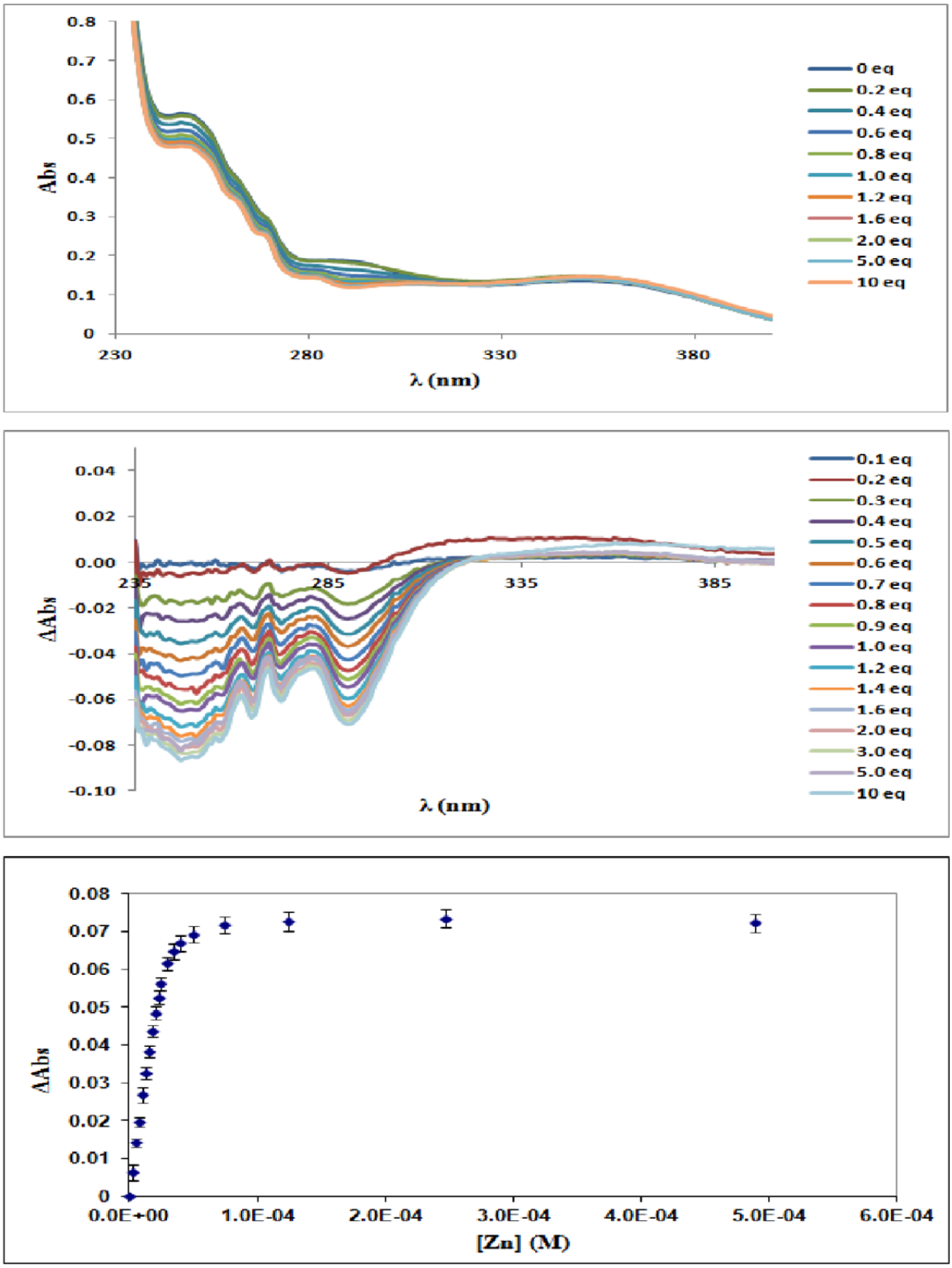


Figure S22 Titration of ZinCast-5 with $Zn(ClO_4)_2$ in water.

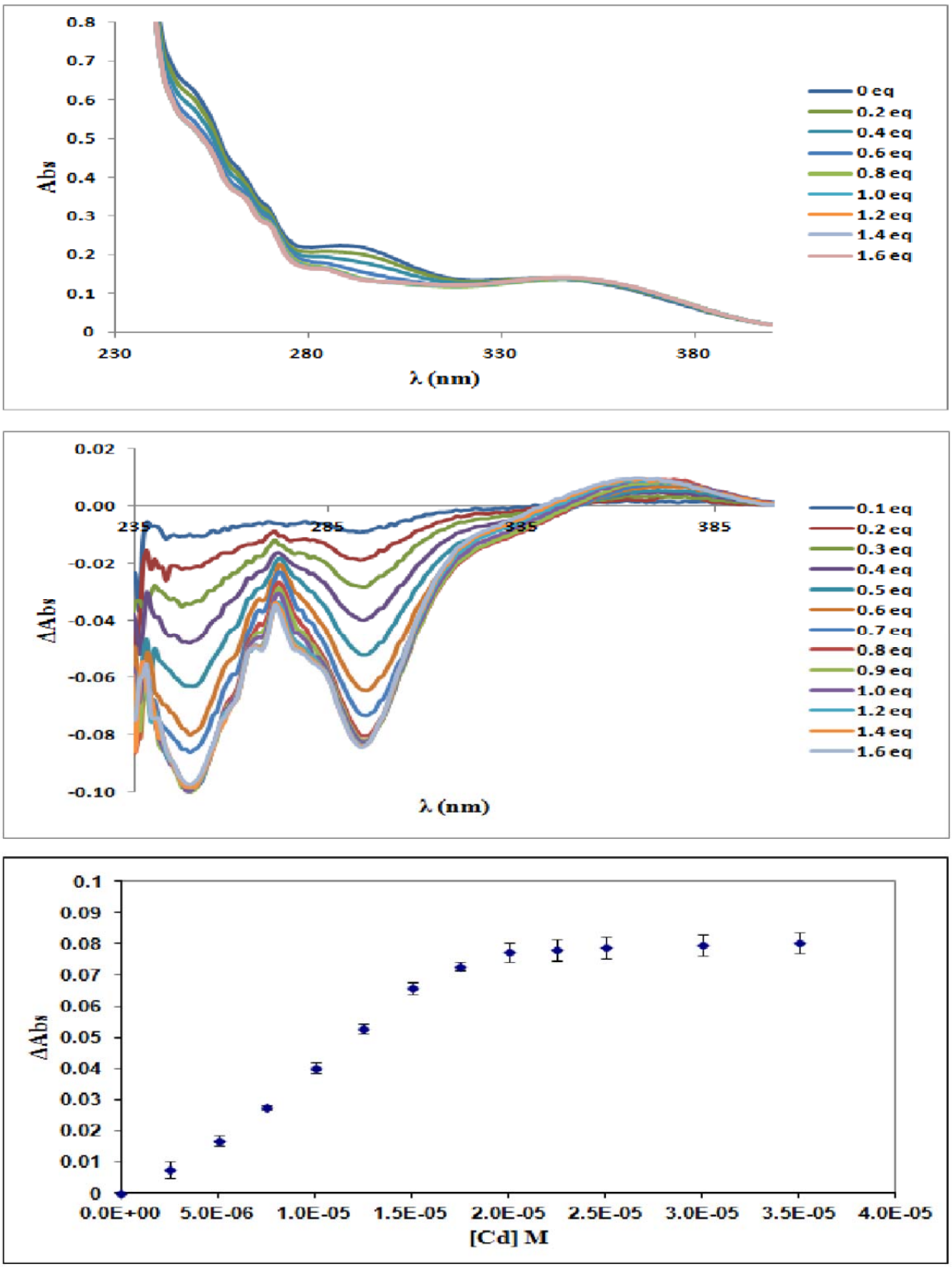


Figure S23 Titration of ZinCast-5 with $Cd(ClO_4)_2$ in EtOH.

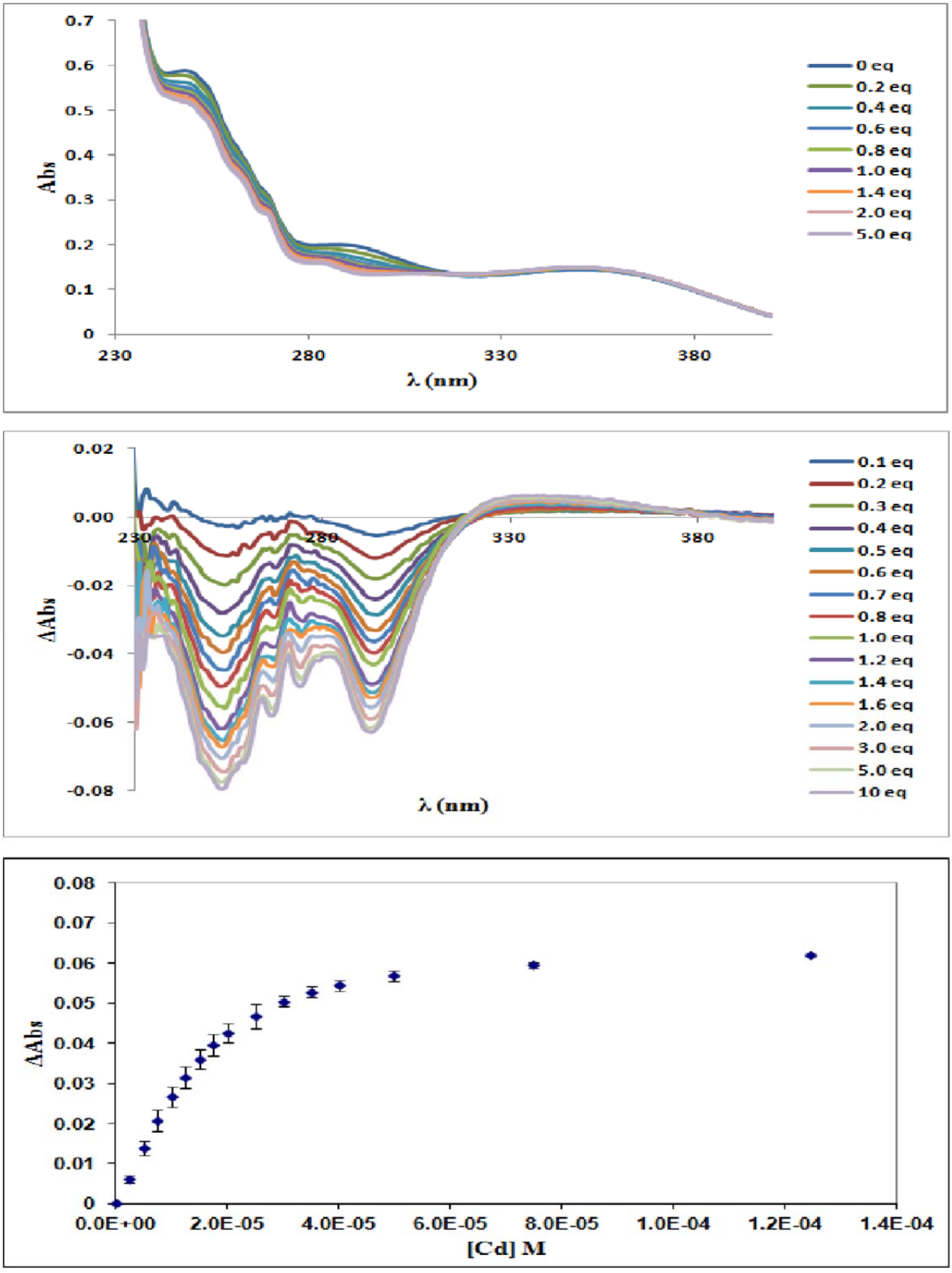


Figure S24 Titration of ZinCast-5 with $Cd(ClO_4)_2$ in water.

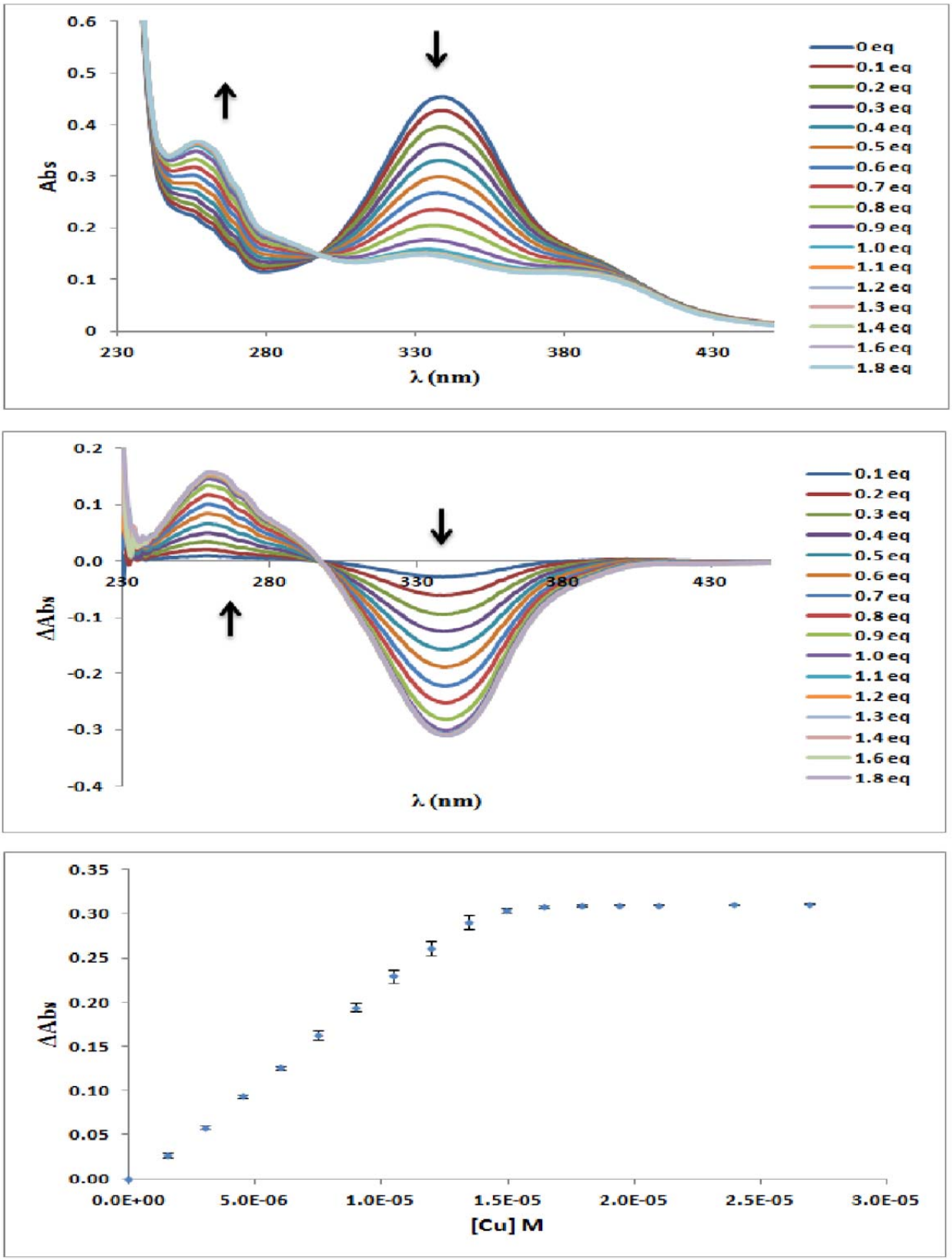
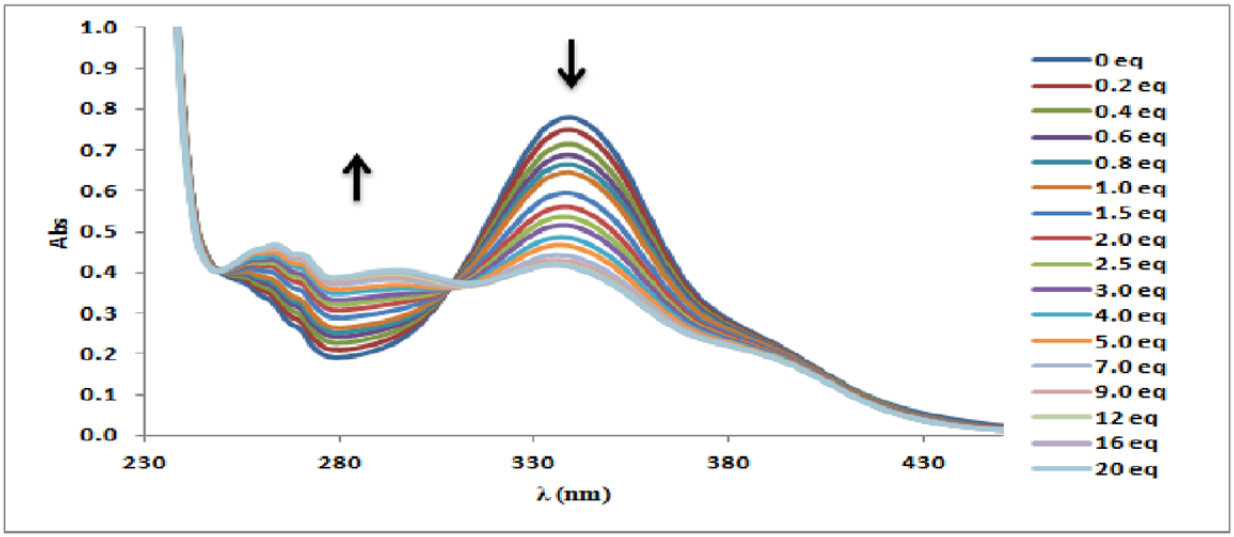
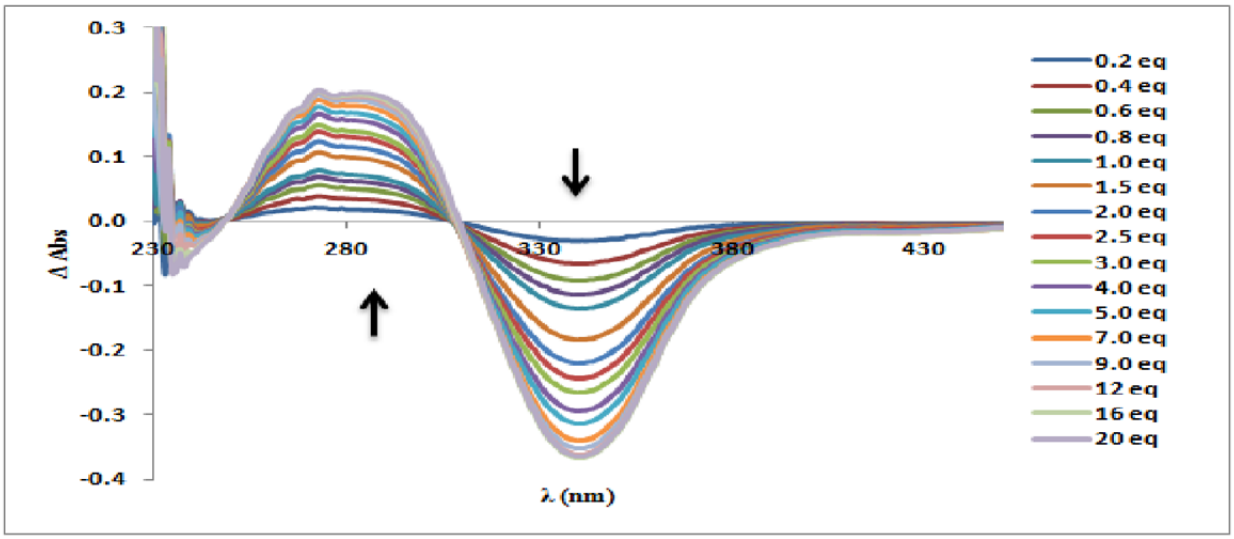


Figure S25 Titration of ZinUnc-1 with $Cu(ClO_4)_2$ in EtOH.





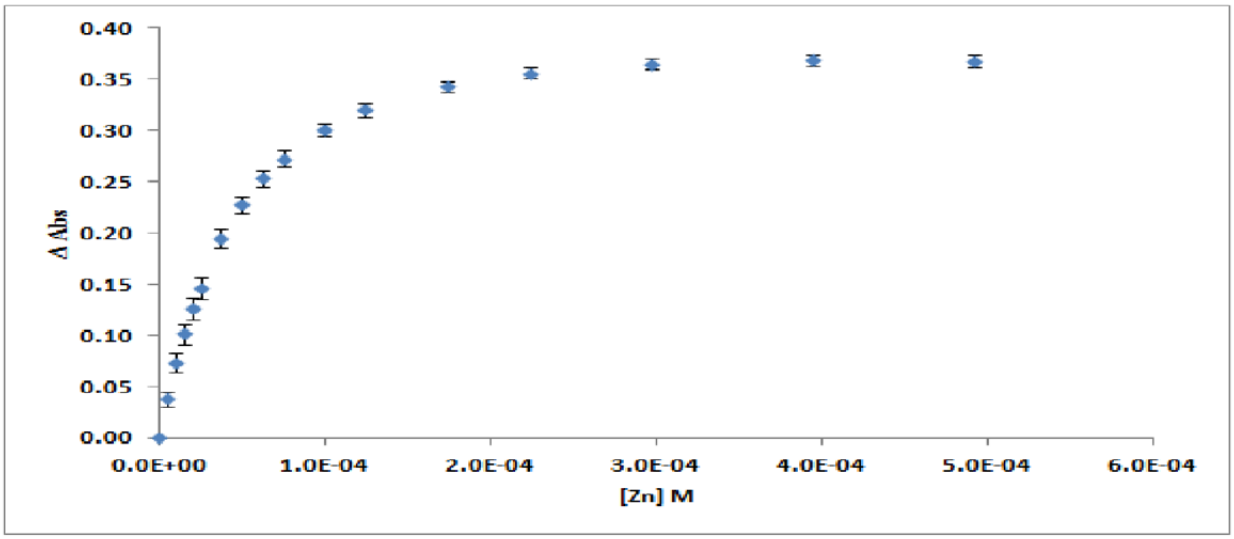


Figure S26 Titration of ZinUnc-1 with $Zn(ClO_4)_2$ in EtOH.

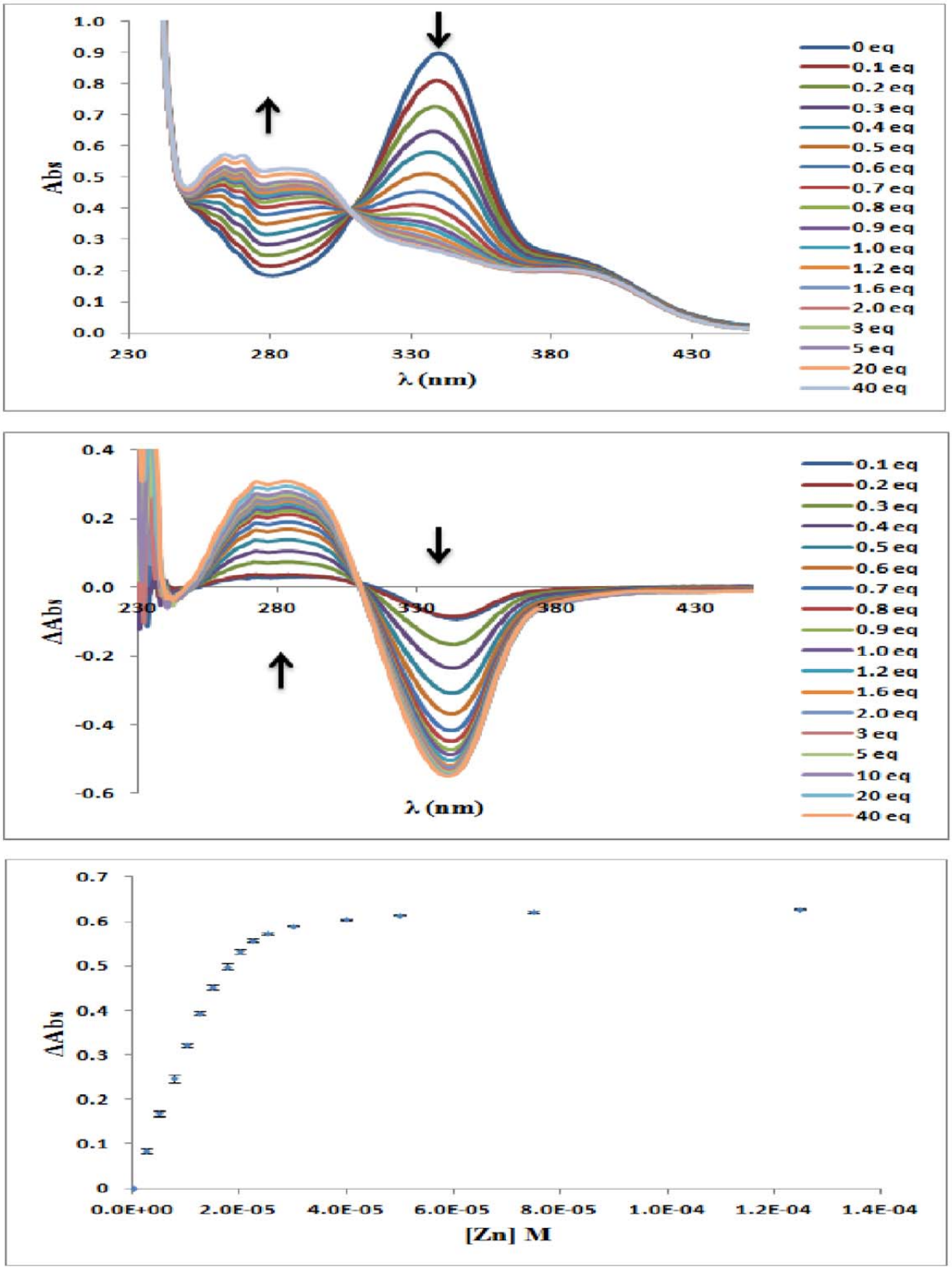


Figure S27 Titration of ZinUnc-1 with $Zn(ClO_4)_2$ in CH_3CN.

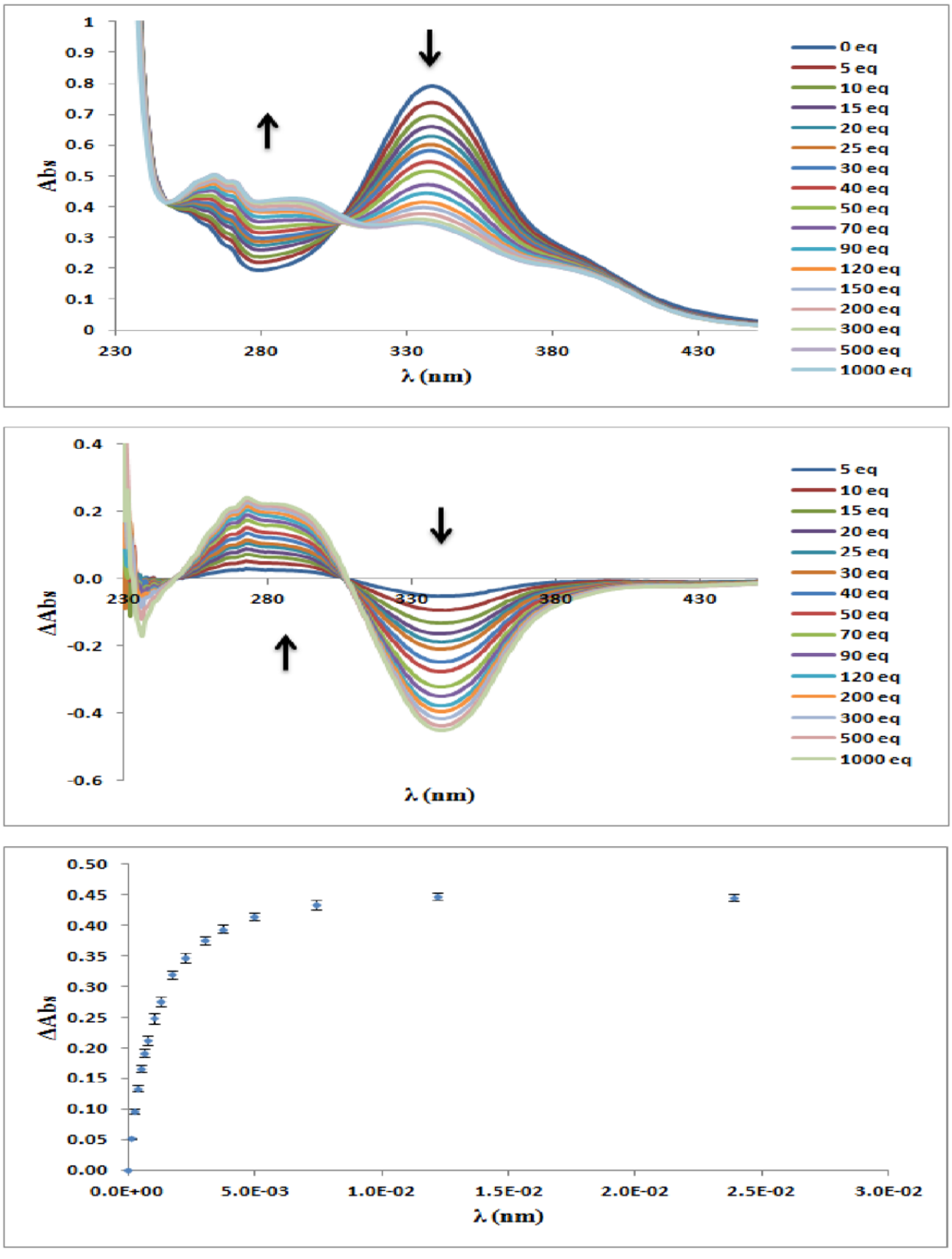


Figure S28 Titration of ZinUnc-1 with $Cd(ClO_4)_2$ in EtOH.

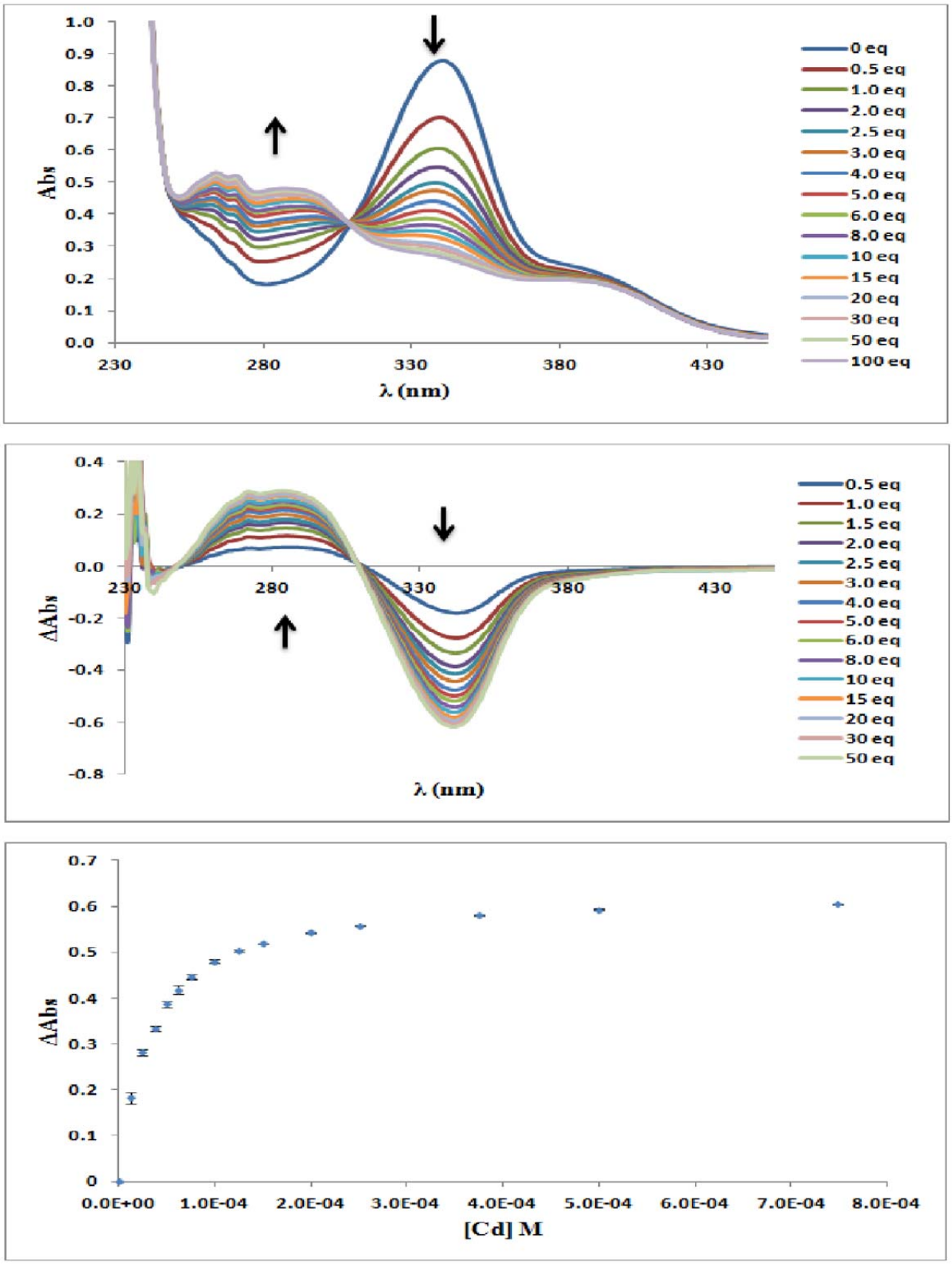


Figure S29 Titration of ZinUnc-1 with $Cd(ClO_4)_2$ in CH_3CN.

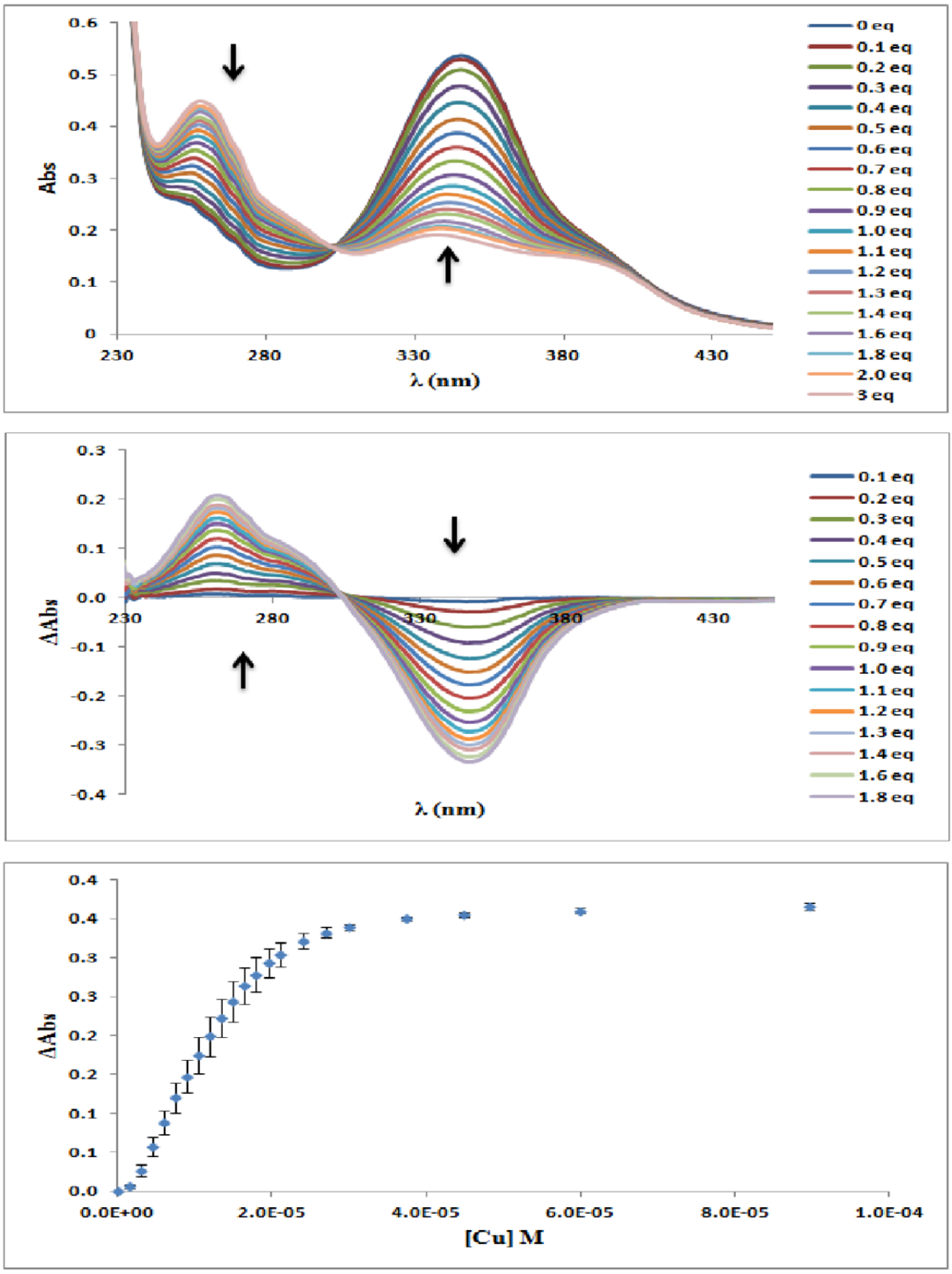


Figure S30 Titration of ZinUnc-2 with $Cu(ClO_4)_2$ in EtOH.

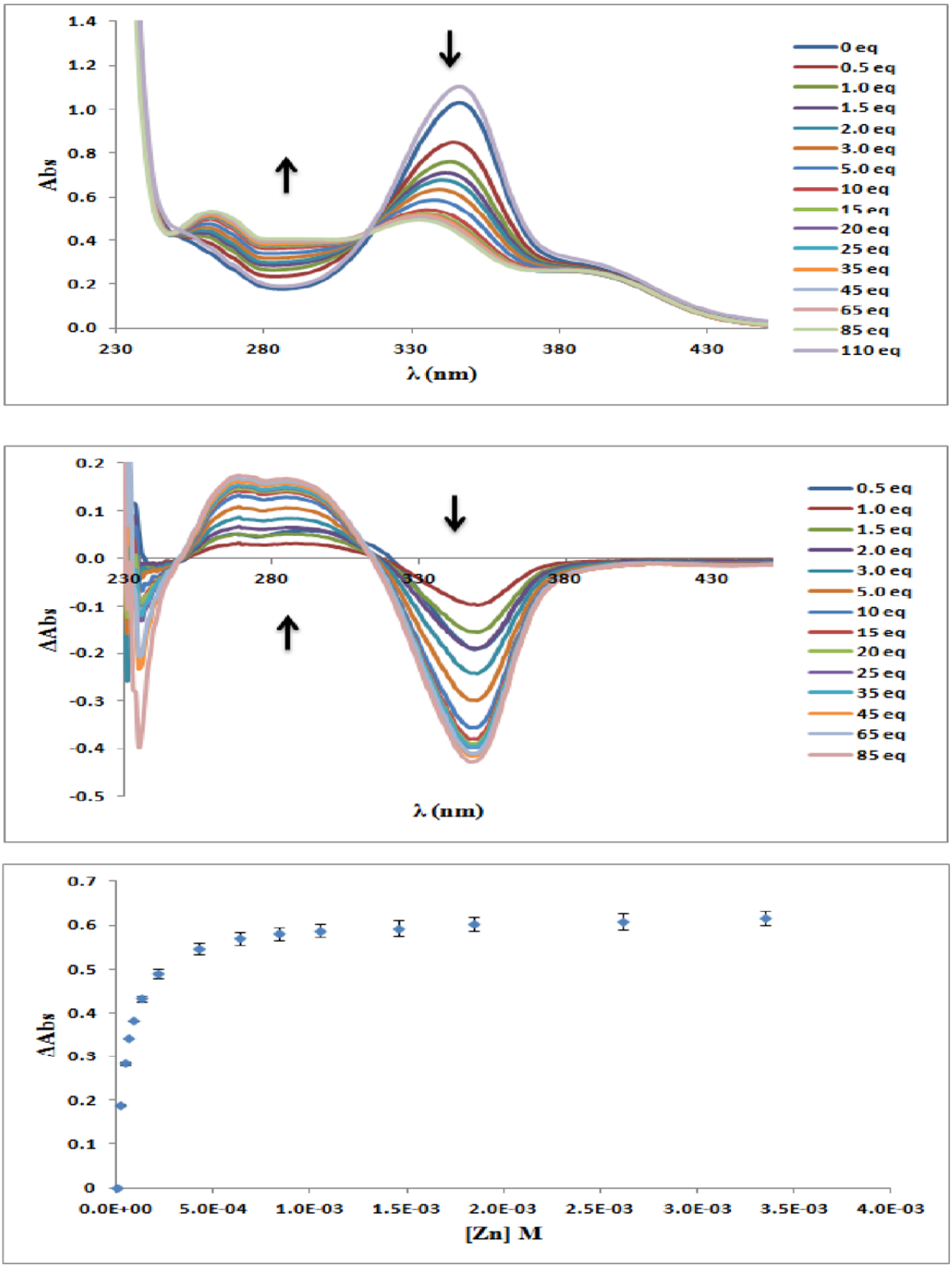


Figure S31 Titration of ZinUnc-2 with $Zn(ClO_4)_2$ in CH_3CN.

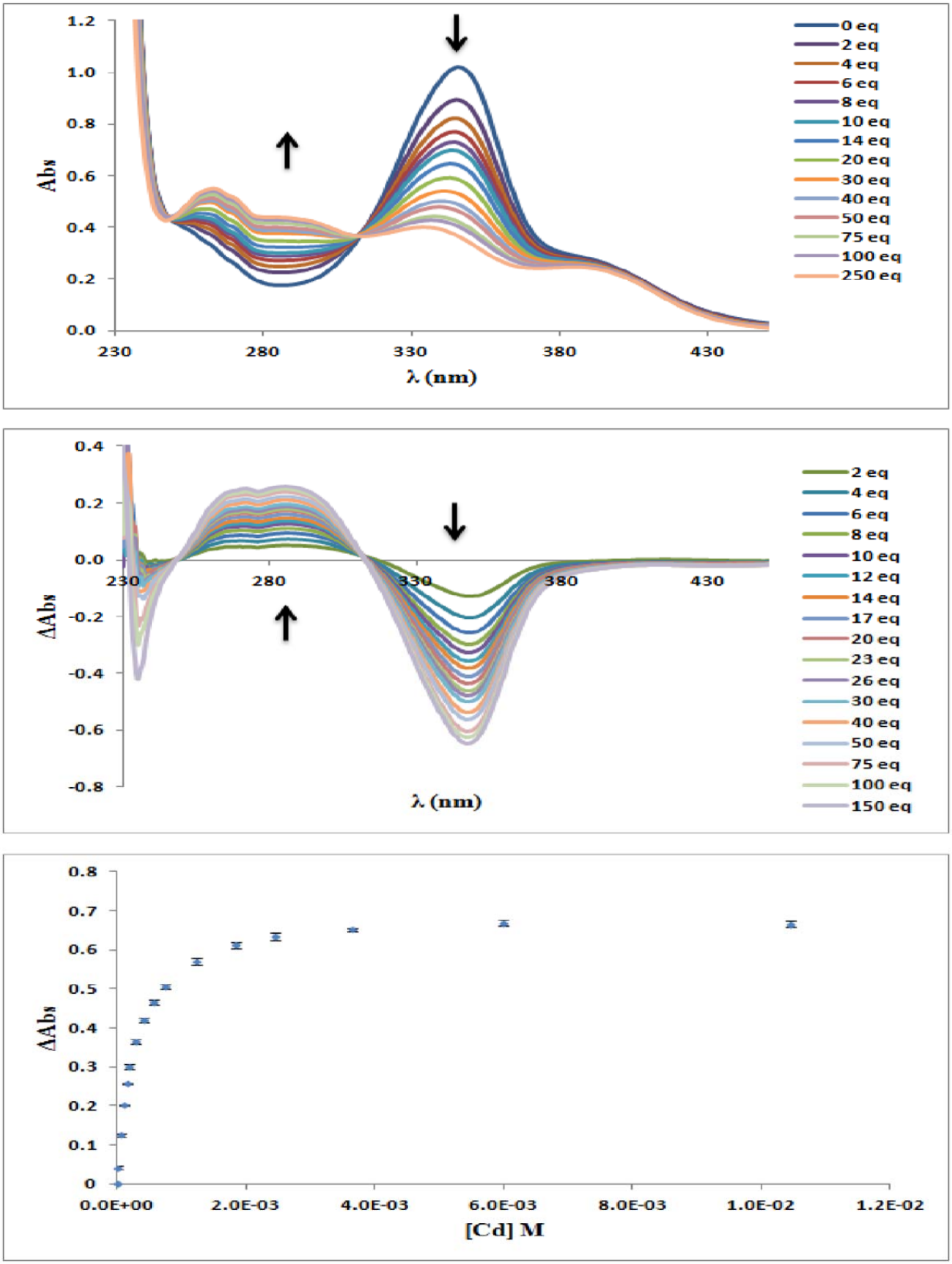


Figure S32 Titration of ZinUnc-2 with $Cd(ClO_4)_2$ in CH_3CN.

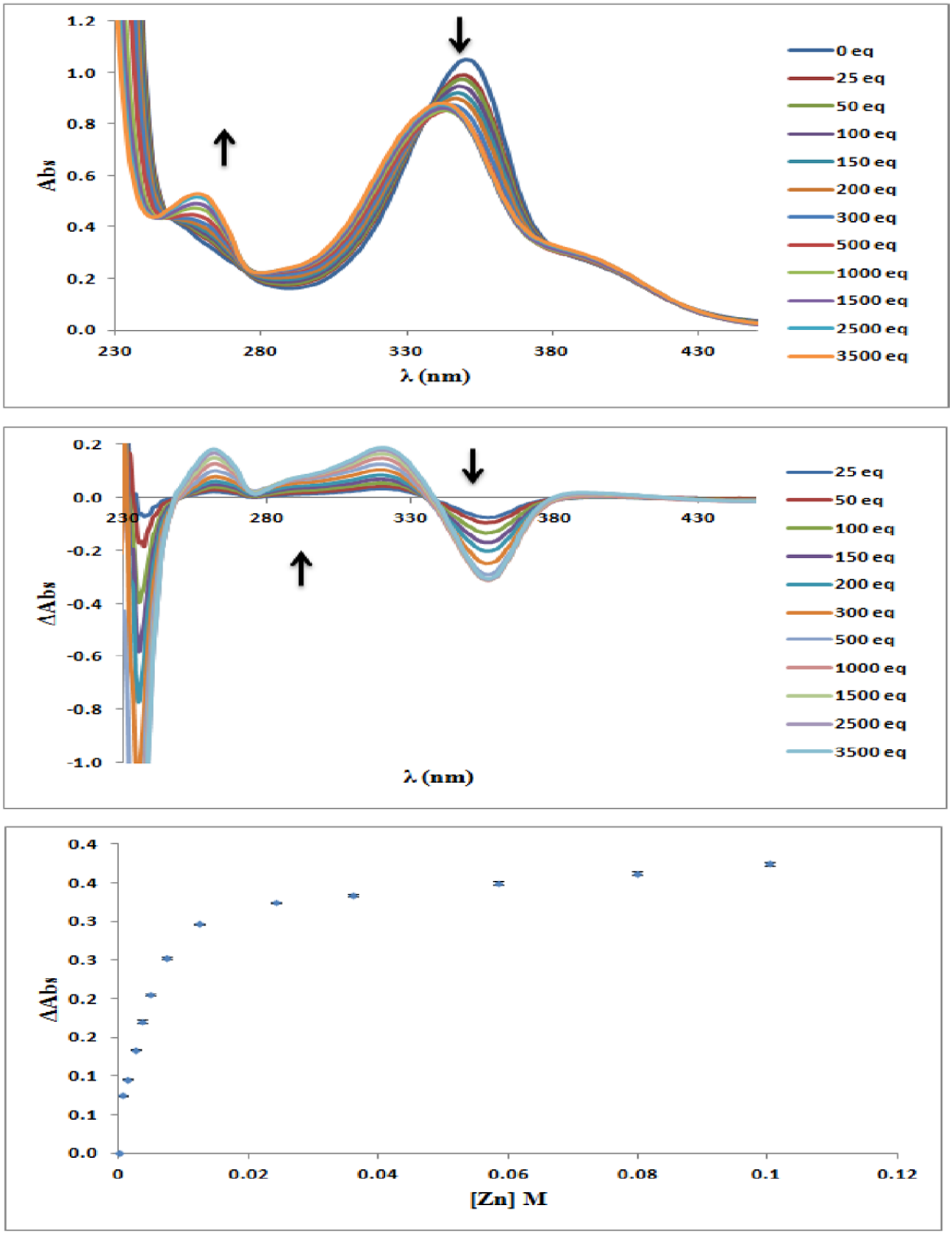


Figure S33 Titration of ZinUnc-3 with $Zn(ClO_4)_2$ in CH_3CN.

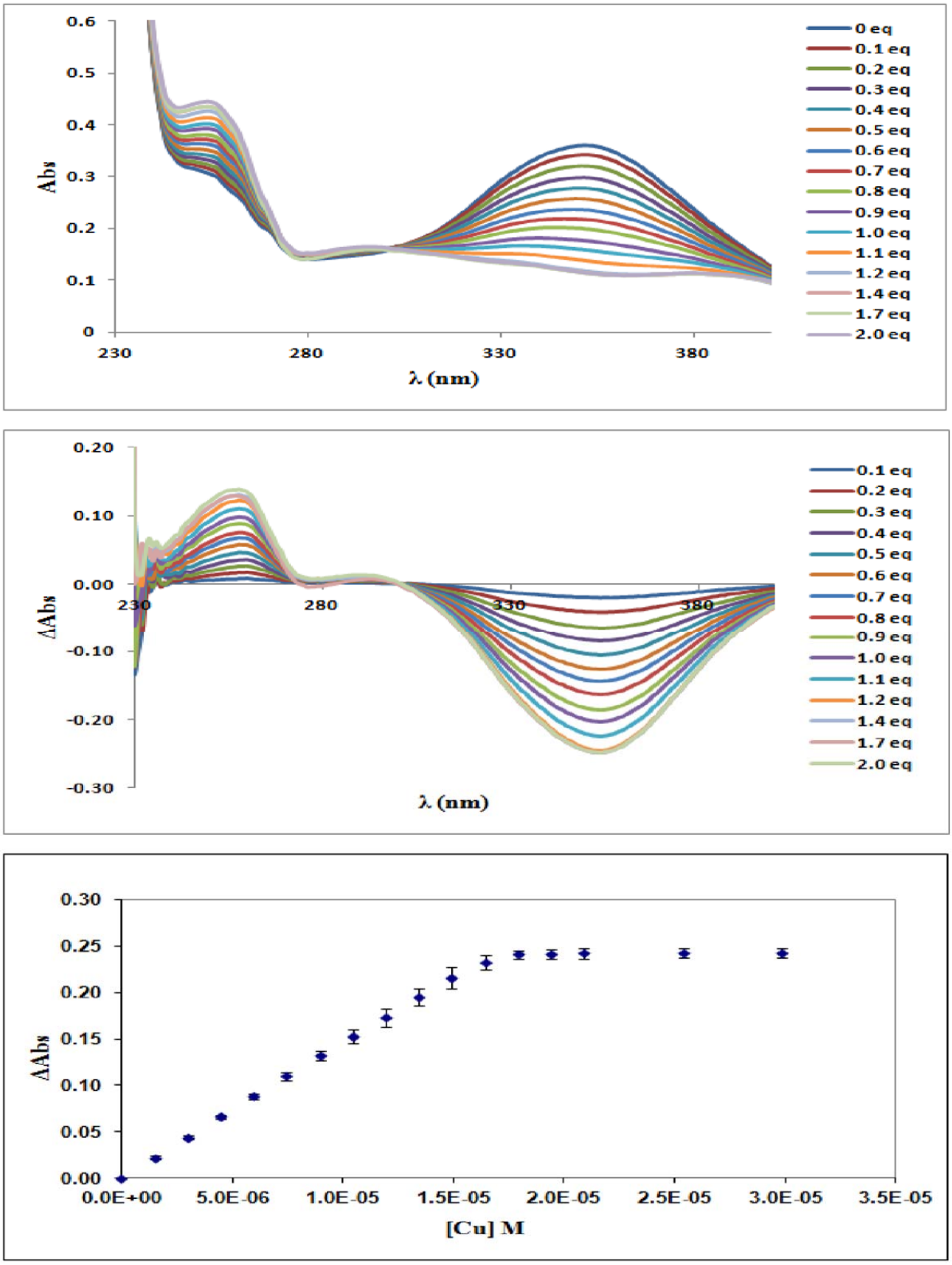


Figure S34 Titration of ZinUnc-4 with $Cu(ClO_4)_2$ in EtOH.

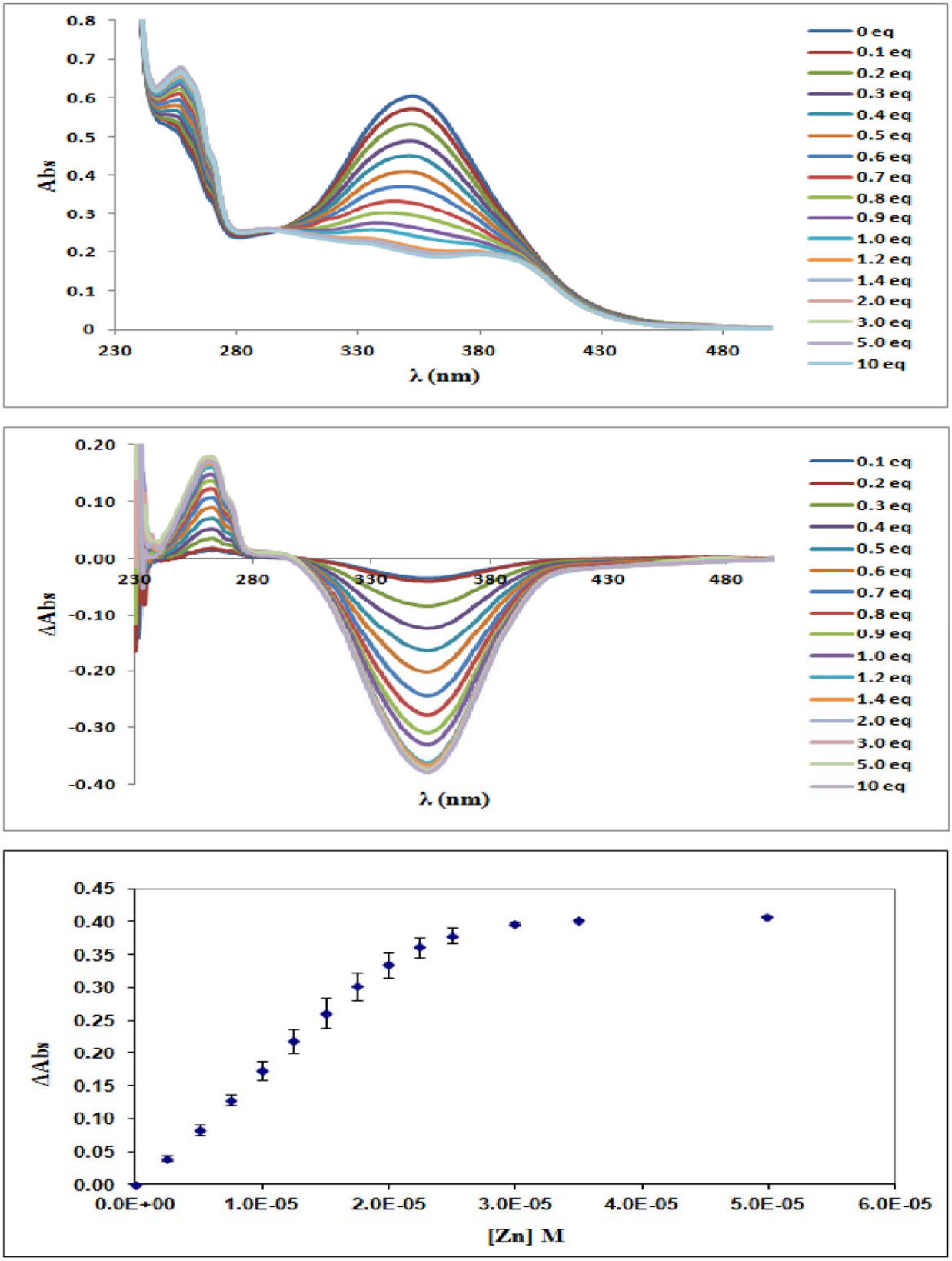


Figure S35 Titration of ZinUnc-4 with $Zn(ClO_4)_2$ in EtOH

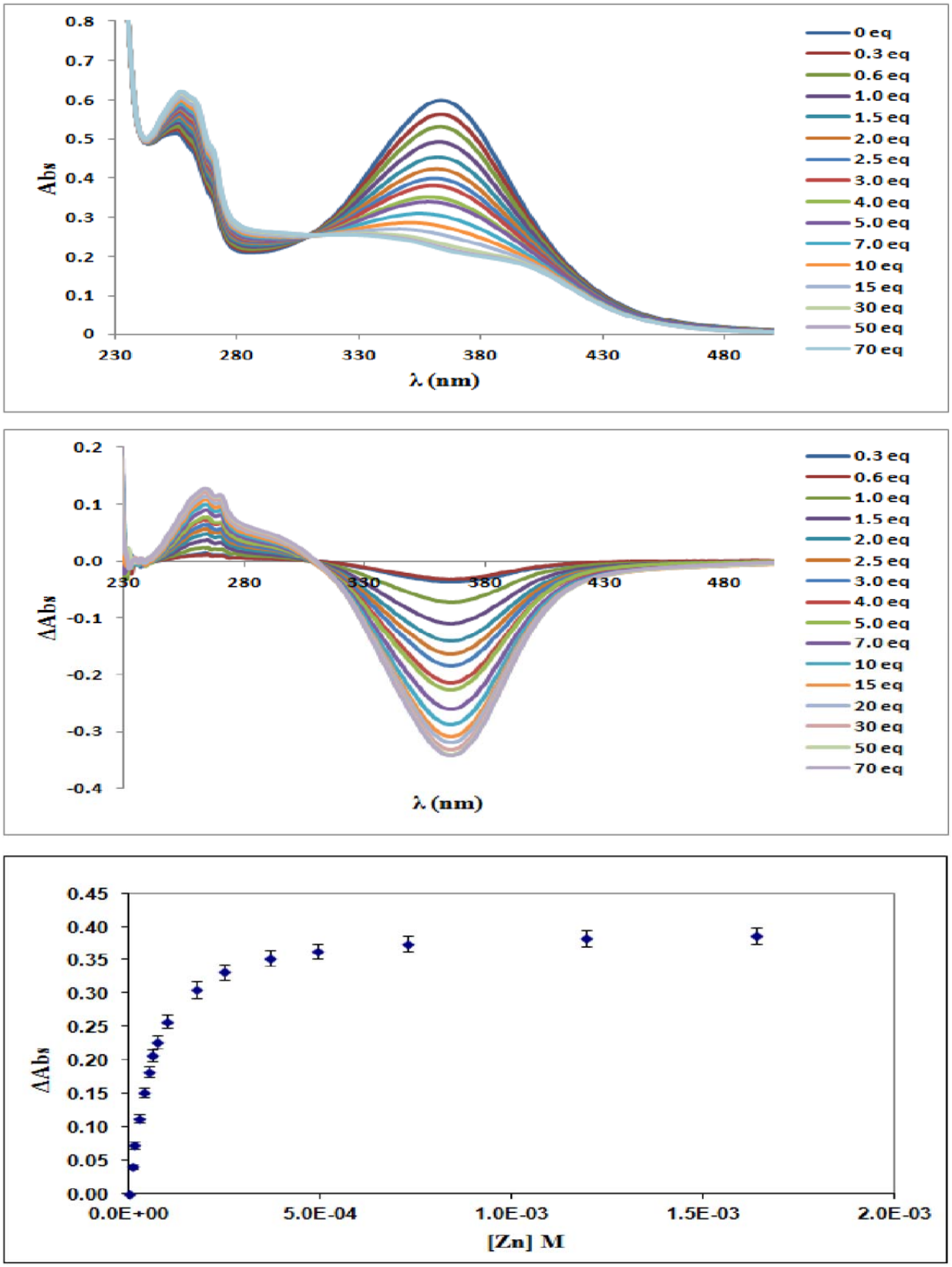
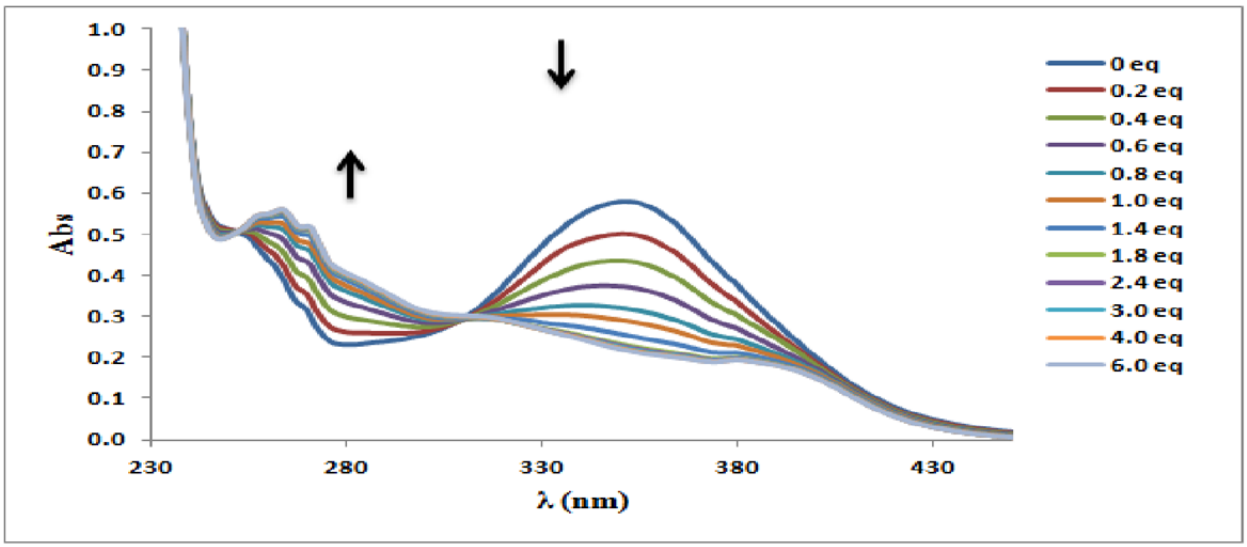
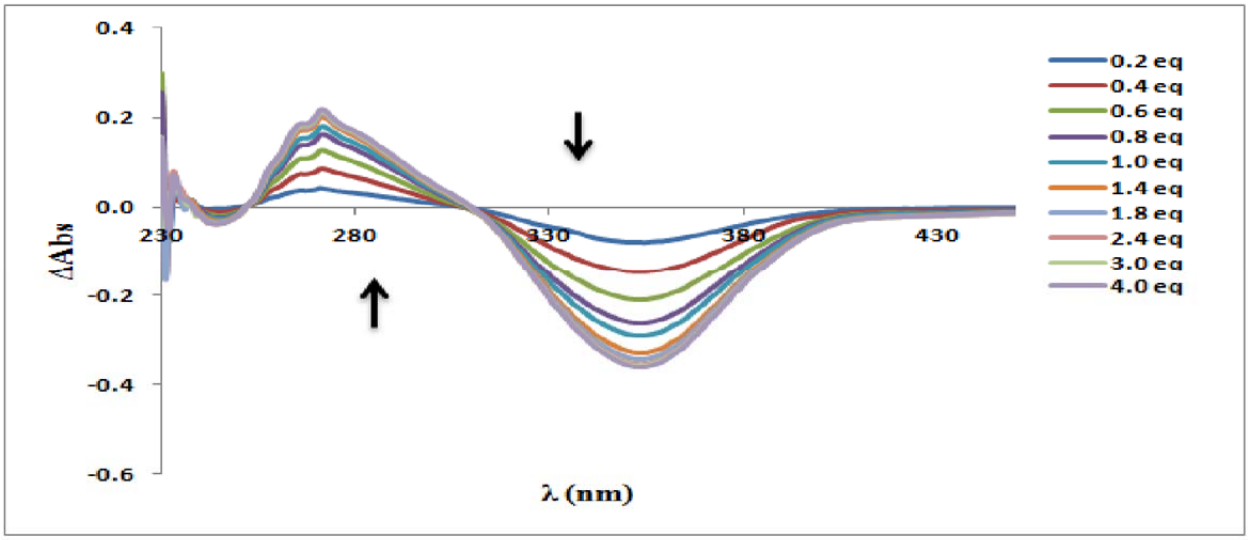


Figure S36 Titration of ZinUnc-4 with $Zn(ClO_4)_2$ in water.





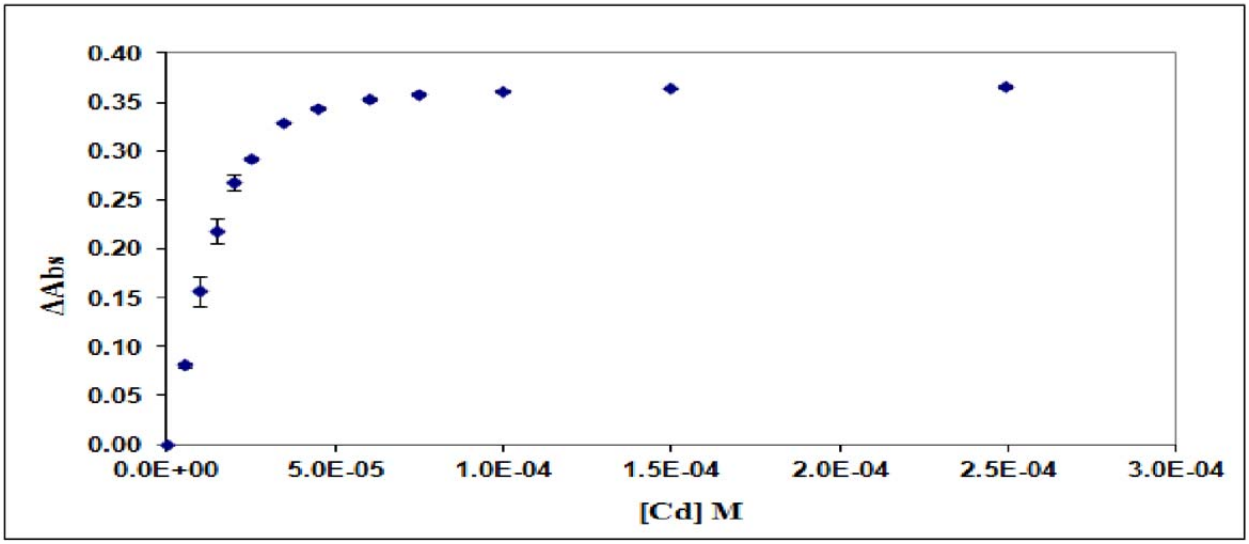


Figure S37 Titration of ZinUnc-4 with $Cd(ClO_4)_2$ in EtOH.

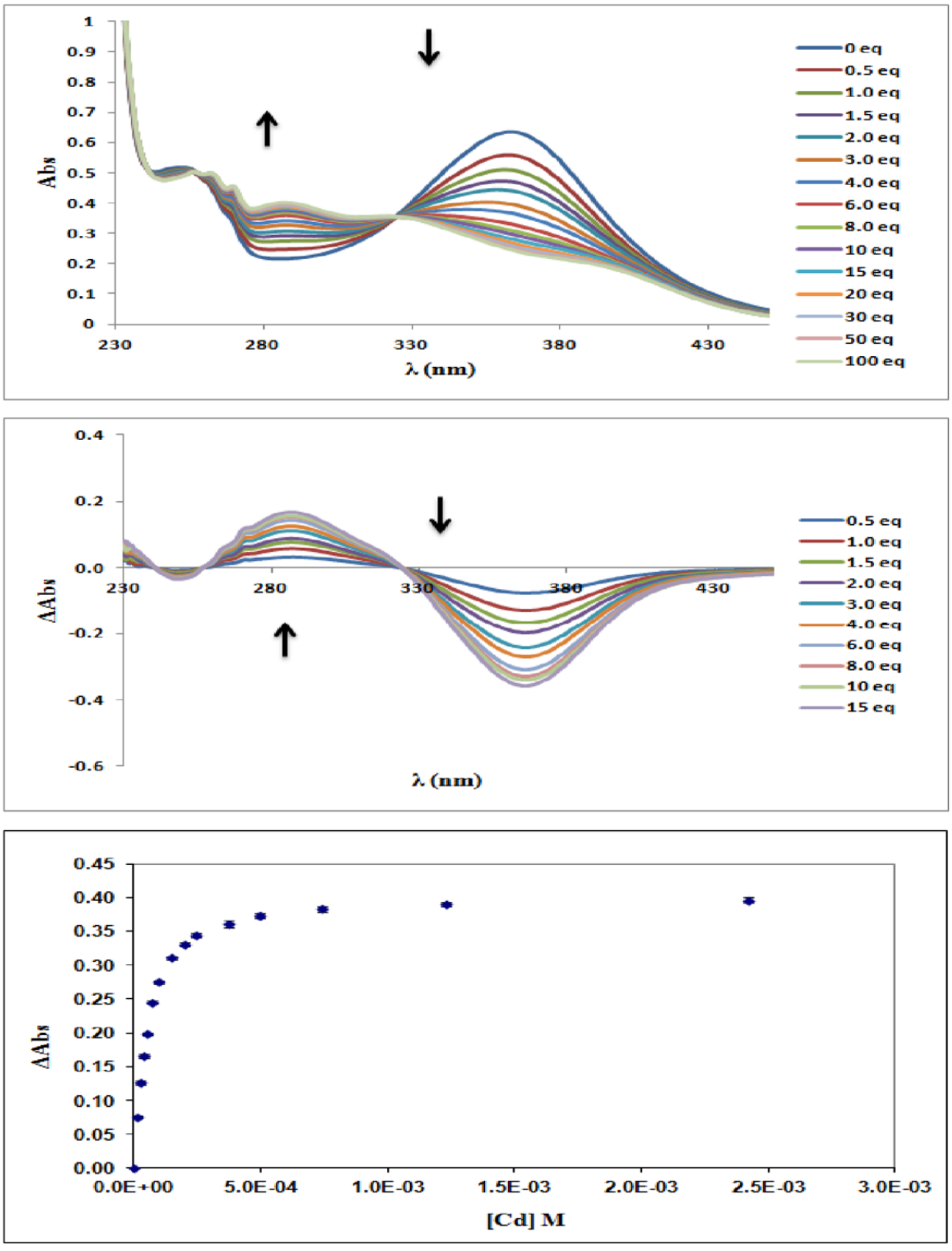


Figure S38 Titration of ZinUnc-4 with $Cd(ClO_4)_2$ in water.

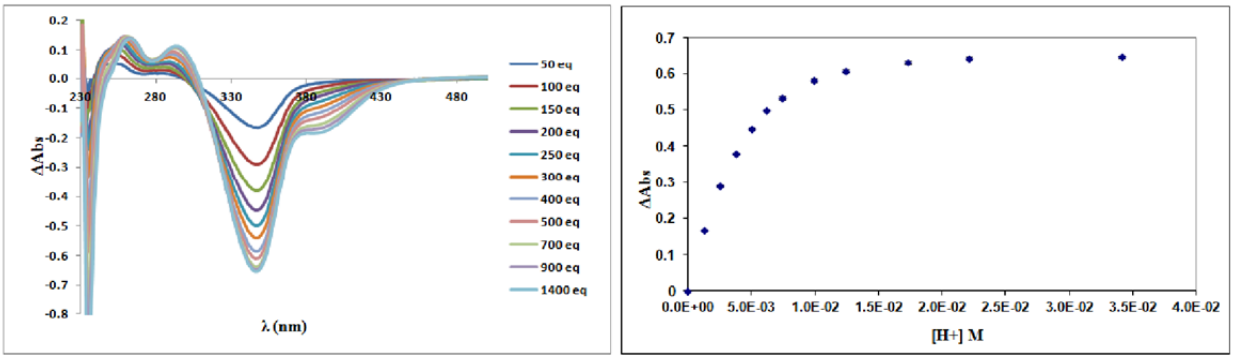


Figure S39 Titration of DMAUnc with HCl in CH_3CN.

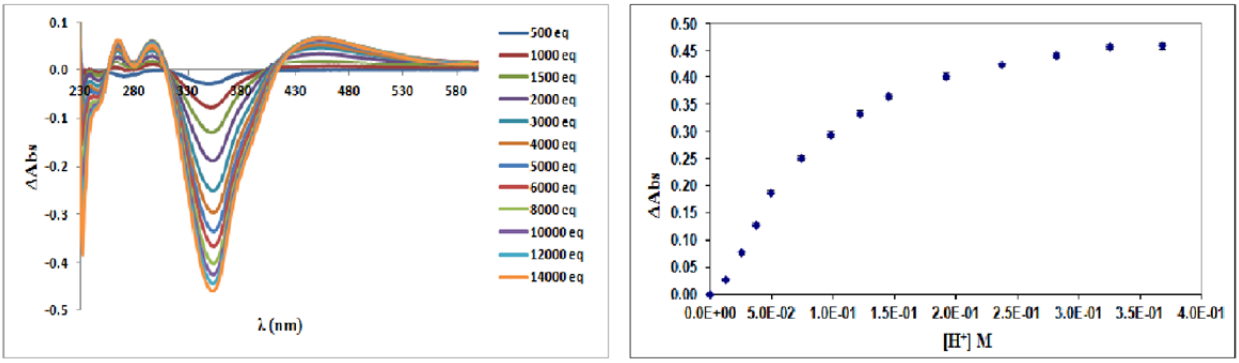


Figure S40 Titration of DMAUnc with HCl in EtOH.

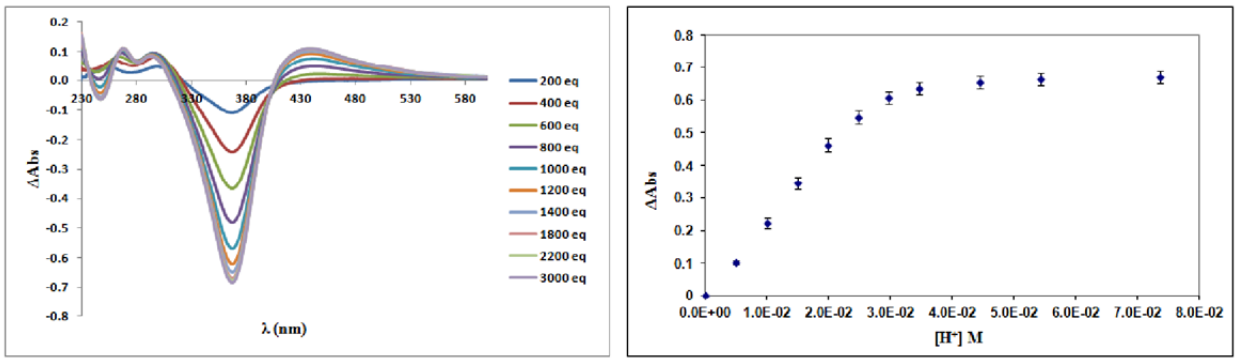


Figure S41 Titration of DMAUnc with HCl in water.

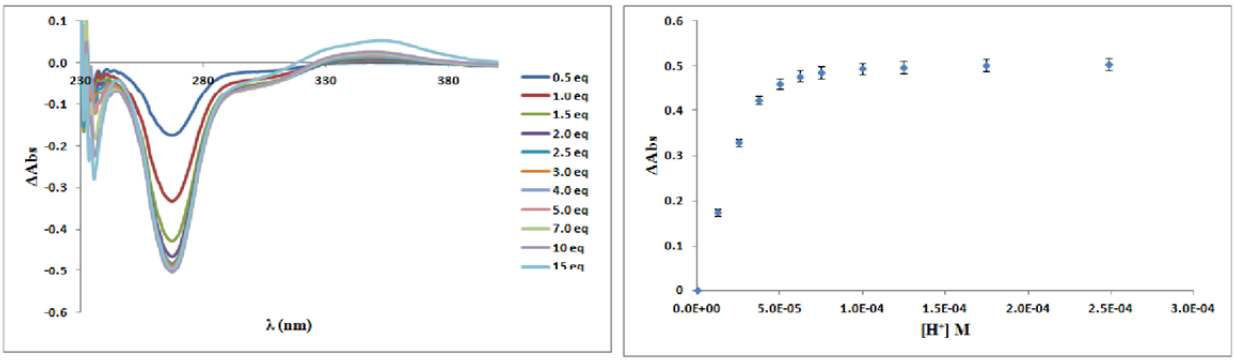


Figure S42 Titration of DMACast with HCl in CH_3CN.

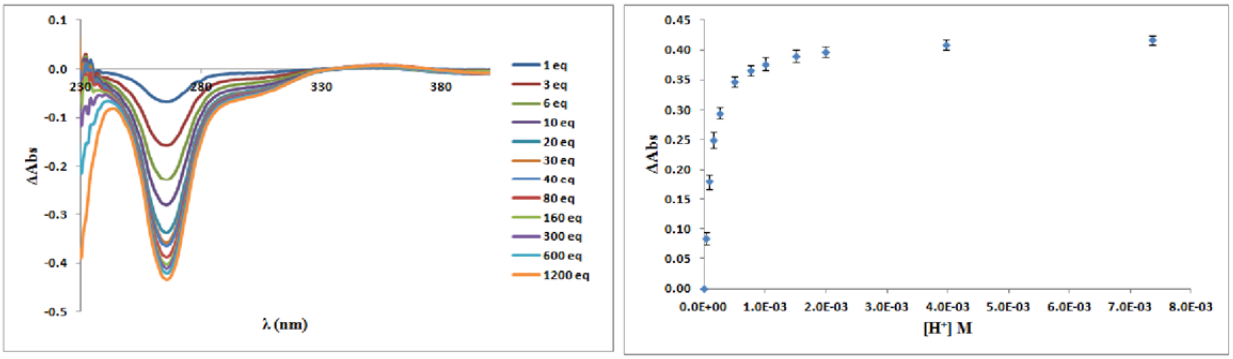


Figure S43 Titration of DMACast with HCl in EtOH.

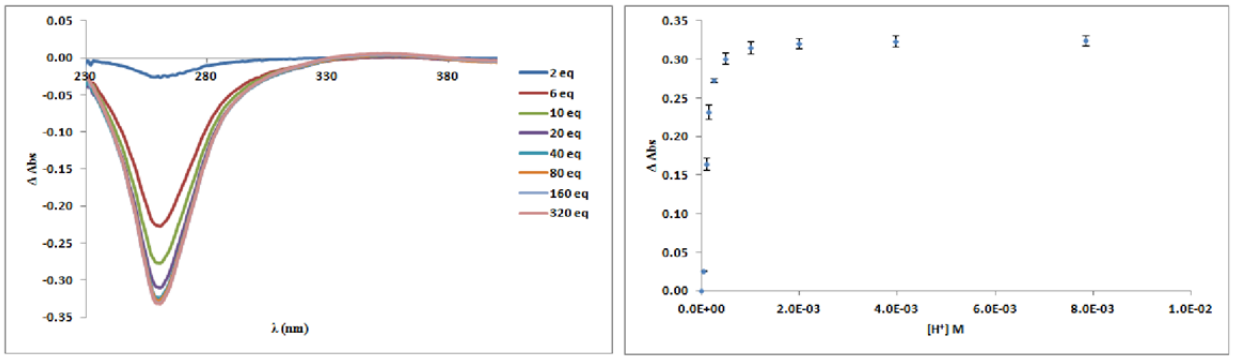


Figure S44 Titration of DMACast with HCl in water.

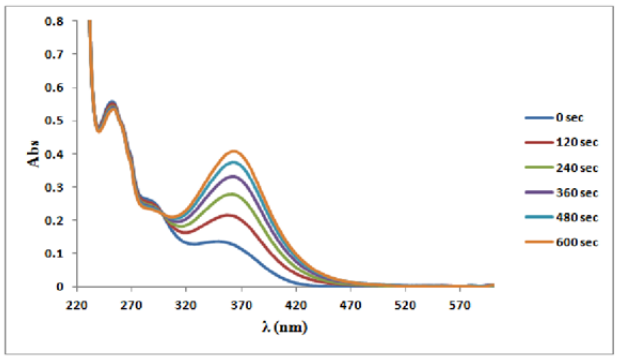


Figure S45 Photolysis of ZinCast-4 in water.

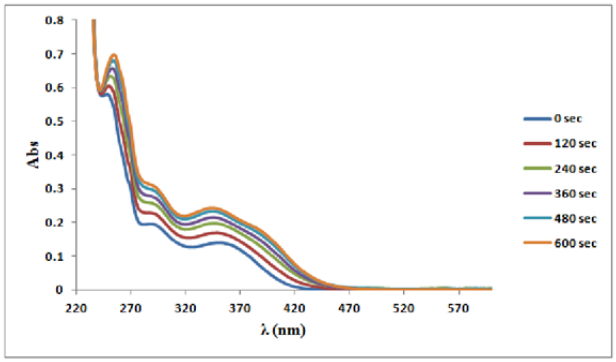


Figure S46 Photolysis of ZinCast-5 in water.

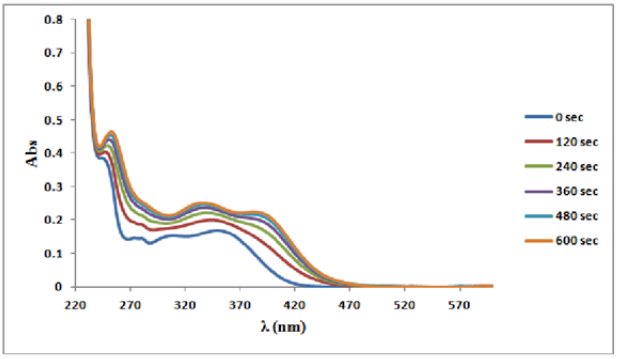


Figure S47 Photolysis of *m*-OMeCast in water.

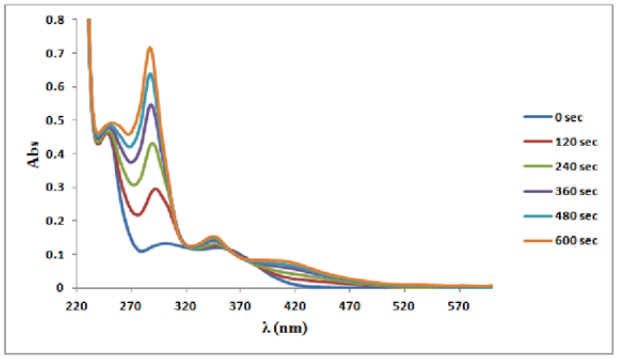


Figure S48 Photolysis of *m*-DMACast in water.

Crystal Structure Report for $[Zn(23)]Cl_2$

A colorless plate-like specimen of $C_{19}H_{19}Cl_2N_3OZn$, approximate dimensions 0.02 mm x 0.10 mm x 0.20 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Table S1: Data collection details for $[Zn(23)]Cl_2$.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Phi	49.323	-27.50	316.94	-339.53	-44.32	0.50	646	30.00	0.71073	20.00	5.00	100.02
Phi	49.323	-2.50	40.56	-59.45	-93.52	0.50	97	30.00	0.71073	20.00	5.00	100.02
Phi	49.323	10.00	5.69	-138.10	95.73	0.50	150	30.00	0.71073	20.00	5.00	100.02
Omega	49.323	25.00	3.90	-79.56	-33.35	0.50	260	30.00	0.71073	20.00	5.00	100.02
Omega	49.323	25.00	135.31	-60.34	-99.80	0.50	139	30.00	0.71073	20.00	5.00	100.02

A total of 1292 frames were collected. The total exposure time was 10.77 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 17291 reflections to a maximum θ angle of 26.19° (0.81 Å resolution), of which 3997 were independent (average redundancy 4.326, completeness = 98.7%, R_{int} = 3.61%, R_{sig} = 3.94%) and 2910 (72.80%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 7.7523(3) Å, $\underline{b}$ = 25.2982(11) Å, $\underline{c}$ = 10.7609(4) Å, β = 106.849(2)°, volume = 2019.82(14) $Å^3$, are based upon the refinement of the XYZ-centroids of 4748 reflections above 20 σ(I) with 5.100° < 2θ < 48.92°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.867. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7545 and 0.9708.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{19}H_{19}Cl_2N_3OZn$. The final anisotropic full-matrix least-squares refinement on F^2 with 236 variables converged at R1 = 3.43%, for the observed data and wR2 = 7.56% for all data. The goodness-of-fit was 1.006. The largest peak in the final difference electron density synthesis was 0.569 $e^-/Å^3$ and the largest hole was -0.264 $e^-/Å^3$ with an RMS deviation of 0.056 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.452 g/cm^3 and F(000), 904 e^-.

Table S2. Sample and crystal data for $[Zn(23)]Cl_2$.

Identification code	**$[Zn(23)]Cl_2$**	
Chemical formula	$C_{19}H_{19}Cl_2N_3OZn$	
Formula weight	441.64	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.02 x 0.10 x 0.20 mm	
Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 7.7523(3) Å	α = 90°
	b = 25.2982(11) Å	β = 106.849(2)°
	c = 10.7609(4) Å	γ = 90°
Volume	2019.82(14) $Å^3$	
Z	4	
Density (calculated)	1.452 Mg/cm^3	
Absorption coefficient	1.493 mm^{-1}	
F(000)	904	

Table S3. Data collection and structure refinement for [Zn(23)]Cl_2.

Theta range for data collection	1.61 to 26.19°	
Index ranges	-9<=h<=8, -27<=k<=31, -11<=l<=13	
Reflections collected	17291	
Independent reflections	3997 [R(int) = 0.0361]	
Coverage of independent reflections	98.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9708 and 0.7545	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 1997)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3997 / 0 / 236	
Goodness-of-fit on F^2	1.006	
Δ/σ_{max}	0.001	
Final R indices	2910 data; I>2σ(I)	R1 = 0.0343, wR2 = 0.0681
	all data	R1 = 0.0608, wR2 = 0.0756
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0321P)^2+0.8051P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.569 and -0.264 eÅ^{-3}	
R.M.S. deviation from mean	0.056 eÅ^{-3}	

Table S4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for [Zn(23)]Cl$_2$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Zn1	0.31496(4)	0.626483(12)	0.61727(3)	0.03314(10)
N1	0.1927(3)	0.55605(8)	0.65092(19)	0.0336(5)
N2	0.4504(3)	0.69325(8)	0.7157(2)	0.0346(5)
C19	0.2352(4)	0.50801(11)	0.6180(3)	0.0412(7)
C15	0.0543(3)	0.56119(11)	0.7016(2)	0.0349(6)
C9	0.3635(3)	0.72222(11)	0.7834(2)	0.0345(6)
C16	0.9566(4)	0.51796(12)	0.7197(3)	0.0482(7)
C10	0.4392(4)	0.76679(12)	0.8502(3)	0.0464(7)
C13	0.6141(4)	0.70930(12)	0.7140(3)	0.0431(7)
C18	0.1434(4)	0.46350(12)	0.6330(3)	0.0499(8)
C17	0.0013(5)	0.46872(13)	0.6839(3)	0.0565(9)
C12	0.6969(4)	0.75322(12)	0.7790(3)	0.0497(8)
C11	0.6078(4)	0.78259(13)	0.8477(3)	0.0524(8)
C14	0.0125(3)	0.61666(10)	0.7339(2)	0.0359(6)
C8	0.1783(3)	0.70271(10)	0.7795(3)	0.0361(6)
N4	0.1836(3)	0.64473(8)	0.79058(19)	0.0322(5)
C1	0.2711(3)	0.62687(11)	0.9218(2)	0.0378(6)
C6	0.1957(4)	0.63679(12)	0.0233(3)	0.0455(7)
C2	0.4294(4)	0.59838(12)	0.9476(3)	0.0537(8)
C5	0.2795(5)	0.61885(14)	0.1467(3)	0.0607(9)
C4	0.4357(5)	0.59025(16)	0.1697(4)	0.0787(12)
C3	0.5103(5)	0.57957(15)	0.0726(4)	0.0751(11)
C7	0.9436(5)	0.67061(18)	0.0836(4)	0.0913(14)
O1	0.0385(3)	0.66395(9)	0.98985(19)	0.0596(6)
Cl1	0.09130(9)	0.66432(3)	0.45323(6)	0.04294(18)
Cl2	0.54220(10)	0.59284(3)	0.54751(8)	0.0549(2)

Table S5. Bond lengths (Å) for $[Zn(23)]Cl_2$..

Zn1-N1	2.099(2)	Zn1-N2	2.105(2)
Zn1-Cl2	2.2712(7)	Zn1-Cl1	2.2943(7)
Zn1-N4	2.414(2)	N1-C19	1.334(3)
N1-C15	1.343(3)	N2-C13	1.337(3)
N2-C9	1.344(3)	C19-C18	1.367(4)
C15-C16	1.376(4)	C15-C14	1.504(4)
C9-C10	1.374(4)	C9-C8	1.507(3)
C16-C17	1.377(4)	C10-C11	1.375(4)
C13-C12	1.370(4)	C18-C17	1.371(4)
C12-C11	1.368(4)	C14-N4	1.472(3)
C8-N4	1.471(3)	N4-C1	1.450(3)
C1-C2	1.380(4)	C1-C6	1.403(4)
C6-O1	1.354(3)	C6-C5	1.375(4)
C2-C3	1.393(4)	C5-C4	1.370(5)
C4-C3	1.360(5)	C7-O1	1.420(4)

Table S6. Bond angles (°) for [Zn(23)]Cl_2..

N1-Zn1-N2	141.14(8)	N1-Zn1-Cl2	99.87(6)
N2-Zn1-Cl2	98.37(6)	N1-Zn1-Cl1	102.03(6)
N2-Zn1-Cl1	102.00(6)	Cl2-Zn1-Cl1	112.81(3)
N1-Zn1-N4	73.51(8)	N2-Zn1-N4	73.64(7)
Cl2-Zn1-N4	150.25(5)	Cl1-Zn1-N4	96.93(5)
C19-N1-C15	119.0(2)	C19-N1-Zn1	124.67(18)
C15-N1-Zn1	116.22(18)	C13-N2-C9	117.9(2)
C13-N2-Zn1	124.99(18)	C9-N2-Zn1	117.07(17)
N1-C19-C18	122.8(3)	N1-C15-C16	121.2(3)
N1-C15-C14	115.8(2)	C16-C15-C14	123.0(2)
N2-C9-C10	121.7(2)	N2-C9-C8	115.4(2)
C10-C9-C8	122.9(2)	C15-C16-C17	119.1(3)
C9-C10-C11	119.5(3)	N2-C13-C12	123.1(3)
C19-C18-C17	118.3(3)	C18-C17-C16	119.7(3)
C11-C12-C13	118.8(3)	C12-C11-C10	119.0(3)
N4-C14-C15	108.5(2)	N4-C8-C9	108.7(2)
C1-N4-C8	112.6(2)	C1-N4-C14	111.4(2)
C8-N4-C14	116.5(2)	C1-N4-Zn1	120.63(15)
C8-N4-Zn1	97.83(14)	C14-N4-Zn1	96.82(14)
C2-C1-C6	118.9(3)	C2-C1-N4	119.8(2)
C6-C1-N4	121.3(2)	O1-C6-C5	124.1(3)
O1-C6-C1	115.4(2)	C5-C6-C1	120.4(3)
C1-C2-C3	119.8(3)	C4-C5-C6	119.6(3)
C3-C4-C5	121.1(3)	C4-C3-C2	120.1(3)
C6-O1-C7	118.9(3)		

Table S7. Anisotropic atomic displacement parameters ($Å^2$) for $[Zn(23)]Cl_2$..

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn1	0.03179(17)	0.03425(18)	0.03475(17)	-0.00113(14)	0.01180(12)	0.00203(14)
N1	0.0323(12)	0.0352(13)	0.0320(12)	0.0013(10)	0.0071(9)	0.0017(10)
N2	0.0306(12)	0.0385(14)	0.0375(12)	-0.0036(10)	0.0142(10)	0.0010(10)
C19	0.0422(16)	0.0343(17)	0.0416(16)	-0.0004(13)	0.0036(13)	0.0079(14)
C15	0.0334(15)	0.0389(17)	0.0288(13)	0.0028(12)	0.0034(11)	-0.0038(13)
C9	0.0358(15)	0.0333(15)	0.0364(14)	-0.0003(12)	0.0135(12)	0.0034(12)
C16	0.0487(18)	0.050(2)	0.0474(17)	0.0033(15)	0.0155(14)	-0.0087(16)
C10	0.0496(18)	0.0405(18)	0.0528(18)	-0.0104(14)	0.0207(15)	0.0012(15)
C13	0.0386(16)	0.0484(19)	0.0461(17)	-0.0055(14)	0.0184(13)	0.0026(14)
C18	0.057(2)	0.0343(18)	0.0480(17)	0.0043(14)	-0.0011(15)	0.0042(15)
C17	0.067(2)	0.040(2)	0.056(2)	0.0091(15)	0.0064(17)	-0.0149(17)
C12	0.0396(16)	0.051(2)	0.0611(19)	-0.0071(16)	0.0191(15)	-0.0095(15)
C11	0.0520(19)	0.0422(19)	0.063(2)	-0.0134(16)	0.0159(16)	-0.0110(16)
C14	0.0296(14)	0.0433(18)	0.0361(14)	0.0007(12)	0.0116(12)	0.0004(12)
C8	0.0374(15)	0.0333(16)	0.0433(15)	-0.0006(12)	0.0206(12)	0.0053(13)
N4	0.0290(11)	0.0331(13)	0.0349(12)	-0.0023(10)	0.0098(9)	0.0013(10)
C1	0.0362(15)	0.0384(16)	0.0366(14)	-0.0010(13)	0.0070(12)	-0.0038(13)
C6	0.0493(18)	0.0471(19)	0.0414(16)	0.0001(14)	0.0152(14)	-0.0049(15)
C2	0.0431(18)	0.059(2)	0.0526(19)	0.0055(16)	0.0033(15)	0.0062(16)
C5	0.075(2)	0.067(2)	0.0388(18)	0.0019(16)	0.0145(16)	-0.011(2)
C4	0.075(3)	0.098(3)	0.049(2)	0.015(2)	-0.004(2)	0.003(2)
C3	0.058(2)	0.088(3)	0.065(2)	0.014(2)	-0.0036(19)	0.018(2)
C7	0.094(3)	0.129(4)	0.069(3)	0.005(2)	0.051(2)	0.021(3)
O1	0.0663(15)	0.0727(16)	0.0486(12)	0.0025(11)	0.0305(11)	0.0110(12)
Cl1	0.0403(4)	0.0460(4)	0.0399(4)	0.0101(3)	0.0075(3)	0.0017(3)
Cl2	0.0462(4)	0.0541(5)	0.0733(5)	-0.0163(4)	0.0313(4)	0.0028(4)

Table S8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for $[Zn(23)]Cl_2$..

	x/a	y/b	z/c	U(eq)
H19	0.3335	0.5046	0.5825	0.049
H16	-0.1402	0.5220	0.7564	0.058
H10	0.3755	0.7866	0.8978	0.056
H13	0.6758	0.6893	0.6655	0.052
H18	0.1771	0.4298	0.6089	0.06
H17	-0.0660	0.4385	0.6943	0.068
H12	0.8140	0.7631	0.7764	0.06
H11	0.6617	0.8134	0.8929	0.063
H14A	-0.0588	0.6350	0.6543	0.043
H14B	-0.0591	0.6160	0.7965	0.043
H8A	0.1409	0.7183	0.8520	0.043
H8B	0.0899	0.7134	0.6968	0.043
H2	0.4831	0.5916	0.8802	0.064
H5	0.2293	0.6262	1.2156	0.073
H4	0.4928	0.5777	1.2549	0.094
H3	0.6178	0.5593	1.0901	0.09
H7A	-0.0914	0.6359	1.1089	0.137
H7B	-0.1646	0.6919	1.0464	0.137
H7C	0.0213	0.6886	1.1602	0.137

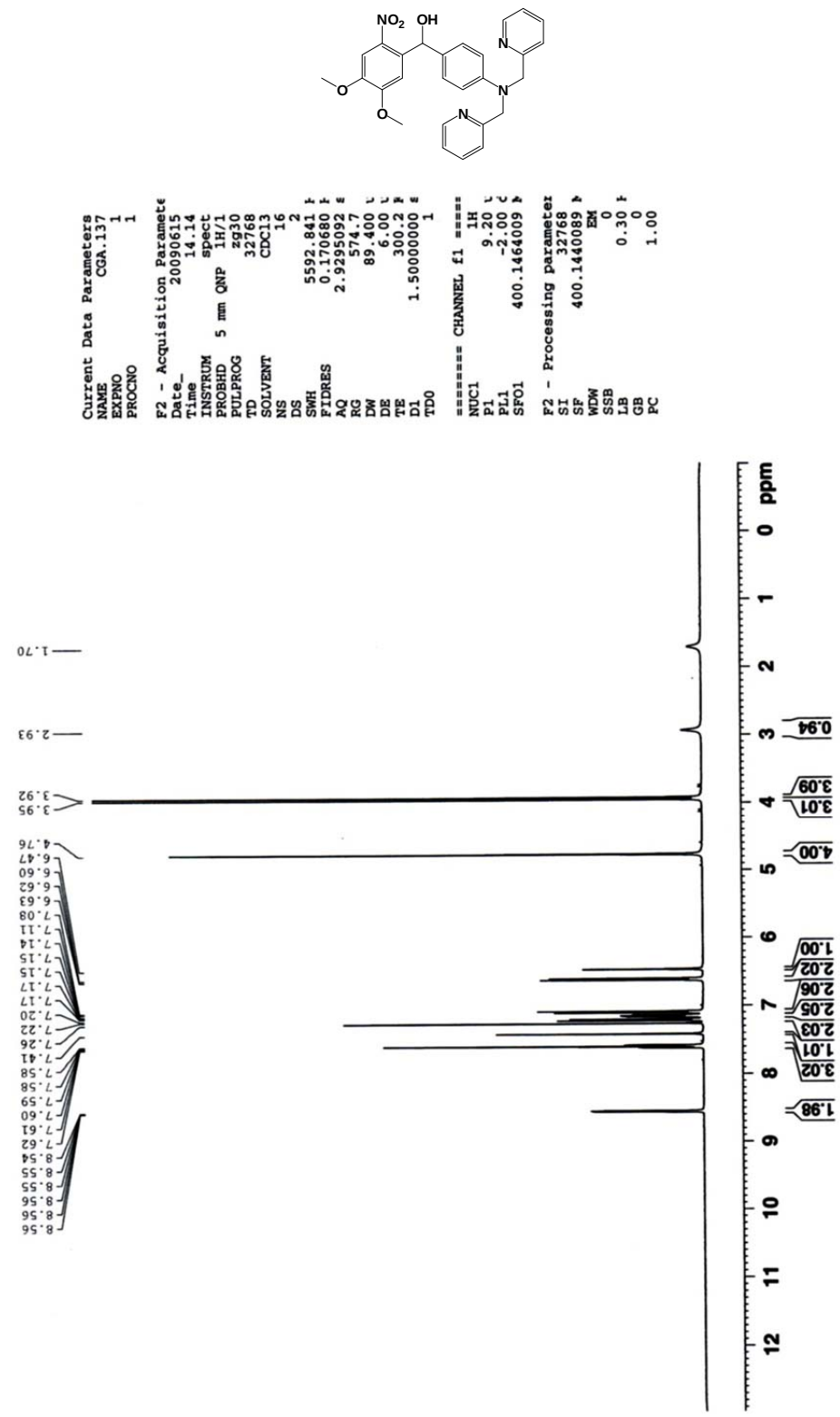


Figure S49 ^{1}H NMR of compound ZinCast-1, **1.**

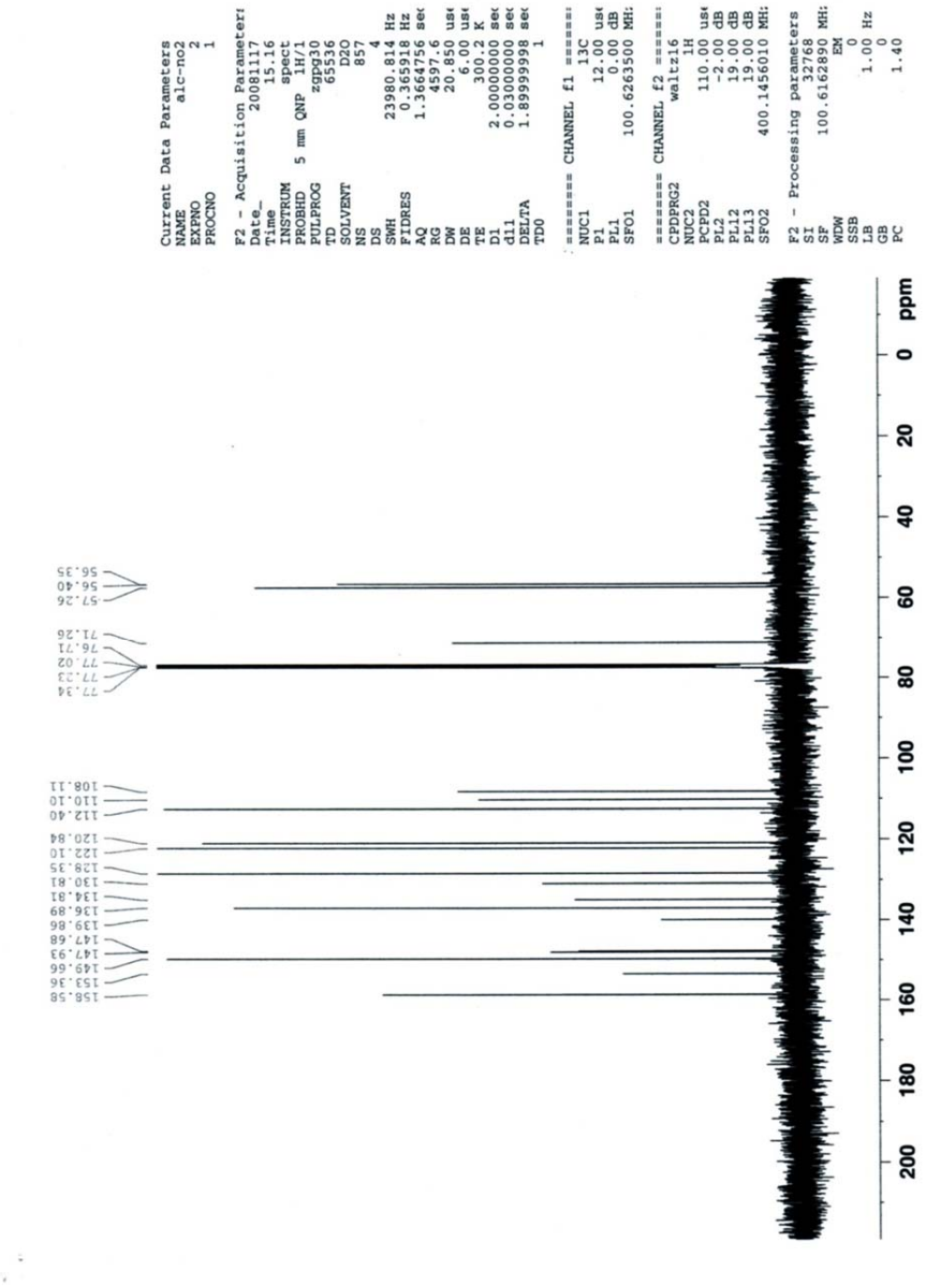


Figure S50 ^{13}C NMR of compound ZinCast-1**, 1.**

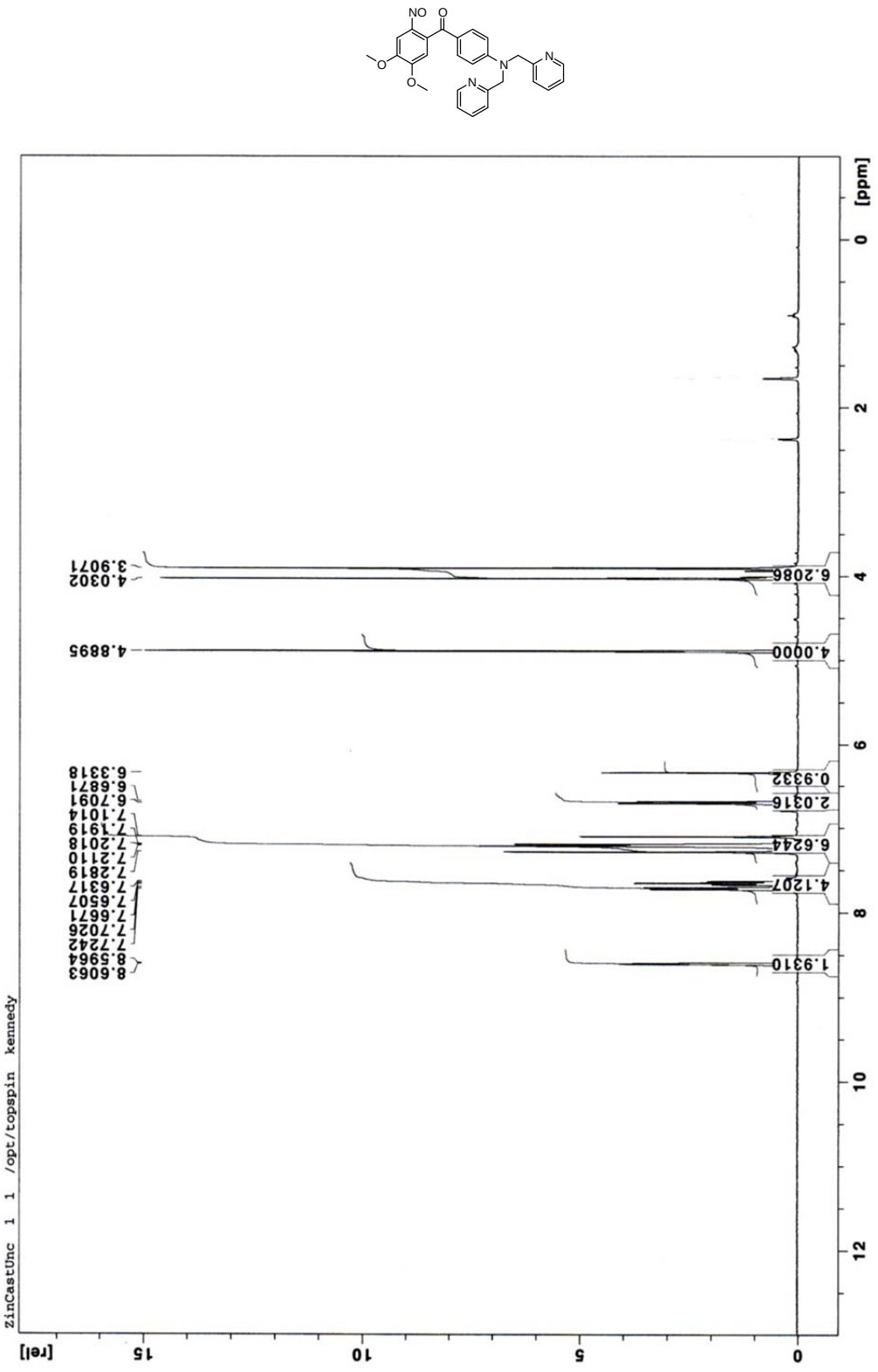


Figure S51. ^{1}H NMR of ZinUnc-1**, 2.**

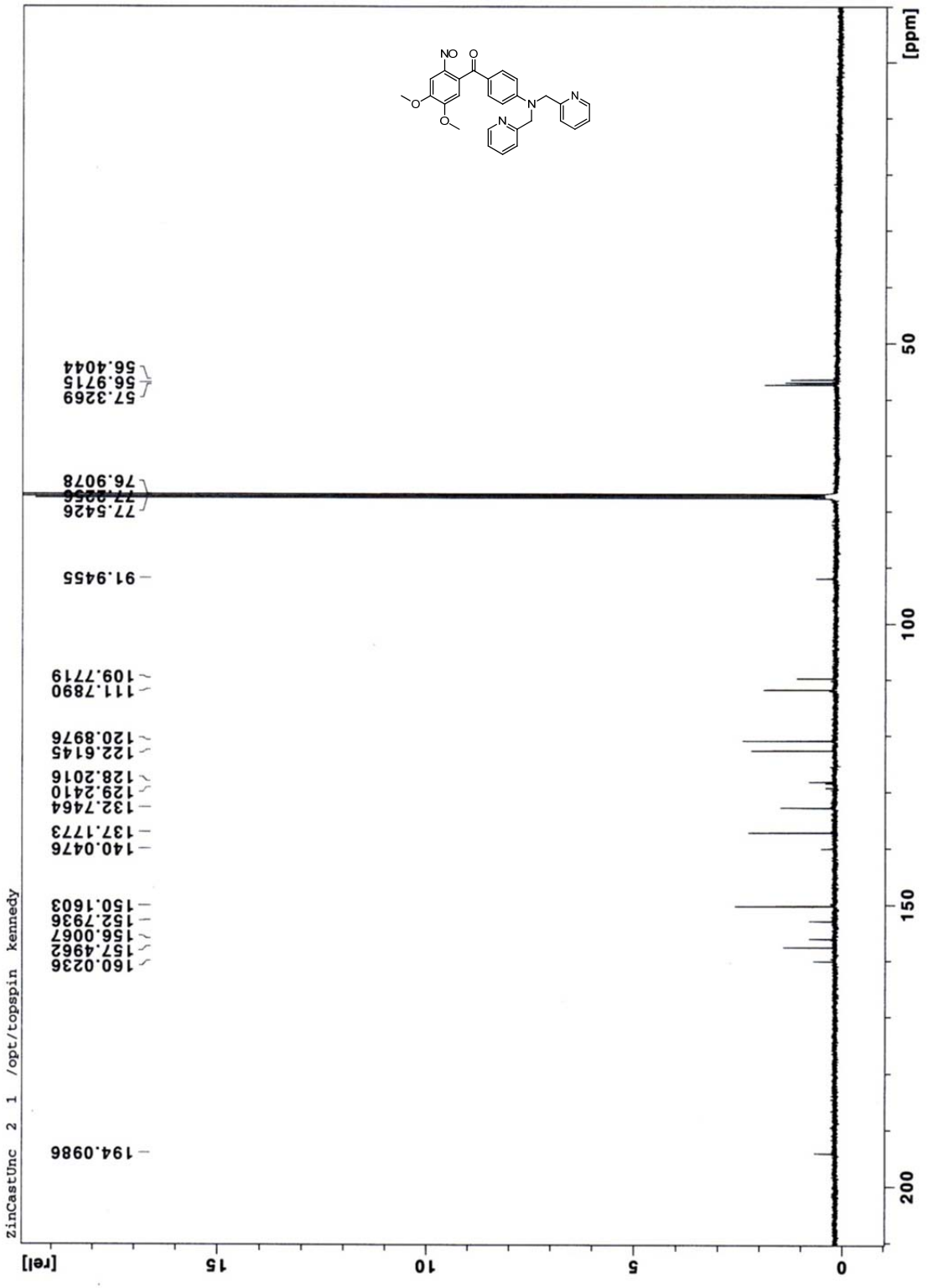


Figure S52. ^{13}C NMR of ZinUnc-1 **2.**

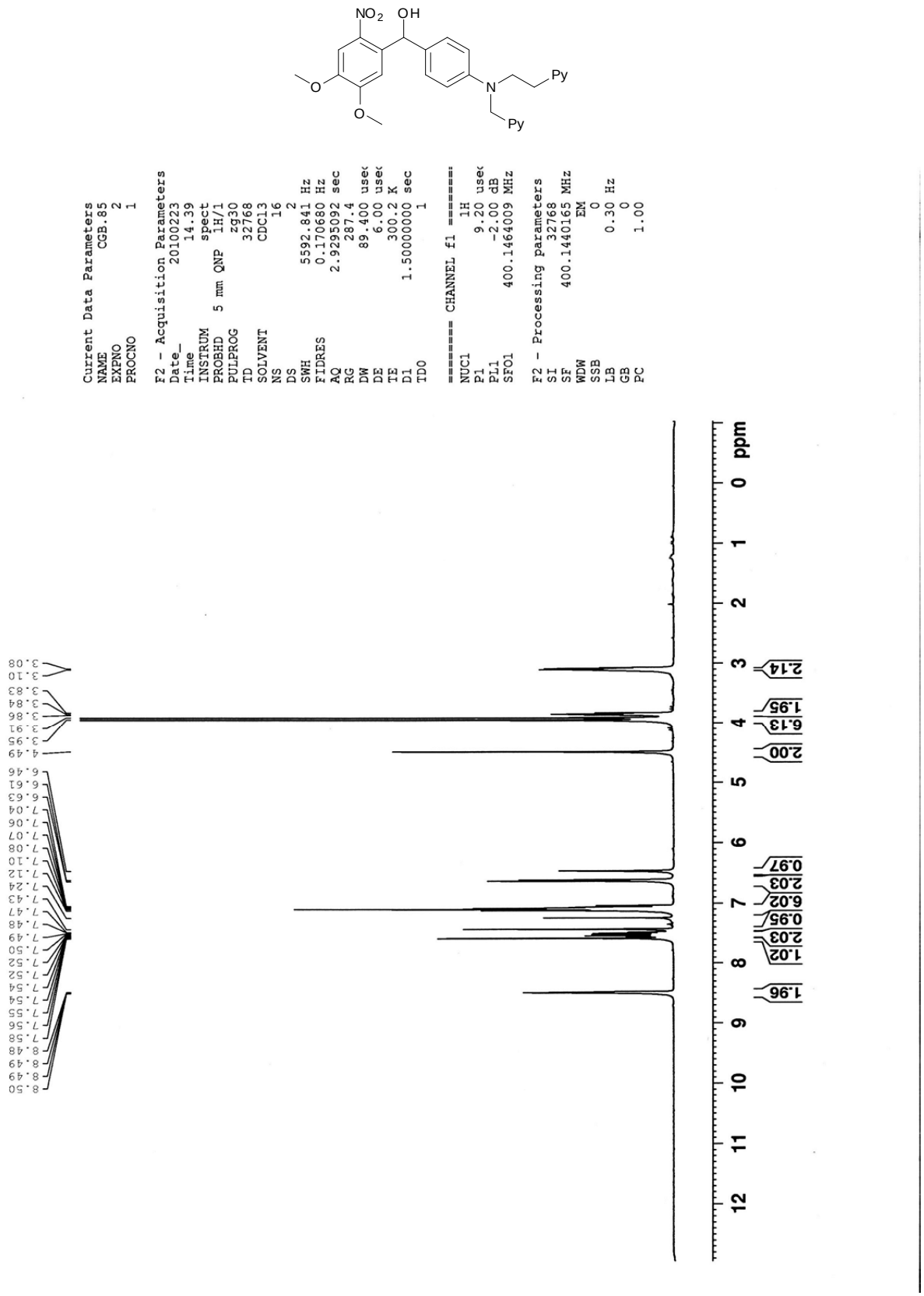


Figure S53 ^{1}H NMR of compound ZinCast-2, **3**.

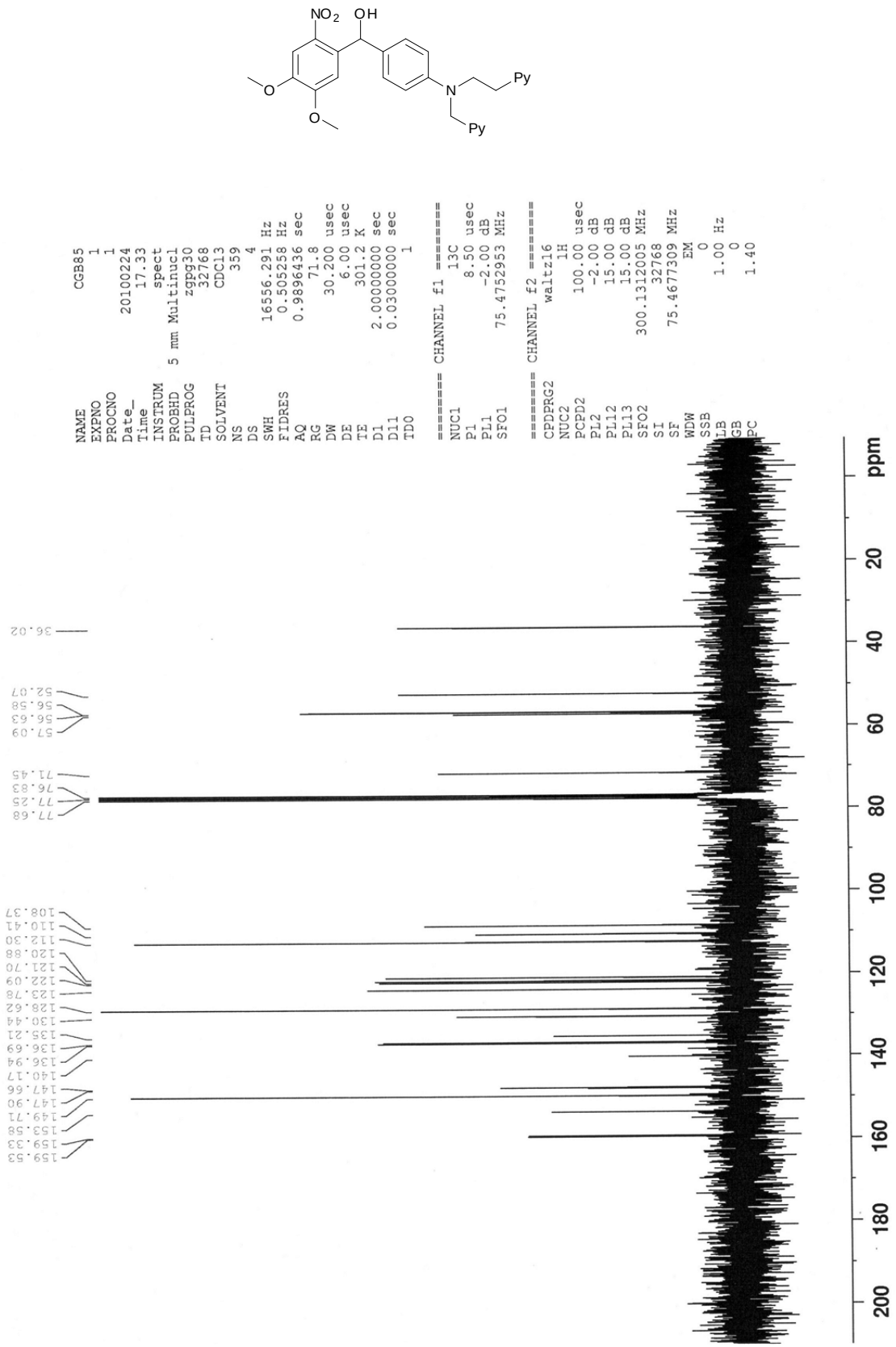


Figure S54 ^{13}C NMR of compound ZinCast-2, **3**

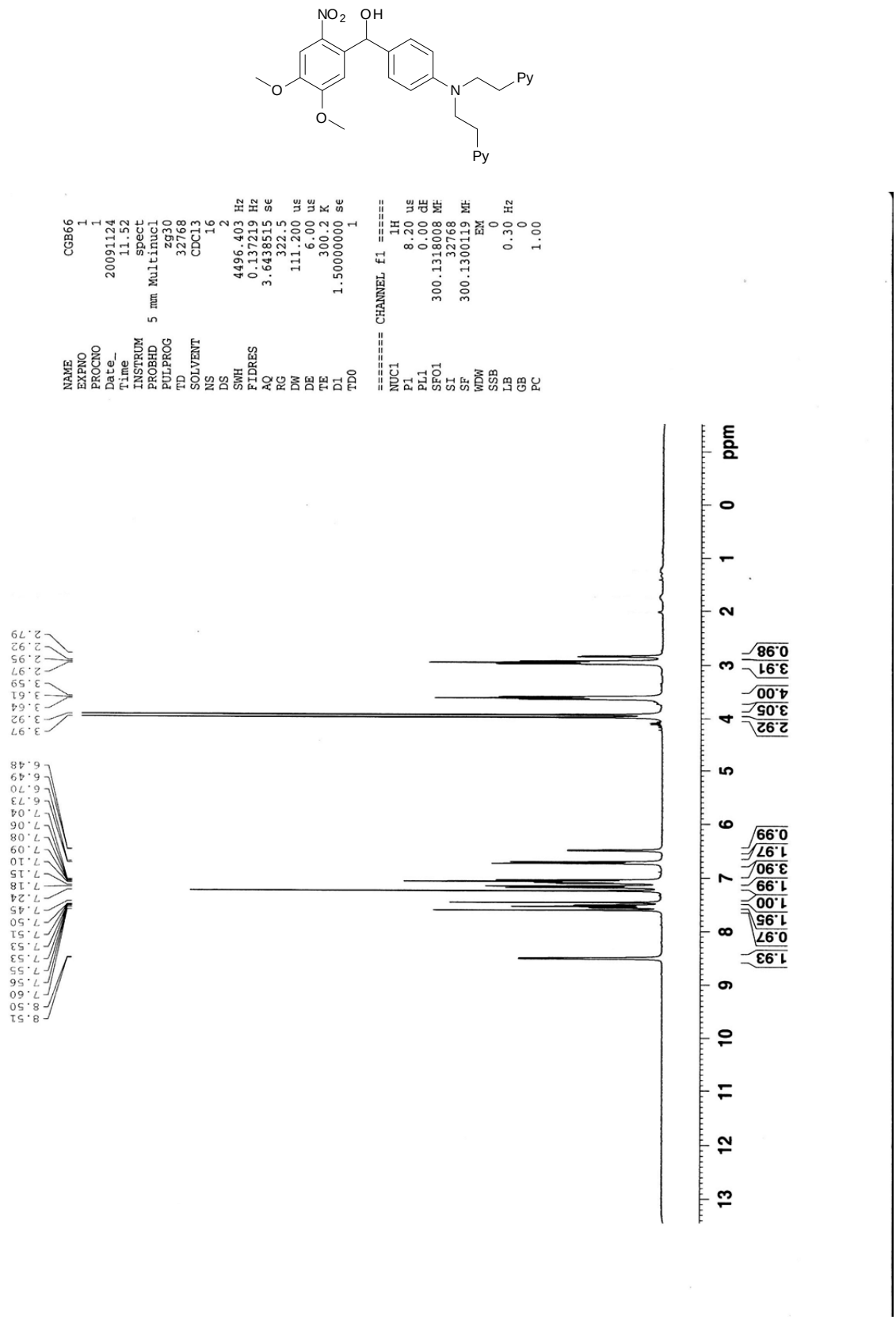


Figure S55 ^{1}H NMR of compound ZinCast-3, **4**

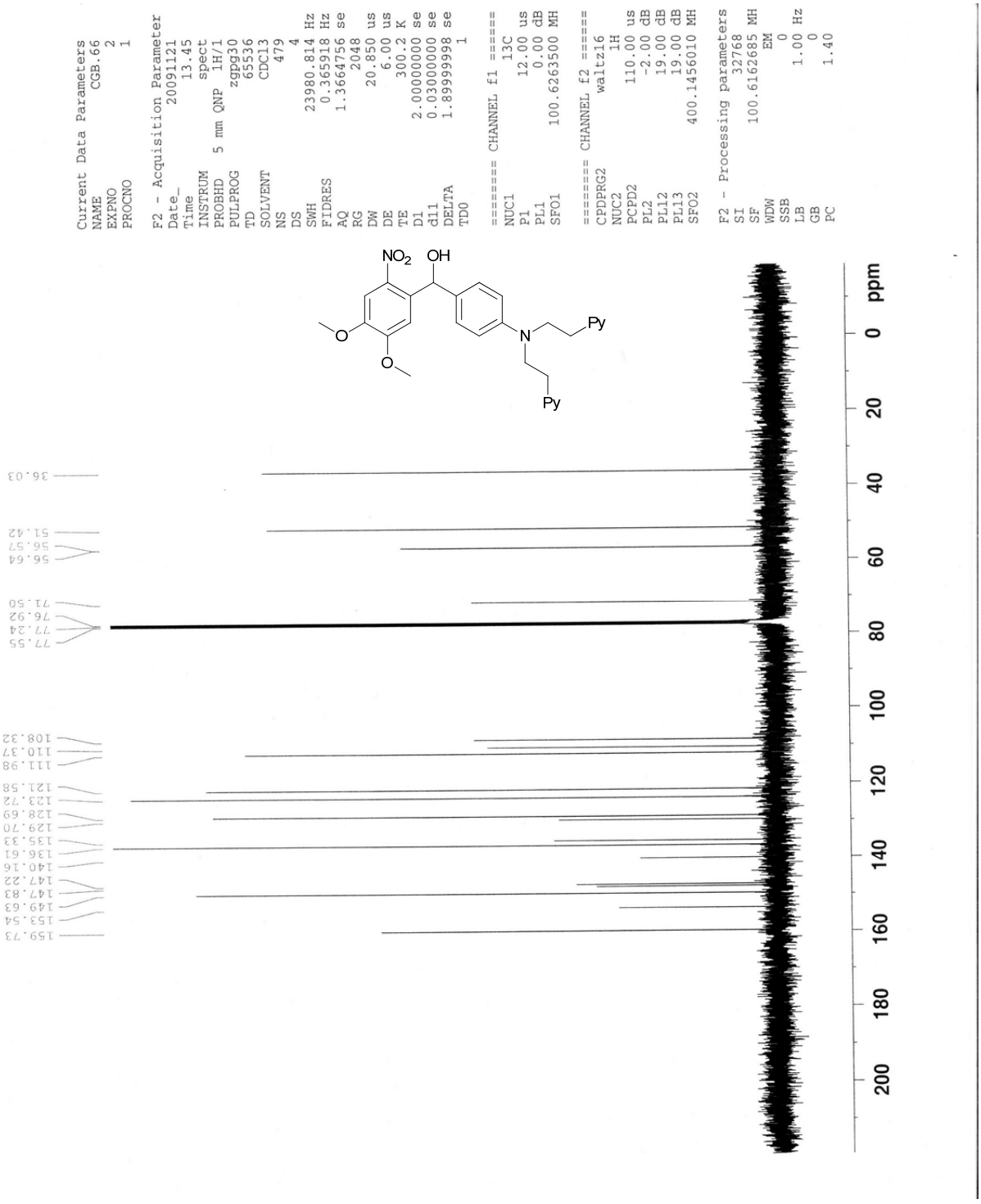


Figure S56 ^{13}C NMR of compound ZinCast-3, **4**.

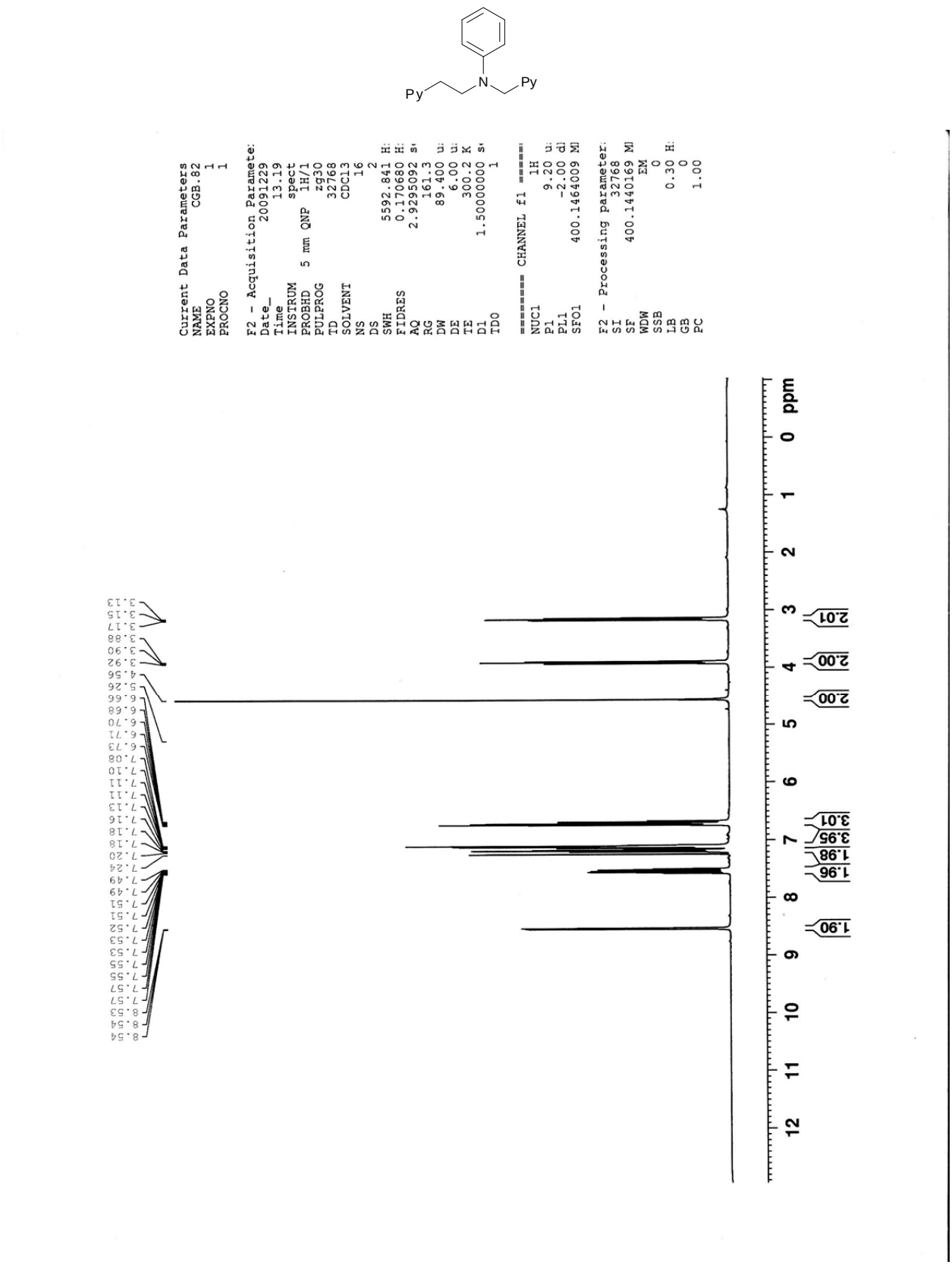


Figure S57 ^{1}H NMR of compound **9**.

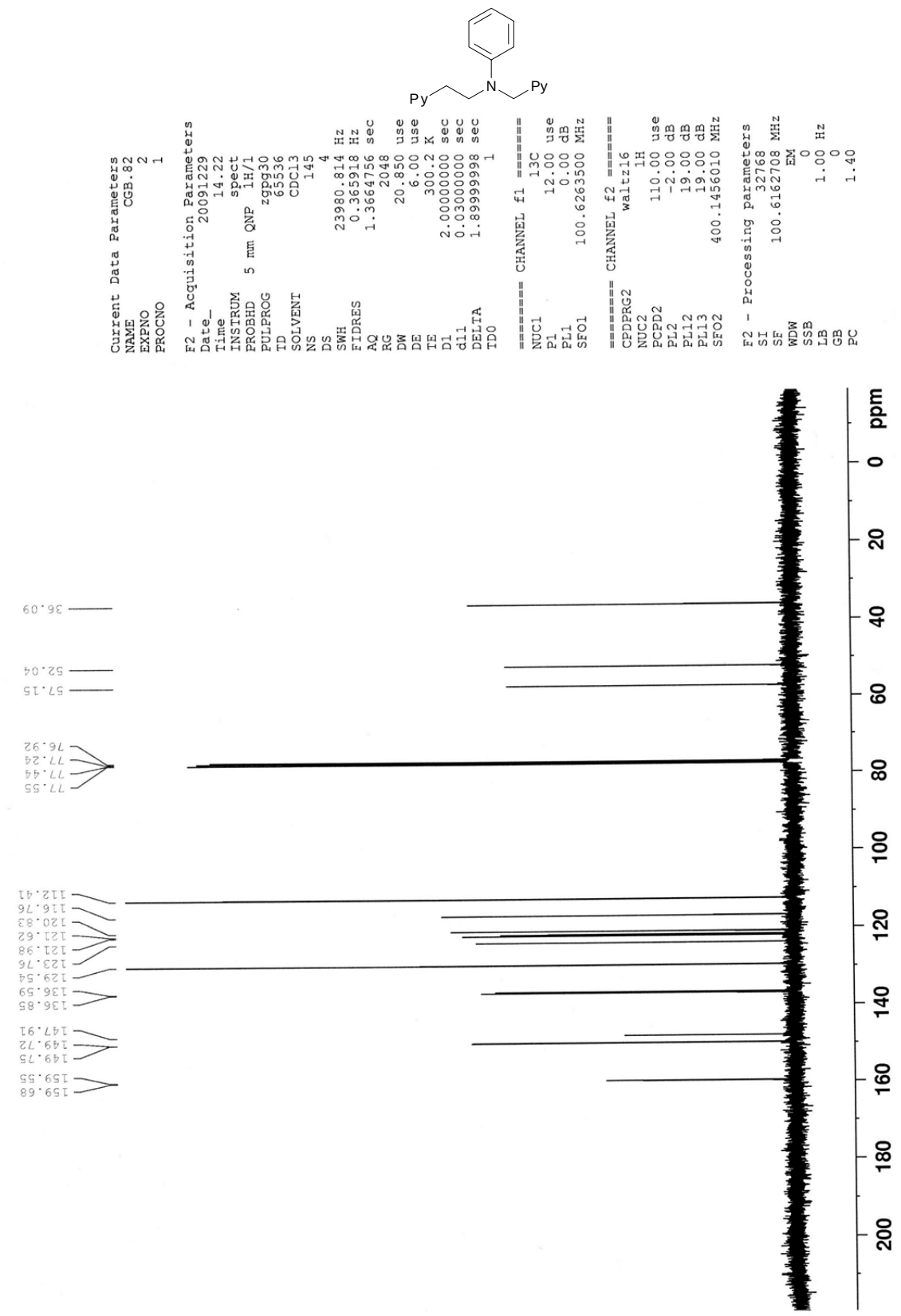


Figure S58 ^{13}C NMR of compound **9**.

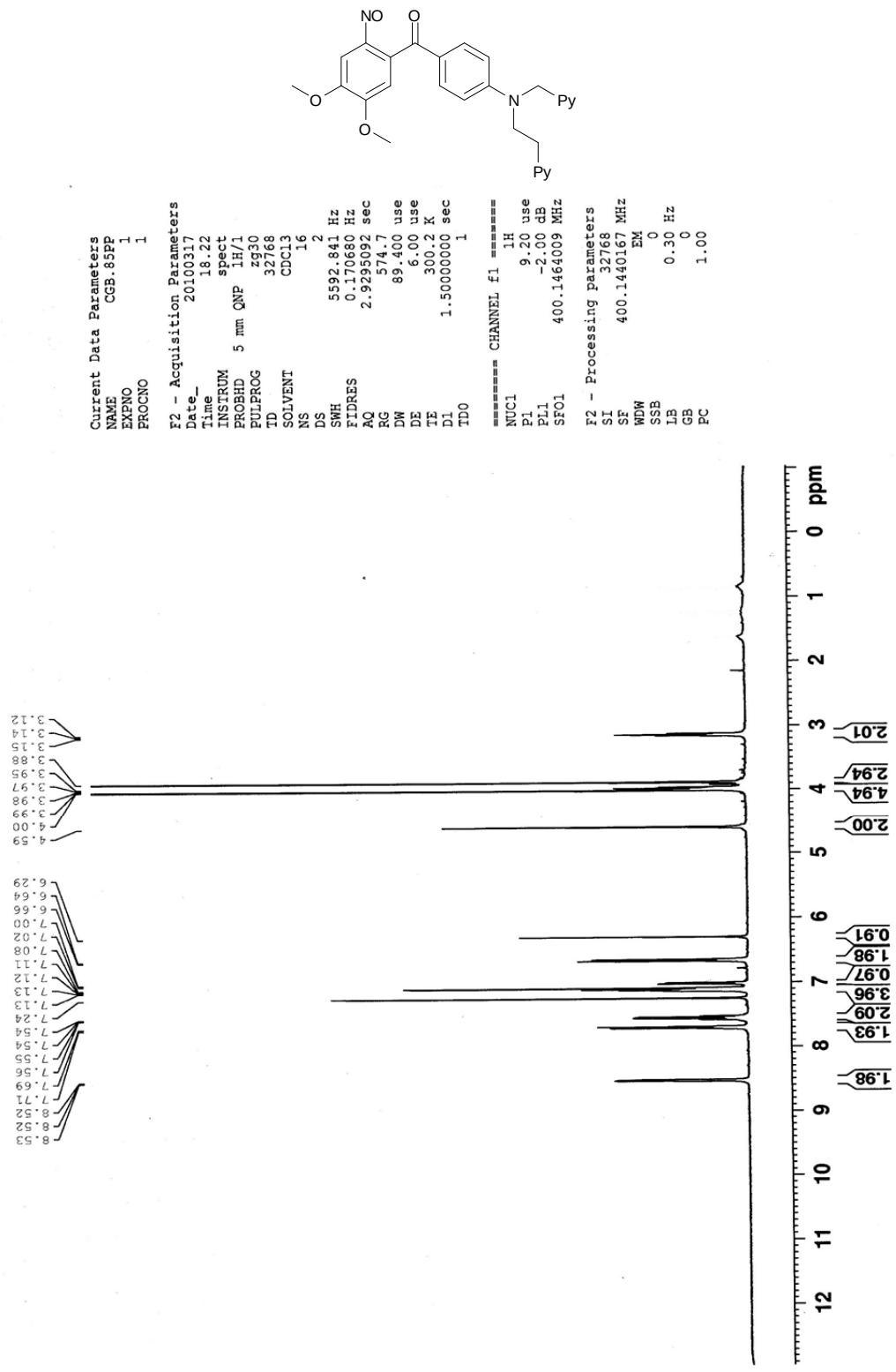


Figure S59 ^{1}H NMR of compound ZinUnc-2, **12**.

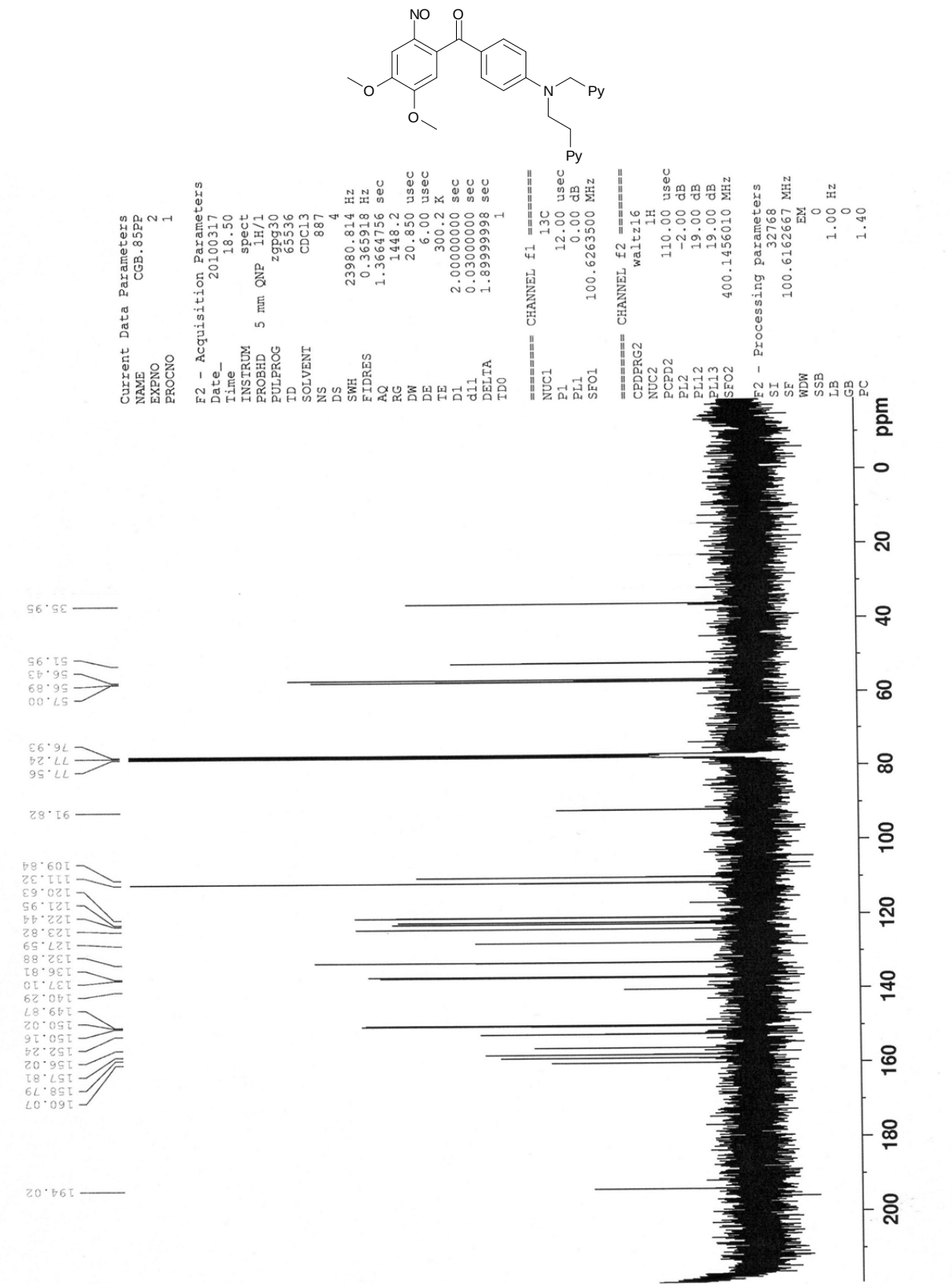


Figure S60 ^{13}C NMR of compound ZinUnc-2, **12**.

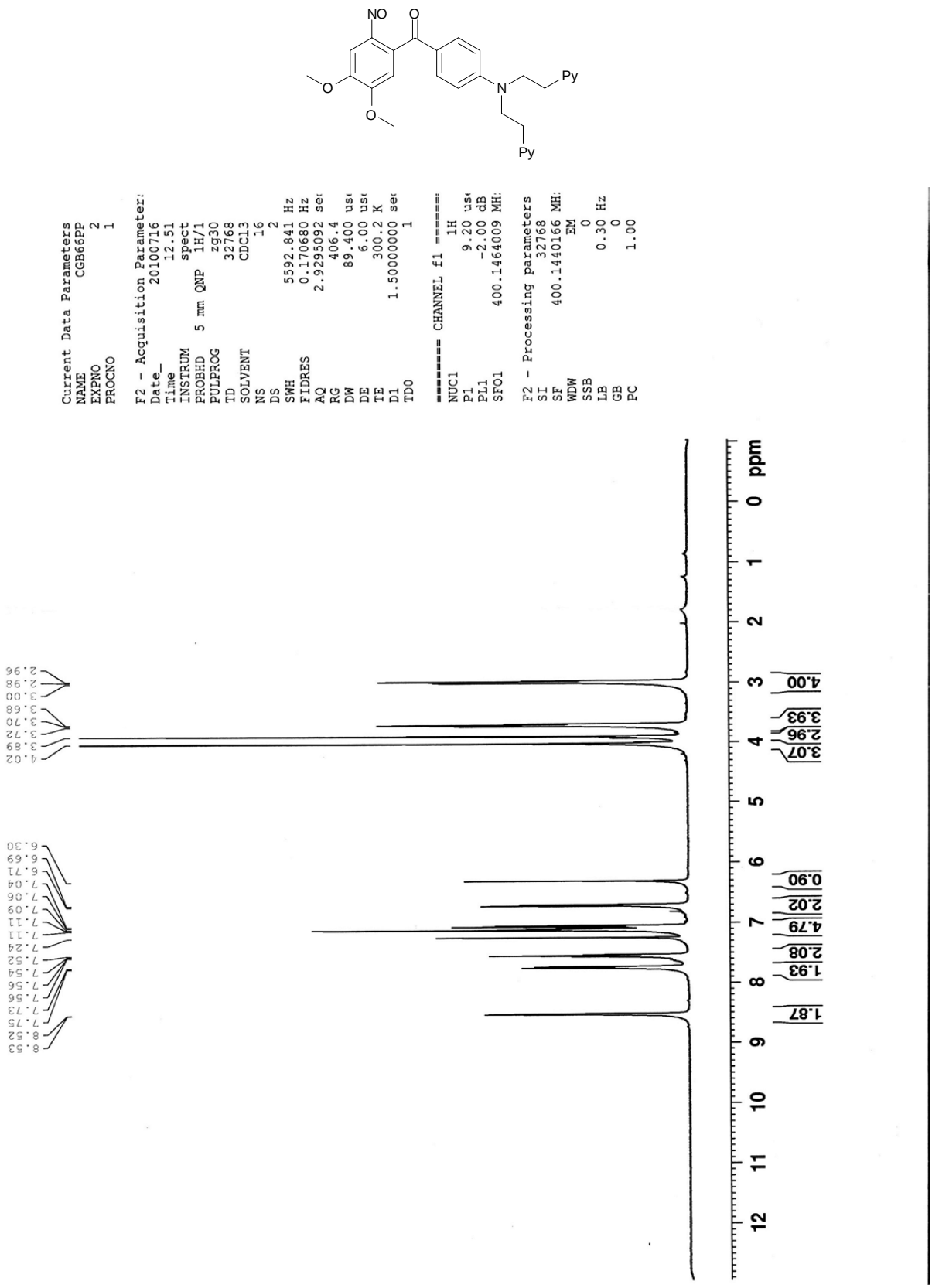


Figure S61 ^{1}H NMR of compound ZinUnc-3, **13**.

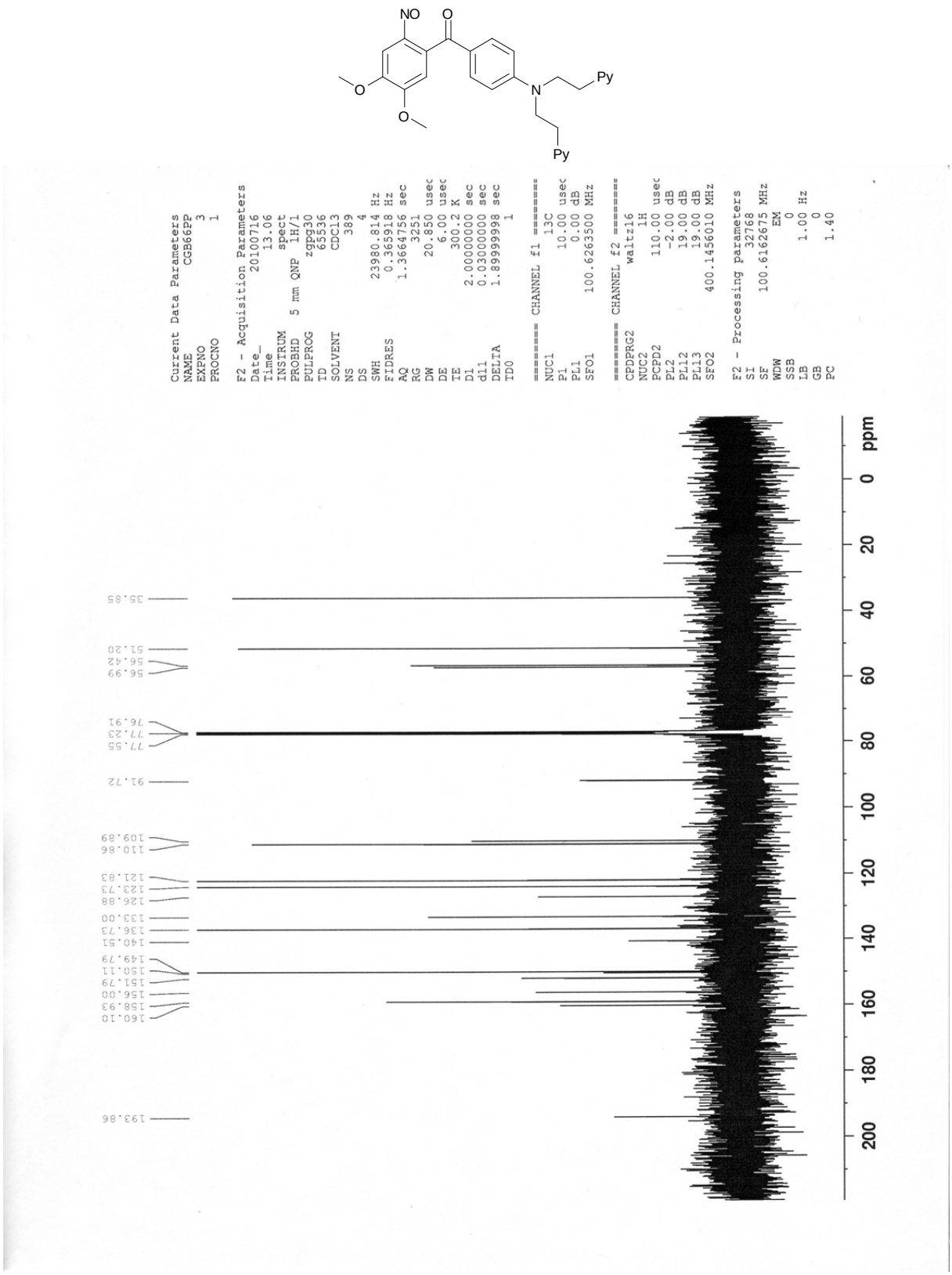


Figure S62 ^{13}C NMR of compound ZinUnc-3, **13**.

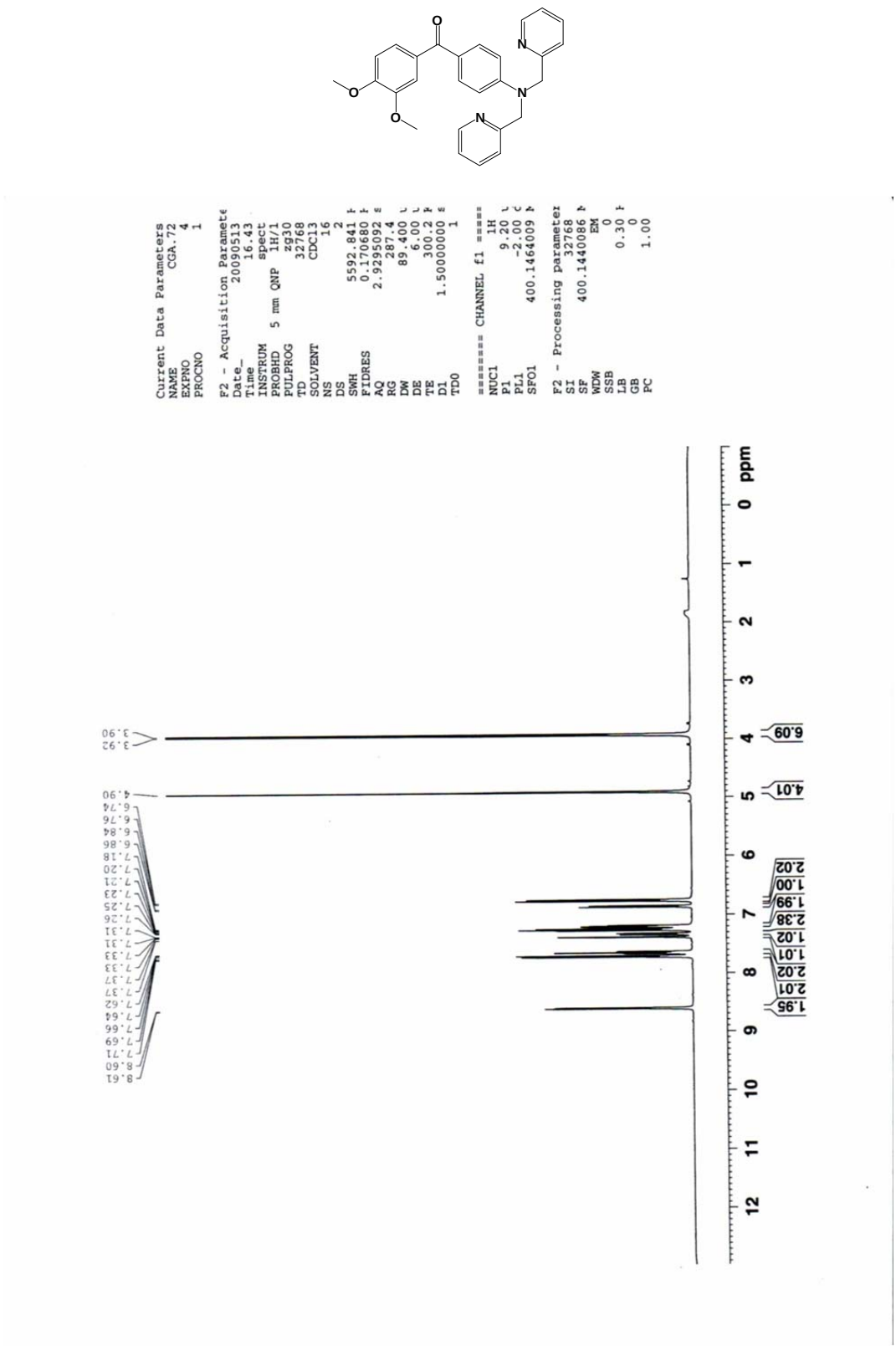


Figure S63 ^{1}H NMR of compound **15.**

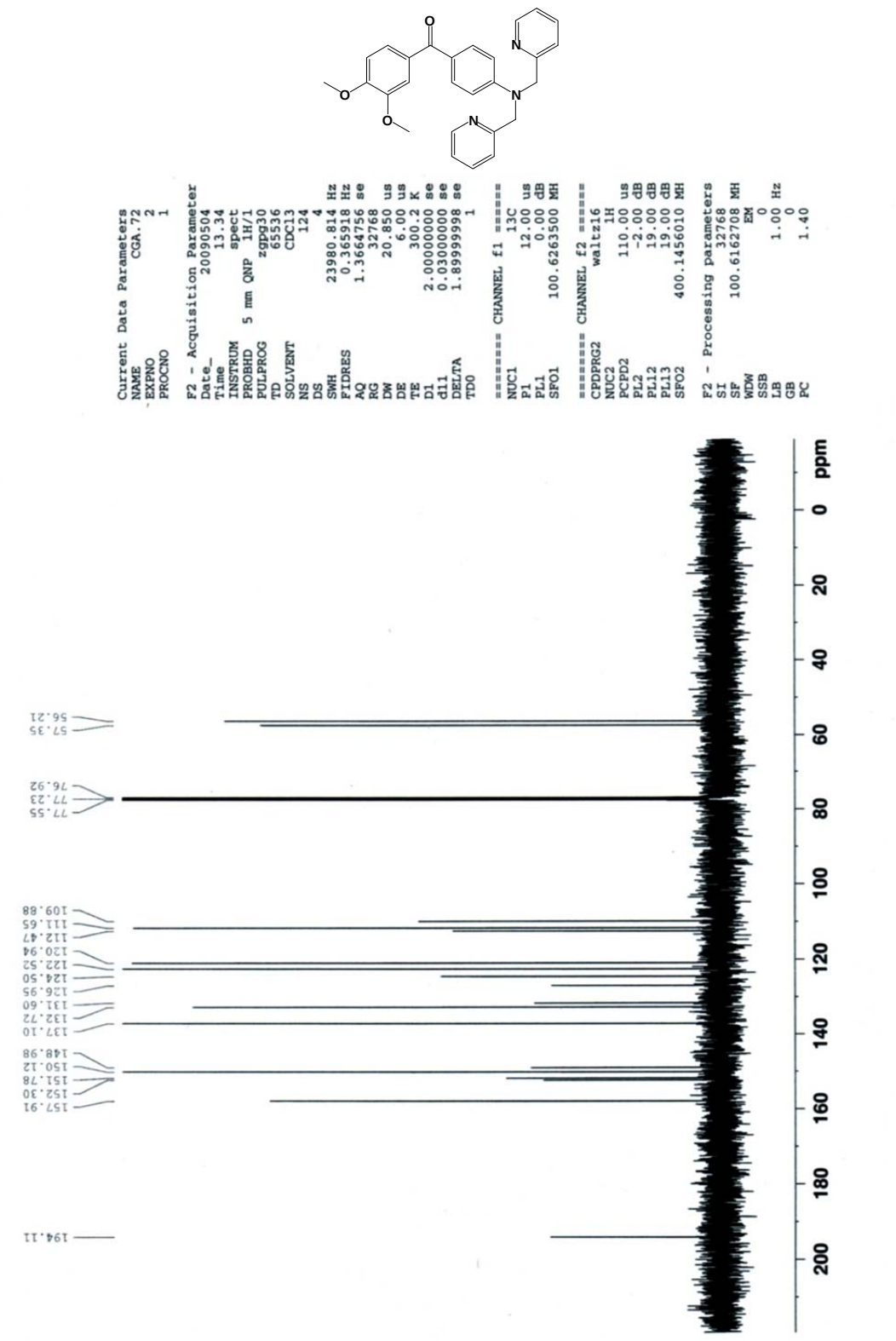


Figure S64 ^{13}C NMR of compound **15.**

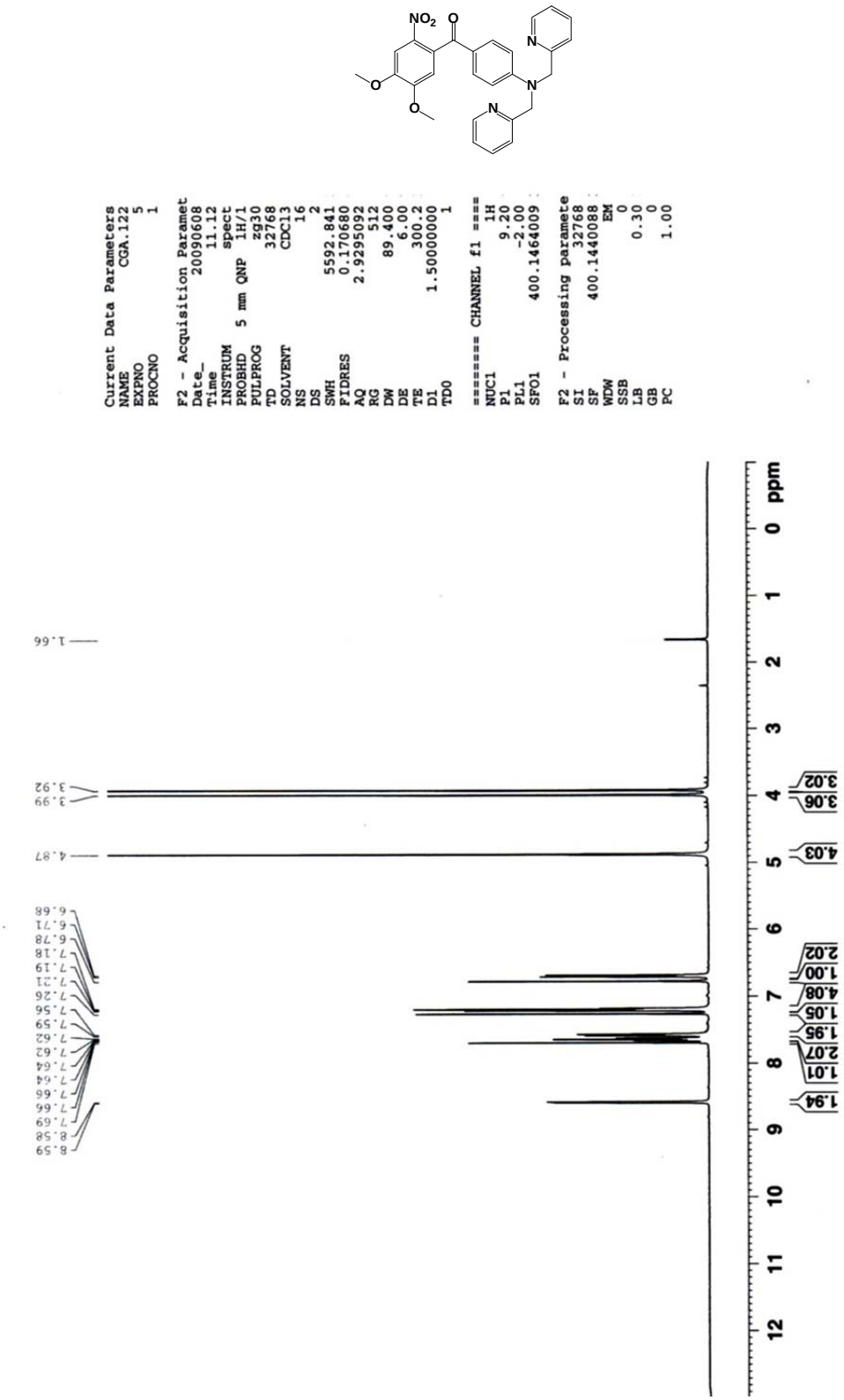


Figure S65 ^{1}H NMR of compound **16.**

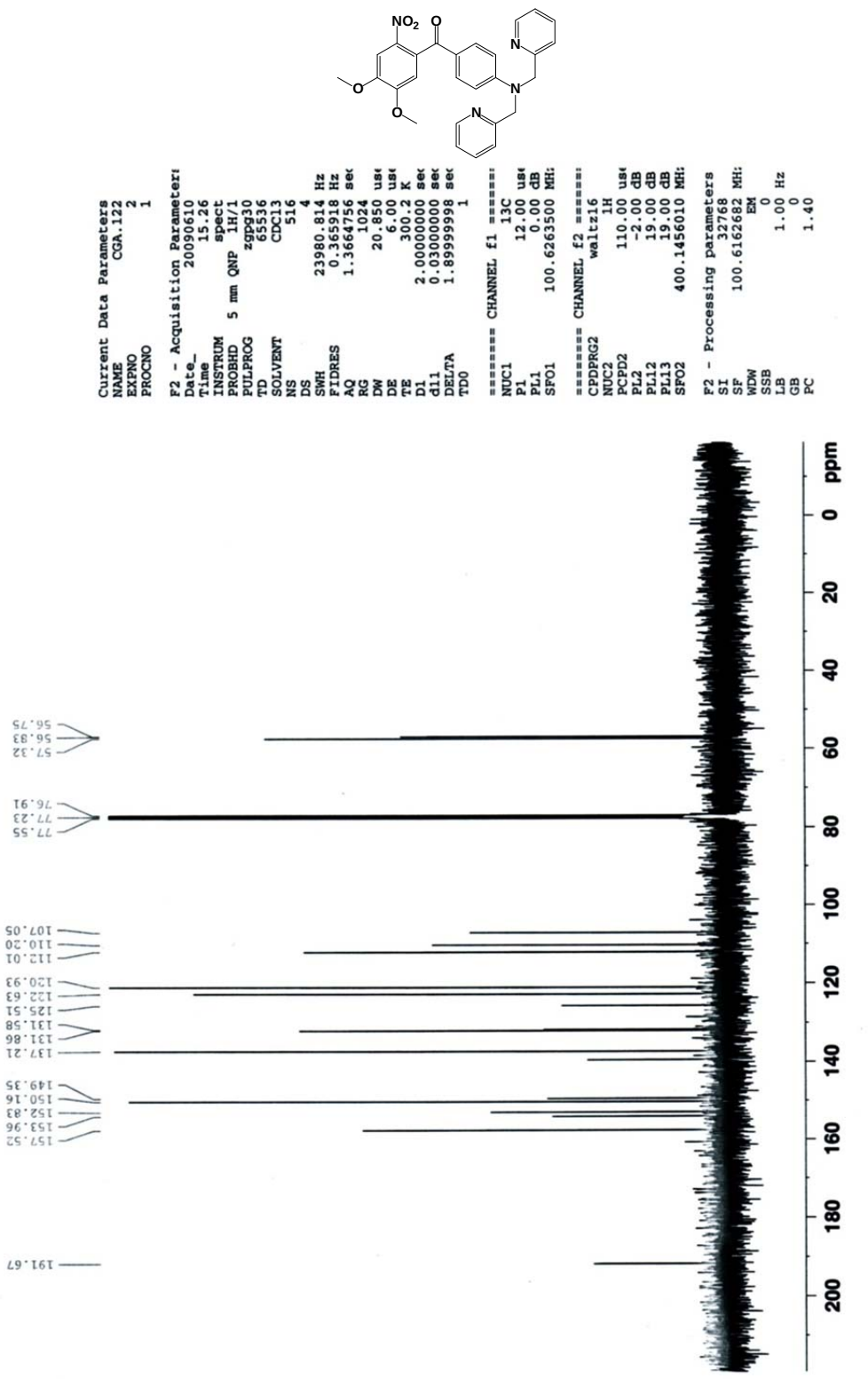


Figure S66. ^{13}C NMR of compound **16.**

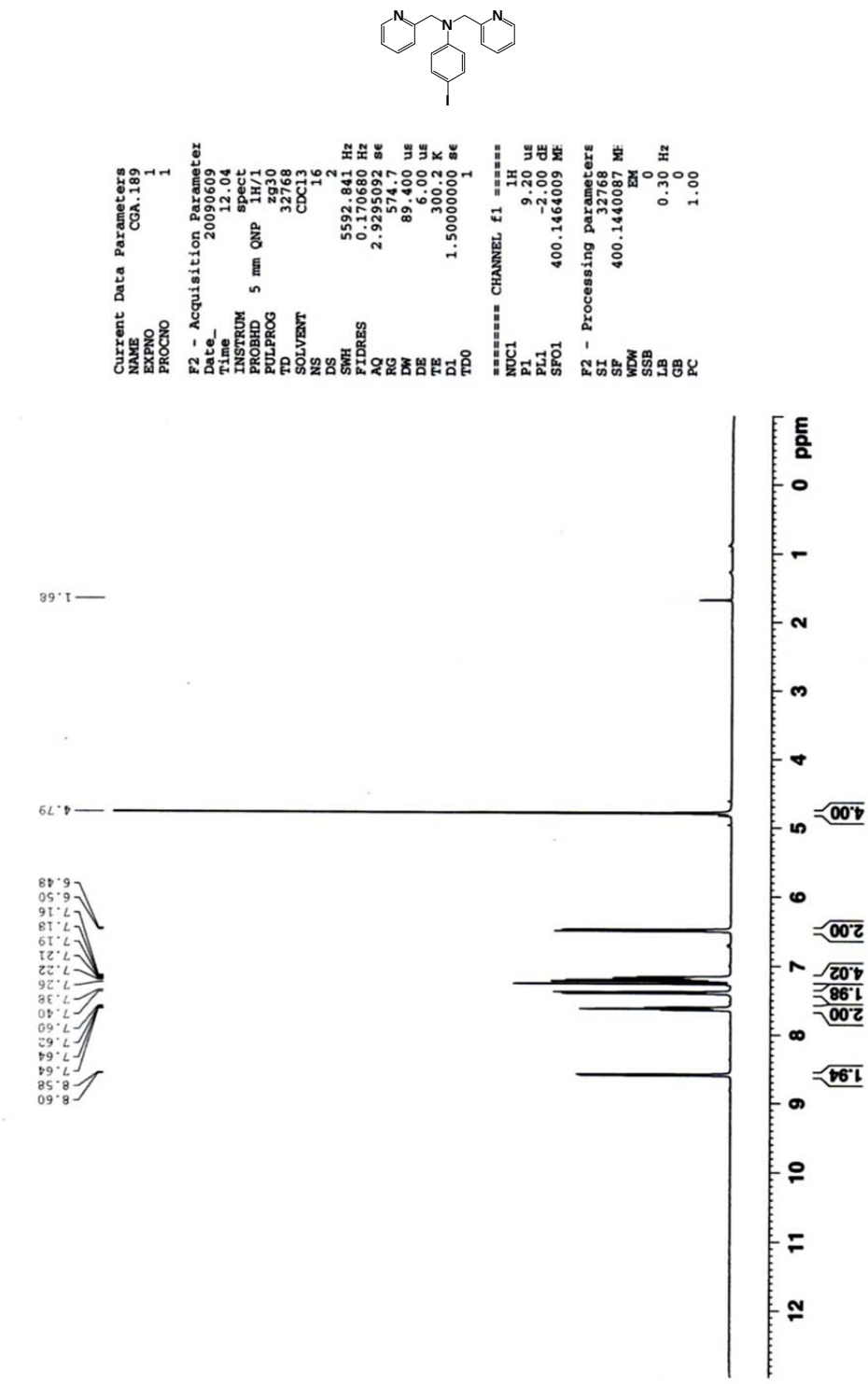
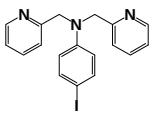


Figure S67 ^{1}H NMR of compound **17.**



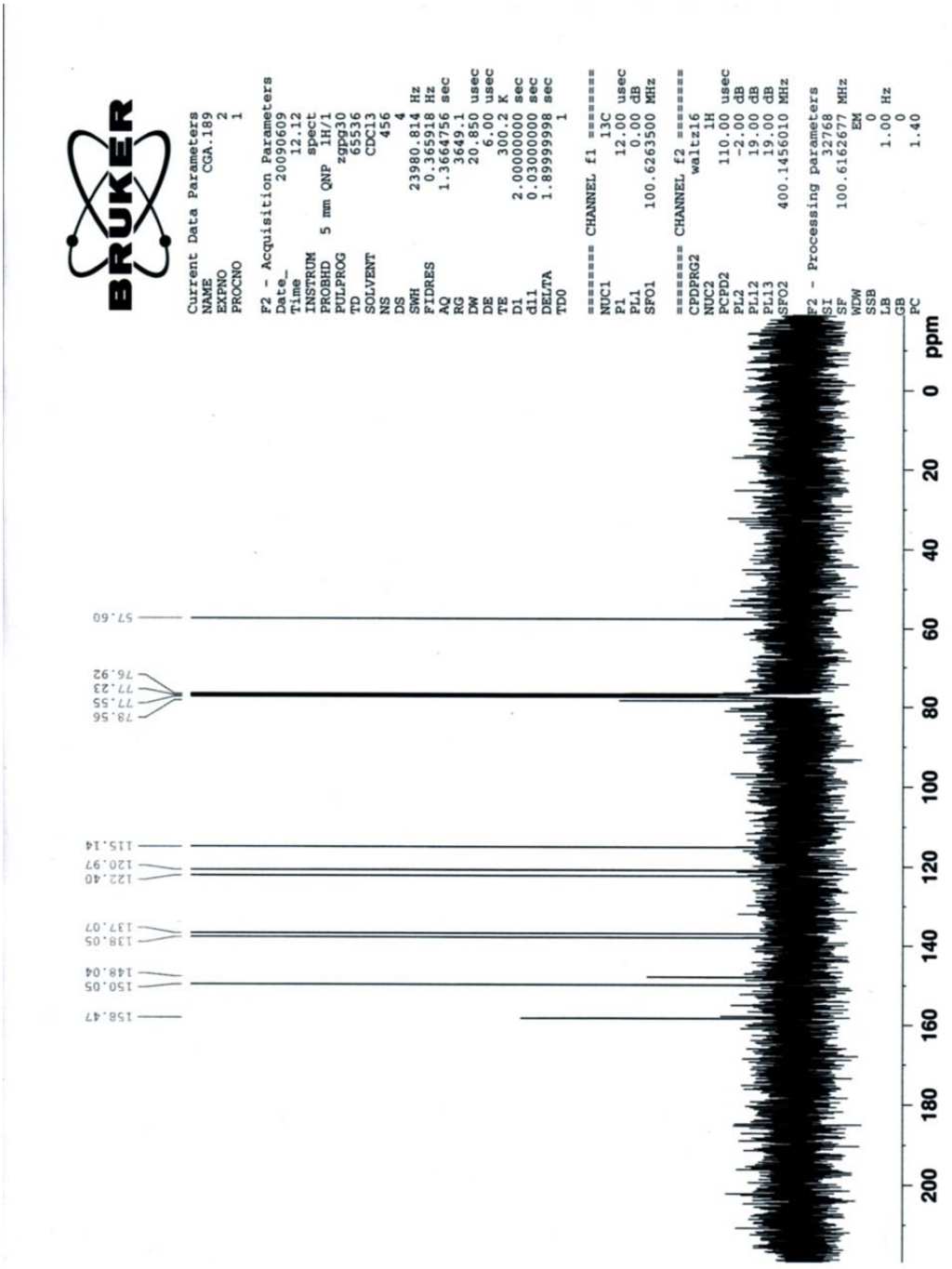


Figure S68 ^{13}C NMR of compound **17.**

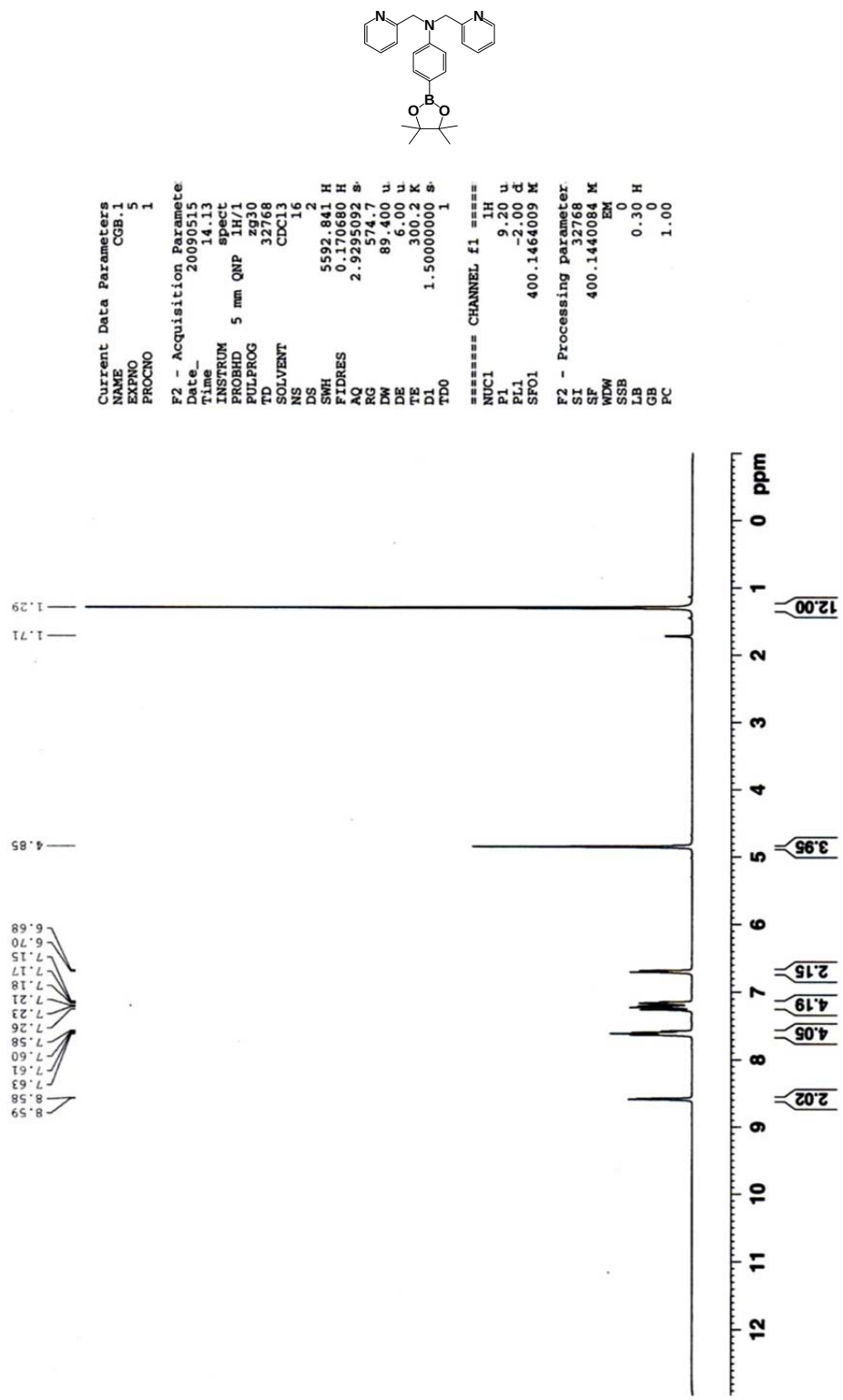


Figure S69. ^{1}H NMR of compound **18.**

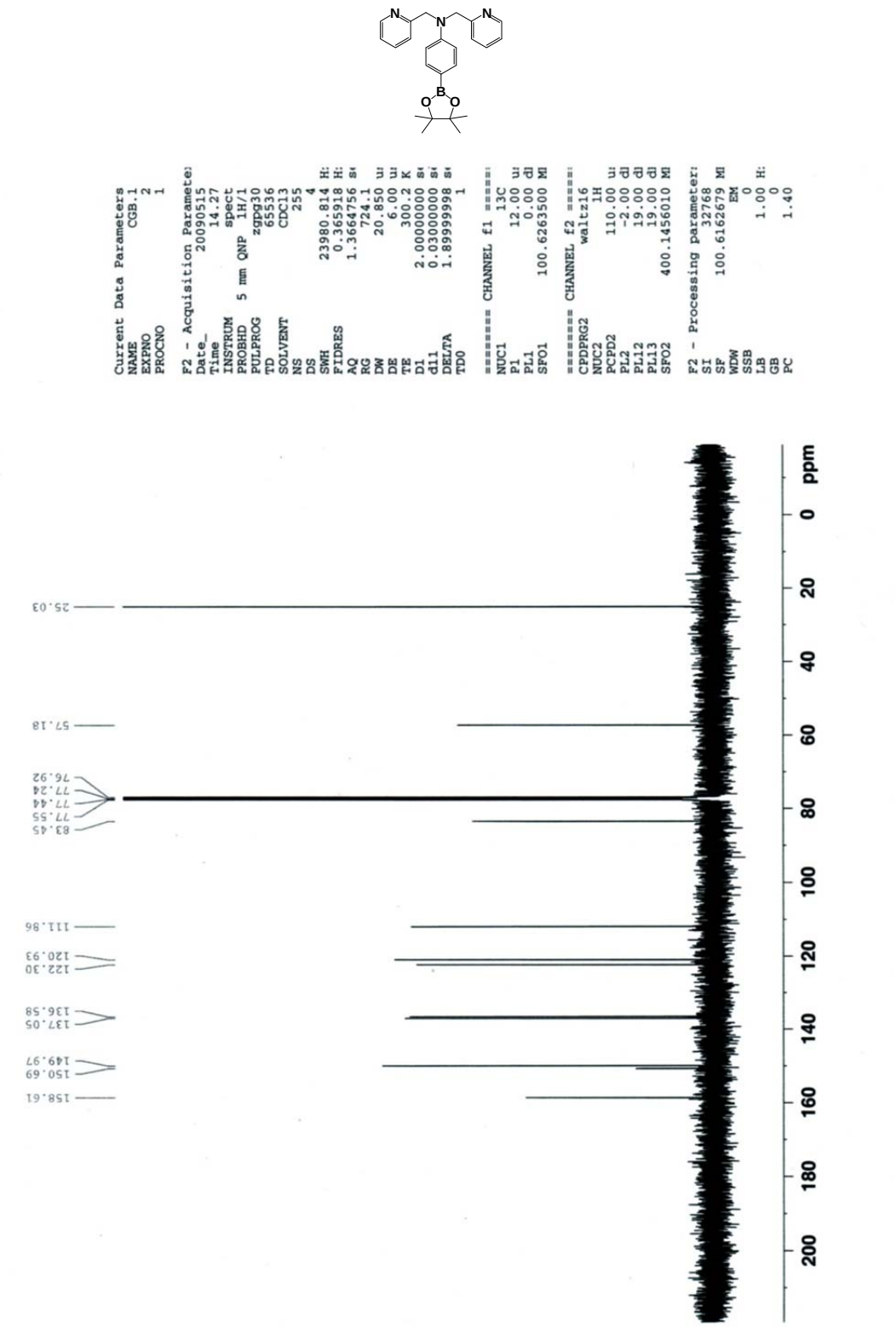
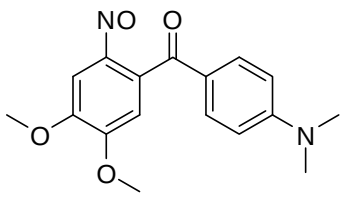
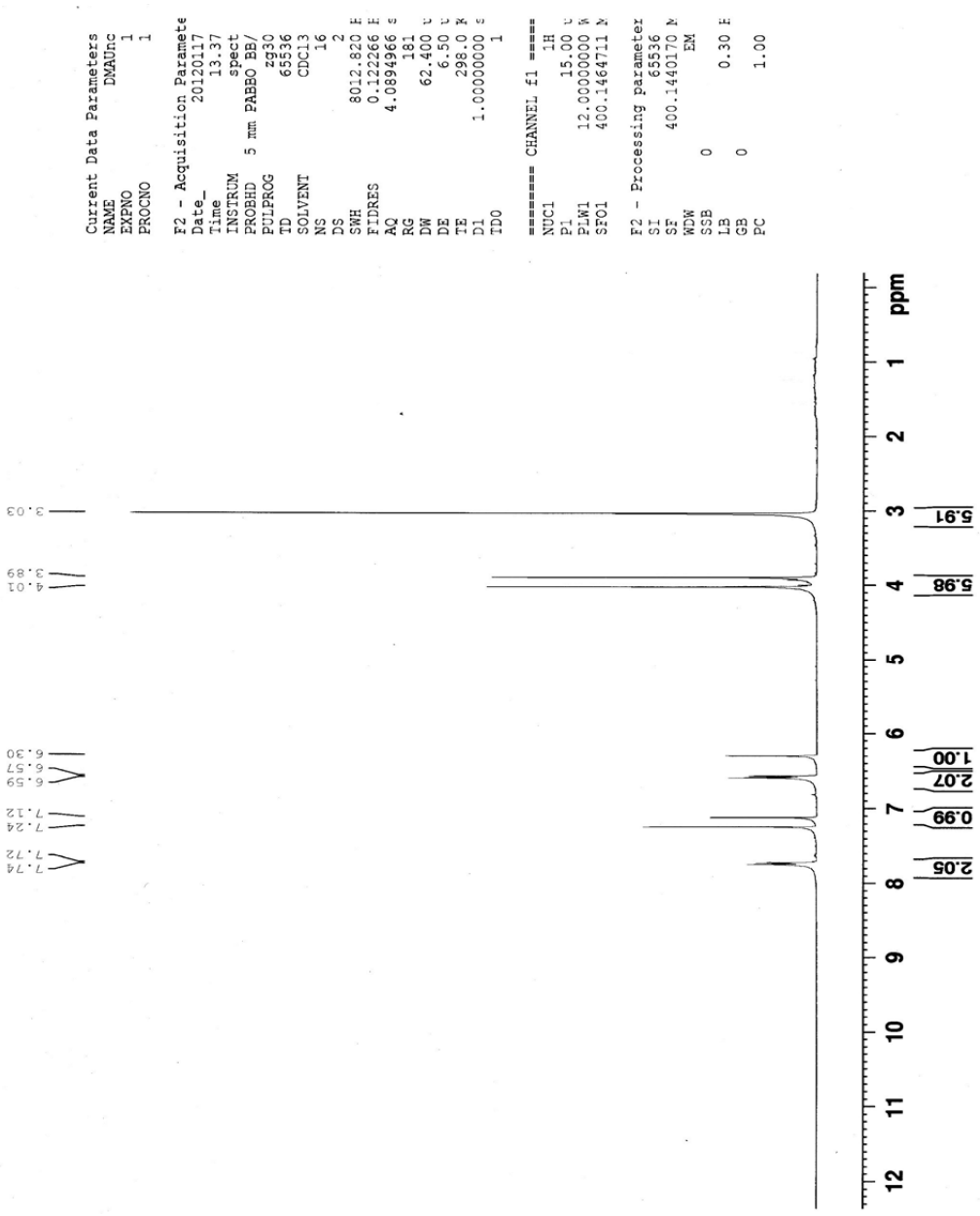


Figure S70 ^{13}C NMR of compound **18.**





S71 ^{1}H NMR of compound DMAUnc, **21**.

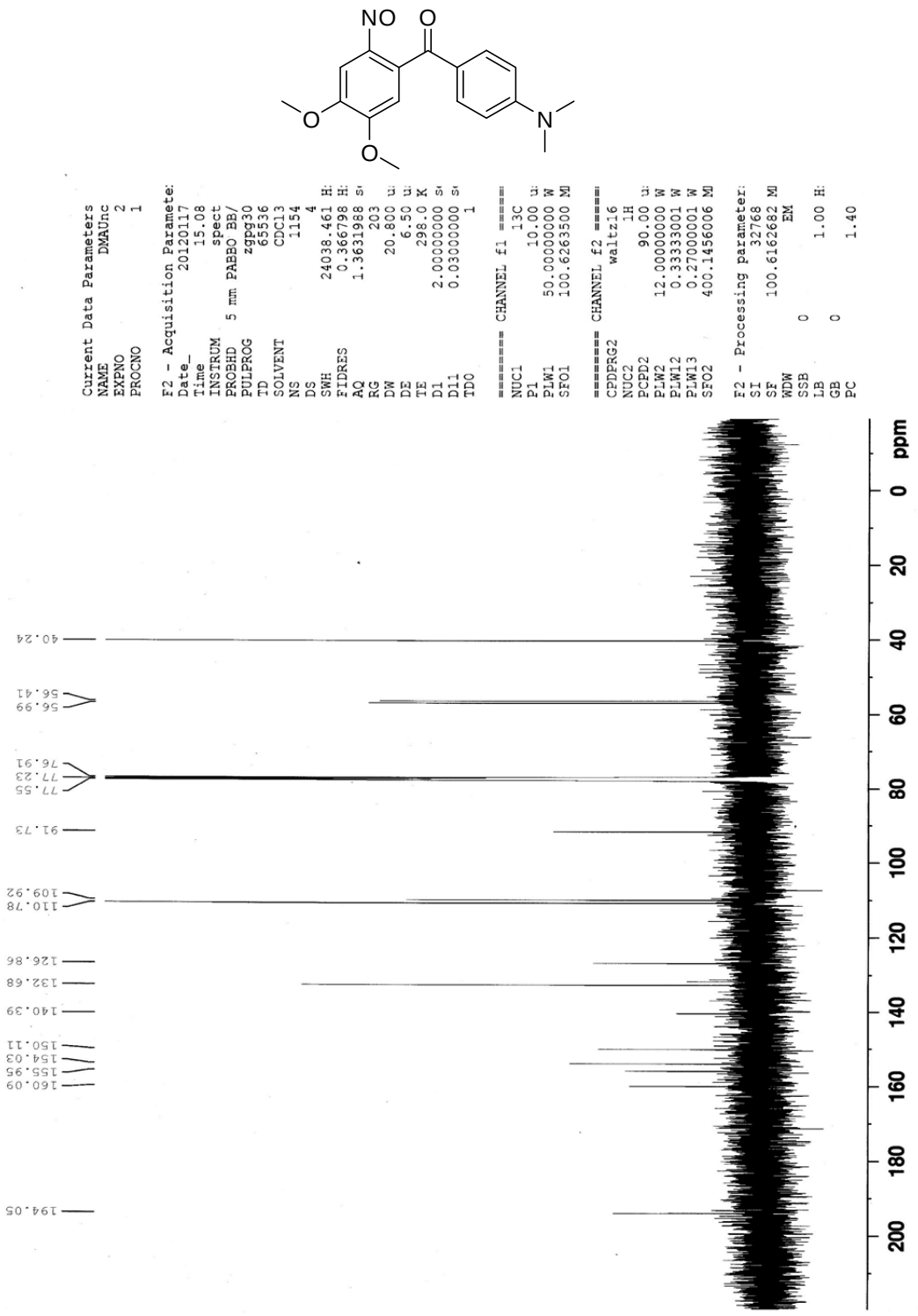


Figure S72 ^{13}C NMR of compound DMAUnc, **21**.

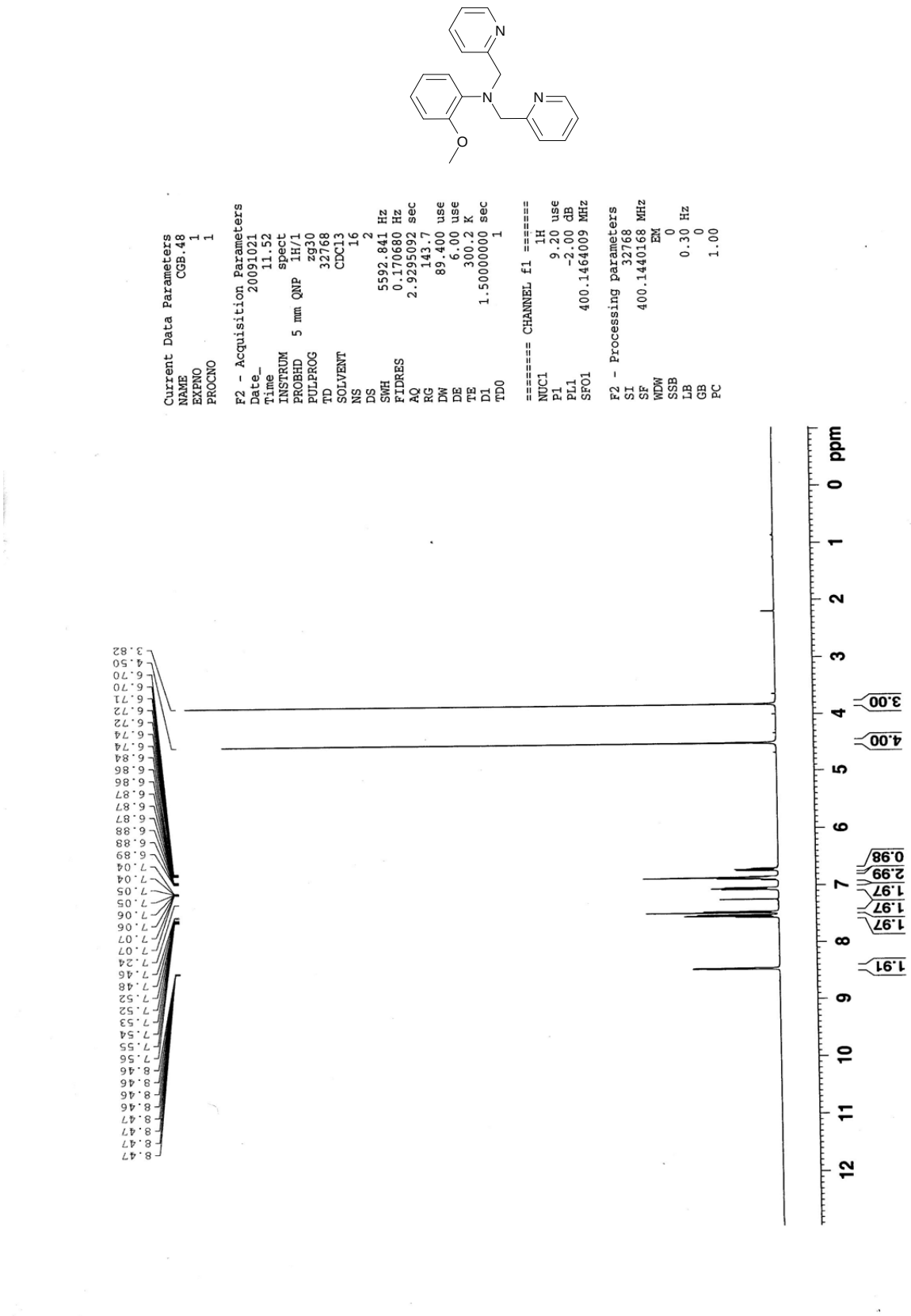


Figure S73 ^{1}H NMR of compound **23**.

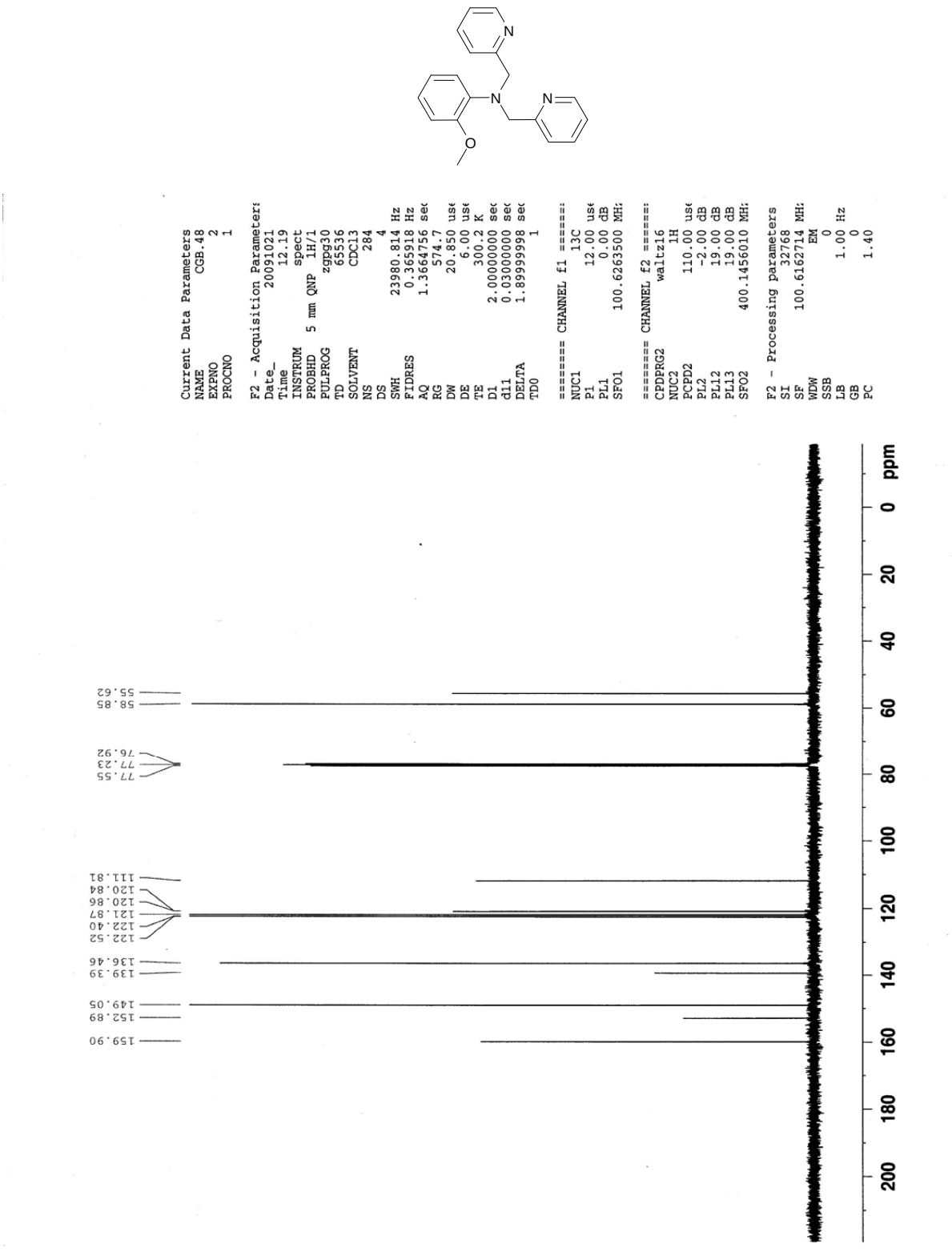


Figure S74 ^{13}C NMR of compound **23**.

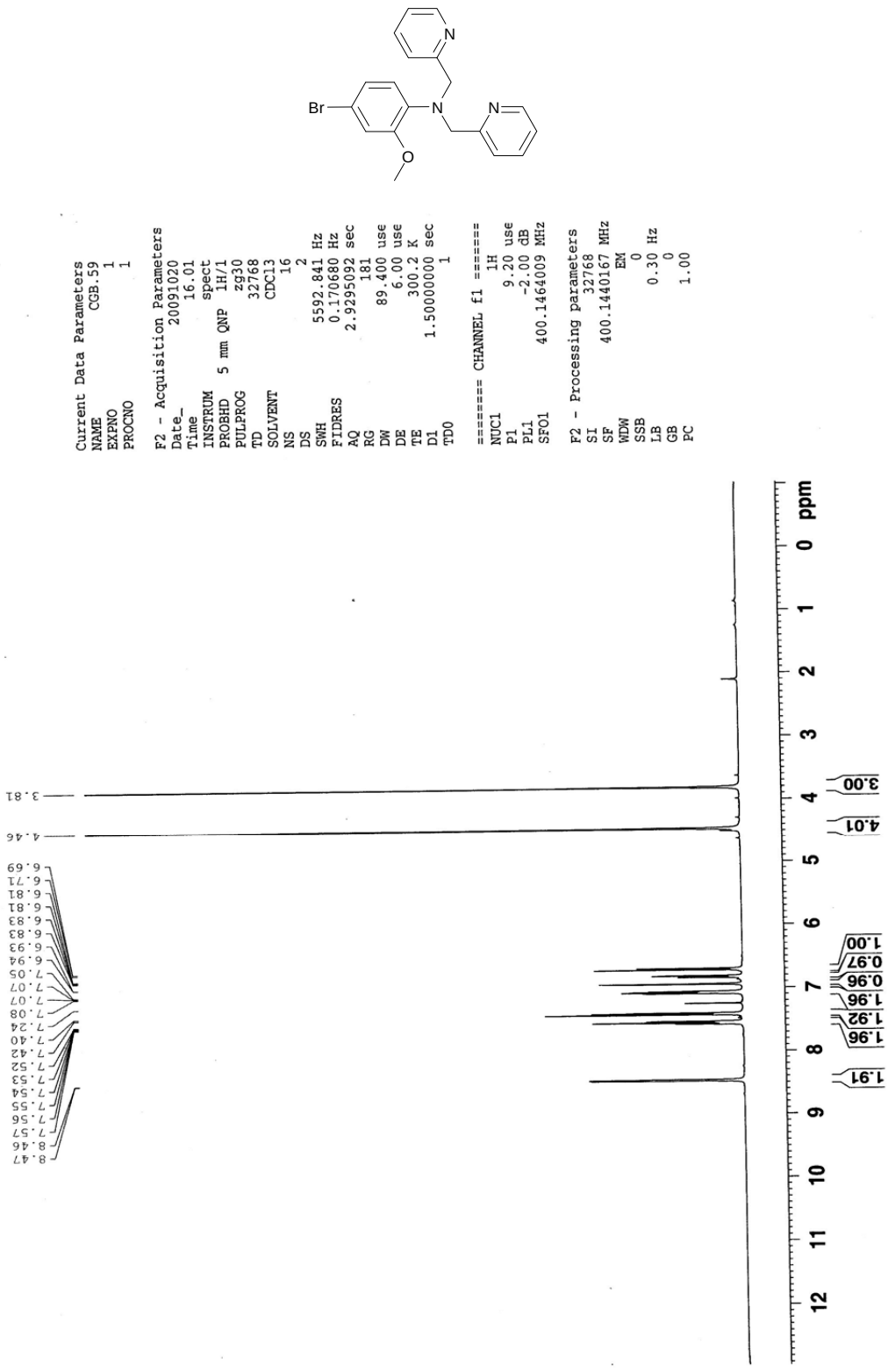


Figure S75 ^{1}H NMR of compound **24**.

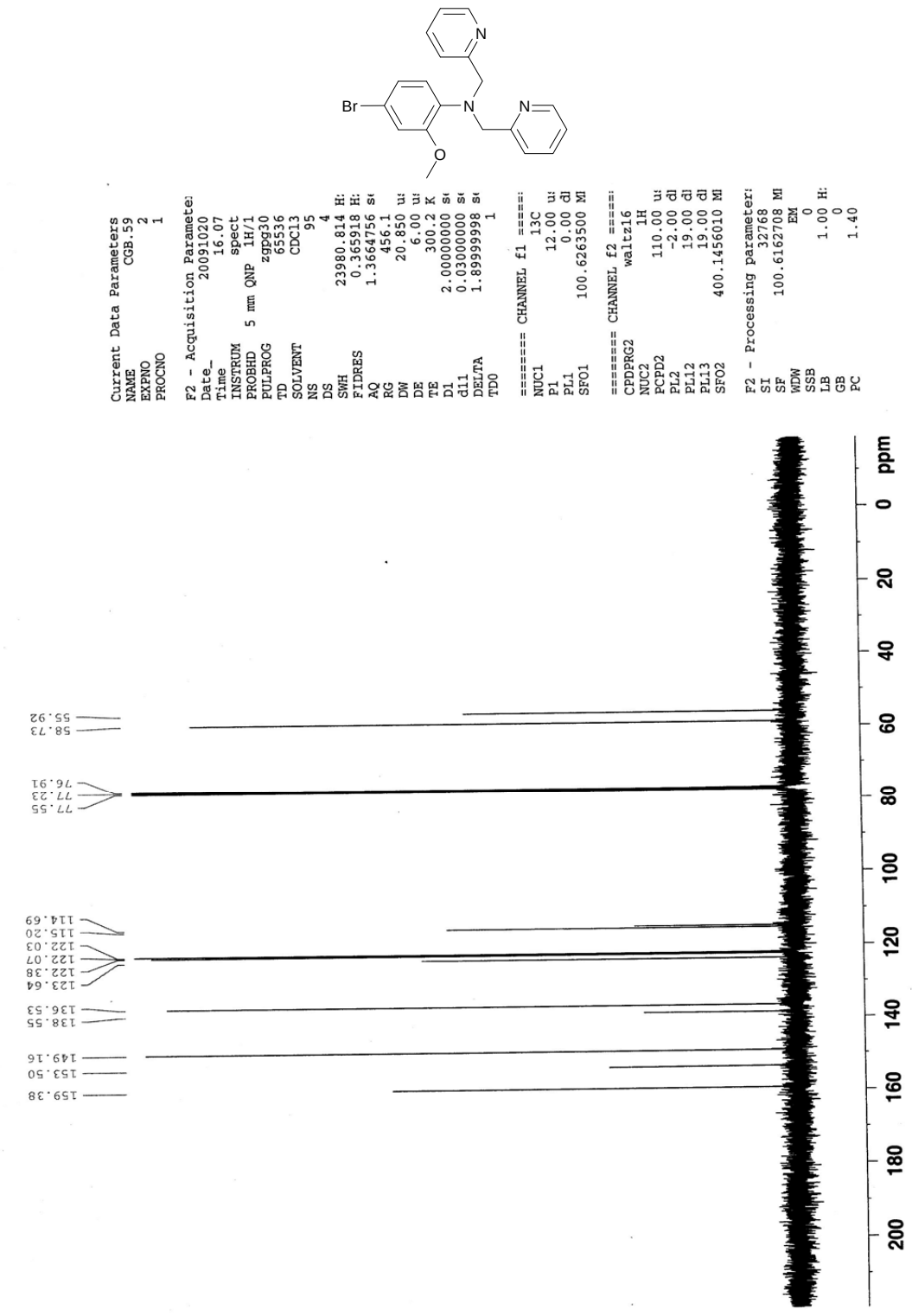


Figure S76 ^{13}C NMR of compound **24**.

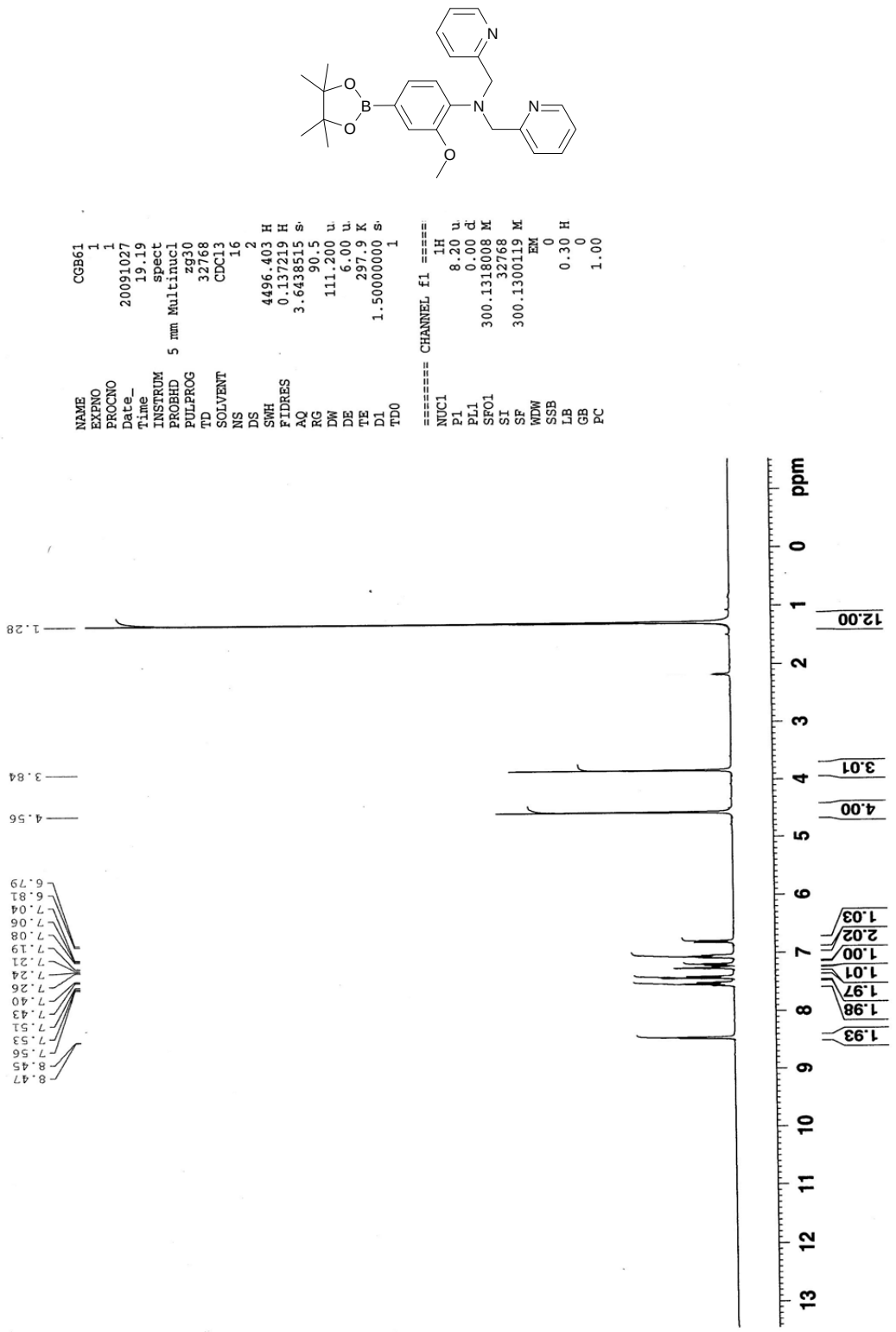


Figure S77 ^{1}H NMR of compound **25**.

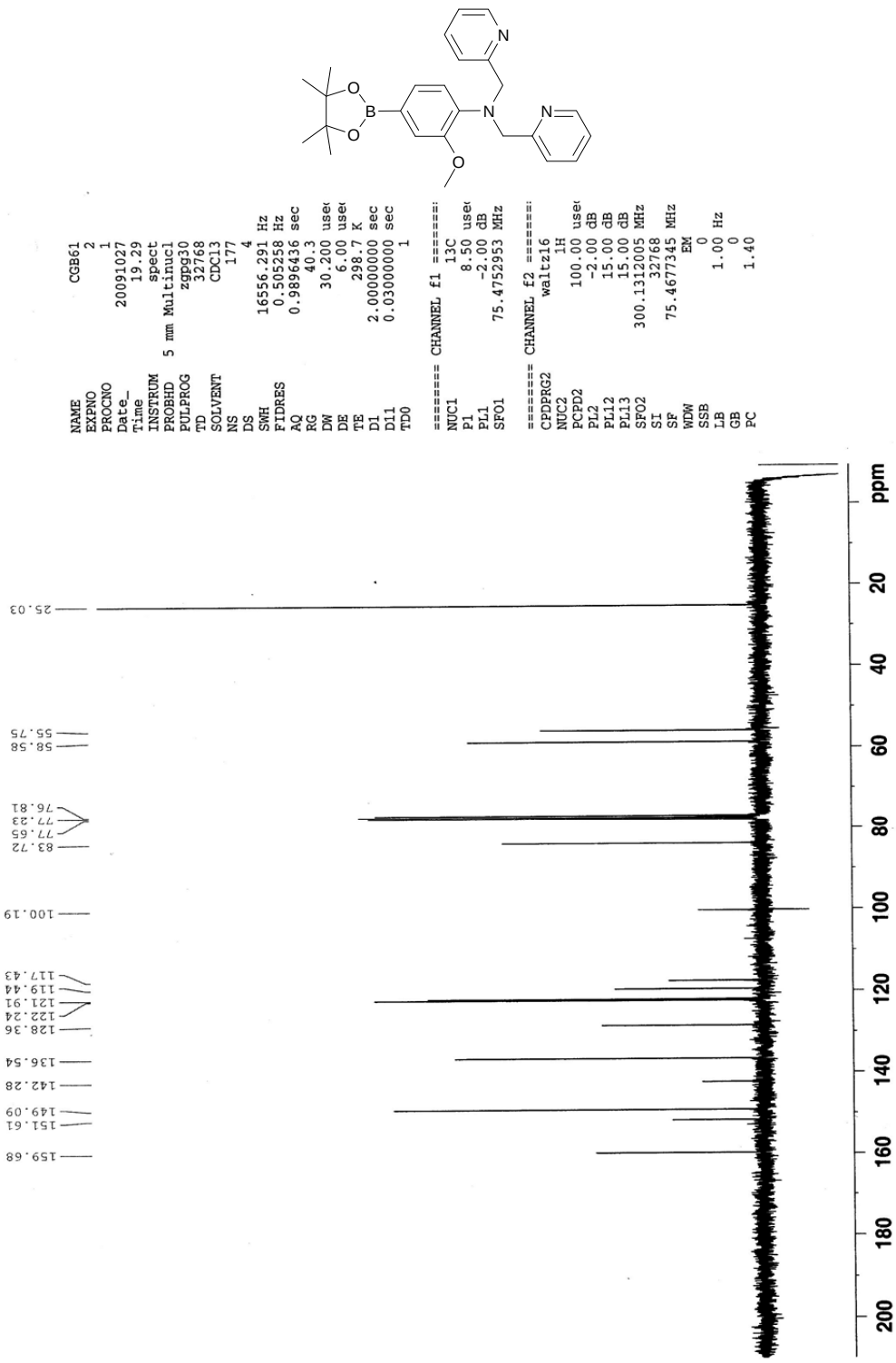


Figure S78 ^{13}C NMR of compound **25**.

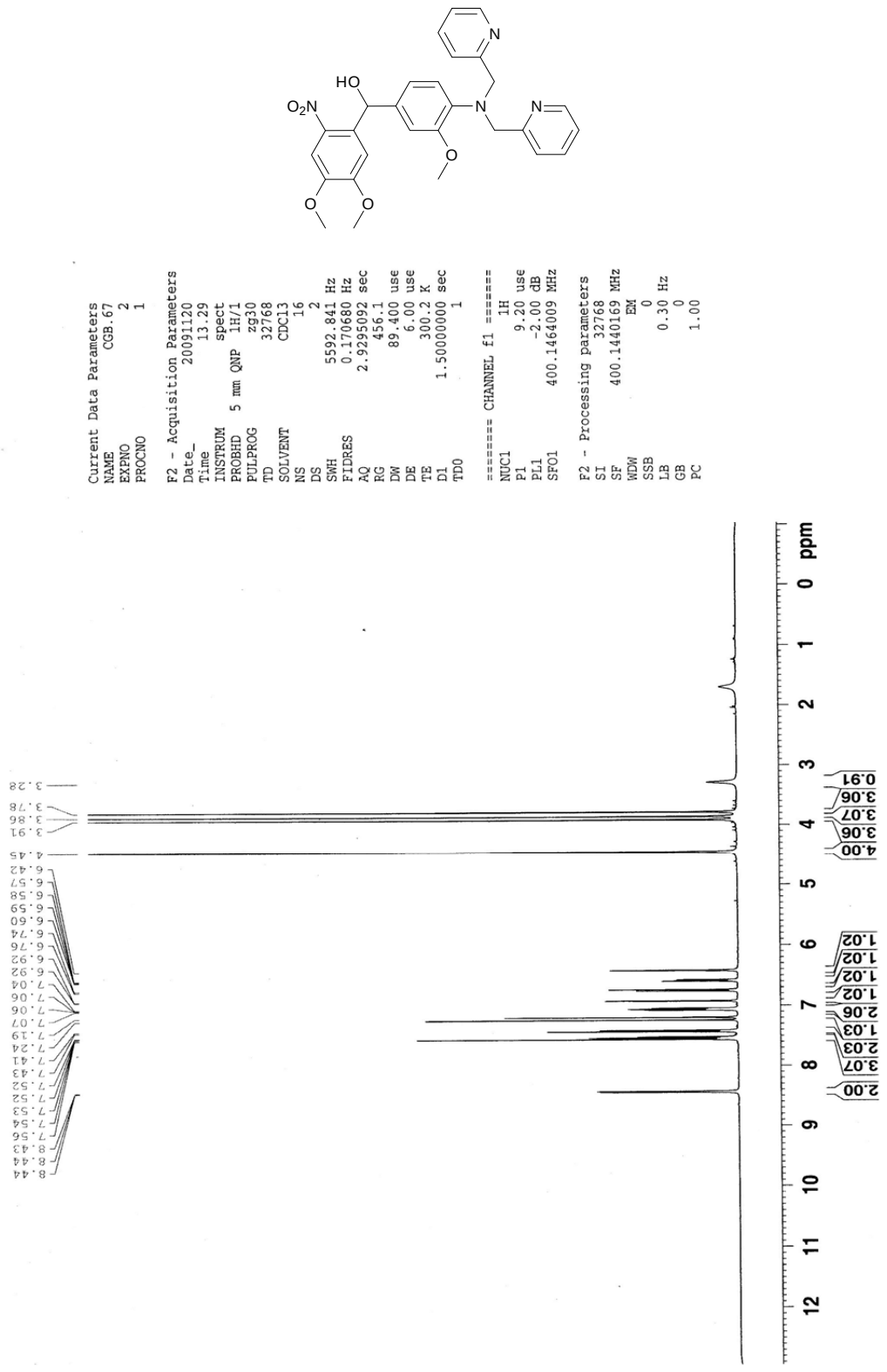


Figure S79 [1]H NMR of compound ZinCast-4, **26**.

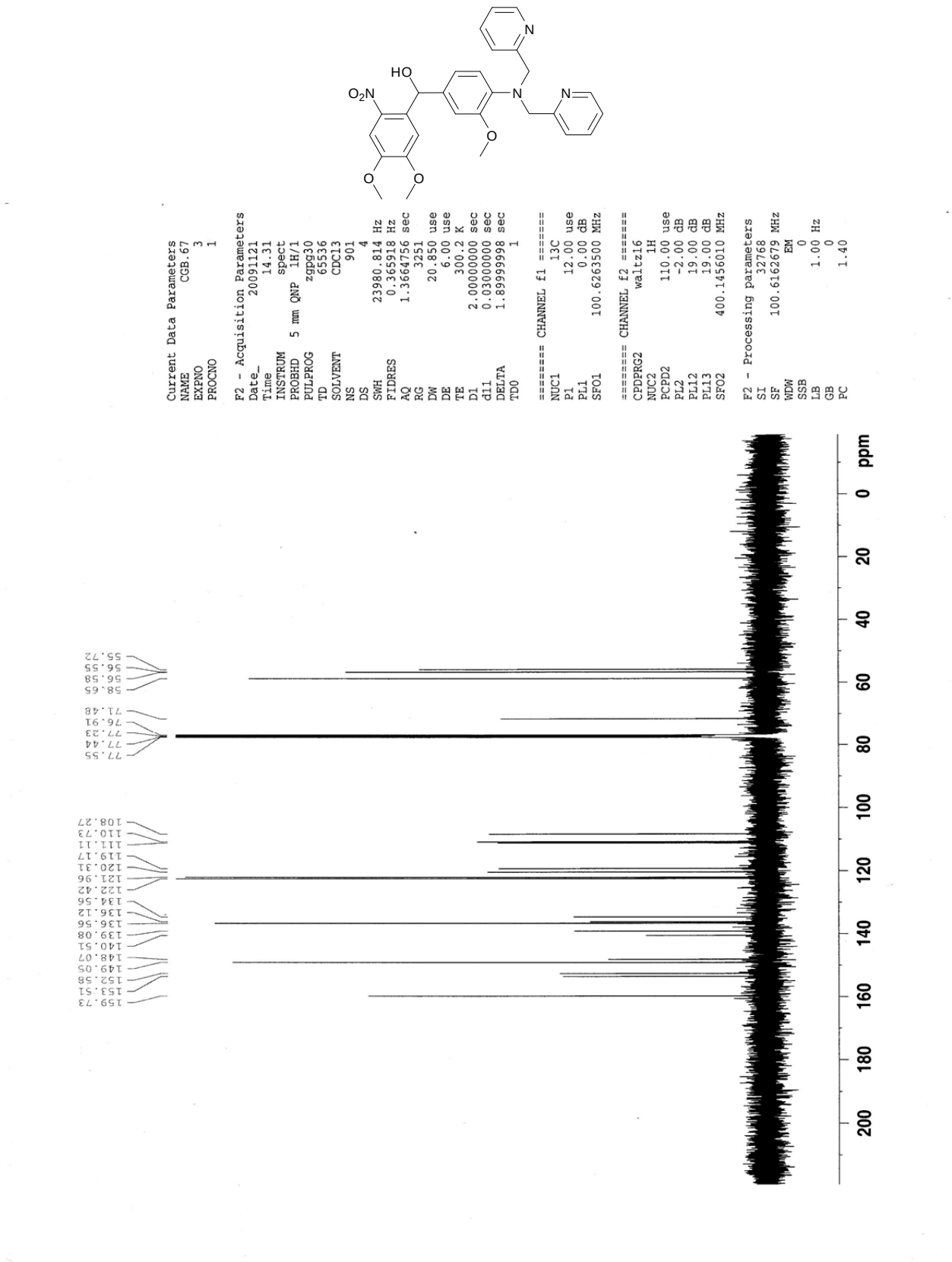


Figure S80 ^{13}C NMR of compound ZinCast-4**, 26**.

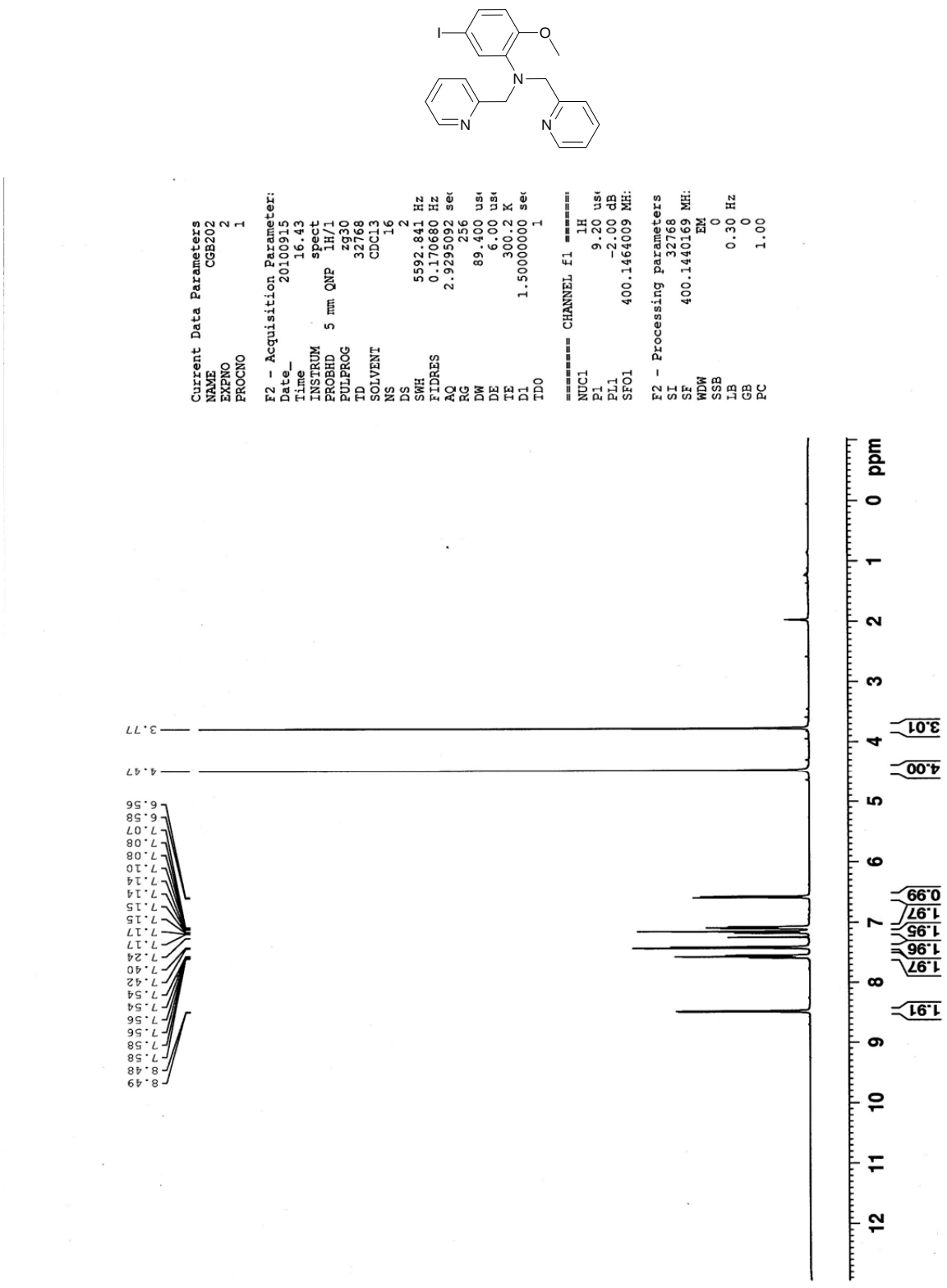


Figure S81 ^{1}H NMR of compound **28**.

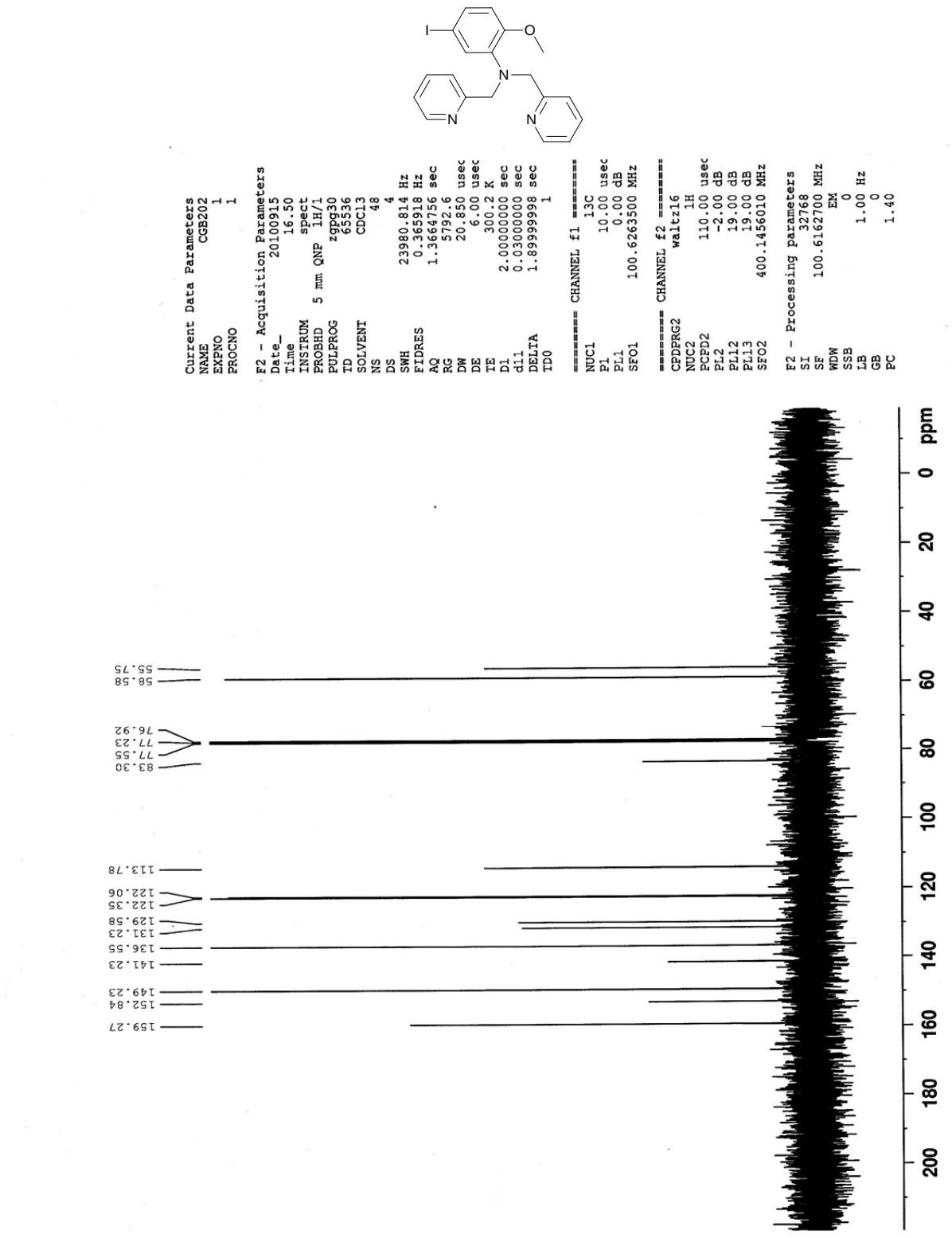


Figure S82 ^{13}C NMR of compound **28**

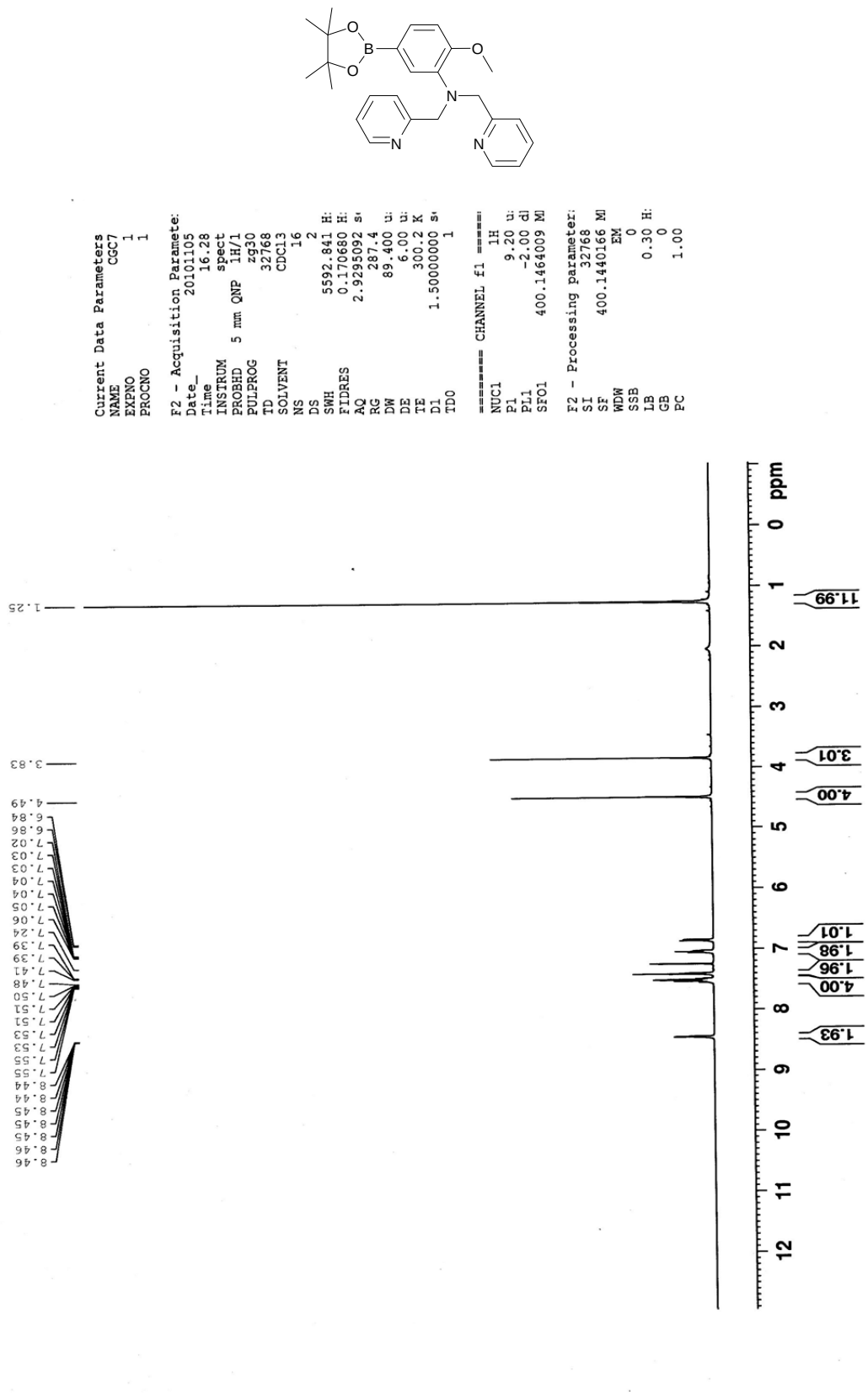


Figure S83 ^{1}H NMR of compound **29**.

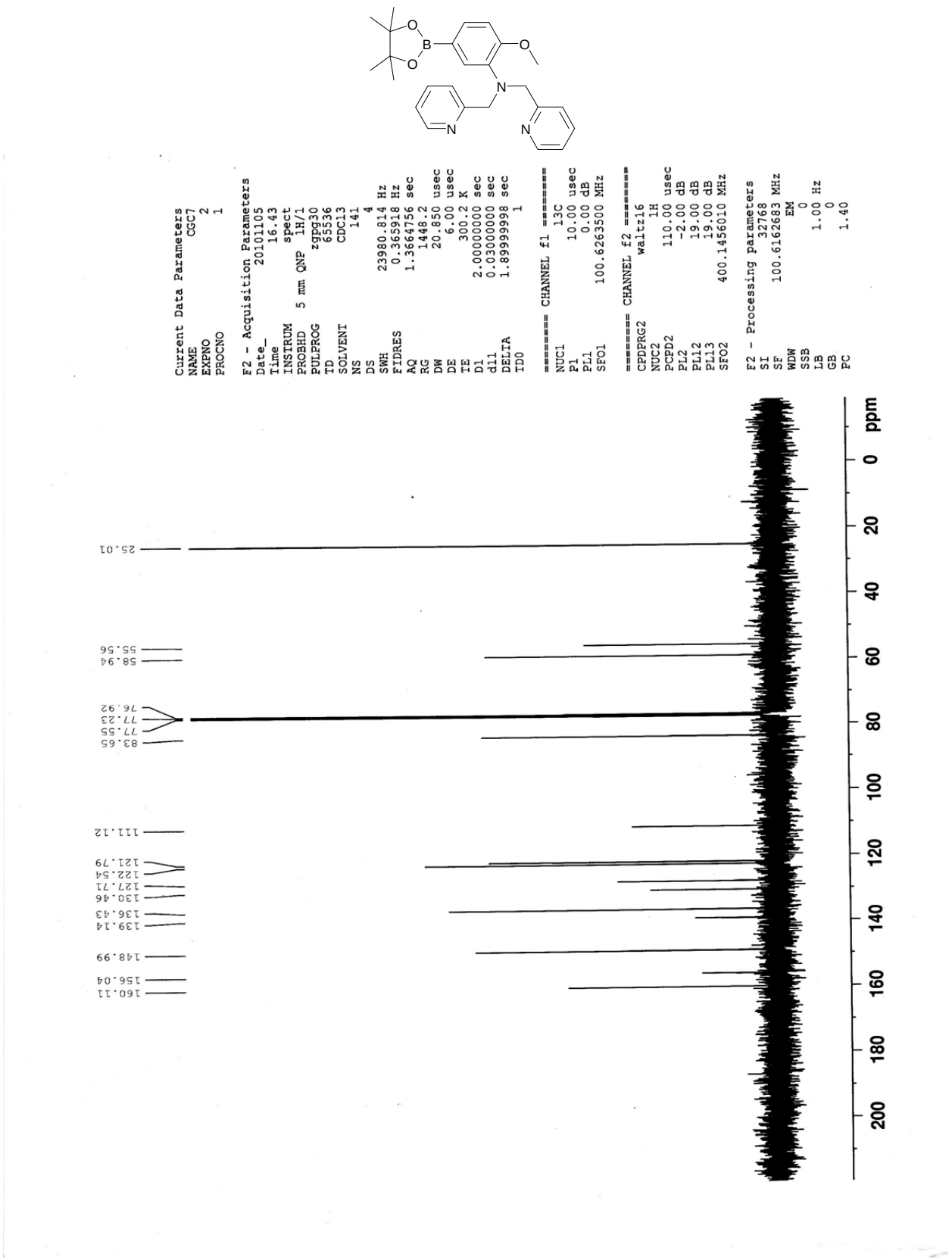


Figure S84 ^{13}C NMR of compound **29**.

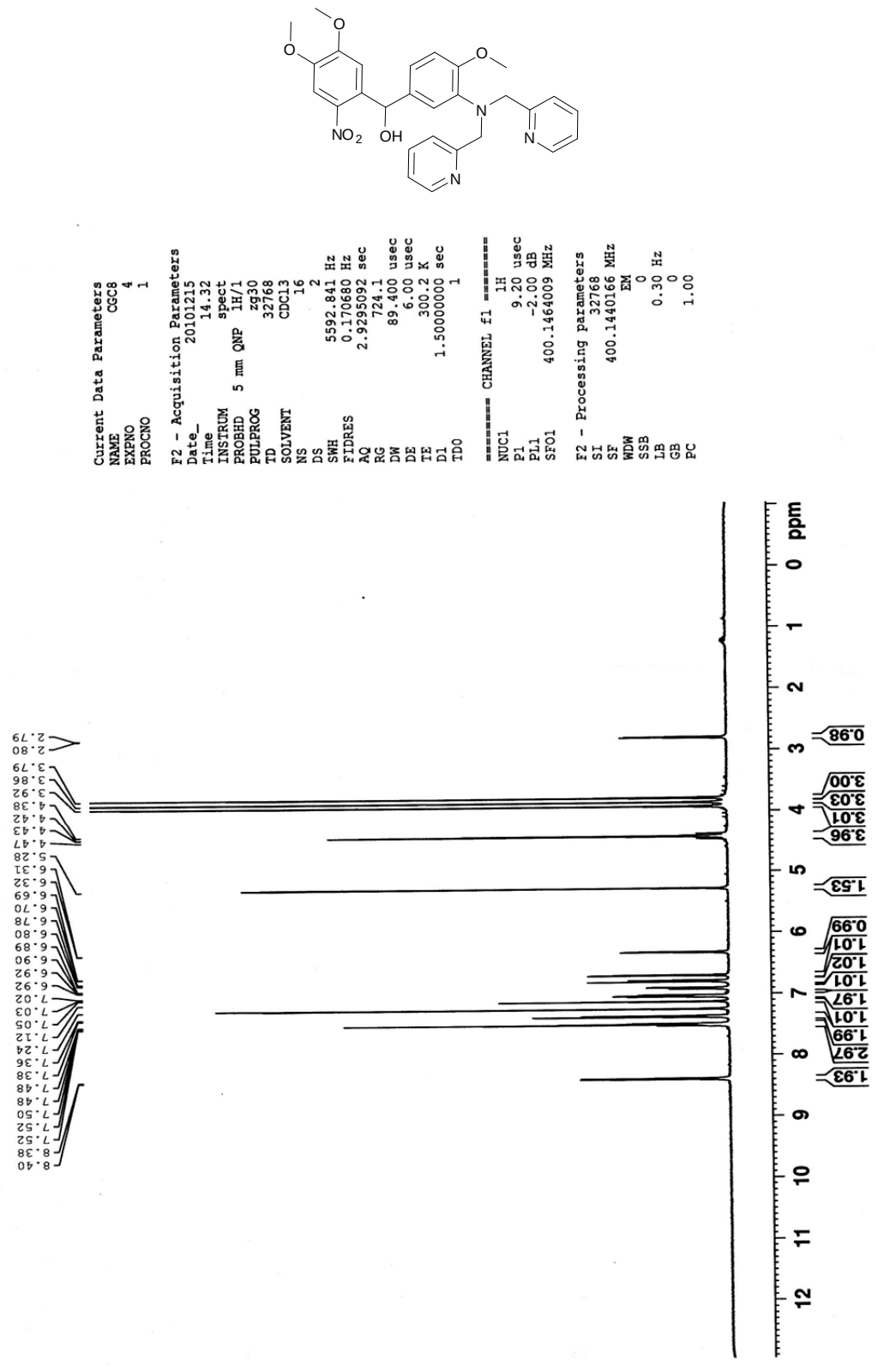


Figure S85 ^{1}H NMR of compound ZinCast-5, **30.**

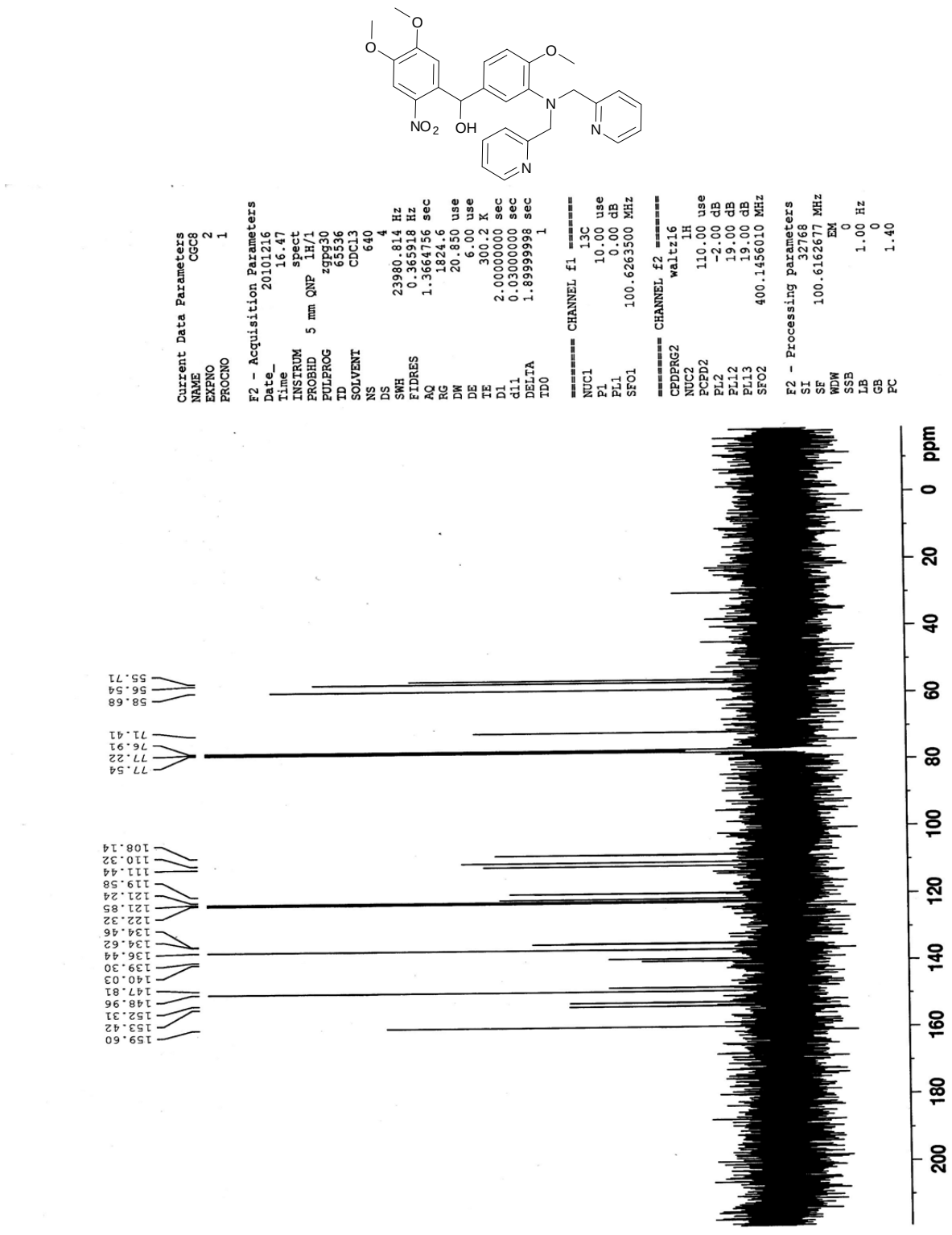


Figure S86 ^{13}C NMR of compound ZinCast-5, **30**.

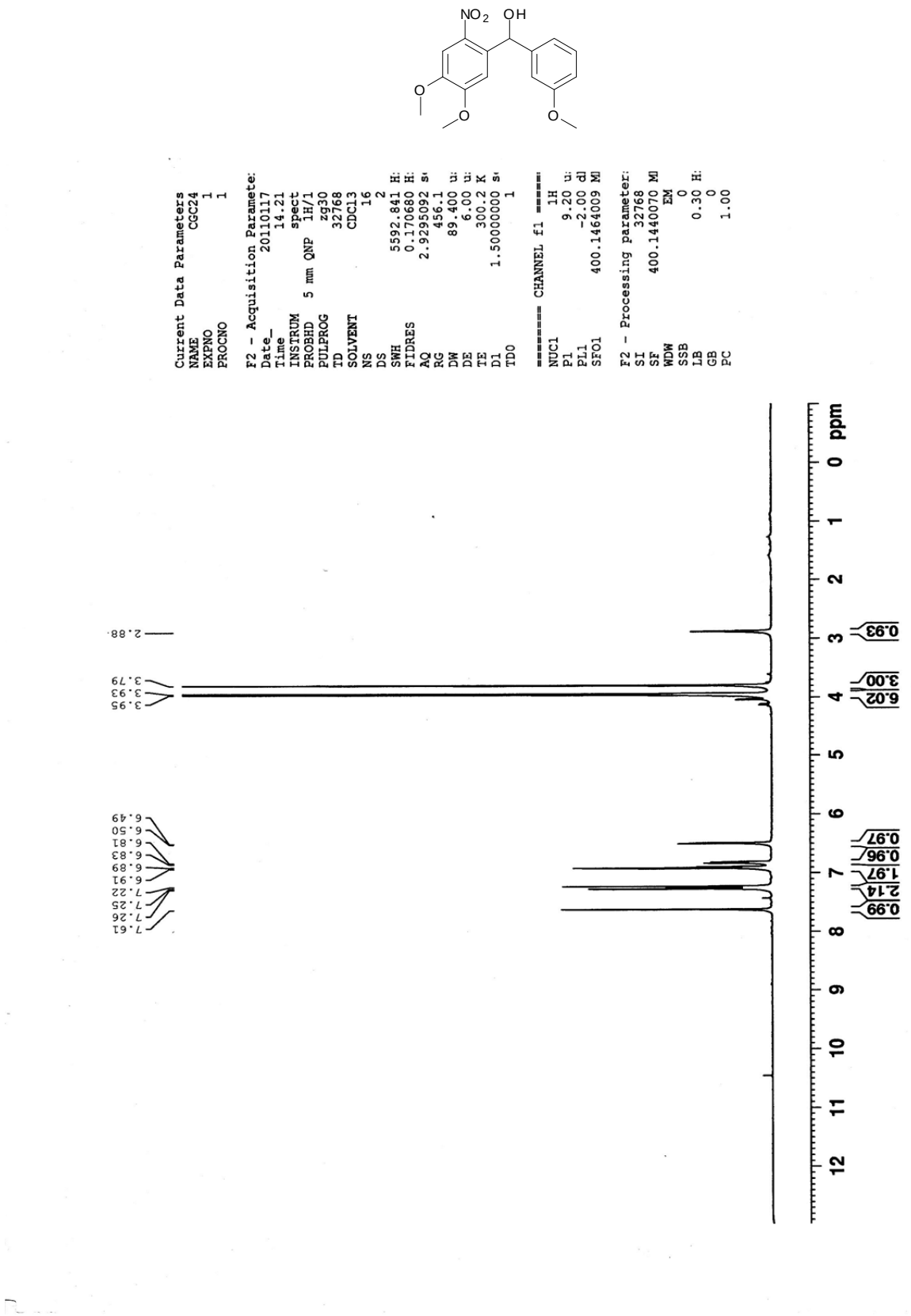


Figure S87 ^{1}H NMR of compound *m*-OMeCast, **33**.

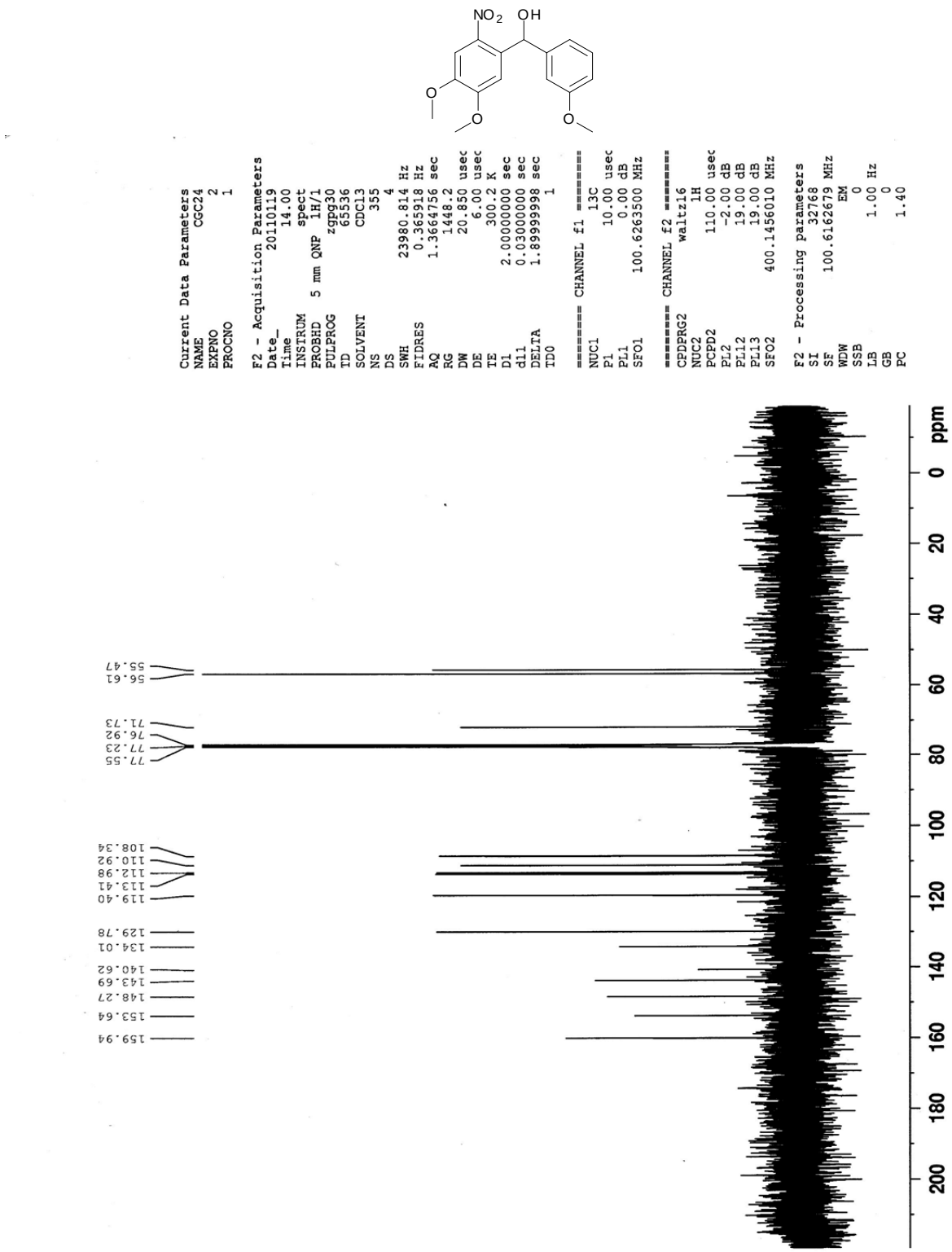
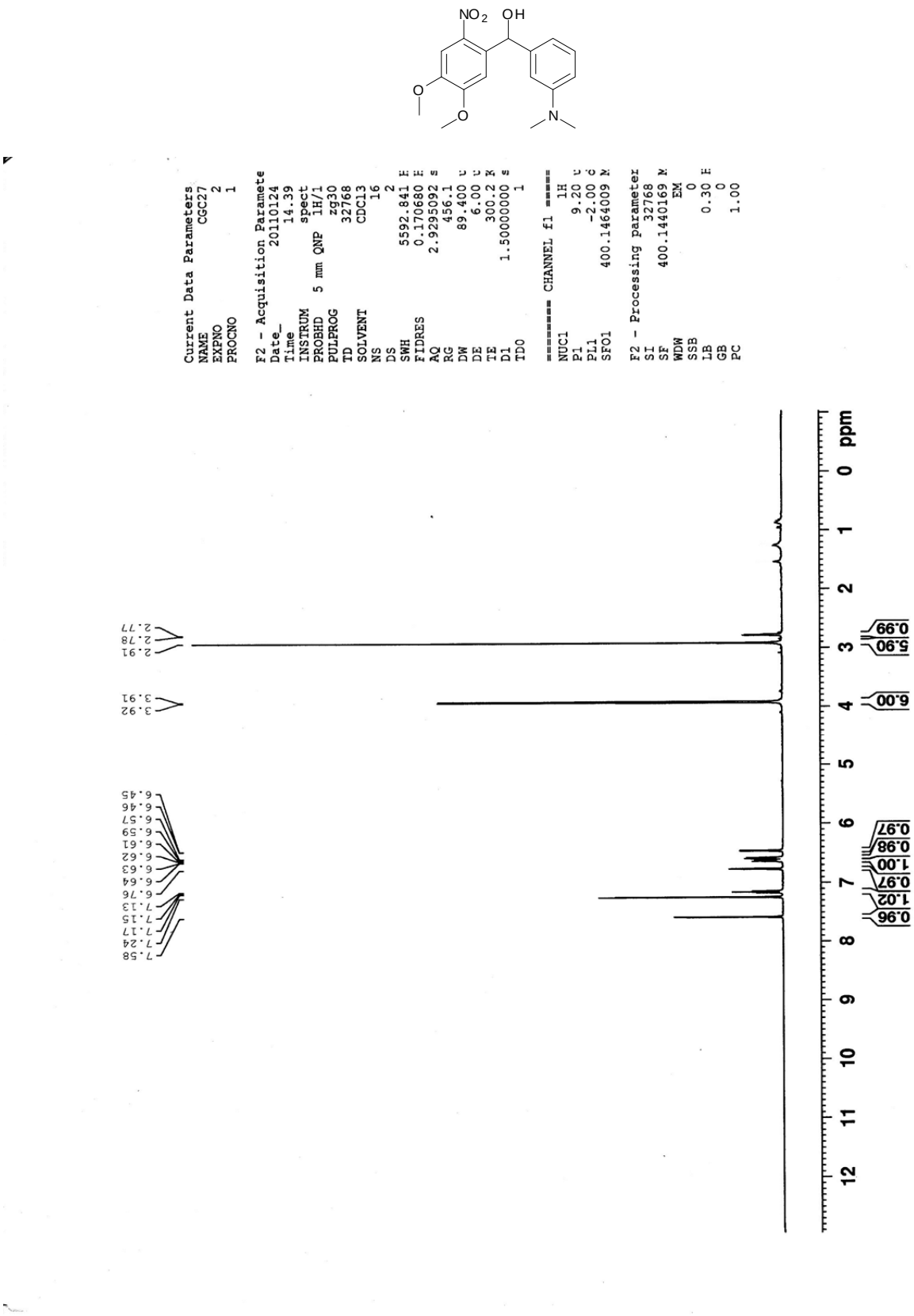


Figure S88 ^{13}C NMR of compound *m*-OMeCast, **33**.



S89 ^{1}H NMR of compound *m*-DMACast, **34**.

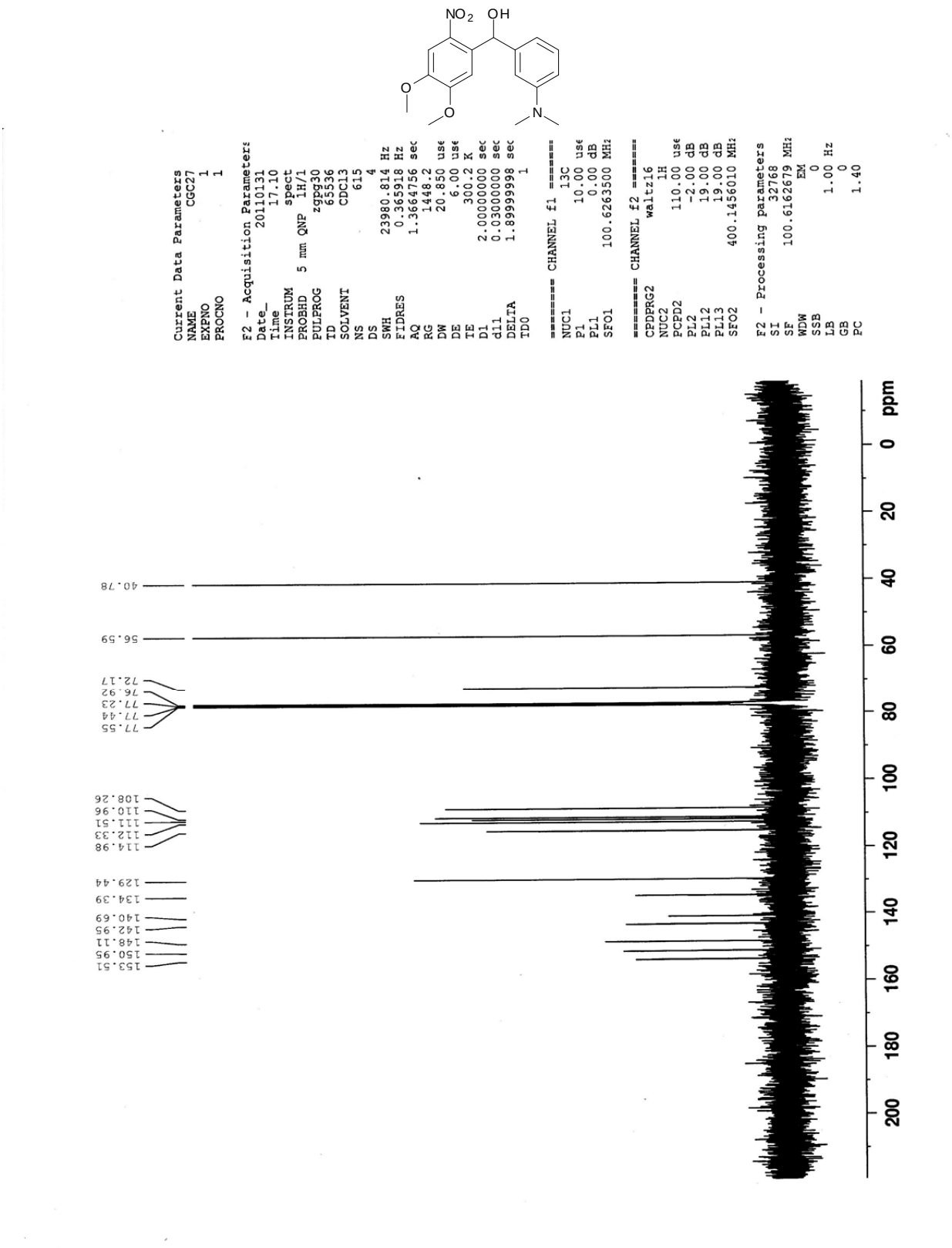


Figure S90 ^{13}C NMR of compound *m*-DMACast, **34**.

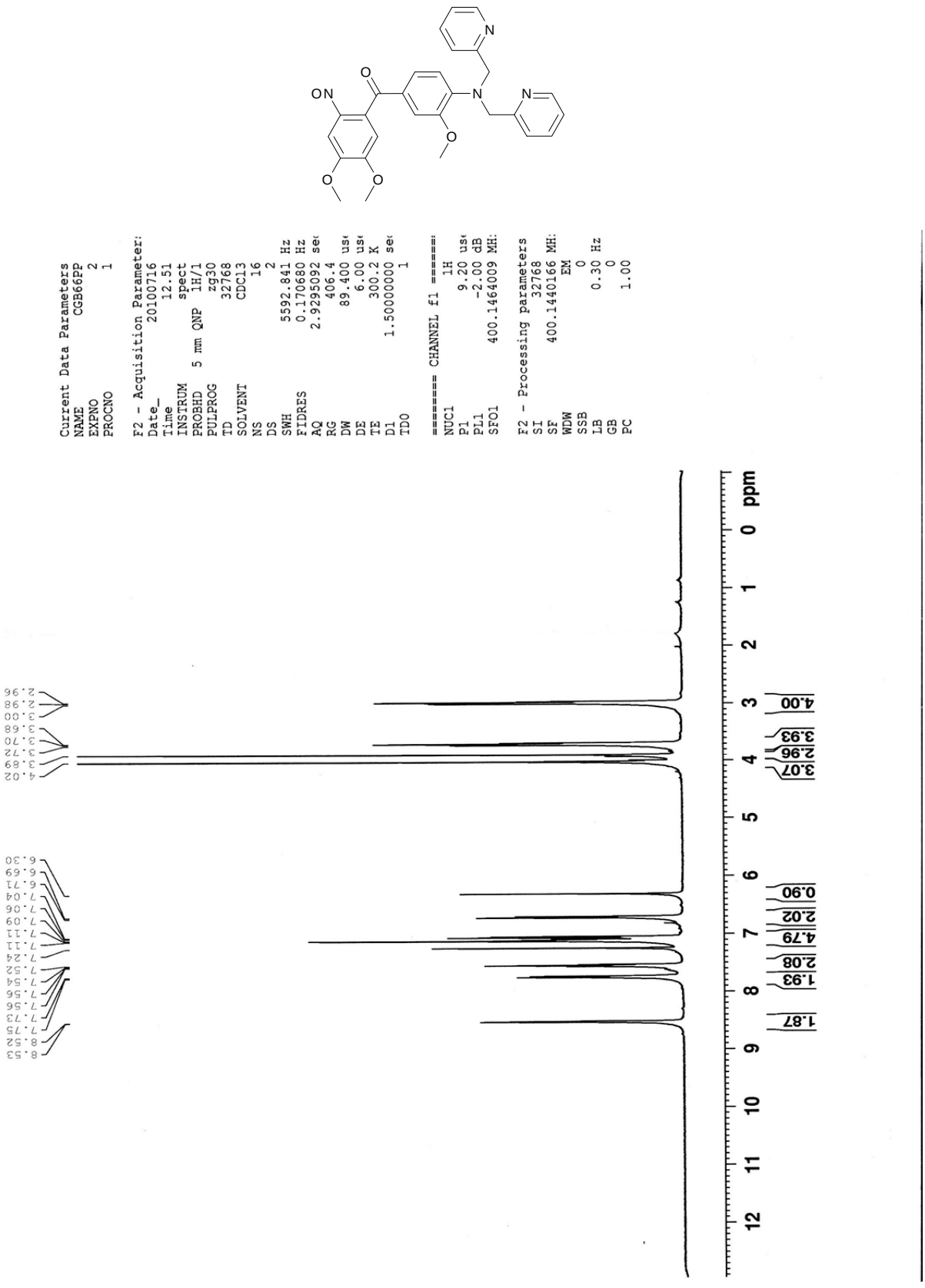


Figure S91 [1]H NMR of compound ZinUnc-4, **35**.

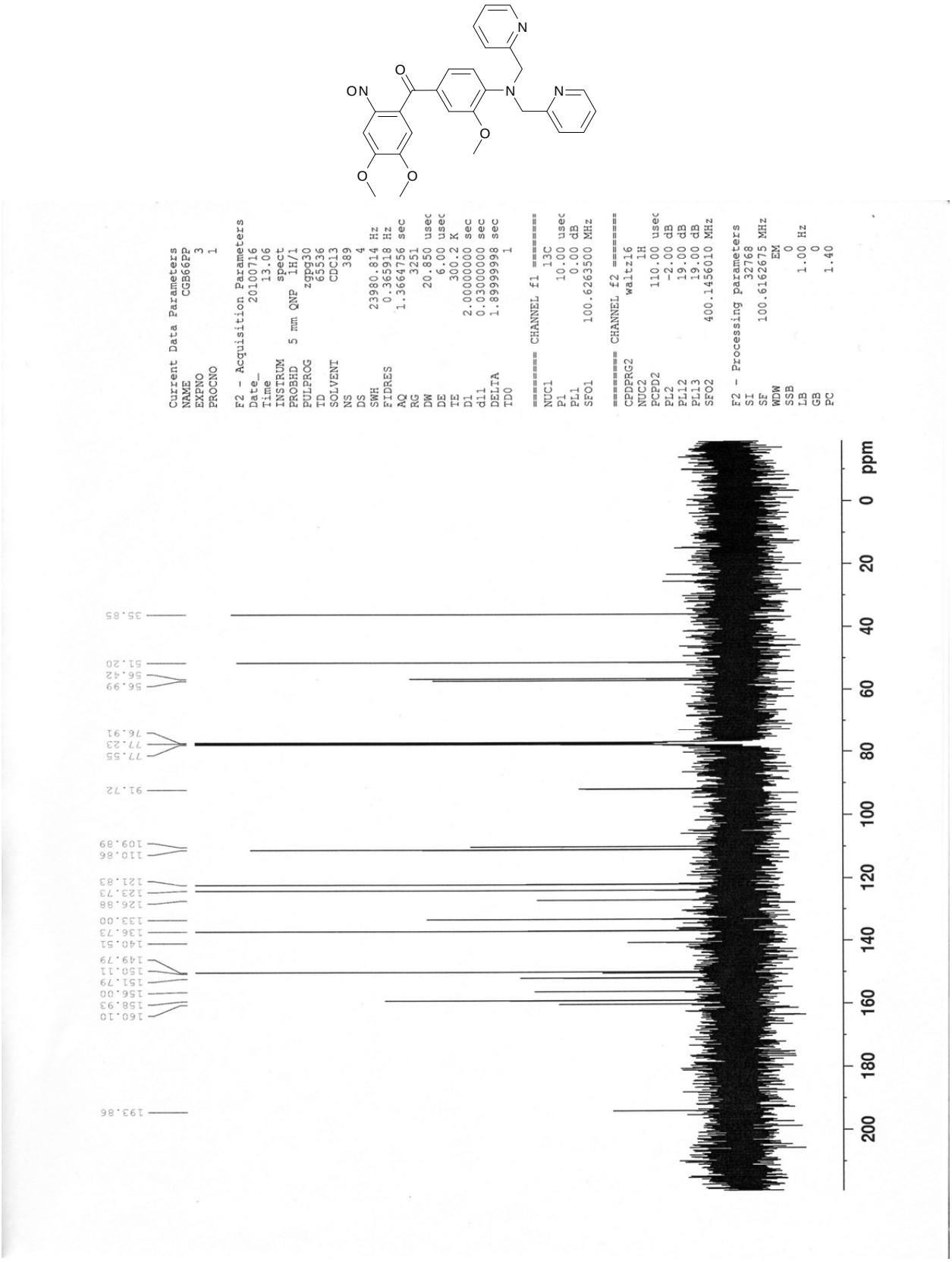


Figure S92 ^{13}C NMR of compound ZinUnc-4, **35**.