Supplementary Information for

Zinc-specific intramolecular excimer formation in TQEN derivatives: fluorescence and zinc binding property of TPEN-based hexadentate ligands

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Table S1 Crystallographic Data for *N,N*-1-isoBQBPEN (**1b**) and *N,N′*-1-isoBQBPEN·$4H_2O$ (**2b**·$4H_2O$)

	N,N-1-isoBQBPEN (**1b**)	*N,N′*-1-isoBQBPEN·$4H_2O$ (**2b**·$4H_2O$)
Formula	$C_{34}H_{32}N_6$	$C_{34}H_{40}N_6O_4$
FW	524.67	596.73
Crystal system	triclinic	monoclinic
Space group	*P*-1	$P2_1/a$
a, Å	10.183(6)	9.4162(8)
b, Å	11.355(7)	14.2496(9)
c, Å	13.428(7)	11.8720(12)
α, deg	107.863(10)	90
β, deg	92.769(9)	105.124(4)
γ, deg	102.293(7)	90
V, Å^3	1433(2)	1537.8(3)
Z	2	2
D_{calc}, g cm^{-3}	1.216	1.289
μ, mm^{-1}	0.0737	0.0862
$2\theta_{max}$, deg	62.8	55
temp, K	153	123
no. reflns collected	11895	11810
no. reflns used	6331	3501
no. of params	489	279
R_{int}	0.0302	0.0255
Final $R1$ ($I > 2\sigma(I)$)[a]	0.0552	0.0463
$wR2$ (all data)[b]	0.1424	0.1185
GOF	1.065	1.159

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S2 Crystallographic Data for [Zn(**1b**)]$(ClO_4)_2$·$2CH_3OH$ and [Zn(**2b**)]$(ClO_4)_2$·DMF

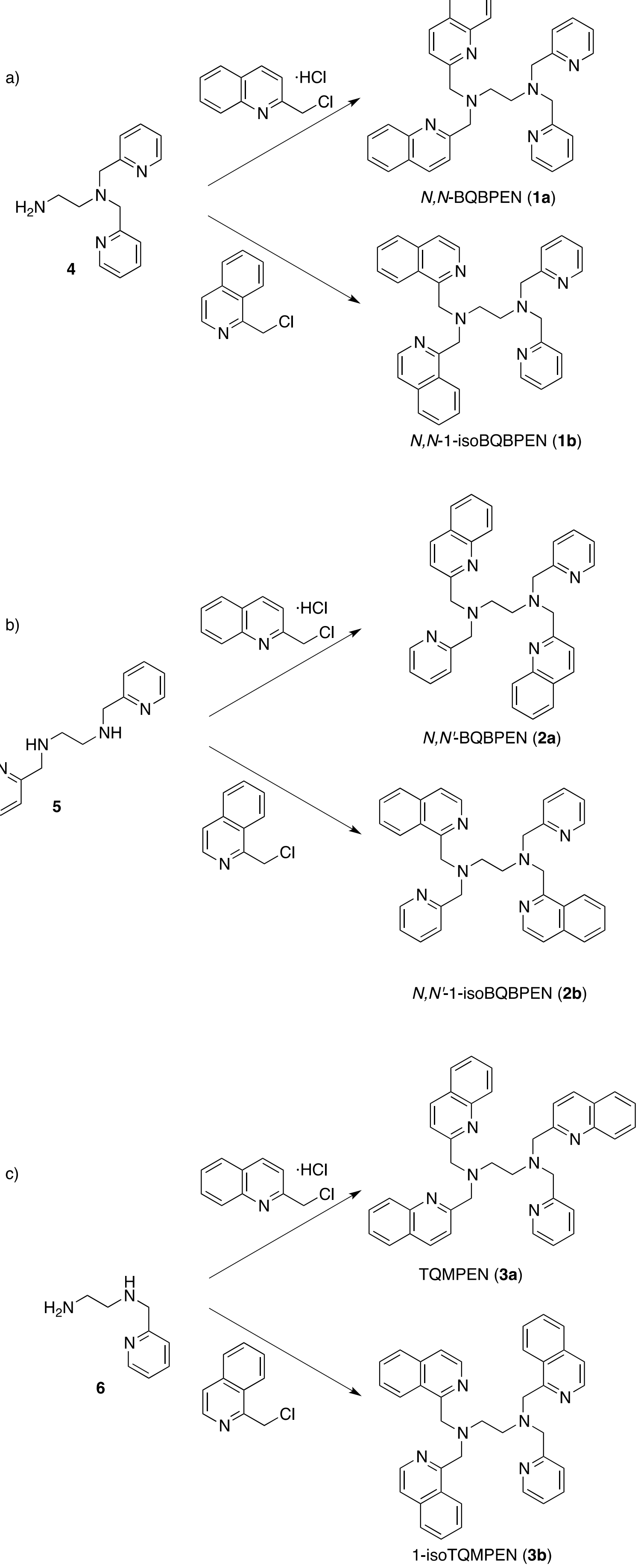
	[Zn(**1b**)]$(ClO_4)_2$· ·$2CH_3OH$	[Zn(**2b**)]$(ClO_4)_2$· ·DMF
Formula	$C_{36}H_{38}Cl_2N_6O_{10}Zn$	$C_{37}H_{39}Cl_2N_7O_9Zn$
FW	851.02	862.04
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a, Å	12.0540(9)	13.4515(13)
b, Å	14.3530(8)	18.682(2)
c, Å	21.7345(12)	14.935(2)
β, deg	92.903(4)	97.4707(11)
V, Å^3	3755.5(4)	3721.2(6)
Z	4	4
D_{calc}, g cm^{-3}	1.505	1.539
μ, mm^{-1}	0.8622	0.08701
$2\theta_{max}$, deg	55	55
temp, K	123	153
no. reflns collected	28756	28520
no. reflns used	8511	8509
no. of params	541	633
R_{int}	0.0210	0.0247
Final $R1$ ($I > 2\sigma(I)$)^a	0.0490	0.0667
$wR2$ (all data)^b	0.1377	0.2058
GOF	1.047	1.173

$^aR1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S3 Calculated Absorption Properties for $[Zn(\mathbf{1b})]^{2+}$ and $[Zn(\mathbf{2b})]^{2+}$

State	Wavelength (nm)	Oscillator Strength	Orbital Composition	CI (%)
		*[Zn(**1b**)]*^{2}		
S_1	290	0.050	HOMO-1 -> LUMO	43
			HOMO -> LUMO+1	2
S_2	285	0.084	HOMO -> LUMO+1	39
			HOMO-1 -> LUMO	2
S_3	261	0.0040	HOMO-3 -> LUMO	21
			HOMO-1 -> LUMO+4	15
		*[Zn(**2b**)]*$^{2+}$		
S_1	285	0.10	HOMO-1 -> LUMO+1	48
			HOMO -> LUMO	20
S_2	285	0.035	HOMO -> LUMO+1	22
			HOMO-1 -> LUMO	20
S_3	260	0.016	HOMO-3 -> LUMO+1	10
			HOMO-1 -> LUMO+6	10

Scheme S1


a)
·HCl
Cl
N
H₂N
4
N,N-BQBPEN (1a)
N,N-1-isoBQBPEN (1b)
b)
HN
NH
5
N,N'-BQBPEN (2a)
N,N'-1-isoBQBPEN (2b)
c)
6
TQMPEN (3a)
1-isoTQMPEN (3b)

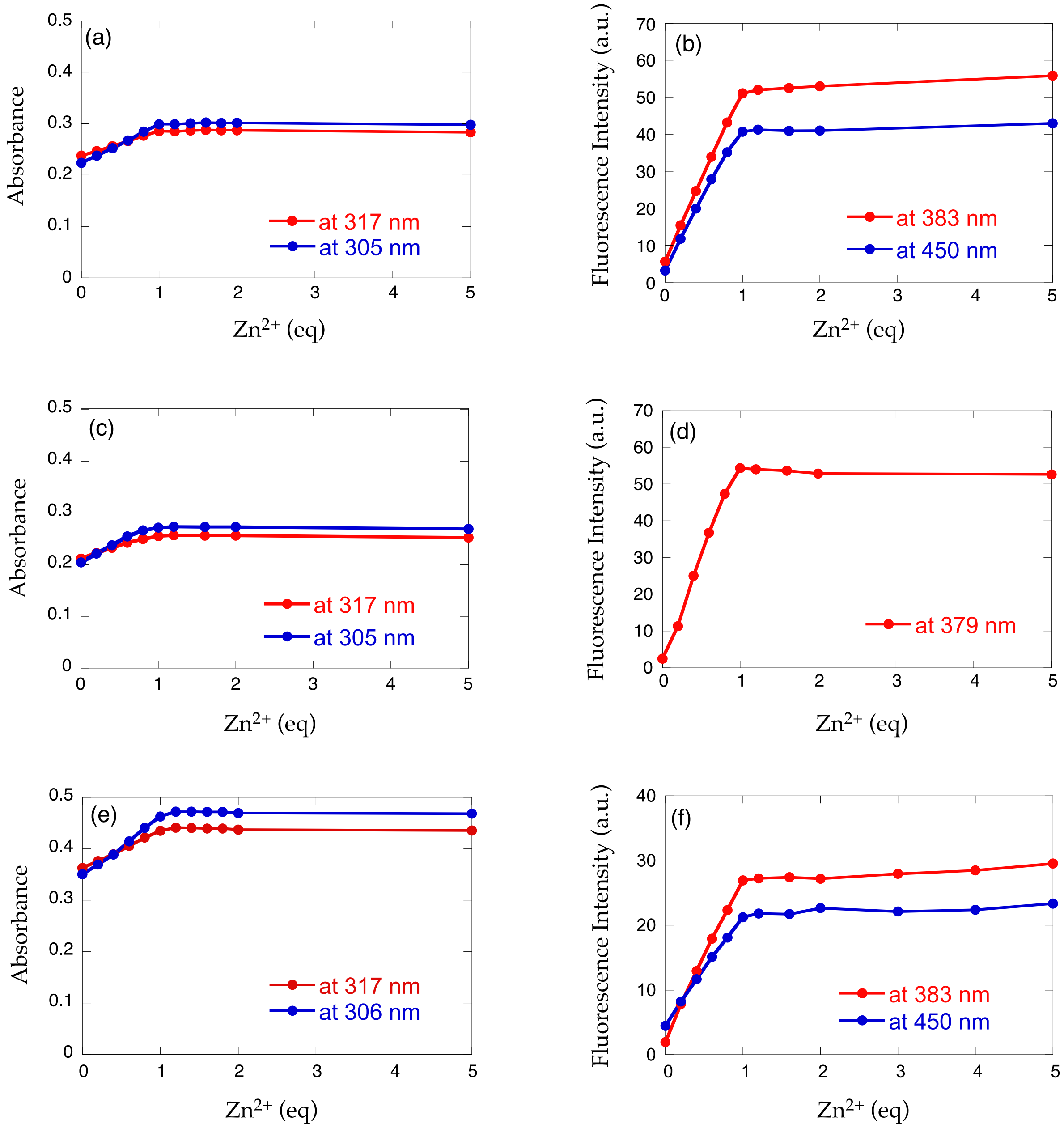


Fig. S1 Zinc titration profile for 34 μM *N*,*N*-BQBPEN (**1a**) (a, b), *N*,*N'*-BQBPEN (**2a**) (c, d) and TQMPEN (**3a**) (e, f) in DMF/H_2O (1:1) at 25 °C. (a, c, e) Absorbance changes. (b, d, f) Fluorescence intensity changes.

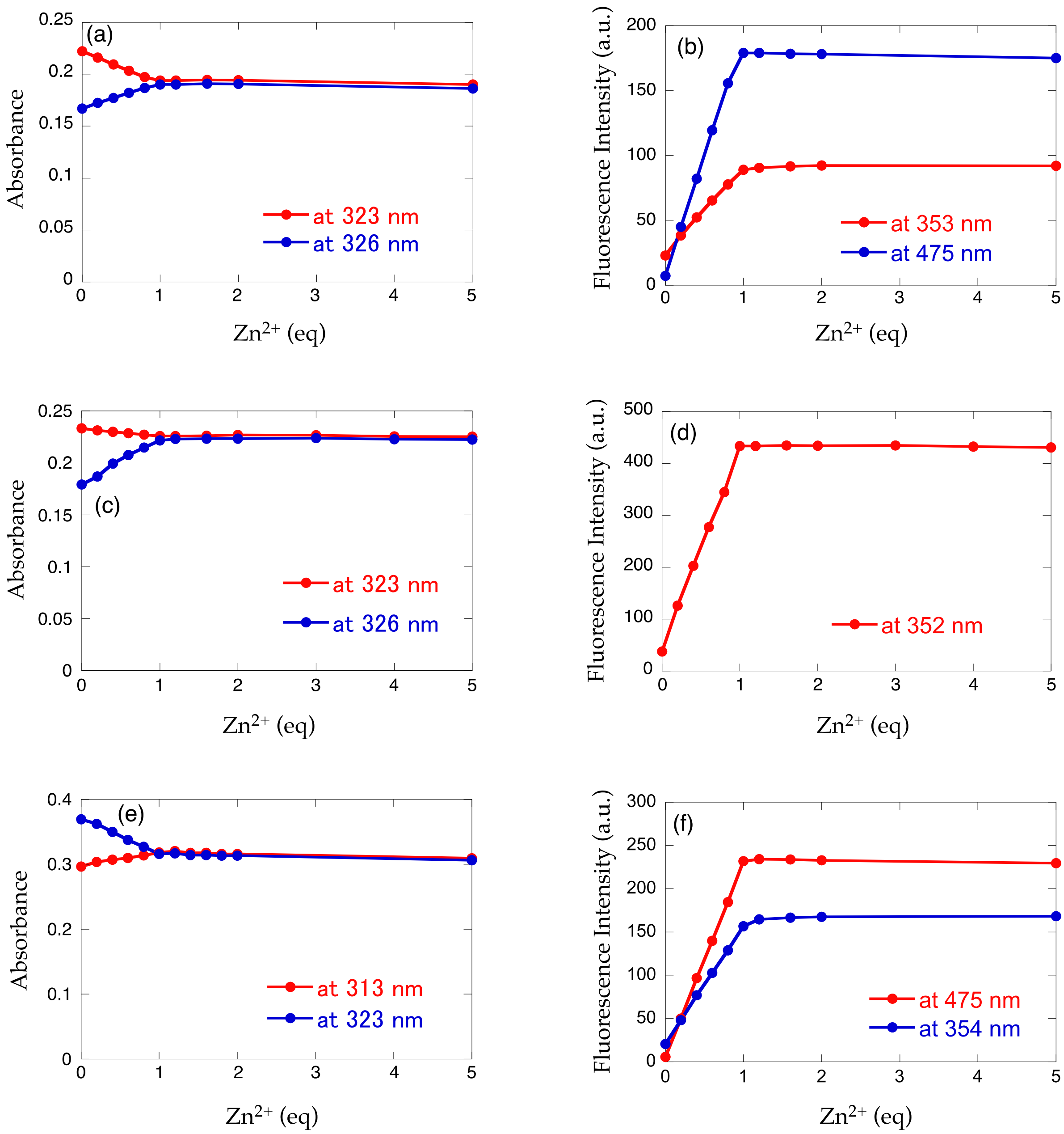


Fig. S2 Zinc titration profile for 34 μM *N,N*-1-isoBQBPEN (**1b**) (a, b), *N,N′*-1-isoBQBPEN (**2b**) (c, d) and 1-isoTQMPEN (**3b**) (e, f) in DMF/H_2O (1:1) at 25 °C. (a, c, e) Absorbance changes. (b, d, f) Fluorescence intensity changes.

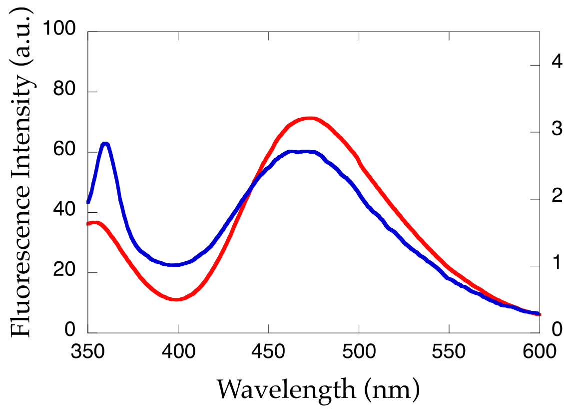


Fig. S3 Fluorescence spectra of zinc complex of *N*,*N*-1-isoBQBPEN (**1b**) at 34 μM (red, left Y axis) and 1 μM (blue, right Y axis) in DMF/H_2O (1:1) at 25 °C (λ_{ex} = 326 nm).

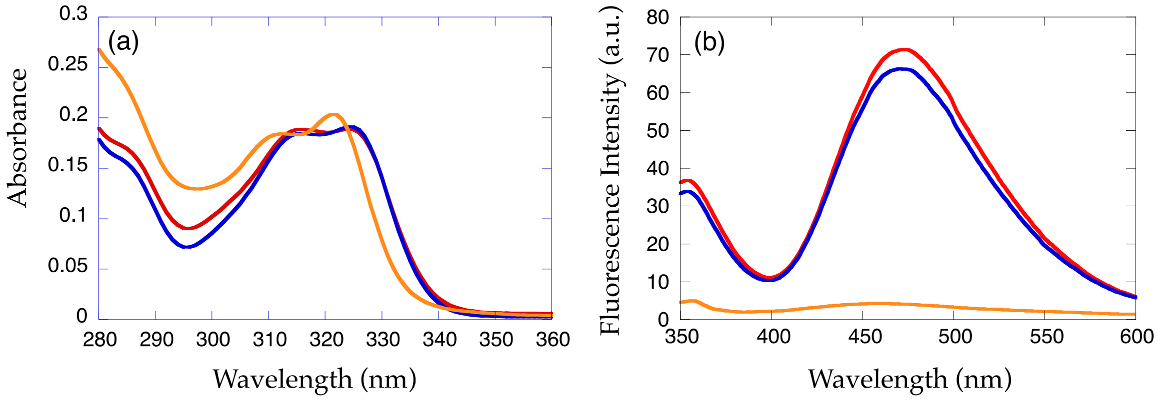
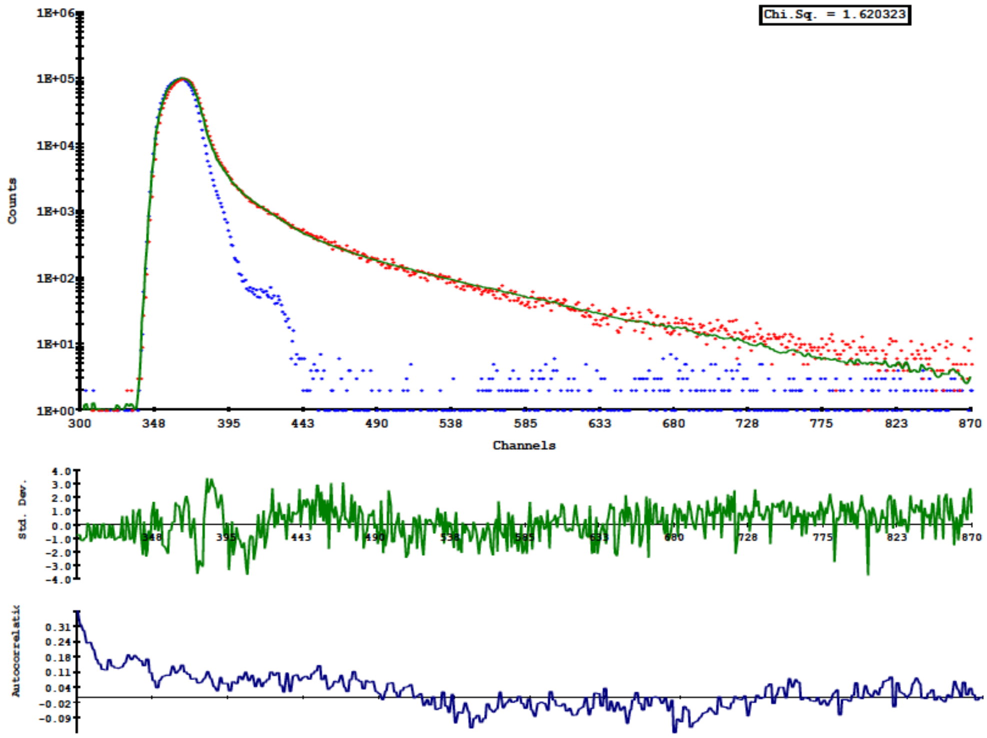


Fig. S4 Fluorescence spectra of 34 μM of zinc complex of *N*,*N*-1-isoBQBPEN (**1b**) in DMF/H_2O (1:1) (red), DMF/H_2O (4:1) (blue) and DMF (orange) at 25 °C (λ_{ex} = 326 nm).




```
Calculated using 3 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

 Shift Value = 0          ch;          0              sec
 Shift Limit = 30         ch;          1.677618E-09   sec

 T1 Estimate = 2.669495 ch;            1.492797E-10   sec
 T2 Estimate = 5.338989 ch;            2.985595E-10   sec
 T3 Estimate = 10.67798 ch;            5.97119E-10    sec

 A Free
 B1 Free
 B2 Free
 B3 Free

 Prompt and decay LO = 300     ch;     1.677618E-08   sec
 Prompt and decay HI = 900     ch;     5.032854E-08   sec

 Background on prompt = 0.4285714
 Time calibration = 5.59206E-11 sec/ch

The fitted parameters are:

 Hi reduced to: 870 ch

 SHIFT = 0.3566583     ch;   1.994455E-11  sec     S.Dev = 4.304355E-13   sec
 T1    = 2.029763      ch;   1.135055E-10  sec     S.Dev = 2.015821E-12   sec
 T2    = 18.38545      ch;   1.028126E-09  sec     S.Dev = 1.78468E-11    sec
 T3    = 77.43118      ch;   4.329998E-09  sec     S.Dev = 5.101761E-11   sec
 A     = 0.7804149                                 S.Dev = 0.1262916
 B1    = 0.6164292     [ 90.67 Rel.Ampl][ 0.99 Alpha] S.Dev = 5.023048E-04
 B2    = 5.283901E-03  [ 7.04 Rel.Ampl][ 0.01 Alpha] S.Dev = 3.017124E-05
 B3    = 4.082497E-04  [ 2.29 Rel.Ampl][ 0.00 Alpha] S.Dev = 2.869185E-06
 Average Life Time = 1.240407E-10  sec
 CHISQ = 1.620323              [ 563 degrees of freedom ]
  Chi-squared Probability = 5.8224E-17 percent
  Durbin-Watson Parameter =    1.248984
  Negative residuals      =    41.50613 percent
  Residuals < 1 s.dev     =    54.11559 percent
  Residuals < 2 s.dev     =    88.61646 percent
  Residuals < 3 s.dev     =    98.24869 percent
  Residuals < 4 s.dev     =         100 percent
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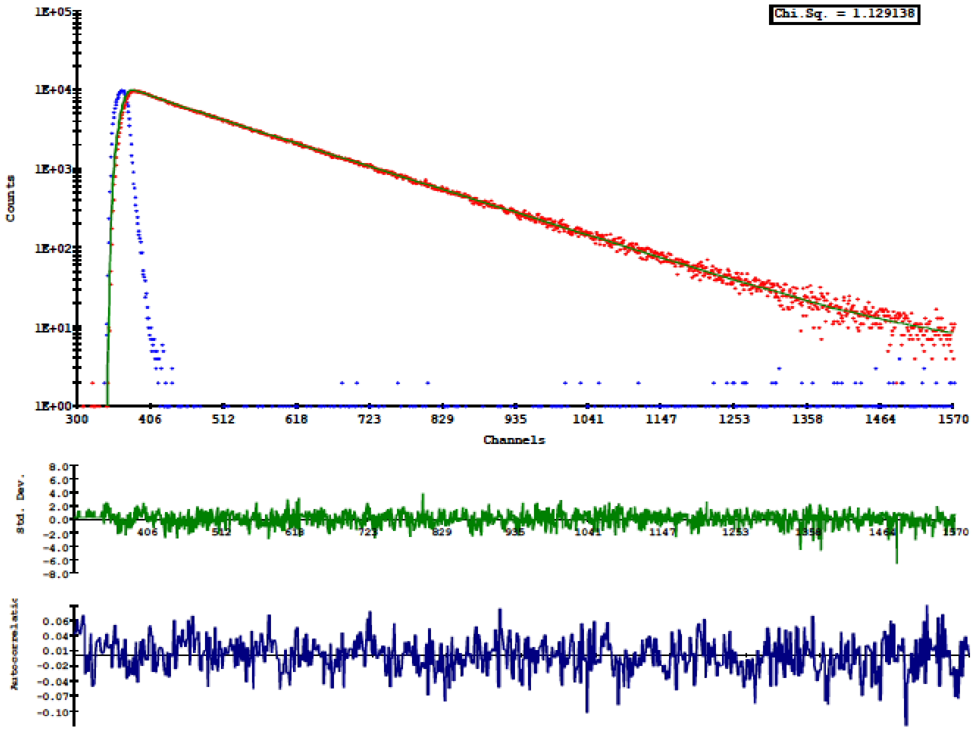
Fig. S5 Fluorescence lifetime measurement for 34 μM **1b** in DMF/H_2O (1:1) at 353 nm (λ_{ex} = 333 nm, 25 °C).




```
Calculated using 2 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

 Shift Value = 0          ch;          0              sec
 Shift Limit = 30         ch;          1.677618E-09   sec

 T1 Estimate = 75.99924 ch;            4.249923E-09   sec
 T2 Estimate = 303.9969 ch;            1.699969E-08   sec

 A Free
 B1 Free
 B2 Free

 Prompt and decay LO = 300    ch;      1.677618E-08   sec
 Prompt and decay HI = 1600   ch;      8.947296E-08   sec

 Background on prompt = 5.128205E-02
 Time calibration = 5.59206E-11 sec/ch

The fitted parameters are:

 Hi reduced to: 1570 ch

 SHIFT = 2.208822       ch;   1.235187E-10  sec     S.Dev = 1.832464E-12   sec
 T1    = 54.03464       ch;   3.02165E-09   sec     S.Dev = 2.191955E-10   sec
 T2    = 158.0185       ch;   8.836488E-09  sec     S.Dev = 1.27492E-11    sec
 A     = -0.2151939                                 S.Dev = 0.1206584
 B1    = 5.085289E-03  [ 3.37 Rel.Ampl][ 0.09 Alpha] S.Dev = 1.363726E-04
 B2    = 4.991136E-02  [ 96.63 Rel.Ampl][ 0.91 Alpha] S.Dev = 6.062928E-05
 Average Life Time = 8.298816E-09  sec
 CHISQ = 1.129138             [ 1265 degrees of freedom ]

 Chi-squared Probability = 8.7523E-02 percent
 Durbin-Watson Parameter =    1.921839
 Negative residuals      =    44.92525 percent
 Residuals < 1 s.dev     =     65.6963 percent
 Residuals < 2 s.dev     =    94.80724 percent
 Residuals < 3 s.dev     =    99.21322 percent
 Residuals < 4 s.dev     =    99.76396 percent
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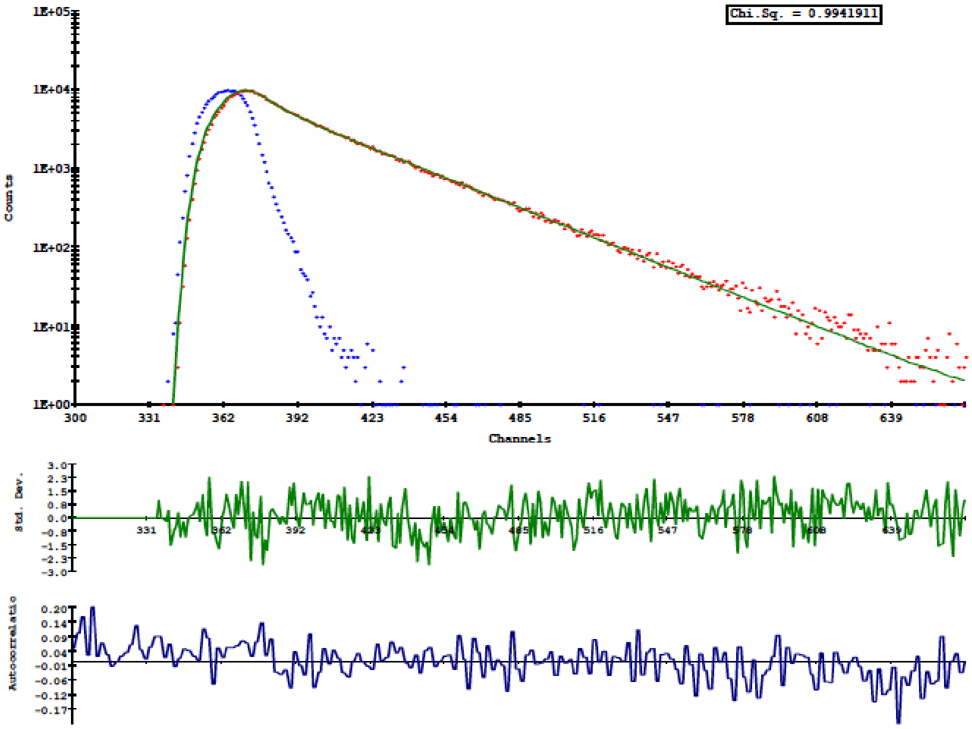
Fig. S6 Fluorescence lifetime measurement for 34 μM **1b** in DMF/H_2O (1:1) at 475 nm (λ_{ex} = 333 nm, 25 °C).




```
Calculated using 2 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

 Shift Value = 0         ch;          0              sec
 Shift Limit = 30        ch;          1.677618E-09   sec

 T1 Estimate = 14.5312   ch;          8.125937E-10   sec
 T2 Estimate = 58.12482  ch;          3.250375E-09   sec

 A Free
 B1 Free
 B2 Free

 Prompt and decay LO = 300     ch;    1.677618E-08   sec
 Prompt and decay HI = 700     ch;    3.914442E-08   sec

 Background on prompt = 5.128205E-02
 Time calibration = 5.59206E-11 sec/ch

The fitted parameters are:

 Hi reduced to: 670 ch

 SHIFT = 0.5384116      ch;    3.01083E-11   sec     S.Dev = 1.753064E-12   sec
 T1    = 6.26983        ch;    3.506127E-10  sec     S.Dev = 1.373984E-11   sec
 T2    = 35.30278       ch;    1.974152E-09  sec     S.Dev = 5.103789E-12   sec
 A     = 1.458923E-02                                S.Dev = 0.1260993
 B1    = 7.432063E-02  [ 21.75 Rel.Ampl][ 0.61 Alpha] S.Dev = 5.150422E-04
 B2    = 4.747551E-02  [ 78.25 Rel.Ampl][ 0.39 Alpha] S.Dev = 1.105757E-04
 Average Life Time = 9.834602E-10  sec
 CHISQ = 0.9941911             [ 365 degrees of freedom ]

 Chi-squared Probability =    52.14775 percent
 Durbin-Watson Parameter =    1.897539
 Negative residuals      =    49.86523 percent
 Residuals < 1 s.dev     =    66.57682 percent
 Residuals < 2 s.dev     =    95.68733 percent
 Residuals < 3 s.dev     =         100 percent
 Residuals < 4 s.dev     =         100 percent
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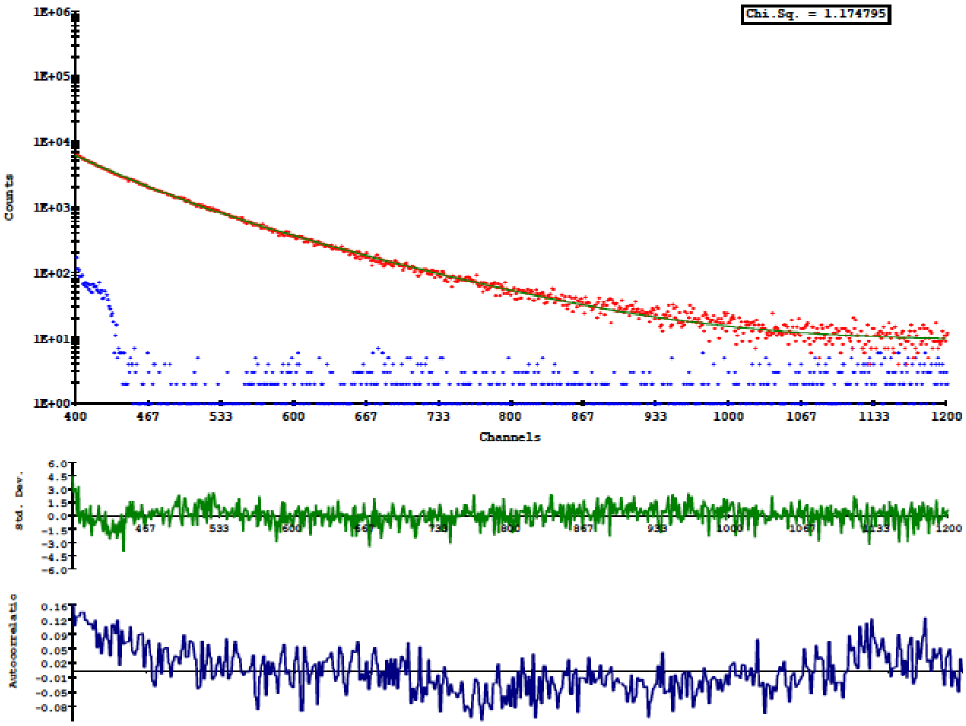
Fig. S7 Fluorescence lifetime measurement for 34 μM **2b** in DMF/H_2O (1:1) at 352 nm (λ_{ex} = 333 nm, 25 °C).




```
Calculated using 2 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

 Shift Value = Fixed @ 0        ch;          0               sec

 T1 Estimate = 37.2776  ch;          2.084586E-09    sec
 T2 Estimate = 149.1104 ch;          8.338344E-09    sec

 A Free
 B1 Free
 B2 Free

 Prompt and decay LO = 400    ch;   2.236824E-08    sec
 Prompt and decay HI = 1200   ch;   6.710472E-08    sec

 Background on prompt = 176
 Time calibration = 5.59206E-11 sec/ch

The fitted parameters are:

 SHIFT = 0 ch

 T1     = 44.8611       ch;   2.50866E-09    sec     S.Dev = 6.1016E-11    sec
 T2     = 101.9488      ch;   5.70104E-09    sec     S.Dev = 3.90837E-11   sec
 A      = 8.71542                                    S.Dev = 0.1989453
 B1     = 3969.181      [ 44.10 Rel.Ampl][ 0.64 Alpha] S.Dev = 21.71085
 B2     = 2214.35       [ 55.90 Rel.Ampl][ 0.36 Alpha] S.Dev = 10.27692
 Average Life Time = 3.651865E-09   sec
 CHISQ = 1.174795             [ 796 degrees of freedom ]

 Chi-squared Probability = 4.5179E-02 percent
 Durbin-Watson Parameter =    1.661178
 Negative residuals      =    42.94632 percent
 Residuals < 1 s.dev     =    67.54057 percent
 Residuals < 2 s.dev     =    93.13358 percent
 Residuals < 3 s.dev     =    99.00125 percent
 Residuals < 4 s.dev     =    99.75031 percent
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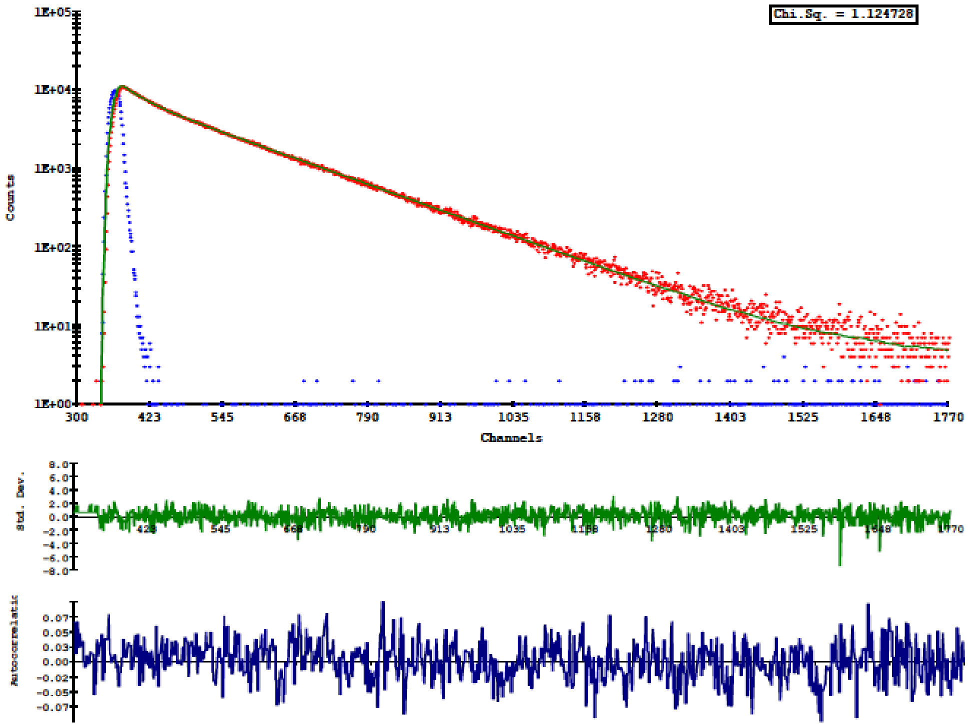
Fig. S8 Fluorescence lifetime measurement for 34 μM 1-isoTQEN in DMF/H_2O (1:1) at 357 nm (λ_{ex} = 333 nm, 25 °C).




```
Calculated using 2 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

 Shift Value = 0         ch;          0              sec
 Shift Limit = 30        ch;          1.677618E-09   sec

 T1 Estimate = 71.70784 ch;           4.009946E-09   sec
 T2 Estimate = 286.8314 ch;           1.603978E-08   sec

 A Free
 B1 Free
 B2 Free

 Prompt and decay LO = 300    ch;     1.677618E-08   sec
 Prompt and decay HI = 1800   ch;     1.006571E-07   sec

 Background on prompt = 5.128205E-02
 Time calibration = 5.59206E-11 sec/ch

The fitted parameters are:

 Hi reduced to: 1770 ch

 SHIFT = 0.4110158      ch;   2.298425E-11  sec     S.Dev = 1.634583E-12   sec
 T1    = 34.27012       ch;   1.916406E-09  sec     S.Dev = 3.202362E-11   sec
 T2    = 161.4141       ch;   9.026375E-09  sec     S.Dev = 1.159869E-11   sec
 A     = -0.5997773                                 S.Dev = 9.739386E-02
 B1    = 2.499236E-02  [ 11.08 Rel.Ampl][ 0.37 Alpha] S.Dev = 1.542642E-04
 B2    = 4.256321E-02  [ 88.92 Rel.Ampl][ 0.63 Alpha] S.Dev = 4.682044E-05
 Average Life Time = 6.396023E-09  sec
 CHISQ = 1.124728              [ 1465 degrees of freedom ]

 Chi-squared Probability = 5.6506E-02 percent
 Durbin-Watson Parameter =   1.872047
 Negative residuals      =   43.64378 percent
 Residuals < 1 s.dev     =   67.43712 percent
 Residuals < 2 s.dev       =    94.2896 percent
 Residuals < 3 s.dev       =   99.52413 percent
 Residuals < 4 s.dev       =   99.86404 percent
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Fig. S9 Fluorescence lifetime measurement for 34 μM 1-isoTQEN in DMF/H_2O (1:1) at 477 nm (λ_{ex} = 333 nm, 25 °C).

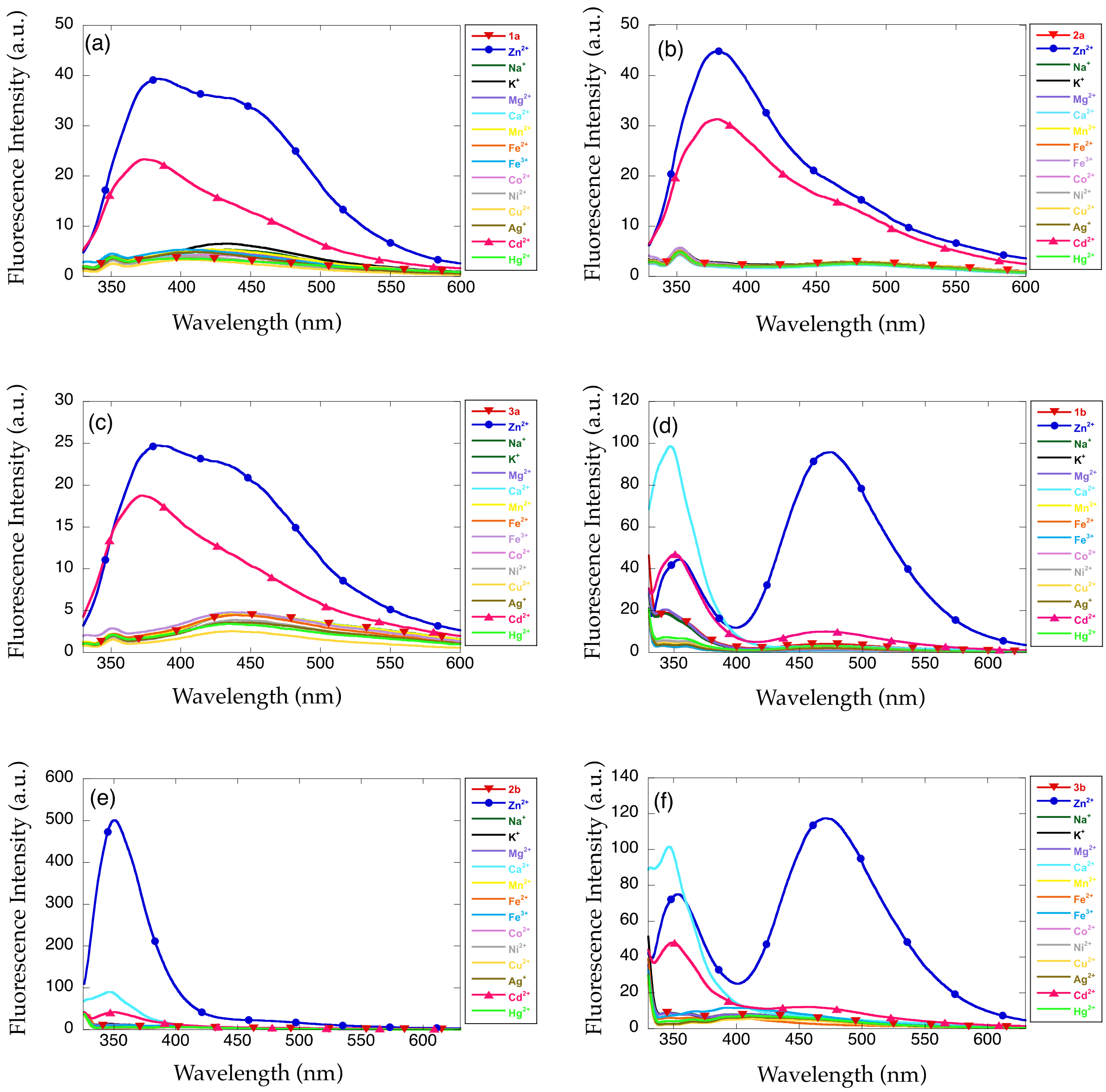

Fig. S10 Comparison of fluorescence spectra of 34 μM **1-3a** and **1-3b** in DMF/H_2O (1:1) at 25 °C in the presence of 1 equivalent of various metal ions.

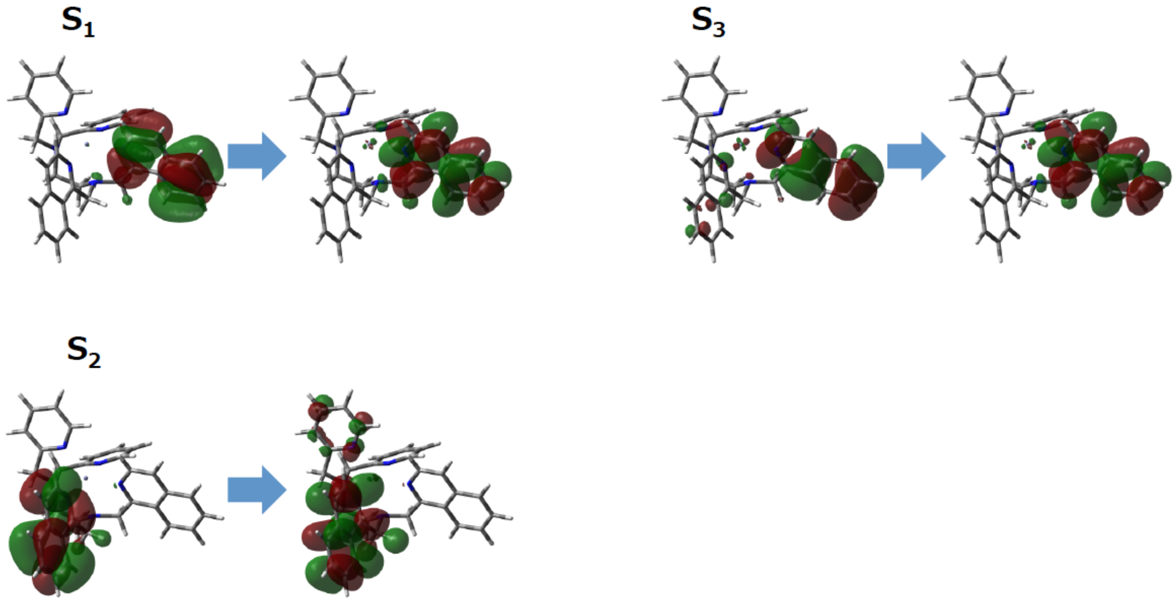

Fig. S11 Schematic representation of molecular orbitals for absorption of [Zn(**1b**)]$^{2+}$.

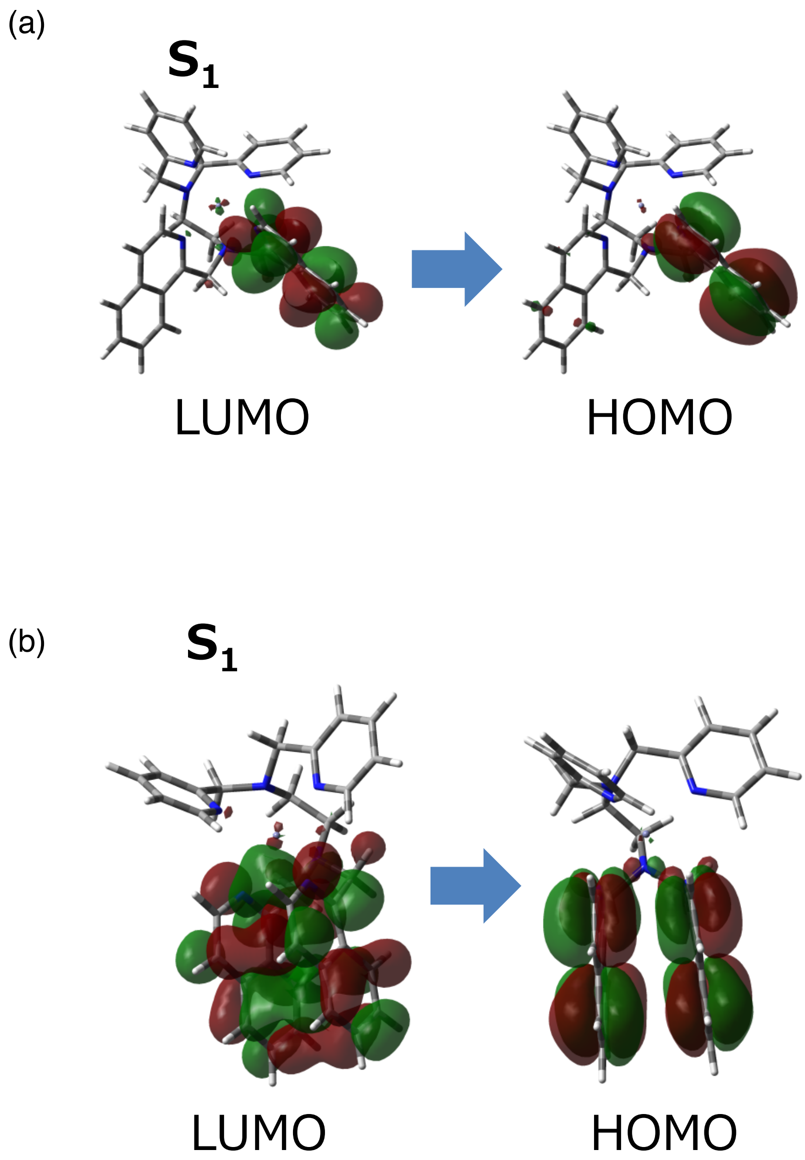

Fig. S12 Schematic representation of molecular orbitals for emission of [Zn(**1b**)]$^{2+}$ with (a) Franck Condon and (b) excimer conformation.

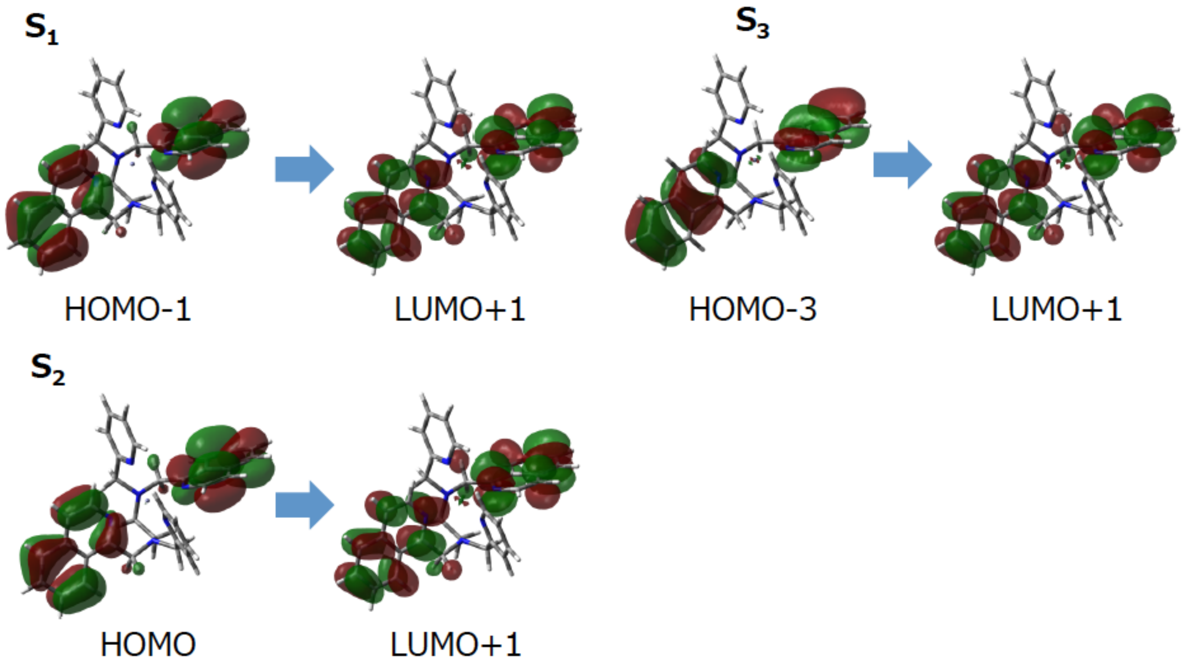

Fig. S13 Schematic representation of molecular orbitals for absorption of [Zn(**2b**)]$^{2+}$.

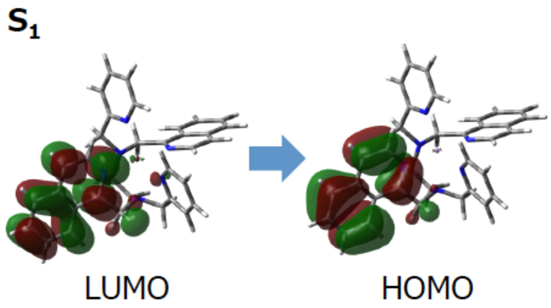

Fig. S14 Schematic representation of molecular orbitals for emission of [Zn(**2b**)]$^{2+}$.

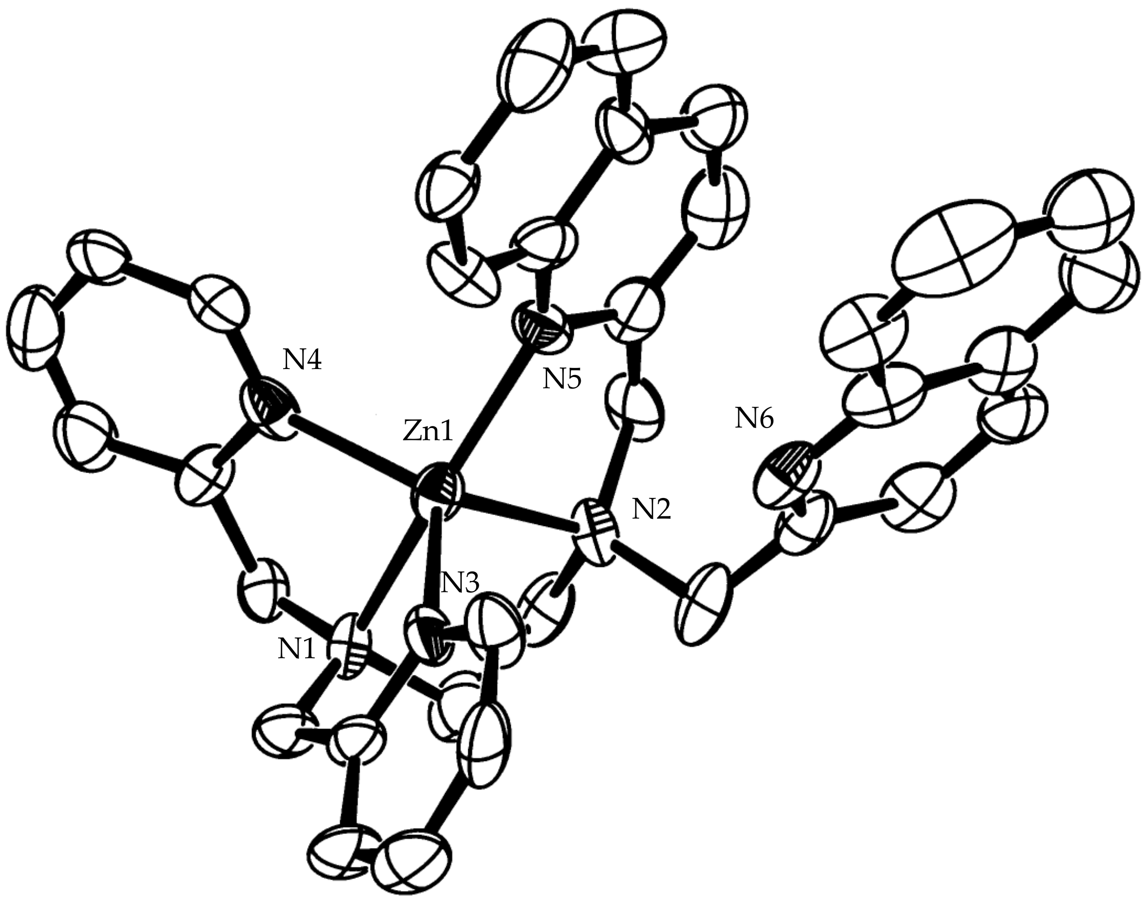

Fig. S15 Preliminary X-ray analysis of [Zn(**1a**)](ClO_4)$_2$ in 50% probability. One of the crystallographically independent molecules, hydrogen atoms and counter anions were omitted for clarity. Crystal data for $C_{34}H_{32}Cl_2N_6O_8Zn$: monoclinic, space group $P2_1/c$, a = 12.450(11) Å, b = 13.933(13) Å, c = 38.54(3) Å, β = 92.234(10) °, V = 6681(10) Å^3, Z = 8, $R1$ = 0.250, $wR2$ = 0.598, GOF = 1.937.

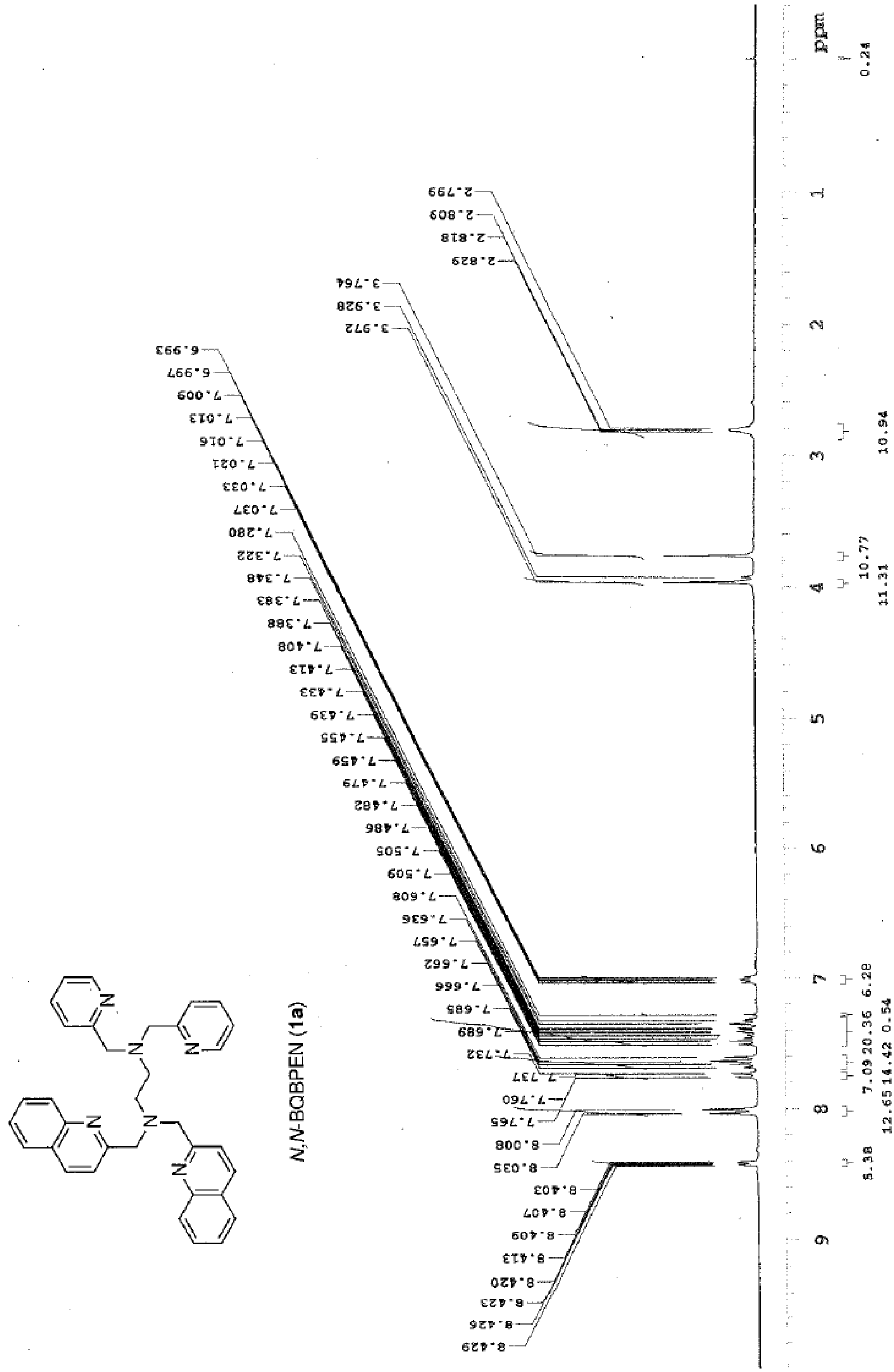

Fig. S16 ^{1}H NMR spectrum of *N,N*-BQBPEN (**1a**) in $CDCl_3$.

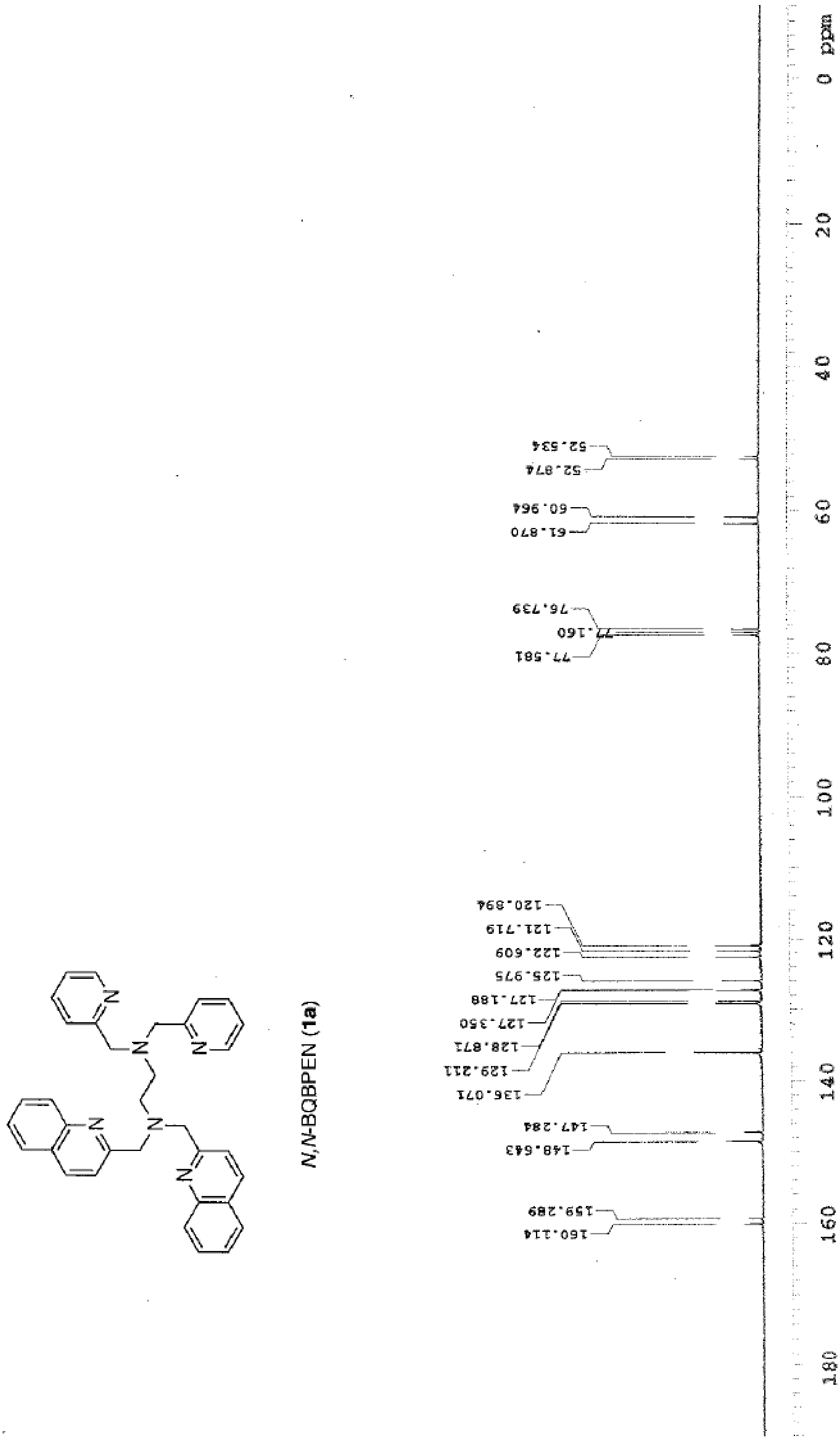

Fig. S17 ^{13}C NMR spectrum of *N,N*-BQBPEN (**1a**) in $CDCl_3$.

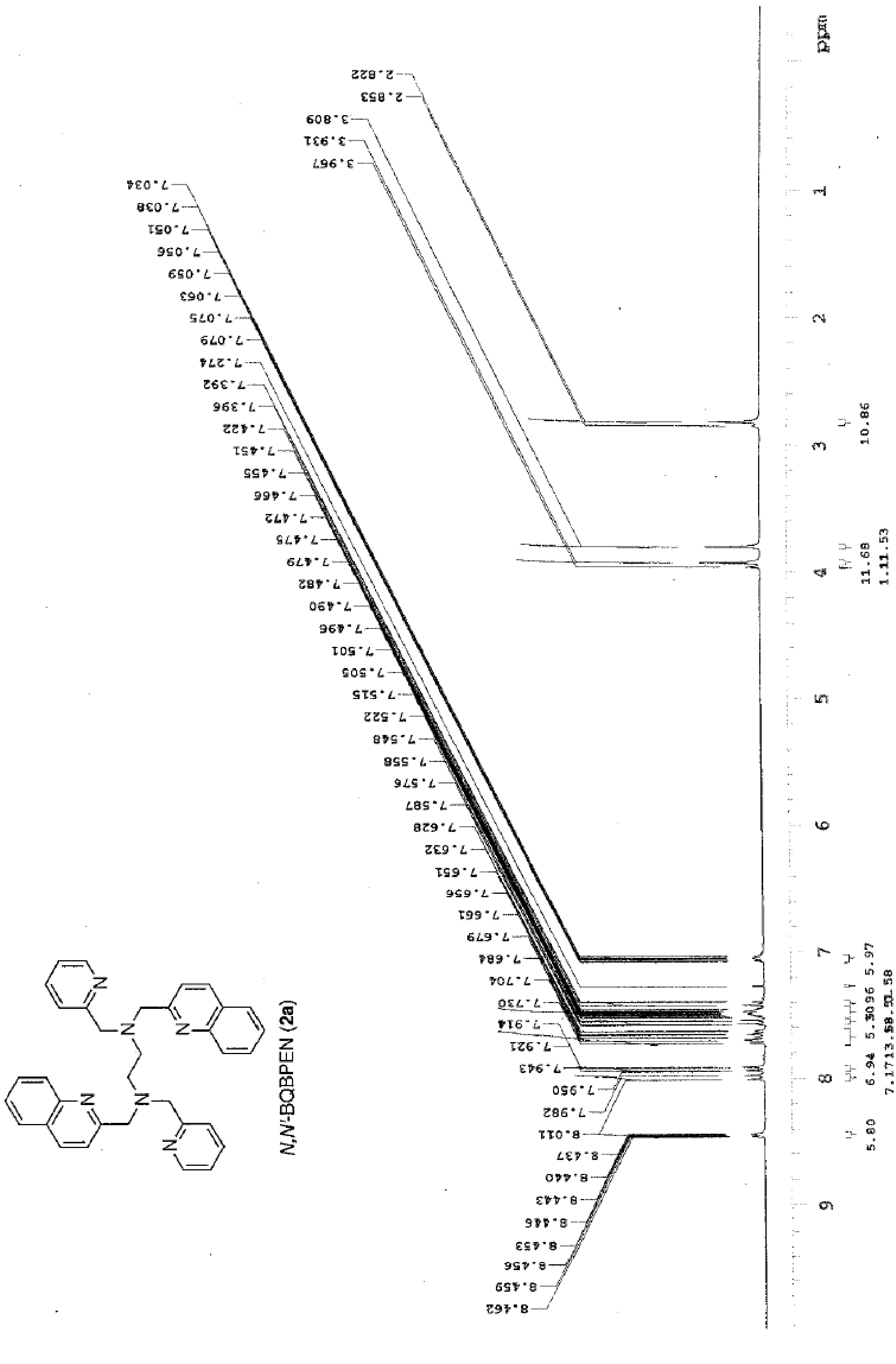

Fig. S18 ^{1}H NMR spectrum of *N,N′*-BQBPEN (**2a**) in $CDCl_3$.

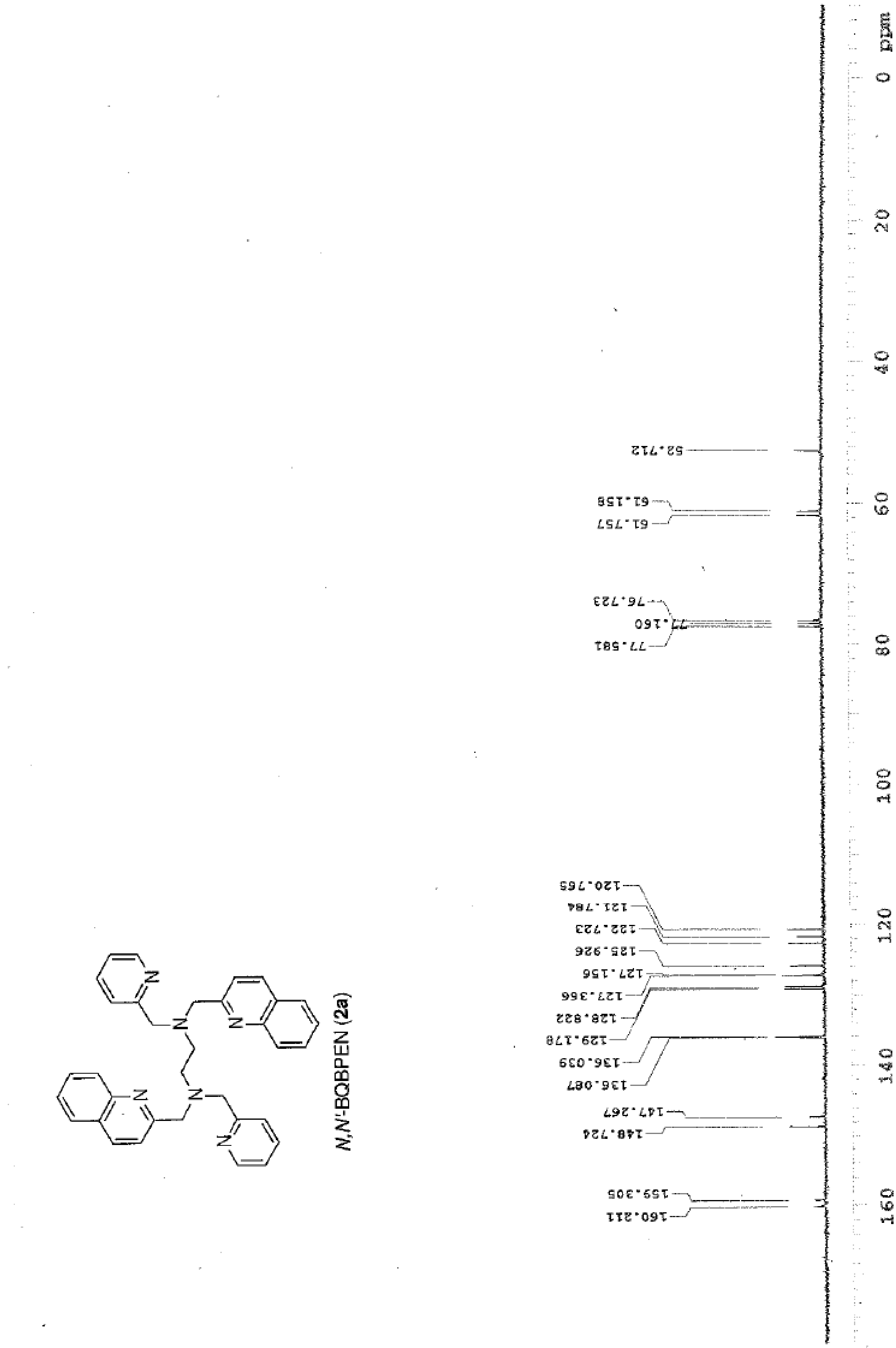

Fig. S19 ^{13}C NMR spectrum of *N,N′*-BQBPEN (**2a**) in $CDCl_3$.

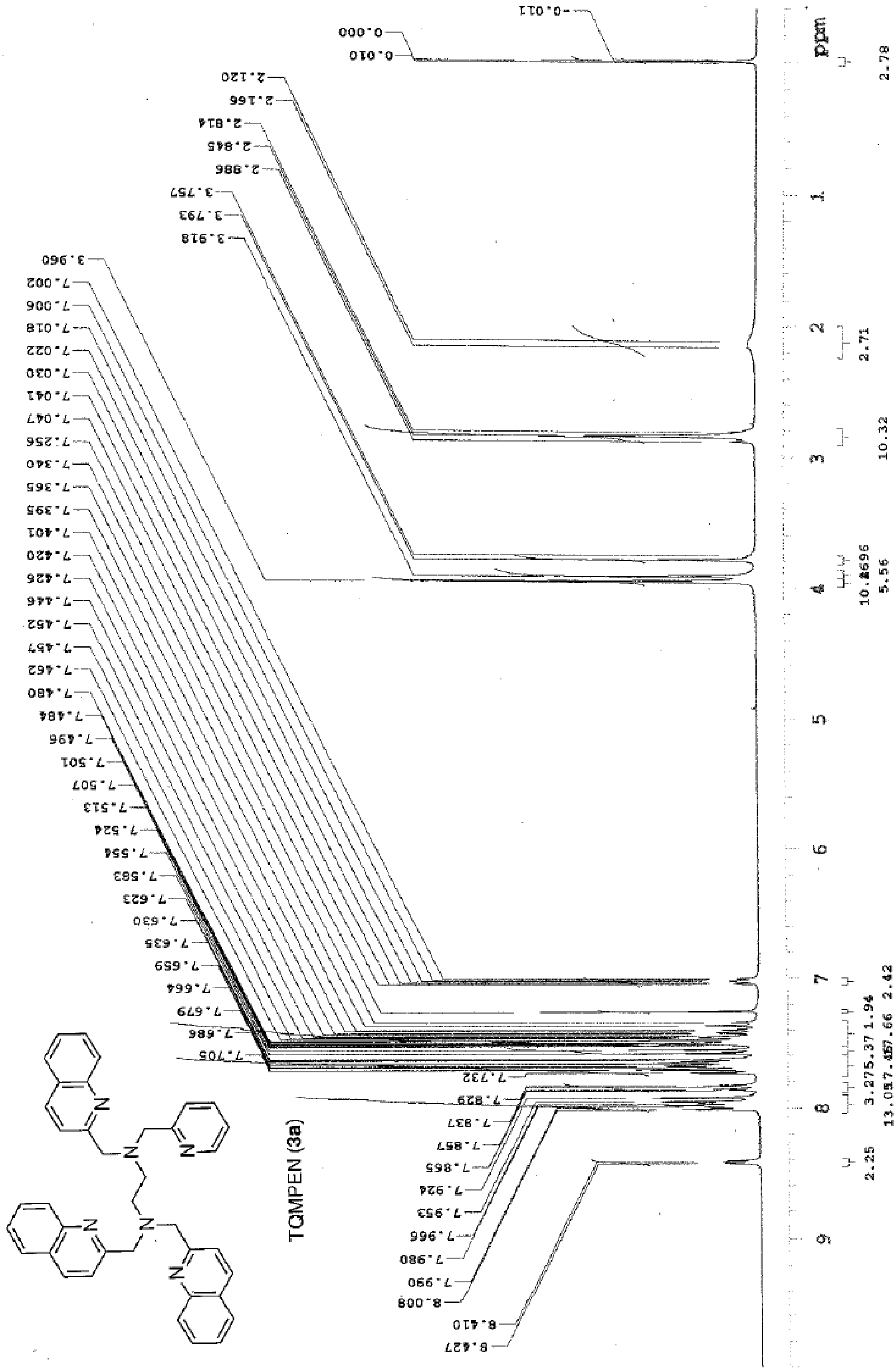

Fig. S20 ^{1}H NMR spectrum of TQMPEN (**3a**) in $CDCl_3$.

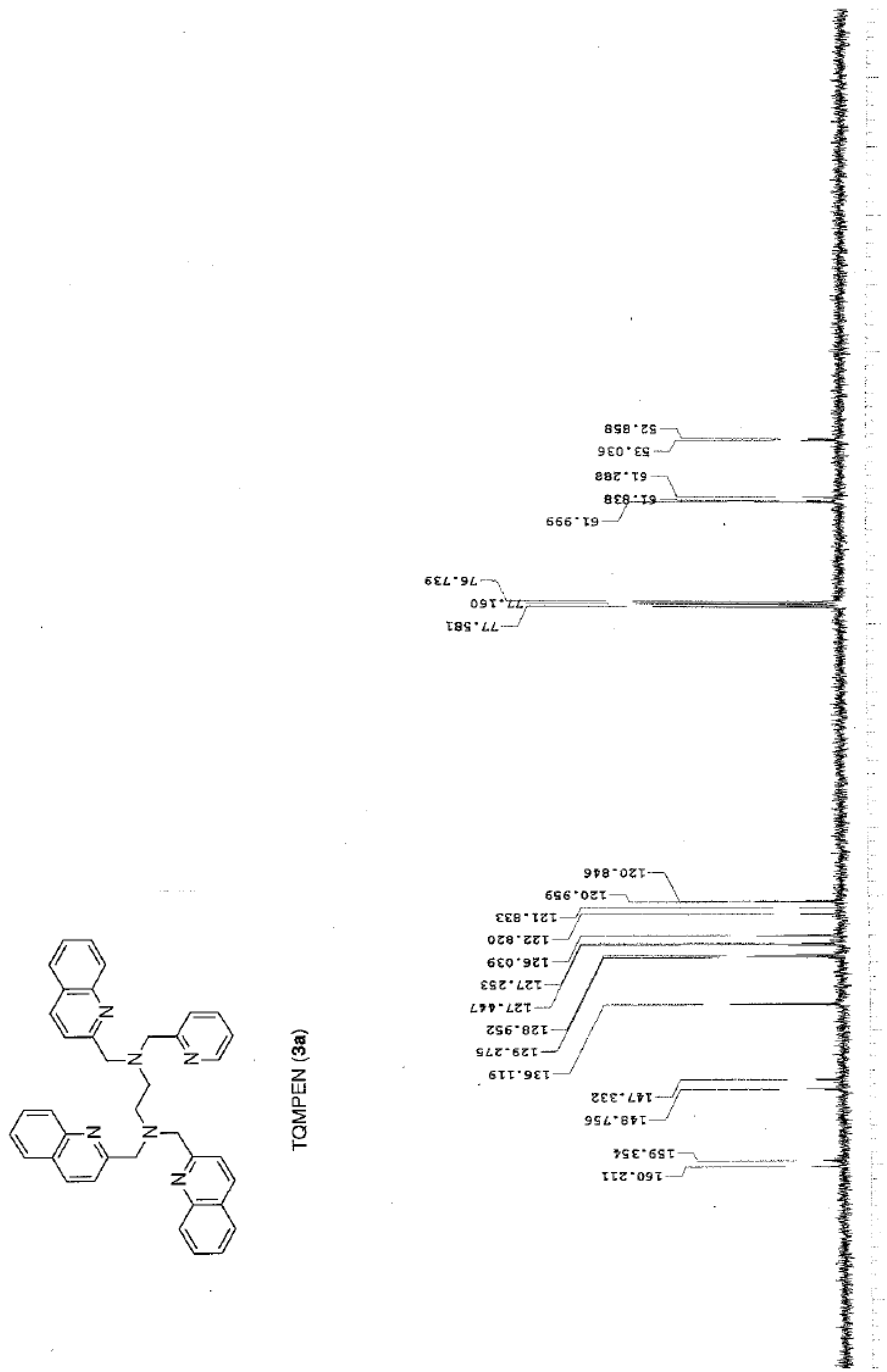

Fig. S21 ^{13}C NMR spectrum of TQMPEN (**3a**) in $CDCl_3$.

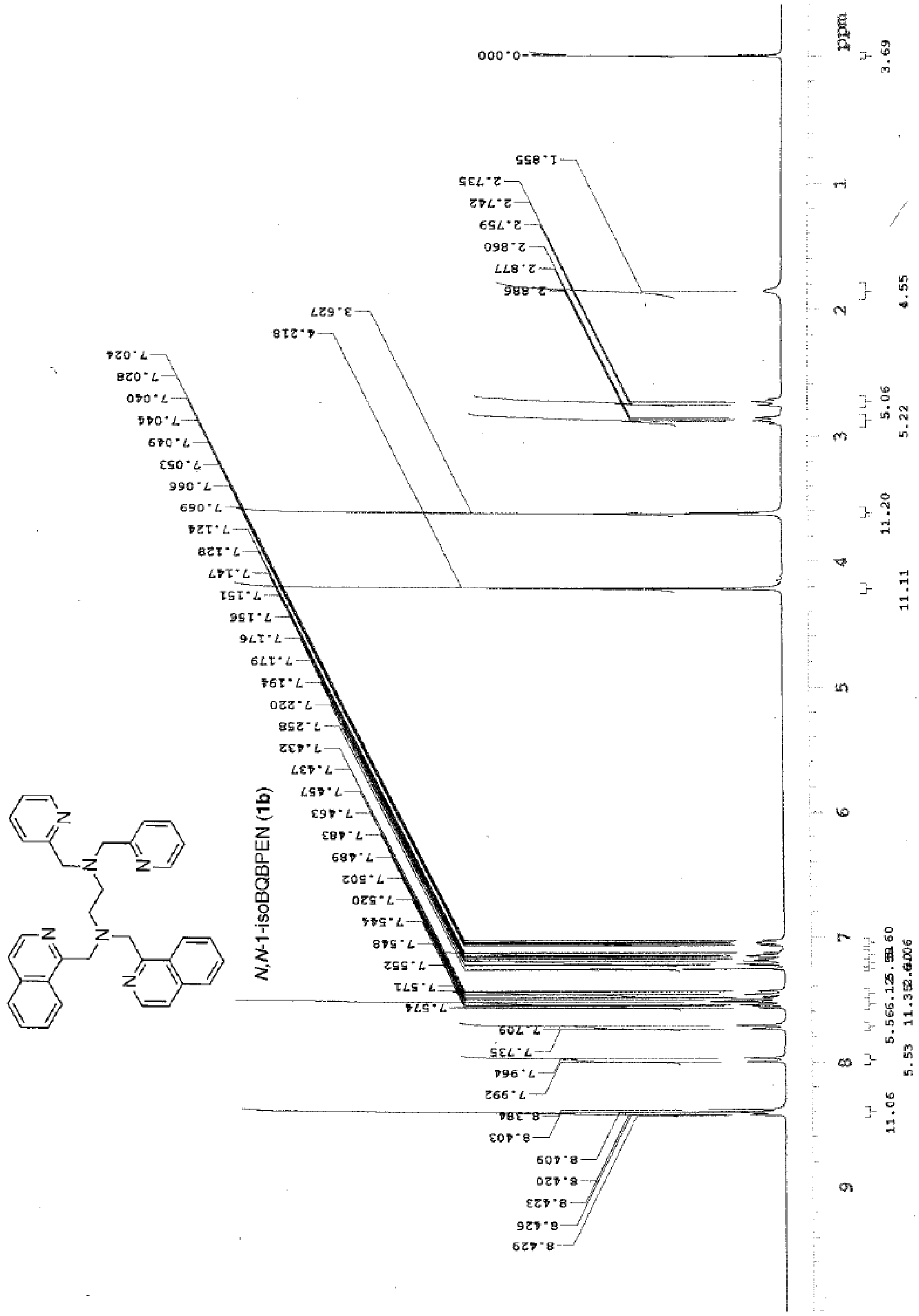

Fig. S22 [1]H NMR spectrum of *N,N*-1-isoBQBPEN (**1b**) in $CDCl_3$.

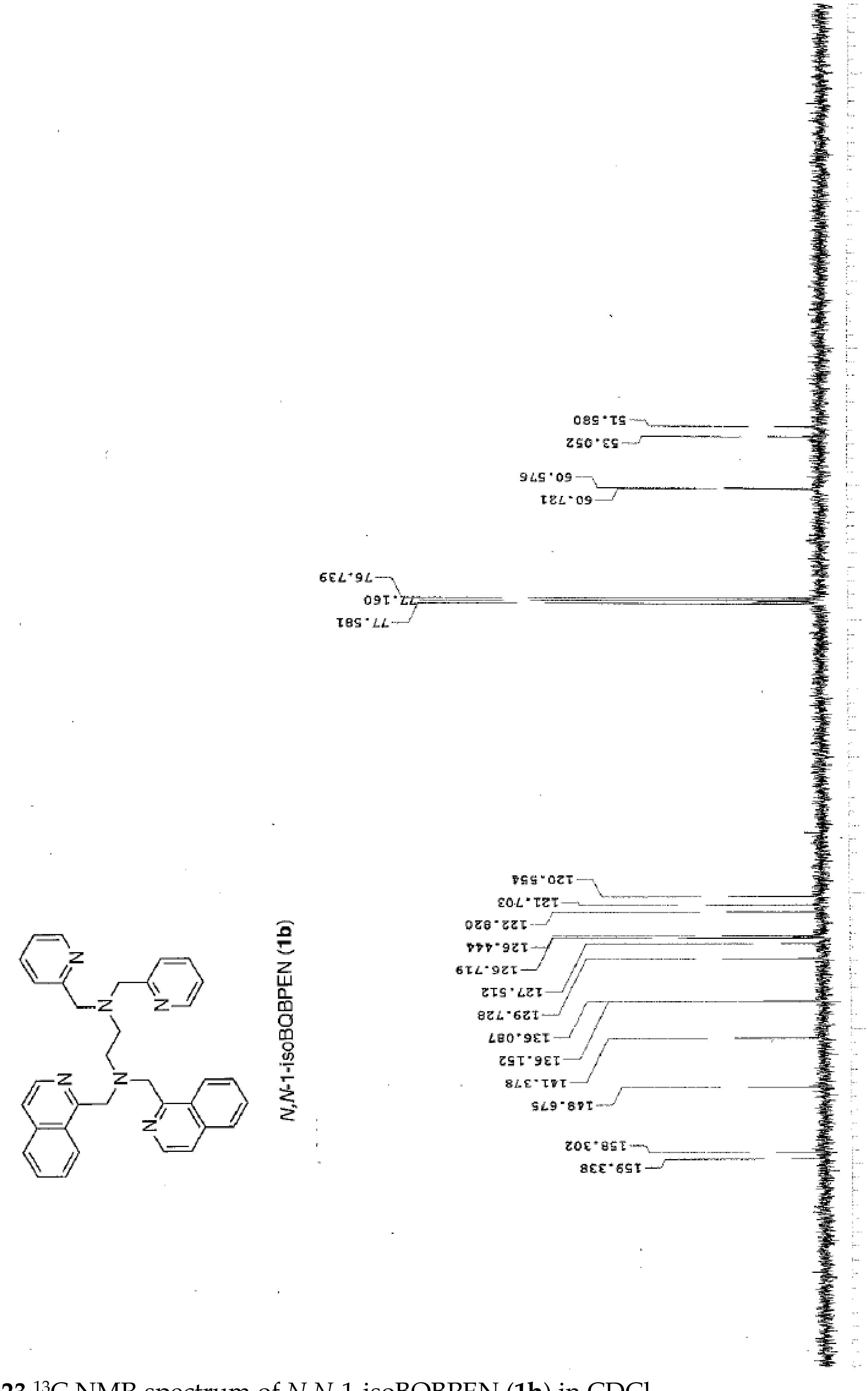

Fig. S23 ^{13}C NMR spectrum of *N,N*-1-isoBQBPEN (**1b**) in $CDCl_3$.

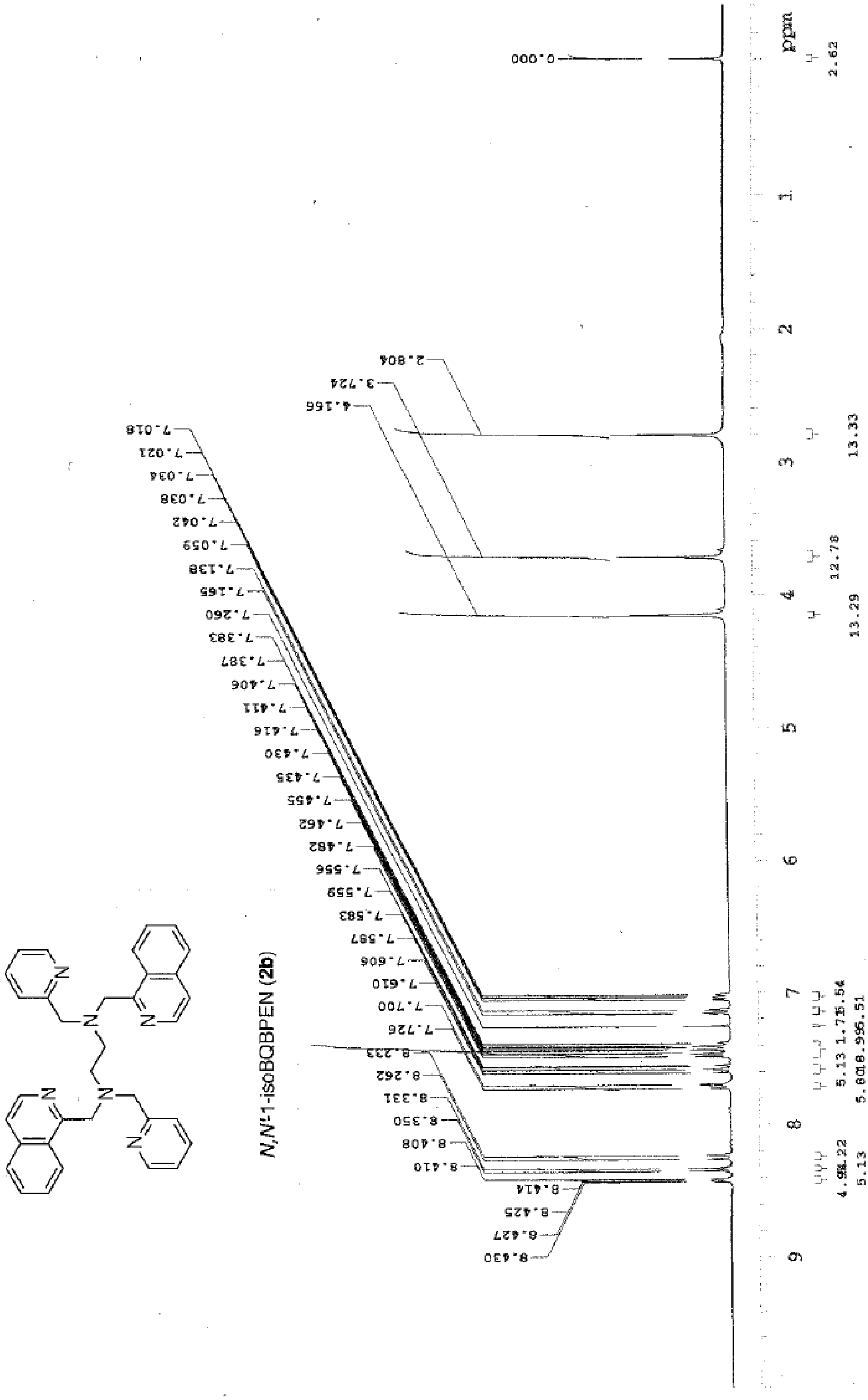

Fig. S24 ^{1}H NMR spectrum of *N,N′*-1-isoBQBPEN (**2b**) in $CDCl_3$.

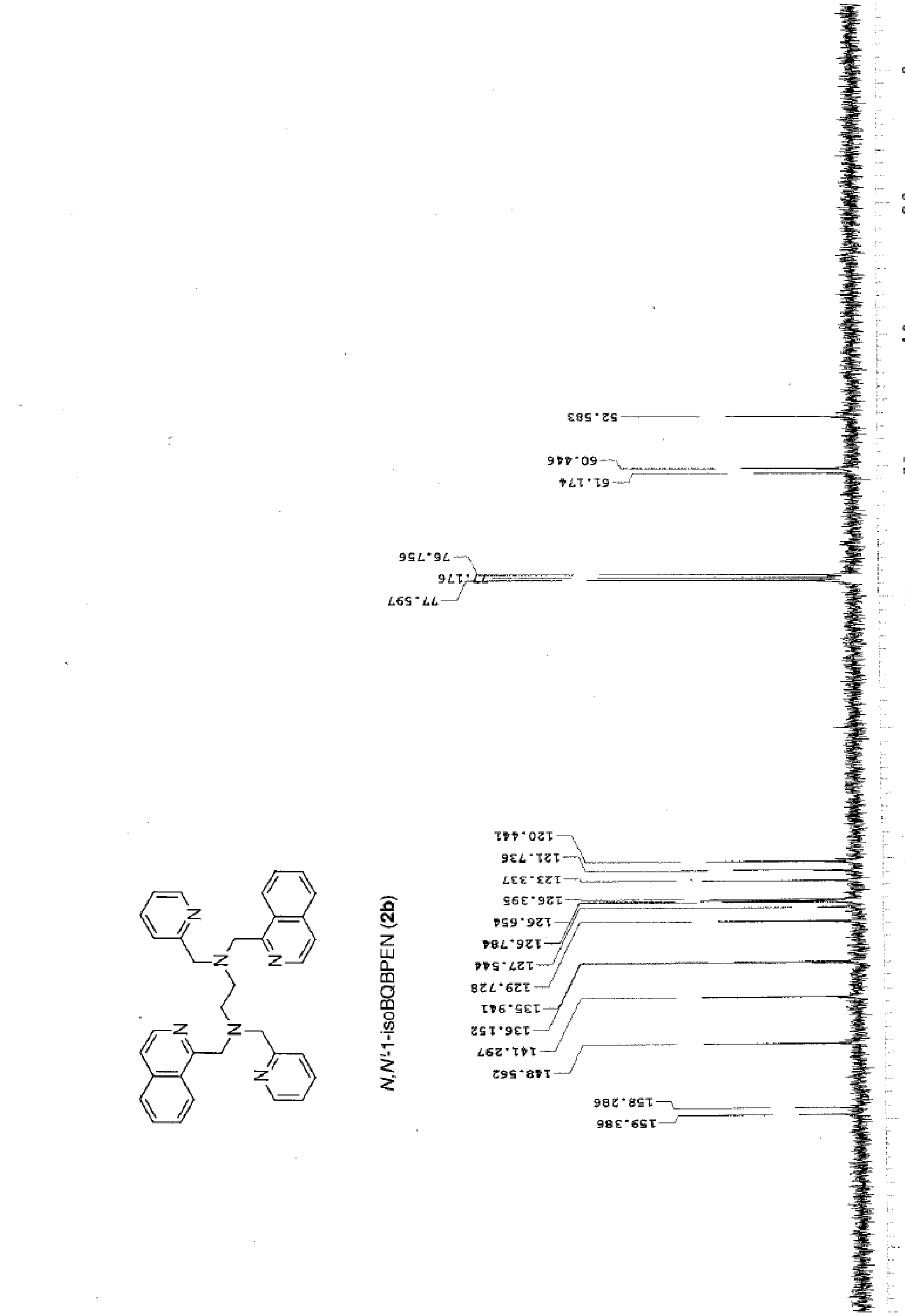

Fig. S25 ^{13}C NMR spectrum of *N,N′*-1-isoBQBPEN (**2b**) in $CDCl_3$.

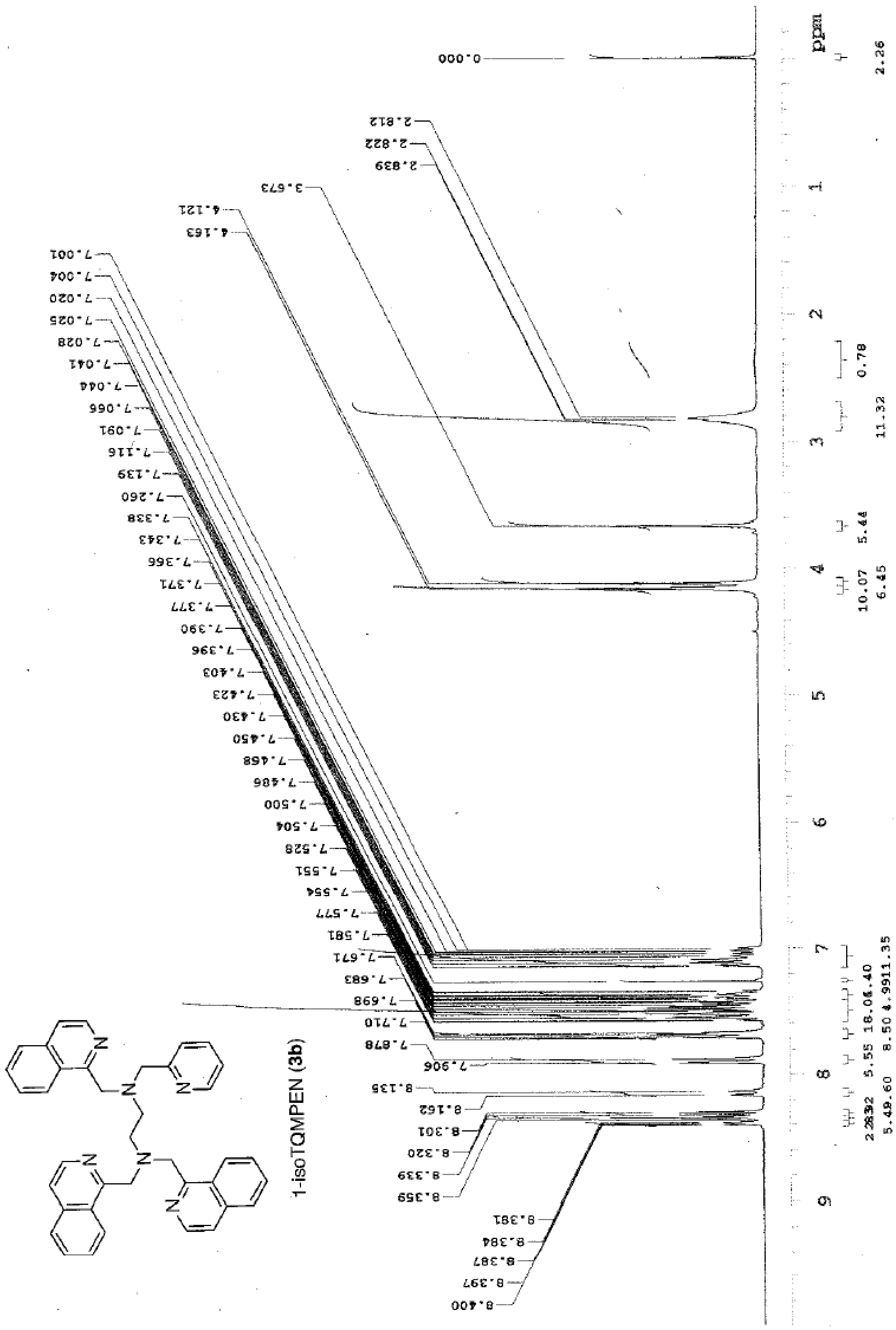

Fig. S26 ^{1}H NMR spectrum of 1-isoTQMPEN (**3b**) in $CDCl_3$.

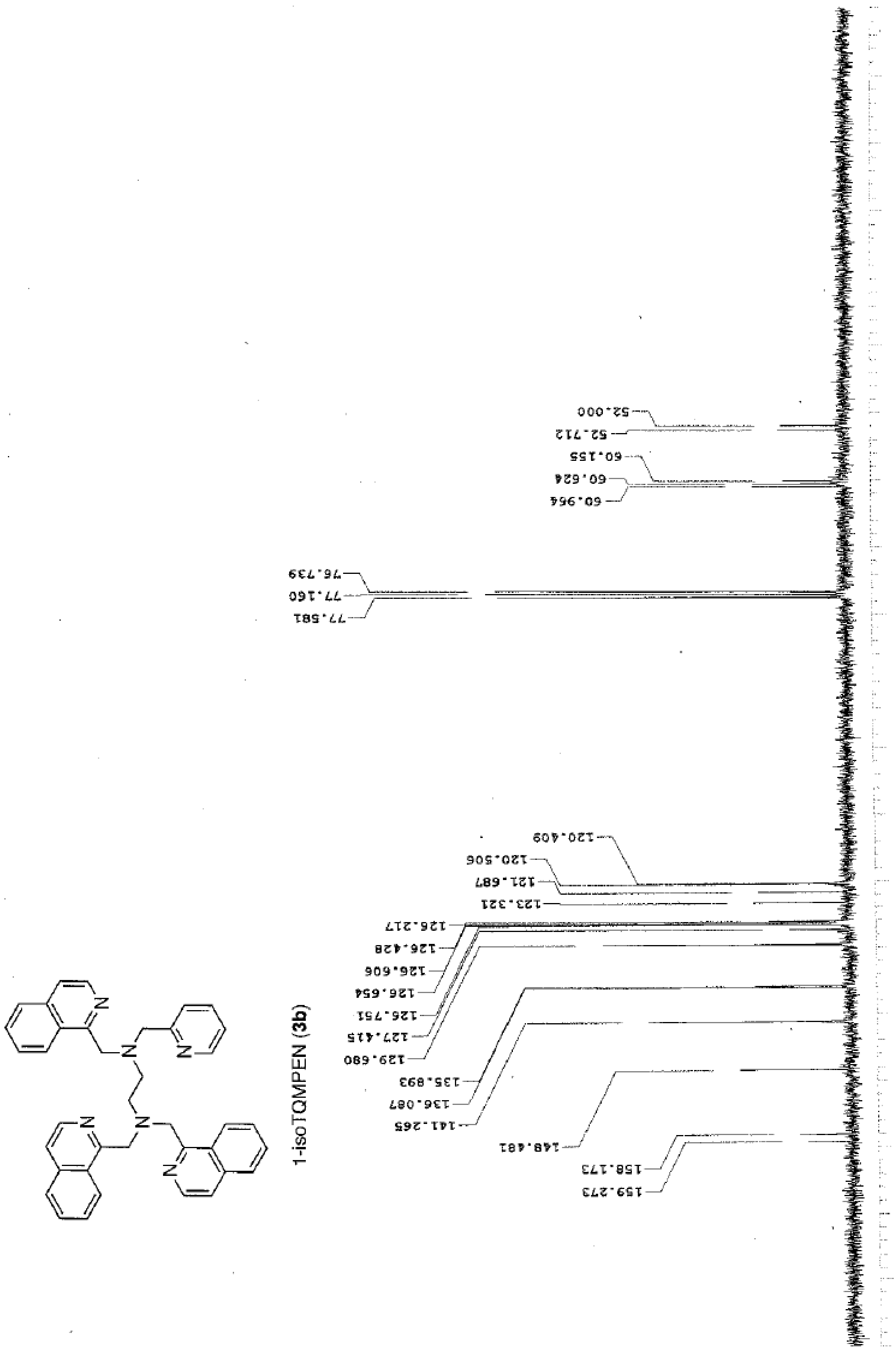

Fig. S27 ^{13}C NMR spectrum of 1-isoTQMPEN (**3b**) in $CDCl_3$.

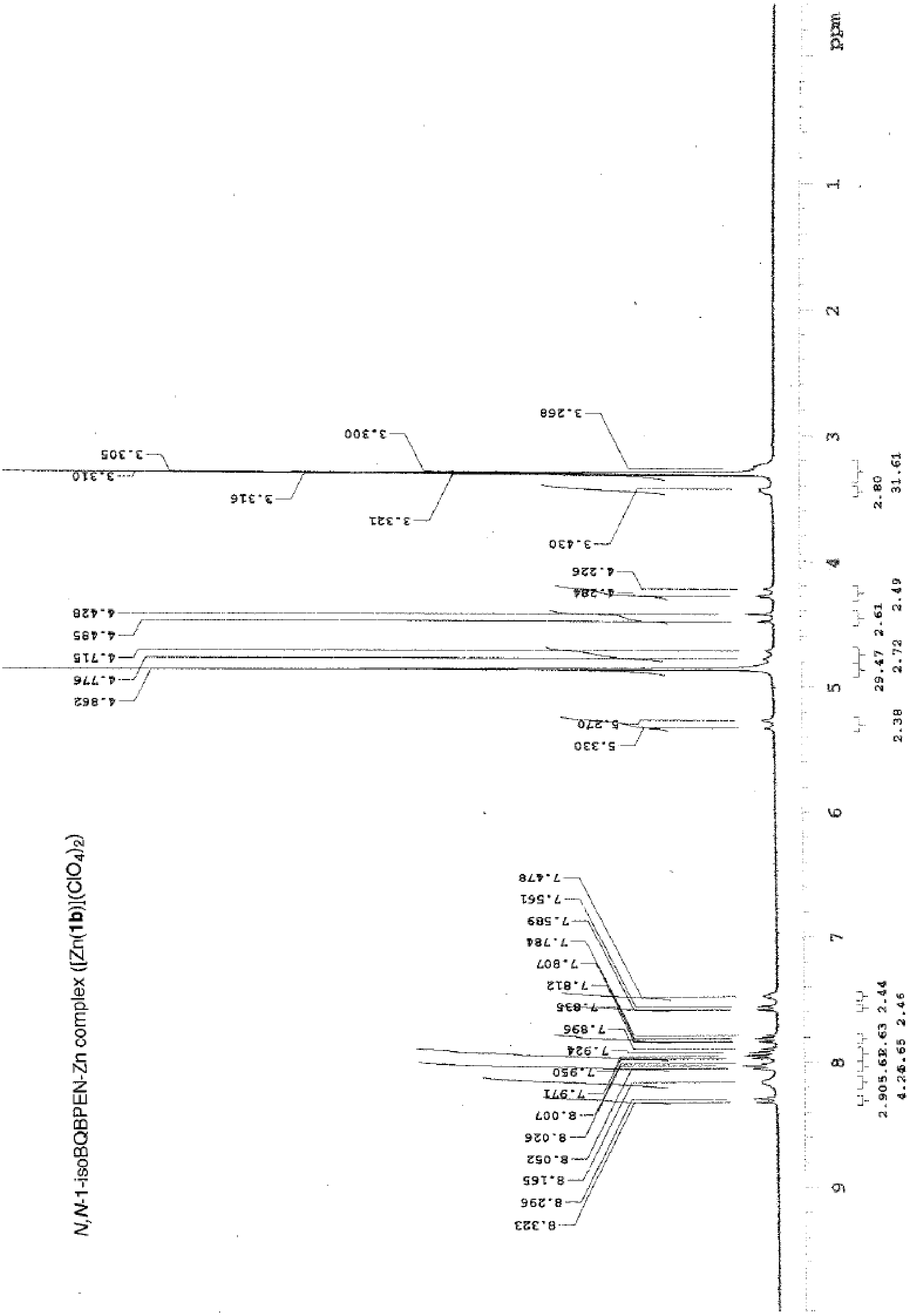

Fig. S28 ^{1}H NMR spectrum of $[Zn(\mathbf{1b})](ClO_4)_2$ in CD_3OD.

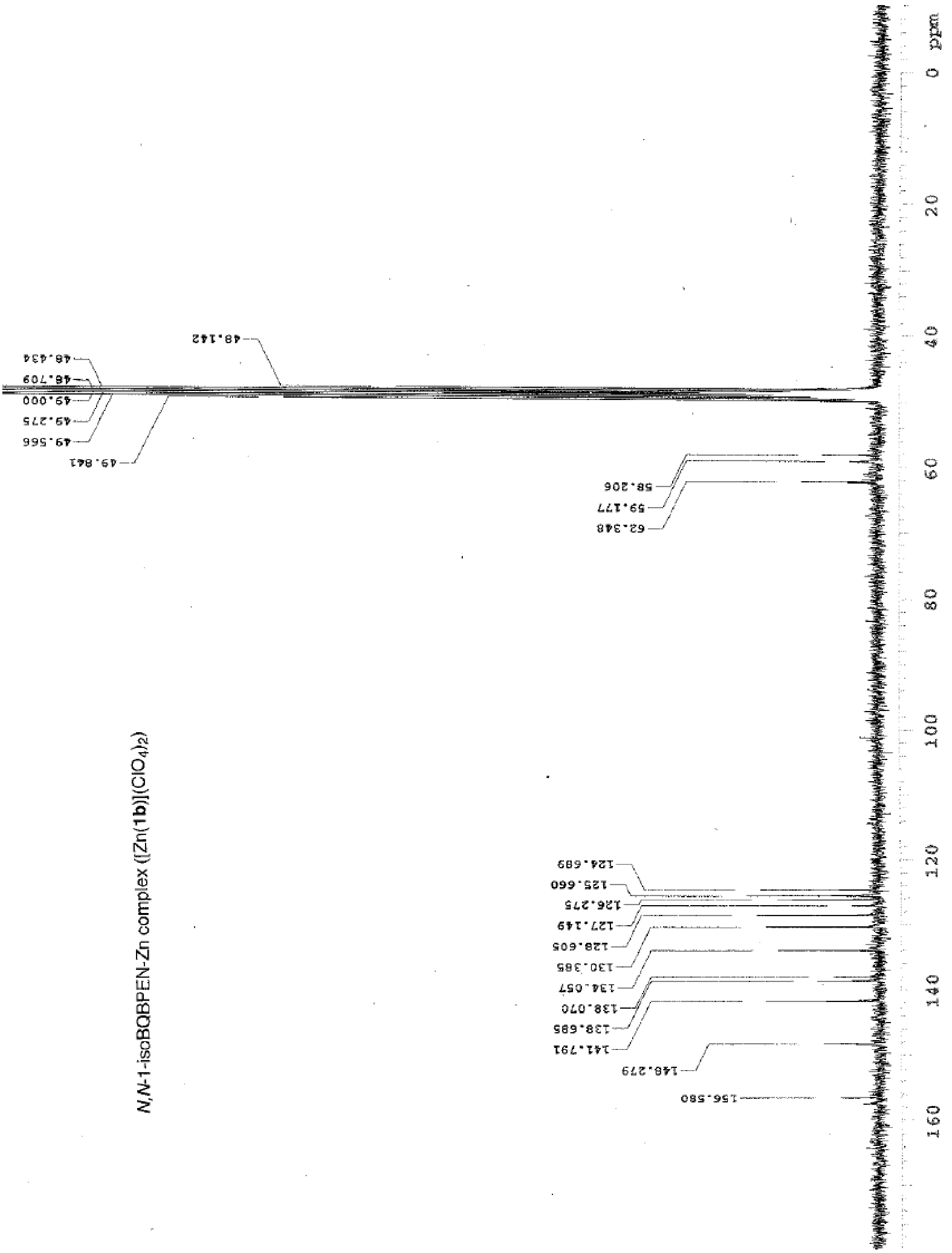

Fig. S29 ^{13}C NMR spectrum of $[Zn(\mathbf{1b})](ClO_4)_2$ in CD_3OD.

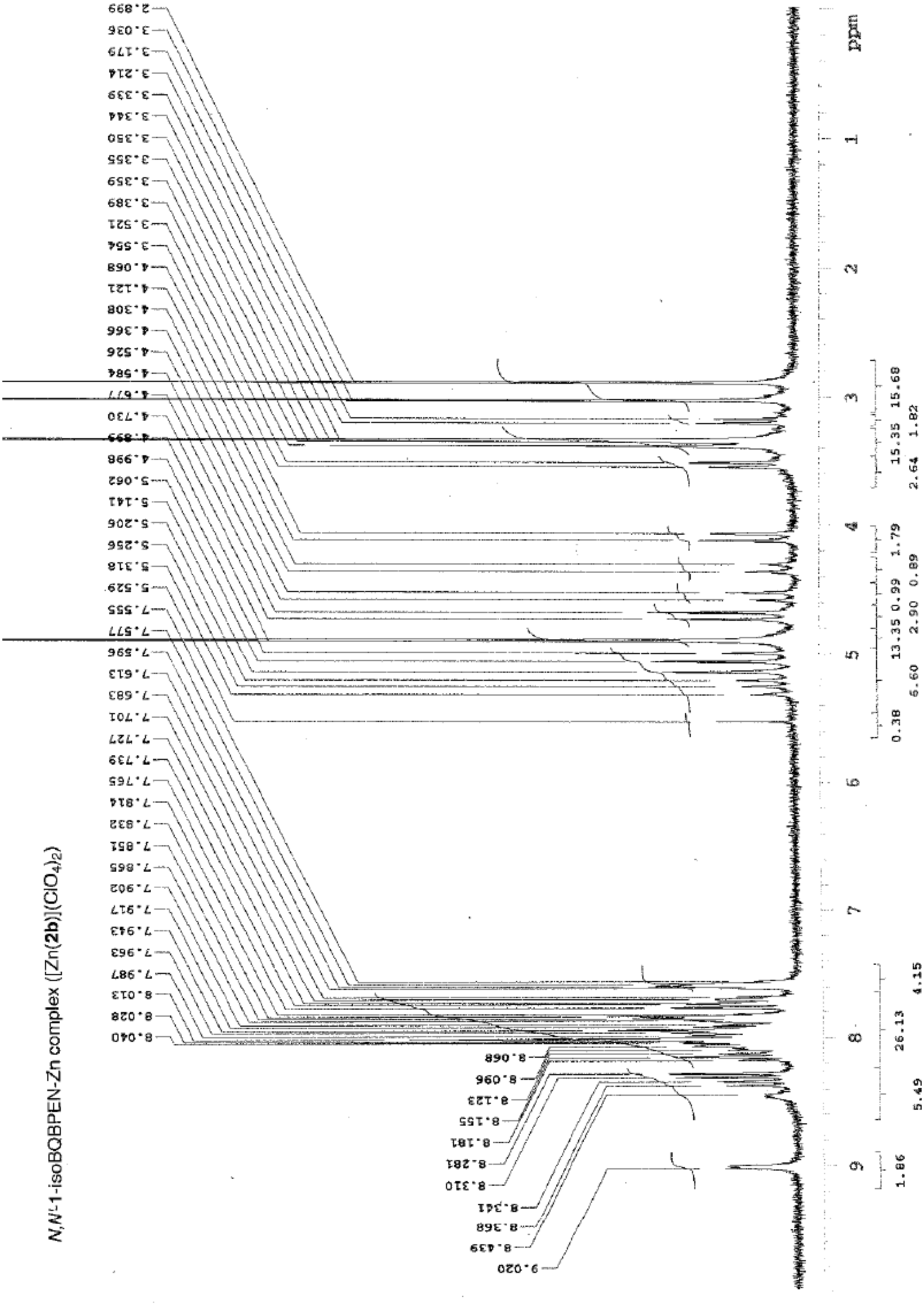

Fig. S30 ^{1}H NMR spectrum of [Zn(**2b**)]$(ClO_4)_2$ in CD_3OD.

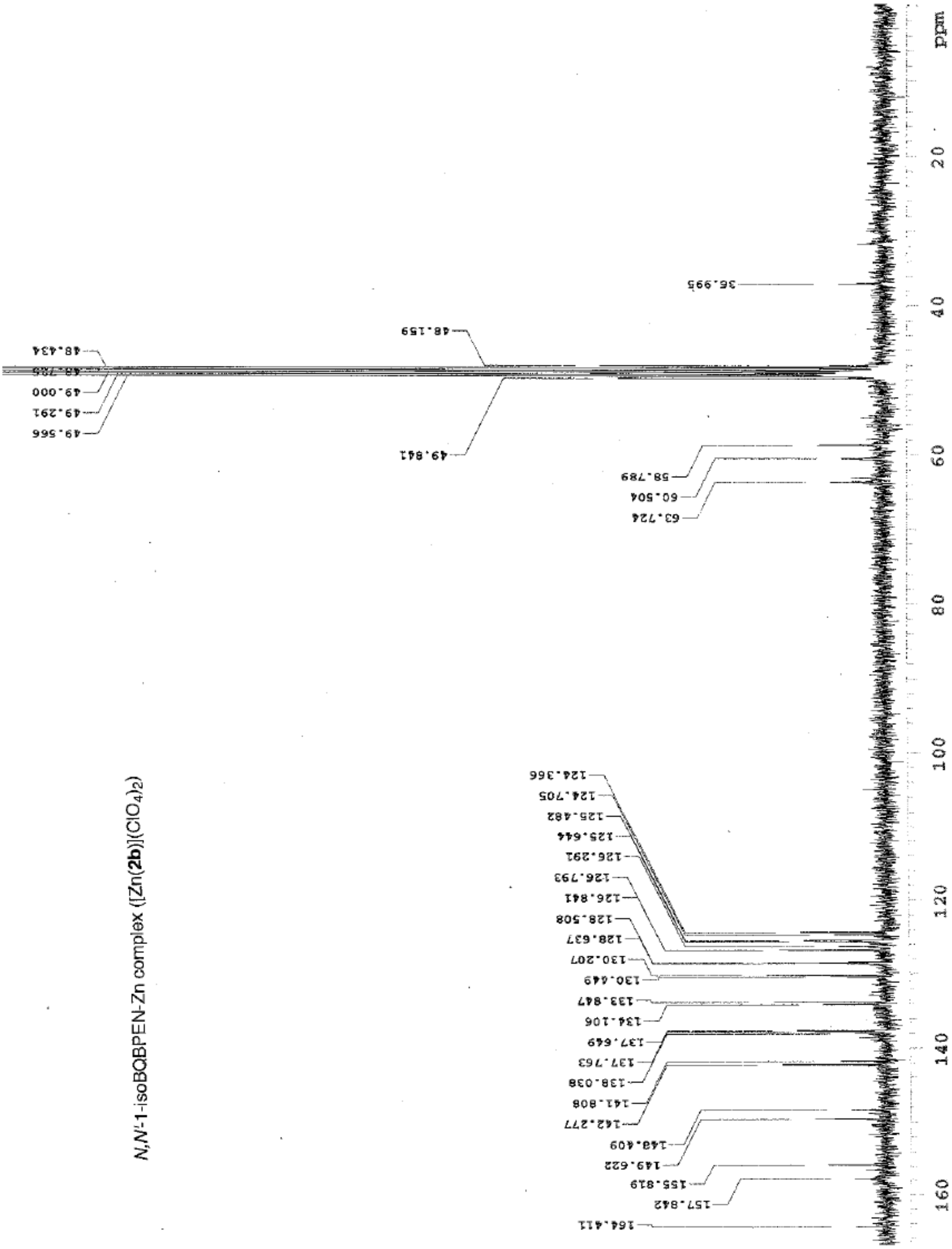

Fig. S31 ^{13}C NMR spectrum of $[Zn(\mathbf{2b})](ClO_4)_2$ in CD_3OD.