

Supplementary Information for
**Cd²⁺-selective fluorescent response of TQEN (*N,N,N',N'*-tetrakis(2-
quinolylmethyl)ethylenediamine) derivatives bearing ether oxygen binding
sites**

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Table S1. Crystallographic Data for [Cd(8-MOMOTQEN)](ClO₄)₂ and [Zn(8-OHTQEN)](ClO₄)₂·2CH₃CN

	[Cd(8-MOMO-TQEN)](ClO ₄) ₂	[Zn(8-OHTQEN)]-(ClO ₄) ₂ ·2CH ₃ CN
Formula	C ₄₄ H ₄₀ CdCl ₂ N ₆ O ₁₀	C ₄₆ H ₄₂ Cl ₂ N ₈ O ₉ Zn
FW	996.15	987.17
Crystal system	monoclinic	triclinic
Space group	P2 ₁ /c	P-1
<i>a</i> , Å	12.1523(6)	10.352(2)
<i>b</i> , Å	16.5107(15)	12.177(3)
<i>c</i> , Å	20.3375(13)	20.024(4)
α, deg	90	68.874(5)
β, deg	94.160(3)	71.806(7)
γ, deg	90	84.582(8)
<i>V</i> , Å ³	4069.8(5)	2236.3(8)
<i>Z</i>	4	2
<i>D</i> _{calc} , g cm ⁻³	1.626	1.466
μ, mm ⁻¹	0.7386	0.7351
2θ _{max} , deg	55	55
temp, K	153	153
no. reflns collected	30977	23466
no. reflns used	9310	10158
no. of params	569	601
<i>R</i> _{int}	0.0183	0.0354
Final <i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0391	0.0608
<i>wR</i> 2 (all data) ^b	0.1021	0.1959
GOF	1.051	1.103

^a*R*1 = Σ ||*F*_o|| - ||*F*_c|| / Σ ||*F*_o||. ^b*wR*2 = [Σ*w*[(*F*_o² - *F*_c²)²]] / Σ [*w*(*F*_o²)²]]^{1/2}.

Table S2. Interatomic Distances (\AA) for $[\text{Cd(8-MOMOTQEN)}](\text{ClO}_4)_2$ and $[\text{Zn(8-OHTQEN)}](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$

	$[\text{Cd(8-MOMO-TQEN)}](\text{ClO}_4)_2$	$[\text{Zn(8-OHTQEN)}] \cdot (\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$
M-N1	2.369(2)	2.291(3)
M-N2	2.421(2)	2.250(3)
M-N3	2.359(2)	2.078(4)
M-N4	2.409(2)	2.206(3)
M-N5	2.442(2)	2.199(3)
M-N6	2.363(2)	3.580(3)
M-O1	3.011(2)	2.142(3)
M...O2	5.221(2)	—

Table S3. Fluorescence Lifetimes for Cd²⁺ and Zn²⁺ Complexes of 8-MOMOTQEN^a

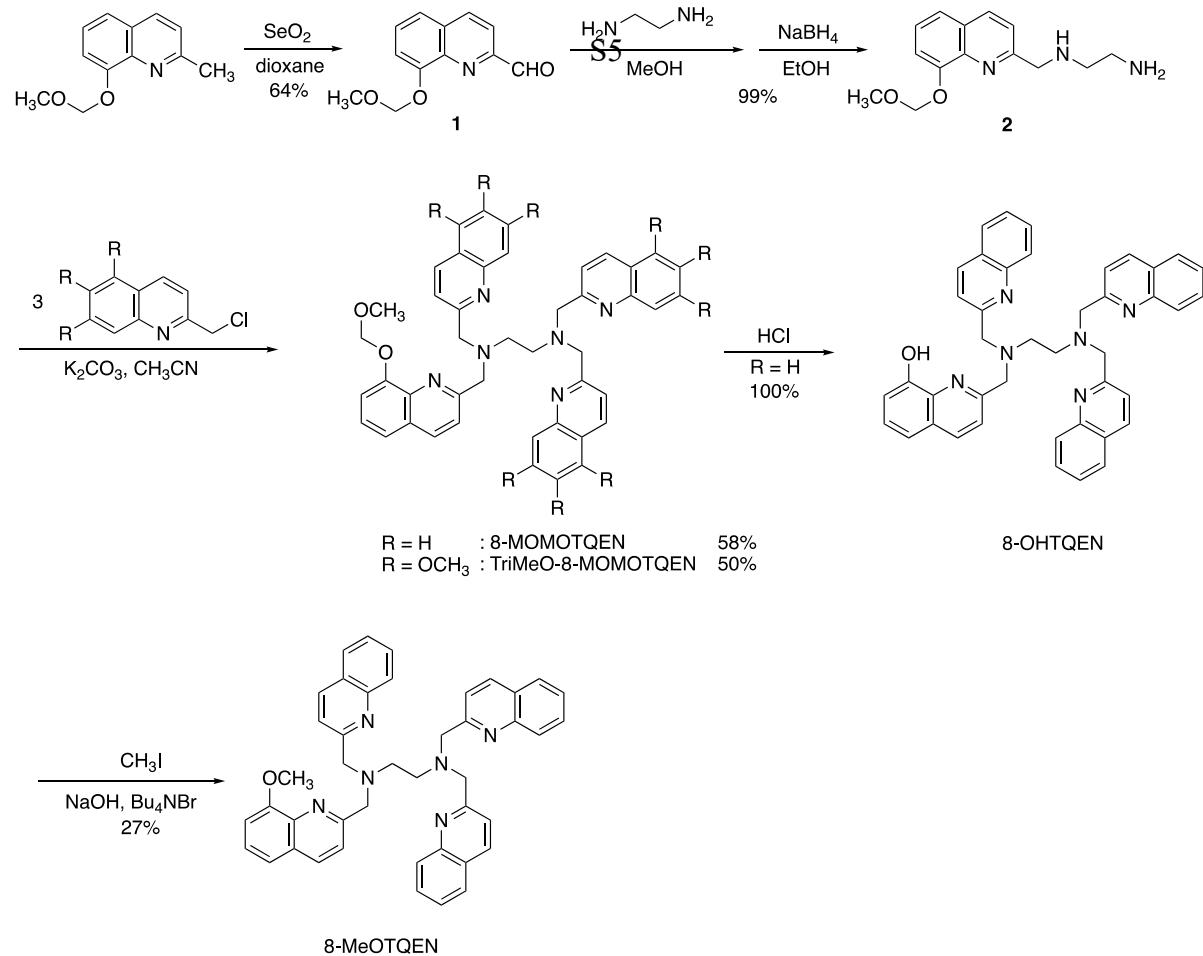
Metal Ion	λ_{em} (nm)	BPF ^b	τ (nsec) ^c
none	434	430	4.28 (24%), 19.5 (49%)
Cd ²⁺	436	430	1.89 (7%), 9.33 (60%), 15.8 (33%)
Zn ²⁺	451	460	7.30 (37%), 23.2 (54%)

^a Conditions: 34 μM solution in DMF-H₂O (1:1) at 25 °C in the presence of 1 equiv. of metal ion ($\lambda_{\text{ex}} = 331$ nm).

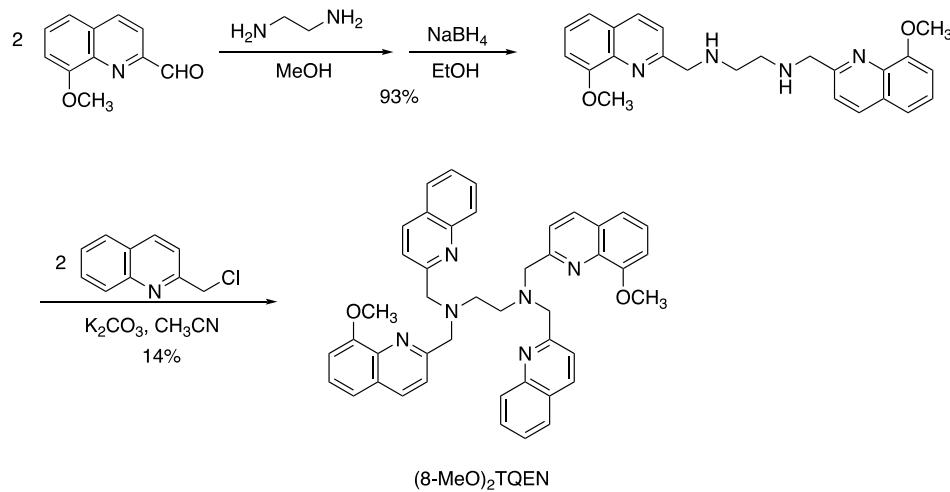
^b Bandpath filter used (± 10 nm).

^c Components with extremely short lifetime (< 1 nsec) were omitted.

Scheme S1



Scheme S2



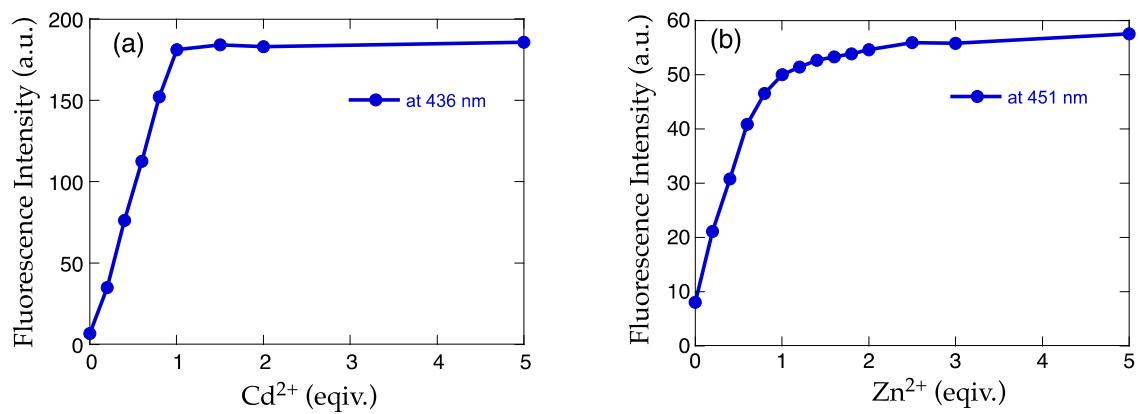
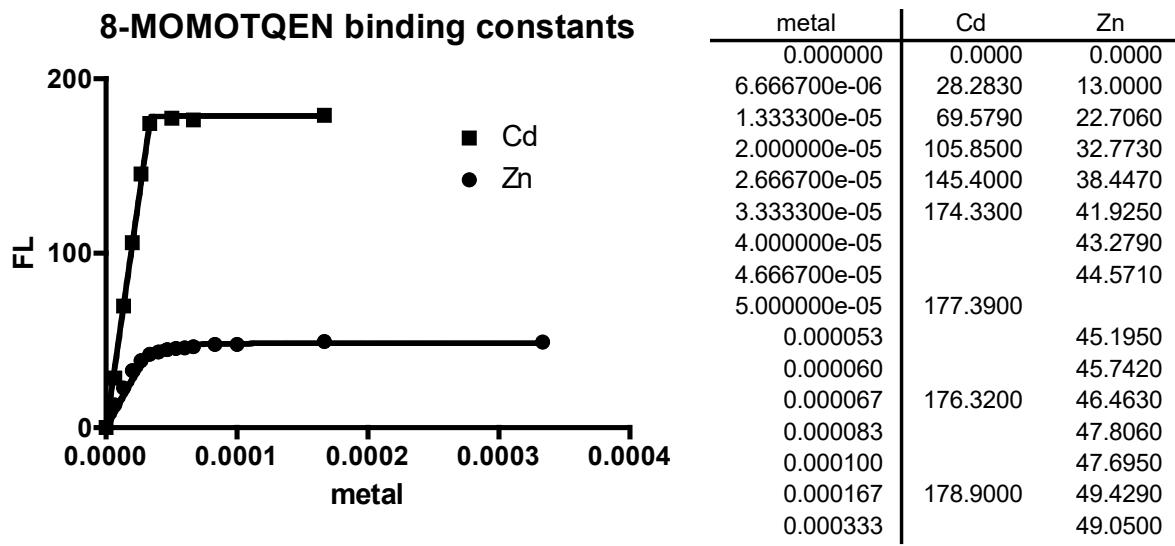


Fig. S1. Plot of fluorescence intensity changes of 34 μM 8-MOMOTQEN in the presence of 1 equiv. of (a) Cd²⁺ and (b) Zn²⁺ in DMF-H₂O (1:1) at 25 °C ($\lambda_{\text{ex}} = 317 \text{ nm}$).



	Cd	Zn
zinc binding 2/7/2008		
Best-fit values		
BMAX	178.5	48.55
KD	1.4353e-009	6.0952e-007
L0	3.4000e-005	3.4000e-005
Std. Error		
BMAX	1.754	1.303
KD	1.7978e-008	5.0052e-007
95% Confidence Intervals		
BMAX	174.4 to 182.7	45.73 to 51.36
KD	-4.1082e-008 to 4.3953e-008	-4.7161e-007 to 1.6906e-006
Goodness of Fit		
Degrees of Freedom	7	13
R squared	0.9979	0.9720
Absolute Sum of Squares	81.63	85.23
Sy.x	3.415	2.560
Constraints		
L0	L0 = 3.4000e-005	L0 = 3.4000e-005
Data		
Number of X values	15	16
Number of Y replicates	1	1
Total number of values	9	15
Number of missing values	6	1

Fig. S2. Estimation of dissociation constants (K_d) for 8-MOMOTQEN with Cd^{2+} and Zn^{2+} in DMF- H_2O (1:1) at 25°C.

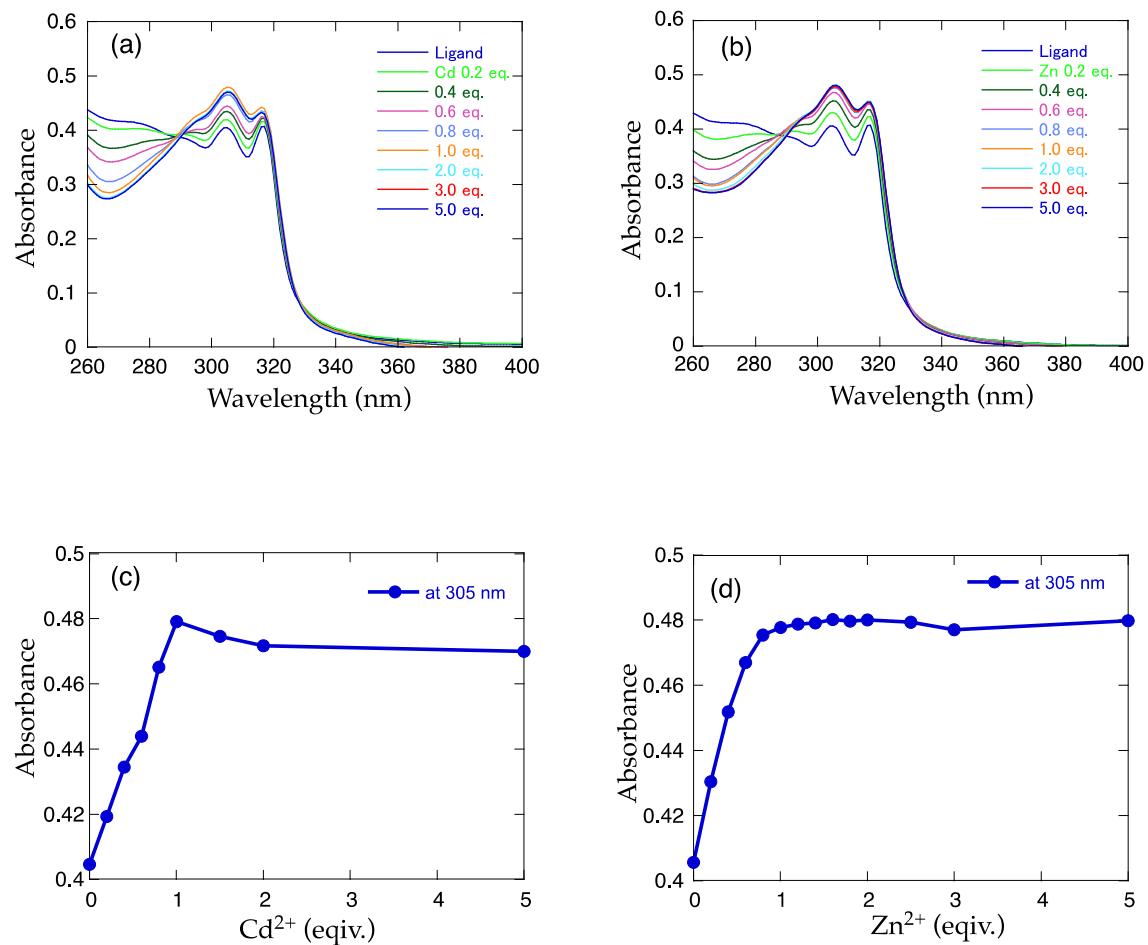


Fig. S3. (a,b) UV-vis absorption spectra of 34 μM 8-MOMOTQEN in DMF-H₂O (1:1) at 25 °C in the presence of increasing amount of (a) Cd²⁺ and (b) Zn²⁺. (c,d) Plot of absorbance changes in the presence of increasing amount of (c) Cd²⁺ and (d) Zn²⁺.

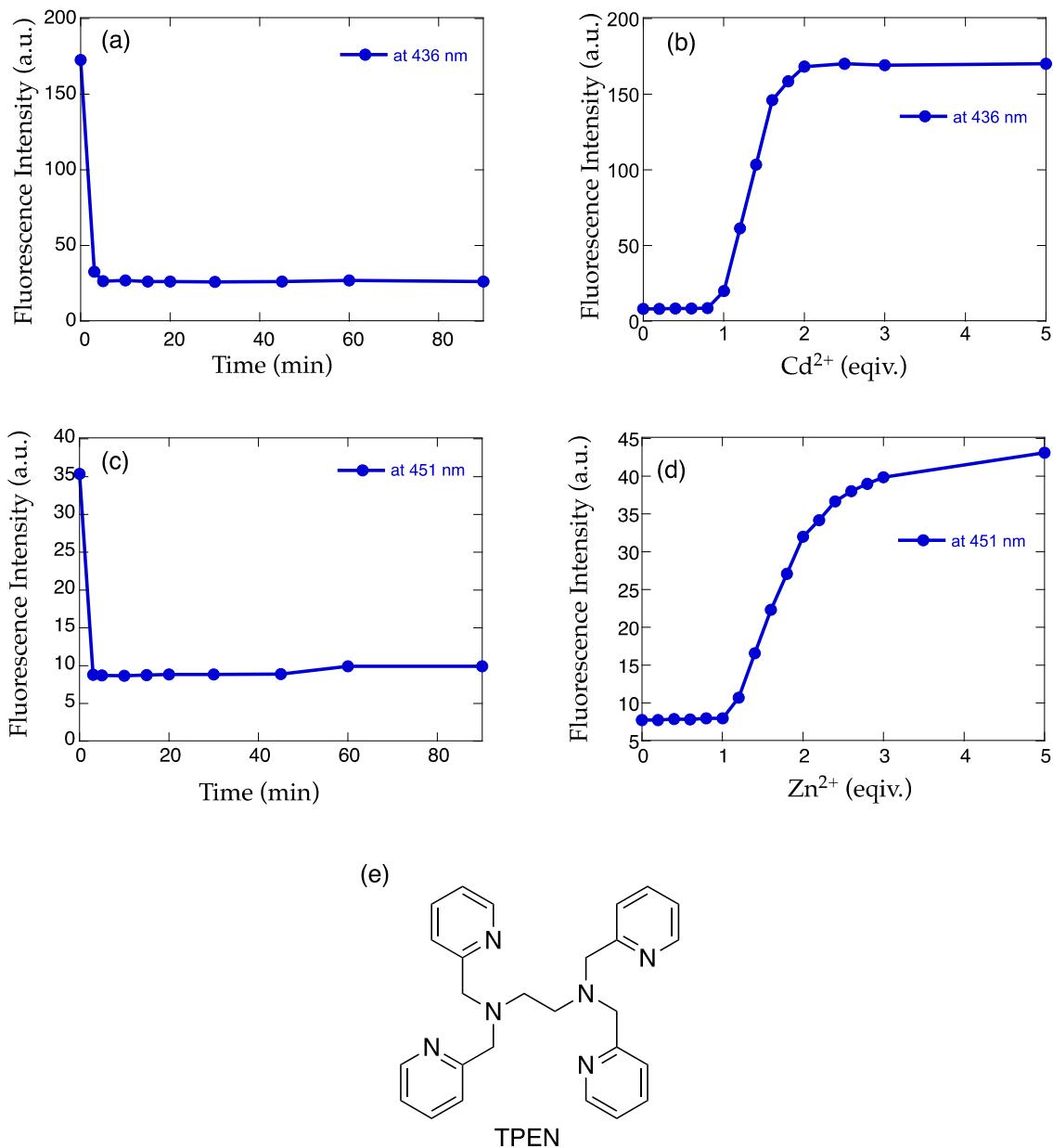


Fig. S4. Plot of fluorescence intensity changes of 34 μM 8-MOMOTQEN in the presence of 1 equiv. of (a,b) Cd²⁺, (c,d) Zn²⁺ and (a-d) TPEN in DMF-H₂O (1:1) at 25 °C ($\lambda_{\text{ex}} = 317 \text{ nm}$). (a,c) Time course of fluorescence intensity of (a) Cd²⁺ and (c) Zn²⁺ complexes of 8-MOMOTQEN after addition of 1 equiv. of TPEN. (b,d) fluorescence intensity of 8-MOMOTQEN with increasing amount of (b) Cd²⁺ and (d) Zn²⁺ in the presence of 1 equiv. of TPEN. (e) Structure of TPEN.

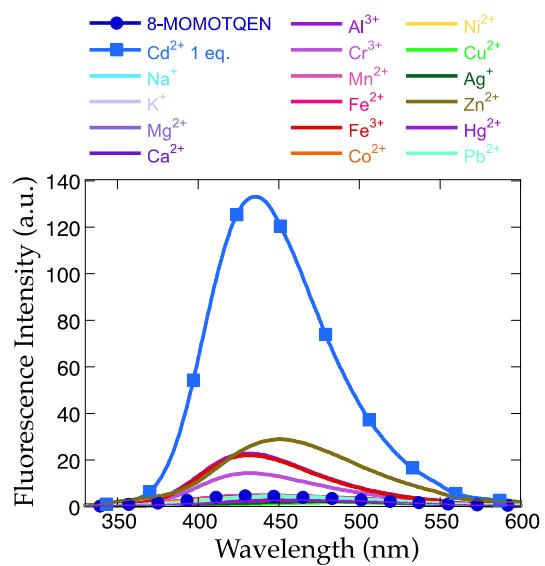


Fig. S5. Fluorescence spectra of 34 μ M 8-MOMOTQEN in the presence of 1 equiv. of various metal ions in DMF-H₂O (1:1) at 25 °C ($\lambda_{\text{ex}} = 317$ nm).

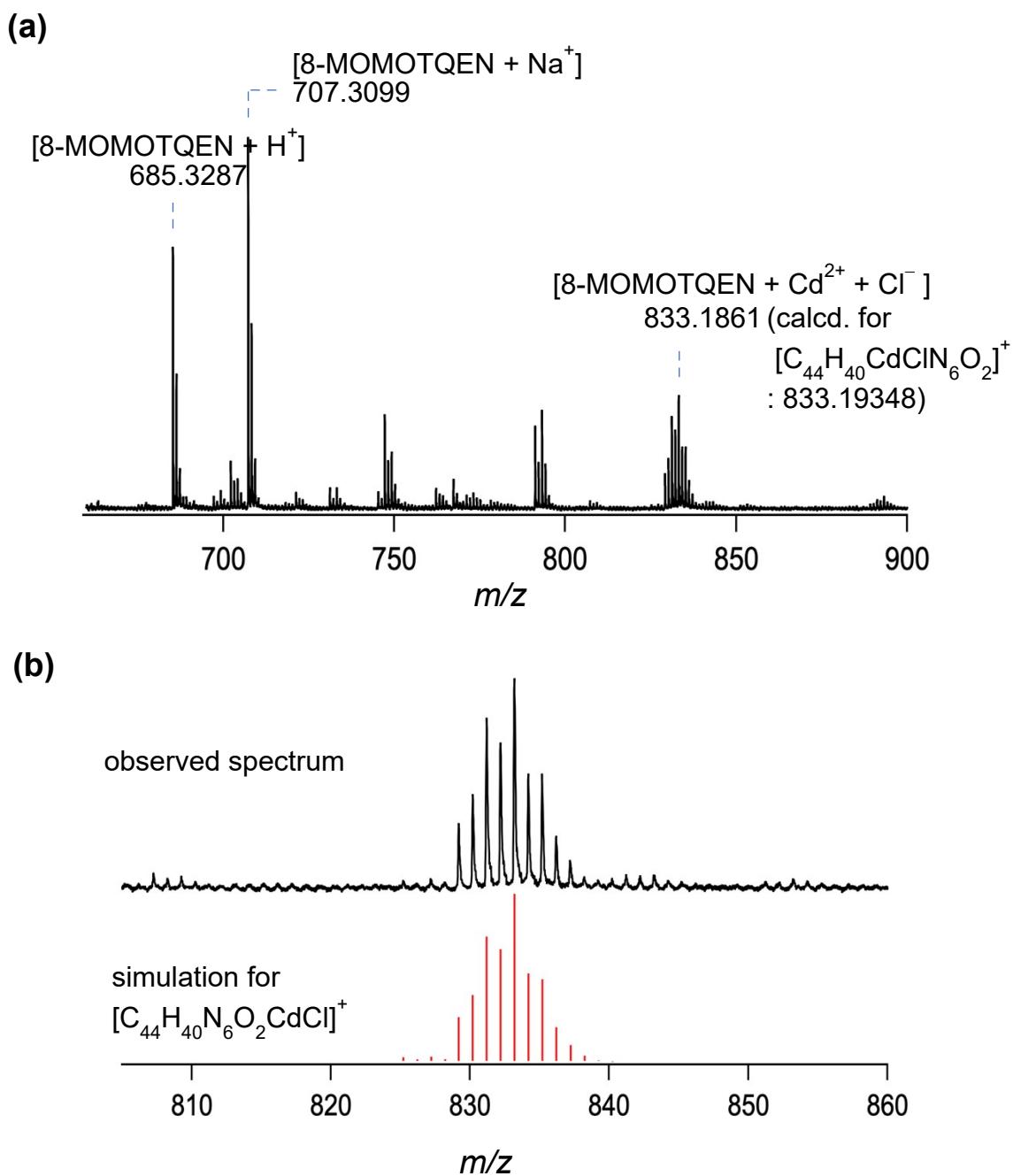


Fig. S6. ESI-MS spectrrm of 8-MOMOTQEN in methanol solution in the presence of 1 equiv. of Cd^{2+} . (a) Observed spectrum. (b) Comparison of observed and simulated spectra for 8-MOMOTQEN- Cd^{2+} complex.

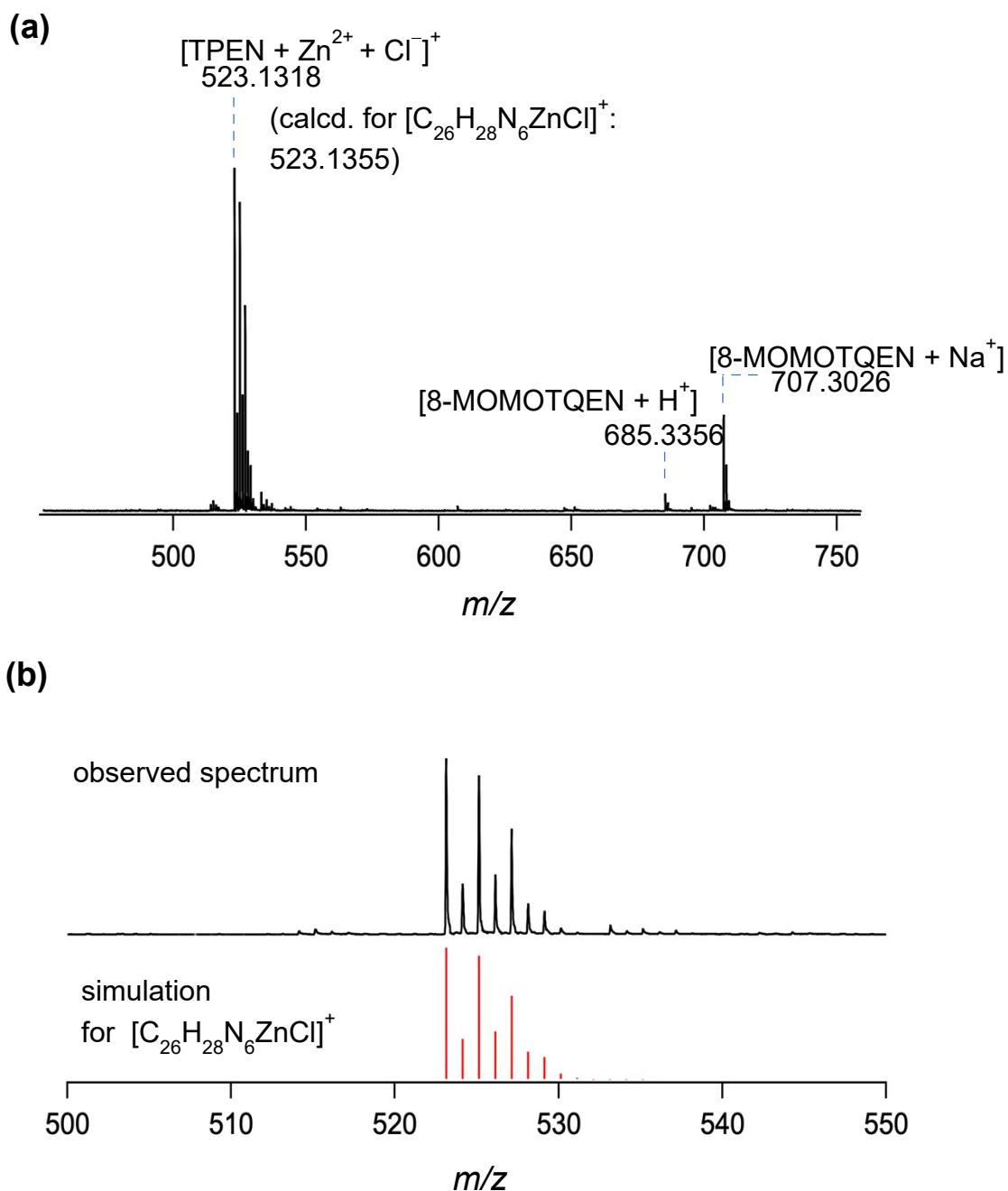


Fig. S7. ESI-MS spectrum of 8-MOMOTQEN-Zn²⁺ complex in methanol solution in the presence of 1 equiv. of TPEN. (a) Observed spectrum. (b) Comparison of observed and simulated spectra for TPEN-Zn²⁺ complex produced by ligand replacement.

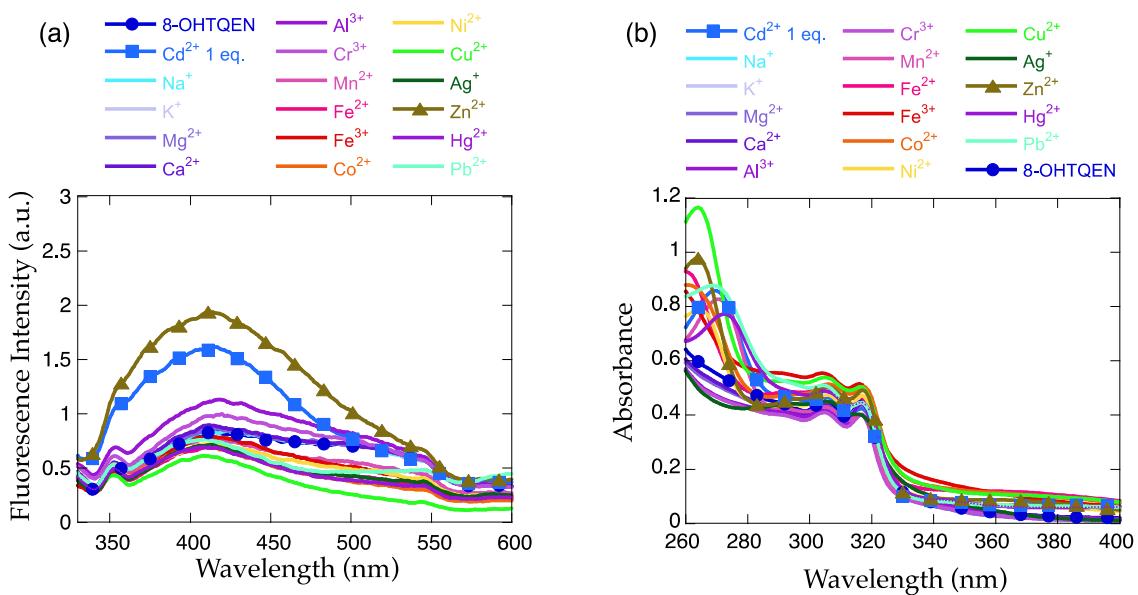


Fig. S8. (a) Fluorescence and (b) UV-vis spectra of 34 μM 8-OHTQEN in the presence of 1 equiv. of various metal ions in DMF-H₂O (1:1) at 25 °C ($\lambda_{\text{ex}} = 317 \text{ nm}$).

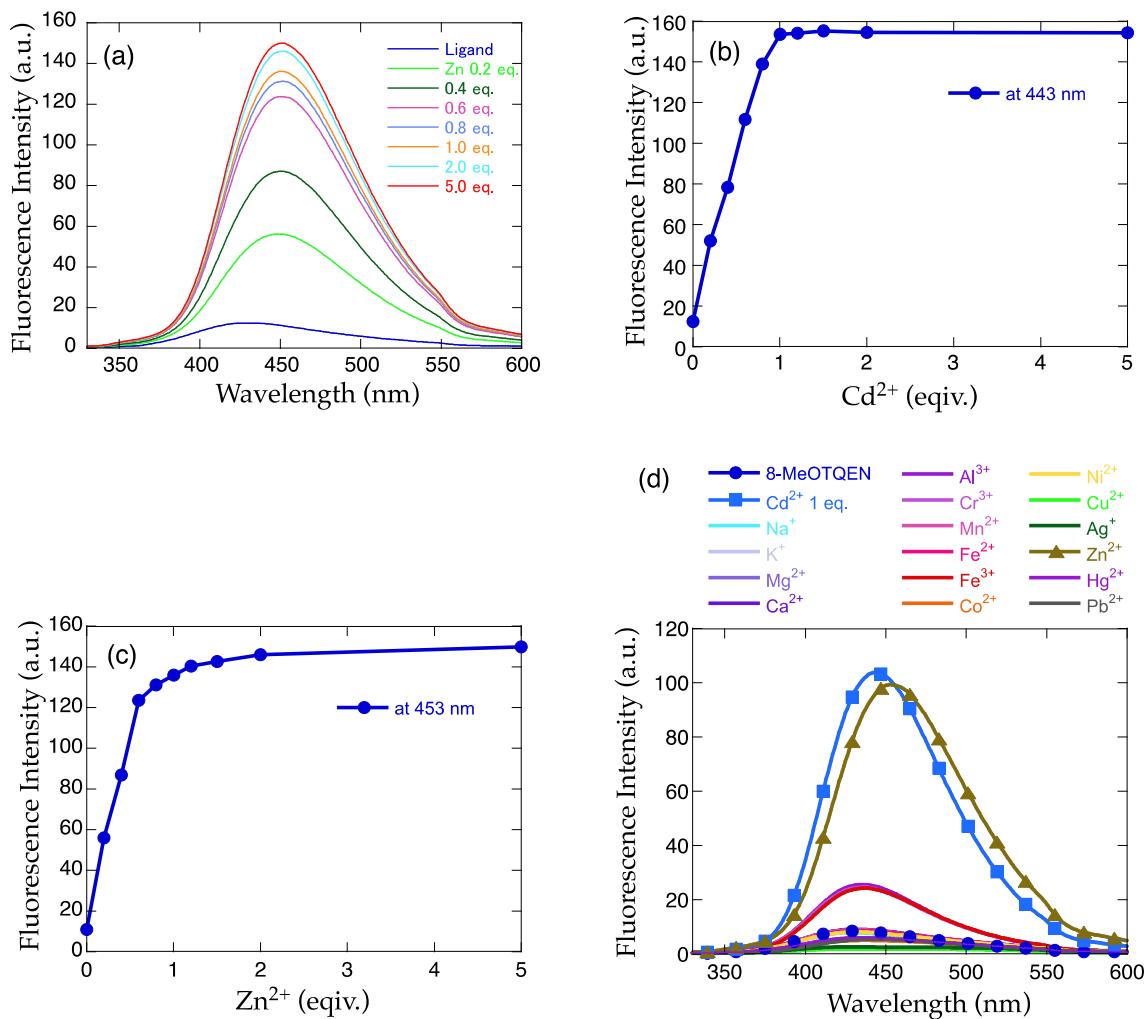


Fig. S9. (a) Fluorescence spectra of 34 μM 8-MeOTQEN in DMF-H₂O (1:1) at 25 °C in the presence of increasing amount of Zn²⁺ ($\lambda_{\text{ex}} = 317 \text{ nm}$). (b,c) Plot of fluorescence intensity changes for (b) Cd²⁺ and (c) Zn²⁺ titration. (d) Fluorescence spectra in the presence of 1 equiv. of various metal ions.

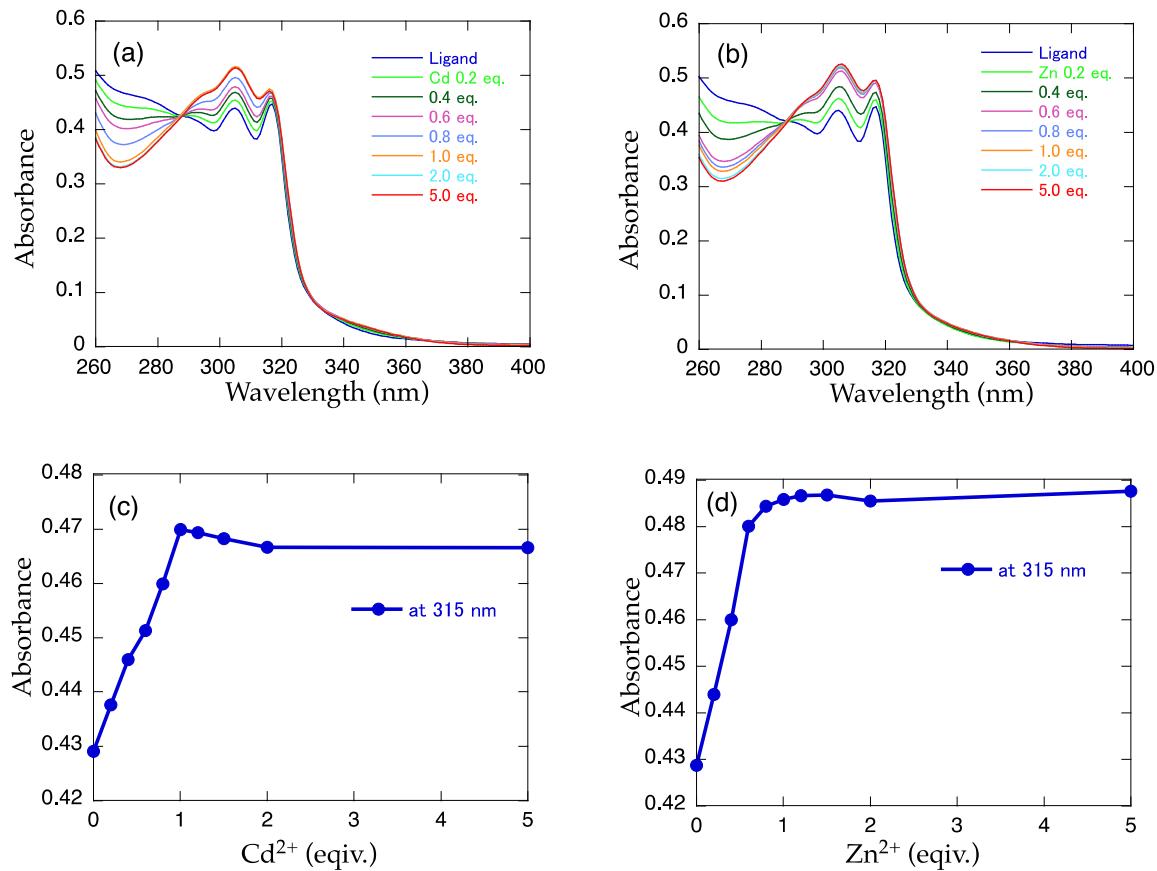


Fig. S10. (a,b) UV-vis absorption spectra of 34 μM 8-MeOTQEN in DMF- H_2O (1:1) at 25 °C in the presence of increasing amount of (a) Cd²⁺ and (b) Zn²⁺. (c,d) Plot of absorbance changes in the presence of increasing amount of (c) Cd²⁺ and (d) Zn²⁺.

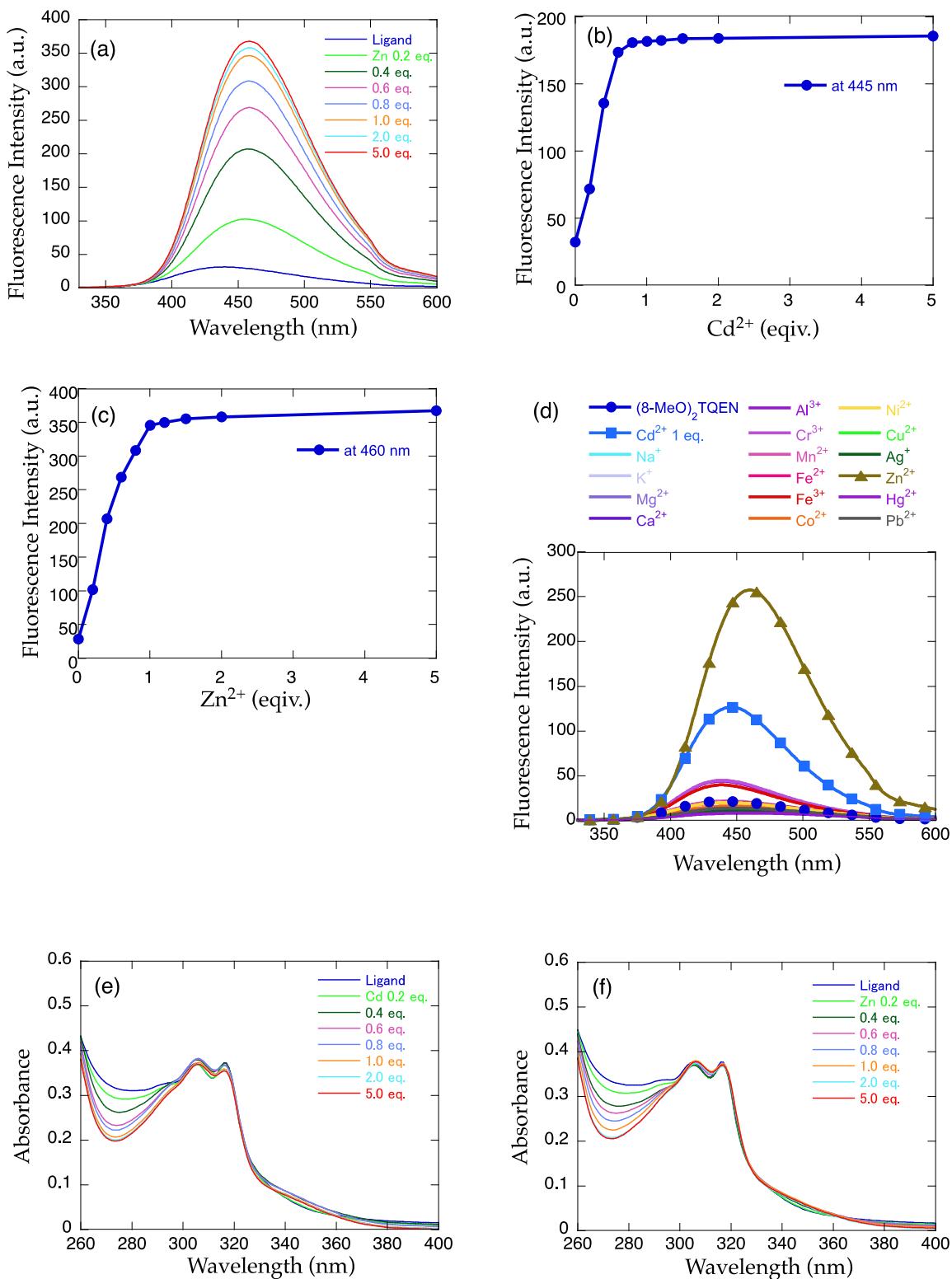
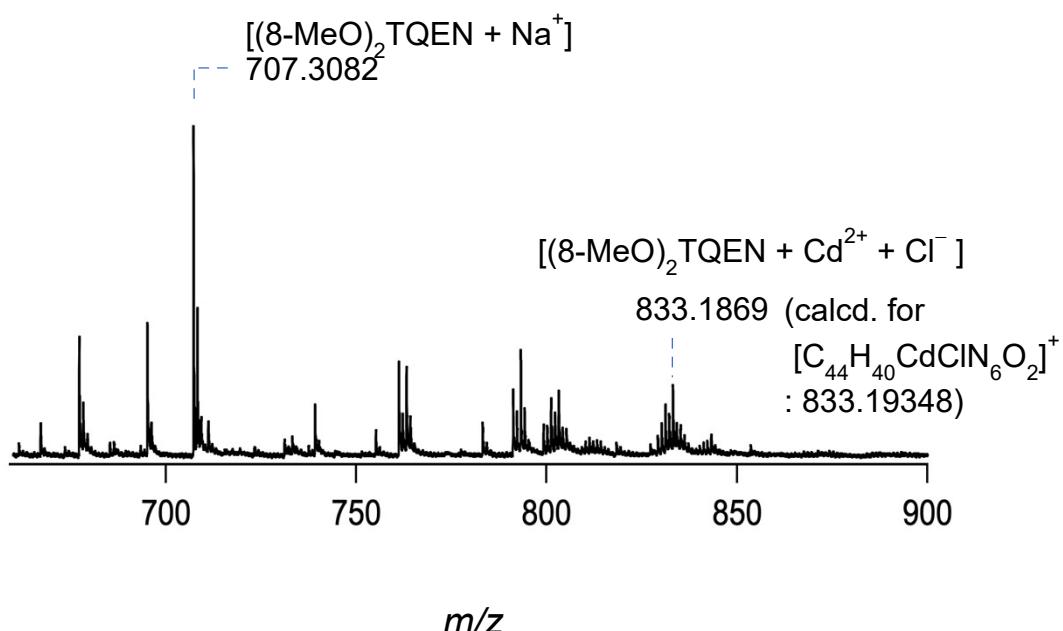


Fig. S11. (a) Fluorescence spectra of 34 μM $(8\text{-MeO})_2\text{TQEN}$ in DMF-H₂O (1:1) at 25 °C in the presence of increasing amount of Zn²⁺ ($\lambda_{\text{ex}} = 317 \text{ nm}$). (b,c) Plot of fluorescence intensity changes for (b) Cd²⁺ and (c) Zn²⁺ titration. (d) Fluorescence spectra in the presence of 1 equiv. of various metal ions. (e,f) UV-vis absorption spectra in the presence of increasing amount of (e) Cd²⁺ and (f) Zn²⁺.

(a)



(b)

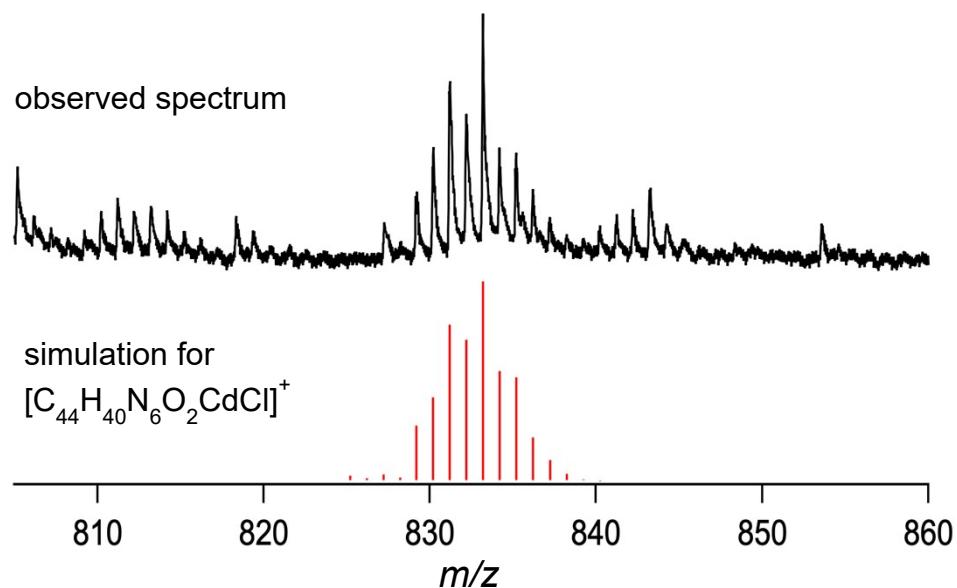


Fig. S12. ESI-MS spectrrm of $(8\text{-MeO})_2\text{TQEN}$ in methanol solution in the presence of 1 equiv. of Cd^{2+} . (a) Observed spectrum. (b) Comparison of observed and simulated spectra for $(8\text{-MeO})_2\text{TQEN}\text{-Cd}^{2+}$ complex.

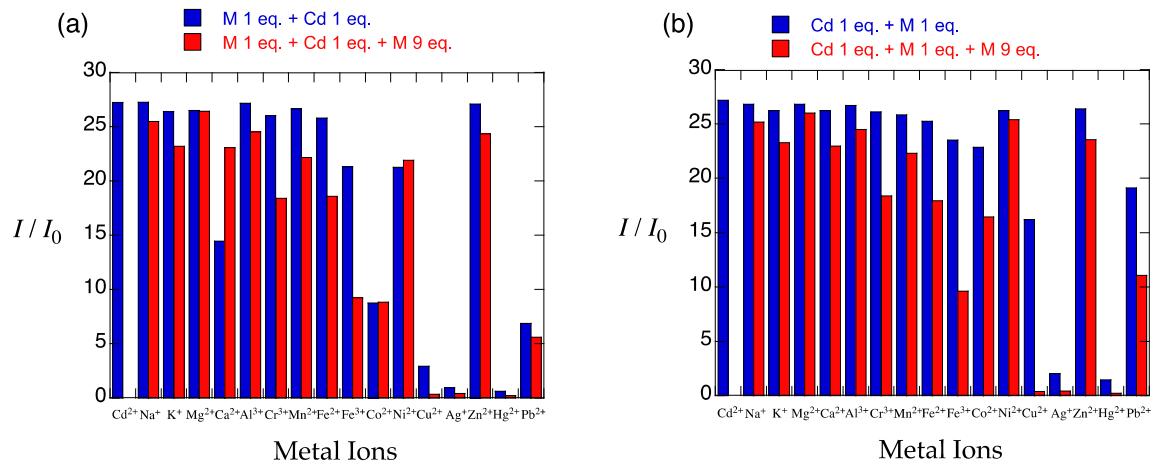


Fig. S13. The relative fluorescence intensity of 8-MOMOTQEN at 436 nm in the presence of (a) 1 equiv. of metal ions followed by addition of 1 equiv. of Cd^{2+} (blue) and further addition of 9 equiv. of metal ions (total 10 equiv. of metal ions and 1 equiv. of Cd^{2+}) (red) and (b) 1 equiv. of Cd^{2+} followed by addition of 1 equiv. of metal ions (blue) and further addition of 9 equiv. of metal ions (total 10 equiv. of metal ions and 1 equiv. of Cd^{2+}) (red) in DMF- H_2O (1:1) at 25 °C ($\lambda_{\text{ex}} = 317$ nm). I_0 is the emission intensity of free ligand.

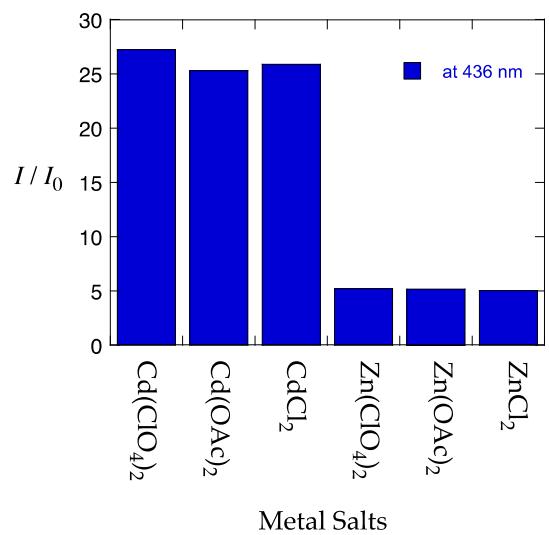


Fig. S14. Effect of counter anions on the relative fluorescence intensity of 8-MOMOTQEN at 436 nm in the presence of 1 equiv. of Cd^{2+} and Zn^{2+} in DMF- H_2O (1:1) at 25 °C ($\lambda_{\text{ex}} = 317$ nm). I_0 is the emission intensity of free ligand.

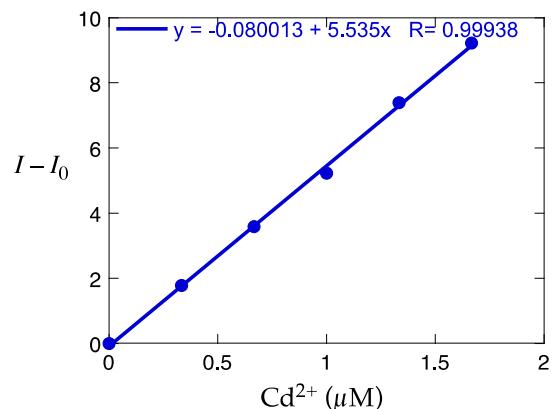
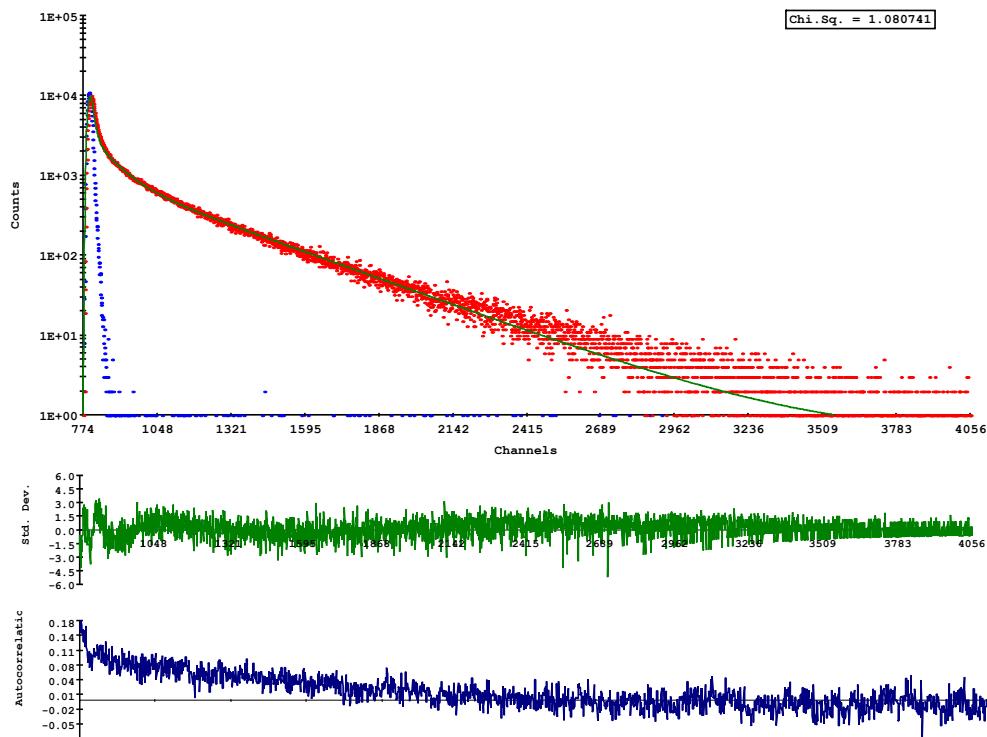


Fig. S15. Estimation of LOD (limit of detection) for Cd²⁺ with 8-MOMOTQEN in DMF-H₂O (1:1) at 25 °C ($\lambda_{\text{ex}} = 317 \text{ nm}$). The 3σ value (σ corresponds to standard deviation from 7 measurements) of blank solution (34 μM 8-MOMOTQEN) is 0.103 in fluorescence intensity unit, which corresponds to 18.5 nM from the slope of the liner dynamic fluorescence intensity plot (k) shown above (LOD = $3\sigma/k$).



Calculated using 3 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

Shift Value = 0	ch;	0	sec
Shift Limit = 40	ch;	2.194787E-09	sec
T1 Estimate = 102.6277	ch;	5.631151E-09	sec
T2 Estimate = 205.2554	ch;	1.12623E-08	sec
T3 Estimate = 410.5109	ch;	2.25246E-08	sec

A Free
B1 Free
B2 Free
B3 Free

Prompt and decay LO = 774 ch; 4.246914E-08 sec
Prompt and decay HI = 4096 ch; 2.247462E-07 sec

Background on prompt = 2
Time calibration = 5.486969E-11 sec/ch

The fitted parameters are:

Hi reduced to: 4056 ch

SHIFT = 0.3367705	ch;	1.847849E-11	sec	S.Dev = 1.450421E-12	sec
T1 = 78.00881	ch;	4.280319E-09	sec	S.Dev = 8.732682E-11	sec
T2 = 356.2304	ch;	1.954625E-08	sec	S.Dev = 5.988601E-11	sec
T3 = 9.182409	ch;	5.038359E-10	sec	S.Dev = 5.686153E-12	sec
A = 0.5486421				S.Dev = 0.0337956	
B1 = 1.117342E-02	[23.87 Rel.Ampl]	[0.09 Alpha]	S.Dev = 6.379103E-05		
B2 = 4.996874E-03	[48.74 Rel.Ampl]	[0.04 Alpha]	S.Dev = 1.221199E-05		
B3 = 0.1089253	[27.39 Rel.Ampl]	[0.87 Alpha]	S.Dev = 3.921117E-04		
Average Life Time = 1.601786E-09 sec					
CHISQ = 1.080741 [3275 degrees of freedom]					
Chi-squared Probability = 7.0898E-02 percent					
Durbin-Watson Parameter = 1.660464					
Negative residuals = 41.60828 percent					
Residuals < 1 s.dev = 67.10326 percent					
Residuals < 2 s.dev = 94.97411 percent					
Residuals < 3 s.dev = 99.48218 percent					
Residuals < 4 s.dev = 99.90862 percent					

Fig. S16. Fluorescence lifetime measurement of 34 μ M 8-MOMOTQEN in DMF-H₂O (1:1) with 430 nm bandpath filter (BPF) at 25 °C ($\lambda_{\text{ex}} = 331$ nm).

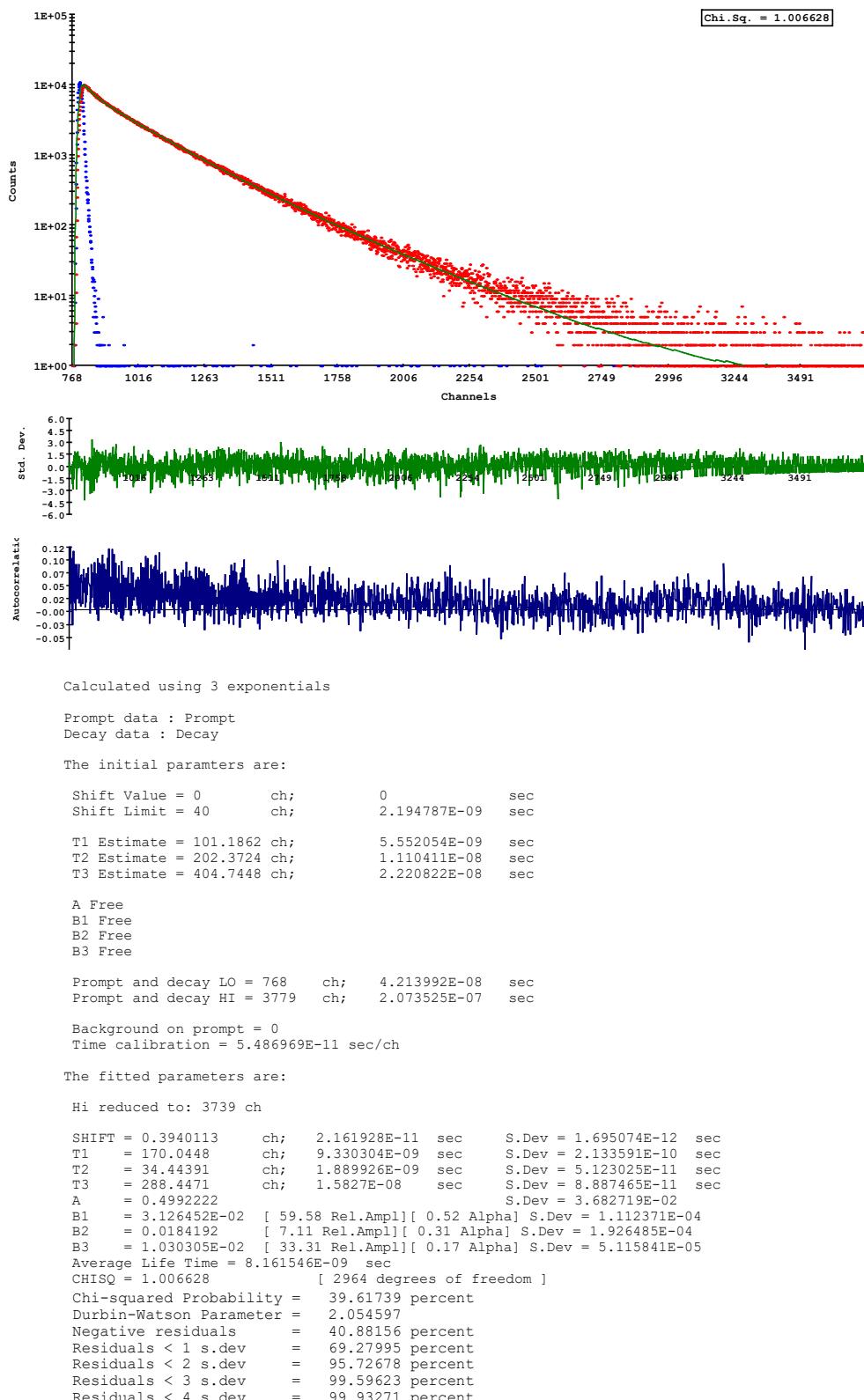


Fig. S17. Fluorescence lifetime measurement of 34 μM 8-MOMOTQEN in the presence of 1 equiv. of Cd^{2+} in DMF- H_2O (1:1) with 430 nm bandpath filter (BPF) at 25 °C ($\lambda_{\text{ex}} = 331$ nm).

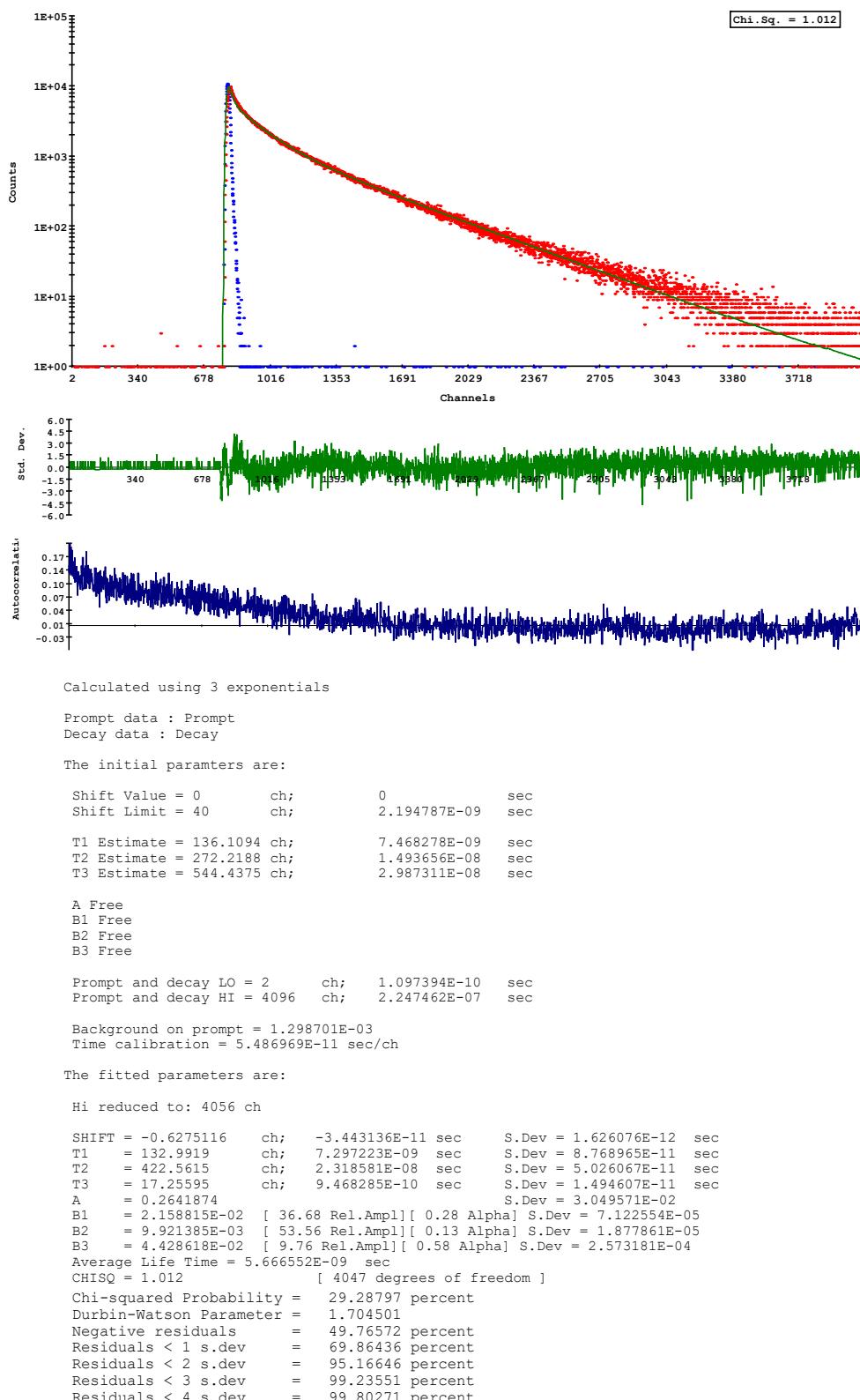


Fig. S18. Fluorescence lifetime measurement of 34 μ M 8-MOMOTQEN in the presence of 1 equiv. of Zn²⁺ in DMF-H₂O (1:1) with 460 nm bandpath filter (BPF) at 25 °C ($\lambda_{\text{ex}} = 331$ nm).

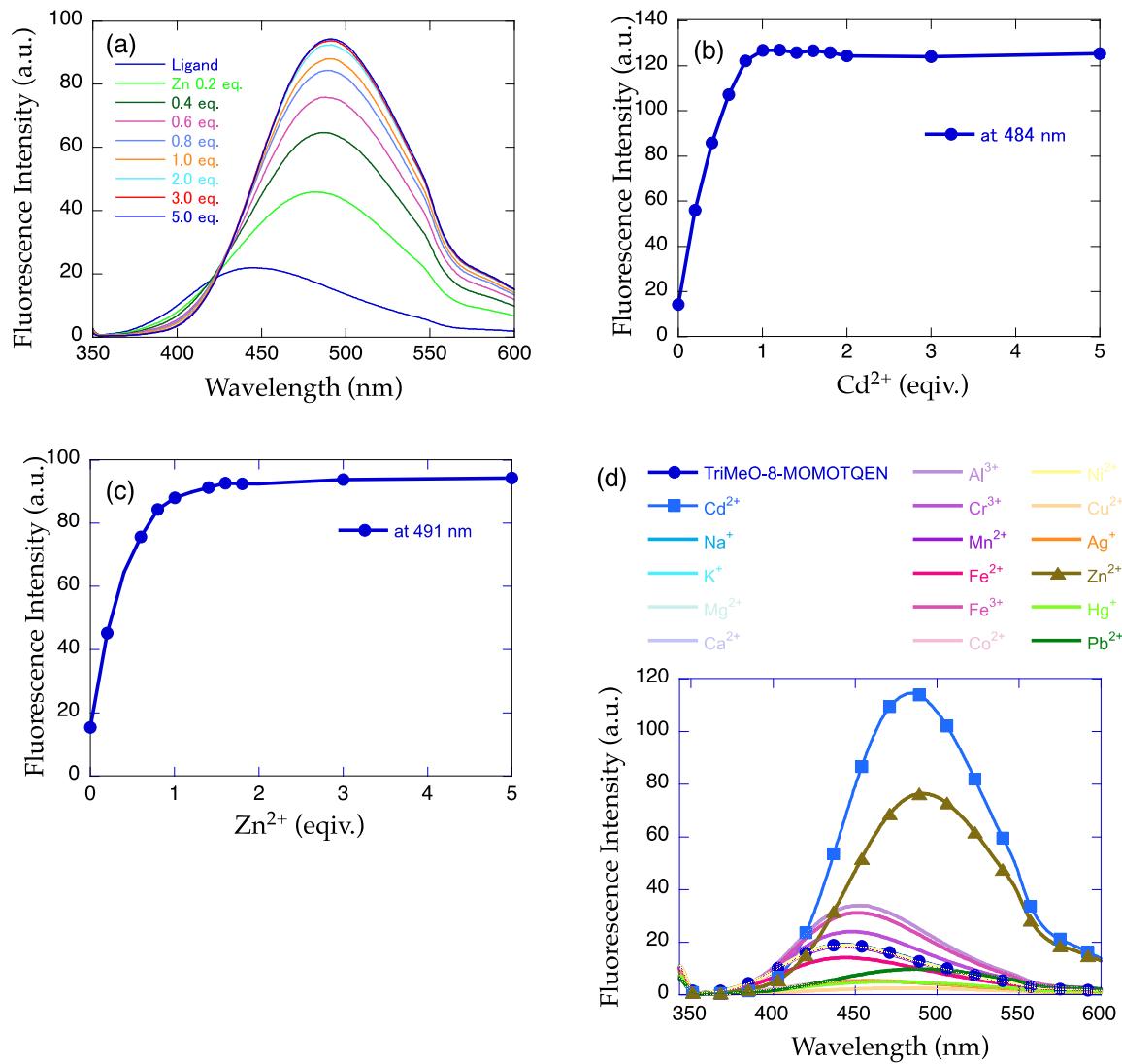


Fig. S19. (a) Fluorescence spectra of 34 μM TriMeO-8-MOMOTQEN in DMF- H_2O (1:1) at 25 °C in the presence of increasing amount of Zn^{2+} ($\lambda_{\text{ex}} = 343$ nm). (b,c) Plot of fluorescence intensity changes for (b) Cd^{2+} and (c) Zn^{2+} titration. (d) Fluorescence spectra in the presence of 1 equiv. of various metal ions.

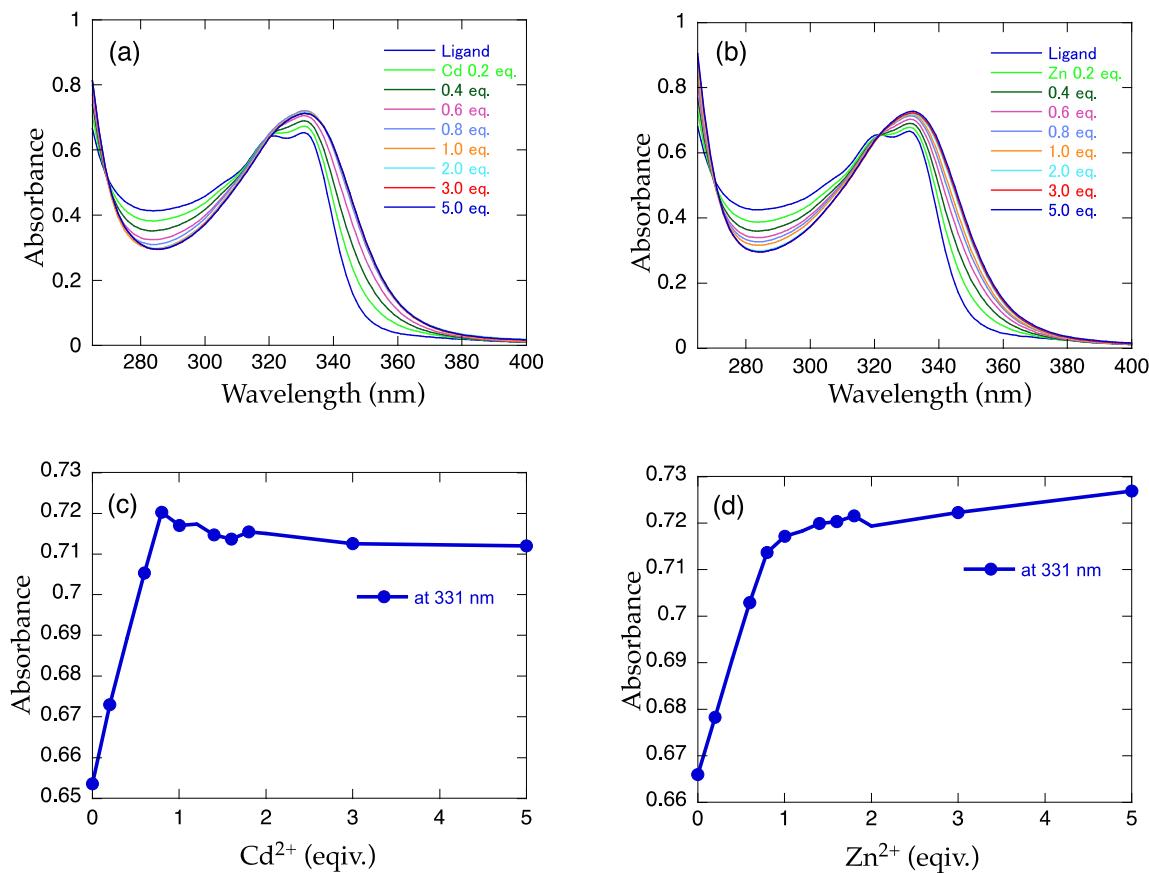


Fig. S20. (a,b) UV-vis absorption spectra of 34 μM TriMeO-8-MOMOTQEN in DMF-H₂O (1:1) at 25 °C in the presence of increasing amount of (a) Cd²⁺ and (b) Zn²⁺. (c,d) Plot of absorbance changes in the presence of increasing amount of (c) Cd²⁺ and (d) Zn²⁺.

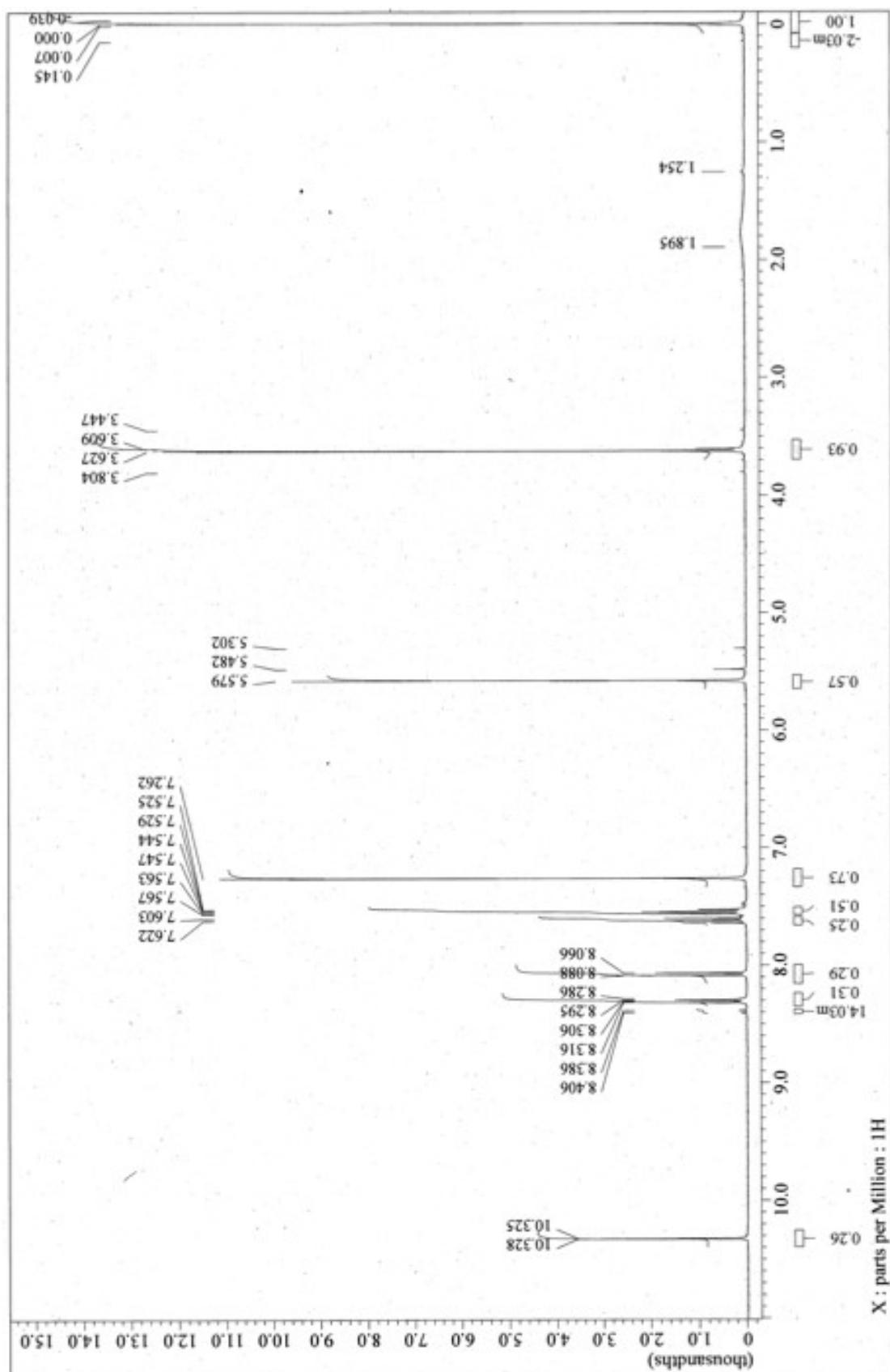


Fig. S21. ¹H NMR spectrum for 8-methoxymethoxy-2-quinolinecarboaldehyde (**1**) in CDCl_3 .

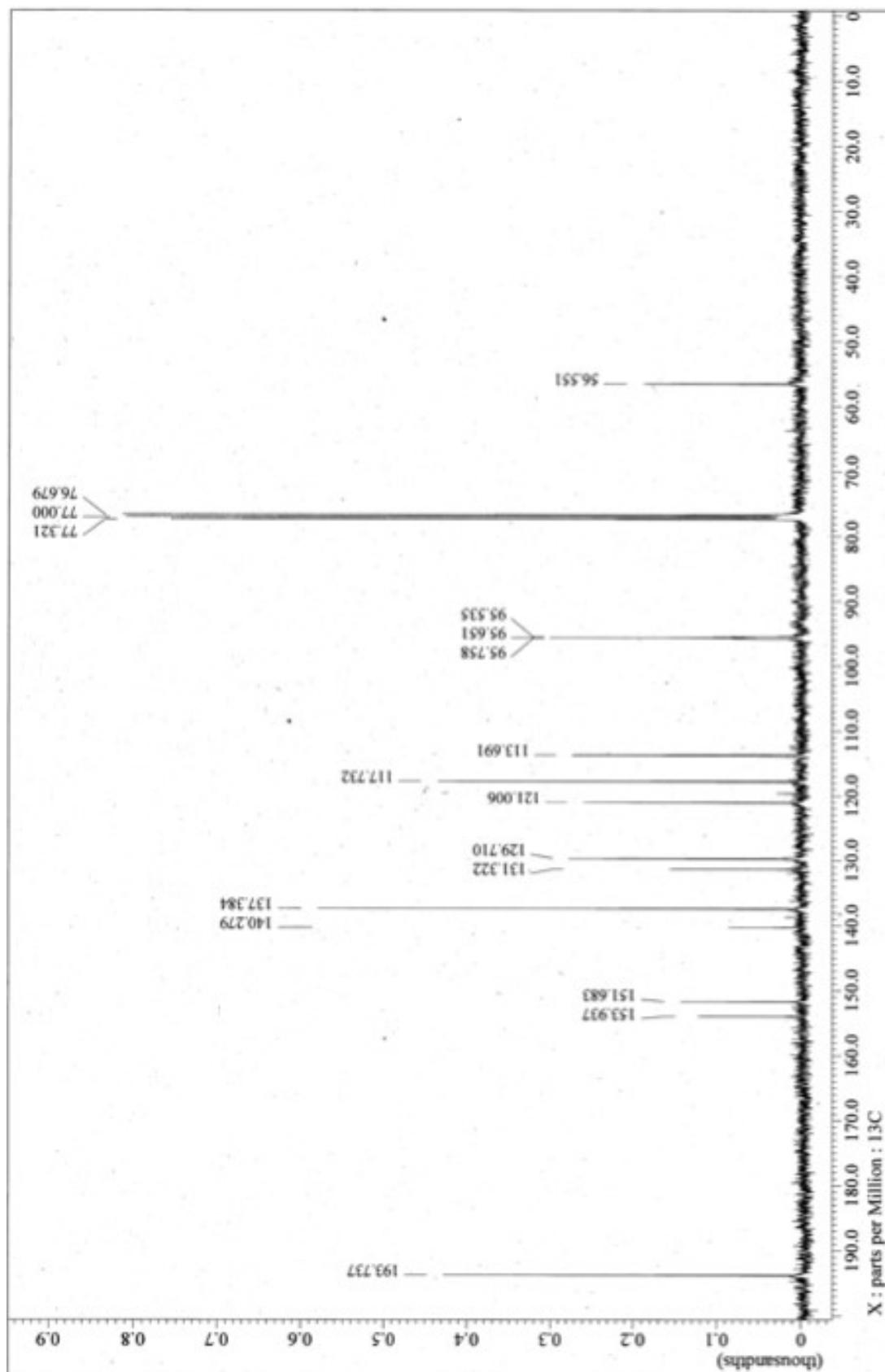


Fig. S22. ^{13}C NMR spectrum for 8-methoxymethoxy-2-quinolinecarboaldehyde (**1**) in CDCl_3 .

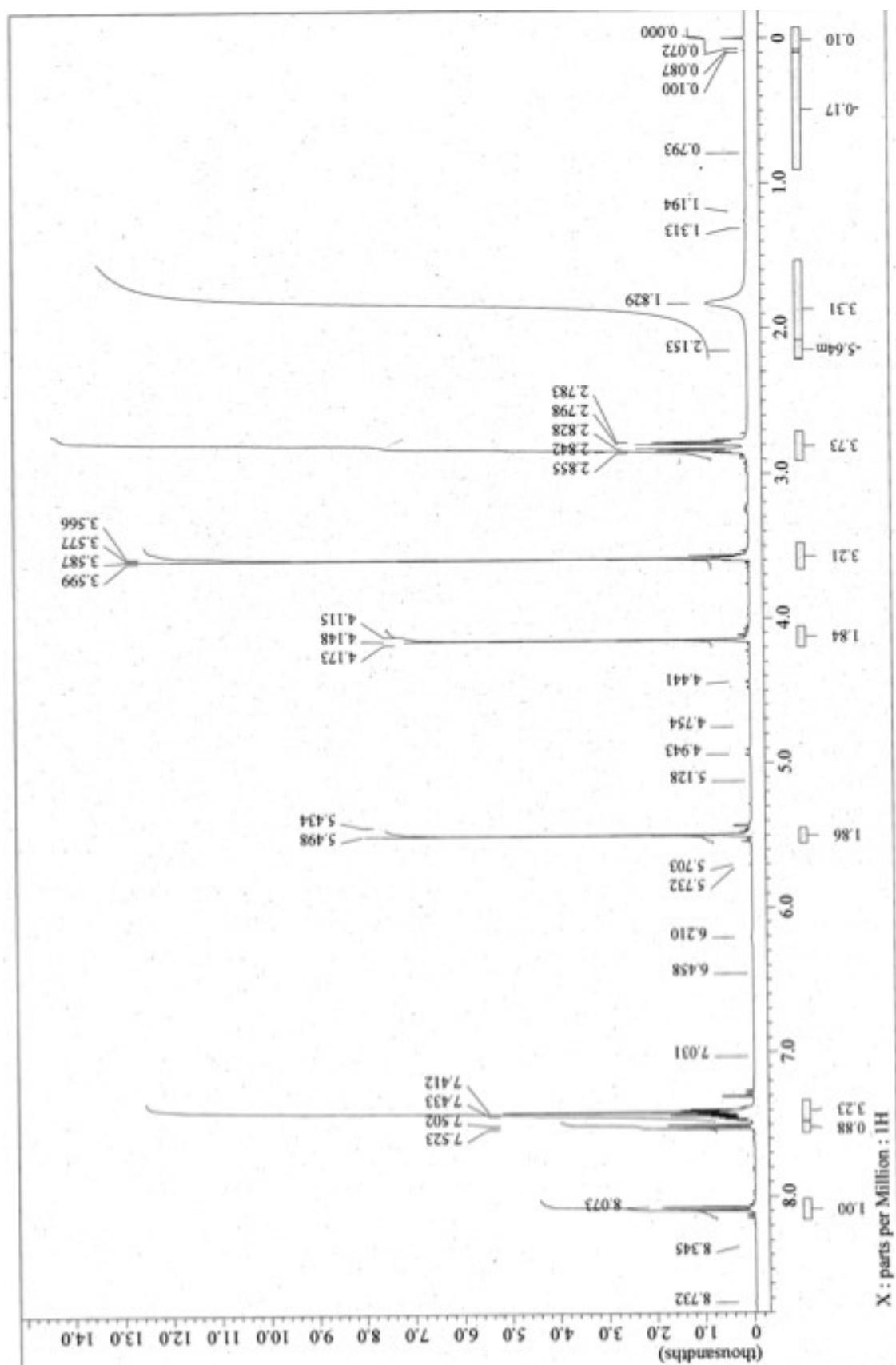


Fig. S23. ^1H NMR spectrum for *N*-(8-methoxymethoxy-2-quinolylmethyl)-ethylenediamine (**2**) in CDCl_3 .

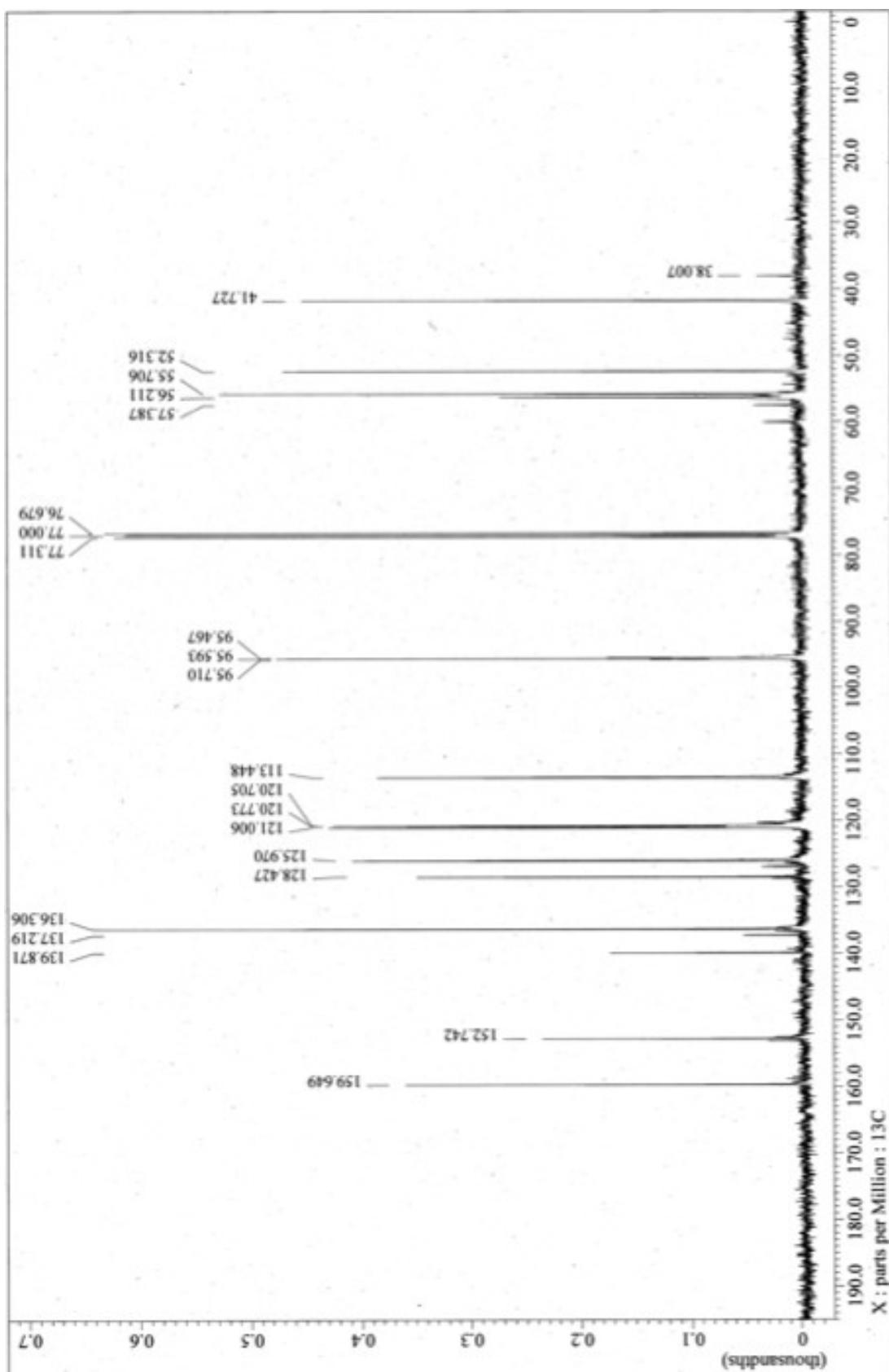


Fig. S24. ^{13}C NMR spectrum for *N*-(8-methoxymethoxy-2-quinolylmethyl)-ethylenediamine (**2**) in CDCl_3 .

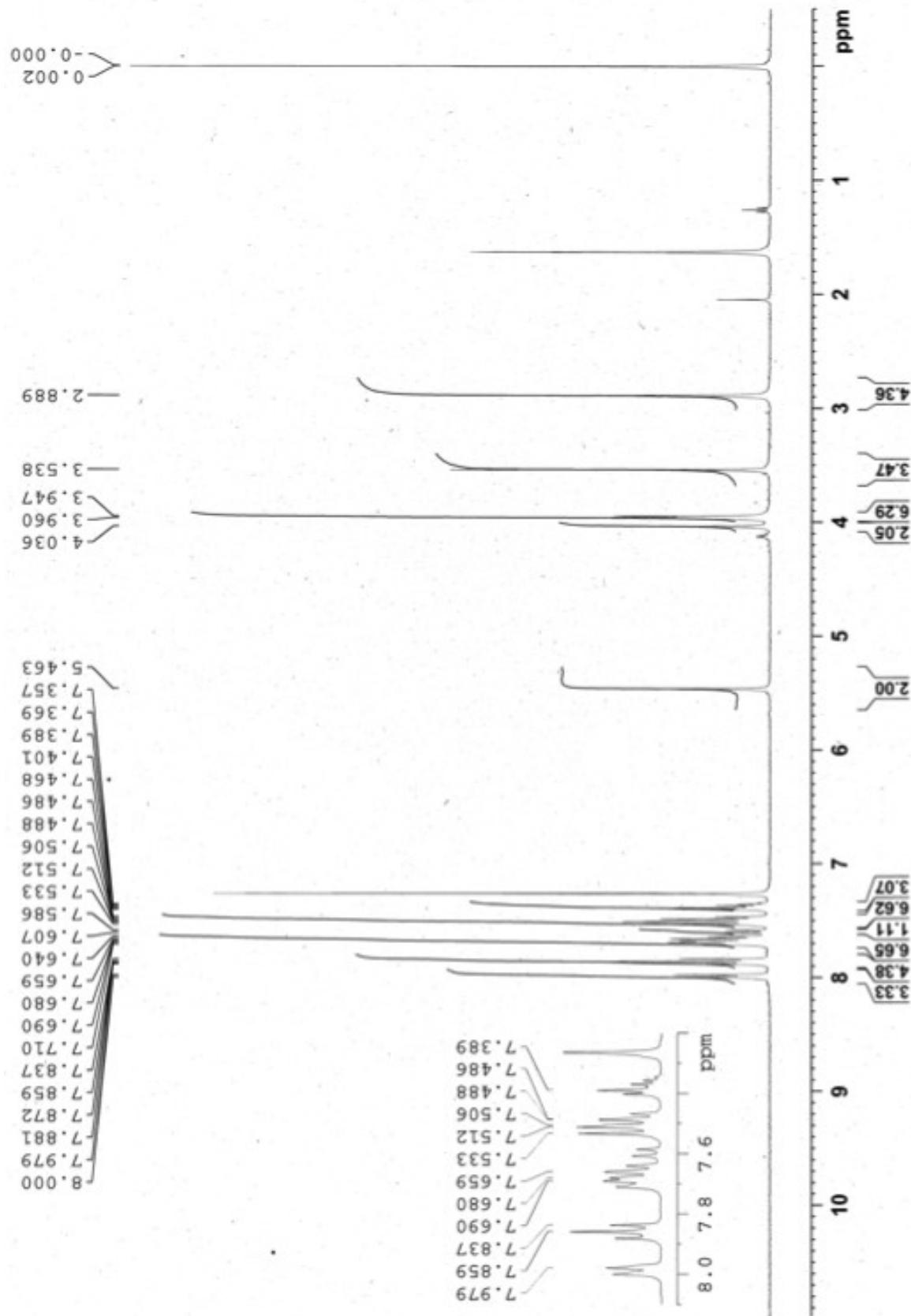


Fig. S25. ^1H NMR spectrum for 8-MOMOTQEN in CDCl_3 .

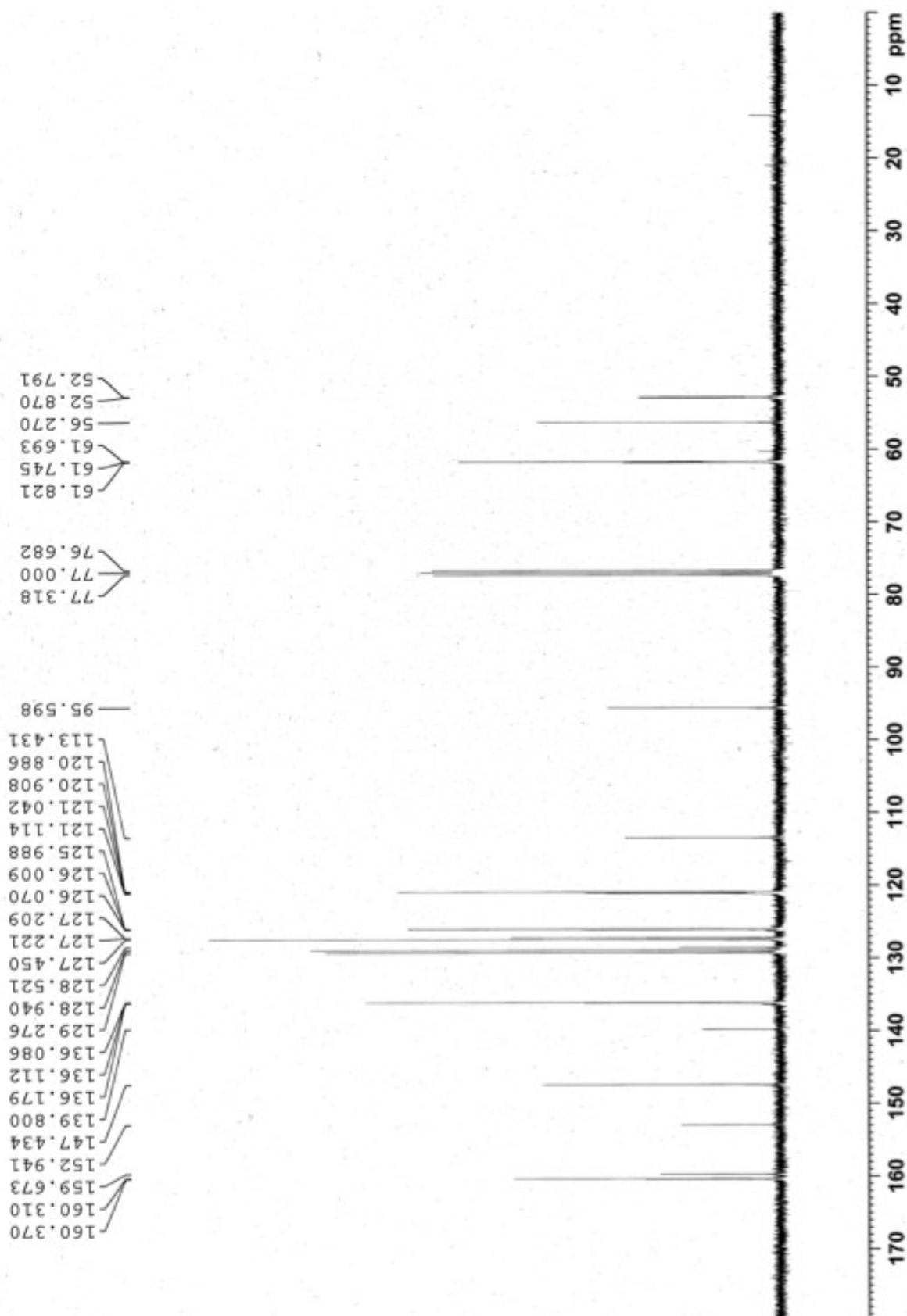


Fig. S26. ^{13}C NMR spectrum for 8-MOMOTQEN in CDCl_3 .

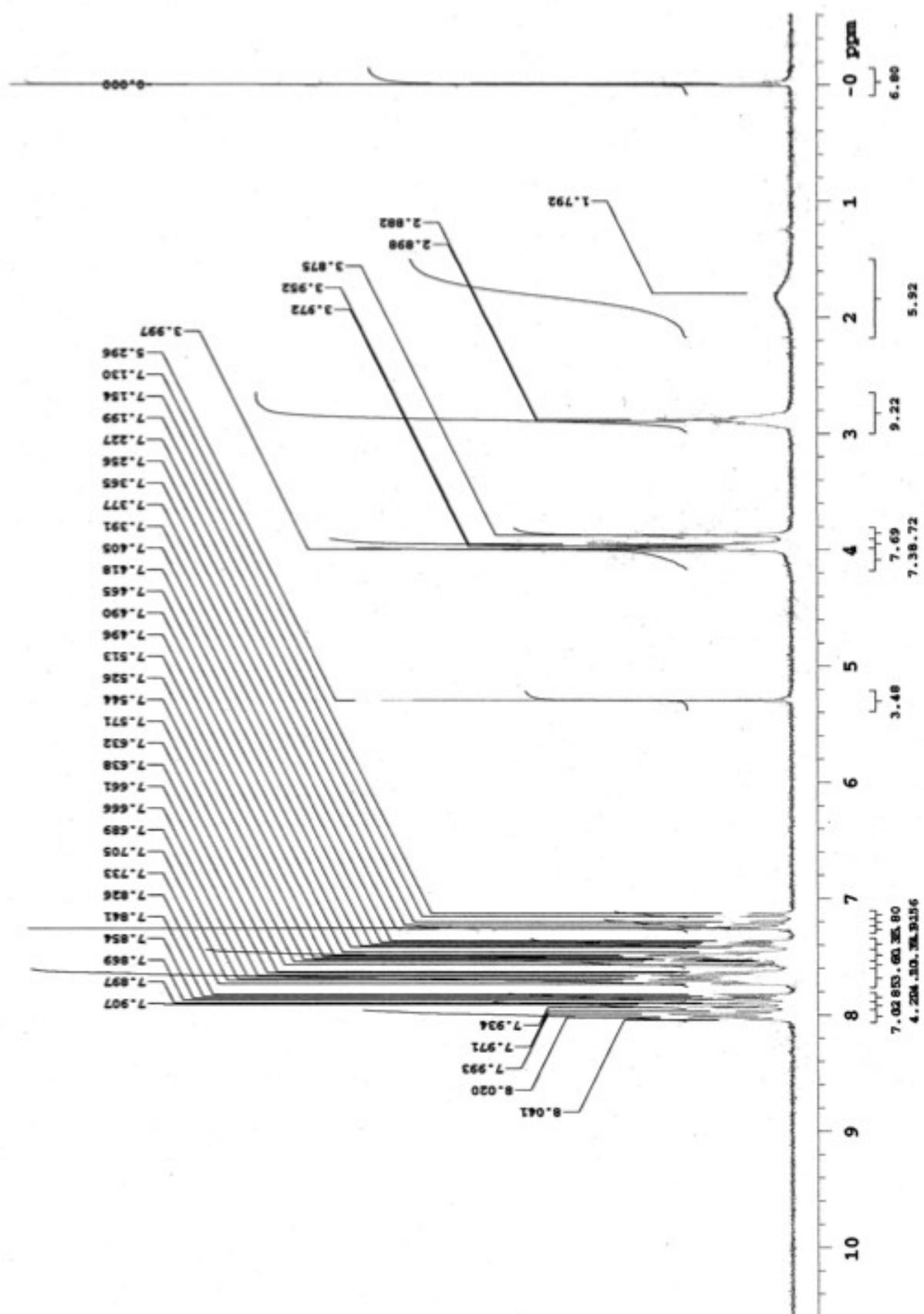


Fig. S27. ¹H NMR spectrum for 8-OHTQEN in CDCl₃.

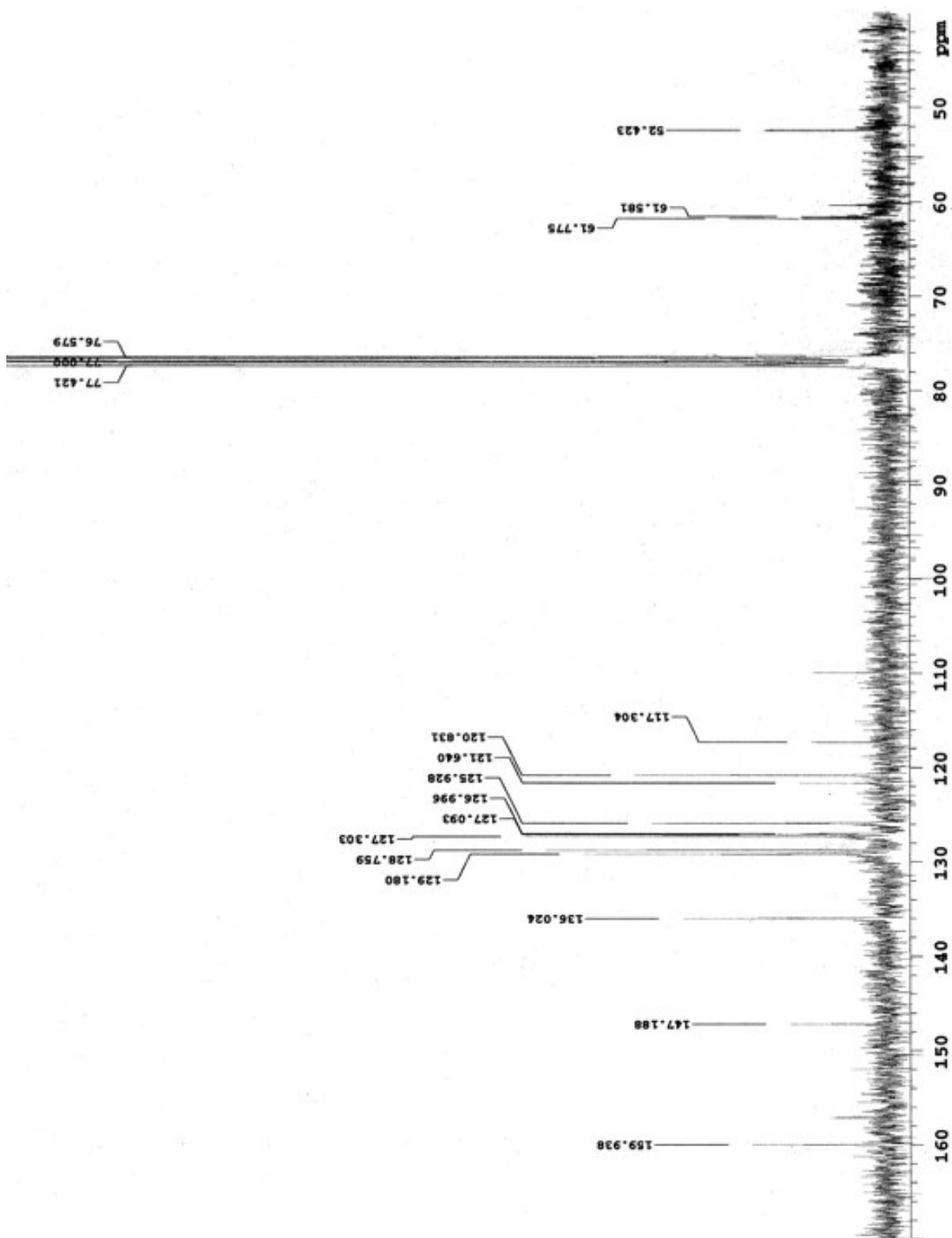


Fig. S28. ^{13}C NMR spectrum for 8-OHTQEN in CDCl_3 .

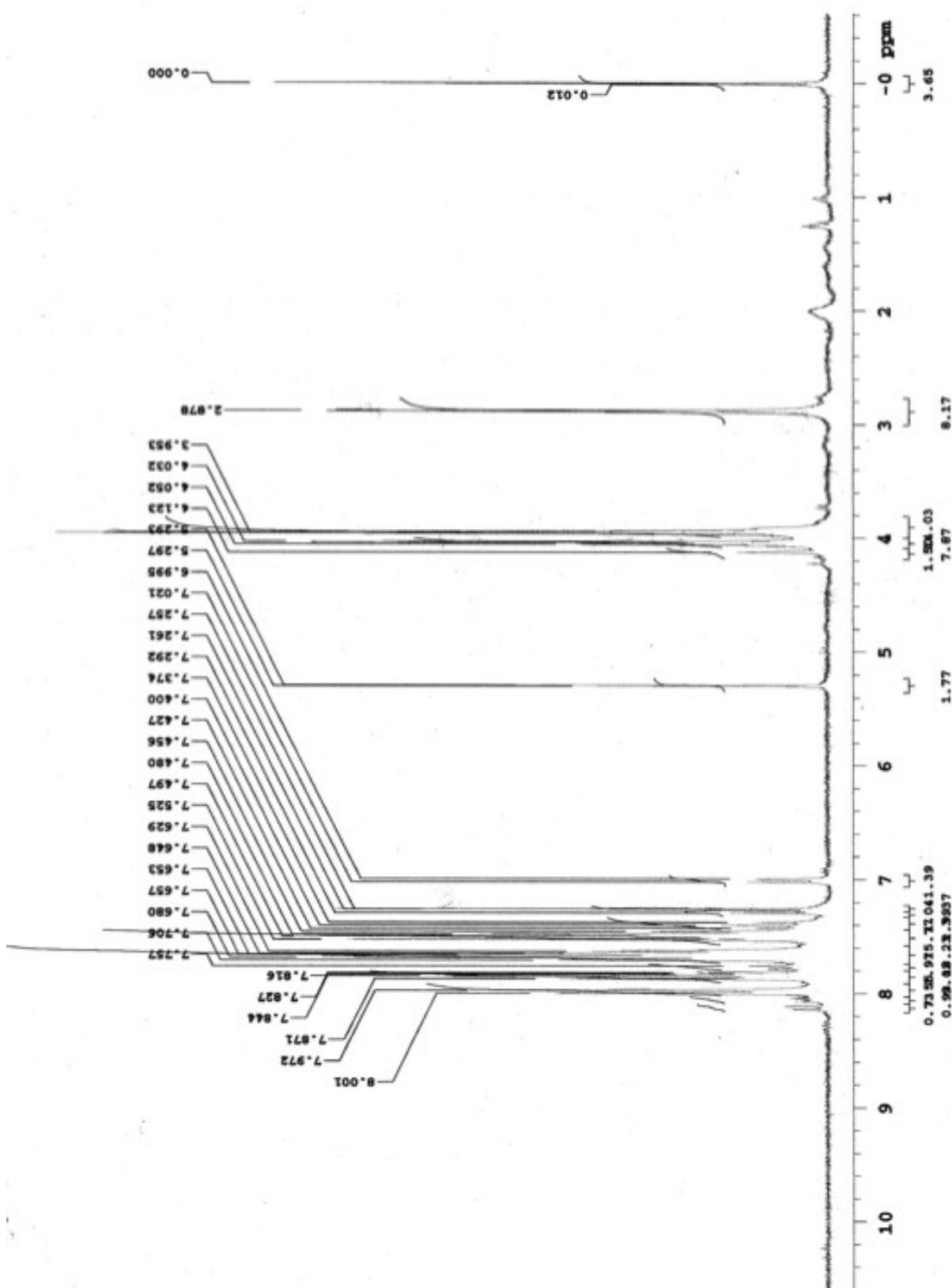


Fig. S29. ${}^1\text{H}$ NMR spectrum for 8-MeOTQEN in CDCl_3 .

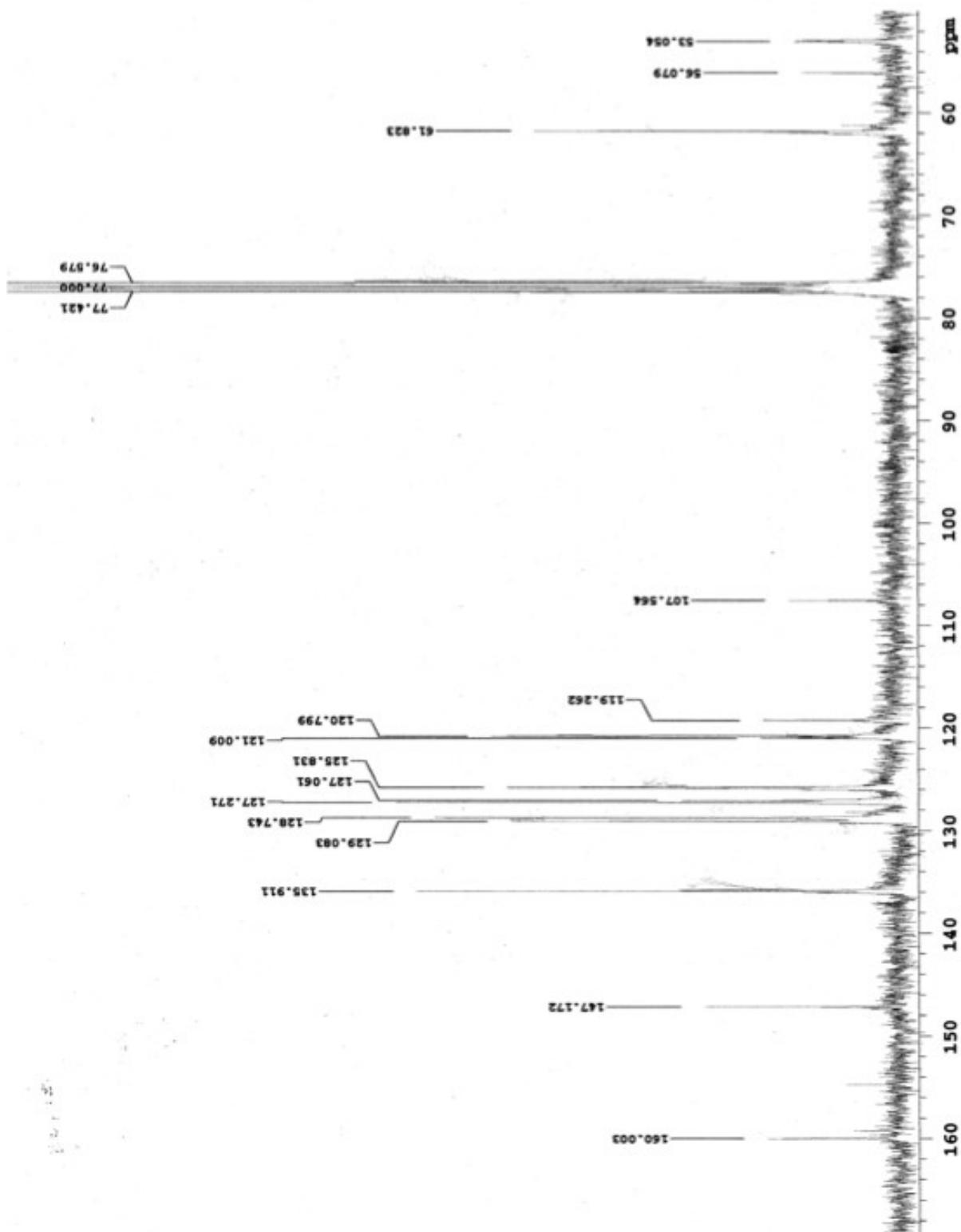


Fig. S30. ^{13}C NMR spectrum for 8-MeOTQEN in CDCl_3 .

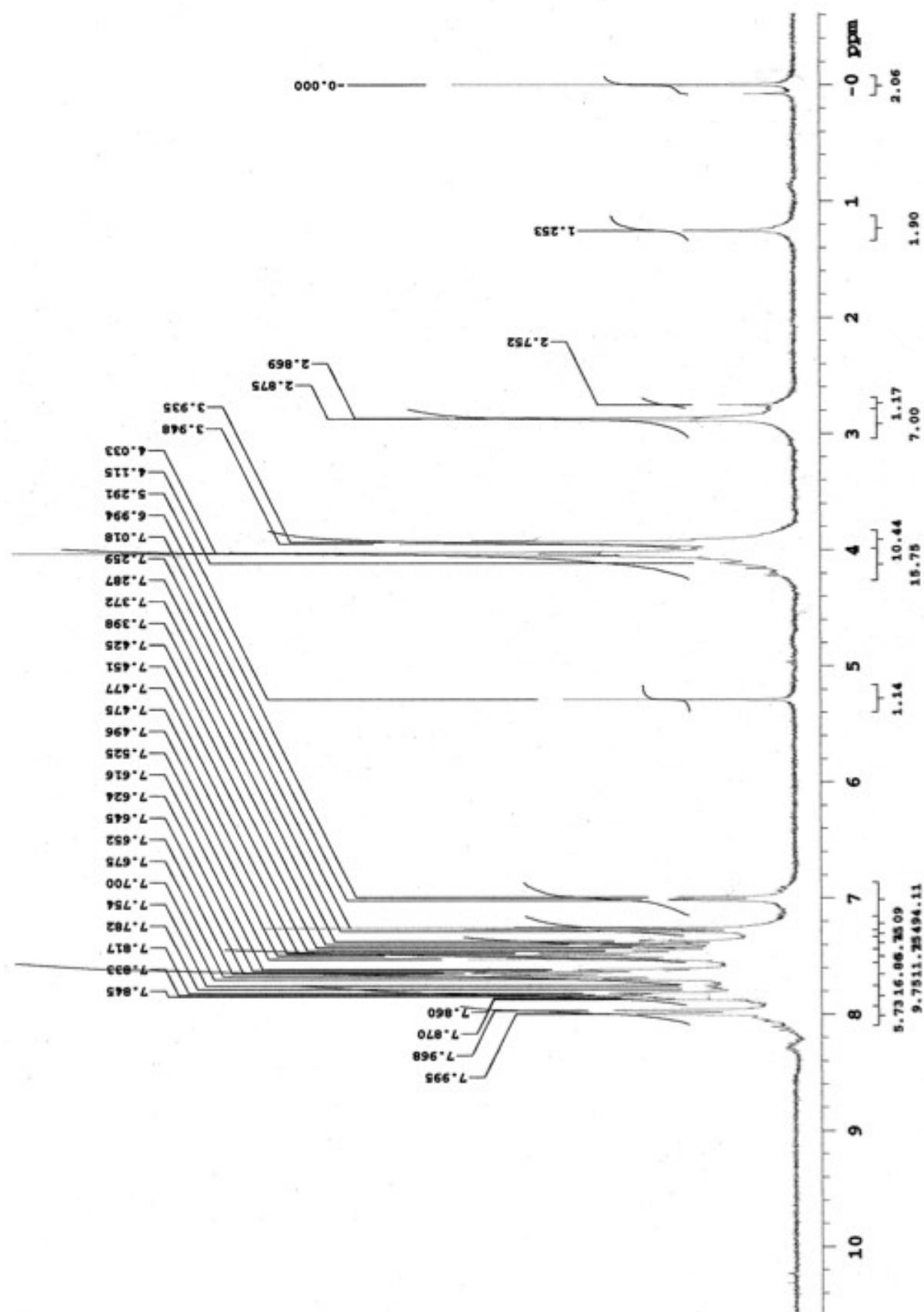


Fig. S31. ^1H NMR spectrum for $(8\text{-MeO})_2\text{TQEN}$ in CDCl_3 .

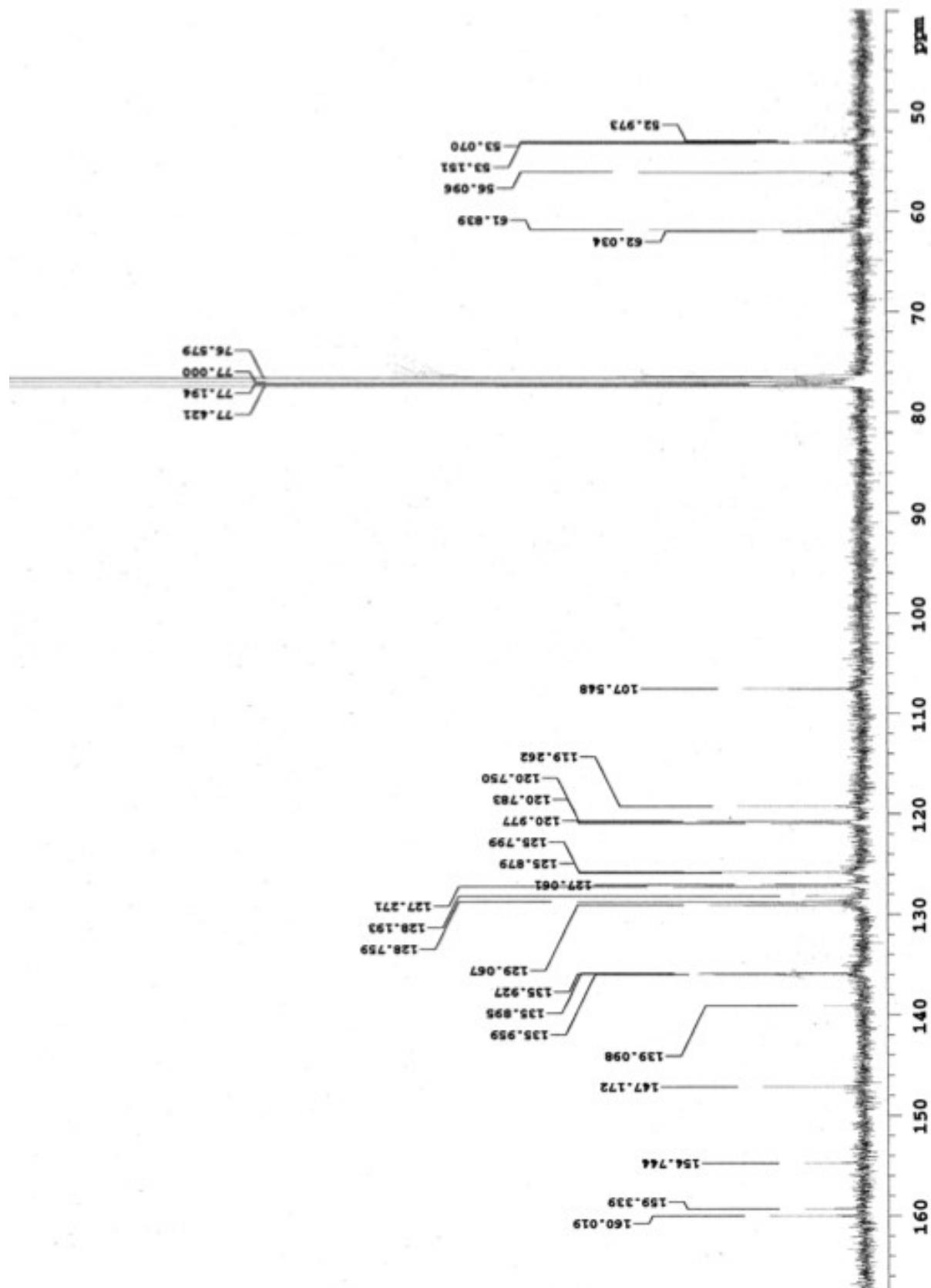


Fig. S32. ^{13}C NMR spectrum for $(8\text{-MeO})_2\text{TQEN}$ in CDCl_3 .

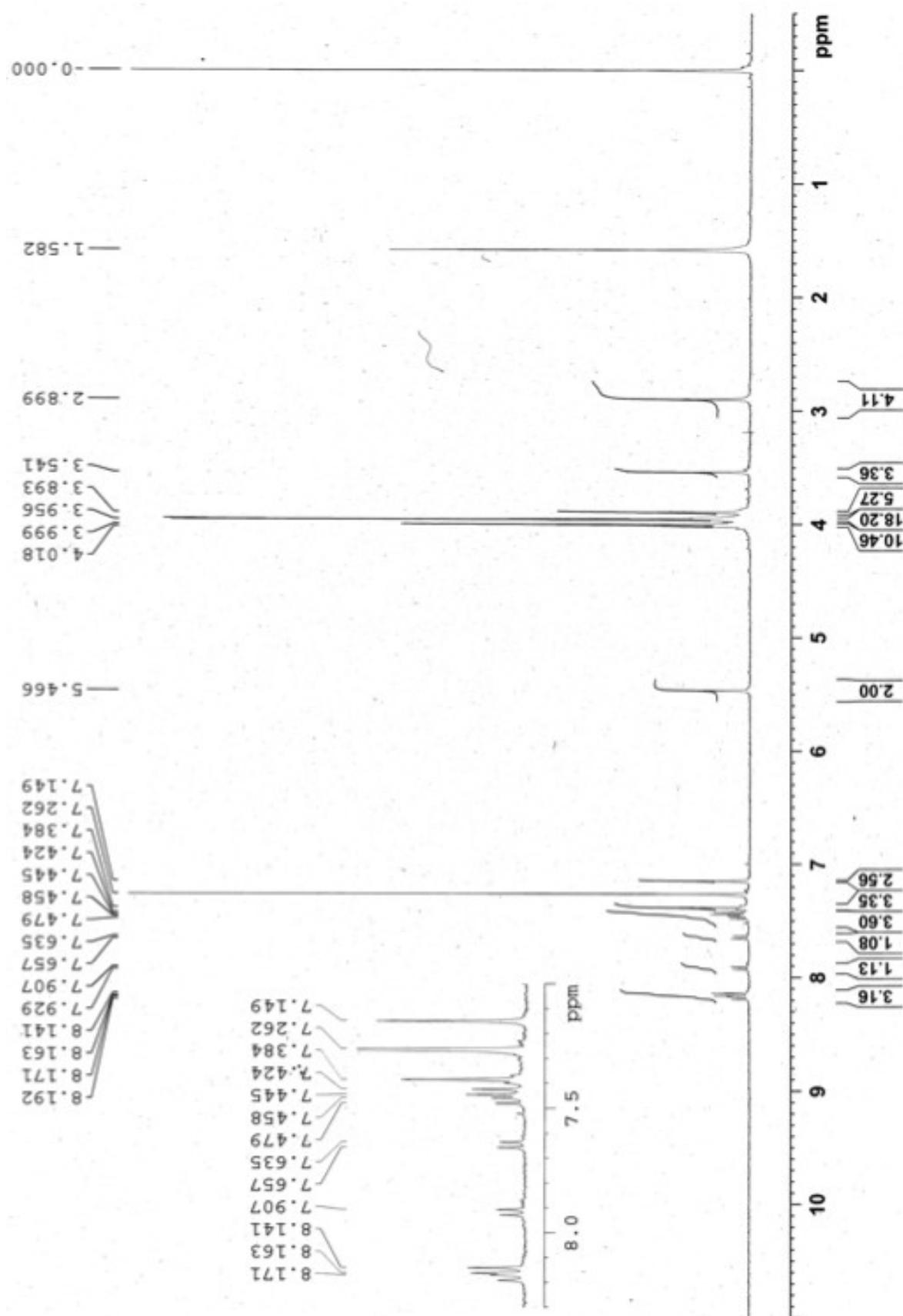


Fig. S33. ^1H NMR spectrum for TriMeO-8-MOMOTQEN in CDCl_3 .

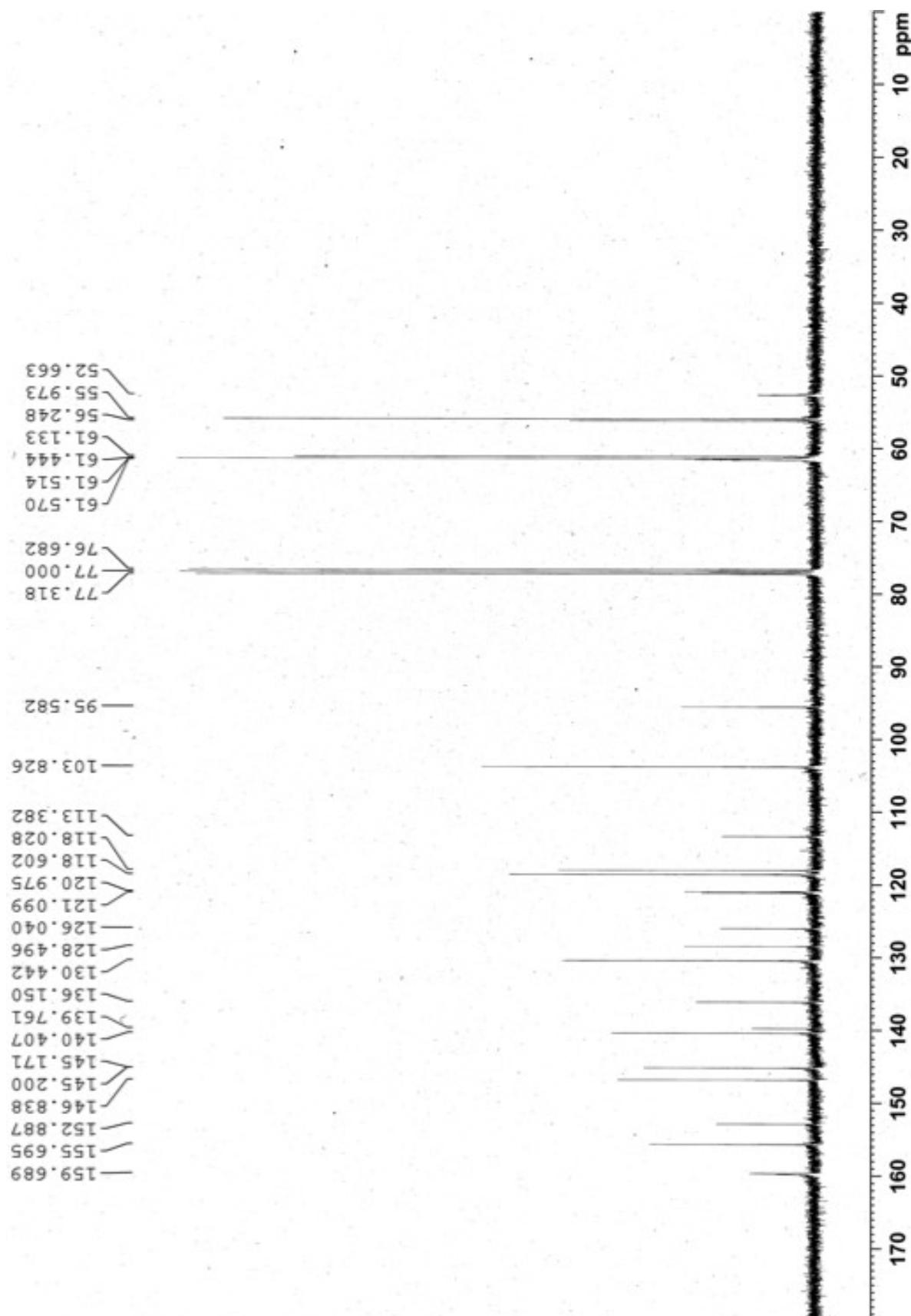


Fig. S34. ^{13}C NMR spectrum for TriMeO-8-MOMOTQEN in CDCl_3 .