Supplementary Information for

Quinoline-attached triazacyclononane(TACN) derivatives as fluorescent zinc sensors

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Table S1. Crystallographic Data for 6-MeOTQTACN (**5**), [Zn(6-MeOTQTACN)]$(ClO_4)_2$ (**5-Zn**) and [Cd(6-MeOTQTACN)]$(ClO_4)_2$ (**5-Cd**)

	6-MeOTQ-TACN·CH_3OH (**1**·CH_3OH)	[Zn(6-MeOTQ-TACN)]$(ClO_4)_2$ (**5-Zn**)	[Cd(6-MeOTQ-TACN)]$(ClO_4)_2$ (**5-Cd**)
Formula	$C_{40}H_{46}N_6O_4$	$C_{39}H_{42}Cl_2N_6O_{11}Zn$	$C_{39}H_{42}CdCl_2N_6O_{11}$
FW	674.84	907.08	954.11
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/c$
a, Å	10.257(2)	9.7431(4)	21.944(6)
b, Å	13.830(3)	37.9514(11)	9.938(3)
c, Å	13.985(3)	11.4609(4)	18.534(5)
α, deg	68.153(7)	90	90
β, deg	71.191(7)	112.976(2)	107.020(3)
γ, deg	80.492(9)	90	90
V, Å^3	1740.8(6)	3901.6(3)	3865(2)
Z	2	4	4
D_{calc}, g cm^{-3}	1.287	1.544	1.640
μ, mm^{-1}	0.0845	0.8371	0.7753
$2\theta_{max}$, deg	55	55	55
temp, K	123	123	123
no. reflns collected	13703	33276	29253
no. reflns used	7595	8893	8768
no. of params	619	727	700
R_{int}	0.0215	0.0240	0.0425
Final *R*1 ($I > 2\sigma(I)$)[a]	0.0744	0.0391	0.0563
*wR*2 (all data)[b]	0.2269	0.0953	0.1595
GOF	1.055	1.069	1.168

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

Table S2. Crystallographic Data for [Zn(1-isoTQTACN)]$(ClO_4)_2 \cdot CH_3OH$ (**6-Zn** $\cdot CH_3OH$) and [Cd(1-isoTQTACN)]$(ClO_4)_2 \cdot 0.5CH_3OH$ (**6-Cd** $\cdot 0.5CH_3OH$)

	[Zn(1-isoTQTACN)]-$(ClO_4)_2 \cdot CH_3OH$ (**6-Zn** $\cdot CH_3OH$)	[Cd(1-isoTQTACN)]-$(ClO_4)_2 \cdot 0.5CH_3OH$ (**6-Cd** $\cdot 0.5CH_3OH$)
Formula	$C_{37}H_{40}Cl_2N_6O_9Zn$	$C_{36.5}H_{38}CdCl_2N_6O_{8.5}$
FW	849.04	880.05
Crystal system	orthorhombic	triclinic
Space group	*Pbca*	*P*-1
a, Å	7.721(3)	11.370(2)
b, Å	19.269(3)	16.276(3)
c, Å	21.462(3)	22.279(3)
α, deg	90	69.744(3)
β, deg	90	75.434(3)
γ, deg	90	88.391(5)
V, Å^3	7328(2)	3735.6(9)
Z	8	4
D_{calc}, g cm^{-3}	1.539	1.565
μ, mm^{-1}	0.8816	0.7901
$2\theta_{max}$, deg	55	55
temp, K	123	173
no. reflns collected	54863	37386
no. reflns used	8393	16828
no. of params	649	1027
R_{int}	0.0456	0.0227
Final *R*1 ($I > 2\sigma(I)$)[a]	0.0596	0.0517
*wR*2 (all data)[b]	0.1410	0.1517
GOF	1.169	1.075

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

Table S3. Crystallographic Data for [Cd(6-MeOTQEN)]$(ClO_4)_2 \cdot 2CH_3OH$ (**2-Cd** $\cdot 2CH_3OH$)

	[Cd(6-MeOTQEN)]$(ClO_4)_2 \cdot 2CH_3OH$ (**2-Cd** $\cdot 2CH_3OH$)
Formula	$C_{48}H_{52}CdCl_2N_6O_{14}$
FW	1120.29
Crystal system	orthorhombic
Space group	*P*-1
a, Å	11.006(2)
b, Å	11.191(2)
c, Å	20.600(4)
α, deg	78.273(5)
β, deg	79.581(5)
γ, deg	74.864(5)
V, Å^3	2376.2(7)
Z	2
D_{calc}, g cm^{-3}	1.566
μ, mm^{-1}	0.6479
$2\theta_{max}$, deg	55
temp, K	153
no. reflns collected	23551
no. reflns used	10707
no. of params	828
R_{int}	0.0176
Final *R*1 ($I > 2\sigma(I)$)[a]	0.0408
*wR*2 (all data)[b]	0.1137
GOF	1.063

[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 S4. Selected Bond Distances for Zinc and Cadmium Complexes with 6-MeOTQTACN (**5**) and 1-isoTQTACN (**6**) in the Crystal Structure

	[Zn(6-MeO-TQTACN)]-$(ClO_4)_2$ (**5-Zn**)	[Cd(6-MeO-TQTACN)]-$(ClO_4)_2$ (**5-Cd**)	[Zn(1-isoTQ-TACN)$(ClO_4)_2$·CH_3OH (**6-Zn**·CH_3OH)	[Cd(1-isoTQ-TACN]$(ClO_4)_2$·$0.5CH_3OH$ (**6-Cd**·$0.5CH_3OH$)
M-N1[a]	2.2227(19)	2.417(4)	2.205(3)	2.359(4), 2.402(4)
M-N2[a]	2.2260(17)	2.370(4)	2.212(3)	2.366(4), 2.379(4)
M-N3[a]	2.1853(15)	2.387(4)	2.175(3)	2.392(3), 2.354(4)
Mean M-$N_{aliphatic}$	2.211	2.391(0.180)[c]	2.197	2.375(0.178)[c]
M-N4[b]		2.2085(13)	2.307(4)	2.146(3) 2.284(3), 2.275(3)
M-N5[b]		2.196(2)	2.335(4)	2.120(3) 2.290(3), 2.288(4)
M-N6[b]		2.2357(17)	2.342(5)	2.163(3) 2.316(4), 2.305(4)
Mean M-$N_{aromatic}$	2.213	2.328(0.115)[c]	2.143	2.293(0.150)[c]

[a] Aliphatic nitrogen atoms.

[b] Aromatic nitrogen atoms.

[c] Values in parentheses indicate the difference between zinc and cadmium complexes.

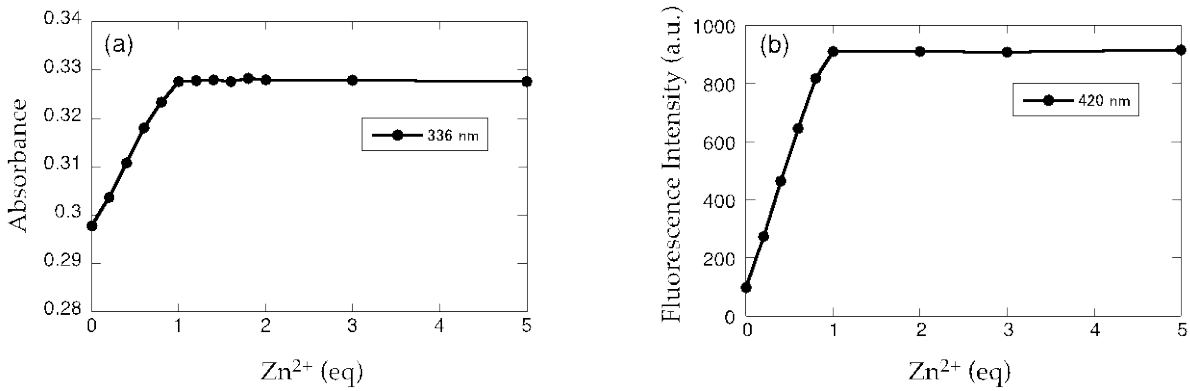

Figure S1. Zinc titration profile for 34 μM 6-MeOTQTACN (**5**) in DMF/H_2O (1:1) at 25 °C. (a) UV-vis absorbance changes at 322 and 334 nm. (b) Fluorescence intensity changes (λ_{ex} = 341 nm) at 420 nm.

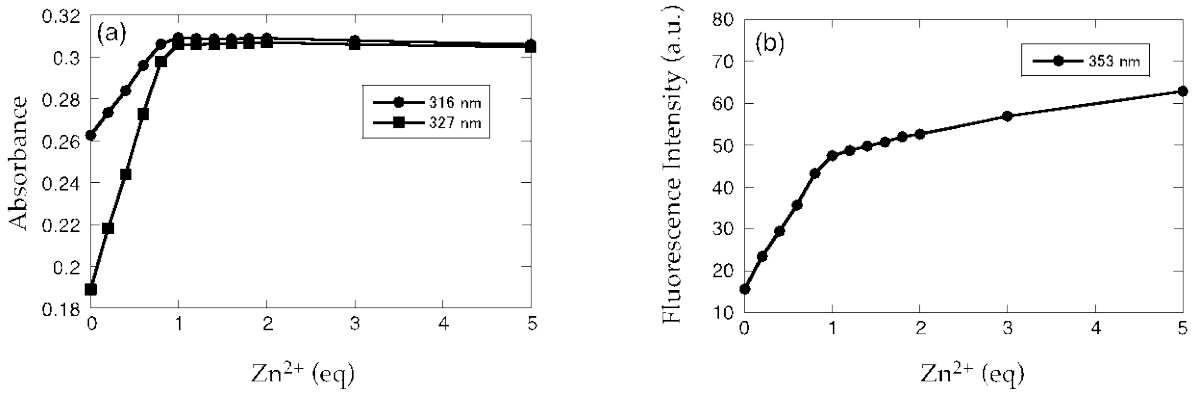

Figure S2. Zinc titration profile for 34 μM 1-isoTQTACN (**6**) in DMF/H_2O (1:1) at 25 °C. (a) UV-vis absorbance changes at 316 and 327 nm. (b) Fluorescence intensity changes (λ_{ex} = 327 nm) at 353 nm.

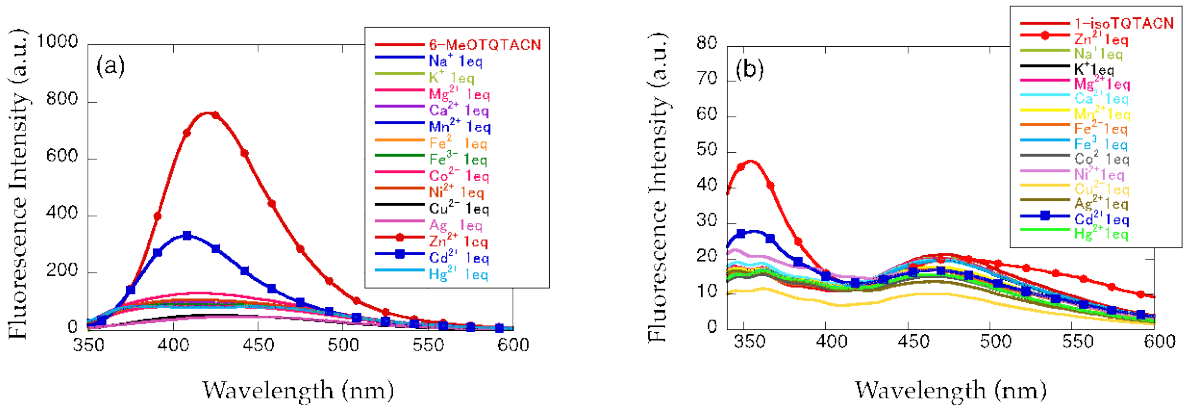

Figure S3. Comparison of fluorescence spectra of 34 μM (a) 6-MeOTQTACN (**5**) (λ_{ex} = 341 nm) and (b) 1-isoTQTACN (**6**) (λ_{ex} = 327 nm) in DMF/H_2O (1:1) at 25 °C in the presence of 1 equivalent of zinc (red, circles), cadmium (blue, squares) and other metal ions (various colors, no marks).

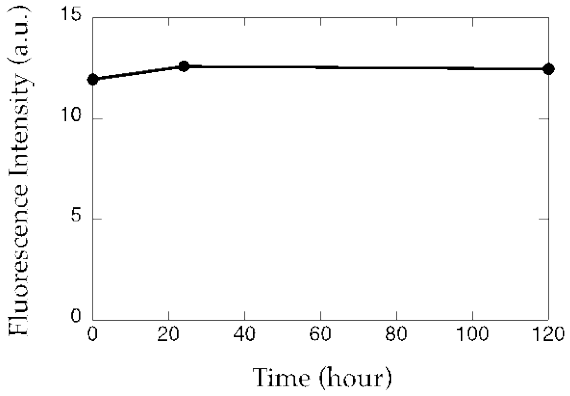

Figure S4. Fluorescence intensity change of 34 μM TQTACN-Zn complex (**4-Zn**) at 388 nm (λ_{ex} = 317 nm) in the presence of one equivalent of TPEN in DMF/H_2O (1:1) at 25 °C.

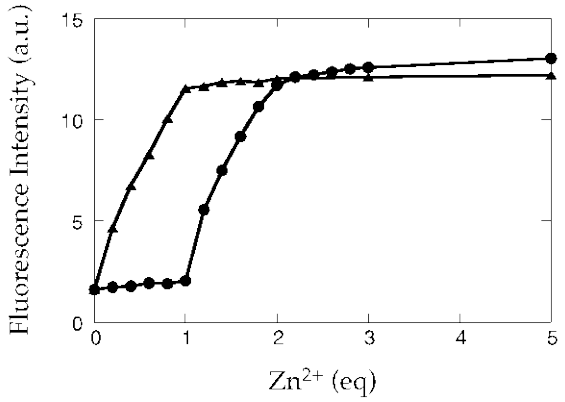

Figure S5. Competitive fluorescence intensity change of 34 μM TQTACN (**4**) at 388 nm (λ_{ex} = 317 nm) in the presence (circle) and absence (triangles) of one equivalent of TPEN with increasing amount of zinc in DMF/H_2O (1:1) at 25 °C.

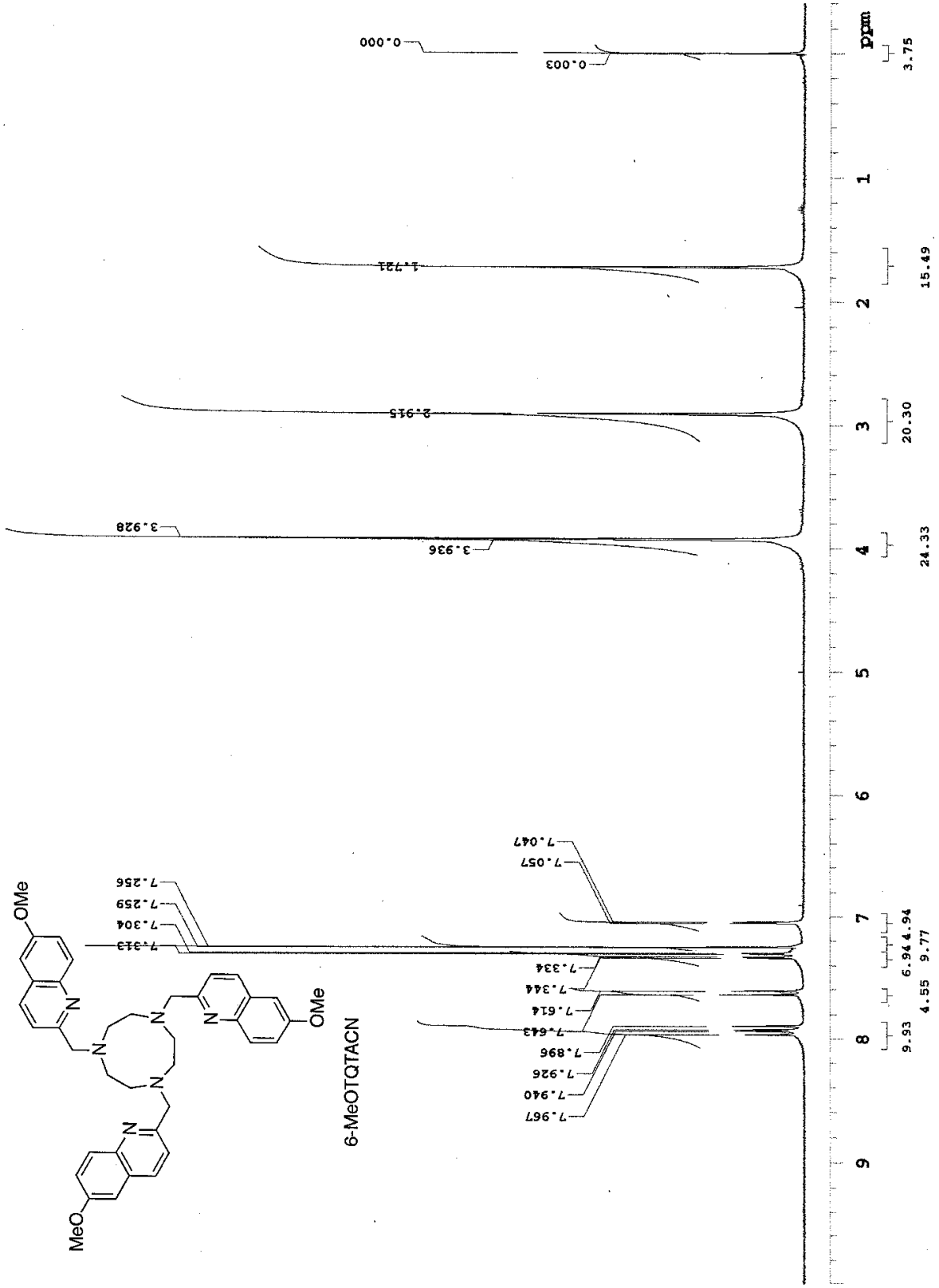

Figure S6. ^{1}H NMR spectrum of 6-MeOTQTACN (**5**) in $CDCl_3$.

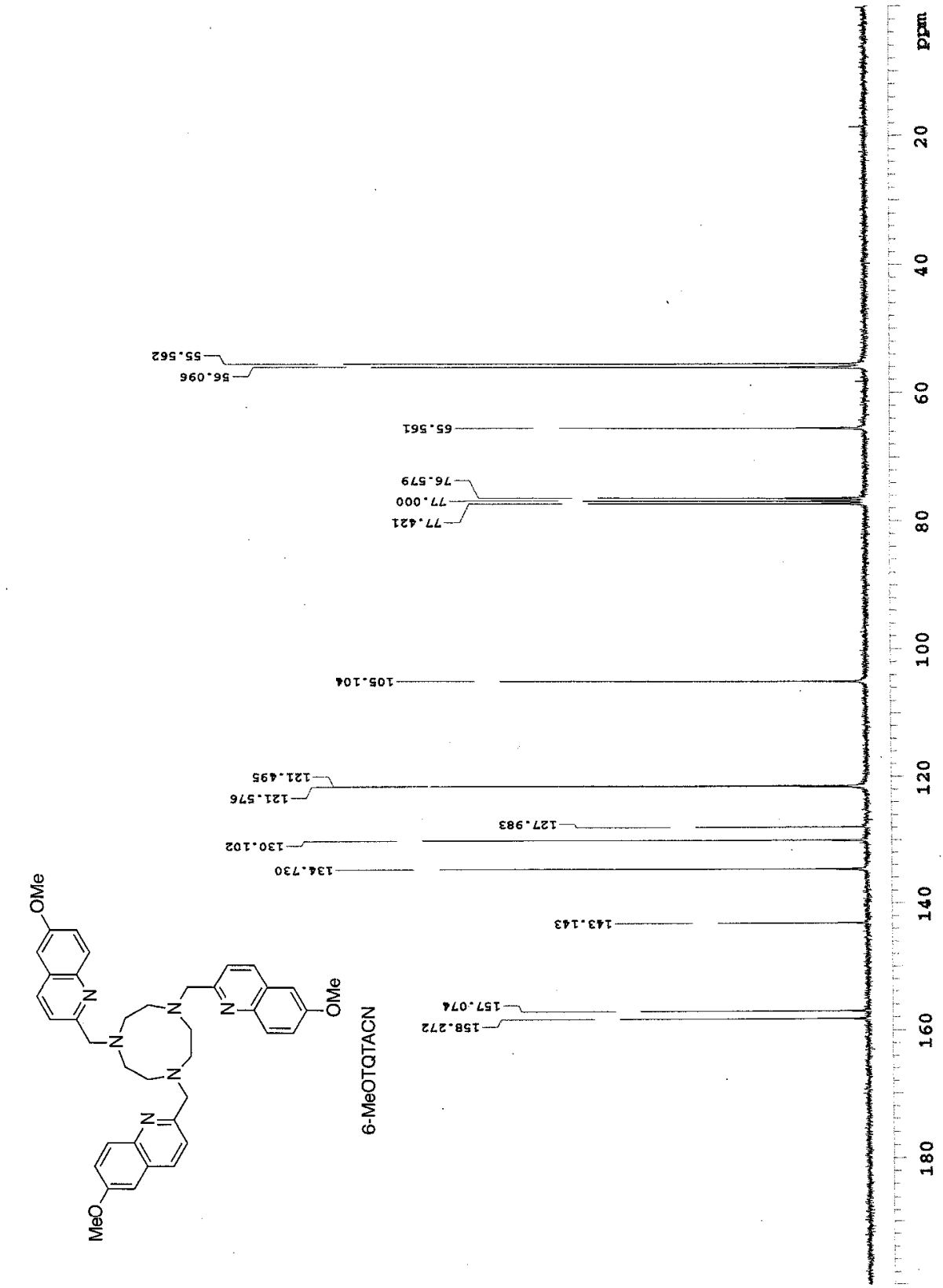

Figure S7. ^{13}C NMR spectrum of 6-MeOTQTACN (**5**) in $CDCl_3$.

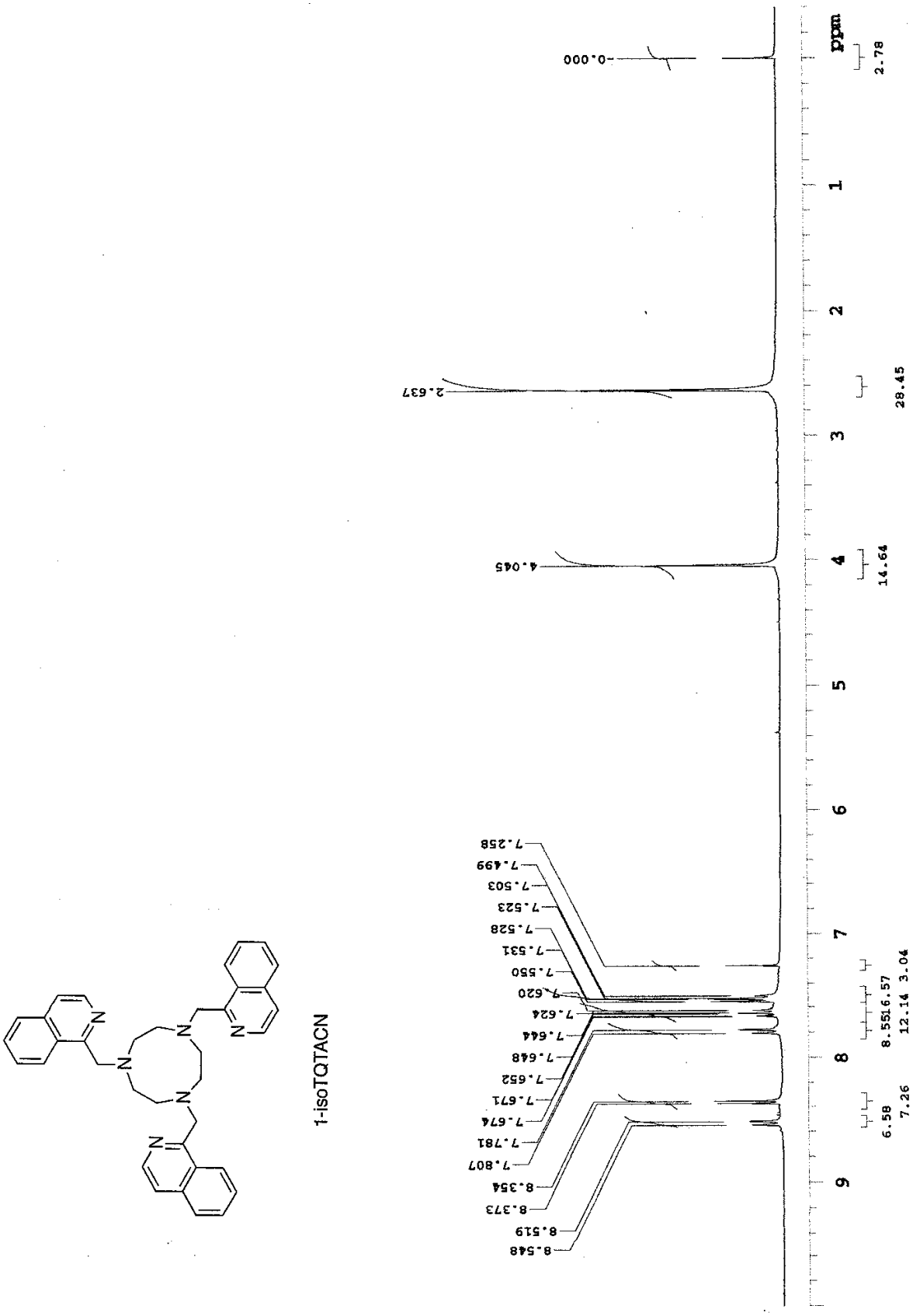

Figure S8. ^{1}H NMR spectrum of 1-isoTQTACN (**6**) in $CDCl_3$.

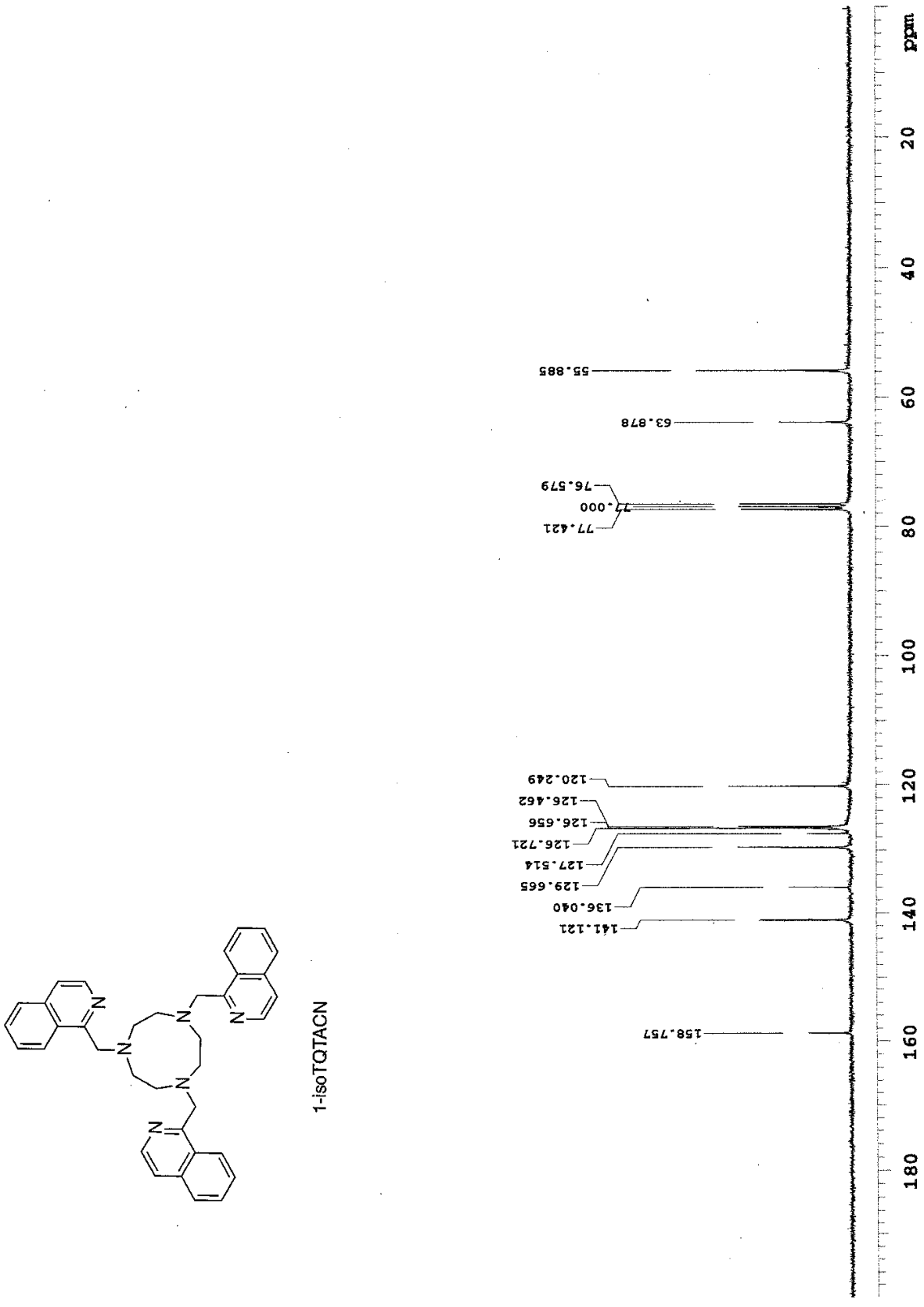

Figure S9. ^{13}C NMR spectrum of 1-isoTQTACN (**6**) in $CDCl_3$.

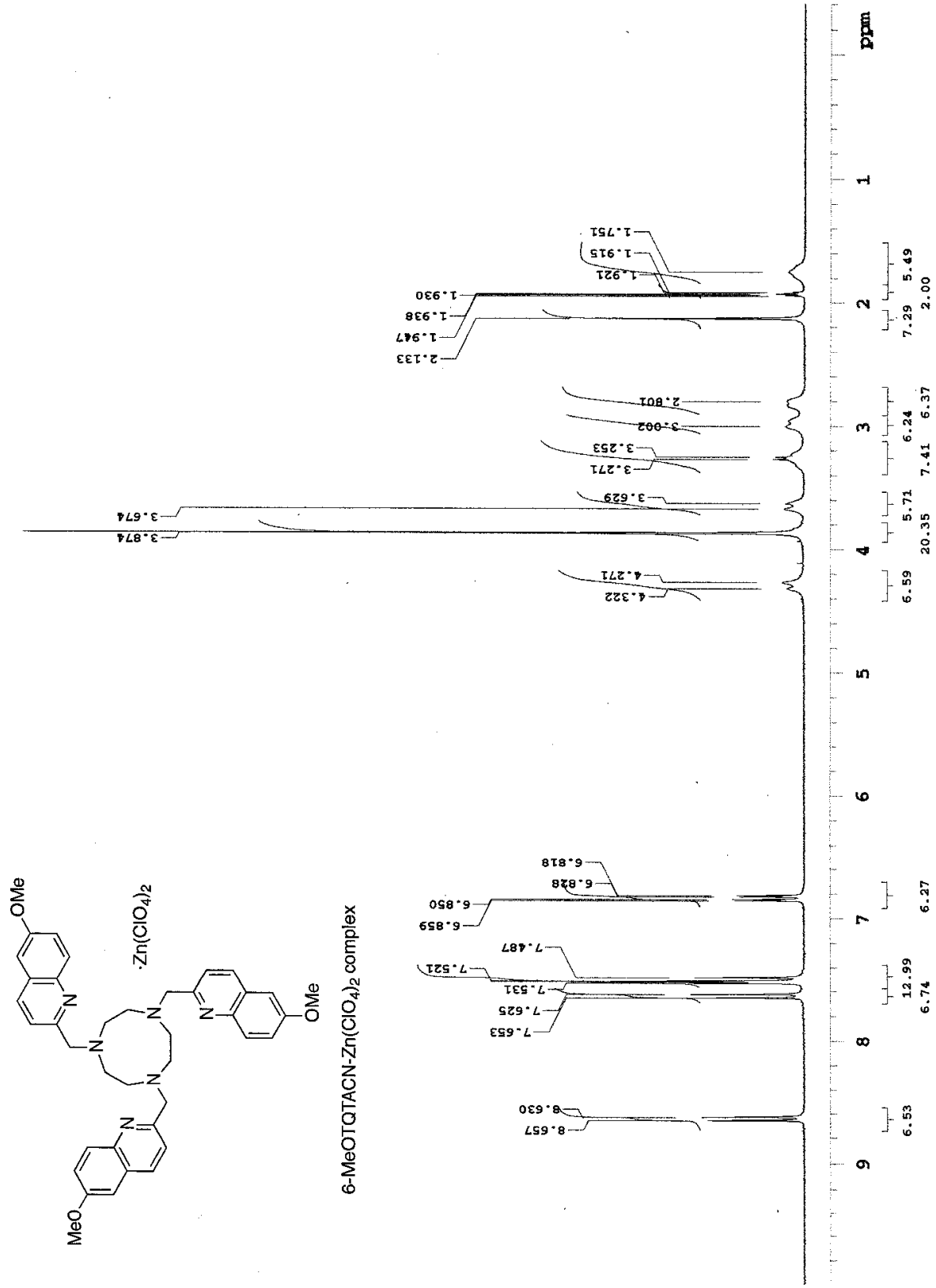

Figure S10. ^{1}H NMR spectrum of [Zn(6-MeOTQTACN)]$(ClO_4)_2$ (**5-Zn**) in CD_3CN.

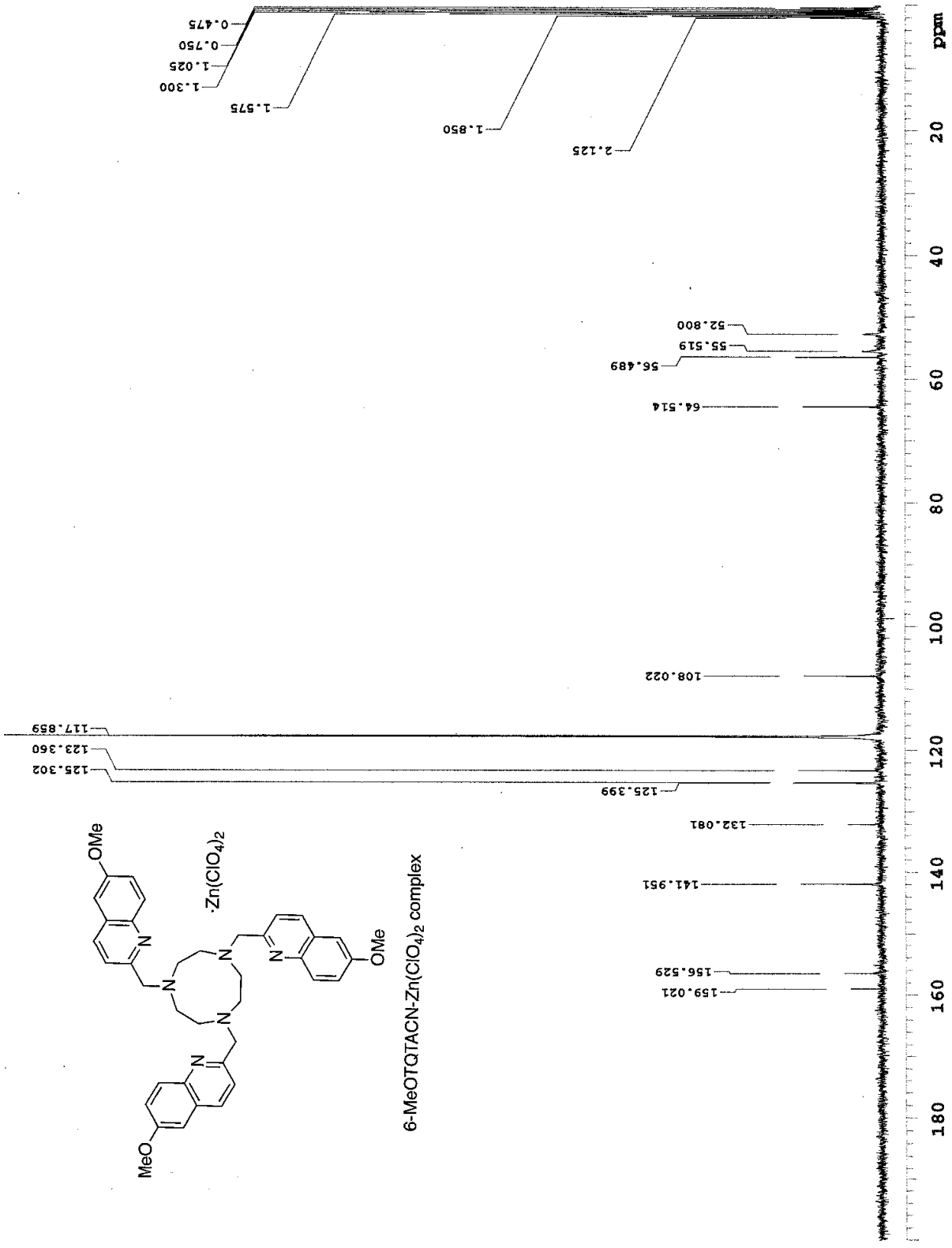

Figure S11. ^{13}C NMR spectrum of [Zn(6-MeOTQTACN)]$(ClO_4)_2$ (**5-Zn**) in CD_3CN.

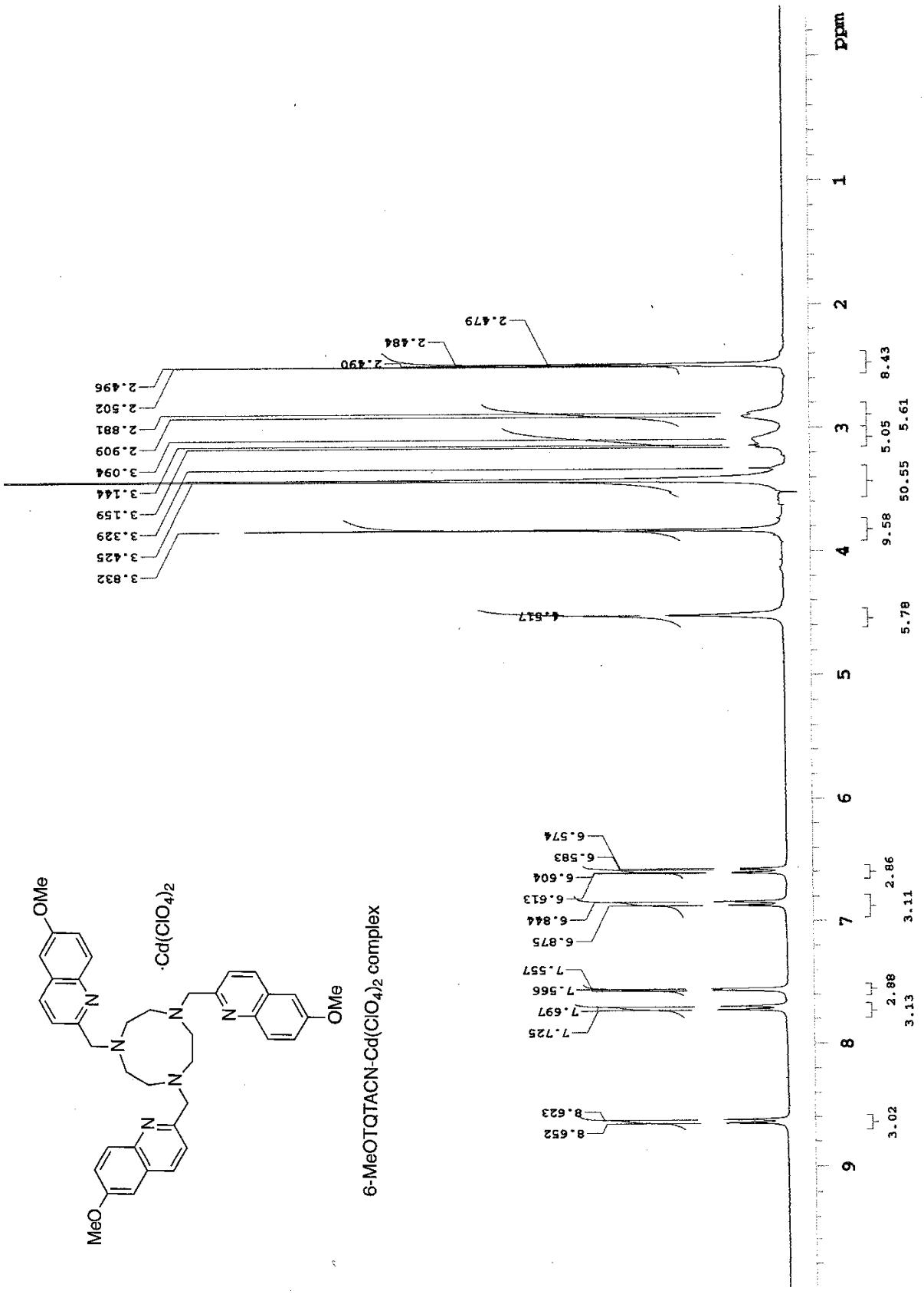

Figure S12. ^{1}H NMR spectrum of [Cd(6-MeOTQTACN)]$(ClO_4)_2$ (**5-Cd**) in DMSO-d_6.

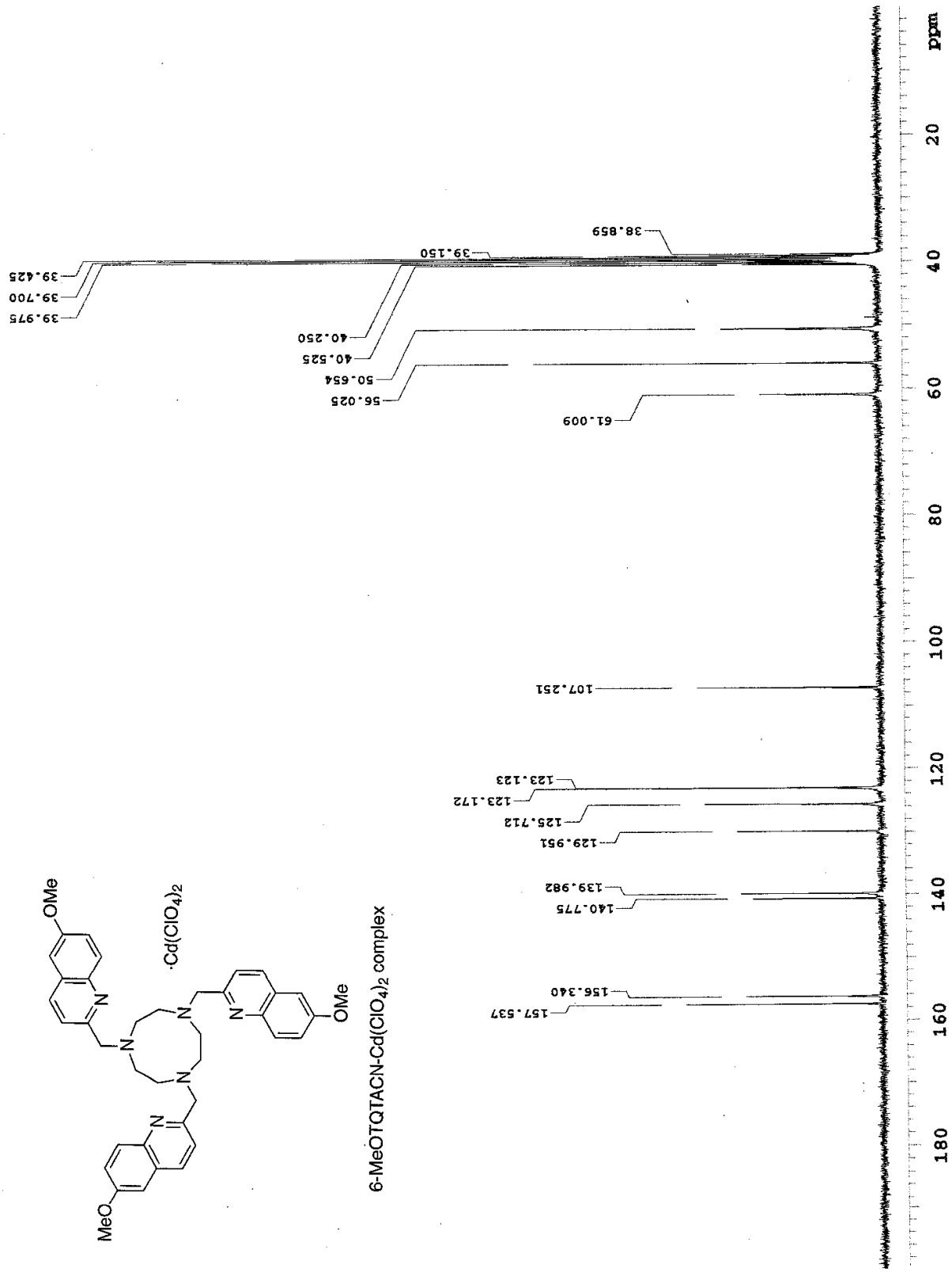

Figure S13. ^{13}C NMR spectrum of [Cd(6-MeOTQTACN)]$(ClO_4)_2$ (**5-Cd**) in DMSO-d_6.

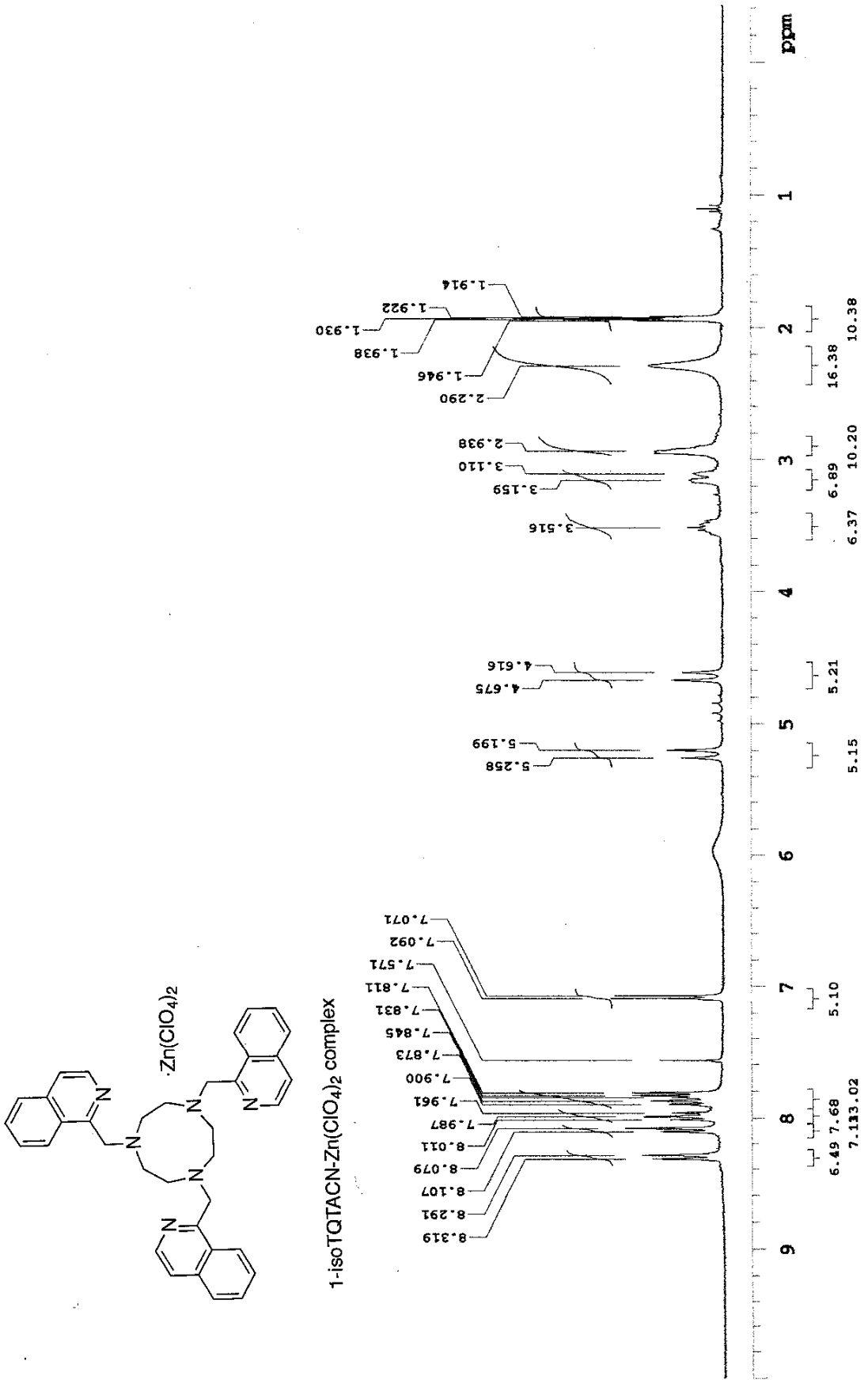

Figure S14. ^{1}H NMR spectrum of [Zn(1-isoTQTACN)]$(ClO_4)_2$ (**6-Zn**) in CD_3CN.

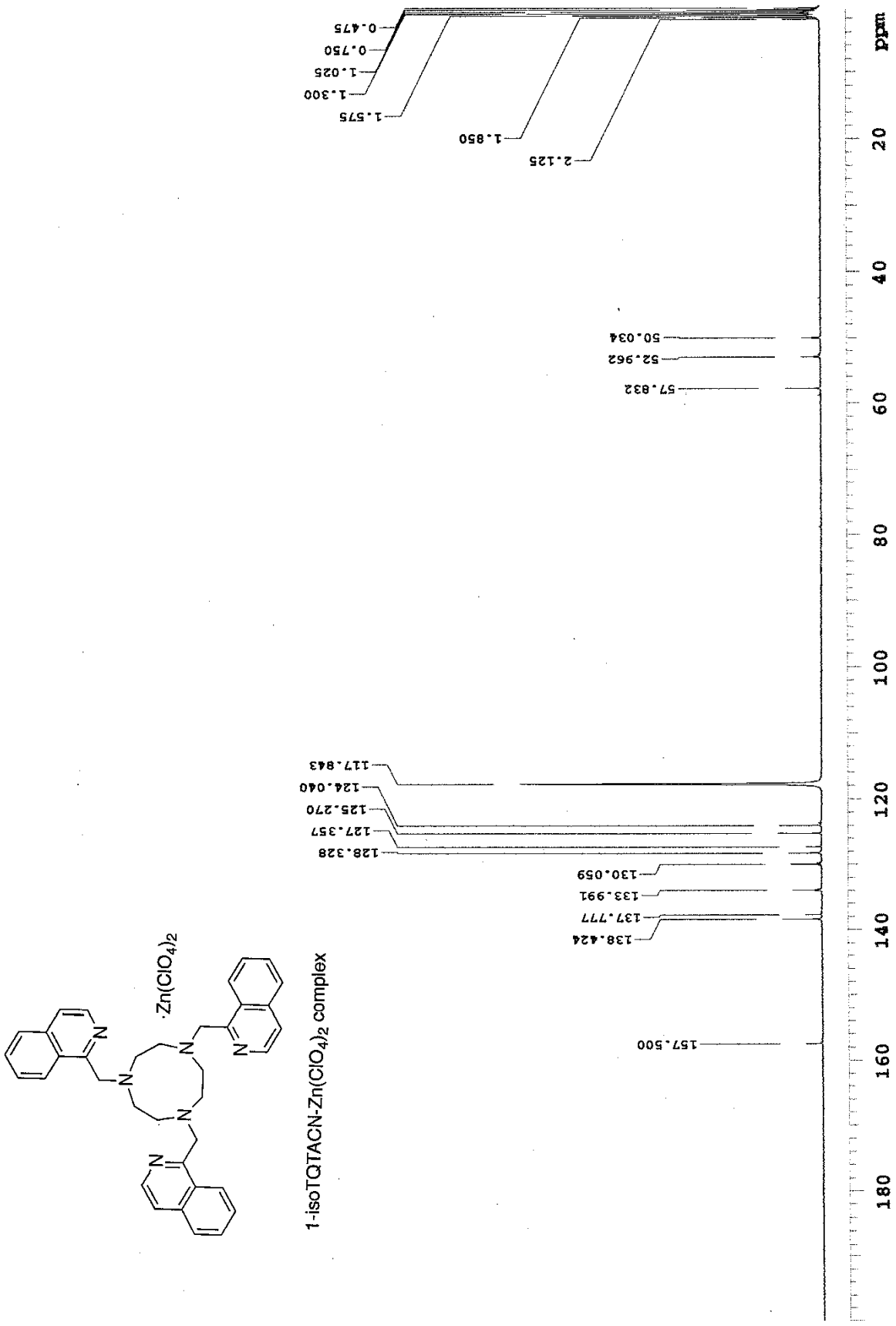

Figure S15. ^{13}C NMR spectrum of [Zn(1-isoTQTACN)]$(ClO_4)_2$ (**6-Zn**) in CD_3CN.

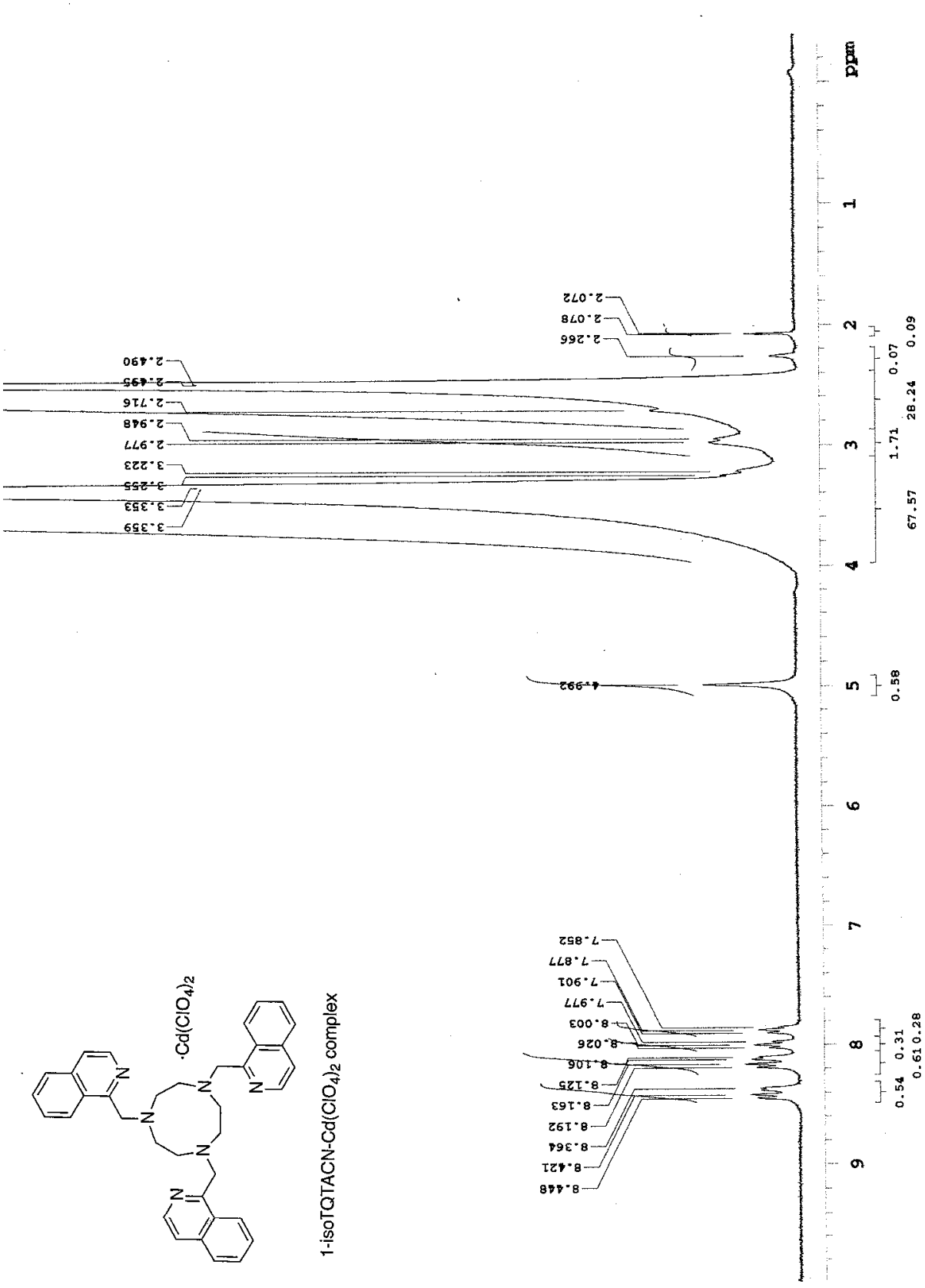

Figure S16. ^{1}H NMR spectrum of [Cd(1-isoTQTACN)]$(ClO_4)_2$ (**6-Cd**) in DMSO-d_6.

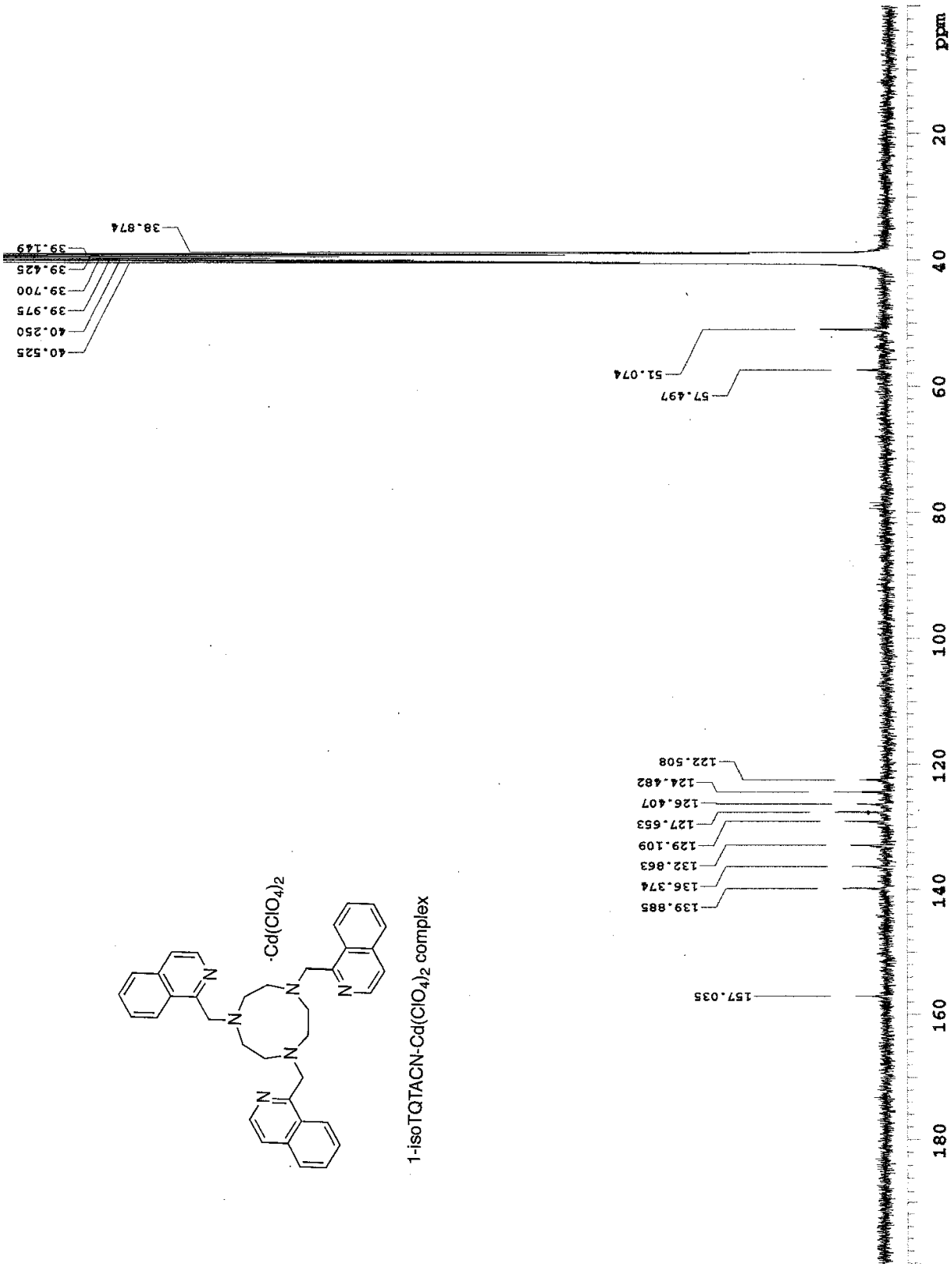

Figure S17. ^{13}C NMR spectrum of [Cd(1-isoTQTACN)]$(ClO_4)_2$ (**6-Cd**) in DMSO-d_6.

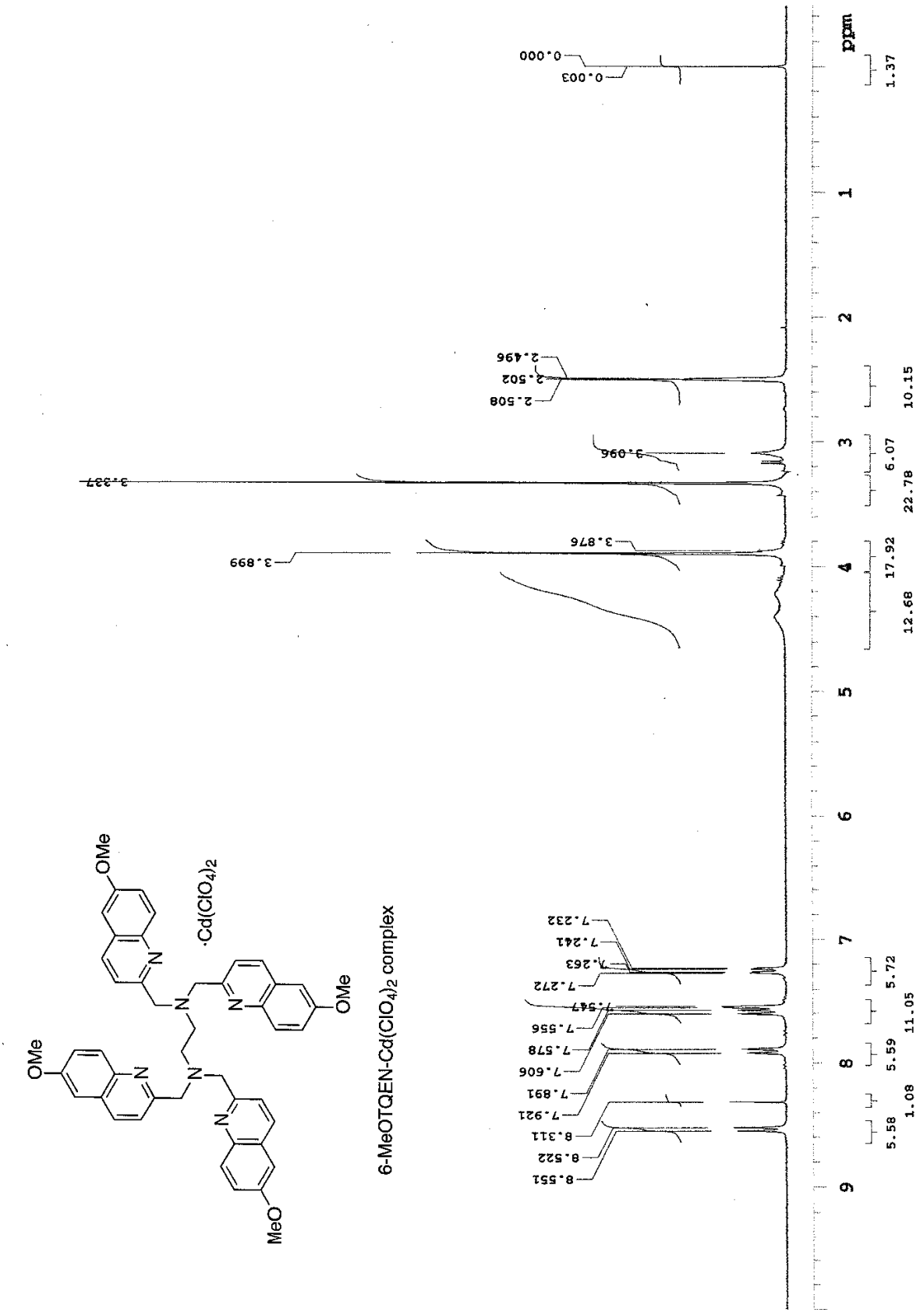

Figure S18. ^{1}H NMR spectrum of [Cd(6-MeOTQEN)](ClO$_4$)$_2$ (**2-Cd**) in DMSO-d_6.

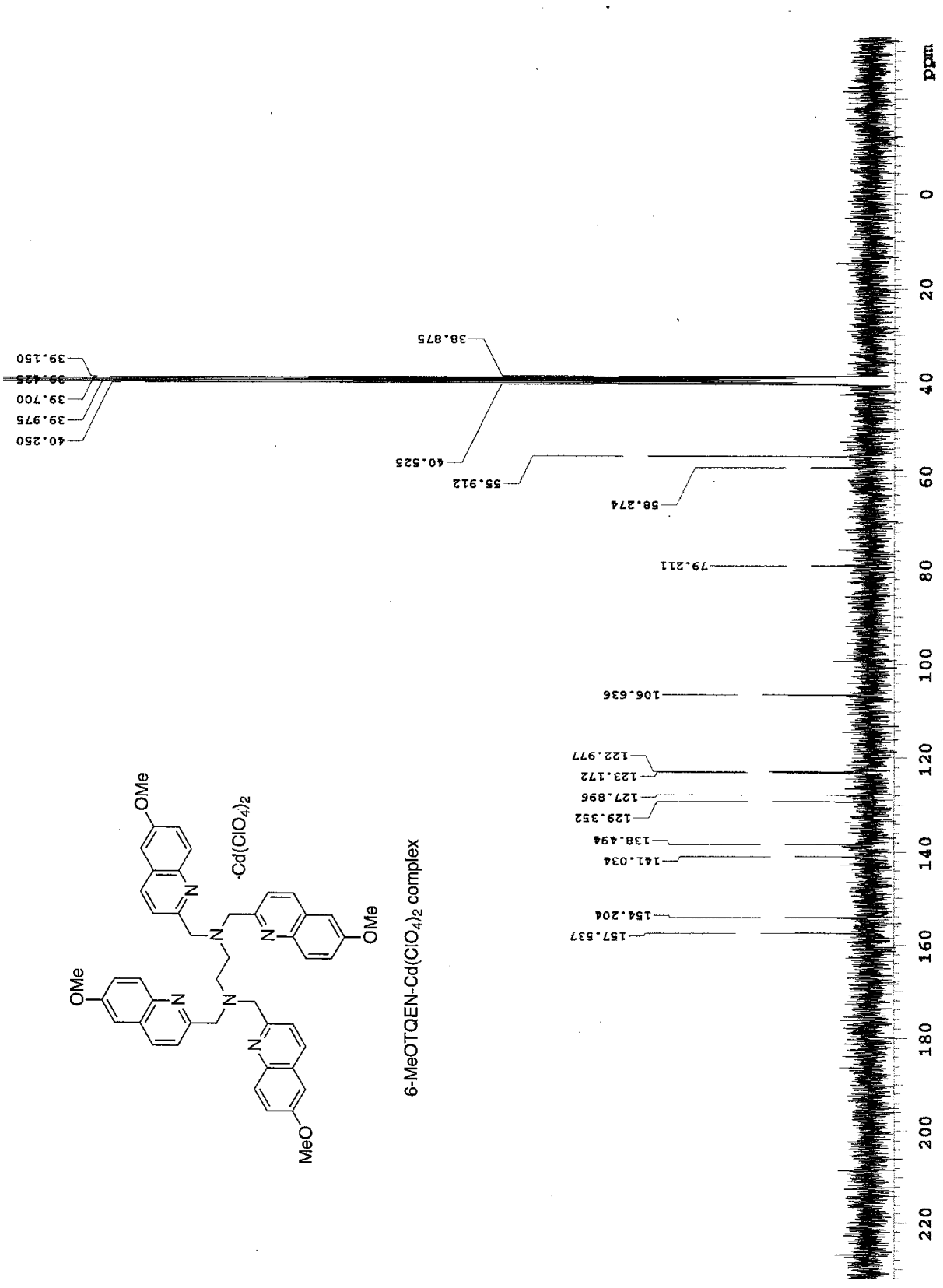

Figure S19. ^{13}C NMR spectrum of [Cd(6-MeOTQEN)]$(ClO_4)_2$ (**2-Cd**) in DMSO-d_6.