Supplementary Information for

Thioether-tethered bisquinoline derivatives as fluorescent probes for mercury(II) and iron(III) ions

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Experimental

General

All reagents and solvents used for synthesis were from commercial sources and used as received. Acetonitrile (Dojin) was spectral grade (Spectrosol). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL JNM AL-400 spectrometer and referenced to internal $Si(CH_3)_4$ or solvent signals. UV-vis and fluorescence spectra were measured on a Jasco V-660 spectrophotometer and Jasco FP-6300 spectrofluorometer, respectively. *CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive. All due precautions should be taken.*

BQET[1]

To the acetonitrile suspension (30 mL) of 2-chloromethylquinoline hydrochloride

(535 mg, 2.50 mmol) and 1,2-ethanedithiol (100 μL, 1.25 mmol) was added potassium carbonate (1.38 g, 10.0 mmol) and stirred for 2 days under reflux. After removal of the solvent, the residue was extracted with chloroform/water. The organic layer was dried, evaporated, and washed with acetonitrile to give BQET as white powder. Yield, 445 mg (1.18 mmol, 94%).

^{1}H NMR ($CDCl_3$): δ 8.08 (d, 2H, *J* = 8.3 Hz), 8.00 (d, 2H, *J* = 8.3 Hz), 7.77 (m, 2H), 7.67 (m, 2H), 7.51 (m, 4H), 3.98 (s, 4H), 2.71 (s, 4H).

^{13}C NMR ($CDCl_3$): δ 158.5, 147.1, 136.6, 129.3, 128.8, 127.2, 126.7, 126.1, 120.1, 38.5, 31.1.

6-MeOBQET

To the acetonitrile suspension (50 mL) of 6-methoxy-2-chloromethylquinoline (1.14 g, 5.51 mmol) and 1,2-ethanedithiol (226 μL, 2.75 mmol) was added potassium carbonate (3.46 g, 25.0 mmol) and stirred for 2 days under reflux. After removal of the solvent, the residue was extracted with chloroform/water. The organic layer was dried, evaporated, and purified by silica gel column chromatography (AcOEt/CH_2Cl_2 = 1/3) to give 6-MeOBQET as white powder. Yield, 738 mg (1.69 mmol, 61%). Recrystallization from chloroform-acetonitrile afforded single crystals suitable for X-ray crystallography.

^{1}H NMR ($CDCl_3$): δ 8.07 (d, 2H, *J* = 9.0 Hz), 7.78 (d, 2H, *J* = 9.2 Hz), 7.43 (d, 2H, *J* = 9.0 Hz), 7.30 (dd, 2H, *J* = 2.8, 9.2 Hz), 7.21 (d, 2H, *J* = 2.8 Hz), 3.91 (s, 4H), 3.89 (s, 6H), 2.66, (s, 4H).

^{13}C NMR ($CDCl_3$): δ 158.5, 157.7, 144.2, 131.0, 128.9, 122.7, 122.5, 106.5, 56.2, 38.6, 31.9.

Anal calcd for $C_{24}H_{24}N_2O_2S_2$ (6-MeOBQET): H, 5.54; C, 66.03; N, 6.42. Found: H, 5.58; C, 66.06; N, 6.35.

TriMeOBQET

To the acetonitrile suspension (50 mL) of 5,6,7-trimethoxy-2-chloromethylquinoline (535 mg, 2.00 mmol) and 1,2-ethanedithiol (80.0 μL, 1.00 mmol) was added potassium carbonate (1.39 g, 10.0 mmol) and stirred for 2 days under reflux. After removal of the solvent, the residue was extracted with chloroform/water. The organic layer was dried, evaporated, and purified by silica gel column chromatography (AcOEt) to give TriMeOBQET as yellow oil. Yield, 253 mg (0.46 mmol, 46%).

^{1}H NMR (CD_3OD): δ 8.29 (d, 2H, *J* = 9.0 Hz), 7.34 (d, 2H, *J* = 9.0 Hz), 7.18 (s, 2H), 4.06 (s, 6H), 4.02 (s, 6H), 4.00 (s, 6H), 3.96 (s, 4H), 2.71, (s, 4H).

^{13}C NMR (CD_3OD): δ 157.9, 155.9, 146.7, 145.0, 140.4, 131.1, 118.6, 117.8, 103.7, 61.6, 61.2, 56.1, 38.5, 31.3.

Anal. calcd for $C_{28}H_{33}N_2O_{6.5}S_2$ (TriMeOBQET·0.5H_2O): H, 5.88; C, 59.45; N, 4.95. Found: H, 5.80; C, 59.68; N, 5.11.

[Hg(BQET)(ClO_4)]ClO_4

In an acetonitrile solution of BQET was added equimolar amount of $Hg(ClO_4)_2$·6H_2O in ethanol, and the solution was kept at 4 °C under ether diffusion condition to give colorless crystals. Yield, 23%.

^{1}H NMR (DMSO-d_6): δ 8.64 (d, 2H, *J* = 8.4 Hz), 8.42 (d, 2H, *J* = 8.4 Hz), 8.17 (d, 2H, *J* =

7.3 Hz), 7.94 (m, 2H), 7.82 (m, 2H), 7.73 (d, 2H, J = 8.5 Hz), 4.63 (s, 4H), 3.03 (s, 4H). ^{13}C NMR (DMSO-d_6): δ 154.6, 145.0, 139.8, 131.5, 128.8, 128.2, 127.9, 127.4, 123.5, 36.8, 31.1.

Anal. calcd for $C_{22}H_{20}Cl_2HgN_2O_8S_2$ ([Hg(BQET)(ClO_4)$_2$]): H, 2.60; C, 34.05; N, 3.61. Found: H, 2.78; C, 34.25; N, 3.82.

X-ray crystallography

Single crystals of 6-MeOBQET and [Hg(BQET)(ClO_4)]ClO_4 were covered by Paraton-N oil and mounted on a glass fiber. All data were collected at 123 K on a Rigaku Mercury CCD detector, with monochromatic MoK□ radiation, operating at 50 kV/40 mA. Data were processed on a PC using CrystalClear Software (Rigaku). Structures were solved by direct methods (SIR-92)[2] and refined by full-matrix least-squares methods on F^2 (SHELXL-97).[3] Crystal data are summarized in Tables S1. CCDC-924739 and 924740 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

References

1 V. Amendola, C. Mangano, P. Pallavicini and M. Zema, *Inorg. Chem.*, 2003, **42**, 6056.

2 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435.

3 G. M. Sheldrick, *SHELXL-97, Program for refinement of cystal structures, University of Göttingen, Germany, 1997*.

Table S1. Crystallographic Data for 6-MeOBQET and $[Hg(BQET)(ClO_4)]ClO_4$

	6-MeOBQET	$[Hg(BQET)(ClO_4)]ClO_4$
Formula	$C_{24}H_{24}N_2O_2S_2$	$C_{22}H_{20}Cl_2HgN_2O_8S_2$
FW	436.59	776.02
Crystal system	monoclinic	triclinic
Space group	*C*2/*c*	*P*-1
a, Å	45.859(4)	14.2333(7)
b, Å	6.0059(4)	14.4741(7)
c, Å	15.7820(10)	15.0775(9)
α, deg	90	101.0406(15)
β, deg	105.080(4)	113.0721(8)
γ, deg	90	111.1031(3)
V, Å^3	4197.1(5)	2457.8(2)
Z	8	4
D_{calc}, g cm^{-3}	1.382	2.097
μ, mm^{-1}	0.2780	6.7189
$2\theta_{max}$, deg	55	55
temp, K	123	123
no. reflns collected	19768	24541
no. reflns used	4804	11047
no. of params	367	668
R_{int}	0.0259	0.028
Final *R*1 ($I > 2\sigma(I)$)[a]	0.0424	0.0364
*wR*2 (all data)[b]	0.1105	0.0856
GOF	1.086	1.097

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

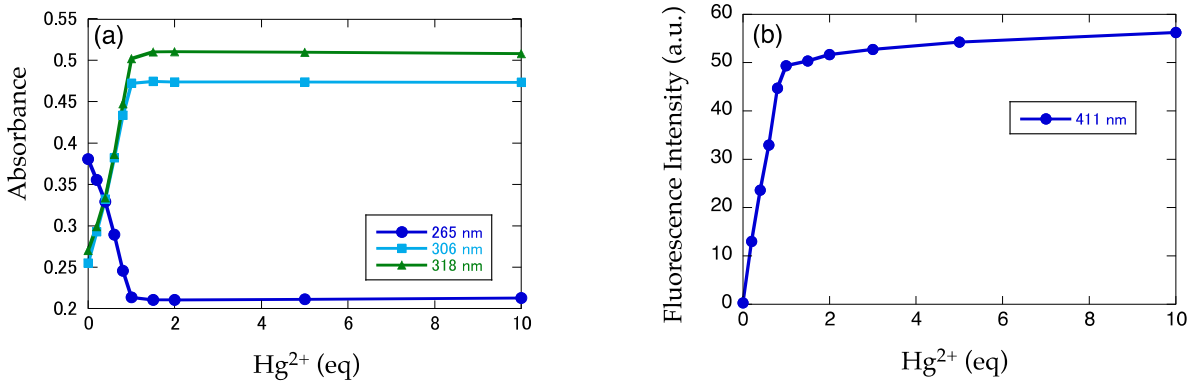

Fig. S1 Hg^{2+} titration profile for 34 μM BQET in CH_3CN at 25 °C. (a) UV-vis absorbance changes at 265, 306 and 318 nm. (b) Fluorescence intensity changes (λ_{ex} = 317 nm) at 411 nm.

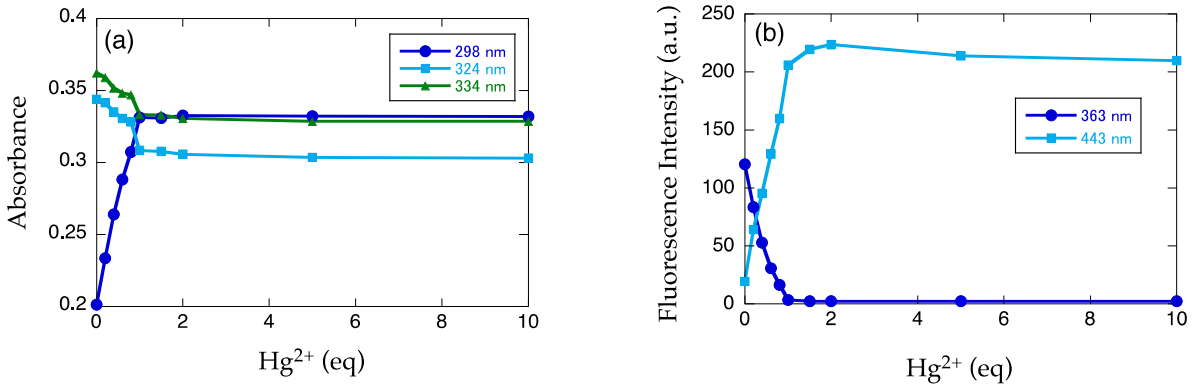

Fig. S2 Hg^{2+} titration profile for 34 μM 6-MeOBQET in CH_3CN at 25 °C. (a) UV-vis absorbance changes at 298, 324 and 334 nm. (b) Fluorescence intensity changes (λ_{ex} = 334 nm) at 363 and 443 nm.

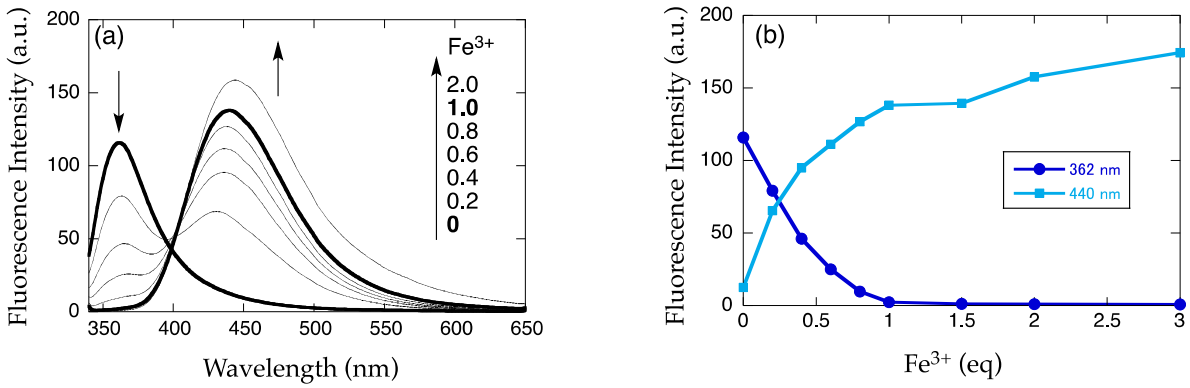

Fig. S3 (a) Fluorescence (λ_{ex} = 334 nm) spectra of 34 μM 6-MeOBQET in acetonitrile at 25 °C in the presence of various concentration of Fe^{3+} ranging from 0 to 68 μM. (b) Fluorescence intensity changes at 363 and 443 nm.

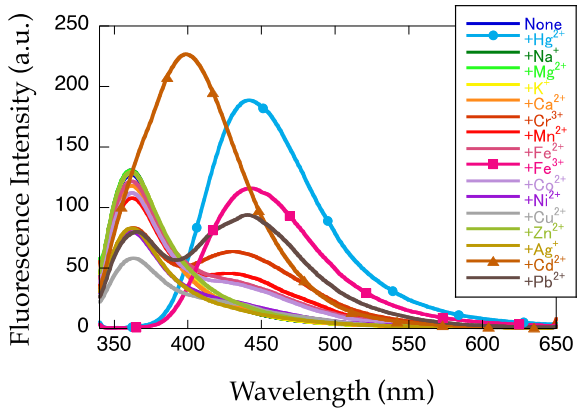

Fig. S4 Comparison of fluorescence spectra of 34 μM 6-MeOBQET (λ_{ex} = 334 nm) in CH_3CN at 25 °C in the presence of 1 equivalent of Hg^{2+} (light blue, circles), Fe^{3+} (red magenta, squares) cadmium (light brown, triangles) and other metal ions (various colors, no marks).

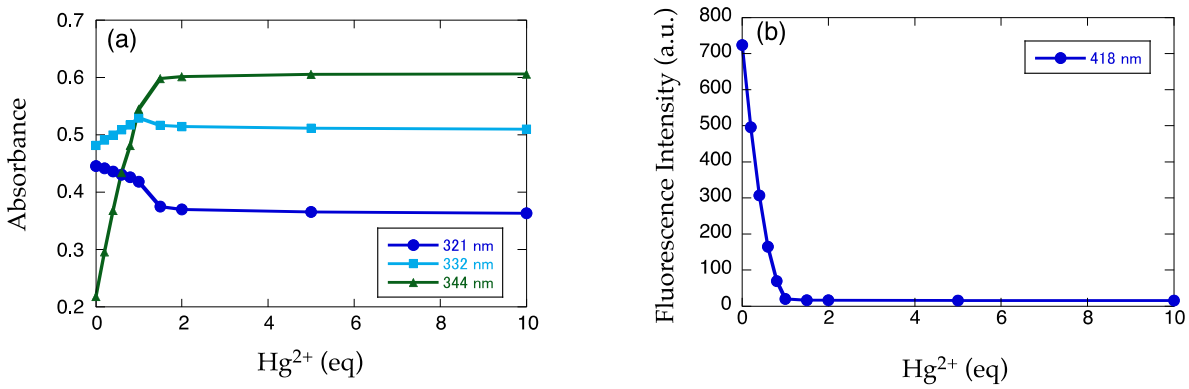

Fig. S5 Hg^{2+} titration profile for 34 μM TriMeOBQET in CH_3CN at 25 °C. (a) UV-vis absorbance changes at 321, 332 and 344 nm. (b) Fluorescence intensity changes (λ_{ex} = 334 nm) at 418 nm.

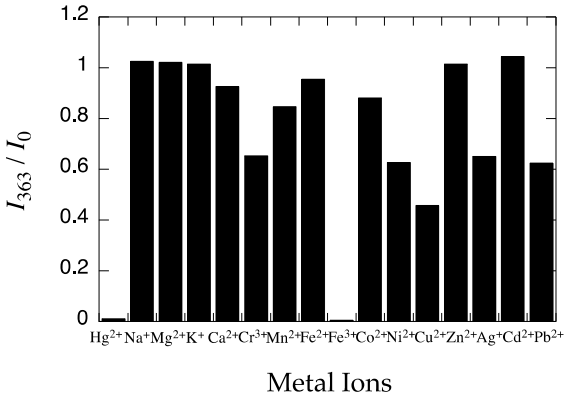

Fig. S6 The relative fluorescence intensity of 6-MeOBQET at 363 nm in the presence of 1 equivalent of metal ions in acetonitrile at 25 °C. I_0 is the emission intensity of free ligand.

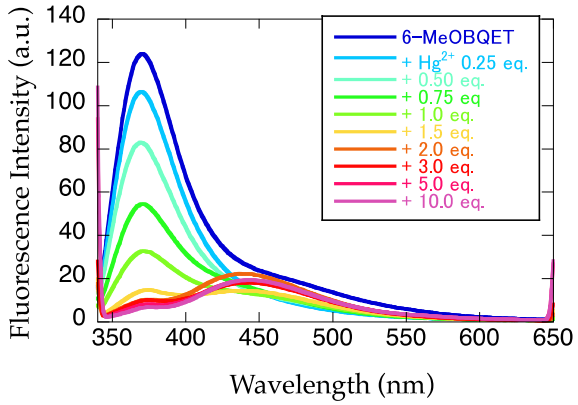

Fig. S7 Fluorescence (λ_{ex} = 334 nm) spectra of 34 µM 6-MeOBQET in acetonitrile/water (1/1) at 25 °C in the presence of various concentration of Hg^{2+} ranging from 0 to 340 µM.

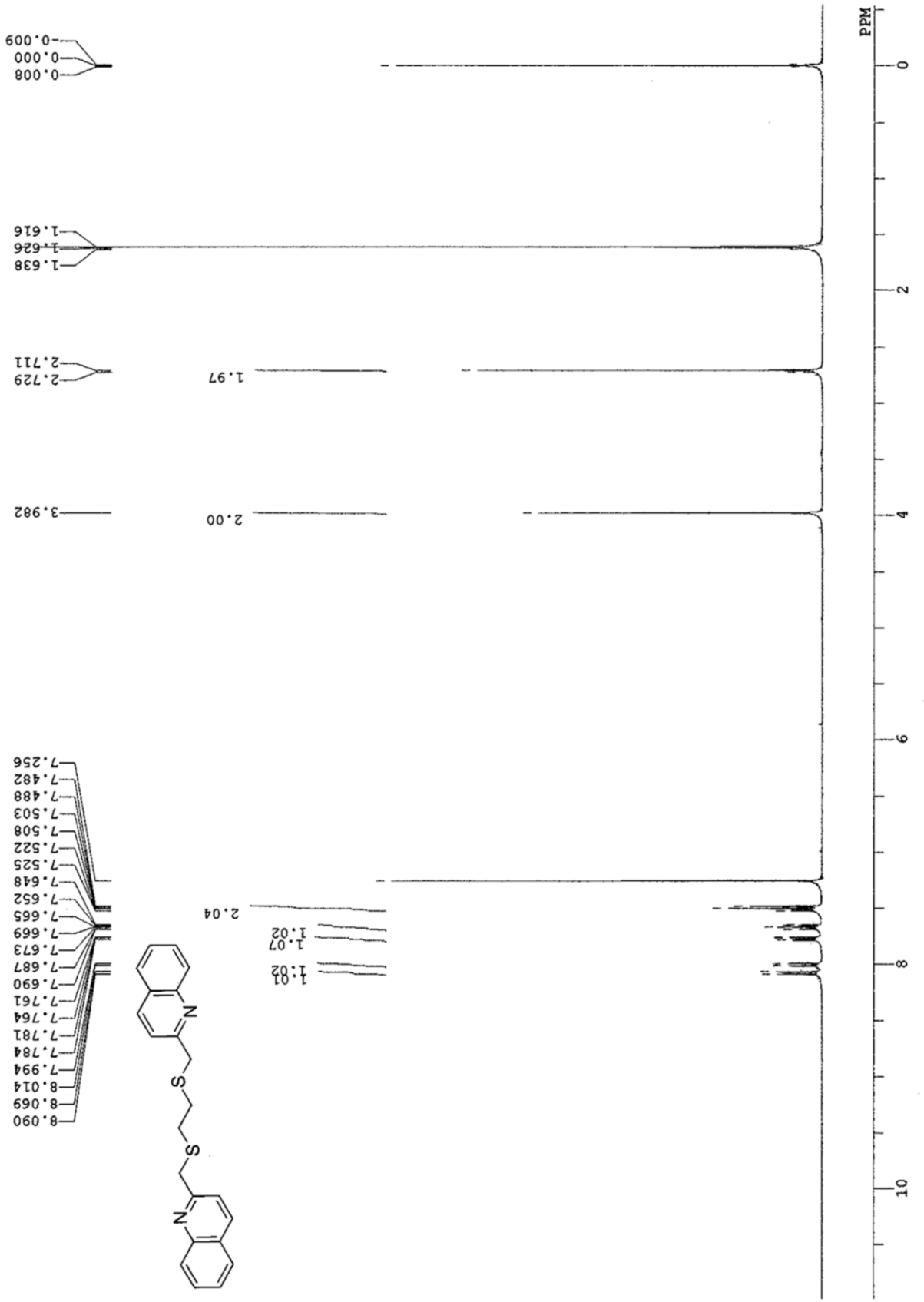

Fig. S8 ^{1}H NMR spectrum of BQET in $CDCl_3$.

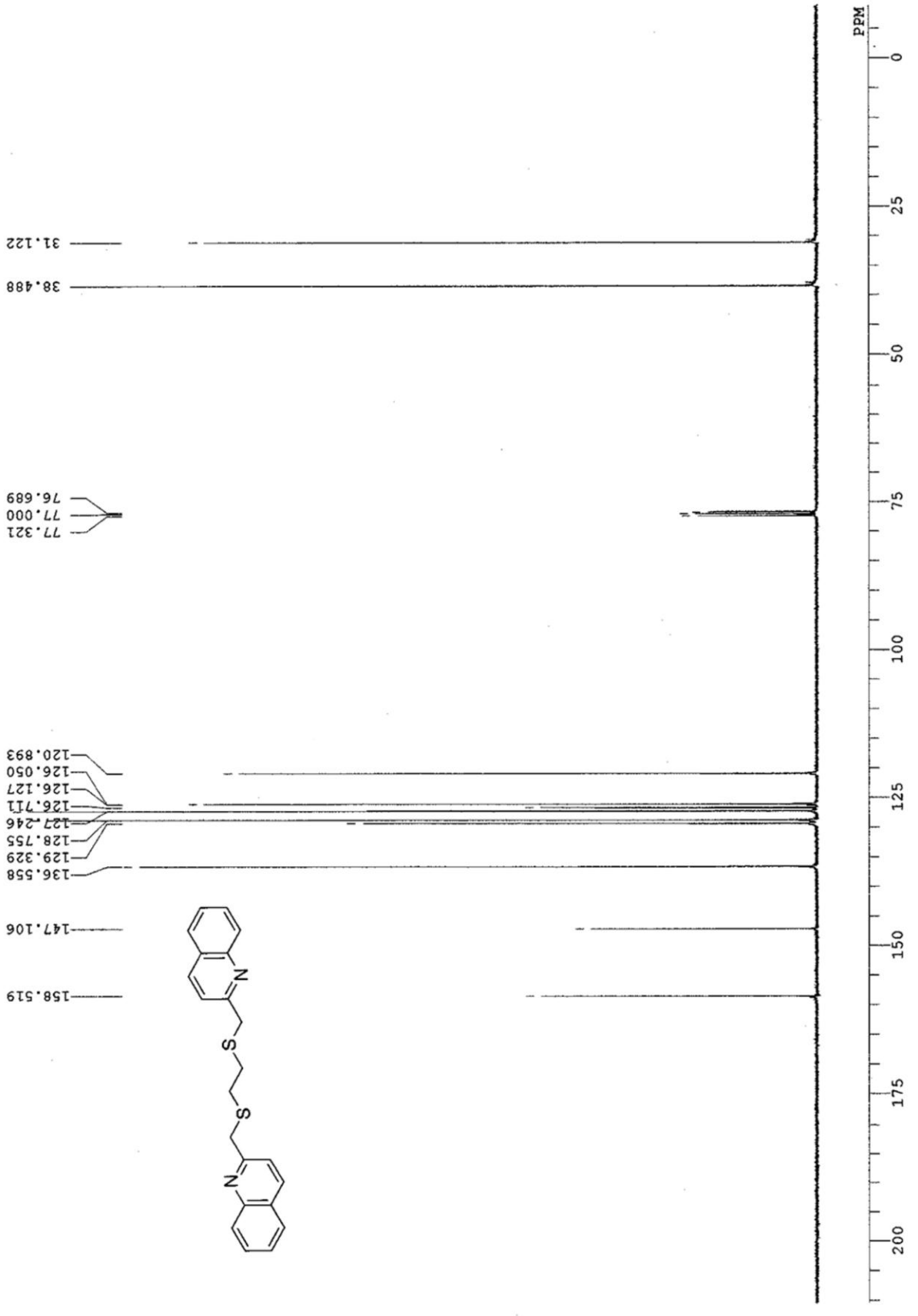

Fig. S9 ^{13}C NMR spectrum of BQET in $CDCl_3$.

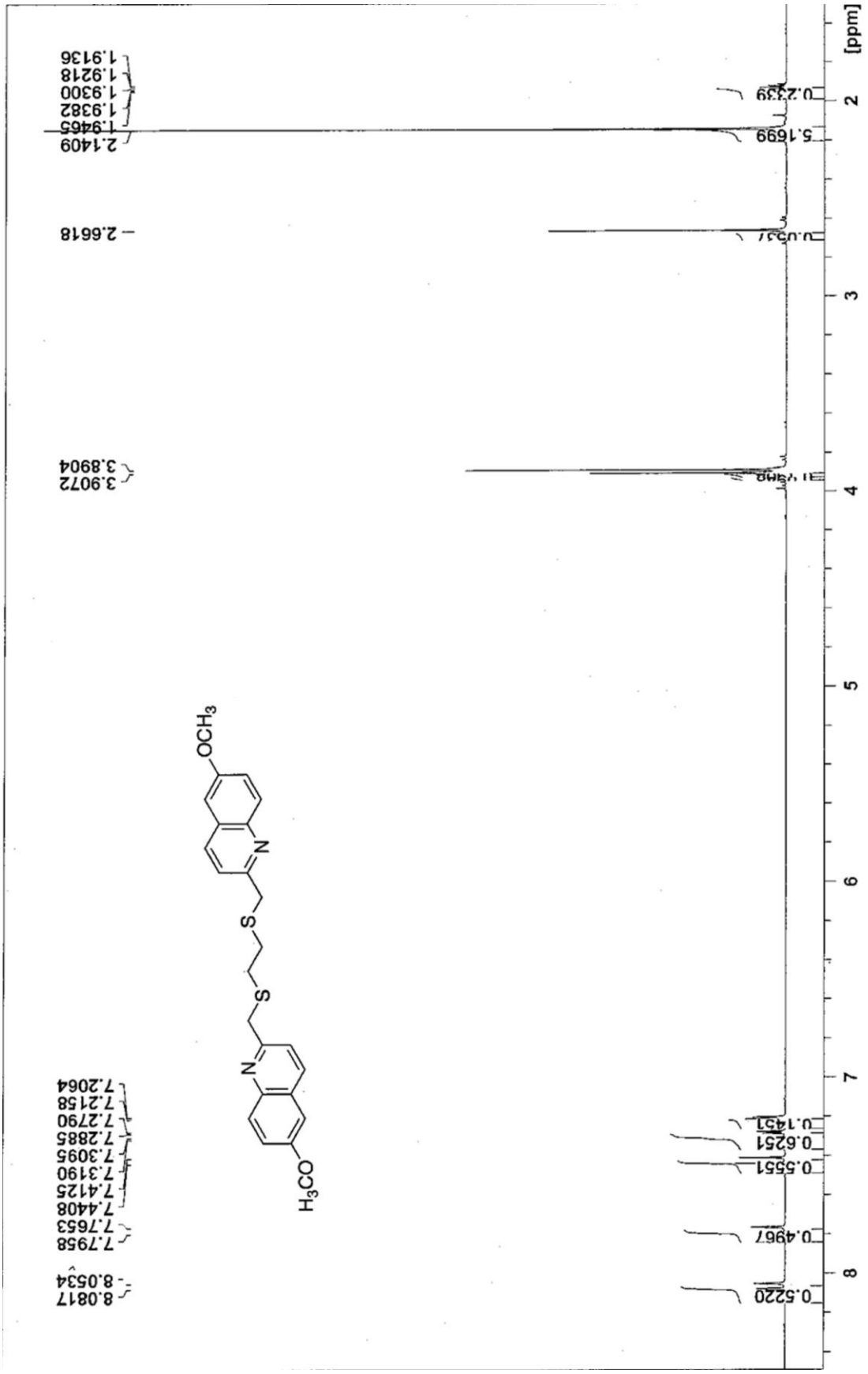

Fig. S10 ^{1}H NMR spectrum of 6-MeOBQET in CD_3CN.

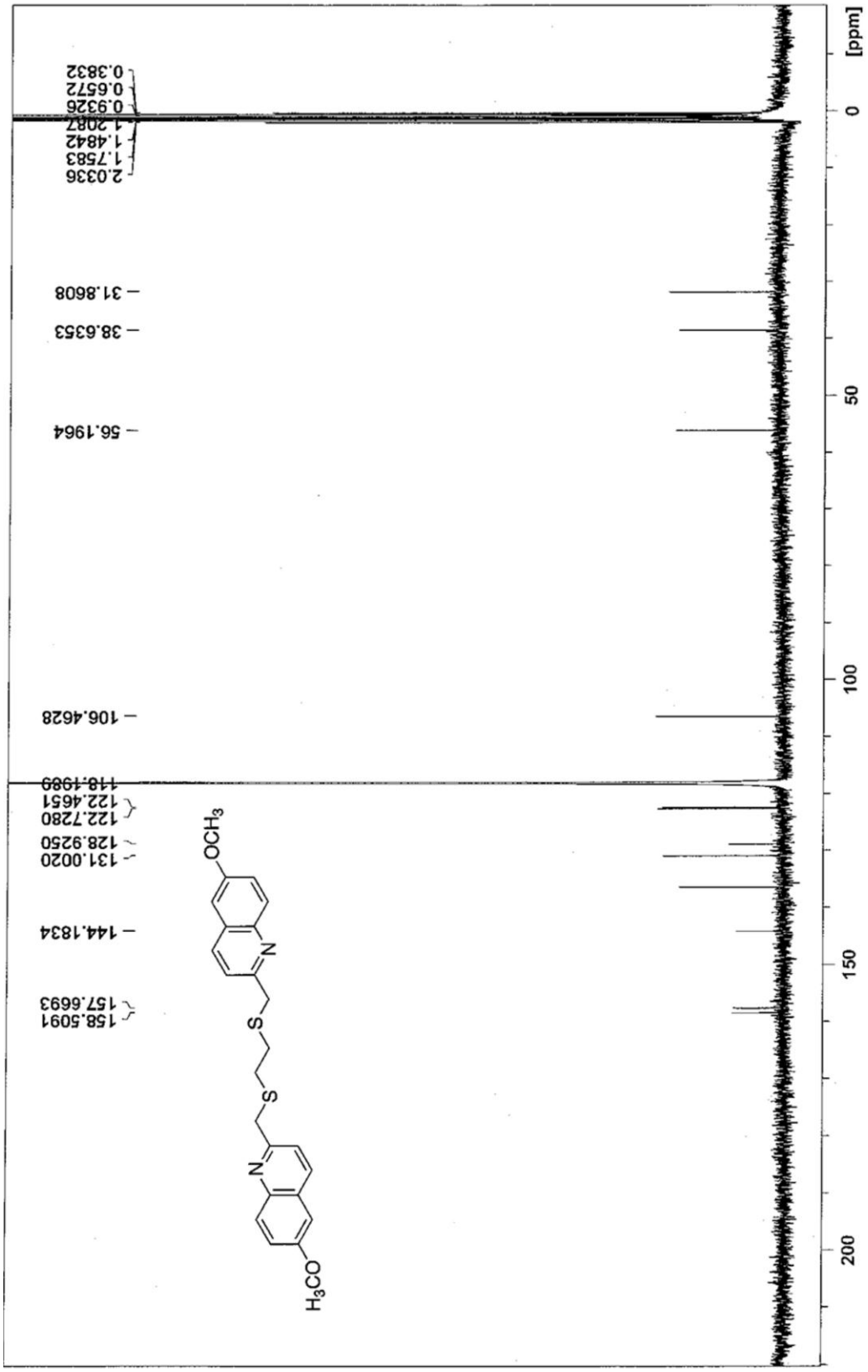

Fig. S11 ^{13}C NMR spectrum of 6-MeOBQET in CD_3CN.

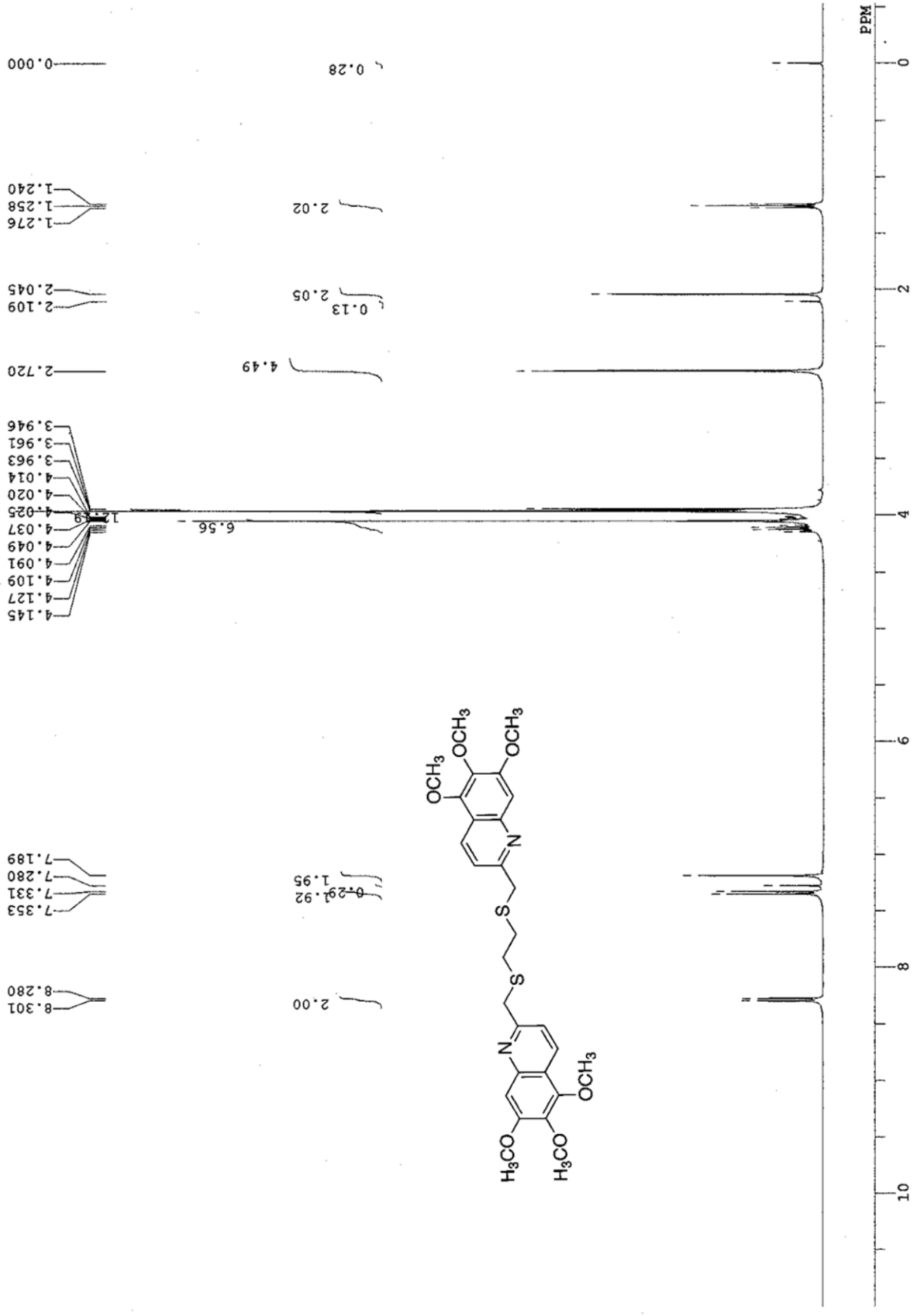

Fig. S12 ^{1}H NMR spectrum of TriMeOBQET in $CDCl_3$.

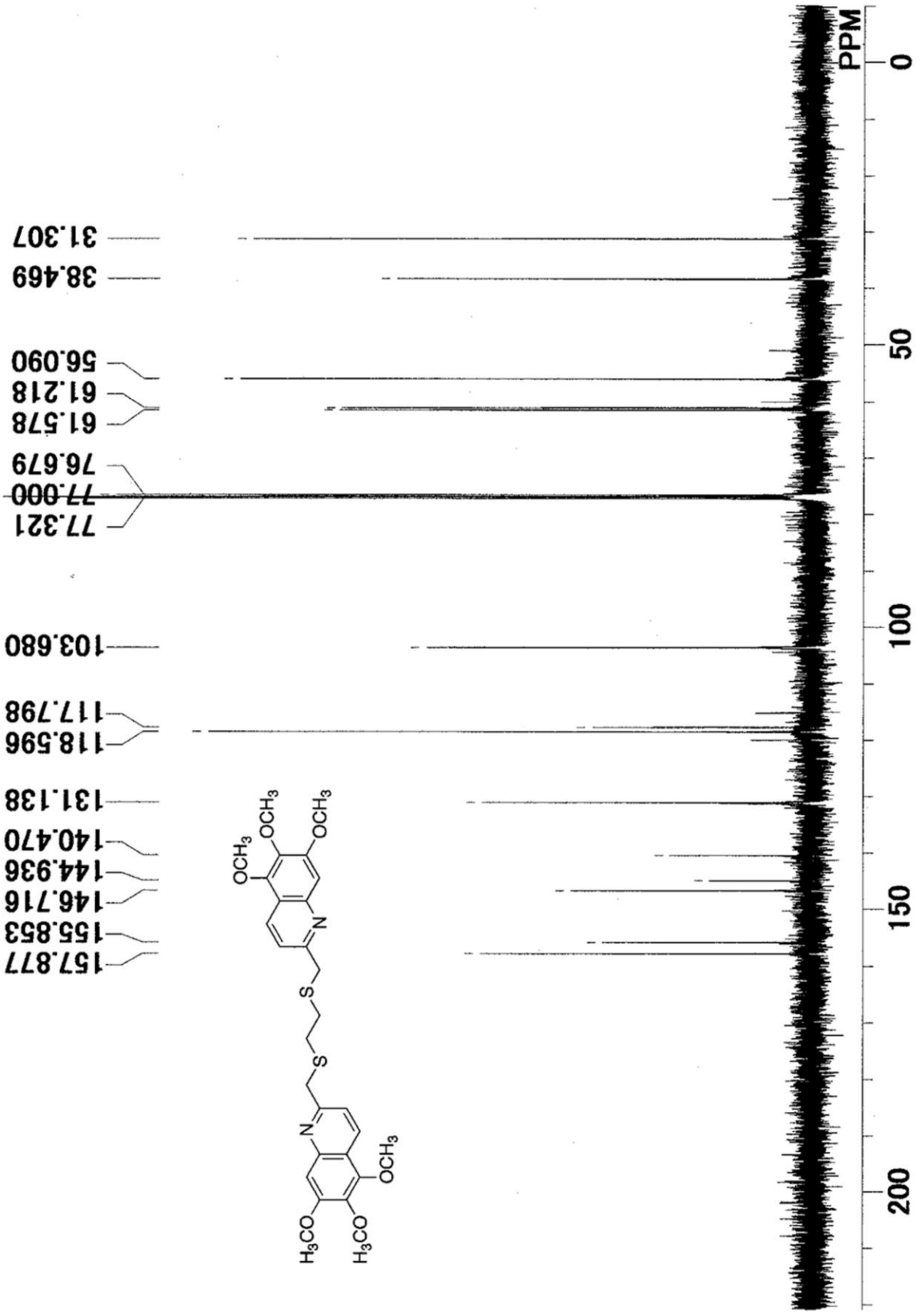

Fig. S13 ^{13}C NMR spectrum of TriMeOBQET in $CDCl_3$.

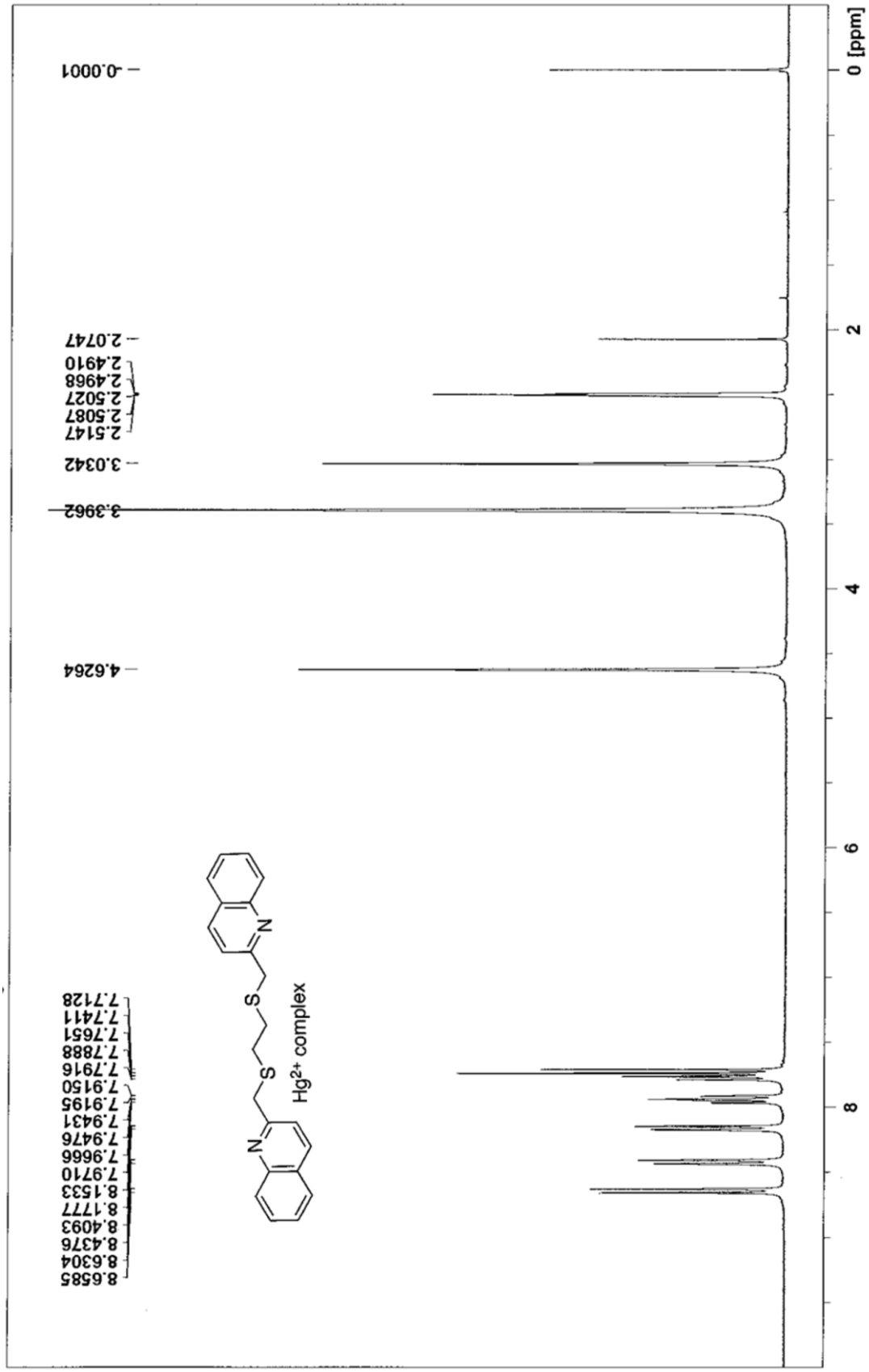

Fig. S14 ^{1}H NMR spectrum of [Hg(BQET)(ClO_4)]ClO_4 in DMSO-d_6.

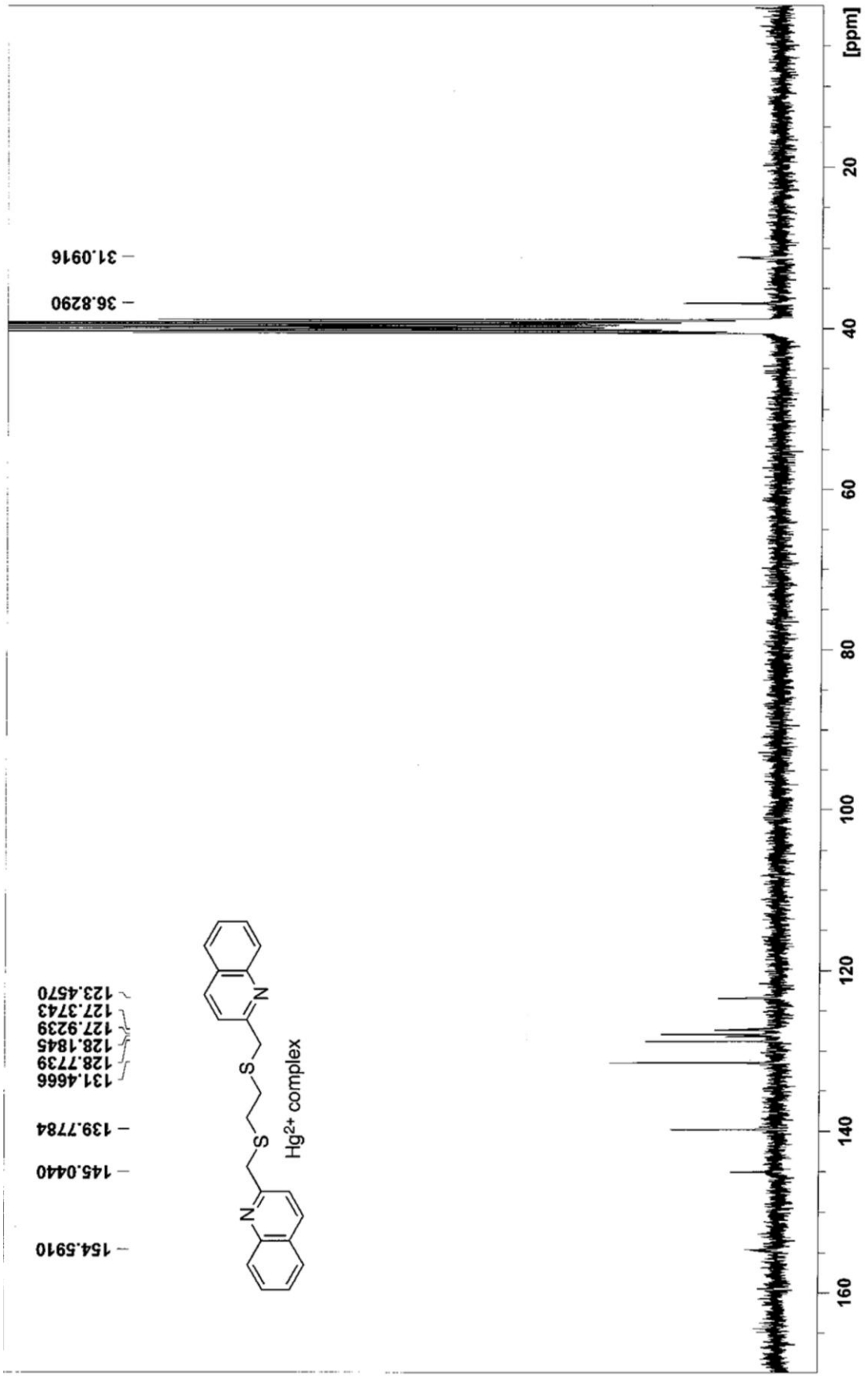

Fig. S15 ^{13}C NMR spectrum of $[Hg(BQET)(ClO_4)]ClO_4$ in DMSO-d_6.