Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Material

for

A turn-on chemsensor for Hg^{2+} in aqueous media and its application in "MCT" imaging in living cells

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1. Synthesis routes and characteristic data

1.1 Experiment Procedure

Absorption spectra were determined on a Varian UV-Cary100 spectrophotometer. Fluorescence spectra measurements were performed on a Hitachi F-4500 spectrofluorimeter. All pH measurements were made with a pH-10C digital pH meter. ^{1}H and ^{13}C NMR spectra were taken on a Varian mercury-400 spectrometer with TMS as an internal standard and $CDCl_3$ and DMSO-d_6 as solvent. HRMS were determined on a Bruker Daltonics APEXII 47e FT-ICR spectrometer. A white crystal having dimensions of 0.27 x 0.25 x 0.21 mm was chosen for X-ray diffraction studies. The measurements were made on a BRUKER SMART 1000 CCD diffractometer equipped with graphite crystal monochromatized Mo Kα radiation (λ = 0.71073 Å) at 296(2) K. The structure was solved by direct methods with the SHELXS-97 program, and refined anisotropically by full-matrix least-squares methods for all non-H atoms. All H atoms were added according to theoretical calculations and refined isotropically.

All the materials for synthesis were purchased from commercial suppliers and used without further purification. The solutions of metal ions were prepared from their perchlorate salts. HEPES buffer solutions (20mM, pH = 7.0) were prepared in deionized water.

The SPC-A-1 (lung cancer) cells lines were provided by Institute of Biochemistry and Cell Biology (China). Cells were grown in H-DMEM (Dulbecco's Modified Eagle's Medium, High Glucose) supplemented with 10 % FBS (Fetal Bovine Serum) in an atmosphere of 5 % CO_2, 95 % air at 37°C. Cells (5×10^8/L) were placed on 18 mm glass cover slips and allowed to adhere for 24 hours. Experiments to asses Hg^{2+} uptake were performed in the same media supplemented with 50 μM $Hg(ClO_4)_2$ for 0.5 h.

Fluorescent pictures were taken on Lecia TCS-SP2 confocal fluorescence microscope inverted epifluorescence /reflectance laser scanning confocal microscope. Excitation of L1-loaded cells at 515 nm was carried out with a HeNe laser. Emission was collected using a 560 nm long-pass filter. Emission was collected from 570 to 625 nm. Before the experiments, cells were washed with PBS buffer and then incubated with 10 μM L1 in DMSO-PBS (1:49, v/v) for 10 min at 37 °C. Cell imaging was then carried out after washing cells with PBS.

1.2 Synthesis of fluorescence chemsensor L1

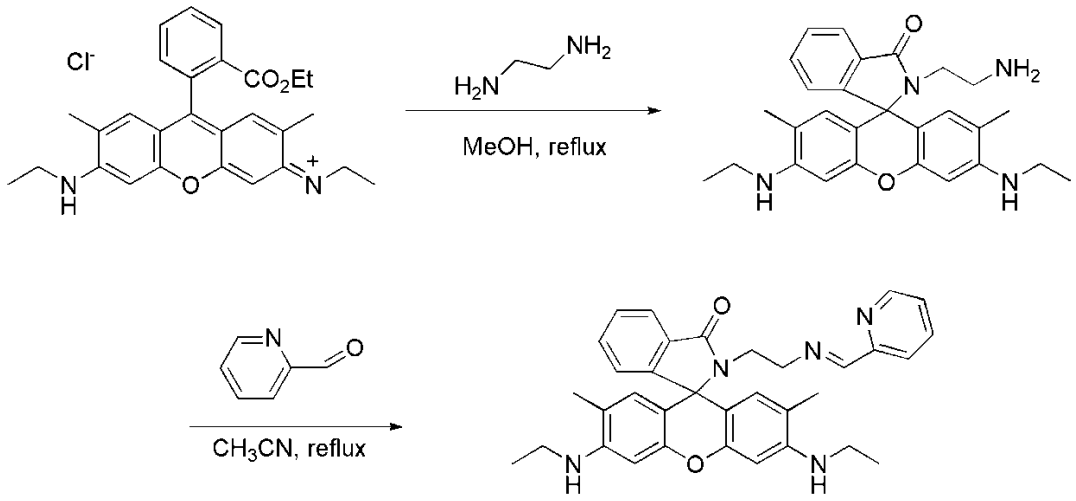
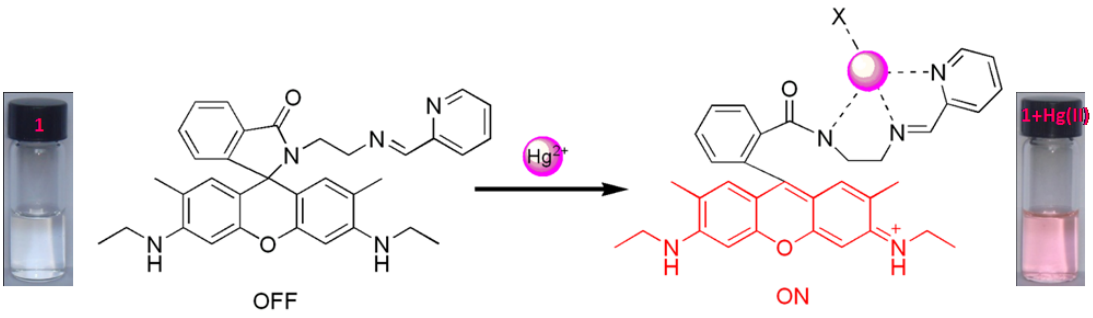


Fig. S1 Synthetic Route of chemsensor L1

N-(rhodamine-6G)lactam-ethylenediamine is prepared according to the literature mothod.[1]

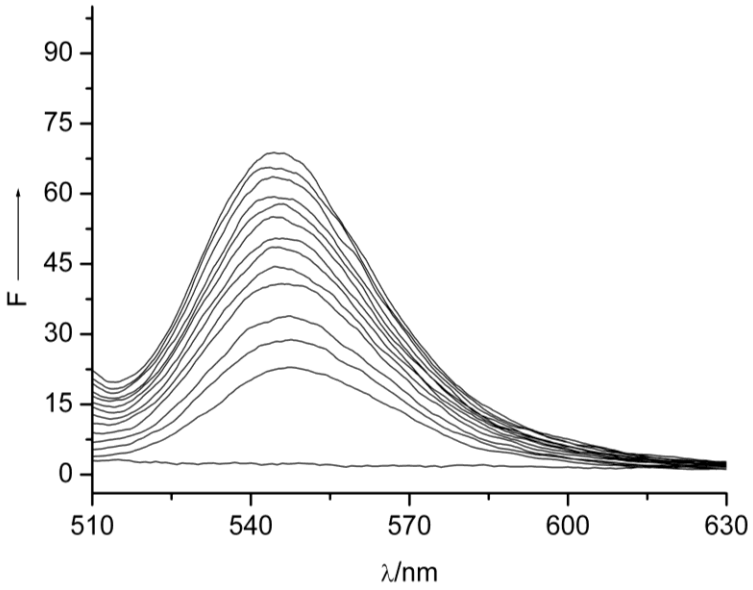
A portion of N-(rhodamine-6G)lactam-ethylenediamine (228 mg, 0.5 mmol) and 2,4-2-Pyridinecarboxaldehyde (82.8 mg, 0.6 mmol) were combined in fresh distilled acetonitrile (50 mL). The reaction solution was refluxed for 24 hours under N_2 atmosphere. After that, the solution was cooled (concentrated to 10 mL) and allowed to stand at room temperature overnight. The precipitate which appeared next day was filtered and the crude product was purified by recrystallization from acetonitrile to give 259.2 mg of **L1** (white solid) in 95% yield; mp: 263-265 ℃; ^{1}H-NMR (DMSO-d_6): 8.58 (d, 2H), 7.94 (s, 1H), 7.79-7.51 (m, 3H), 7.5 (s, 1H), 6.28 (s, 2H), 6.07 (s, 2H), 3.31 (s, 4H), 3.15 (s, 4H), 3.14-3.09 (m, 4H), 1.83 (s, 6H),

1.23-1.19 (t, 6H). ^{13}C-NMR (DMSO-d_6): δ 167.40, 163.11, 154.33, 153.80, 151.58, 1459.63, 148.16, 137.10, 133.13, 131.02, 128.71, 128.11, 125.46, 124.11, 122.74, 120.91, 118.77, 105.17, 96.05, 64.78, 58.57, 40.94, 40.63, 40.42, 40.21, 40.00, 39.79, 39.58, 39.37, 37.93, 17.43, 14.58 ppm. IR (film, cm^{-1}) 3441, 3156, 2978, 2918, 2898, 1657, 1603, 1673, 1518, 1472, 1401, 1328, 1268, 1218, 1157, 1107, 936; ESI-MS (M+H$^+$): m/z = 546.26 Element analysis (%): found: C 74.72, H 6.49, N 13.05, calcd: C 74.84, H 6.47, N 12.83.



[a]X is the coordinating anion or solvent

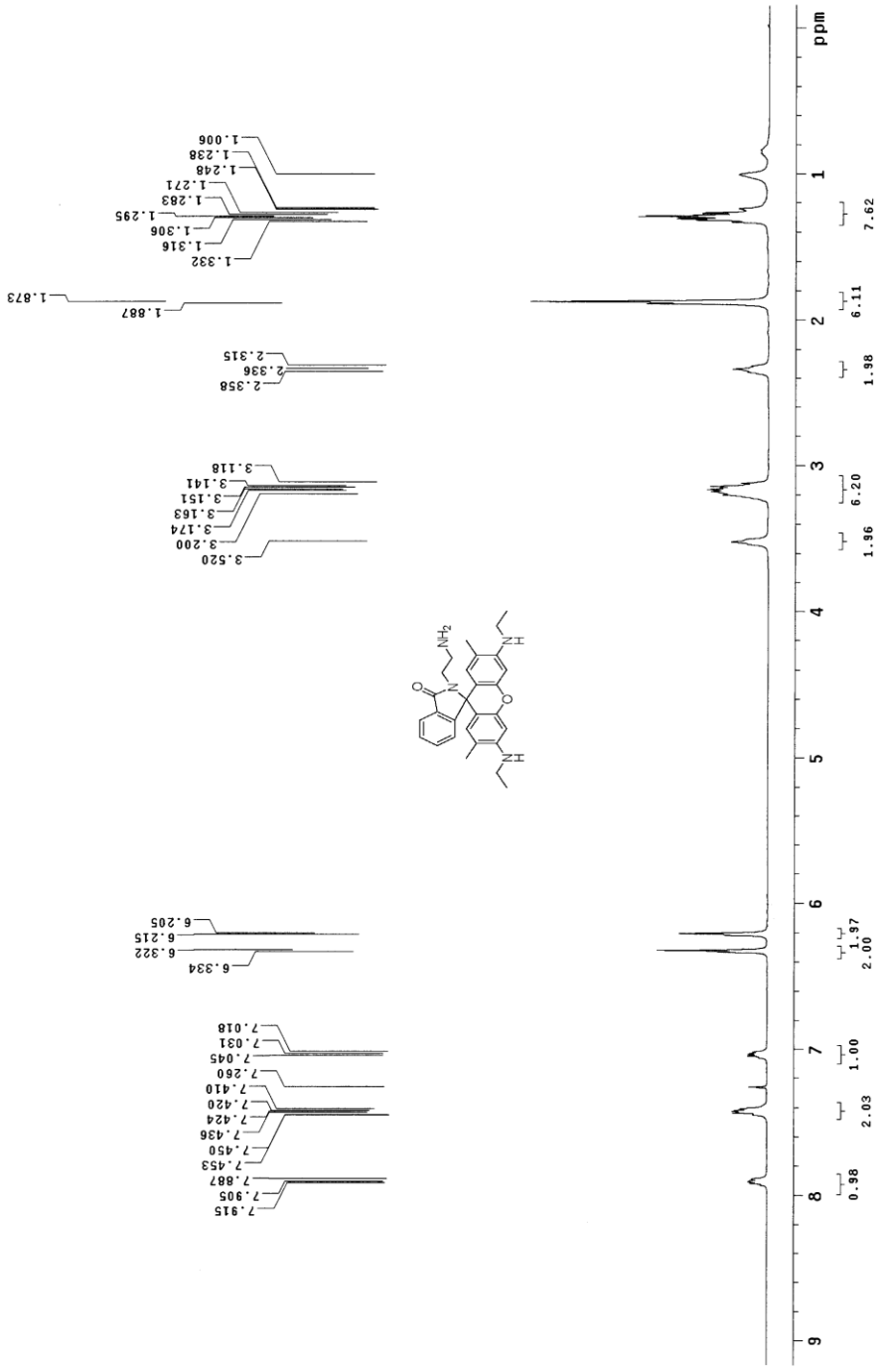
Fig s2 Proposed Binding Mode of Chemsensor L1 with



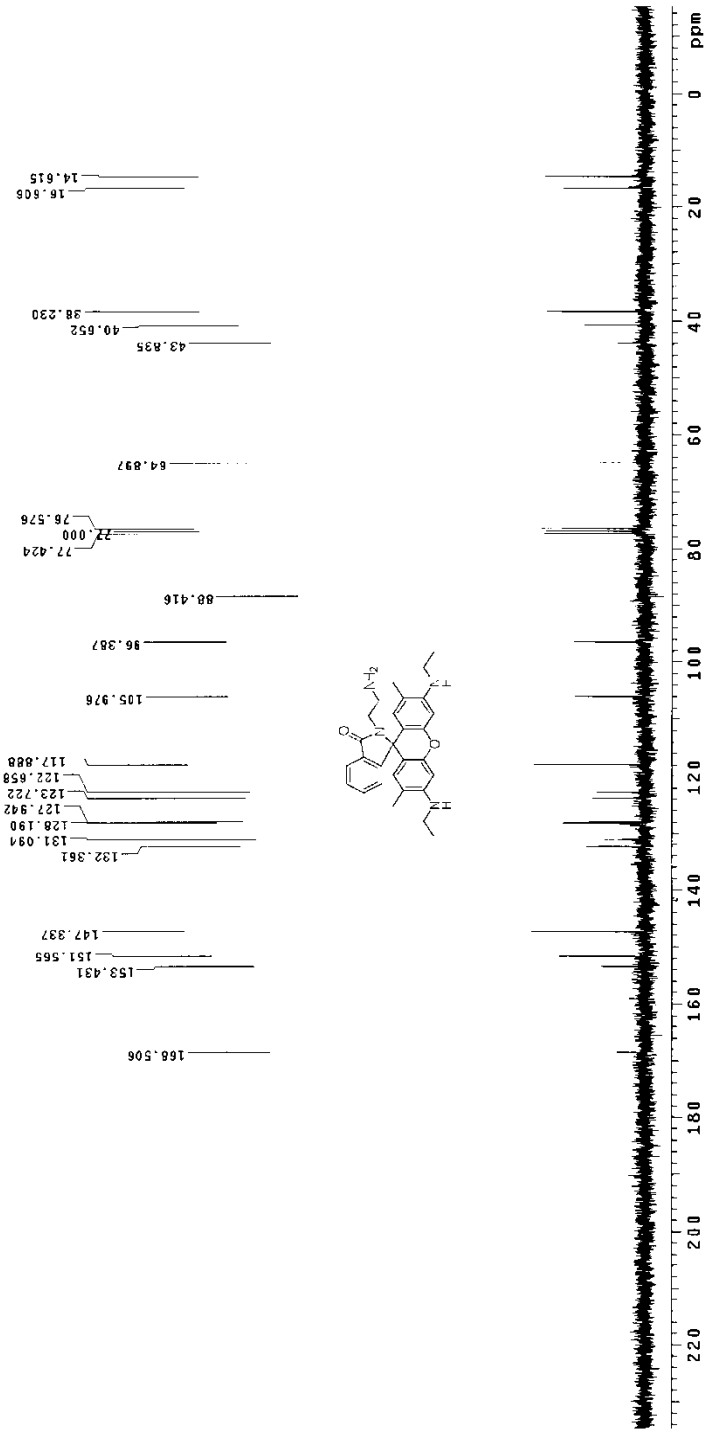
Hg^{2+a}

Fig. S3 Detection limit test of chemsensor L1: Fluorescence emission changes of L1 (10^{-7} M) upon additions of Hg^{2+} (by 2 ppb) in methanol at 25℃.

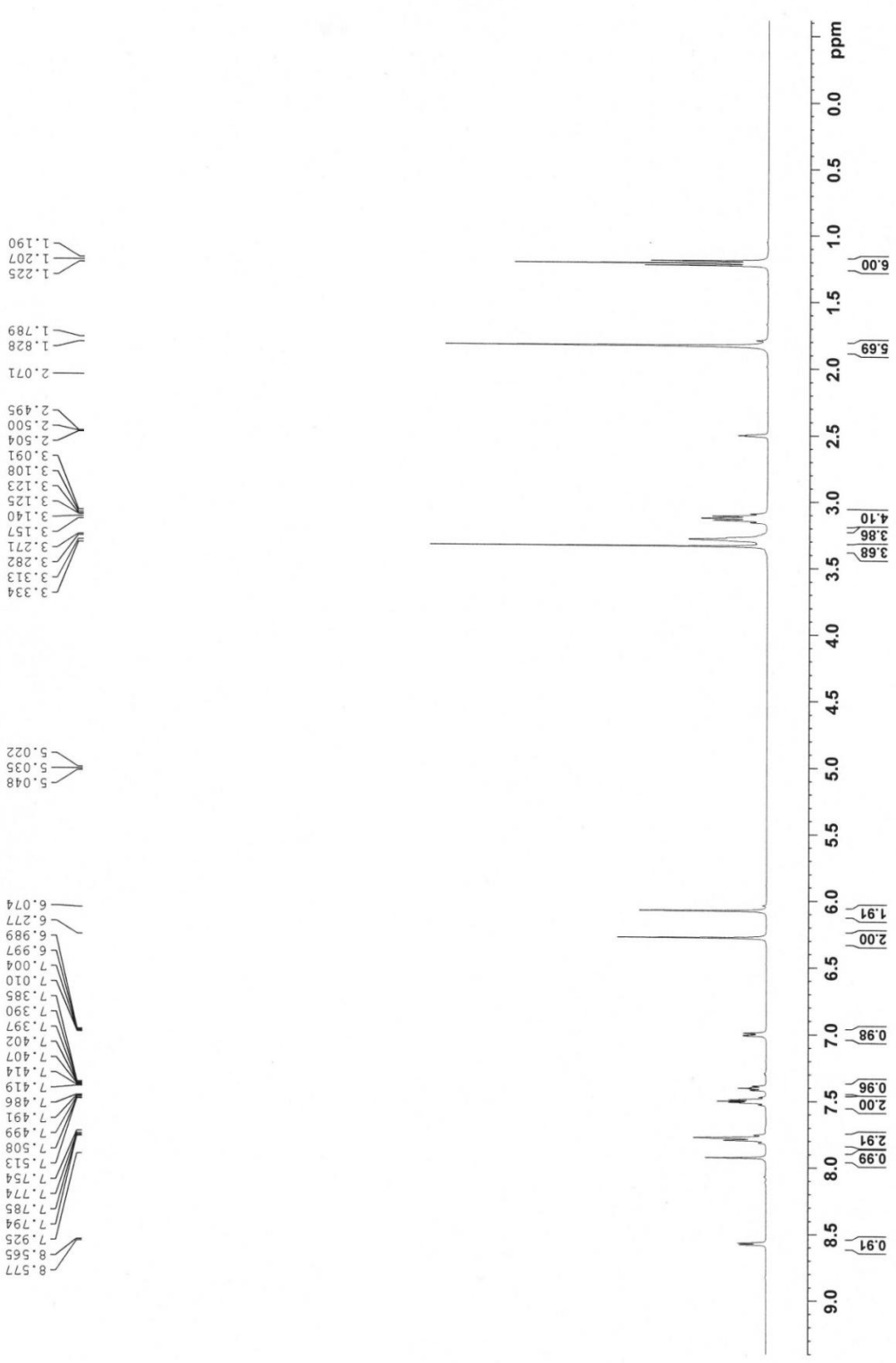
Ref：1. Wu JS, Hwang IC, Kim KS (2007) Org Lett 9:907-910



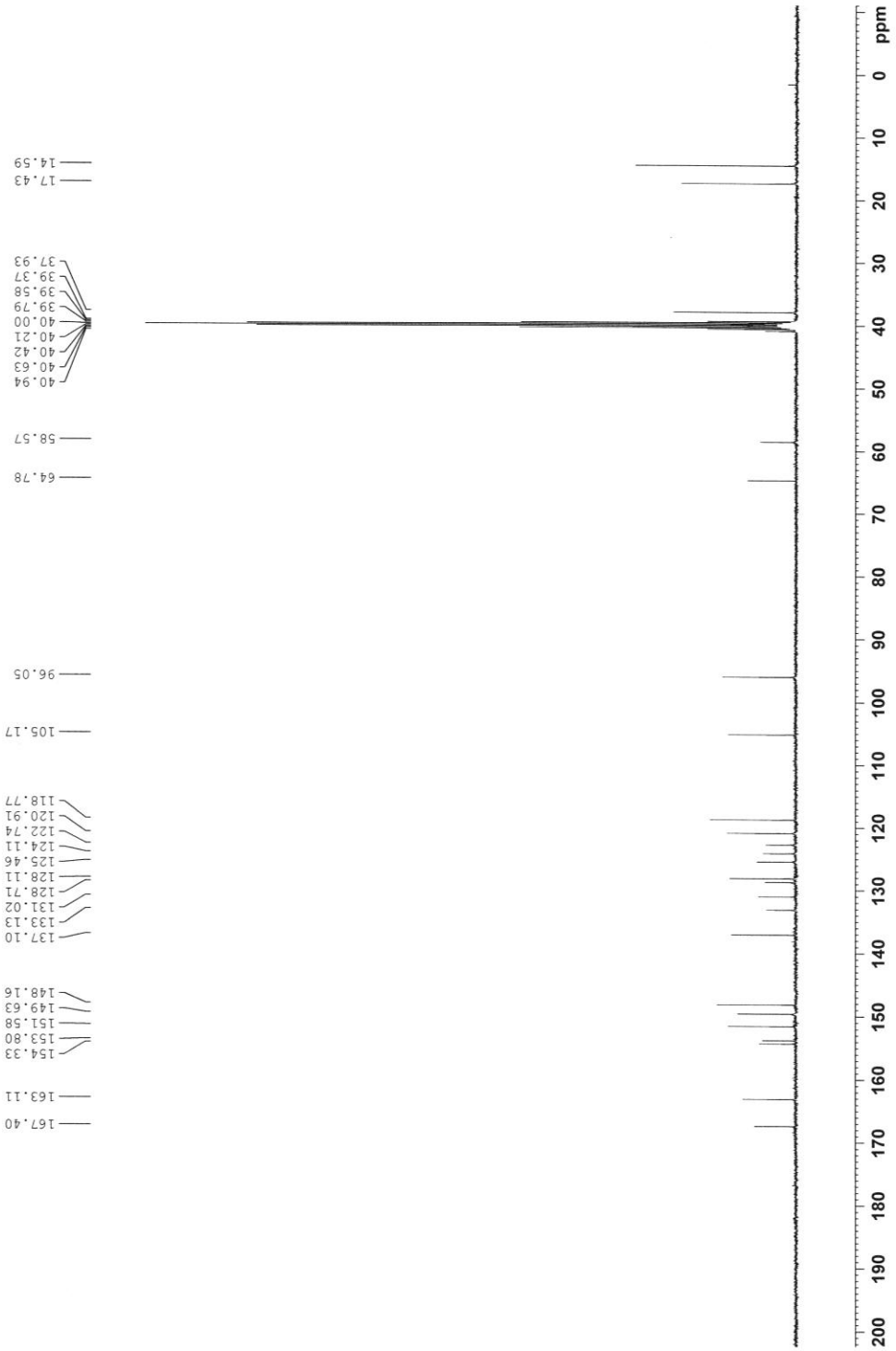
^{1}H-NMR spectra of N-(rhodamine-6G)lactam-ethylenediamine



^{13}C-NMR spectra of N-(rhodamine-6G)lactam-ethylenediamine



^{1}H-NMR spectra of L1



^{13}C-NMR spectra of L1