Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.
This journal is © The Royal Society of Chemistry 2017

Electronic Supplementary Information

A NIR fluorescent chemodosimeter for imaging endogenous hydrogen polysulfides *via* the CSE enzymatic pathway

Jianhua Ma,[a] Jiangli Fan,[a] Haidong Li,[a] Qichao Yao,[a] Feng Xu,[a] Jingyun Wang[b] and Xiaojun Peng*[a]

[a]State Key Laboratory of Fine Chemicals, Dalian University of Technology, 2 Linggong Road, Dalian 116024, P.R. China.

[b]School of Life Science and Biotechnology, Dalian University of Technology, 2 Linggong Road, Dalian 116024, P.R. China.

Email: Pengxj@dlut.edu.cn.

Contents

Scheme S1 The synthetic route of probe **Cy-S$_n$**.....S2

Fig. S1 Photostability test of **Cy-S$_n$** and traditional cyanine dye **Cy7-Cl**.....S2

Fig. S2 HRMS analysis of **Cy-S$_n$** before and after addition of Na_2S_4.....S3

Fig. S3 Fluorescence intensity of **Cy-S$_n$** and **Cy-S$_n$** treated with Na_2S_4 at various pH values.....S3

Fig. S4 Fluorescence intensity of **Cy-S$_n$** and **Cy-S$_n$** treated with various RSS.....S4

Fig. S5 Fluorescence intensity of **Cy-S$_n$** and **Cy-S$_n$** treated with Na_2S_4 and various RSS.....S4

Fig. S6 Fluorescence intensity of **Cy-S$_n$** and **Cy-S$_n$** treated with various ROS.....S5

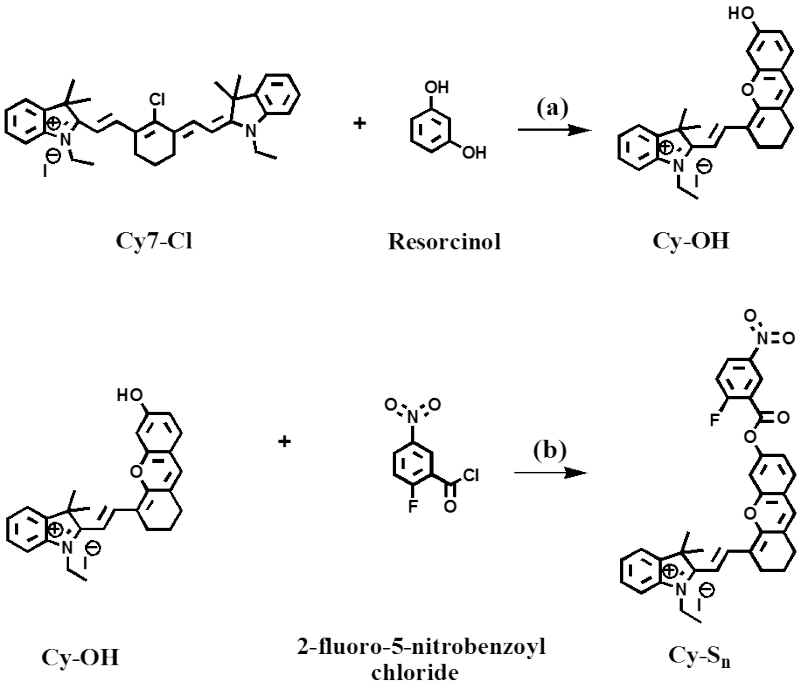
Fig. S7 Fluorescence intensity of **Cy-S$_n$** and **Cy-S$_n$** treated with H_2S and various ROS.....S5

Fig. S8 Confocal images of exogenous H_2S_n in RAW264.7 cells.....S6

Fig. S9 Confocal images of H_2S_n from H_2S/ClO^- system in RAW264.7 cells.....S6

Fig. S10 Confocal images of endogenous H_2S_n in RAW264.7 cells.....S7

Fig. S11 ^{1}H NMR and ^{13}C NMR spectrum of compound **Cy-S$_n$** in $CDCl_3$.....S8



Scheme S1. The synthetic route of probe **Cy-S$_n$**. Reagent and conditions: (a) Et_3N, DMF, 50°C, 5 h, 60.2%; (b) DMAP, CH_2Cl_2, 30 min, r.t., 77.1%.

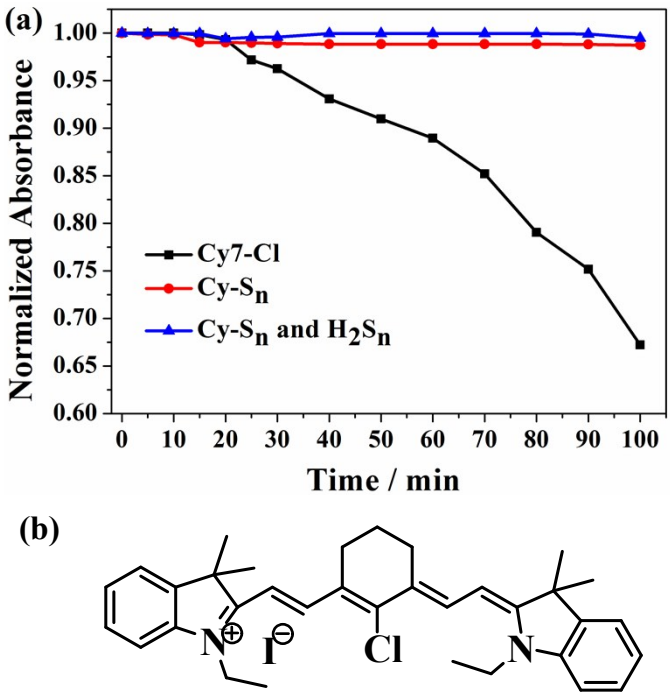


Fig. S1. (a) Time-dependent normalized absorbance intensity of probe **Cy-S$_n$** (5 μM, monitored at 590 nm), **Cy-S$_n$** (5 μM) treated with Na_2S_4 (300 μM, monitored at 700 nm), and **Cy7-Cl** (10 μM, monitored at 780 nm) in solution (DMSO/PBS = 5/5, pH = 7.4) under sustained illumination; (b) the structure of compound **Cy7-Cl** as reference for photo-stability experiment.

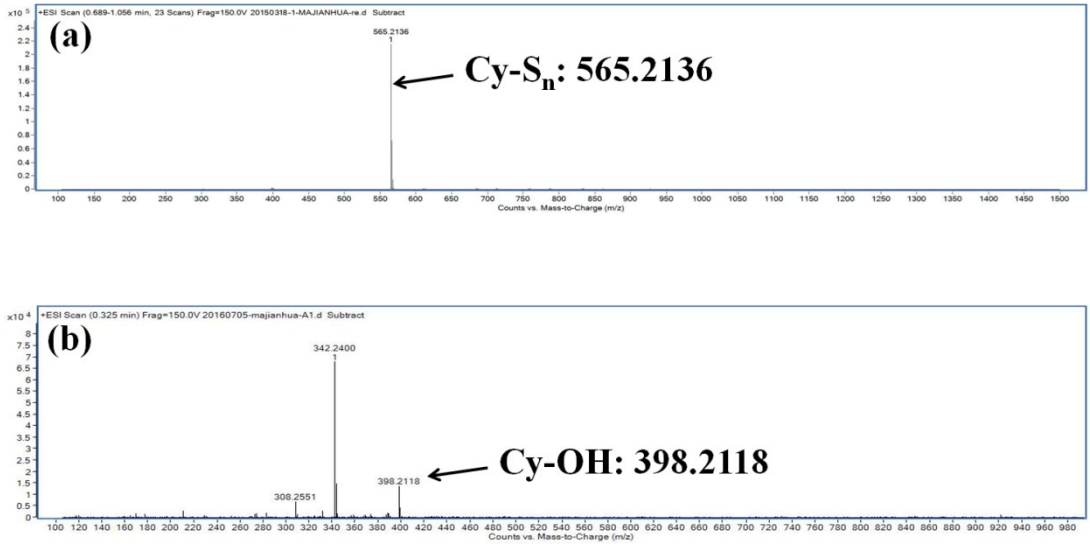


Fig. S2. HRMS spectra of **Cy-S$_n$** (a) and **Cy-S$_n$** + Na_2S_4 (b) in solution (DMSO/PBS = 5/5, pH = 7.4).

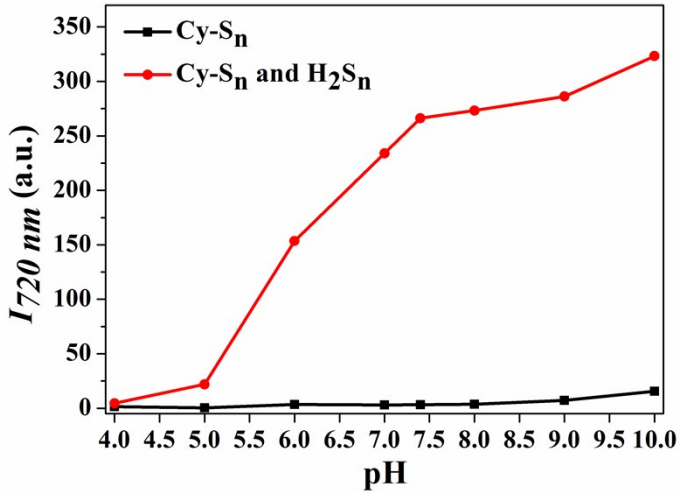


Fig. S3. Fluorescence intensity of **Cy-S$_n$** (5 μM) and **Cy-S$_n$** treated with Na_2S_4 (300 μM) in 5 min in solution (DMSO/PBS = 5/5, pH = 7.4) at various pH values, respectively. The excitation wavelength was 680 nm.

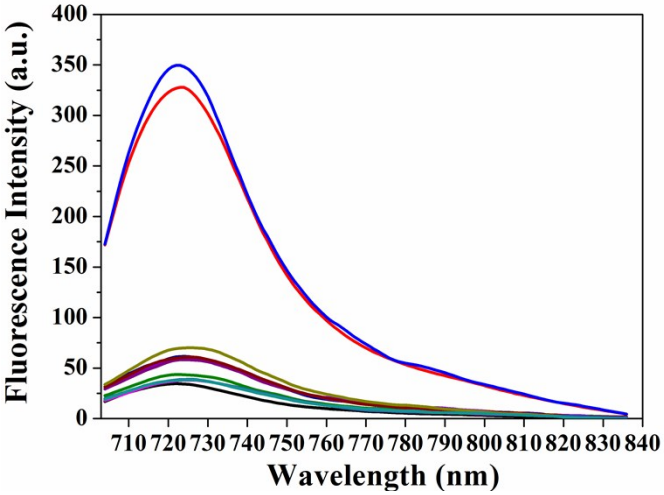


Fig. S4. Fluorescence intensity of **Cy-S$_n$** (5 μM) and **Cy-S$_n$** treated with 300 μM of Na_2S_2, Na_2S_4, ascorbic acid, tocopherol, GSSG, GSH, HCy, Cys, H_2S, SO_4^{2-}, S_8 in 5 min in solution (DMSO/PBS = 5/5, pH = 7.4). The excitation wavelength was 680 nm.

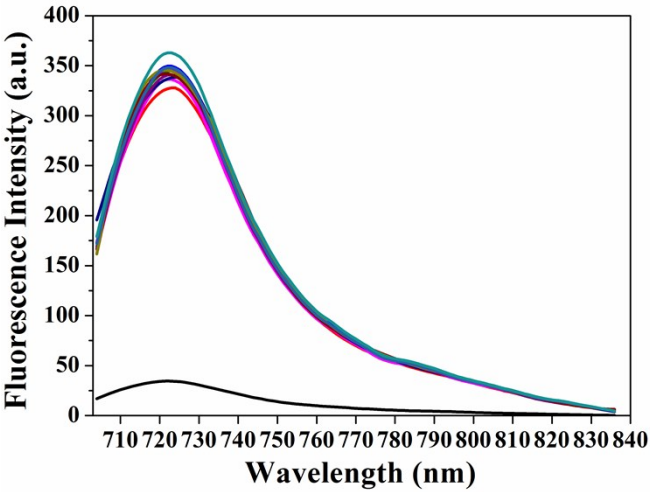


Fig. S5. Fluorescence intensity of **Cy-S$_n$** (5 μM) and **Cy-S$_n$** with the mixture of Na_2S_4 and various RSS (ascorbic acid, tocopherol, GSSG, GSH, HCy, Cys, H_2S, SO_4^{2-}, S_8, 300 μM) in 5 min in solution (DMSO/PBS = 5/5, pH = 7.4). The excitation wavelength was 680 nm.

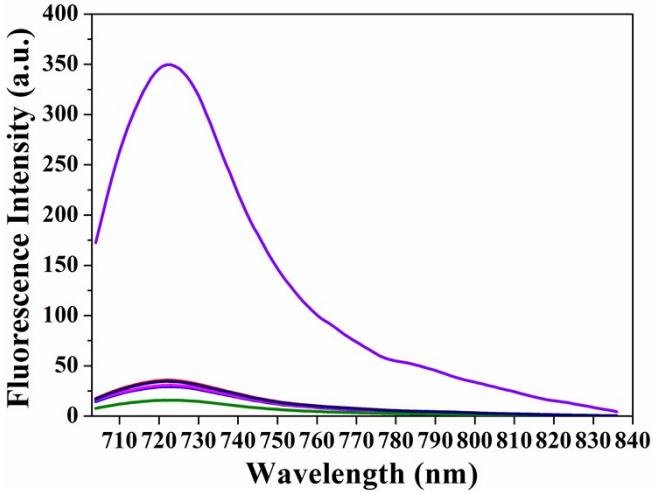


Fig. S6. Fluorescence intensity of **Cy-S$_n$** (5 μM) and **Cy-S$_n$** treated with 300 μM of Na_2S_4, H_2O_2, ·OH, O_2^-, $^1O_2$ and ClO^- in 5 min in solution (DMSO/PBS = 5/5, pH = 7.4). The excitation wavelength was 680 nm.

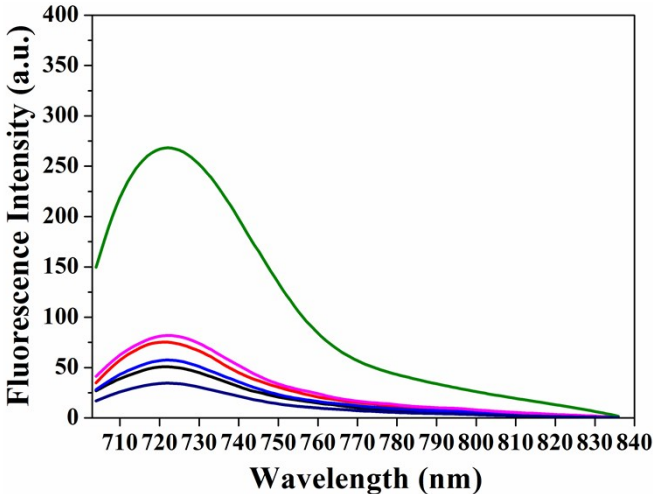


Fig. S7. Fluorescence intensity of **Cy-S$_n$** (5 μM) and **Cy-S$_n$** with the mixture of H_2S (300 μM) and various ROS (H_2O_2, ·OH, O_2^-, $^1O_2$ and ClO^- , 300 μM) in solution (DMSO/PBS = 5/5, pH = 7.4). The reactions were carried out for 20 min at 37 °C. The excitation wavelength was 680 nm.

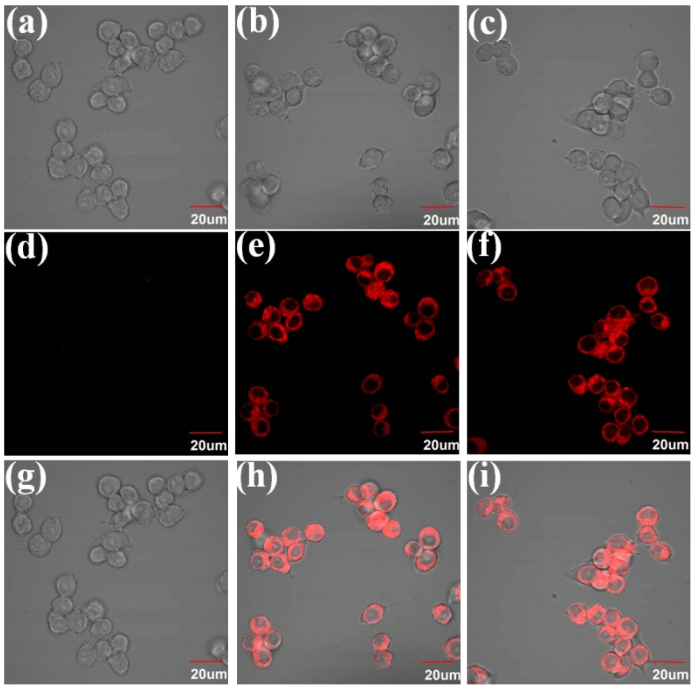


Fig. S8. Confocal microscope images of RAW264.7 cells. Cells were treated with **Cy-S$_n$** for 15 min, then PBS (a), (d), (g), Na_2S_2 (b), (e), (h) and Na_2S_4 (c), (f), (i) for 20 min. Confocal microscope image of cells upon excitation at 635 nm, emission window 650 nm—750 nm.

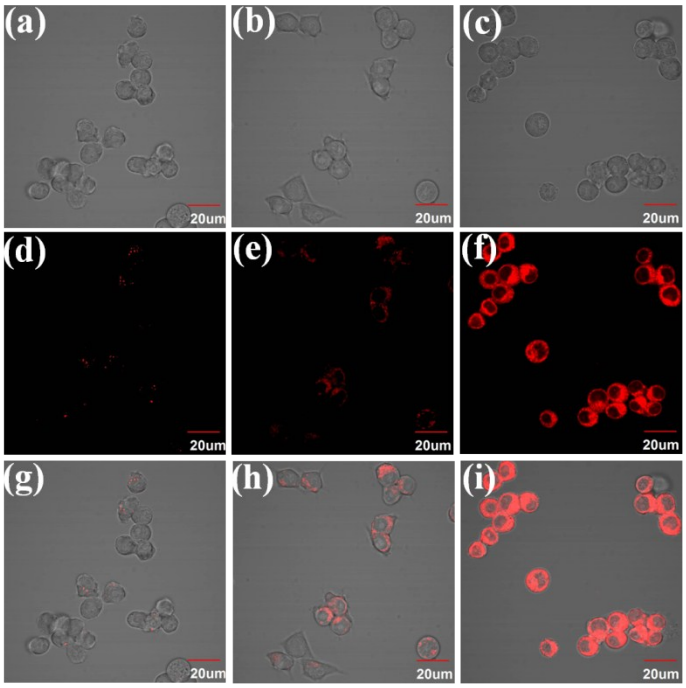


Fig. S9. Confocal microscope images of RAW264.7 cells. Cells were treated with **Cy-S$_n$** for 15 min, then NaClO (a), (d), (g), H_2S (b), (e), (h) and mixture of NaClO and H_2S (c), (f), (i) for 20 min. Confocal microscope image of cells upon excitation at 635 nm, emission window 650 nm—750 nm

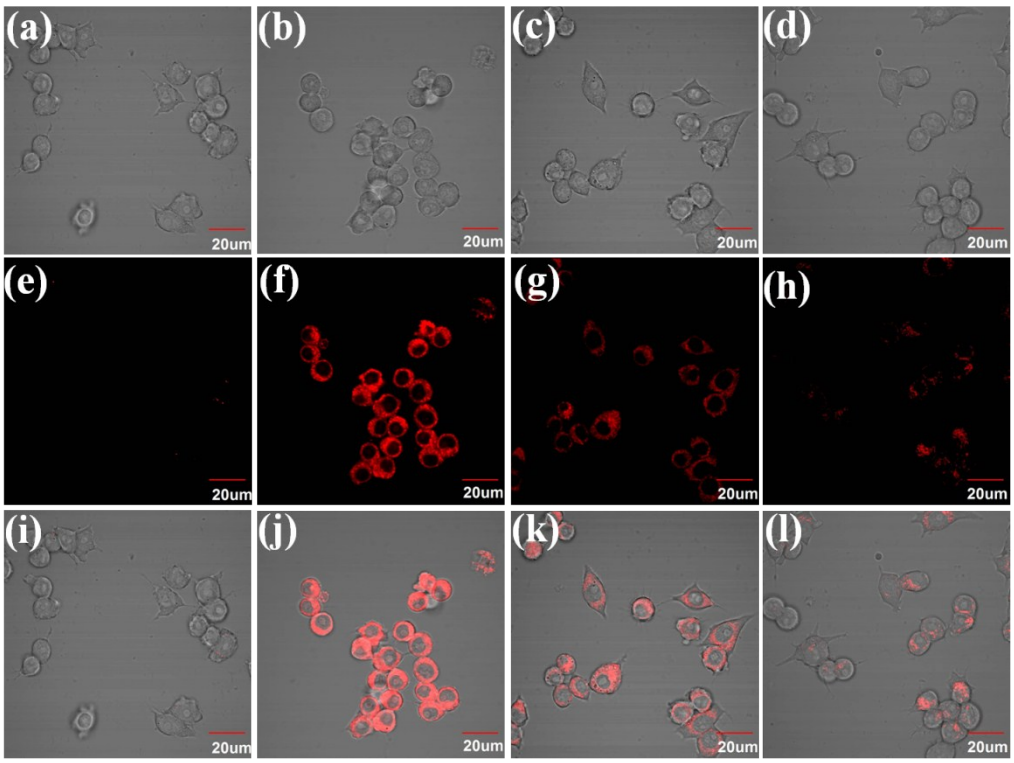


Fig. S10. Confocal microscope images of RAW264.7 cells. Cells were treated with **Cy-S$_n$** for 15 min, then PBS (a), (e), (i); 1 μg/mL LPS for 24 h (b), (f), (j); 1 μg/mL LPS and 1 nM dexamethasone for 24 h (c), (g), (k); pretreated with 1mM PPG 8 h then 1 μg/mL LPS for 24 h (d), (h), (l). Confocal microscope image of cells upon excitation at 635 nm, emission window 650 nm—750 nm

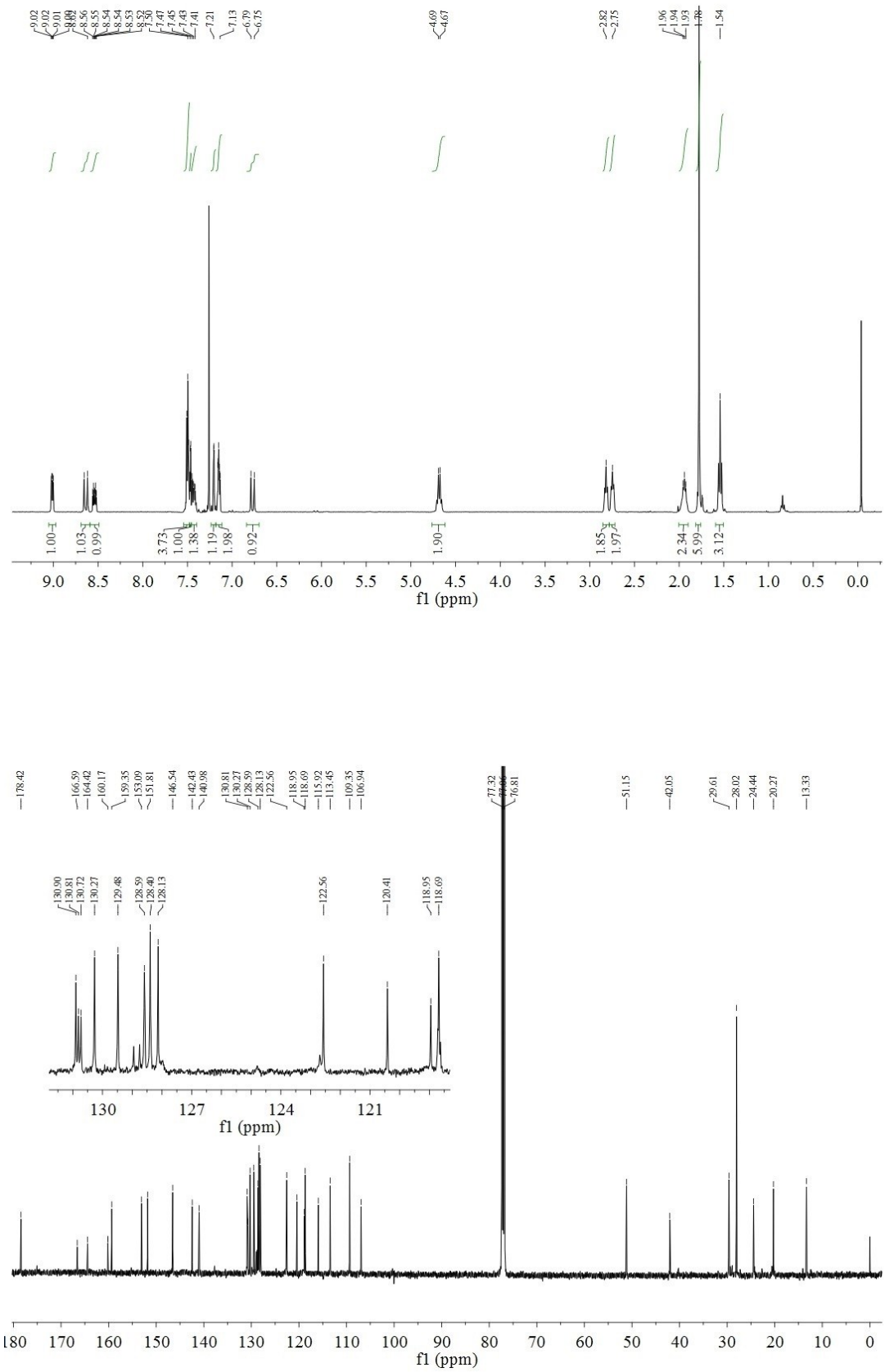


Fig. S11. ^{1}H NMR (top) and ^{13}C NMR (down) spectrum of compound **Cy-S$_n$** in $CDCl_3$.