Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Zn(II) phthalocyanines Tetra Substituted by Aryl and Alkyl Azides: Design, Synthesis and Optical Detection of H_2S

Electronic Supplementary Information

Mohamad Albakour[a], Merve Zeyrek Ongun[b], Sevinc Zehra Topal[a,*], Ayşe Gül Gürek[a,*]

[a] *Gebze Technical University, Department of Chemisytry, 41400 Gebze, Kocaeli, Turkey*

[b] *Dokuz Eylul University, Chemistry Technology Program, Izmir Vocational High School, 35160, Izmir, Turkey*

Table of Contents

Fig. S27 Absorption spectra of **3** in DMF, pyridine, THF and DMSO at the same concentration (10^{-5} M).
Fig. S28 Absorption spectra of **7** in DMF, pyridine, THF and DMSO at the same concentration (10^{-5} M).

Fig. S29 UV-Vis spectra of compound **3** at the different concentrations in DMSO.

Fig. S30 UV-Vis spectra of compound **7** at the different concentrations in DMSO

Fig. S31 Fluorescence integrate area *vs* absorbance of **3**, **7** and **ZnPc** in DMSO to determine their Φ_F values

Fig. S32 Determination of singlet oxygen quantum yield of **3** in DMSO. Inset: Plot of DPBF absorbance at 417 nm

Fig. S33 Determination of singlet oxygen quantum yield of **7** in DMSO. Inset: Plot of DPBF absorbance at 417 nm

Fig. S34 Determination of singlet oxygen quantum yield of **ZnPc** in DMSO. Inset: Plot of DPBF absorbance at 417 nm

Fig. S35 Changes in the absorption spectra of compound **7** (5.0×10^{-7} M) in DMSO by the addition of hydrogen sulfide ($Na_2S.9H_2O$ in HEPES/ DMSO (5:5, pH= 7.0)).

Fig. S36 Changes in the emission spectra of compound **7** (5.0×10^{-7} M) in DMSO by the addition of hydrogen sulfide ($Na_2S.9H_2O$ in HEPES/ DMSO (5:5, pH= 7.0))

Fig. S37 Proposed mechanism for reduction of azide group to amine group [1,2].

Fig. S38 MALDI-TOF mass spectrum of 2,9(10),16(17),23(24) (amino) phthalocyaninato zinc (II) (**Pc-NH_2**). It is obtained the reaction of 500 μM compound **3** with 10 mM Na_2S

Synthesis of tetra 2,9(10),16(17),23(24) (amino) phthalocyaninato zinc (II) (Pc-NH_2)

Fig. S39 FT-IR spectrum of 2,9(10),16(17),23(24) (amino) phthalocyaninato zinc (II) **(Pc-NH_2)**

Fig. S40 ^{1}H-NMR spectrum of 2,9(10),16(17),23(24) (amino) phthalocyaninato zinc (II) **(Pc-NH_2)** in DMSO-d_6

Fig. S41 MALDI-TOF mass spectrum of 2,9(10),16(17),23(24) (amino) phthalocyaninato zinc (II) **(Pc-NH_2)** (matrix: DIT)

EXPERIMENTAL

Fluorescence Quantum Yield Determination

Fluorescence quantum yield values (Φ_F) were determined by the comparative William's method [15]. Accordingly, the UV-Vis absorption and corrected emission spectra at different concentrations of the reference standard (ZnPc) and samples were measured under identical conditions. Note that the absorbance value at the excitation wavelength was used. Integrated fluorescence intensities (the area of the fluorescence emission spectrum) versus absorbance for using reference molecule **ZnPc** (Φ_F = 0.18 in DMSO [16] and samples were plotted. Quantum yield (Φ_F) values were calculated according to Eq. 1. Grad was the gradient of the plot, and the gradients of the plots were proportional to the quantum yield of the samples.

$$\Phi_F = \Phi_F^{Std}\left(\frac{Grad}{Grad_{Std}}\right) \qquad \text{(Eq. 1)}$$

Singlet Oxygen Quantum Yield Determination

Singlet oxygen quantum yields (Φ_Δ) of the molecules were determined by indirect measurement based on the quenching of the absorbance of DPBF by singlet oxygen generated by the Pc irradiation. **ZnPc** was used as a reference (Φ_Δ = 0.67 in DMSO). DPBF degradation at 417 nm was monitored by UV-Vis spectroscopy. The solutions of photosensitizers containing DPBF (~1×10^{-5} M) were prepared in the dark and irradiated in the Q band region. The light intensity of 7.05×10^{15} photons s^{-1} cm^{-2} was used for Φ_Δ determinations. Singlet oxygen quantum yields were calculated using the Equation 2:

$$\Phi_\Delta = \Phi_\Delta^{Std}\frac{R \cdot I_{Abs}^{Std}}{R_{Std} \cdot I_{Abs}} \qquad \text{(Eq. 2)}$$

In the equation, R and R_{Std} were DPBF photobleaching rates in the presence of the respective samples and standard, respectively, while I_{abs} and $I_{abs\ std}$ were the rates of light absorption by the samples and standard, respectively.

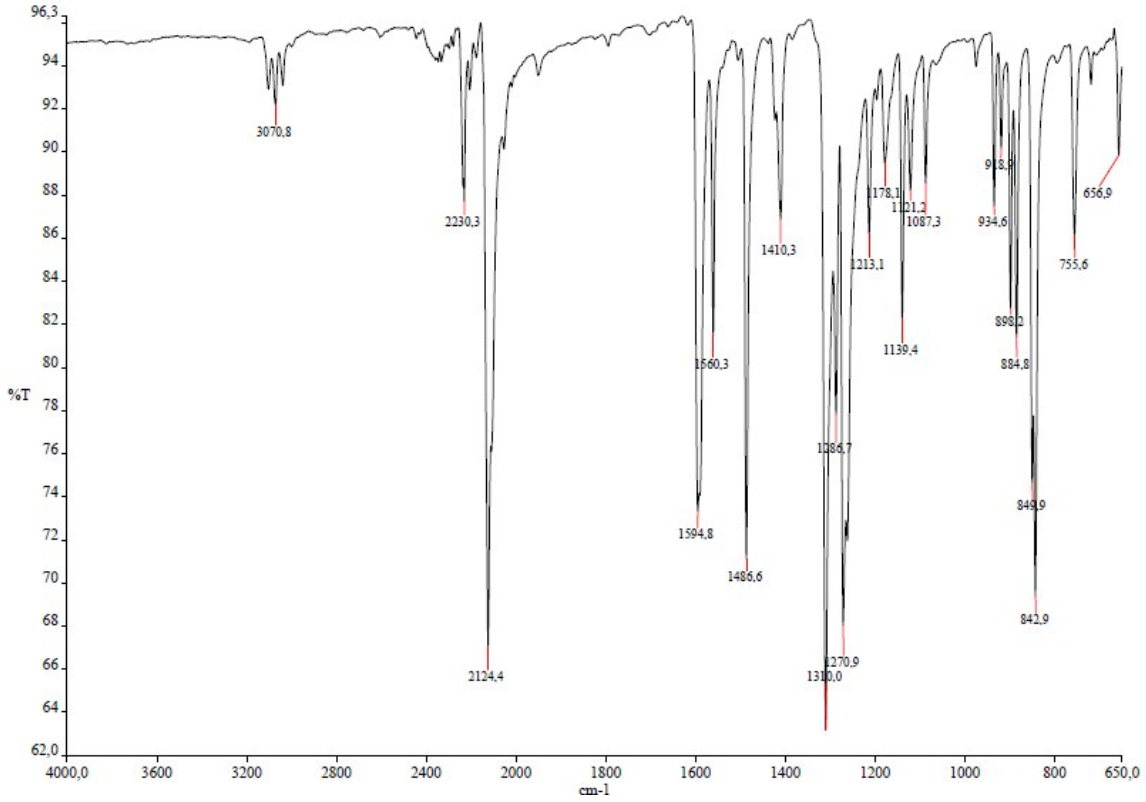


Fig. S1 FT-IR spectrum of 4- azido phthalonitrile (**2**)

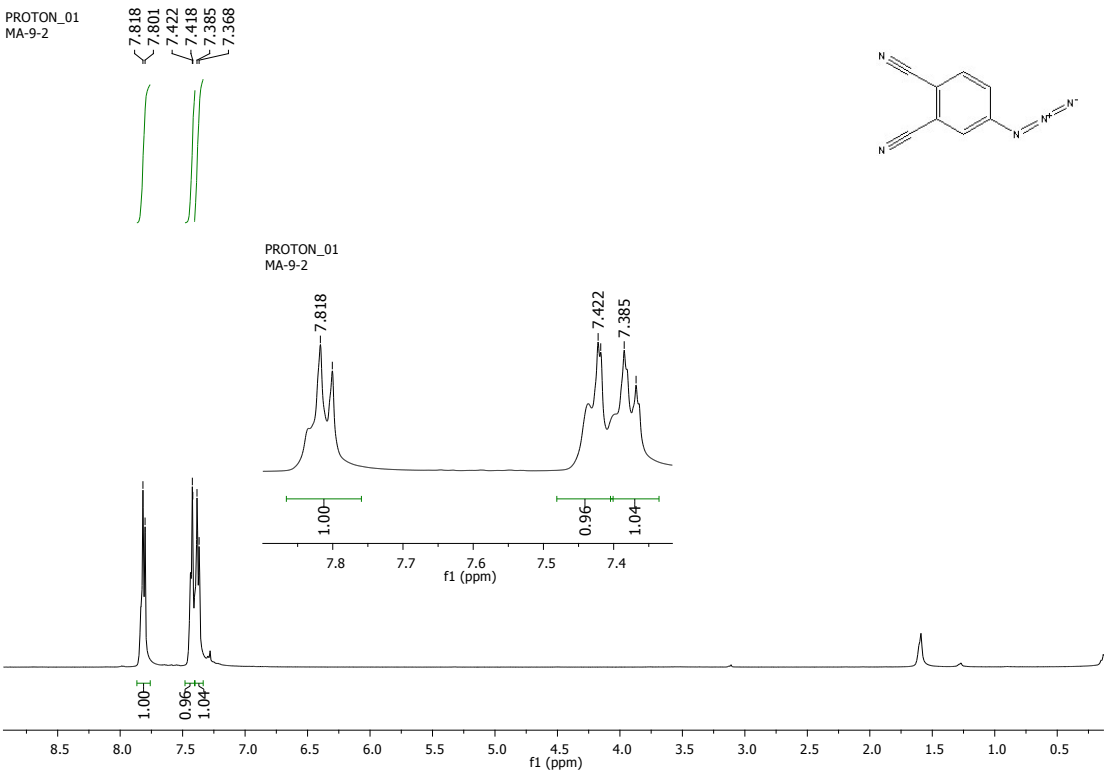
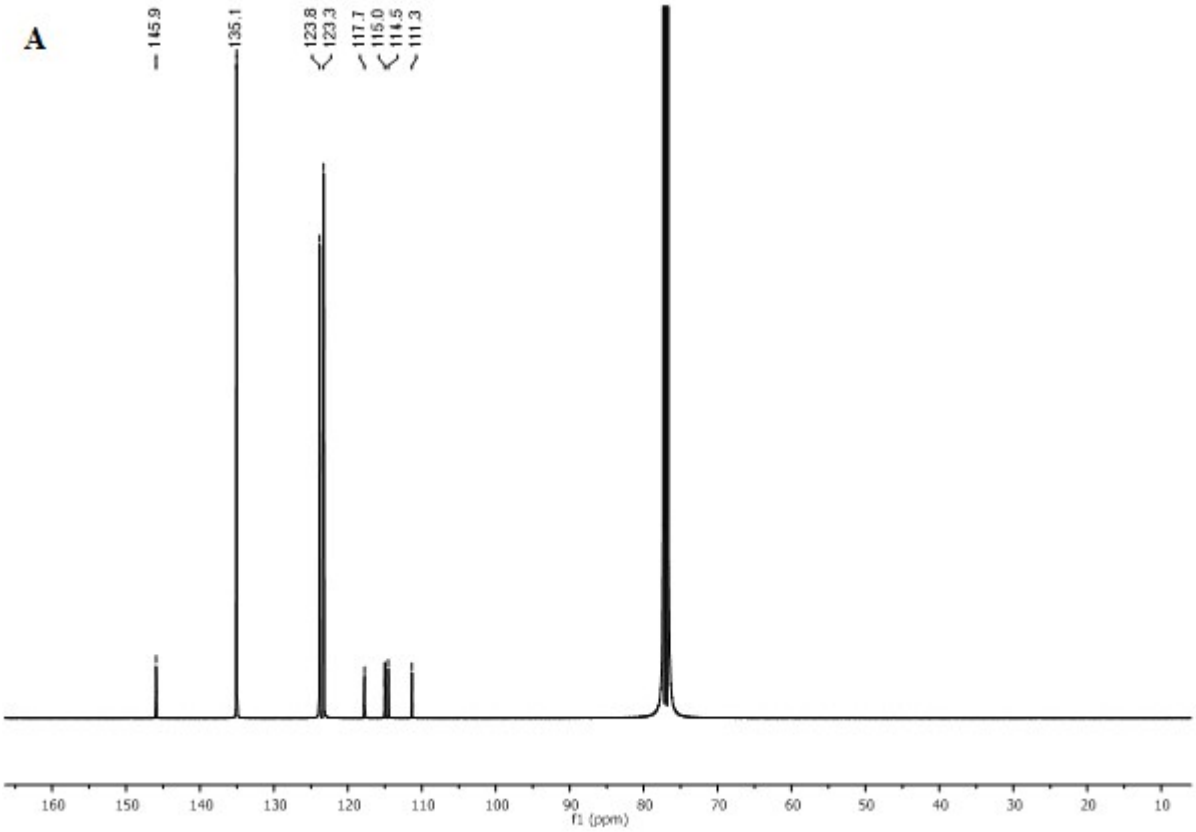


Fig. S2 ^{1}H- NMR spectrum of 4- azido phthalonitrile (**2**) in $CDCl_3$



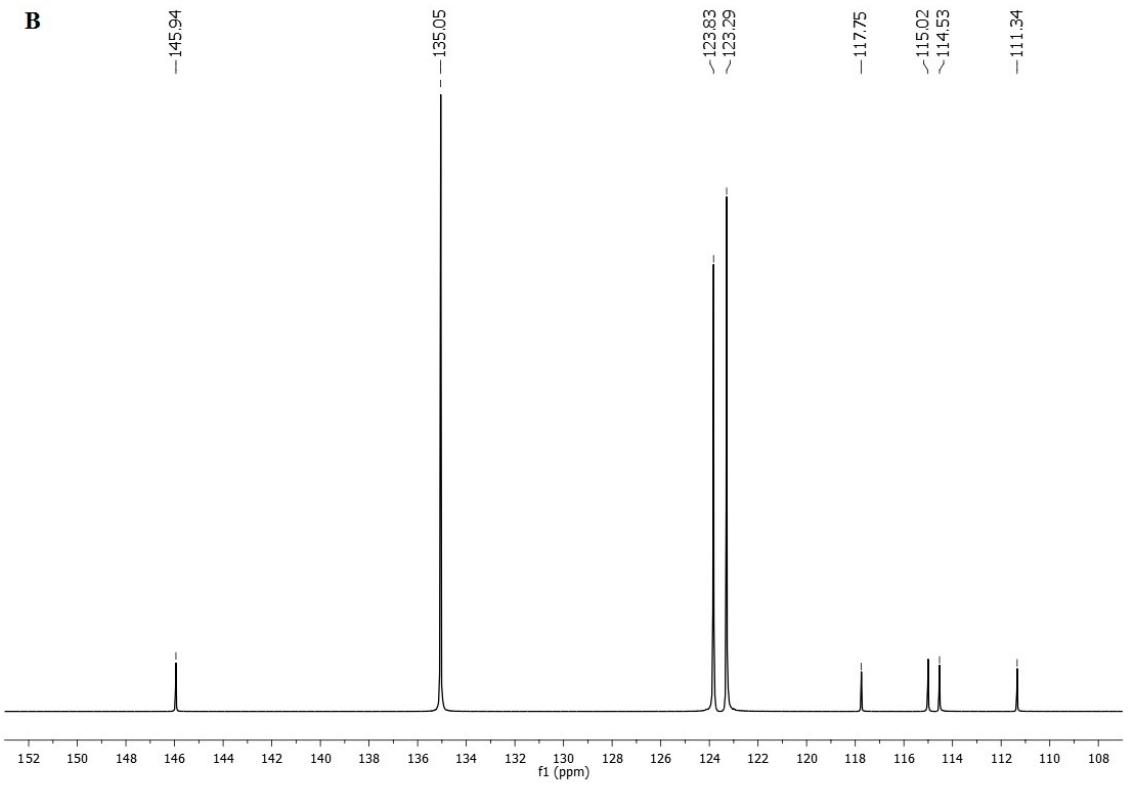


Fig. S3 ^{13}C- NMR spectrum of 4- azido phthalonitrile (**2**) in $CDCl_3$ (A) full spectra (B) the spectra between 150 and100 ppm

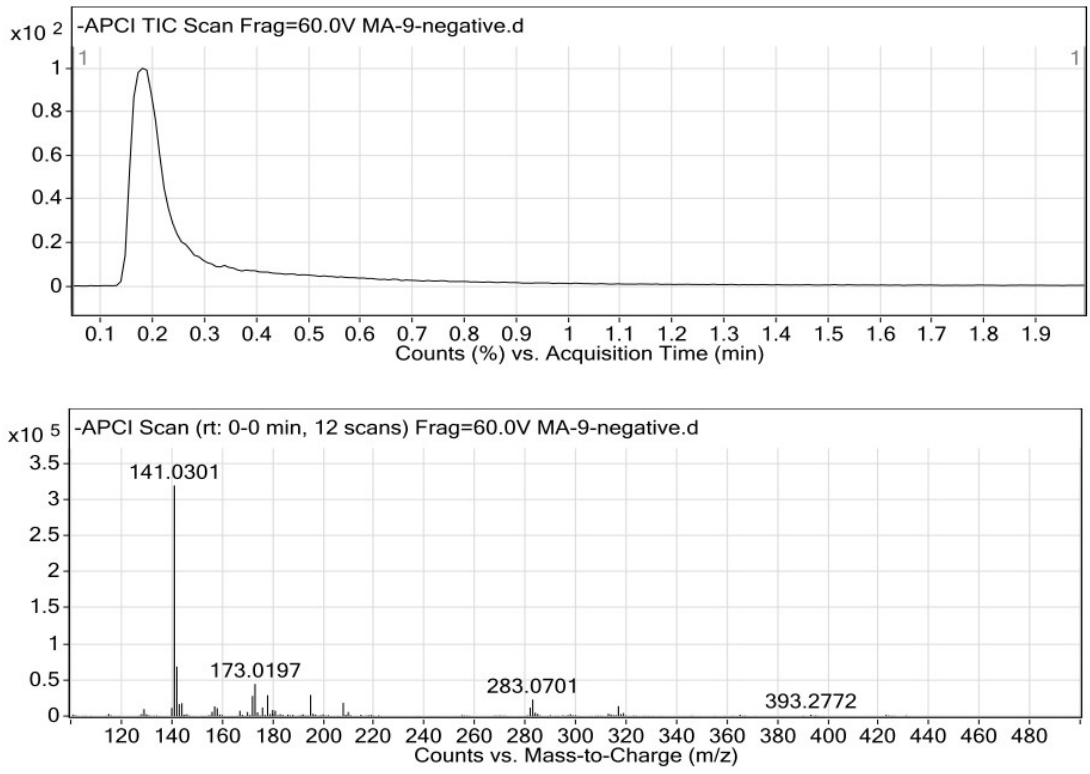


Fig. S4 Mass spectrum of 4- azido phthalonitrile (**2**)

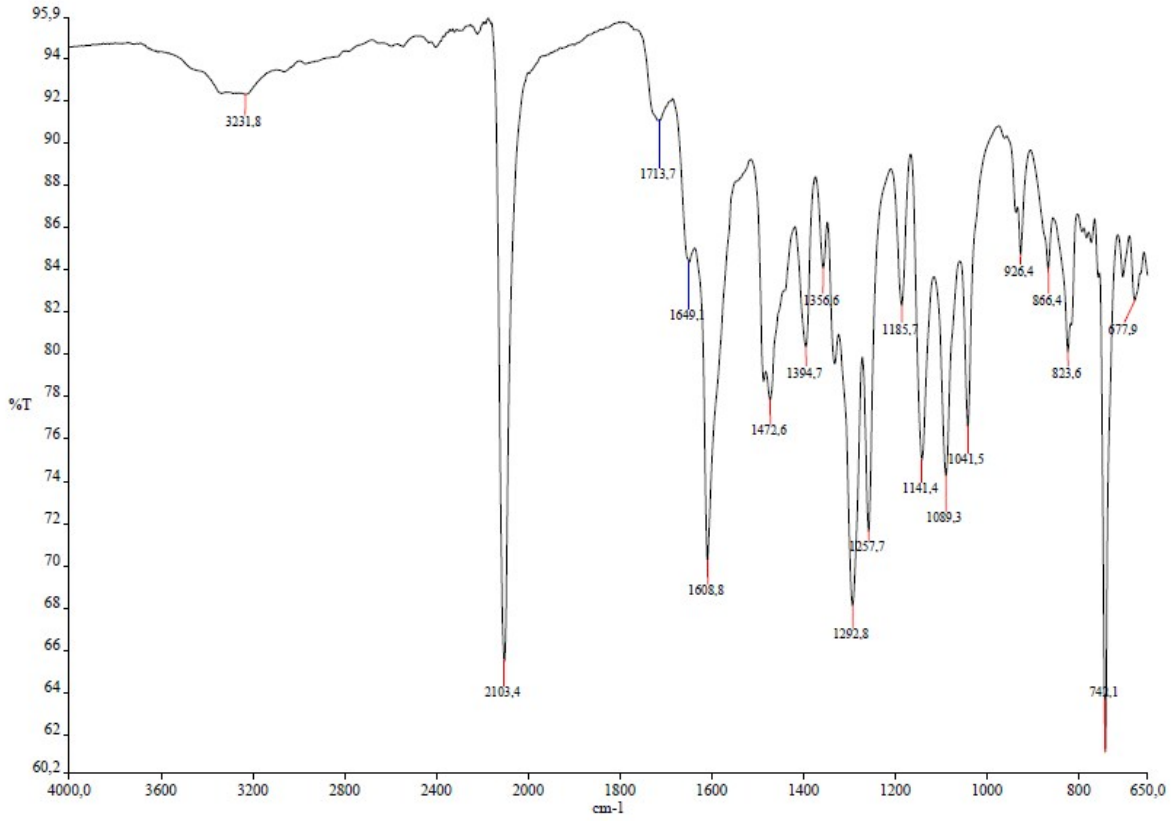


Fig. S5 FT-IR spectrum of tetra 2,9(10),16(17),23(24) azido phthalocyaninato zinc (II) (**3**)

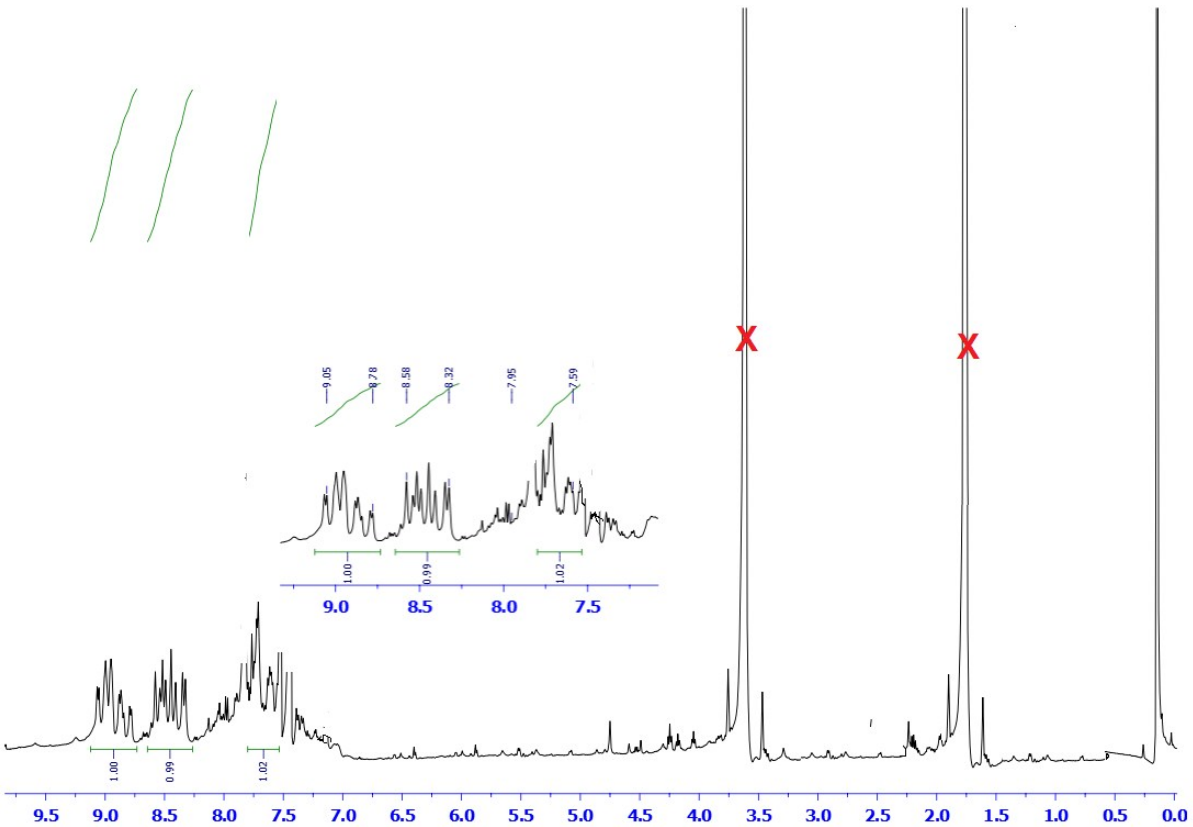


Fig. S6 ^{1}H- NMR spectrum of tetra 2,9(10),16(17),23(24) azido phthalocyaninato zinc (II) (**3**) in THF-d_8

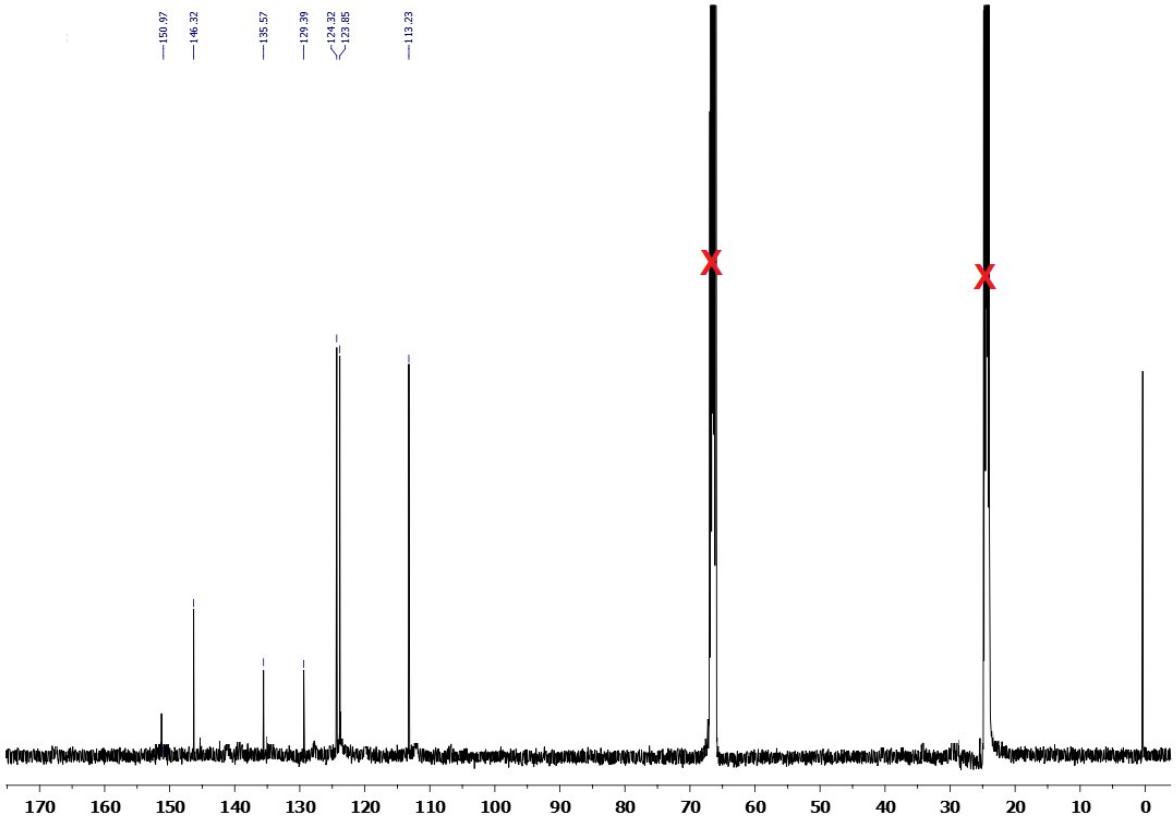


Fig. S7 ^{13}C- NMR spectrum of tetra 2,9(10),16(17),23(24) azido phthalocyaninato zinc (II) (**3**) in THF-d_8

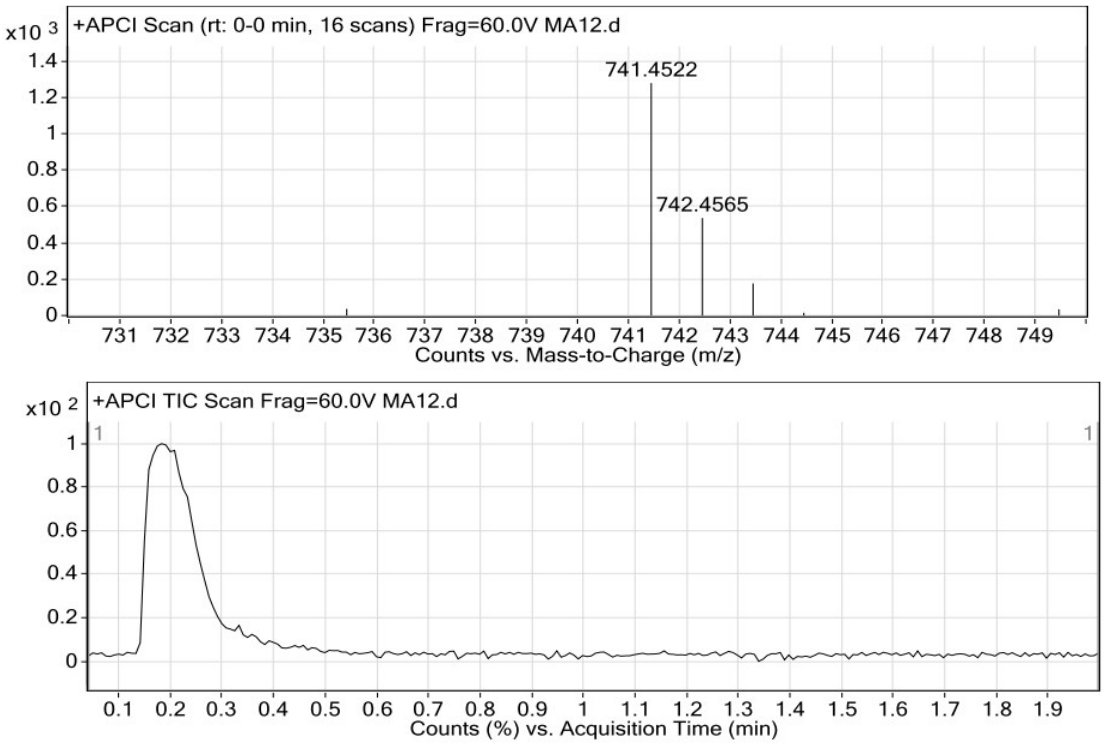


Fig. S8 Mass spectrum of tetra 2,9(10),16(17),23(24) azido phthalocyaninato zinc (II) (**3**)

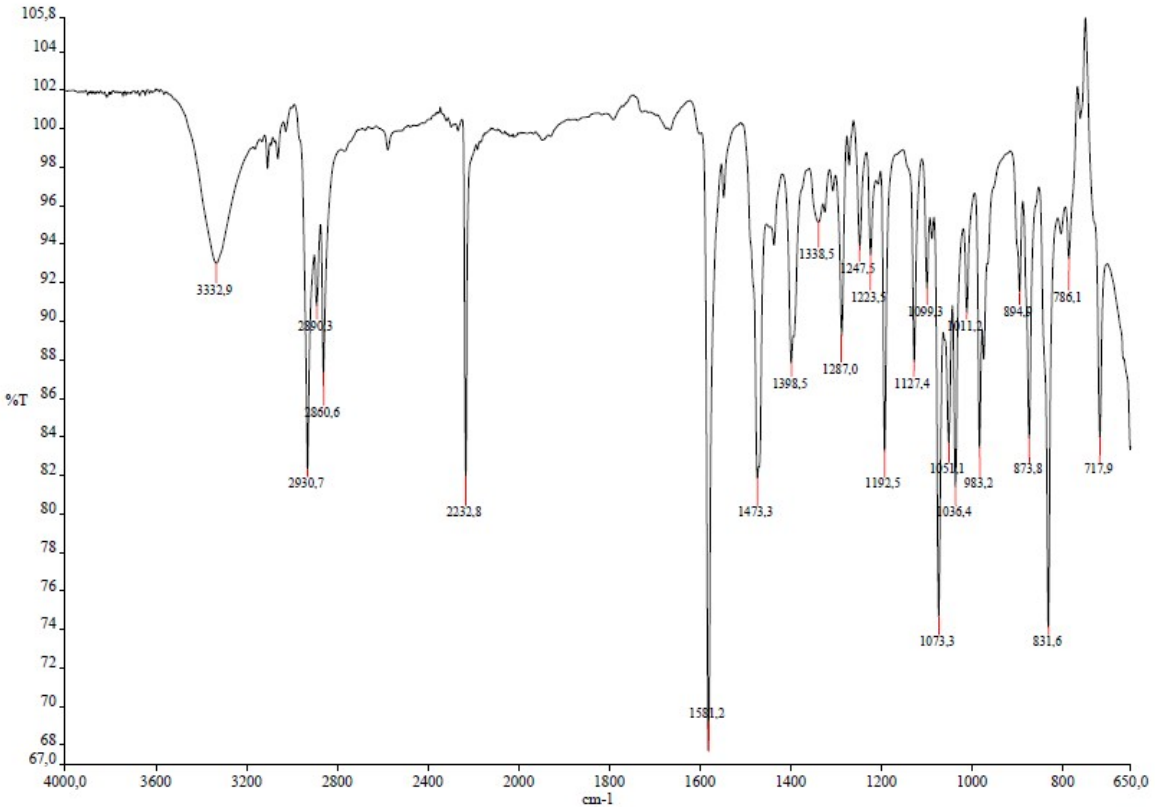


Fig. S9 FT-IR spectrum of 4 -(6-hydroxyhexylsulfanyl)-1,2-dicyanobenzene (**4**)

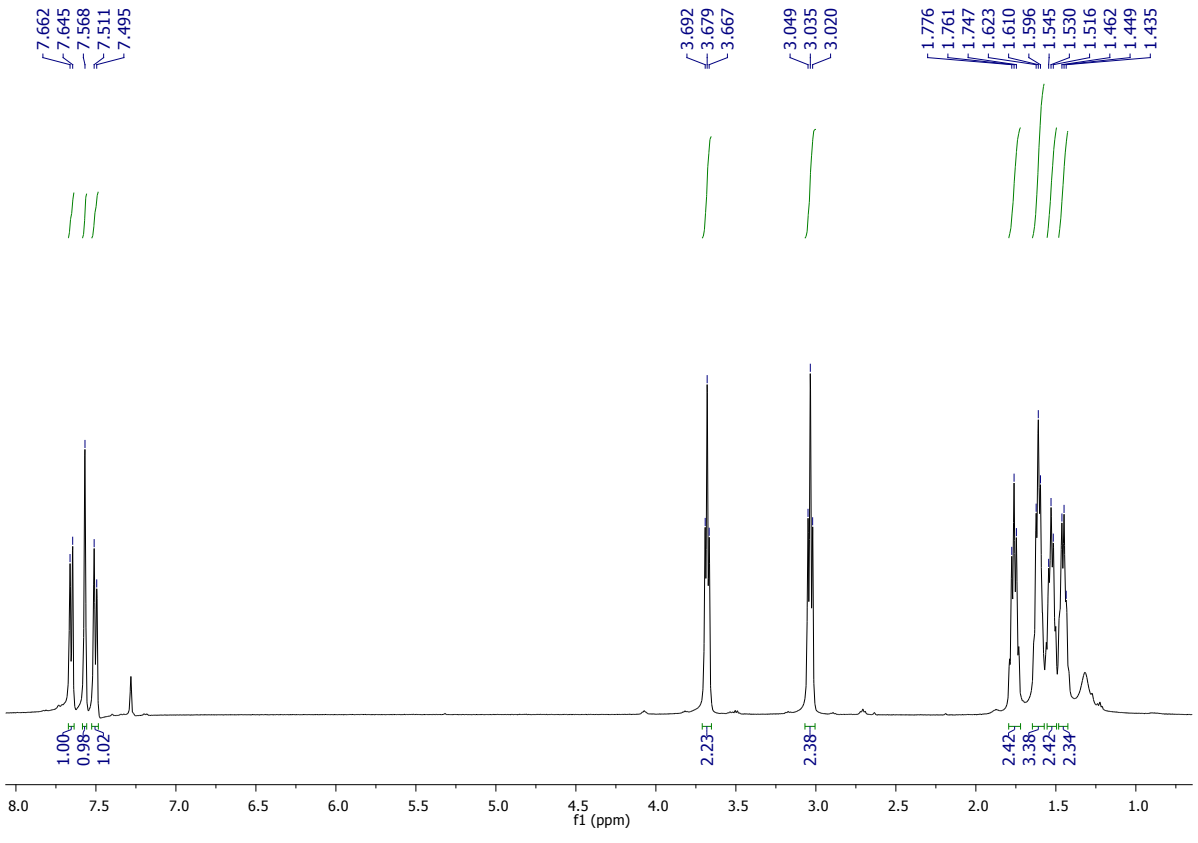


Fig. S10 ^{1}H-NMR spectrum of 4 -(6-hydroxyhexylsulfanyl)-1,2-dicyanobenzene (**4**) in $CDCl_3$

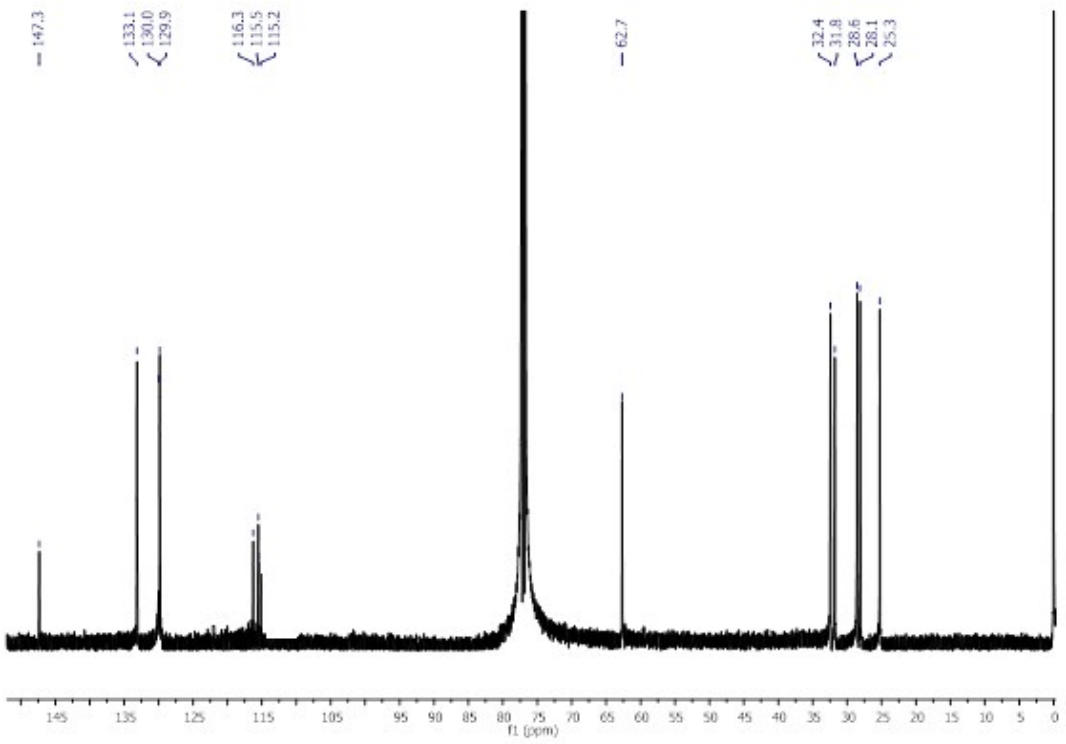


Fig. S11 ^{13}C-NMR spectrum of 4 -(6-hydroxyhexylsulfanyl)-1,2-dicyanobenzene (**4**) in $CDCl_3$

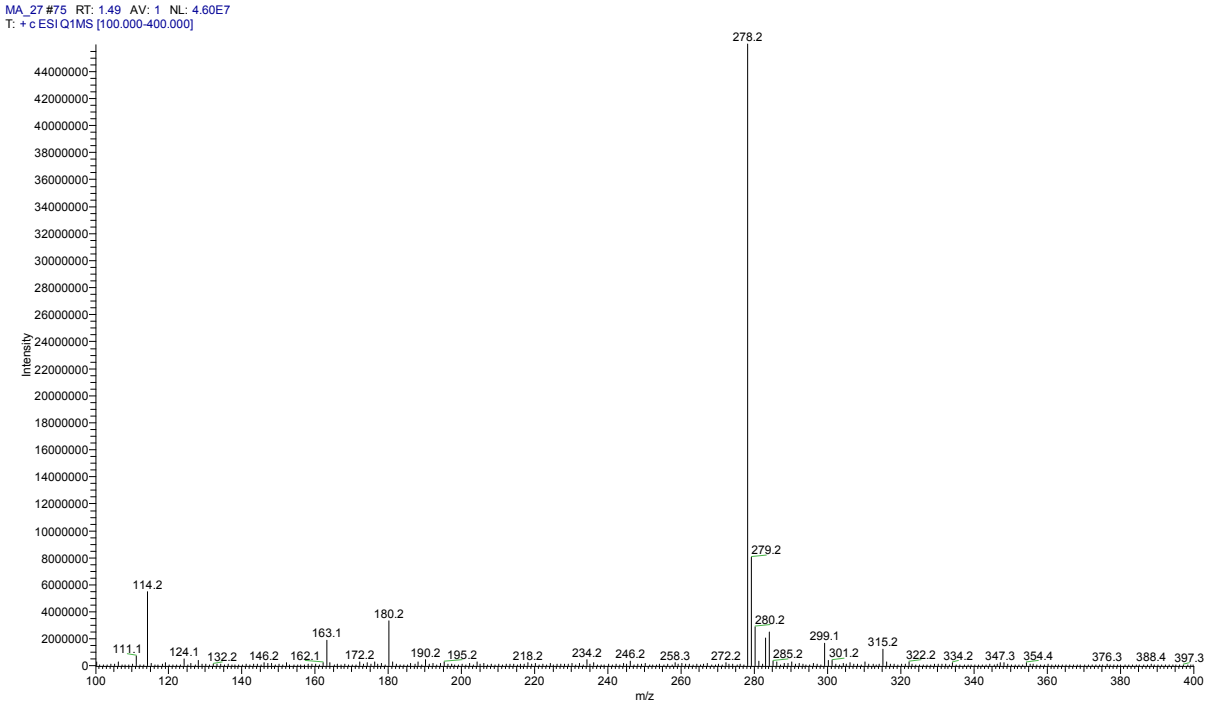


Fig. S12 Mass spectrum of 4 -(6-hydroxyhexylsulfanyl)-1,2-dicyanobenzene (**4**)

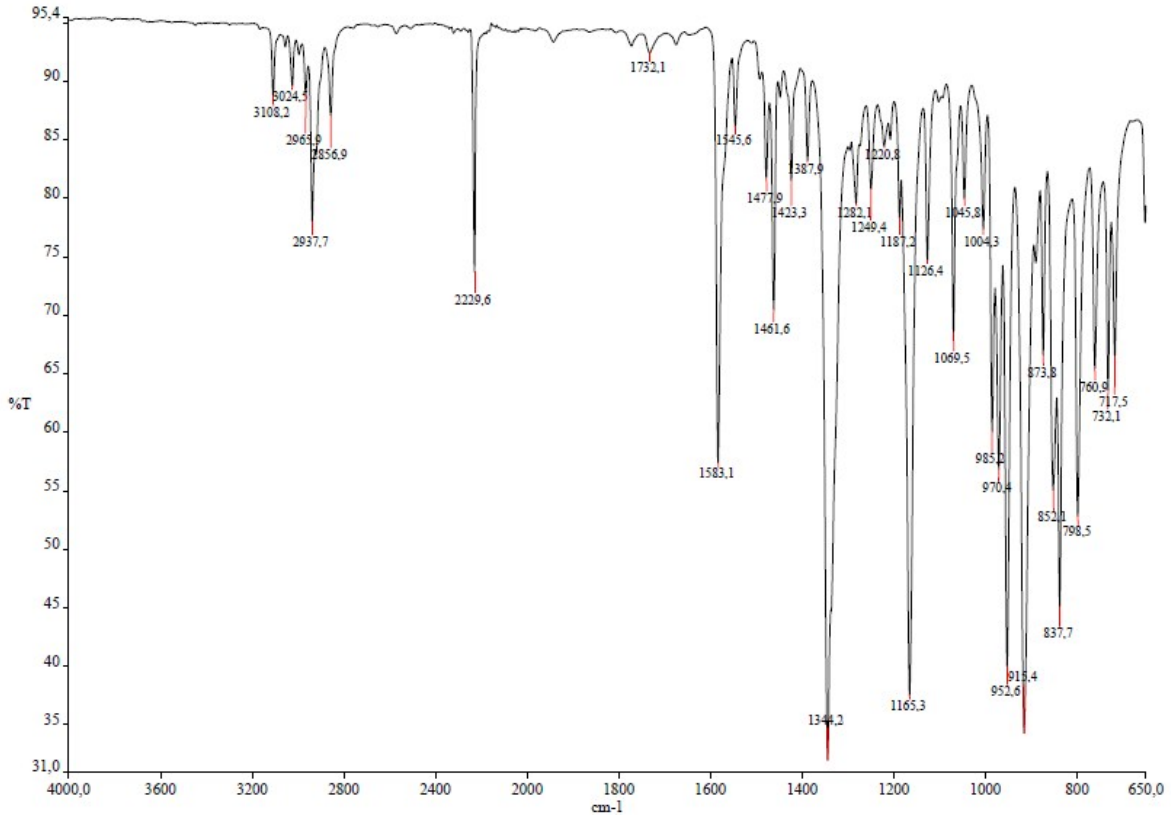


Fig. S13 FT-IR spectrum of 4 -(6-methanesulfonatehexylsulfanyl)-1,2-dicyanobenzene (**5**)

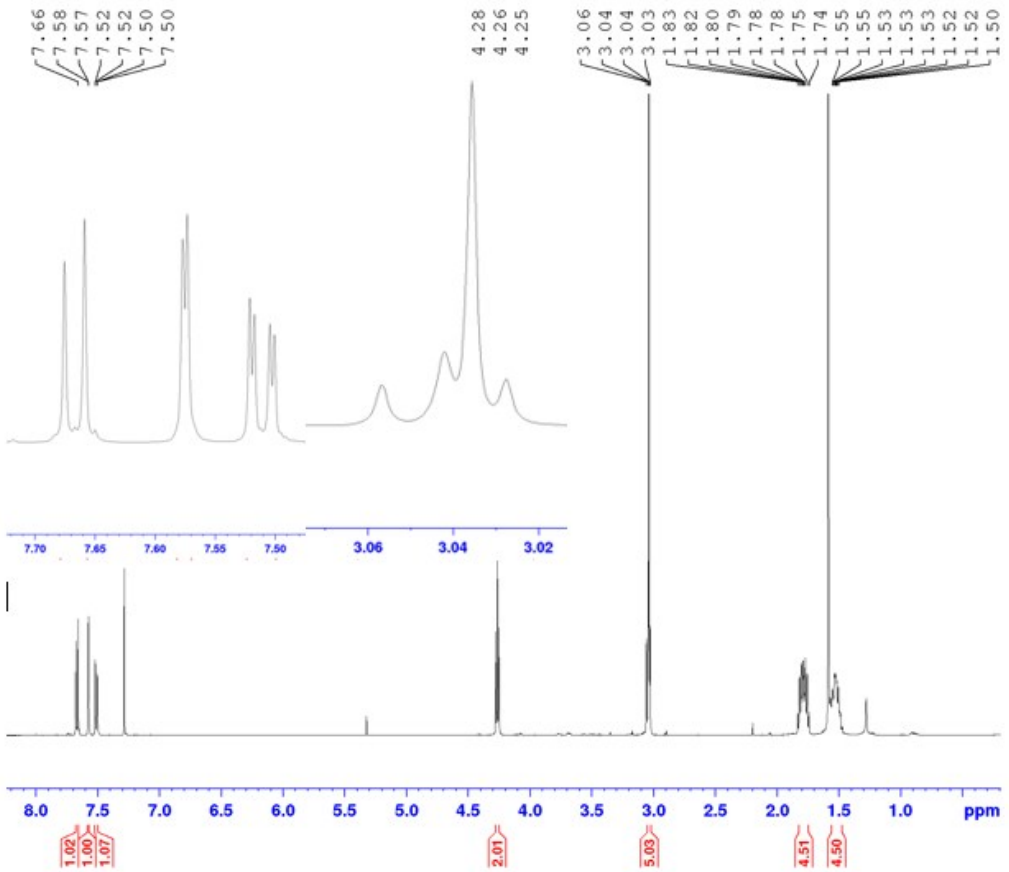


Fig. S14 ^{1}H-NMR spectrum of 4 -(6-methanesulfonatehexylsulfanyl)-1,2-dicyanobenzene (**5**)

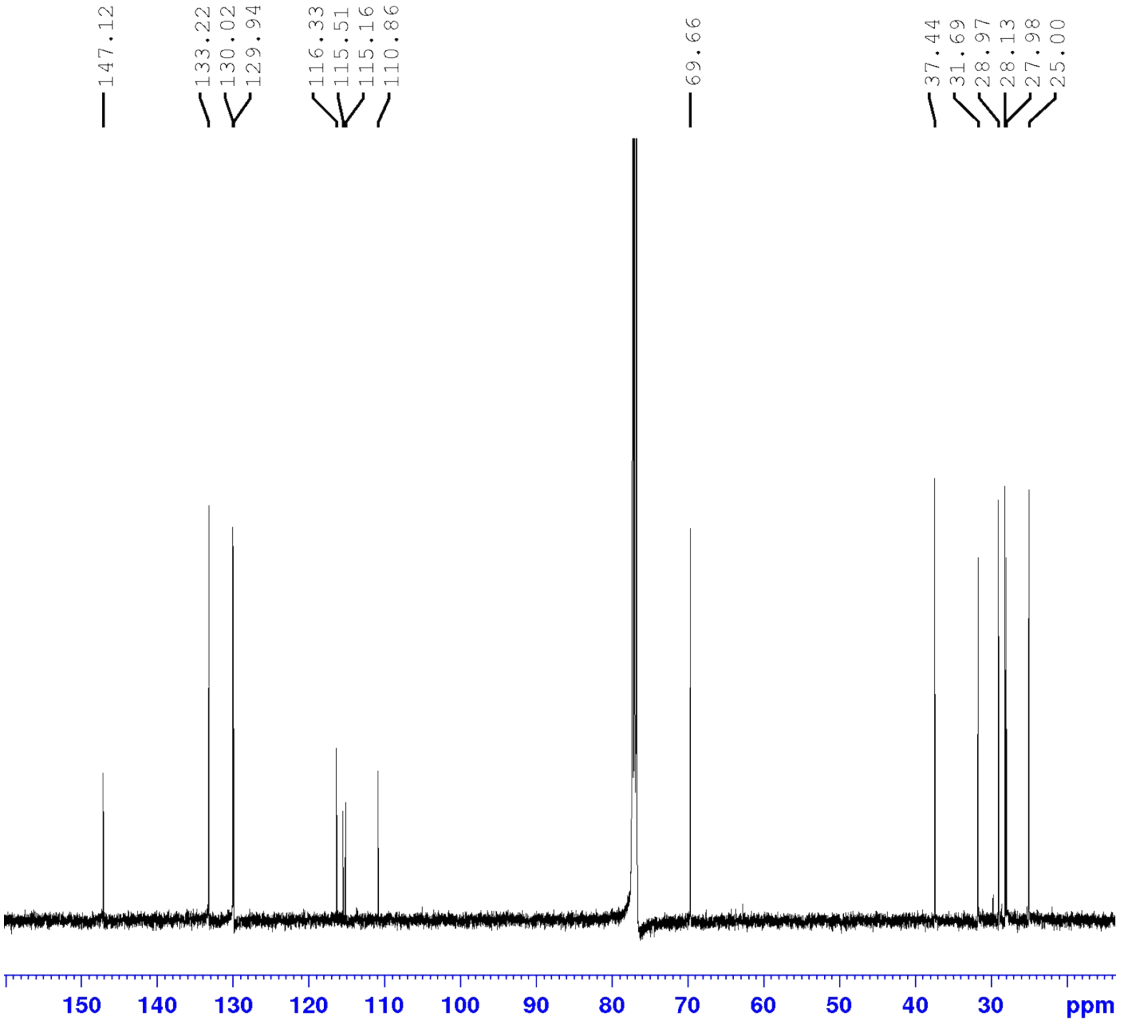


Fig. S15 ^{13}C-NMR spectrum of 4 -(6-methanesulfonatehexylsulfanyl)-1,2-dicyanobenzene (**5**)

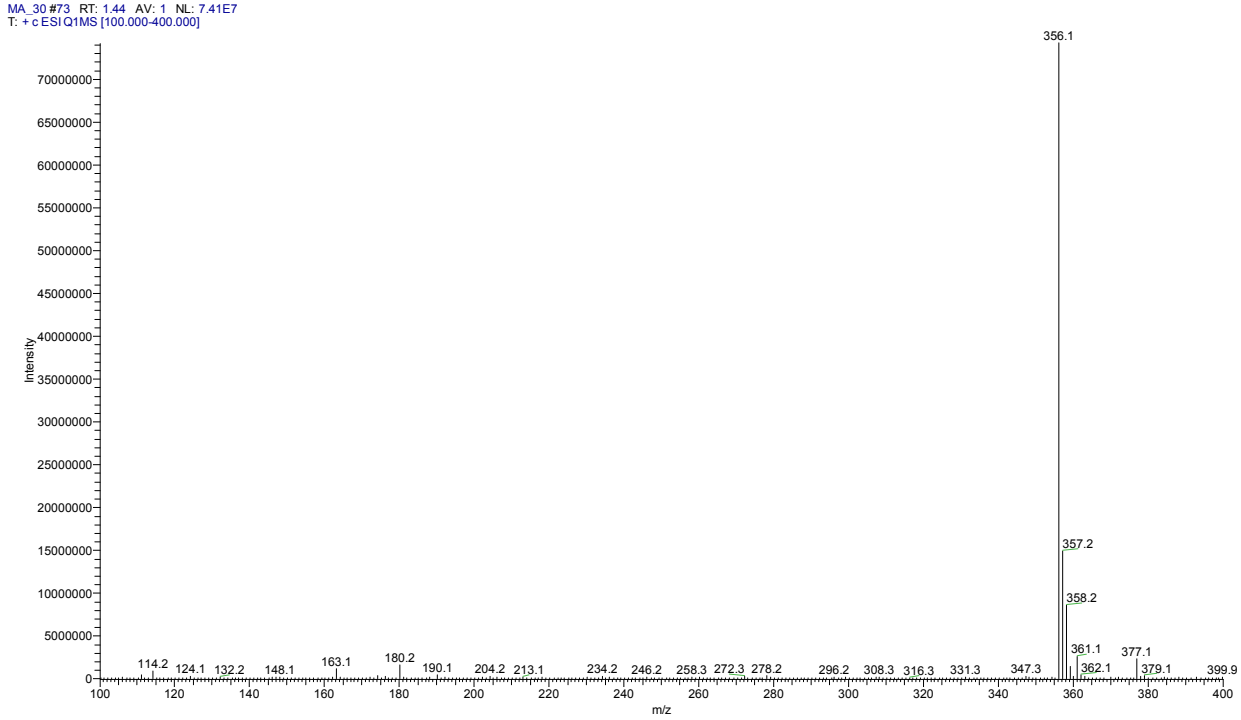


Fig. S16 Mass spectrum of 4 -(6-methanesulfonatehexylsulfanyl)-1,2-dicyanobenzene (**5**)

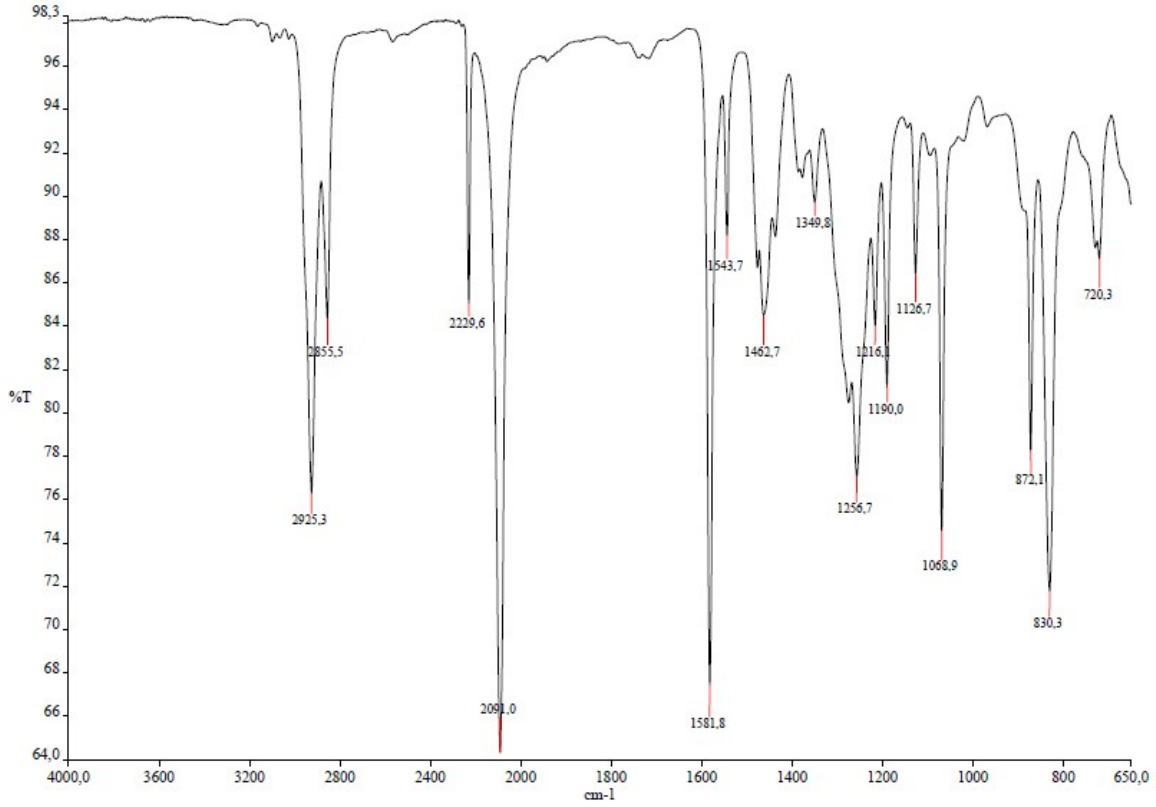


Fig. S17 FT-IR spectrum of 4 -(6-azidohexylsulfanyl)-1,2-dicyanobenzene (**6**)

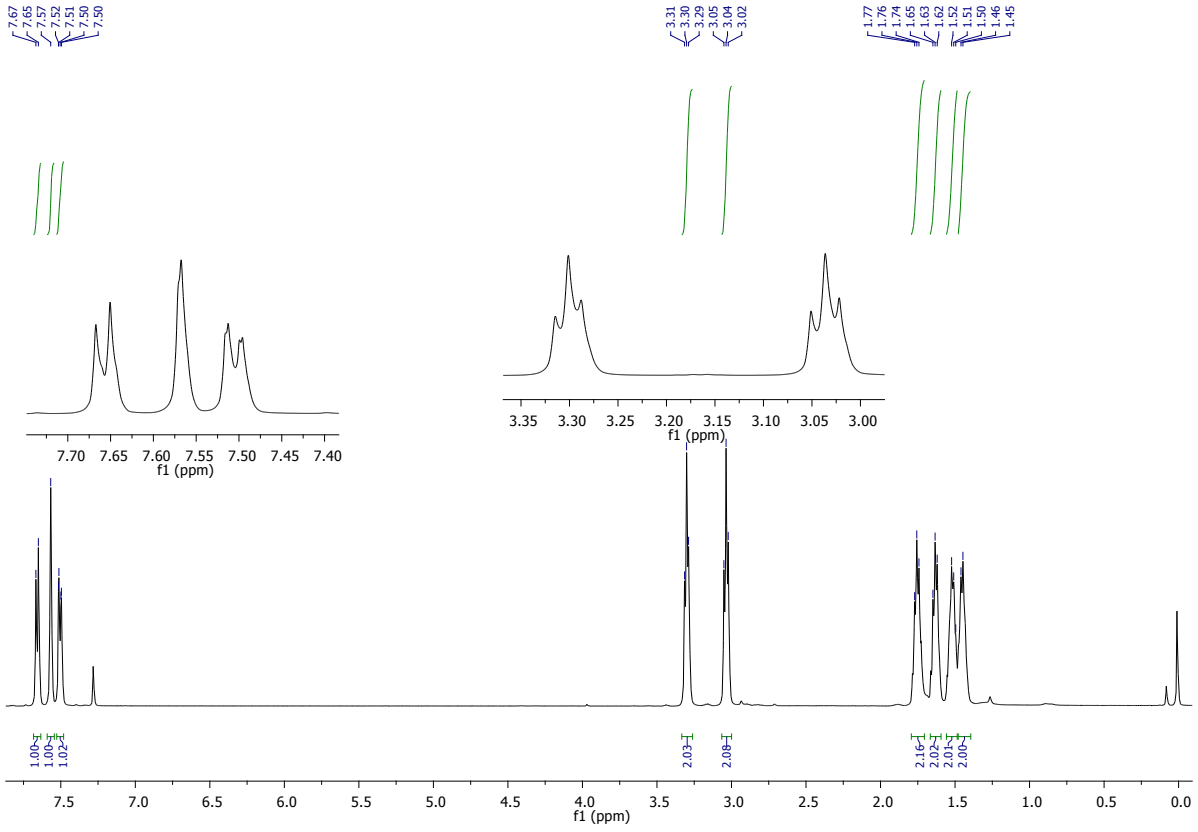


Fig. S18 ^{1}H-NMR spectrum of 4 -(6-azidohexylsulfanyl)-1,2-dicyanobenzene (**6**)

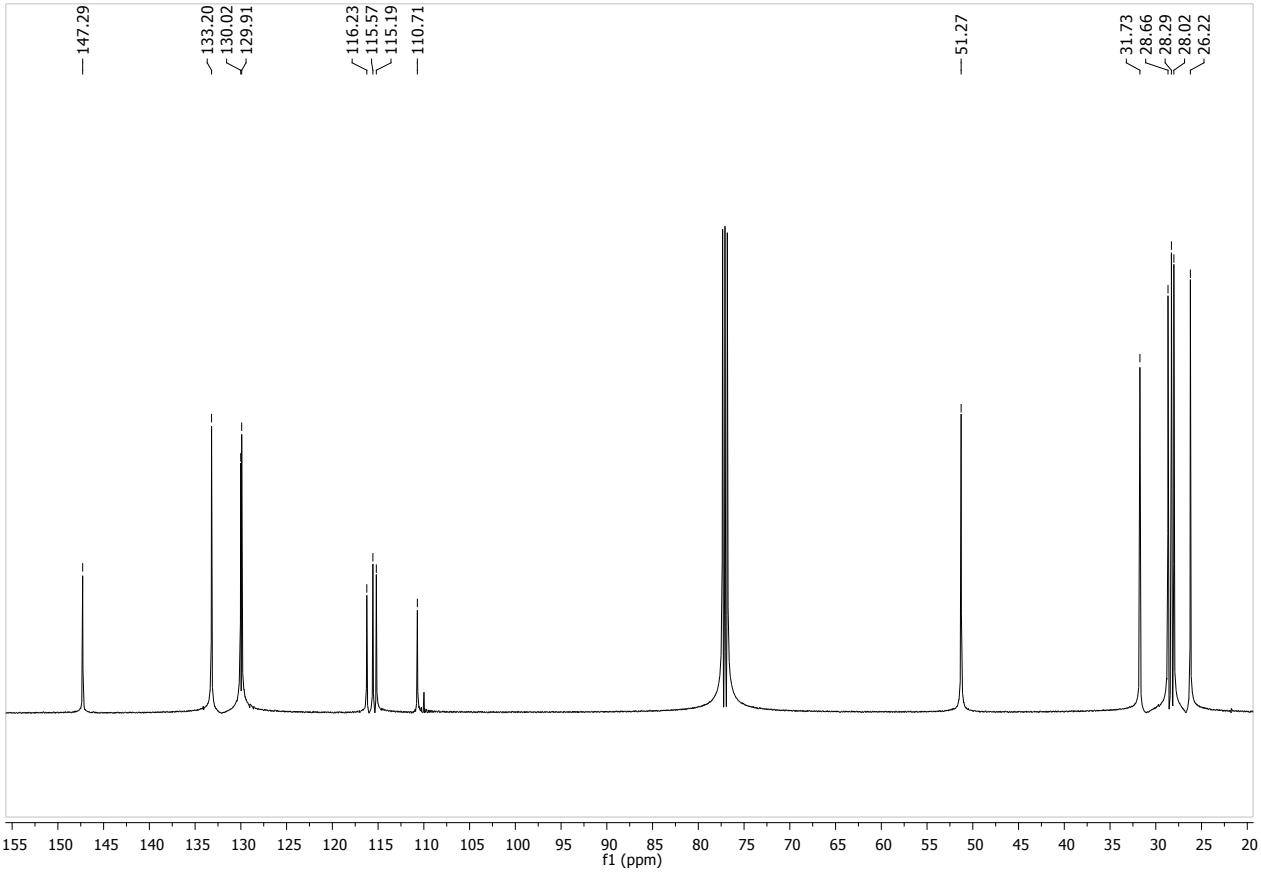


Fig. S19 ^{13}C-NMR spectrum of 4 -(6-azidohexylsulfanyl)-1,2-dicyanobenzene (**6**)

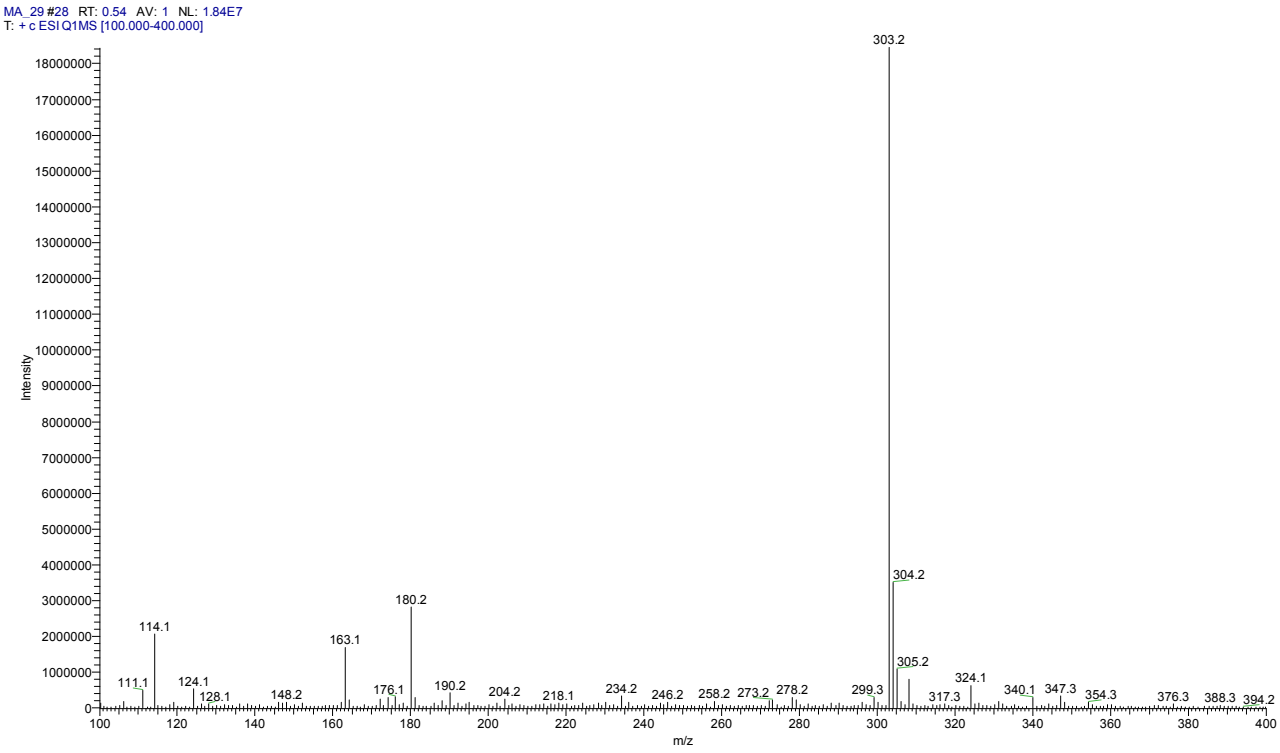


Fig. S20 Mass spectrum of 4 -(6-azidohexylsulfanyl)-1,2-dicyanobenzene (**6**)

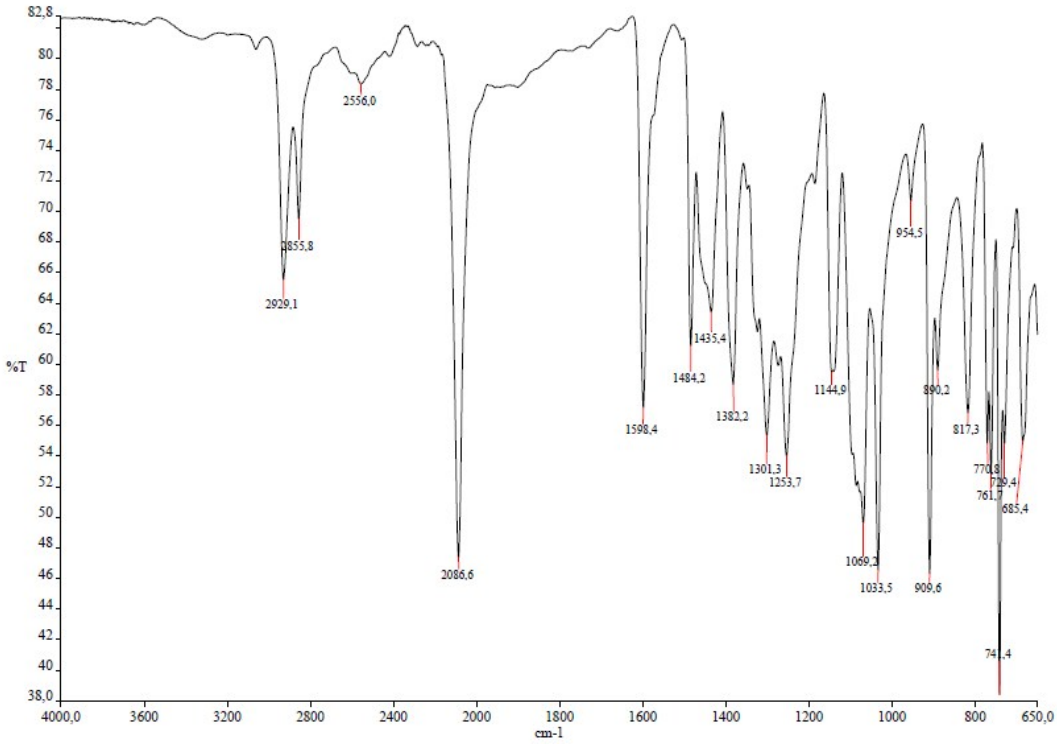


Fig. S21 FT-IR spectrum of compound **7**

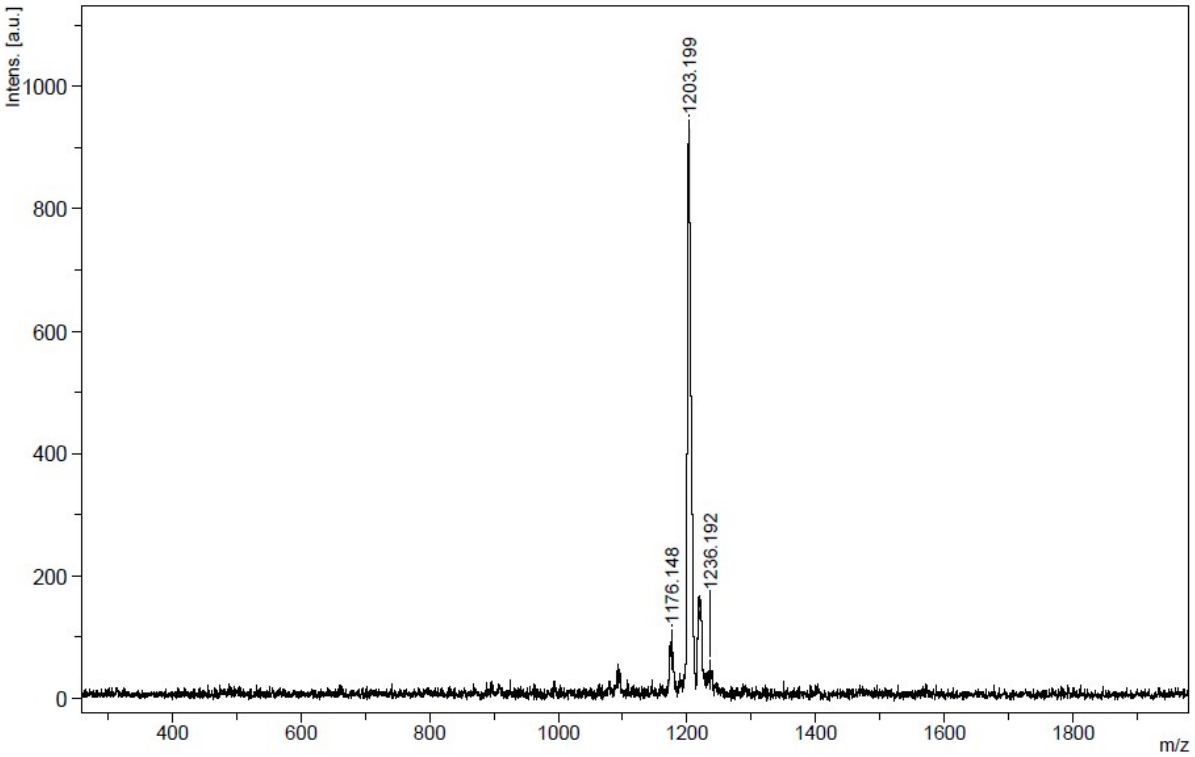


Fig. S22 mass spectrum of compound **7**

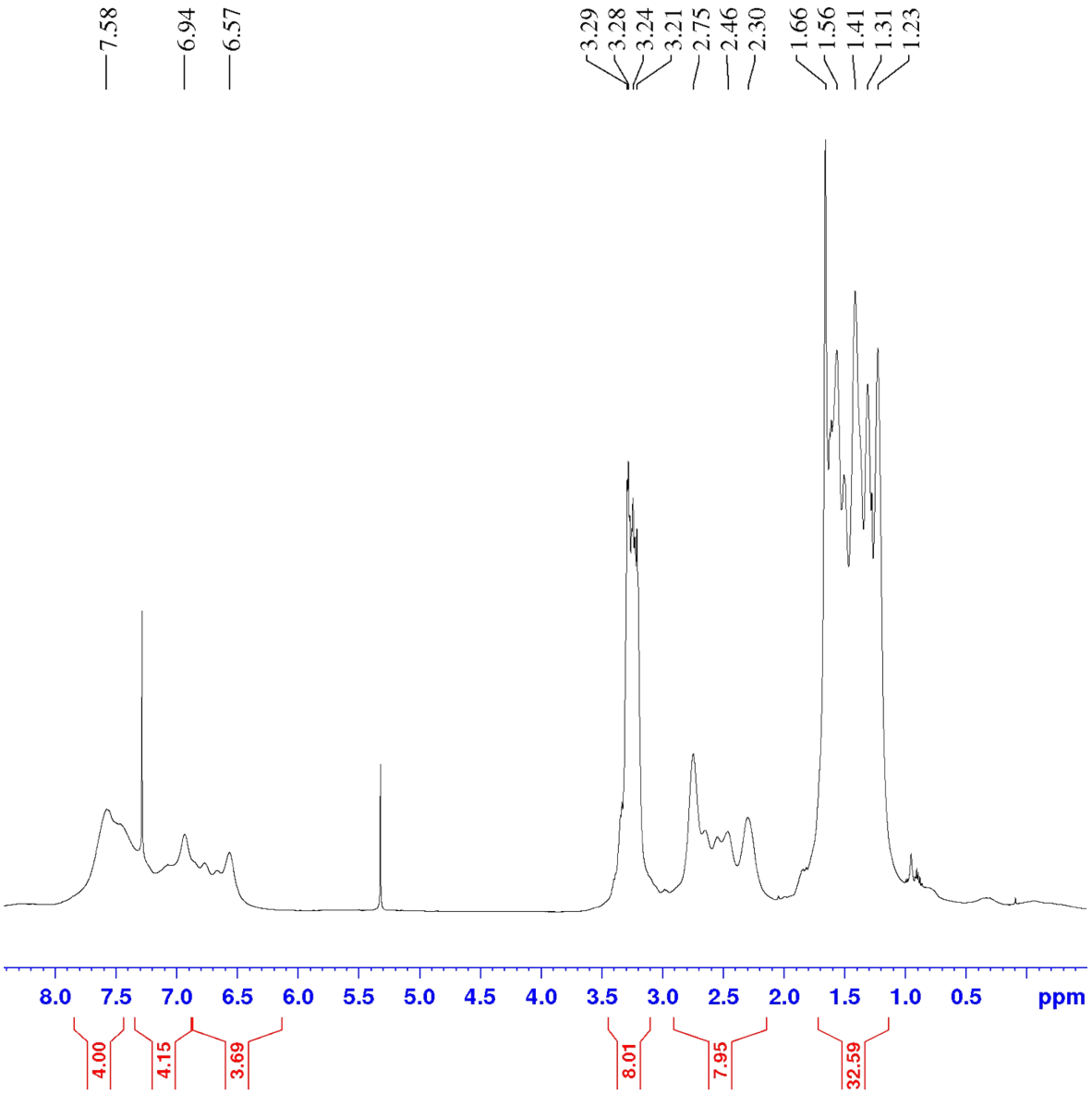


Fig. S23 ^{1}H-NMR spectrum of compound **7** in $CDCl_3$

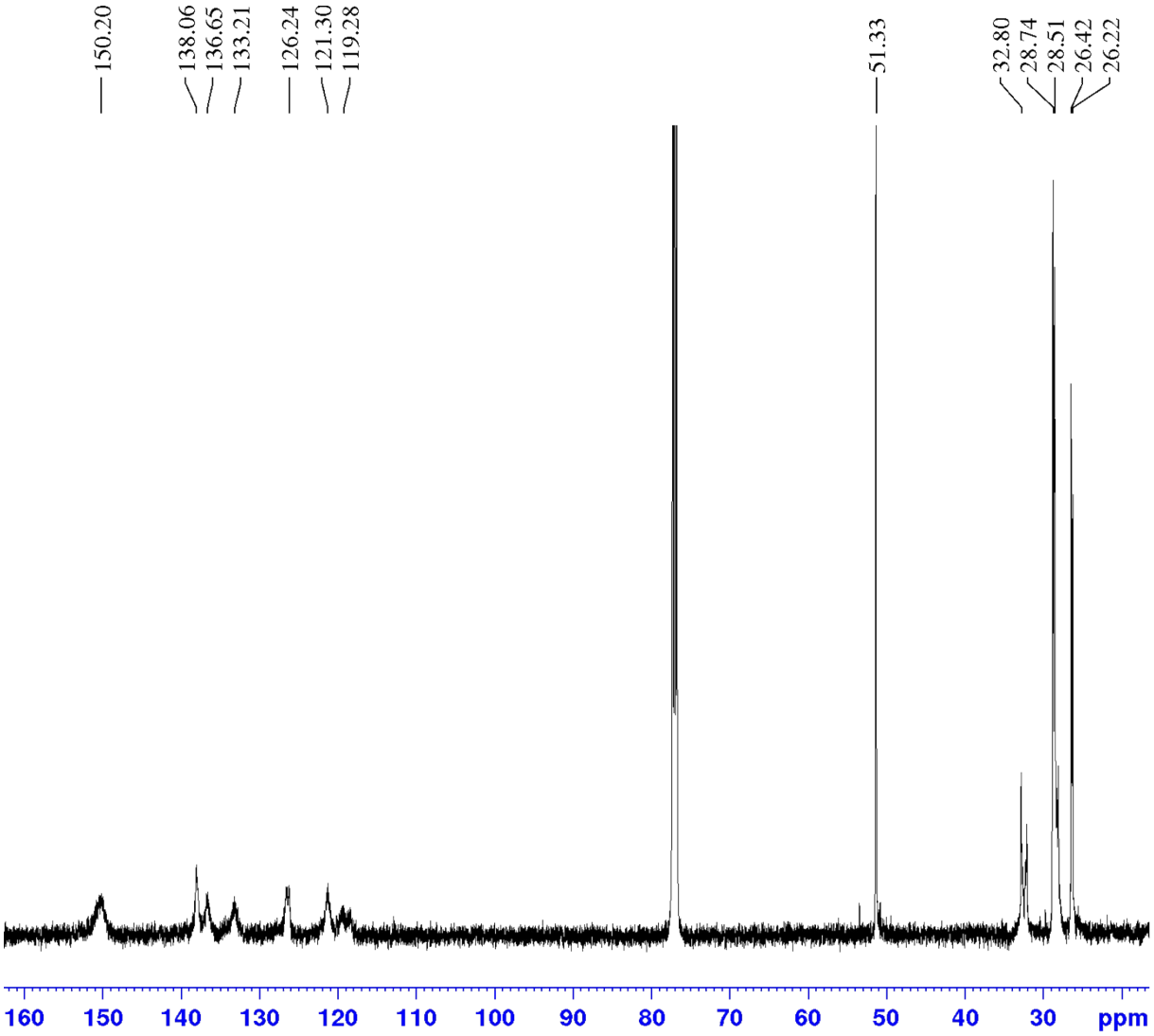


Fig. S24 ^{13}C-NMR spectrum of compound **7** in $CDCl_3$

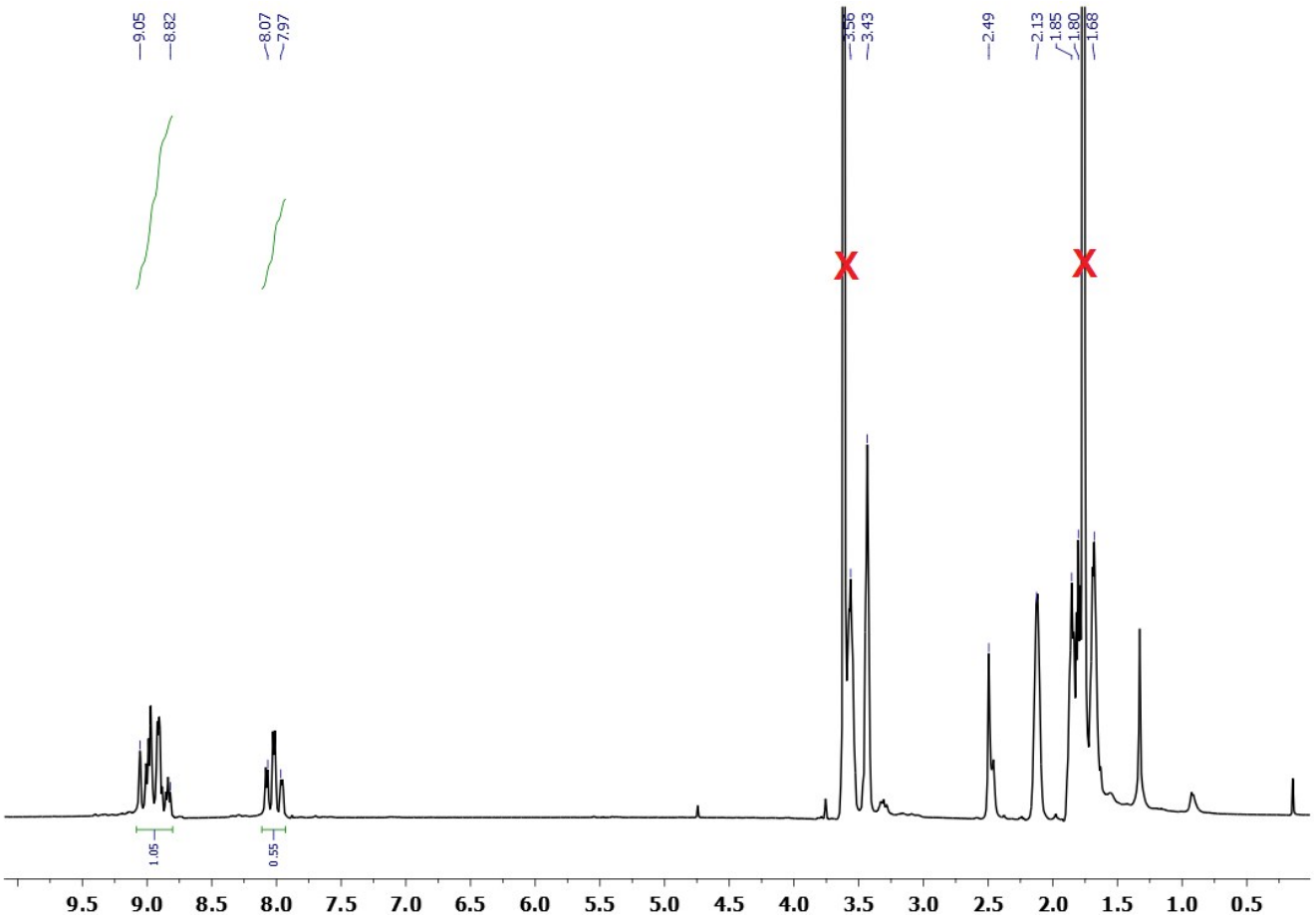


Fig. S25 ^{1}H-NMR spectrum of compound **7** in THF-d_8

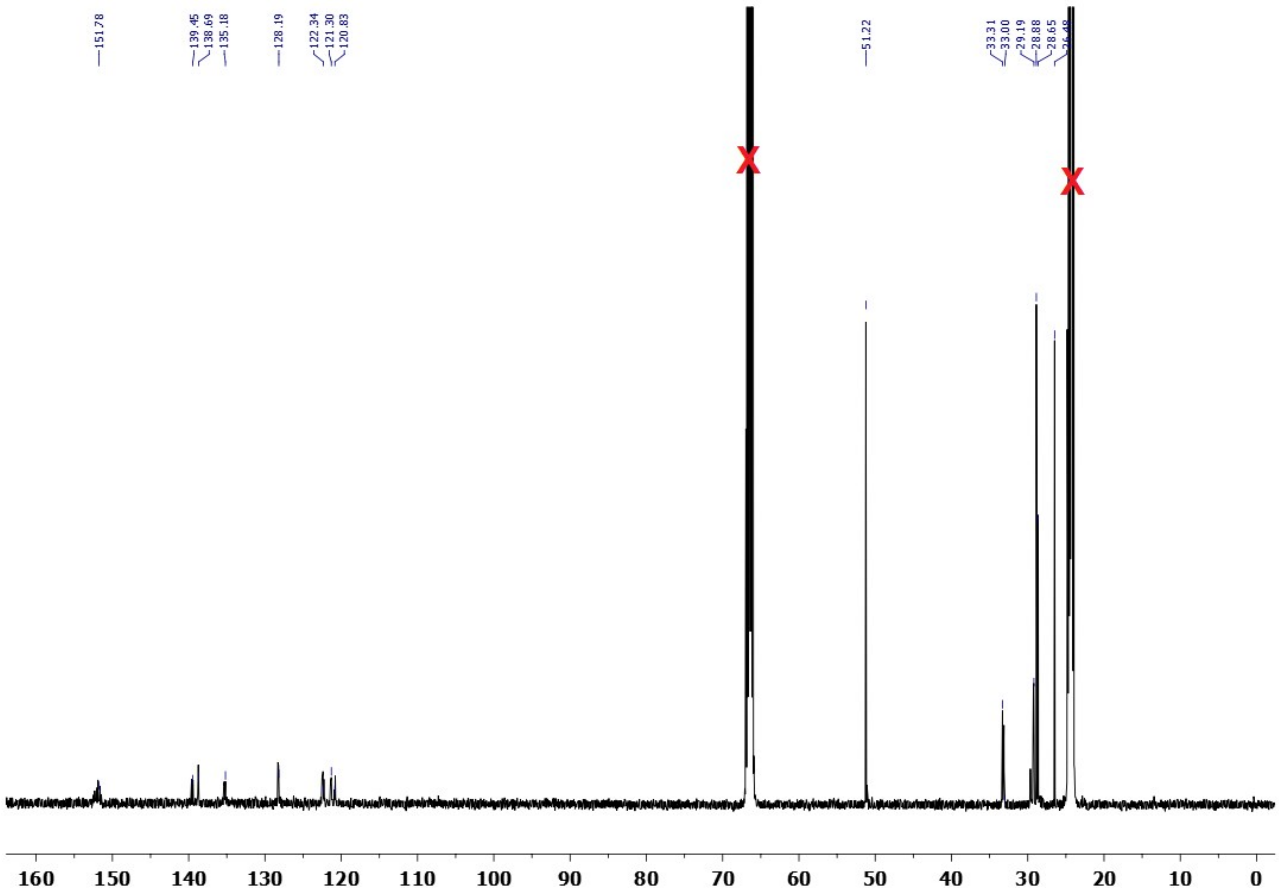


Fig. S26 ^{13}C-NMR spectrum of compound **7** in THF-d_8

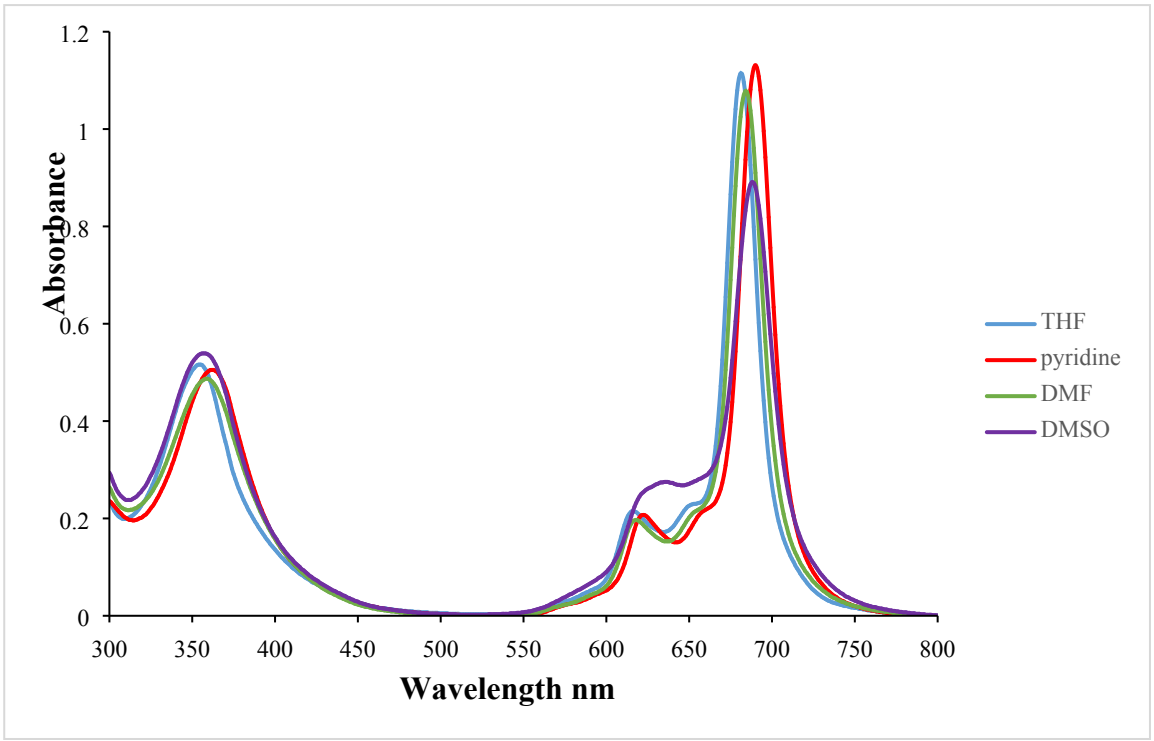


Fig. S27 Absorption spectra of **3** in DMF, pyridine, THF and DMSO at the same concentration (10^{-5} M).

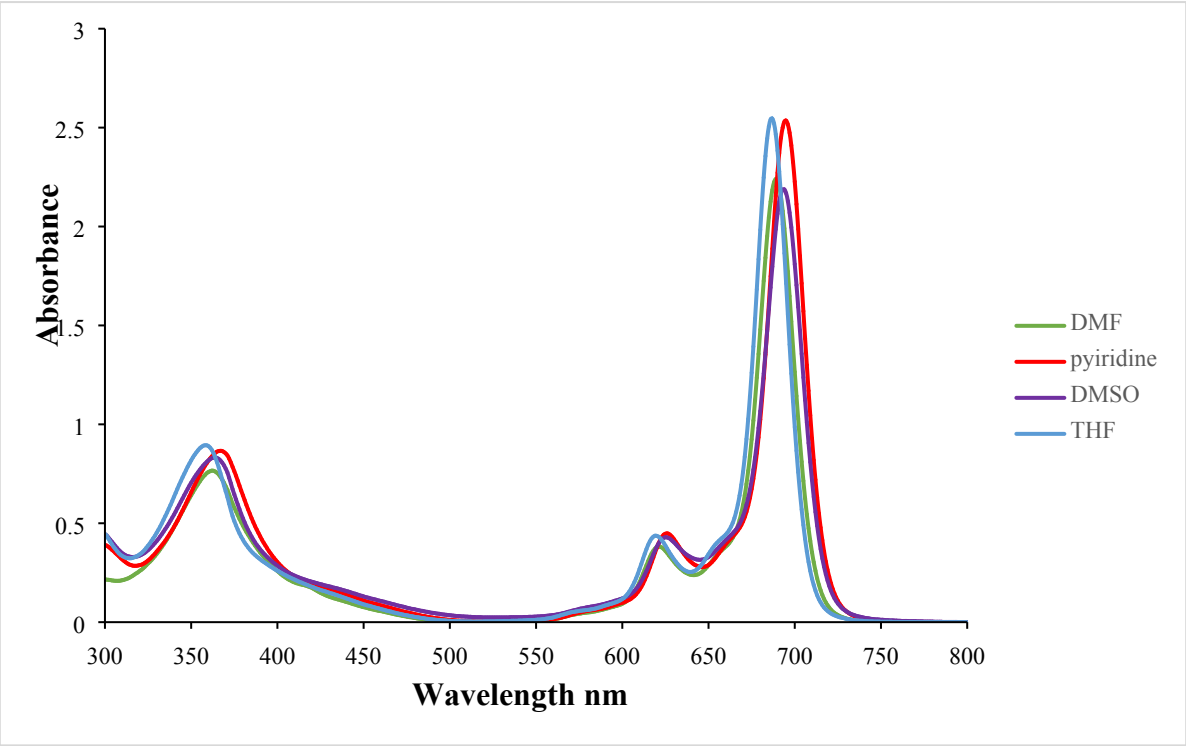


Fig. S28 Absorption spectra of **7** in DMF, pyridine, THF and DMSO at the same concentration (10^{-5} M).

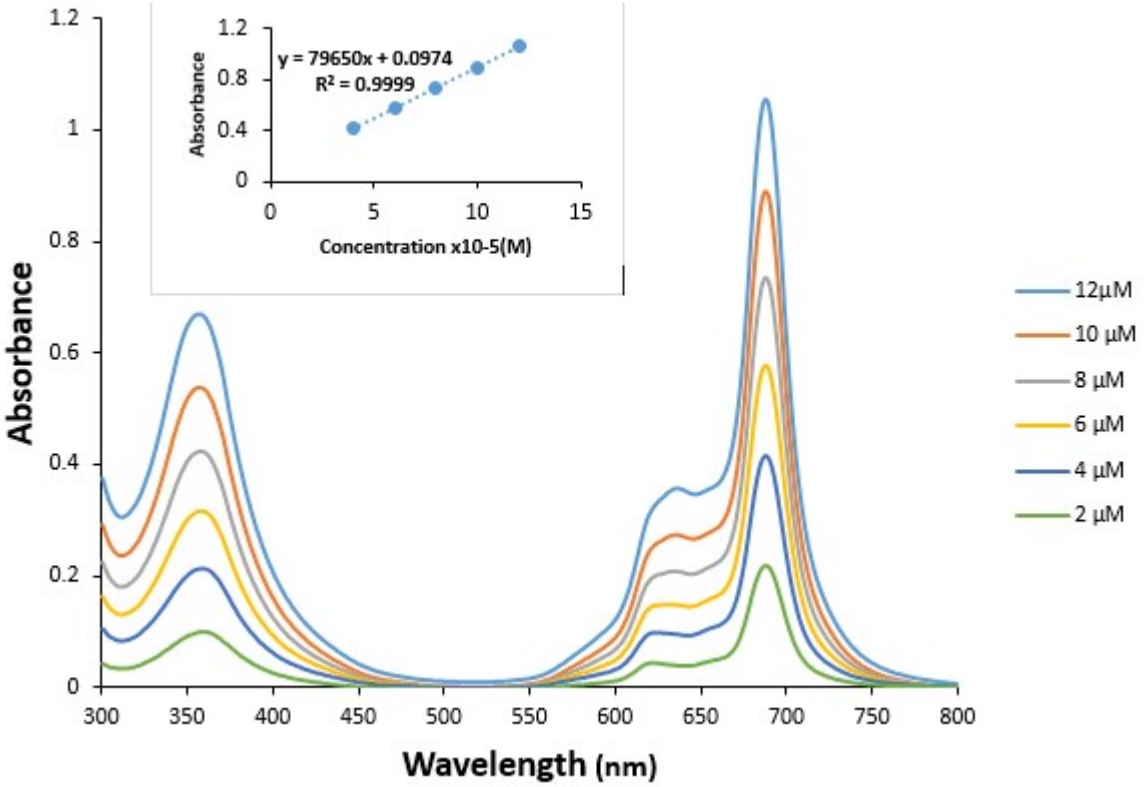


Fig. S29 UV-Vis spectra of compound **3** at the different concentrations in DMSO.

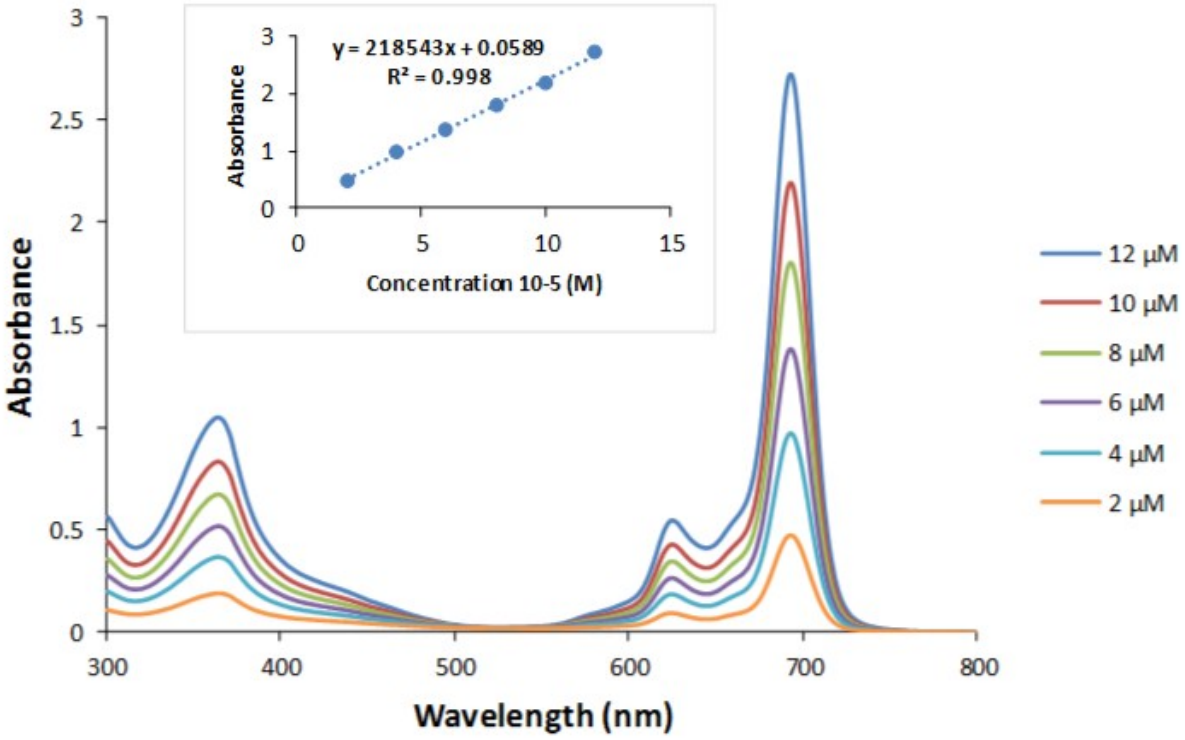


Fig. S30 UV-Vis spectra of compound **7** at the different concentrations in DMSO

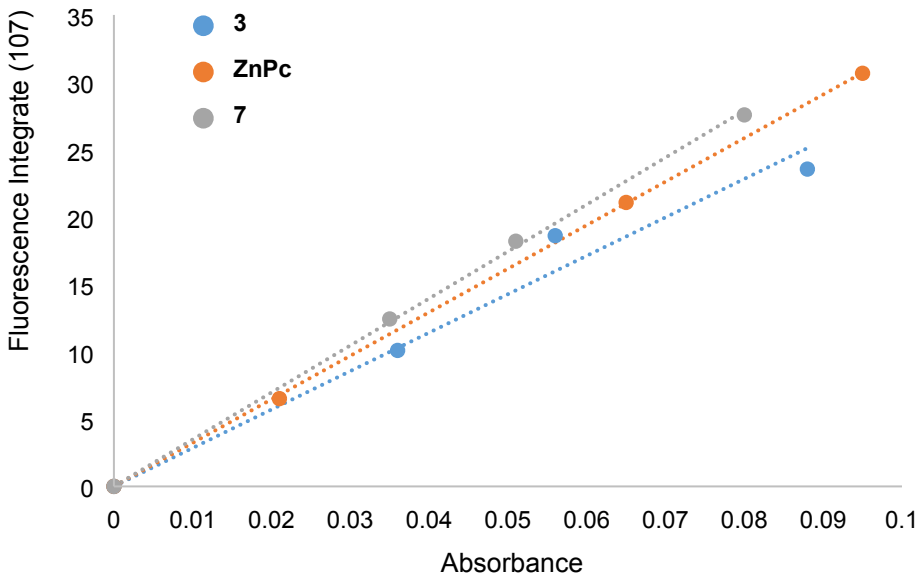


Fig. S31 Fluorescence integrate area *vs* absorbance of **3**, **7** and **ZnPc** in DMSO to determine their Φ_F values

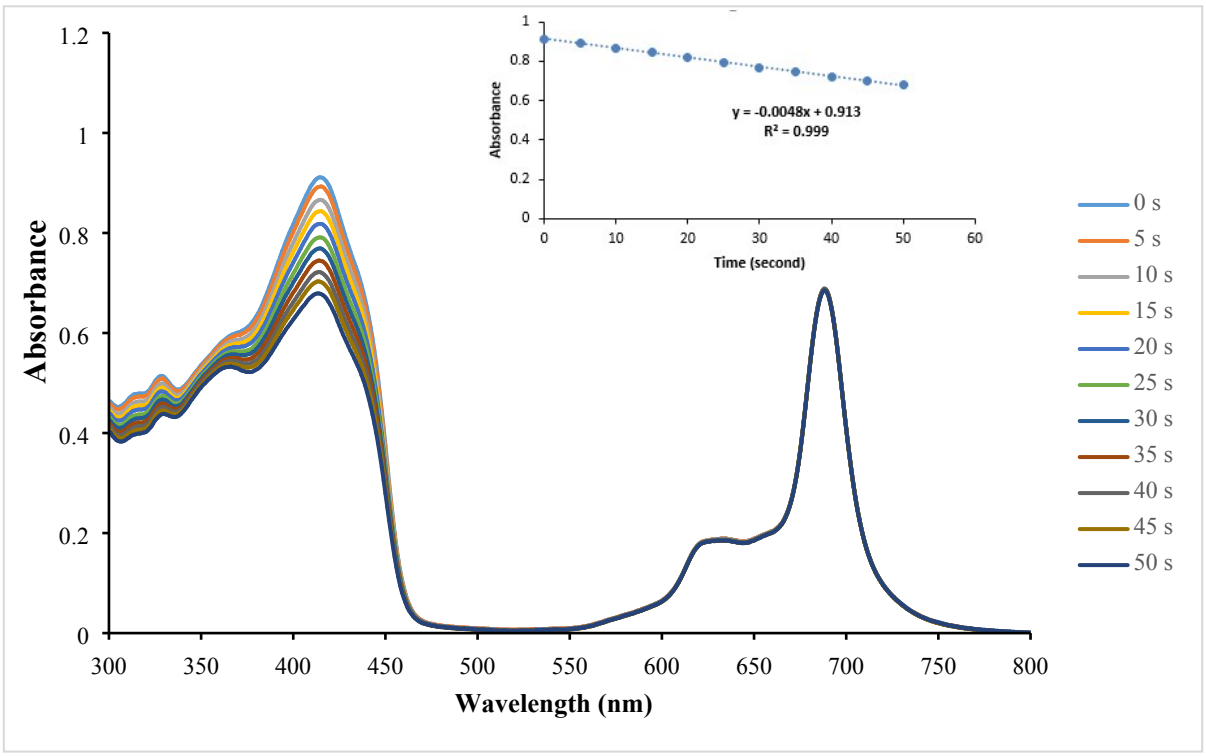


Fig. S32 Determination of singlet oxygen quantum yield of **3** in DMSO. Inset: Plot of DPBF absorbance at 417 nm

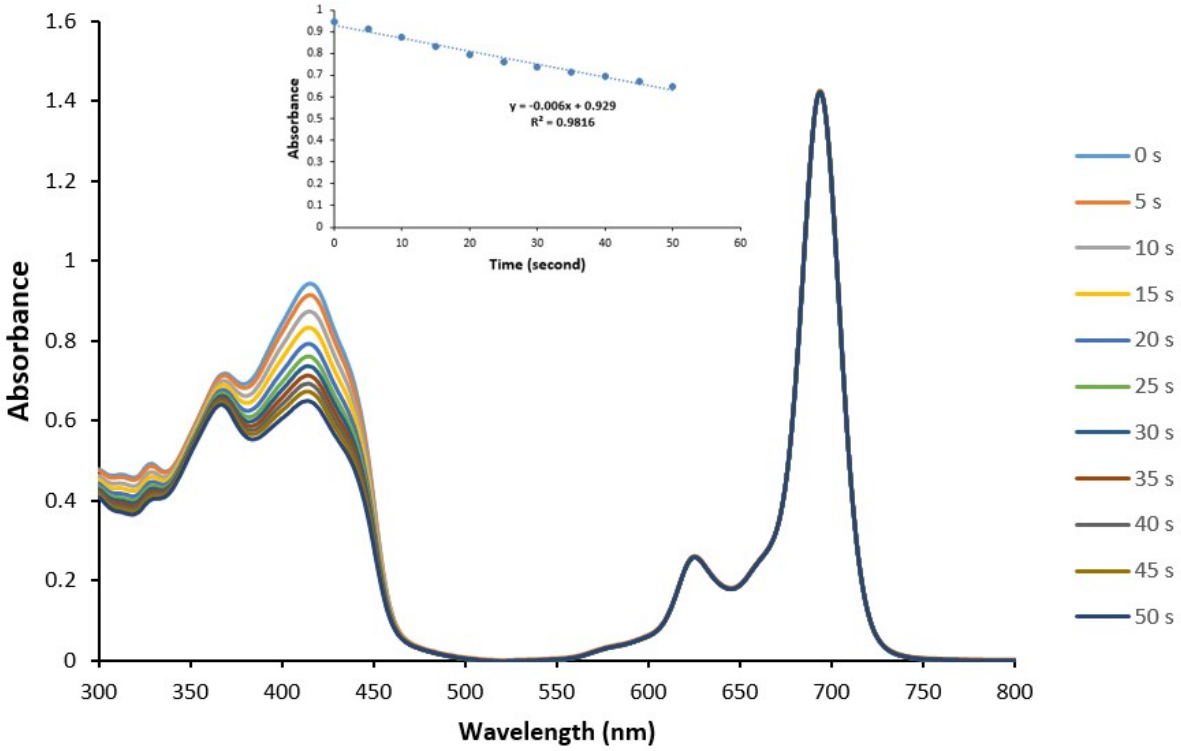


Fig. S33 Determination of singlet oxygen quantum yield of **7** in DMSO. Inset: Plot of DPBF absorbance at 417 nm

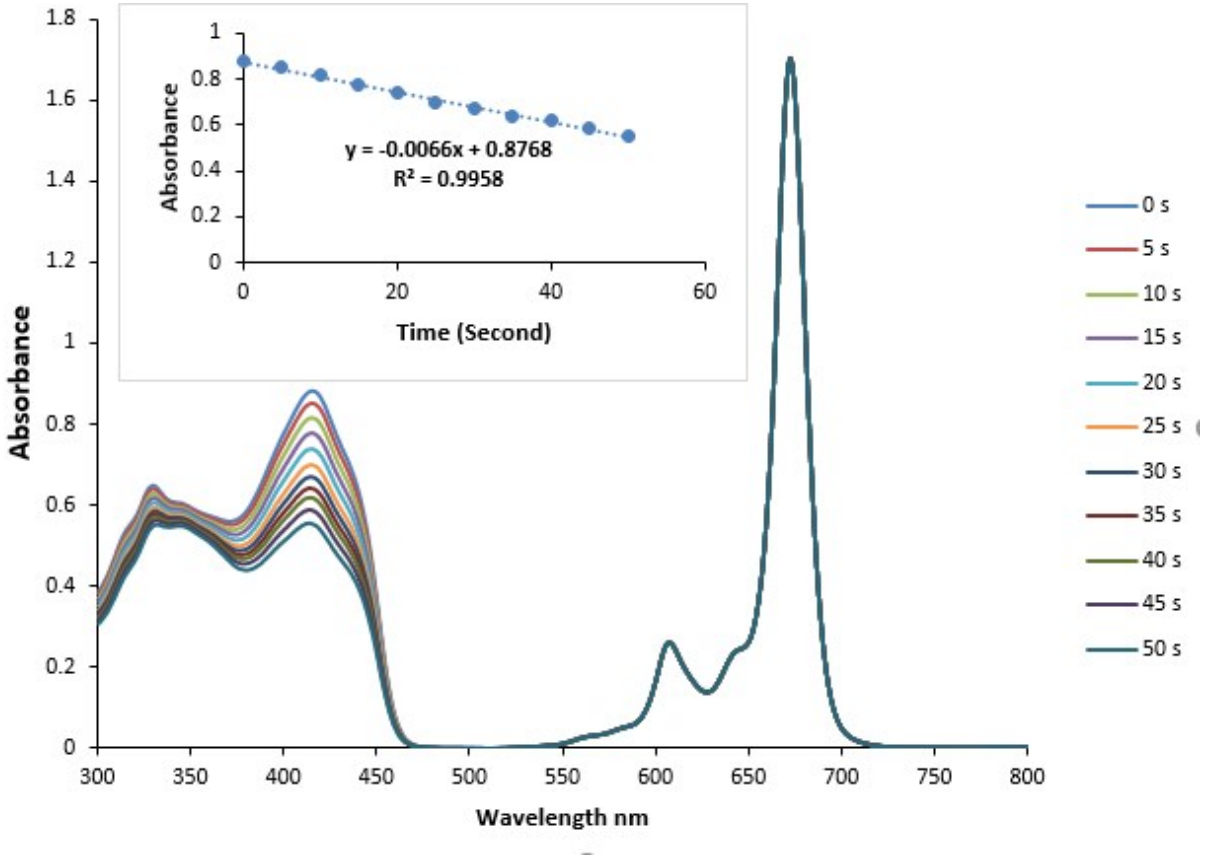


Fig. S34 Determination of singlet oxygen quantum yield of **ZnPc** in DMSO. Inset: Plot of DPBF absorbance at 417 nm

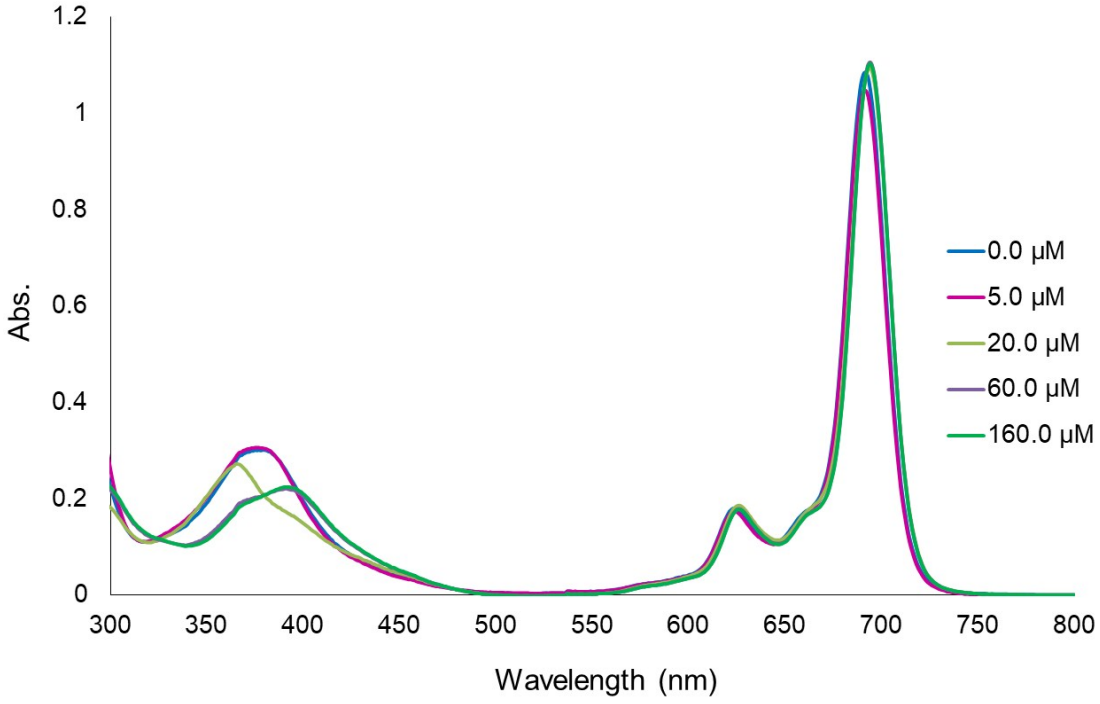


Fig. S35 Changes in the absorption spectra of compound **7** (5.0×10^{-7} M) in DMSO by the addition of hydrogen sulfide ($Na_2S.9H_2O$ in HEPES/ DMSO (5:5, pH= 7.0)).

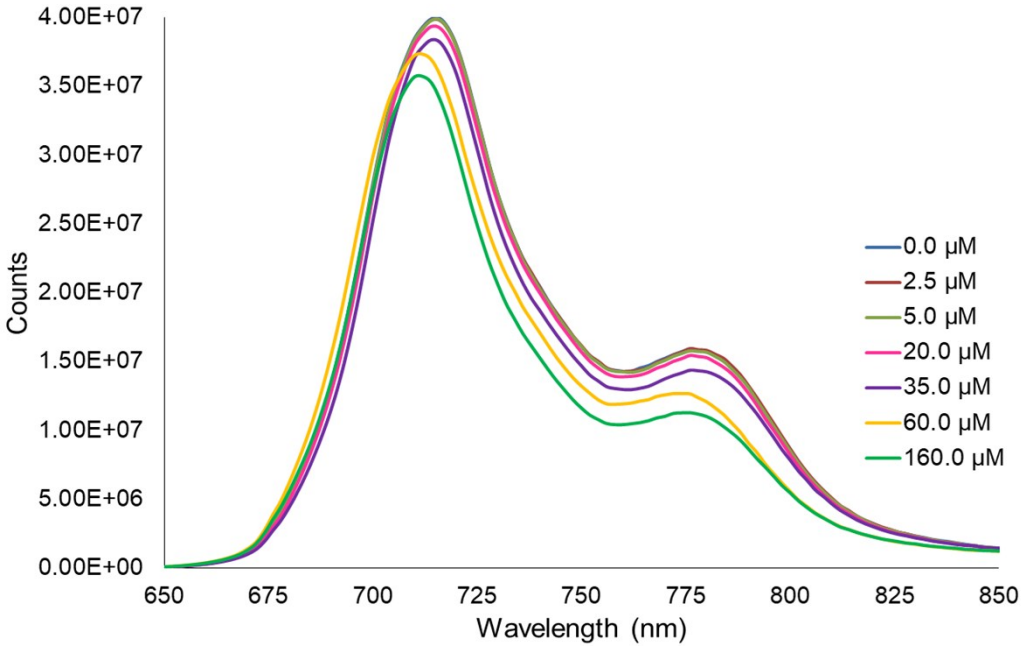


Fig. S36 Changes in the emission spectra of compound **7** (5.0×10^{-7} M) in DMSO by the addition of hydrogen sulfide ($Na_2S.9H_2O$ in HEPES/ DMSO (5:5, pH= 7.0))

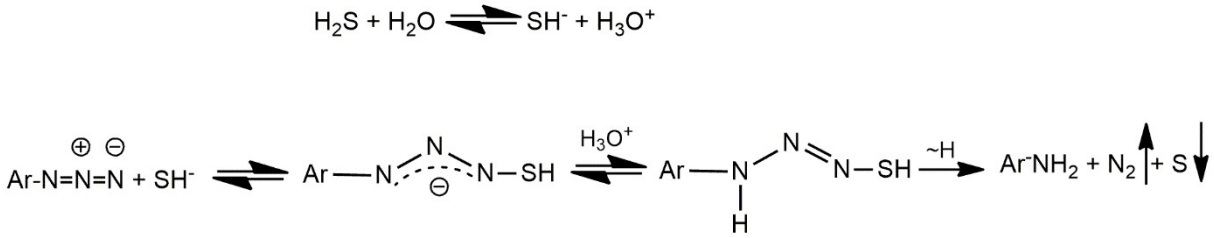


Fig. S37. Proposed mechanism for reduction of azide group to amine group [1,2].

References

[1] Gronowitz S, Westerlund C, Hörnfeldt AB, The synthetic utility of heteroaromatic azido compounds. I. Preparation and reduction of some 3-azido-2-substituted furans, thiophenes and selenophenes. Acta Chem. Scand., Ser. B 1975; *B29*: 224-32.

[2] Ozdemir T, Sozmen F, Mamur S, Tekinay T, Akkaya EU. Fast responding and selective near-IR Bodipy dye for hydrogen sulfide sensing. Chem Commun. 2014;50:5455–57.

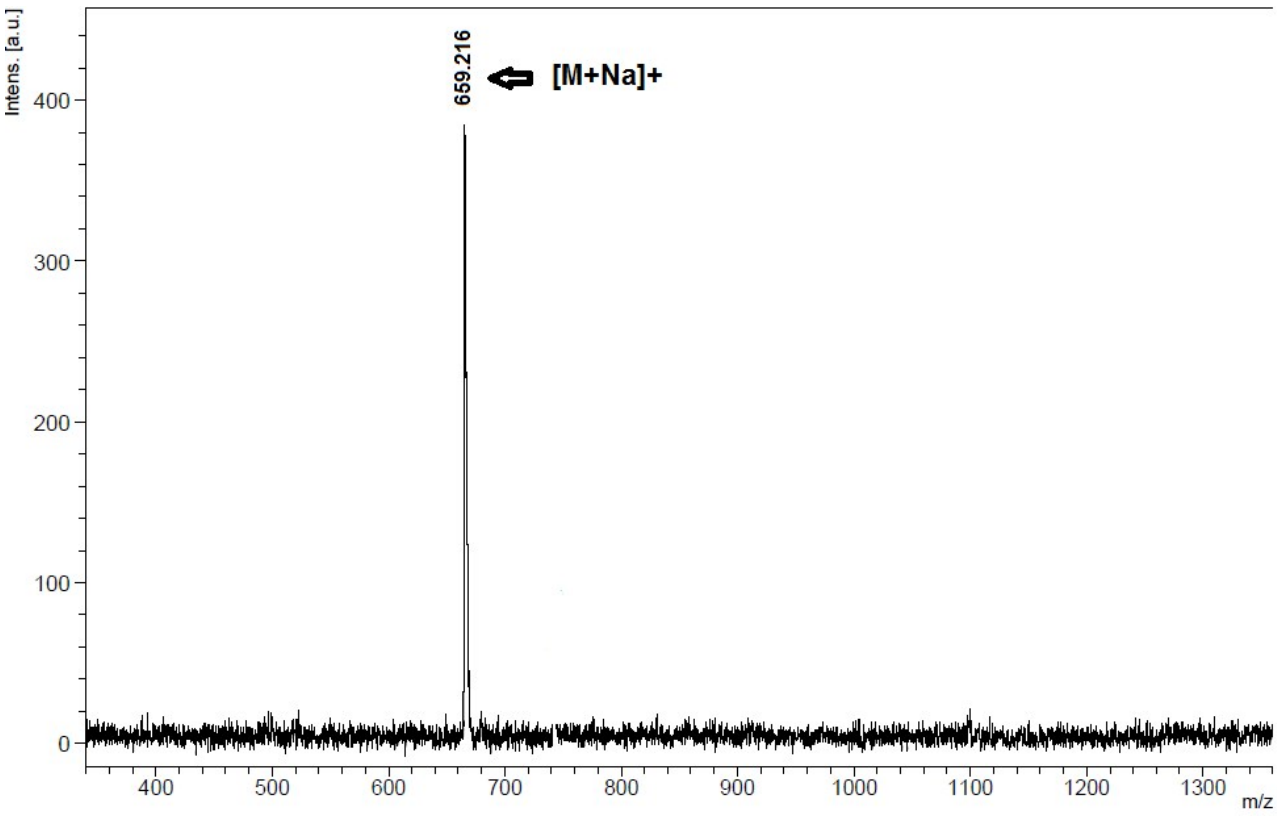


Fig. S38 MALDI-TOF mass spectrum of 2,9(10),16(17),23(24) (amino) phthalocyaninato zinc (II) (**Pc-NH_2**). It is obtained the reaction of 500 μM compound **3** with 10 mM Na_2S

Synthesis of tetra 2,9(10),16(17),23(24) (amino) phthalocyaninato zinc (II) (Pc-NH_2)

Sodium sulfide nonahydrate (48 mg, 0.2 mmol) was added to the solution of compound **3** (15 mg, 0.02 mmol) in 5 mL DMSO/H_2O (v/v 9:1) mix-solvent. The mixture was stirred for 1.5 h at room temperature in the dark. The reaction mixture was poured into 100 mL of water. The resulting dark green precipitate collected by centrifugation.The product was washed with hot ethanol, ethyl acetate, DCM, and diethyl ether, and dried in *vacuo* over P_2O_5 to give 11.2 mg of **Pc-NH_2**, yield: 86.97%. FT-IR [(ATR) υ_{max}/cm^{-1}]: 3328.9, 3203.7, 1605.6, 1492.9, 1454.3, 1405.9, 1345.6, 1252.3, 1134.4, 1090.8, 1045.9, 940.5, 822.8, 719.9 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6, ppm): δ 8.93(d, 4H, ArH), 8.42 (d, 4H, ArH), 7.37 (s, 4H, ArH), 6.22 (br s, 8H, NH). MALDI-TOF-MS *m/z*: 637.466 $[M+H]^+$, 663.590$[M+4H+Na]^+$, 689.726$[M+2(4H+Na)]^+$, 862.128 $[M+DIT]^+$.

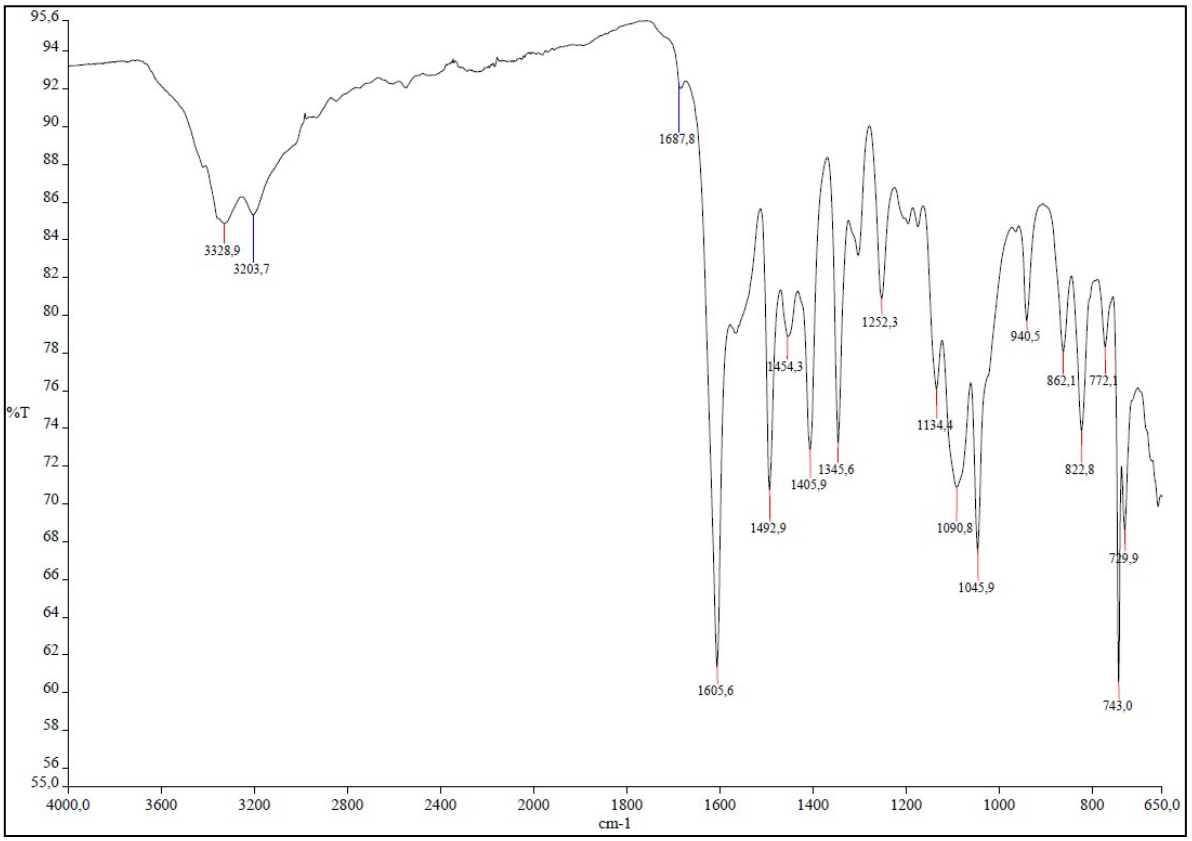


Fig. S39 FT-IR spectrum of 2,9(10),16(17),23(24) (amino) phthalocyaninato zinc (II) **(Pc-NH_2)**

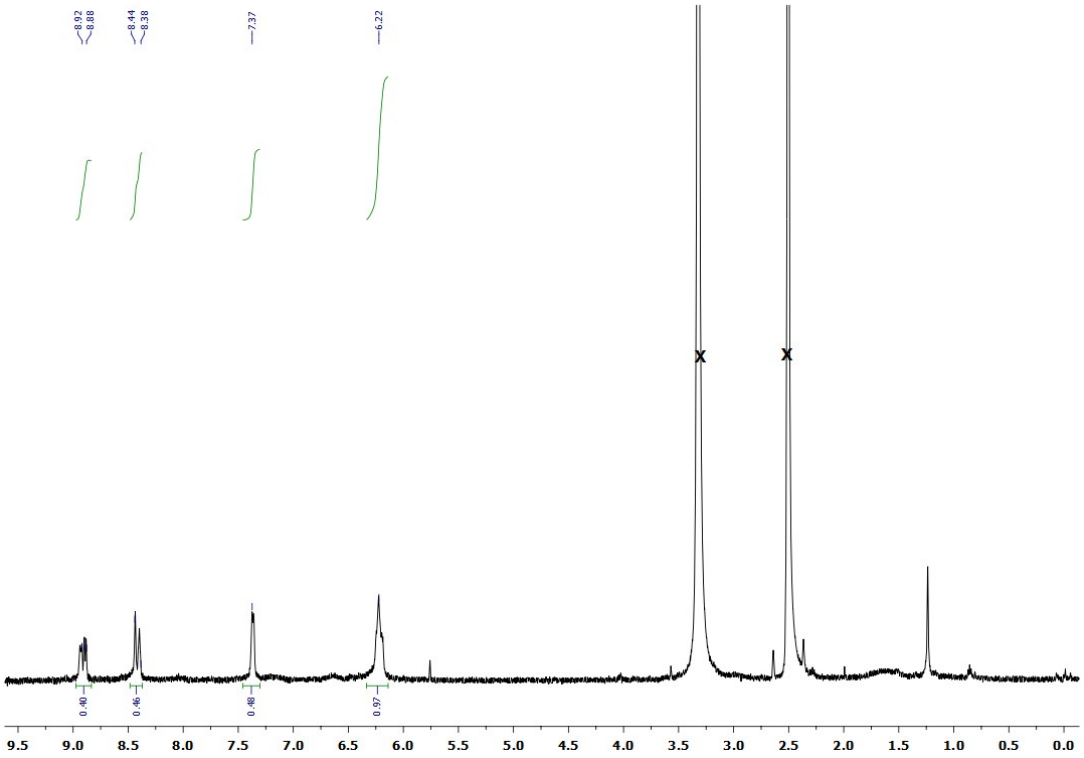


Fig. S40 ^{1}H-NMR spectrum of 2,9(10),16(17),23(24) (amino) phthalocyaninato zinc (II) **(Pc-NH_2)** in DMSO-d_6

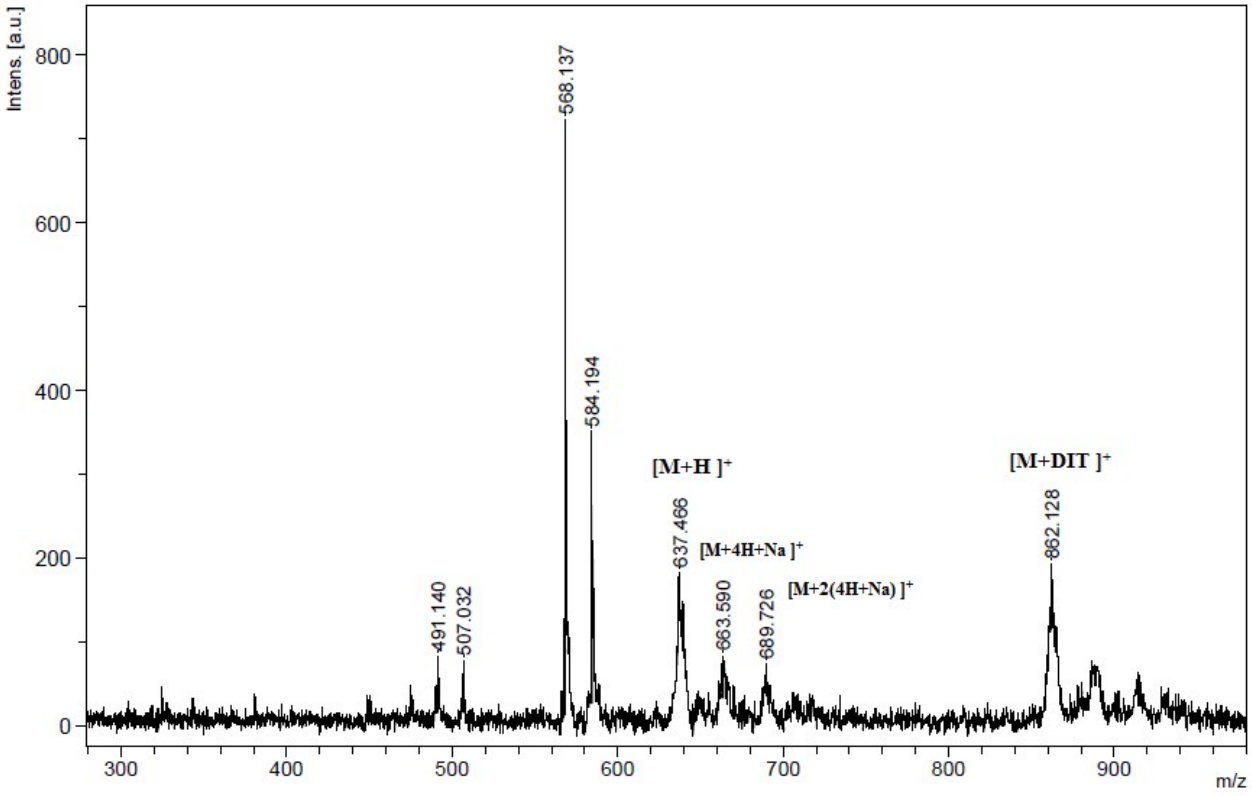


Fig. S41 MALDI-TOF mass spectrum of 2,9(10),16(17),23(24) (amino) phthalocyaninato zinc (II) **(Pc-NH_2)** (matrix: DIT)