

Supplementary Information

Efficiency Enhancement of Ruthenium Based DSSCs Employing A- π -D- π -A Organic Co-sensitizers

Islam M. Abdellah¹ and Ahmed El-Shafei^{2*}

¹*Department of Chemistry, Faculty of Science, Aswan University, Aswan, Egypt 81528*

²*Polymer and Color Chemistry Program, North Carolina State University, Raleigh, USA 27606*

*Corresponding Author: Ahmed_El-Shafei@ncsu.edu.

1. Device fabrication

1.1. Device fabrication for IMA1-4 dyes

Fluorine-doped tin oxide (FTO) coated glass (2.2 mm thickness, sheet resistance of 8 Ω/cm^2 , TEC, Pilkington) were washed with detergent, water, acetone and ethanol, respectively. Then, FTO glass plates are immersed in a 40 mM aqueous TiCl_4 solution at 70 °C for 30 minutes and washed with water and ethanol. A thin layer (8-12 μm thick) of TiO_2 (Solaronix, Ti-Nanoxide D/SP) (active area, 0.18 cm^2) was deposited on transparent conducting glass by printing, then dried at 350 °C for 10 minutes and curing at 500 °C for 30 min. Then, after the electrodes are dried, the TiO_2 particles of the scattering layer (5 μm thick) (Solaronix, Ti-Nanoxide R/SP) are printed on the already deposited TiO_2 layer. TiO_2 electrodes were heated under airflow at 350 °C for 10 minutes, then heated at 500 °C for 30 minutes. After cooling to room temperature, the TiO_2 electrodes were treated with 40 mM aqueous solution of TiCl_4 at 70 °C for 30 minute and then washed off with water and ethanol. The electrodes were heated again at 500 °C for 30 minutes, and allowed to cool to 80 °C before dipping in IMA1-4 solutions. The IMA1-4 solutions (0.2 mM) were prepared in 10 mL 1: 1 acetonitrile and tert-butanol. Chenodeoxycholic acid (CDCA) was added at a concentration of 20 mM. The electrodes were immersed in IMA5 solution (0.2 mM) and then kept

at 25 ° C for 20 hours to adsorb IMA1-4 on the TiO₂ surface. The counter electrode was prepared from pre-cut TCO glass (transparent conductive oxides) washed with water followed by 0.1M HCl in EtOH, and then sonication in an acetone bath for 10 min. These washed TCO was then dried at 400 °C for 15 minutes. A thin layer of Pt paste (Solaronix, Platisol T/SP) was printed on TCO and the printed electrodes were cured at 450 ° C for 10 minutes. The dye sensitized TiO₂ electrodes were sandwiched with Pt counter electrodes and the electrolyte (Solaronix, Iodolyte HI-30) was injected into the cells, while the two electrodes were held together with clips.

1.2. Device fabrication for IMA5 complex

The fabrication was performed using the same procedure as IMA1-4 devices fabrication utilizing a thin layer (8-12 μm thick) of TiO₂ (Solaronix, Ti-Nanoxide T/SP) was deposited instead of TiO₂ (Solaronix, Ti-Nanoxide D/SP).

1.3. Device fabrication for the co-sensitized devices

The fabrication was performed using the same procedure as IMA1-4 devices fabrication. While the TiO₂ electrodes were immersed in a mixture of IMA5 (0.2 mM) and IMA1-4 (0.2 mM).

2. Synthesis

2.1. Synthesis of 2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid

The 2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid was synthesized according to published procedure [3]. In a three neck round bottom flask 4,4'-Dimethyl-2,2'-bipyridine (3 g, 16.3 mmol) was gradually added to a stirred solution of sodium dichromate (Na₂Cr₂O₇) (10.9g, 36.5 mmol) in concentrated sulfuric acid (H₂SO₄) (93%, 45 ml) and stirred for 30 min at 75°C. After 30 min, the dark green reaction mixture was poured into cold water forming a light-yellow precipitate. The precipitate was then filtered under vacuum and dissolved in 10 % aq. Sodium hydroxide. The product was crystallized by slowly acidifying the solution with 10 % aq. hydrochloric acid at a pH

of 2. The precipitation and acidification process were repeated three times to obtain the white chromium free precipitates of 2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid (2.56g, 90%).

2.2. N,N-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (7)

To a three-necked flask adding 1,4-dioxane solution of 4-bromo triphenyl amine (5 g, 15.42 mmol), bis(pinacolato)diboron (4.7 g, 18.5 mmol) and CH₃COOK (4.54 g, 46.62 mmol), The solution was purged with argon for 30 min, and then Pd(dppf)Cl₂ (0.38 g, 0.465 mmol) was added. The reaction was stirred at 85°C overnight. The reaction followed by TLC until reaction completion, then let the reaction to cool down and the reaction quenched by adding (50ml) of water then extracted by ethyl acetate (3 x 30 ml) The combined organic layers were dried over anhydrous Mg₂SO₄, and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica with hexane/ethyl acetate mixture (6: 1). The compound crystalized from anhydrous ethanol and give the pure white powder. Yield (80 %), melting point (m.p) 93 °C.

2.3. Synthesis of 2-(3,4-Ethylenedioxythiophene) carbaldehyde

3,4-Ethylenedioxythiophene (25 g, 0.1755 mmol) was dissolved in dry DMF (100 mL). The mixture was cooled to -10 °C and POCl₃ (17 mL, 0.18 mmol) was added drop-wise (15 min) in the cold solution. The mixture stirred 1 h at -10 °C, ice water (200 mL) was added and the mixture stirred overnight at room temperature. The aldehyde was filtered off, dissolved in CH₂Cl₂ (200 mL) and dried (Na₂SO₄). The CH₂Cl₂ filtrate was eluted through a short silica plug to remove colored byproducts, giving the dry product as white crystals (21g, 71%).

2.4. Synthesis of 2-Bromo-(3,4-ethylenedioxythiophene)-5-carbaldehyde (8).

2-(3,4-Ethylenedioxythiophene) carbaldehyde (4.04 g, 23.7 mmol) was suspended in dry acetonitrile (100 mL) and cooled to 0 °C. NBS (4.36 g, 26.0 mmol), 1.1 equiv, was added and the mixture was stirred for 60 hrs at room temperature, shielded from light and under nitrogen. The

color changed from yellow to purple. The mixture was transferred with 150 mL of ethyl acetate to a separation funnel, washed with 10% aqueous Na_2CO_3 (2×200 mL), saturated $\text{Na}_2\text{S}_2\text{O}_3$ (2×200 mL) and water (2×200 mL), dried with MgSO_4 , and evaporated in vacuo. Recrystallization twice from ethanol (60 mL) of the bromide as yellow needles (5.35 g, 91%).

3. Electrochemical measurements (CV)

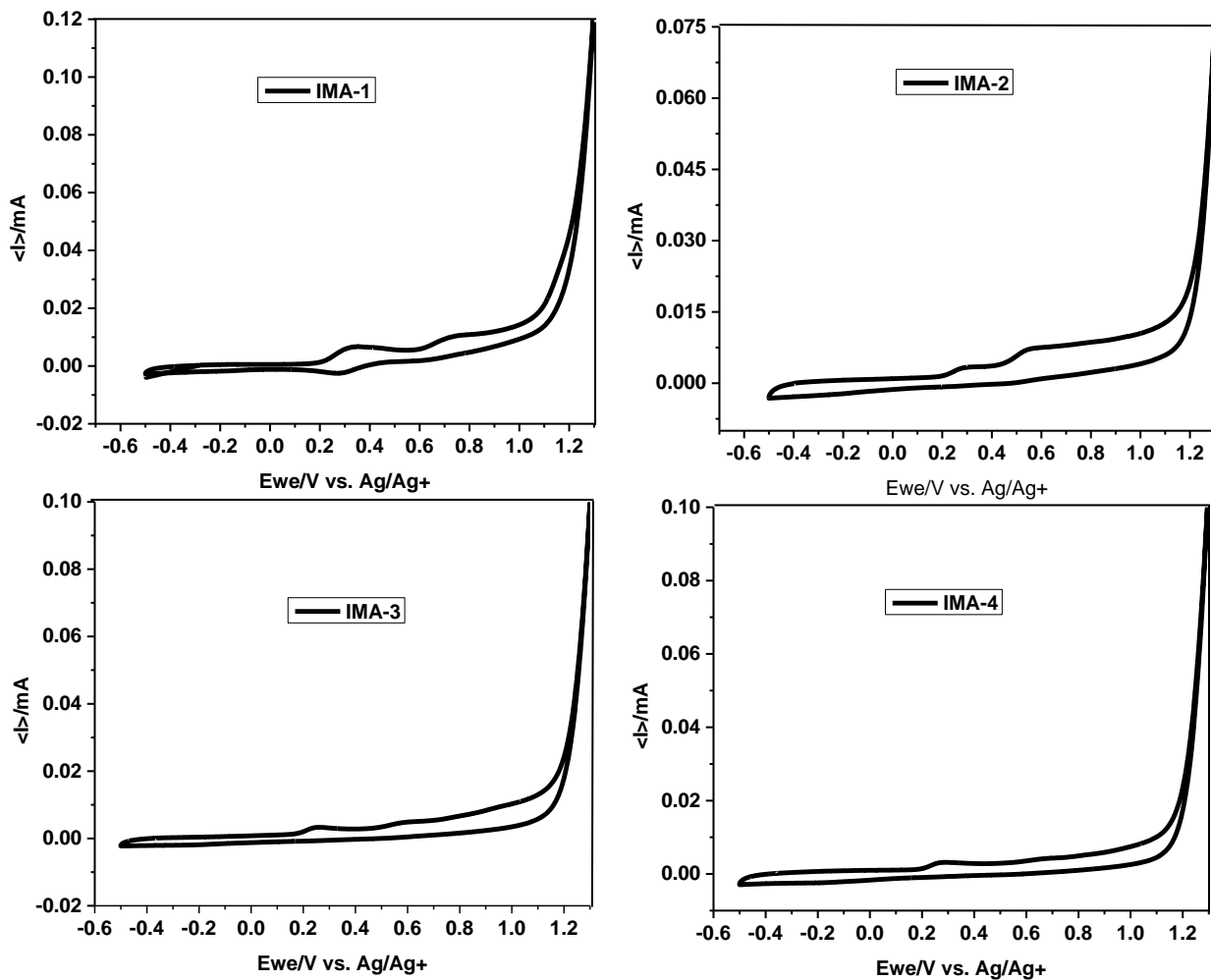


Fig. S1. Cyclic voltammogram of IMA-(1-4) in DMSO solution

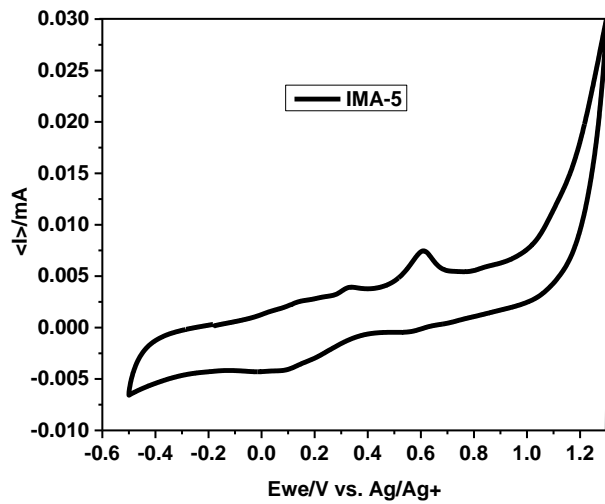


Fig. S2. Cyclic voltammogram of IMA-5 complex in chloroform solution

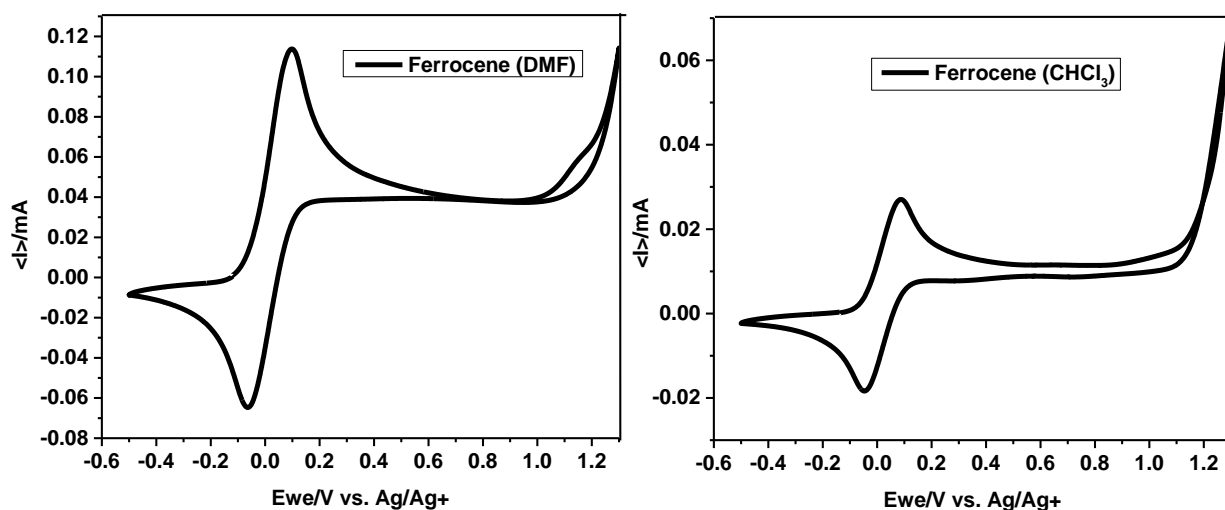


Fig. S3. Cyclic voltammogram of ferrocene compound in DMF/ CHCl_3 solution

4. Spectral results

4.1. High resolution mass spectra

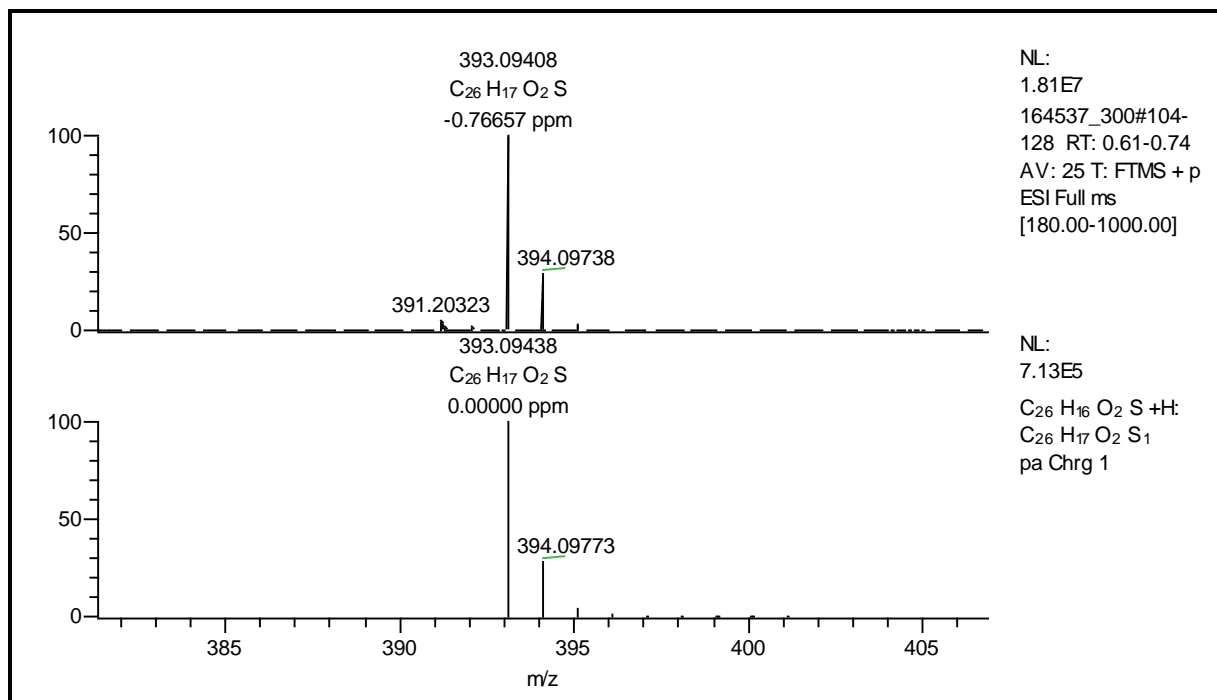


Fig. S4. Experimental and Theoretical Isotopic Distribution for **2**, $[\text{M}+\text{H}]^+$

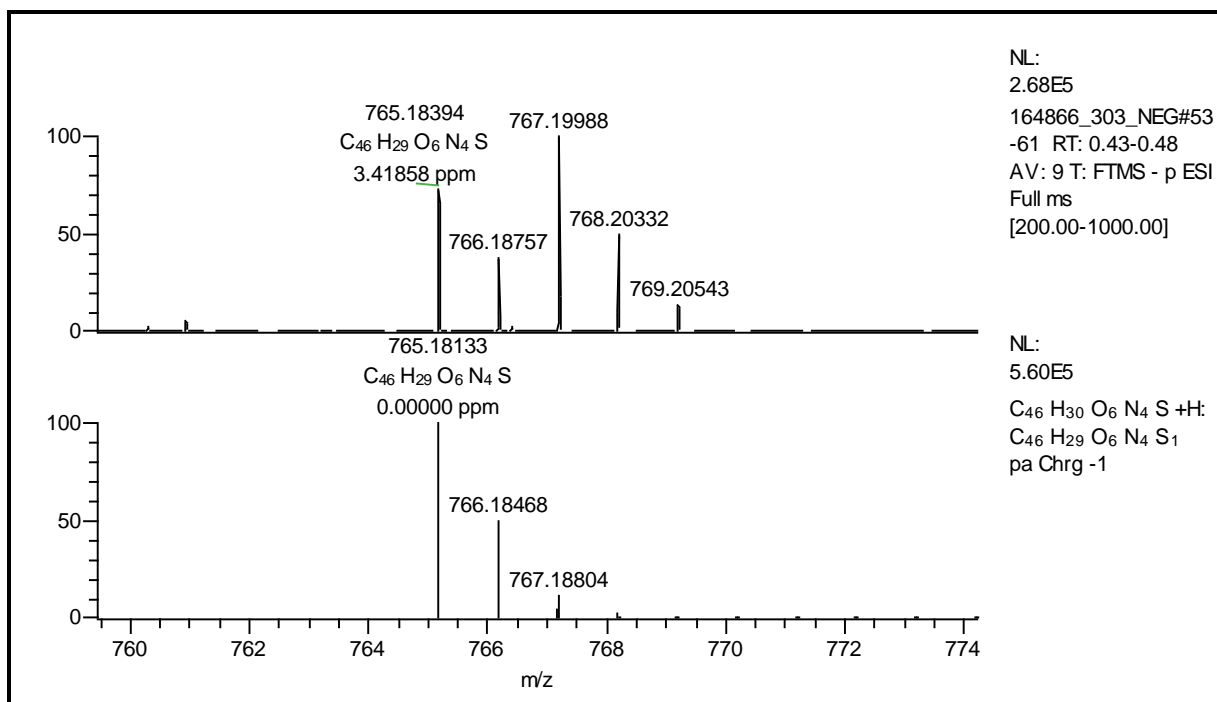


Fig. S5. Experimental and Theoretical Isotopic Distribution for **IMA1**, [M-H]⁻

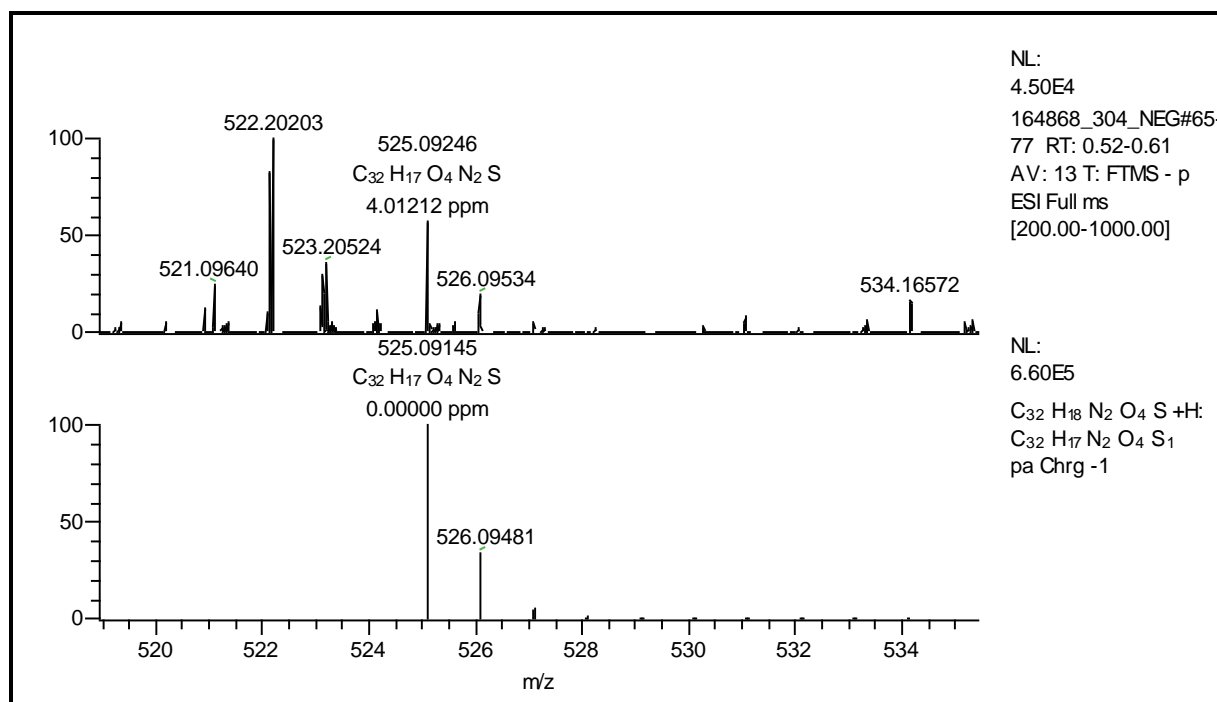


Fig. S6. Experimental and Theoretical Isotopic Distribution for **IMA2**, [M-H]⁻

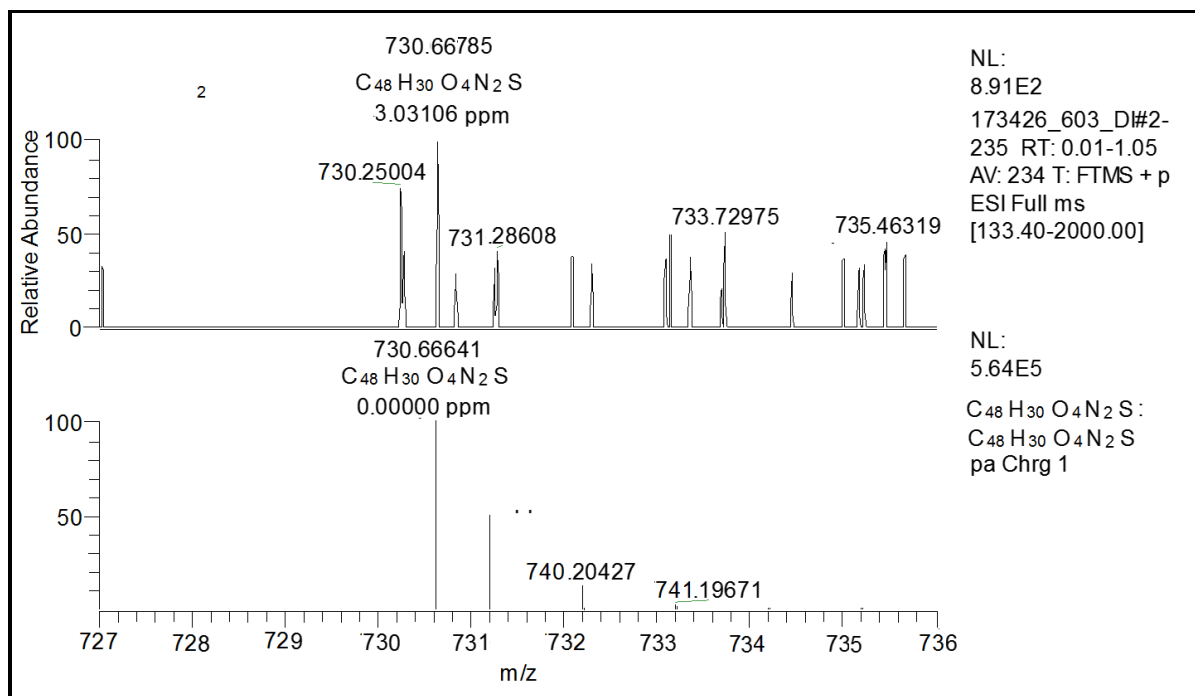


Fig. S7. Experimental and Theoretical Isotopic Distribution for **IMA-3**, [M]⁺

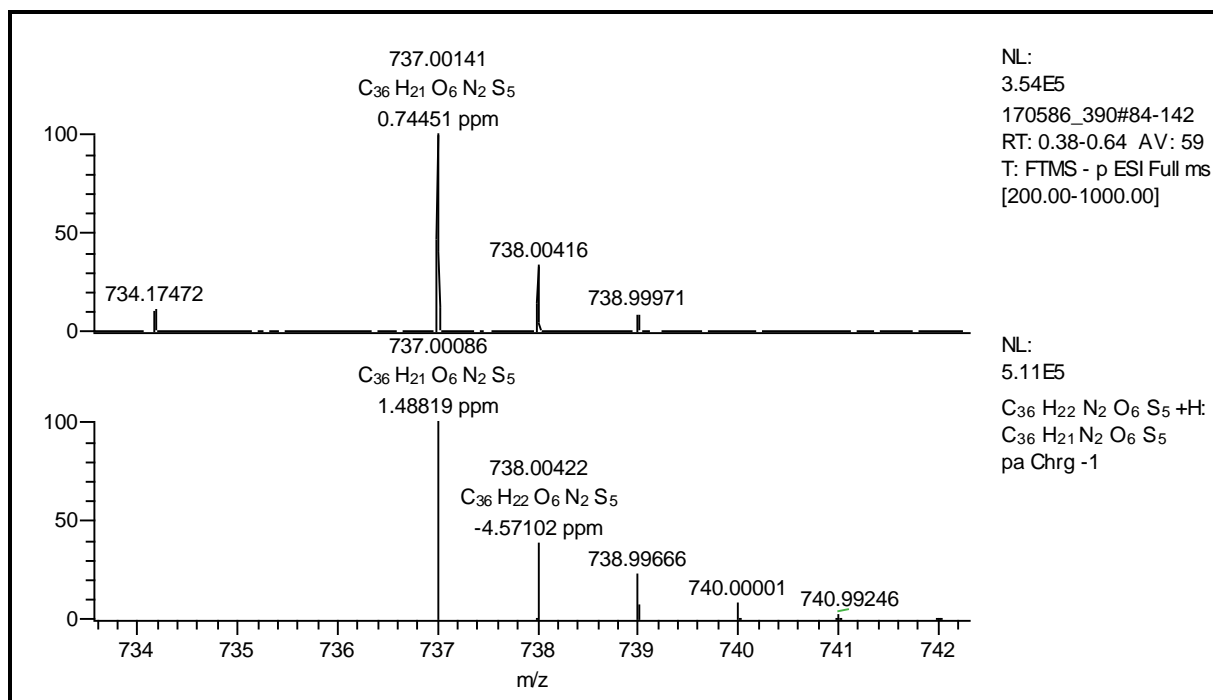


Fig. S8. Experimental and Theoretical Isotopic Distribution for **IMA4**, [M-H]⁻

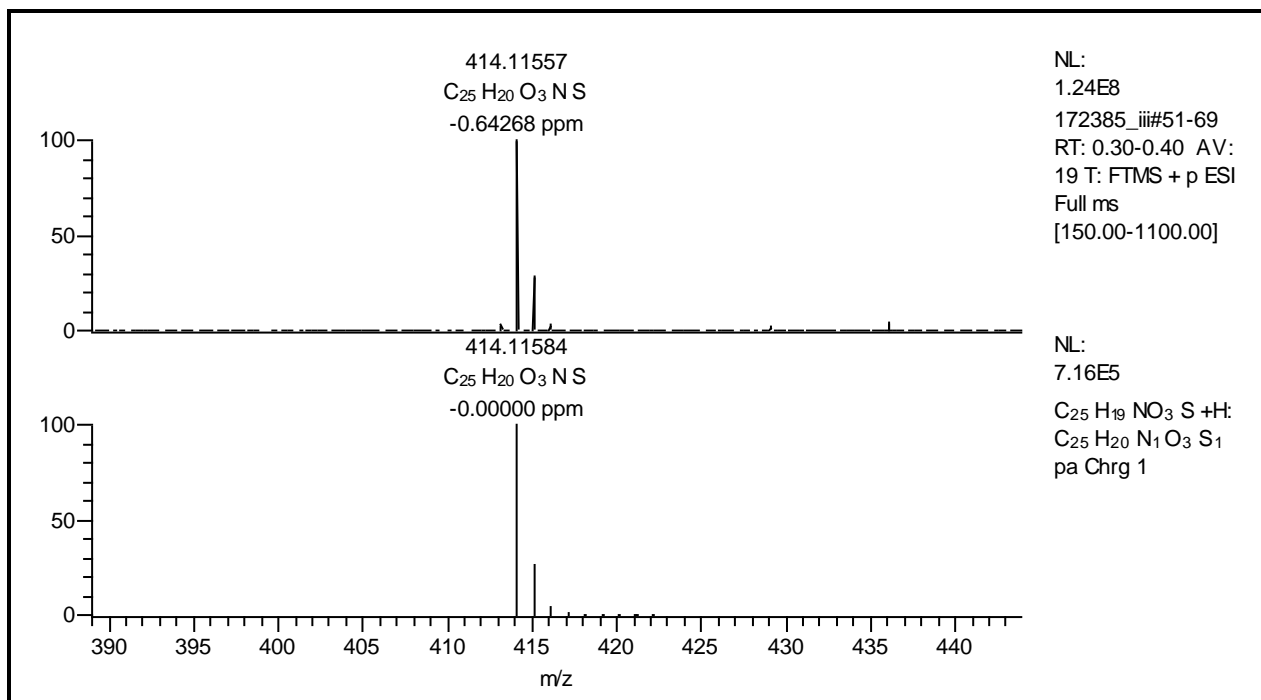


Fig. S9. Experimental and Theoretical Isotopic Distribution for **9**, $[M+H]^+$

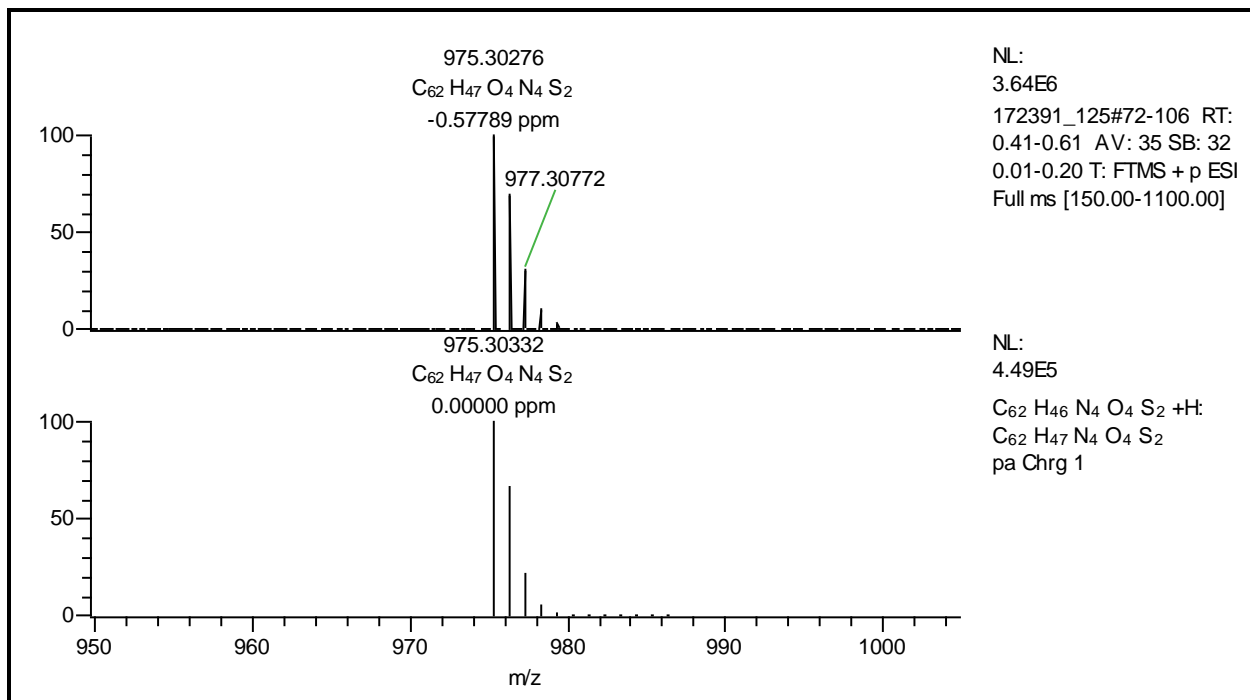


Fig. S10. Experimental and Theoretical Isotopic Distribution for **10**, $[M+H]^+$

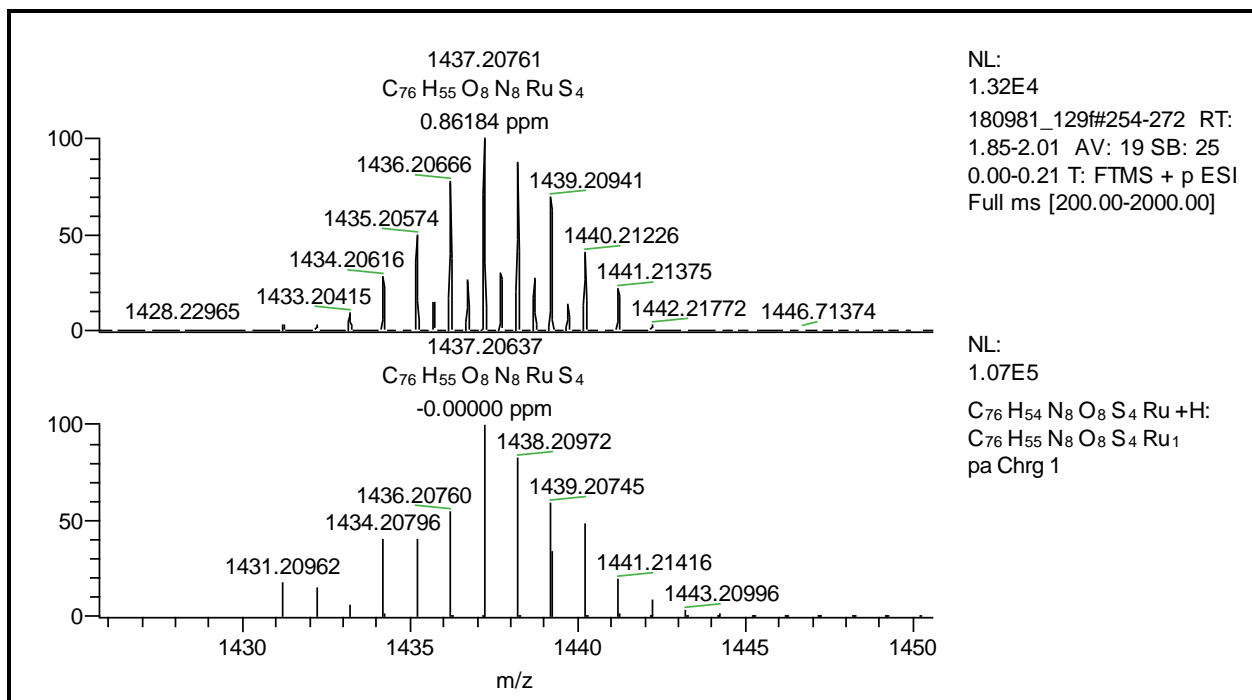


Fig. S11. Experimental and Theoretical Isotopic Distribution **IMA5**, $[M+H]^+$

4.2. FTIR Spectra

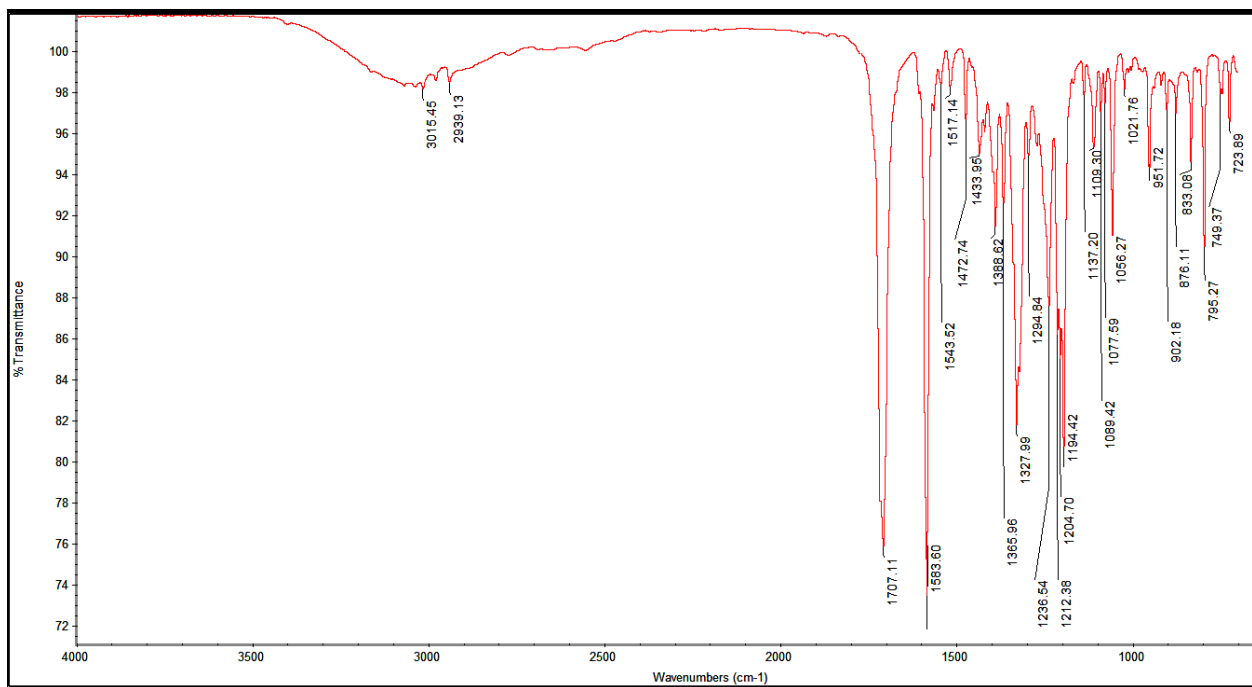


Fig. S12. FTIR spectra for **2**

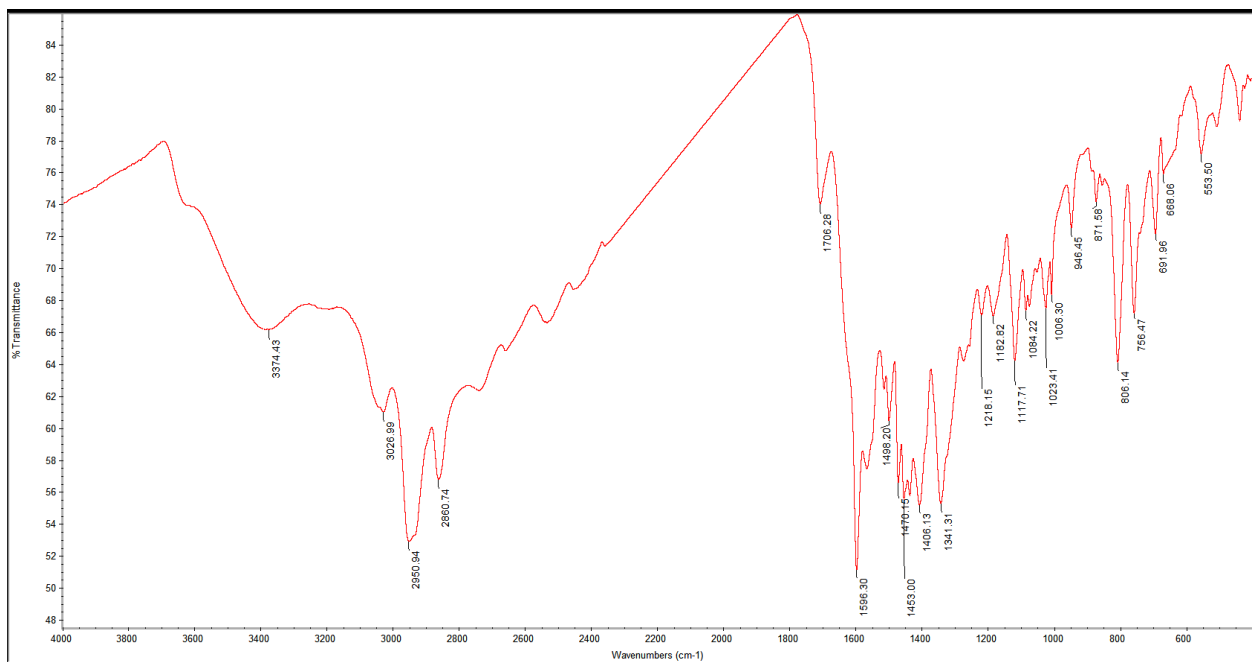


Fig. S13. FTIR spectra for IMA1

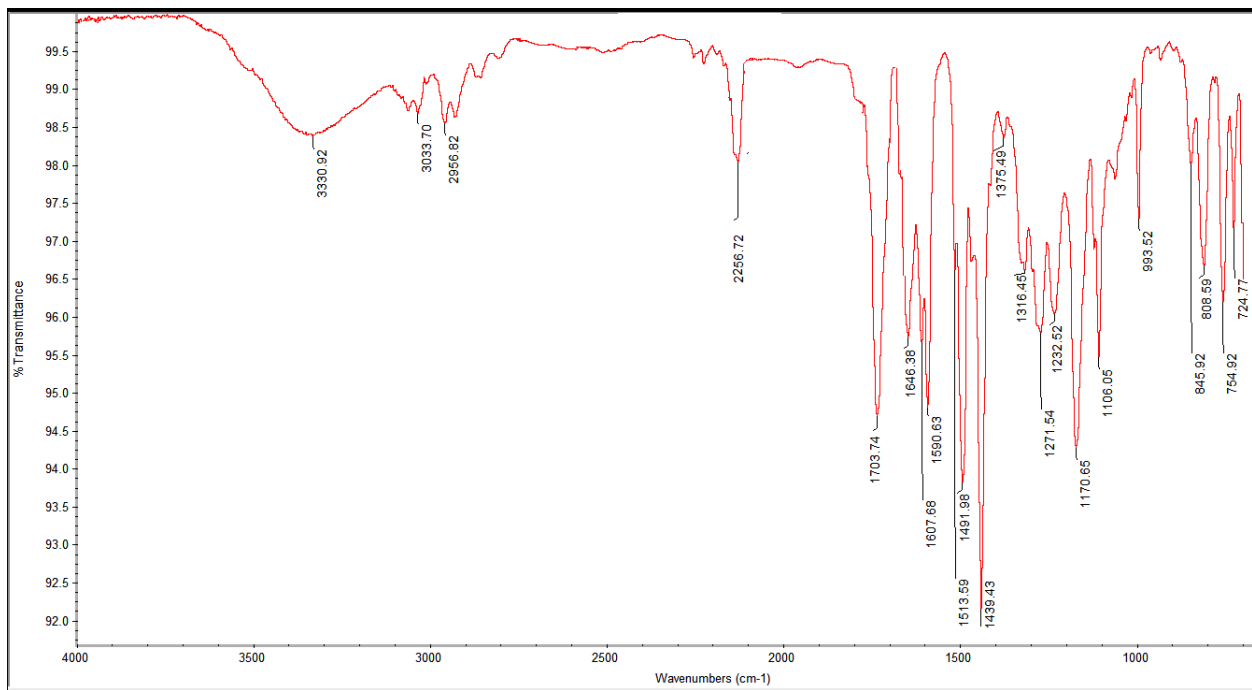


Fig. S14. FTIR spectra for IMA2

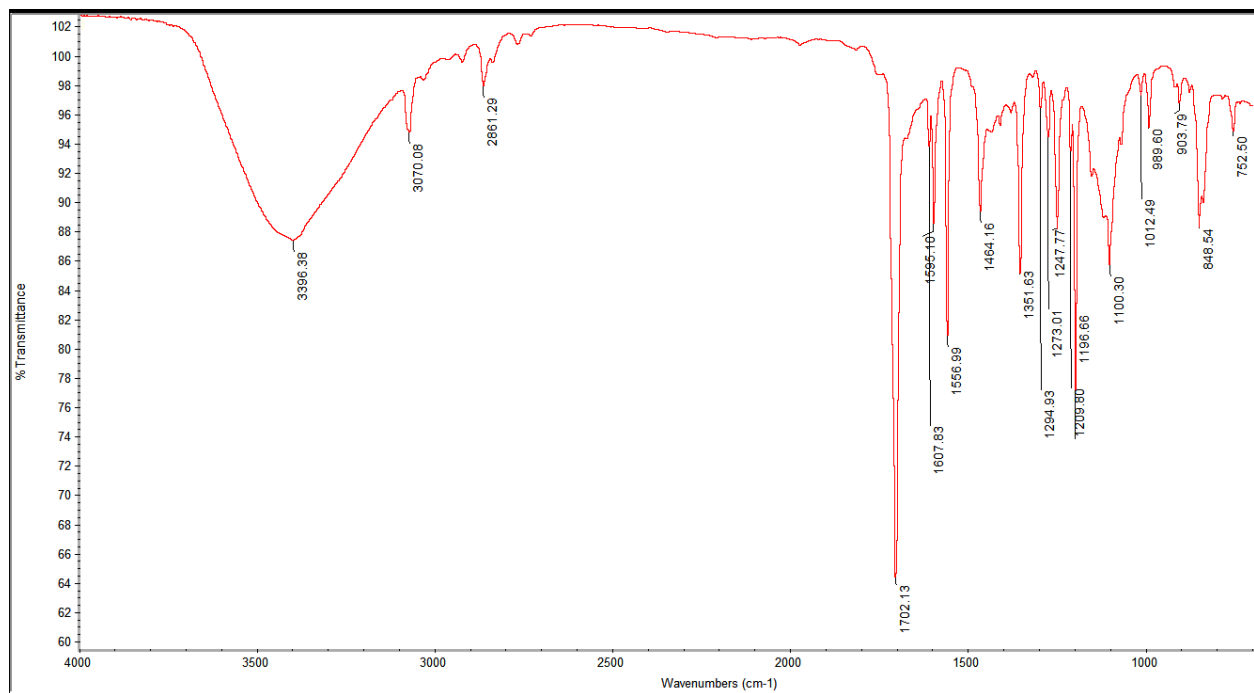


Fig. S15. FTIR spectra for IMA3

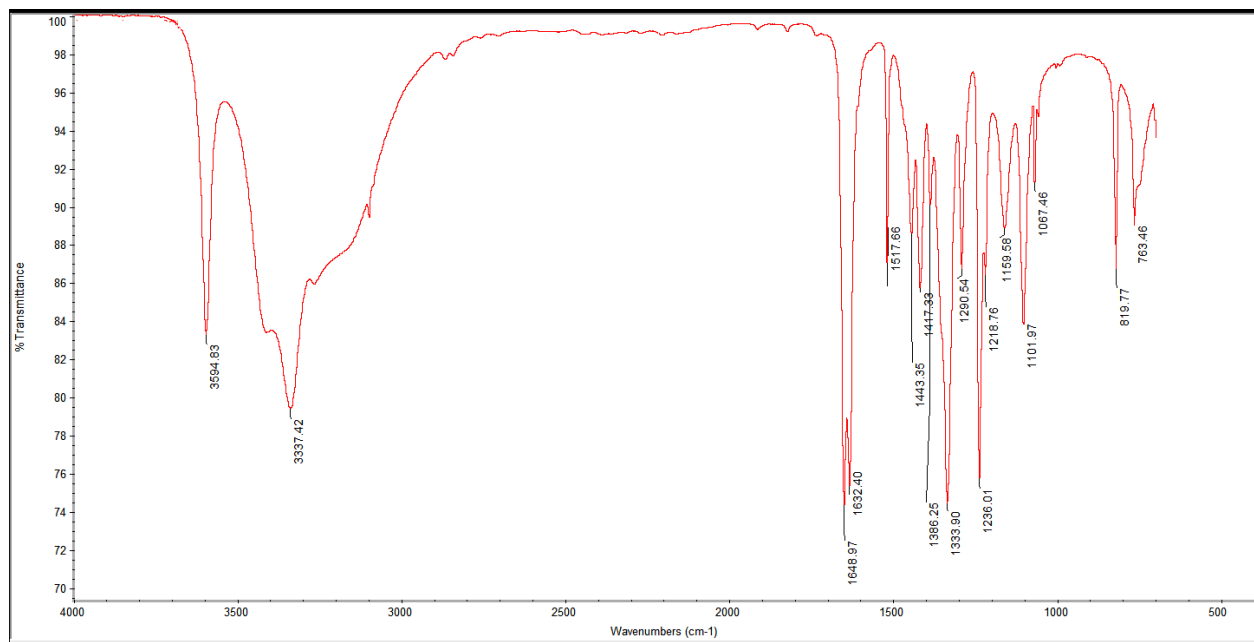


Fig. S16. FTIR spectra for IMA4

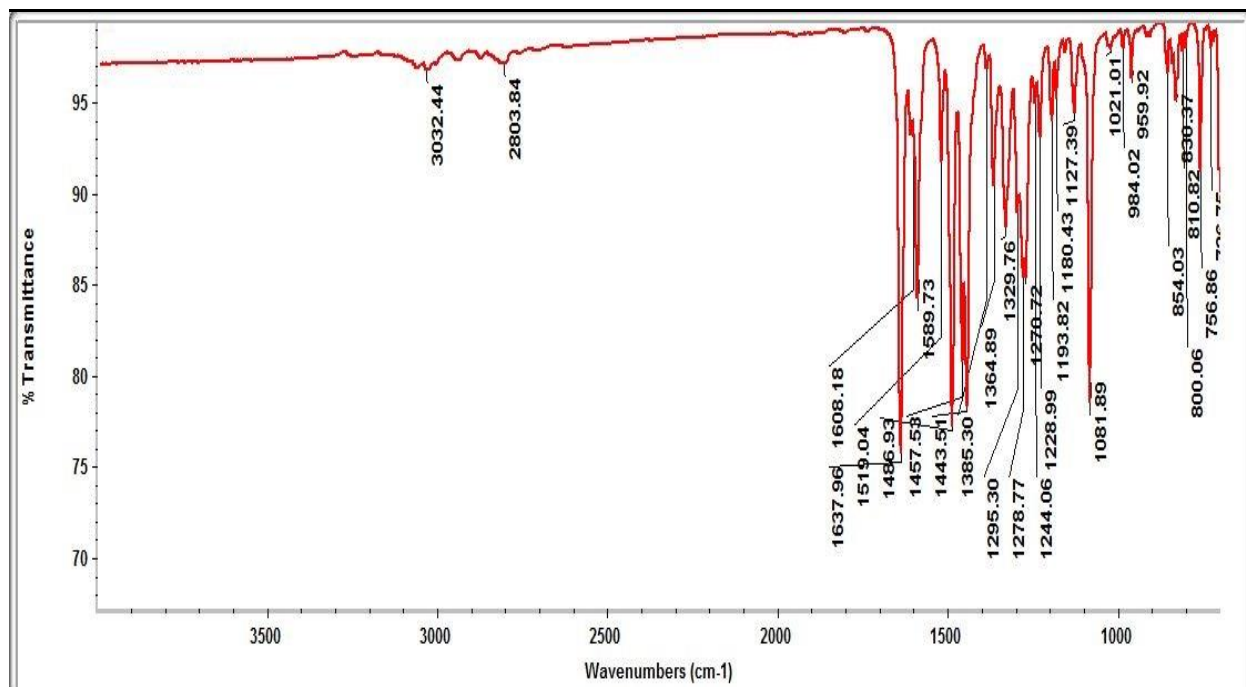


Fig. S17. FTIR spectra for **9**

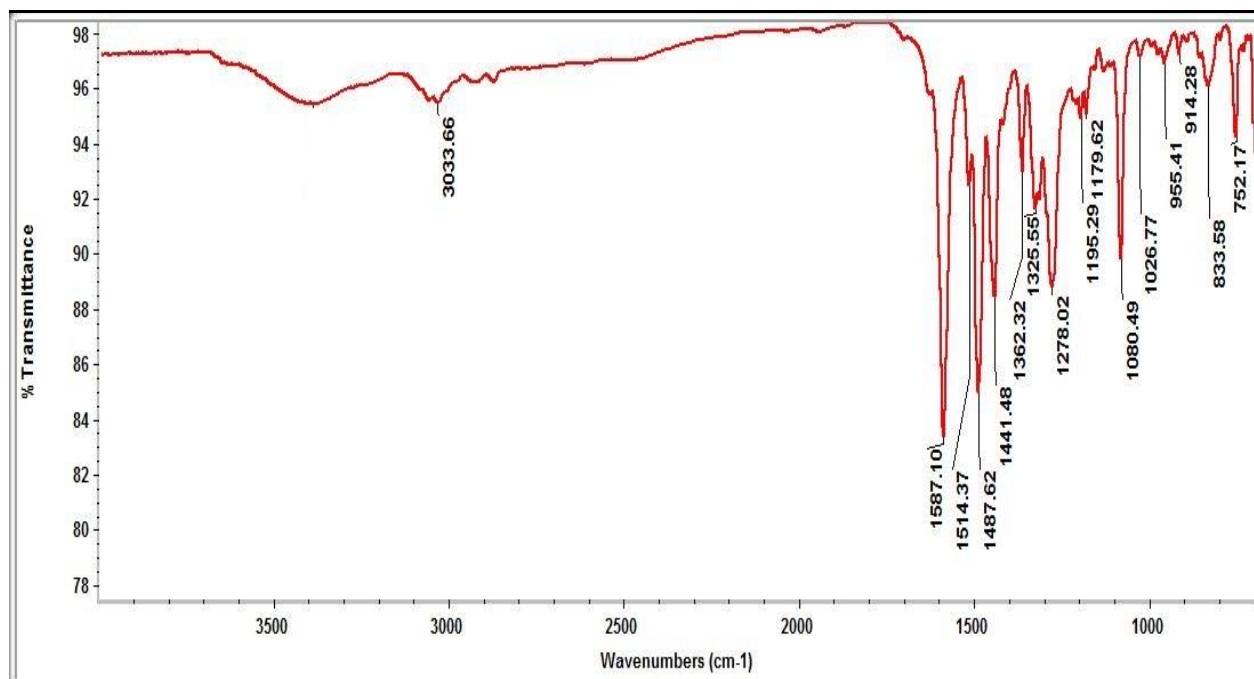


Fig. S18. FTIR spectra for **10**

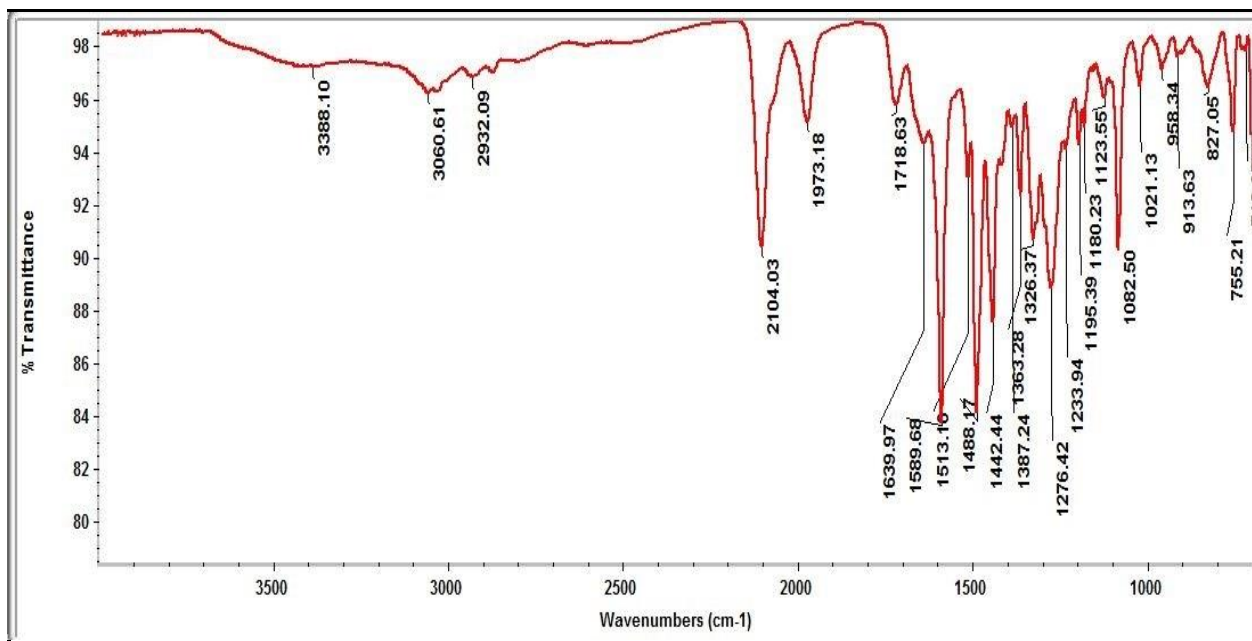


Fig. S19. FTIR spectra for IMA5

4.3. ¹H-NMR spectra

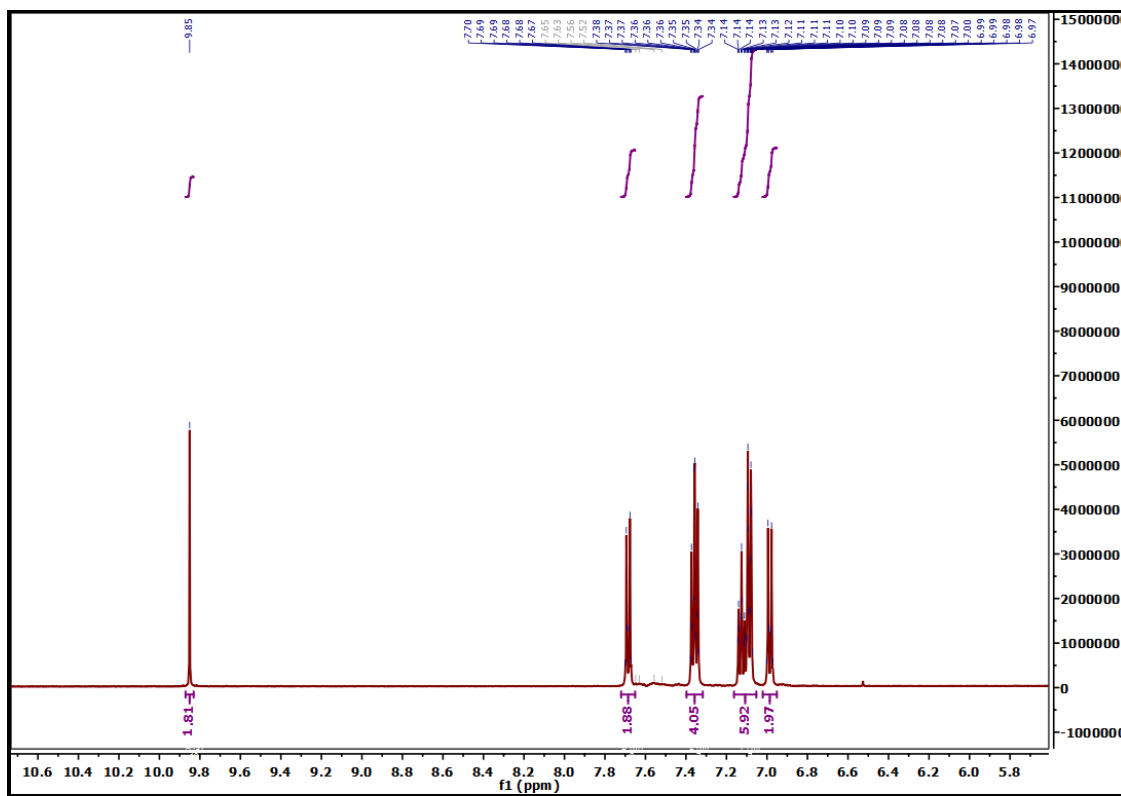


Fig. S20. ¹H-NMR spectra for 2

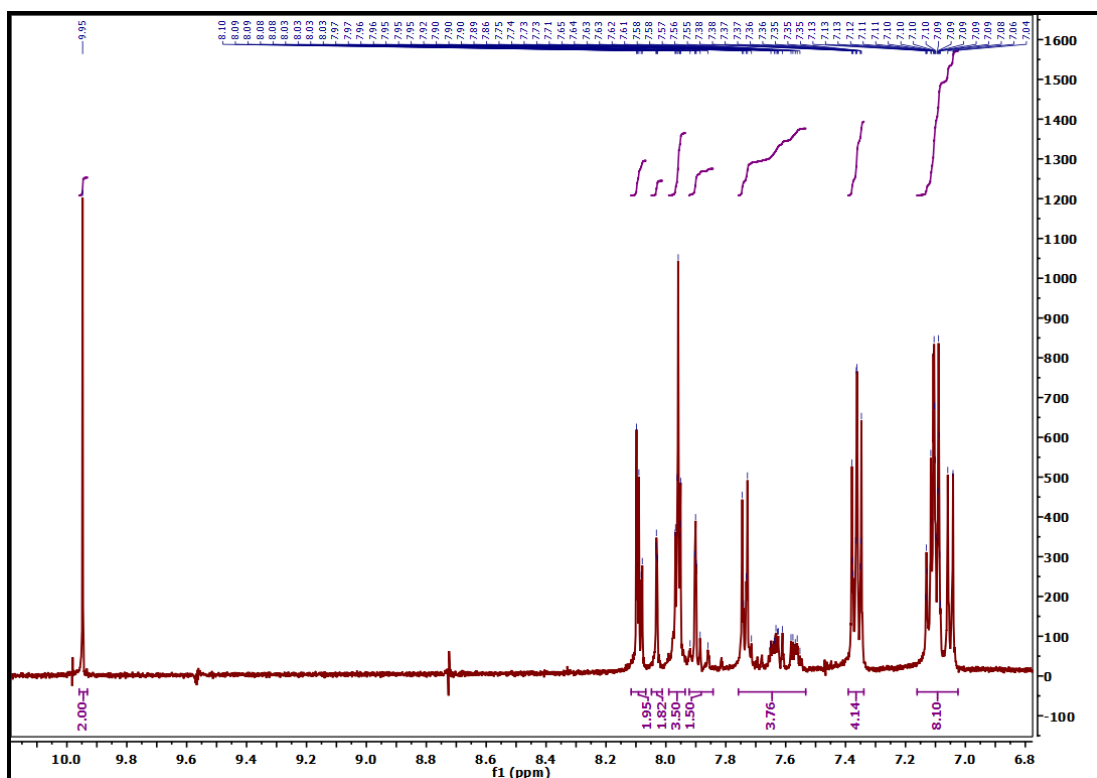


Fig. S21. ¹H-NMR spectra for IMA1

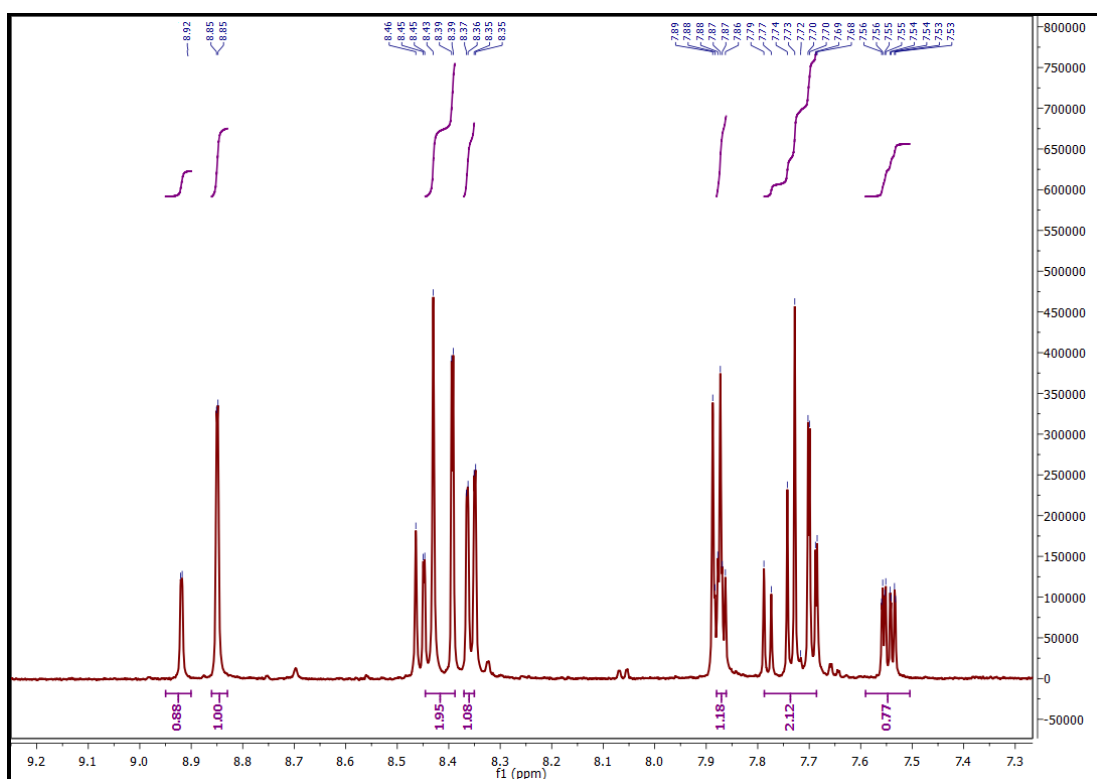


Fig. S22. ¹H-NMR spectra for IMA2

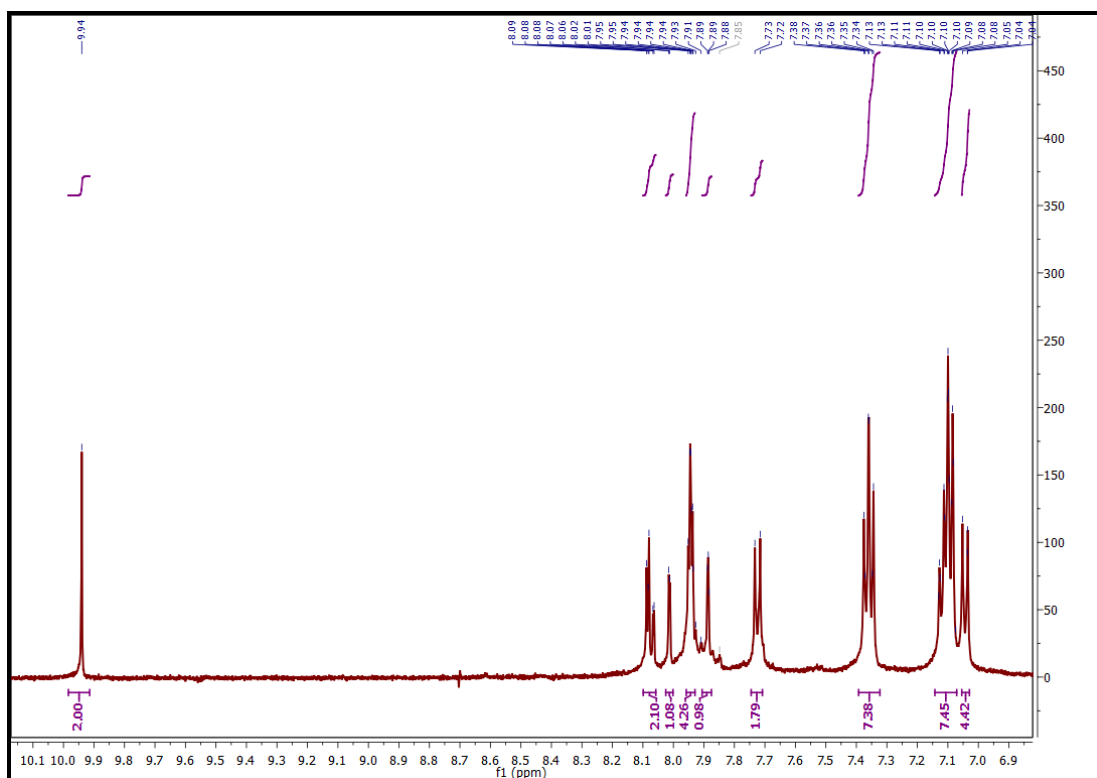


Fig. S23. $^1\text{H-NMR}$ spectra for IMA3

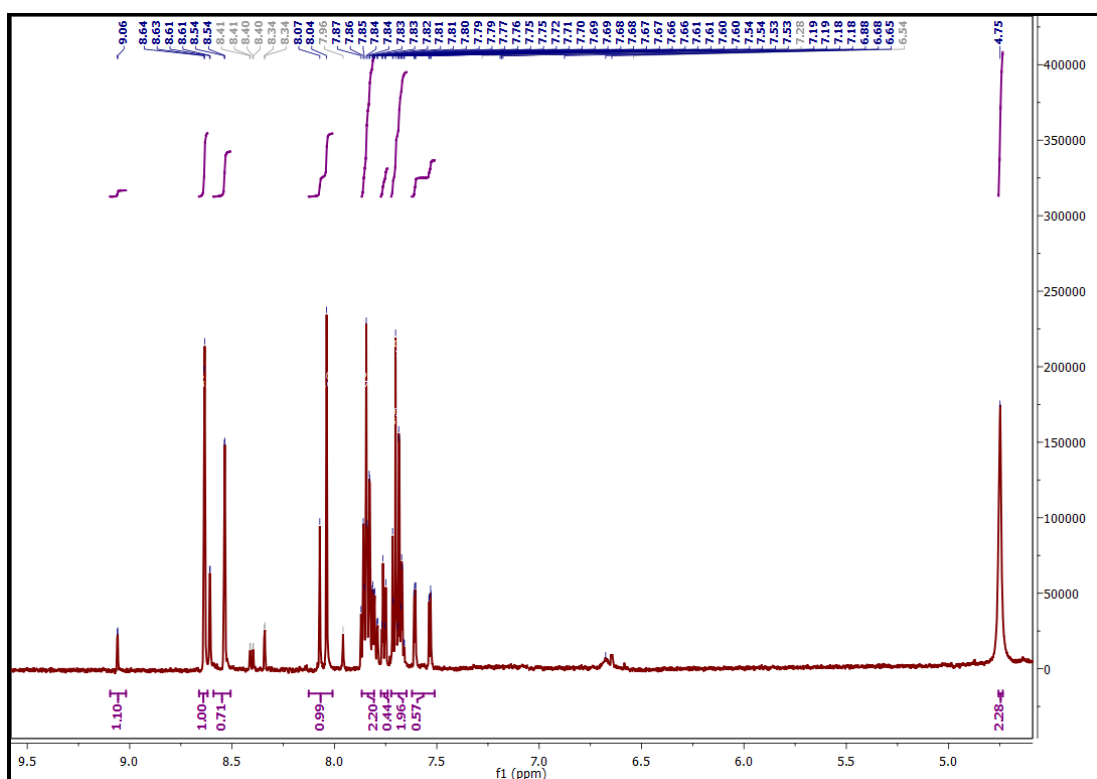


Fig. S24. $^1\text{H-NMR}$ spectra for IMA4

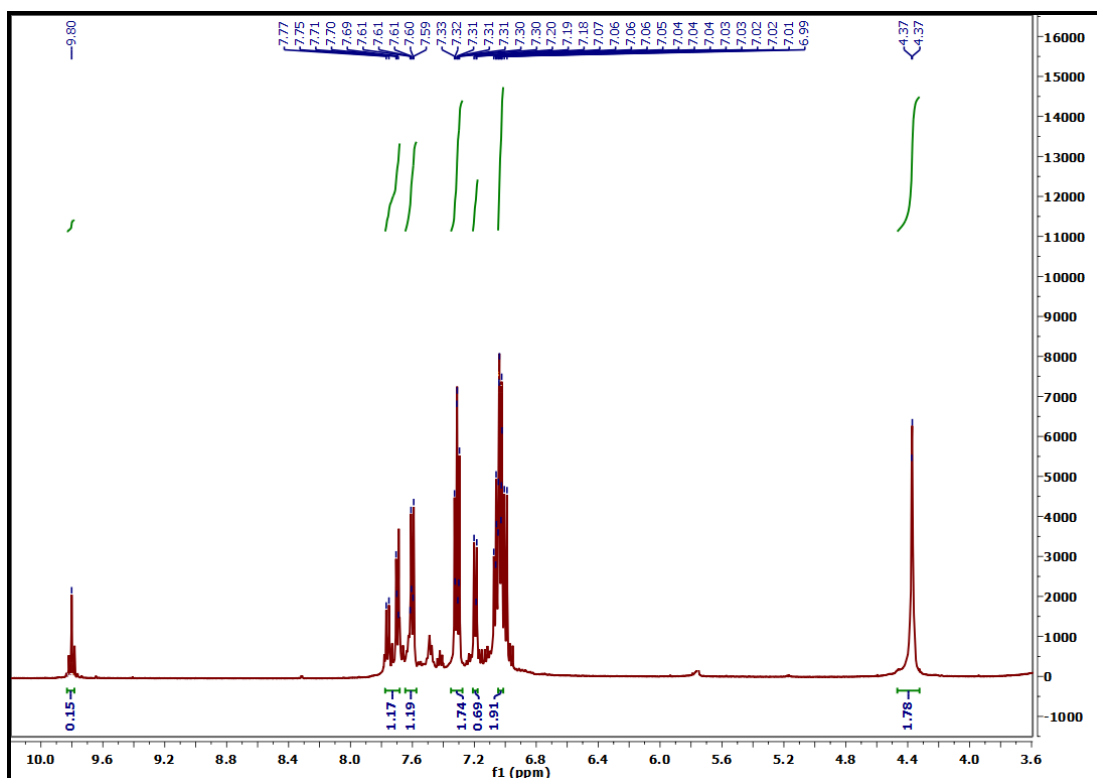


Fig. S25. ¹H-NMR spectra for 9

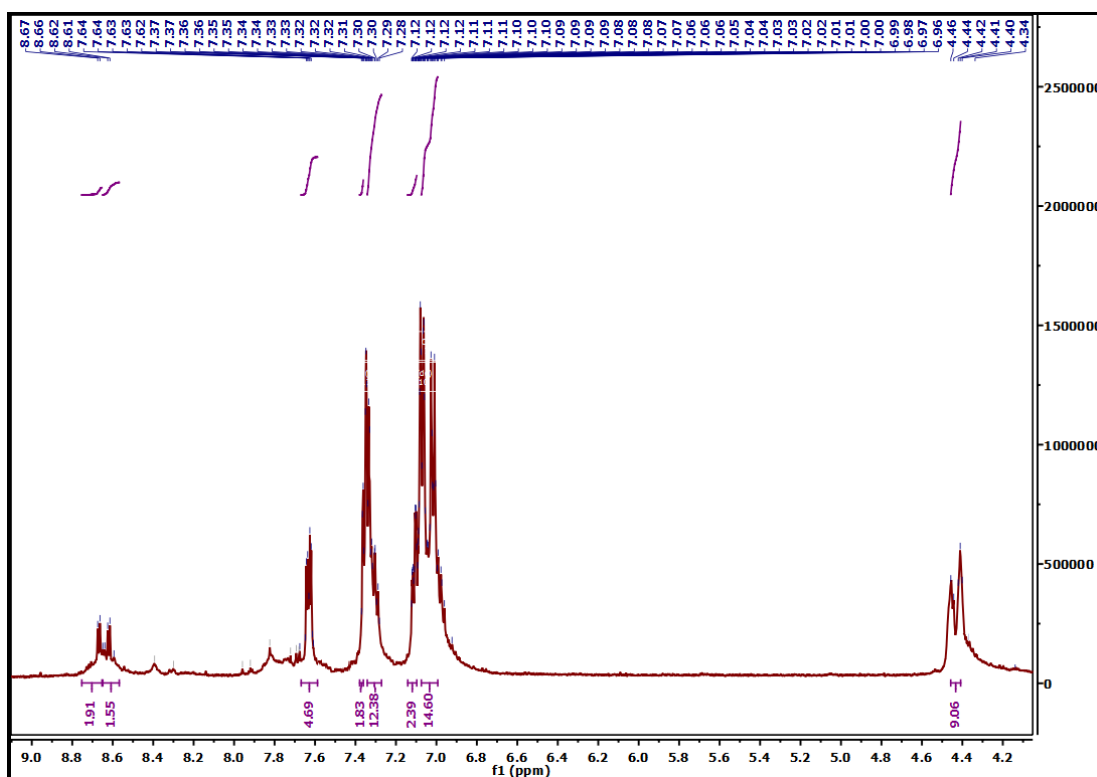


Fig. S26. ¹H-NMR spectra for 10

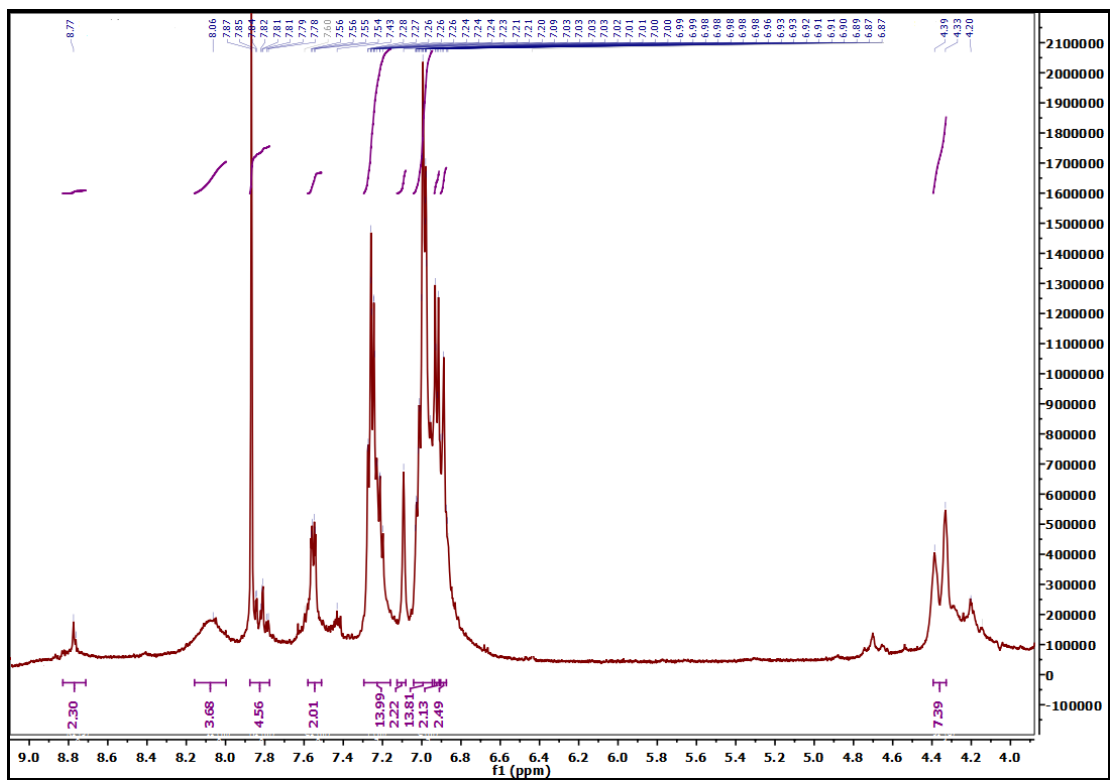


Fig. S27. ¹H-NMR spectra for IMA5