Electronic Supplementary Information (ESI) for

A Thiadiazolopyridine-Functionalized Zr(IV)-Based Metal-Organic Framework for Enhanced Photocatalytic Synthesis of Tetrahydroquinolines under Visible Light

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General method and materials

Unless specifically mentioned, all chemicals are commercially available and were used as received. NMR spectra were taken on a Bruker AV400 at room temperature. The powder X-ray diffraction (PXRD) measurements were taken on a Bruker D8 diffractometer using Cu-K_α radiation (λ = 1.5418 Å) at room temperature. Low-pressure gas sorption measurements were performed by using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with the extra-high pure gases. The infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrometer as KBr pellets. Thermal gravimetric analyses (TGA) were performed on a TA-Q50 thermoanalyzer thermogravimetric analyzer in nitrogen atmosphere from 45 °C to 800 °C at the rate of 10 °C min^{-1}.

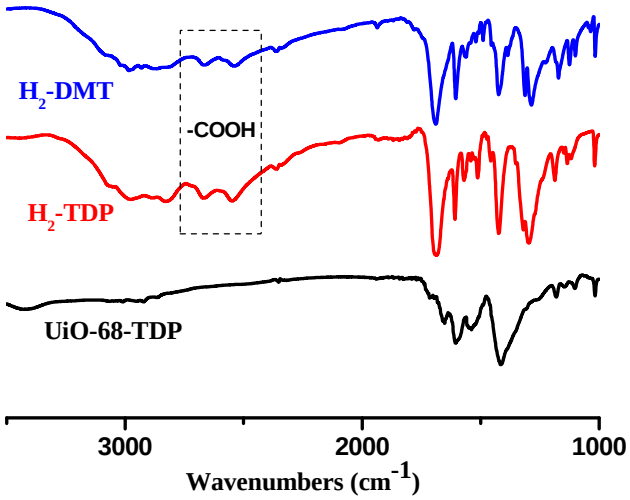


Fig. S1 The FT-IR comparison of H_2-DMT, H_2-TDP ligands and MOF UiO-68-TDP, the disappearance of peak COOH at 2500 ~cm^{-1} in MOF indicative of the coordination of carboxylic acid with Zr^{4+}.

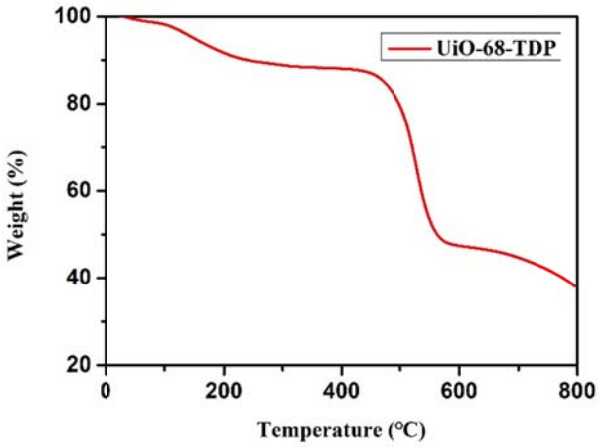


Fig. S2 TGA of UiO-68-TDP under N_2 atmosphere with a heating rate of 10 ^{o}C/min, suggesting it can be stable as high as ~500 ^{o}C.

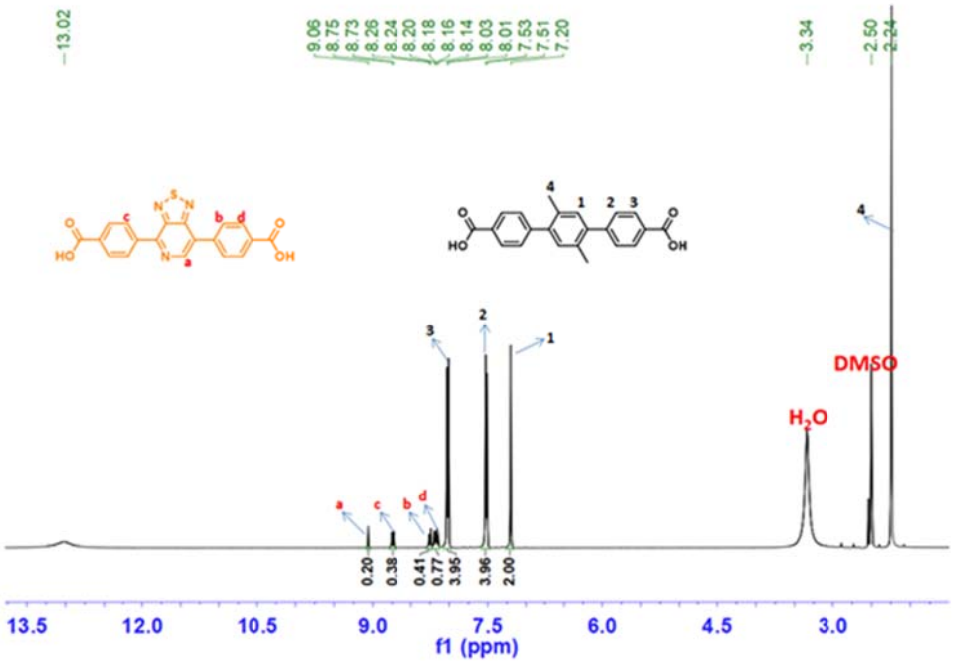


Fig.S3 ^{1}H NMR of digested UiO-68-TDP in DMSO-d_6. The ratio of linkers H_2TDP and H_2DMT in as-prepared MOF UiO-68-TDP was calculated from the integration of Ha (H_2TDP) and H1 (H_2DMT), giving the ratio of 1:5, which is slightly lower the initial ratio of 1:3 in preparation of MOF. The low content of H_2-TDP linker in MOF should be ascribed to its lower solubility in comparison to H_2-DMT.

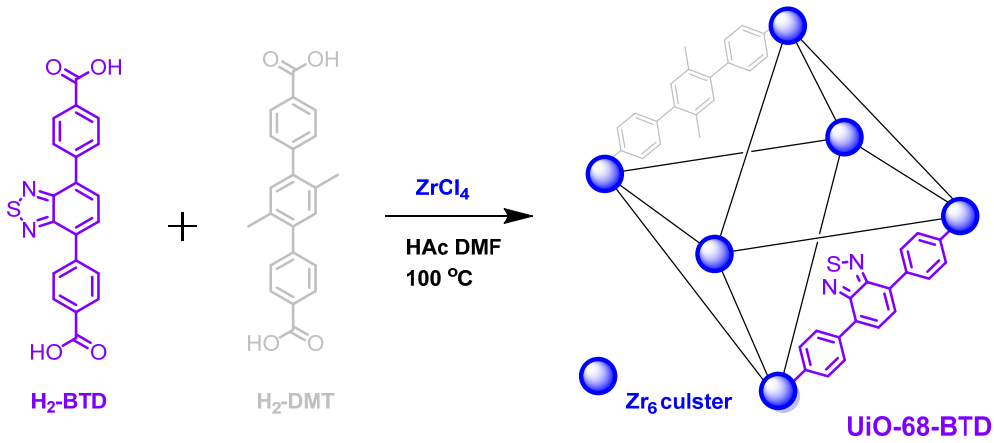


Fig. S4 The preparation for MOF UiO-68-BTD composed by the mixed linkers of H_2-BTD and H_2-DMT, which was prepared according to our previous work (*Acta Chim. Sinica* 2017, *75*, 80-85).

General Procedure for Photocatalysis

The weighed various photocatalysts (including MOF UiO-68-TDP, UiO-68-BTD, organic linkers, $ZrCl_4$ and others) *N,N*-dimethylanilines (0.2 mmol) and maleimides (0.1 mmol) were added into CH_3CN (1 mL). The reaction mixture with stirring was irradiated by blue LEDs for 12 hours under air at room temperature. After that, 0.1 mmol 1-methyl-2,4-dinitrobenzene as an internal standard was added into the mixture and stirred at room temperature for 10 min in dark. Then, the reaction mixture was extracted by dichloromethane (20 mL). The organic layer was dried over Na_2SO_4 and evaporated for subsequent ^1H NMR analysis to determine the yield by integration of H_A from internal standard and H_B from product (as shown in below.)

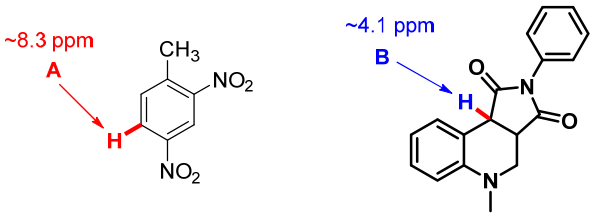
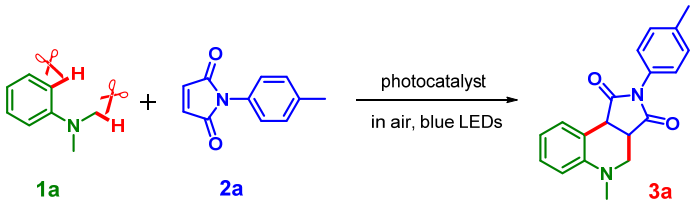


Table S1. Screening of the photocatalytic reaction conditions of **1a** and **2a** under other conditions.[a]



1a **2a** **3a**

Entry	Conditions	Light	Solvent	Yield[b]
1	UiO-68-TDP, 4 mg	+	DMF	64%
2	UiO-68-TDP, 4 mg	+	THF	30%
3	UiO-68-TDP, 4 mg	+	DCM	28%
4	$ZrCl_4$, 4 mg	+	CH_3CN	12%
5	H_2-TDP, 4 mg	+	DMF	66%
6	H_2-DMT, 4 mg	+	DMF	16%

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol) in solvent (1 mL) under an air atmosphere at room temperature for 12 h, blue LEDs (λ_{max} = 450 nm, 3 W). [b]Yield was determined by ^{1}H-NMR analysis based on **2a**.

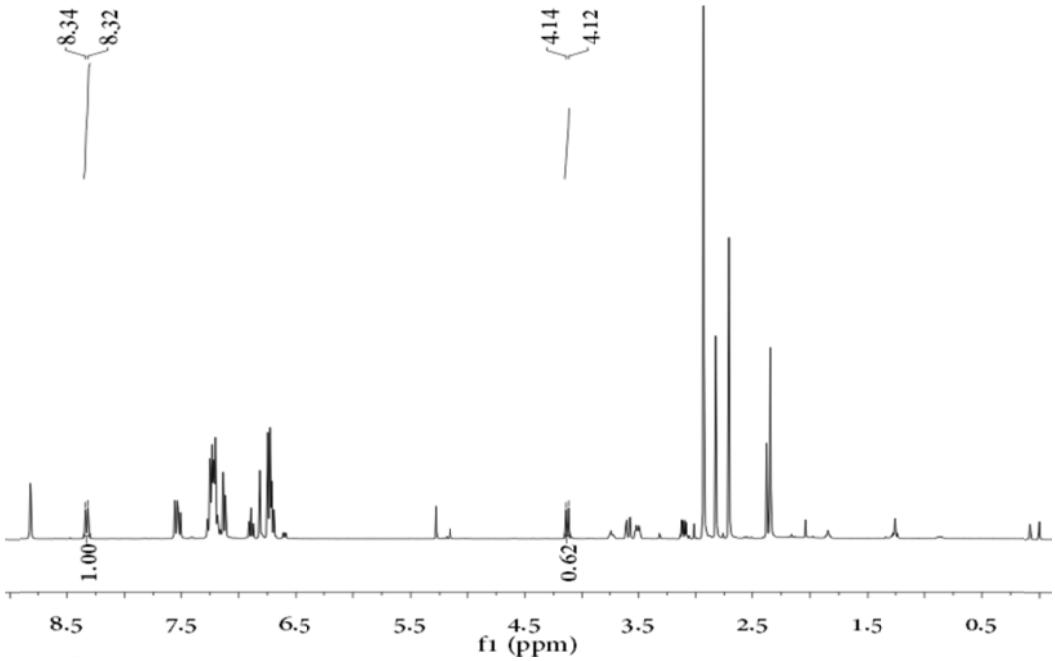


Fig. S5 ^{1}H NMR (Entry 1, Table 1).

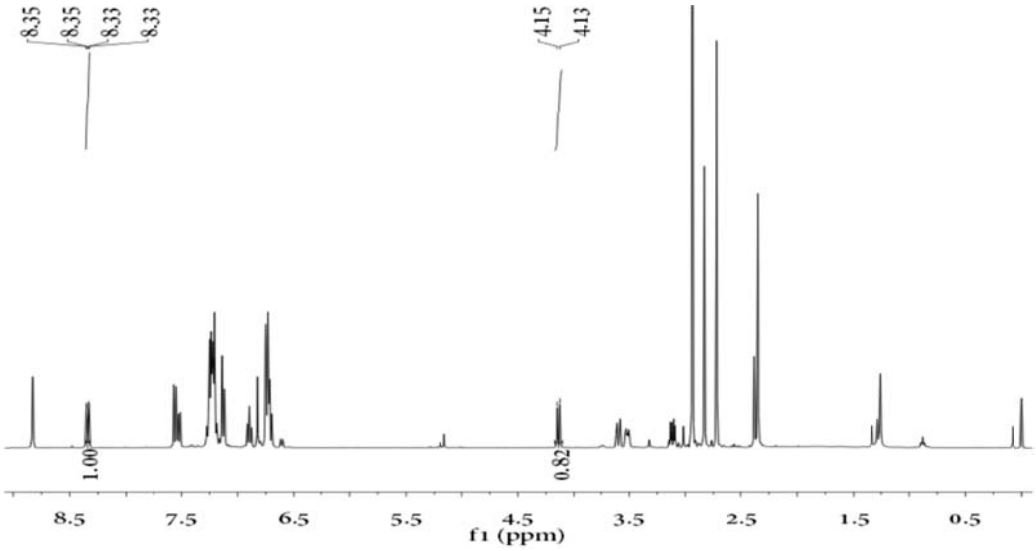


Fig. S6 ^{1}H NMR (Entry 2, Table 1).

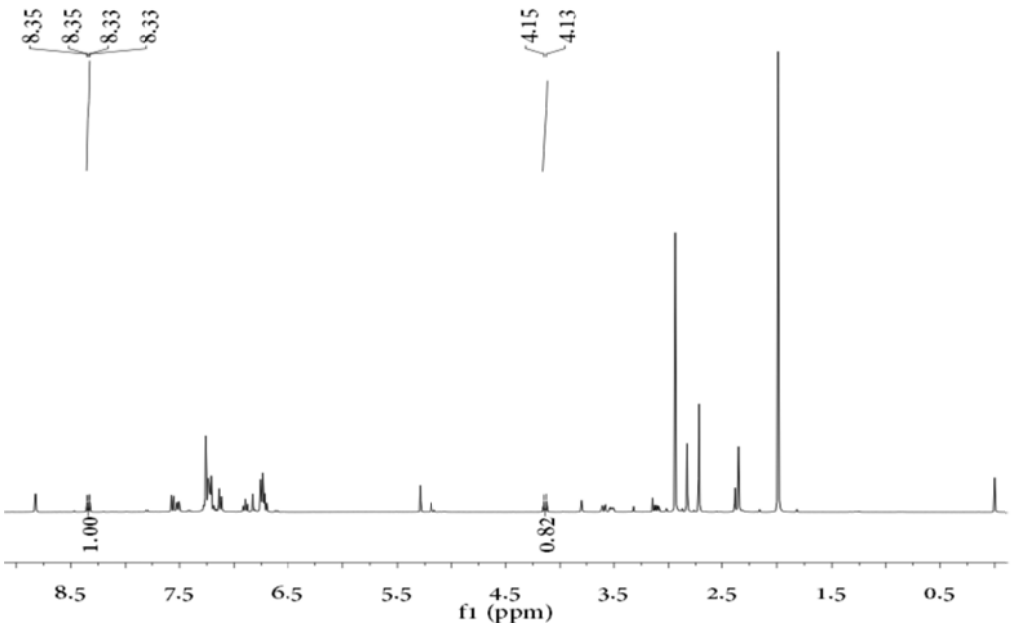


Fig. S7 ^{1}H NMR (Entry 3, Table 1).

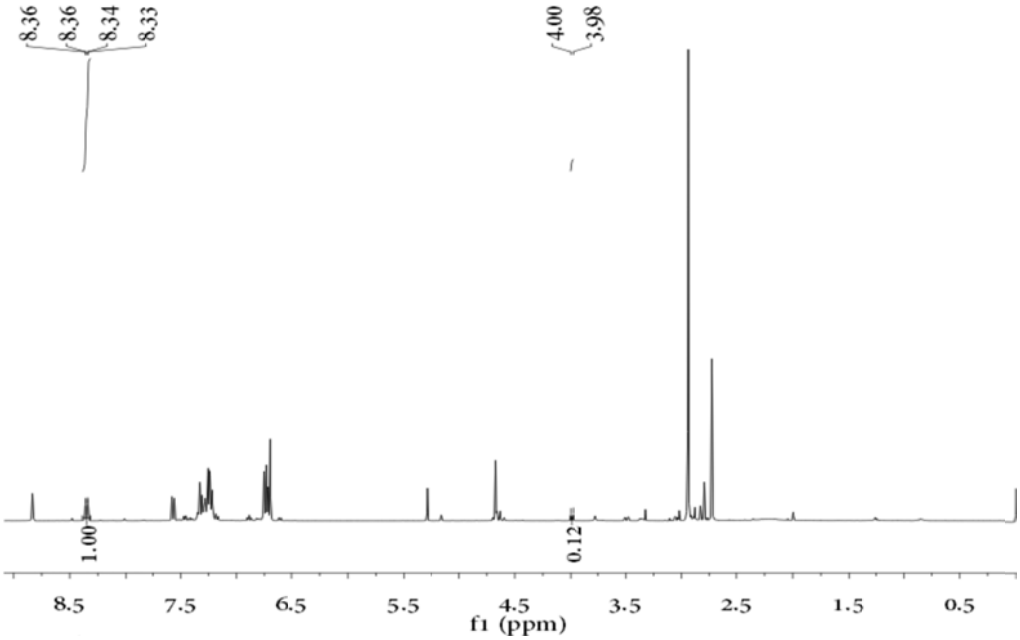


Fig. S8 ^{1}H NMR (Entry 4, Table 1).

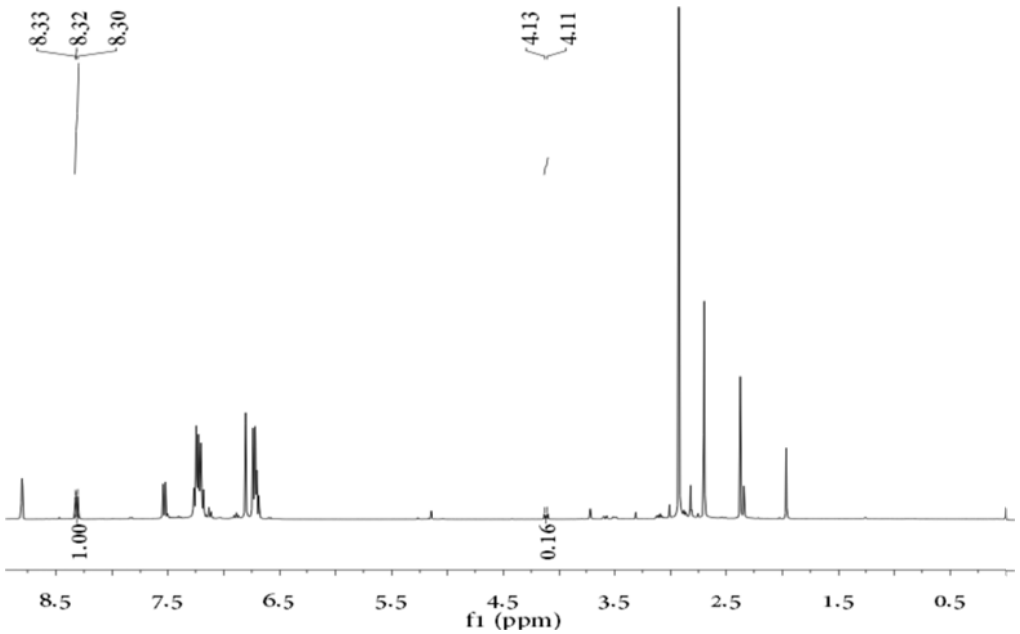


Fig. S9 ^{1}H NMR (Entry 5, Table 1).

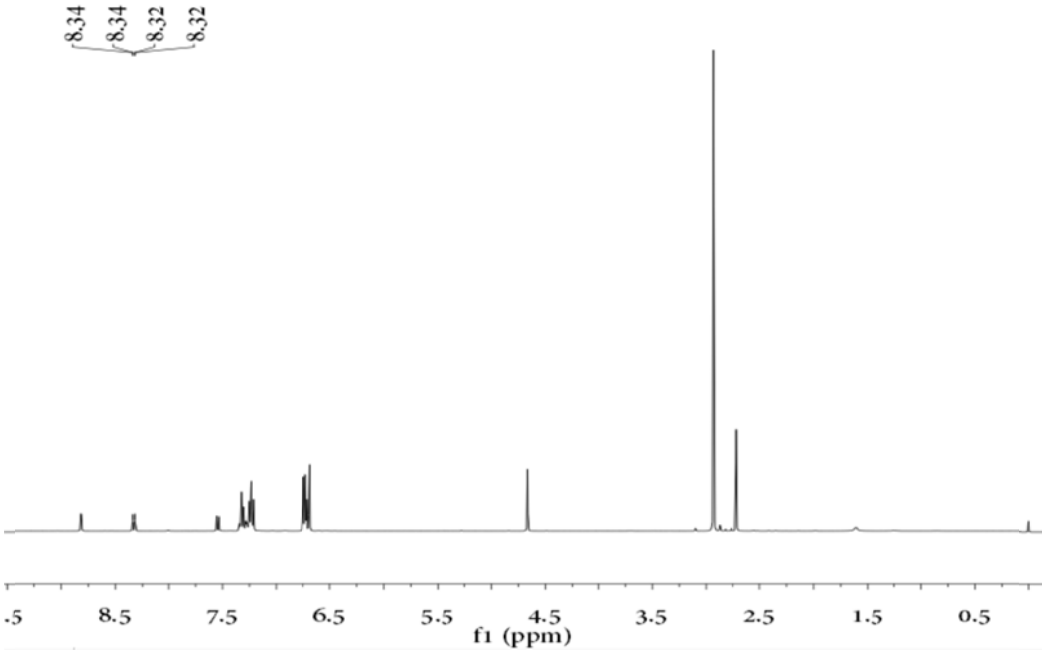


Fig. S10 ^{1}H NMR (Entry 6, Table 1).

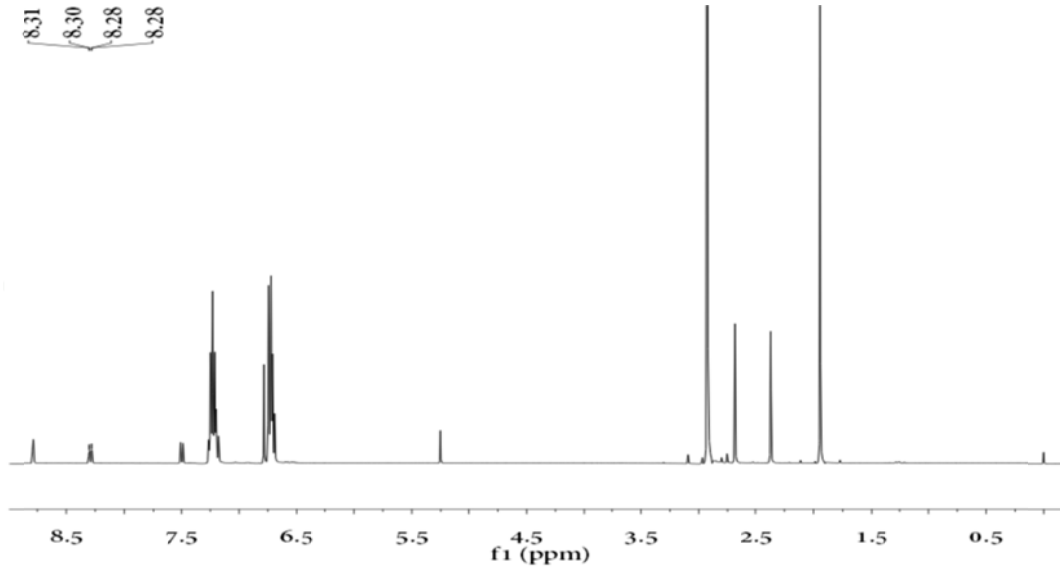


Fig. S11 ^{1}H NMR (Entry 7, Table 1).

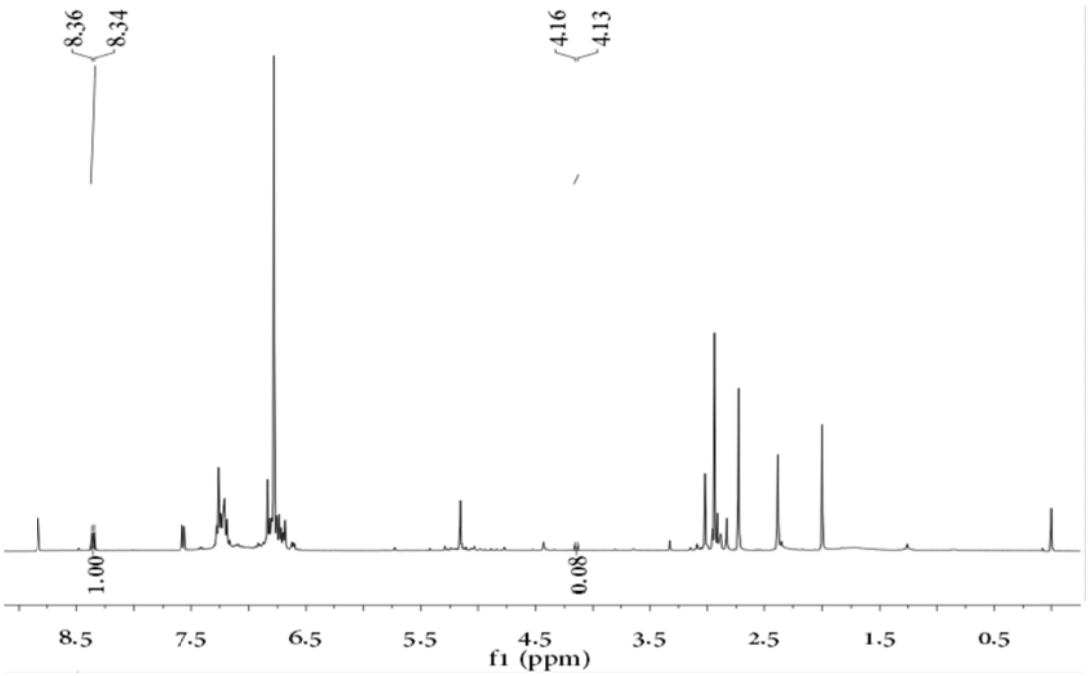


Fig. S12 ^{1}H NMR (Entry 8, Table 1).

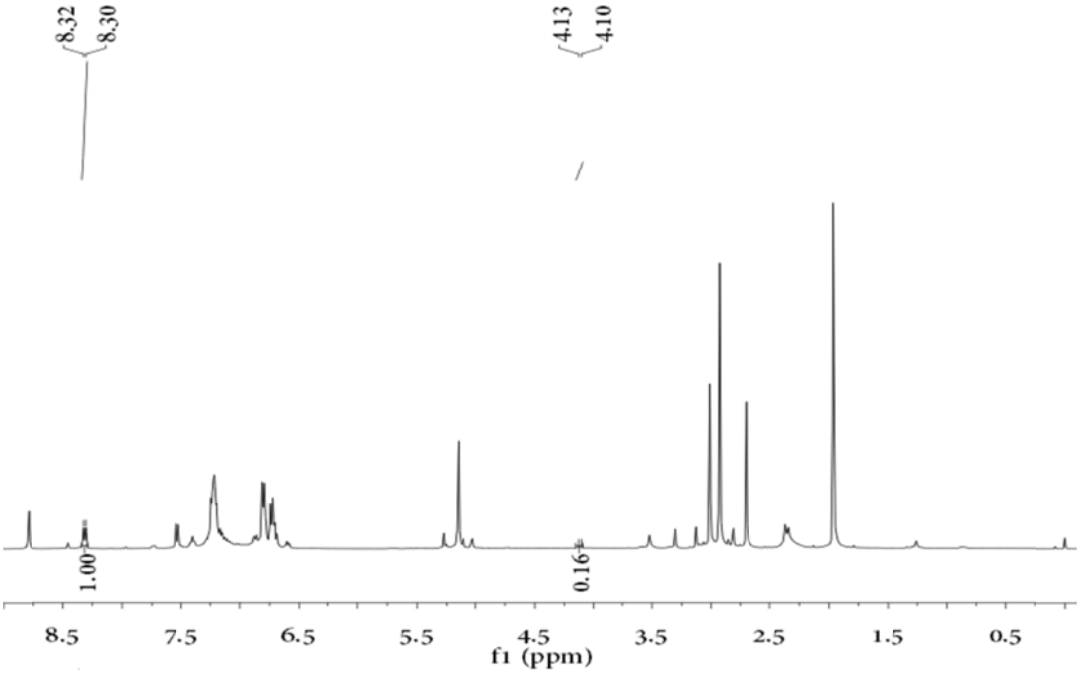


Fig. S13 ^{1}H NMR (Entry 9, Table 1).

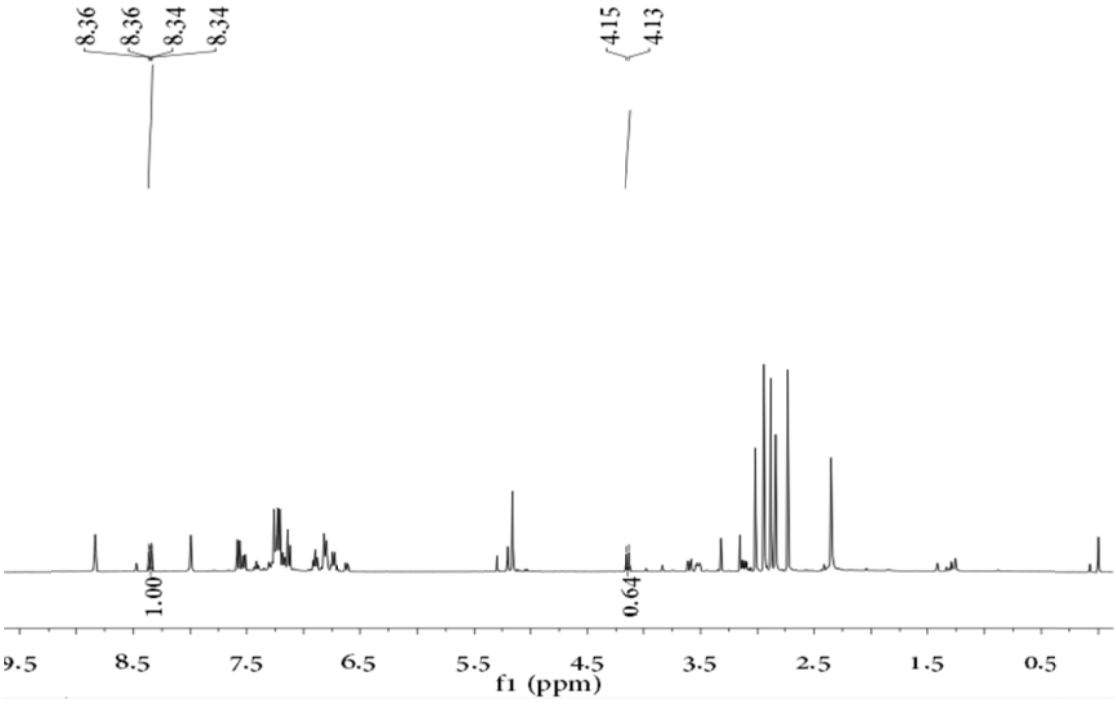


Fig. S14 ^{1}H NMR (Entry 1, Table S1).

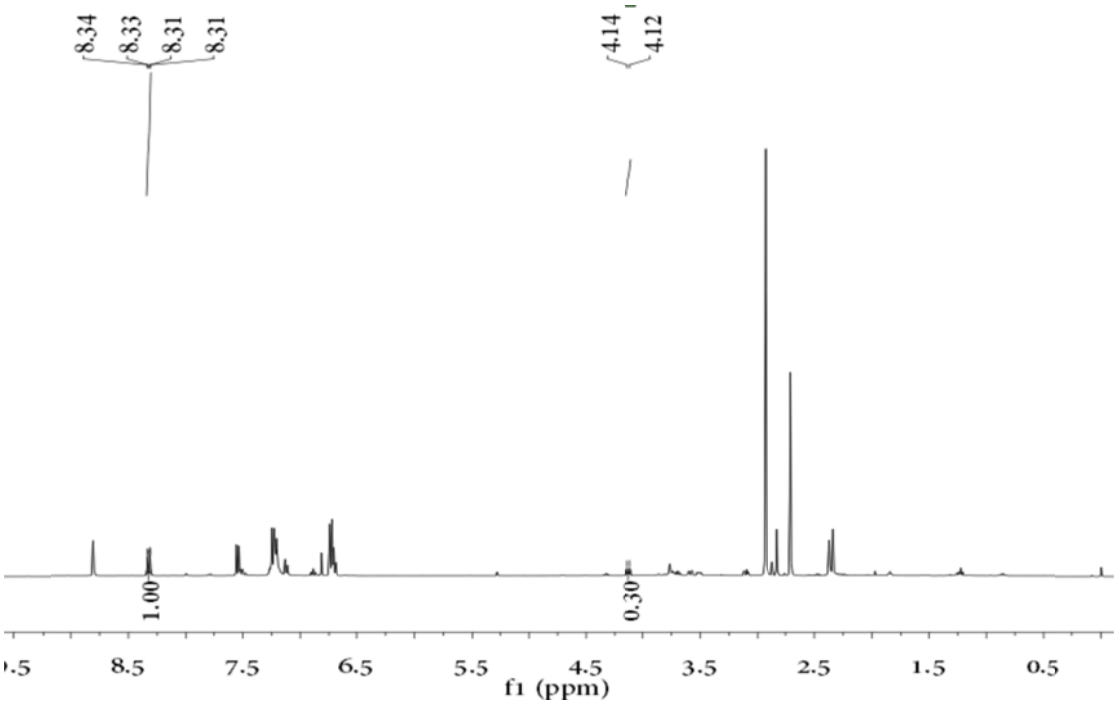


Fig. S15 ^{1}H NMR (Entry 2, Table S1).

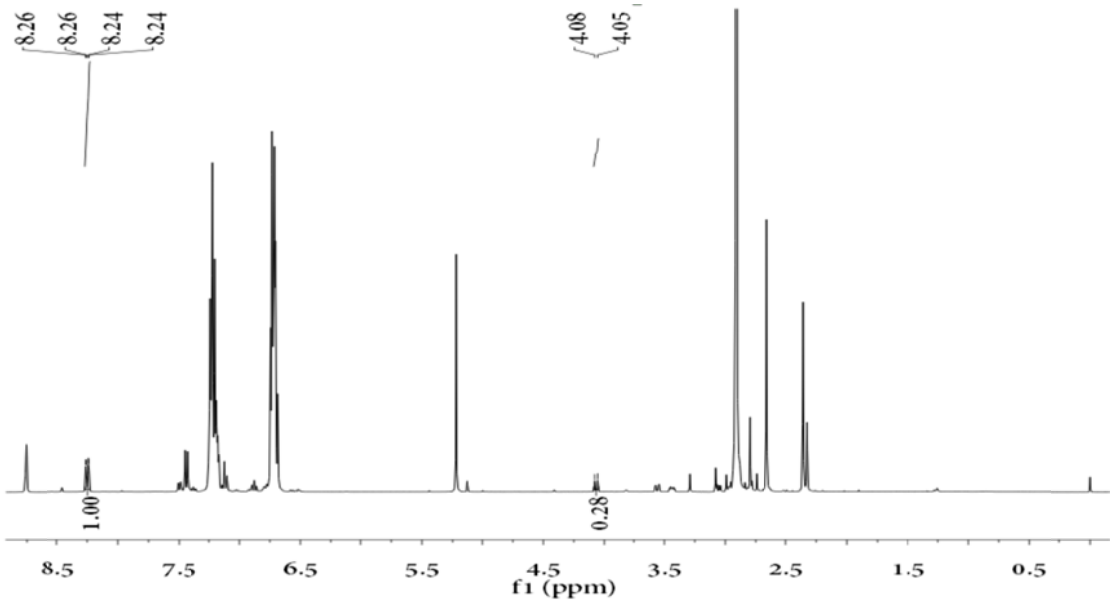


Fig. S16 ^{1}H NMR (Entry 3, Table S1).

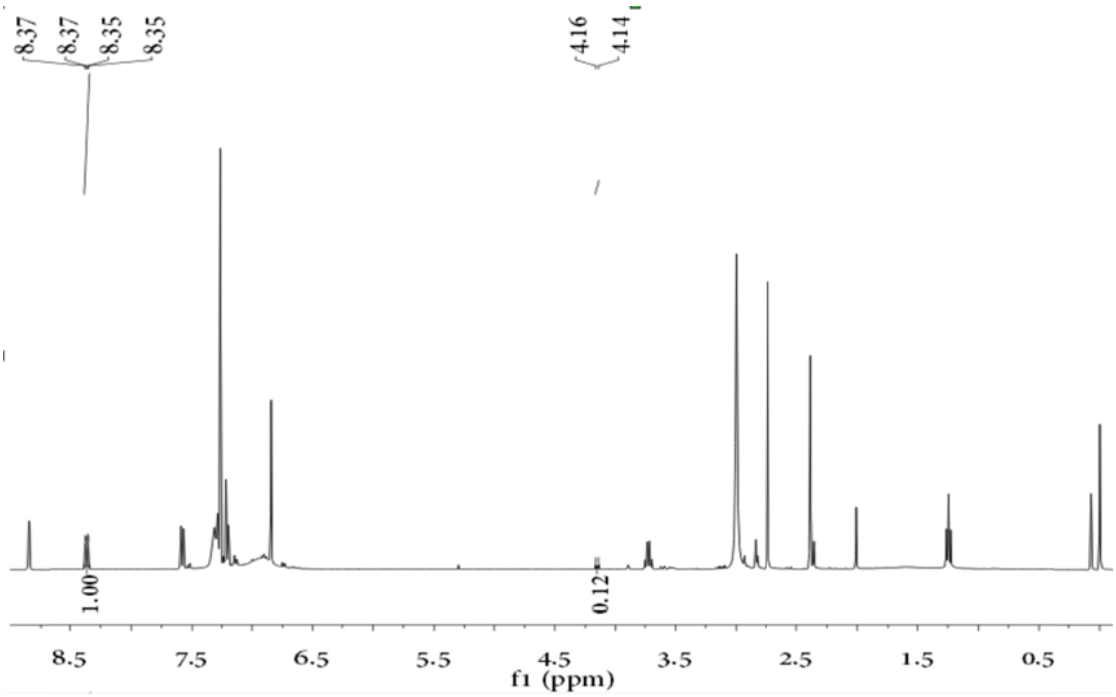


Fig. S17 ^{1}H NMR (Entry 4, Table S1).

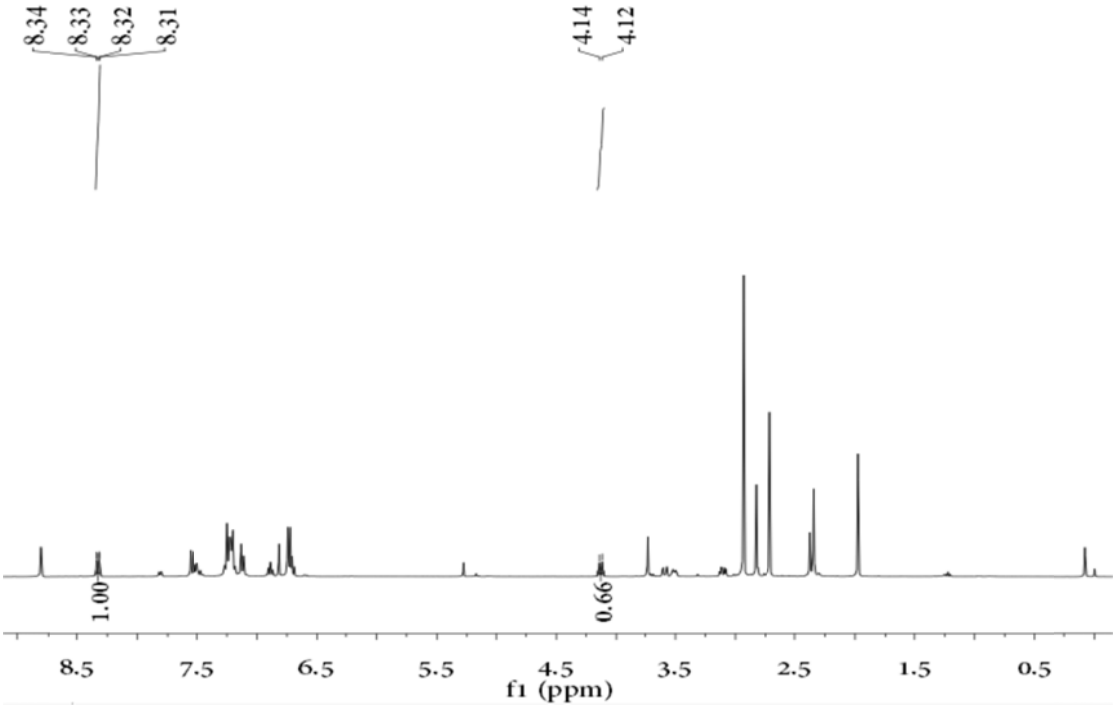


Fig. S18 ^{1}H NMR (Entry 5 , Table S1).

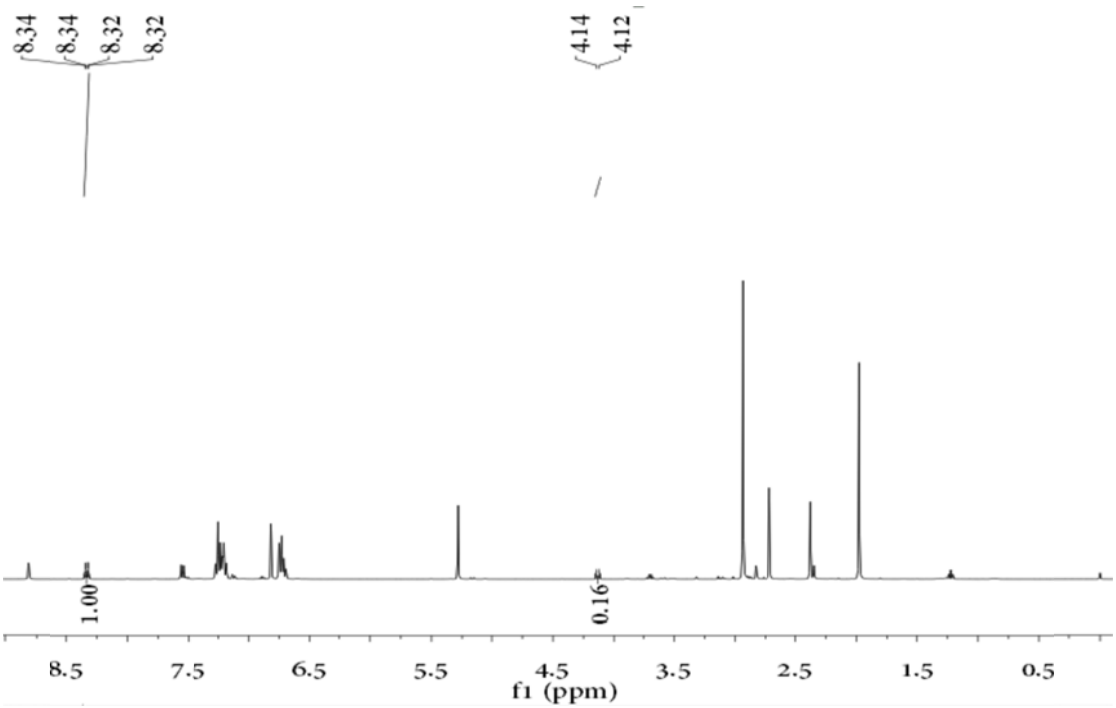


Fig. S19 ^{1}H NMR (Entry 6, Table S1).

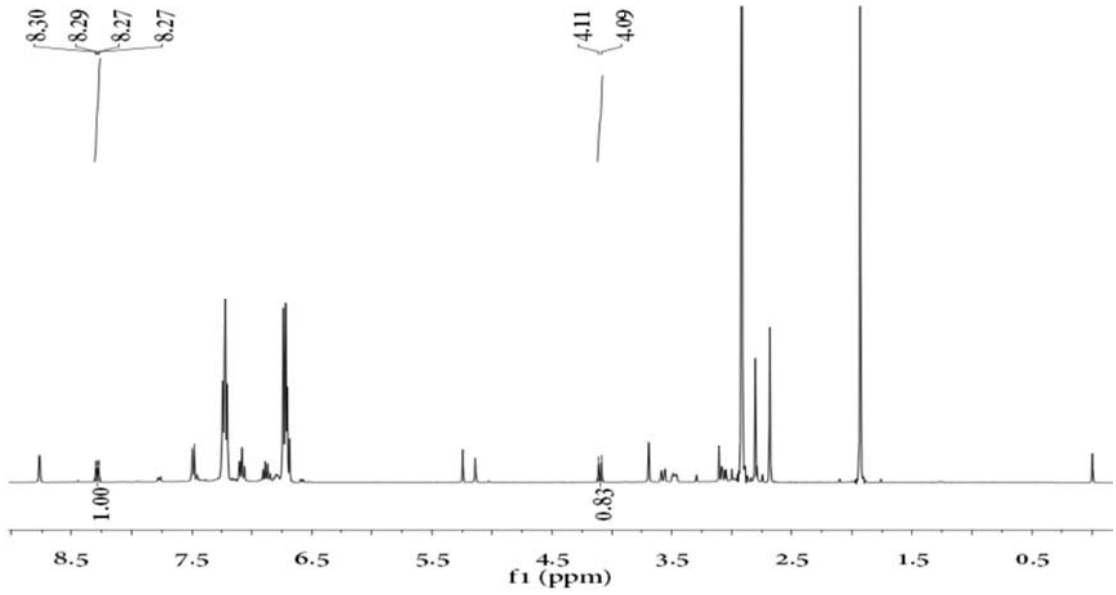


Fig. S20 ^{1}H NMR (3b, Table 2).

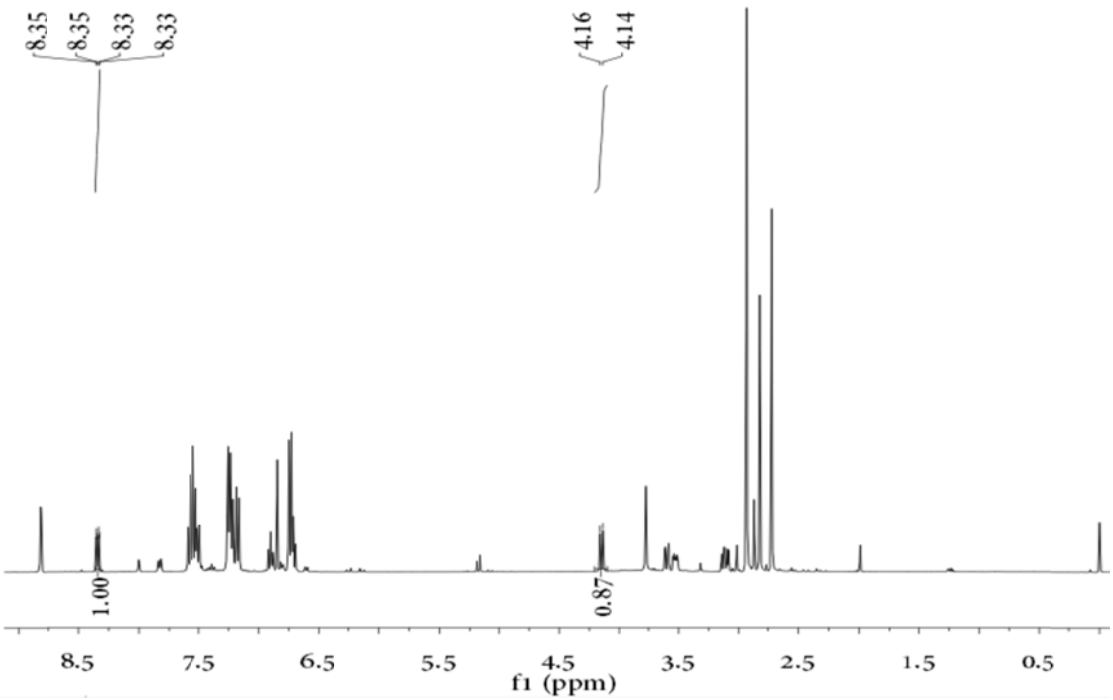


Fig. S21 ^{1}H NMR (3c, Table 2).

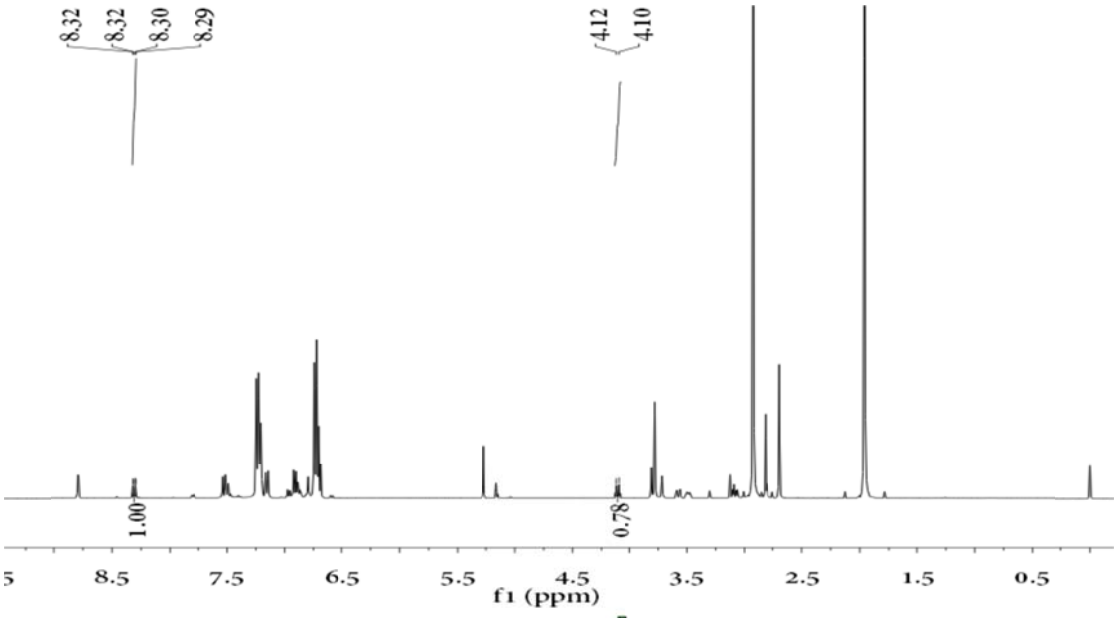


Fig. S22 ^{1}H NMR (3d, Table 2).

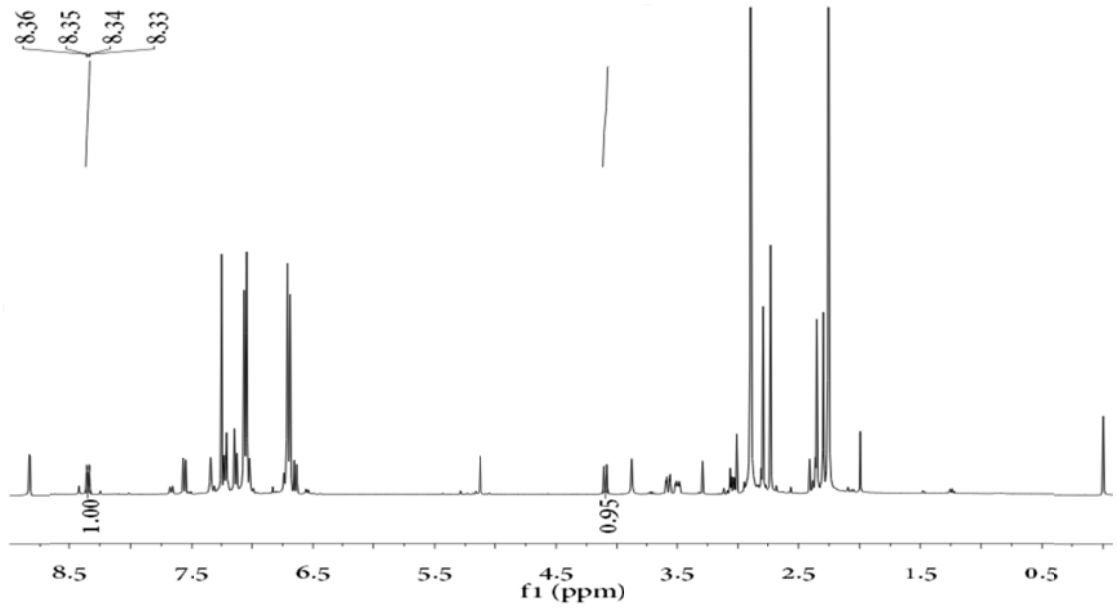


Fig. S23 ^{1}H NMR (3e, Table 2).

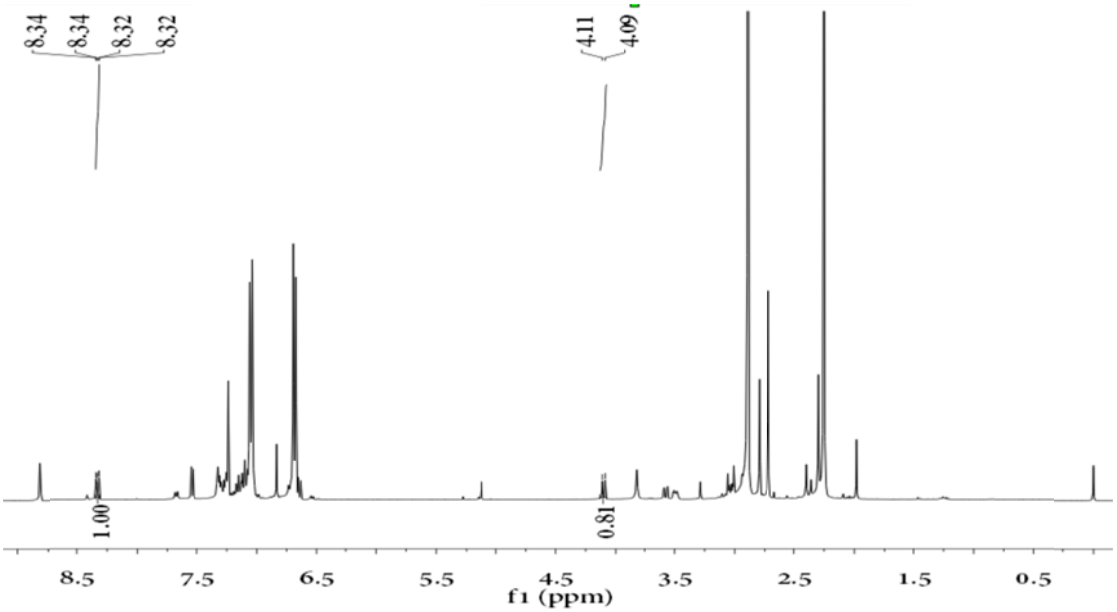


Fig. S24 ^{1}H NMR (3f, Table 2).

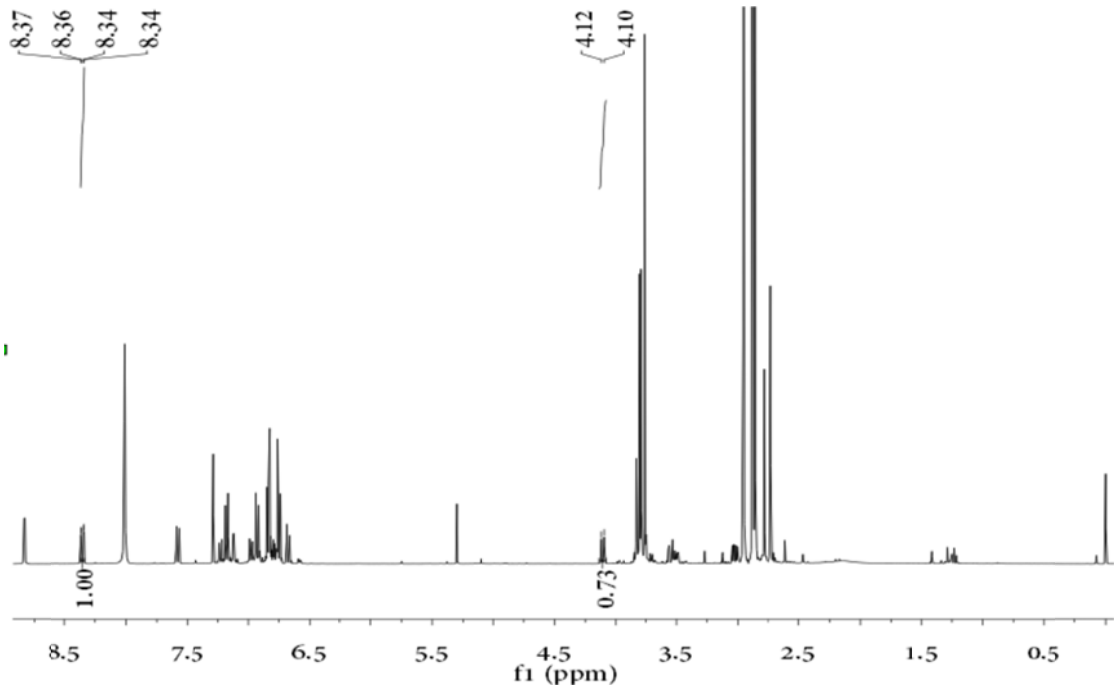


Fig. S25 ^{1}H NMR (3g, Table 2).

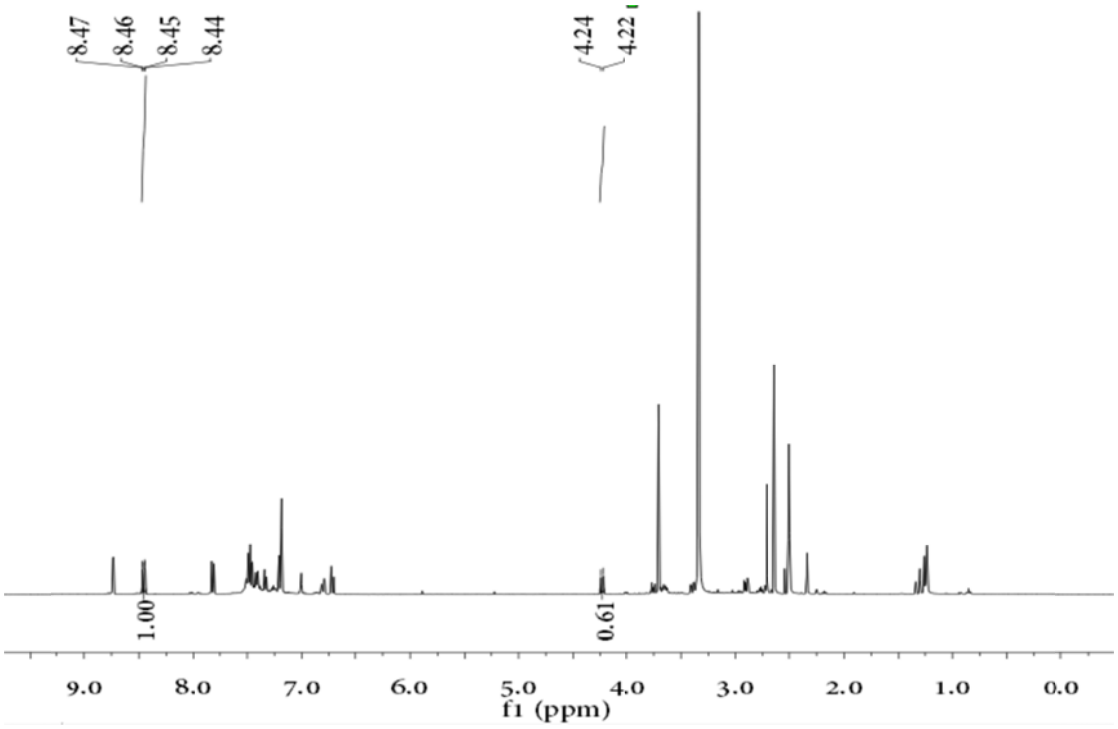


Fig. S26 ^{1}H NMR (3h, Table 2).

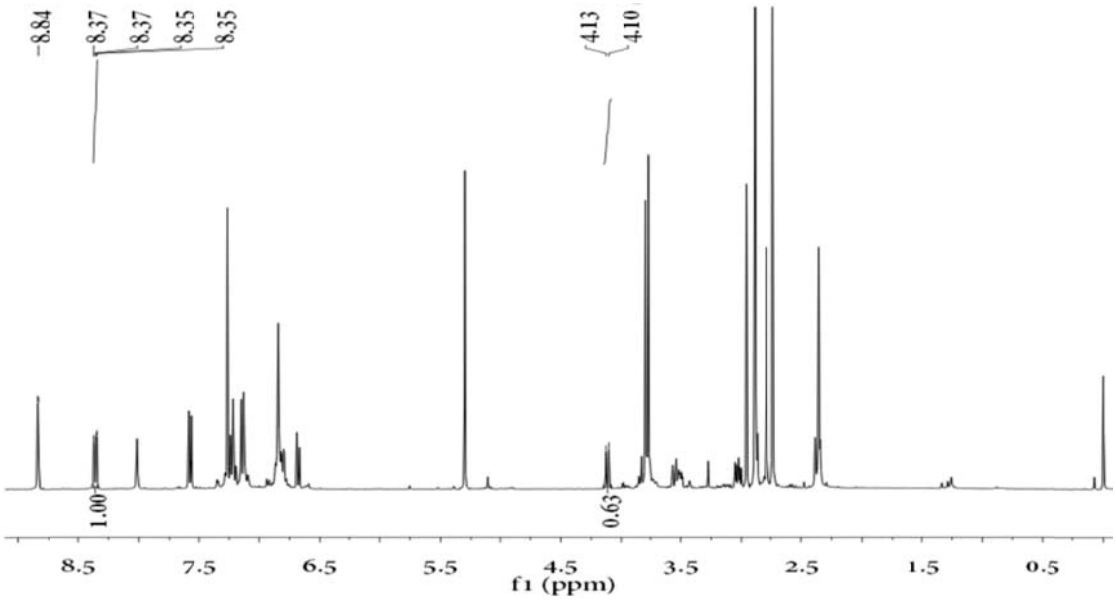


Fig. S27 ^{1}H NMR (3i, Table 2).

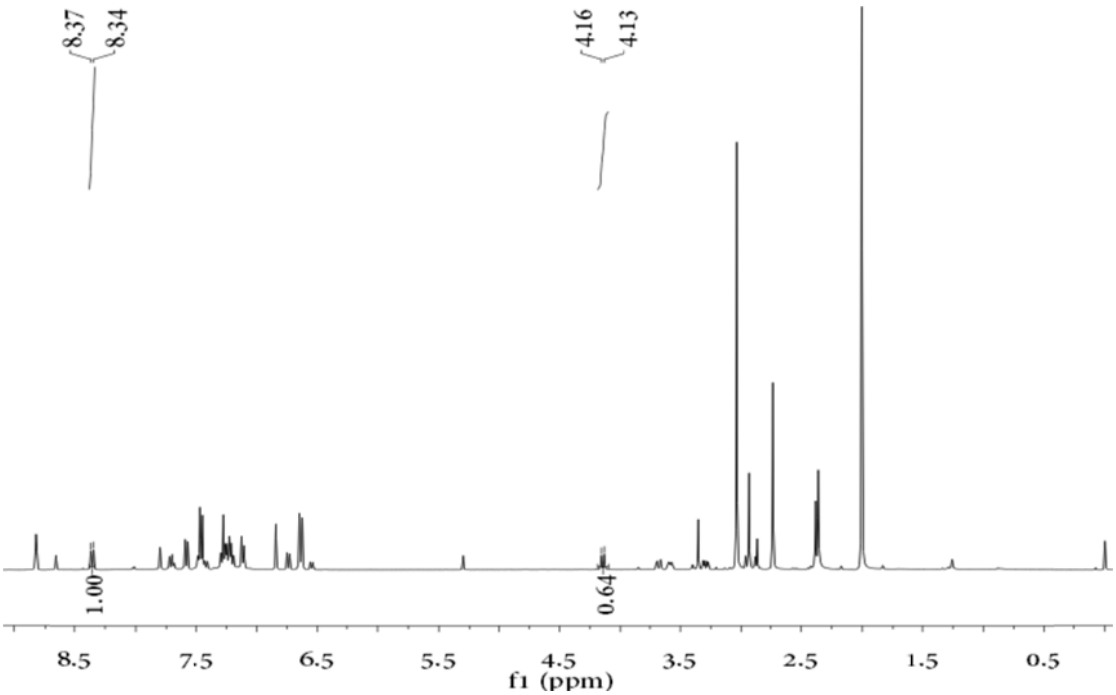


Fig. S28 ^{1}H NMR (3j, Table 2).

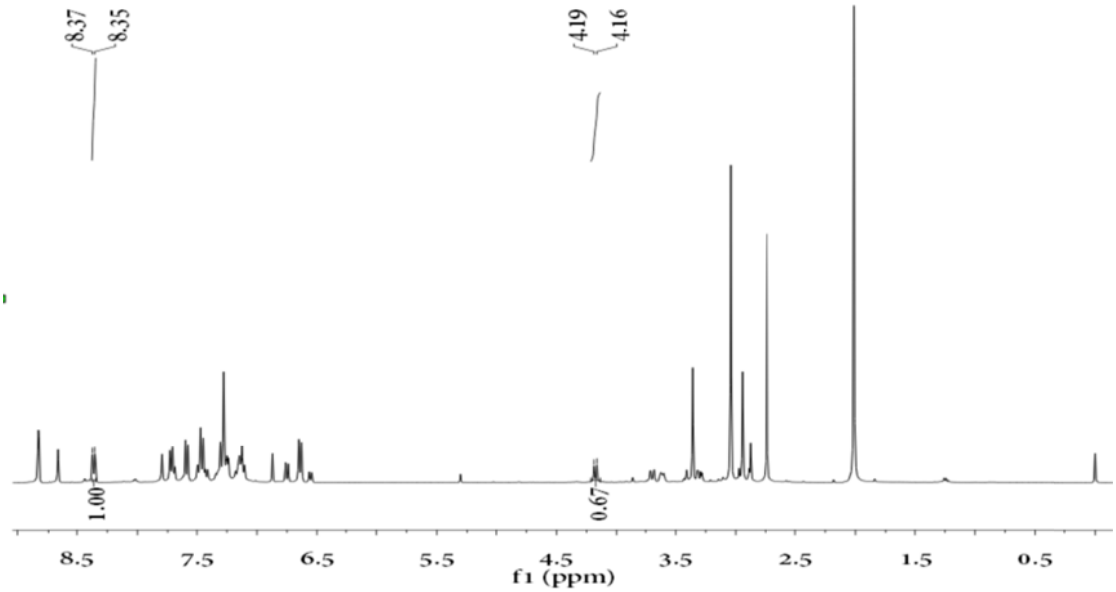


Fig. S29 ^{1}H NMR (3k, Table 2).

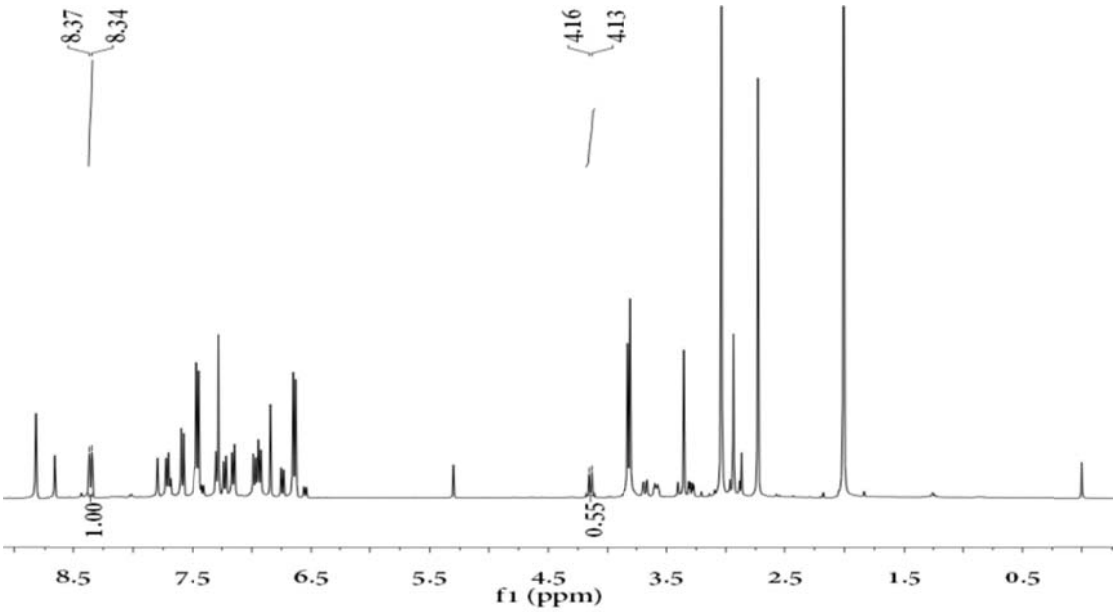


Fig. S30 ^{1}H NMR (3l, Table 2).

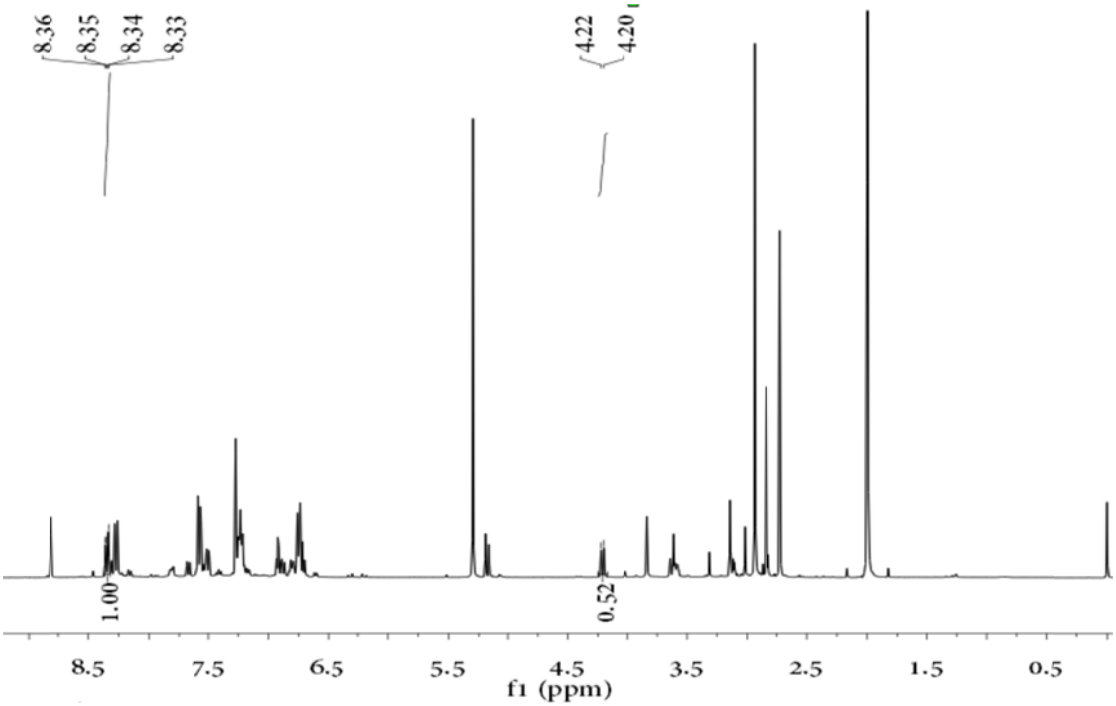


Fig. S31 ^{1}H NMR (3m, Table 2).

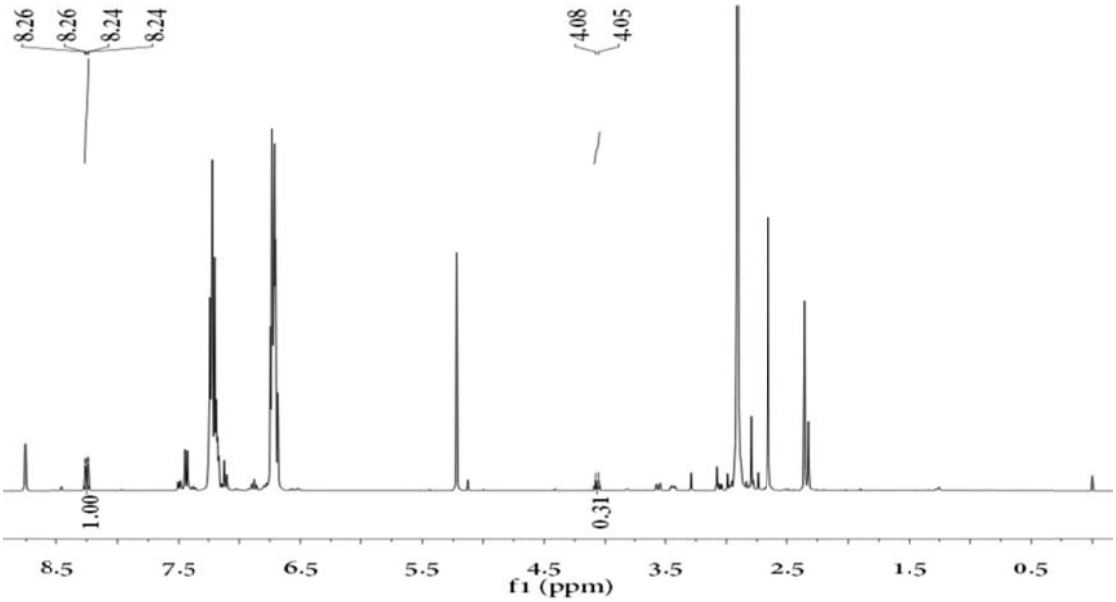


Fig. S32 ^{1}H NMR (3n, Table 2).

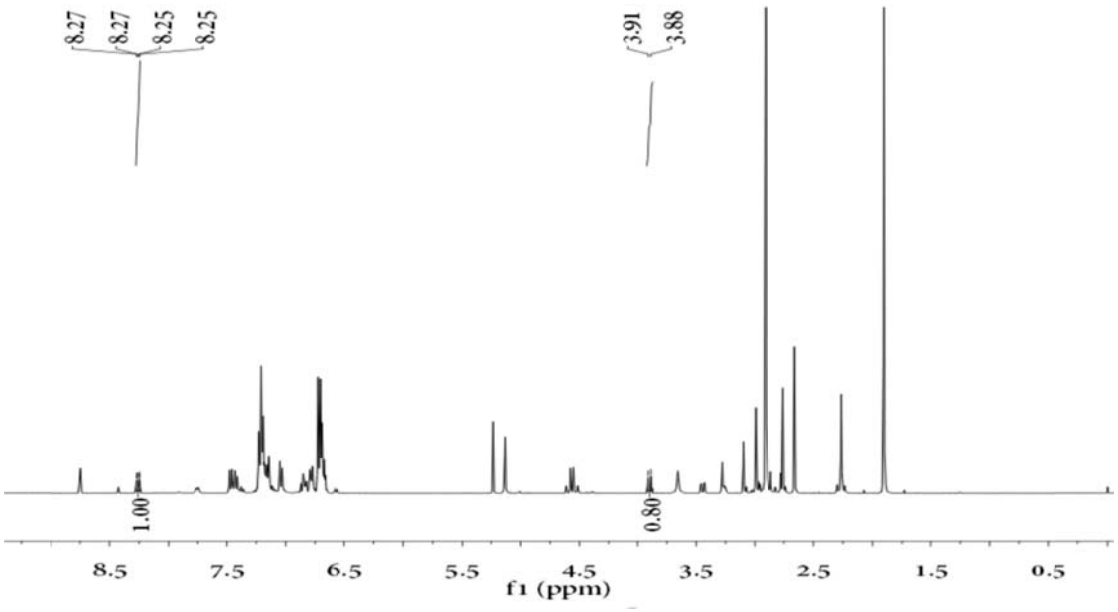


Fig. S33 ^{1}H NMR (3o, Table 2).

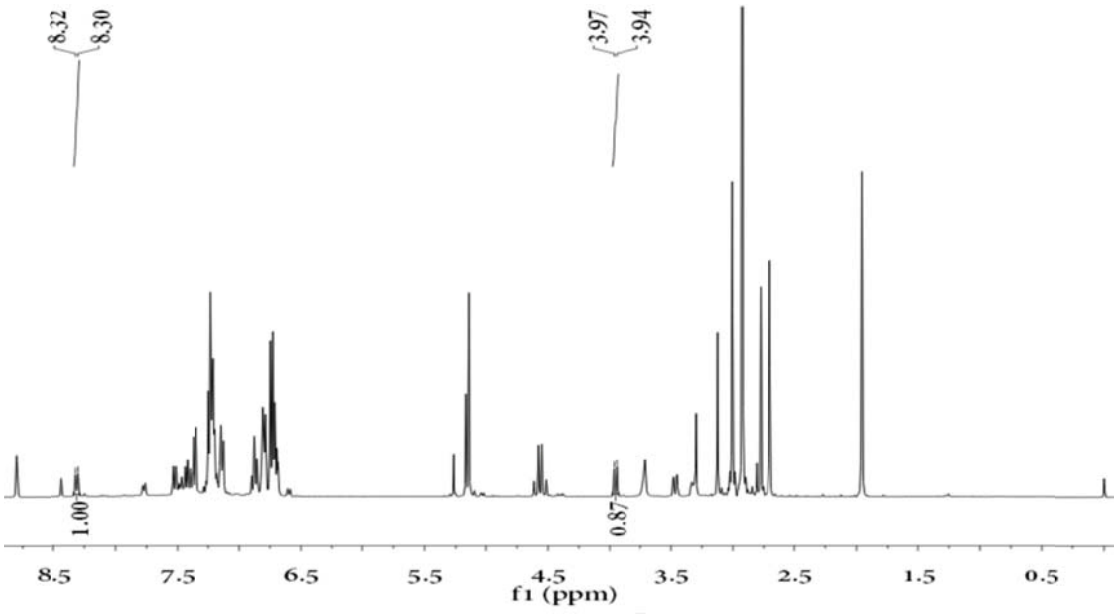


Fig. S34 ^{1}H NMR (3p, Table 2)