

Synthesis, Thermal and Optical Characterizations of New Lateral Organic Systems

Laila Ahmed Al-Mutabagani ¹, Latifah A. Alshabanah ¹, Sobhi M. Gomha ^{2,3} and Hoda A. Ahmed ^{2,4,*}

¹ Department of Chemistry, College of Science, Princess Nourah bint Abdulrahman University, Riyadh 11671, Saudi Arabia; laalmutbagani@pnu.edu.sa (L.A.A.-M.); Laalsabanah@pnu.edu.sa (L.A.A.)

² Department of Chemistry, Faculty of Science, Cairo University, Cairo 12613, Egypt; sm.gomha@iu.edu.sa

³ Chemistry Department, Faculty of Science, Islamic University in Almadinah Almonawara, Almadinah Almonawara, Medina 42351, Saudi Arabia

⁴ Chemistry Department, College of Sciences, Yanbu, Taibah University, Yanbu 30799, Saudi Arabia

* Correspondence: ahoda@sci.cu.edu.eg

1. Materials

4-Hexyloxybenzoic acid, 4-octyloxybenzoic acid, 4-decyloxybenzoic acid, 4-dodecyloxybenzoic acid, 4-hexadecyloxybenzoic, vaniline, and 4-hexyloxyaniline, were purchased from Sigma Aldrich (Germany). Dichloromethane, *N,N'*-dicyclohexylcarbodiimide (DCC), ethanol and 4-dimethylaminopyridine (DMAP) were purchased from Aldrich (Wisconsin, USA).

2. Synthesis of 4-((4-(hexyloxyphenyl)iminomethyl)-3-methoxyphenol (3)

A mixture of 4-hydroxy-2-methoxybenzaldehyde (1.52 g, 10 mmol) and 4-(hexyloxy)aniline (1.93 g, 10 mmol) in ethanol (20 mL) were refluxed for two hours (monitored by Thin Layer Chromatography ;TLC). The mixture was cooled to room temperature and filtered. The obtained solid was washed with cold ethanol and recrystallized twice from hot ethanol to give pure imine compound **3**, as indicated by TLC analysis.

3. General procedure for synthesis of 4-((4-(hexyloxyphenyl)iminomethyl)-3-methoxyphenyl 4-alkoxybenzoates, In

A mixture of imine compound **3** (1.93g, 10 mmol) and the appropriate 4-substituted benzoic acid derivatives (10 mmol for each) in dry methylene chloride (25 mL), containing *N,N'*-dicyclohexylcarbodiimide (DCC, 10 mmol) and a few crystals of 4-dimethylaminopyridine (DMAP) as a catalyst, were left to stand for 72 h at room temperature with continuous stirring. The solid separated was then filtered off and the solution evaporated. The solid residue obtained was recrystallized from ethanol to give TLC pure products. The purity of the prepared samples was checked with thin-layer chromatography (TLC) using TLC sheets coated with silica gel (E Merck), and CH₂Cl₂/CH₃OH (9:1) as eluent, whereby only one spot was detected by a UV-lamp.

Infrared spectra (IR), ¹H-NMR, and elemental analyses for compounds investigated were consistent with the structures assigned. ¹H-NMR data showed the expected integrated aliphatic to aromatic proton ratios in all compounds investigated.

4. Characterization

A Perkin-Elmer B25 (Perkin-Elmer, Inc., Shelton, CT, USA) spectrophotometer was used for infrared spectra measurements. NMR spectra were acquired on a Bruker Avance 400 instrument at 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR with tetramethyl silane as internal standard in CDCl₃; the chemical shift values recorded as δ (ppm units) and coupling constants as J (Hz units) (JEOL, Tokyo, Japan). A Thermo Scientific Flash 2000 CHS/O Elemental Analyzer (Milan, Italy) was used for elemental analyses.

The spectrophotometer (UV-1800, Shimadzu, Japan) was used for UV-vis measurements of a wavelength ranging from 200–800 nm at 25 °C for all compounds.

TA Instruments Inc. (Q20 Differential Scanning Calorimeter, DSC, USA) was used for recording phase transitions. DSC calibration was carried out using lead and indium melting temperature and enthalpy. Samples of 2–3 mg were used in aluminum pans for DSC investigation. The heating rate was 10 °C/min in nitrogen gas as an inert atmosphere (30 ml/min). All transitions measured from the second heating scan.

Transition temperatures for the prepared compounds were checked and phases identified by polarized optical microscope (POM, Wild, Germany) attached with Mettler FP82HT hot stage.

Thermogravimetric analysis (TGA) was carried out using a Shimadzu TGA-50H Thermal Analyzer under nitrogen at a heating rate of 10 °C/min. The experiments were conducted from room temperature up to 600 °C and the reference material was α -alumina. The sample weights for all the experiments were taken in the range of 3–4 mg.

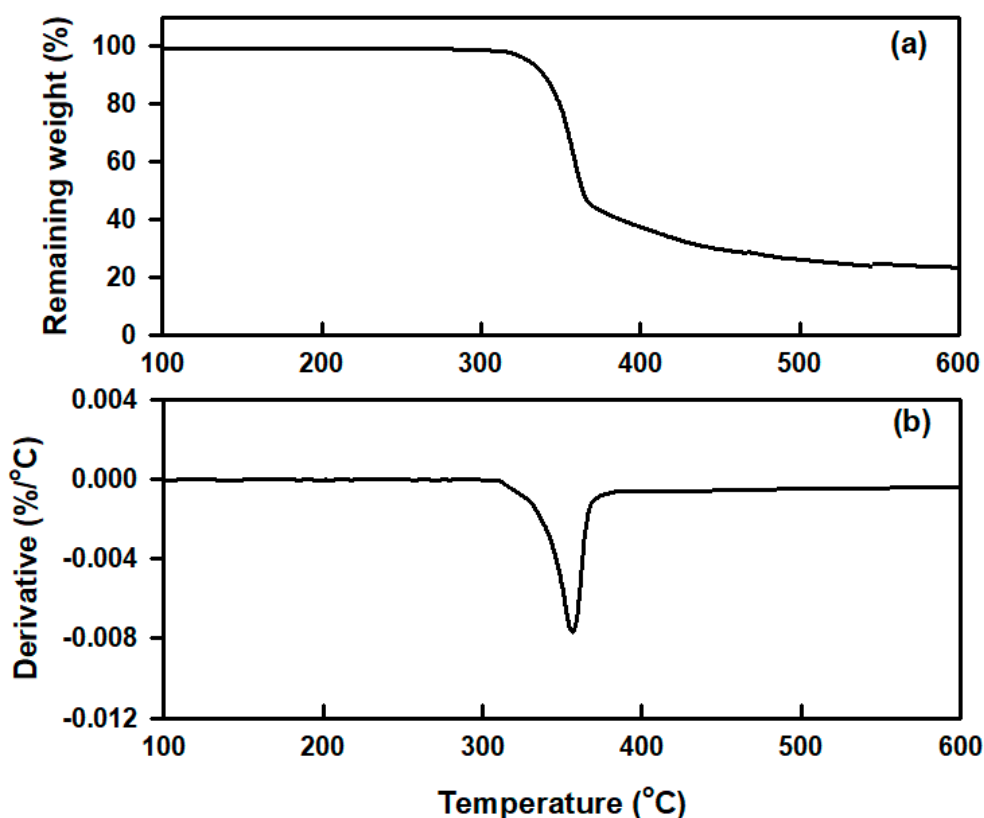


Figure S1. TG (a) and DTG (b) curves of the compound I8.

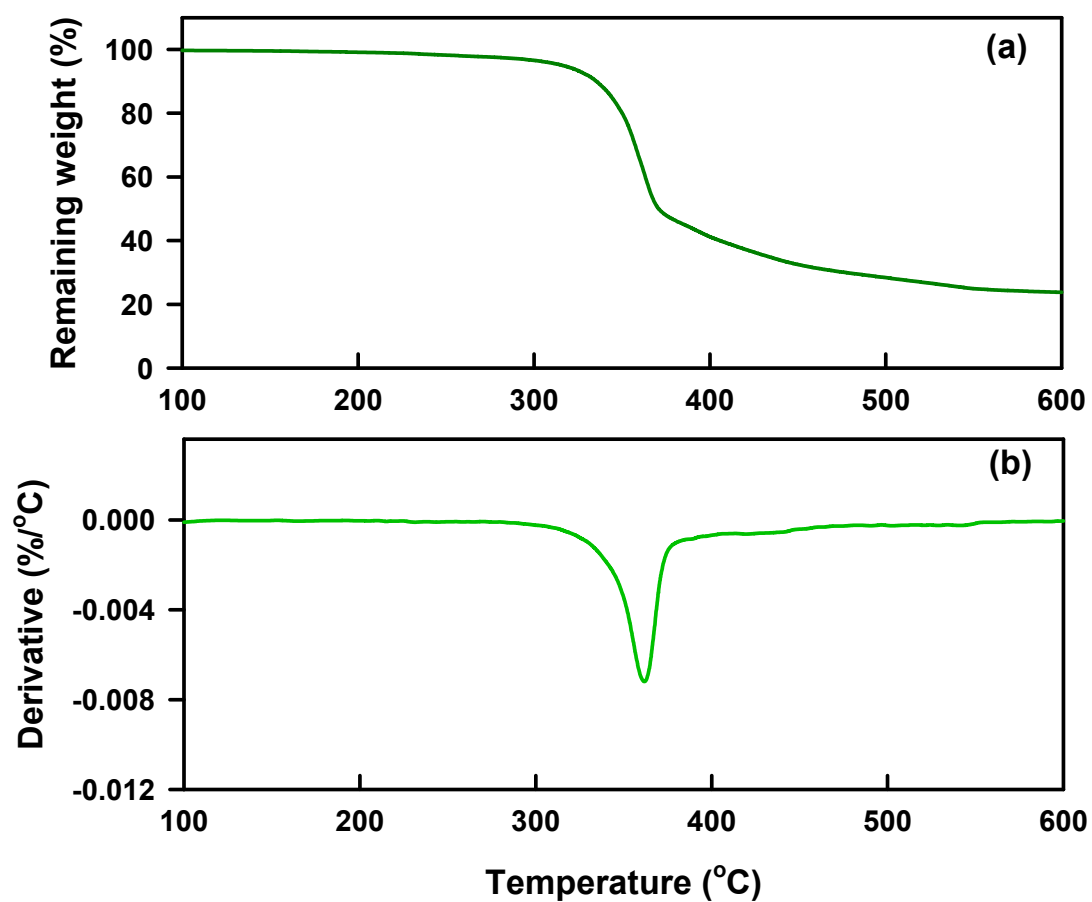


Figure S2. TG (a) and DTG (b) curves of the compound I10.

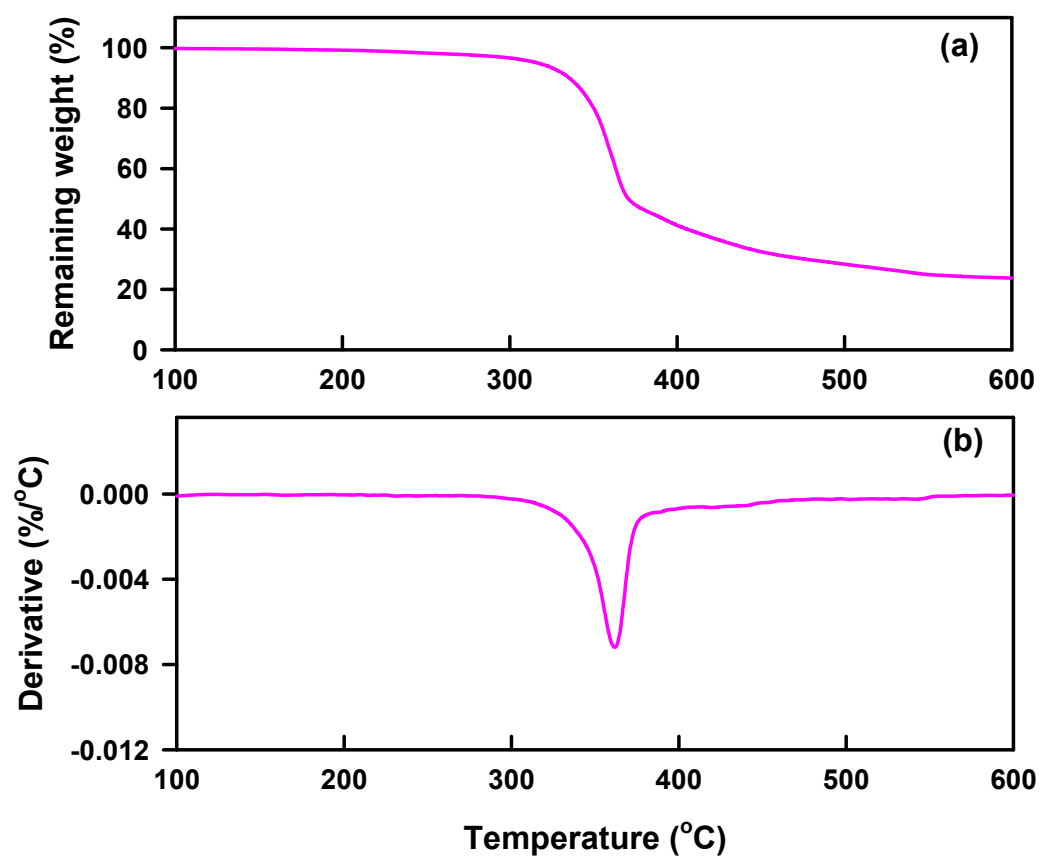


Figure S3. TG (a) and DTG (b) curves of the compound I12.

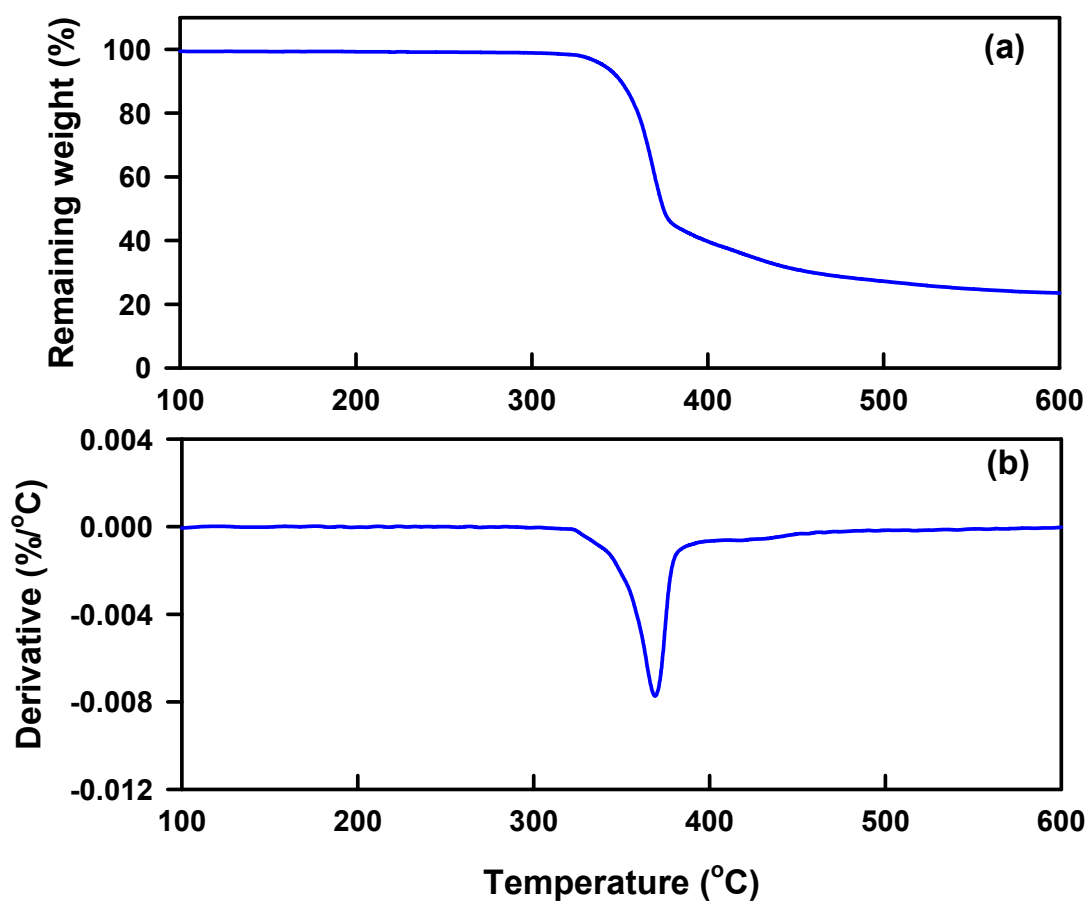


Figure S4. TG (a) and DTG (b) curves of the compound I16.

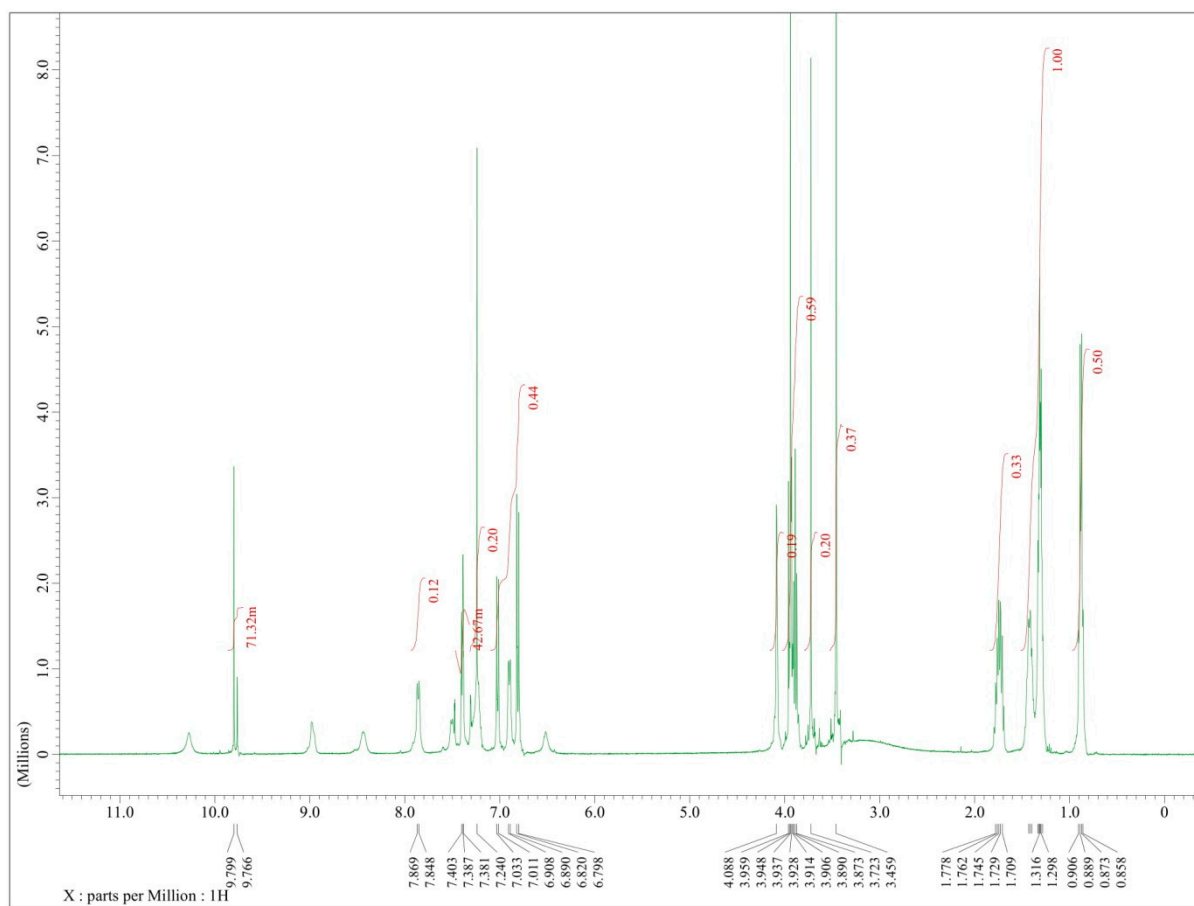


Figure S5. ^1H -NMR spectra of compound 3.

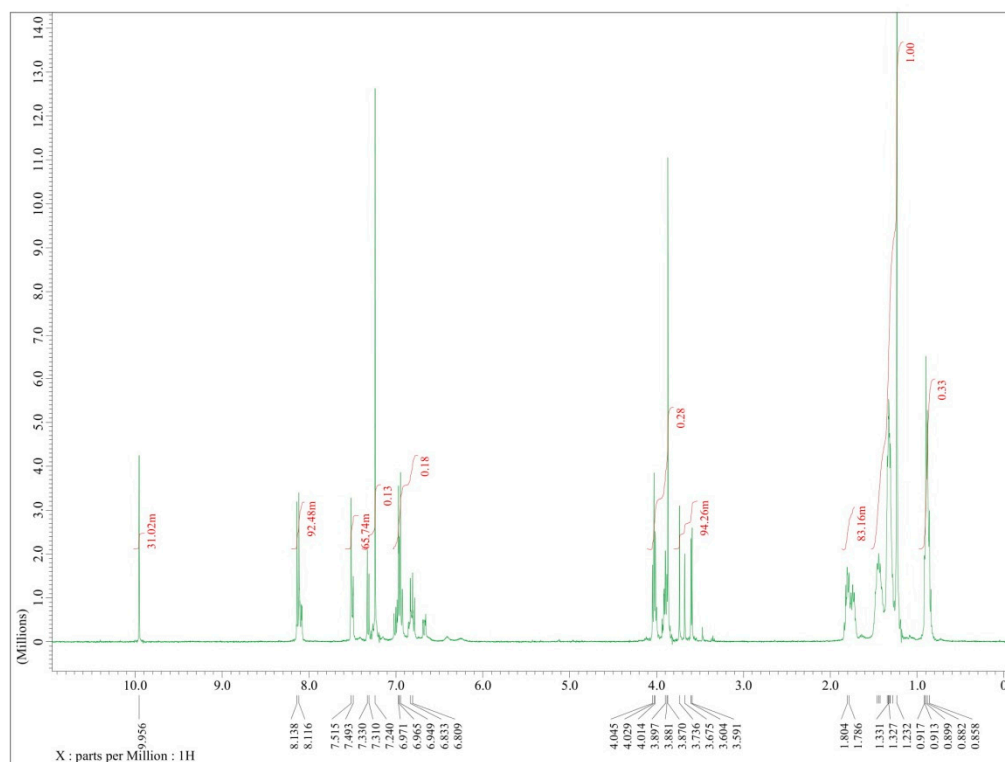


Figure S6. ¹H-NMR spectra of compound I6.

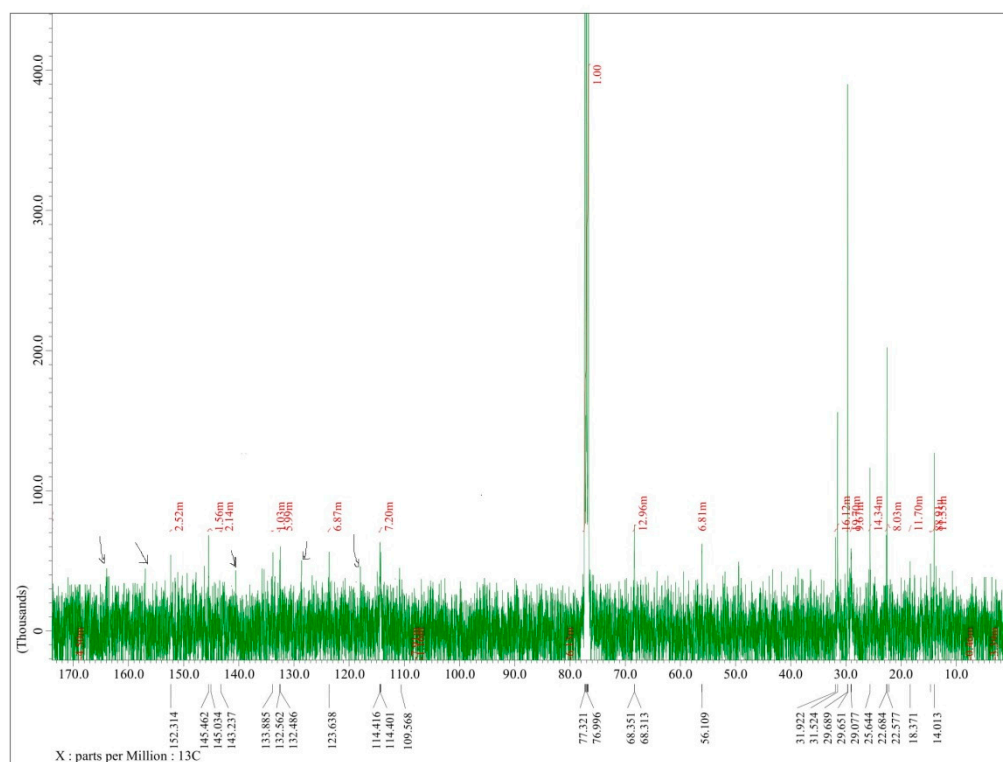


Figure S7. ¹³C-NMR spectra of compound I6.

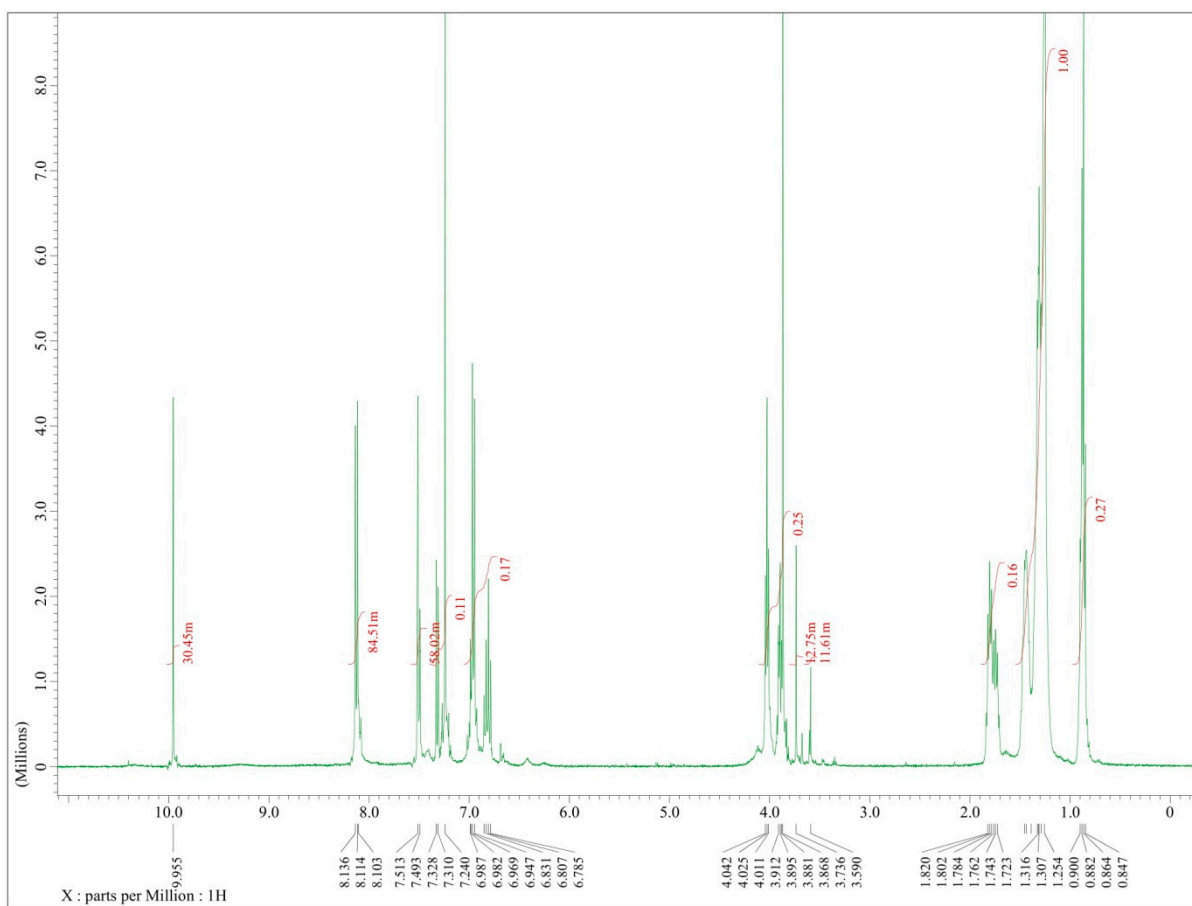


Figure S8. ^1H -NMR spectra of compound I10.

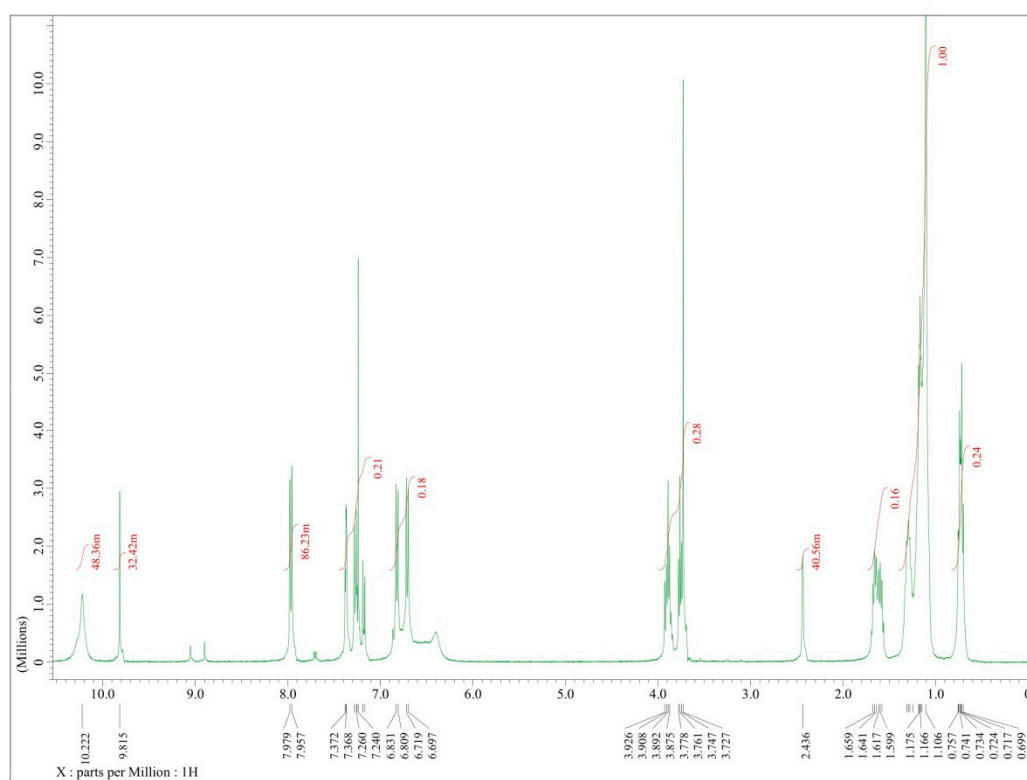


Figure S9. ^1H -NMR spectra of compound I12.

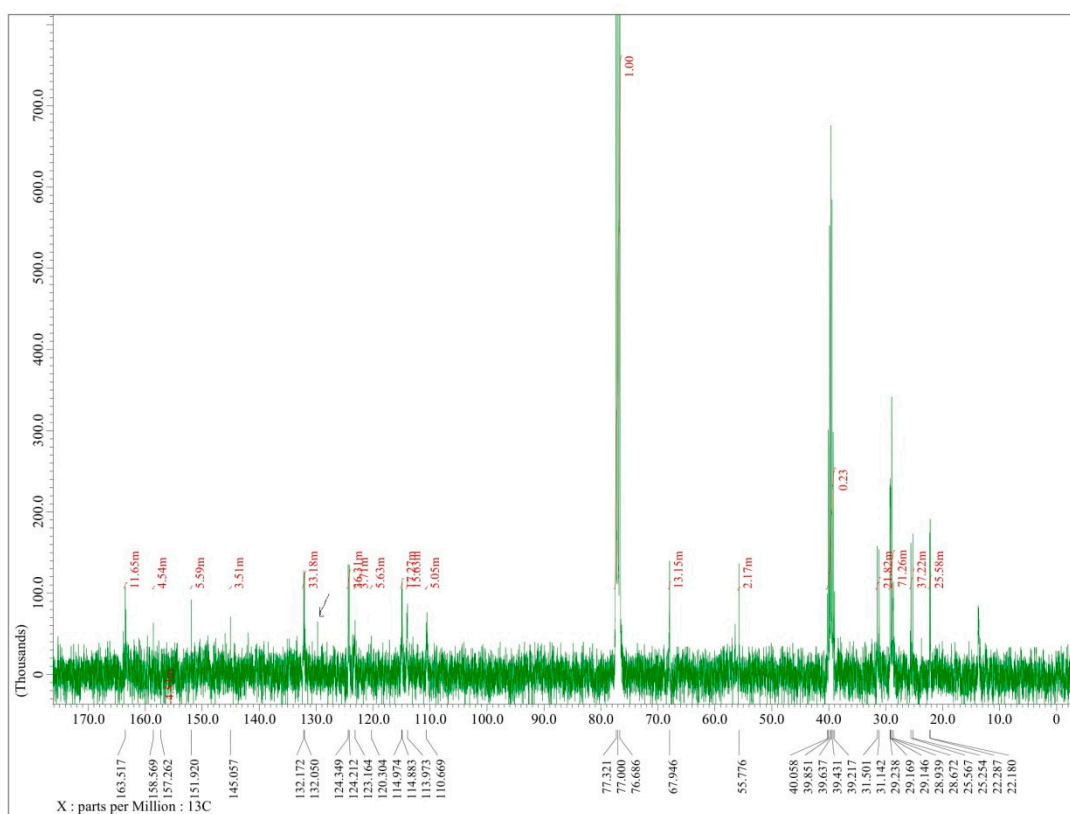


Figure S10. ^{13}C -NMR spectra of compound I12.

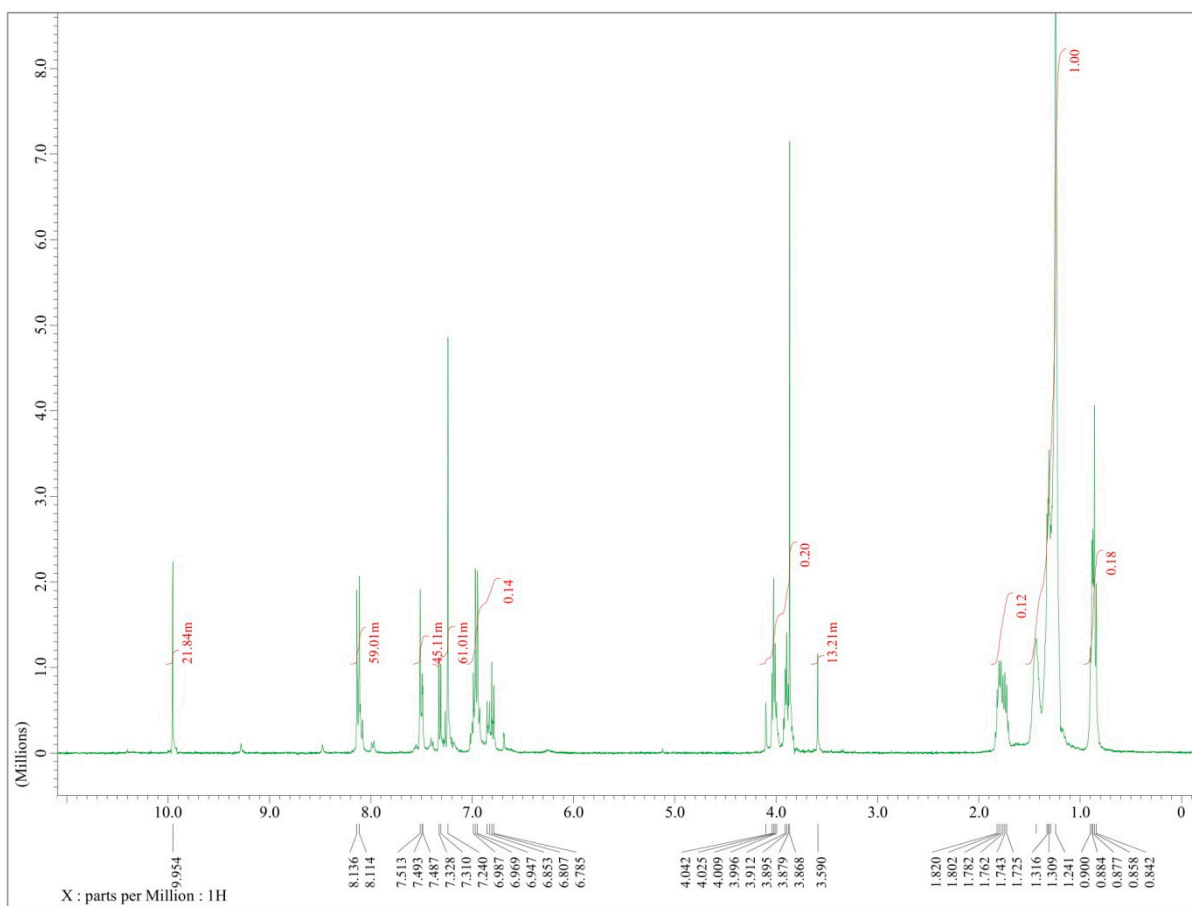


Figure S11. ^1H -NMR spectra of compound **I16**.