

Supplementary material

Mesomorphic, Optical and DFT Aspects of Near to Room Temperature Calamitic Liquid Crystal

Ayman A. Zaki ^{1,2}, Mohamed Hagar ^{3,4,*}, Rua B. Alnoman ³, Mariusz Jaremko ⁵, Abdul-Hamid Emwas ⁶ and Hoda A. Ahmed ^{7,*}

¹ Physics Department, College of Sciences, Yanbu, Taibah University, Yanbu 30799, Saudi Arabia; aismail@taibahu.edu.sa

² Physics Department, Faculty of Sciences, Banha University, Banha 13511, Egypt

³ Chemistry Department, College of Sciences, Taibah University, Yanbu 30799, Saudi Arabia; mhagar@taibahu.edu.sa (M.H.), rua-b-n@live.co.uk (R.B.A.),

⁴ Faculty of Science, Chemistry Department, Alexandria University, Alexandria 21321, Egypt

⁵ Biological and Environmental Sciences & Engineering Division (BESE), King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia; Mariusz.jaremko@kaust.edu.sa

⁶ Core Labs., King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia; abdelhamid.emwas@kaust.edu.sa

⁷ Department of Chemistry, Faculty of Science, Cairo University, Cairo 12613, Egypt;

* Correspondence: mohamedhagar@gmail.com (M.H.), ahoda@sci.cu.edu.eg (H.A.A.)

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Materials

4-methoxyaniline, oleic acid, and 4-hydroxybenzaldehyde were obtained from Sigma-Aldrich (Hamburg, Germany). *N,N'*-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), dichloromethane ethanol and methanol were purchased from Aldrich (Wisconsin, USA). All chemicals were used without further purification.

Characterization of synthesized compound

The purity of the prepared samples was checked with TLC (Thin Layer Chromatography) sheets coated with silica gel (Sigma, Homburg)

Infrared spectra were measured using Perkin-Elmer B25 (Perkin-Elmer, Inc., Shelton, CT USA) spectrophotometer. ¹HNMR spectra were recorded using a Varian EM 350L 300 MHz spectrometer (Oxford, UK) using tetramethylsilane as internal standard and CDCl₃ as solvent; the chemical shift values recorded as δ (ppm units).

Elemental analyses for final products were carried out on Thermo Scientific Flash 2000 CHS/O Elemental Analyzer, Milan, Italy.

Calorimetric measurements were carried out using a TA Instruments Co. Q20 Differential Scanning Calorimeter (DSC; USA). The DSC was calibrated using the melting temperature and enthalpy of indium and lead. DSC investigation was carried out for small samples (2–3 mg) placed in aluminum pans. All measurements were achieved at a heating rate of 10 °C/min in inert atmosphere of nitrogen gas (30 mL/min) and all transition recorded from the second heating scan.

Transition temperatures were checked and types of mesophases identified, for all compounds prepared and their binary mixtures, with a standard polarized light microscope (PLM, Wild, Germany) attached with Mettler FP82HT hot stage.

NMR measurements

The NMR have been recoded for compound **I** that was prepared by dissolving in 600 μL of deuterated solvents DMSO- d_6 inside a 3mL glass vial, then vigorously vortexed until completely dissolved. Then, 500 μL was transferred to 5 mm NMR tubes. A Bruker 600 NMR spectrometer (Bruker BioSpin, Rheinstetten, Germany) operating at 600.13 MHz for proton equipped with a triple resonance probe was used to record all NMR spectra. The ^1H NMR spectrum was recorded by collecting 64 scans with a recycle delay time of 10 s, using one pulse sequence through a standard (zg) program from the Bruker pulse library. The ^{13}C NMR spectra were recoded using the reported methods and parameters [1]. Chemical shifts were corrected using the TMS signal at 0.0 pp as an internal chemical shift reference for both ^{13}C and ^1H NMR spectra. Bruker Topspin 3.5pl7 software (Bruker BioSpin, Rheinstetten, Germany) was used to collect and analysis the data.

Computational Method

Gaussian 09 software was used for DFT calculations for the studied compounds [2]. DFT/B3LYP methods using 6-31G (d,p) basis set was selected for the calculations. The geometries were optimized by minimizing the energies with respect to all geometrical parameters without imposing any molecular symmetry constraints. The structures of the optimized geometries had been drawn with Gauss View [3]. Moreover, calculations frequencies were carried out by the same level of theory. The frequency calculations showed that all structures were stationary points in the geometry optimization method with non-imaginary frequencies.

Table S1. H-1NMR chemical shifts.

Temperature	305	310	315	320	325	335	345	355	365
CH3	0.87	0.88	0.89	0.89	0.9	0.9	0.91	0.92	0.93
CH2	1.33	1.29	1.29	1.3	1.3	1.31	1.31	1.32	1.33
CH2	1.34	1.34	1.35	1.35	1.36	1.41	1.55	1.59	1.59
CH2	1.75	1.75	1.75	1.75	1.77	1.77	1.77	1.79	1.79
CH2	2.55	2.55	2.56	2.03	2.04	2.05	2.05	2.06	2.07
CH2O	3.87	3.87	3.88	3.88	3.88	3.88	3.89	3.9	3.9
OCH3	5.36	5.36	5.36	5.36	5.38	5.38	5.38	5.4	5.4
2CH=	5.98	5.98	5.98	5.98	5.98	5.98	5.98	5.98	5.98
CH Ar	6.99	6.99	7	7	7	7	7.01	7.01	7.01
CH Ar	7.09	7.09	7.1	7.1	7.1	7.11	7.11	7.12	7.12
CH Ar	7.2	7.2	7.2	7.2	7.2	7.2	7.2	7.2	7.2
CH Ar	7.85	7.85	7.86	7.86	7.86	7.86	7.86	7.87	7.87
CH=N <i>E</i> isomer	8.37	8.37	8.38	8.38	8.38	8.39	8.39	8.4	8.4
CH=N <i>Z</i> isomer	-	-	-	-	-	-	9.9	9.9	9.9

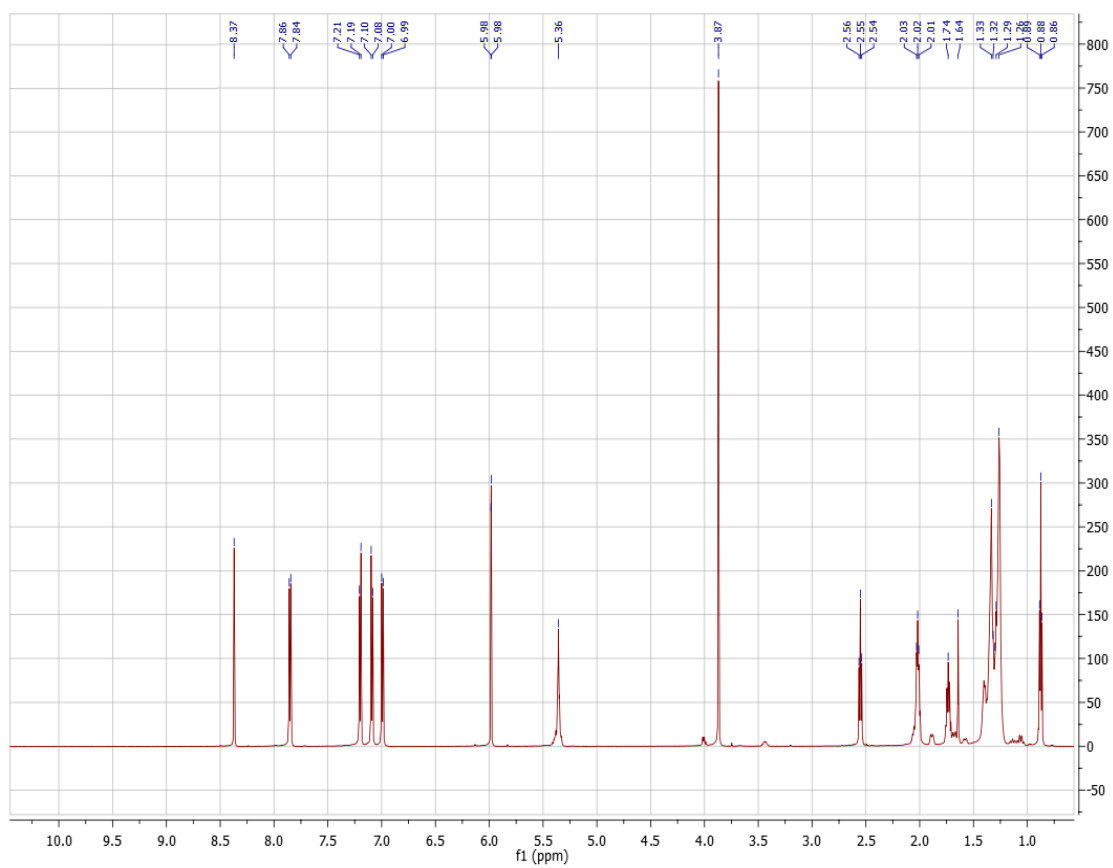


Figure S1. ^1H -NMR of (4-methoxybenzylideneamino)phenyl oleate at 305 K.

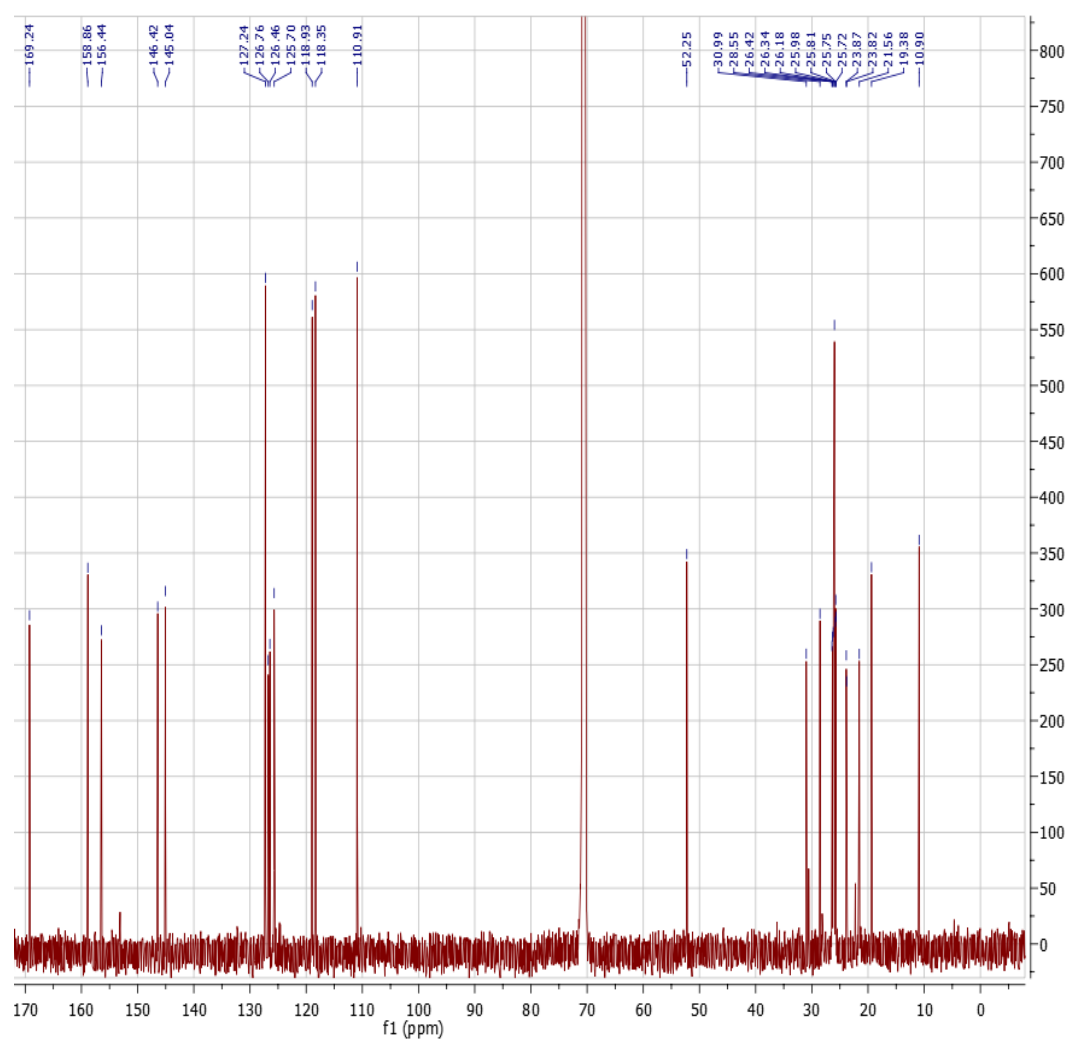


Figure S2. ^{13}C -NMR of (4-methoxybenzylideneamino)phenyl oleate at 305 K.

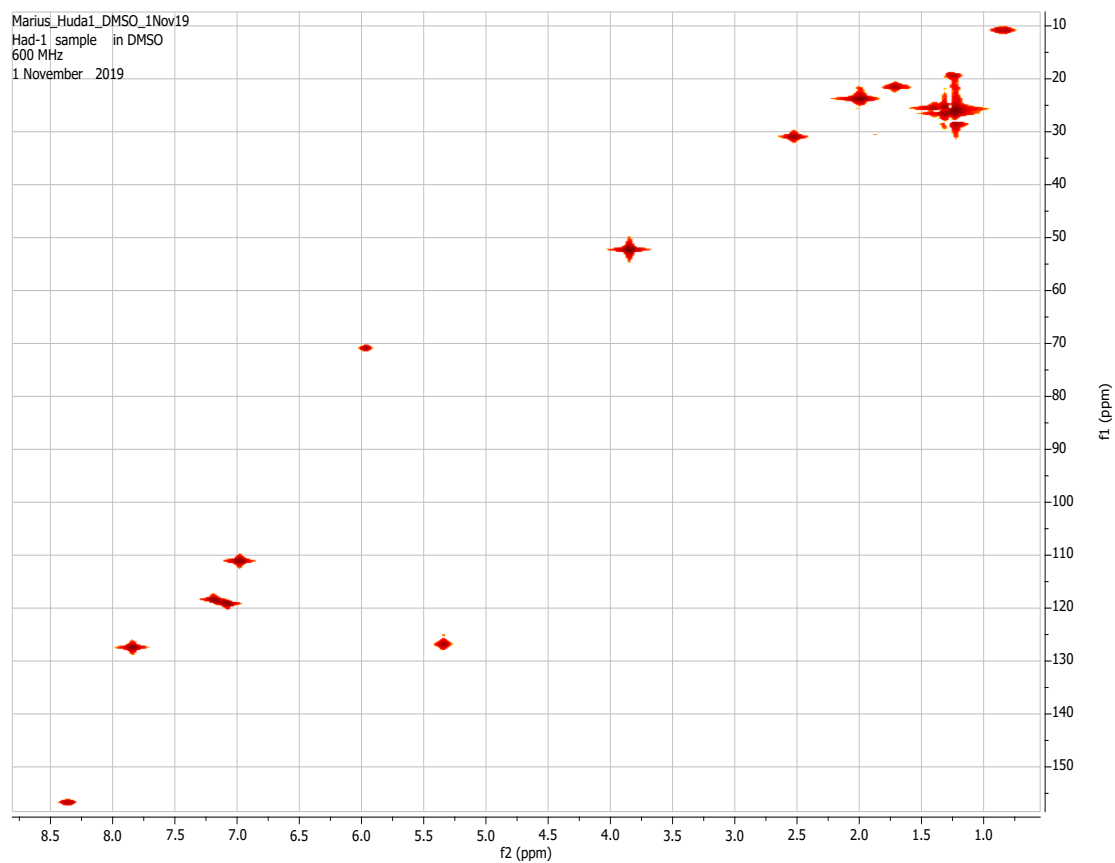


Figure S3. HSQC-NMR of (4-methoxybenzylideneamino)phenyl oleate at 305 K.

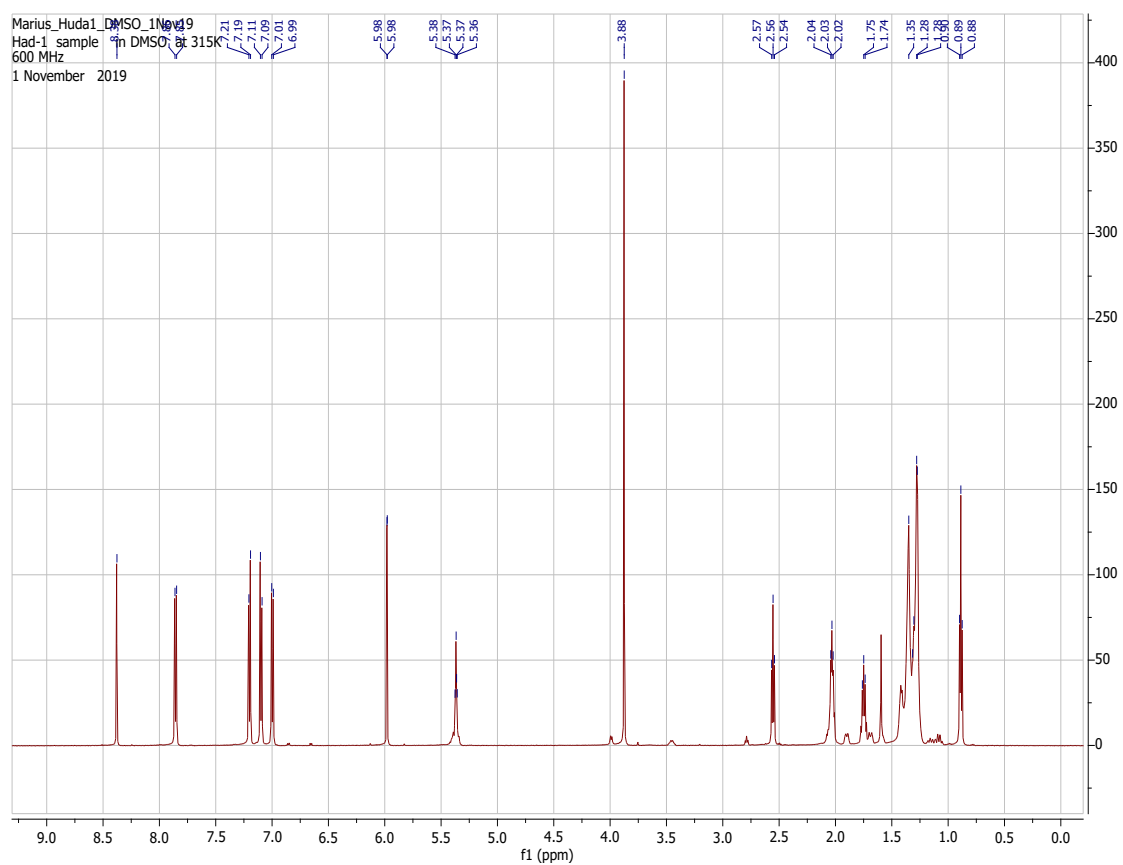


Figure S4. ^1H -NMR of (4-methoxybenzylideneamino)phenyl oleate at 310 K.

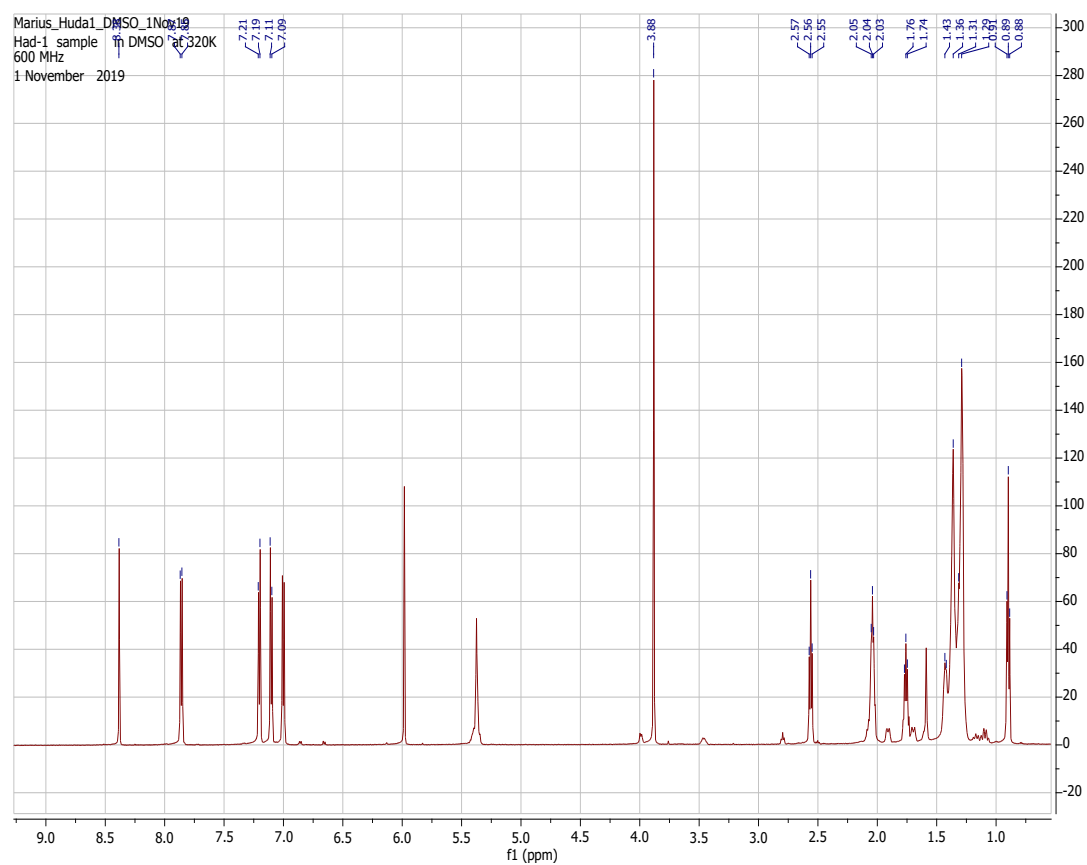


Figure S5. ^1H -NMR of (4-methoxybenzylideneamino)phenyl oleate at 315 K.

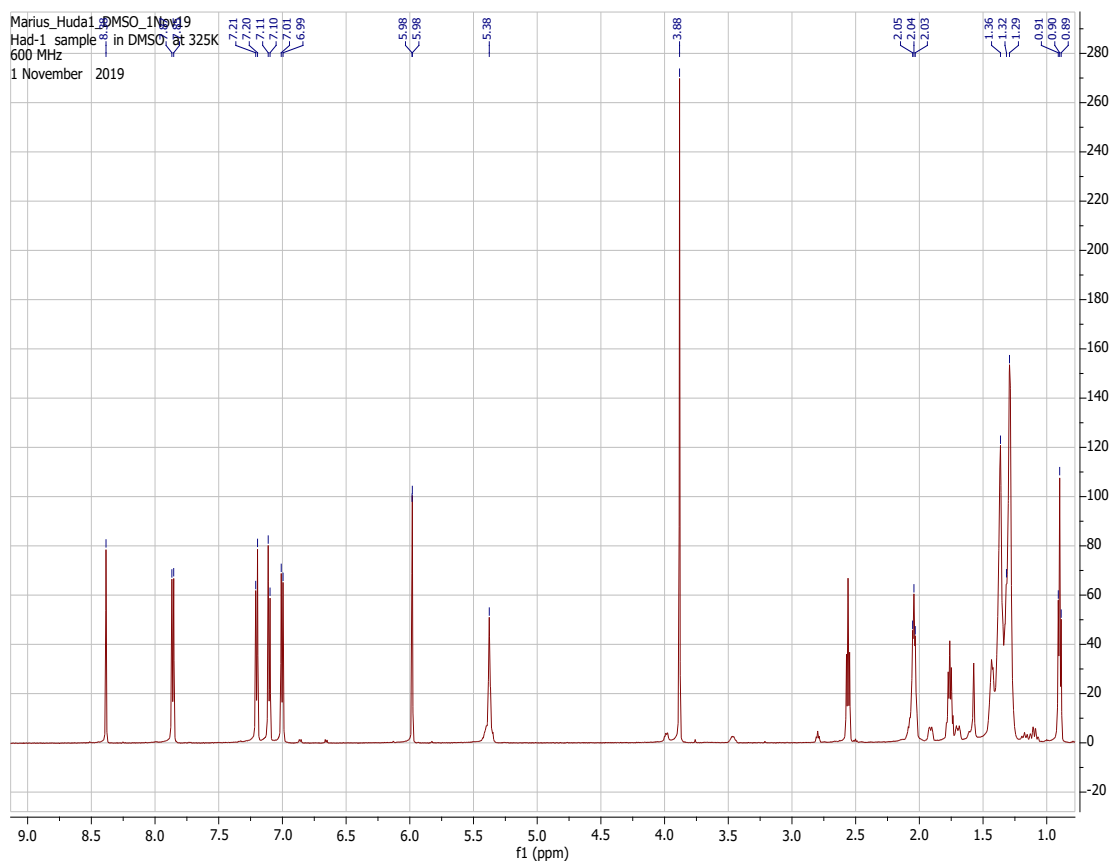


Figure S6. ¹H-NMR of (4-methoxybenzylideneamino)phenyl oleate at 320 K.

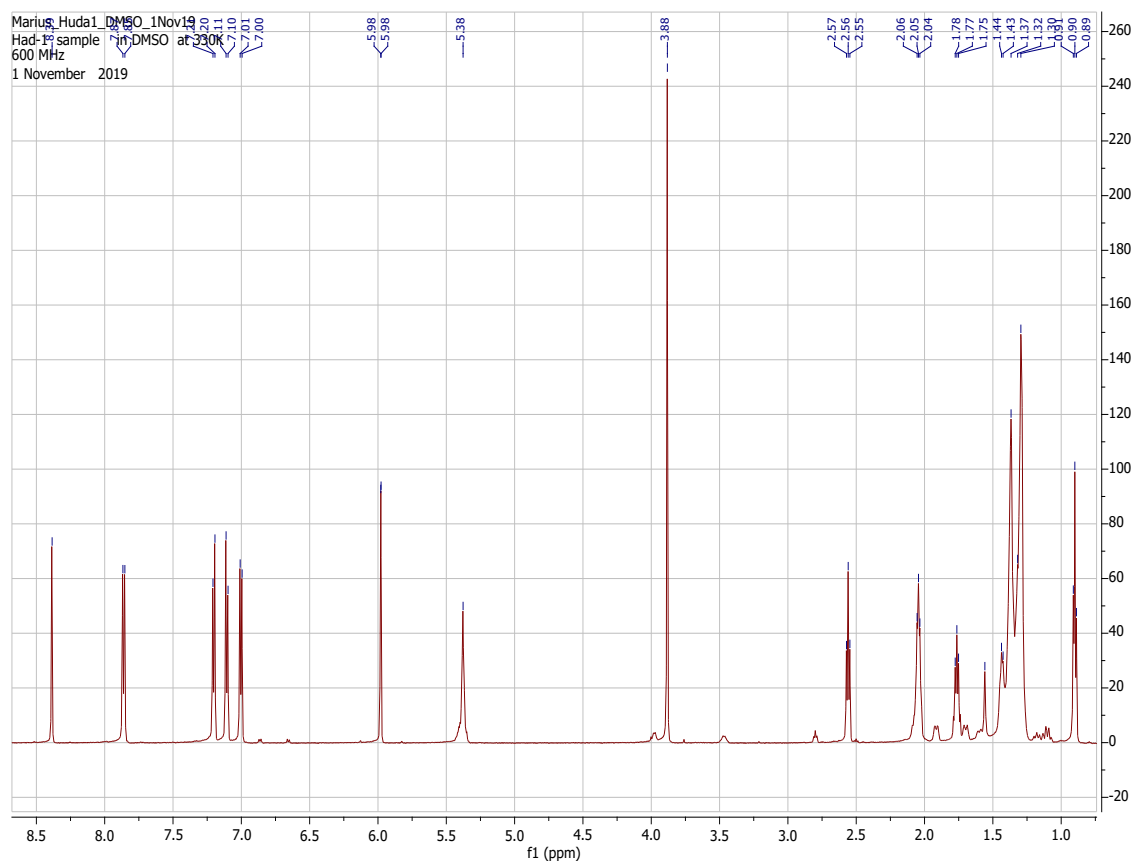


Figure S7. ^1H -NMR of (4-methoxybenzylideneamino)phenyl oleate at 325 K.



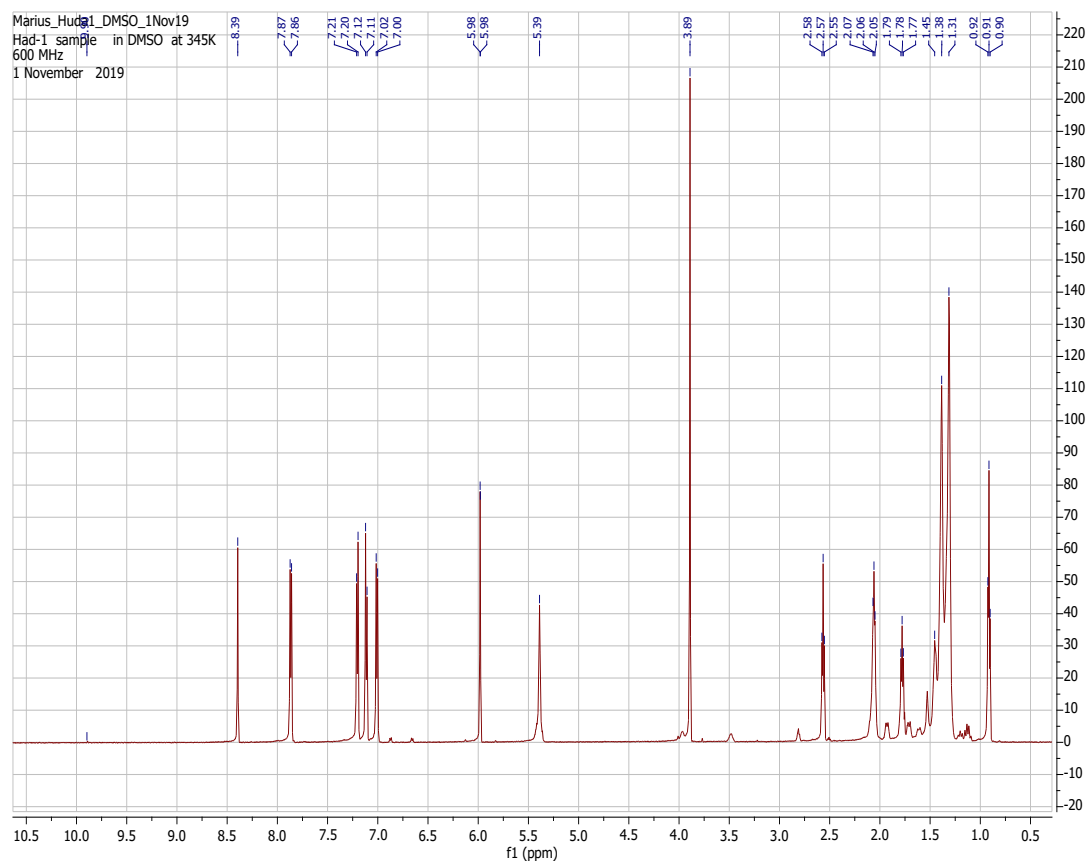


Figure S9. ^1H -NMR of (4-methoxybenzylideneamino)phenyl oleate at 345 K.

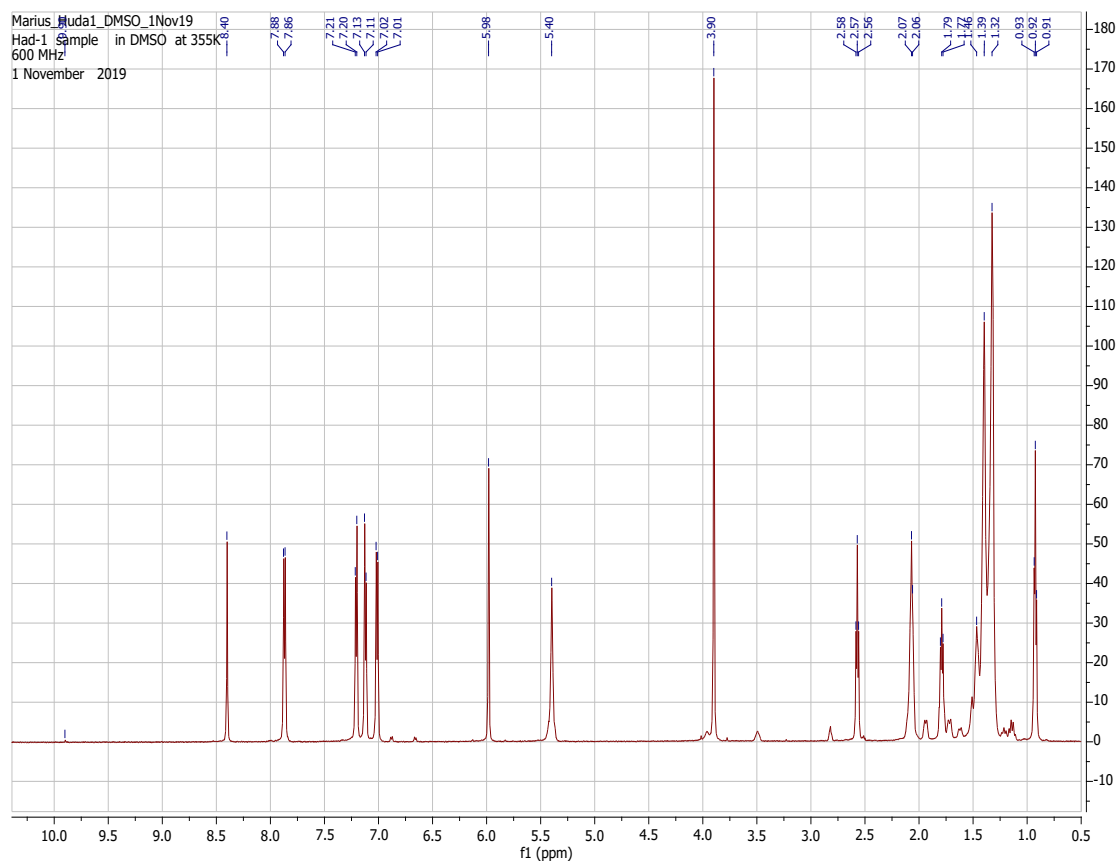


Figure S10. ^1H -NMR of (4-methoxybenzylideneamino)phenyl oleate at 355 K.

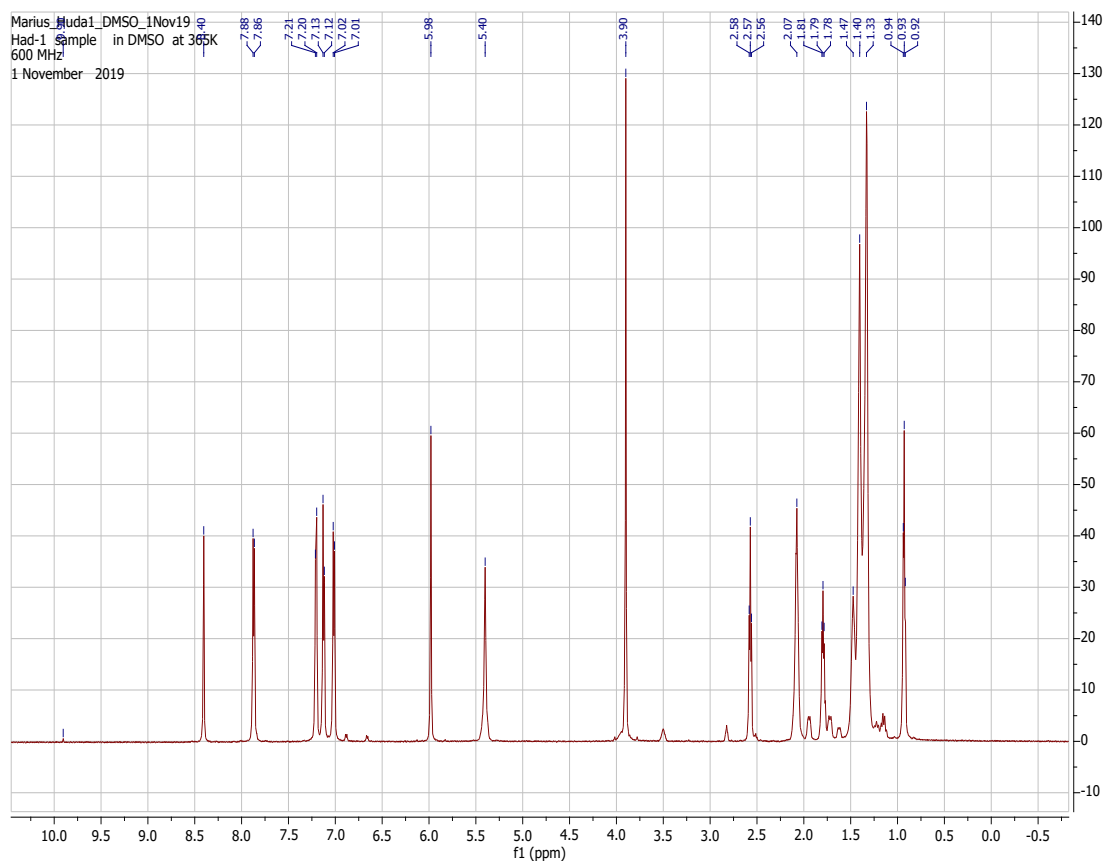


Figure S11. ^1H -NMR of (4-methoxybenzylideneamino)phenyl oleate at 365 K.

References

1. Baltisberger, J.; Mabrouk, P.A. Book Reviews: 200 and More NMR Experiments, Introductory Raman Spectroscopy. *Appl. Spectrosc.* 2005, 59, 113A–114A, doi:10.1366/0003702053946065.
2. *Gaussian 09*, revision a.02, Gaussian, Inc.: Wallingford, CT, 2009.
3. *GaussView*, version 5, Semichem Inc.: Shawnee Mission, Edinburgh, UK, 2009.

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