

Supplementary data

New widely stable four ring azo/ester/Schiff base liquid crystals: synthesis, mesomorphic, photophysical and DFT approaches

Nagwa H.S. Ahmed^a, Gamal R. Saad^{b*}, Hoda .A. Ahmed^{b*}, Mohamed Hagar^c

^aHigher Institute of Engineering and Technology, Department of Mathematics and Physical Science, New Cairo Academy, 5th settlement, New Cairo City, Egypt.

^bFaculty of Science, Department of Chemistry, Cairo University, Giza 12631, Egypt.

^cFaculty of Science, Chemistry Department, Alexandria University, Alexandria, Egypt.

Experimental

Materials

Ethyl 4-aminobenzoate, 4-hydroxybenzaldehyde obtained from Sigma-Aldrich (Germany). Aniline, 4-methylaniline, 4-methoxyaniline, 4-chloroaniline, 1-bromoalkanes, were obtained from Merck (Germany). *N,N'*-Dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were purchased from Aldrich (Milwaukee, WI, USA). All chemicals were used without further purification. All the solvents used such as dichloromethane, ethanol, and methanol were of pure grade and purchased Aldrich.

Preparation of Ethyl [2-(4-hydroxyphenyl)diazenyl]benzoate (**A**)

Ethyl 4-aminobenzoate (0.01 mol) was dissolved in a concentrated hydrochloric acid then the reaction mixture was cooled in an ice-salt bath to -2°C. To the resulting solution, a cold aqueous solution of sodium nitrite (0.03 mol) was added drop-wise with stirring, the reaction temperature did not exceed to 2°C. After complete addition, the cold mixture was added drop-wise to an ice-cold solution of the phenol (0.01 mol) in sodium hydroxide (0.03 mol). The mixture was further stirred at -2°C for one hour then acidified with dilute hydrochloric acid. The solid separated was filtered and crystallized twice from ethanol. The product was TLC pure and gave transition temperatures as reported ¹.

Preparation of Ethyl 4-[2-(4-alkoxyphenyl)diazenyl]benzoate (**Bn**)

The esters were prepared according to the previously described method ². Ethyl [2-(4-hydroxyphenyl)diazenyl]benzoate (**A**) (0.001 mol) was dissolved in alcoholic KOH (0.02 mol), then appropriate amount of 1-bromoalkane (0.0012 mol) was added drop-wise while stirring. Stirring was continued at room temperature for two days. The separated solid was filtered off, evaporated and the residue was crystallized twice from ethanol.

Preparation of 4-[2-(4-methoxyphenyl)diazenyl]benzoic acid (**An**)

The esters (**Bn**) were hydrolyzed to their corresponding acids by refluxing in aqueous ethanolic potassium hydroxide for 24 hours then acidified with dilute HCl to give the corresponding acids **An**^{3, 4}. The products were crystallized twice from ethanol to give TLC pure compounds.

Preparation of (4-substitutedphenylimino)methylphenol (Cn)

Equimolar equivalents of the 4-hydroxybenzaldehyde (0.5 g, 4.1 mmol) and 4-substitutedaniline (4.1 mmol) were dissolved in ethanol (10 ml) and refluxed for 2 h. 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 compounds, as indicated by thin-layer chromatography (TLC) analysis. The melting points and infrared (IR) data determined of the four prepared imines A as X=CH₃O, CH₃, H, and Cl; mp = 228.0°C, 232.0°C, 218.0°C, and 220.0°C, respectively,⁵.

Characterization

IR spectra of all investigated compounds *In*_{a-d} were measured by Perkin-Elmer B25 (Perkin-Elmer, Inc., Shelton, CT USA) spectrophotometer. ¹H NMR spectra were performed using a Varian EM 350L 300 MHz spectrometer (Oxford, UK) using 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). Mass spectra were performed with GCMS-QP1000EX Mass spectrometer (Shimadzu, Japan) and microanalyses with a Perkin-Elmer Series II 2400-CHN Analyser (Shelton, CT USA). The UV–vis absorption spectra were measured on a UV-1800 SHIMADZU (Japan) spectrophotometer in dichloromethane solutions.

Differential Scanning Calorimeter, TA instrument Co. Q20 (DSC; USA), was used for calorimetric measurements. The melting point and enthalpy of indium and lead was used for DSC calibration. Aluminum pans and 2–3 mg sample amounts were used for DSC measurements investigation. 30 ml/min nitrogen gas inert atmosphere and 10°C/min heating rate were selected for all measurements and all transitions were recorded from the heating scan. The texture of the mesophases was identified by a polarized light microscope (PLM, Wild, Germany) with Mettler FP82HT hot stage.

Thermogravimetric analysis (TGA) was carried out using 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.

2.4. Computational Method

Gaussian 09 software was used for DFT calculations for the studied compounds⁶. 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 ⁷. Also, 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 none imaginary frequencies.

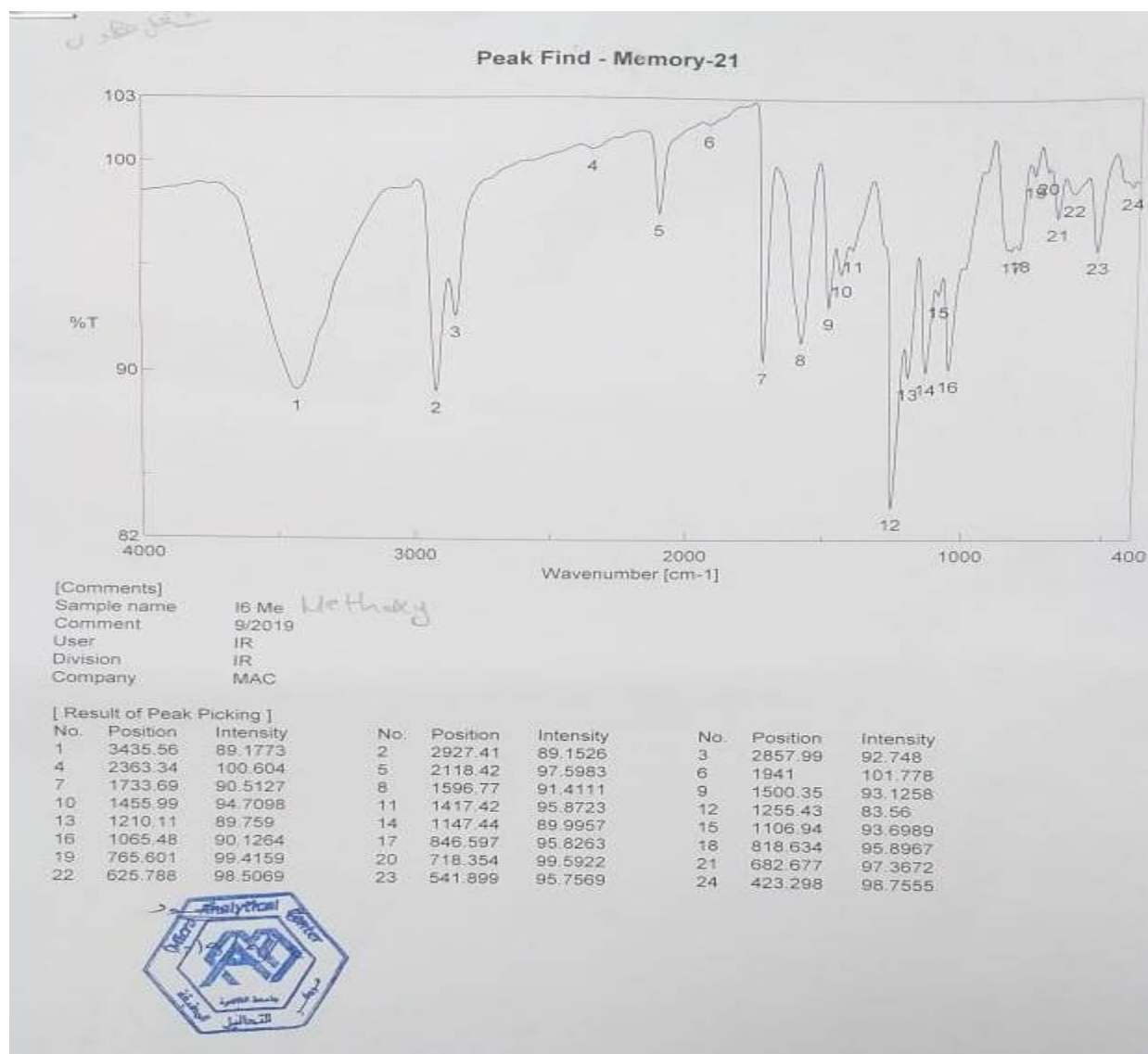


Fig S1: FTIR of (4-methoxyphenylimino)methyl)phenyl 4-[2-(4-hexadecyloxyphenyl)diazenyl]benzoate, I16_a

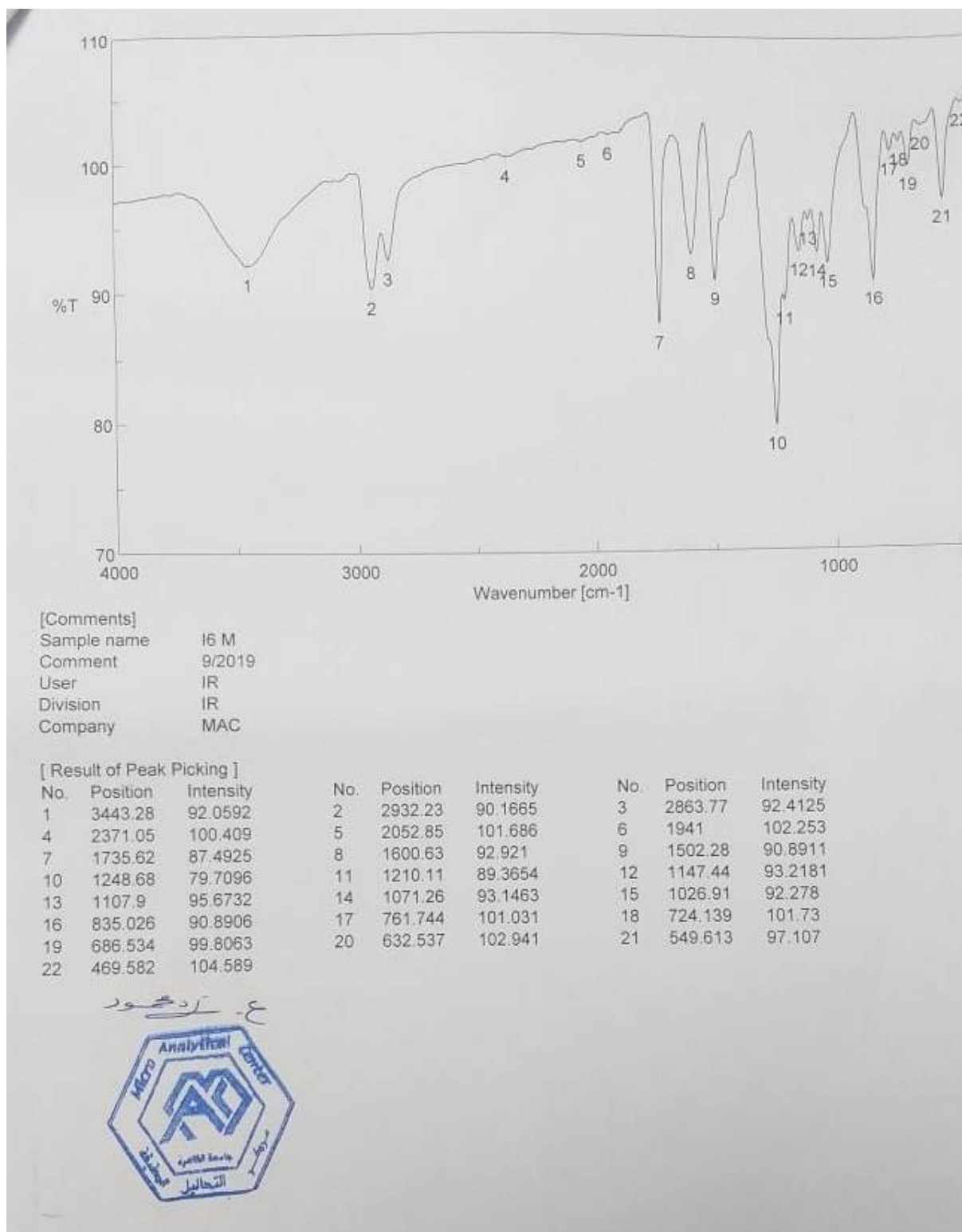


Fig S2: FTIR of (4-methylphenylimino)methyl)phenyl 4-[2-(4-hexadecyloxyphenyl)diazenyl]benzoate, I16_b

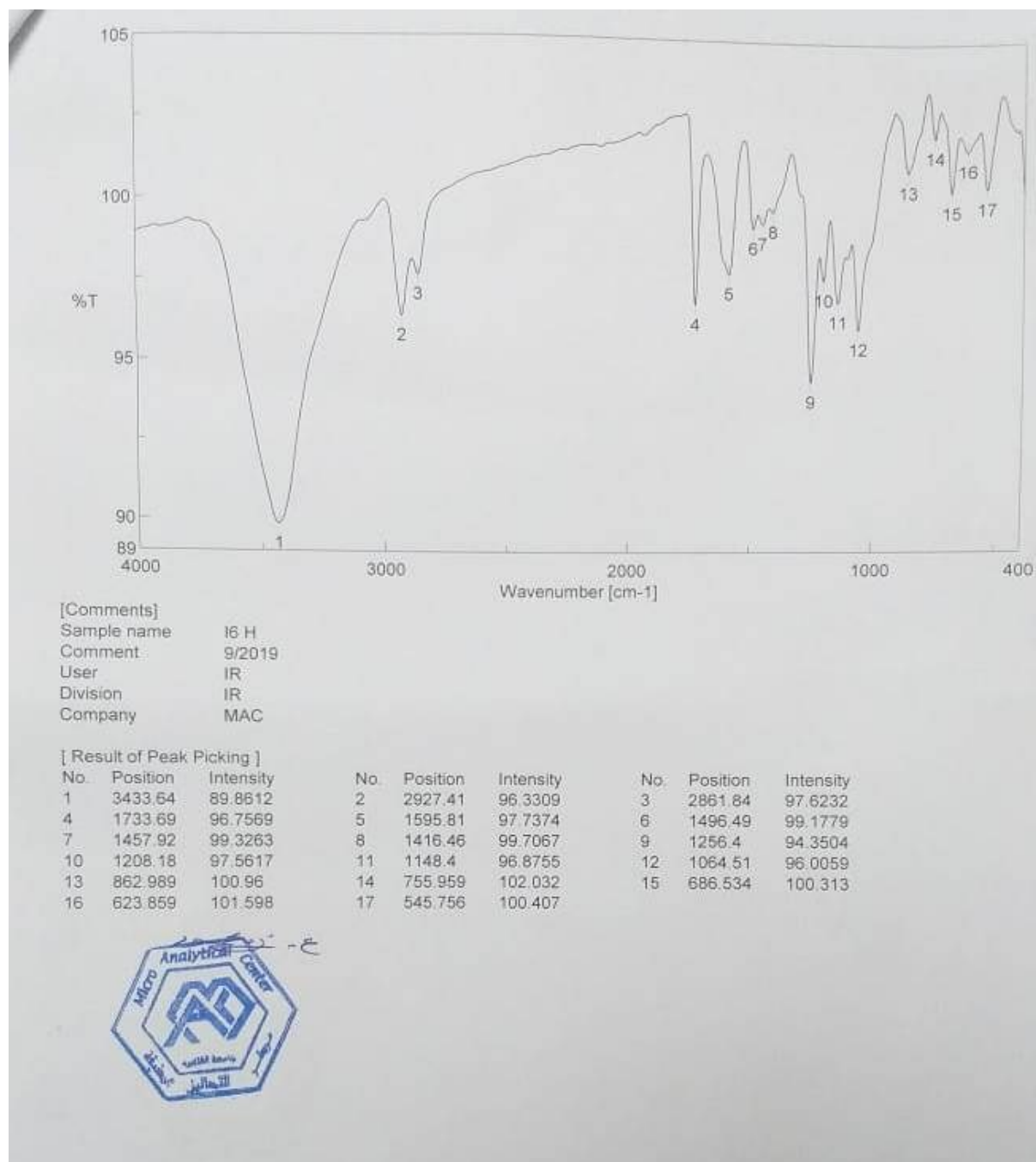


Fig S3: FTIR of (4-phenylimino)methyl)phenyl 4-[2-(4-hexadecyloxyphenyl)diazenyl]benzoate, I16c

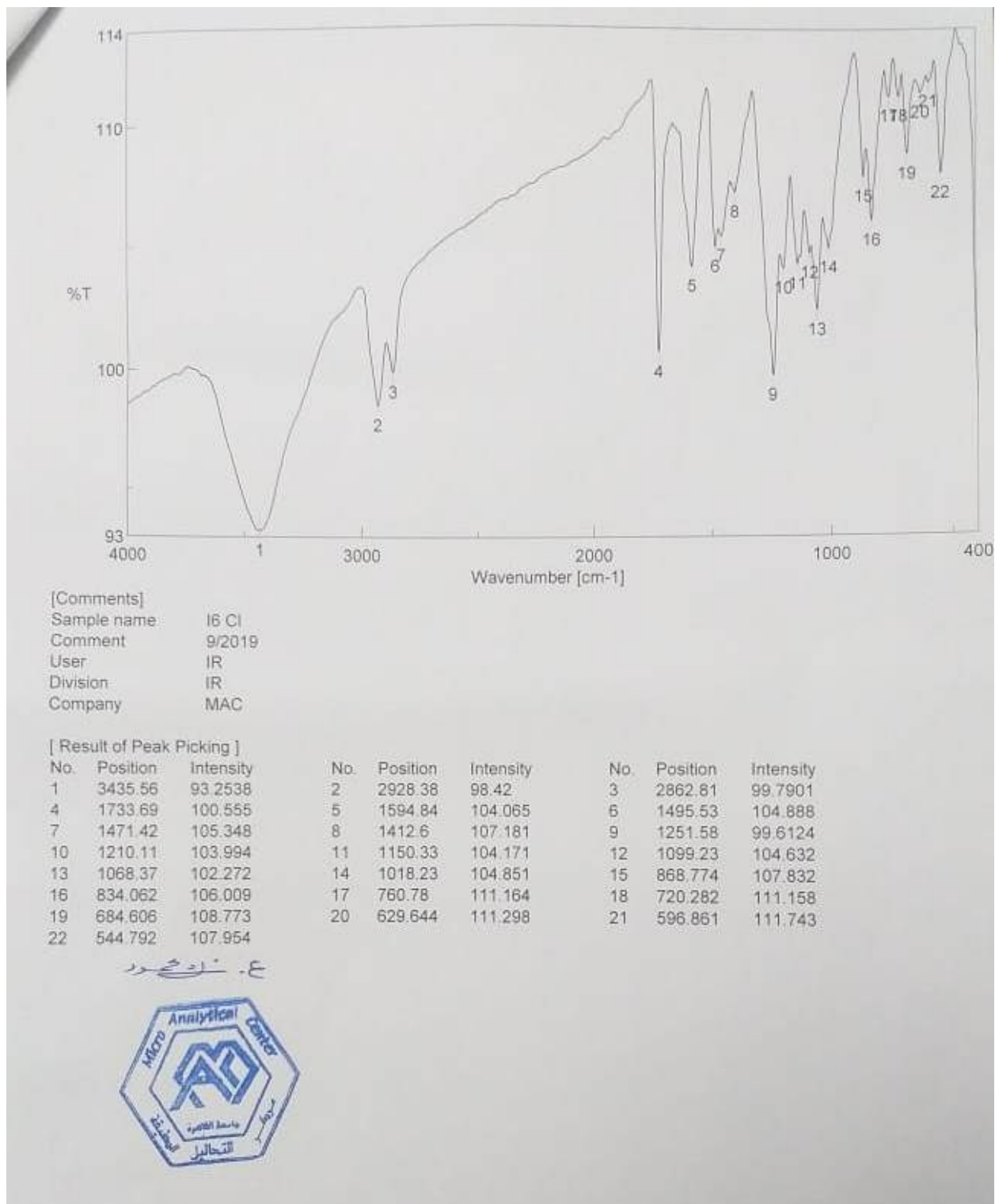


Fig S4: FTIR of (4-chlorophenylimino)methyl)phenyl 4-[2-(4-hexadecyloxyphenyl)diazenyl]benzoate, 116_d

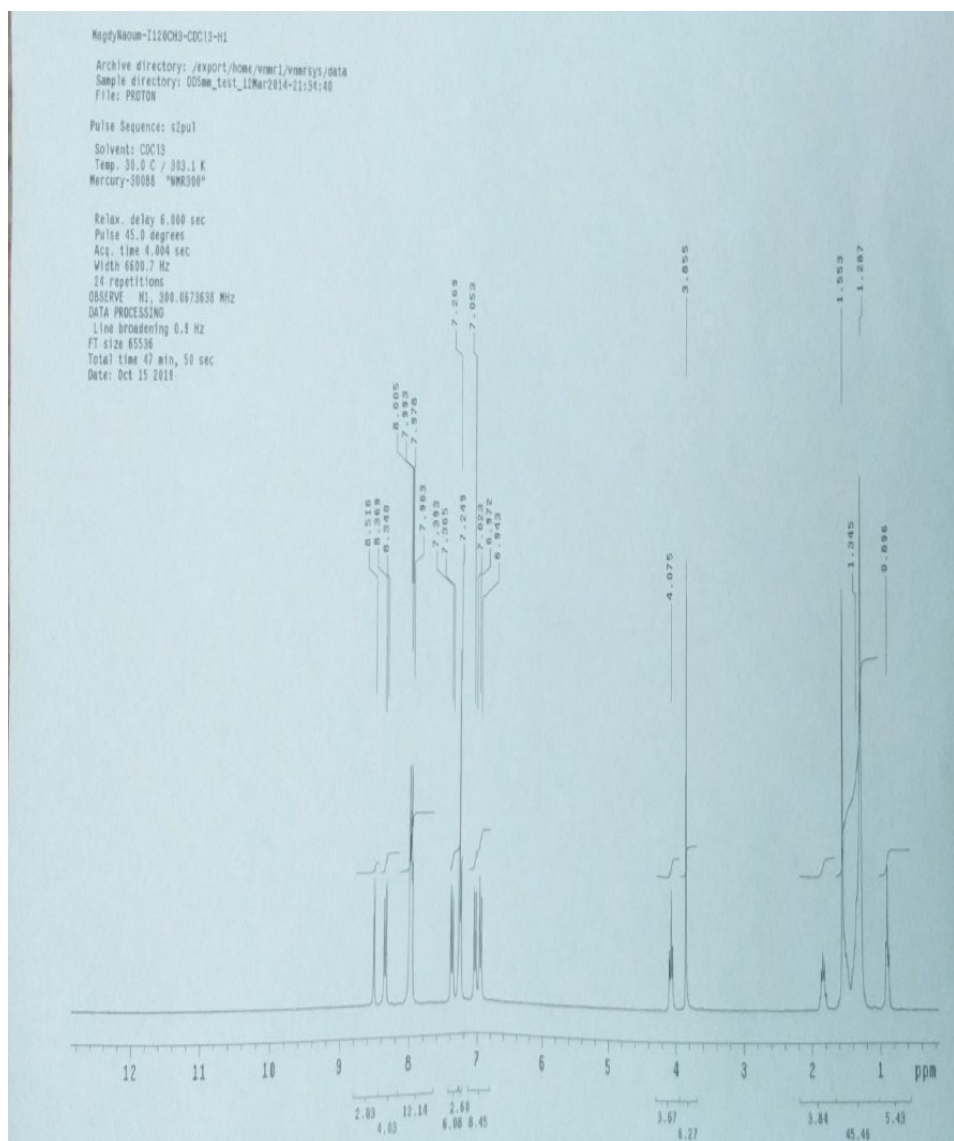


Fig S5: ¹H NMR of (4-methoxyphenylimino)methyl)phenyl 4-[2-(4-dodecyloxyphenyl)diazenyl]benzoate, I12_a

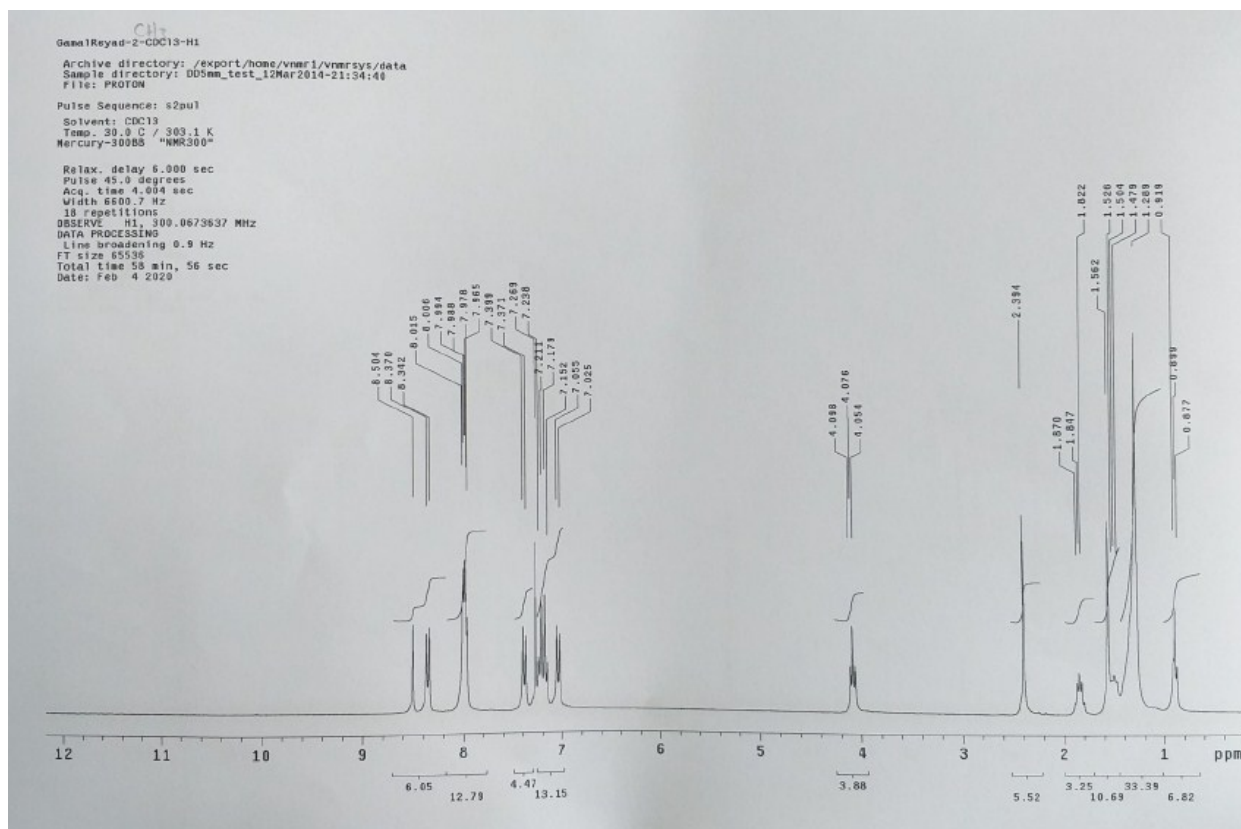


Fig S6: ¹HNMR of (4-methylphenylimino)methyl)phenyl 4-[2-(4-dodecyloxyphenyl)diazeryl]benzoate, I12_b

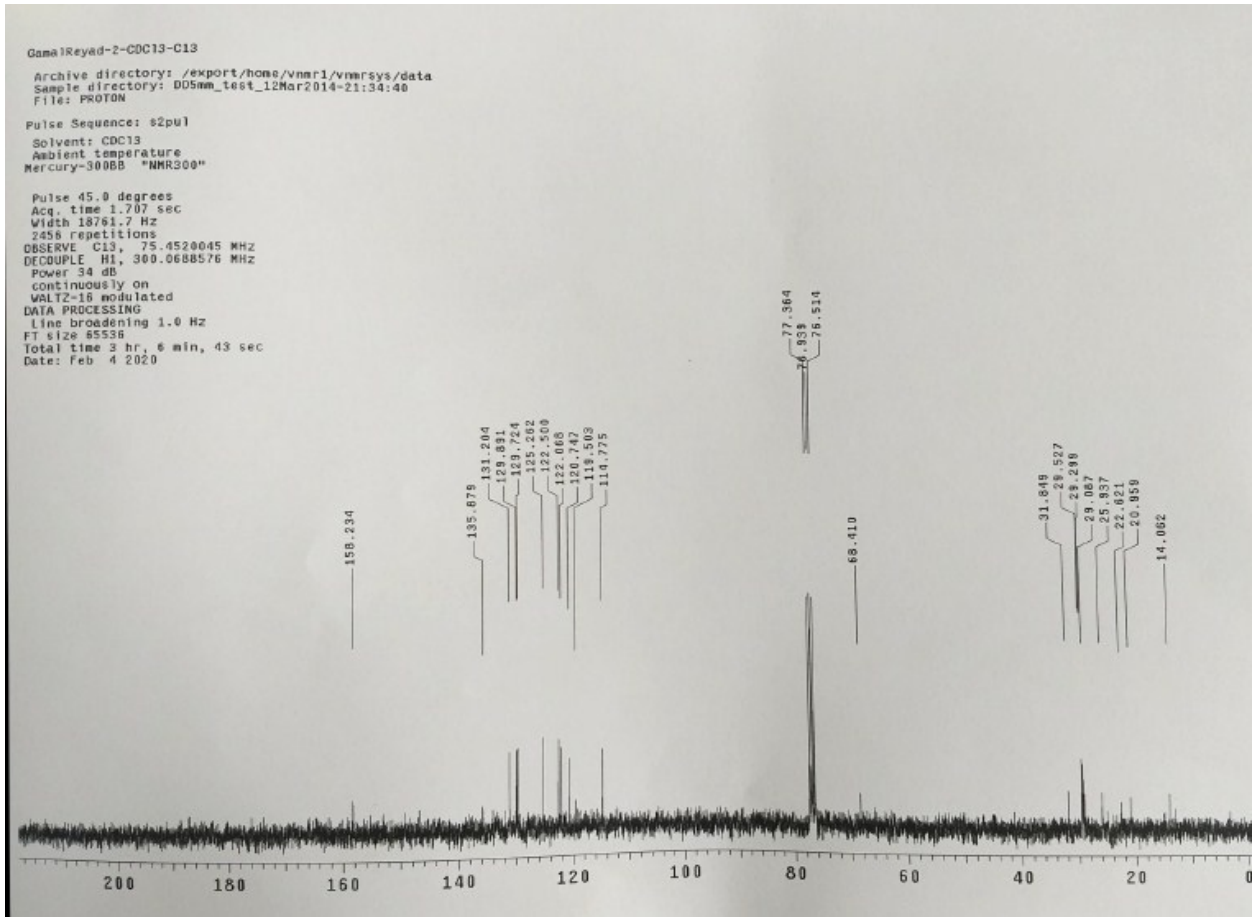


Fig S7: ¹³C-NMR of (4-methylphenylimino)methyl)phenyl 4-[2-(4-dodecyloxyphenyl)diazenyl]benzoate, **112_b**

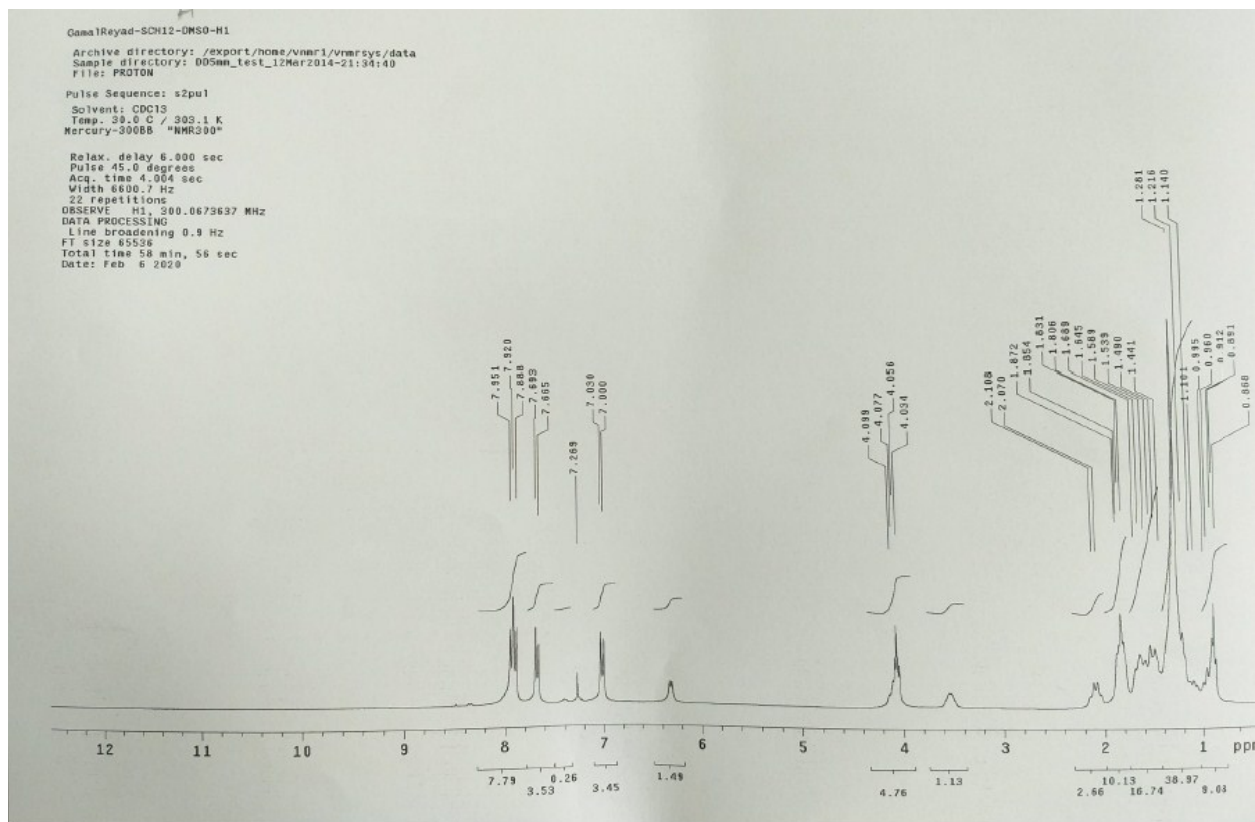


Fig S8: ^1H NMR of phenyliminomethyl)phenyl 4-[2-(4-dodecyloxyphenyl)diazenyl]benzoate, 112c

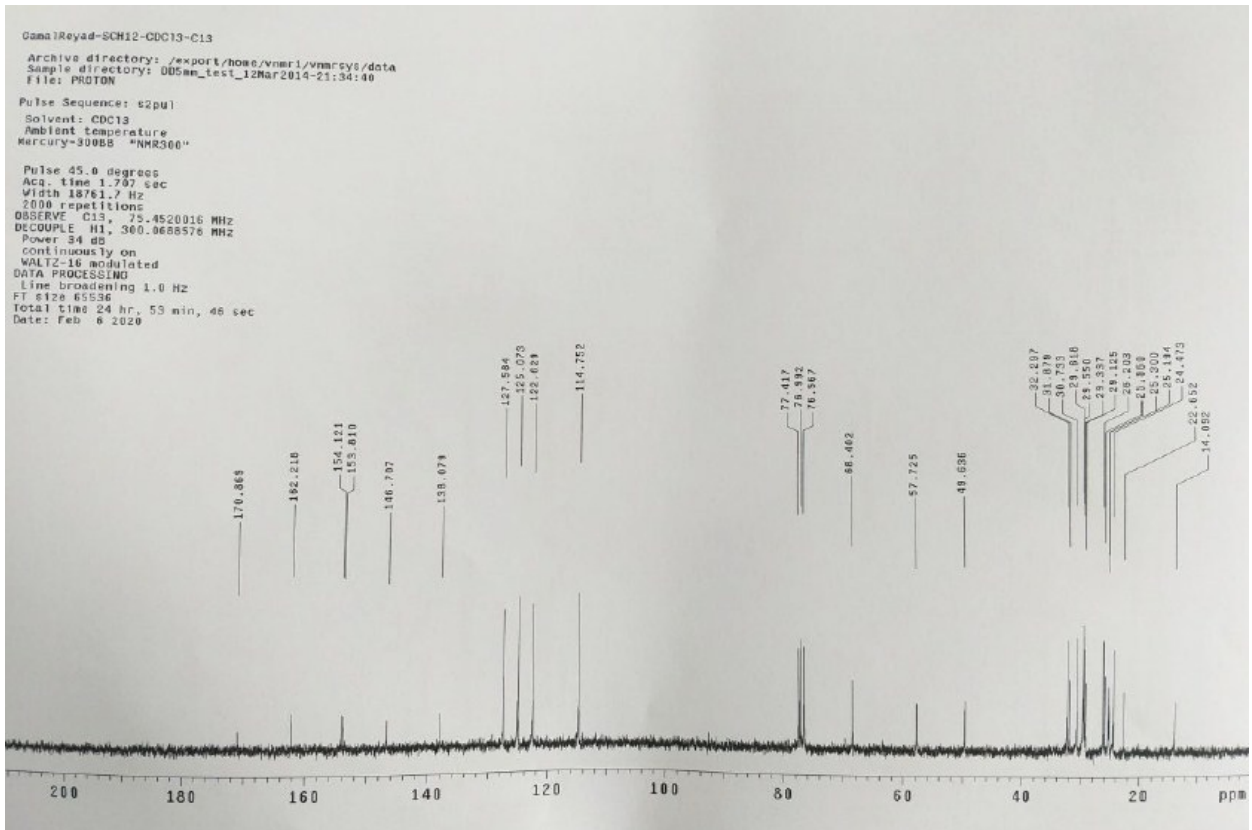


Fig S9: ^{13}C NMR of phenyliminomethylphenyl 4-[2-(4-dodecyloxyphenyl)diazenyl]benzoate, I12_c

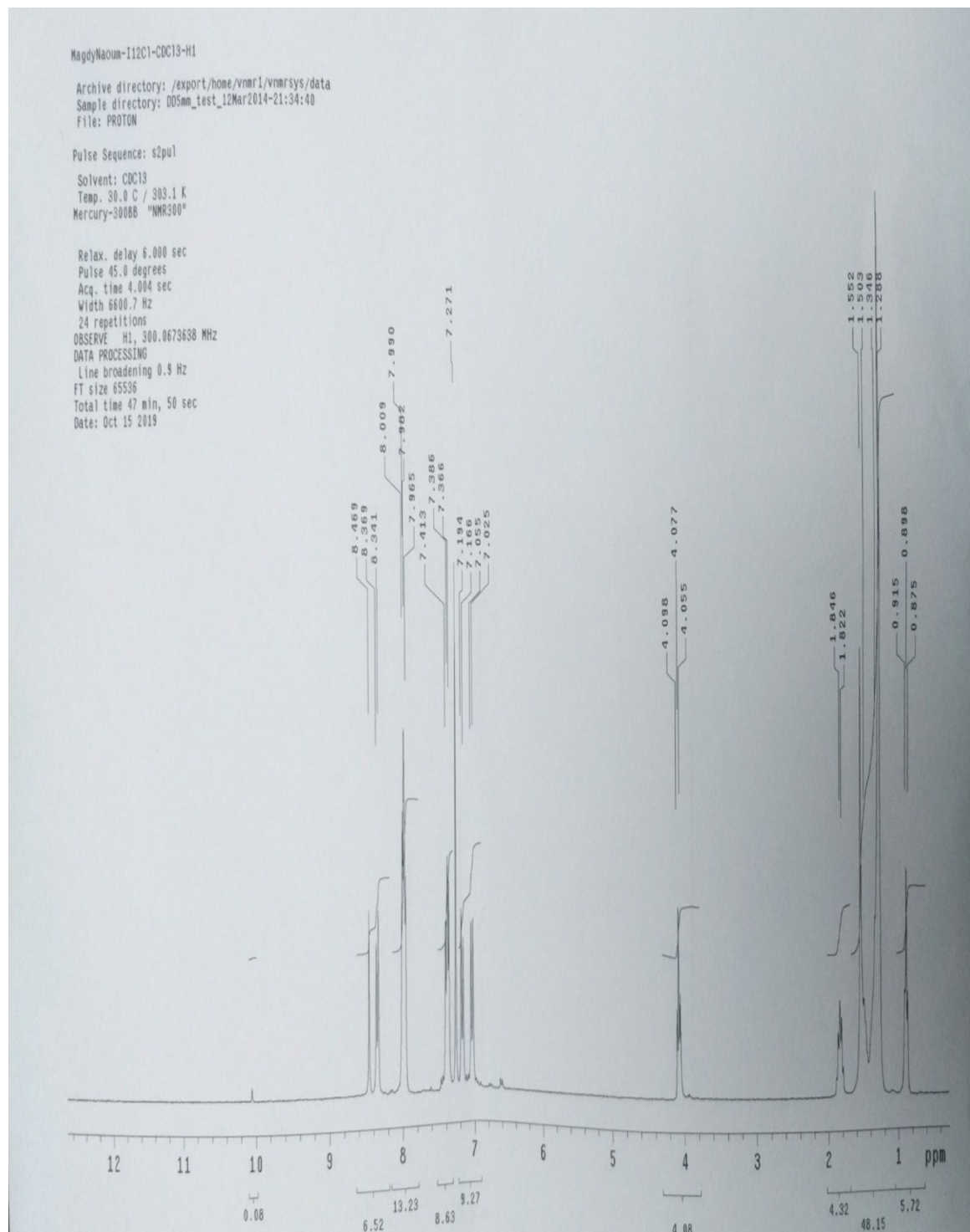
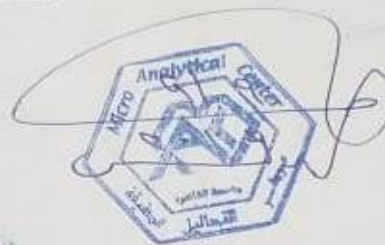


Fig S10: ^1H NMR of (4-chlorophenylimino)methyl)phenyl 4-[2-(4-dodecyloxyphenyl)diazenyl]benzoate, I12_d

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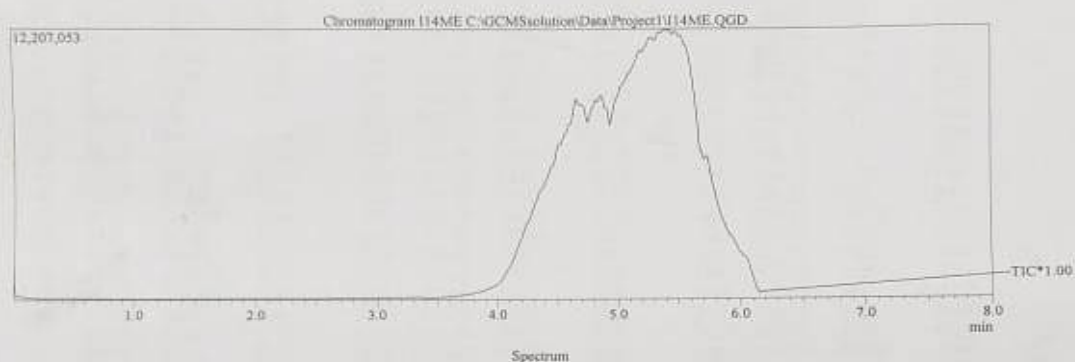
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Shimadzu Qp-2010 Plus**



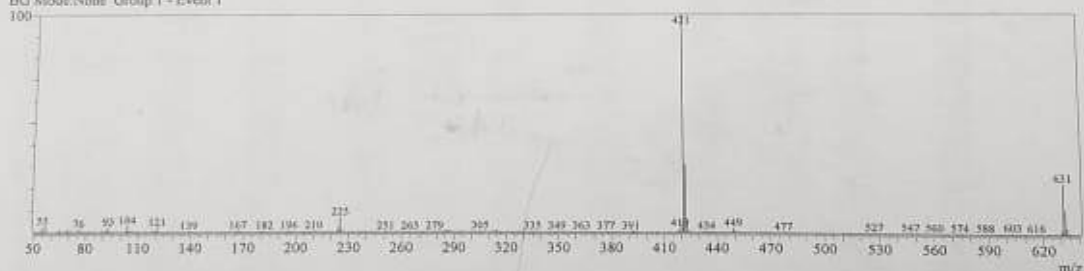
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 Ionization Mode: EI

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| 2 | 51.00 | 9297 | 0.18 | 5 | 54.05 | 7604 | 0.15 | 8 | 57.00 | 150146 | 2.90 |
| 3 | 52.00 | 4286 | 0.08 | 6 | 55.00 | 136119 | 2.62 | 9 | 58.00 | 6567 | 0.13 |

Fig S11: Mass spectra of (4-methoxyphenylimino)methyl)phenyl 4-[2-(4-tetradecyloxyphenyl)diazenyl]benzoate, I14_a

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**DI Analysis
Shimadzu Qp-2010 Plus**

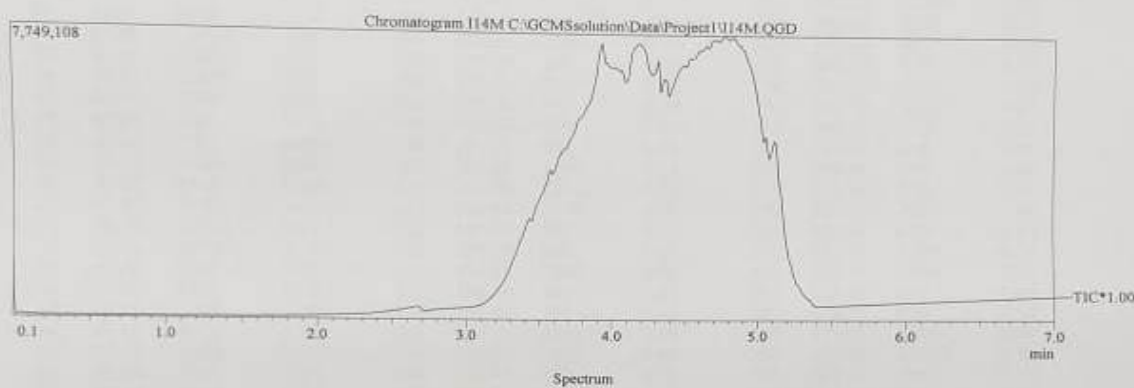


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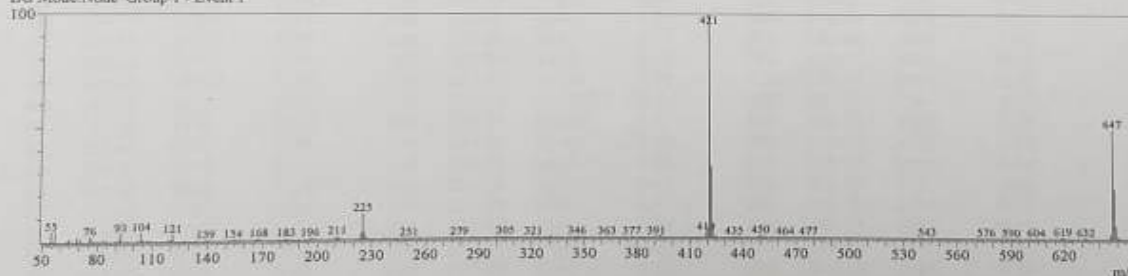
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Electron Voltage: 70 eV
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Mass Table
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| 1 | 49.95 | 5196 | 0.21 | 4 | 53.00 | 6542 | 0.26 | 7 | 56.05 | 14244 | 0.57 |
| 2 | 51.00 | 7258 | 0.29 | 5 | 54.05 | 6397 | 0.26 | 8 | 57.05 | 121668 | 4.88 |
| 3 | 52.00 | 4254 | 0.17 | 6 | 55.00 | 112513 | 4.51 | 9 | 58.05 | 5615 | 0.23 |

Fig S12: Mass spectra of (4-methylphenylimino)methyl)phenyl 4-[2-(4-tetradecyloxyphenyl)diazenyl]benzoate, I14_b

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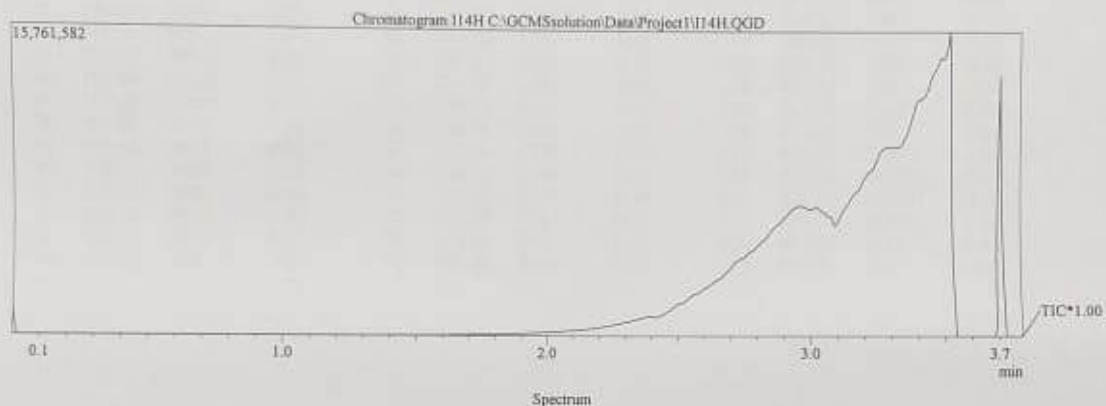
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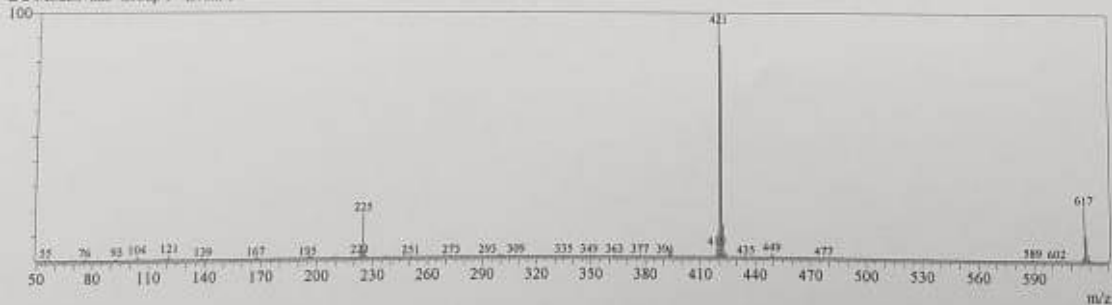
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 BG Mode: None Group 1 - Event 1



Mass Table
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 RawMode: Single 3.7(447) BasePeak: 421(2096881)
 BG Mode: None Group 1 - Event 1

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|---|-------|---------|-----------|---|-------|---------|-----------|---|-------|---------|-----------|
| 1 | 55.00 | 8598 | 0.41 | 4 | 69.05 | 7244 | 0.35 | 7 | 77.00 | 7182 | 0.34 |
| 2 | 57.05 | 10841 | 0.52 | 5 | 71.05 | 4907 | 0.23 | 8 | 83.05 | 2995 | 0.14 |
| 3 | 65.00 | 3033 | 0.14 | 6 | 76.00 | 8986 | 0.43 | 9 | 85.00 | 1884 | 0.09 |

Fig S13: Mass spectra of (phenylimino)methyl)phenyl 4-[2-(4-tetradecyloxyphenyl)diazenyl]benzoate, I14.

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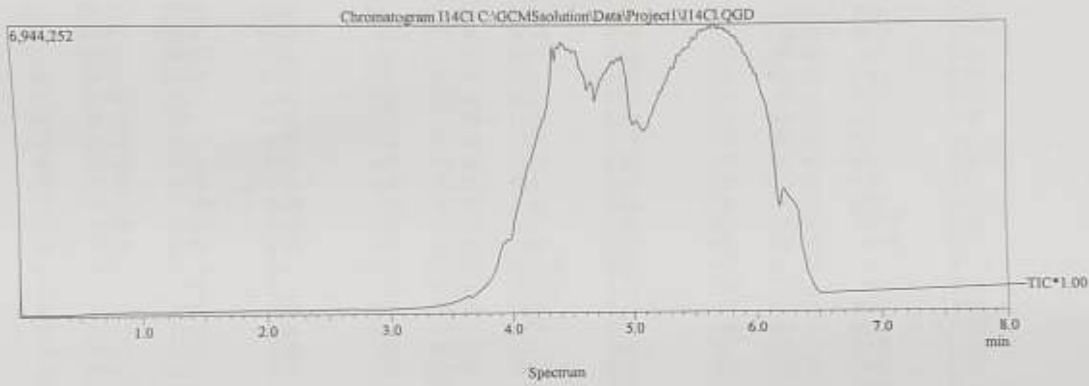
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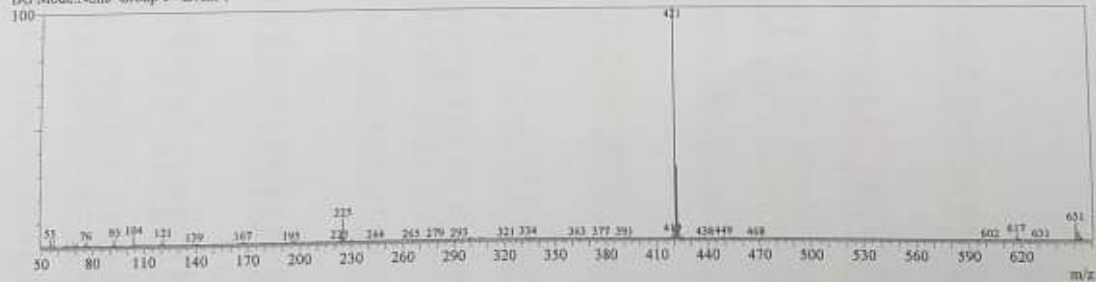
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 Ionization Mode : EI

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Mass Table
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| 2 | 51.00 | 8428 | 0.28 | 5 | 54.05 | 6070 | 0.20 |
| 3 | 52.05 | 2711 | 0.09 | 6 | 55.00 | 91468 | 3.08 |
| | | | | 7 | 56.05 | 13522 | 0.46 |
| | | | | 8 | 57.05 | 102314 | 3.44 |
| | | | | 9 | 58.05 | 5034 | 0.17 |

Fig S14: Mass spectra of (4-chlorophenylimino)methyl)phenyl 4-[2-(4-tetradecyloxyphenyl)diazanyl]benzoate, I14_d

References

1. M. L. Rahman, J. Asik, S. Kumar and C. Tschierske, *Liquid Crystals*, 2008, 35, 1263-1270.
2. N. Shah, R. Vora and N. Jadav, *Molecular Crystals and Liquid Crystals*, 1991, 209, 291-296.
3. M. Lutfor, G. Hegde, S. Kumar, C. Tschierske and V. Chigrinov, *Optical Materials*, 2009, 32, 176-183.
4. M. Alaasar, M. Prehm and C. Tschierske, *Liquid Crystals*, 2013, 40, 656-668.
5. M. Hagar, H. Ahmed and G. Saad, *Liquid Crystals*, 2018, 45, 1324-1332.
6. M. Frisch, G. Trucks, H. B. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. Petersson, *Inc., Wallingford, CT*, 2009, 200.
7. R. Dennington, T. Keith and J. Millam, 2009.