

Supplementary Materials

Synthesis, phase behavior and computational simulations of pyridyl based liquid crystal system

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1. Materials

Ethyl 4-aminobenzoate and nicotinaldehyde obtained from Sigma-Aldrich (Germany). 4-hydroxyaniline and 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.

2. Preparation of (E)-4-((pyridin-3-ylmethylene)amino)phenol (**A**)

(0.5 g, 4.1 mmol) of nicotinaldehyde mixed with equimolar equivalents of the and 4-hydroxyaniline (0.45 g, 4.1 mmol) in EtOH (10 ml) and refluxed for 2 h. The mixture was cooled to room temperature and filtered. The obtained solid was washed with cold EtOH and recrystallized twice from hot EtOH to give pure compounds, as indicated by thin-layer chromatography (TLC) analysis; mp = 204.0°C.

3. Preparation of (E)-4-((pyridin-3-ylmethylene)amino)phenyl 4-(alkoxy) benzoate **Tn**

Molar equivalents of the (E)-4-((pyridin-3-ylmethylene)amino)phenol (**A**) and 4-(alkoxy)benzoic acid (0.01 mol each) were dissolved in 25 ml dry methylene chloride (DCM). To the resulting mixture, DCC (0.02 mol) and few crystals of 4-(dimethylamino) pyridine (DMAP), as catalyst, were added and the solution left to stand for 72 h at room temperature with

continuous stirring. The solid was separated then filtered off and the solution evaporated. The solid residue obtained was recrystallized twice from acetic acid and twice from ethanol to give TLC pure products. The purity of the prepared samples was checked with TLC using TLC sheets coated with silica gel (E Merck), and CH₂Cl₂/CHOH (9:1) as eluent, whereby only one spot was detected by a UV-lamp.

4. 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 (POM, Wild, Germany) with Mettler FP82HT hot stage. The transitions from liquid crystal phase to isotropic liquid under POM for all prepared derivatives were in all cases quite sharp, and there was no indication whatsoever that any of the transitions took place over a range of temperature.

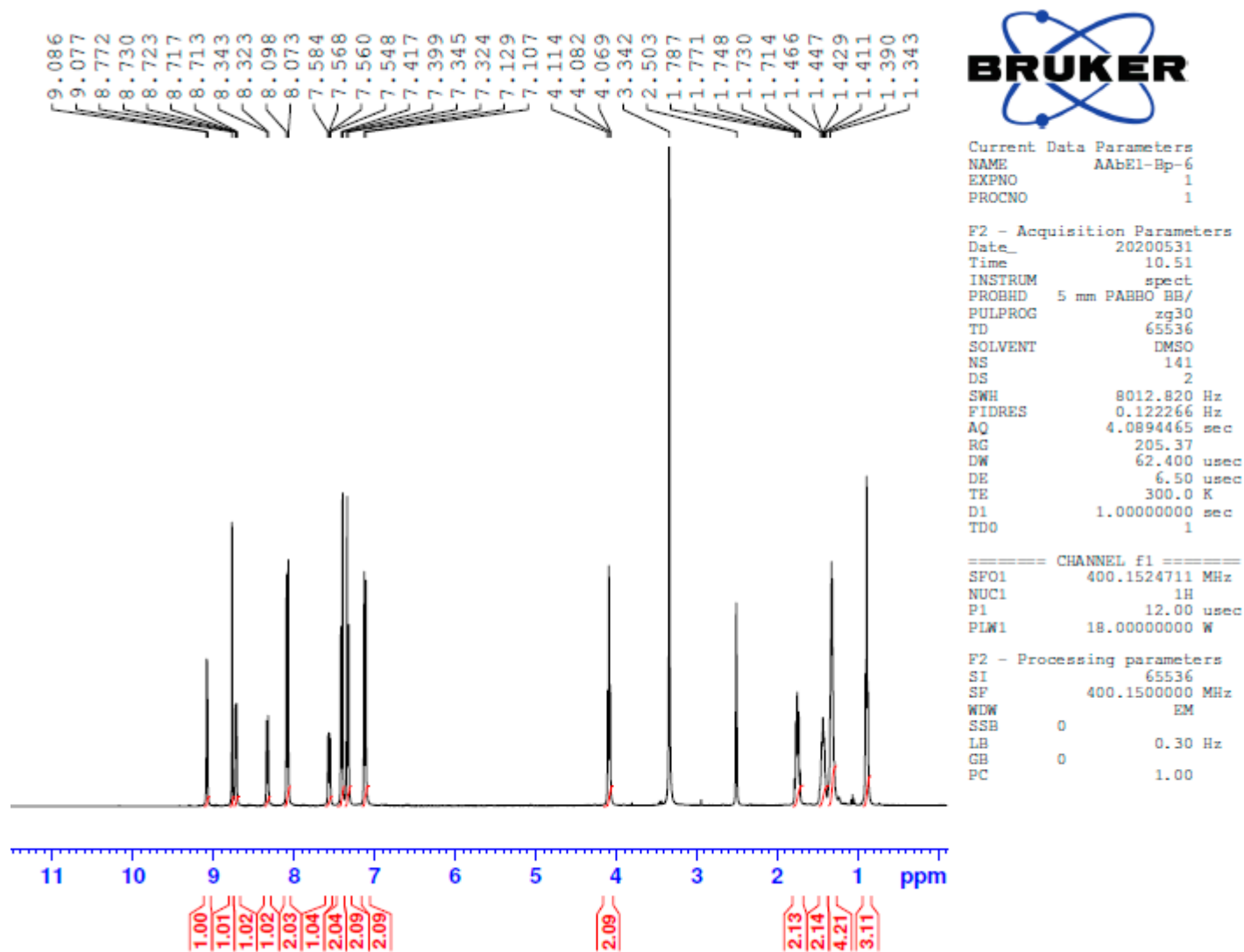
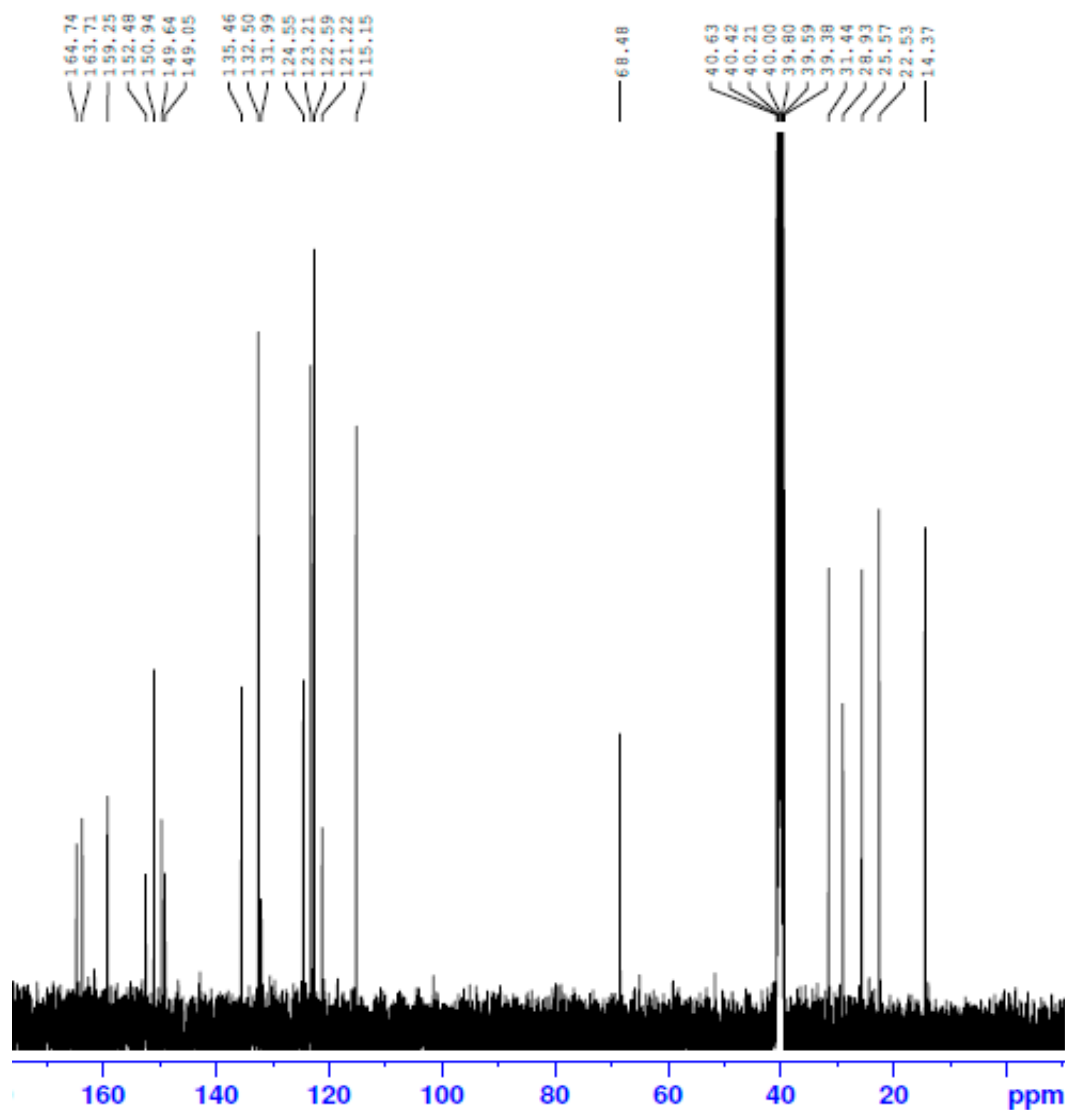


Figure S1. ¹H-NMR spectrum of T6



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 PROCNO 1

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 D11 0.03000000 sec
 TD0 1

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 PLW1 47.00000000 W

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 CPDPRG[2] waltz16
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 PLW13 0.28125000 W

F2 - Processing parameters
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Figure S2. ^{13}C -NMR spectrum of T6

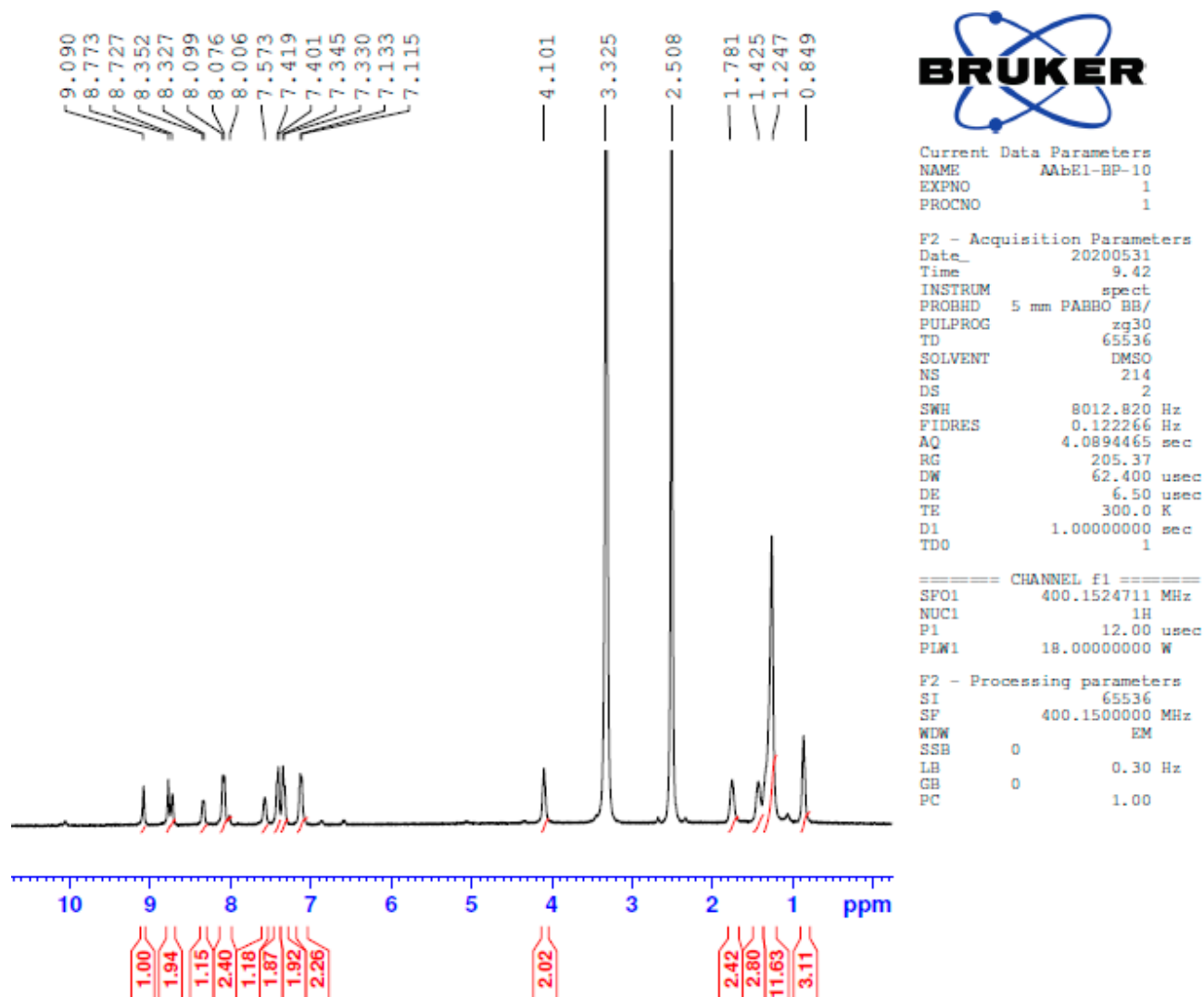
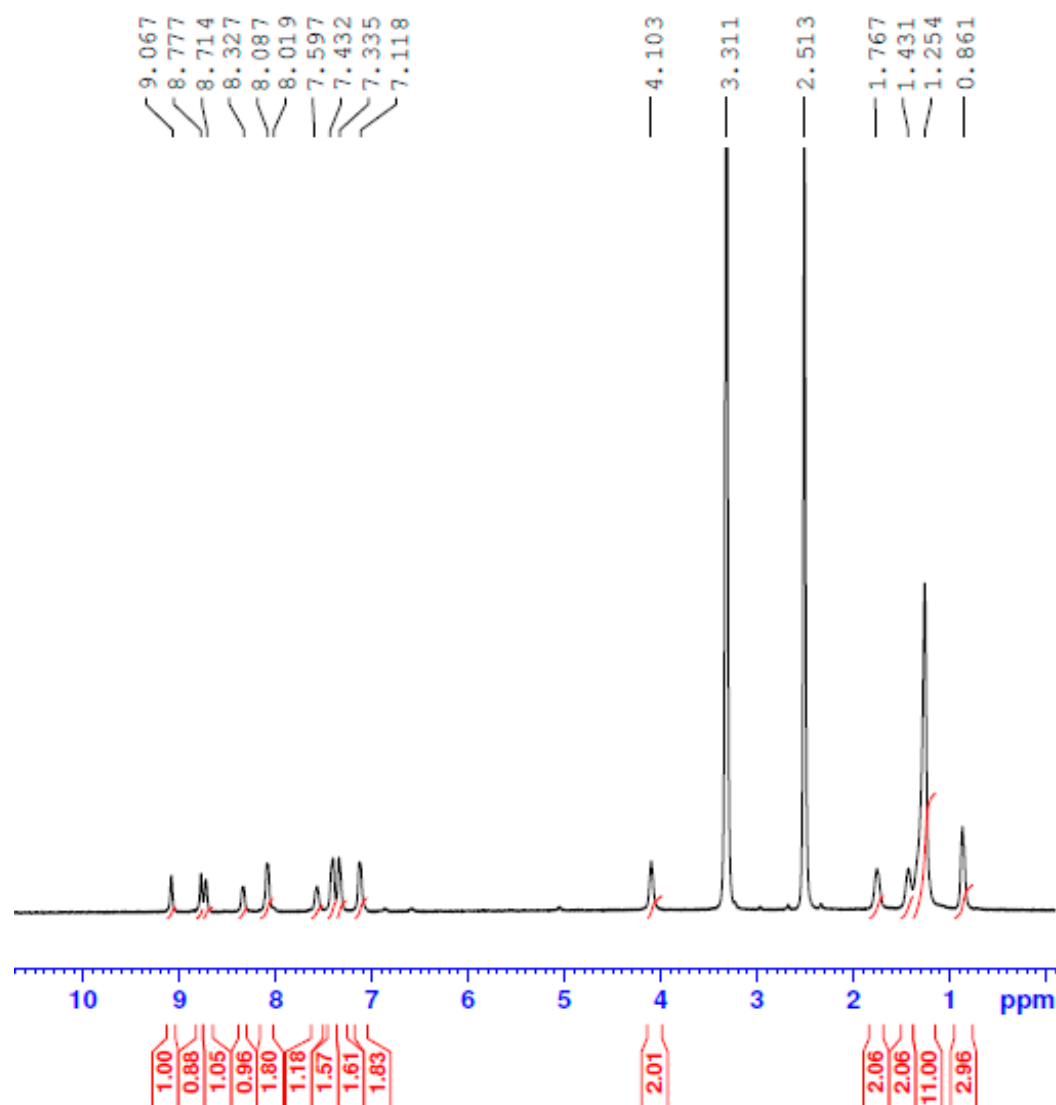


Figure S3. ^1H -NMR spectrum of T10



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 TD0 1

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Figure S4. ^1H -NMR spectrum of T12

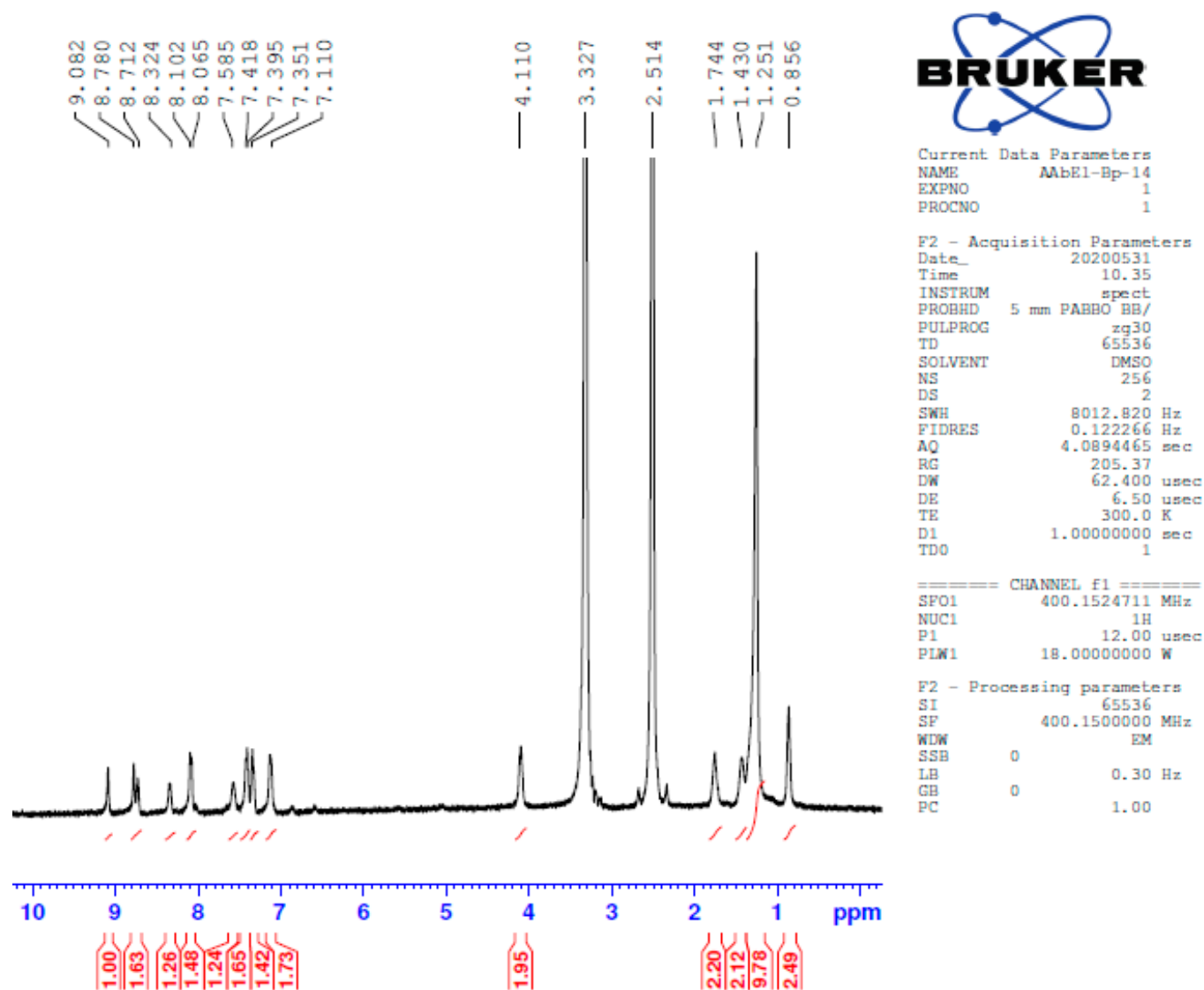
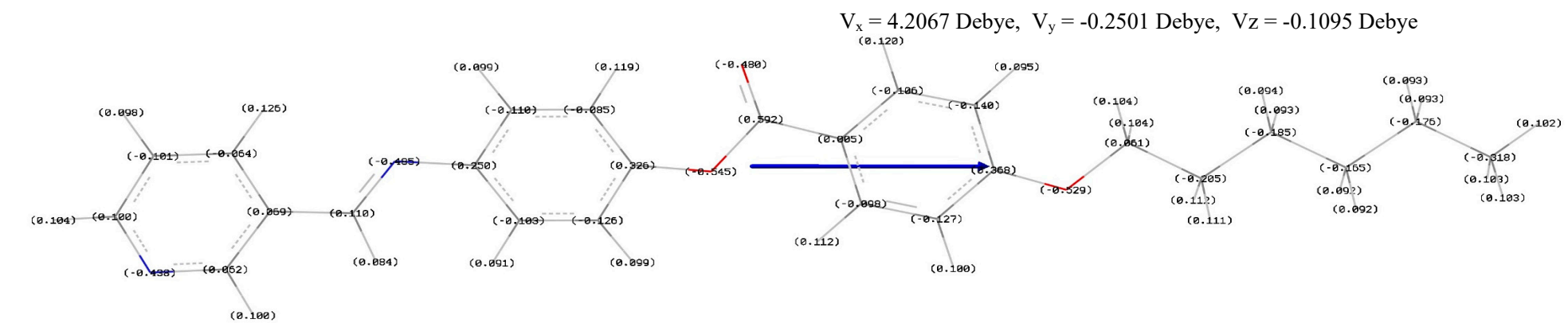
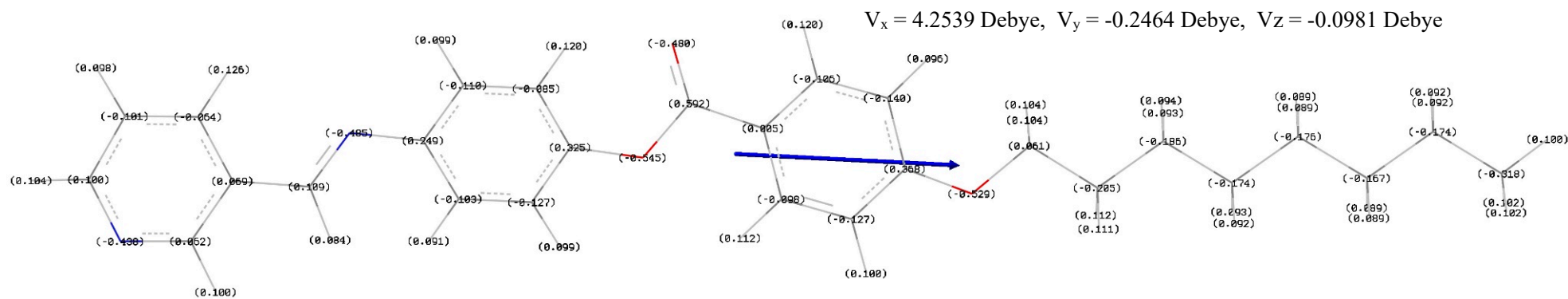


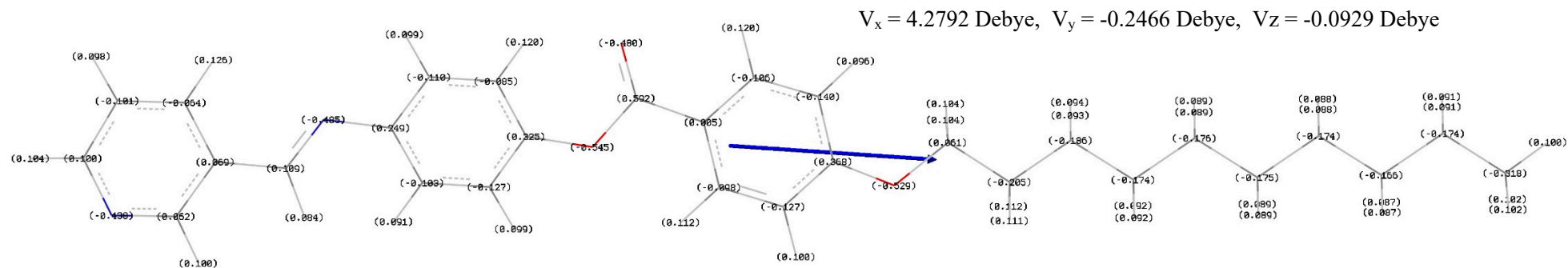
Figure S5. $^1\text{H-NMR}$ spectrum of T14



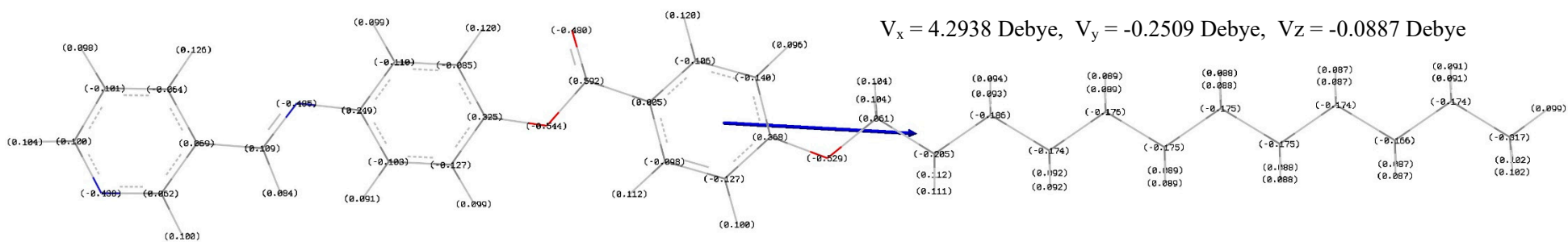
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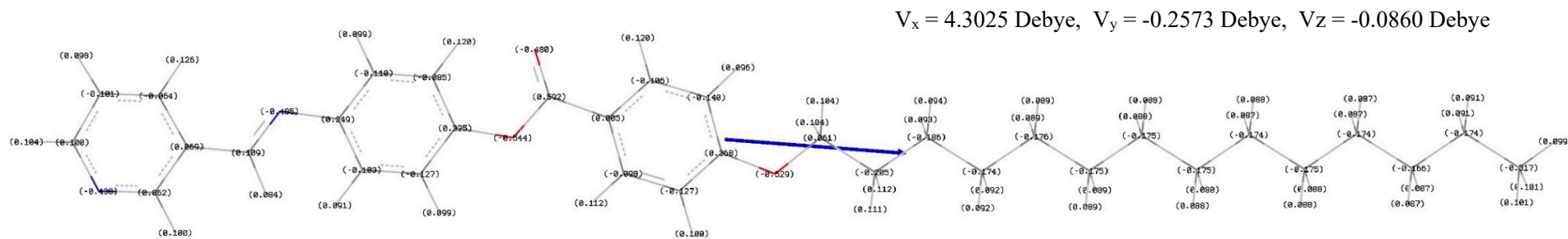
T8



T10



T12



T14

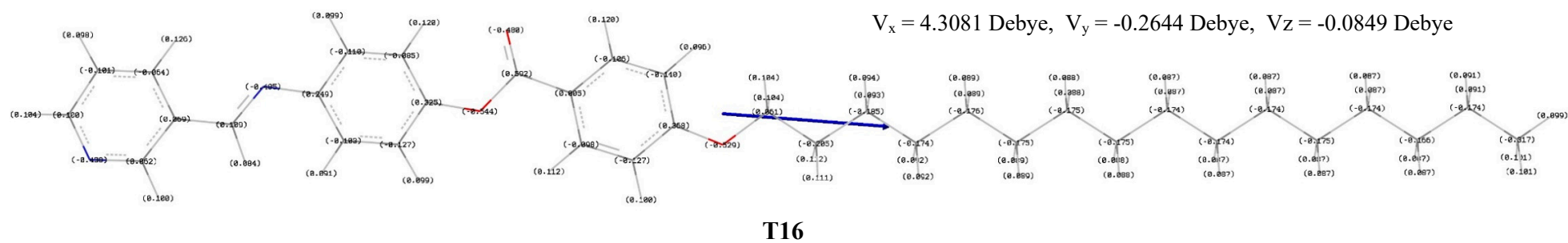


Figure S6. Atomic charges and dipole moment vectors, calculated at B3LYP/6-31G(d,p) level for the **T_n** series