

Effect of the relative positions of di-laterally substituted Schiff base derivatives: Phase transition and computational investigations

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1. Materials

4-Octyloxybenzoic acid, 4-dodecyloxybenzoic acid, 4-hydroxy-2-methoxy benzaldehyde, and 2-chloroaniline, were purchased from Sigma Aldrich (Germany) while the dichloromethane, *N,N'*-dicyclohexylcarbodiimide (DCC), ethanol and 4-dimethylaminopyridine (DMAP) were procured from Aldrich (Wisconsin, USA).

2. Synthesis of (E)-4-(((2-chlorophenyl)imino)methyl)-3-methoxyphenol (3)

A mixture of 4-hydroxy-2-methoxybenzaldehyde (1.52g, 10 mmol) and 2-chloroaniline (1.27g, 10 mmol) in ethanol (20 mL) was refluxed for two hours (monitored by TLC). The mixture was cooled to room temperature and then 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. The melting points and IR data of the prepared imine **3** were then recorded. Yield: 86%; mp 136 °C, FTIR (ν , cm^{-1}): 3039, 2921 (C-H), 1613 (C=N). ¹H-NMR (400 MHz, DMSO): δ /ppm: 3.81 (s, 3H, OCH₃), 5.17 (s, 3H, OH), 6.69-6.73 (m, 2H, Ar-H), 7.07-7.47 (m, 5H, Ar-H), 8.65 (s, 1H, CH=N). Anal. Calcd. for C₁₄H₁₂ClNO₂ (261.70): C, 64.25; H, 4.62; N, 5.35. Found: C, 64.09; H, 4.53; N, 5.27%.

3. Synthesis of (E)-4-(((2-Chlorophenyl)imino)methyl)-3-methoxyphenyl 4-(alkoxy)benzoate, In

A mixture of imine compound **3** (2.61g, 10 mmol) and the appropriate 4-alkoxy benzoic acid derivatives **4** (10 mmol for each) in dry methylene chloride (25 mL) containing *N,N'*-dicyclohexylcarbodiimide (DCC, 10 mmol) and few crystals of 4-dimethylaminopyridine (DMAP), as catalyst, were left to stand for 72 hours at room temperature with continuous stirring. The resulting solid was then filtered off while 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.

The physical data of products **I8** and **I12** are listed below:

(E)-4-(((2-Chlorophenyl)imino)methyl)-3-methoxyphenyl 4-(octyloxy)benzoate **I8**:

Yield: 91.3%; mp 110.0 °C, FTIR (ν , cm^{-1}): 3070, 2958, 2916 (C-H), 1743 (C=O), 1604 (C=N). ^1H -NMR (400 MHz, CDCl_3): δ /ppm: 0.91-0.95 (t, 3H, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{O}-$), 1.13-1.51 (m, 10H, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{O}-$), 1.78-1.85 (m, 2H, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{O}-$), 3.93 (s, 3H, OCH_3), 4.01-4.06 (t, 2H, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{O}-$), 6.94-6.96 (m, 2H, Ar-H), 7.25-7.68 (m, 6H, Ar-H), 7.76 (s, 1H, Ar-H), 8.23-8.25 (m, 2H, Ar-H), 8.47 (s, 1H, CH=N); ^{13}C -NMR (100 MHz, CDCl_3): δ /ppm: 14.09 (CH_3), 18.49, 22.68, 24.75, 25.54, 29.36, 31.73, 34.99 (CH_2), 58.22 (OCH_3), 68.37 ($\text{CH}_2\text{-O}$), 106.65, 110.56, 113.91, 115.04, 122.24, 122.88, 123.23, 129.16, 132.53, 135.43, 139.87, 142.67, 144.64, 149.45, 152.06 (Ar-C), 157.44 (C=N), 158.09 (Ar-C-OR), 163.99 (C=O). Anal. Calcd. for $\text{C}_{29}\text{H}_{32}\text{ClNO}_4$ (494.02): C, 70.51; H, 6.53; N, 2.84. Found: C, 70.70; H, 6.43; N, 2.69%.

(E)-4-(((2-Chlorophenyl)imino)methyl)-3-methoxyphenyl 4-(dodecyloxy)benzoate **I12**:

Yield: 93.9 %; mp 107.0 °C, FTIR (ν , cm^{-1}): 3057, 2955, 2915 (C-H), 1739 (C=O), 1604 (C=N). ^1H -NMR (400 MHz, CDCl_3): δ /ppm: 0.90-0.93 (t, 3H, $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{CH}_2\text{O}-$), 1.10-1.16 (m, 18H, $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{CH}_2\text{O}-$), 1.71-1.79 (m, 2H, $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{CH}_2\text{O}-$), 3.89 (s, 3H, OCH_3), 4.00-4.03 (t, 2H, $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{CH}_2\text{O}-$), 6.92-6.95 (m, 2H, Ar-H), 7.15-7.62 (m, 6H, Ar-H), 7.76 (s, 1H, Ar-H), 8.16-8.18 (m, 2H, Ar-H), 8.46 (s, 1H, CH=N). Anal. Calcd. for $\text{C}_{33}\text{H}_{40}\text{ClNO}_4$ (550.13): C, 72.05; H, 7.33; N, 2.55. Found: C, 71.85; H, 7.48; N, 2.37%.

4. Characterization

The IR spectra were measured on a Pye-Unicam SP300 instrument in potassium bromide discs. NMR spectra were acquired on a Bruker Avance 400 instrument at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR with tetramethyl silane as internal standard in CDCl_3 ; the chemical shift values recorded as (ppm units) and coupling constants as J (Hz units). (JEOL, Tokyo, Japan). Thermo Scientific Flash 2000 CHS/O Elemental Analyzer, Milan, Italy was used for Elemental analyses.

TA Instruments Co. (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 were measured for the second heating scan.

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

5. Computational details

The structures of investigated compounds were completely optimized without geometrical constraint utilizing GAUSSIAN 09 program [41]. The convergence nature of the compounds was ensured by frequency calculation which established all the frequencies to be real. Moreover the molecular electrostatic potential surfaces and the Frontier molecular orbitals were obtained from the optimized structures' formatted check (.Fchk) files. All the density functional theory (DFT) calculations were conducted using B3LYP method [42, 43] with the basis set of 6-31g(d,p).

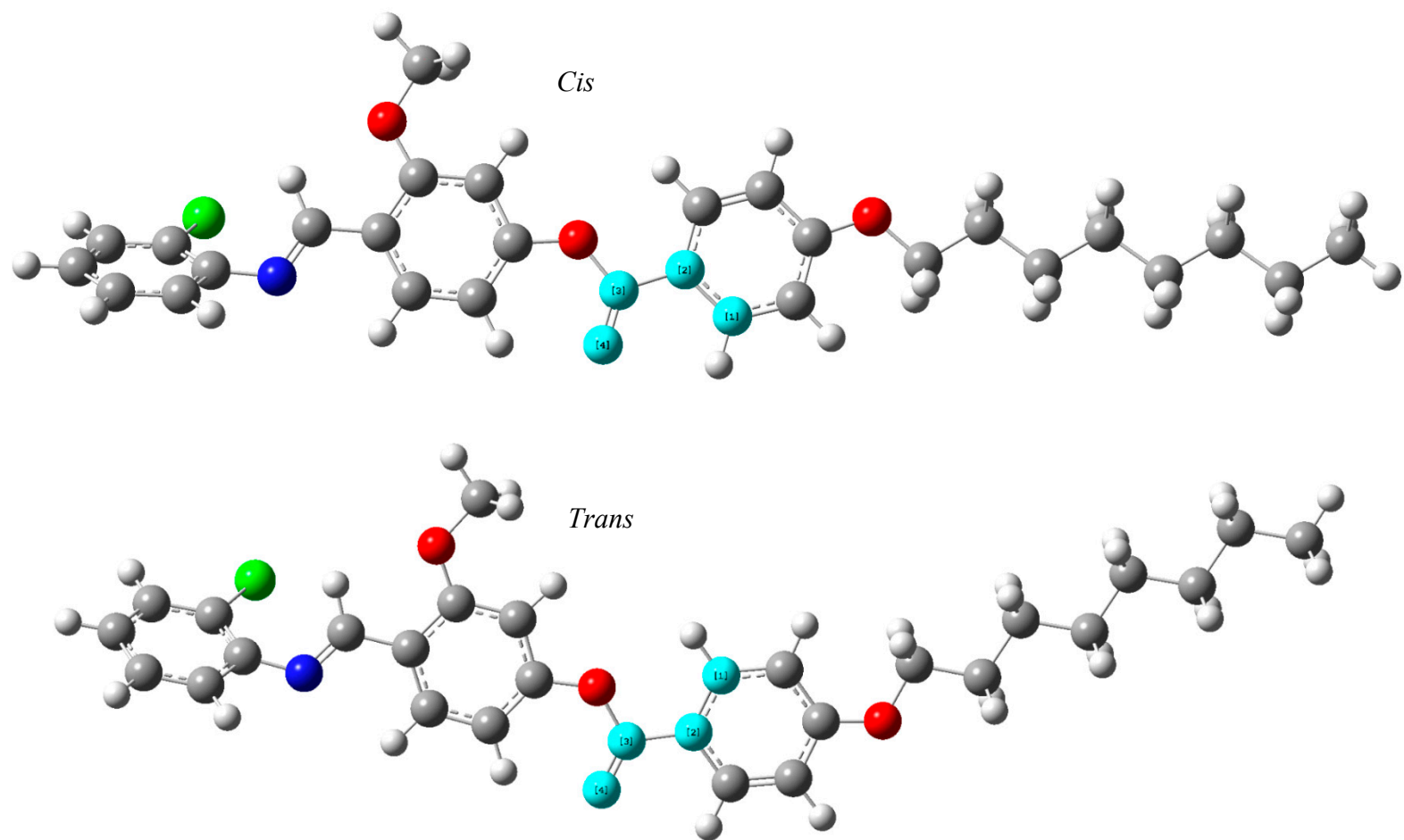
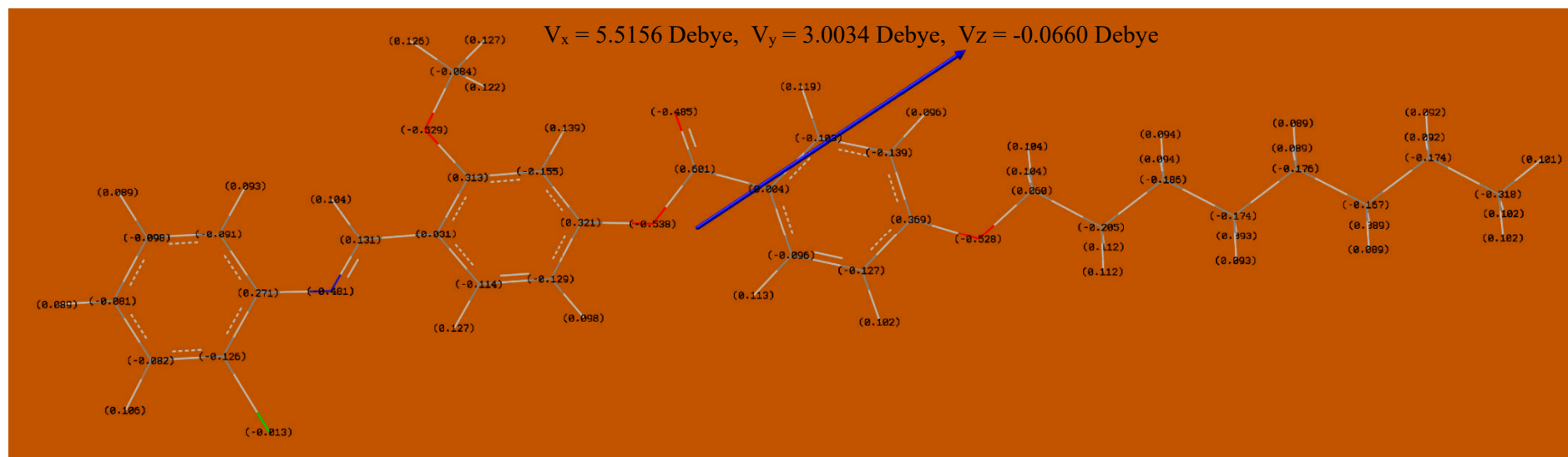
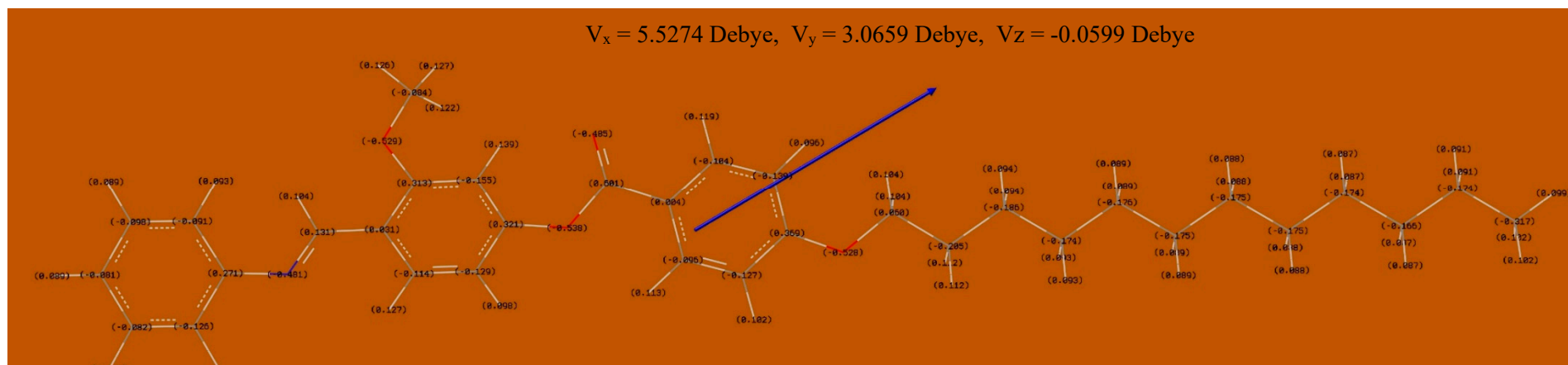


Figure S1. The geometry of C=O established from the potential energy of C-C-C=O dihedral angle of **I8** derivative.



I8



I12

Figure S2. Atomic charges and dipole moment vectors, calculated at B3LYP/6-31G(d,p) level for the **I8** and **I12** derivatives.

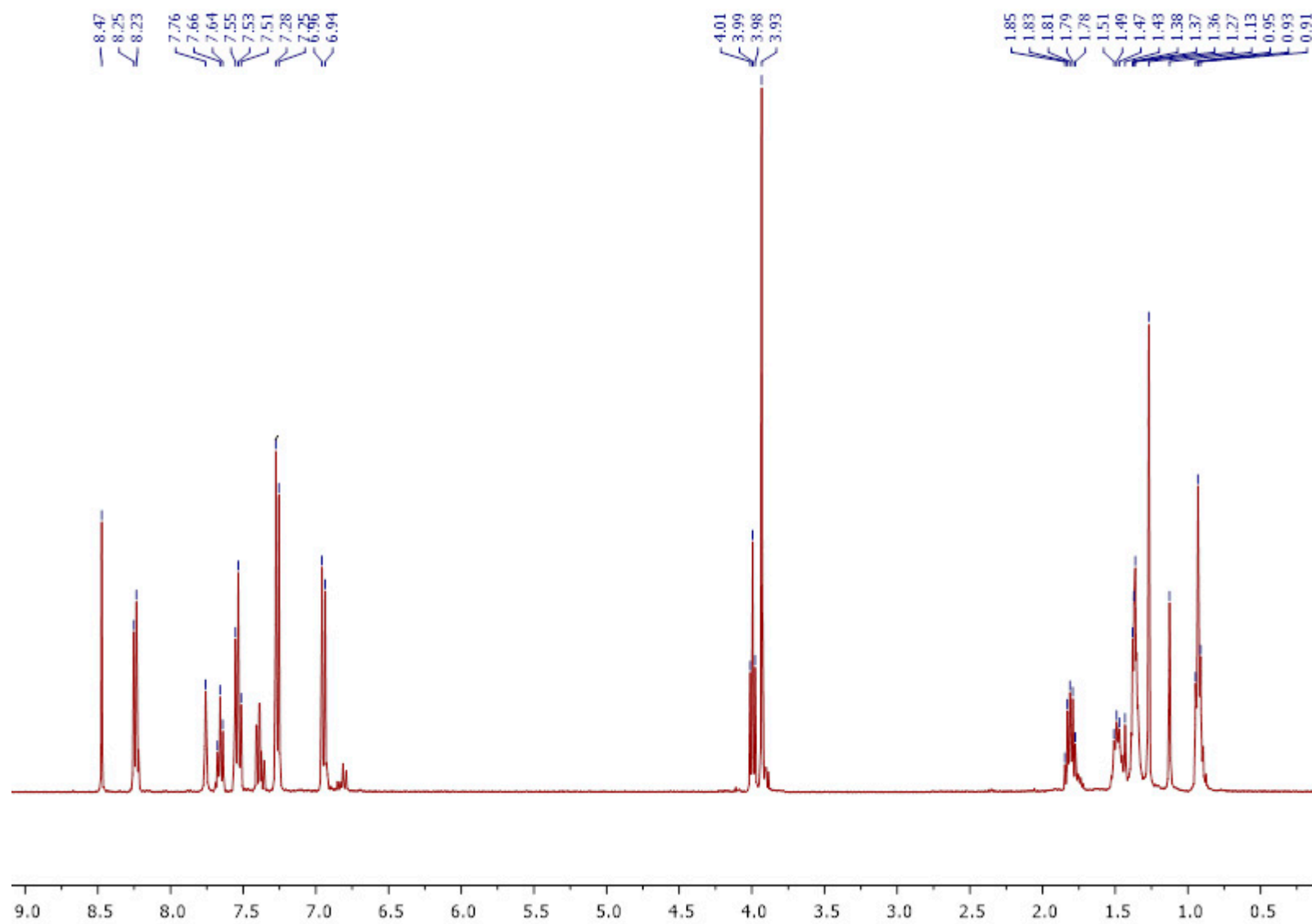


Figure S3. ¹H-NMR spectra of compound I8.

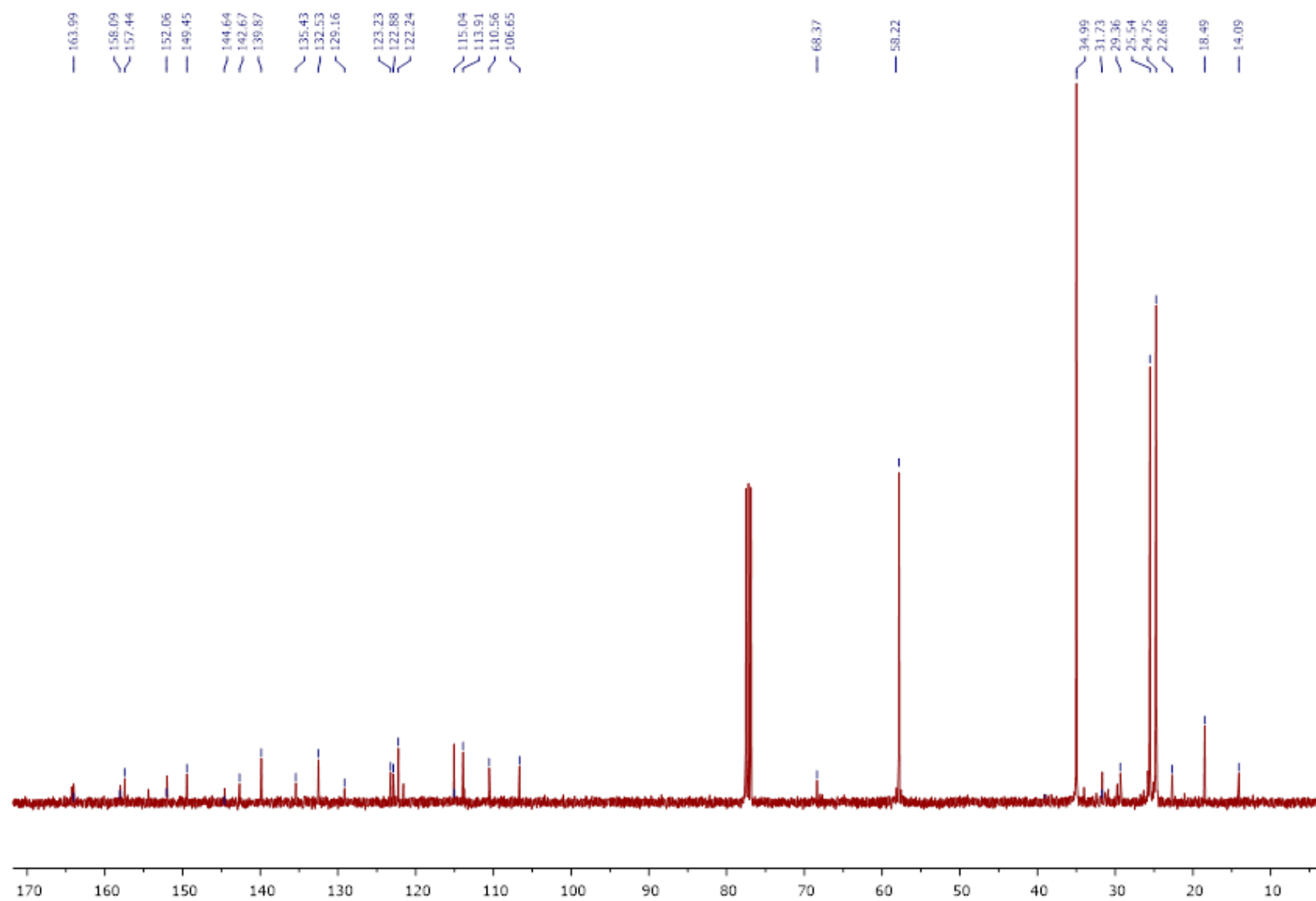


Figure S4. ^{13}C -NMR spectra of compound **18**.

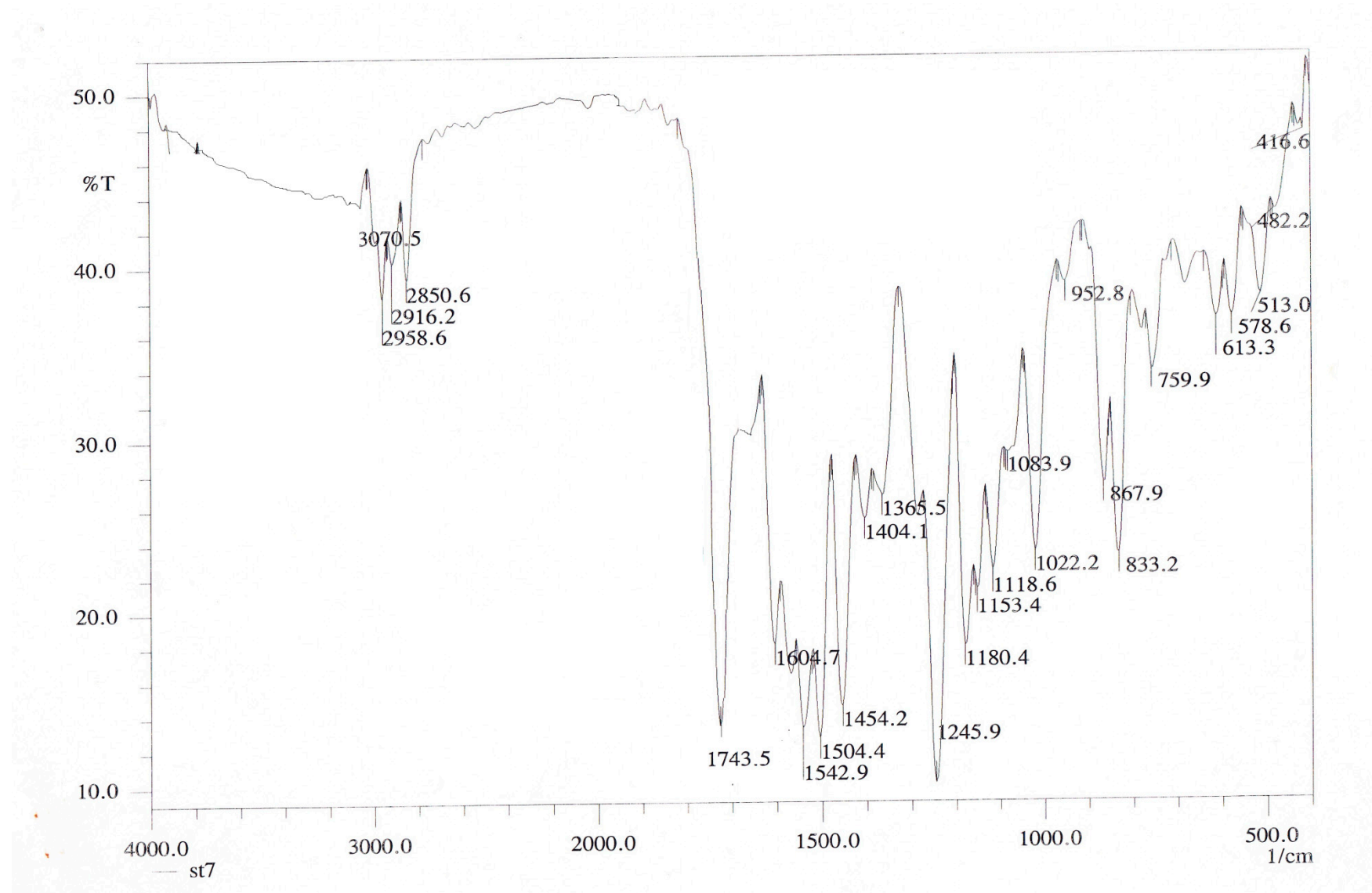


Figure S5. IR spectra of compound I8.