Electronic Supplementary Information

Azulene-Based Conjugate Polymers: Unique Seven-Membered Ring Connectivity Leading to Stimuli-Responsiveness

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General Procedures.

Chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF) and dichloromethane (DCM) were purchased from Fisher Scientific, and were all purified by passage under N2 pressure through two packed columns of neutral alumina. 4,7-Dibromo-6-dodecylazulene **M1,**[S1] 4,7-dibromoazulene **M3**,[S1] and 1,3-polyazulene **P4**[S2] were prepared according to the procedure reported previously. Flash chromatography was performed using silica gel (particle size 40-63 μm) or basic alumina (particle size 50-200 μm). All compounds were characterized by ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) on Varian 600 instruments with the solvent signal as internal reference with the spectra being acquired at room temperature. Chemical shifts and coupling constants are reported in ppm and in Hz, respectively. Microwave assisted reactions were conducted on a Biotage Microwave reactor at a frequency of 2.5 GHz. High-resolution mass spectrometry (HRMS) was performed on a Waters GCT Premier Time of Flight Mass Spectrometer equipped with a field ionization source (12000 V extraction voltage), and the values reported represent the most abundant molecular ion. VG70 Magnetic Sector and Waters GCT Premier TOF instruments were used for low and high resolution mass analysis by electron ionization (EI). For polymer molecular weight determination, polymer samples were dissolved in chloroform at a concentration of 1 mg/ml, briefly heated and then allowed to return to room temperature prior to filtering through a 0.45 μm filter. Gel permeation chromatography (GPC) was performed in chloroform on a Waters 2690 Separation Module equipped with a Waters 2414 Refractive Index Detector. Molecular weights were calculated relative to linear PS standards. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of 10 °C/min. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 with a Universal ATR sampling accessory. UV-vis spectra were recorded on an Agilent 8453 spectrophotometer using quartz cuvettes and dichloromethane as a solvent.

Synthesis of 4,7-dibromo-1-hexylazulene M2 (Scheme S1).

To a solution of 2,5-dibromo-3-hexylthiophene-*S*,*S*-dioxide[S1] (2.51 g, 7.0 mmol) in 20 ml of CH_2Cl_2 was added dimethylaminofulvene[S3] (852 mg, 7.0 mmol) dissolved in 5 ml of CH_2Cl_2 at 0 ^oC over a period of 30 mins. After stirring the mixture at 0 ^oC for 2 h, an additional dimethylaminofulvene (7.0 mmol) in CH_2Cl_2 was added. Stirring was continued at 0 ^oC for 2 h then at room temperature overnight. The reaction mixture was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with water and dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on basic alumina with hexane as an eluent to afford 4,7-dibromo-6-hexylazulene **M2** (829 mg, 2.2 mmol, 32% yield) as a blue solid. ^1H NMR (600 MHz, $CDCl_3$, ppm): δ 0.92 (t, J = 7.8 Hz, 3H), 1.33-1.39 (m, 4H), 1.46 (q, J = 7.8 Hz, 2H), 1.71 (q, J = 7.8 Hz, 2H), 3.00 (t, J = 7.8 Hz, 2H), 7.36 (d, J = 3.6 Hz, 1H), 7.52 (d, J = 3.6 Hz, 1H), 7.63 (s, 1H), 7.85 (t, J = 3.6 Hz, 1H), 8.70 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 14.1, 22.6, 29.2, 30.6, 31.6, 44.9, 120.2, 121.2, 122.3, 128.5, 133.1, 134.9, 136.3, 138.3, 140.9, 149.2. HRMS (EI): m/z $[M]^+$ calcd for $C_{16}H_{18}Br_2$ 367.9775; found, 367.9792.

Synthesis of 4,7-diethynyl-6-dodecylazulene 6 (Scheme S2).

To a Schlenk tube charged with 4,7-dibromo-6-dodecylazulene **M1**[S1] (136 mg, 0.30 mmol), $Pd(PPh_3)_4$ (10 mg, 0.0090 mmol), CuI (3.4 mg, 0.018 mmol) was added *i*-Pr_2NH (3 mL) and toluene (8 mL), and degassed by the three freeze pump thaw cycles. Trimethylsilylacetylene (89 mg, 0.90 mmol) was then added slowly over a period of 2 h at 70 ^oC under an argon atmosphere. The

reaction mixture was stirred at 70 °C for a further 15 h and then quenched with a saturated aqueous NH_4Cl solution. The aqueous layer was extracted with CH_2Cl_2 (20 mL × 3), and the combined organic layer was washed with brine followed by drying over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on silica gel with hexane as an eluent to afford 4,7-bis(trimethylsilylethynyl)-6-dodecylazulene **5** (146 mg, 0.30 mmol, quant) as a blue solid. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 0.31 (s, 9H), 0.37 (s, 9H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.26-1.33 (m, 14H), 1.37 (q, *J* = 7.2 Hz, 2H), 1.45 (q, *J* = 7.2 Hz, 2H), 1.75 (q, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 7.32 (s, 1H), 7.33 (d, *J* = 3.6 Hz, 1H), 7.59 (d, *J* = 3.6 Hz, 1H), 7.79 (t, *J* = 3.6 Hz, 1H), 8.48 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ -0.09, 0.01, 14.1, 22.7, 29.4, 29.60, 29.64, 29.67, 29.68, 29.7, 30.1, 31.6, 31.9, 42.2, 98.0, 101.5, 106.2, 107.7, 117.6, 120.1, 120.9, 128.3, 128.8, 136.8, 137.2, 137.8, 140.7, 153.6. HRMS (EI): m/*z* $[M]^+$ calcd for $C_{32}H_{48}Si_2$ 488.3305; found, 488.3295.

To a solution of **5** (146 mg, 0.30 mmol) in THF (2 mL) and MeOH (5 mL) was added K_2CO_3 (83 mg, 0.60 mmol) and stirred at rt for 2 days. The reaction mixture was quenched with a saturated aqueous NH_4Cl solution, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with water and dried over $MgSO_4$ followed by filtration. The organic solvent was removed under reduced pressure to afford 4,7-diethynyl-6-dodecylazulene **6** (103 mg, 0.30 mmol, quant) as a blue solid. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.25-1.32 (m, 14H), 1.35 (q, *J* = 7.2 Hz, 2H), 1.43 (q, *J* = 7.2 Hz, 2H), 1.74 (q, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.2 Hz, 2H), 3.38 (s, 1H), 3.58 (s, 1H), 7.34 (s, 1H), 7.35 (d, *J* = 3.6 Hz, 1H), 7.64 (d, *J* = 3.6 Hz, 1H), 7.82 (t, *J* = 3.6 Hz, 1H), 8.51 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 14.1, 22.7, 29.3, 29.4, 29.5, 29.64, 29.65, 29.67, 29.7, 31.5, 31.9, 41.8, 80.8, 83.1, 84.8, 85.9, 116.8, 120.3, 121.1, 128.0, 128.5, 137.3, 137.4, 137.8, 140.9, 153.7. HRMS (EI): m/*z* $[M]^+$ calcd for $C_{26}H_{32}$ 344.2504; found, 344.2490.

Optimization of the Homopolymerization Conditions for M1.

A solution of 4,7-dibromo-6-dodecylazulene **M1**[S1] (22.6 mg, 0.050 mmol), palladium or nickel complexes, ligands in dry solvent (2 mL) was stirred under the conditions specified in Tables S1 and S2. The reaction was quenched with *dil*. HCl *aq*. and organic solvent was removed under reduced pressure. The resulting solid was washed with MeOH, then M_n and PDI were checked by GPC.

General Procedure for Yamamoto Dehalogenative Polymerization of M1-M3.

In a drybox, a 5 mL glass vial was charged with 4,7-dibromoazulene **M1**-**M3** (0.10 mmol), $Ni(cod)_2$ (33 mg, 0.12 mmol), bipyridine (19 mg, 0.12 mmol), 1,5-cyclooctadiene (13 mg, 0.12 mmol), and DMF (1 mL). The vial was sealed with a cap and taken out of the drybox, then placed into a microwave reactor and heated at 150 ^{o}C for 1 h with stirring. The reaction was quenched with *dil*. HCl *aq*. and organic solvent was removed under reduced pressure. The residue was dissolved in a minimum volume of CH_2Cl_2 and added into excess methanol with vigorous stirring. The obtained precipitate was washed successively with a warm solution of EDTA and water, and then filtered. Soxhlet extractions with MeOH followed by hexanes removed catalytic residues and low-molecular weight materials. Polymers were then extracted with $CHCl_3$. Insoluble black solid residue was observed in the Soxhlet extractor in all cases. The solvent was reduced to about 1 mL and the mixture was poured into cold methanol. **P1**-**P3** was finally dried under vacuum at 60 °C for overnight.

4,7-Poly(6-dodecylazulene) P1. Yield: 72%. GPC ($CHCl_3$): M_n = 7.2 K; M_w = 13.9 K; PDI = 1.9. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ0.78-0.94 (m, 3H), 0.94-1.48 (m, 18H), 1.48-1.82 (m, 2H), 2.57-2.94 (m, 2H), 6.88-7.04 (m, 1H), 7.29-7.56 (m, 2H), 7.60-7.88 (m, 1H), 8.40-8.54 (m, 1H).

4,7-Poly(6-hexylazulene) P2. Yield: 79%. GPC ($CHCl_3$): M_n = 6.6 K; M_w = 14.5 K; PDI = 2.2. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ0.73-1.92 (m, 11H), 2.63-2.91 (m, 2H), 6.92-7.12 (m, 1H), 7.35-7.52 (m, 2H), 7.60-7.92 (m, 1H), 8.38-8.59 (m, 1H).

4,7-Polyazulene P3. Yield: 60%. GPC ($CHCl_3$): M_n = 2.4 K, M_w = 5.0 K, PDI = 2.1. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ7.01-7.32 (m, 1H), 7.42-7.68 (m, 2H), 7.82-8.16 (m, 2H), 8.82-8.93 (m, 1H).

Synthesis of Poly[1,2-ethynyl-*alt*-4',7'-(6'-dodecylazulenyl)] P4 (Scheme S3).

To a Schlenk tube charged with 4,7-dibromo-6-dodecylazulene **M1**[S1] (45 mg, 0.10 mmol), $Pd(PPh_3)_4$ (6.0 mg, 0.0050 mmol), CuI (1.9 mg, 0.010 mmol) was added *i*-Pr_2NH (1.0 mL) and toluene (1.0 mL) was degassed by the three freeze pump thaw cycles. 4,7-Bisethynyl-6-dodecyl-azulene **5** (34 mg, 0.10 mmol) in toluene (1.0 mL) was then added and the reaction mixture was stirred at 70 ^oC for 15 h. The mixture was poured into MeOH and the resulting precipitate was isolated by filtration. The obtained precipitate was filtered, and extracted with MeOH followed by hexanes to remove catalytic residues and low-molecular weight materials. Polymer was then extracted with $CHCl_3$. The solvent was reduced to about 1 mL and the mixture was poured into cold methanol. The resulting solid was dried under vacuum at 60 °C for overnight to afford poly[1,2-ethynyl-*alt*-4',7'-(6'-dodecylazulenyl)] **P4** (48 mg, 76% yield) as a green solid. GPC ($CHCl_3$): M_n = 6.6 K; M_w = 11.9 K; PDI = 1.8. ^1H NMR (600 MHz, $CDCl_3$, ppm): δ 0.83-0.92 (m, 3H), 1.16-1.37 (m, 18H), 1.43-1.68 (m, 2H), 3.03-3.09 (m, 1H), 3.24-3.33 (m, 1H), 7.33-7.35 (m, 1H), 7.45-7.55 (m, 1H), 7.63-7.79 (m, 1H), 7.86-7.92 (m, 1H), 8.73-8.77 (m, 1H).

Synthesis of Poly[2,5-thienyl-*alt*-4',7'-(6'-dodecylazulenyl)] P5 (Scheme S4).

To a Schlenk tube charged with 4,7-dibromo-6-dodecylazulene **M1**[S1] (45 mg, 0.10 mmol), 2,5-di(trimethylstannyl)thiophene (41 mg, 0.10 mmol), Pd_2dba_3 (4.6 mg, 0.0050 mmol), P(*o*-Tol)$_3$ (6.0 mg, 0.020 mmol), CsF (45 mg, 0.30 mmol), and DMF (2 mL) was stirred at 100 ^oC for 15 h under an argon atmosphere. The reaction was quenched with *dil*. HCl *aq*. and organic solvent was

removed under reduced pressure. The residue was dissolved in a minimum volume of CH_2Cl_2 and added into excess methanol with vigorous stirring. The obtained precipitate was filtered, and extracted with MeOH followed by hexanes to remove catalytic residues and low-molecular weight materials. Polymer was then extracted with $CHCl_3$. The solvent was reduced to about 1 mL and the mixture was poured into cold methanol. The resulting solid was dried under vacuum at 60 °C for overnight to afford poly[2,5-thienyl-*alt*-4',7'-(6'-dodecylazulenyl)] **P5** (23 mg, 62% yield) as a green solid. GPC ($CHCl_3$): M_n = 5.1 K; M_w = 9.7 K; PDI = 1.4. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 0.81-0.89 (m, 3H), 1.16-1.31 (m, 18H), 1.64-1.83 (m, 2H), 2.63-2.86 (m, 1H), 2.92-2.98 (m, 1H), 7.04-7.19 (m, 1H), 7.39-7.49 (m, 3H), 7.65-7.91 (m, 2H), 8.58-8.67 (m, 1H).

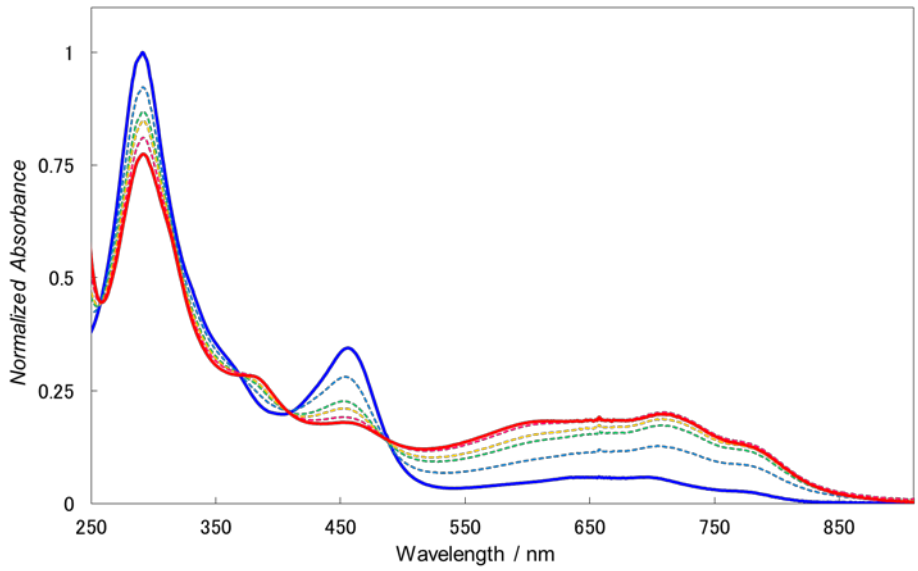
Theoretical Calculations.

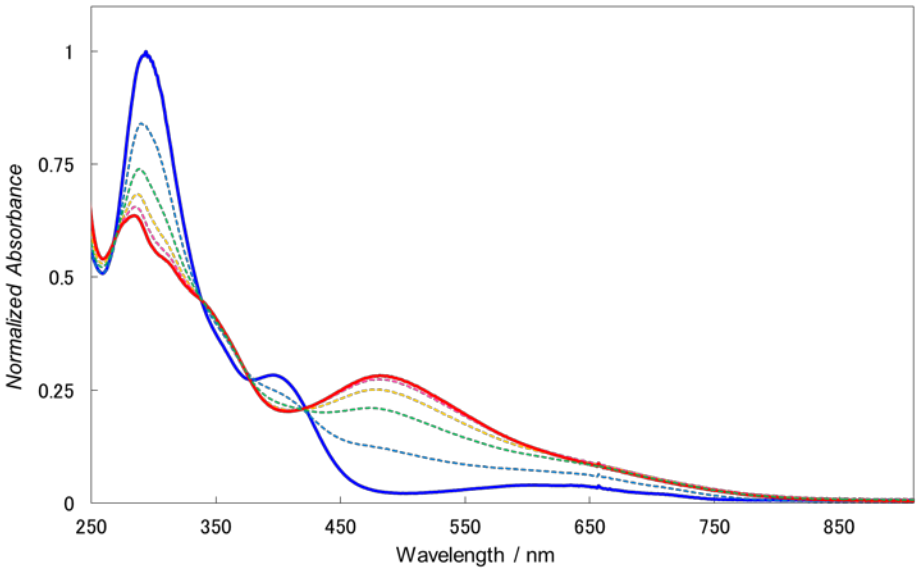
Geometry optimizations were carried out using the Gaussian 09 quantum chemistry program package[S4] at the B3LYP functional.[S5] All compounds were fully optimized with the 6-31G* basis set.[S6] Plots of molecular orbitals and spin densities were constructed using the MOLEKEL program 4.1.[S7]

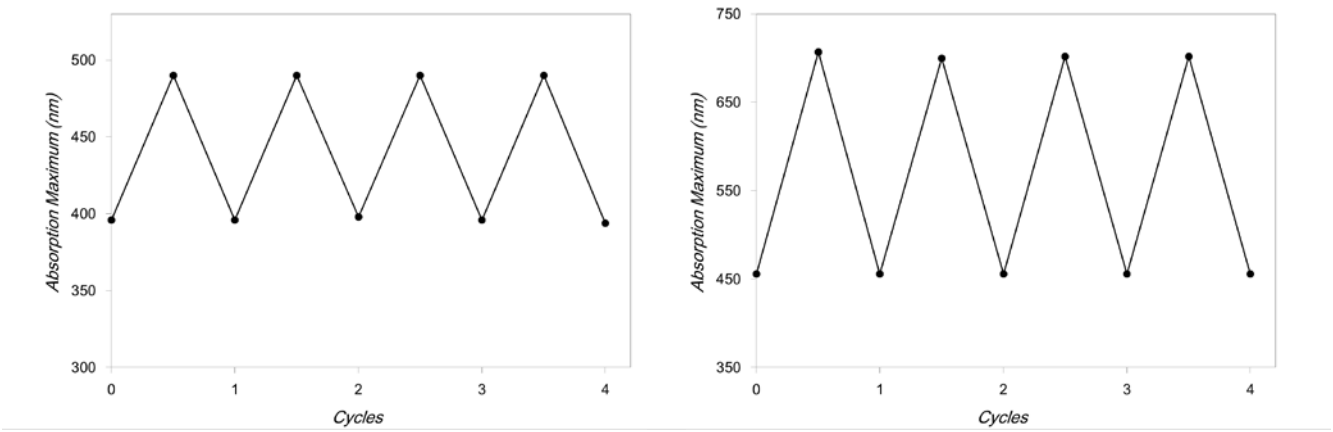
Cartesian Atomic Coordinates for the Geometry Optimized Structure

UV-Vis Titration Curves for P4 and P5.

To avoid dilution effect, paralleled samples were prepared by adding TFA to the stock solutions of **P4** and **P5** in CH_2Cl_2 at rt, respectively. Additional CH_2Cl_2, if needed, is added to ensure that the final polyazulene concentrations of all samples are identical.







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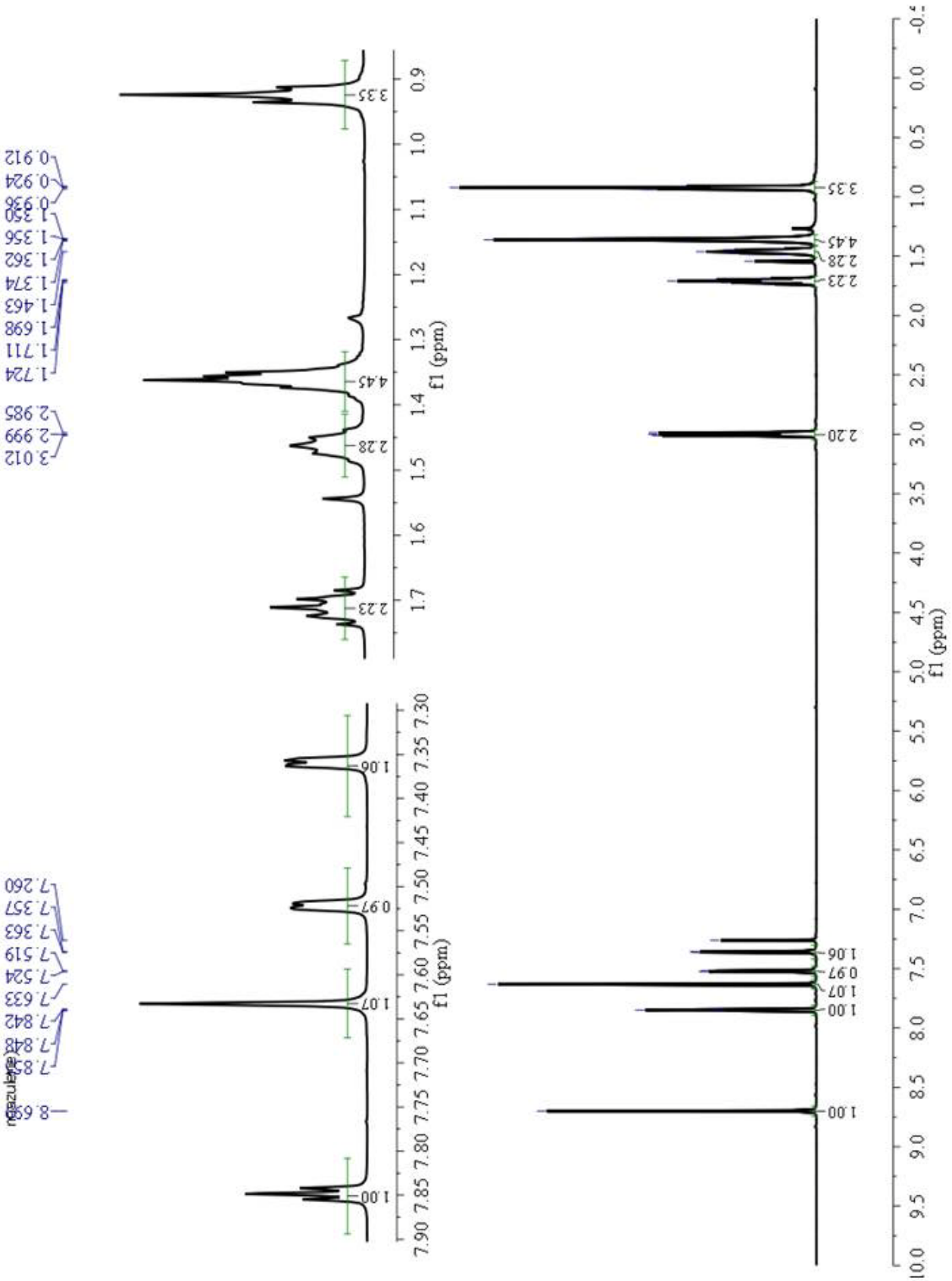
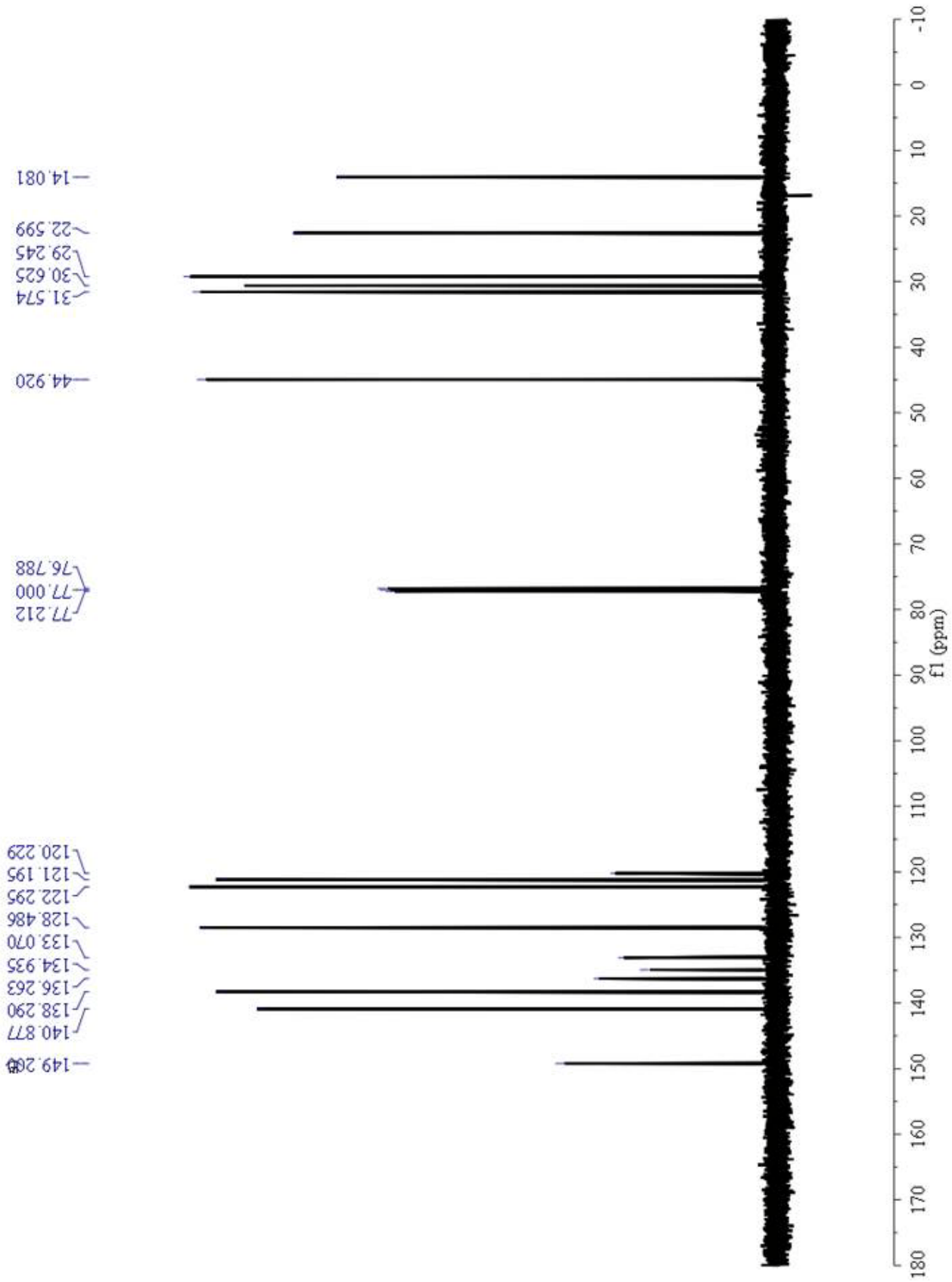
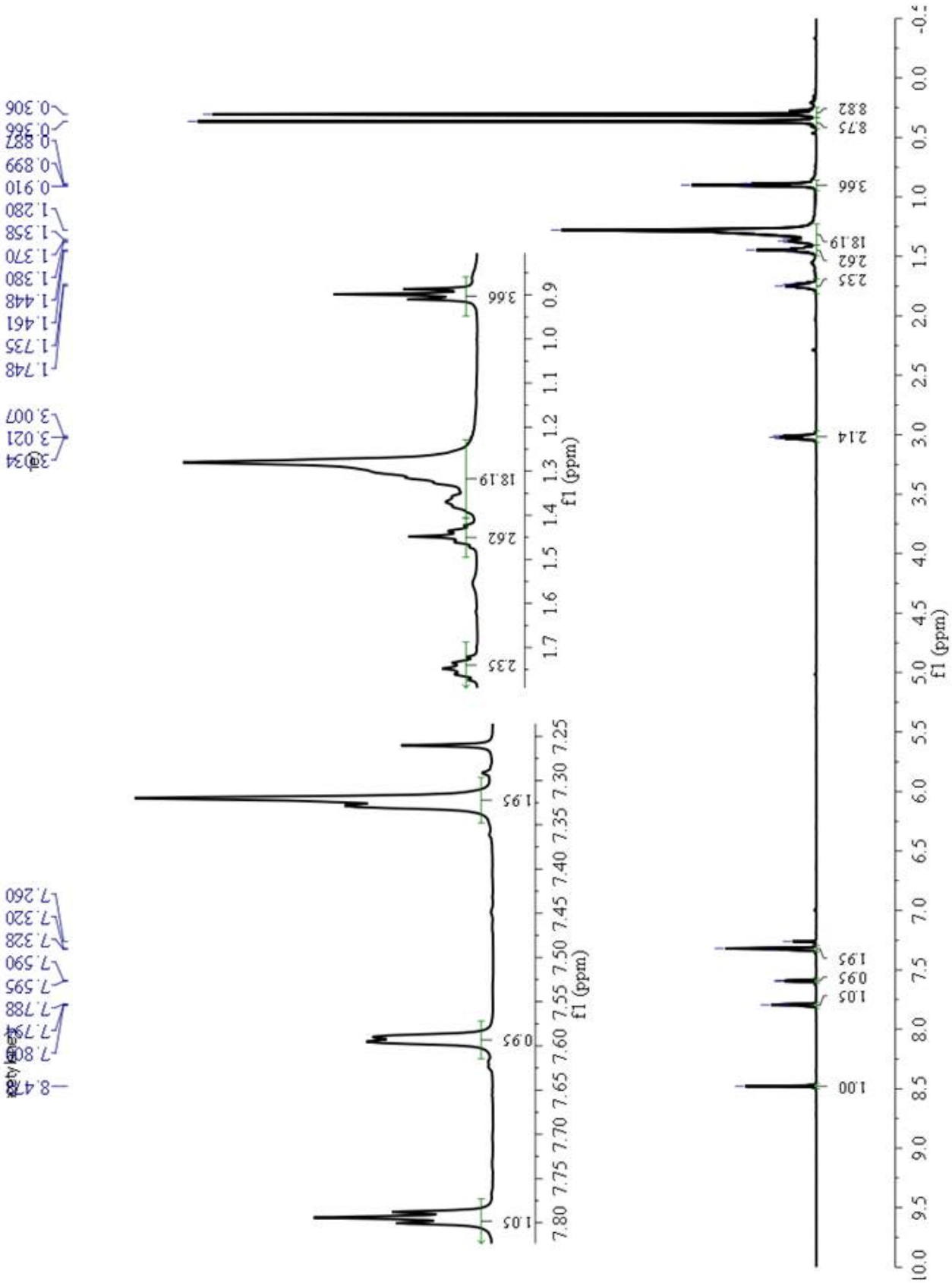
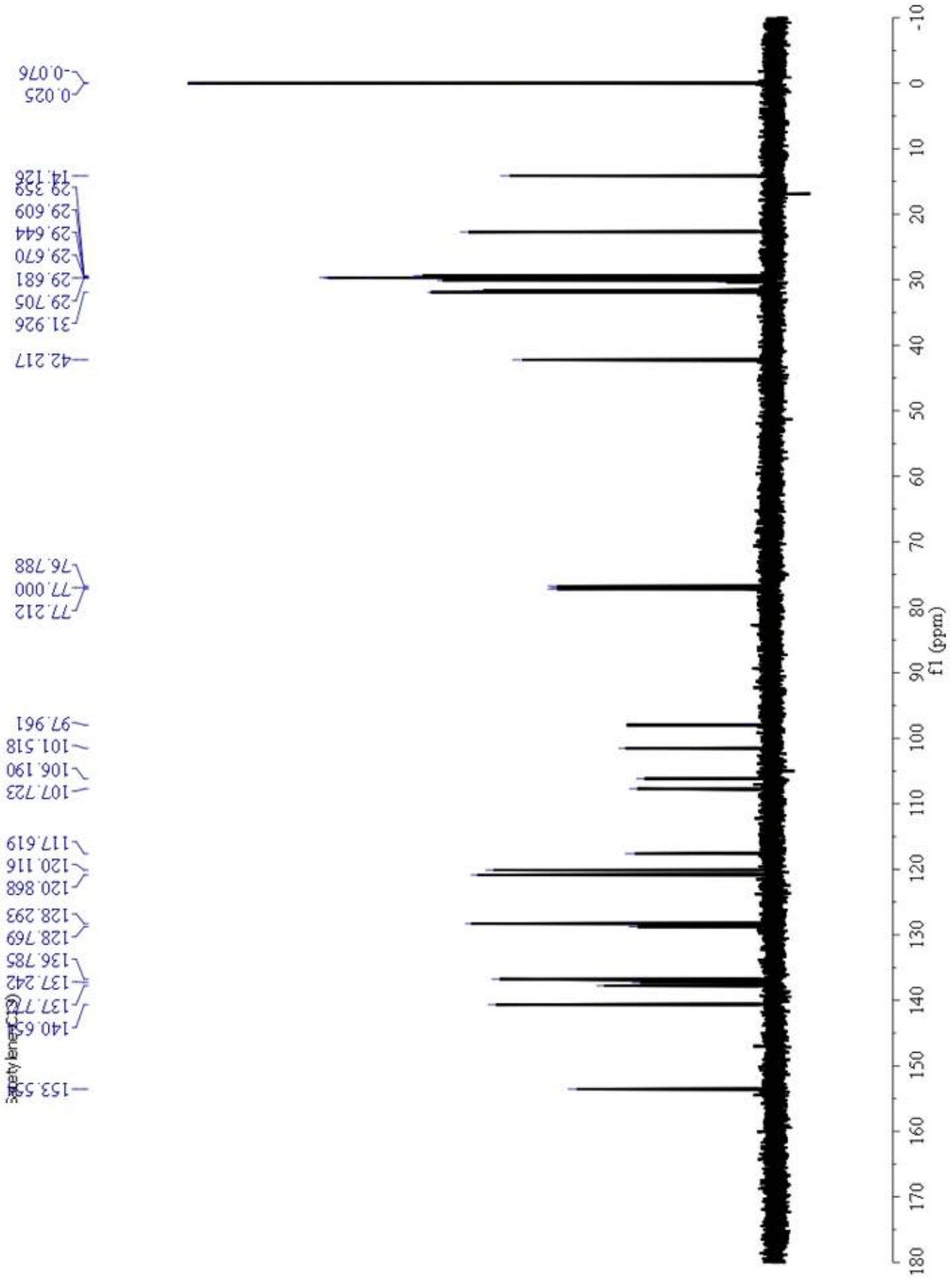
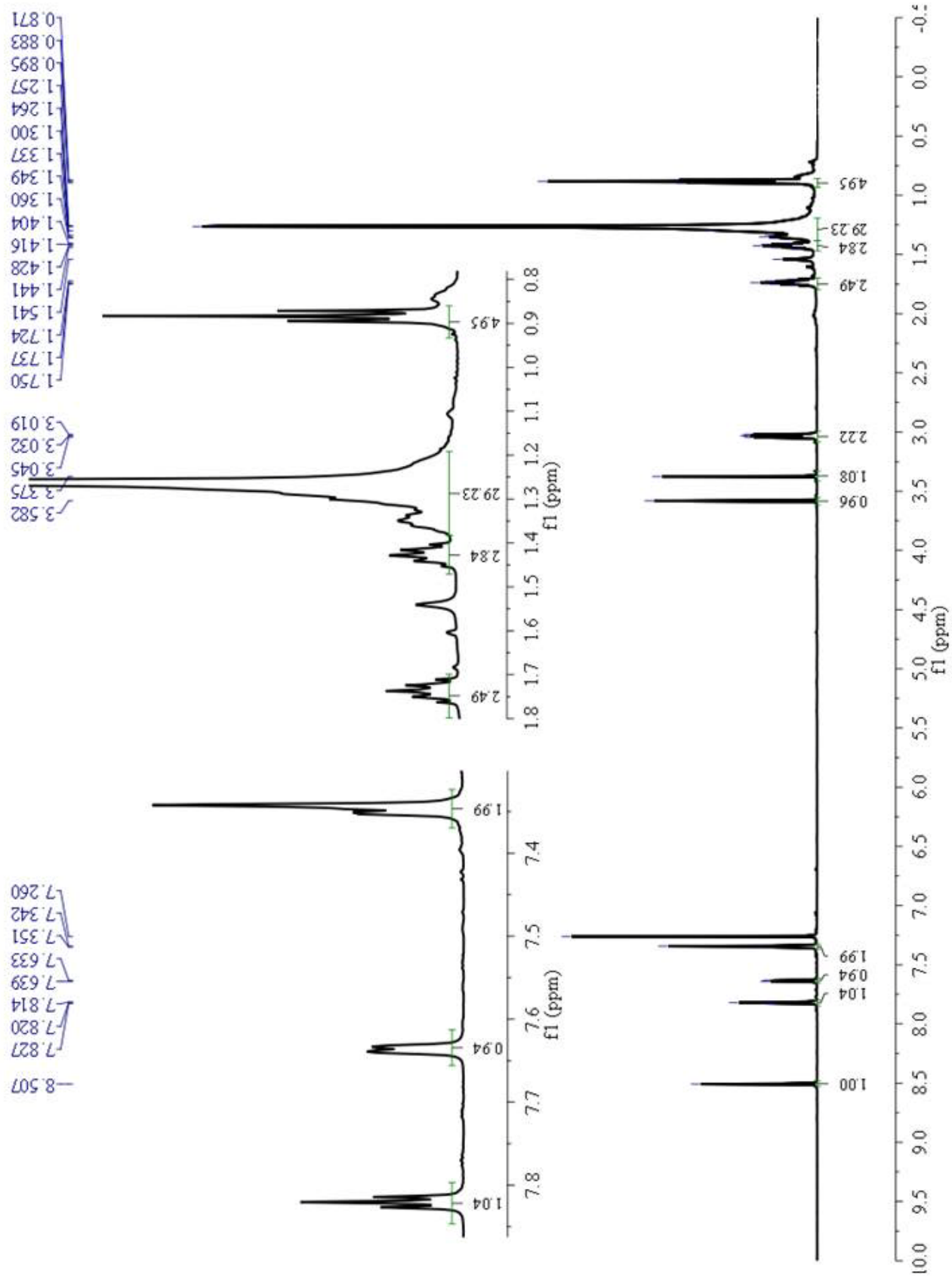
^{1}H NMR and ^{13}C NMR Spectra of Selected Compounds







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