

Synthesis, Molecular and Photovoltaic/Transistor Properties of Heptacyclic Ladder-Type Di(thienobenzofluorene)-Based Copolymers

Chia-Hao Lee^a, Yu-Ying Lai^{a,b}, Fong-Yi Cao^a, Jhih-Yang Hsu^a, Zong-Liang Lin^a, U-Ser Jeng^c, Chun-Jen Su^c and Yen-Ju Cheng^{a*}

^aDepartment of Applied Chemistry, National Chiao Tung University, 1001 University Road, Hsin-Chu, 30010 Taiwan, ROC.

^bInstitute of Polymer Science and Engineering, National Taiwan University, Taipei, 10617 Taiwan.

^cNational Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsin-Chu Science Park, Hsin-Chu 30076 Taiwan.

*Email: yjcheng@mail.nctu.edu.tw

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1. General measurement and characterization.

^1H and ^{13}C NMR spectra were measured by Varian 400 MHz instrument spectrometer in deuterated chloroform (CDCl_3) with tetramethylsilane as internal reference unless otherwise stated and chemical shifts (δ) are reported in parts per million. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) with a PN5300 of Postnova using THF as a solvent and calibrated with polystyrene standards. Absorption spectra were taken on a HP8453 UV-vis spectrophotometer. Differential scanning calorimetry (DSC) was conducted on a TA Q200 Instrument under nitrogen atmosphere at a heating/cooling rate of $10\text{ }^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) was recorded on a Perkin-Elmer Pyris under nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Electrochemical cyclic voltammetry was conducted on a CH instruments electrochemical analyzer. A carbon glass was used as the working electrode and a Ag/AgCl electrode as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile was the electrolyte. Cyclic voltammetry (CV) curves were calibrated using ferrocene as the standard, whose HOMO is set at -4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation $\text{HOMO} = -(E_{\text{ox}}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}} + 4.8)\text{ eV}$. The LUMO levels were obtained from the equation $\text{LUMO} = -(E_{\text{red}}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}} + 4.8)\text{ eV}$. Grazing-incidence X-ray scattering (GIXS) experiments were conducted on the SAXS beamline BL23A in the National Synchrotron Radiation Research Center, Taiwan.^{S1} The samples were irradiated with an X-ray beam of 10.09 keV energy (wavelength $\lambda = 1.23\text{ \AA}$) at a fixed incident angle of 0.2° , and the GIXS patterns were recorded using a C10158DK-3957(x) 2D flat panel detector (Hamamatsu Photonics KK). The scattering vector q is defined by $4\pi\lambda^{-1}\sin\theta$ with λ and scattering angle 2θ . The polymer films for GIXS measurement were prepared under identical conditions used for the PSCs devices.

2. Fabrication and Characterization of OPV Devices.

ITO/glass substrates were ultrasonically cleaned sequentially in detergent, water, acetone, and isopropyl alcohol. For the inverted architectures, the ZnO precursor solution was spin-coated onto an ITO-coated glass and followed by thermal annealing at 170 °C in air for 15 min to crystallize the film (thickness = ca. 50 nm). Subsequently, each polymer was dissolved in *o*-dichlorobenzene (*o*-DCB) and PC₇₁BM (purchased from UR) was added to reach the desired ratio. The mixture was stirred at 80 °C overnight. The photoactive layers was then spin-coated on top of the ZnO/ITO at different spin-coating speed without annealing in a glovebox. The detailed processing parameters (polymer/*o*-DCB concentration; spin coating speed/spin coating time) are shown as follows: **PDTBFFBT**/ (6 mg/mL; 450 rpm/20 s) and **PDTBFNT**/ (10 mg/mL; 800 rpm/40 s). A MoO₃ layer (thickness = ca. 7 nm) and silver top anode (thickness = ca. 150 nm) were then thermally evaporated through a shadow mask under high vacuum ($<1 \times 10^{-6}$ Torr) to complete the inverted devices. Each device is composed of 4 pixels defined by an active area of 0.04 cm². Finally, the *J-V* curves were measured in air under AM 1.5 G spectrum from a solar simulator.

3. OFET Fabrication.

An n-type heavily doped Si wafer with a SiO₂ layer of 325 nm and a capacitance of 10.6 nF/cm² was used as the gate electrode and dielectric layer. Thin films (40–60 nm in thickness) of polymers were deposited on octadecyltrichlorosilane-treated SiO₂/Si substrates by spin-coating (1000 rpm) their hot CHCl₃ solutions (10 mg/mL). Thermal annealing was then conducted at 200 °C for 10 min. Gold source and drain contacts (40 nm in thickness) were deposited by vacuum evaporation on the polymer layer to complete the bottom-gate/top-contact OFET devices. Electrical measurements of all OFET devices were carried out at room temperature in air on a 4156C (Agilent Technologies). The field-effect mobility was calculated in the saturation regime by

using the equation $I_{ds} = (\mu WC_i/2L)(V_g - V_t)^2$, where I_{ds} is the drain-source current, μ is the field-effect mobility, W is the channel width (1 mm), L is the channel length (100 μ m), C_i is the capacitance per unit area of the gate dielectric layer, V_g is the gate voltage, and V_t is threshold voltage.

4. Experimental Procedures.

Sn-DTFBT and **Sn-DTNT** were synthesized as reported.^{S2}

Synthesis of 2. To a degassed toluene (10 mL) solution of compound **1** (1 g, 1.25 mmol) were added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (35 mg, 0.05 mmol) and 2-tributylstannyl thiophene (0.83 mL, 2.62 mmol). The mixture was stirred for 12 h at 110 °C and water (10 mL) was then added. The resultant precipitate was collected, dissolved with ethyl acetate (50 mL $\times$ 3), and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane) to give a transparent oil **2** (445 mg, yield: 50%): ^1H NMR (CDCl_3 , 400 MHz): δ 7.97 (s, 2 H), 7.43 (s, 2 H), 7.42 (d, $J=5.0$ Hz, 2 H), 7.35 (dd, $J=3.6$ Hz, $J=1.2$ Hz, 2 H), 7.15 (dd, $J=5.0$ Hz, $J=3.6$ Hz, 2 H), 1.93 (m, 4 H), 1.26–1.07 (m, 20 H), 0.82 (t, $J=7$ Hz, 6 H), 0.69 (br, 4 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.5, 142.3, 140.5, 134.2, 128.0, 127.0, 126.3, 126.1, 125.2, 121.5, 55.3, 39.9, 31.7, 29.8, 29.2, 29.1, 23.8, 22.6, 14.1; HRMS (EI, $\text{C}_{37}\text{H}_{44}\text{Br}_2\text{S}_2^+$): calcd, 712.1231; found, 712.1232.

Synthesis of 3. To a degassed toluene (25 mL) solution of compound **2** (670 mg, 0.94 mmol) and diisopropylamine (25 mL) were added PPh_3 (62 mg, 0.24 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (164 mg, 0.24 mmol), CuI (45 mg, 0.24 mmol), and 4-octyl-1-tetradecyne (864 mg, 2.81 mmol). The reaction mixture was stirred for 3 days at 110 °C. After cooling to room temperature, the mixture was diluted with water (100 mL), extracted with ethyl acetate (50 mL $\times$ 3), dried over MgSO_4 , and concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexane) to give a transparent oil **3** (660 mg, yield: 60%): ^1H NMR (CDCl_3 , 400 MHz): δ 7.80 (s, 2 H), 7.62 (dd, $J=3.6$ Hz, $J=1.2$ Hz, 2 H), 7.45 (s, 2 H), 7.34 (dd, $J=5.2$ Hz, $J=1.2$ Hz, 2

H), 7.10 (dd, $J = 5.2$ Hz, $J = 3.6$ Hz, 2 H), 2.44 (d, $J = 6.8$ Hz, 4 H), 1.94 (m, 4 H), 1.61 (m, 2 H), 1.42–0.87 (m, 84 H), 0.85 (m, 12 H), 0.80 (t, $J = 3.6$ Hz, 6 H), 0.67 (br, 4 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.7, 143.1, 139.2, 134.9, 127.0, 126.6, 125.3, 125.2, 123.3, 120.5, 93.6, 81.5, 55.5, 40.3, 37.3, 33.7, 32.0, 31.8, 30.0, 30.0, 29.7, 29.7, 29.4, 29.2, 29.2, 27.0, 24.1, 23.8, 22.7, 22.6, 14.1, 14.1; HRMS (FAB, $\text{C}_{81}\text{H}_{126}\text{S}_2^+$): calcd, 1162.9301; found, 1163.9342.

Synthesis of DTBF. To a degassed *N*-methyl-2-pyrrolidone (NMP, 2.5 mL) solution of compound **3** (500 mg, 0.43 mmol) was added 1,8-diazabicycloundec-7-ene (DBU, 0.07 mL, 0.47 mmol). The resulting mixture was refluxed for 3 days, cooled to rt, diluted with water (20 mL), and extracted with ethyl acetate (10 mL $\times$ 3). The combined organic layer was washed with brine solution (5 mL) and dried over anhydrous MgSO_4 . After filtration, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (hexane) to give a yellow oil **DTBF** (300 mg, yield: 60%). ^1H NMR (CDCl_3 , 400 MHz): δ 8.28 (s, 2 H), 8.00 (s, 2 H), 7.57 (s, 2 H), 7.55 (d, $J = 5.6$ Hz, 2 H), 7.53 (d, $J = 5.6$ Hz, 2 H), 2.97 (d, $J = 6.8$ Hz, 4 H), 2.20 (m, 4 H), 1.88 (m, 2 H), 1.39–1.00 (m, 88 H), 0.86 (t, $J = 6.4$ Hz, 12 H), 0.72 (t, $J = 6.8$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 149.4, 139.5, 137.9, 137.7, 134.5, 131.0, 128.0, 125.5, 124.3, 123.6, 118.7, 117.0, 54.9, 42.2, 39.3, 38.7, 33.5, 31.9, 31.7, 30.1, 30.0, 29.7, 29.7, 29.7, 29.4, 29.3, 29.2, 29.2, 26.6, 24.0, 22.7, 22.5, 14.1, 14.0; HRMS (field desorption (FD), $\text{C}_{81}\text{H}_{126}\text{S}_2^+$): calcd, 1162.9295; found, 1162.9318.

Synthesis of Br-DTBF. To an anhydrous THF (10 mL) solution of **DTBF** (200 mg, 0.17 mmol) was added *n*-butyllithium (0.2 mL, 2.5 M) slowly at -78 °C. The stirring was continued for 40 min at -78 °C and 1, 2-dibromotetrachloroethane (223 mg, 0.69 mmol) was added. The mixture was warmed to room temperature gradually and stirred for 12 h. It was quenched with saturated NH_4Cl solution (10 mL), cooled to room temperature, and extracted with ethyl acetate (200 mL $\times$ 3) and water (200 mL). The

combined organic layer was dried over MgSO_4 , filtrated, and concentrated *in vacuo*. A transparent oil **Br-DTBF** was obtained (160 mg, 70%). ^1H NMR (CDCl_3 , 400 MHz): δ 8.24 (s, 2 H), 7.84 (s, 2 H), 7.53 (s, 2 H), 7.50 (s, 2 H), 2.88 (d, $J = 6.8$ Hz, 4 H), 2.17 (m, 4 H), 1.84 (m, 2 H), 1.41–0.92 (m, 88 H), 0.89–0.82 (m, 12 H), 0.76–0.70 (m, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 149.7, 139.5, 139.0, 137.7, 133.7, 130.8, 127.1, 126.4, 125.8, 118.9, 116.7, 113.0, 54.9, 42.1, 39.1, 38.6, 33.4, 31.9, 31.7, 30.1, 30.0, 29.7, 29.7, 29.4, 29.4, 29.2, 29.1, 26.5, 24.0, 22.7, 22.5, 14.1, 14.0; HRMS (FD, $\text{C}_{81}\text{H}_{124}\text{Br}_2\text{S}_2^+$): calcd, 1318.7505; found, 1318.7488.

Synthesis of PDTBFFBT. To a mixture of **Br-DTBF** (212 mg, 0.16 mmol), **Sn-DTFT** (106 mg, 0.16 mmol), $\text{Pd}_2(\text{dba})_3$ (3.1 mg, 0.003 mmol) and $\text{P}(o\text{-tol})_3$ (4.1 mg, 0.013 mmol) was added 5 mL of chlorobenzene in a glove box protected with N_2 . The reaction mixture was then sealed and heated at 145 °C for 2 days. The resultant mixture was added into methanol dropwise. The precipitate was collected by filtration and washed by Soxhlet extraction with acetone (24 h) and hexane (24 h), sequentially. The crude product was re-dissolved in THF (200 mL). After filtration and removal of the solvent under reduced pressure, the polymer was re-precipitated again from methanol/THF, collected by filtration, and dried under vacuum for 1 day to give a green black solid (120 mg, 50%, $M_n = 7800$, PDI = 1.2). ^1H NMR (CDCl_3 , 400 MHz): δ 8.28 (br, 2 H), 7.74–7.46 (br, 10 H), 2.90 (br, 4 H), 2.22–2.16 (br, 6 H), 1.85–1.26 (br, 76 H), 0.87–0.46 (br, 30 H).

Synthesis of PDTBFNT. To a mixture of monomer **Br-DTBF** (160 mg, 0.12 mmol), **Sn-DTNT** (89 mg, 0.12 mmol), $\text{Pd}_2(\text{dba})_3$ (2.3 mg, 0.003 mmol) and $\text{P}(o\text{-tol})_3$ (3.1 mg, 0.010 mmol) was added 5 mL of chlorobenzene in a glove box protected with N_2 . The reaction mixture was then sealed and heated at 145 °C for 2 days. The resultant mixture was added into methanol dropwise. The precipitate was collected by filtration and washed sequentially by Soxhlet extraction with acetone (24 h), hexane (24 h), and THF

(24 h). The crude product was re-dissolved in chlorobenzene (200 mL). After filtration and removal of the solvent under reduced pressure, the polymer was re-precipitated again from methanol/chlorobenzene, collected by filtration, and dried under vacuum for 1 day to give a green black solid (150 mg, 79%, $M_n = 14300$, PDI = 3.4). ^1H NMR (CDCl_3 , 400 MHz): δ 8.27-8.25 (br, 2 H), 7.97 (br, 4 H), 7.57-7.52 (br, 8 H), 2.97 (br, 4 H), 2.17-1.84 (br, 20 H), 1.40-1.06 (br, 70 H) 0.86-0.74 (br, 22 H).

5. Differential scanning calorimetry (DSC)

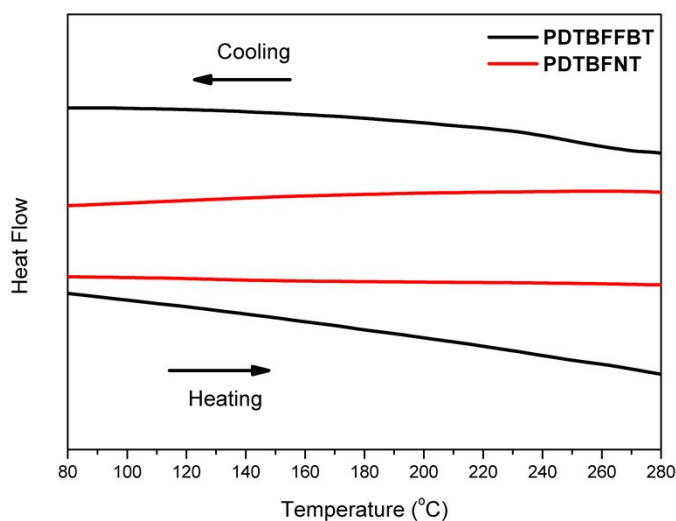
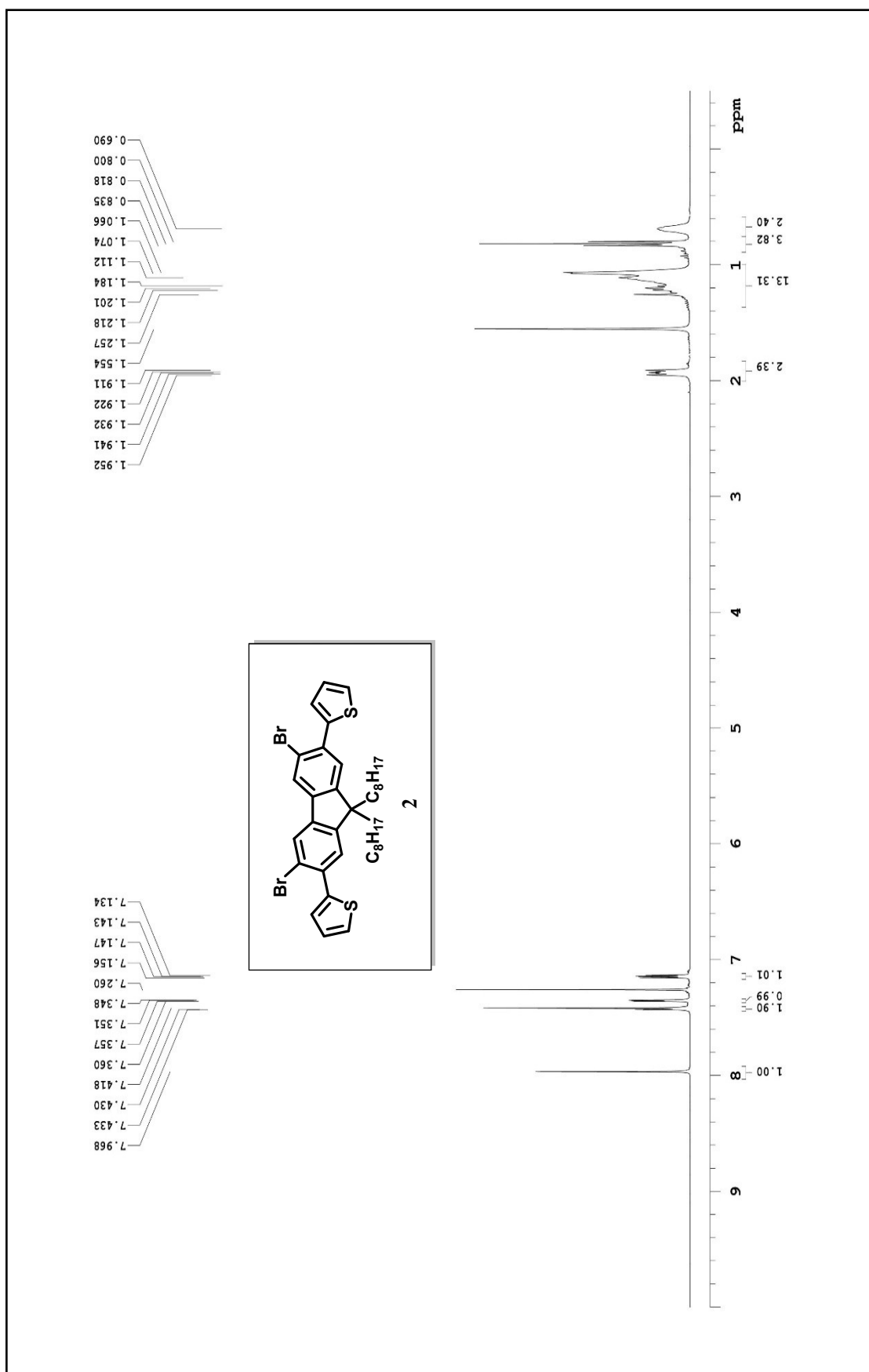
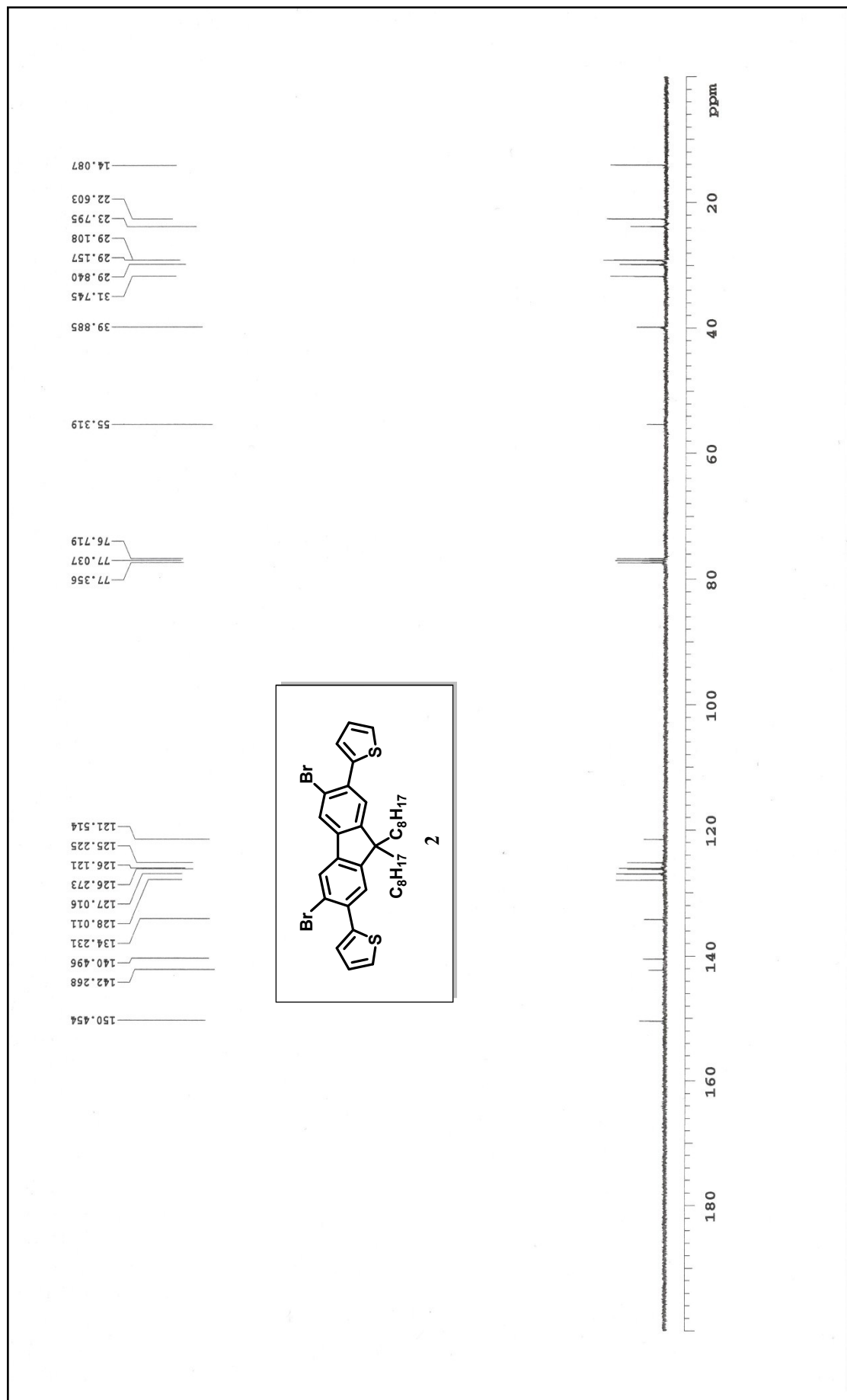
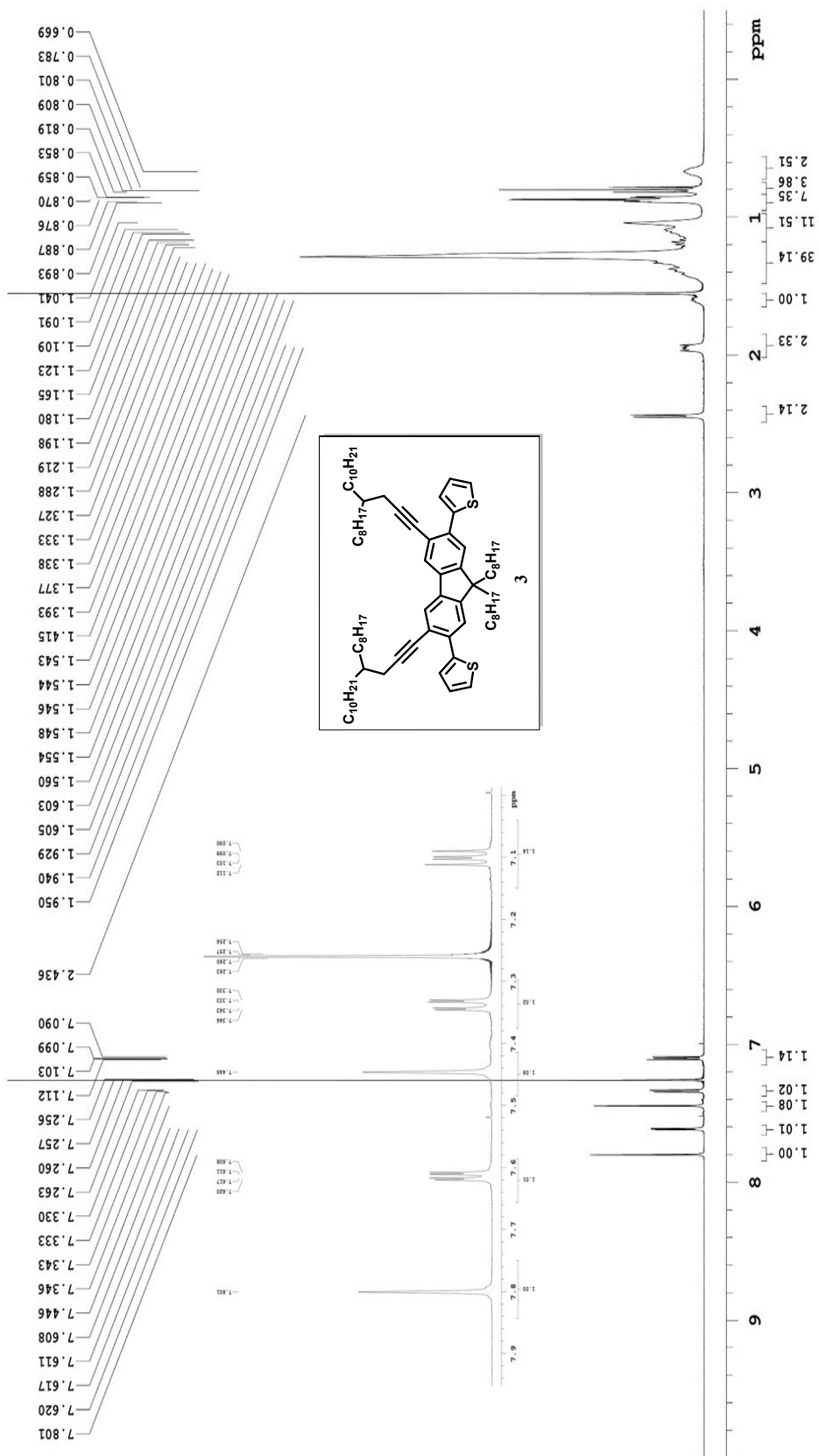


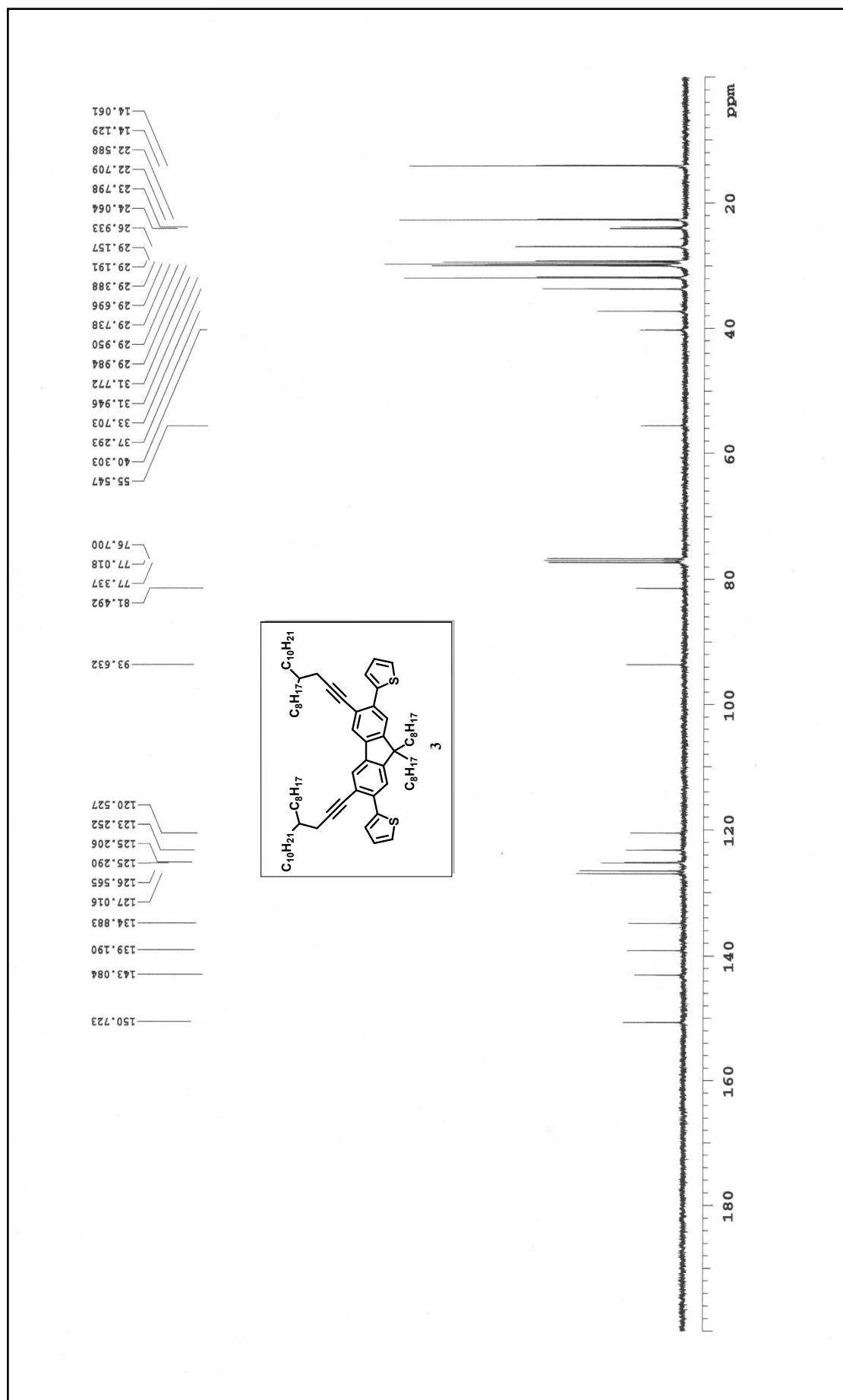
Figure S1. Differential scanning calorimetry of **PDTBFFBT** and **PDTBFNT** with a heating/cooling rate of 10 °C/min.

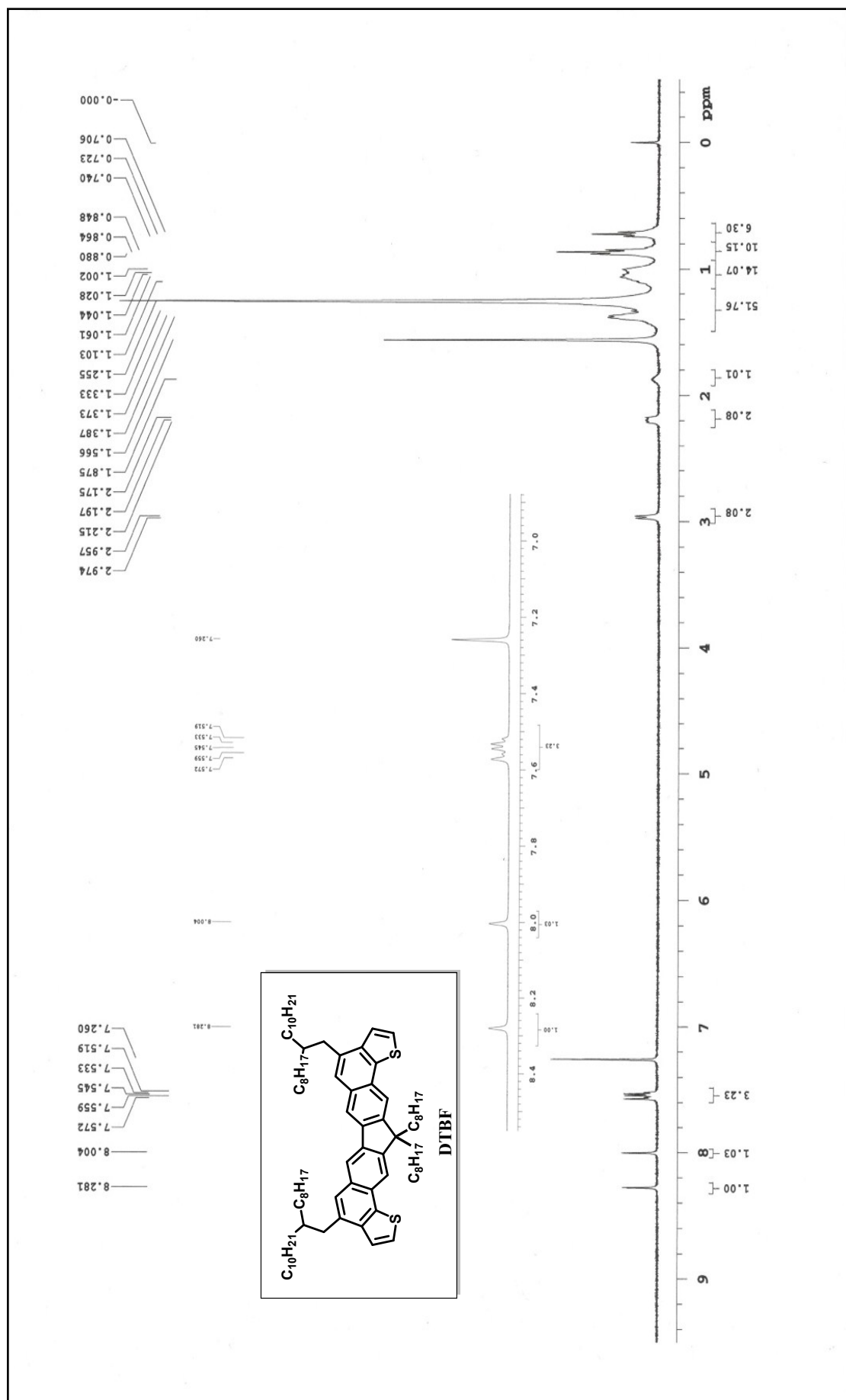
6. ^1H and ^{13}C NMR spectra

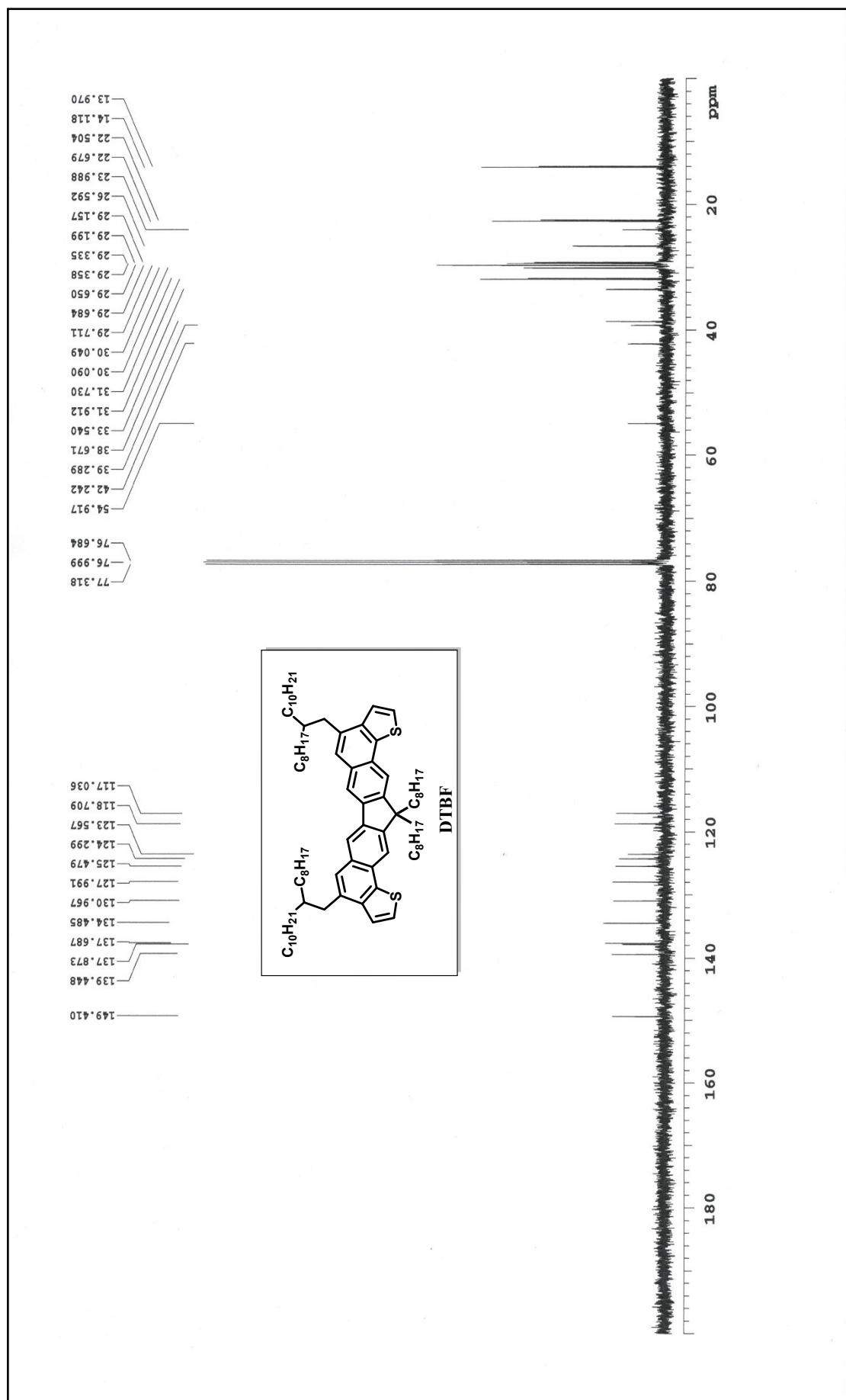


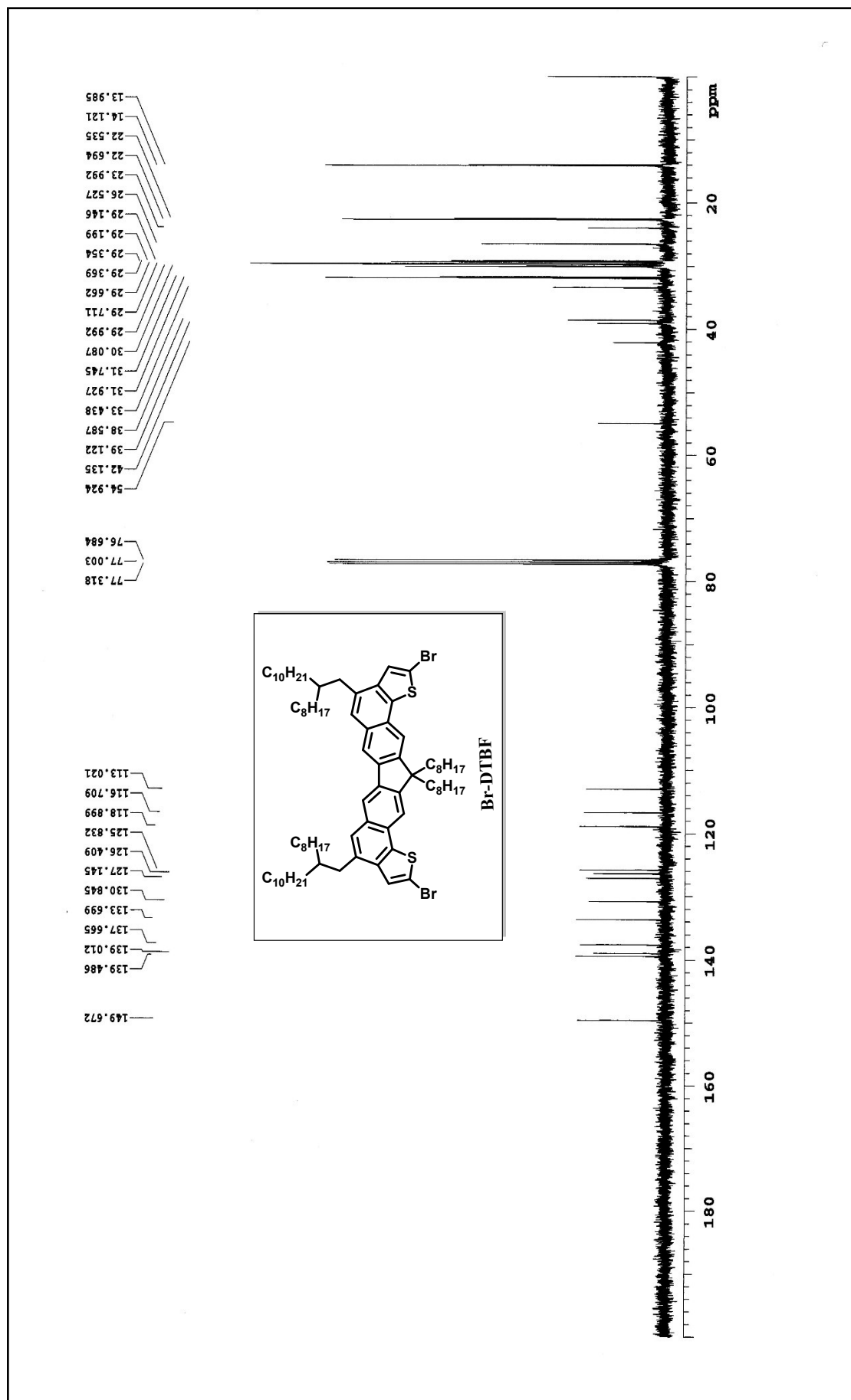


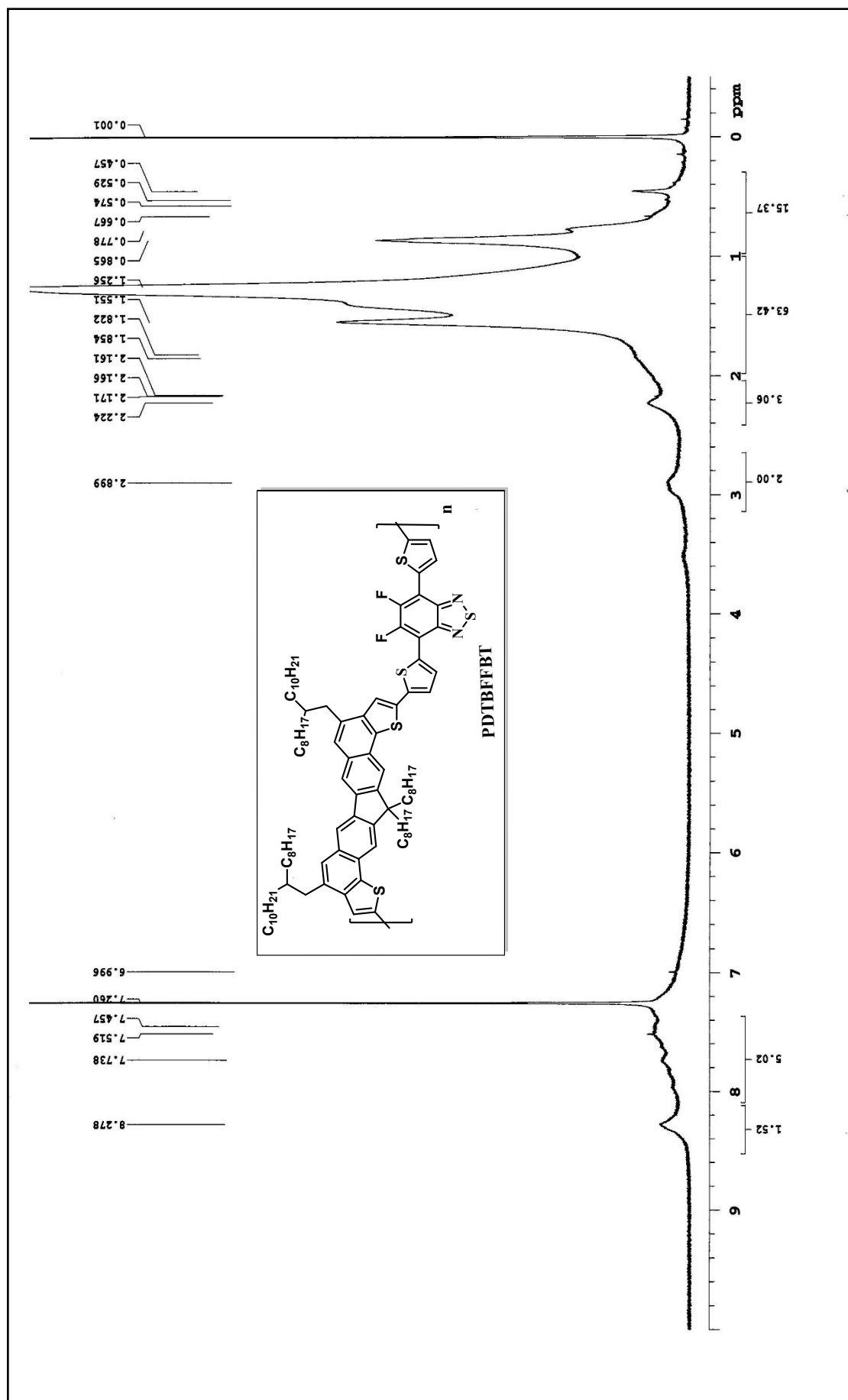














7. Computational details.

Quantum-chemical calculations were performed with the Gaussian09 suite^{S3}.

Cartesian coordinates (Å) of the Gaussian (B3LYP/6-31G(d)) optimized structures

P-FBT

C	20.499458724368	-5.865000098380	-0.075492159189
C	19.562446845371	-4.855692820490	-0.131964728170
C	19.967600431724	-3.497009735358	-0.252557660686
C	21.298114979801	-3.171032559424	-0.313281287780
H	20.197753656391	-6.903568089334	0.015361752030
H	21.611511207651	-2.135869797001	-0.403526771873
C	18.754856851833	-2.566333613011	-0.296747730054
C	18.099773905563	-4.900806965241	-0.090262495450
C	17.605343017981	-3.568824252401	-0.186275958646
C	17.231793963789	-5.965608717619	0.019015285435
H	17.602110586857	-6.982991441429	0.094422239740
C	15.340254014137	-4.404614277488	-0.063592447763
C	18.693178834400	-1.787001149012	-1.628583233530
H	17.788377833068	-1.174601903446	-1.675678569062
H	19.555453673214	-1.121592895190	-1.726138039513
C	18.759244416816	-1.581377743692	0.892506245874
H	17.856433796031	-0.964314487397	0.885595371672
H	19.624026928958	-0.914547561138	0.835711766722
C	13.930559435360	-4.246956862374	-0.039202098167
C	13.039437767431	-5.327885530070	0.065215193074
S	13.073489415620	-2.722820594071	-0.140042121047

C	11.676404133566	-4.896617080501	0.079161905107
H	10.835723136396	-5.568868727747	0.176907668787
C	14.913642385820	-6.829399965219	0.147500519199
C	13.551810866715	-6.663862418988	0.160234898376
H	15.325597107772	-7.830845022327	0.231859211651
C	12.640299512054	-7.869362595066	0.266528242104
C	12.452199077310	-8.657734692070	-1.055385744048
C	11.660790108691	-9.961416596401	-0.828275685666
H	13.061601298873	-8.541247973548	1.019064833479
H	11.655479416556	-7.573815368934	0.642146231457
C	11.781282752700	-7.806703917457	-2.141024338169
H	11.708413689272	-8.364355576310	-3.079090931980
H	10.765038907968	-7.523243641271	-1.846080597453
H	13.453106978558	-8.932457618574	-1.414599720159
C	23.682733957482	-3.944541871610	-0.308725974240
S	24.445989317520	-2.371111371279	-0.425069615110
C	25.980402668013	-4.452427129915	-0.302456852356
C	26.028829204071	-3.099505466857	-0.393826660528
H	26.867619604846	-5.068900245259	-0.265896810351
H	26.901108748374	-2.465794247727	-0.444385176367
C	24.638838693765	-4.967849923382	-0.254260656171
C	21.879300965375	-5.558753338028	-0.137797139644
C	22.870031523915	-6.586087807543	-0.084229867436
C	24.216344030272	-6.334347208234	-0.147056008171
C	25.231498579653	-7.453803301700	-0.106901543038

H	24.751223794223	-8.354116162277	0.292350245483
H	26.022289838140	-7.188583072201	0.601346077241
C	25.869190545274	-7.811316254581	-1.475532552330
C	27.033337459599	-8.809064041278	-1.309974464818
C	24.822348923684	-8.365509781400	-2.450503406632
C	28.276451469175	-8.255281889052	-0.605196994963
H	29.074023005387	-9.002738215188	-0.579097299207
H	28.666722294879	-7.377028736746	-1.129573573691
H	26.669077099105	-9.695450070532	-0.774414980654
H	27.325053721644	-9.159798118152	-2.306415992246
H	28.074271026813	-7.964487994370	0.429115049540
H	25.268238139257	-8.560383230831	-3.429956475615
H	24.407177707295	-9.310097658729	-2.080942701531
H	23.993577954240	-7.668742694289	-2.591393479148
H	26.278169864322	-6.890681773431	-1.911213849698
H	11.442340137515	-10.399197021279	-1.808967782341
C	12.363572664912	-11.016815211434	0.032382847347
H	10.686359780997	-9.714358102319	-0.386811482162
H	13.340838137153	-11.278296927054	-0.386057357206
H	12.521563869049	-10.678319881363	1.059569365099
H	11.770782861892	-11.934187721910	0.082380290943
H	22.526434681554	-7.611507284894	0.011308193101
C	10.288802010994	-2.776373229596	-0.030432174571
C	10.113617885233	-1.425843516327	0.189964929927
S	8.758701455450	-3.552467725195	-0.357172804314

C	8.771326926060	-1.013296422656	0.116753782879
H	10.929780659314	-0.753218790879	0.418727085715
H	8.463491278745	0.007308390050	0.272774181052
C	6.434194674923	-1.958007563756	-0.295610732744
C	5.706290236194	-0.797874245045	-0.111262621136
C	5.599594755213	-3.085640843648	-0.631174098754
C	4.299547732967	-0.701166530487	-0.237634920207
C	4.150273091558	-2.989349269947	-0.760461043580
C	7.878165019063	-2.037159407064	-0.163021075881
S	4.777967133277	-5.268775699525	-1.201012257741
N	6.060848958750	-4.310887184257	-0.855272339917
N	3.585733277777	-4.151711212009	-1.076788397959
H	18.801391862683	-2.115011469058	1.844347080768
H	18.689277566983	-2.468349657086	-2.481977834008
C	22.283043911419	-4.190414954655	-0.257773085690
C	11.514552509298	-3.540214594197	-0.017716835733
C	15.834305479341	-5.745819488561	0.033739574984
C	16.256782590650	-3.325516761487	-0.172387376292
H	15.875630543907	-2.311764468579	-0.244415065671
H	12.339072142126	-6.889389550295	-2.340826906406
F	6.314266531256	0.356737729051	0.211779864918
F	3.801992095666	0.529501509318	-0.014127968628
C	2.009090788690	-1.607516588858	-0.676587716787
C	1.089635408476	-2.588677000301	-1.005437150071
S	1.167919510606	-0.081622334790	-0.391744794362

C	-0.242561018658	-2.136512820210	-1.042717979585
H	1.385953002579	-3.602725074524	-1.219208948166
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C	-20.707032360418	4.810636033882	0.714002010799
C	-21.648931584968	3.865857172426	0.359100262715
C	-21.214466328022	6.152424390500	0.927389556128
H	-21.346516712963	2.838650161095	0.195327150011
C	-22.626069532243	6.448304133108	0.762406694838
N	-20.502245013026	7.220861651401	1.276917718025
C	-23.976424754962	3.125295543841	-0.174474231954
N	-22.935239863368	7.720490407156	0.990392429453
S	-21.540432479622	8.489492782348	1.386170253158
C	-25.383396042132	3.430873482461	-0.342977816562
N	-23.679676040466	1.847717414114	-0.389482162381
C	-24.953770375468	5.712280383252	0.224765932668
N	-26.108989662470	2.368550533849	-0.680284688517
S	-25.084153089222	1.088297935160	-0.774506833658
H	-25.263030717034	6.729891685771	0.422869847850
C	-27.817141901605	6.394675022641	-0.448434894779
S	-28.590651047369	3.939042597054	-0.386405493517

C	-29.227271095556	6.427445455082	-0.565193222156
H	-27.201705630885	7.283781853113	-0.468167249534
C	-29.782843829204	5.177964862195	-0.538347344731
H	-29.802387508029	7.337226073530	-0.673611681656
H	-30.824719270178	4.907459730435	-0.619044810019
C	24.559351522411	0.137612854257	-0.494970133964
C	13.781249022624	0.671642935864	-0.548784008581
C	3.623230937419	1.227112036753	0.524449292164
C	18.311509066254	2.383647327629	-0.379799993811
C	18.474571910239	-0.070264185463	-0.546586423681
H	17.987357942310	-1.037519958788	-0.616982001905
C	-13.735274348820	1.233051808964	0.666197549614
C	-14.536962324222	-1.076873508228	0.403485504112
C	-5.502598209424	-0.179491932456	0.632187198433
C	-4.083428048206	-0.187676471315	0.646266042378
C	-15.991351704023	2.341452602595	0.777758773441
C	-27.294237916489	5.121837439404	-0.330883192767
C	-25.889572342496	4.769372262132	-0.145897108654
C	-23.568388149299	5.428934153925	0.383061720916
C	-23.032552996614	4.147034582277	0.192236069821
C	-12.128313869434	-0.570613108707	0.498674875999
H	-14.264283437127	-2.758881382169	-1.927746504997
H	16.912114913264	5.243052018081	1.924322890981

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