Supporting Information

Synthesis, Properties, and Crystal Structures of π-Extended Double [6]Helicenes: Contorted Multi-Dimensional Stacking Lattices

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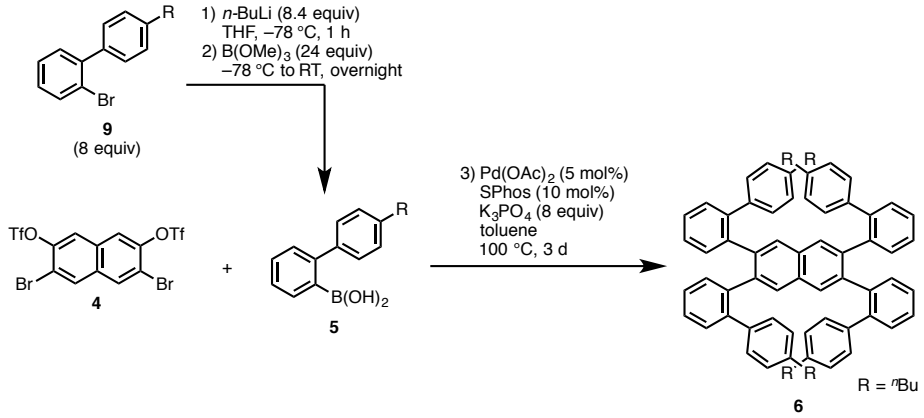
1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. 2-Bromo-4'-butyl-1,1'-biphenyl (**9**),[S1] 3,6-dibromonaphthalene-2,7-diyl bis(trifluoromethanesulfonate) (**4**),[S2] and compound **7**[S3] were prepared according to the procedures reported in the literature. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen in dried glassware with standard vacuum-line techniques. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm and 365 nm). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-S3000 SpiralTOF (MALDI-TOF MS). Cyclic voltammetry (CV) measurements were performed by BAS ALS-600D Electrochemical Analyzer. Melting points were measured on a MPA100 Optimelt automated melting point system. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz) or a JEOL ECA 600II spectrometer with Ultra COOLTM probe (^{1}H 600 MHz, ^{13}C 150 MHz). Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to $CHCl_3$ (δ 7.26 ppm) or C_2DHCl_4 (δ 6.00 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.16 ppm) or $C_2D_2Cl_4$ (δ 73.78 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

2. Synthesis of 6, 2, 8, and 3

Synthesis of 2,3,6,7-tetrakis(4'-butyl-[1,1'-biphenyl]-2-yl)naphthalene (6)

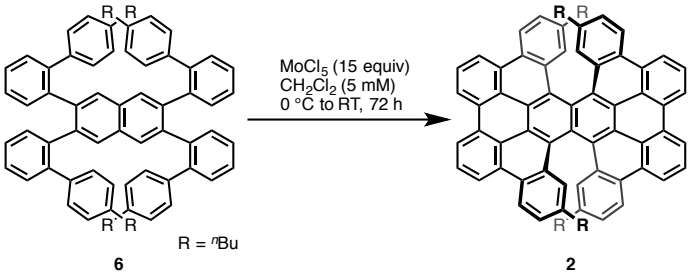


To a solution of 2-bromo-4'-butyl-1,1'-biphenyl (**9**) (11.6 g, 40.0 mmol, 8 equiv) in THF (130 mL) was added a pentane solution of *n*-butyllithium (1.6 M, 26.3 mL, 42.0 mmol, 8.4 equiv) at –78 °C dropwise over 10 min, and the mixture was stirred for 1 h under nitrogen. Trimethoxyborane (13.4 mL, 120 mmol, 24 equiv) was added, and then the reaction mixture was allowed to warm to room temperature. After stirring the mixture overnight, the reaction was quenched by the addition of 2N HCl aqueous solution. The organic layer was extracted with Et_2O, washed with brine, dried over Na_2SO_4, and then concentrated *in vacuo* to afford a crude mixture of (4'-butyl-[1,1'-biphenyl]-2-yl)boronic acid (**5**) as a white solid. Compound **5** was used in the next step without further purification.

A mixture of 3,6-dibromonaphthalene-2,7-diyl bis(trifluoromethanesulfonate) (**4**) (2.91 g, 5.00 mmol, 1 equiv), **5**, $Pd(OAc)_2$ (56.1 mg, 0.250 mmol, 5 mol%), SPhos (205 mg, 0.500 mmol, 10 mol%), and K_3PO_4 (8.49 g, 40.0 mmol, 8 equiv) in toluene (20 mL) was stirred at 100 °C for 3 days under nitrogen. After cooling to room temperature, the mixture was passed through a pad of silica-gel and eluted with dichloromethane, and then the residue was concentrated *in vacuo*. Recrystallization from dichloromethane/*n*-hexane bilayer system afforded **6** (4.24 g, 88%) as a white solid.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 130 °C) δ 7.56 (s, 4H), 7.24 (t, J = 7.5 Hz, 4H), 7.17 (d, J = 7.6 Hz, 4H), 6.99 (t, J = 7.2 Hz, 4H), 6.90 (d, J = 7.8 Hz, 8H), 6.65 (d, J = 7.0 Hz, 8H), 6.50 (broad s, 4H), 2.62 (t, J = 7.5 Hz, 8H), 1.71–1.63 (m, 8H), 1.49–1.38 (m, 8H), 1.00 (t, J = 7.2 Hz, 12H); ^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 130 °C) δ 140.5 (4º), 140.4 (4º), 139.4 (4º), 139.3 (4º), 138.7 (4º), 131.7 (CH), 131.4 (4º), 130.1 (CH), 129.3 (CH), 129.2 (CH), 127.2 (CH), 126.5 (CH), 126.1 (CH), 35.0 (CH_2), 33.1 (CH_2), 22.0 (CH_2), 13.4 (CH_3); HRMS (MALDI TOF-MS) *m/z* calcd for $C_{74}H_{72}Na$ $[M+Na]^+$: 983.5532, found: 983.5526; mp: 219–220 ºC (recrystallized from dichloromethane/*n*-hexane).

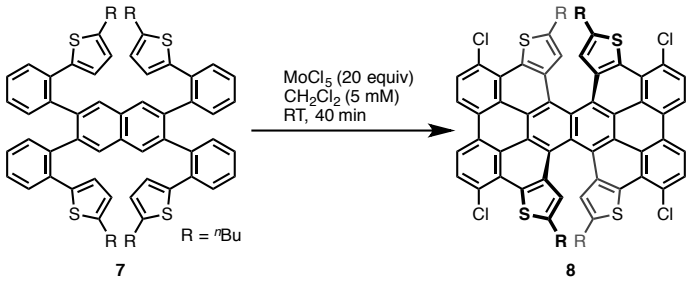
Synthesis of 2



To a solution of **6** (19.2 mg, 0.020 mmol, 1 equiv) in dichloromethane (4 mL) was added $MoCl_5$ (82.0 mg, 0.300 mmol, 15 equiv) at 0 °C, and then the reaction mixture was stirred at room temperature for 3 days under nitrogen. The reaction was quenched by the addition of MeOH/$CHCl_3$ (1:1, 5 mL) and the resultant solution was directly passed through a pad of silica-gel with *n*-hexane/dichloromethane solution (9:1) eluent. The filtrate was concentrated *in vacuo*, and the crude residue was purified by preparative thin-layer chromatography (eluent: *n*-hexane/$CHCl_3$ = 17:3) to afford **2** (2.4 mg, 13%) as a red solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.08 (d, *J* = 7.7 Hz, 4H), 8.96 (d, *J* = 7.7 Hz, 4H), 8.58 (d, *J* = 8.4 Hz, 4H), 8.15 (t, *J* = 7.8 Hz, 4H), 7.84 (d, *J* = 1.4 Hz, 4H), 7.18 (dd, *J* = 8.1, 1.6 Hz, 4H), 2.17–2.11 (m, 4H), 2.02–1.97 (m, 4H), 1.04–0.85 (m, 16H), 0.72 (t, *J* = 7.0 Hz, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.3 (4º), 131.3 (4º), 131.1 (4º), 130.2 (4º), 129.7 (CH), 128.0 (4º), 127.7 (CH), 127.0 (CH), 125.6 (4º), 125.2 (4º), 123.2 (CH), 123.0 (4º), 121.9 (CH), 121.8 (CH), 121.5 (4º), 35.6 (CH_2), 33.3 (CH_2), 22.3 (CH_2), 14.1 (CH_3); HRMS (MALDI TOF-MS) *m/z* calcd for $C_{74}H_{60}$ $[M]^+$: 948.4695, found: 948.4685; mp: >300 ºC (recrystallized from chloroform/*n*-pentane).

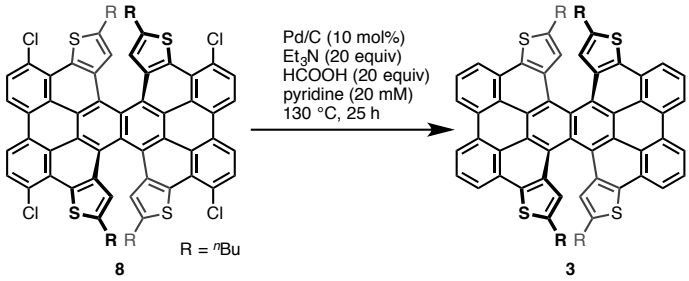
Synthesis of 8



To a solution of **7** (493 mg, 0.500 mmol, 1 equiv) in dichloromethane (100 mL) was added $MoCl_5$ (2.73 g, 10.0 mmol, 20 equiv) at room temperature, and then the reaction mixture was stirred for 40 min under nitrogen. The reaction was quenched by the addition of MeOH/$CHCl_3$ (7:3, 100 mL) and the resultant solution was directly passed through a pad of silica-gel with $CHCl_3$ eluent. The filtrate was concentrated *in vacuo*. Recrystallization from nitrobenzene afforded **8** (143 mg, 26%) as a red crystal.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.92 (d, J = 8.6 Hz, 4H), 8.18 (d, J = 8.5 Hz, 4H), 6.99 (s, 4H), 2.57 (dt, ^2J = 14.9, ^3J = 7.3 Hz, 4H), 2.49 (dt, ^2J = 15.1, ^3J = 7.4 Hz, 4H), 1.39 (quintet, J = 7.5 Hz, 8H), 1.17–1.07 (m, 8H), 0.83 (t, J = 7.7 Hz, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 132.5 (4º), 130.3 (4º), 129.2 (CH), 129.1 (4º), 127.1 (4º), 125.7 (4º), 123.6 (CH), 123.0 (4º), 122.7 (4º), 121.8 (4º), 120.5 (CH), 33.7 (CH_2), 29.6 (CH_2), 21.9 (CH_2), 14.0 (CH_3); HRMS (MALDI TOF-MS) *m/z* calcd for $C_{66}H_{48}Cl_4S_4$ $[M]^+$: 1110.1363, found: 1110.1371; mp: >300 ºC (recrystallized from nitrobenzene).

Synthesis of 3



A mixture of **8** (22.2 mg, 0.0200 mmol, 1 equiv), 5% Pd/C containing 55% water (9.5 mg, 2.0 μmol, 10 mol%), triethylamine (40.5 mg, 0.400 mmol, 20 equiv), and formic acid (18.4 mg, 0.400 mmol, 20 equiv) in pyridine (1 mL) was stirred at 130 °C for 25 h in a 20-mL Schlenk tube sealed with J. Young® O-ring tap. After cooling to room temperature, the precipitate was dissolved in $CHCl_3$ and Pd/C residue was removed by filtration through Celite®. The filtrate was washed with water, dried with over Na_2SO_4, and then concentrated *in vacuo* to afford **3** (20.1 mg, quant) as a red solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.07 (dd, J = 7.9, 0.7 Hz, 4H), 8.45 (dd, J = 7.7, 0.7 Hz, 4H), 8.10 (t, J = 7.7 Hz, 4H), 6.97 (s, 4H), 2.61 (dt, ^2J = 15.4, ^3J = 7.4 Hz, 4H), 2.56 (dt, ^2J = 14.9, ^3J = 7.6 Hz, 4H), 1.46–1.40 (m, 8H), 1.22–1.13 (m, 8H), 0.83 (t, J = 7.4 Hz, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.9 (4º), 136.5 (4º), 135.6 (4º), 131.8 (4º), 129.2 (4º), 127.0 (CH), 125.2 (CH), 123.8 (4º), 122.9 (4º), 122.6 (CH), 122.1 (4º), 121.8 (4º), 120.4 (CH). 33.7 (CH_2), 30.2 (CH_2), 21.9 (CH_2), 14.1 (CH_3); HRMS (MALDI TOF-MS) *m/z* calcd for $C_{66}H_{52}S_4$ $[M]^+$: 972.2952, found: 972.2965; mp: >300 ºC (recrystallized from nitrobenzene).

3. Photophysical Study

UV-vis absorption spectra were recorded on a Shimadzu UV-3510 spectrometer with a resolution of 0.5 nm. Emission spectra were measured with an FP-6600 Hitachi spectrometer with a resolution of 0.2 nm. Dilute solutions in degassed spectral grade chloroform in a 1 cm square quartz cell were used for measurements. Absolute fluorescence quantum yields were determined with a Hamamatsu C9920-02 calibrated integrating sphere system upon excitation at 390 nm for **2** or at 405 nm for **3**.

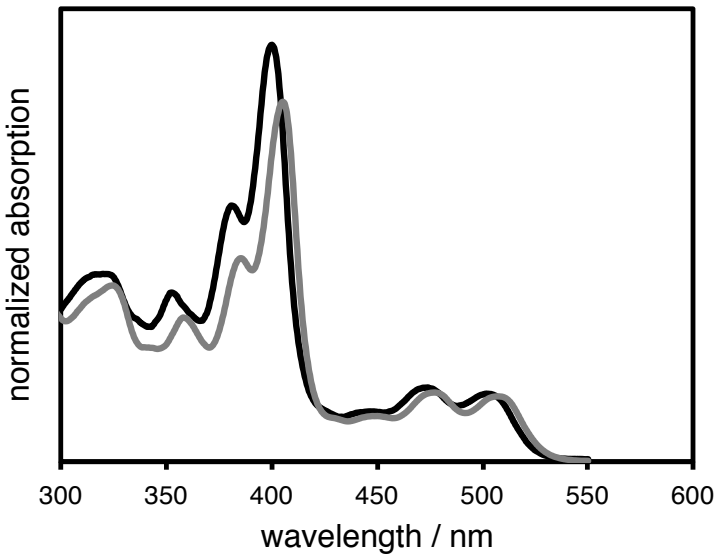


Figure S1. UV–vis absorption spectra of **1** (black line) and **2** (gray line) in chloroform.

4. X-ray Crystallography

Recrystallization of a racemic mixture of **2** from $CHCl_3$/*n*-pentane in vapor diffusion method yielded red crystals suitable for X-ray crystal structure analysis, and a racemic mixture of **3** from hot nitrobenzene yielded red crystals suitable for X-ray crystal structure analysis. Details of the crystal data and a summary of the intensity data collection parameters for **2** and **3** are listed in Table S1. A suitable crystal was mounted with mineral oil on a glass fiber and transferred to the goniometer of a Rigaku PILATUS diffractometer. Graphite-monochromated Mo Kα radiation (λ = 0.71075 Å) was used. The structures were solved by direct methods with (SIR-97)[S4a] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/3)[S4b] by using Yadokari-XG software package.[S5] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

Table S1. Crystallographic data and structure refinement details for **2** and **3**.

	2	**3**
formula	$C_{76.5}H_{64}$	$C_{66}H_{52}S_4$
fw	983.27	973.31
T (K)	123(2)	123(2)
λ (Å)	0.71075	0.71075
cryst syst	Triclinic	Monoclinic
space group	*P*-1	*C*2/*c*
a (Å)	11.0983(7)	16.046(3)
b (Å)	16.4648(10)	26.399(5)
c (Å)	16.7317(8)	11.908(2)
α (°)	63.011(5)	90°
β (°)	72.188(7)	110.469(3)
γ (°)	78.909(7)	90°
V (Å^3)	2588.7(3)	4725.7(15)
Z	2	4
D_{calc} (g / cm^3)	1.261	1.368
μ (mm^{-1})	0.071	0.247
F(000)	1046	2048
cryst size (mm)	0.20 × 0.10 × 0.10	0.20 × 0.05 × 0.01
θ range (°))	3.011–24.999˚	3.087–25.00˚
reflns collected	19357	17282
indep reflns/R_{int}	8814/ 0.0414	4144/ 0.0344
params	788	354
GOF on F^2	1.187	1.114
R_1, wR_2 [I>2σ(I)]	0.0713, 0.1617	0.0753, 0.1903
R_1, wR_2 (all data)	0.1027, 0.1990	0.0927, 0.2061

5. Time-Resolved Microwave Conductivity Measurement

Transient photoconductivity was measured by flash-photolysis time-resolved microwave conductivity (FP-TRMC). A resonant cavity was used to obtain a high degree of sensitivity in the measurement of conductivity. The resonant frequency was set at ~9.1 GHz and the microwave power was set at 3 mW, so that the electric field of the microwave was sufficiently small not to disturb the motion of charge carriers. The value of conductivity is converted to the product of the quantum yield ϕ and the sum of charge carrier mobilities $\Sigma\mu$, by $\phi\Sigma\mu = \Delta\sigma(eI_0F_{\text{light}})^{-1}$, where e, I_0, F_{light}, and $\Delta\sigma$ are the unit charge of a single electron, incident photon density of excitation laser (photons/m^2), a correction (or filling) factor (/m), and a transient photoconductivity, respectively. The charge of conductivity is equivalent with $\Delta P_r/(AP_r)$, where ΔP_r, P_r, and A are change of reflected microwave power, a power of reflected microwave, and a sensitivity factor [(S/m)$^{-1}$], respectively. Third harmonic generation (355 nm) from an Optical Parametric Oscillator (OPO) of a ND:YAG laser (Continuum Surelite II, 5–8 ns pulse duration) was used as an excitation source. The incident photon density was set at 4.6×10^{15} photons/cm^2. The sample was set at the highest electric field in a resonant cavity. FP-TRMC experiments were performed at room temperature.

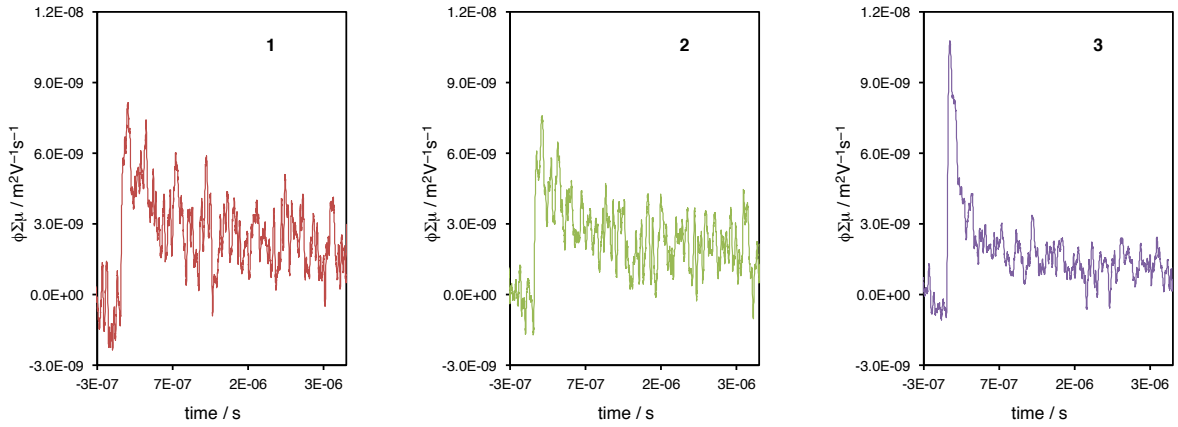


Figure S2. Conductivity transients observed for **1**–**3**. Recrystallized samples were used in each case.

6. Organic Field-Effect Transistor Fabrication

OFETs were fabricated in a top-contact/bottom-gate configuration on a heavily doped n^+-Si (100) wafer with 300-nm thermal silicon oxide (SiO_2) as the dielectric layer. The Si/SiO_2 substrate was cleaned by a sonication in acetone and 2-propanol, and dried before use. A thin film of **3** was grown on the Si/SiO_2 substrate by drop-coat method using a saturated toluene solution at room temperature under a vapor of toluene. Then, gold films (~200 nm) as drain and source electrodes were deposited through a shadow mask. The transfer characteristics of the devices were measured at room temperature in a nitrogen atmosphere with a Keithley 4200-SCS. Field-effect hole mobility (μ_h) was calculated in the saturation regime (V_{DS} = –60 V) of the I_{DS} using the following equation, $I_{DS} = (WC_i/2L)\mu_h(V_{GS}–V_{th})^2$, where W and L are the drain-source channel width (W) and length (L), C_i is the capacitance of the SiO_2 insulator, and V_{GS} and V_{th} are the gate and threshold voltages, respectively.

7. Computational Study

The Gaussian 09 program[S6] running on a SGI Altix4700 system was used for optimization (B3LYP/6-31G(d)).[S7] All structures were optimized without any symmetry assumptions. Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated from the gas-phase studies unless otherwise noted. Harmonic vibration frequency calculations at the same level were performed to verify all stationary points as local minima (with no imaginary frequency) or transition states (with one imaginary frequency). Visualization of the results was performed by use of GaussView 5.0 software.

Table S2. Uncorrected and thermal-corrected (298 K) energies of stationary points (Hartree).[a]

structure	*E*	*E* + *ZPE*	*H*	*G*
twisted-**1**$^{+}$	-2226.99821760	-	-	-
twisted-**2'**	-2384.48556171	-2383.708006	-2383.662450	-2383.784239
twisted-**2'**$^{+}$	-2384.27537950	-	-	-
twisted-**3'**	-3667.55069824	-3666.906436	-3666.862250	-3666.979972
twisted-**3'**$^{+}$	-3667.33927934	-	-	-
meso-**3'**	-3667.53900632	-3666.895159	-3666.850933	-3666.968493
TS-**3'**	-3667.47120342	-3666.827778	-3666.784555	-3666.899034

a) *E*: electronic energy; *ZPE*: zero-point energy; *H* (= $E + ZPE + E_{vib} + E_{rot} + E_{trans} + RT$): sum of electronic and thermal enthalpies; *G* (= *H* – *TS*): sum of electronic and thermal free energies.

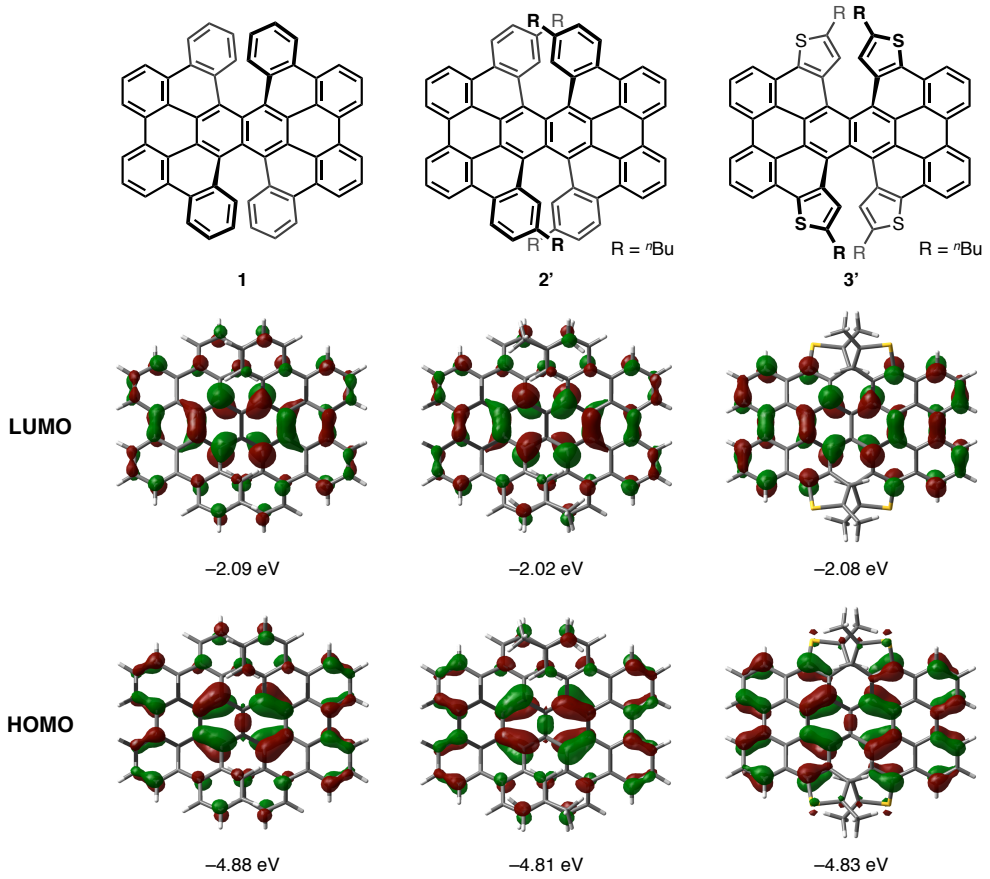


Figure S3. Distributions and energy levels of frontier molecular orbitals (isovalue = 0.03) of **1**, **2'**, and **3'**.

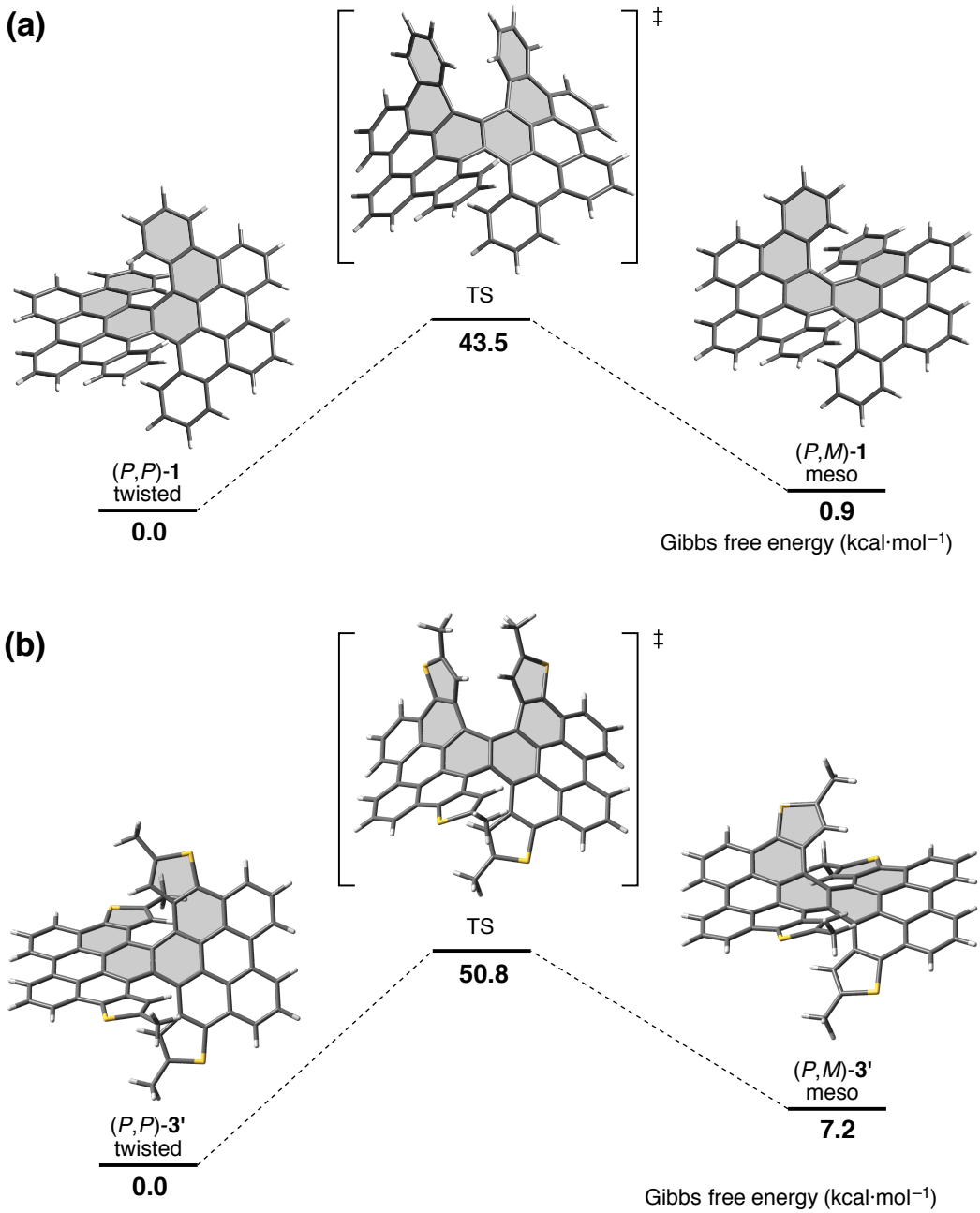


Figure S4. Isomerization between (*P*,*P*)-isomer and (*P*,*M*)-isomer of (a) **1** and (b) **3'**. Calculated at the B3LYP/6-31G(d) level.

Table S3. Cartesian coordinates of optimized species.

twisted-**1**$^{+}$

C	2.452082	0.672197	0.241276	C	-3.695171	-2.720842	0.892685	H	7.068858	-0.987087	0.004381
C	2.452078	-0.672165	-0.241269	C	-4.909796	-3.415833	0.937395	H	7.036599	-3.351191	-0.630985
C	1.218458	-1.365155	-0.404097	C	-6.108597	-2.788182	0.606883	H	4.931501	-4.461727	-1.219093
C	-0.000003	-0.713899	0.000005	C	-6.123047	-1.447361	0.253447	H	4.931523	4.461734	1.219137
C	0.000002	0.713948	0.000004	C	-4.930947	-0.705030	0.183710	H	7.036605	3.351224	0.630921
C	1.218464	1.365183	0.404152	C	2.439954	3.322062	1.337265	H	7.068854	0.987132	-0.004495
C	-1.218469	-1.365145	0.404108	C	-2.439927	3.322076	-1.337271	H	-7.068849	0.987175	0.004466
C	-2.452084	-0.672148	0.241274	C	2.439918	-3.322084	-1.337140	H	-7.036583	3.351264	-0.630957
C	-2.452077	0.672213	-0.241276	C	-2.439945	-3.322064	1.337151	H	-4.931491	4.461761	-1.219164
C	-1.218455	1.365190	-0.404148	C	2.413456	-4.547055	-2.034871	H	-4.931533	-4.461694	1.219090
C	3.695819	1.362316	0.459544	C	1.235911	-5.063392	-2.548621	H	-7.036621	-3.351147	0.630967
C	3.695811	-1.362290	-0.459553	C	0.039578	-4.344173	-2.411219	H	-7.068864	-0.987044	-0.004404
C	-3.695821	-1.362264	0.459553	C	0.036534	-3.146234	-1.723667	H	3.335391	-5.087050	-2.214583
C	-3.695809	1.362339	-0.459552	C	1.214305	-2.627586	-1.131286	H	1.250601	-6.003339	-3.092258
C	4.930942	-0.705062	-0.183720	C	-1.214327	-2.627574	1.131300	H	-0.882534	-2.577769	-1.667540
C	6.123037	-1.447399	-0.253463	C	-0.036562	-3.146228	1.723689	H	0.882510	-2.577770	1.667564
C	6.108577	-2.788221	-0.606896	C	-0.039618	-4.344164	2.411245	H	-1.250654	-6.003320	3.092286
C	4.909771	-3.415866	-0.937399	C	-1.235956	-5.063375	2.548644	H	-3.335434	-5.087020	2.214597
C	3.695150	-2.720869	-0.892683	C	-2.413494	-4.547032	2.034887	H	-3.335421	5.086999	-2.214779
C	3.695167	2.720881	0.892713	C	-2.413485	4.547000	-2.035085	H	-1.250671	6.003185	-3.092653
C	4.909787	3.415882	0.937408	C	-1.235965	5.063276	-2.548949	H	0.882478	2.577656	-1.667866
C	6.108584	2.788251	0.606845	C	-0.039642	4.344033	-2.411588	H	-0.882452	2.577664	1.667885
C	6.123039	1.447437	0.253383	C	-0.036578	3.146142	-1.723953	H	1.250727	6.003180	3.092654
C	4.930944	0.705096	0.183662	C	-1.214315	2.627568	-1.131437	H	3.335466	5.086979	2.214767
C	-4.930940	0.705127	-0.183676	C	1.214336	2.627563	1.131439	H	0.876322	4.711510	-2.864081
C	-6.123030	1.447474	-0.253407	C	0.036607	3.146144	1.723964	H	-0.876275	4.711518	2.864097
C	-6.108565	2.788287	-0.606874	C	0.039683	4.344036	2.411598	H	-0.876411	-4.711707	-2.863615
C	-4.909763	3.415910	-0.937431	C	1.236011	5.063271	2.548950	H	0.876367	-4.711704	2.863646
C	-3.695147	2.720902	-0.892726	C	2.413525	4.546987	2.035078				

twisted-**2'**

C	-2.444355	0.676942	-0.246126	C	4.931565	-0.708984	-0.183621	H	4.938819	4.469151	1.211625
C	-2.444146	-0.677660	0.246308	C	-2.450626	3.328285	-1.328433	H	4.940095	-4.467701	-1.211313
C	-1.225545	-1.367107	0.398262	C	2.449610	3.329141	1.328377	H	7.044641	-3.352414	-0.616226
C	0.000106	-0.709906	0.000052	C	-2.449603	-3.329166	1.328271	H	7.062248	-0.985113	0.026124
C	-0.000103	0.709936	0.000051	C	2.450628	-3.328300	-1.328365	H	-3.349171	-5.082055	2.228824
C	-1.225962	1.366742	-0.398167	C	-2.422876	-4.553032	2.034451	H	-1.269065	-6.017469	3.082529
C	1.225966	-1.366707	-0.398177	C	-1.248645	-5.077422	2.535438	H	0.877332	-2.630327	1.604506
C	2.444356	-0.676911	-0.246140	C	-0.033034	-4.381153	2.385975	H	-0.876503	-2.630400	-1.604636
C	2.444150	0.677689	0.246300	C	-0.048742	-3.184352	1.688092	H	1.271010	-6.016556	-3.083309
C	1.225549	1.367140	0.398253	C	-1.224349	-2.647264	1.110505	H	3.350801	-5.080686	-2.229266
C	-3.698030	1.363000	-0.466064	C	1.225167	-2.646787	-1.110565	H	3.349224	5.081874	2.229174
C	-3.697622	-1.364059	0.466332	C	0.049748	-3.184121	-1.688301	H	1.269104	6.017295	3.082888
C	3.698035	-1.362970	-0.466081	C	0.034446	-4.380783	-2.386434	H	-0.877357	2.630383	1.604440
C	3.697627	1.364086	0.466326	C	1.250276	-5.076646	-2.535994	H	0.876521	2.630437	-1.604605
C	-4.931358	-0.710365	0.184073	C	2.424321	-4.552014	-2.034818	H	-1.271041	6.016416	-3.083608
C	-6.119407	-1.449436	0.243426	C	2.422907	4.552928	2.034694	H	-3.350849	5.080556	-2.229507

C	-6.112540	-2.794597	0.600666	C	1.248674	5.077312	2.535687	C	-1.240419	-4.921857	-2.987920
C	-4.921448	-3.420996	0.935991	C	0.033043	4.381112	2.386088	H	-1.500167	-5.896318	-2.554814
C	-3.702664	-2.723237	0.895225	C	0.048735	3.184366	1.688108	H	-2.083009	-4.245871	-2.814236
C	-3.703470	2.722137	-0.895081	C	1.224348	2.647278	1.110532	H	-1.142339	-5.068434	-4.070983
C	-4.922412	3.419628	-0.935648	C	-1.225169	2.646803	-1.110583	C	1.242035	-4.921981	2.987244
C	-6.113296	2.792977	-0.600045	C	-0.049738	3.184133	-1.688337	H	1.502236	-5.896093	2.553623
C	-6.119789	1.447828	-0.242749	C	-0.034457	4.380728	-2.386558	H	2.084337	-4.245533	2.813956
C	-4.931562	0.709028	-0.183571	C	-1.250314	5.076558	-2.536205	H	1.143964	-5.069188	4.070221
C	4.931361	0.710410	0.184021	C	-2.424344	4.551947	-2.035003	C	1.240378	4.921810	-2.988098
C	6.119400	1.449498	0.243344	H	-7.062009	-0.986992	-0.025335	H	1.142225	5.068423	-4.071151
C	6.112527	2.794655	0.600602	H	-7.043733	-3.354307	0.616948	H	1.500160	5.896257	-2.554982
C	4.921440	3.421029	0.935993	H	-4.938843	-4.469118	1.211620	H	2.082975	4.245811	-2.814495
C	3.702666	2.723249	0.895264	H	-4.940069	4.467739	-1.211305	C	-1.242031	4.921922	2.987368
C	3.703477	-2.722116	-0.895064	H	-7.044619	3.352475	-0.616156	H	-1.501986	5.896256	2.554099
C	4.922426	-3.419590	-0.935656	H	-7.062240	0.985182	0.026198	H	-2.084422	4.245690	2.813674
C	6.113314	-2.792924	-0.600094	H	7.062000	0.987074	-0.025461	H	-1.144112	5.068675	4.070422
C	6.119800	-1.447772	-0.242809	H	7.043711	3.354380	0.616846				

twisted-**2'**$^{+}$

C	-2.451898	-0.671871	0.242698	C	4.931747	0.704229	0.188011	H	4.931855	-4.454133	-1.246547
C	-2.451973	0.671601	-0.242721	C	-2.438836	-3.316825	1.342286	H	4.931349	4.454658	1.246634
C	-1.218091	1.364943	-0.406391	C	2.439223	-3.316554	-1.342309	H	7.038287	3.345452	0.660656
C	-0.000037	0.713801	-0.000021	C	-2.439215	3.316561	-1.342297	H	7.070636	0.985868	0.009328
C	0.000042	-0.713804	-0.000024	C	2.438831	3.316817	1.342312	H	-3.321547	5.087855	-2.223136
C	-1.217939	-1.365080	0.406349	C	-2.403525	4.542168	-2.039333	H	-1.240781	5.995754	-3.089363
C	1.217941	1.365074	0.406362	C	-1.224180	5.054205	-2.546001	H	0.882784	2.576151	-1.658387
C	2.451901	0.671867	0.242712	C	-0.011687	4.346422	-2.416153	H	-0.883101	2.576048	1.658286
C	2.451979	-0.671600	-0.242716	C	-0.034479	3.147760	-1.722804	H	1.240050	5.995872	3.089352
C	1.218097	-1.364942	-0.406392	C	-1.213674	2.626439	-1.135126	H	3.320941	5.088205	2.223184
C	-3.696111	-1.360293	0.464084	C	1.213371	2.626562	1.135104	H	3.321552	-5.087842	-2.223161
C	-3.696264	1.359893	-0.464076	C	0.034099	3.147755	1.722741	H	1.240784	-5.995739	-3.089383
C	3.696113	1.360289	0.464107	C	0.011155	4.346411	2.416097	H	-0.882781	-2.576150	-1.658373
C	3.696271	-1.359890	-0.464074	C	1.223569	5.054323	2.545987	H	0.883090	-2.576053	1.658304
C	-4.931822	0.703701	-0.187951	C	2.402986	4.542417	2.039352	H	-1.240074	-5.995881	3.089338
C	-6.124313	1.444628	-0.266189	C	2.403531	-4.542157	-2.039352	H	-3.320956	-5.088213	2.223149
C	-6.109901	2.783221	-0.628464	C	1.224184	-5.054193	-2.546017	C	-1.257066	4.875501	3.038968
C	-4.910570	3.410230	-0.957393	C	0.011689	-4.346414	-2.416158	H	-1.523249	5.853613	2.619811
C	-3.695092	2.716749	-0.903051	C	0.034483	-3.147755	-1.722803	H	-2.099798	4.198447	2.871717
C	-3.694787	-2.717147	0.903066	C	1.213682	-2.626433	-1.135133	H	-1.142291	5.011141	4.121051
C	-4.910192	-3.410753	0.957443	C	-1.213374	-2.626571	1.135089	C	1.256458	4.875651	-3.039064
C	-6.109596	-2.783870	0.628543	C	-0.034109	-3.147761	1.722743	H	1.522547	5.853792	-2.619916
C	-6.124156	-1.445279	0.266263	C	-0.011172	-4.346418	2.416097	H	2.099268	4.198689	-2.871839
C	-4.931744	-0.704230	0.187989	C	-1.223587	-5.054333	2.545972	H	1.141635	5.011278	-4.121143
C	4.931827	-0.703699	-0.187940	C	-2.402998	-4.542426	2.039325	C	1.257042	-4.875507	3.038984
C	6.124319	-1.444625	-0.266180	H	-7.070735	0.985115	-0.009201	H	1.142253	-5.011147	4.121066
C	6.109908	-2.783217	-0.628464	H	-7.038651	3.344709	-0.660505	H	1.523231	-5.853619	2.619832
C	4.910579	-3.410224	-0.957401	H	-4.931845	4.454141	-1.246534	H	2.099775	-4.198452	2.871744
C	3.695100	-2.716743	-0.903060	H	-4.931353	-4.454664	1.246592	C	-1.256458	-4.875643	-3.039061
C	3.694786	2.717141	0.903097	H	-7.038288	-3.345452	0.660614	H	-1.522543	-5.853786	-2.619914

C	4.910190	3.410748	0.957481	H	-7.070633	-0.985864	0.009299	H	-2.099269	-4.198683	-2.871830
C	6.109596	2.783868	0.628580	H	7.070740	-0.985114	-0.009185	H	-1.141642	-5.011269	-4.121142
C	6.124158	1.445279	0.266292	H	7.038659	-3.344703	-0.660506				

twisted-**3'**

C	-0.000011	0.707603	-0.000073	C	-3.713121	-2.623747	1.149570	H	7.074196	-3.105656	-1.410008
C	0.000013	-0.707601	0.000061	C	-4.934526	-3.256387	1.445558	H	4.931838	-4.251878	-1.880336
C	-1.227701	-1.366738	0.387798	C	-6.131847	-2.615545	1.181731	H	-7.095401	0.869990	-0.425068
C	-2.454929	-0.674160	0.253929	C	-6.137559	-1.337982	0.618272	H	-7.074138	3.105355	-1.410966
C	-2.454940	0.674086	-0.254037	C	-4.949493	-0.668373	0.304147	H	-4.931762	4.251505	-1.881387
C	-1.227729	1.366702	-0.387859	C	2.448007	3.219102	1.434222	H	-4.931693	-4.251667	1.881175
C	1.227684	1.366814	0.387588	C	2.448174	-3.219024	-1.434115	H	-7.074092	-3.105594	1.410659
C	2.454918	0.674208	0.253904	C	-2.448065	-3.218822	1.434738	H	-7.095391	-0.870231	0.424759
C	2.454951	-0.674132	-0.253805	C	-2.448114	3.218746	-1.434843	H	-0.916702	3.097737	1.488863
C	1.227744	-1.366775	-0.387545	C	1.231371	2.635769	1.085715	H	0.916602	3.097508	-1.489443
C	3.704988	1.315190	0.572298	C	0.117697	3.391312	1.603263	H	0.916644	-3.097475	1.489465
C	3.705056	-1.315072	-0.572141	C	0.472162	4.514339	2.285219	H	-0.916537	-3.097771	-1.488911
C	-3.705032	1.314961	-0.572552	S	2.218286	4.702544	2.338928	C	-0.424216	5.514959	2.949206
C	-3.705011	-1.315079	0.572395	S	-2.218445	4.702063	-2.339772	H	-0.212778	5.604022	4.021903
C	3.713074	2.623968	1.149222	C	-0.472313	4.513910	-2.286057	H	-0.315088	6.514265	2.509681
C	4.934466	3.256671	1.445127	C	-0.117811	3.391008	-1.603918	H	-1.468699	5.209900	2.834088
C	6.131799	2.615787	1.181452	C	-1.231457	2.635517	-1.086236	C	0.424027	5.514345	-2.950379
C	6.137535	1.338117	0.618238	C	-1.231415	-2.635556	1.086172	H	0.212933	5.602623	-4.023216
C	4.949480	0.668435	0.304218	C	-0.117762	-3.391009	1.603900	H	0.314472	6.513915	-2.511578
C	4.949514	-0.668272	-0.304011	C	-0.472254	-4.513916	2.286037	H	1.468553	5.209645	-2.834705
C	6.137605	-1.337915	-0.617981	S	-2.218382	-4.702122	2.339691	C	-0.423908	-5.514977	-2.949225
C	6.131936	-2.615586	-1.181191	S	2.218542	-4.702488	-2.338811	H	-0.212446	-5.603987	-4.021922
C	4.934636	-3.256513	-1.444914	C	0.472410	-4.514333	-2.285191	H	-0.314740	-6.514294	-2.509739
C	3.713210	-2.623851	-1.149061	C	0.117877	-3.391309	-1.603265	H	-1.468408	-5.209973	-2.834116
C	-4.949502	0.668209	-0.304359	C	1.231503	-2.635728	-1.085672	C	0.424090	-5.514322	2.950395
C	-6.137578	1.337777	-0.618536	H	4.931614	4.252035	1.880550	H	0.212951	-5.602615	4.023221
C	-6.131886	2.615341	-1.181994	H	7.074035	3.105889	1.410305	H	0.314588	-6.513892	2.511581
C	-4.934577	3.256226	-1.445769	H	7.095375	0.870341	0.424828	H	1.468611	-5.209586	2.834769
C	-3.713162	2.623629	-1.149727	H	7.095421	-0.870105	-0.424534				

twisted-**3'**$^{+}$

C	-0.000612	0.710520	-0.000264	C	-3.713062	-2.625834	1.136246	H	7.079602	-3.117403	-1.363415
C	0.000614	-0.710537	-0.000113	C	-4.930469	-3.264167	1.419697	H	4.937169	-4.251172	-1.853725
C	-1.220770	-1.367385	0.394714	C	-6.135425	-2.629594	1.146136	H	-7.104782	0.879346	-0.392075
C	-2.461441	-0.670330	0.251834	C	-6.144976	-1.353739	0.593121	H	-7.079542	3.117142	-1.364278
C	-2.462607	0.666100	-0.252036	C	-4.951254	-0.671868	0.293684	H	-4.937089	4.250807	-1.854737
C	-1.223141	1.365274	-0.395035	C	2.446704	3.214891	1.437393	H	-4.929609	-4.259181	1.855009
C	1.220754	1.367454	0.394469	C	2.452480	-3.210729	-1.437350	H	-7.074053	-3.129164	1.364833
C	2.461430	0.670365	0.251798	C	-2.446767	-3.214599	1.437979	H	-7.103227	-0.891438	0.392581
C	2.462618	-0.666170	-0.251793	C	-2.452417	3.210432	-1.438083	H	-0.923431	3.080571	1.518775
C	1.223158	-1.365373	-0.394704	C	1.223085	2.623645	1.097514	H	0.917920	3.081799	-1.520133
C	3.708039	1.317398	0.561375	C	0.111268	3.377587	1.619119	H	0.923361	-3.080218	1.519557
C	3.710393	-1.311085	-0.561077	C	0.469874	4.502827	2.294407	H	-0.917853	-3.082117	-1.519579
C	-3.710369	1.310958	-0.561495	S	2.219468	4.693863	2.330989	C	-0.413935	5.503991	2.972112

C	-3.708063	-1.317301	0.561483	S	-2.227866	4.689623	-2.331996	H	-0.183841	5.589280	4.040630
C	3.713012	2.626049	1.135868	C	-0.477945	4.501547	-2.295745	H	-0.304951	6.502650	2.532418
C	4.930408	3.264432	1.419261	C	-0.117299	3.377049	-1.620307	H	-1.460908	5.203320	2.873104
C	6.135375	2.629794	1.145902	C	-1.227730	2.621330	-1.098319	C	0.404030	5.504057	-2.973847
C	6.144950	1.353829	0.593142	C	-1.223132	-2.623416	1.098045	H	0.173618	5.588676	-4.042350
C	4.951242	0.671907	0.293770	C	-0.111341	-3.377225	1.619898	H	0.293400	6.502640	-2.534391
C	4.952439	-0.663487	-0.293181	C	-0.469978	-4.502316	2.295418	H	1.451534	5.205211	-2.874931
C	6.147372	-1.343392	-0.592254	S	-2.219572	-4.693367	2.331923	C	-0.403894	-5.504656	-2.972794
C	6.140087	-2.619380	-1.144999	S	2.227971	-4.690097	-2.330981	H	-0.173391	-5.589535	-4.041256
C	4.936261	-3.256059	-1.418637	C	0.478050	-4.502012	-2.294850	H	-0.293332	-6.503139	-2.533092
C	3.717718	-2.619735	-1.135543	C	0.117371	-3.377385	-1.619644	H	-1.451399	-5.205758	-2.874040
C	-4.952426	0.663414	-0.293521	C	1.227777	-2.621565	-1.097747	C	0.413796	-5.503308	2.973421
C	-6.147345	1.343270	-0.592758	H	4.929528	4.259535	1.854368	H	0.183676	-5.588294	4.041958
C	-6.140037	2.619154	-1.145742	H	7.073993	3.129401	1.364555	H	0.304805	-6.502087	2.534003
C	-4.936199	3.255776	-1.419463	H	7.103210	0.891480	0.392754	H	1.460778	-5.202683	2.874355
C	-3.717669	2.619500	-1.136210	H	7.104799	-0.879422	-0.391636				

meso-**3'**

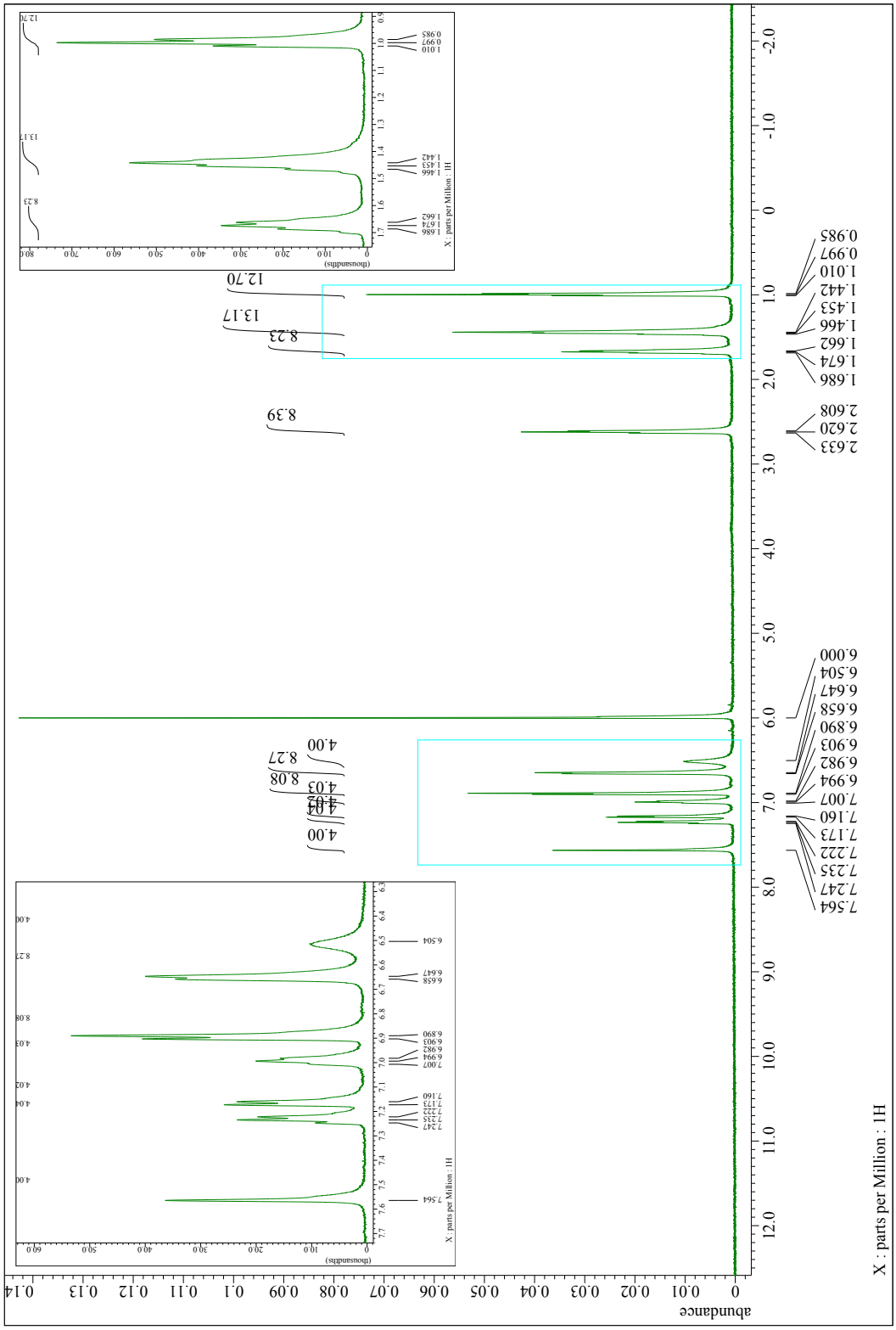
C	-0.715071	0.000047	-0.000058	C	2.836406	-3.746254	0.075653	H	4.621895	4.958912	0.029499
C	0.715010	0.000021	-0.000124	C	3.546129	-4.932246	-0.182190	H	-4.621481	4.959286	0.030665
C	1.408357	-1.246711	0.233815	C	2.874994	-6.059882	-0.627917	H	-3.426849	6.970870	0.842782
C	0.716481	-2.456398	-0.007258	C	1.485634	-6.047053	-0.772843	H	-0.991564	6.962088	1.079660
C	-0.716540	-2.456375	-0.007346	C	0.734597	-4.895579	-0.507810	H	-0.992023	-6.961737	-1.080604
C	-1.408435	-1.246678	0.233743	C	-3.431792	2.572024	-0.632934	H	-3.427292	-6.970464	-0.843435
C	-1.408370	1.246814	-0.233844	C	3.431865	2.571649	-0.633591	H	-4.621724	-4.958985	-0.030691
C	-0.716409	2.456478	0.007134	C	3.431685	-2.571836	0.633556	H	4.621578	-4.959160	-0.029364
C	0.716608	2.456416	0.006999	C	-3.431830	-2.571845	0.633044	H	3.427164	-6.970901	-0.841508
C	1.408392	1.246676	-0.234075	C	-2.752383	1.362025	-0.759908	H	0.991990	-6.962171	-1.079085
C	-1.424618	3.702149	0.142444	C	-4.739632	0.846586	-1.908238	H	3.152081	0.585821	1.770128
C	1.424954	3.702009	0.142143	S	-5.019964	2.497052	-1.369560	H	3.152029	-0.585890	-1.770393
C	-1.424808	-3.701992	-0.142645	S	-5.019923	-2.496862	1.369803	H	-5.405137	-0.875298	-2.977072
C	1.424747	-3.702053	-0.142325	C	-4.739519	-0.846428	1.908465	H	-6.706068	-0.019452	-2.135169
C	0.734870	4.895562	0.507636	C	-2.752367	-1.361863	0.759952	H	-6.035071	0.649049	-3.628605
C	1.486016	6.046944	0.772930	C	2.752253	-1.361792	0.760153	H	-6.033258	-0.648305	3.630002
C	2.875362	6.059662	0.628095	C	3.515752	-0.400406	1.512778	H	-5.405318	0.875939	2.976323
C	3.546442	4.932008	0.182277	C	4.739311	-0.846241	1.908793	H	-6.706467	0.018178	2.136671
C	2.836657	3.746114	-0.075676	S	5.019713	-2.496769	1.370466	H	6.033835	0.647615	-3.629788
C	-2.836337	3.746386	-0.075087	S	5.019942	2.496495	-1.370363	H	6.706152	-0.019414	-2.136314
C	-3.545978	4.932321	0.183128	C	4.739492	0.845947	-1.908726	H	5.404994	-0.876474	-2.976643
C	-2.874703	6.059910	0.628841	C	3.515816	0.400254	-1.512923	H	5.405748	0.877165	2.974535
C	-1.485321	6.047063	0.773318	C	2.752326	1.361707	-0.760342	H	6.030702	-0.646722	3.631935
C	-0.734345	4.895624	0.507803	C	-5.778288	0.116547	-2.704550	H	6.707064	0.016172	2.138450
C	-0.734618	-4.895483	-0.508160	C	-5.777940	-0.116478	2.705154	C	-3.515882	-0.400599	1.512731
C	-1.485690	-6.046774	-0.773909	C	5.777919	0.115737	-2.705150	C	-3.515990	0.400732	-1.512528
C	-2.875082	-6.059568	-0.629337	C	5.777493	-0.116226	2.705729	H	-3.152147	0.585542	1.770353
C	-3.546253	-4.932051	-0.183319	H	0.992410	6.961998	1.079399	H	-3.152221	-0.585380	-1.770158
C	-2.836523	-3.746190	0.075001	H	3.427636	6.970602	0.841842				

TS-**3'**

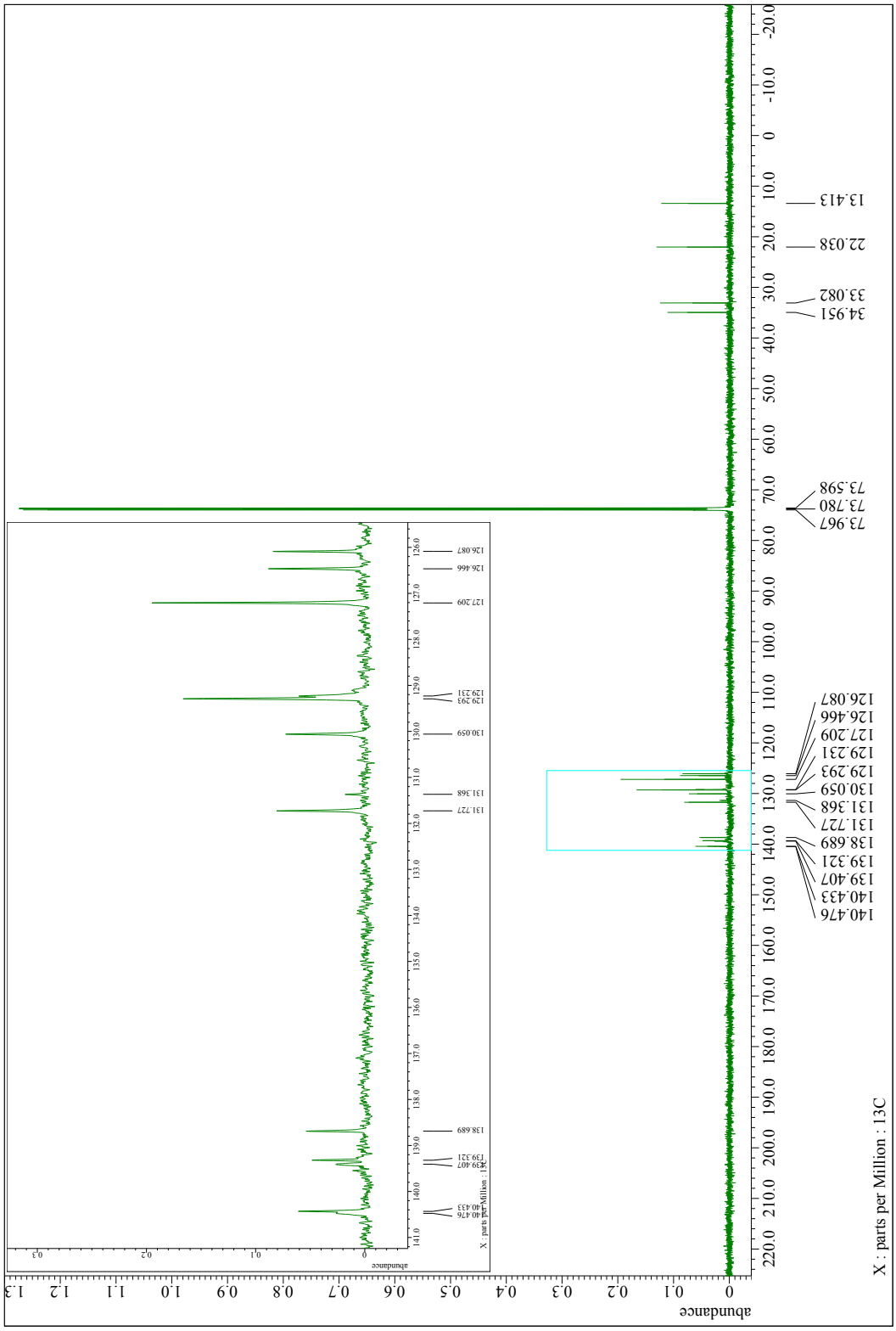
C	-0.855938	-0.025172	0.408040	C	3.299734	-3.120507	0.246974	H	3.940628	5.494315	-0.119250
C	0.570222	0.189183	0.399388	C	4.236122	-4.124176	-0.072233	H	-5.102595	4.258681	-1.538982
C	1.445531	-0.954210	0.585687	C	3.906568	-5.120891	-0.976807	H	-4.015866	6.401922	-2.154196
C	1.062951	-2.119135	-0.081987	C	2.639410	-5.162883	-1.571798	H	-1.637284	6.767576	-1.628583
C	-0.318624	-2.295917	-0.400196	C	1.669409	-4.201783	-1.273949	H	0.633563	-5.781984	-3.294528
C	-1.276132	-1.427838	0.186948	C	-3.893584	2.227254	-0.162665	H	-1.728091	-6.006076	-3.923583
C	-1.702771	1.171415	0.312173	C	3.105425	2.890359	-0.356249	H	-3.484740	-4.762333	-2.691894
C	-1.103156	2.422915	-0.037192	C	3.542320	-2.057503	1.173812	H	5.219162	-4.110429	0.390698
C	0.322461	2.582292	-0.091400	C	-2.962033	-3.089893	-0.509286	H	4.635544	-5.888344	-1.222105
C	1.154195	1.449240	0.048519	C	-3.157187	1.229812	0.477812	H	2.410438	-5.976124	-2.251888
C	-1.905840	3.551156	-0.484990	C	-5.333019	0.813985	1.310824	H	2.612170	0.872317	2.571211
C	0.902720	3.894961	-0.268901	S	-5.608713	2.107864	0.167468	H	3.252032	-0.386592	-1.069088
C	-0.692985	-3.415062	-1.221584	S	-4.404957	-3.931713	0.035346	H	-6.077439	-0.469676	2.845316
C	2.009045	-3.157467	-0.365876	C	-4.310485	-3.161892	1.606630	H	-7.055879	0.989128	2.607409
C	0.085468	5.037812	-0.463844	C	-2.539762	-2.135410	0.419403	H	-7.153131	-0.340539	1.445964
C	0.657953	6.314792	-0.412006	C	2.671523	-0.974835	1.330857	H	-5.306056	-4.606267	2.872343
C	2.033350	6.479004	-0.245438	C	3.151485	-0.027962	2.300230	H	-4.961267	-3.045841	3.637740
C	2.863341	5.369296	-0.186256	C	4.344074	-0.368430	2.861082	H	-6.290167	-3.192342	2.476874
C	2.317583	4.075106	-0.222811	S	4.945709	-1.889986	2.208091	H	6.230469	0.864953	-2.702385
C	-3.299930	3.394513	-0.724098	S	4.779528	2.883115	-0.873325	H	6.750117	0.456225	-1.062086
C	-4.046390	4.415010	-1.338267	C	4.711077	1.159497	-1.191654	H	5.637727	-0.615914	-1.925615
C	-3.443359	5.617057	-1.667886	C	3.488144	0.649516	-0.877900	H	4.583743	1.276011	4.198320
C	-2.099166	5.823894	-1.360872	C	2.554093	1.613316	-0.348198	H	5.273200	-0.239086	4.808935
C	-1.325061	4.821129	-0.763418	C	-6.466118	0.221558	2.091615	H	6.112723	0.667455	3.543875
C	0.297561	-4.257984	-1.802507	C	-5.268245	-3.523679	2.701493	C	-3.280242	-2.270552	1.648121
C	-0.103808	-5.165874	-2.790915	C	5.896521	0.432849	-1.750965	C	-4.009898	0.495564	1.366354
C	-1.449073	-5.302214	-3.144361	C	5.122168	0.368693	3.908290	H	-2.976031	-1.801071	2.576008
C	-2.434802	-4.589443	-2.471578	H	0.025989	7.192988	-0.486895	H	-3.638035	-0.186037	2.102423
C	-2.071459	-3.663799	-1.482189	H	2.455689	7.478577	-0.191166				

8. ^{1}H and ^{13}C NMR Spectra of Products

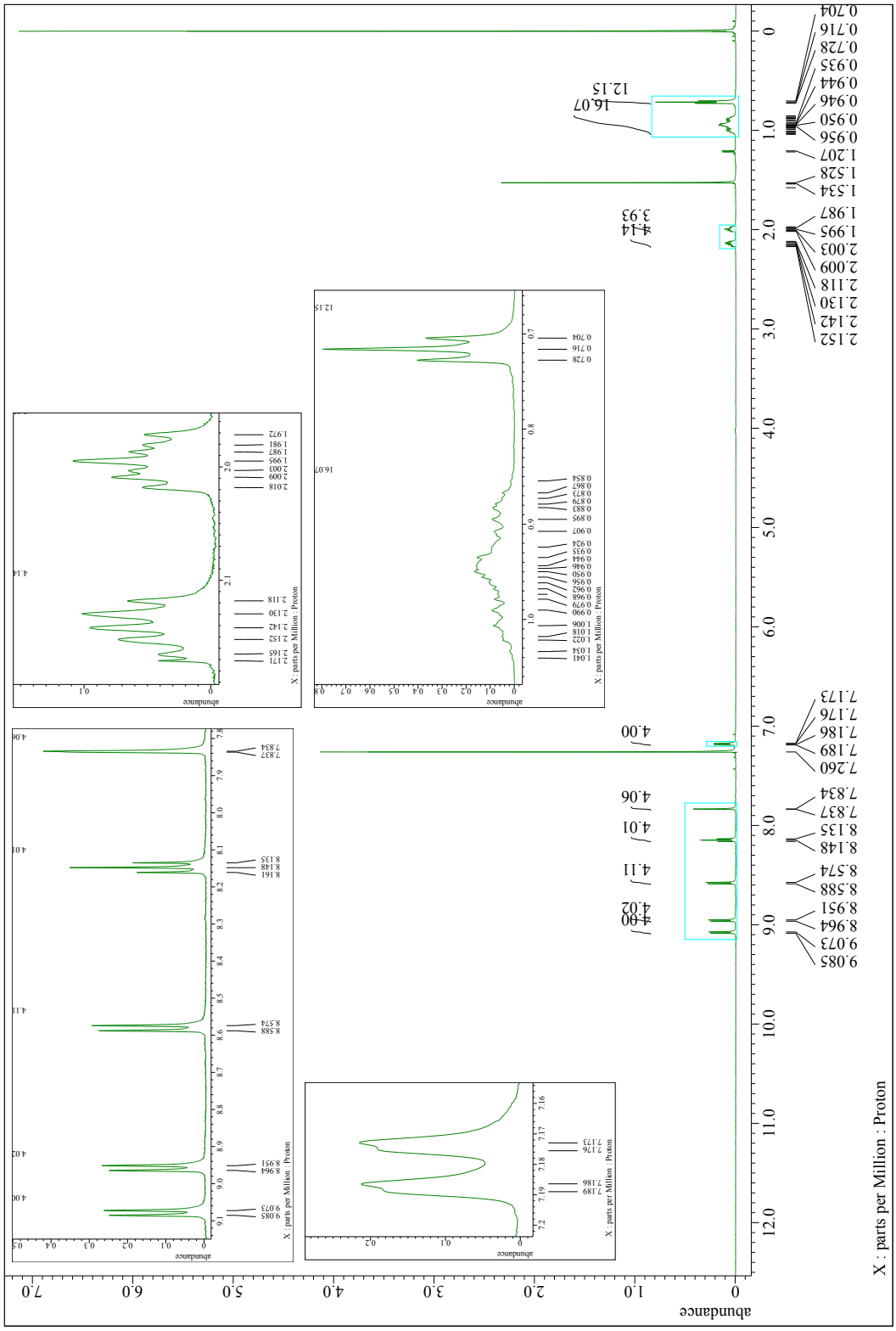
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 130 °C) of **6**



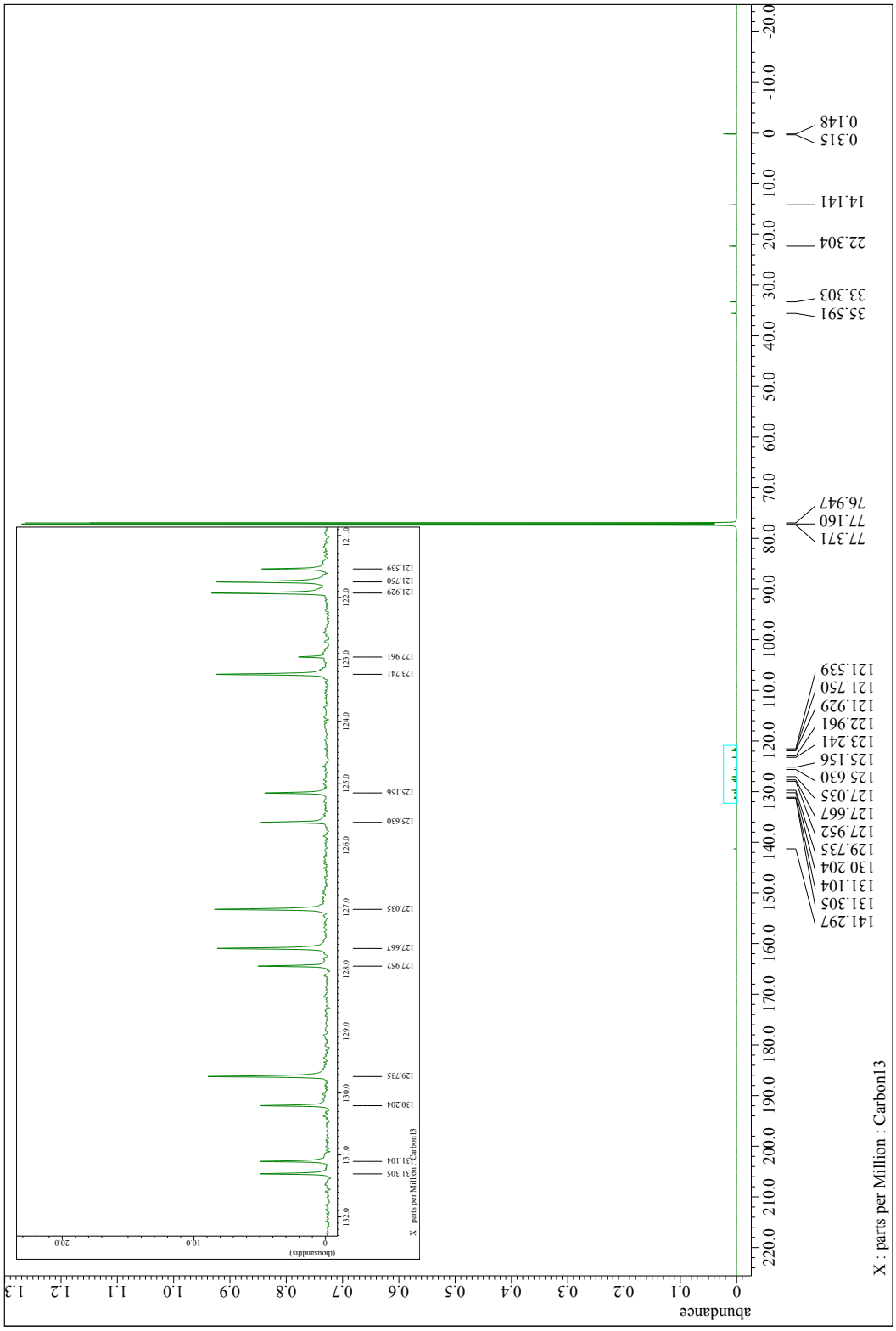
^{13}C NMR (150 MHz, $C_2D_2Cl_4$, 130 °C) of **6**



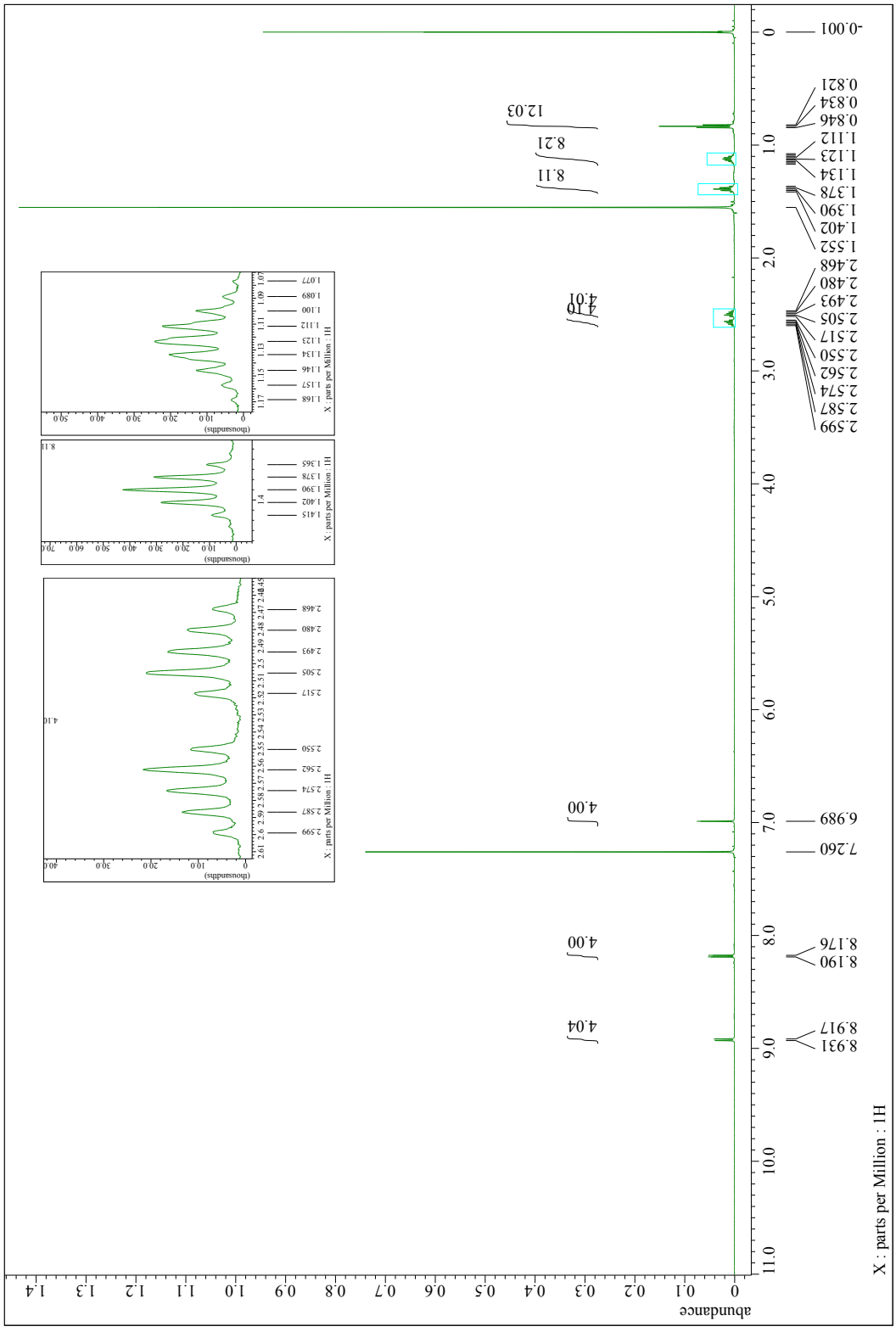
^{1}H NMR (600 MHz, $CDCl_3$) of **2**



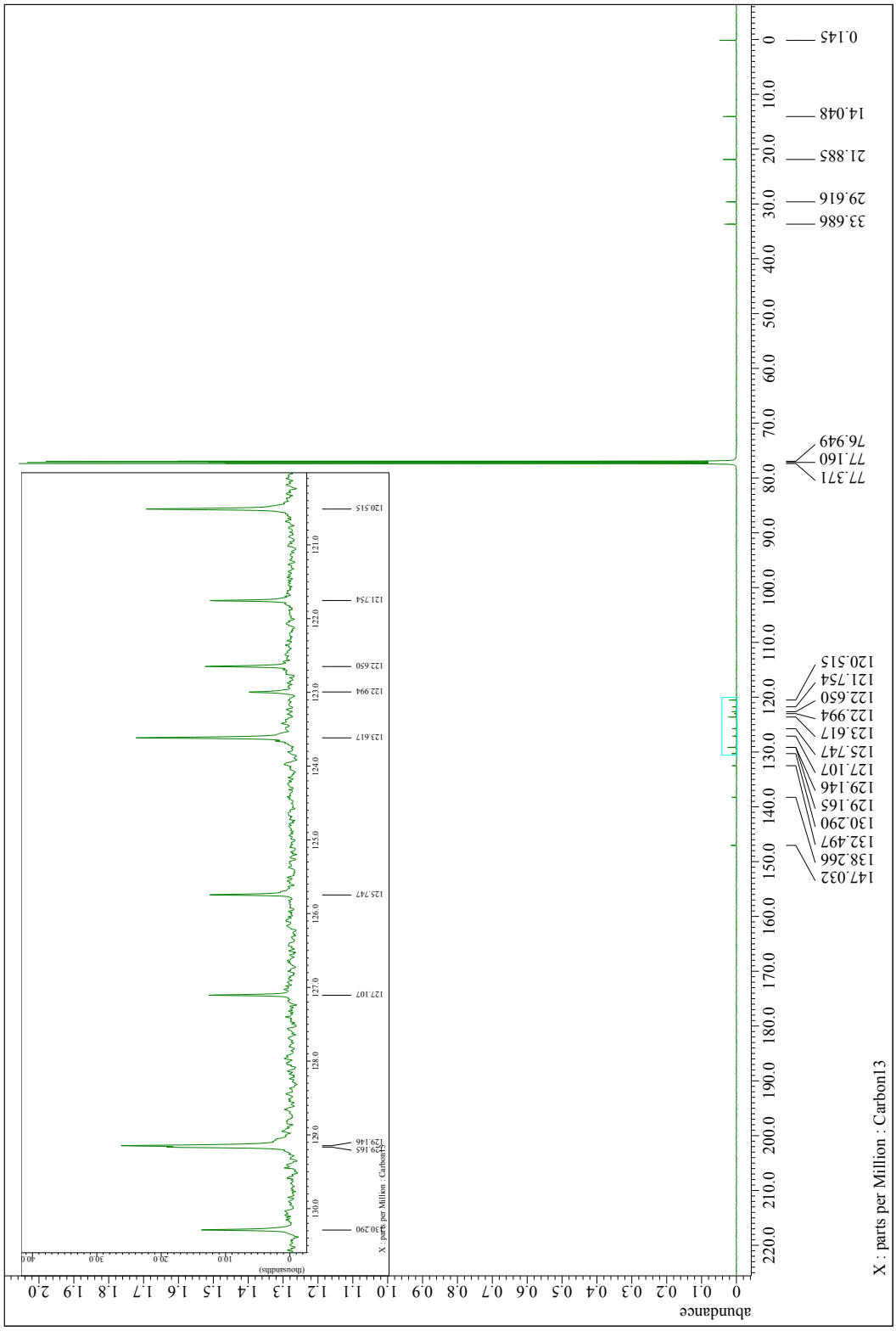
^{13}C NMR (150 MHz, $CDCl_3$) of **2**



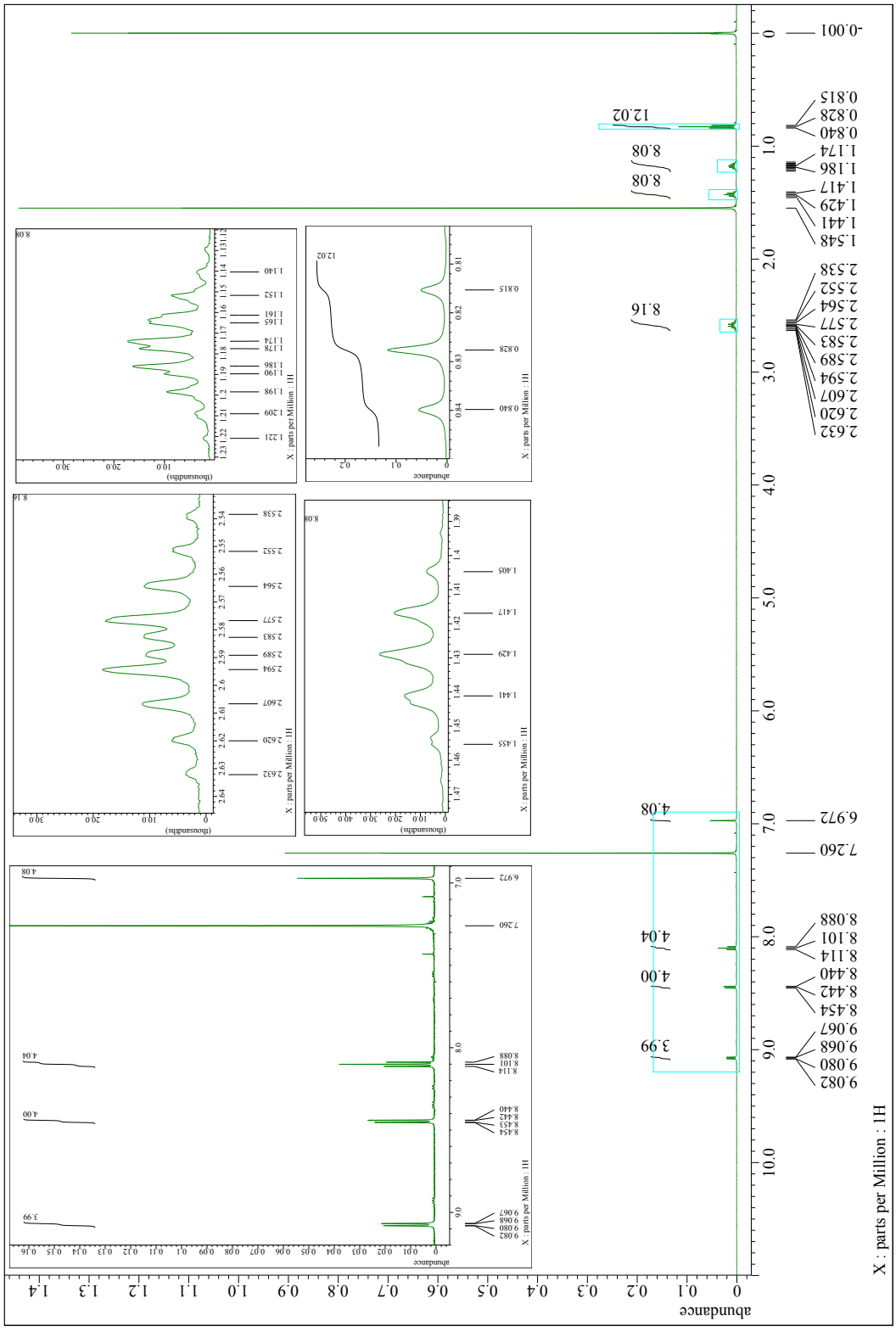
^{1}H NMR (600 MHz, $CDCl_3$) of **8**



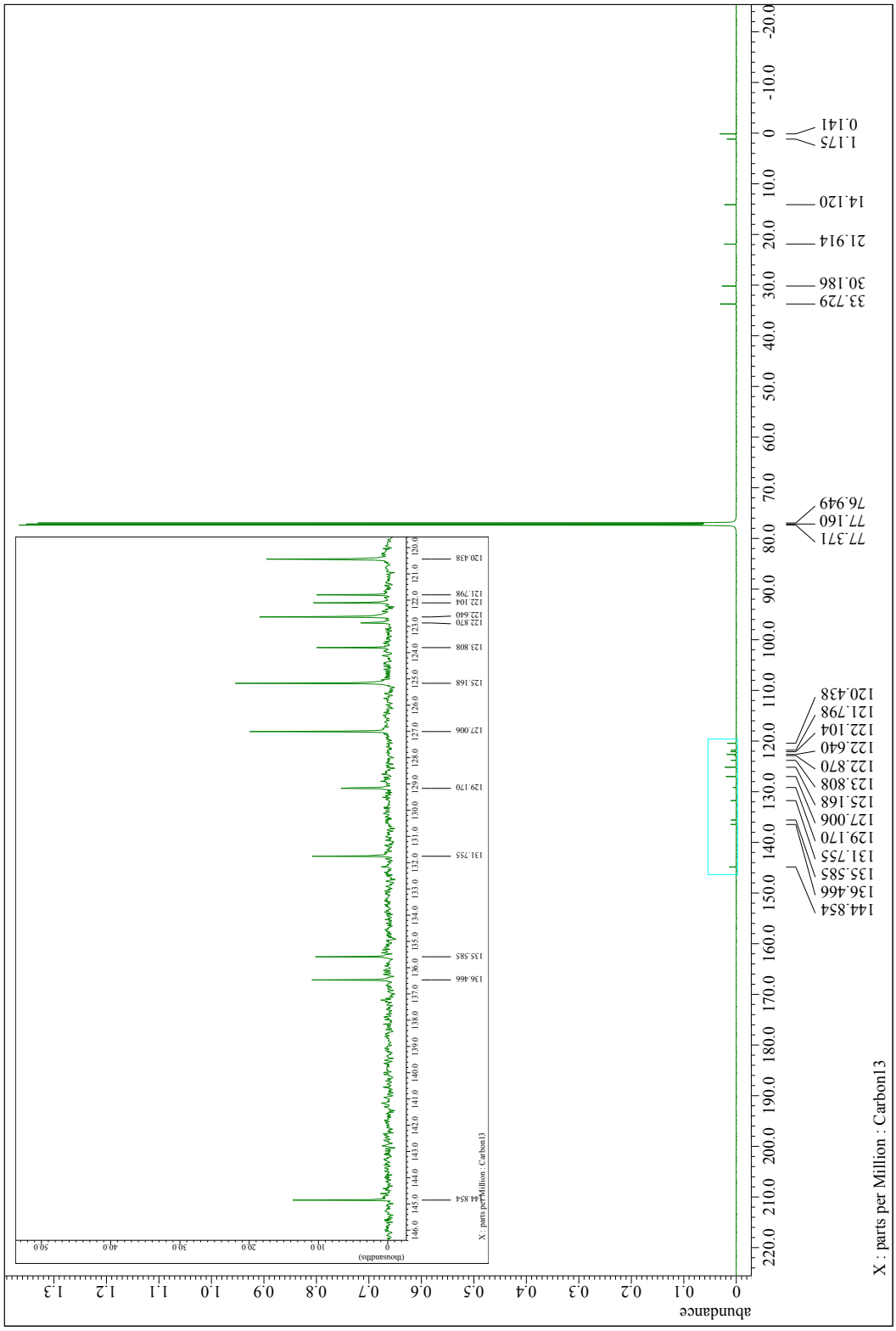
^{13}C NMR (150 MHz, $CDCl_3$) of **8**



^{1}H NMR (600 MHz, $CDCl_3$) of **3**



^{13}C NMR (150 MHz, $CDCl_3$) of **3**



9. References

S1) N. Suzuki, T. Fujita, J. Ichikawa, *Org. Lett.,* 2015, **17**, 4984.

S2) T. Oyamada, H. Uchiuzo, C. Adachi, T. Takahashi, S. Akiyama, S. JP Patent 084485, 2007.

S3) T. Fujikawa, Y. Segawa, K. Itami, *J. Am. Chem. Soc.,* 2016, **138**, 3587.

S4) (a) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.,* 1999, **32**, 115; (b) G. M. Sheldrick, *Acta Crystallogr., Sect. A,* 2008, **64**, 112.

S5) (a) K. Wakita, Yadokari-XG, Software for Crystal Structure Analyses, 2001; (b) C. Kabuto, S. Akine, T. Nemoto, E. Kwon, *J. Crystallogr. Soc. Jpn.,* 2009, **51**, 218.

S6) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2013.

S7) (a) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648; (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.,* 1988, **37**, 785.