Supporting Information for

Synthesis of a Double Spiro Polyindenofluorene with Stable Blue Emission

Doojin Vak, Bogyu Lim, Soo-Hyoung Lee, and Dong-Yu Kim

Material Synthesis. Synthesis of 1-bromo-2-benzylbenzene was reported in our previous work.[1] 1-chlorododecane was purchased from TCI chemicals. Other starting materials were purchased from Aldrich Chemical Co. and used without further purification except THF, which was dried by refluxing over calcium hydride

4,4,5,5-tetramethyl-2-(2,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,2-dioxaborolane (1). 1,4-dibromoxylene (13.2 g, 50 mmol) was dissolved in 300 ml THF and cooled to -80 ^{o}C. *tert*-buthyllithium (1.7 M) (100 ml, 170 mmol) was added very slowly through a cannula under nitrogen. The solution was stirred at -40 ^{o}C for 12 h. The solution was cooled to -80 ^{o}C again and then 2-isopropoxy-4,4,5,6,-tetramethyl-1,3,2-dioxaborolane (25 ml, 123 mmol) was added quickly. The solution was stirred at rt for 1 h. The solution was extracted using 500 ml of ether, dried over $MgSO_4$, and evaporated. The crude product was dissolved in 300 ml of boiling hexane and recrystallized in the refrigerator. The product was white powder with 47 % yield. Mp: 178 ^{o}C . ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (s, 24H), 2,48 (s, 6H), 7,54 (s, 2H). ^{13}C NMR (75 MHz, CDCl3): δ 21.37, 24.78, 83.39, 136.98, 140.62. Anal. Calcd for $C_{20}H_{32}B_2O_4$: C, 97.08, H, 9.01. Found: C, 97.34, H, 9.31. MS(EI): m/z 358.15 (M^+)

4,4''-Dibromo-2',5'-dimethyl-[1,1';4',1'']terphenyl (2). 1 (7.16 g, 20 mmol), bromoiodobenzene (22.6 g, 80 mmol) and $Pd(PPh_3)_4$ (0.22 g, 0.2 mmol) were dissolved in 400 ml of THF and 100 ml of degassed K_2CO_3 (2 M) solution was added to the THF solution. The reaction mixture was refluxed under nitrogen for 6 h. The reaction mixture was transferred to separatory funnel and 500 ml of ether was added. The organic solution was washed by water several times. The organic layer was dried over $MgSO_4$, and evaporated. The crude product was recrystallized from dichloromethane and hexane. The product was yellowish white powder with 93 % yield. Mp: 202 ^{o}C . ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 6H), 7.11 (s, 2H), 7.23 (d, J = 6.6 Hz, 2H), 7.56 (d, J = 6.6 Hz, 2H). ^{13}C NMR (75 MHz, CDCl3):19.73, 121.12, 130.93,

[1] Vak, D.; Chun, C.; Lee, C. L.; Kim, J.-J.; Kim, D.-Y. *J. Mater. Chem.* **2004**, *14*, 1342.

131.35, 131.80, 132.73, 140.03, 140.51. Anal. Calcd for $C_{20}H_8Br_2$: C, 57.72, H, 3.88. Found: C, 57.53, H, 3.86. MS(EI): m/z 413.95 (M^+)

2,8-Dibromo-indeno[1,2-b]fluorene-6,12-dione (3). KMnO4 (15.8 g, 100 mmol) was placed in 3-neck flask and 20 ml of water was added. To the slurry, 2 (8.33 g, 20 mmol) in 500 ml of pyridine was added. The reaction mixture was stirred using mechanical stirrer and refluxed. $KMnO_4$ (7.9 g, 50 mmol) in 20 ml of water solution was added to the reaction mixture four times every 30 min. The reaction mixture was further refluxed for 6 h. The hot solution was filtered to remove the dark-brown solid (MnO_2) and evaporated to remove pyridine. 250 ml of H_2SO_4 was added to the flask and the mixture was stirred for 12 h at 80 ^oC. The hot reaction mixture was added to ice. Precipitates were filtered and washed by water, methanol and hot THF several times. The precipitate was dried in vacuum oven at 150 ^oC for 4 days. The product was violet colored insoluble powder with yield of 76 %. Anal. Calcd for $C_{20}H_8Br_2O_2$: C, 54.58, H, 1.83. Found: C, 54.51, H, 1.82. MS(DI): m/z 437.80 (M^+)

2',8'-dibromo-dispiro[[9,10]dihydro-anthracene-9,6'-[6,12]dihydro-indeno[1,2-b]fluorene-12',9"-[9,10]dihydro-anthracene] (4) Mg (2.88 g, 12 mmol) was charged into a two-neck flask and flame-dried under nitrogen. 1-benzyl-2-bromobenzene (2.96 g, 12 mmol) in 100 ml of THF was added and refluxed for 1 h. 3 was added quickly with the protection of already formed Grignard reagent from air by the flow of nitrogen. The mixture was stirred for 12 h at rt 10 ml of HCl (2 M) solution was added and the mixture was extracted using 300 ml of ether, dried over $MgSO_4$, and evaporated. Unreacted starting materials were removed using short liquid column chromatography and the remaining was charged into two-neck flask and 100 ml of acetic acid and 1 ml of conc. HCl solution were added. The mixture was refluxed for 6 h and white precipitates were appeared during the period. The mixture was cooled to rt and the precipitates were filtered and dried in vacuum oven. The product was recrystallized from hot chloroform and methanol twice. The product was white powder with 43 % yield. ^1H NMR (300 MHz, $CDCl_3$): δ 4.57 (s, 4H), 6.50 (d, J = 7.9 Hz, 4H), 6.99 (t, J = 8.2 Hz, 4H), 7.09 (s, 2H). 7.25 (t, J = 7.4 Hz, 4H), 7.33-7.47 (m, 10H) ^{13}C NMR (75 MHz, CDCl3): 34.75, 59.33, 117.03, 121.53, 121.73, 126.91, 127.09, 127.86, 128.50, 128.61, 130.68, 134.29, 138.35, 138.94, 140.22, 155.59, 157.91. Anal. Calcd for $C_{46}H_{28}Br_2$: C, 74.61, H, 3.81. Found: C, 74.40, H, 3.80.

2',8'-dibromo-10,10,10",10"-tetradodecyl-dispiro[[9,10]dihydro-anthracene-9,6'-[6,12]dihydro-indeno[1,2-b]fluorene-12',9"-[9,10]dihydro-anthracene] (5) 4 (1.4 g, 1.9 mmol), 1-chlorododecane (1.68 g, 12 mmol) and a peace of 18-crown-6 was dissolved in 150 ml of THF. To the solution, excess amount of KH, which was dispersed in mineral oil, was

added under nitrogen. The mixture was stirred at rt for 5 h and unreacted KH was deactivated by addition of methanol under nitrogen. The solution was extracted by ether, dried over $MgSO_4$, and evaporated. The crude product was purified by liquid chromatography using hexane and dichloromethane (9.8: 0.22) as eluents. The product was white powder with 49 % yield. (R_f = 0.44) Mp: 152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.8-1.3 (m, 92H), 2.24 (br, 8H), 6.33 (d, J = 8.1 Hz, 4H), 6.90 (t, J = 7.5 Hz, 4H), 7.03 (s, 2H). 7.25 (m, J = 7.4 Hz, 8H), 7.32 (s, 2H), 7.52 (d, J = 8.1 Hz , 4H) ^{13}C NMR (75 MHz, CDCl3): δ 13.99, 22.58, 25.91, 26.36, 29.25, 29.55, 29.64, 29.81, 29.85 30.09, 31.87, 45.68, 46.87, 57.58, 117.12, 121.05, 121.87, 125.91, 126.25, 127.35, 128.89, 129.07, 130.20, 137.32, 139.04, 139.25, 140.20, 158.20, 160.67. Anal. Calcd for $C_{94}H_{124}Br_2$: C, 79.86, H, 8.84. Found: C, 80.51, H, 9.28.

Poly[10,10,10”,10”-tetradodecyl-dispiro[[9,10]dihydro-anthracene-9,6’-[6,12]dihydro-indeno[1,2-b]fluorene-12’,9”-[9,10]dihydro-anthracene]-2’,8’-diyl] P12SIF bis(2,5-cyclooctadiene)-nickel(0) (0.36 g, 1.3 mmol), dipyridyl (0.20 g, 1.3 mmol) and 1,5-cyclooctadiene were placed in two-neck flask and 10ml of DMF was added. The solution was stirred at 80 °C for 30 min and **5** (0.71 g, 0.5 mmol) in 40 ml of toluene was added to the dark-blue solution under nitrogen. The solution was stirred for a day at 80 °C and poured into a mixture of methanol and conc. HCl solution (8 : 2). Precipitates were filtered and redissolved in 50 ml of hot chloroform. The solution was dropwised into 200 ml of methanol. The polymer was collected and purified by Soxhlet extraction using acetone for 2 days. The precipitation process was repeated again. The polymer was greenish yellow solid with 72 % yield. . ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.6-1.3 (br, 92H), 2.2 (br, 8H), 6.21 (br, 4H), 6.7 (br, 16H), 7.4 (br, 4H). Anal. Calcd for $C_{94}H_{124}$: C, 90.03, H, 9.97. Found: C, 90.01, H, 9.72.

Characterization and Measurements. ^{1}H and ^{13}C NMR spectra were measured by JEOL JNM-LA300WB 300 MHz and processed by ACD/SpecManager. Mass data were obtained by GCMS (Shimadzu, GCMS-QP2010). Thermal properties including glass transition temperature (T_g) were determined by means of differential scanning calorimetry (DSC; TA2010) and thermo-gravimetric analysis (TGA; TA-2050) at a heating rate of 10 °C/min under nitrogen. Melting point (mp) was determined by means of DSC. Elemental analyses were performed by National Center for Inter-University Research Facilities, Seoul National University. (Elemental analyzer; CE Instruments Flash EA 1110). Absorption spectra were measured using a UV/Vis spectrophotometer (K-MAC, Spectraview-2000). Molecular weight of the polymer was measured gel permeation chromatography (GPC, Futecs, NS2001) using tetrahydrofuran (THF) as a solvent and calibrated against polystrene standards.. PL and EL spectra were obtained using a CCD detecter (Princeton Instruments, SPEC-10) with monochromator (Acton Research Co.

SpectraPro-300i) and excitation sources were a xenon lamp with monochromator (Acton Research Co. SpectraPro-150) and Keithley 237 Source Measurement Unit, respectively.

Device Fabrication. The polymer LEDs were fabricated with the structure of ITO / PEDOT (60 nm) / emitting polymer (60 nm) / LiF (5 nm) / Ca (10 nm) / Ag . The glass substrate pre-coated with indium-tin-oxide was cleaned in an ultrasonic bath with acetone, followed by boiling 2-propanol. Surface treatment was carried out by exposing the ITO to UV-ozone. The hole injecting poly(3,4-ethylene dioxythiophene) (PEDOT) layer was spin coated on the ITO with a thickness of 60 nm and baked at 200 °C for 10 min on a hot plate. A 1 wt % solution of polymer in a toluene was spin coated on the PEDOT layer as an emitting layer and baked at 200 °C for 1 hr. LiF and Ca were deposited as the cathode through a shadow mask by thermal evaporation. Finally, a Ag layer was deposited as a protecting layer.

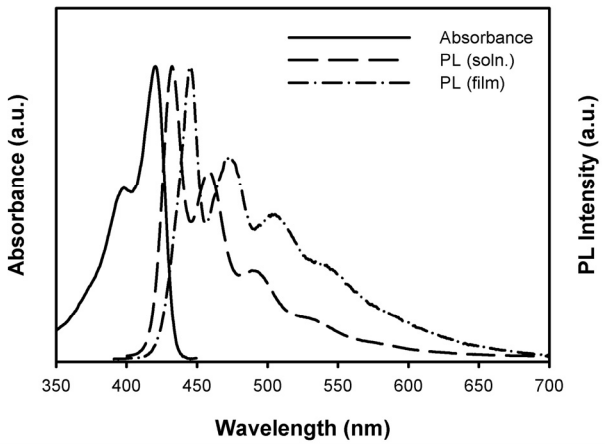

Figure S1. Absorption (solid line) and PL spectra of PSIF in film (long dash line) and in dichloromethane solution (dash dot line).

Cyclic voltammetry (CV) measurements were conducted in a 0.1 M Bu_4NClO_4 acetonitrile solutions using a potentiostat (Eco Chemie, AUTOLAB) at a scan rate of 50 mV/sec at room temperature. To estimate the energy levels of polymers from the vacuum energy level, ferrocene/ferrocenium (Fc/Fc^+) redox couple (4.8 eV from vacuum energy level) was used as a calibration reference.

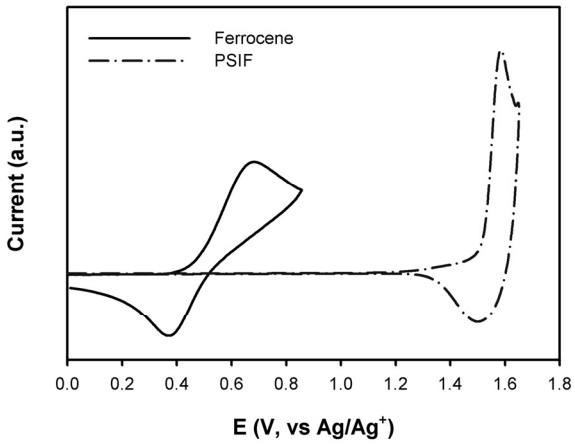

Figure S2. Cyclic voltmmogram of PSIF. CV curve of PSIF (dash dot line) and ferrocene (solid line)

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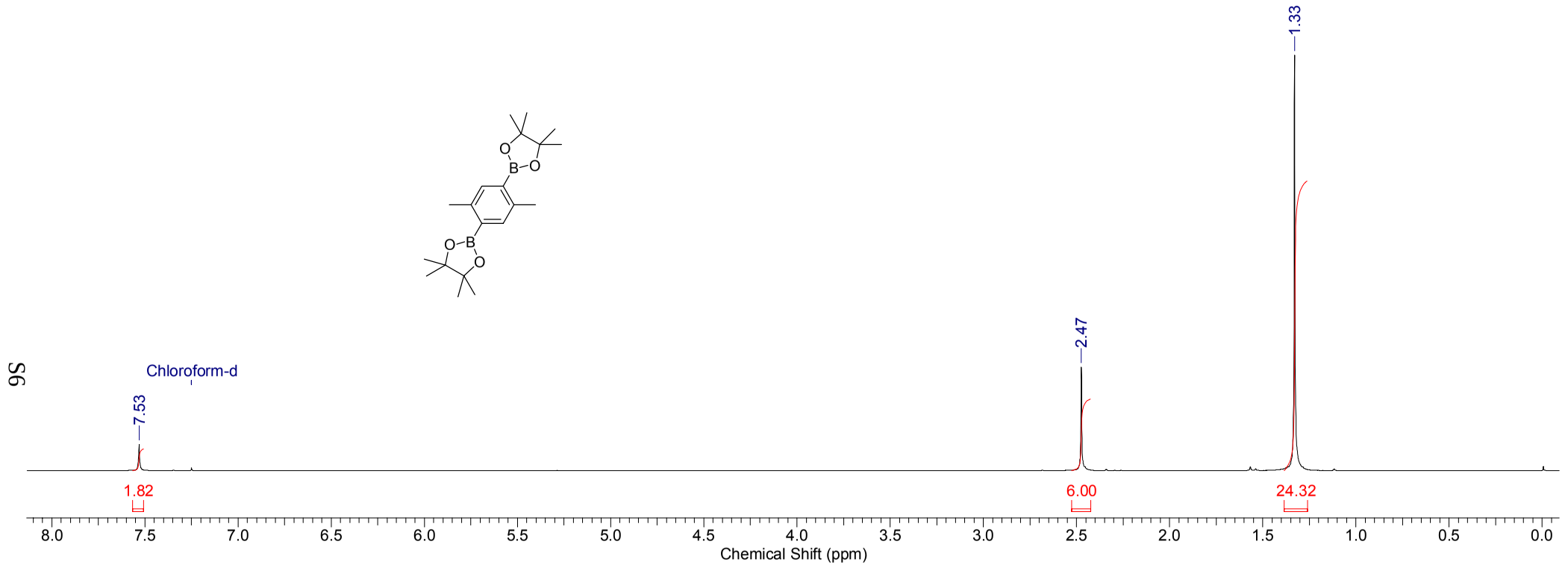
Solvent	CHLOROFORM-D	***Sweep Width (Hz)***	6009.62	***Temperature (degree C)***	0.000		



No.	(ppm)	(Hz)	Height
1	1.33	399.4	1.0000
2	2.47	743.3	0.2489
3	7.53	2262.4	0.0628

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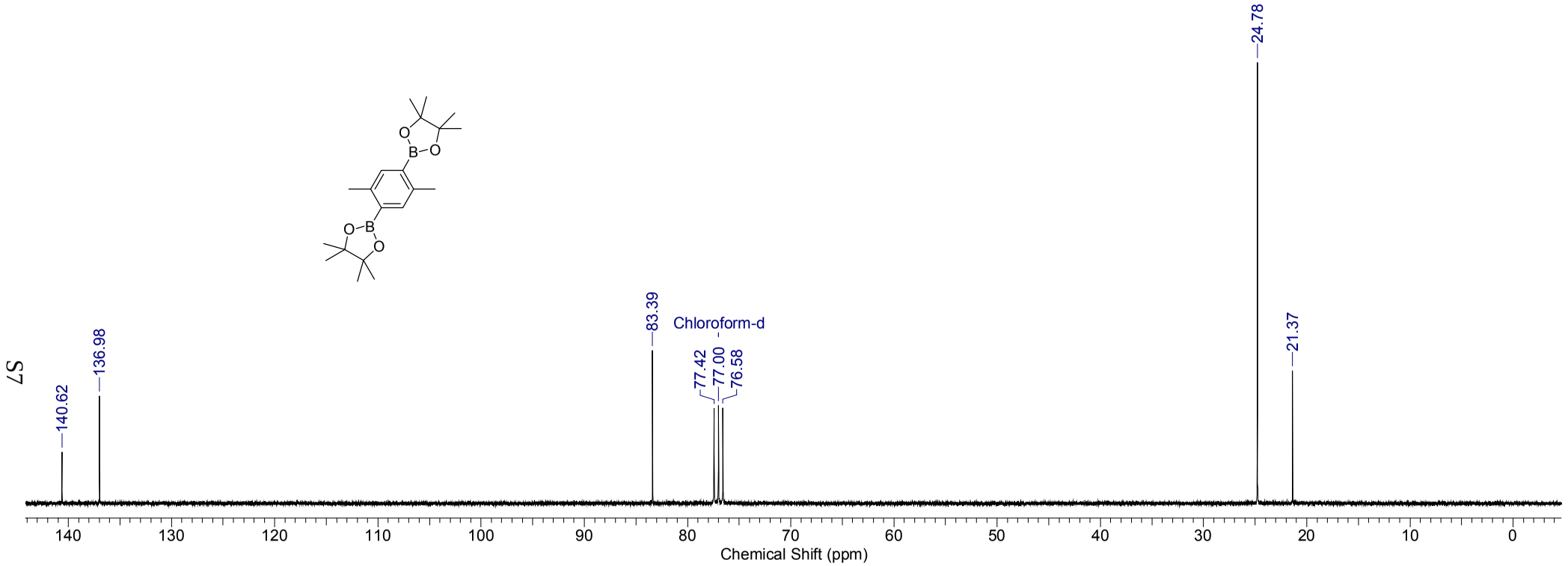
Solvent	CHLOROFORM-D	***Sweep Width (Hz)***	20366.60	***Temperature (degree C)***	0.000		



No.	(ppm)	(Hz)	Height
1	21.37	1612.6	0.3020
2	24.78	1869.7	1.0000
3	76.58	5777.6	0.2163
4	77.00	5809.7	0.2222
5	77.42	5841.7	0.2160
6	83.39	6292.0	0.3472
7	136.98	10335.5	0.2442
8	140.62	10609.9	0.1172

Acquisition Time (sec)	5.4526	***Date***	Sat Jul 10 00:26:47 2004				
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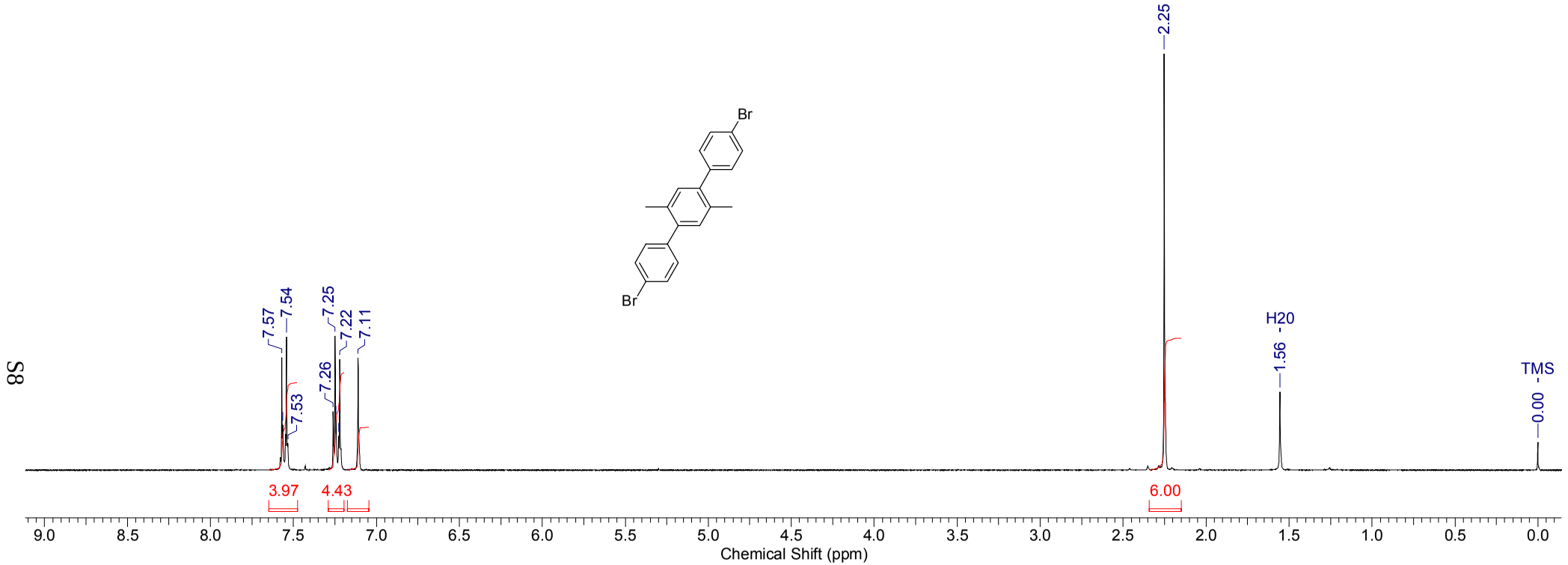
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	6009.62	***Temperature (degree C)***	0.000



No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	-0.00	-0.0	0.0673	8	7.25	2177.7	0.3223
2	1.56	467.1	0.1878	9	7.26	2181.0	0.1410
3	2.25	676.6	1.0000	10	7.53	2263.2	0.0639
4	7.11	2136.1	0.2691	11	7.54	2265.6	0.3196
5	7.22	2169.1	0.2659	12	7.55	2267.6	0.0864
6	7.23	2171.1	0.0817	13	7.56	2272.2	0.1089
7	7.24	2175.7	0.1230	14	7.57	2274.0	0.2705

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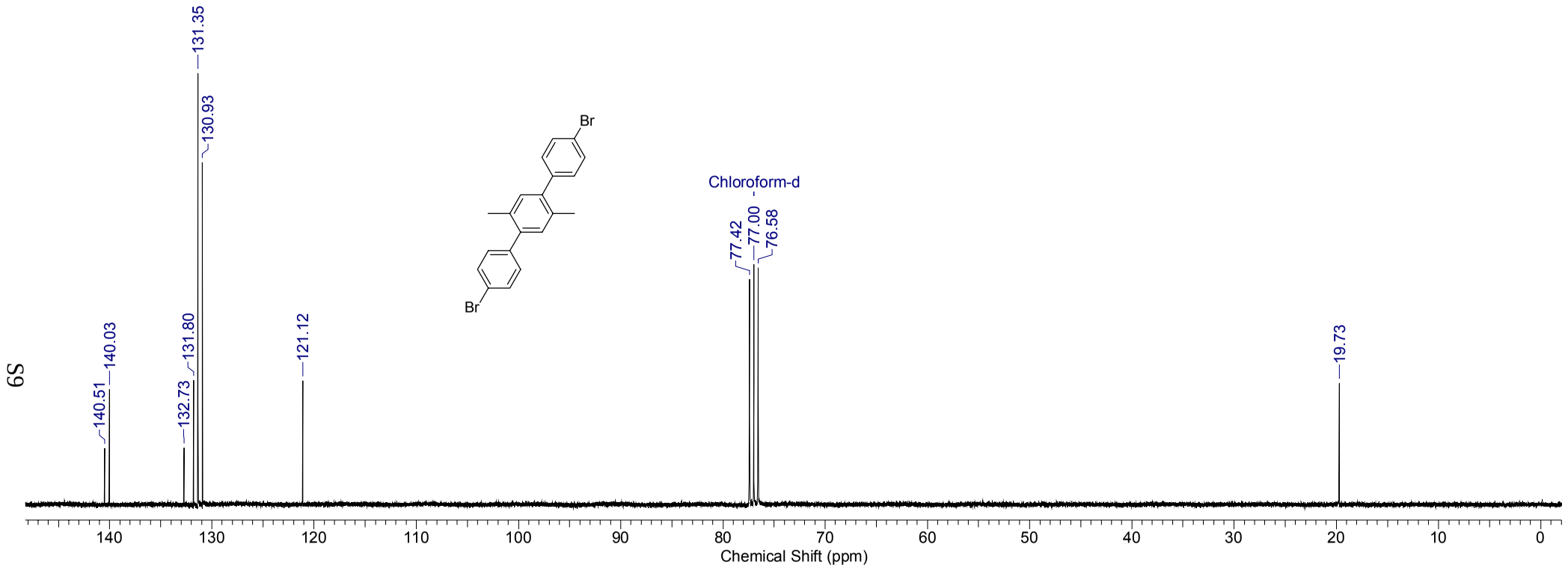
Solvent	CHLOROFORM-D	***Sweep Width (Hz)***	20366.60	***Temperature (degree C)***	0.000		



No.	(ppm)	(Hz)	Height
1	19.73	1488.3	0.2807
2	76.58	5777.6	0.5484
3	77.00	5809.7	0.5562
4	77.42	5841.3	0.5223
5	121.12	9138.7	0.2869
6	130.93	9878.3	0.7931
7	131.35	9910.6	1.0000
8	131.80	9944.2	0.2884
9	132.73	10014.4	0.1316
10	140.03	10565.1	0.2667
11	140.51	10601.2	0.1298

Acquisition Time (sec)	5.4526	***Date***	Sat Jul 31 03:52:26 2004				
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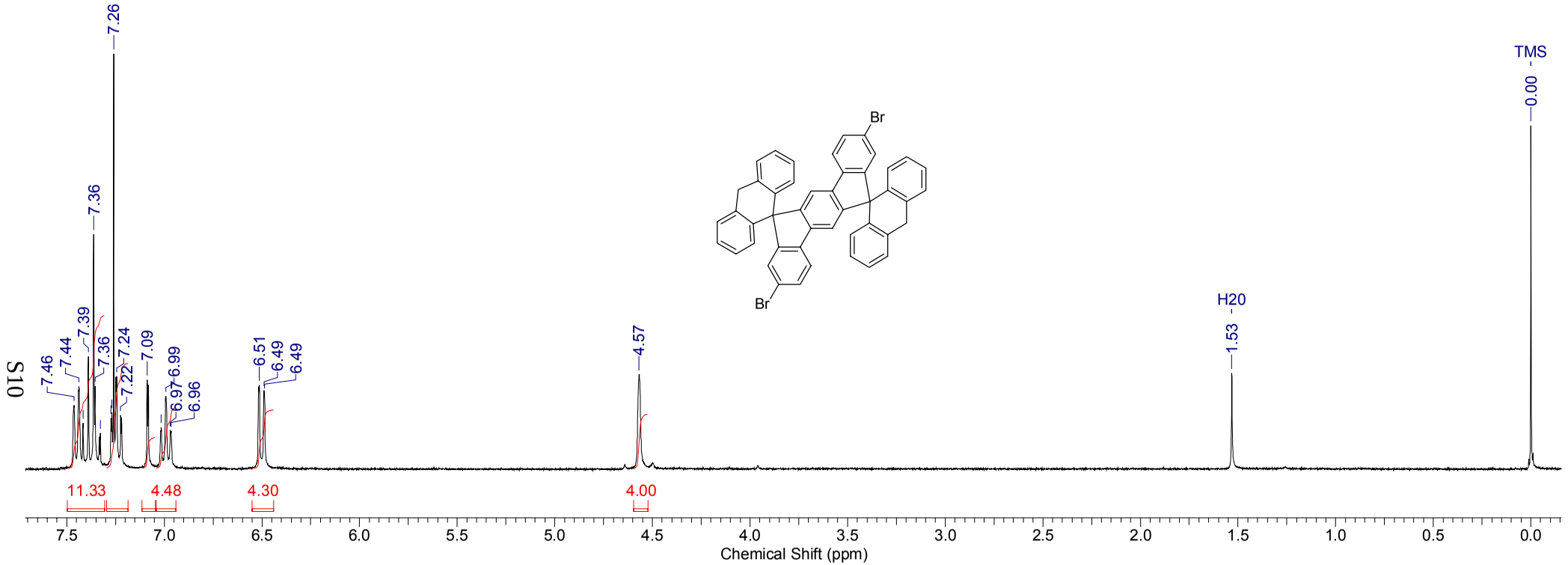

No.	(ppm)	(Hz)	Height
1	0.00	0.0	0.8262
2	1.53	460.2	0.2287
3	4.57	1372.2	0.2259
4	6.49	1948.5	0.1813
5	6.49	1949.6	0.1875
6	6.51	1956.6	0.2005
7	6.52	1957.7	0.1963
8	6.96	2092.1	0.0888
9	6.97	2093.6	0.0905
10	6.99	2100.2	0.1732

No.	(ppm)	(Hz)	Height
11	7.02	2107.3	0.0984
12	7.08	2127.3	0.2009
13	7.09	2129.0	0.2128
14	7.22	2168.8	0.1215
15	7.22	2170.0	0.1270
16	7.24	2176.1	0.2208
17	7.25	2177.4	0.2196
18	7.26	2180.9	1.0000
19	7.27	2183.6	0.1344
20	7.27	2184.7	0.1207

No.	(ppm)	(Hz)	Height
21	7.33	2201.4	0.0846
22	7.33	2203.1	0.0754
23	7.36	2209.5	0.1974
24	7.36	2211.9	0.5640
25	7.39	2219.7	0.2693
26	7.42	2228.0	0.1092
27	7.44	2234.1	0.1963
28	7.46	2241.8	0.1518

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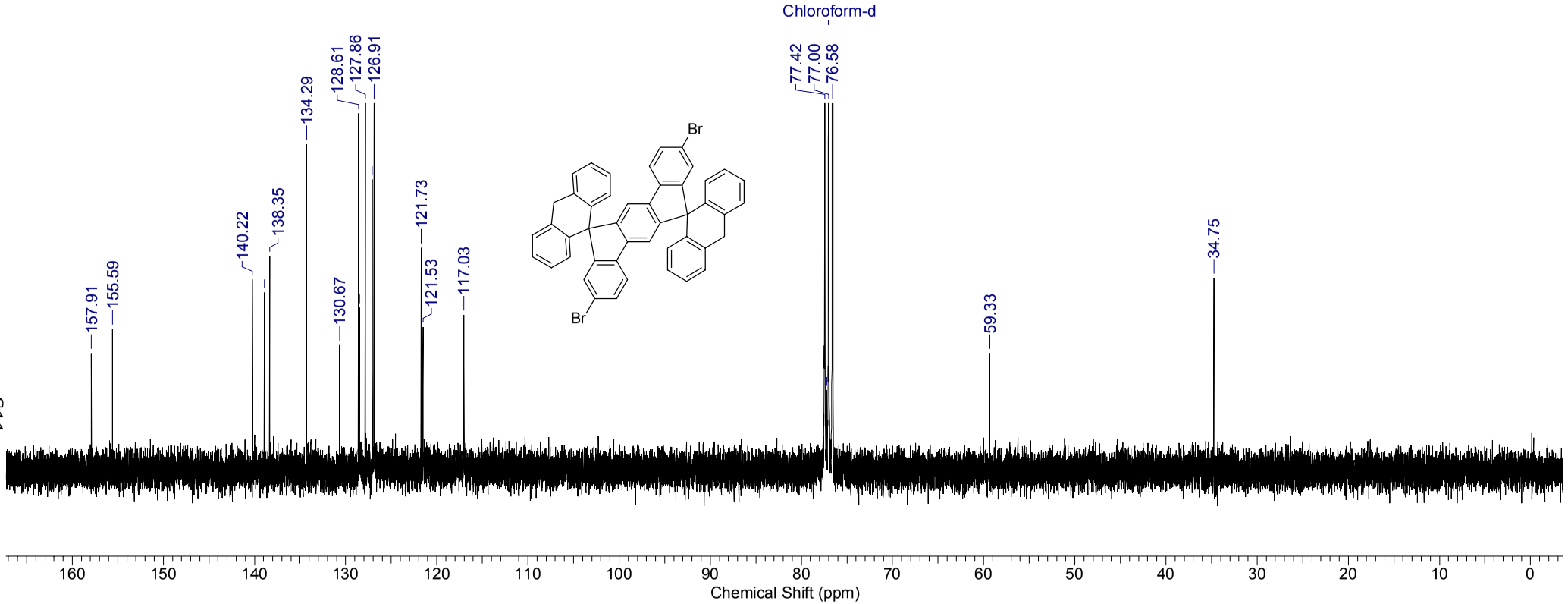

No.	(ppm)	(Hz)	Height
1	34.75	2622.0	0.0984
2	59.33	4476.4	0.0596
3	76.58	5777.6	0.9574
4	77.00	5809.6	1.0000
5	77.21	5825.2	0.0406
6	77.42	5841.7	0.9725
7	117.03	8829.8	0.0792
8	121.53	9169.4	0.0732
9	121.73	9184.7	0.1140
10	126.91	9575.0	0.1944
11	127.09	9588.7	0.1492

No.	(ppm)	(Hz)	Height
12	127.86	9647.1	0.2094
13	128.50	9695.3	0.0832
14	128.61	9703.3	0.1832
15	130.67	9859.4	0.0638
16	134.29	10132.2	0.1672
17	138.35	10438.3	0.1096
18	138.94	10482.8	0.0909
19	140.22	10579.4	0.0975
20	155.59	11739.5	0.0722
21	157.91	11914.5	0.0597

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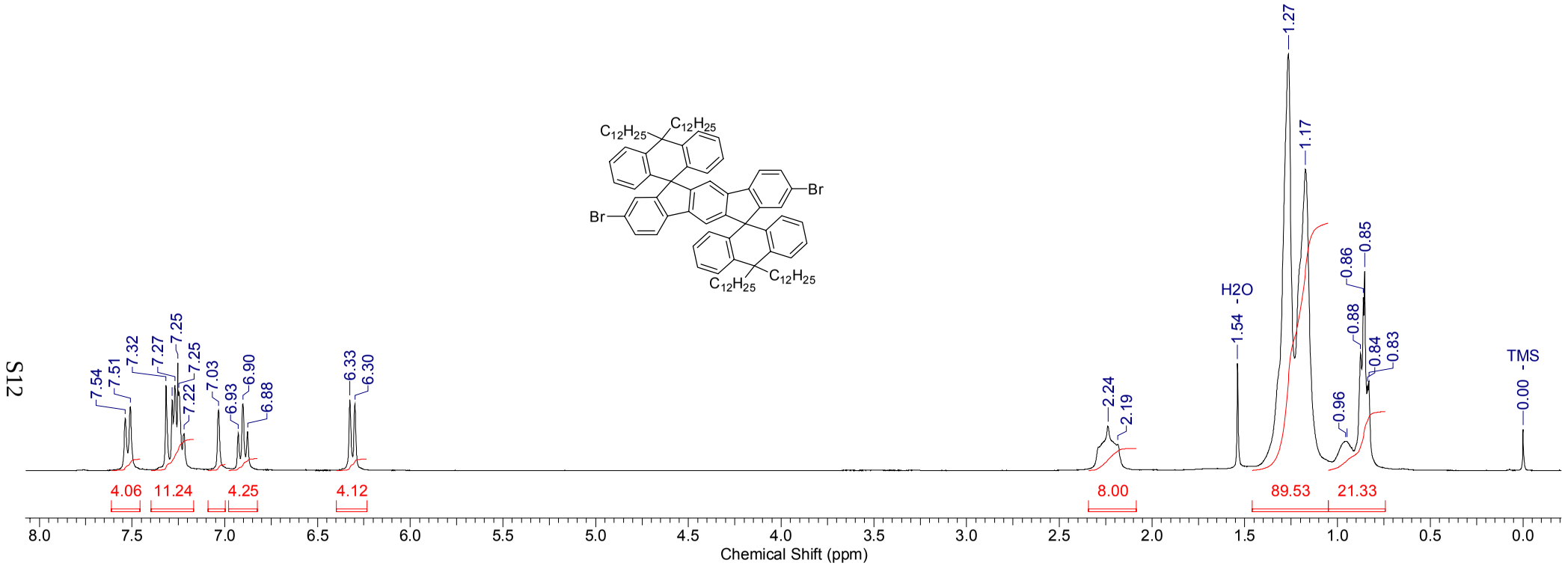

No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	-0.00	-0.0	0.0980	10	1.27	380.0	1.0000	19	7.03	2112.8	0.1445
2	0.83	249.6	0.2143	11	1.54	462.4	0.2577	20	7.22	2168.8	0.0883
3	0.84	251.6	0.2031	12	2.19	656.4	0.0630	21	7.25	2176.8	0.1877
4	0.85	256.6	0.4776	13	2.24	672.4	0.1061	22	7.25	2179.0	0.2583
5	0.86	258.8	0.4155	14	6.30	1892.0	0.1593	23	7.27	2183.6	0.2044
6	0.88	263.0	0.2812	15	6.33	1900.1	0.1701	24	7.28	2187.8	0.1691
7	0.95	284.8	0.0694	16	6.88	2065.9	0.0925	25	7.32	2198.1	0.2039
8	0.96	287.2	0.0704	17	6.90	2073.6	0.1598	26	7.51	2255.9	0.1531
9	1.17	352.1	0.7222	18	6.93	2080.9	0.0894	27	7.54	2263.9	0.1248

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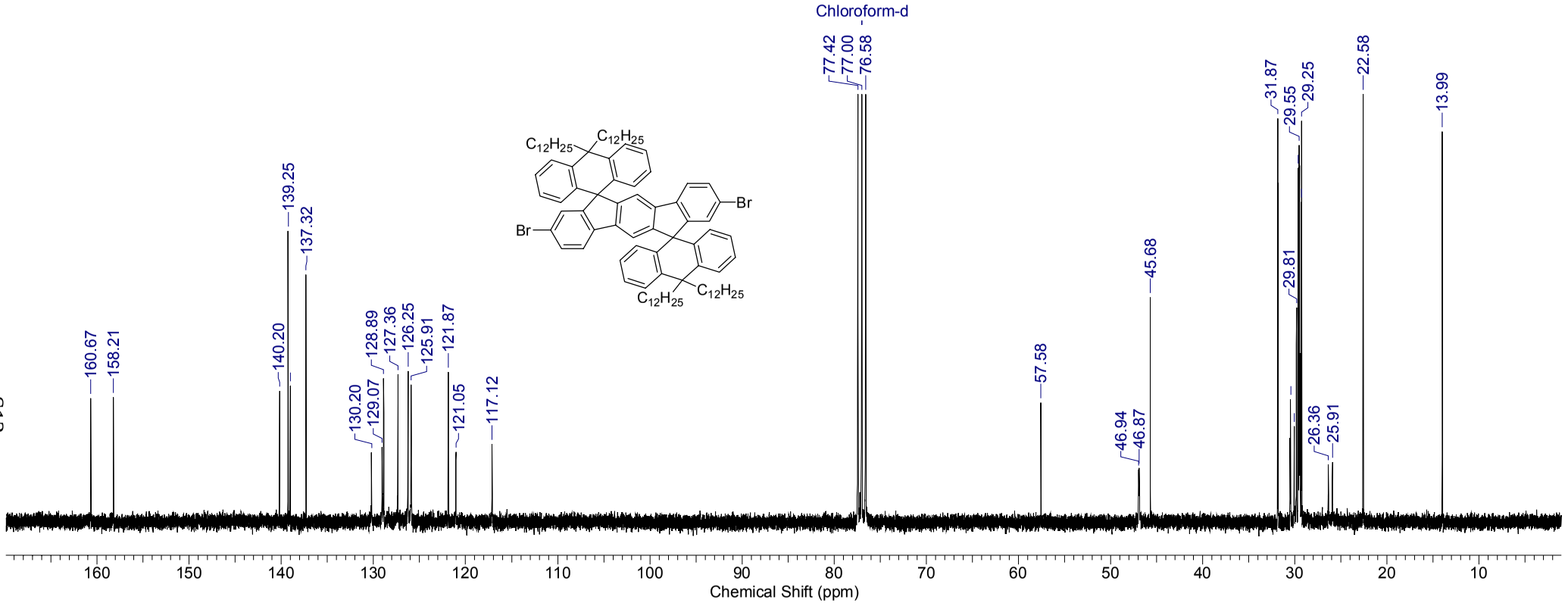
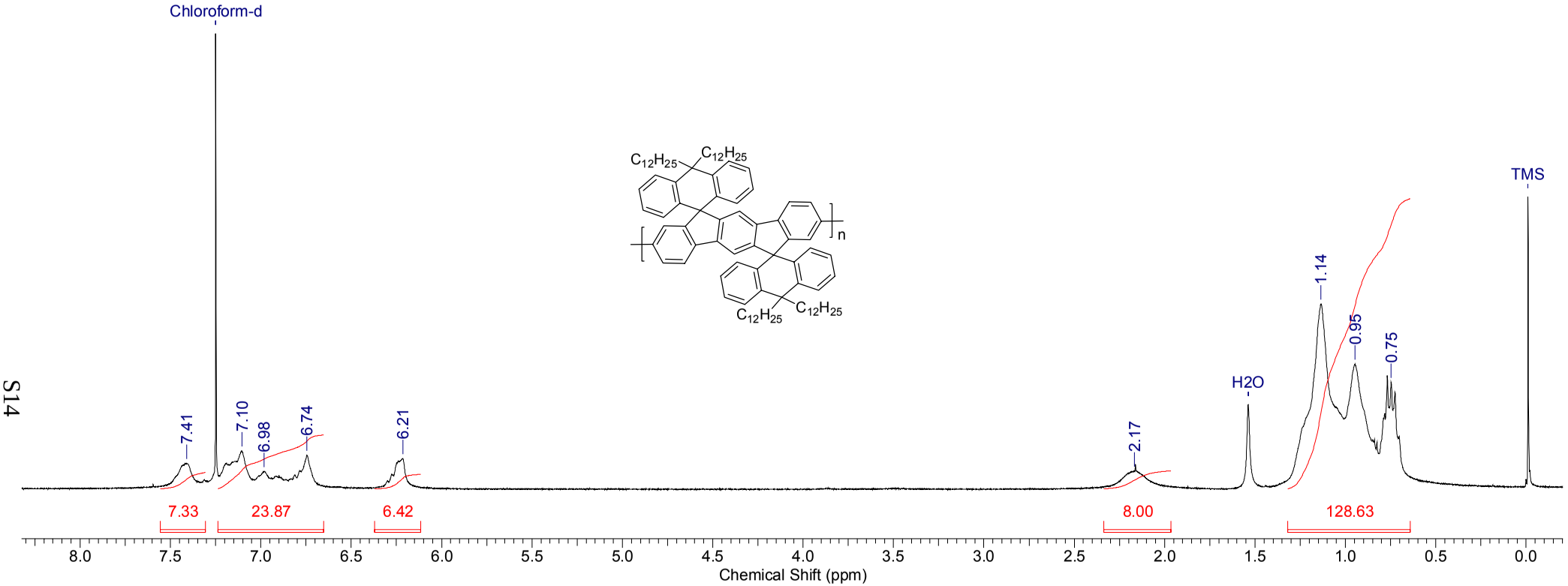
Solvent	CHLOROFORM-D	***Sweep Width (Hz)***	20366.60	***Temperature (degree C)***	0.000		



No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	13.99	1055.4	0.5470	12	29.55	2229.5	0.5282	23	45.68	3446.2	0.3144	34	126.25	9525.6	0.2105
2	14.00	1056.7	0.5278	13	29.57	2230.8	0.4538	24	46.87	3536.3	0.0746	35	127.36	9609.2	0.2060
3	22.58	1703.4	0.6543	14	29.62	2234.8	0.1430	25	46.94	3541.9	0.0722	36	128.89	9724.8	0.2003
4	22.59	1704.6	0.6147	15	29.64	2236.7	0.4961	26	57.58	4344.0	0.1662	37	129.07	9738.1	0.1036
5	25.91	1954.8	0.0829	16	29.81	2249.4	0.2998	27	76.58	5777.6	0.9762	38	130.20	9823.9	0.0961
6	26.36	1988.7	0.0794	17	29.85	2252.2	0.2485	28	77.00	5809.6	1.0000	39	137.32	10360.9	0.3462
7	29.25	2206.8	0.5618	18	30.09	2269.9	0.1334	29	77.42	5841.7	0.9442	40	139.04	10490.2	0.1901
8	29.29	2209.9	0.4484	19	30.45	2297.6	0.1710	30	117.12	8836.6	0.1078	41	139.25	10506.7	0.4075
9	29.44	2221.4	0.2361	20	30.52	2302.9	0.1165	31	121.05	9133.1	0.0970	42	140.20	10578.2	0.1827
10	29.48	2224.6	0.4992	21	31.82	2400.5	0.4748	32	121.87	9194.9	0.2094	43	158.21	11936.9	0.1738
11	29.52	2227.4	0.3727	22	31.87	2404.8	0.5655	33	125.91	9499.8	0.1919	44	160.67	12122.7	0.1725

Acquisition Time (sec)	5.4624	***Date***	Mon Oct 4 22:46:04 2004				
File Name	C:\2004 박두진\2004 논문용 NMR files\41014-pddsaif\41014-pddsaif.nmfid					***Frequency (MHz)***	300.40
Nucleus	1H	***Number of Transients***	147	***Original Points Count***	32768	***Points Count***	32768
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	0.000



No.	(ppm)	(Hz)	Height
1	0.75	224.3	0.2348
2	0.95	284.7	0.2743
3	1.14	341.1	0.4062
4	2.17	651.1	0.0389
5	6.21	1866.7	0.0668
6	6.74	2026.1	0.0736
7	6.98	2097.5	0.0381
8	7.10	2134.3	0.0835
9	7.41	2225.9	0.0557