Supporting Information

Rational Design of Diketopyrrolopyrrole-based Oligomers with Deep HOMO Level and Tunable Liquid Crystal Behavior by Modulating the Sequence and Strength of Donor Moiety

Jin-Liang Wang,* Zheng-Feng Chang, Xiao-Xin Song, Kai-Kai Liu, Ling-Min Jing
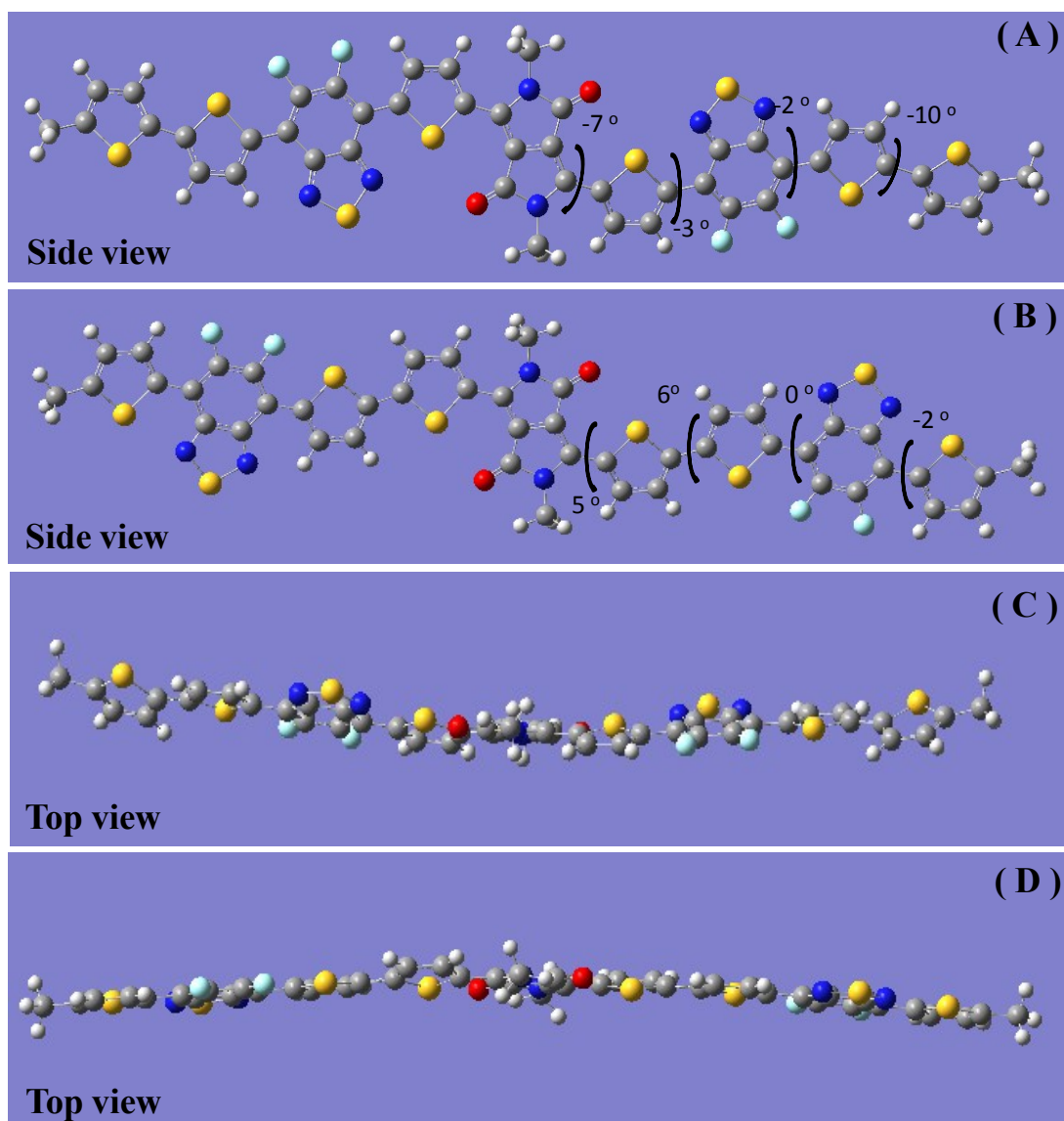
1. Experimental Details

Figure S1: DFT-optimized geometries and the side, top views of **DTFB2T** (A and C) and **D2TFBT** (B and D) based on density functional theory (DFT) calculation.
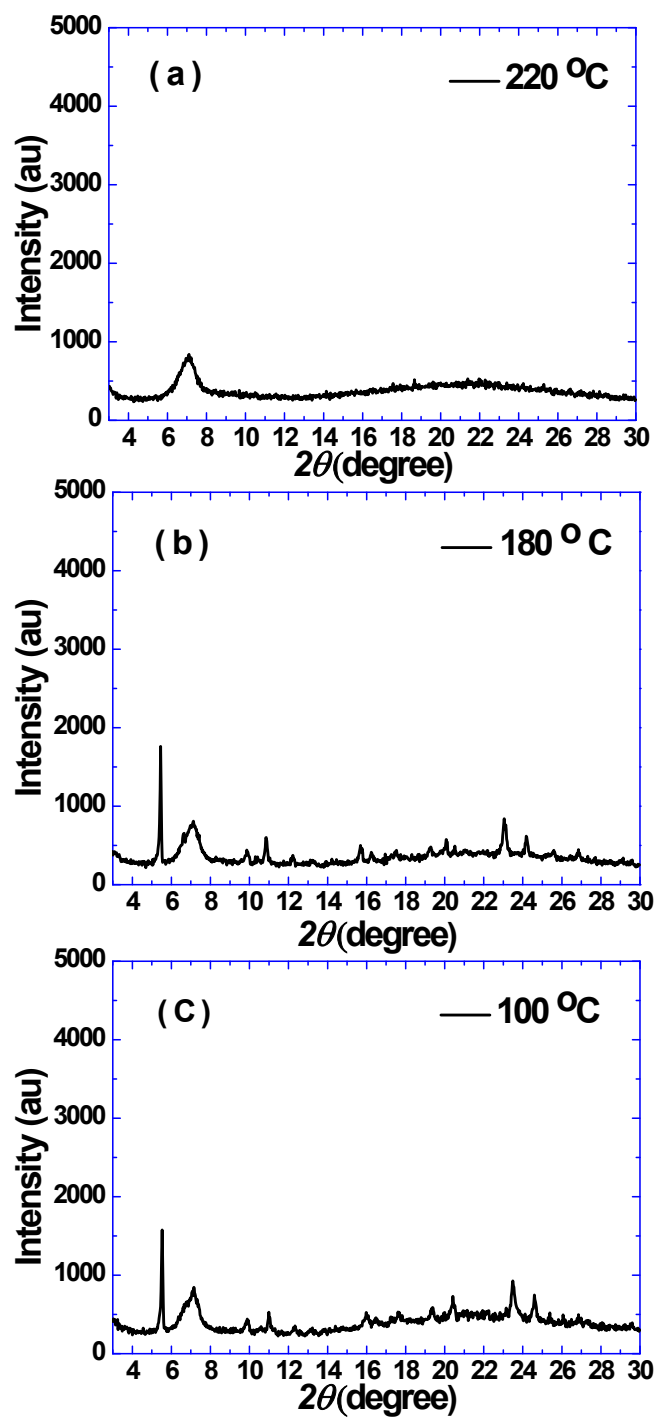
Figure S2. XRD patterns of **D2TFBT** from 1º-30º (2θ) (a) at 220 ºC, (b) at 180 ºC, (c) at 100 ºC. The peak at about 7 º denotes reflection from the peak of background.
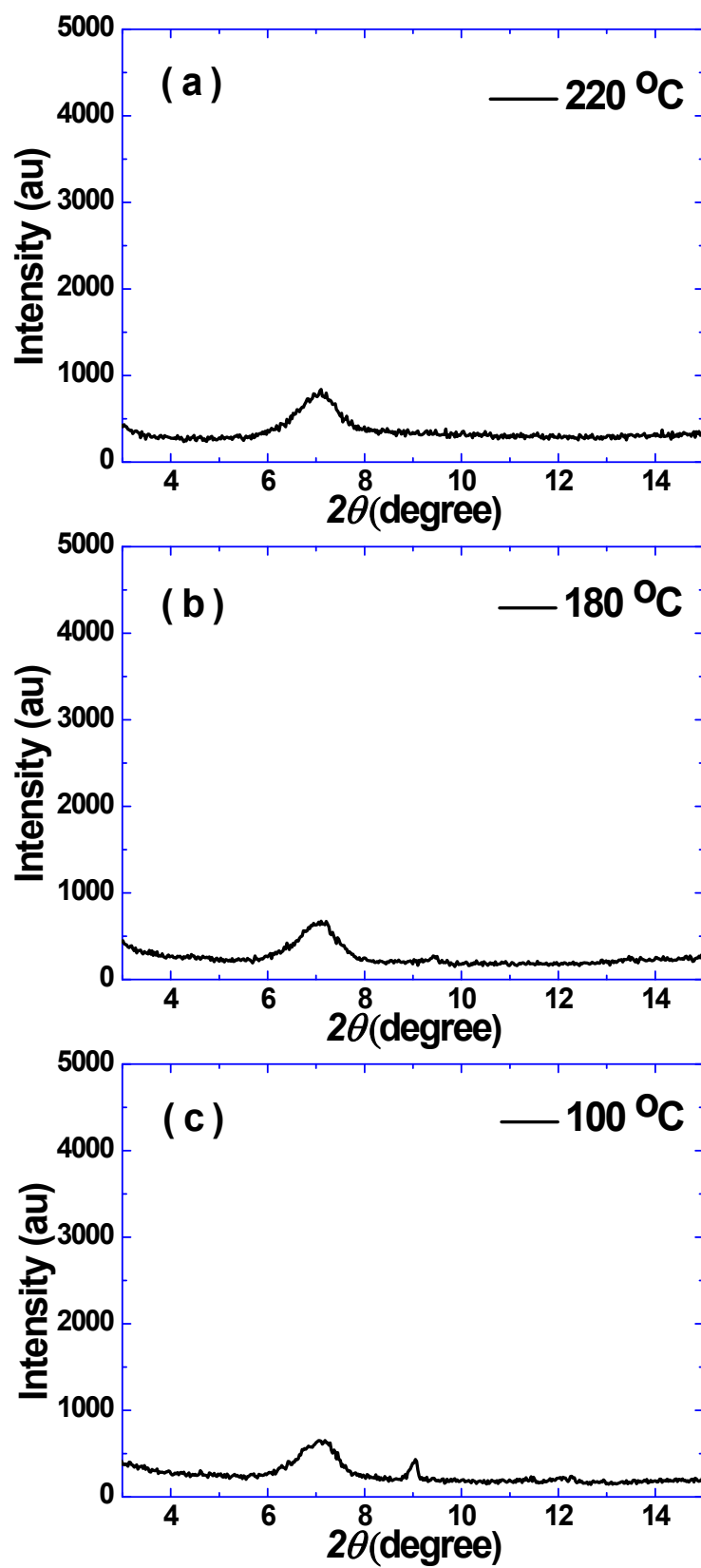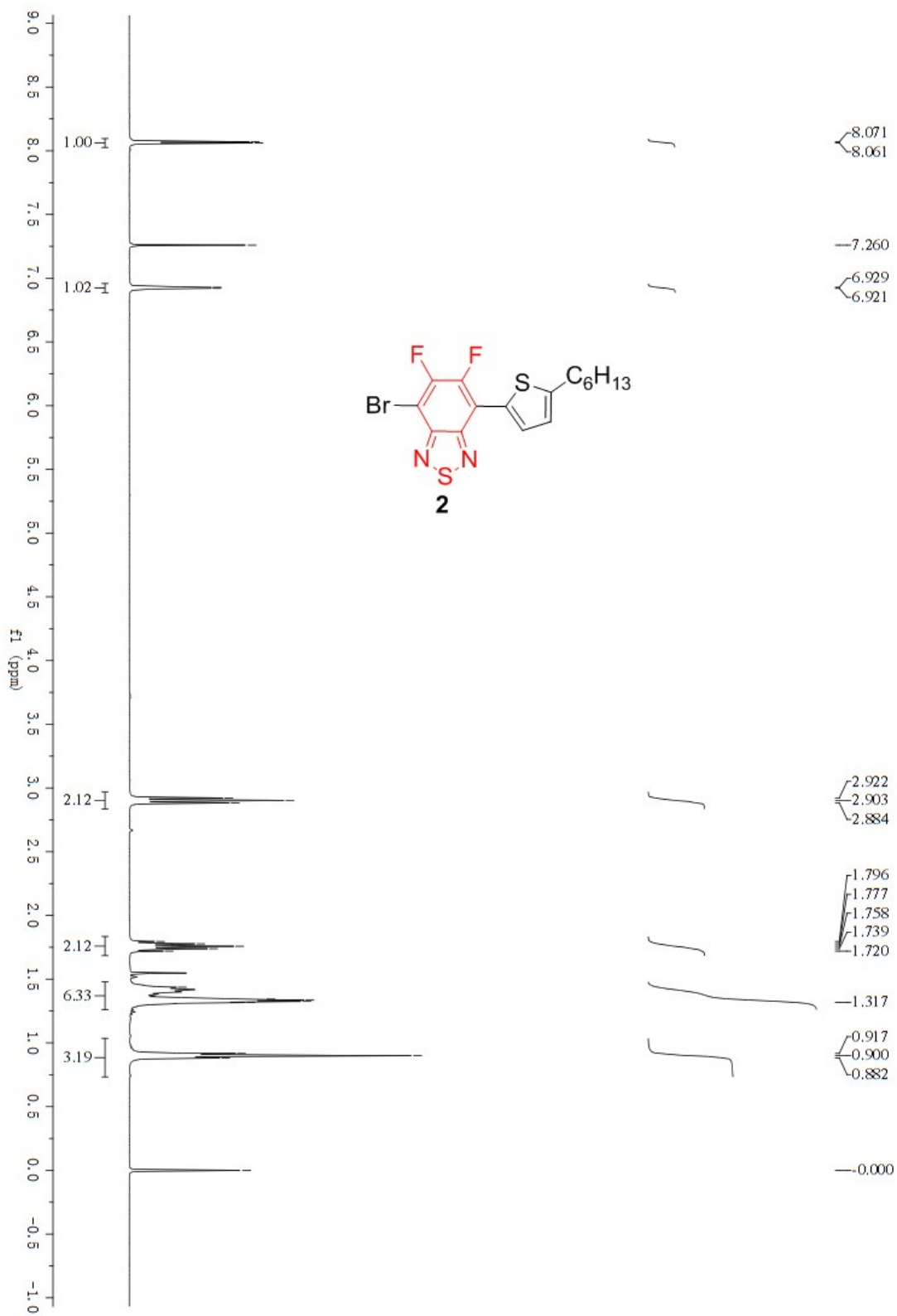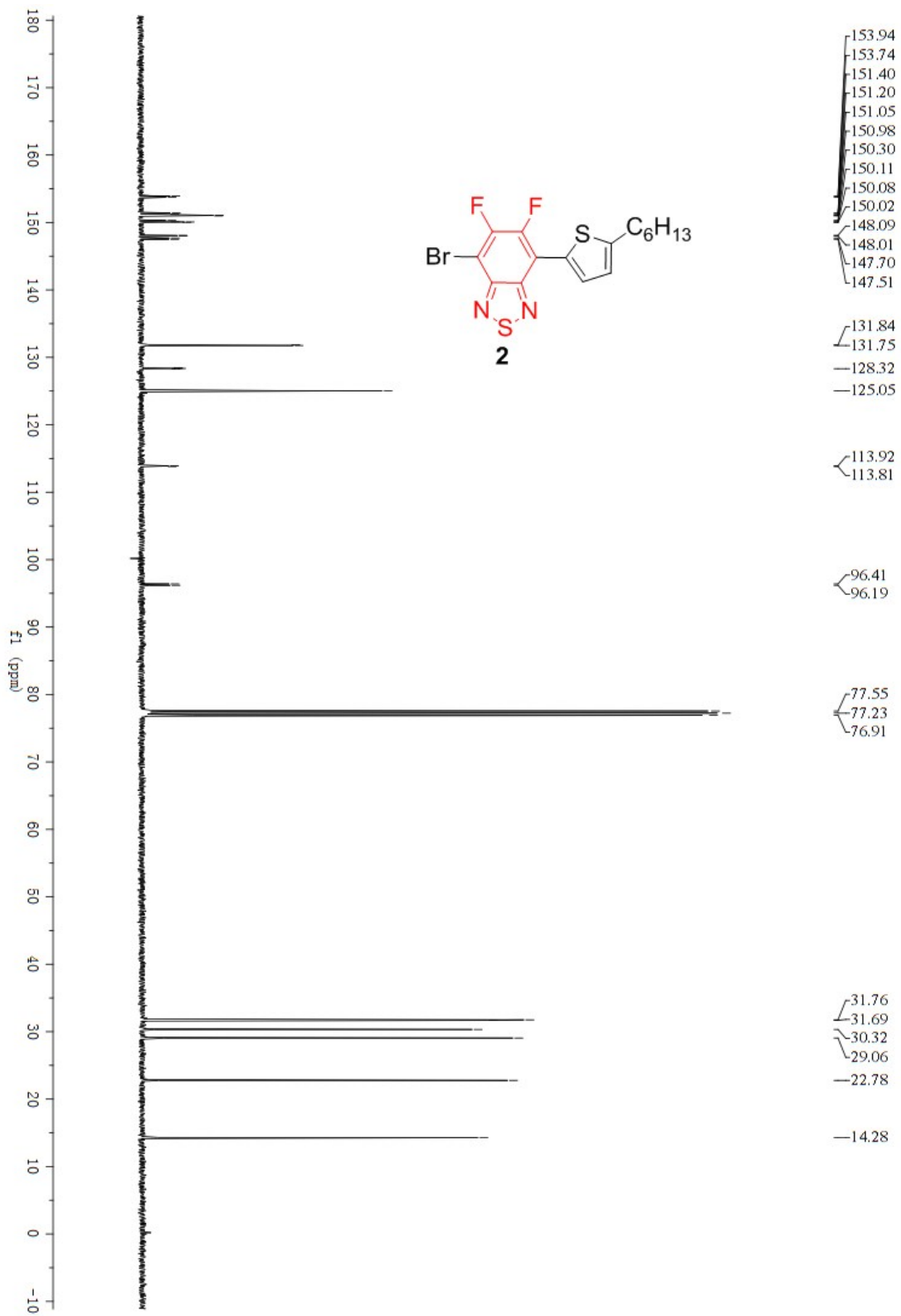
Figure S3. XRD patterns of **DTFB2T** (a) at 220 ºC, (b) at 180 ºC, (c) at 100 ºC. The peak at about 7 º denotes reflection from the peak of background.
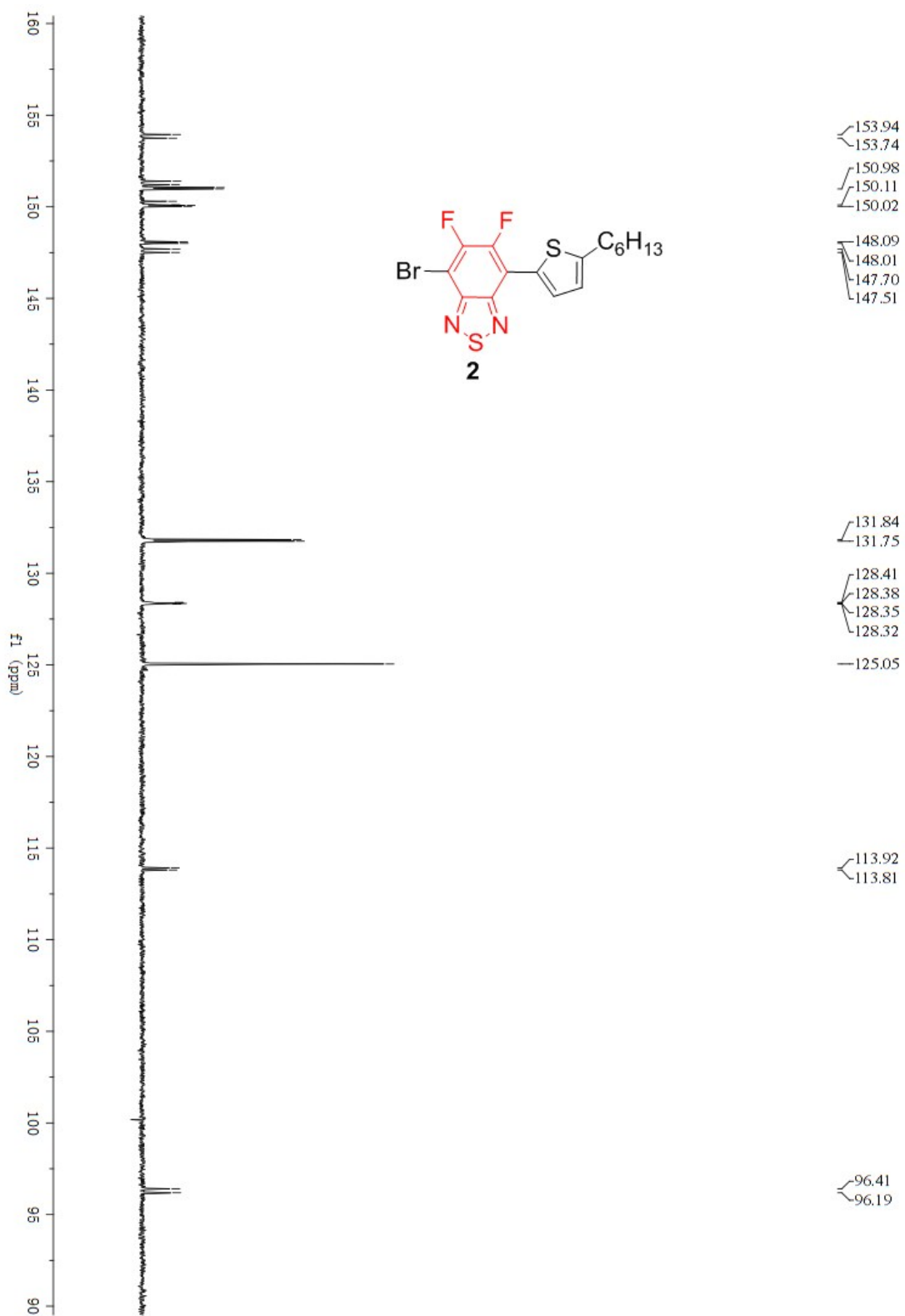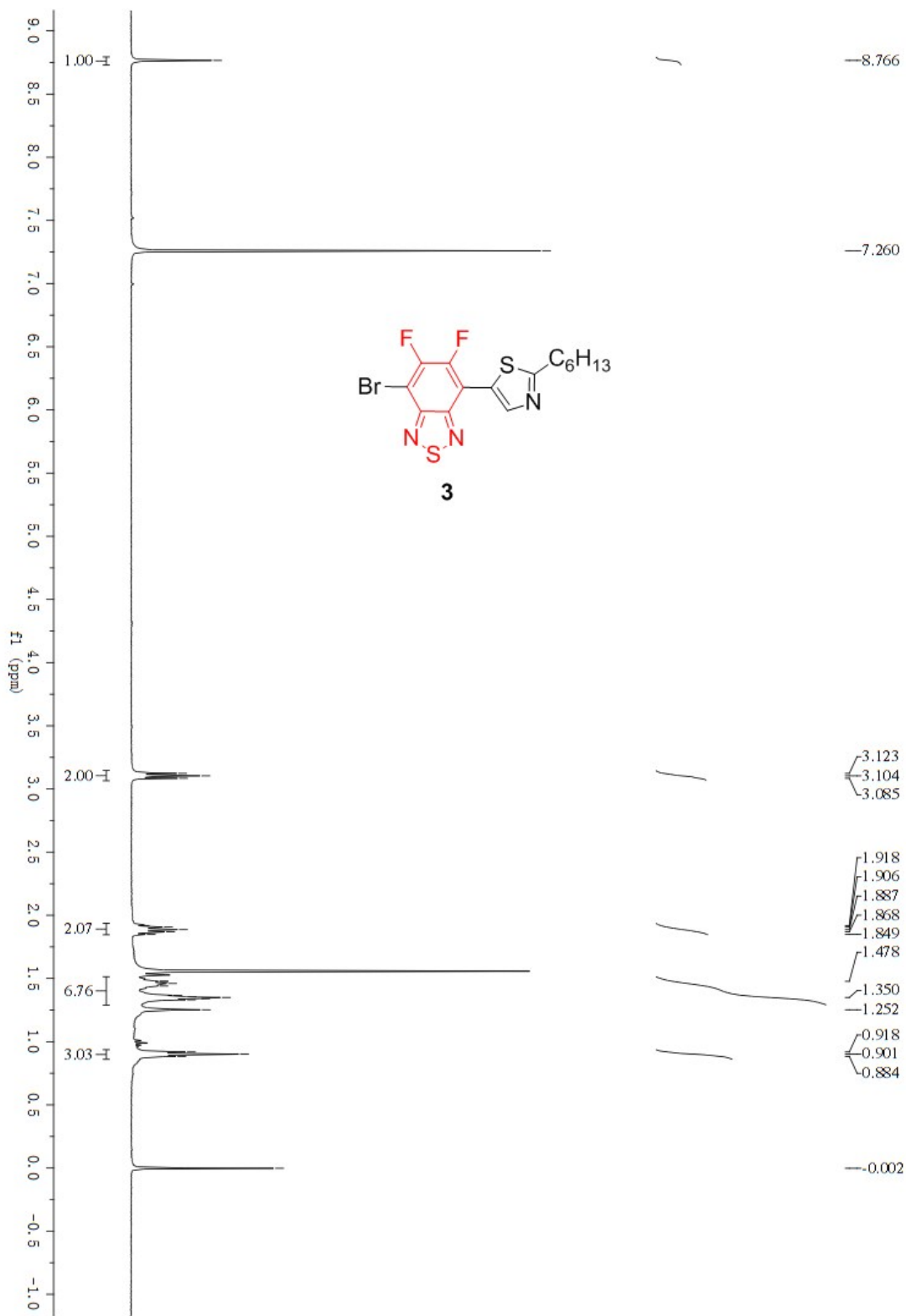
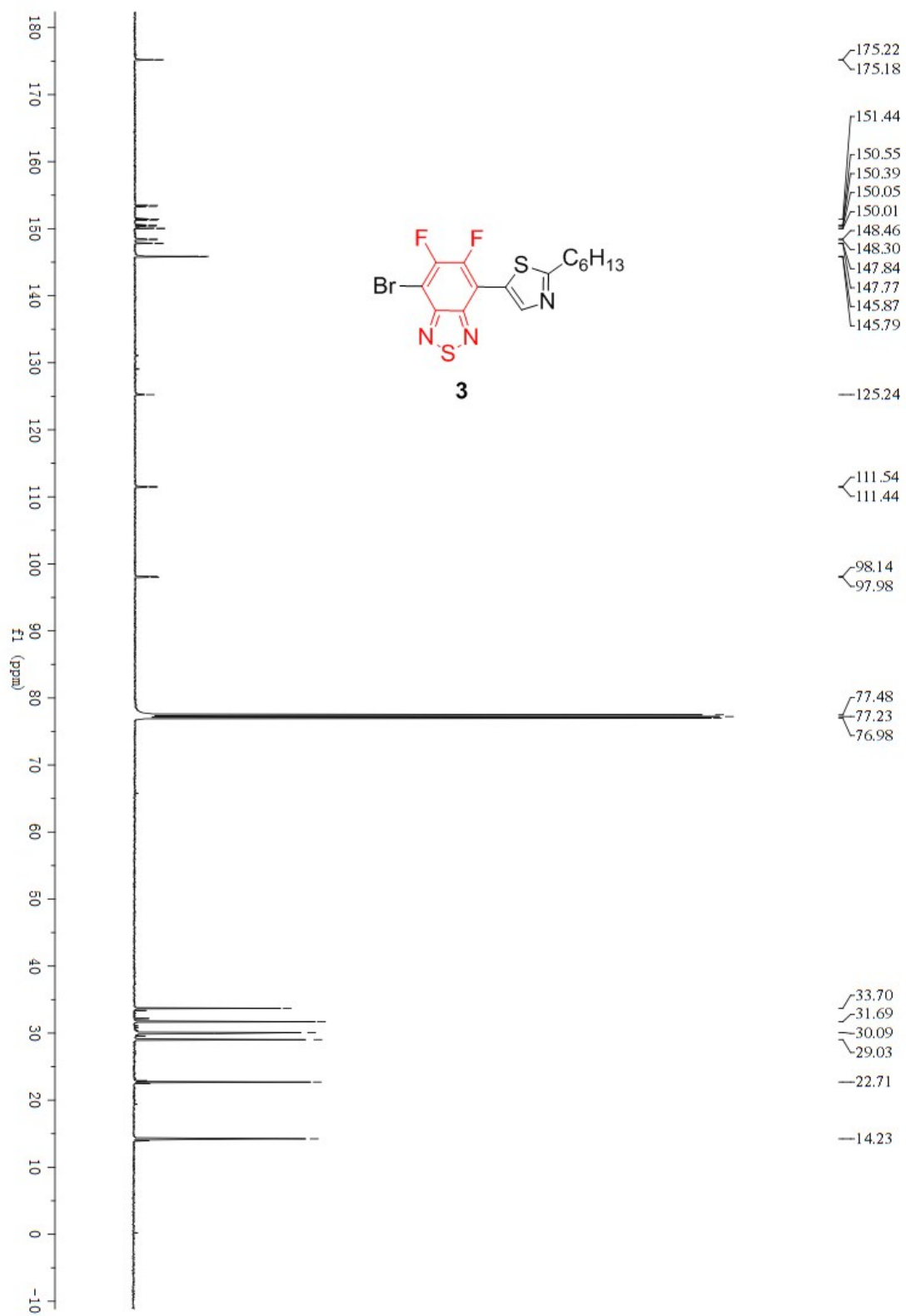## 2. Copies of ¹H and ¹³C NMR Spectra

¹H NMR spectrum of **2** in CDCl₃.
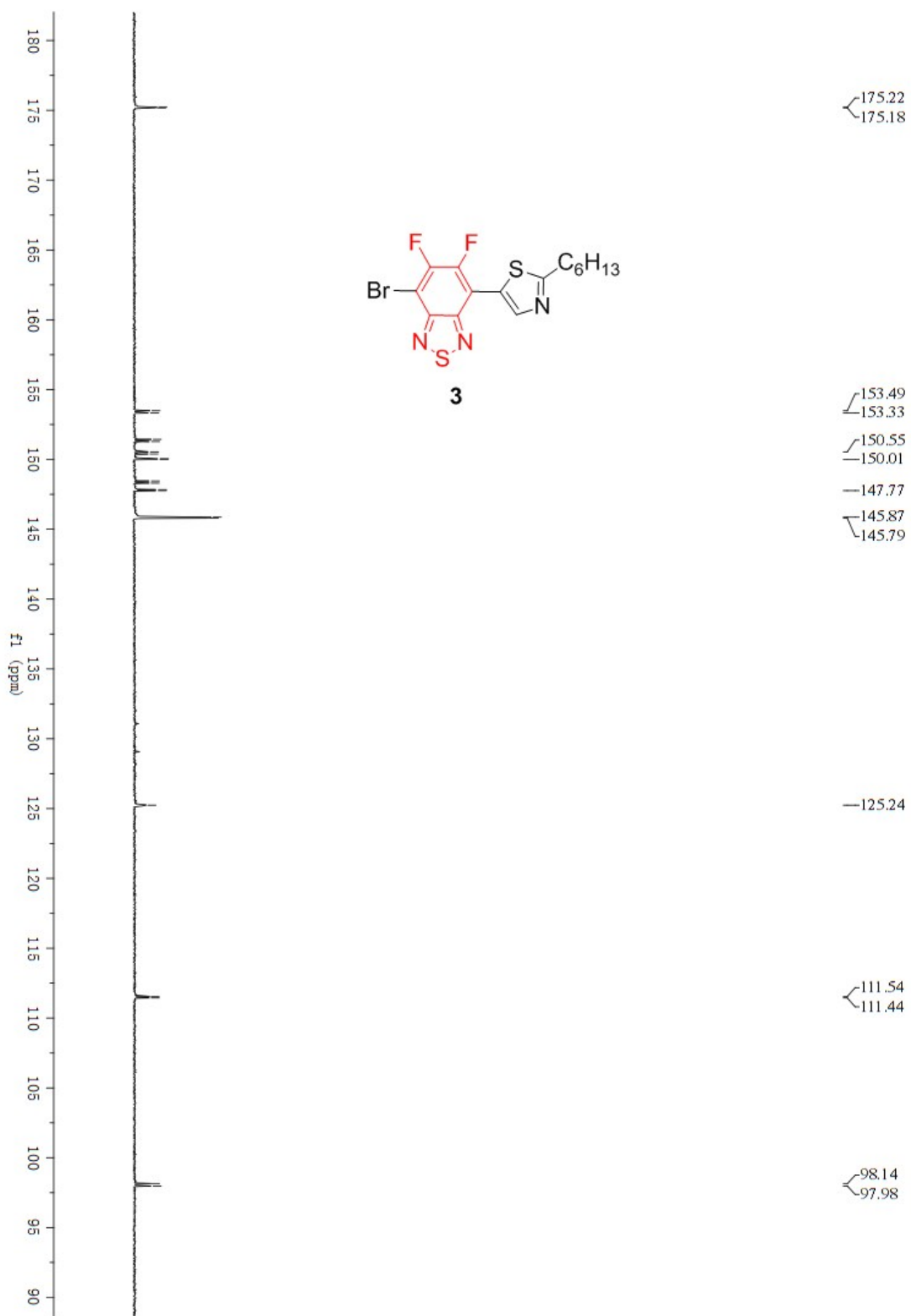
^{13}C NMR spectrum of **2** in CDCl$_3$.

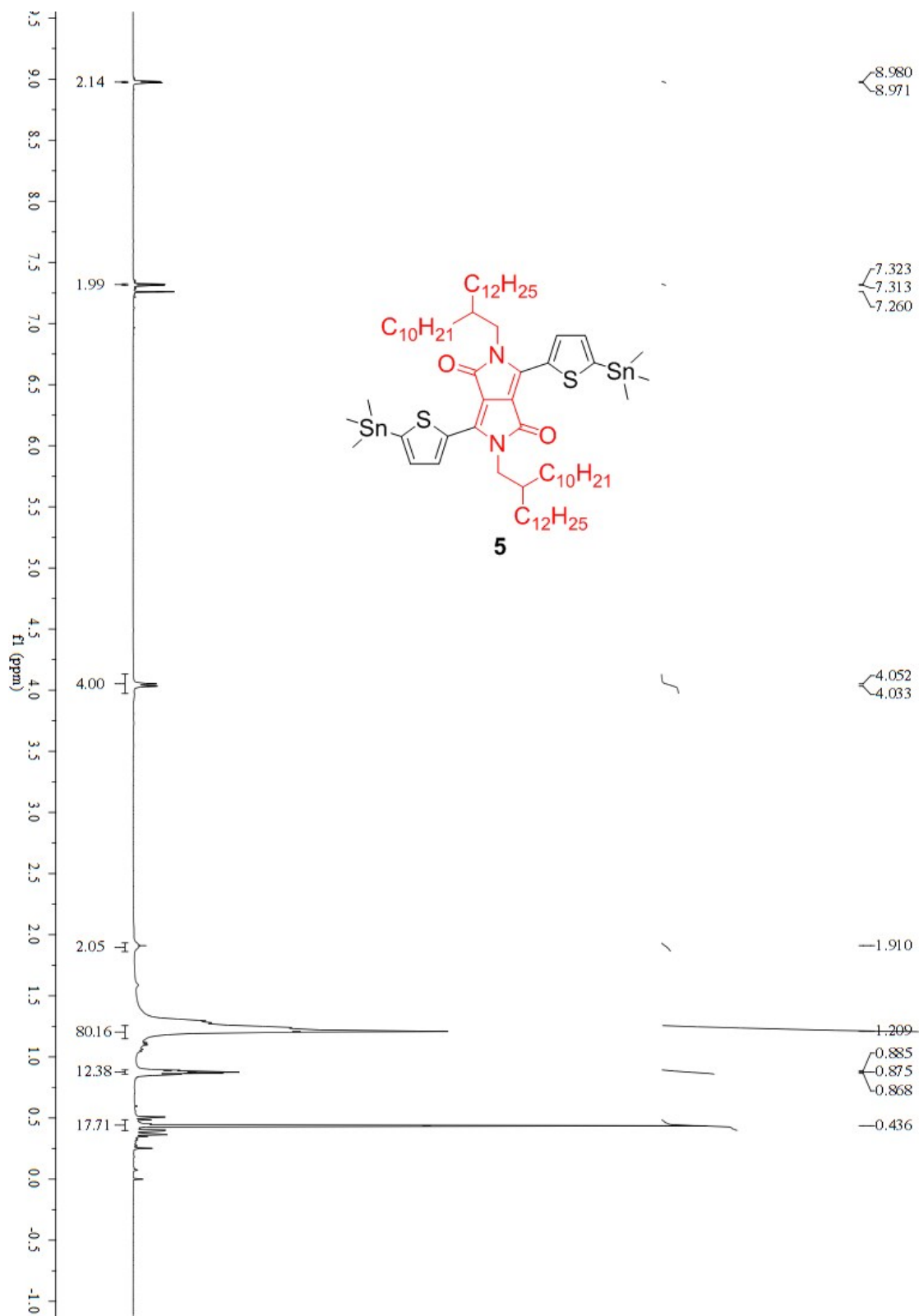The expended ^{13}C NMR spectrum of **2** in CDCl$_3$.

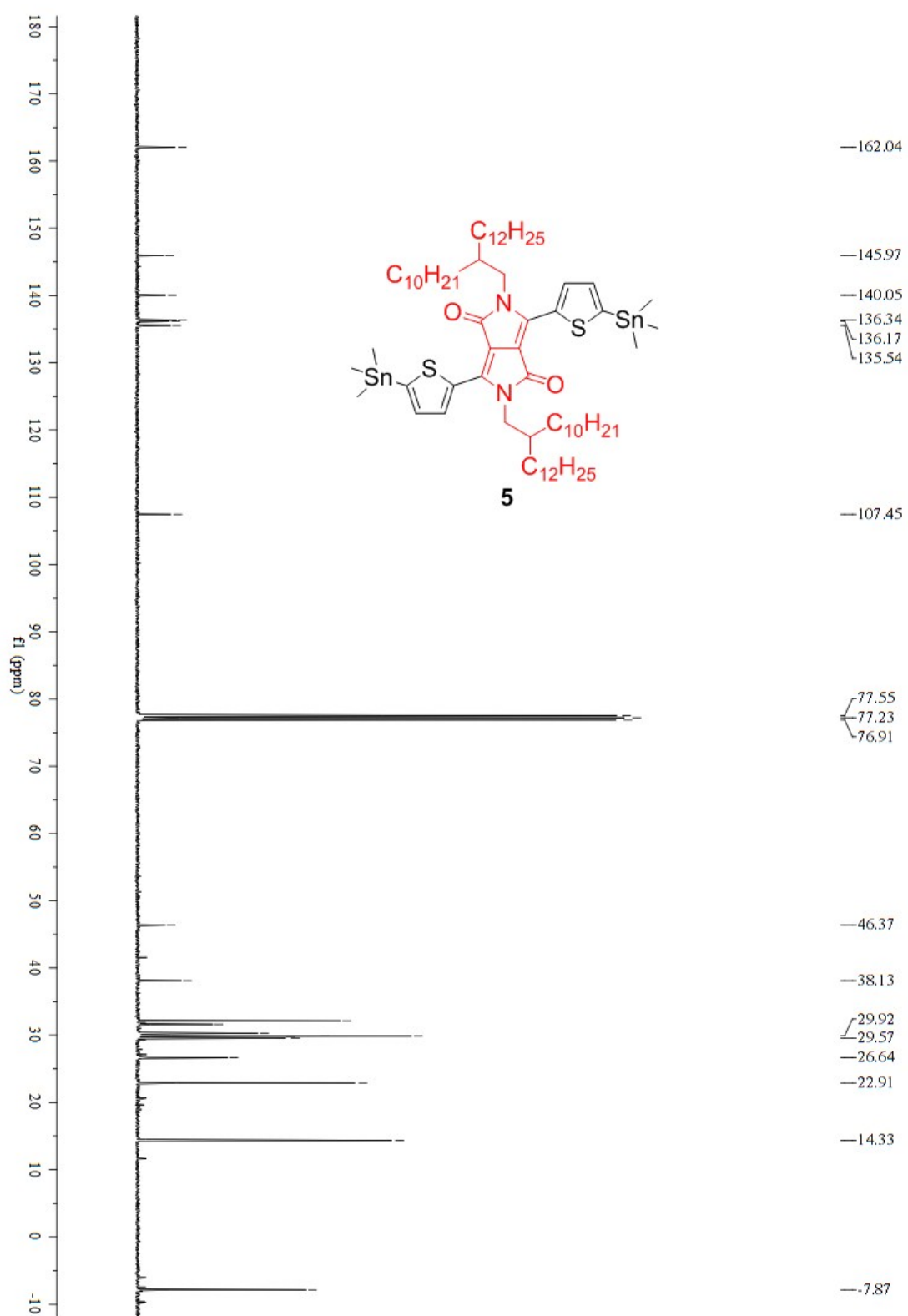^{1}H NMR spectrum of **3** in CDCl$_3$.
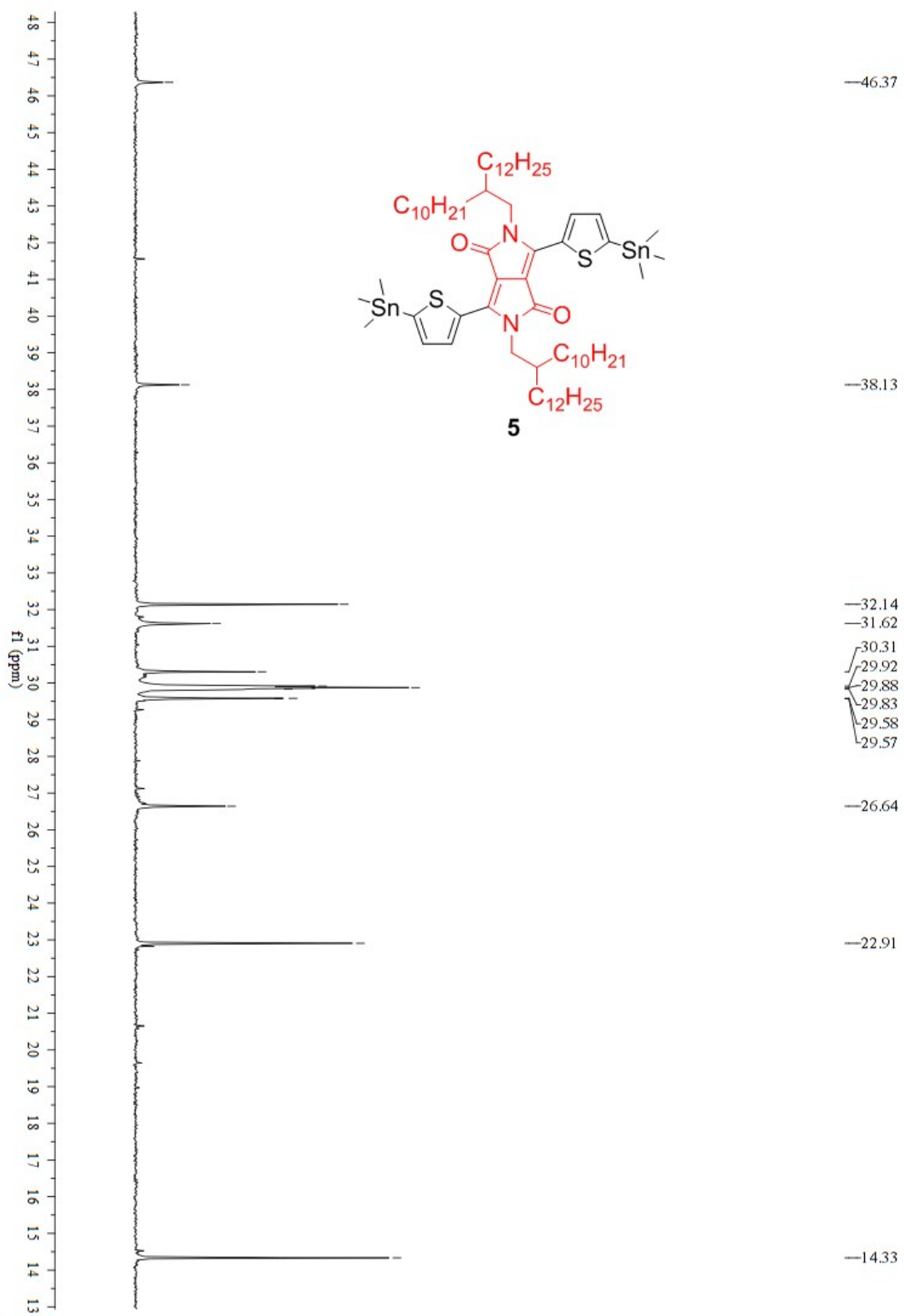
^{13}C NMR spectrum of **3** in CDCl$_3$.

The expended ^{13}C NMR spectrum of **3** in CDCl$_3$.
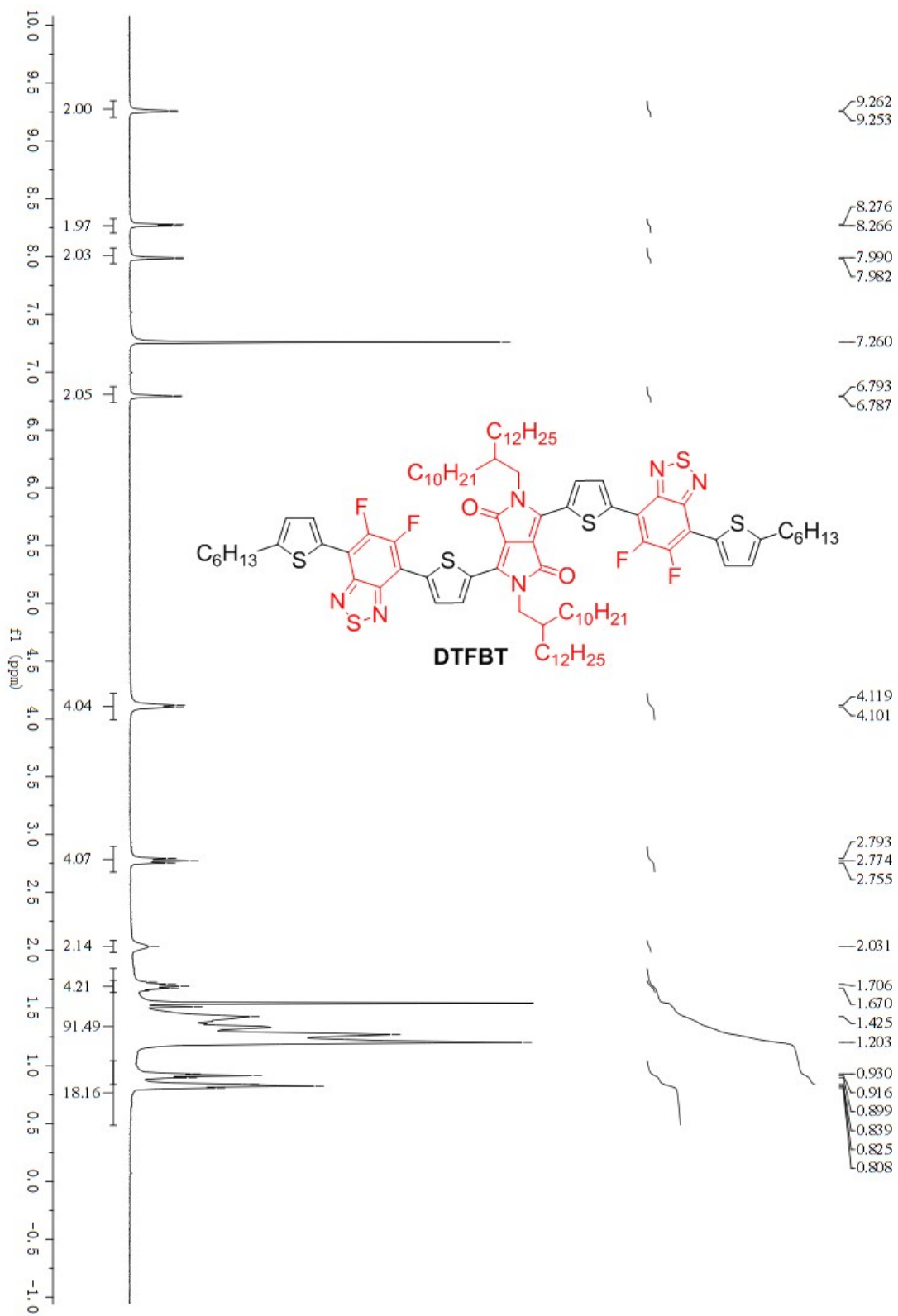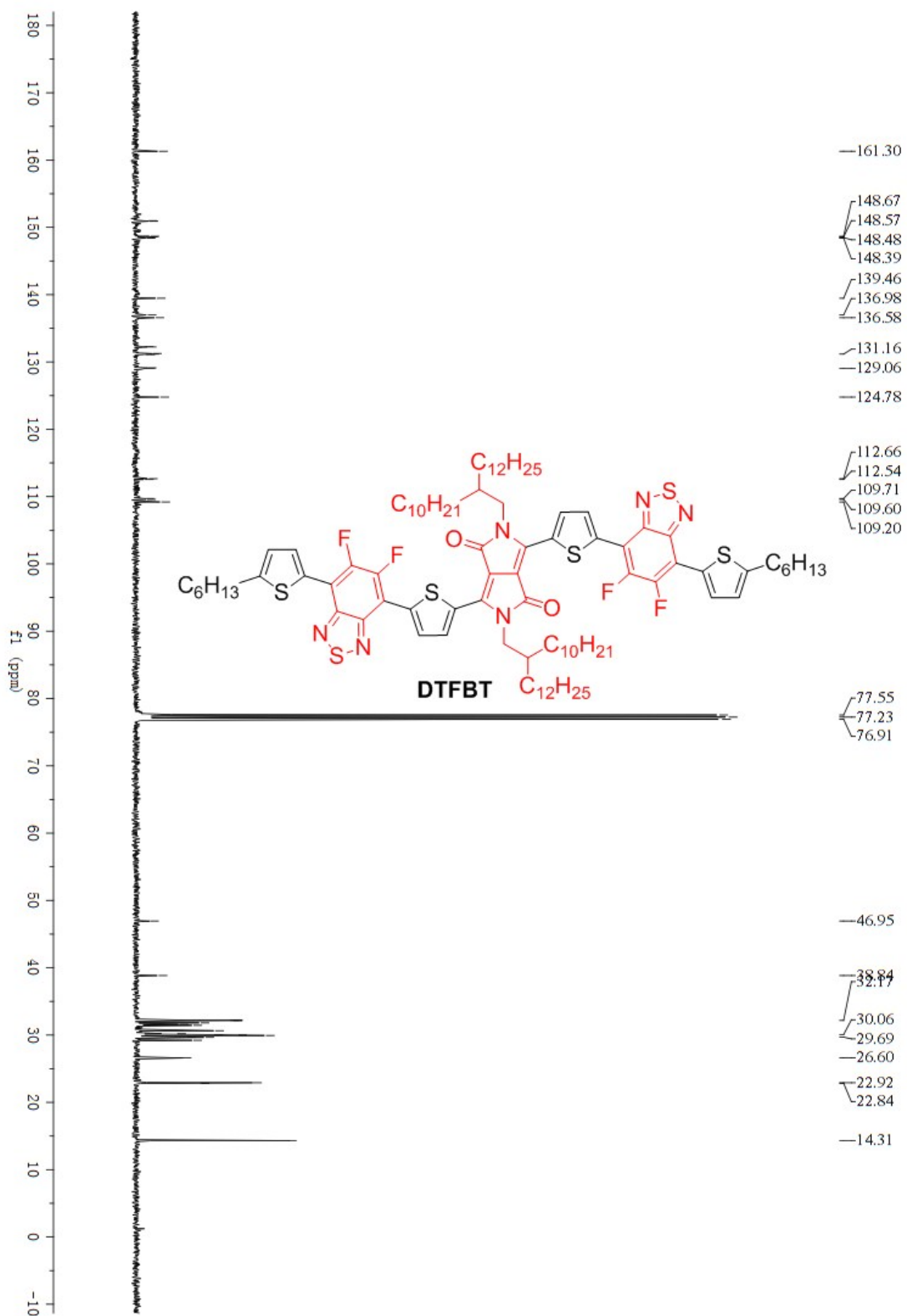
^{1}H NMR spectrum of **5** in CDCl$_3$.
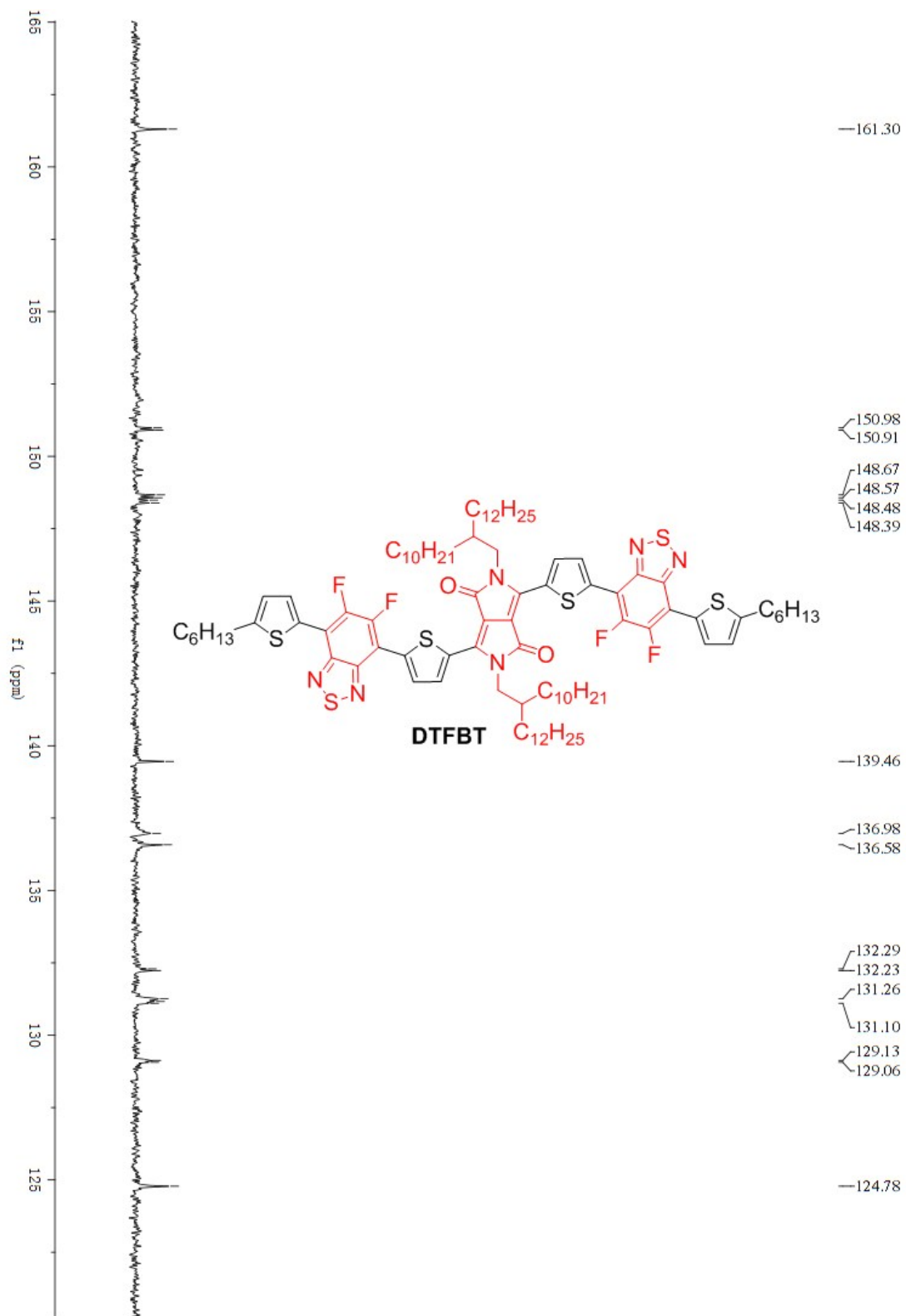
^{13}C NMR spectrum of **5** in CDCl$_3$.

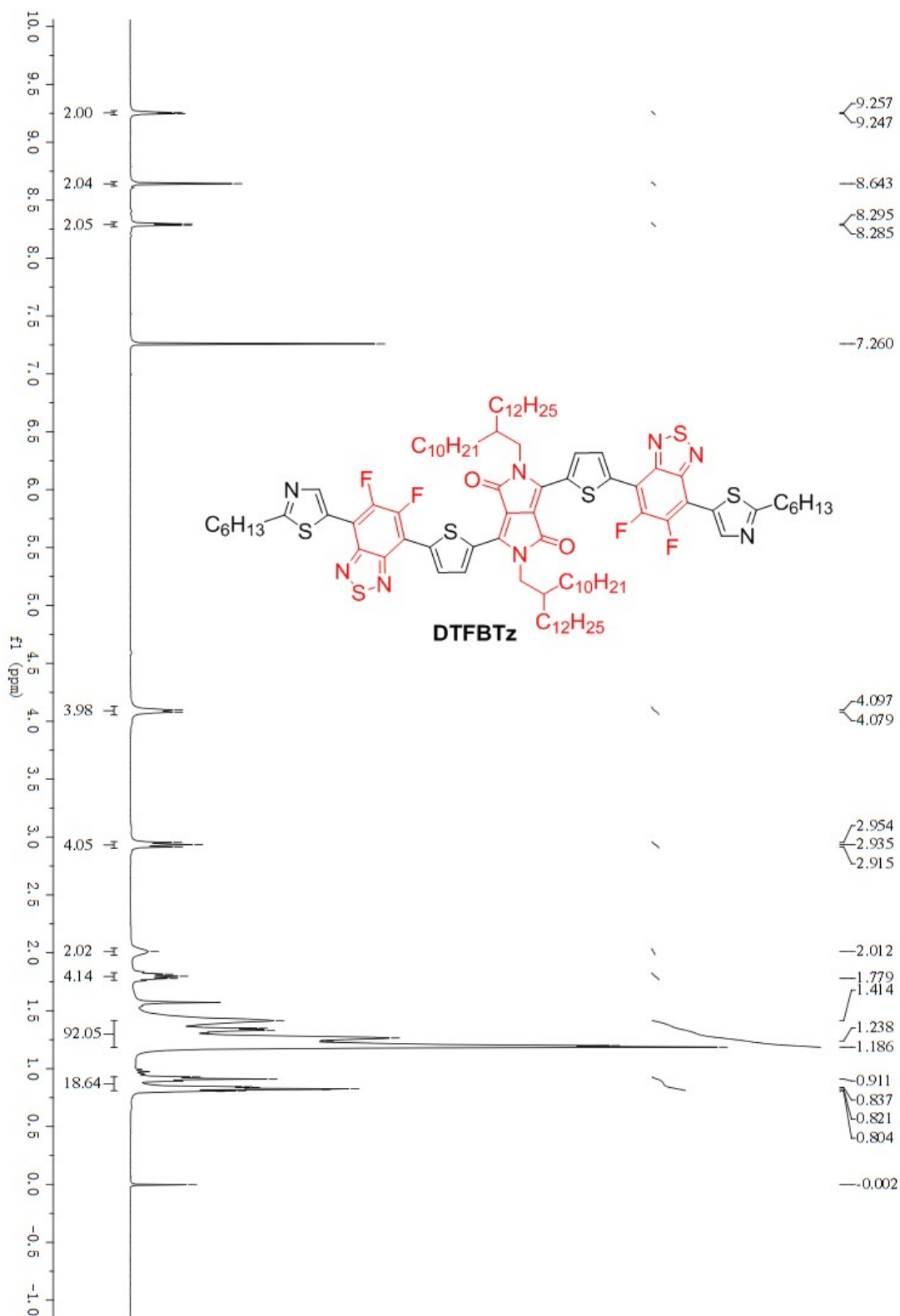The expended ^{13}C NMR spectrum of **5** in $CDCl_3$.

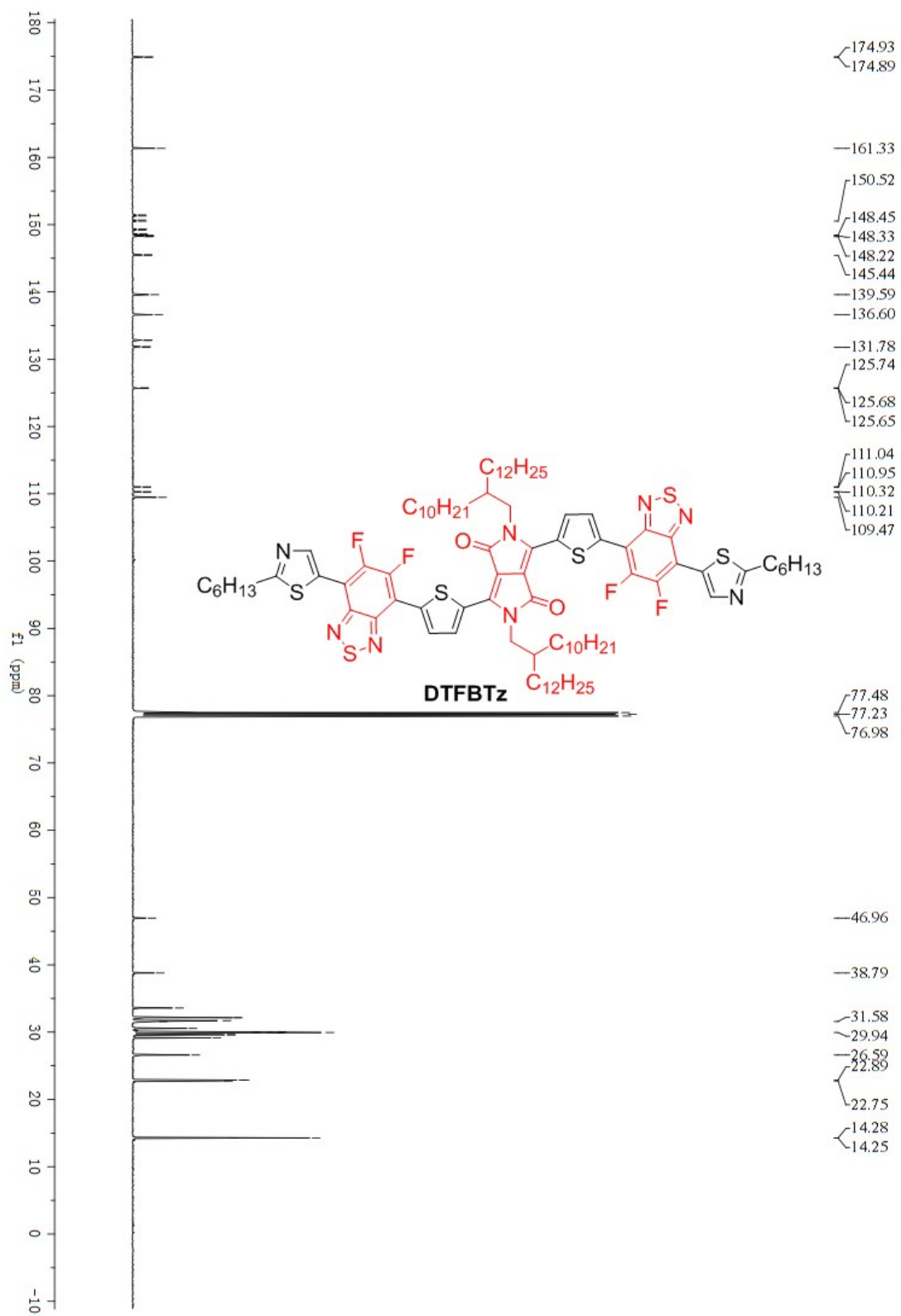^{1}H NMR spectrum of **DTFBT** in CDCl$_3$.
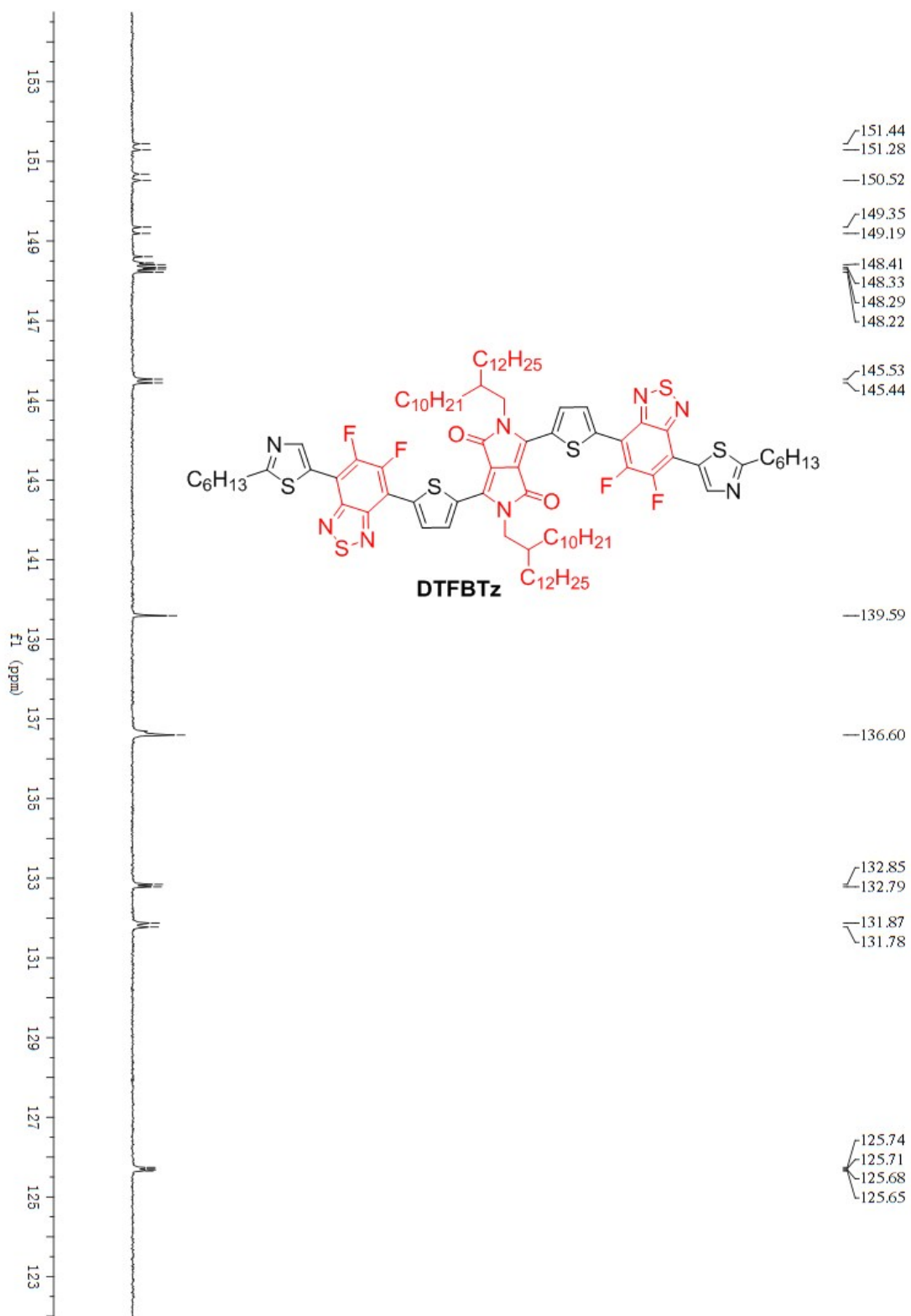
^{13}C NMR spectrum of **DTFBT** in CDCl$_3$.

The expended ^{13}C NMR spectrum of **DTFBT** in CDCl$_3$.

^{1}H NMR spectrum of **DTFBTz** in CDCl$_3$.

^{13}C NMR spectrum of **DTFBT**z in CDCl$_3$.

The expended ^{13}C NMR spectrum of **DTFBTz** in CDCl$_3$.
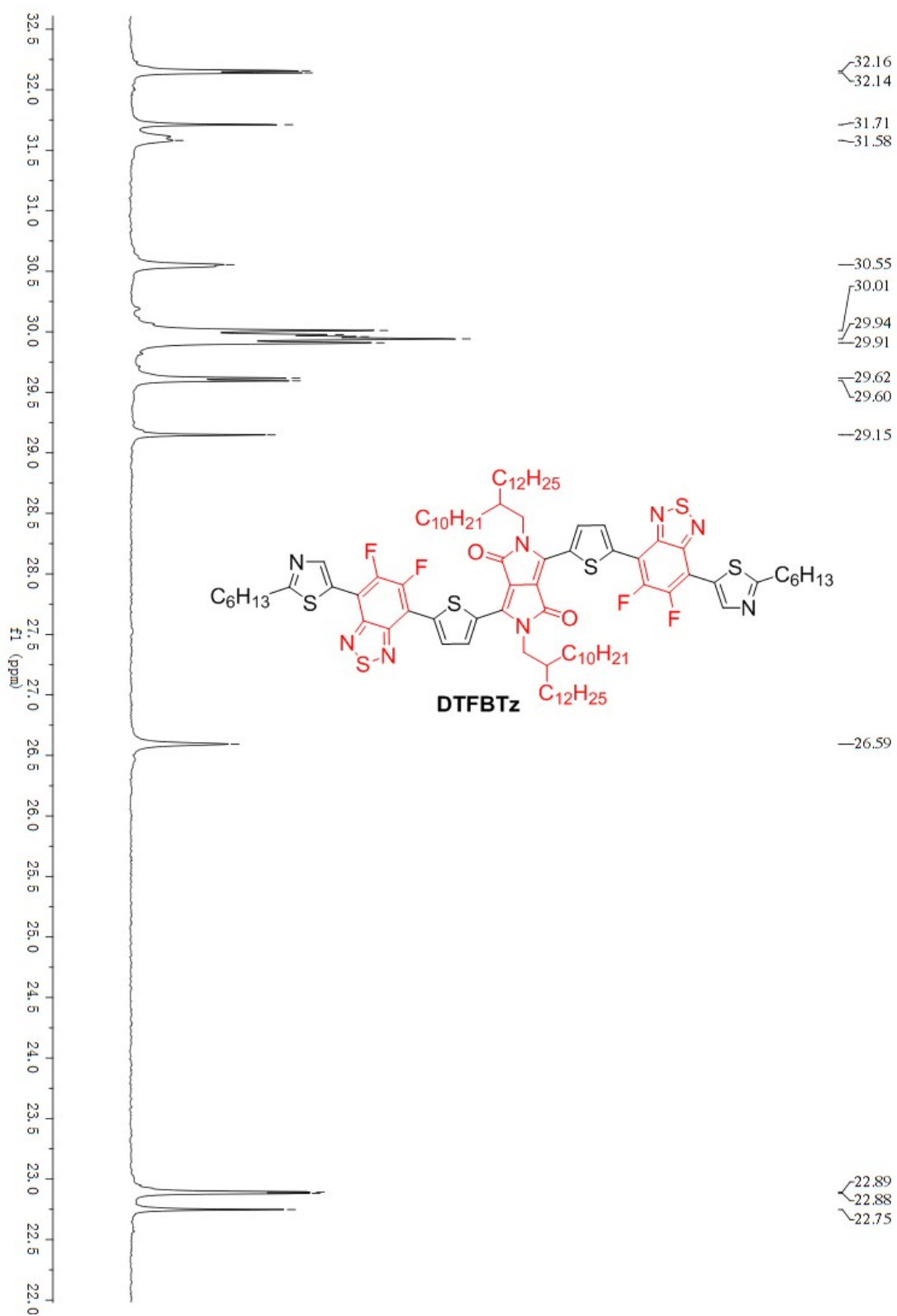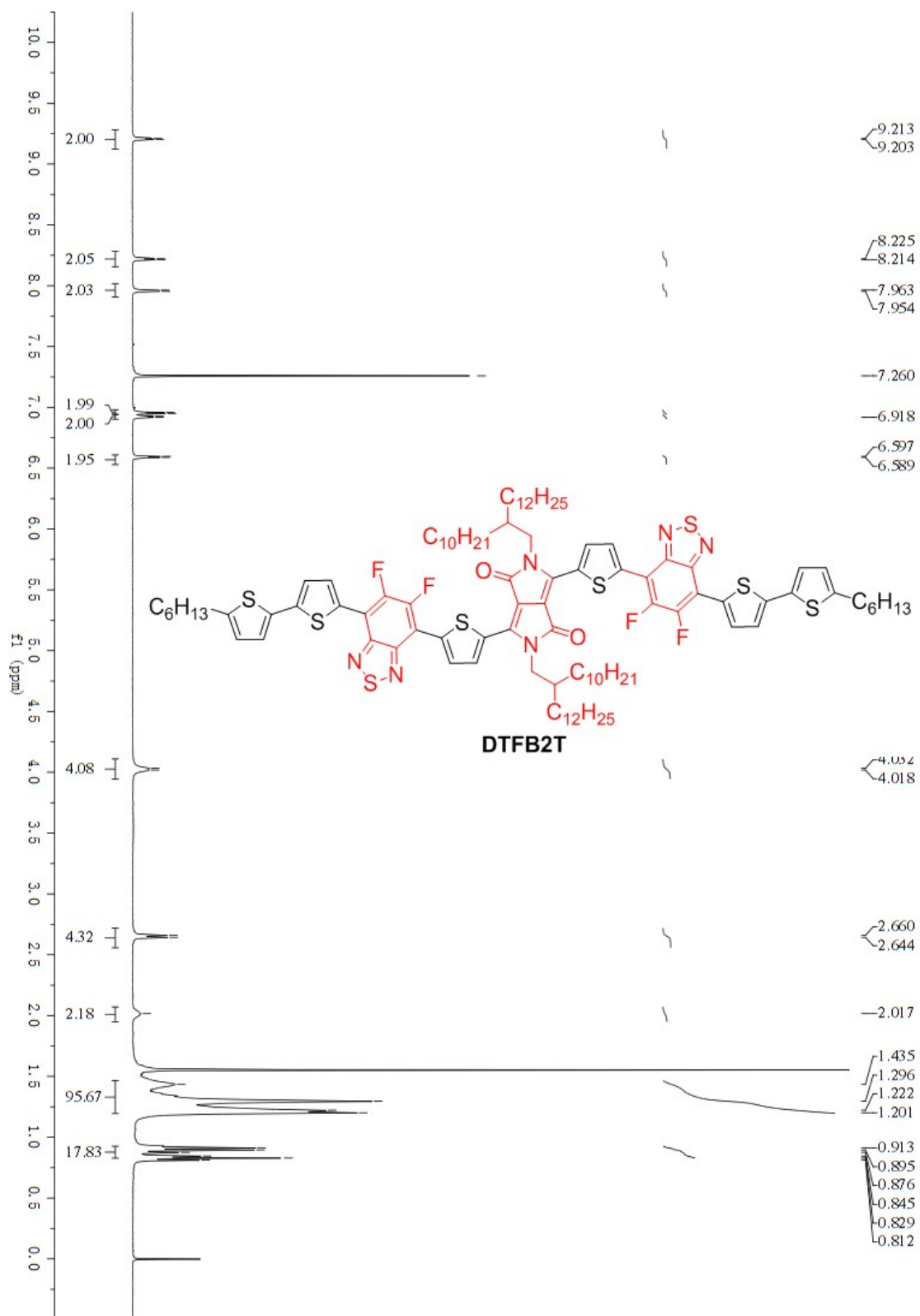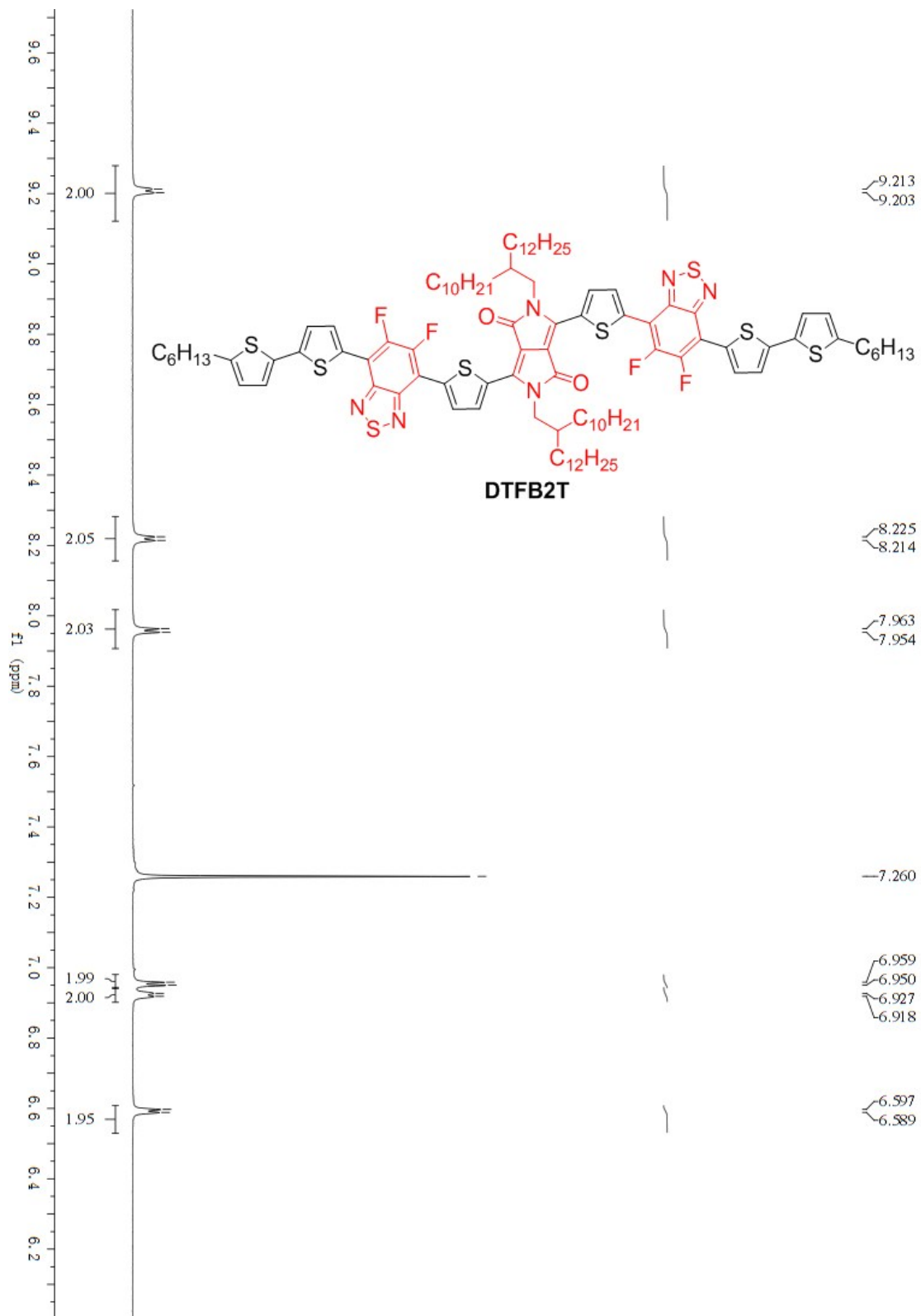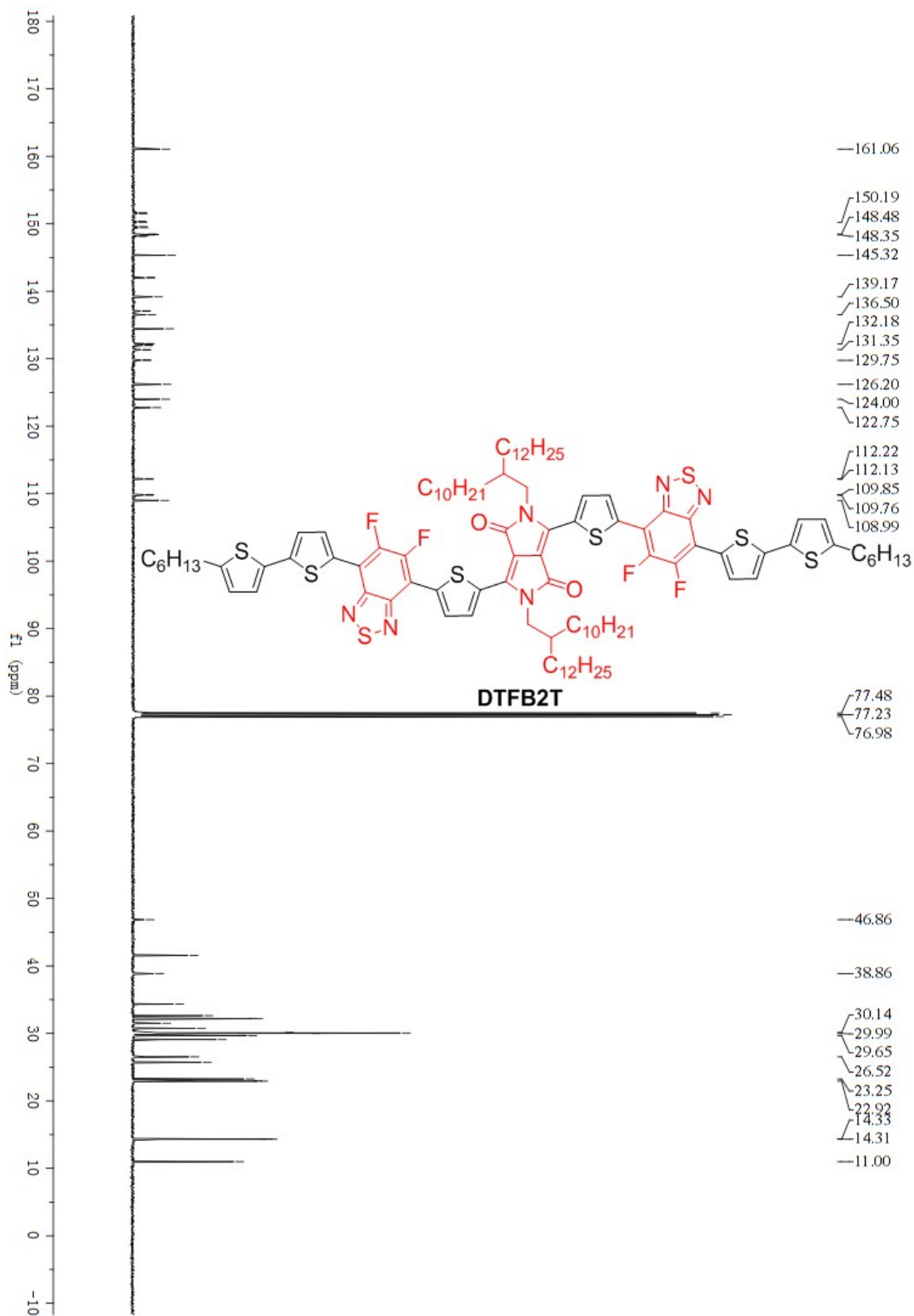
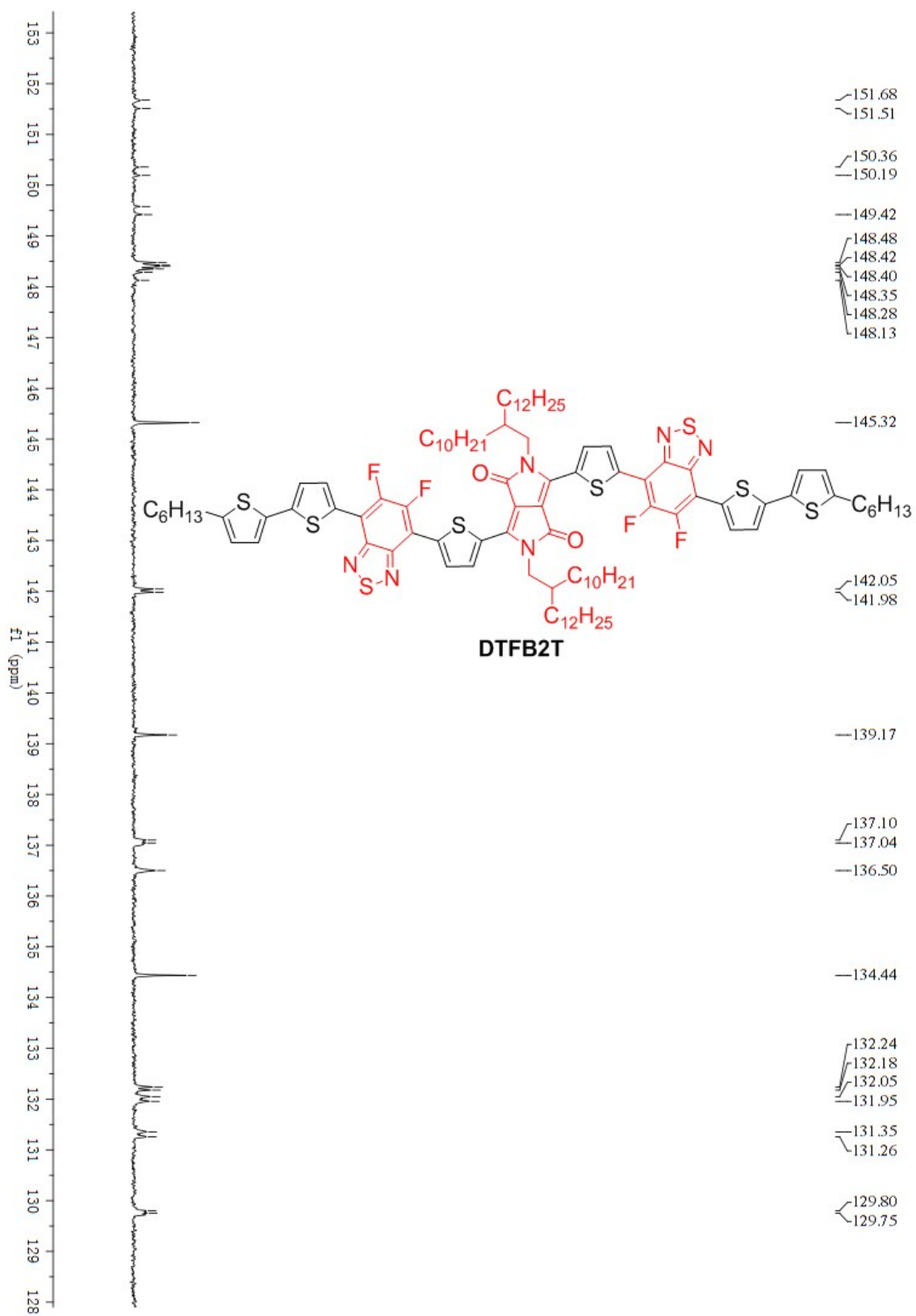The expended ^{13}C NMR spectrum of **DTFBTz** in CDCl$_3$.
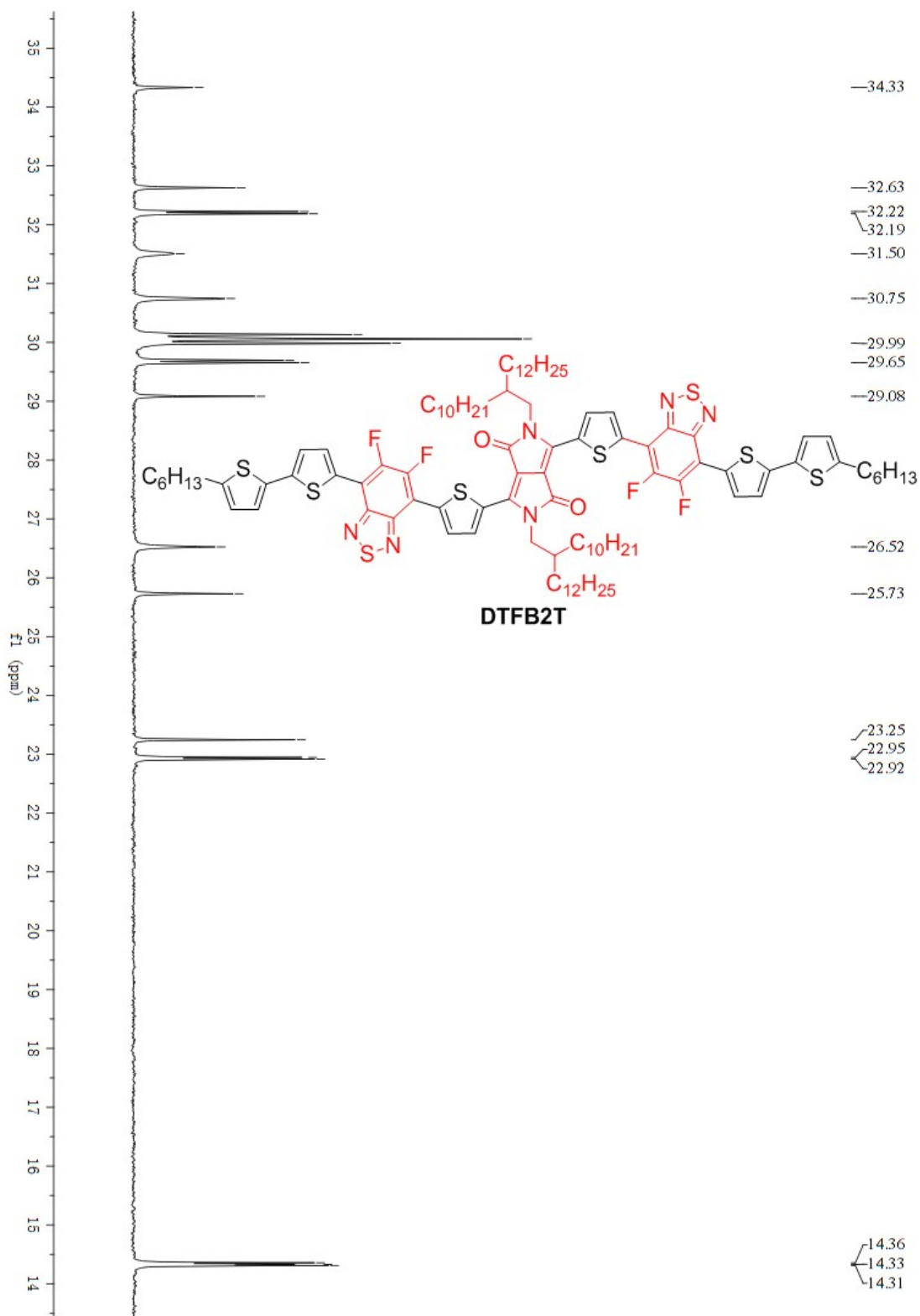
^{1}H NMR spectrum of **DTFB2T** in CDCl$_3$.

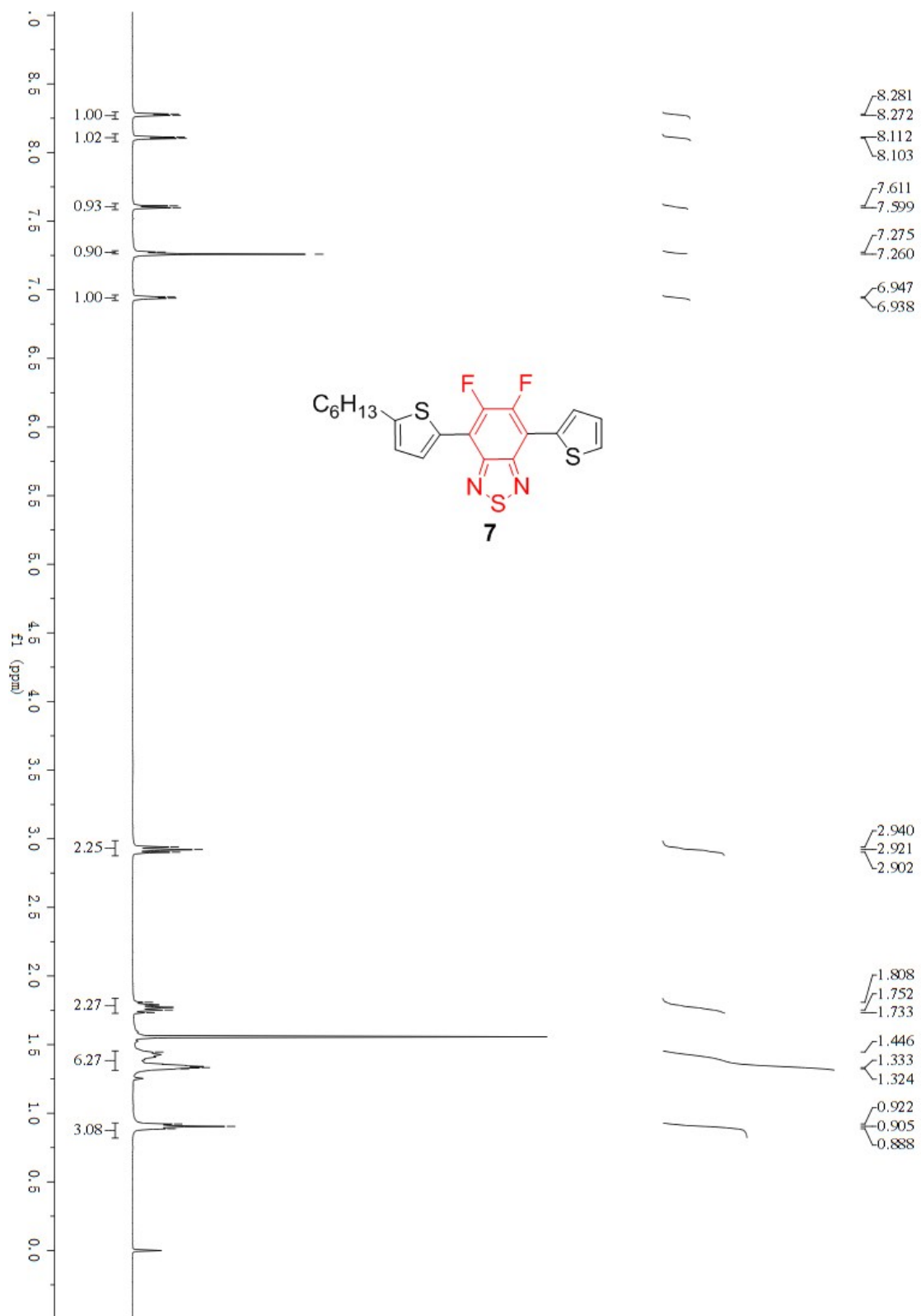The expended ^{1}H NMR spectrum of **DTFB2T** in CDCl$_3$.
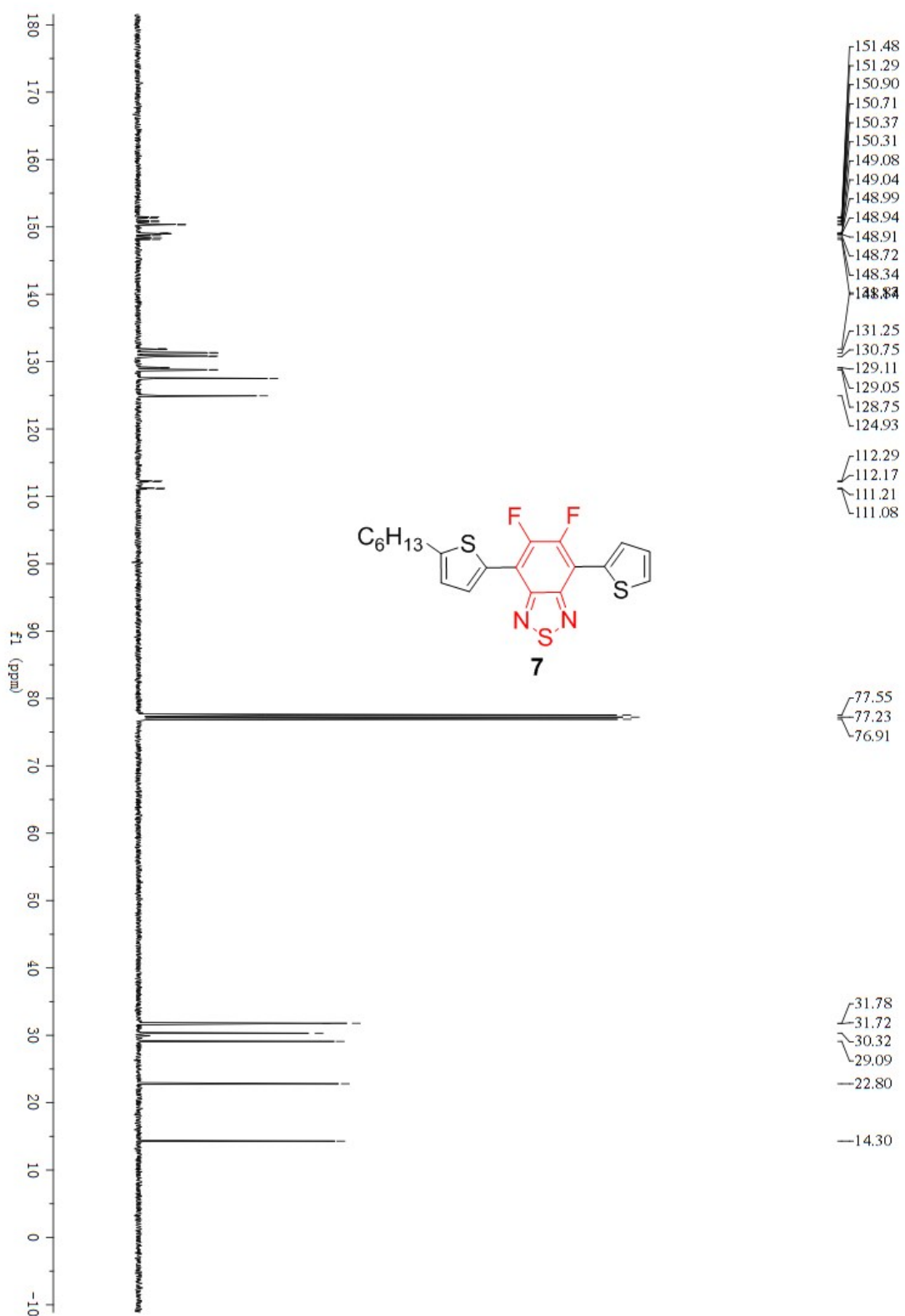
^{13}C NMR spectrum of **DTFB2T** in CDCl$_3$.

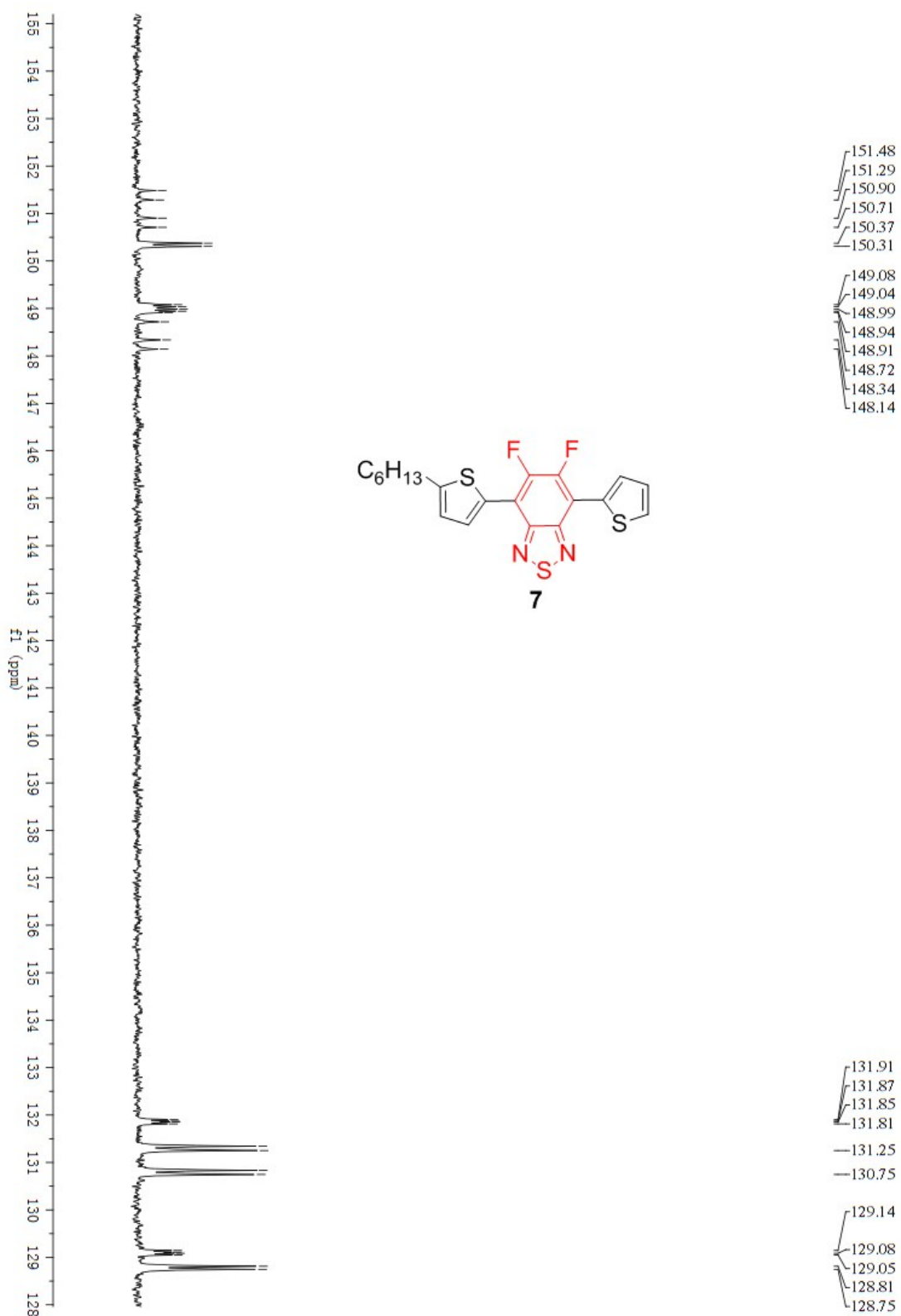The expended ^{13}C NMR spectrum of **DTFB2T** in CDCl$_3$.

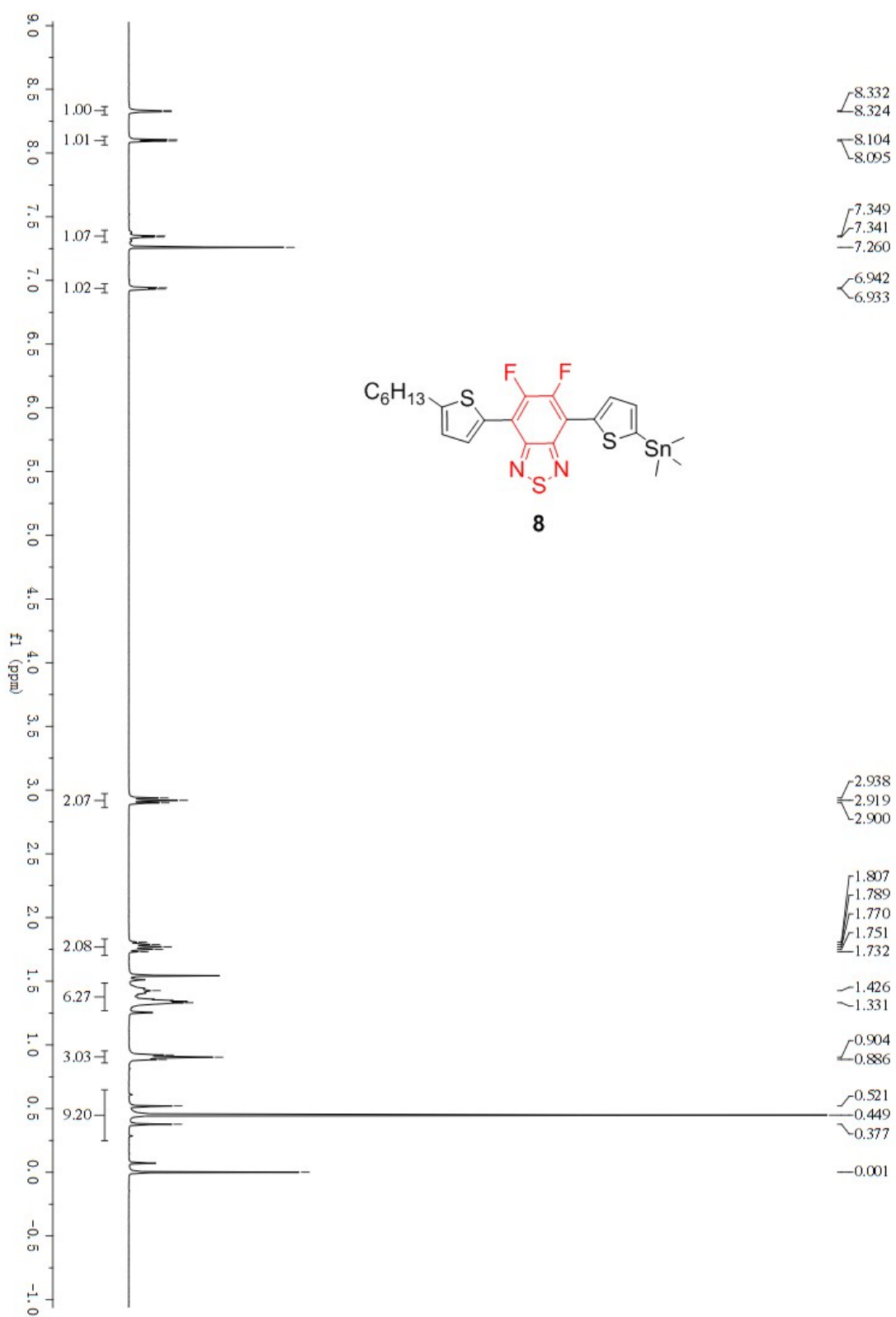The expended ^{13}C NMR spectrum of **DTFB2T** in CDCl$_3$.
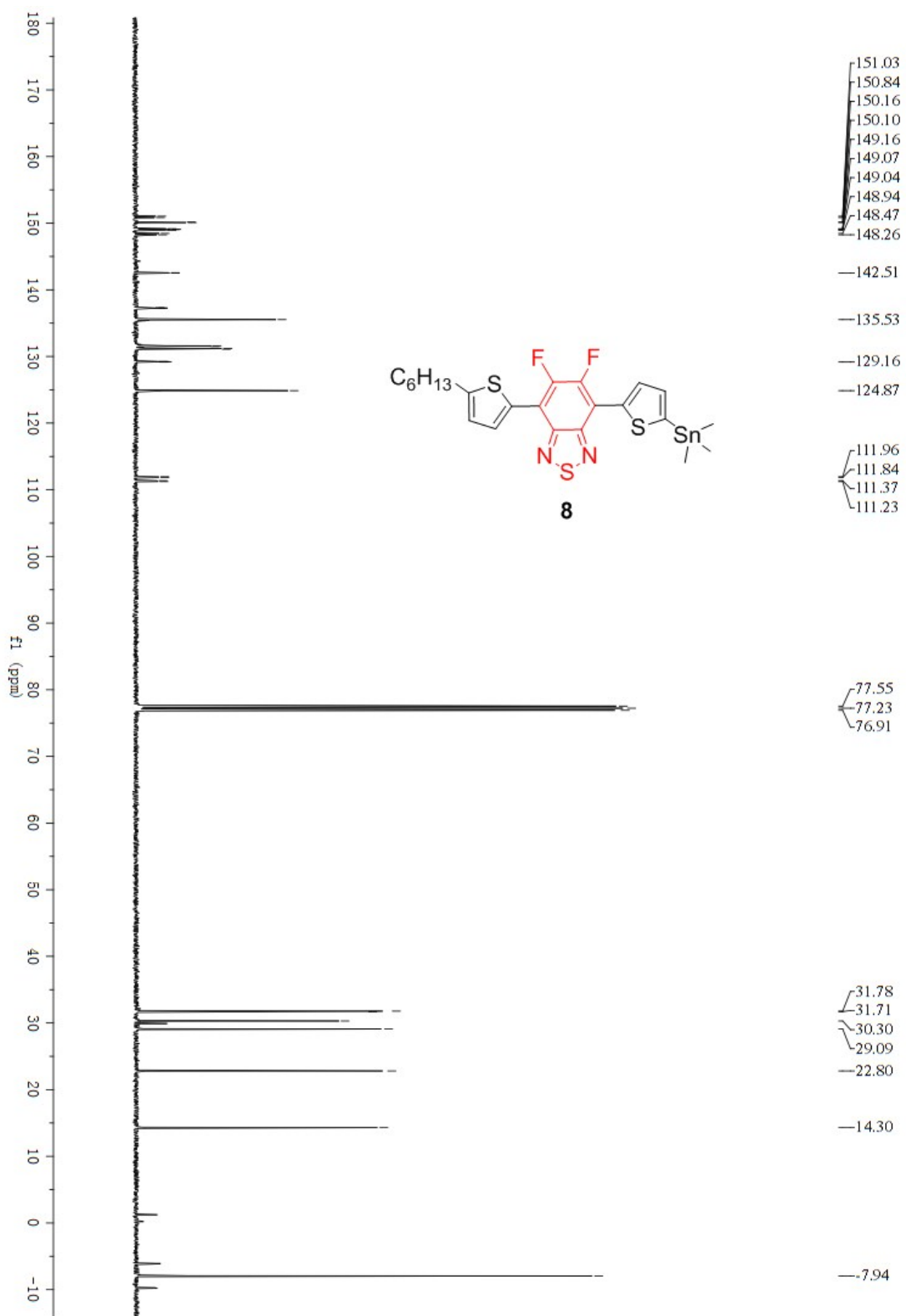
^{1}H NMR spectrum of **7** in CDCl$_3$.

^{13}C NMR spectrum of **7** in CDCl$_3$.

The expended ^{13}C NMR spectrum of **7** in CDCl$_3$.

8.332
8.324

8.104
8.095

7.349
7.341
7.260

6.942
6.933

2.938
2.919
2.900

1.807
1.789
1.770
1.751
1.732

1.426
1.331

0.904
0.886

0.521
0.449
0.377

0.001

1.00
1.01
1.07
1.02
2.07
2.08
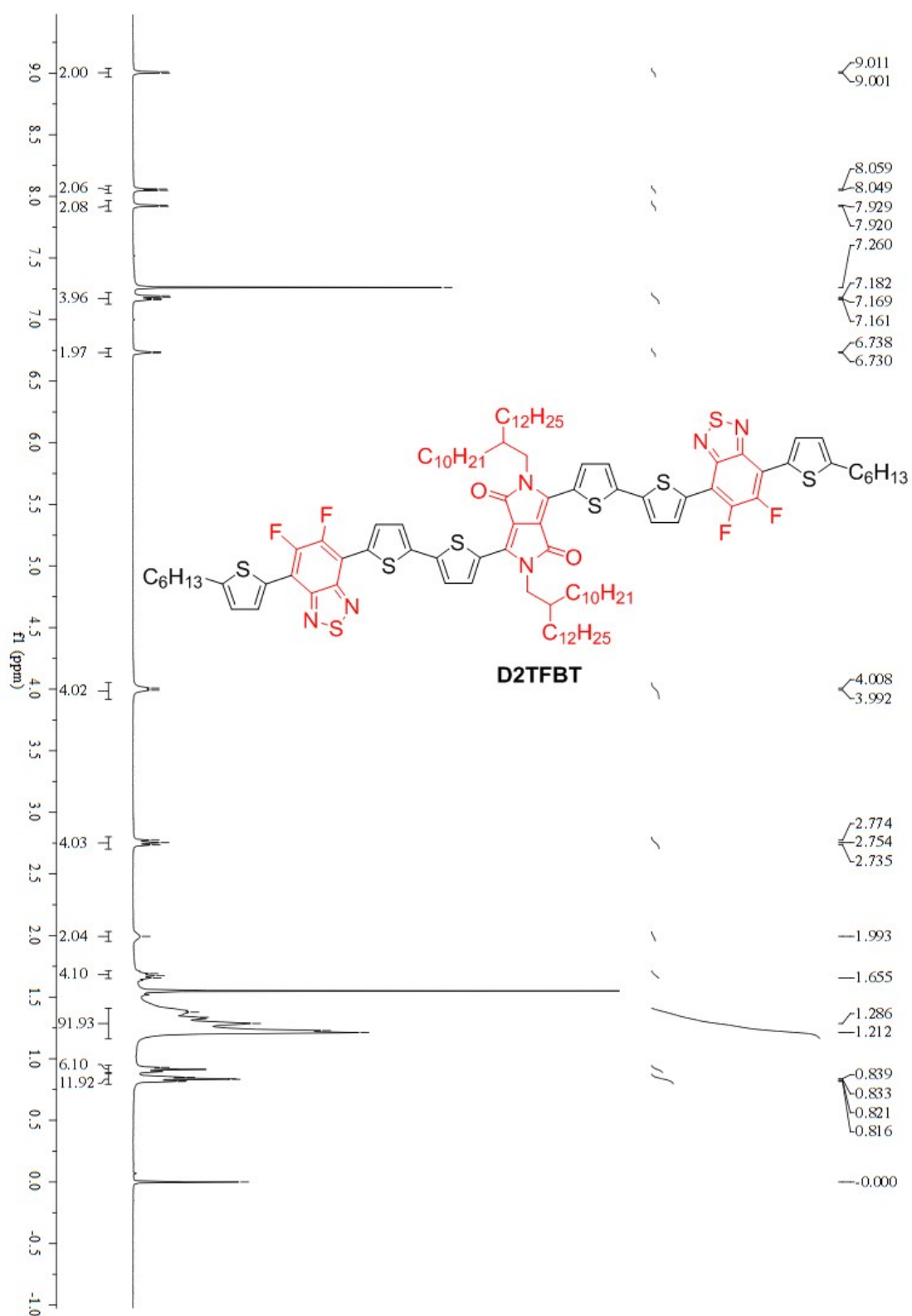6.27
3.03
9.20

f1 (ppm)

^{1}H NMR spectrum of **8** in CDCl$_3$.

^{13}C NMR spectrum of **8** in CDCl$_3$.

The expended ^{13}C NMR spectrum of **8** in CDCl$_3$.

^{1}H NMR spectrum of **D2TFBT** in CDCl$_3$.