Supporting Information

A new synthetic approach to fused nine-ring systems of the indolo[3,2-*b*]carbazole family through the double Pd-catalyzed intramolecular C-H arylation

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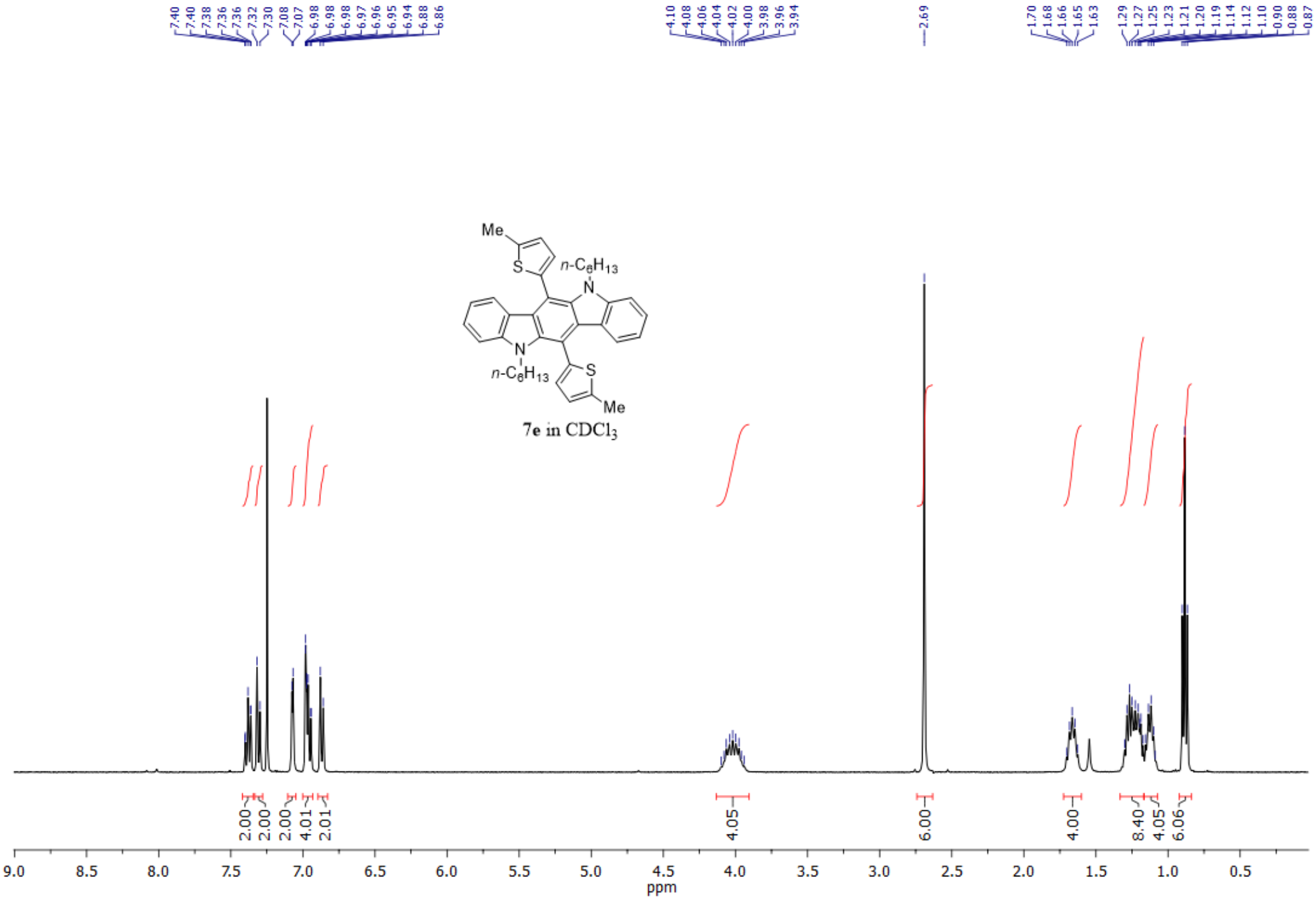
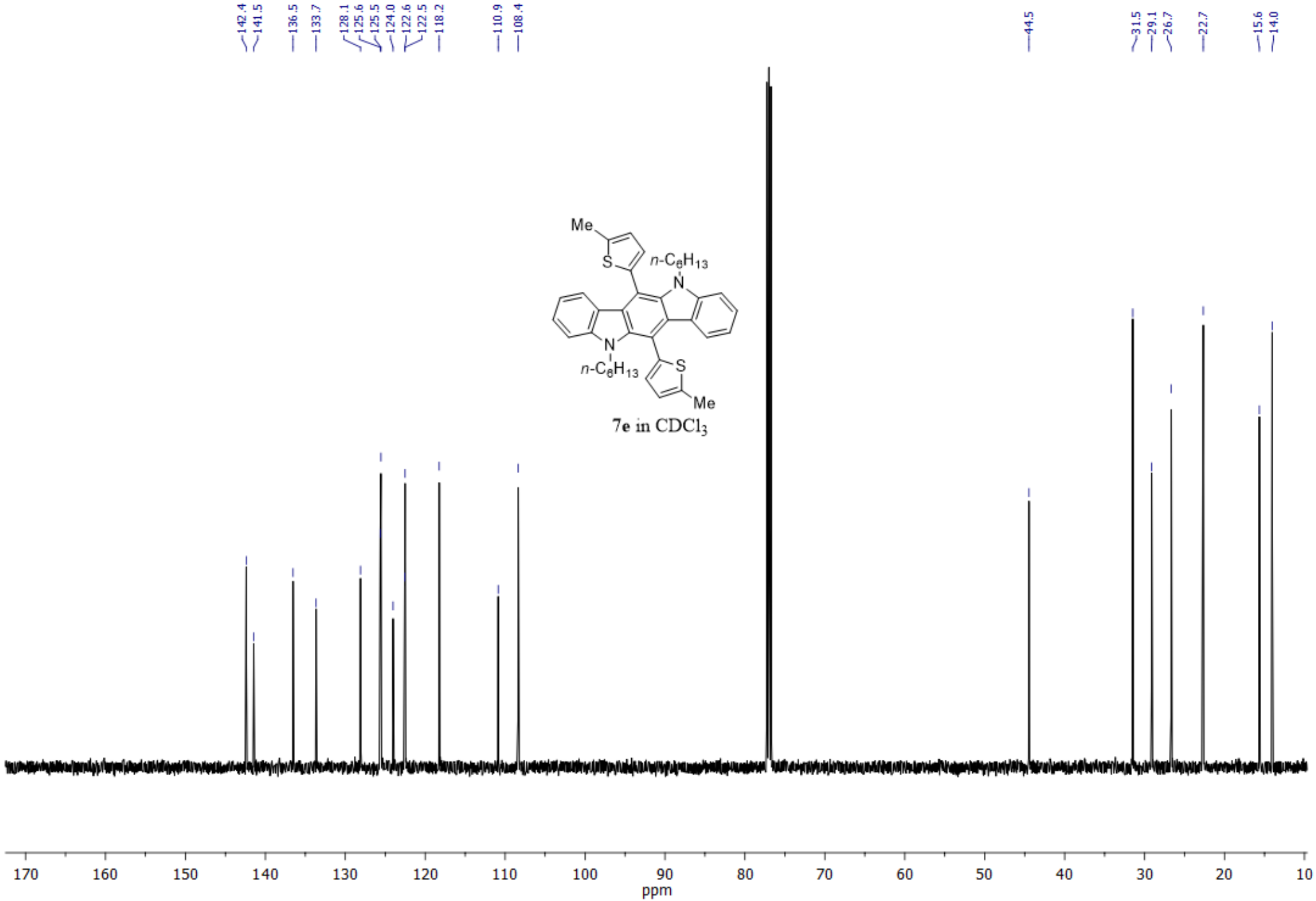
^{1}H NMR

1. Copies of ^{1}H and ^{13}C NMR spectra of new compounds



^{13}C NMR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44.5
31.5
29.1
26.7
22.7
15.6
14.0
Me
S
n-C6H13
N
N
n-C6H13
S
Me
7e in CDCl3
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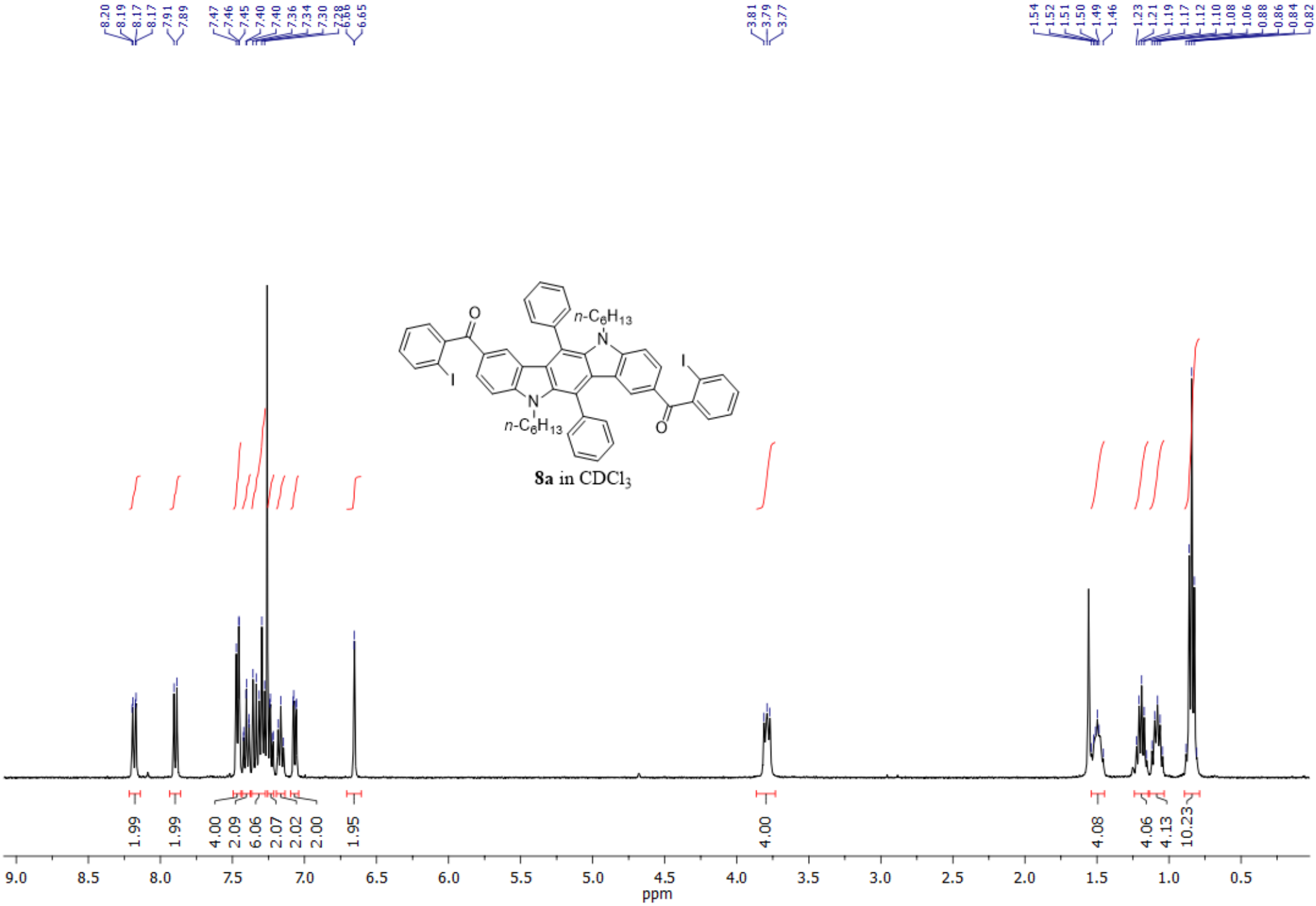
ppm

^{1}H NMR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7.30
7.28
6.68
6.65
3.81
3.79
3.77
1.54
1.52
1.51
1.50
1.49
1.46
1.23
1.21
1.19
1.17
1.12
1.10
1.08
1.06
0.88
0.86
0.84
0.82
n-C6H13
N
I
O
N
n-C6H13
I
O
8a in CDCl3
1.99
1.99
4.00
2.09
6.06
2.07
2.02
2.00
1.95
4.00
4.08
4.06
4.13
10.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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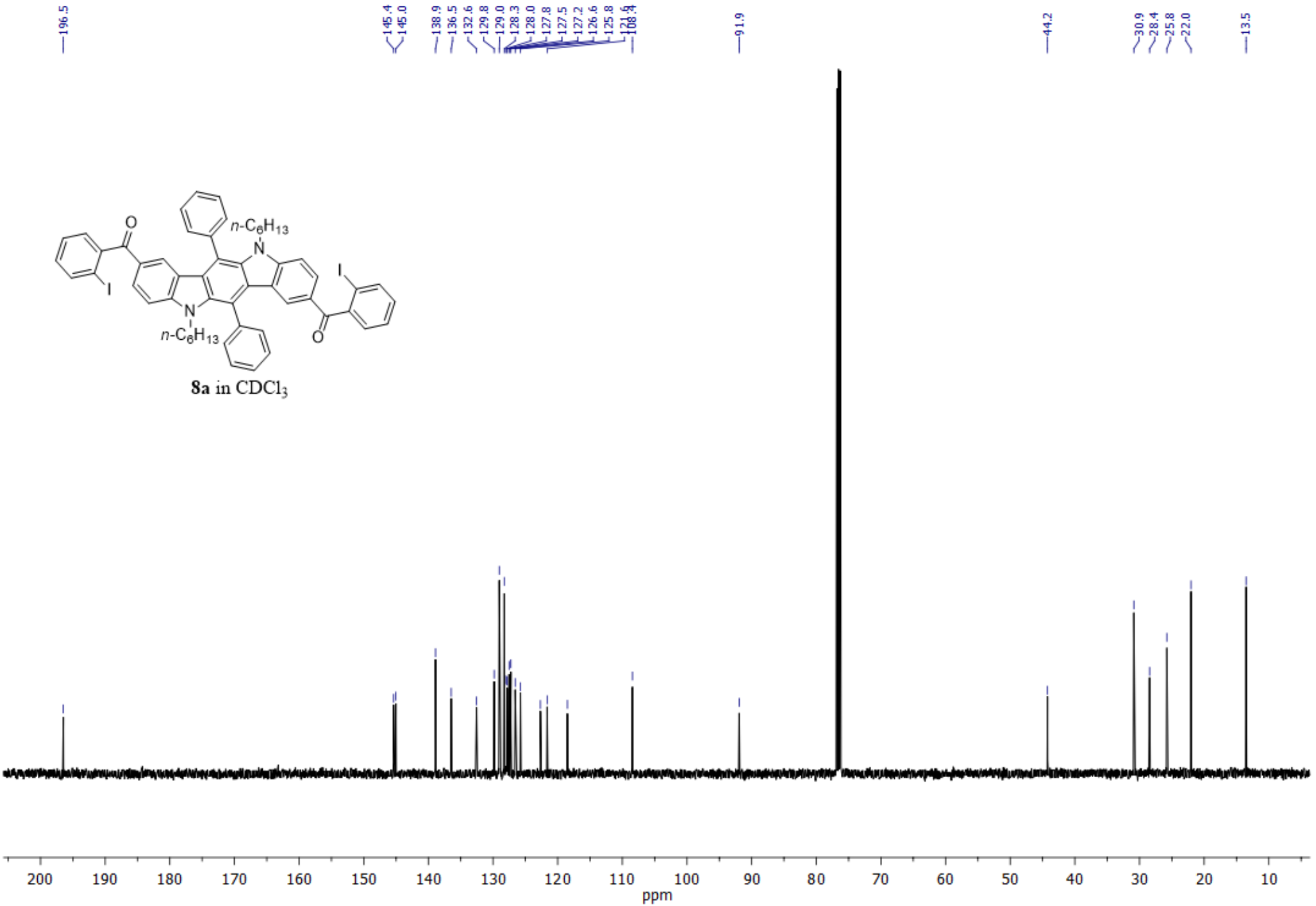
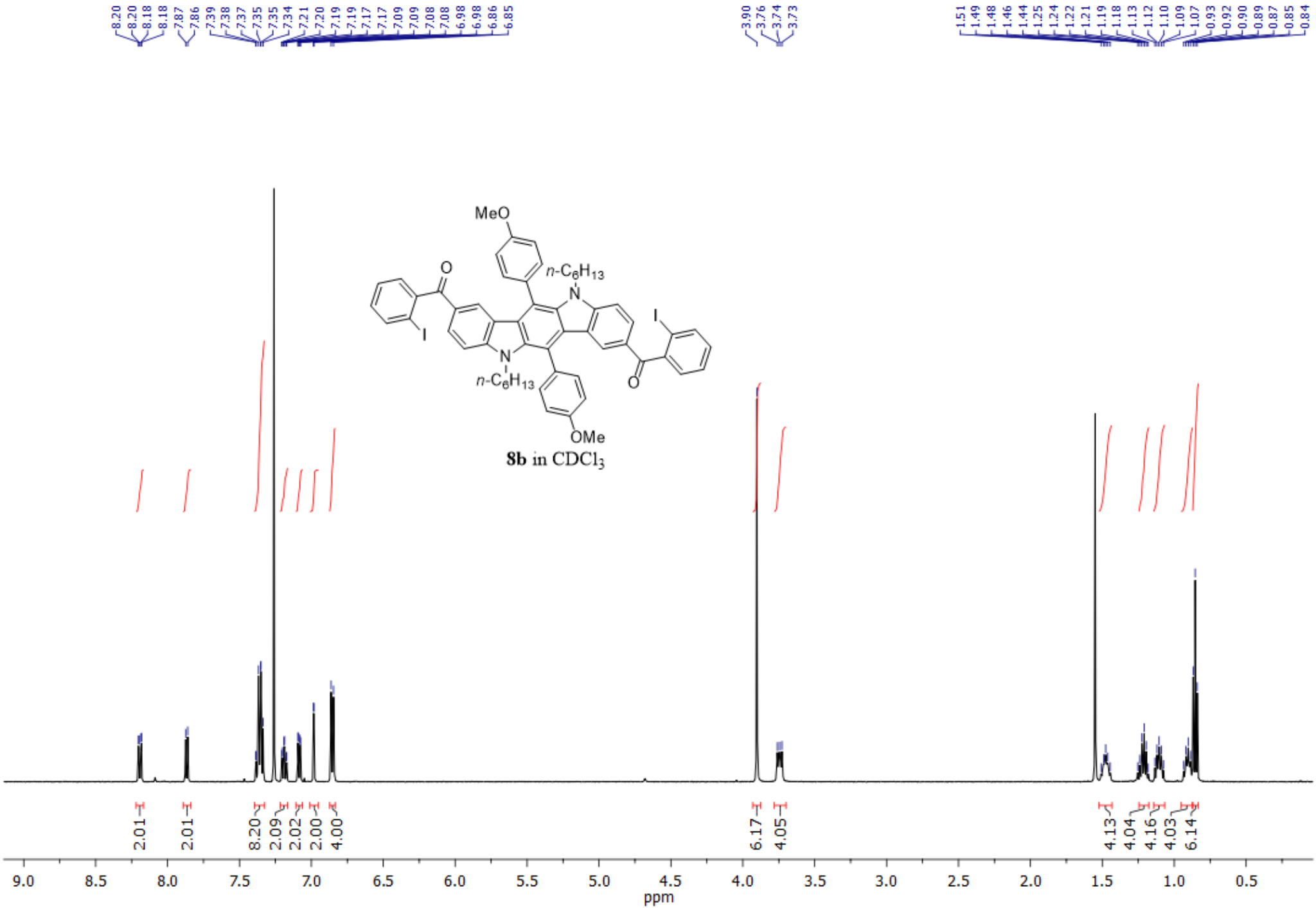
^{13}C NMR



8a in $CDCl_3$

^{1}H NMR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n-C6H13
I
O
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2.01
8.20
2.09
2.02
2.00
4.00
6.17
4.05
4.13
4.04
4.16
4.03
6.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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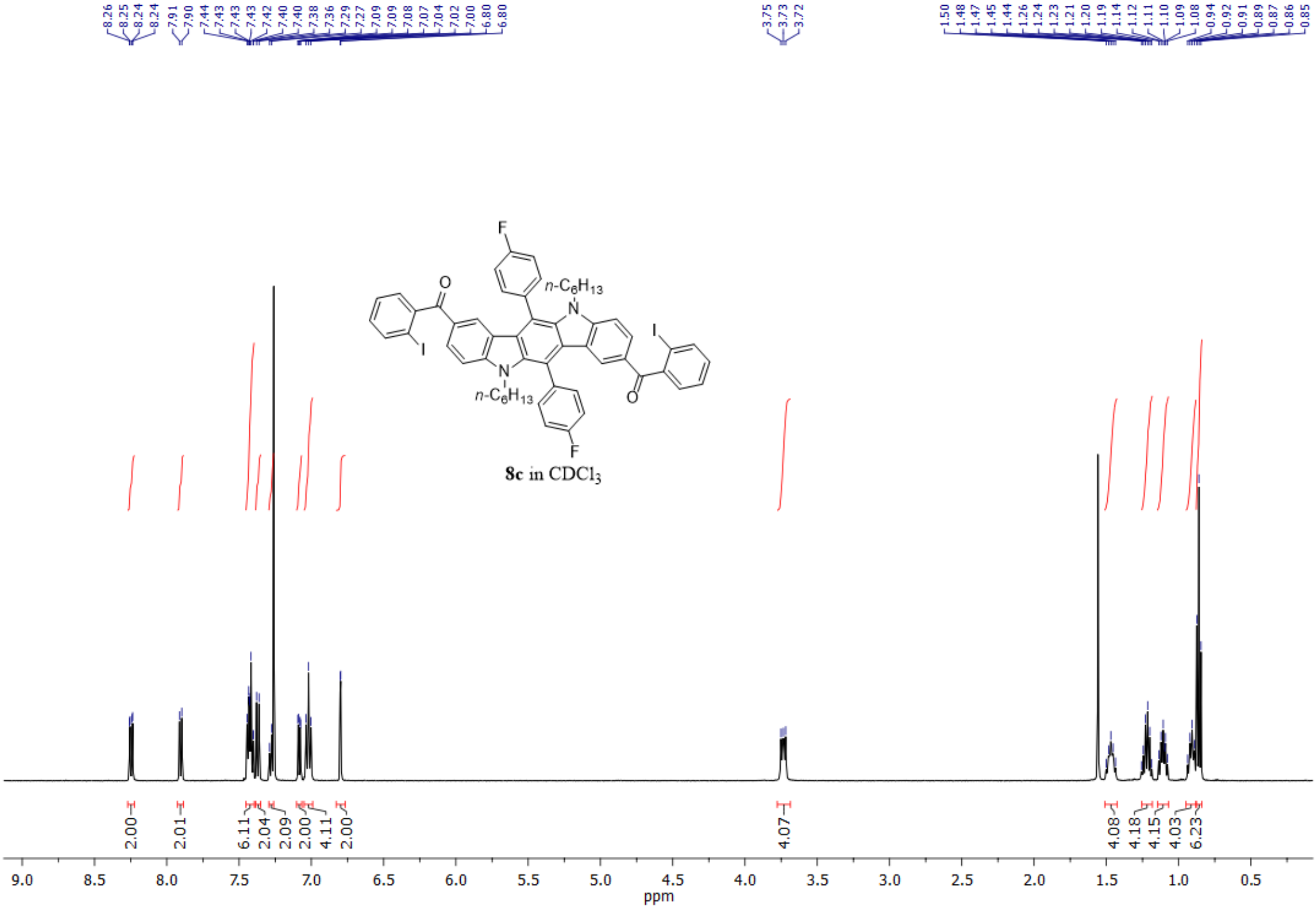
ppm

^{1}H NMR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7.40
7.38
7.36
7.29
7.27
7.09
7.09
7.08
7.07
7.04
7.02
7.00
6.80
6.80
3.75
3.73
3.72
1.50
1.48
1.47
1.45
1.44
1.26
1.24
1.23
1.21
1.20
1.19
1.14
1.12
1.11
1.10
1.09
1.08
0.94
0.92
0.91
0.89
0.87
0.86
0.85
F
n-C6H13
N
I
O
N
n-C6H13
I
O
F
8c in CDCl3
2.00
2.01
6.11
2.04
2.09
2.00
4.11
2.00
4.07
4.08
4.18
4.15
4.03
6.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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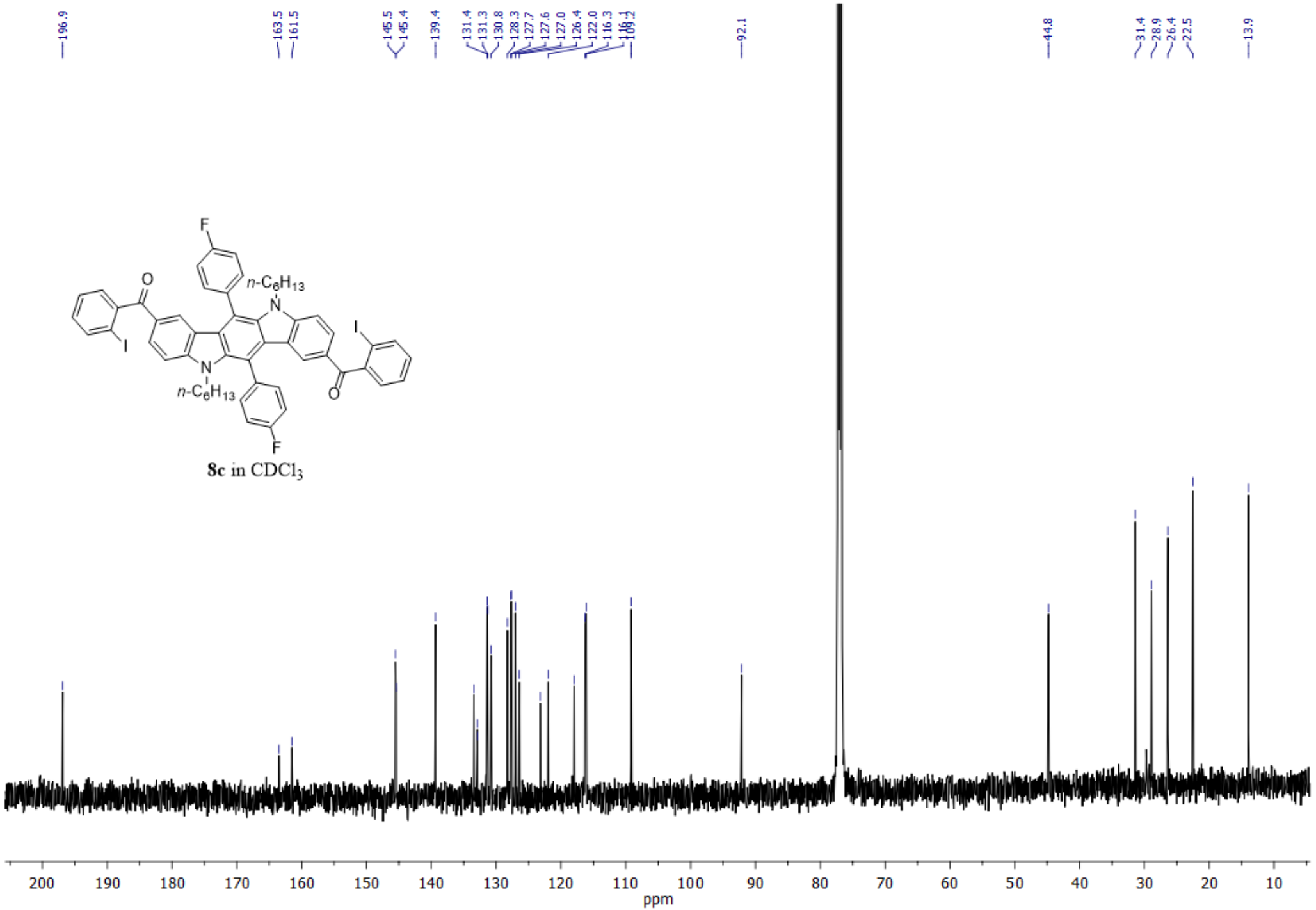
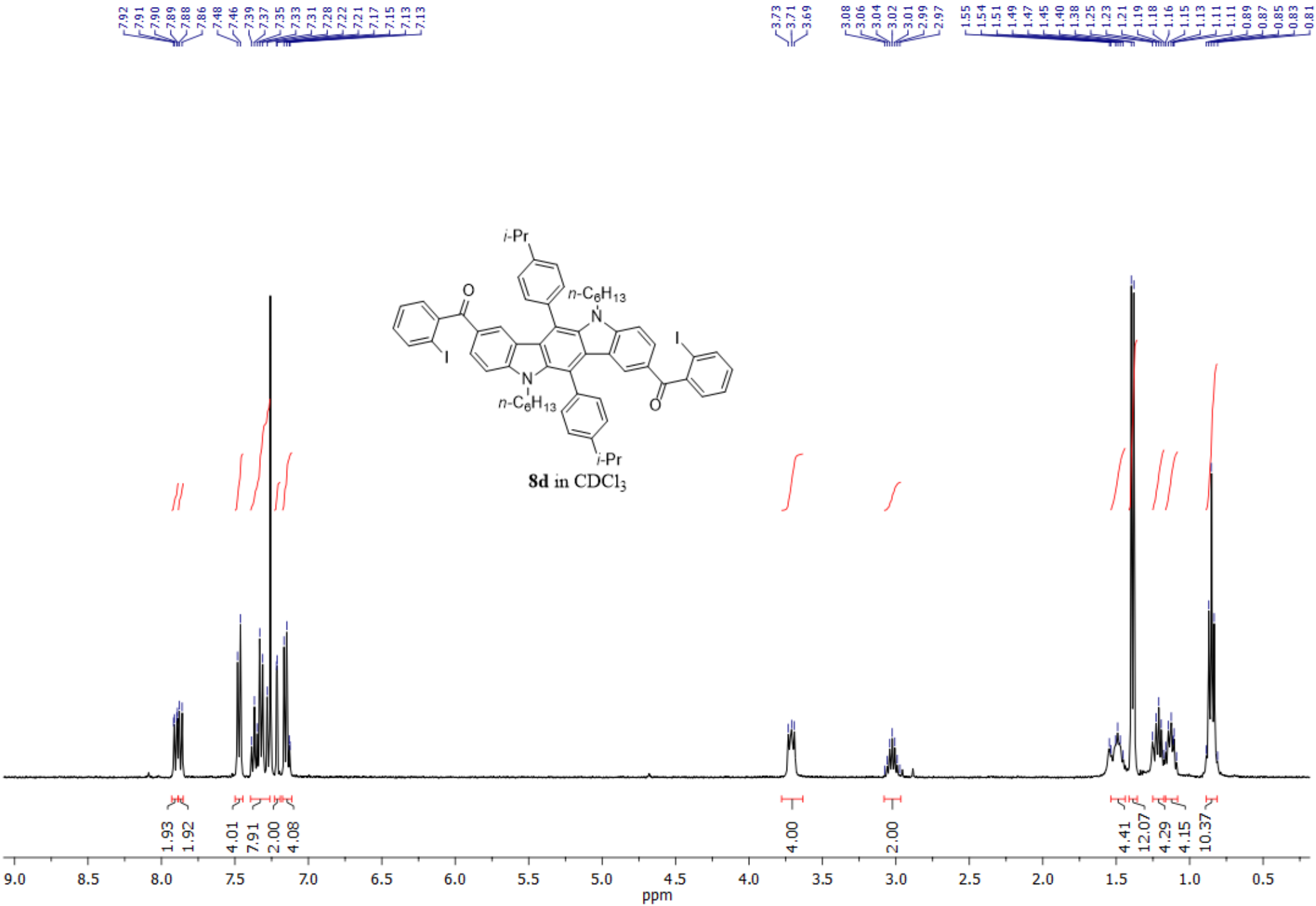
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{13}C NMR



8c in $CDCl_3$

^{1}H NMR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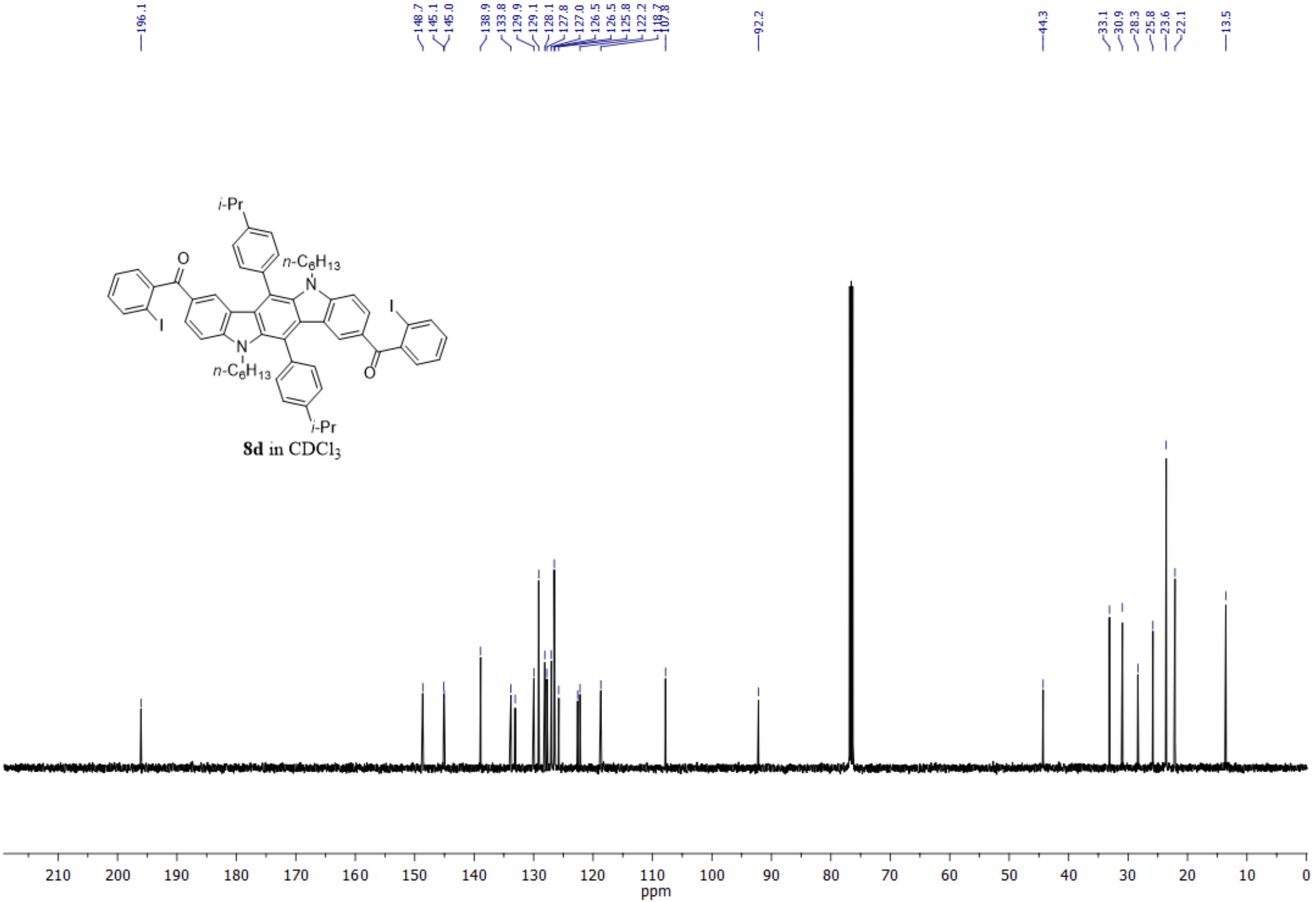
3.73 3.71 3.69 3.08 3.06 3.04 3.02 3.01 2.99 2.97
1.55 1.54 1.51 1.49 1.47 1.45 1.40 1.38 1.25 1.23 1.21 1.19 1.18 1.16 1.15 1.13 1.11 1.11 0.89 0.87 0.85 0.83 0.81
i-Pr
n-C6H13
N
O
I
I
O
N
n-C6H13
i-Pr
8d in CDCl3
1.93 1.92 4.01 7.91 2.00 4.08 4.00 2.00 4.41 12.07 4.29 4.15 10.37
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

^{13}C NMR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126.5
125.8
122.2
92.2
44.3
33.1
30.9
28.3
25.8
23.6
22.1
13.5
i-Pr
n-C6H13
O
I
N
n-C6H13
i-Pr
8d in CDCl3
210
200
190
180
170
160
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140
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120
110
100
90
80
70
60
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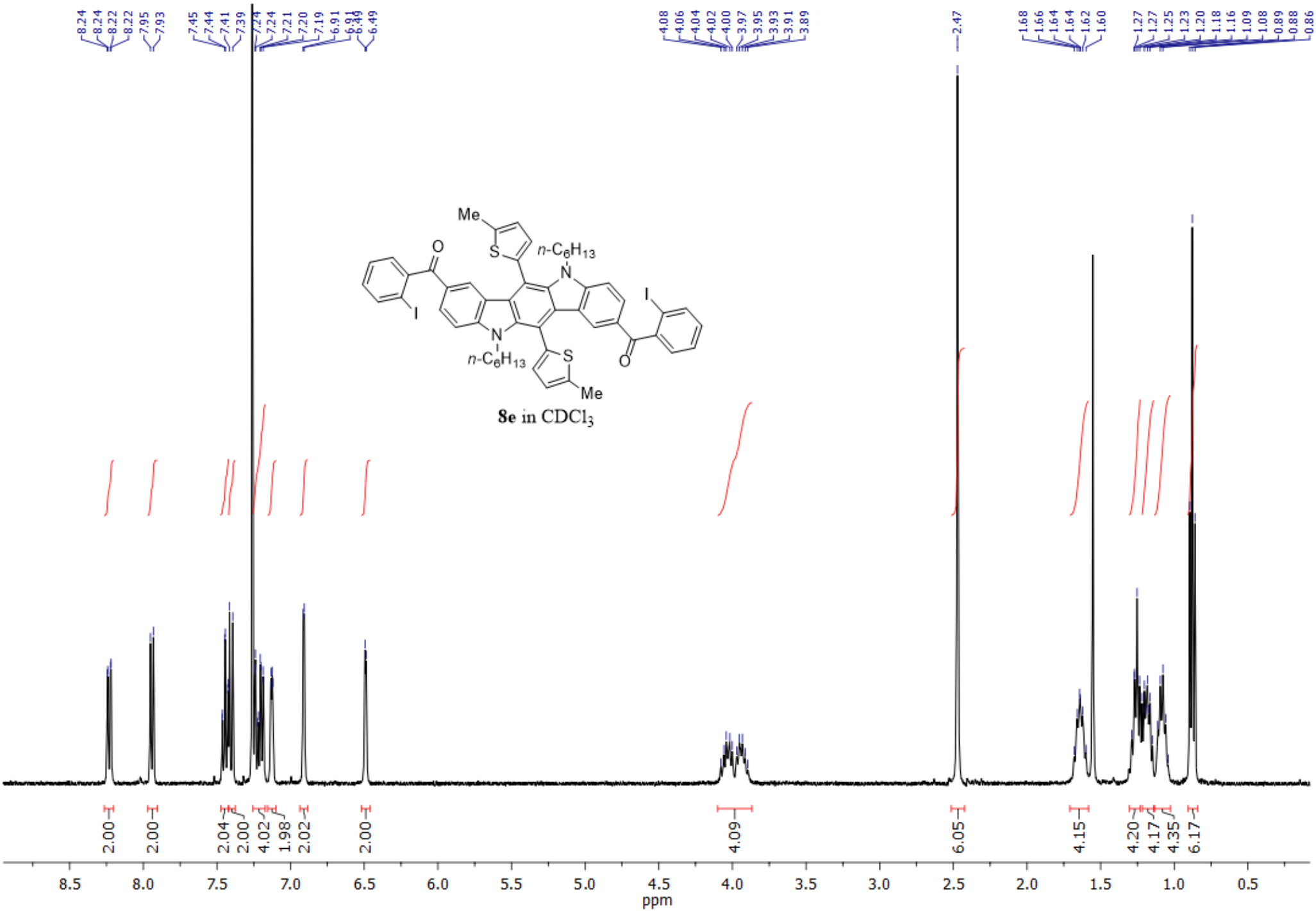
40
30
20
10
0
ppm

^{1}H NMR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7.20
7.19
6.91
6.91
6.49
4.08
4.06
4.04
4.02
4.00
3.97
3.95
3.93
3.91
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1.68
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1.64
1.62
1.60
1.27
1.27
1.25
1.23
1.20
1.18
1.16
1.09
1.08
0.89
0.88
0.86
Me
S
n-C6H13
N
I
O
O
I
N
n-C6H13
S
Me
8e in CDCl3
2.00
2.00
2.04
2.00
4.02
1.98
2.02
2.00
4.09
6.05
4.15
4.20
4.17
4.35
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6.5
6.0
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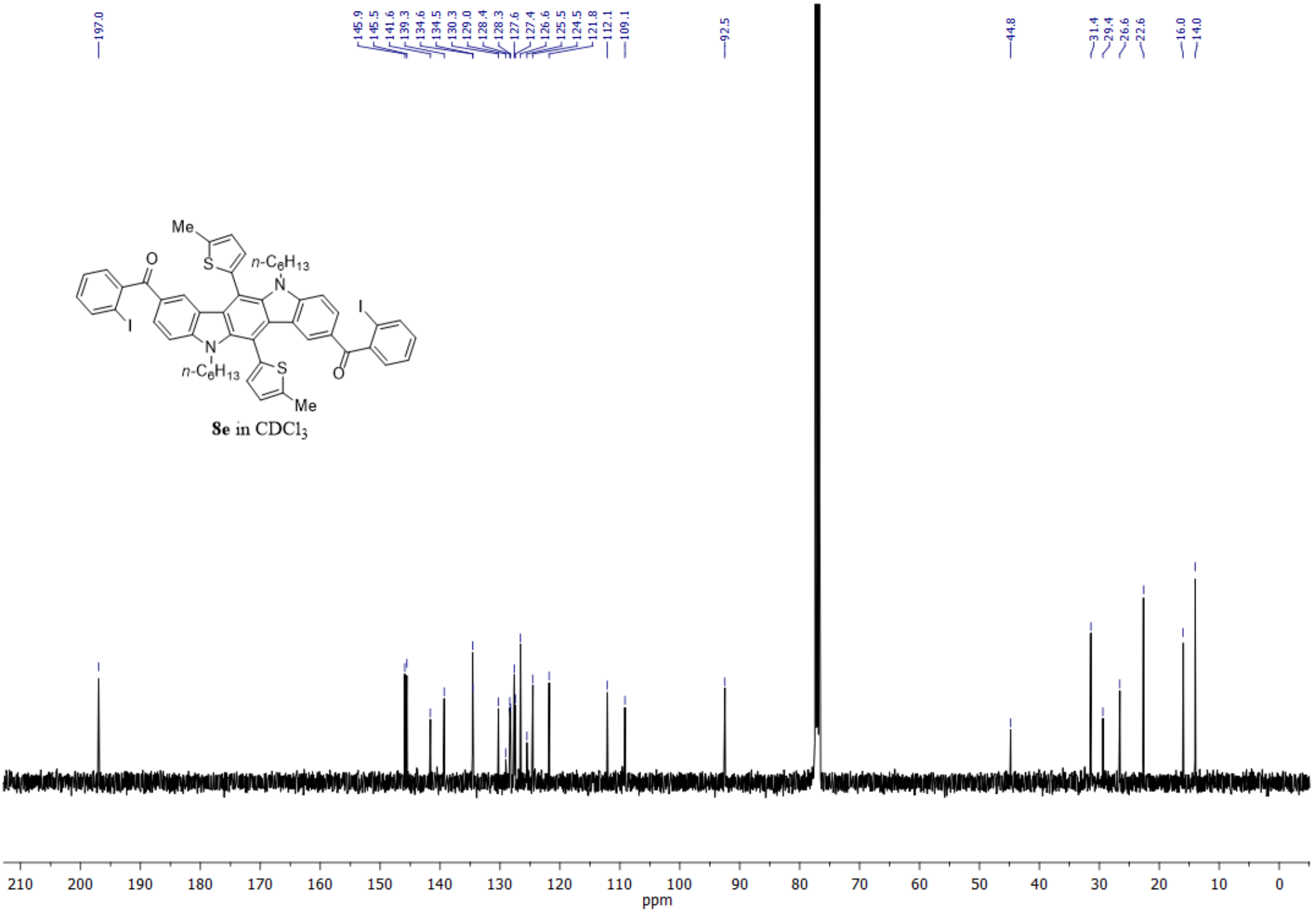
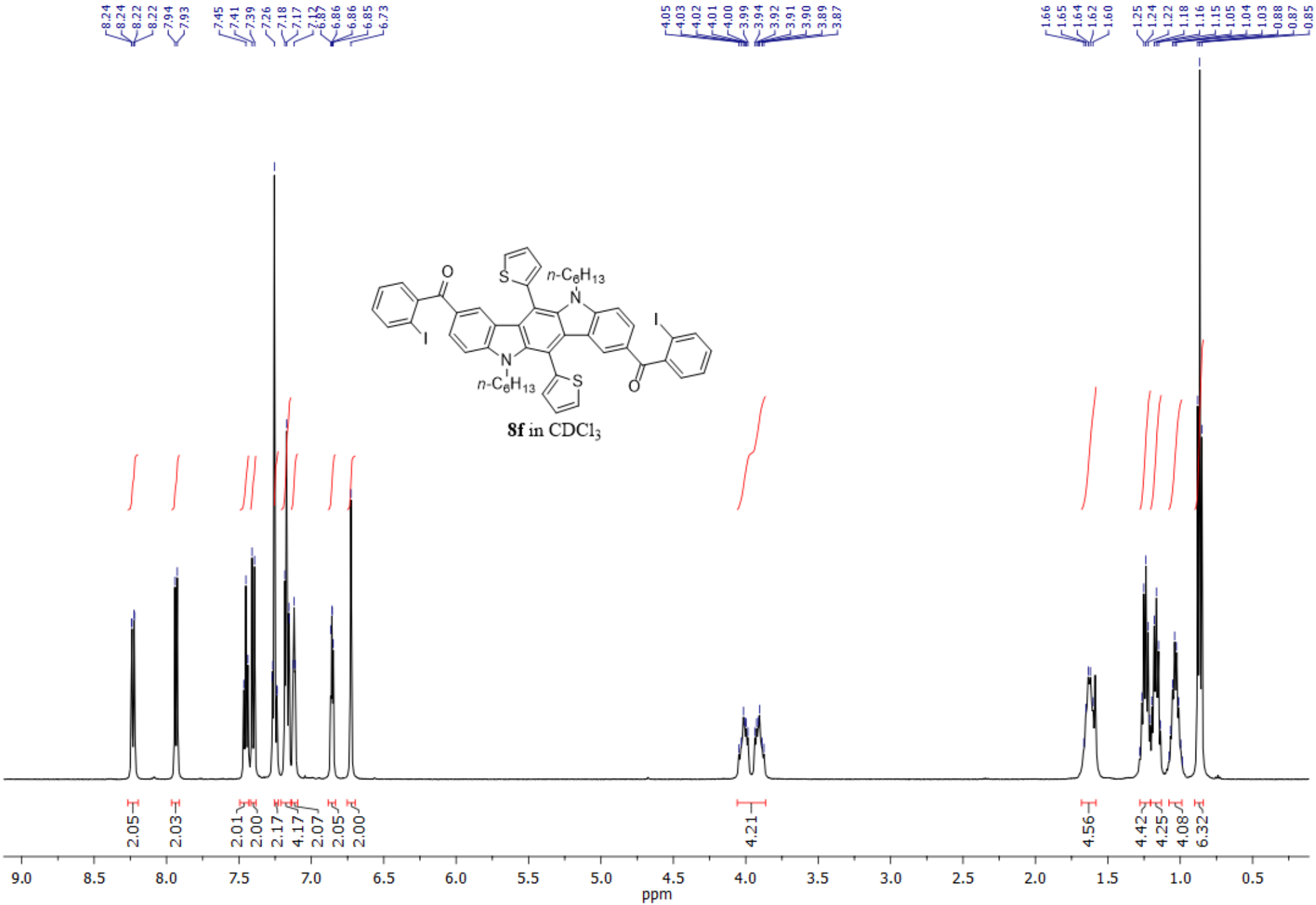
ppm

^{13}C NMR



8e in $CDCl_3$

^{1}H NMR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1.62
1.60
1.25
1.24
1.22
1.18
1.16
1.15
1.05
1.04
1.03
0.88
0.87
0.85
O
S
n-C6H13
N
I
I
N
n-C6H13
S
O
8f in CDCl3
2.05
2.03
2.01
2.00
2.17
4.17
2.07
2.05
2.00
4.21
4.56
4.42
4.25
4.08
6.32
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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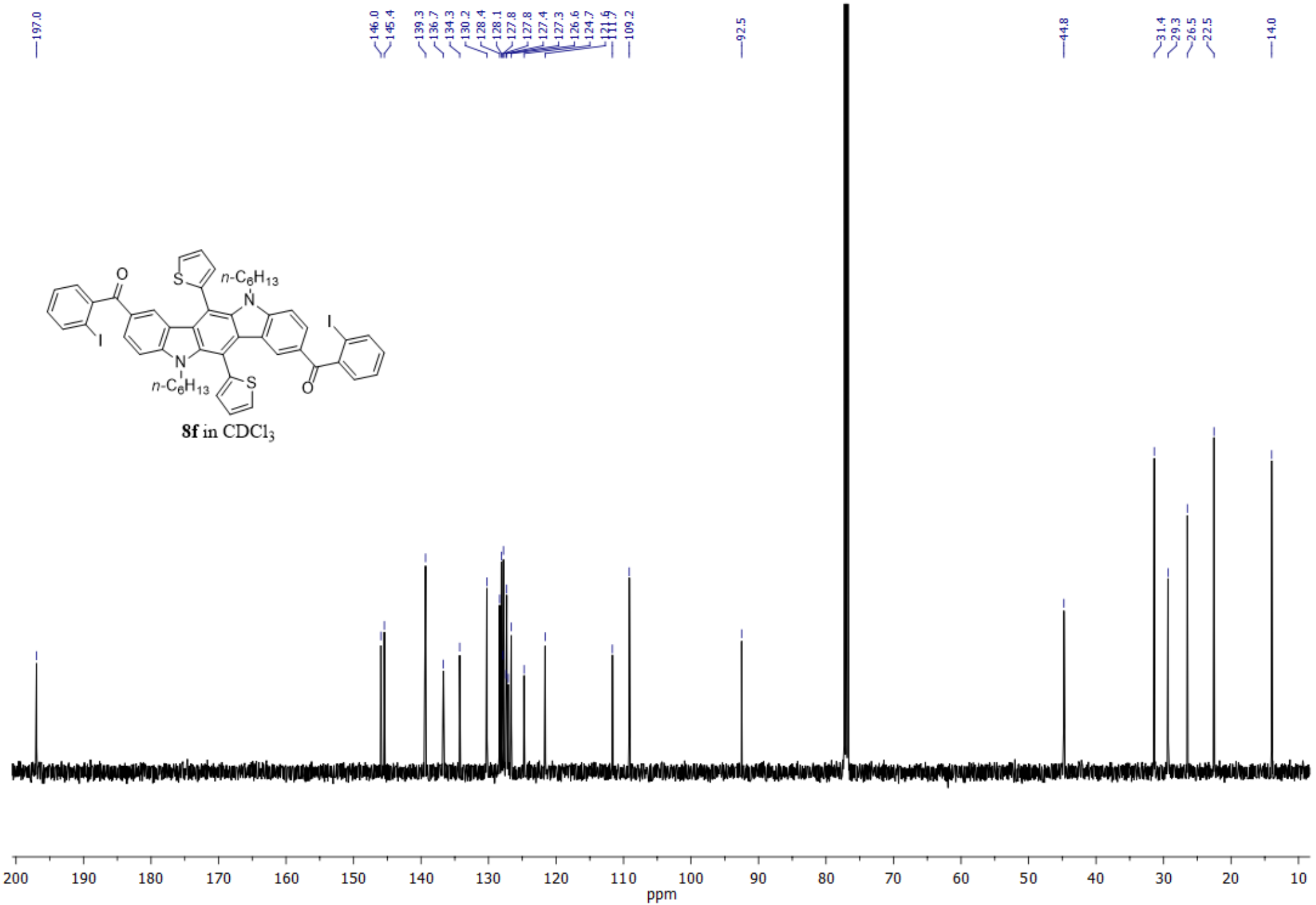
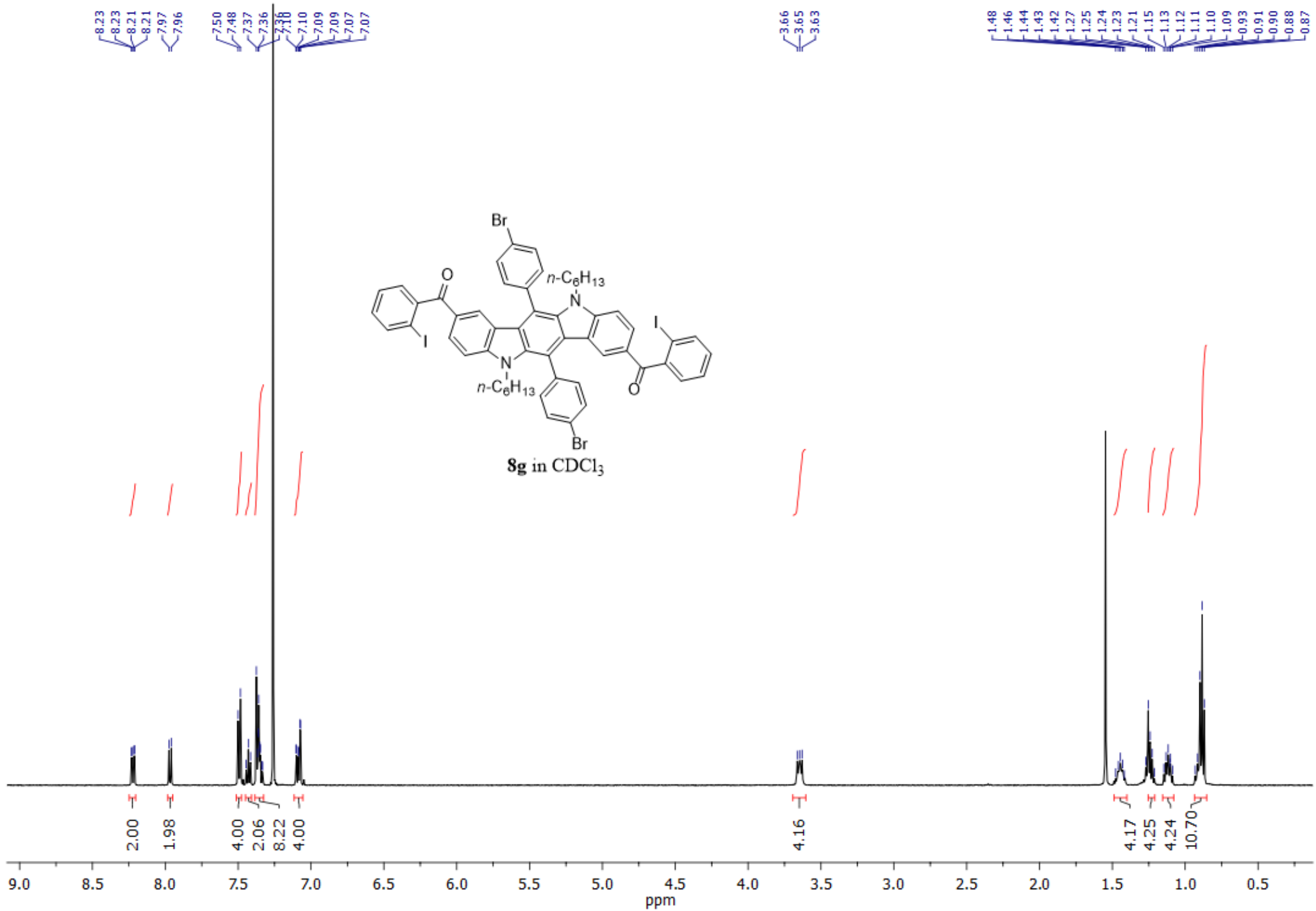
ppm

^{13}C NMR



8f in $CDCl_3$

^{1}H NMR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1.23
1.21
1.15
1.13
1.12
1.11
1.10
1.09
0.93
0.91
0.90
0.88
0.87
Br
O
I
n-C6H13
N
N
n-C6H13
I
O
Br
8g in CDCl3
2.00
1.98
4.00
2.06
8.22
4.00
4.16
4.17
4.25
4.24
10.70
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8.5
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7.0
6.5
6.0
5.5
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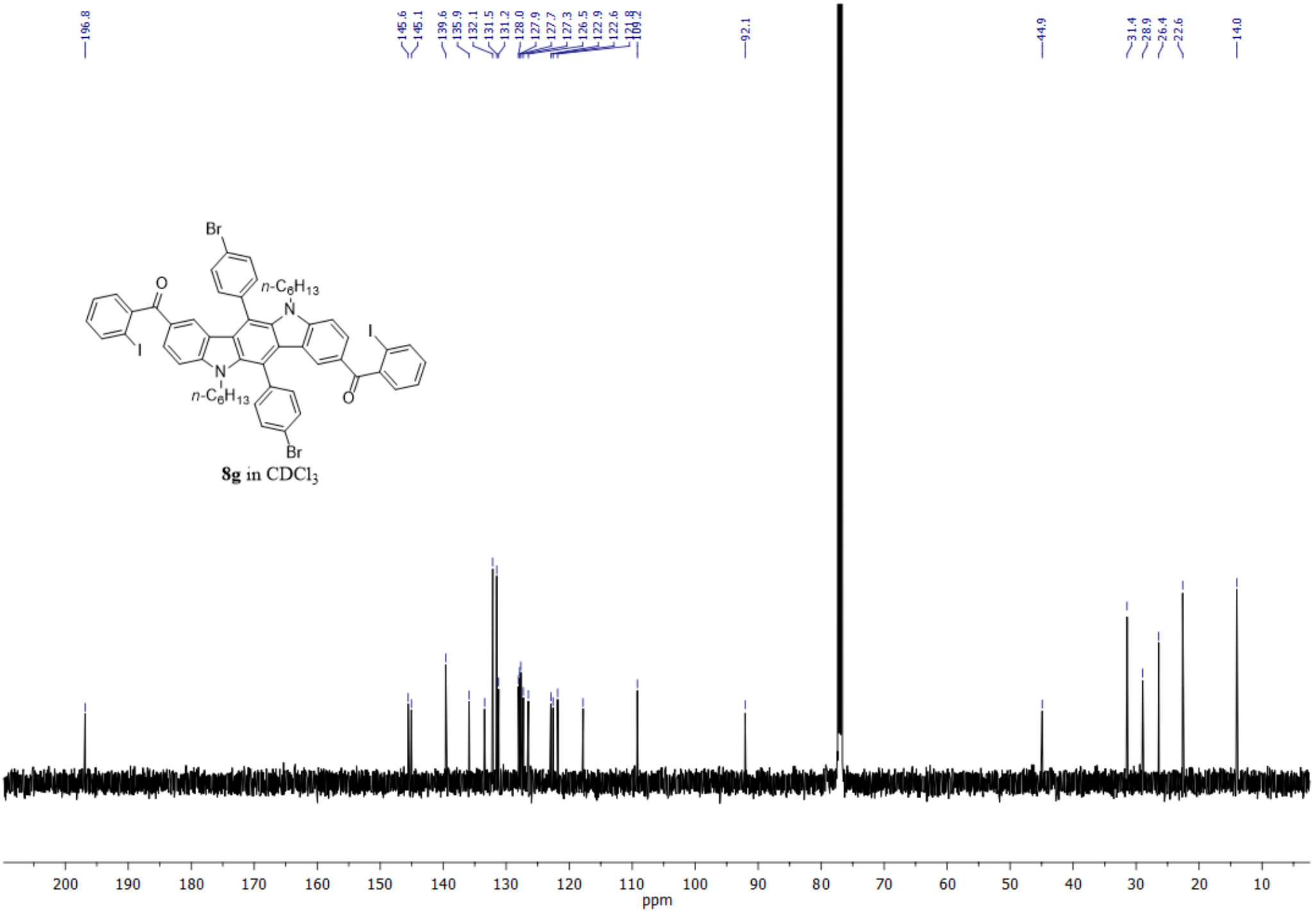
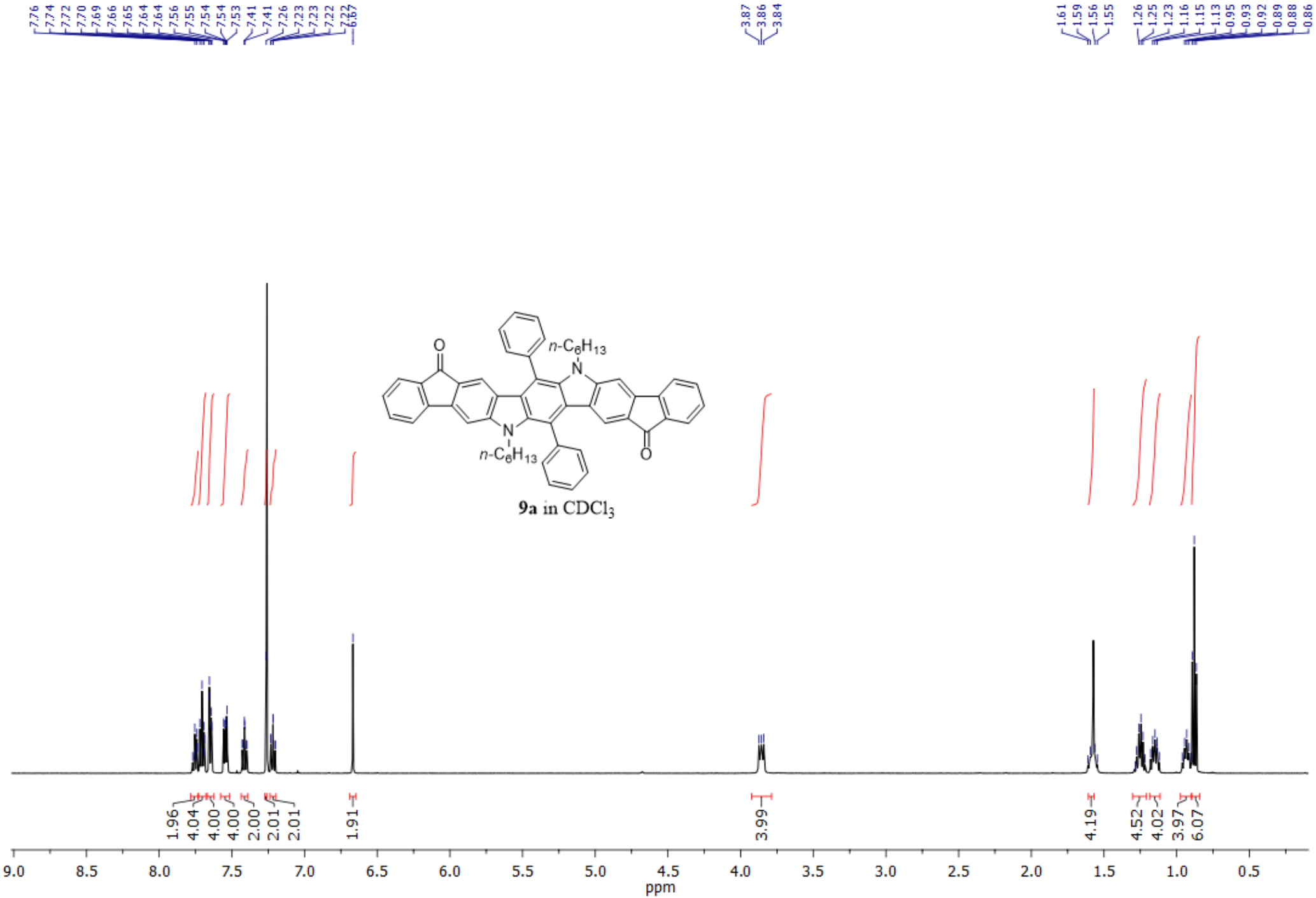
^{13}C NMR



8g in $CDCl_3$

^{1}H NMR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7.23
7.22
7.22
6.67
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3.84
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1.59
1.56
1.55
1.26
1.25
1.23
1.16
1.15
1.13
0.95
0.93
0.92
0.89
0.88
0.86
O
n-C6H13
N
N
n-C6H13
O
9a in CDCl3
1.96
4.04
4.00
4.00
2.00
2.01
2.01
1.91
3.99
4.19
4.52
4.02
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6.07
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8.0
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5.5
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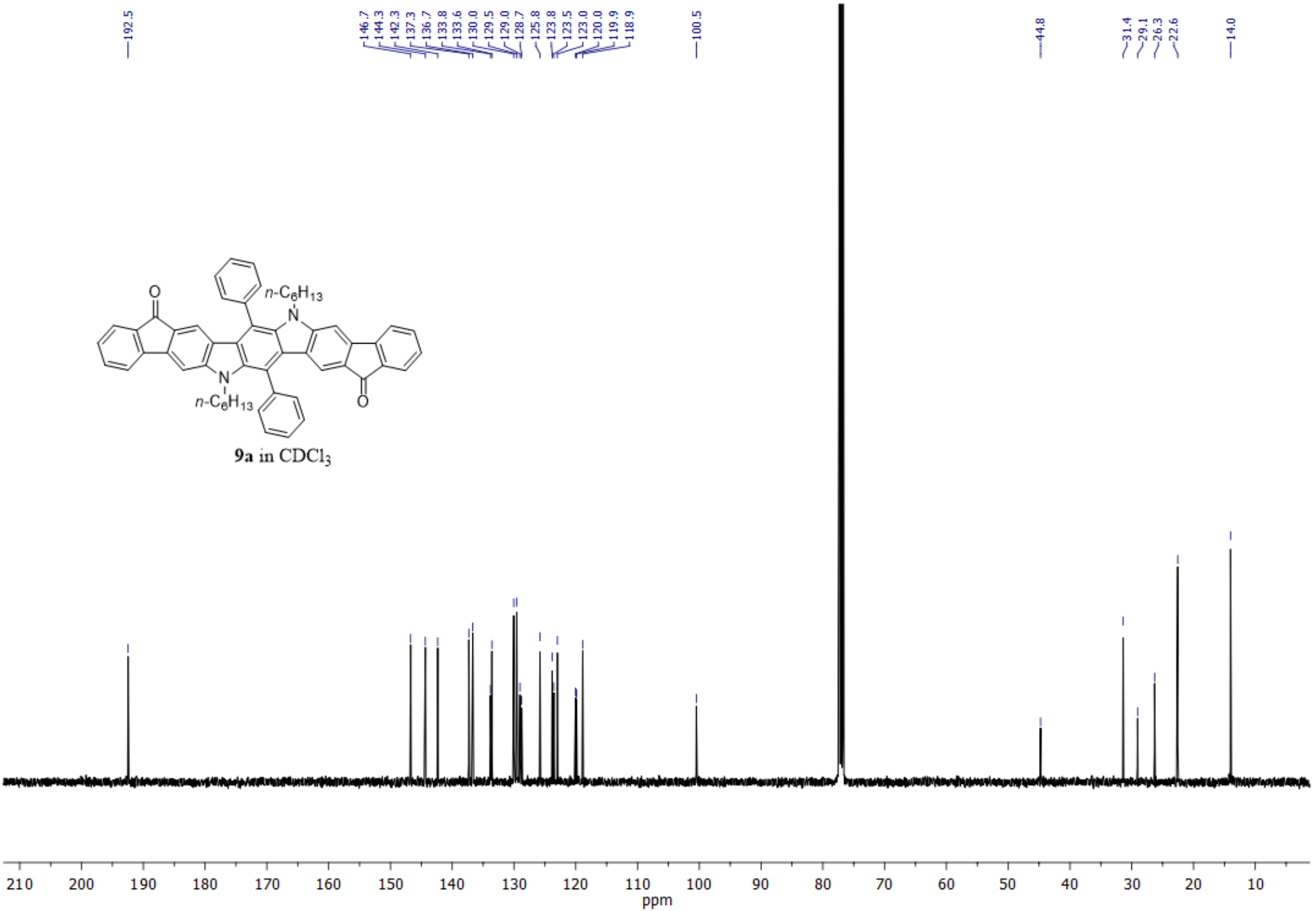
ppm

^{13}C NMR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123.8
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119.9
118.9
100.5
44.8
31.4
29.1
26.3
22.6
14.0
O
n-C6H13
N
N
n-C6H13
O
9a in CDCl3
210
200
190
180
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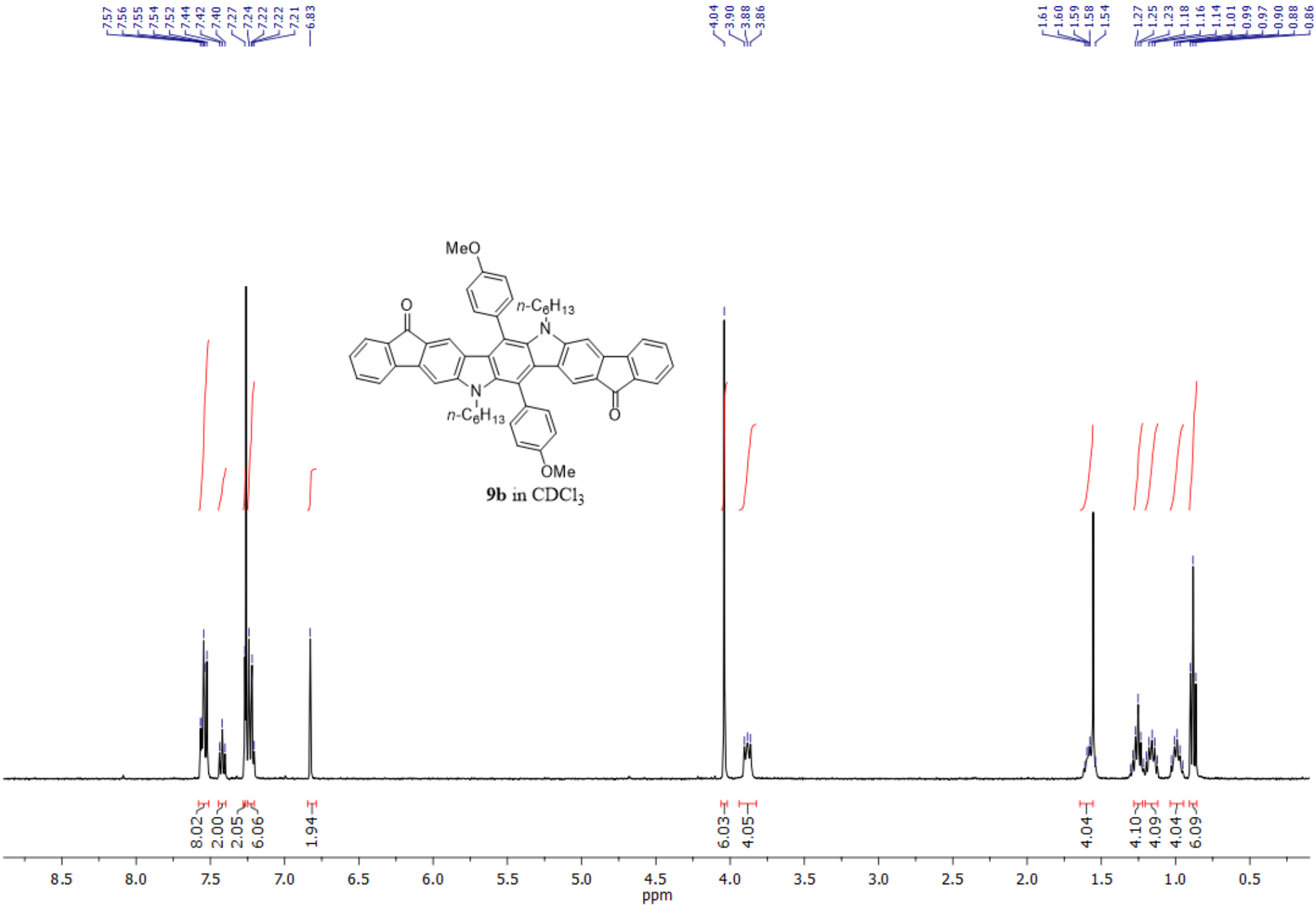
^{1}H NMR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3.86
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1.60
1.59
1.58
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1.27
1.25
1.23
1.18
1.16
1.14
1.01
0.99
0.97
0.90
0.88
0.86
MeO
n-C6H13
O
N
N
n-C6H13
O
OMe
9b in CDCl3
8.02
2.00
2.05
6.06
1.94
6.03
4.05
4.04
4.10
4.09
4.04
6.09
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7.5
7.0
6.5
6.0
5.5
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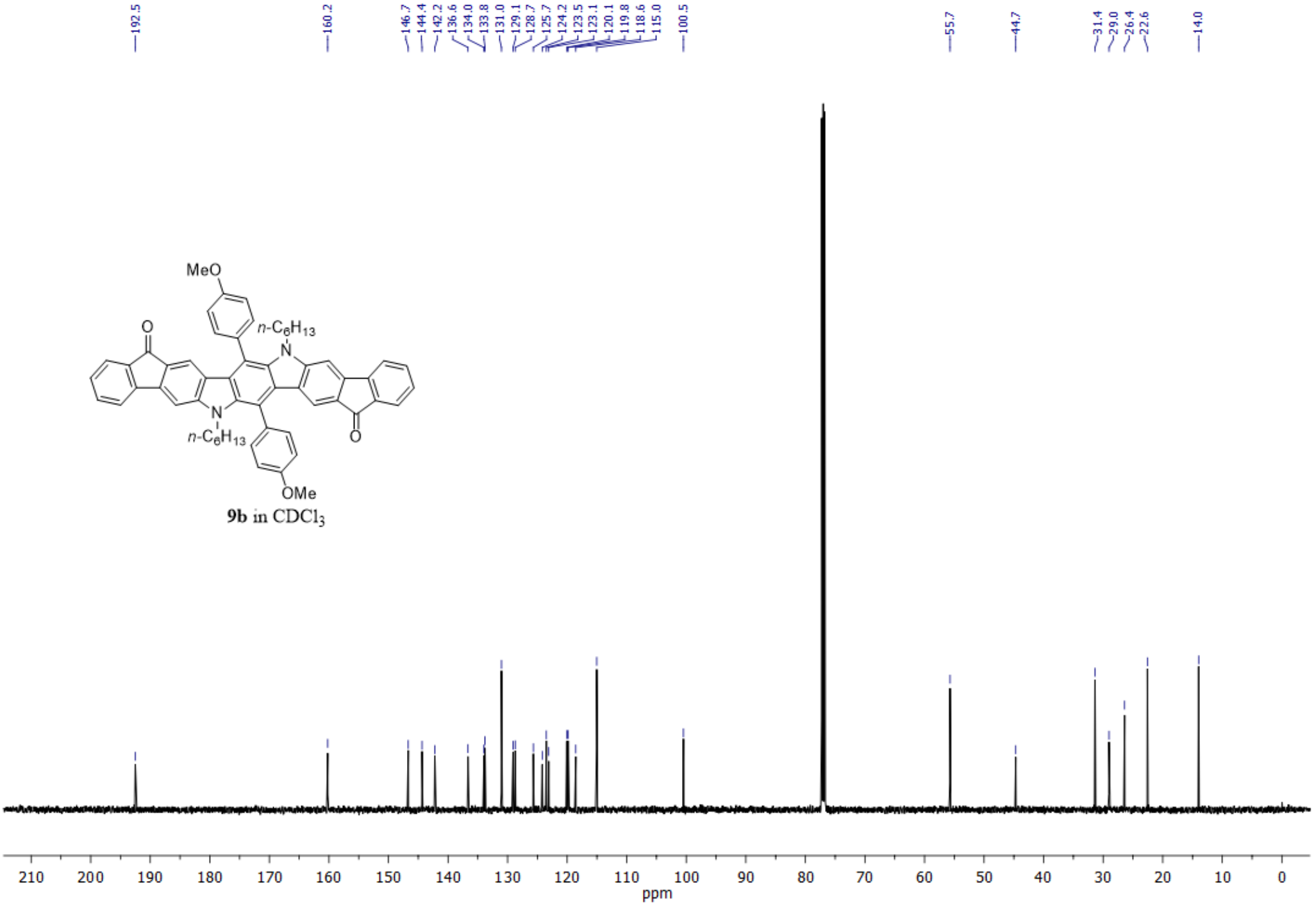
ppm

^{13}C NMR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133.8
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124.2
123.5
123.1
120.1
119.8
118.6
115.0
100.5
55.7
44.7
31.4
29.0
26.4
22.6
14.0
MeO
n-C6H13
N
O
N
n-C6H13
O
OMe
9b in CDCl3
210
200
190
180
170
160
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120
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100
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40
30
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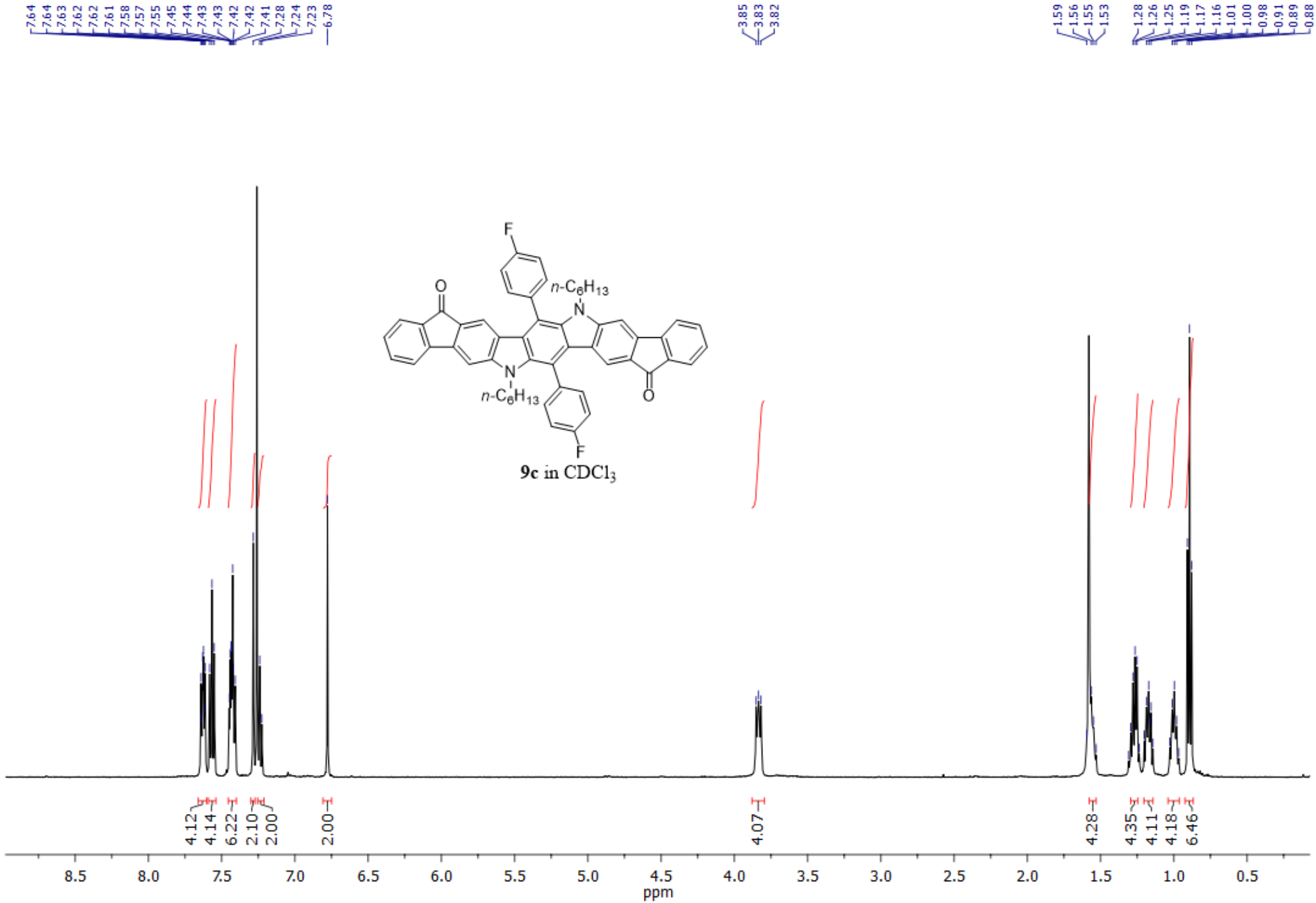
0
ppm

^{1}H NMR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7.43
7.42
7.42
7.41
7.28
7.24
7.23
6.78
3.85
3.83
3.82
1.59
1.56
1.55
1.53
1.28
1.26
1.25
1.19
1.17
1.16
1.01
1.00
0.98
0.91
0.89
0.88
F
O
n-C6H13
N
N
n-C6H13
O
F
9c in CDCl3
4.12
4.14
6.22
2.10
2.00
2.00
4.07
4.28
4.35
4.11
4.18
6.46
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7.0
6.5
6.0
5.5
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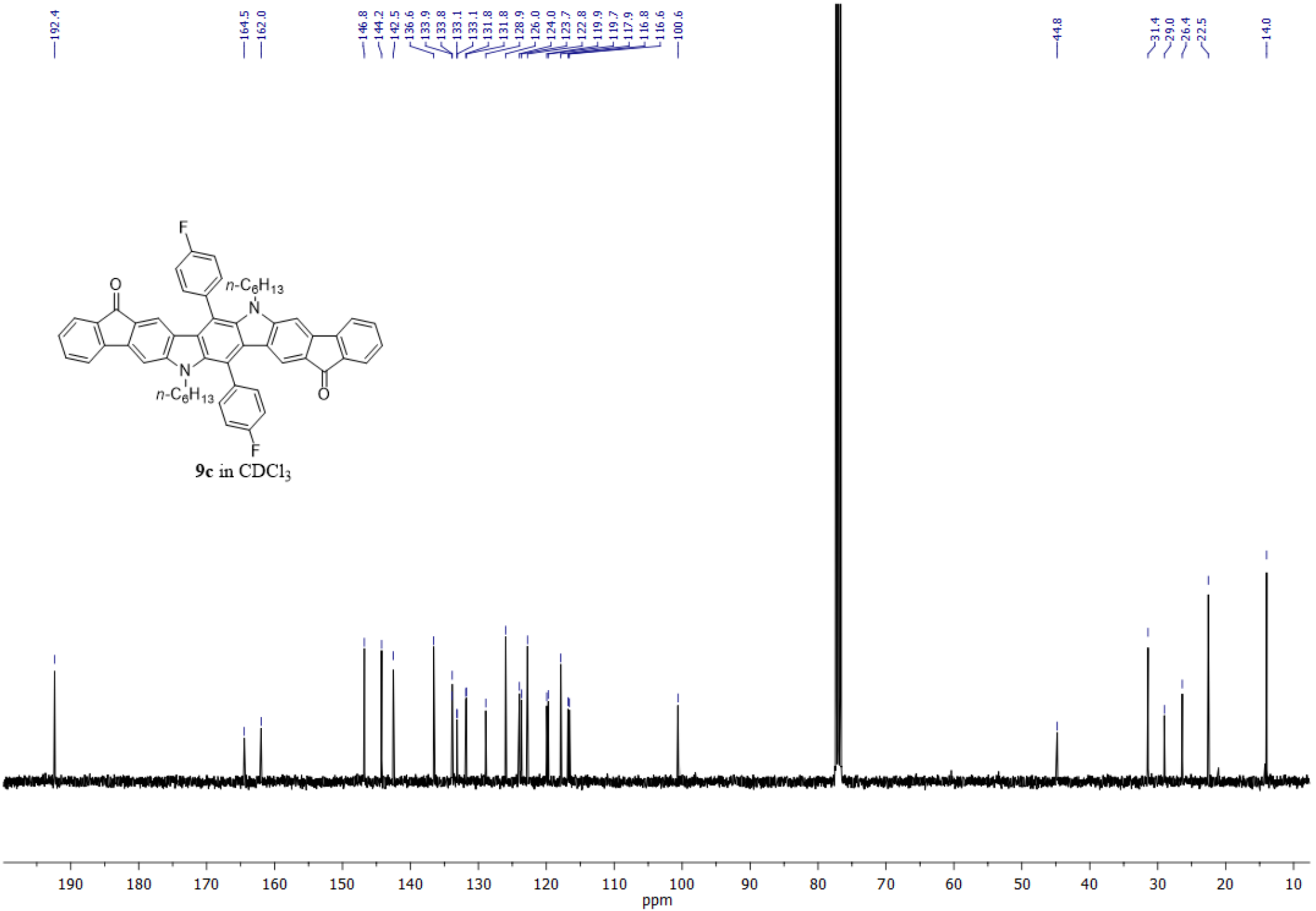
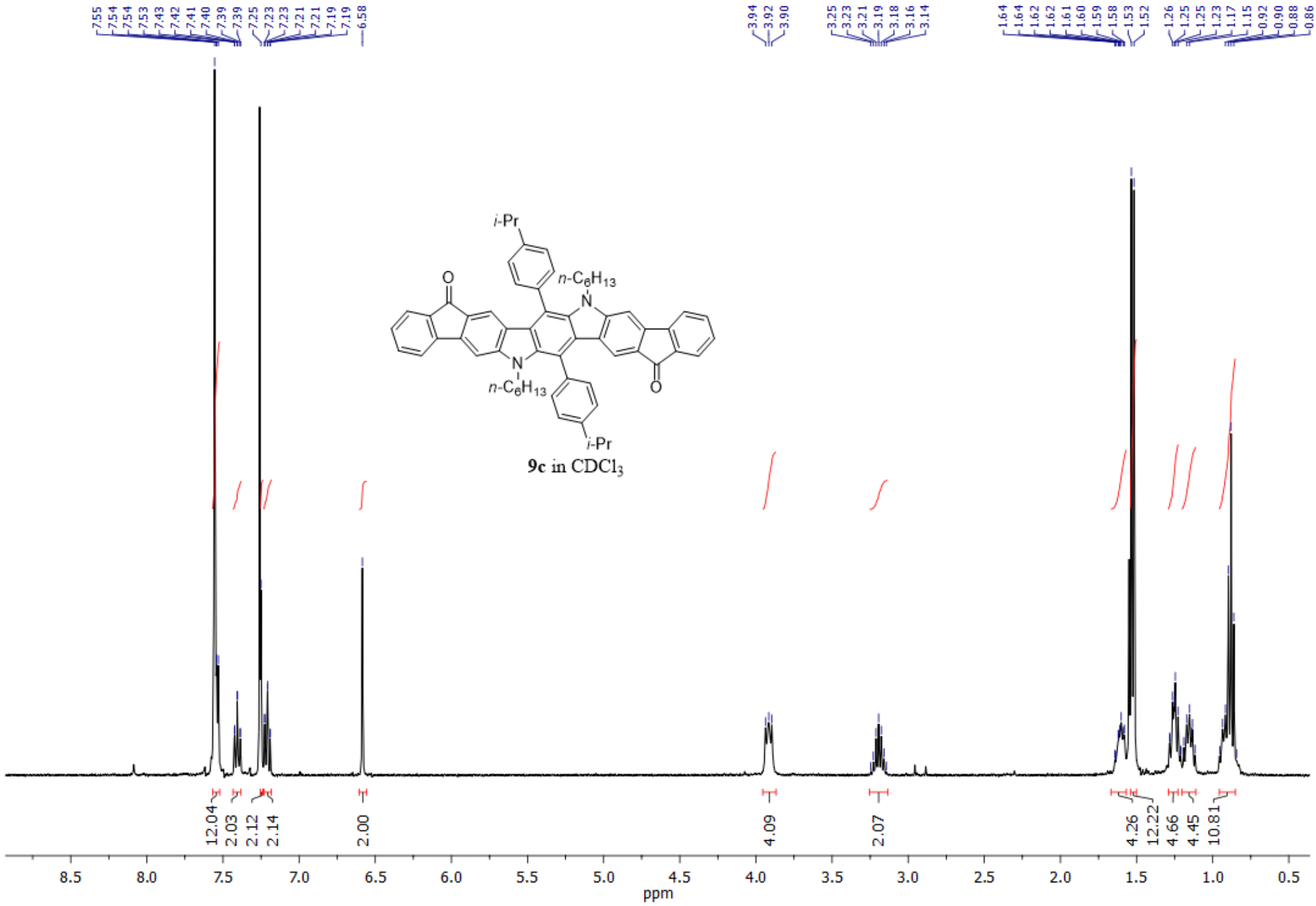
ppm

^{13}C NMR



9c in $CDCl_3$

^{1}H NMR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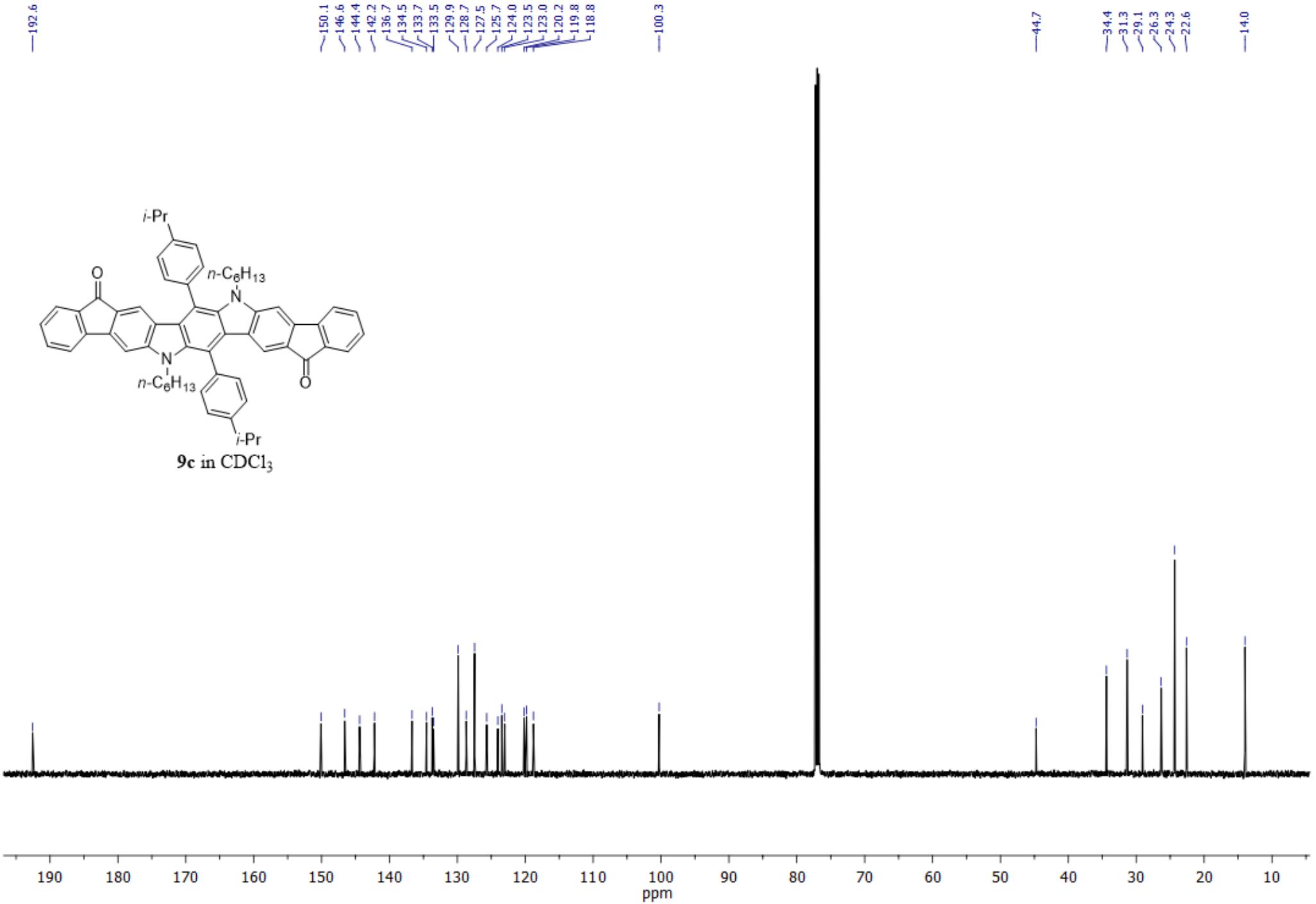
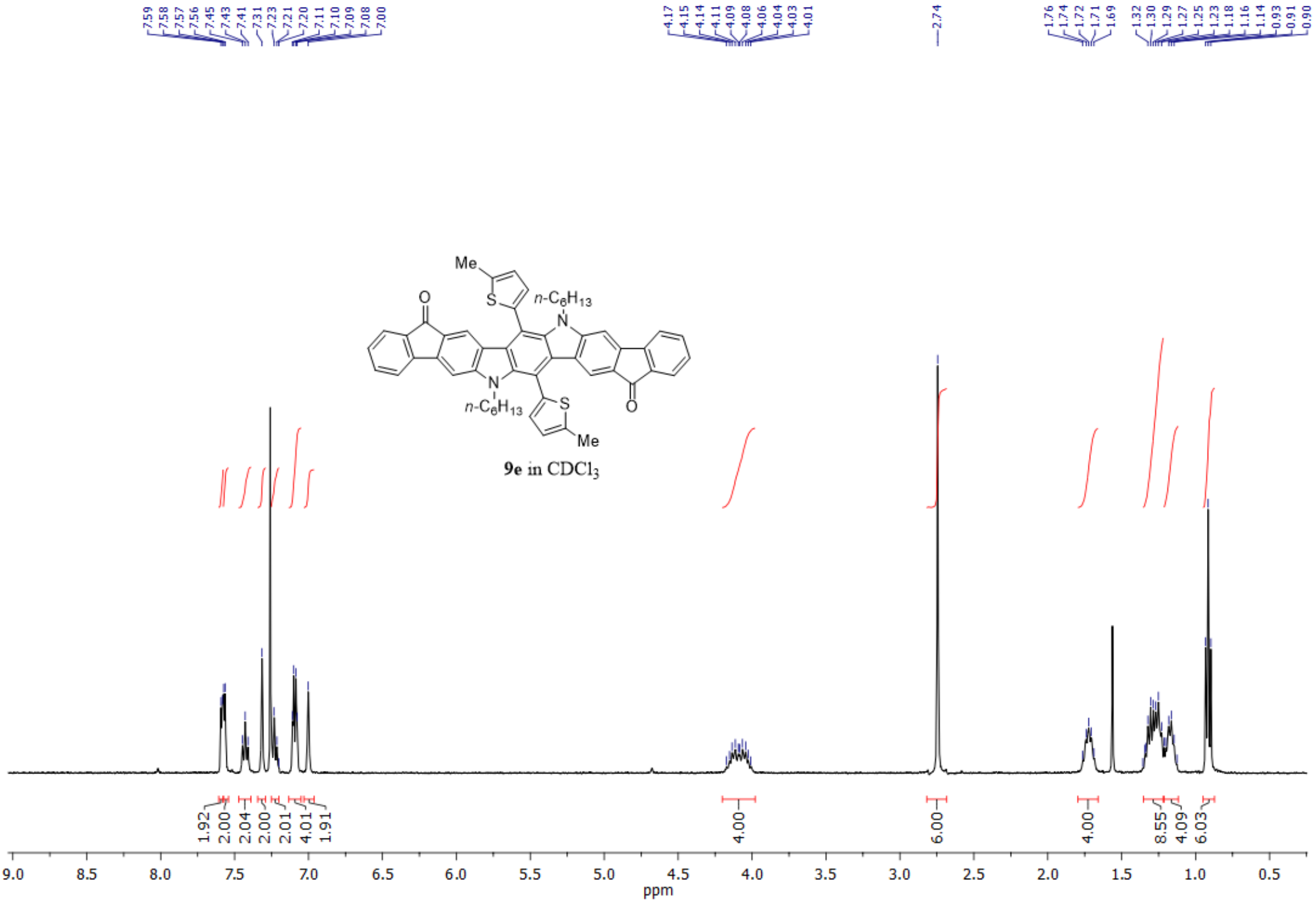
1.64 1.64 1.62 1.62 1.61 1.60 1.59 1.58 1.53 1.52 1.26 1.25 1.25 1.23 1.17 1.15 0.92 0.90 0.88 0.86
i-Pr
n-C6H13
N
O
n-C6H13
i-Pr
9c in CDCl3
12.04 2.03 2.12 2.14 2.00 4.09 2.07 4.26 12.22 4.66 4.45 10.81
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

^{13}C NMR

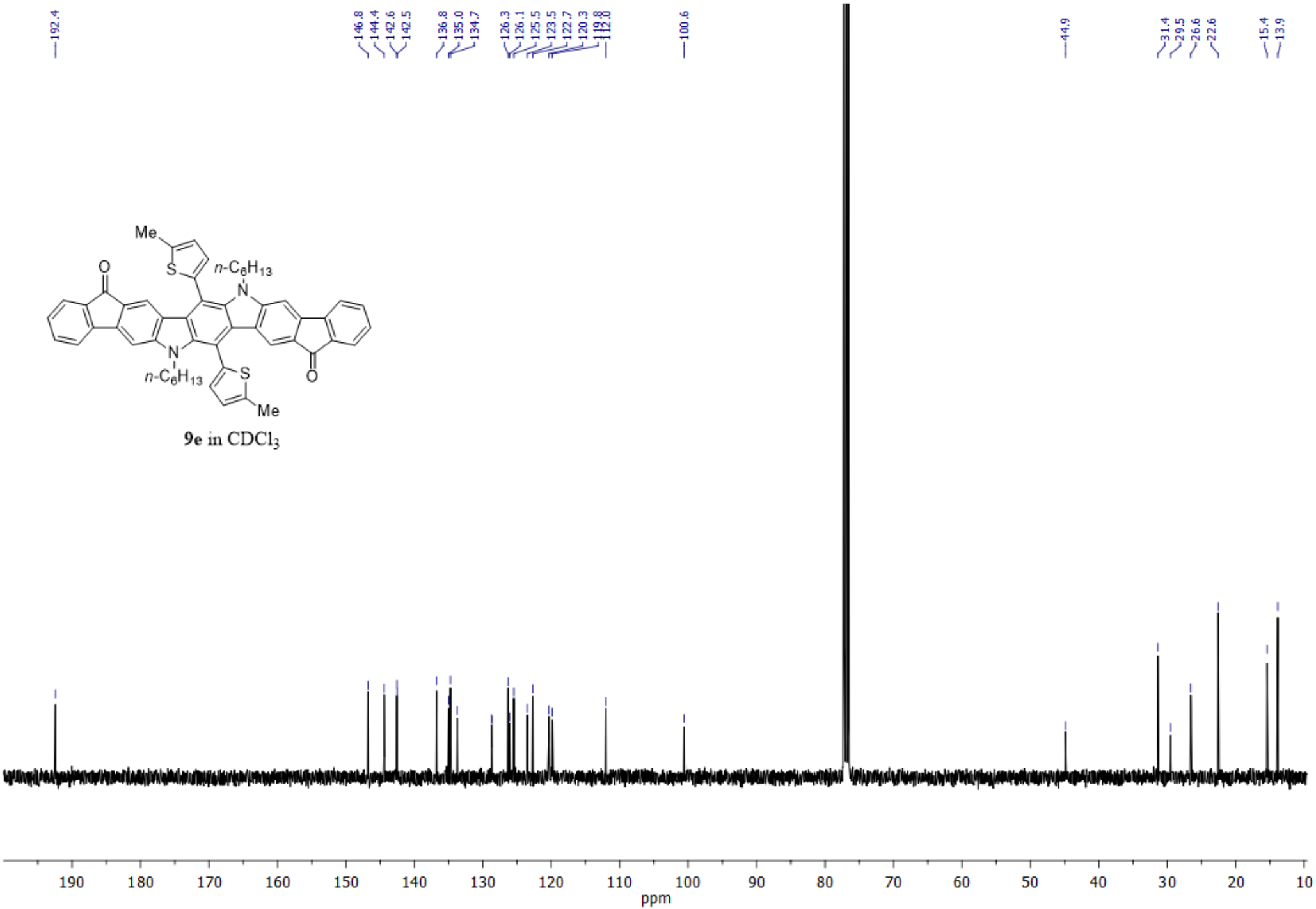


9c in $CDCl_3$

^{1}H NMR

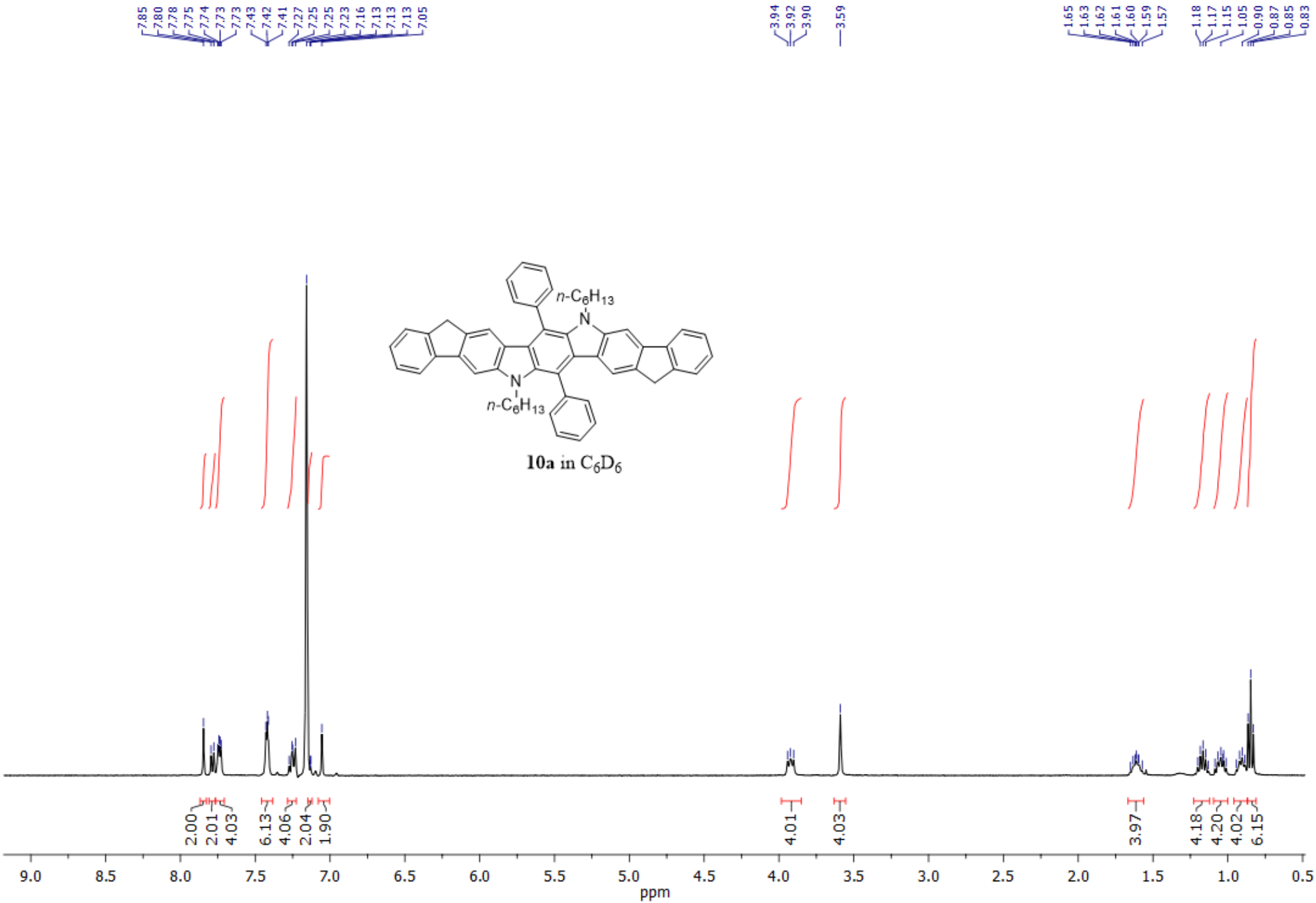

7.59
7.58
7.57
7.56
7.45
7.43
7.41
7.31
7.23
7.21
7.20
7.11
7.10
7.09
7.08
7.00
4.17
4.15
4.14
4.11
4.09
4.08
4.06
4.04
4.03
4.01
2.74
1.76
1.74
1.72
1.71
1.69
1.32
1.30
1.29
1.27
1.25
1.23
1.18
1.16
1.14
0.93
0.91
0.90
Me
S
n-C6H13
N
O
O
N
n-C6H13
S
Me
9e in CDCl3
1.92
2.00
2.04
2.00
2.01
4.01
1.91
4.00
6.00
4.00
8.55
4.09
6.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{13}C NMR

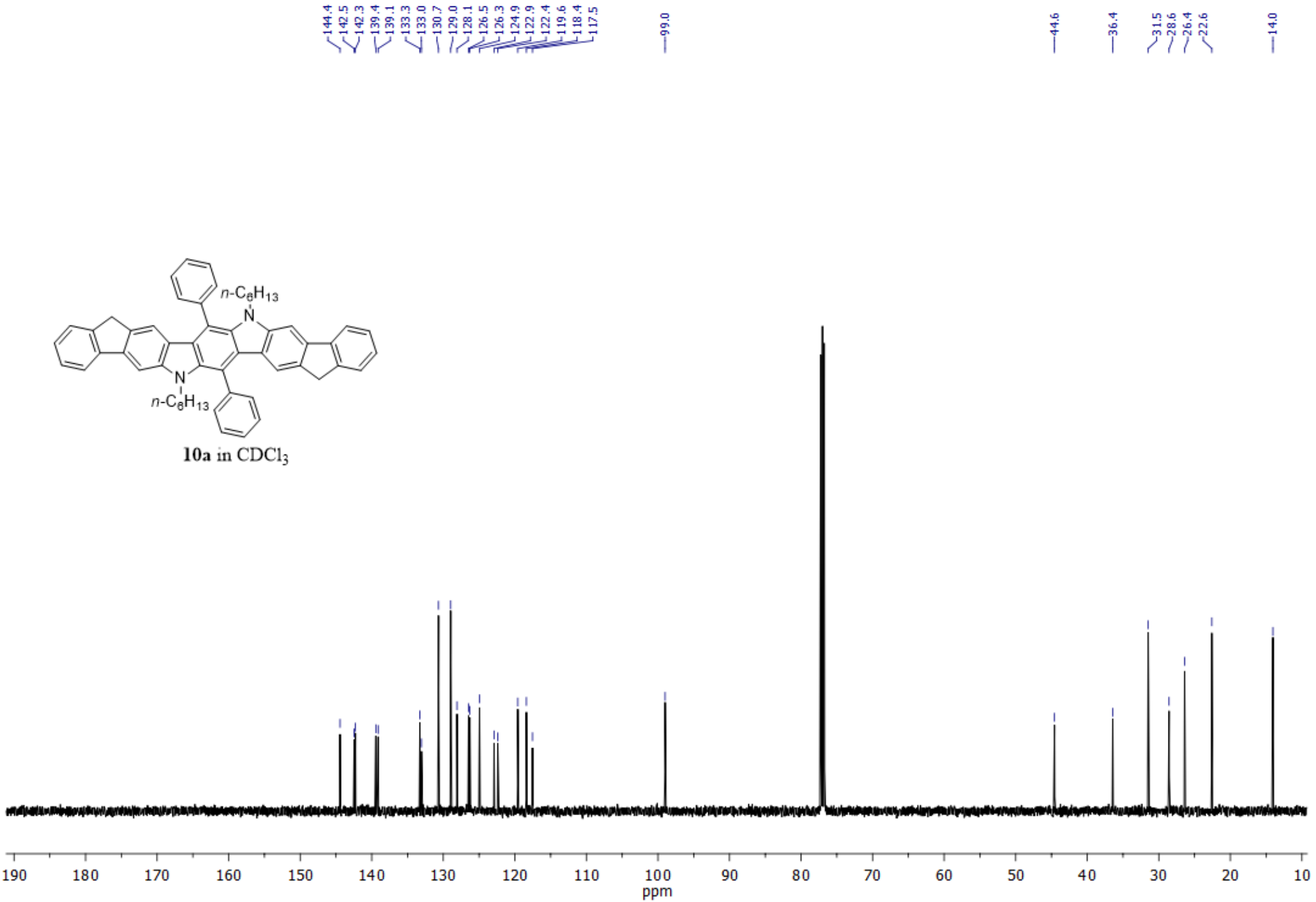


9e in $CDCl_3$

^{1}H NMR

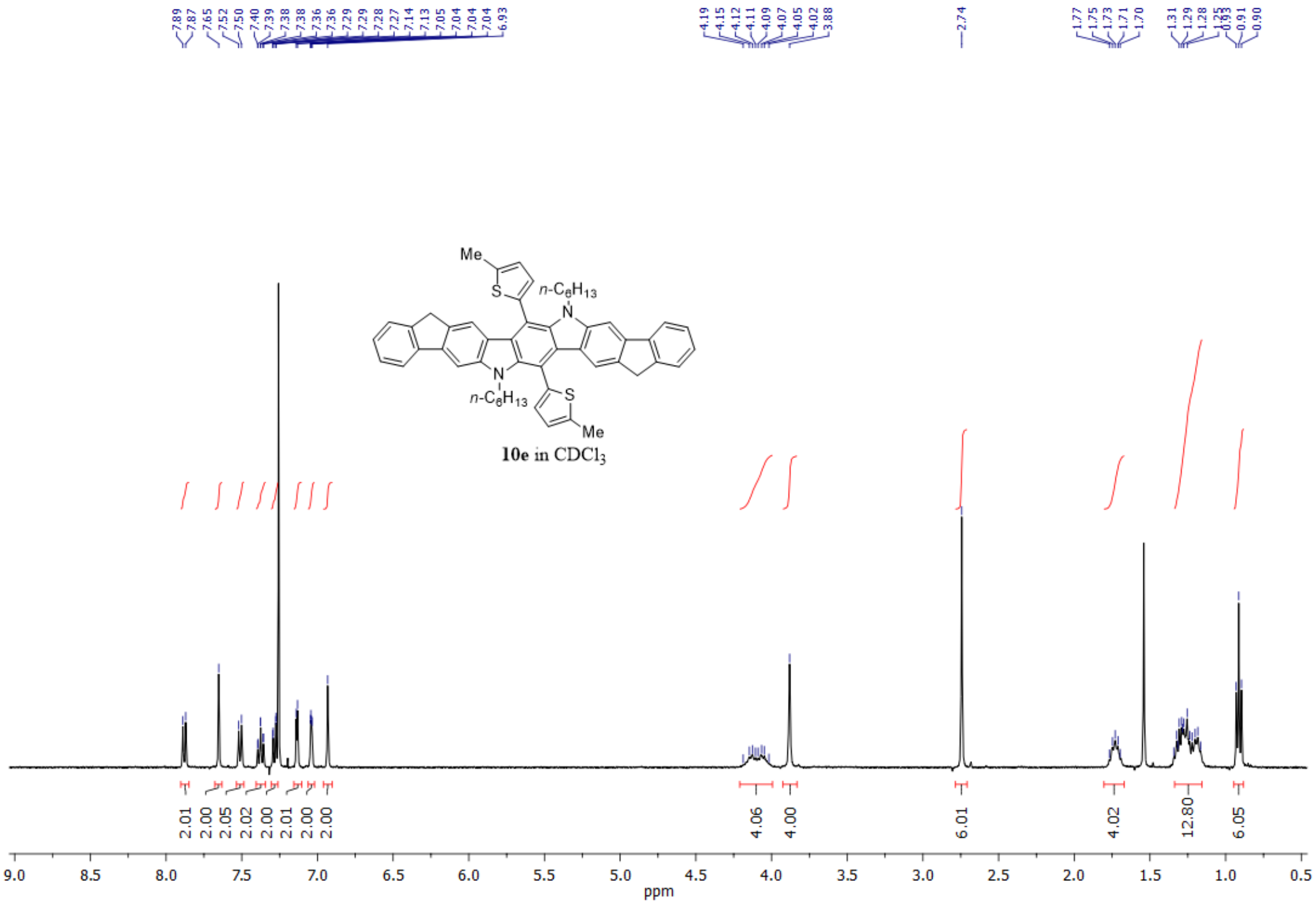

7.85
7.80
7.78
7.75
7.74
7.73
7.73
7.43
7.42
7.41
7.27
7.25
7.25
7.23
7.16
7.13
7.13
7.13
7.05
3.94
3.92
3.90
3.59
1.65
1.63
1.62
1.61
1.60
1.59
1.57
1.18
1.17
1.15
1.05
0.90
0.87
0.85
0.83
n-C6H13
N
N
n-C6H13
10a in C6D6
2.00
2.01
4.03
6.13
4.06
2.04
1.90
4.01
4.03
3.97
4.18
4.20
4.02
6.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{13}C NMR

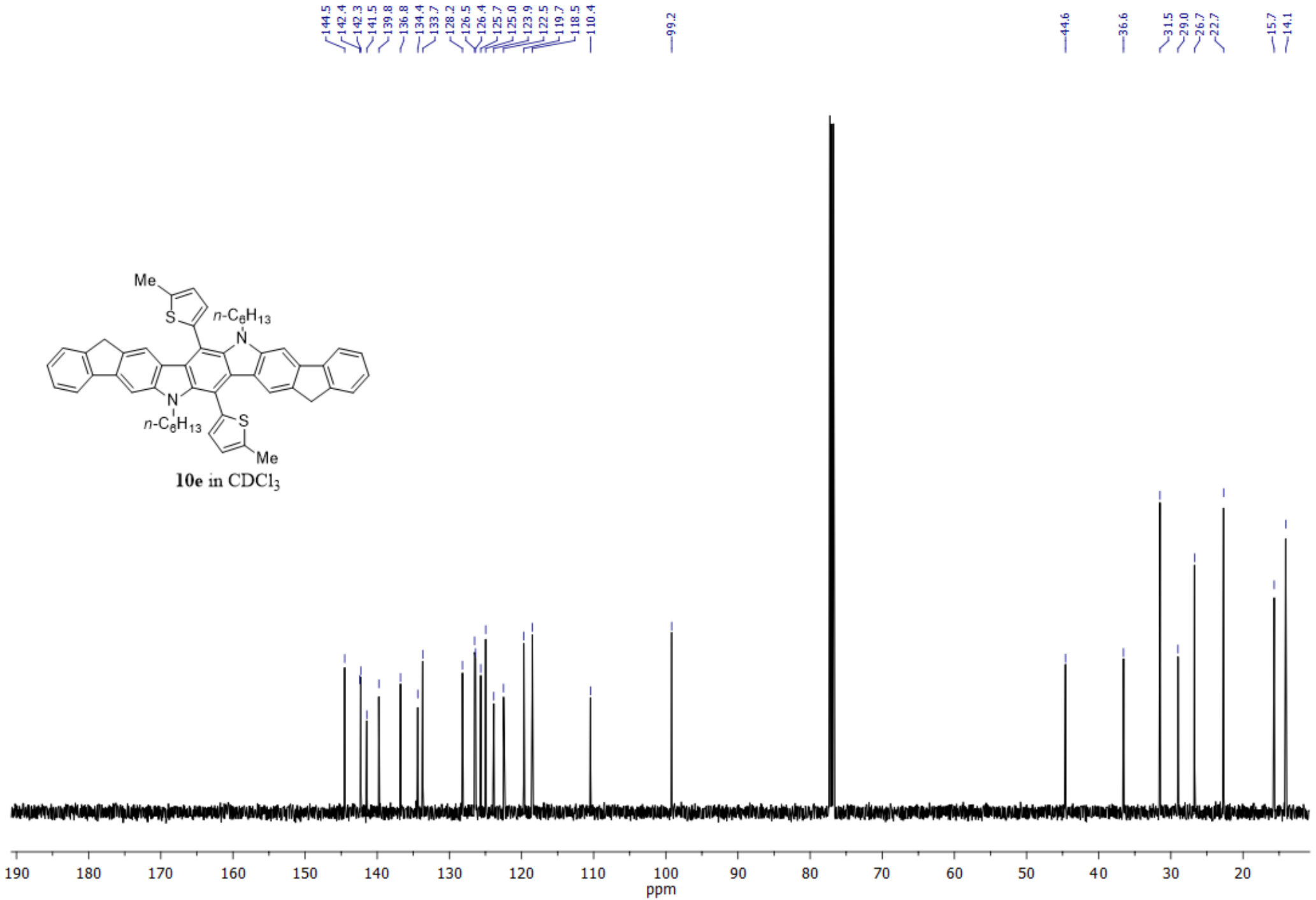


10a in $CDCl_3$

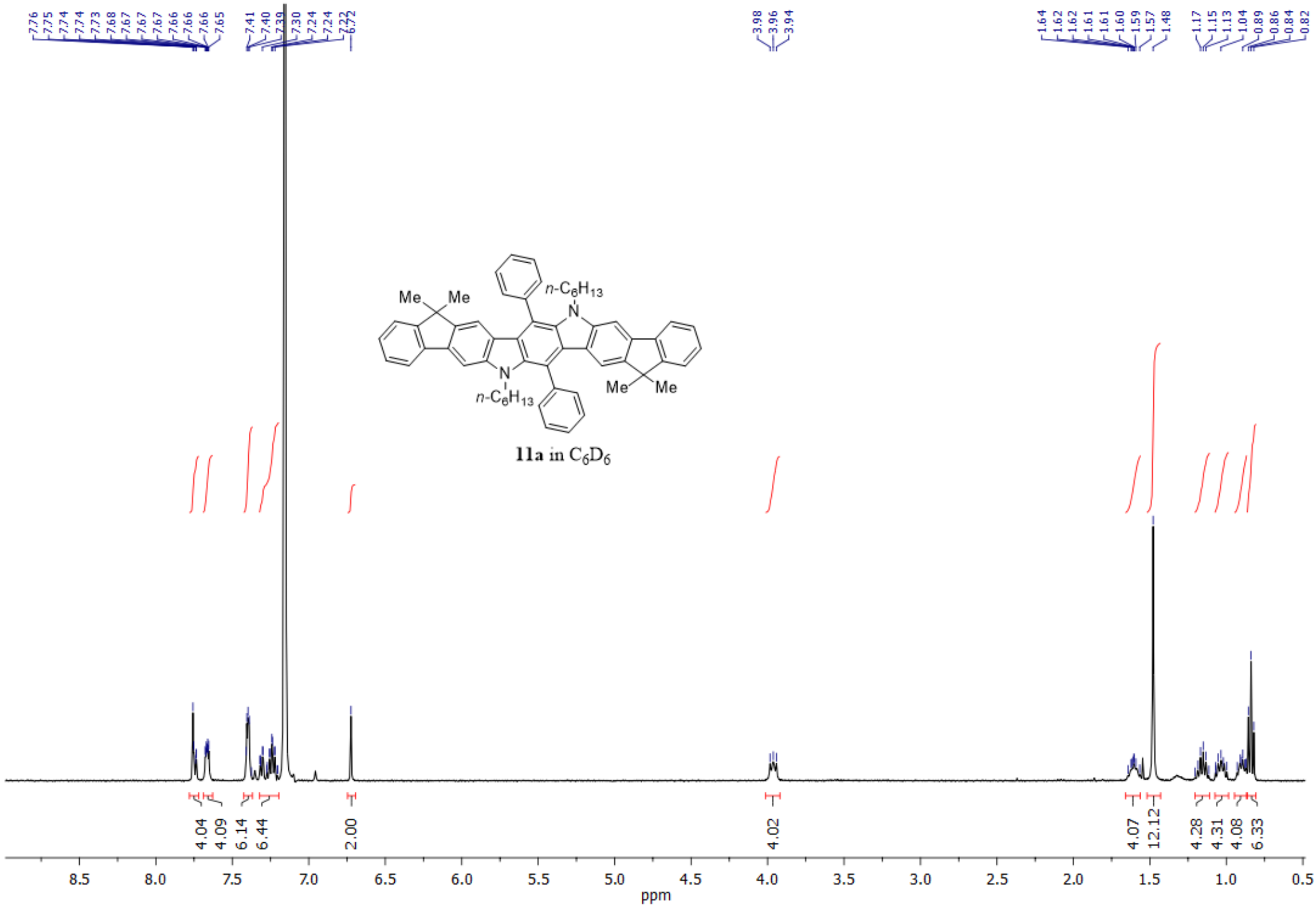
^{1}H NMR


7.89
7.87
7.65
7.52
7.50
7.40
7.39
7.38
7.38
7.36
7.36
7.29
7.29
7.28
7.27
7.14
7.13
7.05
7.04
7.04
7.04
6.93
4.19
4.15
4.12
4.11
4.09
4.07
4.05
4.02
3.88
2.74
1.77
1.75
1.73
1.71
1.70
1.31
1.29
1.28
0.91
0.90
Me
S
n-C6H13
N
N
n-C6H13
S
Me
10e in CDCl3
2.01
2.00
2.05
2.02
2.00
2.01
2.00
2.00
4.06
4.00
6.01
4.02
12.80
6.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

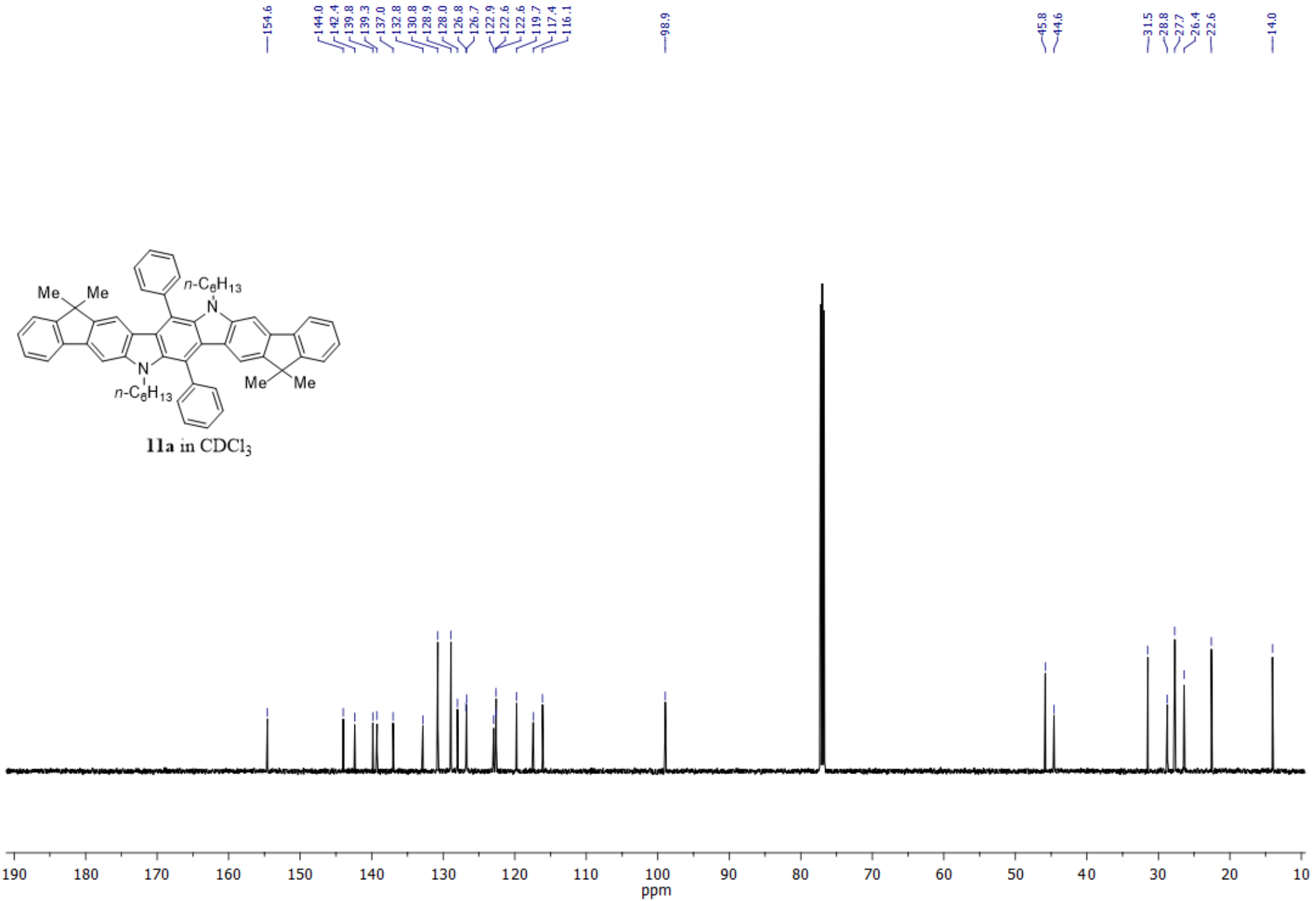
^{13}C NMR


144.5
142.4
142.3
141.5
139.8
136.8
134.4
133.7
128.2
126.5
126.4
125.7
125.0
123.9
122.5
119.7
118.5
110.4
99.2
44.6
36.6
31.5
29.0
26.7
22.7
15.7
14.1
Me
S
n-C6H13
N
N
n-C6H13
S
Me
10e in CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

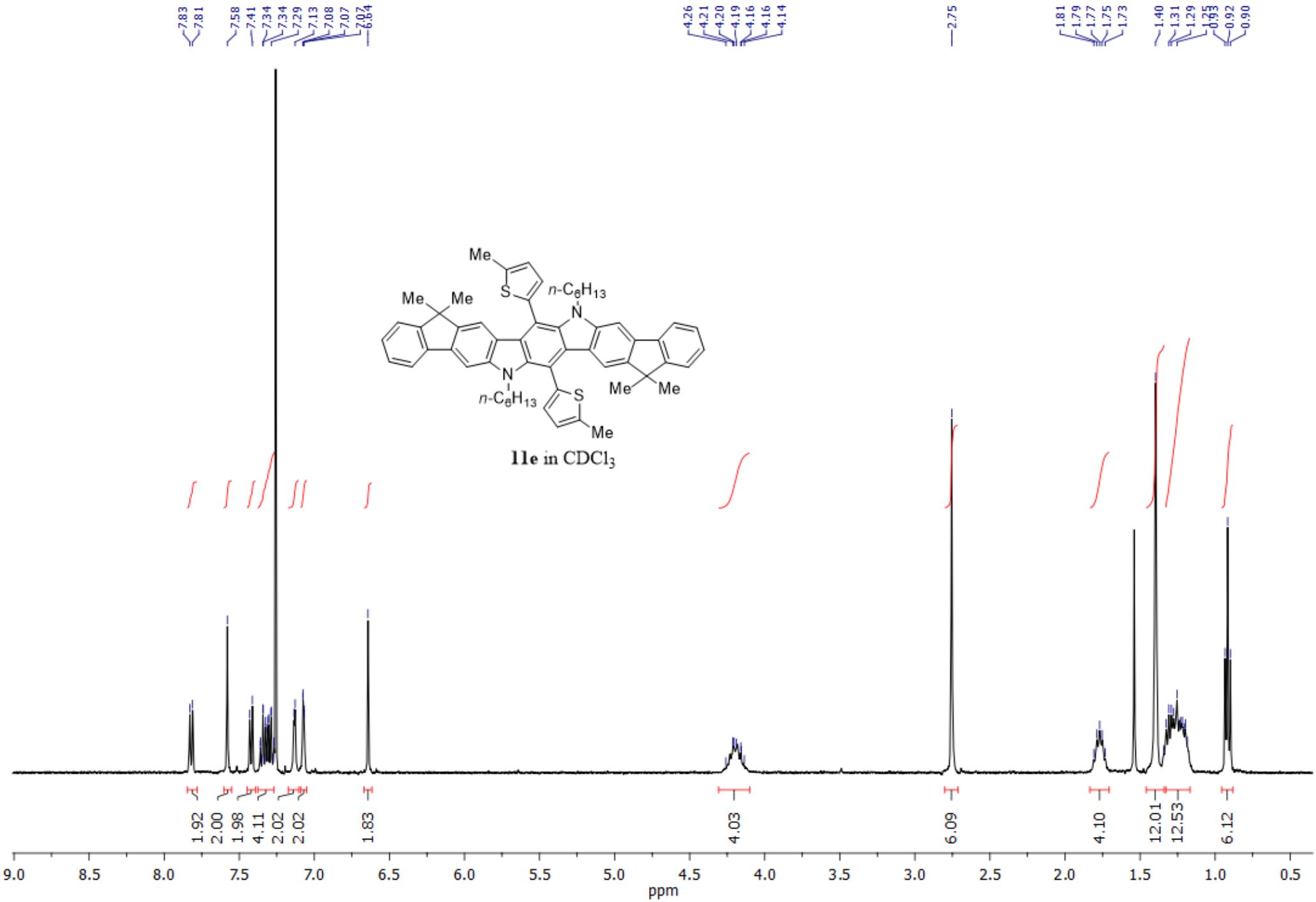
^{1}H NMR



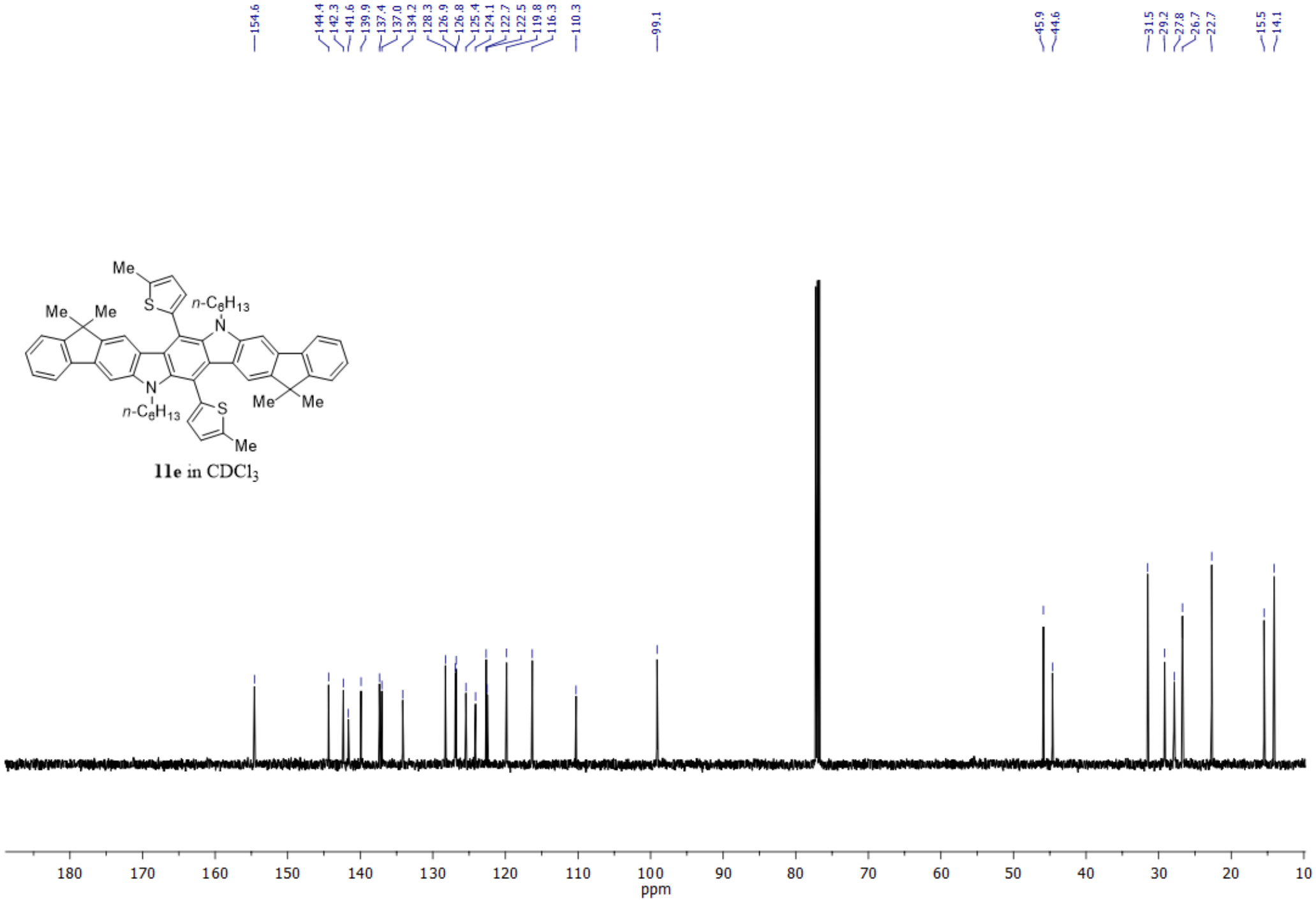
^{13}C NMR


154.6
144.0
142.4
139.8
139.3
137.0
132.8
130.8
128.9
128.0
126.8
126.7
122.9
122.6
122.6
119.7
117.4
116.1
98.9
45.8
44.6
31.5
28.8
27.7
26.4
22.6
14.0
Me
Me
n-C6H13
N
N
n-C6H13
Me
Me
11a in CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{1}H NMR

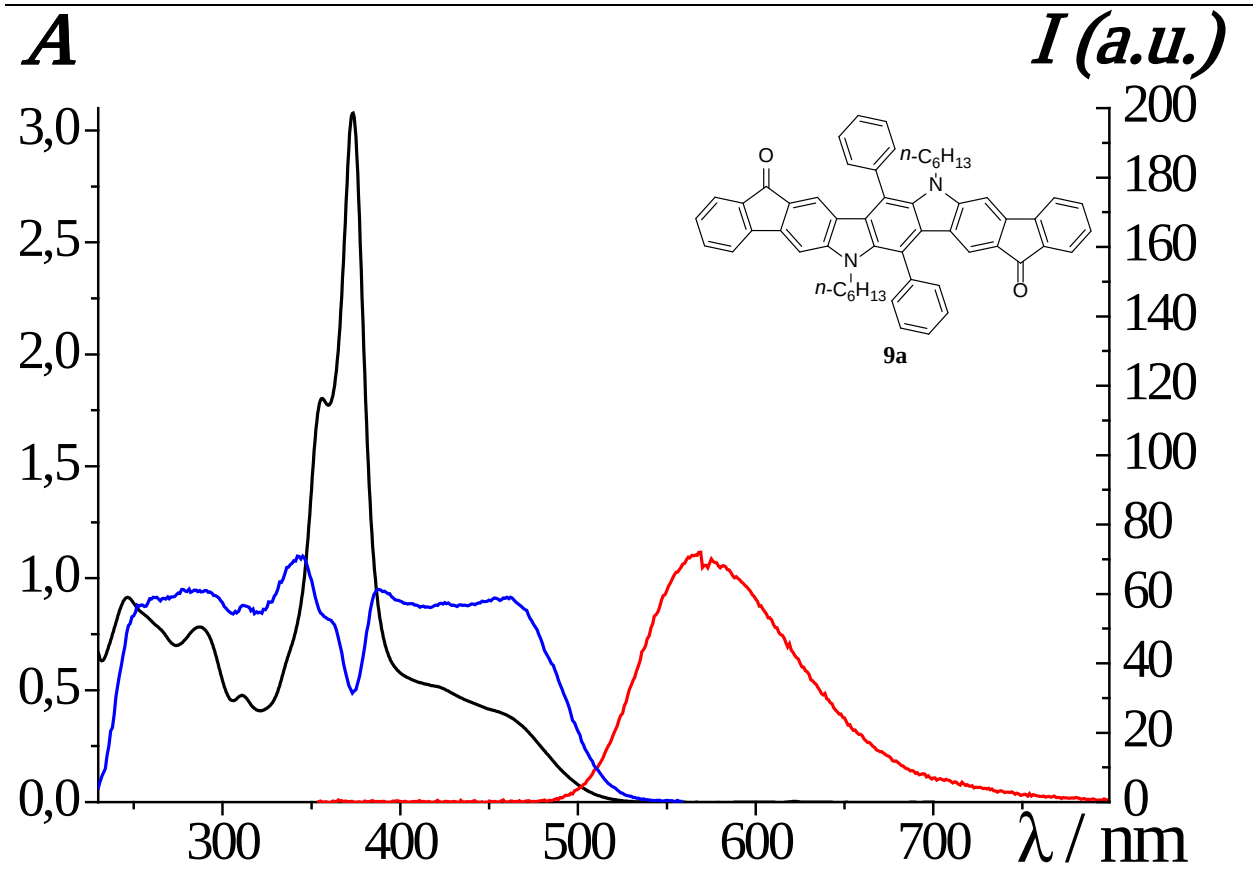

7.83
7.81
7.58
7.41
7.34
7.34
7.29
7.13
7.08
7.07
7.02
6.84
4.26
4.21
4.20
4.19
4.16
4.16
4.14
2.75
1.81
1.79
1.77
1.75
1.73
1.40
1.31
1.29
1.25
0.93
0.92
0.90
Me
Me
Me
S
n-C8H13
N
n-C8H13
N
S
Me
Me
Me
11e in CDCl3
1.92
2.00
1.98
4.11
2.02
2.02
1.83
4.03
6.09
4.10
12.01
12.53
6.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{13}C NMR



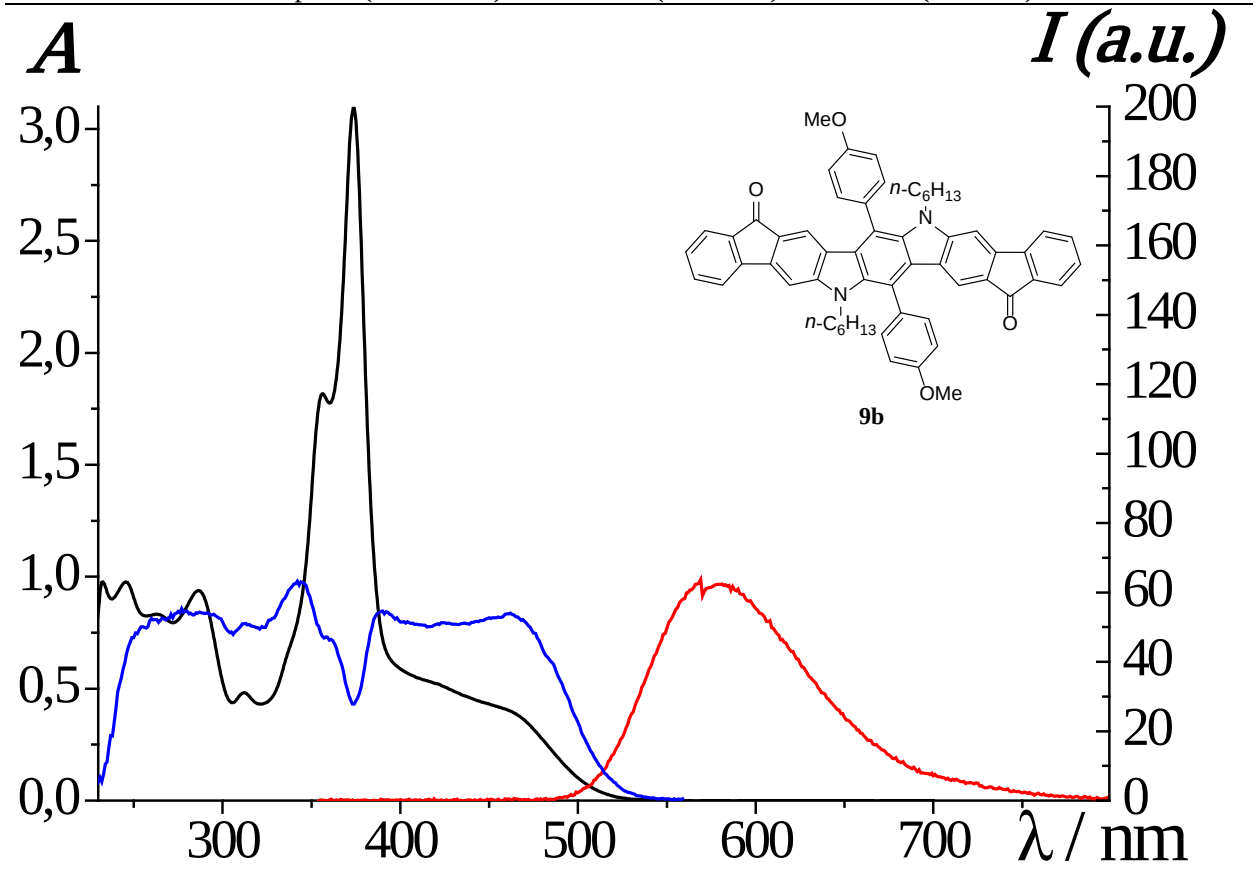
11e in $CDCl_3$

*2. Absorption, excitation and emission spectra of compounds **9a-e** and **11a,e***



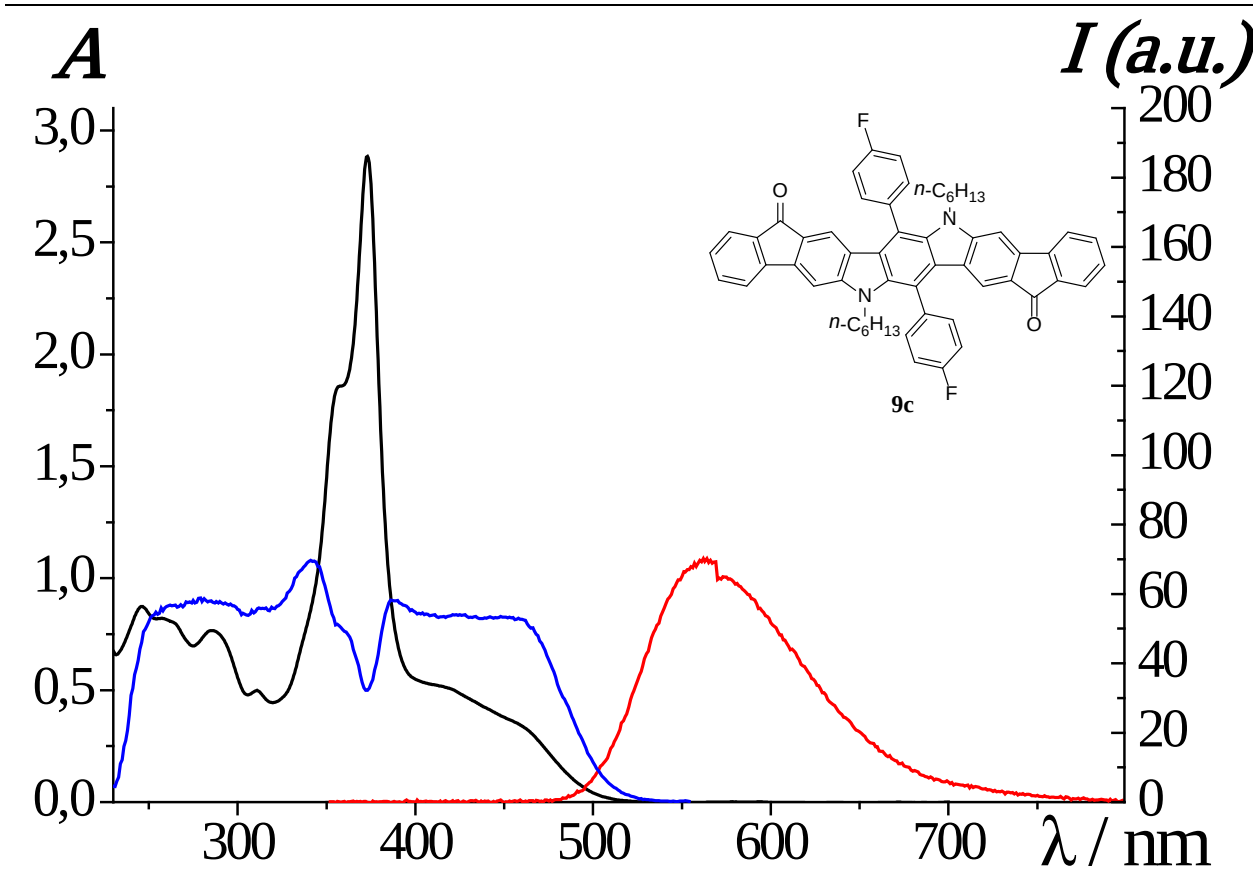
9a

Absorption (**black line**) / Excitation (**blue line**) / Emission (**red line**)

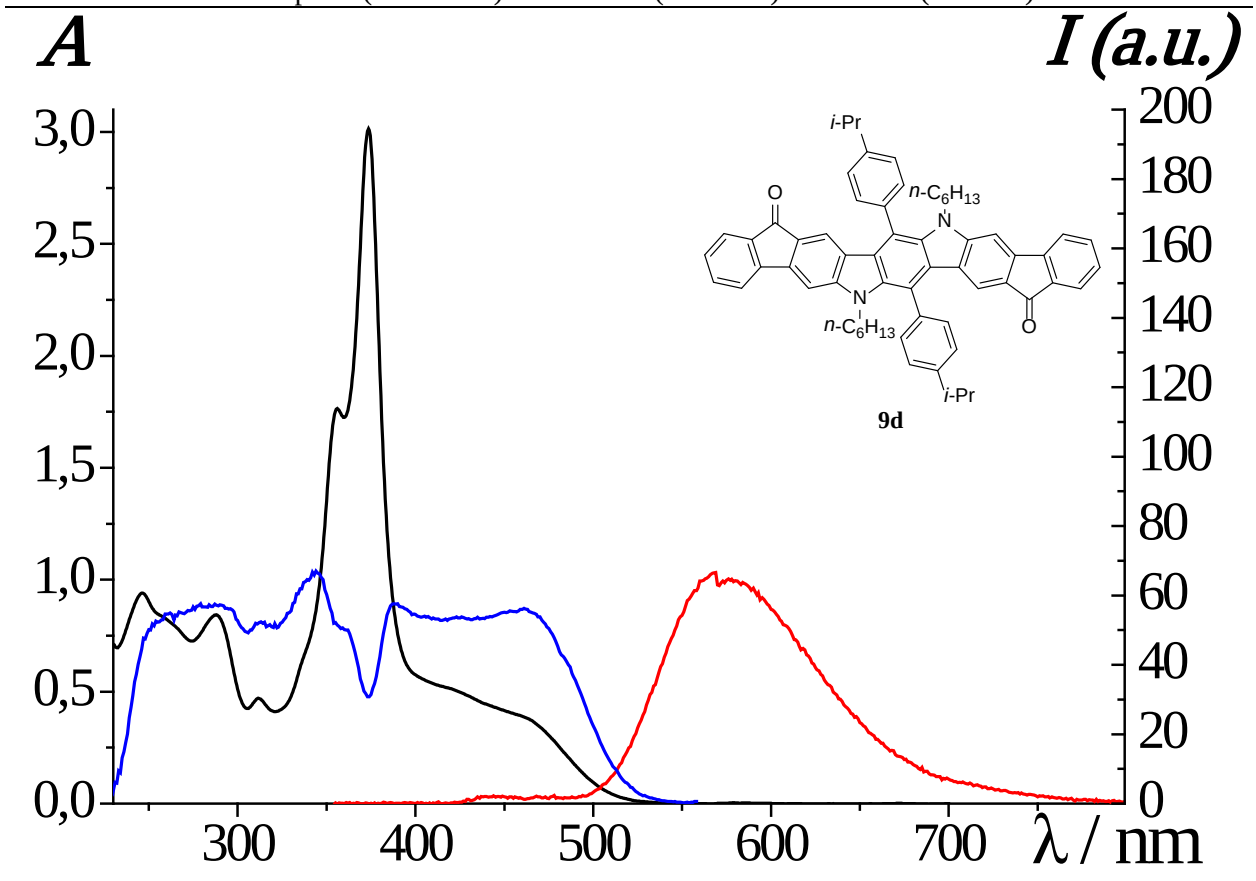


9b

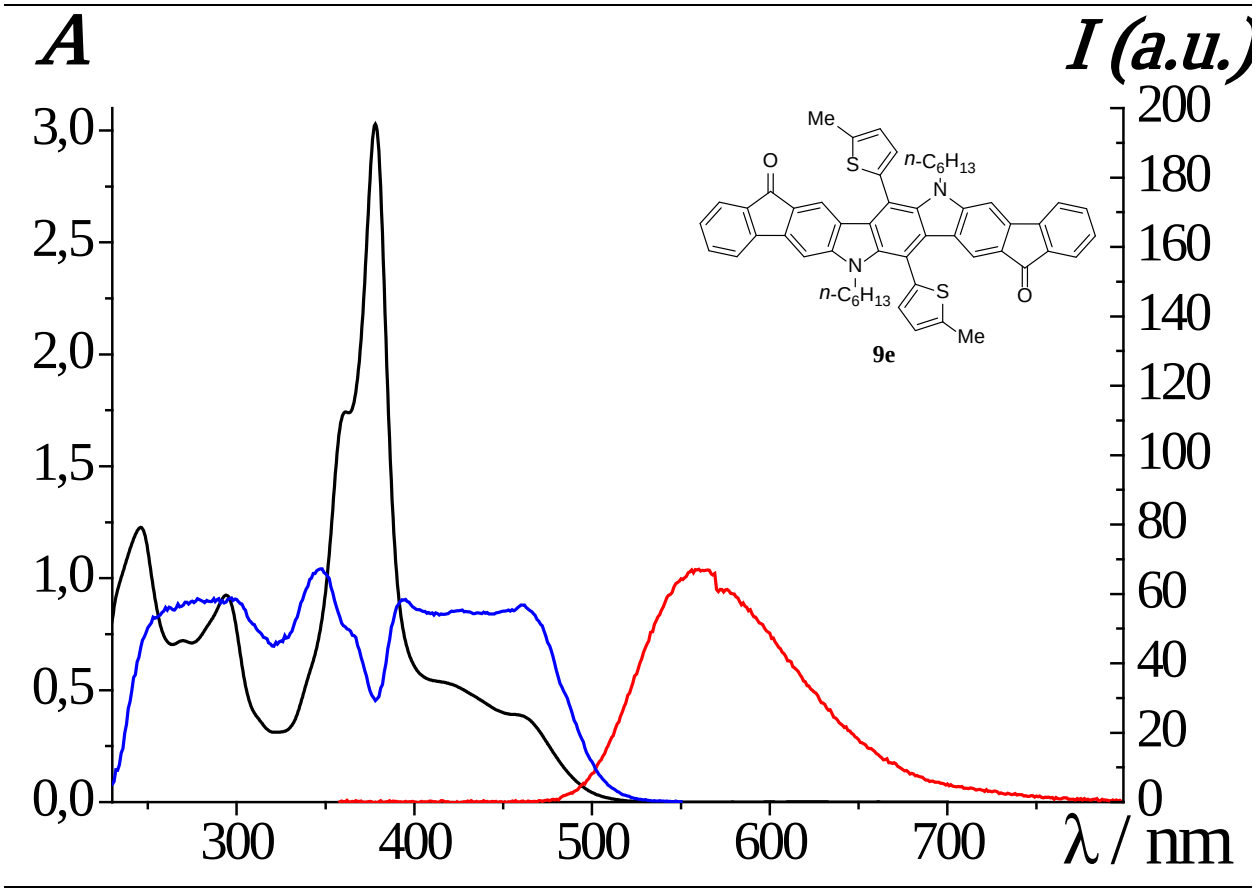
Absorption (**black line**) / Excitation (**blue line**) / Emission (**red line**)



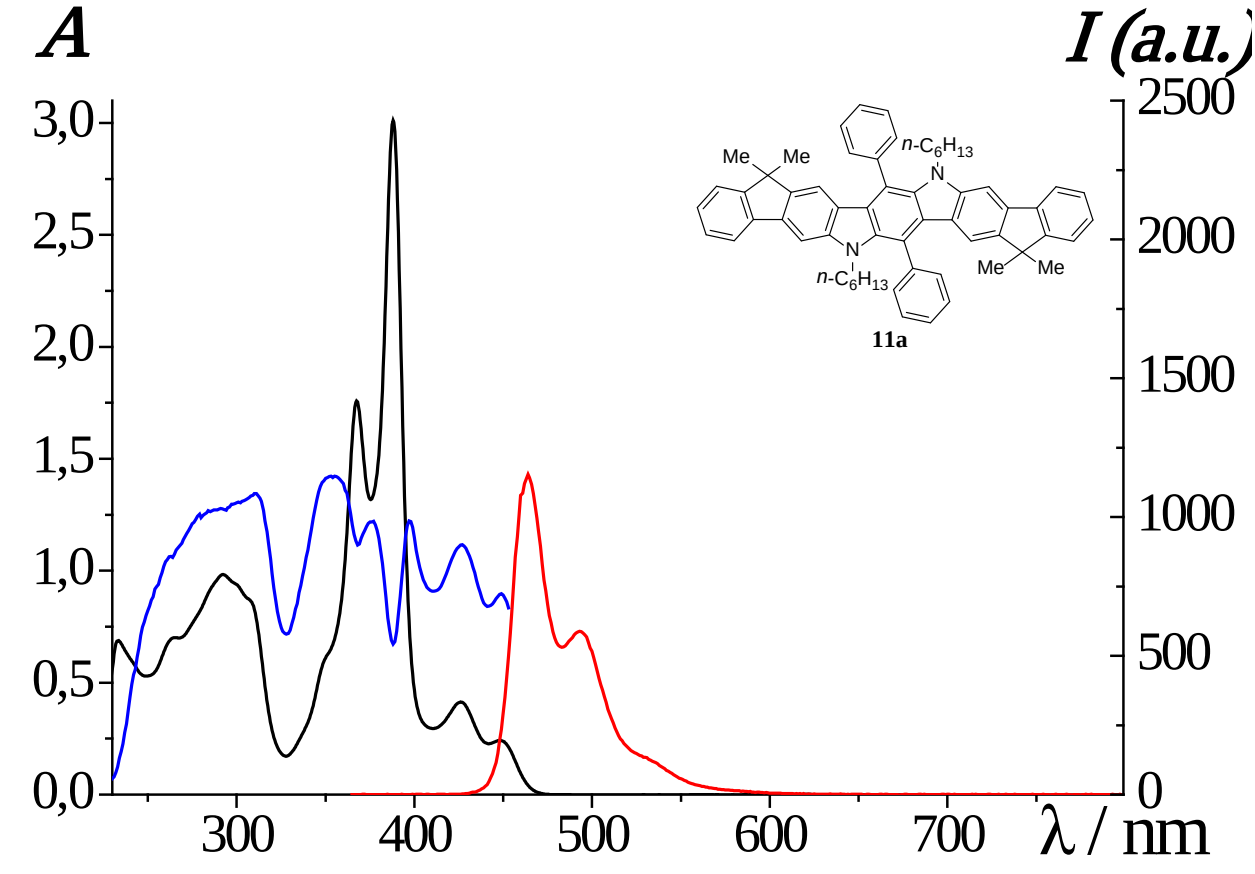
Absorption (**black line**) / Excitation (**blue line**) / Emission (**red line**)



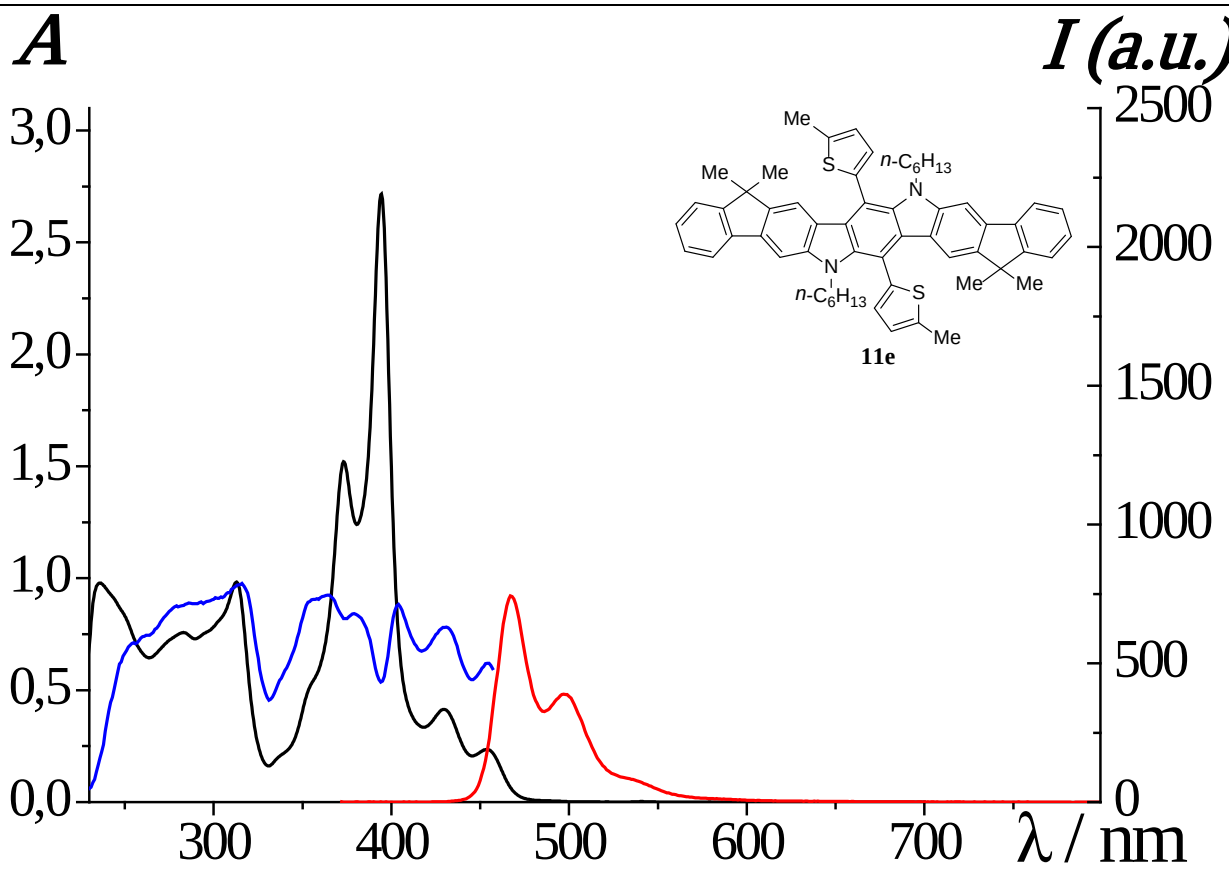
Absorption (**black line**) / Excitation (**blue line**) / Emission (**red line**)



Absorption (**black line**) / Excitation (**blue line**) / Emission (**red line**)



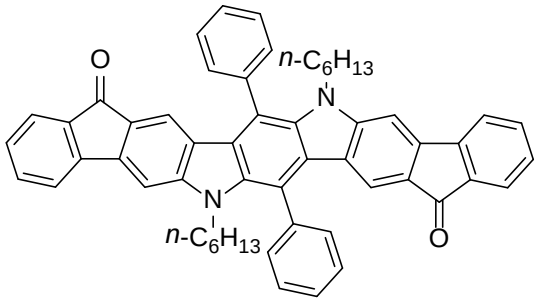
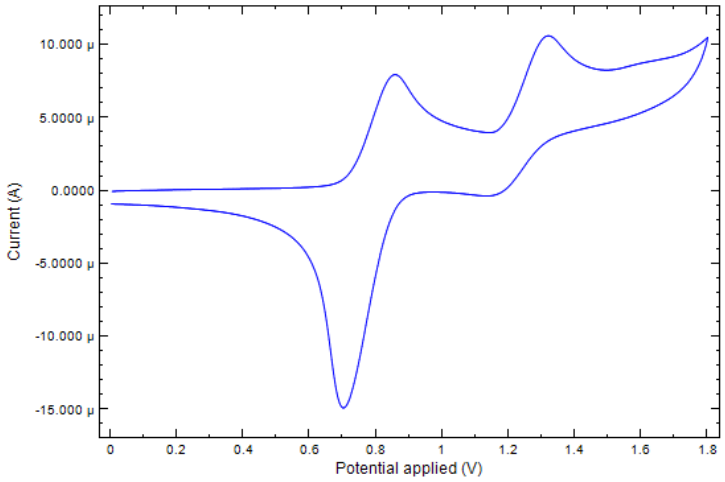
Absorption (**black line**) / Excitation (**blue line**) / Emission (**red line**)

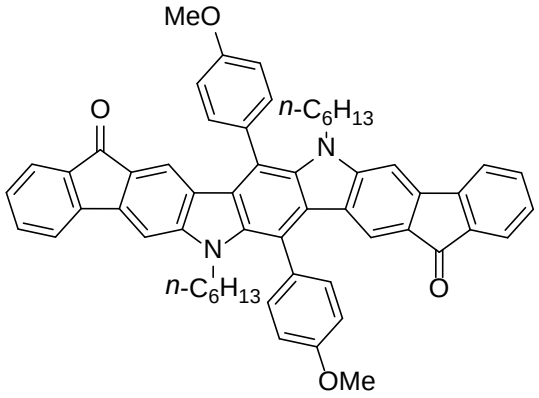
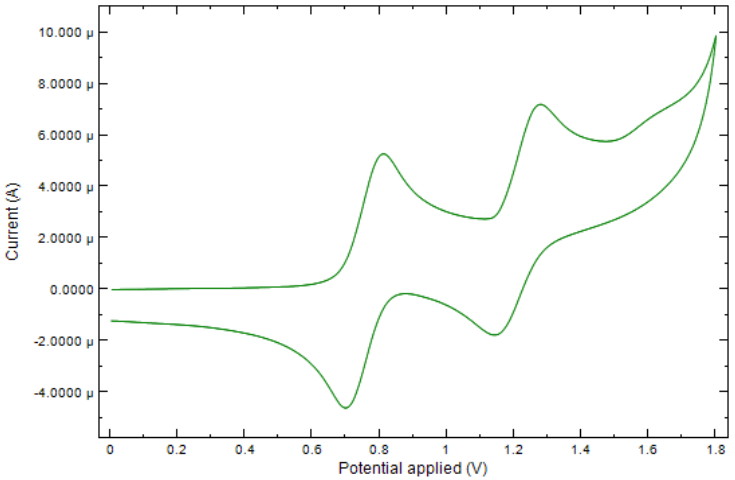
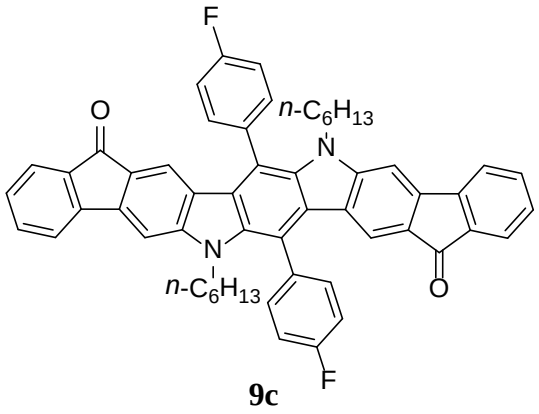
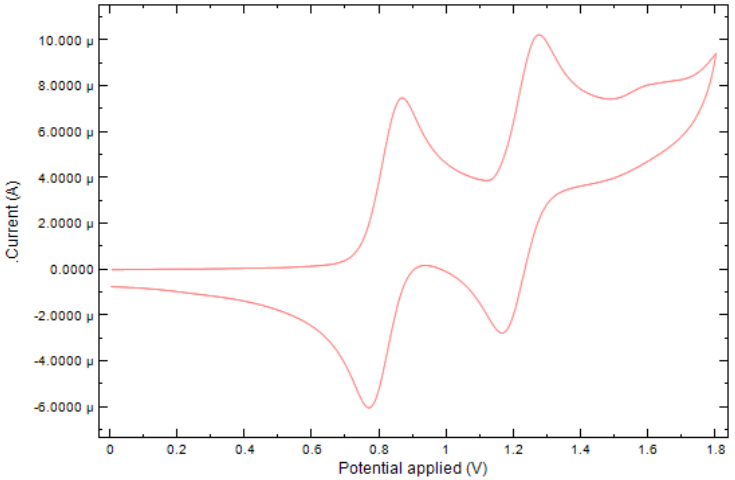


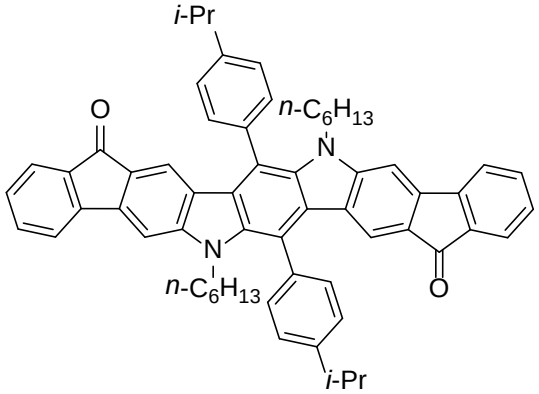
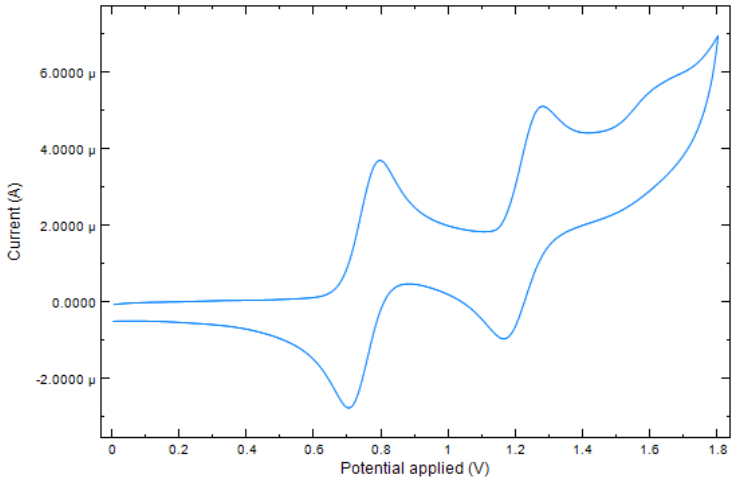
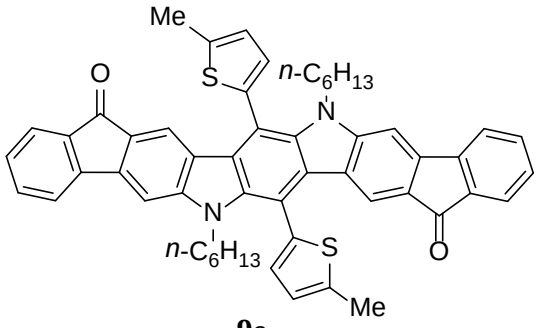
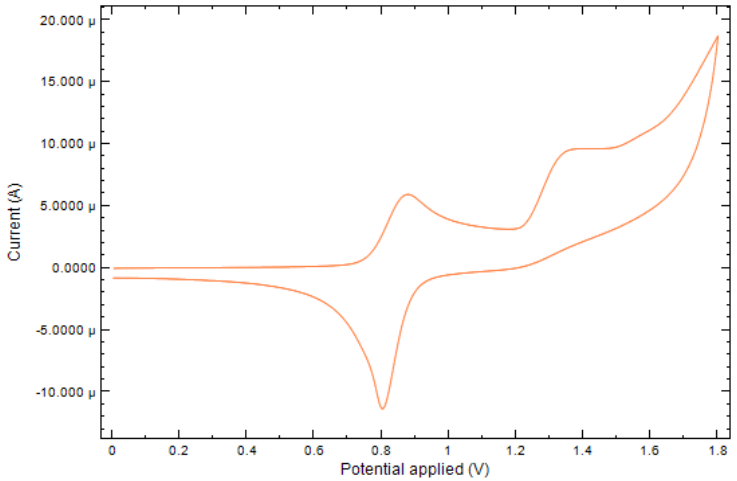
Absorption (**black line**) / Excitation (**blue line**) / Emission (**red line**)

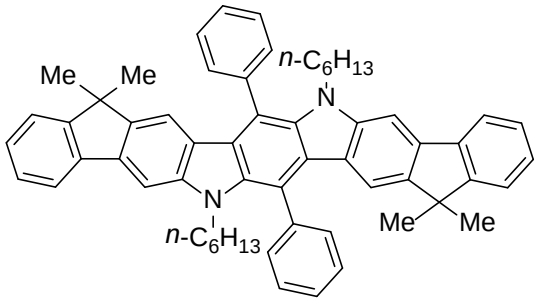
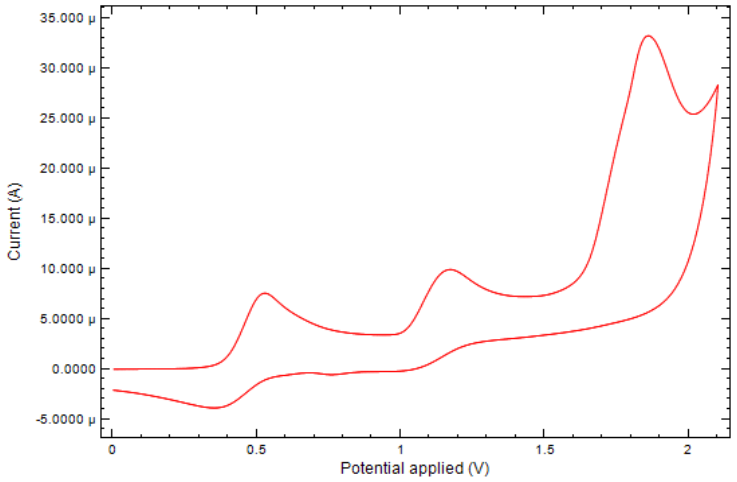
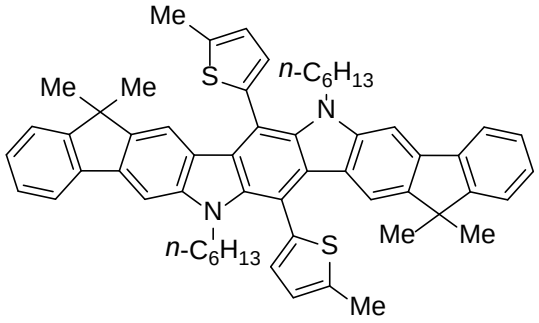
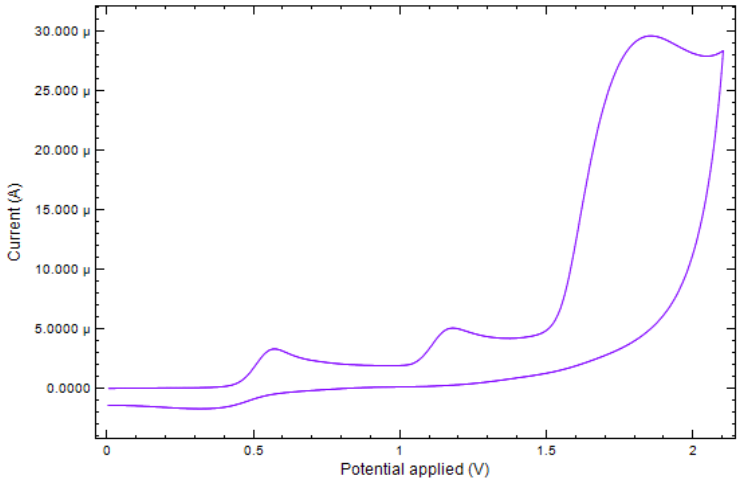
*3. Cyclic voltammetry data for compounds **9a-e** and **11a,e***

Cyclic voltammetry was carried out on a Metrohm Autolab PGSTAT**128N** potentiostat with a standard three-electrode configuration. Typically, a three electrodes cell equipped with a glass carbon working electrode, a $Ag/AgNO_3$ (0.01M) reference electrode, and a glass carbon rod counter electrode was employed. The all measurements were done in anhydrous CH_2Cl_2 with tetrabutylammonium tetrafluoroborate (0.1 M) as the supporting electrolyte under an argon atmosphere at a scan rate of 100 mV/s. The potential of the reference electrode was calibrated using the ferrocene/ferrocenium redox couple (Fc/Fc^+). The HOMO energy values were estimated from the onset potentials (E_{ox}^{onset}) of the first oxidation event according to the following equation: E_{HOMO} (eV) = – [E_{ox}^{onset} – $E_{1/2}(Fc/Fc^+)$ + 5.1], where $E_{1/2}(Fc/Fc^+)$, as the half-wave potential of the Fc/Fc^+ couple against the Ag/Ag^+ electrode. It was defined at 0.22 V in the calibration experiment.

Structure of compound	CV graphic	Oxidation potential
 **9a**		E_{ox}^{onset} = 0.67 V **E_{HOMO} (eV) = – 5.55** E_{ox}^{peak1} = 0.85 V E_{ox}^{peak2} = 1.31 V

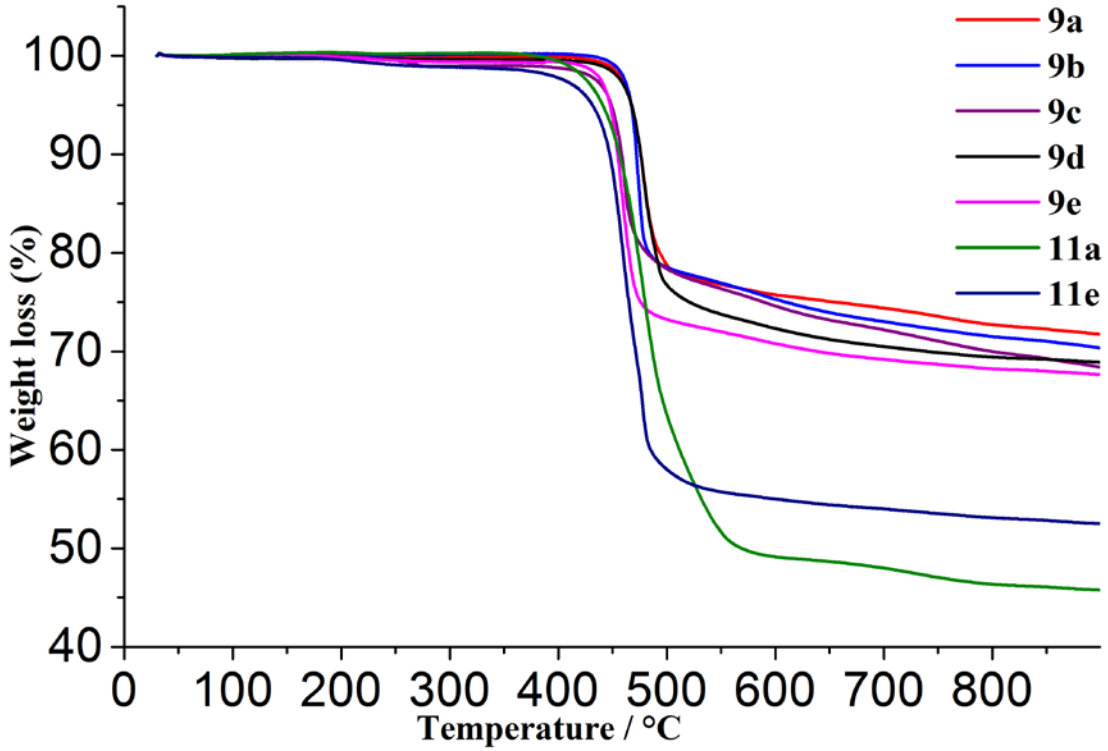
 **9b**		E_{ox}^{onset} = 0.64 V **E_{HOMO} (eV) = – 5.52** E_{ox}^{peak1} = 0.81 V E_{ox}^{peak2} = 1.13 V
 **9c**		E_{ox}^{onset} = 0.70 V **E_{HOMO} (eV) = – 5.58** E_{ox}^{peak1} = 0.86 V E_{ox}^{peak2} = 1.26 V

 **9d**		E_{ox}^{onset} = 0.63 V **E_{HOMO} (eV) = – 5.51** E_{ox}^{peak1} = 0.79 V E_{ox}^{peak2} = 1.27 V
 **9e**		E_{ox}^{onset} = 0.71 V **E_{HOMO} (eV) = – 5.59** E_{ox}^{peak1} = 0.87 V E_{ox}^{peak2} = 1.33 V

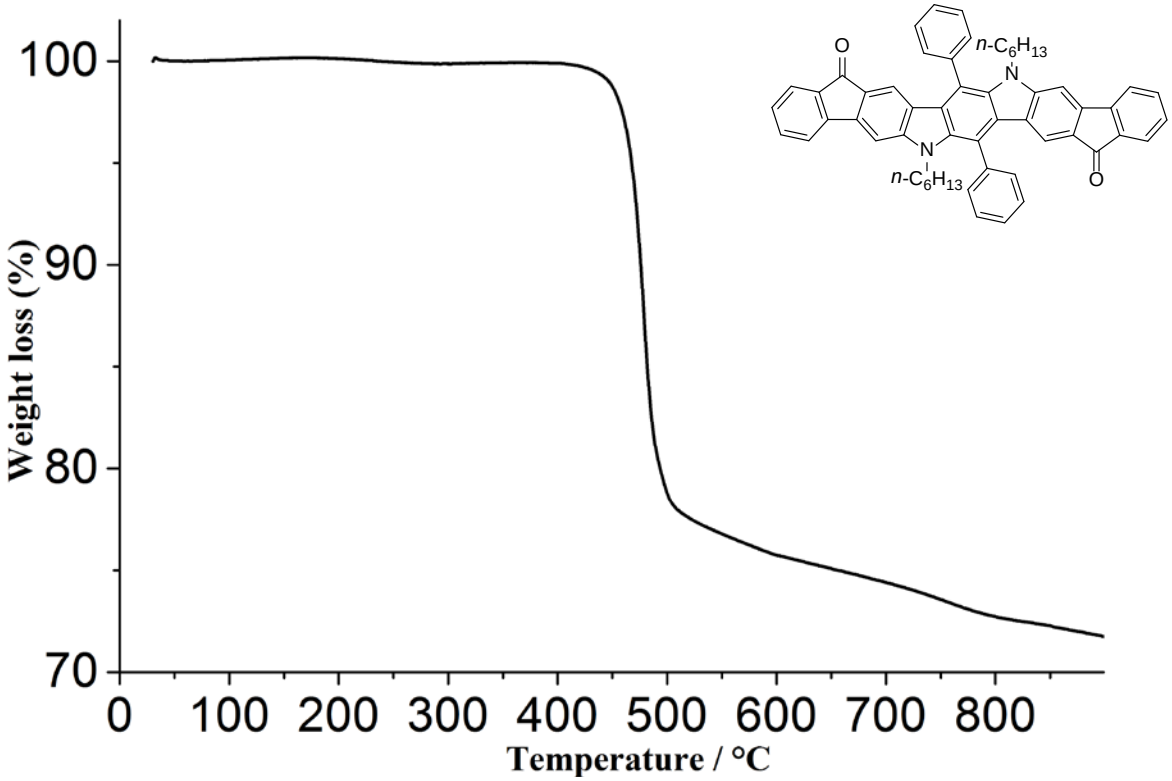
 **11a**		E_{ox}^{onset} = 0.33 V **E_{HOMO} (eV) = – 5.21** E_{ox}^{peak1} = 0.52 V E_{ox}^{peak2} = 1.16 V E_{ox}^{peak3} = 1.84 V
 **11e**		E_{ox}^{onset} = 0.39 V **E_{HOMO} (eV) = – 5.27** E_{ox}^{peak1} = 0.56 V E_{ox}^{peak2} = 1.17 V E_{ox}^{peak3} = 1.76 V

*4. Thermogravimetric analysis (TGA) data for compounds **9a-e** and **11a,e***

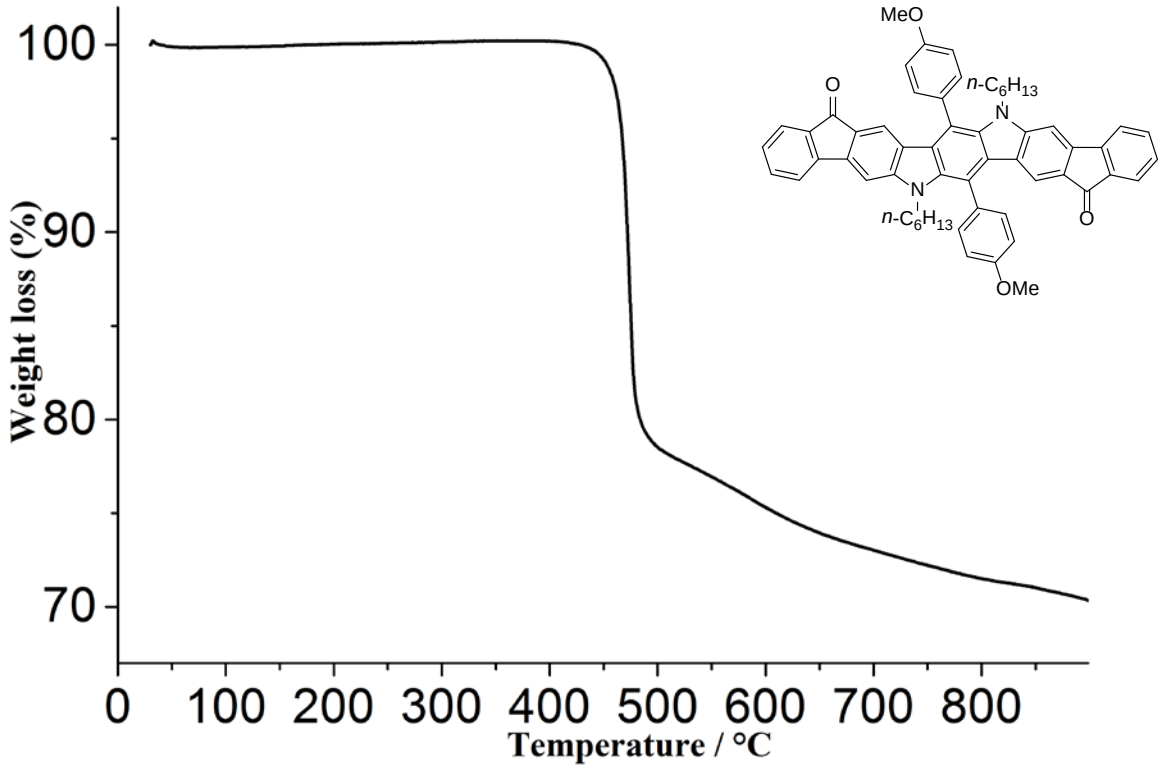
TGA curves of compounds **9a-e** and **11a**,**e**:



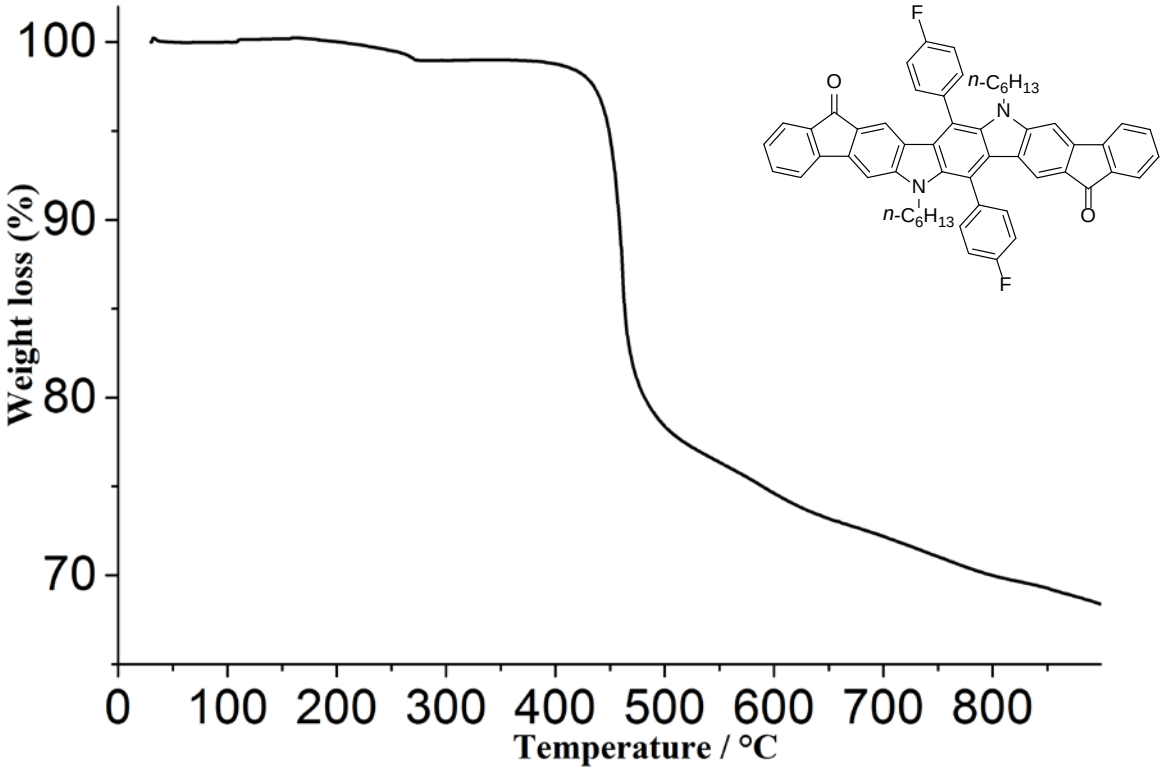
TGA curve of compound **9a**:



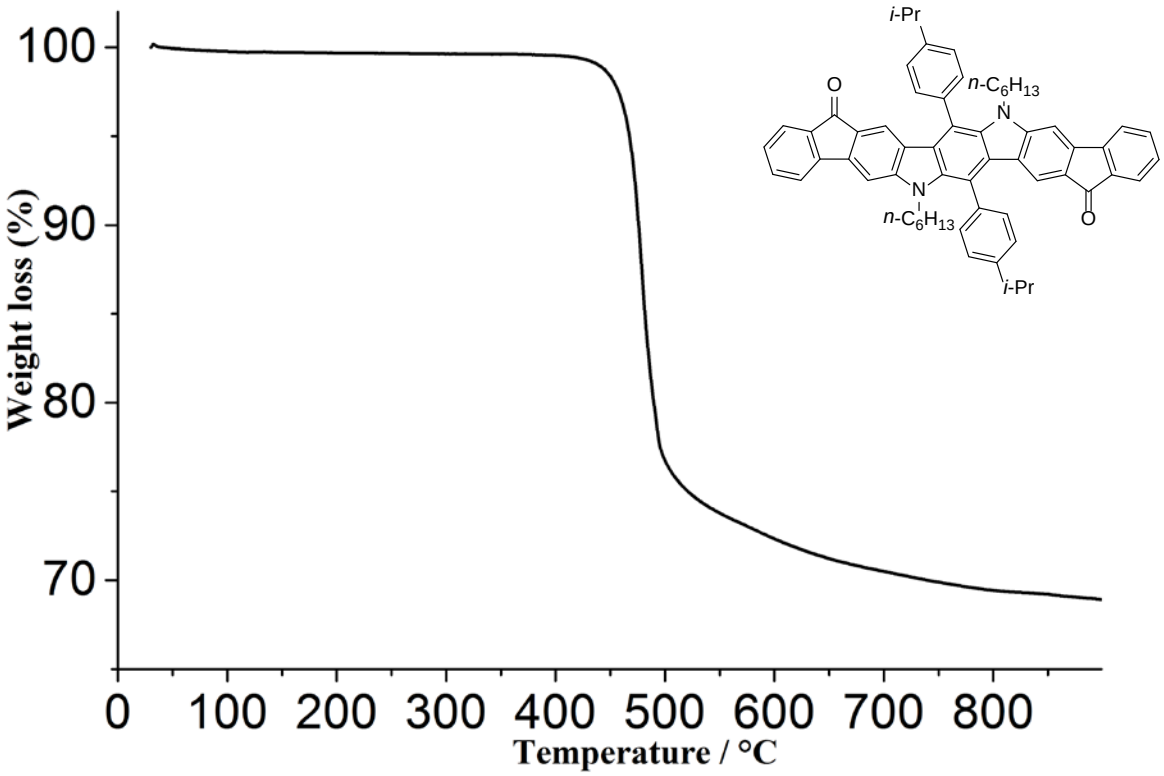
TGA curve of compound **9b**:



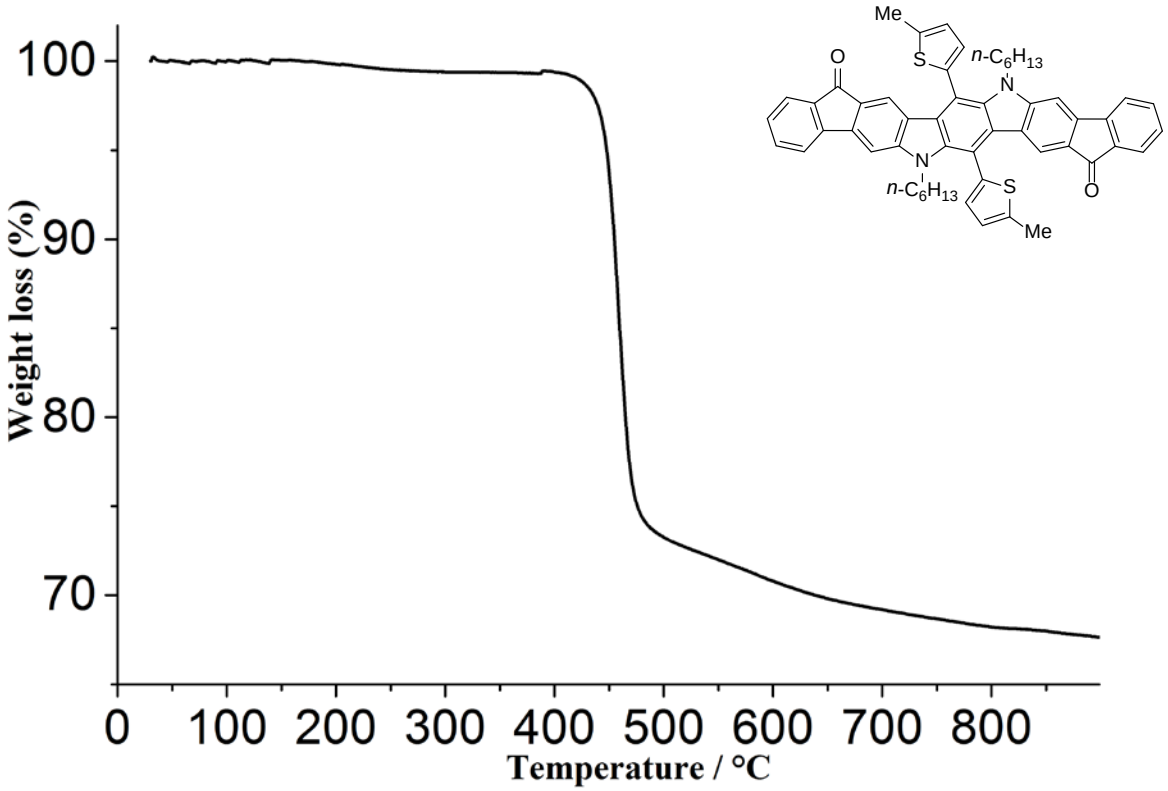
TGA curve of compound **9c**:



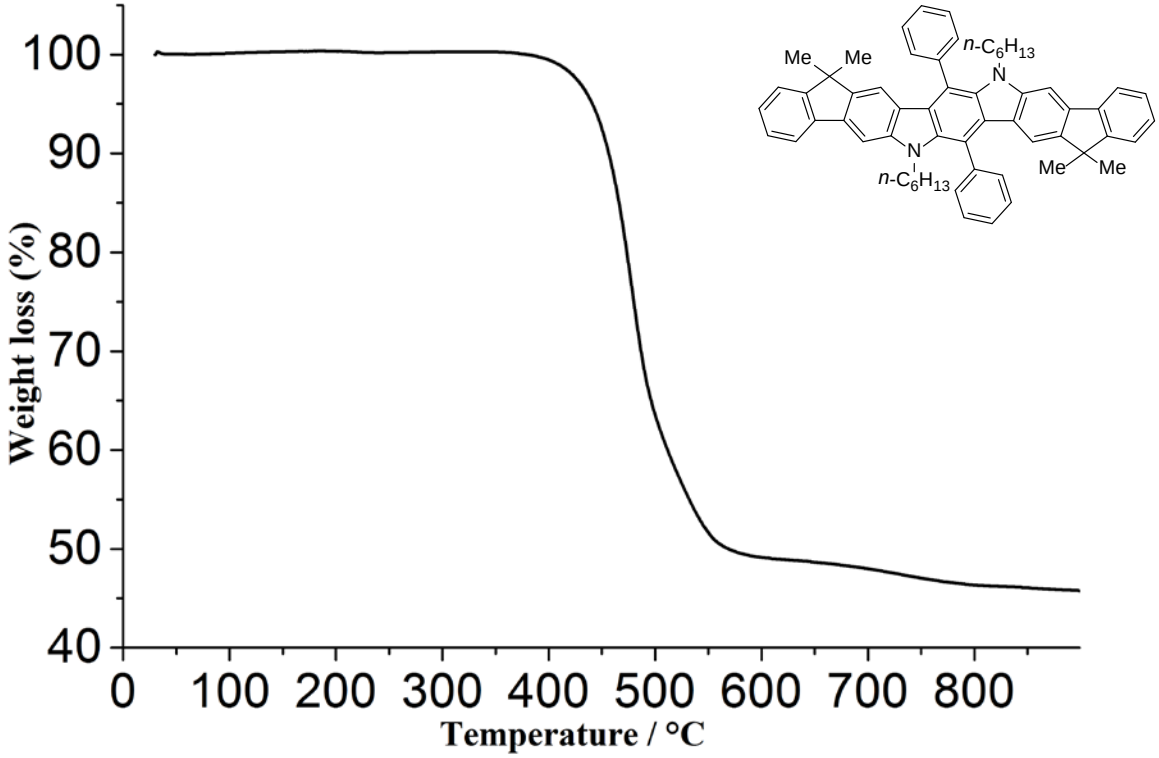
TGA curve of compound **9d**:



TGA curve of compound **9e**:



TGA curve of compound **11a**:



TGA curve of compound **11e**: