Electronic Supplementary Information

4,5-Diaminophthalimides: highly efficient solid-state fluorophores and turn-on type fluorescent probe for hydrazine

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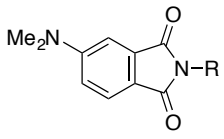
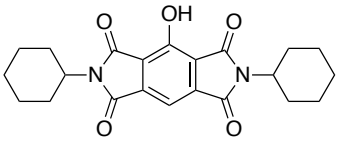


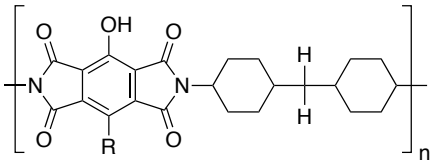
$\Phi_{crystal}$ = 0.58 (R = 4-$CH_3C_6H_4$)
$\Phi_{crystal}$ = 0.25 (R = 4-pyridiyl)
$\Phi_{crystal}$ = 0.25 (R = 4-$CF_3C_6H_4$)

ChemPhotoChem, *2018*, ***2***, *42–52*



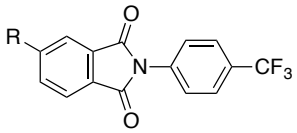
Φ_{powder} = 0.14

Macromolecules, *2016*, ***49***, *1848–1857*



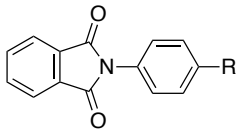
$\Phi_{neat\ film}$ = 0.07 (R = H)
$\Phi_{neat\ film}$ = 0.01 (R = OH)

Macromolecules, *2016*, ***49***, *1848–1857*
Macromolecules, *2015*, ***48***, *1777–1785*



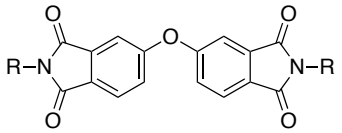
Φ_{solid} = 0.27 (R = 2-thienyl)
Φ_{solid} = 0.22 (R = 4-biphenylyl)
Φ_{solid} = 0.25 (R = 2-napthyl)
$\Phi_{solid,\ fluorescence}$ = 0.02 (R = Br)
$\Phi_{solid,\ phosphorescence}$ = 0.04 (R = Br)

J. Org. Chem., *2016*, ***81***, *433–441*
Angew. Chem. Int. Ed., *2018*, ***57***, *6449–6453*



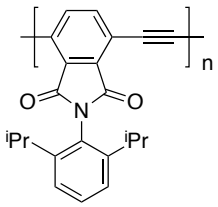
Φ_{solid} = 0.04 (R = H)
Φ_{solid} = 0.03 (R = SF_5)

Chem. Mater., *2012*, ***24***, *671–676*



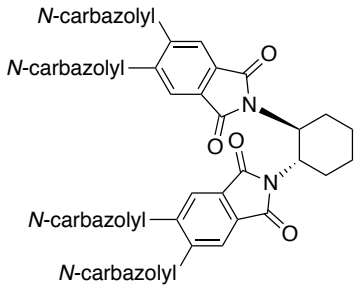
$\Phi_{crystal}$ = 0.27 (R = $(CH_2)_2OH$)
$\Phi_{crystal}$ = 0.08 (R = $(CH_2)_2CH_3$)
$\Phi_{crystal}$ = 0.10 (R = C_5H_9)
$\Phi_{crystal}$ = 0.09 (R = C_7H_{13})

CrystEngComm, *2017*, ***19***, *419–425*



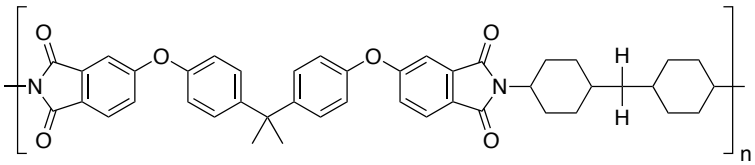
Macromol. Rapid Commun., *2005*, ***26***, *889–894*

$\Phi_{neat\ film}$ = 0.11



$\Phi_{neat\ film}$ = 0.41

Angew. Chem. Int. Ed., *2018*, ***57***, *2889–2893*



$\Phi_{neat\ film}$ = 0.11

J. Phys. Chem. B, *2009*, ***113***, *15212–15224*

Fig. S1 Molecular structures and solid-state fluorescence quantum yields of known fluorescent phthalimides.

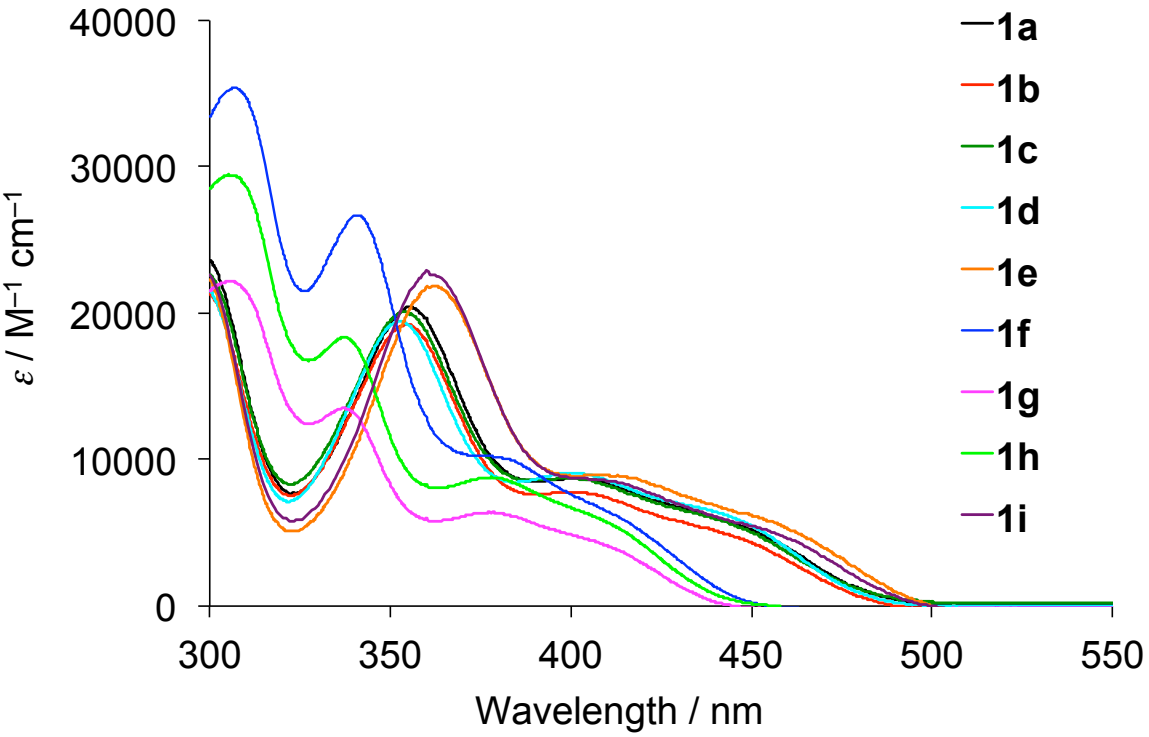


Fig. S2 Absorption spectra of **1** in toluene (10^{-5} M).

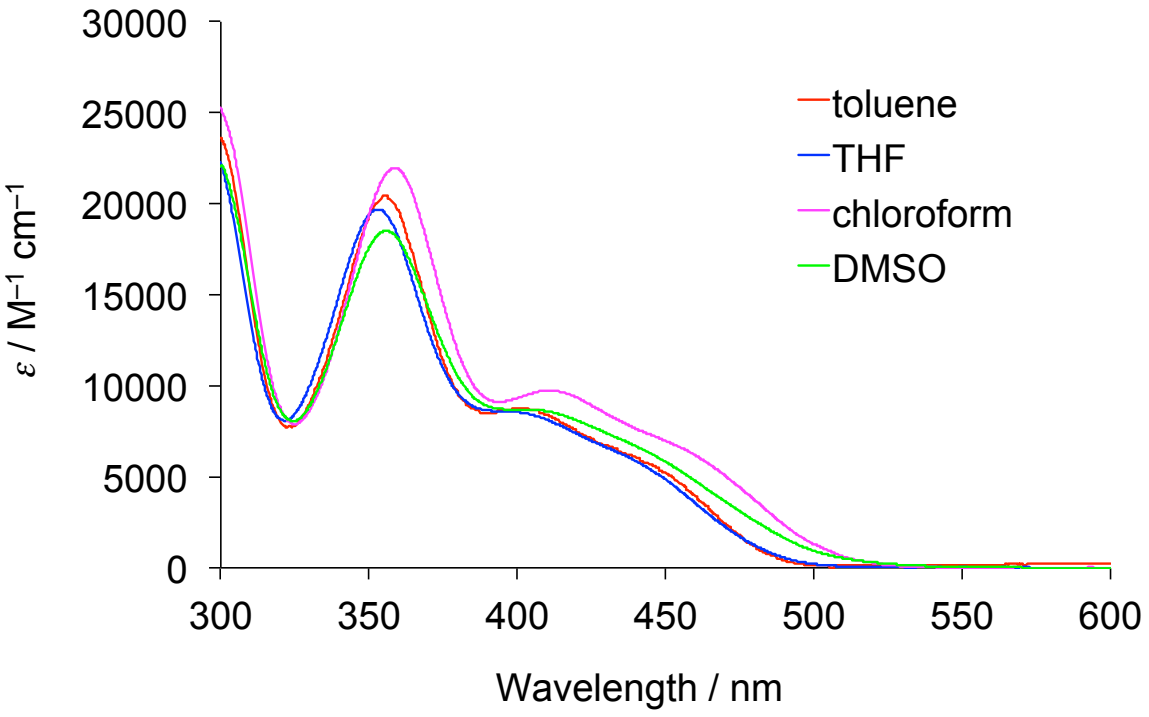


Fig. S3 Absorption spectra of **1a** in toluene, THF, chloroform, and DMSO.

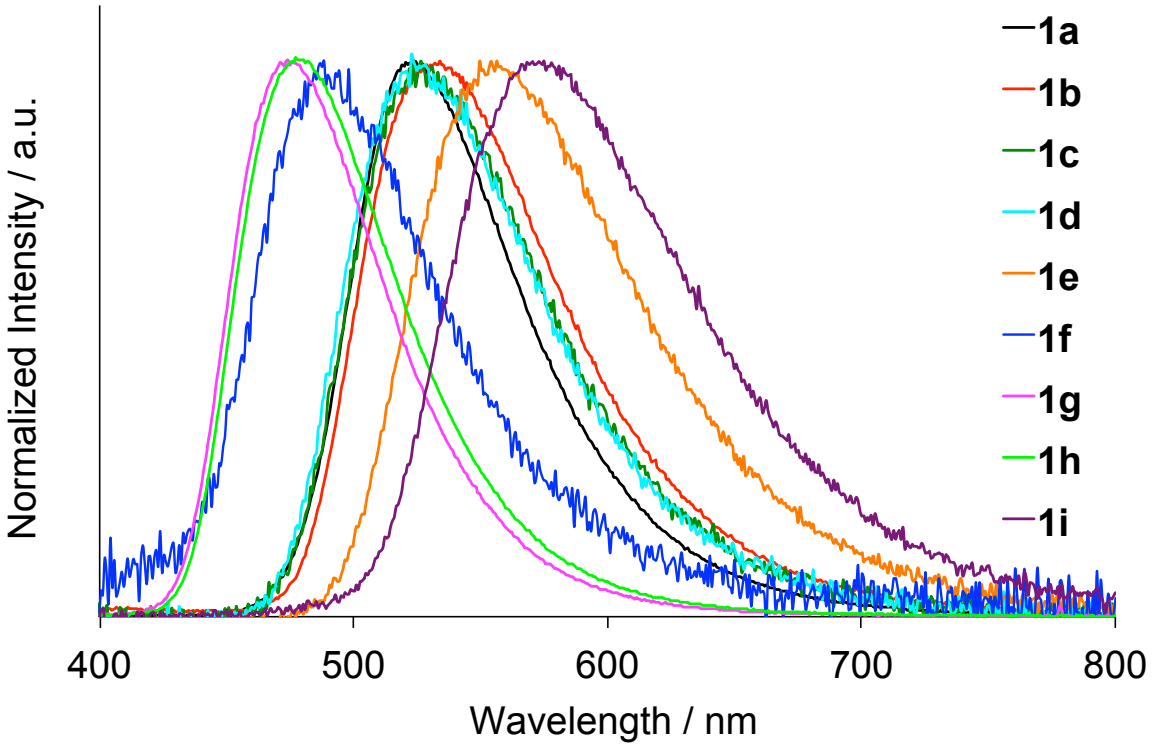


Fig. S4 Fluorescence spectra of **1** in toluene (10^{-5} M, λ_{ex} = 320 nm).

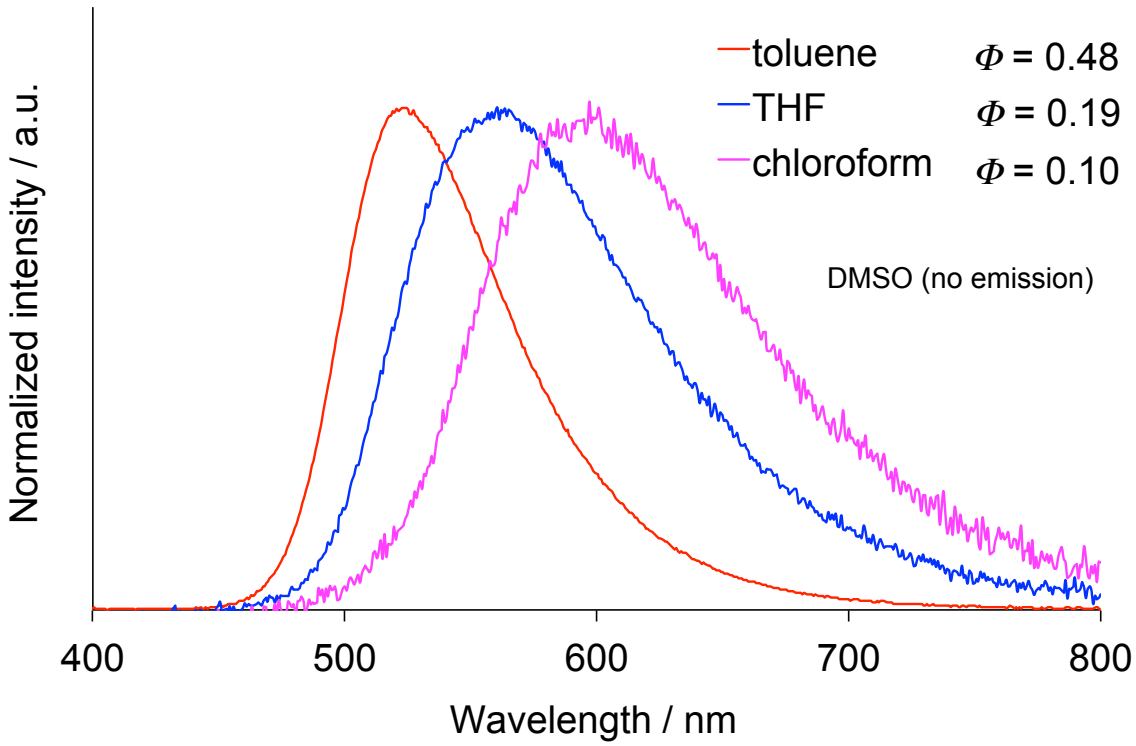


Fig. S5 Fluorescence spectra of **1a** in toluene, THF, and chloroform.

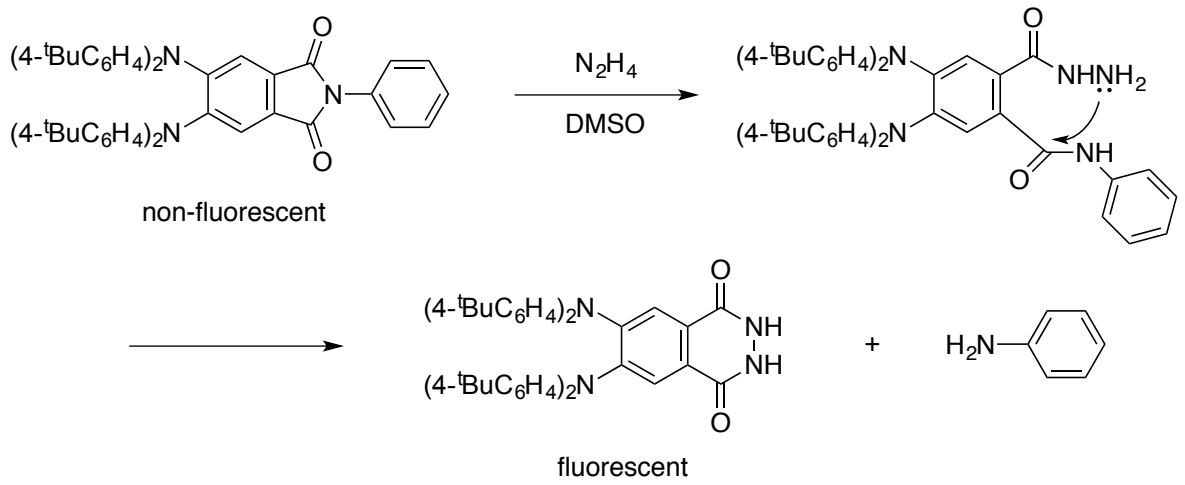


Fig. S6 A plausible mechanism for hydrazine sensing with **1i** in DMSO.

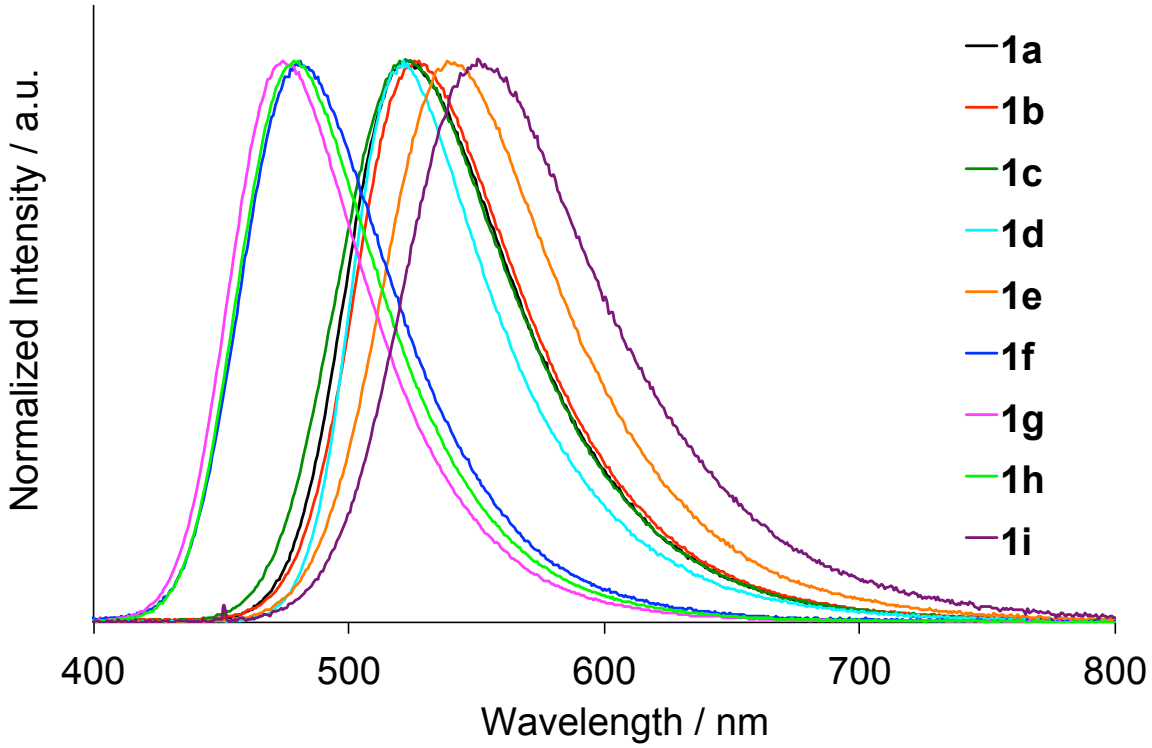


Fig. S7 Fluorescence spectra of **1** in PMMA film (λ_{ex} = 320 nm).

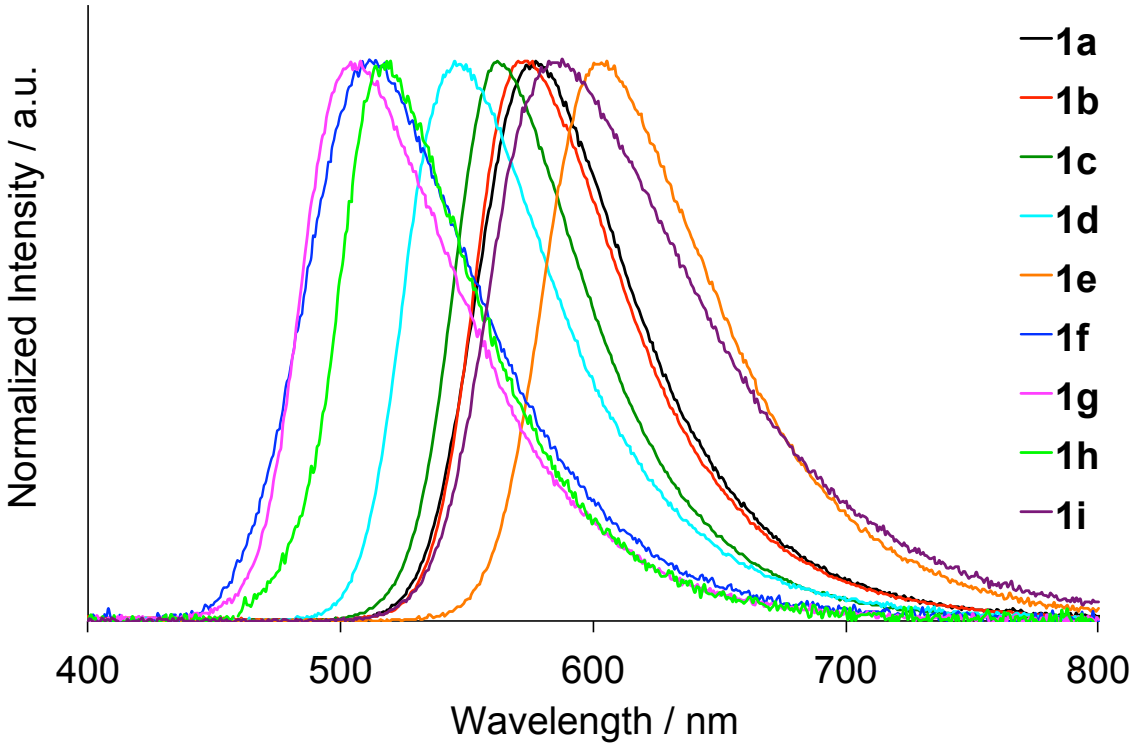


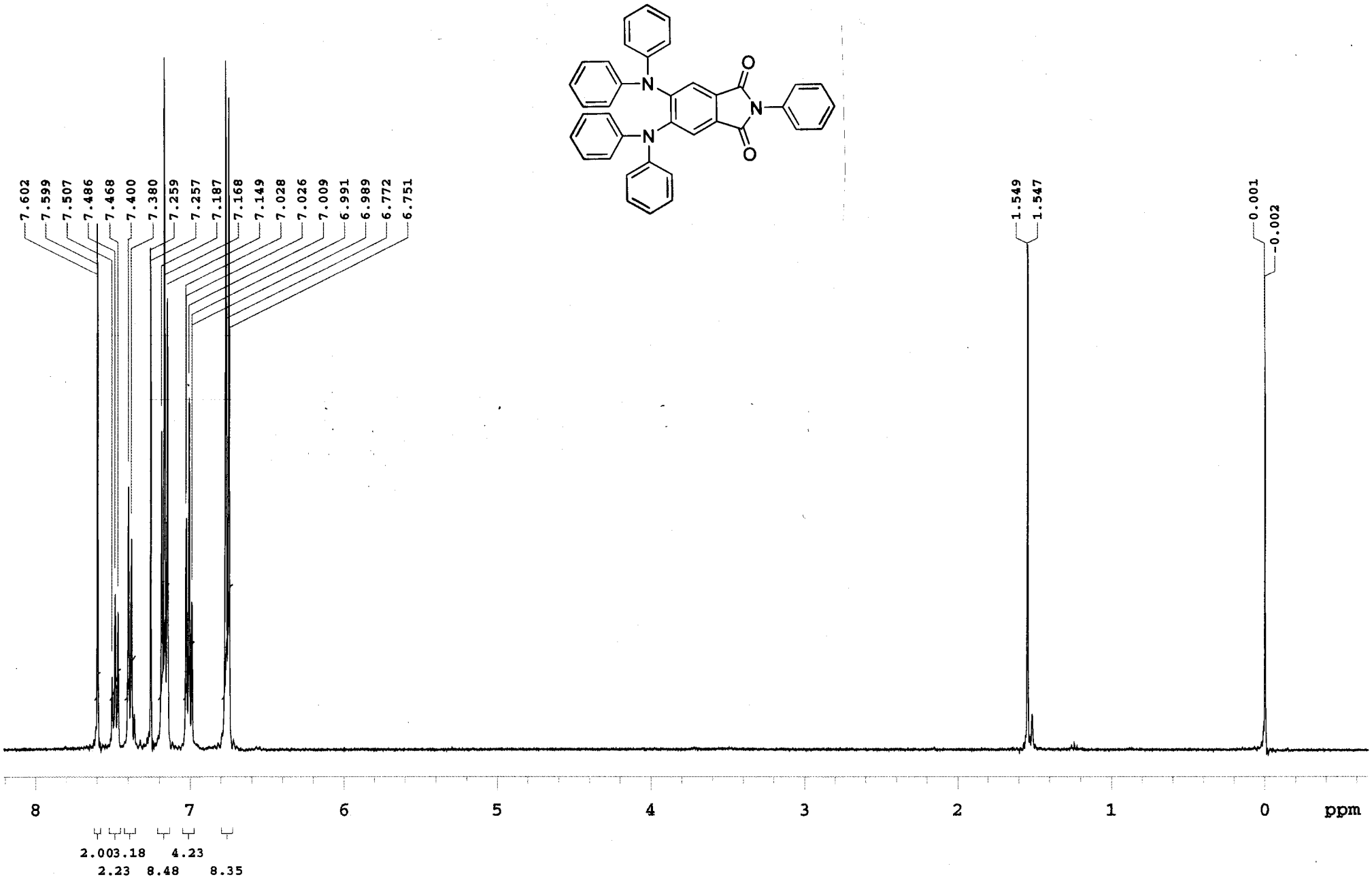
Fig. S8 Fluorescence spectra of **1** in powder (λ_{ex} = 320 nm).

Table S1 HOMO and LUMO energies, transition configuration, and oscillator strength of **1a**, **1f**, **1f'**, and **1i** [a]

	1a	**1f**	**1f'**	**1i**
LUMO (eV)	–1.005	–1.533	–1.571	–0.908
HOMO (eV)	–6.684	–7.414	–7.448	–6.474
$\Delta E_{LUMO–HOMO}$ (eV)	5.679	5.881	5.877	5.566
ΔE_{exp} (eV)[b]	3.49	3.65	Not available	3.32
Transition configuration (coefficient)	HOMO→LUMO (0.67071)	HOMO→LUMO (0.66776)	HOMO→LUMO (0.66575)	HOMO→LUMO (0.67083)
Oscillator strength	0.0150	0.0885	0.0984	0.1225

[a] Calculated at the cam-B3LYP/cc-pVDZ level using the Gaussian 09 (Revision D01). [b] ΔE_{exp}: Energy gap between HOMO and LUMO, estimated from the wavelength of the absorption edge.

^{1}H NMR of **1a**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7.507
7.486
7.468
7.400
7.380
7.259
7.257
7.187
7.168
7.149
7.028
7.026
7.009
6.991
6.989
6.772
6.751
1.549
1.547
0.001
-0.002
8
7
6
5
4
3
2
1
0
ppm
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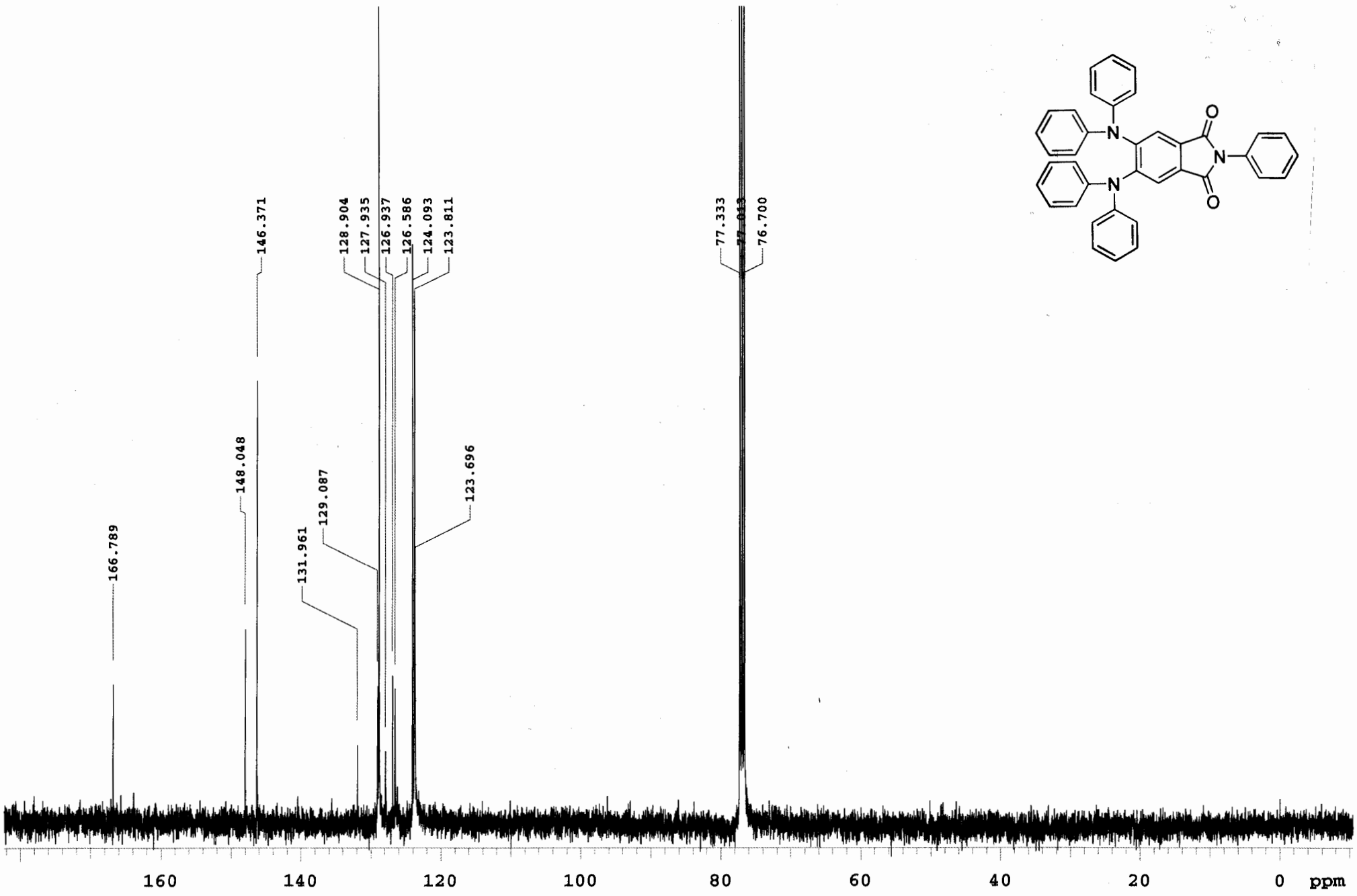
3.18
4.23
2.23
8.48
8.35

^{13}C NMR of **1a**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146.371
131.961
129.087
128.904
127.935
126.937
126.586
124.093
123.811
123.696
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77.013
76.700
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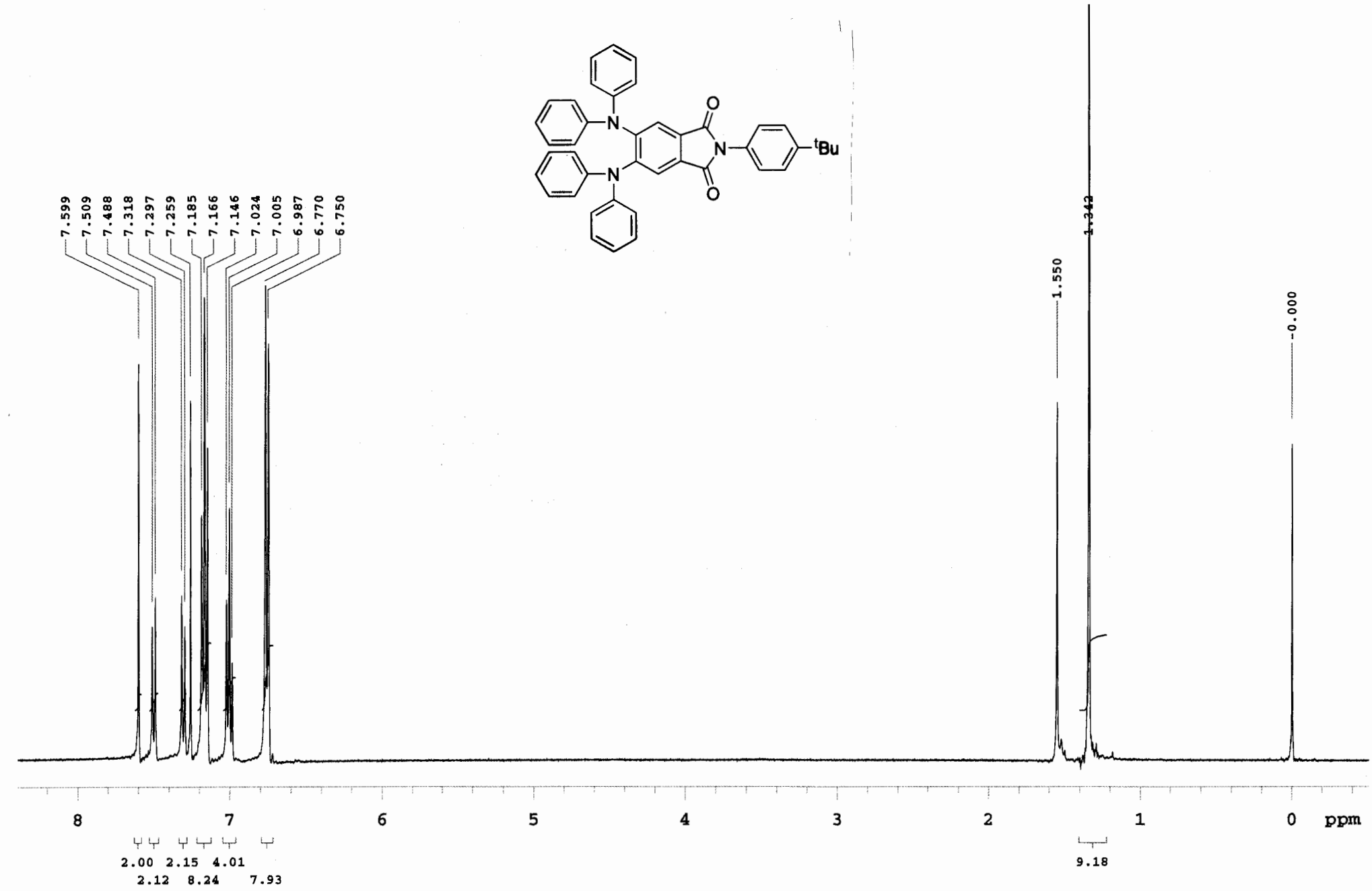
140
120
100
80
60
40
20
0
ppm

^{1}H NMR of **1b**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7.297
7.259
7.185
7.166
7.146
7.024
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6.750
1.550
1.342
0.000
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N
N
O
N
tBu
8
7
6
5
4
3
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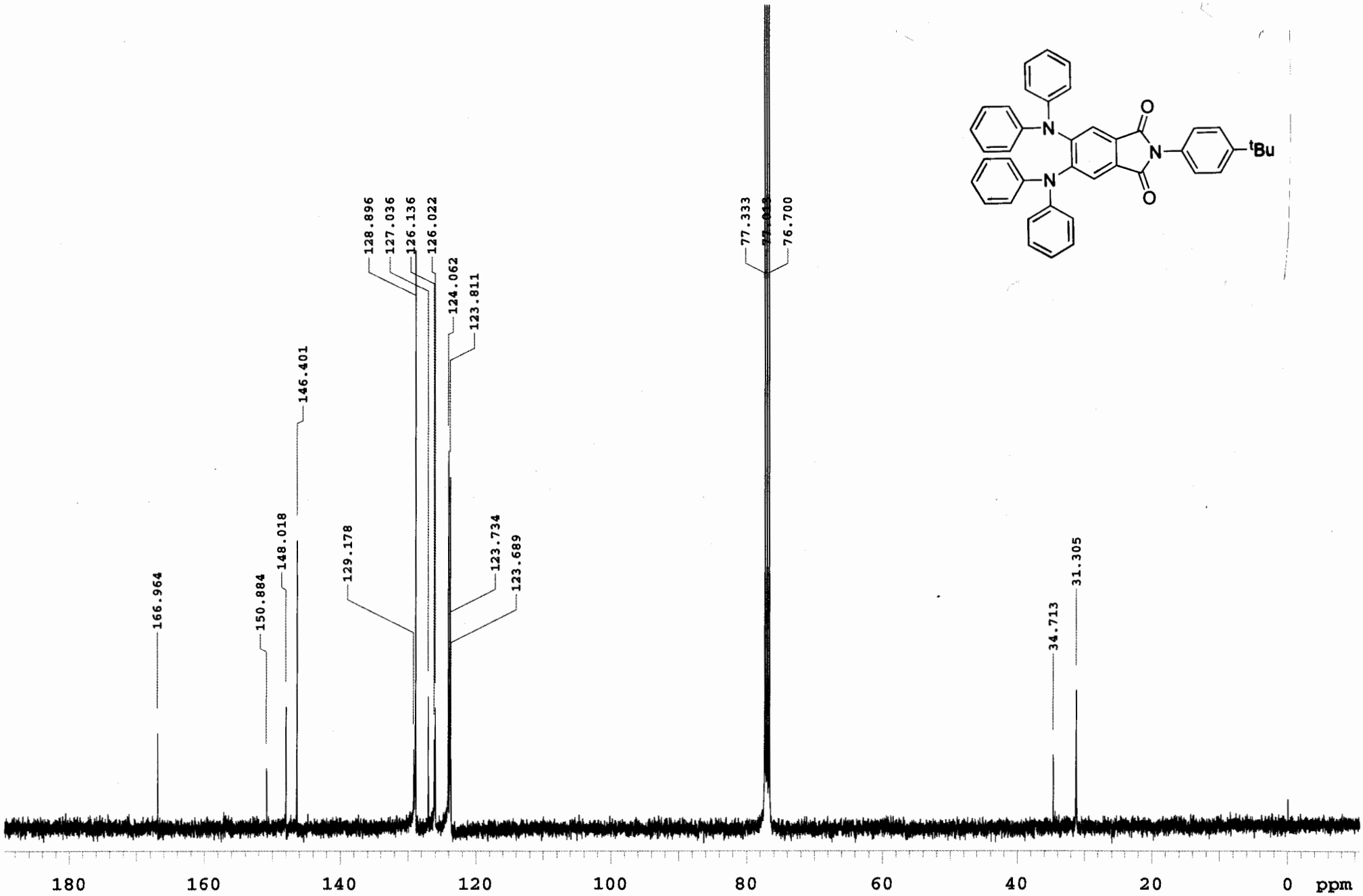
2.12
8.24
7.93
9.18

^{13}C NMR of **1b**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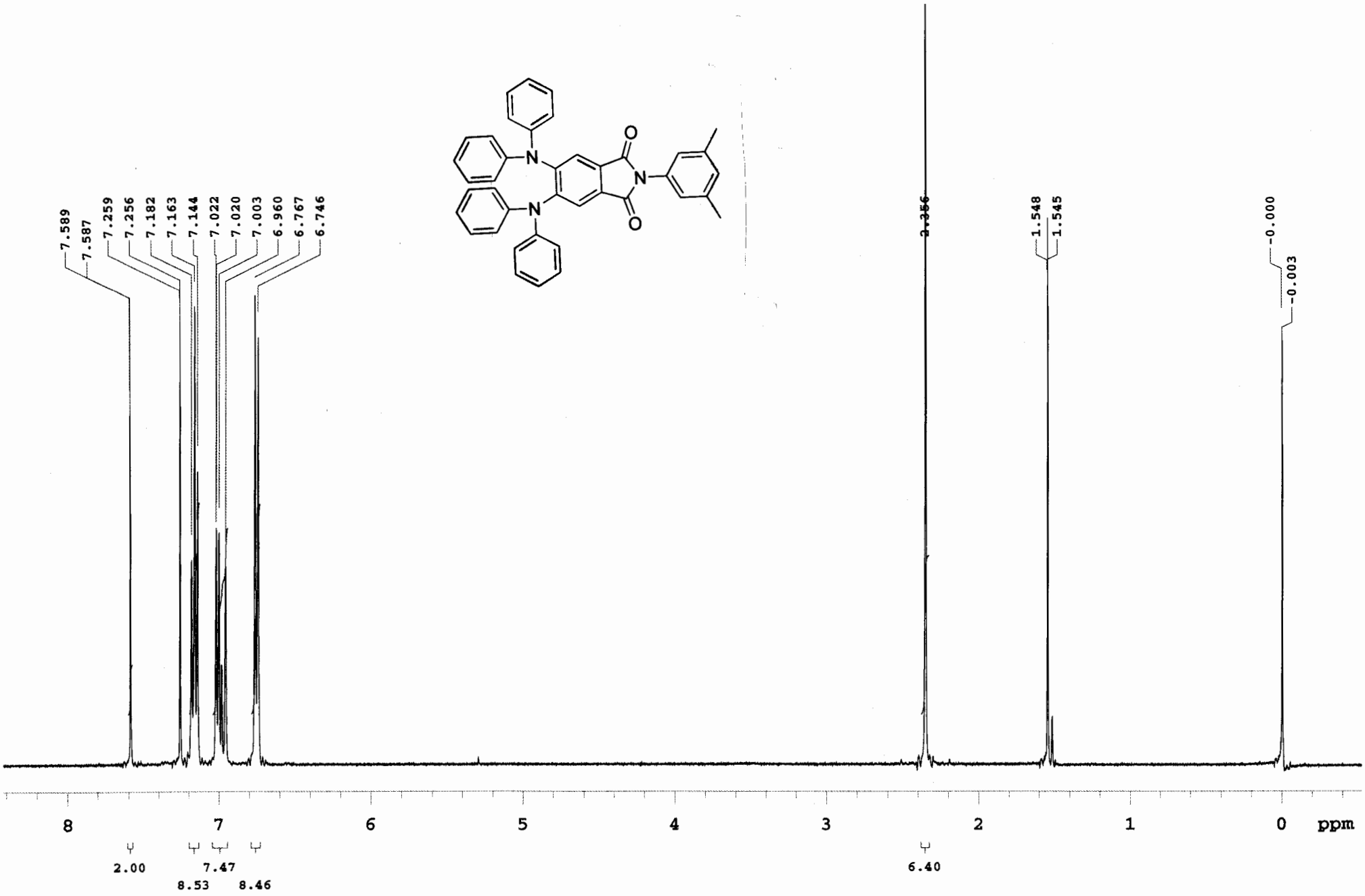
146.401
129.178
128.896
127.036
126.136
126.022
124.062
123.811
123.734
123.689
77.333
76.700
34.713
31.305
N
N
N
O
O
O
tBu
180
160
140
120
100
80
60
40
20
0
ppm

^{1}H NMR of **1c**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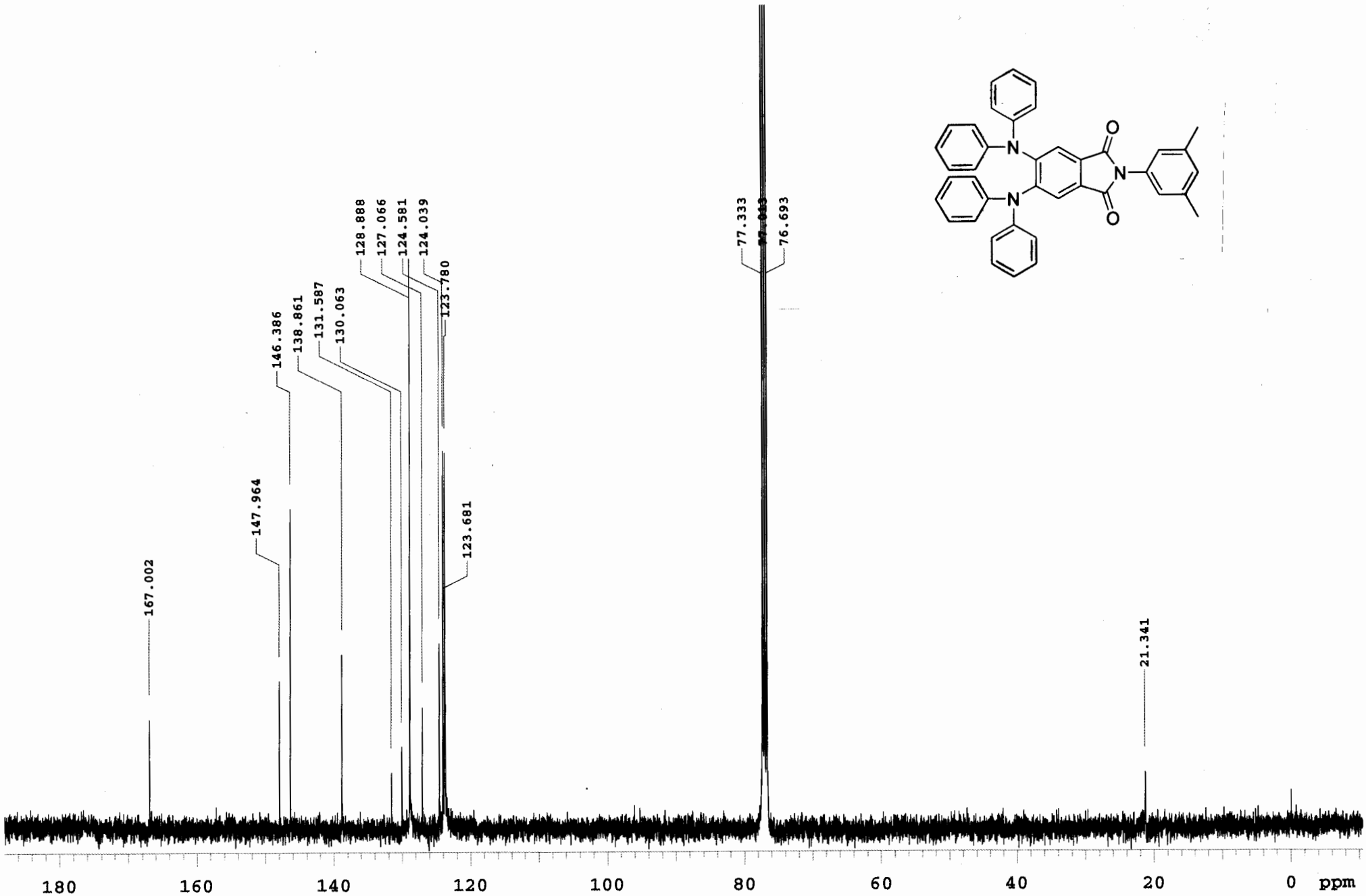
7.256
7.182
7.163
7.144
7.022
7.020
7.003
6.960
6.767
6.746
2.356
1.548
1.545
-0.000
-0.003
O
N
N
O
O
8
7
6
5
4
3
2
1
0
ppm
2.00
7.47
8.53
8.46
6.40

^{13}C NMR of **1c**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120
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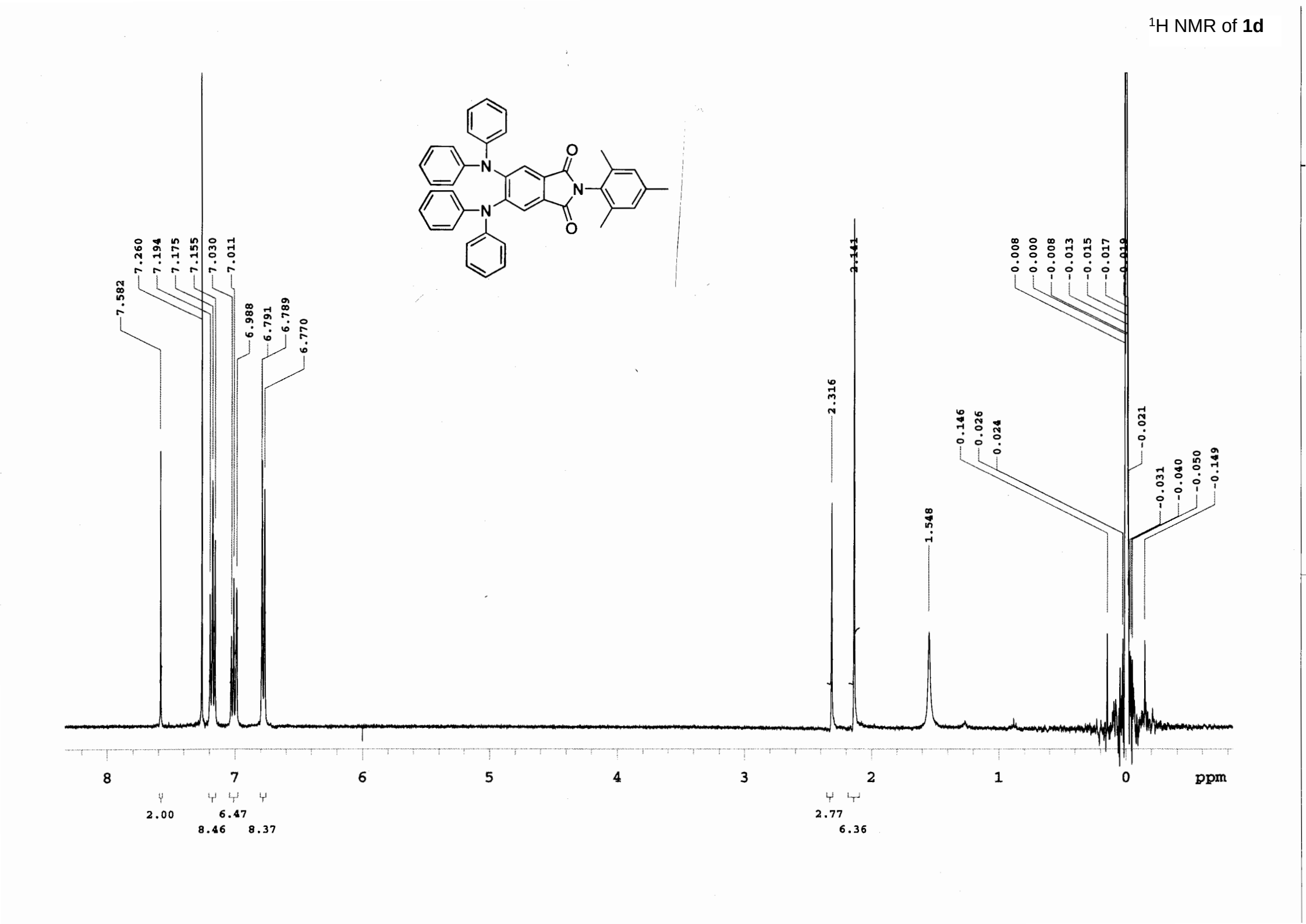
80
60
40
20
0
ppm

^{1}H NMR of **1d**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-0.015
-0.017
-0.021
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-0.050
-0.149
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6
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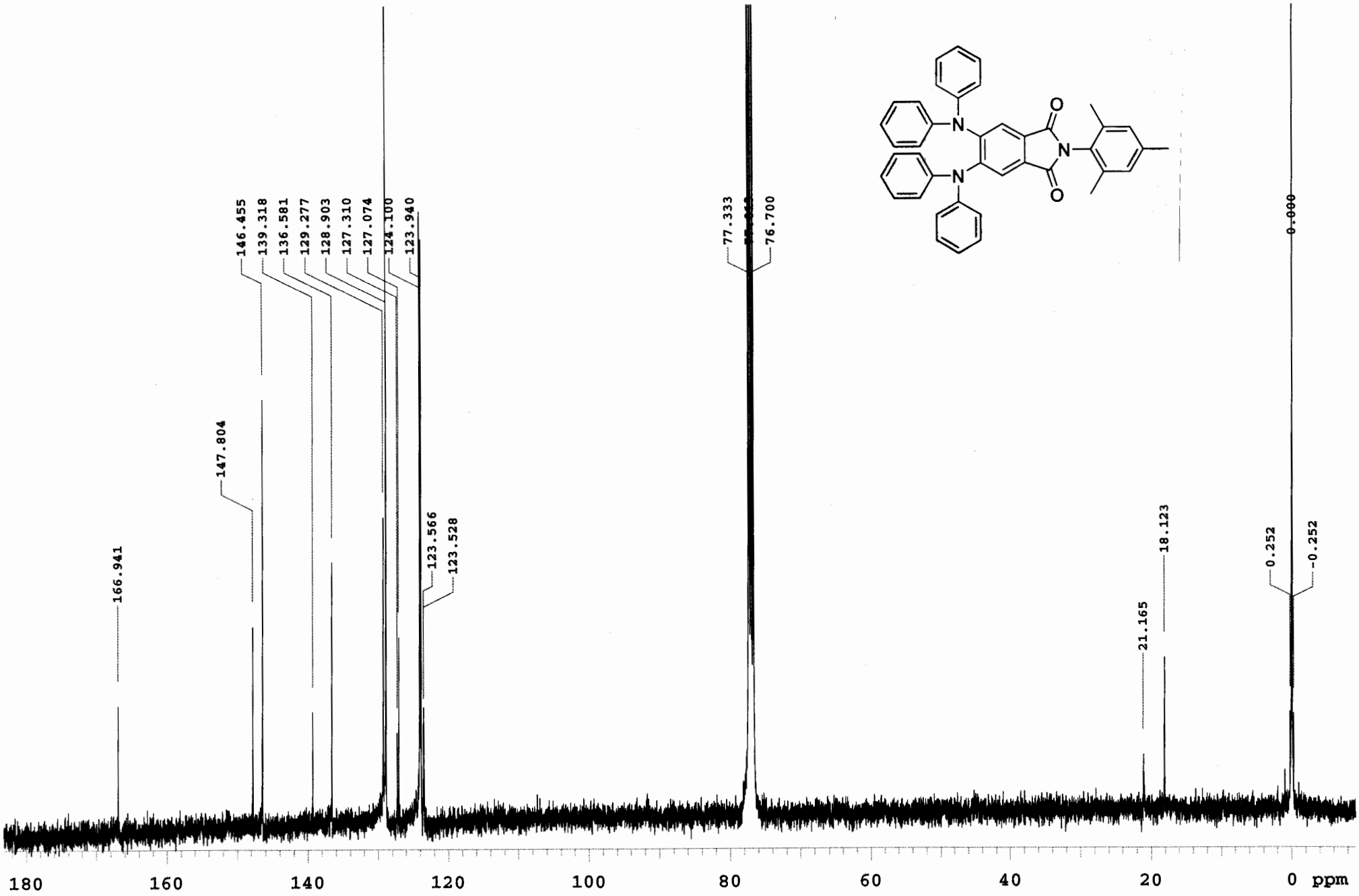
^{13}C NMR of **1d**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136.581
129.277
128.903
127.310
127.074
124.100
123.940
123.566
123.528
77.333
76.700
21.165
18.123
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0.000
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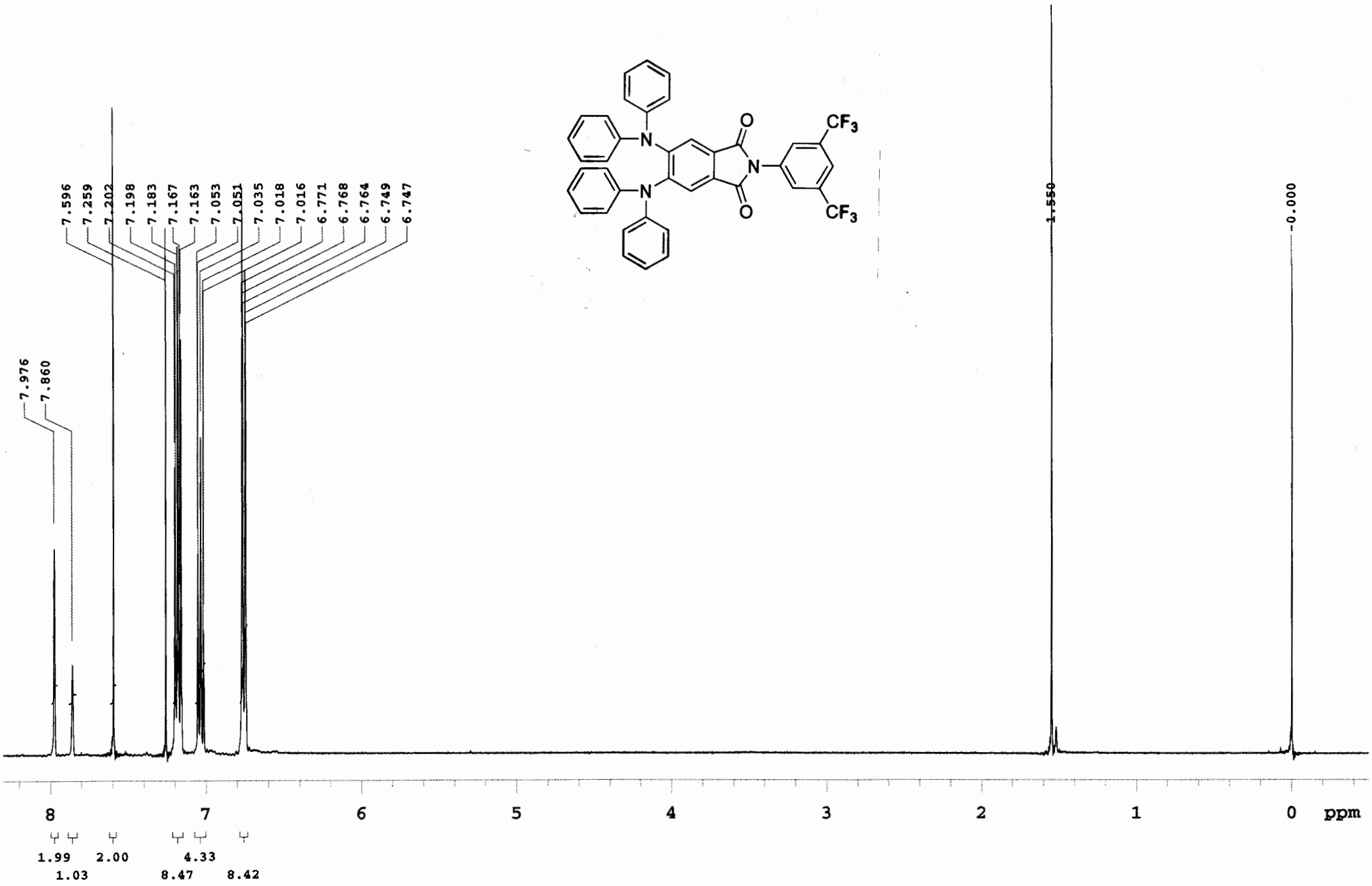
120
100
80
60
40
20
0
ppm

^{1}H NMR of 1**e**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7.202
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7.183
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7.163
7.053
7.051
7.035
7.018
7.016
6.771
6.768
6.764
6.749
6.747
1.550
0.000
8
7
6
5
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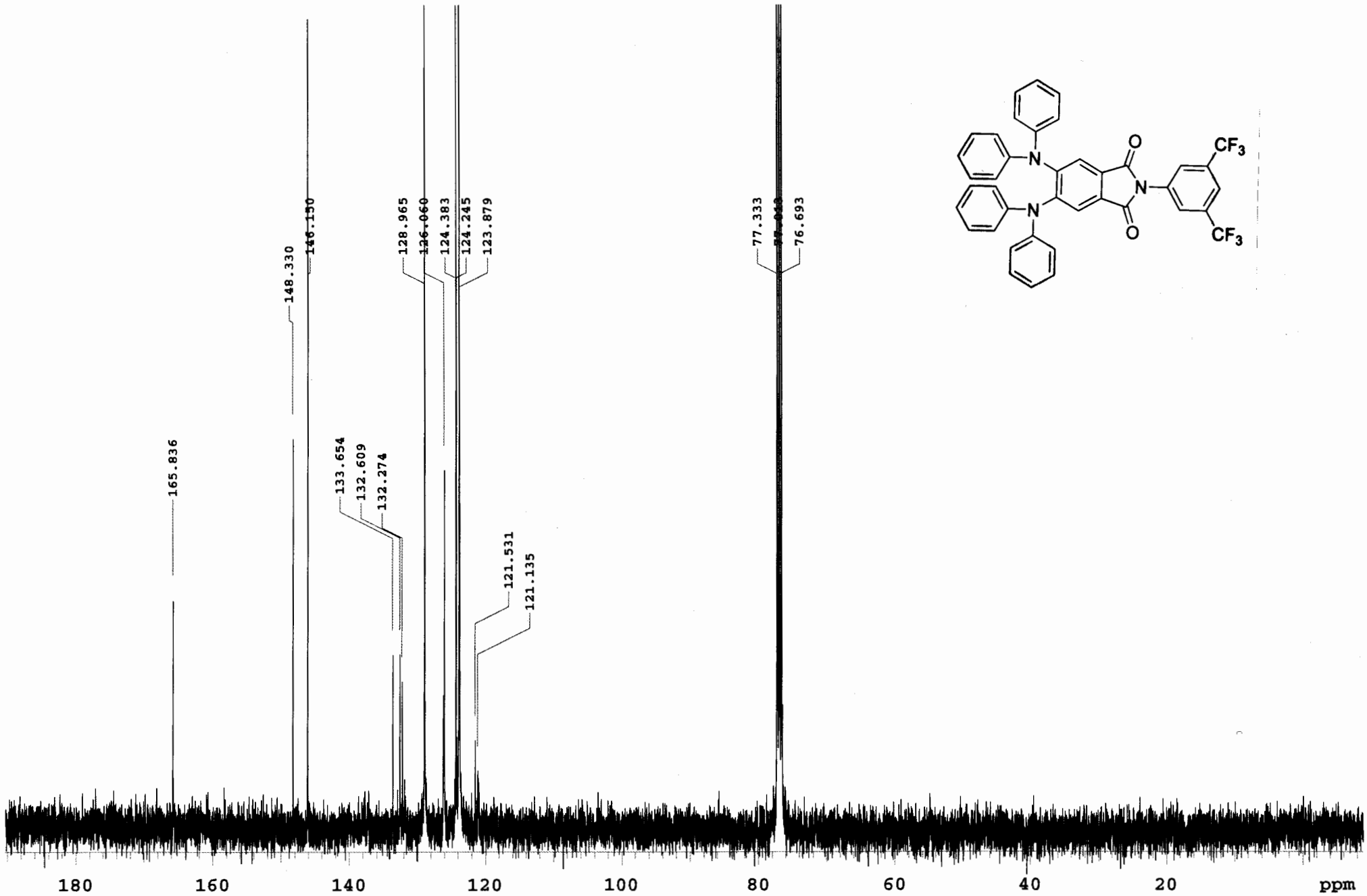
8.42

^{13}C NMR of **1e**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121.135
77.333
76.693
O
N
N
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N
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CF3
CF3
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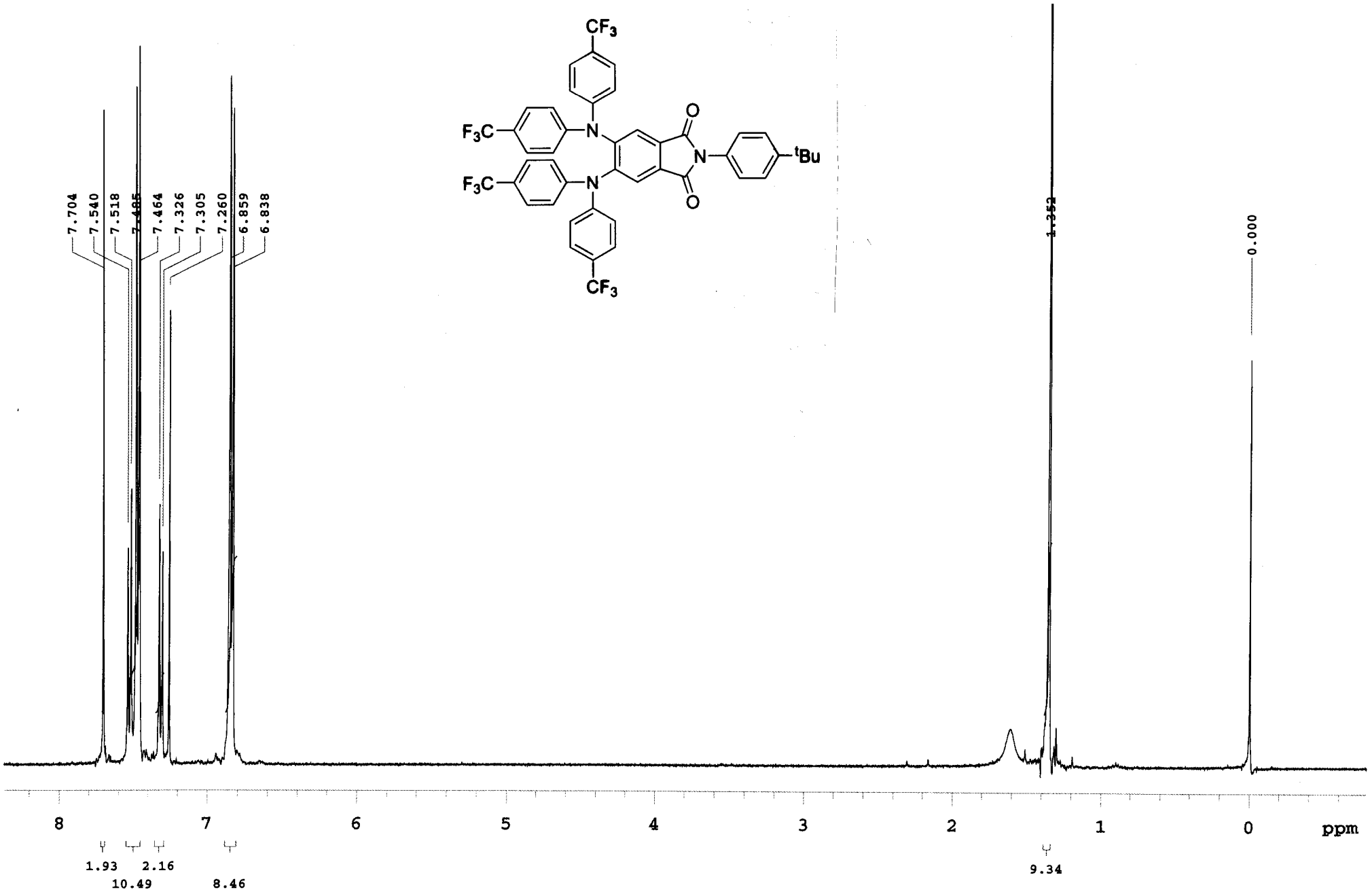
160
140
120
100
80
60
40
20
ppm

^{1}H NMR of **1f**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F3C
N
O
CF3
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7.326
7.305
7.260
6.859
6.838
1.352
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8
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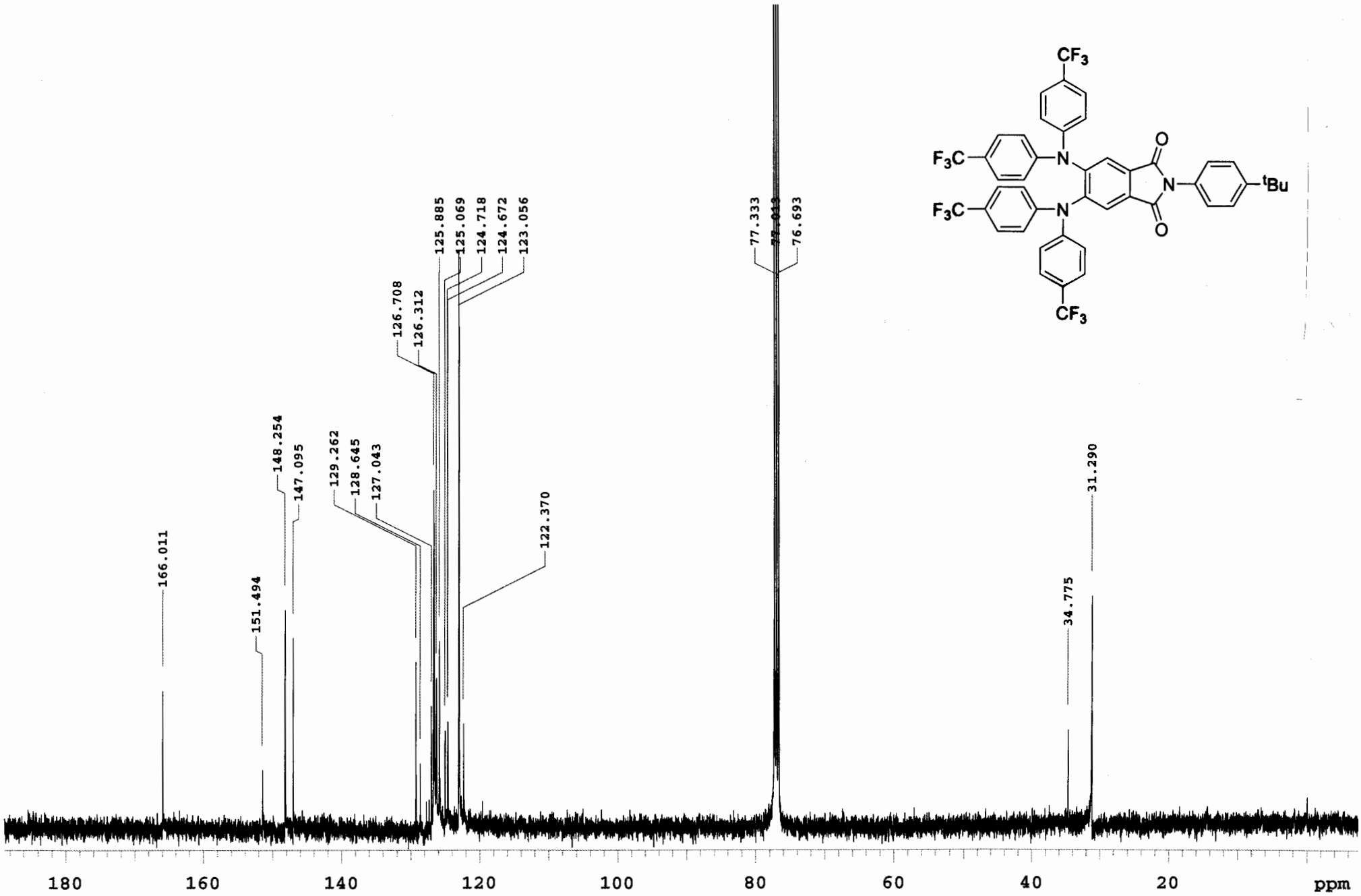
^{13}C NMR of **1f**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123.056
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31.290
180
160
140
120
100
80
60
40
20
ppm
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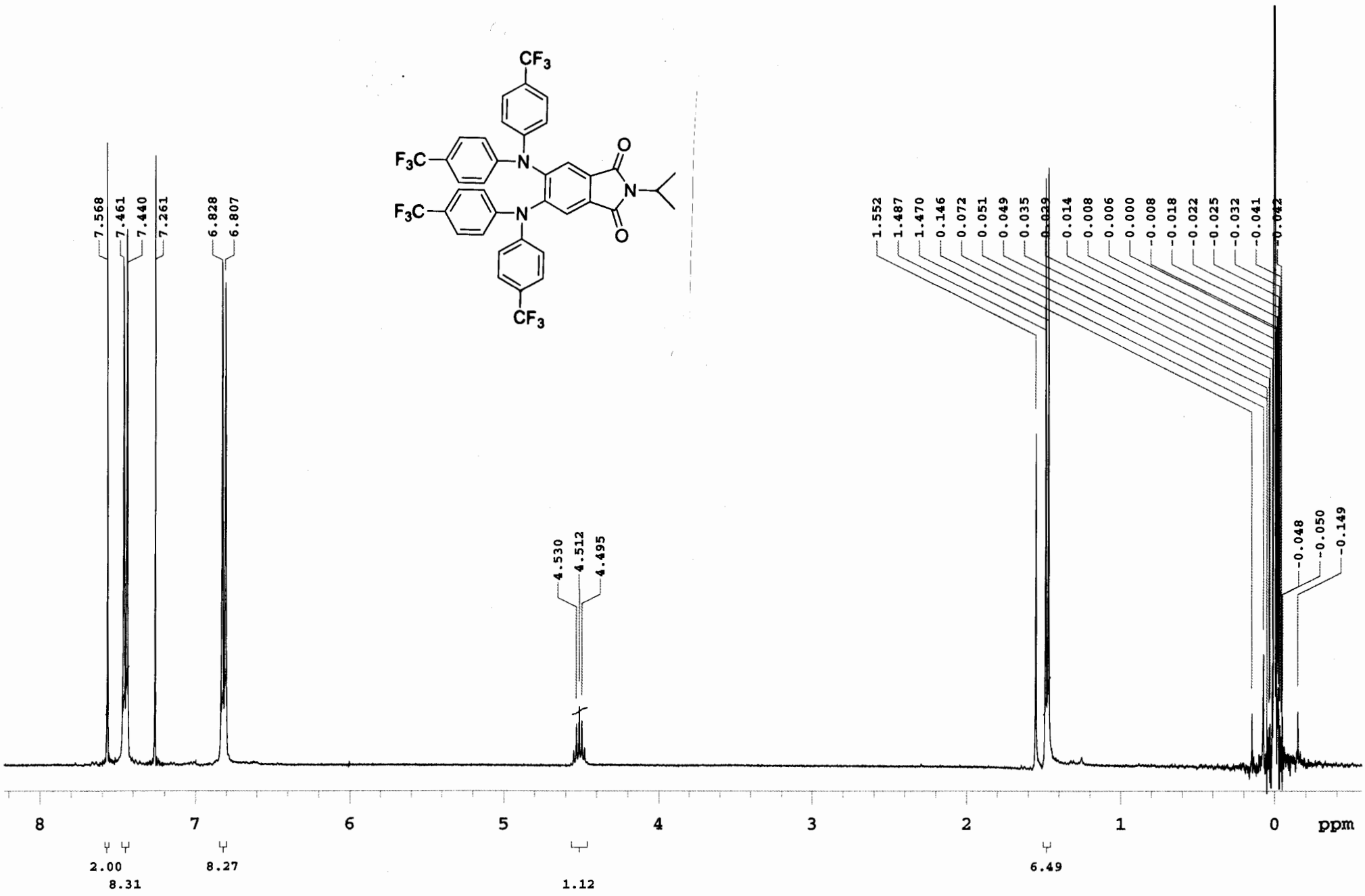
F3C
F3C
CF3
N
N
N
O
O
O
tBu

^{1}H NMR of **1g**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6.828
6.807
4.530
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4.495
1.552
1.487
1.470
0.146
0.072
0.051
0.049
0.035
0.029
0.014
0.008
0.006
0.000
-0.008
-0.018
-0.022
-0.025
-0.032
-0.041
-0.042
-0.048
-0.050
-0.149
8
7
6
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1.12
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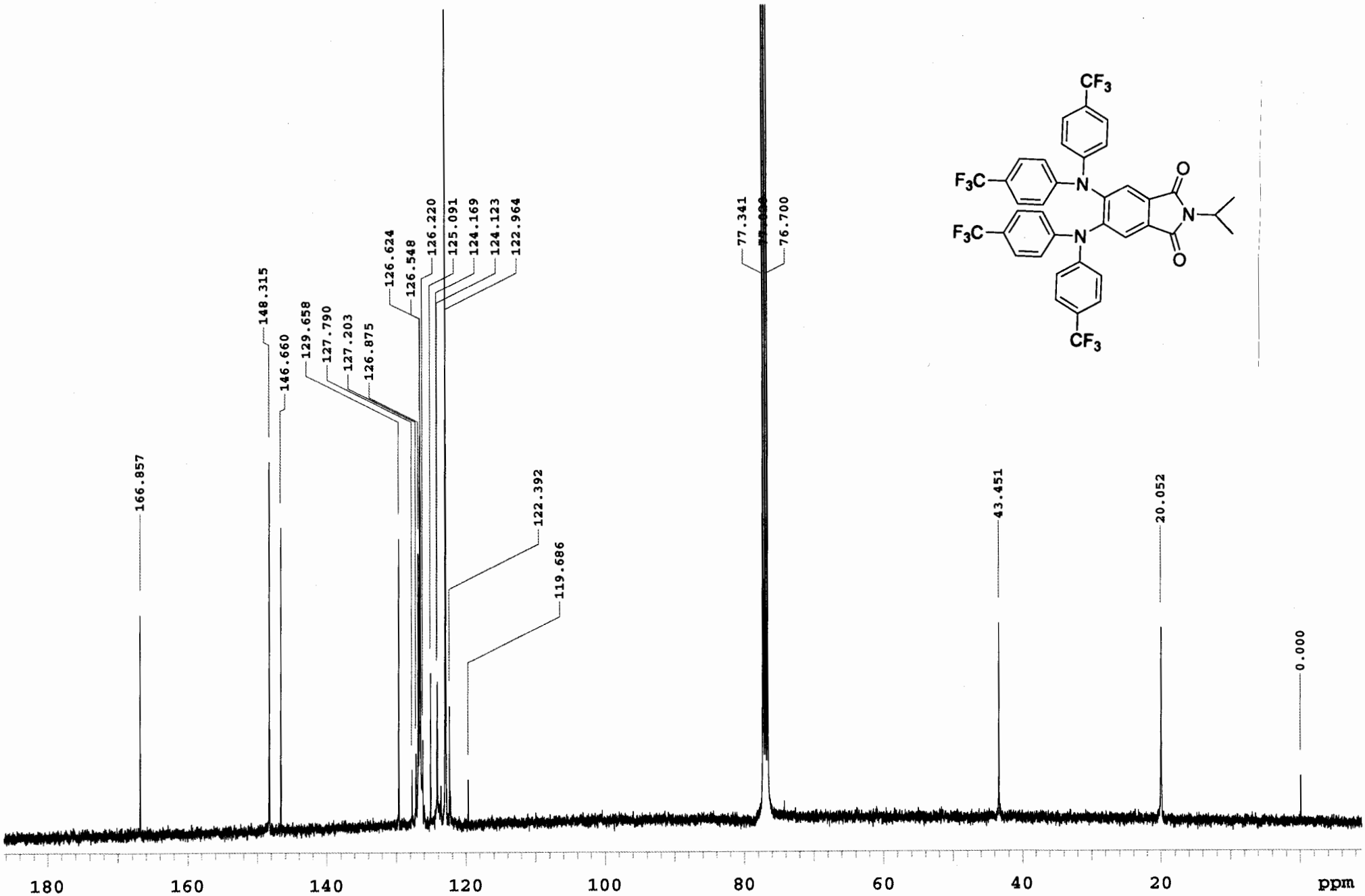
^{13}C NMR of **1g**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125.091
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122.964
122.392
119.686
77.341
76.700
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160
140
120
100
80
60
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F3C
CF3
N
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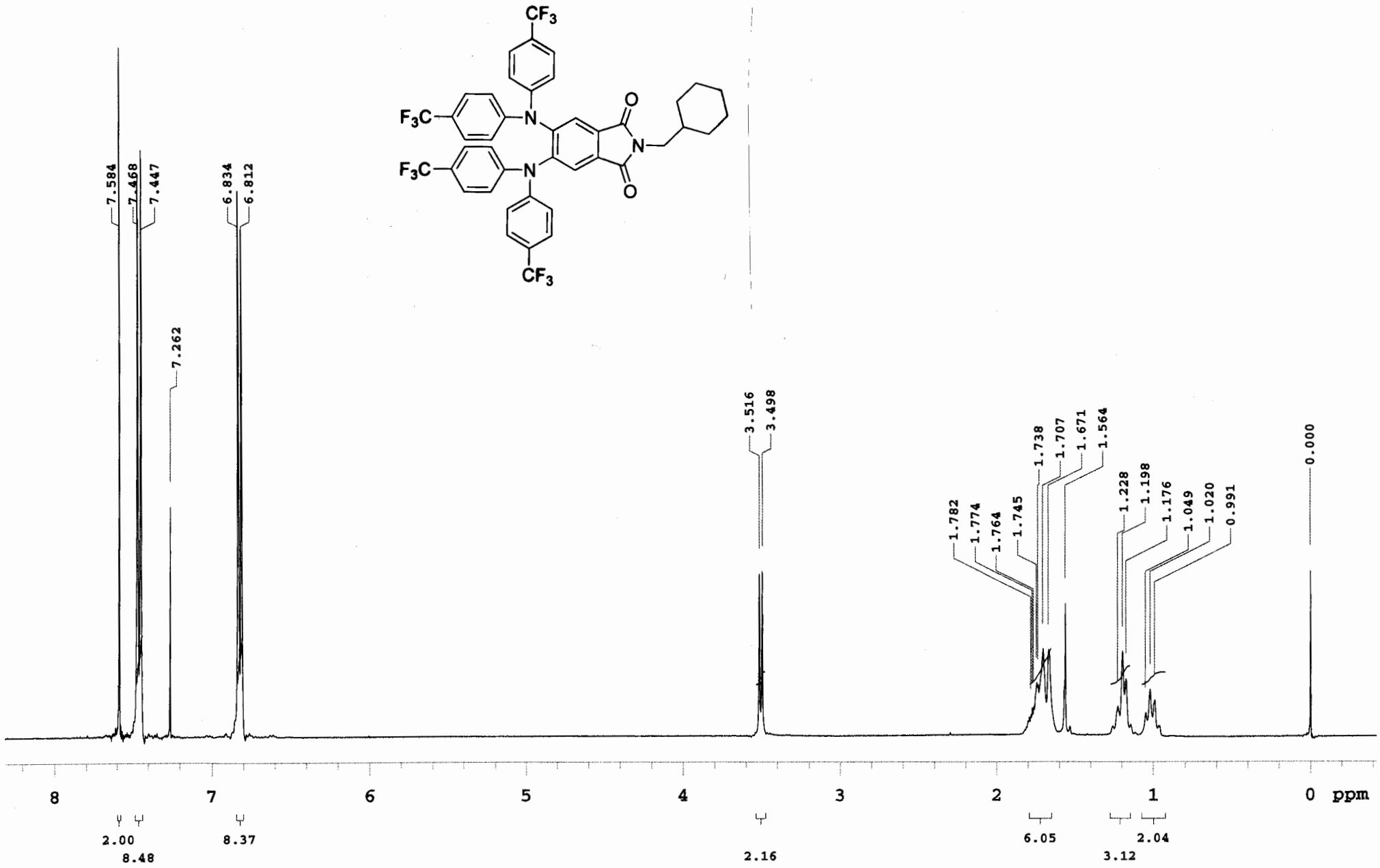
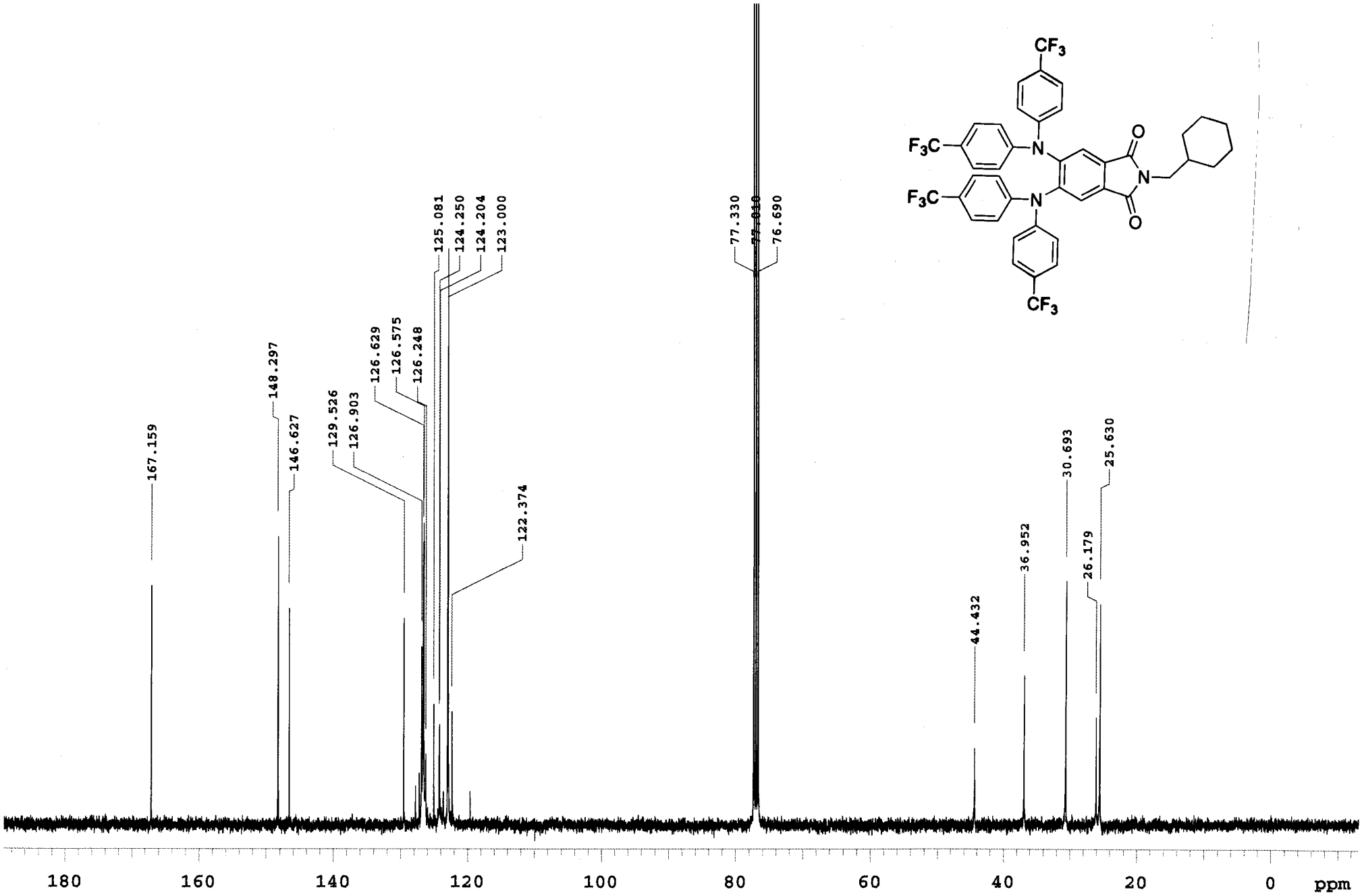
N
O
O
O

^{1}H NMR of **1h**


CF3
F3C
N
O
N
O
F3C
N
CF3
7.584
7.468
7.447
7.262
6.834
6.812
3.516
3.498
1.782
1.774
1.764
1.745
1.738
1.707
1.671
1.564
1.228
1.198
1.176
1.049
1.020
0.991
0.000
8
7
6
5
4
3
2
1
0
ppm
2.00
8.48
8.37
2.16
6.05
3.12
2.04

^{13}C NMR of **1h**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126.903
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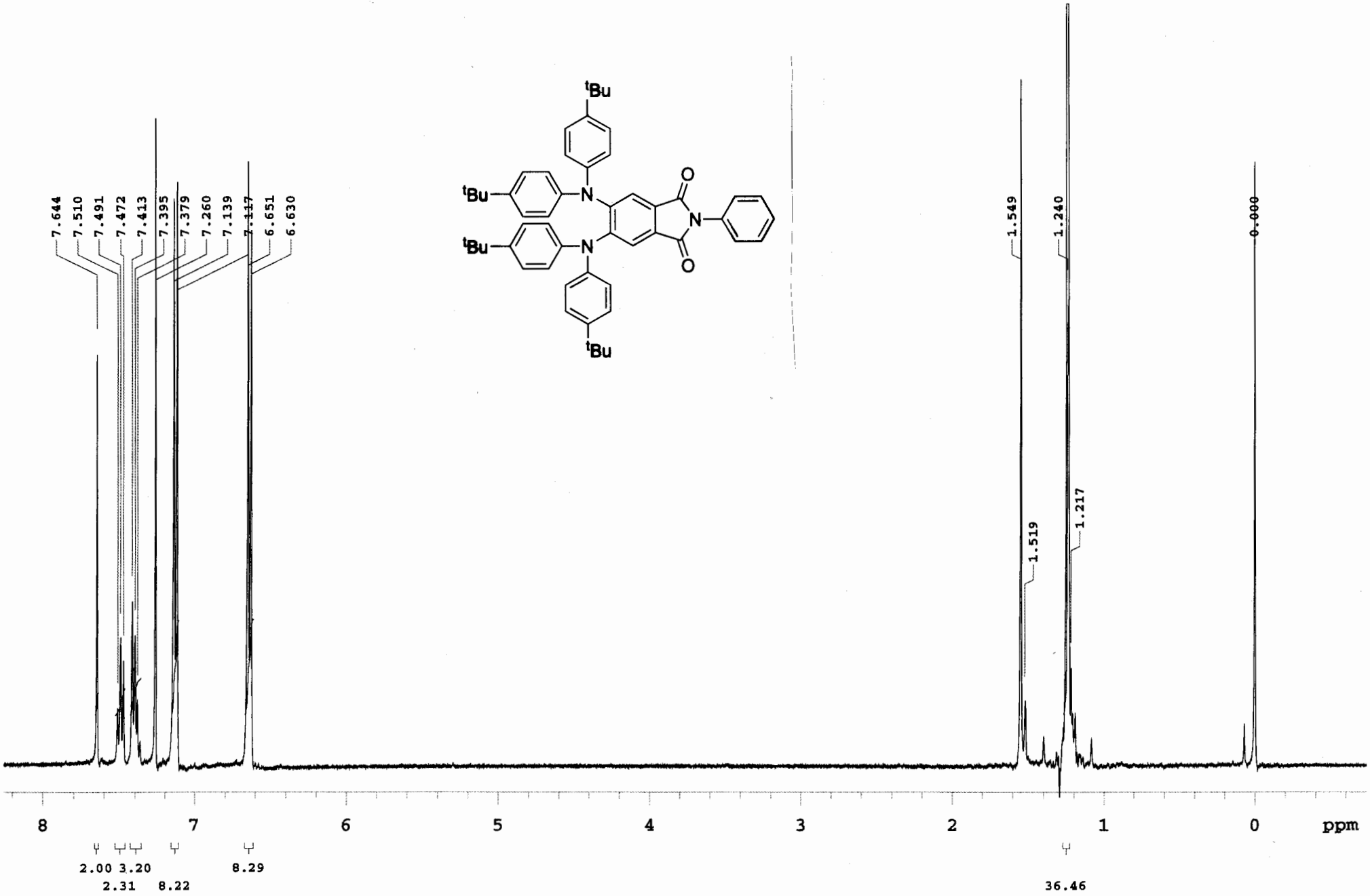
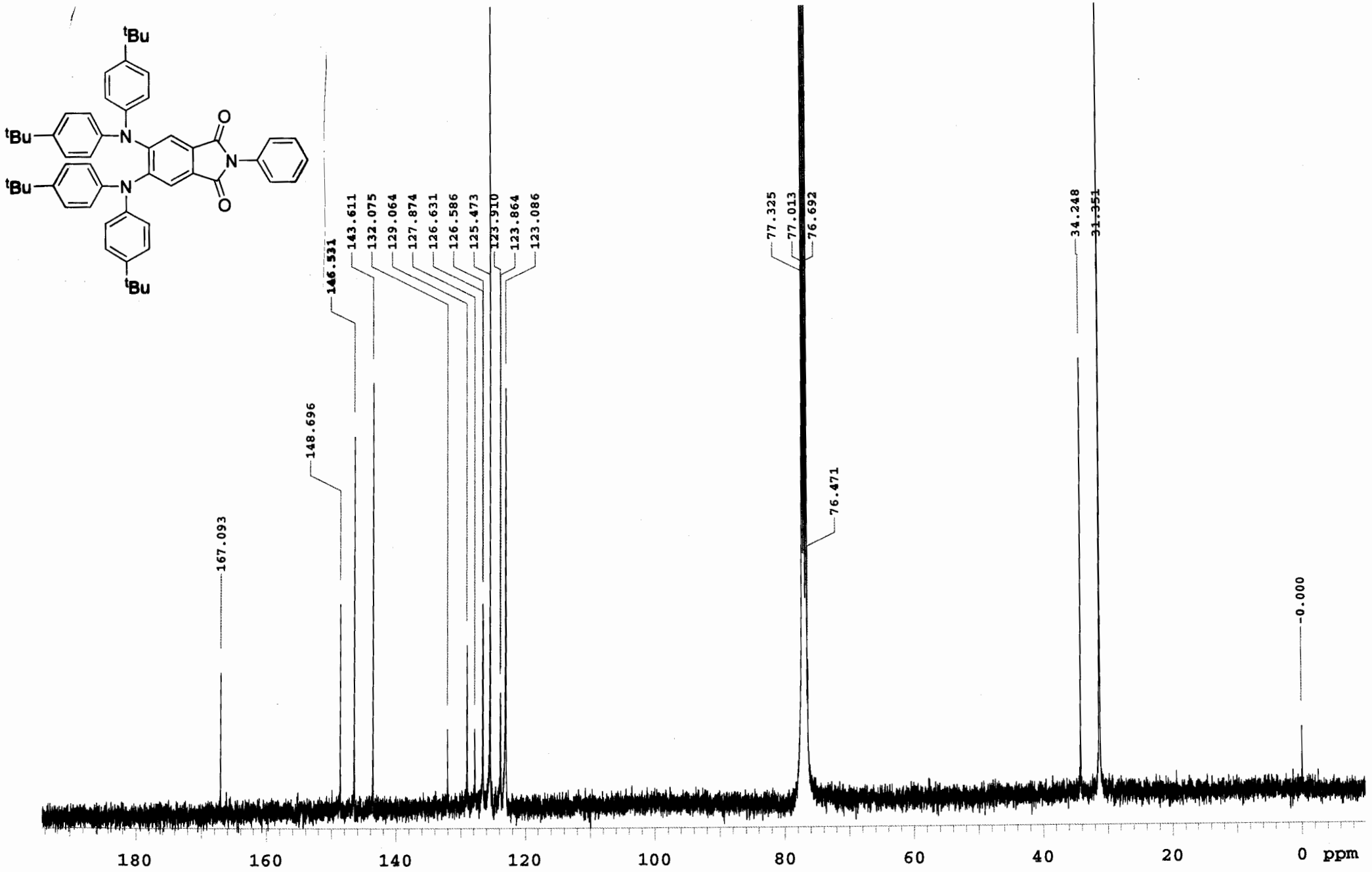
126.575
126.248
125.081
124.250
124.204
123.000
122.374
77.330
77.010
76.690
44.432
36.952
30.693
26.179
25.630
180
160
140
120
100
80
60
40
20
0
ppm
CF3
F3C
F3C
CF3
N
N
N
O
O
O

^{1}H NMR of **1i**


7.644
7.510
7.491
7.472
7.413
7.395
7.379
7.260
7.139
7.117
6.651
6.630
1.549
1.519
1.240
1.217
0.000
tBu
tBu
tBu
tBu
N
N
N
O
O
O
8
7
6
5
4
3
2
1
0
ppm
2.00
3.20
2.31
8.22
8.29
36.46

^{13}C NMR of **1i**


tBu
tBu
tBu
tBu
N
N
O
O
N
146.531
143.611
132.075
129.064
127.874
126.631
126.586
125.473
123.910
123.864
123.086
148.696
167.093
77.325
77.013
76.692
76.471
34.248
31.351
-0.000
180
160
140
120
100
80
60
40
20
0
ppm