Supporting Information

Palladium Catalyzed Direct Arylation of Polysubstituted Benzofurans

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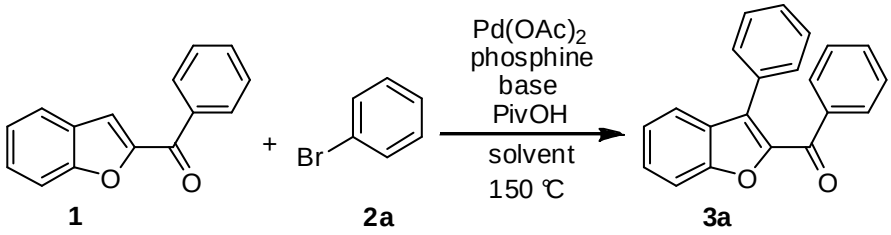
GENERAL INFORMATION

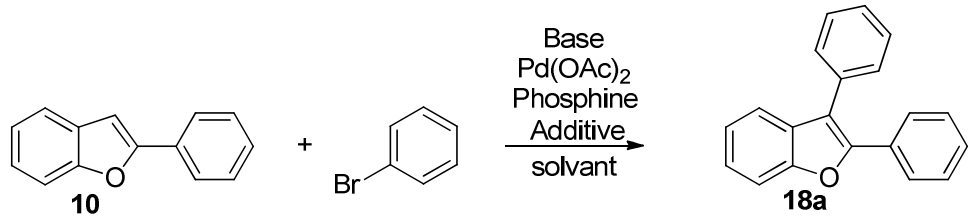
All reactions were performed under argon atmosphere unless otherwise noted. DMA and mesitylene were stored over molecular sieves. Catalyst $Pd(OAc)_2$ was purchased from Aldrich. All other commercial reagents and solvents were used as received without additional purification. $Pd(OAc)_2$ and $P(t\text{-}Bu)_2Me{\bullet}HBF_4$ were stored under argon and weighed to air. Reactions were followed with TLC (0.25 mm silica gel 60-F plates). Vizualisation was accomplished with UV light. Flash chromatographies were carried out on silica gel 320-400 mesh. Yields refer to chromatographically and spectroscopically pure materials. ^1H NMR spectra were recorded at 300MHz. ^{13}C NMR spectra were recorded at 75 MHz with complete proton decoupling. Chemical shifts are reported in ppm relative to the residual solvent peak ($CDCl_3$) as the internal reference, coupling constants are given in Hertz. Peak assignment was unambiguously performed using HMQC and HMBC technics. IR spectra were taken with FT-IR. Melting points were determined by capillary method and are uncorrected.



1 **2a** **3a**

Base [a]	**Phosphine (mol%)**	**Additive (mol%)**	**Solvent**	**Time (h)**	**Conversion (%)**
Cs_2CO_3	P(*t*-Bu)$_2$Me (4)	PivOH (30)	DMA	16	22
Cs_2CO_3	P(*t*-Bu)$_2$Me (10)	PivOH (30)	DMA	16	55
K_2CO_3	P(*t*-Bu)$_2$Me (10)	PivOH (30)	DMA	16	73
KOAc	P(*t*-Bu)$_2$Me (10)	PivOH (30)	DMA	16	59
CsOAc	P(*t*-Bu)$_2$Me (10)	PivOH (30)	DMA	16	59
Cs_2CO_3	PPh_3 (10)	PivOH (30)	DMA	16	10
Cs_2CO_3	PCy_3 (10)	PivOH (30)	DMA	16	11
Cs_2CO_3	PEt_3 (10)	PivOH (30)	DMA	16	21
Cs_2CO_3	P(*t*-Bu)$_2$Me (10)	PivOH (60)	DMA	16	74
Cs_2CO_3	P(*t*-Bu)$_2$Me (10)	PivOH (120)	DMA	16	78
Cs_2CO_3	P(*t*-Bu)$_2$Me (10)	PivOH (60)	Mesitylene	16	94
K_2CO_3	P(*t*-Bu)$_2$Me (10)	PivOH (60)	mesitylene	16	97
K_2CO_3	P(*t*-Bu)$_2$Me (10)	PivOH (30)	Mesitylene	16	96
Cs_2CO_3	PCy_3 (10)	PivOH (60)	Mesitylene	16	95
K_2CO_3	PPh_3 (10)	PivOH (30)	Mesitylene	16	32
K_2CO_3	P(*t*-Bu)$_2$Me (10)	PivOH (60)	Mesitylene	4	68
K_2CO_3	P(*t*-Bu)$_2$Me (10)	PivOH (60)	Mesitylene	8	88
K_2CO_3	P(*t*-Bu)$_2$Me (10)	PivOH (30)	Mesitylene	24	95
K_2CO_3	P(*t*-Bu)$_2$Me (4)	PivOH (30)	Mesitylene	16	84
K_2CO_3	P(*t*-Bu)$_2$Me (6)	PivOH (30)	Mesitylene	16	98
K_2CO_3	P(*t*-Bu)$_2$Me (8)	PivOH (30)	Mesitylene	16	99
K_2CO_3	P(*t*-Bu)$_2$Me (8)	-	Mesitylene	16	22

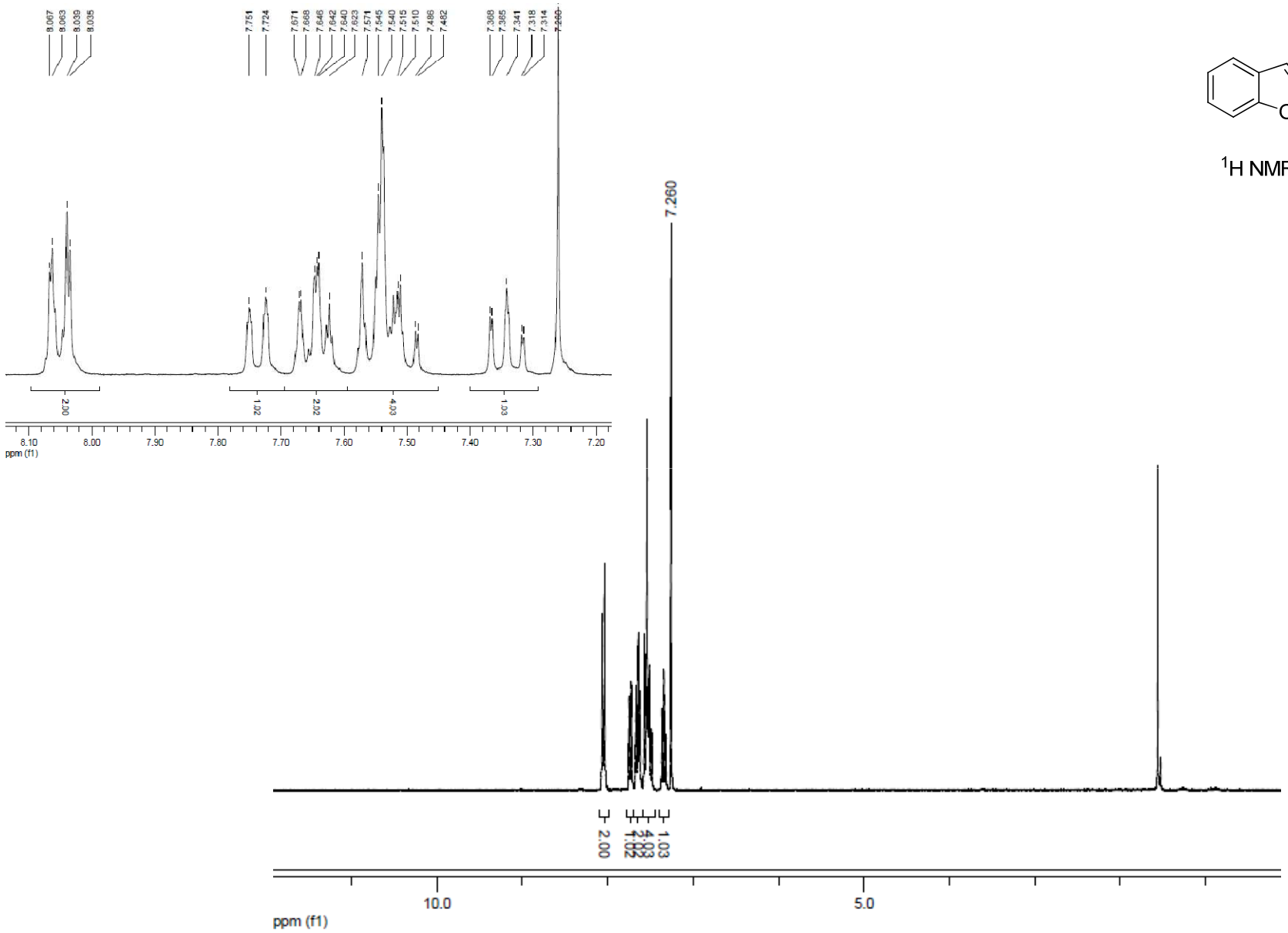
[a] Conditions: 2-benzoylbenzofuran (1 equiv.), bromobenzene (2 equiv.), $Pd(OAc)_2$ (2 mol%), phosphine, base (2 equiv.) and PivOH, 150 °C, solvent.

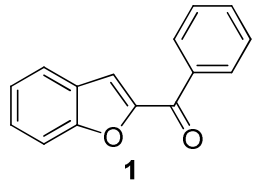


10 **18a**

Base	Mol% $Pd(OAc)_2$	Phosphine (mol%)	Additive	Solvent	T (°C)	Yield (%)
KOAc	2.5	PPh_3 (5)	-	DMA	150	Traces
KOAc	2.5	Johnphos (5)	-	DMA	150	62
KOAc	2.5	PCy_3•HBF_4 (5)	-	DMA	150	57
KOAc	2.5	P(*t*-Bu)$_2$Me •HBF_4 (5)	-	DMA	150	68
K_2CO_3	2.5	Johnphos (5)	-	DMA	150	21
K_3PO_4	2.5	Johnphos (5)	-	DMA	150	39
KOAc	5	Johnphos (15)	-	DMA	125	63
KOAc	5	Johnphos (15)	-	DMA	100	60
KOAc	2	P(*t*-Bu)$_2$Me •HBF_4 (8)	-	DMA	150	69
KOAc	2	P(*t*-Bu)$_2$Me •HBF_4 (8)	PivOH	DMA	150	67

[a] Conditions: 2-phenylbenzofuran (1 equiv.), bromobenzene (2 equiv.), $Pd(OAc)_2$, phosphine, base (2 equiv.), 16 h.





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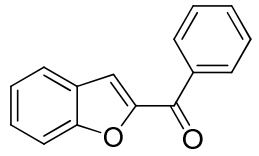
^{1}H NMR in $CDCl_3$



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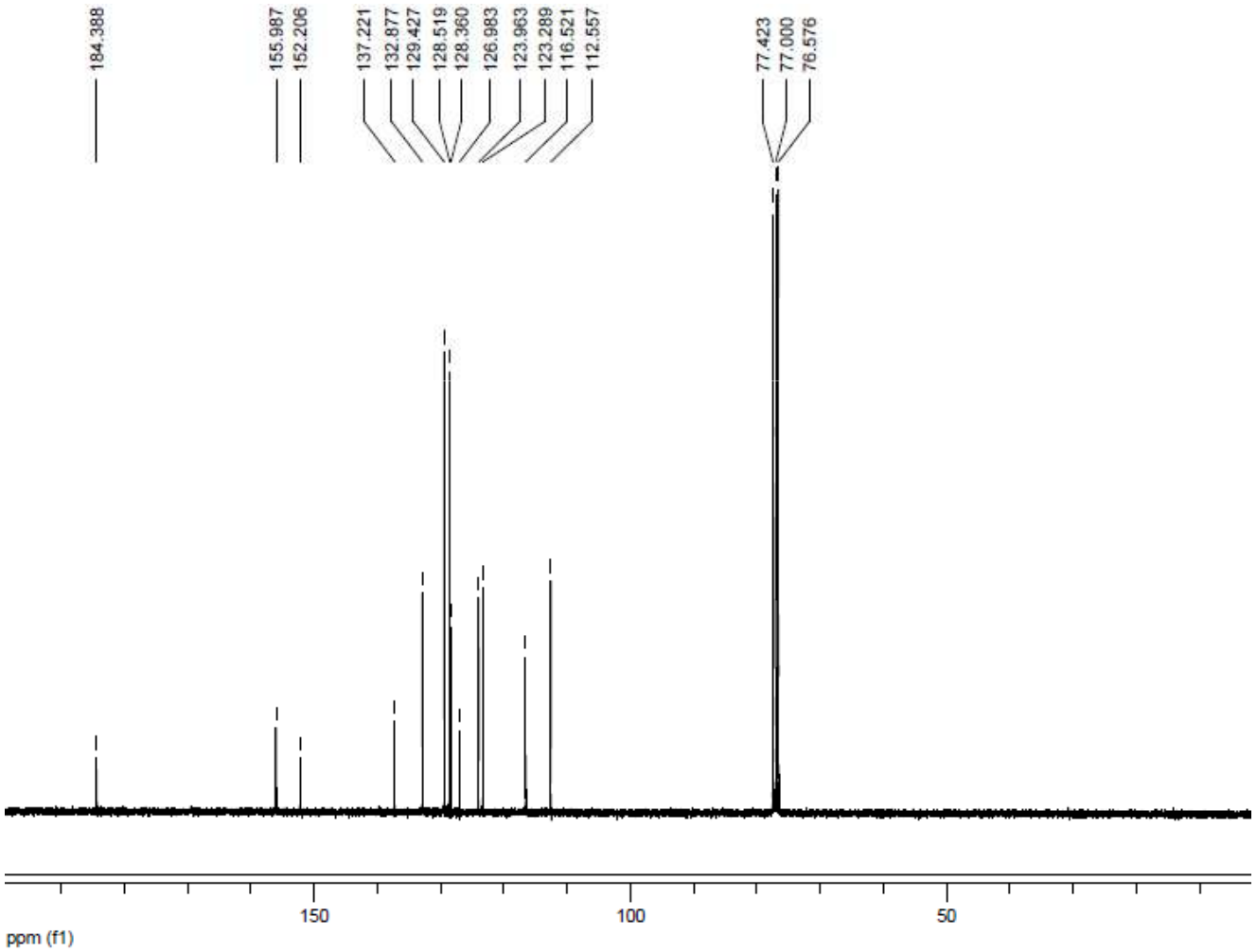
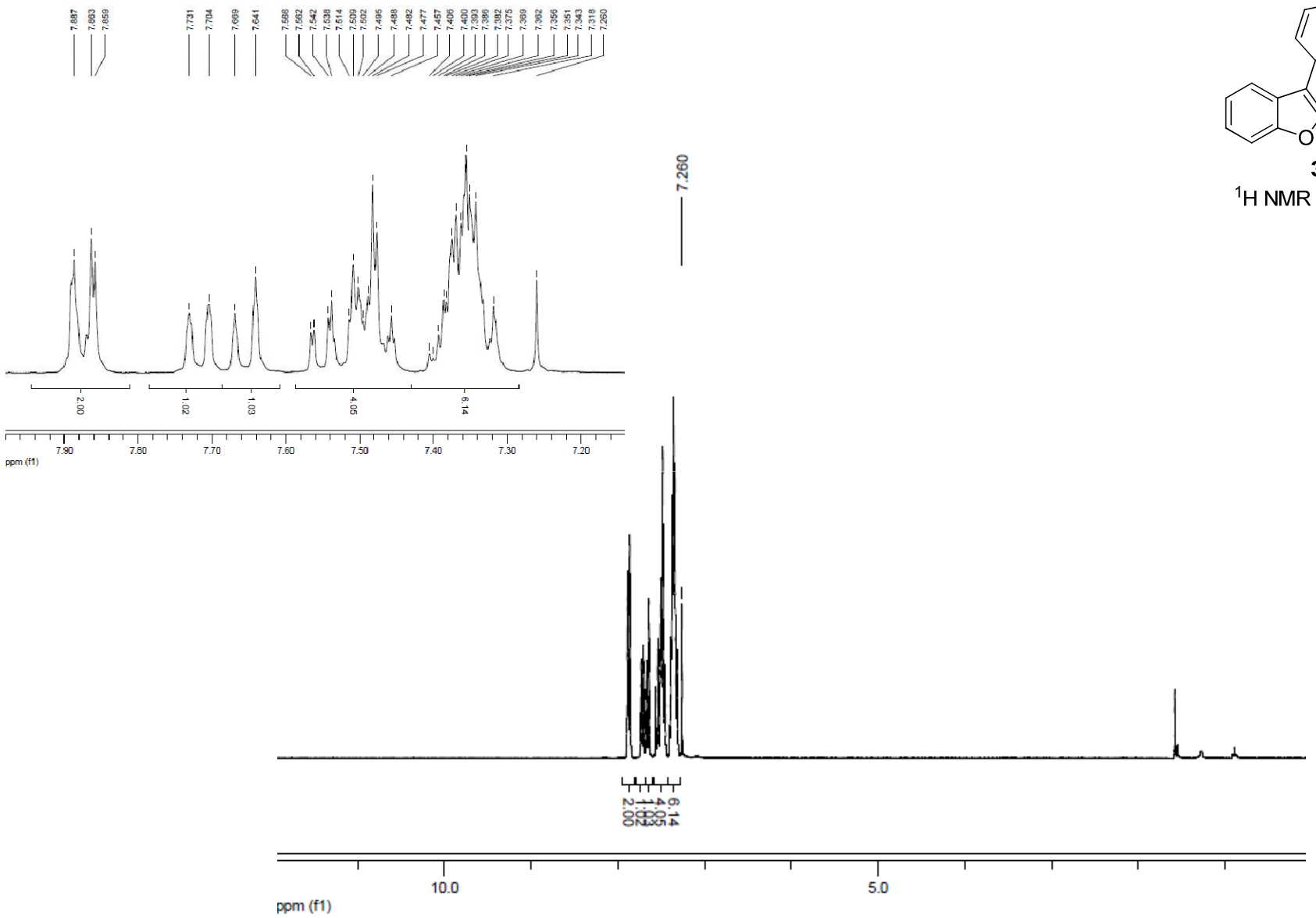
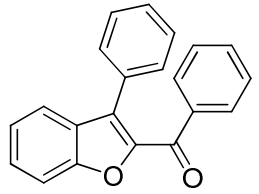
^{13}C NMR in $CDCl_3$

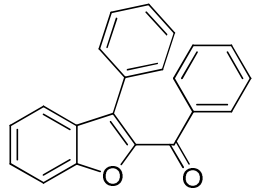






3a

^{1}H NMR in $CDCl_3$



3a

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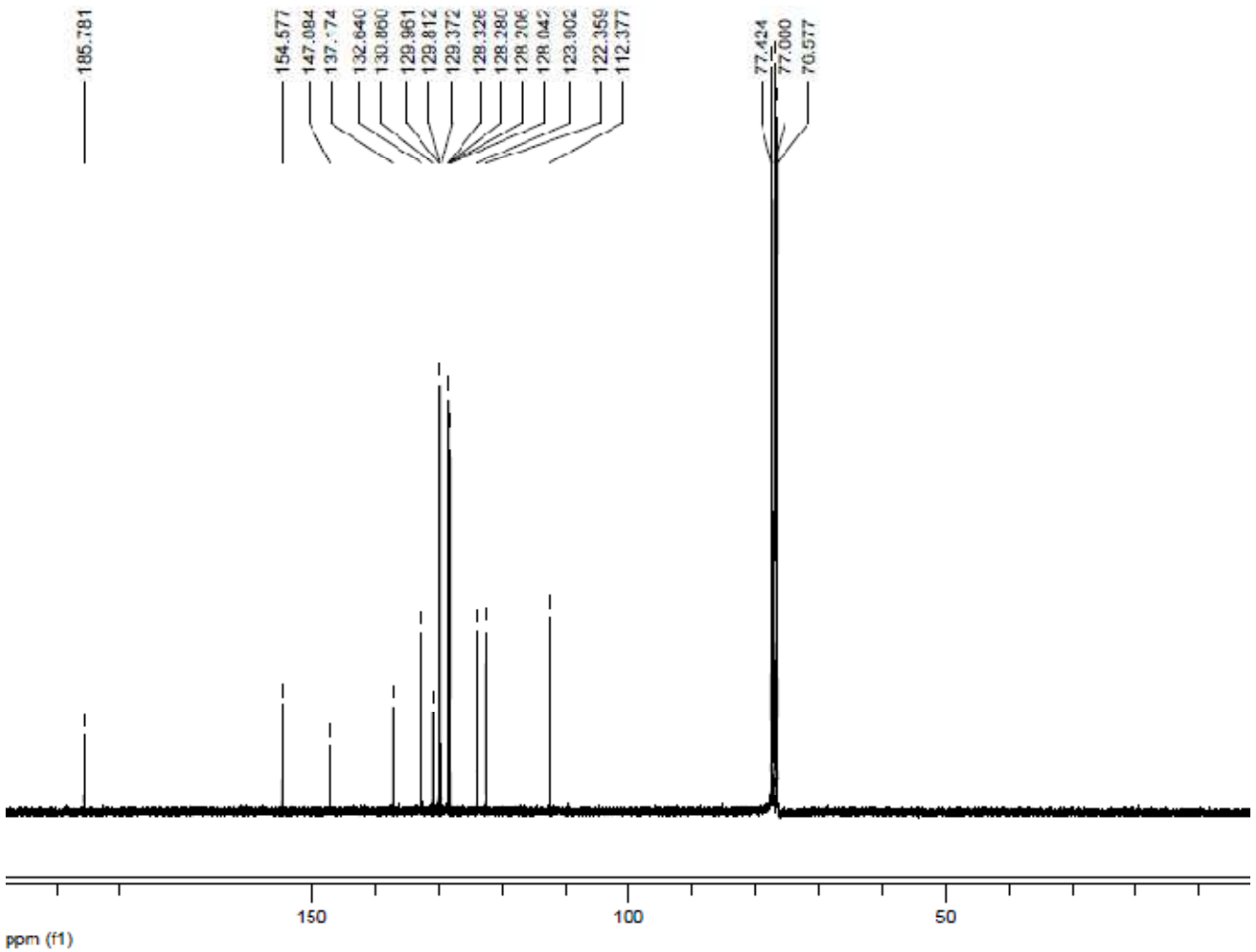
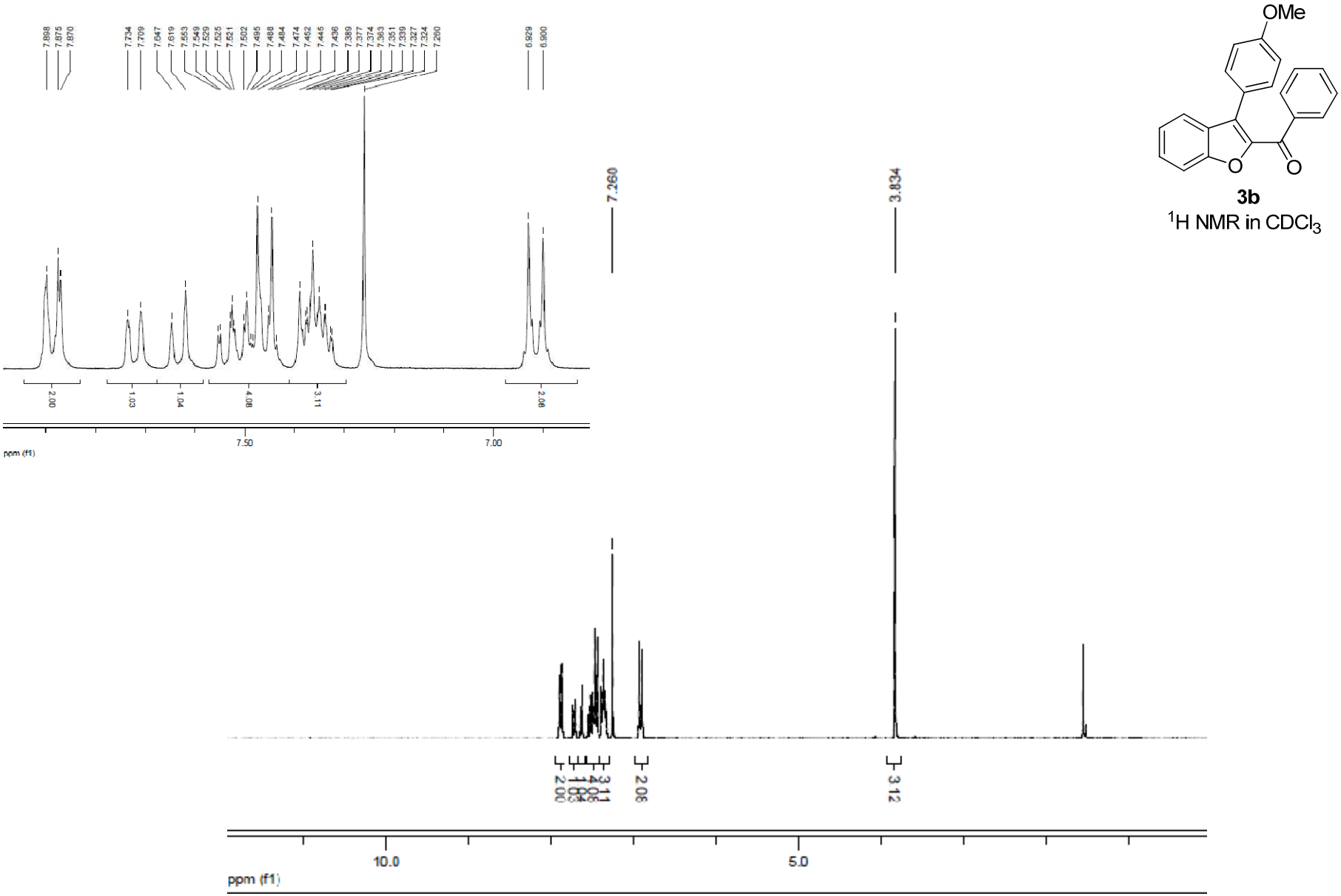
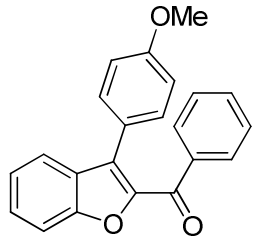




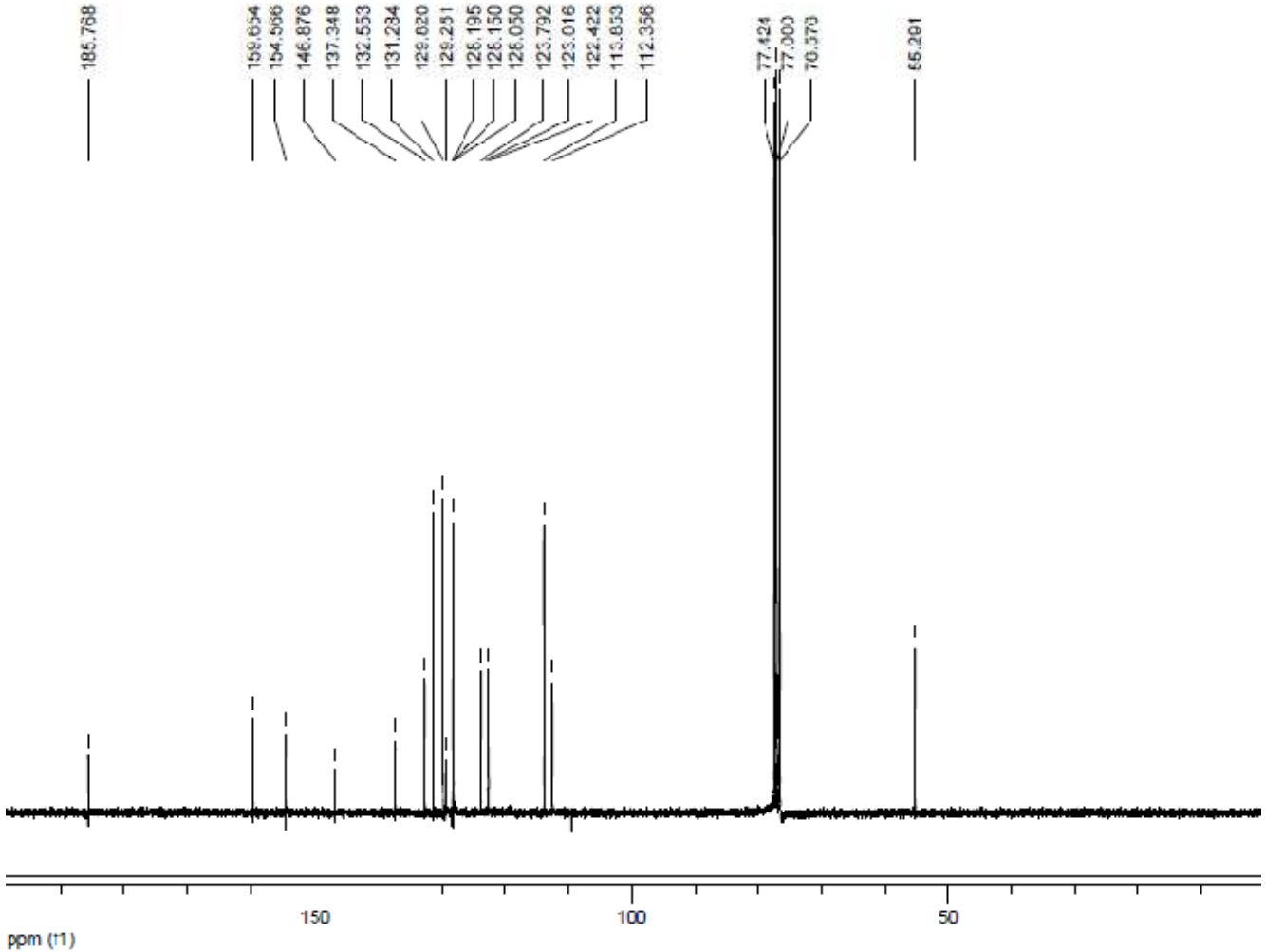
3b

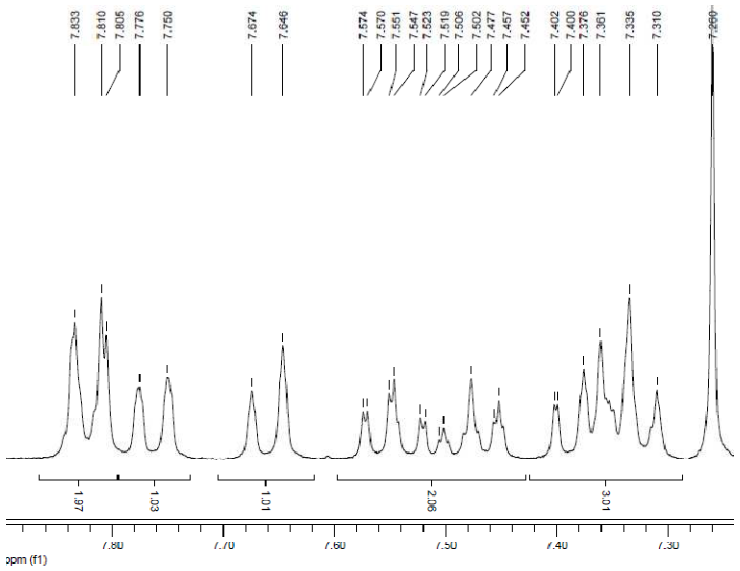
^{1}H NMR in $CDCl_3$

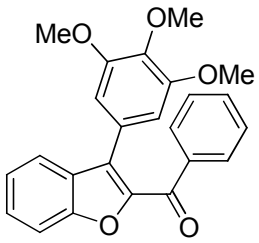


3b

^{13}C NMR in $CDCl_3$

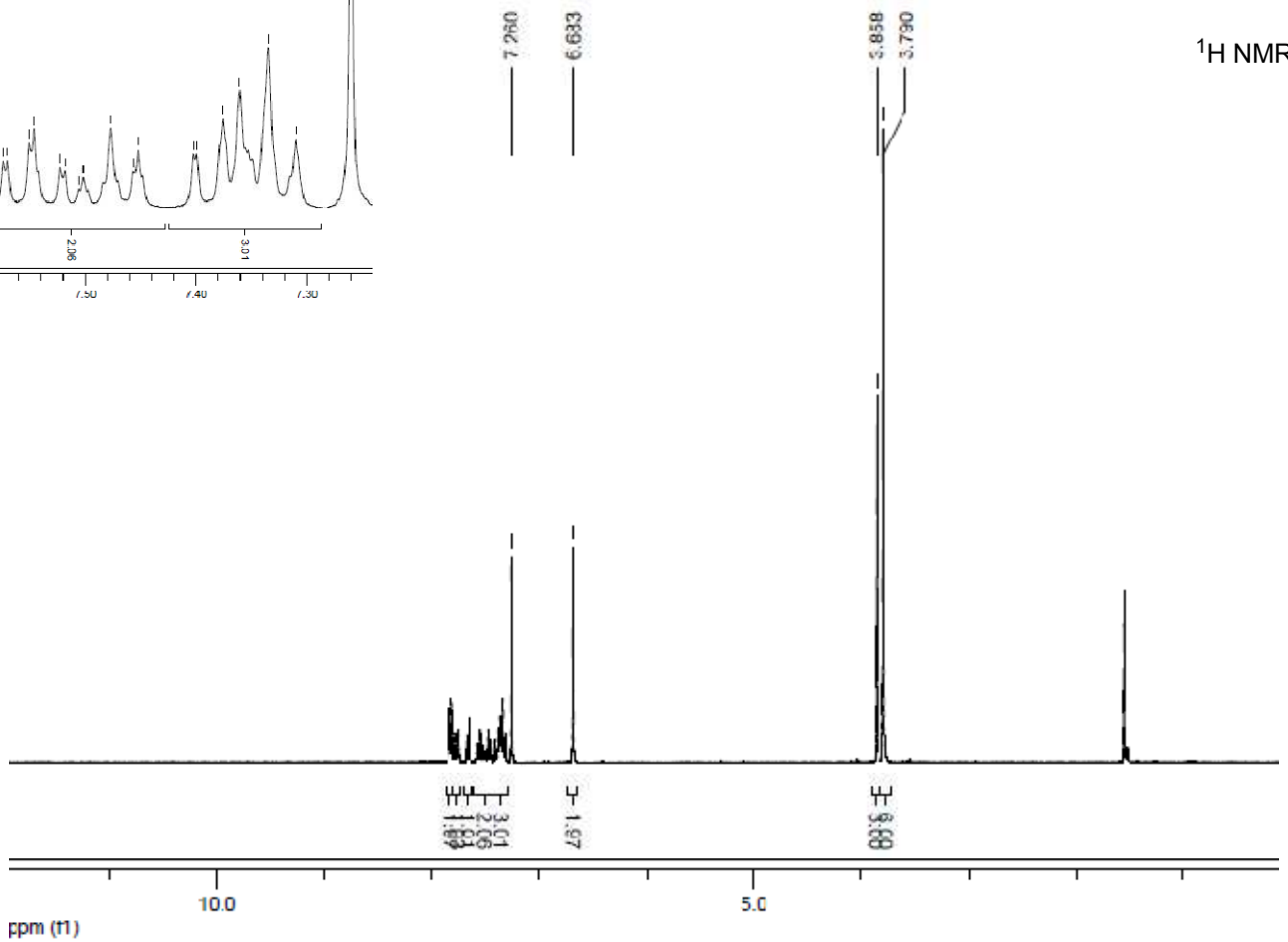


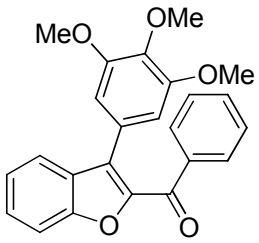




3c

^{1}H NMR in $CDCl_3$





3c

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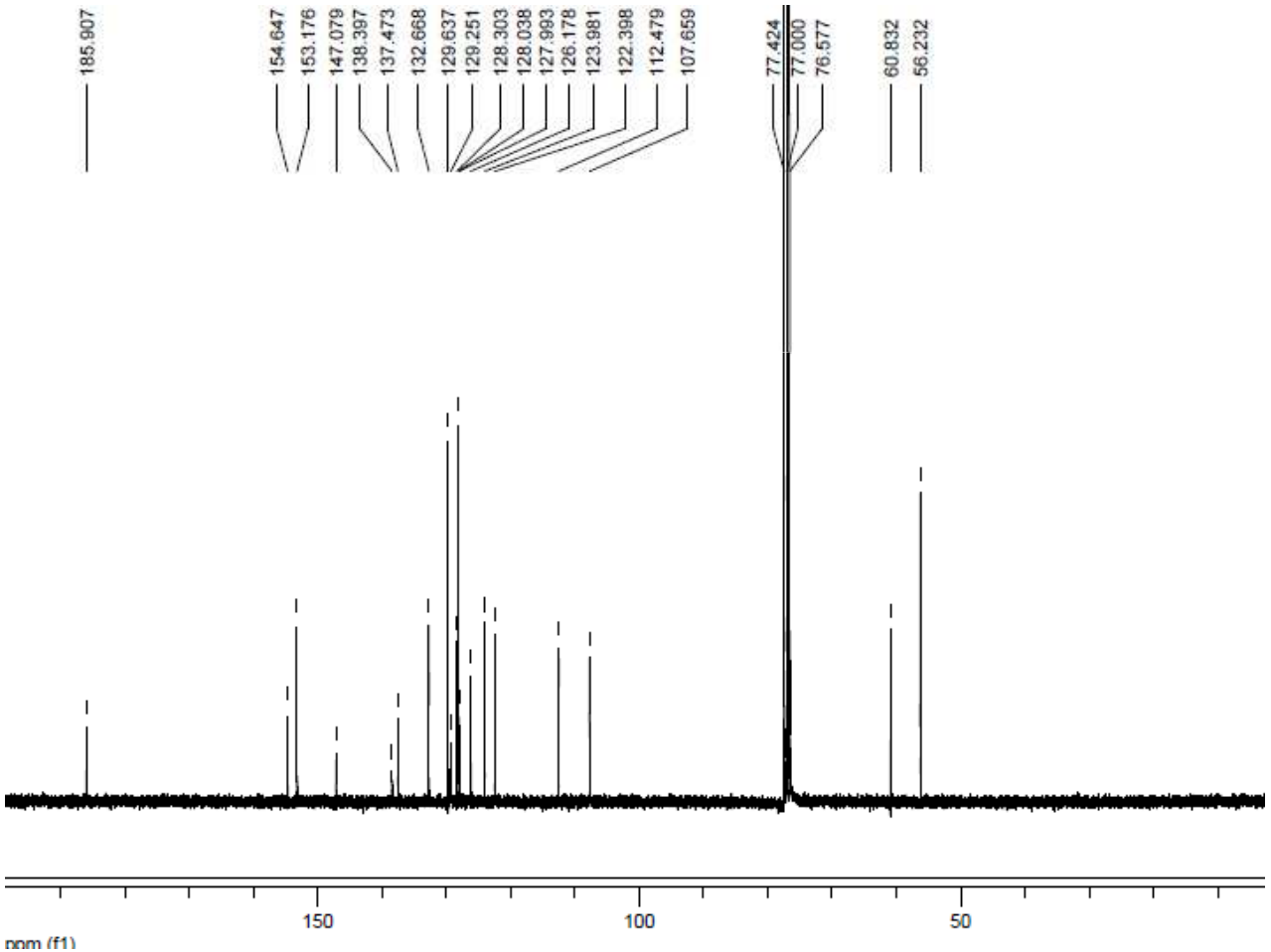
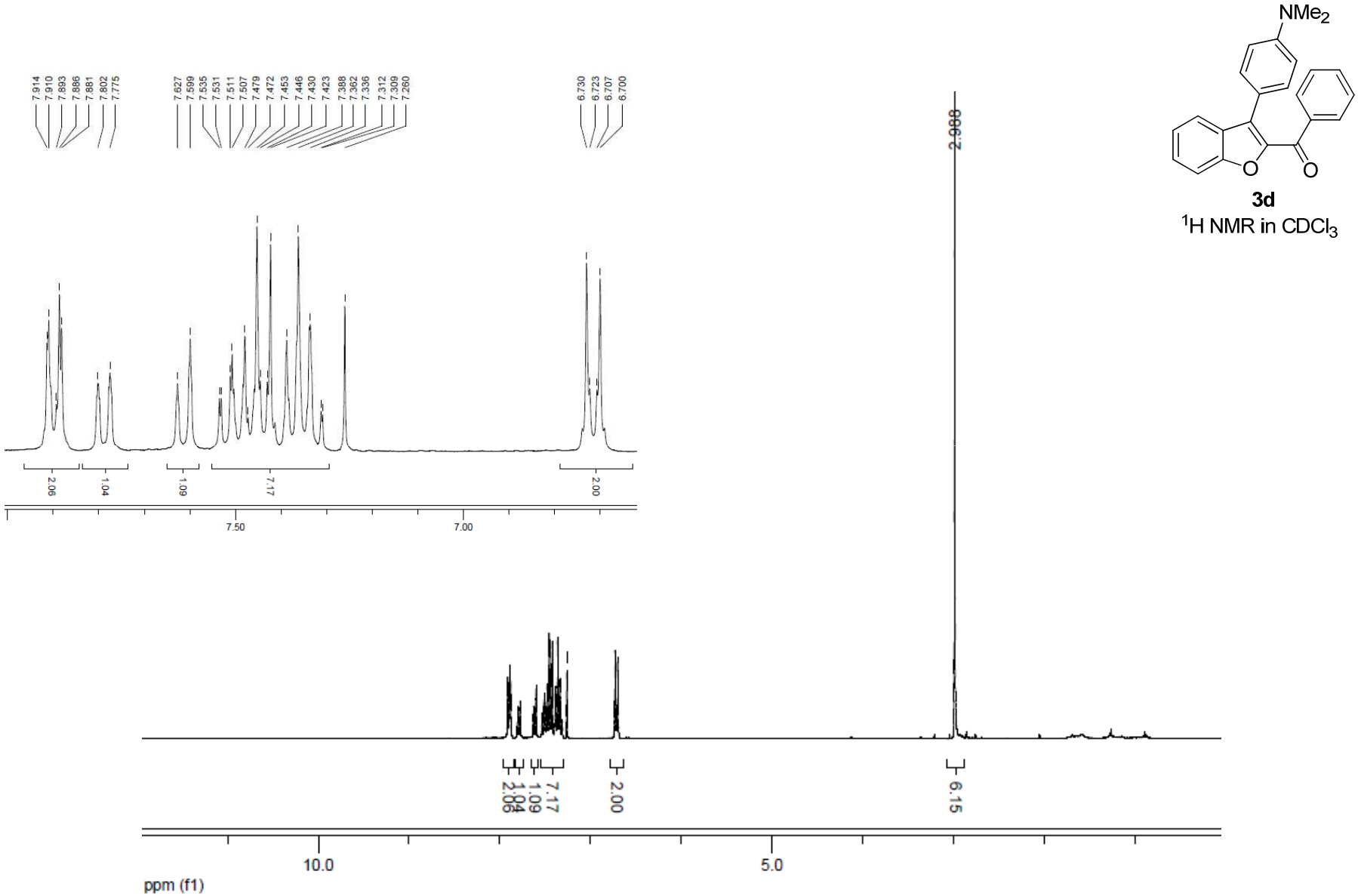
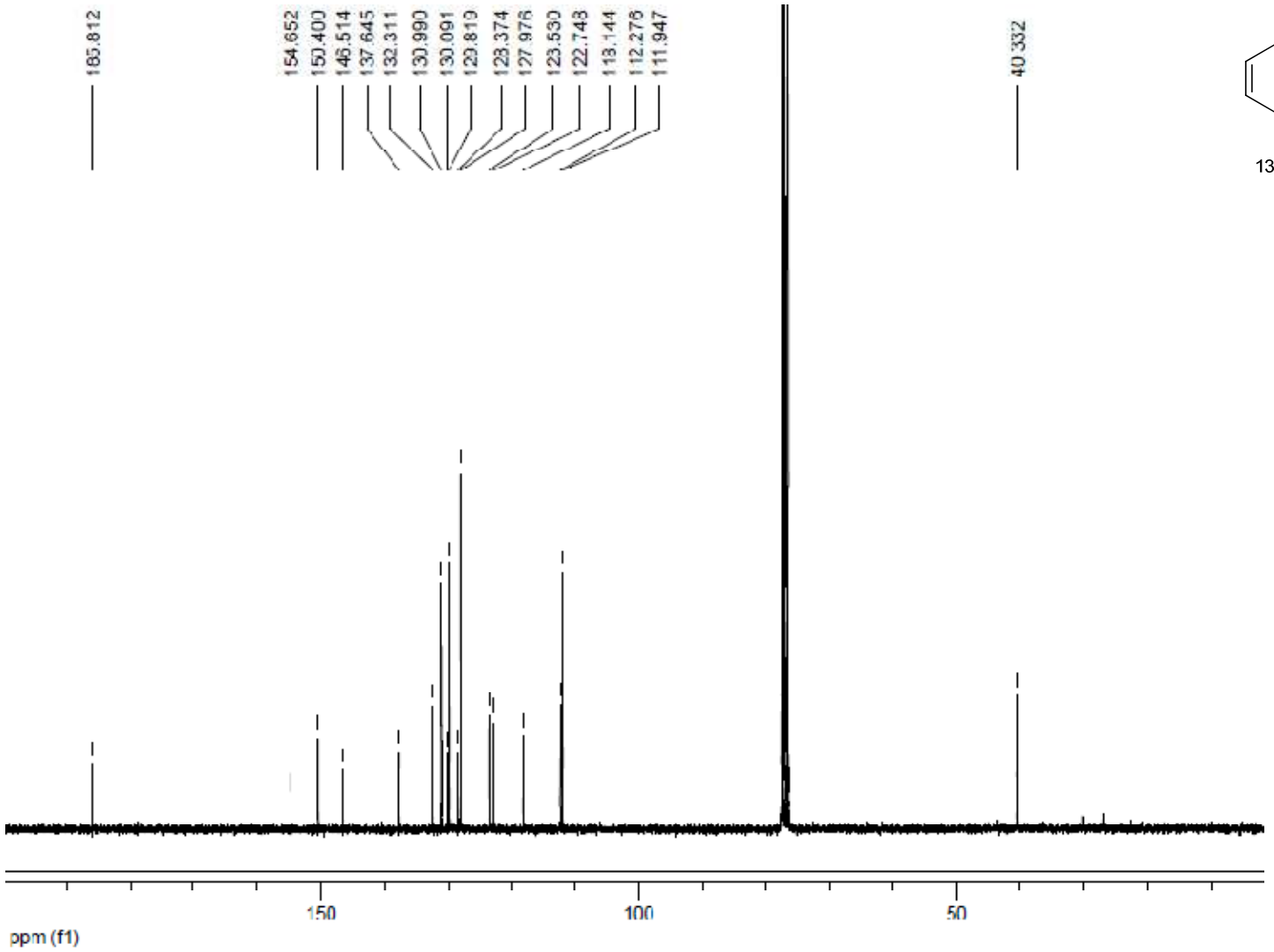
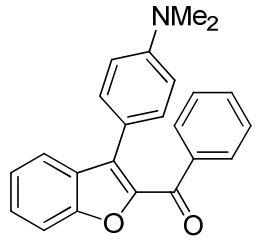


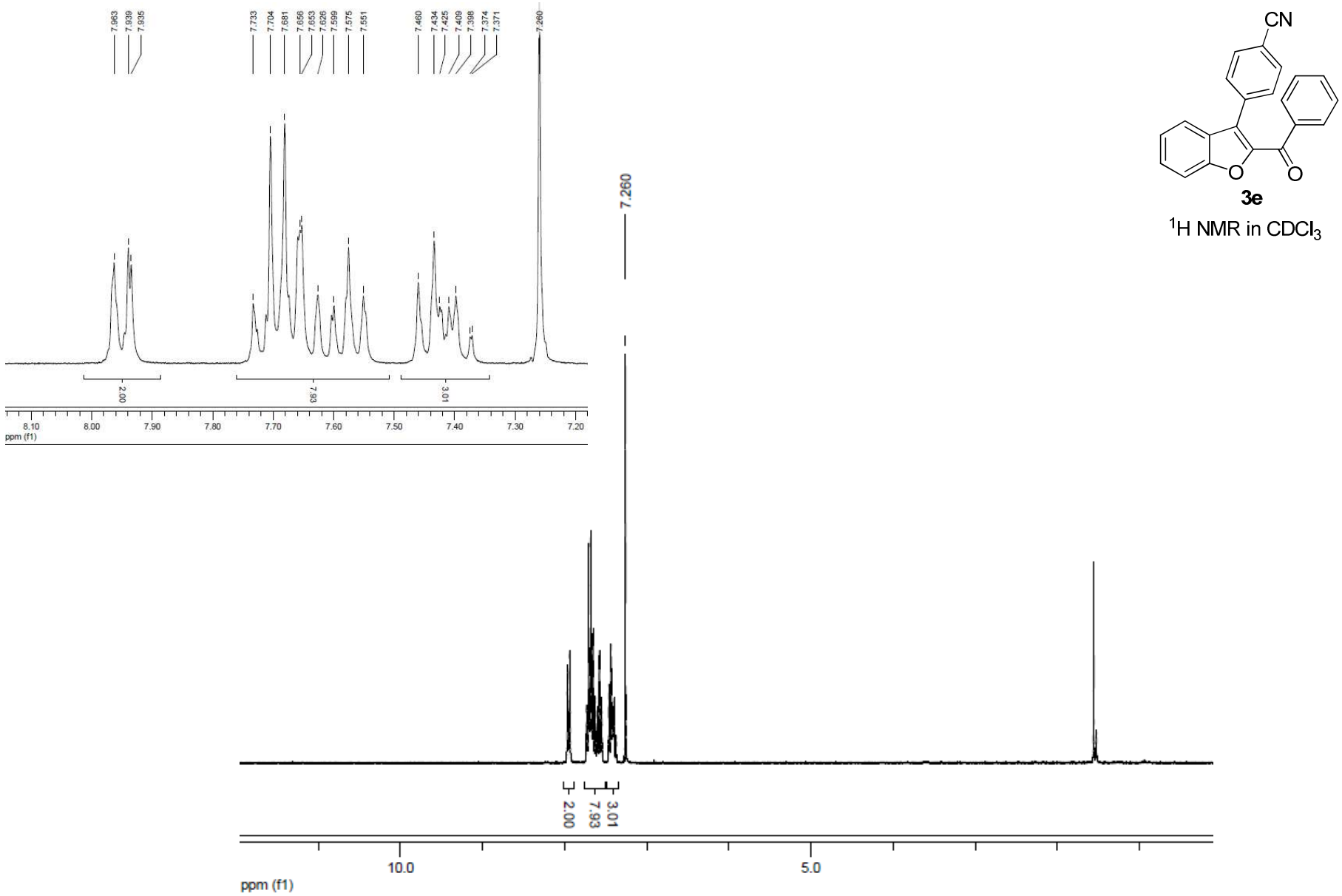

NMe2
O
O
3d
1H NMR in CDCl3
7.914
7.910
7.893
7.886
7.881
7.802
7.775
7.627
7.599
7.535
7.531
7.511
7.507
7.479
7.472
7.453
7.446
7.430
7.423
7.388
7.362
7.336
7.312
7.309
7.260
6.730
6.723
6.707
6.700
2.06
1.04
1.09
7.17
2.00
7.50
7.00
2.908
2.06
1.04
1.09
7.17
2.00
6.15
10.0
5.0
ppm (f1)





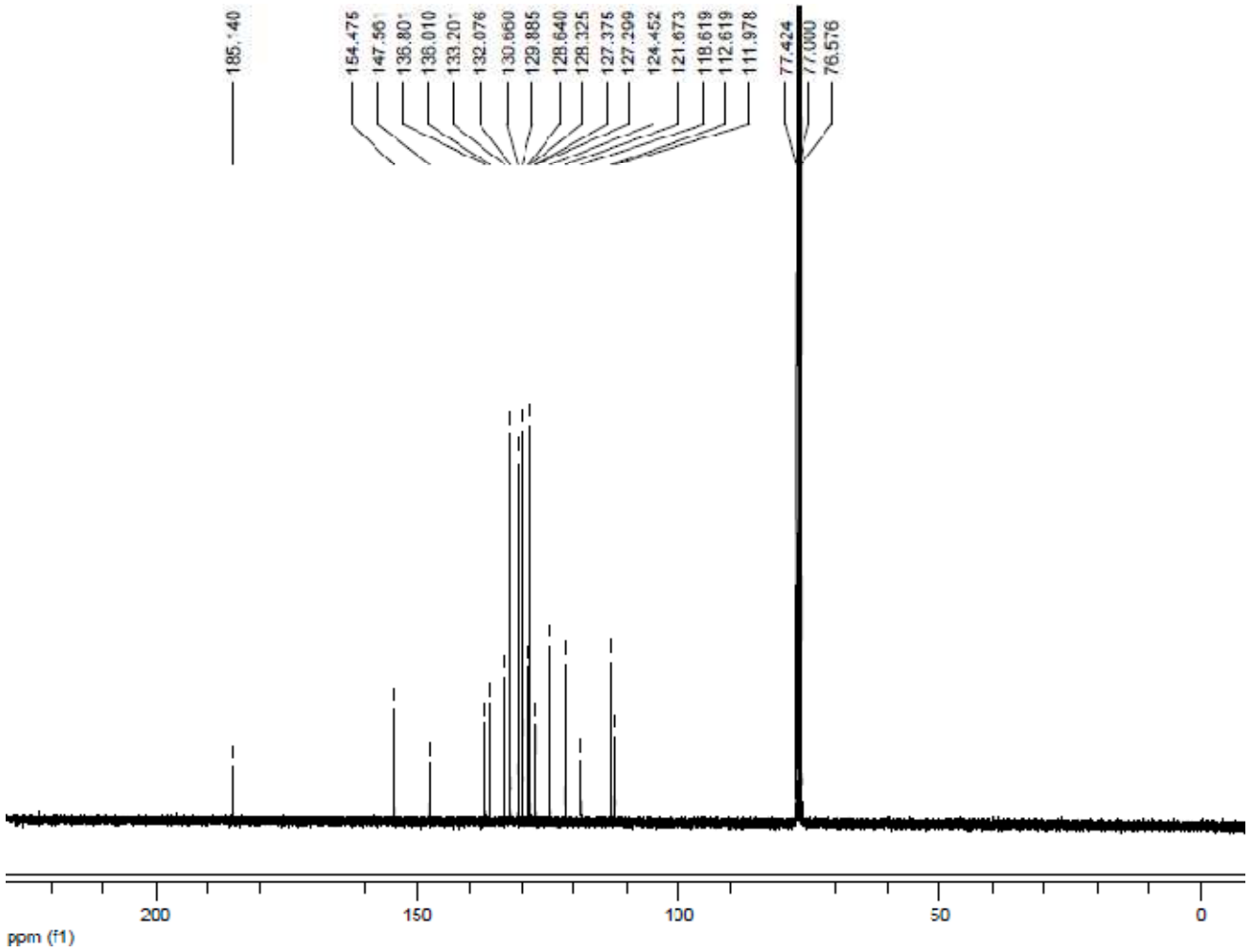
3d

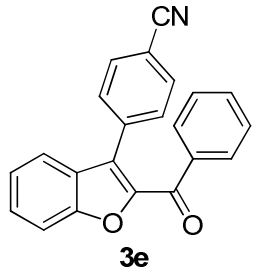
^{13}C NMR in $CDCl_3$



3e

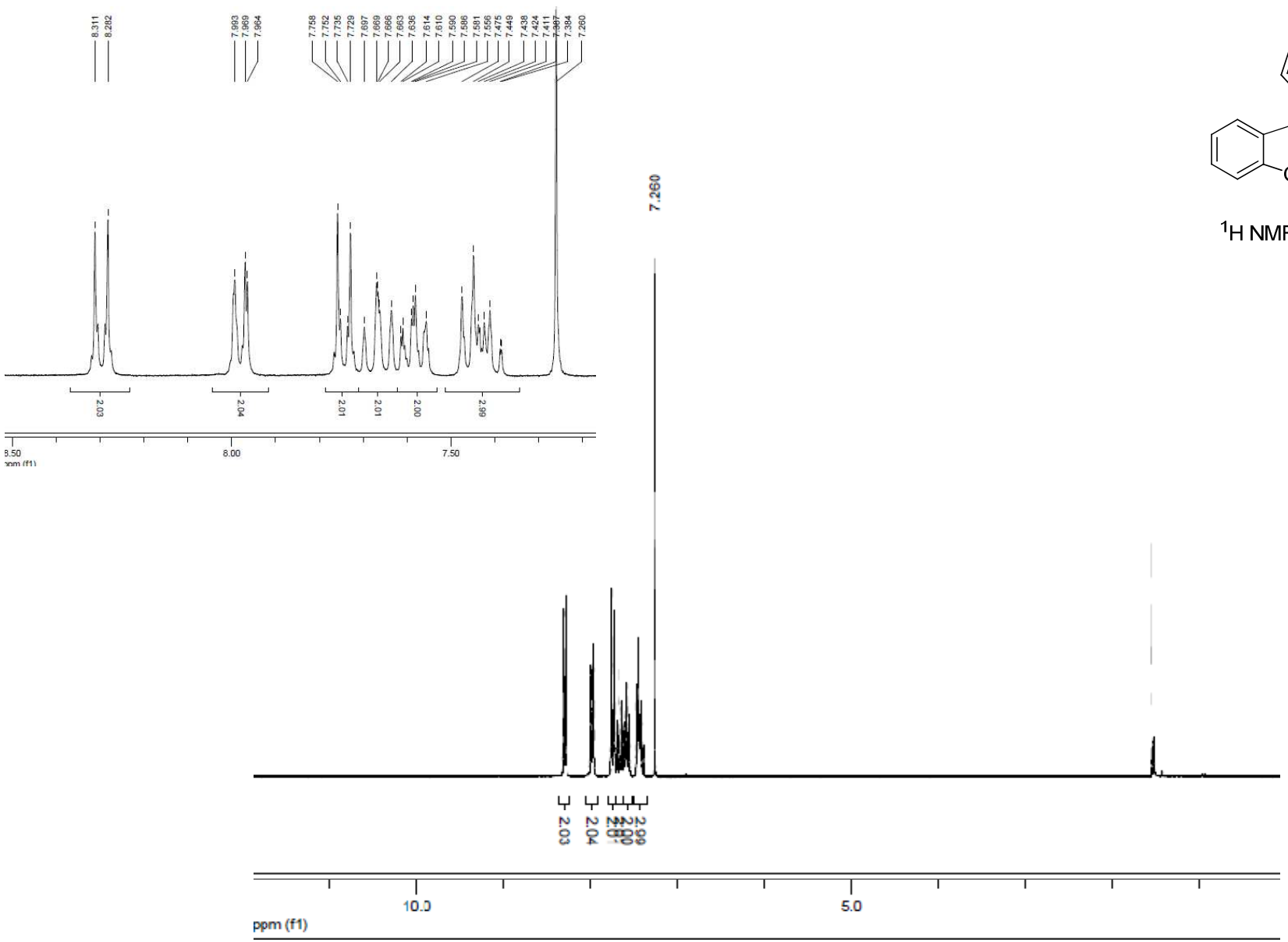
^{1}H NMR in $CDCl_3$

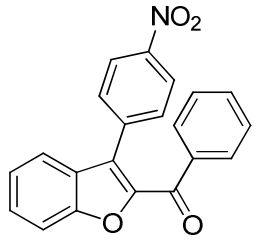




3e

^{13}C NMR in $CDCl_3$





3f

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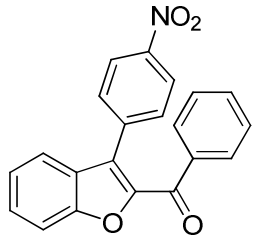

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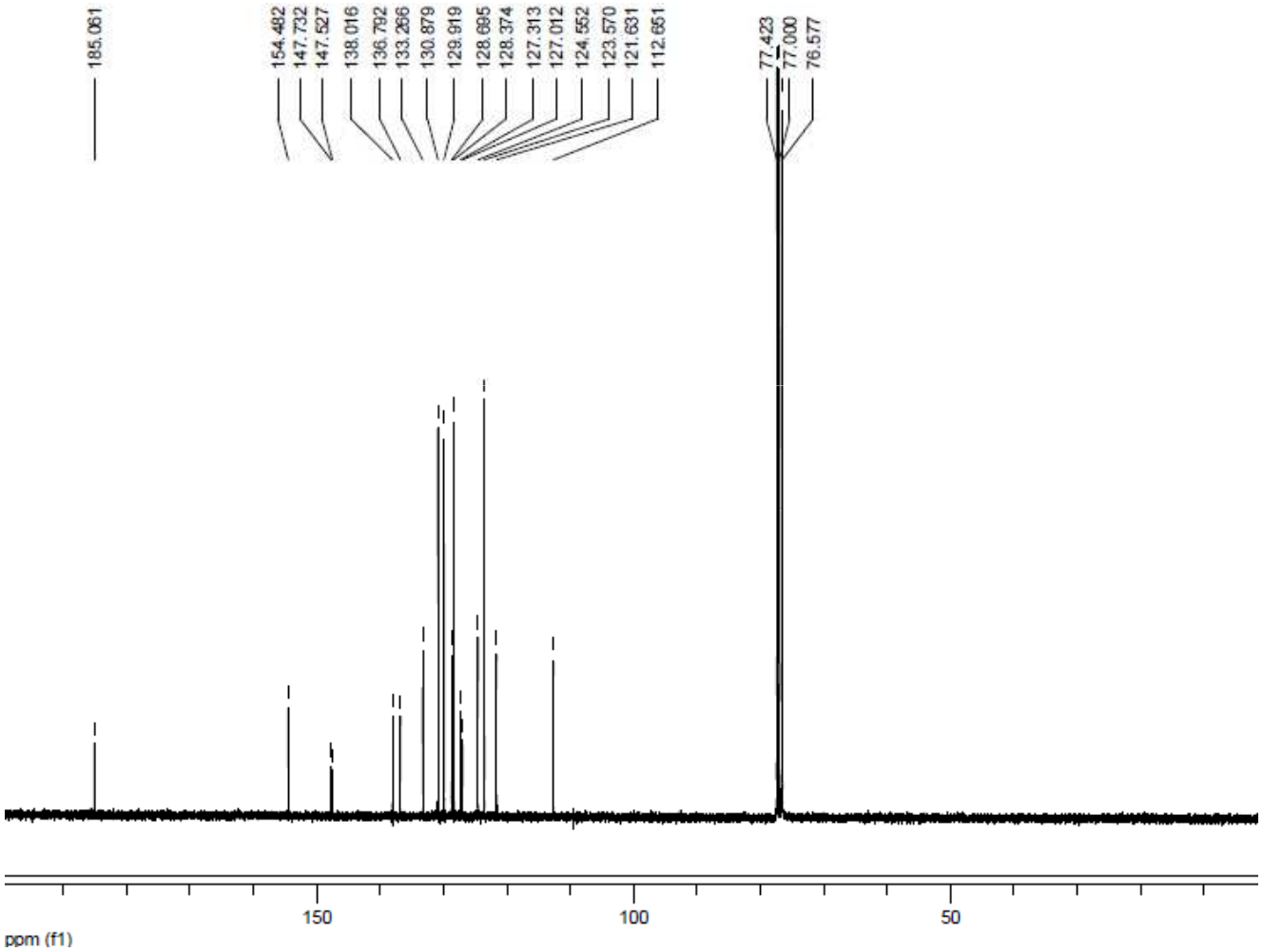
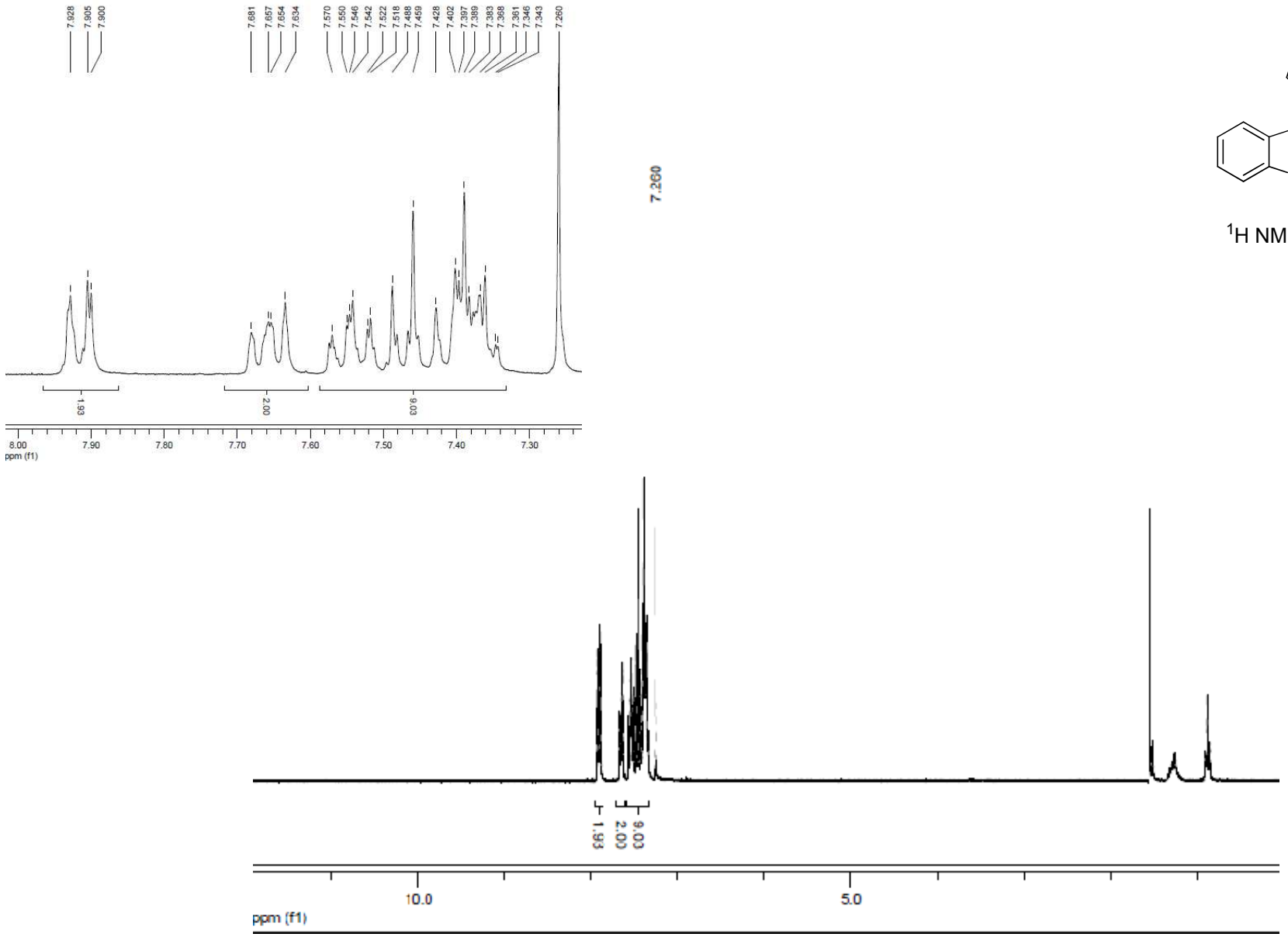
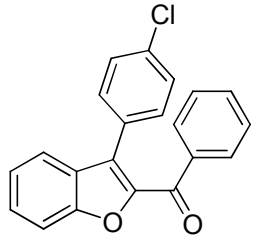
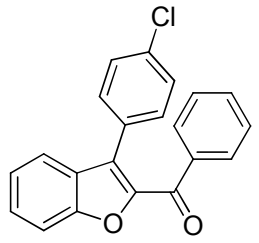






3g

^{1}H NMR in $CDCl_3$



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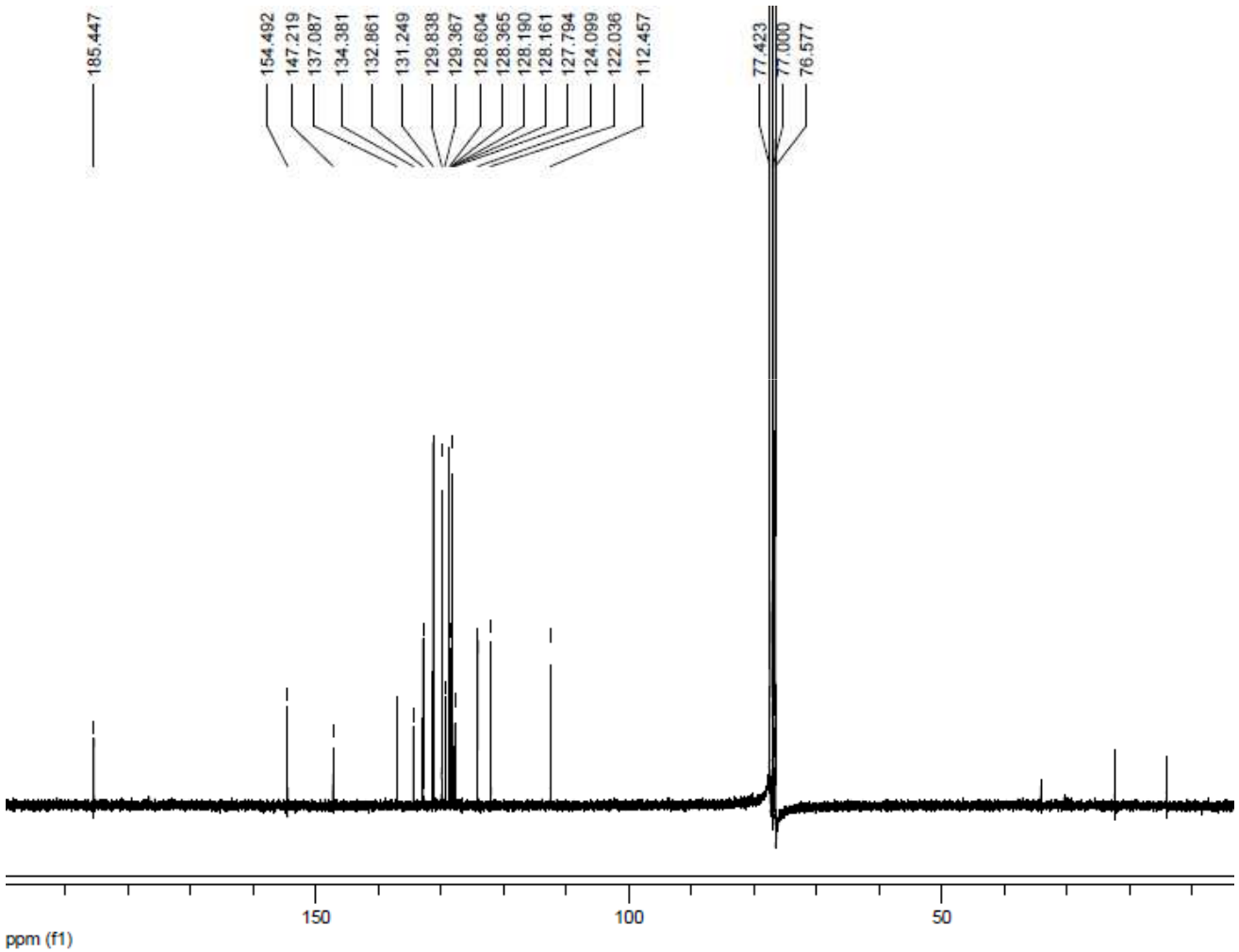

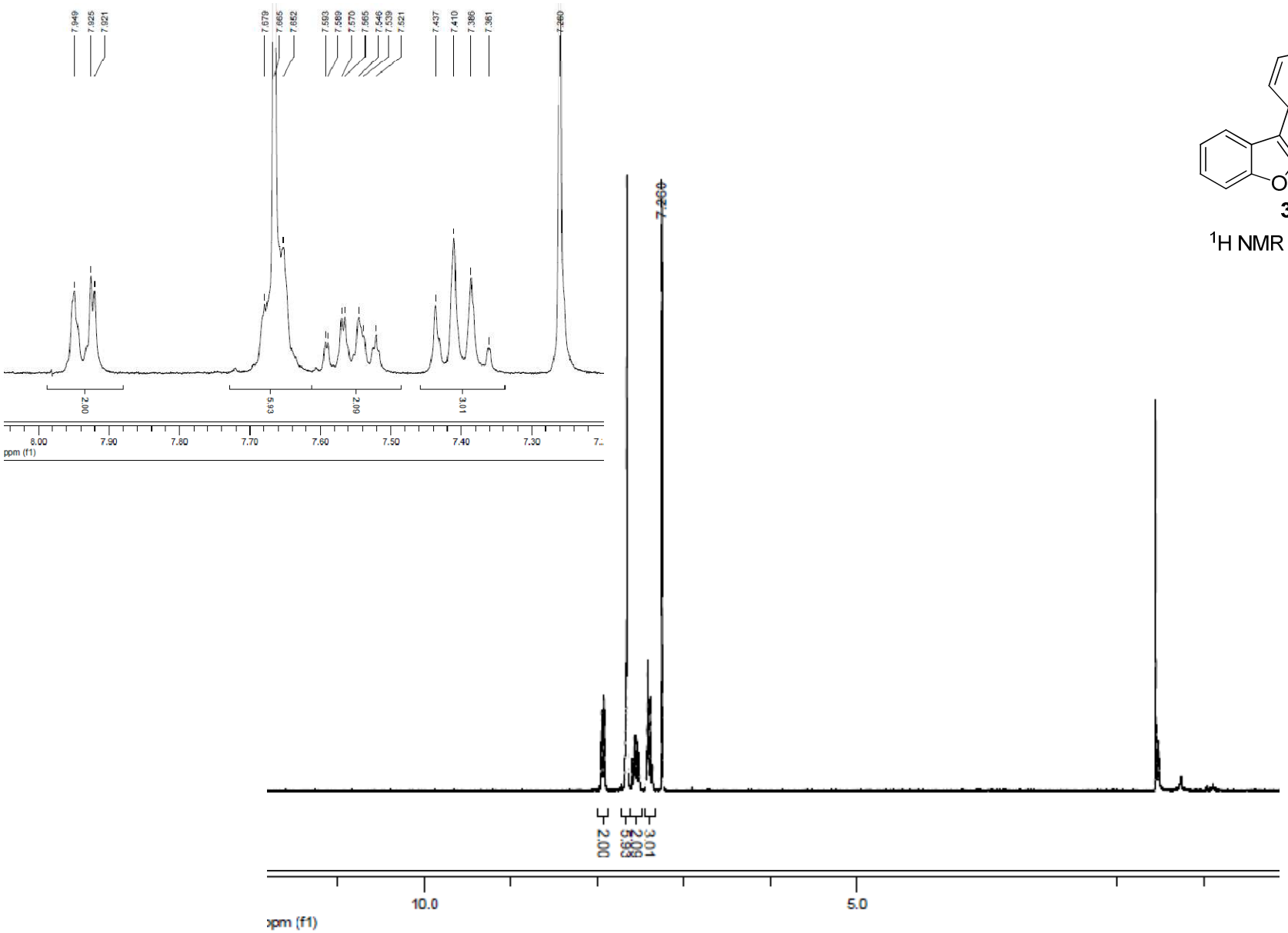

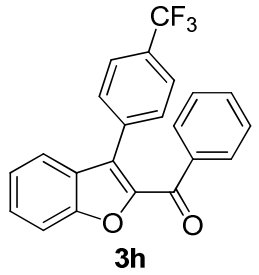

3h

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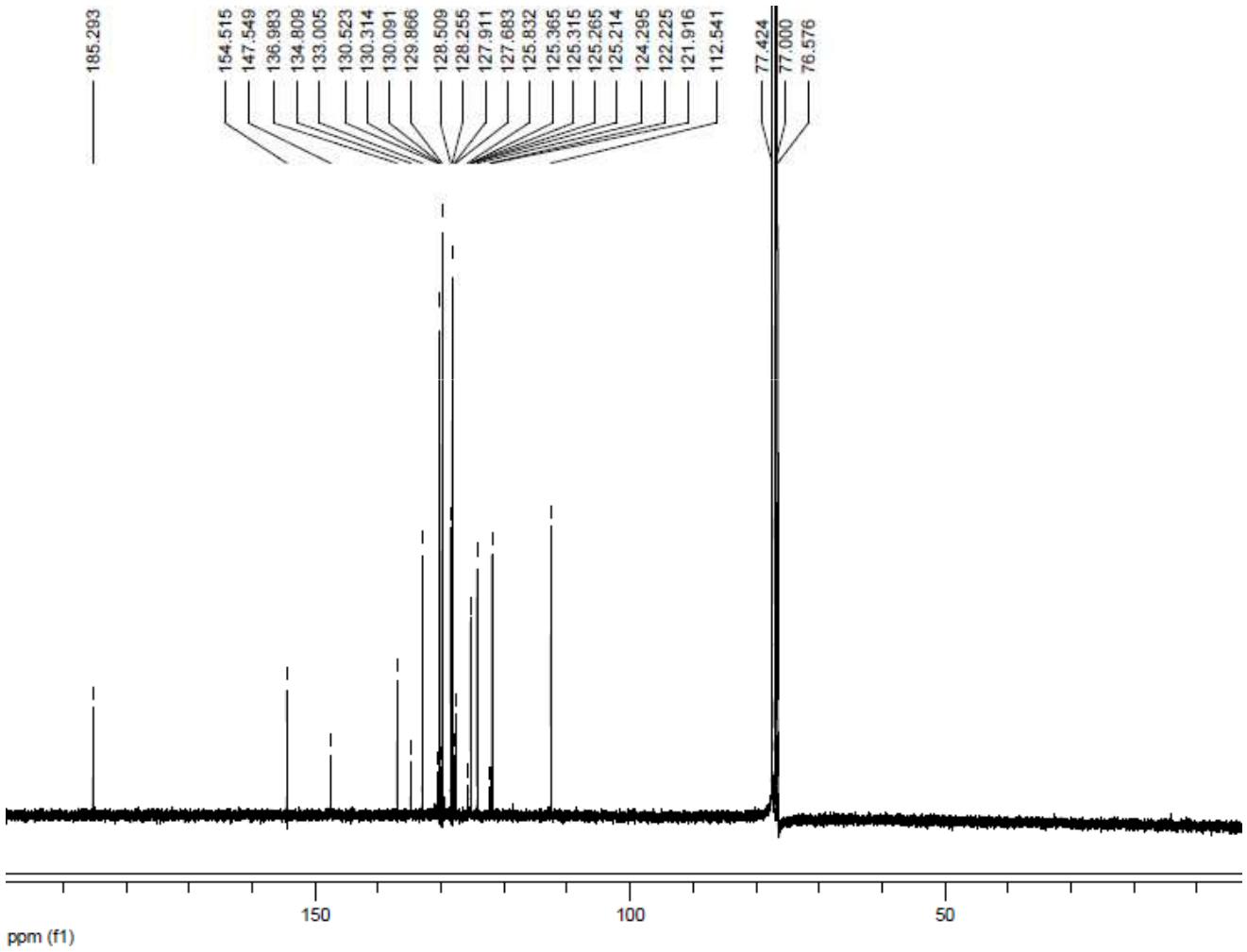

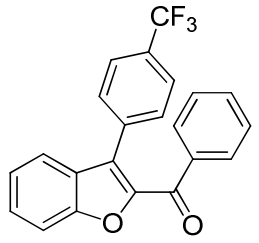

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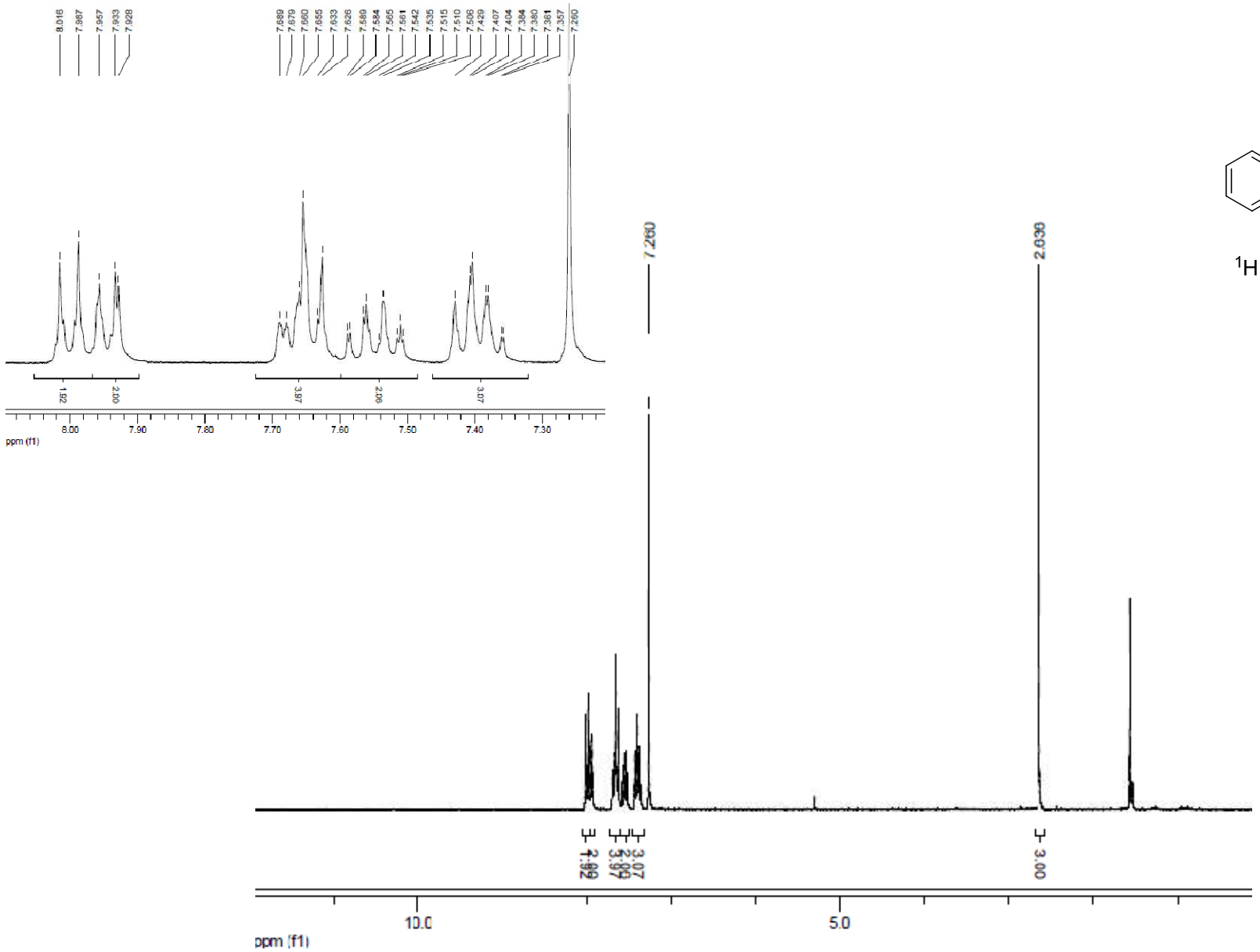
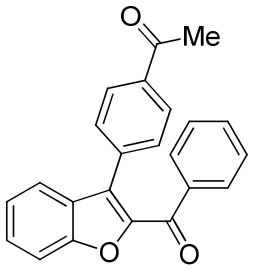
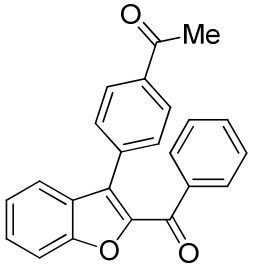




3i

^{1}H NMR in $CDCl_3$



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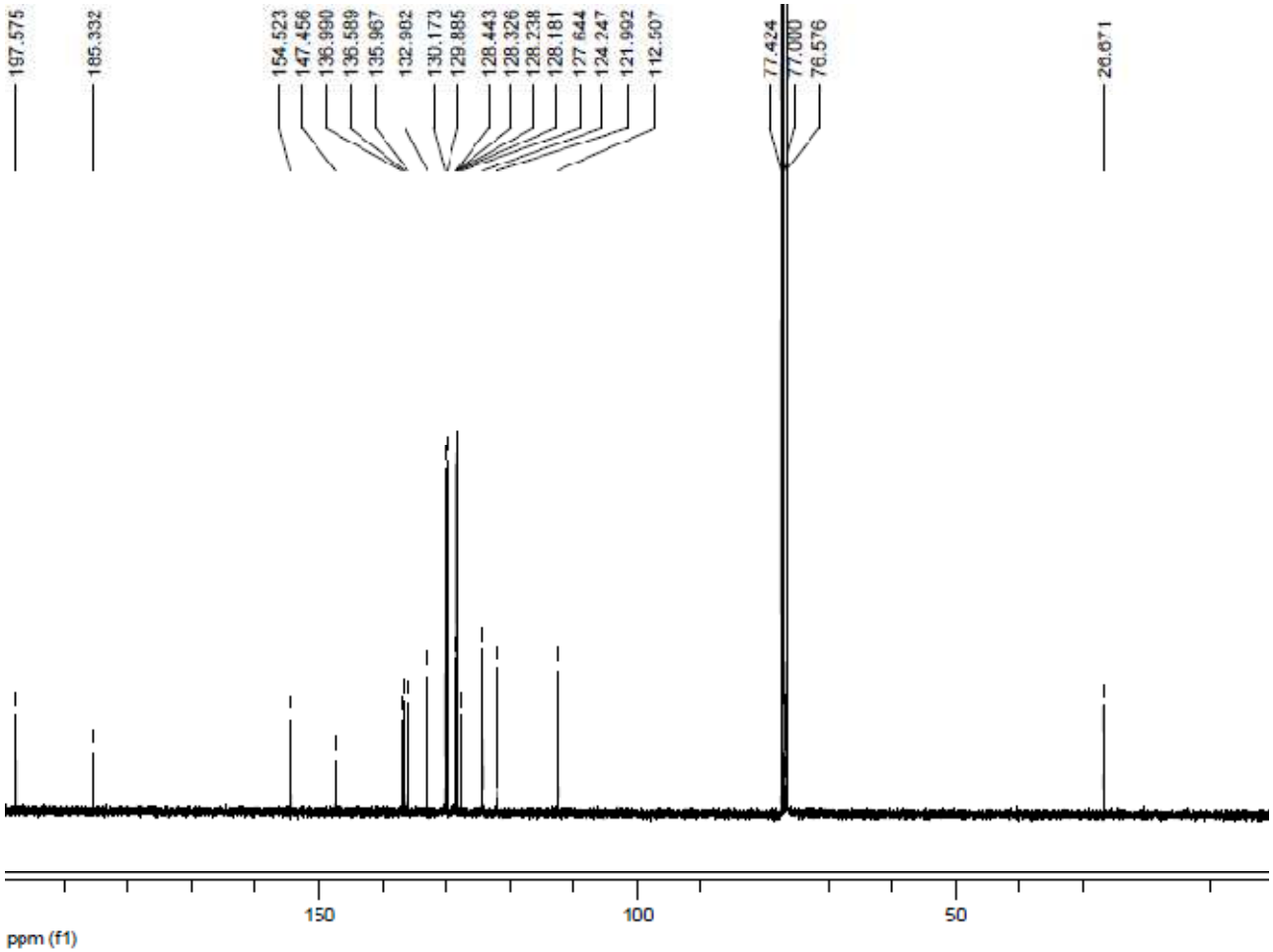

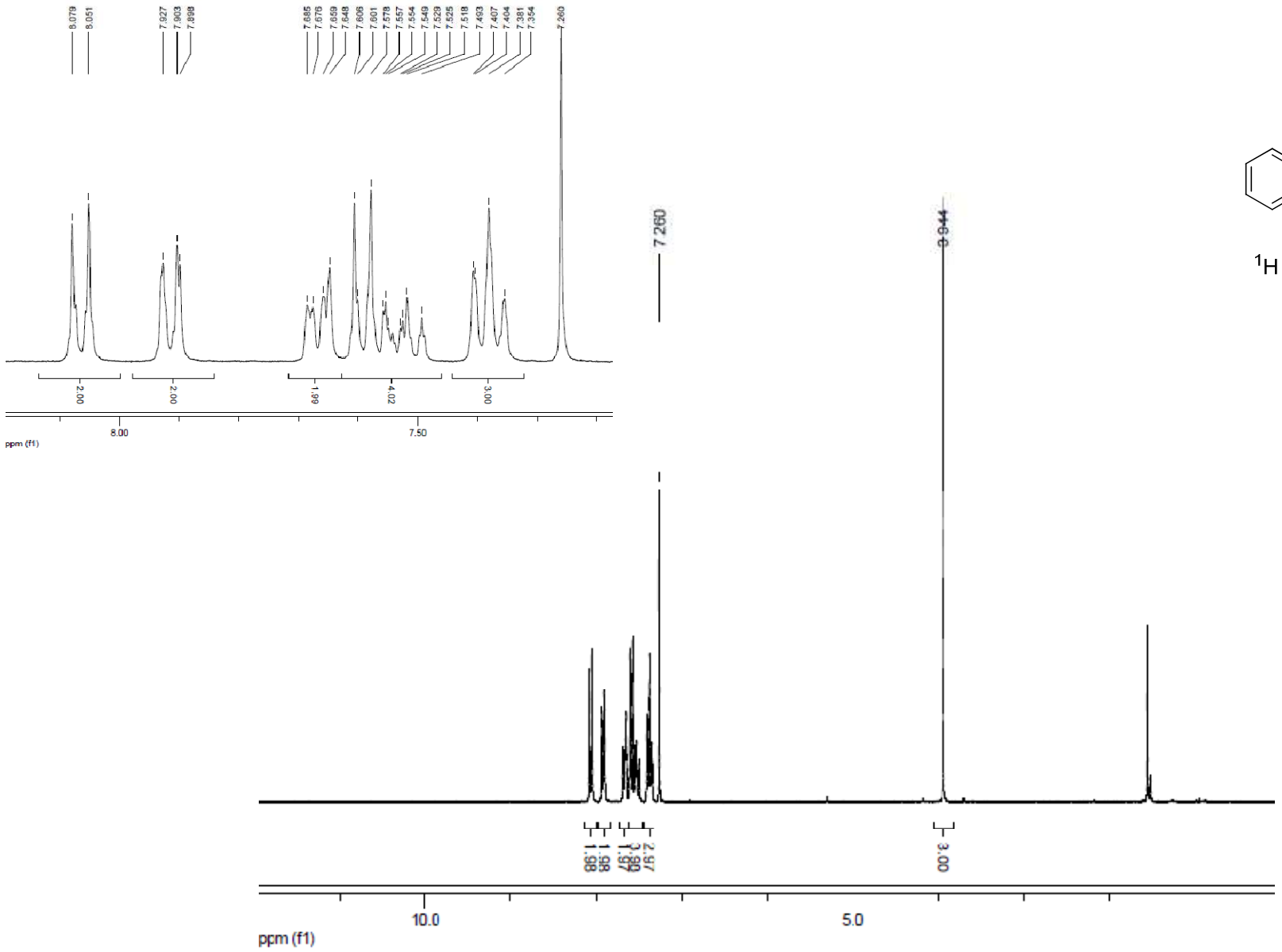

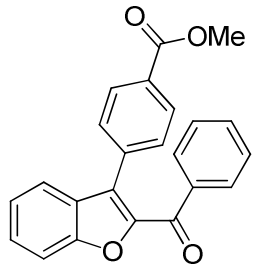

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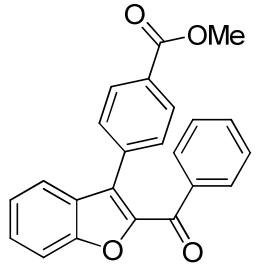

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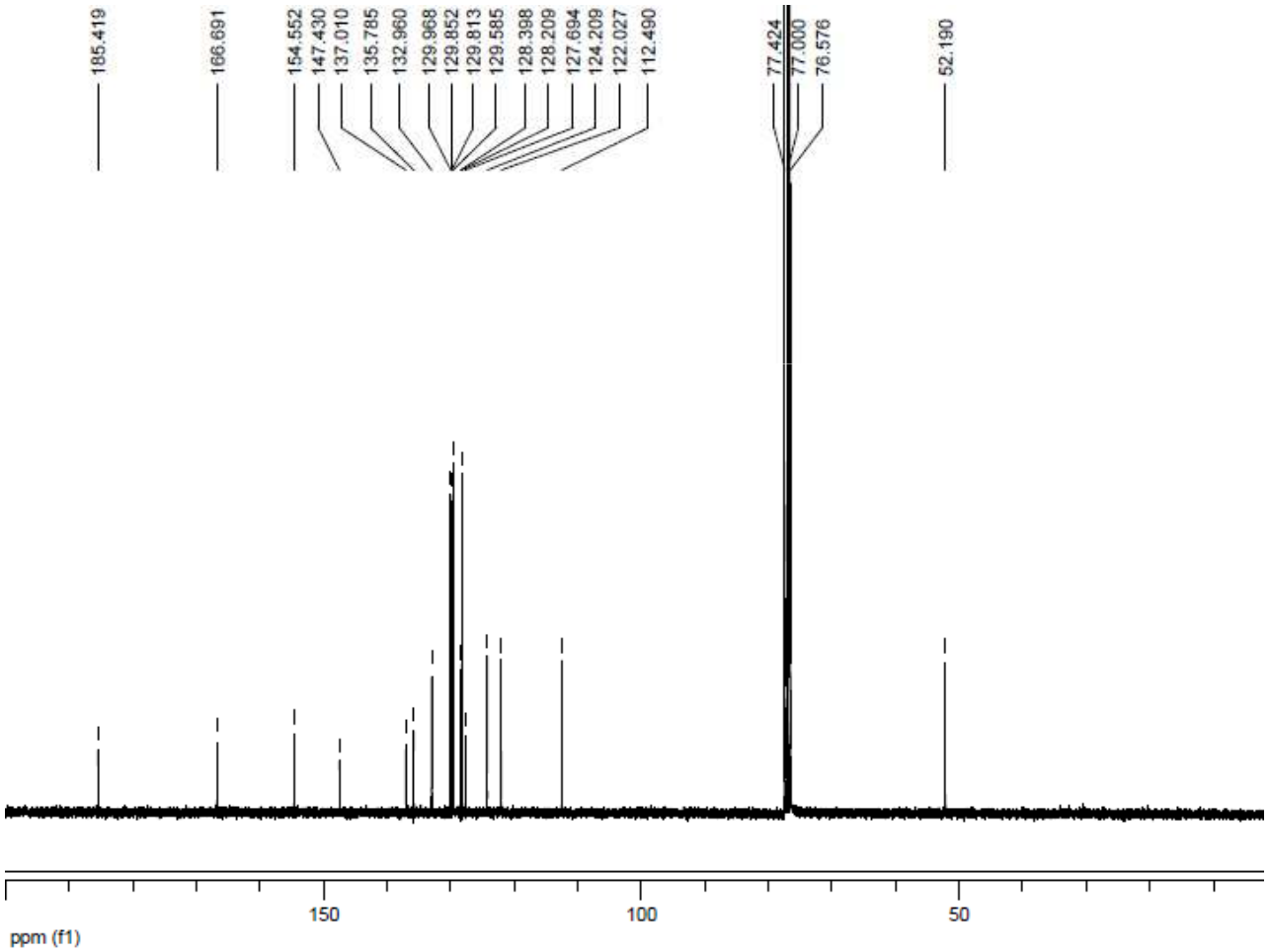
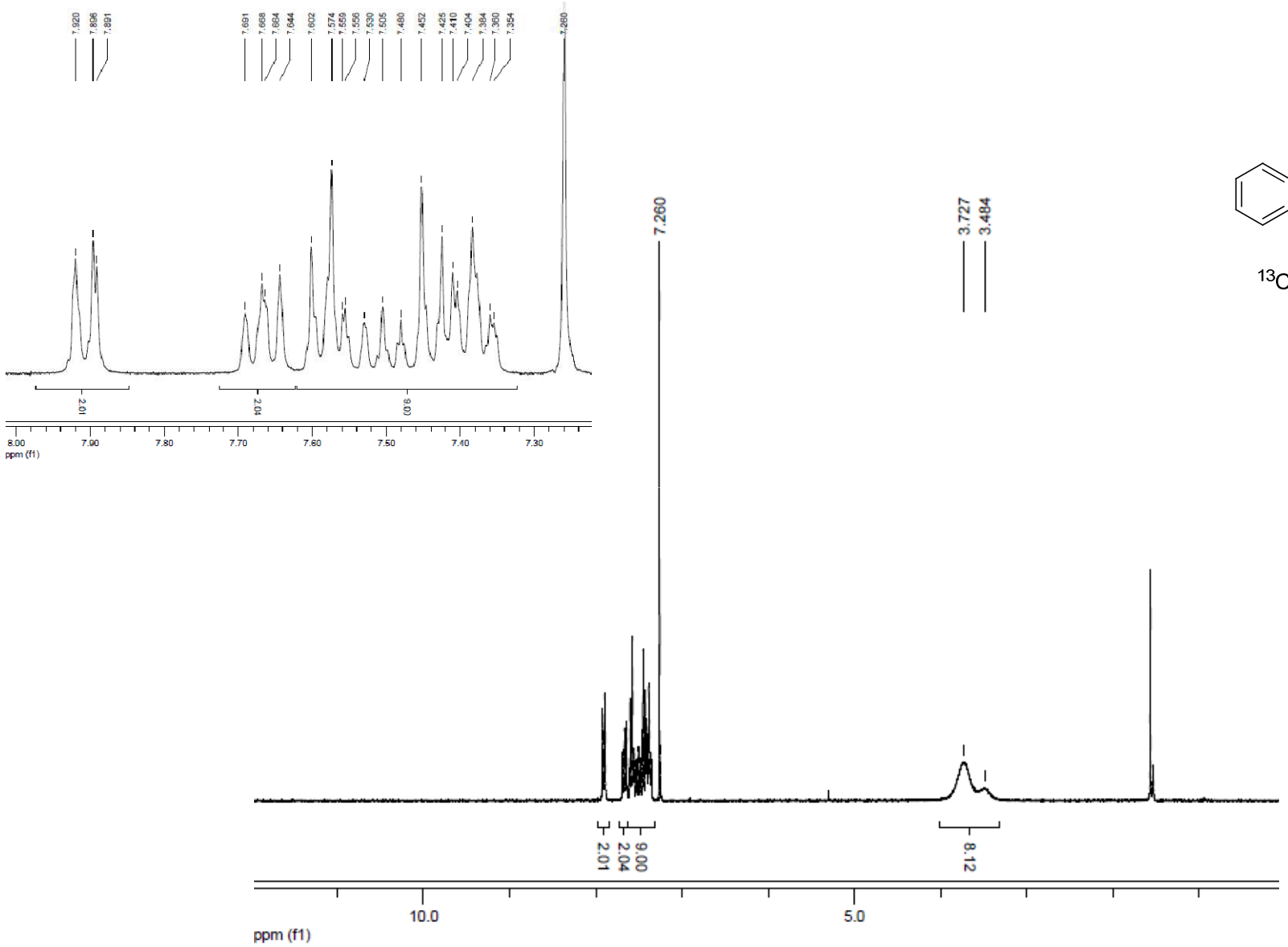
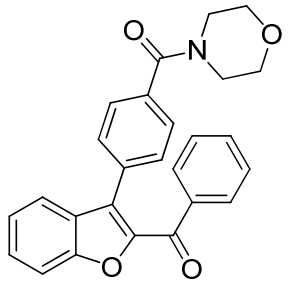
^{13}C NMR in $CDCl_3$

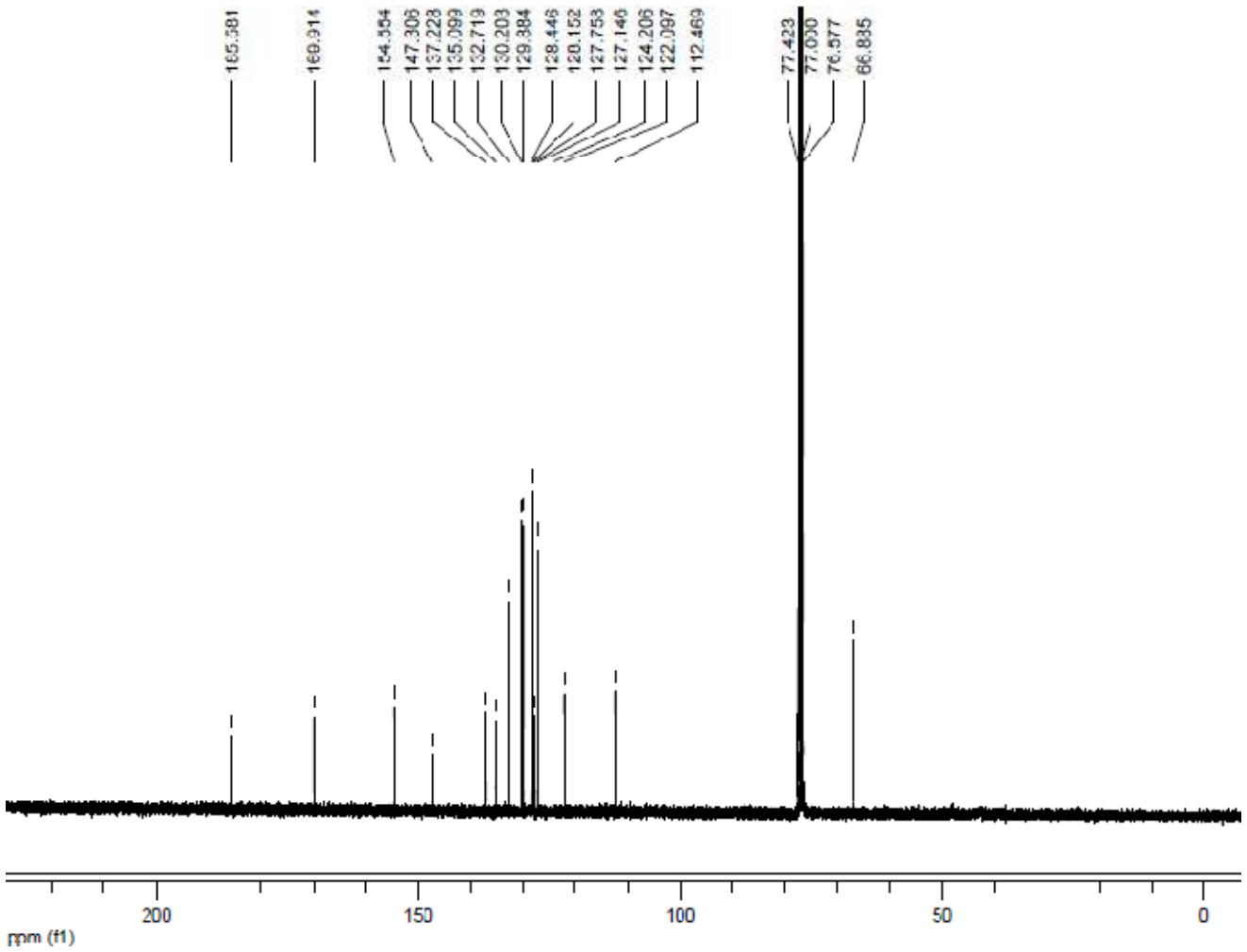


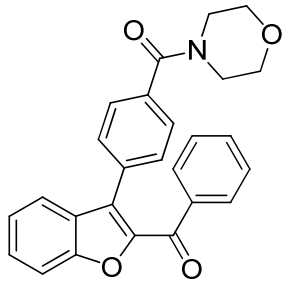




3k

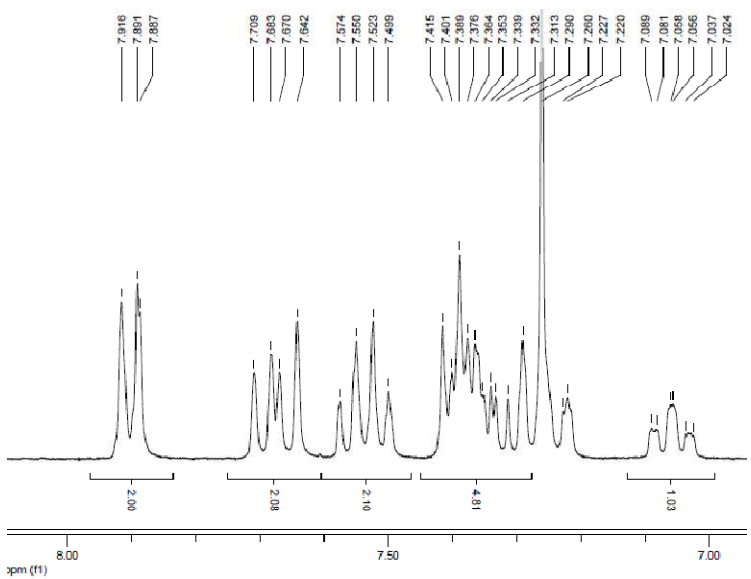
^{13}C NMR in $CDCl_3$

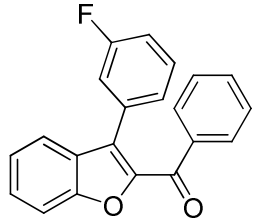




3k

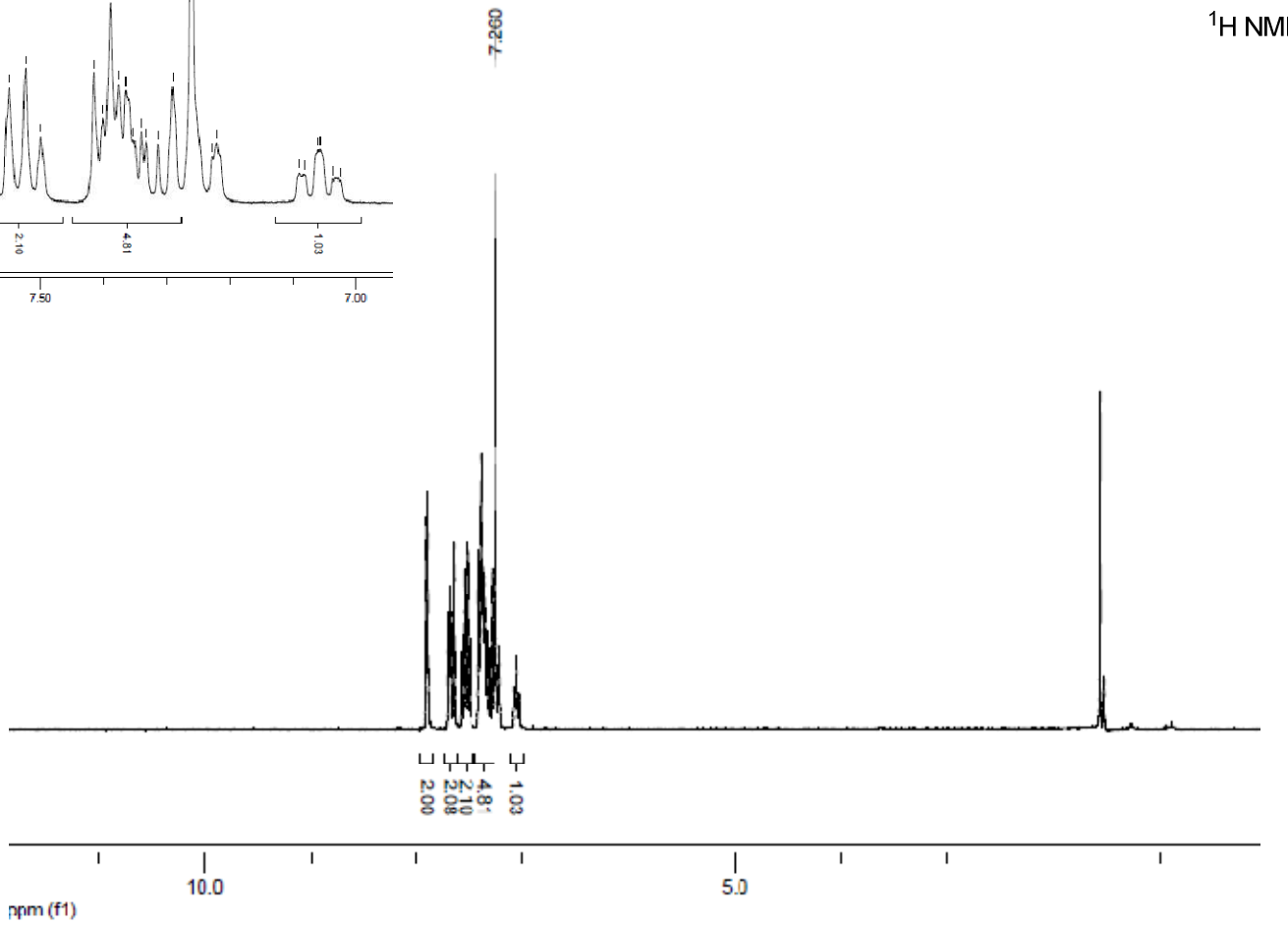
^{13}C NMR in $CDCl_3$

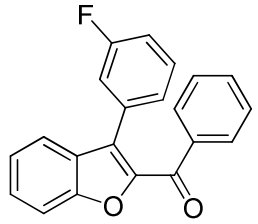




3l

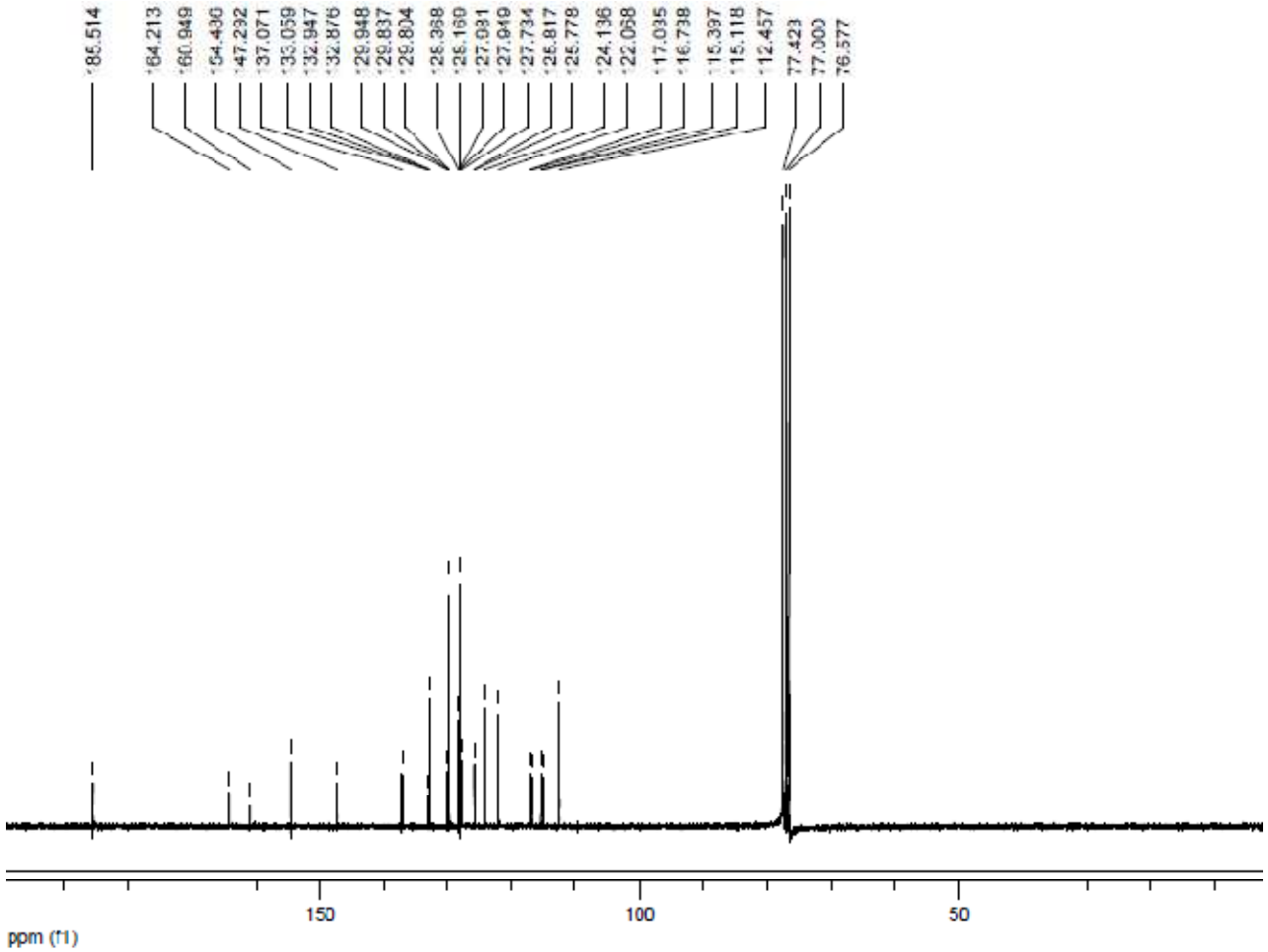
^{1}H NMR in $CDCl_3$

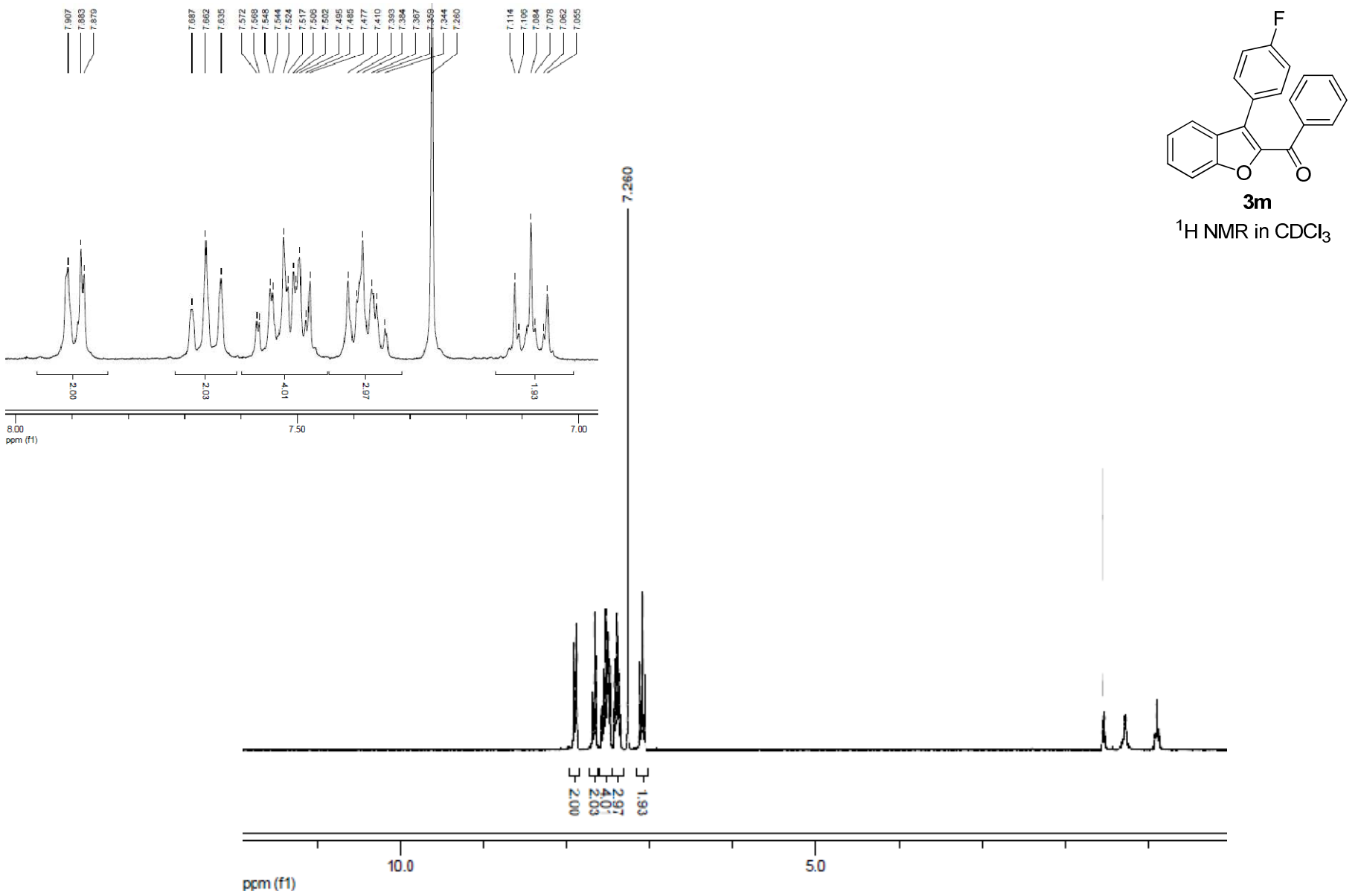




3l

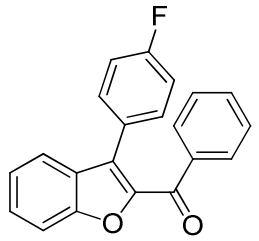
^{13}C NMR in $CDCl_3$





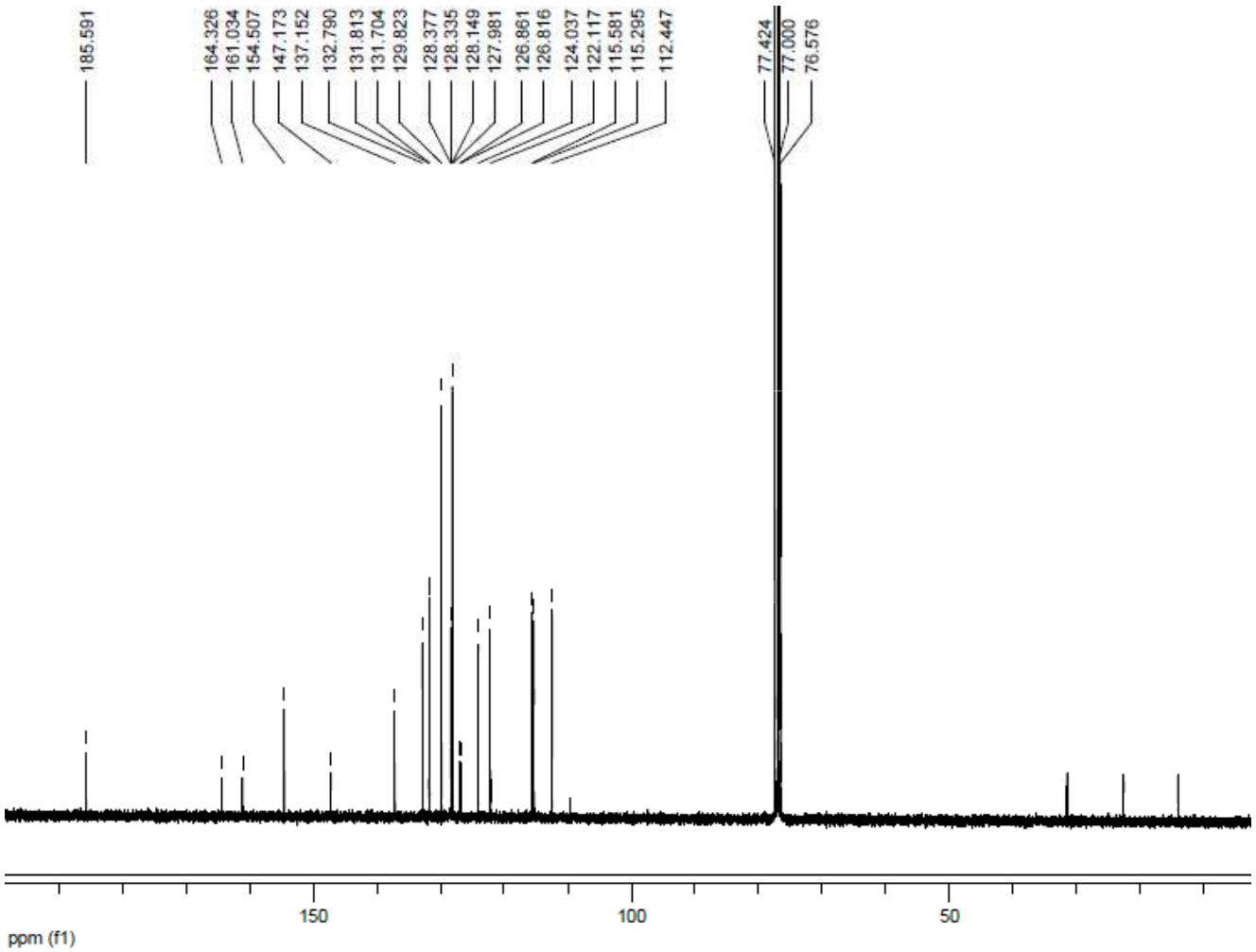
3m

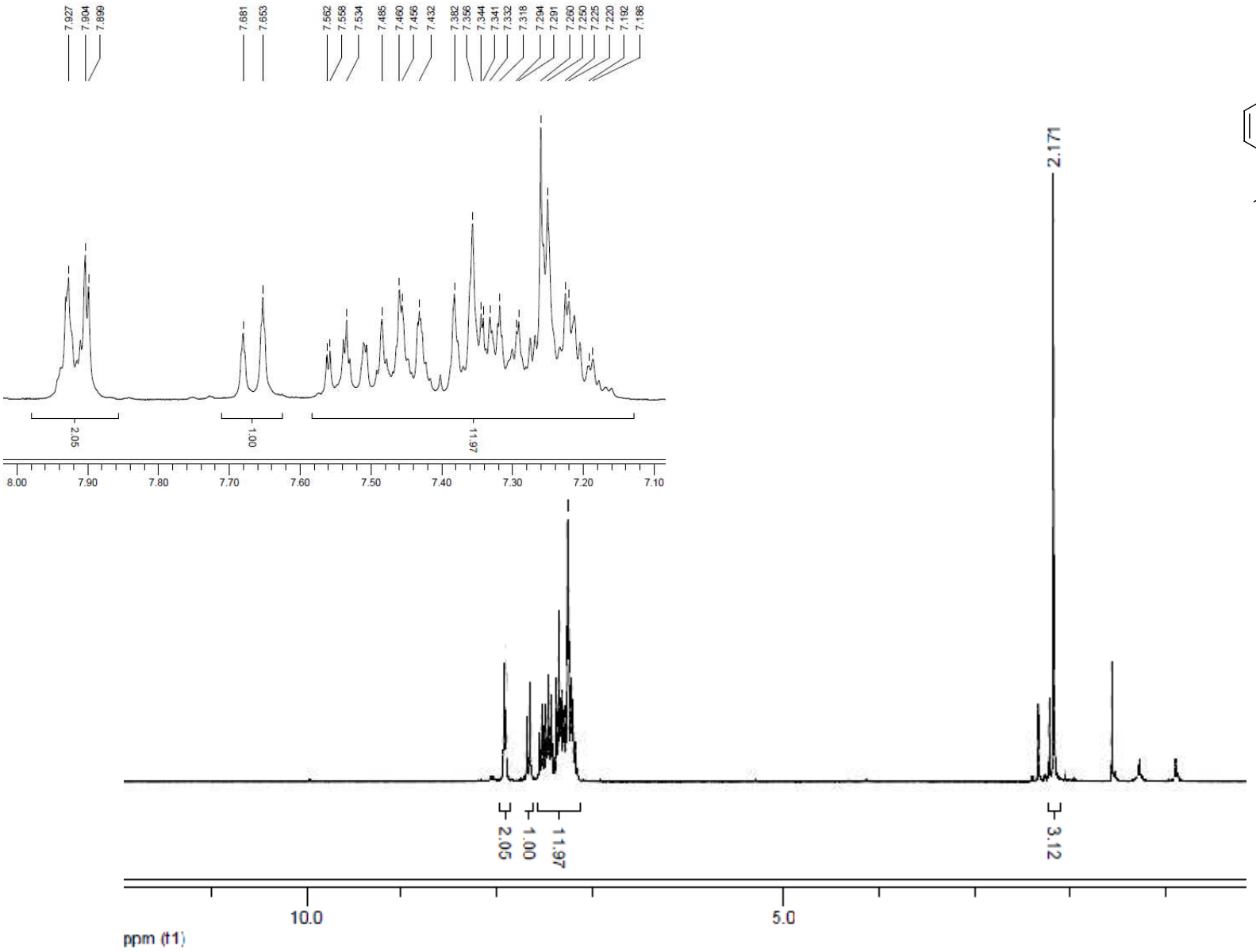
^{1}H NMR in $CDCl_3$

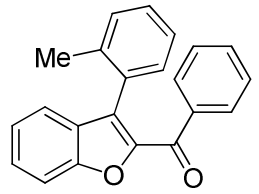


3m

^{13}C NMR in $CDCl_3$

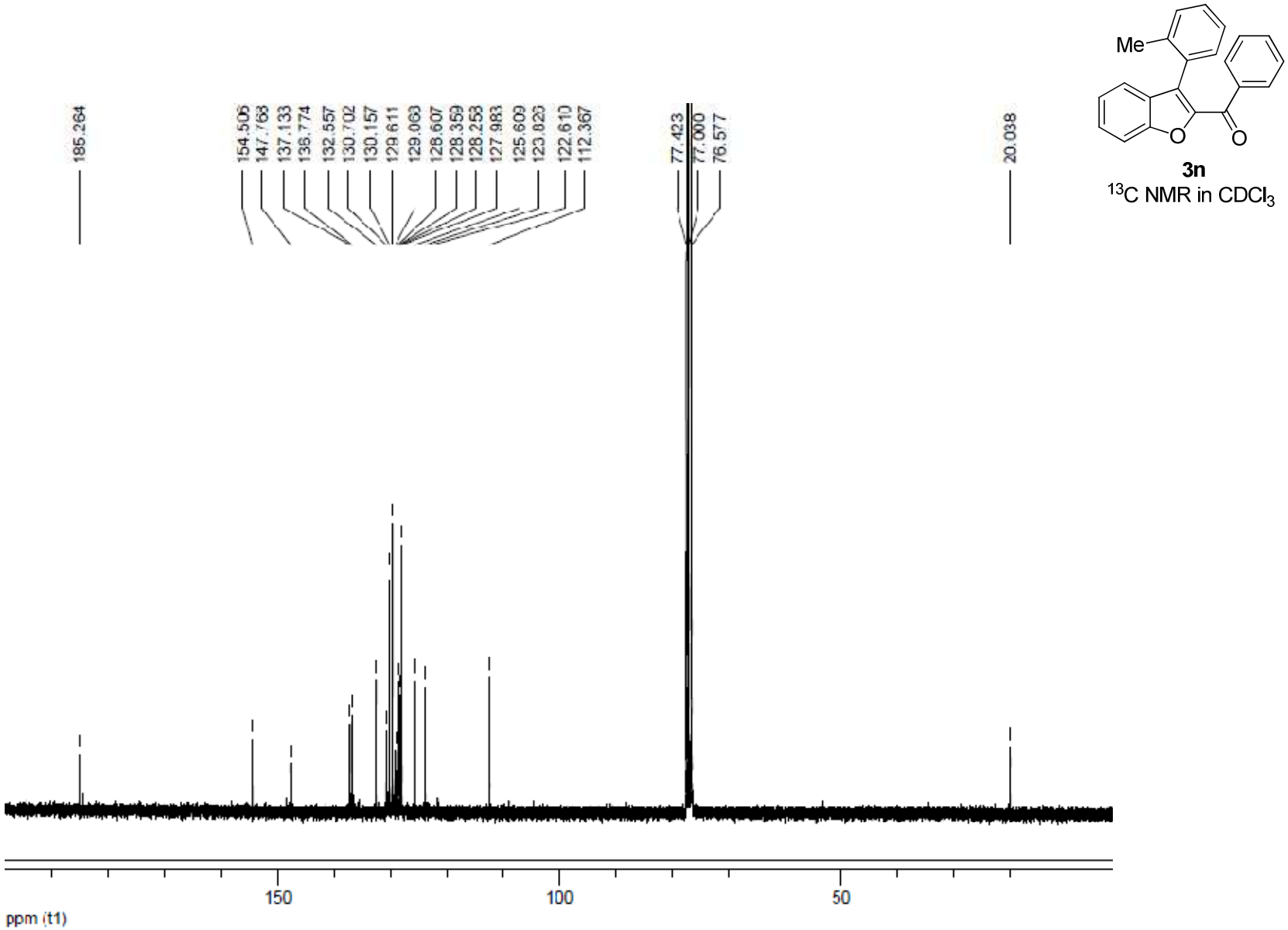


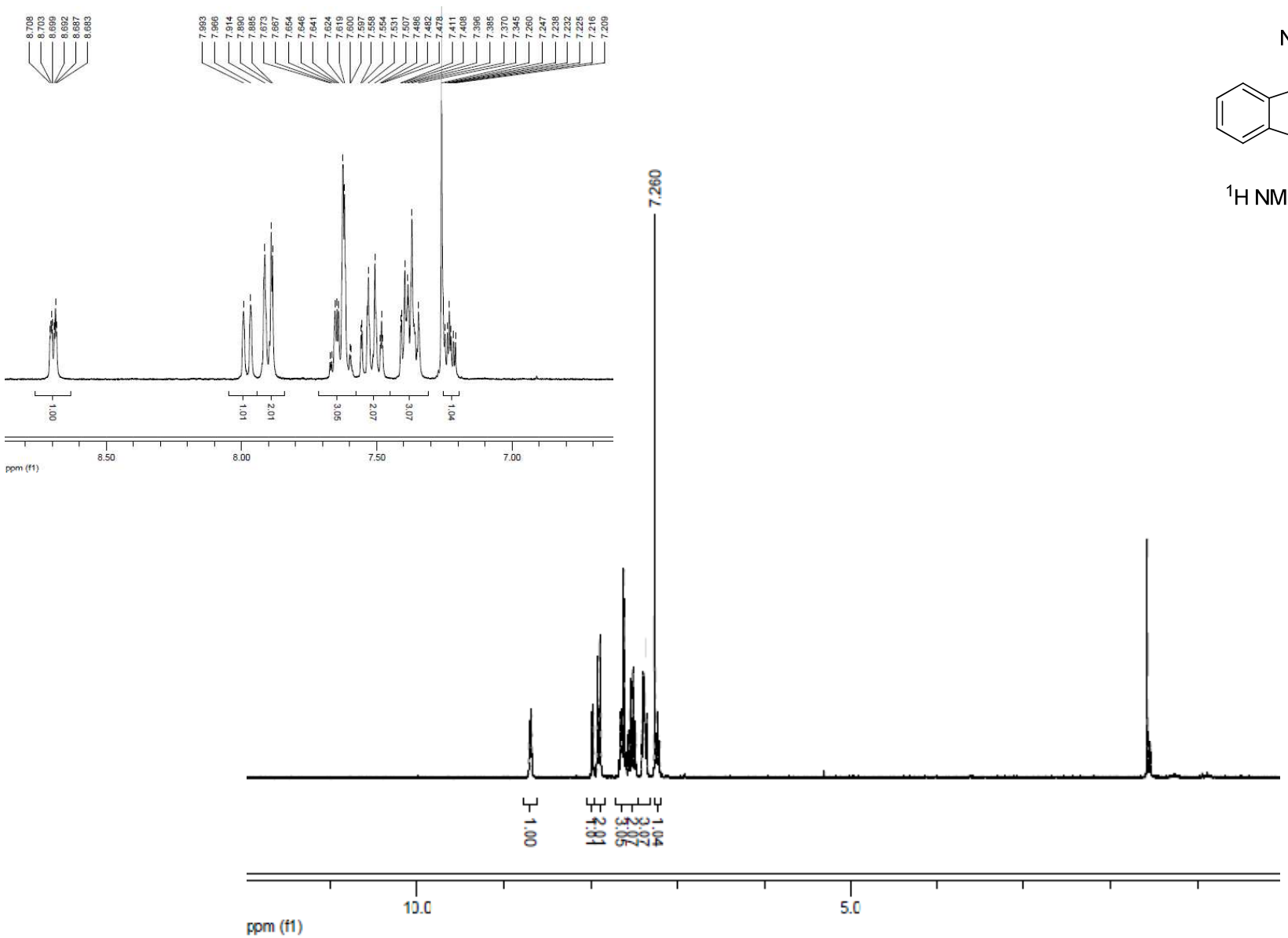


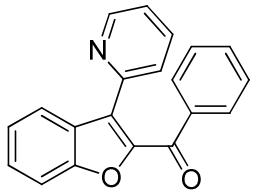


3n

^{1}H NMR in $CDCl_3$

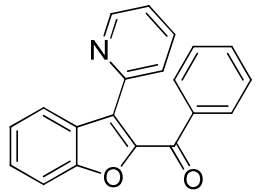

Me
O
O
3n
^{13}C NMR in $CDCl_3$
185.264
154.505
147.768
137.133
136.774
132.557
130.702
130.157
129.611
129.063
128.607
128.359
128.253
127.983
125.609
123.826
122.610
112.367
77.423
77.000
76.577
20.038
150
100
50
ppm (t1)





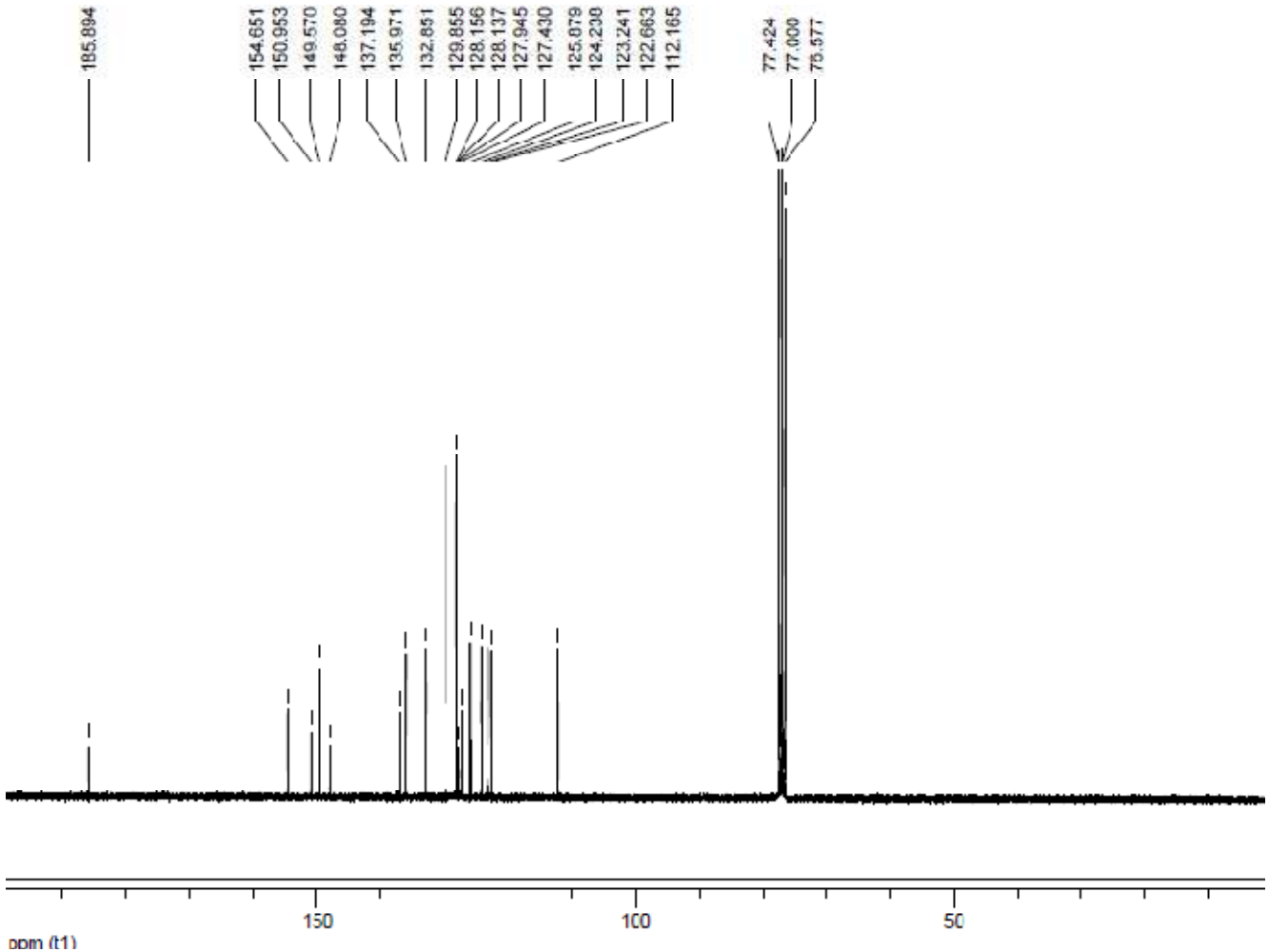
3o

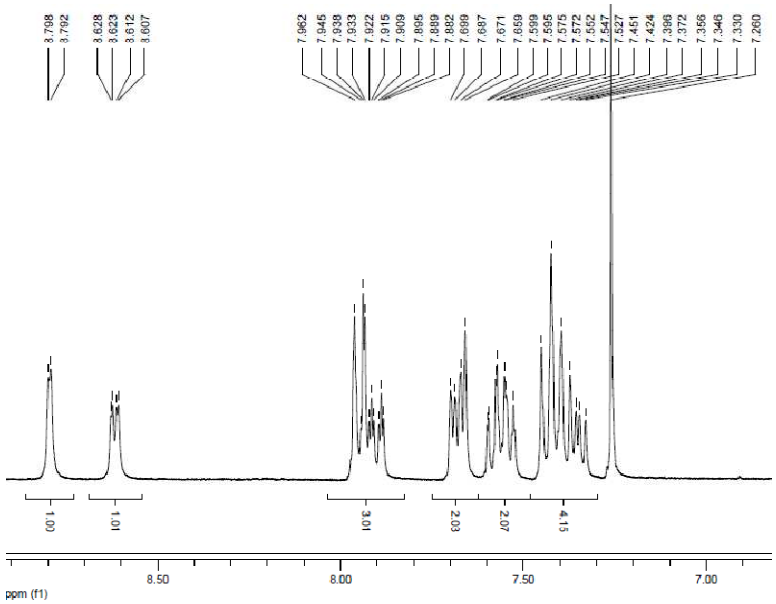
^{1}H NMR in $CDCl_3$

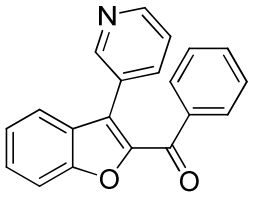


3o

^{13}C NMR in $CDCl_3$

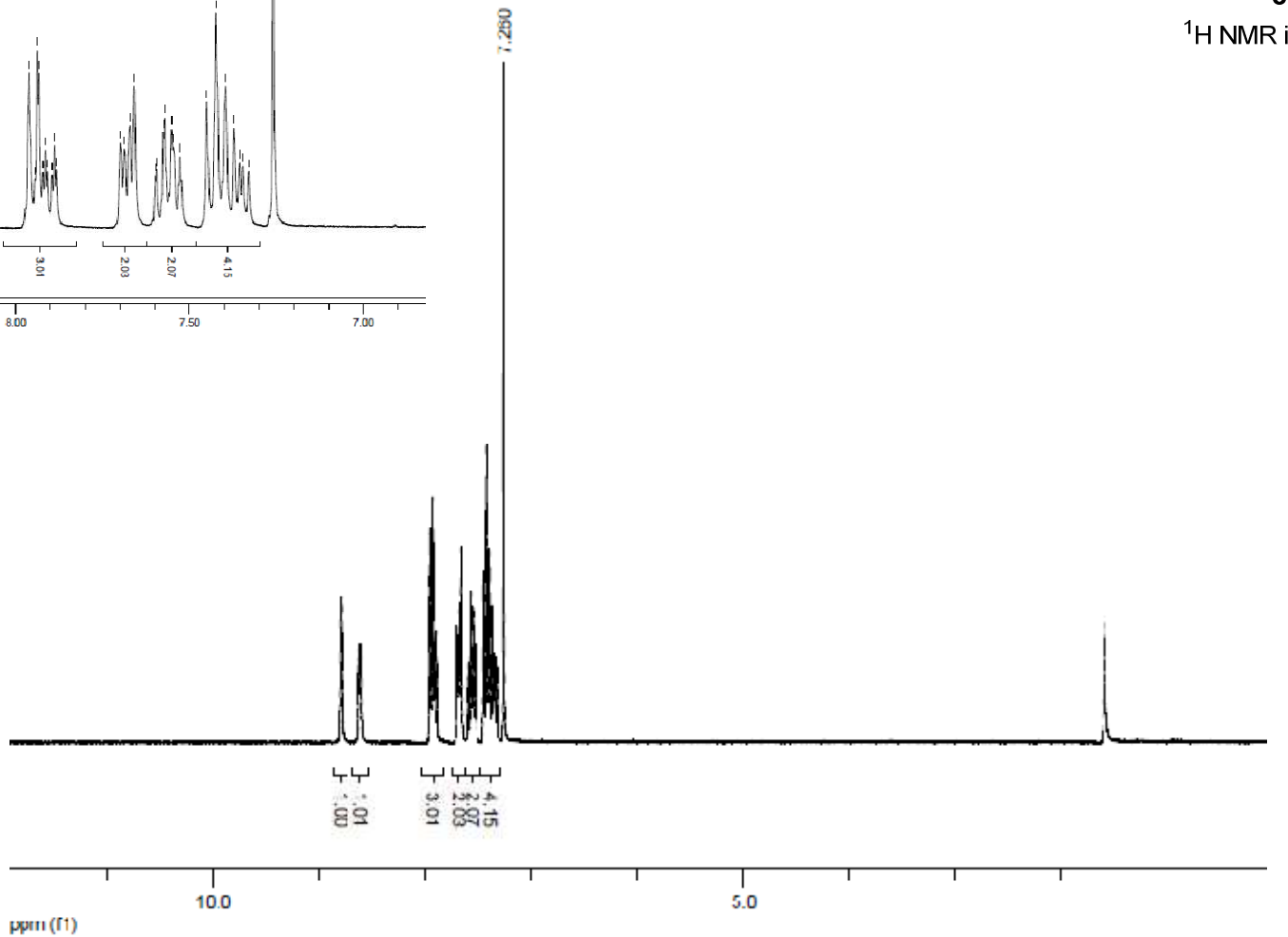


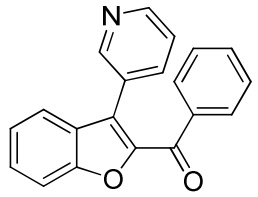




3p

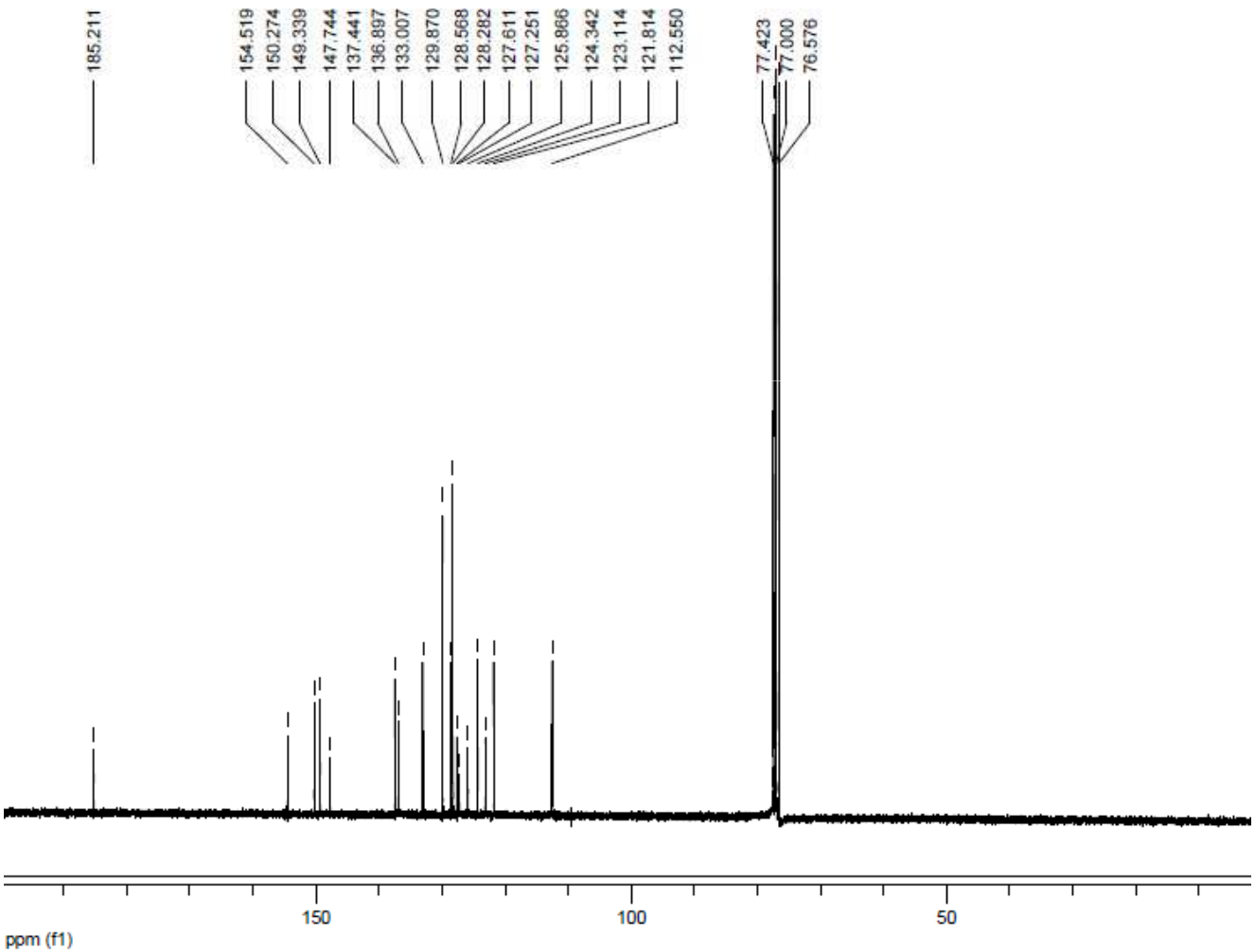
^{1}H NMR in $CDCl_3$

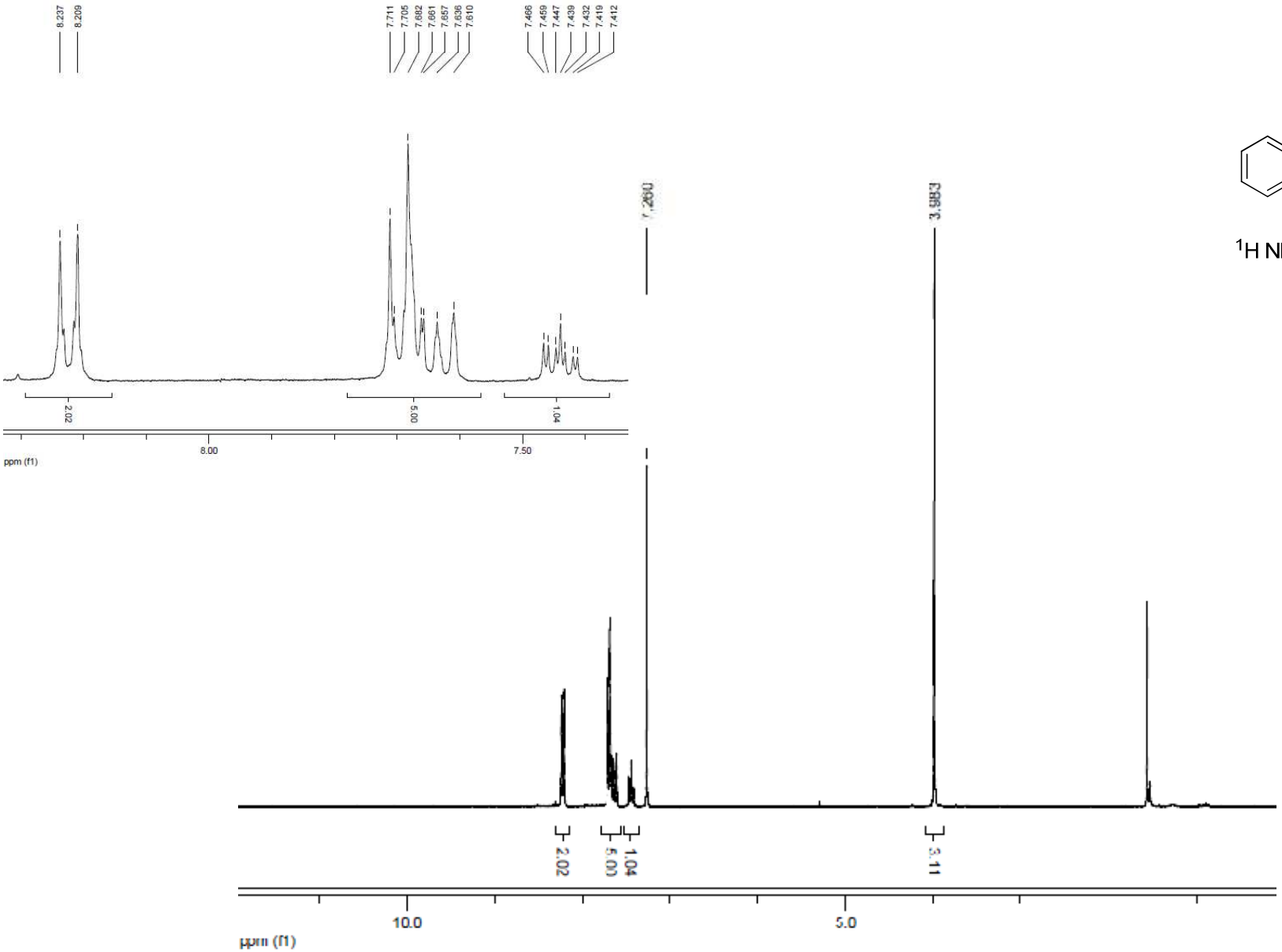


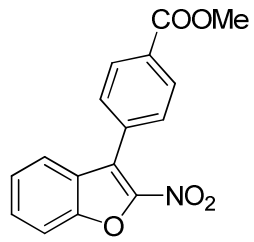


3p

^{13}C NMR in $CDCl_3$

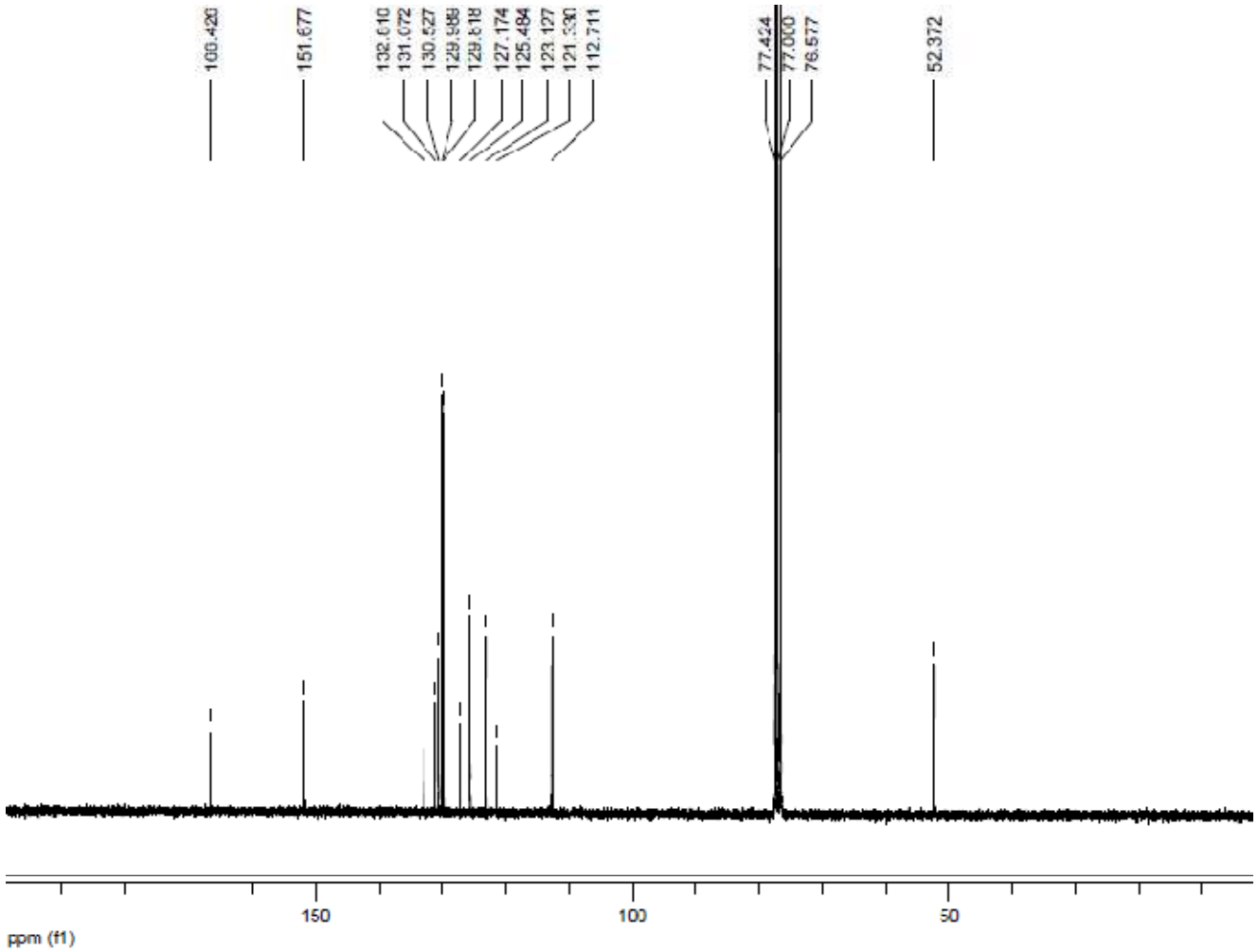


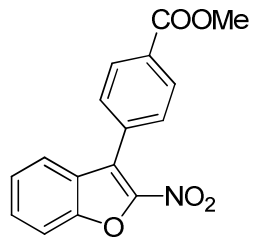




12j

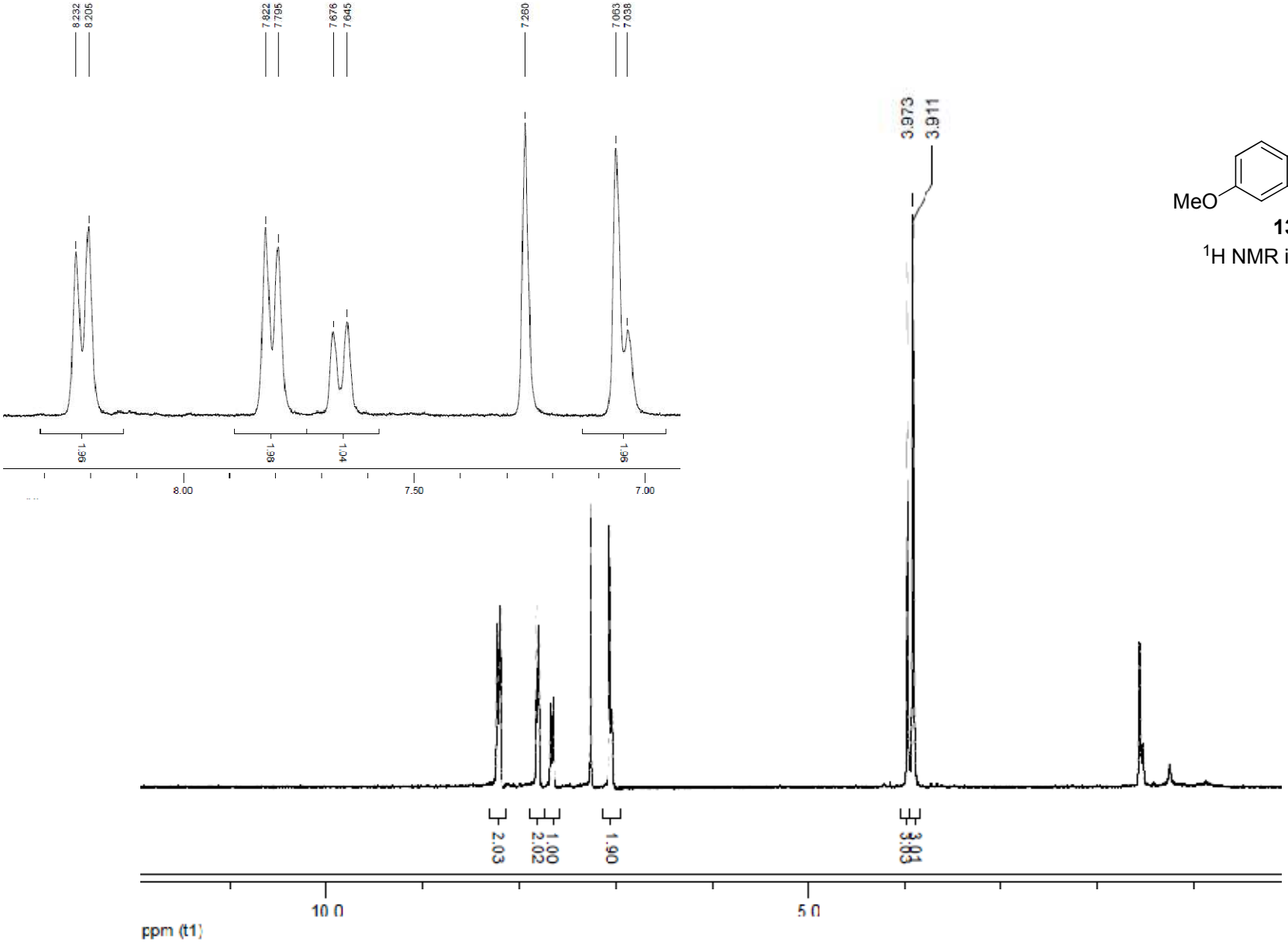
^{1}H NMR in $CDCl_3$

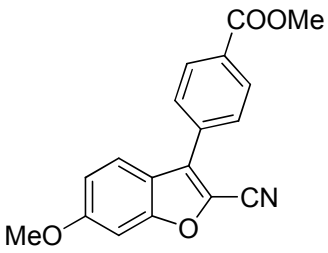




12j

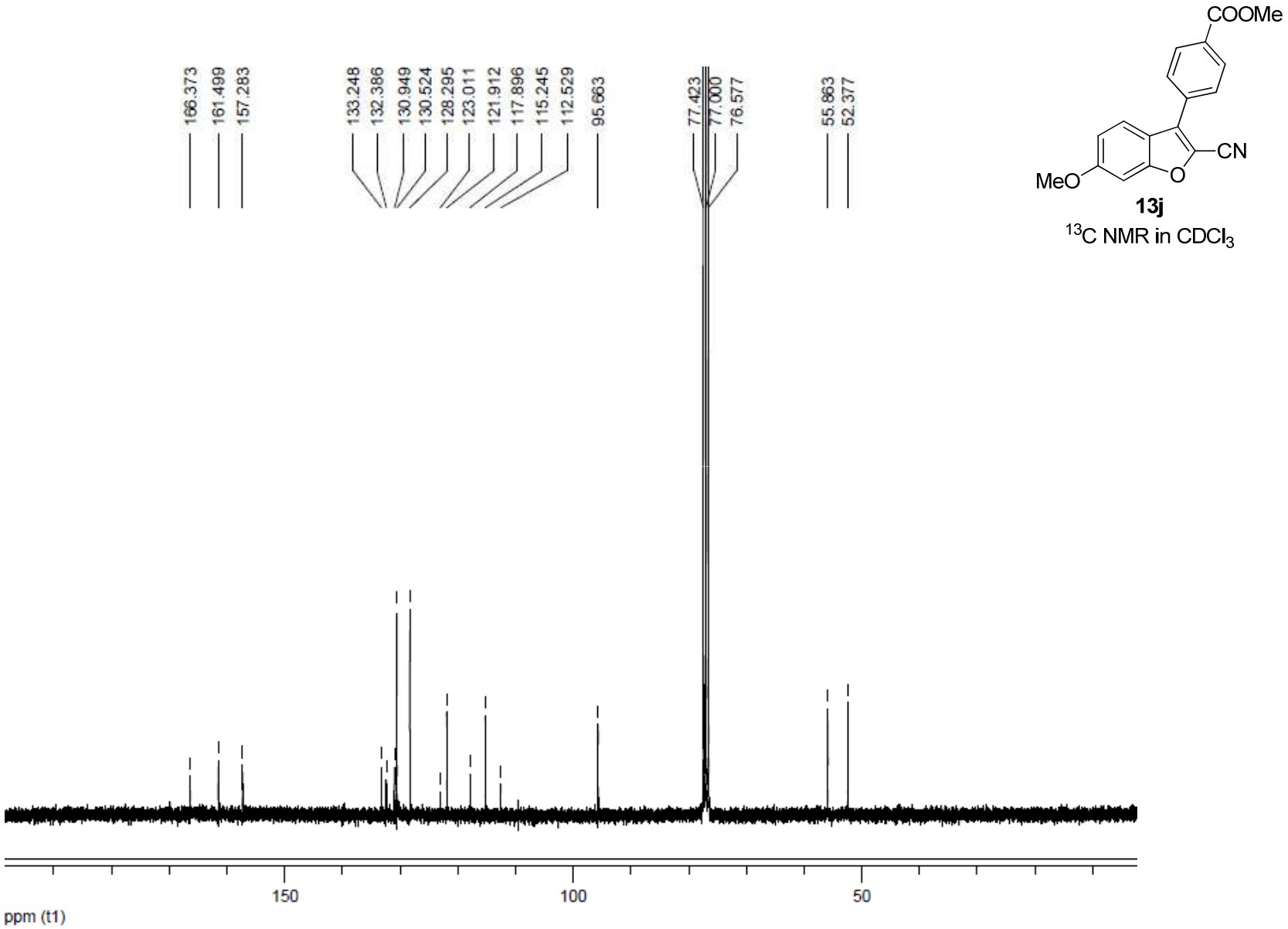
^{13}C NMR in $CDCl_3$

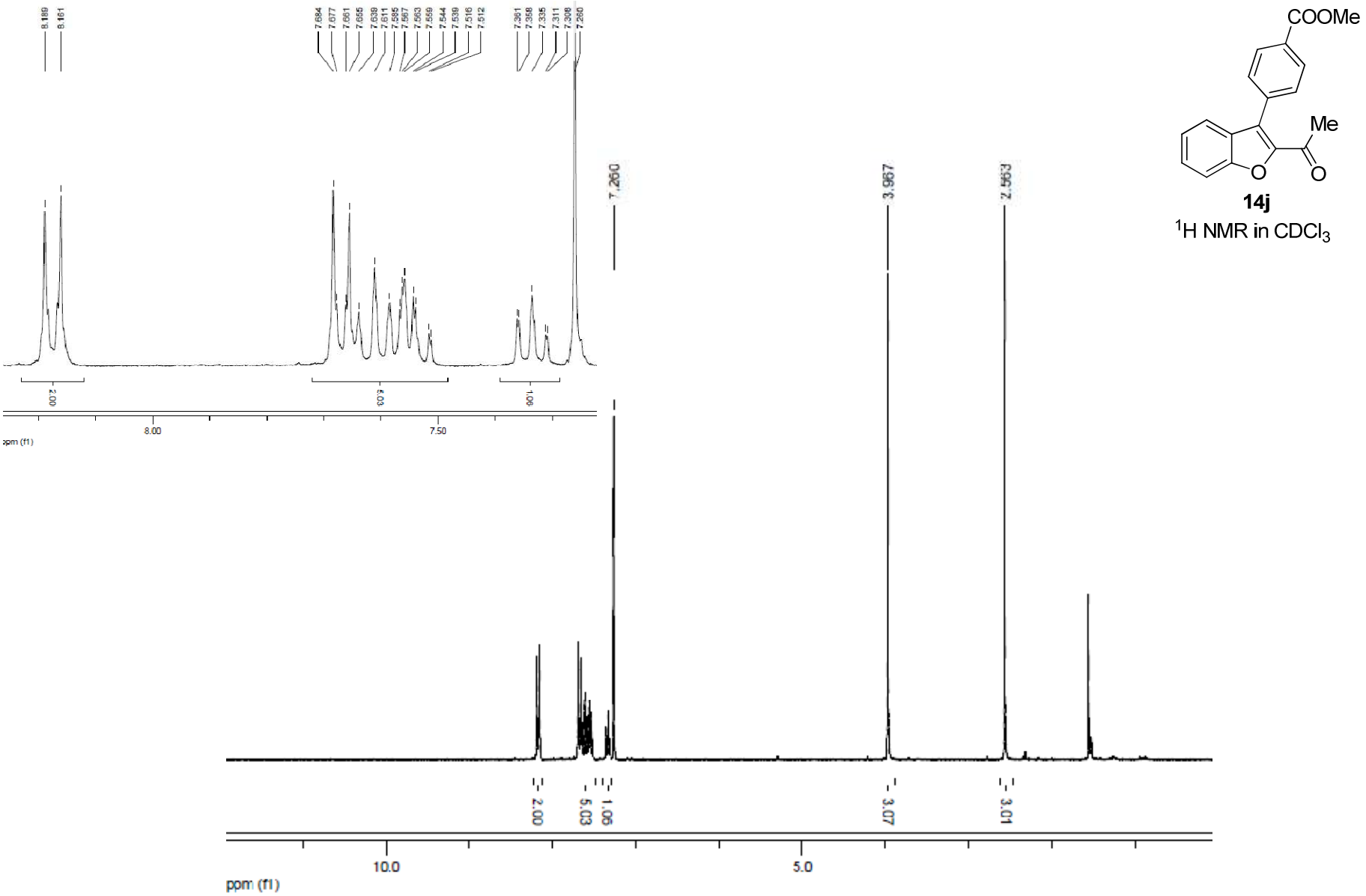




13j

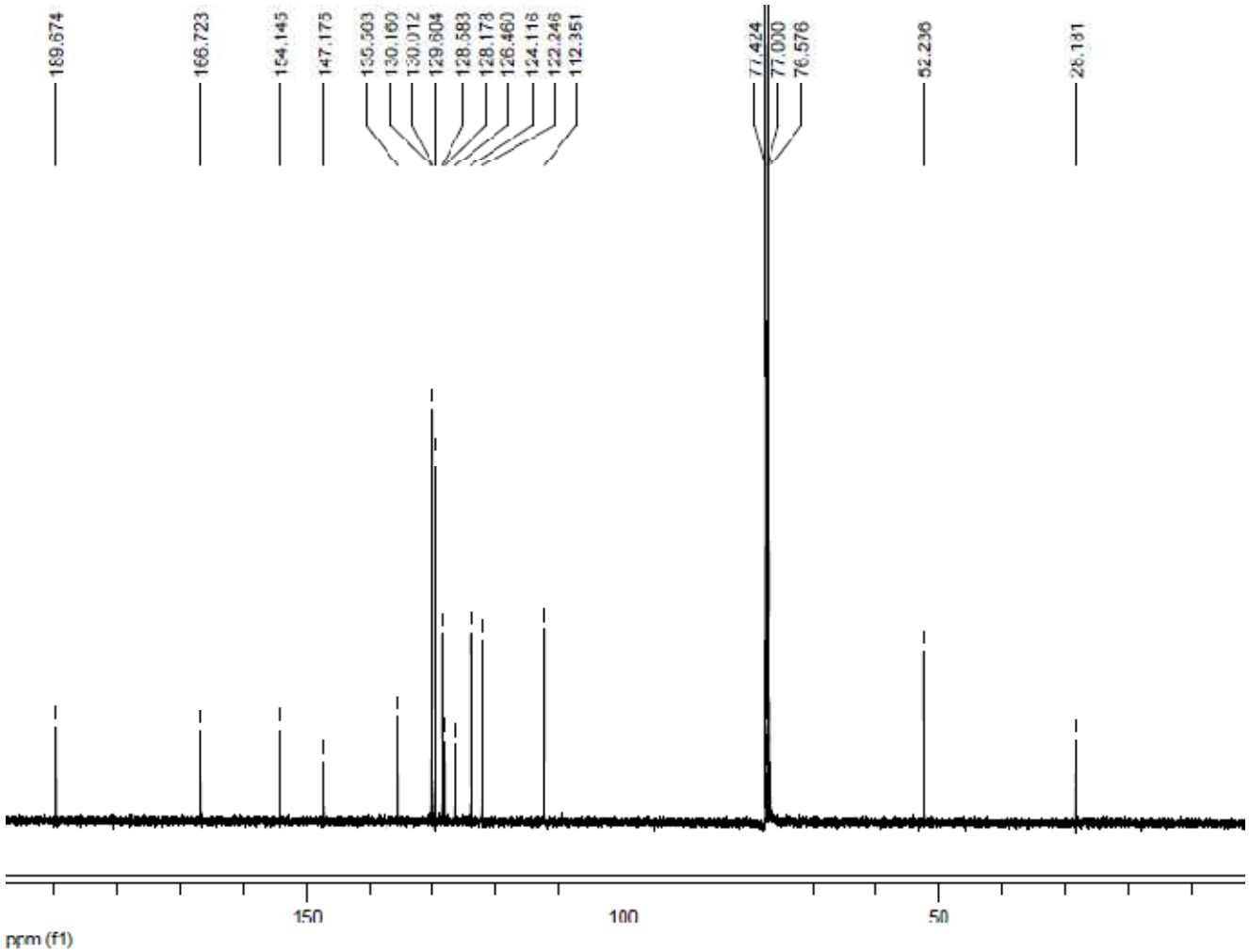
^{1}H NMR in $CDCl_3$

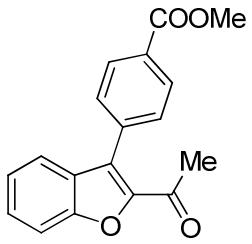

166.373
161.499
157.283
133.248
132.386
130.949
130.524
128.295
123.011
121.912
117.896
115.245
112.529
95.663
77.423
77.000
76.577
55.863
52.377
COOMe
CN
MeO
O
13j
13C NMR in CDCl3
150
100
50
ppm (t1)



14j

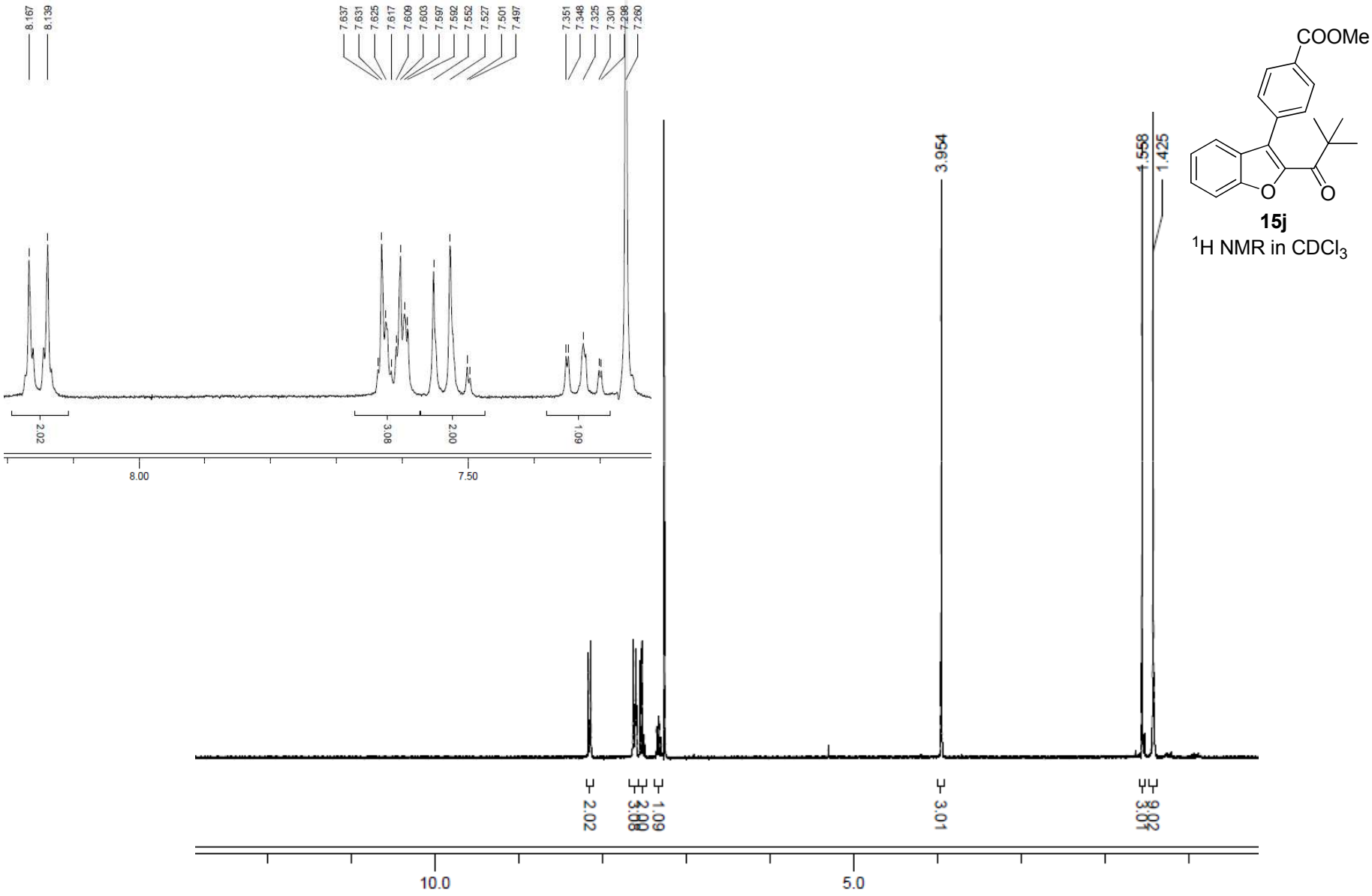
^{1}H NMR in $CDCl_3$





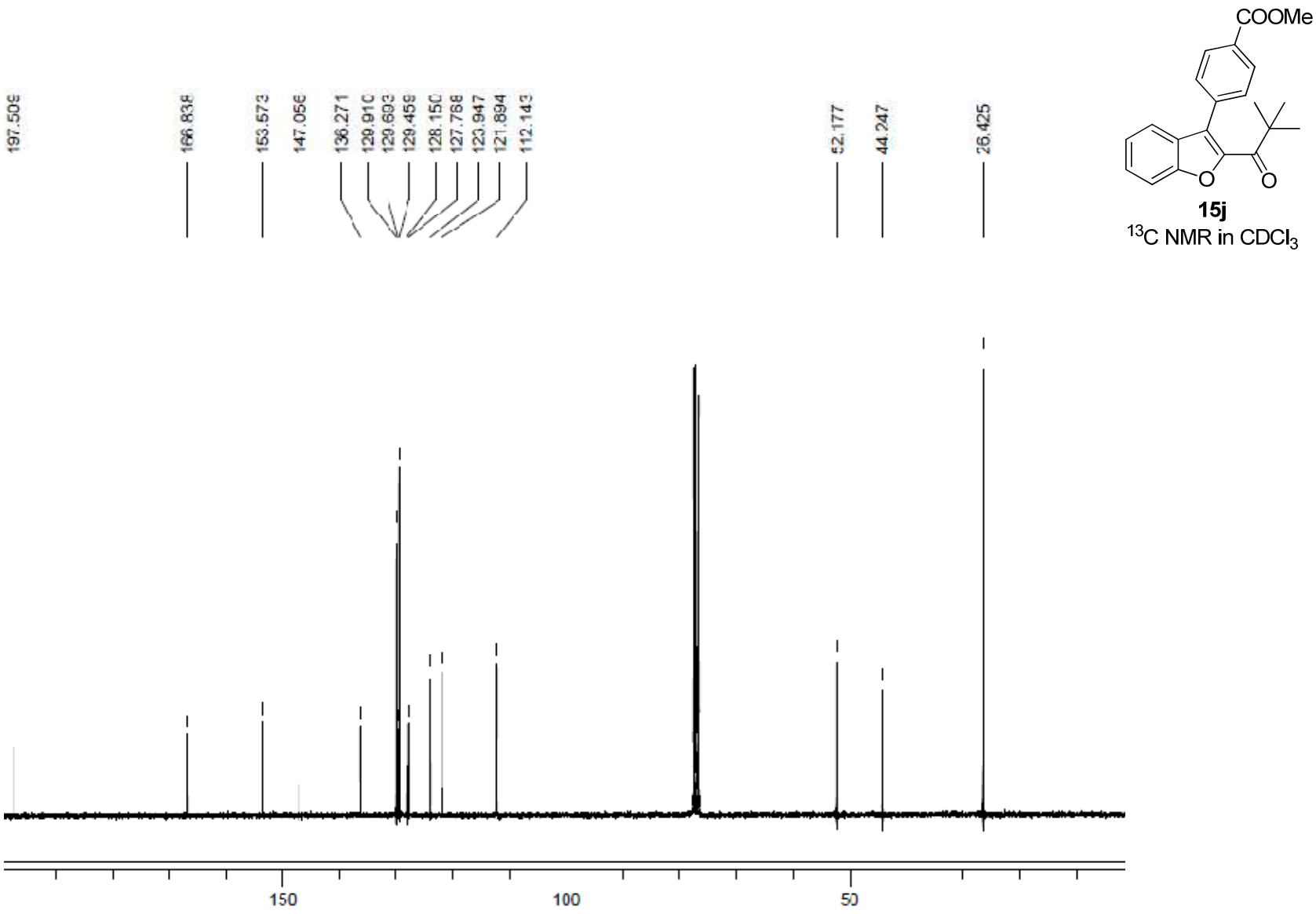
14j

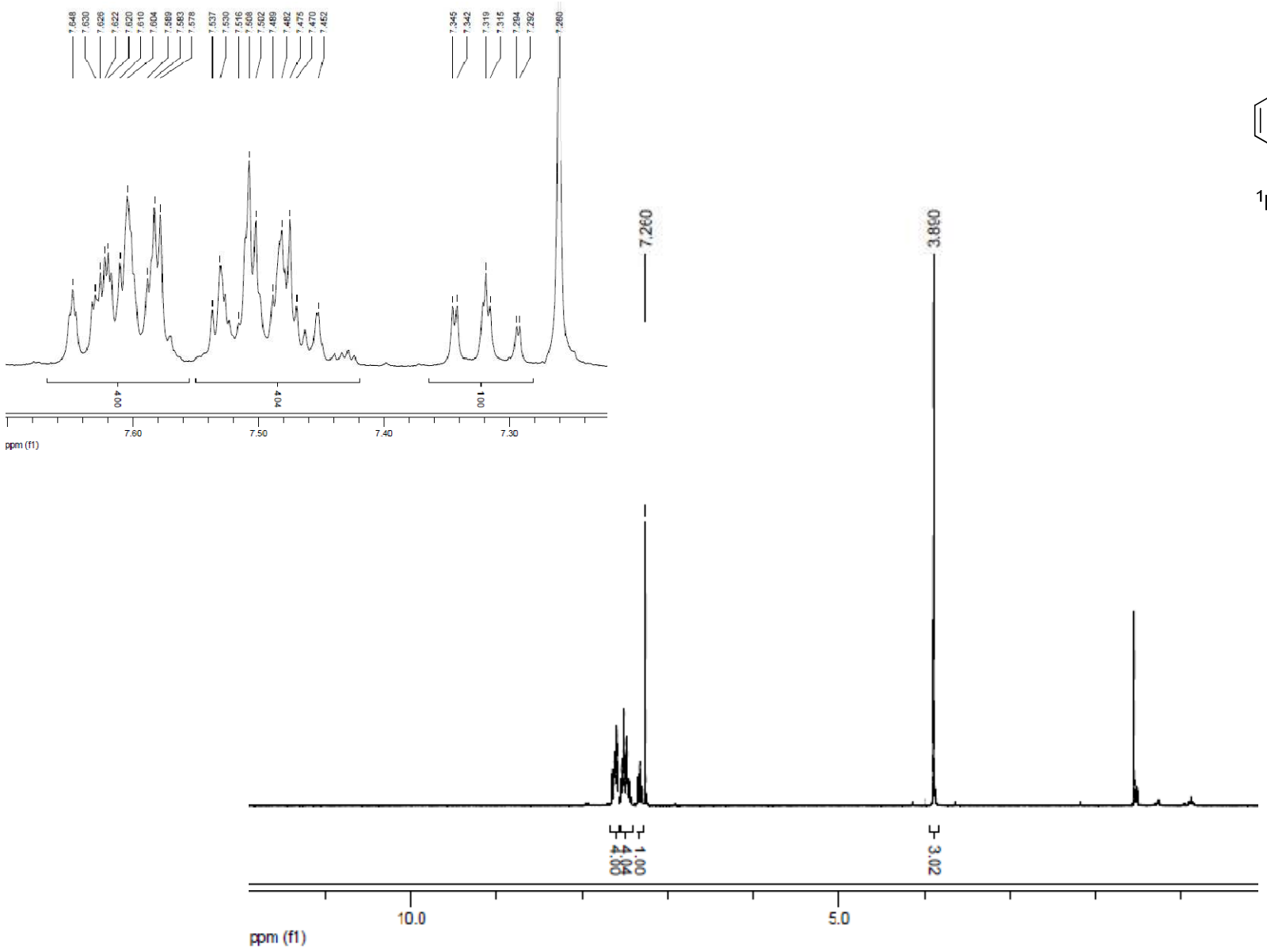
^{13}C NMR in $CDCl_3$

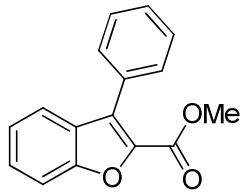


15j

^{1}H NMR in $CDCl_3$

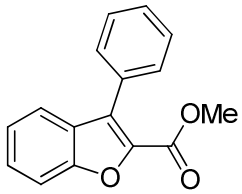

197.508
166.838
153.573
147.058
136.271
129.910
129.693
129.459
128.150
127.768
123.947
121.894
112.143
52.177
44.247
26.425
150
100
50
COOMe
O
O
15j
13C NMR in CDCl3





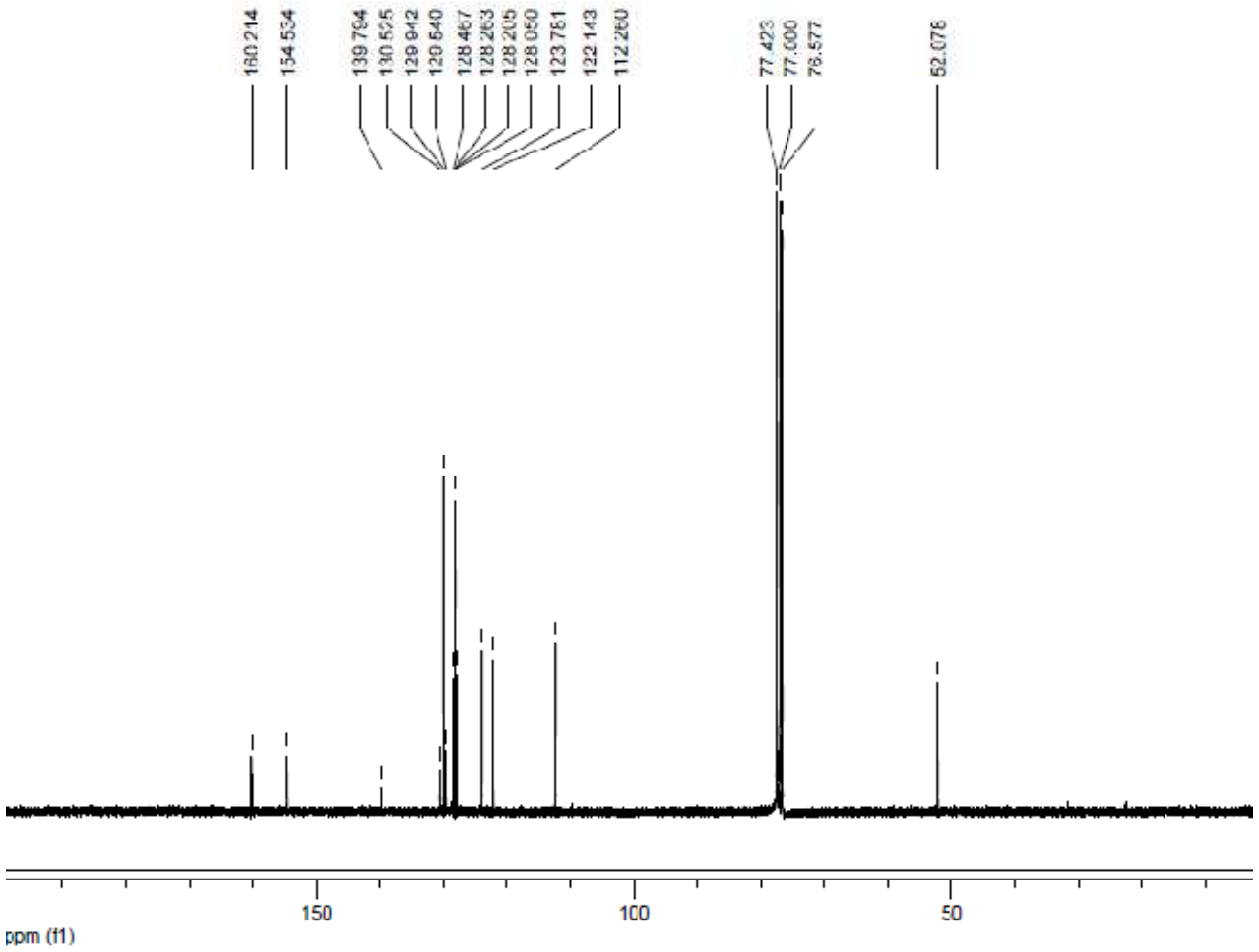
16a

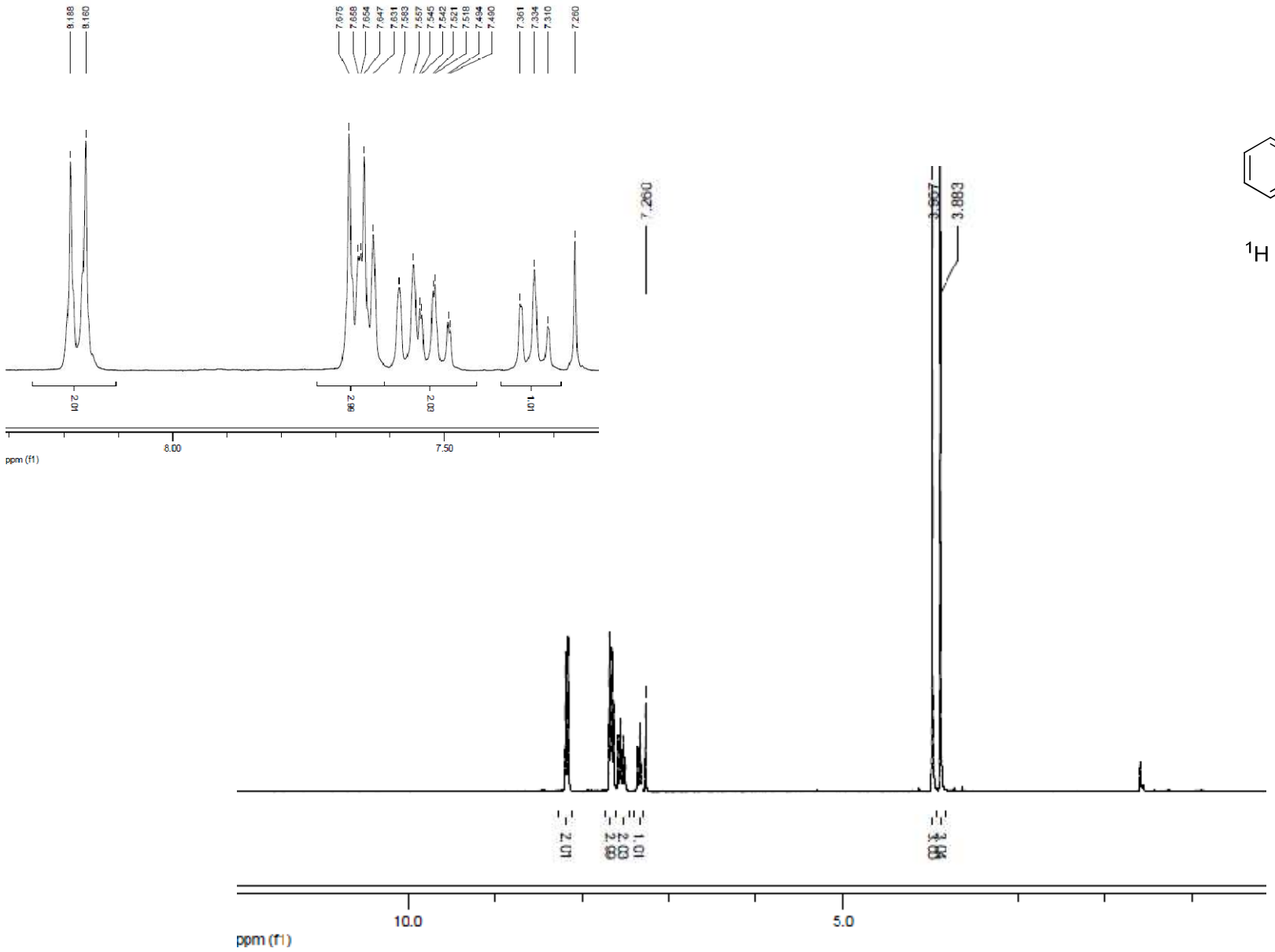
^{1}H NMR in $CDCl_3$

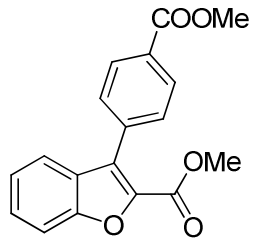


16a

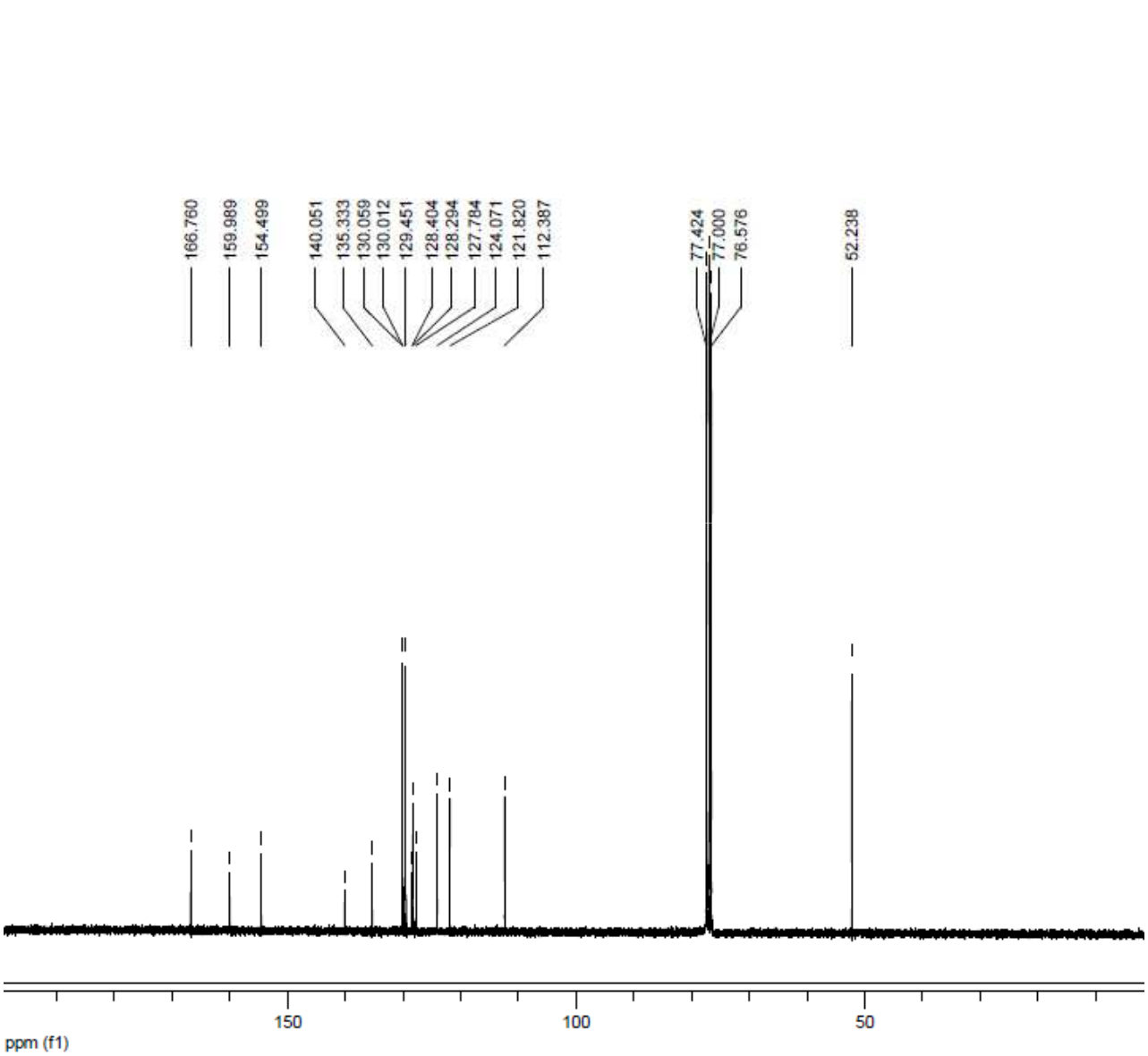
^{13}C NMR in $CDCl_3$

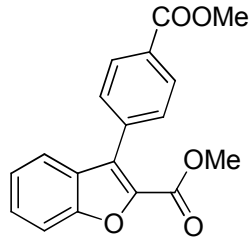






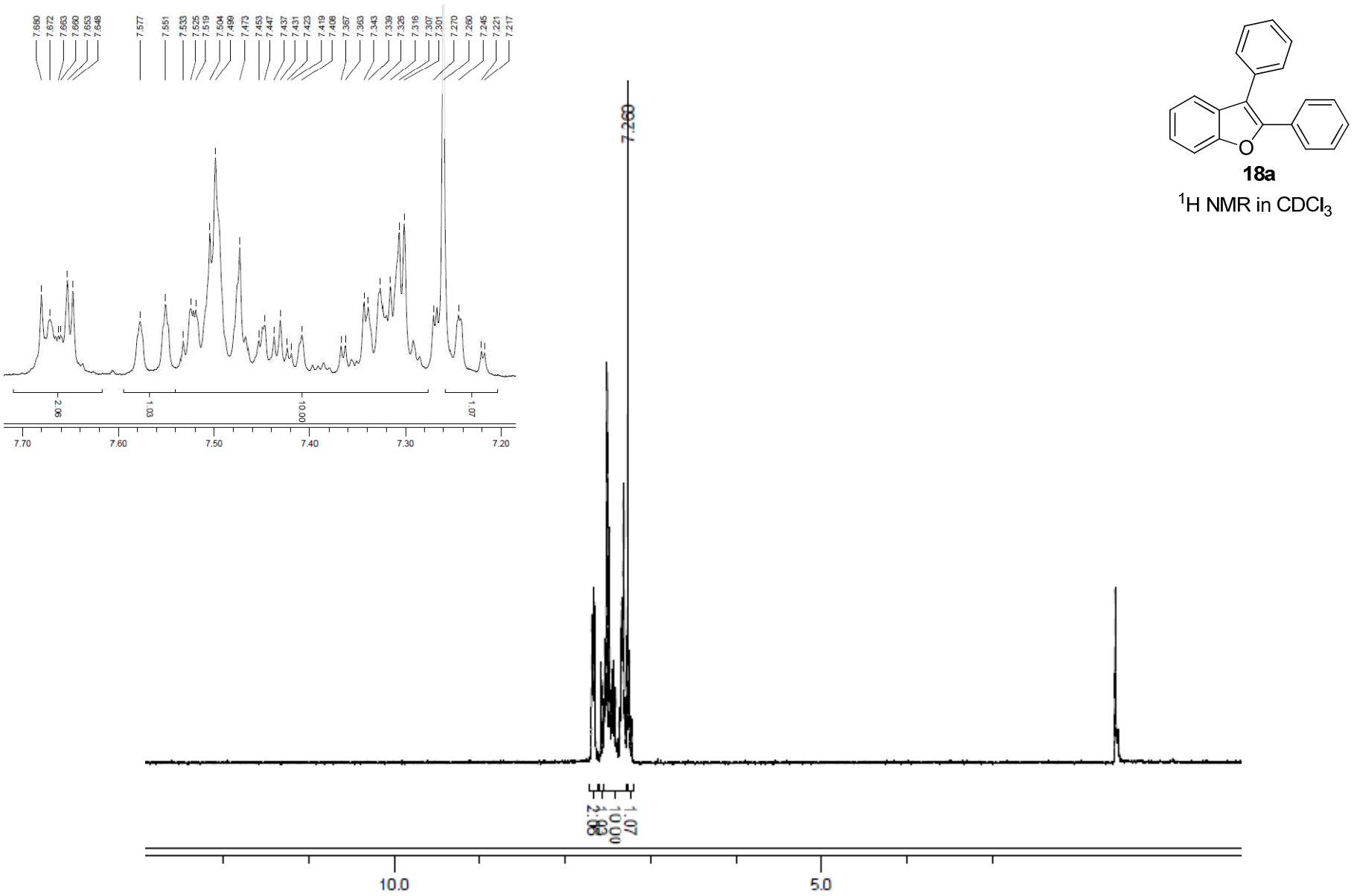
16j
^{1}H NMR in $CDCl_3$





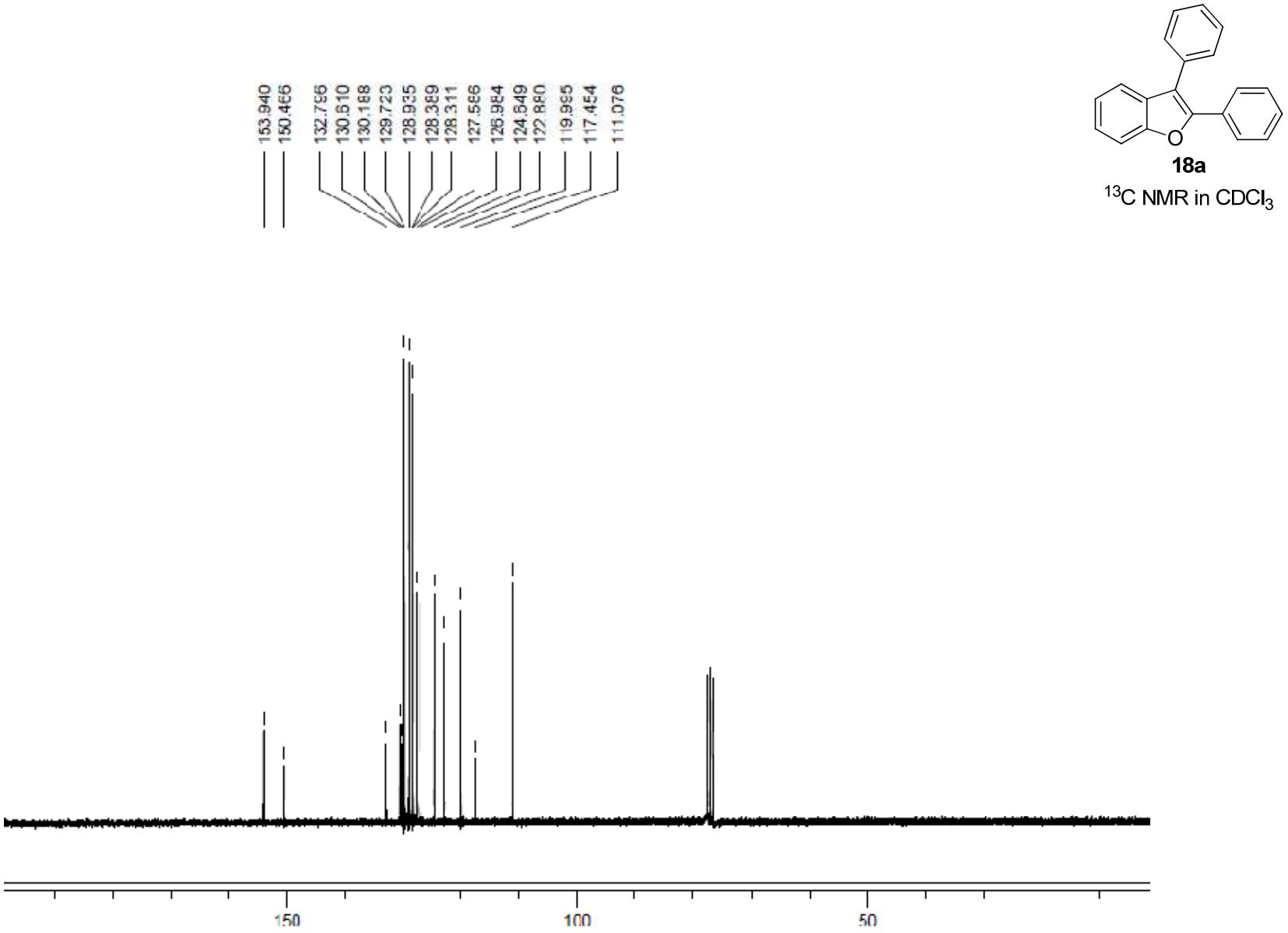
16j

^{13}C NMR in $CDCl_3$



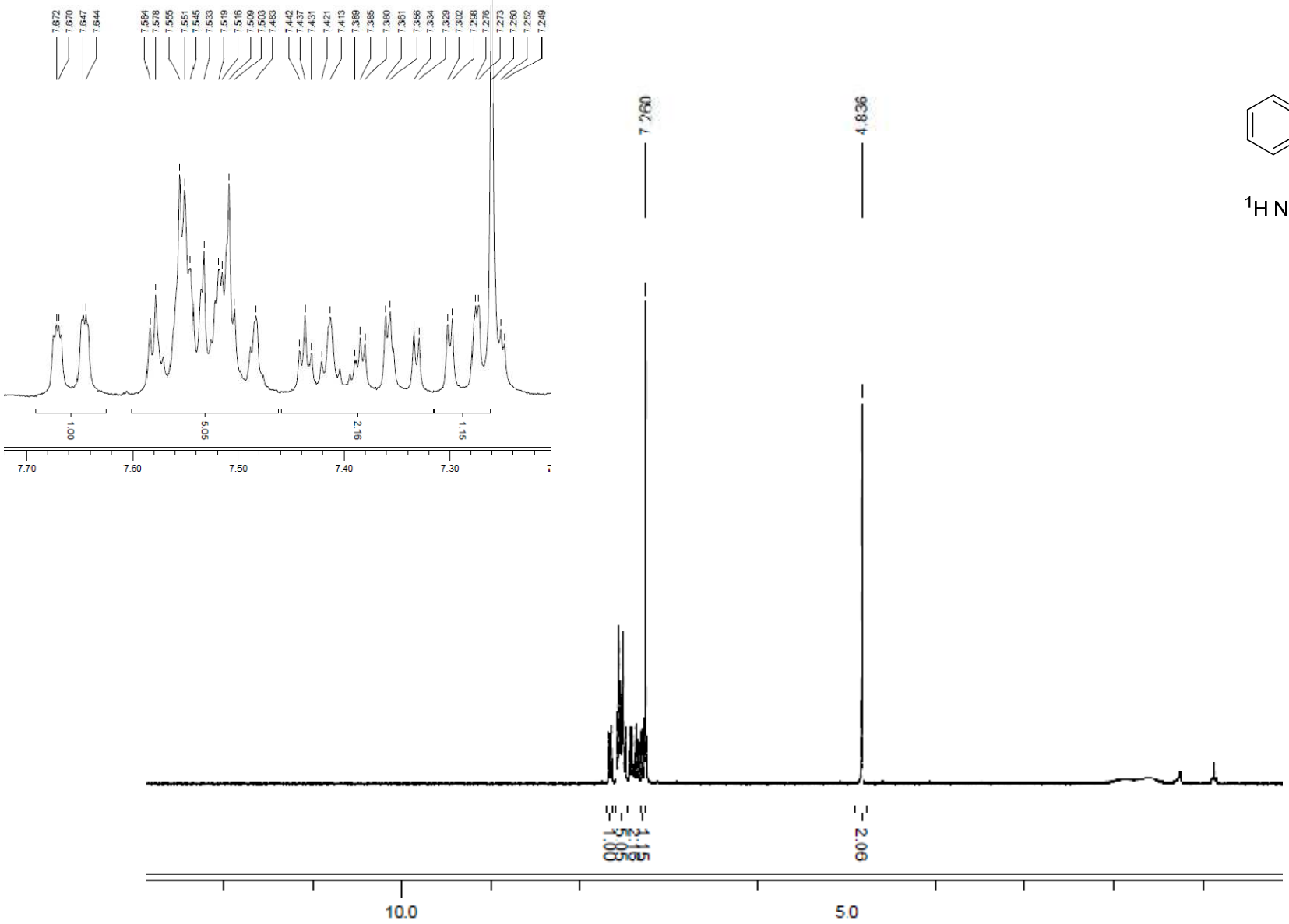
18a

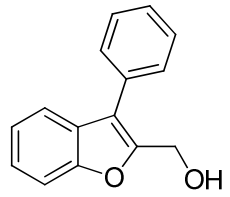
^{1}H NMR in $CDCl_3$



18a

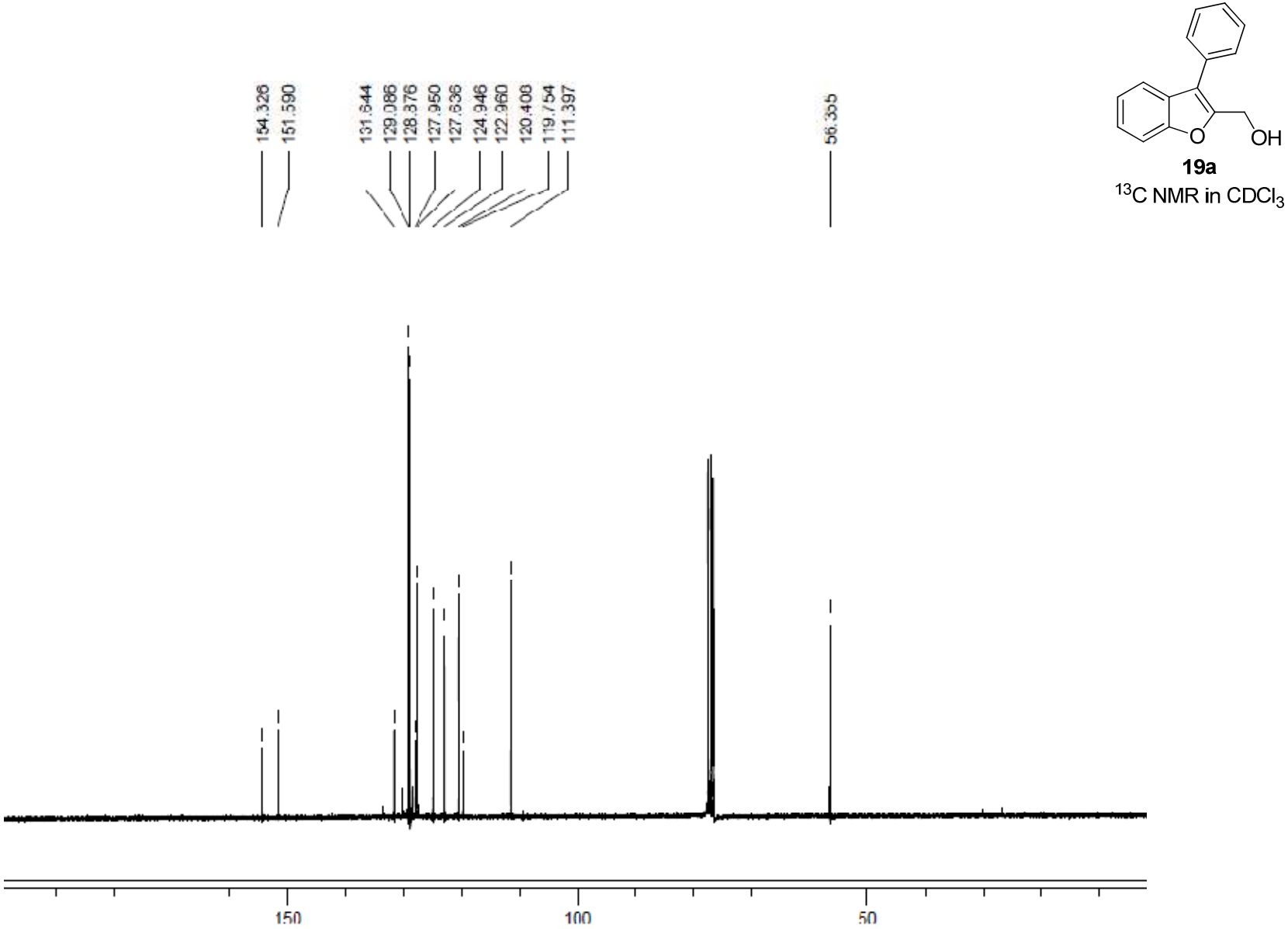
^{13}C NMR in $CDCl_3$





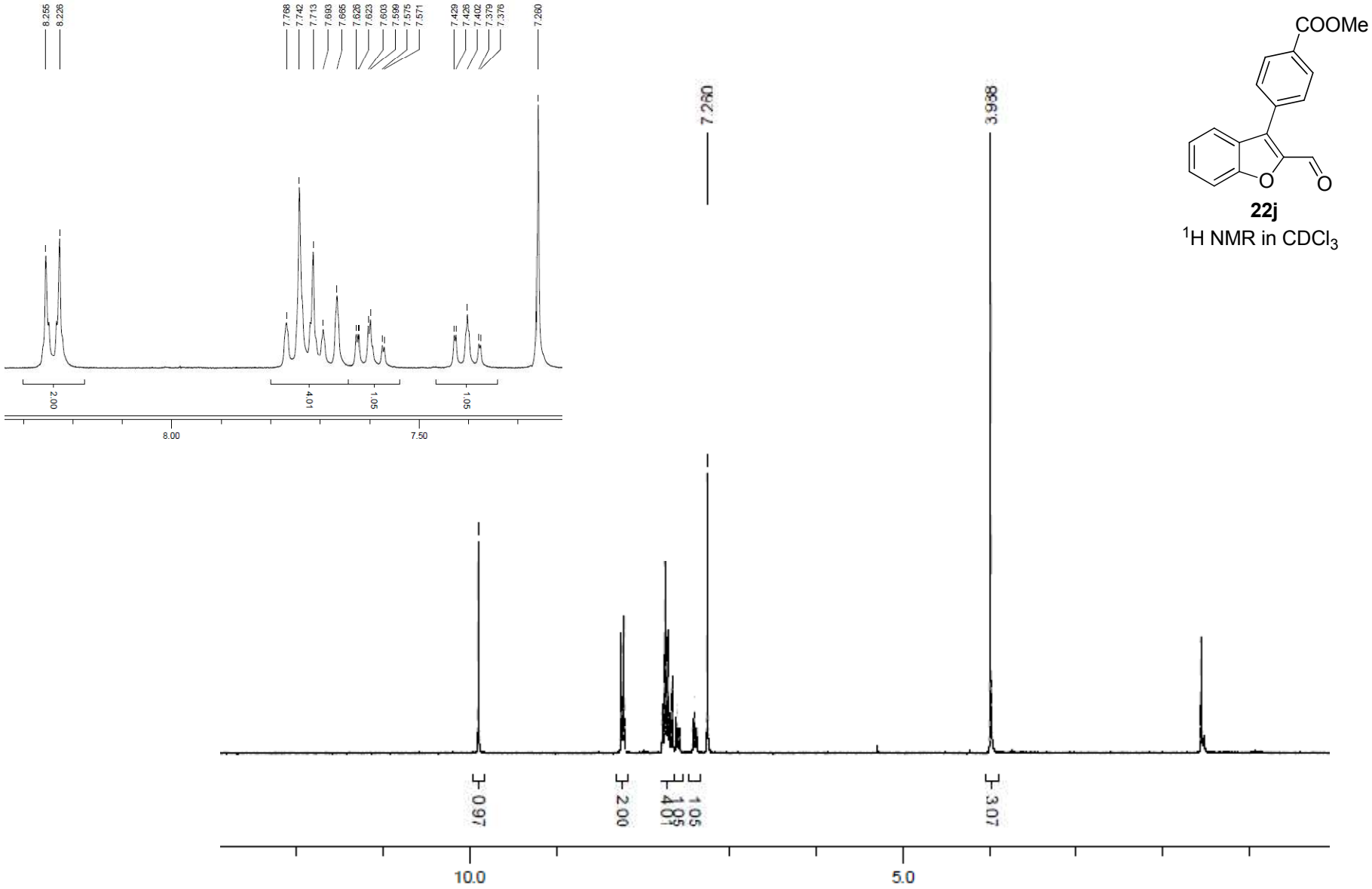
19a

^{1}H NMR in $CDCl_3$



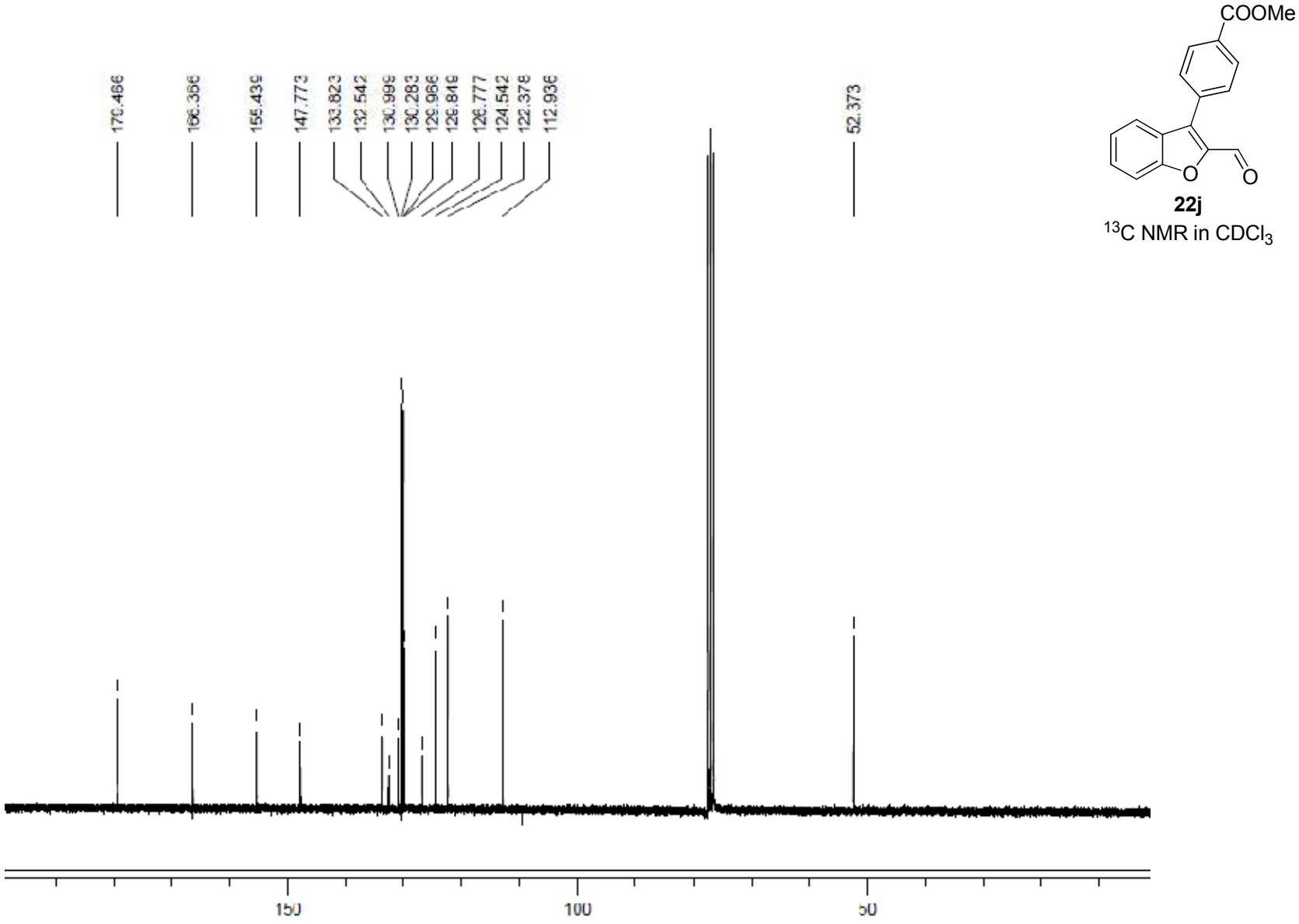
19a

^{13}C NMR in $CDCl_3$



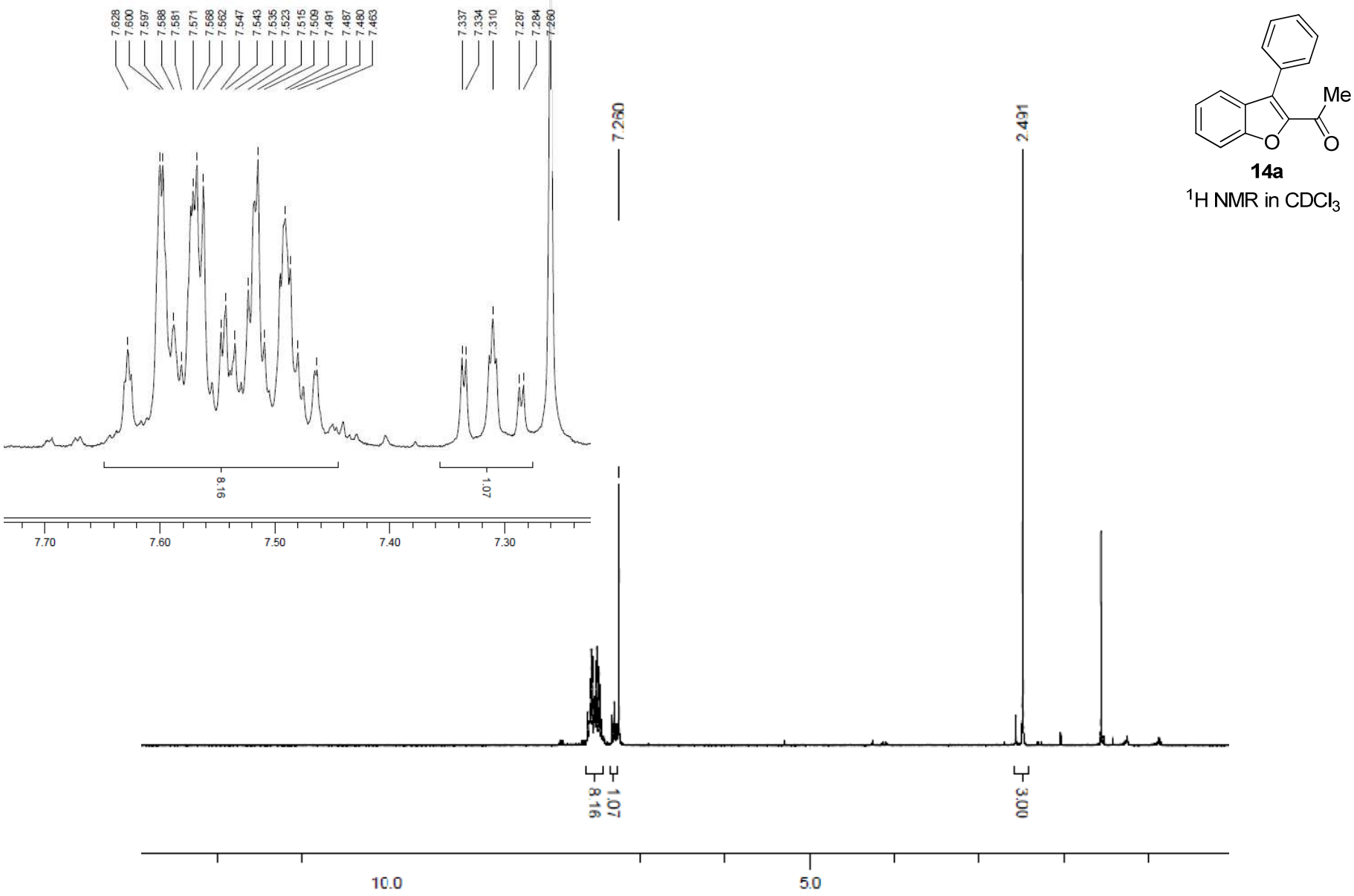
22j

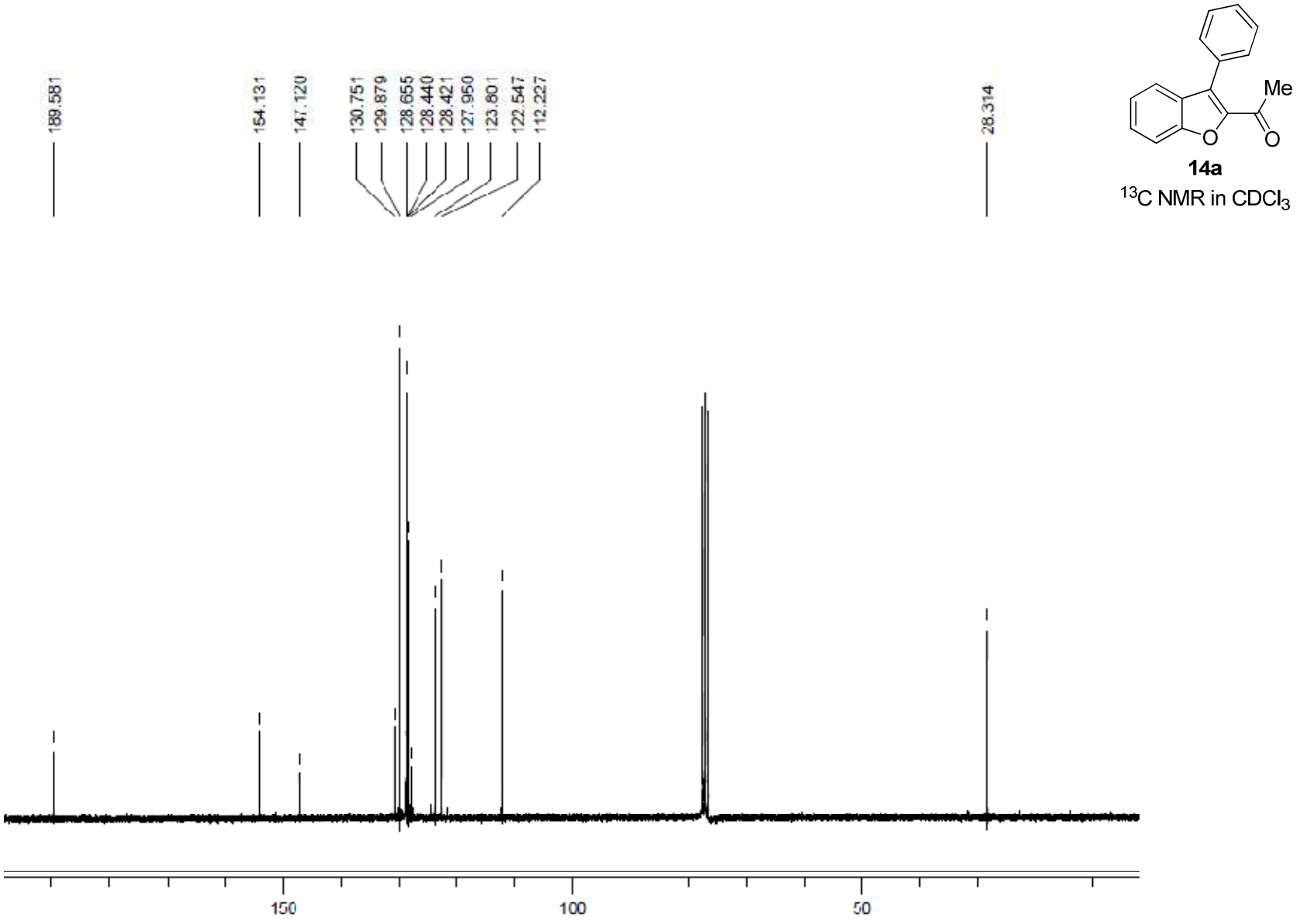
^{1}H NMR in $CDCl_3$



22j

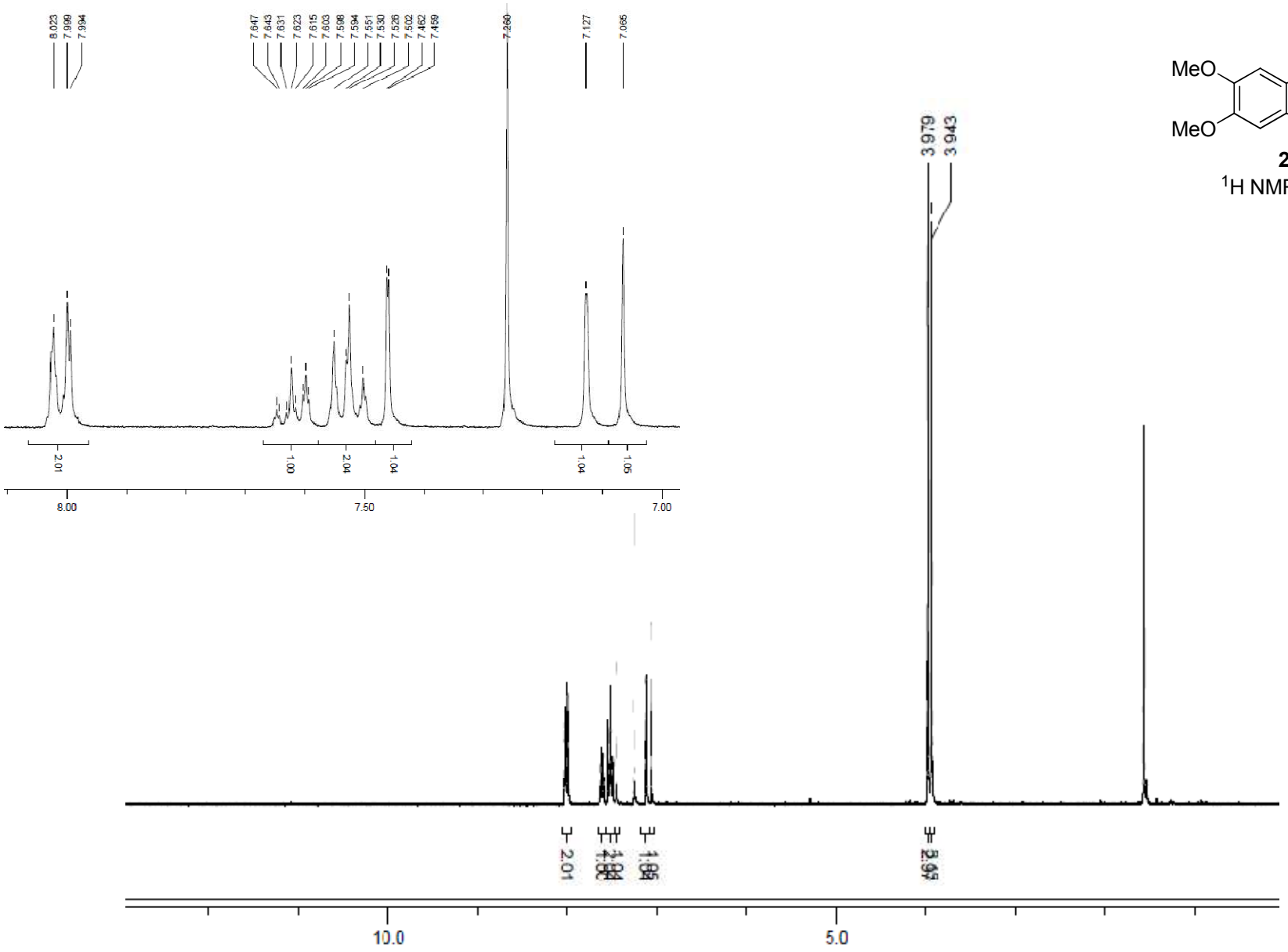
^{13}C NMR in $CDCl_3$


7.628
7.600
7.597
7.588
7.581
7.571
7.568
7.562
7.547
7.543
7.535
7.523
7.515
7.509
7.491
7.487
7.480
7.463
7.337
7.334
7.310
7.287
7.284
7.260
8.16
1.07
7.70
7.60
7.50
7.40
7.30
7.260
2.491
8.16
1.07
3.00
10.0
5.0
Me
O
O
14a
^{1}H NMR in $CDCl_3$



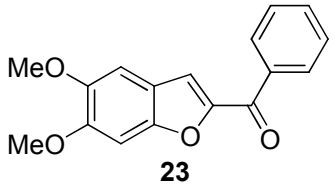
14a

^{13}C NMR in $CDCl_3$



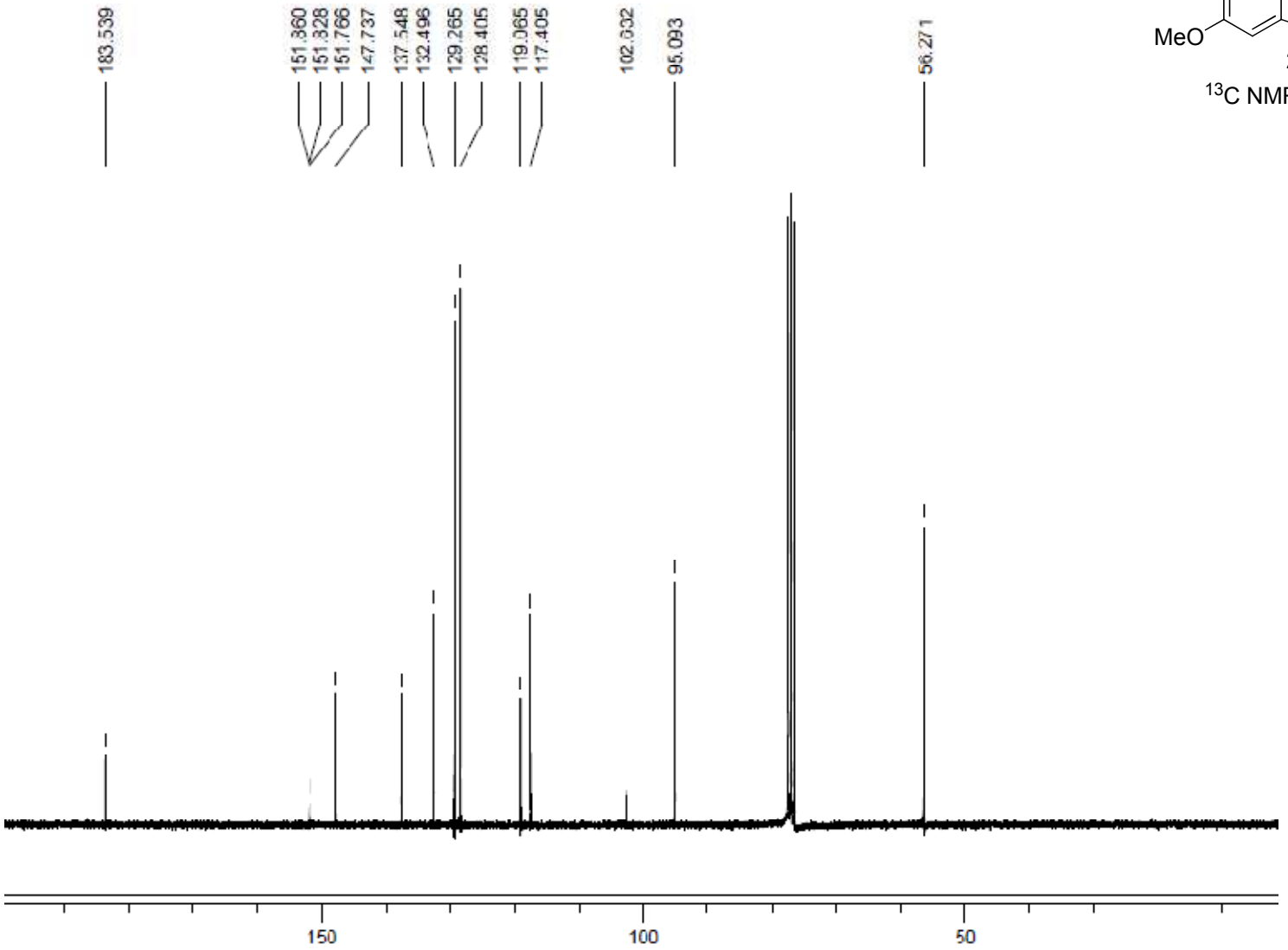
23

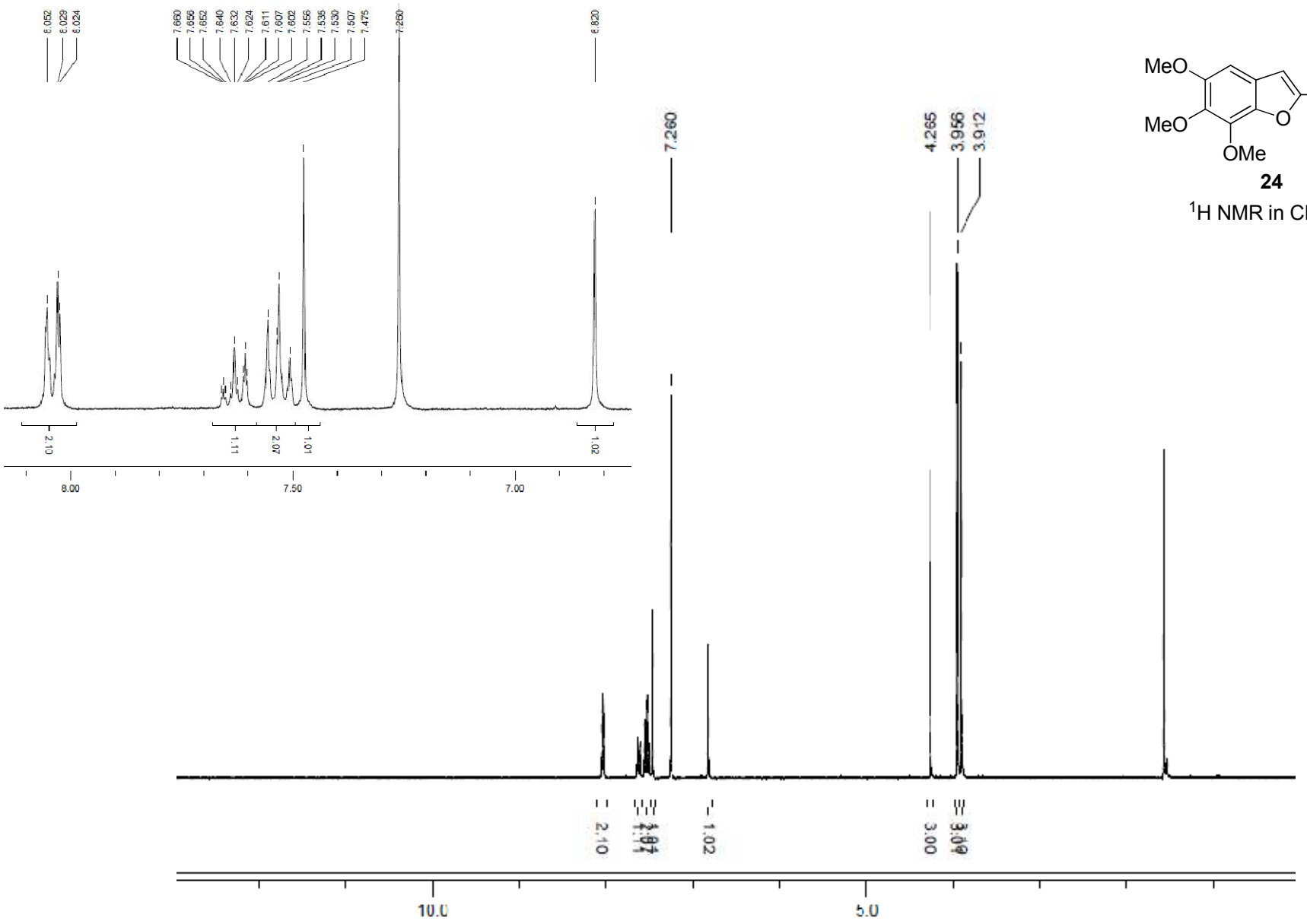
^{1}H NMR in $CDCl_3$



23

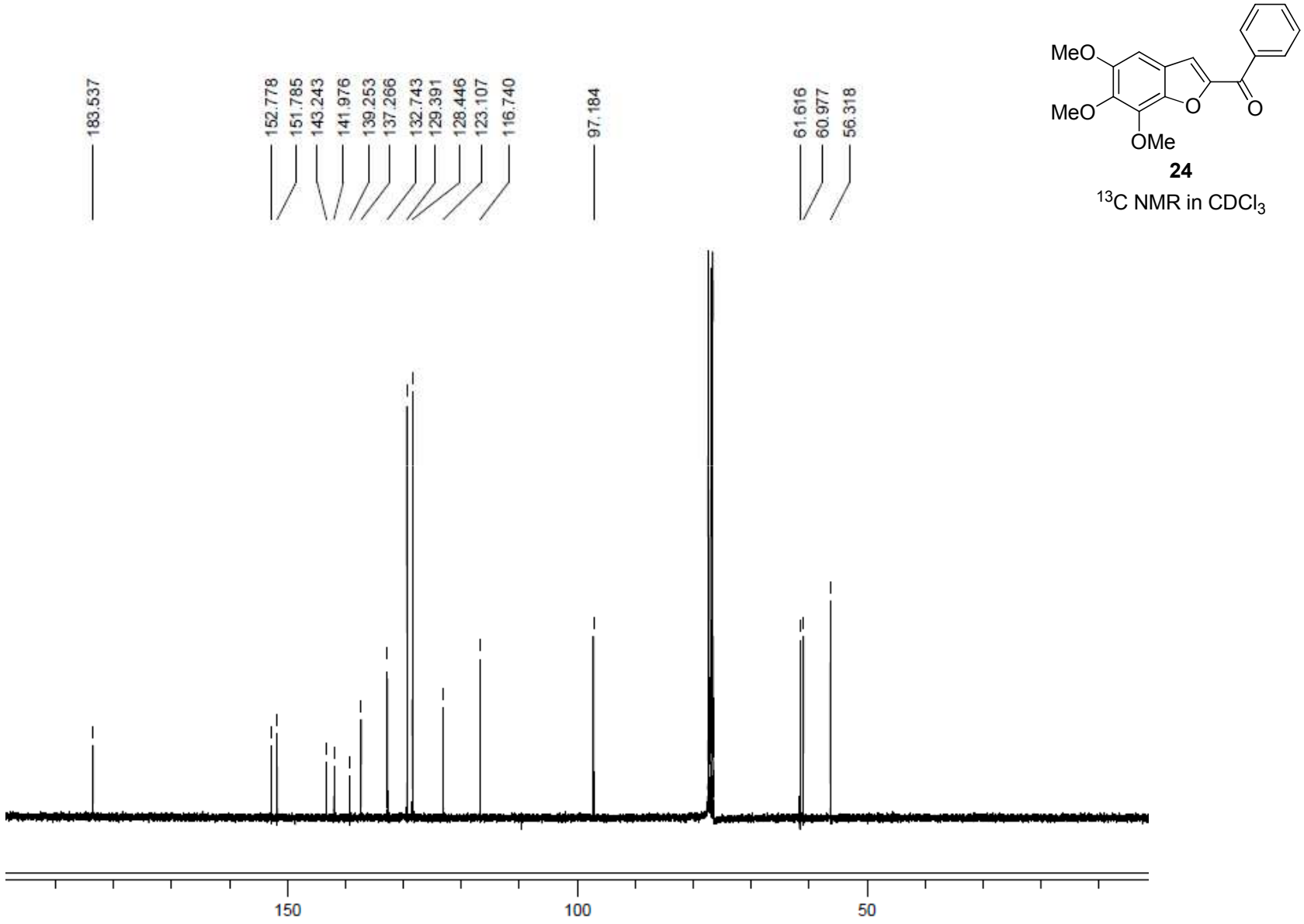
^{13}C NMR in $CDCl_3$





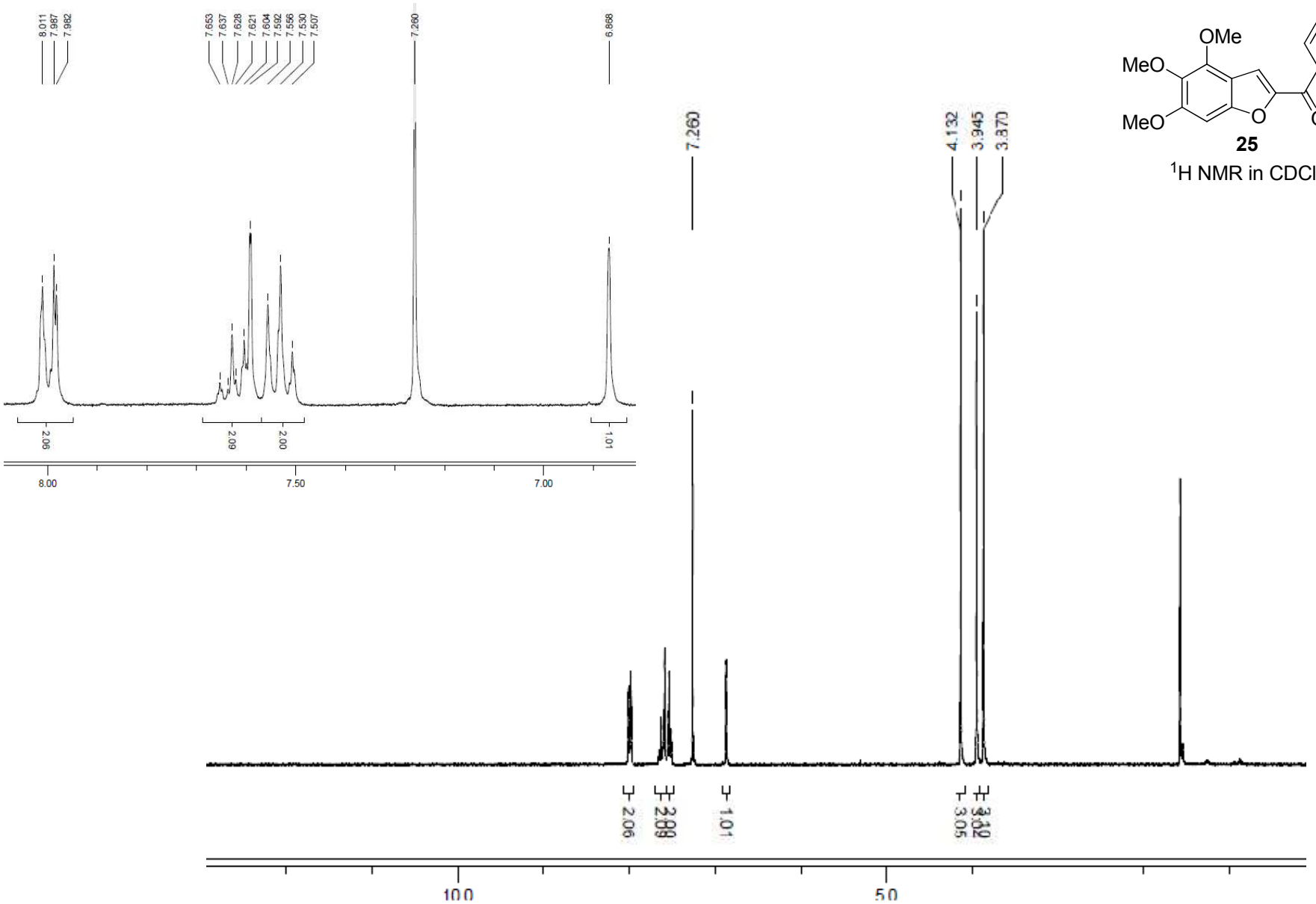
24

^{1}H NMR in $CDCl_3$



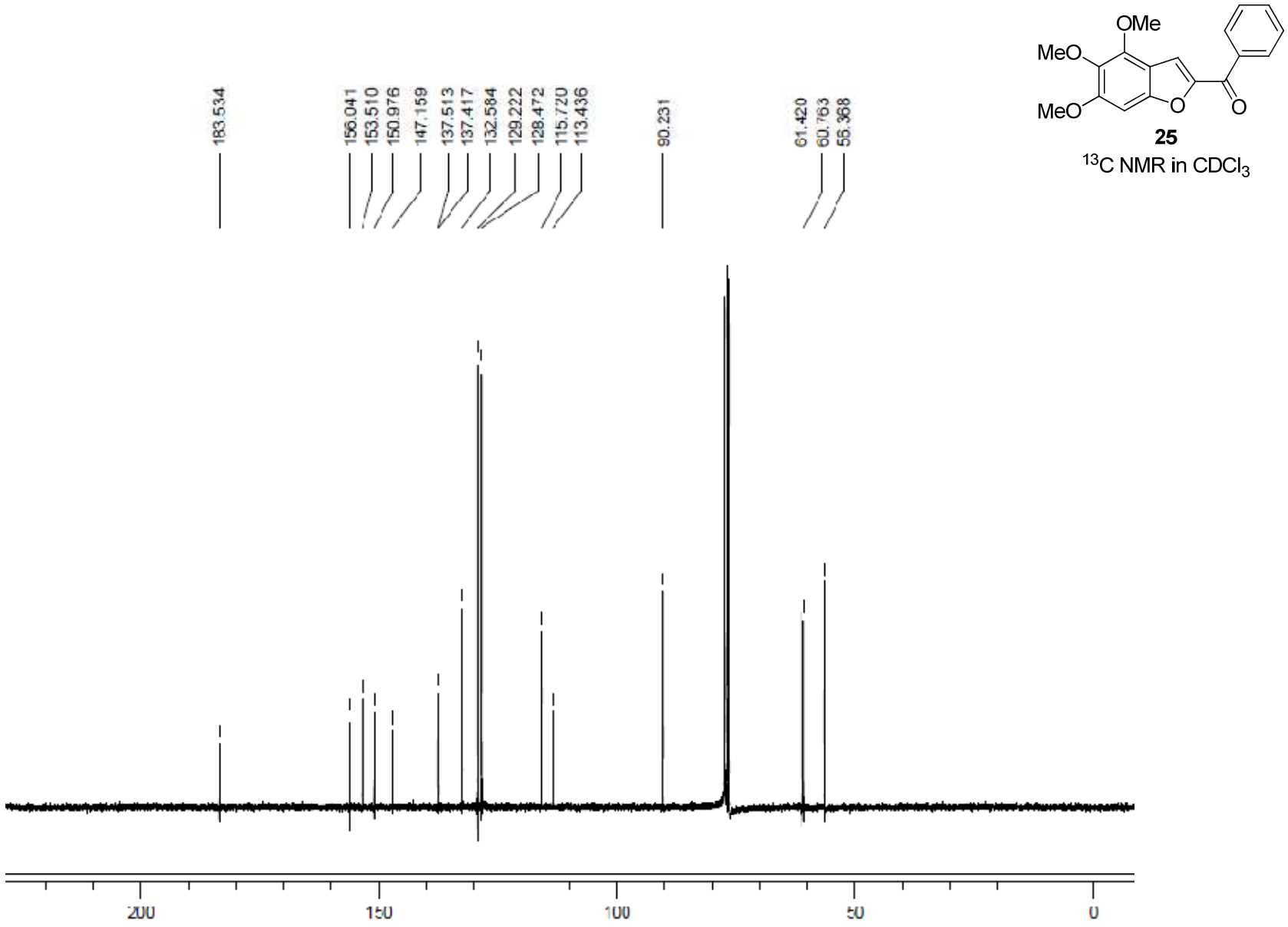
24

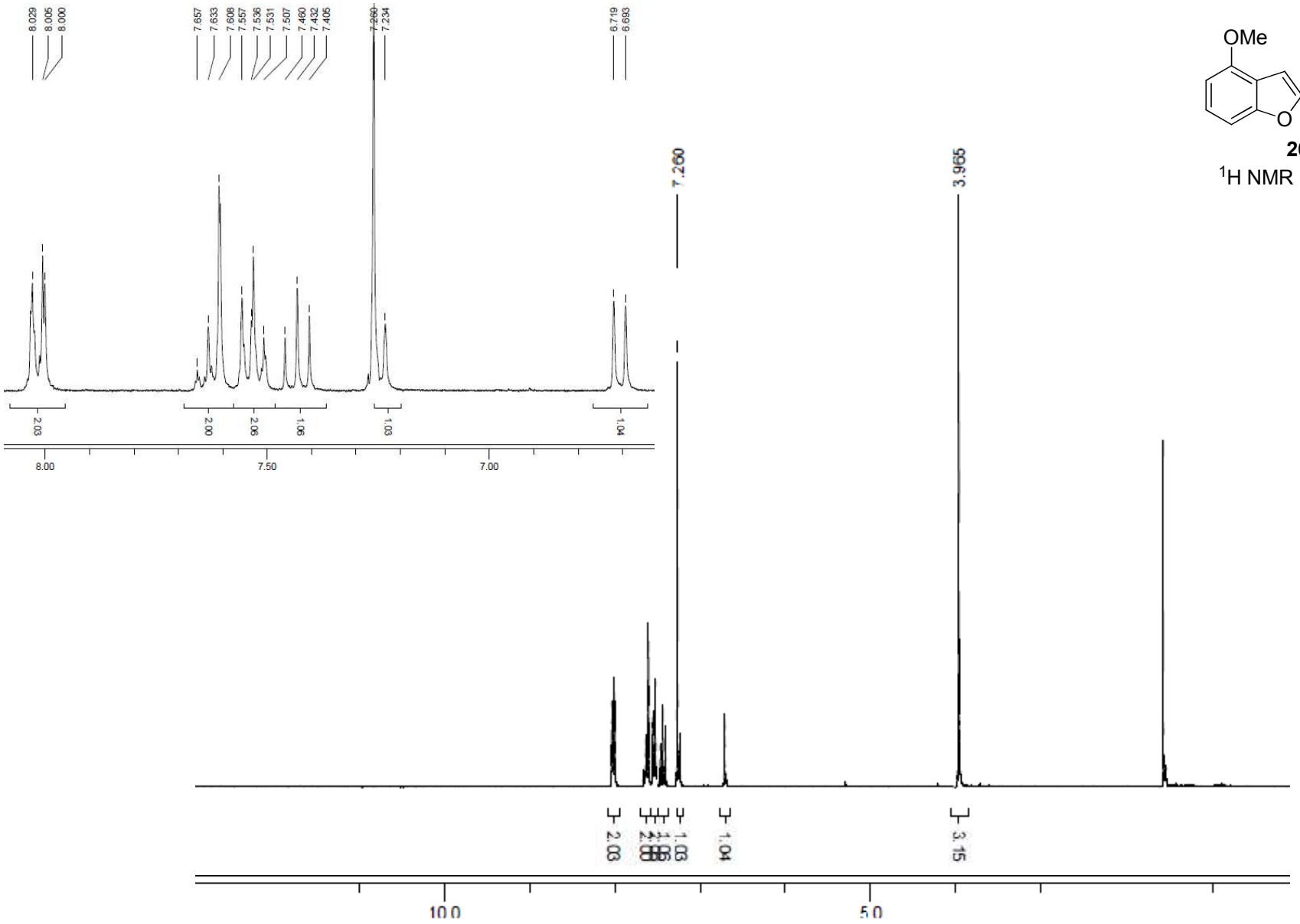
^{13}C NMR in $CDCl_3$

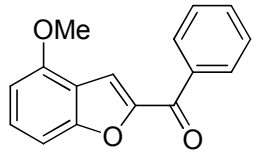


25

^{1}H NMR in $CDCl_3$

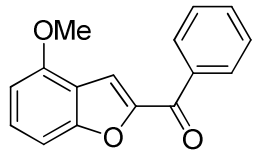

OMe
MeO
MeO
O
O
25
^{13}C NMR in $CDCl_3$
183.534
156.041
153.510
150.976
147.159
137.513
137.417
132.584
129.222
128.472
115.720
113.436
90.231
61.420
60.763
56.368
200
150
100
50
0





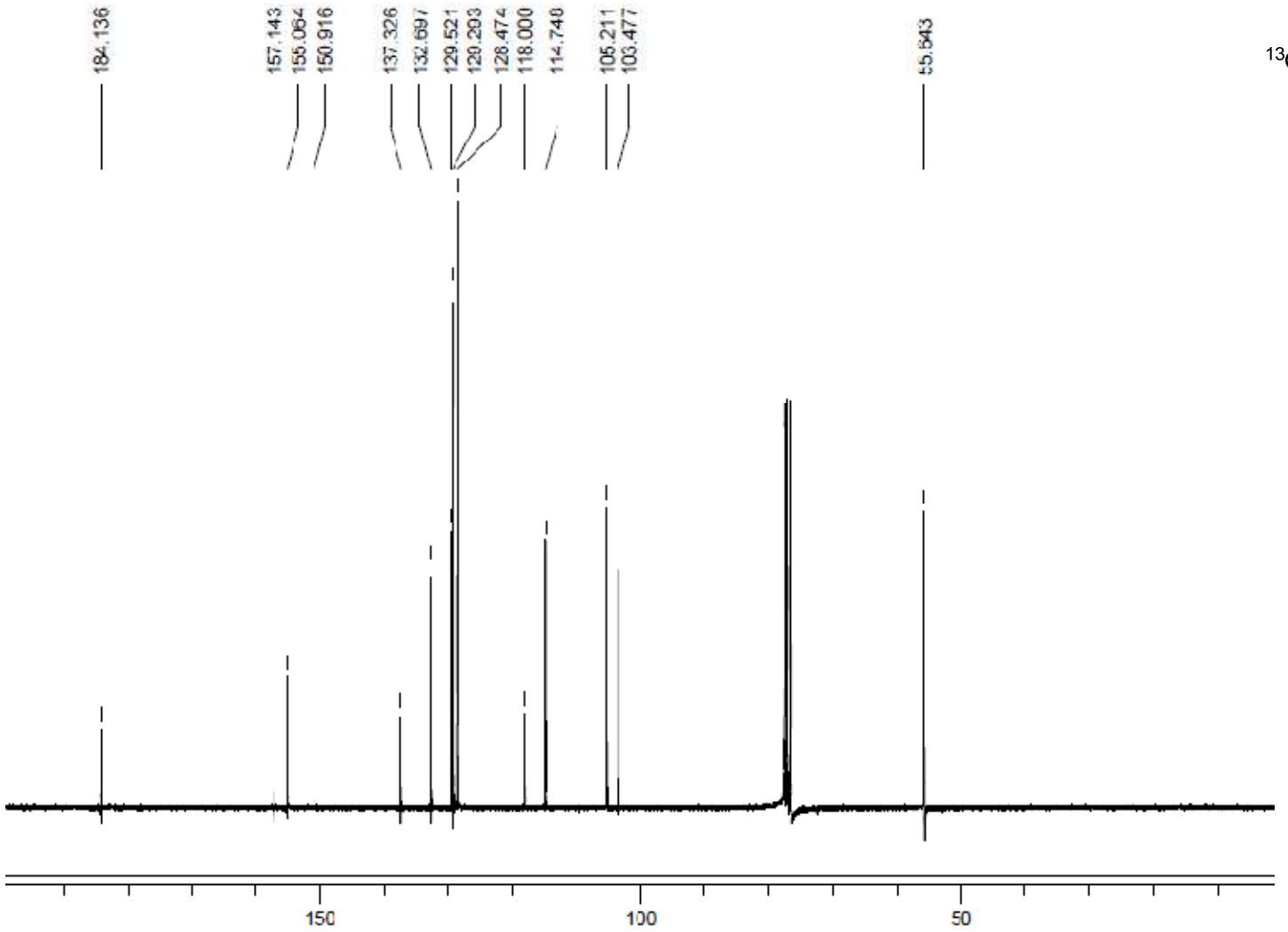
26

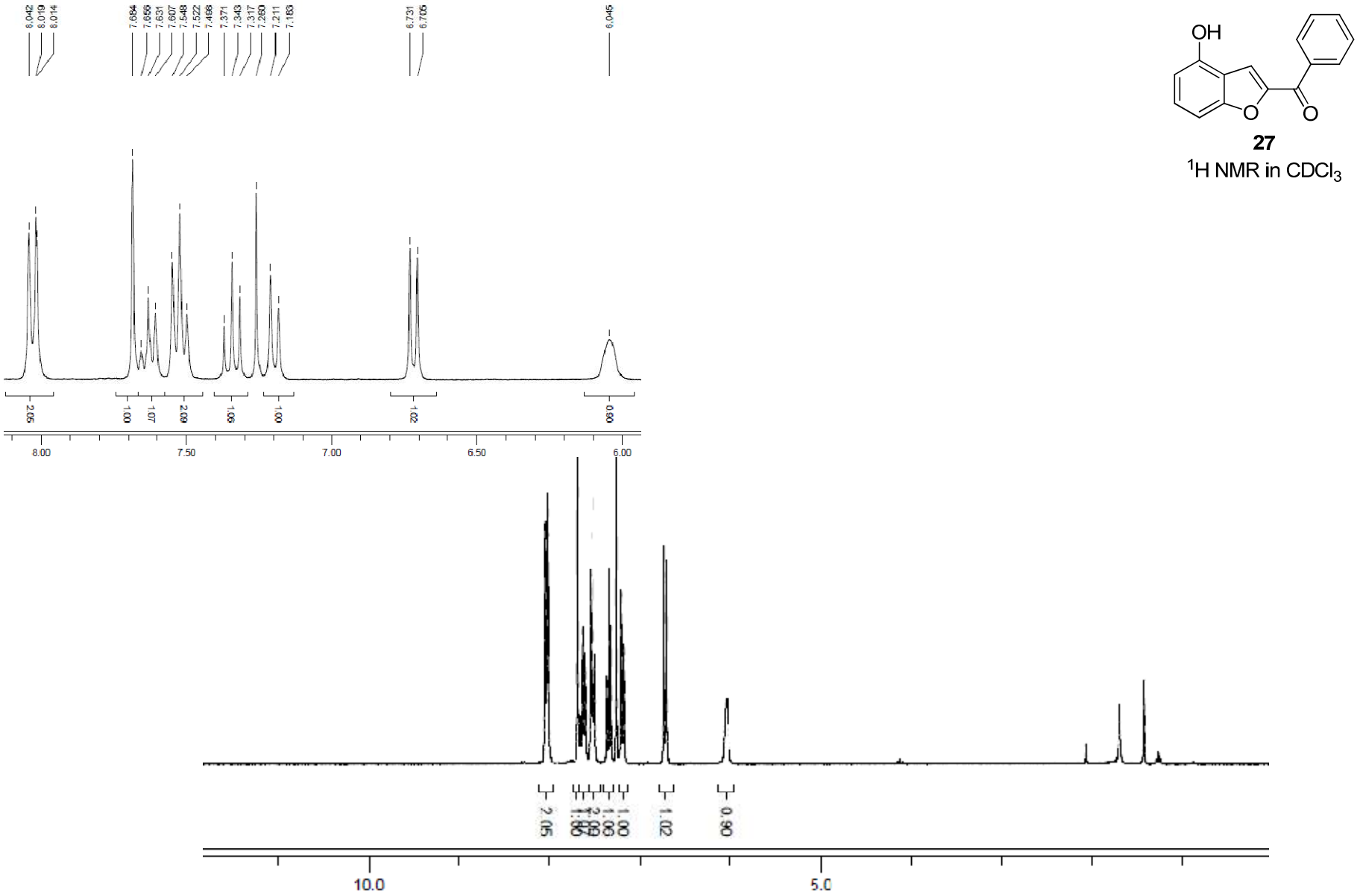
^{1}H NMR in $CDCl_3$



26

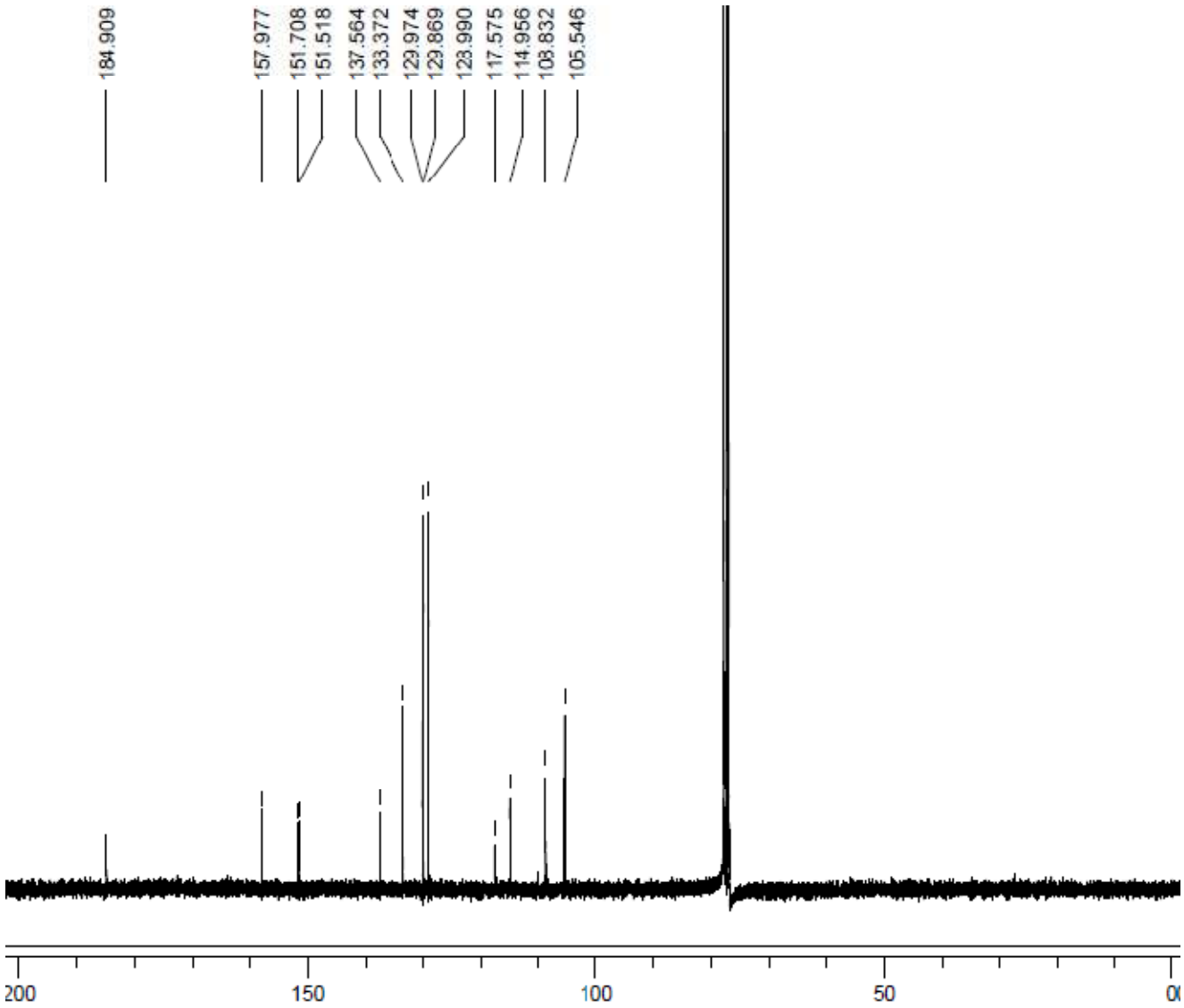
^{13}C NMR in $CDCl_3$

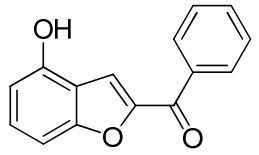




27

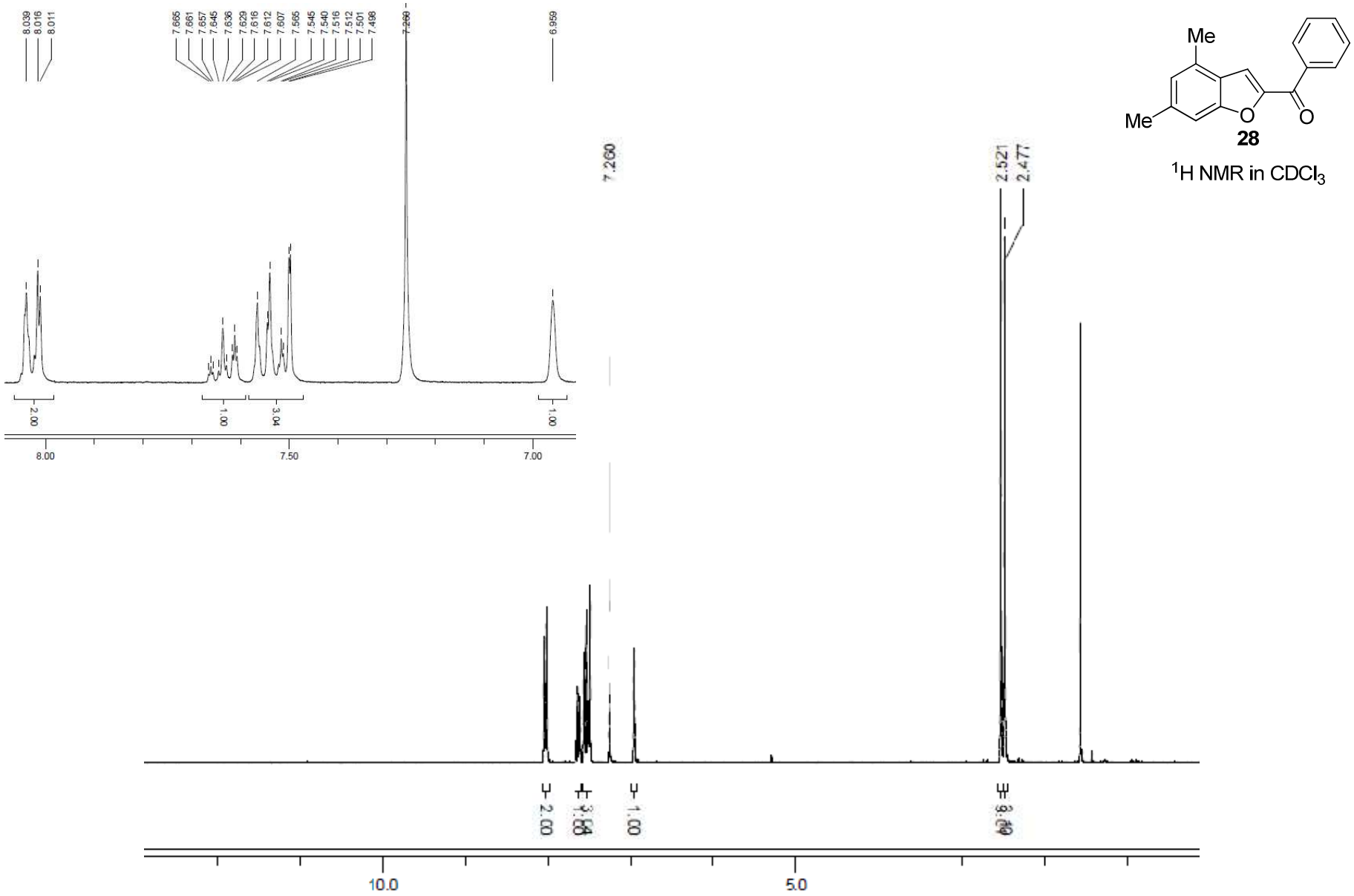
^{1}H NMR in $CDCl_3$

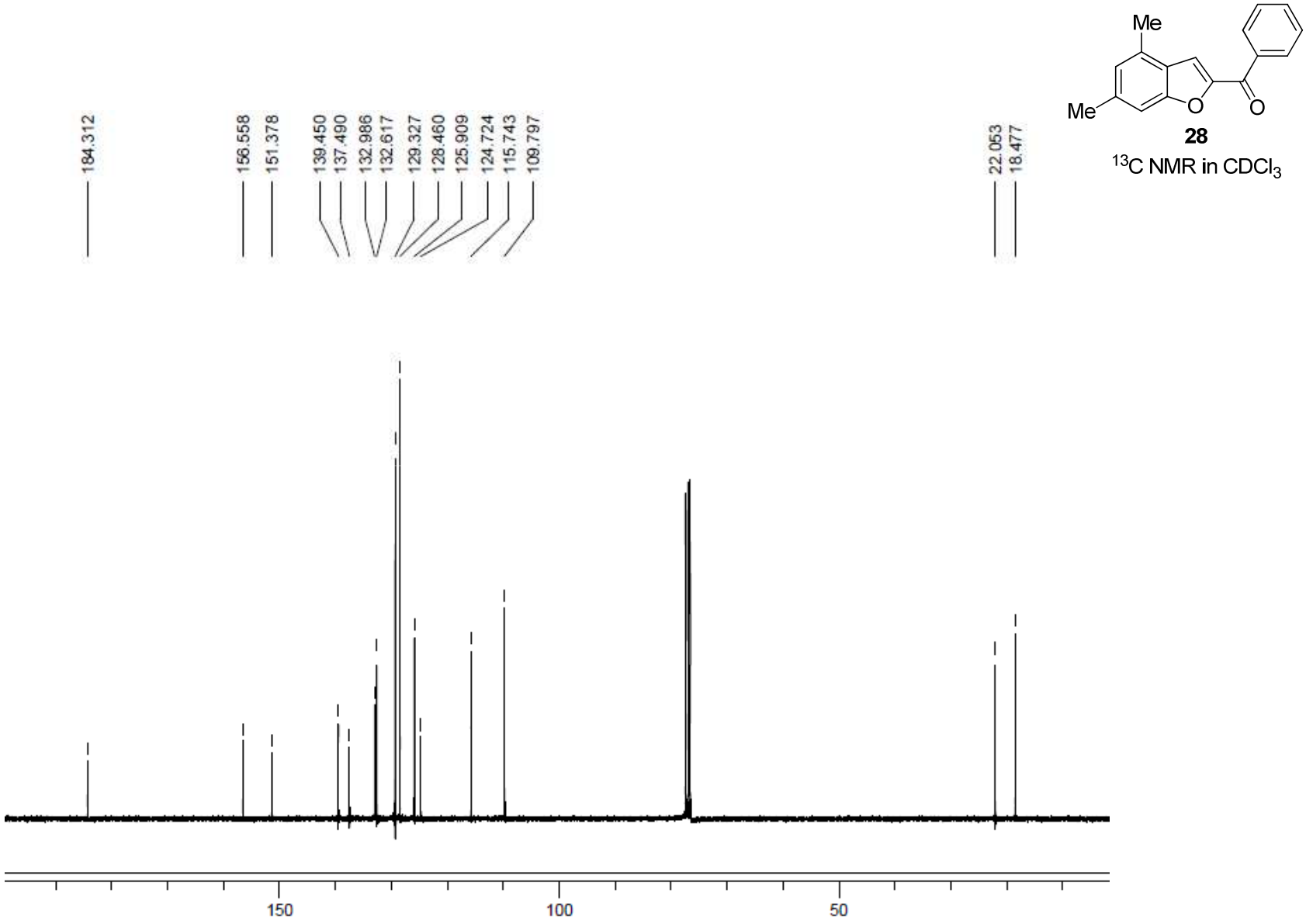


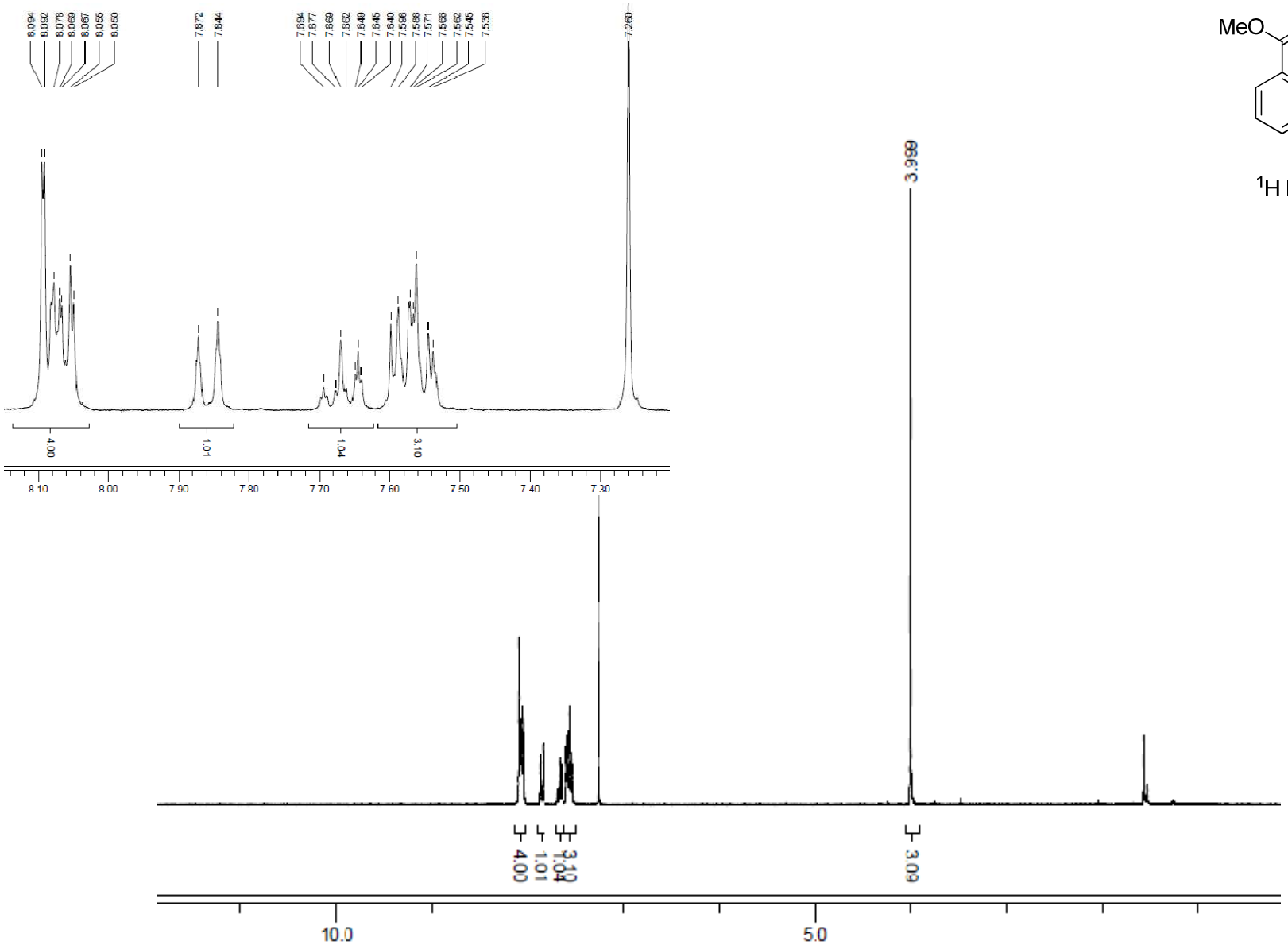


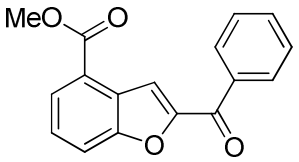
27

^{13}C NMR in $CDCl_3$


8.039
8.016
8.011
7.665
7.661
7.657
7.645
7.636
7.629
7.616
7.612
7.607
7.565
7.545
7.540
7.516
7.512
7.501
7.498
7.260
6.959
2.00
1.00
3.04
1.00
8.00
7.50
7.00
7.260
2.521
2.477
2.00
1.00
10.0
5.0
Me
Me
O
O
28
^{1}H NMR in $CDCl_3$

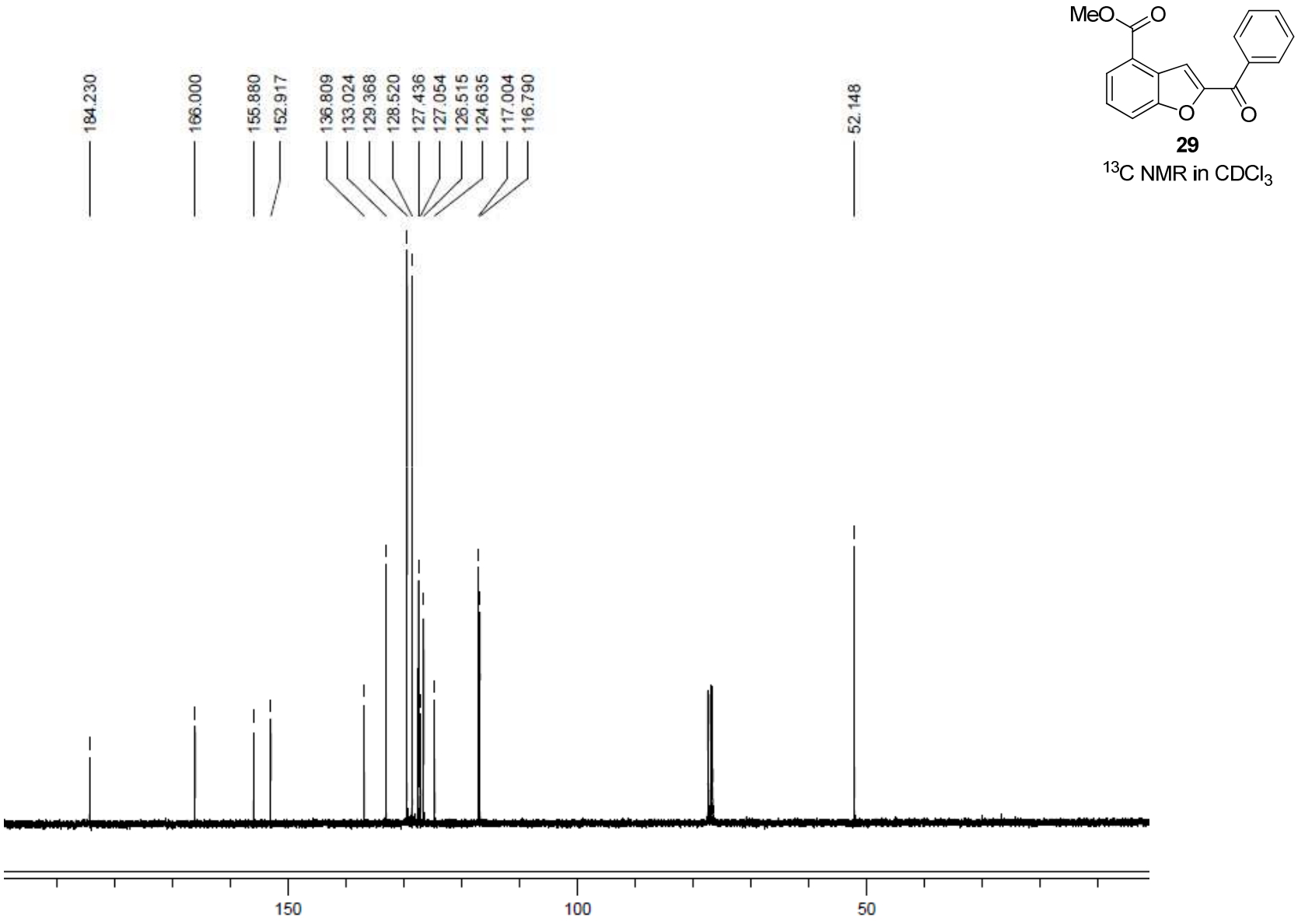

Me
Me
O
O
28
^{13}C NMR in $CDCl_3$
184.312
156.558
151.378
139.450
137.490
132.986
132.617
129.327
128.460
125.909
124.724
115.743
109.797
22.053
18.477
150
100
50





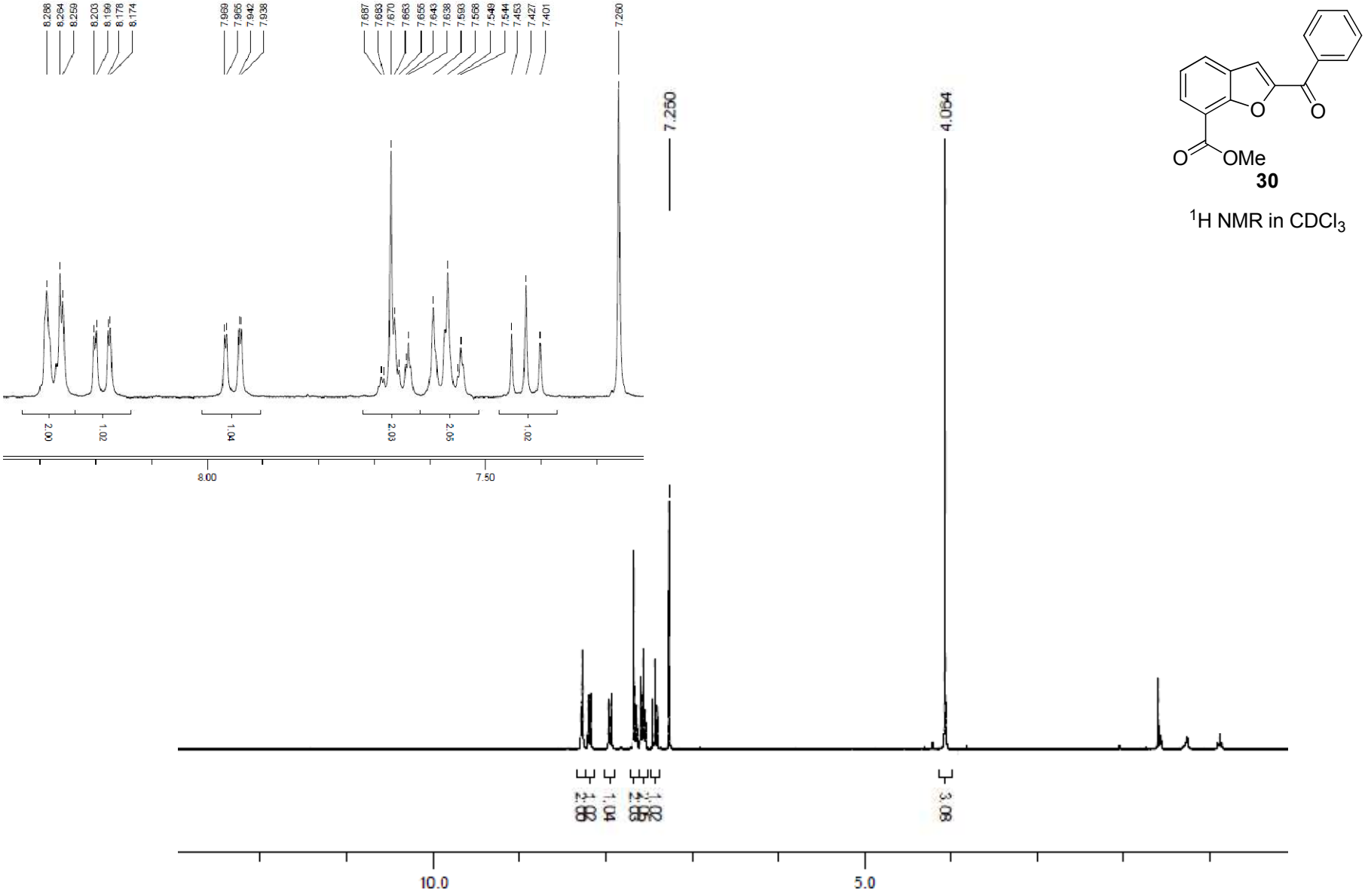
29

^{1}H NMR in $CDCl_3$



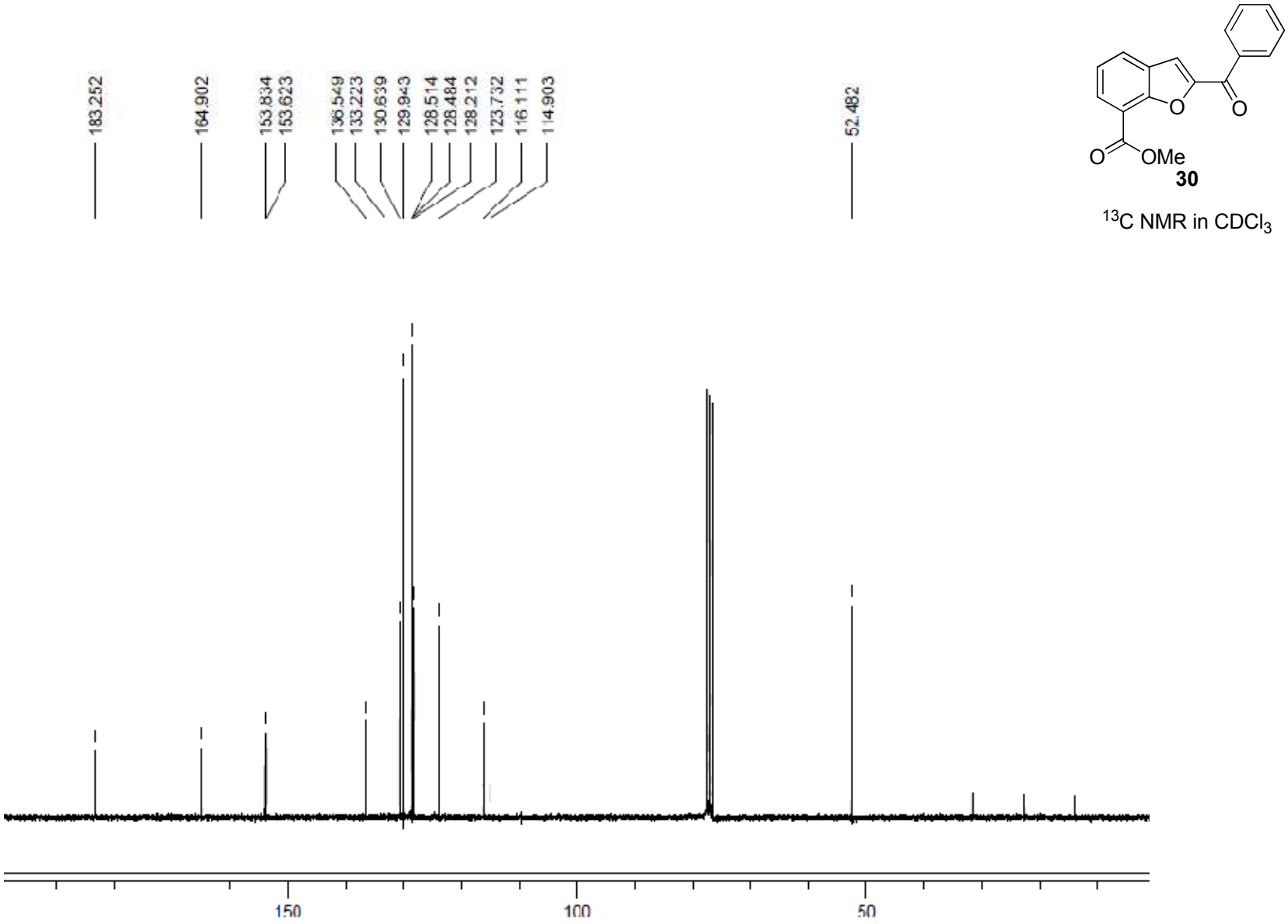
29

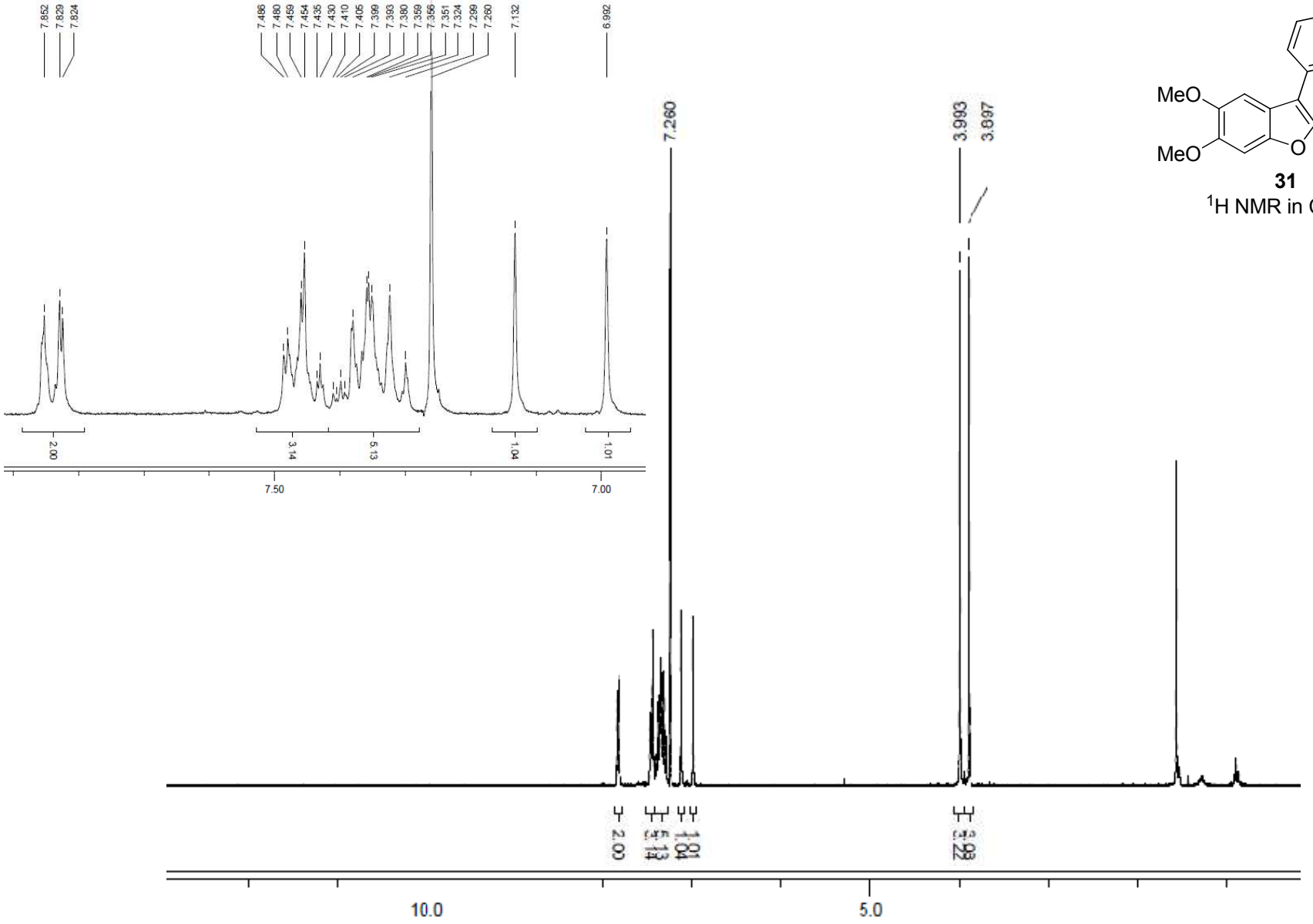
^{13}C NMR in $CDCl_3$



30

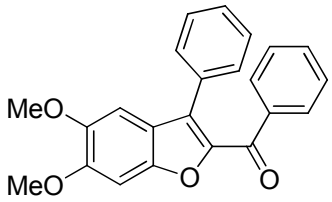
^{1}H NMR in $CDCl_3$


183.252
164.902
153.834
153.623
136.549
133.223
130.639
129.943
128.514
128.484
128.212
123.732
116.111
114.903
52.482
O
O
O
OMe
30
^{13}C NMR in $CDCl_3$
150
100
50



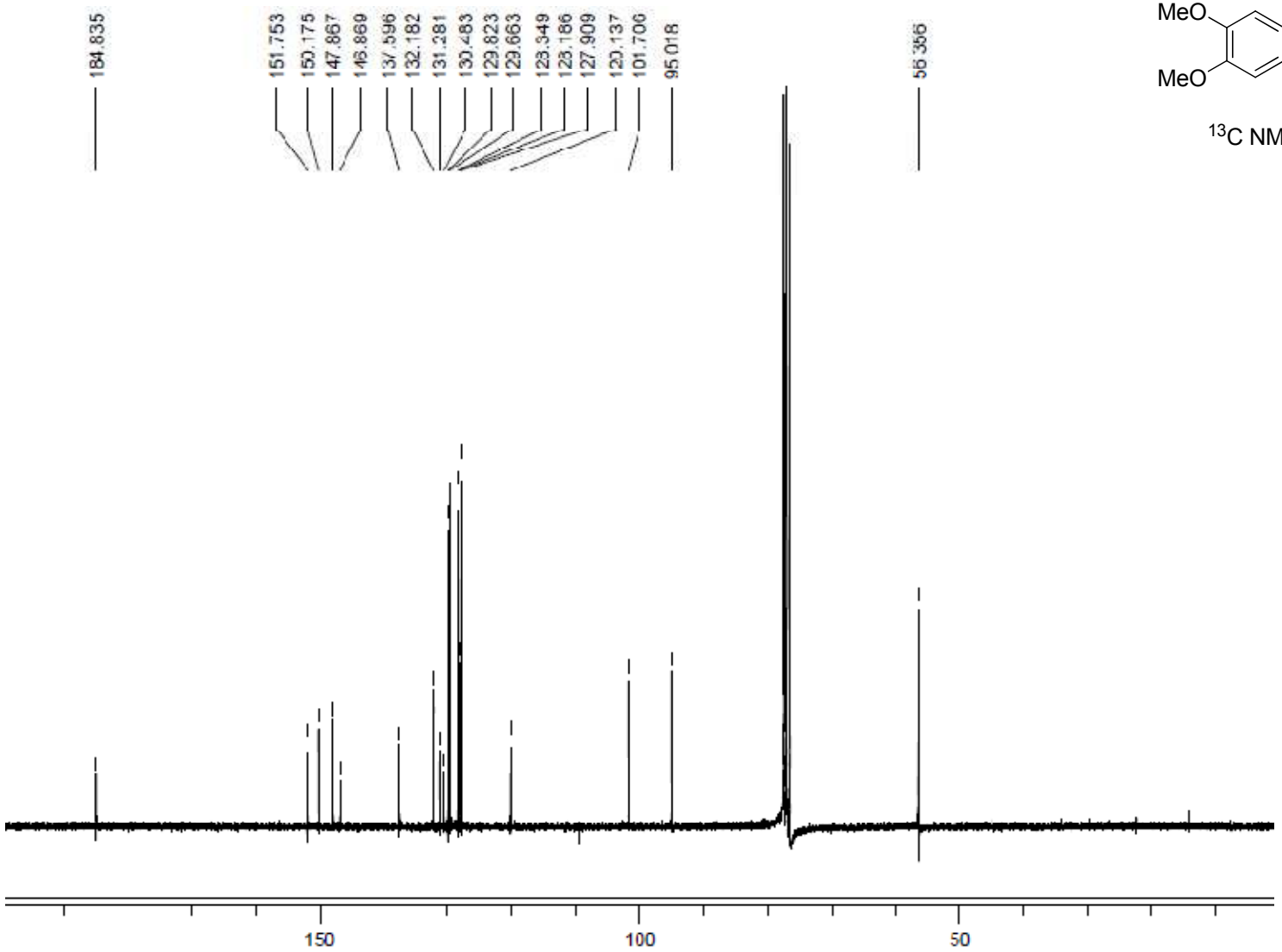
31

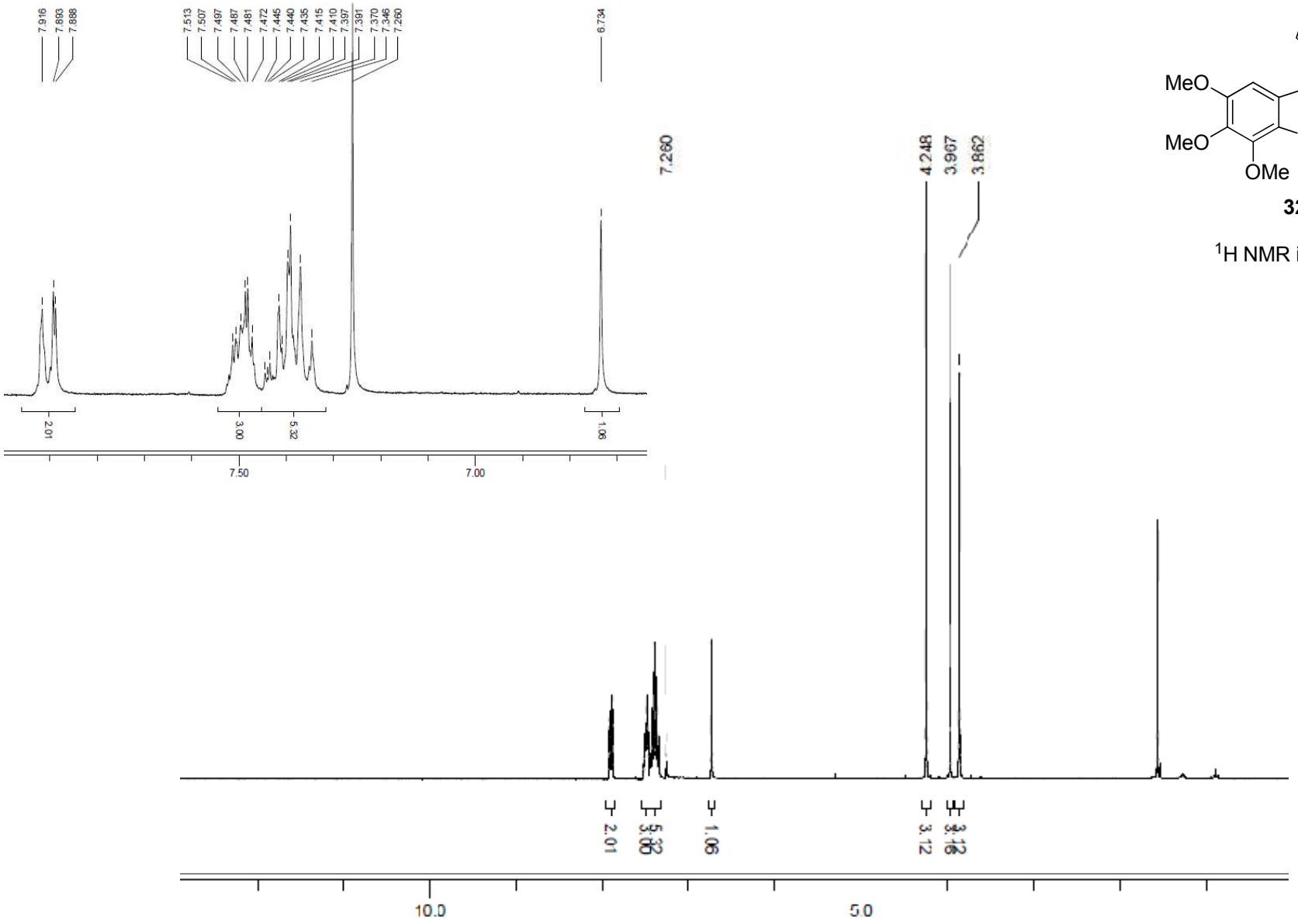
^{1}H NMR in $CDCl_3$



31

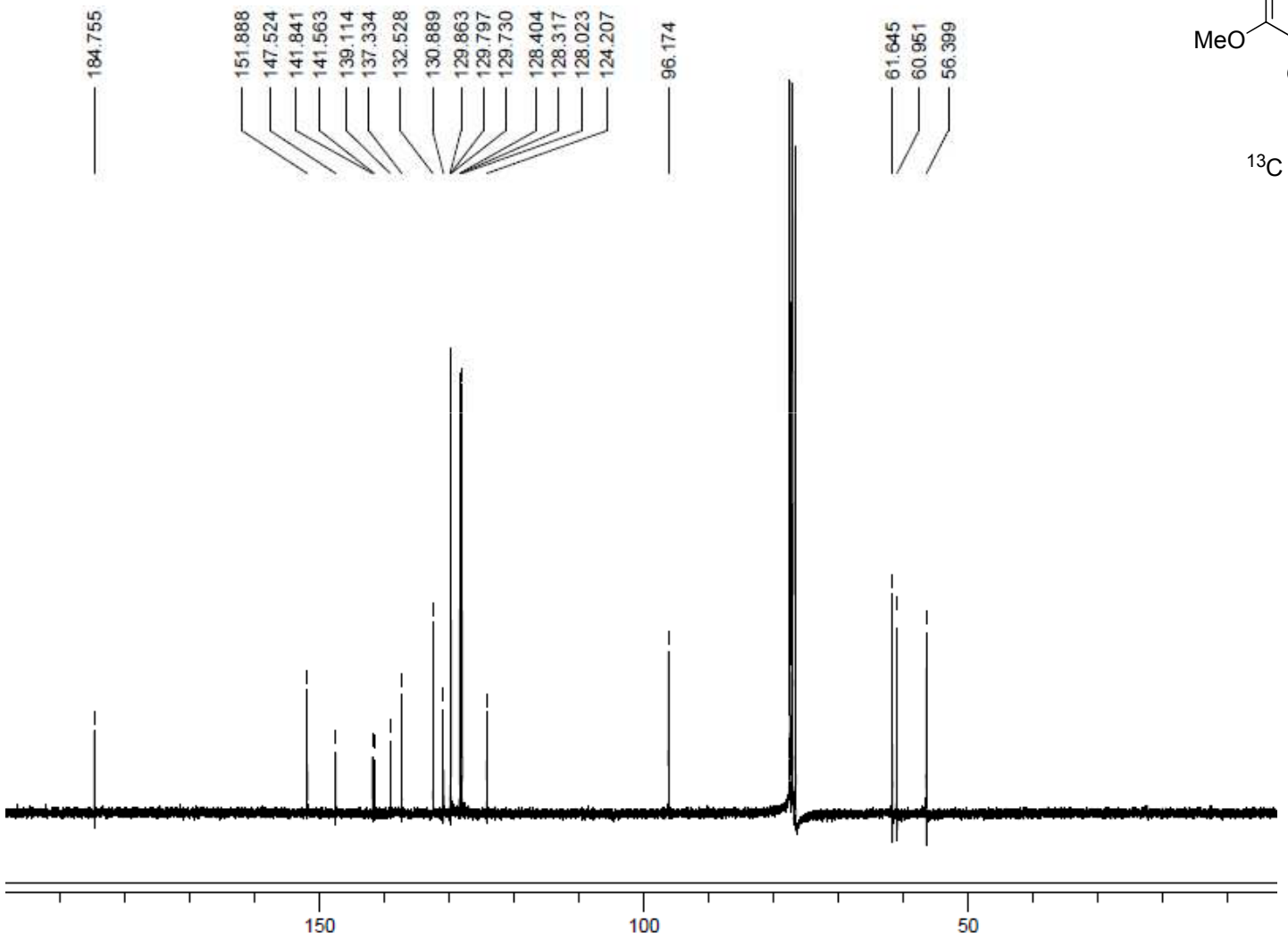
^{13}C NMR in $CDCl_3$

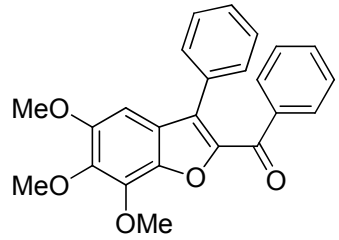




32

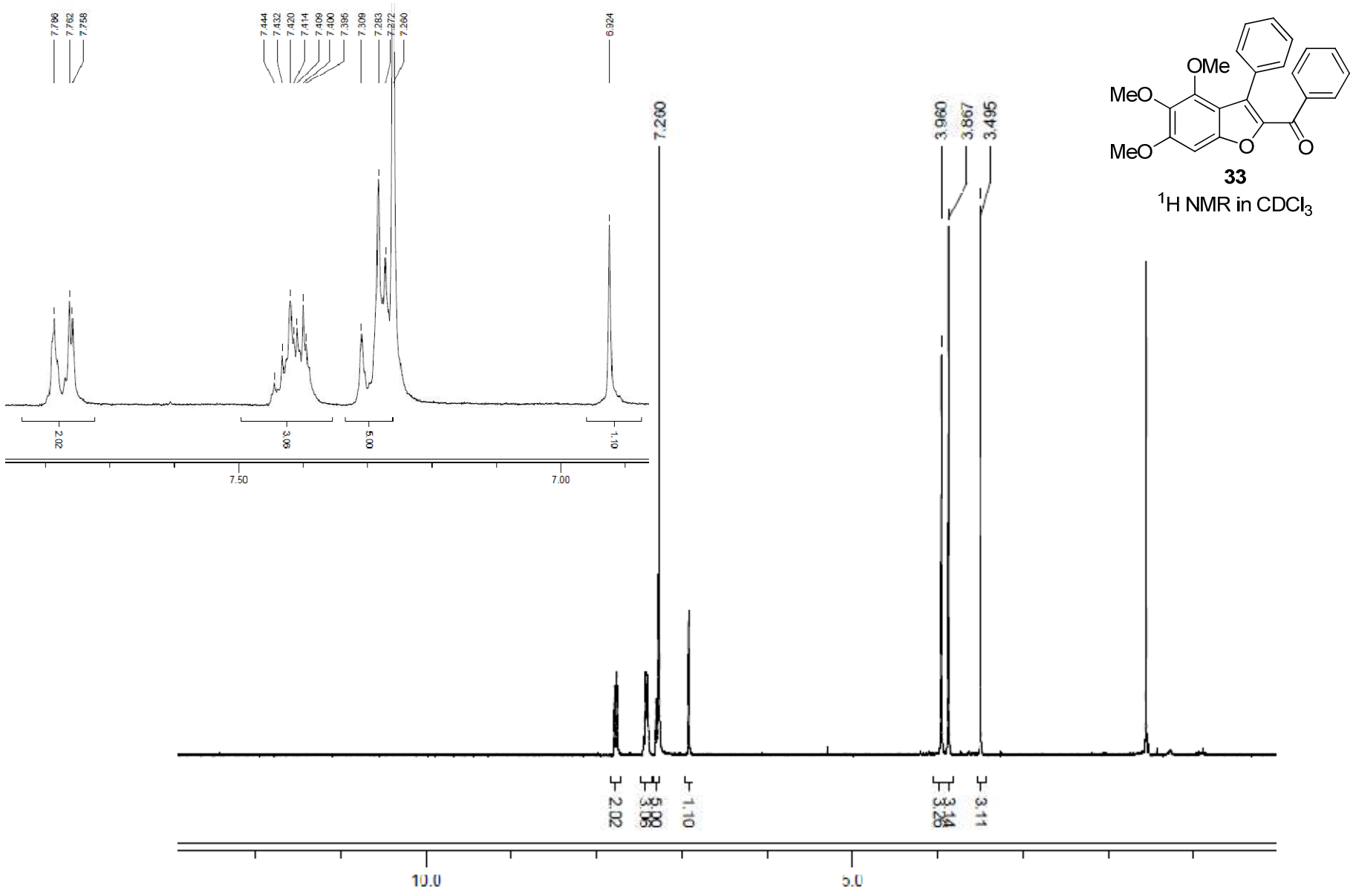
^{1}H NMR in $CDCl_3$





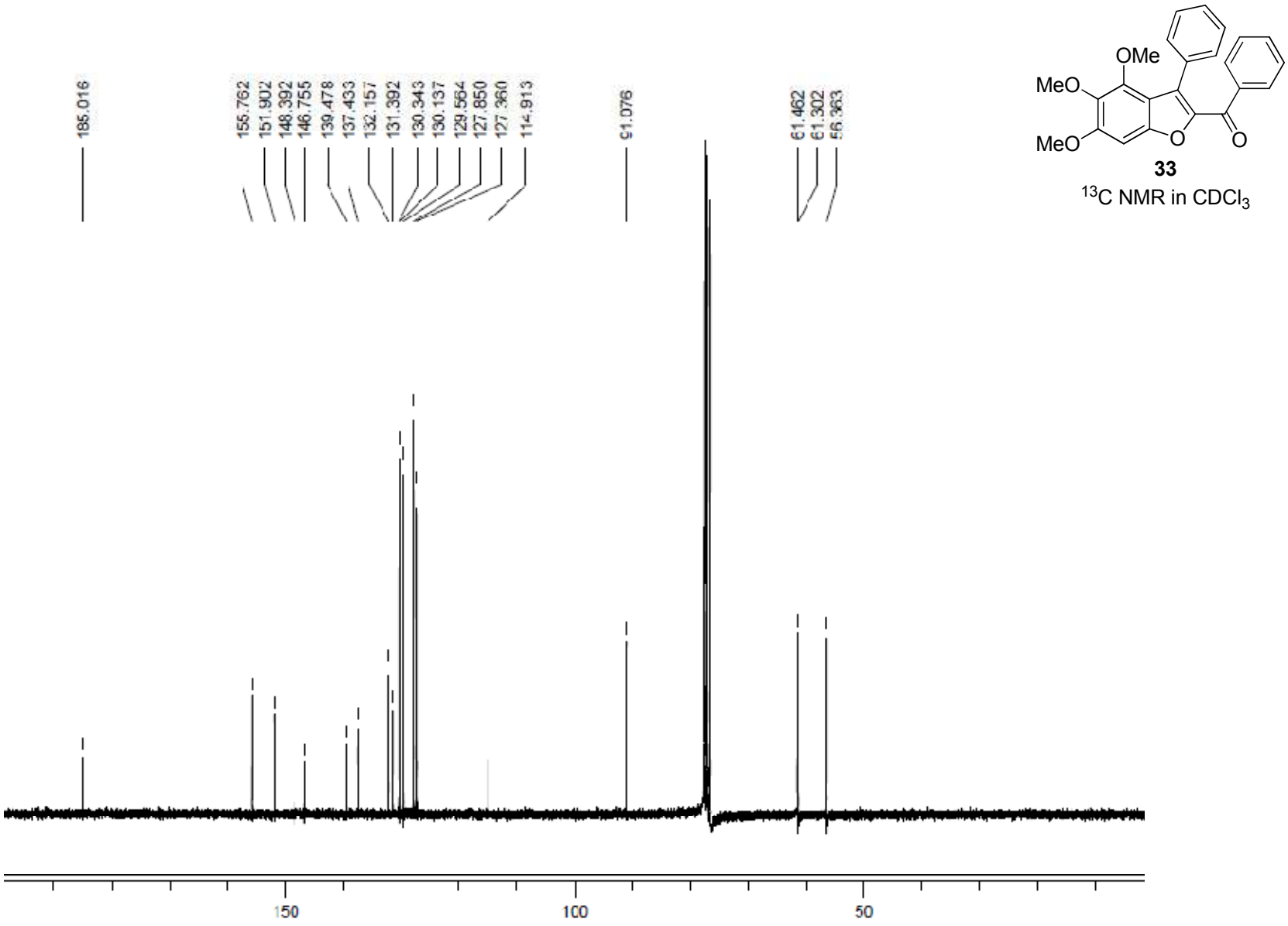
32

^{13}C NMR in $CDCl_3$



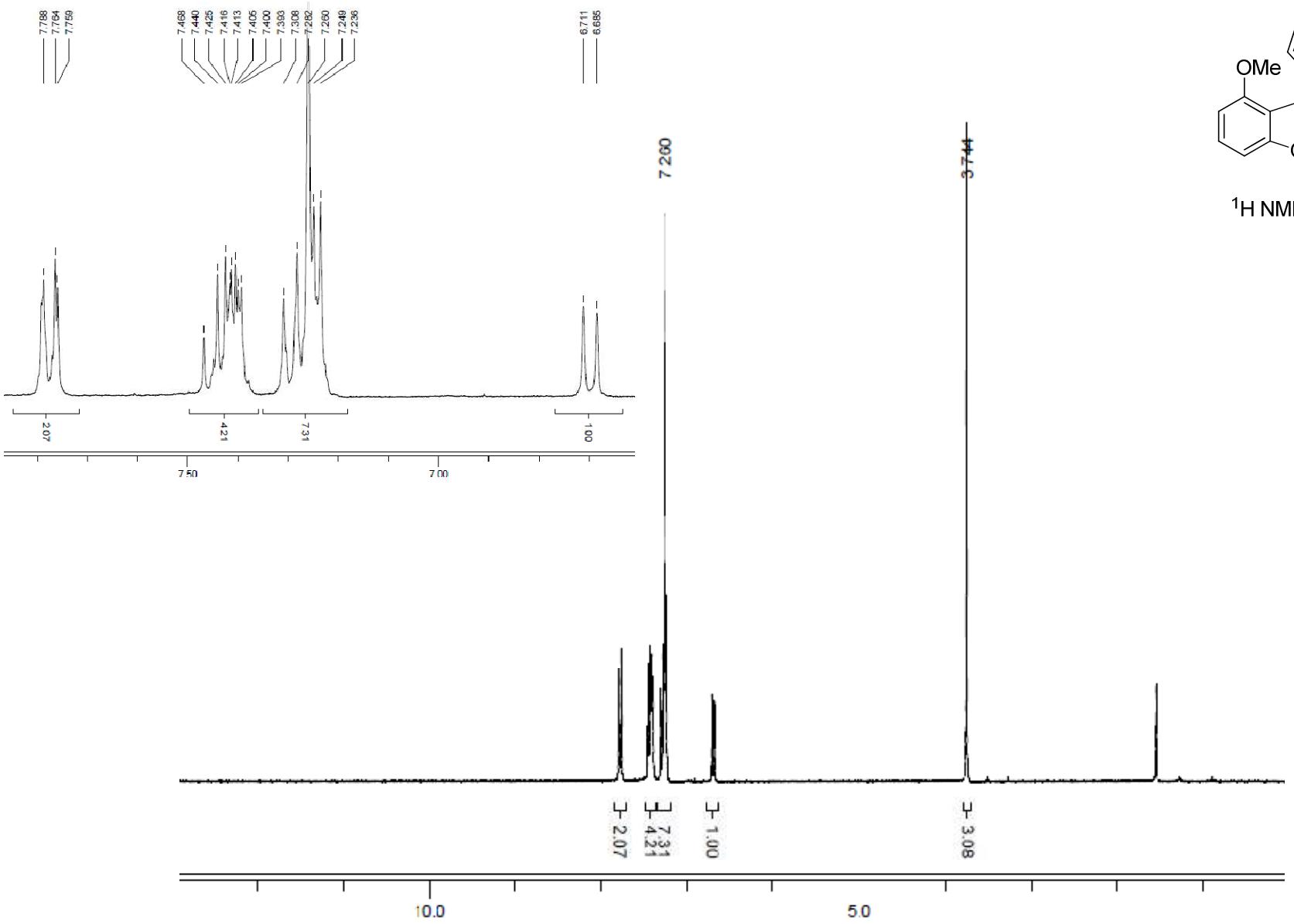
33

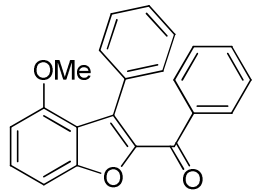
^{1}H NMR in $CDCl_3$



33

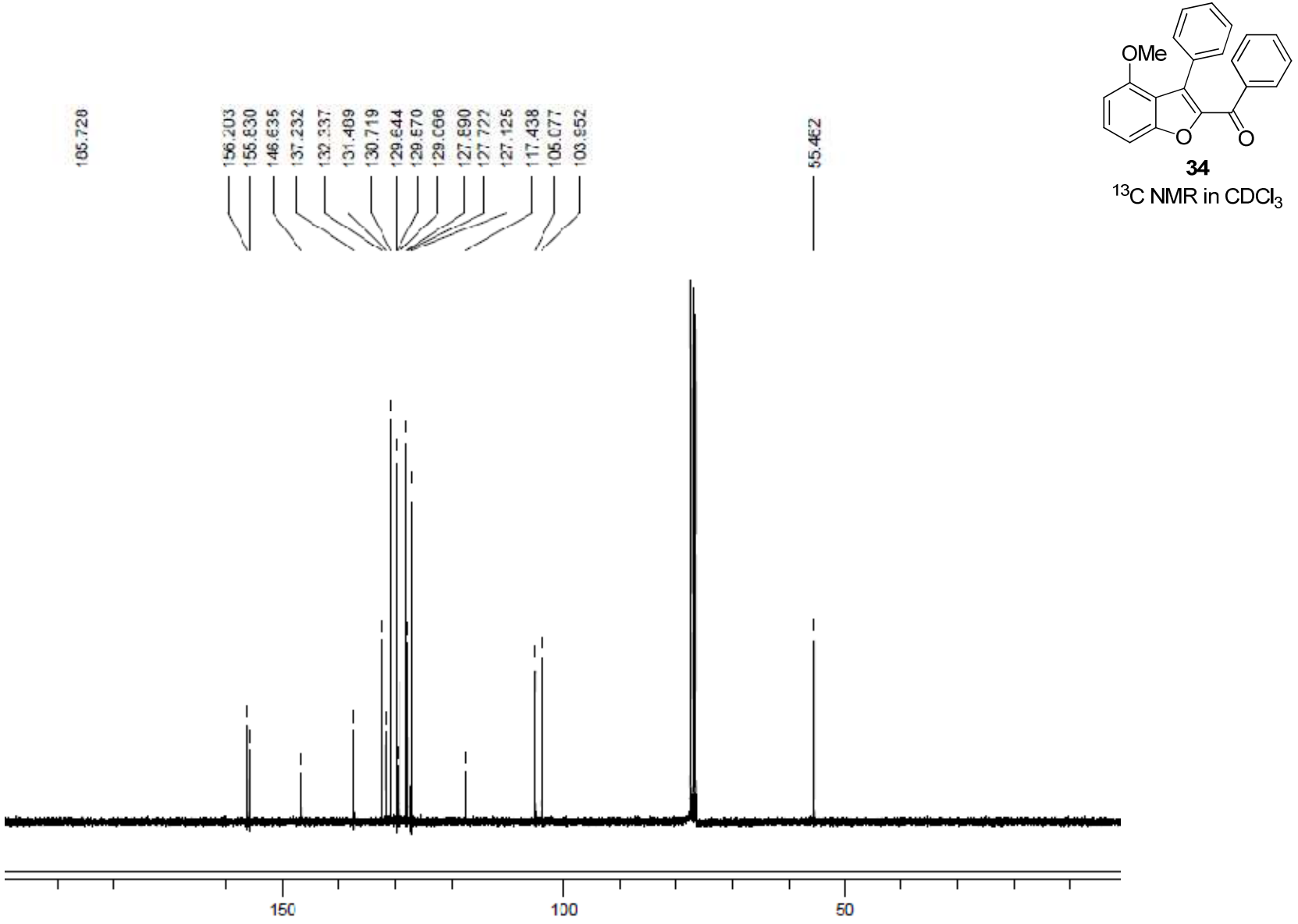
^{13}C NMR in $CDCl_3$

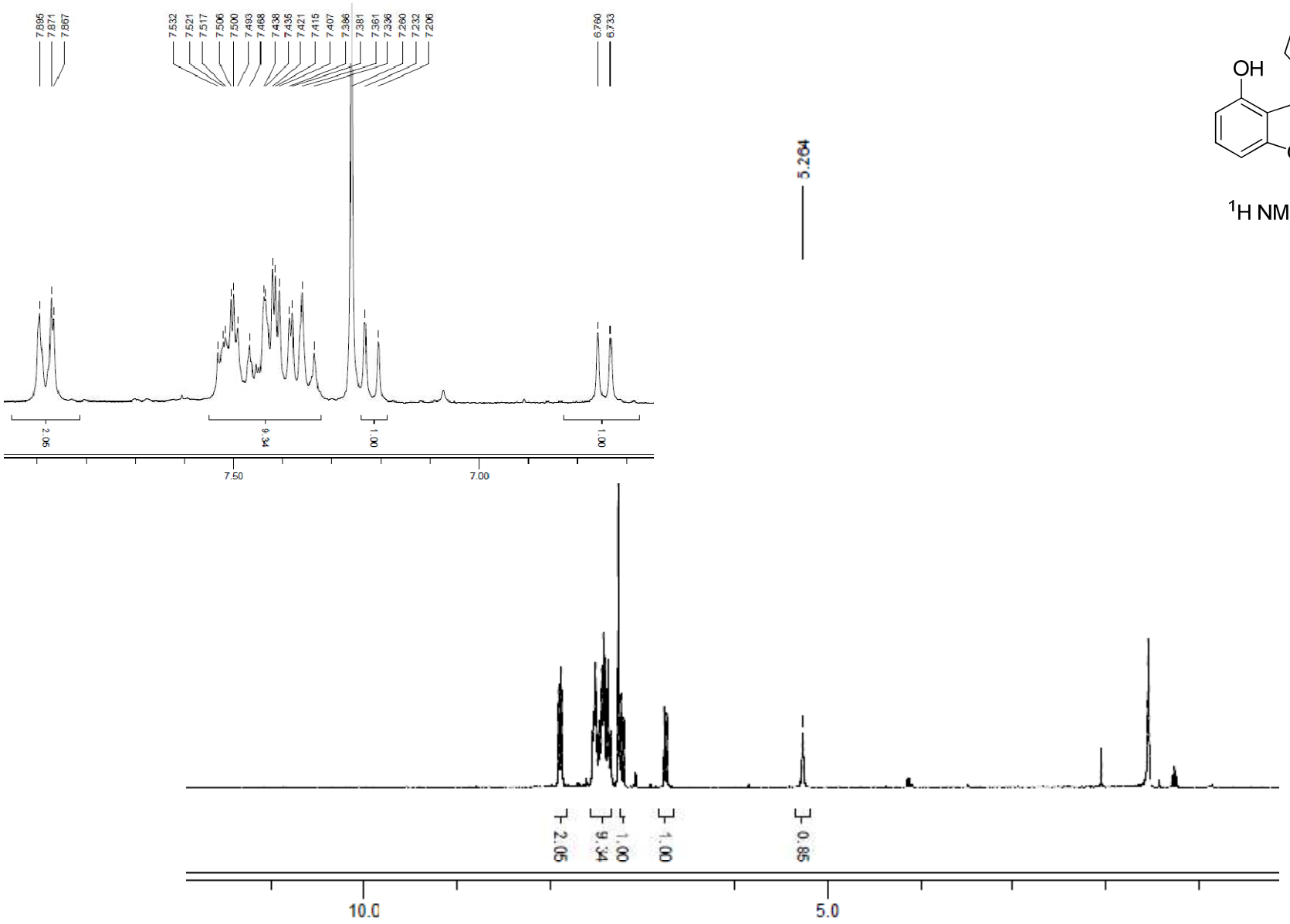


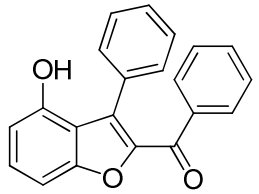


34

^{1}H NMR in $CDCl_3$

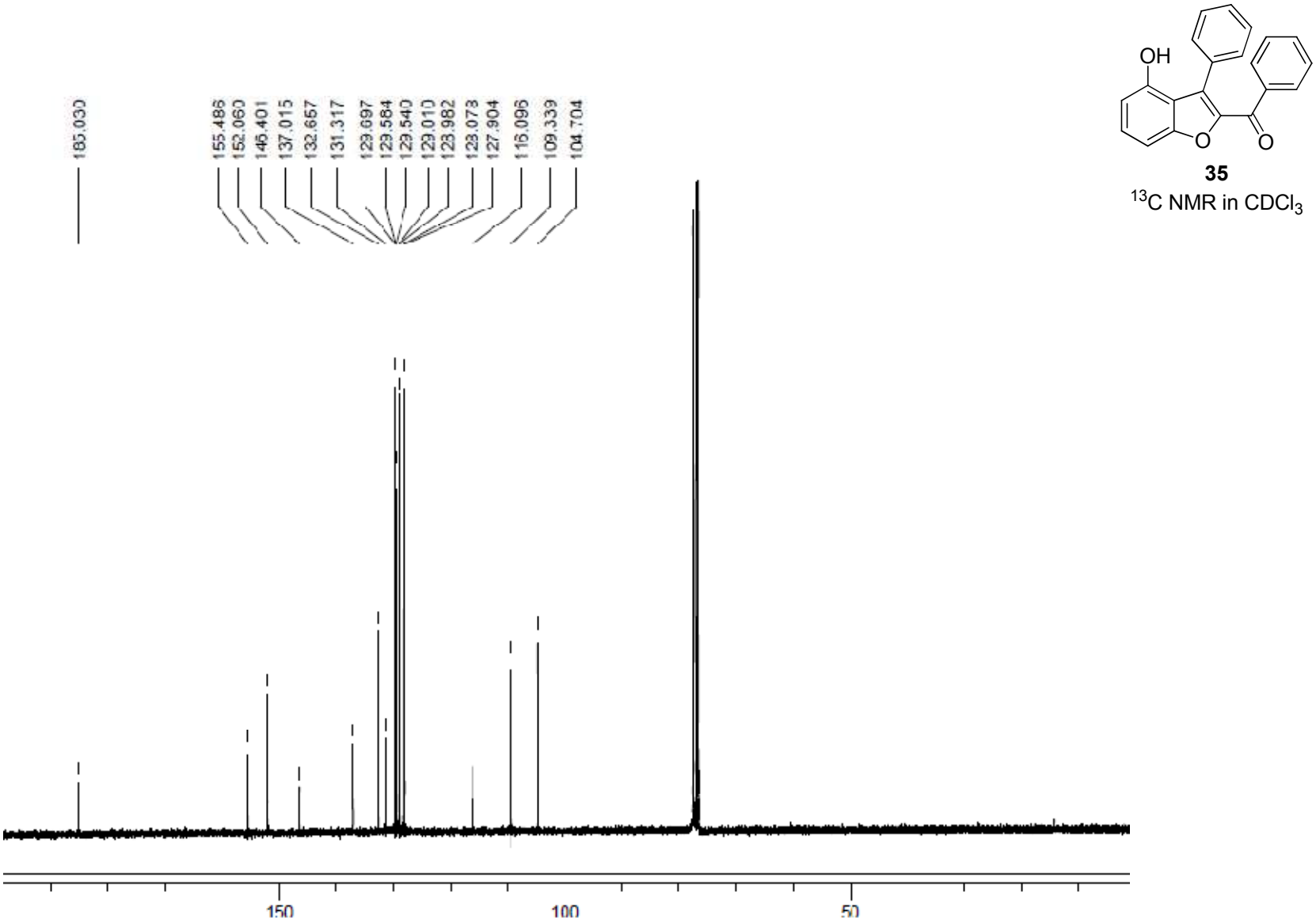

OMe
O
O
34
13C NMR in CDCl3
185.728
156.203
155.830
146.635
137.232
132.337
131.469
130.719
129.644
129.670
129.066
127.890
127.722
127.125
117.438
105.077
103.952
55.462
150
100
50





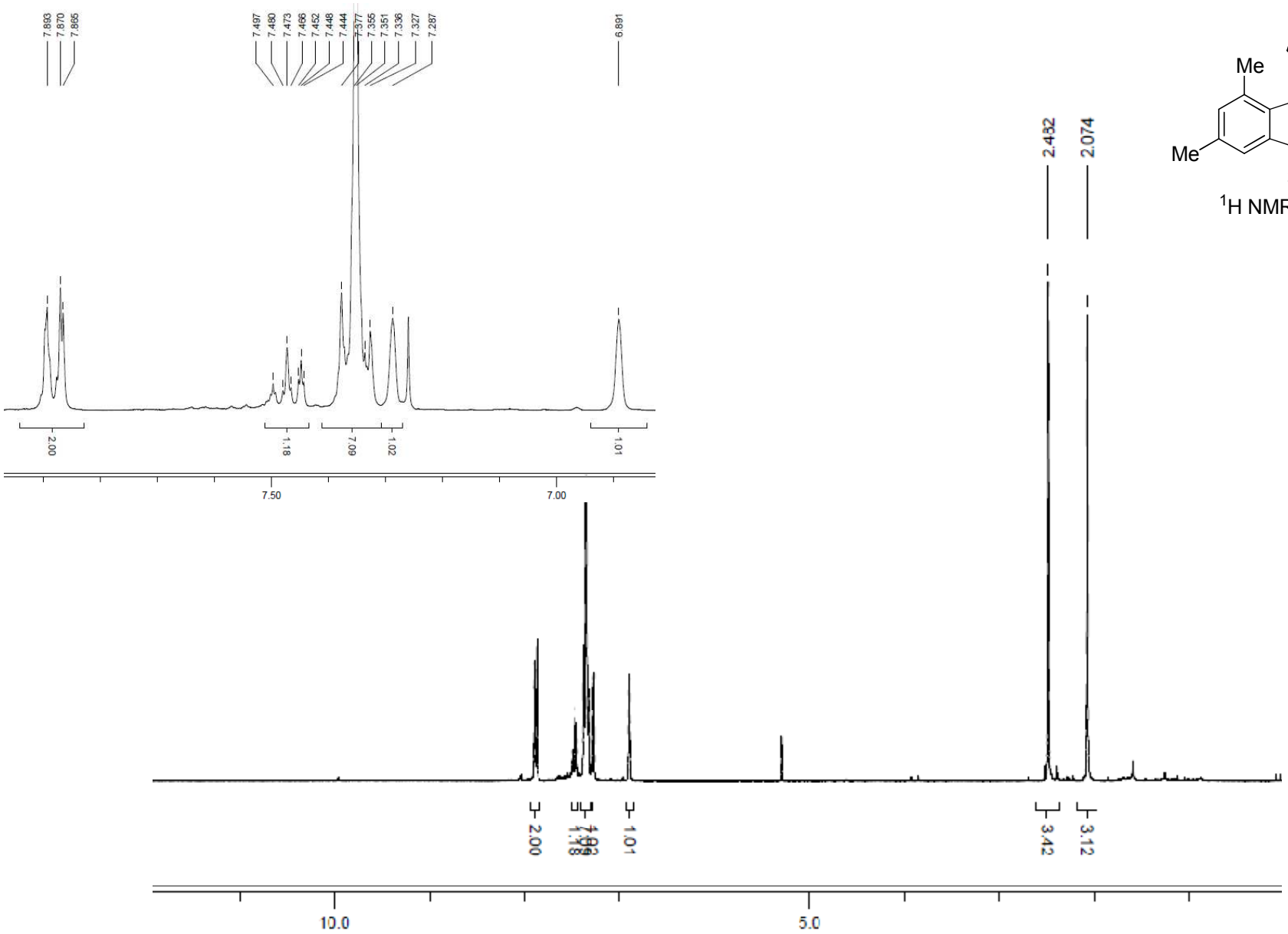
35

^{1}H NMR in $CDCl_3$



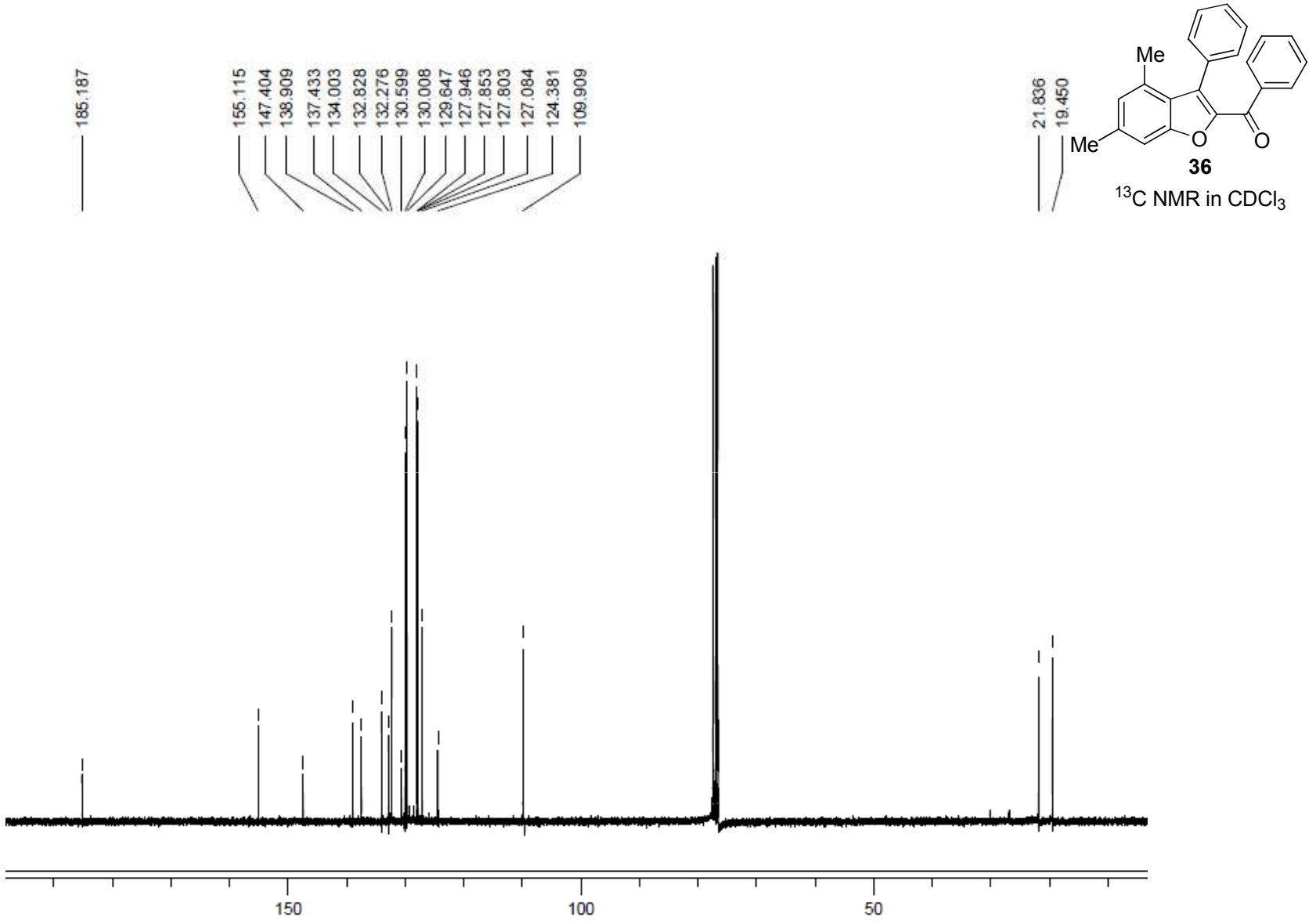
35

^{13}C NMR in $CDCl_3$



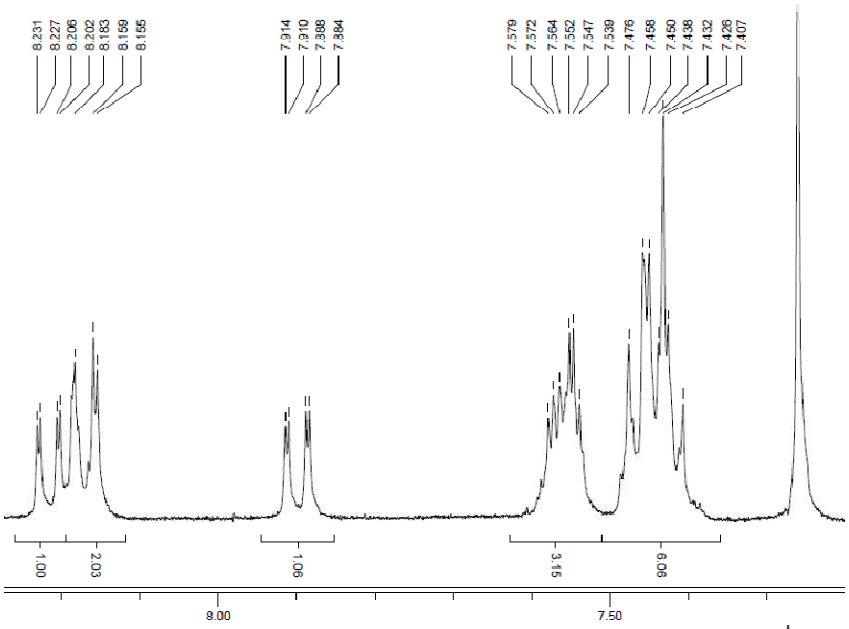
36

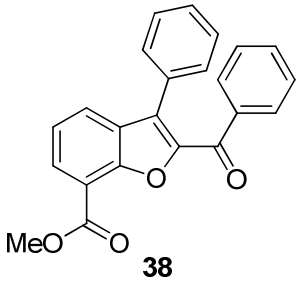
^{1}H NMR in $CDCl_3$



36

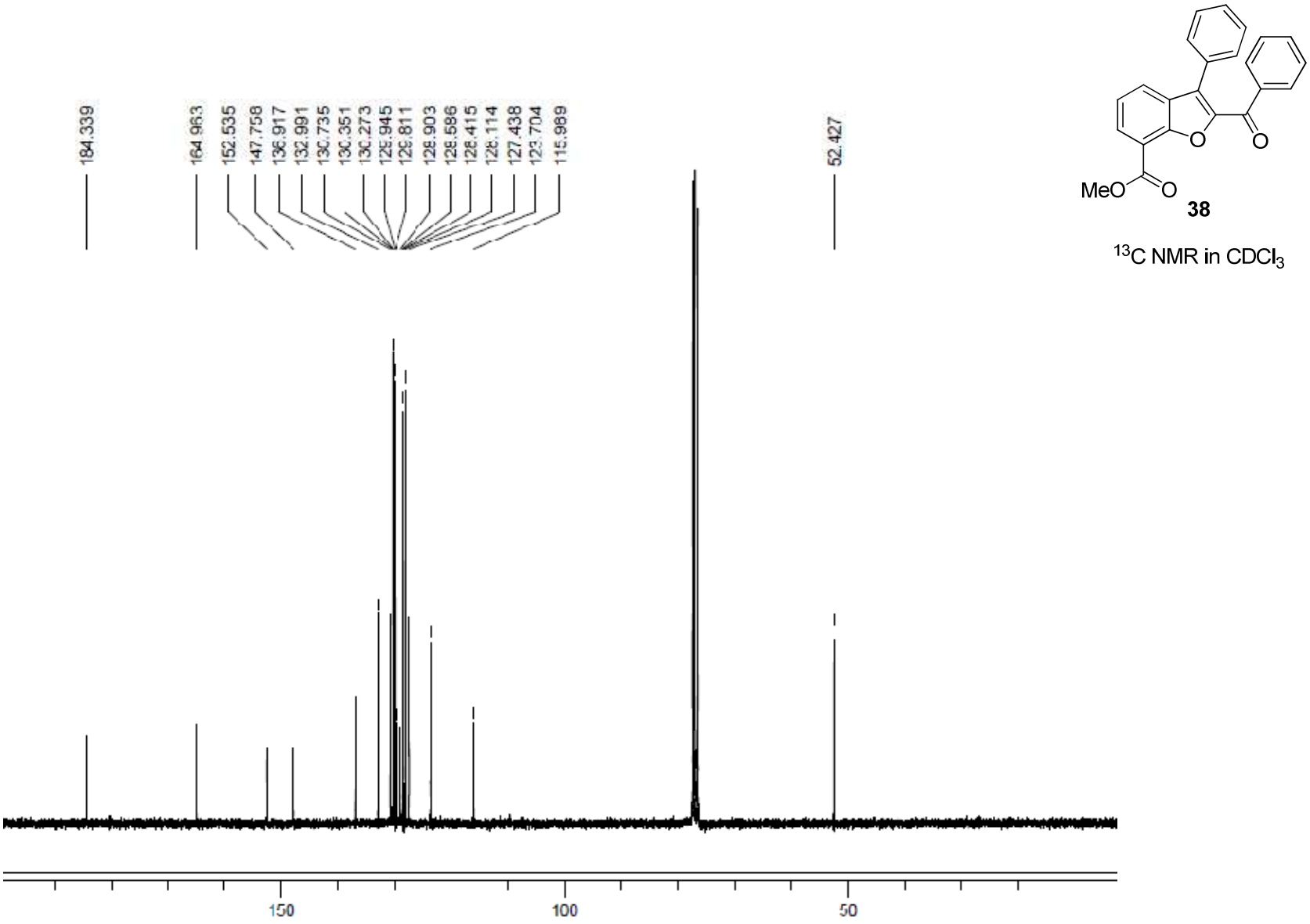
^{13}C NMR in $CDCl_3$





38

^{1}H NMR in $CDCl_3$


184.339
164.963
152.535
147.758
136.917
132.991
130.735
130.351
130.273
129.945
129.811
128.903
128.586
128.415
128.114
127.438
123.704
115.989
52.427
MeO
O
O
O
38
^{13}C NMR in $CDCl_3$
150
100
50