SUPPLEMENTARY INFORMATION

Visible-Light Photocatalytic Functionalization of Isocyanides for the Synthesis of Secondary Amides and Ketene Aminals

Rolando Cannalire,[a] Jussara Amato, [a] Vincenzo Summa,[a] Ettore Novellino,[a] Gian Cesare Tron,[b] and Mariateresa Giustiniano*[a]

[a] *Department of Pharmacy, University of Naples Federico II, via D. Montesano 49, 80131, Napoli, Italy*

[b] *Department of Pharmaceutical Sciences, University of Piemonte Orientale, Largo Donegani 2, 28100, Novara, Italy*

Contents:

HRMS spectra for control experiments

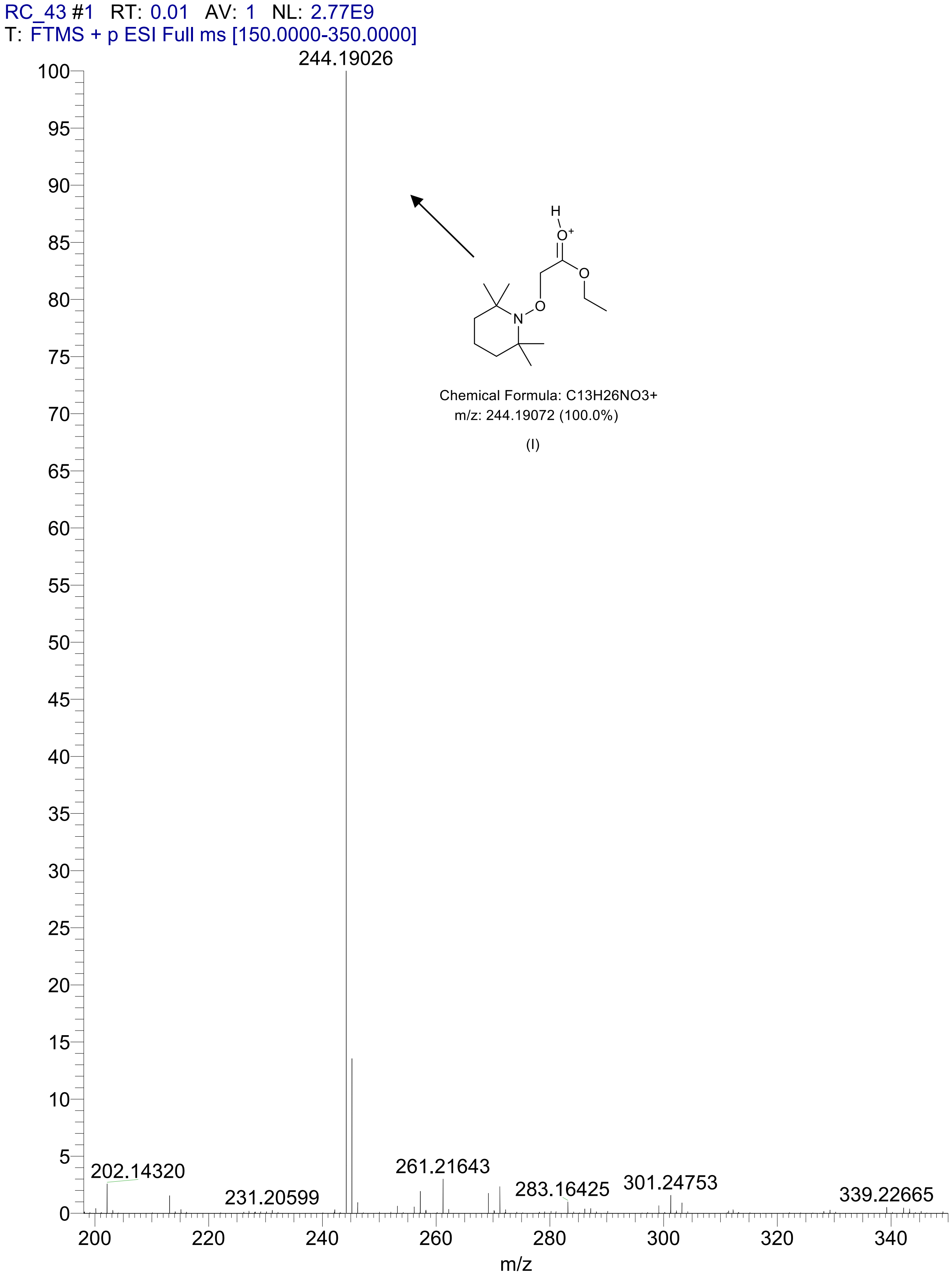


Figure S1. TEMPO adduct with an alkyl radical intermediate.

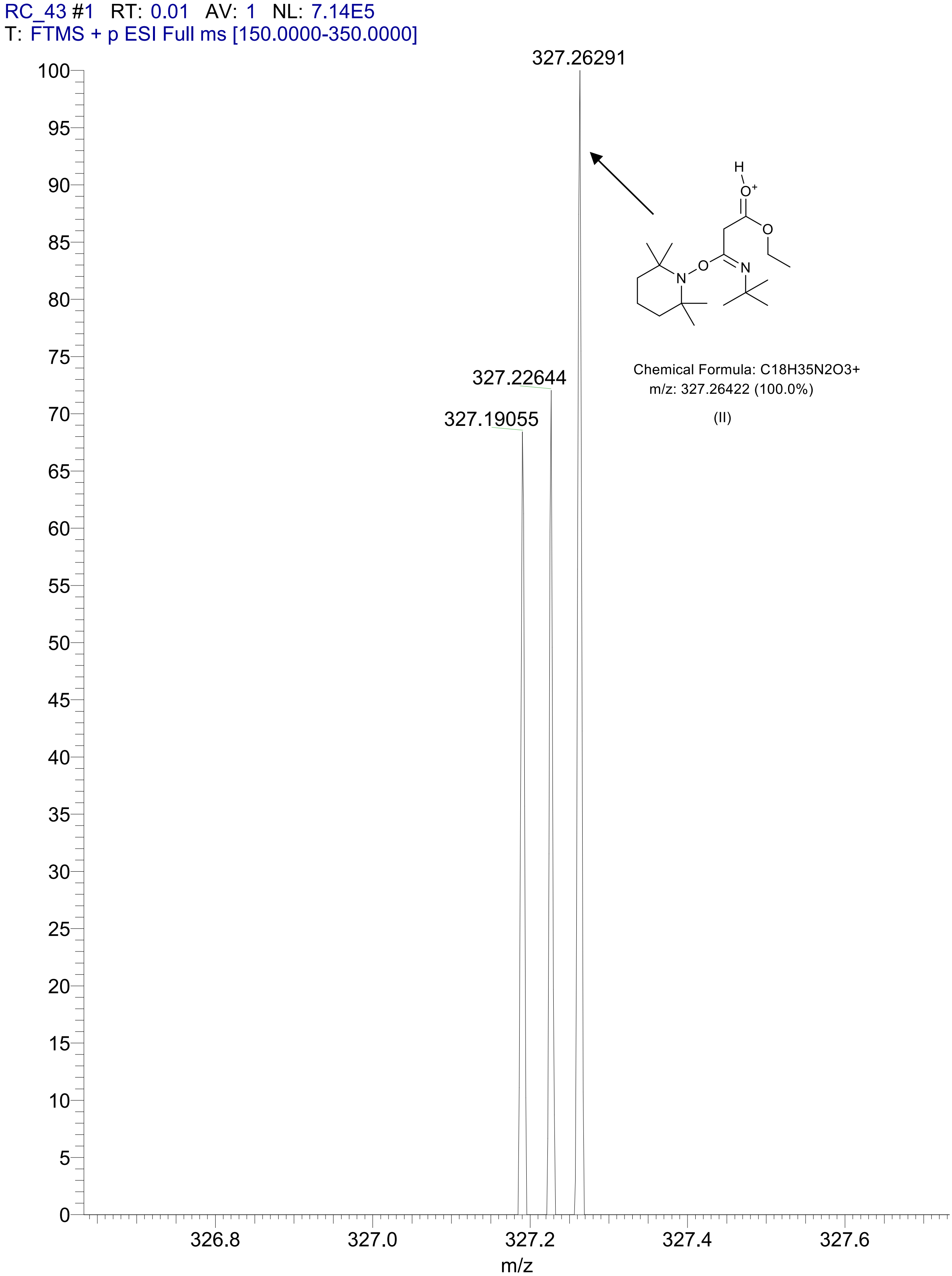


Figure S2. TEMPO adduct with an imidoyl radical intermediate.

The NMR data of known compounds (**3**, **4**, **5**, **7**, **8**, **9**, **12**, **15**, **17**, **18**, **21**, **22**, **23**, **25**, **26** and **29**) are consistent to literature data.[1-15]

References

1 S. Rohe, T. McCallum, A. O. Morris and L. Barriault, *J. Org. Chem.*, 2018, **83**, 10015–10024.

2 Z. W. Wicks and K.-J. Wu, *J. Org. Chem.*, 2002, **45**, 2446–2448.

3 1992 P. Jakobsen, A. Kanstrup, Lundbeck, M. Jane, WO Pat. 9201672 A1 19920206, .

4 R. K. Rapolu, B. Nabamukul, S. R. Bommineni, R. Potham, N. Mulakayala and S. Oruganti, *RSC Adv.*, 2013, **3**, 5332–5337.

5 S. Sumino, A. Fusano, T. Fukuyama and I. Ryu, *Synlett*, 2012, **23**, 1331–1334.

6 WO 2009117659 A1 20090924, 2009.

7 S. Pelliccia, A. I. Alfano, P. Luciano, E. Novellino, A. Massarotti, G. C. Tron, D. Ravelli and M. Giustiniano, *J. Org. Chem.*, 2020, **85**, 1981–1990.

8 H. Stamm and L. Schneider, *Chem. Ber.*, 1975, **108**, 500–510.

9 A. P. Gurevich, A. I.; Kolosov, M. N.; Konnova, G. S.; Nametkina, L. N.; Prudnikova, *Zhurnal Org. Khimii*, 1969, **5**, 1766–1771.

10 Z. W. Wicks and P. P. Patel, *J. Org. Chem.*, 1981, **46**, 4068–4069.

11 D. J. Woodman and A. I. Davidson, *J. Org. Chem.*, 1973, **38**, 4288–4295.

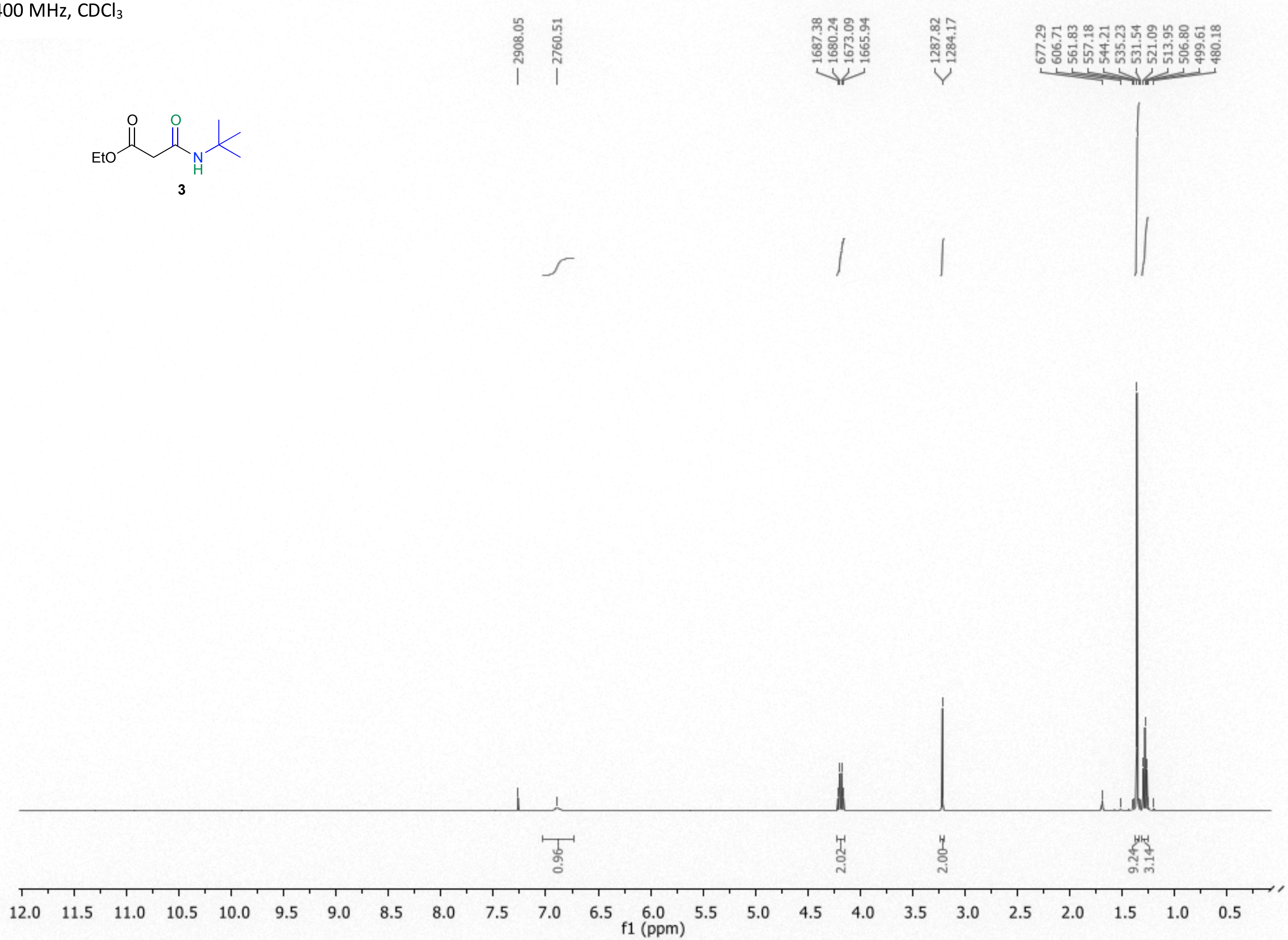
12 J. K. Vandavasi, C.-T. Hsiao, W.-P. Hu, S. S. K. Boominathan and J.-J. Wang, *European J. Org. Chem.*, 2015, **2015**, 3171–3177.

13 A. G. Neo, J. Delgado, C. Polo, S. Marcaccini and C. F. Marcos, *Tetrahedron Lett.*, 2005, **46**, 23–26.

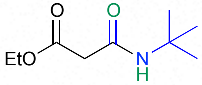
14 T. Nishio and H. Yamamoto, *J. Heterocycl. Chem.*, 1995, **32**, 883–891.

15 H.-R. Müller and M. Seefelder, *Justus Liebigs Ann. Chem.*, 1969, **728**, 88–98.

[1]H NMR
400 MHz, $CDCl_3$



^{13}C NMR
100 MHz, $CDCl_3$



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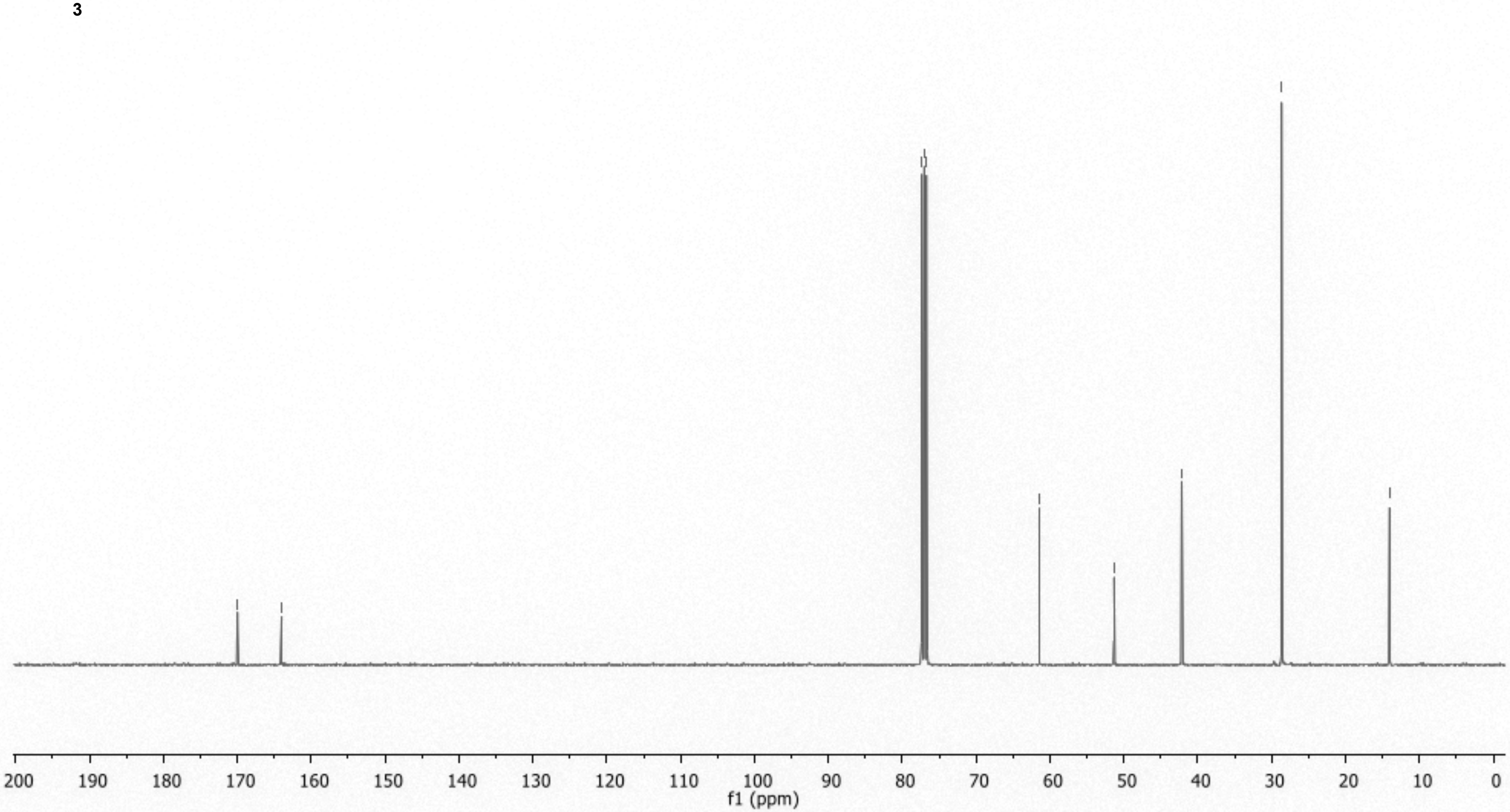
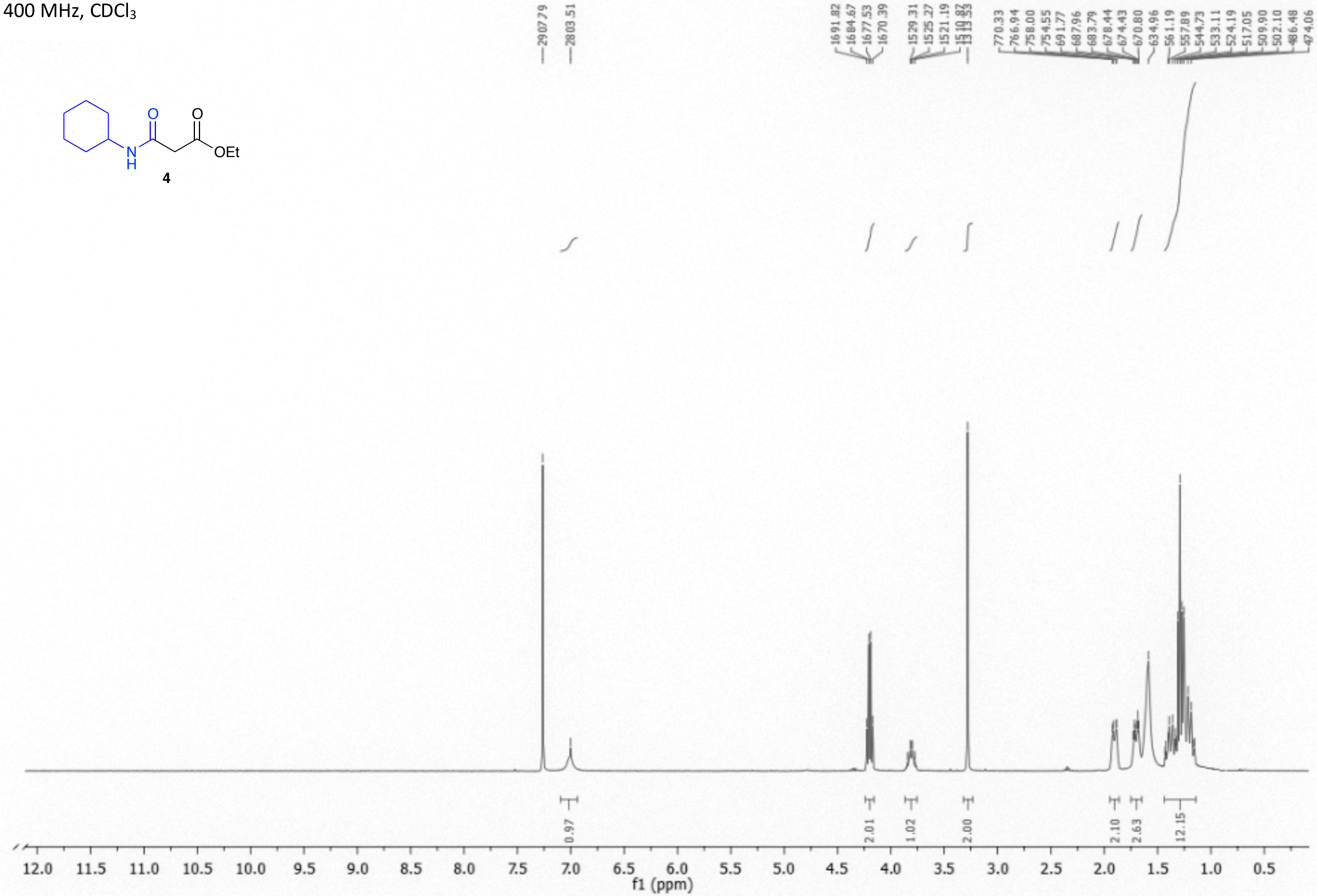


^{1}H NMR
400 MHz, $CDCl_3$



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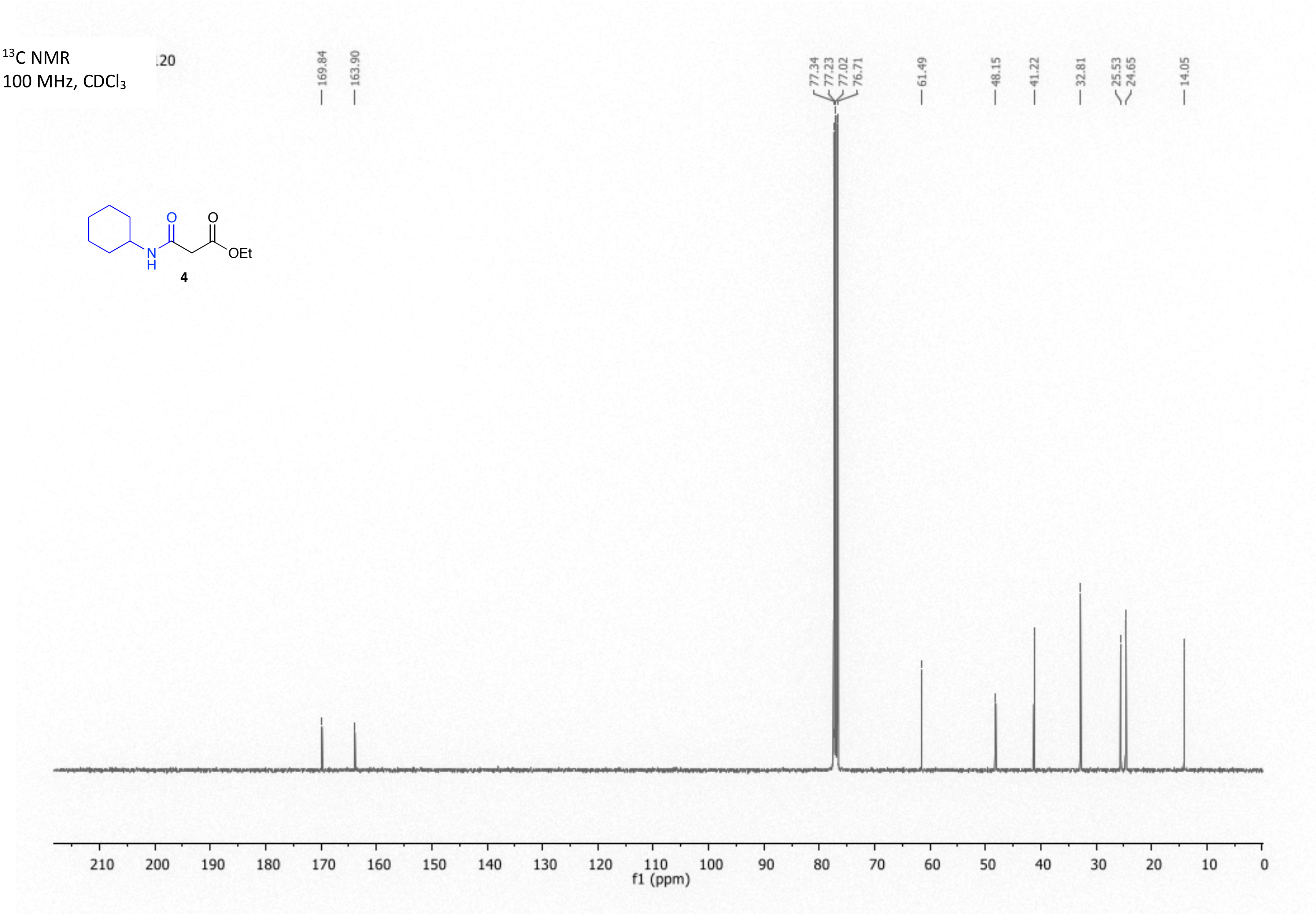

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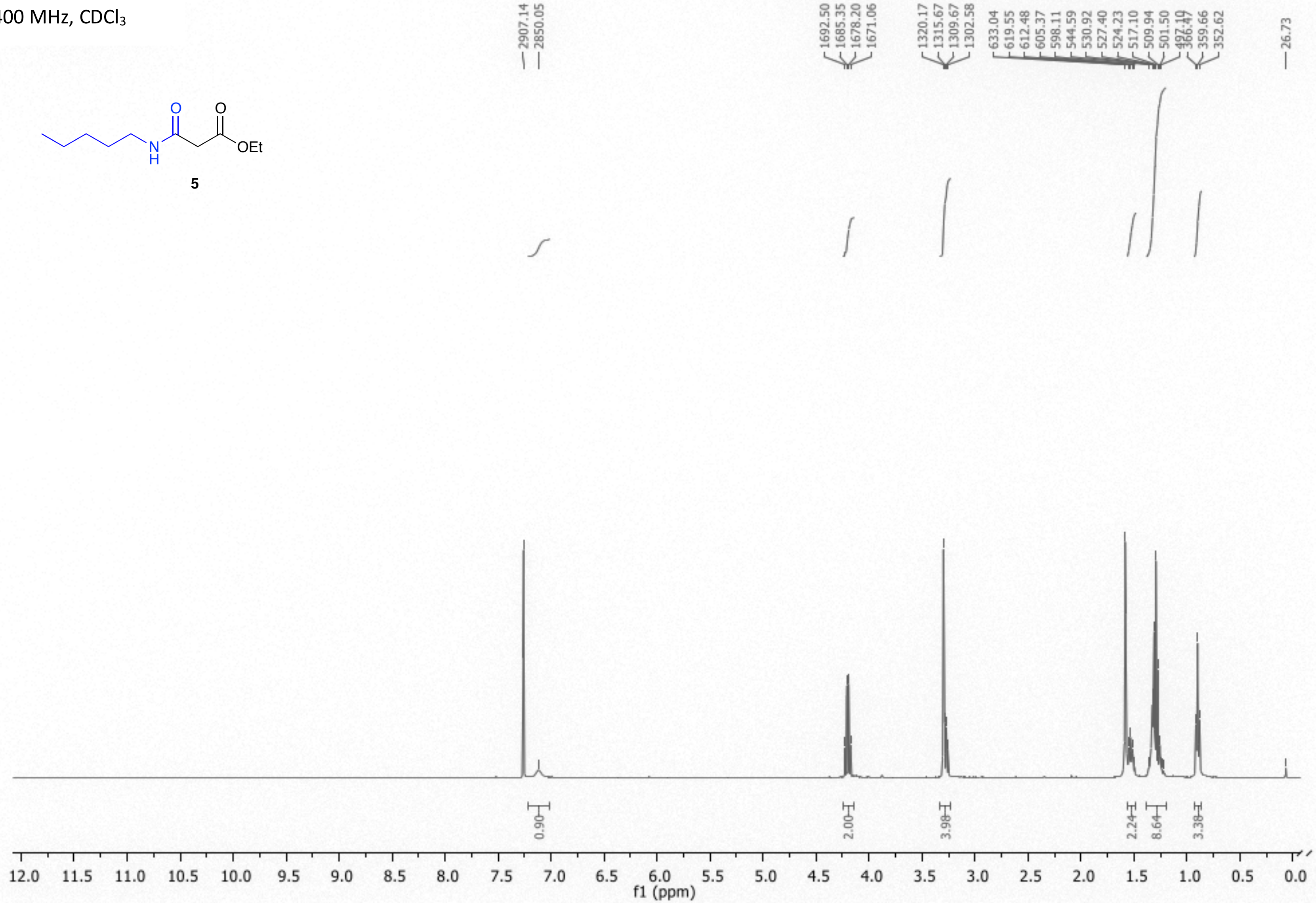

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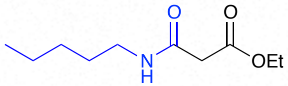

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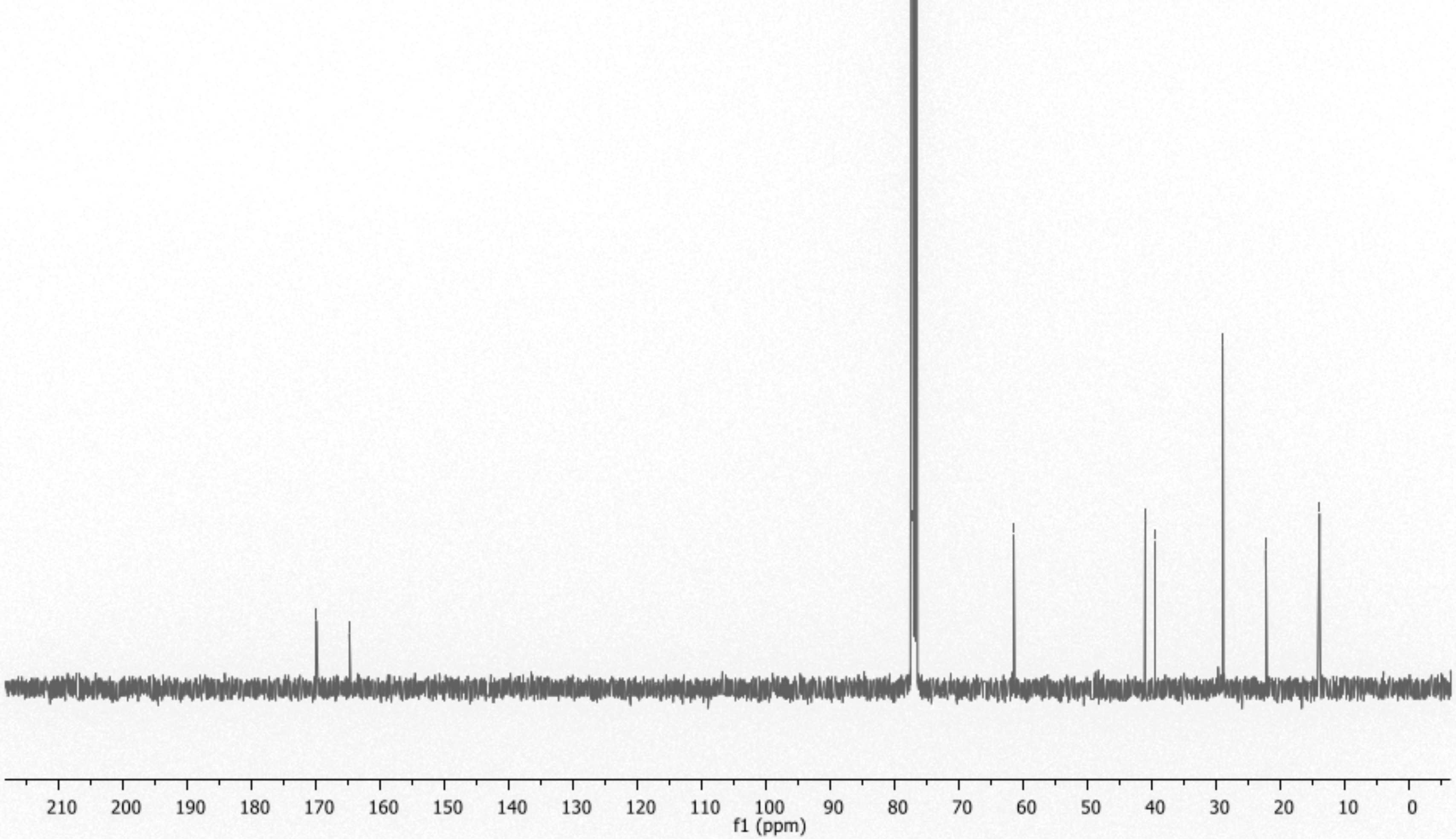

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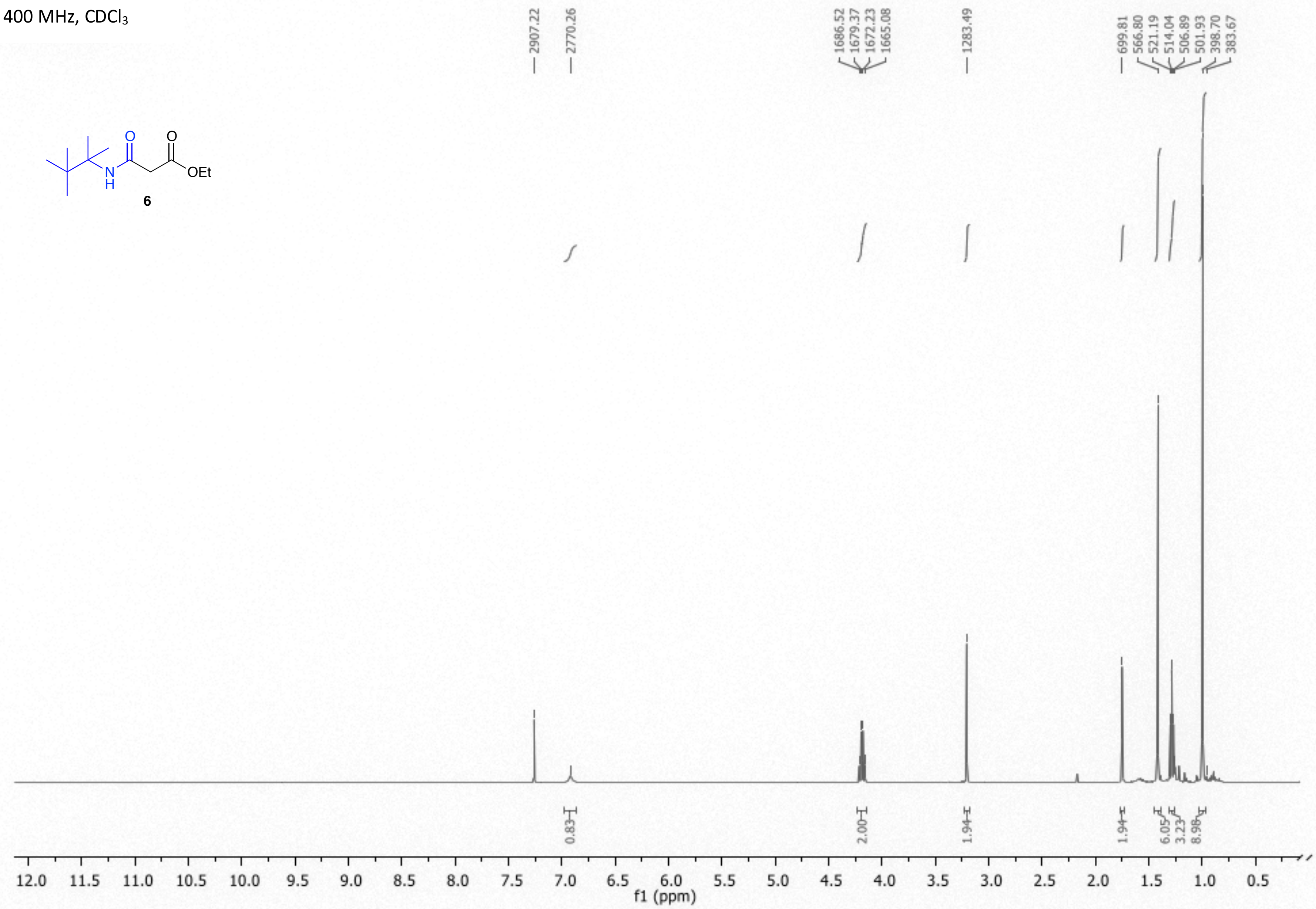
400 MHz, $CDCl_3$



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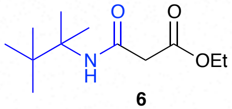

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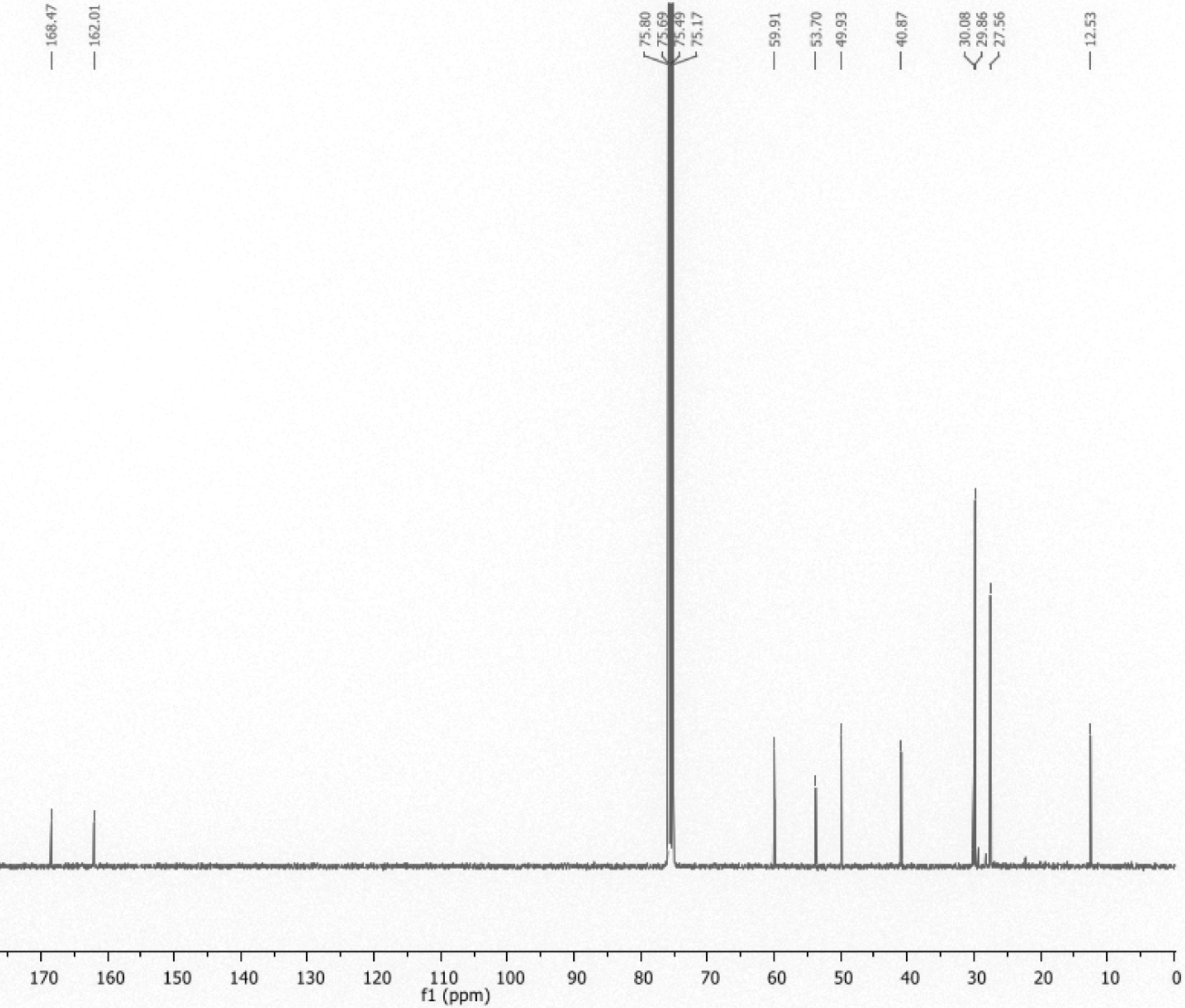

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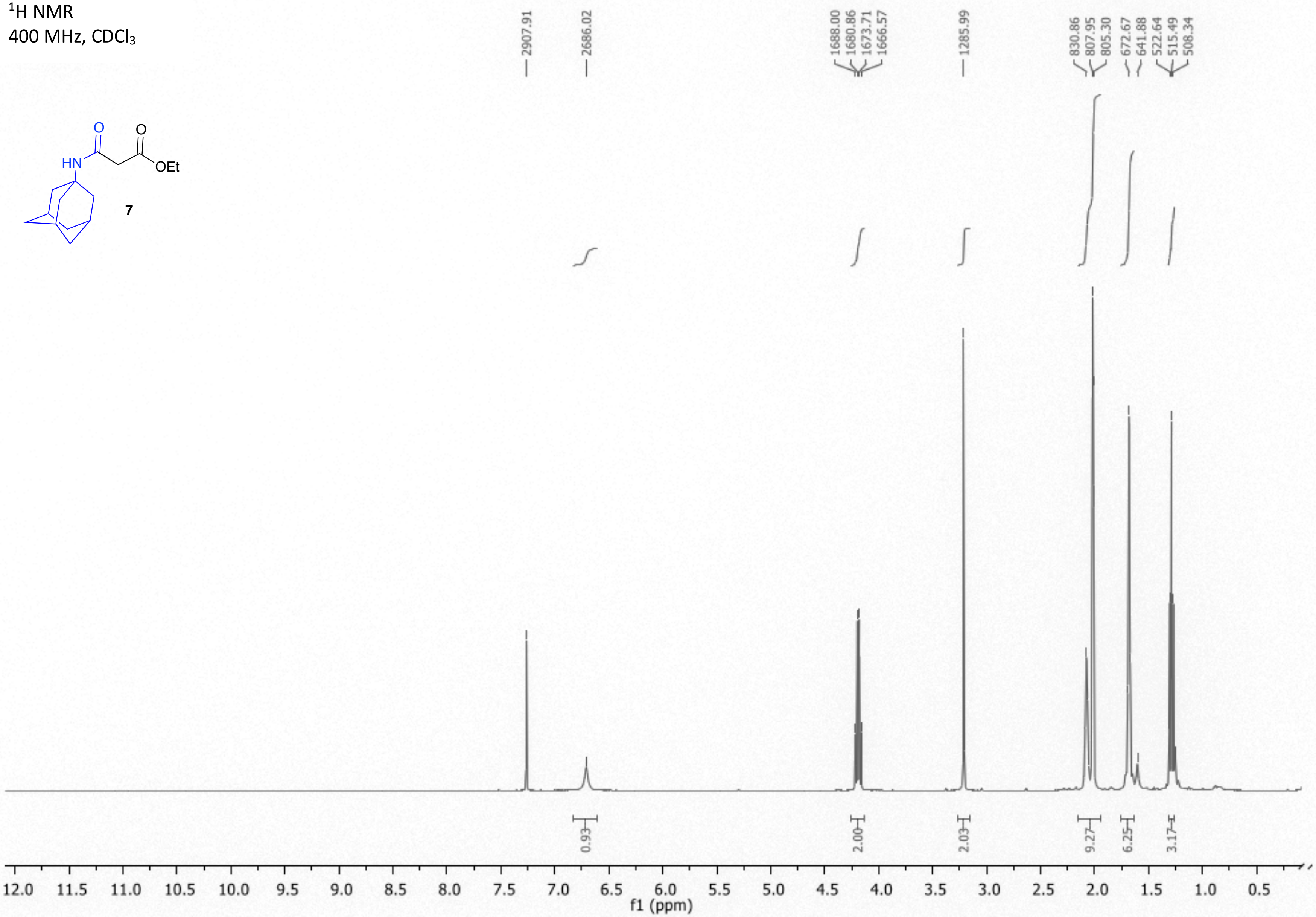
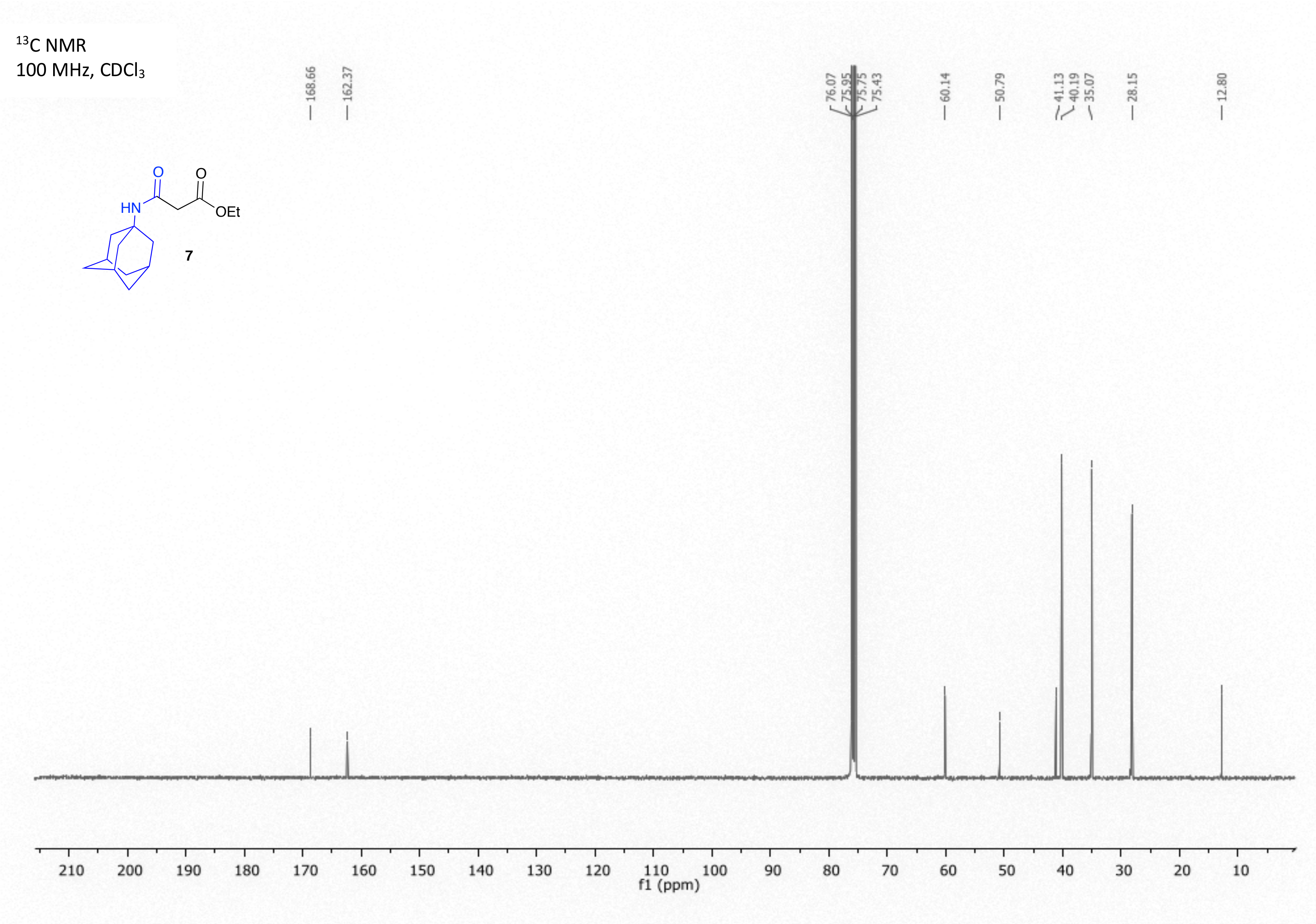
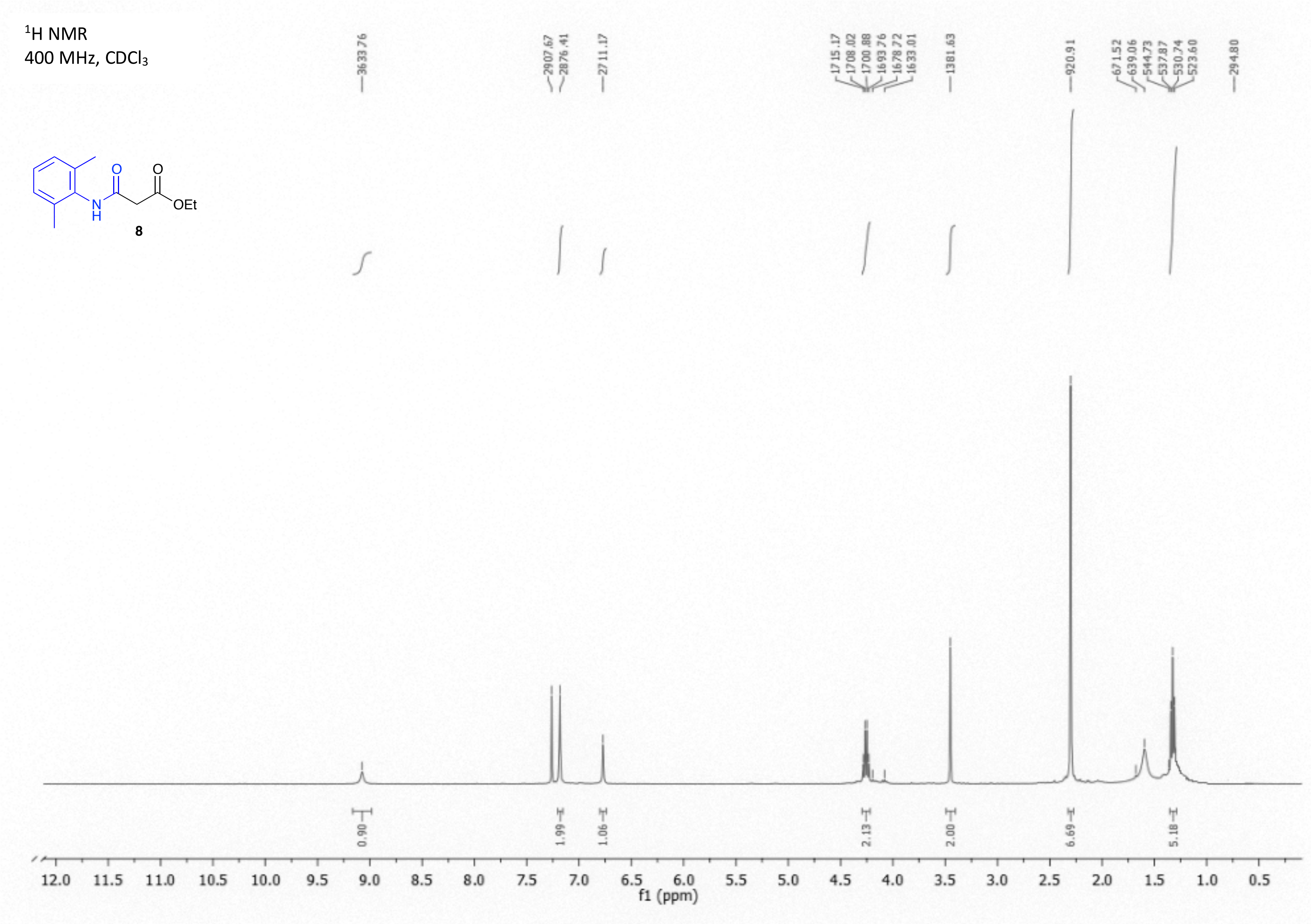
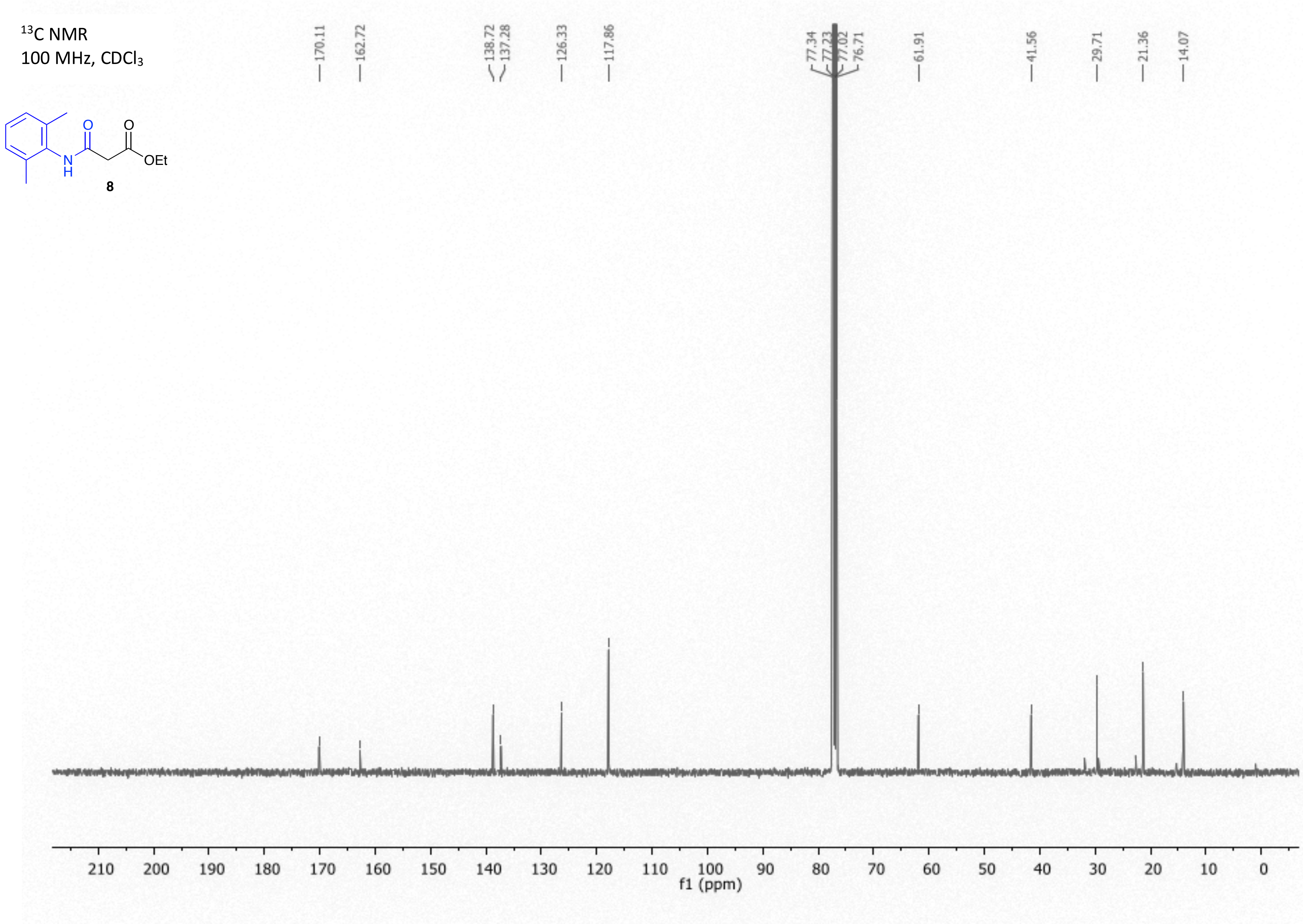




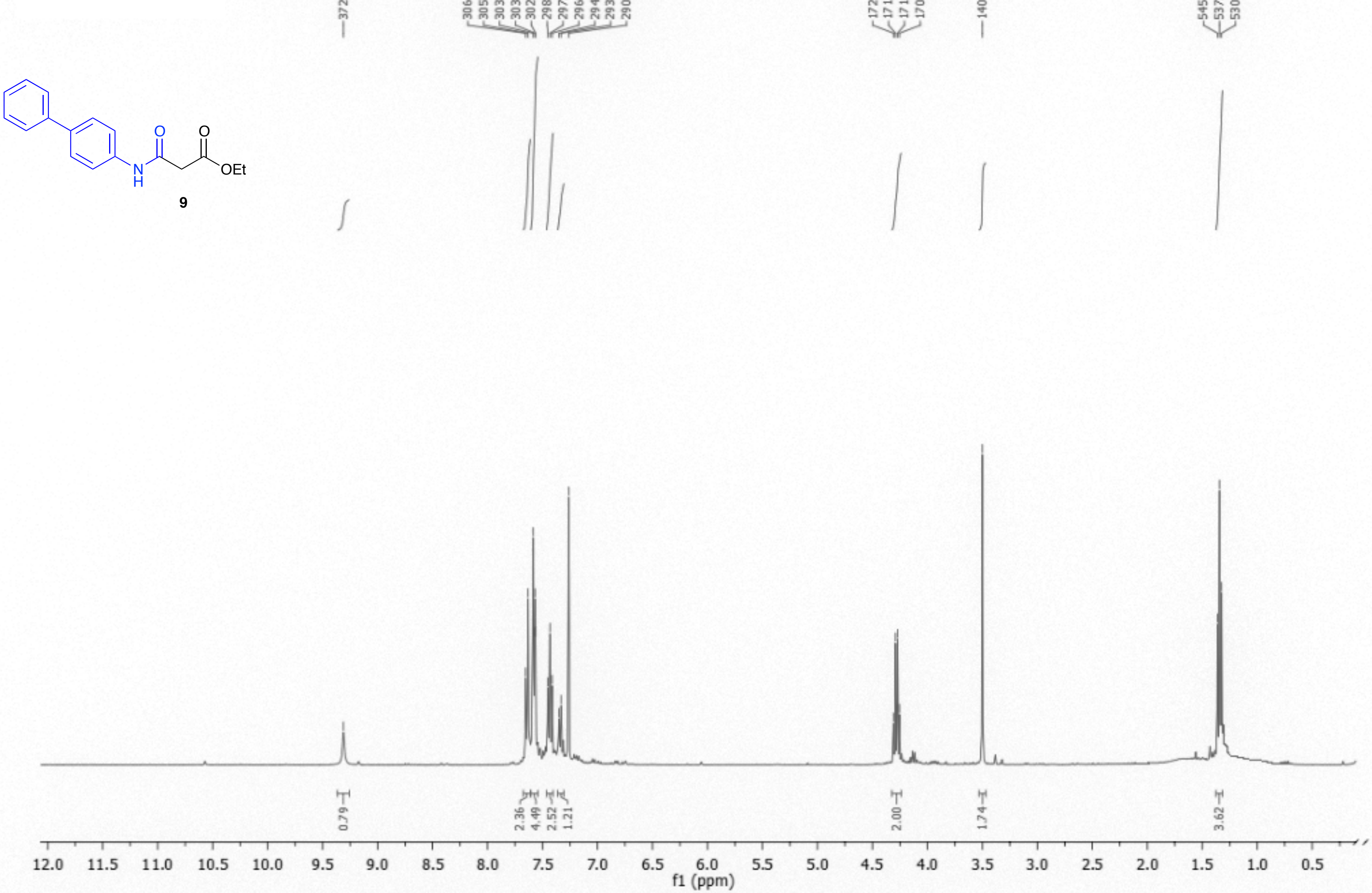
13C NMR
100 MHz, CDCl3
168.66
162.37
76.07
75.95
75.75
75.43
60.14
50.79
41.13
40.19
35.07
28.15
12.80
O
O
HN
OEt
7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

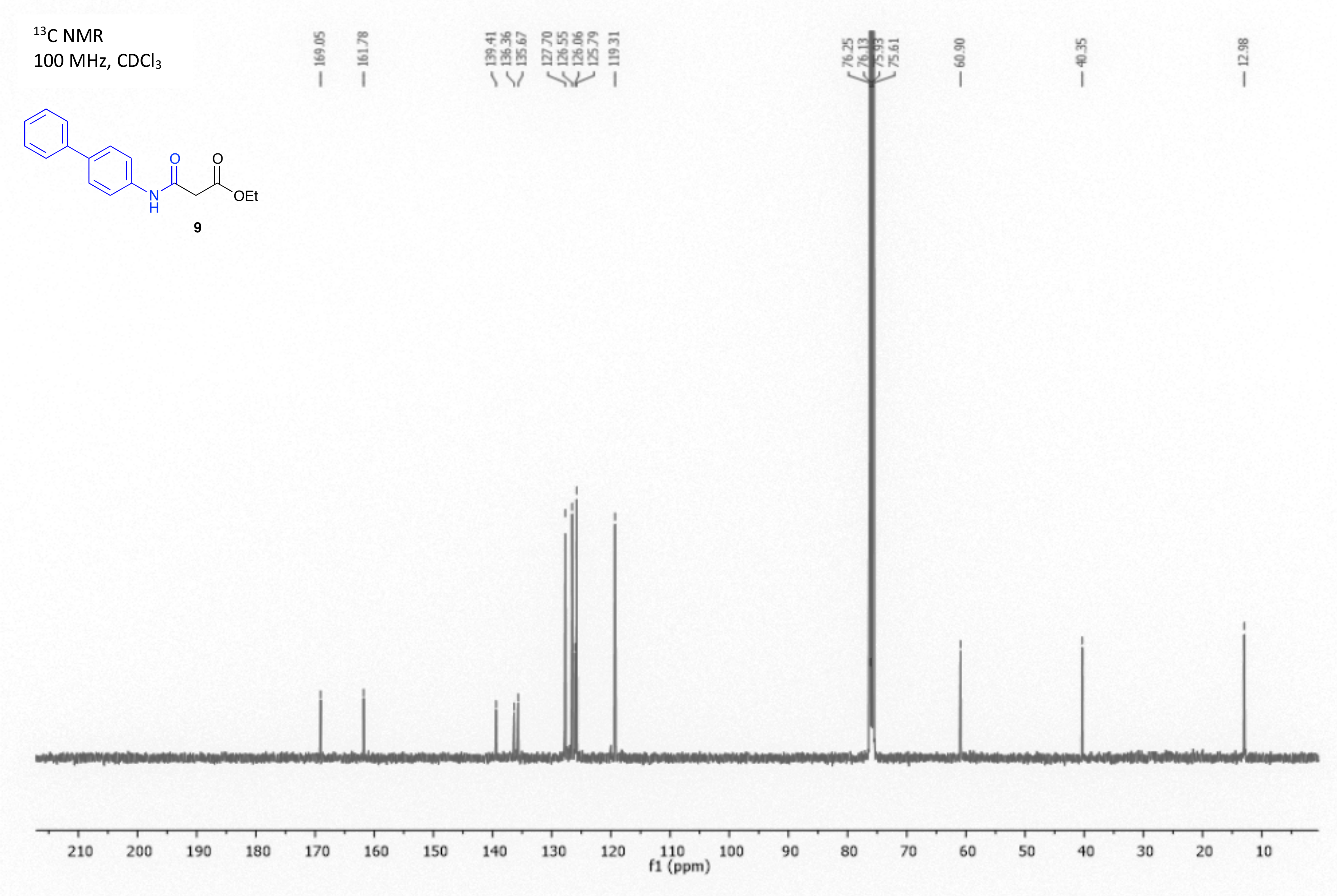

^{1}H NMR
400 MHz, CDCl$_3$
OEt
O
O
N
H
8
3633.76
2907.67
2876.41
2711.17
1715.17
1708.02
1700.88
1693.76
1678.72
1633.01
1381.63
920.91
671.52
639.06
544.73
537.87
530.74
523.60
294.80
0.90
1.99
1.06
2.13
2.00
6.69
5.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

^{13}C NMR
100 MHz, $CDCl_3$



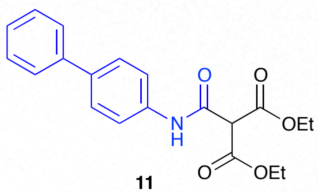
[1]H NMR
400 MHz, $CDCl_3$





^{13}C NMR
100 MHz, CDCl$_3$
OEt
9
169.05
161.78
139.41
136.36
135.67
127.70
126.55
126.06
125.79
119.31
76.25
76.13
75.93
75.61
60.90
40.35
12.98
f1 (ppm)

[1]H NMR
400 MHz, $CDCl_3$



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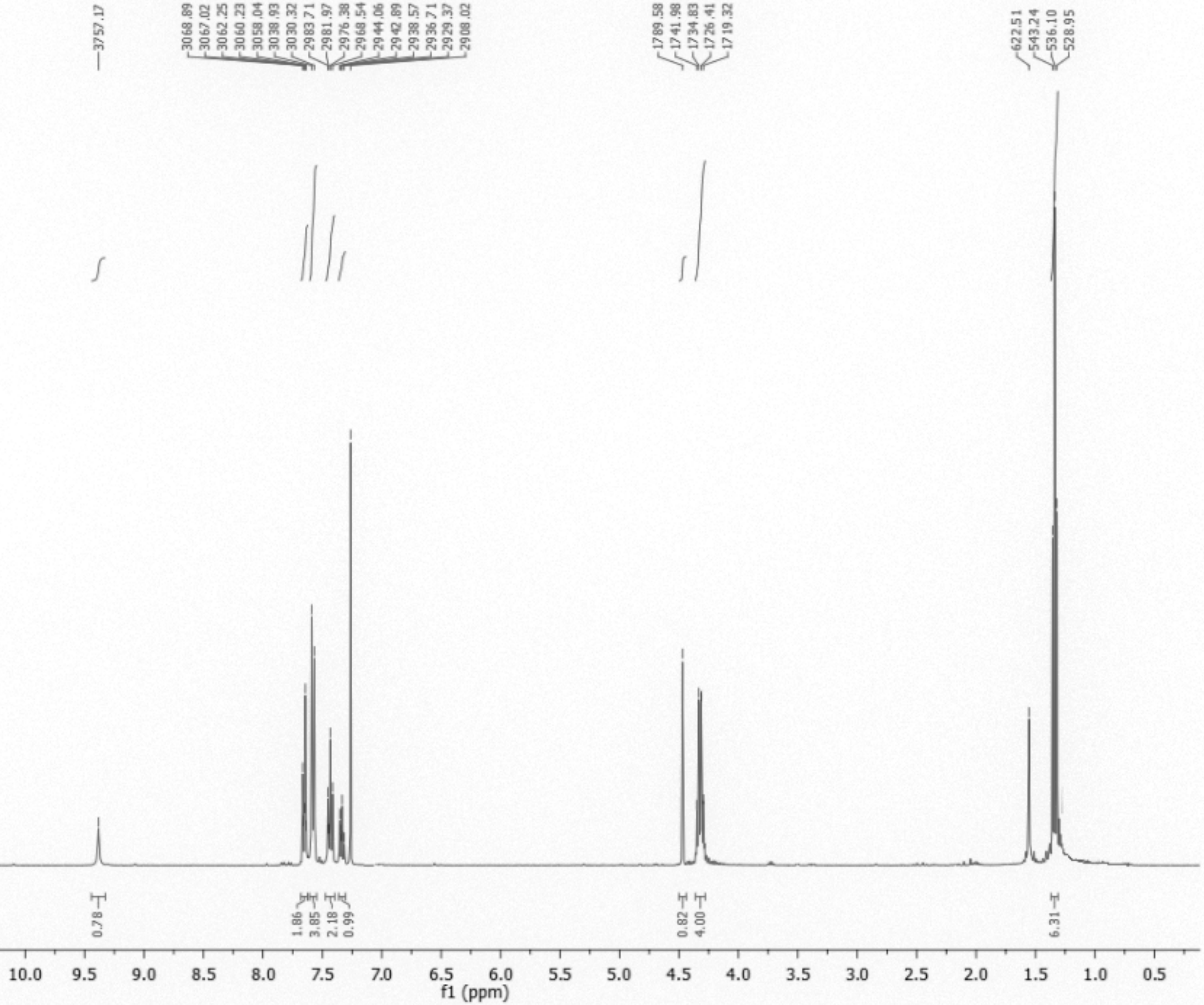
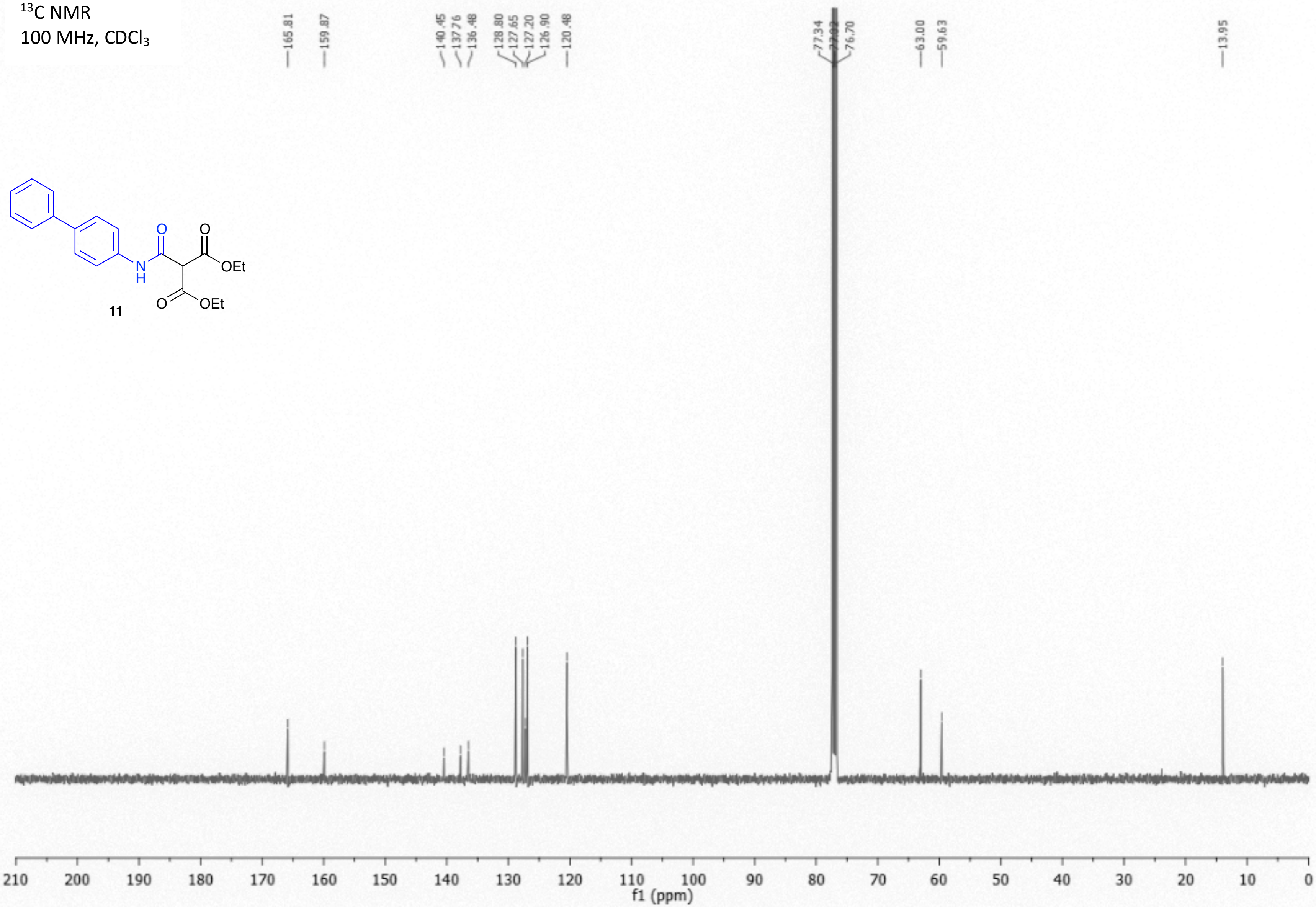
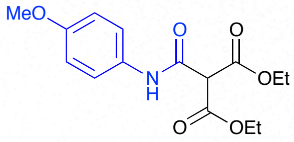


^{13}C NMR
100 MHz, $CDCl_3$



^1H NMR
400 MHz, $CDCl_3$



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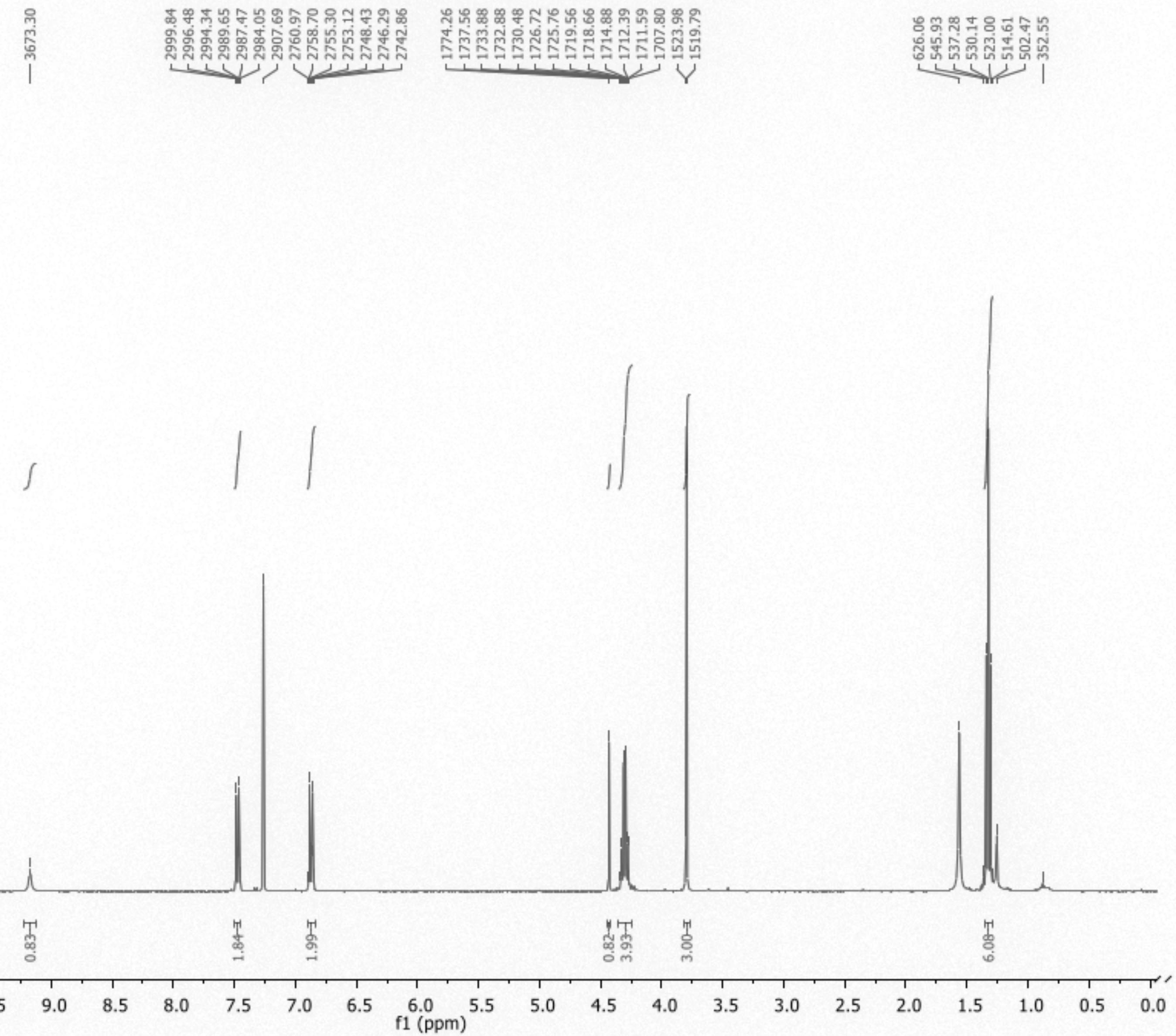
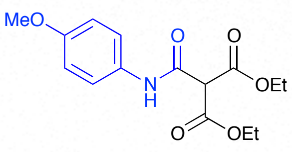


^{13}C NMR
100 MHz, $CDCl_3$



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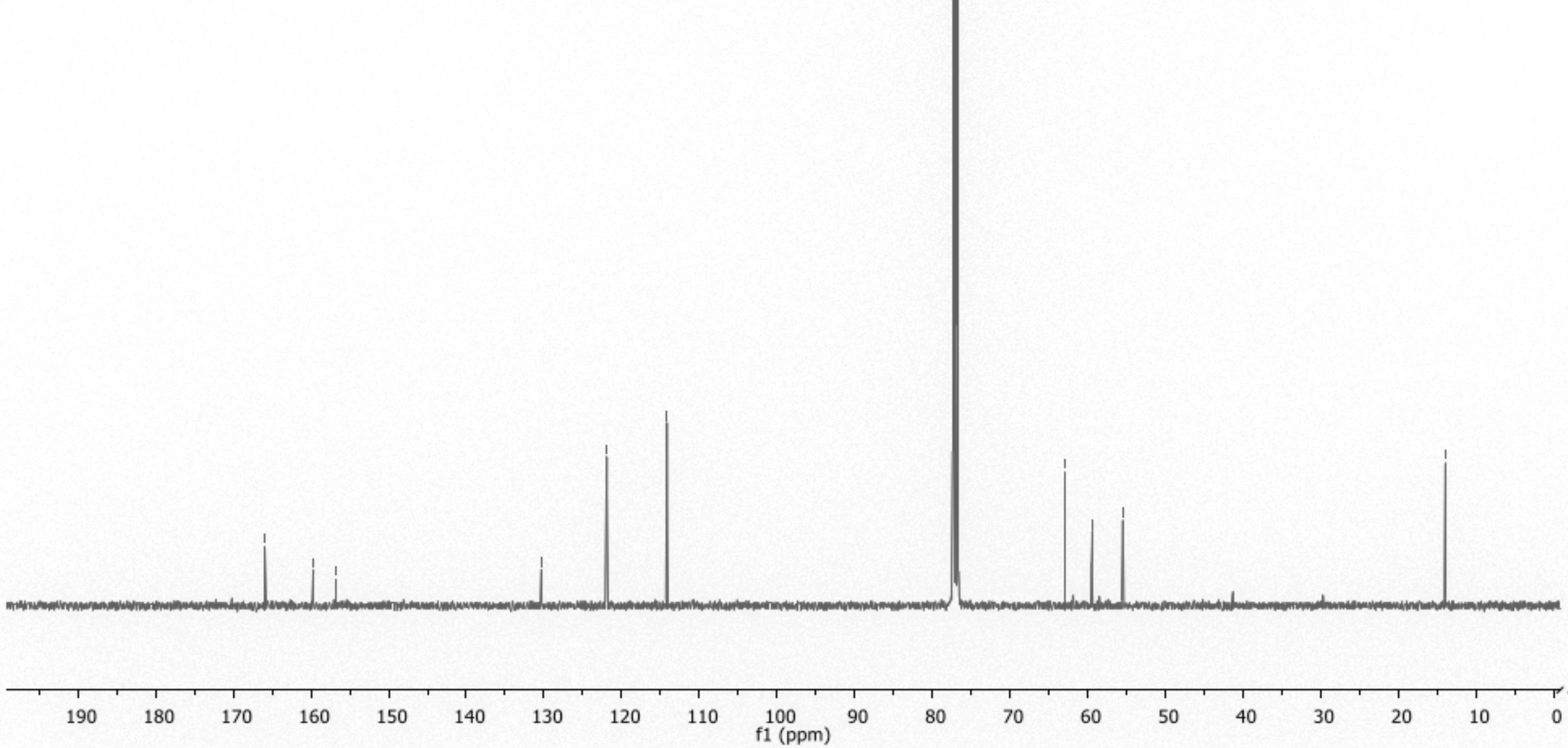
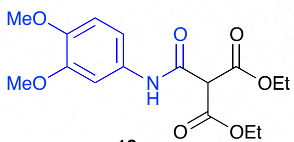


^{1}H NMR
400 MHz, $CDCl_3$



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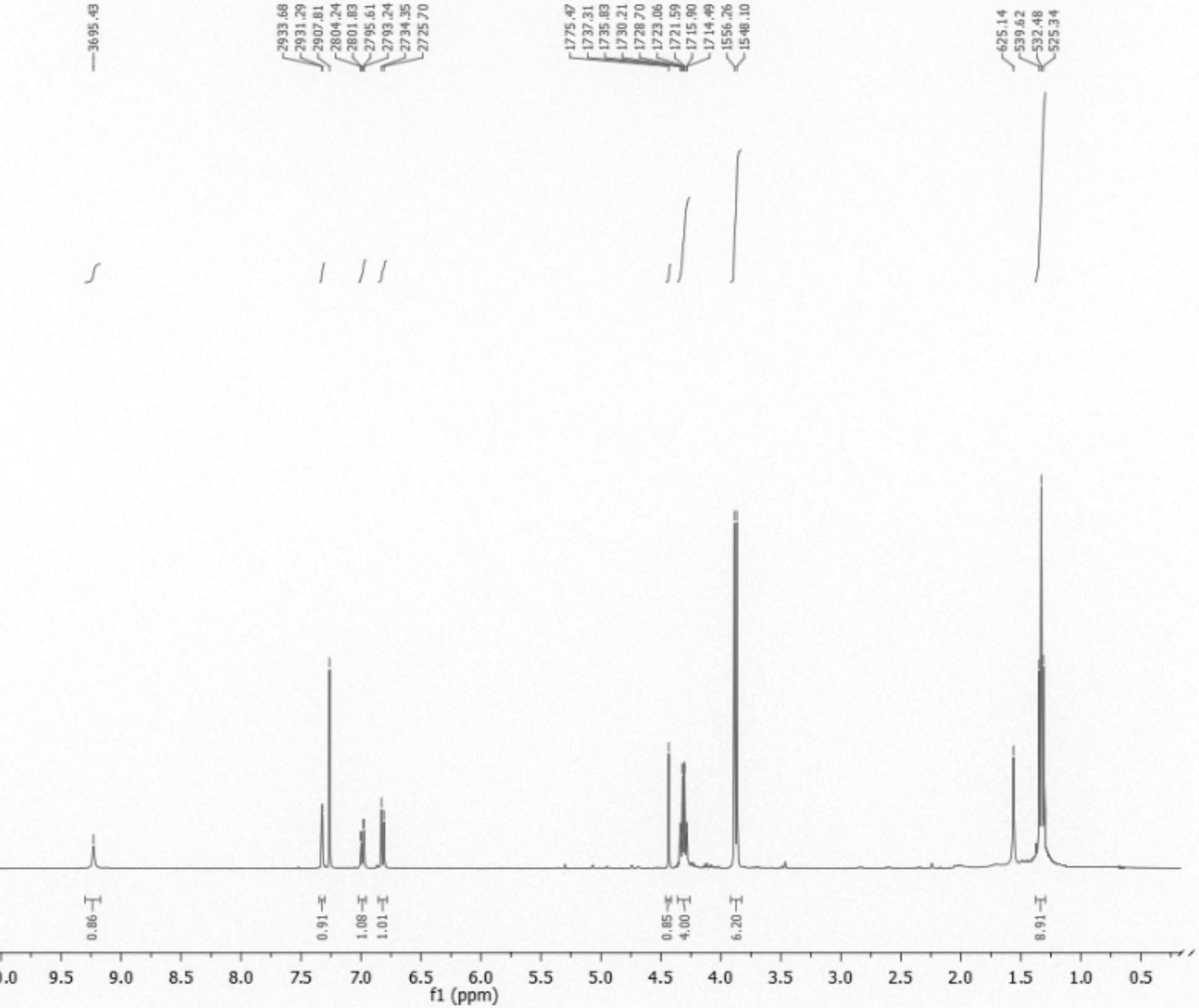
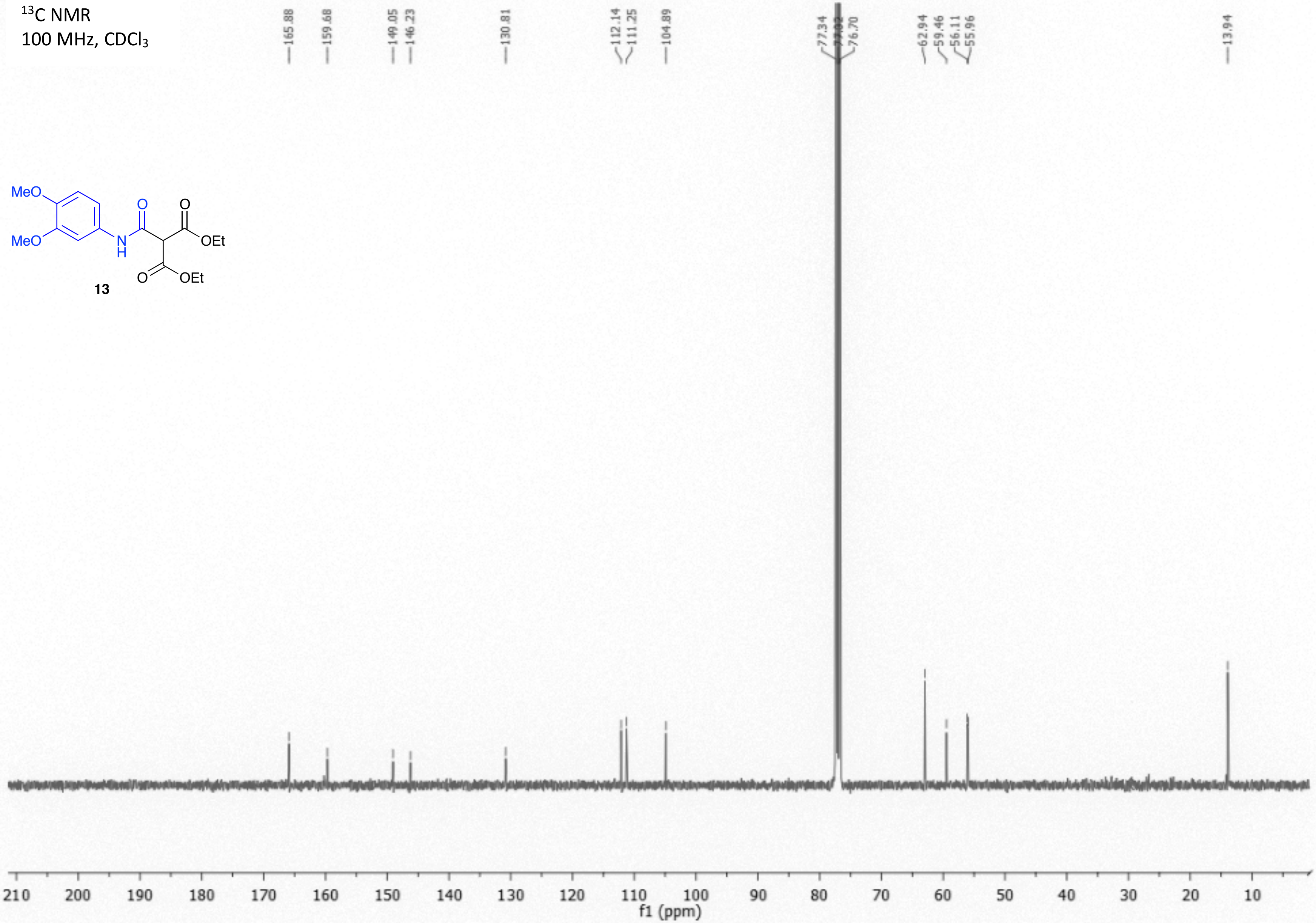


^{13}C NMR
100 MHz, $CDCl_3$



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^{1}H NMR
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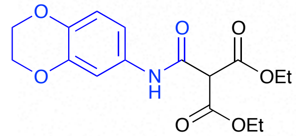

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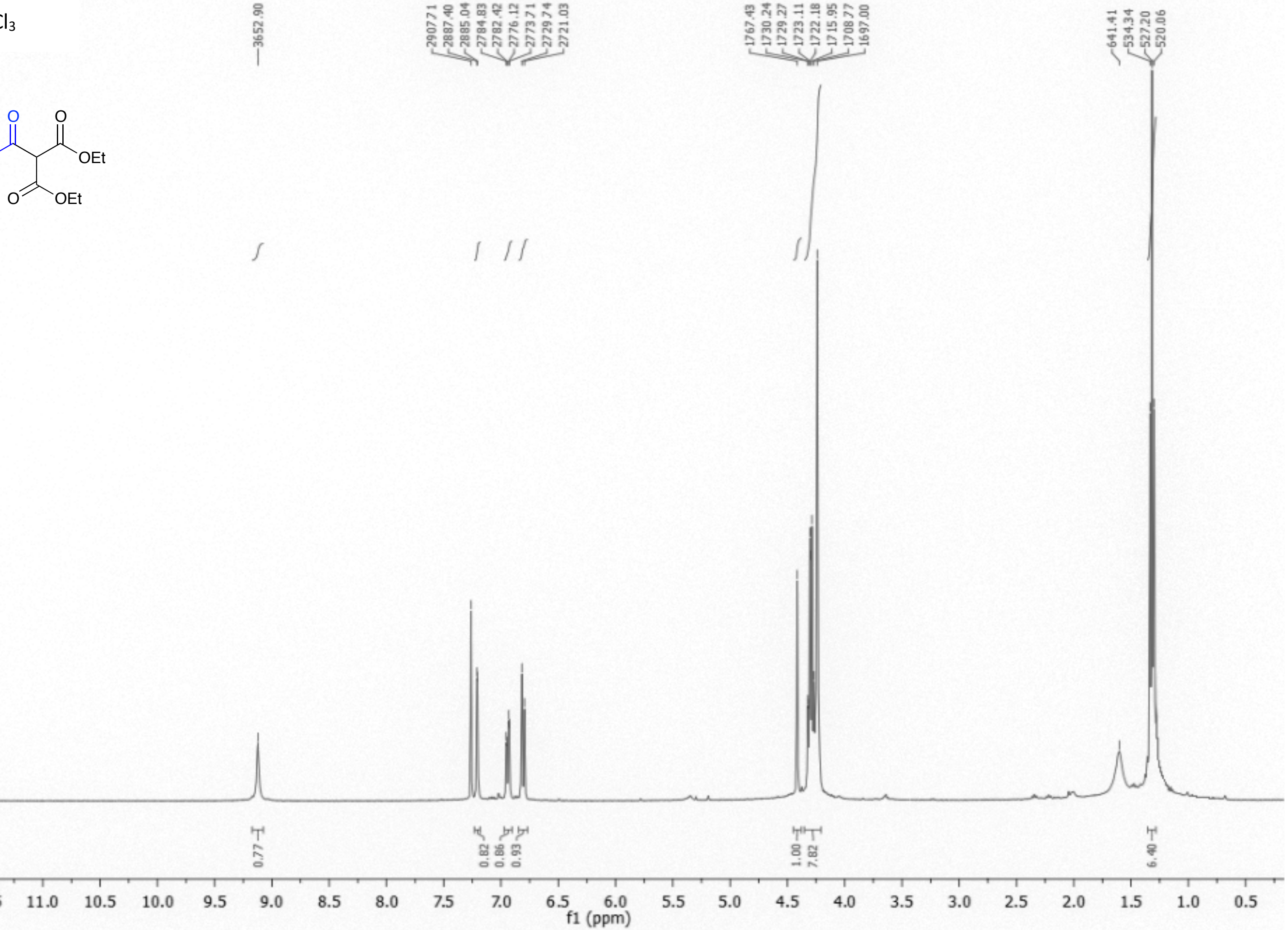
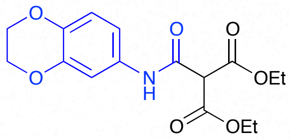


^{13}C NMR
100 MHz, $CDCl_3$



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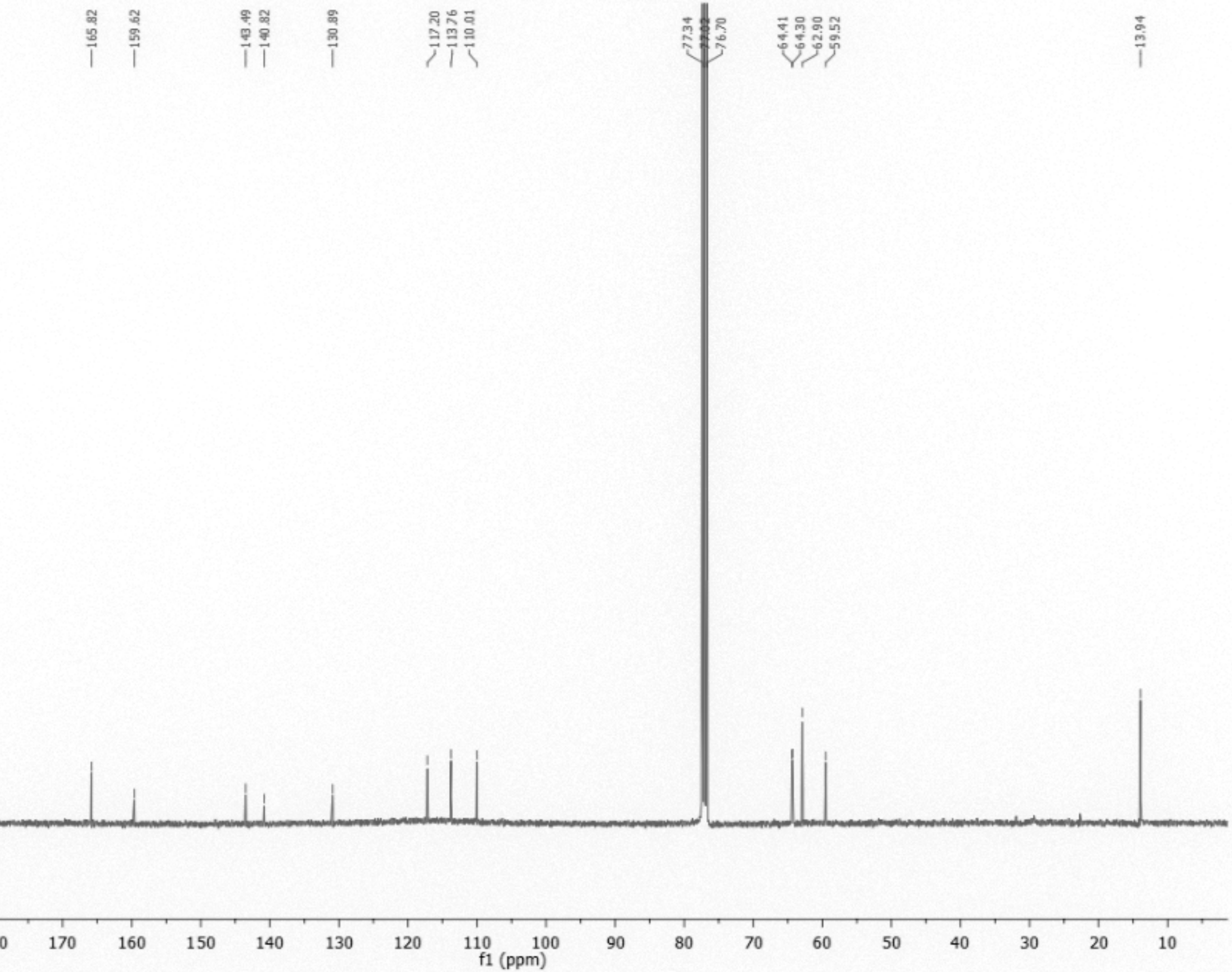

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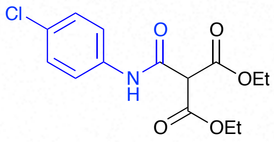

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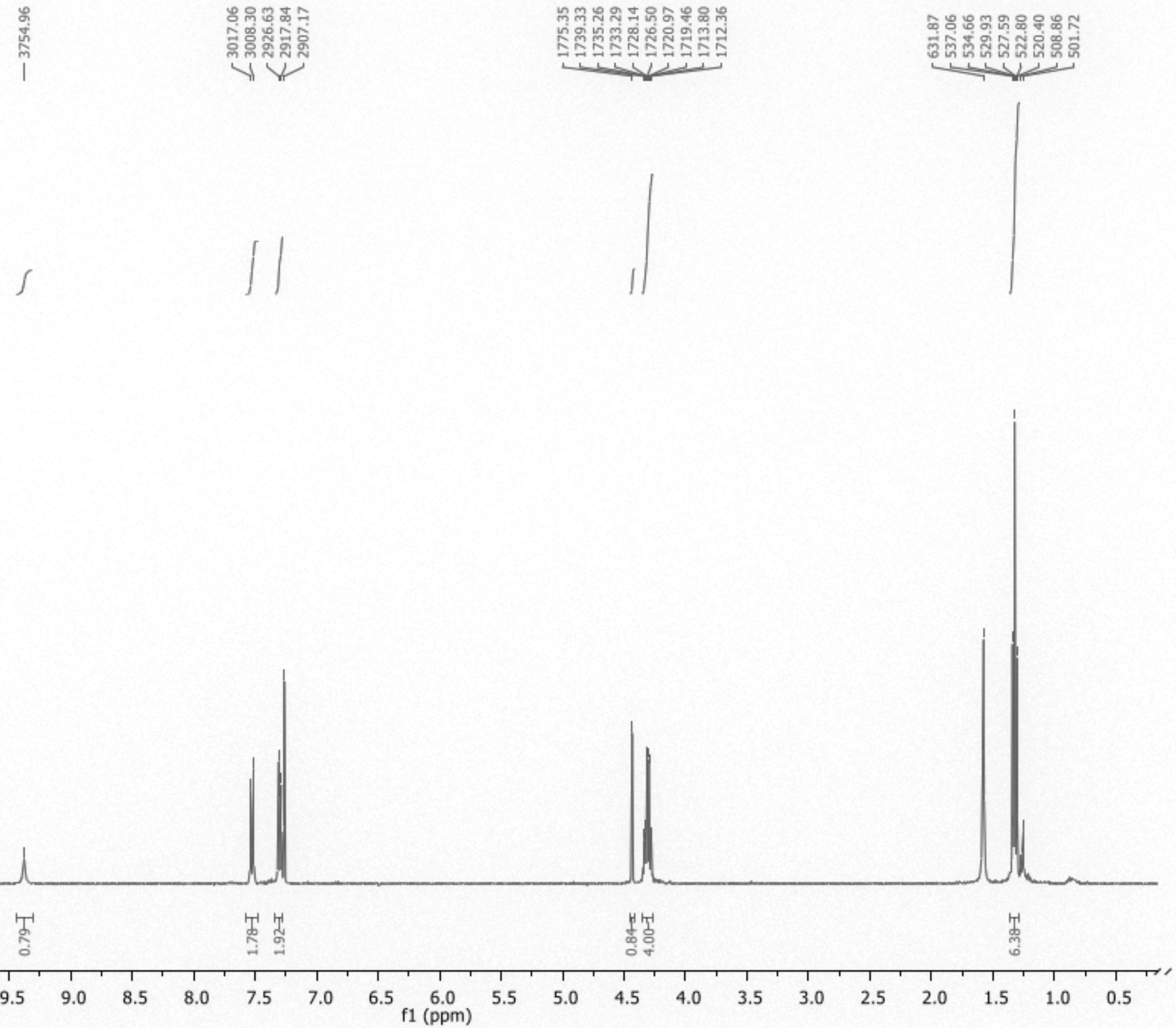
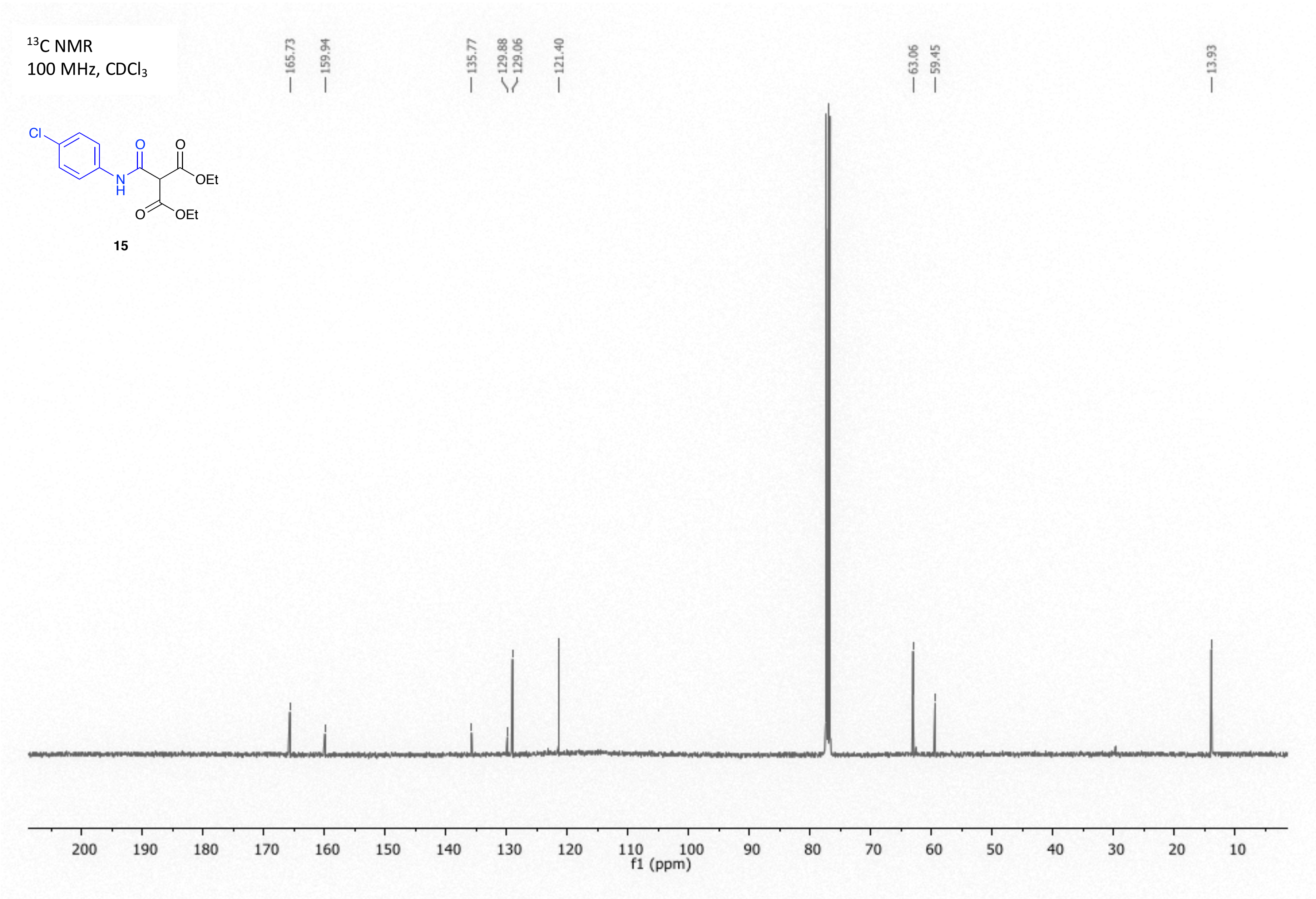
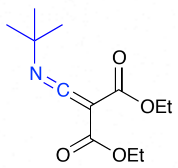




^{13}C NMR
100 MHz, $CDCl_3$
Cl
O
O
N
H
OEt
O
OEt
15
165.73
159.94
135.77
129.88
129.06
121.40
63.06
59.45
13.93
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

^{1}H NMR
400 MHz, $CDCl_3$



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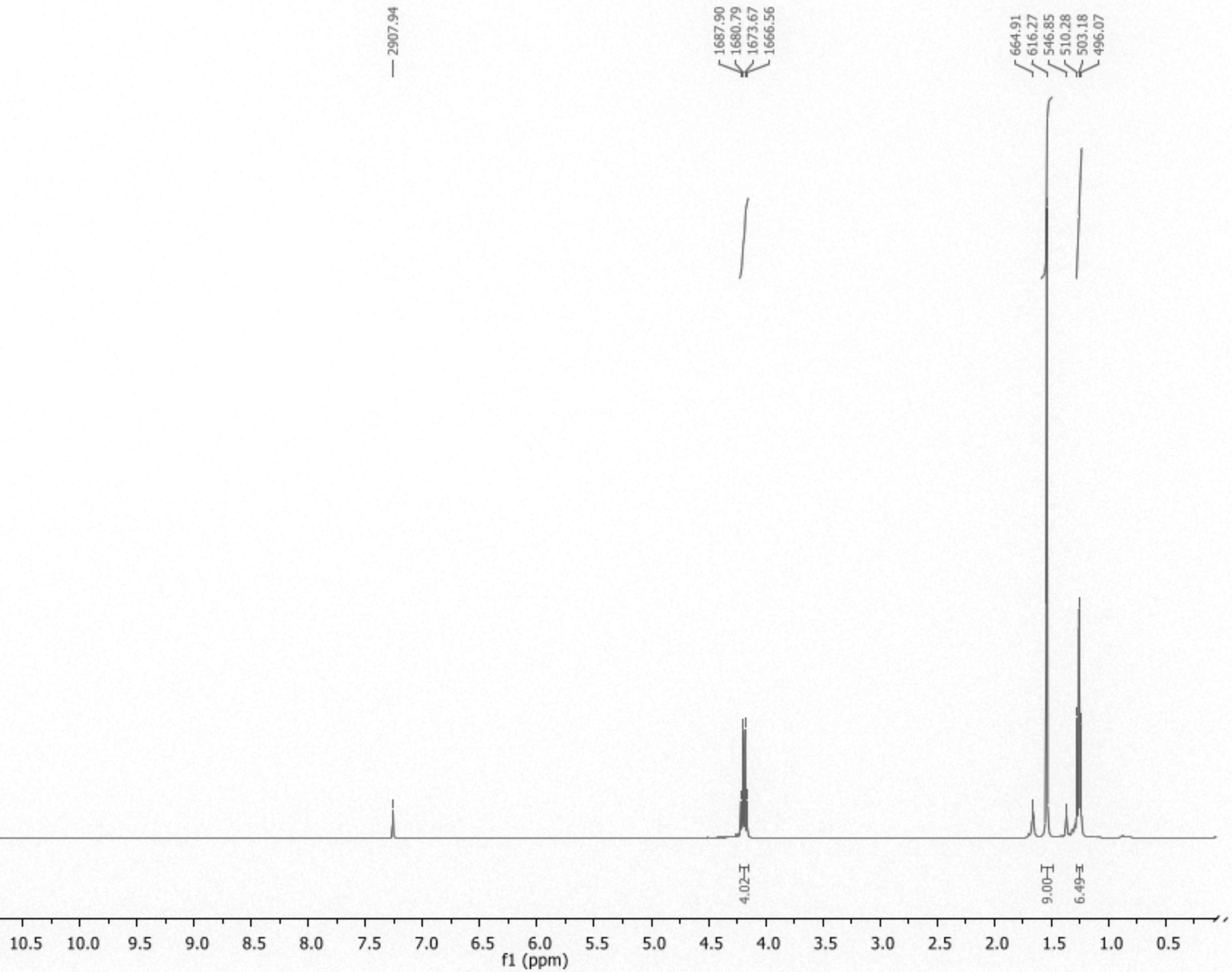

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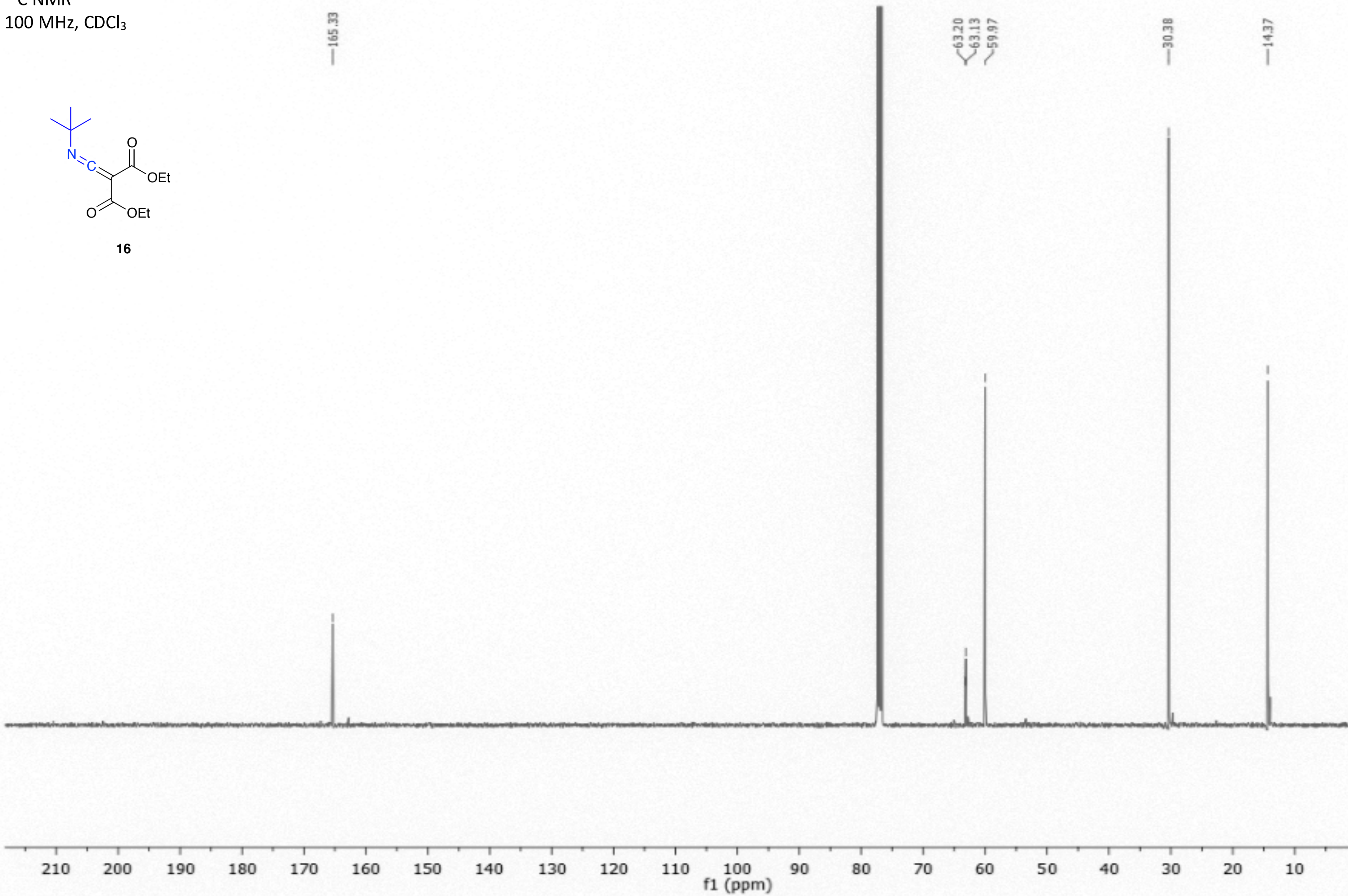

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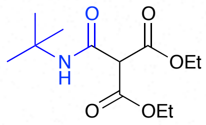

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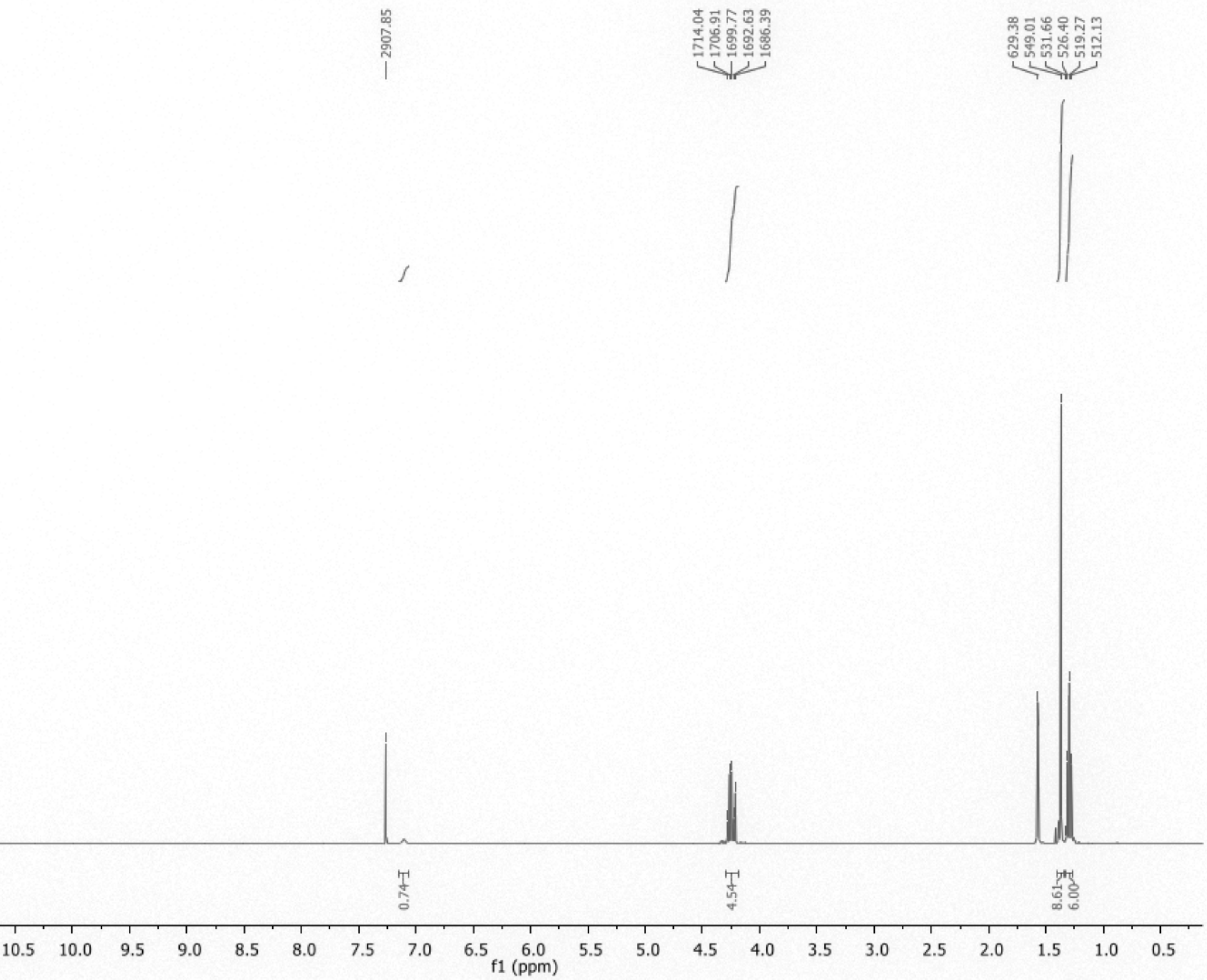

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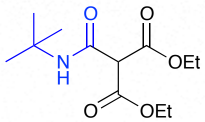

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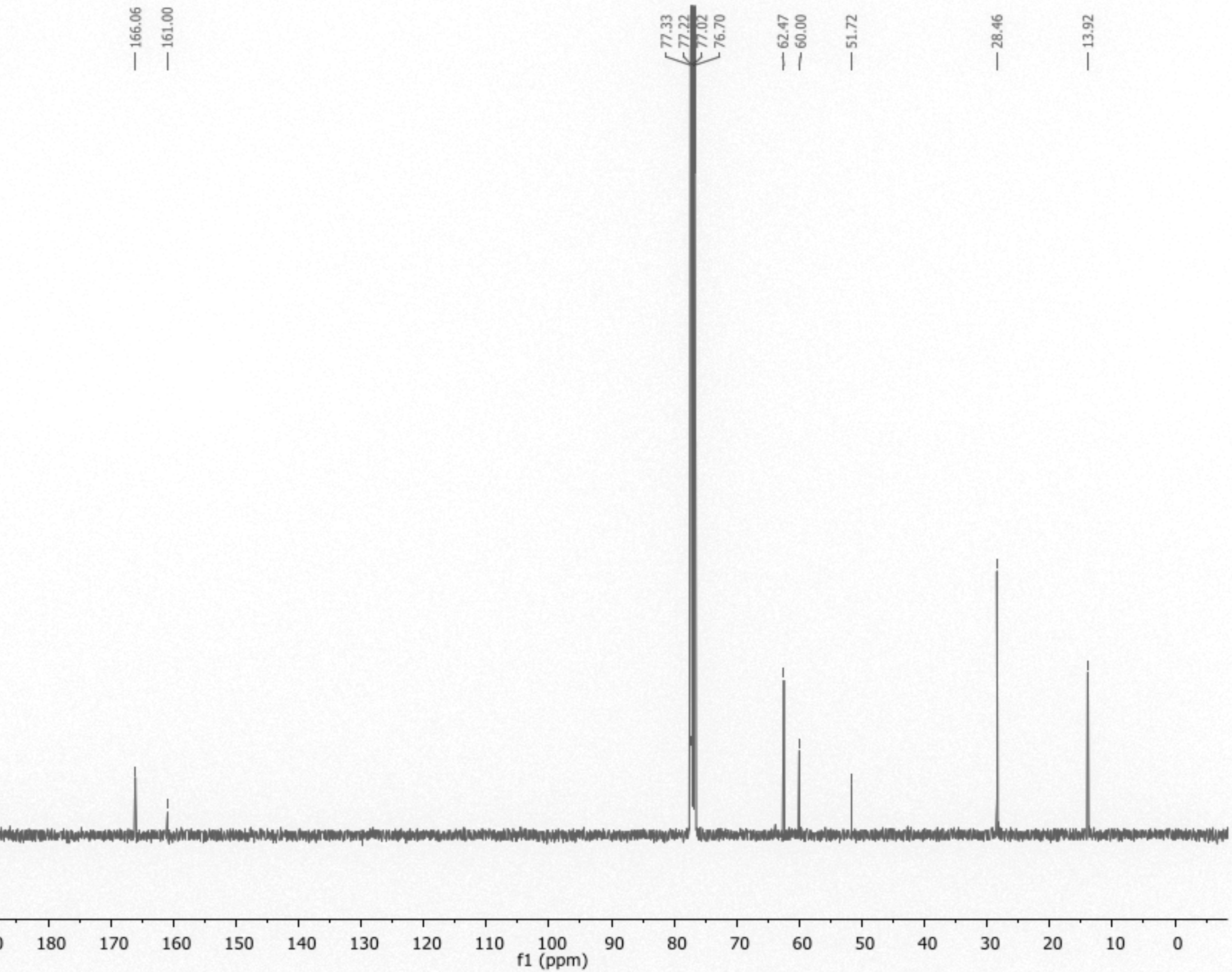
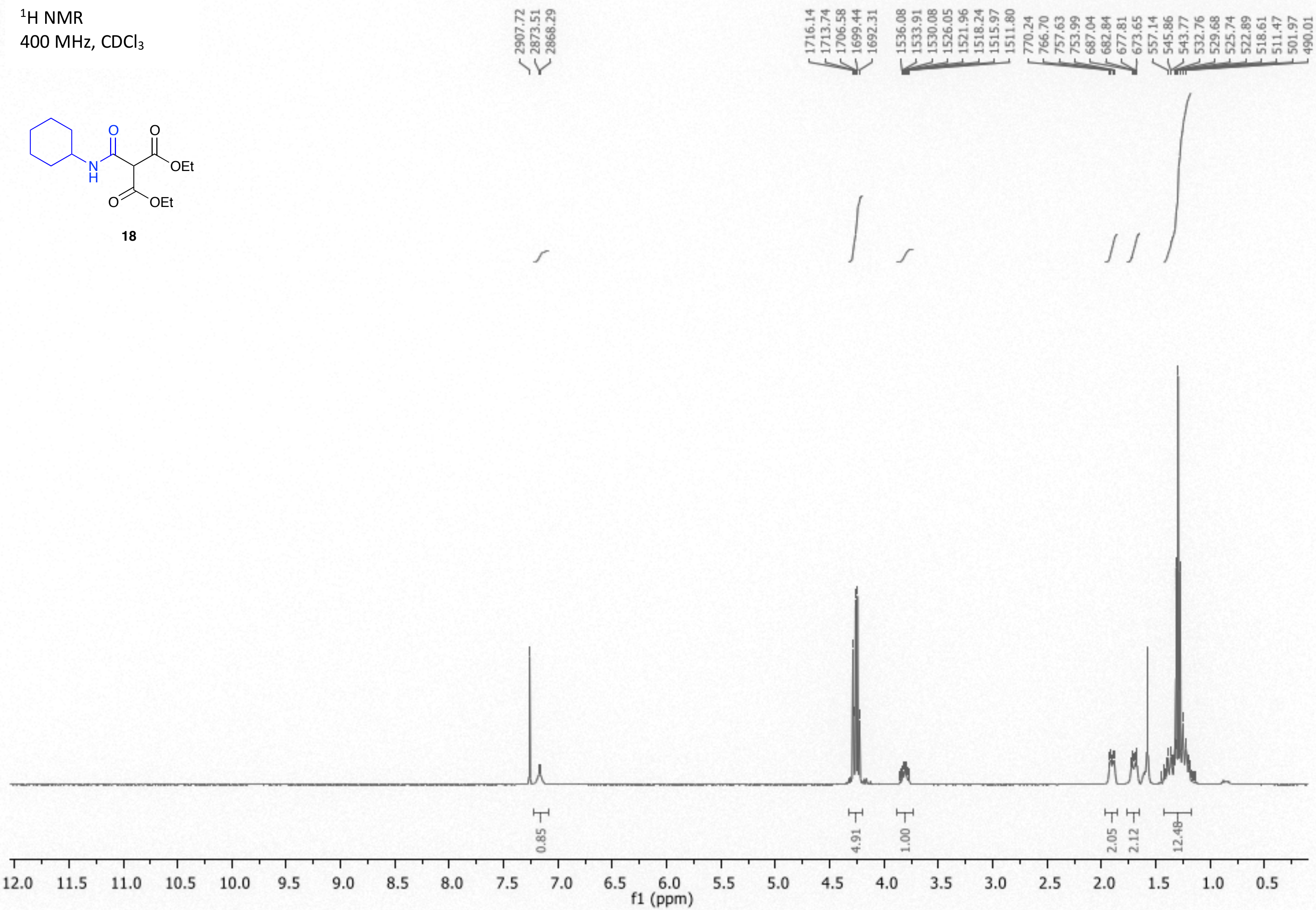
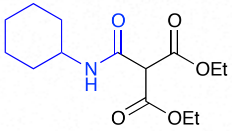



1H NMR
400 MHz, CDCl3
O
O
N
H
OEt
O
OEt
18
2907.72
2873.51
2868.29
1716.14
1713.74
1706.58
1699.44
1692.31
1536.08
1533.91
1530.08
1526.05
1521.96
1518.24
1515.97
1511.80
770.24
766.70
757.63
753.99
687.04
682.84
677.81
673.65
557.14
545.86
543.77
532.76
529.68
525.74
522.89
518.61
511.47
501.97
490.01
0.85
4.91
1.00
2.05
2.12
12.48
12.0 11.5 11.0 10.5 10.0 9.5 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
f1 (ppm)

^{13}C NMR
100 MHz, $CDCl_3$



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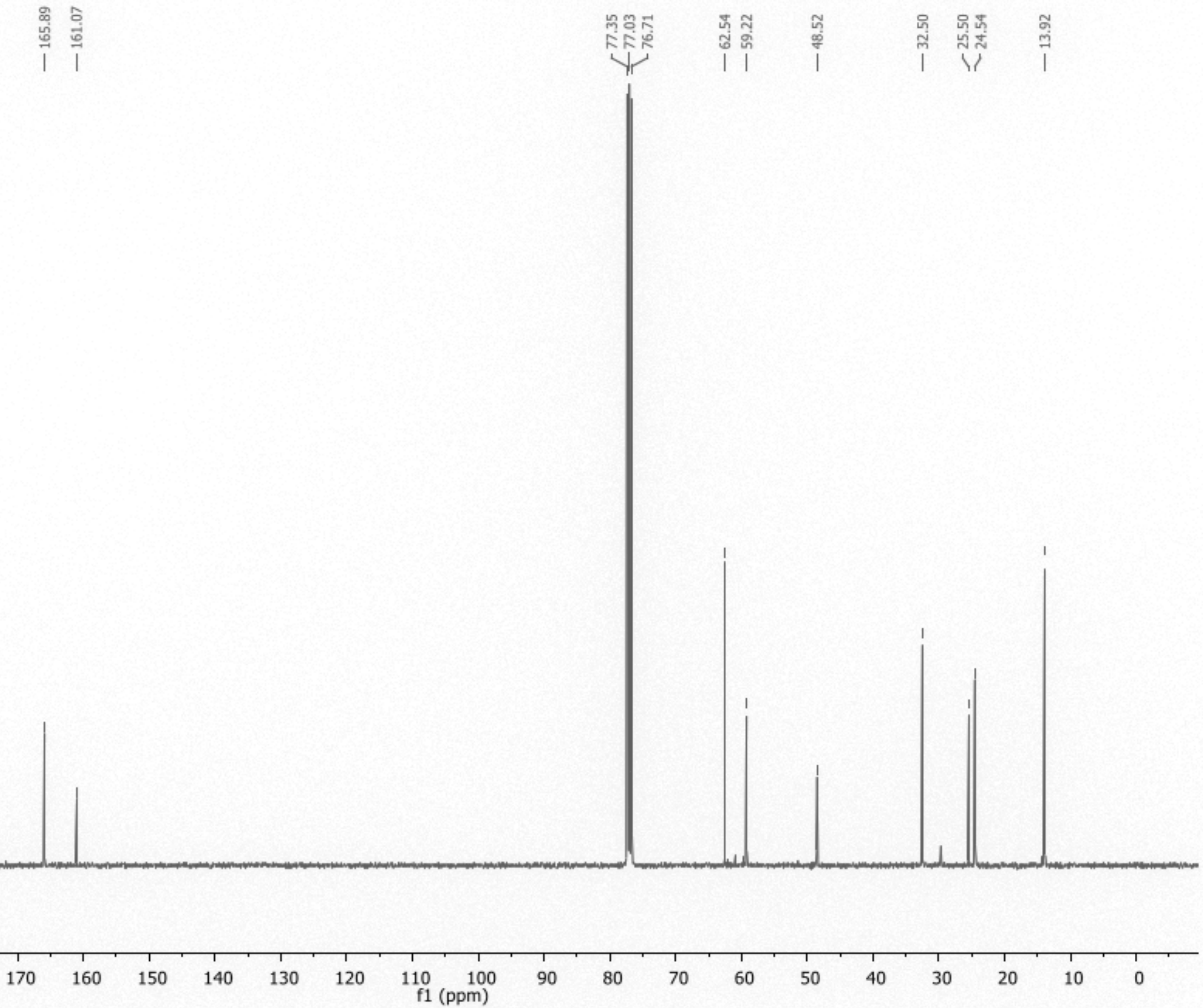

^{1}H NMR
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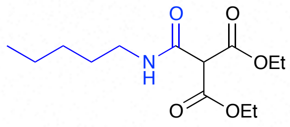

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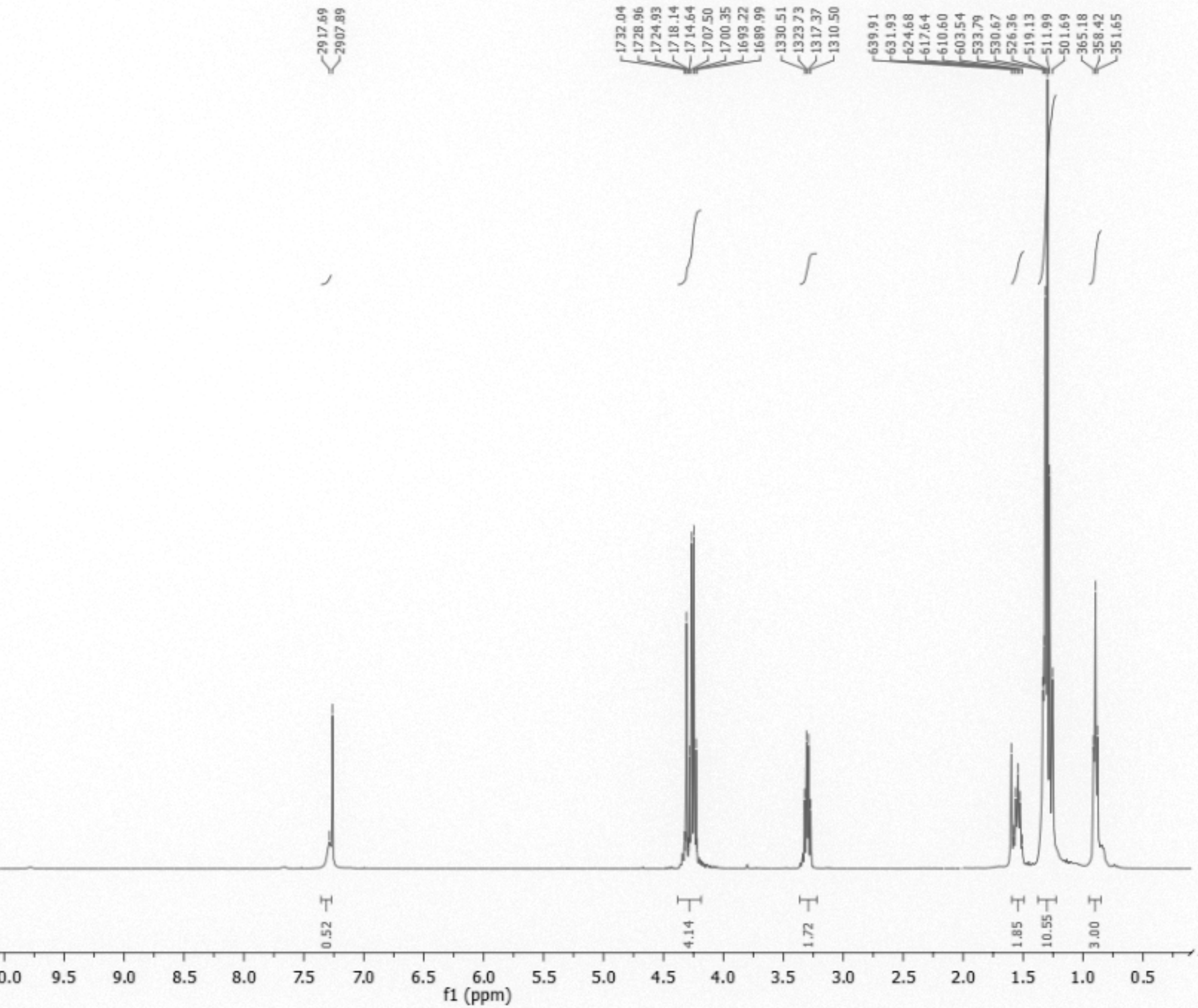

^{13}C NMR
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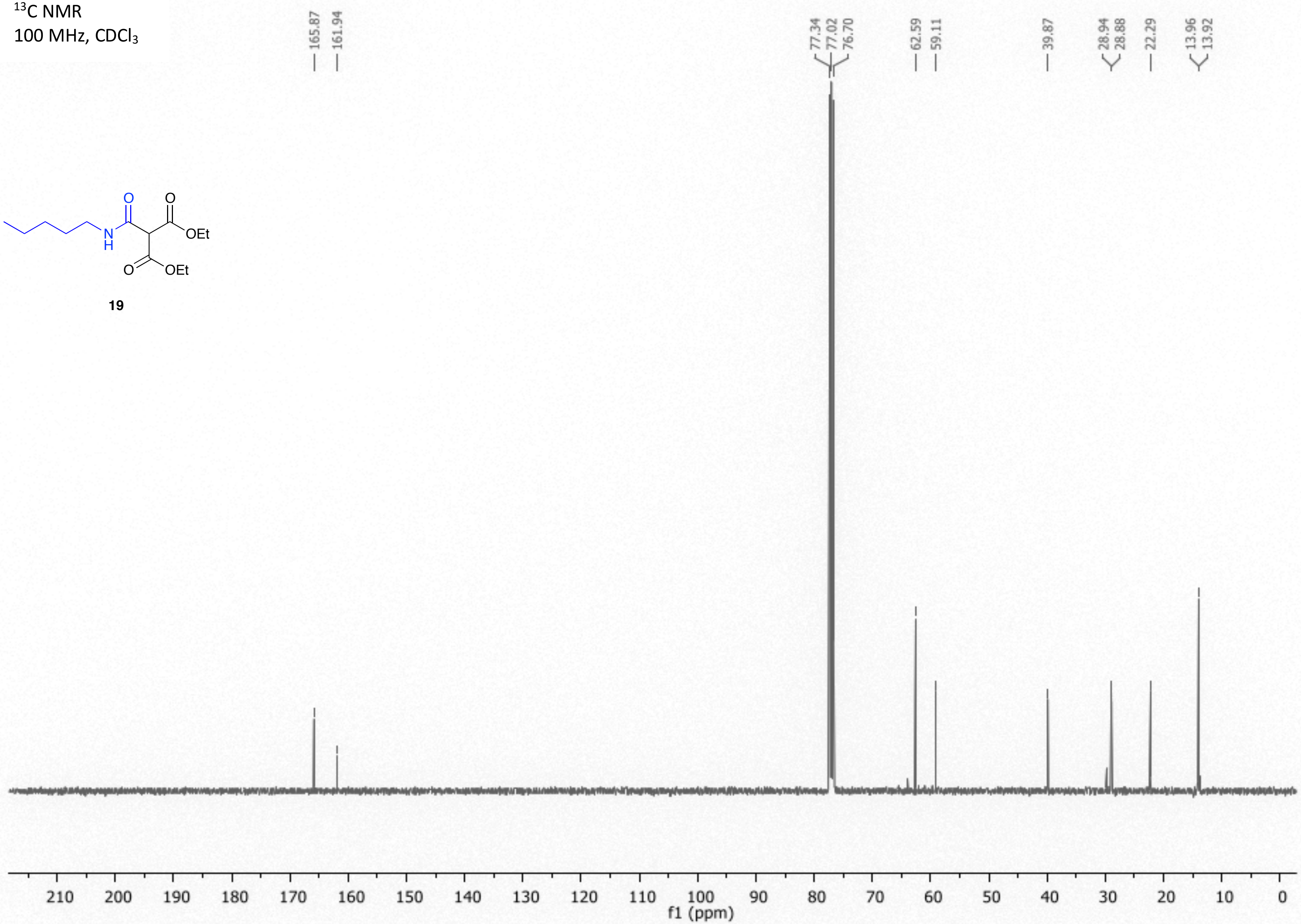
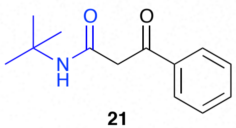


[1]H NMR
400 MHz, $CDCl_3$



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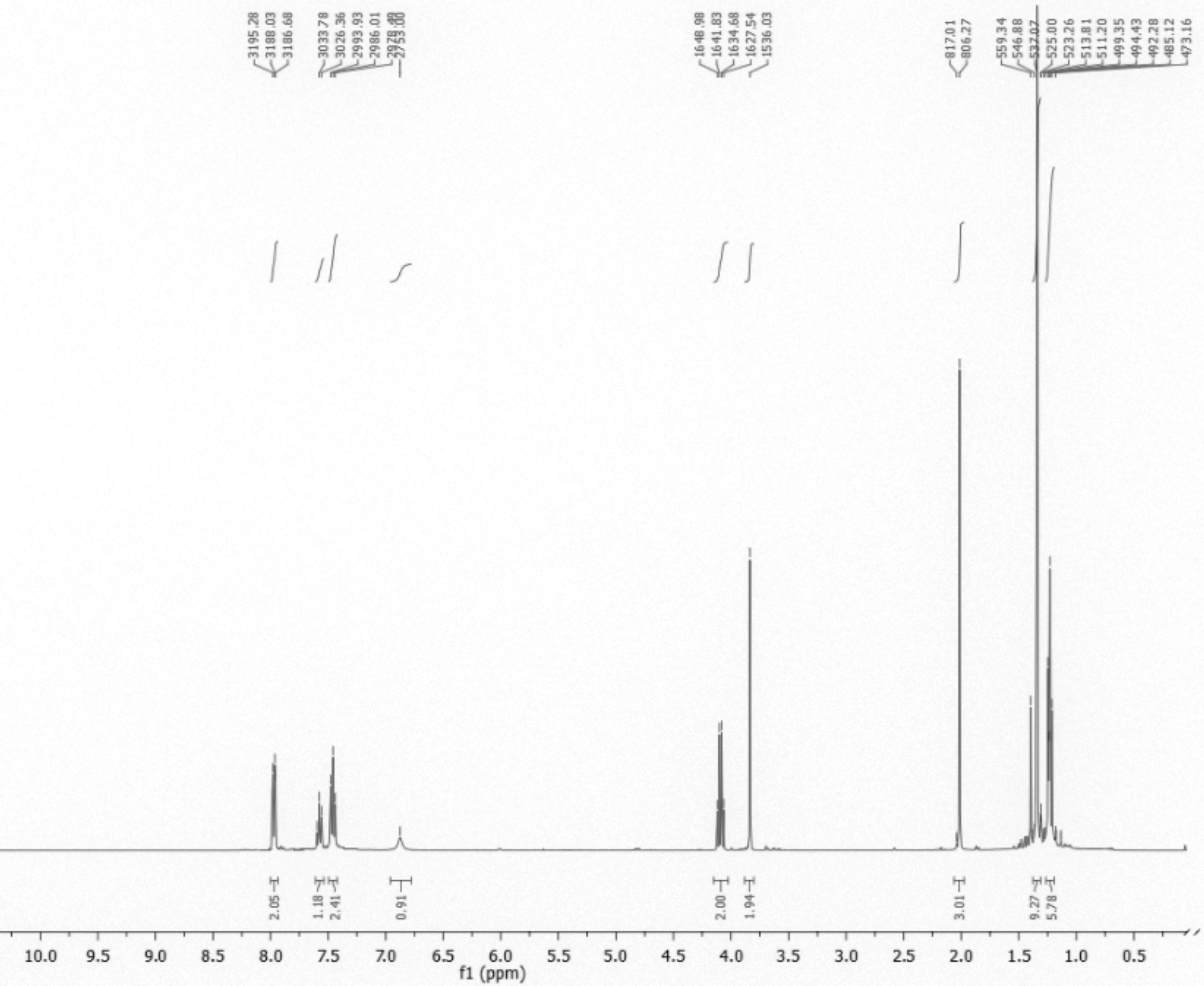
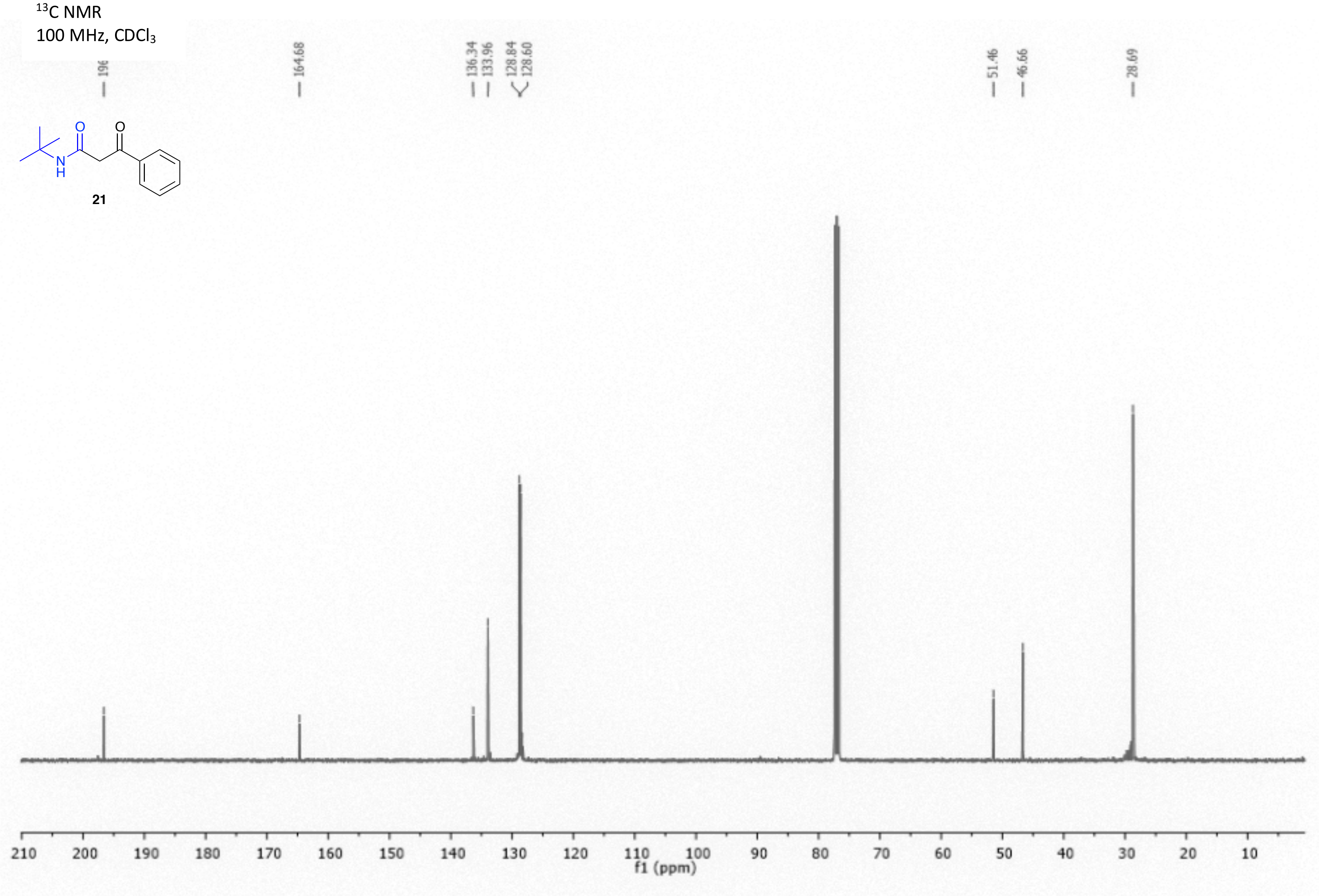
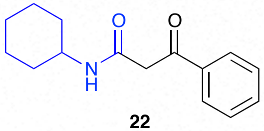




^{13}C NMR
100 MHz, $CDCl_3$
196
164.68
136.34
133.96
128.84
128.60
51.46
46.66
28.69
O
O
N
H
21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

[1]H NMR
400 MHz, $CDCl_3$



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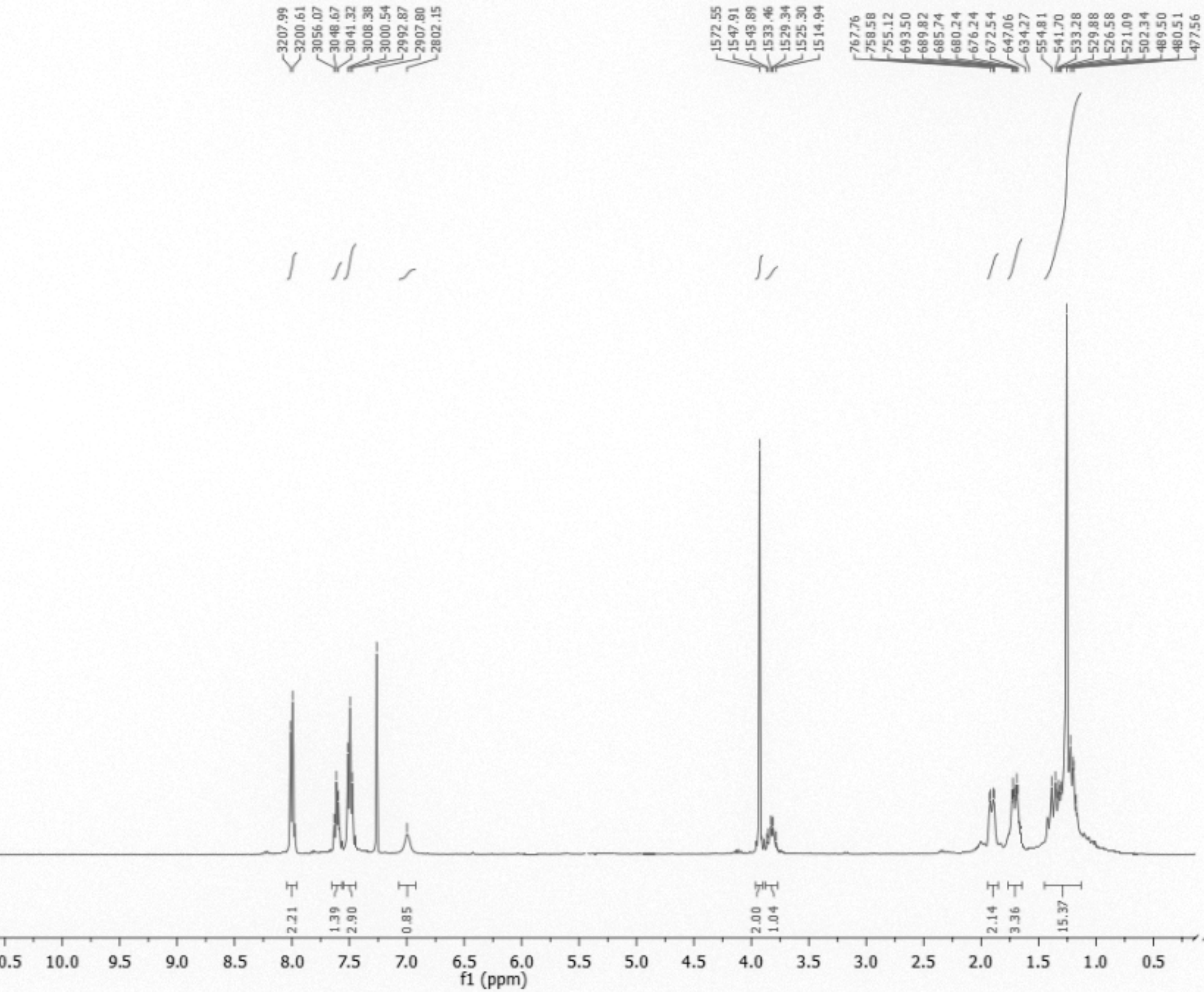
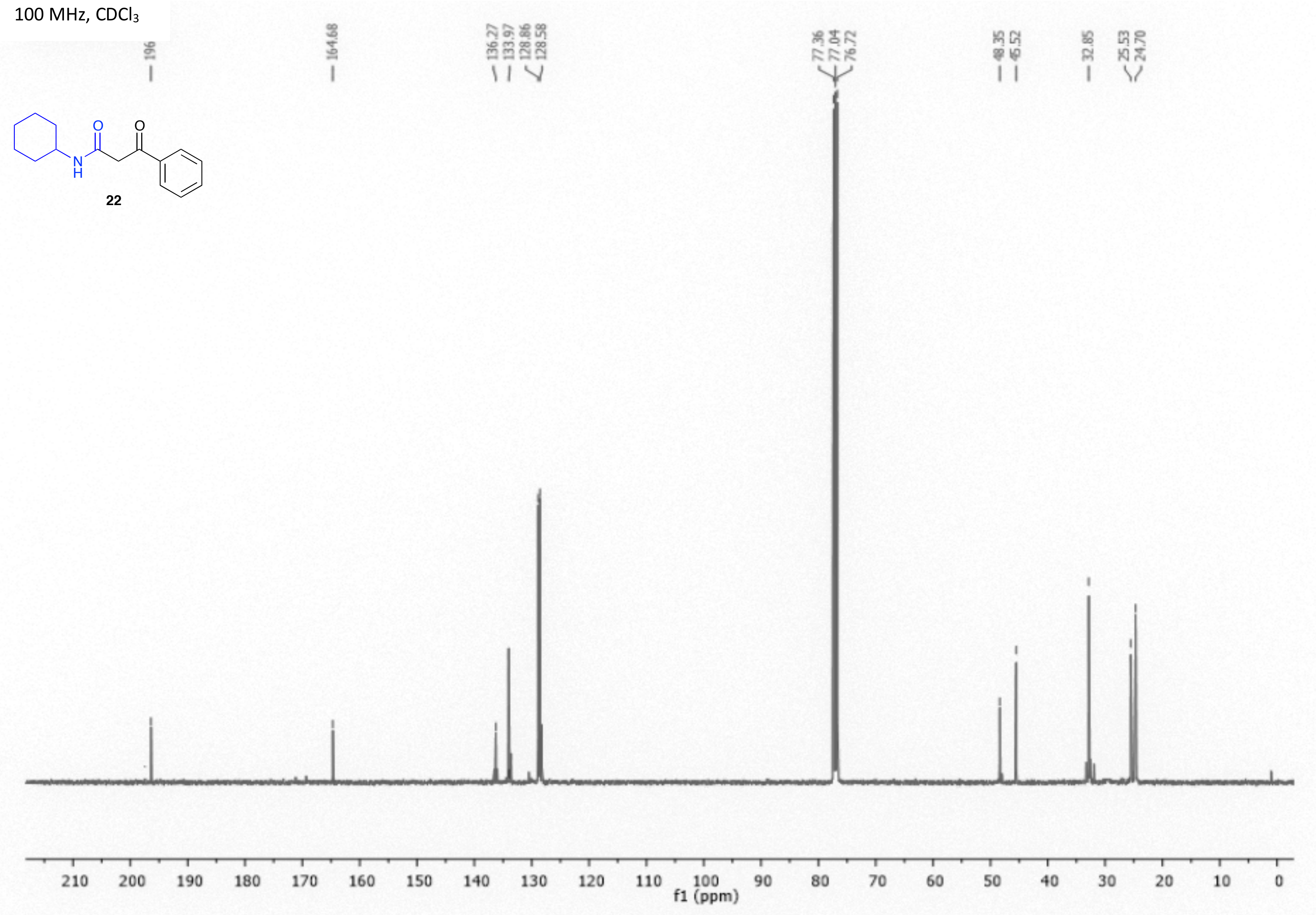
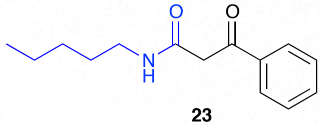


^{13}C NMR
100 MHz, $CDCl_3$



^{1}H NMR
400 MHz, $CDCl_3$



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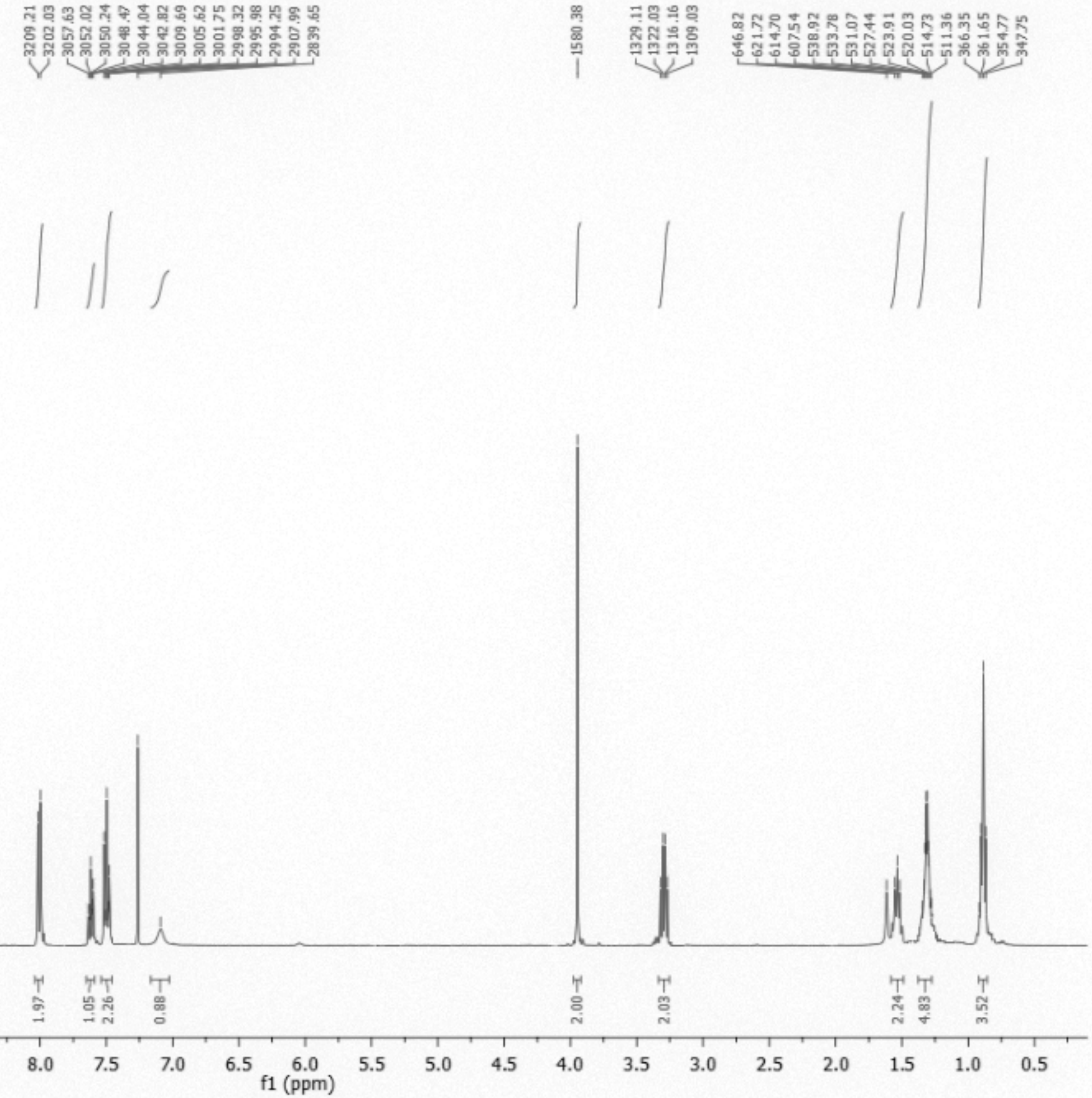
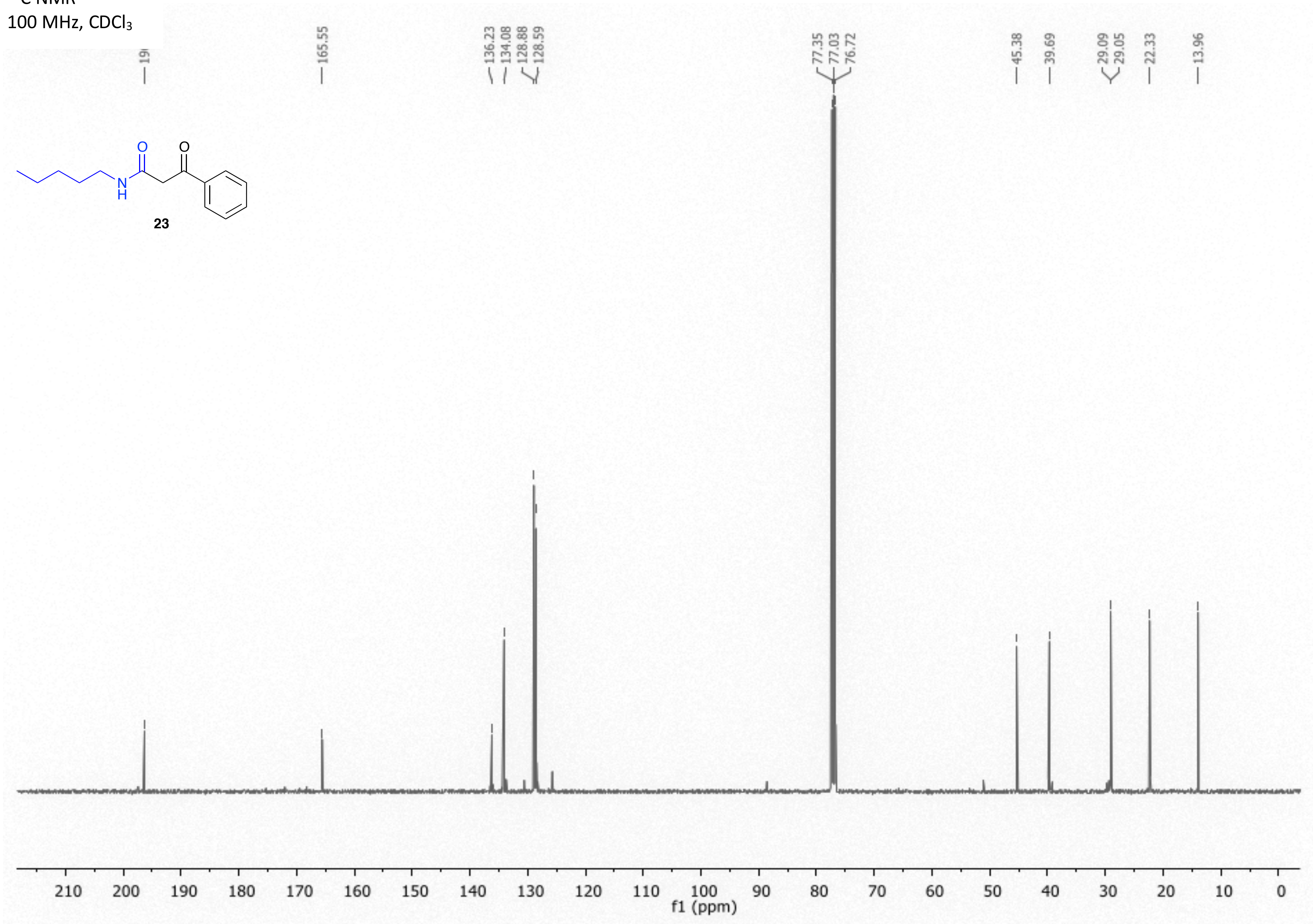
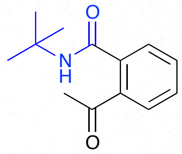


^{13}C NMR
100 MHz, $CDCl_3$



^1H NMR
400 MHz, $CDCl_3$



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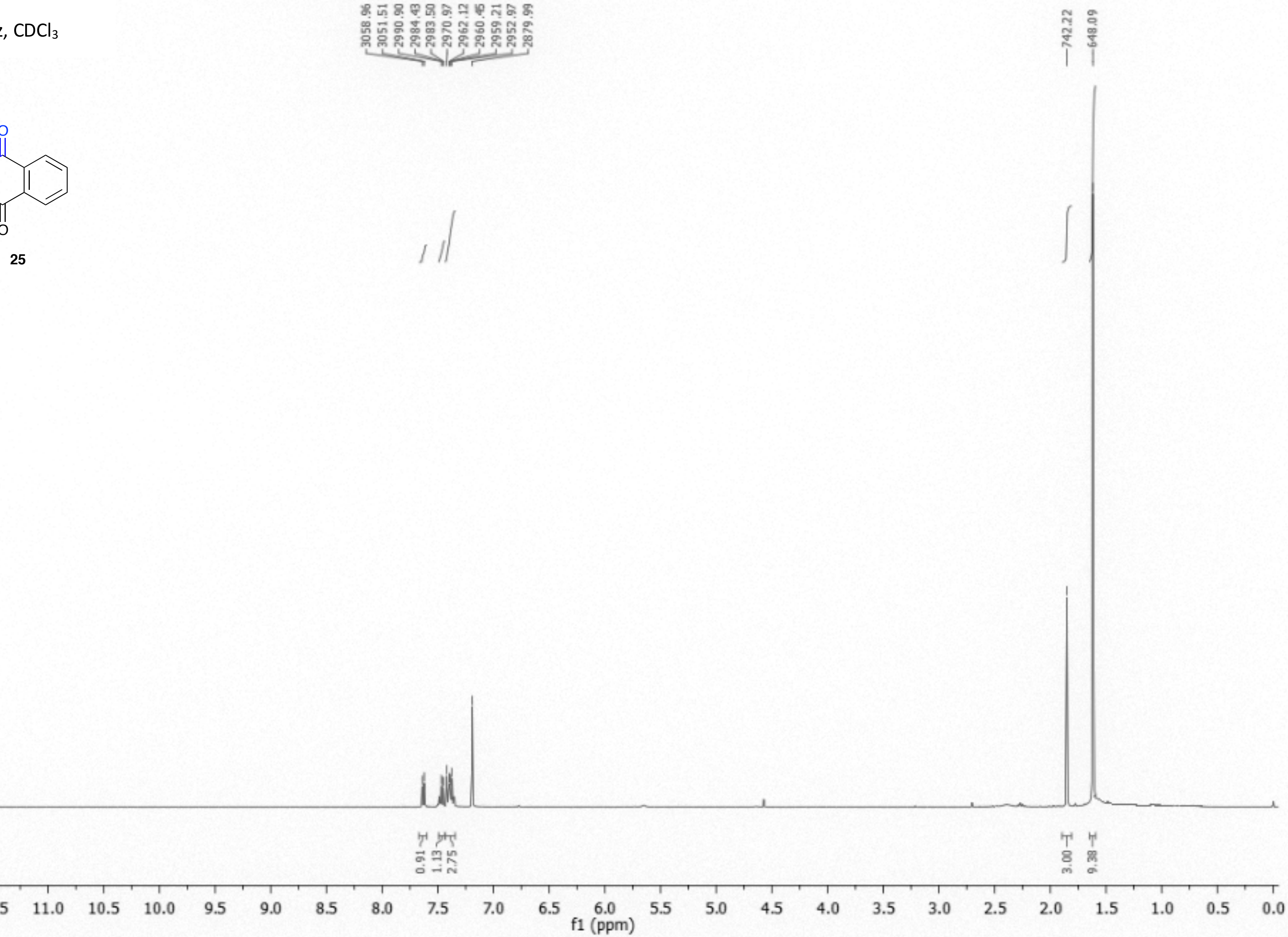
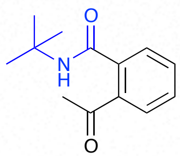


^{13}C NMR
100 MHz, $CDCl_3$



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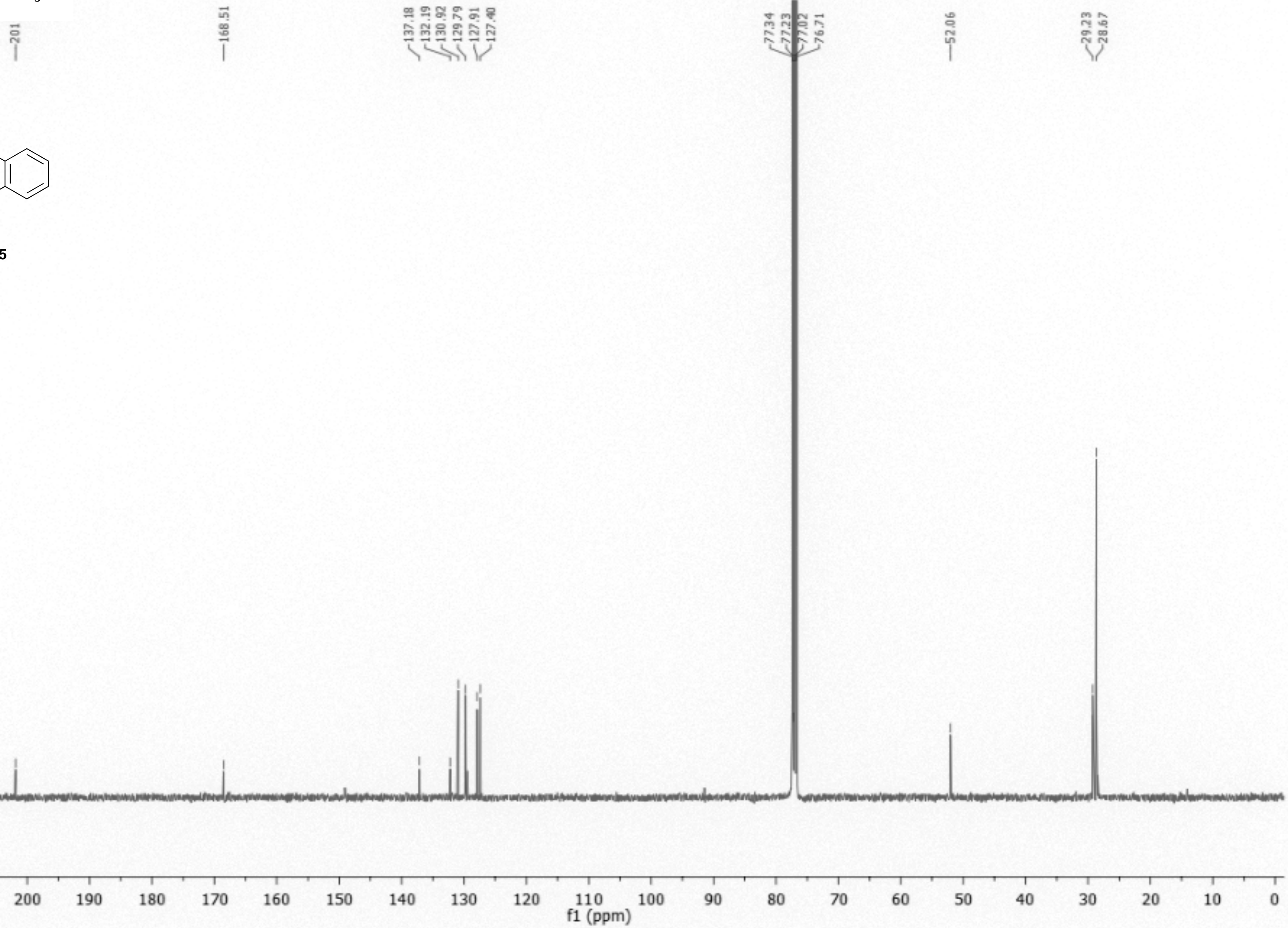
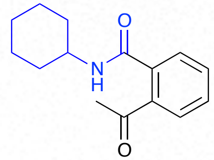


^{1}H NMR
400 MHz, CD_3OD



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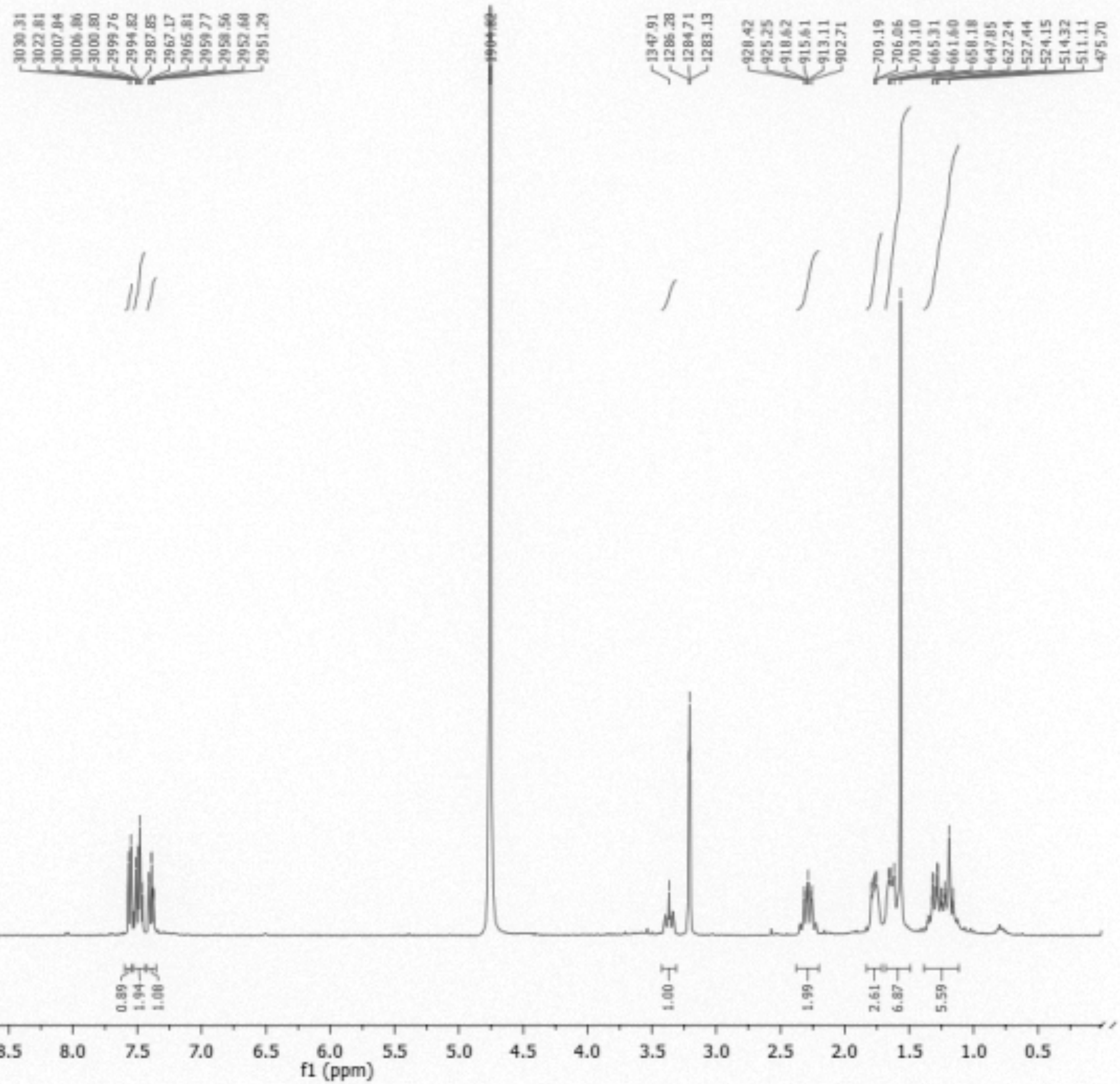
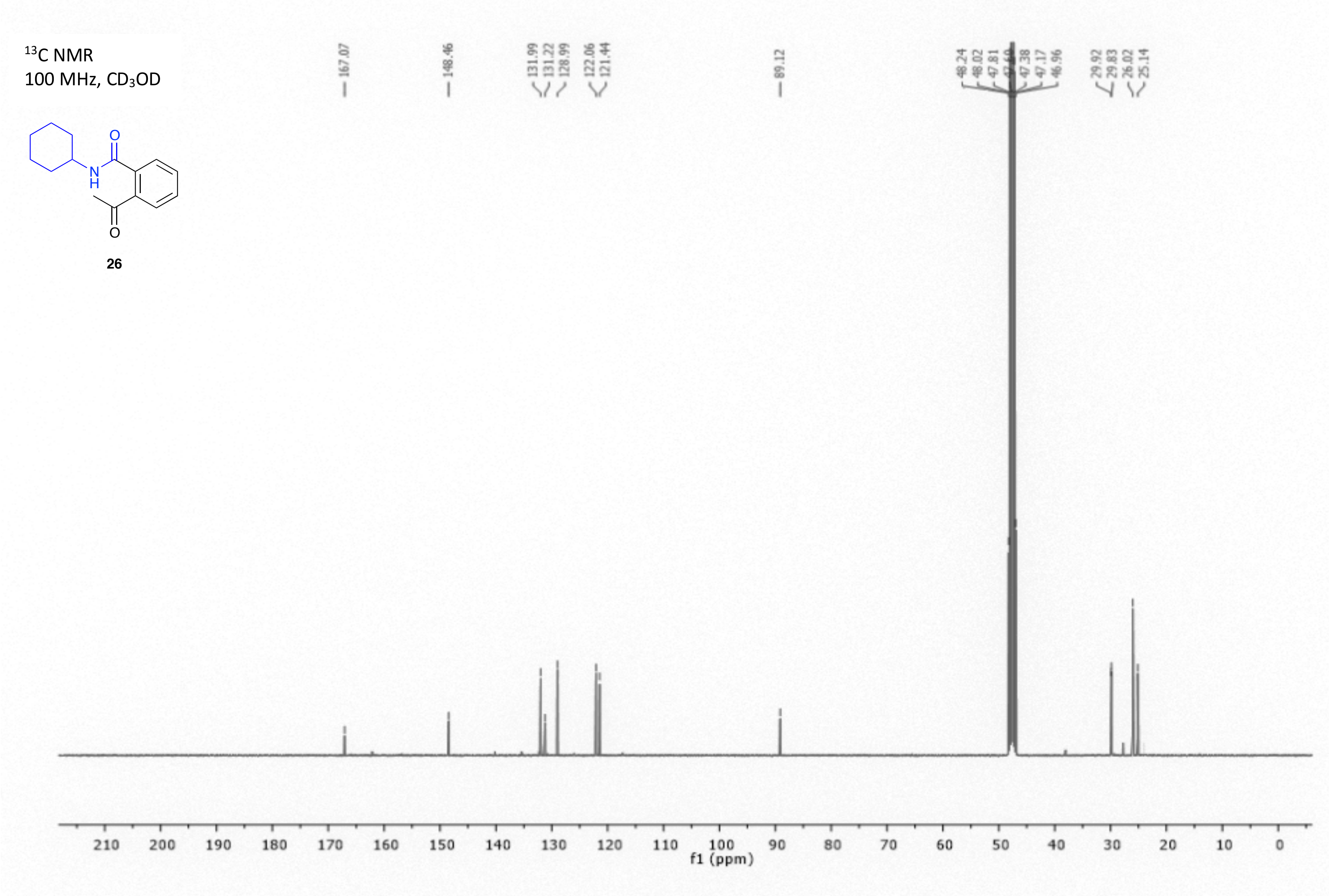
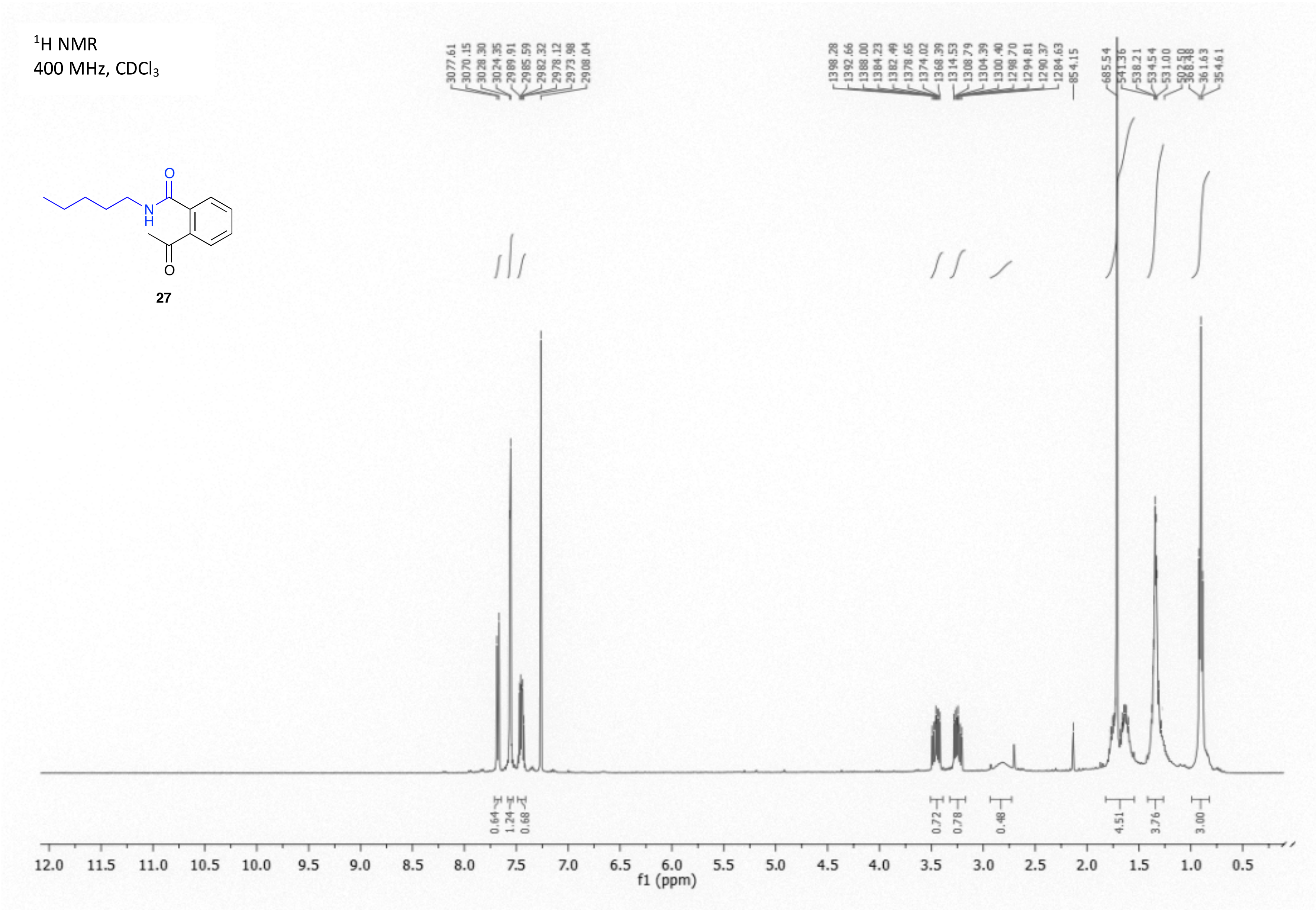




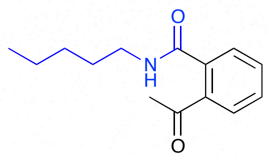
^{13}C NMR
100 MHz, CD$_3$OD
167.07
148.46
131.99
131.22
128.99
122.06
121.44
89.12
48.24
48.02
47.81
47.38
47.17
46.96
29.92
29.83
26.02
25.14
f1 (ppm)

26

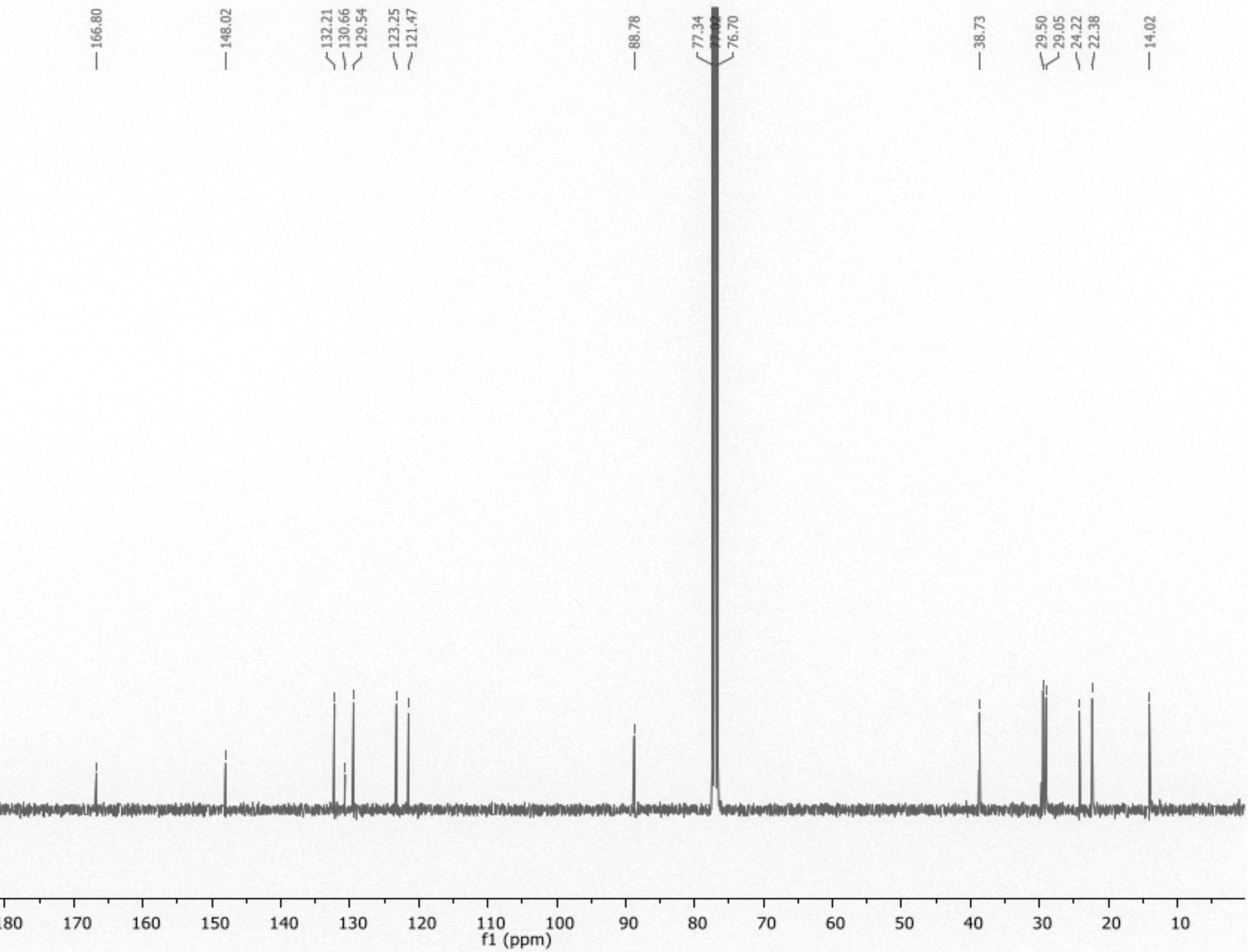


^1H NMR
400 MHz, $CDCl_3$
O
N
H
O
27
f1 (ppm)

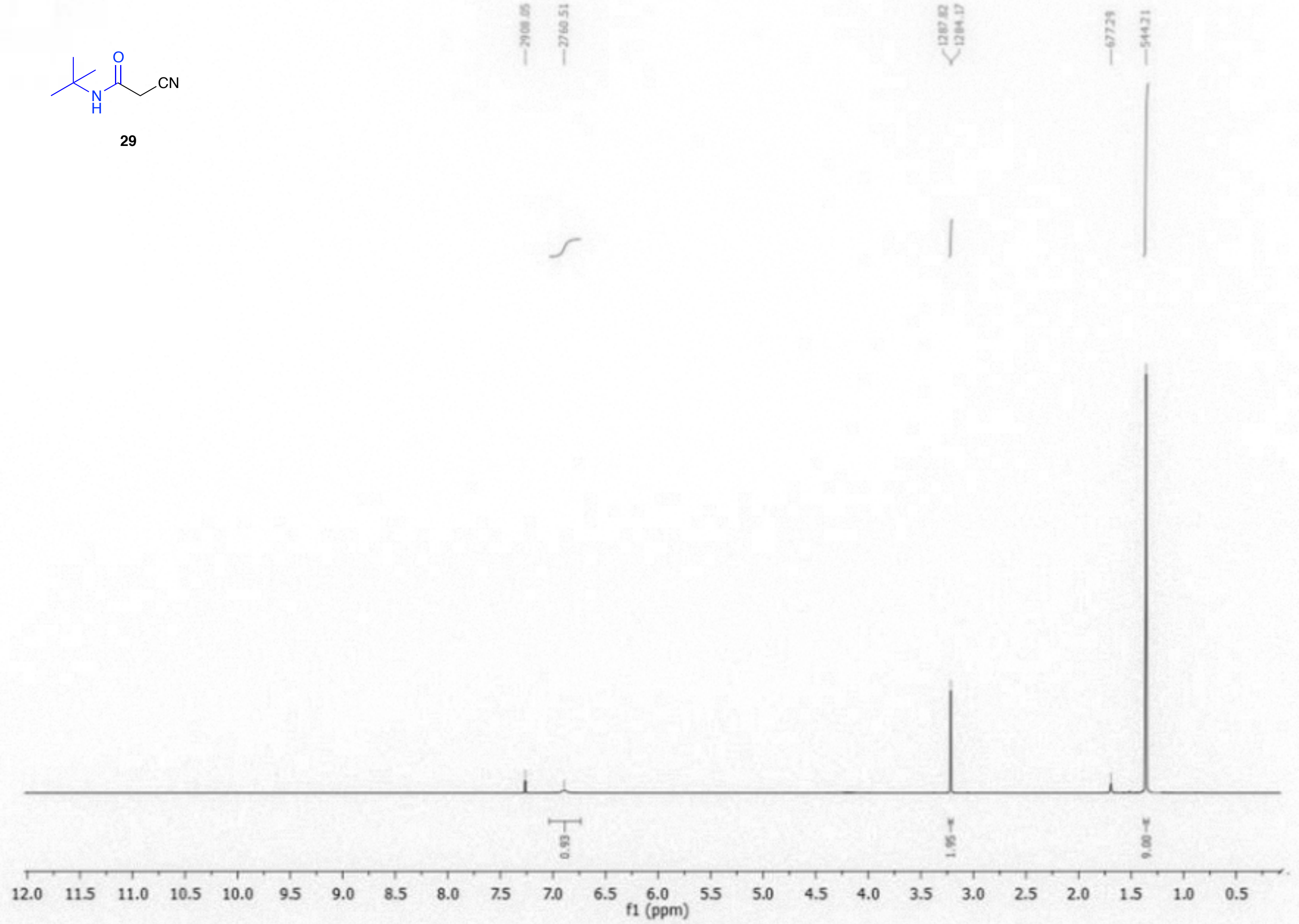
^{13}C NMR
100 MHz, $CDCl_3$



27

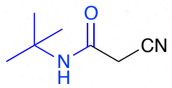


^{1}H NMR
400 MHz, $CDCl_3$

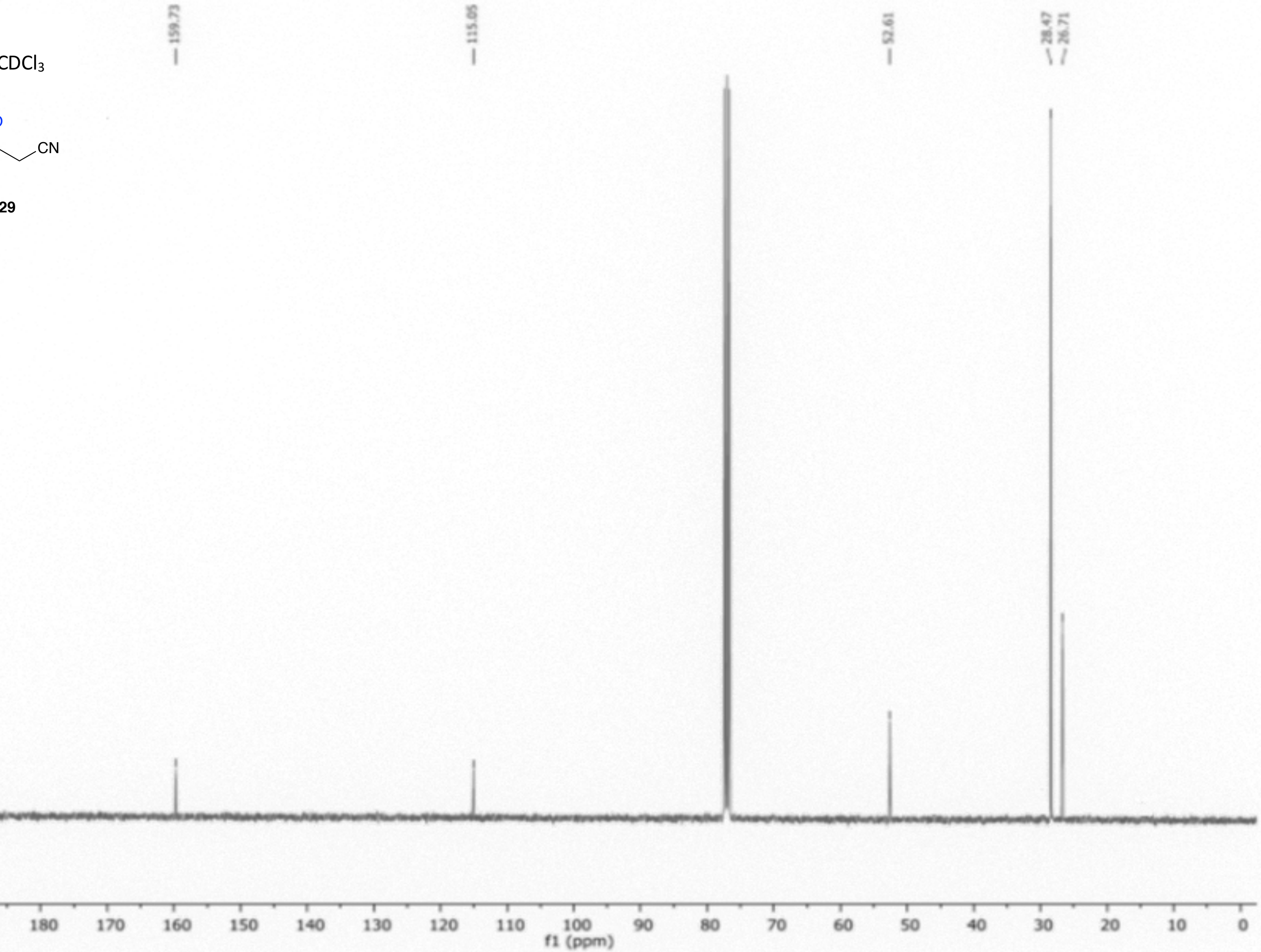


29

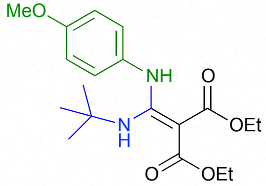
^{13}C NMR
100 MHz, $CDCl_3$



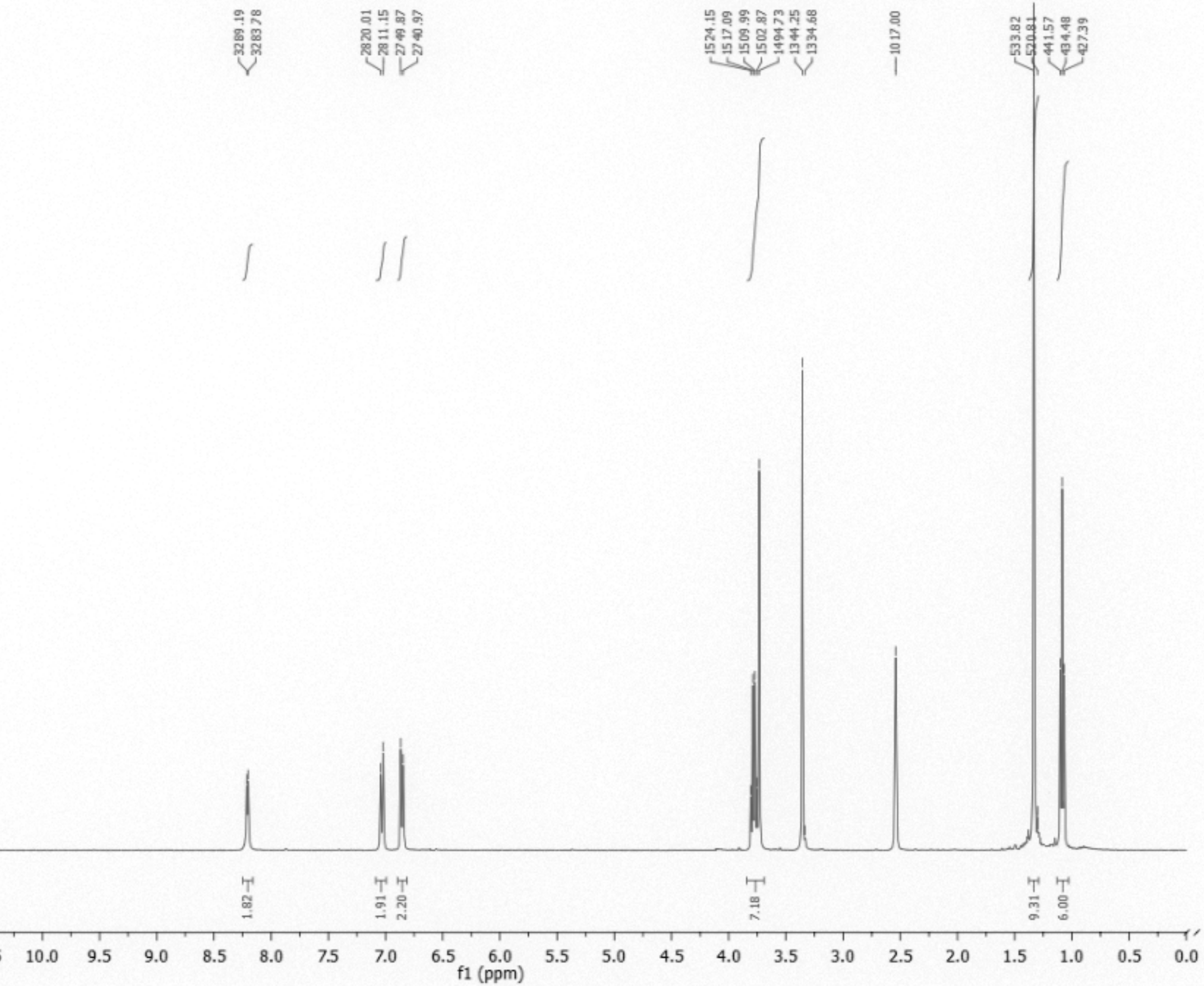
29



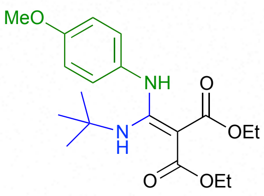
^{1}H NMR
400 MHz, DMSO-d_6



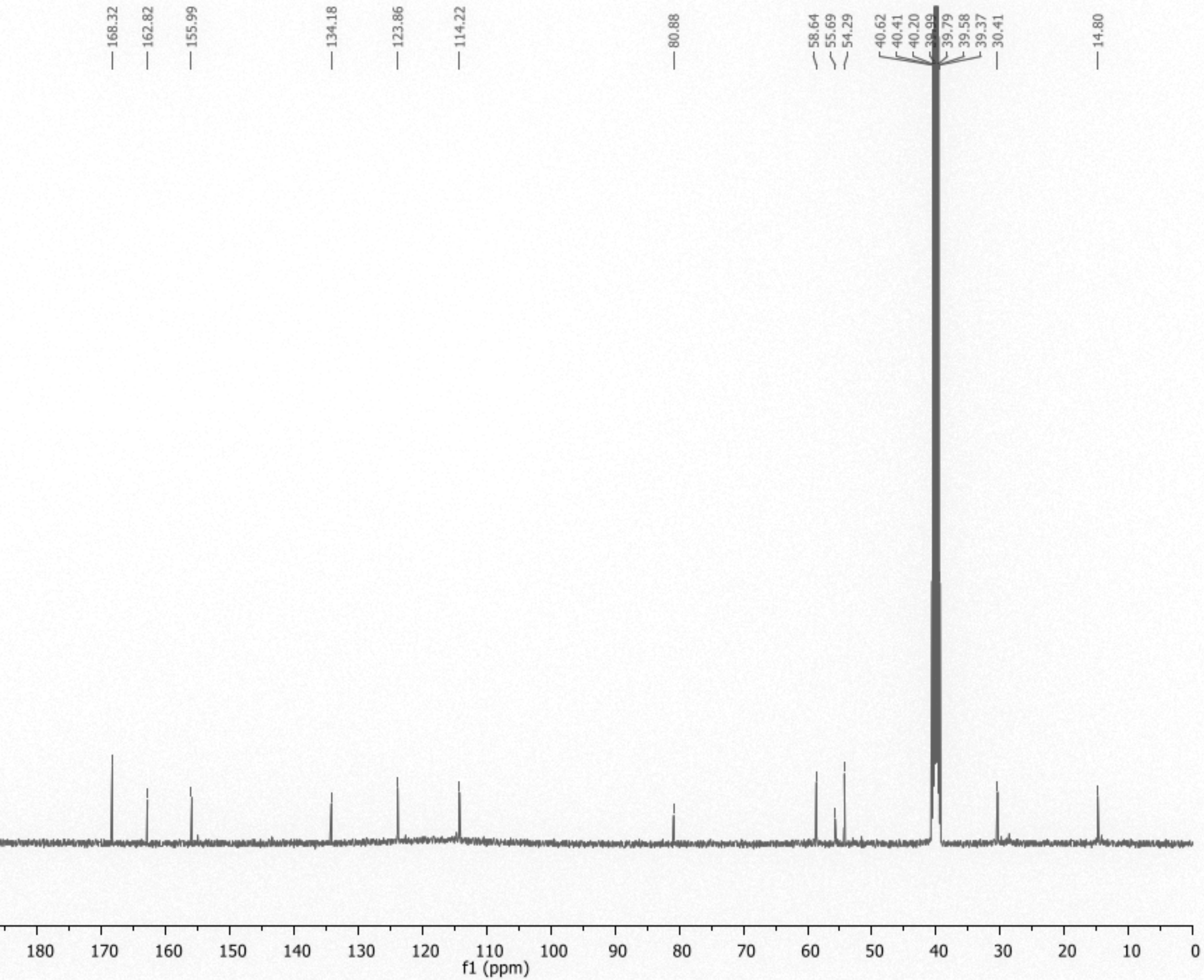
30



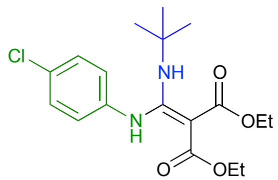
^{13}C NMR
100 MHz, DMSO-d_6



30



^{1}H NMR
400 MHz, DMSO-d_6



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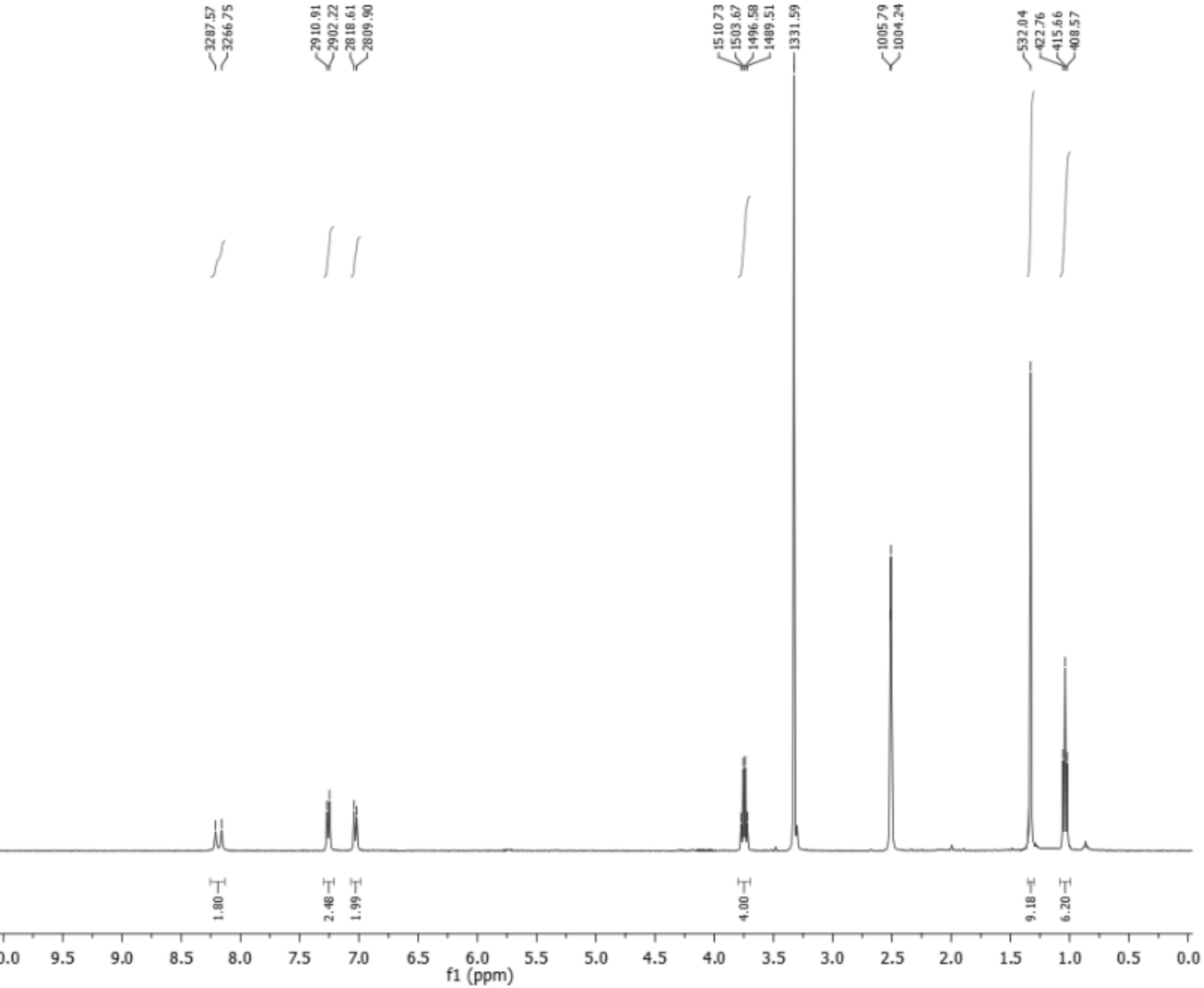
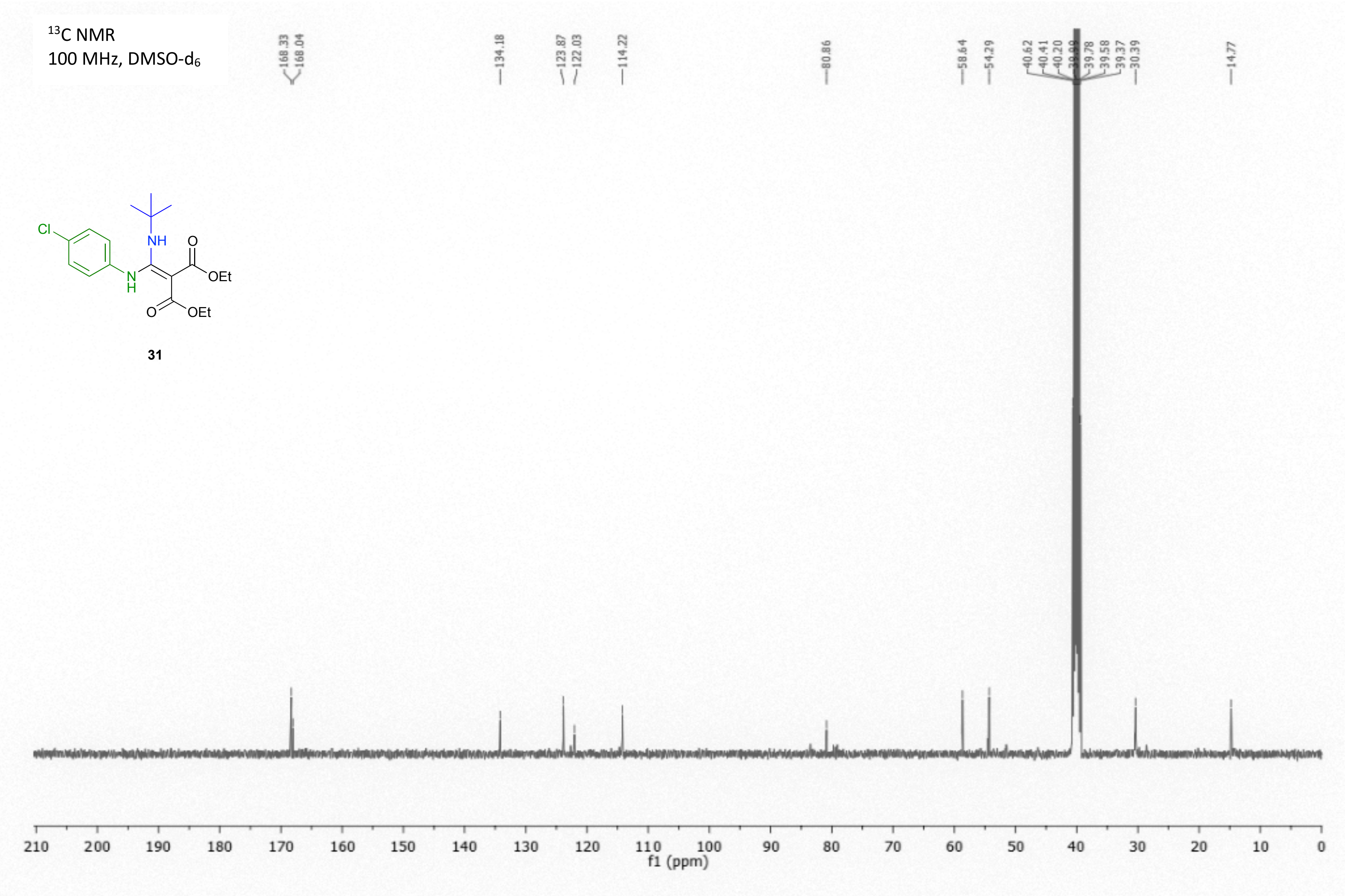
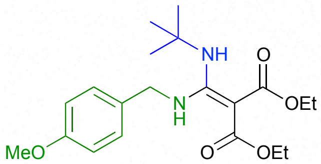


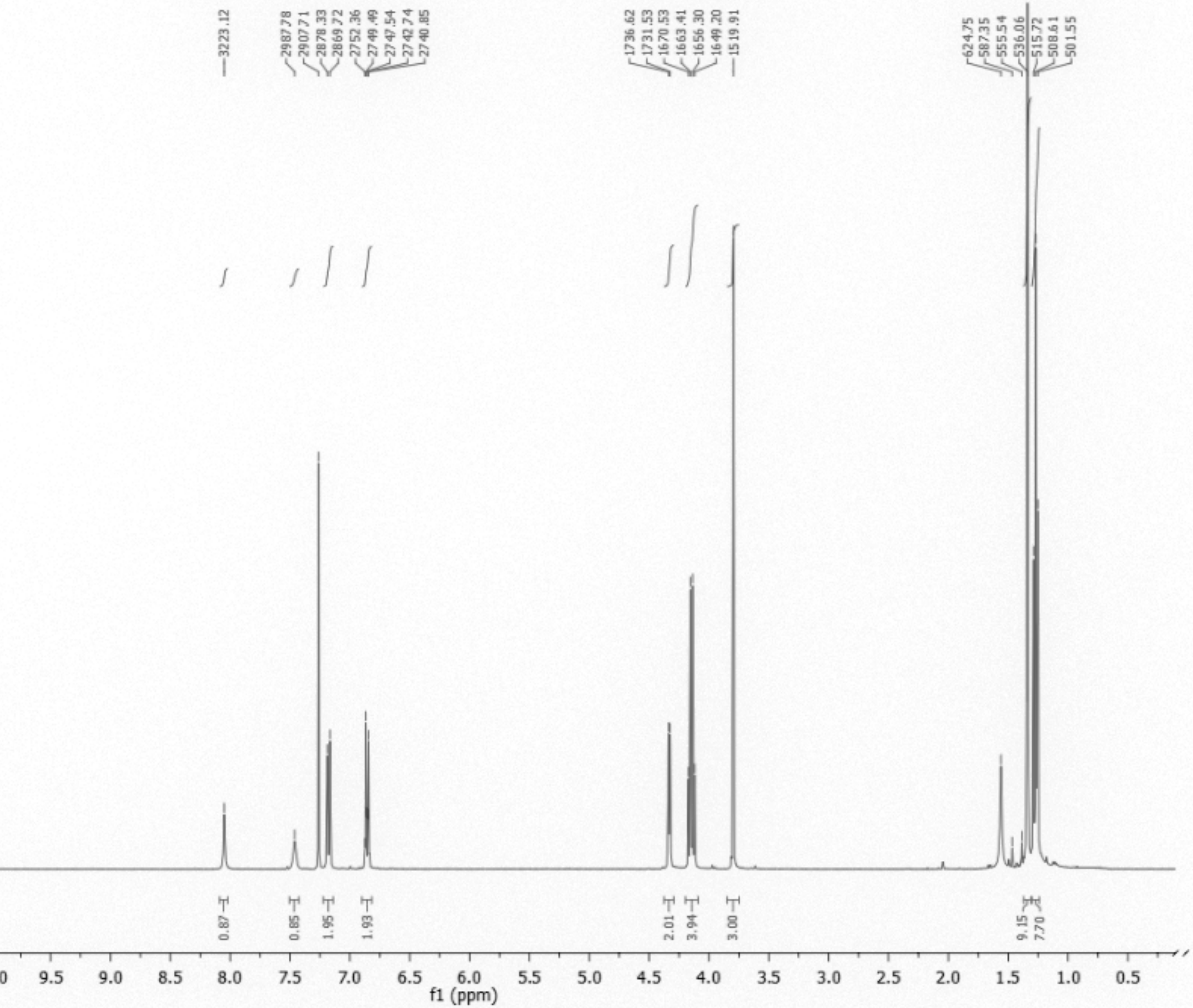


^{13}C NMR
100 MHz, DMSO-d_6
168.33
168.04
134.18
123.87
122.03
114.22
80.86
58.64
54.29
40.62
40.41
40.20
39.99
39.78
39.58
39.37
30.39
14.77
Cl
NH
N
H
O
OEt
O
OEt
31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

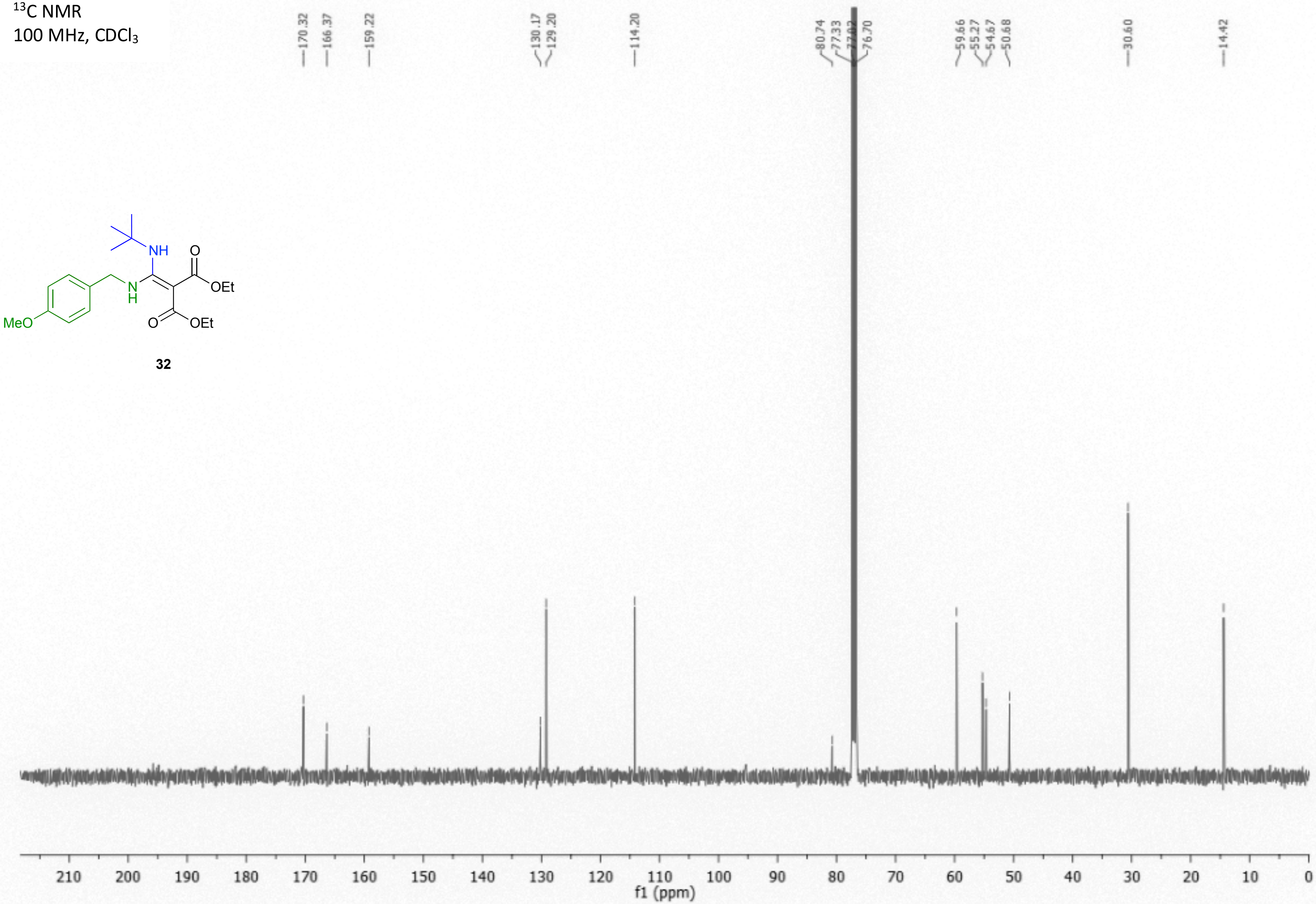
^{1}H NMR
400 MHz, $CDCl_3$



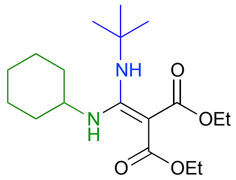
32



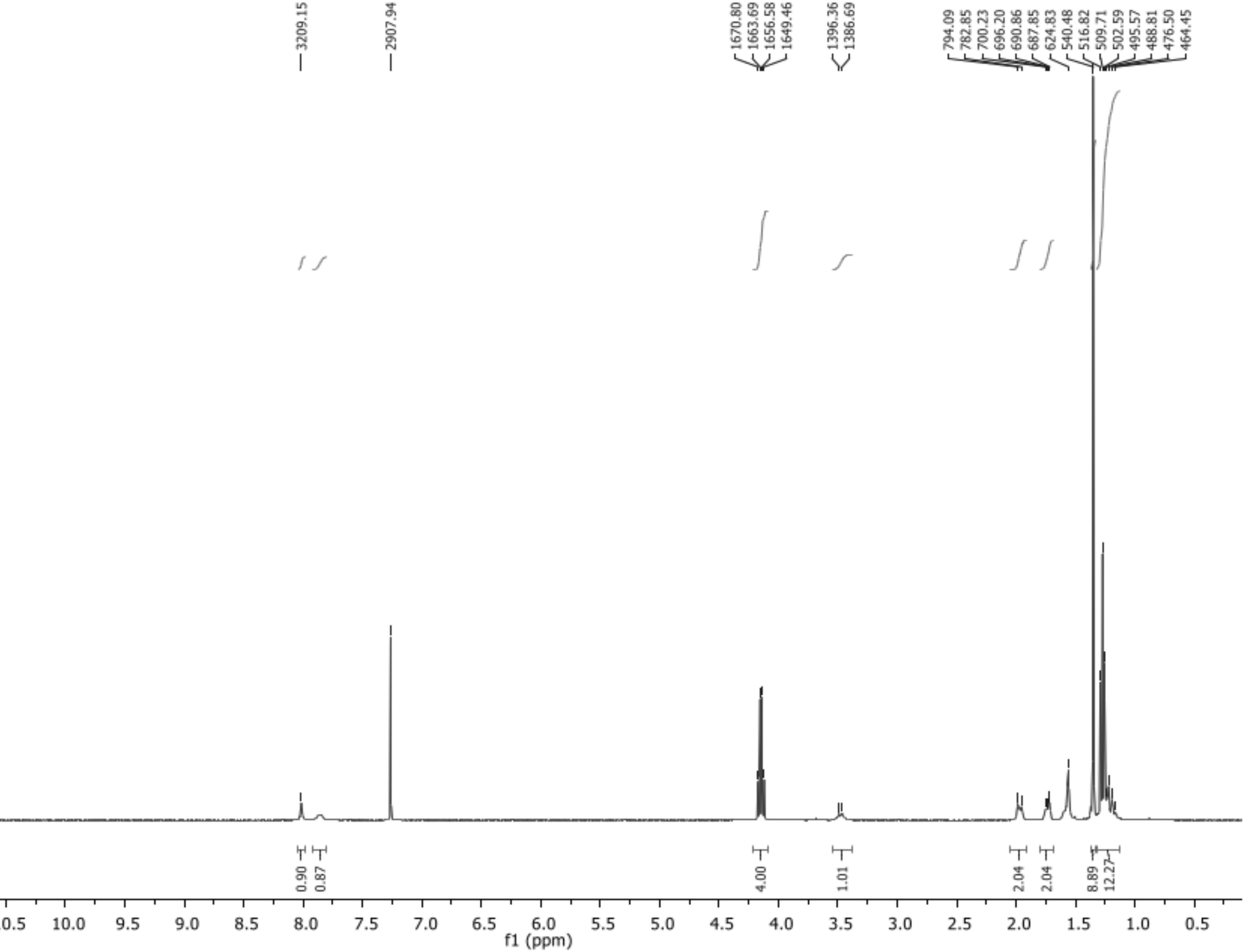
^{13}C NMR
100 MHz, $CDCl_3$



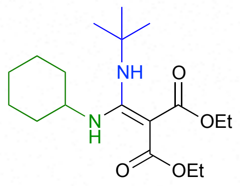
^{1}H NMR
400 MHz, $CDCl_3$



33



^{13}C NMR
100 MHz, $CDCl_3$



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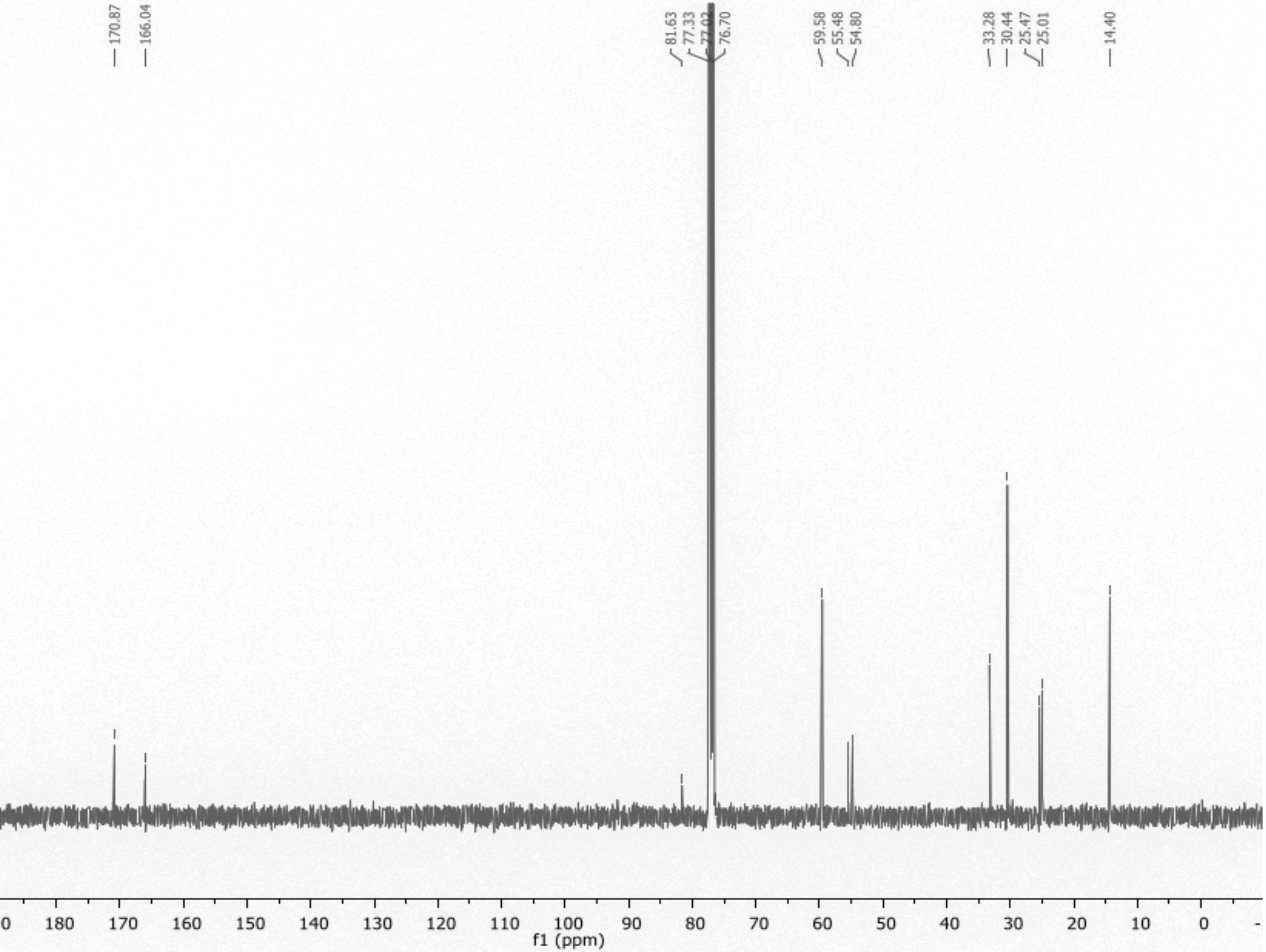
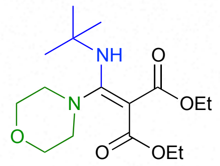
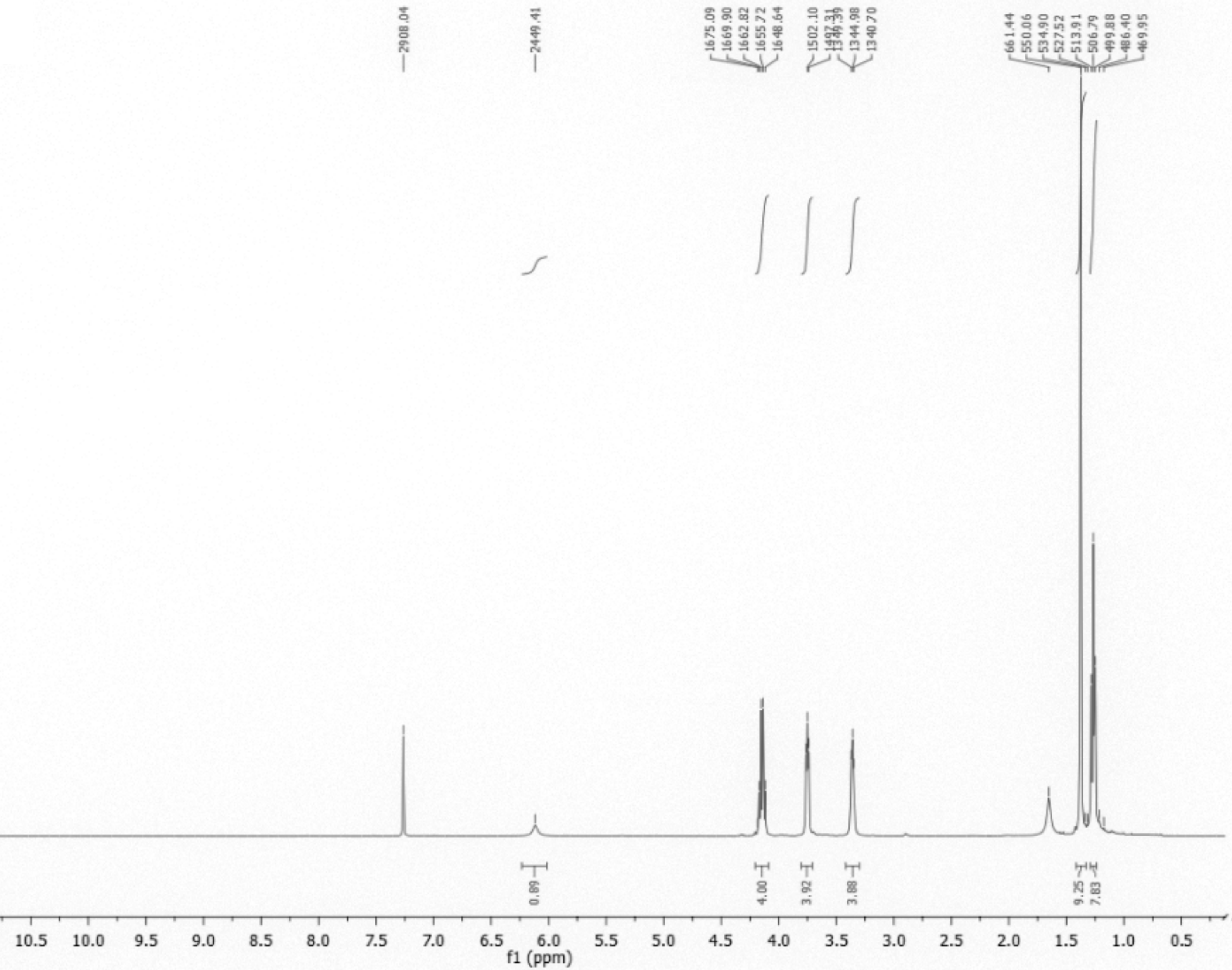
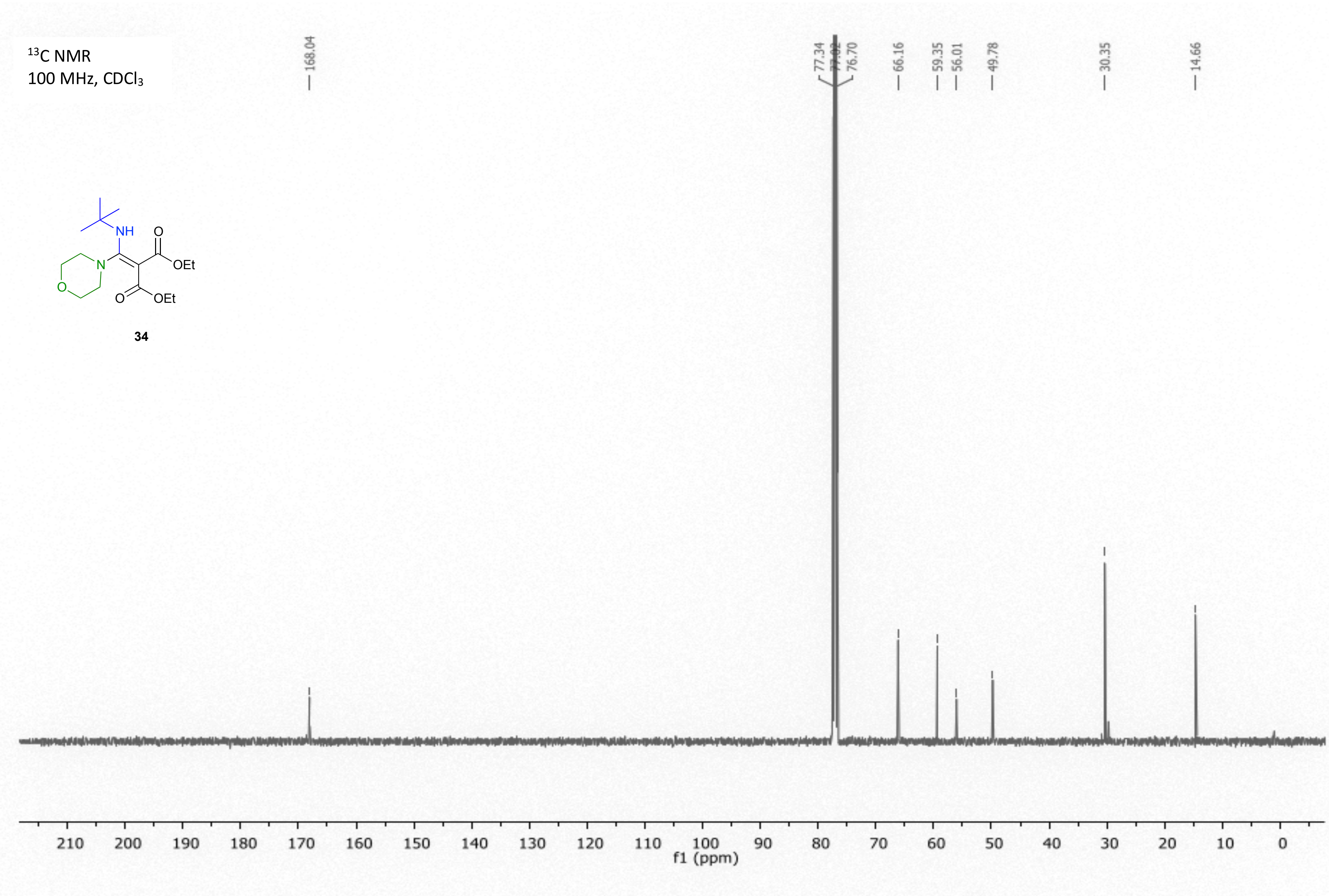


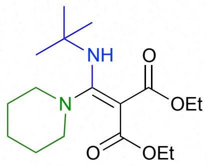


34




^{13}C NMR
100 MHz, $CDCl_3$
NH
O
OEt
N
O
O
OEt
34
168.04
77.34
77.02
76.70
66.16
59.35
56.01
49.78
30.35
14.66
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

[1]H NMR
400 MHz, $CDCl_3$



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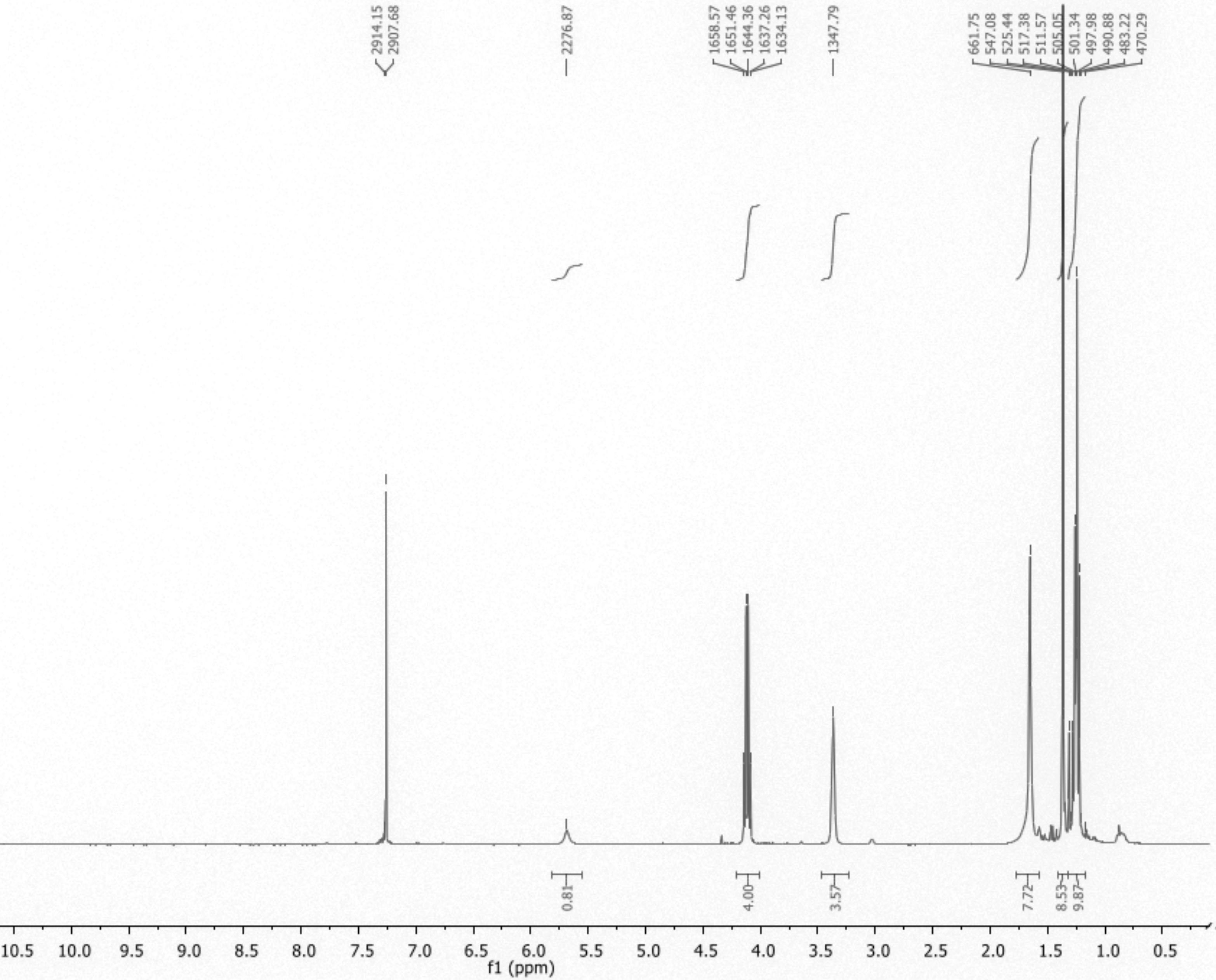
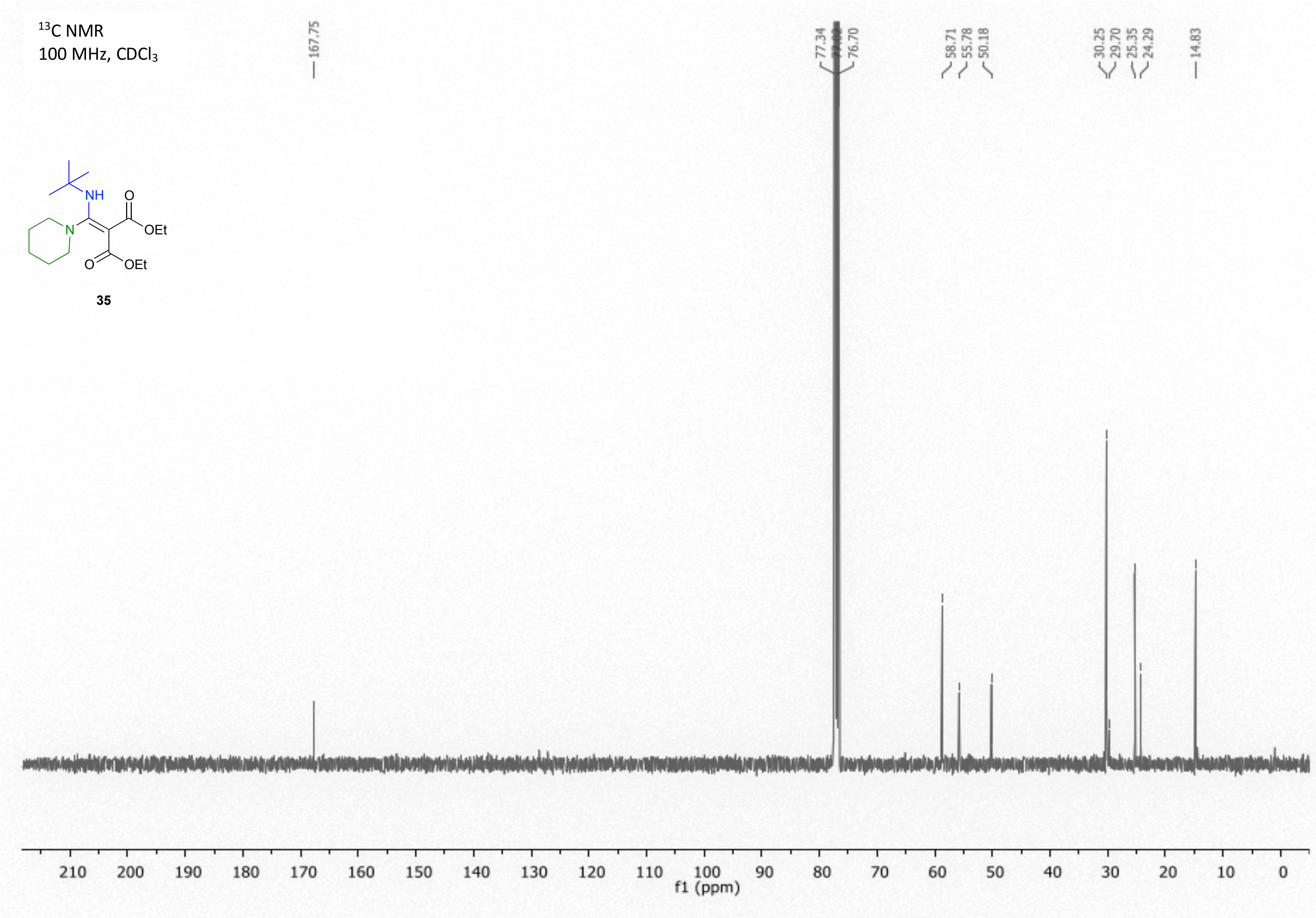
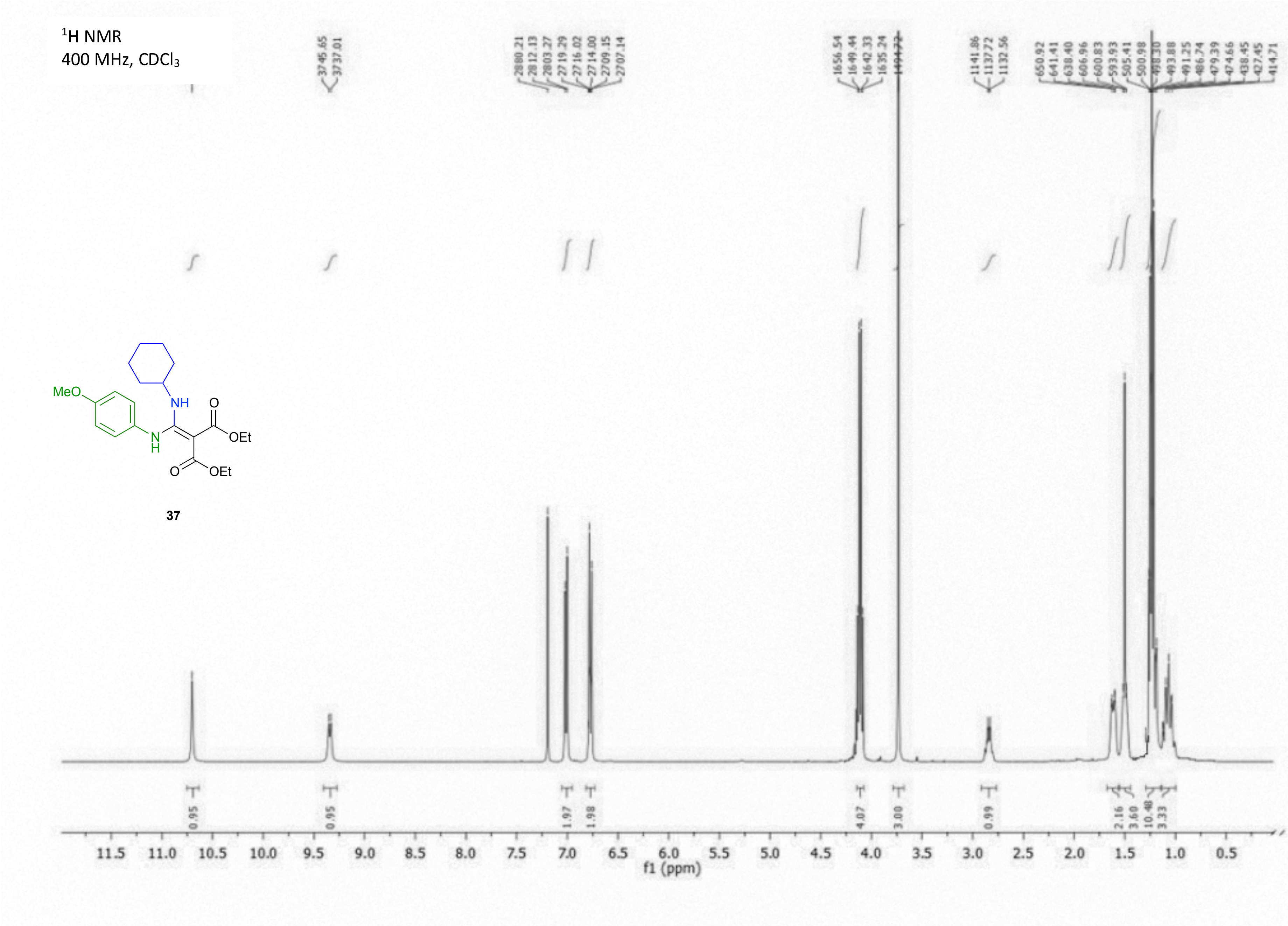
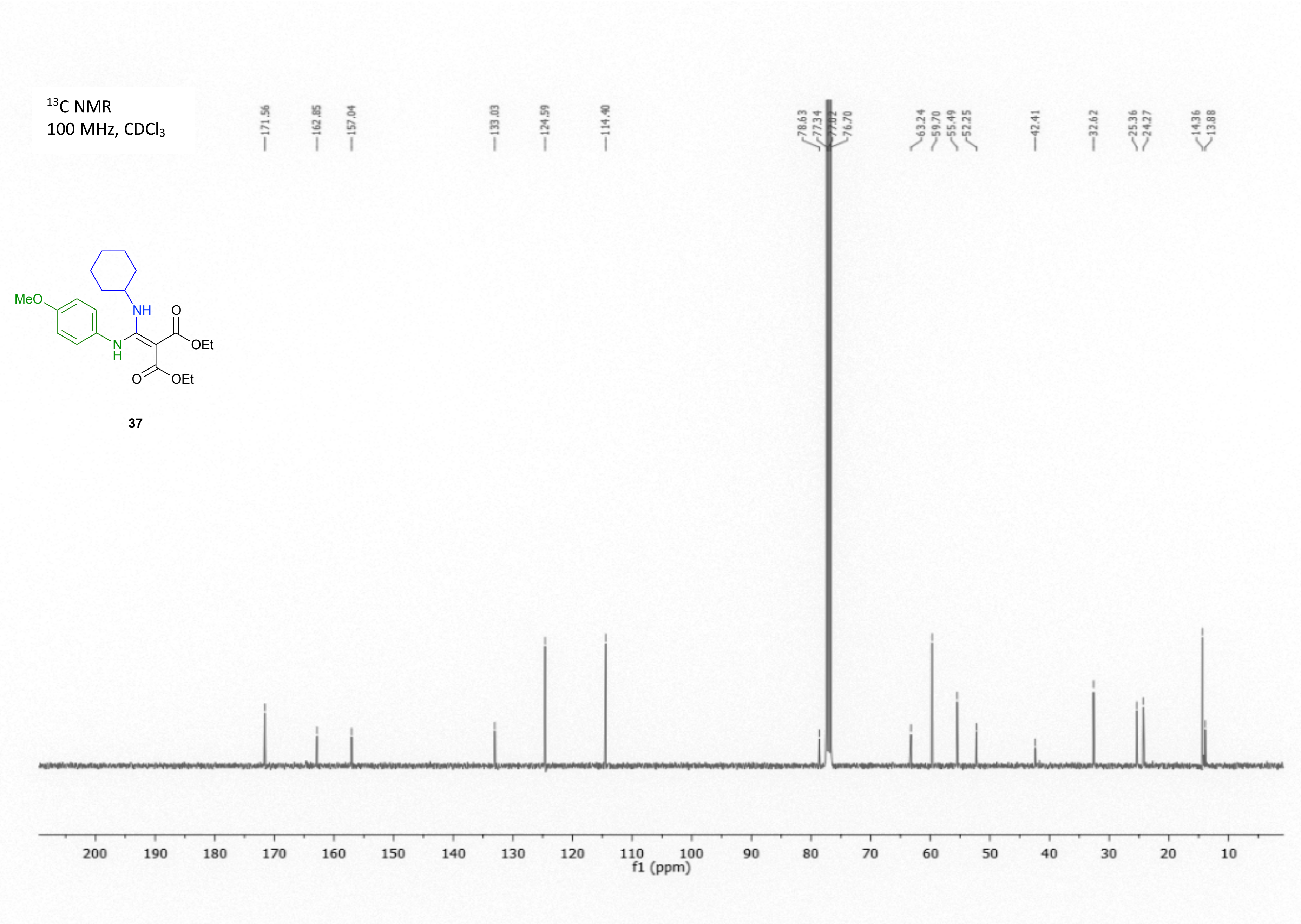
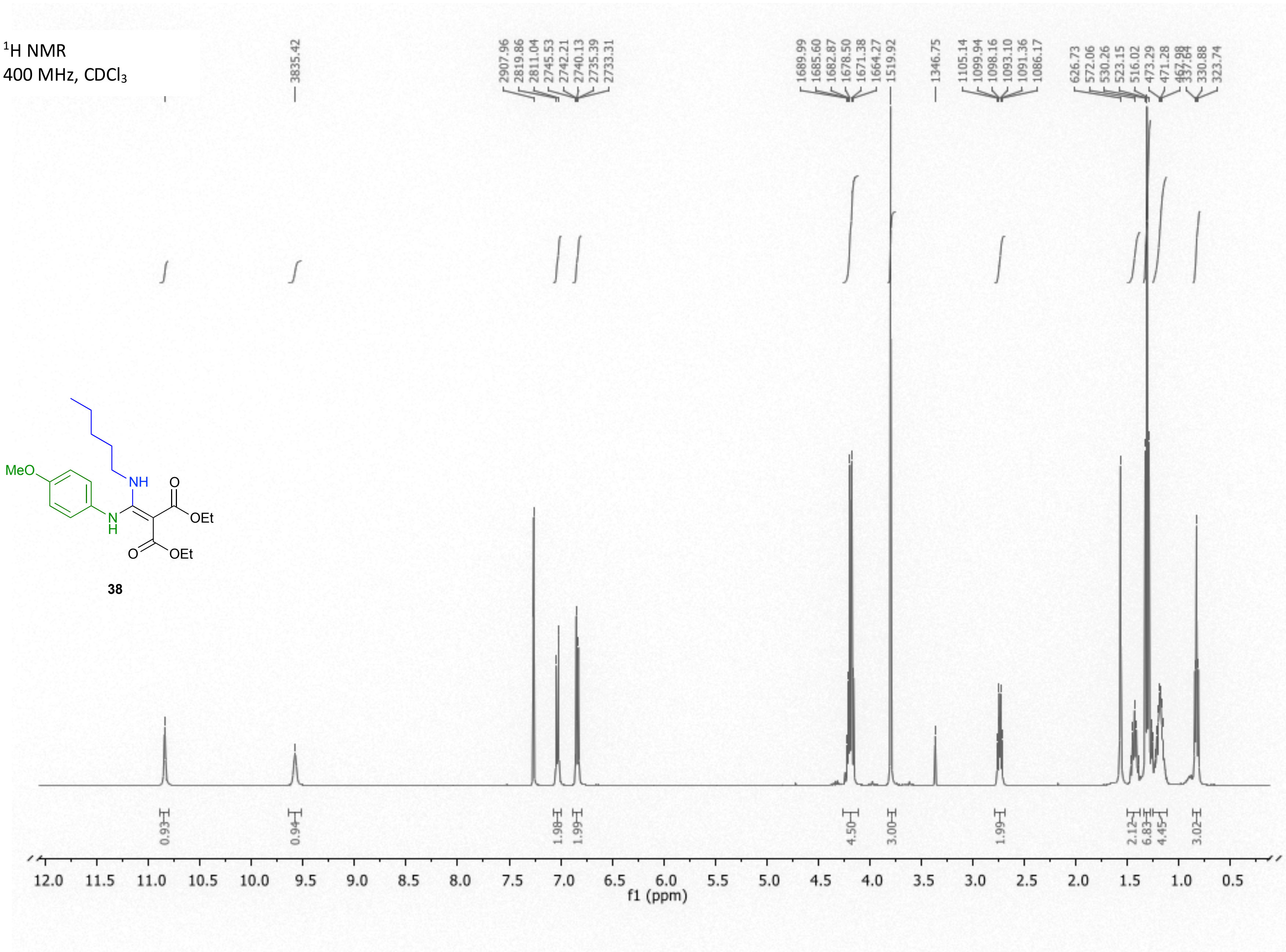



^{13}C NMR
100 MHz, $CDCl_3$
NH
O
N
OEt
O
OEt
35
167.75
77.34
77.02
76.70
58.71
55.78
50.18
30.25
29.70
25.35
24.29
14.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

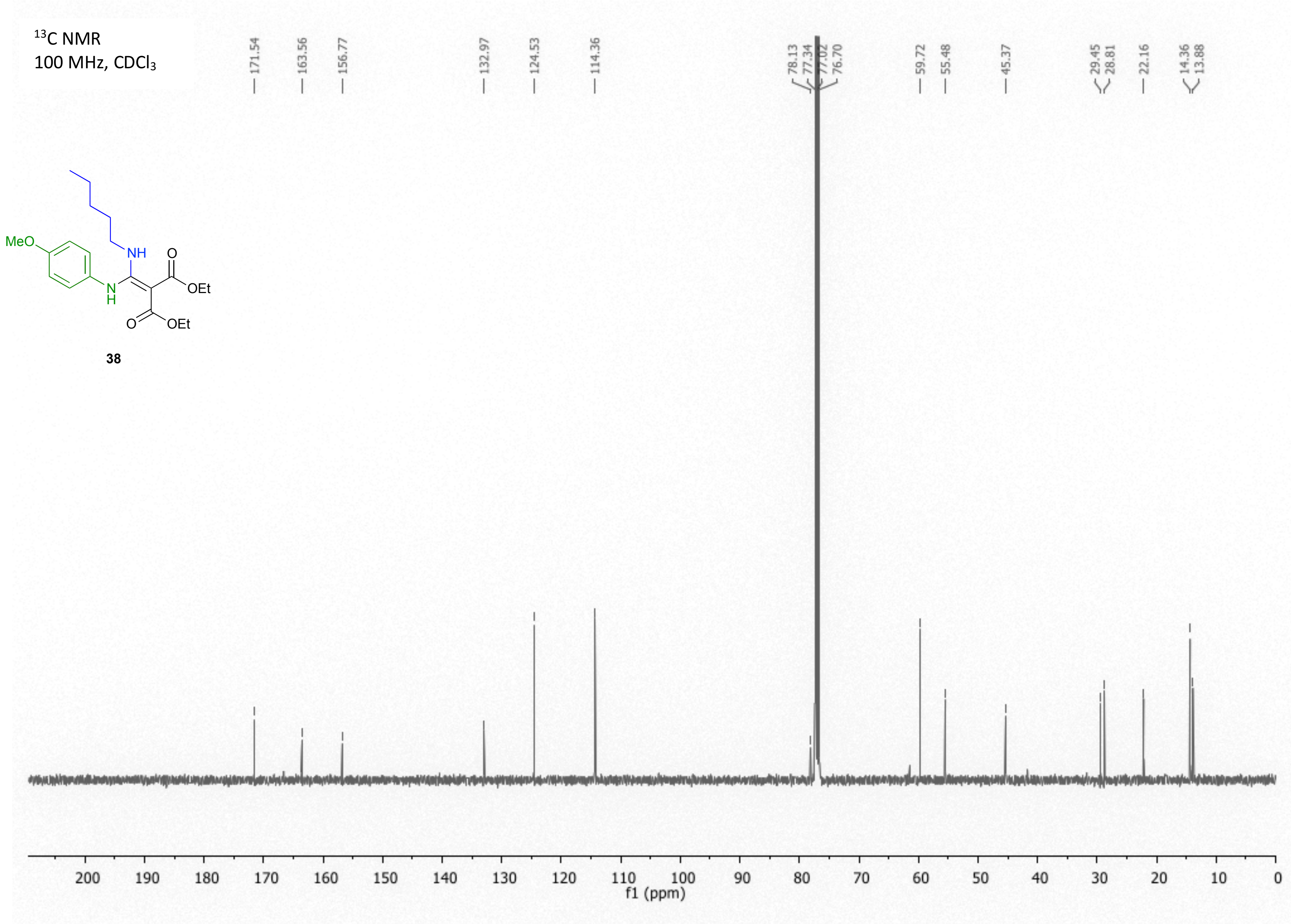

1H NMR
400 MHz, CDCl3
MeO
NH
H
O
OEt
37
f1 (ppm)



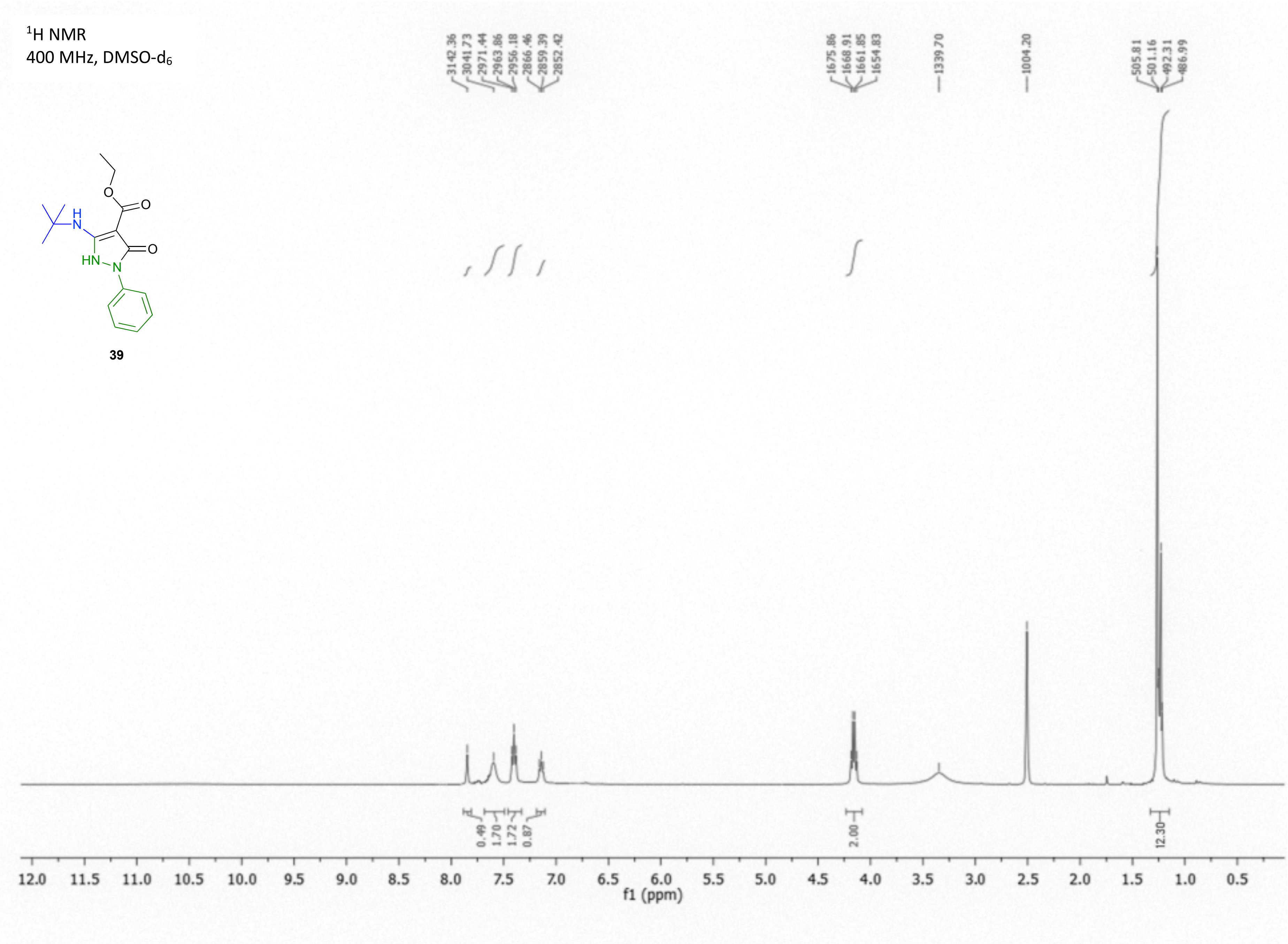
^{13}C NMR
100 MHz, $CDCl_3$
MeO
NH
N
H
O
OEt
O
OEt
37
171.56
162.85
157.04
133.03
124.59
114.40
78.63
77.34
77.02
76.70
63.24
59.70
55.49
52.25
42.41
32.62
25.36
24.27
14.36
13.88
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



[1]H NMR
400 MHz, CDCl3
MeO
NH
N
H
O
OEt
O
OEt
38
f1 (ppm)

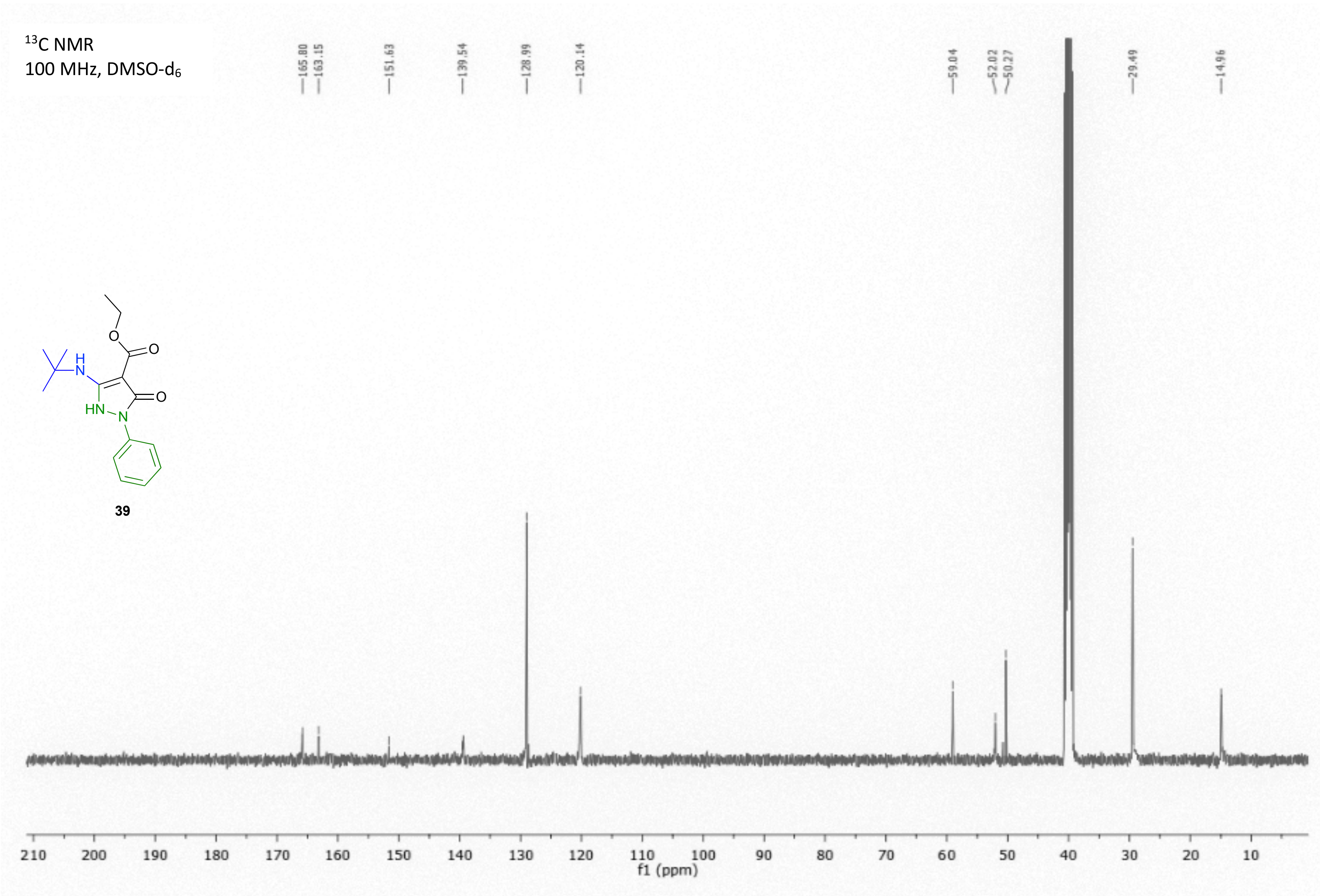


^{13}C NMR
100 MHz, CDCl$_3$
171.54
163.56
156.77
132.97
124.53
114.36
78.13
77.34
77.02
76.70
59.72
55.48
45.37
29.45
28.81
22.16
14.36
13.88
MeO
NH
O
N
H
OEt
O
OEt
38
f1 (ppm)



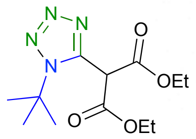
1H NMR
400 MHz, DMSO-d6
39
3142.36
3041.73
2971.44
2963.86
2956.18
2866.46
2859.39
2852.42
1675.86
1668.91
1661.85
1654.83
1339.70
1004.20
505.81
501.16
492.31
486.99
0.49
1.70
1.72
0.87
2.00
12.30
f1 (ppm)

^{13}C NMR
100 MHz, DMSO-d_6

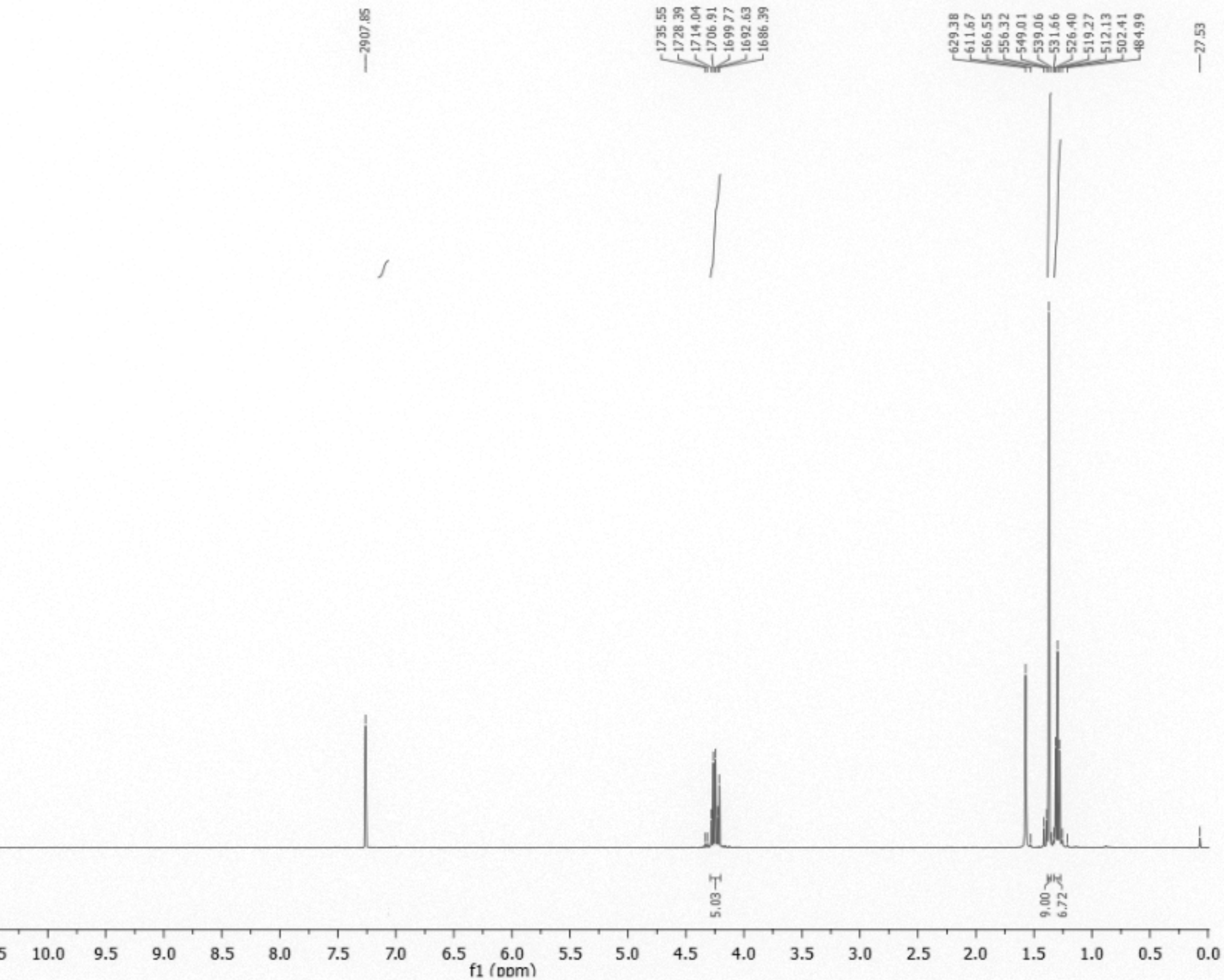


39

[1]H NMR
400 MHz, $CDCl_3$



40



^{13}C NMR
100 MHz, $CDCl_3$