Supporting Information

Entry to 4,5-Fused Coumarin frameworks via Radical-Promoted Alkylative Intramolecular C5-Annulation

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Table of Contents

1. Structures of starting materials used in this study…… S2

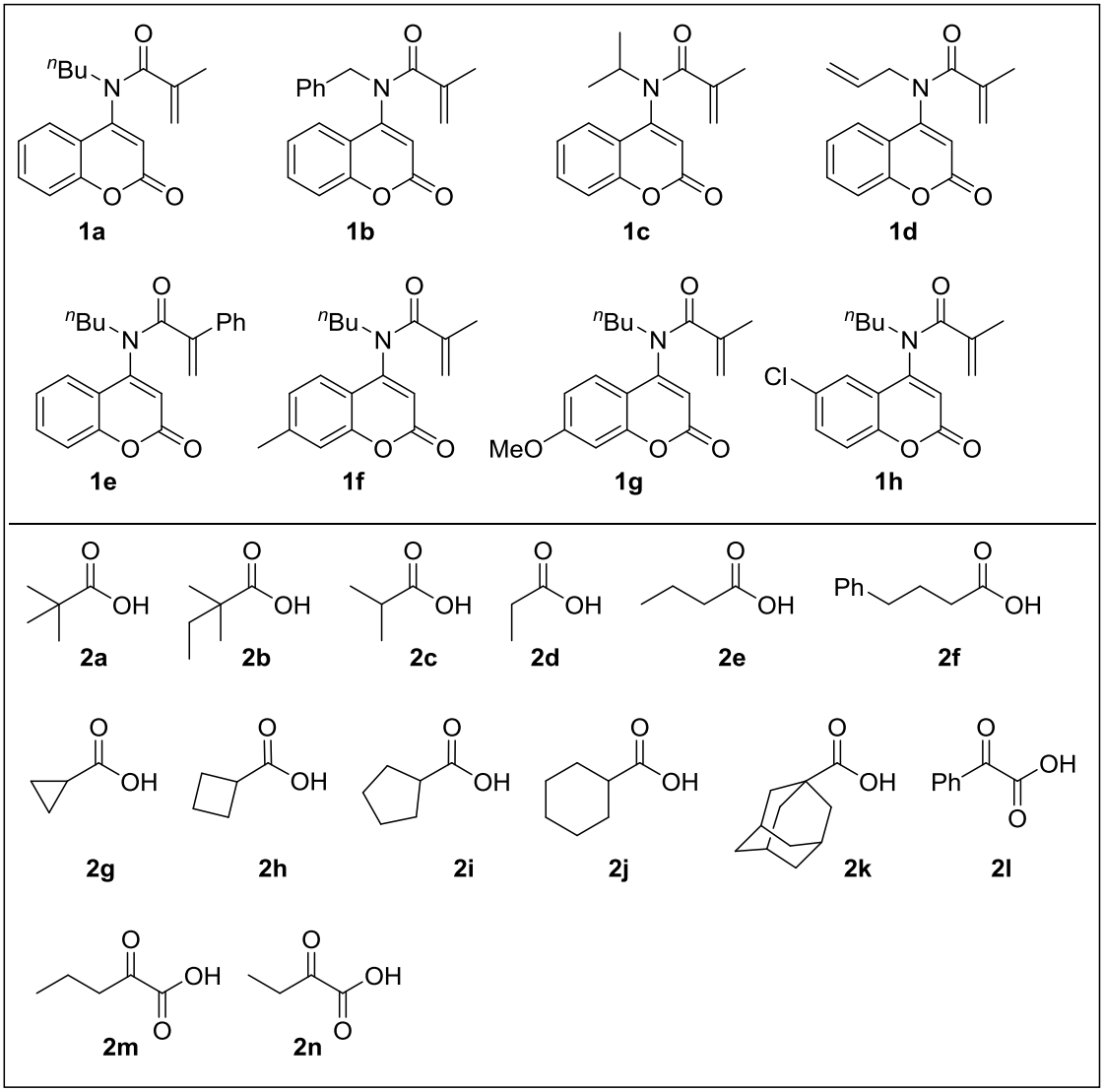
2. Preparation of *N*-acryloyl amino coumarin ……. S2-S6

3. Control Experiment ……. S6-S7

4. X-ray Data ……... S7-S8

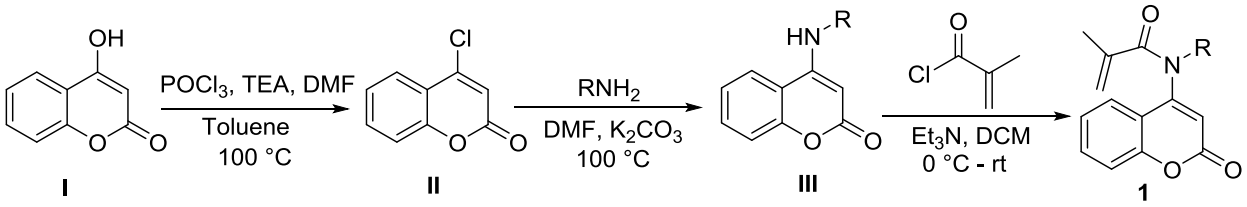
5. ^{1}H NMR and ^{13}C NMR spectra …… S9-S71

Figure S1: Structures of starting materials used in this study



EXPERIMENTAL SECTION

2. Preparation of *N*-acryloyl amino coumarin:

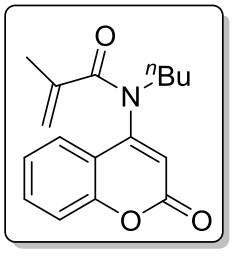


4-Hydroxy-2H-chromen-2-one (**I**) (5 g, 1 equiv) and a catalytic amount of DMF were dissolved in 25 mL of toluene, triethylamine (6.5 mL, 1.5 equiv) and phosphorus oxychloride (5.8 mL, 2

equiv) were added. The mixture was heated to 100 °C for 12 h. The reaction was quenched with water (100 mL) and extracted with toluene (2 x 50 mL). Separated organic layer and concentrated. The crude product was purified by flash column chromatography on silica gel to give 4-Chloro-2H-chromen-2-one (**II**) as cream solid.

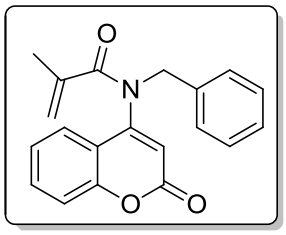
4-Chloro-2H-chromen-2-one (**II**) (2 g, 1 equiv) is dissolved in DMF in 10 mL, potassium carbonate (2.15 g, 1.5 equiv) and n-butylamine (2 mL, 2 equiv) was added. The mixture was heated to 100 °C for 12 h. The reaction was quenched with water (40 mL) and extracted with ethyl acetate (2 x 30 mL). Separated organic layer and concentrated. The crude product was purified by flash column chromatography on silica gel to give 4-Amino coumarin (**III**) as light yellow solid.

To a solution of 4-amino coumarin **III** (1.9 g, 1.0 equiv) in DCM (30 mL), was added triethylamine (4.0 equiv) and the mixture was stirred at 0 °C, and methacryloyl chloride (2.0 equiv) was slowly added under nitrogen atmosphere. The resulting solution was stirred at rt. After completion, the reaction was quenched with 30 mL water and separated organic layer was washed with 30 mL of $NaHCO_3$ saturated solution), brine, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give *N*-acryloyl amino coumarin (**1**).

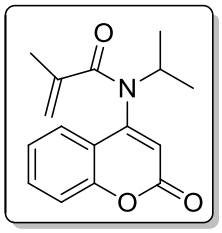


***N*-Butyl-*N*-(2-oxo-2*H*-chromen-4-yl)methacrylamide (1a):** On 7.0 mmol scale, pale yellow viscous oil; yield (**1a**): 90% (1.8 g), **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.62 – 7.59 (m, 1H), 7.48 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.41 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.36 – 7.32 (m, 1H), 6.23 (s, 1H), 5.10 – 5.07 (m, 2H), 3.76 (br s, 2H), 1.88 (s, 3H), 1.63 – 1.58 (m, 2H), 1.33 (dd, *J* = 15.1, 7.5 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 171.3, 160.8, 154.9, 154.1, 140.1, 132.8, 124.7, 124.2,

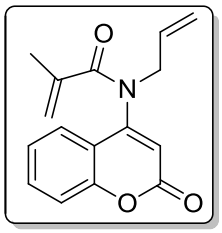
119.3, 117.8, 117.7, 114.3, 49.1, 29.9, 20.1, 20.1, 13.7; **HRMS**: calcd. For $C_{17}H_{20}NO_3$ $[M + H]^+$ 286.1443, found 286.1439.



***N*-Benzyl-*N*-(2-oxo-2H-chromen-4-yl)methacrylamide (1b)**: On 1.0 mmol scale, white solid (mp: 118–120 °C); yield (**1b**): 82% (261.6 mg), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 – 7.56 (m, 1H), 7.43 (dd, J = 8.0, 1.5 Hz, 1H), 7.37 (dd, J = 8.3, 0.8 Hz, 1H), 7.32 – 7.23 (m, 6H), 5.95 (s, 1H), 5.16 – 5.09 (m, 4H), 1.89 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 171.3, 160.6, 154.3, 153.9, 139.9, 135.9, 132.8, 128.8, 128.7, 128.2, 124.7, 124.1, 119.8, 117.7, 117.6, 114.7, 52.2, 20.1; **HRMS**: calcd. For $C_{20}H_{17}NO_3Na$ $[M + Na]^+$ 342.1101, found 342.1092.

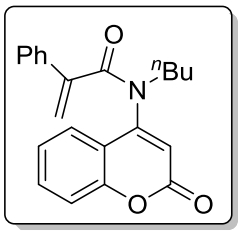


***N*-Isopropyl-*N*-(2-oxo-2H-chromen-4-yl)methacrylamide (1c):** On 1.0 mmol scale, white solid (mp: 88–90 °C); yield (**1c**): 82% (216.8 mg), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 – 7.57 (m, 1H), 7.48 (dd, J = 8.0, 1.5 Hz, 1H), 7.39 (dd, J = 8.3, 1.0 Hz, 1H), 7.34 – 7.30 (m, 1H), 6.27 (s, 1H), 5.07 (s, 1H), 5.04 (d, J = 0.9 Hz, 1H), 4.78 – 4.72 (m, 1H), 1.86 (s, 3H), 1.31 (d, J = 4.2 Hz, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 171.2, 160.7, 153.8, 153.3, 140.7, 132.8, 124.8, 124.5, 119.3, 119.2, 117.6, 115.6, 50.4, 20.8, 20.2; **HRMS**: calcd. For $C_{16}H_{18}NO_3$ $[M + H]^+$ 272.1287, found 272.1272.

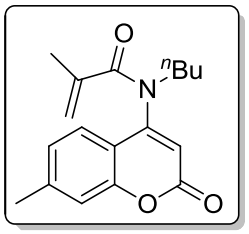


***N*-Allyl-*N*-(2-oxo-2H-chromen-4-yl)methacrylamide (1d)**: On 1.0 mmol scale, white solid (mp: 77–79 °C); yield (**1d**): 78% (209.8 mg), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 – 7.59 (m, 1H), 7.49 (dd, J = 8.0, 1.5 Hz, 1H), 7.40 (dd, J = 8.3, 0.8 Hz, 1H), 7.36 – 7.32 (m, 1H), 6.21 (s, 1H), 5.97 – 5.87 (m, 1H), 5.22 (dd, J = 10.2, 1.0 Hz, 1H), 5.21 – 5.12 (m, 3H), 4.37 (br s, 2H), 1.90 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 171.2, 160.7, 154.5, 154.0, 139.9, 132.8, 131.6, 124.7, 124.1, 119.9,

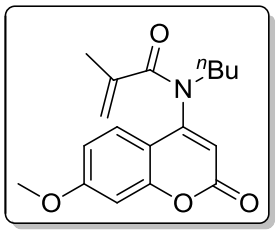
119.8, 117.7, 117.7, 114.2, 51.8, 19.9; **HRMS**: calcd. For $C_{16}H_{16}NO_3$ $[M + H]^+$ 270.1113, found 270.1130.



***N*-Butyl-*N*-(2-oxo-2H-chromen-4-yl)-2-phenylacrylamide (1e):** On 1.0 mmol scale, pale yellow viscous oil; yield (**1e**): 85% (295.4 mg), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 (d, J = 7.6 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.53 – 7.47 (m, 2H), 7.43 – 7.37 (m, 6H), 5.97 (s, 1H), 5.95 (s, 1H), 3.95 – 3.91 (m, 2H), 1.70 – 1.62 (m, 2H), 1.30 – 1.26 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 172.2, 164.9, 144.9, 142.1, 135.0, 133.3, 132.8, 129.3, 129.1, 129.0, 128.9, 128.8, 126.9, 125.8, 124.6, 122.3, 50.5, 30.3, 20.0, 13.6; **HRMS**: calcd. For $C_{22}H_{22}NO_3$ $[M + H]^+$ 347.1421, found 347.1411.

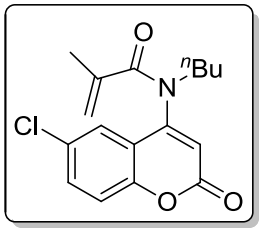


***N*-Butyl-*N*-(7-methyl-2-oxo-2H-chromen-4-yl)methacrylamide (1f)**: On 1.0 mmol scale, white solid (mp: 82–84 °C); yield (**1f**): 83% (248.5 mg), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (d, J = 8.1 Hz, 1H), 7.20 (s, 1H), 7.14 (d, J = 8.2 Hz, 1H), 6.15 (s, 1H), 5.07 (d, J = 14.0 Hz, 2H), 3.75 (br s, 2H), 2.47 (s, 3H), 1.88 (s, 3H), 1.61 – 1.57 (m, 2H), 1.32 (dd, J = 15.1, 7.5 Hz, 2H), 0.90 (t, J = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 171.2, 161.2, 154.9, 154.2, 144.4, 140.1, 125.9, 123.9, 119.2, 117.8, 115.38, 113.0, 49.1, 29.9, 21.7, 20.1, 13.7; **HRMS**: calcd. For $C_{18}H_{22}NO_3$ $[M + H]^+$ 300.1594, found 300.1589.



***N*-Butyl-*N*-(7-methoxy-2-oxo-2H-chromen-4-yl)methacrylamide (1g)**: On 1.0 mmol scale, white solid (mp: 95–97 °C); yield (**1g**): 85% (268.1 mg), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 (d, J = 8.7 Hz, 1H), 6.90 - 6.87 (m, 2H), 6.06 (s, 1H), 5.09 (s, 1H), 5.05 (s, 1H), 3.90 (s, 3H), 3.71 (br s, 2H), 1.88 (s, 3H), 1.62 (d, J = 7.9 Hz, 1H), 1.56 (d, J = 7.9 Hz, 1H), 1.32 (dd, J = 15.1, 7.5 Hz,

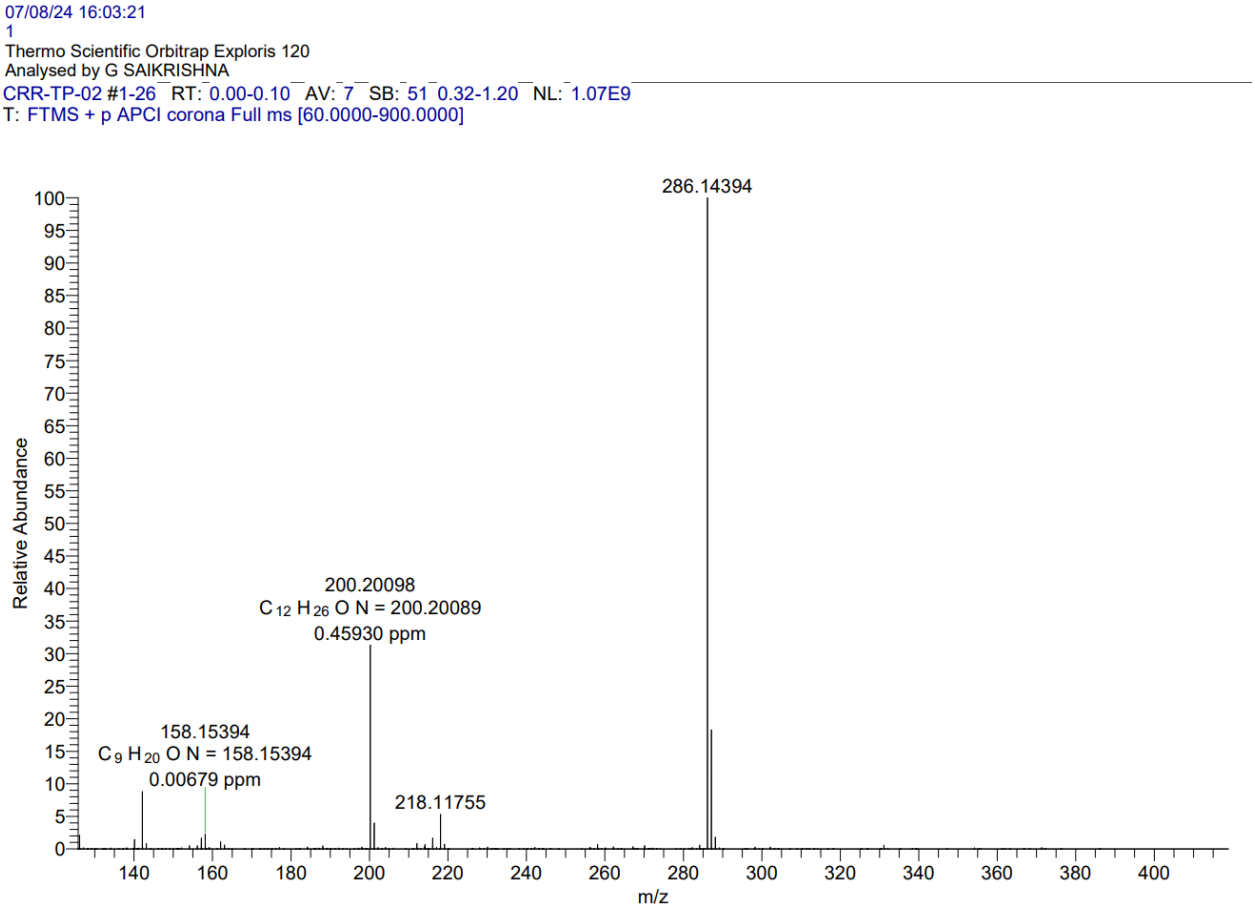
2H), 0.91 (t, *J* = 7.3 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 171.21, 163.52, 161.40, 155.96, 155.13, 140.07, 125.23, 119.12, 113.07, 111.20, 110.86, 101.41, 55.96, 49.12, 30.00, 20.14, 20.12, 13.76; **HRMS**: calcd. For $C_{18}H_{22}NO_4$ $[M + H]^+$ 316.1533, found 316.1549.



***N*-Butyl-*N*-(6-chloro-2-oxo-2H-chromen-4-yl)methacrylamide (1h)**: On 1.0 mmol scale, pale pink solid (mp: 115–117 °C); yield (**1h**): 79% (252.6 mg), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.41 (d, *J* = 2.4 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 6.26 (s, 1H), 5.11 (s, 2H), 3.84 – 3.75 (m, 2H), 1.91 (s, 3H), 1.64 – 1.60 (m, 1H), 1.56 (s, 1H), 1.34 (dd, *J* = 15.2, 7.4 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 171.1, 160.2, 153.9, 152.34, 140.0, 132.8, 130.4, 123.6, 119.6, 119.2, 119.0, 114.8, 49.3, 30.0, 20.1, 13.7; **HRMS**: calcd. For $C_{17}H_{19}NO_3Cl$ $[M + H]^+$ 320.1040, found 320.1053.

3. Control Experiments: Radical trapping with 2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO):

To the solution of *N*-acryloyl amino coumarin **1a** (1.0 equiv, 0.5 mmol scale) in CH_3CN:H_2O (1:1, 3 mL), isobutyric acid **2c** (2.0 equiv.) were added. $K_2S_2O_8$ (4.0 equiv), and Ag_2CO_3 (10 mol%), and 2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) (2.0 equiv) was added to the mixture and stirred for 3 h at 50 °C (an oil bath). The progress of the reaction was monitored by TLC and found that the reaction inhibited and intermediate was confirmed by HRMS. **HRMS**: calcd for $C_{12}H_{26}NO$ $(M+H)^+$ 200.20089, found 200.20098.

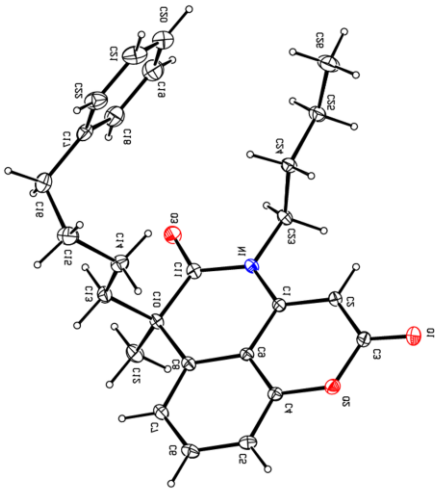


4. X-ray Data:

X-ray data for the compound **3f** was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

Crystal structure determination of 3f:

Crystal Data for $C_{26}H_{29}NO_3$ (M =403.50 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 21.6934(12) Å, b = 9.8813(12) Å, c = 10.474(3) Å, β = 101.399(6)°, V = 2201.0(7) Å^3, Z = 4, T = 294.15 K, μ(MoKα) = 0.079 mm^{-1}, $Dcalc$ = 1.218 g/cm^3, 25218 reflections measured (4.546° ≤ 2Θ ≤ 61.004°), 6461 unique (R_{int} = 0.0588, R_{sigma} = 0.0879) which were used in all calculations. The final R_1 was 0.0632 (I > 2σ(I)) and wR_2 was 0.1473 (all data). CCDC No. 2360230 contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/.



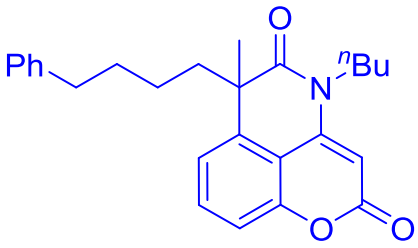


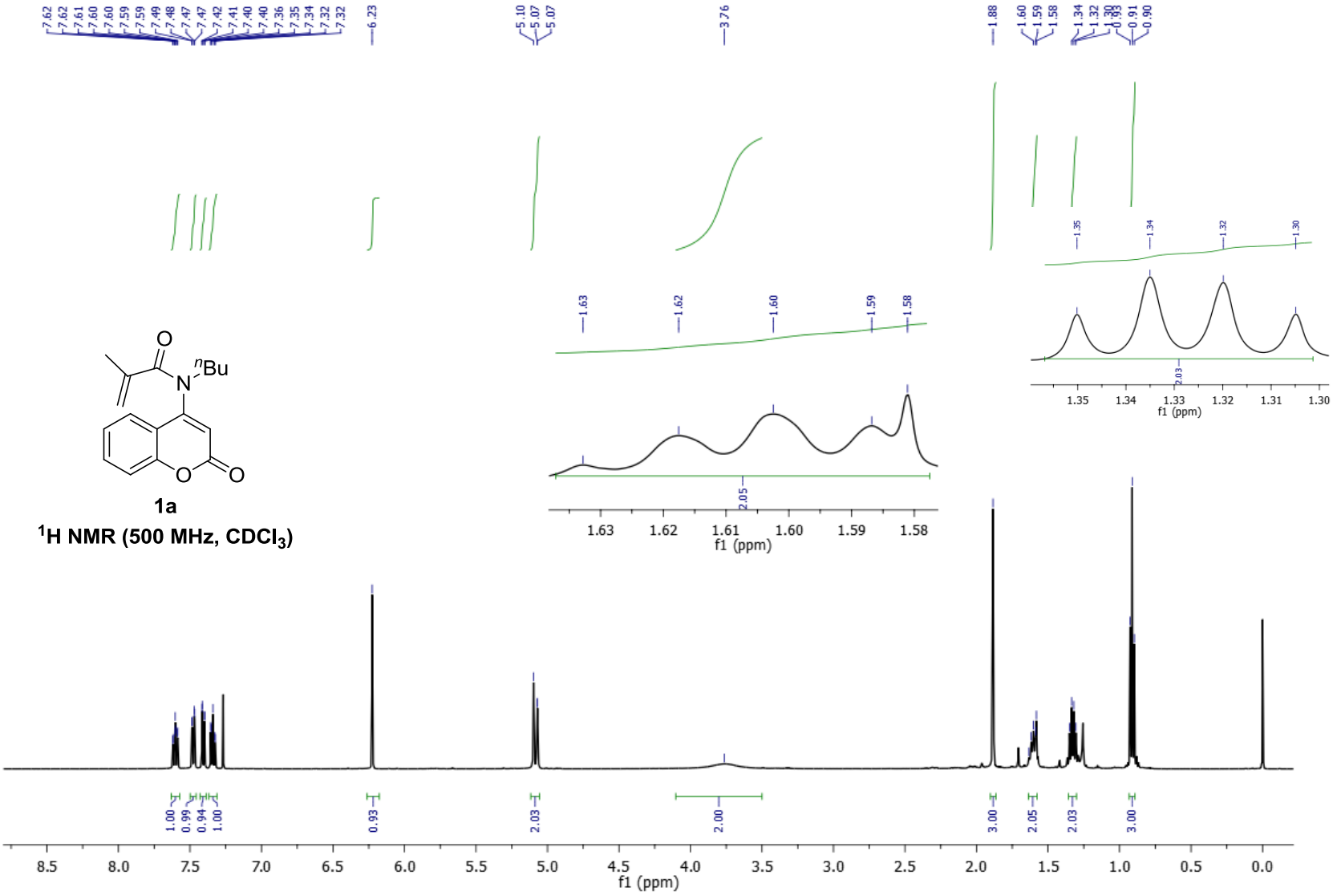
Figure caption: ORTEP diagram of **3f** compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

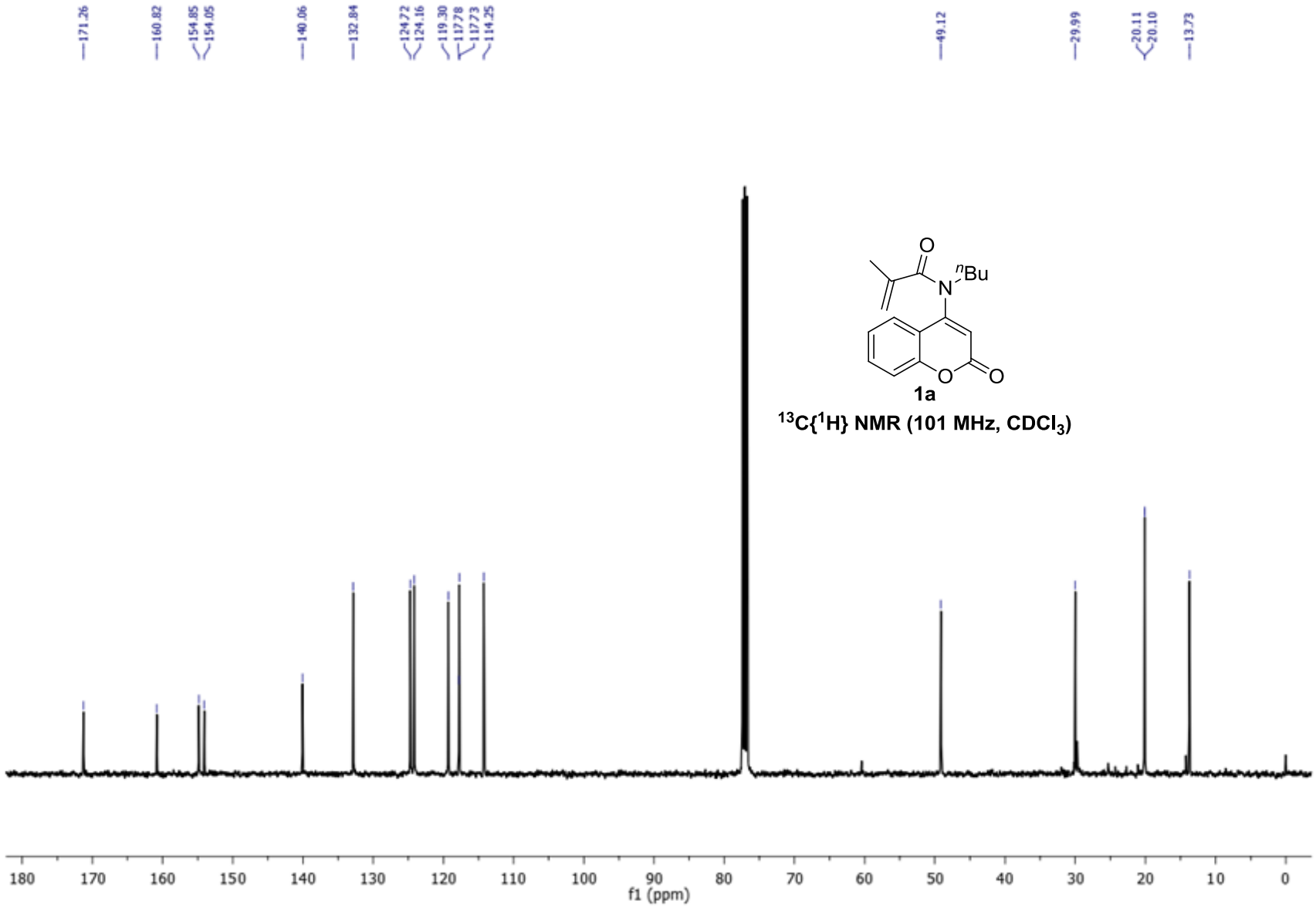
5. References:

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.

2. Sheldrick G. M. (2015).ActaCrystallogr C71: 3-8.

6. ^{1}H NMR and ^{13}C NMR spectra:

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154.05
140.06
132.84
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117.73
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49.12
29.99
20.11
20.10
13.73
O
N
nBu
O
O
1a
13C{1H} NMR (101 MHz, CDCl3)
180
170
160
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140
130
120
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100
90
80
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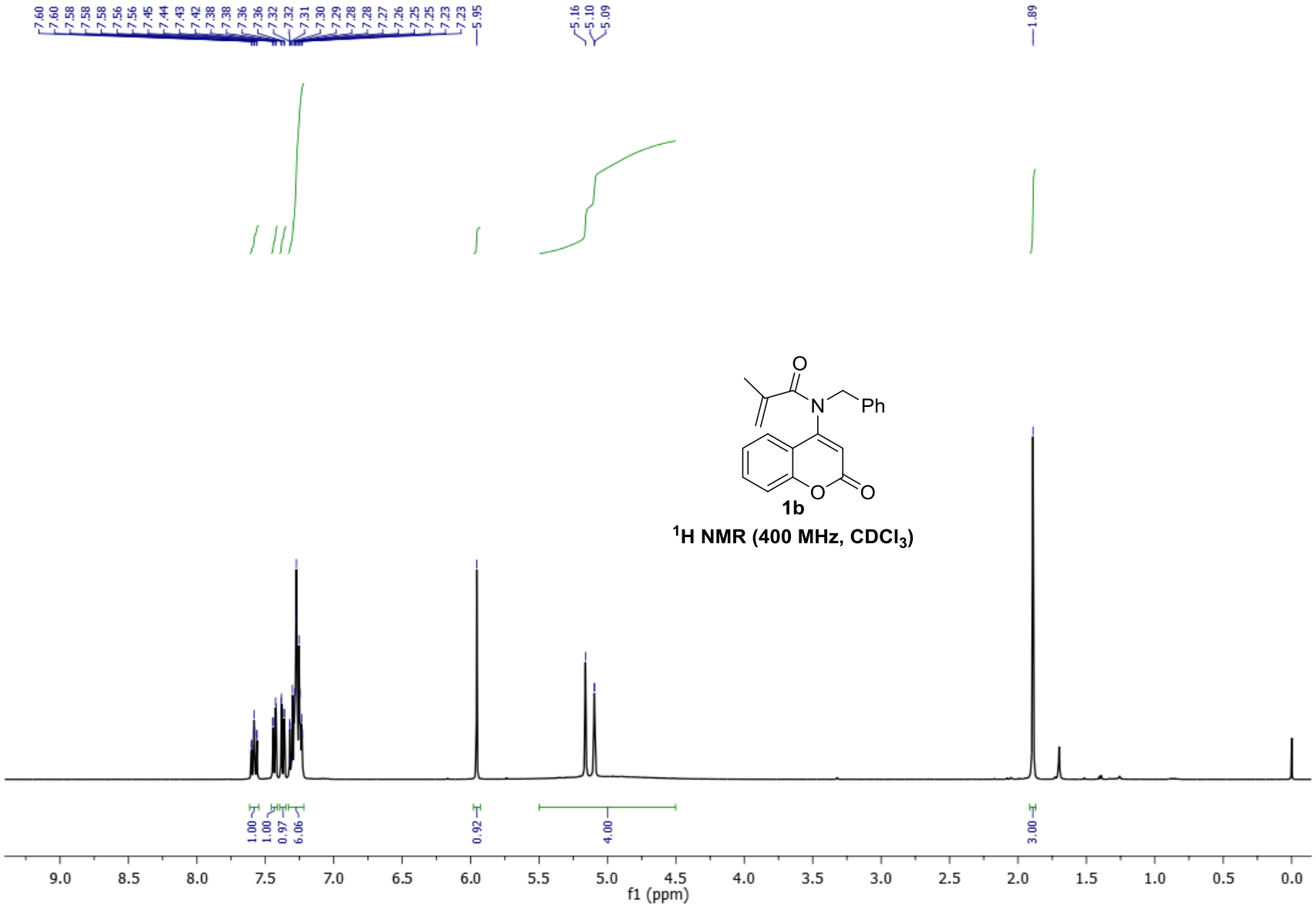
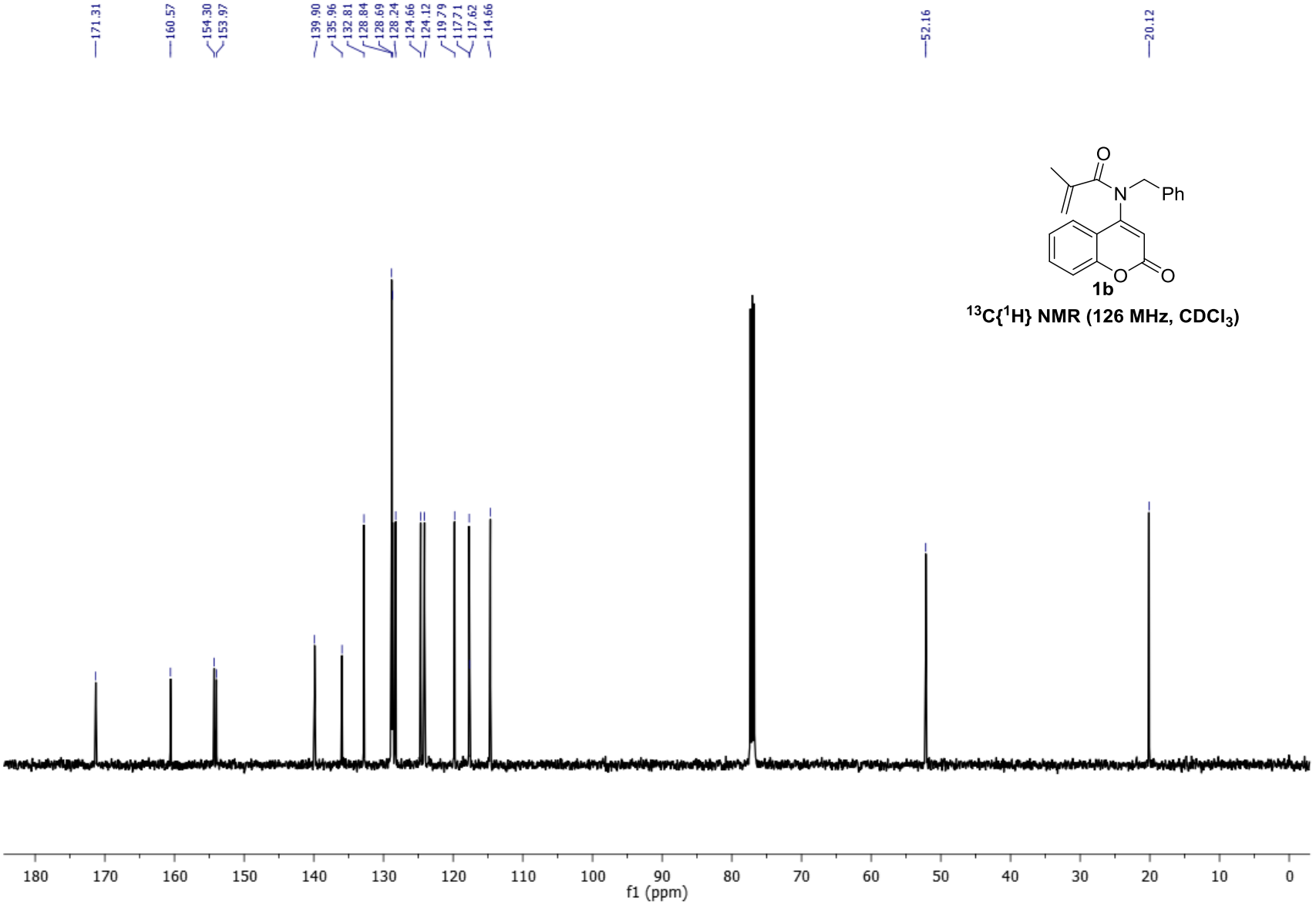
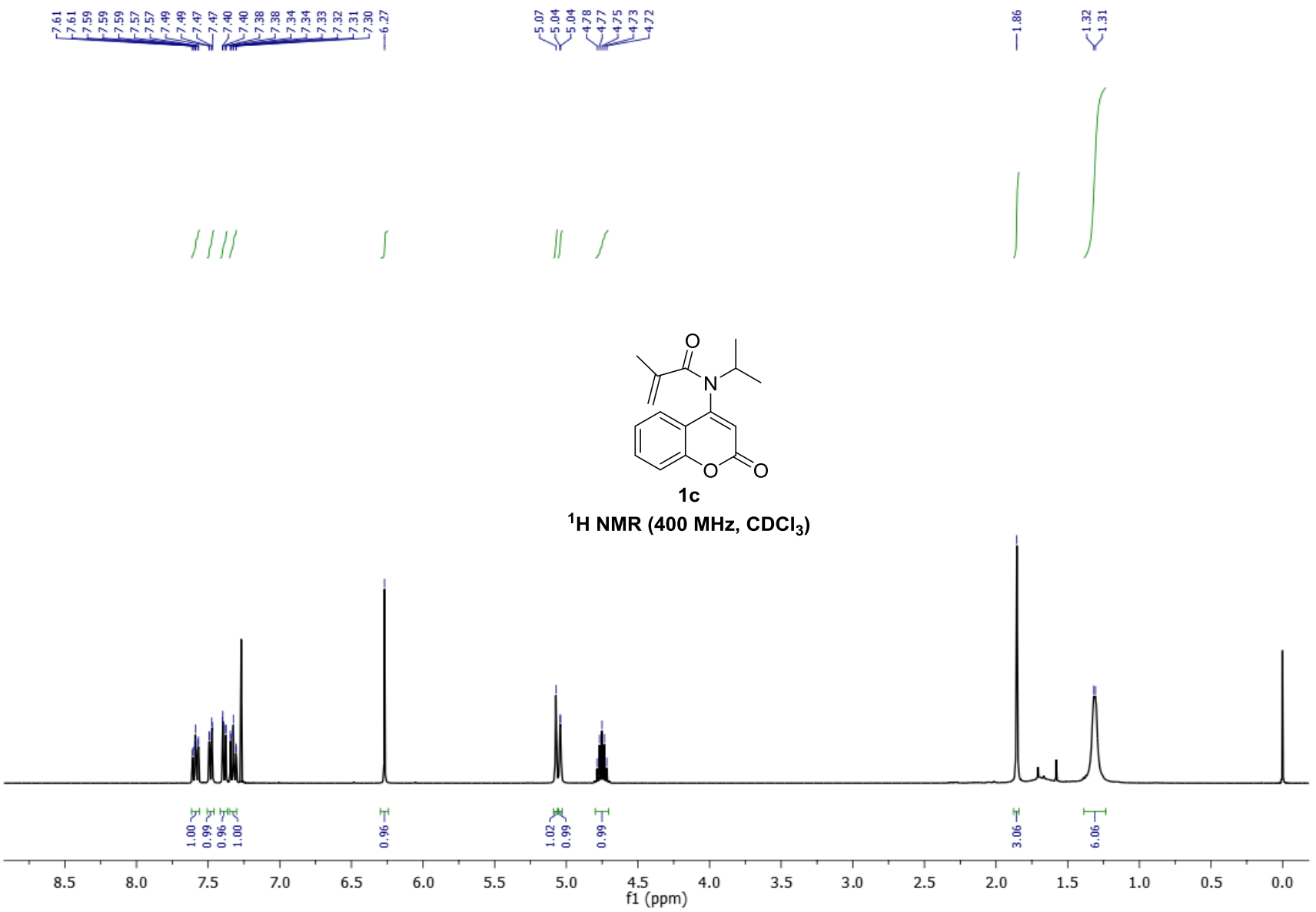
50
40
30
20
10
0
f1 (ppm)



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

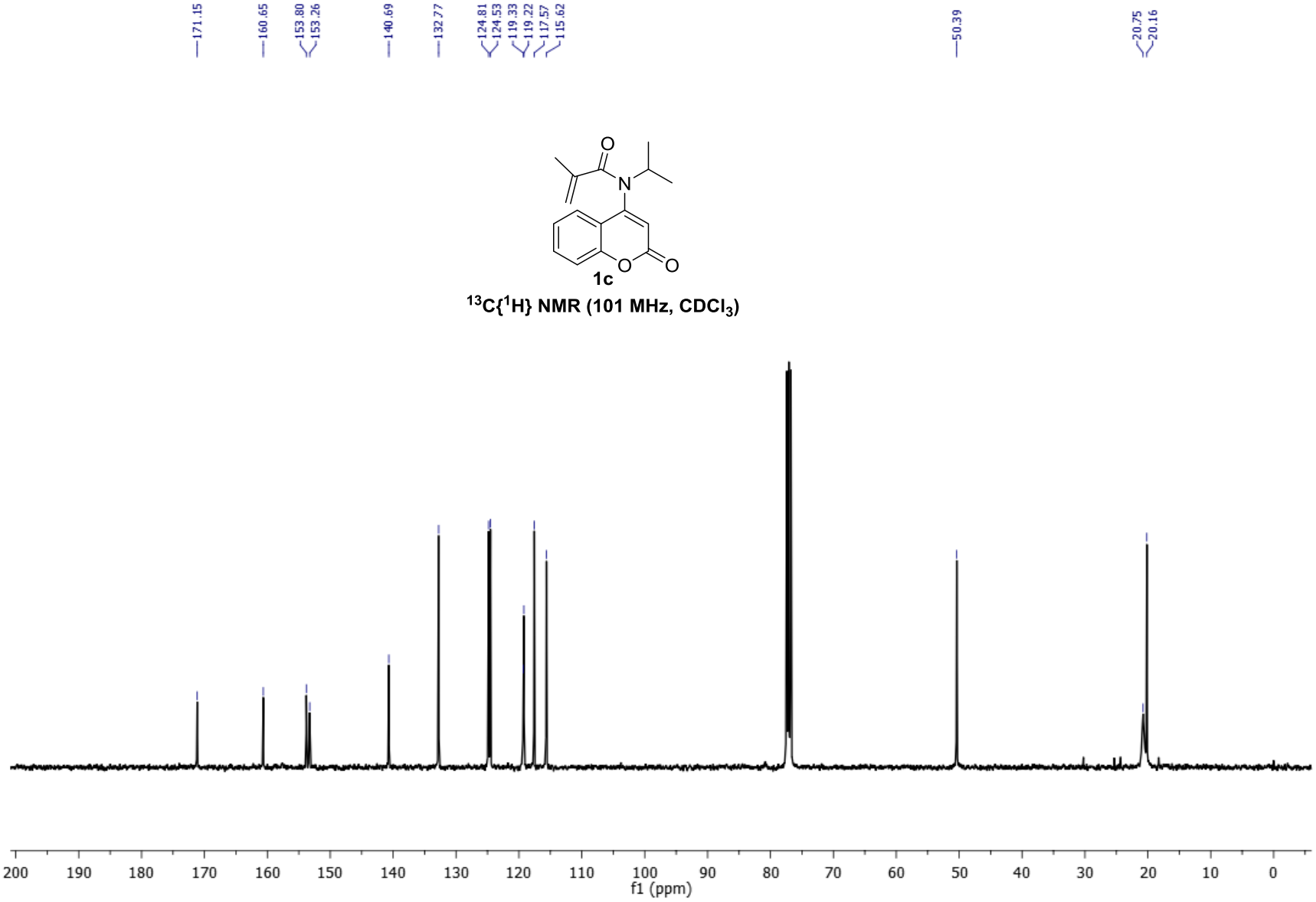


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



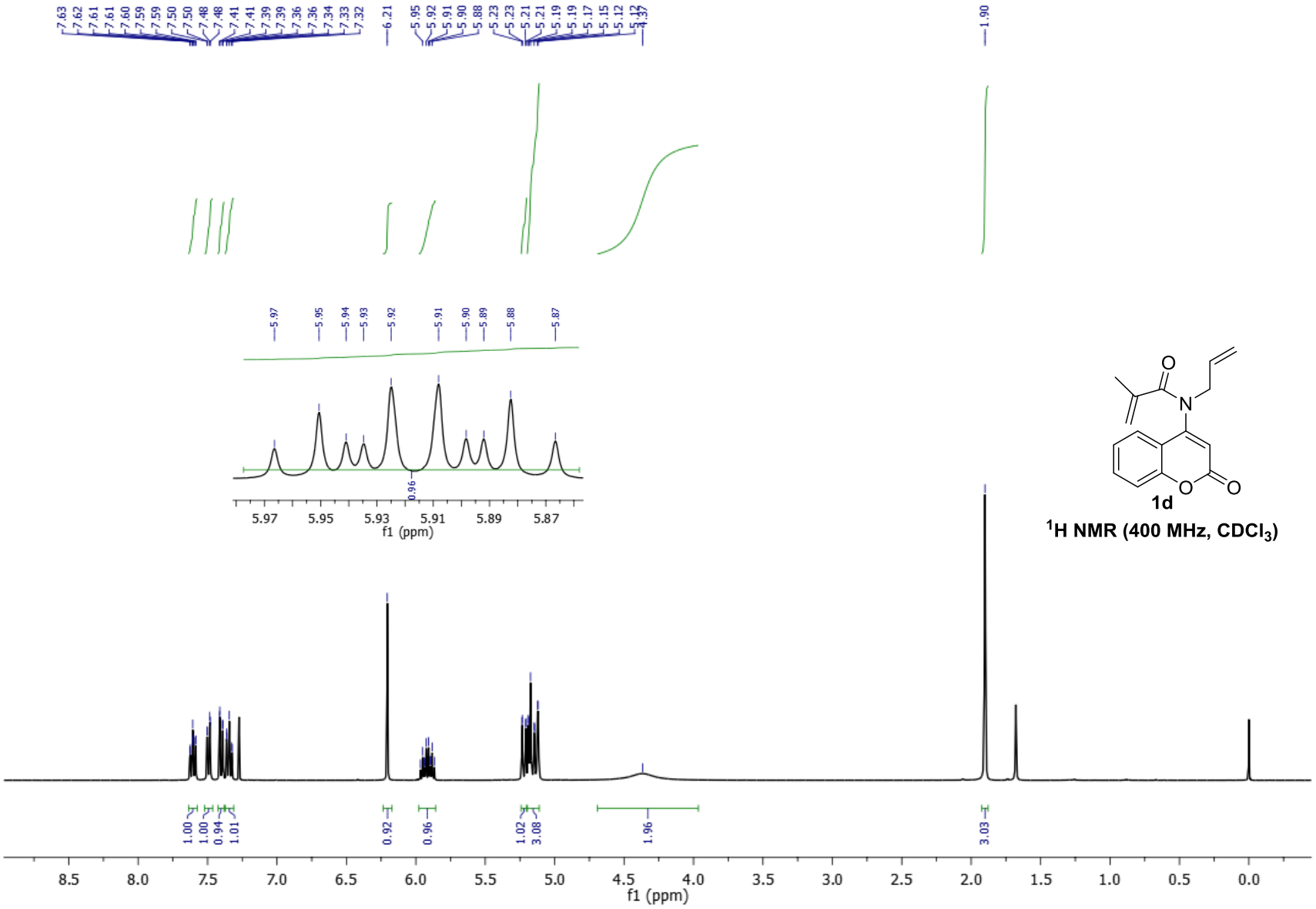
1c

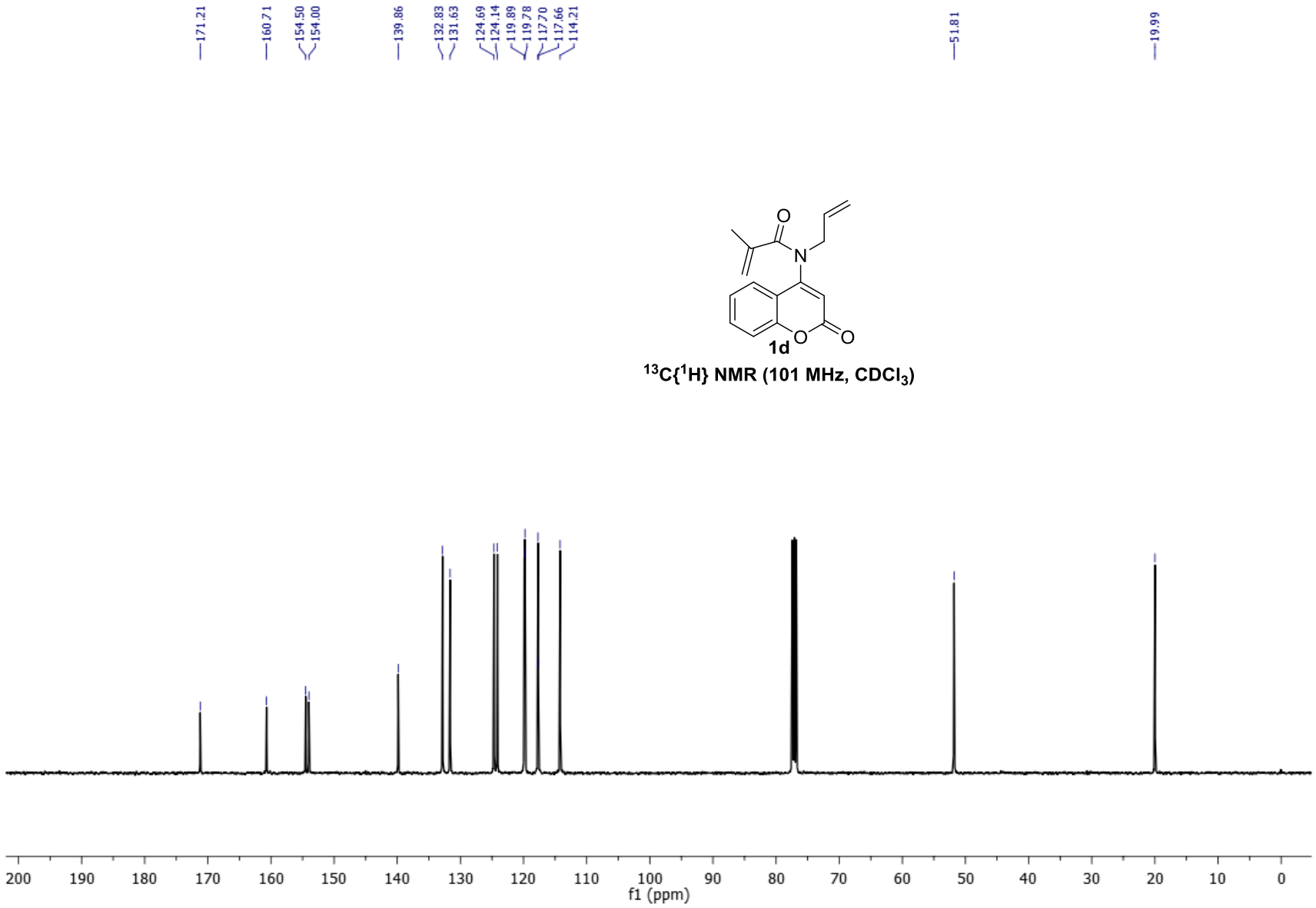
^{1}H NMR (400 MHz, $CDCl_3$)



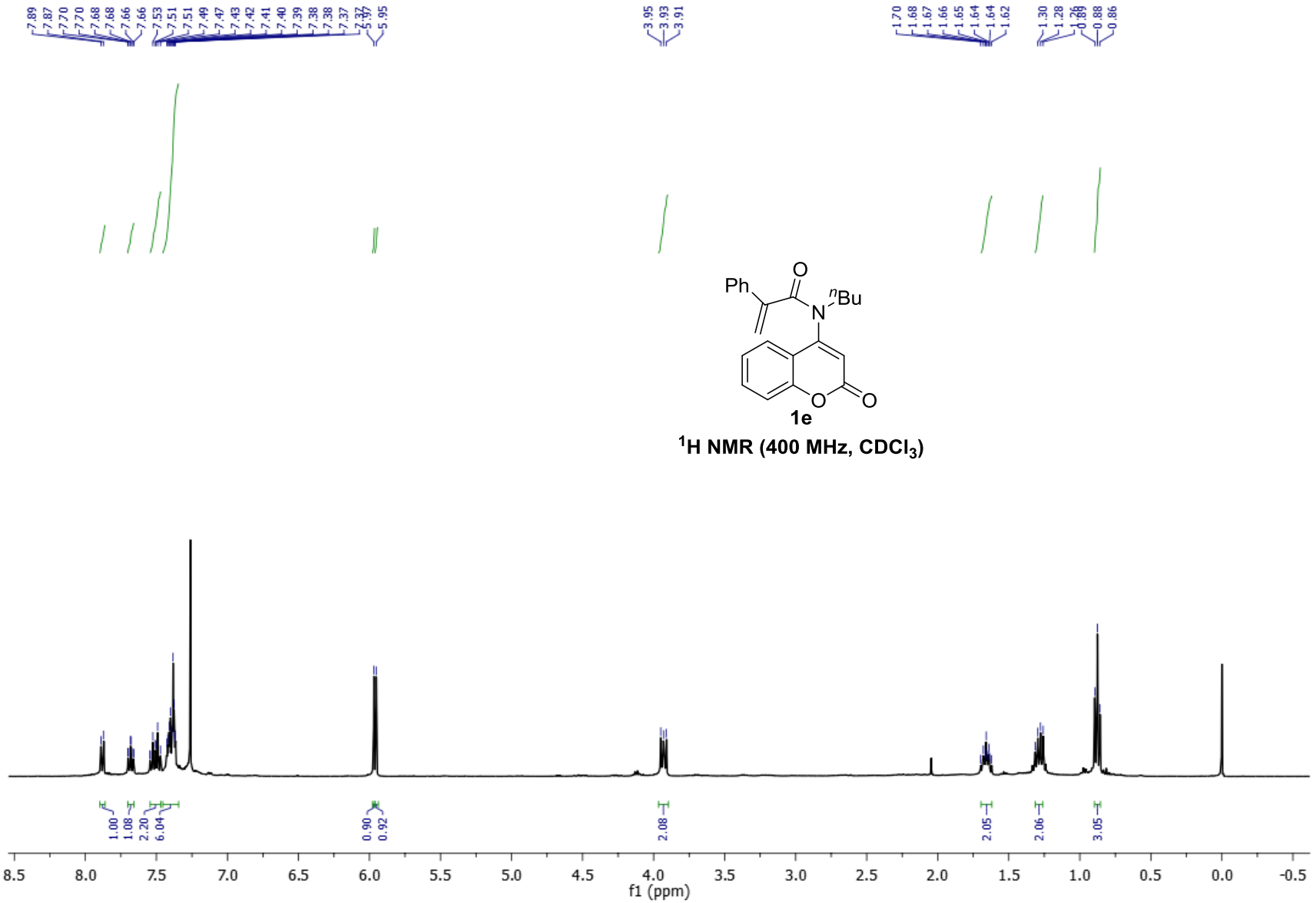
1c

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

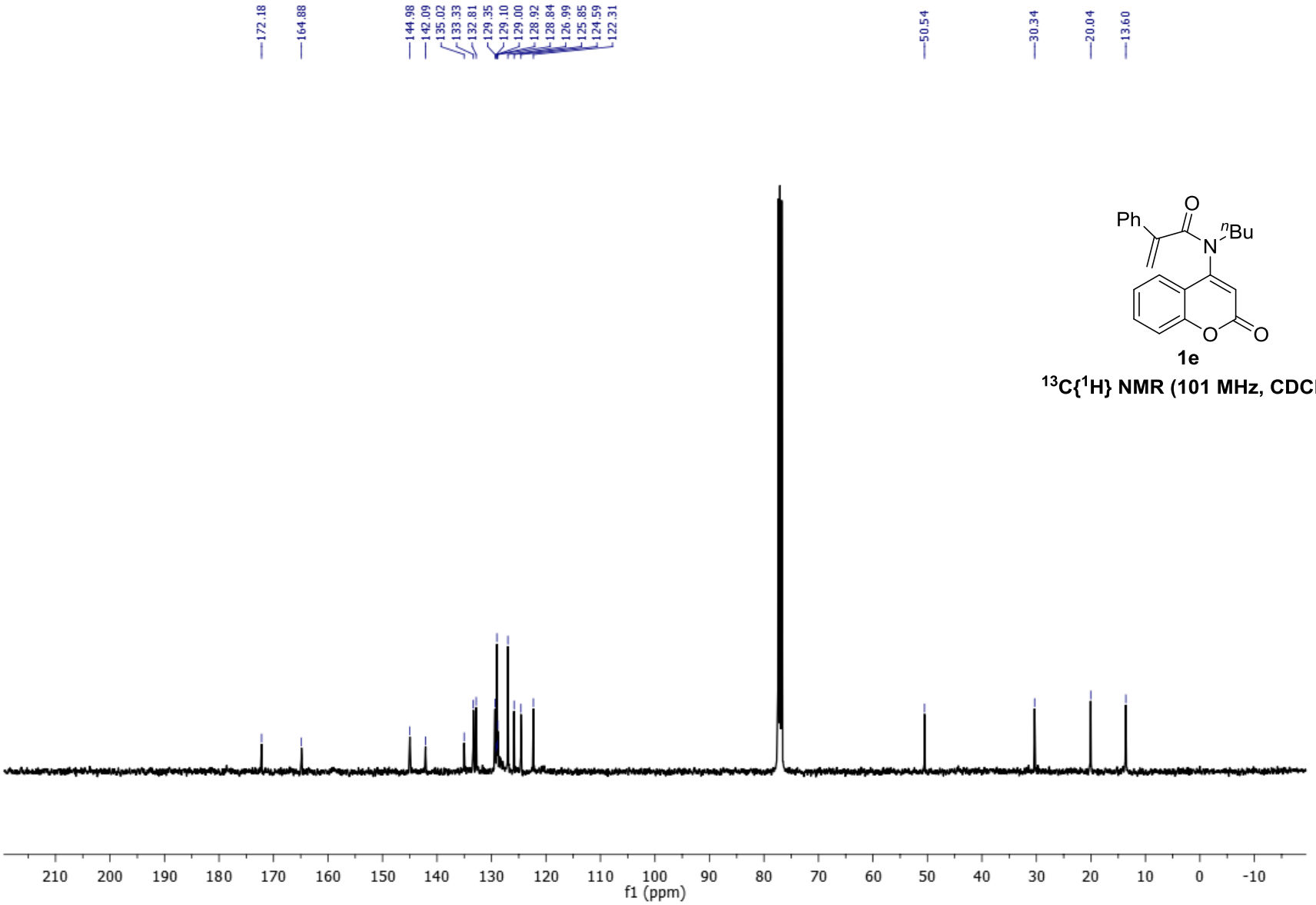

7.63 7.62 7.61 7.61 7.60 7.59 7.59 7.50 7.50 7.48 7.48 7.41 7.41 7.39 7.39 7.36 7.36 7.34 7.33 7.32
6.21
5.95 5.92 5.91 5.90 5.88
5.23 5.21 5.21 5.19 5.19 5.17 5.15 5.12
1.90
5.97 5.95 5.94 5.93 5.92 5.91 5.90 5.89 5.88 5.87
0.96
5.97 5.95 5.93 5.91 5.89 5.87
f1 (ppm)
1d
1H NMR (400 MHz, CDCl3)
1.00 1.00 0.94 1.01 0.92 0.96 1.02 3.08 1.96 3.03
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 0.0
f1 (ppm)



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

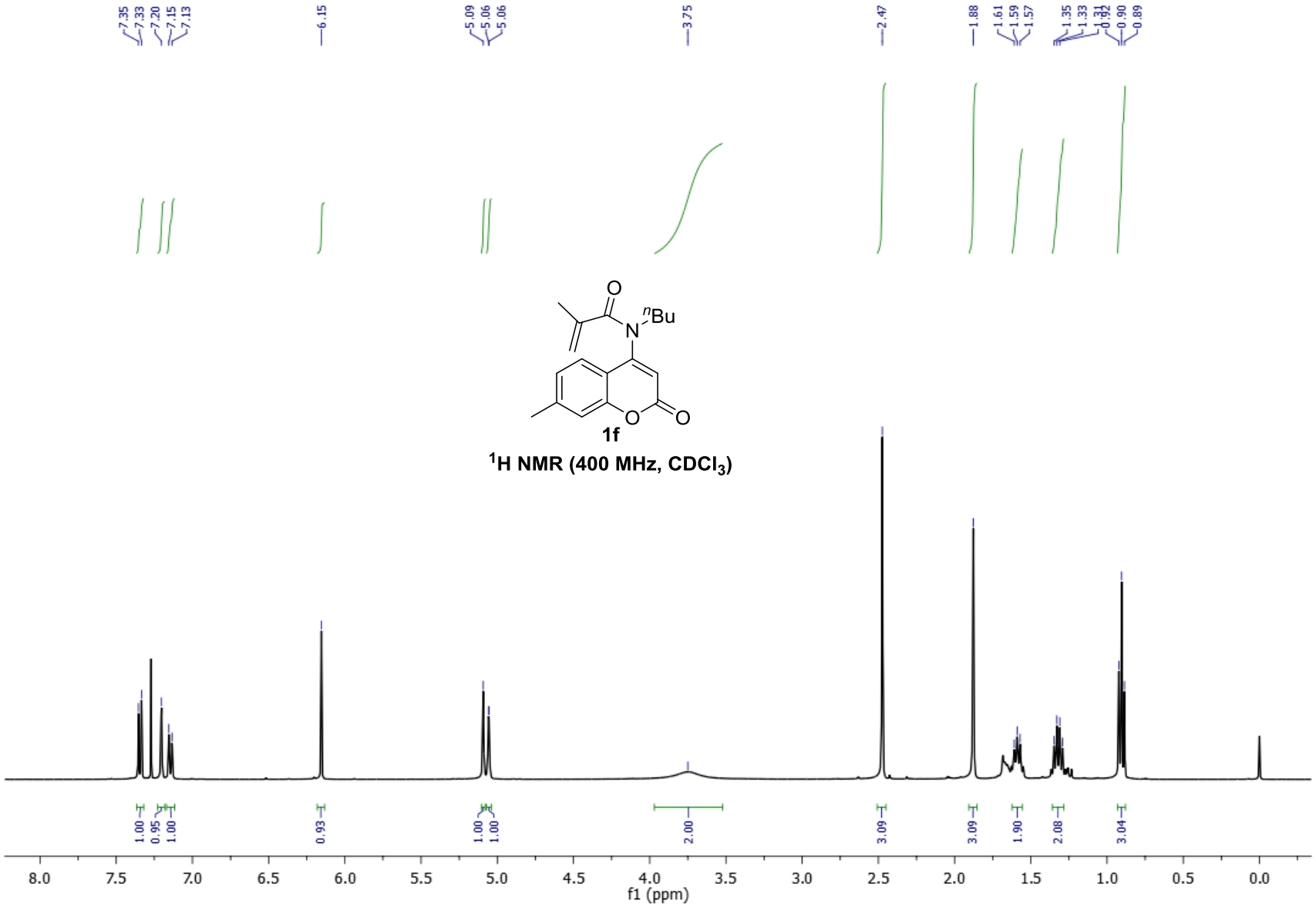


^{1}H NMR (400 MHz, $CDCl_3$)



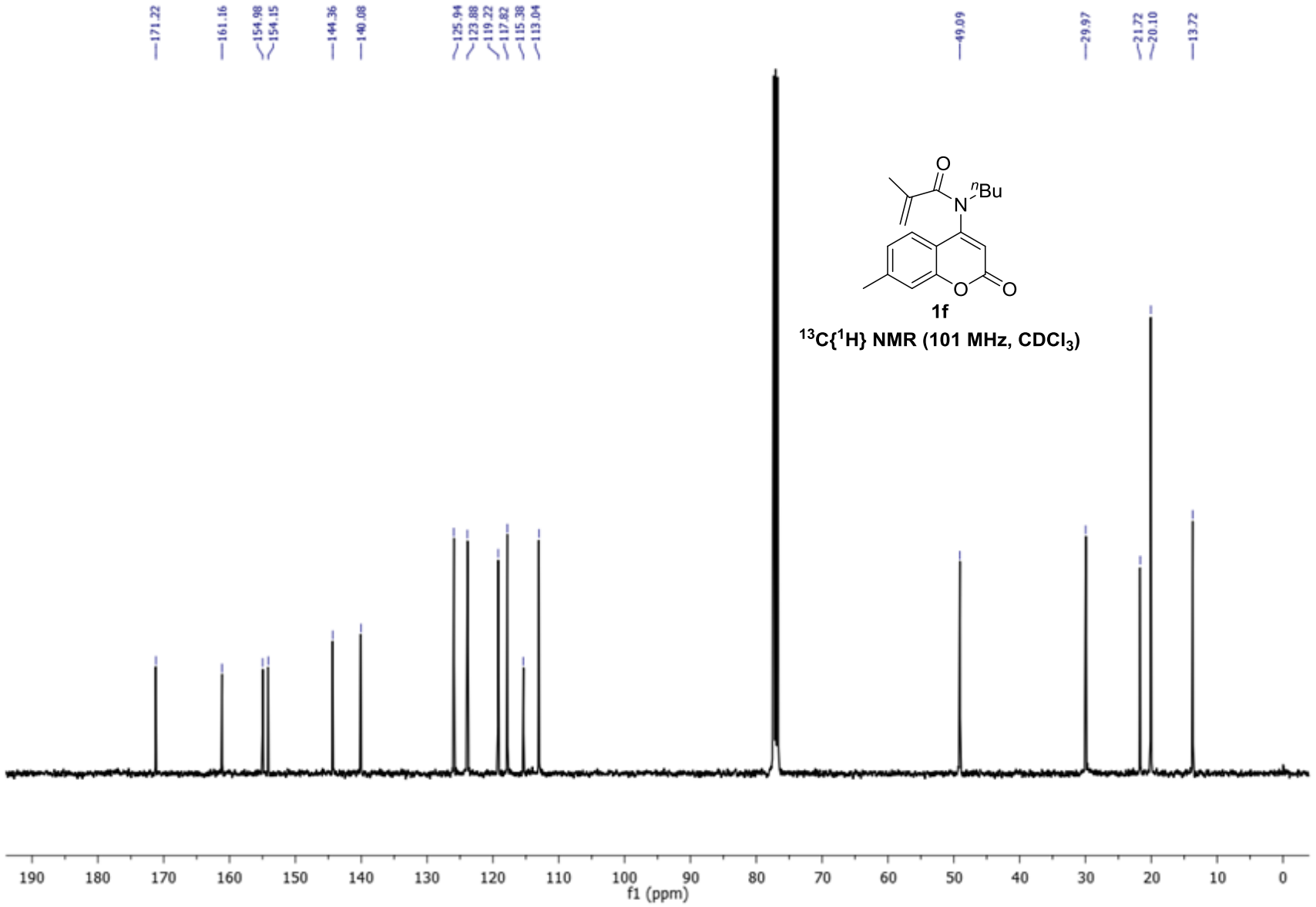
1e

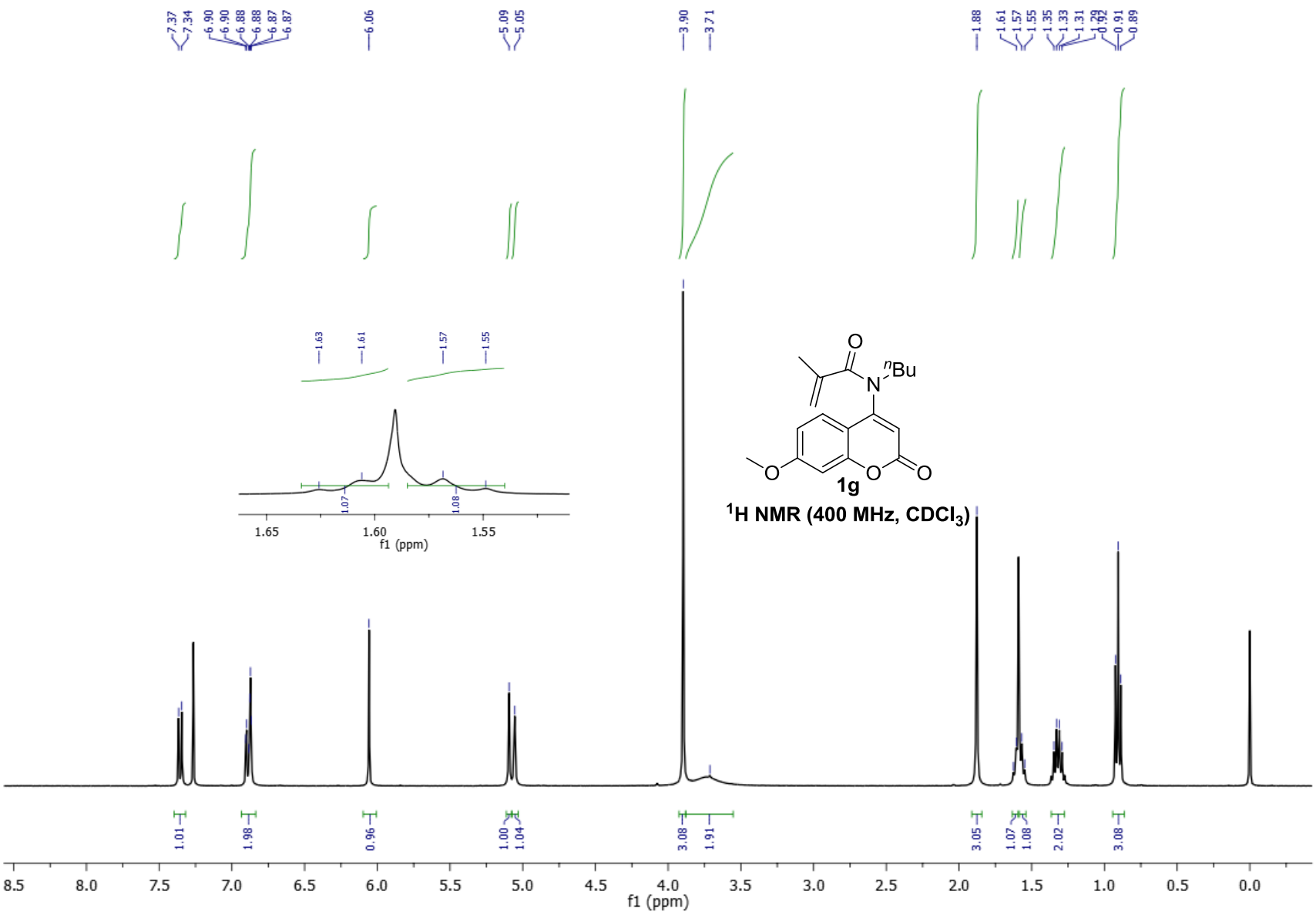
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

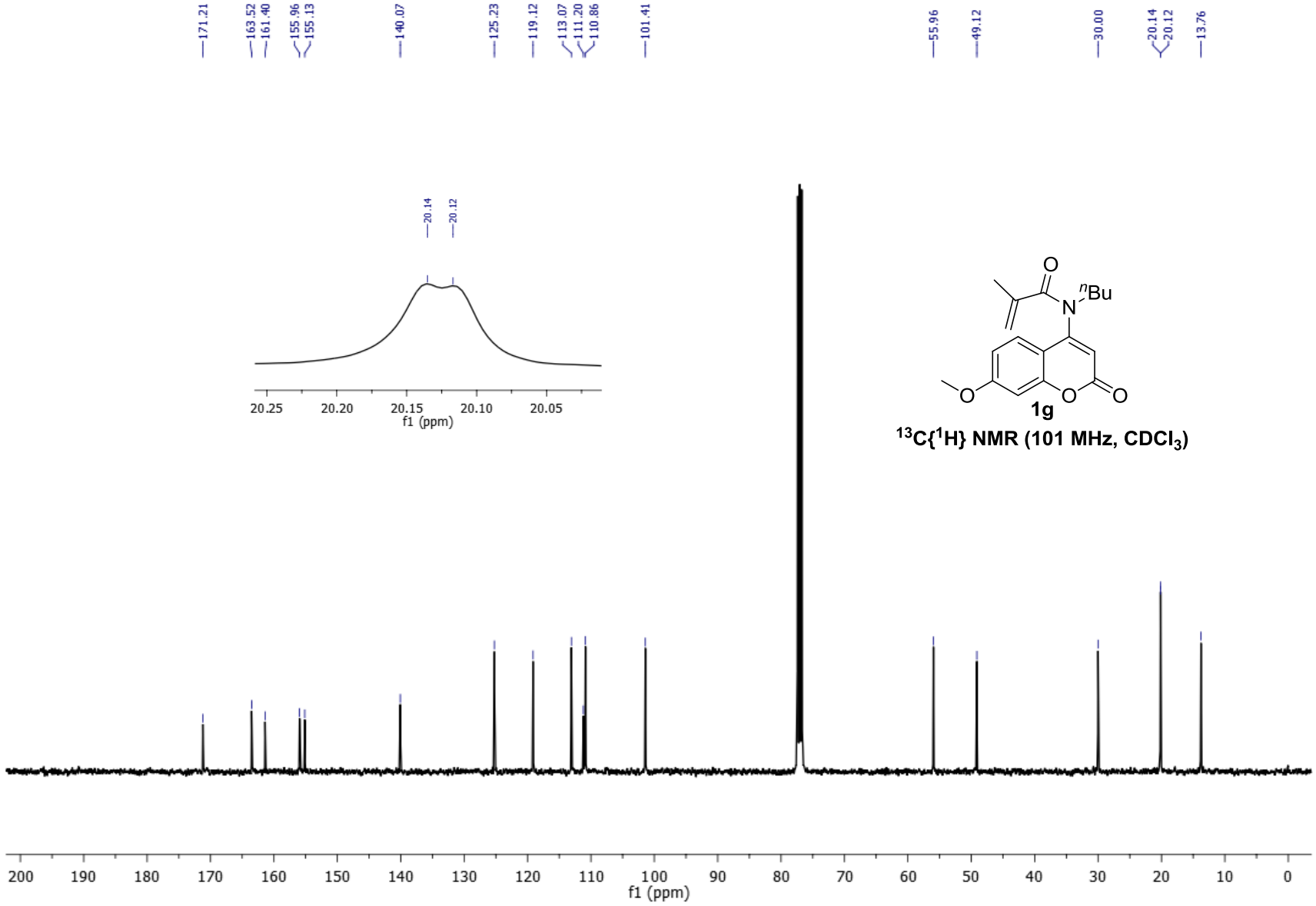


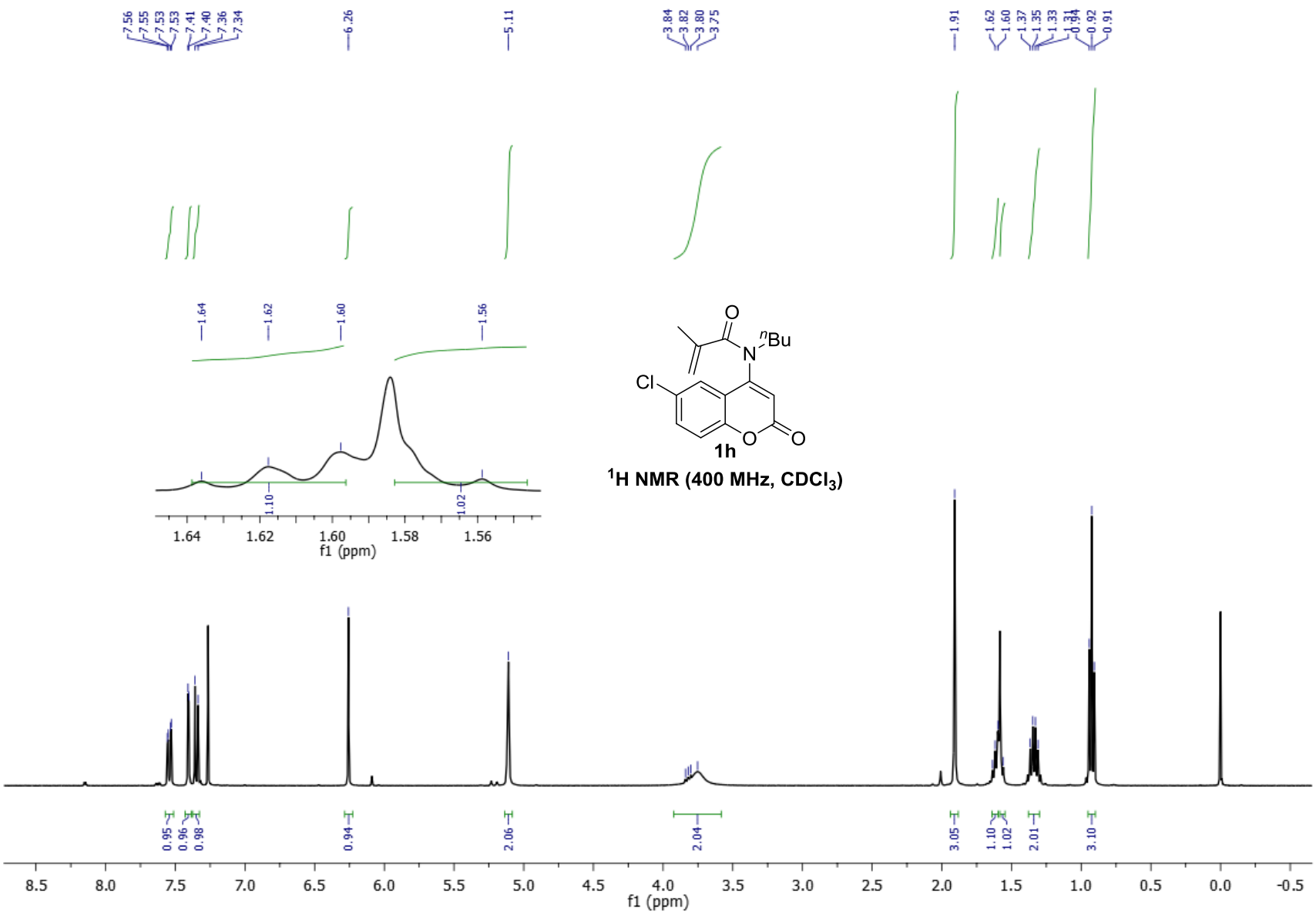
1f

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

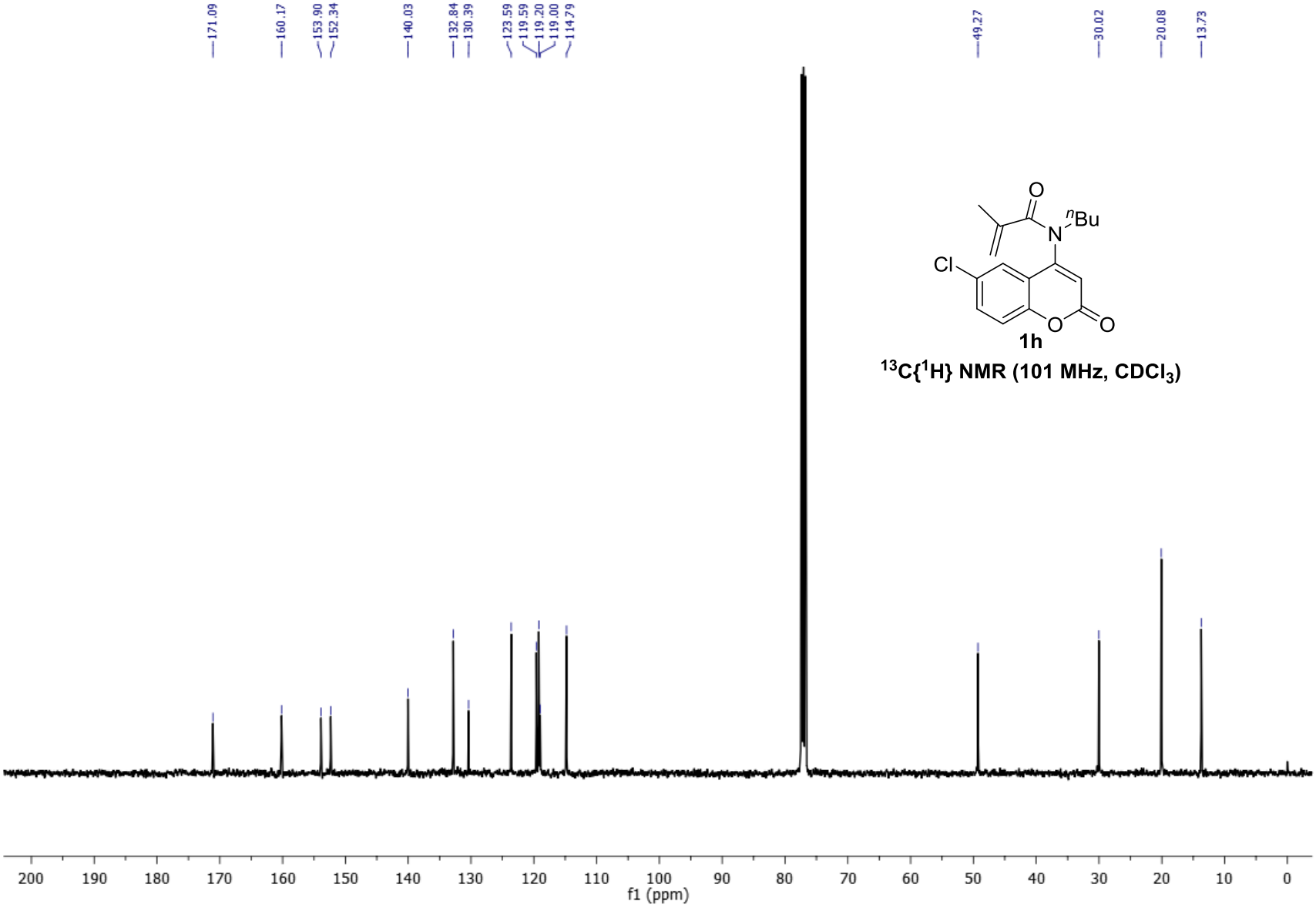

171.22
161.16
154.98
154.15
144.36
140.08
125.94
123.88
119.22
117.82
115.38
113.04
49.09
29.97
21.72
20.10
13.72
O
N
nBu
O
O
1f
13C{1H} NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.37
7.34
6.90
6.90
6.88
6.88
6.87
6.87
6.06
5.09
5.05
3.90
3.71
1.88
1.61
1.57
1.55
1.35
1.33
1.31
1.29
0.92
0.91
0.89
1.63
1.61
1.57
1.55
1.07
1.08
1.65
1.60
1.55
f1 (ppm)
O
nBu
N
O
O
O
1g
1H NMR (400 MHz, CDCl3)
1.01
1.98
0.96
1.00
1.04
3.08
1.91
3.05
1.07
1.08
2.02
3.08
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
0.0
f1 (ppm)

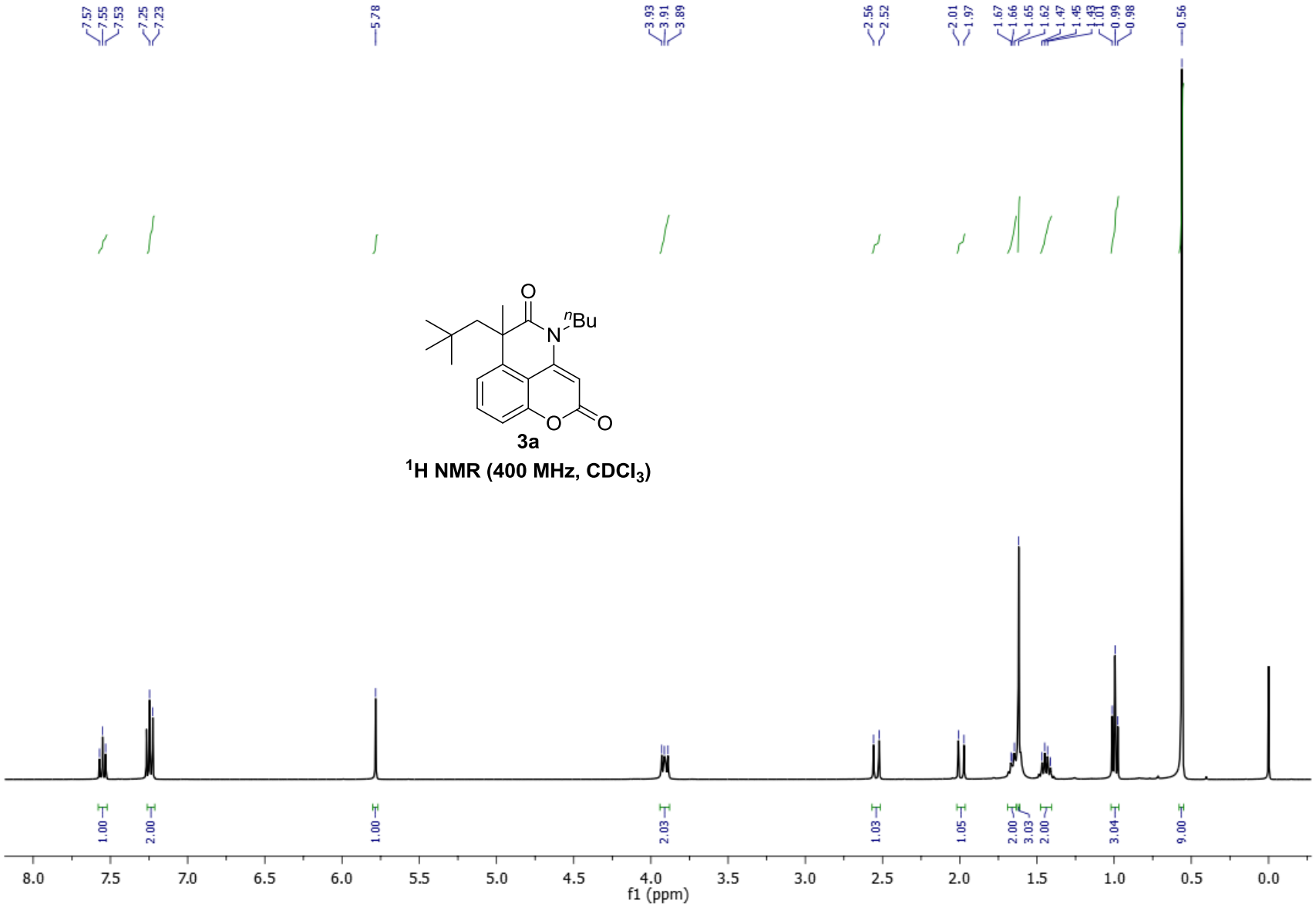

171.21
163.52
161.40
155.96
155.13
140.07
125.23
119.12
113.07
111.20
110.86
101.41
55.96
49.12
30.00
20.14
20.12
13.76
20.14
20.12
20.25
20.20
20.15
20.10
20.05
f1 (ppm)
O
nBu
N
O
O
O
1g
13C{1H} NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



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

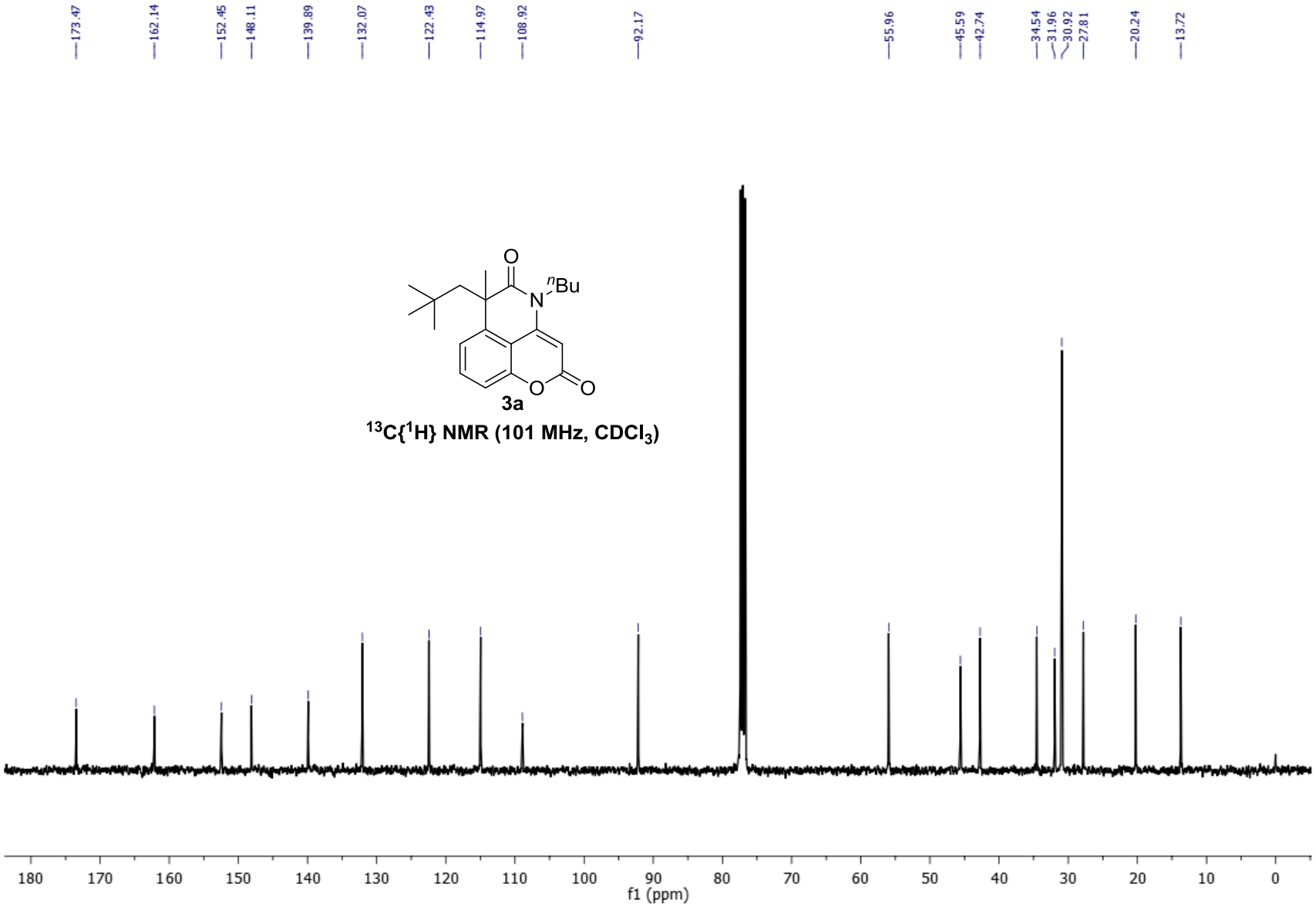


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

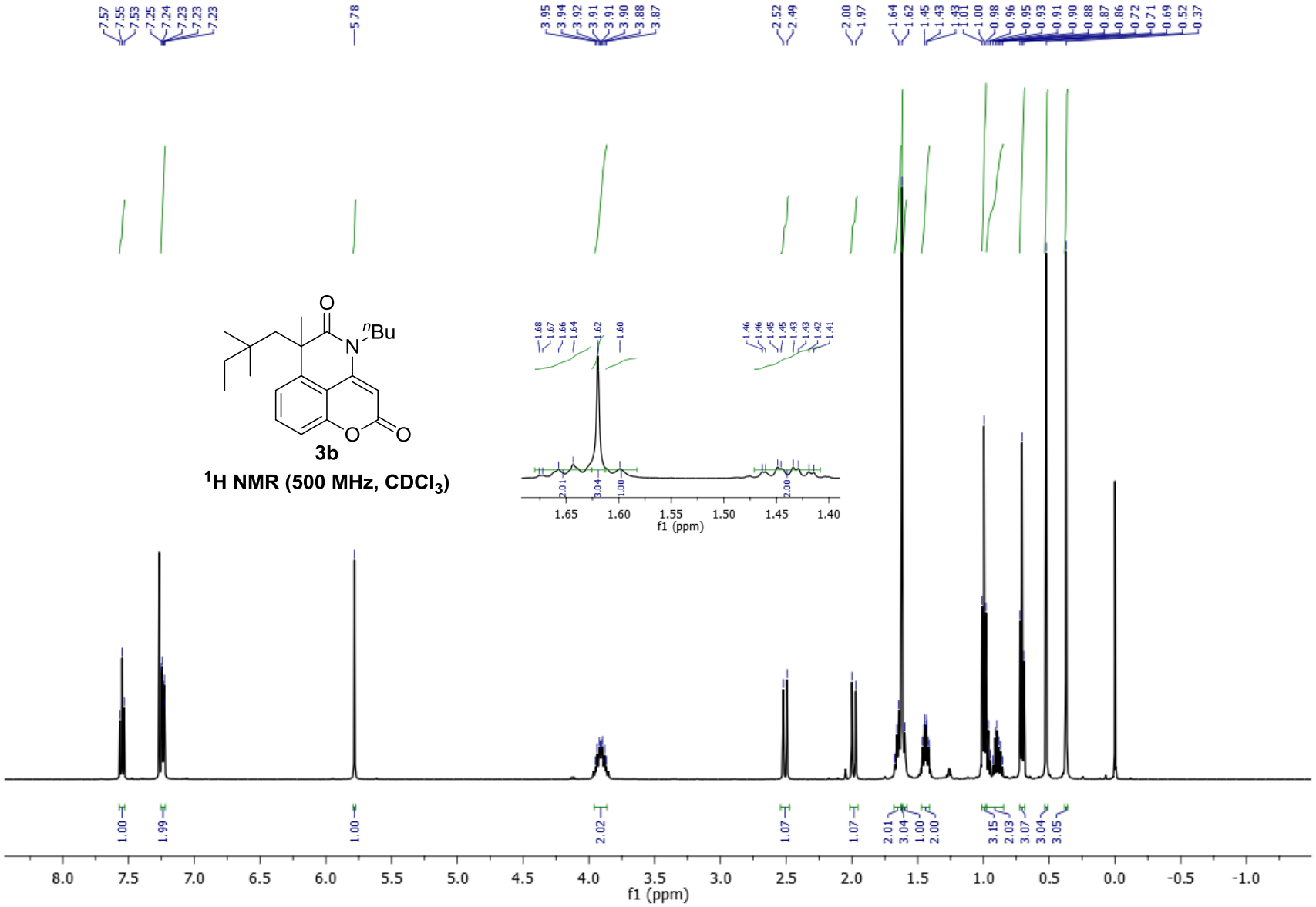


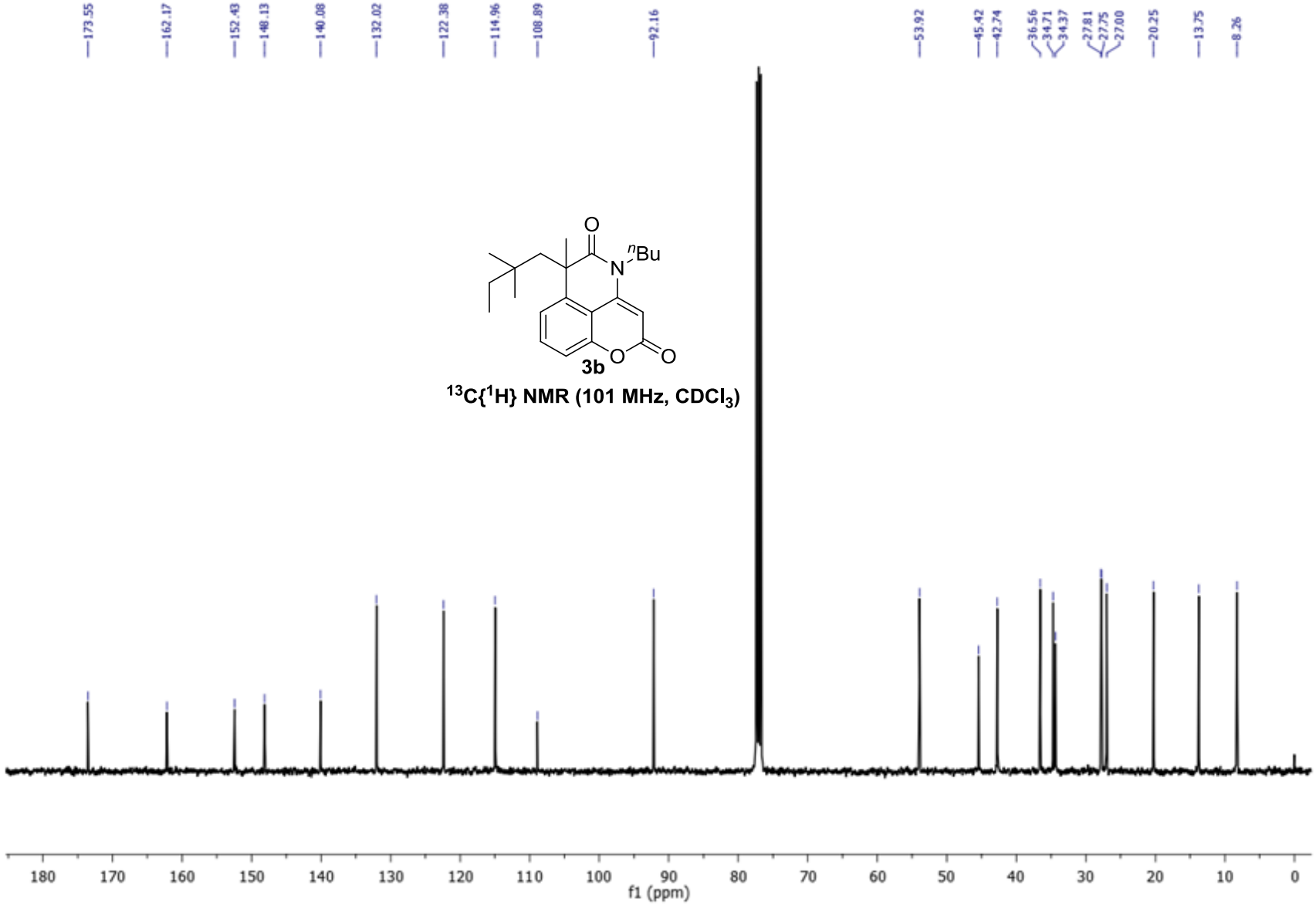
3a

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

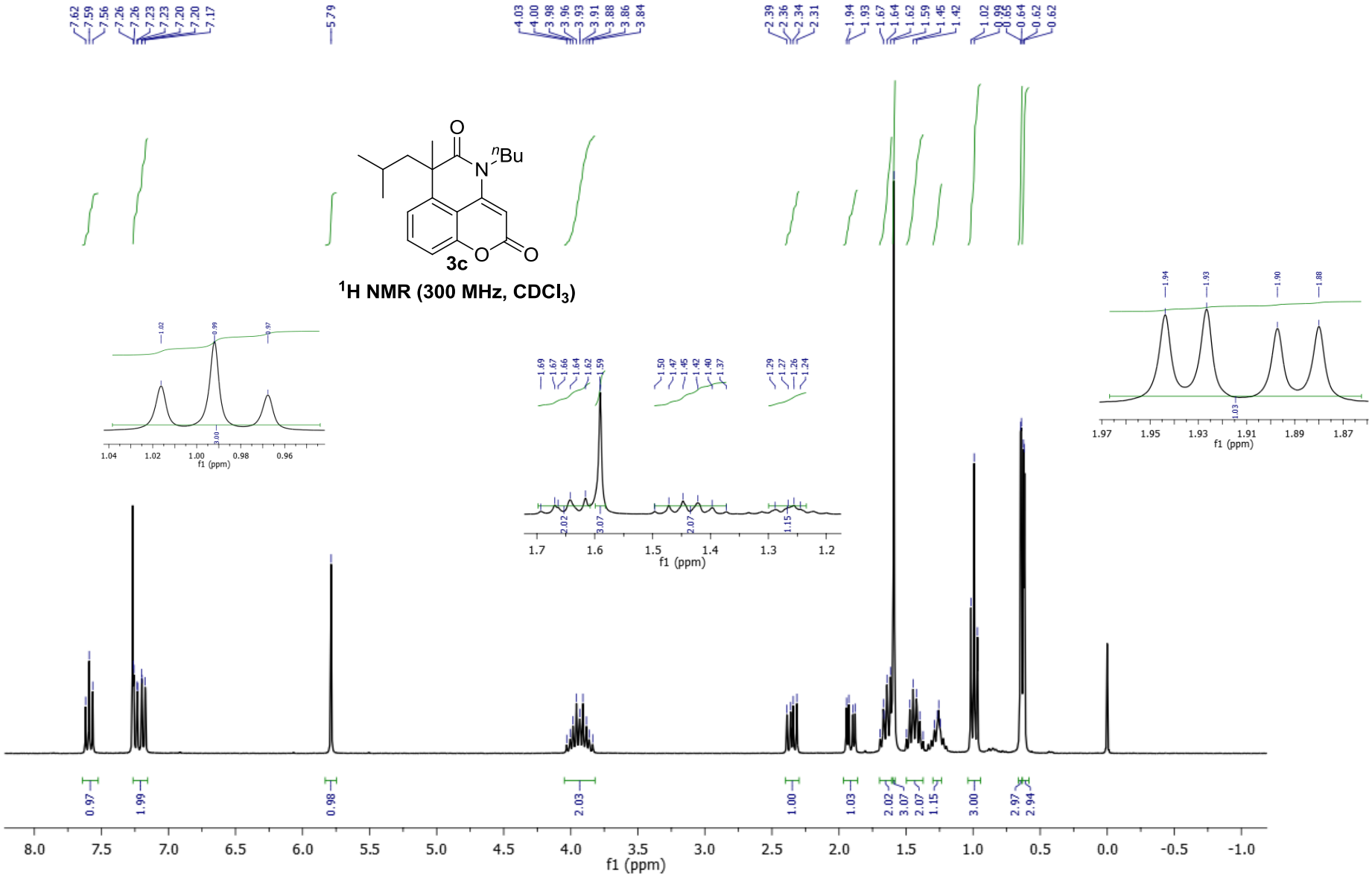


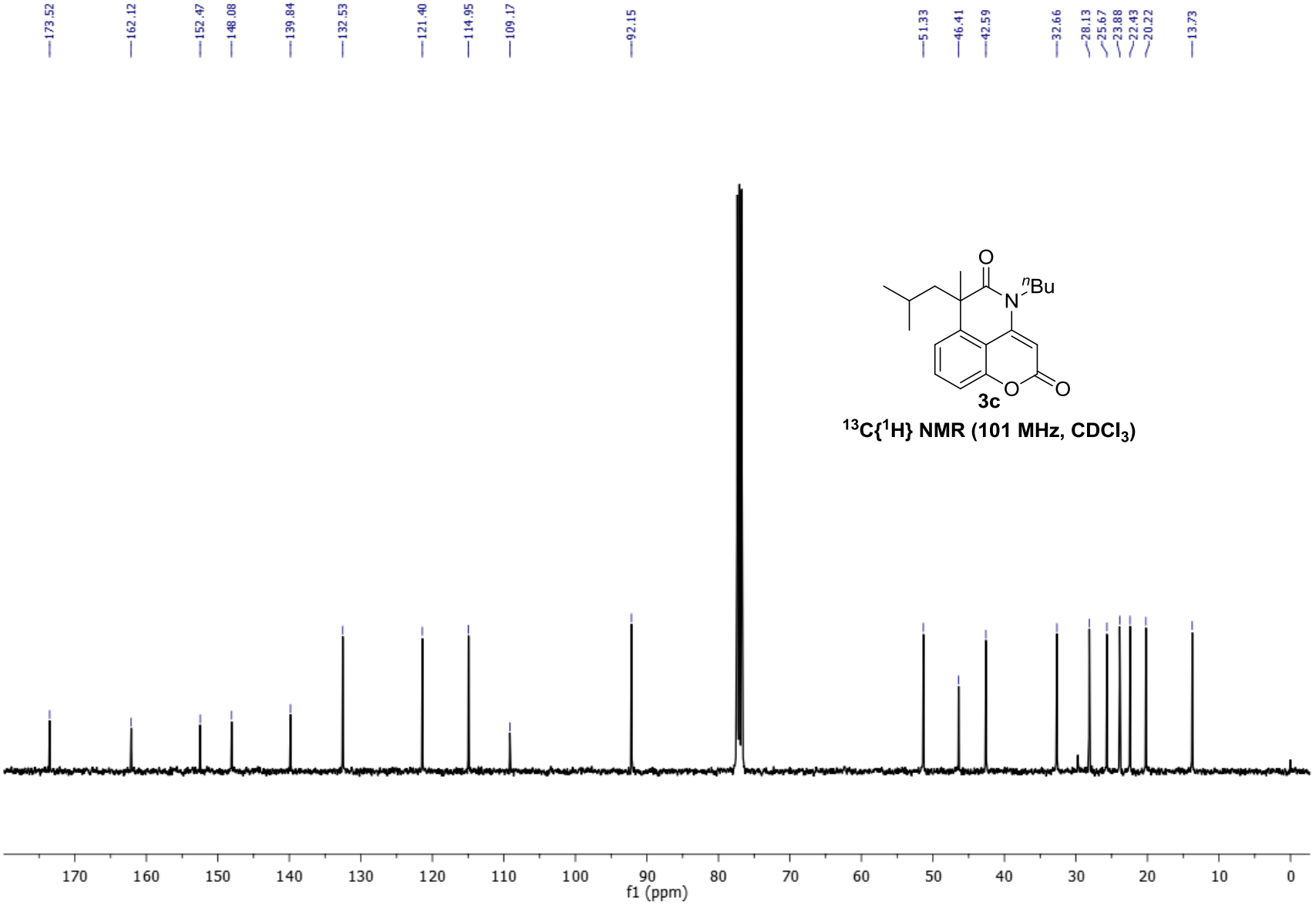
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)


3b
1H NMR (500 MHz, CDCl3)
f1 (ppm)



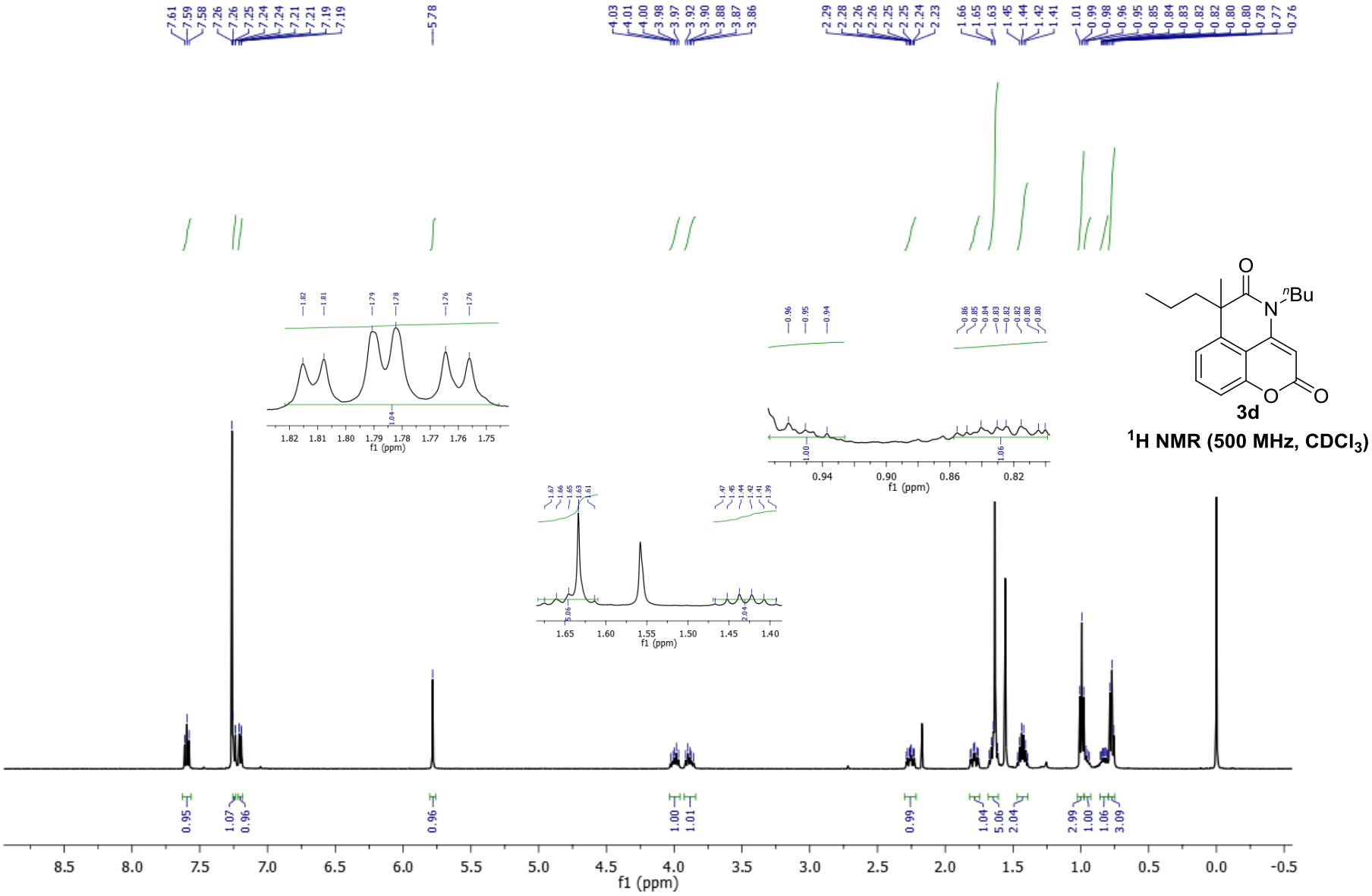
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

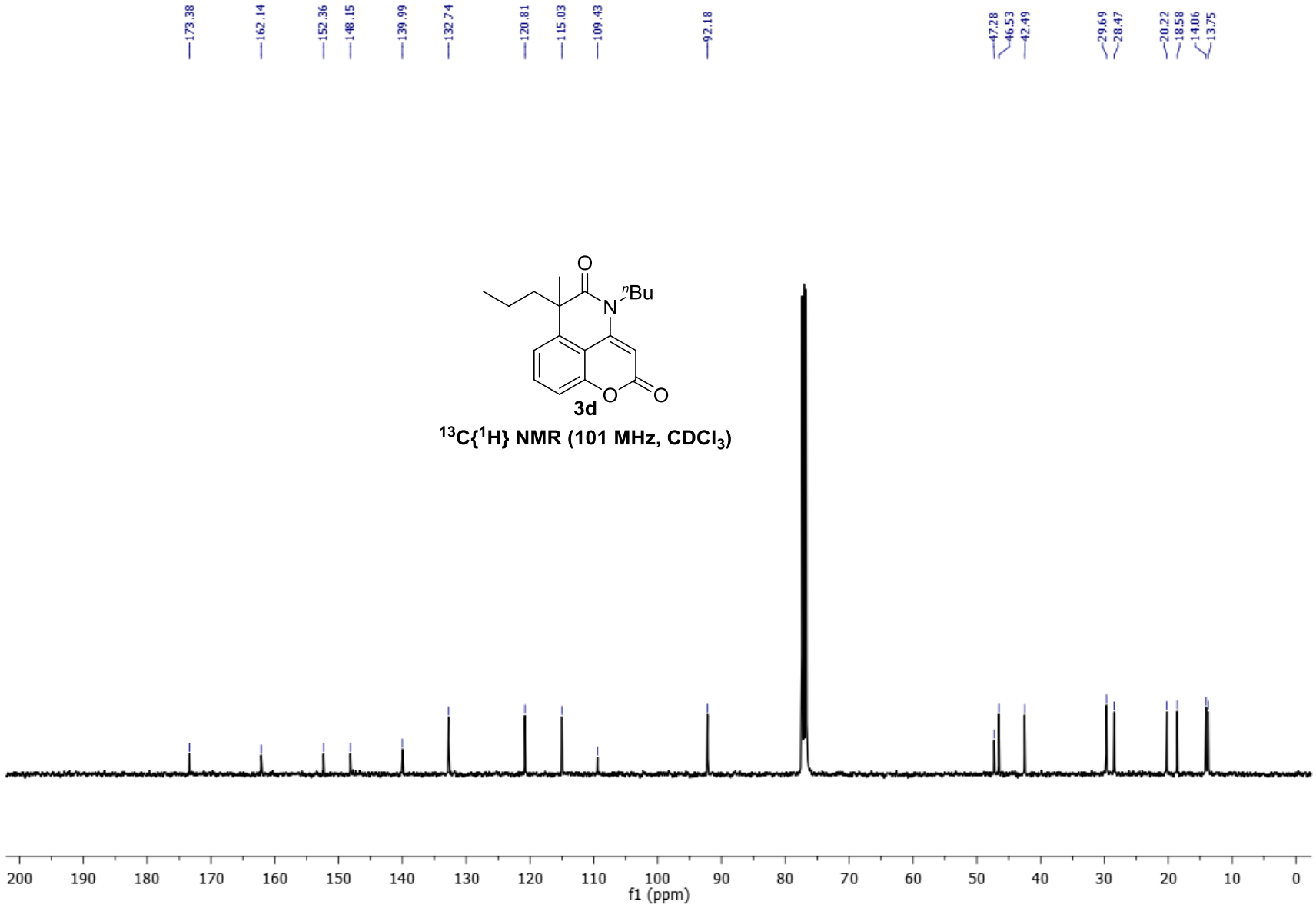

7.62
7.59
7.56
7.26
7.26
7.23
7.23
7.20
7.20
7.17
5.79
4.03
4.00
3.98
3.96
3.93
3.91
3.88
3.86
3.84
2.39
2.36
2.34
2.31
1.94
1.93
1.67
1.64
1.62
1.59
1.45
1.42
1.02
0.99
0.65
0.64
0.62
0.62
O
N
nBu
O
O
3c
1H NMR (300 MHz, CDCl3)
f1 (ppm)



3c

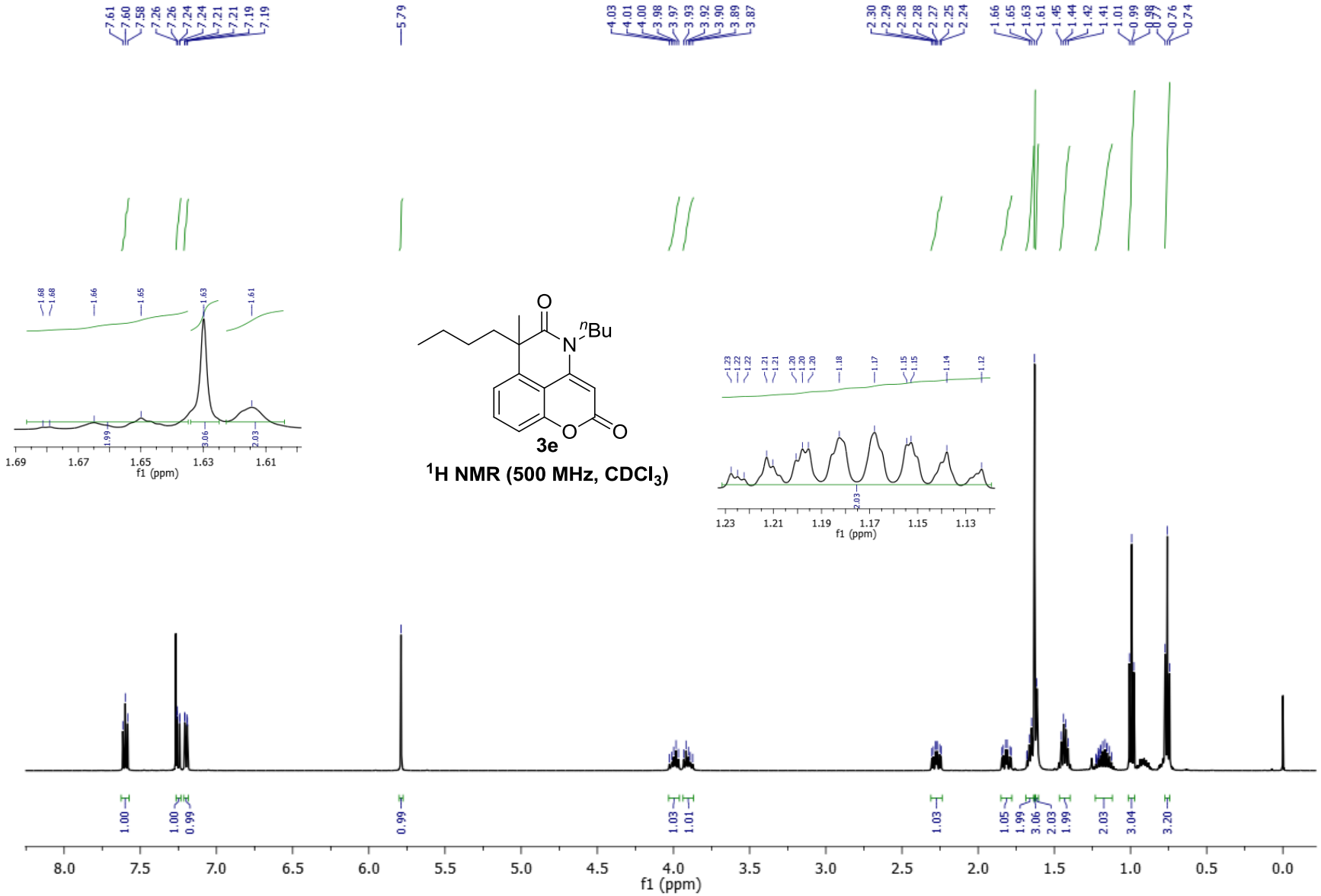
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

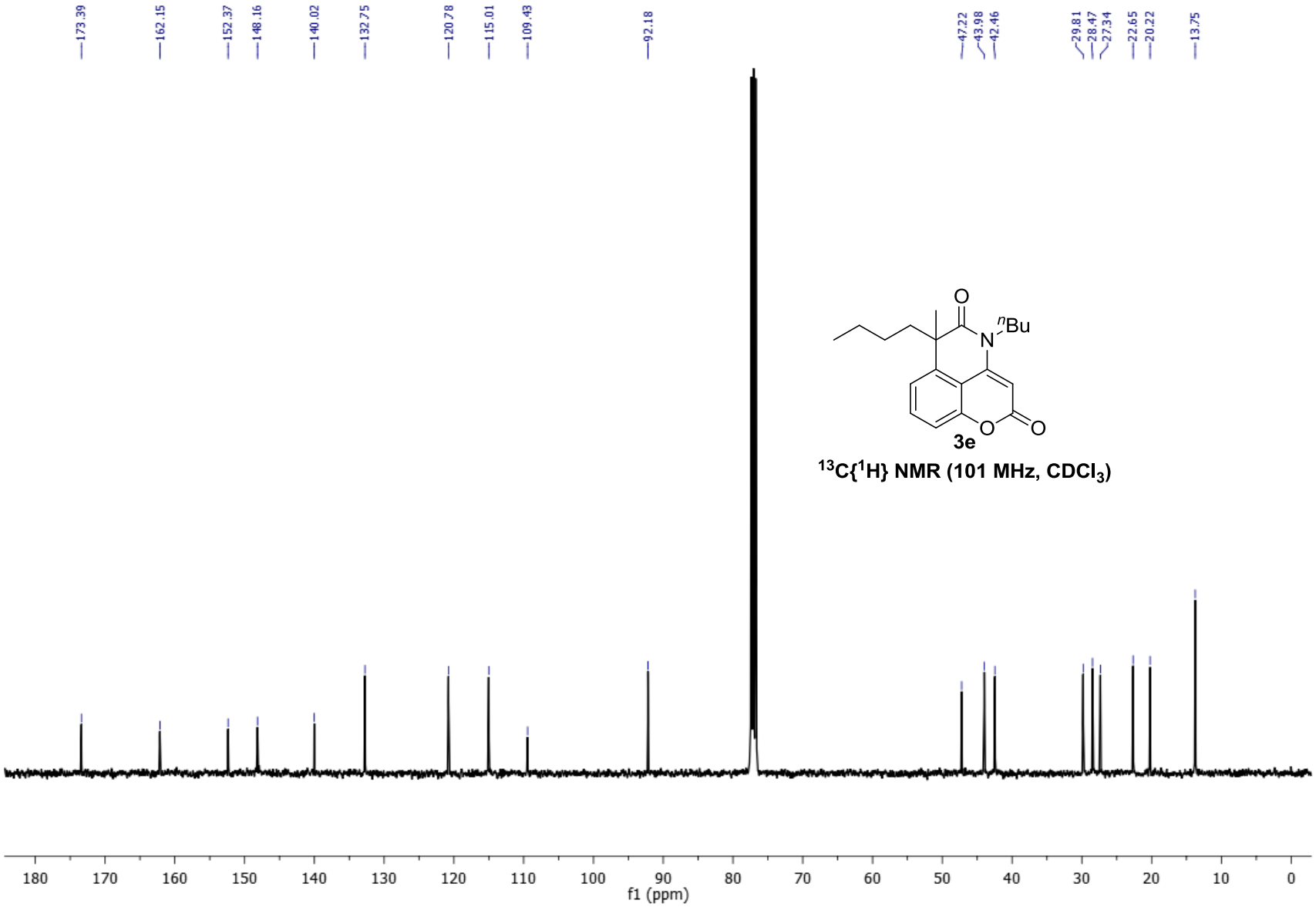

7.61 7.59 7.58 7.26 7.26 7.25 7.24 7.24 7.21 7.21 7.19 7.19
5.78
4.03 4.01 4.00 3.98 3.97 3.92 3.90 3.88 3.87 3.86
2.29 2.28 2.26 2.26 2.25 2.25 2.24 2.23
1.66 1.65 1.63 1.45 1.44 1.42 1.41
1.01 0.99 0.98 0.96 0.95 0.85 0.84 0.83 0.82 0.82 0.80 0.80 0.78 0.77 0.76
1.82 1.81 1.79 1.78 1.76 1.76
1.82 1.81 1.80 1.79 1.78 1.77 1.76 1.75
f1 (ppm)
0.96 0.95 0.94
0.86 0.85 0.84 0.83 0.82 0.82 0.80 0.80
1.00 1.06
0.94 0.90 0.86 0.82
f1 (ppm)
1.67 1.66 1.65 1.63 1.61
1.47 1.45 1.44 1.42 1.41 1.39
3.06 2.04
1.65 1.60 1.55 1.50 1.45 1.40
f1 (ppm)
O
N
nBu
O
O
3d
1H NMR (500 MHz, CDCl3)
0.95 1.07 0.96 0.96 1.00 1.01 0.99 1.04 5.06 2.04 2.99 1.00 1.06 3.09
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 0.0 -0.5
f1 (ppm)



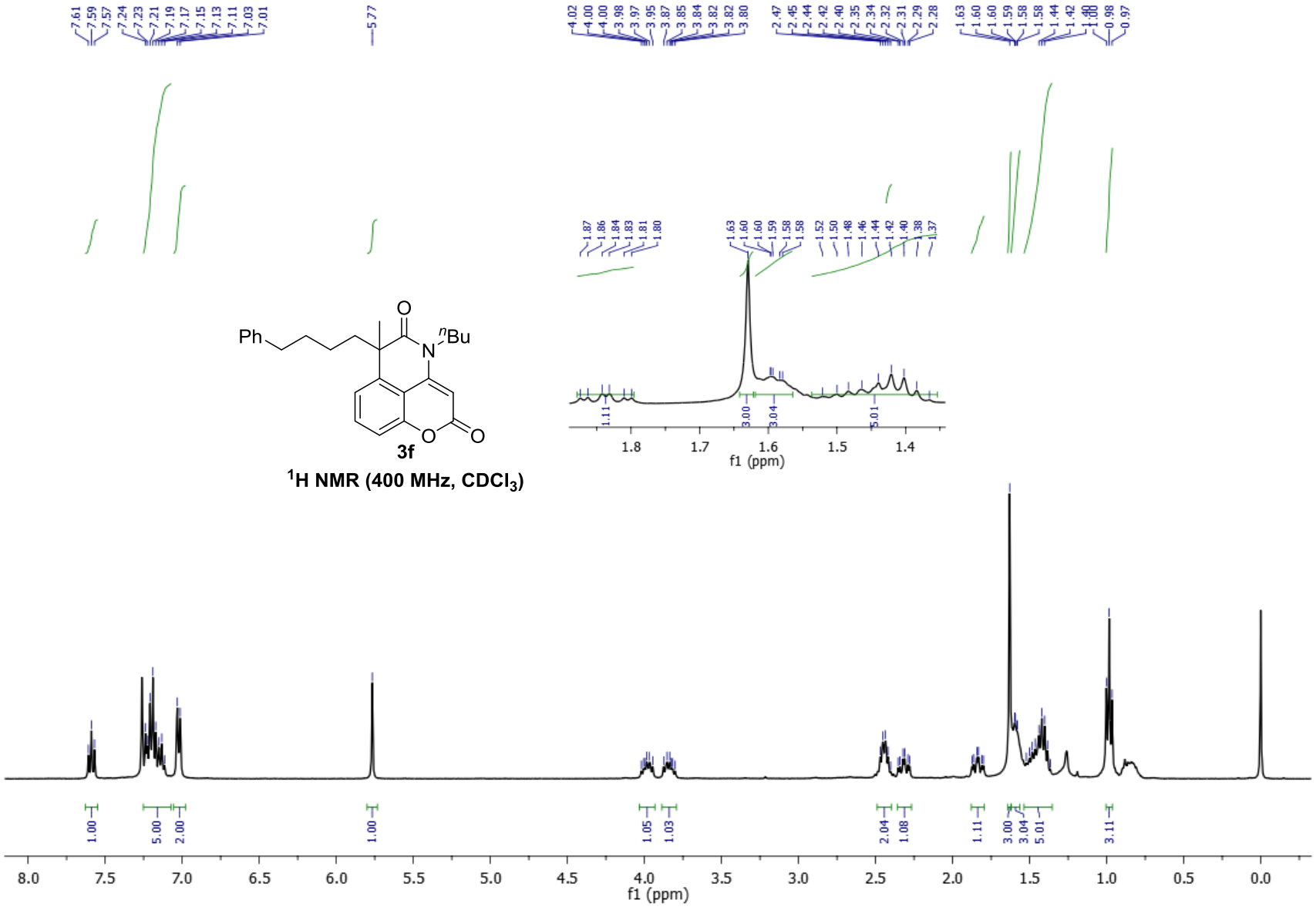
3d

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

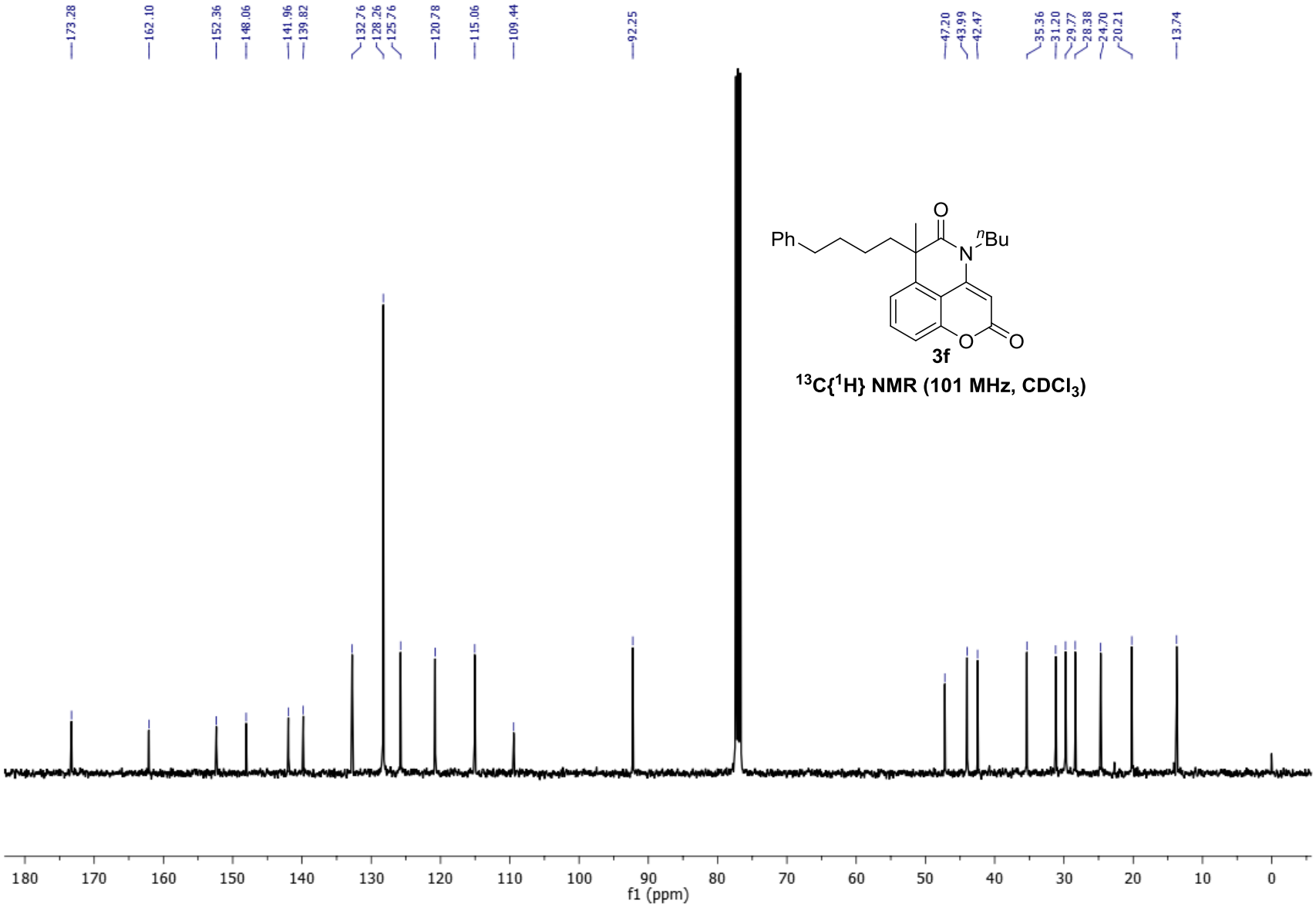

3e
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)



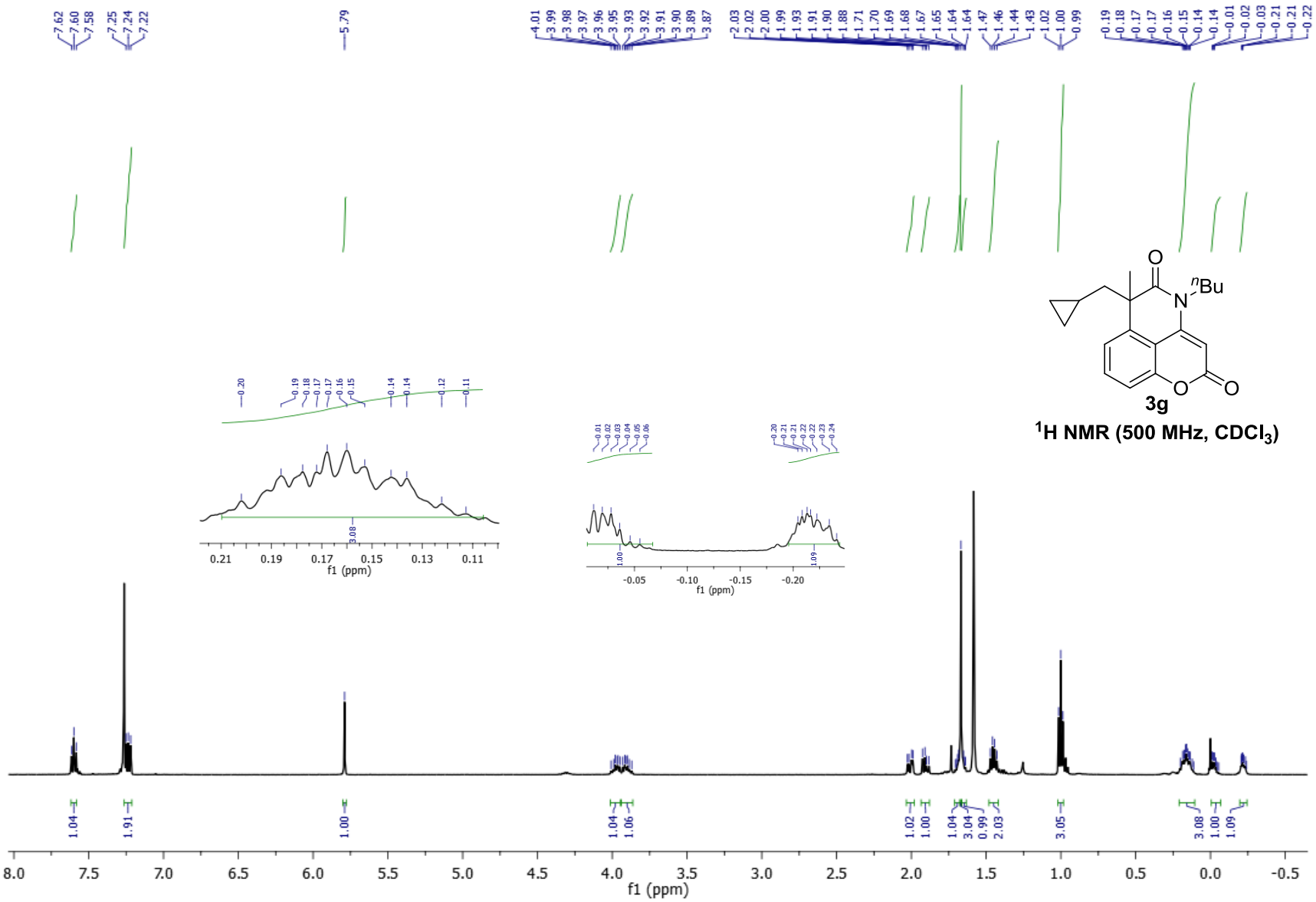
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

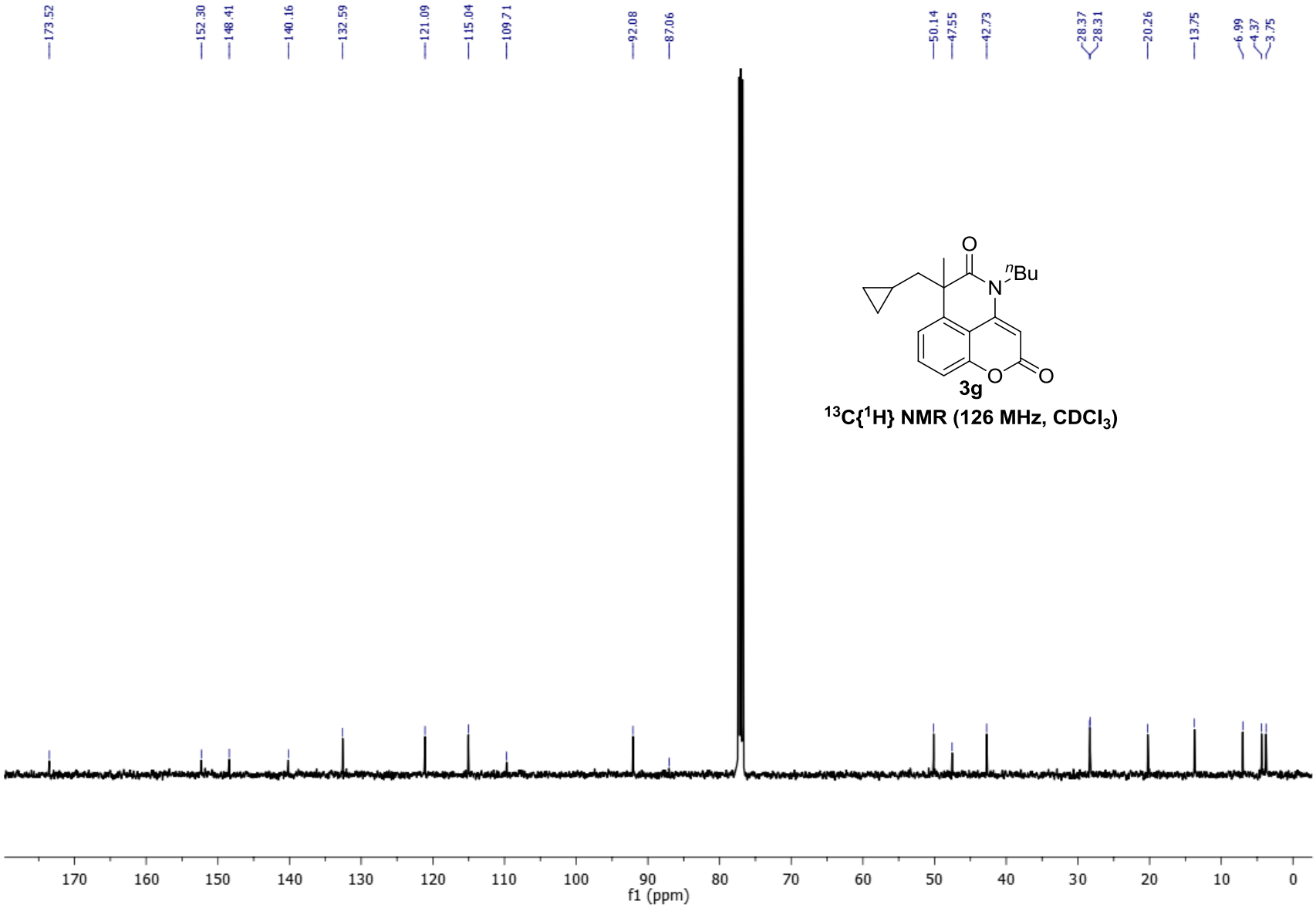


^{1}H NMR (400 MHz, $CDCl_3$)

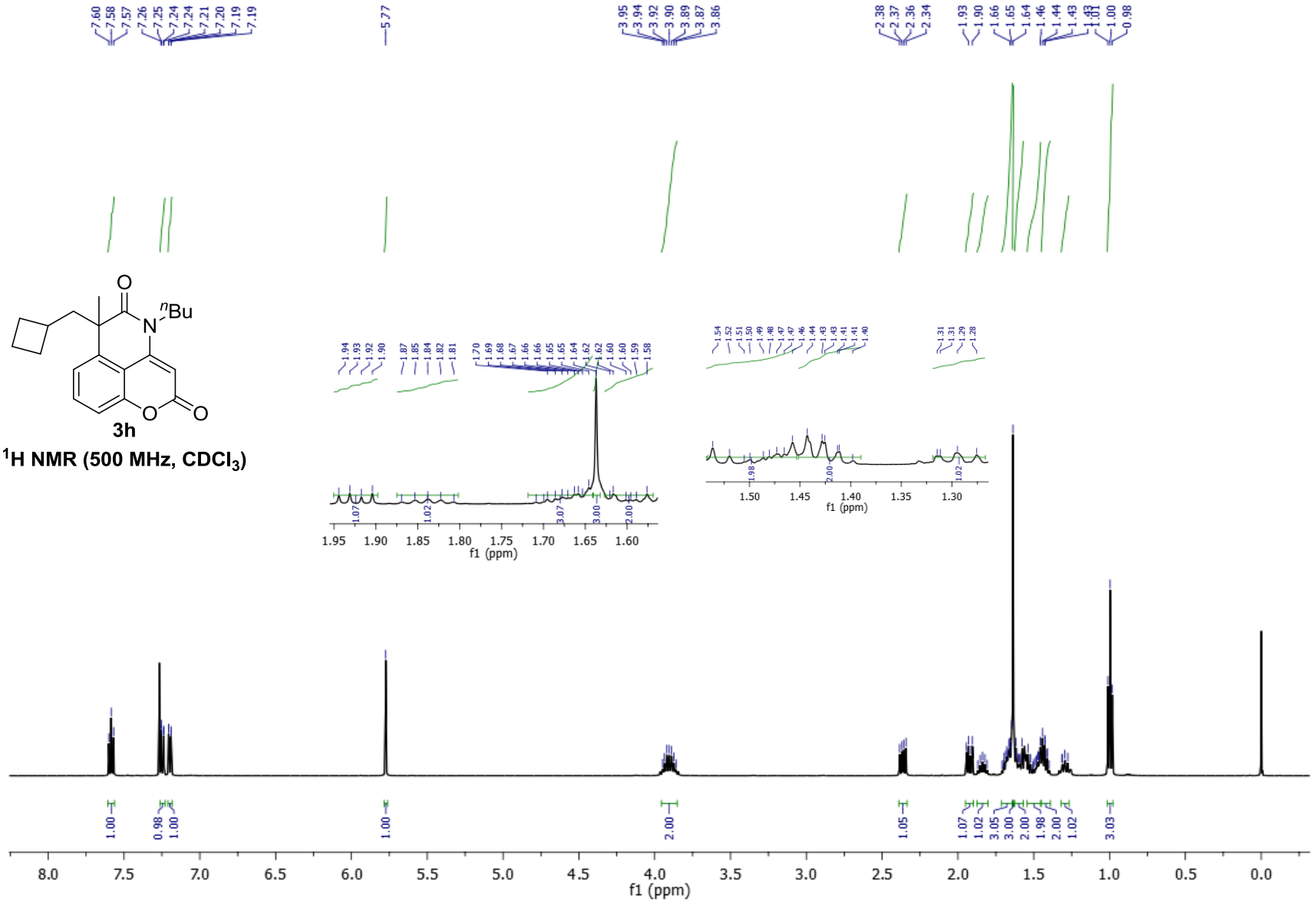


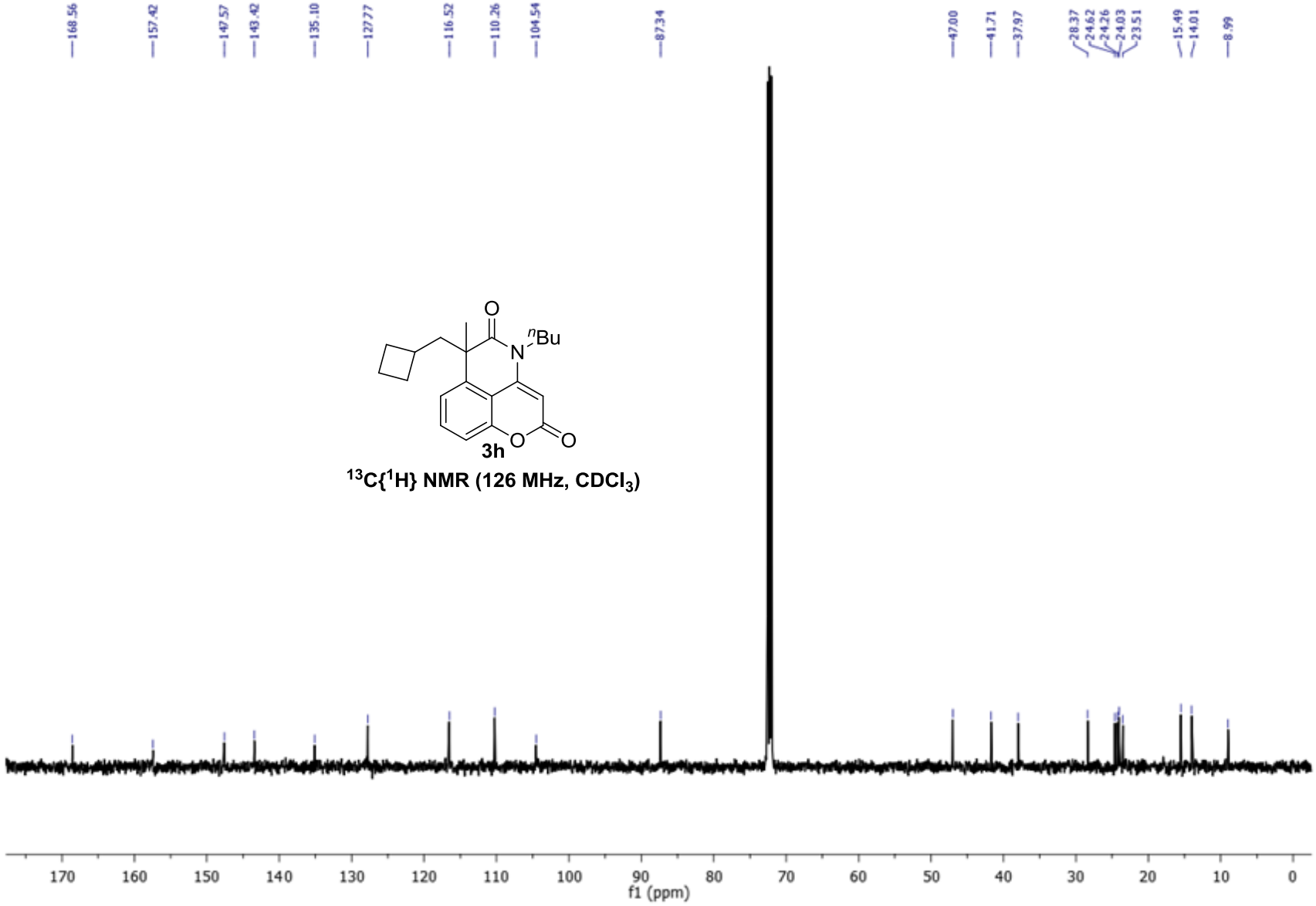
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)


7.62
7.60
7.58
7.25
7.24
7.22
5.79
4.01
3.99
3.98
3.97
3.96
3.95
3.93
3.92
3.91
3.90
3.89
3.87
2.03
2.02
2.00
1.99
1.93
1.91
1.90
1.88
1.71
1.70
1.69
1.68
1.67
1.65
1.64
1.64
1.47
1.46
1.44
1.43
1.02
1.00
0.99
0.19
0.18
0.17
0.17
0.16
0.15
0.14
0.14
0.01
0.02
0.03
0.21
0.21
0.22
O
N
nBu
O
O
3g
1H NMR (500 MHz, CDCl3)
f1 (ppm)
f1 (ppm)
f1 (ppm)

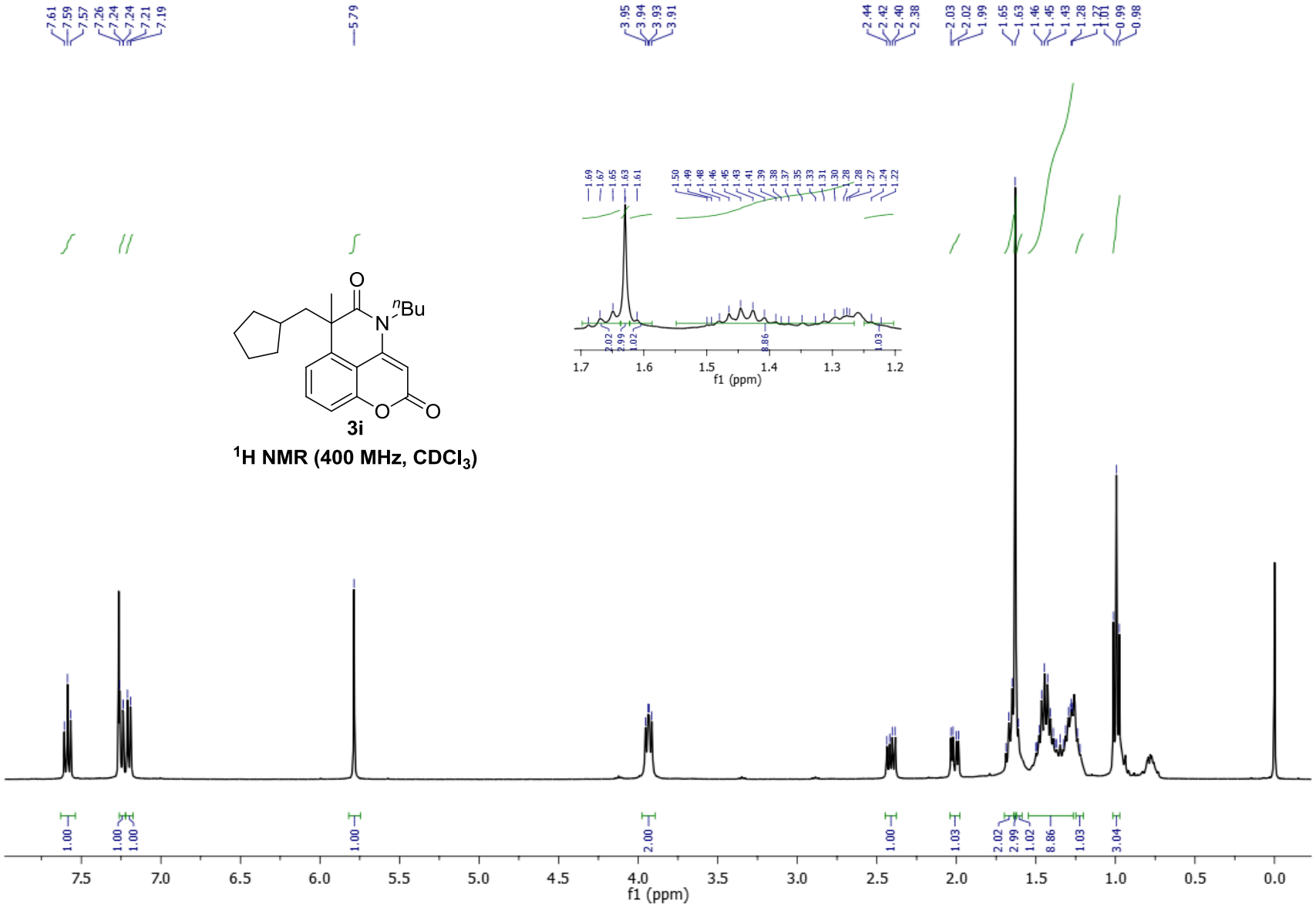


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)


3h
1H NMR (500 MHz, CDCl3)
f1 (ppm)

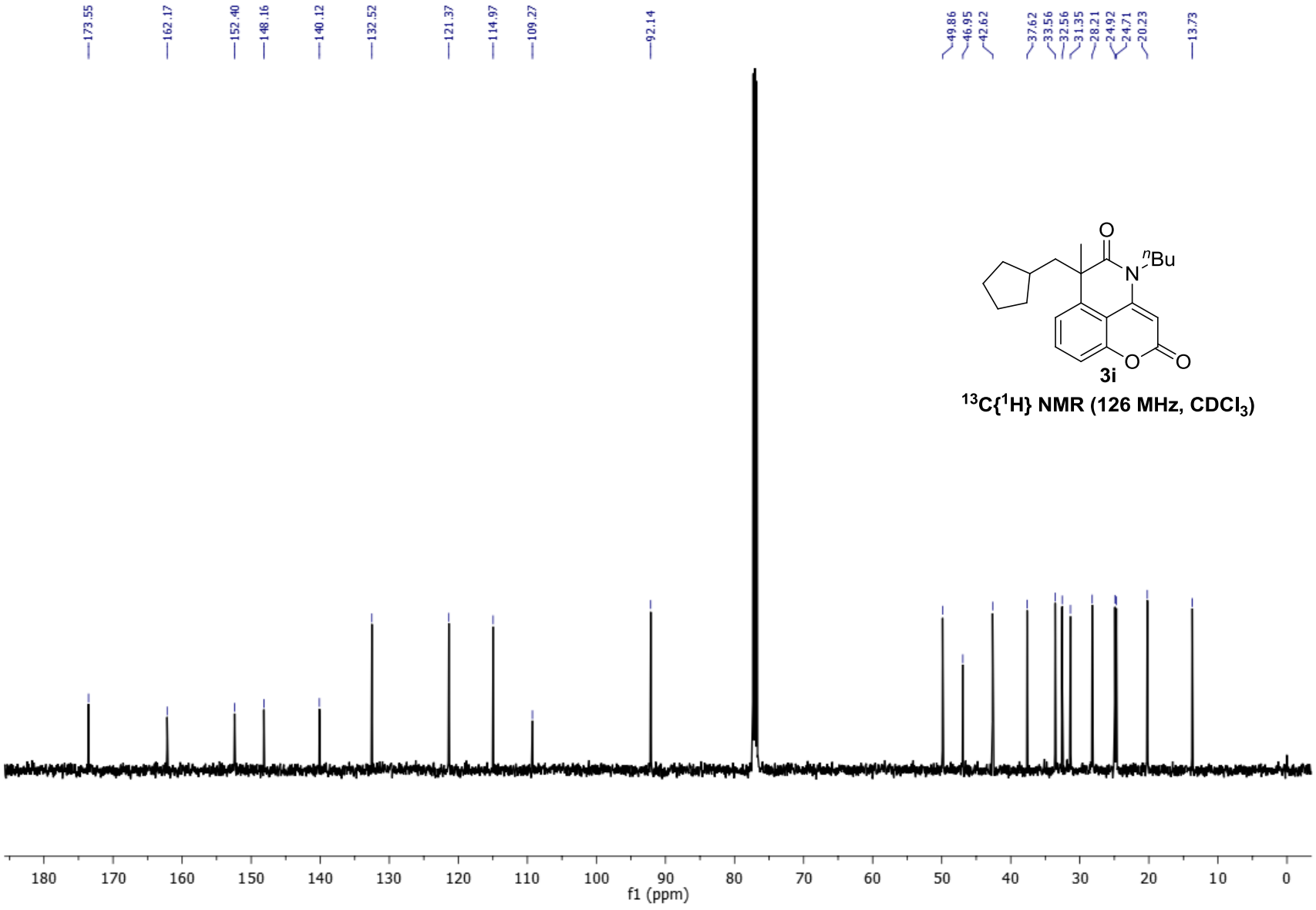


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



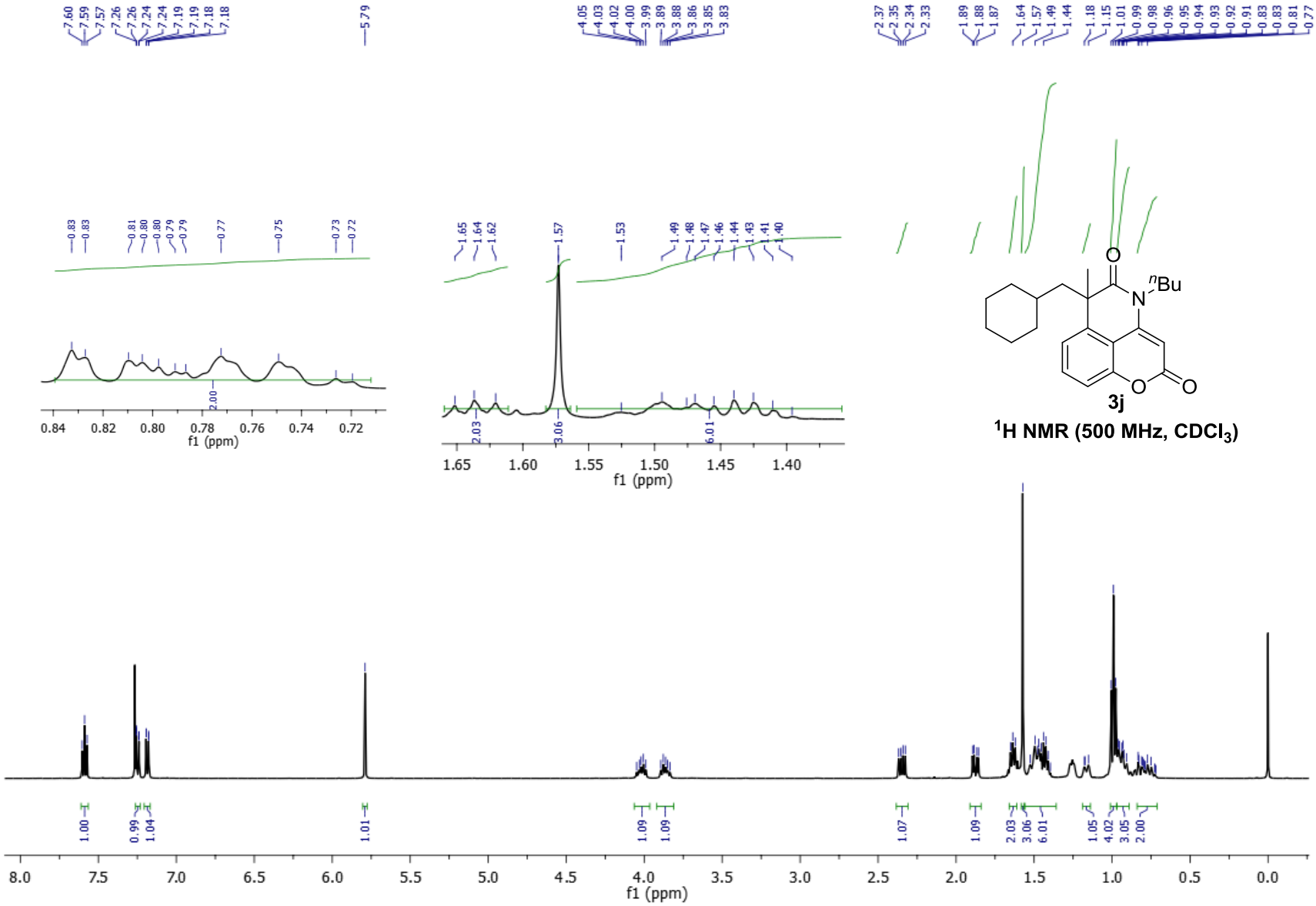
3i

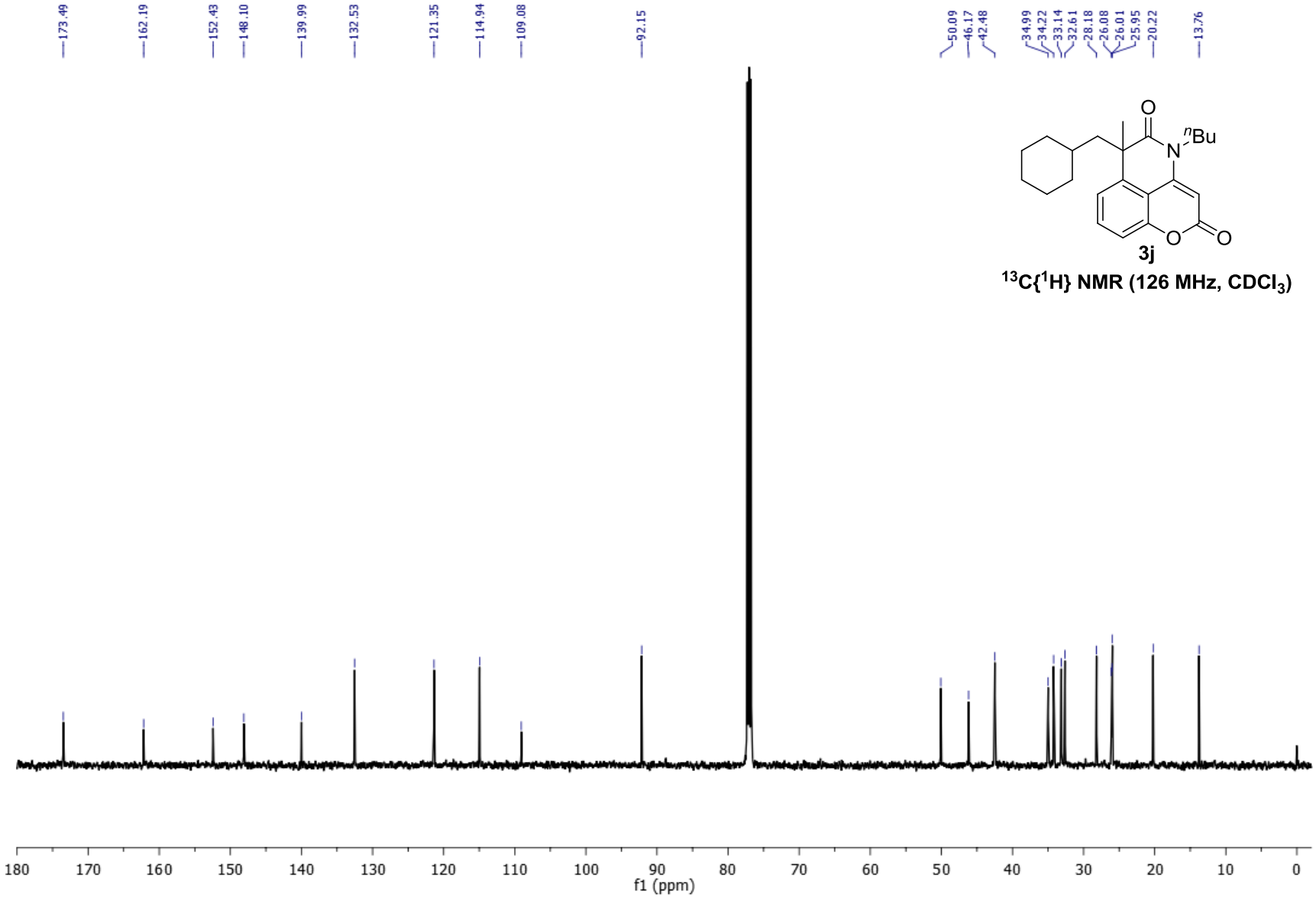
^{1}H NMR (400 MHz, $CDCl_3$)



3i

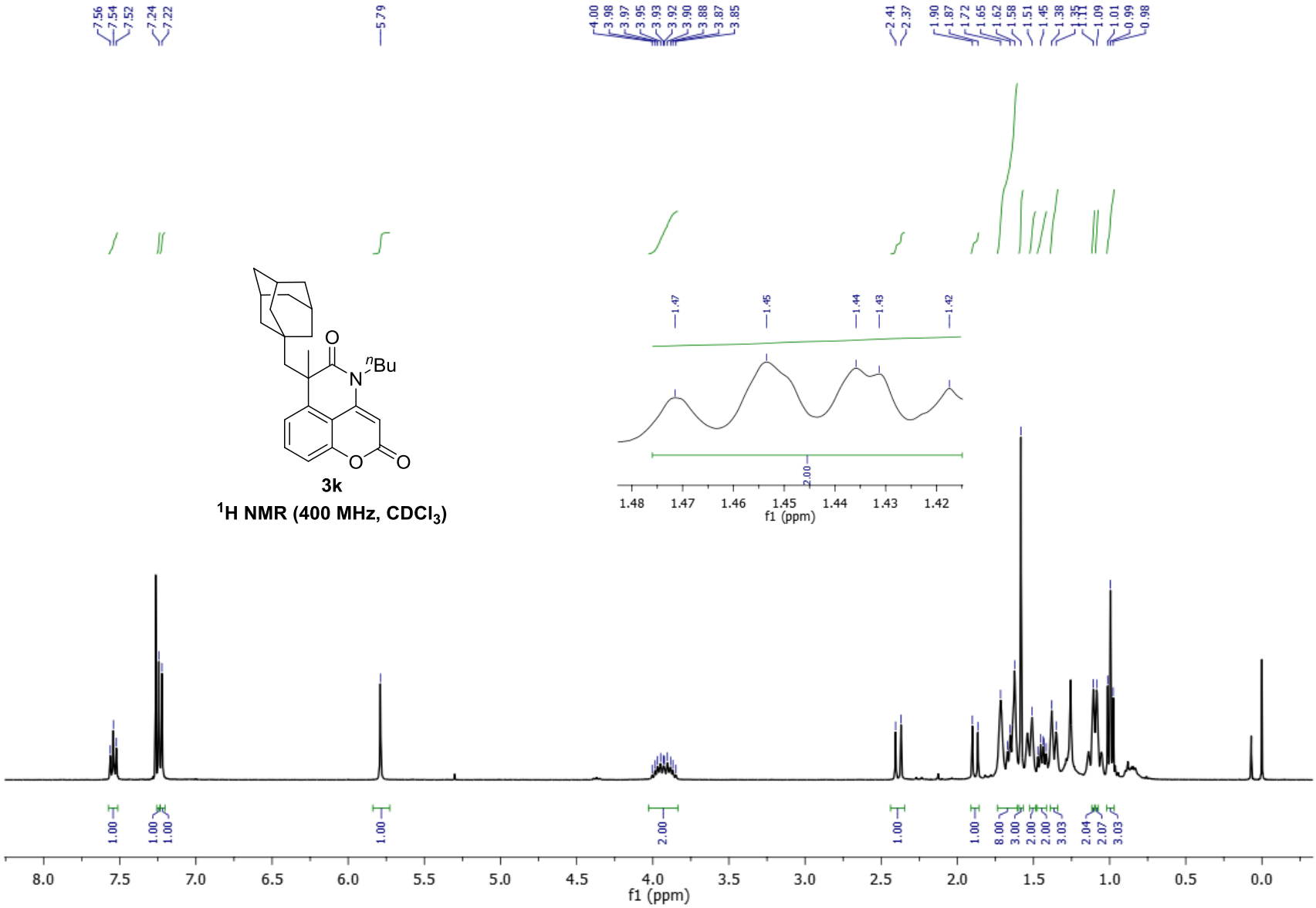
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)


7.60 7.59 7.57 7.26 7.26 7.24 7.24 7.19 7.19 7.18 7.18
5.79
4.05 4.03 4.02 4.00 3.99 3.89 3.88 3.86 3.85 3.83
2.37 2.35 2.34 2.33
1.89 1.88 1.87
1.64 1.57 1.49 1.44
1.18 1.15 1.01 0.99 0.98 0.96 0.95 0.94 0.93 0.92 0.91 0.83 0.83 0.81 0.77
0.83 0.83 0.81 0.80 0.80 0.79 0.79 0.77 0.75 0.73 0.72
2.00
0.84 0.82 0.80 0.78 0.76 0.74 0.72
f1 (ppm)
1.65 1.64 1.62 1.57 1.53 1.49 1.48 1.47 1.46 1.44 1.43 1.41 1.40
2.03 3.06 6.01
1.65 1.60 1.55 1.50 1.45 1.40
f1 (ppm)
O
N
nBu
O
O
3j
1H NMR (500 MHz, CDCl3)
1.00 0.99 1.04 1.01 1.09 1.09 1.07 1.09 2.03 3.06 6.01 1.05 4.02 3.05 2.00
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 0.0
f1 (ppm)



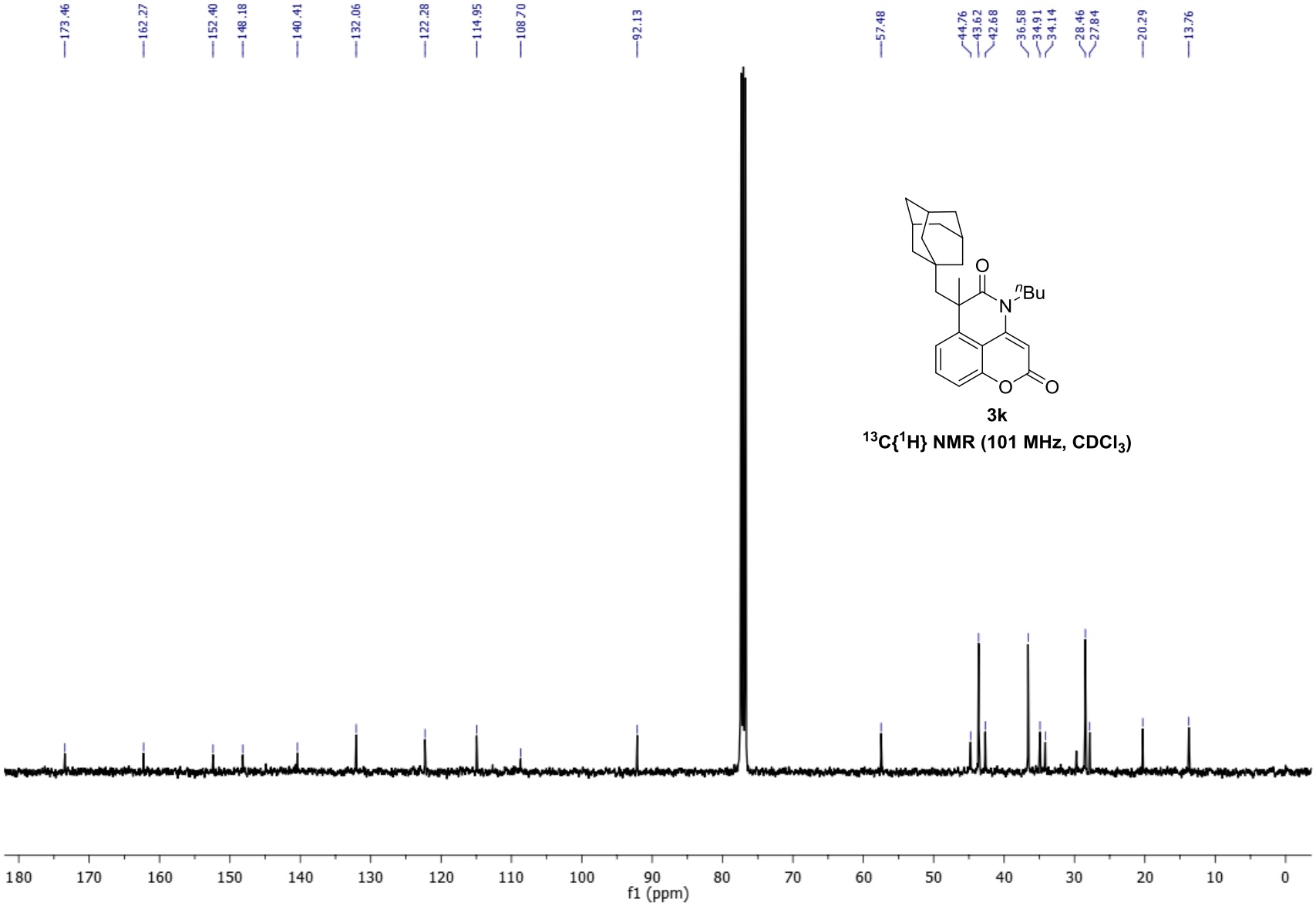
3j

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



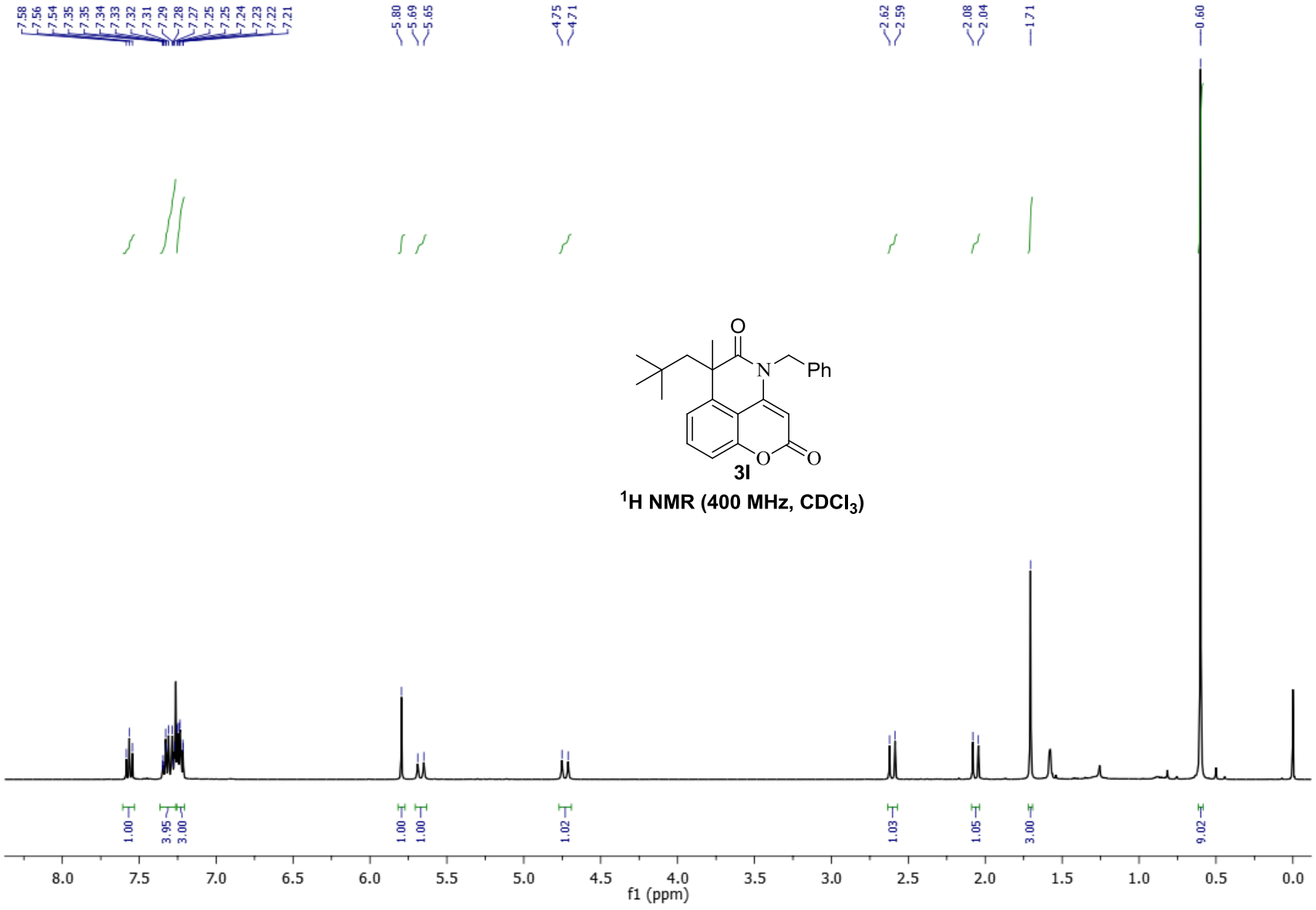
3k

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



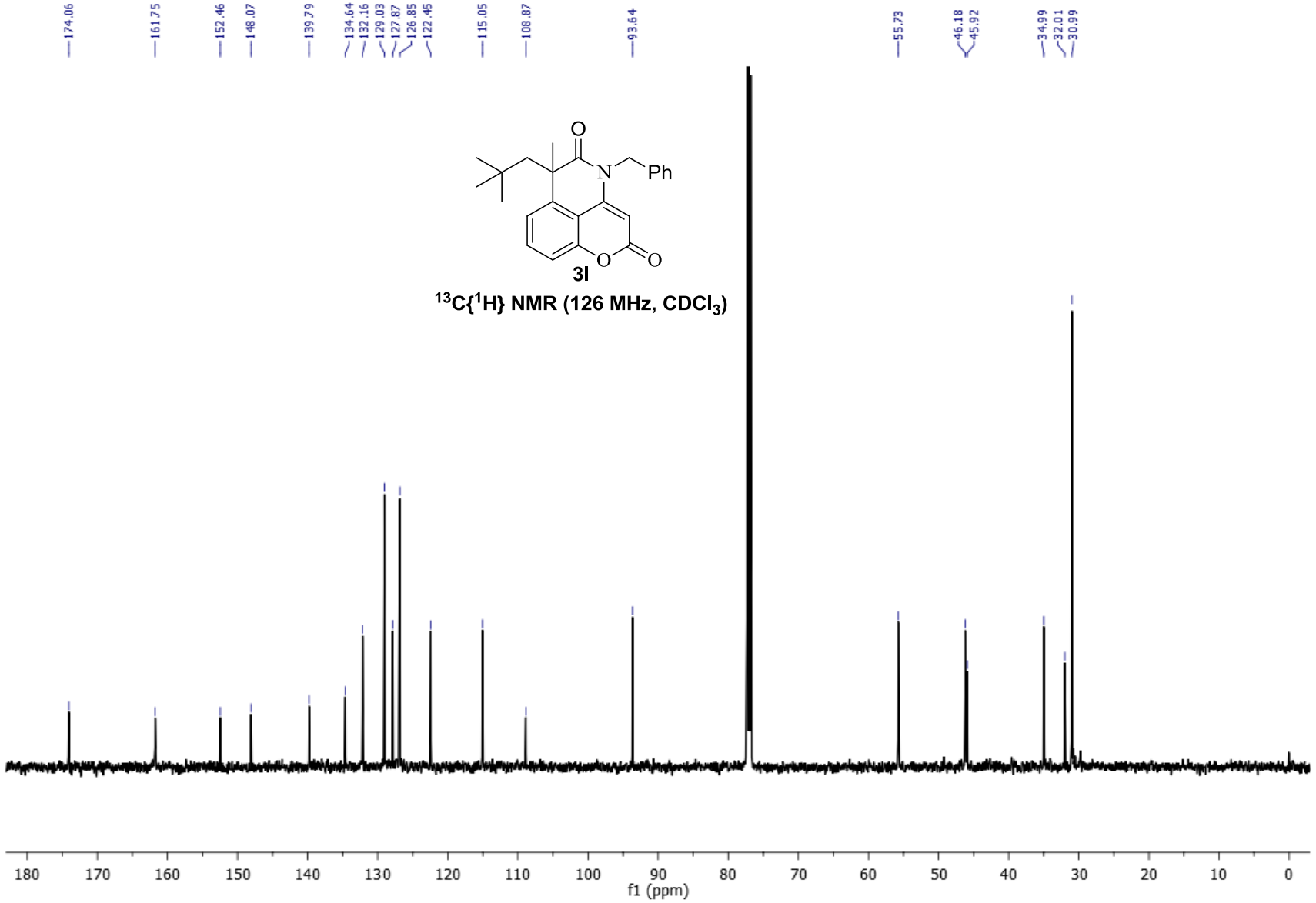
3k

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



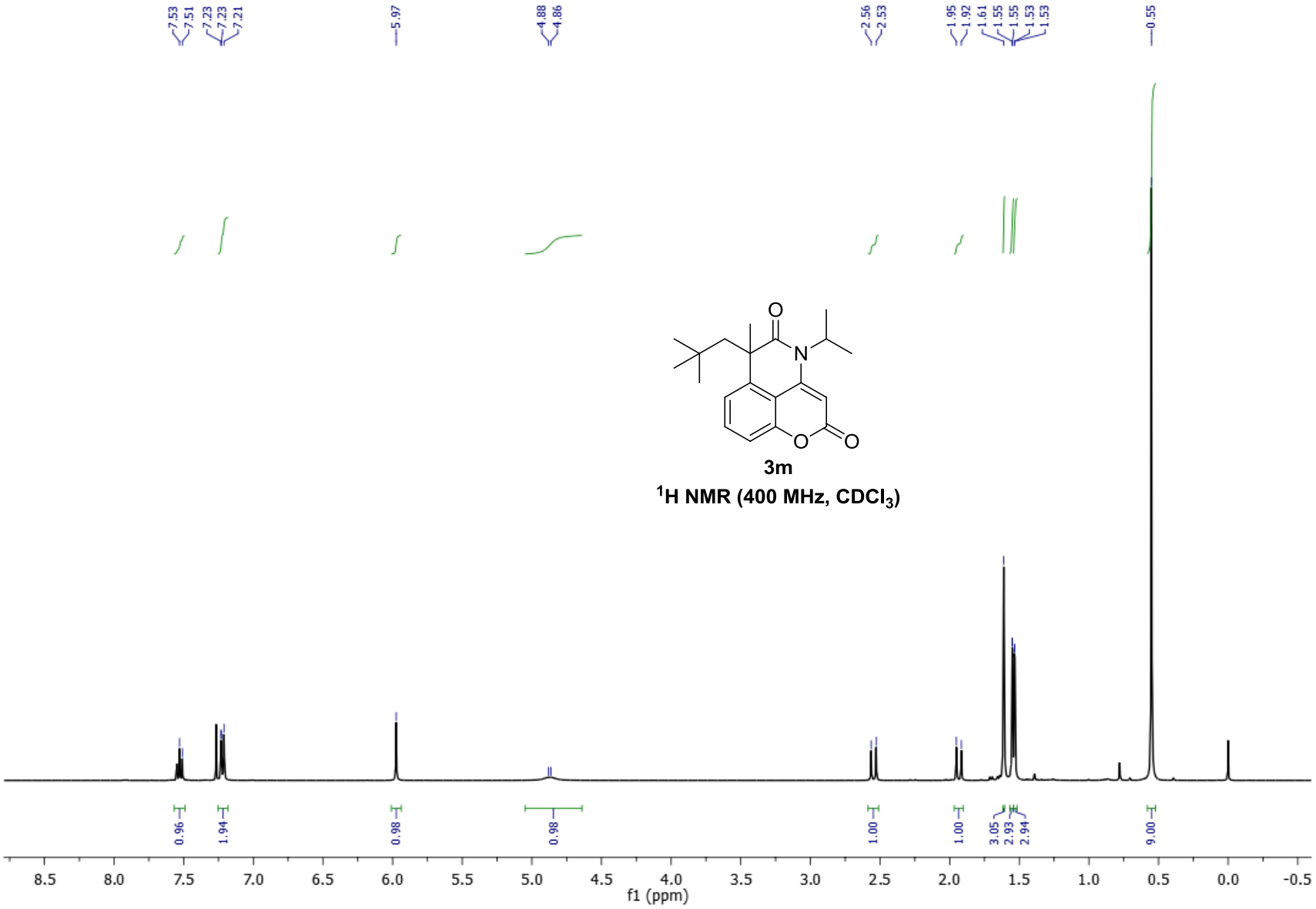
3l

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



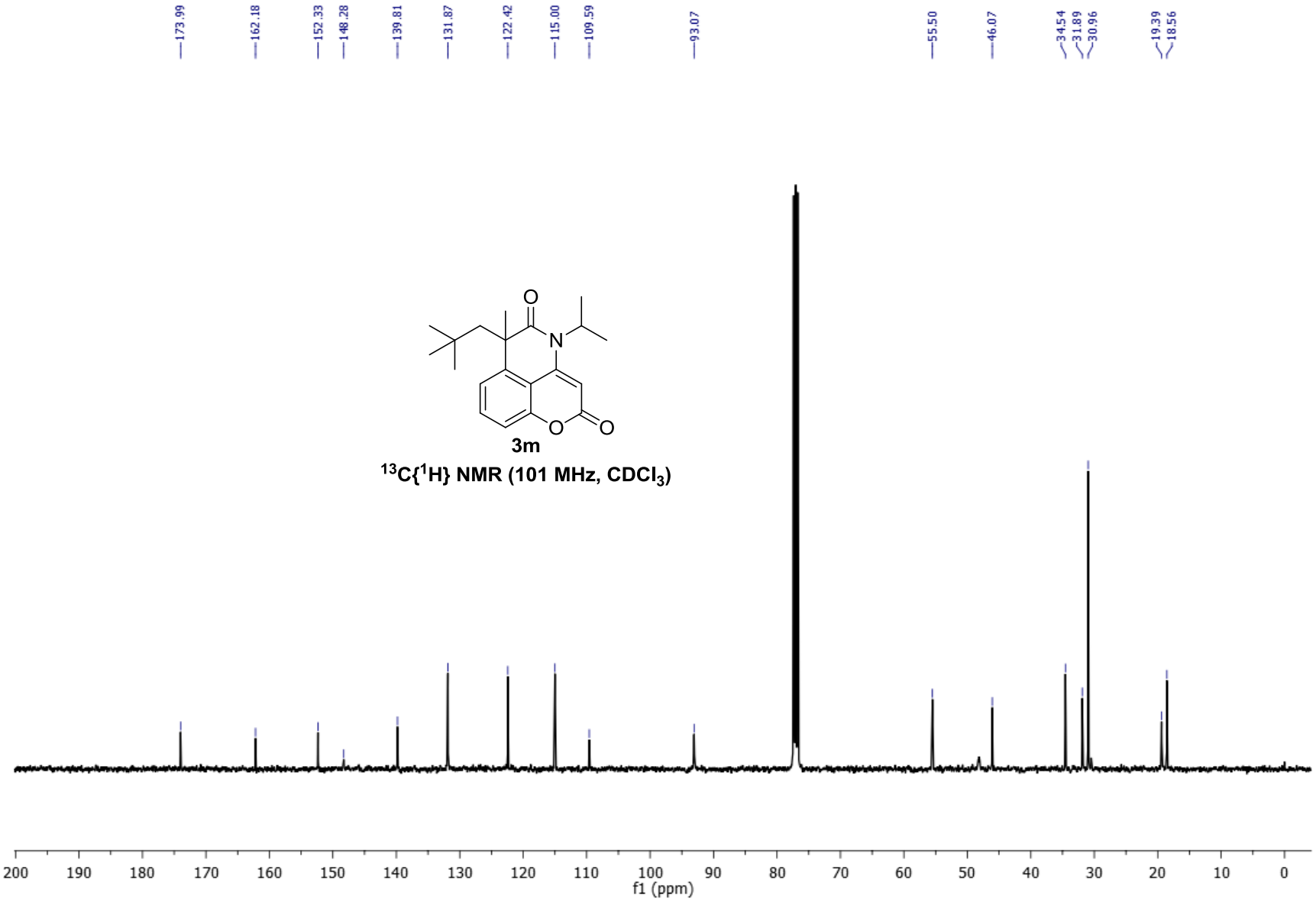
3l

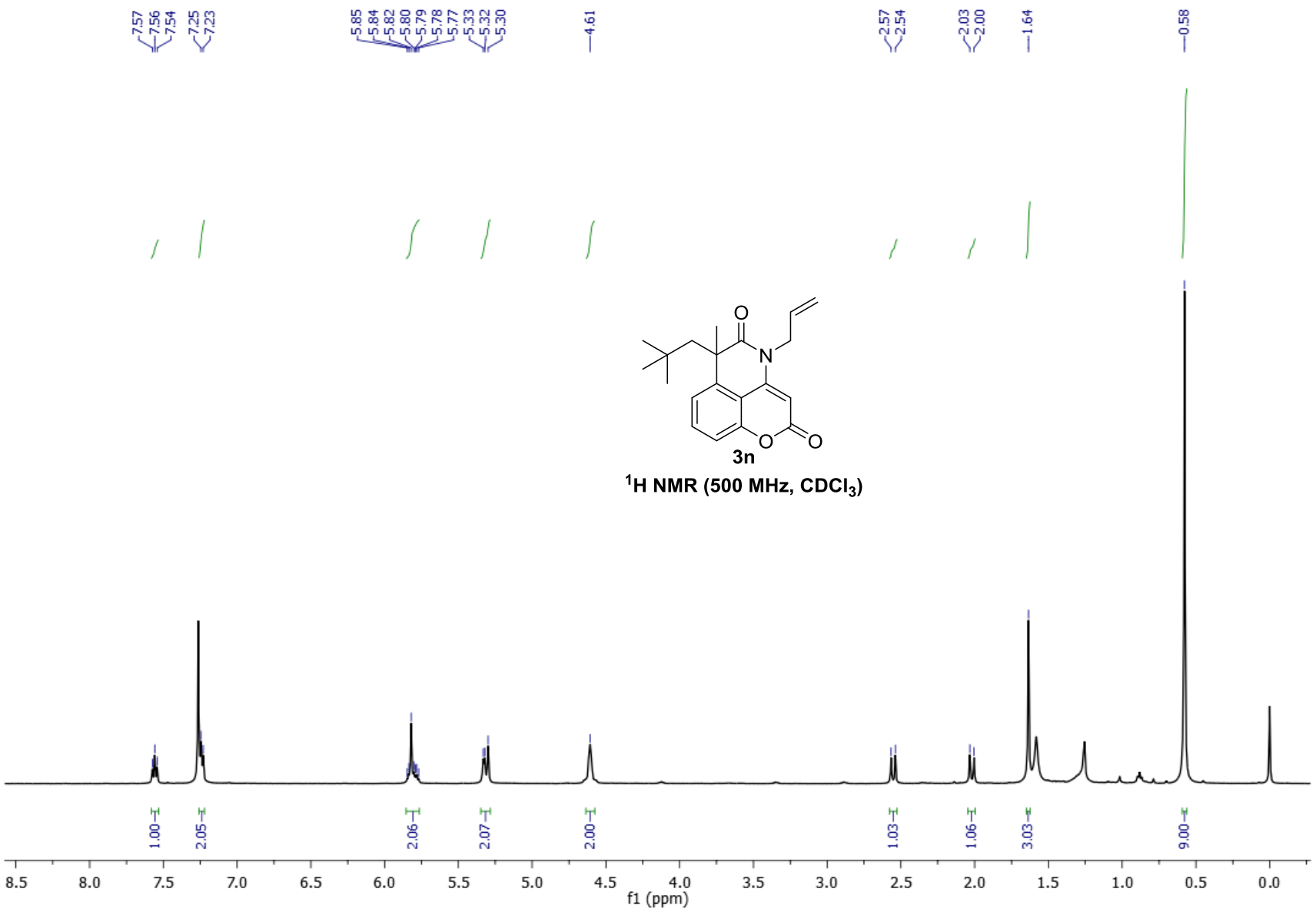
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



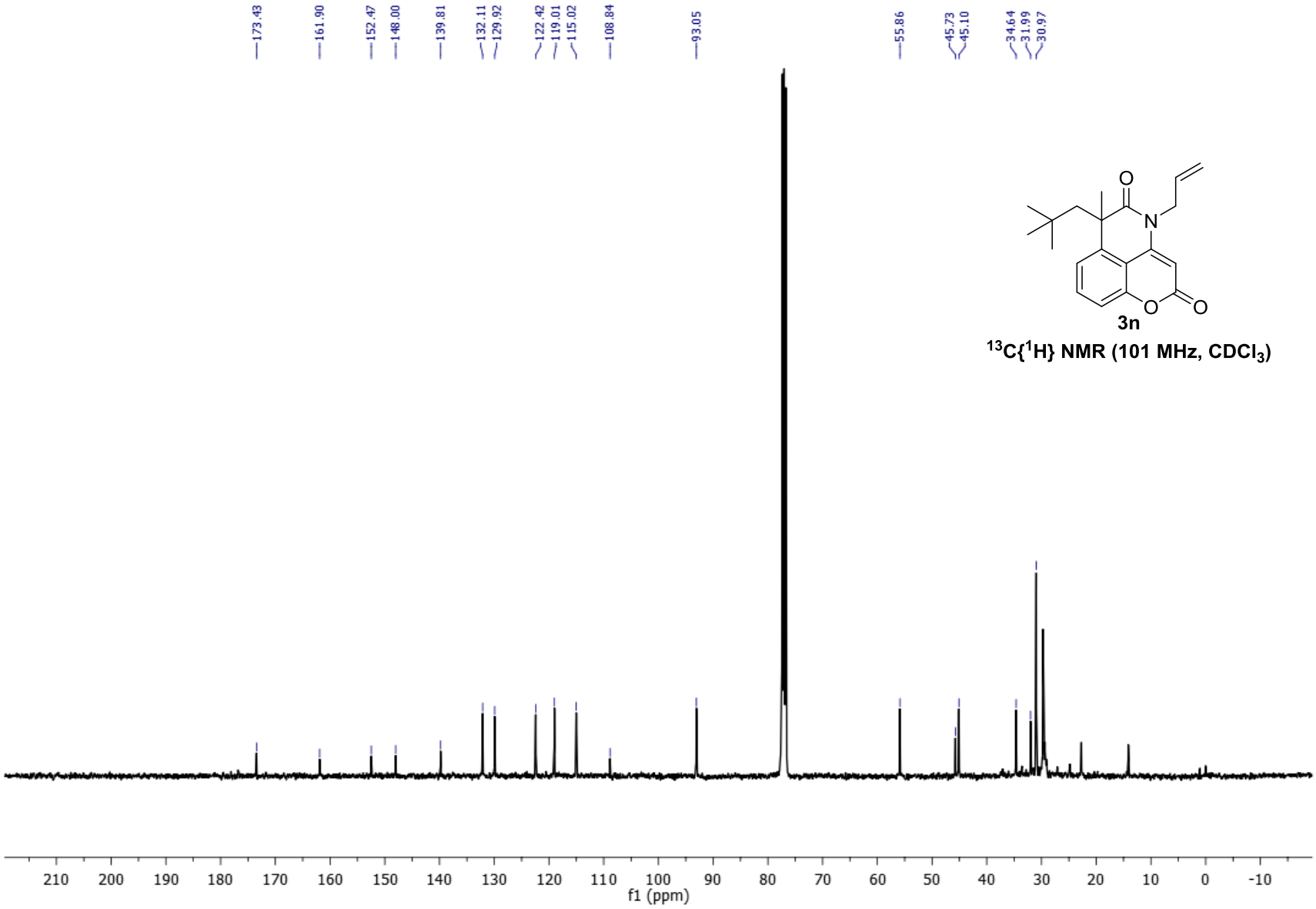
3m

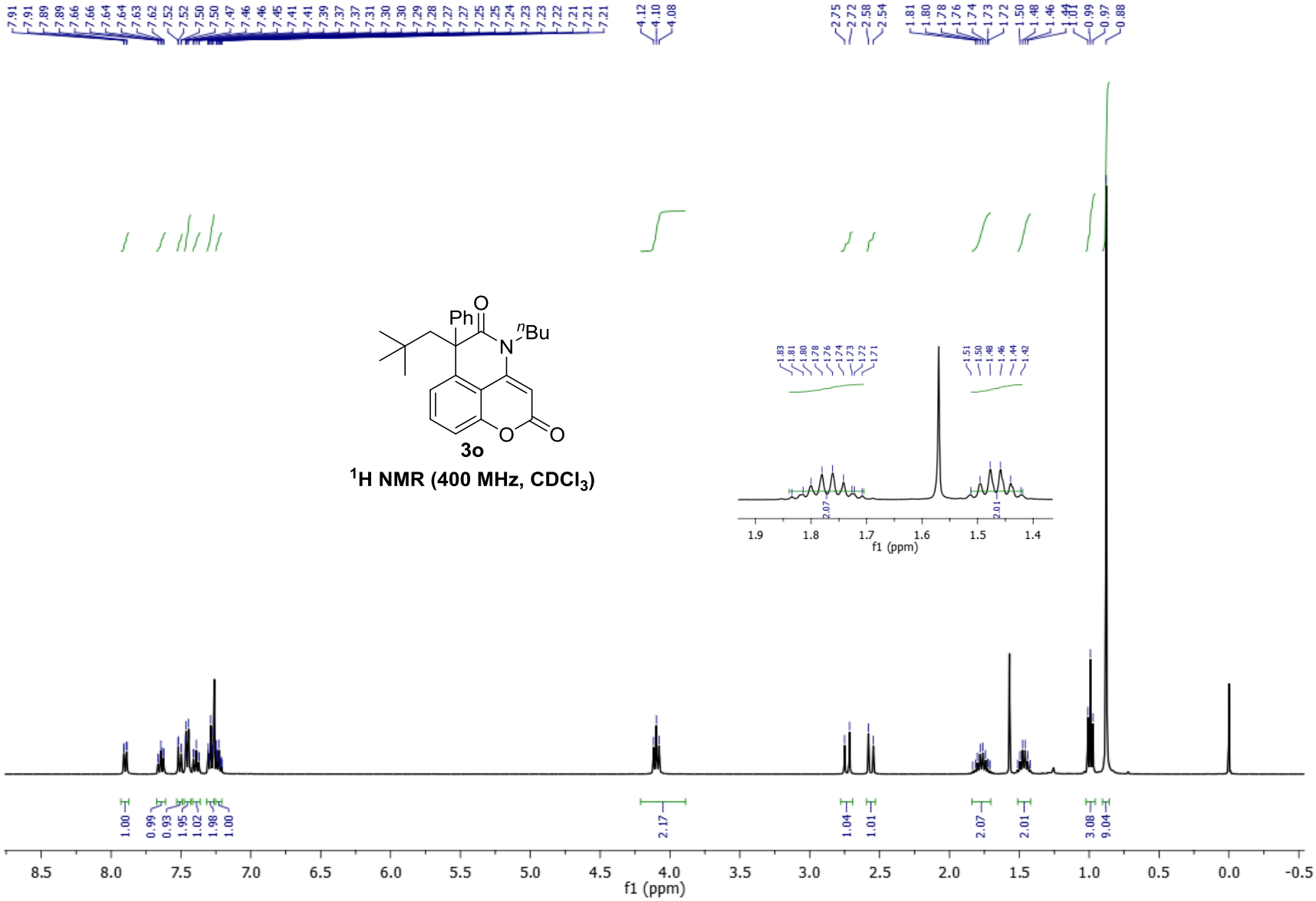
^{1}H NMR (400 MHz, $CDCl_3$)

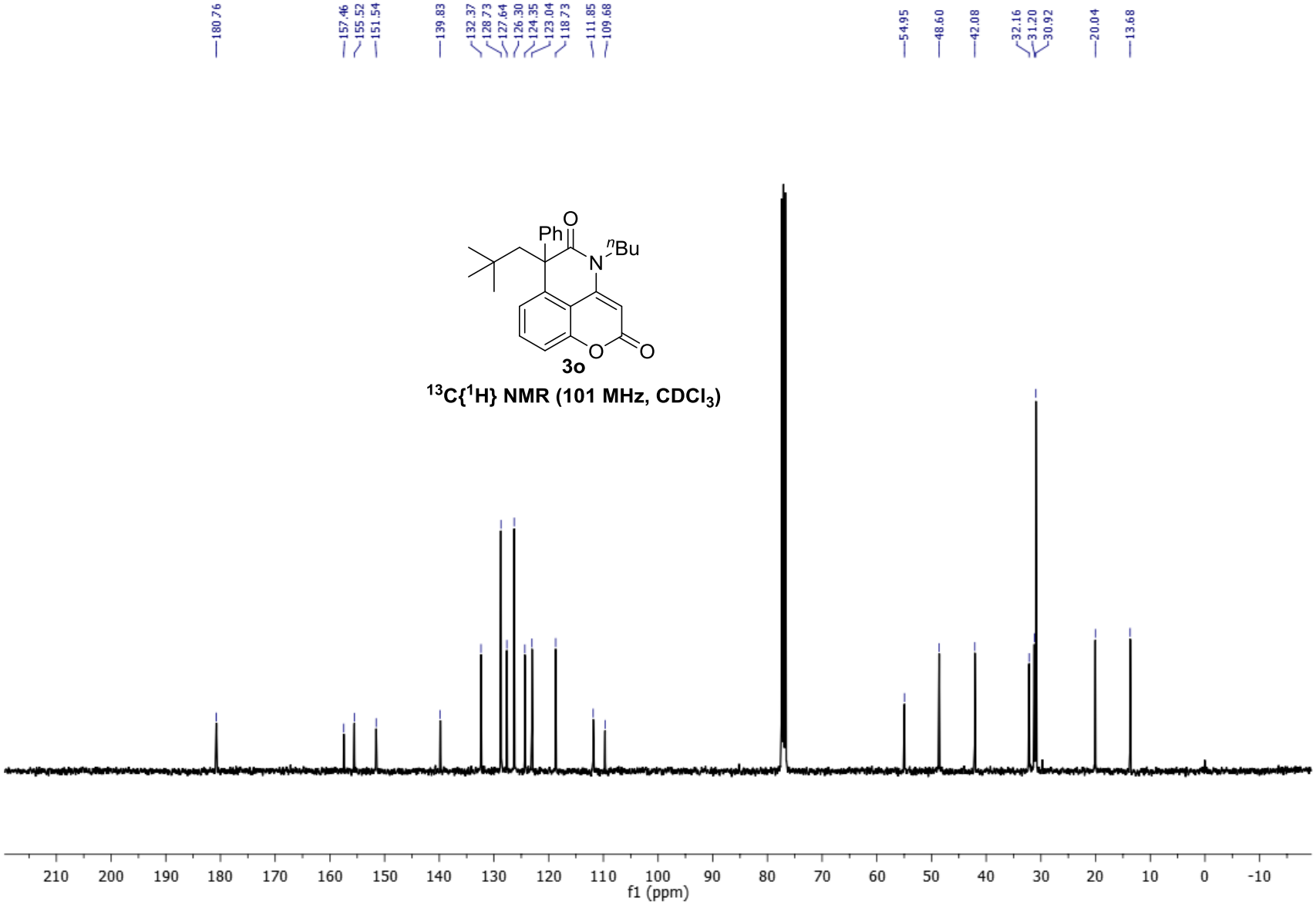

173.99
162.18
152.33
148.28
139.81
131.87
122.42
115.00
109.59
93.07
55.50
46.07
34.54
31.89
30.96
19.39
18.56
O
N
O
O
3m
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



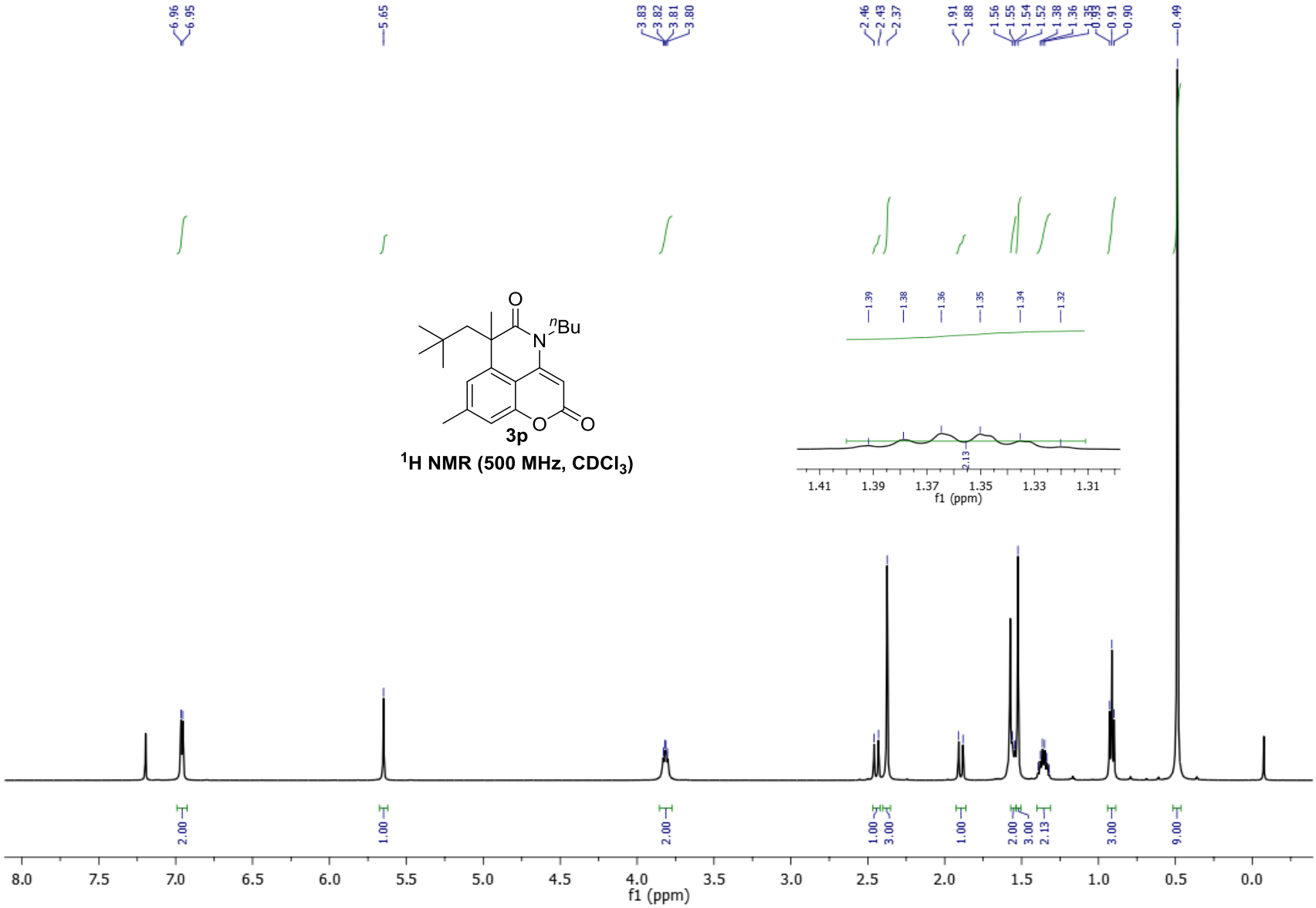
^{1}H NMR (500 MHz, $CDCl_3$)

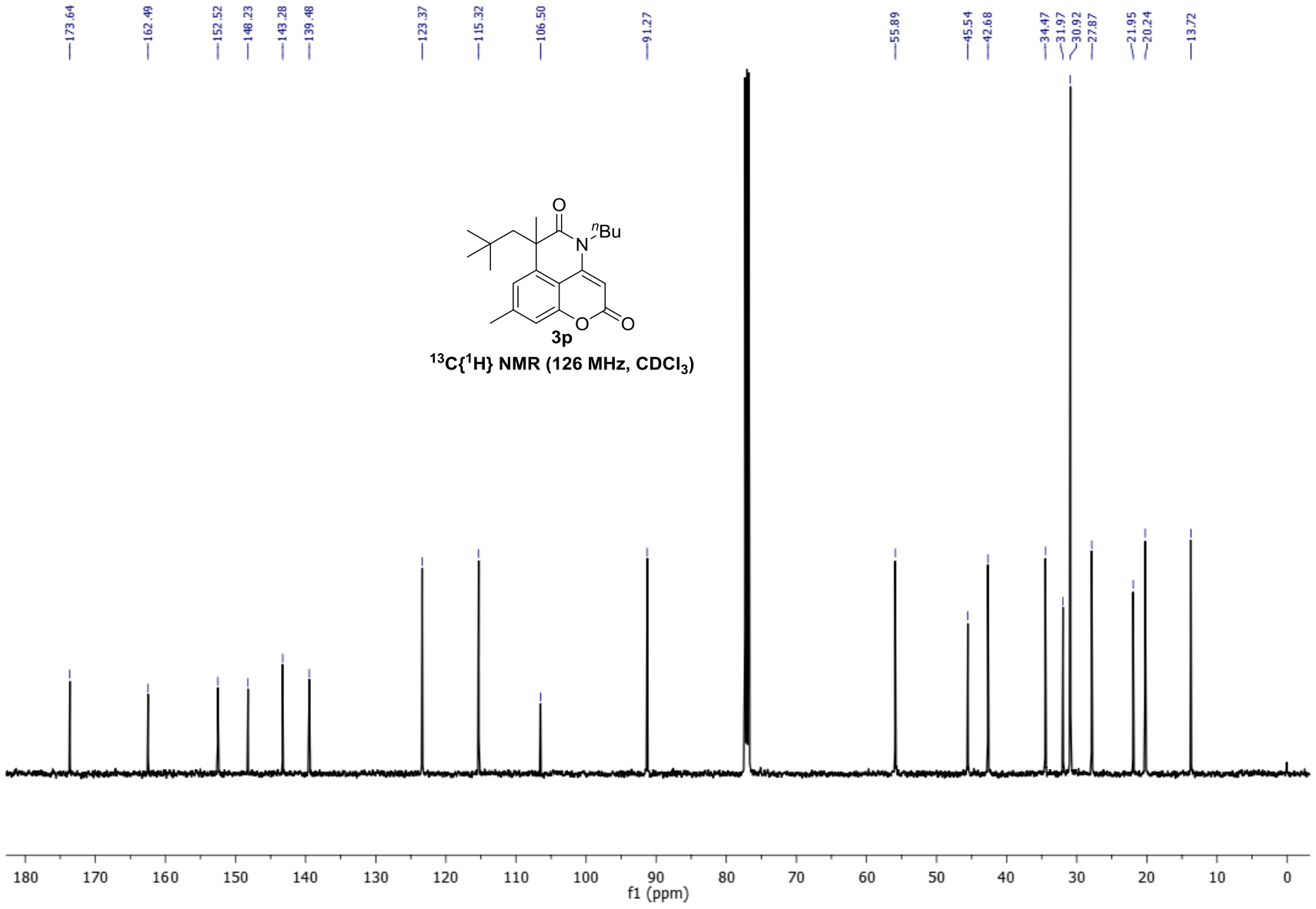

173.43
161.90
152.47
148.00
139.81
132.11
129.92
122.42
119.01
115.02
108.84
93.05
55.86
45.73
45.10
34.64
31.99
30.97
O
N
O
O
3n
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

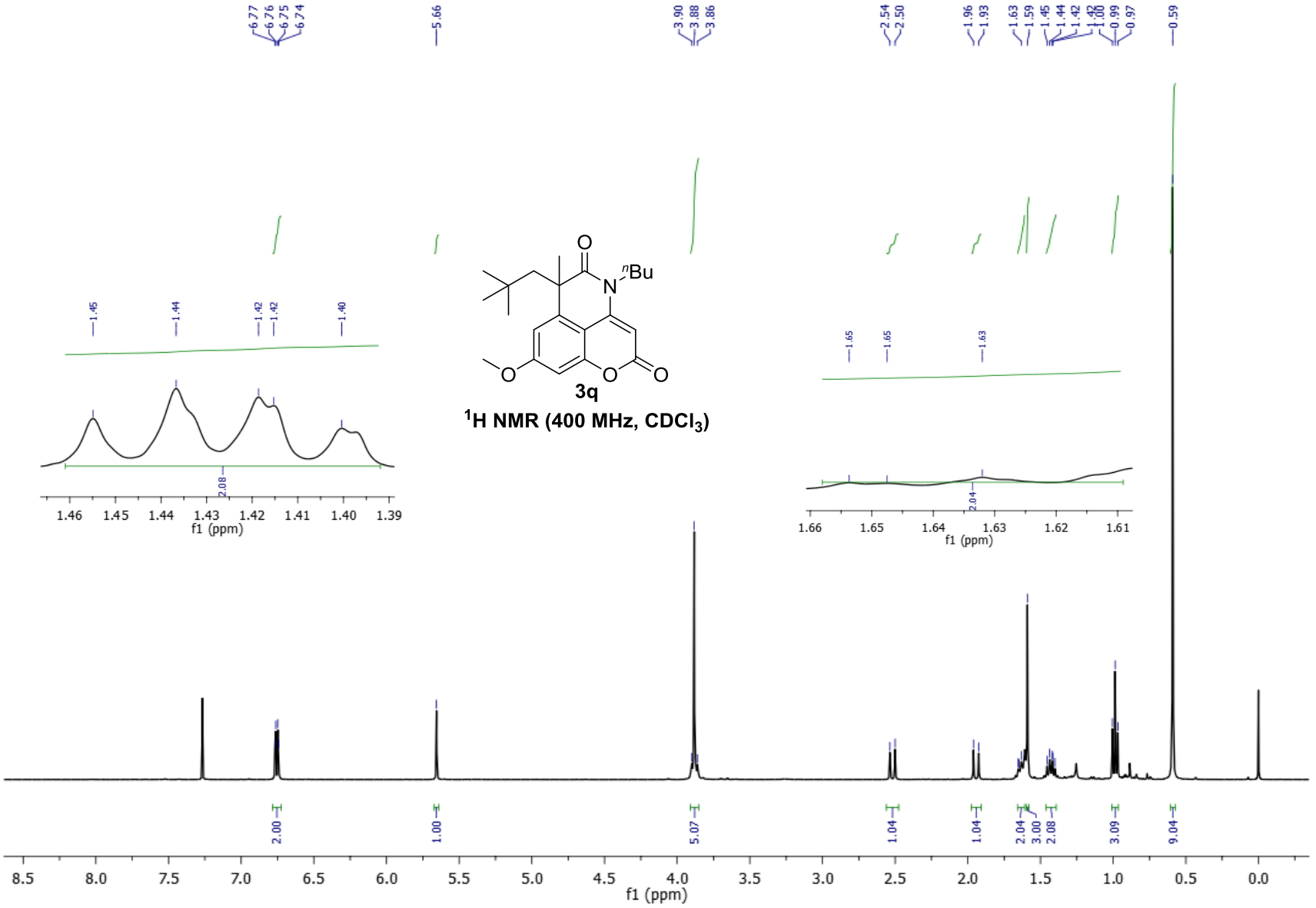

Ph
O
N
nBu
O
O
3o
1H NMR (400 MHz, CDCl3)
f1 (ppm)

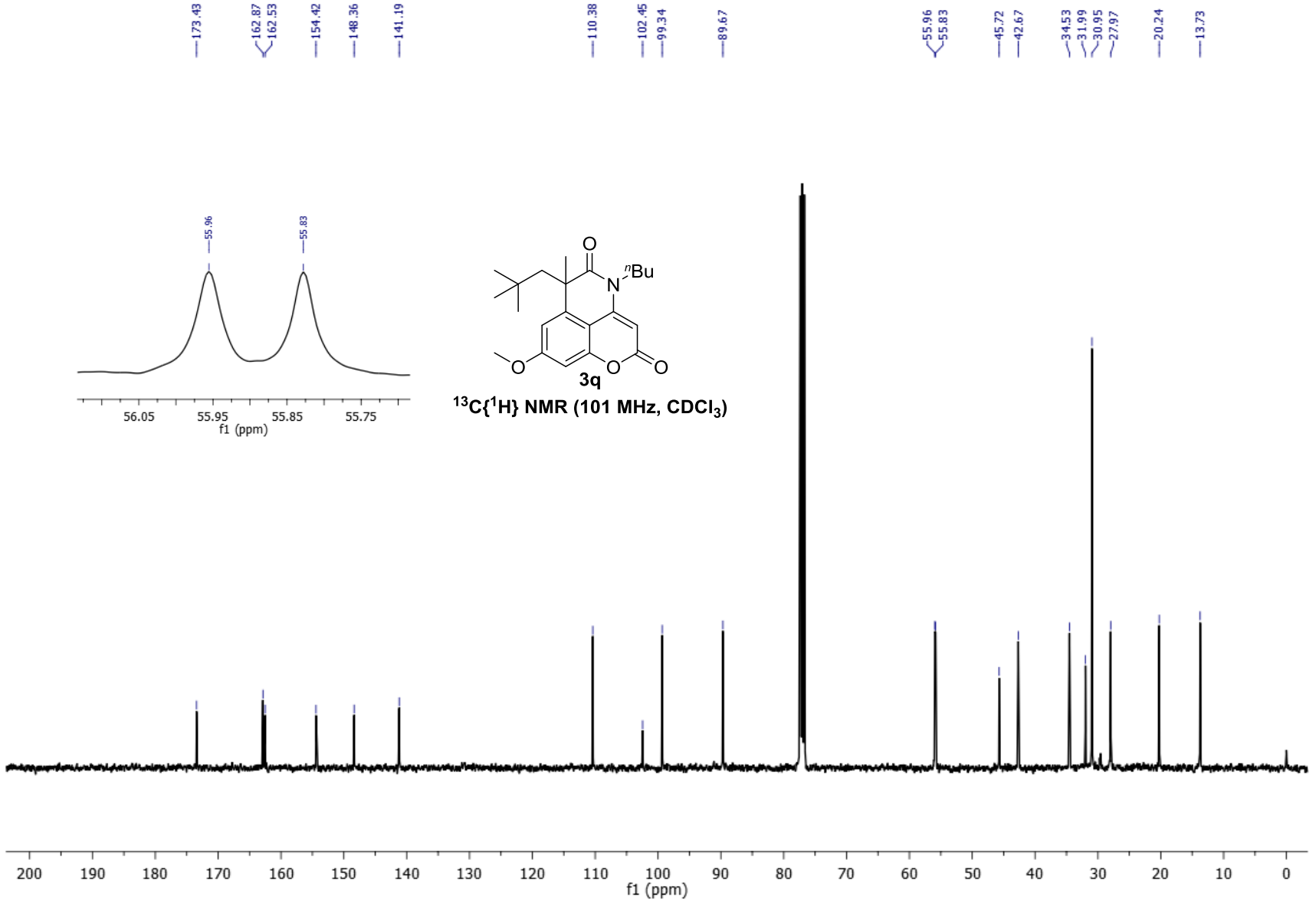


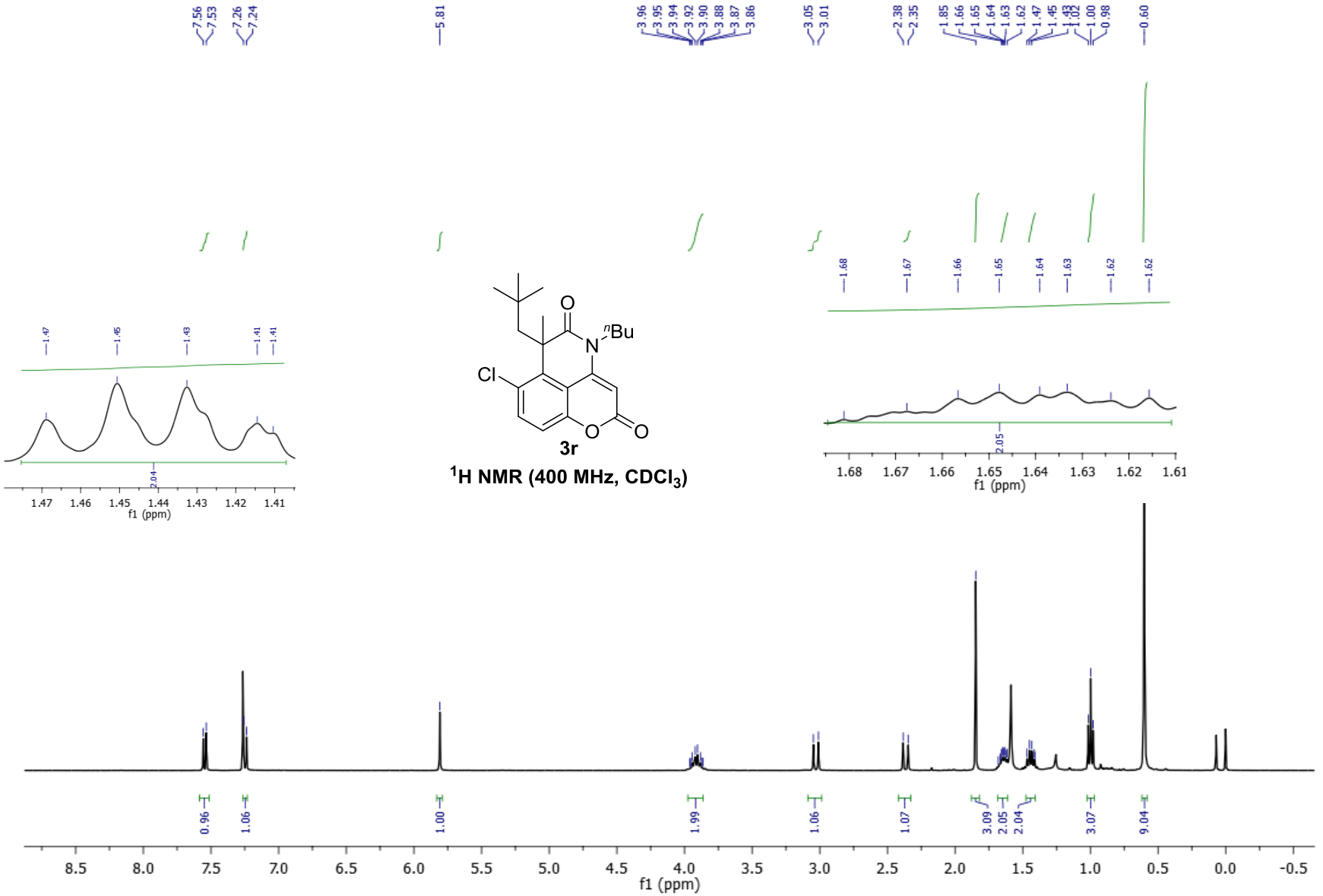
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

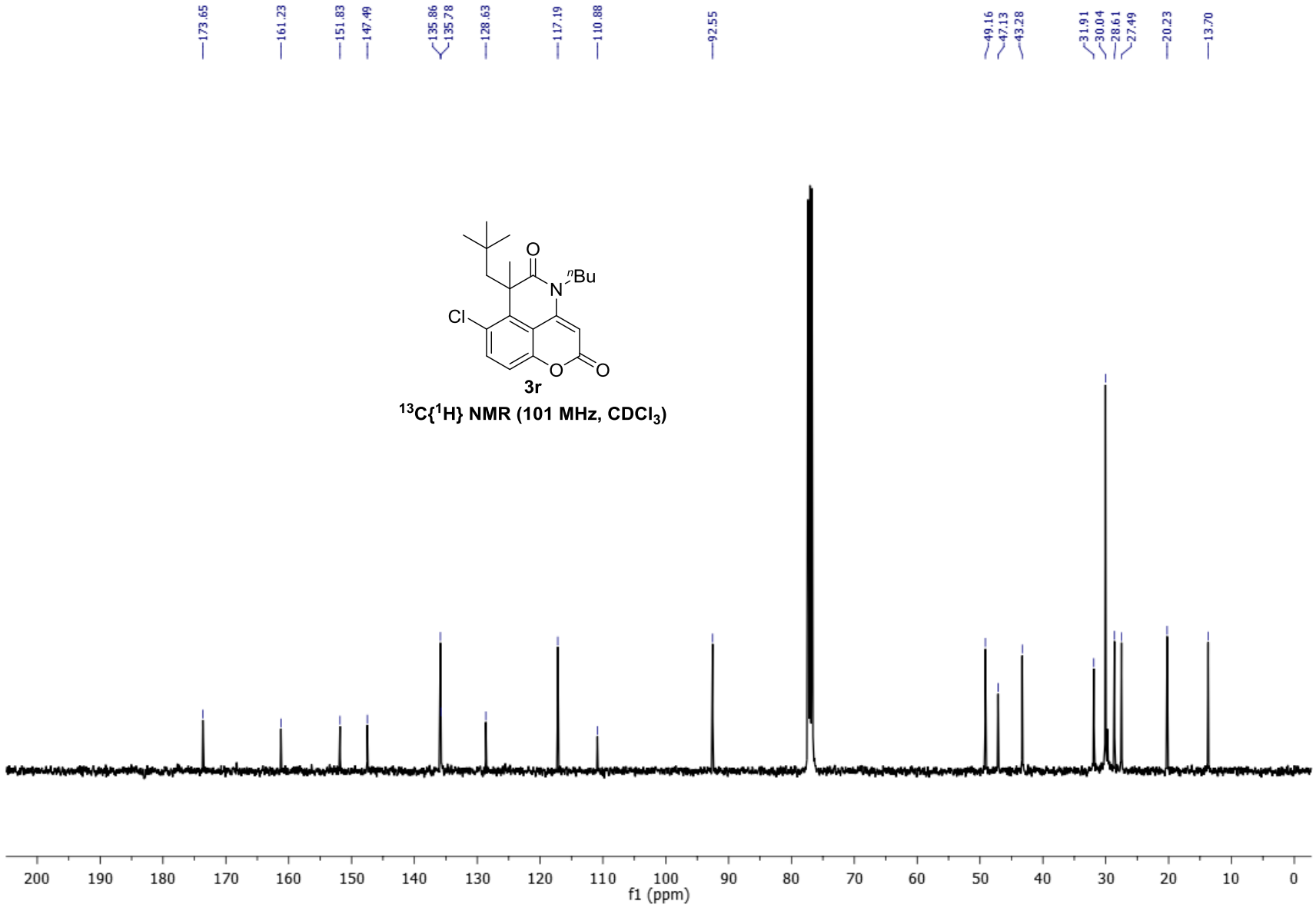

6.96
6.95
5.65
3.83
3.82
3.81
3.80
2.46
2.43
2.37
1.91
1.88
1.56
1.55
1.54
1.52
1.38
1.36
0.91
0.90
0.49
1.39
1.38
1.36
1.35
1.34
1.32
2.13
1.41
1.39
1.37
1.35
1.33
1.31
f1 (ppm)
O
N
nBu
O
O
3p
1H NMR (500 MHz, CDCl3)
2.00
1.00
2.00
1.00
3.00
1.00
2.00
3.00
2.13
3.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.64
162.49
152.52
148.23
143.28
139.48
123.37
115.32
106.50
91.27
55.89
45.54
42.68
34.47
31.97
30.92
27.87
21.95
20.24
13.72
O
N
nBu
O
O
3p
13C{1H} NMR (126 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6.77
6.76
6.75
6.74
5.66
3.90
3.88
3.86
2.54
2.50
1.96
1.93
1.63
1.59
1.45
1.44
1.42
1.42
1.00
0.99
0.97
0.59
O
N
nBu
O
O
O
3q
1H NMR (400 MHz, CDCl3)
1.45
1.44
1.42
1.42
1.40
2.08
1.46 1.45 1.44 1.43 1.42 1.41 1.40 1.39
f1 (ppm)
1.65
1.65
1.63
2.04
1.66 1.65 1.64 1.63 1.62 1.61
f1 (ppm)
2.00
1.00
5.07
1.04
1.04
2.04
3.00
2.08
3.09
9.04
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 0.0
f1 (ppm)

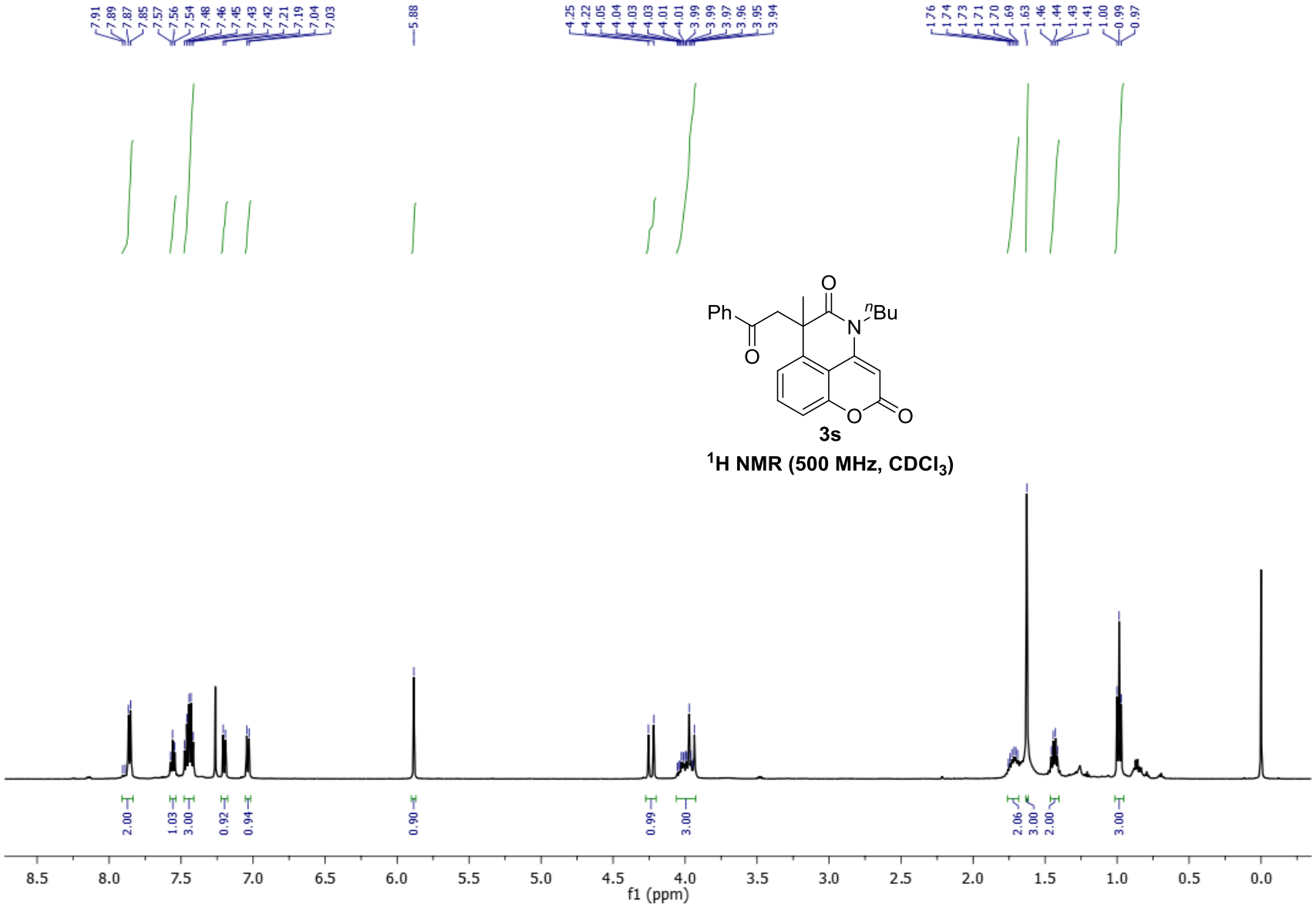

173.43
162.87
162.53
154.42
148.36
141.19
110.38
102.45
99.34
89.67
55.96
55.83
45.72
42.67
34.53
31.99
30.95
27.97
20.24
13.73
55.96
55.83
56.05
55.95
55.85
55.75
f1 (ppm)
O
N
nBu
O
O
O
3q
13C{1H} NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.56
7.53
7.26
7.24
5.81
3.96
3.95
3.94
3.92
3.90
3.88
3.87
3.86
3.05
3.01
2.38
2.35
1.85
1.66
1.65
1.64
1.63
1.62
1.47
1.45
1.00
0.98
0.60
1.68
1.67
1.66
1.65
1.64
1.63
1.62
1.62
1.47
1.46
1.45
1.43
1.41
1.41
2.04
2.05
Cl
O
N
nBu
O
O
3r
1H NMR (400 MHz, CDCl3)
0.96
1.06
1.00
1.99
1.06
1.07
3.09
2.05
2.04
3.07
9.04
f1 (ppm)



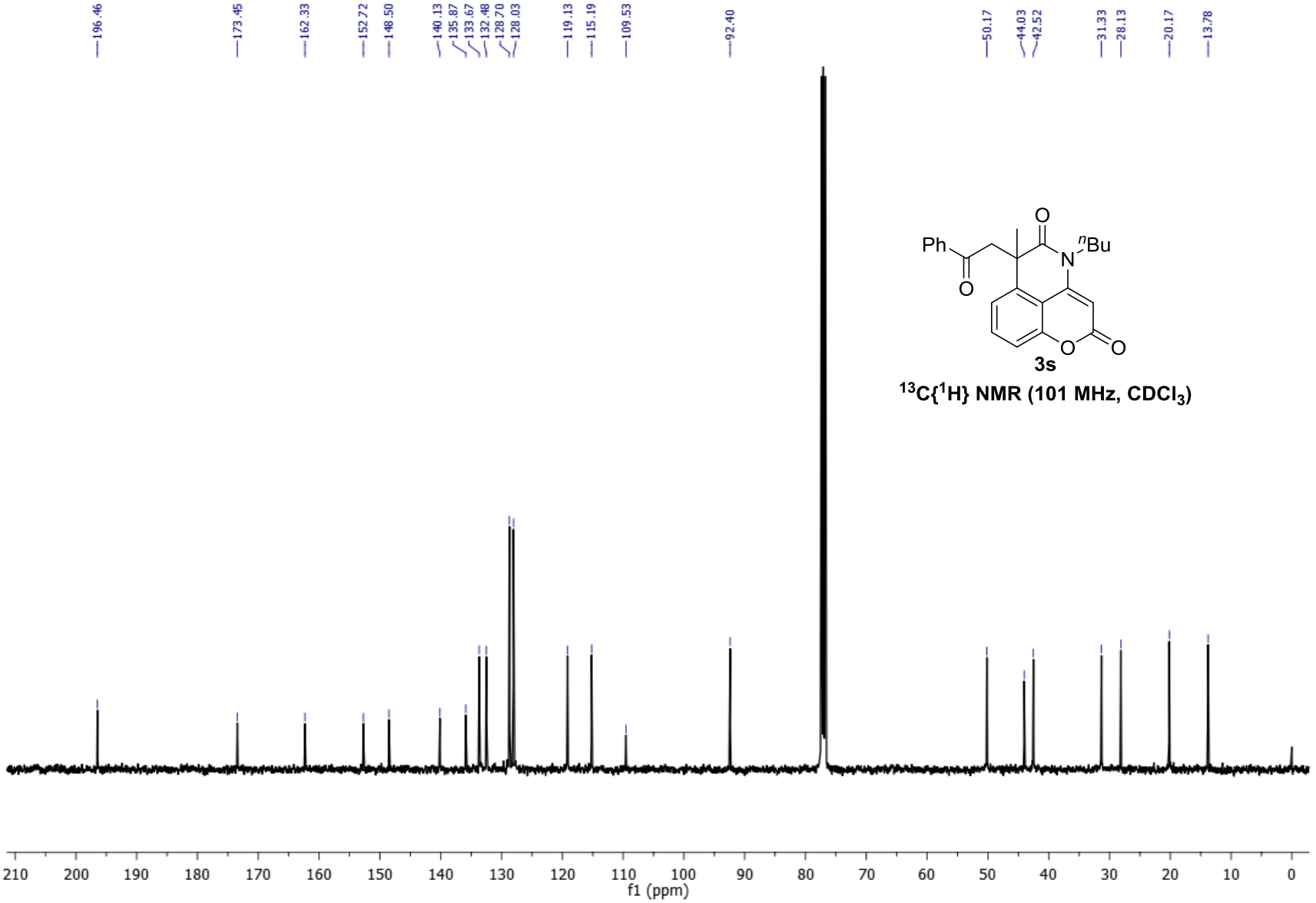
3r

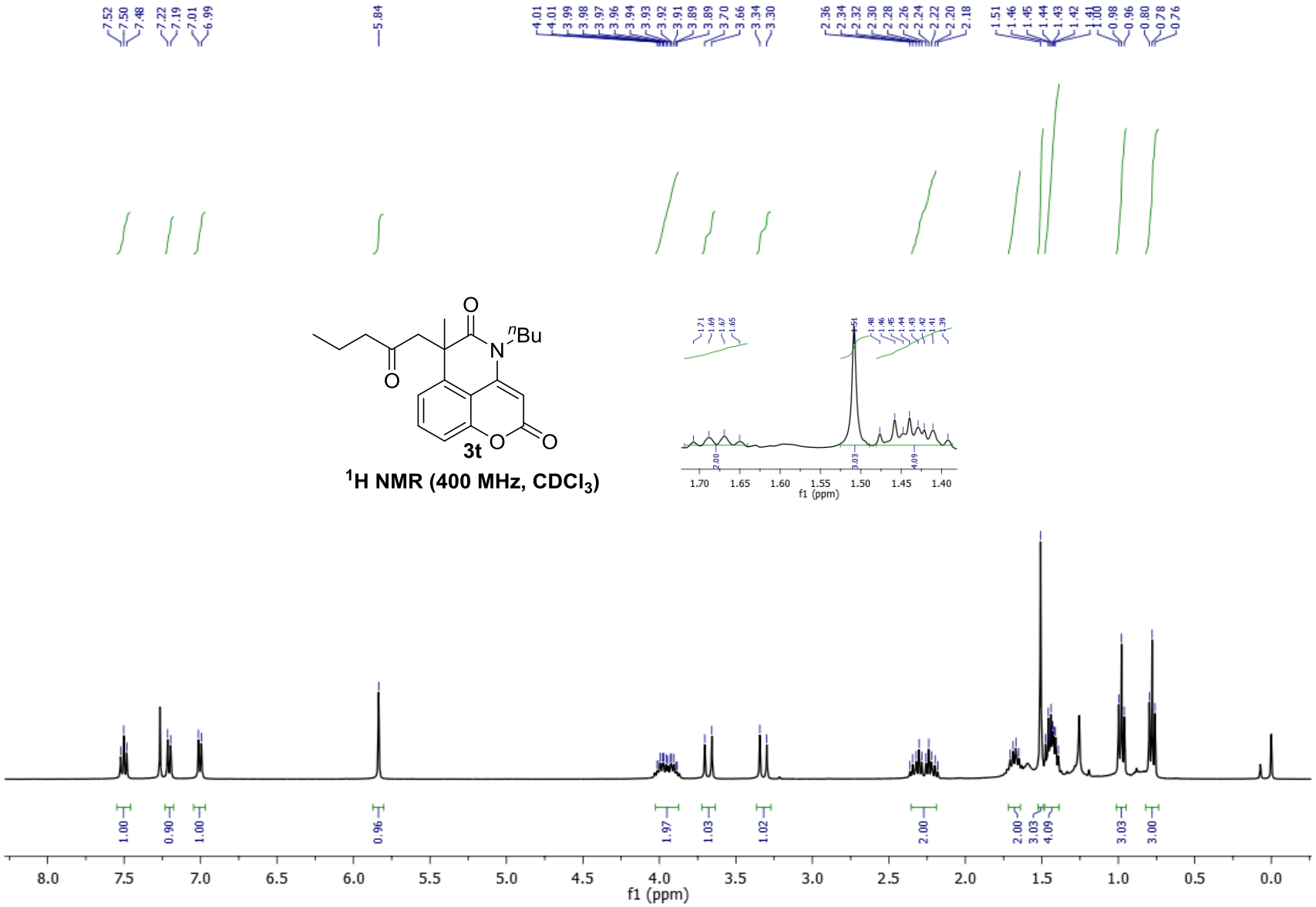
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

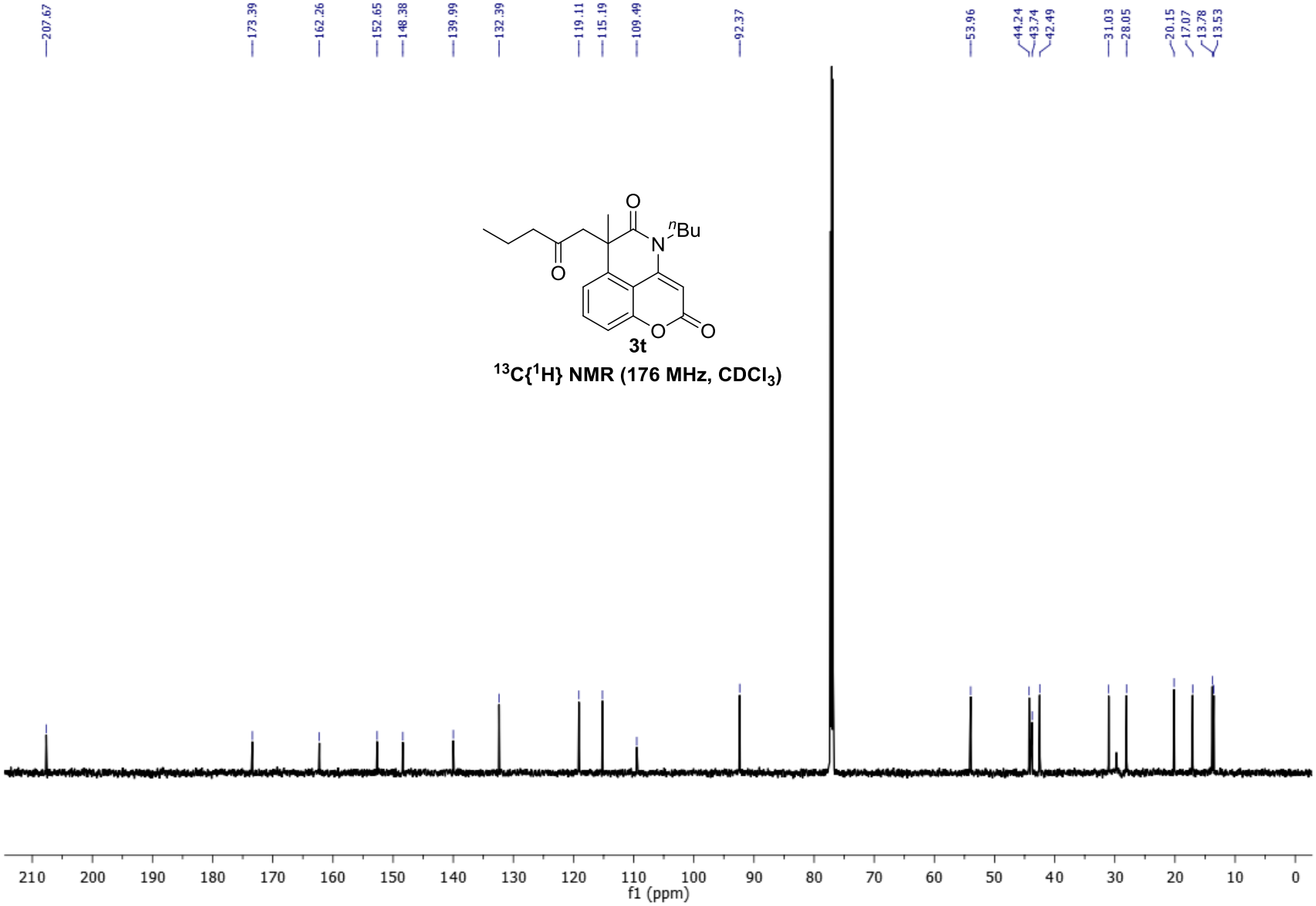


3s

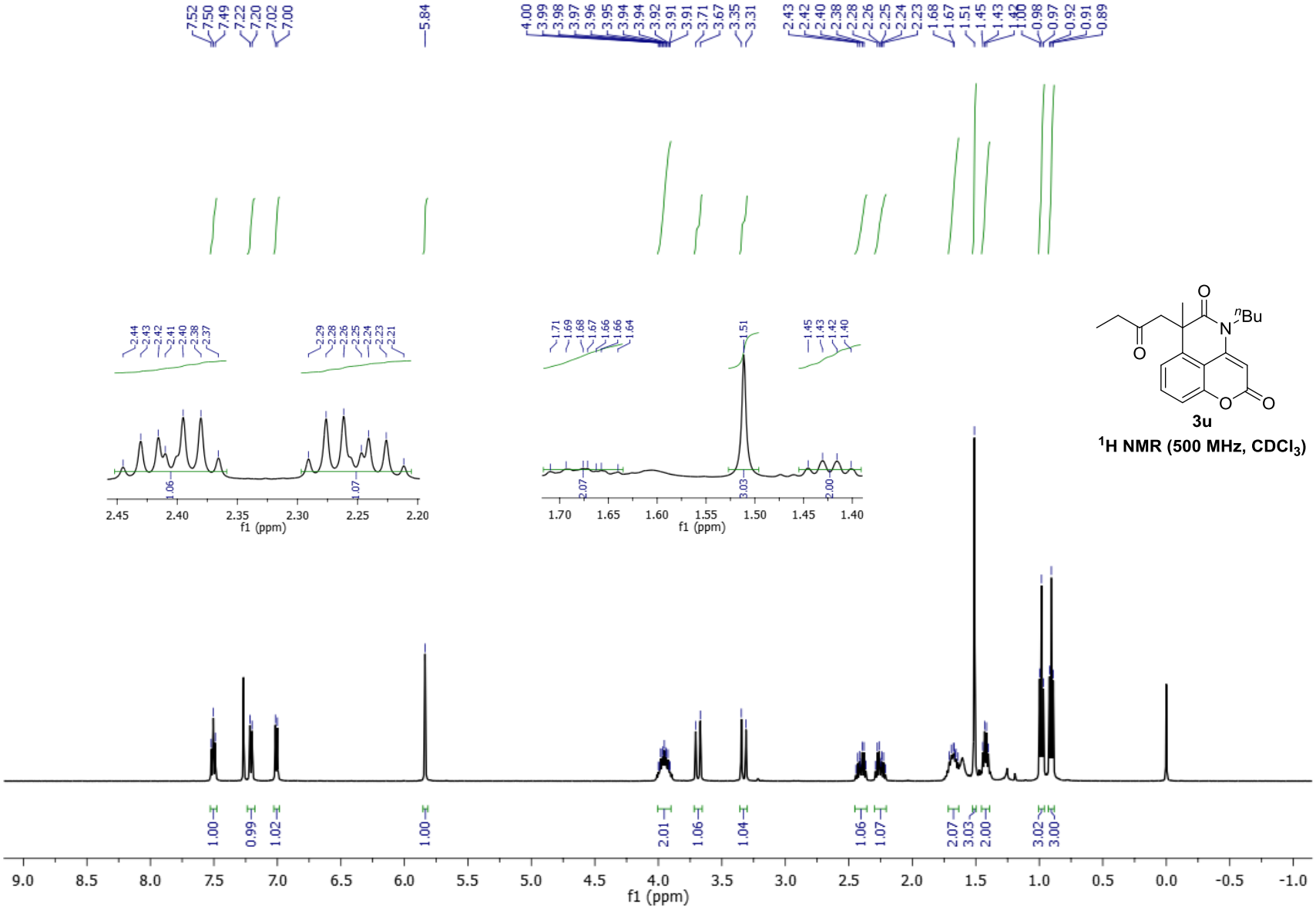
^{1}H NMR (500 MHz, $CDCl_3$)

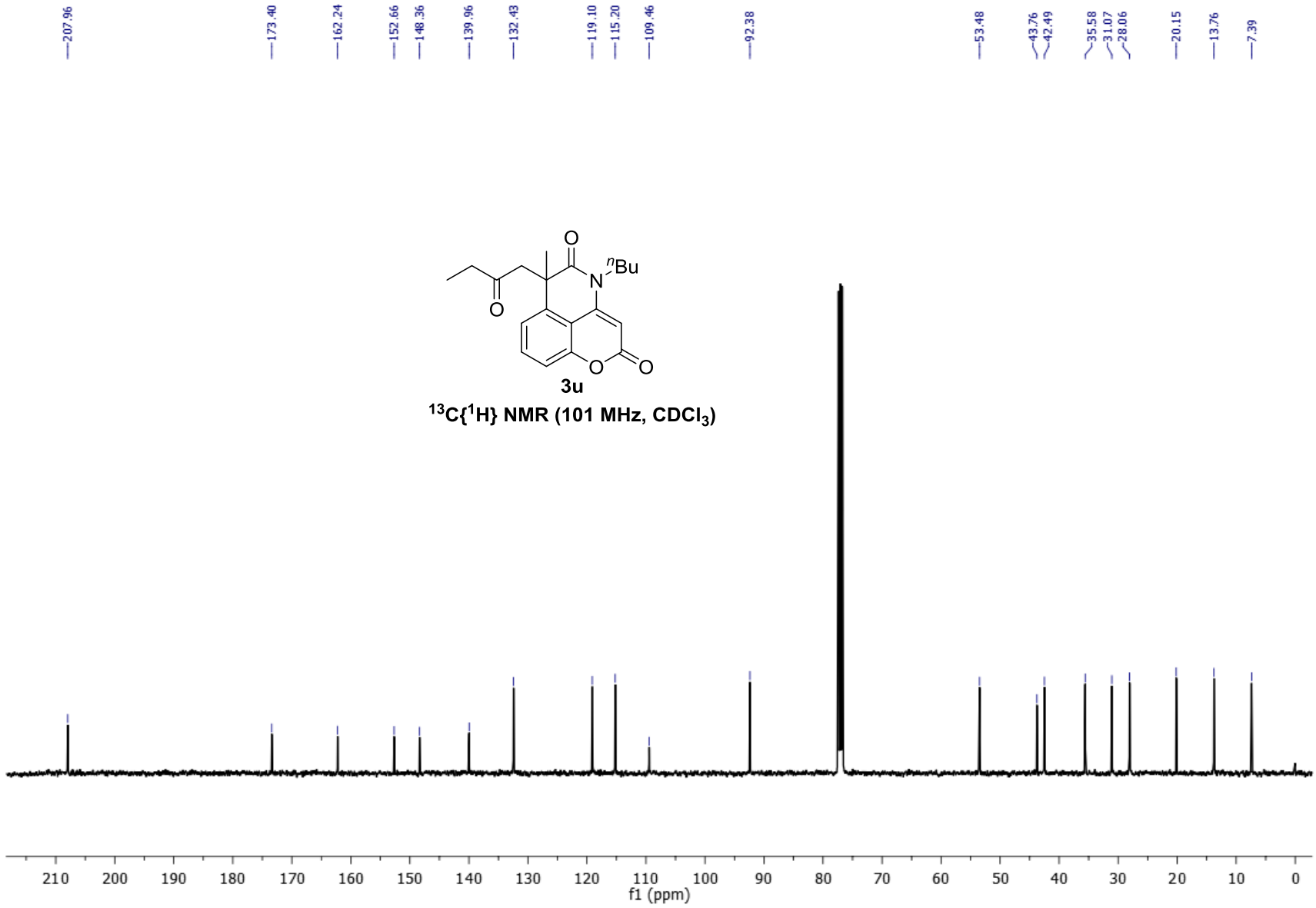

196.46
173.45
162.33
152.72
148.50
140.13
135.87
133.67
132.48
128.70
128.03
119.13
115.19
109.53
92.40
50.17
44.03
42.52
31.33
28.13
20.17
13.78
Ph
O
O
N
nBu
O
O
O
3s
13C{1H} NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

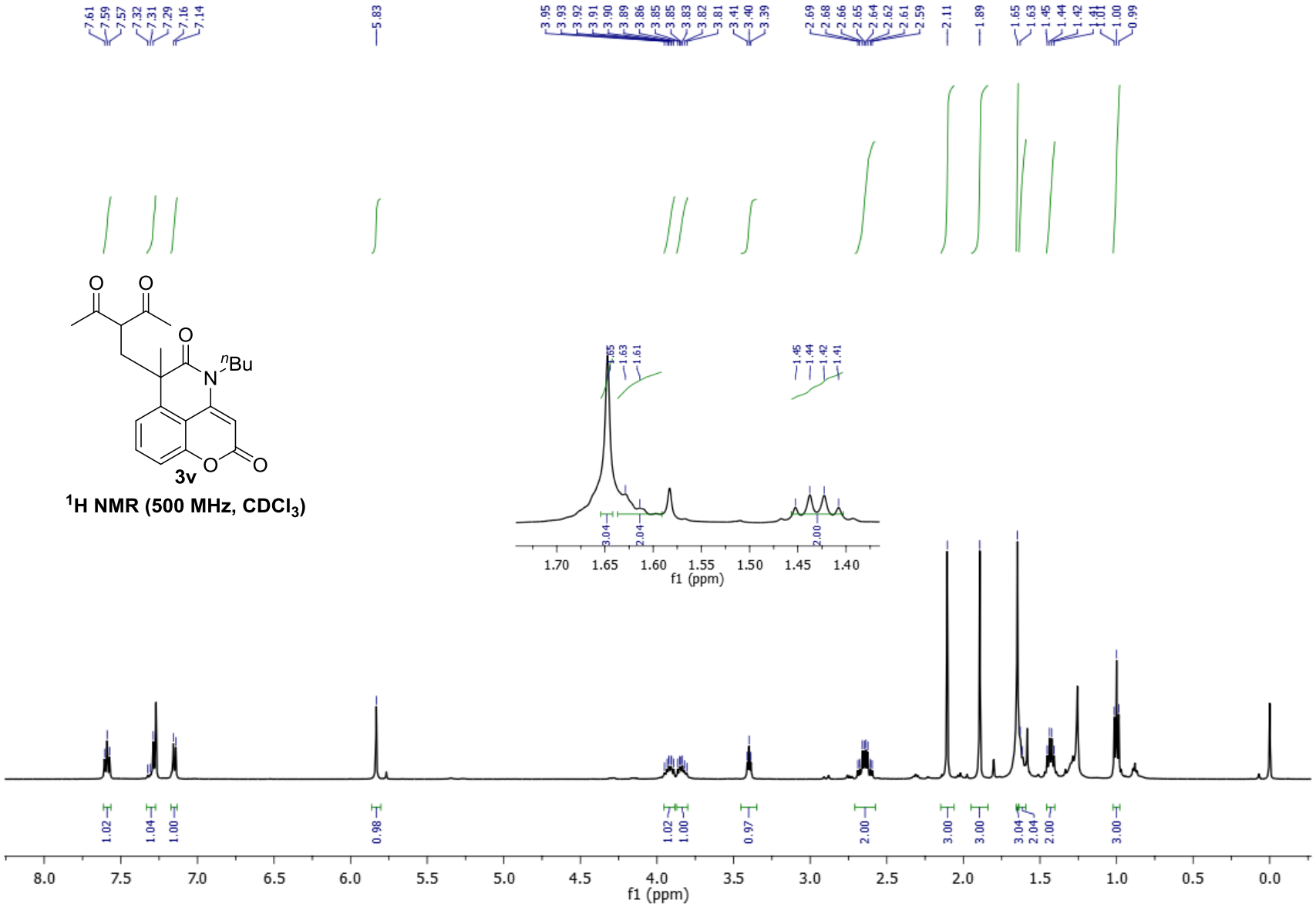

7.52
7.50
7.48
7.22
7.19
7.01
6.99
5.84
4.01
4.01
3.99
3.98
3.97
3.96
3.94
3.93
3.92
3.91
3.89
3.89
3.70
3.66
3.34
3.30
2.36
2.34
2.32
2.30
2.28
2.26
2.24
2.22
2.20
2.18
1.51
1.46
1.45
1.44
1.43
1.42
1.41
1.00
0.98
0.96
0.80
0.78
0.76
O
O
N
nBu
O
O
3t
1H NMR (400 MHz, CDCl3)
1.71
1.69
1.67
1.65
1.51
1.48
1.46
1.45
1.44
1.43
1.42
1.41
1.39
2.00
3.03
4.09
1.70
1.65
1.60
1.55
1.50
1.45
1.40
f1 (ppm)
1.00
0.90
1.00
0.96
1.97
1.03
1.02
2.00
2.00
3.03
4.09
3.03
3.00
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
0.0
f1 (ppm)



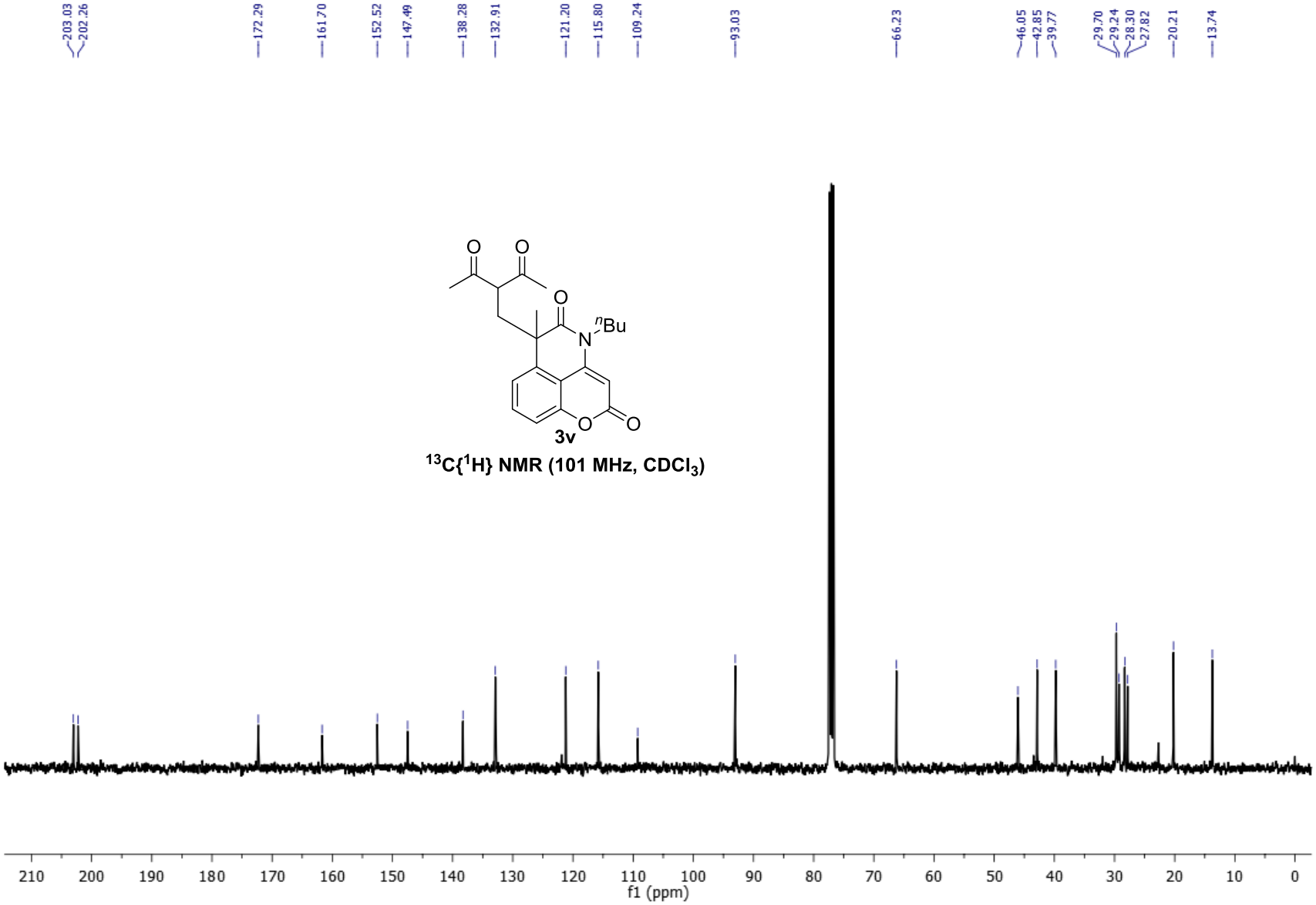
$^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$)

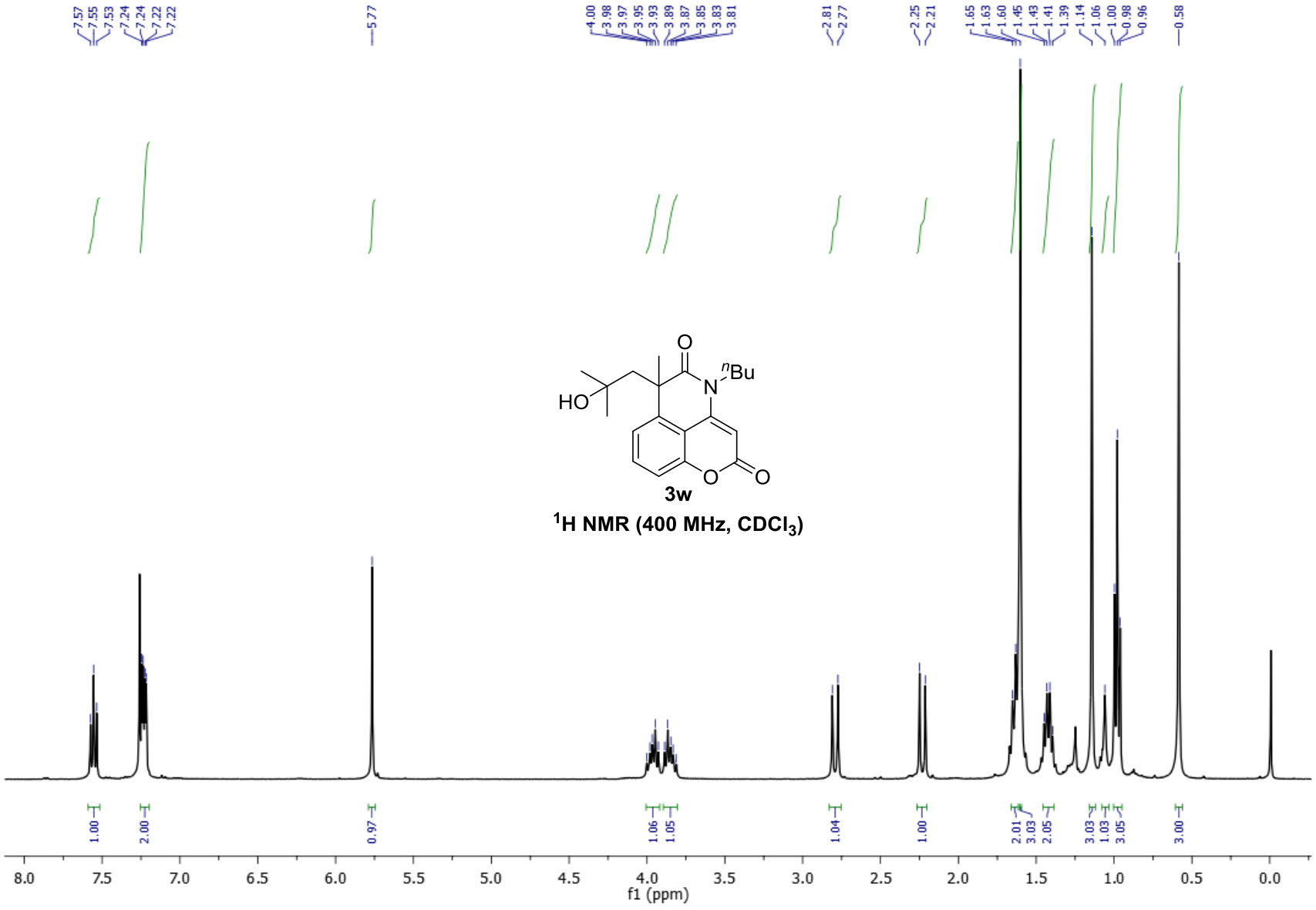

7.52
7.50
7.49
7.22
7.20
7.02
7.00
5.84
4.00
3.99
3.98
3.97
3.96
3.95
3.94
3.94
3.92
3.91
3.91
3.71
3.67
3.35
3.31
2.43
2.42
2.40
2.38
2.28
2.26
2.25
2.24
2.23
1.68
1.67
1.51
1.45
1.43
1.00
0.98
0.97
0.92
0.91
0.89
2.44
2.43
2.42
2.41
2.40
2.38
2.37
2.29
2.28
2.26
2.25
2.24
2.23
2.21
1.71
1.69
1.68
1.67
1.66
1.66
1.64
1.51
1.45
1.43
1.42
1.40
O
O
N
nBu
O
O
3u
1H NMR (500 MHz, CDCl3)
1.00
0.99
1.02
1.00
2.01
1.06
1.04
1.06
1.07
2.07
3.03
2.00
3.02
3.00
f1 (ppm)


207.96
173.40
162.24
152.66
148.36
139.96
132.43
119.10
115.20
109.46
92.38
53.48
43.76
42.49
35.58
31.07
28.06
20.15
13.76
7.39
O
N
nBu
O
O
O
3u
13C{1H} NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



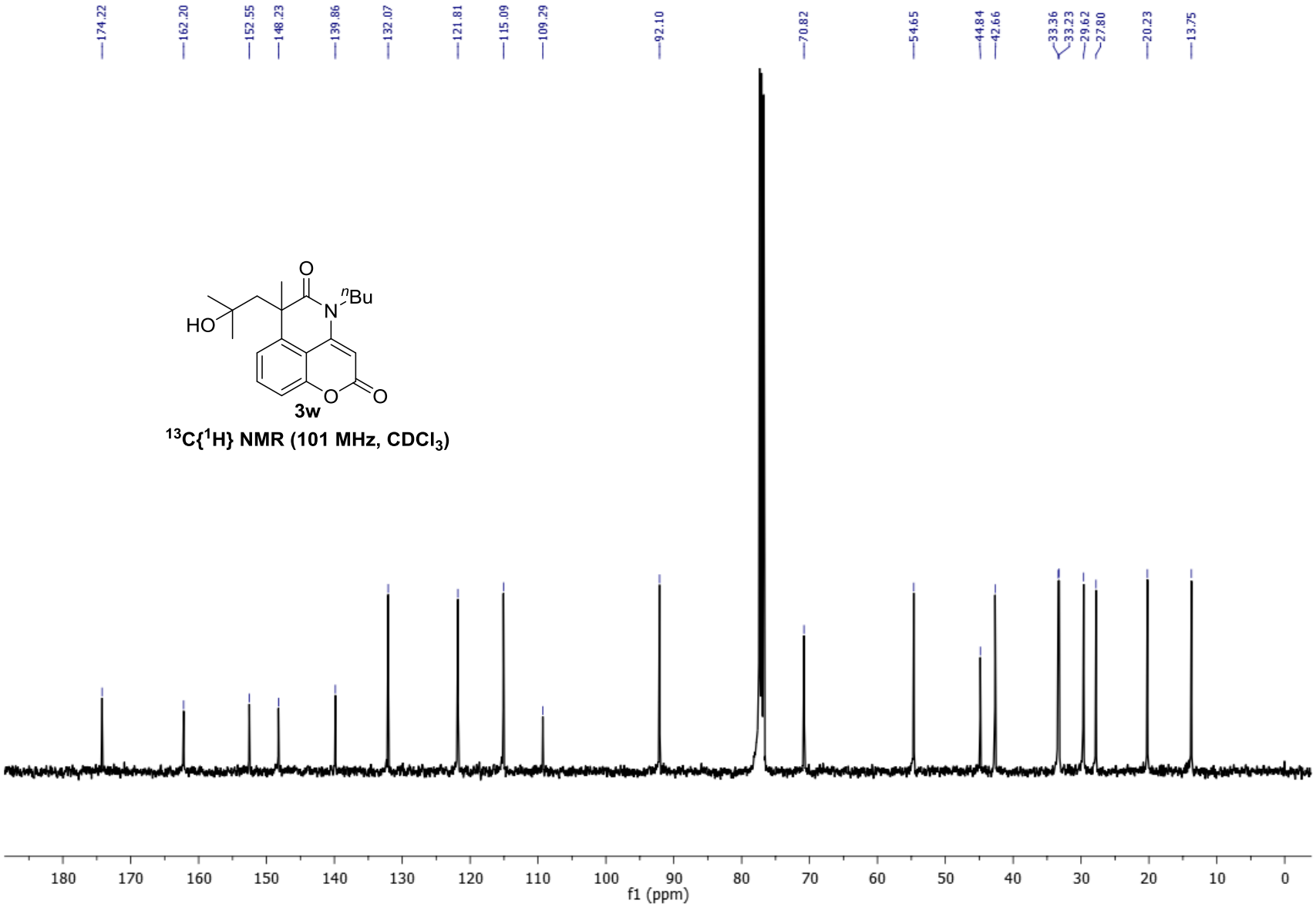
^{1}H NMR (500 MHz, $CDCl_3$)


203.03
202.26
172.29
161.70
152.52
147.49
138.28
132.91
121.20
115.80
109.24
93.03
66.23
46.05
42.85
39.77
29.70
29.24
28.30
27.82
20.21
13.74
O
O
O
N
nBu
O
O
3v
13C{1H} NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

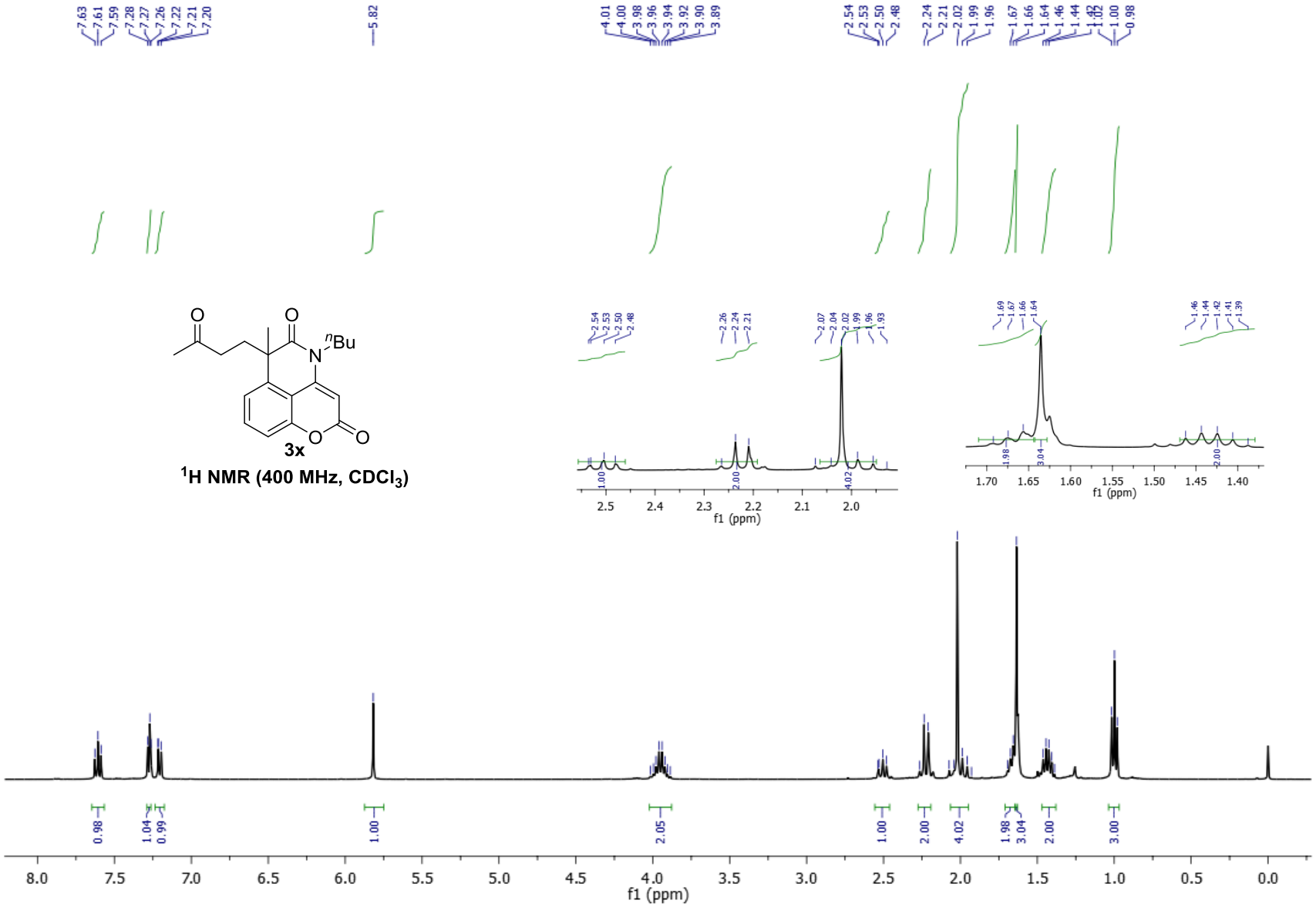


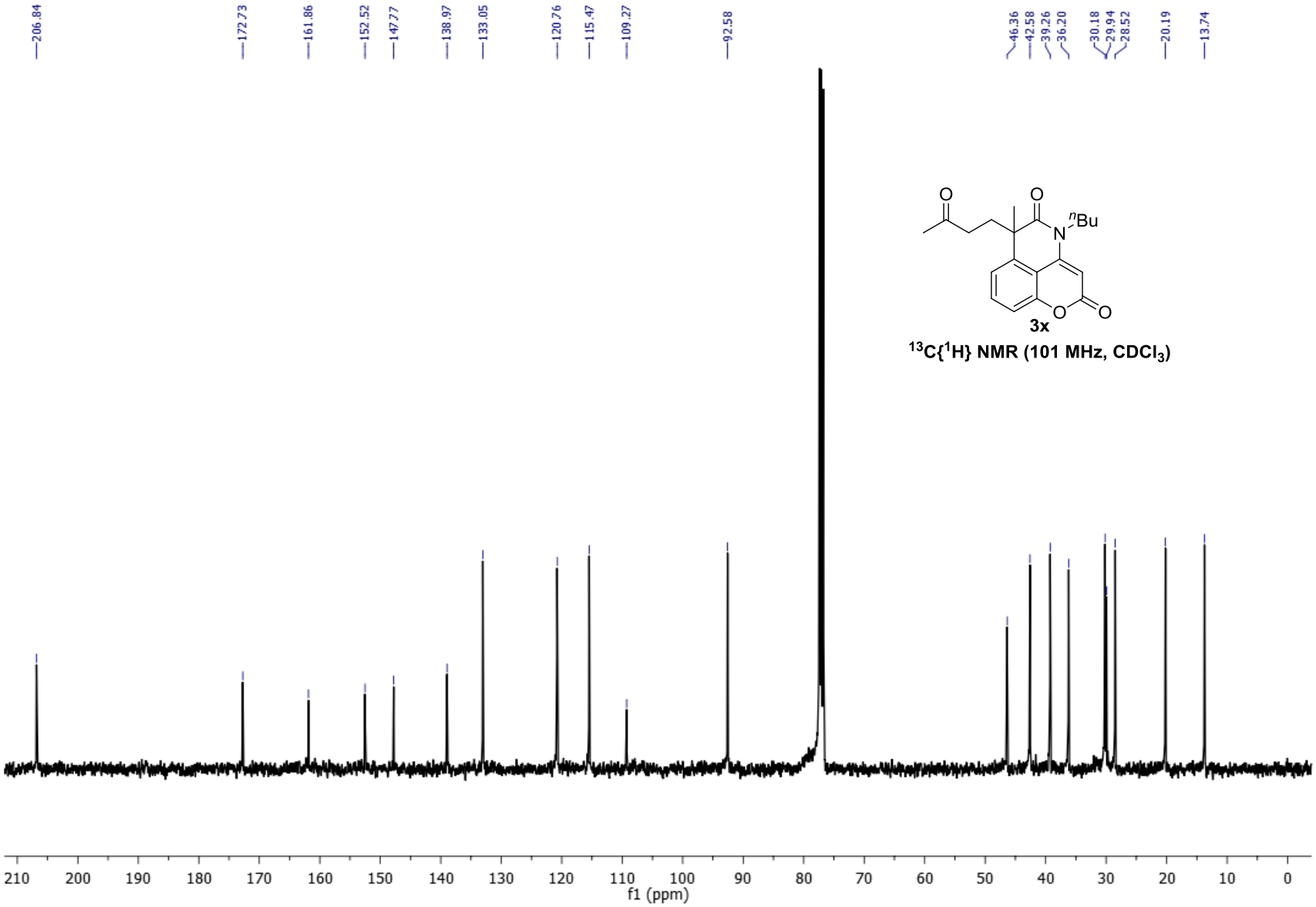
3w

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



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)


7.63
7.61
7.59
7.28
7.27
7.26
7.22
7.21
7.20
5.82
4.01
4.00
3.98
3.96
3.94
3.92
3.90
3.89
2.54
2.53
2.50
2.48
2.24
2.21
2.02
1.99
1.96
1.67
1.66
1.64
1.46
1.44
1.02
1.00
0.98
O
O
nBu
N
O
O
3x
1H NMR (400 MHz, CDCl3)
f1 (ppm)
f1 (ppm)



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)