A Chiral Thiourea as Template for Enantioselective Intramolecular [2+2] Photocycloaddition Reactions

Supporting Information

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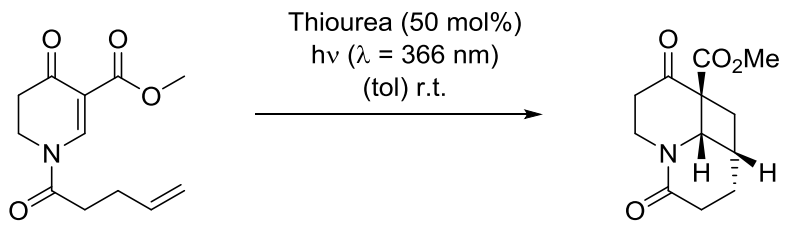
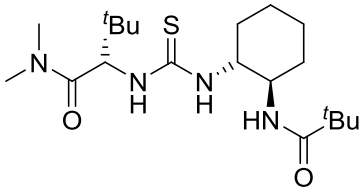
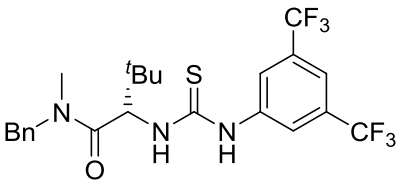
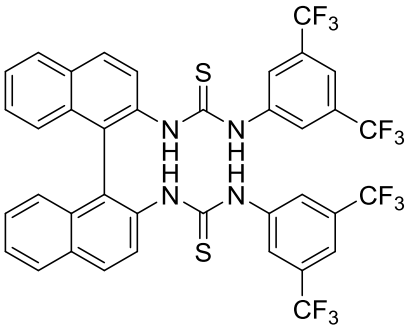
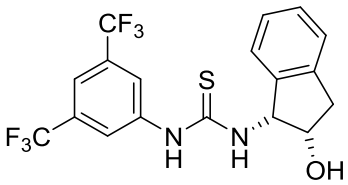
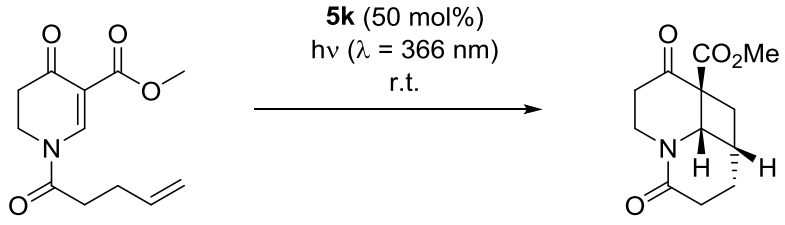
1. Screening for thioureas and reaction conditions



6 **7**

Table 1: Screening of different literature known thioureas.

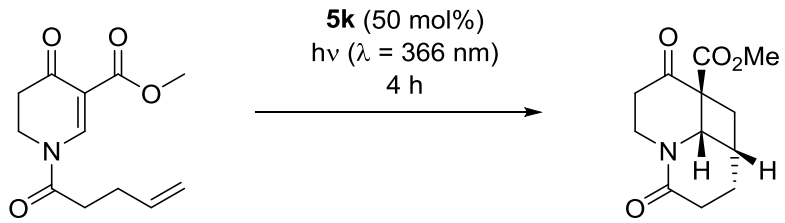
entry	thiourea	time [min]	**7** [%]	*ee* [%]
1	-	30	99	-
2		30	100	1
3		30	n.d.	0
4		480	51	0
5	**5k**	30	51	6
6		30	61	0



6 **7**

Table 2: Screening of different solvents for photoreaction with thiourea **5k**.

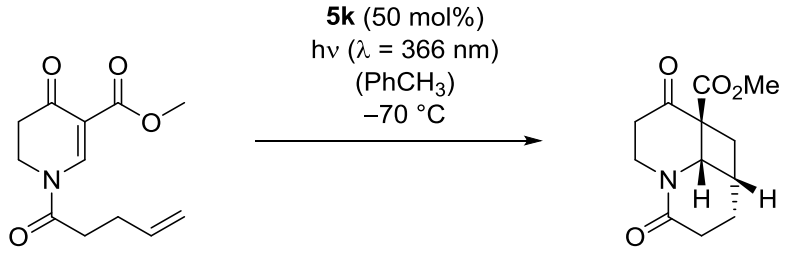
Entry	solvent	t [min]	**7** [%]	*ee* [%]
1	$PhCH_3$	30	51	6
2	$PhCF_3$	45	62	4
3	$1,3\text{-}(CF_3)_2Ph$	40	70	2
4	PhH	30	73	3
5	CH_2Cl_2	30	99	0
6	$(CH_2Cl)_2$	30	99	0
7	Et_2O	80	49	0



6 **7**

Table 3: Solvent screening at low temperature

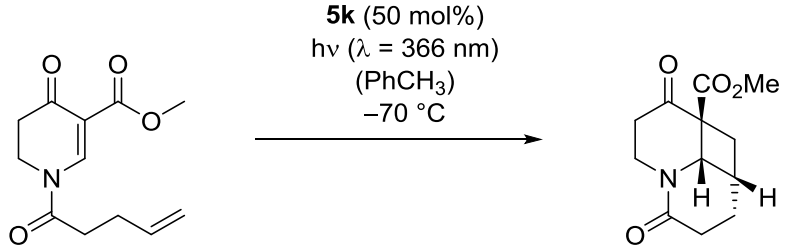
entry	solvent	T [°C]	**7** [%]	*ee* [%]
1	$PhCH_3$	–70	76	56
2	CH_2Cl_2	–70	91	2
3	$PhCF_3$	–25	92	26
4	$PhCF_3$:$1,3\text{-}(CF_3)_2Ph$ 1:2)	–65	86	44



6 **7**

Table 4: Screening for loading of **5k** at low temperature

Entry	**5k** [mol%]	t [h]	**7** [%]	*ee* [%]
1	50	4	76	56
2	10	4	74	4
3	230	18	71	23

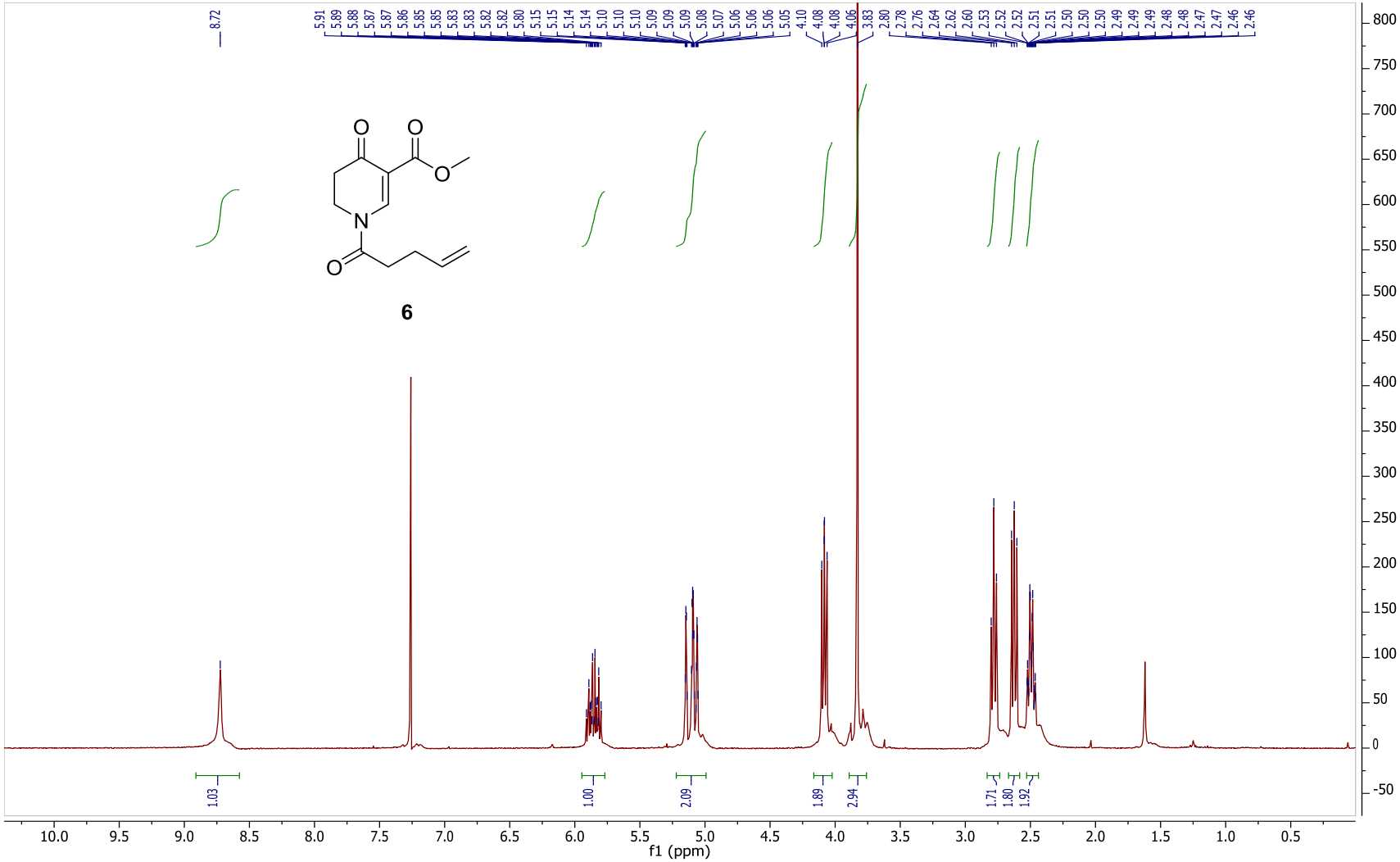


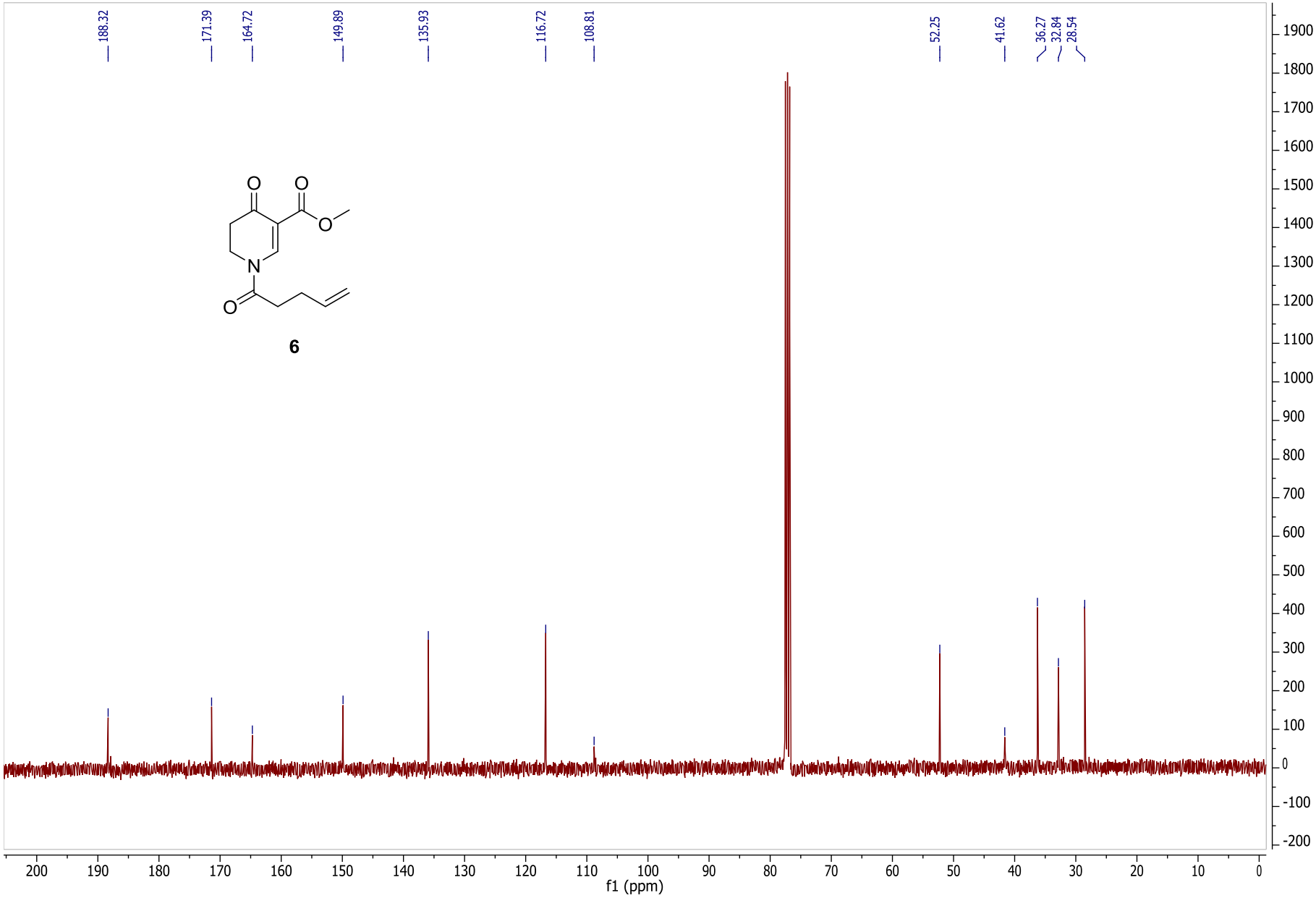
6 **7**

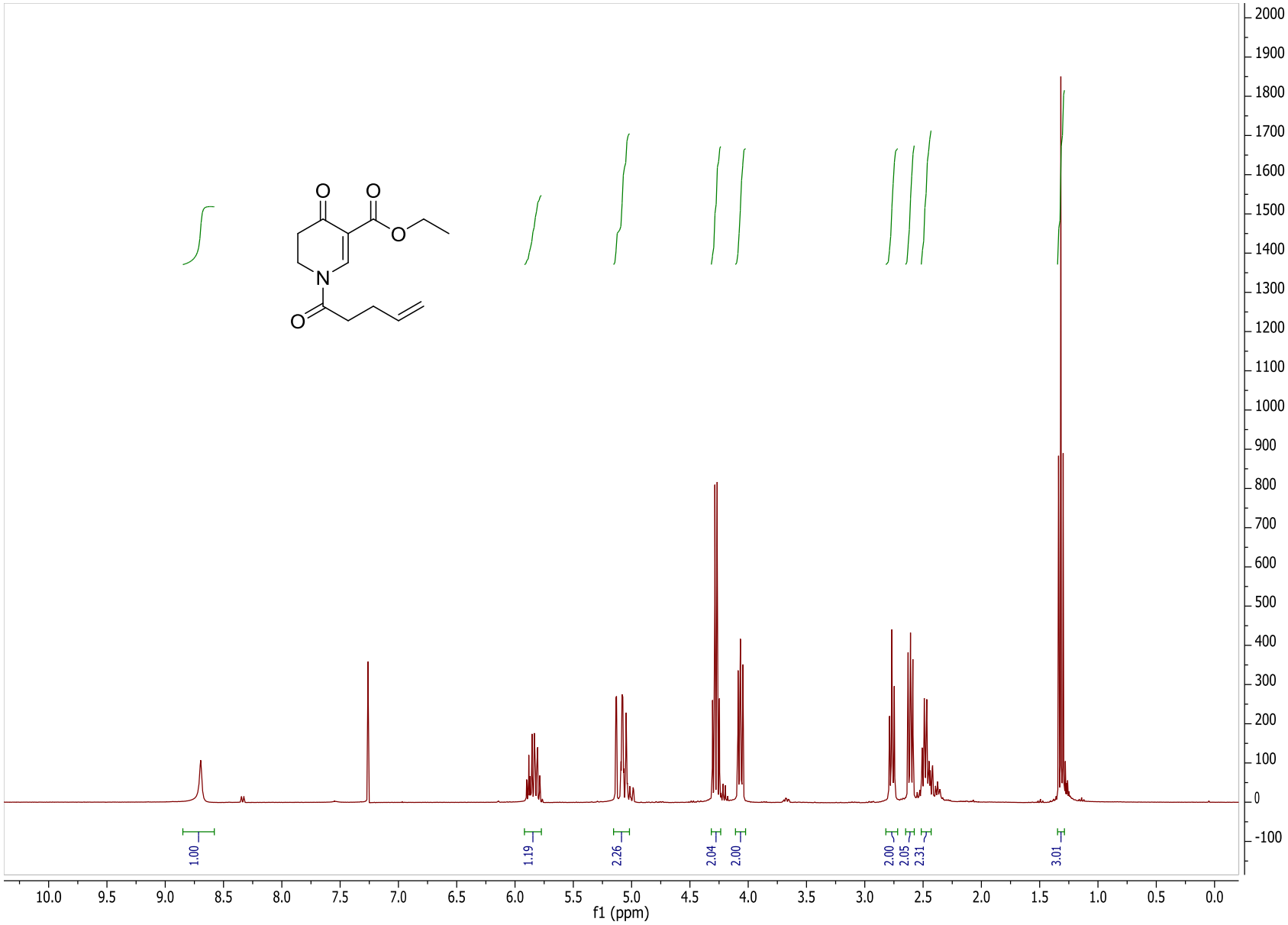
table 5: Screening of different concentrations at low temperature

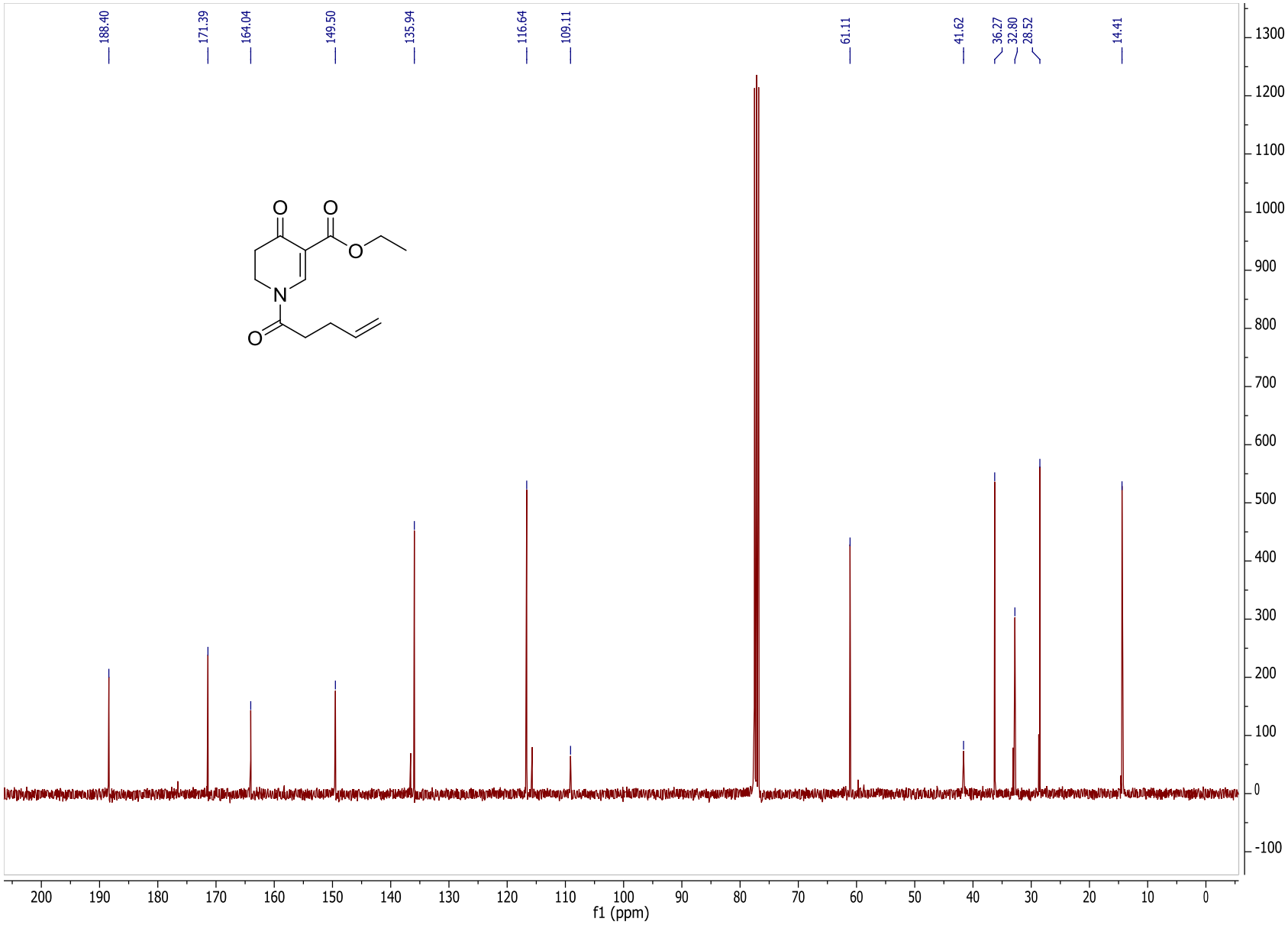
Entry	*c* [mM]	t [h]	**7** [%]	*ee* [%]
1	100	60	59	66
2	40	16	70	57
3	20	4	76	56
4	10	4	88	35

2. NMR-spectra of new compounds




188.32
171.39
164.72
149.89
135.93
116.72
108.81
52.25
41.62
36.27
32.84
28.54
O
O
O
N
O
6
f1 (ppm)


O
O
O
N
O
1.00
1.19
2.26
2.04
2.00
2.00
2.05
2.31
3.01
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
0.0
f1 (ppm)
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100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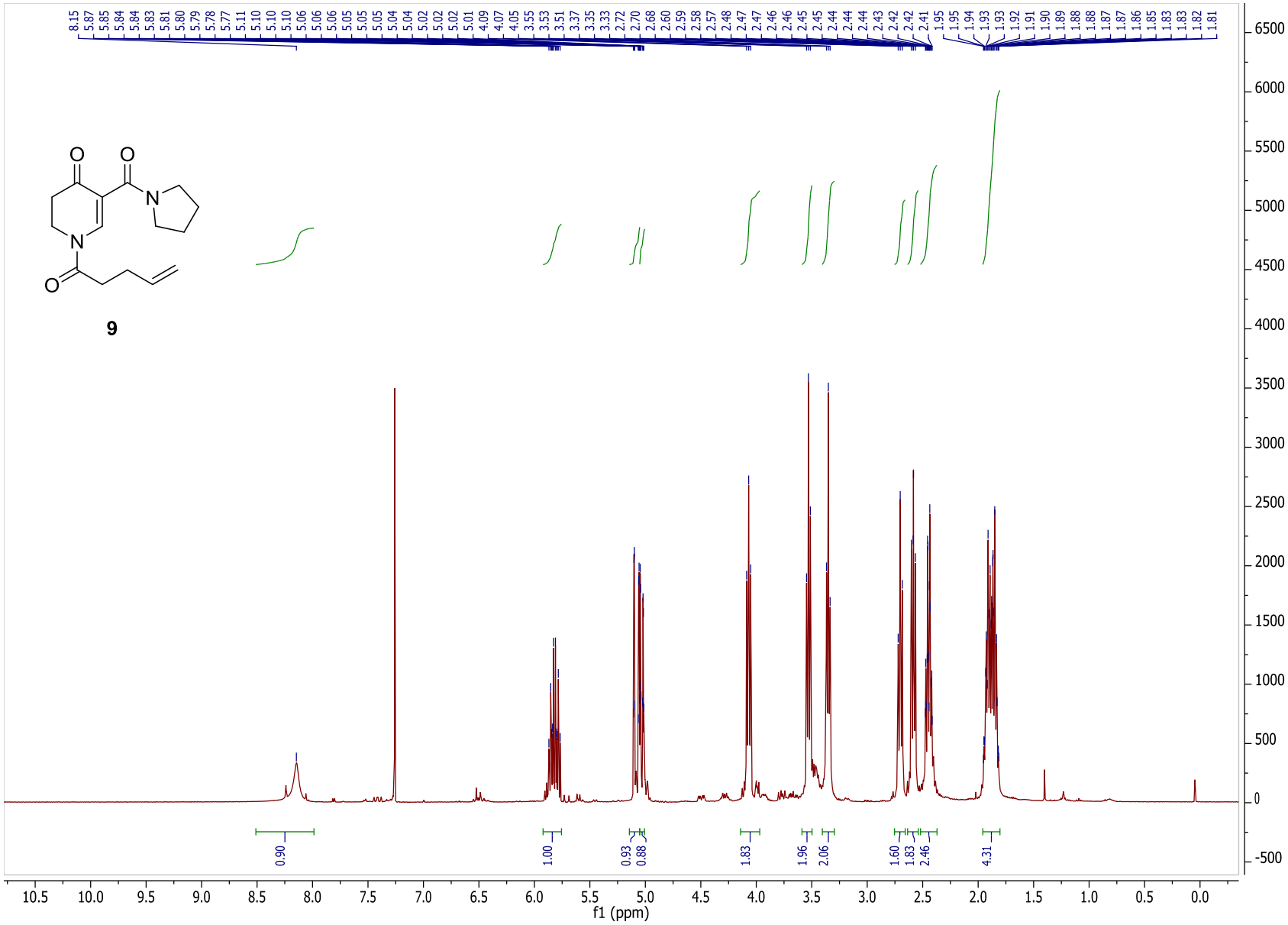
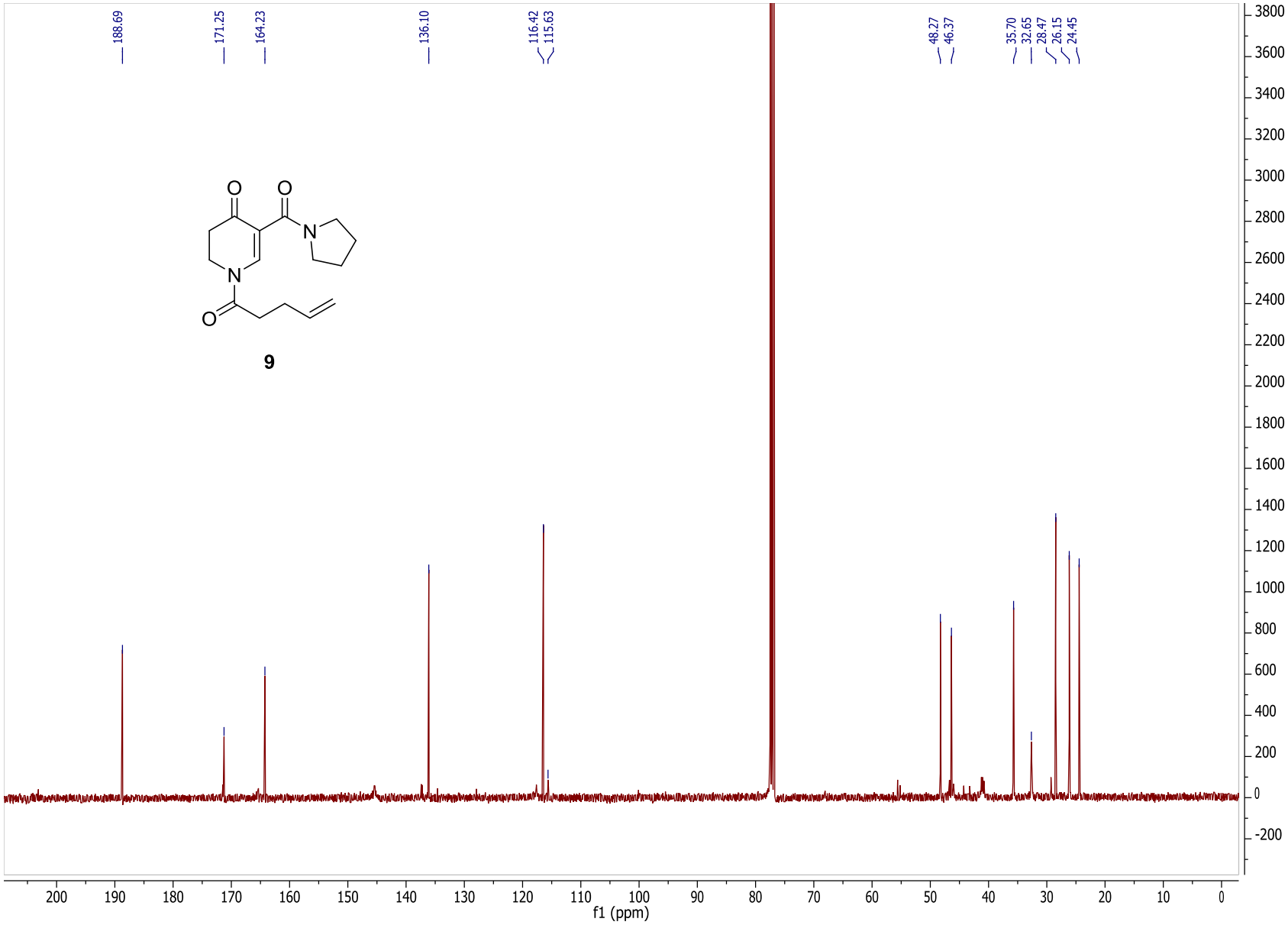
164.04
149.50
135.94
116.64
109.11
61.11
41.62
36.27
32.80
28.52
14.41
O
O
O
N
O
f1 (ppm)


9
f1 (ppm)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115.63
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46.37
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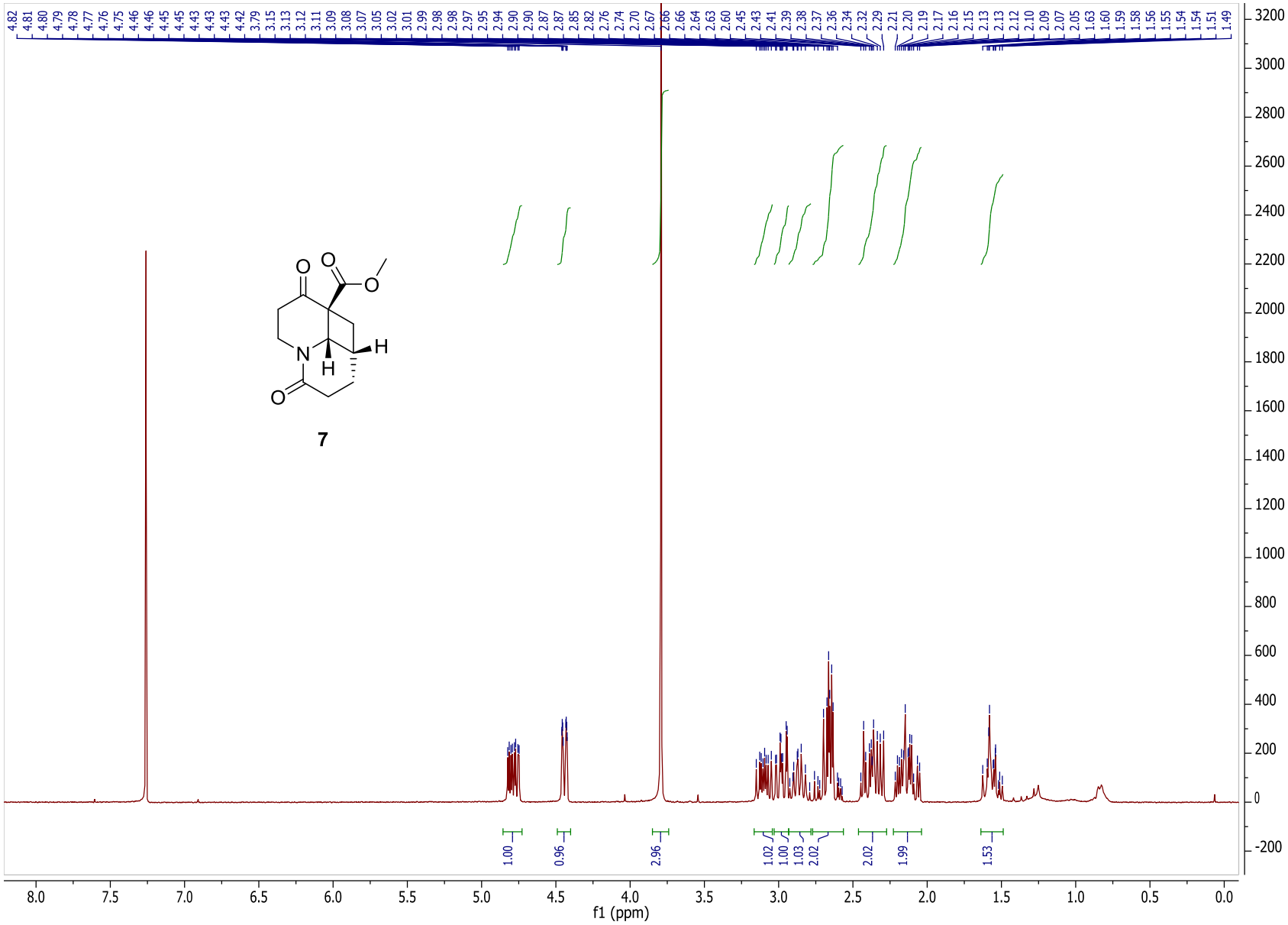
32.65
28.47
26.15
24.45
9
f1 (ppm)


7
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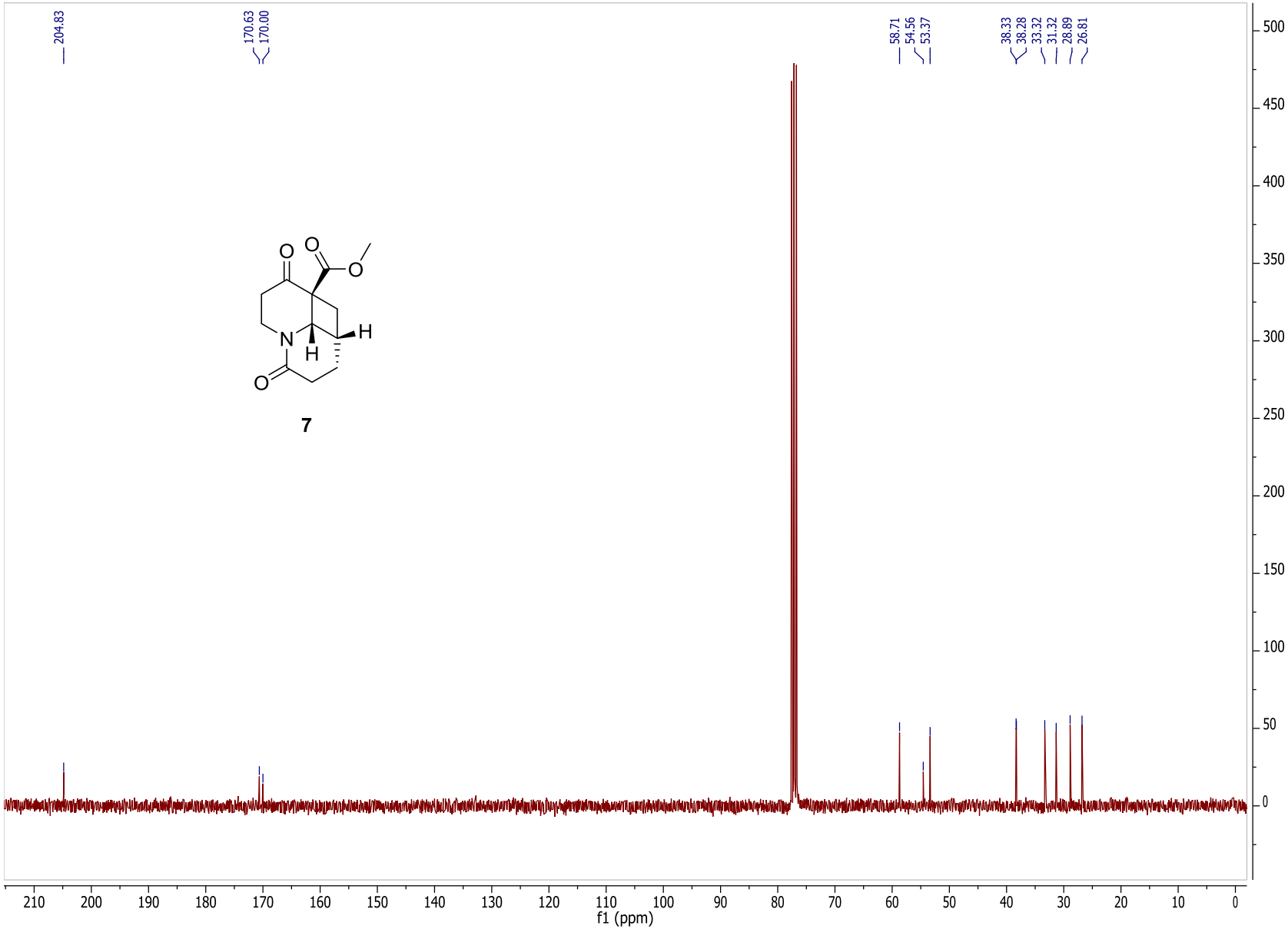
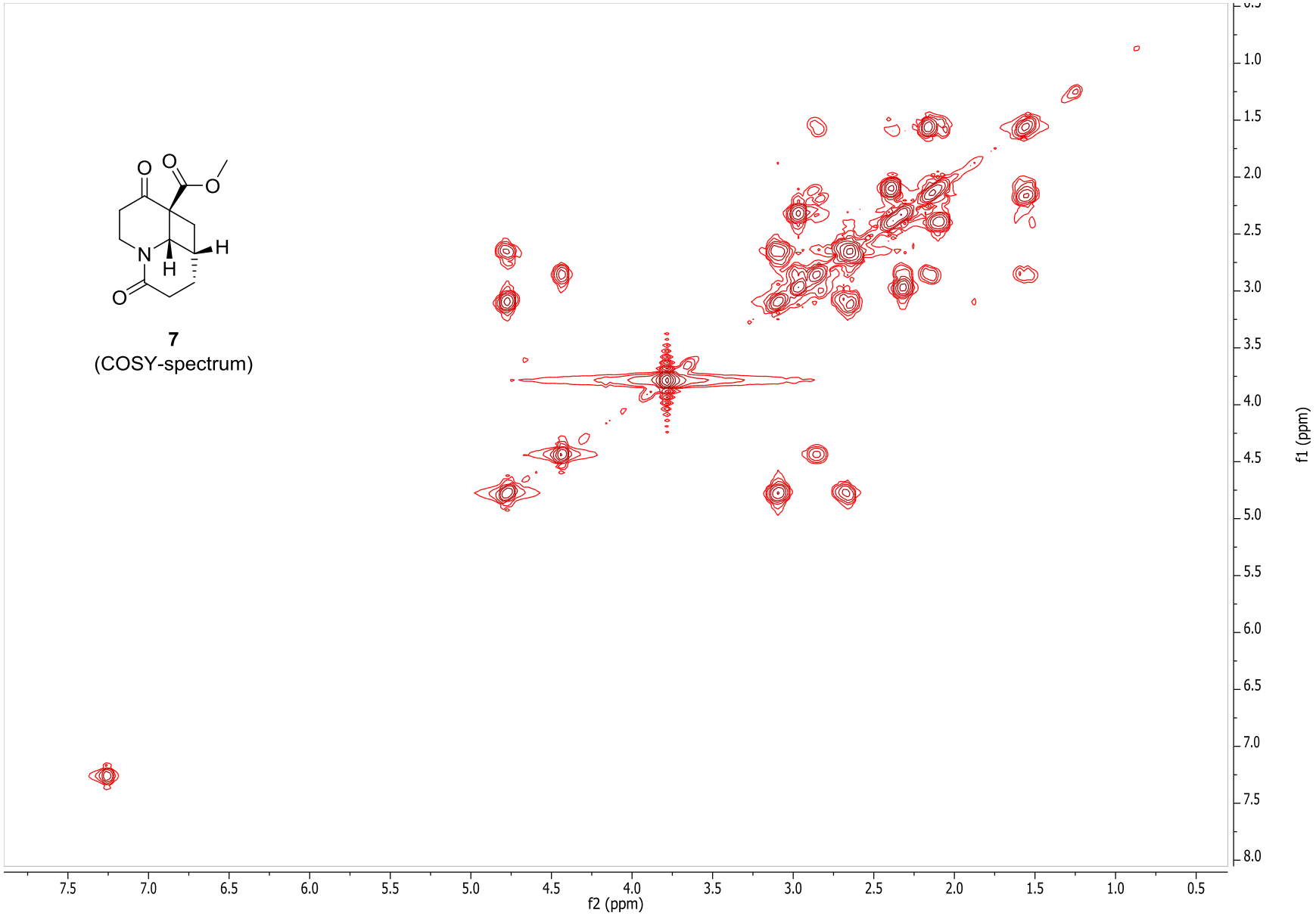
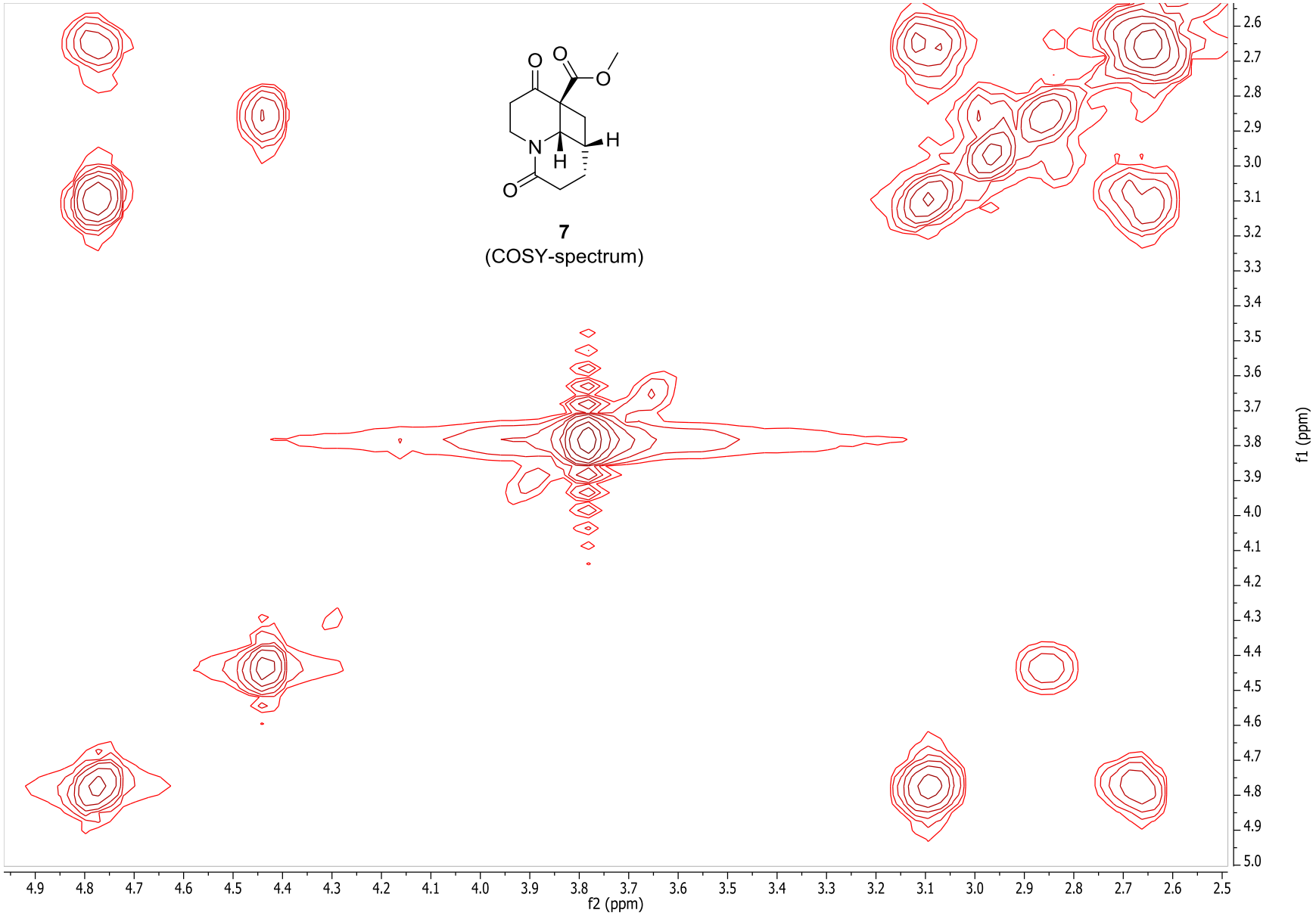
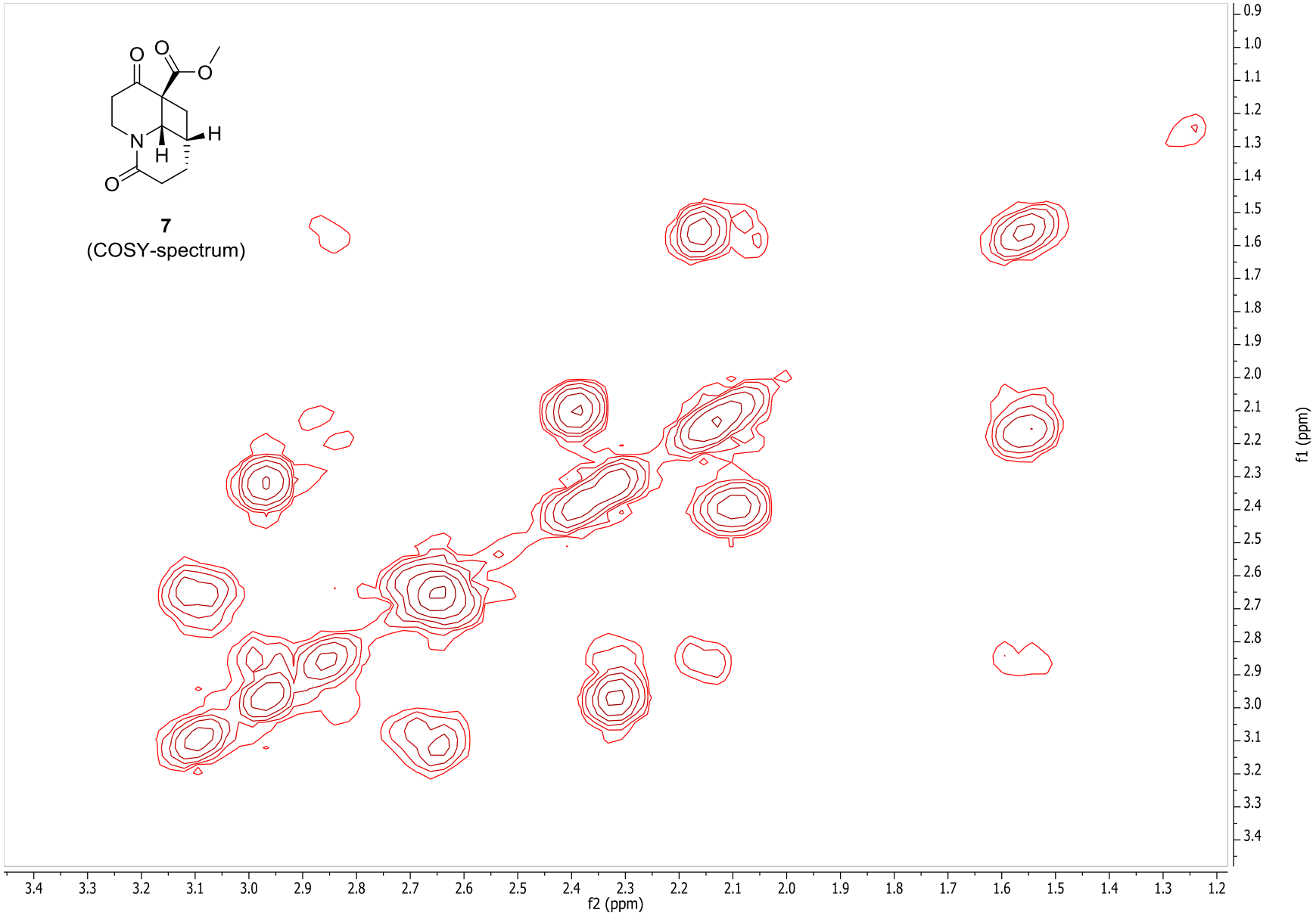
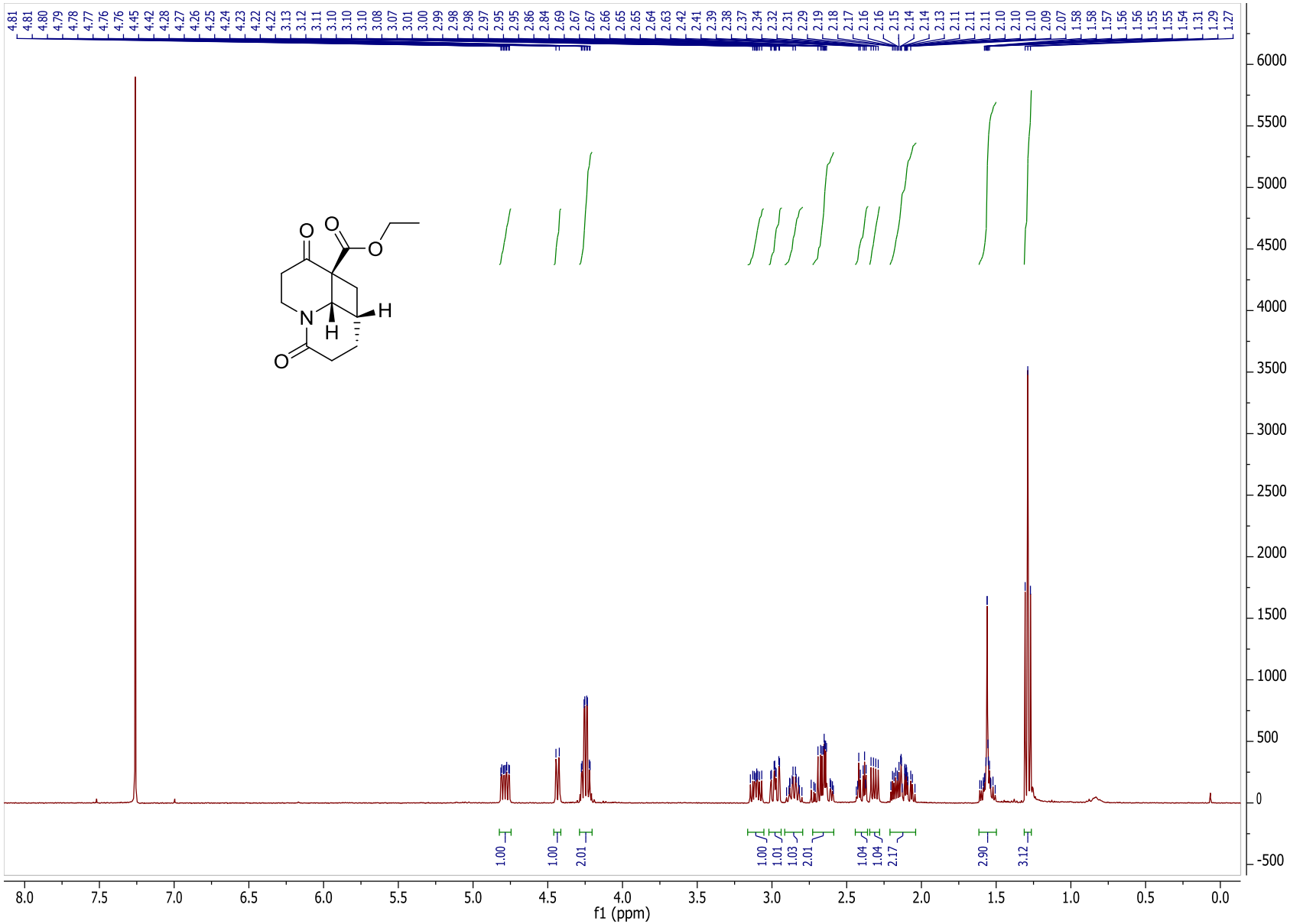

204.83
170.63
170.00
58.71
54.56
53.37
38.33
38.28
33.32
31.32
28.89
26.81
O
O
O
N
H
H
O
7
f1 (ppm)


O
O
O
N
H
H
O
7
(COSY-spectrum)
f2 (ppm)
f1 (ppm)


O
O
O
N
H
H
O
7
(COSY-spectrum)
f2 (ppm)
f1 (ppm)


O
O
O
N
H
H
O
7
(COSY-spectrum)
f2 (ppm)
f1 (ppm)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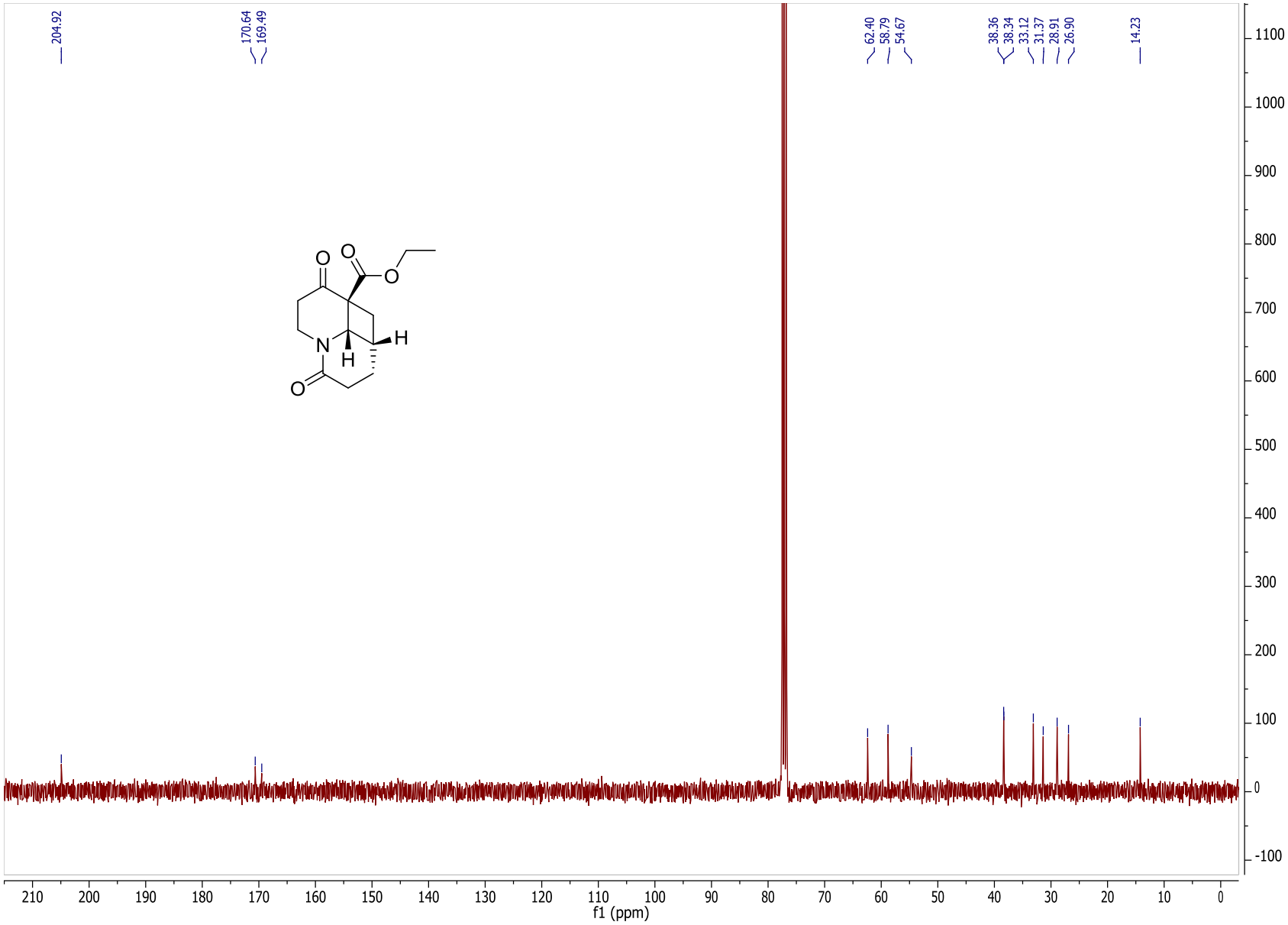
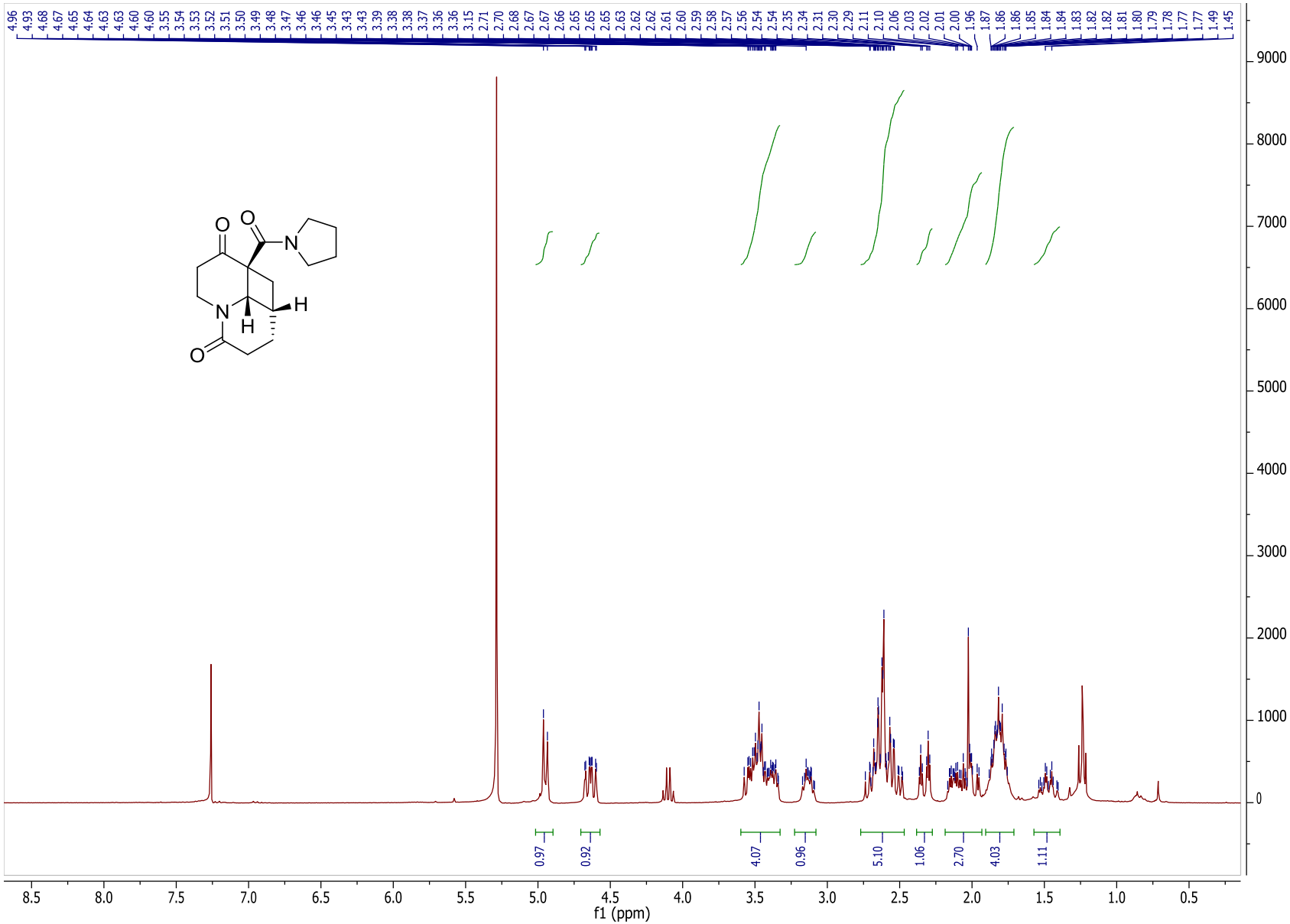
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
1.00
1.00
2.01
1.00
1.01
1.03
2.01
1.04
1.04
2.17
2.90
3.12
O
O
O
N
H
H
O


204.92
170.64
169.49
62.40
58.79
54.67
38.36
38.34
33.12
31.37
28.91
26.90
14.23
O
O
O
N
H
H
O
f1 (ppm)


4.96 4.93 4.68 4.67 4.65 4.64 4.63 4.63 4.60 4.60 3.55 3.54 3.53 3.52 3.51 3.50 3.49 3.48 3.47 3.46 3.46 3.45 3.43 3.43 3.39 3.38 3.38 3.37 3.36 3.36 3.15 2.71 2.70 2.68 2.67 2.67 2.66 2.65 2.65 2.65 2.63 2.62 2.62 2.61 2.60 2.59 2.58 2.57 2.56 2.54 2.54 2.35 2.34 2.31 2.30 2.29 2.11 2.10 2.06 2.03 2.02 2.01 2.00 1.96 1.87 1.86 1.86 1.85 1.84 1.84 1.83 1.82 1.82 1.81 1.80 1.79 1.78 1.77 1.77 1.49 1.45
O
O
N
N
H
H
O
0.97
0.92
4.07
0.96
5.10
1.06
2.70
4.03
1.11
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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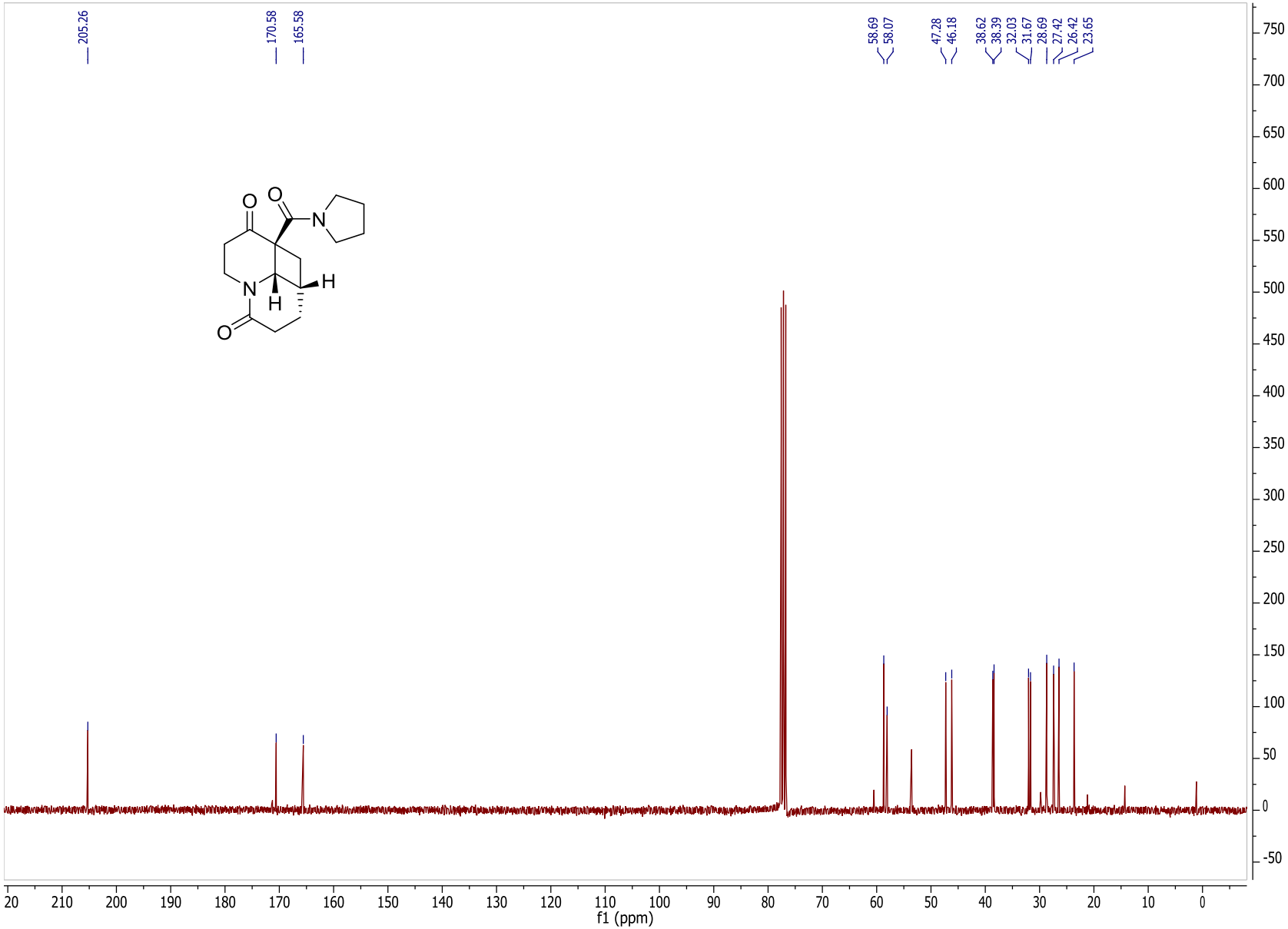
f1 (ppm)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58.69
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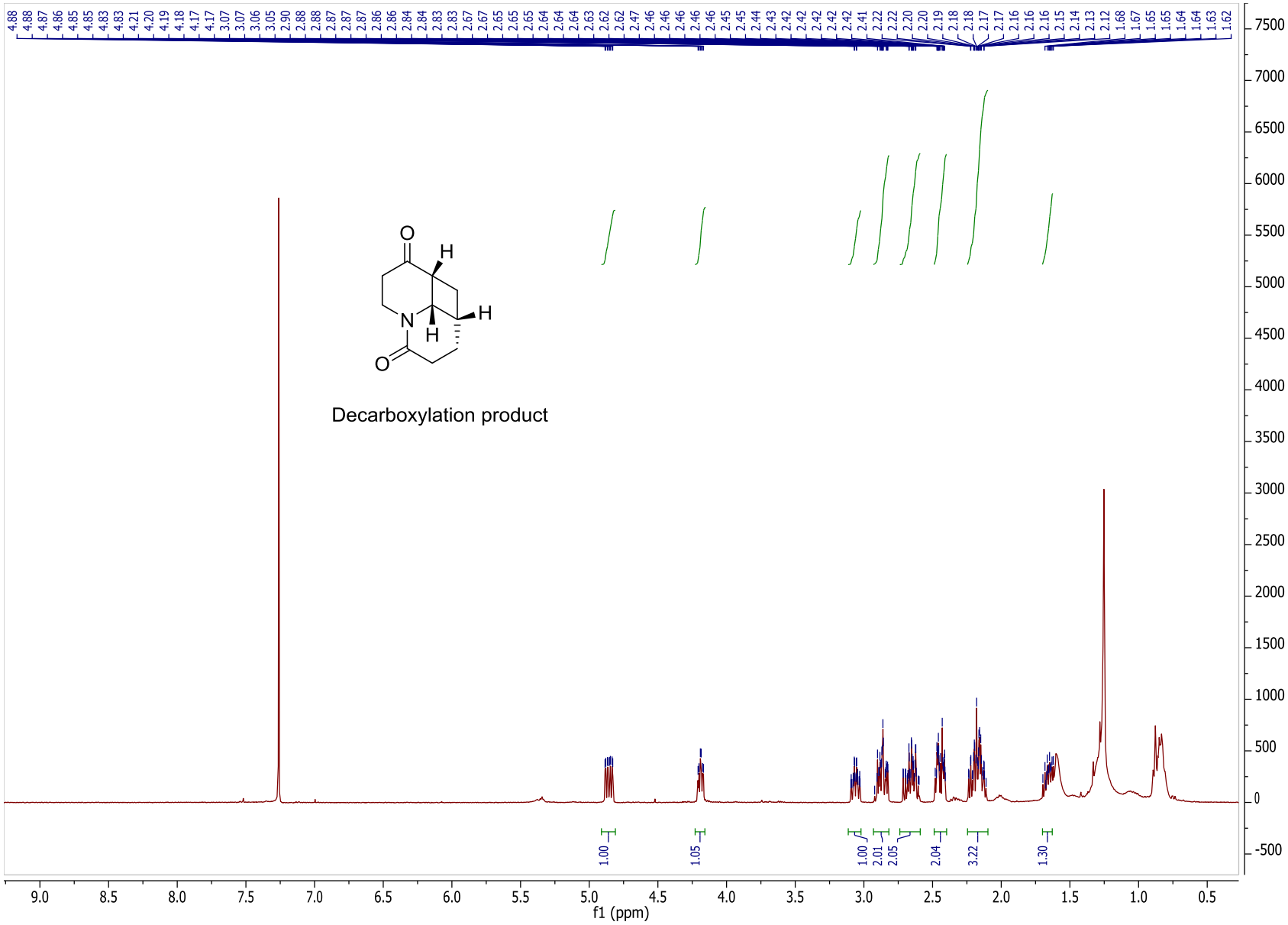
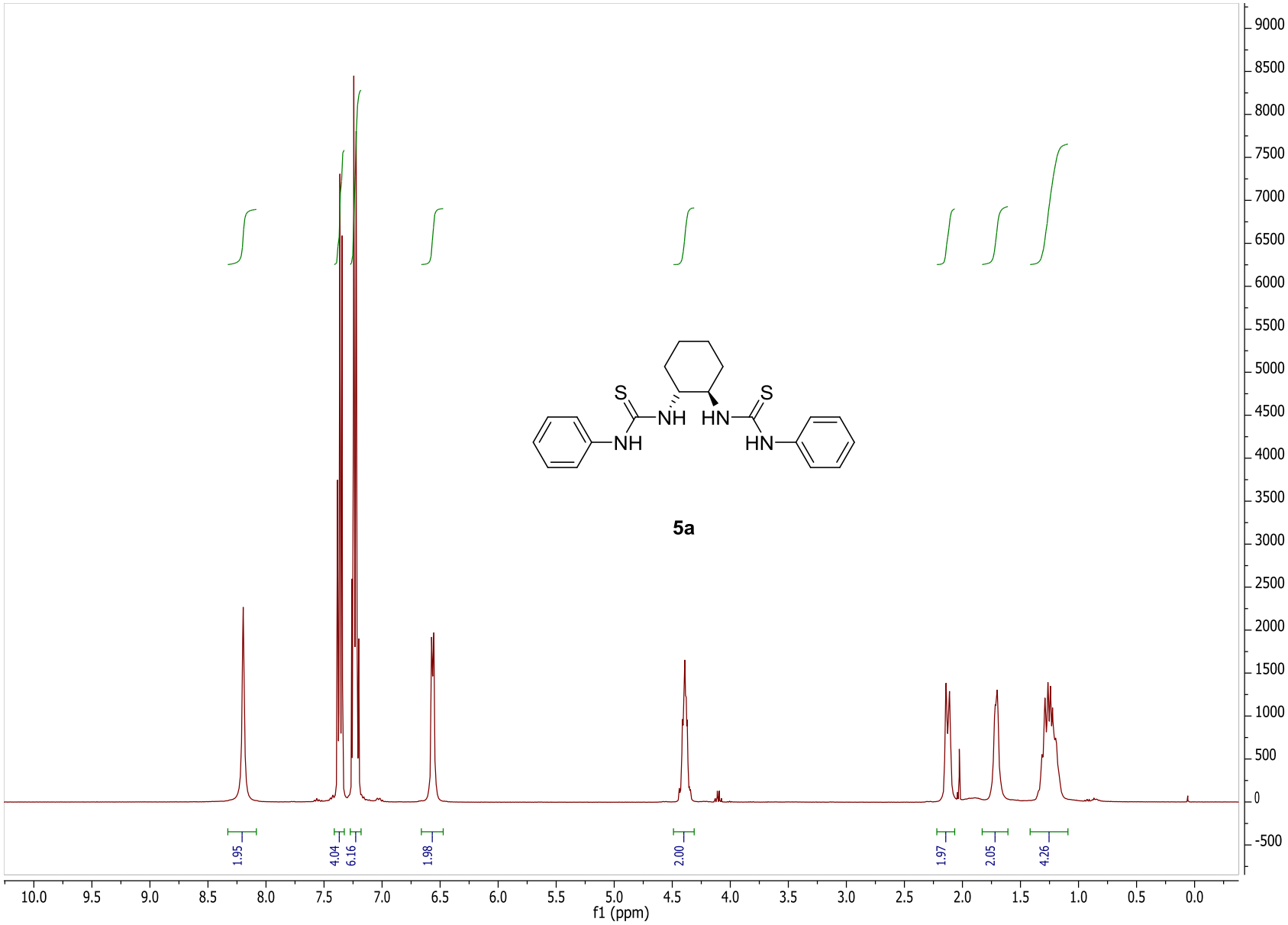
23.65
f1 (ppm)


Decarboxylation product
f1 (ppm)


S
NH
HN
S
NH
HN
5a
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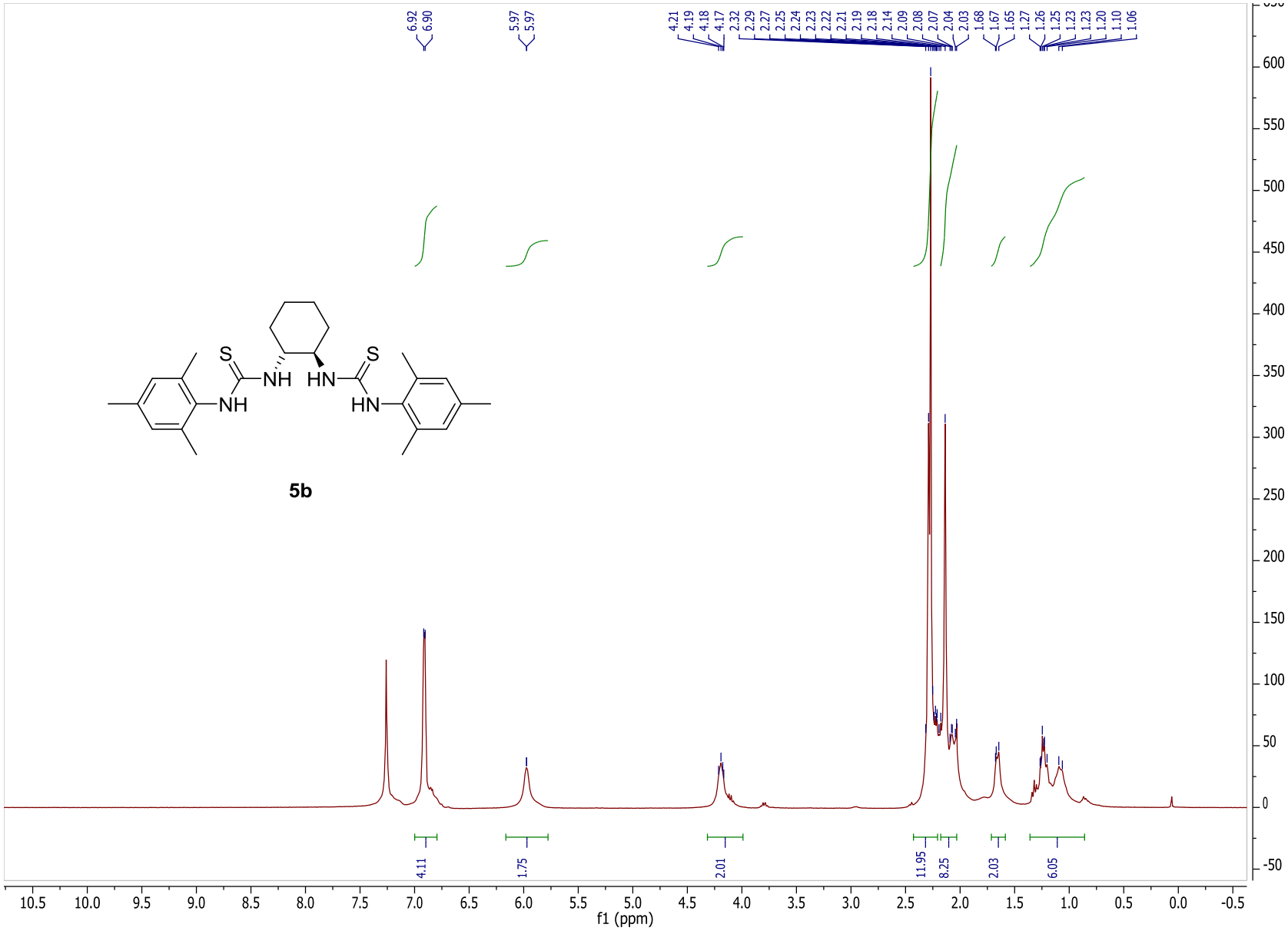
6.16
1.98
2.00
1.97
2.05
4.26
f1 (ppm)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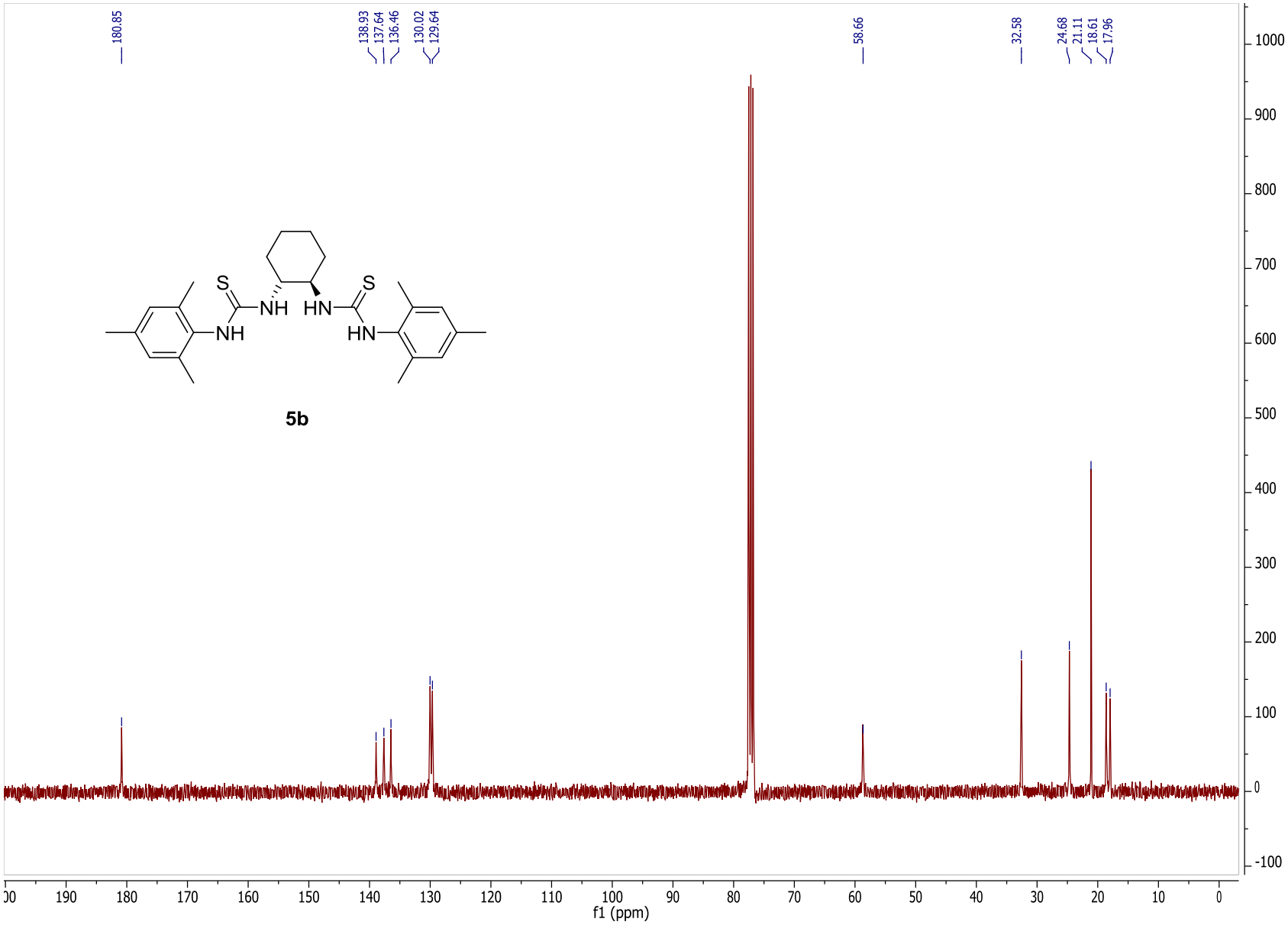
6.90
5.97
5.97
4.21
4.19
4.18
4.17
2.32
2.29
2.27
2.25
2.24
2.23
2.22
2.21
2.19
2.18
2.14
2.09
2.08
2.07
2.04
2.03
1.68
1.67
1.65
1.27
1.26
1.25
1.23
1.23
1.20
1.10
1.06
S
NH
NH
HN
S
HN
5b
4.11
1.75
2.01
11.95
8.25
2.03
6.05
f1 (ppm)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137.64
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130.02
129.64
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24.68
21.11
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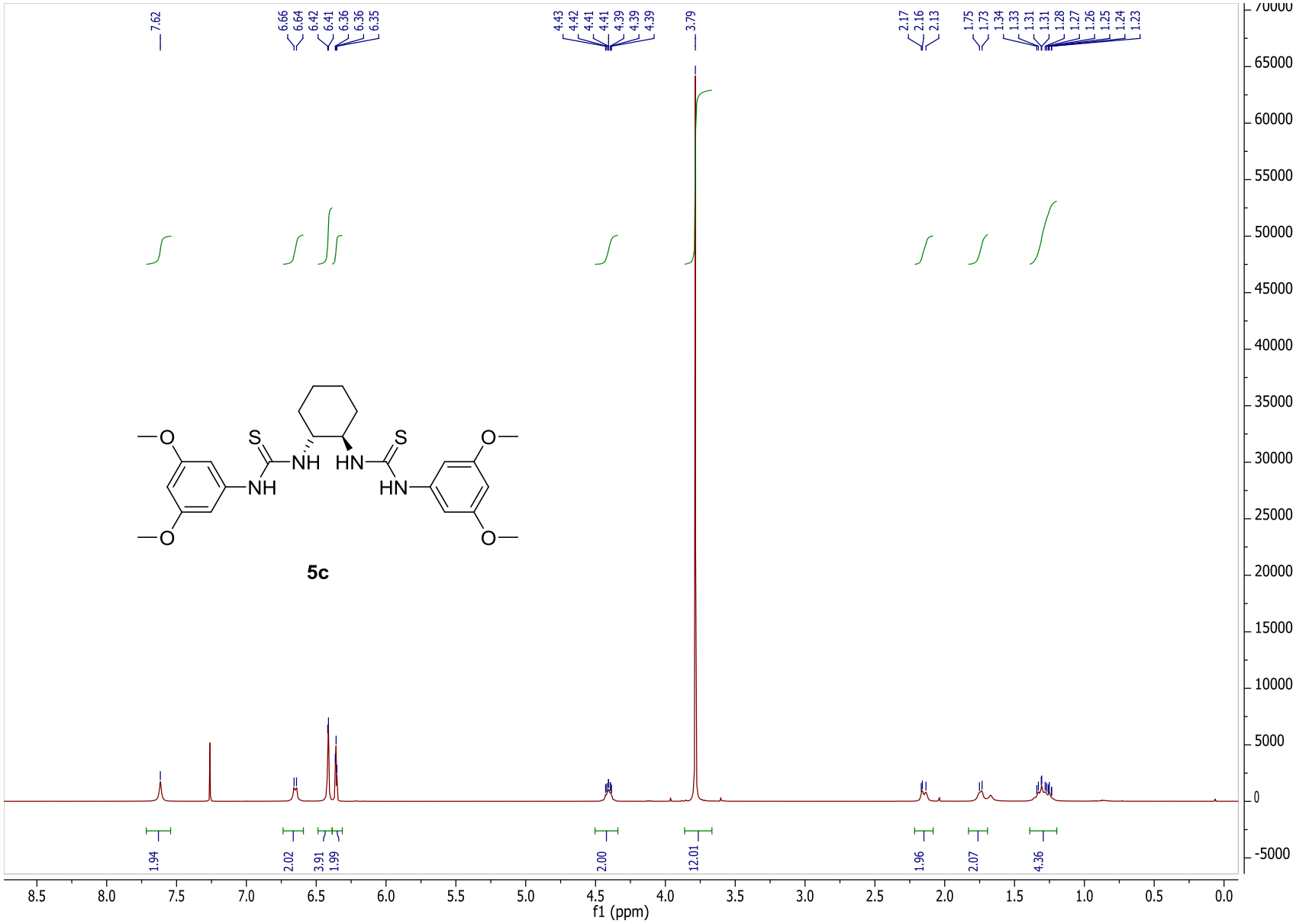
S
NH
HN
S
NH
HN
5b
f1 (ppm)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6.42
6.41
6.36
6.36
6.35
4.43
4.42
4.41
4.41
4.39
4.39
4.39
3.79
2.17
2.16
2.13
1.75
1.73
1.34
1.33
1.31
1.31
1.28
1.27
1.26
1.25
1.24
1.23
1.94
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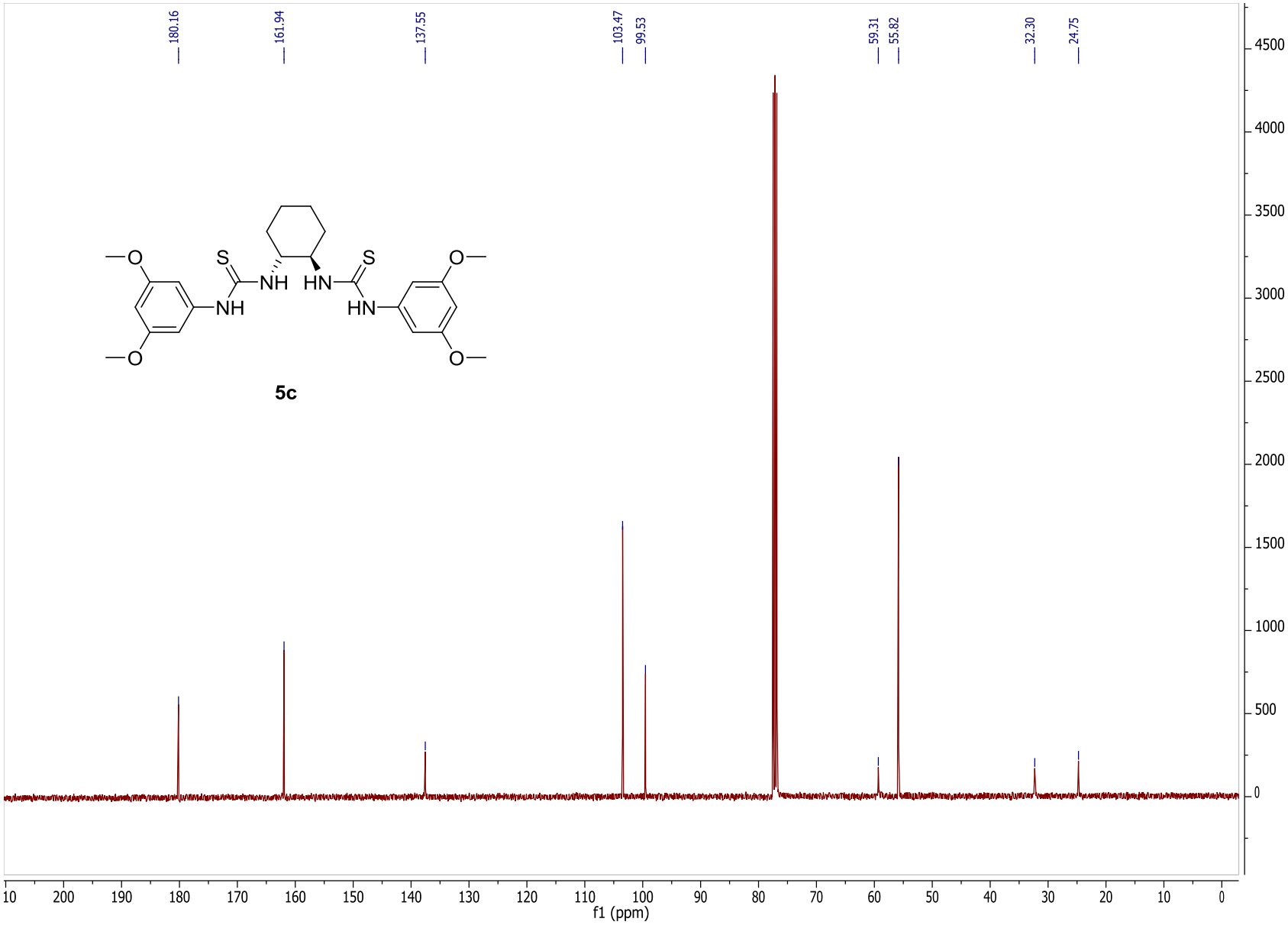
3.91
1.99
2.00
12.01
1.96
2.07
4.36
f1 (ppm)
5c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137.55
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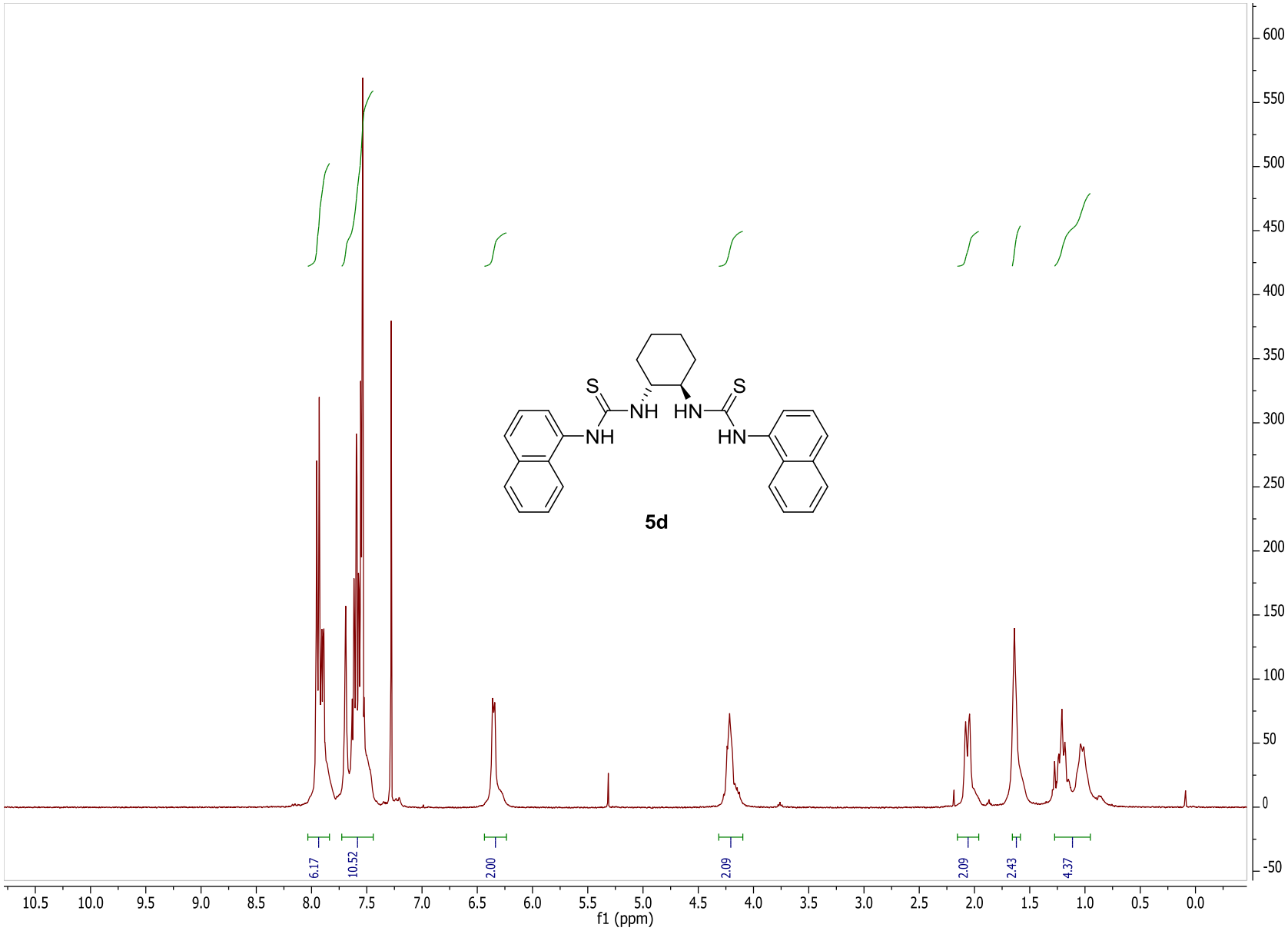
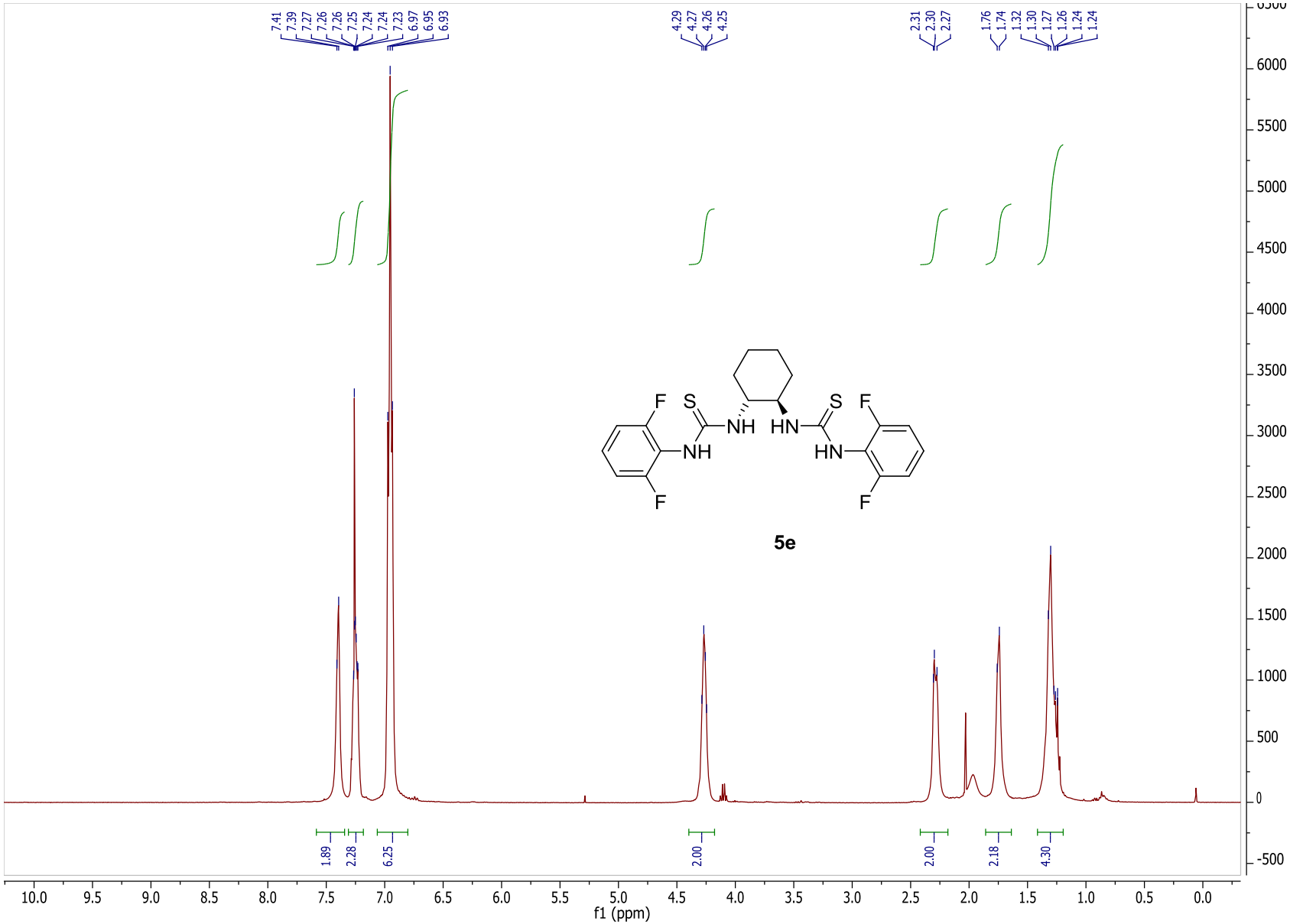
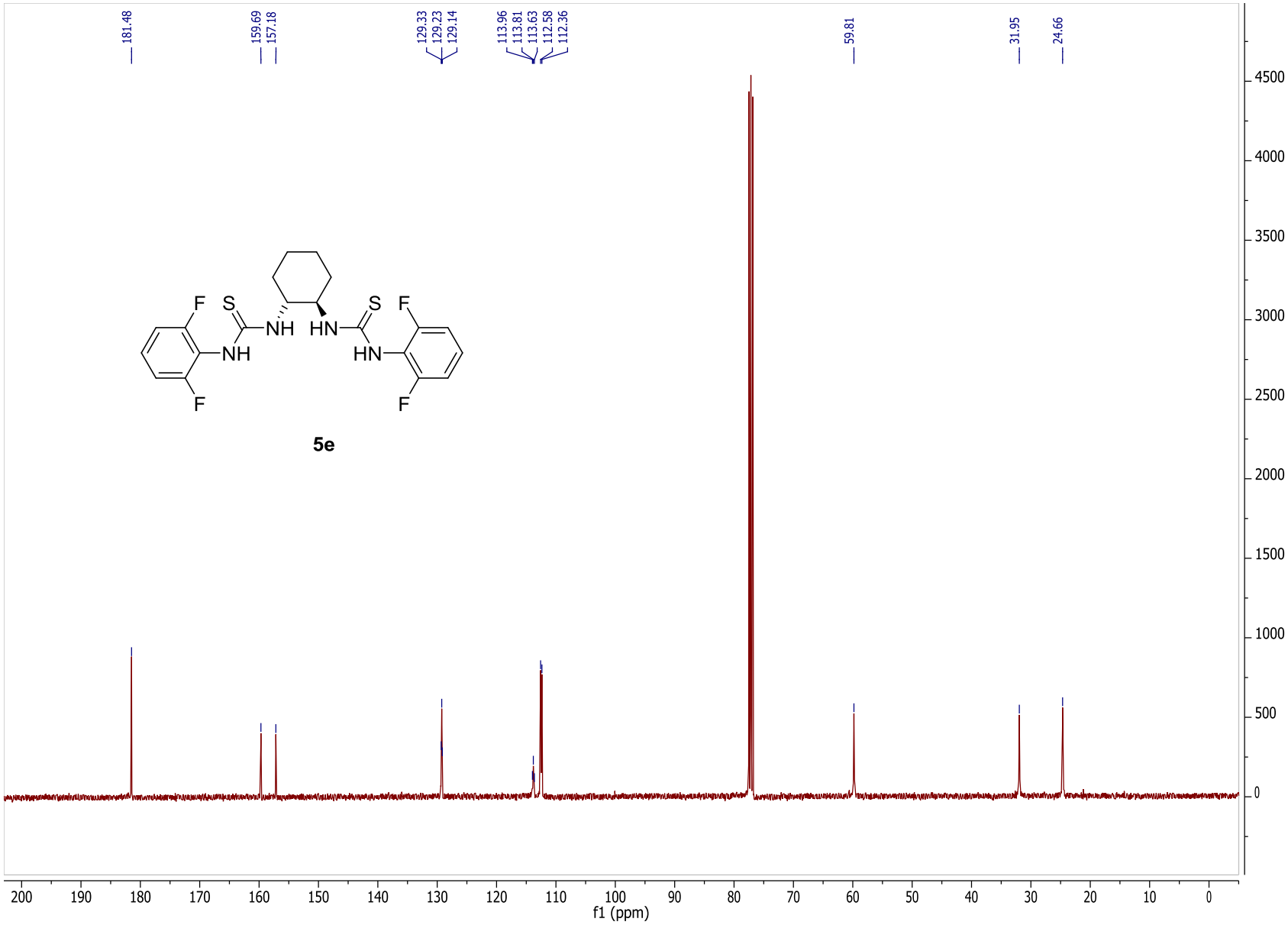
99.53
59.31
55.82
32.30
24.75
5c
f1 (ppm)


S
NH
HN
S
NH
HN
5d
6.17
10.52
2.00
2.09
2.09
2.43
4.37
f1 (ppm)


7.41
7.39
7.27
7.26
7.26
7.25
7.24
7.24
7.23
6.97
6.95
6.93
4.29
4.27
4.26
4.25
2.31
2.30
2.27
1.76
1.74
1.32
1.30
1.27
1.26
1.24
1.24
F
S
NH
HN
S
F
NH
HN
F
F
5e
1.89
2.28
6.25
2.00
2.00
2.18
4.30
f1 (ppm)


181.48
159.69
157.18
129.33
129.23
129.14
113.96
113.81
113.63
112.58
112.36
59.81
31.95
24.66
F
S
NH
HN
S
F
NH
HN
F
F
5e
4500
4000
3500
3000
2500
2000
1500
1000
500
0
200
190
180
170
160
150
140
130
120
110
100
90
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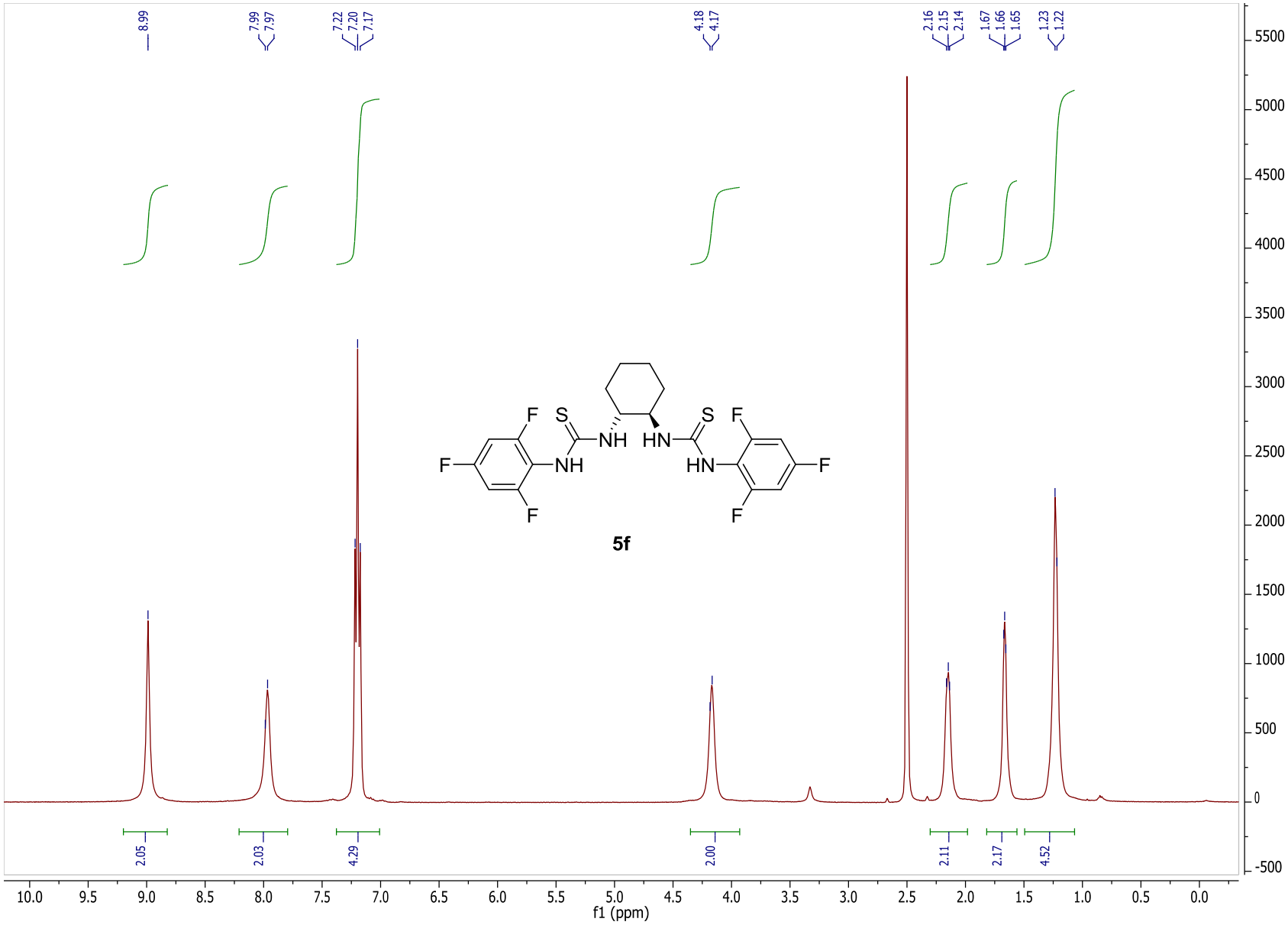
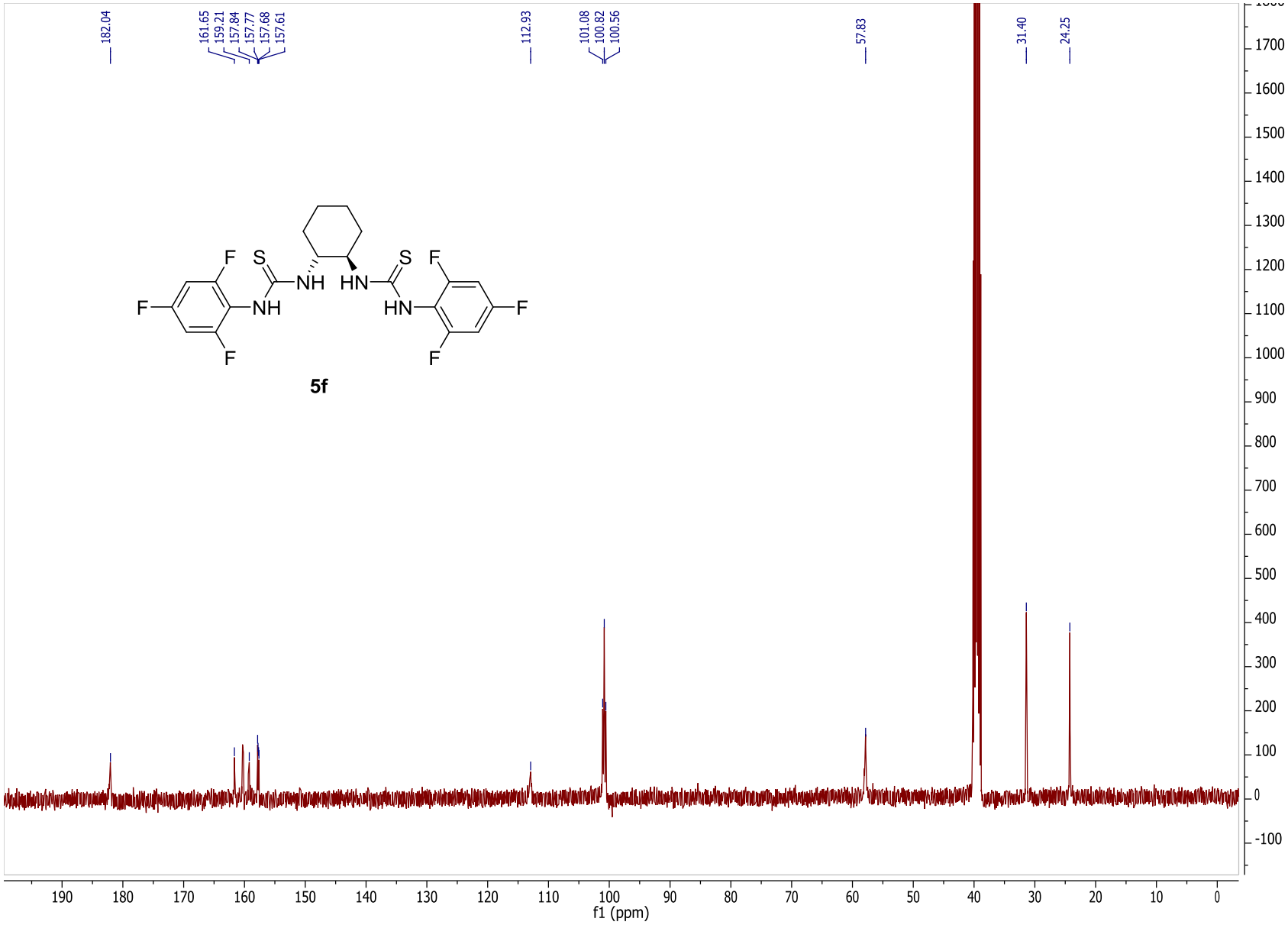
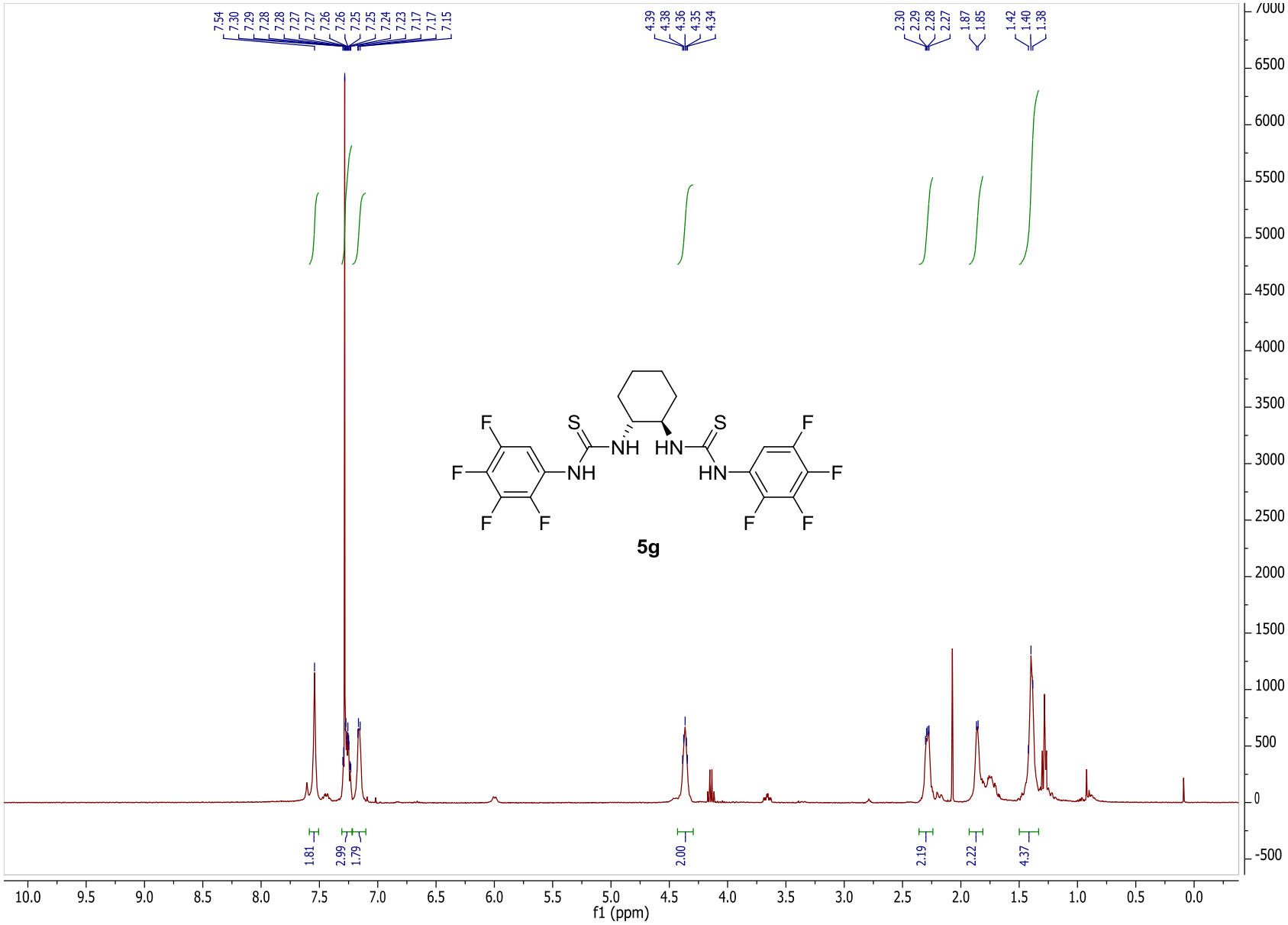
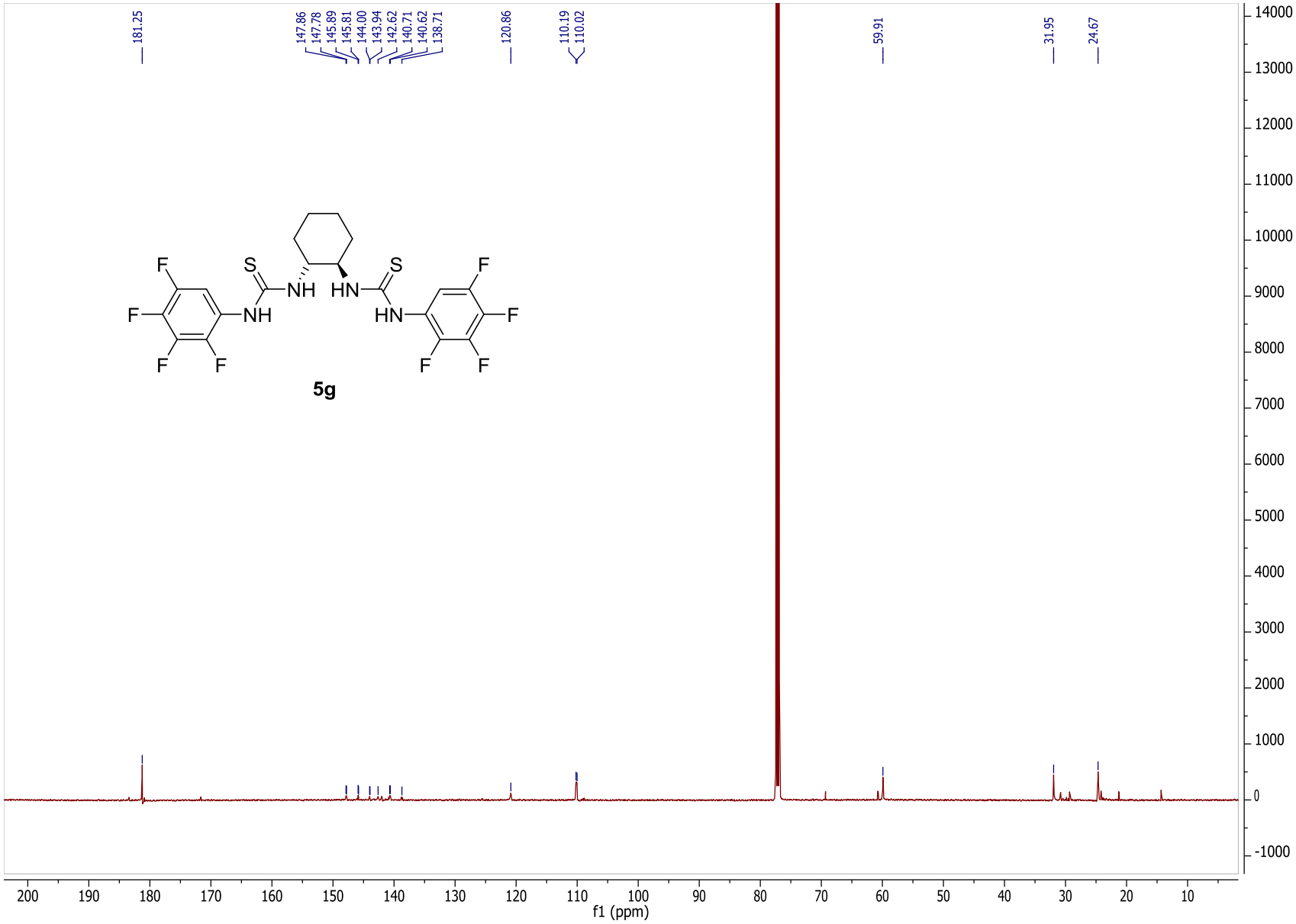
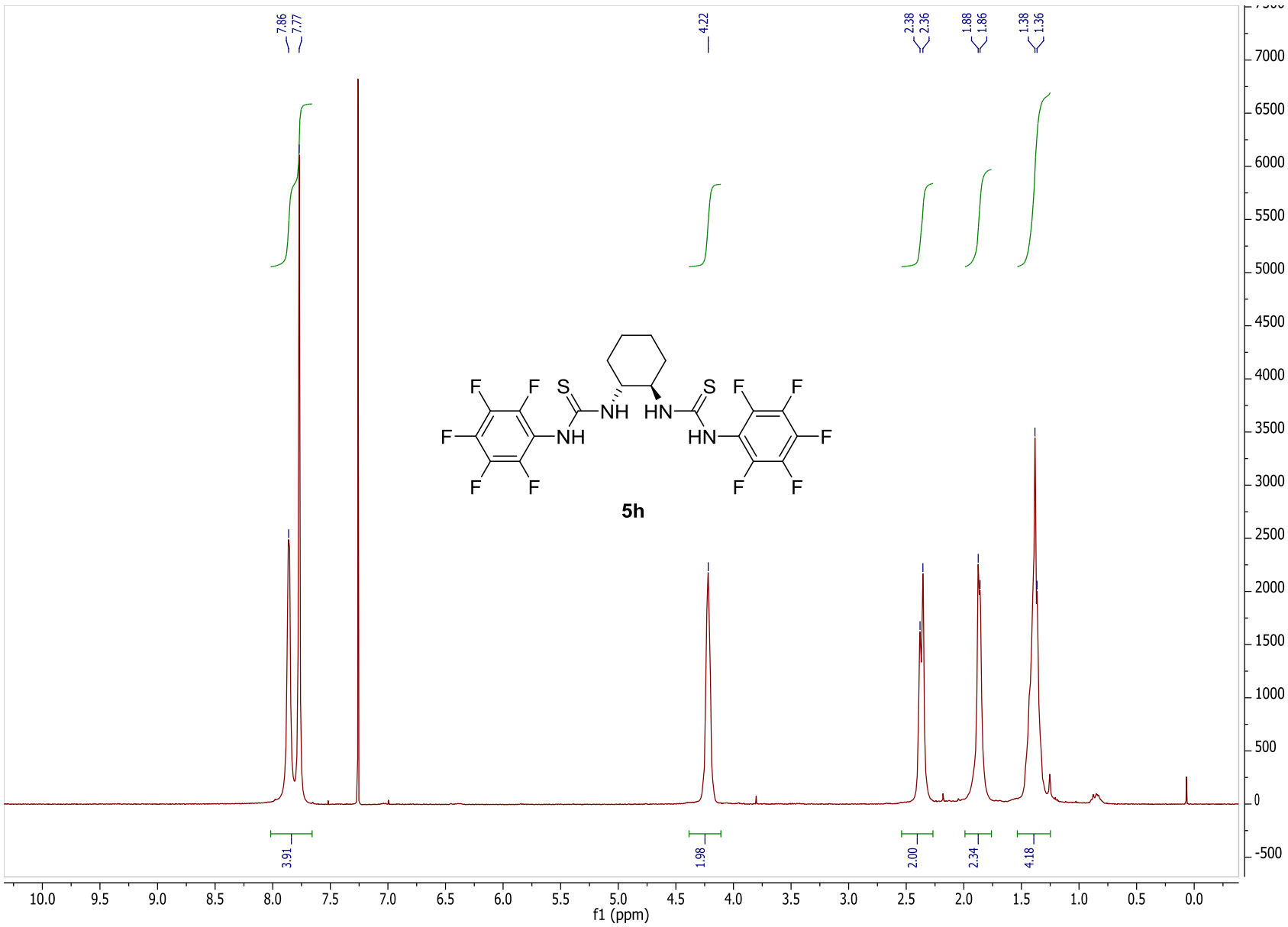
70
60
50
40
30
20
10
0
f1 (ppm)

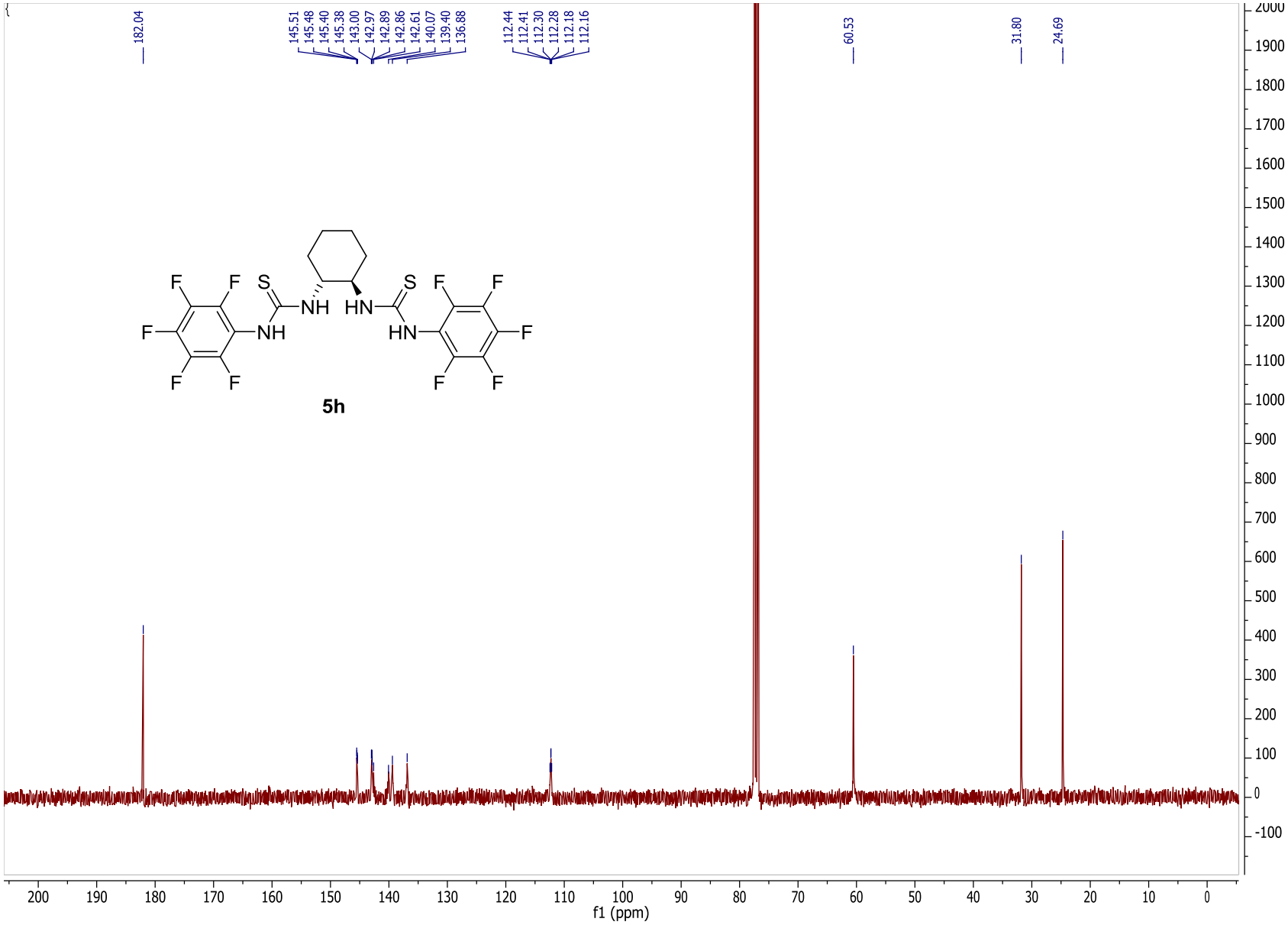

8.99
7.99
7.97
7.22
7.20
7.17
4.18
4.17
2.16
2.15
2.14
1.67
1.66
1.65
1.23
1.22
2.05
2.03
4.29
2.00
2.11
2.17
4.52
f1 (ppm)
5f

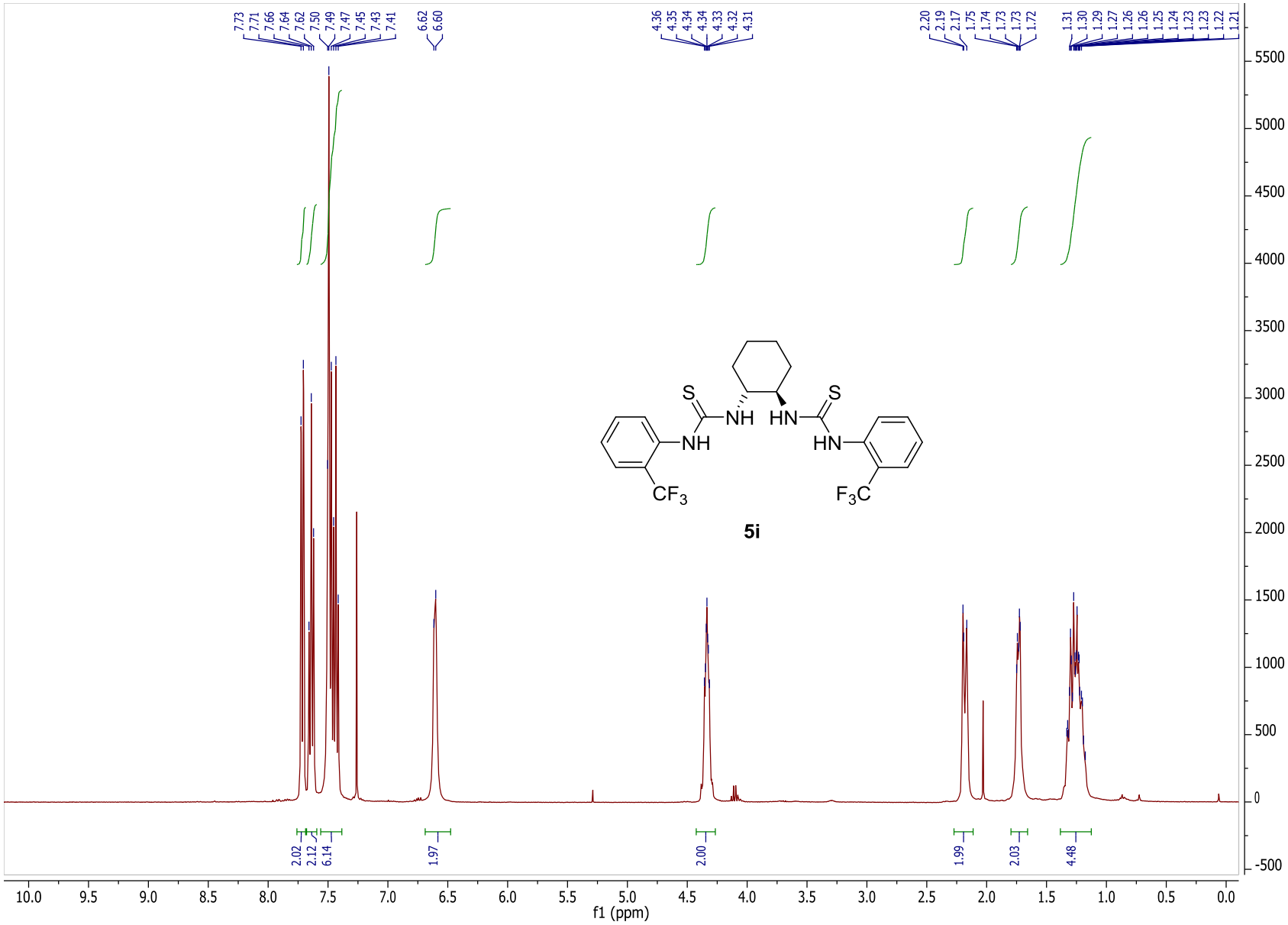

182.04
161.65
159.21
157.84
157.77
157.68
157.61
112.93
101.08
100.82
100.56
57.83
31.40
24.25
F
S
NH
HN
S
F
F
NH
HN
F
F
F
5f
f1 (ppm)

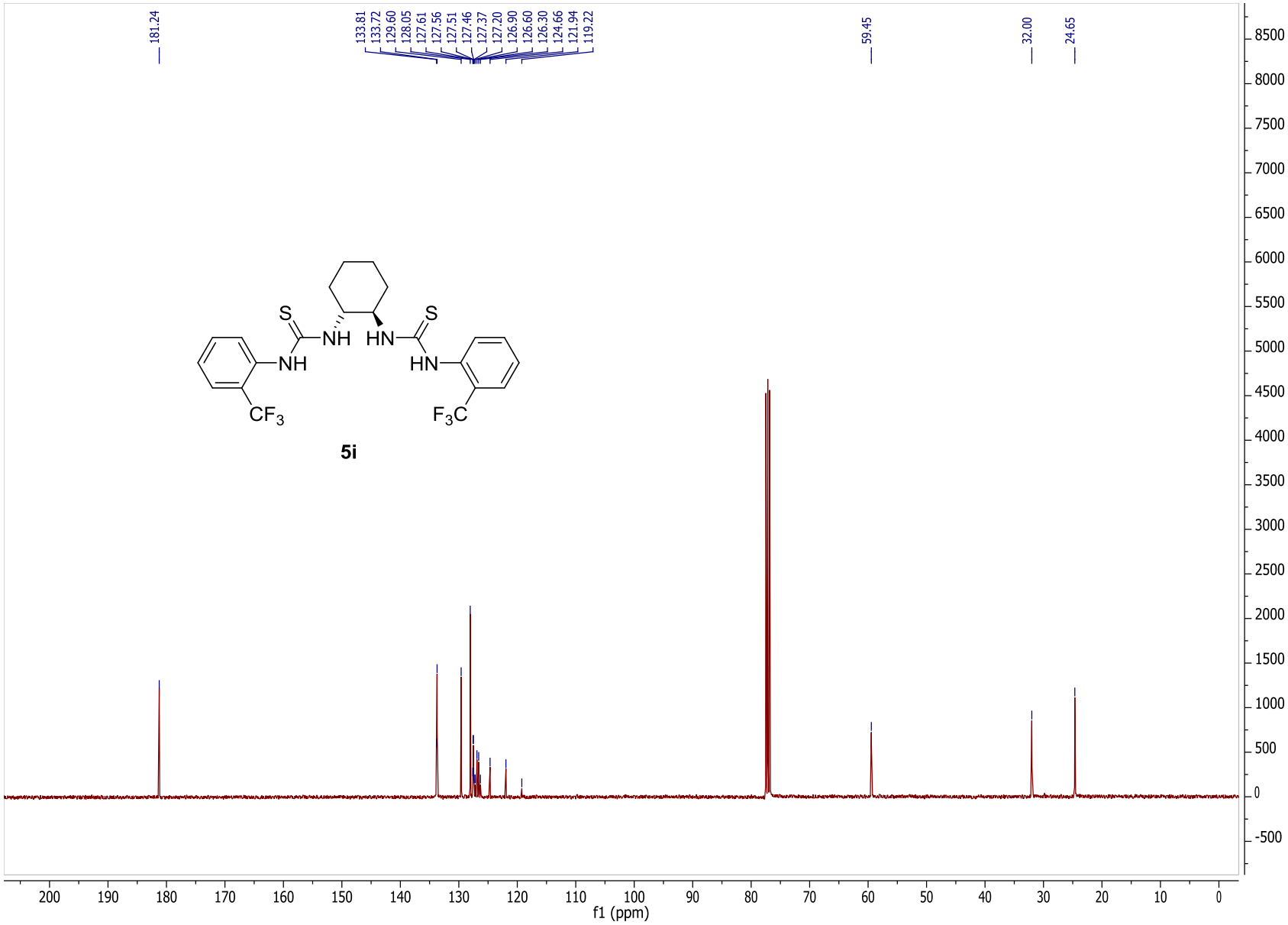

7.54
7.30
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.23
7.17
7.17
7.15
4.39
4.38
4.36
4.35
4.34
2.30
2.29
2.28
2.27
1.87
1.85
1.42
1.40
1.38
F
F
F
F
F
S
NH
NH
S
HN
HN
F
F
F
F
F
5g
1.81
2.99
1.79
2.00
2.19
2.22
4.37
f1 (ppm)

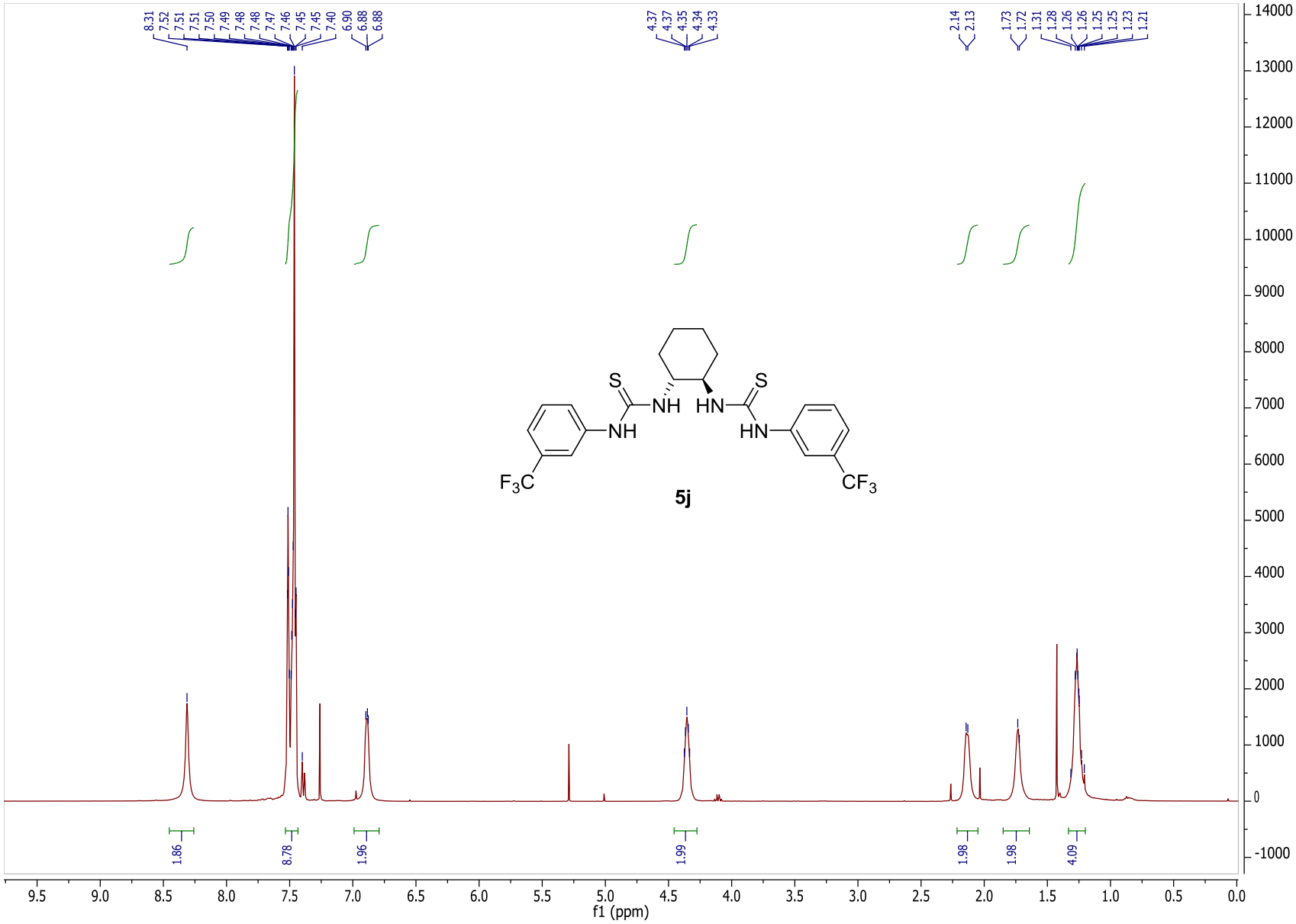

181.25
147.86
147.78
145.89
145.81
144.00
143.94
142.62
140.71
140.62
138.71
120.86
110.19
110.02
59.91
31.95
24.67
5g
f1 (ppm)

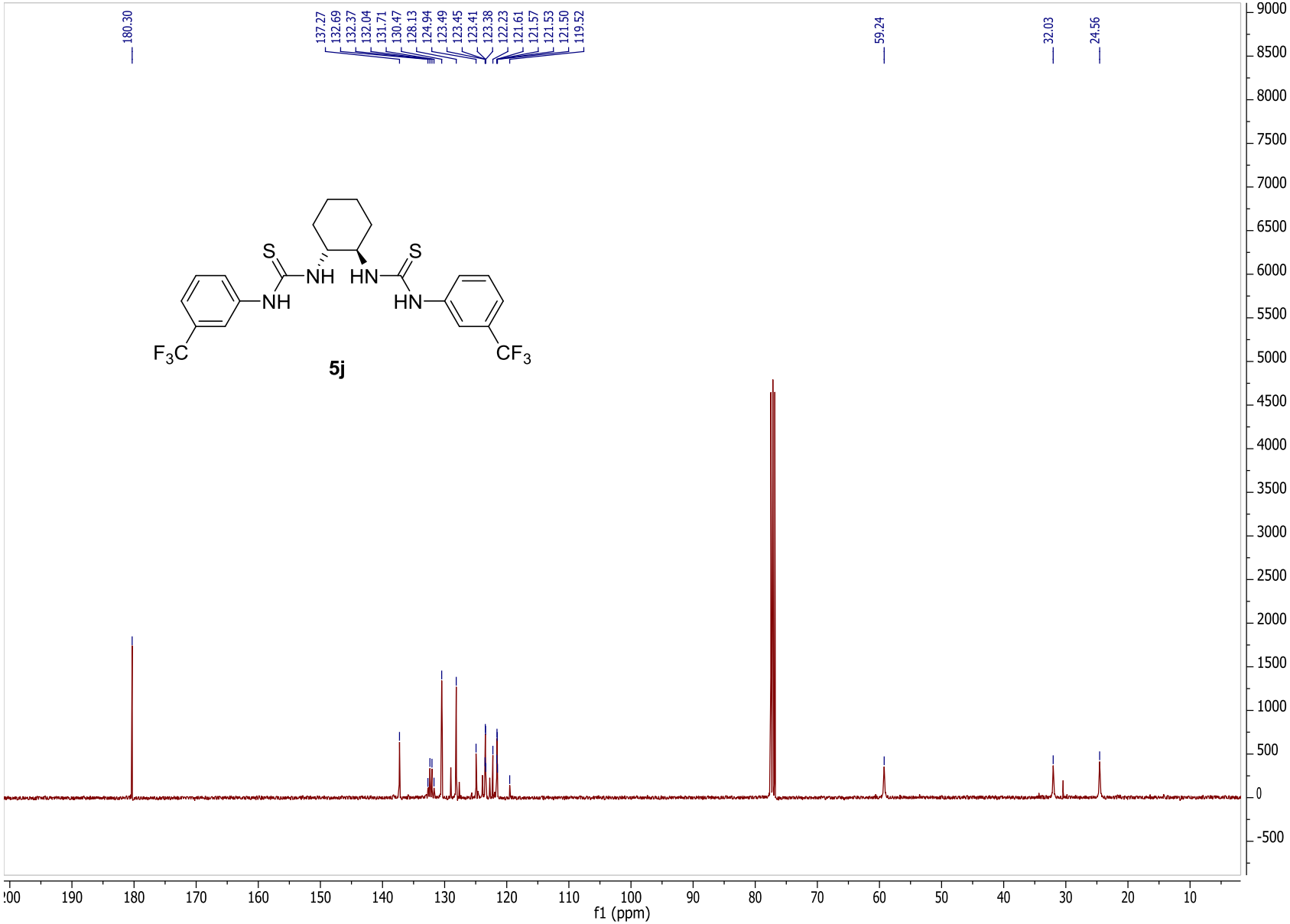

7.86
7.77
4.22
2.38
2.36
1.88
1.86
1.38
1.36
3.91
1.98
2.00
2.34
4.18
5h
f1 (ppm)

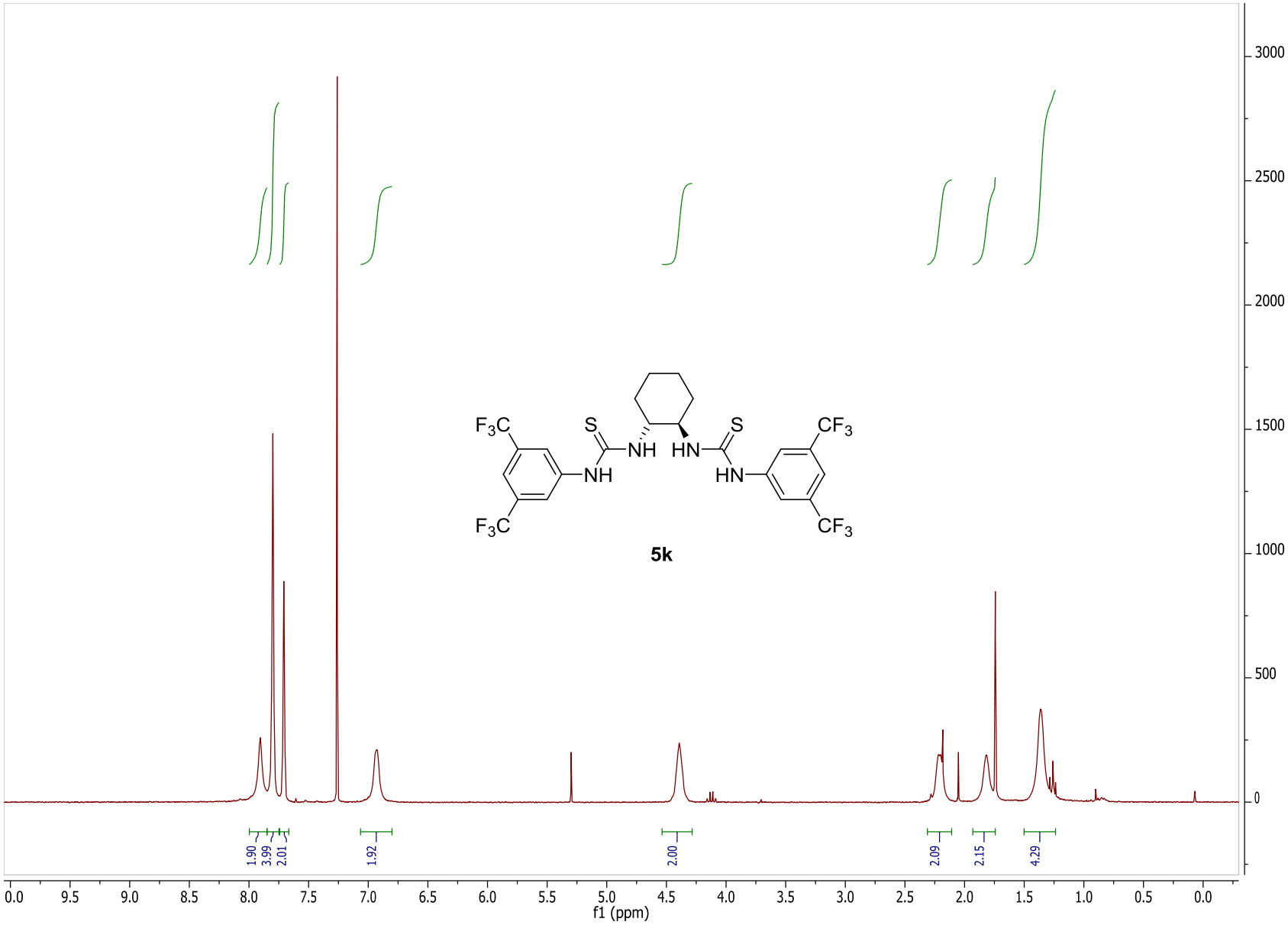

182.04
145.51
145.48
145.40
145.38
143.00
142.97
142.89
142.86
142.61
140.07
139.40
136.88
112.44
112.41
112.30
112.28
112.18
112.16
60.53
31.80
24.69
5h
f1 (ppm)

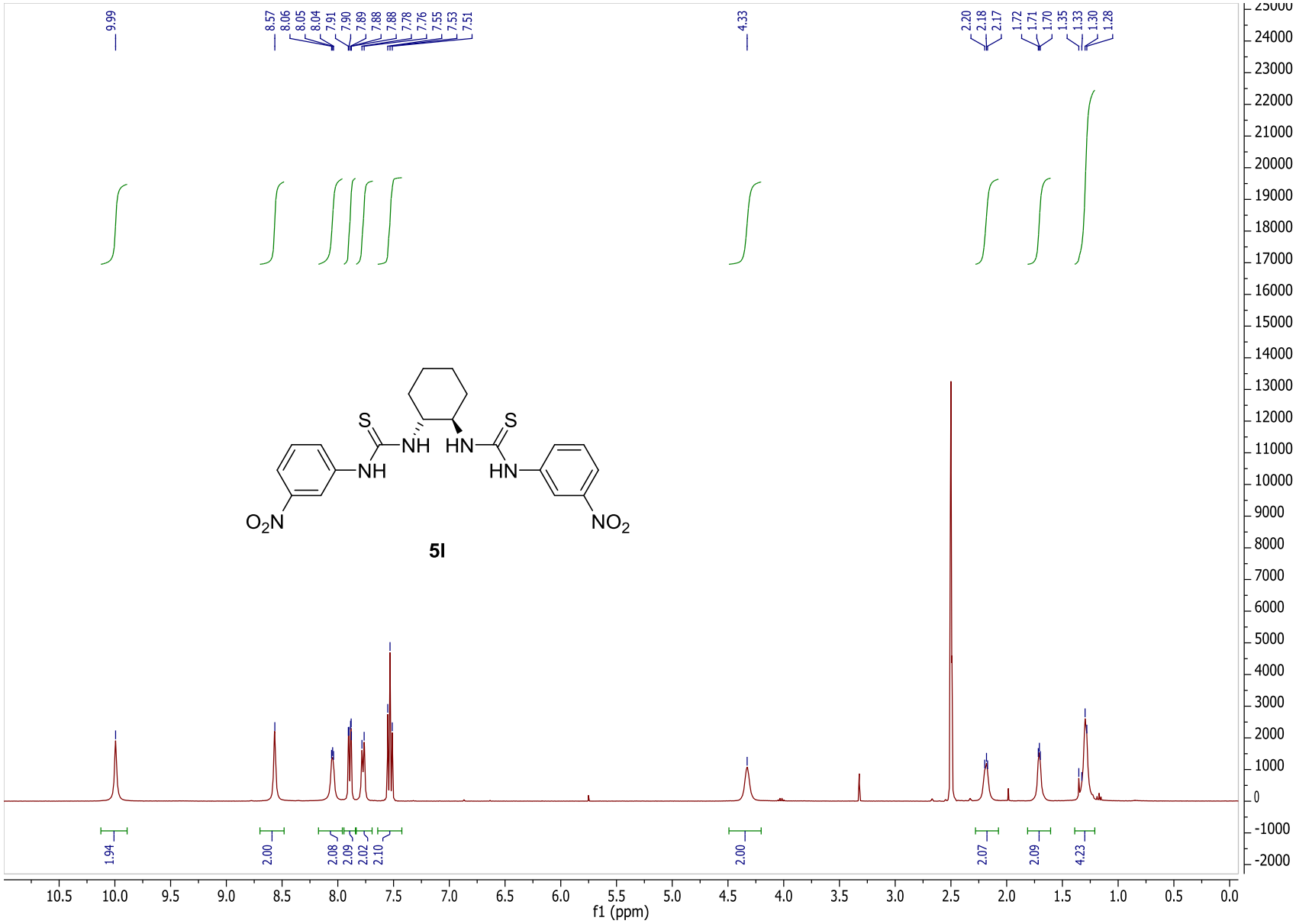

7.73
7.71
7.66
7.64
7.62
7.50
7.49
7.47
7.45
7.43
7.41
6.62
6.60
4.36
4.35
4.34
4.34
4.33
4.32
4.31
2.20
2.19
2.17
1.75
1.74
1.73
1.73
1.72
1.31
1.30
1.29
1.27
1.26
1.26
1.25
1.24
1.23
1.23
1.22
1.21
S
NH
HN
S
NH
HN
CF3
F3C
5i
2.02
2.12
6.14
1.97
2.00
1.99
2.03
4.48
f1 (ppm)

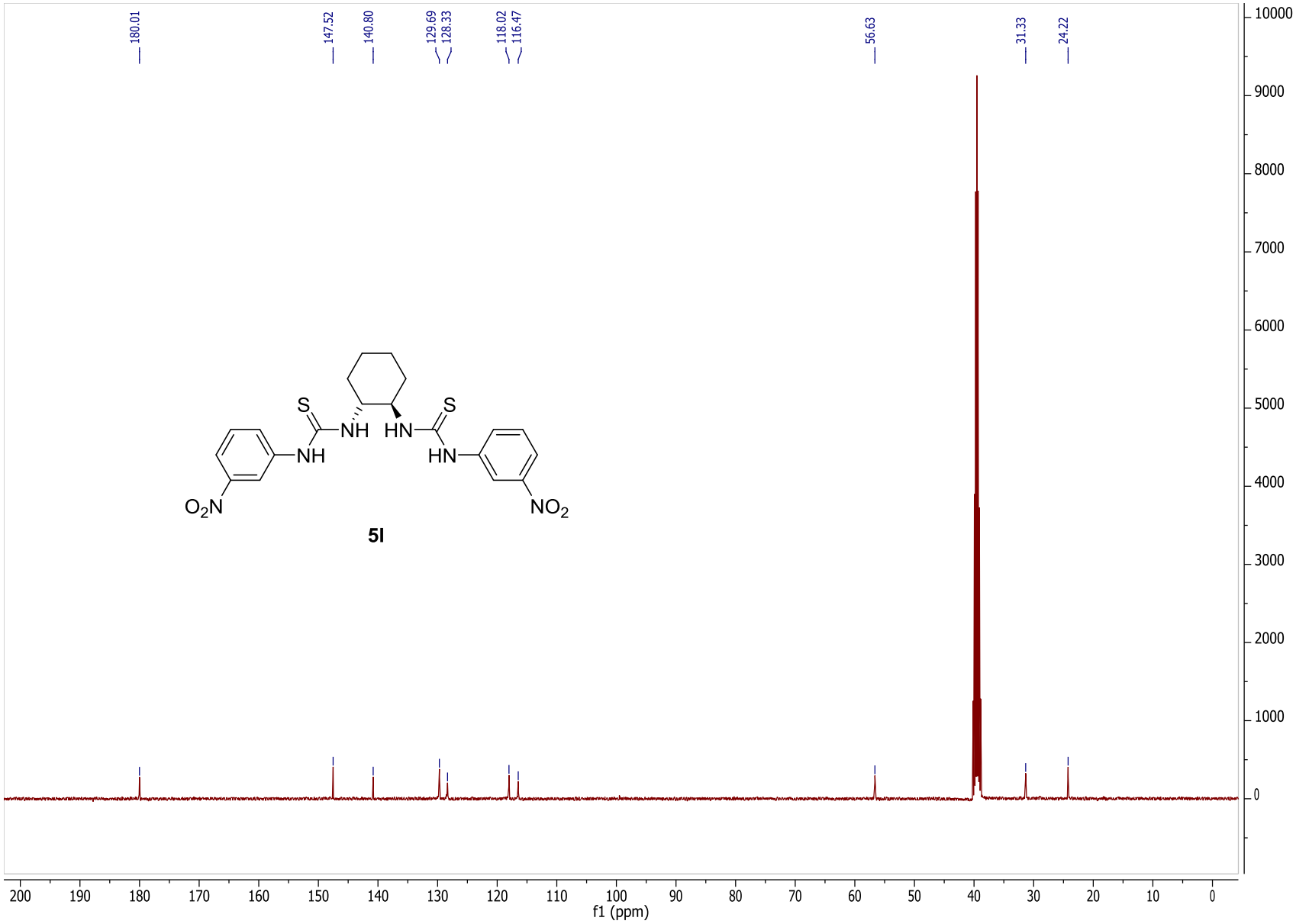

181.24
133.81
133.72
129.60
128.05
127.61
127.56
127.51
127.46
127.37
127.20
126.90
126.60
126.30
124.66
121.94
119.22
59.45
32.00
24.65
S
NH
HN
S
NH
HN
CF3
F3C
5i
f1 (ppm)

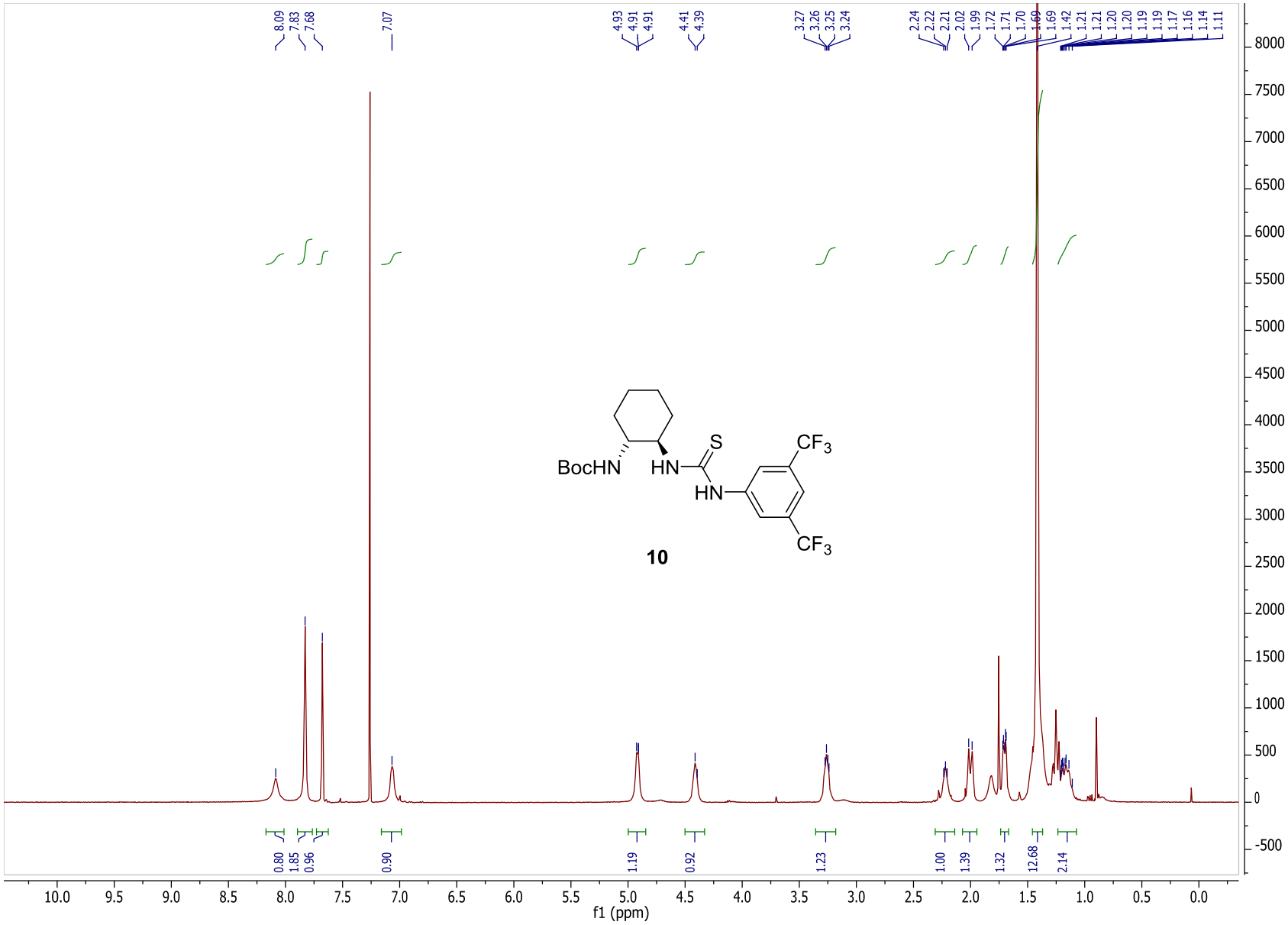

8.31
7.52
7.51
7.51
7.50
7.49
7.48
7.48
7.47
7.46
7.45
7.45
7.40
6.90
6.88
6.88
4.37
4.37
4.35
4.34
4.33
2.14
2.13
1.73
1.72
1.31
1.28
1.26
1.26
1.25
1.25
1.23
1.21
S
NH
HN
S
NH
HN
F3C
CF3
5j
1.86
8.78
1.96
1.99
1.98
1.98
4.09
f1 (ppm)

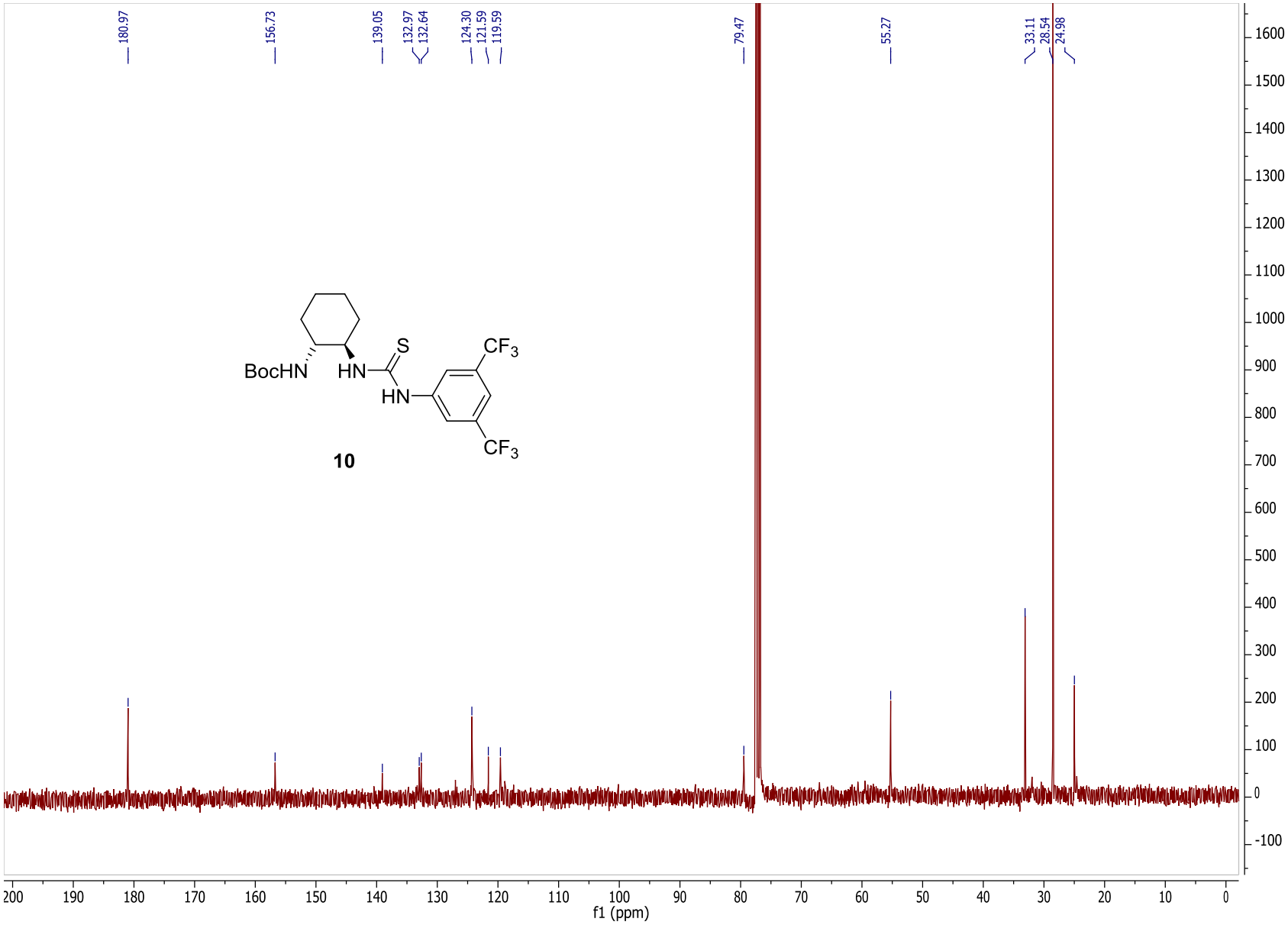

180.30
137.27
132.69
132.37
132.04
131.71
130.47
128.13
124.94
123.49
123.45
123.41
123.38
122.23
121.61
121.57
121.53
121.50
119.52
59.24
32.03
24.56
S
NH
HN
S
NH
HN
F3C
CF3
5j
f1 (ppm)


F3C
S
NH
NH
HN
S
HN
CF3
F3C
CF3
5k
1.90
3.99
2.01
1.92
2.00
2.09
2.15
4.29
3000
2500
2000
1500
1000
500
0
0.0
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
0.0
f1 (ppm)

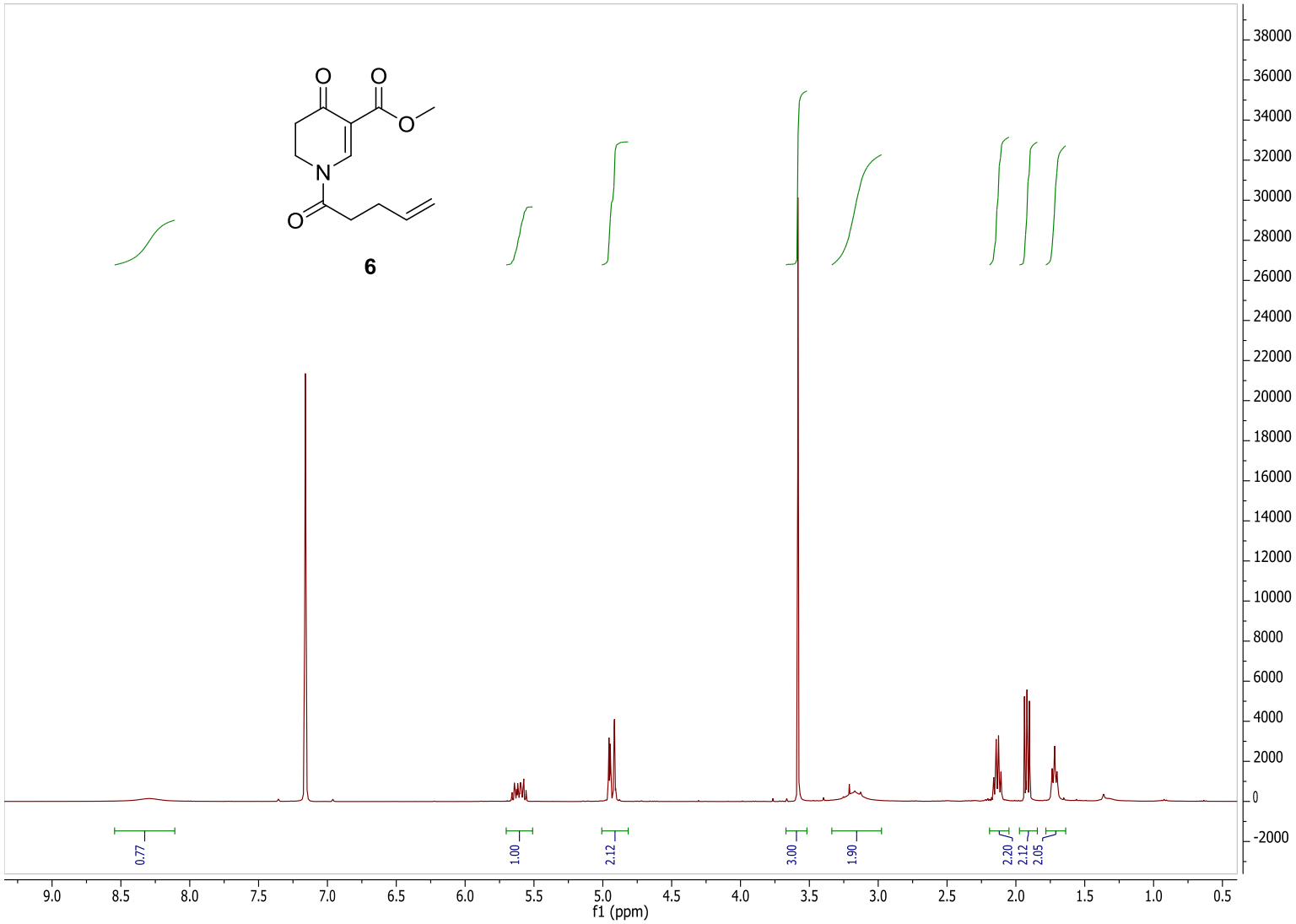

9.99
8.57
8.06
8.05
8.04
7.91
7.90
7.89
7.88
7.88
7.78
7.76
7.55
7.53
7.51
4.33
2.20
2.18
2.17
1.72
1.71
1.70
1.35
1.33
1.30
1.28
S
NH
HN
S
NH
HN
O2N
NO2
5l
1.94
2.00
2.08
2.09
2.02
2.10
2.00
2.07
2.09
4.23
f1 (ppm)

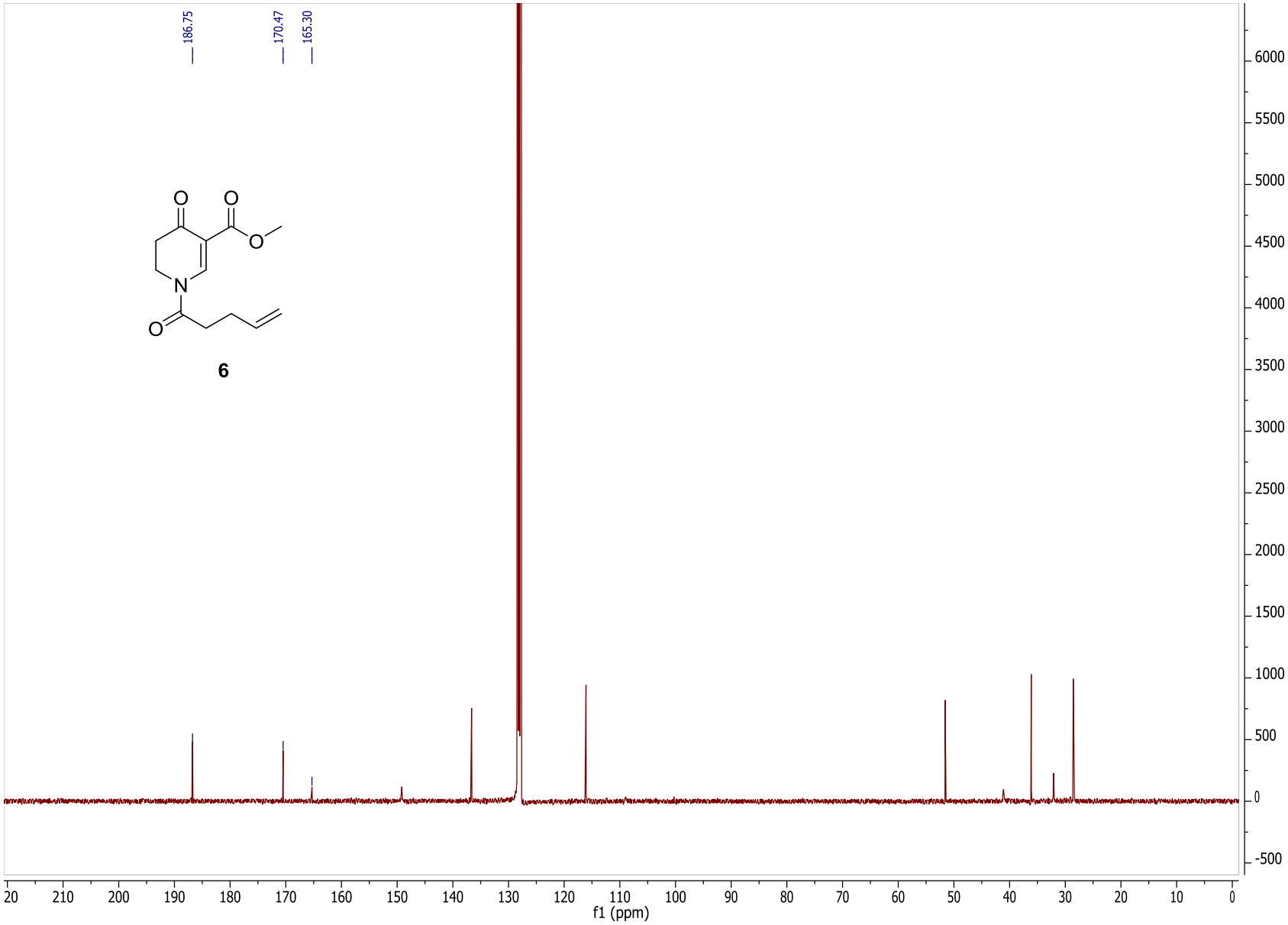

180.01
147.52
140.80
129.69
128.33
118.02
116.47
56.63
31.33
24.22
S
NH
HN
S
NH
HN
O2N
NO2
5l
f1 (ppm)

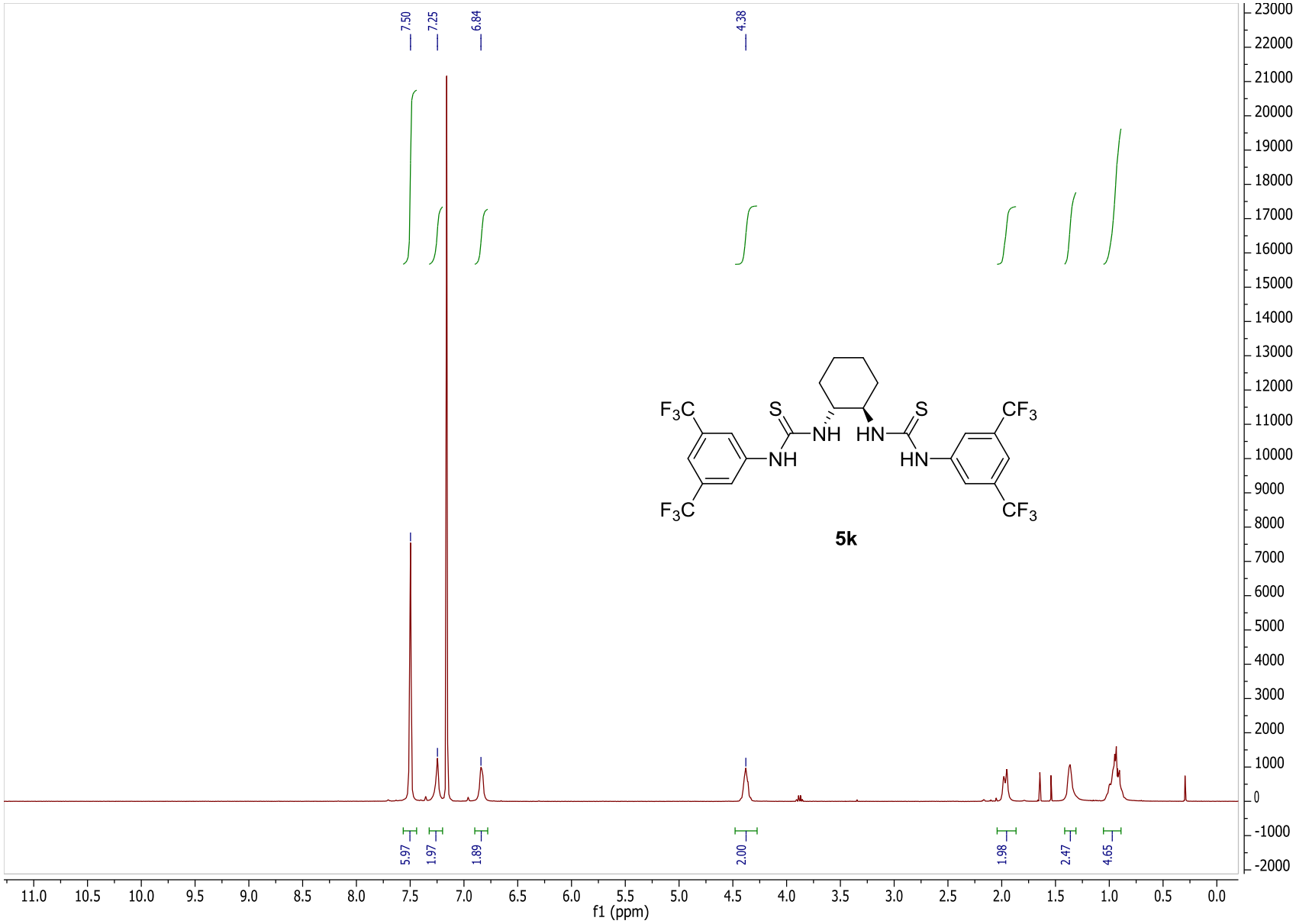

8.09
7.83
7.68
7.07
4.93
4.91
4.91
4.41
4.39
3.27
3.26
3.25
3.24
2.24
2.22
2.21
2.02
1.99
1.72
1.71
1.70
1.69
1.69
1.42
1.21
1.21
1.20
1.20
1.19
1.19
1.17
1.16
1.14
1.11
BocHN
HN
S
HN
CF3
CF3
10
0.80
1.85
0.96
0.90
1.19
0.92
1.23
1.00
1.39
1.32
12.68
2.14
f1 (ppm)

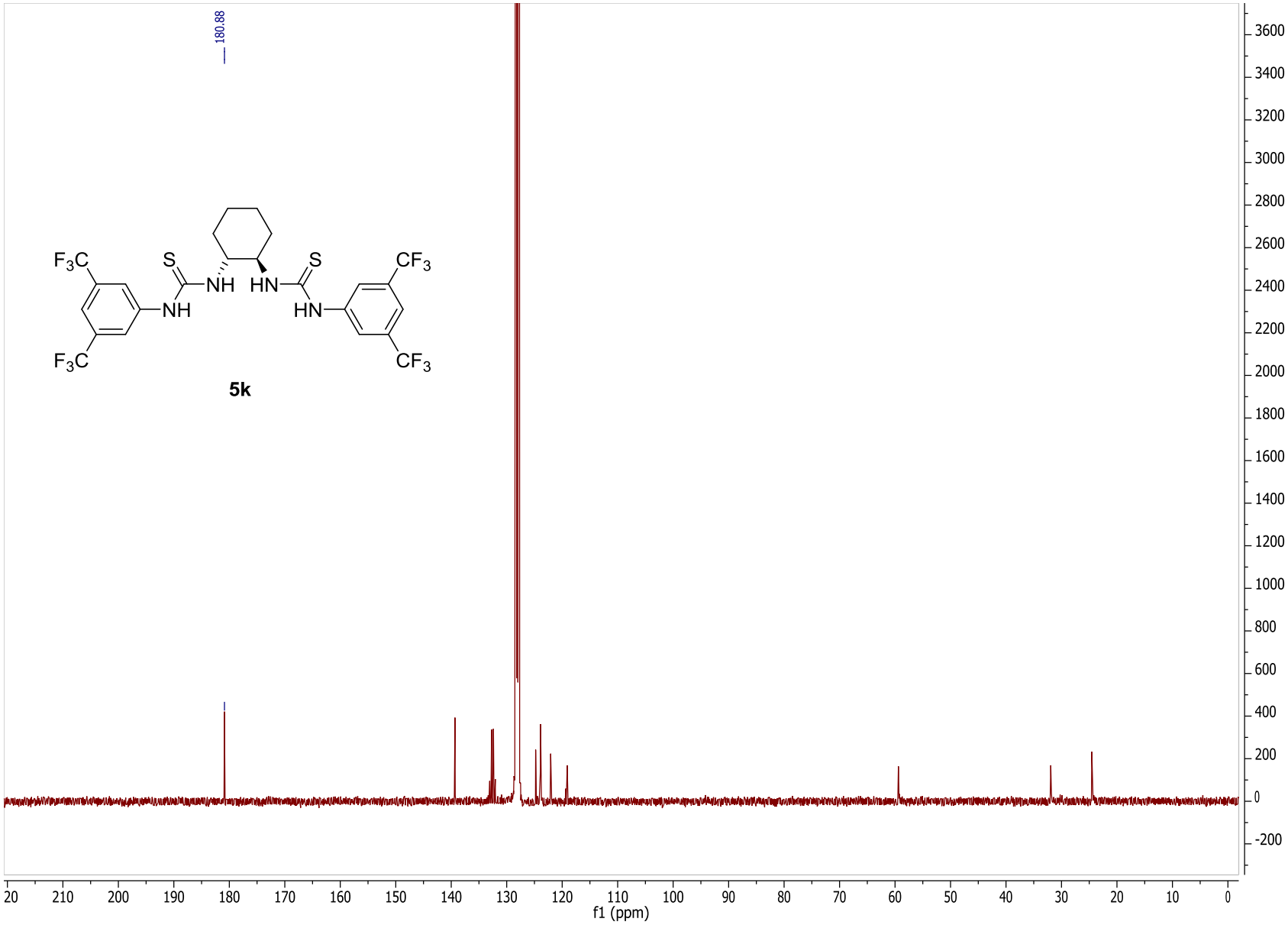

180.97
156.73
139.05
132.97
132.64
124.30
121.59
119.59
79.47
55.27
33.11
28.54
24.98
BocHN
HN
S
HN
CF3
CF3
10
f1 (ppm)

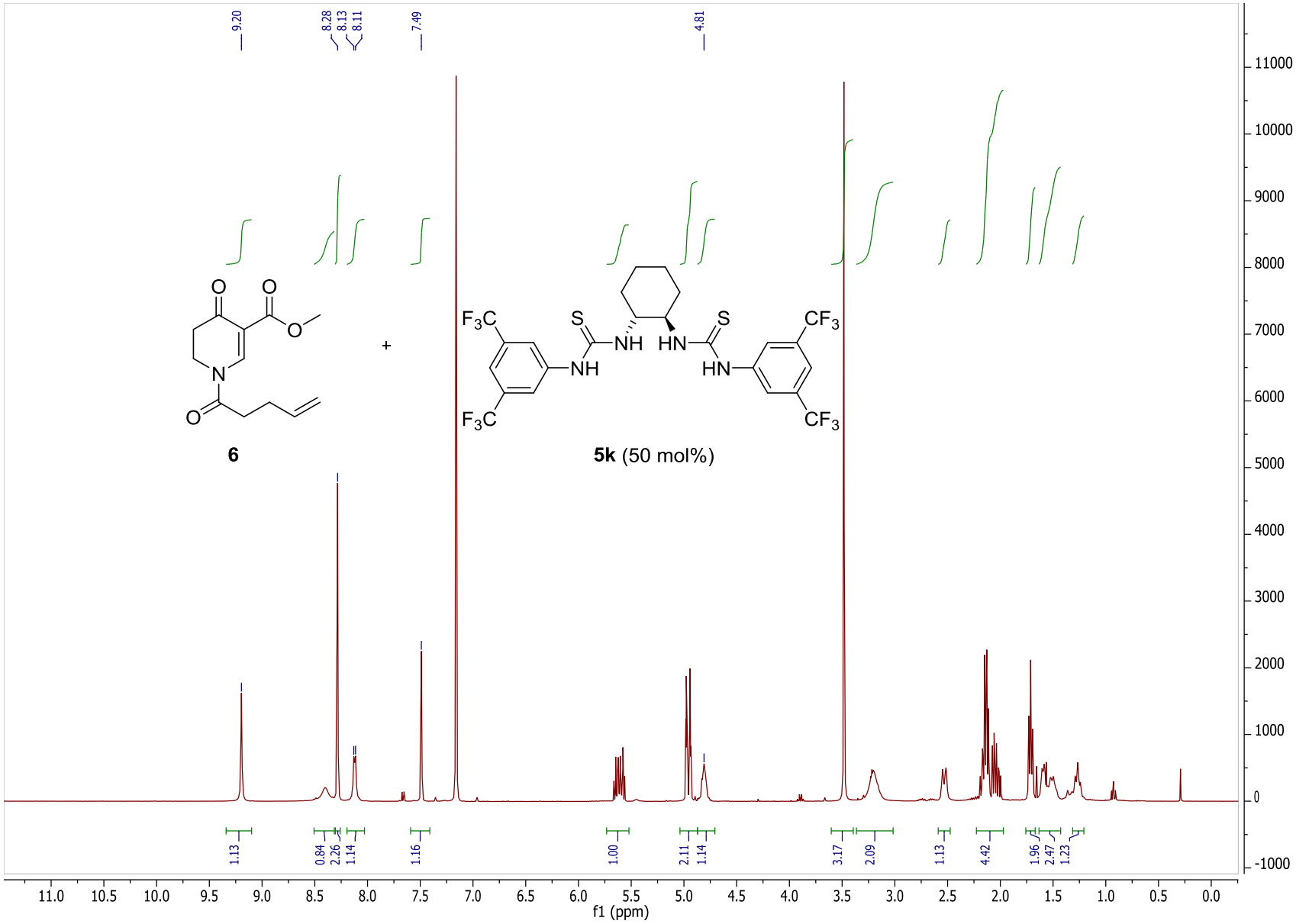
NMR spectra of substrate **6** and thiourea **5k** in benzene-d_6 and combination of both with 50 mol% and 100 mol% of **5k**.

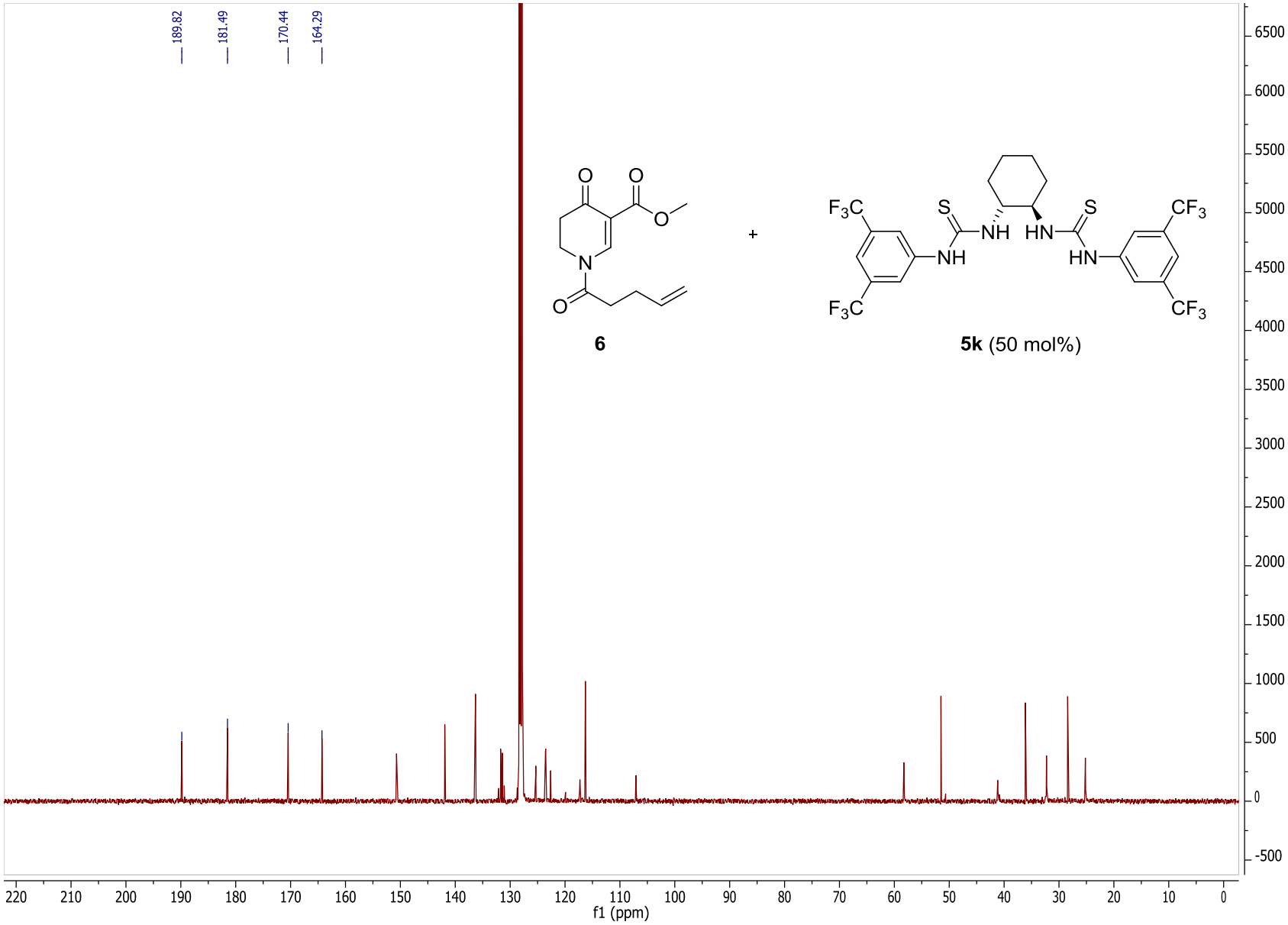


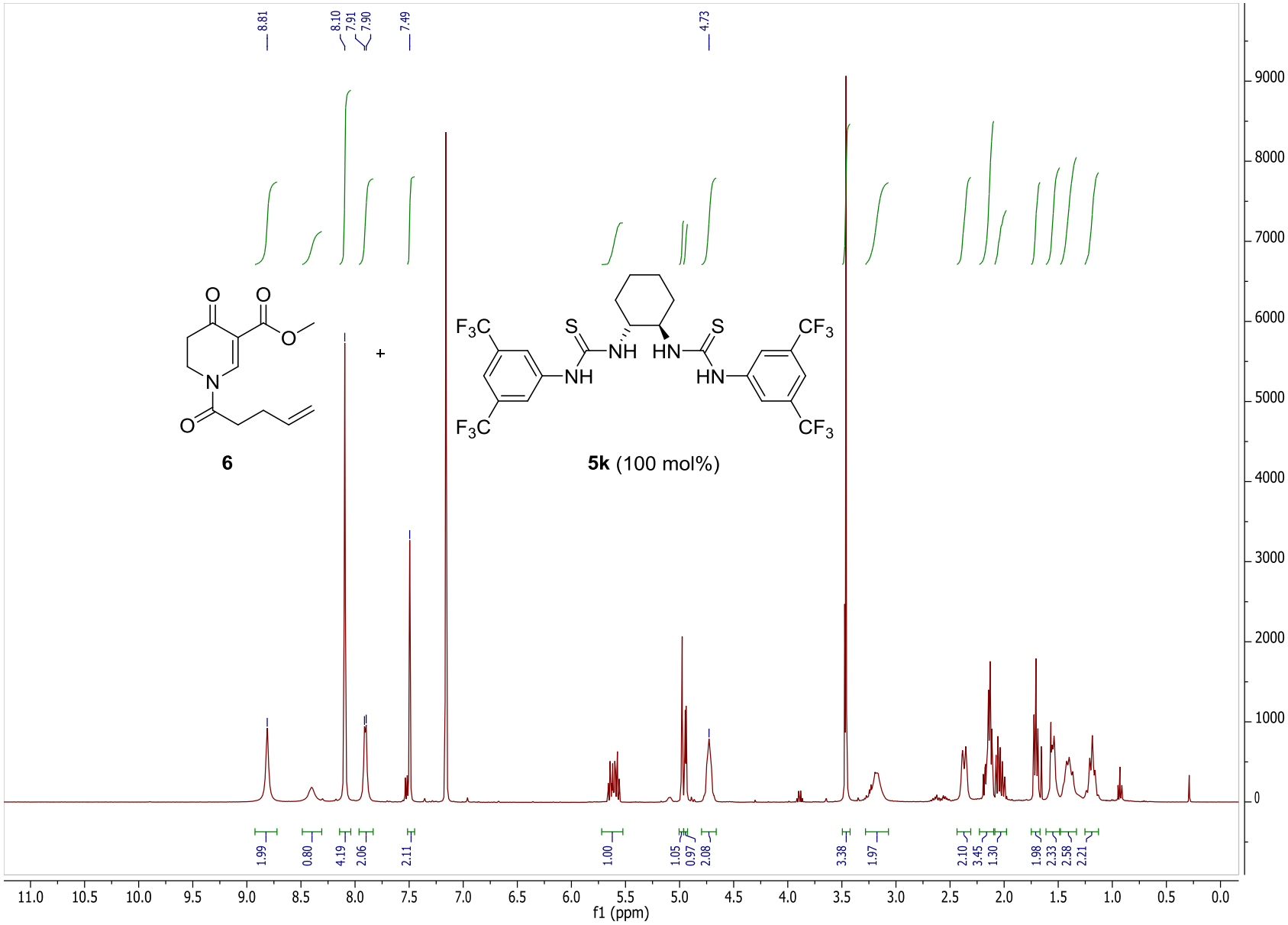

186.75
170.47
165.30
6
f1 (ppm)

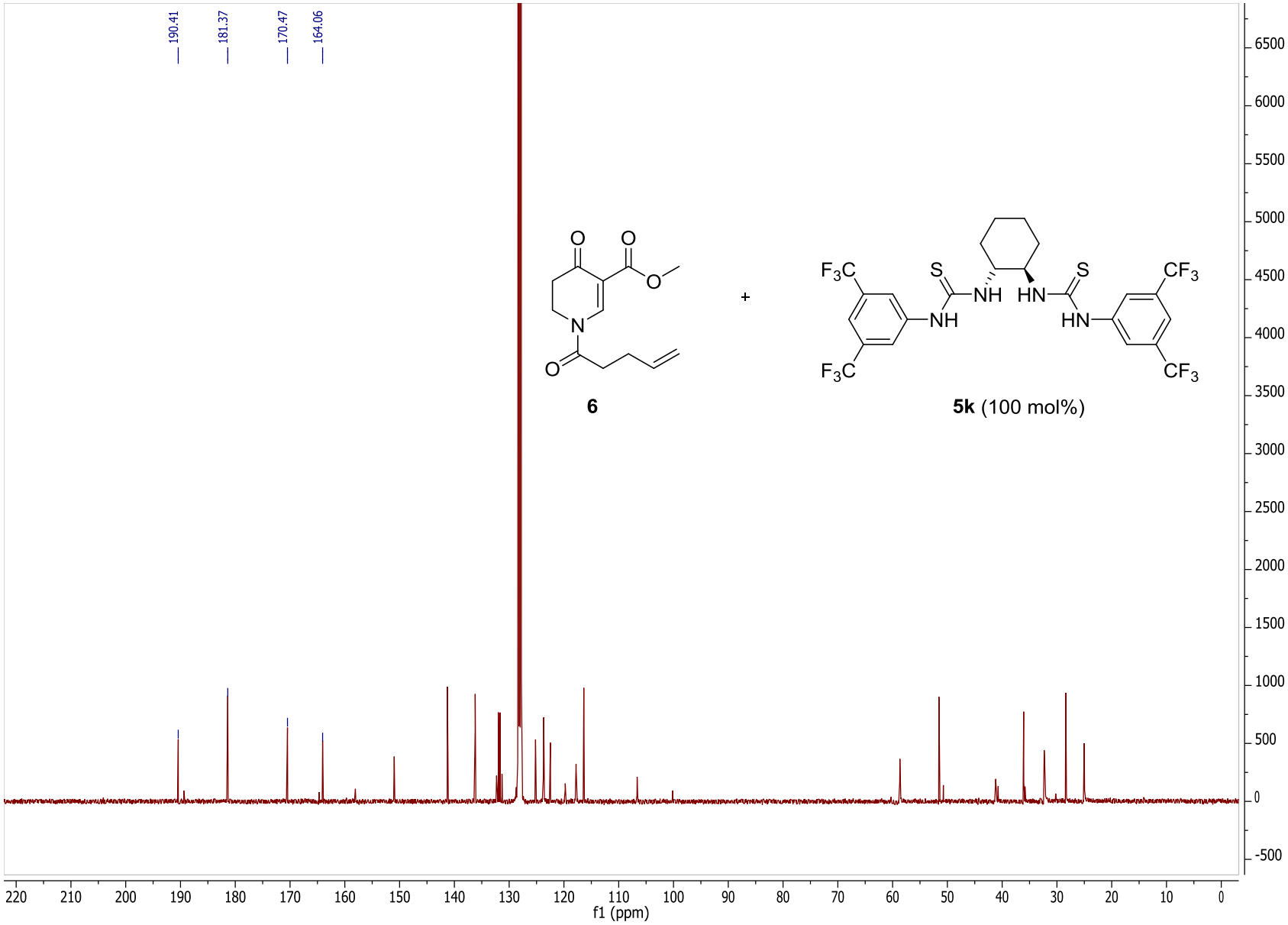

7.50
7.25
6.84
4.38
5.97
1.97
1.89
2.00
1.98
2.47
4.65
F3C
S
NH
NH
HN
S
CF3
HN
F3C
CF3
5k
f1 (ppm)


180.88
F3C
S
NH
HN
S
CF3
NH
HN
F3C
CF3
5k
f1 (ppm)


9.20
8.28
8.13
8.11
7.49
4.81
6
5k (50 mol%)
1.13
0.84
2.26
1.14
1.16
1.00
2.11
1.14
3.17
2.09
1.13
4.42
1.96
2.47
1.23
f1 (ppm)

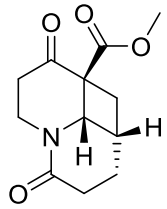

189.82
181.49
170.44
164.29
6
+
5k (50 mol%)
f1 (ppm)


8.81
8.10
7.91
7.90
7.49
4.73
6
5k (100 mol%)
1.99
0.80
4.19
2.06
2.11
1.00
1.05
0.97
2.08
3.38
1.97
2.10
3.45
1.30
1.98
2.33
2.58
2.21
f1 (ppm)


190.41
181.37
170.47
164.06
6
+
5k (100 mol%)
f1 (ppm)

3. HPLC- and chiral GC data of enantioenriched products

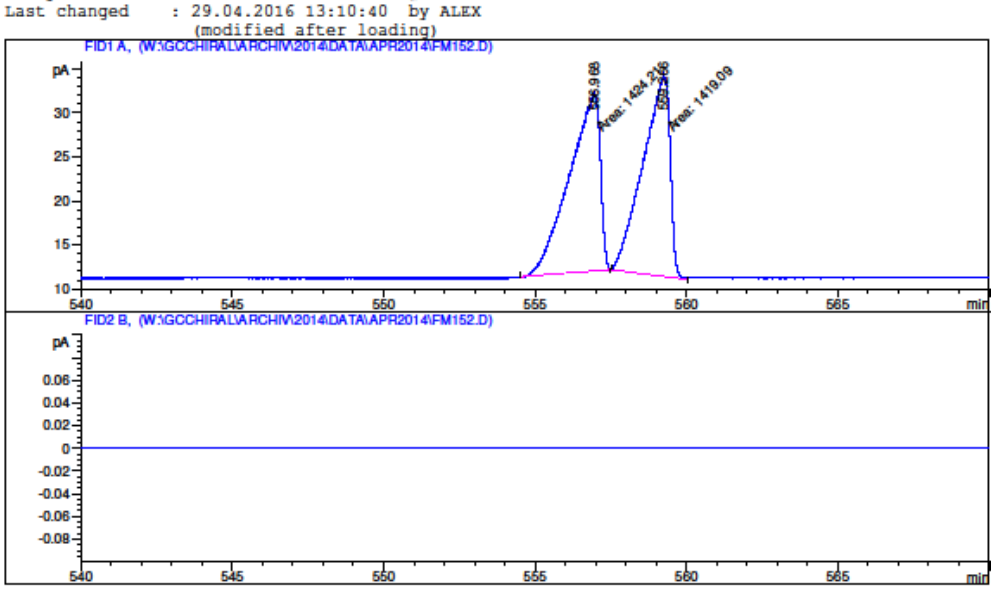
3.1 Data for enantioselective reactions at λ = 366 nm



7

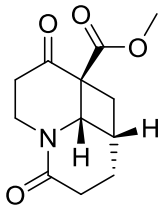
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\APR2014\FM152.D Sample Name: FM152

```
Injection Date  : 10.06.2014 15:20:39          Seq. Line :   1
Sample Name     : FM152                         Location : Vial 104
Acq. Operator   : Ingo                                Inj :   1
                                               Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 29.04.2016 13:10:40  by ALEX
                  (modified after loading)
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 556.968 MM    1.1678 1424.21350   20.32619 50.09004
   2 559.266 MM    1.0200 1419.09326   23.18706 49.90996

Totals :                  2843.30676   43.51325

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

                          *** End of Report ***
```

Instrument 1 29.04.2016 13:10:52 ALEX Page 1 of 1

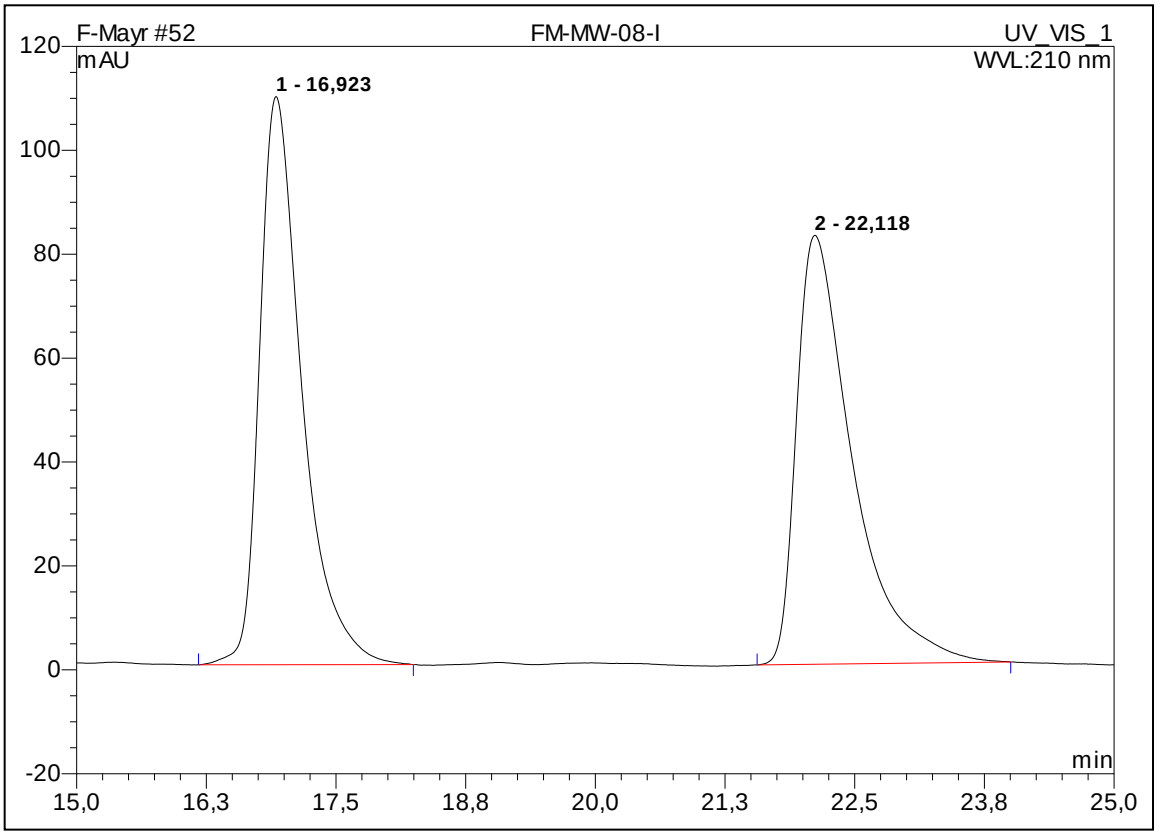


7

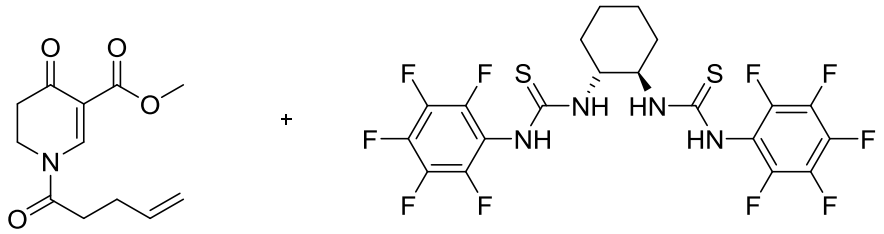
52 FM-MW-08-I

Daicel Chiralpak, AD-H, 250x4.6

Sample Name:	**FM-MW-08-I**	*Injection Volume:*	**10,0**
Vial Number:	**RB4**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210.0**
Control Program:	**Säule1_NP_ISO_90_10_1_50**	*Bandwidth:*	**1**
Quantif. Method:	**gradA**	*Dilution Factor:*	**1,0000**
Recording Time:	**20.03.2015 11:06**	*Sample Weight:*	**1,0000**
Run Time (min):	**50,00**	*Sample Amount:*	**1,0000**



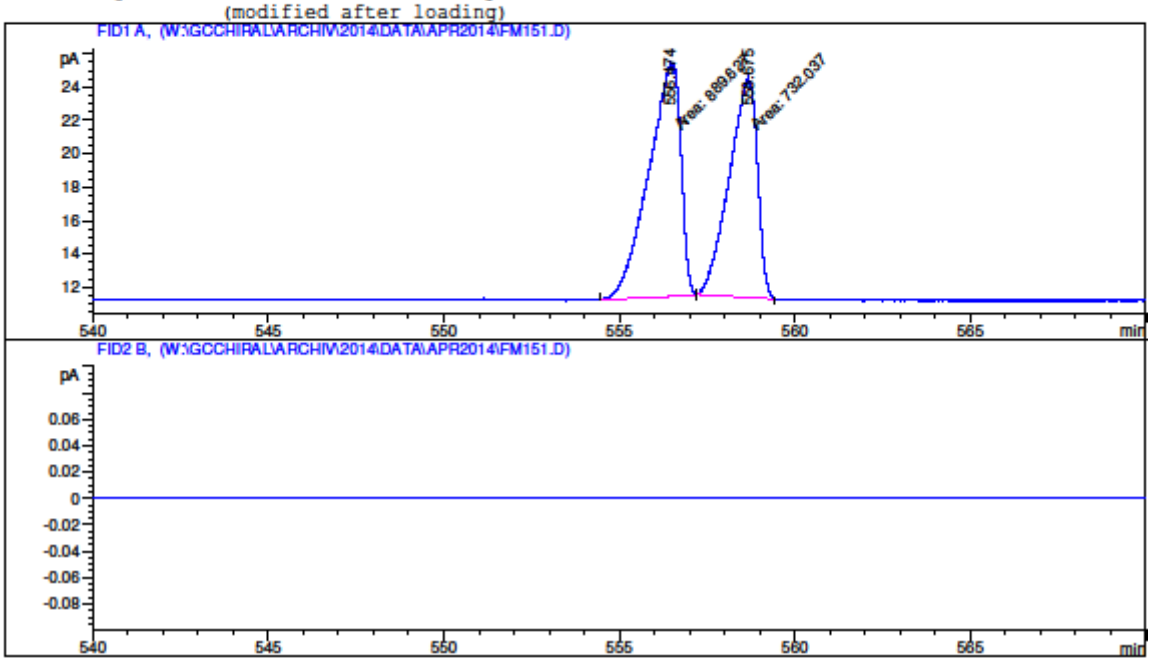
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,92	n.a.	109,367	51,670	50,12	n.a.	BMB
2	22,12	n.a.	82,561	51,414	49,88	n.a.	BMB
Total:			191,928	103,084	100,00	0,000	



6 + **5h** (50 mol%)

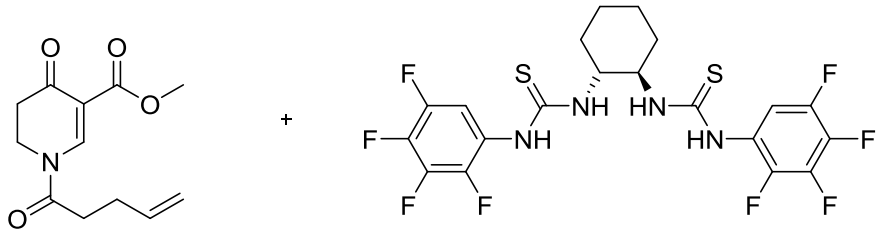
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\APR2014\FM151.D Sample Name: FM151

```
==========================================================================
Injection Date  : 07.06.2014 03:56:51          Seq. Line :   2
Sample Name     : FM151                         Location : Vial 103
Acq. Operator   : Ingo                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 04.05.2016 08:56:13  by ALEX
                  (modified after loading)
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 556.474 MM    1.0525  889.62689   14.08752 54.85890
   2 558.675 MM    0.9176  732.03687   13.29566 45.14110

Totals :                  1621.66376   27.38318

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

==========================================================================
                          *** End of Report ***
```

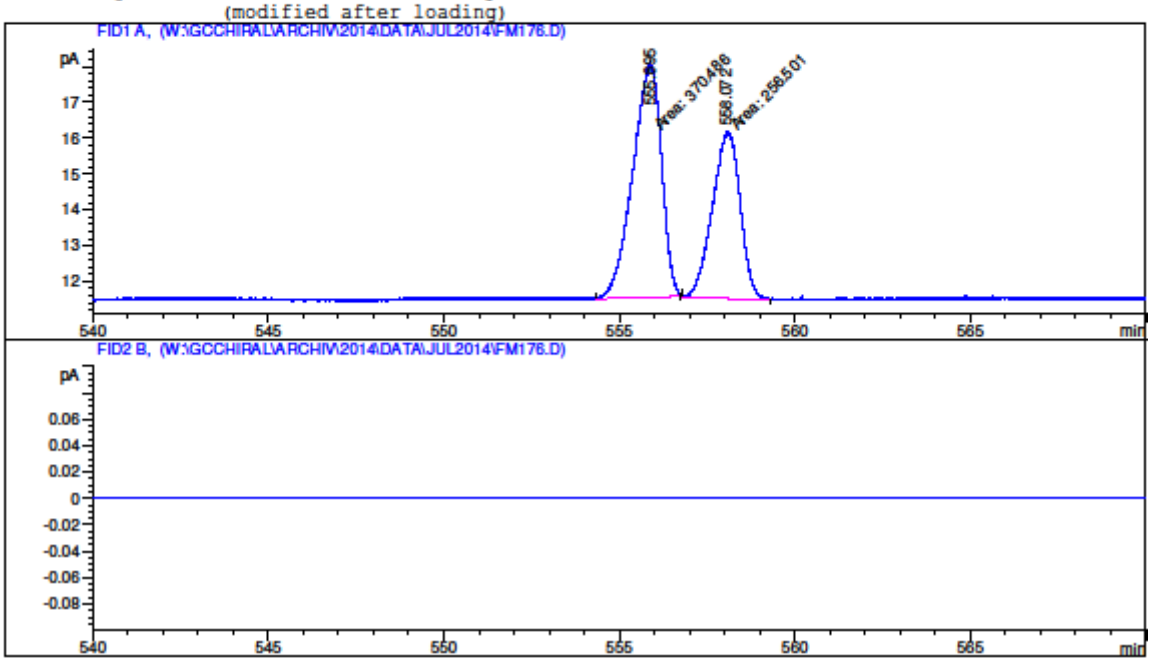
Instrument 1 04.05.2016 08:56:48 ALEX Page 1 of 1



6 **5g** (50 mol%)

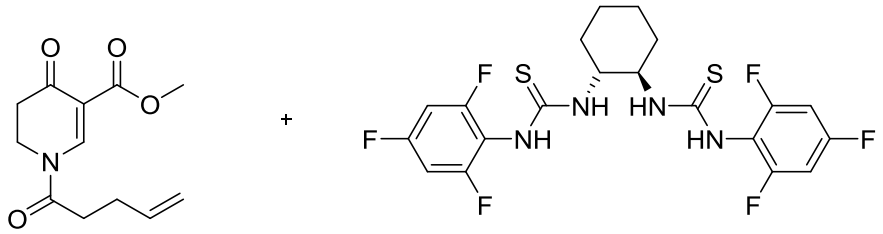
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\JUL2014\FM176.D Sample Name: FM176

```
Injection Date  : 16.07.2014 16:52:41          Seq. Line :   2
Sample Name     : FM176                         Location : Vial 102
Acq. Operator   : Ingo                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 04.05.2016 09:04:30  by ALEX
                  (modified after loading)
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 555.895 MM    0.9401  370.48639    6.56842 59.08992
   2 558.072 MM    0.9186  256.50110    4.65399 40.91008

Totals :                   626.98749   11.22241

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

                          *** End of Report ***
```

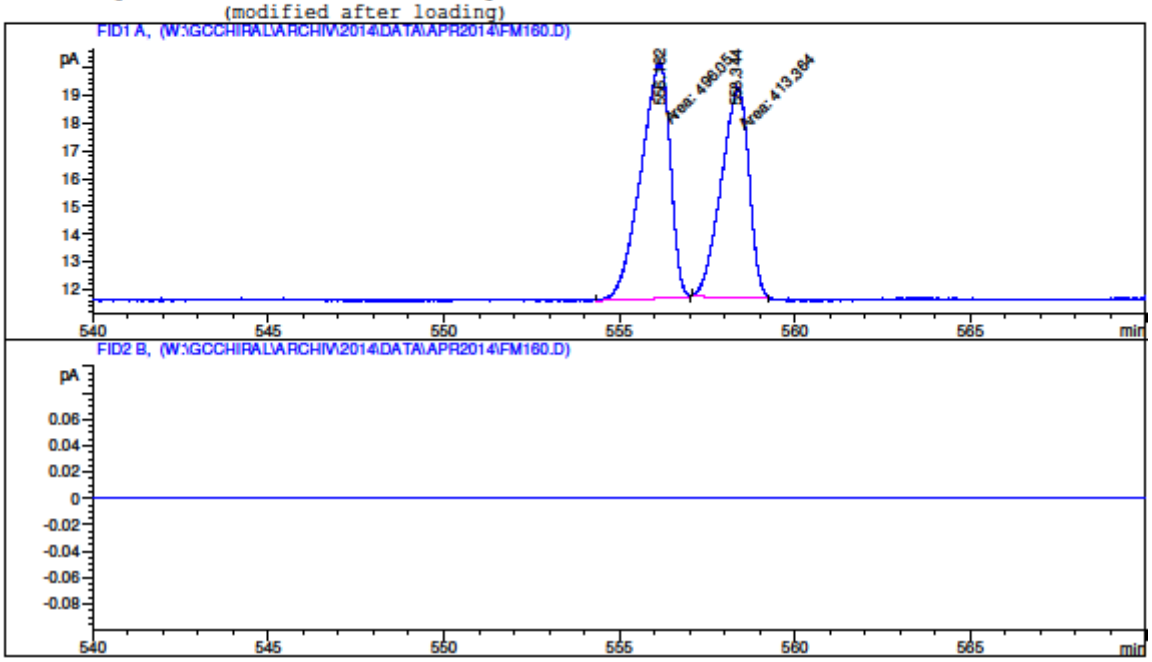
Instrument 1 04.05.2016 09:05:10 ALEX Page 1 of 1



6 + **5f** (50 mol%)

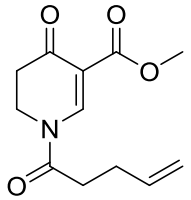
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\APR2014\FM160.D Sample Name: FM160

```
Injection Date  : 18.06.2014 18:18:54          Seq. Line :   1
Sample Name     : FM160                         Location : Vial 102
Acq. Operator   : Ingo                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 04.05.2016 08:58:47  by ALEX
                  (modified after loading)
```



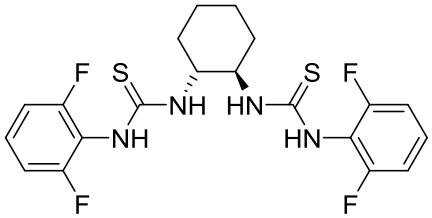

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 556.182 MM    0.9678  496.05032    8.54292 54.54611
   2 558.344 MM    0.9065  413.36435    7.59979 45.45389

Totals :                   909.41467   16.14271

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

                          *** End of Report ***
```

Instrument 1 04.05.2016 08:59:48 ALEX Page 1 of 1



6

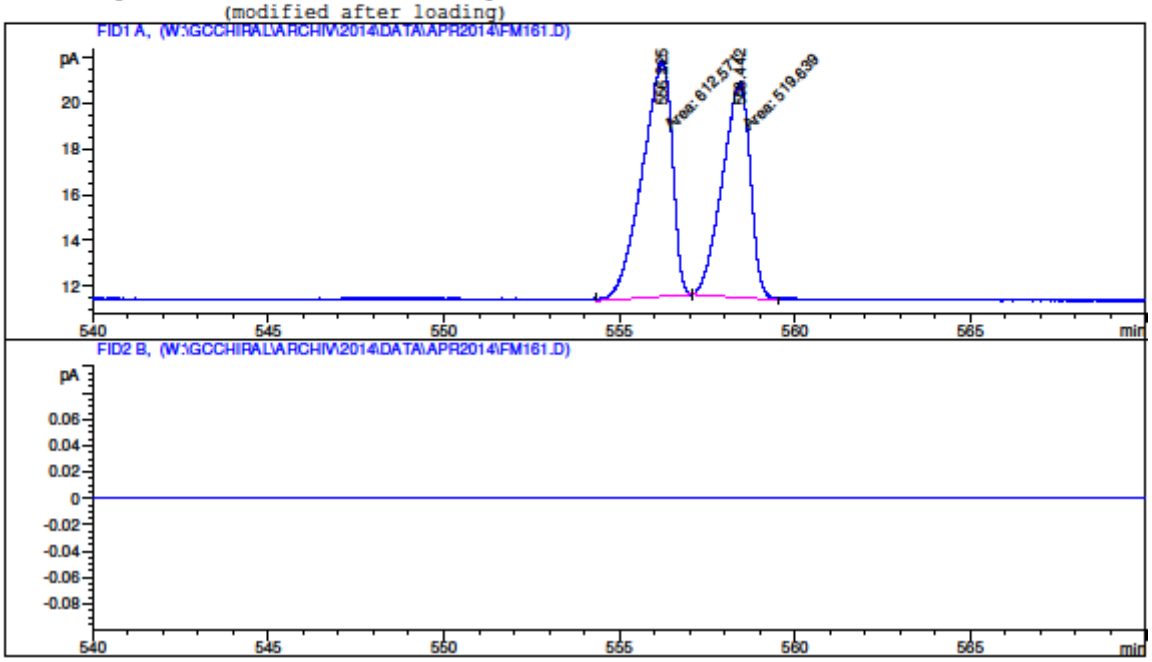
+



5e (50 mol%)

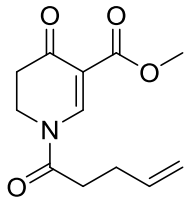
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\APR2014\FM161.D Sample Name: FM161

```
==========================================================================
Injection Date  : 19.06.2014 04:11:16          Seq. Line :   2
Sample Name     : FM161                         Location : Vial 103
Acq. Operator   : Ingo                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 29.04.2016 13:18:24  by ALEX
                  (modified after loading)
```



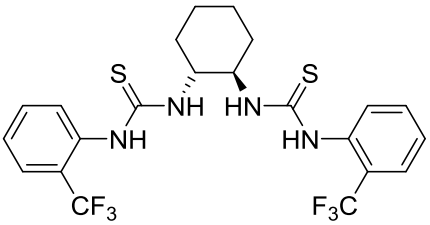

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 556.225 MM    0.9928  612.57056   10.28348 54.10401
   2 558.442 MM    0.9165  519.63861    9.45010 45.89599

Totals :                  1132.20917   19.73358

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

==========================================================================
                          *** End of Report ***
```

Instrument 1 29.04.2016 13:18:34 ALEX Page 1 of 1



6

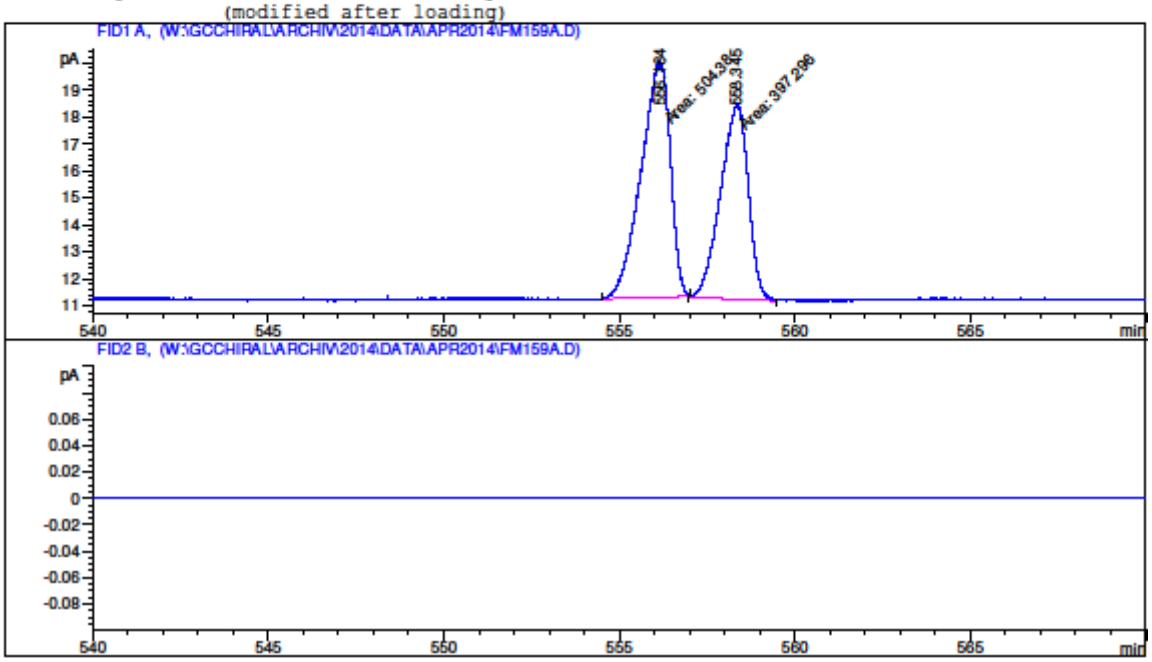
+



5i (50 mol%)

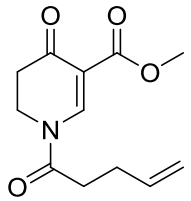
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\APR2014\FM159A.D Sample Name: FM159

```
Injection Date  : 17.06.2014 10:56:18          Seq. Line :   2
Sample Name     : FM159                         Location : Vial 107
Acq. Operator   : Ingo                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 04.05.2016 09:02:43  by ALEX
                  (modified after loading)
```



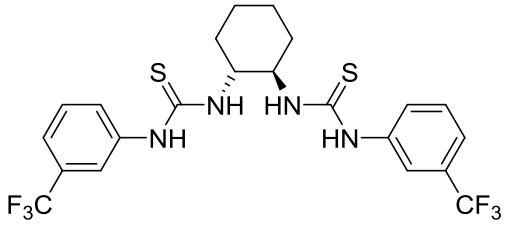

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 556.184 MM    0.9618  504.38013    8.73976 55.93806
   2 558.345 MM    0.9150  397.29605    7.23700 44.06194

Totals :                   901.67618   15.97677

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

                          *** End of Report ***
```

Instrument 1 04.05.2016 09:03:20 ALEX Page 1 of 1



6

+

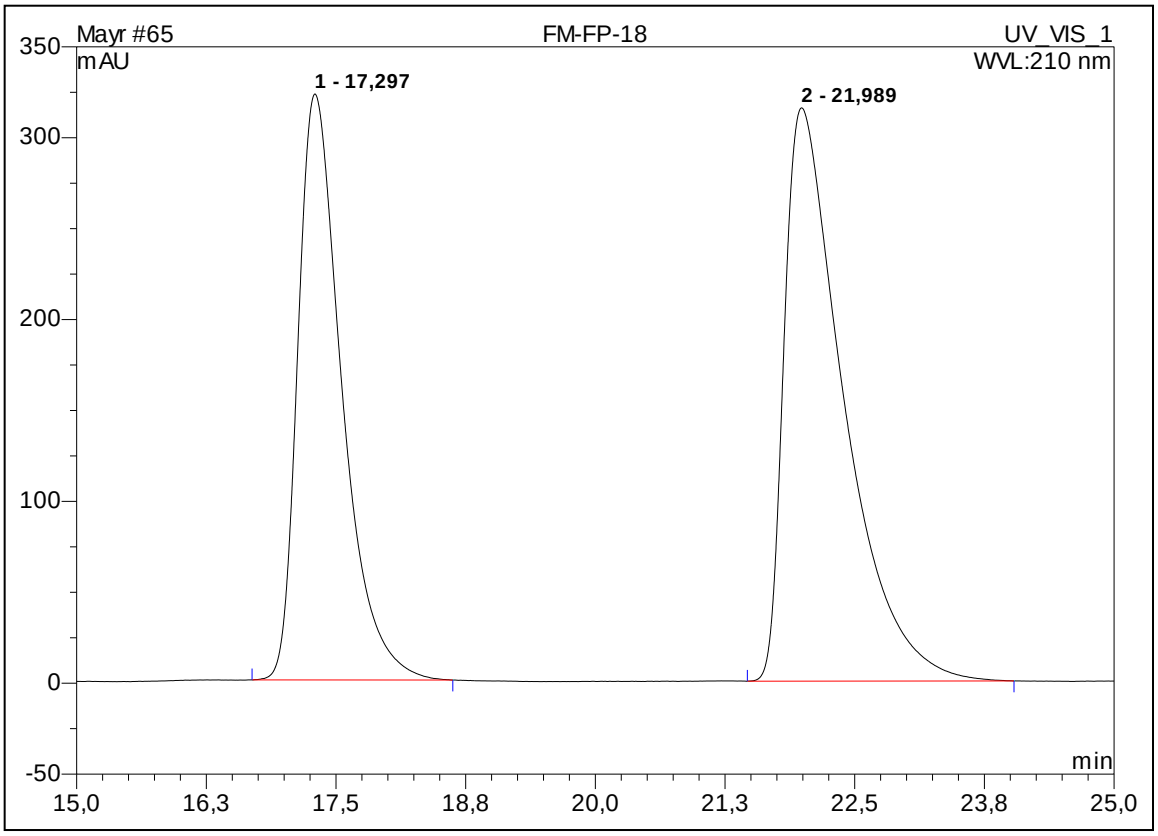


5j (50 mol%)

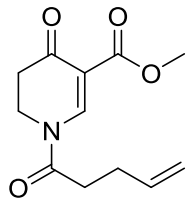
65 FM-FP-18

Daicel Chiralpak, AD-H, 250x4.6

Sample Name:	**FM-FP-18**	*Injection Volume:*	**10,0**
Vial Number:	**GD2**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210.0**
Control Program:	**An3_Säule1_ISO_90_10_0_0_1_30**	*Bandwidth:*	**1**
Quantif. Method:	**gradA**	*Dilution Factor:*	**1,0000**
Recording Time:	**29.03.2016 09:45**	*Sample Weight:*	**1,0000**
Run Time (min):	**30,00**	*Sample Amount:*	**1,0000**

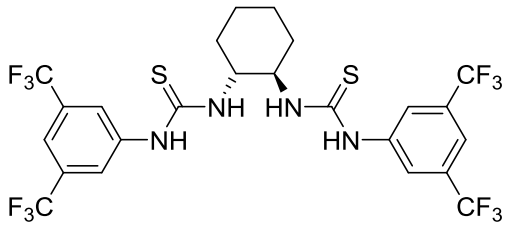


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17,30	n.a.	322,304	158,304	43,06	n.a.	BMB
2	21,99	n.a.	315,306	209,350	56,94	n.a.	BMB
Total:			637,610	367,654	100,00	0,000	



6

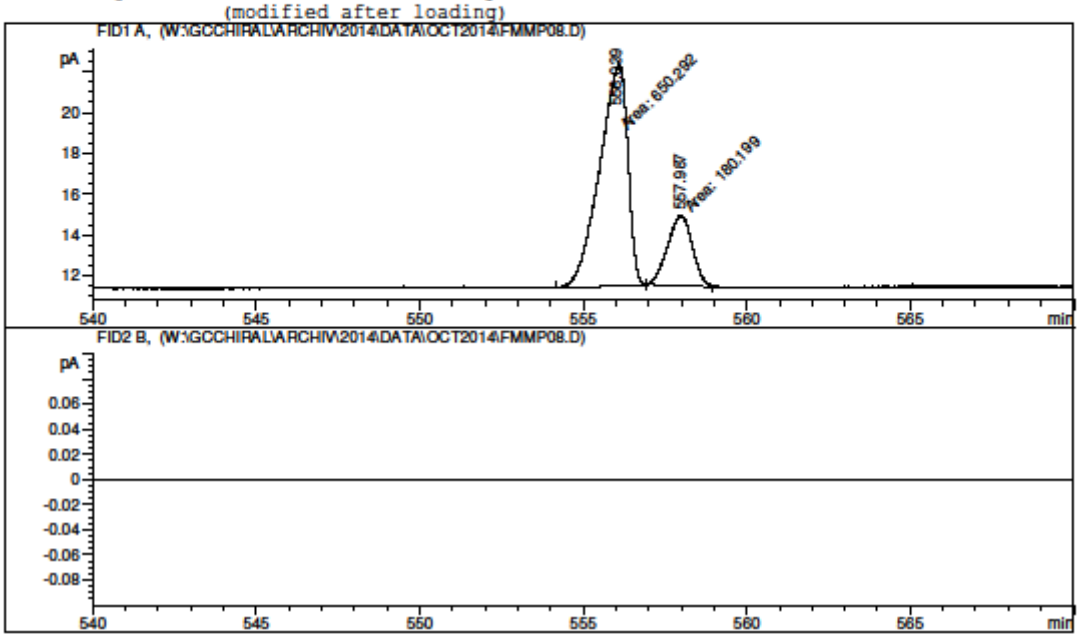
+



5k (50 mol%)

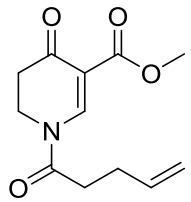
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\OCT2014\FMMP08.D Sample Name: FMMP08

```
Injection Date  : 17.10.2014 17:28:13          Seq. Line :   1
Sample Name     : FMMP08                        Location : Vial 101
Acq. Operator   : Ingo                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 29.04.2016 13:37:25  by ALEX
                  (modified after loading)
```



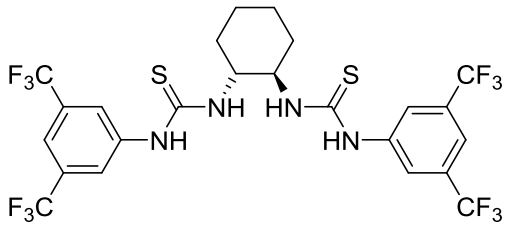

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]     [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 556.039 MM    0.9803  650.29199   11.05585 78.30213
   2 557.987 MM    0.8736  180.19884    3.43793 21.69787

Totals :                   830.49083   14.49378

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

                          *** End of Report ***
```

Instrument 1 29.04.2016 13:38:06 ALEX Page 1 of 1



6

+

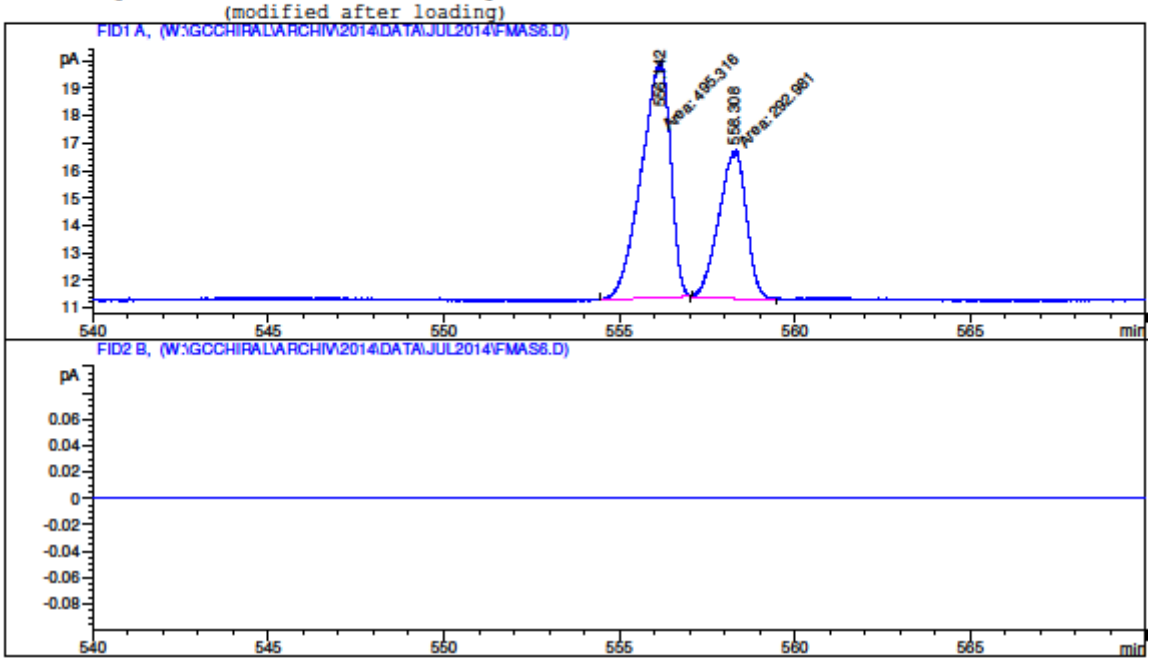


5k (50 mol%)

(TFT as solvent)

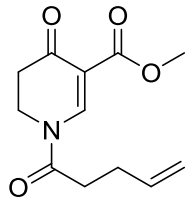
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\JUL2014\FMAS6.D Sample Name: FMAS6

```
Injection Date  : 29.07.2014 17:31:04          Seq. Line :   1
Sample Name     : FMAS6                         Location : Vial 102
Acq. Operator   : Ingo                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 29.04.2016 13:05:24  by ALEX
                  (modified after loading)
```



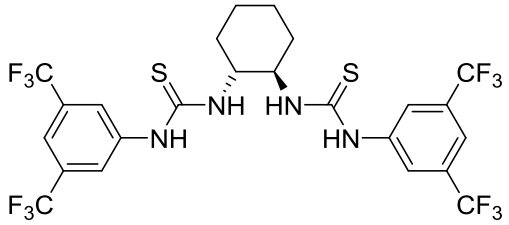

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 556.142 MM    0.9589  495.31628    8.60897 62.83369
   2 558.308 MM    0.9037  292.98096    5.40325 37.16631

Totals :                   788.29724   14.01223

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

                          *** End of Report ***
```

Instrument 1 29.04.2016 13:05:38 ALEX Page 1 of 1



6

+

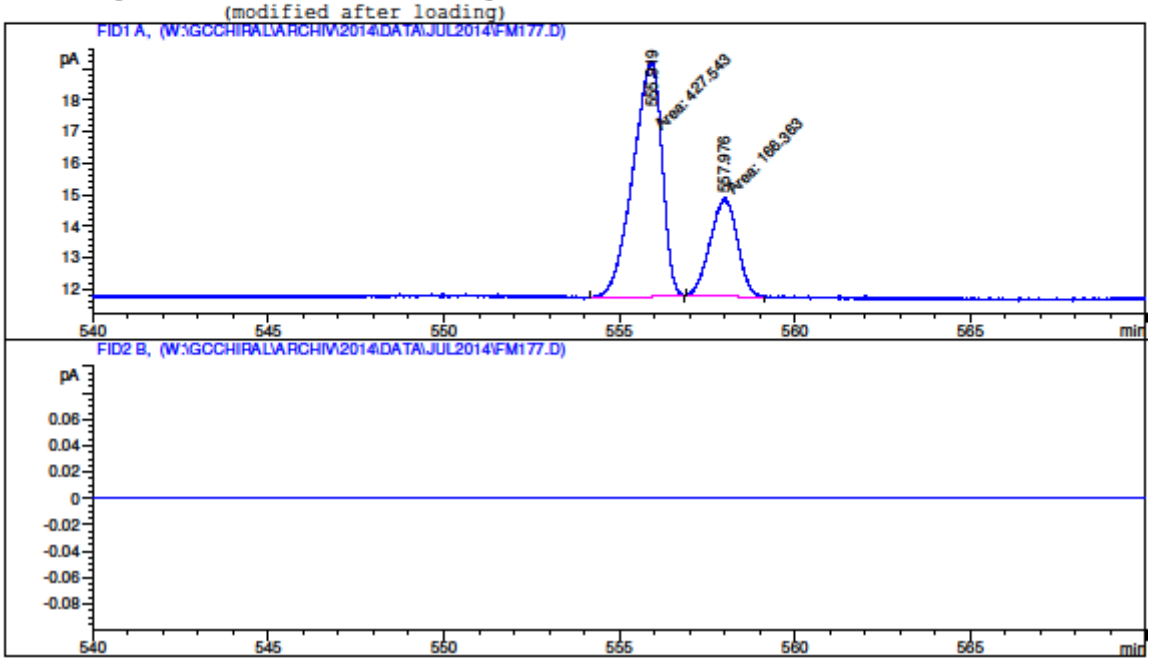


5k (50 mol%)

(TFT/HFX = 1/2 as solvent)

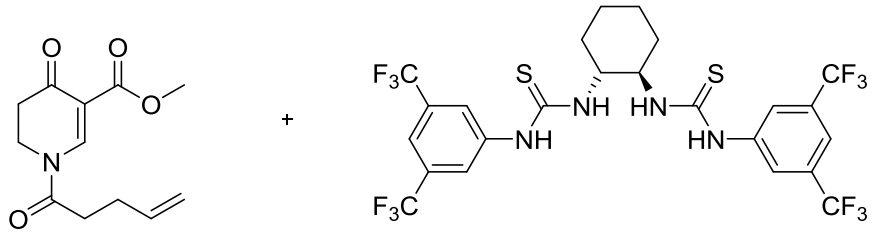
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\JUL2014\FM177.D Sample Name: FM177

```
Injection Date  : 17.07.2014 23:50:37          Seq. Line :   3
Sample Name     : FM177                         Location : Vial 104
Acq. Operator   : Ingo                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 29.04.2016 12:59:43  by ALEX
                  (modified after loading)
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 555.919 MM    0.9545  427.54257    7.46516 71.98831
   2 557.976 MM    0.8858  166.36296    3.13021 28.01169

Totals :                   593.90553   10.59538

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

                          *** End of Report ***
```

Instrument 1 29.04.2016 12:59:52 ALEX Page 1 of 1

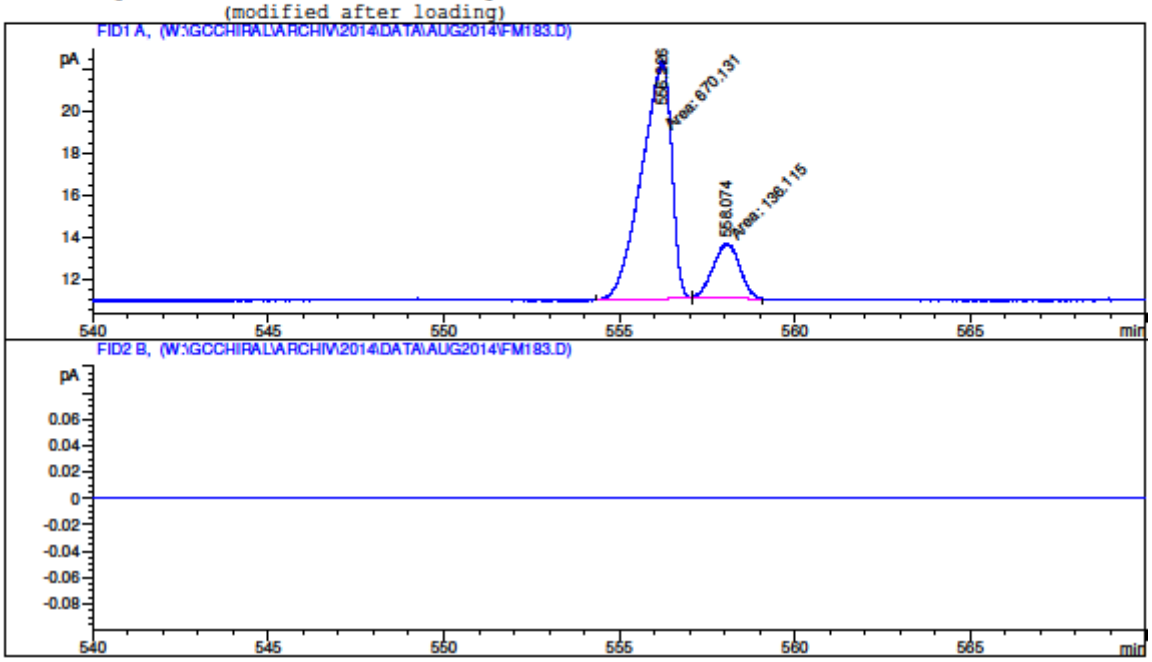


6 + **5k** (50 mol%)

c = 100 mM

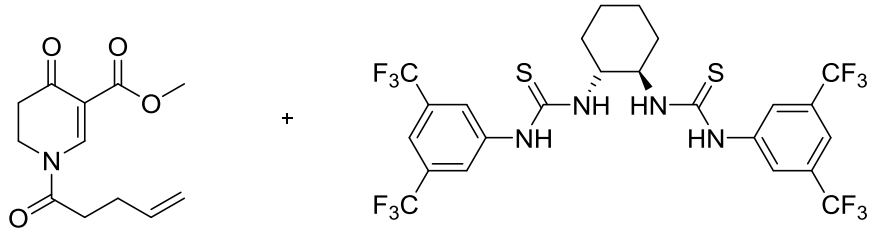
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\AUG2014\FM183.D Sample Name: FM182

```
Injection Date  : 11.08.2014 15:05:31          Seq. Line :   1
Sample Name     : FM182                         Location : Vial 102
Acq. Operator   : Ingo                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 29.04.2016 13:26:52  by ALEX
                  (modified after loading)
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 556.226 MM    0.9857  670.13141   11.33068 83.11747
   2 558.074 MM    0.8626  136.11478    2.62992 16.88253

Totals :                   806.24619   13.96059

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

                          *** End of Report ***
```

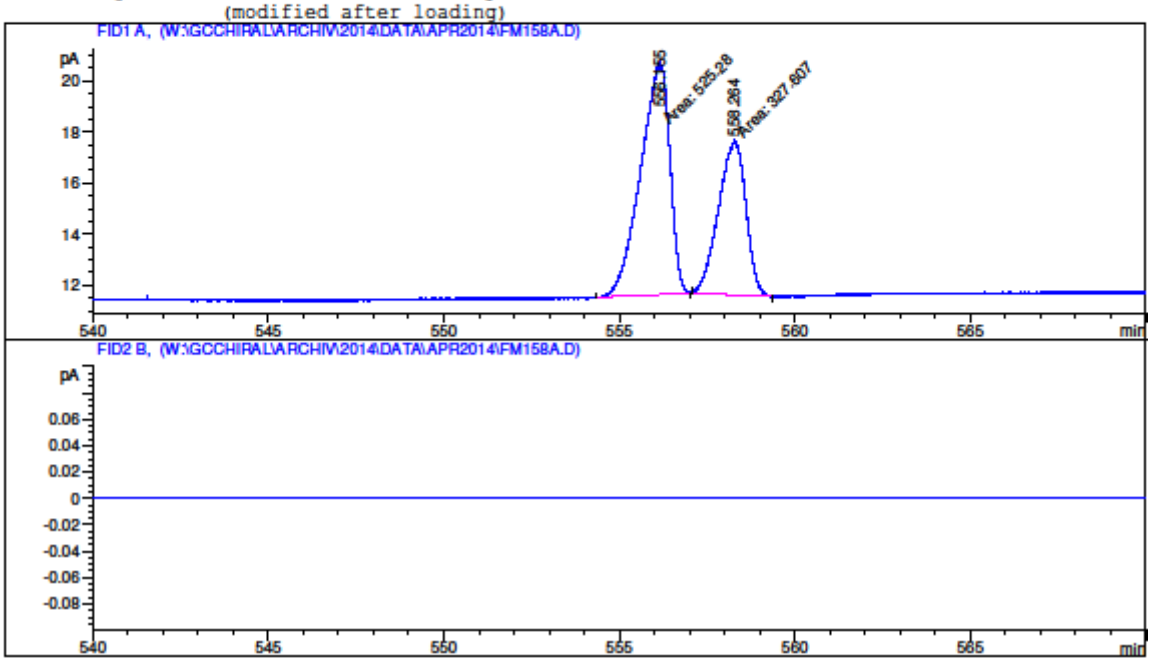
Instrument 1 29.04.2016 13:27:02 ALEX Page 1 of 1



6 + **5k** (230 mol%)

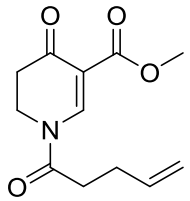
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\APR2014\FM158A.D Sample Name: FM158A

```
Injection Date  : 16.06.2014 19:01:26          Seq. Line :   2
Sample Name     : FM158A                        Location : Vial 106
Acq. Operator   : Ingo                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 29.04.2016 13:14:43  by ALEX
                  (modified after loading)
```



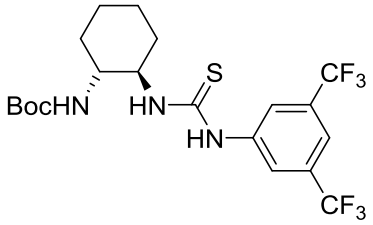

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 556.155 MM    0.9583  525.27960    9.13534 61.58846
   2 558.264 MM    0.9006  327.60678    6.06280 38.41154

Totals :                   852.88638   15.19814

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

                          *** End of Report ***
```

Instrument 1 29.04.2016 13:14:55 ALEX Page 1 of 1



6

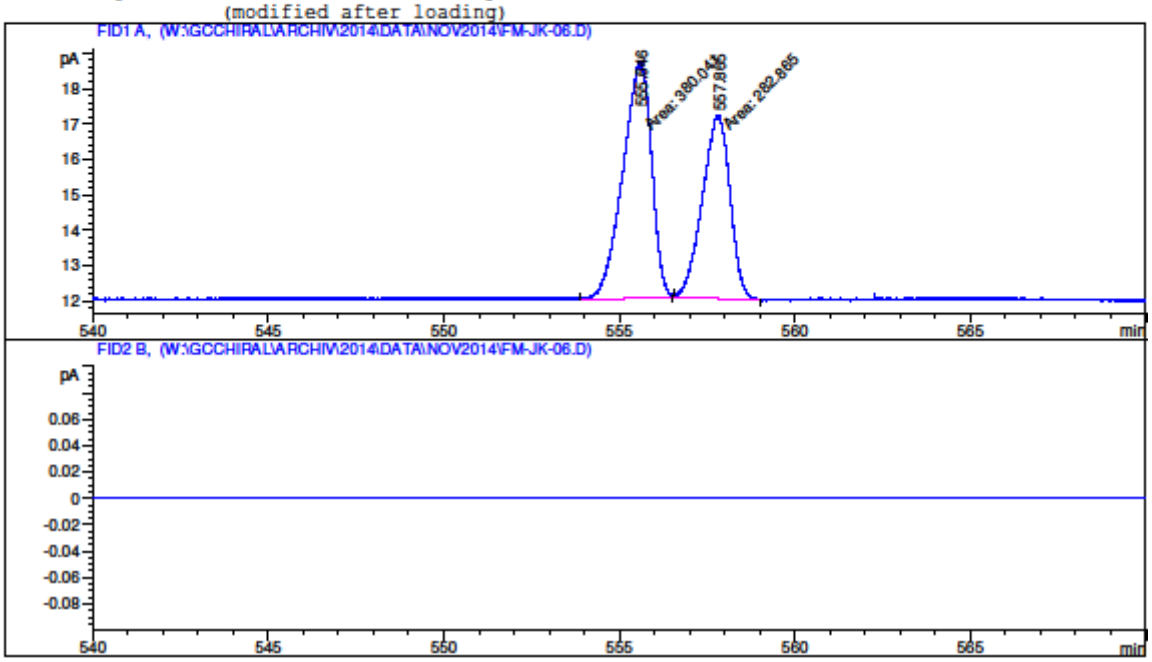
+



10 (50 mol%)

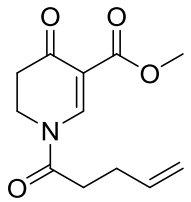
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\NOV2014\FM-JK-06.D Sample Name: FMJK06

```
Injection Date  : 21.11.2014 22:09:05          Seq. Line :   7
Sample Name     : FMJK06                        Location : Vial 107
Acq. Operator   : Alex                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 29.04.2016 13:55:11  by ALEX
                  (modified after loading)
```



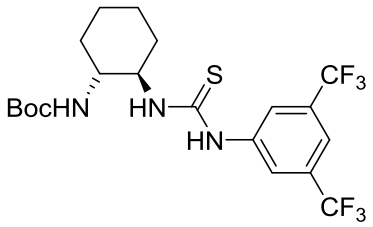

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 555.646 MM    0.9488  380.04089    6.67604 57.32956
   2 557.865 MM    0.9102  282.86481    5.17961 42.67044

Totals :                   662.90570   11.85565

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

                          *** End of Report ***
```

Instrument 1 29.04.2016 13:55:23 ALEX Page 1 of 1



6

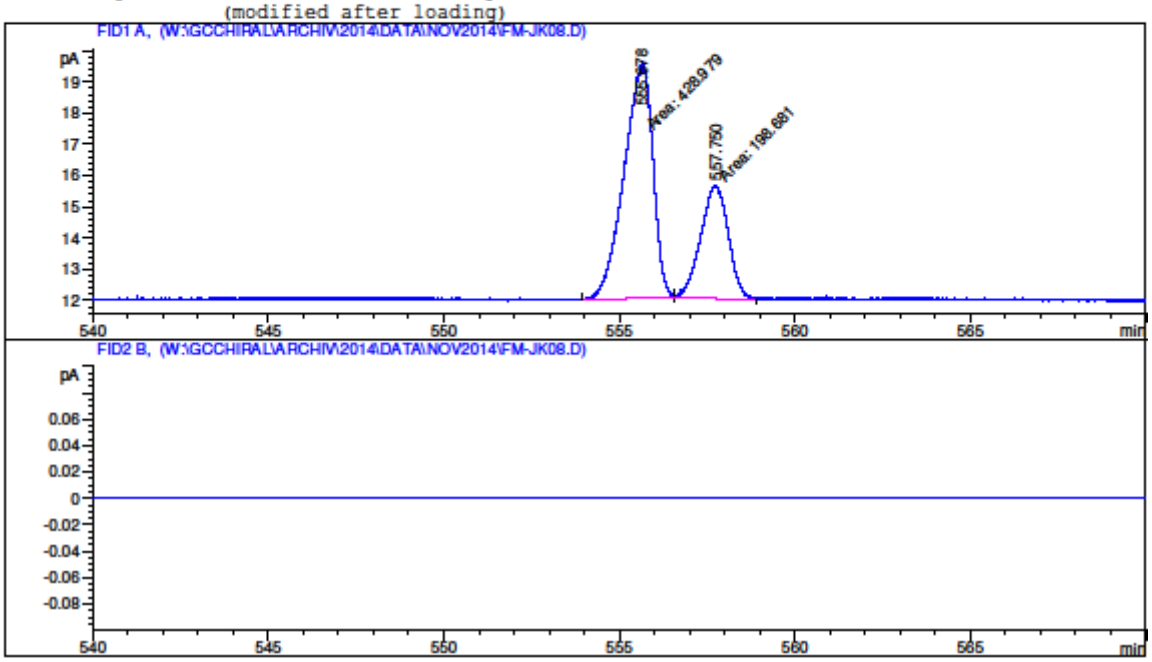
+



10 (100 mol%)

Data File W:\GCCHIRAL\ARCHIV\2014\DATA\NOV2014\FM-JK08.D Sample Name: FMJK08

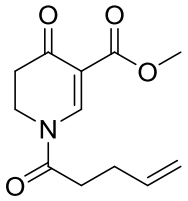
```
Injection Date  : 22.11.2014 08:01:05          Seq. Line :   8
Sample Name     : FMJK08                        Location : Vial 108
Acq. Operator   : Alex                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 29.04.2016 13:56:21  by ALEX
                  (modified after loading)
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 555.678 MM    0.9438  428.97855    7.57575 68.34575
   2 557.750 MM    0.9058  198.68092    3.65554 31.65425

Totals :                   627.65947   11.23129

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

                          *** End of Report ***
```

Instrument 1 29.04.2016 13:56:32 ALEX Page 1 of 1

3.2 Data for sensitized enantioselective reactions at λ = 419 nm

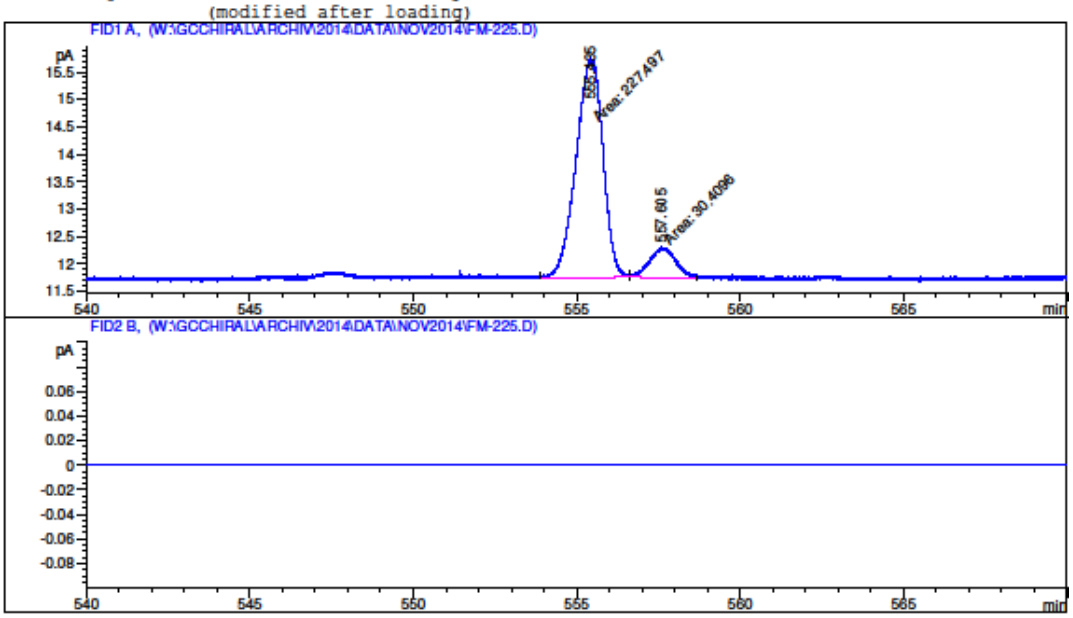


6

+ **5k** (50 mol%)
8 (50 mol%)

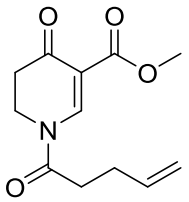
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\NOV2014\FM-225.D Sample Name: FM-225

```
Injection Date  : 05.12.2014 03:20:16          Seq. Line :   2
Sample Name     : FM-225                        Location : Vial 102
Acq. Operator   : Alex                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 29.04.2016 13:52:51  by ALEX
                  (modified after loading)
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 555.435 MM    0.9507  227.49704    3.98843 88.20906
   2 557.605 MM    0.9193   30.40961 5.51320e-1 11.79094

Totals :                   257.90665    4.53975

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

                          *** End of Report ***
```

Instrument 1 29.04.2016 13:52:52 ALEX Page 1 of 1

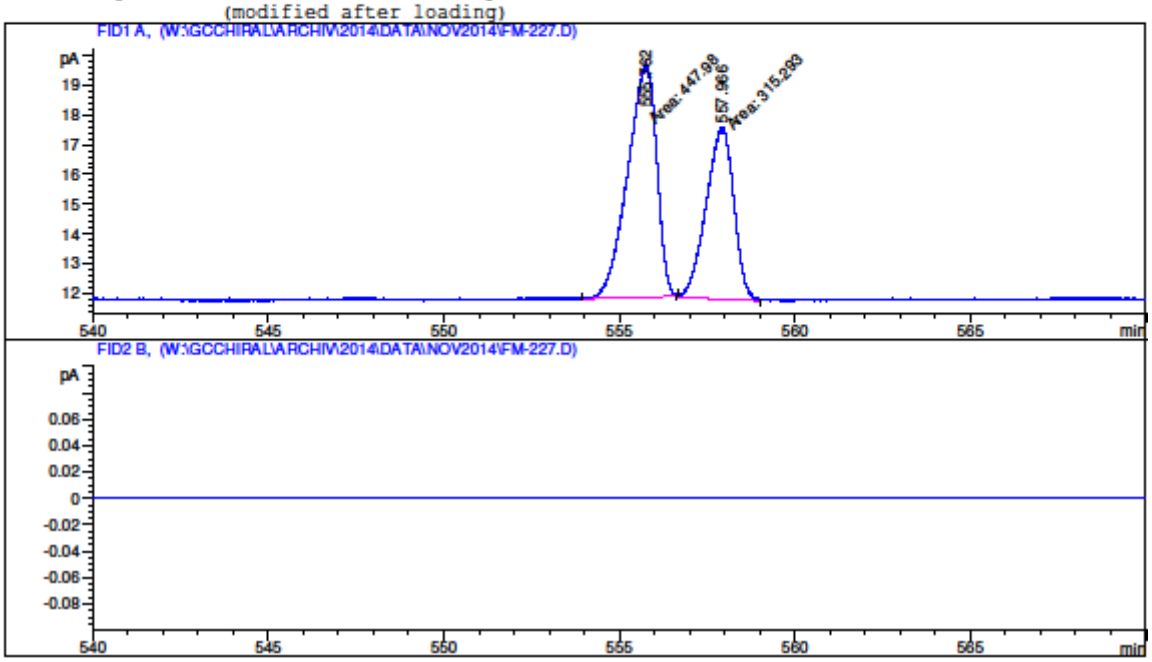


6

+ **5k** (10 mol%)
8 (10 mol%)

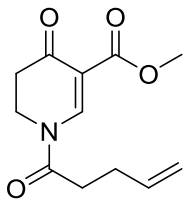
Data File W:\GCCHIRAL\ARCHIV\2014\DATA\NOV2014\FM-227.D Sample Name: FM-227

```
Injection Date  : 04.12.2014 17:28:17          Seq. Line :   1
Sample Name     : FM-227                        Location : Vial 101
Acq. Operator   : Alex                               Inj :   1
                                              Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : D:\HPCHEM1\METHODS\RBIH6A.M
Last changed    : 07.03.2014 07:59:03  by Ingo
Analysis Method : D:\HPCHEM1\METHODS\ZYQ219.M
Last changed    : 29.04.2016 13:54:03  by ALEX
                  (modified after loading)
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 555.762 MM    0.9468  447.97989    7.88572 58.69200
   2 557.966 MM    0.9168  315.29254    5.73183 41.30800

Totals :                   763.27243   13.61755

 Results obtained with enhanced integrator!

Signal 2: FID2 B,

                          *** End of Report ***
```

Instrument 1 29.04.2016 13:54:13 ALEX Page 1 of 1



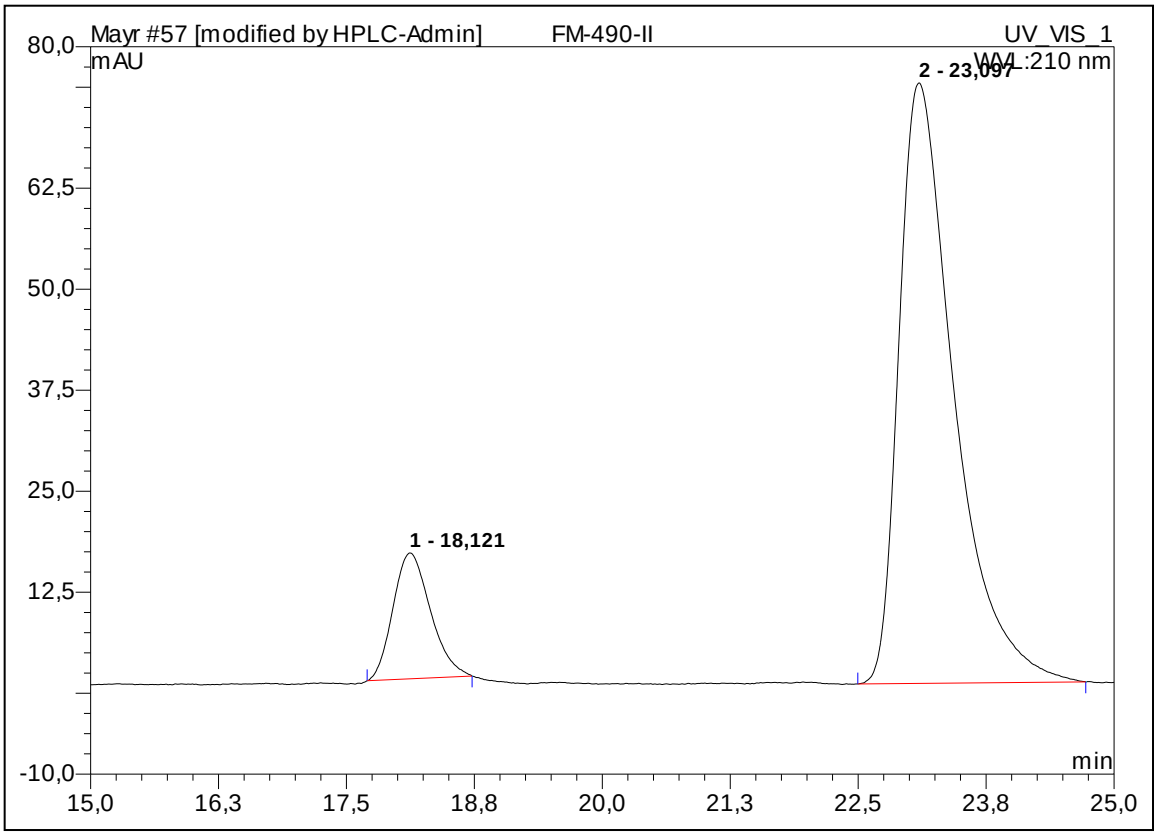
6

+ **5k** (50 mol%)
8 (10 mol%)

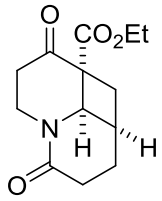
57 FM-490-II

Daicel Chiralpak, AD-H, 250x4.6

Sample Name:	**FM-490-II**	*Injection Volume:*	**10,0**
Vial Number:	**GB8**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210.0**
Control Program:	**An3_Säule1_ISO_90_10_0_0_1_30**	*Bandwidth:*	**1**
Quantif. Method:	**gradA**	*Dilution Factor:*	**1,0000**
Recording Time:	**10.03.2016 16:09**	*Sample Weight:*	**1,0000**
Run Time (min):	**30,00**	*Sample Amount:*	**1,0000**



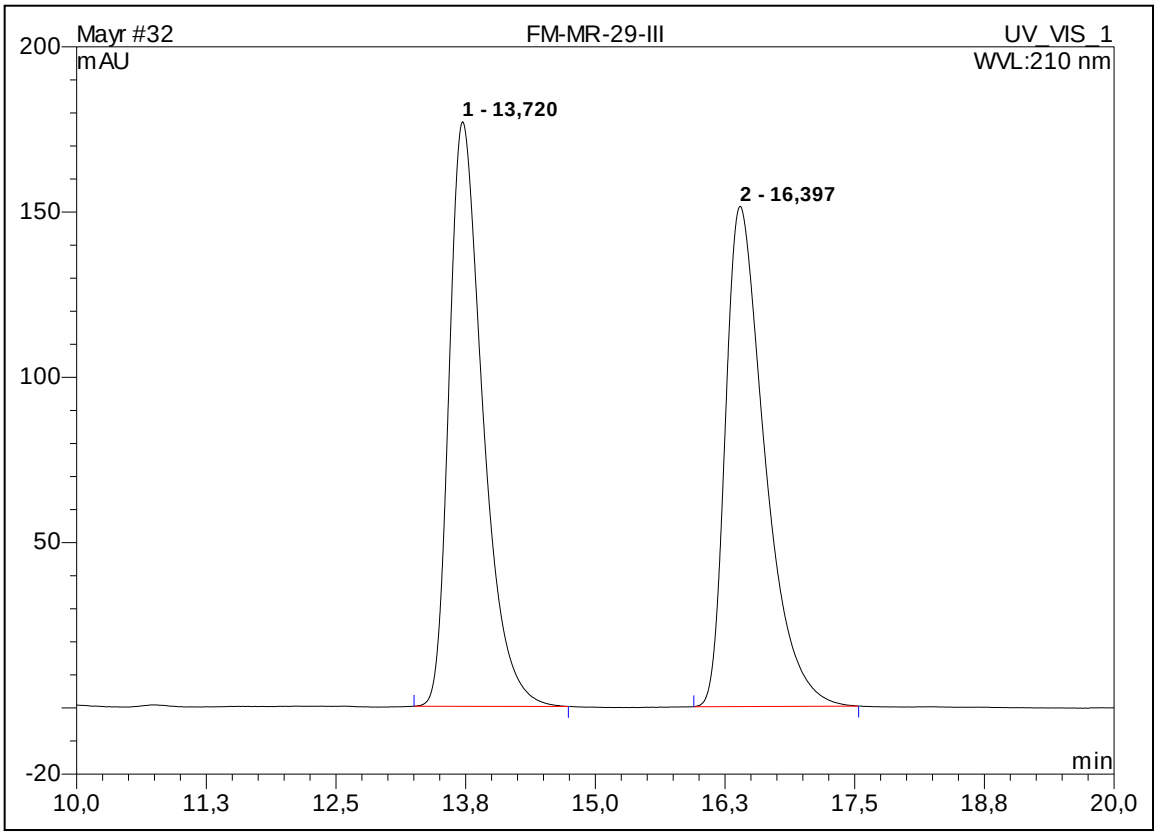
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18,12	n.a.	15,568	6,601	12,50	n.a.	BMB*
2	23,10	n.a.	74,310	46,203	87,50	n.a.	BMB
Total:			89,879	52,803	100,00	0,000	



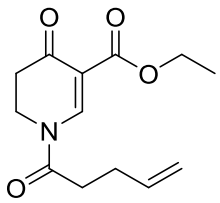
32 FM-MR-29-III

Daicel Chiralpak, AD-H, 250x4.6

Sample Name:	**FM-MR-29-III**	*Injection Volume:*	**10,0**
Vial Number:	**RD4**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210.0**
Control Program:	**An3_Säule1_ISO_90_10_0_0_1_30**	*Bandwidth:*	**1**
Quantif. Method:	**gradA**	*Dilution Factor:*	**1,0000**
Recording Time:	**30.10.2015 09:45**	*Sample Weight:*	**1,0000**
Run Time (min):	**30,00**	*Sample Amount:*	**1,0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13,72	n.a.	176,824	66,732	50,04	n.a.	BMB
2	16,40	n.a.	151,334	66,623	49,96	n.a.	BMB
Total:			328,158	133,355	100,00	0,000	

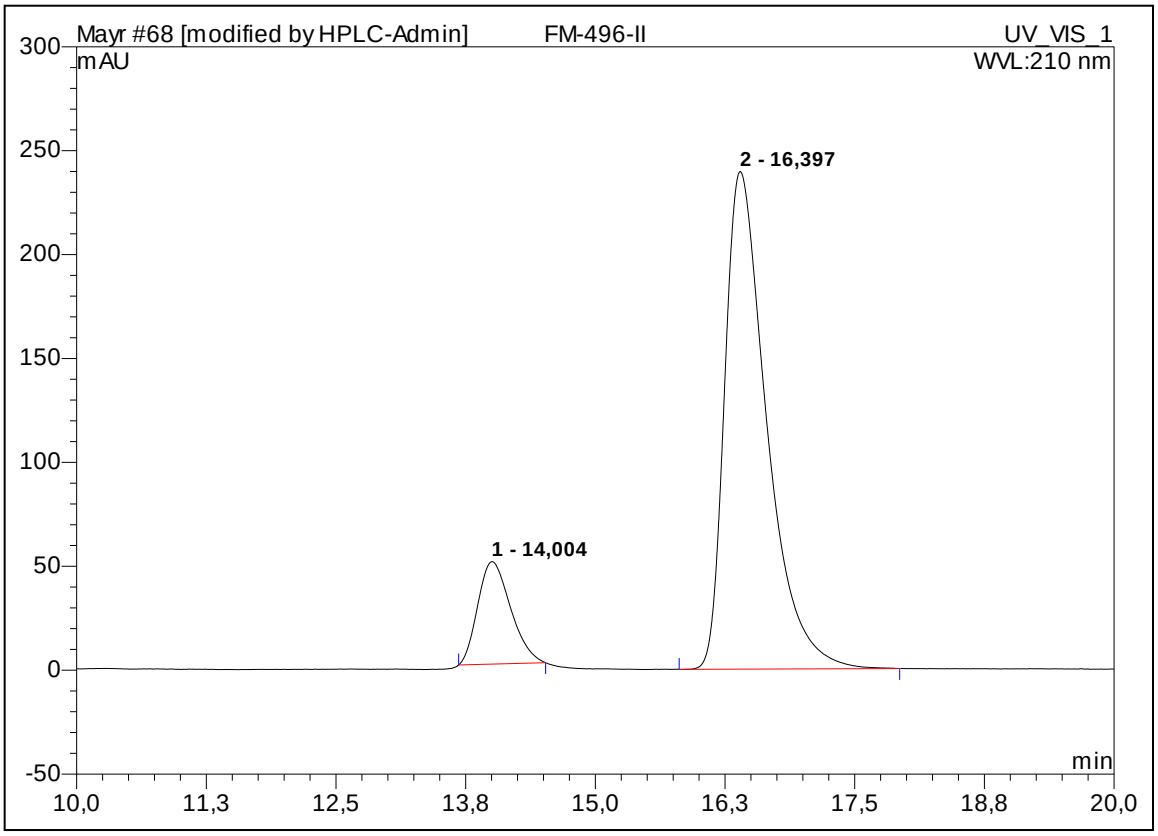


+ **5k** (50 mol%)
8 (10 mol%)

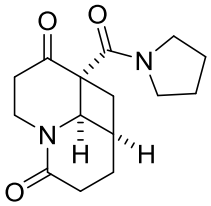
68 FM-496-II

Daicel Chiralpak, AD-H, 250x4.6

Sample Name:	**FM-496-II**	*Injection Volume:*	**10,0**
Vial Number:	**GD6**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210.0**
Control Program:	**An3_Säule1_ISO_90_10_0_0_1_30**	*Bandwidth:*	**1**
Quantif. Method:	**gradA**	*Dilution Factor:*	**1,0000**
Recording Time:	**31.03.2016 14:55**	*Sample Weight:*	**1,0000**
Run Time (min):	**30,00**	*Sample Amount:*	**1,0000**



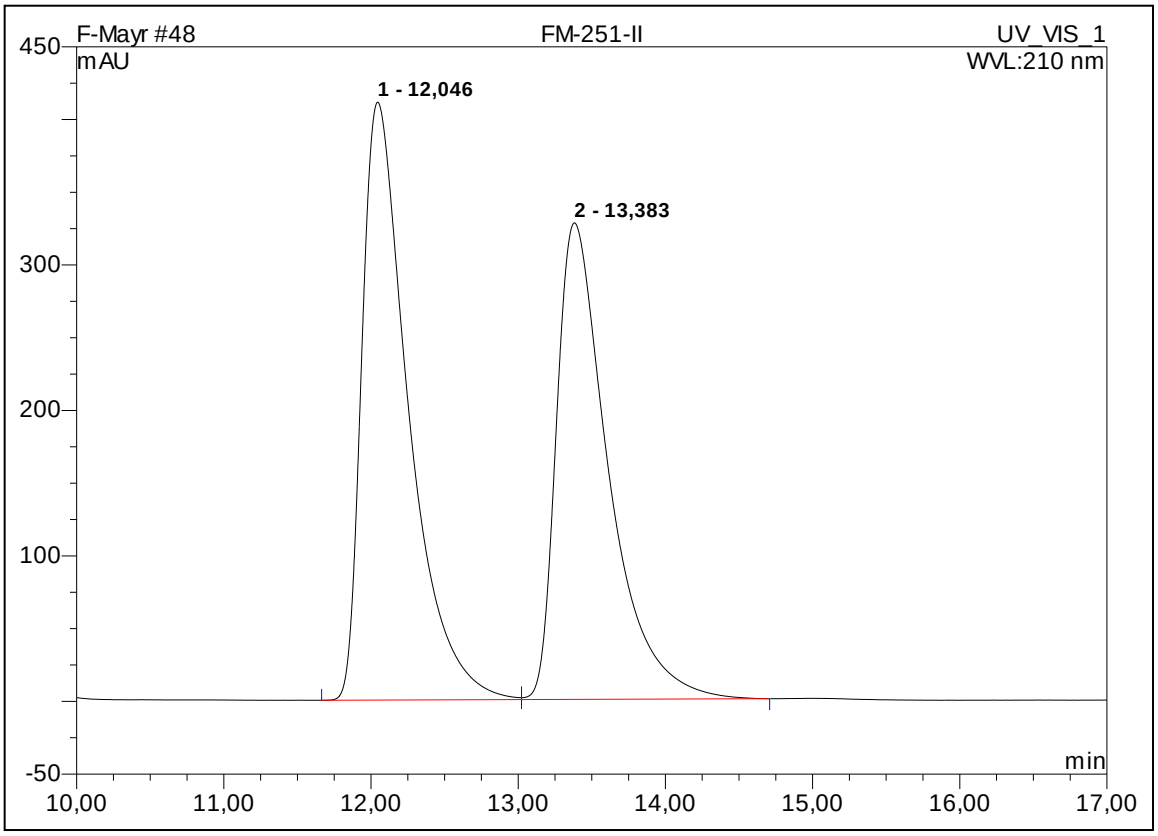
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14,00	n.a.	49,316	18,070	13,87	n.a.	BMB*
2	16,40	n.a.	239,448	112,173	86,13	n.a.	BMB*
Total:			288,764	130,243	100,00	0,000	



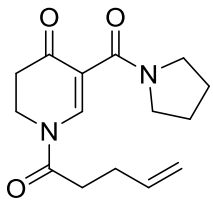
48 FM-251-II

Daicel Chiralpak, AD-H, 250x4.6

Sample Name:	**FM-251-II**	*Injection Volume:*	**5,0**
Vial Number:	**BE2**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210.0**
Control Program:	**Säule1_NP_ISO_80_20_1_50**	*Bandwidth:*	**1**
Quantif. Method:	**gradA**	*Dilution Factor:*	**1,0000**
Recording Time:	**20.01.2015 11:35**	*Sample Weight:*	**1,0000**
Run Time (min):	**50,00**	*Sample Amount:*	**1,0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,05	n.a.	411,054	150,579	52,95	n.a.	BM
2	13,38	n.a.	327,617	133,793	47,05	n.a.	MB
Total:			738,670	284,371	100,00	0,000	

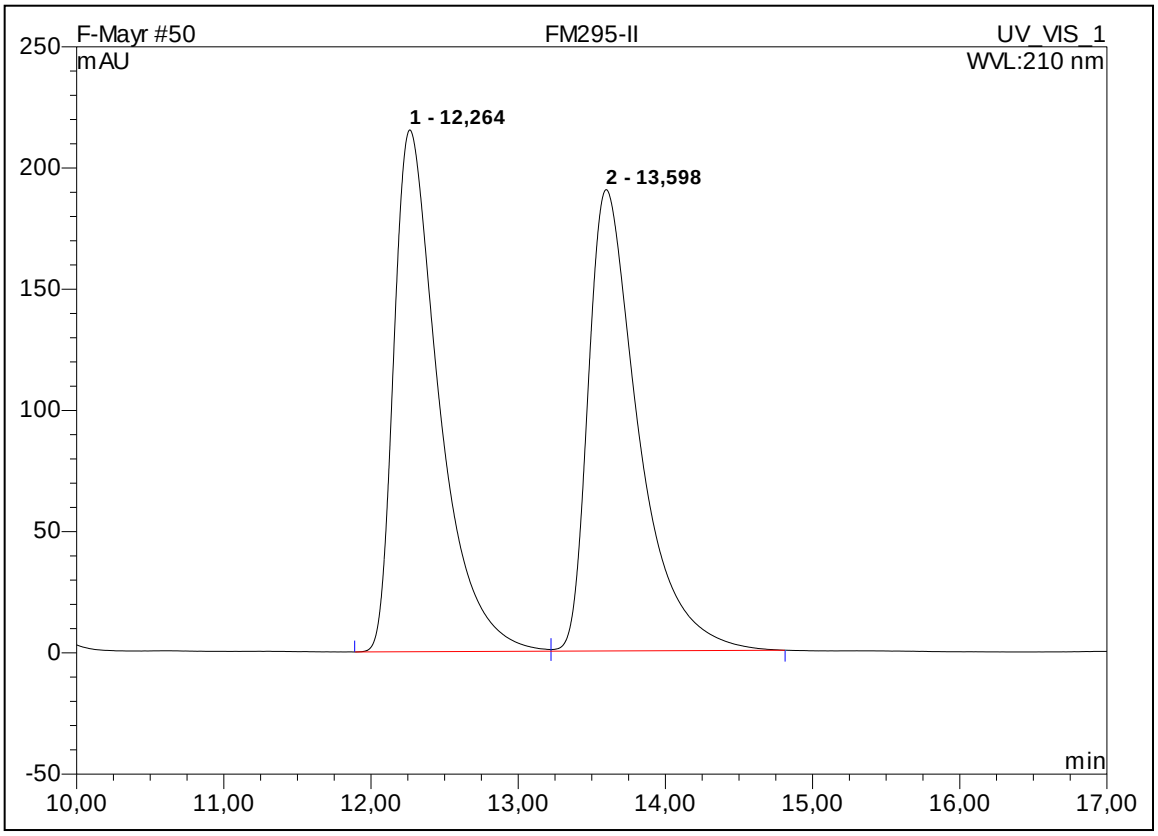


+ **5k** (50 mol%)
8 (10 mol%)

50 FM295-II

Daicel Chiralpak, AD-H, 250x4.6

Sample Name:	**FM295-II**	*Injection Volume:*	**5,0**
Vial Number:	**BA6**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210.0**
Control Program:	**Säule1_NP_ISO_80_20_1_30**	*Bandwidth:*	**1**
Quantif. Method:	**gradA**	*Dilution Factor:*	**1,0000**
Recording Time:	**06.03.2015 13:56**	*Sample Weight:*	**1,0000**
Run Time (min):	**30,00**	*Sample Amount:*	**1,0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,26	n.a.	215,256	76,487	50,40	n.a.	BM
2	13,60	n.a.	190,298	75,276	49,60	n.a.	MB
Total:			405,554	151,762	100,00	0,000	