

## Supplementary Material

### Synthesis of (+)-L-733,060, (+)-CP-99,994 and (2*S*,3*R*)-3-Hydroxypipelic Acid:

#### Application of an Organocatalytic Direct Vinylogous Aldol Reaction

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Memorial University  
St. John's, NL, Canada A1B 3X7

<sup>1</sup> H and <sup>13</sup> C spectra.....	2-34
HPLC traces.....	35-37

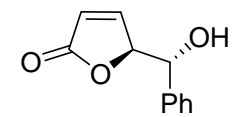
EKP-3473D/1  
EKP-03-90B(CDCI3)

7.44  
7.43  
7.43  
7.42  
7.42  
7.41  
7.41  
7.40  
7.39  
7.39  
7.38  
7.37  
7.37  
7.36  
7.36  
7.35  
7.35  
7.34  
7.34  
7.26  
6.19  
6.19  
6.18  
6.18  
5.19  
5.19  
5.19  
5.18  
5.18  
5.18  
5.10  
5.09  
5.08

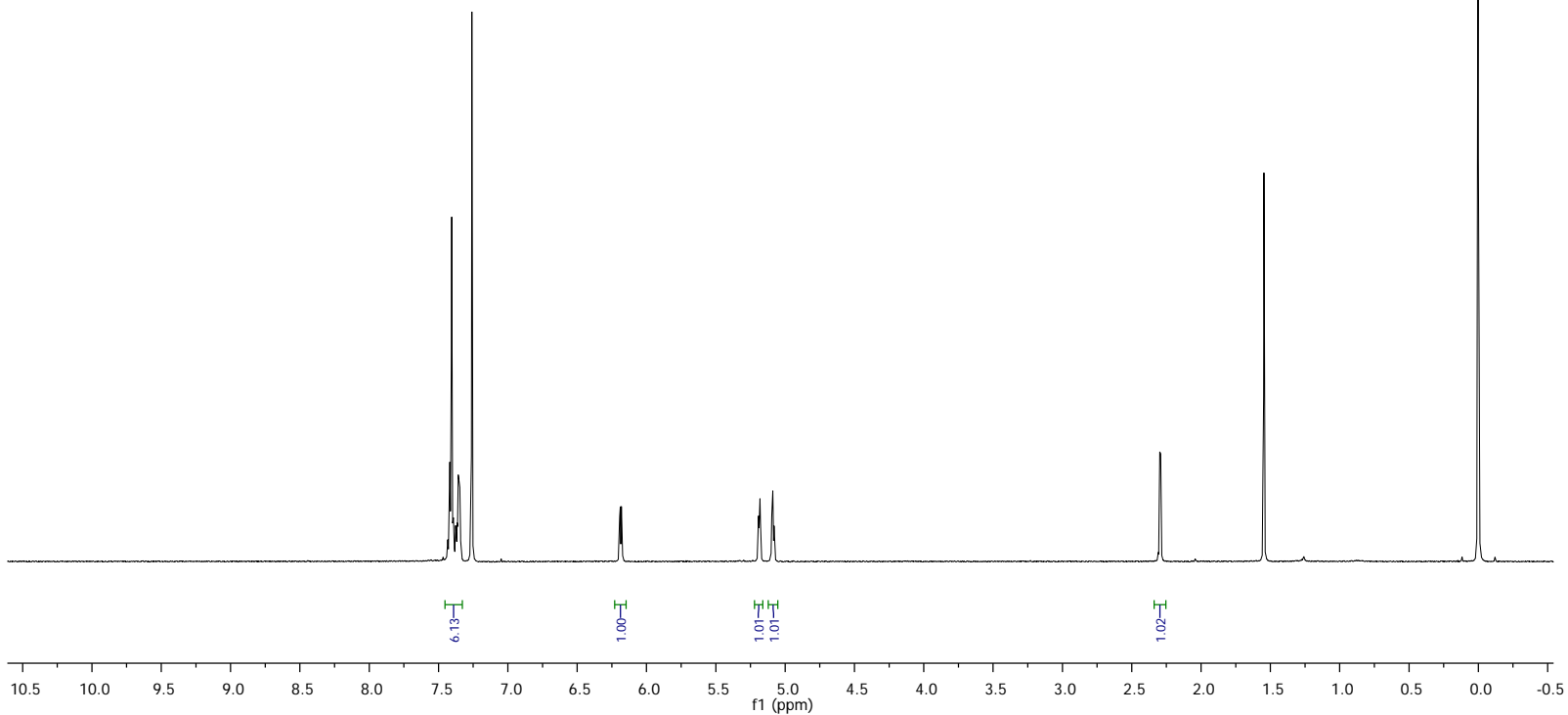
2.30  
2.29

1.55

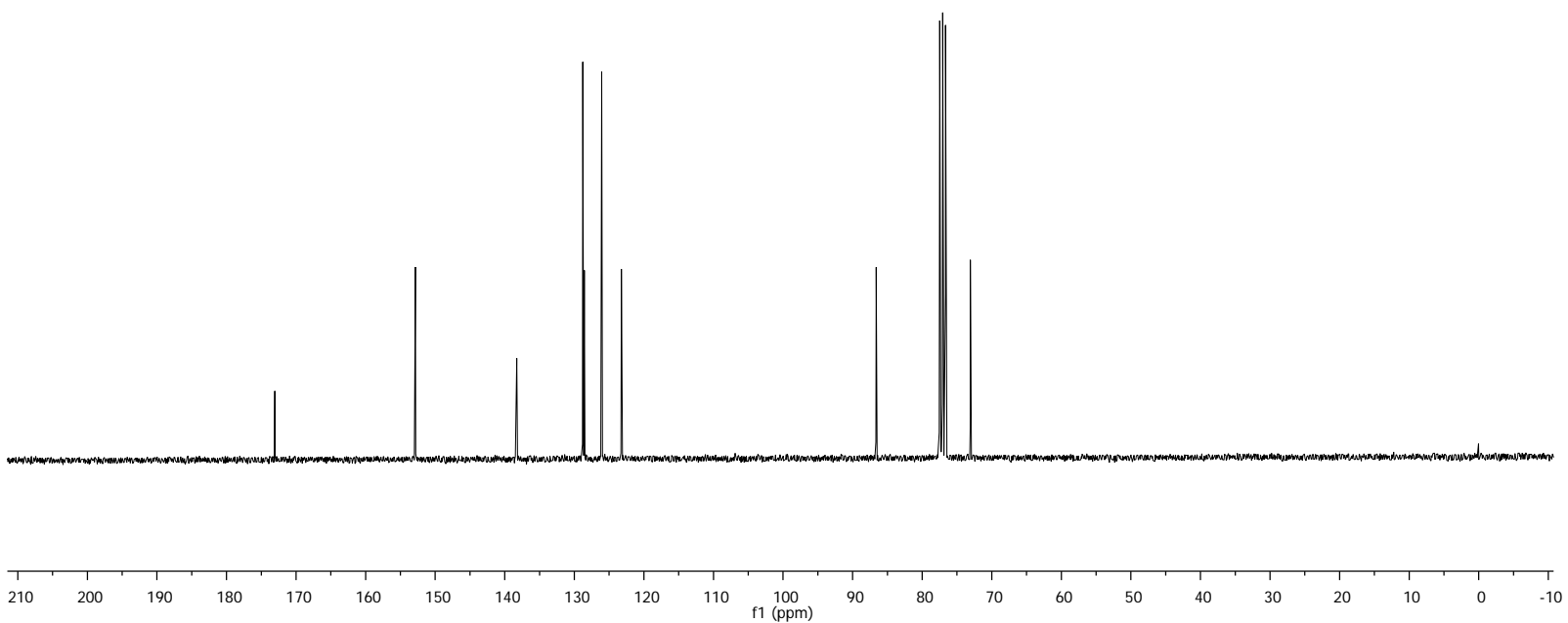
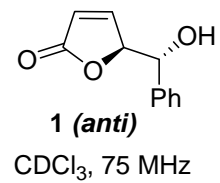
0.00



**1 (anti)**  
CDCl<sub>3</sub>, 500 MHz



EKP-03-90B



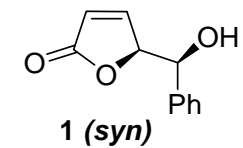
EKP-34215/4  
EKP-03-38C(CDCI3)

7.41  
7.40  
7.40  
7.39  
7.38  
7.37  
7.37  
7.36  
7.36  
7.35  
7.35  
7.34  
7.32  
7.31  
7.26  
7.18  
7.17  
7.17  
7.16  
6.13  
6.13  
6.12  
6.12  
5.17  
5.17  
5.16  
5.16  
5.15  
4.72  
4.70

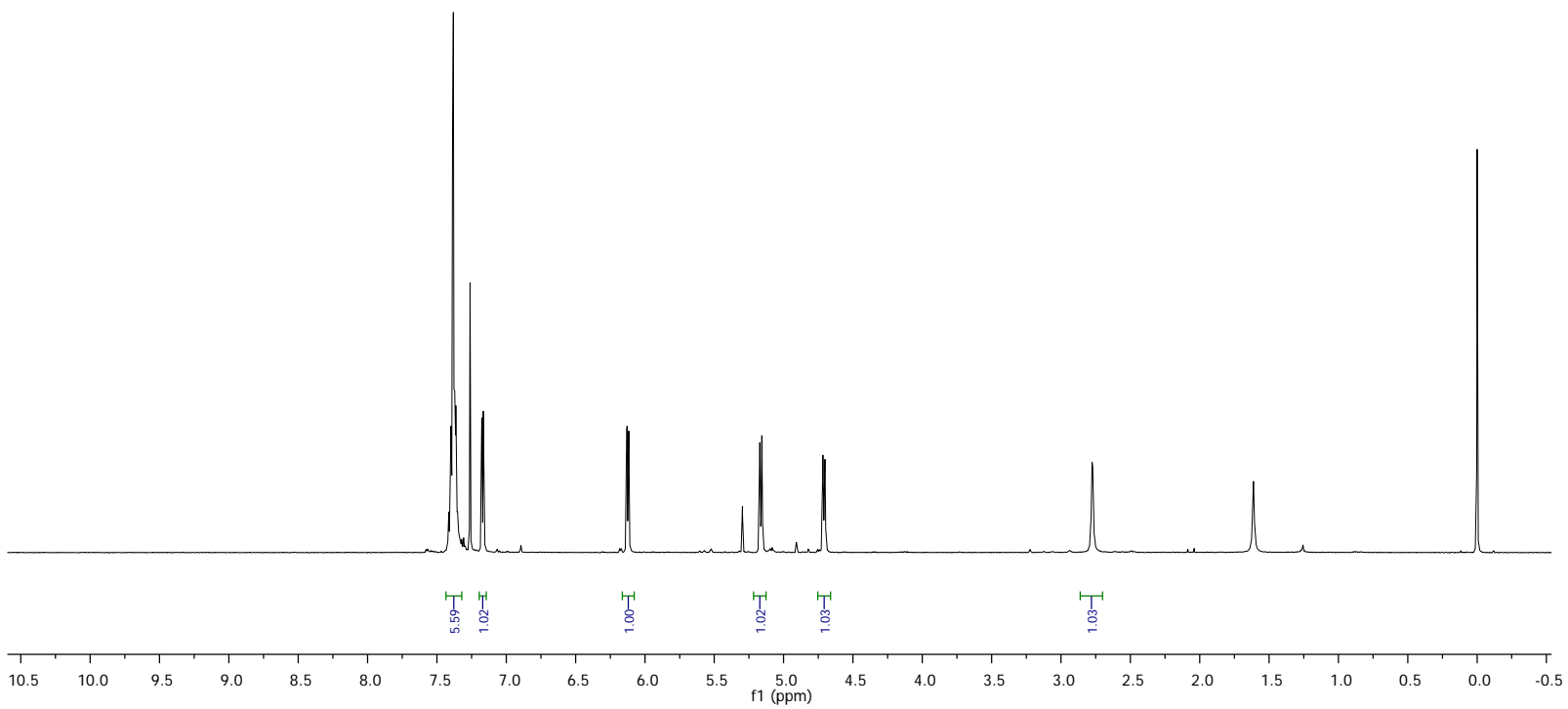
2.78  
2.77

1.61

-0.00



CDCl<sub>3</sub>, 500 MHz



EKP-03-38B

172.40

153.00

137.66

129.01

128.80

126.72

123.01

86.85

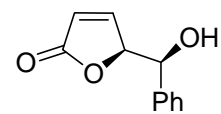
77.44

77.02

76.60

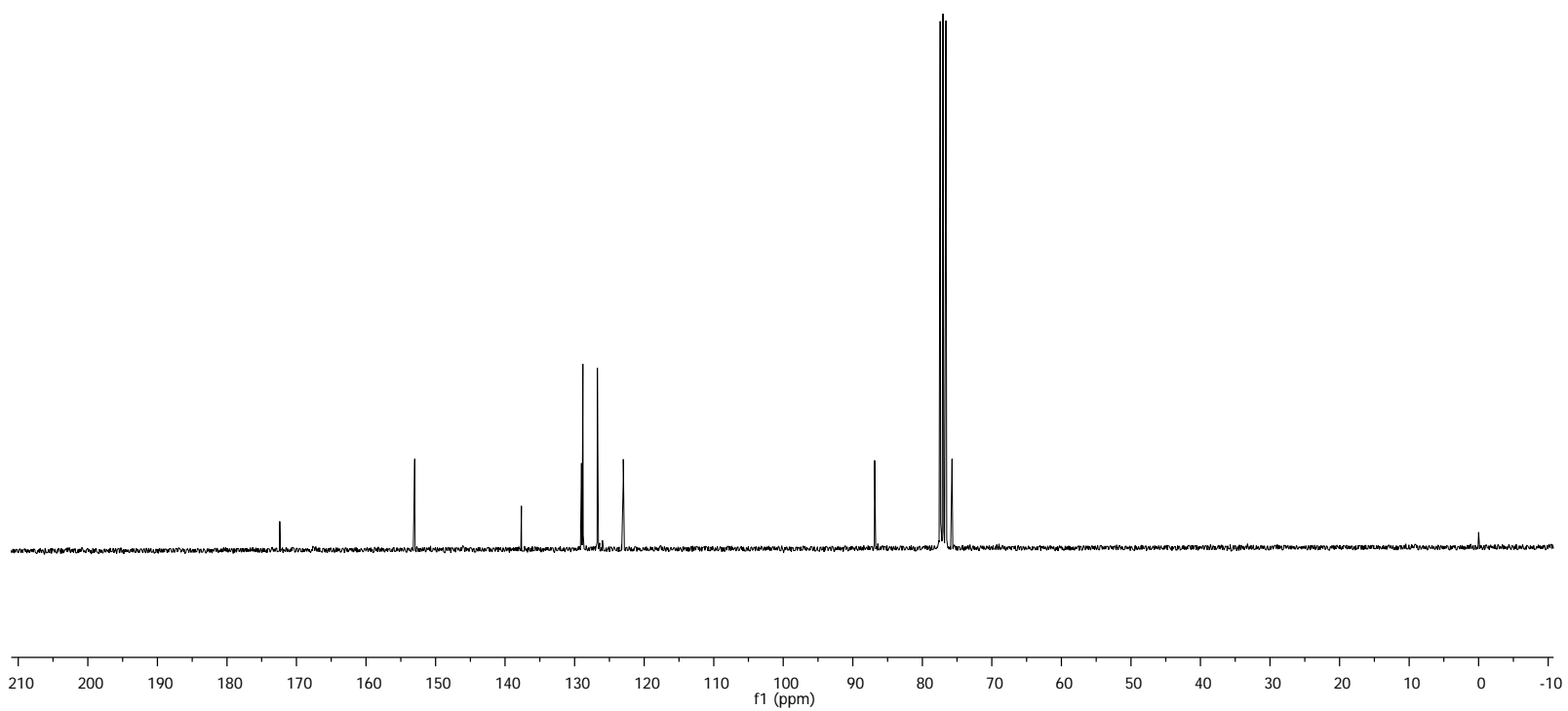
75.72

-0.00



**1 (syn)**

CDCl<sub>3</sub>, 75 MHz



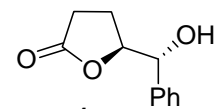
EKP-3554A/1  
EKP-04-41A(CDCI3)

7.39  
7.38  
7.38  
7.37  
7.36  
7.34  
7.33  
7.33  
7.32  
7.32  
7.31  
7.31  
7.30  
7.26

5.13  
5.12

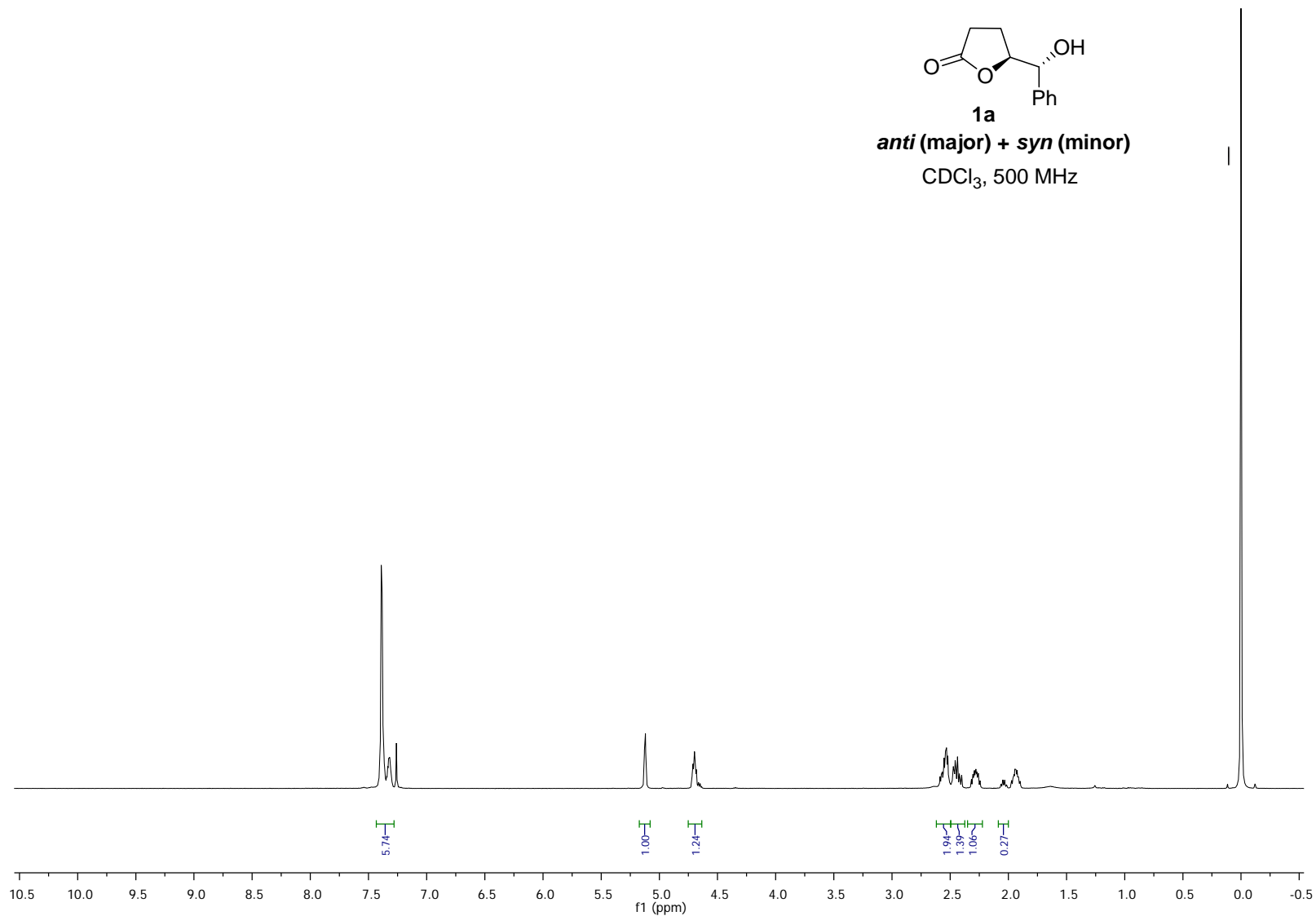
4.72  
4.71  
4.70  
4.70  
4.69  
4.69  
4.68  
4.68

2.57  
2.56  
2.55  
2.54  
2.53  
2.52  
2.47  
2.47  
2.46  
2.46  
2.45  
2.44  
2.42  
2.42  
2.30  
2.29  
2.28  
2.28  
2.27  
2.26  
2.26  
1.94  
1.94  
1.93  
1.93  
1.00

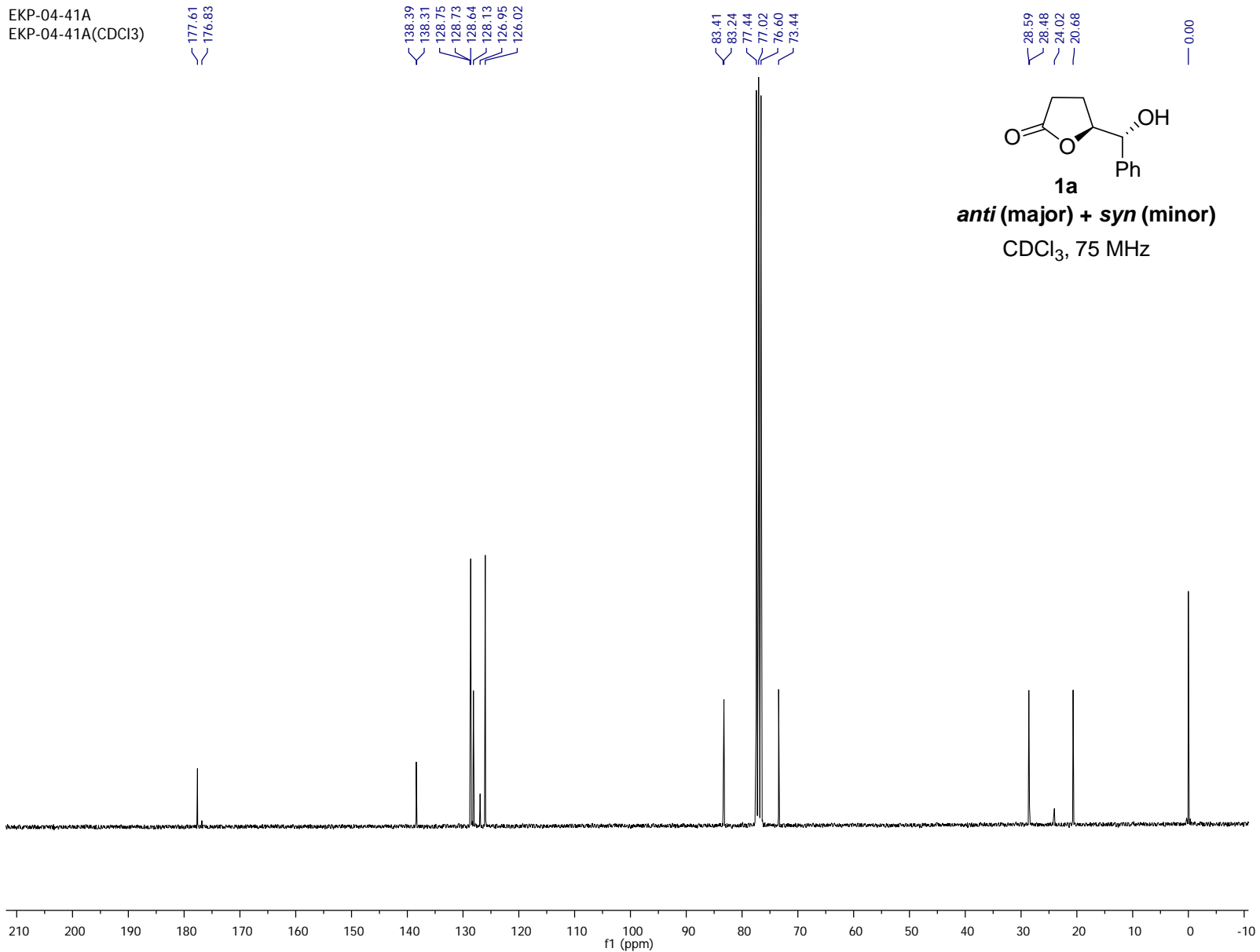


*anti* (major) + *syn* (minor)

CDCl<sub>3</sub>, 500 MHz



EKP-04-41A  
EKP-04-41A(CDCI3)

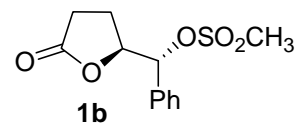


EKP-3602A/1  
EKP-04-57A(CDCI3)

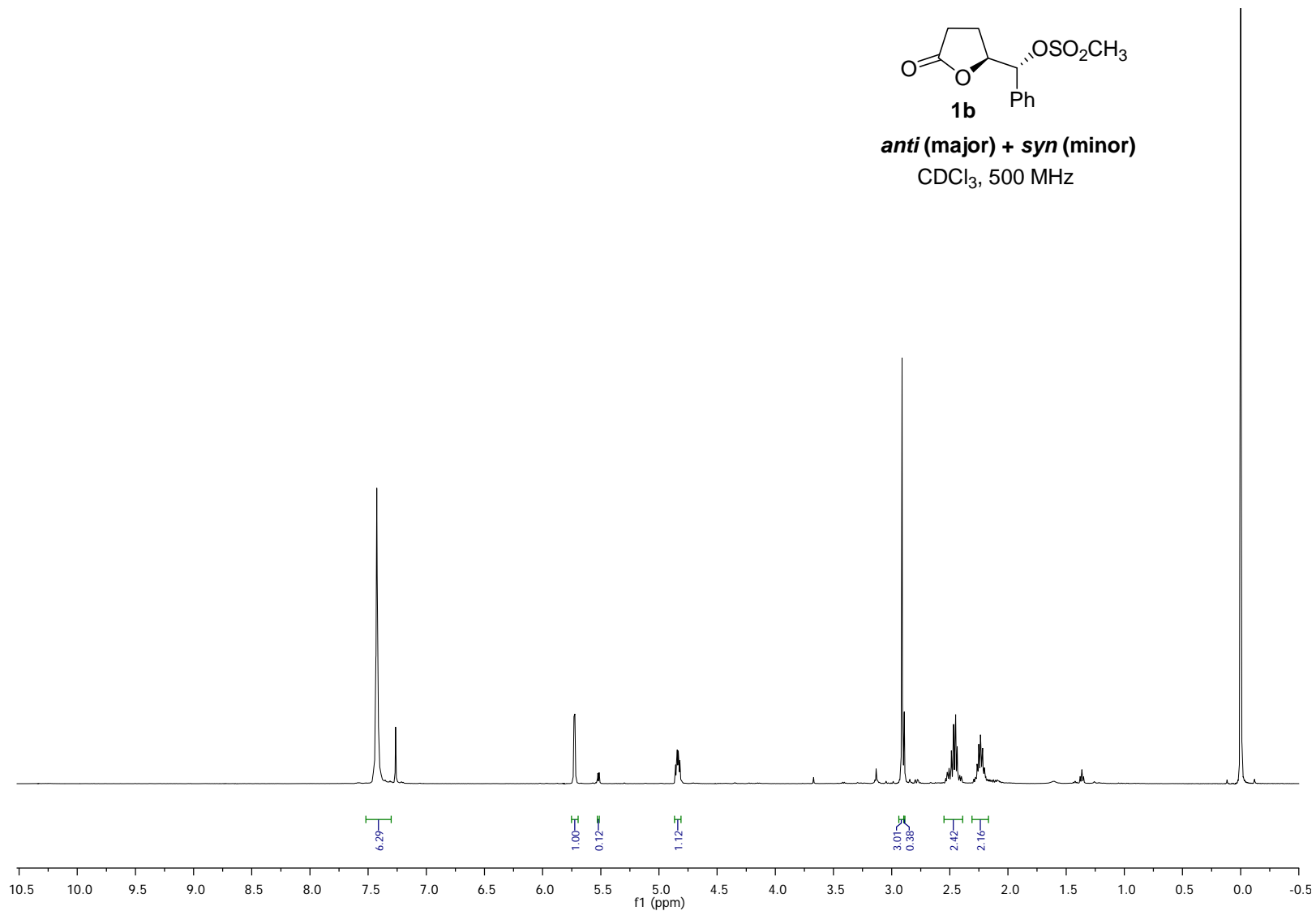
7.43  
7.43  
7.42  
7.42  
7.26

5.73  
5.72  
5.53  
5.51  
4.86  
4.85  
4.84  
4.84  
4.84  
4.83  
4.83  
4.82

2.91  
2.89  
2.52  
2.51  
2.50  
2.49  
2.49  
2.47  
2.47  
2.45  
2.45  
2.44  
2.41  
2.40  
2.27  
2.25  
2.25  
2.24  
2.23  
2.23  
2.22  
0.00

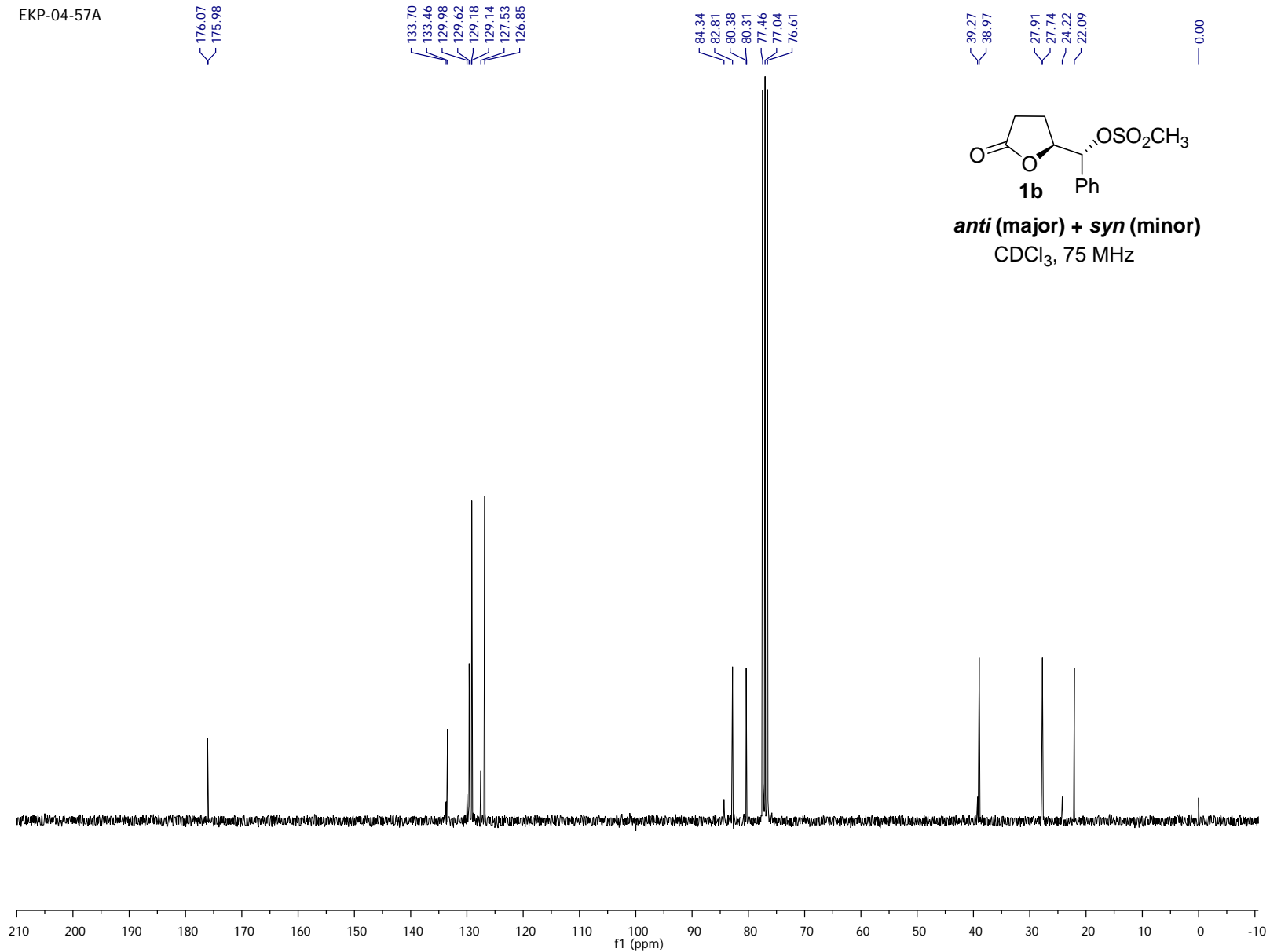


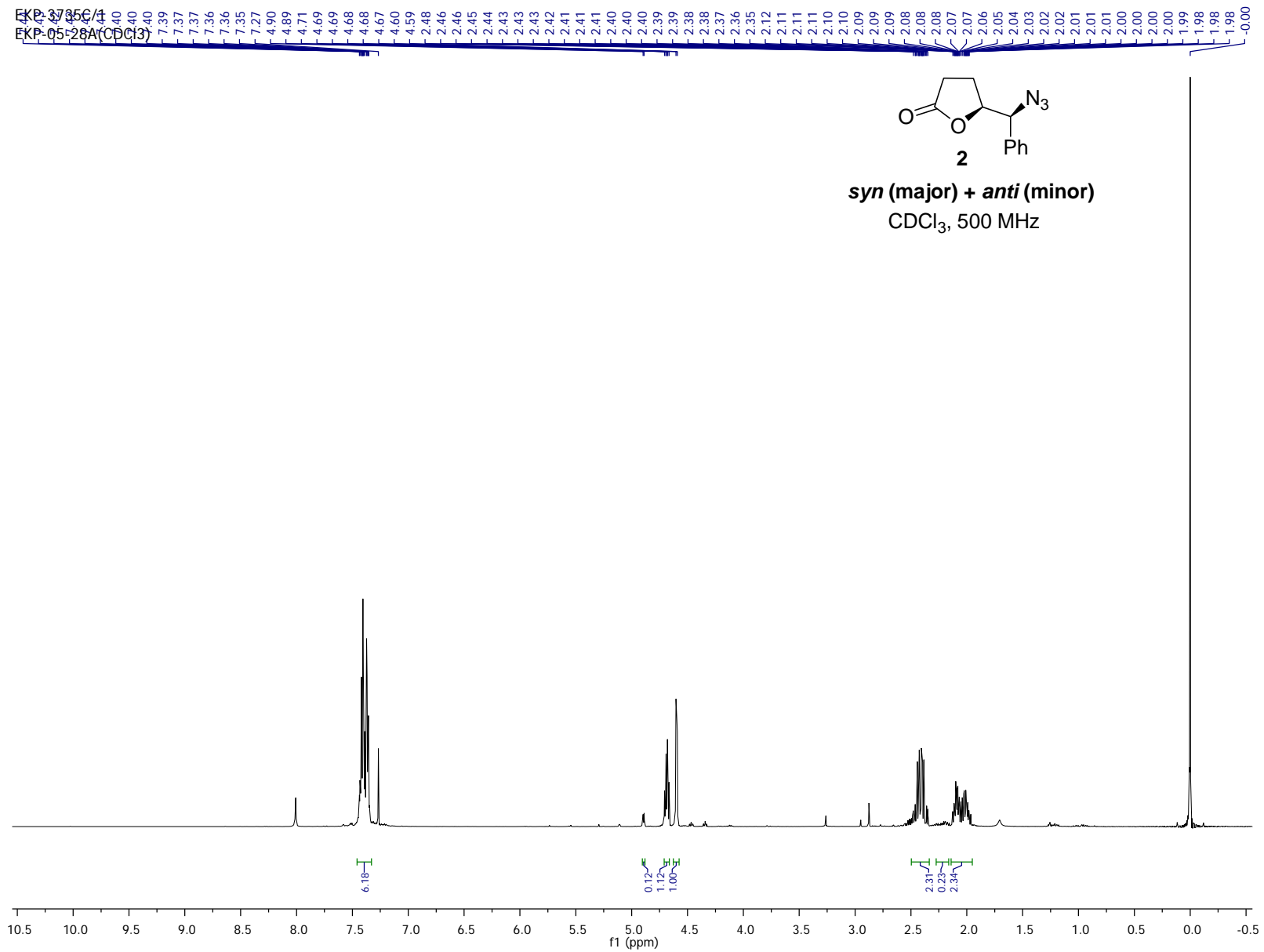
*anti* (major) + *syn* (minor)  
CDCl<sub>3</sub>, 500 MHz



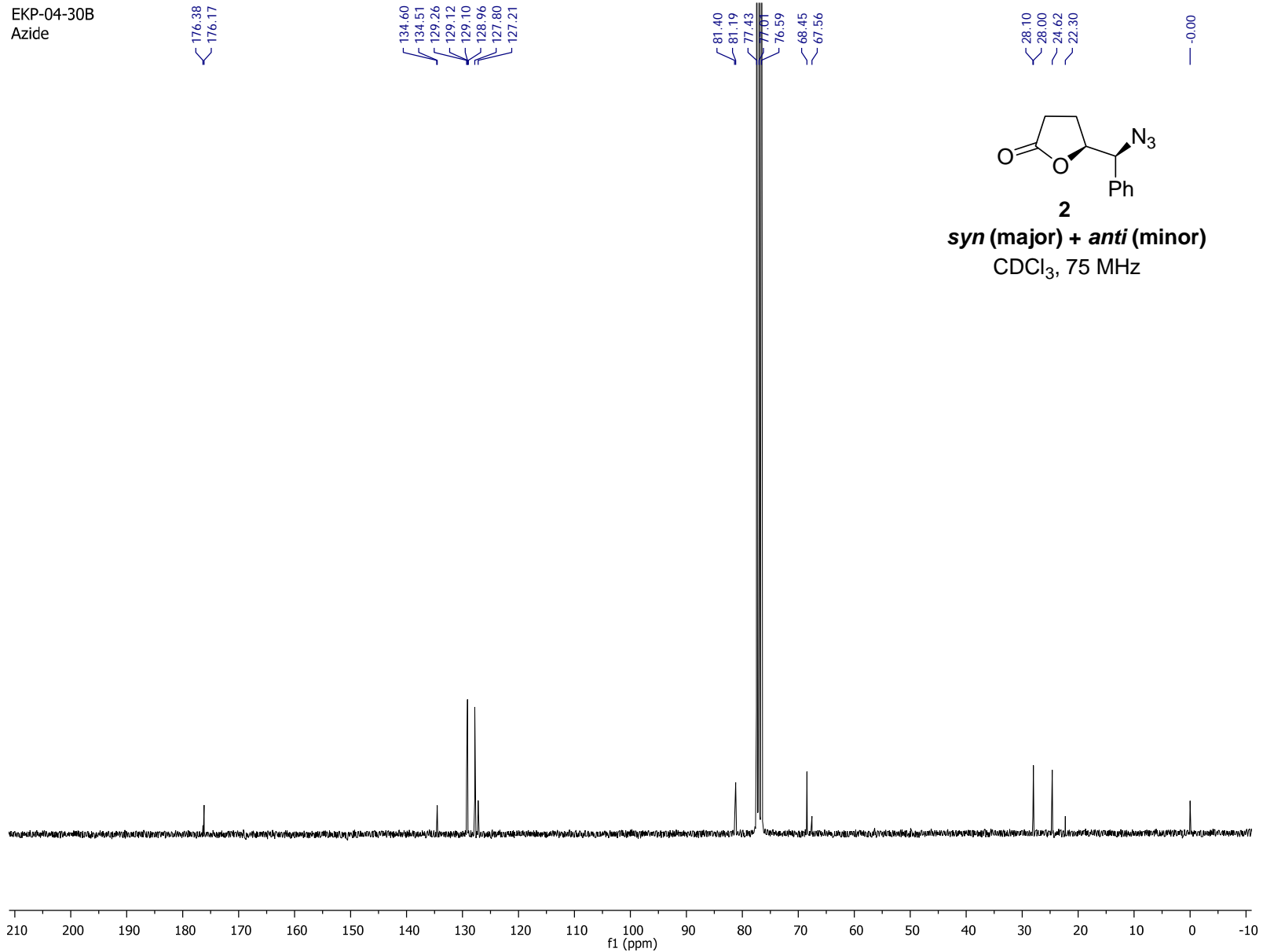


EKP-04-57A





EKP-04-30B  
Azide



EKP-3622A/1  
EKP-04-45C(CDCI3)

7.44  
7.43  
7.42  
7.42  
7.41  
7.37  
7.36  
7.35  
7.35  
7.33  
7.27

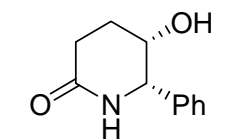
5.85

4.67  
4.67

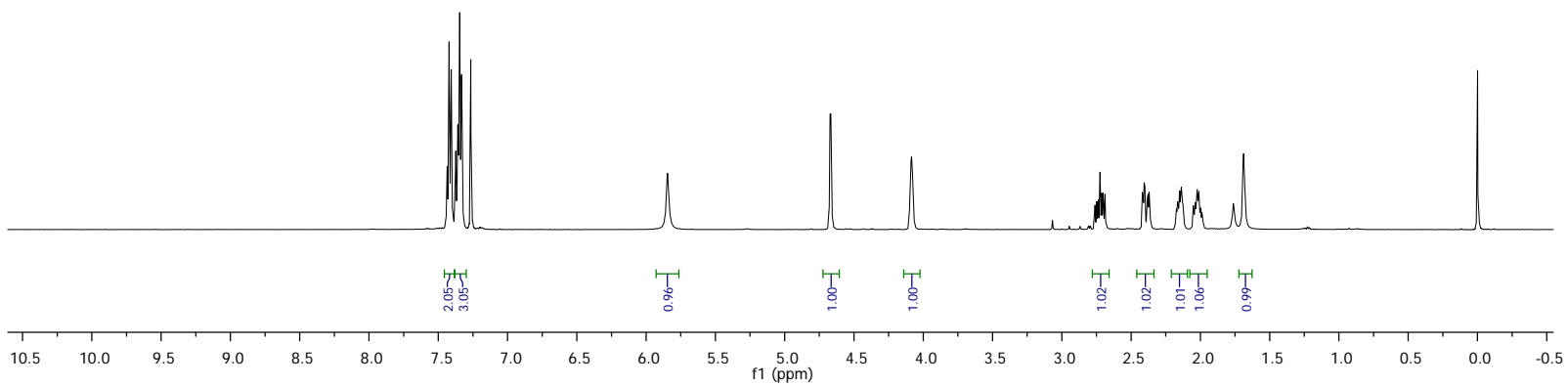
4.08

2.72  
2.71  
2.70  
2.42  
2.41  
2.41  
2.40  
2.38  
2.37  
2.15  
2.14  
2.14  
2.13  
2.13  
2.02  
1.08

-0.00



**cis 3**  
CDCl<sub>3</sub>, 500 MHz



EKP-04-45C  
EKP-04-45C

172.28

137.85

129.15

128.68

127.03

77.46

77.03

76.61

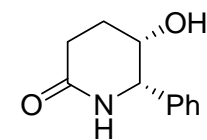
66.23

61.87

26.68

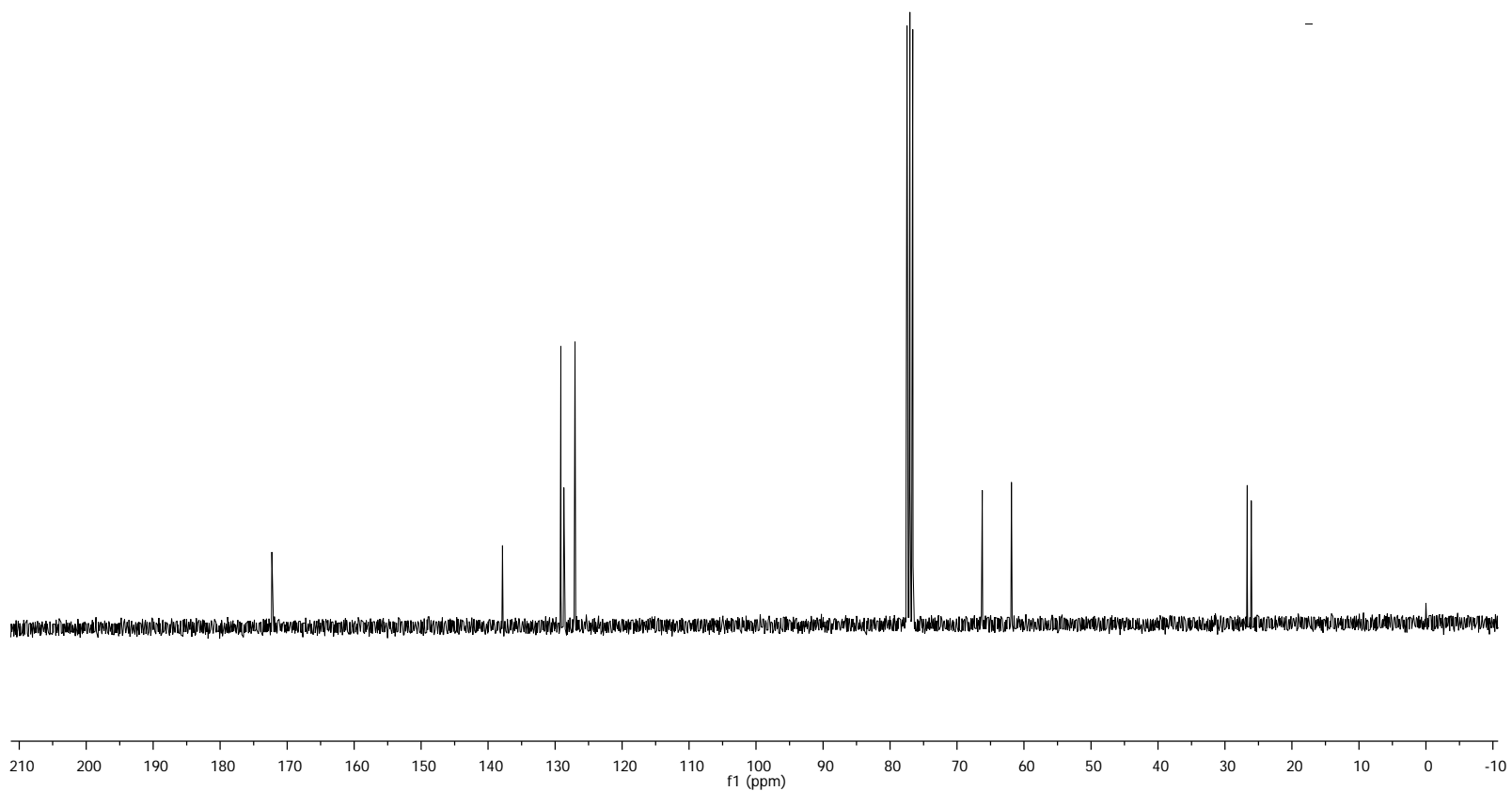
26.06

-0.00



***cis* 3**

CDCl<sub>3</sub>, 75 MHz



EKP-3552B/1  
EKP-04-32C(CDCI3)

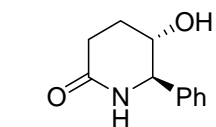
7.46  
7.45  
7.44  
7.44  
7.44  
7.43  
7.43  
7.40  
7.39  
7.39  
7.38  
7.38  
7.36  
7.36  
7.35  
7.26

5.70

4.70  
4.69

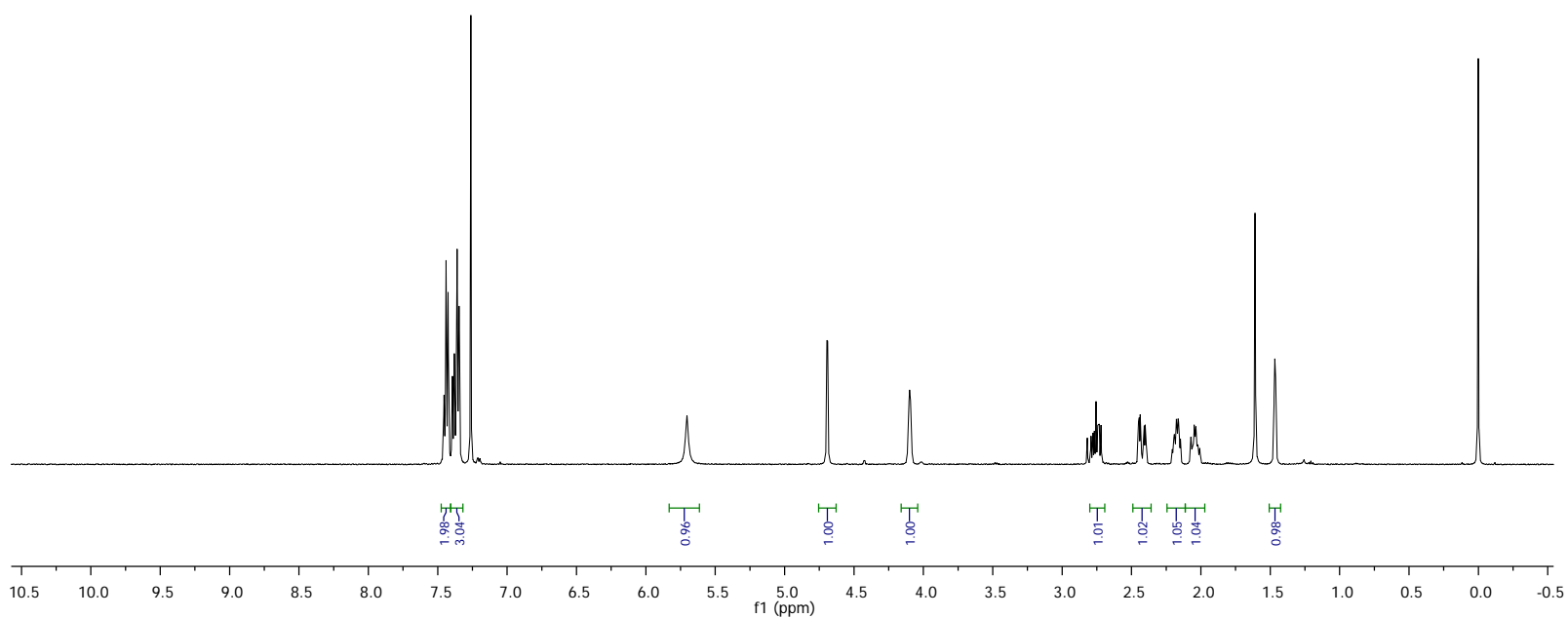
4.10  
4.10  
4.09

2.76  
2.74  
2.73  
2.72  
2.45  
2.44  
2.44  
2.43  
2.40  
2.18  
2.17  
2.17  
2.16  
2.16  
1.85  
1.81

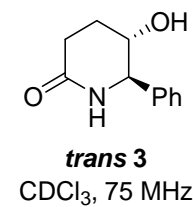
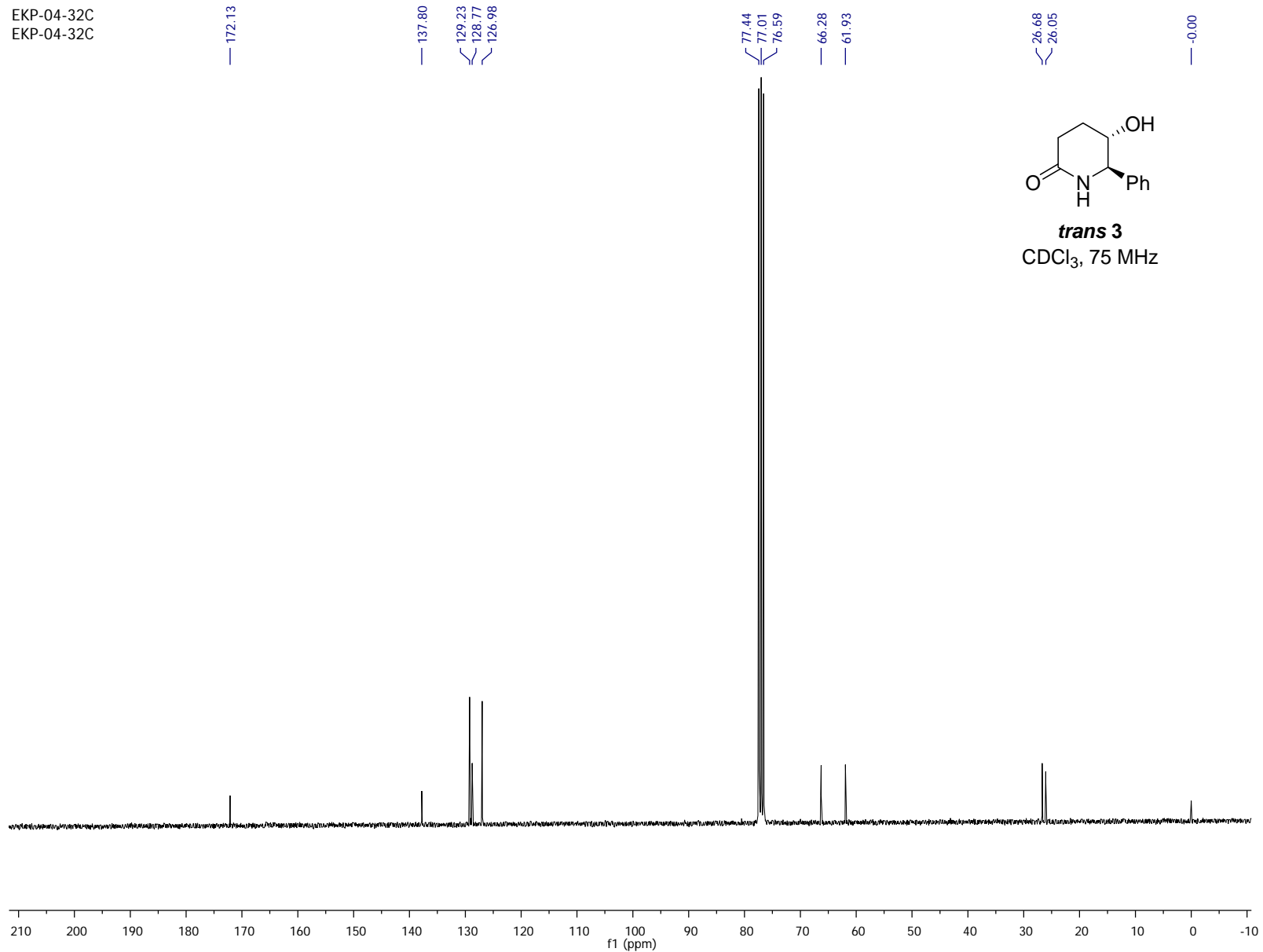


**trans 3**  
CDCl<sub>3</sub>, 500 MHz

0.00



EKP-04-32C  
EKP-04-32C



EKP-3572A/1  
EKP-04-47A(CDCI3)

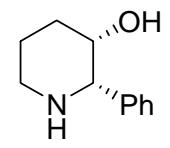
7.36  
7.35  
7.34  
7.34  
7.32  
7.28  
7.27  
7.26  
7.26  
7.25  
7.25

3.86  
3.86  
3.78  
3.78

3.20  
3.19  
3.19

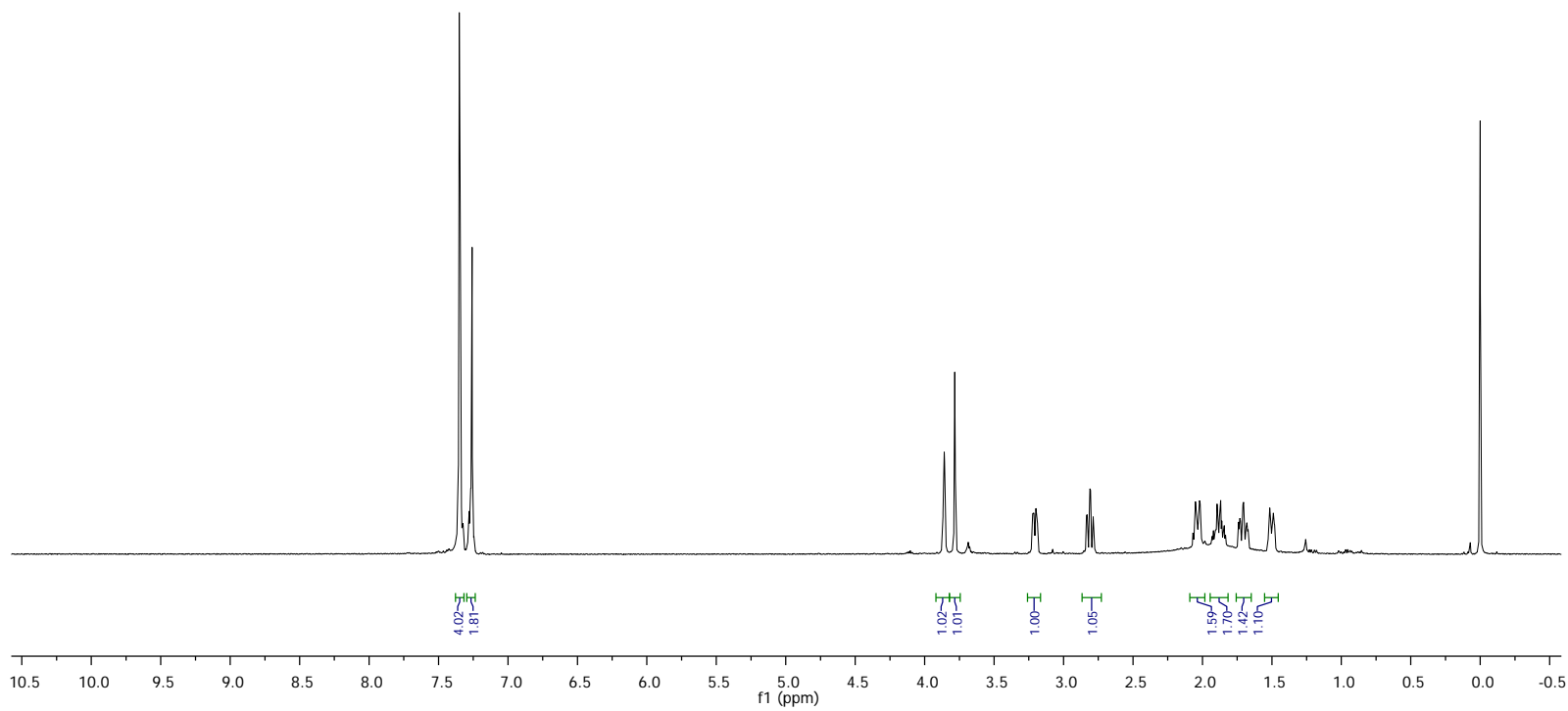
2.83  
2.83  
2.81  
2.81

2.05  
2.05  
2.04  
2.03  
2.02  
2.02  
2.02  
1.89  
1.87  
1.71  
1.71  
1.70  
1.70  
1.52  
1.51  
0.00  
0.00



**3a**

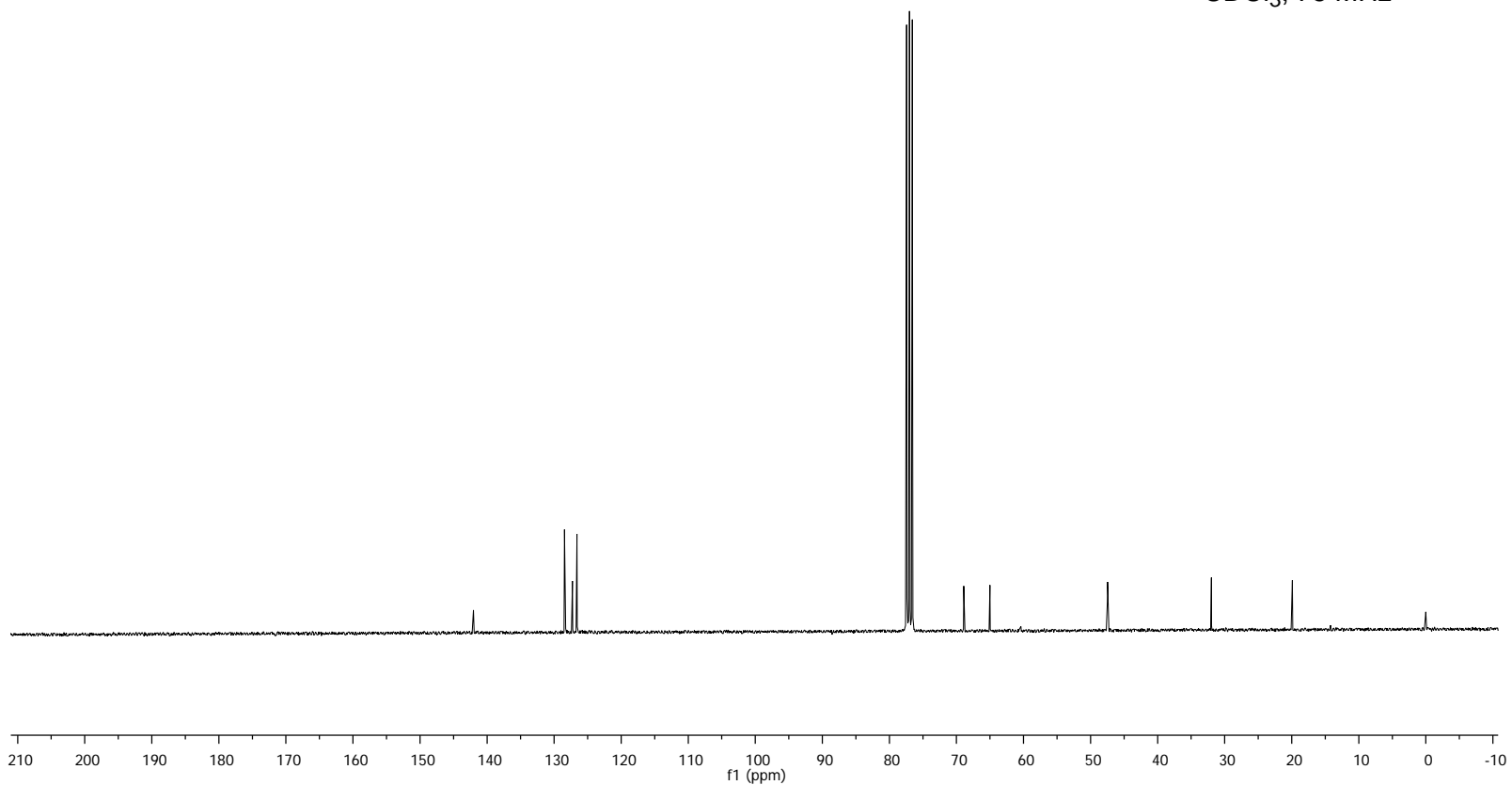
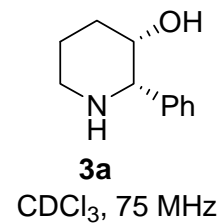
CDCl<sub>3</sub>, 500 MHz



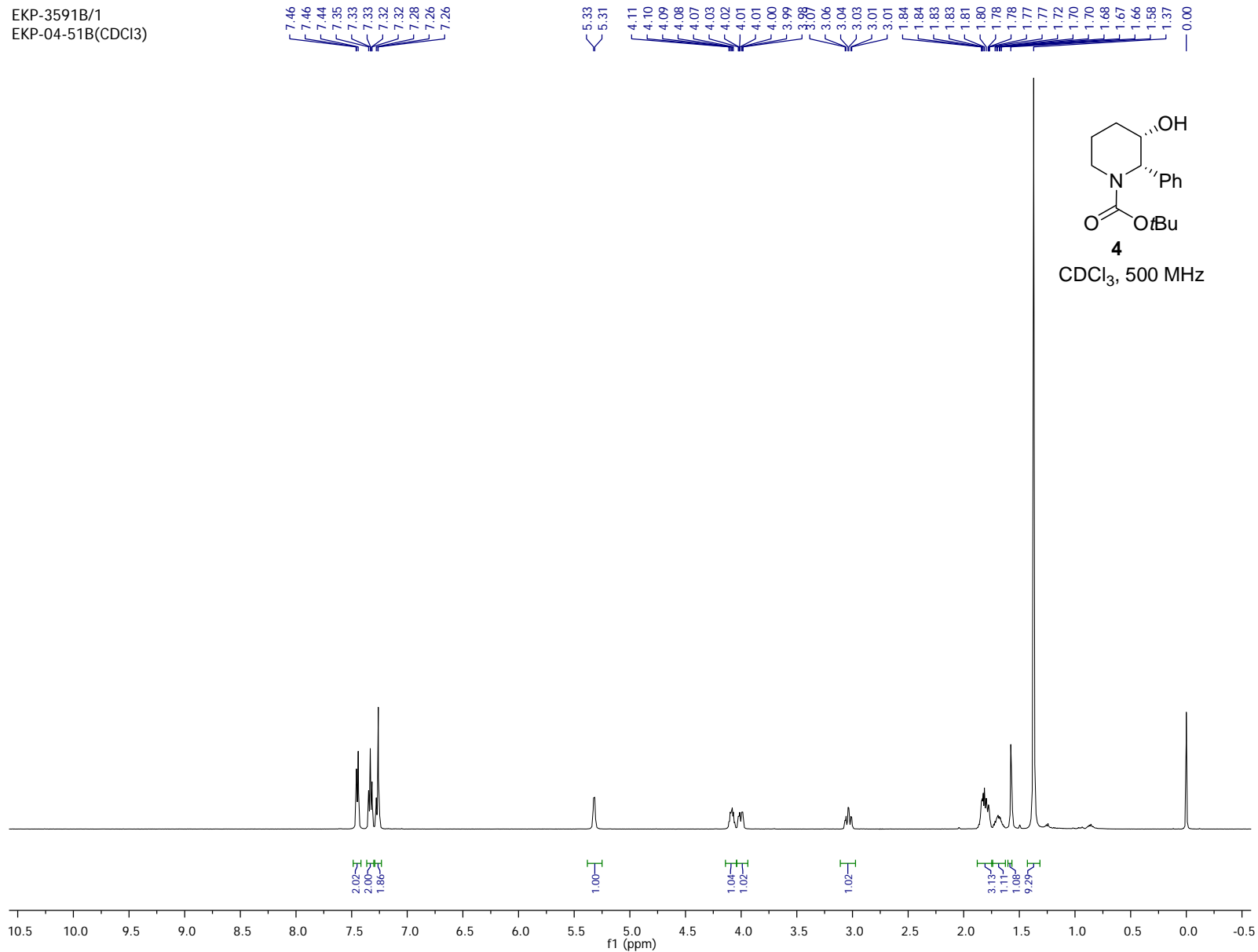


EKP-04-47A  
EKP-04-47A(CDCl<sub>3</sub>)

142.02  
128.45  
127.27  
126.59  
77.44  
77.01  
76.59  
68.92  
65.02  
47.46  
31.98  
19.90  
0.00

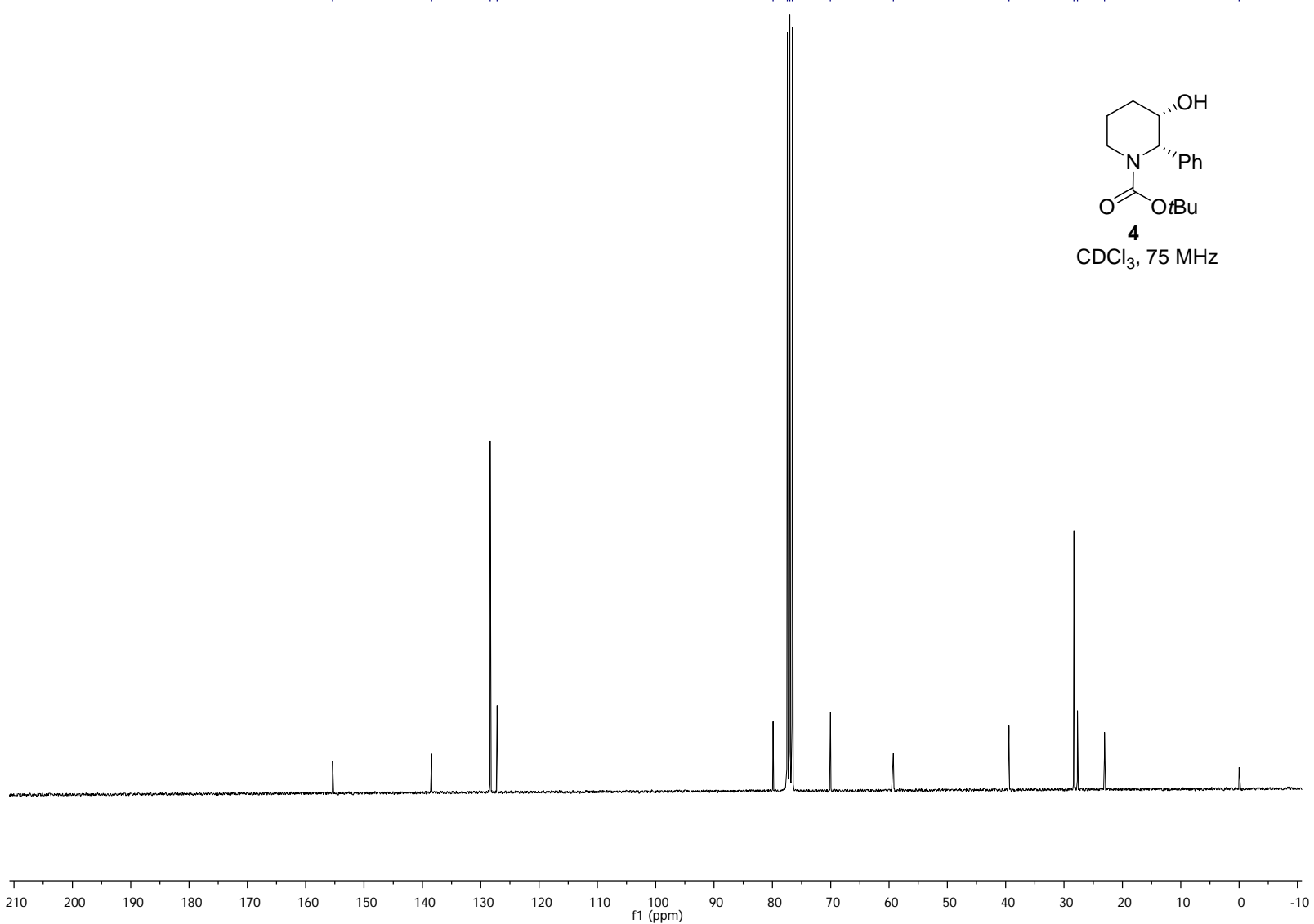


EKP-3591B/1  
EKP-04-51B(CDCl<sub>3</sub>)

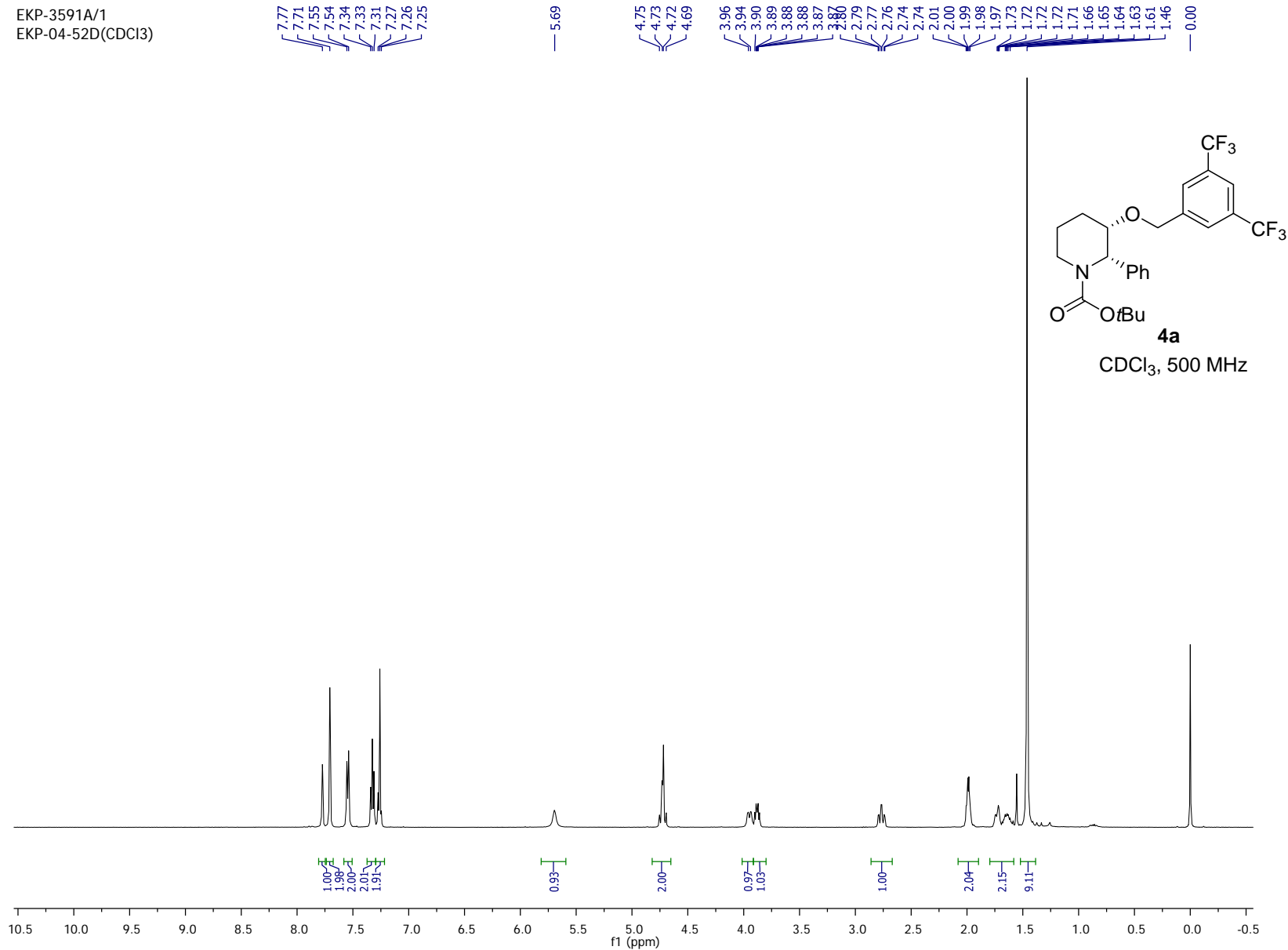


EKP-04-51B  
EKP-04-51B

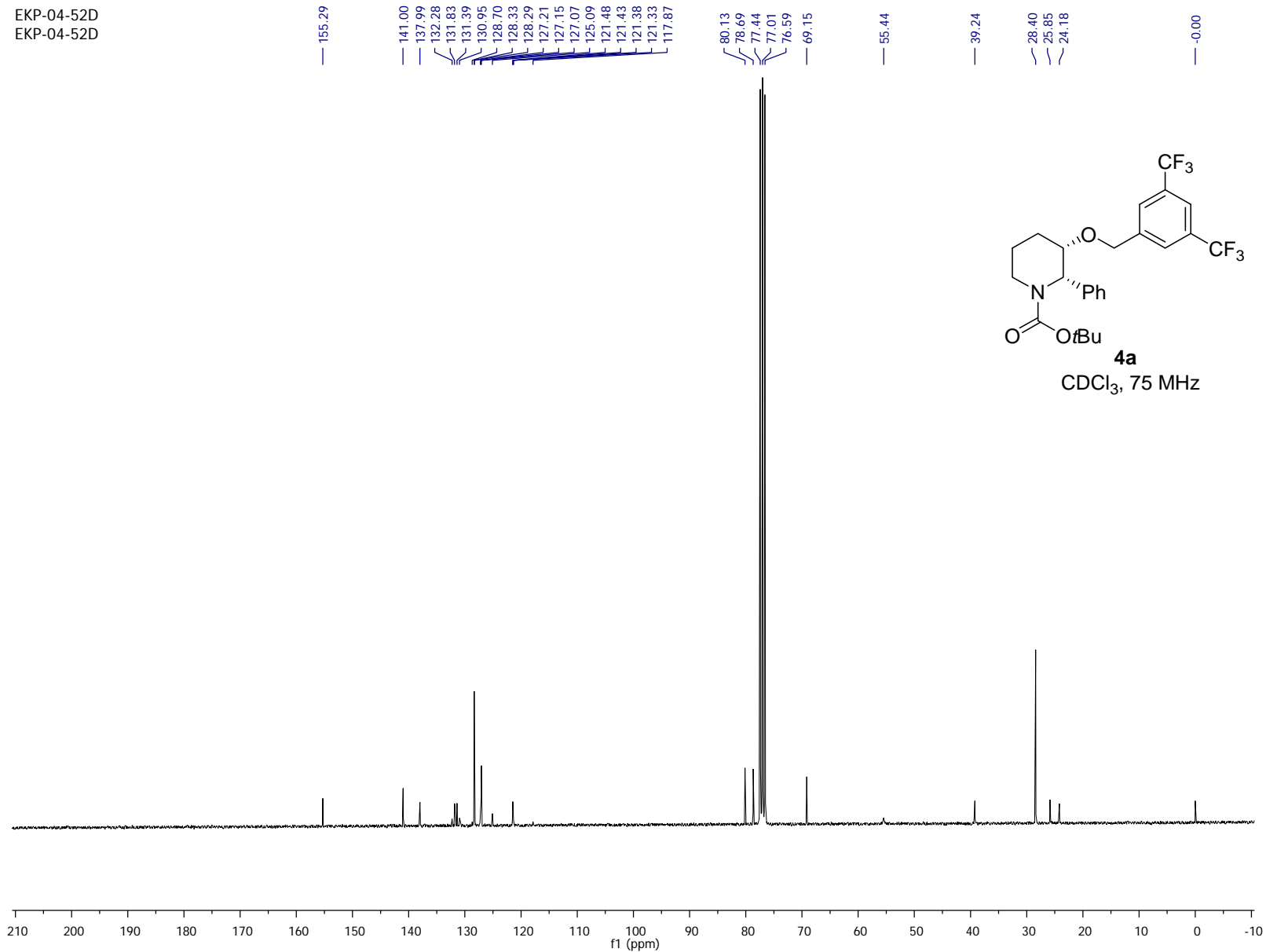
155.39 138.43 128.37 127.19 79.89 77.44 77.01 76.59 70.05 59.25 39.45 28.32 27.70 23.07 -0.00



EKP-3591A/1  
EKP-04-52D(CDCl<sub>3</sub>)



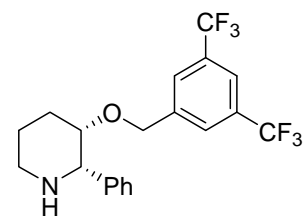
EKP-04-52D  
EKP-04-52D



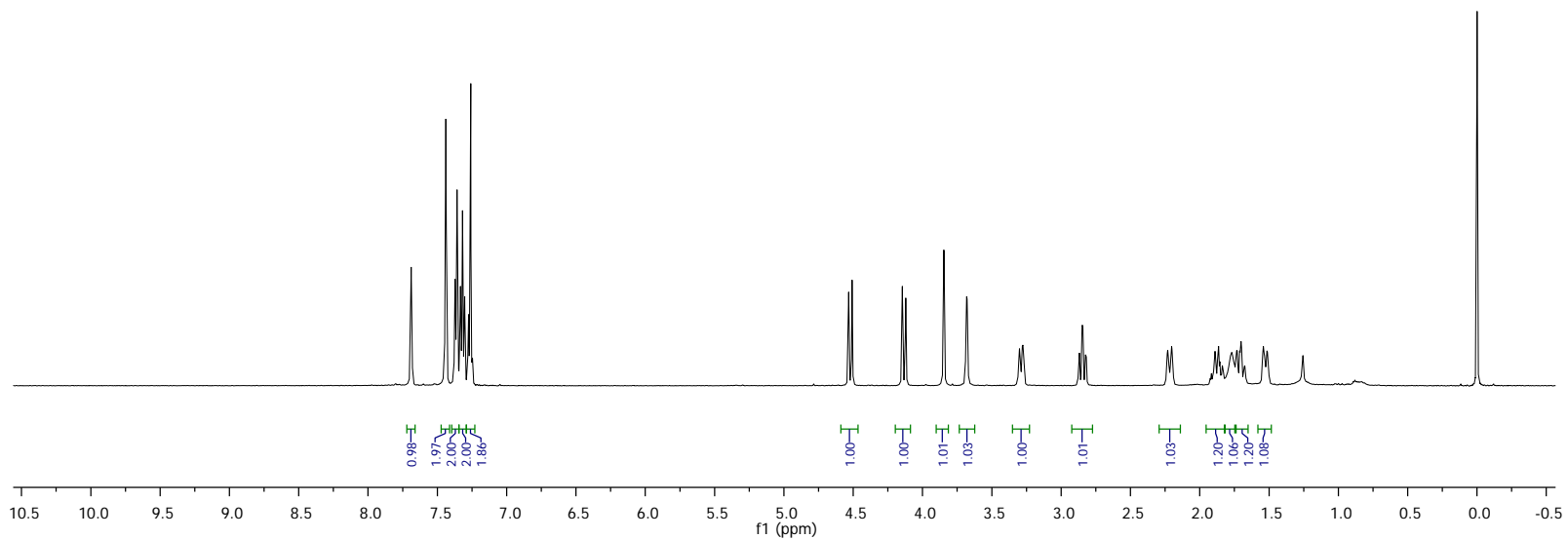
EKP-3594A/1  
EKP-04-53A(CDCI3)

7.69  
7.44  
7.38  
7.37  
7.36  
7.33  
7.32  
7.30  
7.28  
7.28  
7.26  
7.25  
7.25

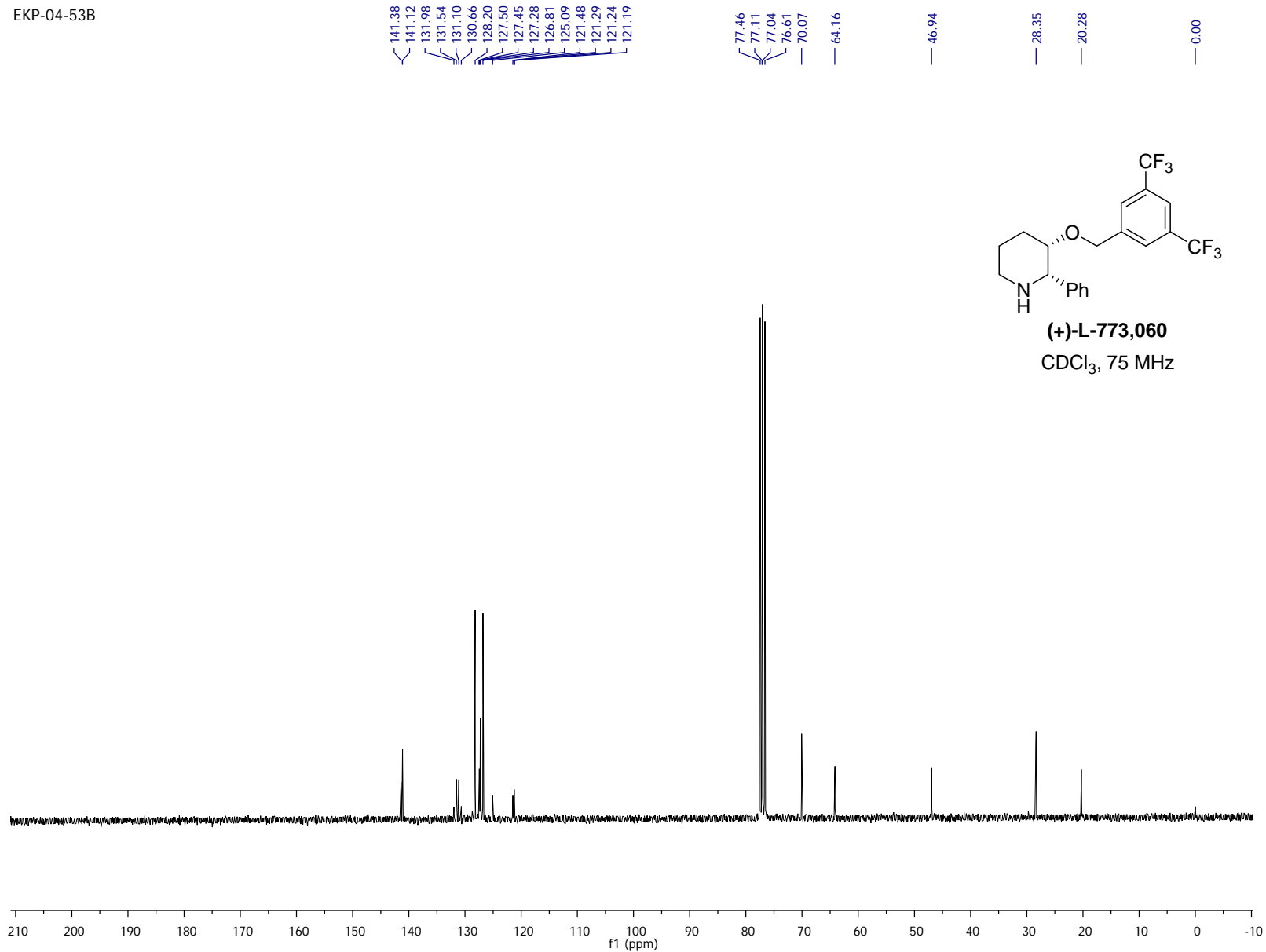
4.53  
4.51  
4.15  
4.12  
3.85  
3.84  
3.68  
3.68  
3.28  
3.27  
3.27  
2.87  
2.85  
2.84  
2.21  
2.20  
2.20  
1.89  
1.86  
1.77  
1.77  
1.74  
1.73  
1.73  
1.71  
1.71  
1.70  
1.70  
1.54  
1.54  
1.54  
0.000



**(+)-L-773,060**  
CDCl<sub>3</sub>, 500 MHz



EKP-04-53B



EKP-3608A/1  
EKP-04-62B(CDCI3)

7.37  
7.36  
7.34  
7.30  
7.28  
7.26  
7.22  
7.20

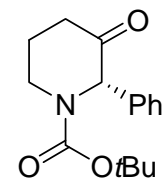
5.66

4.08

3.35  
3.34  
3.33  
3.32  
3.31  
3.30  
3.30

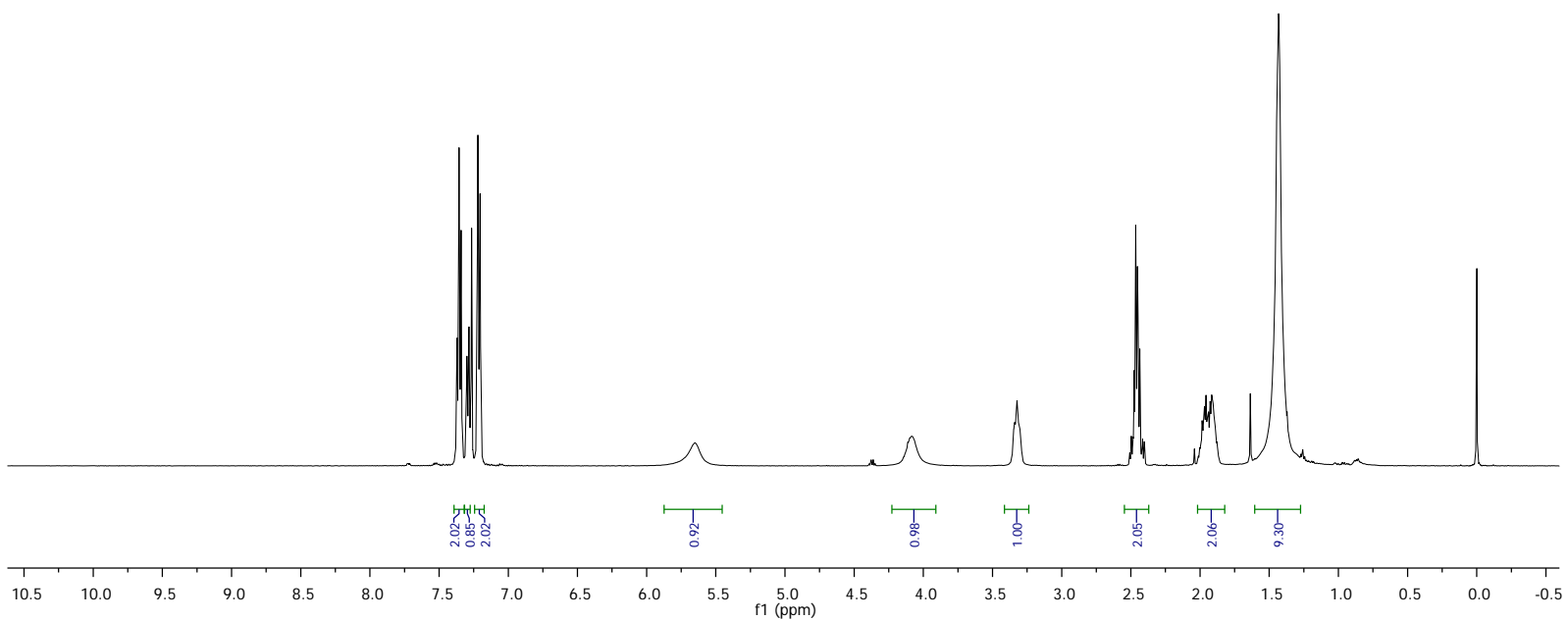
2.46  
2.45  
2.45  
2.44

1.97  
1.97  
1.96  
1.95  
1.94  
1.93  
1.92  
1.91  
1.90  
1.64  
1.49  
1.45  
1.43  
1.39  
1.37  
1.00

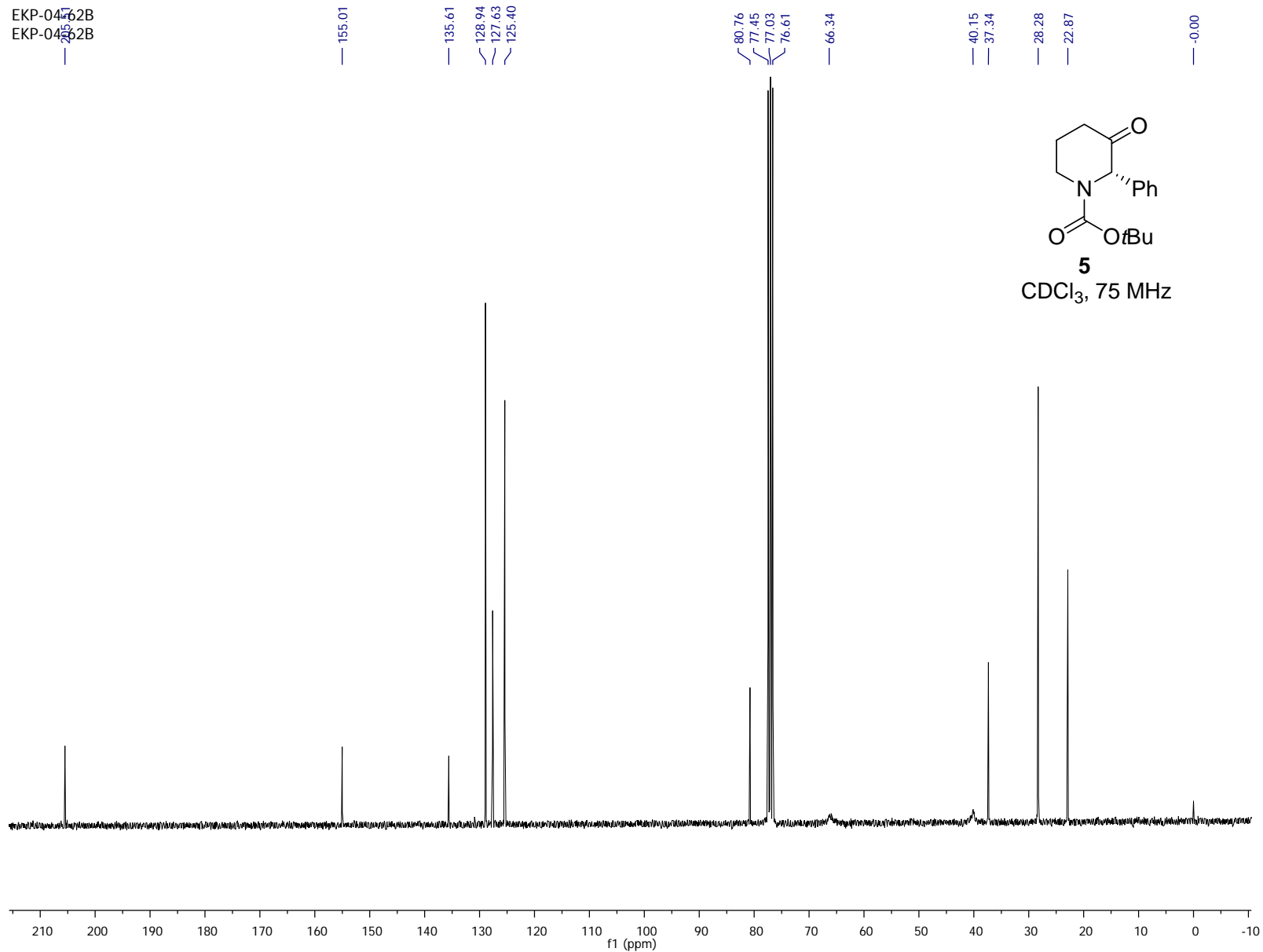


**5**

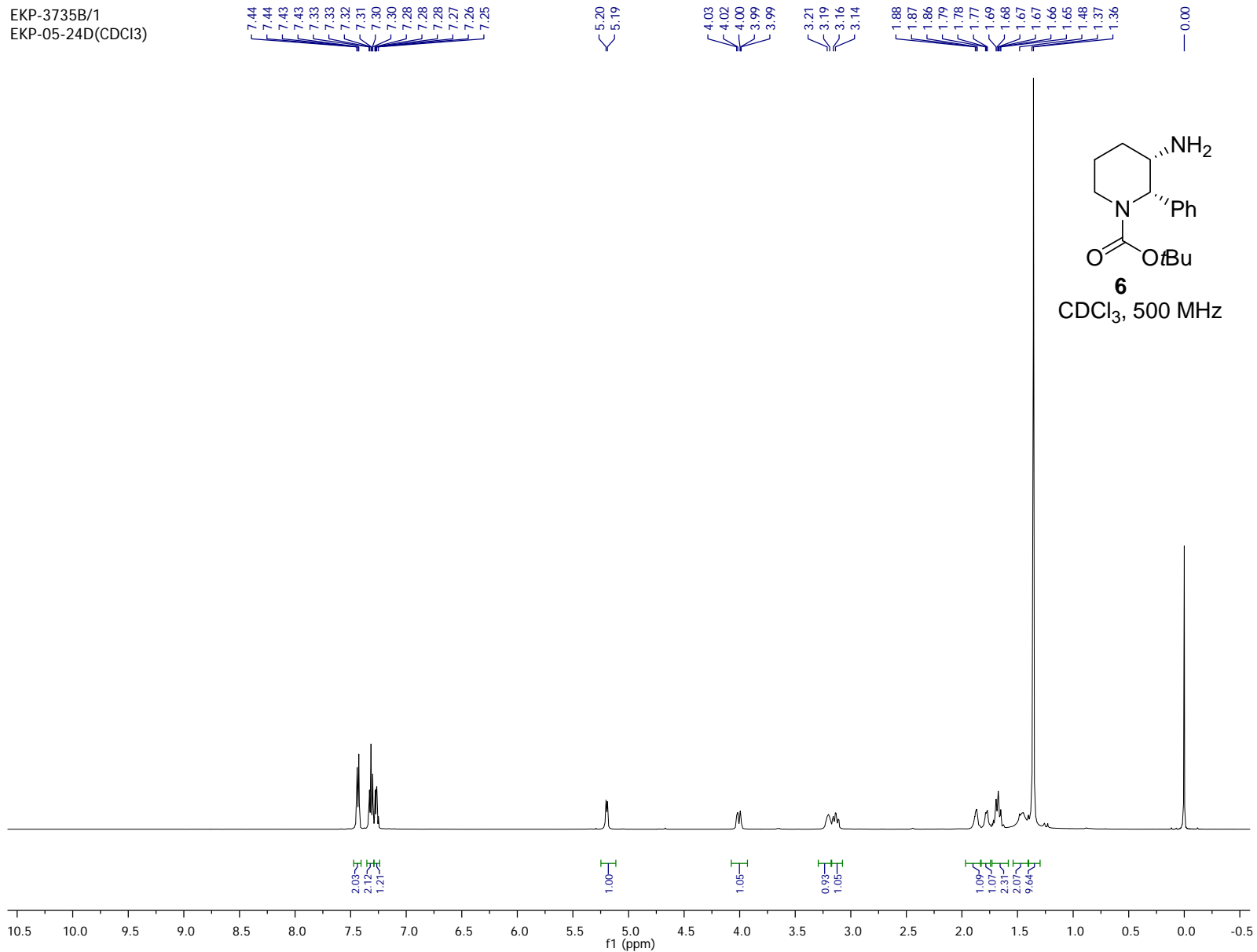
CDCl<sub>3</sub>, 500 MHz

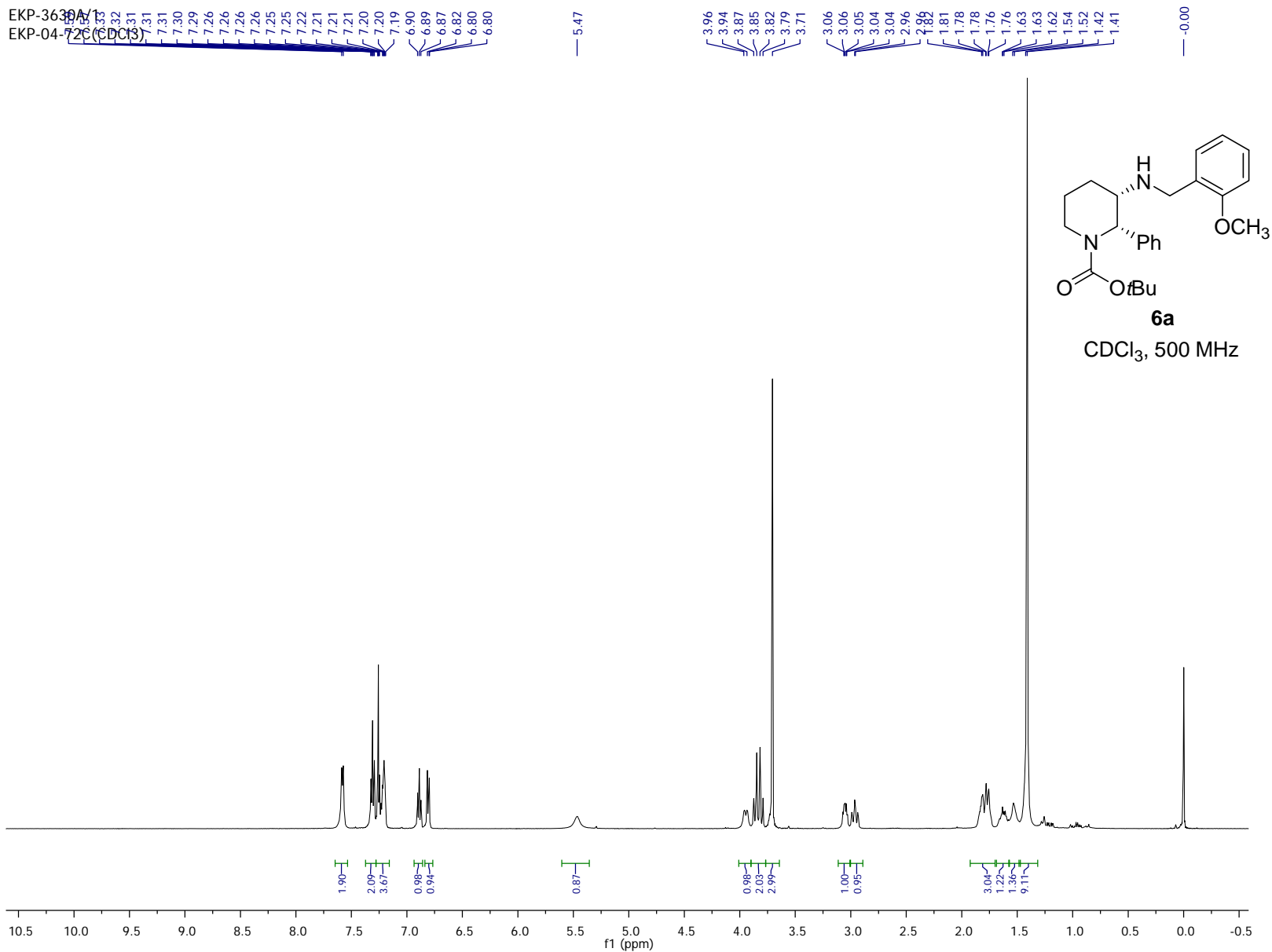






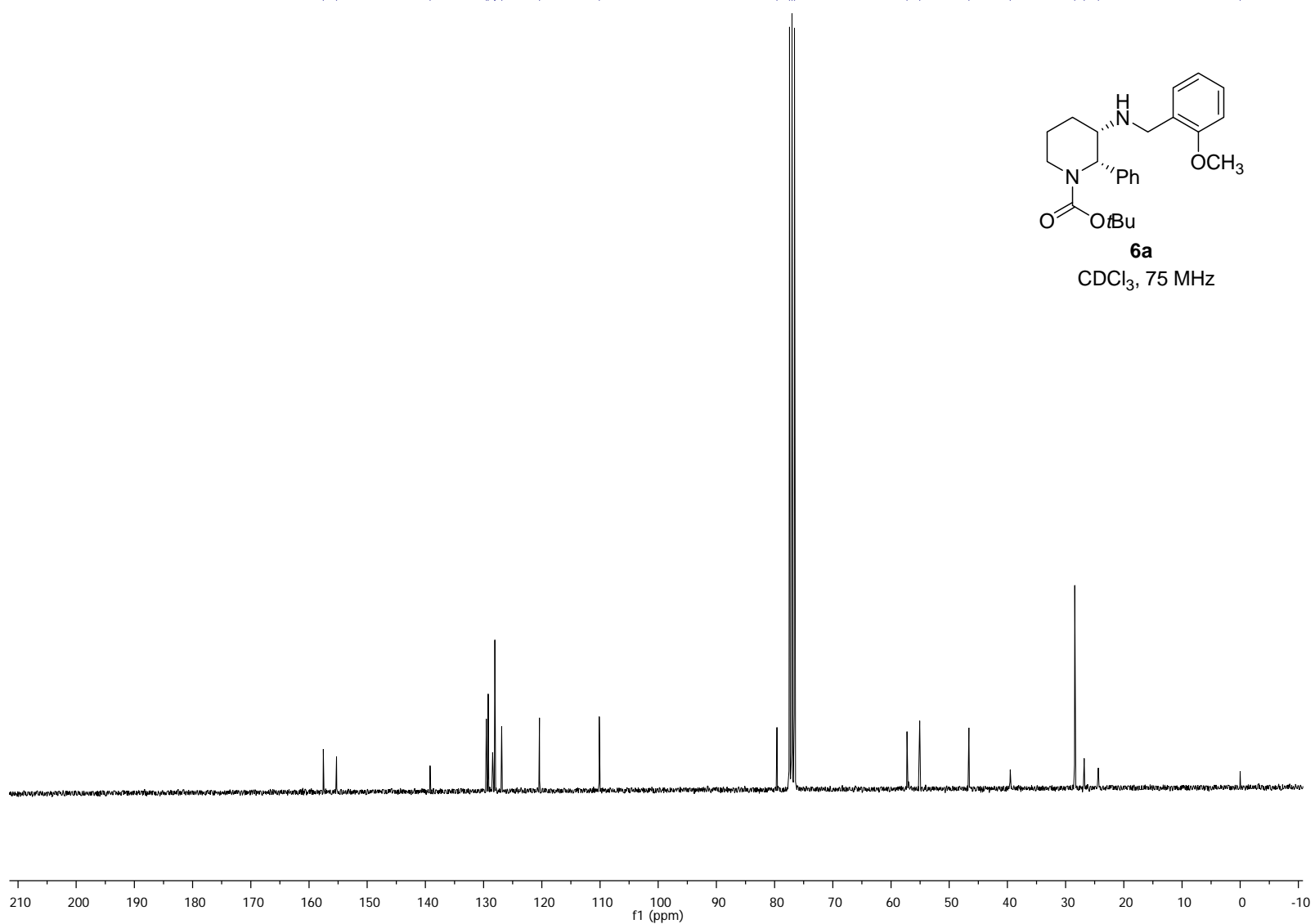
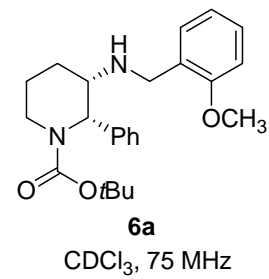
EKP-3735B/1  
EKP-05-24D(CDCl<sub>3</sub>)



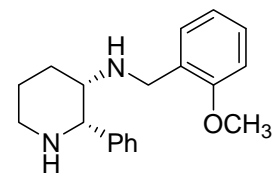
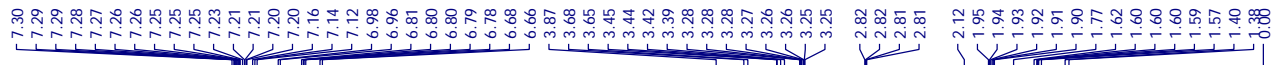


EKP-04-72C  
EKP-04-72C

157.54  
155.27  
139.19  
129.53  
129.22  
128.09  
128.06  
126.89  
110.13  
79.60  
77.44  
77.01  
76.59  
57.26  
55.06  
46.61  
39.51  
28.43  
26.80  
24.36  
-0.00

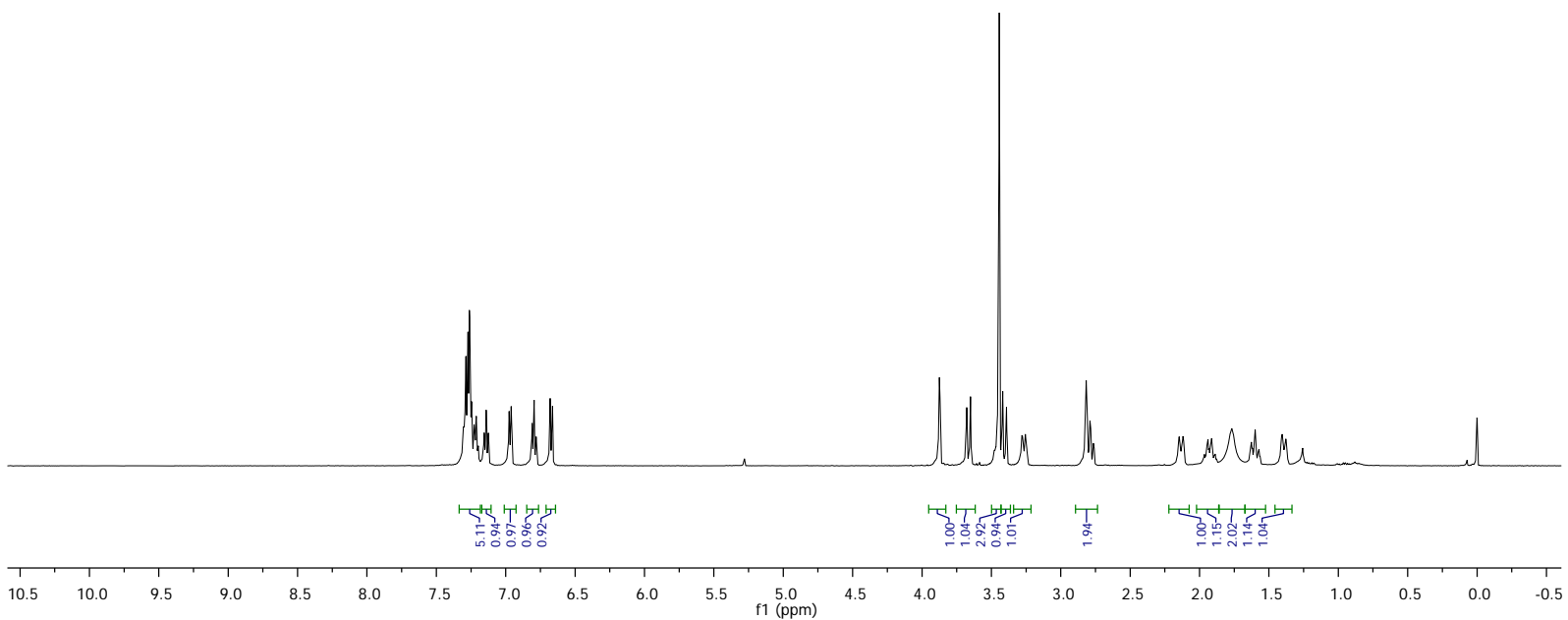


EKP-3634A/1  
EKP-04-74A(CDCl<sub>3</sub>)

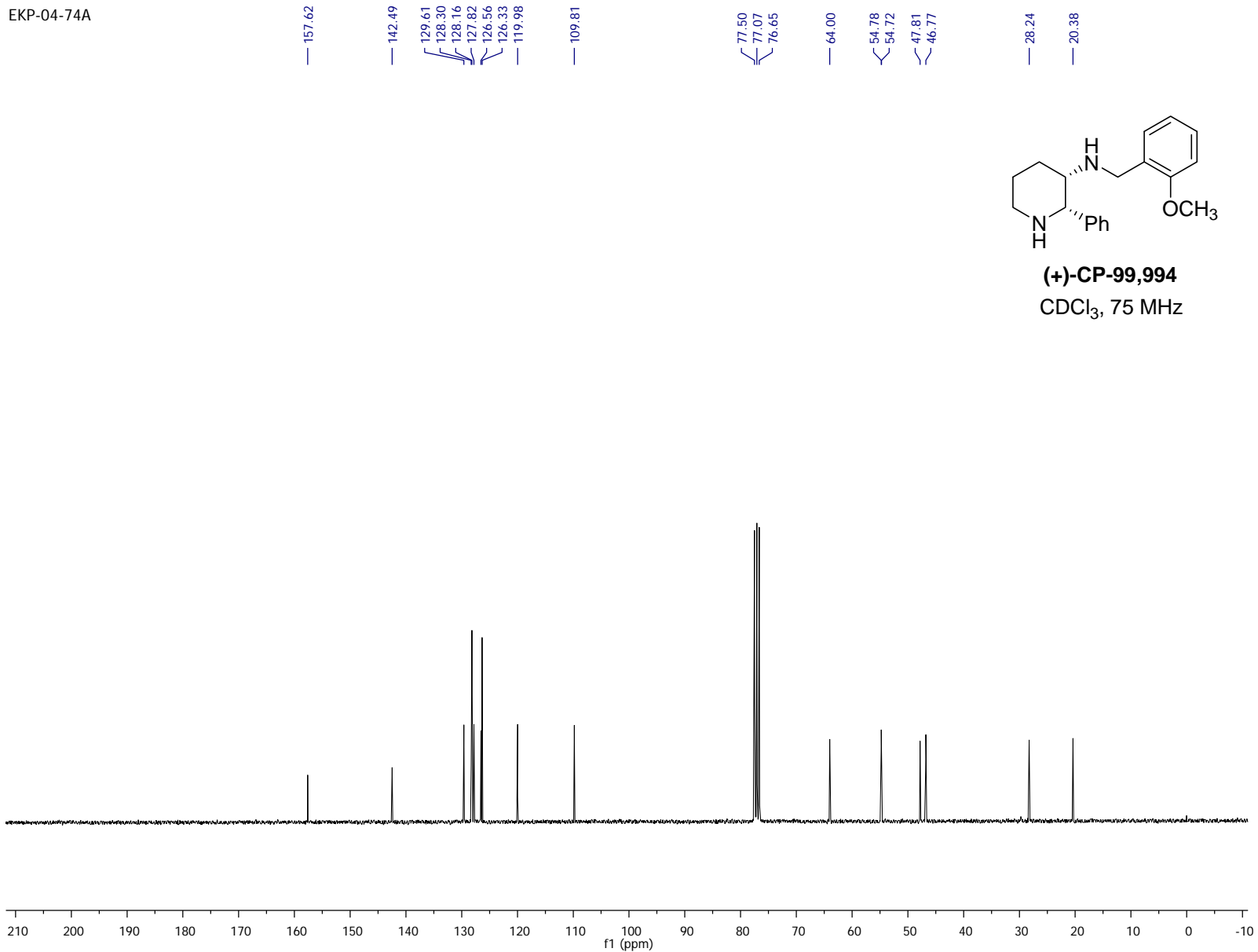


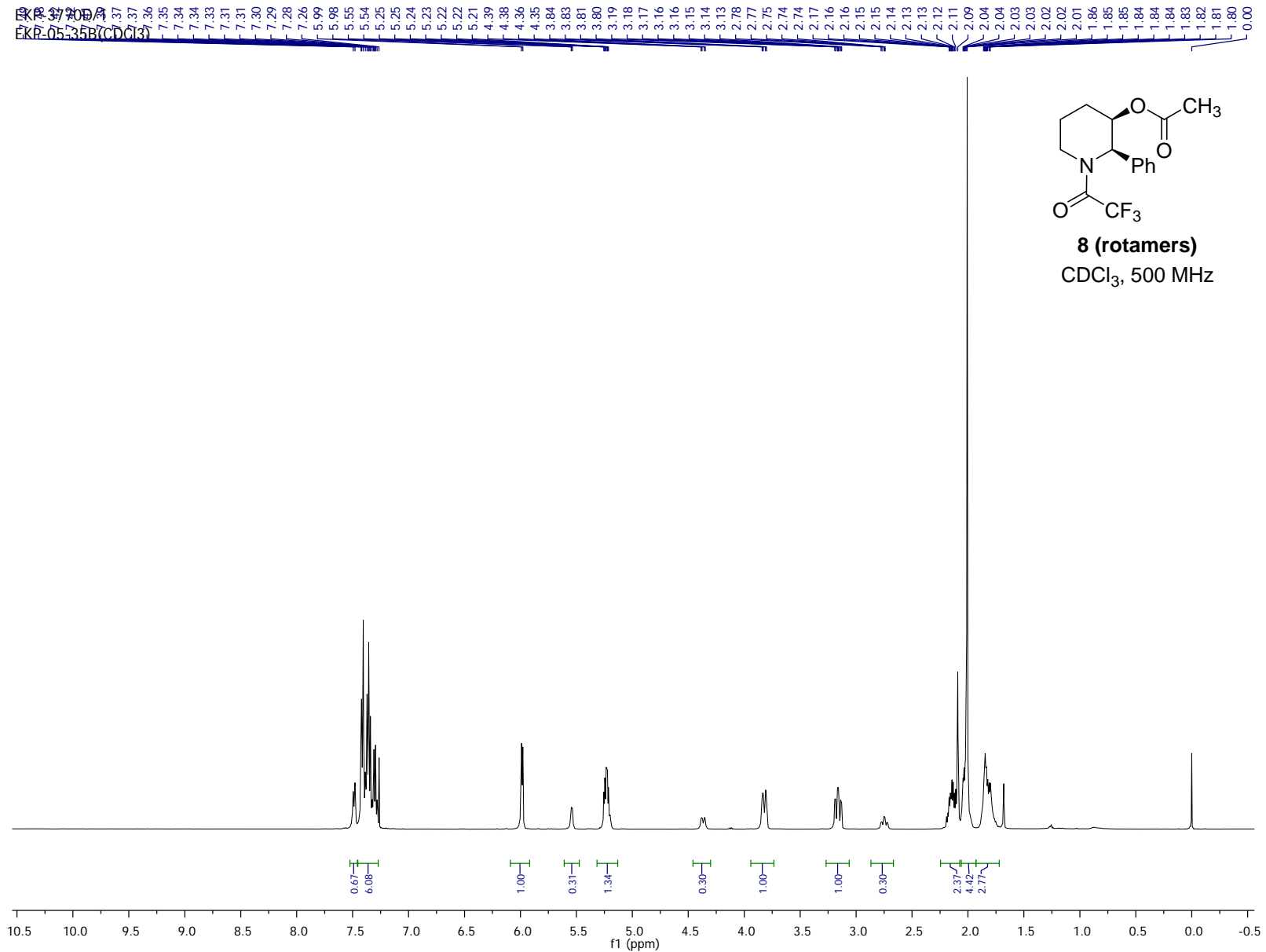
**(+)-CP-99,994**

CDCl<sub>3</sub>, 500 MHz

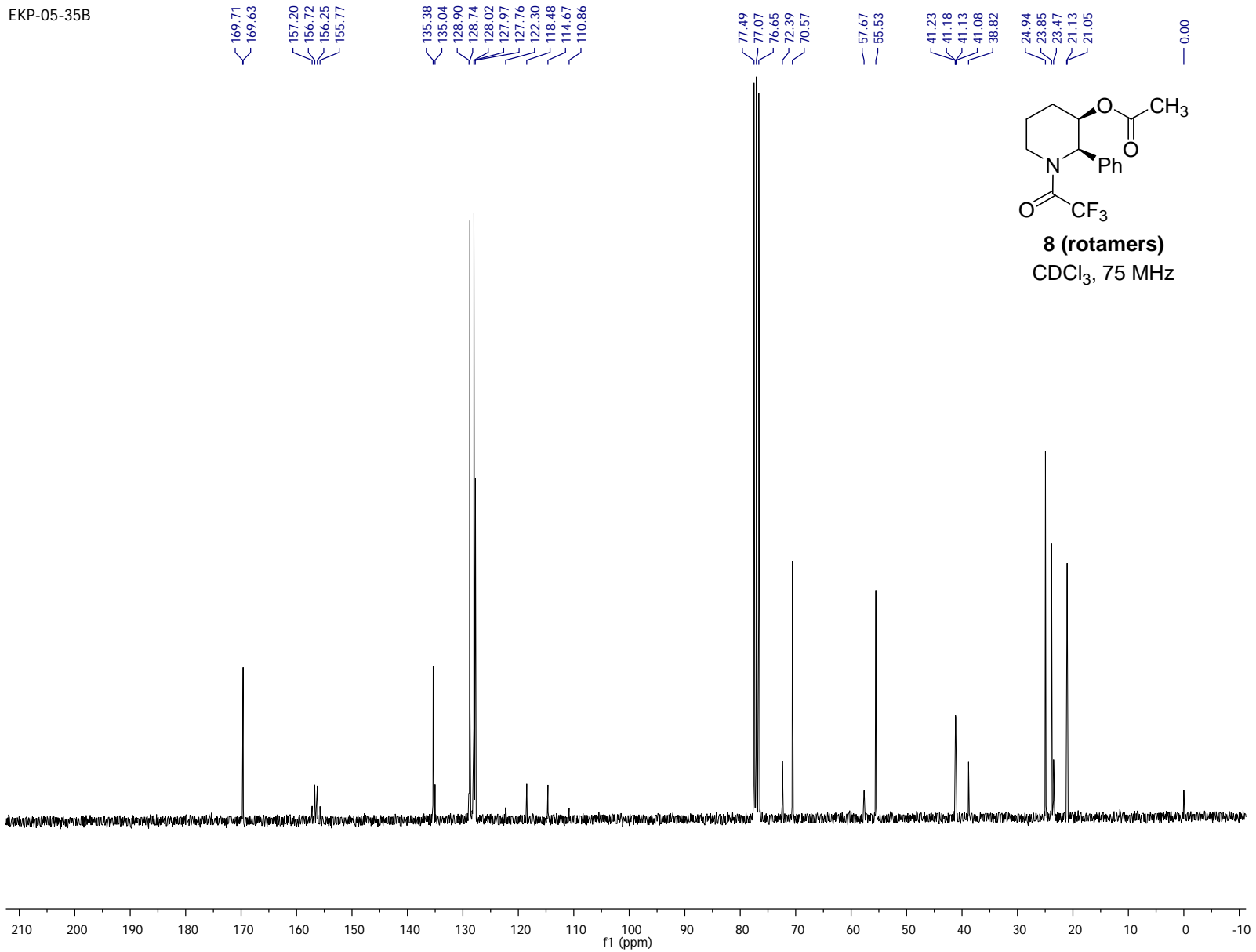


EKP-04-74A



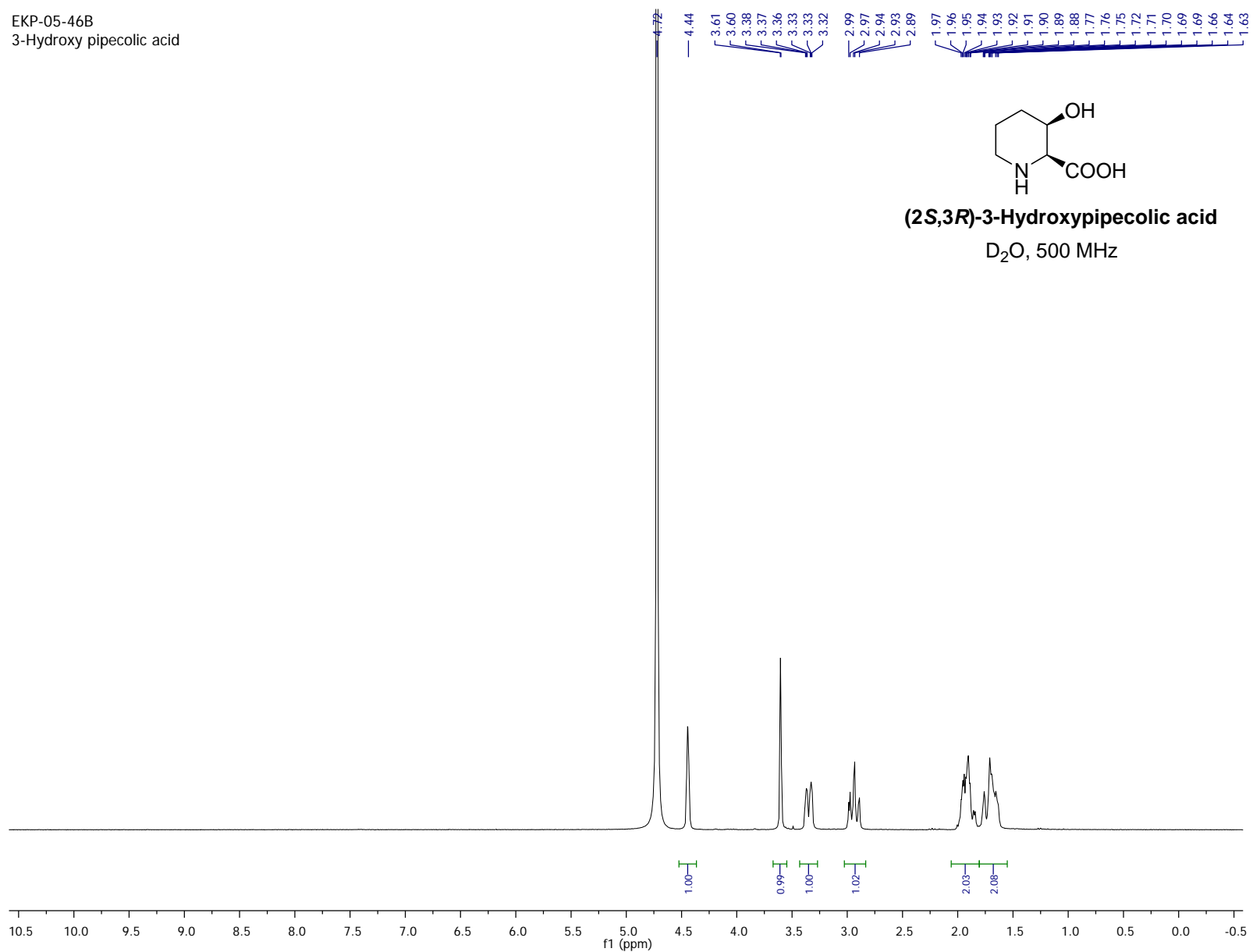


EKP-05-35B





EKP-05-46B  
3-Hydroxy pipercolic acid



EKP-05-46B  
3-Hydroxy pipercolic acid

172.28

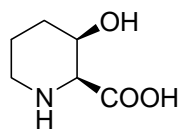
64.10

62.24

43.57

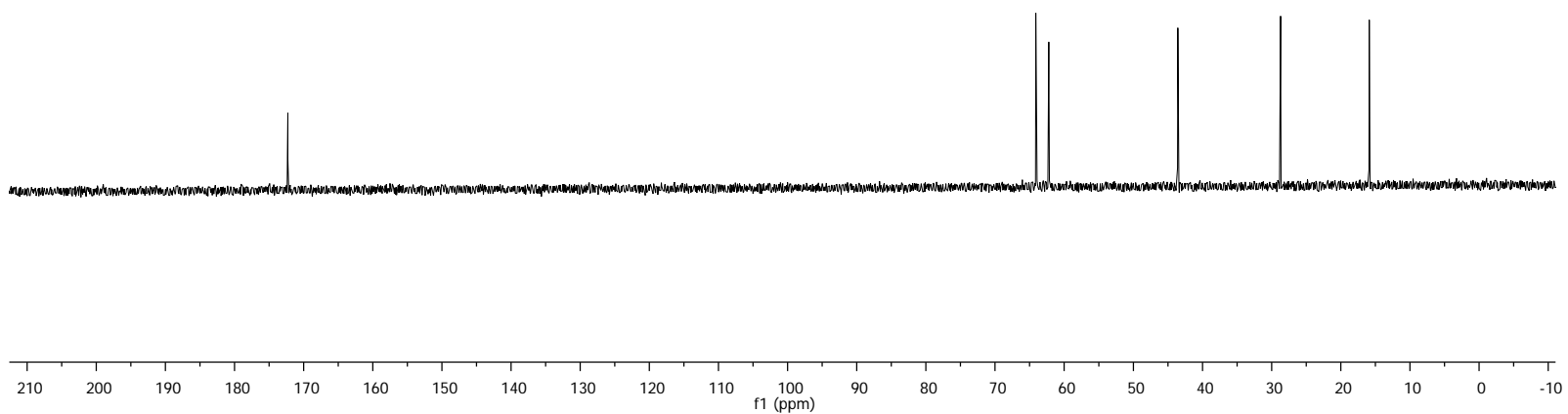
28.70

15.88



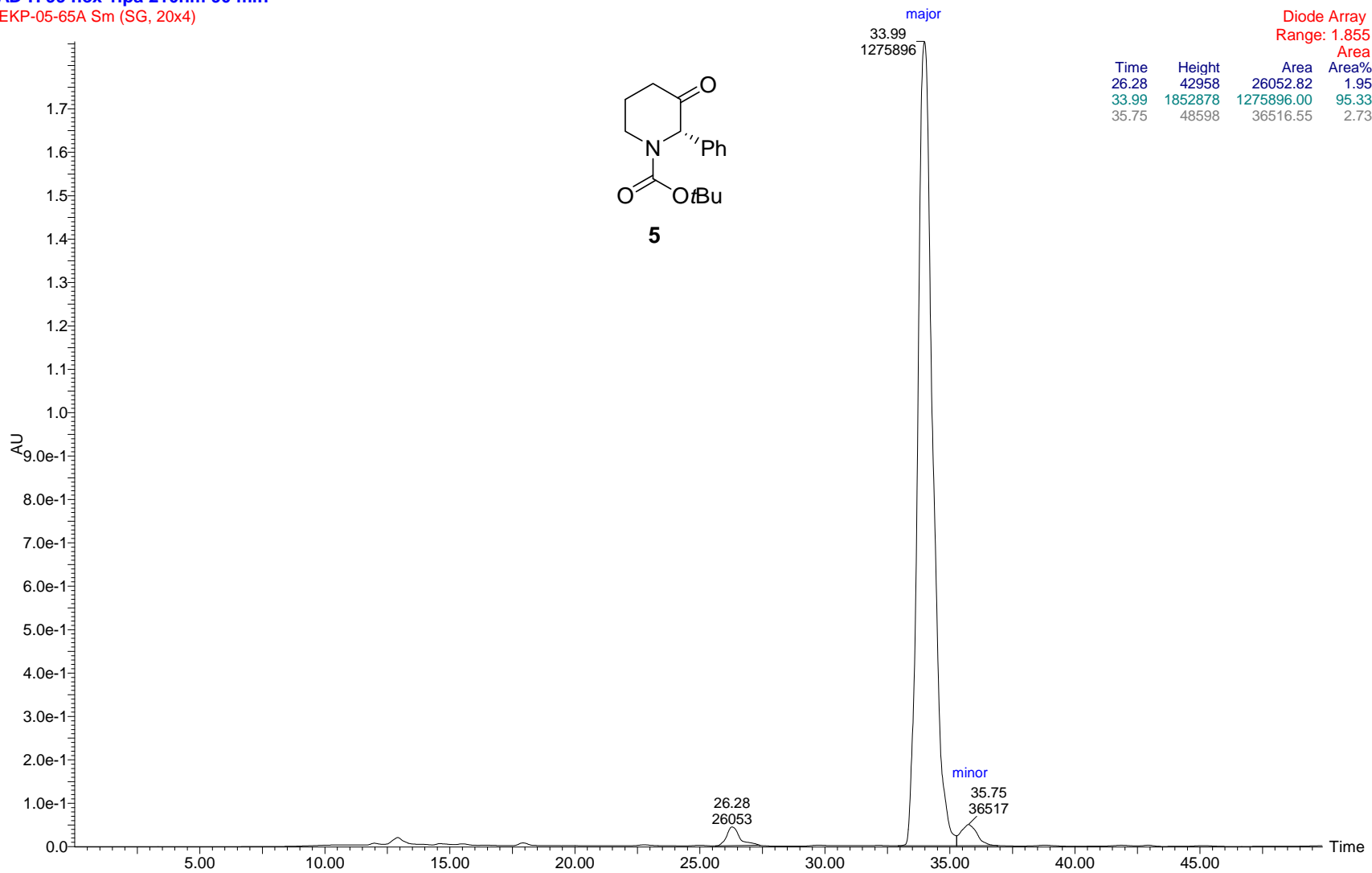
**(2*S*,3*R*)-3-Hydroxypipercolic acid**

D<sub>2</sub>O, 75 MHz

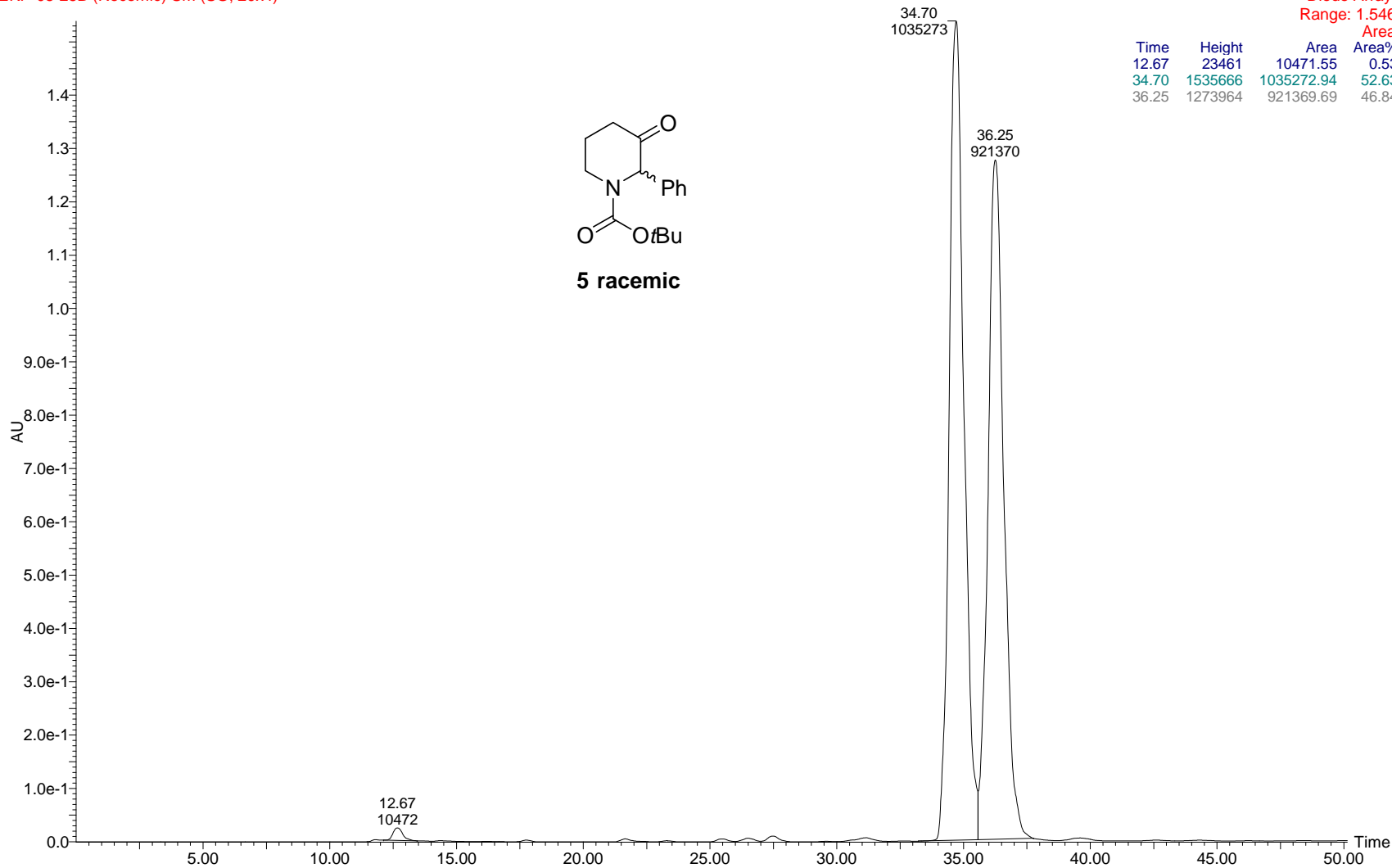


AD-H 99 hex 1ipa 210nm 90 min

EKP-05-65A Sm (SG, 20x4)



AD-H 99 hex 1ipa 210nm 60 min  
EKP-05-25B (Recemic) Sm (SG, 20x4)



OD-H 90 hex 10ipa 210nm 60 min

EKP-05-72A(3rd run) Sm (SG, 20x4)

