Supplementary Materials

Improved Access to Chiral Tetranaphthoazepinium-Based Organocatalysts

Using Aqueous Ammonia as Nitrogen Source

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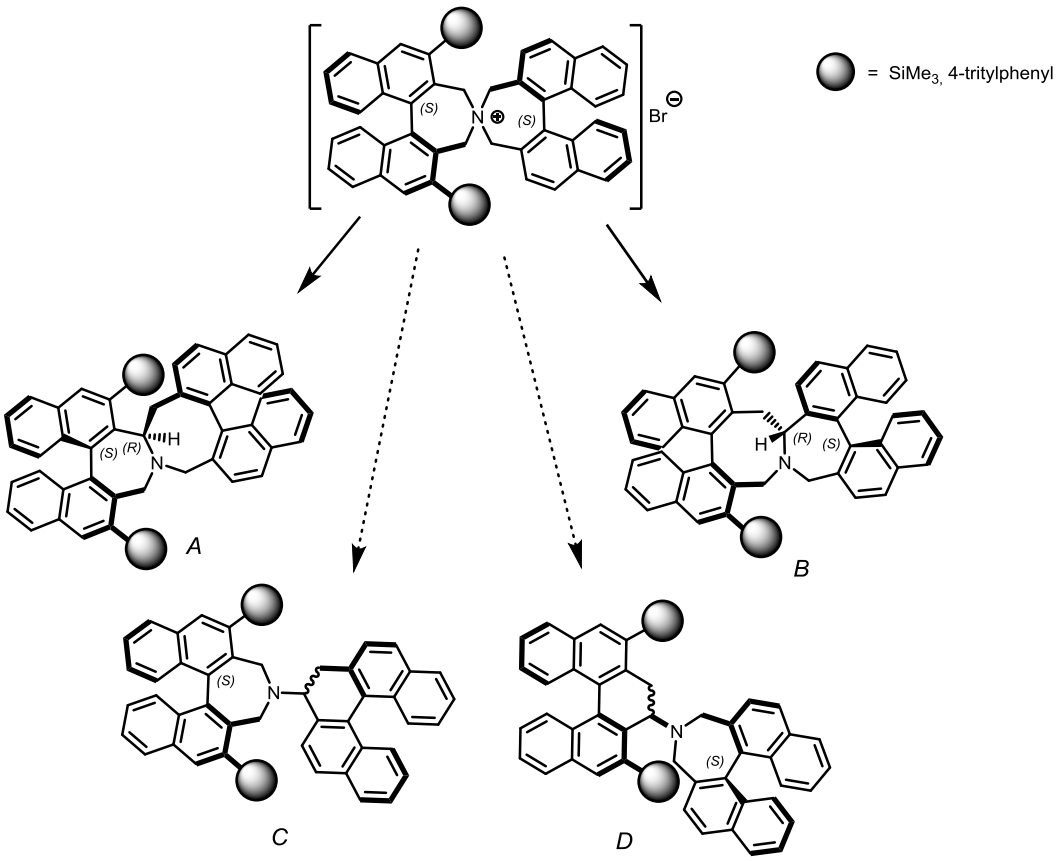
Content

Proposed sequence products of a Stevens rearrangement of **1e** and **5**, respectively

During attempted spirocyclisation of (*S*)-**9e** with (*S*)-2,2'-bisbromomethyl-1,1'-binaphthyl in MeCN the target compound (*S*)(*S*)-**1e** was isolated in small amounts (<10%, ~80% purity). Instead considerable amounts of dinaphthooxepine along with a sequence product **1e-S** from **1e** resulting from Stevens rearrangement was detected. Feasible structures *A*-*D* are depicted in Scheme S1. Based on the ^{1}H NMR spectrum showing seven aliphatic protons in different environment (2x AB, 1x ABX system) structure *C* and *D* can be excluded. From steric reasons an equatorial attack of the CH_2 group will be favored resulting in an axial methine proton in *A* or *B*. Due to the complexity of NMR spectra in the aromatic range only partial assignment of signals was done and no decision between structure *A* and *B* for **1e-S** is possible at the time.

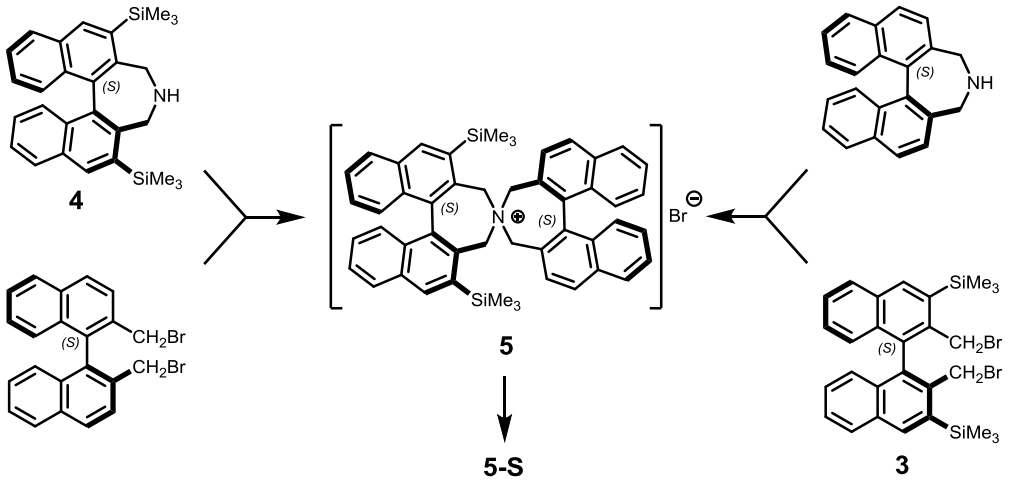
Scheme S1. Stevens Rearrangement of Postulated Dinaphthoazepinium Bromides **1e** and **5** with Bulky Substituents.



Also in case of (*S*)-**5** reaction of **4** with (*S*)-2,2'-bisbromomethyl-1,1'-binaphthyl afforded a rearranged product **5-S** with similar ^{1}H NMR spectrum and correct HRMS. It is worth to note that the same product **5-S** was also obtained from unsubstituted dinaphthoazepine and dibromide **3**, indicative for running

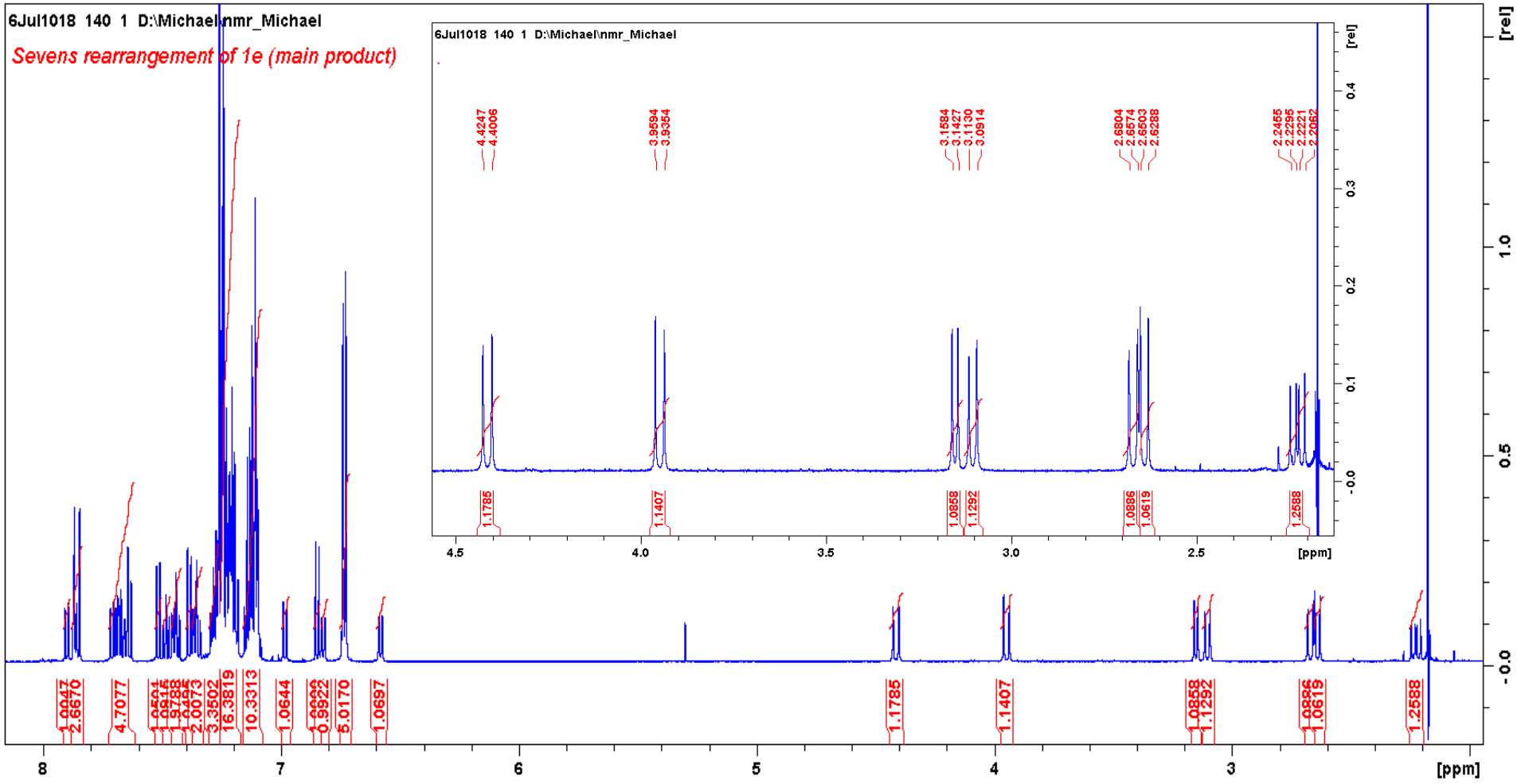
through a common intermediate **5** (Scheme S2). Attempted transformation into corresponding methylammonium salts failed.

Scheme S2. Access of **5-S** from different precursors.



1e-S: HRMS: Calcd for $C_{94}H_{68}N$ $[M + H]^+$: 1210.5347, found: 1210.5337.

5-S: HRMS: Calcd for $C_{50}H_{47}NSi_2$ $[M + H]^+$: 718.3325, found: 716.3314.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Sevens rearrangement of 1e (main product)
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2.6503
2.6288
2.2455
2.2295
2.2221
2.2062
1.1785
1.1407
1.0858
1.1292
1.0886
1.0619
1.2588
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2.6670
4.7077
1.0501
1.0916
1.9788
1.0442
2.0073
3.3502
16.3819
10.3313
1.0644
1.0000
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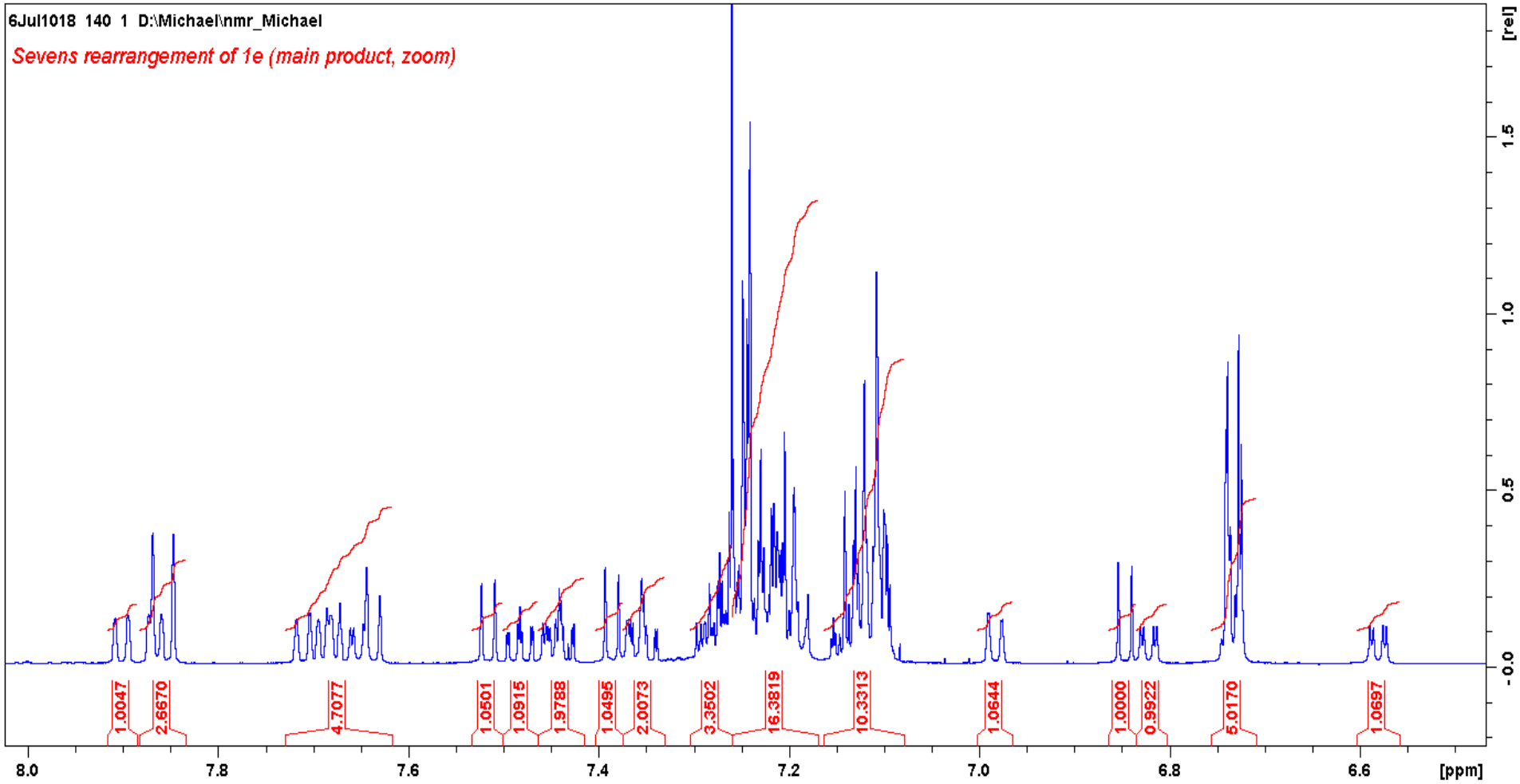
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2.0073
3.3502
16.3819
10.3313
1.0644
1.0000
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6.6
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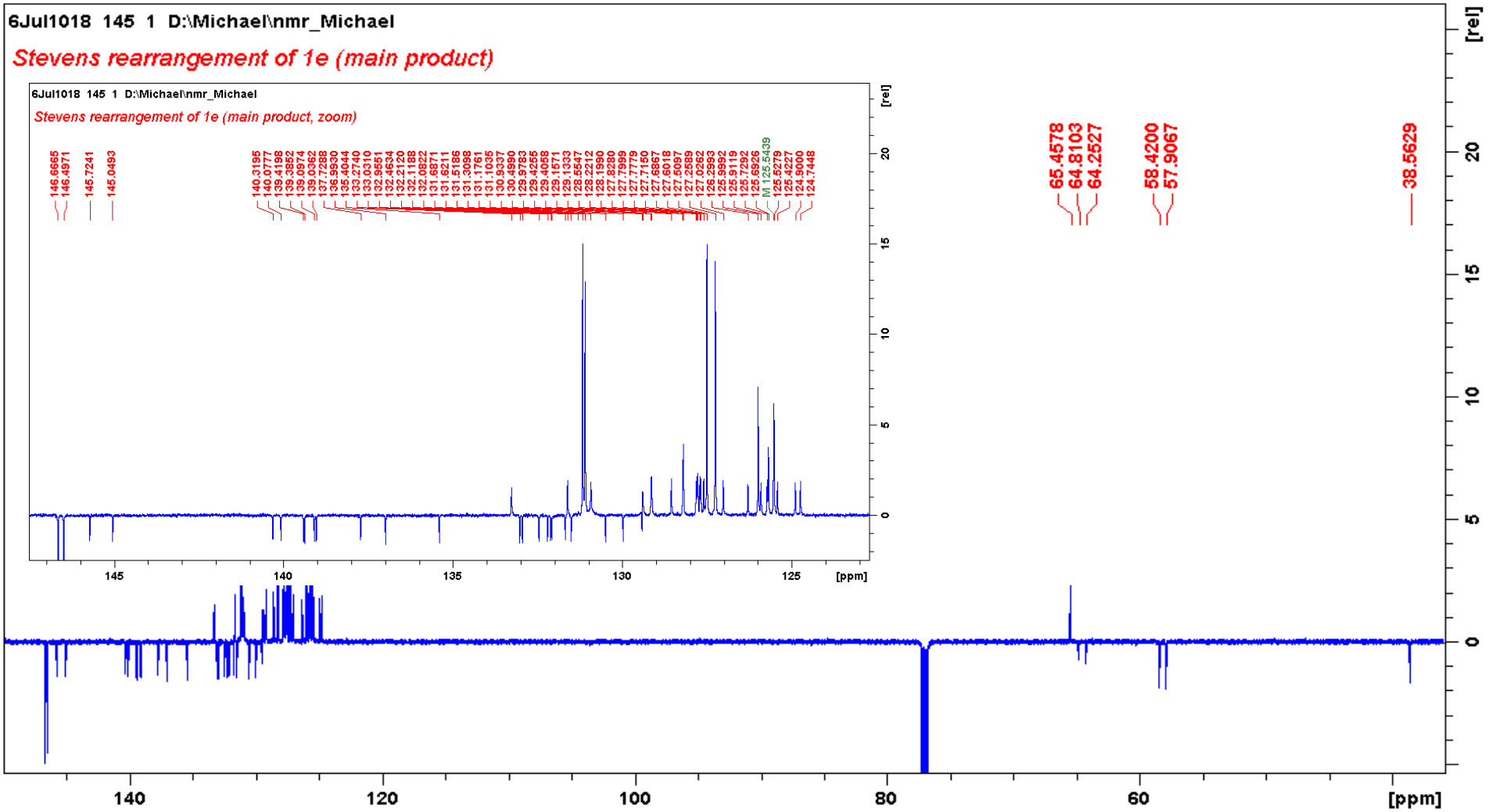
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Stevens rearrangement of 1e (main product, zoom)
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139.0362
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136.9930
135.4044
133.2740
133.0310
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132.1188
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127.8280
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127.6867
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127.5097
127.2589
127.0262
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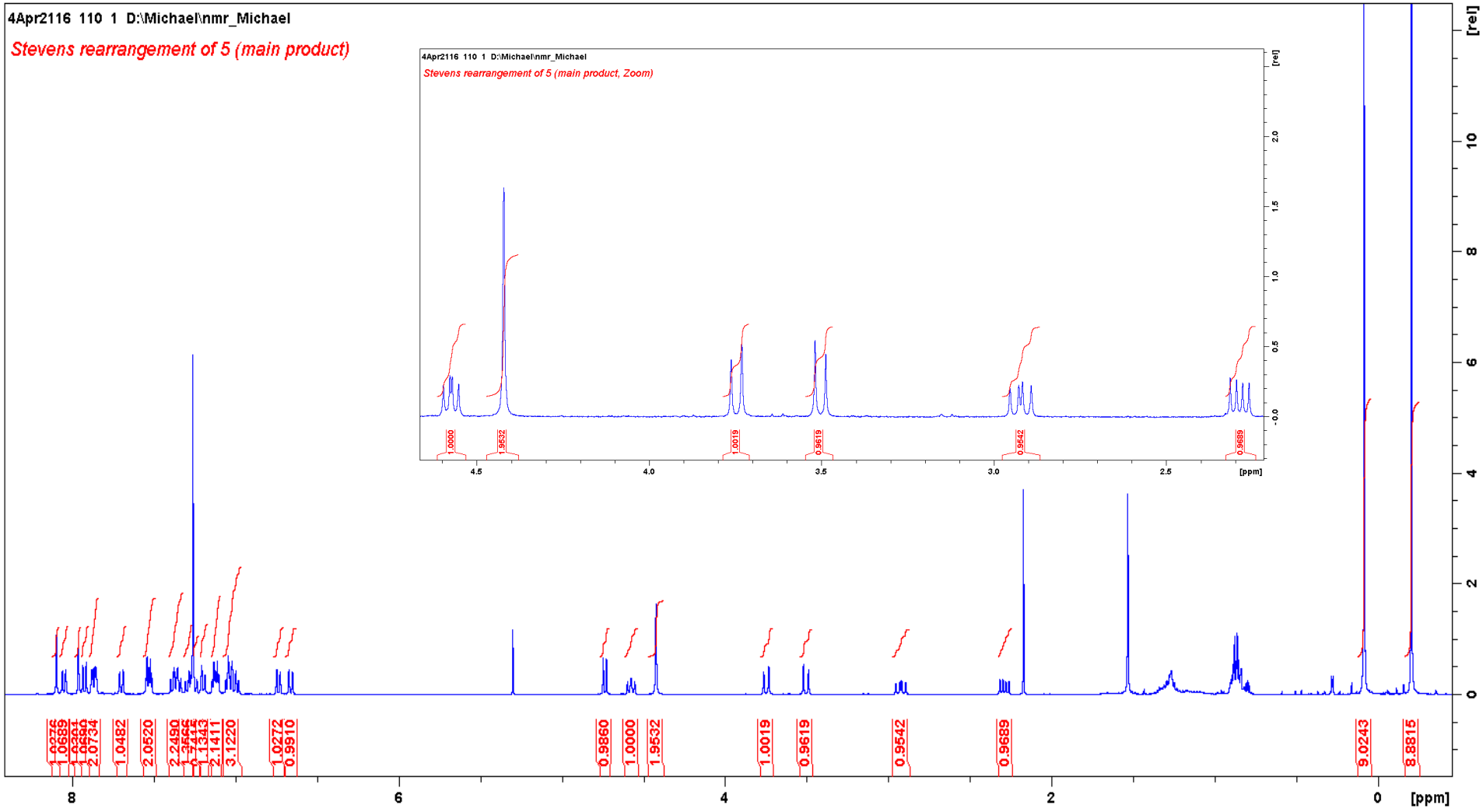
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Stevens rearrangement of 5 (main product, Zoom)
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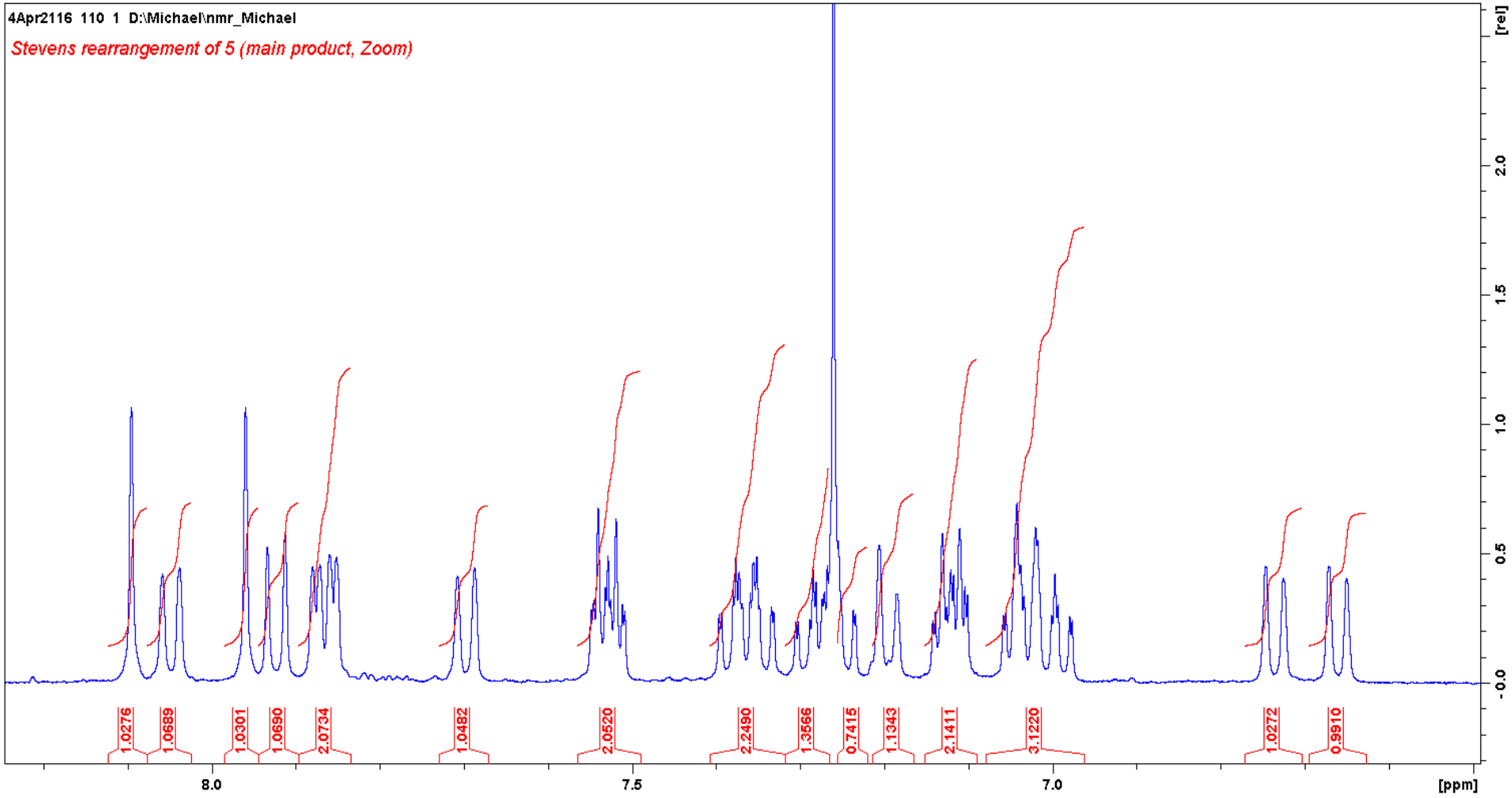
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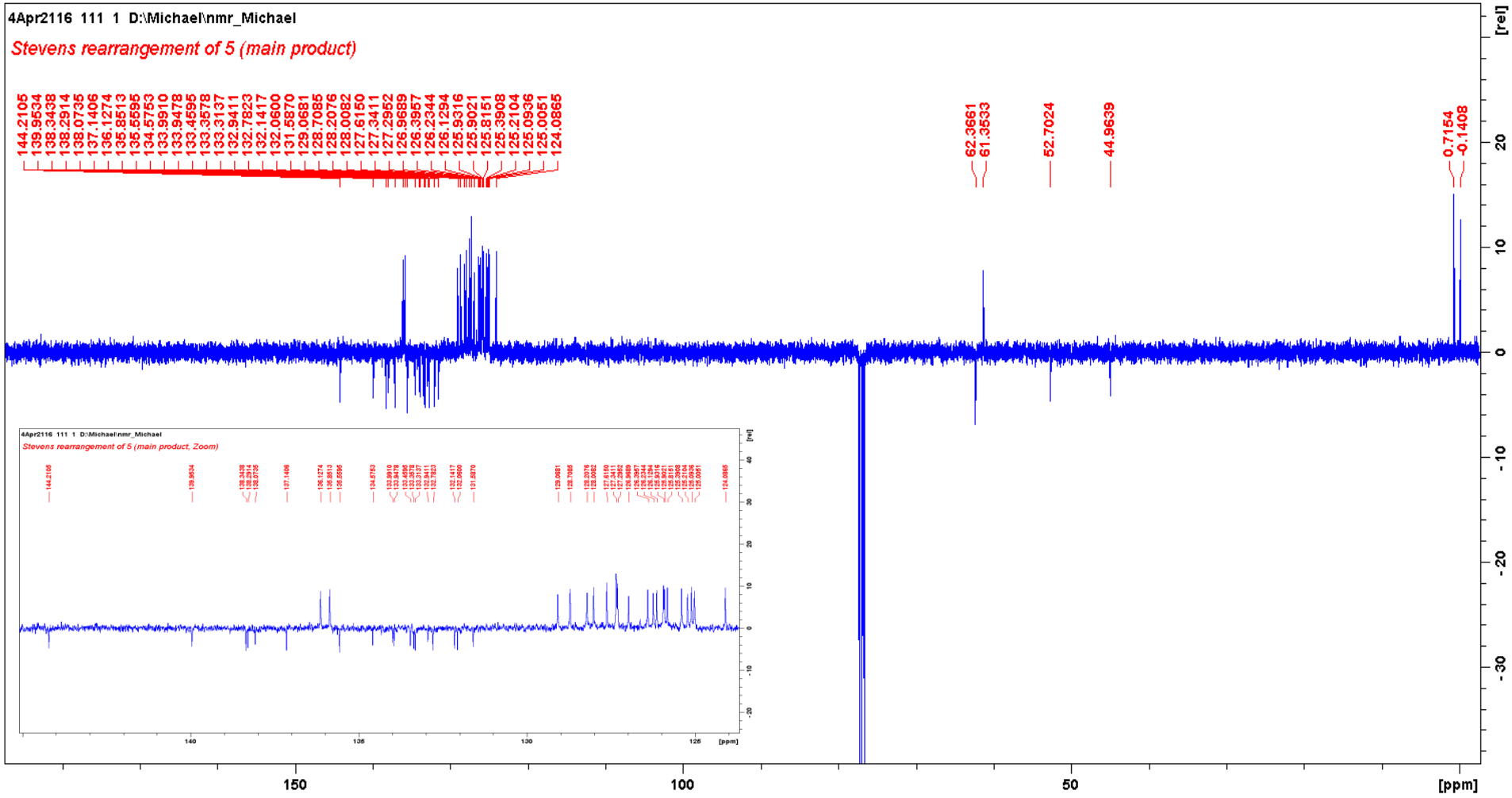
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-20
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100
50
[ppm]
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Stevens rearrangement of 5 (main product, Zoom)
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130
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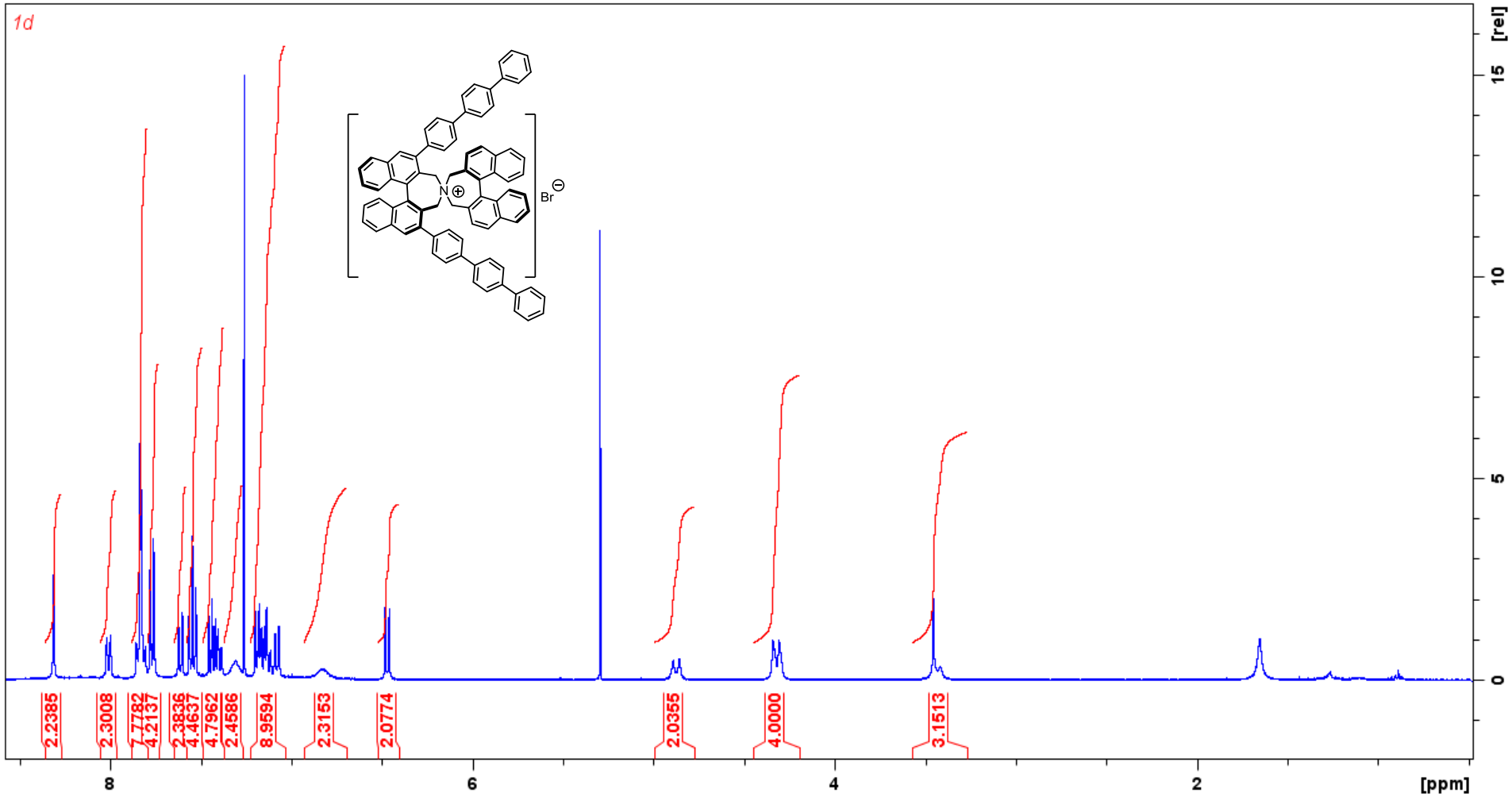
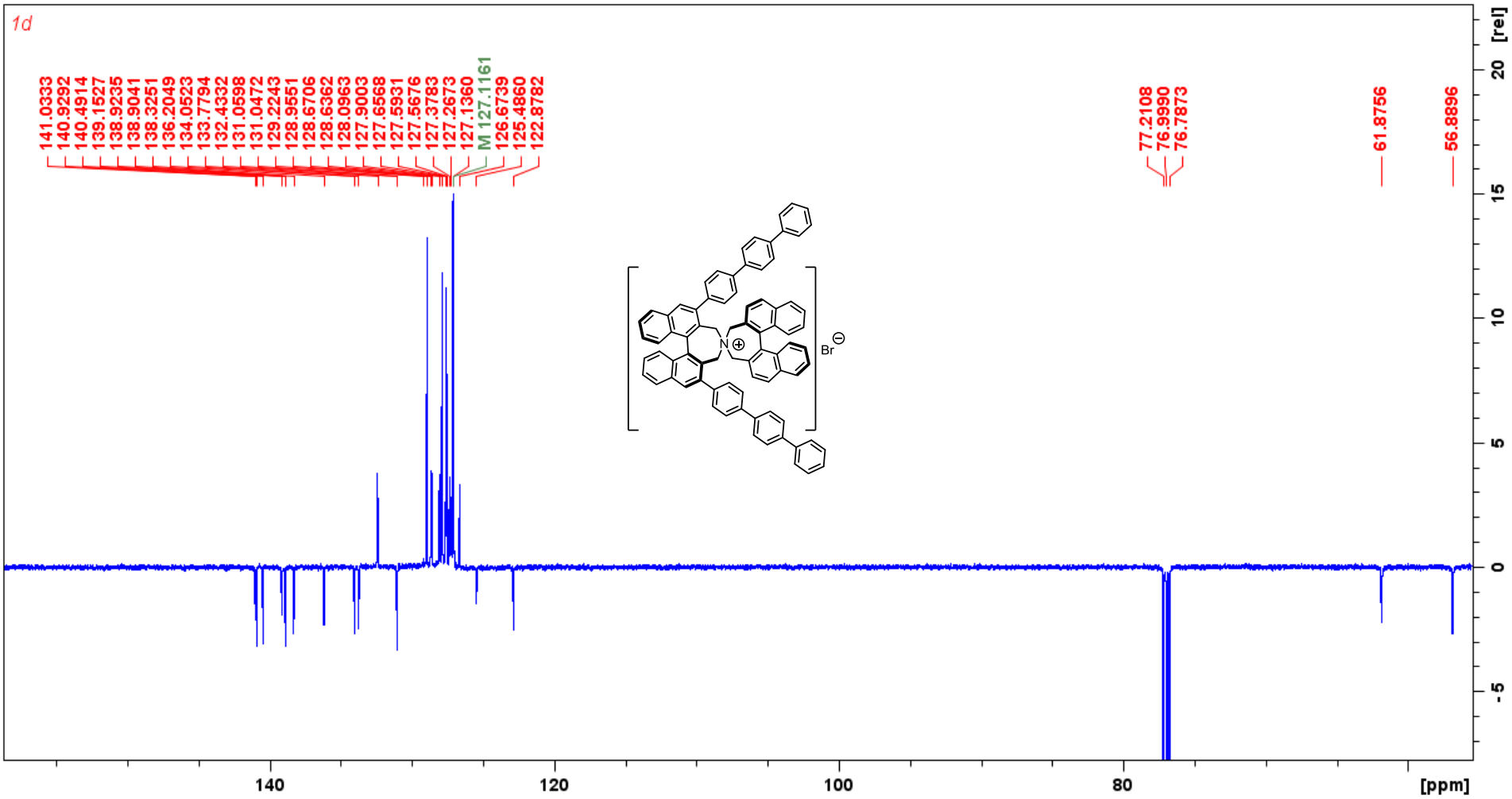
[ppm]

^{1}H- and ^{13}C NMR spectra (If not otherwise noted spectra are recorded at room temperature in $CDCl_3$)

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127.5931
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127.2673
127.1360
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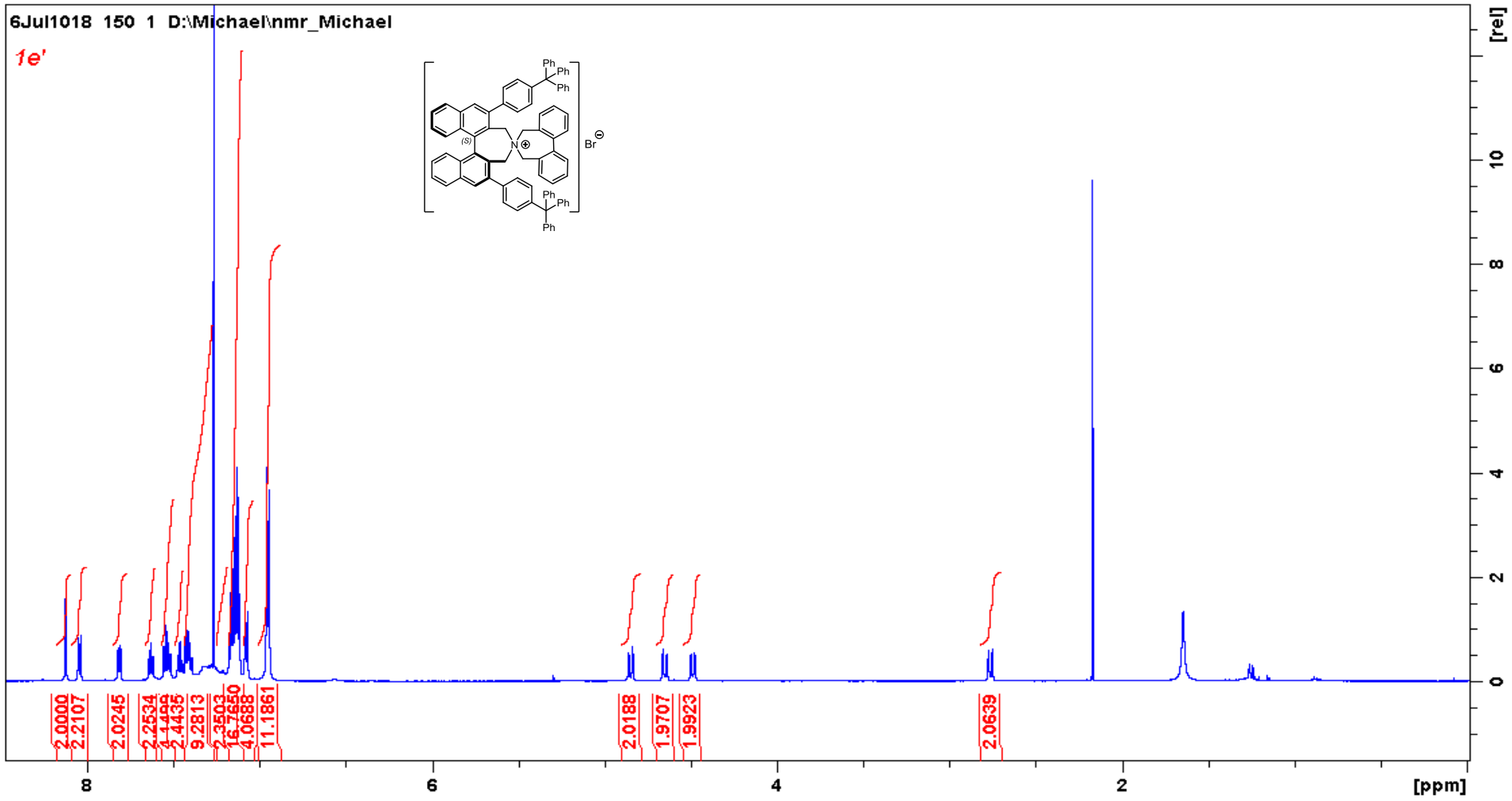
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Ph
Ph
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Br
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Ph
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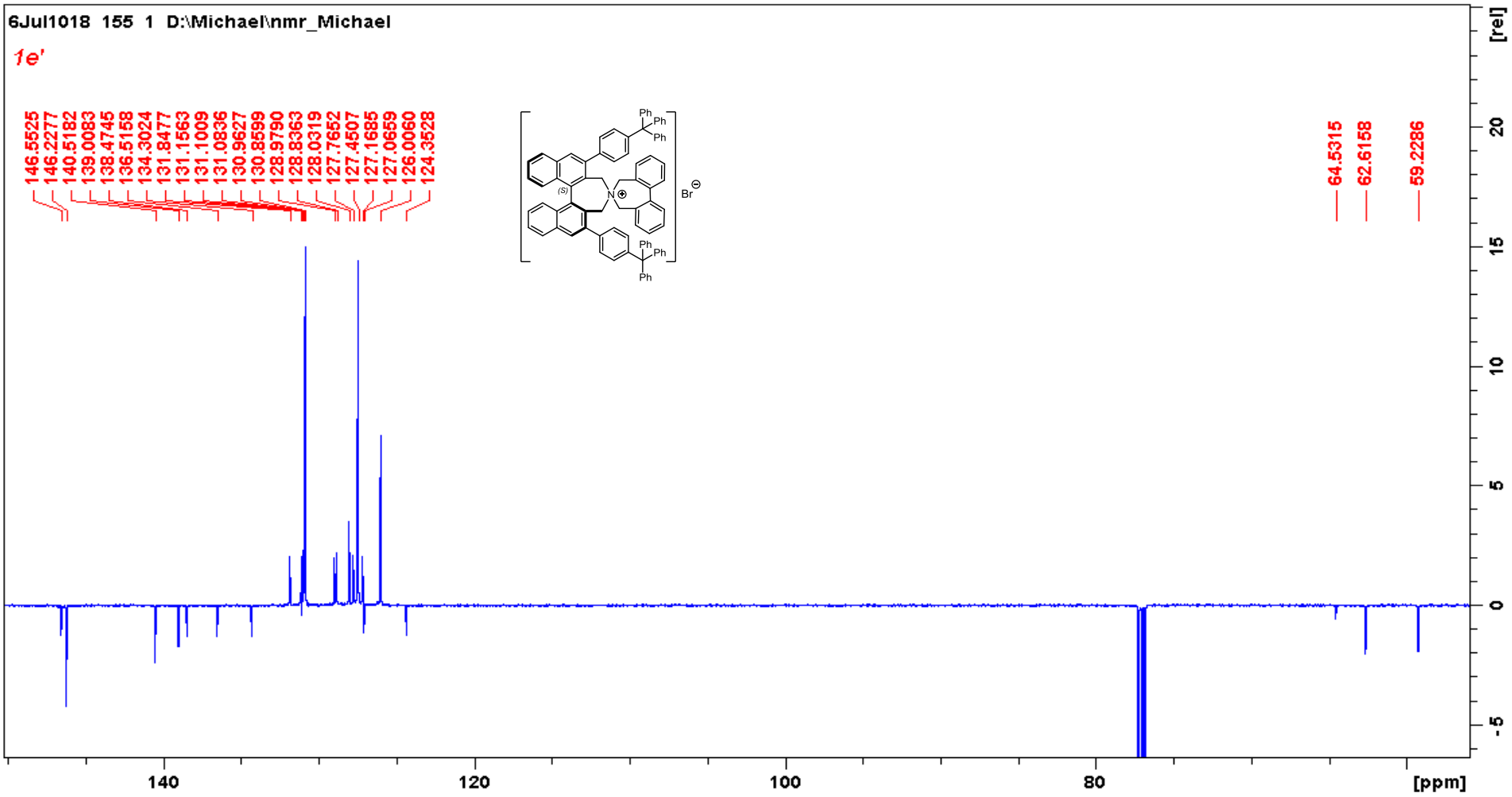
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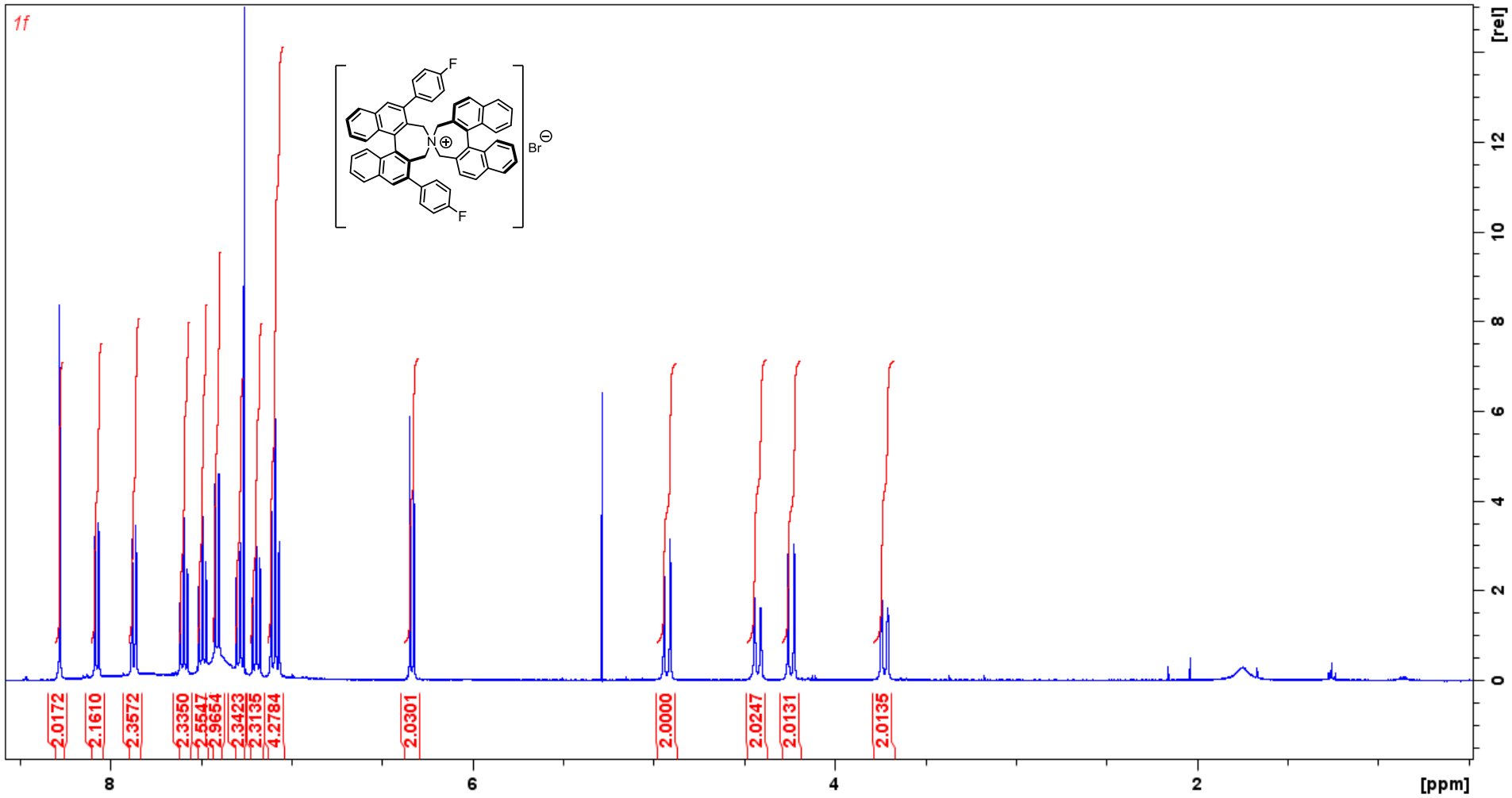
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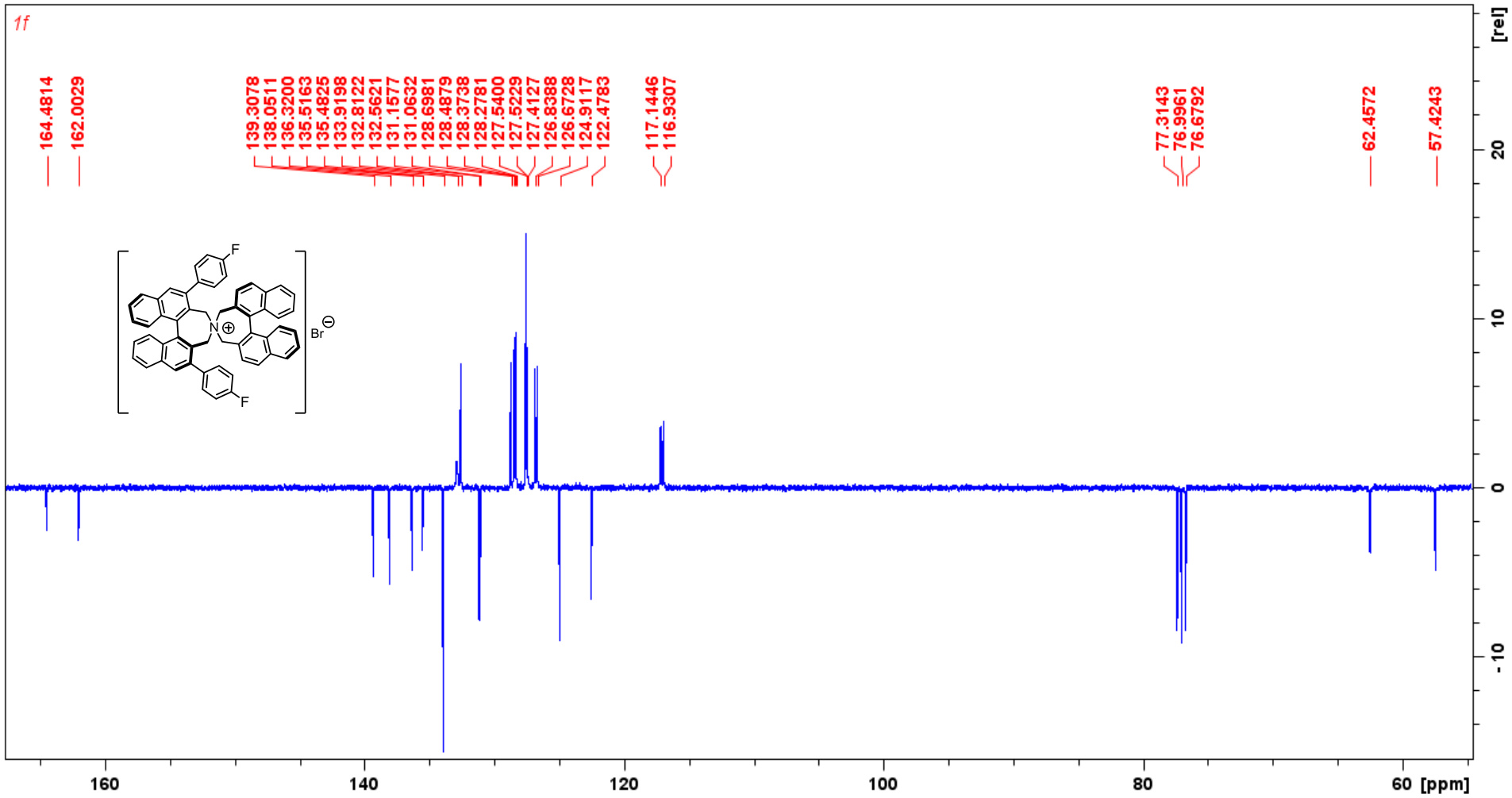
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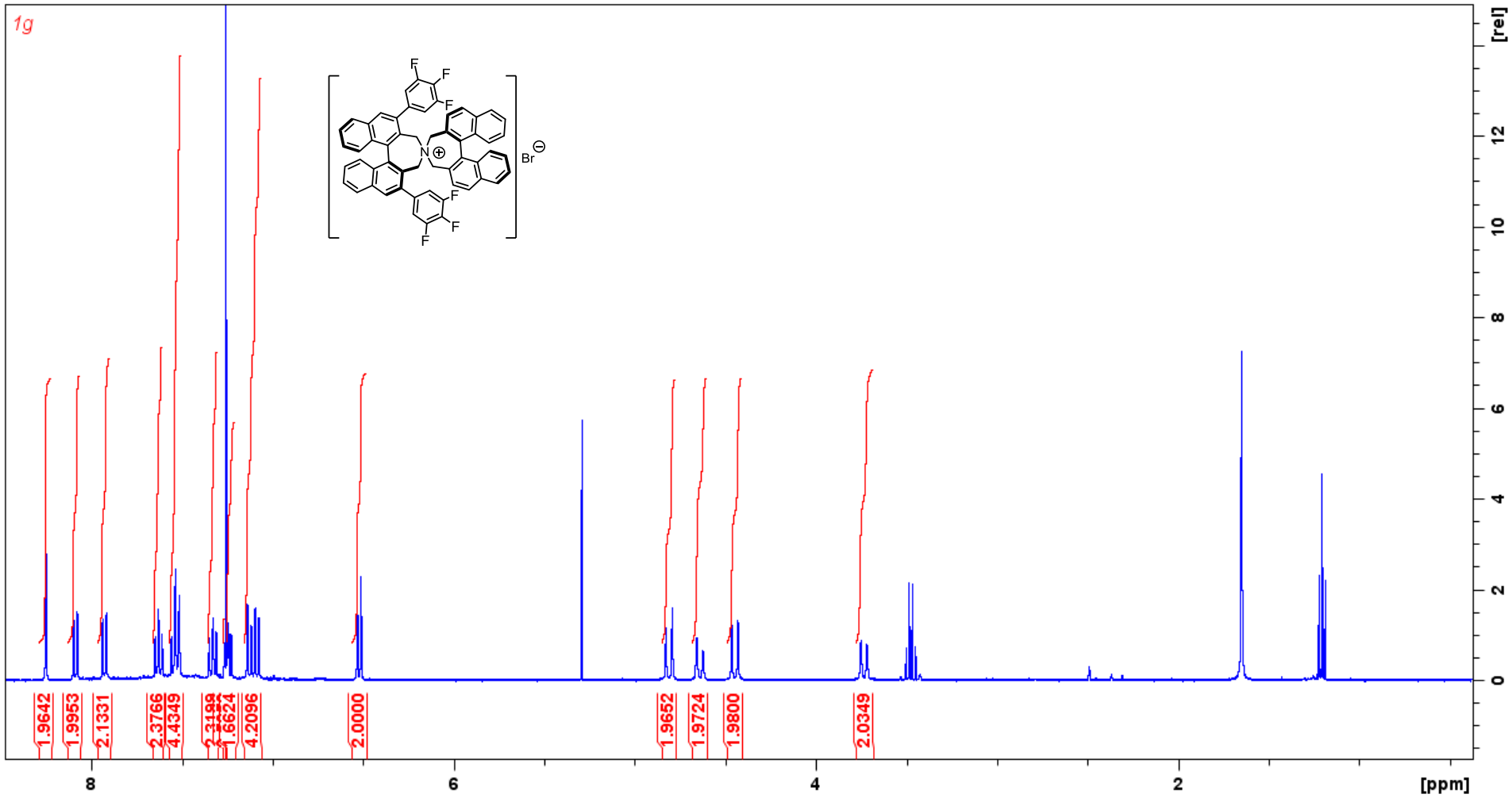
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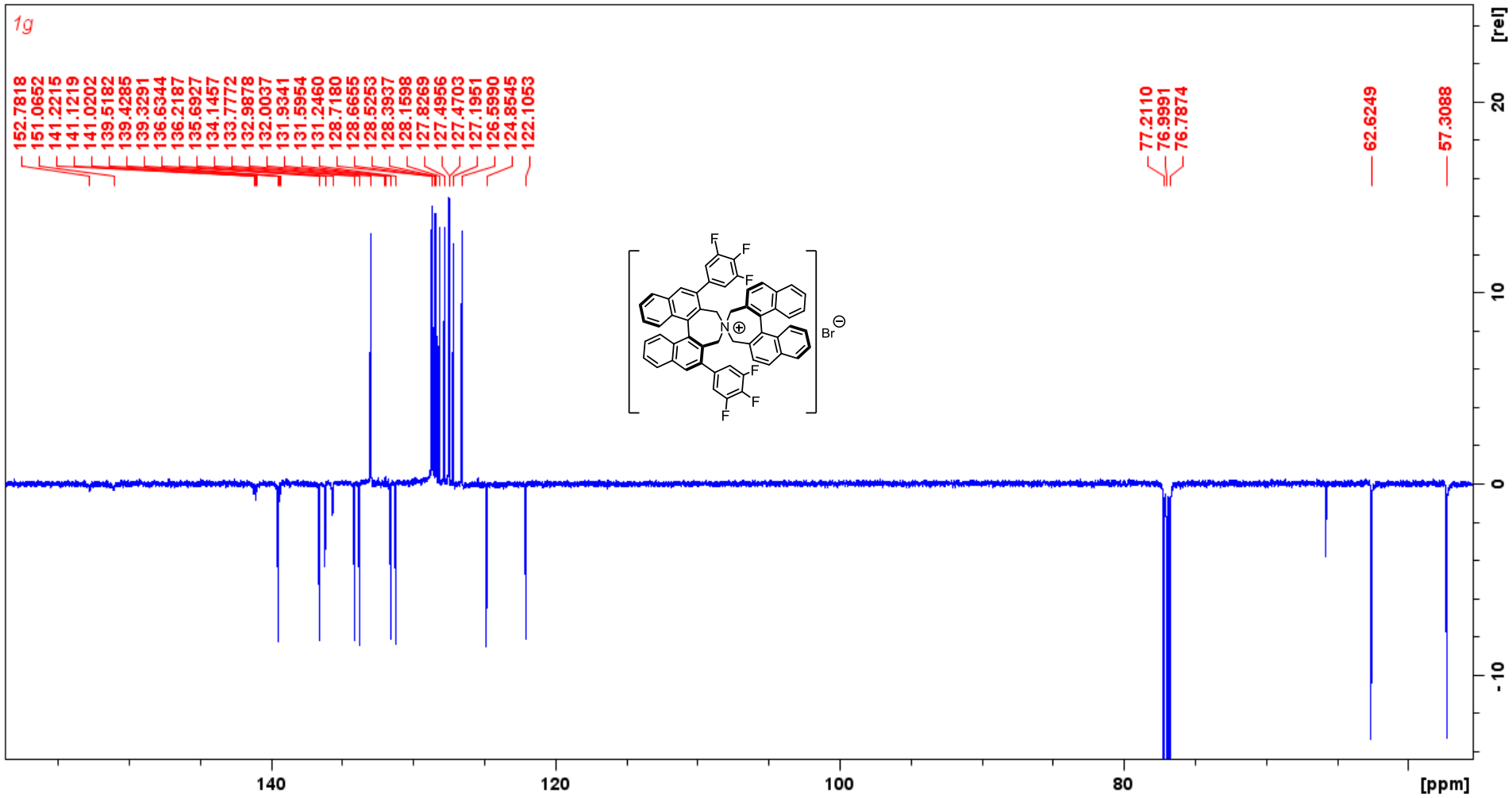
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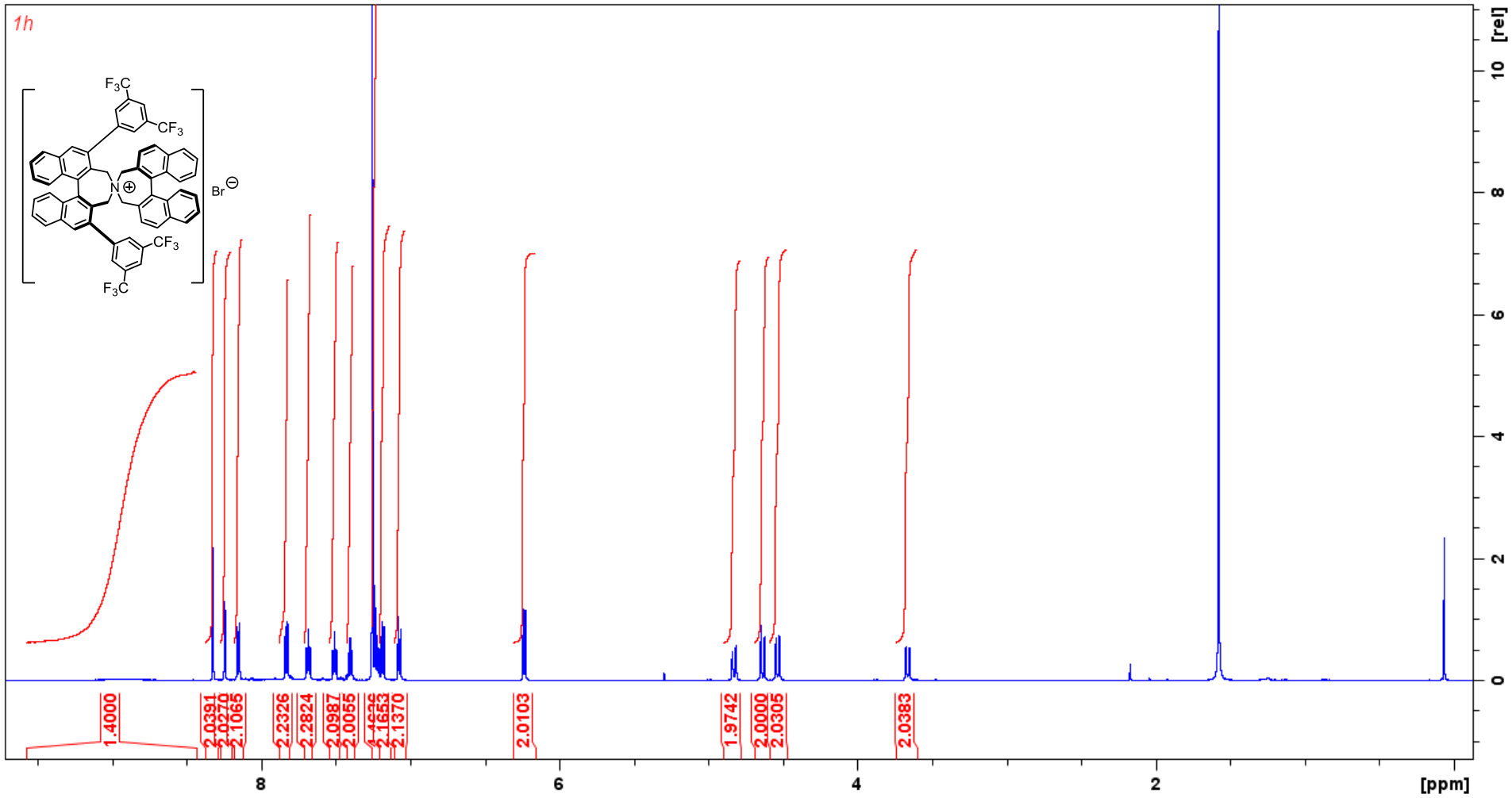
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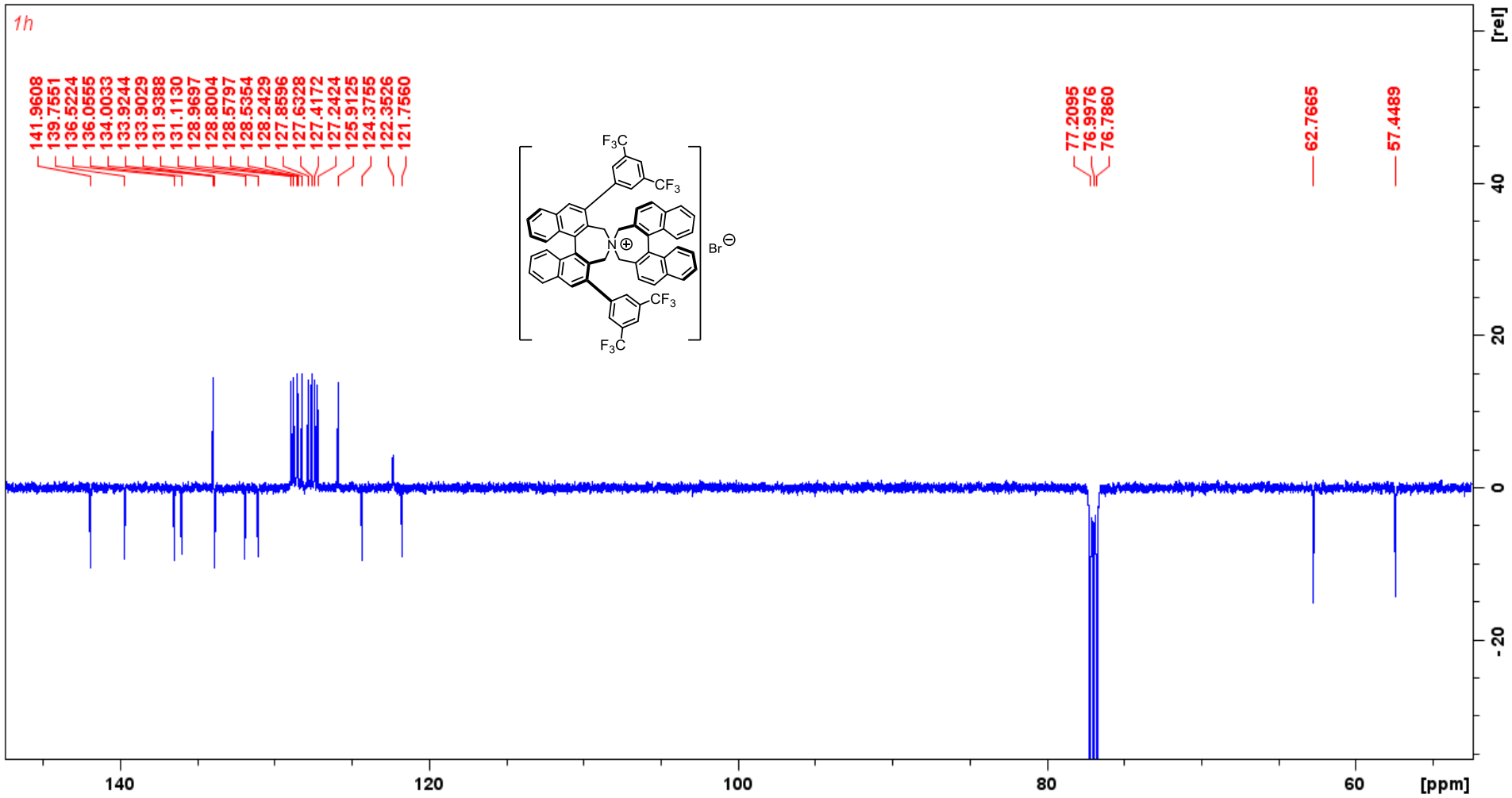
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- 20
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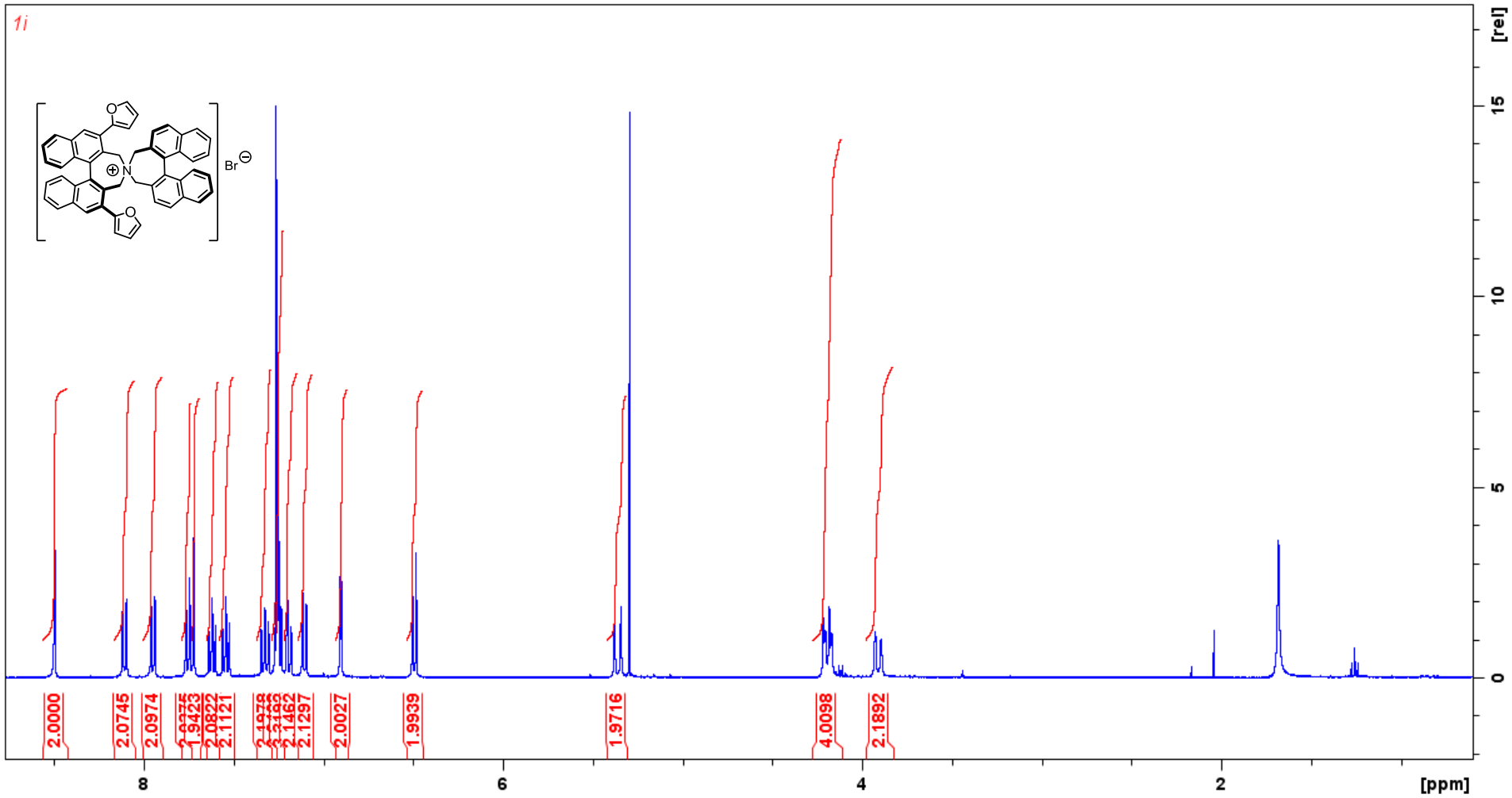
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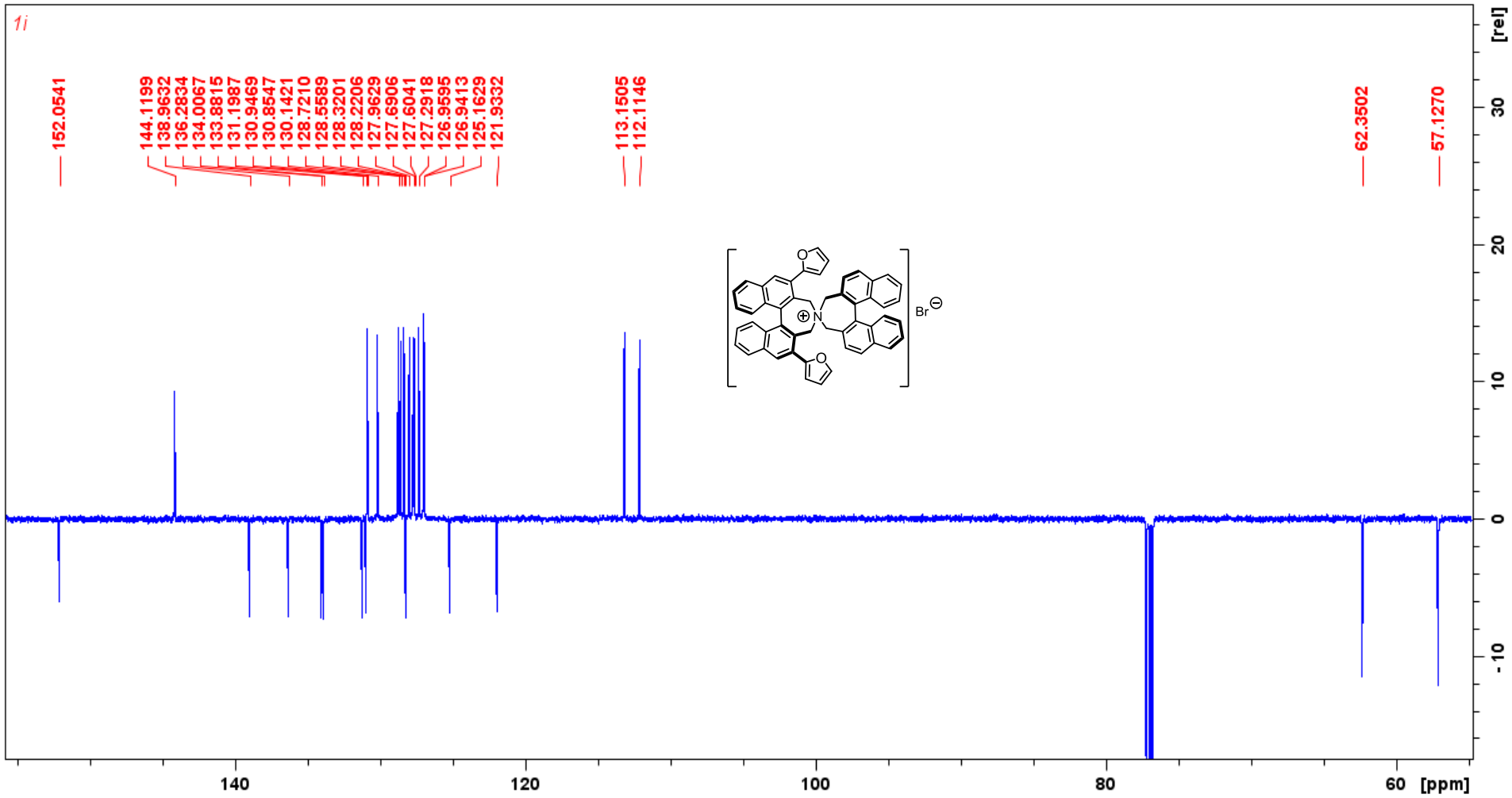
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113.1505
112.1146
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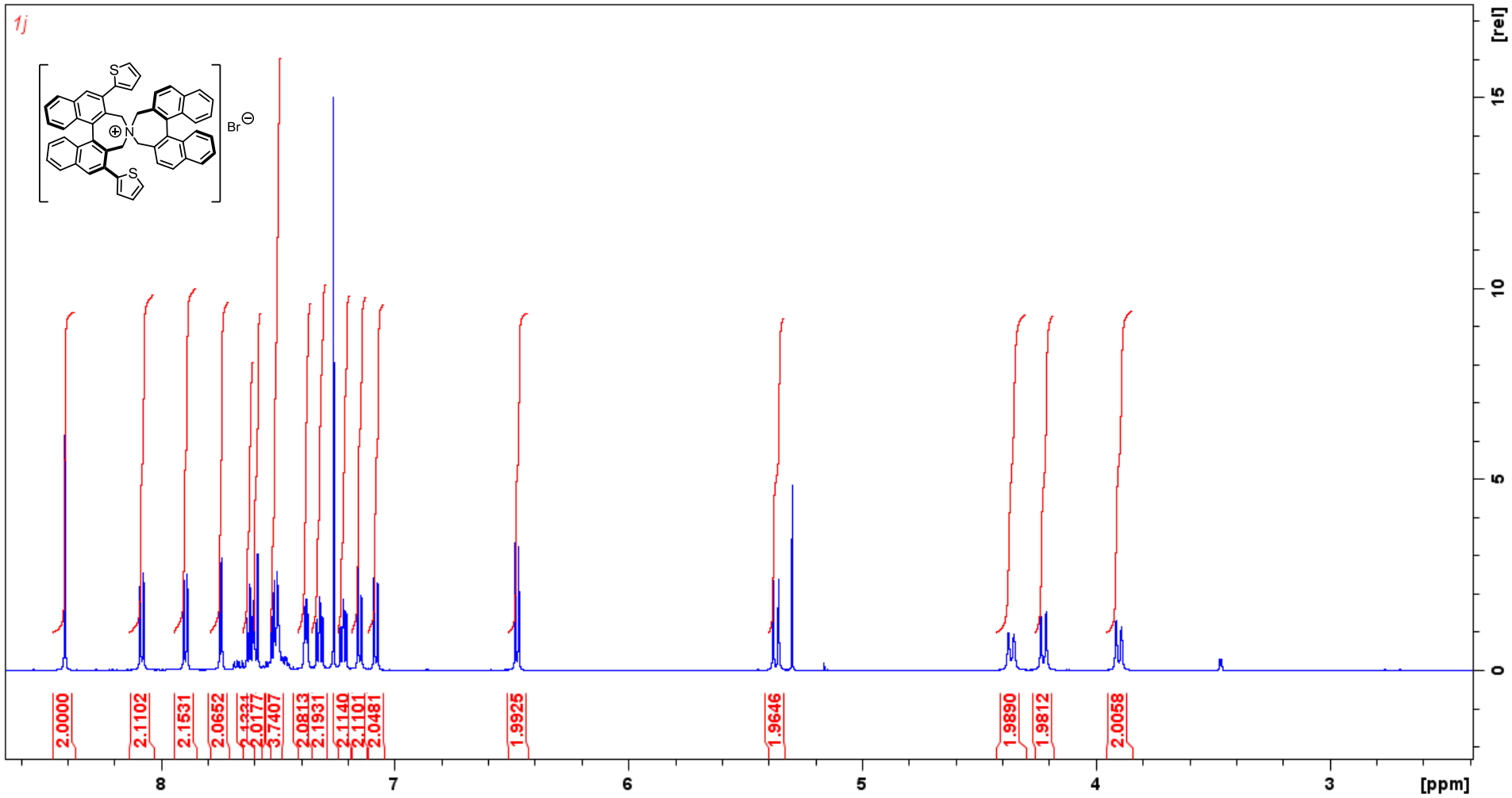
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3
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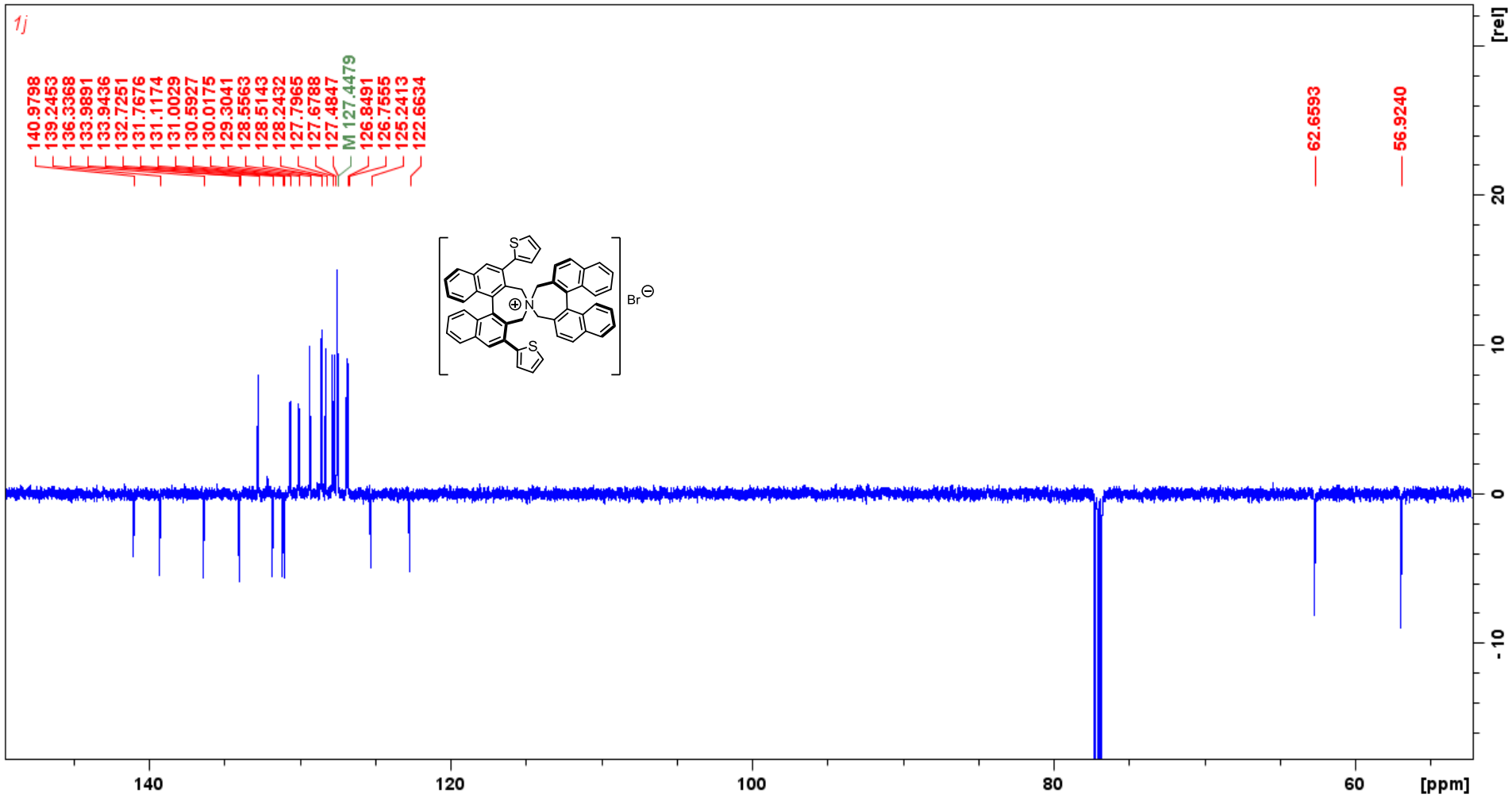
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129.3041
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128.5143
128.2432
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127.6788
127.4847
M 127.4479
126.8491
126.7555
125.2413
122.6634
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Br
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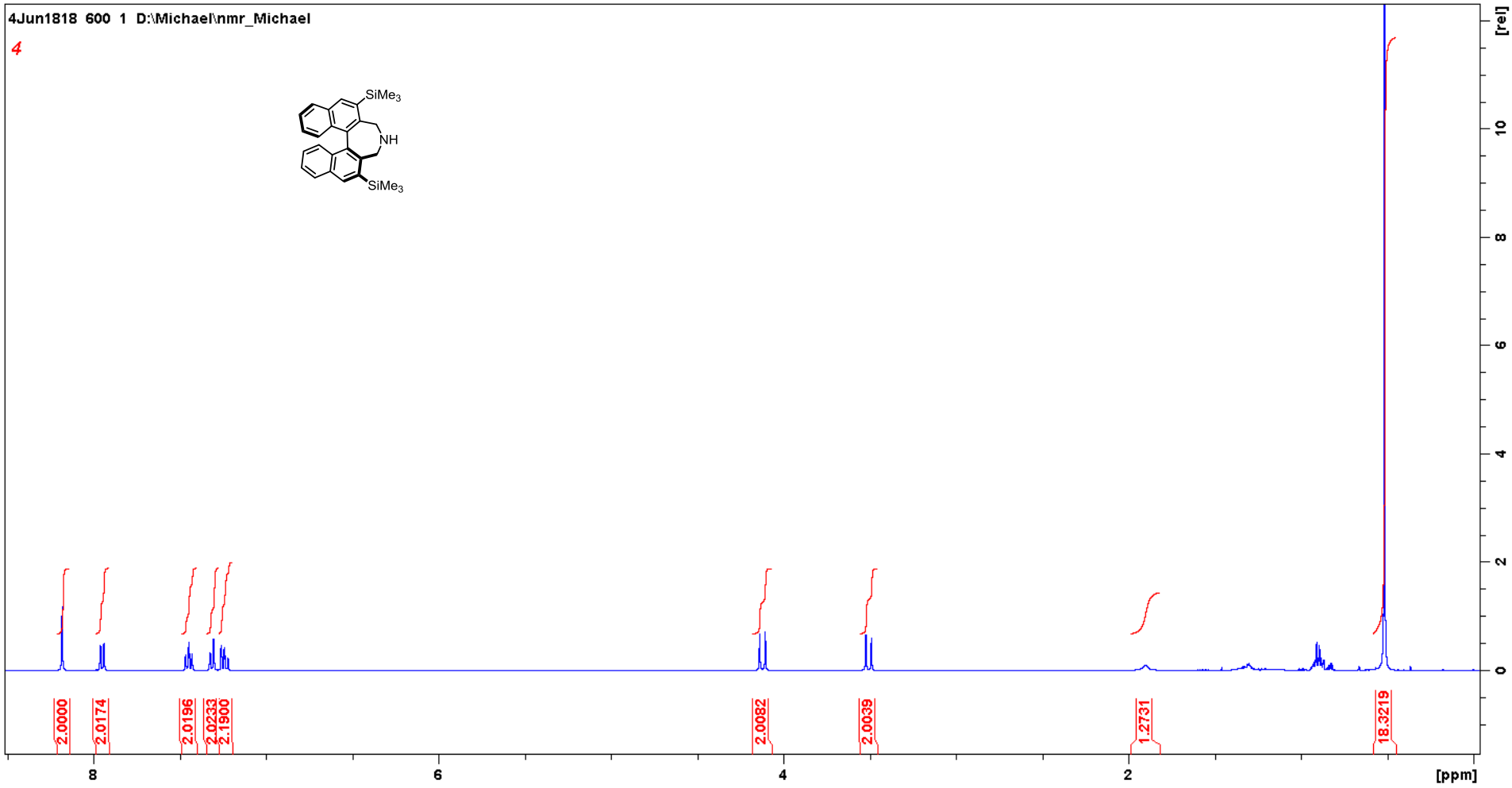
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NH
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4
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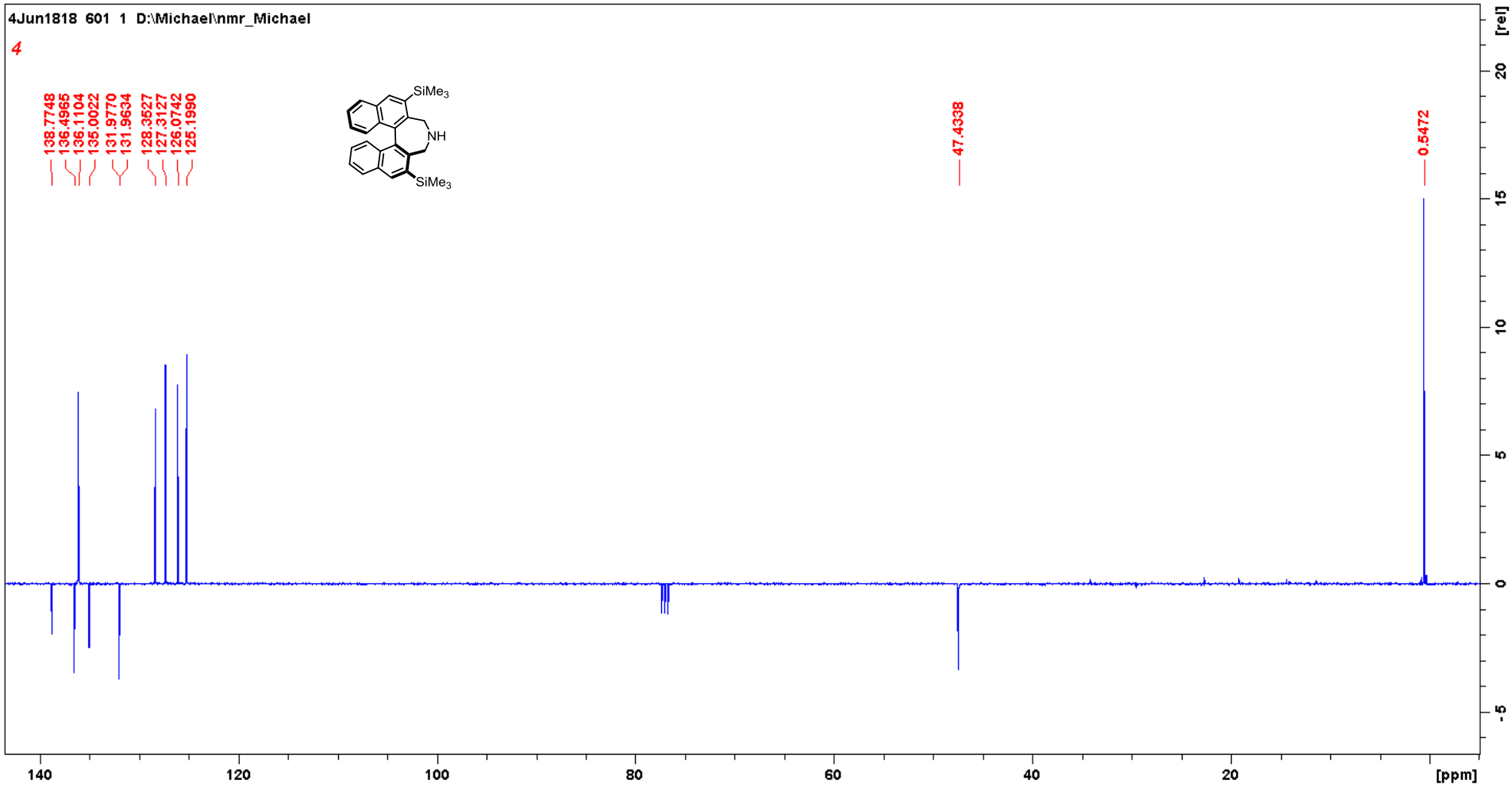
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125.1990
SiMe3
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20
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10
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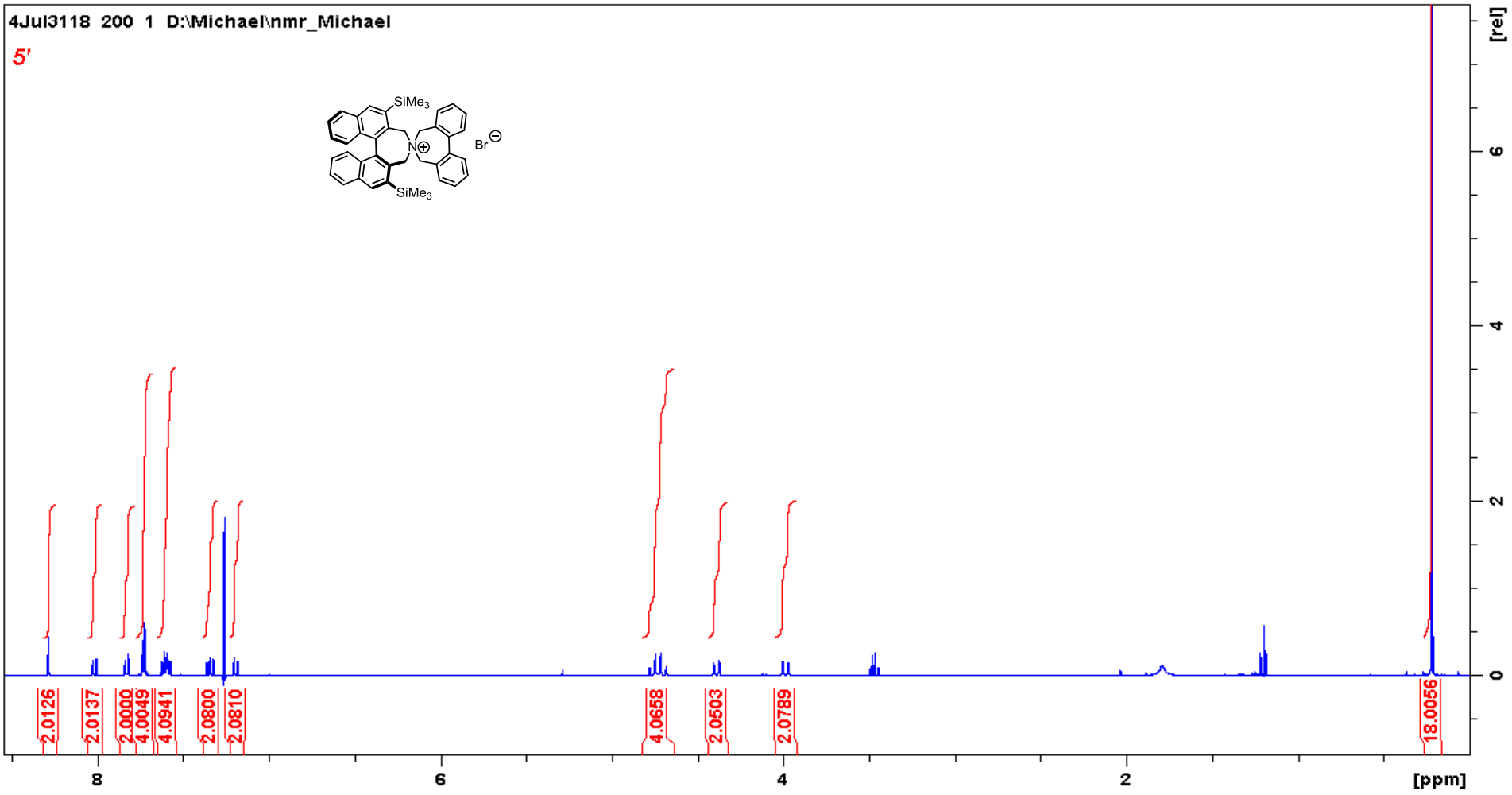
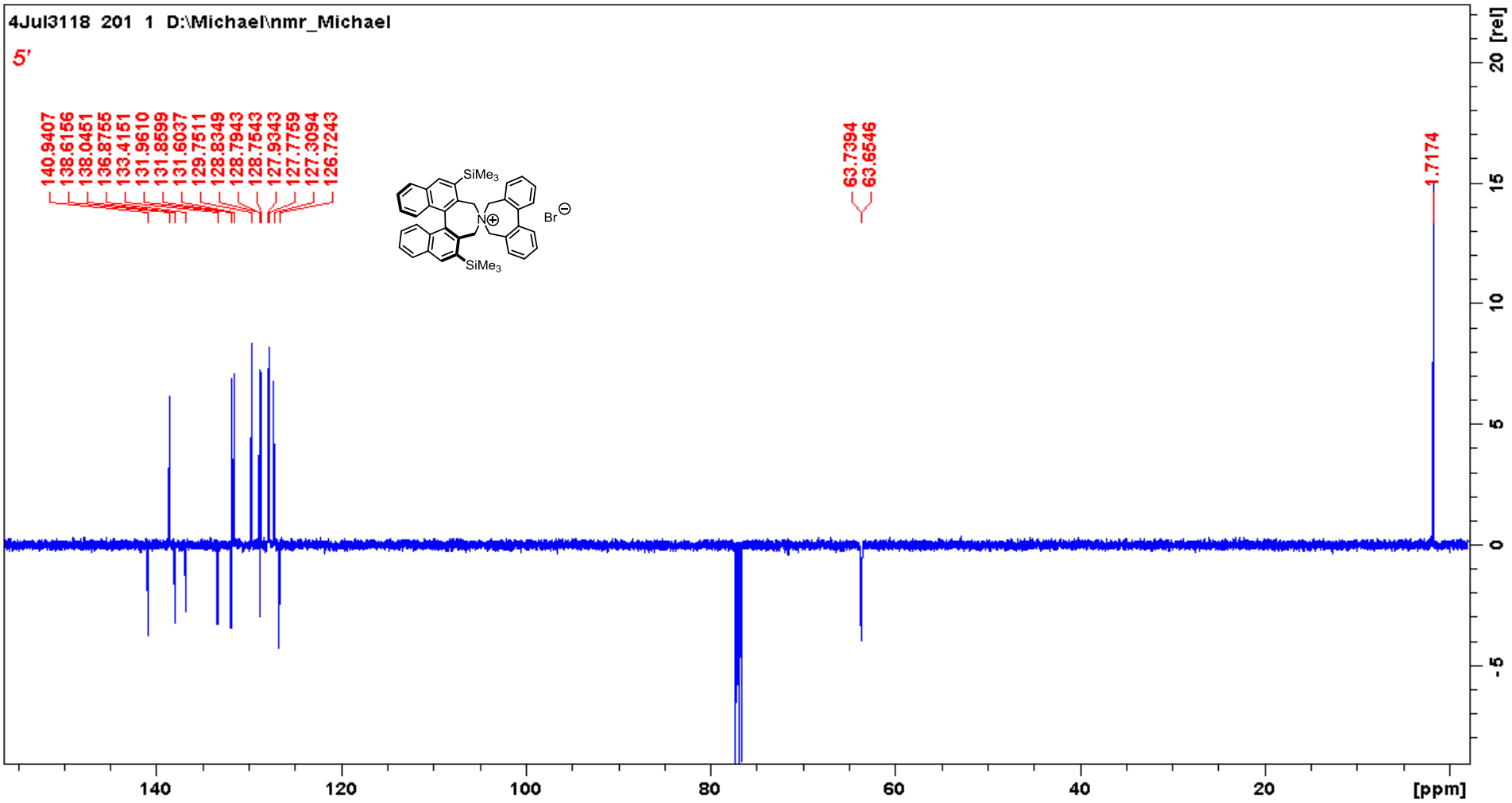
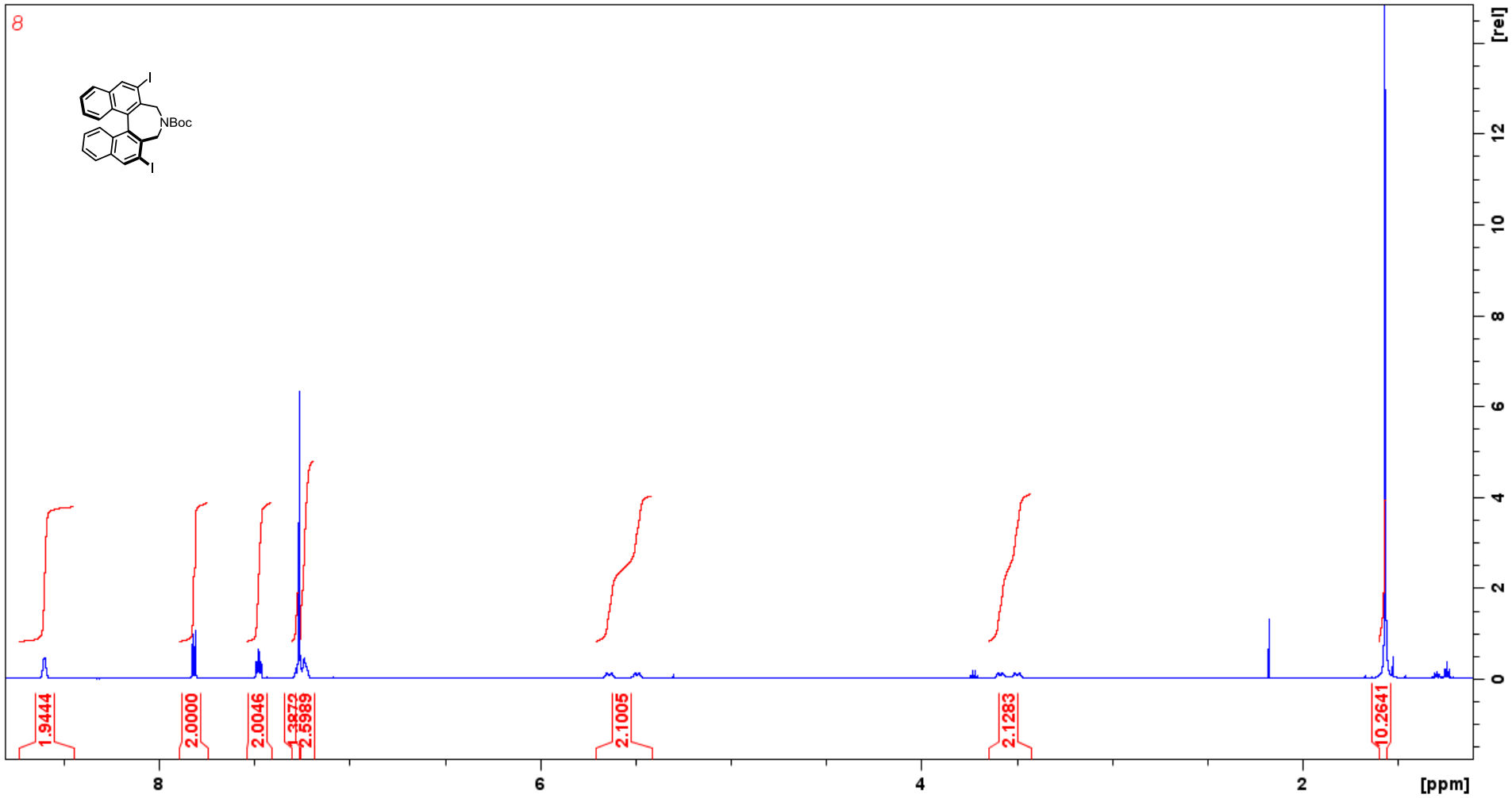
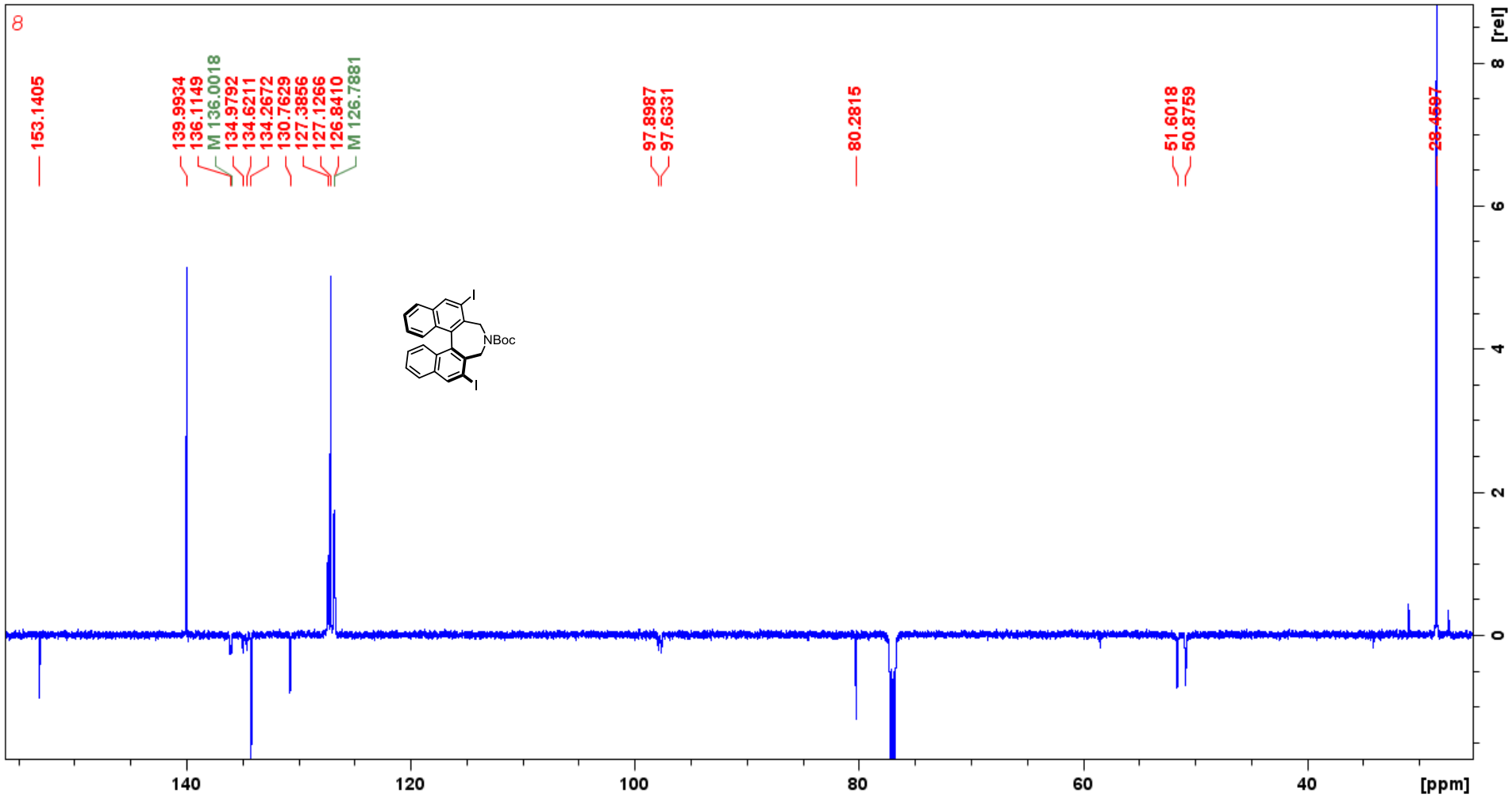
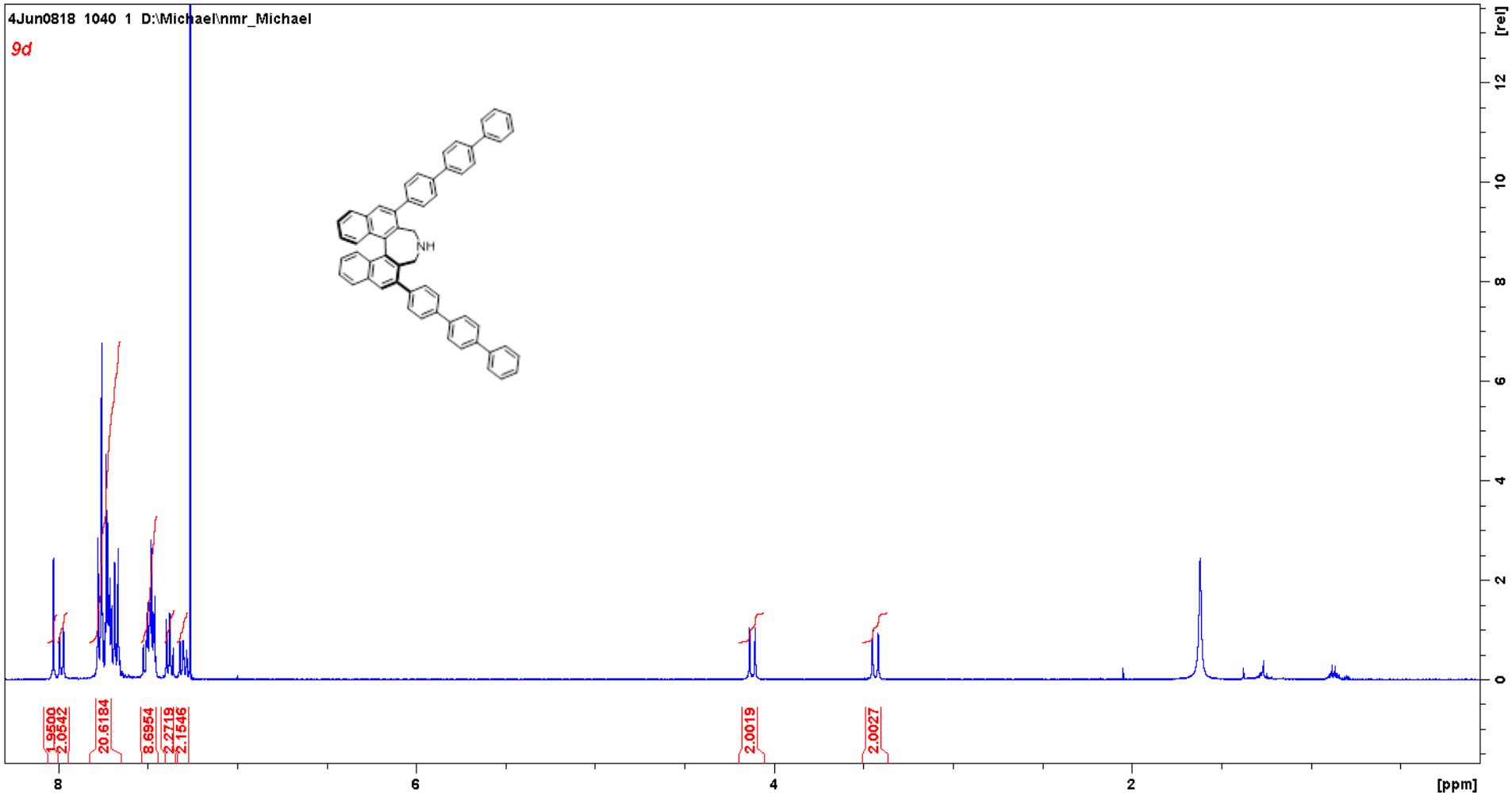
140
120
100
80
60
40
20
[ppm]

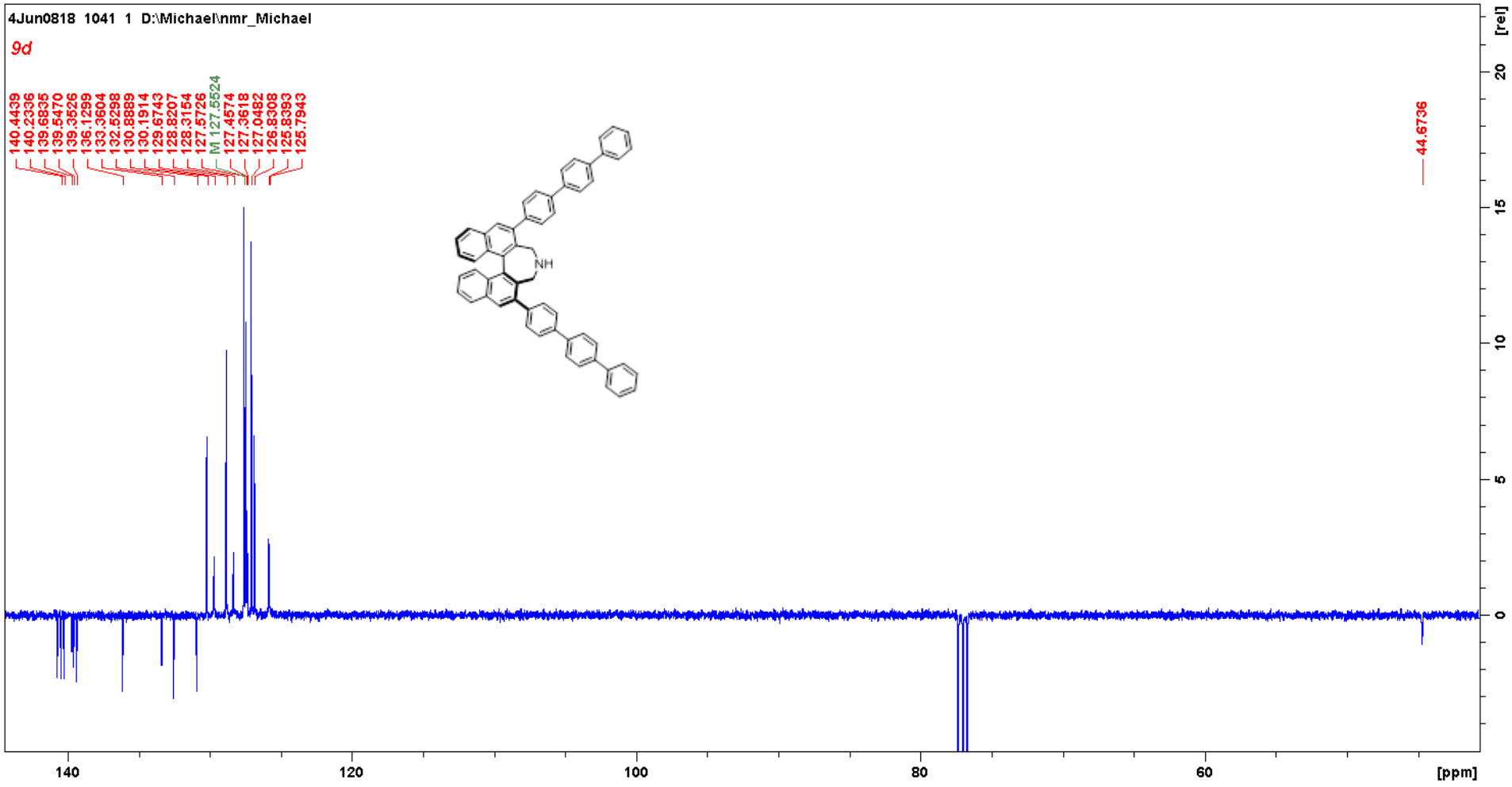

4Jul3118 200 1 D:\Michael\nmr_Michael
5'
SiMe3
Br
N
SiMe3
2.0126
2.0137
2.0000
4.0049
4.0941
2.0800
2.0810
4.0658
2.0503
2.0789
18.0056
8
6
4
2
[ppm]
0
2
4
6
[rel]

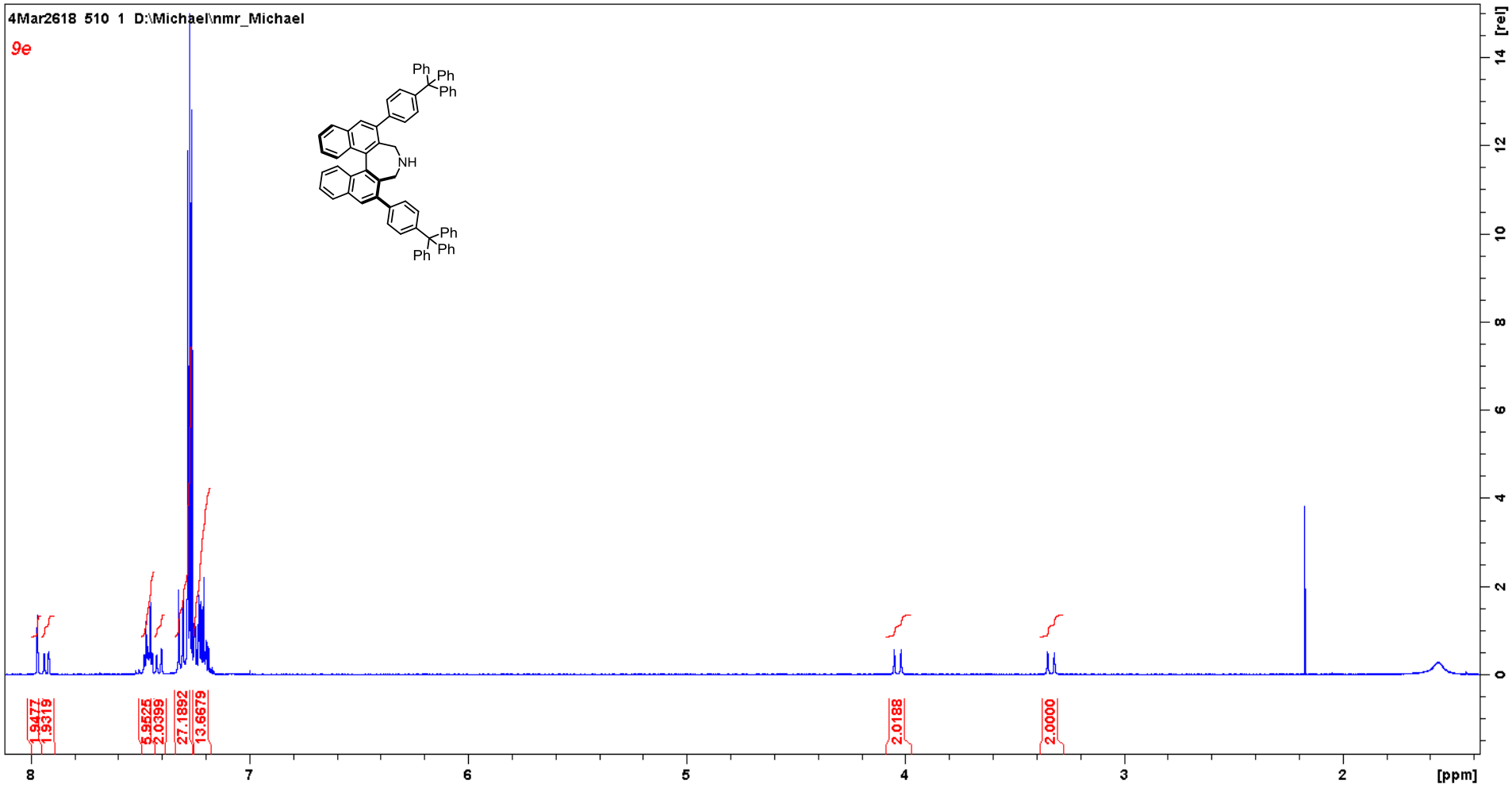

4Jul3118 201 1 D:\Michael\nmr_Michael
5'
140.9407
138.6156
138.0451
136.8755
133.4151
131.9610
131.8599
131.6037
129.7511
128.8349
128.7943
128.7543
127.9343
127.7759
127.3094
126.7243
63.7394
63.6546
1.7174
SiMe3
Br
SiMe3
20 [rel]
15
10
5
0
-5
140
120
100
80
60
40
20
[ppm]

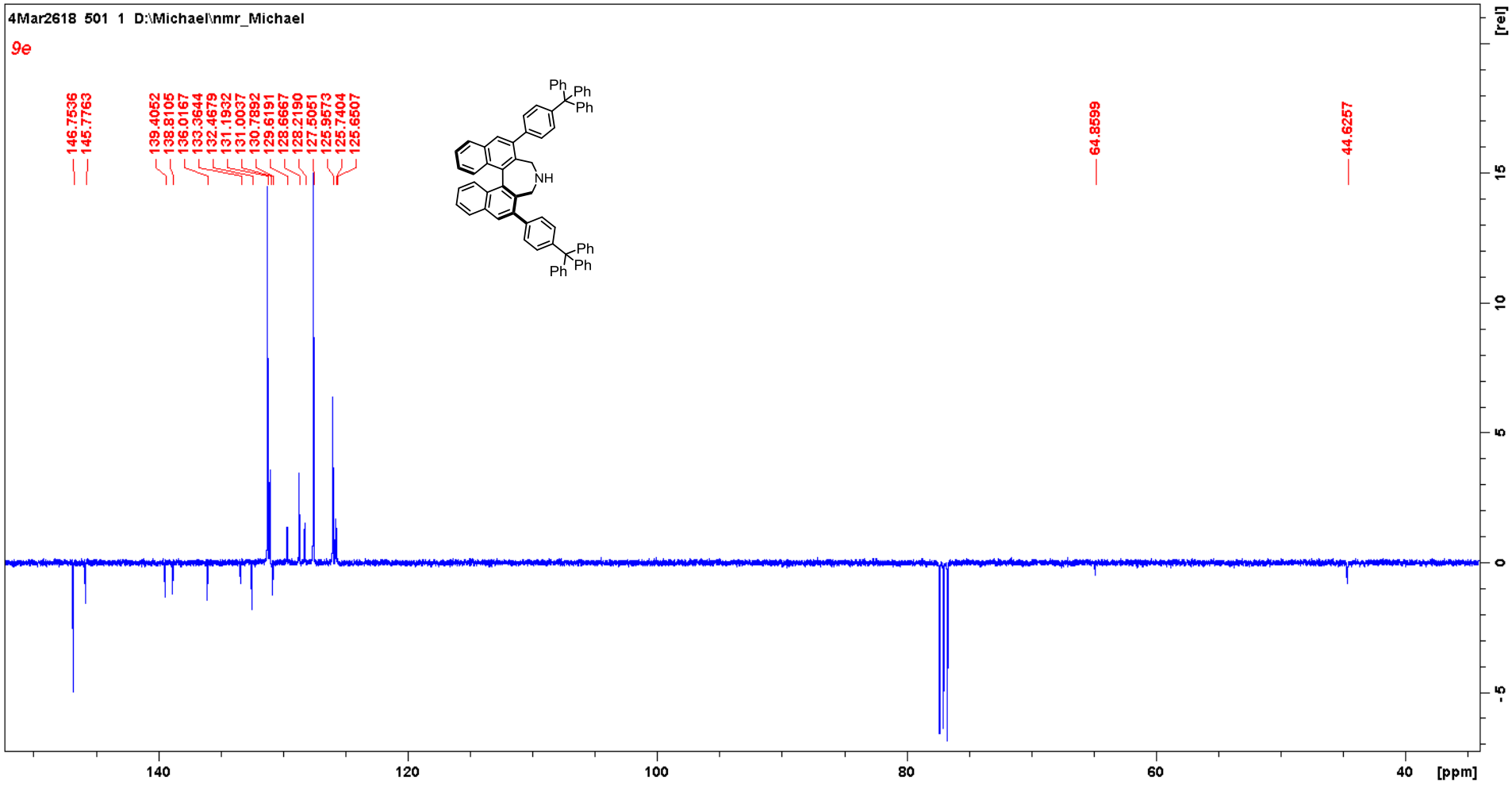

8
I
NBoc
I
1.9444
2.0000
2.0046
1.3872
2.5989
2.1005
2.1283
10.2641
8
6
4
2
[ppm]
0
2
4
6
8
10
12
[rel]

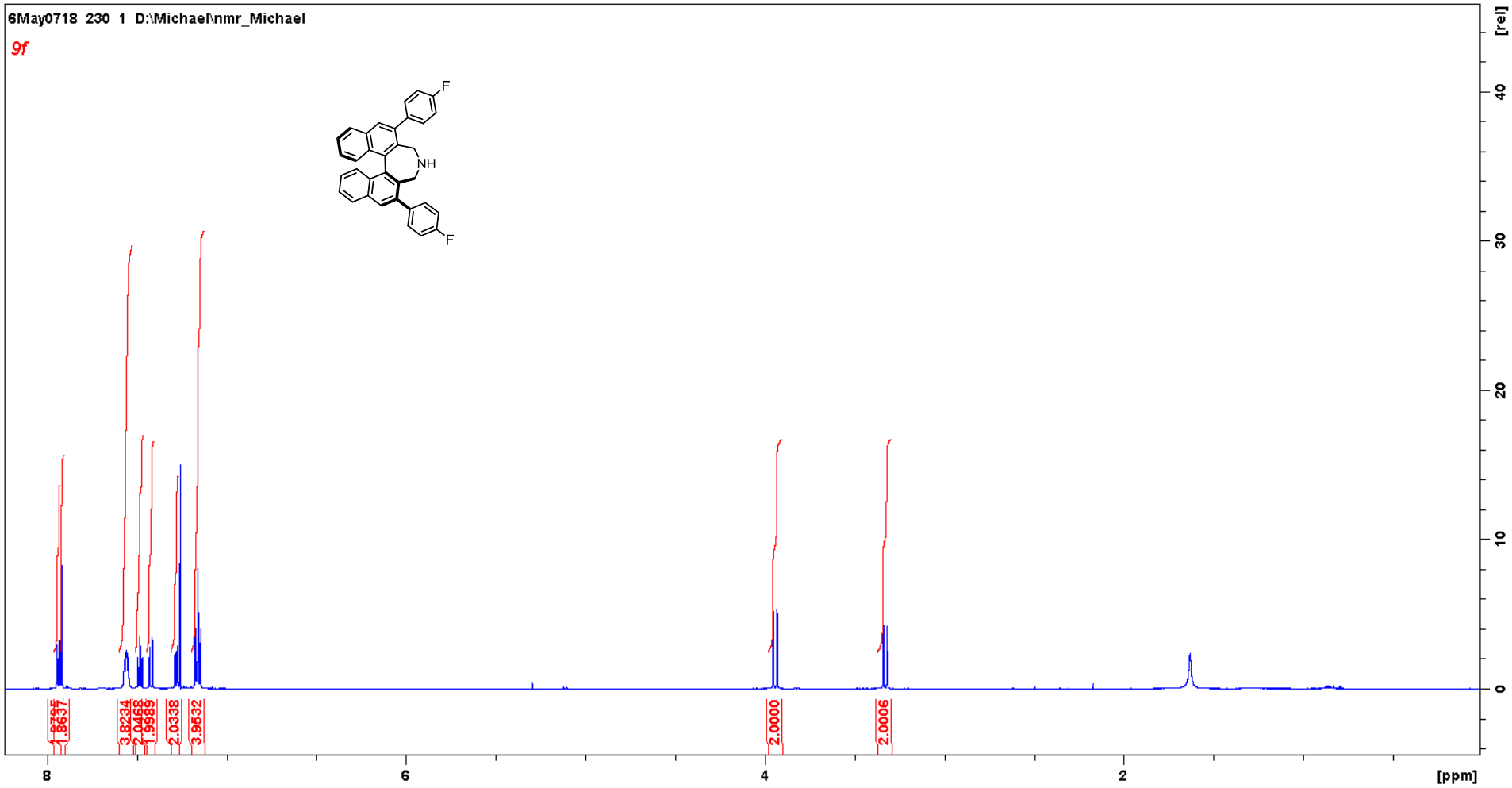

8
153.1405
139.9934
136.1149
M 136.0018
134.9792
134.6211
134.2672
130.7629
127.3856
127.1266
126.8410
M 126.7881
97.8987
97.6331
80.2815
51.6018
50.8759
28.4597
I
NBoc
I
8 [rel]
6
4
2
0
140
120
100
80
60
40
[ppm]

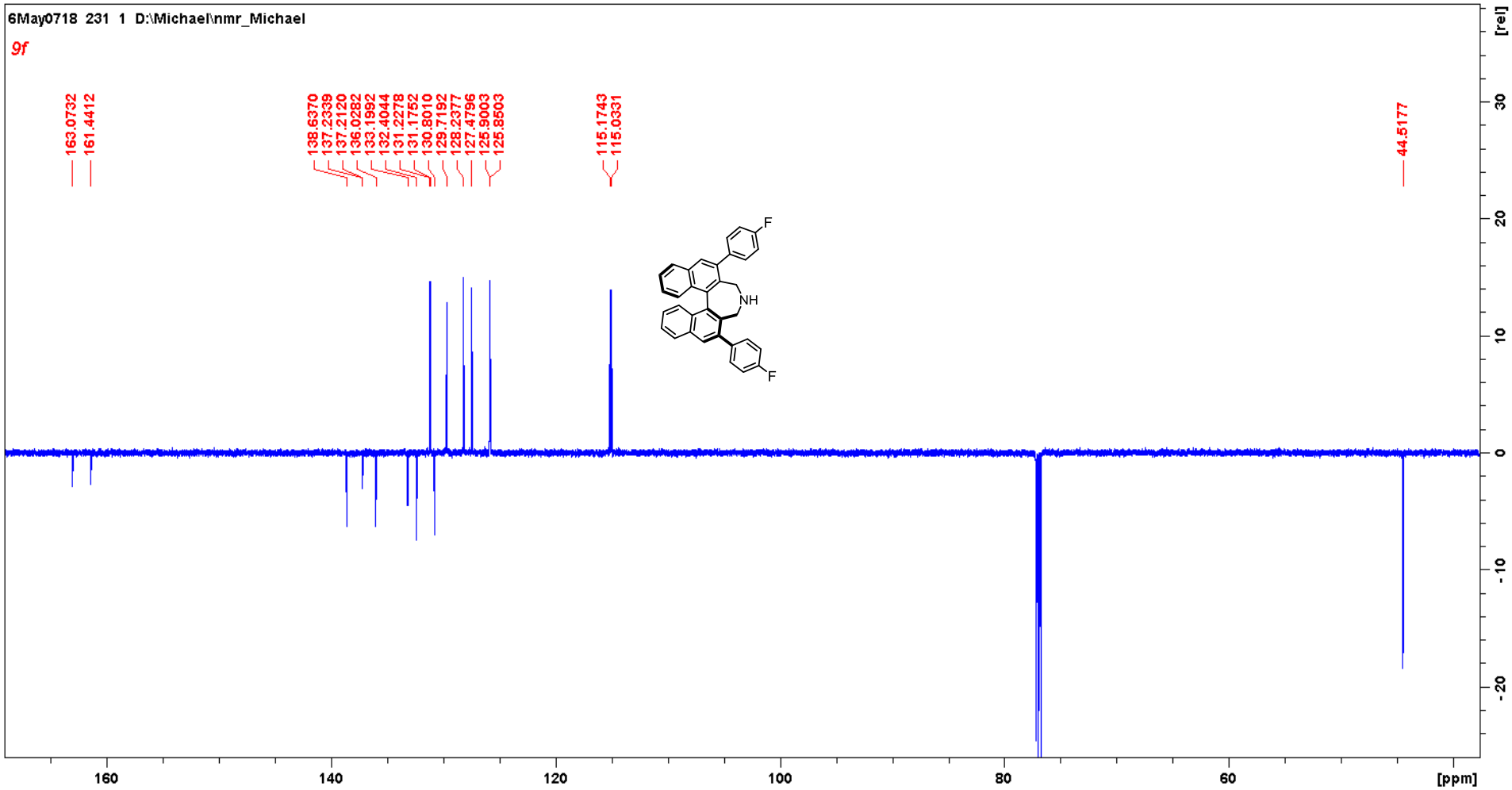

4Jun0818 1040 1 D:\Michael\nmr_Michael
9d
NH
1.9500
2.0542
20.6184
8.6954
2.2719
2.1546
2.0019
2.0027
8
6
4
2
[ppm]
[rel]
0
2
4
6
8
10
12

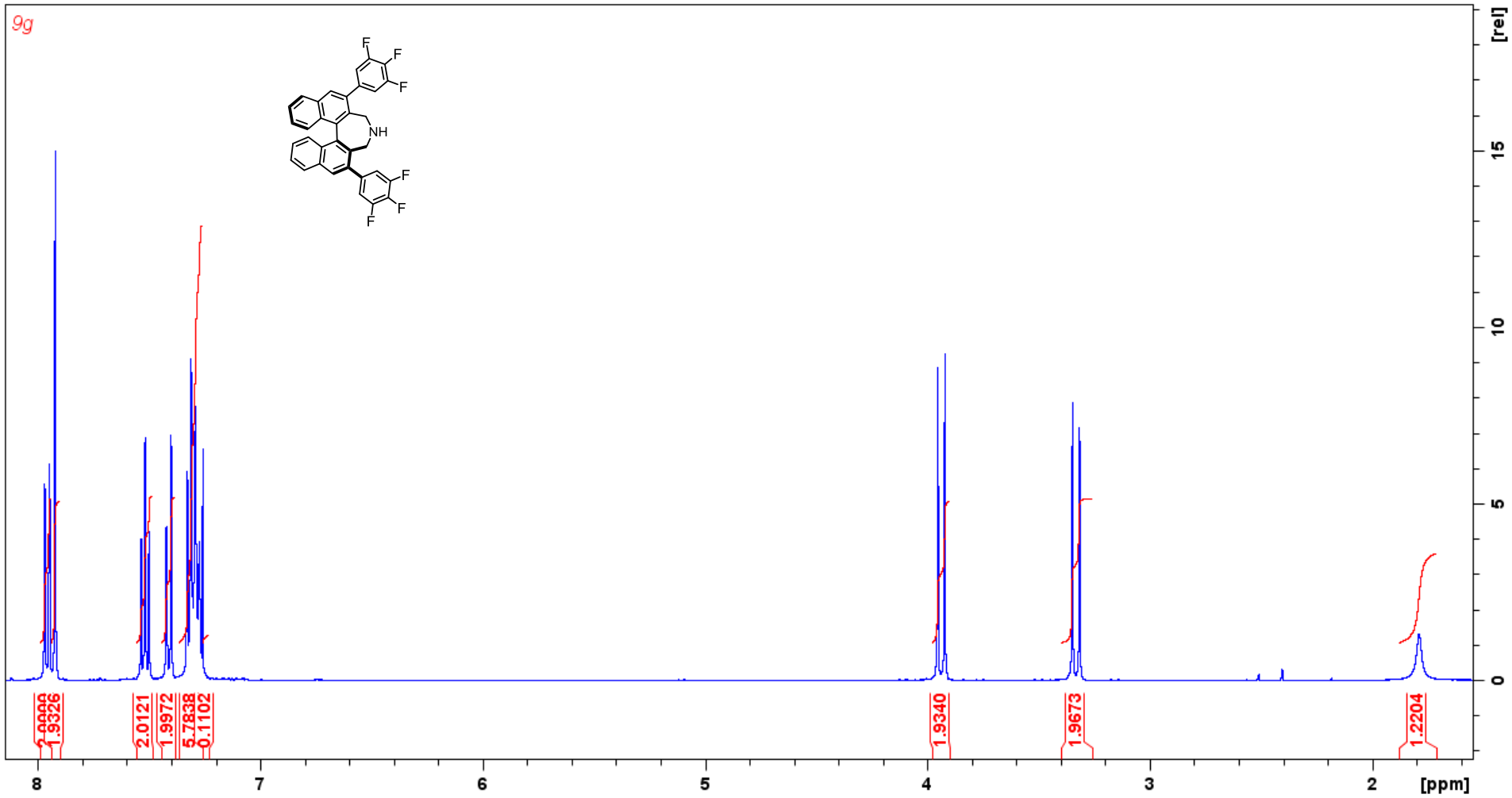

4Jun0818 1041 1 D:\Michael\nmr_Michael
9d
140.4439
140.2336
139.6835
139.5470
139.3526
136.1299
133.3604
132.5298
130.8889
130.1914
129.6743
128.8207
128.3154
127.5726
M 127.5524
127.4574
127.3618
127.0482
126.8308
125.8393
125.7943
44.6736
NH
[rel]
20
15
10
5
0
140
120
100
80
60
[ppm]

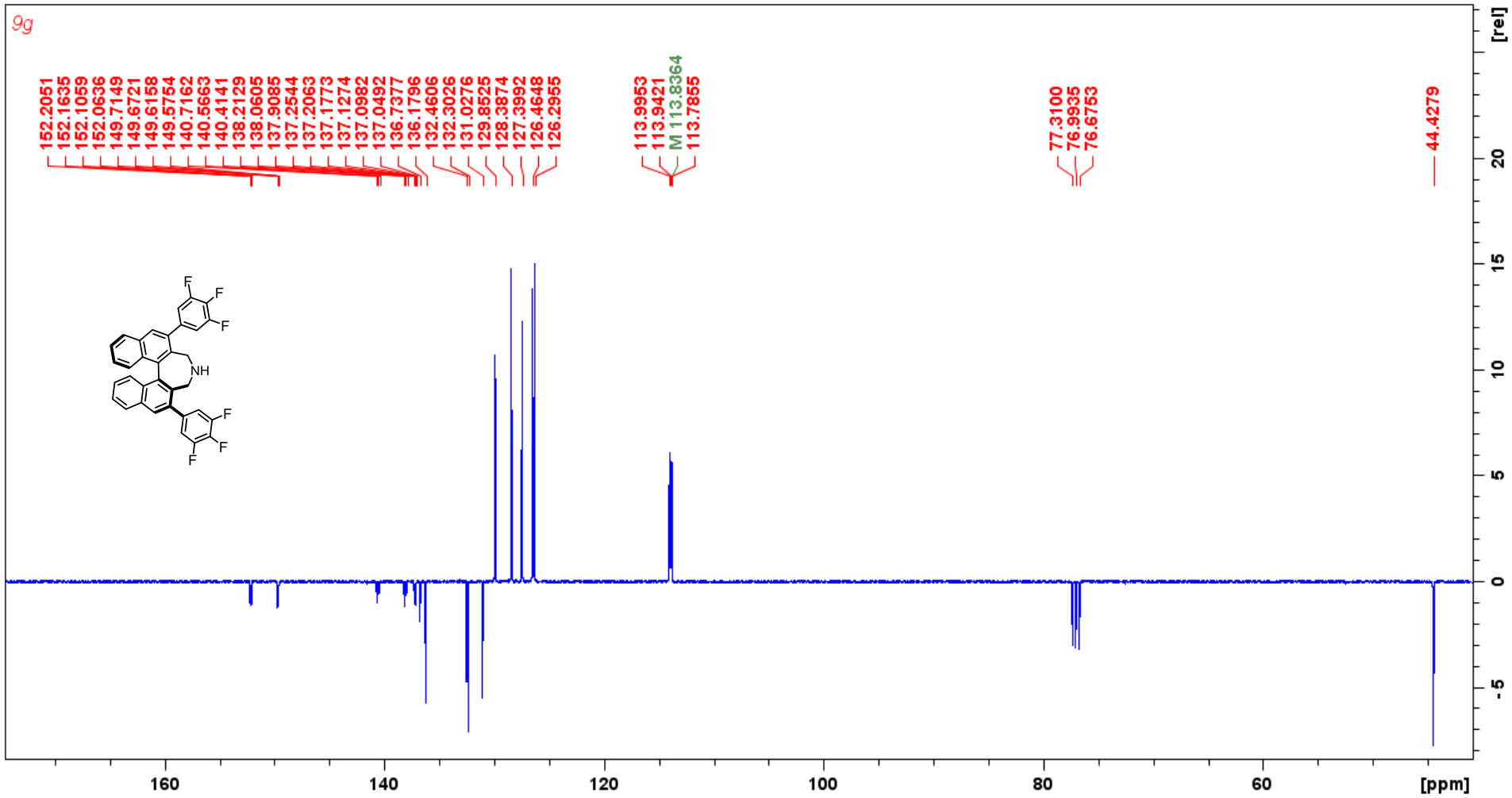

4Mar2618 510 1 D:\Michael\nmr_Michael
9e
Ph
Ph
Ph
NH
Ph
Ph
Ph
1.9477
1.9319
5.9525
2.0399
27.1892
13.6679
2.0188
2.0000
8
7
6
5
4
3
2
[ppm]
0
2
4
6
8
10
12
14
[rel]

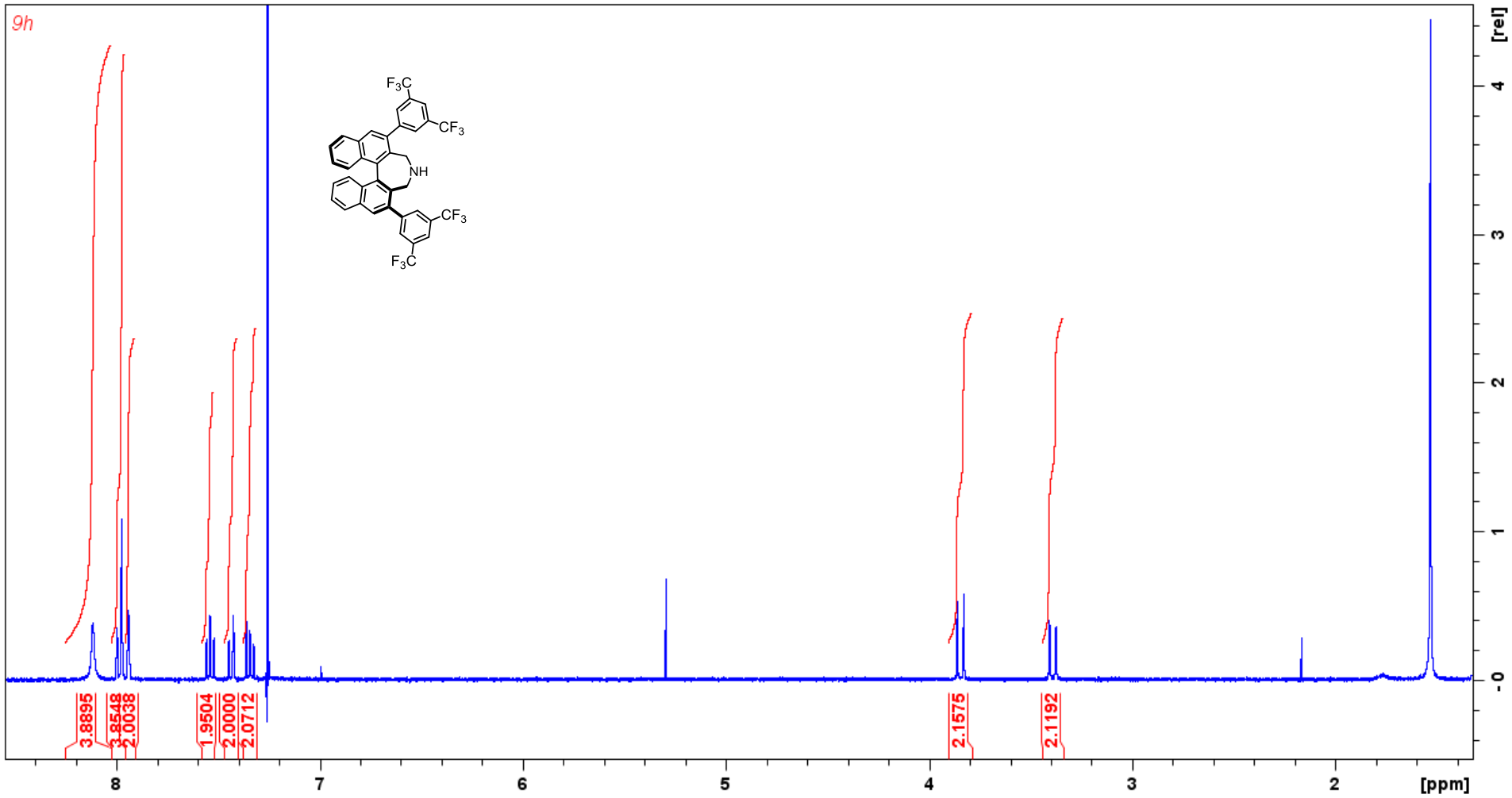

4Mar2618 501 1 D:\Michael\nmr_Michael
9e
146.7536
145.7763
139.4052
138.8105
136.0167
133.3644
132.4679
131.1932
131.0037
130.7892
129.6191
128.6667
128.2190
127.5051
125.9573
125.7404
125.6507
64.8599
44.6257
Ph
Ph
Ph
NH
Ph
Ph
Ph
[rel]
15
10
5
0
-5
140
120
100
80
60
40
[ppm]

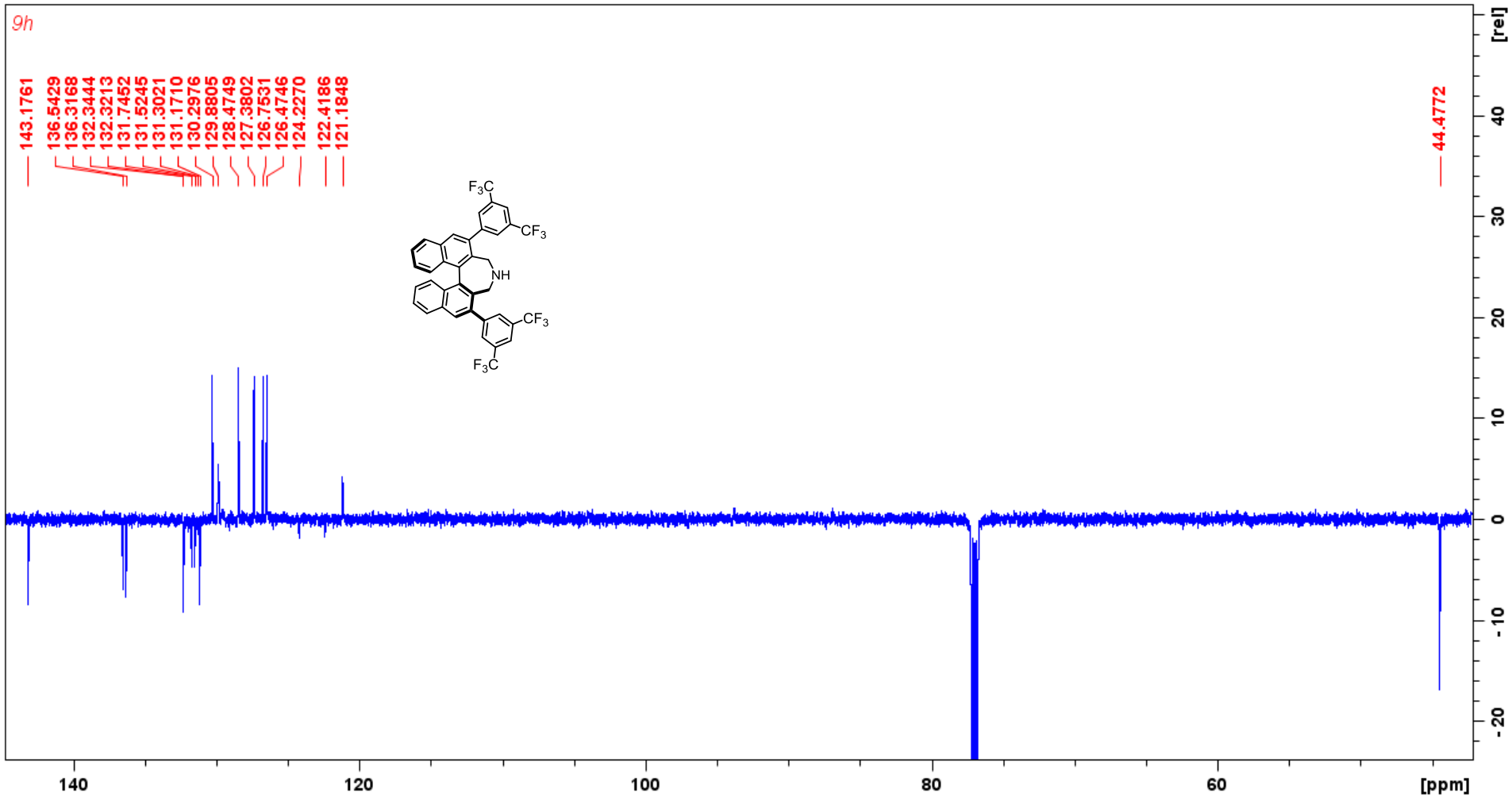

6May0718 230 1 D:\Michael\nmr_Michael
9f
F
NH
F
[rel]
40
30
20
10
0
1.8637
3.8234
2.0468
1.9989
2.0338
3.9532
2.0000
2.0006
8
6
4
2
[ppm]

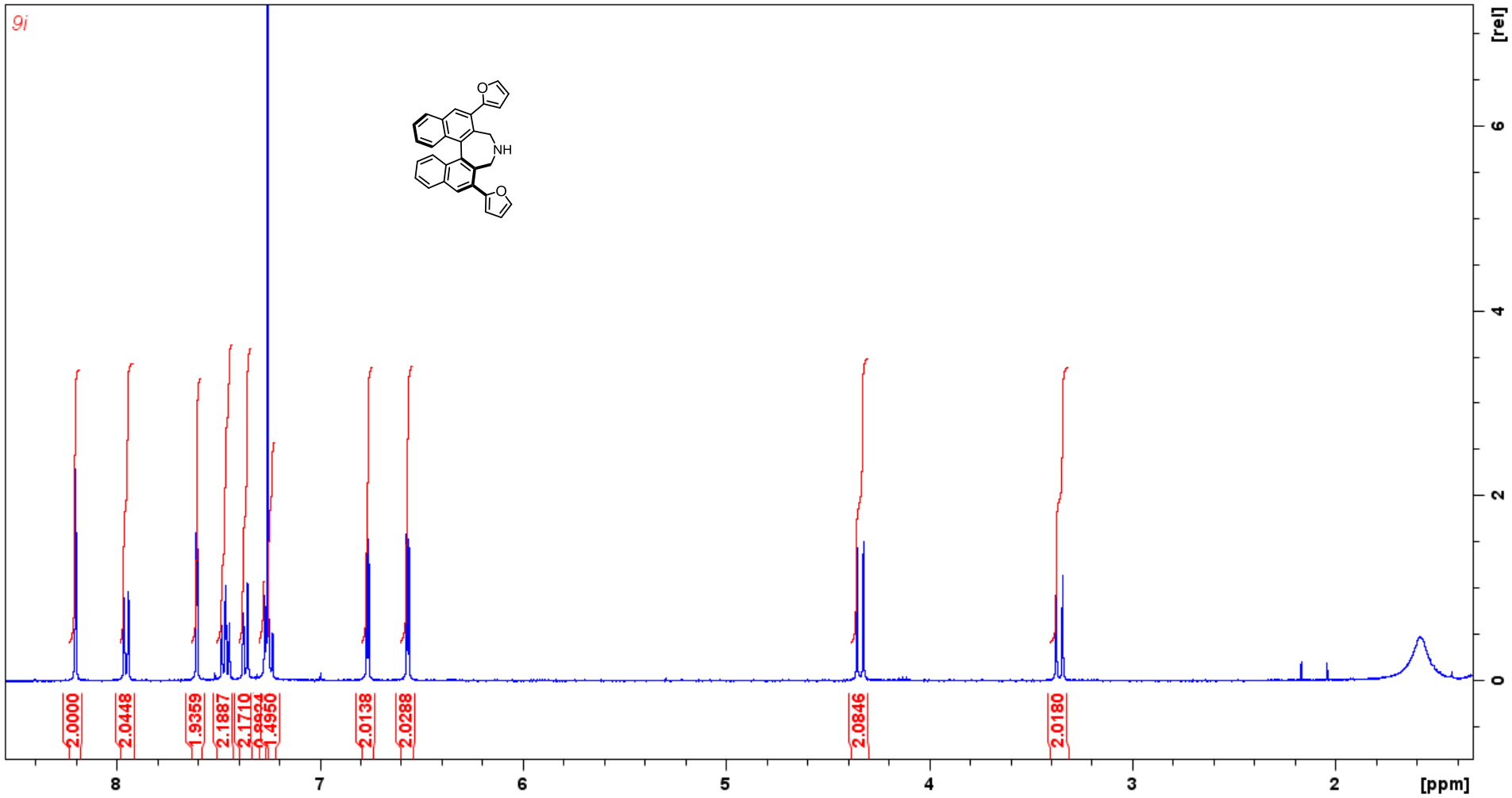

6May0718 231 1 D:\Michael\nmr_Michael
9f
163.0732
161.4412
138.6370
137.2339
137.2120
136.0282
133.1992
132.4044
131.2278
131.1752
130.8010
129.7192
128.2377
127.4796
125.9003
125.8503
115.1743
115.0331
44.5177
F
NH
F
160
140
120
100
80
60
[ppm]
30
20
10
0
-10
-20
[rel]

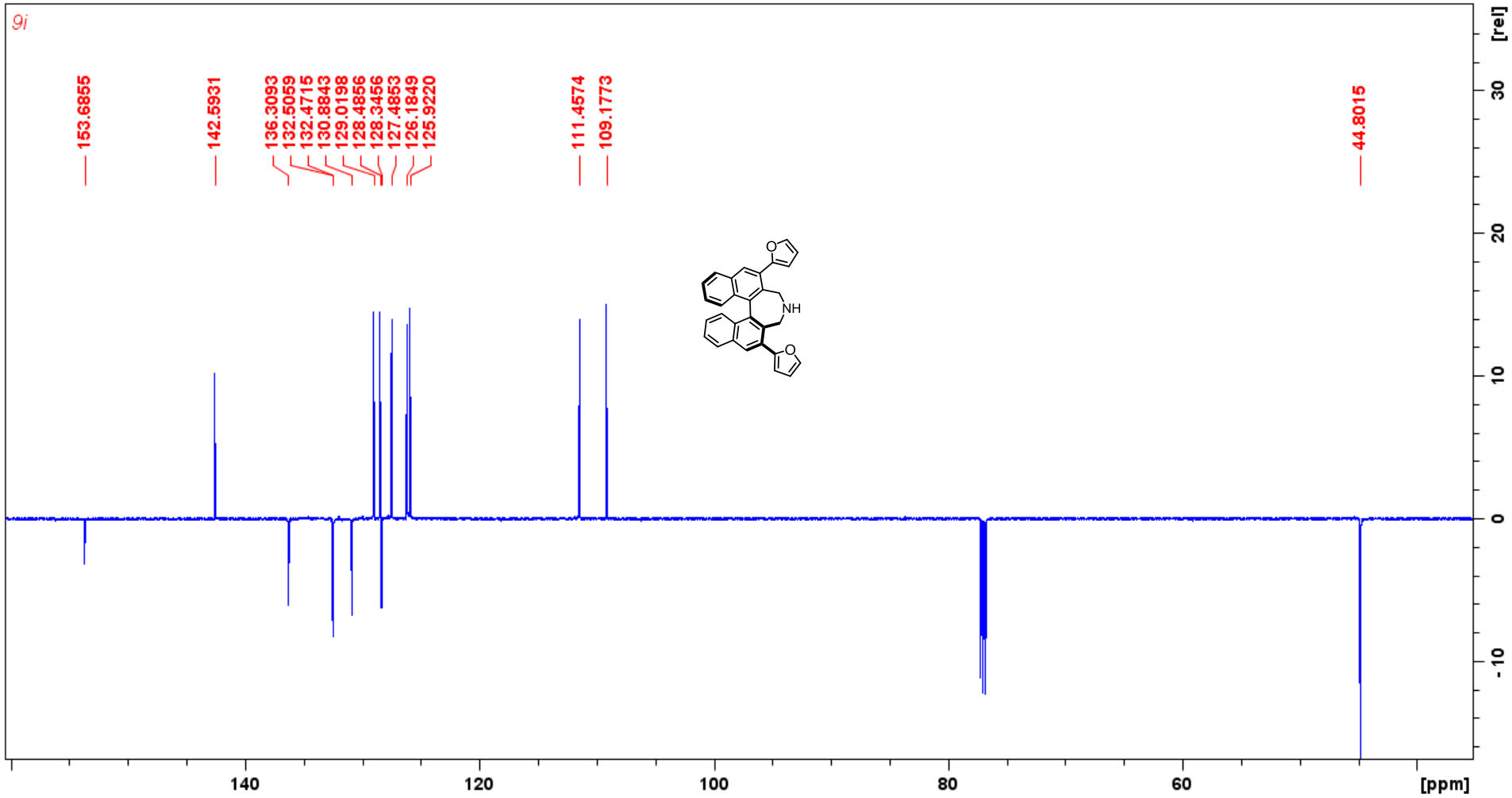

9g
F
F
F
NH
F
F
F
[rel]
15
10
5
0
2.0000
1.9326
2.0121
1.9972
5.7838
0.1102
1.9340
1.9673
1.2204
8
7
6
5
4
3
2
[ppm]

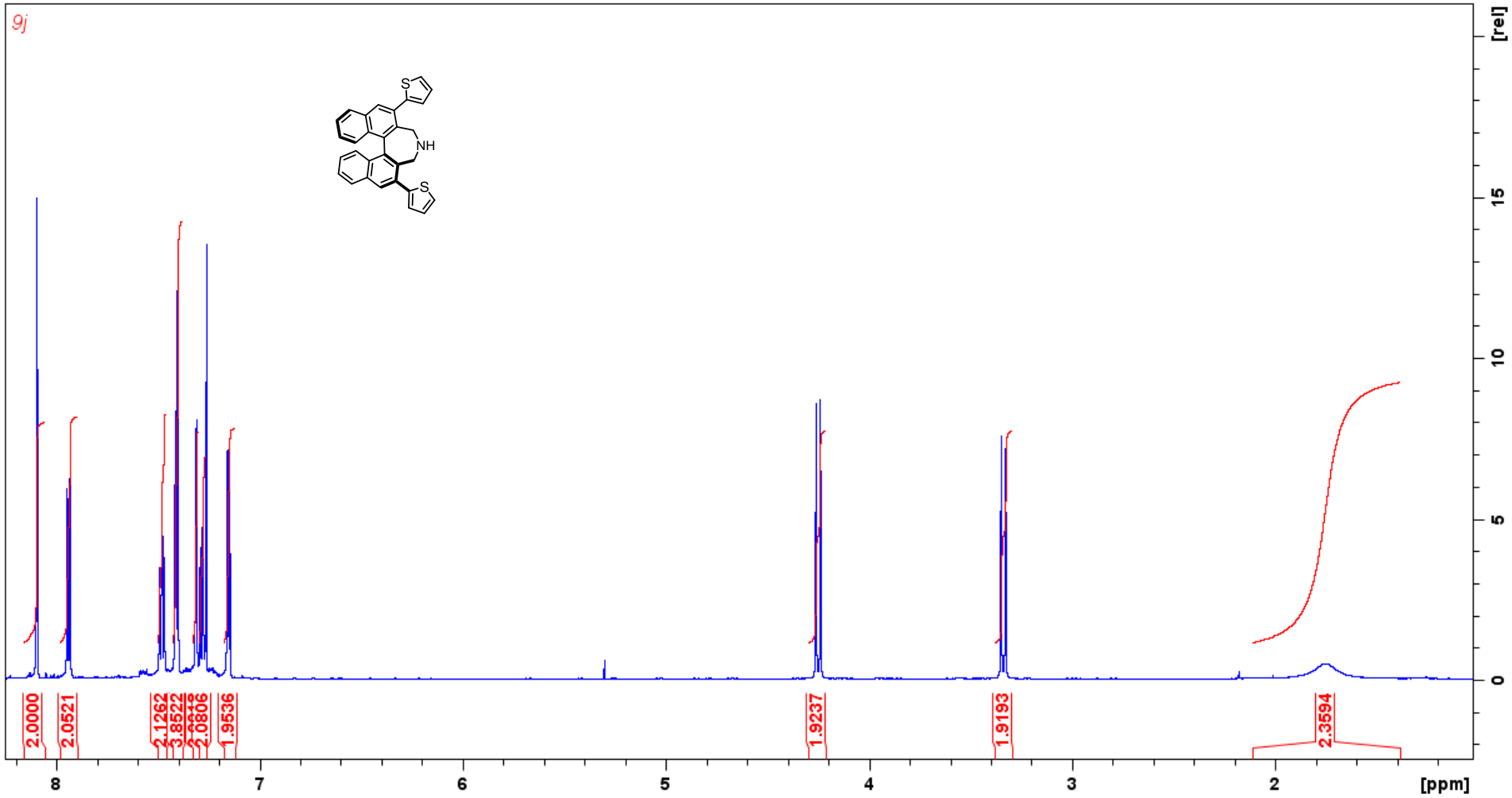

9g
152.2051
152.1635
152.1059
152.0636
149.7149
149.6721
149.6158
149.5754
140.7162
140.5663
140.4141
138.2129
138.0605
137.9085
137.2544
137.2063
137.1773
137.1274
137.0982
137.0492
136.7377
136.1796
132.4606
132.3026
131.0276
129.8525
128.3874
127.3992
126.4648
126.2955
113.9953
113.9421
M 113.8364
113.7855
77.3100
76.9935
76.6753
44.4279
F
F
F
NH
F
F
F
[rel]
20
15
10
5
0
-5
160
140
120
100
80
60
[ppm]

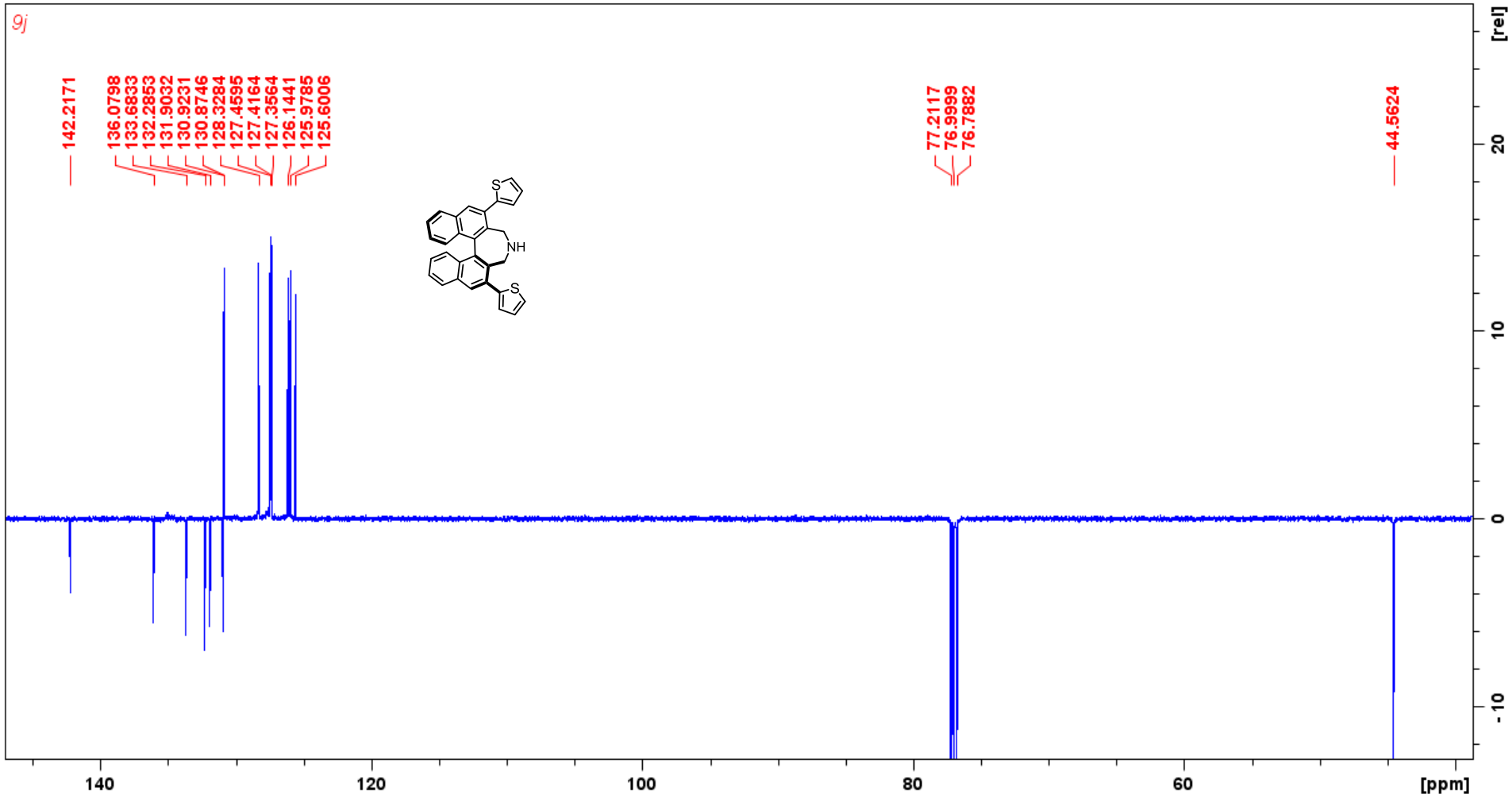

9h
F3C
CF3
NH
CF3
F3C
3.8895
3.8548
2.0038
1.9504
2.0000
2.0712
2.1575
2.1192
8
7
6
5
4
3
2
[ppm]
-0
1
2
3
4
[rel]

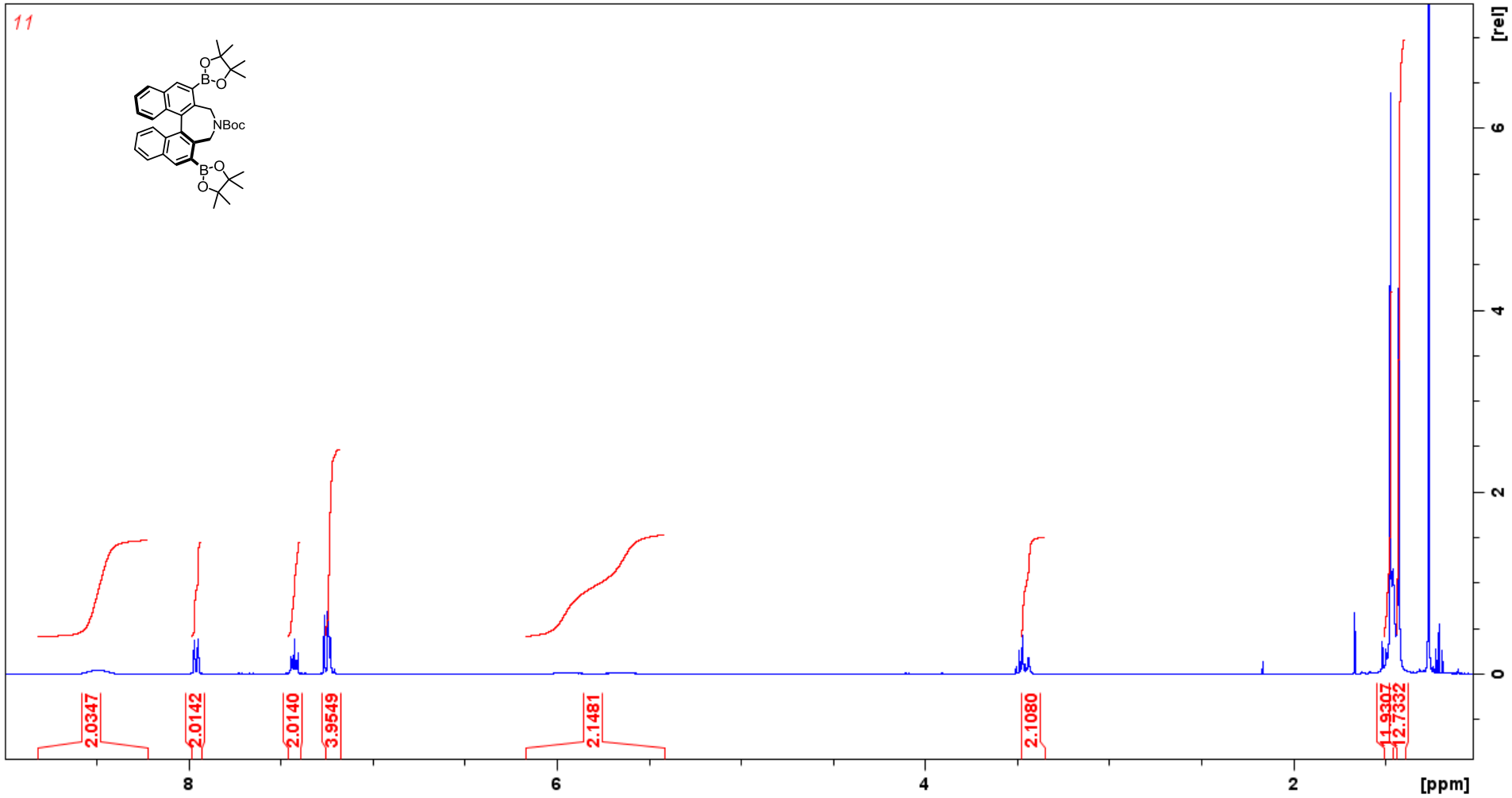

9h
143.1761
136.5429
136.3168
132.3444
132.3213
131.7452
131.5245
131.3021
131.1710
130.2976
129.8805
128.4749
127.3802
126.7531
126.4746
124.2270
122.4186
121.1848
44.4772
F3C
CF3
NH
CF3
F3C
[rel]
40
30
20
10
0
-10
-20
140
120
100
80
60
[ppm]

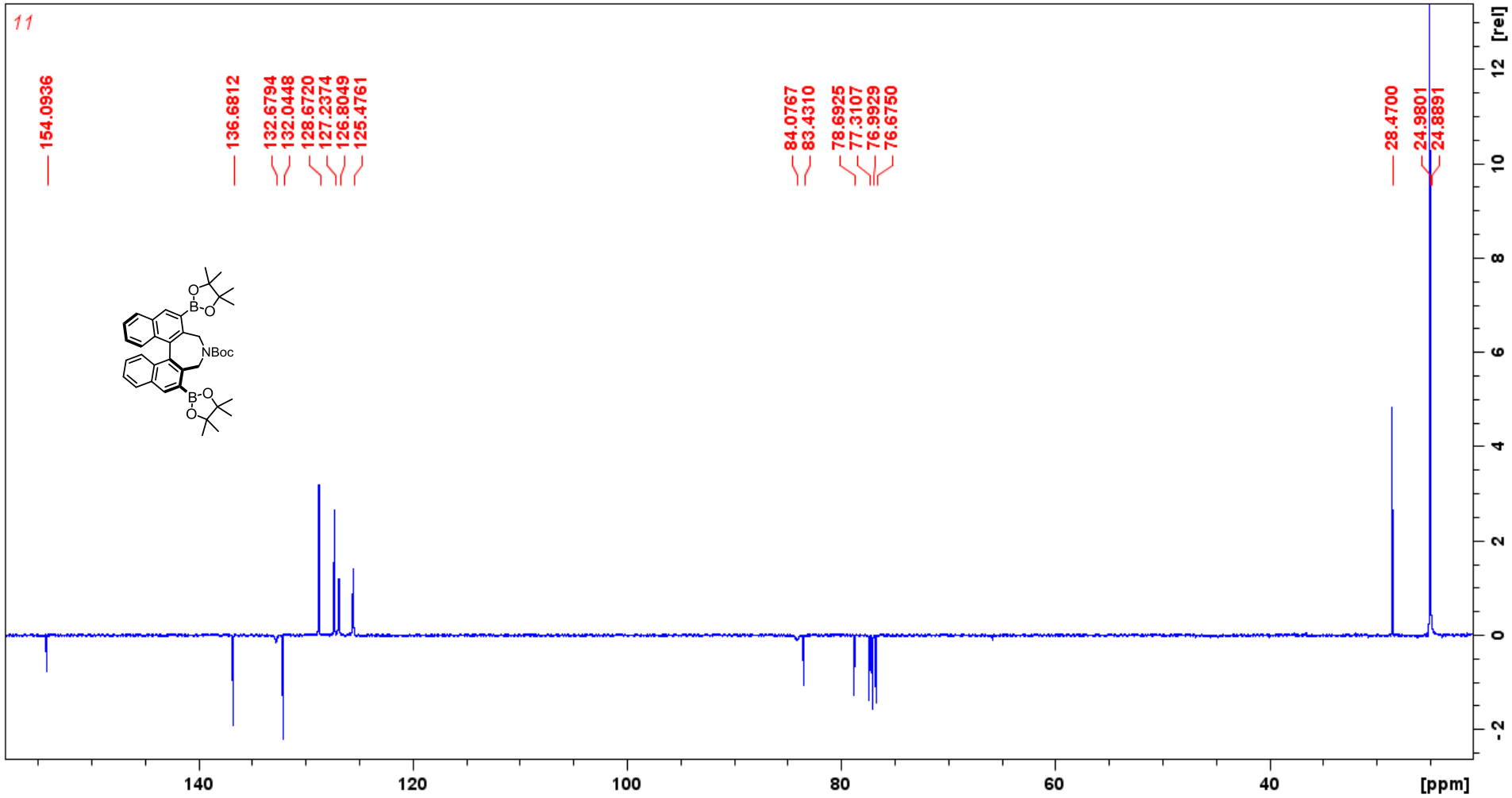

9i
NH
O
O
2.0000
2.0448
1.9359
2.1887
2.1710
2.0138
2.0288
2.0846
2.0180
8
7
6
5
4
3
2
[ppm]
0
2
4
6
[rel]

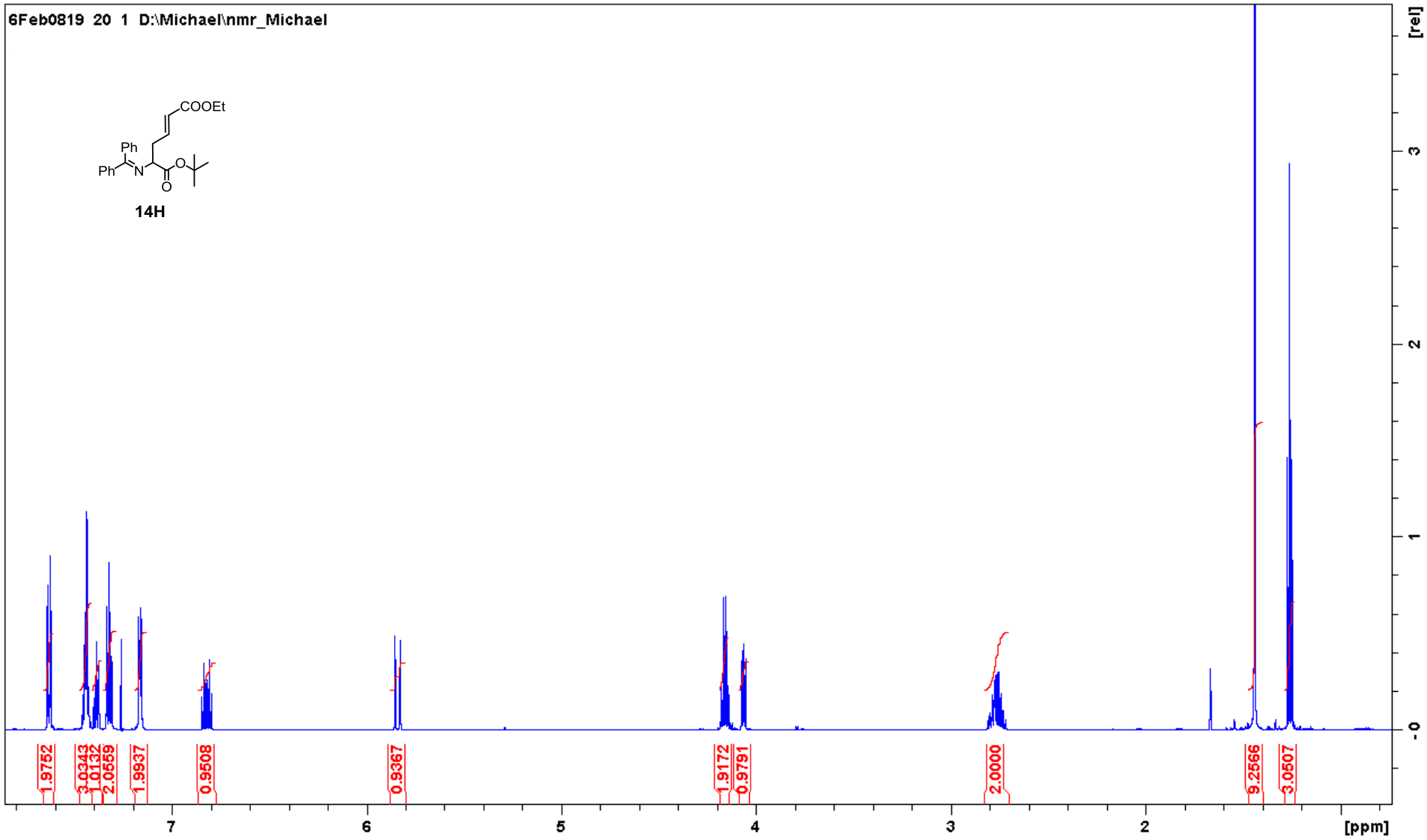

9i
153.6855
142.5931
136.3093
132.5059
132.4715
130.8843
129.0198
128.4856
128.3456
127.4853
126.1849
125.9220
111.4574
109.1773
44.8015
NH
O
O
[rel]
30
20
10
0
- 10
140
120
100
80
60
[ppm]

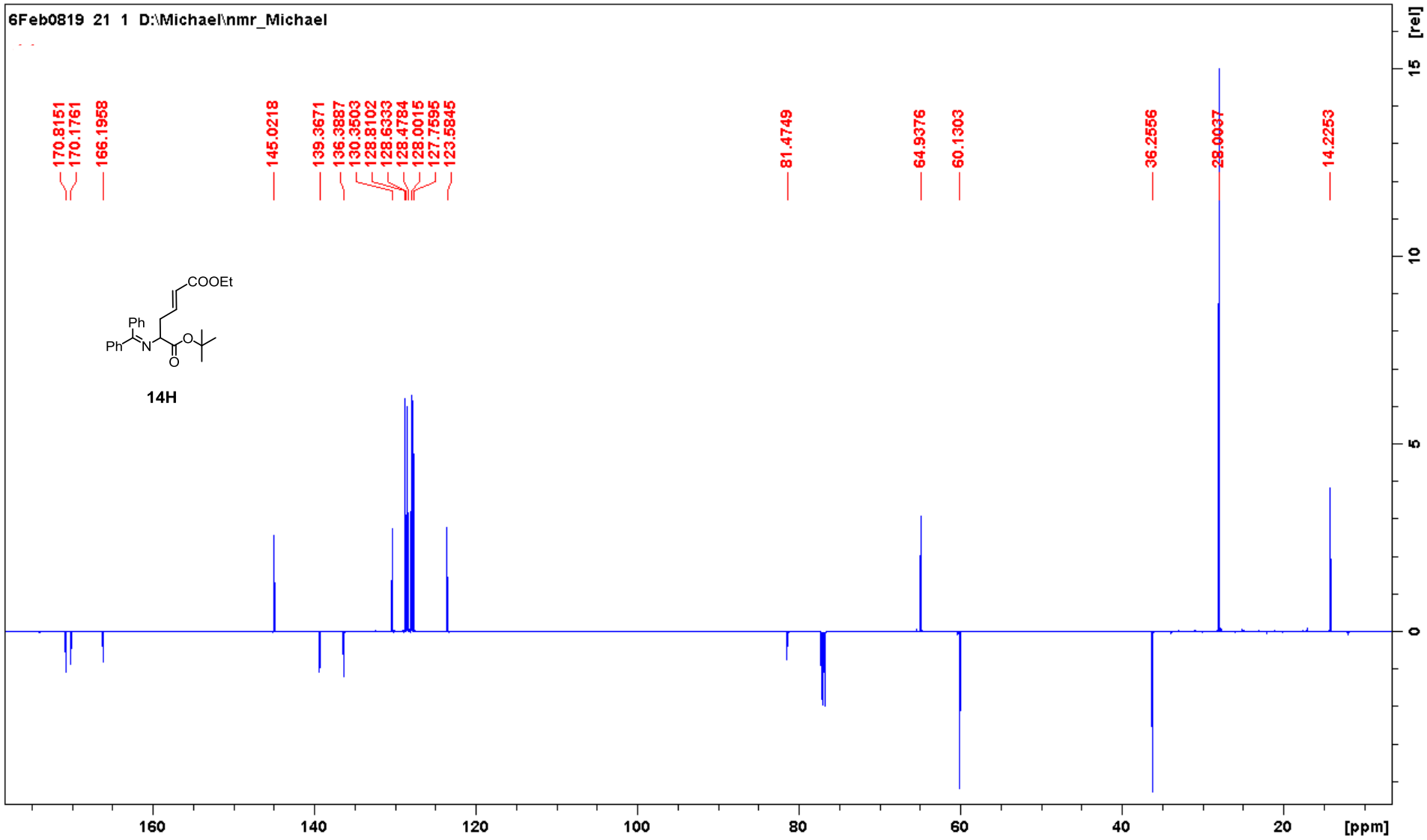

9j
S
NH
S
[rel]
15
10
5
0
2.0000
2.0521
2.1262
3.8522
2.0806
1.9536
1.9237
1.9193
2.3594
8
7
6
5
4
3
2
[ppm]

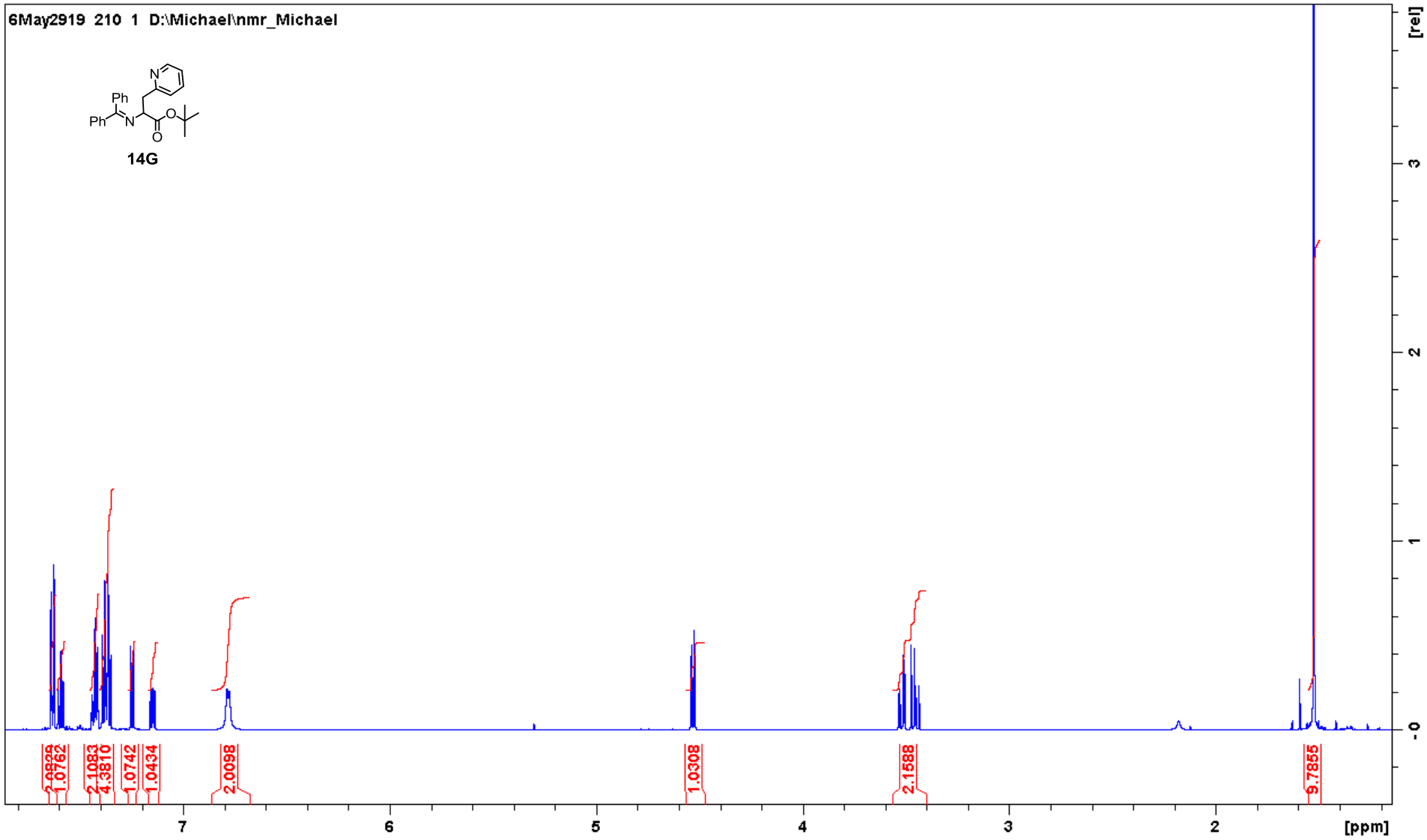

9j
142.2171
136.0798
133.6833
132.2853
131.9032
130.9231
130.8746
128.3284
127.4595
127.4164
127.3564
126.1441
125.9785
125.6006
77.2117
76.9999
76.7882
44.5624
S
NH
S
[rel]
20
10
0
- 10
140
120
100
80
60
[ppm]

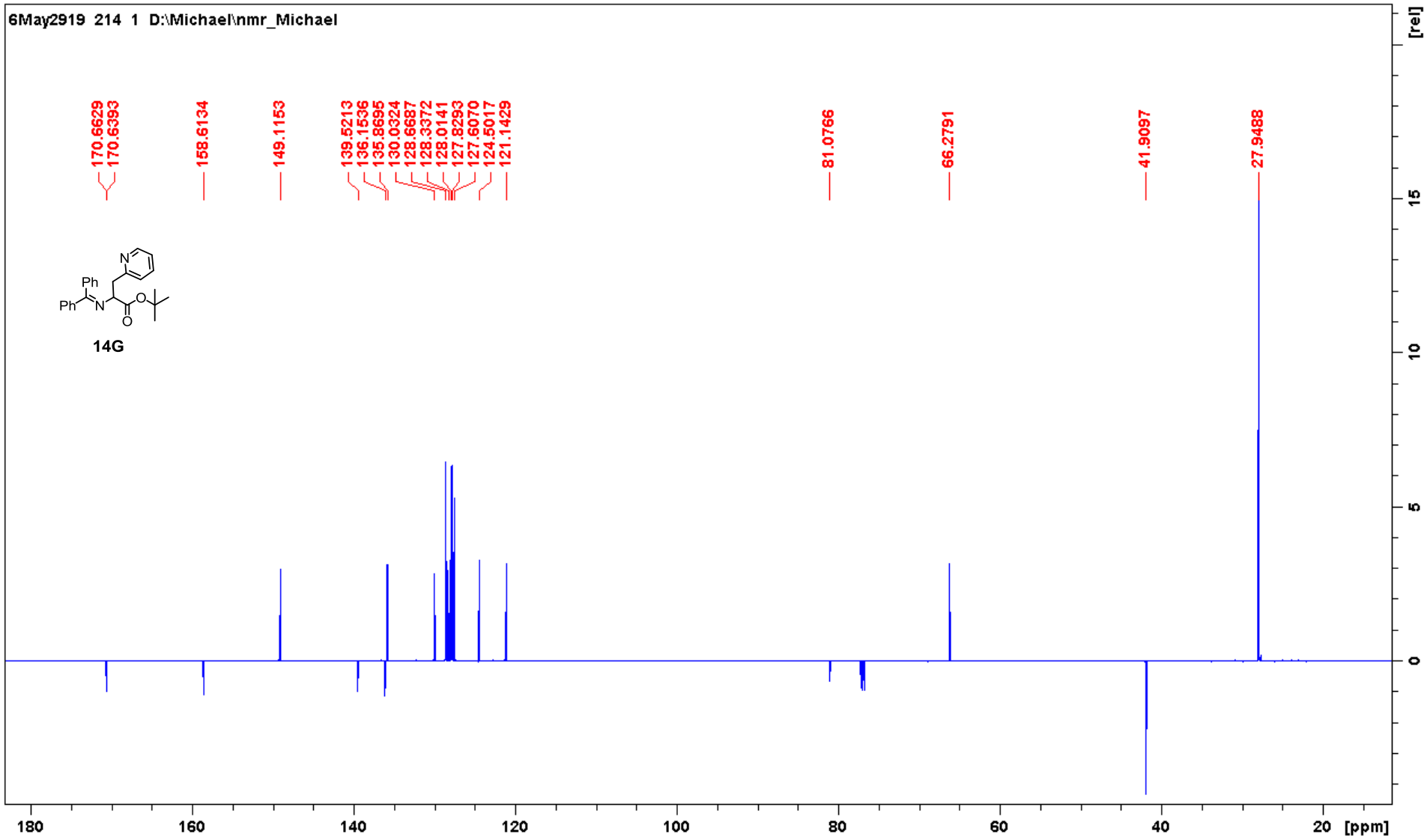

11
NBoc
B-O
B-O
[rel]
0
2
4
6
2.0347
2.0142
2.0140
3.9549
2.1481
2.1080
11.9307
12.7332
8
6
4
2
[ppm]

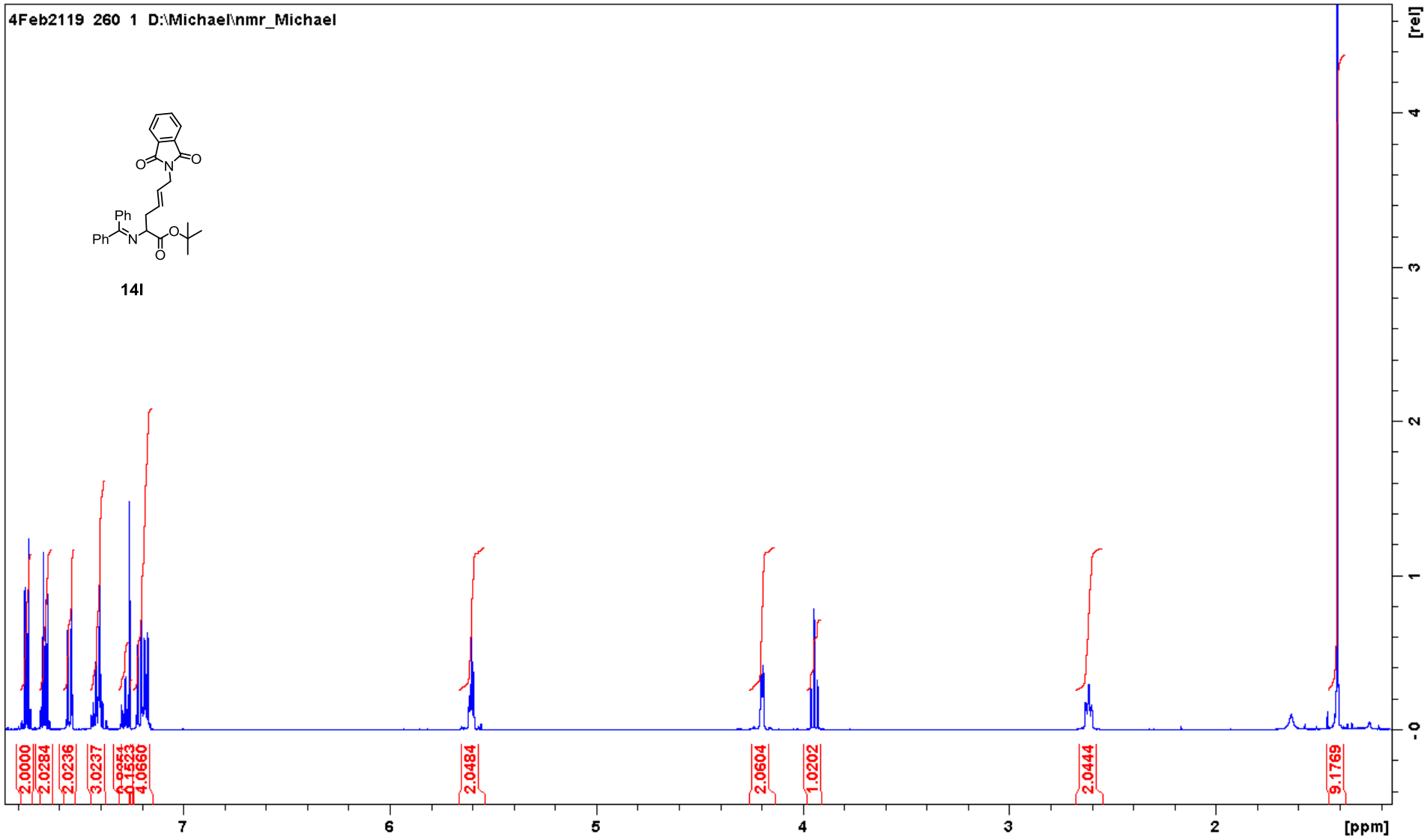

11
154.0936
136.6812
132.6794
132.0448
128.6720
127.2374
126.8049
125.4761
84.0767
83.4310
78.6925
77.3107
76.9929
76.6750
28.4700
24.9801
24.8891
NBoc
[rel]
[ppm]

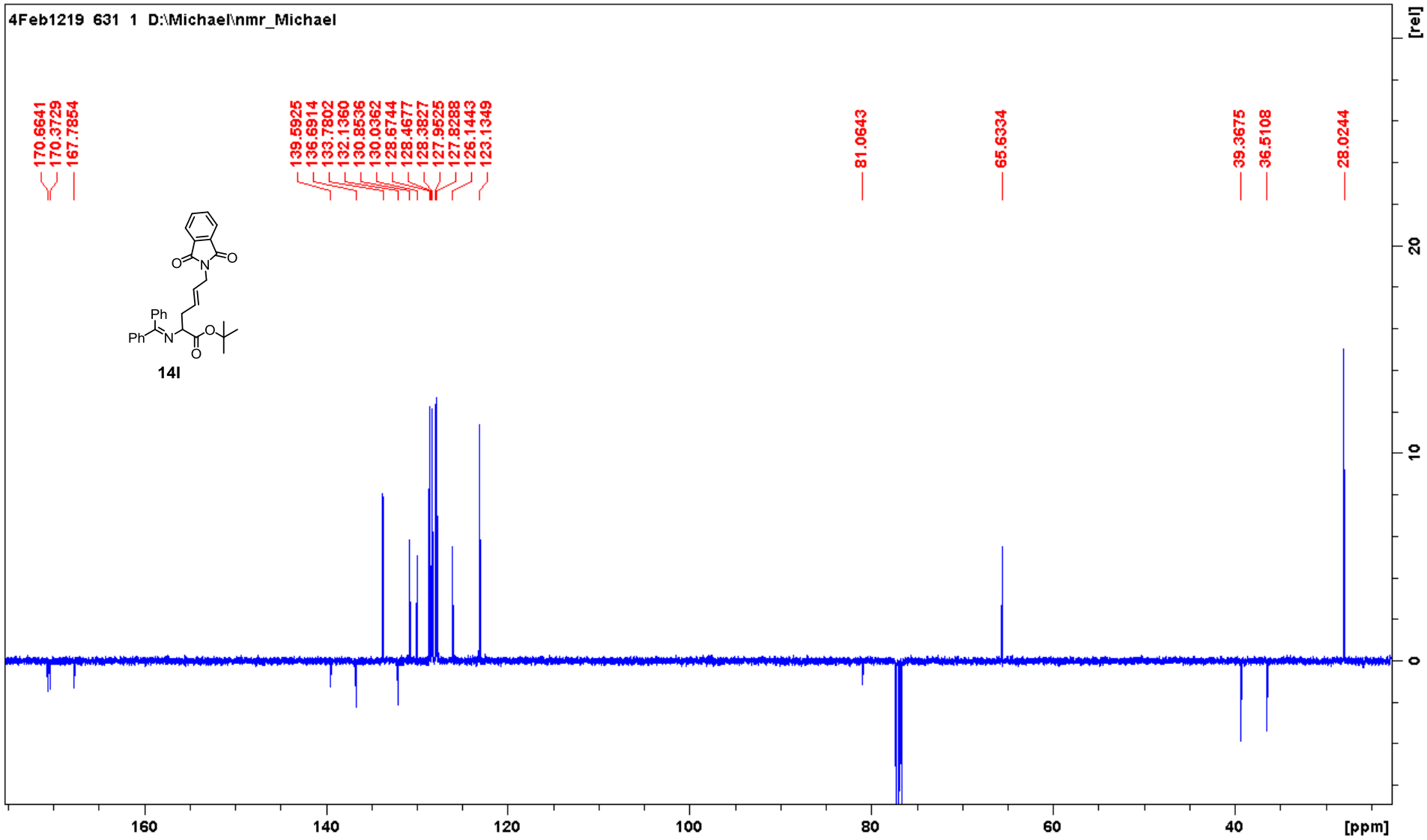

6Feb0819 20 1 D:\Michael\nmr_Michael
COOEt
Ph
Ph
N
O
O
14H
[rel]
3
2
1
-0
1.9752
3.0343
1.0132
2.0559
1.9937
0.9508
0.9367
1.9172
0.9791
2.0000
9.2566
3.0507
7
6
5
4
3
2
[ppm]

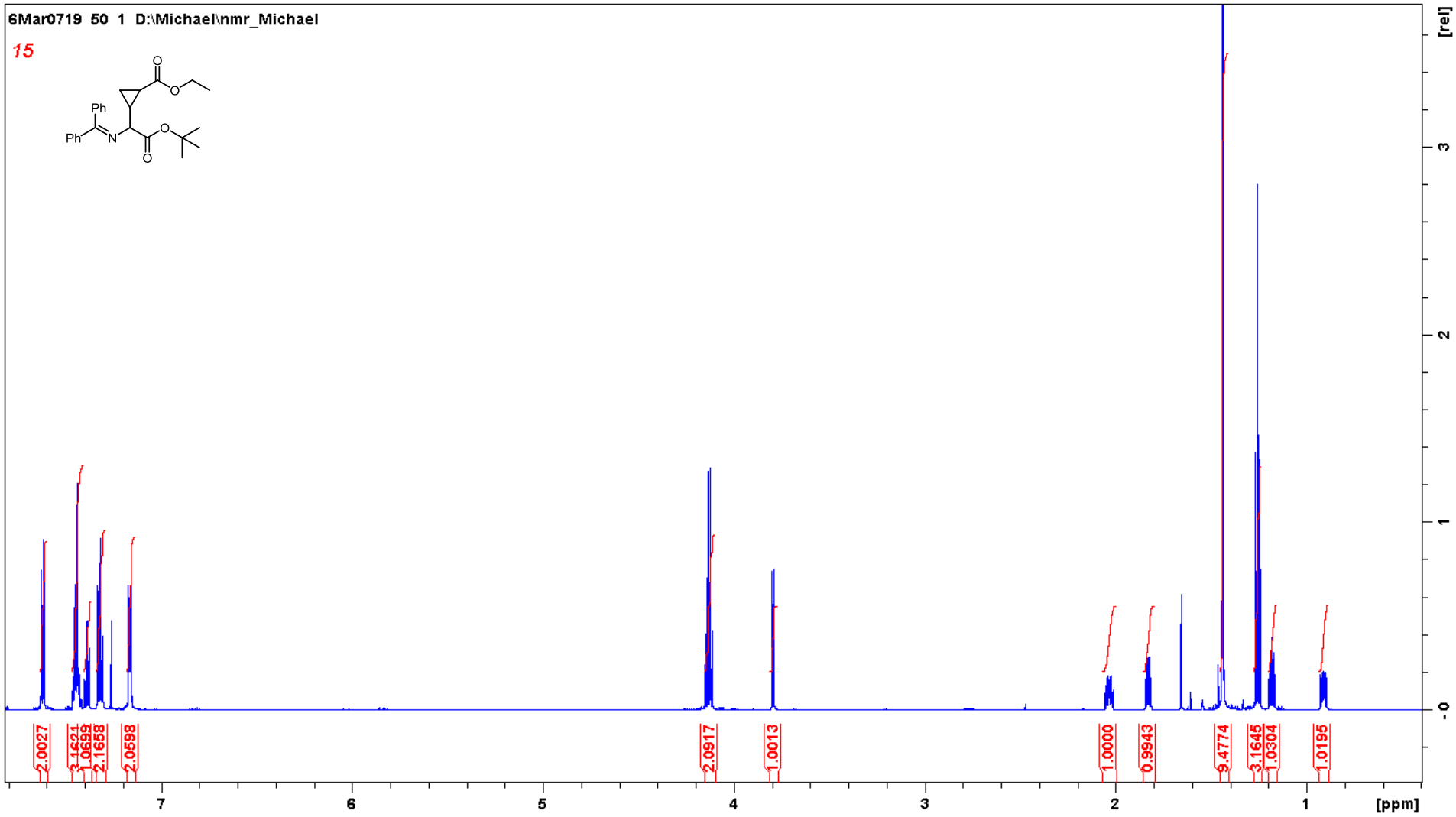

6Feb0819 21 1 D:\Michael\nmr_Michael
170.8151
170.1761
166.1958
145.0218
139.3671
136.3887
130.3503
128.8102
128.6333
128.4784
128.0015
127.7595
123.5845
81.4749
64.9376
60.1303
36.2556
28.0037
14.2253
COOEt
Ph
Ph
N
O
O
14H
[rel]
15
10
5
0
160
140
120
100
80
60
40
20
[ppm]

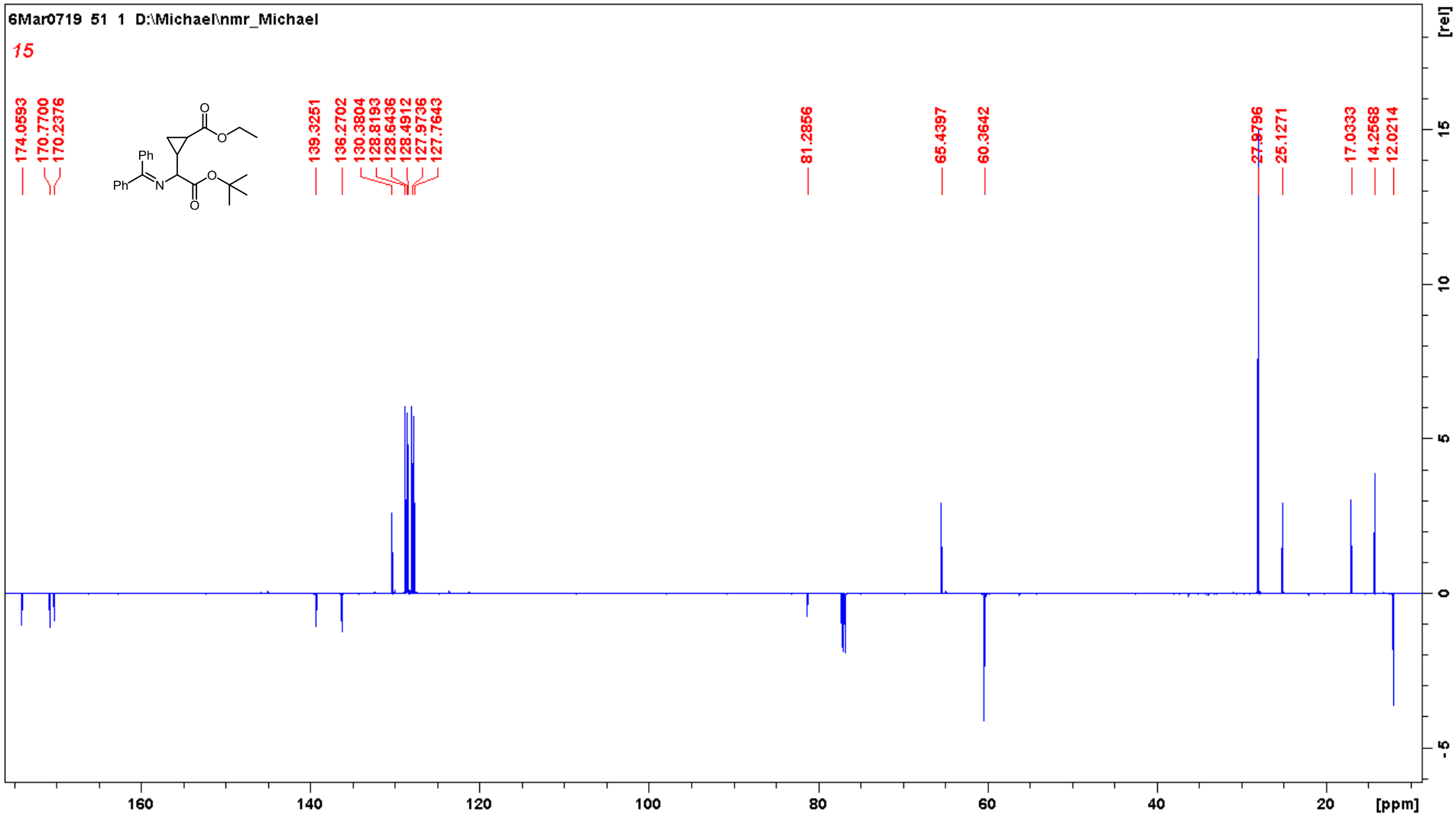

6May2919 210 1 D:\Michael\nmr_Michael
14G
2.0829
1.0762
2.1083
4.3810
1.0742
1.0434
2.0098
1.0308
2.1588
9.7855
7
6
5
4
3
2
[ppm]
[rel]
0
1
2
3

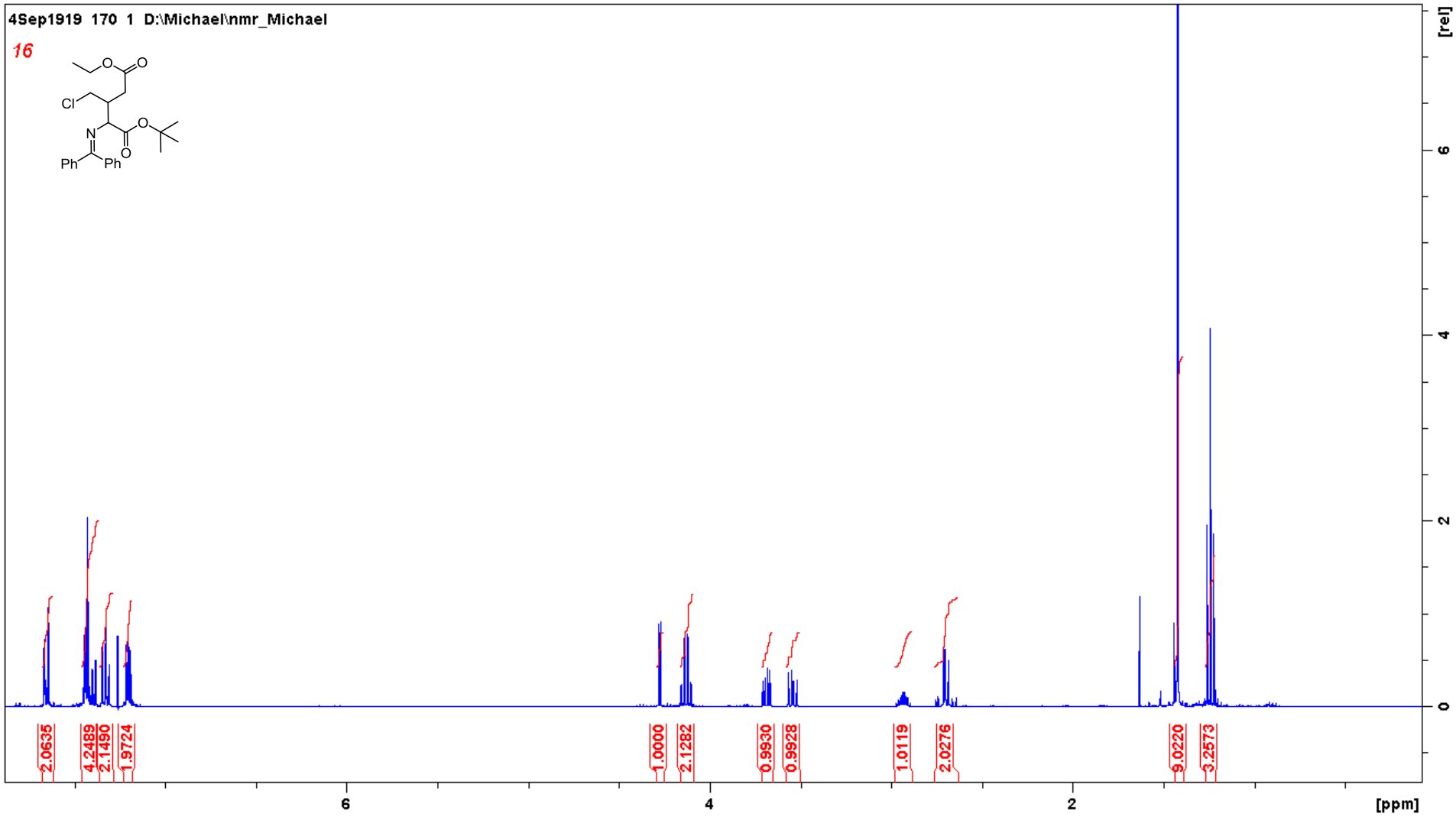

6May2919 214 1 D:\Michael\nmr_Michael
170.6629
170.6393
158.6134
149.1153
139.5213
136.1536
135.8695
130.0324
128.6687
128.3372
128.0141
127.8293
127.6070
124.5017
121.1429
81.0766
66.2791
41.9097
27.9488
14G
[rel]
0
5
10
15
180
160
140
120
100
80
60
40
20
[ppm]


4Feb2119 260 1 D:\Michael\nmr_Michael
Ph
Ph
N
O
O
O
O
O
N
14l
2.0000
2.0284
2.0236
3.0237
2.0484
2.0604
1.0202
2.0444
9.1769
7
6
5
4
3
2
[ppm]
[rel]
0
1
2
3
4


4Feb1219 631 1 D:\Michael\nmr_Michael
170.6641
170.3729
167.7854
139.5925
136.6914
133.7802
132.1360
130.8536
130.0362
128.6744
128.4677
128.3827
127.9525
127.8288
126.1443
123.1349
81.0643
65.6334
39.3675
36.5108
28.0244
[rel]
20
10
0
160
140
120
100
80
60
40
[ppm]
Ph
Ph
N
O
O
O
O
O
14l


6Mar0719 50 1 D:\Michael\nmr_Michael
15
Ph
Ph
N
O
O
O
O
[rel]
3
2
1
-0
2.0027
3.1621
1.0699
2.1658
2.0598
2.0917
1.0013
1.0000
0.9943
9.4774
3.1645
1.0304
1.0195
7
6
5
4
3
2
1
[ppm]


6Mar0719 51 1 D:\Michael\nmr_Michael
15
174.0593
170.7700
170.2376
139.3251
136.2702
130.3804
128.8193
128.6436
128.4912
127.9736
127.7643
81.2856
65.4397
60.3642
27.9796
25.1271
17.0333
14.2568
12.0214
Ph
Ph
N
O
O
O
O
[rel]
15
10
5
0
-5
160
140
120
100
80
60
40
20
[ppm]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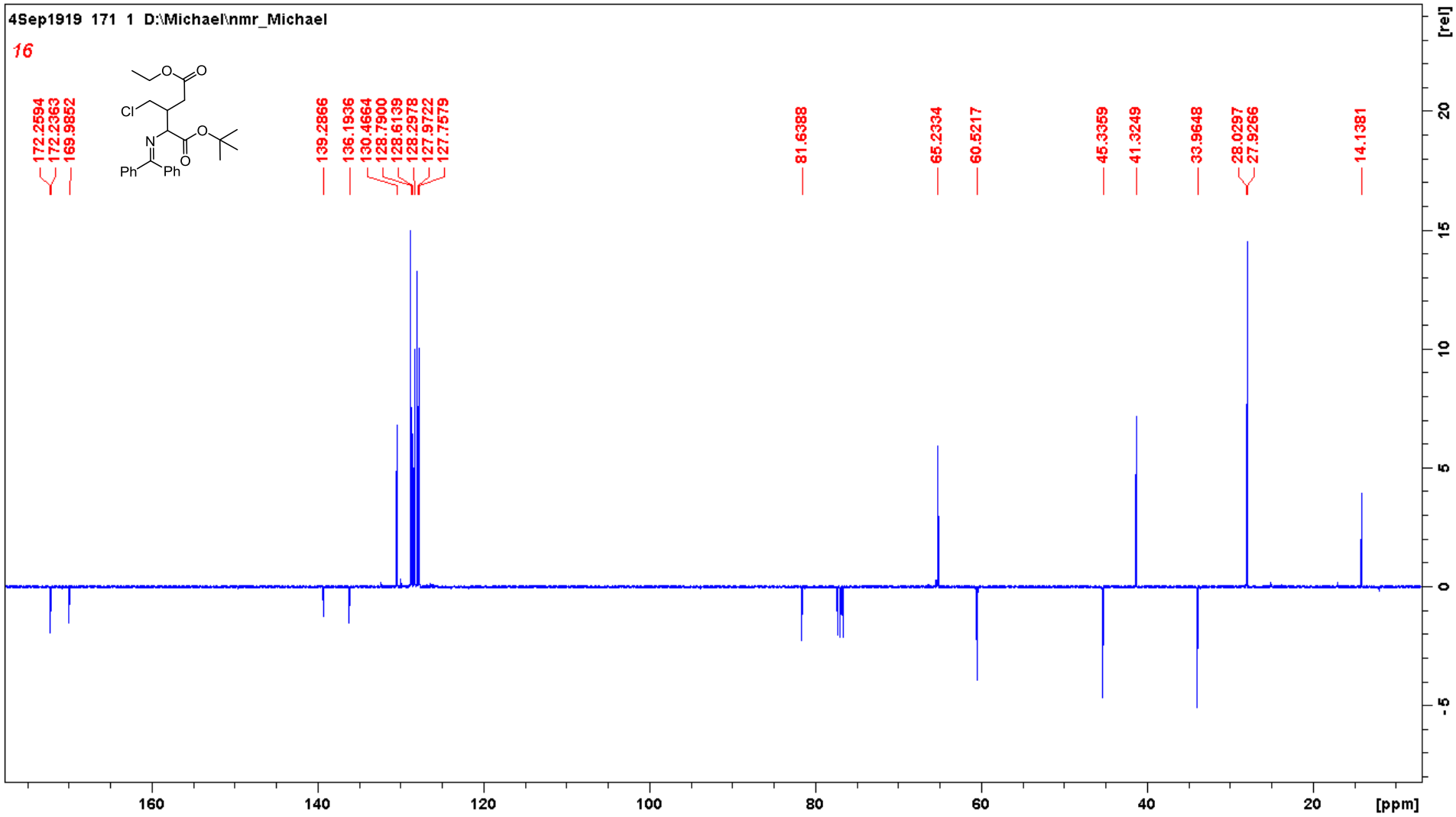
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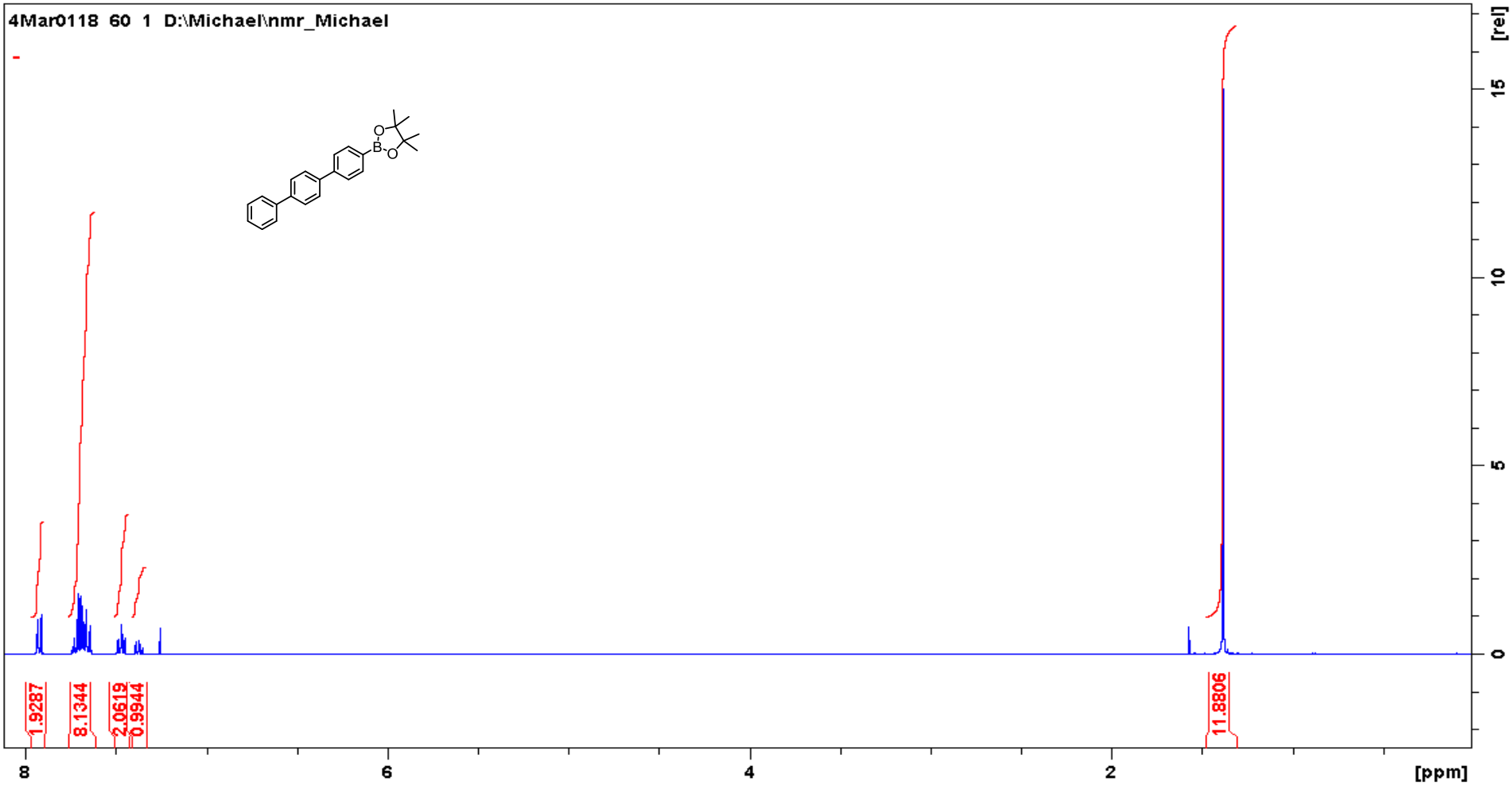
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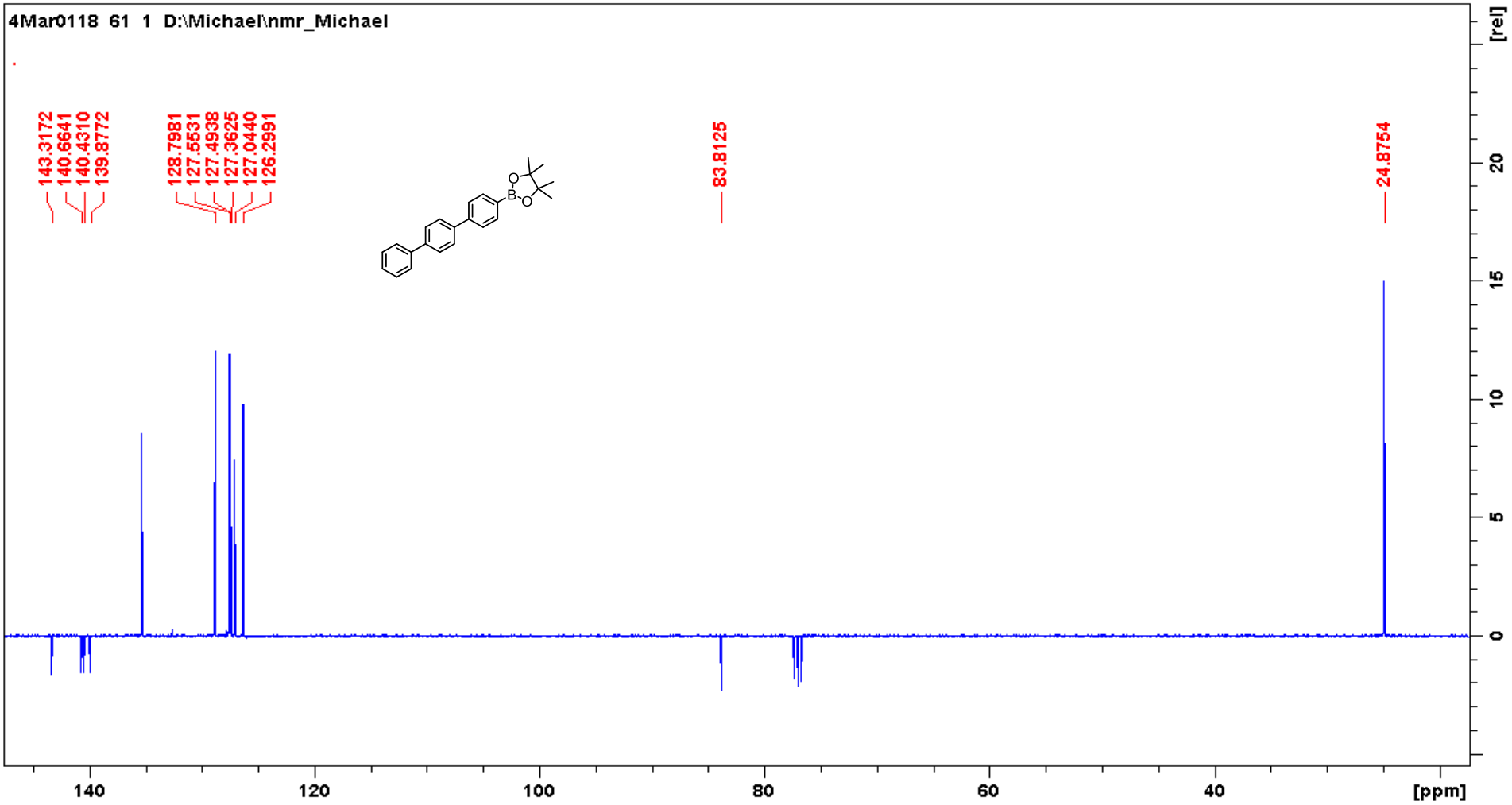
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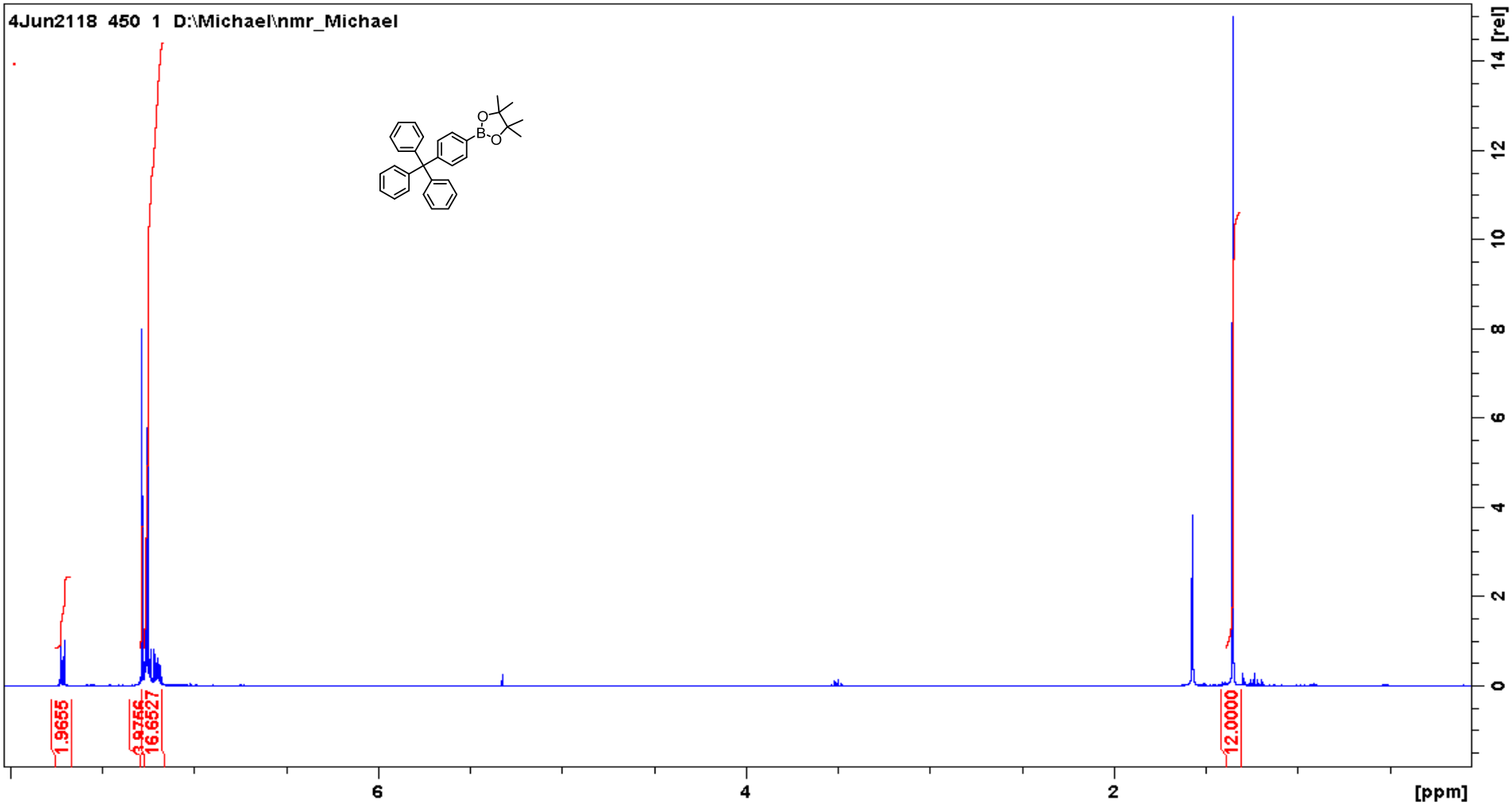
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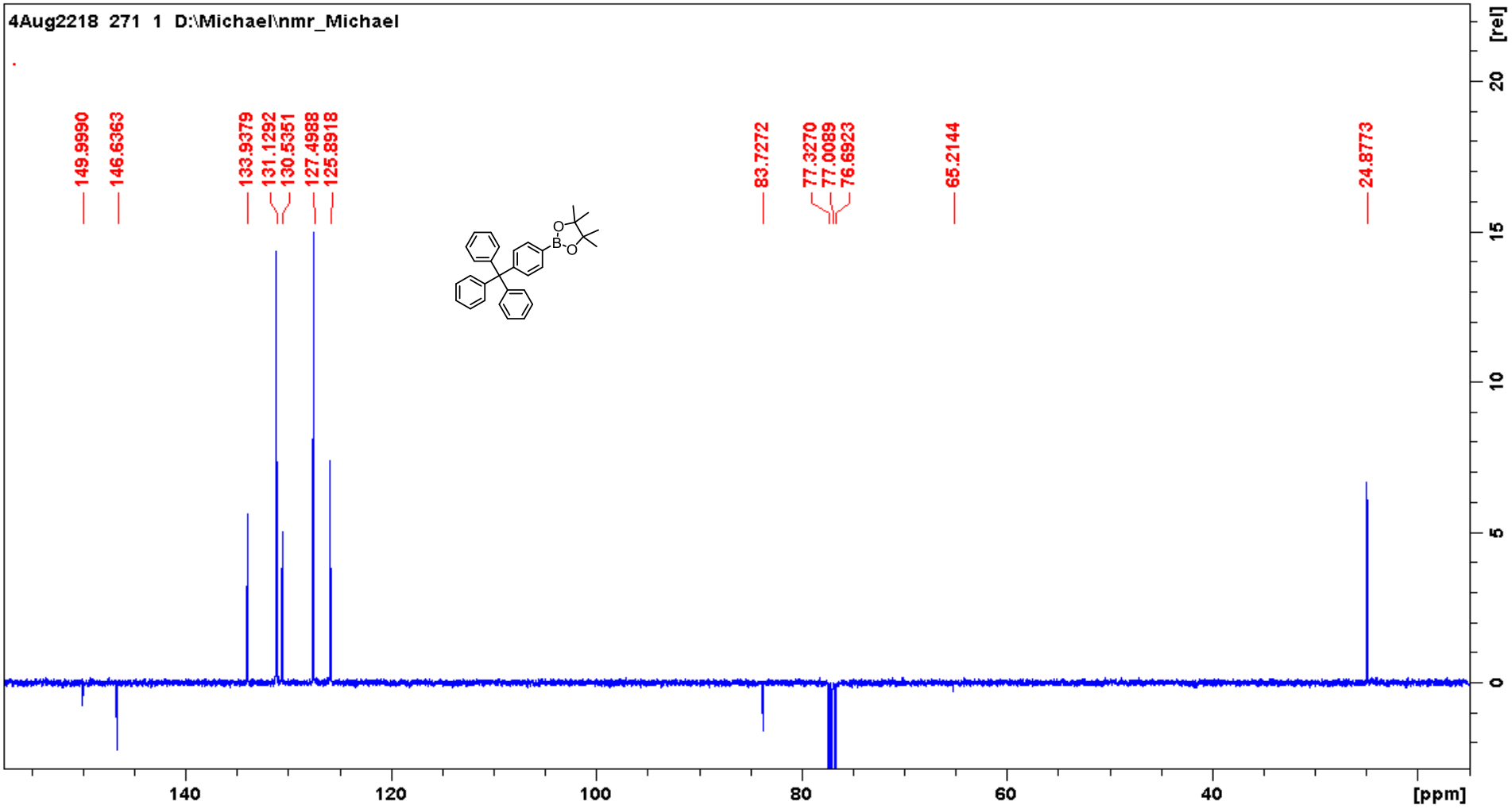
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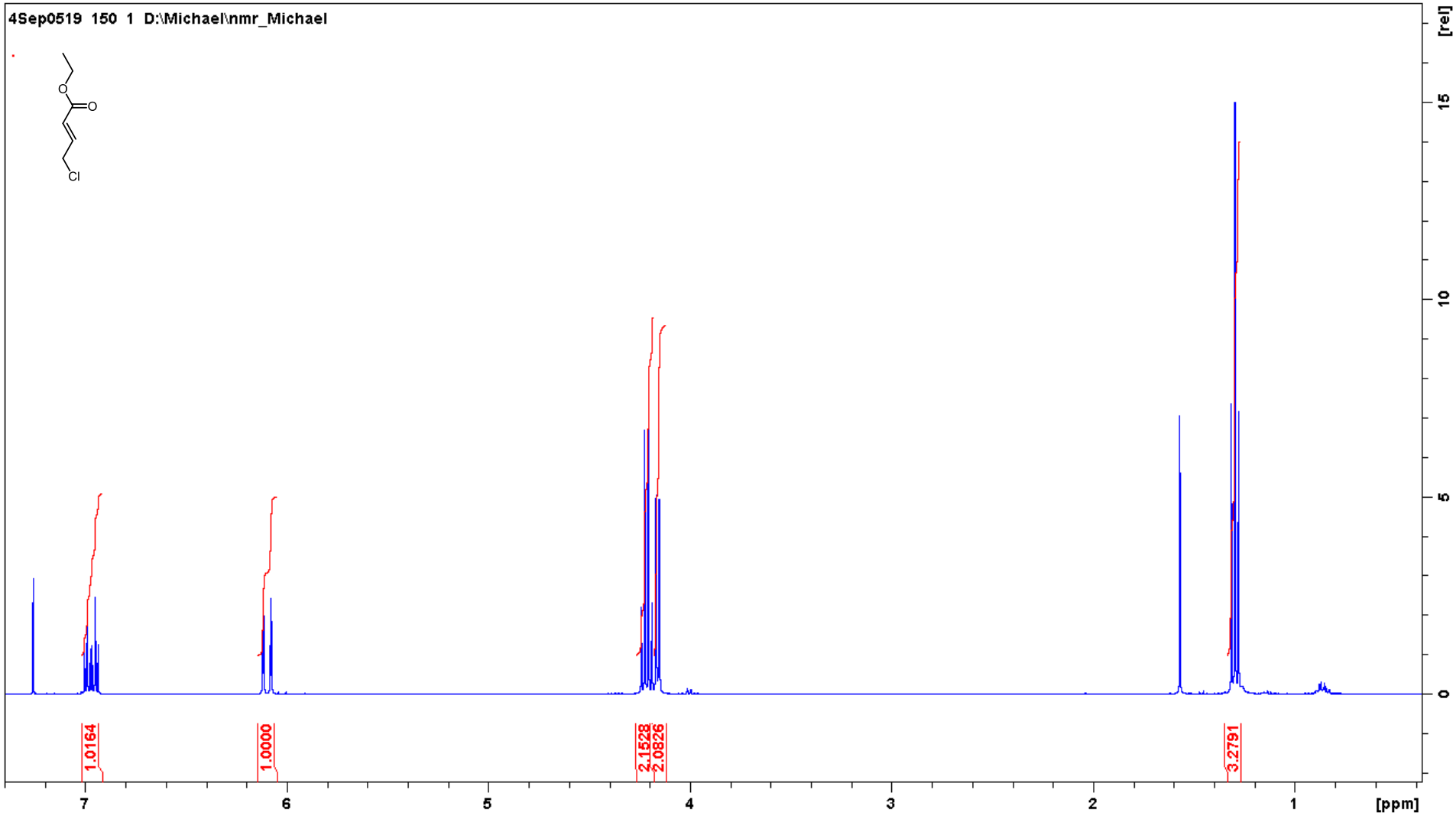
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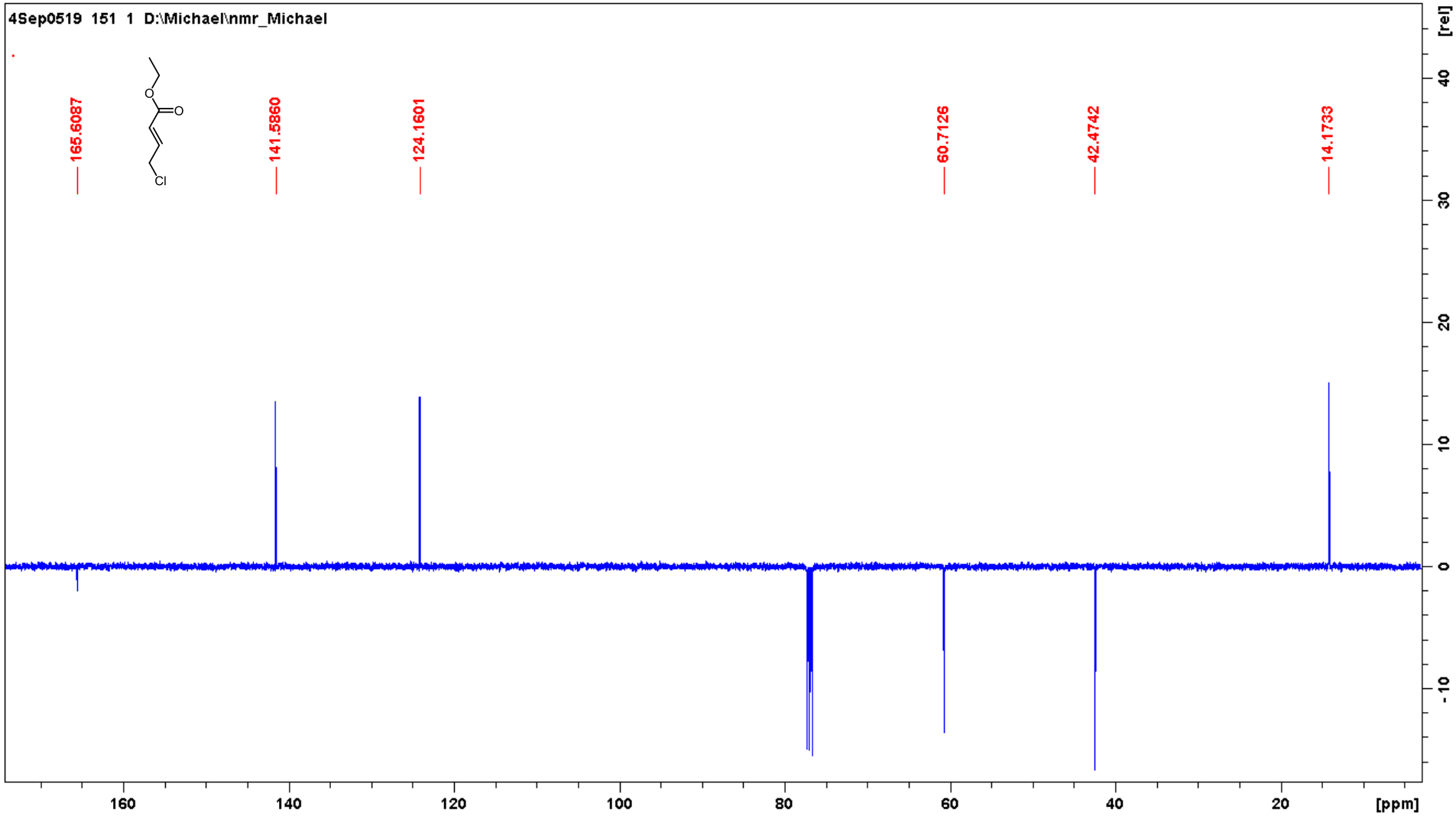
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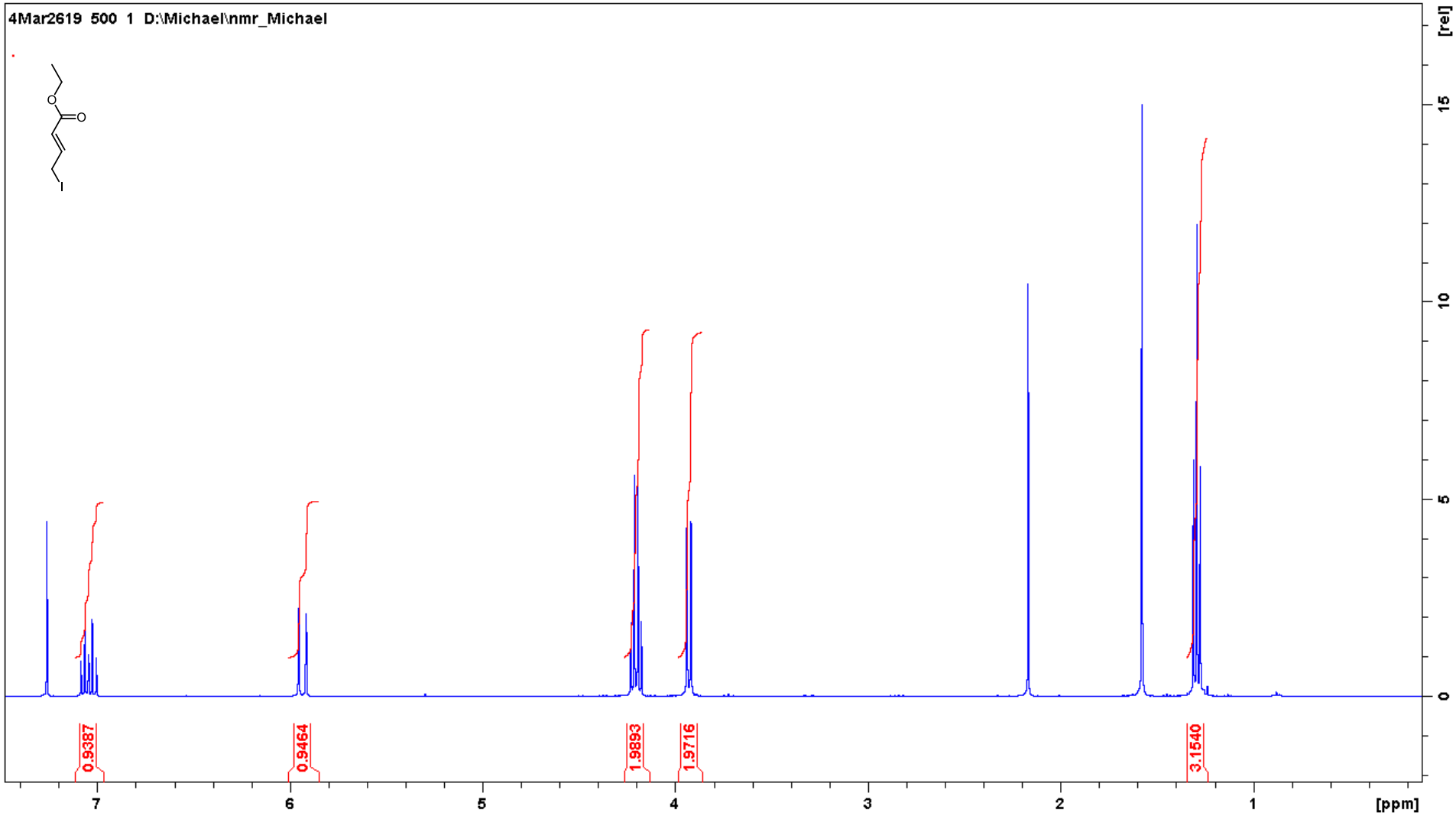
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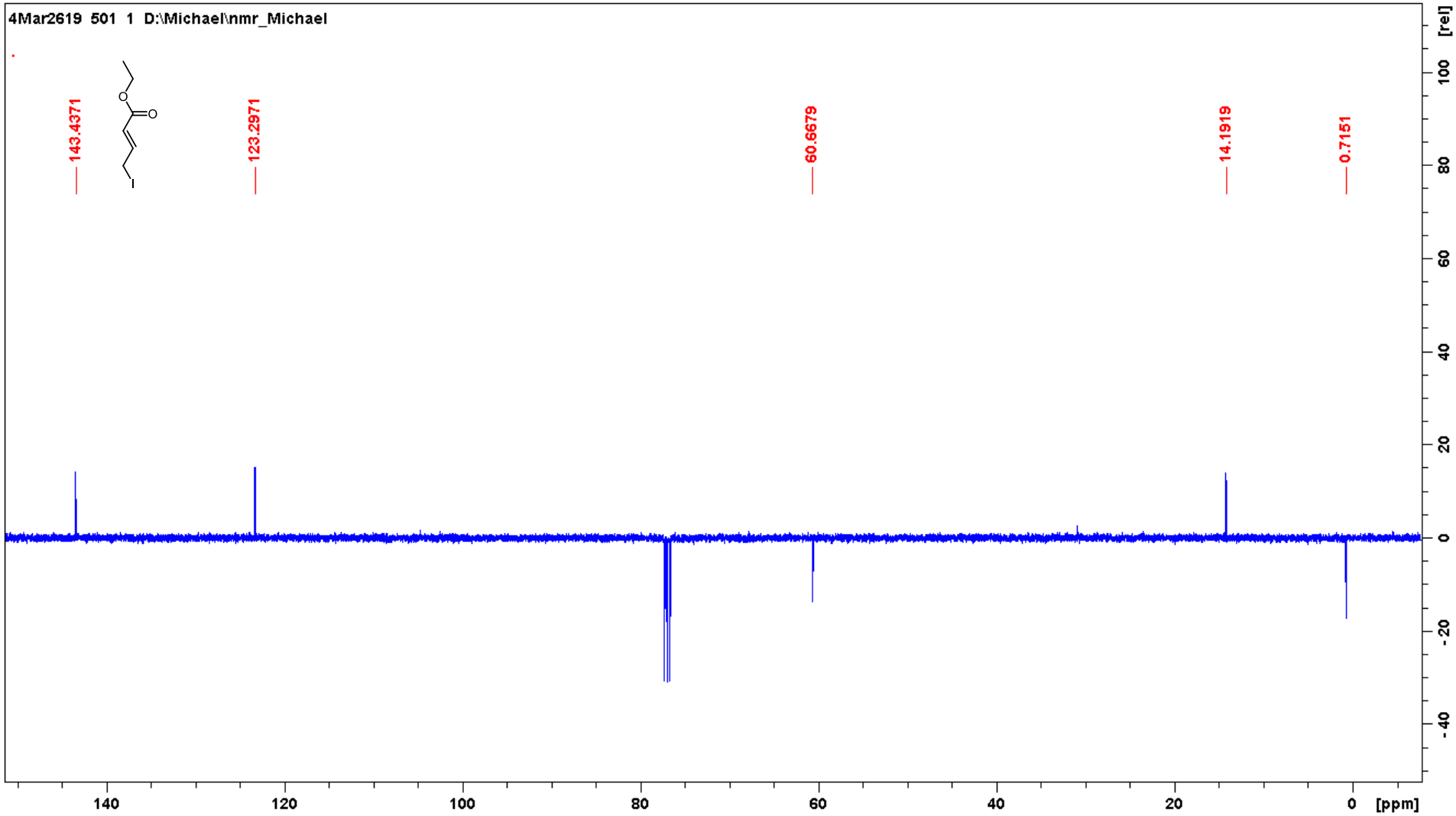
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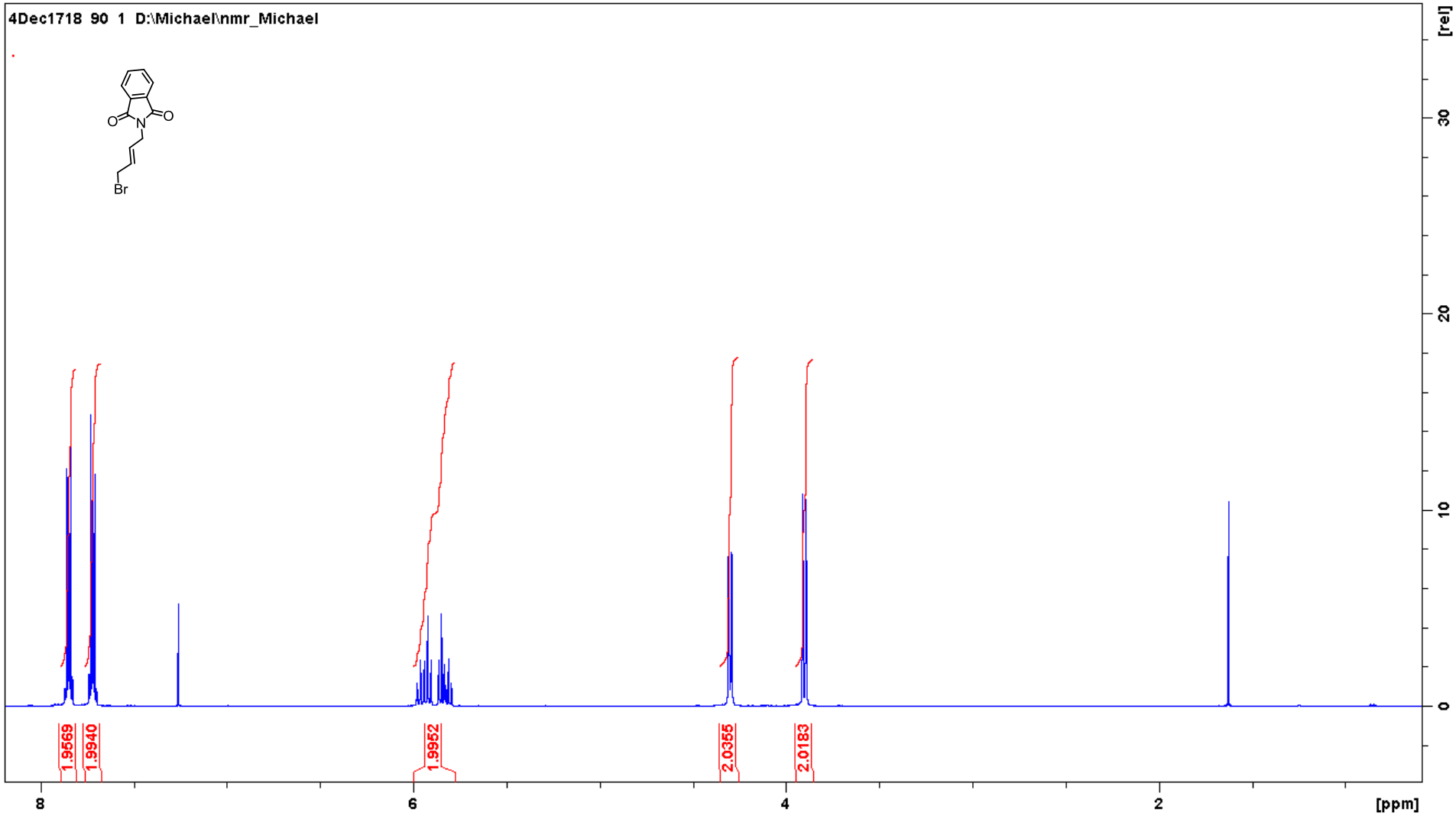
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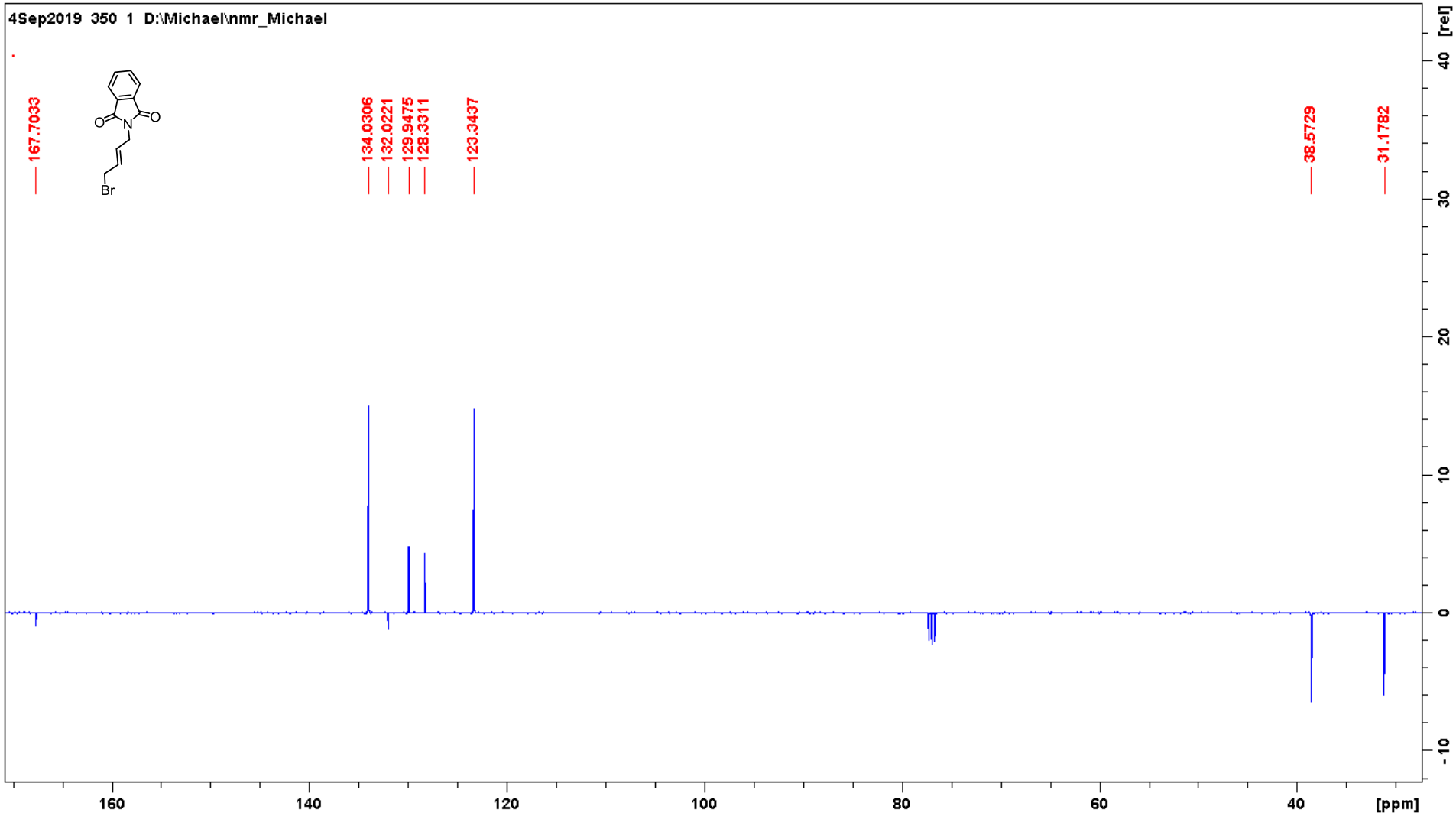
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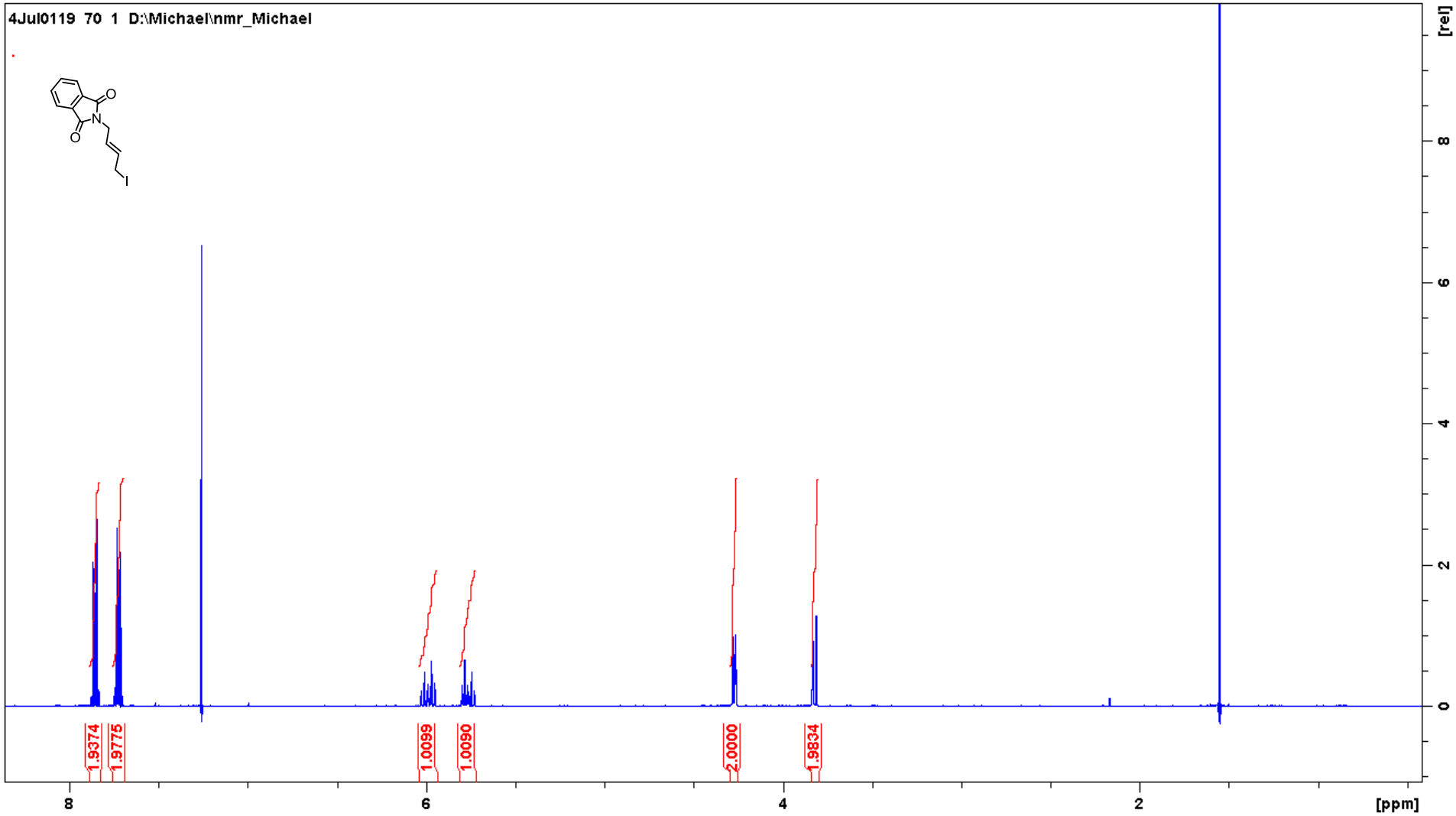
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[ppm]
[rel]
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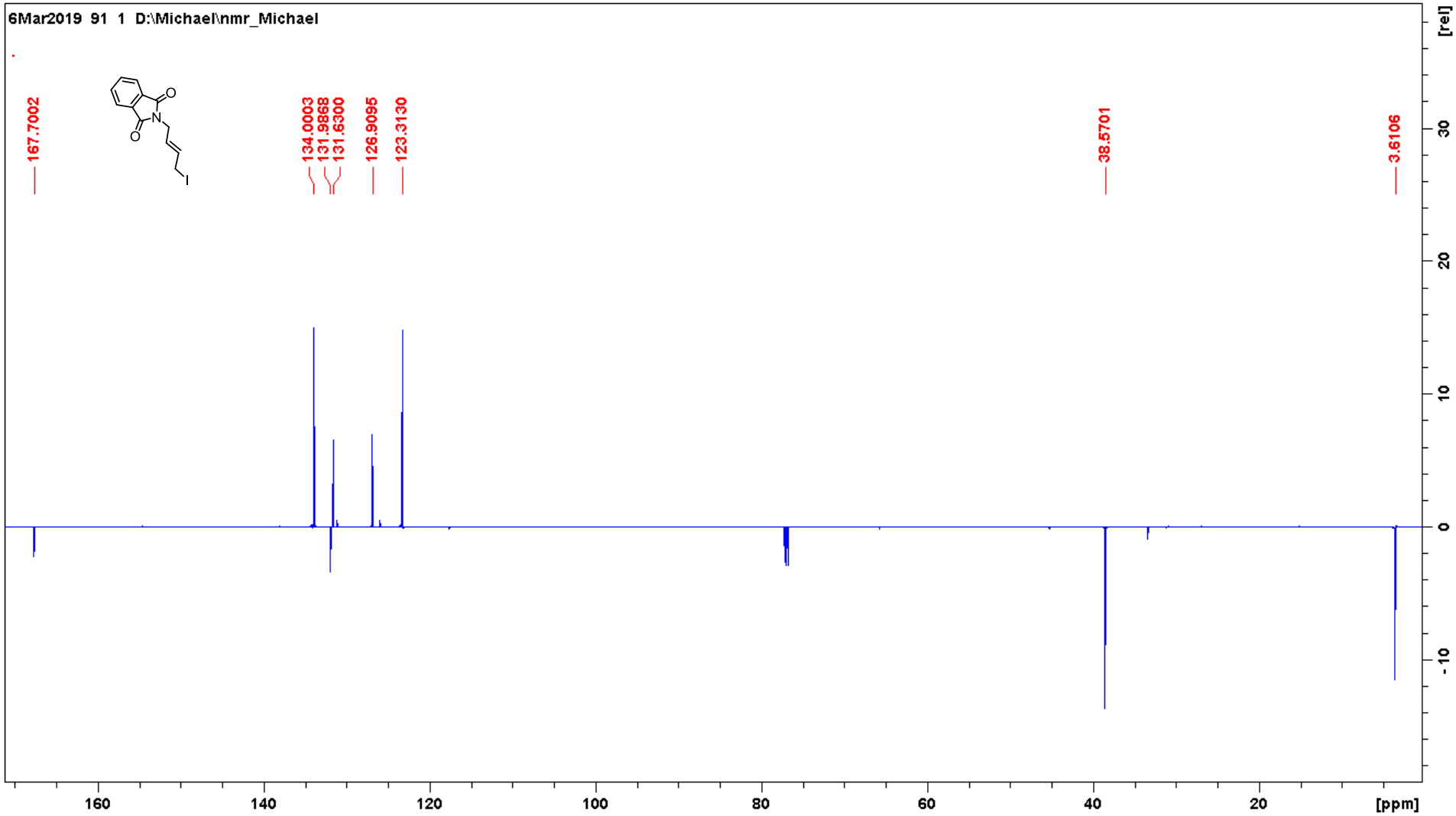
8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80
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40
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[ppm]

Comments on screening experiments in PTC – Practical aspects

For screening experiments it is essential to establish a standardized, reproducible procedure with minimum expenditure of time and resources. Typical key data of interest are conversion, regioselectivity, expressed in relative yields of regioisomers, formation of side and sequence products and dia- and enantioselectivity. Depending on complexity of the reaction mixture a column chromatography is usually performed to obtain "isolated yields". This step will give reproducible and reliable results if conducted on >100 mg scale but becomes increasingly error-prone on small scale. Moreover, this is the most time consuming part of the test reaction runs.

We therefore set out to develop a small scale screening procedure for our ligands, tested first in a prototypical reaction (**12** + **13A**, Scheme 2) which gives information on a) conversion (relativ to starting material), b) amount of product formed and isolated after extraction, and c) determination of enantiomeric excess, preferably without an extra step for purification or chromatographic separation. While a) can be often done by ^{1}H-NMR integration of proper, non-overlapping monitor protons, b) and c) might be more difficult to achieve.

We investigated 1,4-di(*tert*-butyl)benzene, 3,3'-dimethyl-1,1'-biphenyl and bibenzyl as internal standard (IS), added to the crude product mixture after extractive work-up, and recorded the ^{1}H-NMR spectrum in $CDCl_3$. Best results were obtained with bibenzyl. Integration of the well separated singlet of methylene protons (4H) relative to d×d of the methine (1H) or methylene group (2H) of the product gave %-conversion, amount of product formed and eventually side products (if extracted in the organic phase). After evaporation an aliquot was subjected to chiral HPLC measurement (ca. 5 mg dissolved in 1 mL of 2-PrOH/heptane, 5 µL injected). For reaction (1) using reported conditions (Chiralcel ODH, 250 × 4.6 mm, 2-PrOH/heptane, 1:99, 0.5 mL min^{-1}, 25 °C) well resolved peaks in the order of elution of internal standard, (*R*)-product, benzophenone, starting material, (*S*)-product were obtained.

Screening experiments (Details):

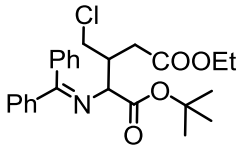
Table S1. Asymmetric substitution of *tert*-butyl 2-((diphenylmethylene)amino)acetate (**12**) with electrophiles **13B-13I** under PT conditions.[a]

entry	cat.	t/h	base	product	yield/%[b]	ee/%[c]	note
1	**1c**	20	KOH	**14B**	89	88	
2	**1d**	20	KOH	**14B**	**90**	88	
3	**1g**	20	KOH	**14B**	89	**98**	[d]
4	**1h**	20	KOH	**14B**	70	**98**	
5	**1c**	20	KOH	**14C**	80	91	
6	**1d**	20	KOH	**14C**	**86**	91	
7	**1g**	20	KOH	**14C**	71	**95**	[e]
8	**1h**	20	KOH	**14C**	45	52	
9	**1c**	20	KOH	**14D**	**90**	75	
10	**1d**	20	KOH	**14D**	**90**	74	
11	**1g**	20	KOH	**14D**	87	**93**	
12	**1h**	20	KOH	**14D**	61	84	

entry	cat.	t/h	base	product	yield/%[b]	ee/%[c]	note
13	**1c**	20	KOH	**14E**	51	83	
14	**1d**	20	KOH	**14E**	55	**88**	
15	**1g**	20	KOH	**14E**	**72**	68	
16	**1h**	20	KOH	**14E**	66	14	
17	**1c**	20	KOH	**14F**	**92**	89	
18	**1d**	20	KOH	**14F**	91	88	
19	**1g**	20	KOH	**14F**	90	**90**	[f]
20	**1h**	20	KOH	**14F**	30	90	
21	**1c**	20	KOH	**14G**	88	72	
22	**1d**	20	KOH	**14G**	**91**	71	
23	**1g**	20	KOH	**14G**	81	**83**	
24	**1h**	20	KOH	**14G**	83	73	
25	**1c**	20	CsOH	**14H**	62	51	[g]
26	**1d**	20	CsOH	**14H**	56	41	[h]
27	**1g**	4	KOH	**14H**	13	69	[i]
28	**1g**	4	KOH	**14H**	39	62	[j]
29	**1g**	4	CsOH	**14H**	54	74	
30	**1g**	20	CsOH	**14H**	**61**	79	[k]
31	**1h**	20	CsOH	**14H**	60	**80**	
32	**1c**	20	CsOH	**14H**	22	35	[l]
33	**1d**	20	CsOH	**14H**	<10	n.d.	[l]
34	**1g**	20	CsOH	**14H**	52	68	[l]
35	**1h**	20	CsOH	**14H**	51	67	[l]
36	**1g**	20	CsOH	**14H**	0	n.d.	[m]
37	**1c**	20	Cs_2CO_3	**14I**	<5	n.d.	
38	**1g**	20	Cs_2CO_3	**14I**	33	**88**	
39	**1h**	20	Cs_2CO_3	**14I**	<5	n.d.	
40	**1c**	20	Cs_2CO_3	**14I**	**33**	57	[n]
41	**1d**	20	Cs_2CO_3	**14I**	26	51	[n]
42	**1g**	20	Cs_2CO_3	**14I**	23	83	[n]
43	**1h**	20	Cs_2CO_3	**14I**	20	83	[n]

[a] 0.25 mmol of substrate, 0.30 mmol of electrophile, 1 mol % of catalyst with (*S,S*)-configuration, 1.5 mL toluene, 0.5 mL KOH or CsOH (50%) or solid Cs_2CO_3 (5 equiv.), vigorous stirring at 0 °C for the time indicated. [b] Yield after extractive work-up based on ^{1}H-NMR integration of signals of product and bibenzyl added as internal standard. [c] Determined by chiral HPLC (Chiralcel ODH or Chiralpak ADH), products with (*R*)-configuration predominating. [d] 99% ee, 80% isolated yield, 0 °C, 24 h [1]. [e] 99%ee 86% over two steps, 0 °C, 24 h [1]. [f] 99% ee 89% isolated yield, 0 °C, 15 h [1]. [g] 12% of **15** formed. [h] 13% of **15** formed. [i] 37% of **15** formed. [j] 10 equ. of KI added, 27% of **15** formed. [k] 8% of **15** formed. [l] Instead of **13H** the corresponding 4-iodocrotonate was used. [m] Instead of **13H** the corresponding 4-chlorocrotonate was used, resulting in formation of 53% of **15** and 27% of intermediate **16** (see structure below). [n] Instead of **13I** the corresponding iodo compound was used.

1-(tert-Butyl) 5-ethyl 3-(chloromethyl)-2-((diphenylmethylene)amino)pentanedioate (**16**): ^{1}H-NMR δ: 7.63–7.67 (m, 2H); 7.37–7.45 (m, 4H); 7.30–7.35 (m, 2H); 7.18–7.22 (m, 2H); 4.18 (d, *J* = 4.1 Hz, 1H); 4.12 (qm, *J* = 7.1 Hz, 2H); 3.69 (dd, *J* = 11.0, 5.0 Hz, 1H); 3.54 (dd, *J* = 10.9, 8.2 Hz, 1H); 2.90–2.97 (m, 1H); 2.73 (dd, *J* = 16.5, 4.8 Hz, 1H); 2.67 (dd, *J* = 16.5, 8.5 Hz, 1H); 1.42 (s, 9H); 1.24 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C-NMR δ: 172.26 (C); 172.24 (C); 169.99 (C); 139.29 (C); 136.19 (C); 130.47 (CH); 128.79 (CH); 128.61 (CH); 128.30 (CH); 127.97 (CH); 127.76 (CH); 81.64 (C); 65.23 (CH); 60.52 (CH_2); 45.34 (CH_2); 41.32 (CH); 33.96 (CH_2); 27.93 (CH_3); 14.14 (CH_3) ppm. HRMS (ESI) calcd for $C_{25}H_{30}ClNaNO_4$ $[M + Na]^+$: 466.1761; found. 466.1746.



16

Ethyl (E)-4-chlorobut-2-enoate: To a stirred solution of ethyl 4-bromocrotonate (772 mg, 3.0 mmol 75% purity) in DMF (1 mL) was added dry LiCl (636 mg, 5 equiv.) at room temperature. After 24 h, the suspension was poured into water/ether (10 mL/30 mL) and the organic phase was washed with water (4 × 10 mL) and dried ($MgSO_4$). The crude product was purified by chromatography (EtOAc (0→15%)/heptane) to afford the product as a colorless oil; yield 80–90%. ^{1}H-NMR δ: 6.97 (dt, *J* = 15.4, 6.1 Hz, 1H); 6.10 (dt, *J* = 15.3, 1.6 Hz, 1H); 4.22 (q, *J* = 7.1 Hz, 2H); 4.16 (dd, *J* = 6.1, 1.6 Hz, 2H); 1.30 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C-NMR δ: 165.61 (C); 141.59 (CH); 124.16 (CH); 60.71 (CH_2); 42.47 (CH_2); 14.17 (CH_3) ppm. HRMS (ESI) calculated for C_4H_4ClO $[M - OC_2H_5]^+$: 102.9951, found 102.9941.

UV traces of chiral HPLC separations

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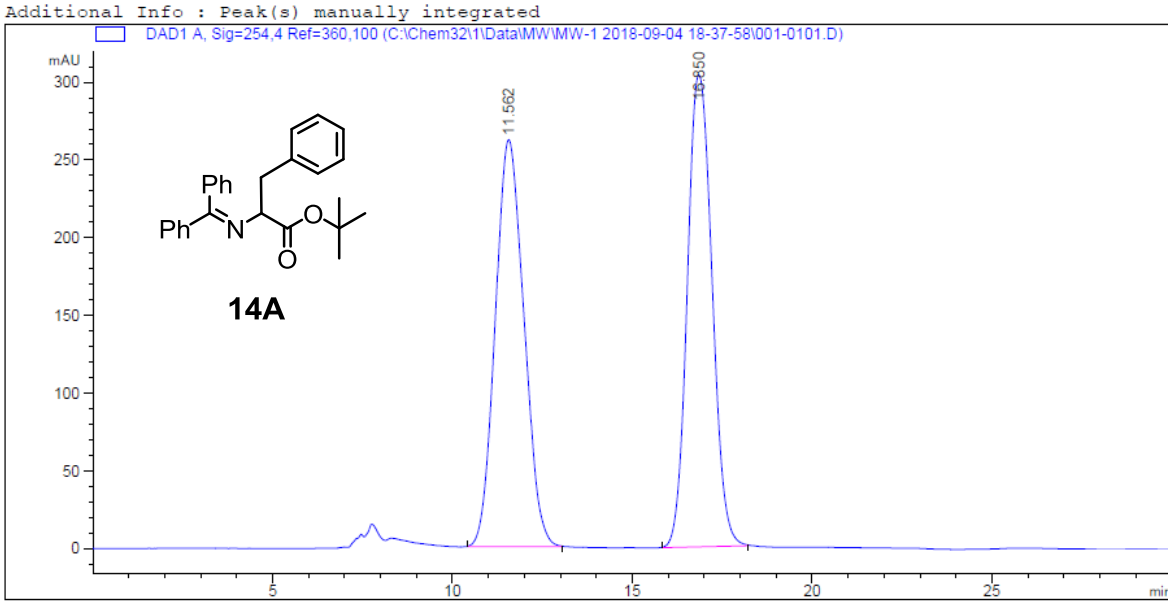


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Additional Info : Peak(s) manually integrated
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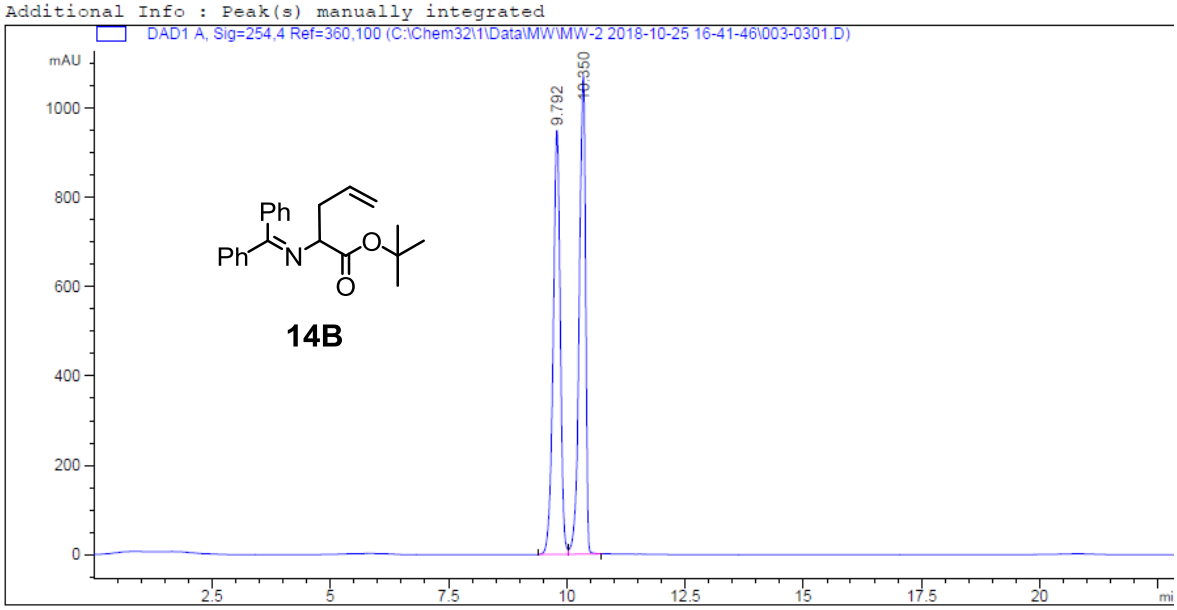


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Do not use Multiplier & Dilution Factor with ISTDs


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Sample Name: STD-C1

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Additional Info : Peak(s) manually integrated
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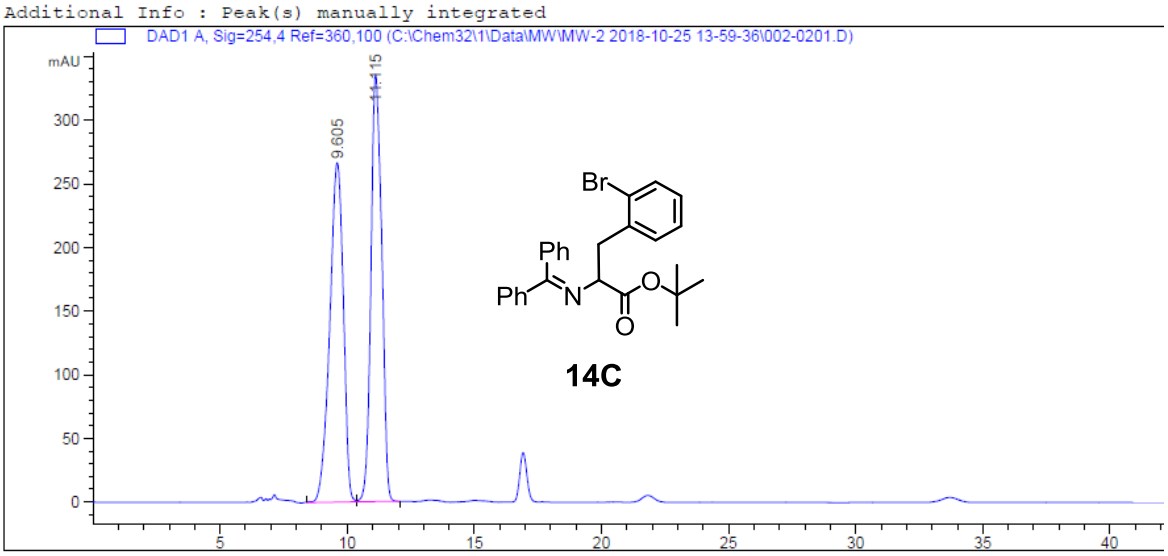


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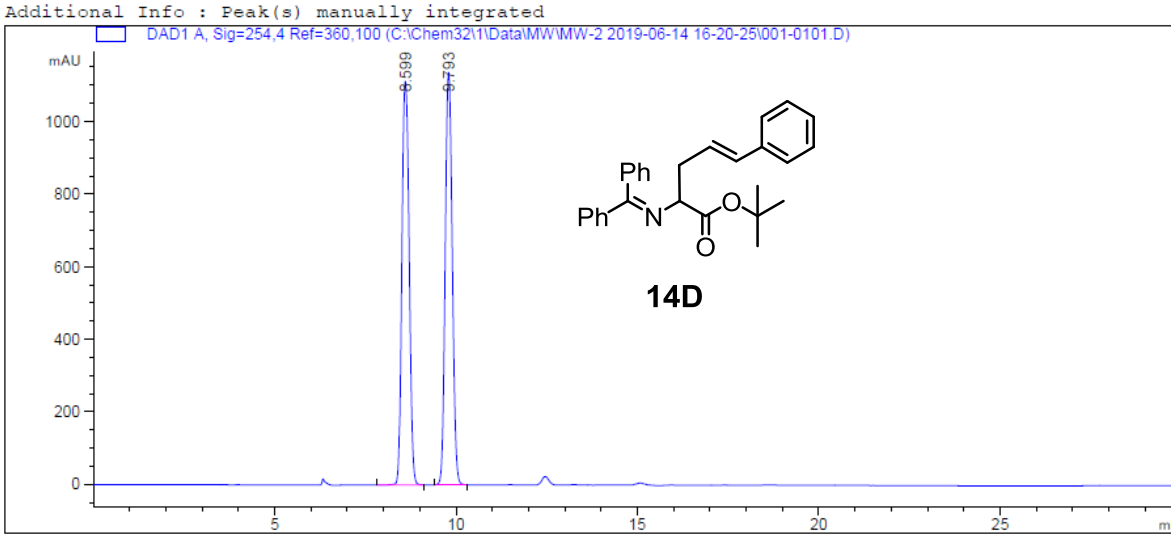
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.605 BV    0.5879 9920.35547  266.72058  50.0998
   2  11.115 VB    0.4896 9880.82813  335.50867  49.9002

Totals :                 1.98012e4   602.22925
```

Sample Name: W STD K01

```
==========================================================================
Acq. Operator    : SYSTEM                          Seq. Line :   1
Acq. Instrument : LC1200                           Location :   1
Injection Date  : 14.06.2019 16:21:31                  Inj :   1
                                                  Inj Volume : 5.000 µl
Method          : C:\Chem32\1\Data\MW\MW-2 2019-06-14 16-20-25\CHIR_ADH.M (Sequence Method)
Last changed    : 14.06.2019 16:20:27 by SYSTEM
Sample Info     : W STD K01/5-6 (RACEMAT)  Chiralpak ADH 2-PrOH/heptane (5:95) 0.5 mL min-1, 25
                  °C

Additional Info : Peak(s) manually integrated
```



14D

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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.599 BB    0.2245 1.54999e4  1112.48364  50.0858
   2   9.793 BB    0.2165 1.54468e4  1136.89917  49.9142

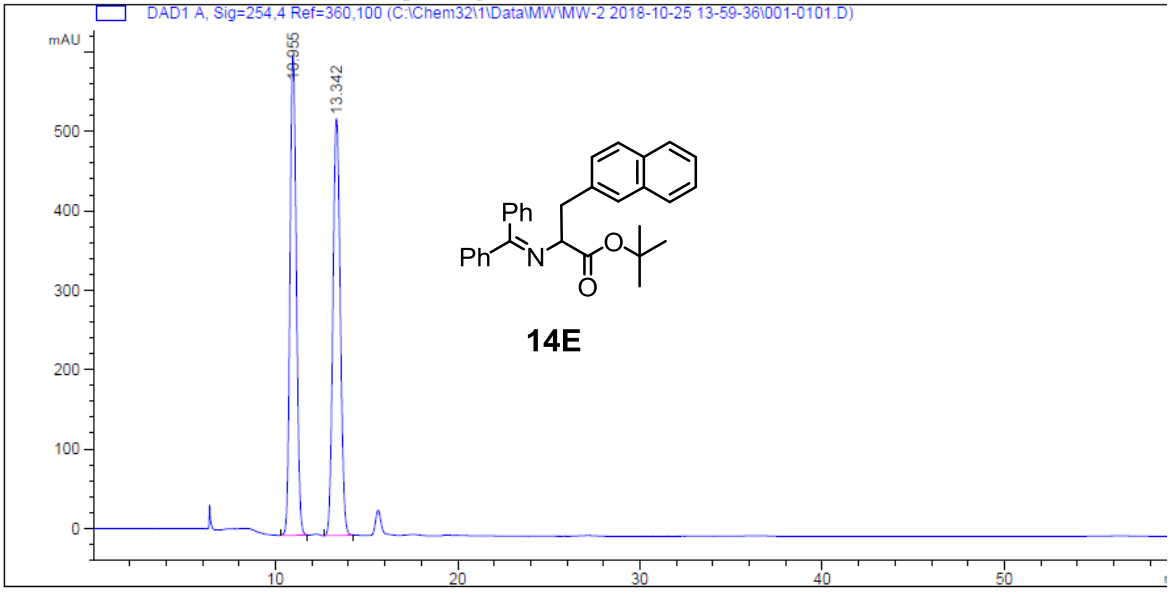
Totals :                  3.09466e4  2249.38281

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

Sample Name: STD-B1

```
==================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   1
Acq. Instrument : LC1200                         Location :   1
Injection Date  : 25.10.2018 14:00:43                Inj :   1
                                               Inj Volume : 5.000 µl
Acq. Method     : C:\Chem32\1\Data\MW\MW-2 2018-10-25 13-59-36\CHIR_ADH.M
Last changed    : 25.10.2018 14:01:05 by SYSTEM
                  (modified after loading)
Analysis Method : C:\Chem32\1\Data\MW\MW-2 2018-10-25 13-59-36\CHIR_ADH.M (Sequence Method)
Last changed    : 25.10.2018 15:00:53 by SYSTEM
Sample Info     : W STD-B1  Chiralpak ADH 2-PrOH/heptane (1:99) 0.5 mL min-1, 25 °C

Additional Info : Peak(s) manually integrated
```



14E

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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

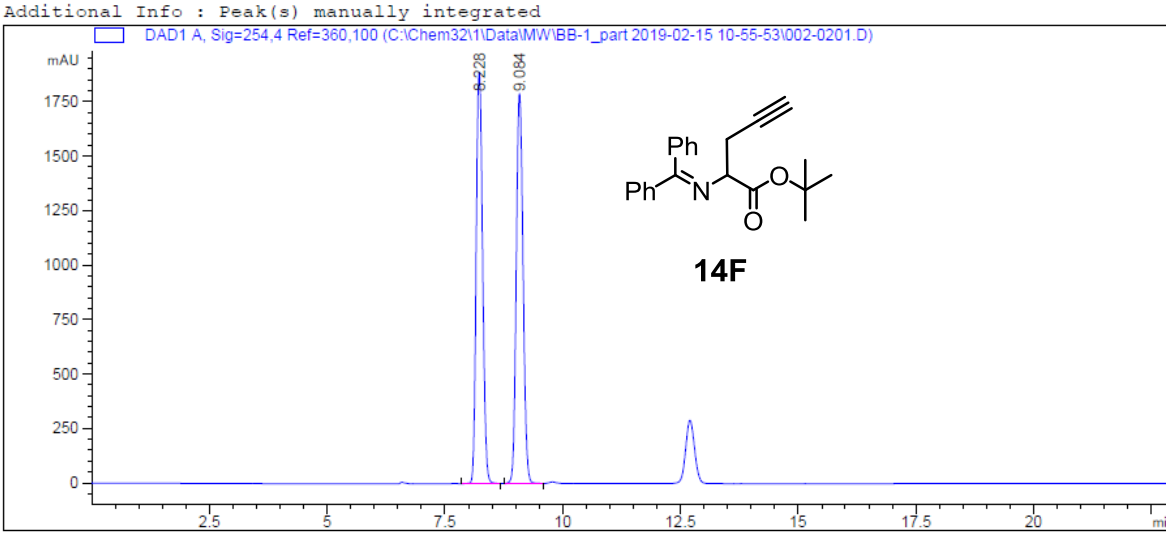
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.955 BB    0.3839 1.47045e4   604.30414  50.1185
   2  13.342 VB    0.4392 1.46350e4   524.99420  49.8815

Totals :                  2.93395e4  1129.29834
```

Sample Name: CHSC3/2

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   2
Acq. Instrument : LC1200                          Location :   2
Injection Date  : 15.02.2019 10:57:09                  Inj :   1
                                                 Inj Volume : 5.000 µl
Acq. Method     : C:\Chem32\1\Data\MW\BB-1_part 2019-02-15 10-55-53\CHIR_ADH.M
Last changed    : 15.02.2019 11:19:19 by SYSTEM
                  (modified after loading)
Analysis Method : C:\Chem32\1\Data\MW\BB-1_part 2019-02-15 10-55-53\CHIR_ADH.M (Sequence Method)
Last changed    : 15.02.2019 11:23:11 by SYSTEM
                  (modified after loading)
Sample Info     : CHSC 03 racem Prod, Chiralpak ADH, 5% 2-PrOH, 95% Heptan, 0.5 mlmin-1, 25 °C

Additional Info : Peak(s) manually integrated
```



14F

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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

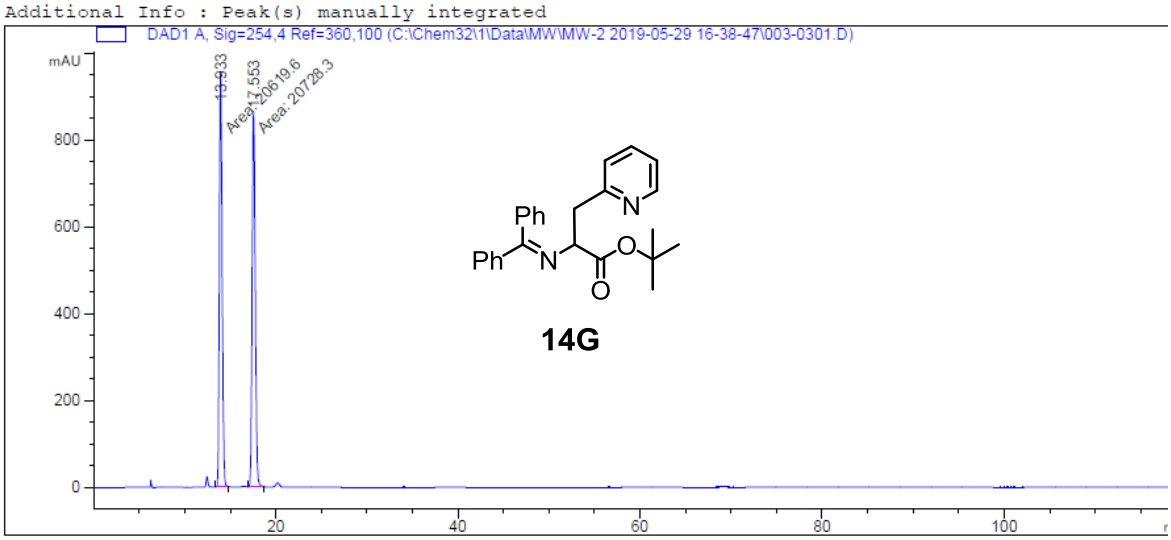
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.228 VB    0.1505 1.78747e4  1887.15088  49.8157
   2   9.084 BV    0.1574 1.80070e4  1790.12805  50.1843

Totals :                  3.58817e4  3677.27893
```

Sample Name: W STD H01

```
=====================================================================
Acq. Operator    : SYSTEM                          Seq. Line :   3
Acq. Instrument : LC1200                           Location :   3
Injection Date  : 29.05.2019 17:42:18                 Inj :   1
                                                  Inj Volume : 5.000 µl
Acq. Method      : C:\Chem32\1\Data\MW\MW-2 2019-05-29 16-38-47\CHIR_ADH.M
Last changed     : 29.05.2019 17:43:15 by SYSTEM
                   (modified after loading)
Analysis Method : C:\Chem32\1\Data\MW\MW-2 2019-05-29 16-38-47\CHIR_ADH.M (Sequence Method)
Last changed     : 29.05.2019 16:38:48 by SYSTEM
Sample Info      : W STD H01/8-9  RACEMAT Chiralpak ADH 2-PrOH/heptane (5:95) 0.5 L min-1, 25 °C

Additional Info : Peak(s) manually integrated
```



14G

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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

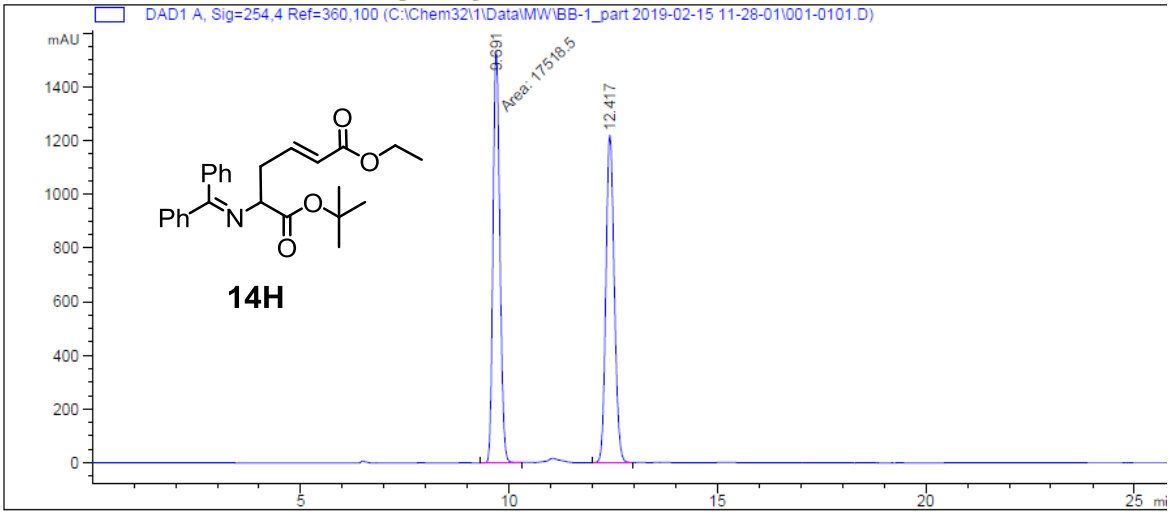
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.933 MF    0.3603 2.06196e4   953.83917  49.8685
   2  17.553 MF    0.4002 2.07283e4   863.33826  50.1315

Totals :                  4.13479e4  1817.17743
```

Sample Name: CHSC 1/3C/8-10

```
=====================================================================
Acq. Operator    : SYSTEM                          Seq. Line :   1
Acq. Instrument  : LC1200                           Location :   1
Injection Date   : 15.02.2019 11:29:05                  Inj :   1
                                                  Inj Volume : 5.000 µl
Acq. Method      : C:\Chem32\1\Data\MW\BB-1_part 2019-02-15 11-28-01\CHIR_ADH.M
Last changed     : 15.02.2019 11:54:50 by SYSTEM
                   (modified after loading)
Analysis Method  : C:\Chem32\1\Data\MW\BB-1_part 2019-02-15 11-28-01\CHIR_ADH.M (Sequence Method)
Last changed     : 15.02.2019 12:07:25 by SYSTEM
                   (modified after loading)
Sample Info      : CHSC 01 racem Prod, Chiralpak ADH, 5% 2-PrOH, 95% Heptan, 0.5 mlmin-1, 25 °C

Additional Info : Peak(s) manually integrated
```




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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

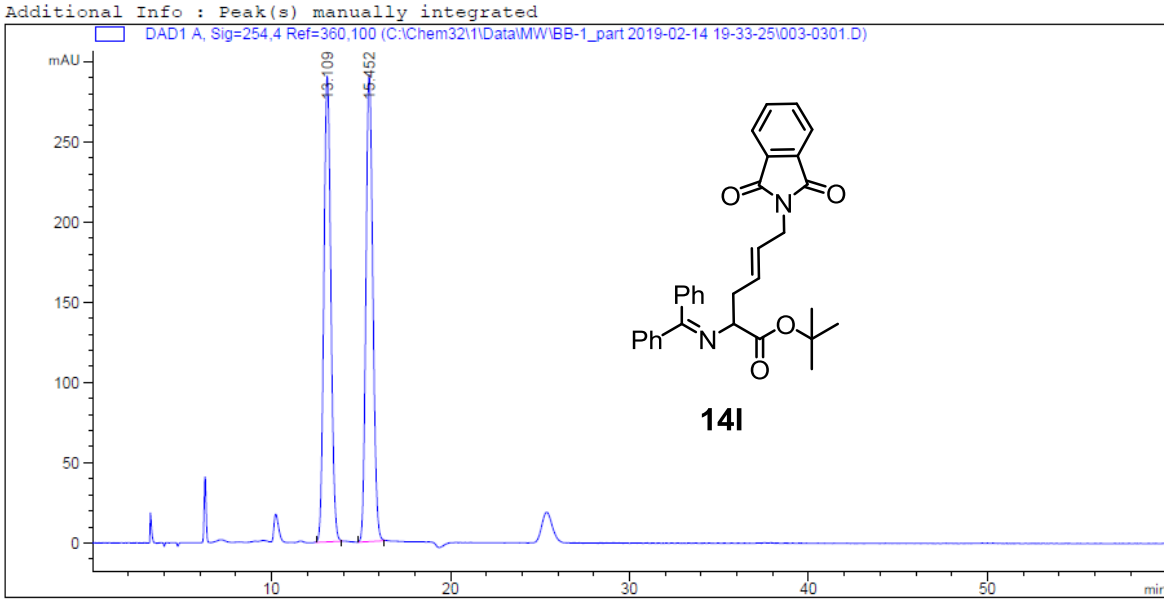
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.691 MF    0.1906 1.75185e4  1531.91235  50.6581
   2  12.417 BB    0.2192 1.70633e4  1220.04663  49.3419

Totals :                  3.45818e4  2751.95898
```

Sample Name: CHSC4/8-9

```
==================================================================
Acq. Operator    : SYSTEM                        Seq. Line :   3
Acq. Instrument : LC1200                          Location :   3
Injection Date  : 14.02.2019 19:35:09                 Inj :   1
                                                 Inj Volume : 20.000 µl
Method          : C:\Chem32\1\Data\MW\BB-1_part 2019-02-14 19-33-25\CHIR_ADH.M (Sequence Method)
Last changed    : 14.02.2019 19:33:26 by SYSTEM
Sample Info     : CHSC 04 racem Prod, Chiralpak ADH, 5% 2-PrOH, 95% Heptan, 0.5 mlmin-1, 25 °C

Additional Info : Peak(s) manually integrated
```



14l

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

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.109 BB    0.4288 7931.43066  290.25415  50.4199
   2  15.452 BB    0.4187 7799.31787  290.97043  49.5801

Totals :                  1.57307e4   581.22458
```

X-ray Structure Analyses

The X-ray intensity data were measured on Bruker D8 Venture and X8 APEX2 diffractometer equipped with multilayer monochromators, Mo K/α INCOATEC micro focus sealed tubes and Oxford and Cryoflex2 cooling systems. The structure was solved by *direct methods.* Non-hydrogen atoms were refined with *anisotropic displacement parameters*. Hydrogen atoms were inserted at calculated positions and refined with riding model. The following software was used: *Bruker SAINT software package* [2] using a narrow-frame algorithm for frame integration, *SADABS* [3] for absorption correction, *OLEX2* [4] for structure solution, refinement, molecular diagrams and graphical user-interface, *Shelxle* [5] for refinement and graphical user-interface *SHELXS-2015* [6] for structure solution, *SHELXL-2015* [7] for refinement*, Platon* [8] for symmetry check. Experimental data and CCDC-Codes (Available online: http://www.ccdc.cam.ac.uk/conts/retrieving.html) can be found in Table S2. Crystal data, data collection parameters, and structure refinement details are given in Tables S3 to S8. Crystal structures are visualized in Figures S1 to S5.

Table S2. Experimental parameter and CCDC-Codes.

Sample	**Machine**	**Source**	**Temp.**	**Detector Distance**	**Time/ Frame**	**#Frames**	**Frame width**	**CCDC**
	Bruker		[K]	[mm]	[s]		[°]	
(*R*)(*R*)-**1d**	X8	Mo	150	30	21	2236	0.700	1956062
$(R)_{bina}(S)_{biphe}$-**1e'**	X8	Mo	150	30	60	1049	0.700	1956063
$[(R)$-**7**$]_2(S,S)$-Dibenzoyltartrate	D8	Mo	100	30	30	1891	0.500	1956064

*(11bR,11b'R)-2,6-Di([1,1':4',1''-terphenyl]-4-yl)-3,3',5,5'-tetrahydro-4,4'-spirobi[dinaphtho[2,1-c:1',2'-e]azepin]-4-ium bromide (R)(R)-***1d**

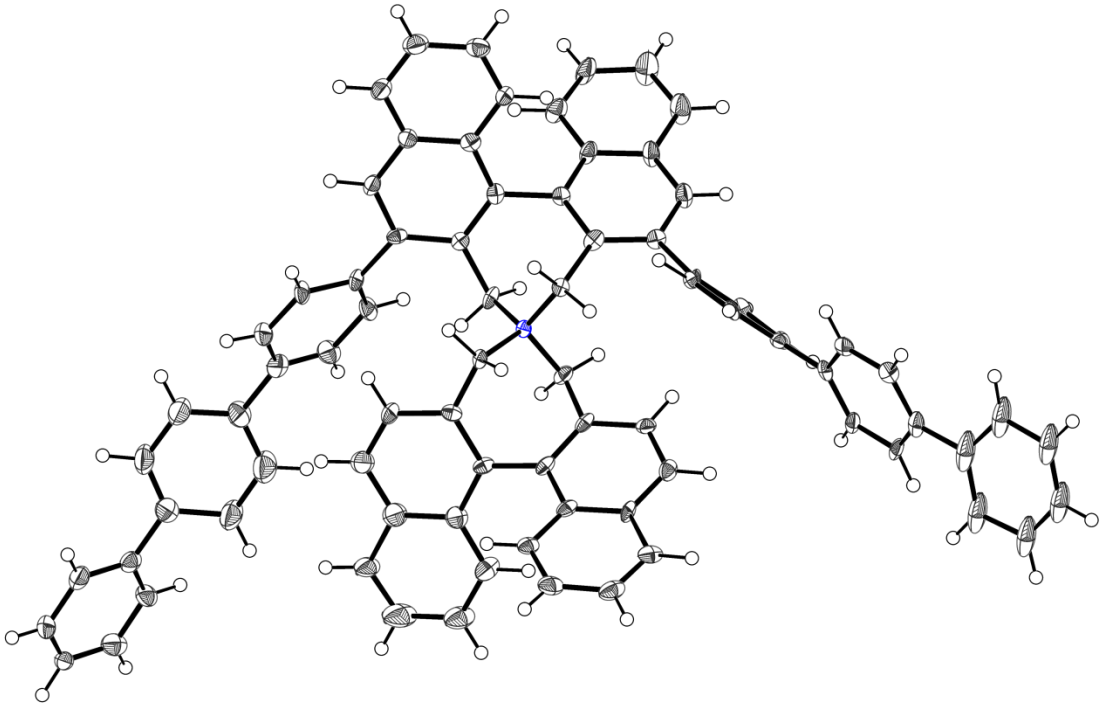


Figure S1. Crystal structure of (*R*)(*R*)-**1d**. C-C- Bond precision: 0.0121 Å. Solvent and counter ion omitted for clarity. Squeeze was used to cut the volume and the corresponding electron densities, because small electron densities in excluded volumes could not be matched. Details see cif-code.

Table S3. Sample and crystal data.

Chemical formula	$C_{82.5}H_{61}BrCl_5N$	**Crystal system**	orthorhombic	
Formula weight [g/mol]	1323.48	**Space group**	*P212121*	
Temperature [K]	150	**Z**	4	
Measurement method	\f and \w scans	**Volume [Å³]**	7229.8(11)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	9.1716(8)	90
Crystal size / [mm³]	0.3 × 0.14 × 0.11		26.018(2)	90
Crystal habit	clear colourless block		30.298(3)	90
Density (calculated) / [g/cm³]	1.216	**Absorption coefficient / [mm⁻¹]**	0.797	
Abs. correction Tmin	0.5297	**Abs. correction Tmax**	0.746	
Abs. correction type	multiscan	**F(000) [e⁻]**	2732	

Table S4. Data collection and structure refinement.

Index ranges	$-11 \le h \le 11$, $-31 \le k \le 31$, $-36 \le l \le 36$	**Theta range for data collection [°]**	2.064 to 50.7	
Reflections number	217019	**Data / restraints / parameters**	13222/0/838	
Refinement method	Least squares	**Final R indices**	all data	R1 = 0.0955, wR2 = 0.2433
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$		$I>2\sigma(I)$	R1 = 0.0812, wR2 = 0.2278
Goodness-of-fit on F^2	1.064	**Weighting scheme**	w=1/[σ2(Fo2)+(0.1579P)2 +14.4721P]	
Largest diff. peak and hole [e $Å^{-3}$]	1.91/-1.02		where $P=(F_o^2+2F_c^2)/3$	

*(R)-2',6'-Bis(4-tritylphenyl)-3',5,5',7-tetrahydrospiro[dibenzo[c,e]azepine-6,4'-dinaphtho[2,1-c:1',2'-e]azepin]-6-ium bromide (R)-**1e'***

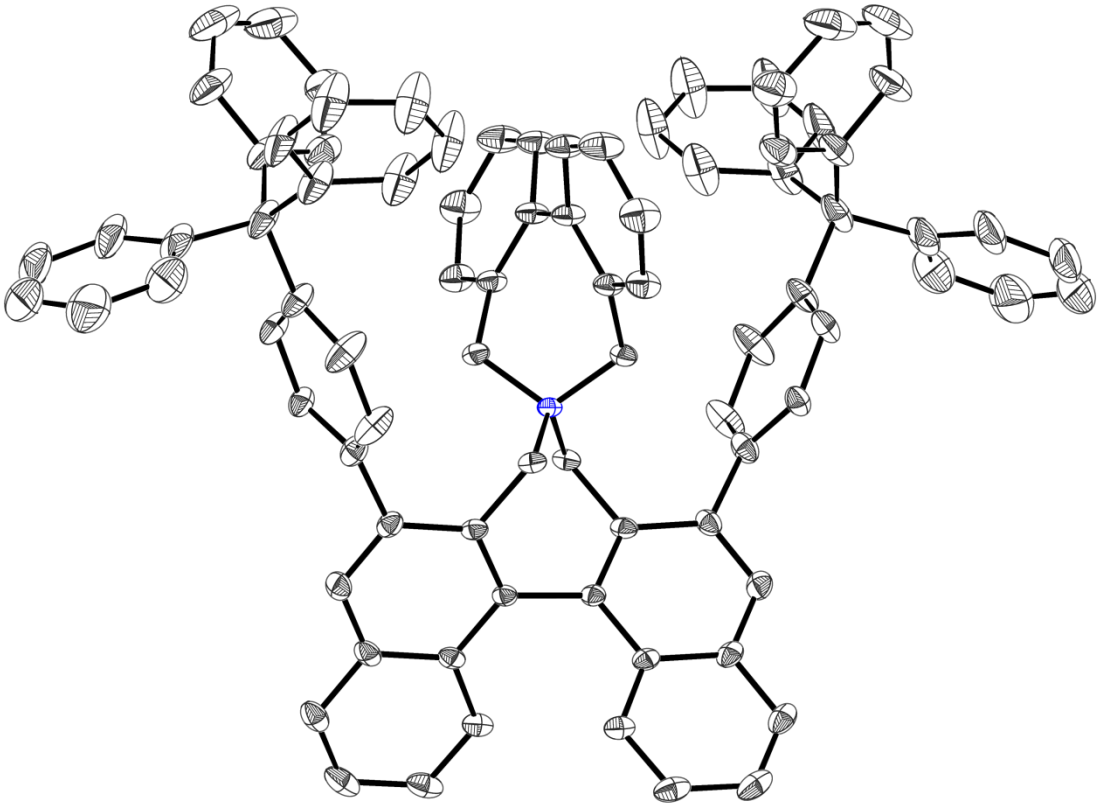


Figure S2. Crystal structure of (*R*)-**1e'**. C-C- Bond precision: 0.0074 Å. Solvent, counter ion and hydrogens omitted for clarity.

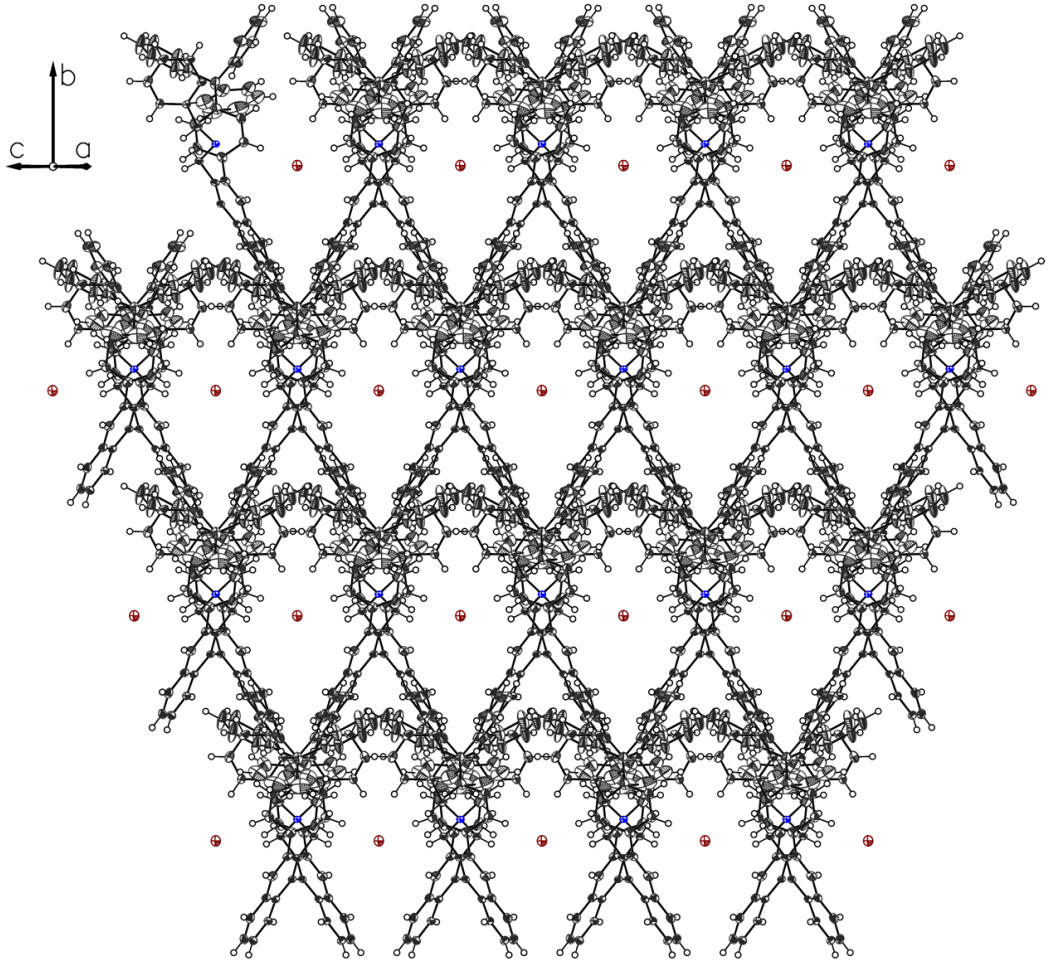


Figure S3. Packing view. Solvent omitted for clarity.

Table S5. Sample and crystal data.

Chemical formula	$C_{58}H_{48}Br_{0.5}N_{0.5}$	**Crystal system**	monoclinic	
Formula weight [g/mol]	791.92	**Space group**	*C2*	
Temperature [K]	150	**Z**	4	
Measurement method	\f and \w scans	**Volume [Å³]**	4478.3(5)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	21.7990(14)	90
Crystal size / [mm³]	0.25 × 0.23 × 0.1		23.2291(13)	94.251(2)
Crystal habit	clear colourless block		8.8684(5)	90
Density (calculated) / [g/cm³]	1.175	**Absorption coefficient / [mm⁻¹]**	0.51	
Abs. correction Tmin	0.5749	**Abs. correction Tmax**	0.746	
Abs. correction type	multiscan	**F(000) [e⁻]**	1668	

Table S6. Data collection and structure refinement.

Index ranges	-30 ≤ h ≤ 29, -32 ≤ k ≤ 32, -12 ≤ l ≤ 12	**Theta range for data collection [°]**	2.566 to 60.592	
Reflections number	43599	**Data / restraints / parameters**	13255/32/450	
Refinement method	Least squares	**Final R indices**	all data	R1 = 0.0876, wR2 = 0.2295
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$		I>2σ(I)	R1 = 0.0802, wR2 = 0.2193
Goodness-of-fit on F^2	1.048	**Weighting scheme**	w=1/[σ2(Fo2)+(0.1825P)2 +2.6917P]	
Largest diff. peak and hole [e $Å^{-3}$]	1.49/-0.65		where $P=(F_o^2+2F_c^2)/3$	

(*R*)-*2,6-Diiodo-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]azepin-4-ium ion* [(*R*)-**7**]$^+$

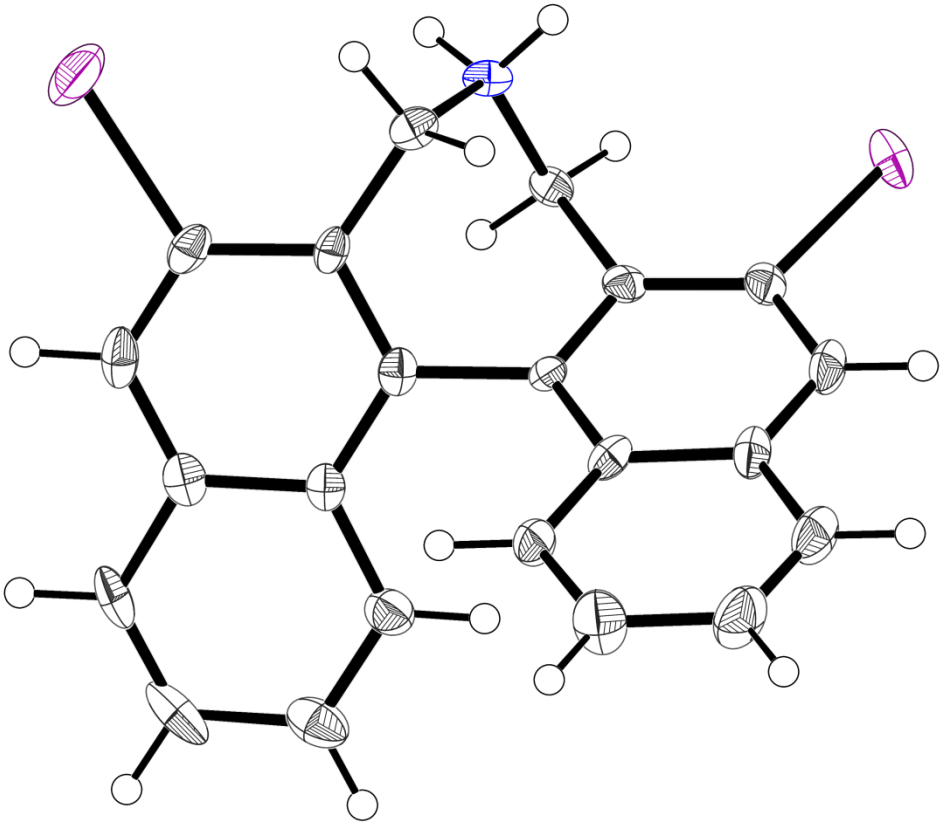


Figure S4. Crystal structure of [(*R*)-**7**]$_2$(*S,S*)-Dibenzoyltartrate. C-C- Bond precision: 0.0129 Å. Solvent and counter ion omitted for clarity.

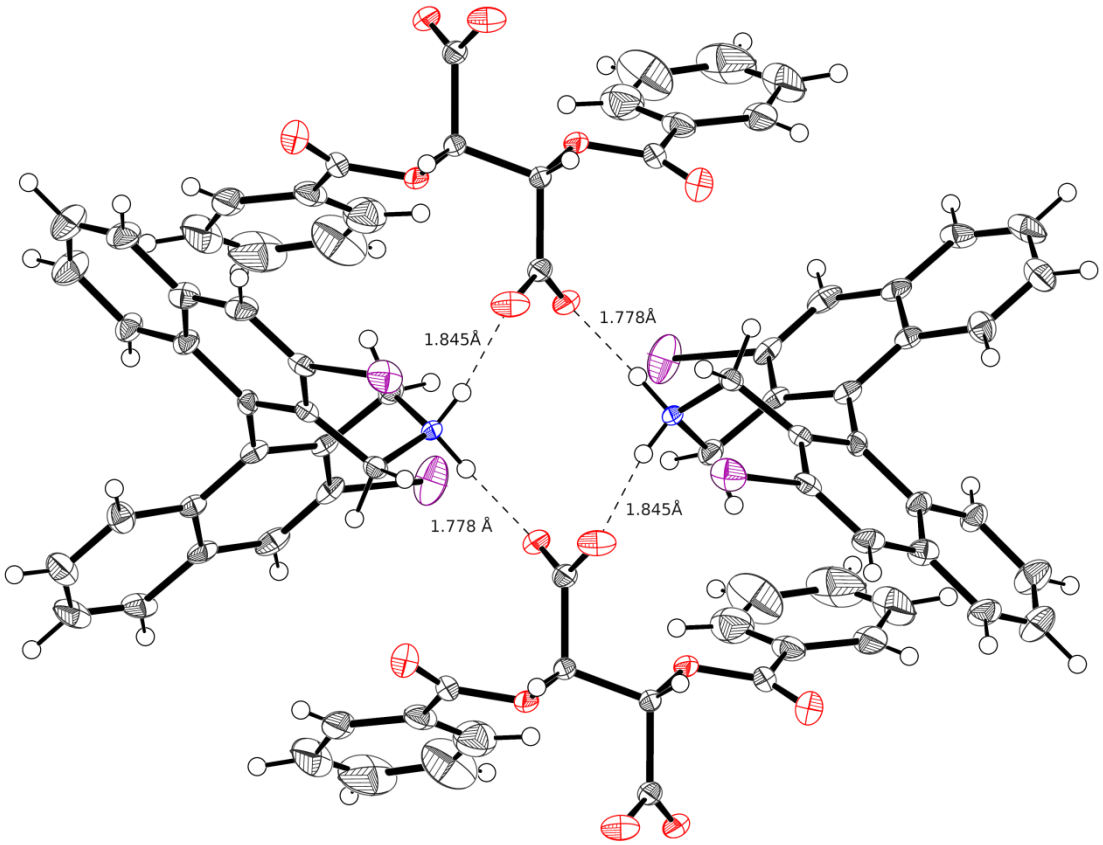


Figure S5. [(*R*)-**7**]$^+$ and counter ion form two independent hydrogen bonds because of symmetry for (two each because of symmetry reasons) construct a rhombus. Bond length and rhombus visualized.

Table S7. Sample and crystal data.

Chemical formula	$C_{32}H_{24}Cl_2I_2NO_4$	**Crystal system**	monoclinic	
Formula weight [g/mol]	811.22	**Space group**	*C2*	
Temperature [K]	100	**Z**	4	
Measurement method	\f and \w scans	**Volume [Å^3]**	3028.14(18)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	28.7403(11)	90
Crystal size / [mm^3]	0.07 × 0.07 × 0.05		12.0555(4)	101.095(2)
Crystal habit	clear colourless block		8.9062(3)	90
Density (calculated) / [g/cm^3]	1.779	**Absorption coefficient / [mm^{-1}]**	2.292	
Abs. correction Tmin	0.2263	**Abs. correction Tmax**	0.265	
Abs. correction type	multiscan	**F(000) [e$^-$]**	1580	

Table S8. Data collection and structure refinement.

Index ranges	-34 ≤ h ≤ 34, -14 ≤ k ≤ 14, -10 ≤ l ≤ 10	**Theta range for data collection [°]**	4.66 to 50.694	
Reflections number	47080	**Data / restraints / parameters**	5534/7/364	
Refinement method	Least squares	**Final R indices**	all data	R1 = 0.0367, wR2 = 0.0897
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$		I>2σ(I)	R1 = 0.0362, wR2 = 0.0894
Goodness-of-fit on F^2	1.129	**Weighting scheme**	w=1/[σ2(Fo2)+(0.0383P)2 +21.9719P]	
Largest diff. peak and hole [e $Å^{-3}$]	0.85/-1.24		where $P=(F_o^2+2F_c^2)/3$	

References

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3. Sheldrick, G.M. *SADABS;* University of Göttingen: Göttingen, Germany, 1996.
4. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42,* 339–341.
5. Huebschle, C.B.; Sheldrick, G.M.; Dittrich, B. ShelXle: A Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.
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7. Sheldrick, G.M. *SHELXL v 2016/4;* University of Göttingen: Göttingen, Germany, 2015.
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