

Electronic Supplementary Information

Formal total synthesis of histrionicotoxin alkaloids *via* Hg(OTf)₂-catalyzed cycloisomerization and SmI₂-induced ring expansion

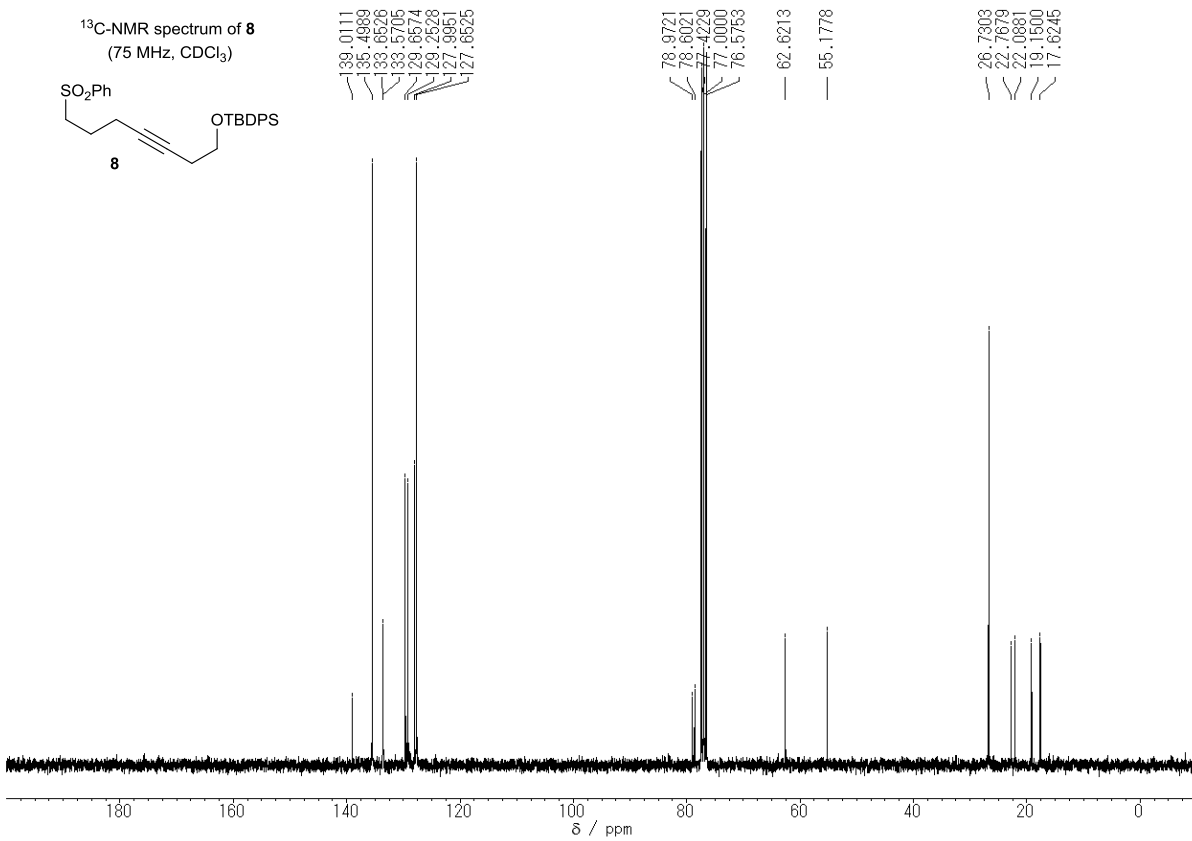
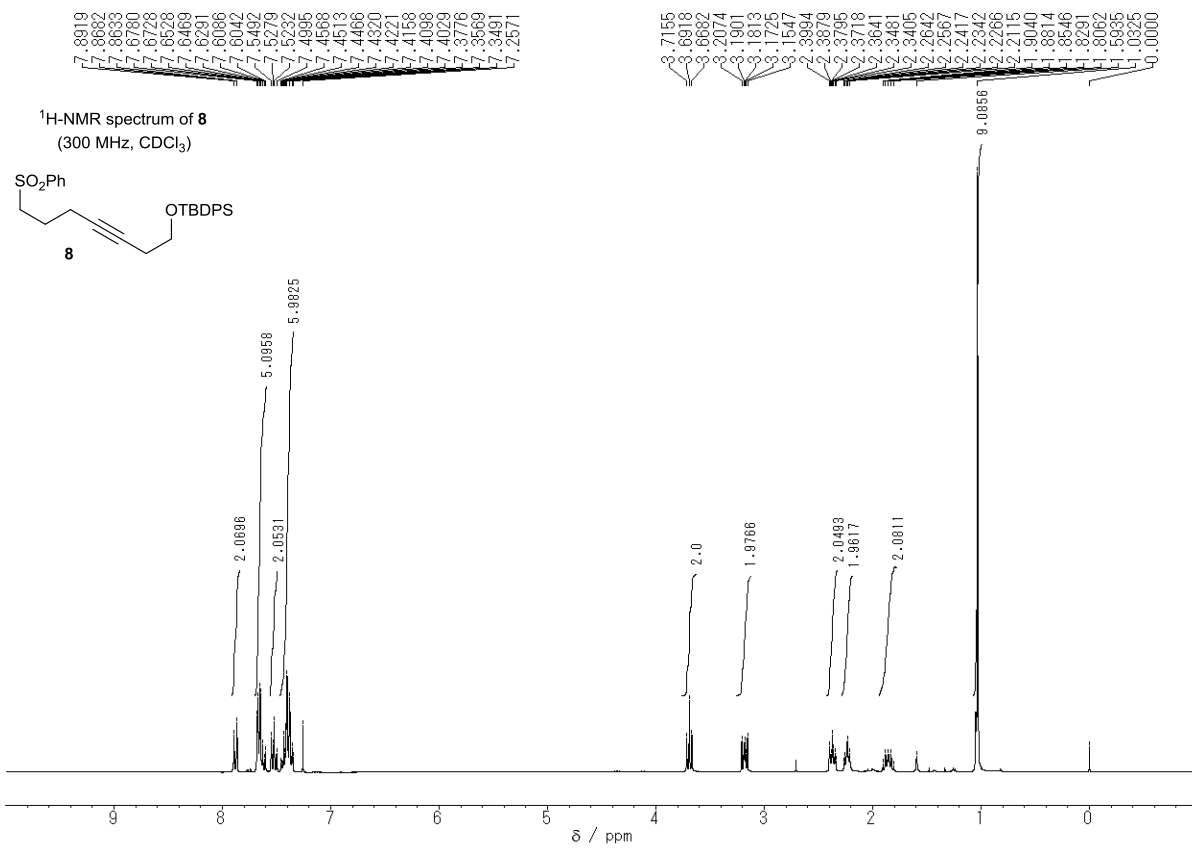
Kunihiro Matsumura,^a Keisuke Nishikawa,^a Hiroaki Yoshida,^a Matsumi Doe^a
and Yoshiki Morimoto^{*a}

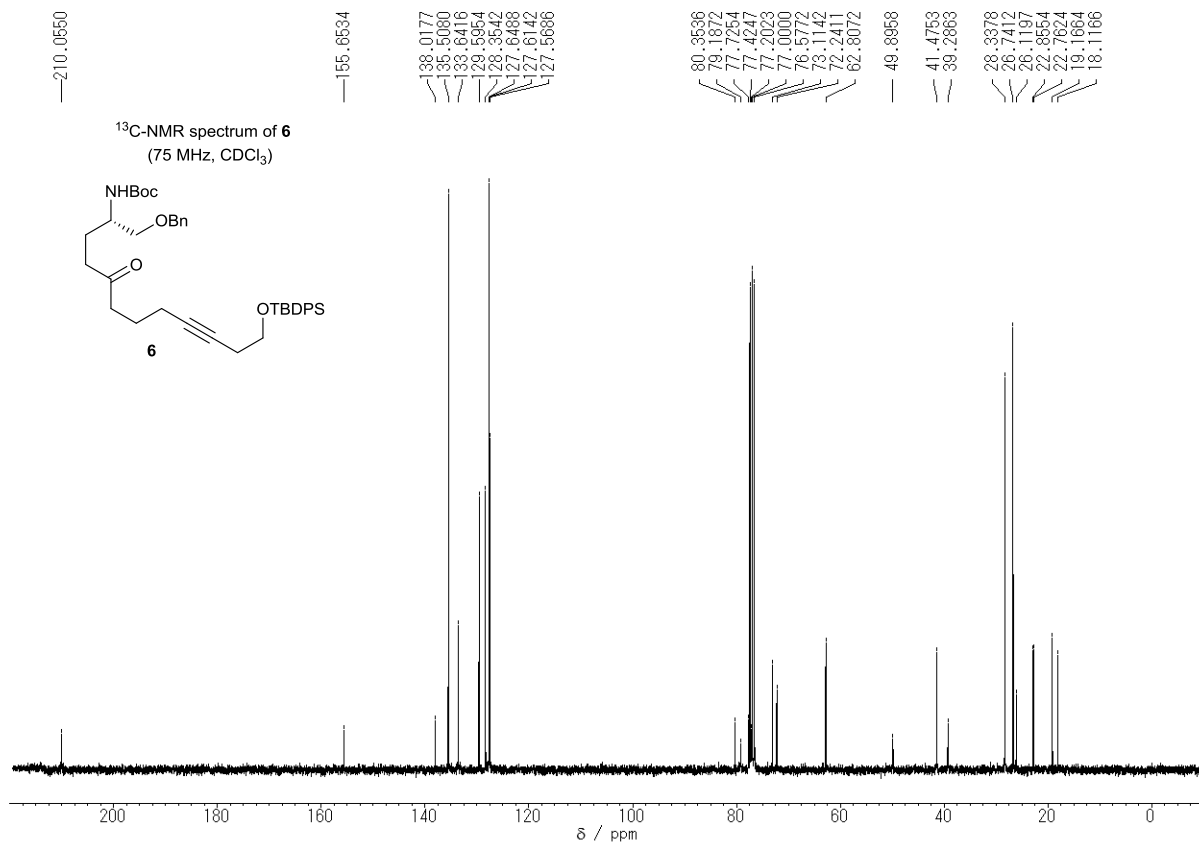
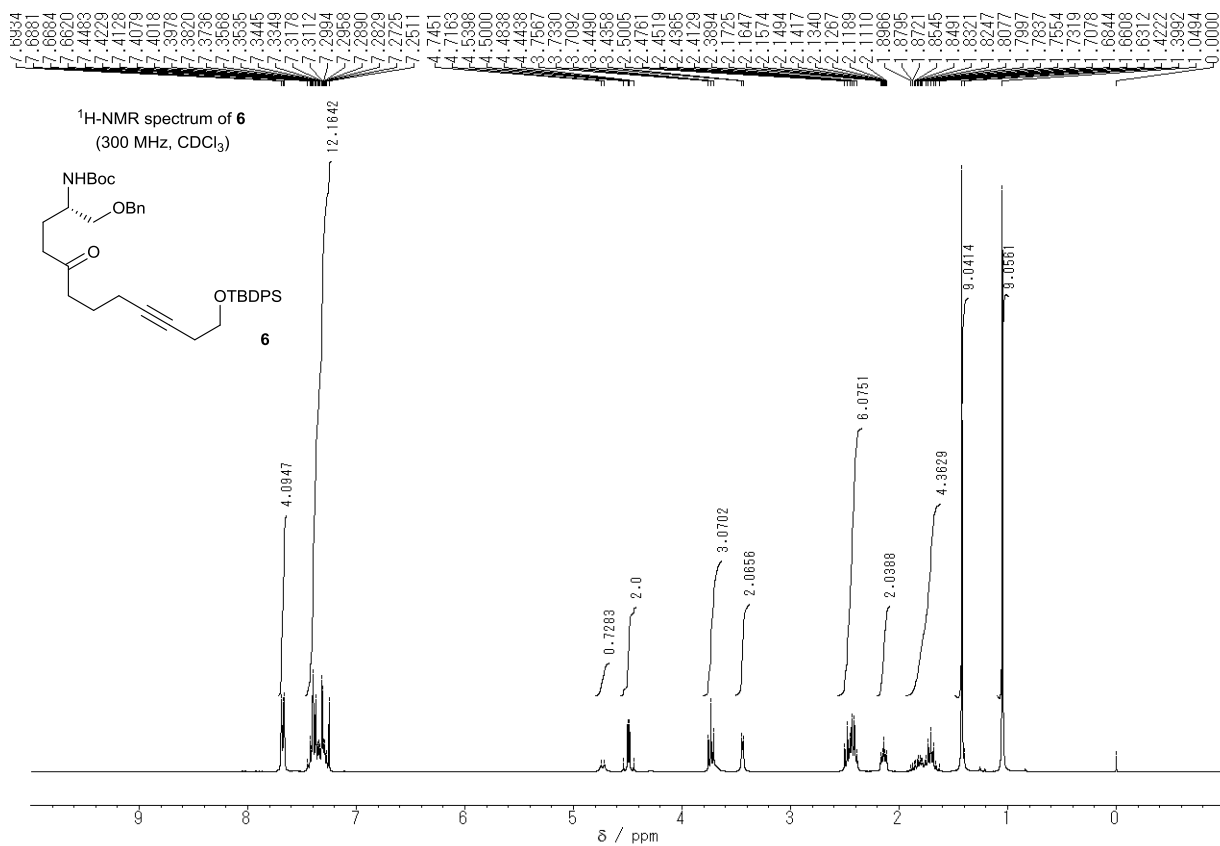
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Osaka 558-8585, Japan

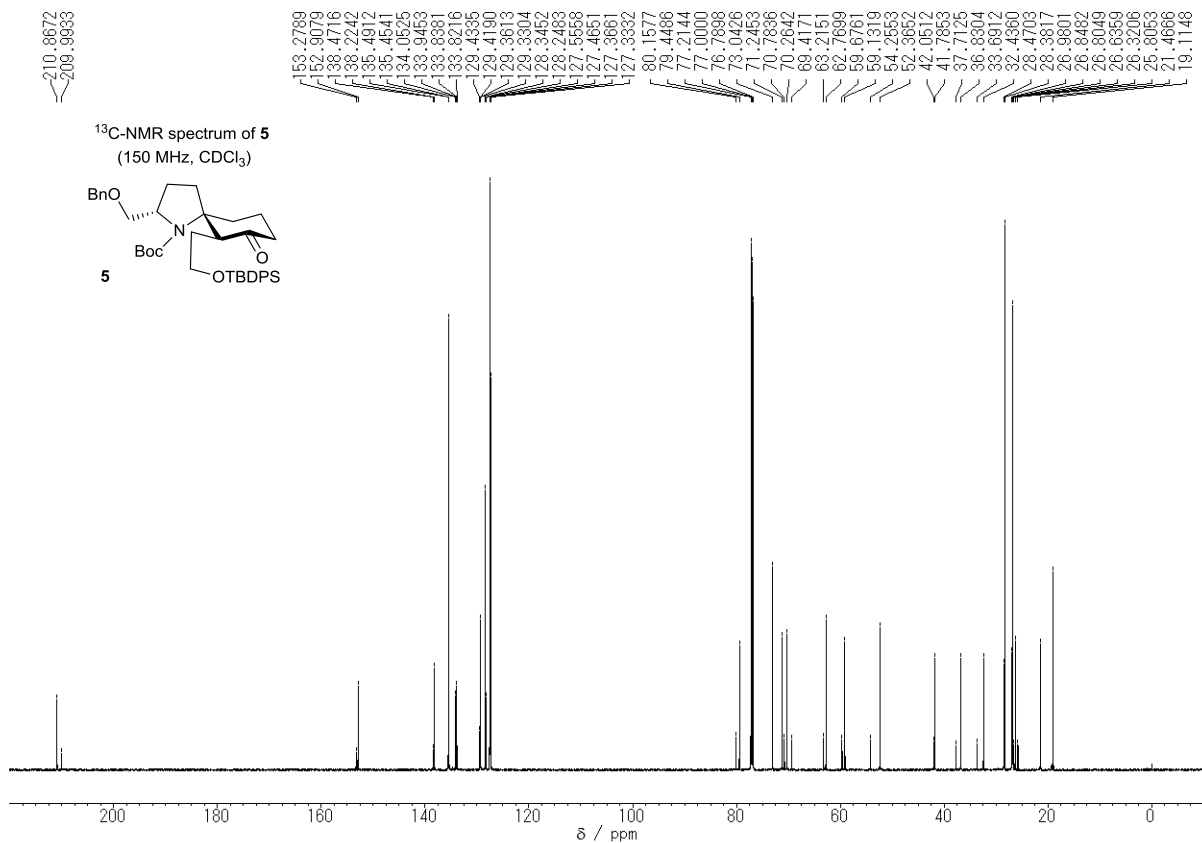
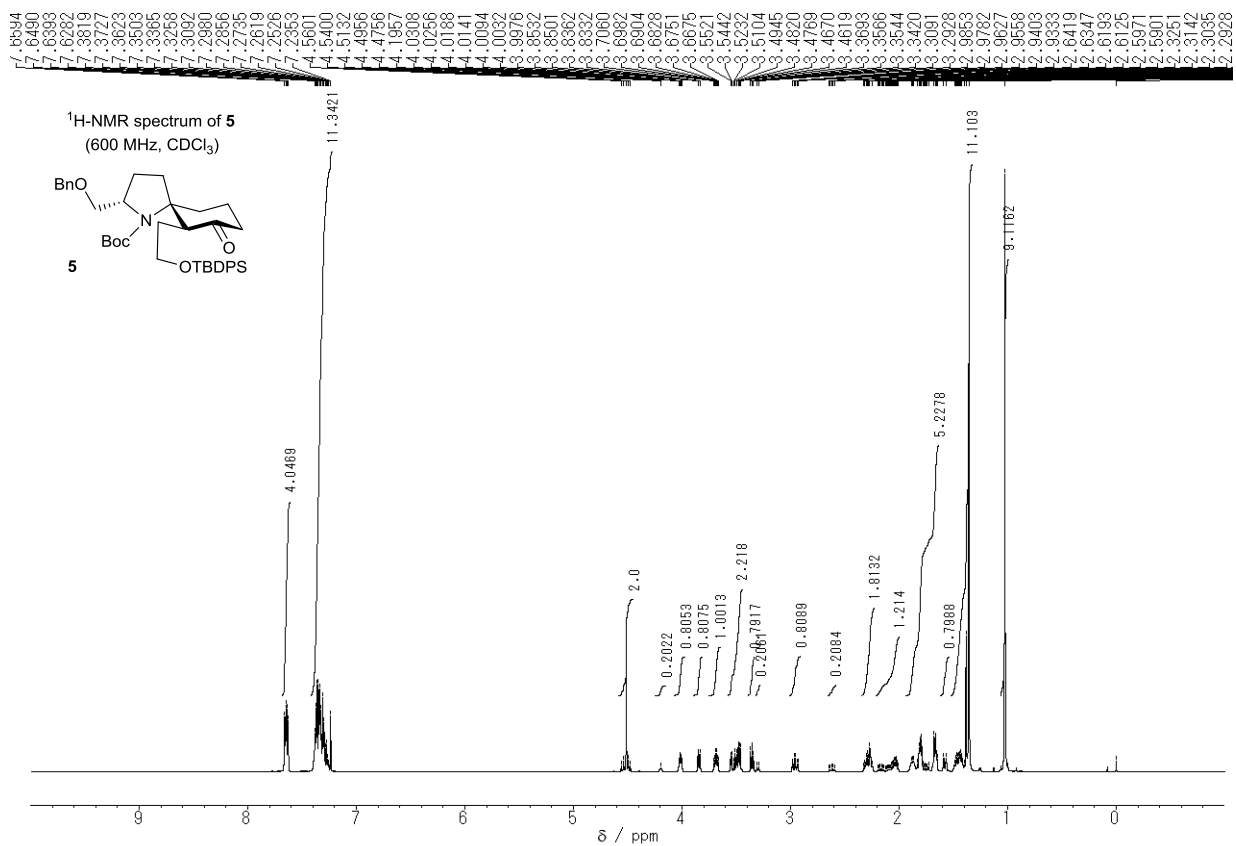
Table of Contents

¹H and ¹³C NMR spectra of synthetic compounds **3–6**, **8**, **11**, *eq-12*, *ax-12*, and **13–16**: S2–S4,
S6, S8, S10, S12–S15, S17, and S19

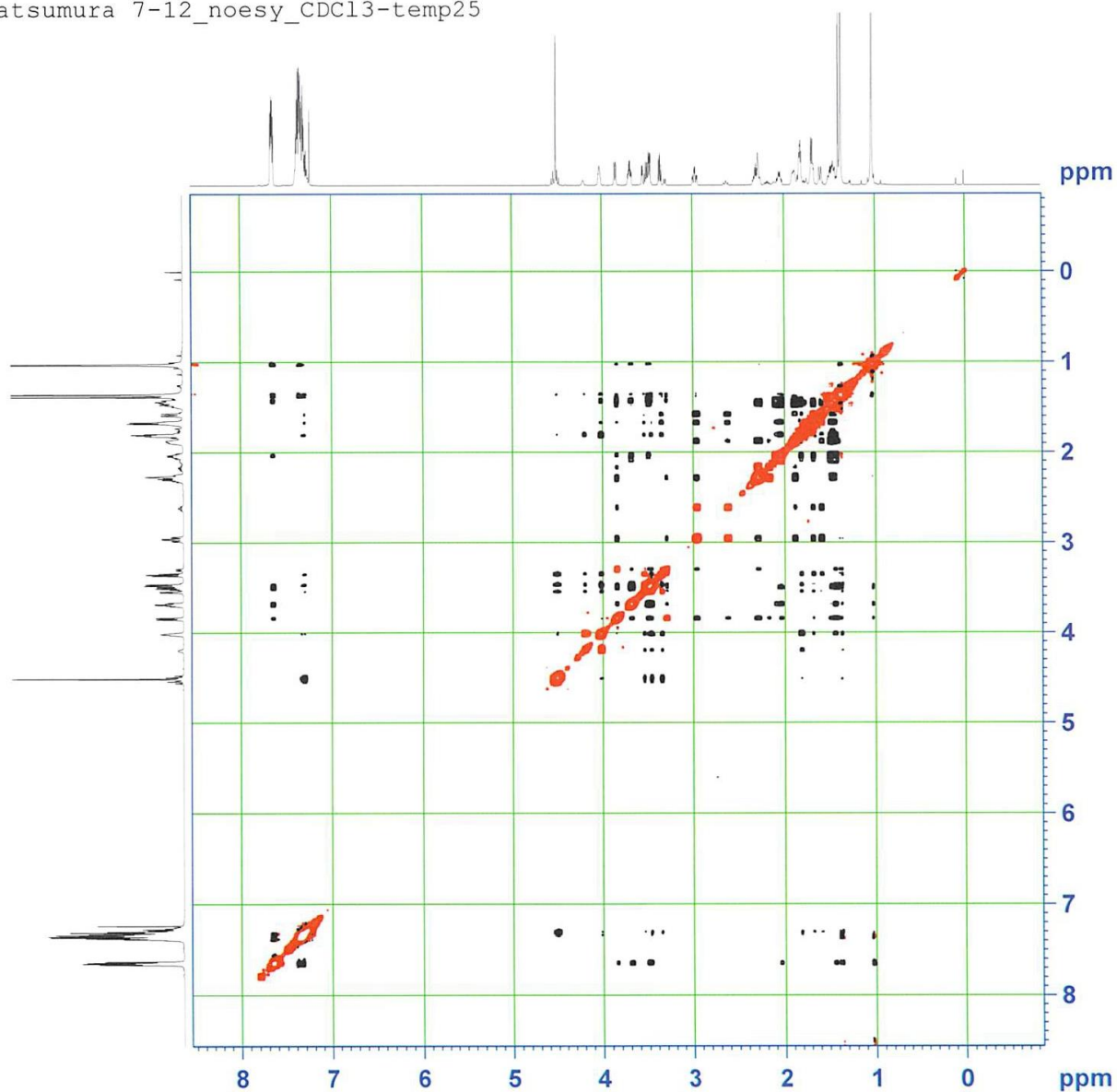
NOESY spectra of compounds **4**, **5**, **11**, *eq-12*, *ax-12*, and **16**: S5, S7, S9, S11, S16, and S18



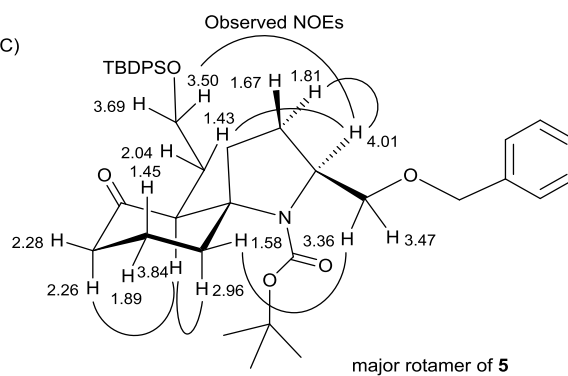
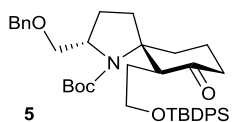


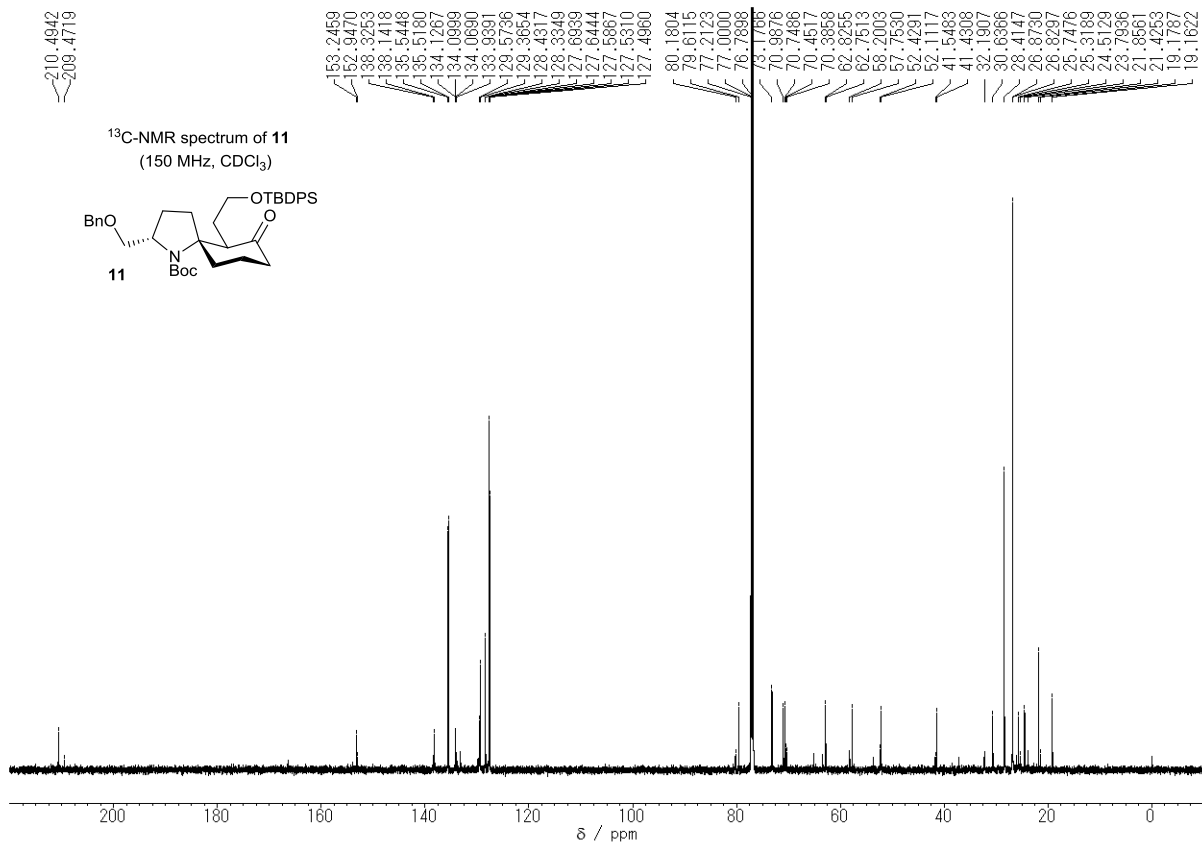
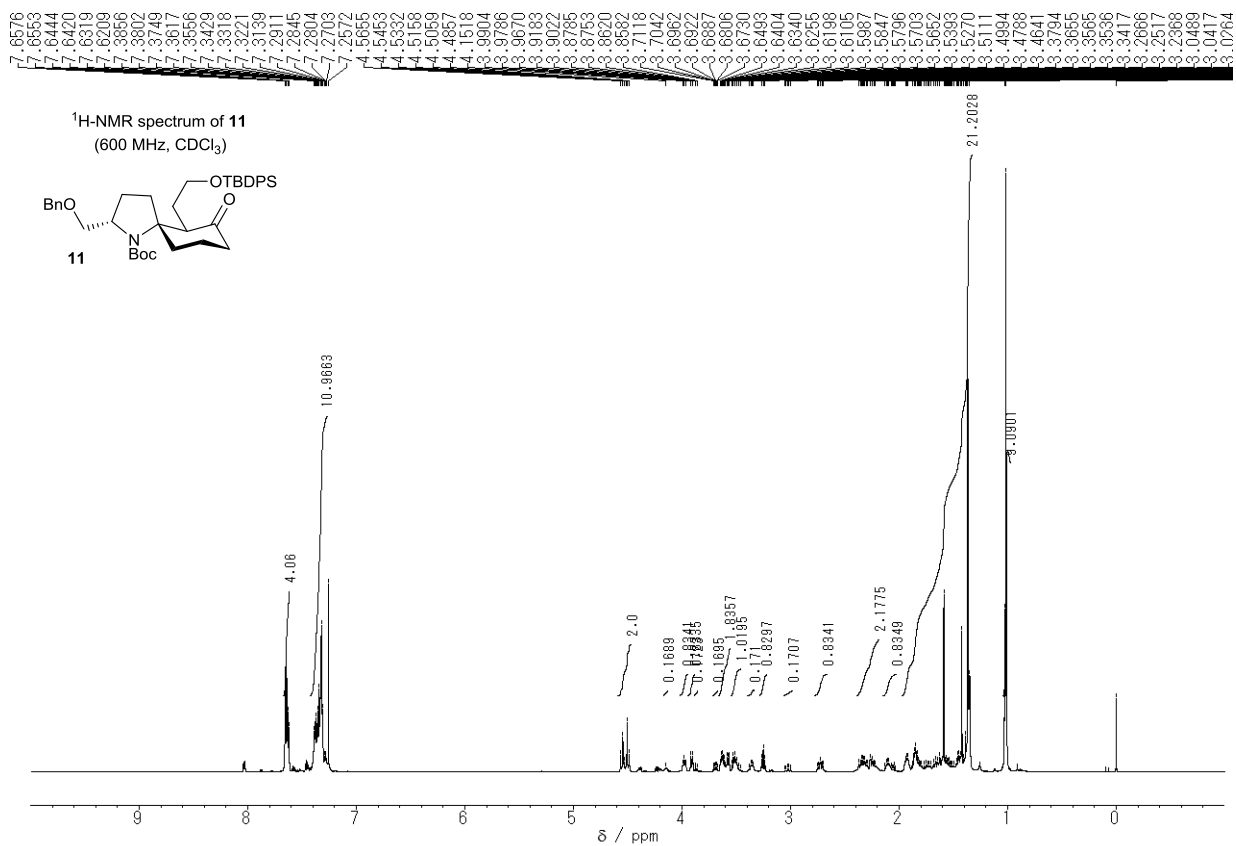


atsumura 7-12_noesy_CDCl3-temp25

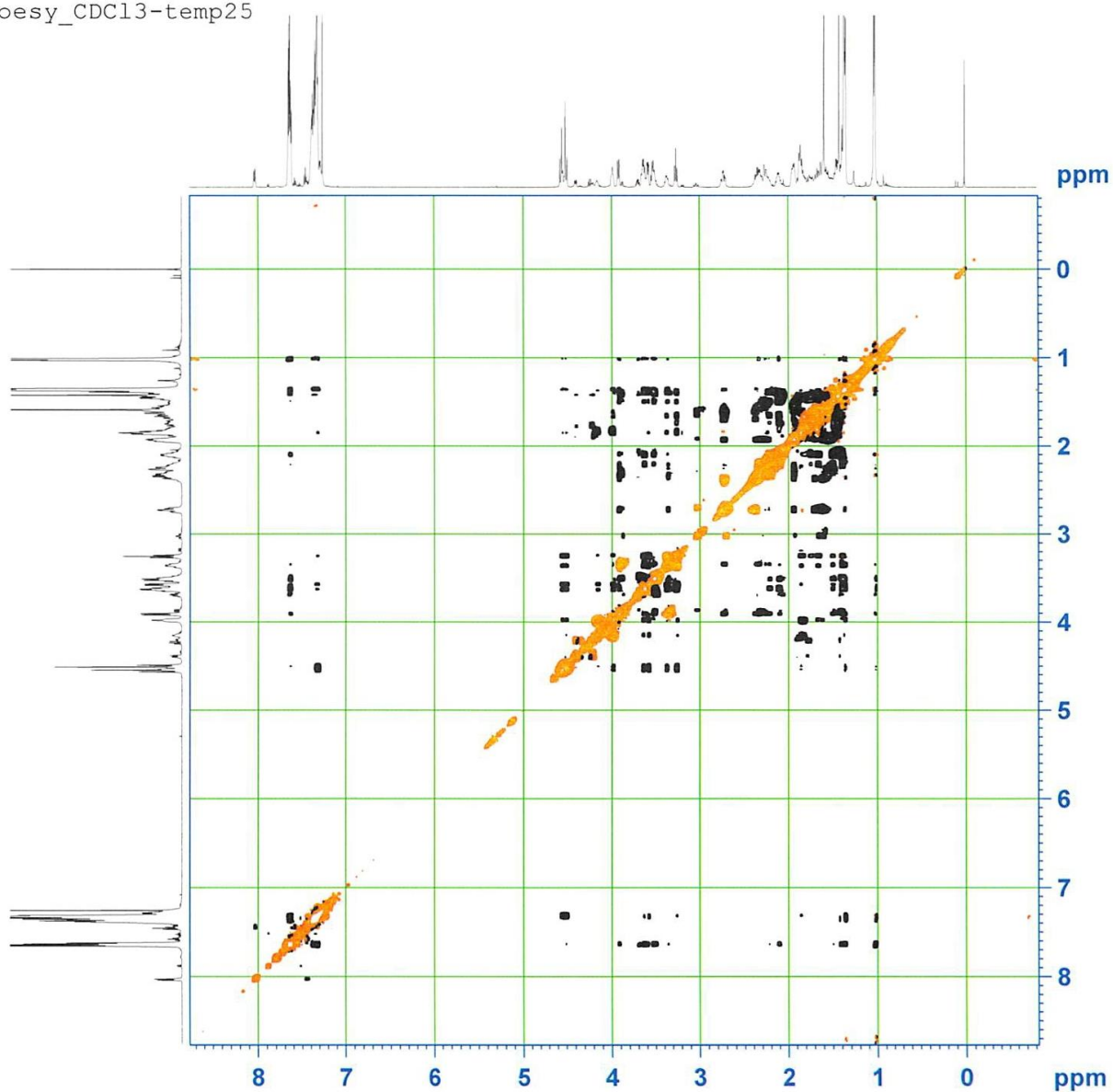


NOESY spectrum of **5**
(two rotamers in a 4:1 ratio, 25 °C)
(CDCl₃)

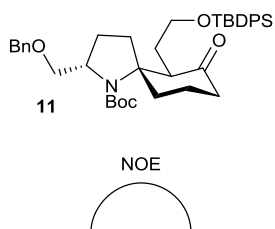




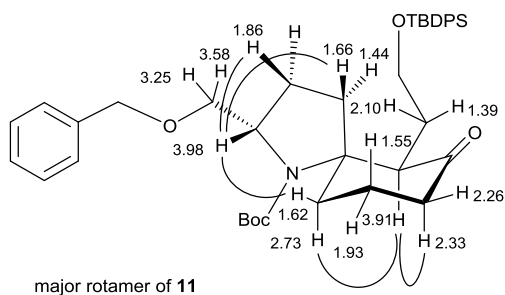
oesy_CDC13-temp25



NOESY spectrum of **11**
(two rotamers in a 5:1 ratio, 25 °C)
(CDCl₃)

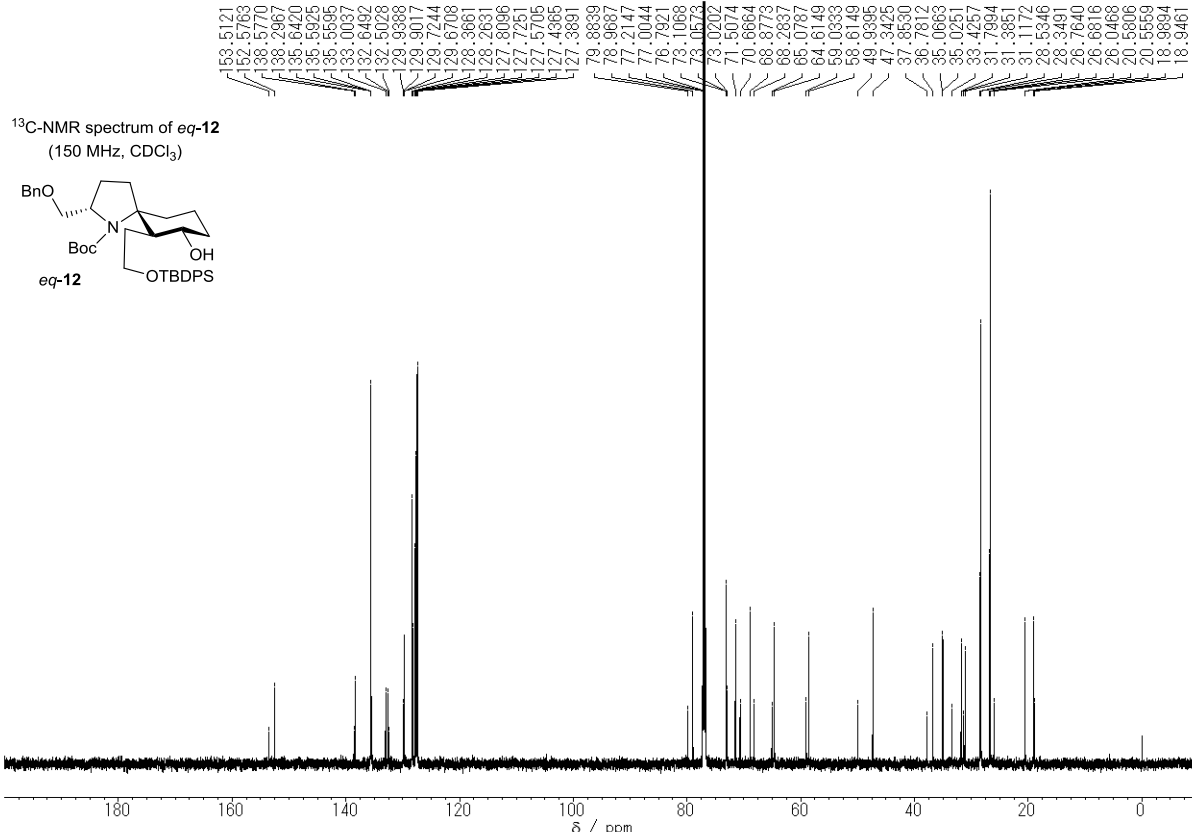
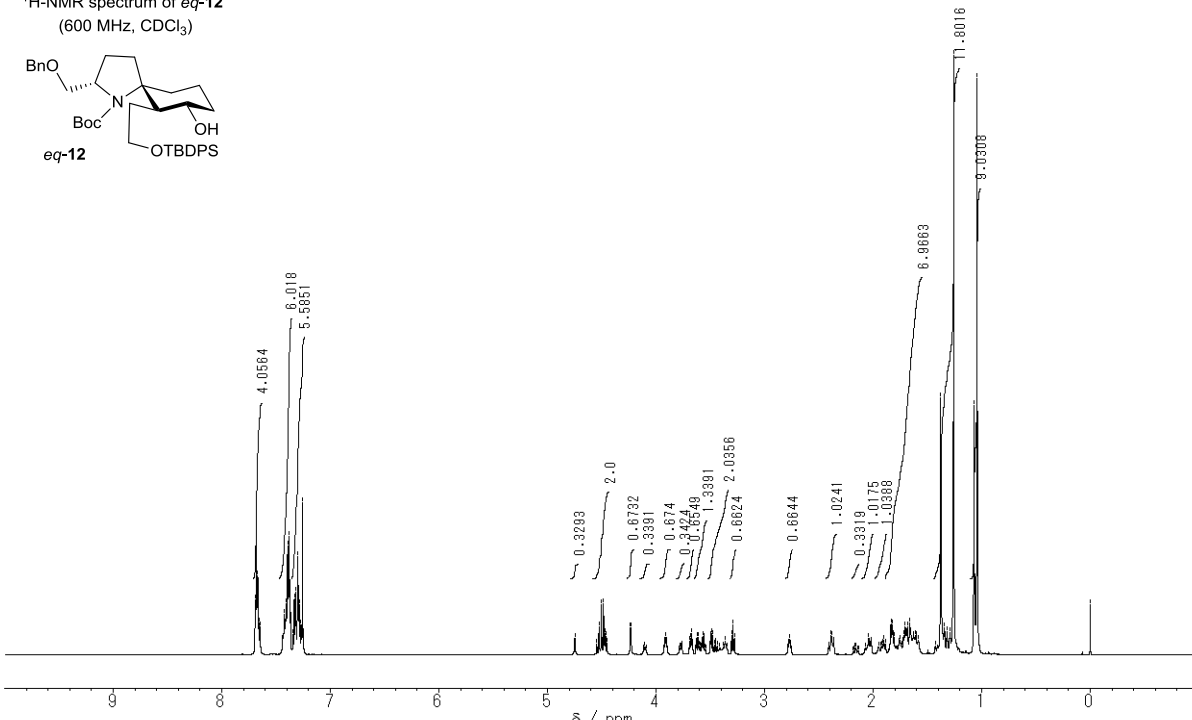
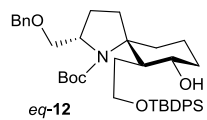


Observed NOEs

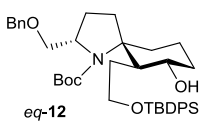


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7.3908
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7.3674
7.3440
7.3315
7.3182
7.2982
7.2868
7.2700
7.2549
4.7475
4.5459
4.5242
4.5030
4.4836
4.4721
4.4626
4.4519
4.2357
4.2305
4.1143
4.1021
4.0917
3.9245
3.9164
3.9120
3.9067
3.8993
3.7895
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3.7722
3.7647
3.7561
3.6939
3.6866
3.6779
3.6699
3.6624
3.6326
3.6264
3.6160
3.6099
3.5993
3.5932
3.5784
3.5741
3.5637
3.5599
3.5477
3.5431
3.4896
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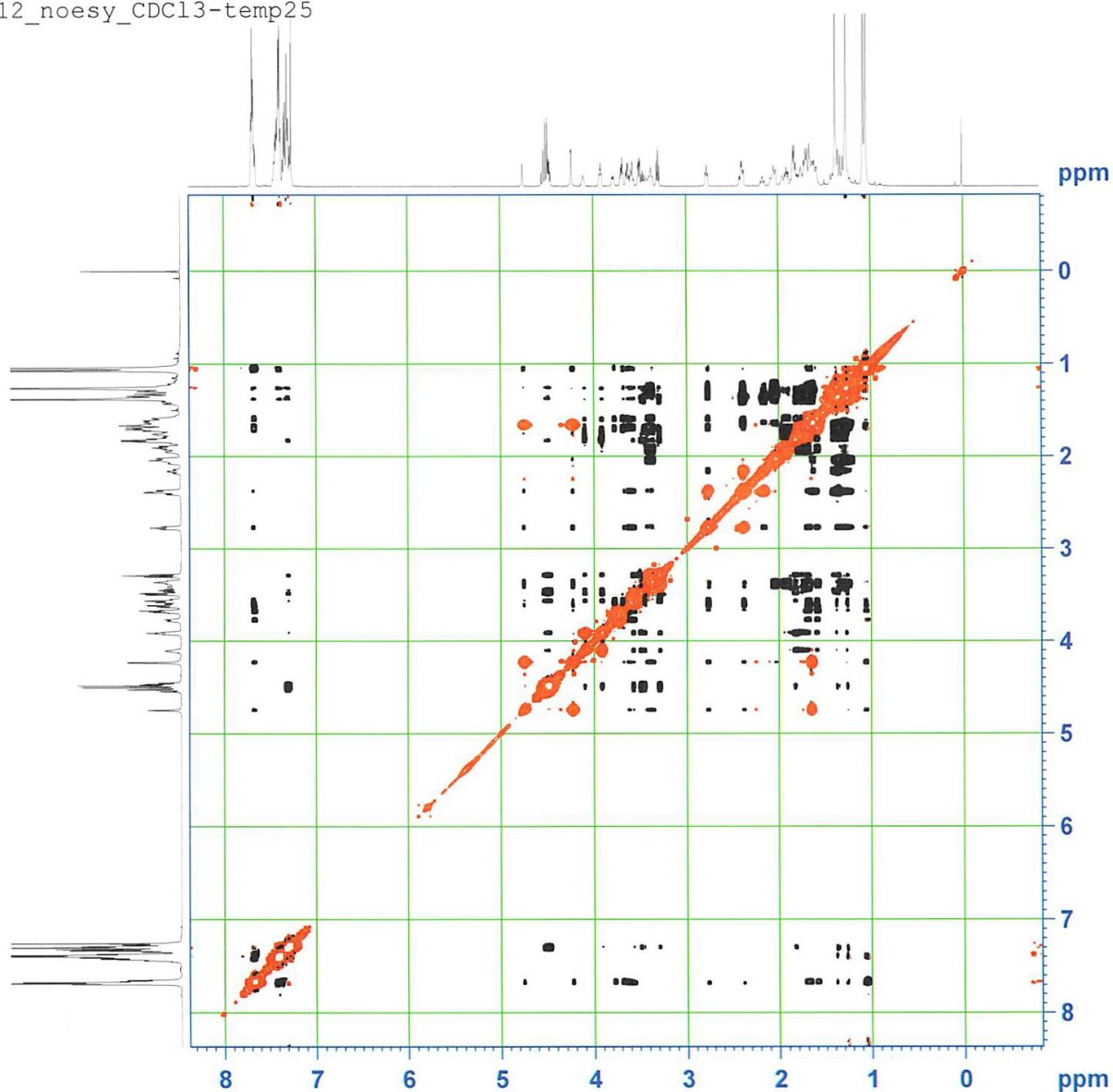
¹H-NMR spectrum of *eq-12*
(600 MHz, CDCl₃)



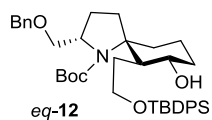
¹³C-NMR spectrum of *eq-12*
(150 MHz, CDCl₃)



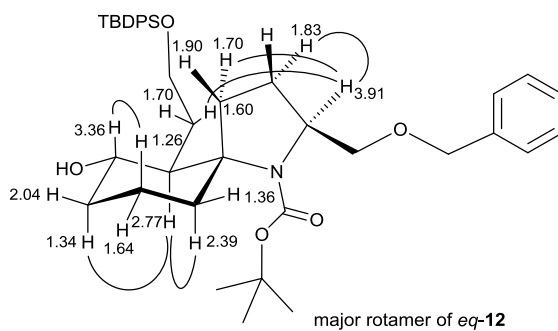
12_noesy_CDC13-temp25

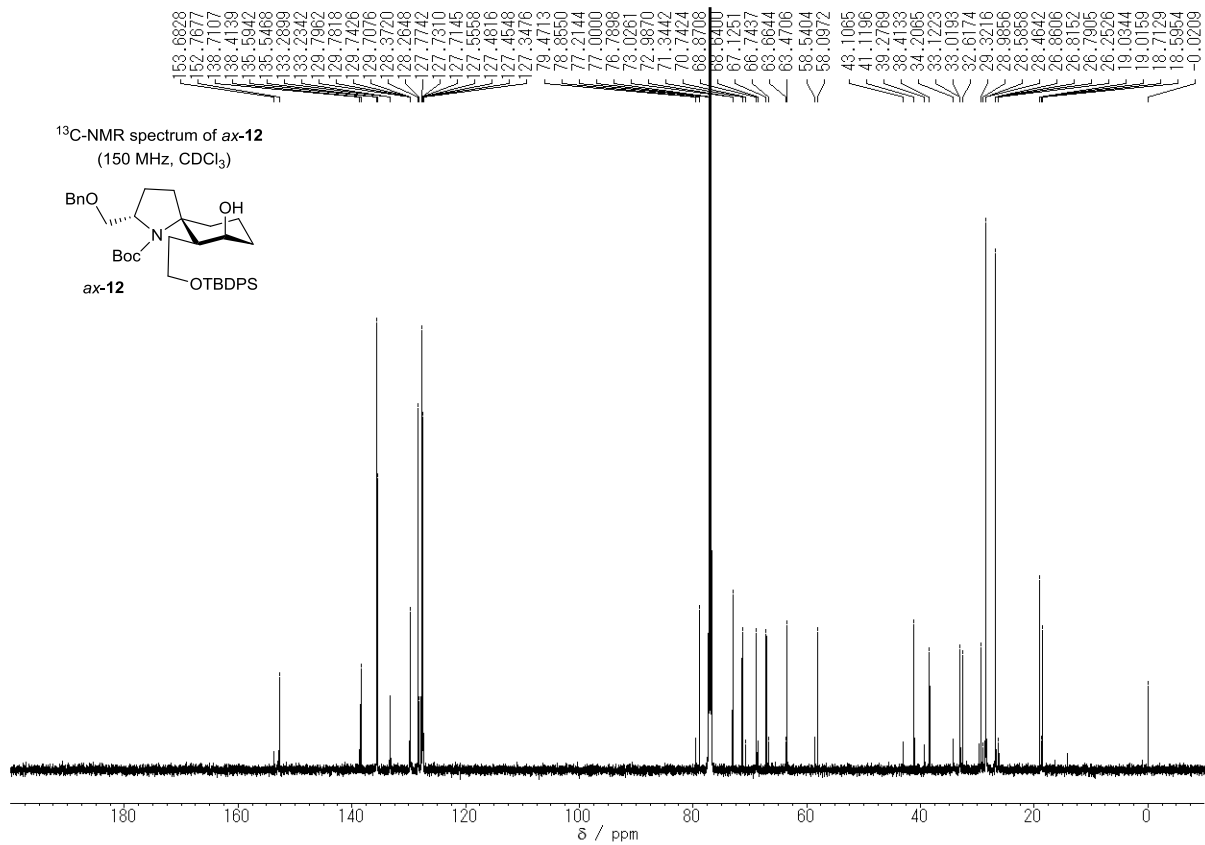
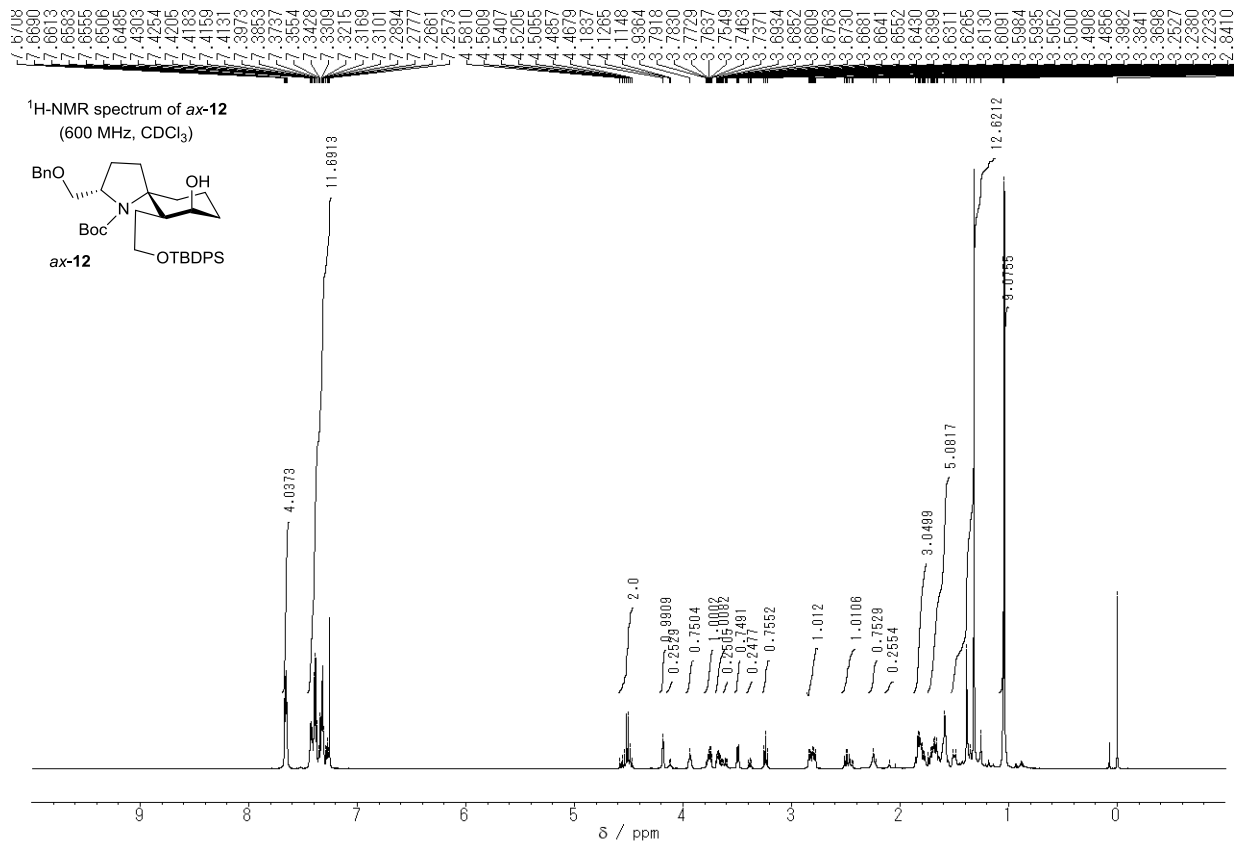


NOESY spectrum of *eq-12*
(two rotamers in a 2:1 ratio, 25 °C)
(CDCl₃)

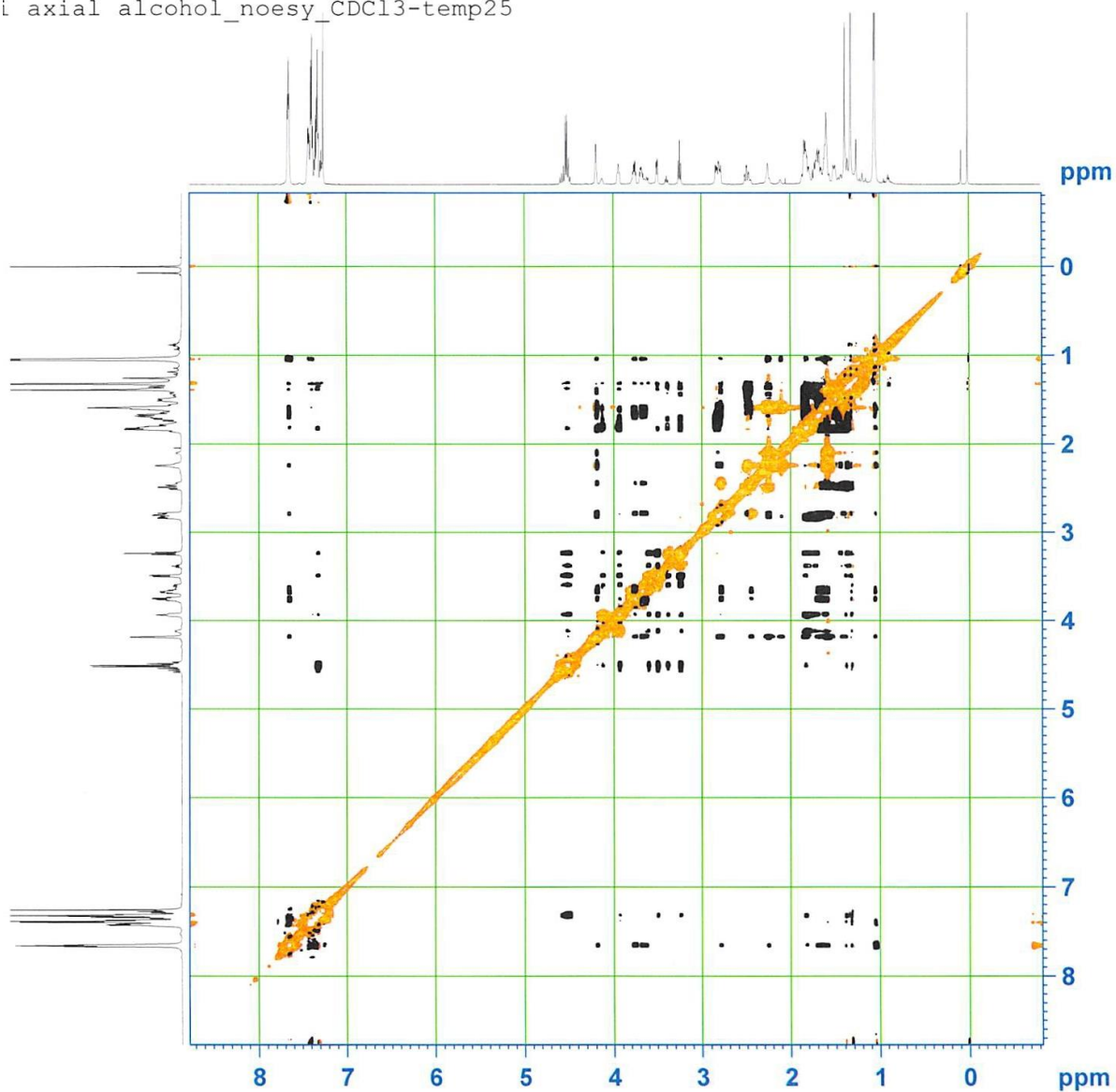


Observed NOEs

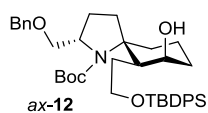




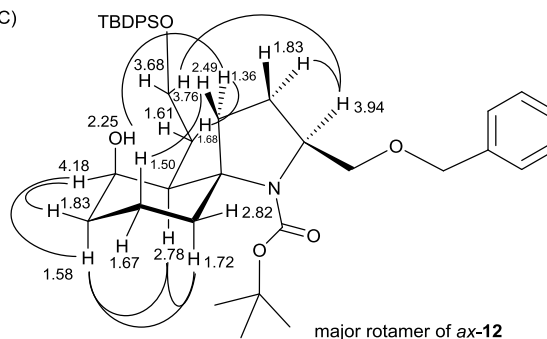
i axial alcohol_noesy_CDCl3-temp25

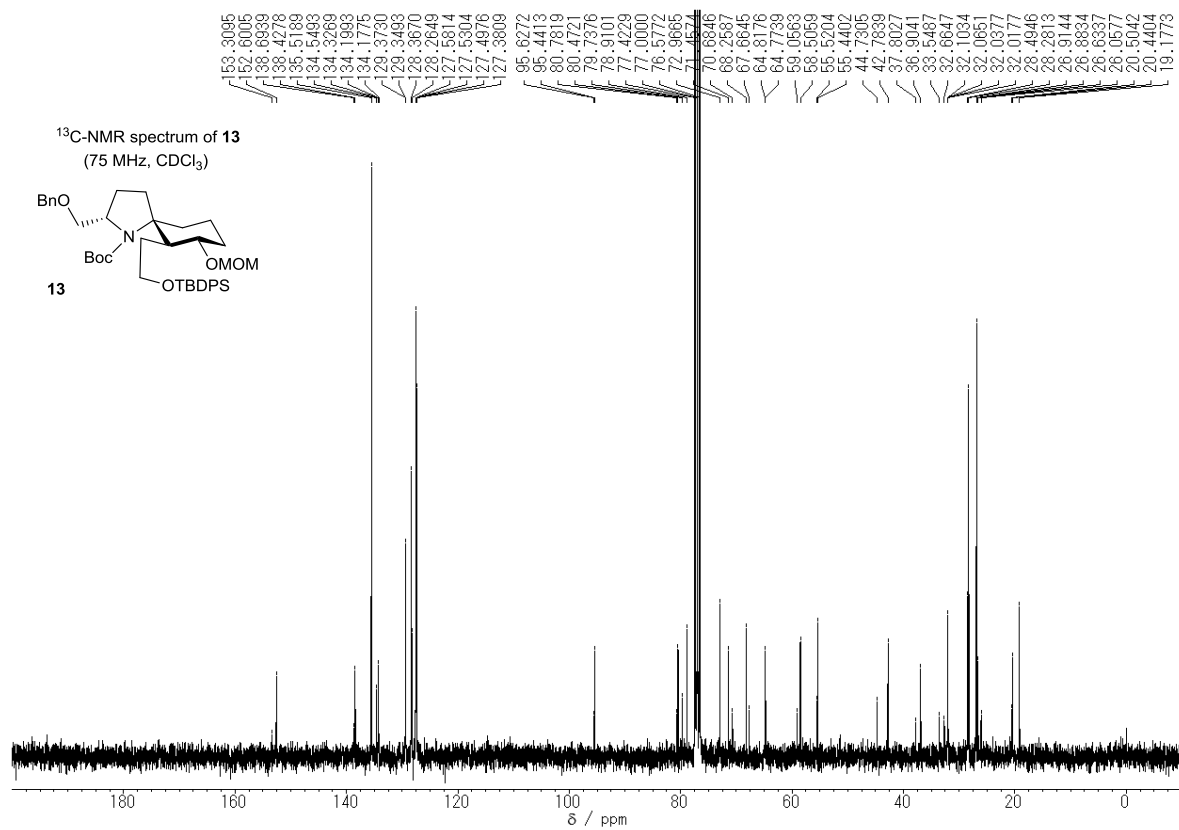
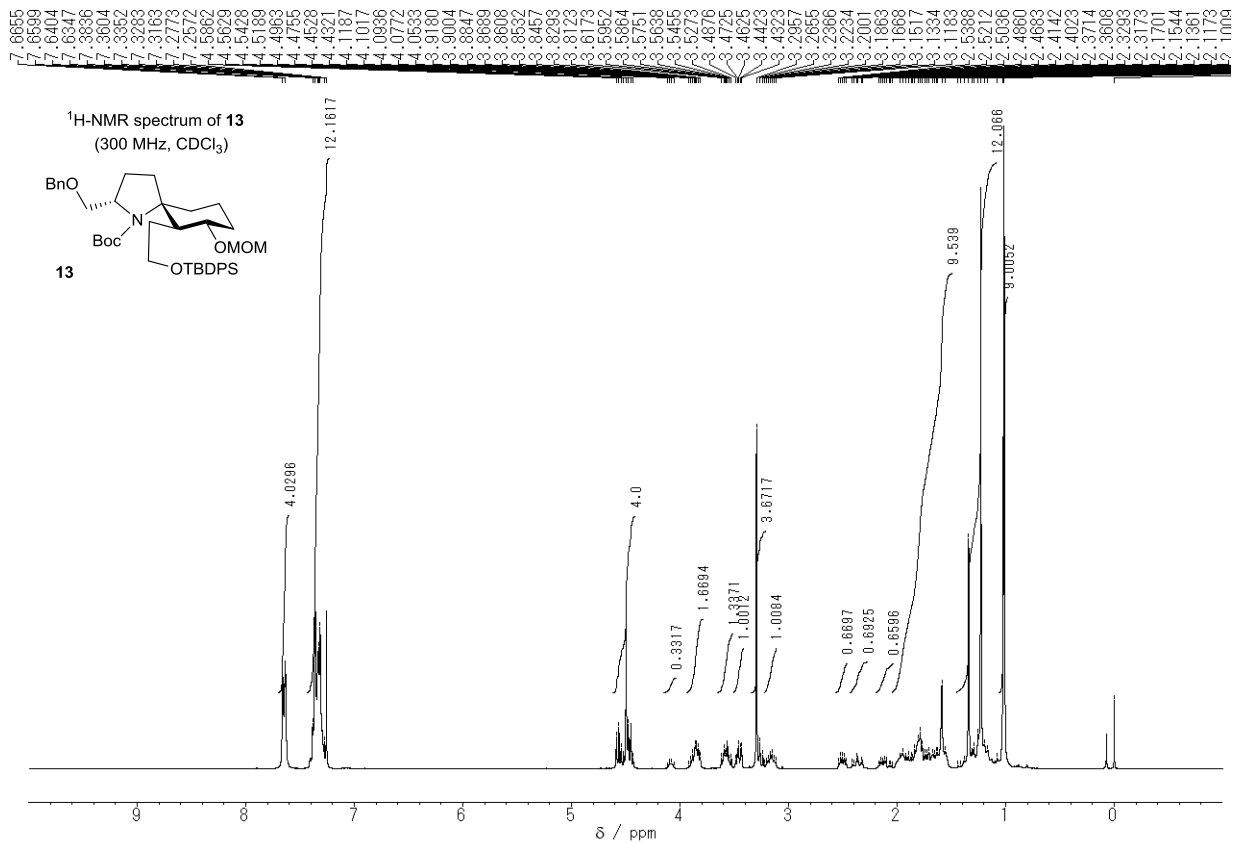


NOESY spectrum of *ax-12*
(two rotamers in a 3:1 ratio, 25 °C)
(CDCl₃)



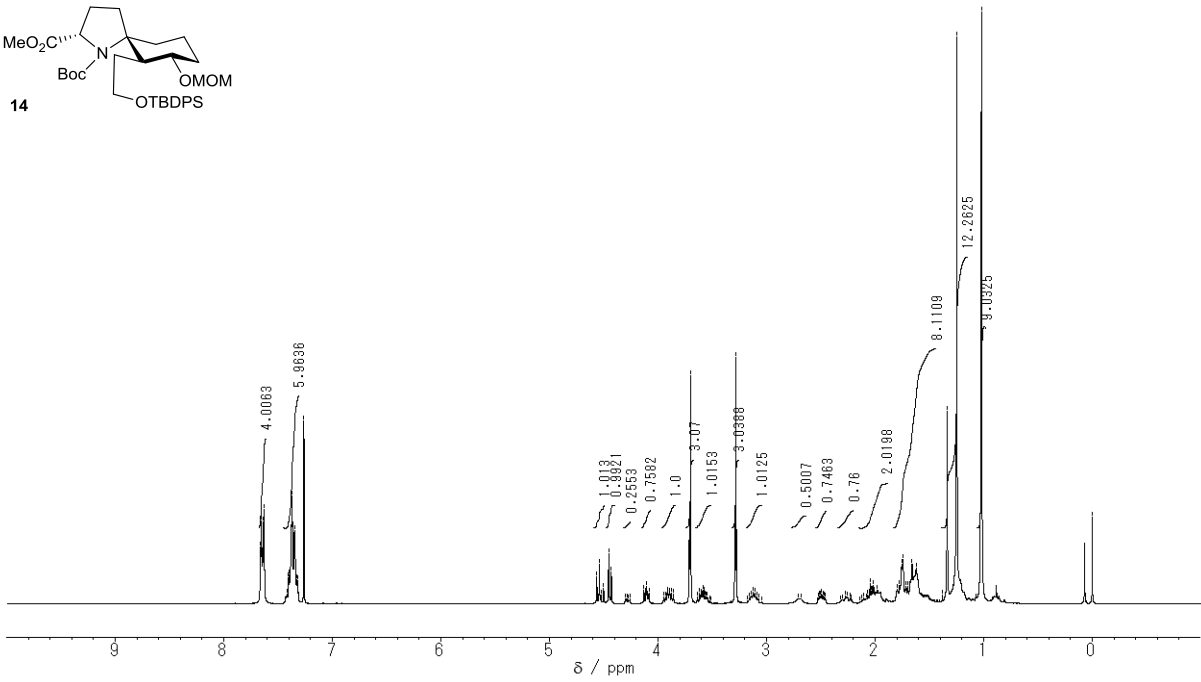
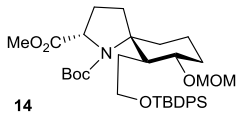
Observed NOEs





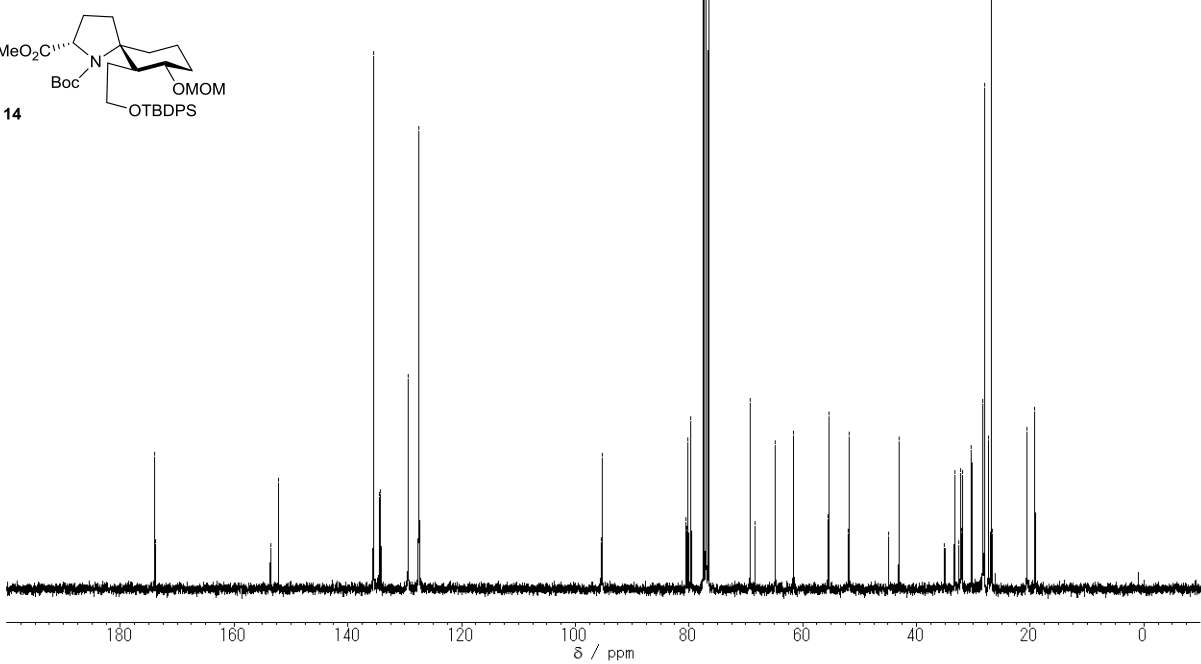
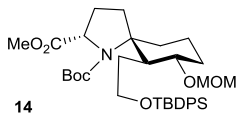
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7.3280
7.2616
4.5637
4.5403
4.5247
4.5012
4.4537
4.4301
4.3019
4.2867
4.2736
4.2564
4.1302
4.1096
4.1045
4.0979
4.0830
3.9466
3.9301
3.9145
3.9085
3.8878
3.8911
3.8760
3.8583
3.7111
3.7001
3.6364
3.6164
3.6041
3.5979
3.5930
3.5834
3.5785
3.5658
3.5576
3.5464
3.5260
3.5156
3.2924
3.2815
3.1738
3.1590
3.1390
3.1241
3.1086
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2.5153
2.5054
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2.4591
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2.3017

¹H-NMR spectrum of **14**
(300 MHz, CDCl₃)



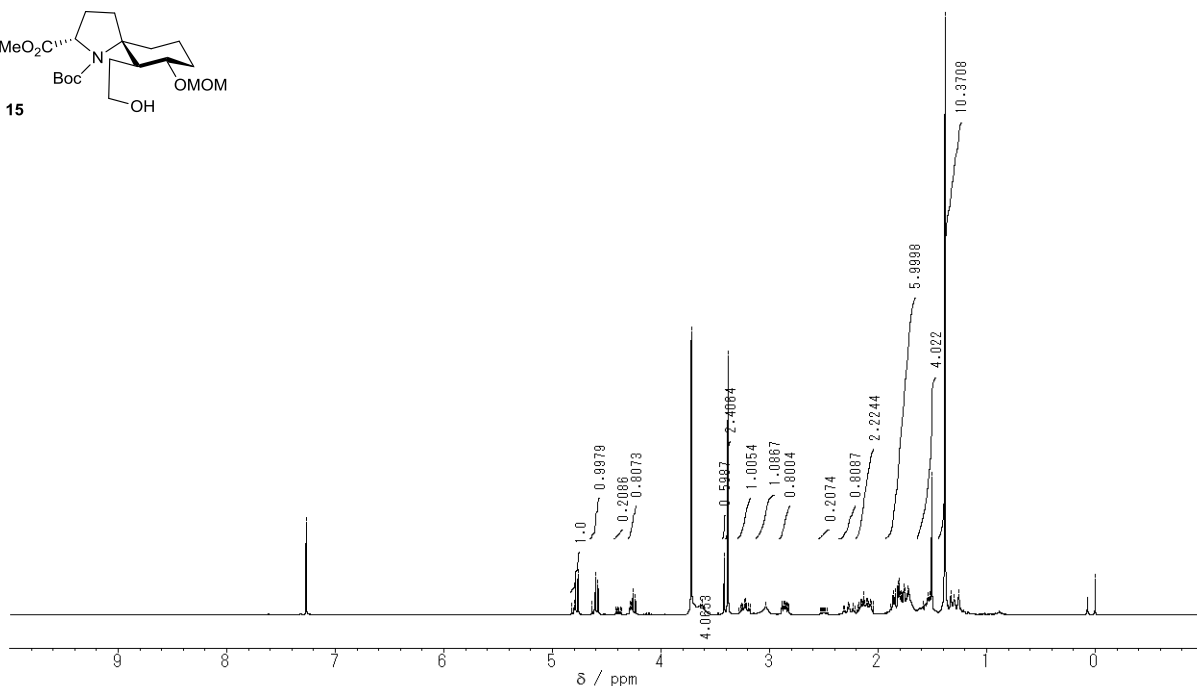
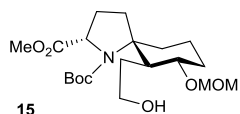
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135.4733
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129.4388
129.4059
129.3894
129.3603
127.5905
127.5158
127.4957
127.4739
95.4759
95.2463
80.5067
80.4265
80.1495
79.6355
77.4247
77.0000
76.5772
69.2739
68.4373
64.8194
64.7976
61.6499
61.5897
55.5022
55.3874
51.9517
51.8167
44.9310
43.1085
35.0250
33.3154
32.5608
32.2473
32.1216
32.0596
31.9175
30.2090
28.3824
28.0389
27.3791
27.3299
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26.6501
20.5771
19.1518
19.1154

¹³C-NMR spectrum of **14**
(75 MHz, CDCl₃)

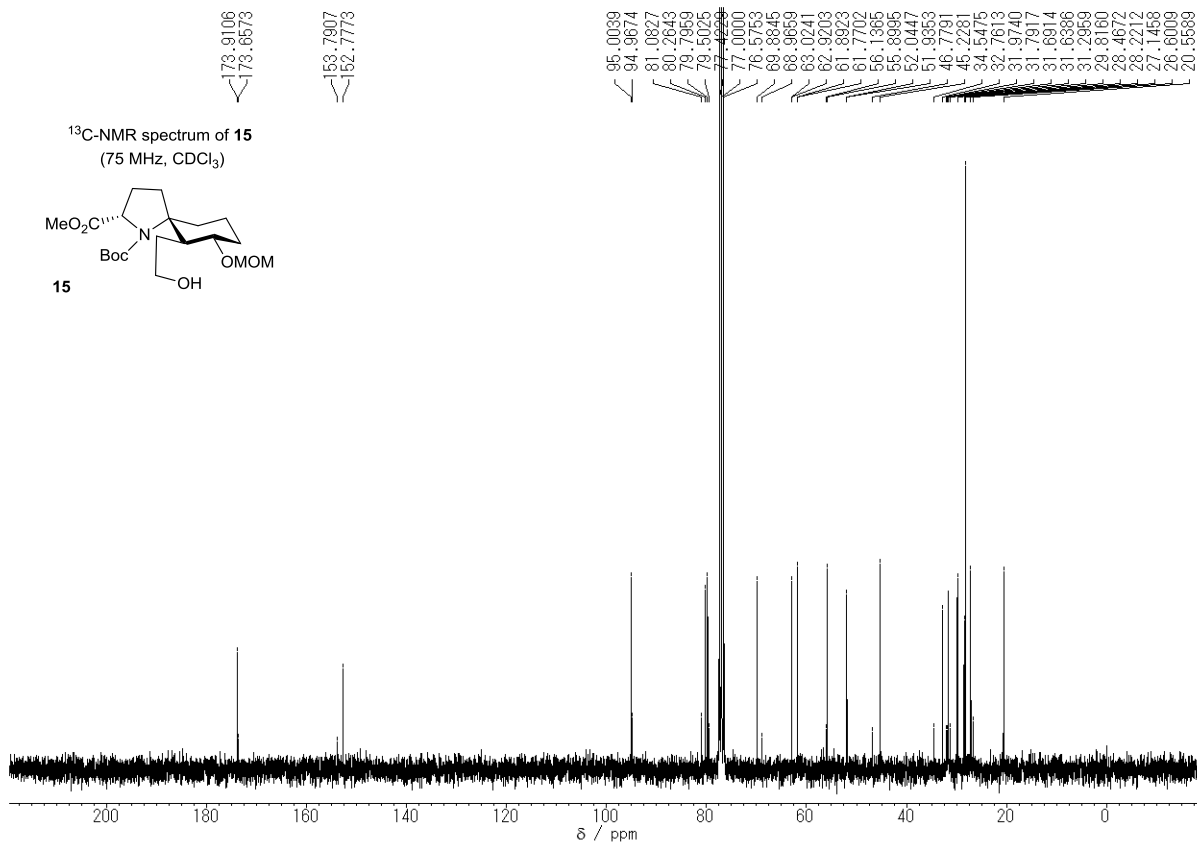
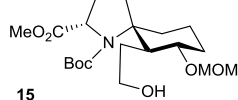


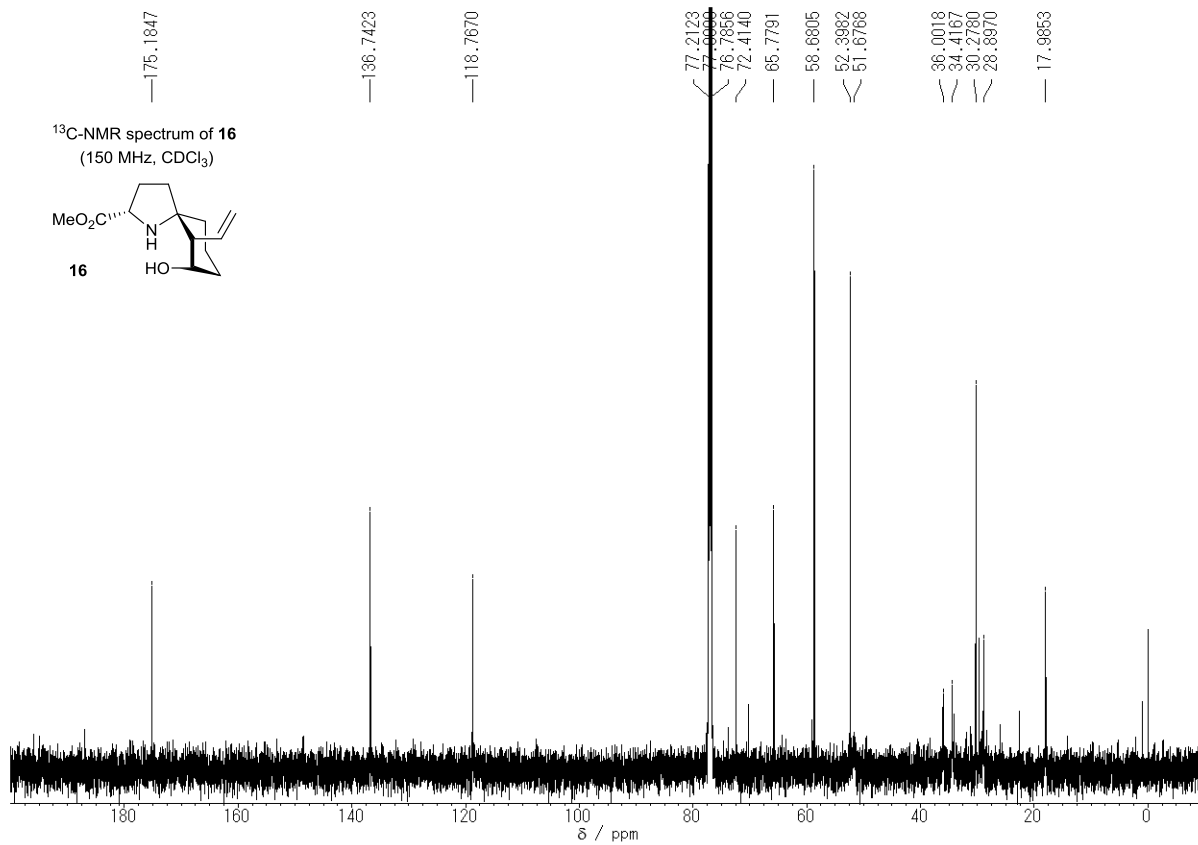
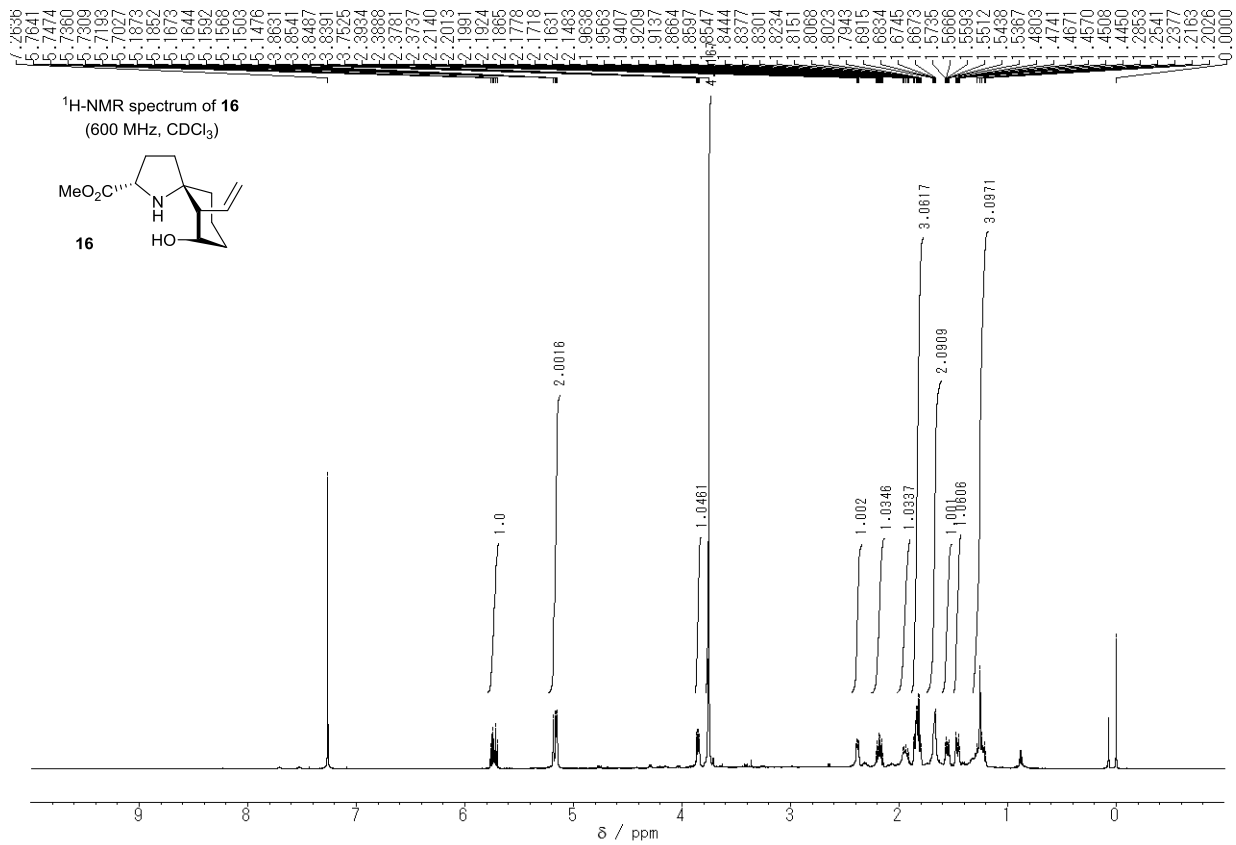
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4.6043
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4.3863
4.3750
4.3671
4.2861
4.2783
4.2711
4.2596
4.2356
3.7209
3.6185
3.4185
3.3830
3.2821
3.2821
3.2664
3.2630
3.2457
3.2312
3.2173
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1.8478

¹H-NMR spectrum of **15**
(300 MHz, CDCl₃)

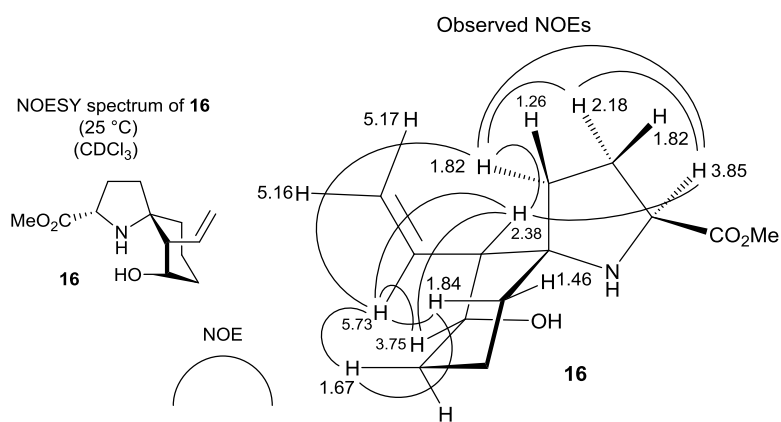
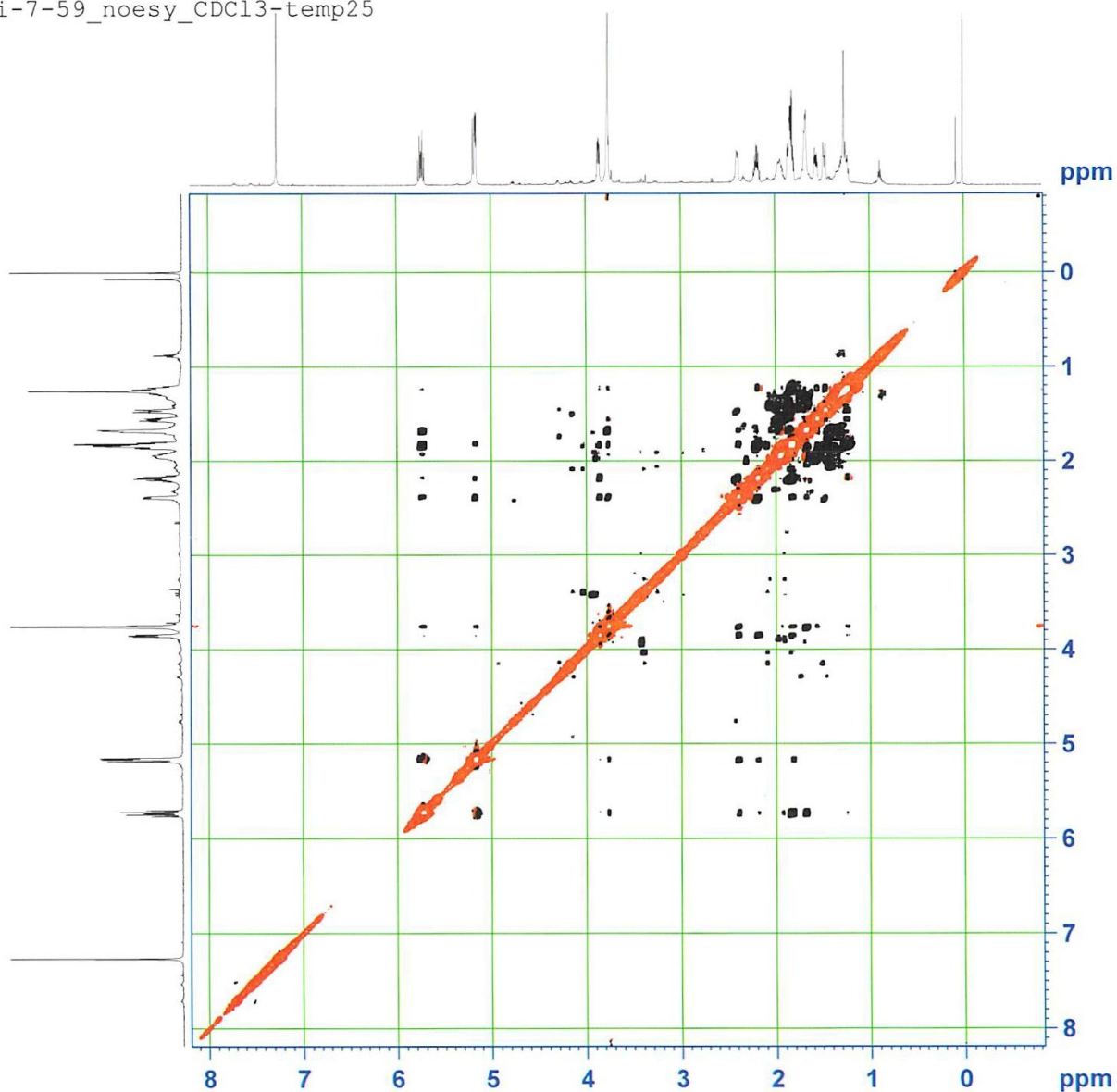


¹³C-NMR spectrum of **15**
(75 MHz, CDCl₃)

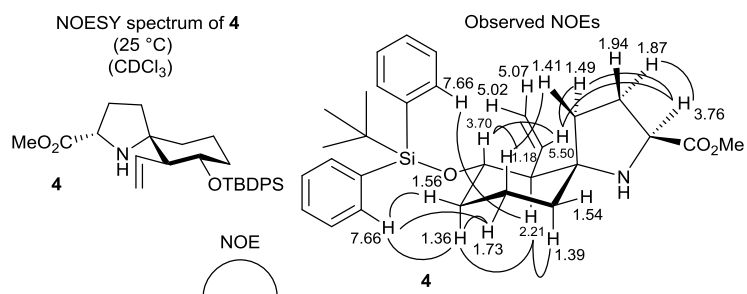
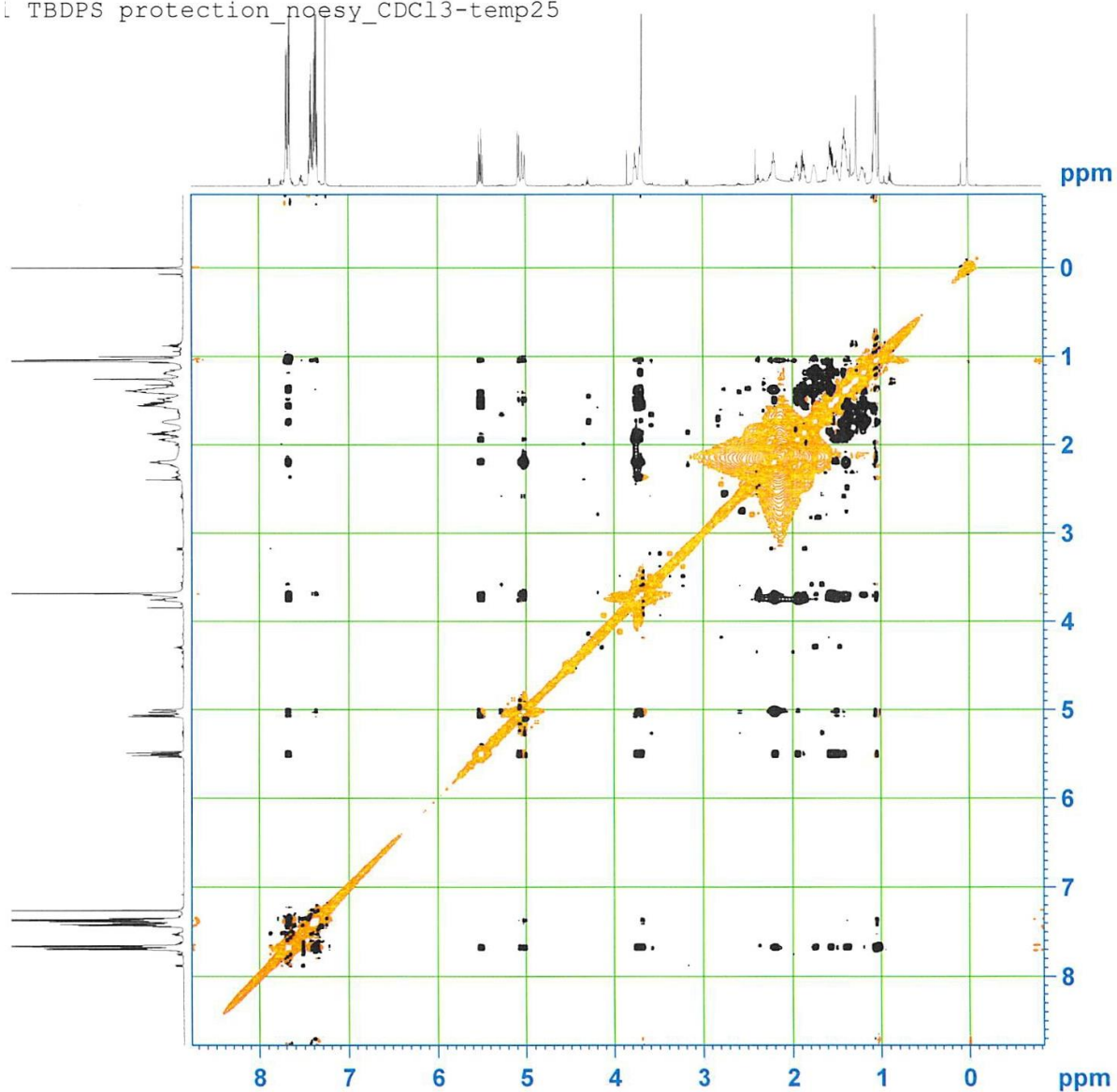




i-7-59_noesy_CDC13-temp25

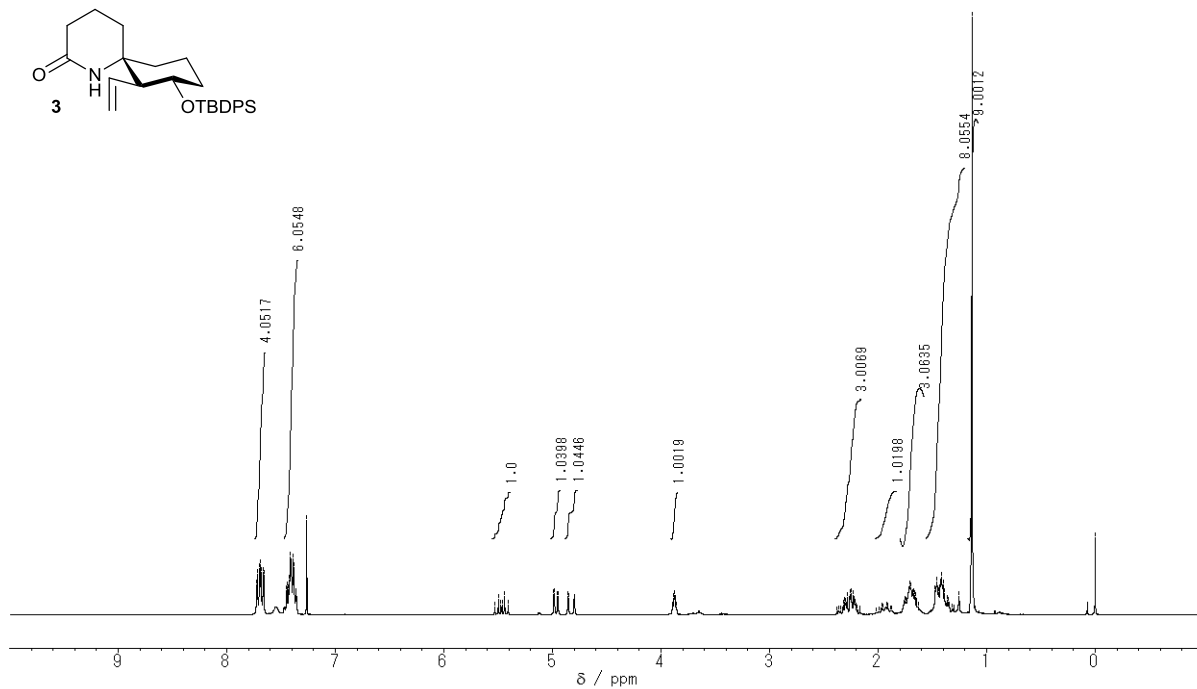
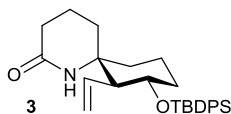


l TBDPS protection_noesy_CDCl3-temp25



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7.6825
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7.4315
7.4262
7.4178
7.4120
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6.4410
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1.6841
1.6769
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1.6580
1.6449
1.6319
1.4735

¹H-NMR spectrum of **3**
(300 MHz, CDCl₃)



¹³C-NMR spectrum of **3**
(75 MHz, CDCl₃)

