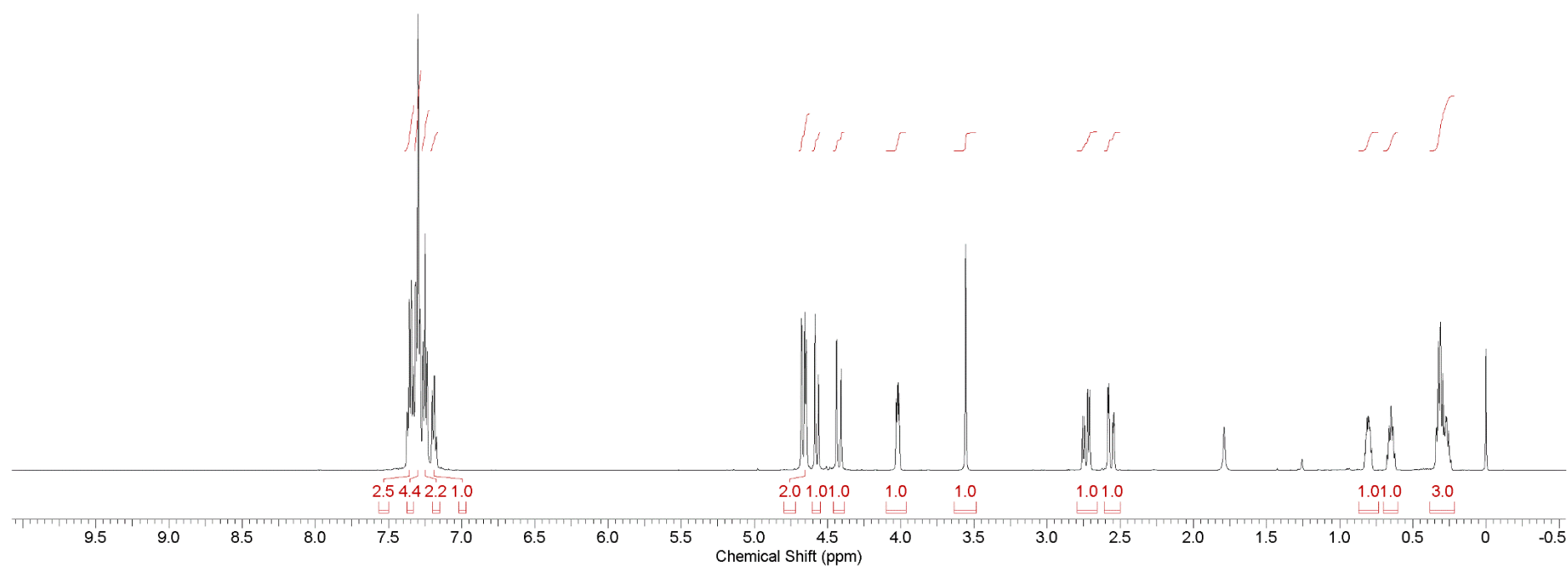
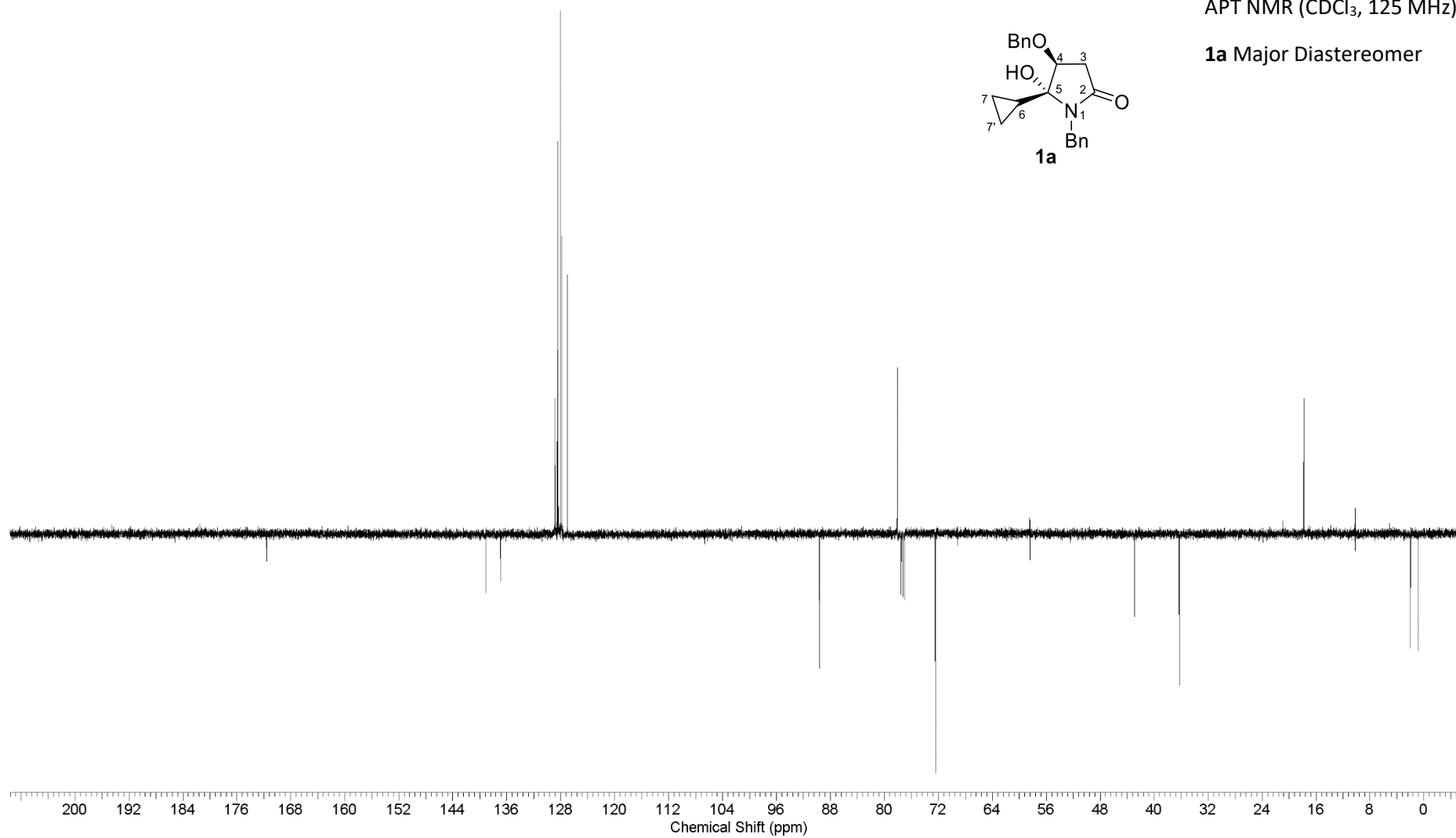
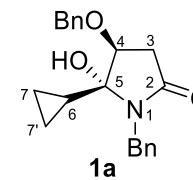


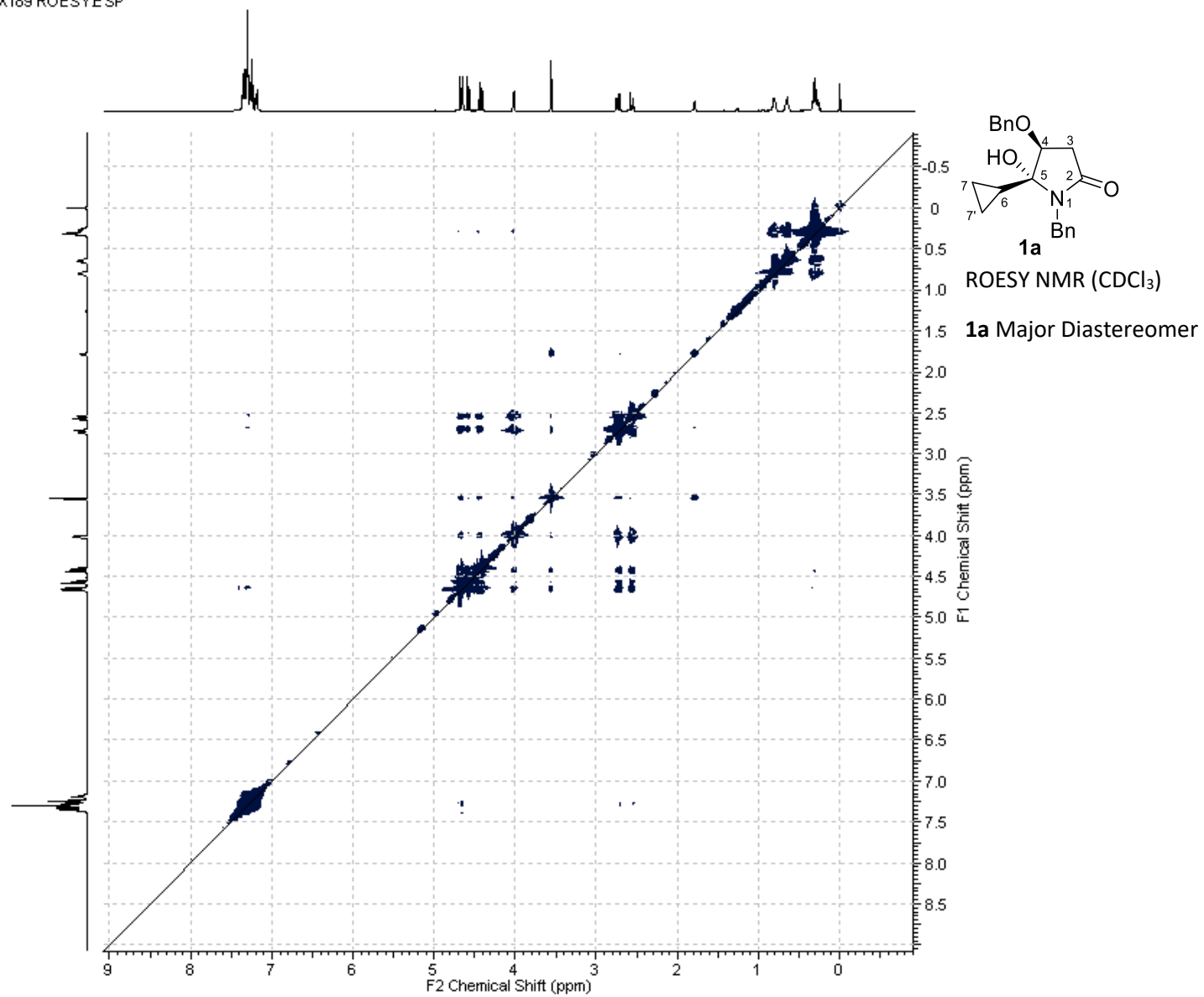
¹H NMR (CDCl₃, 500 MHz)

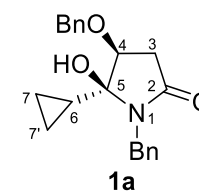
1a Major Diastereomer



APT NMR (CDCl₃, 125 MHz)**1a** Major Diastereomer

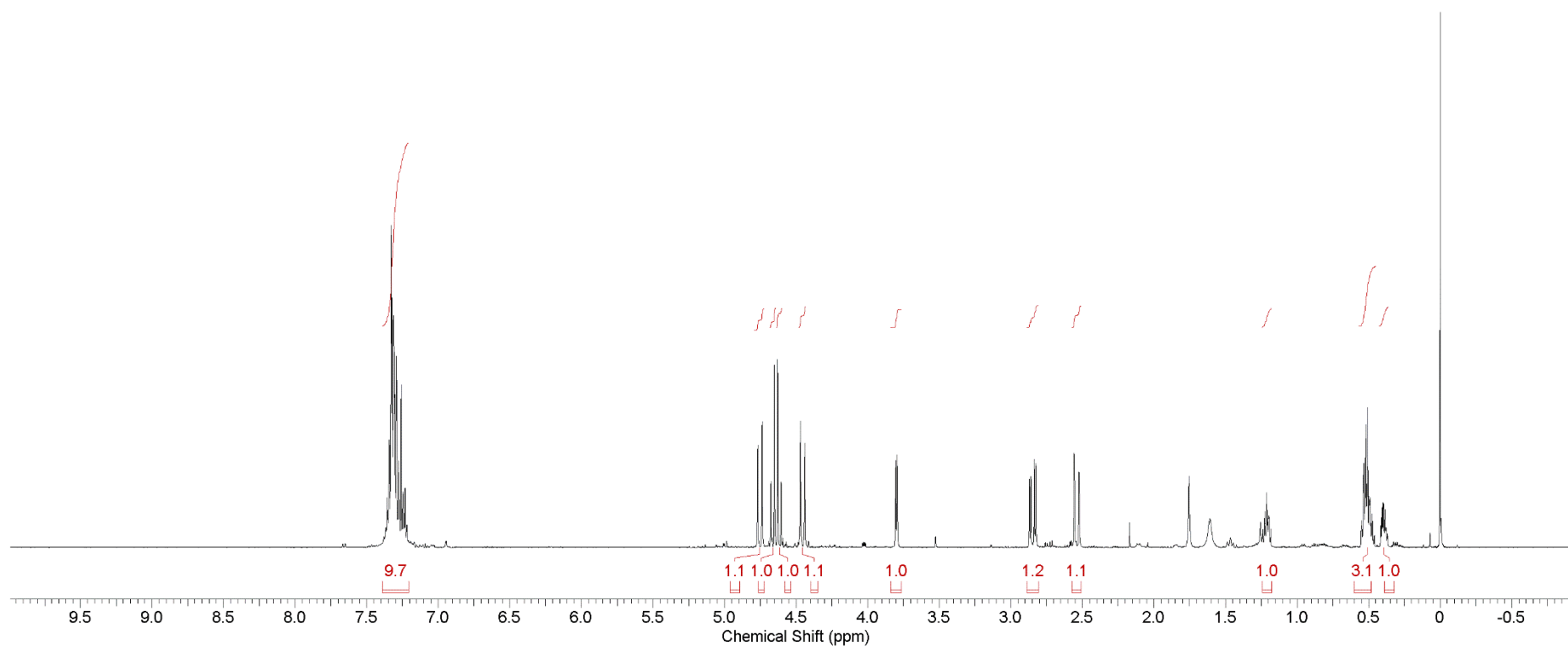
X189 ROESY SP

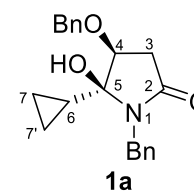




^1H NMR (CDCl_3 , 500 MHz)

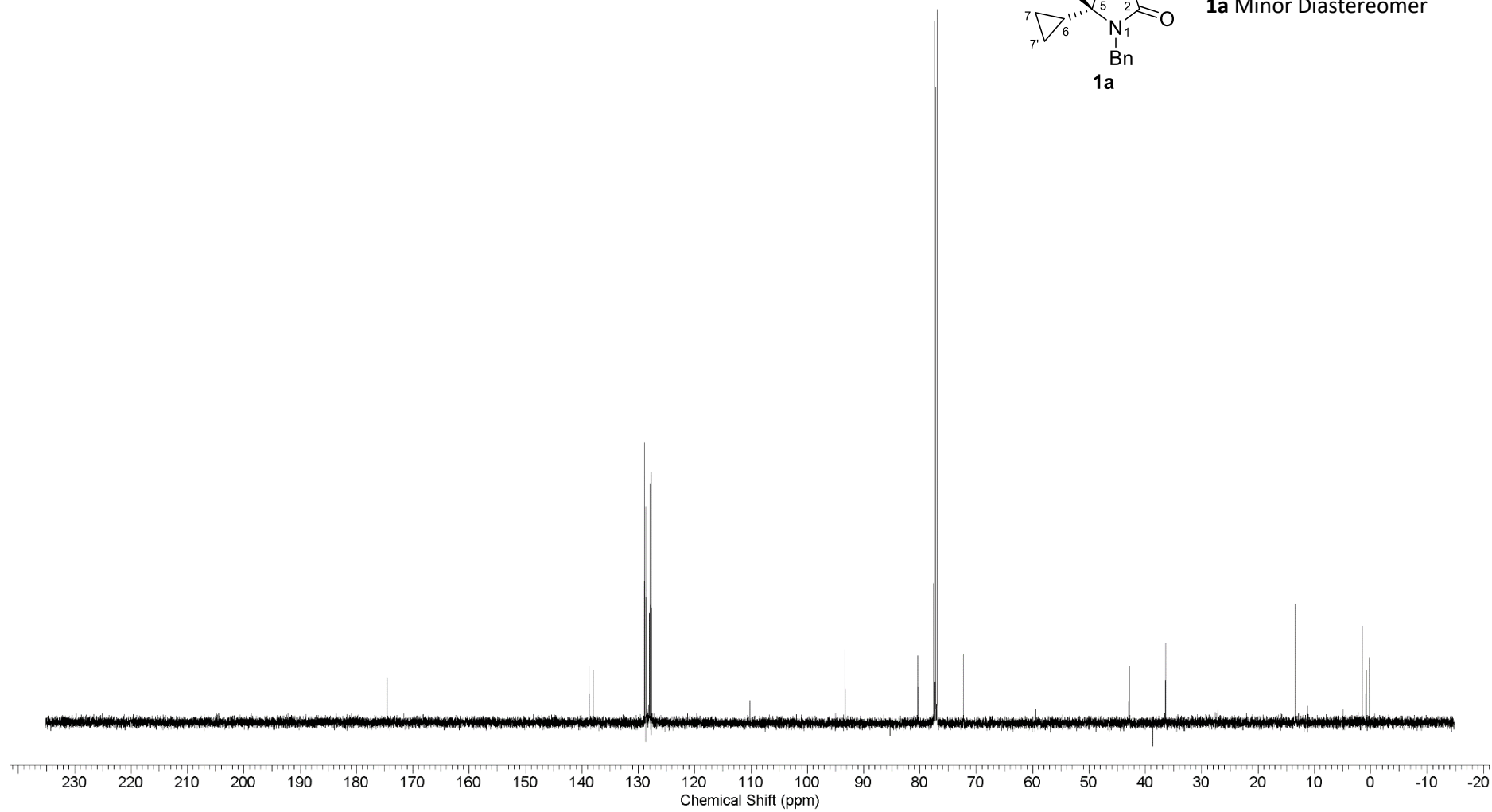
1a Minor Diastereomer

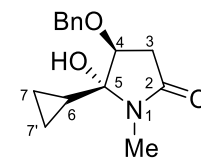




^{13}C NMR (CDCl_3 , 125 MHz)

1a Minor Diastereomer

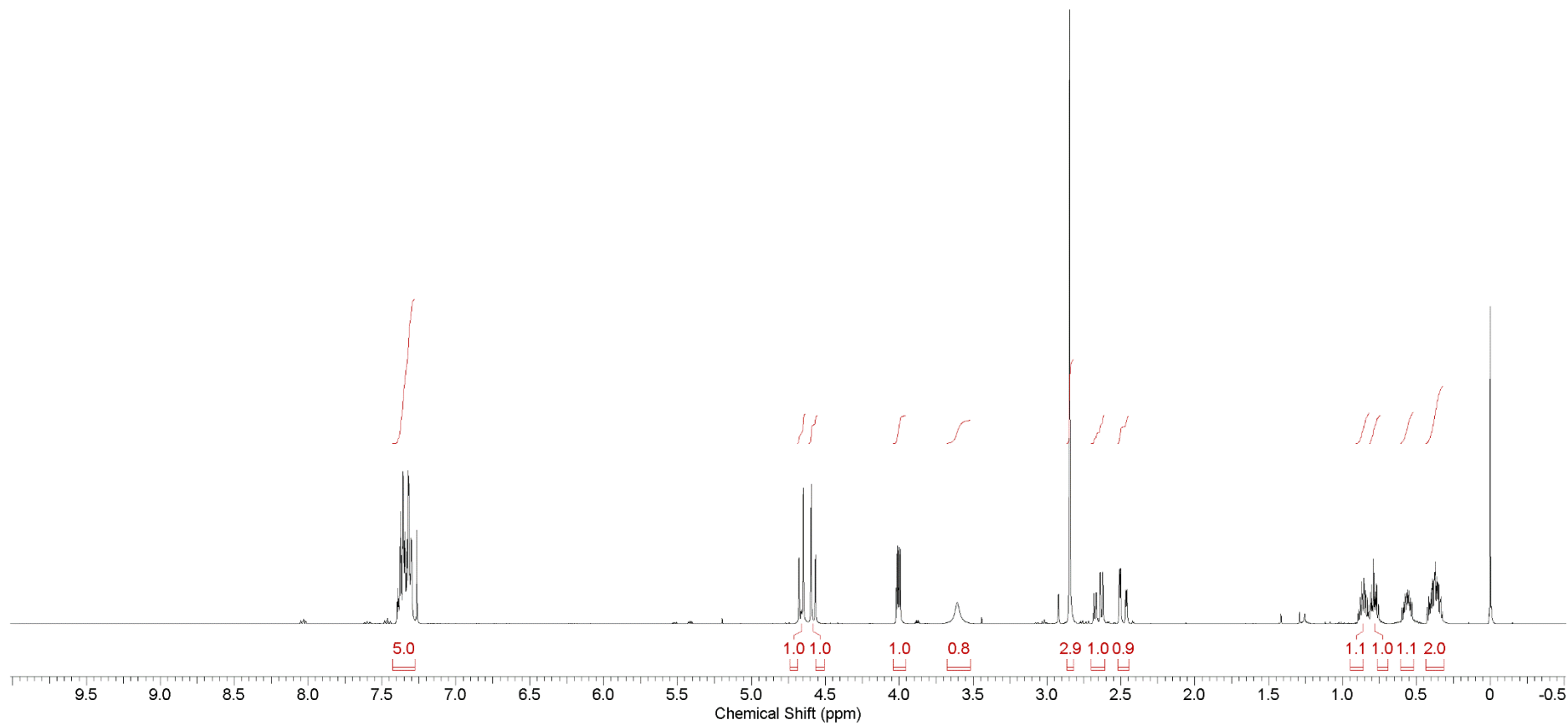


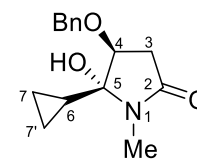


^1H NMR (CDCl_3 , 500 MHz)

1b R = Me Major
Diastereomer

1b R = Me

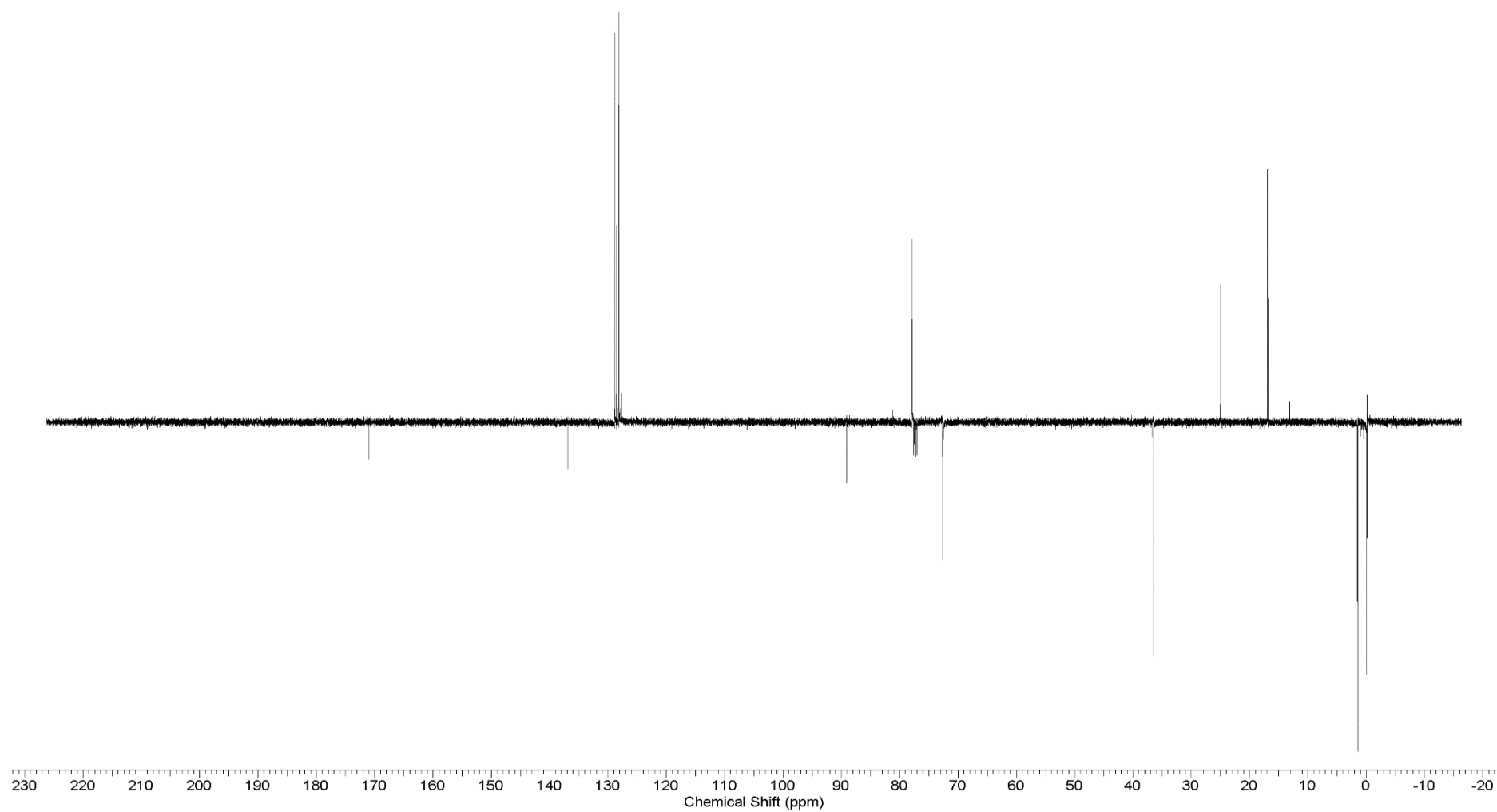




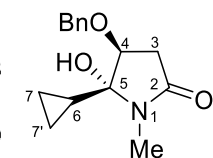
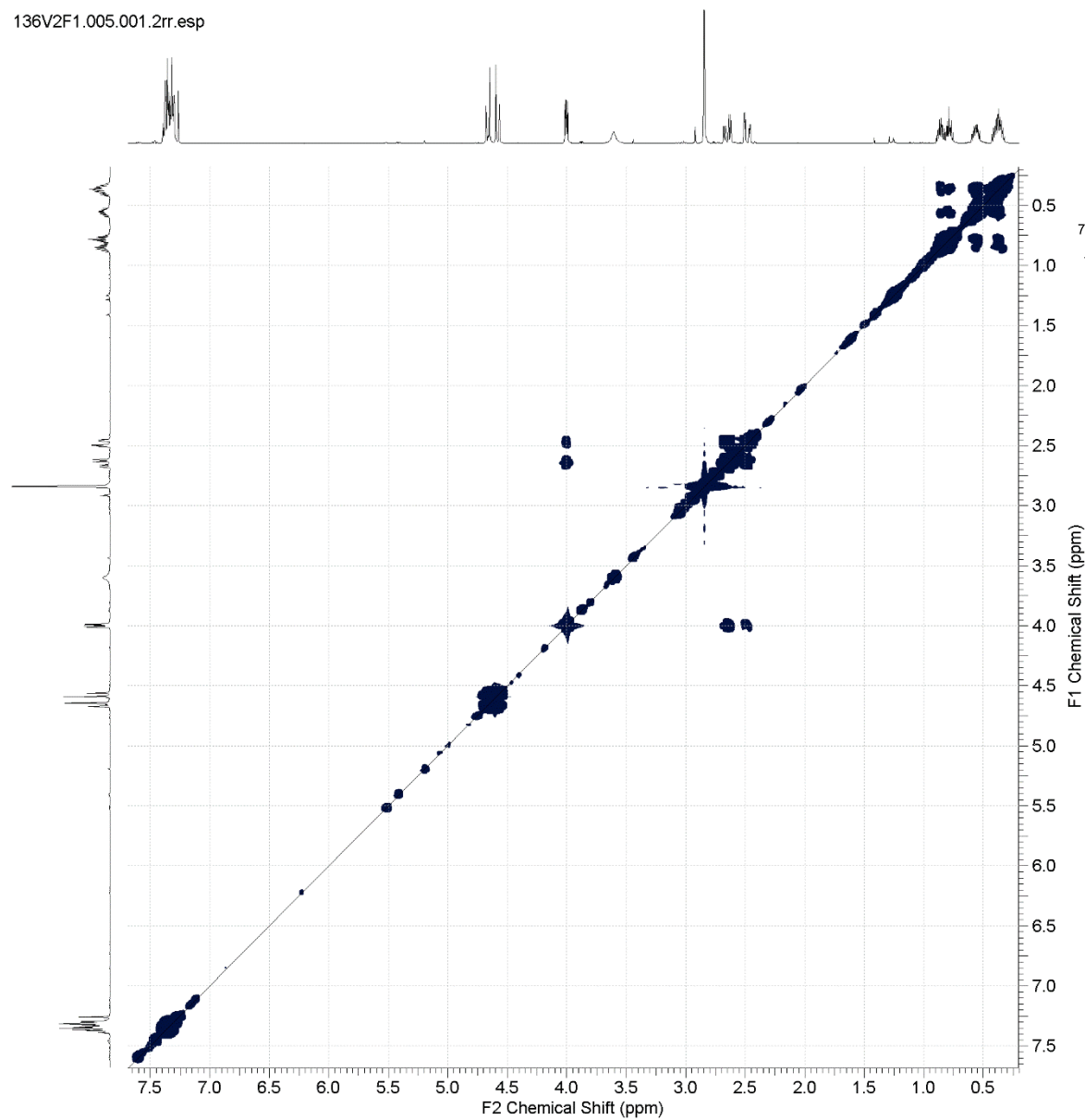
1b R = Me

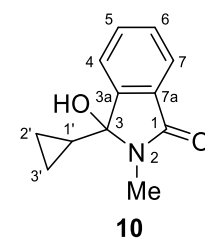
APT NMR (CDCl₃, 125 MHz)

1b R = Me Major
Diastereomer



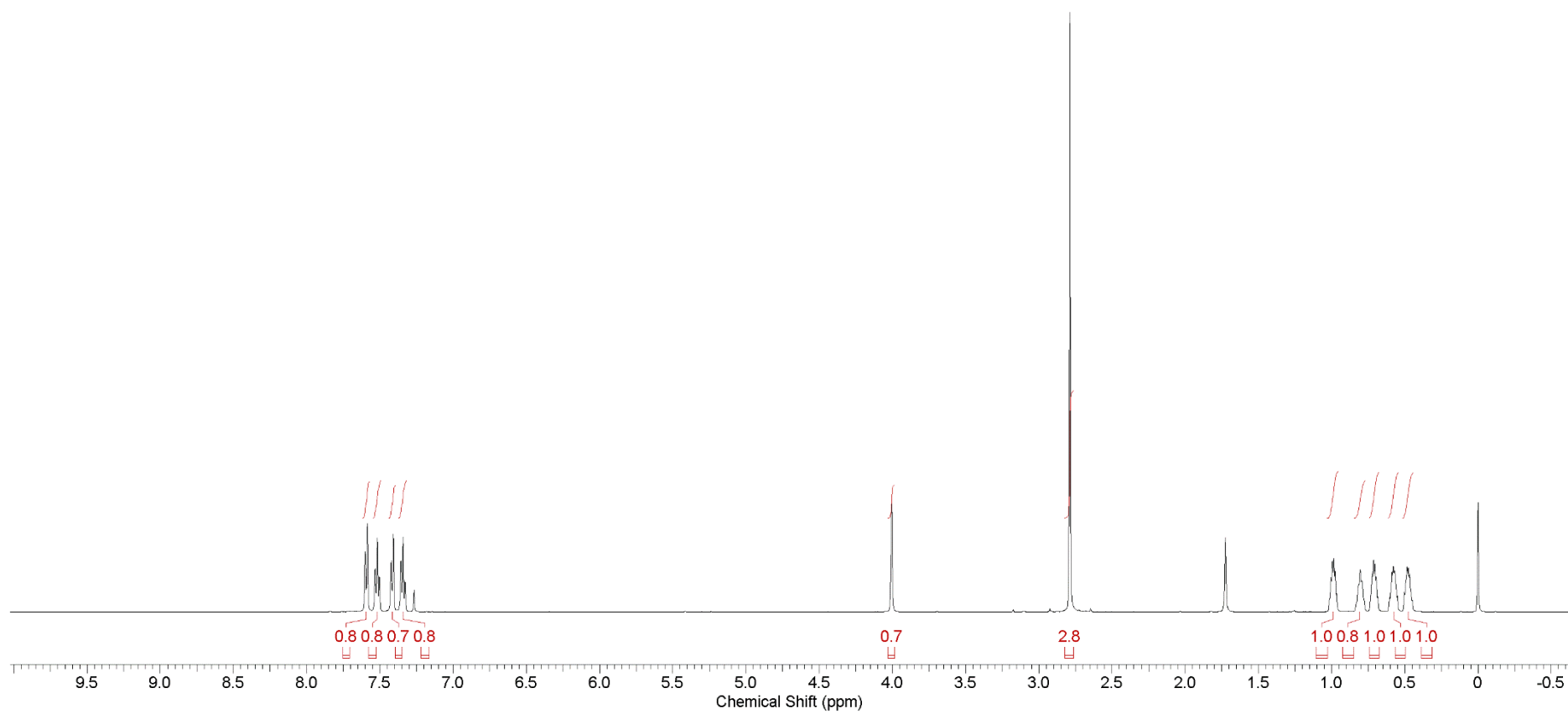
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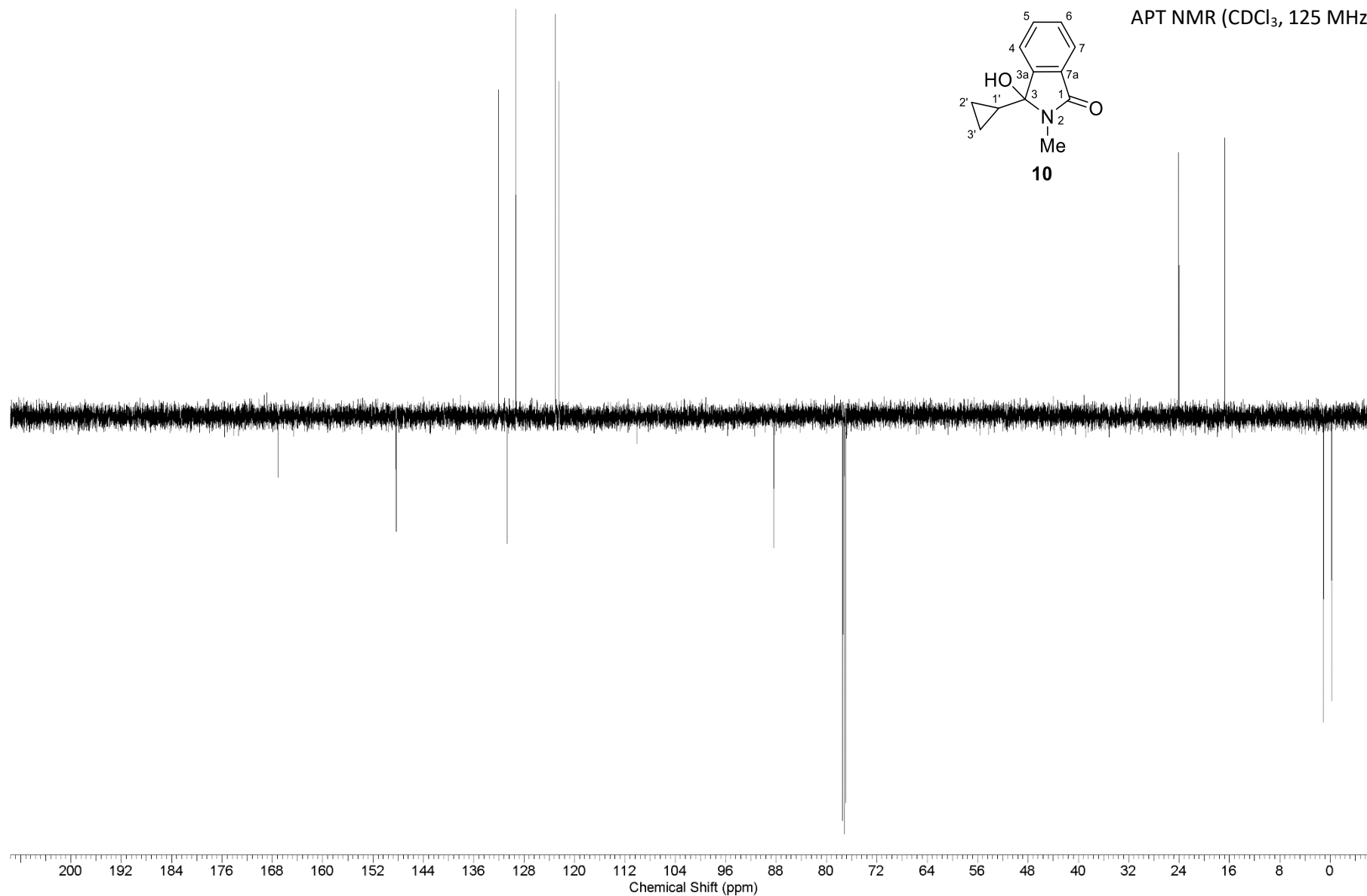
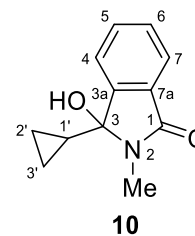


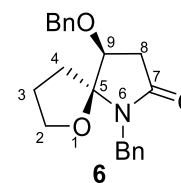


^1H NMR (CDCl_3 , 500 MHz)

10

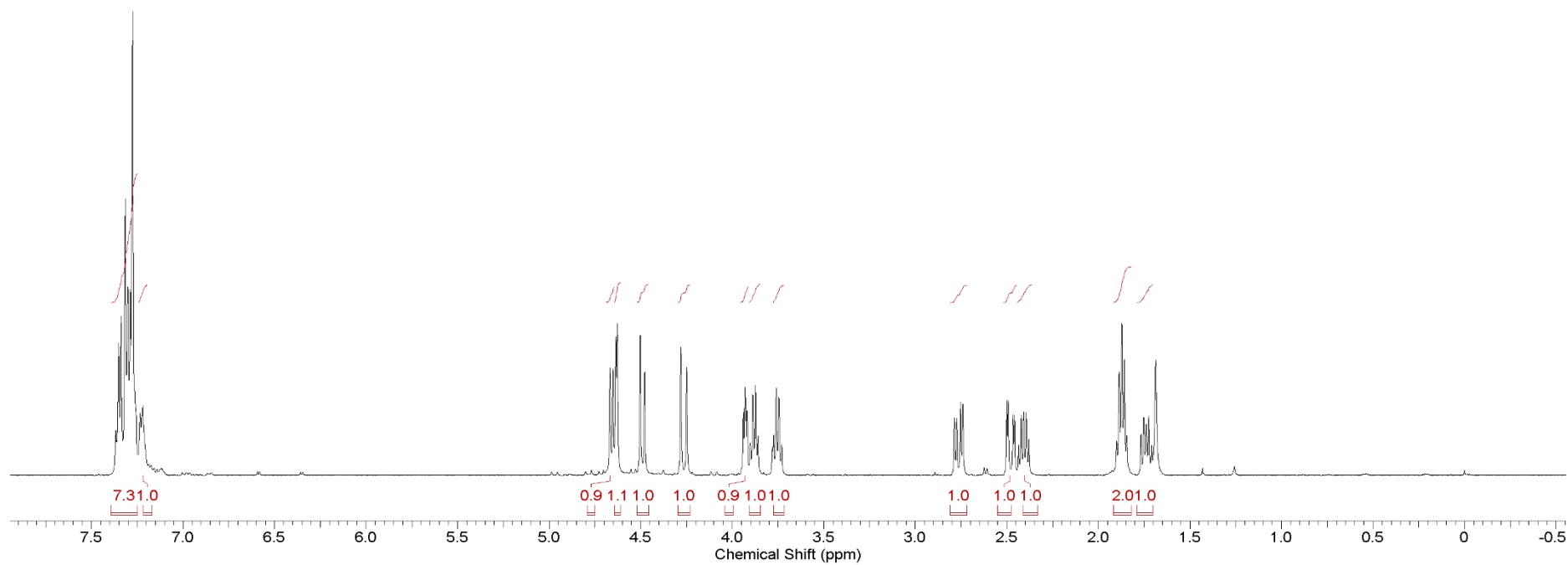


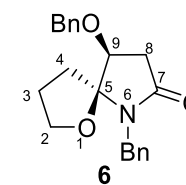
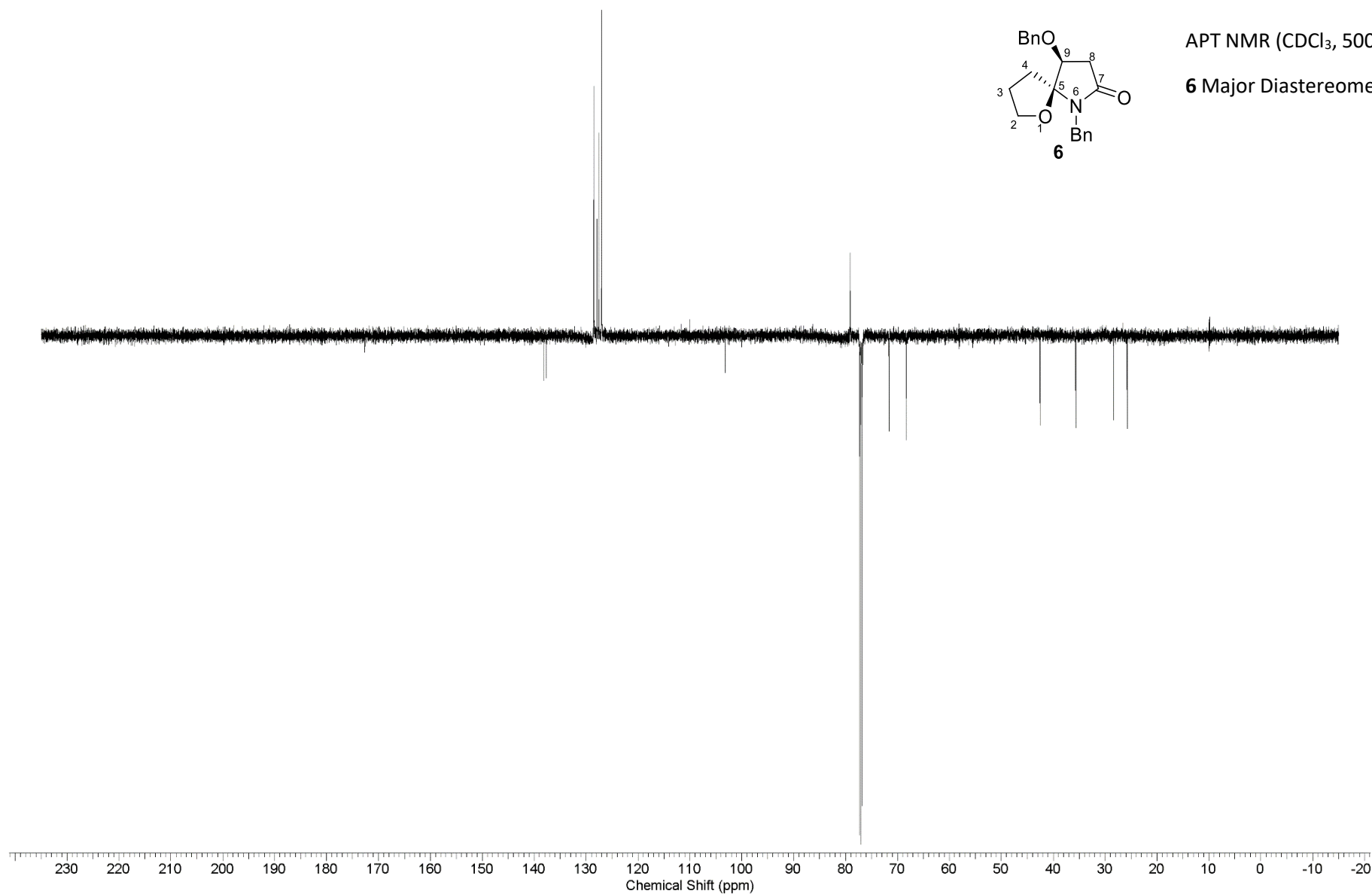
APT NMR (CDCl₃, 125 MHz).



^1H NMR (CDCl_3 , 500 MHz)

6 Major Diastereomer

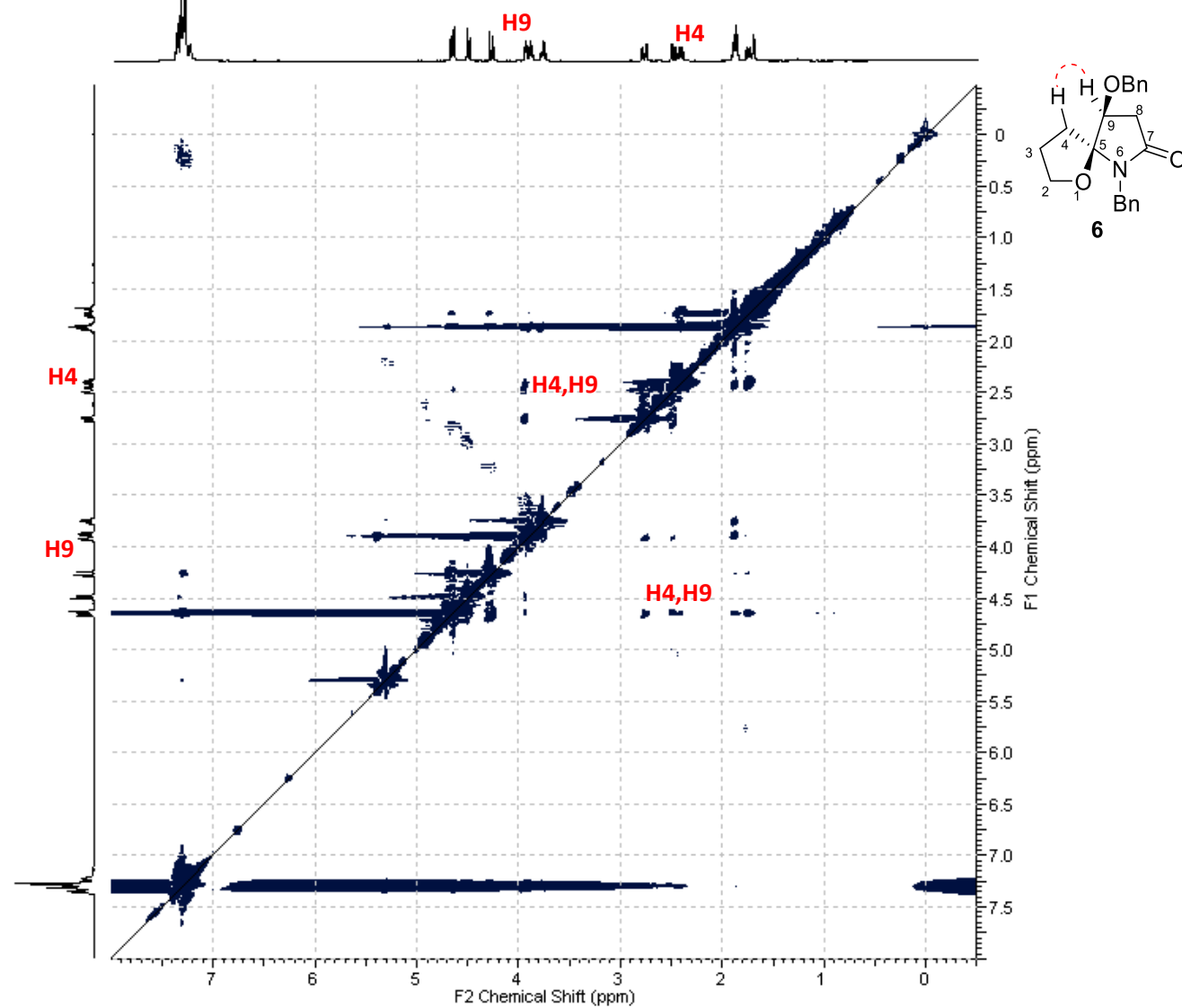


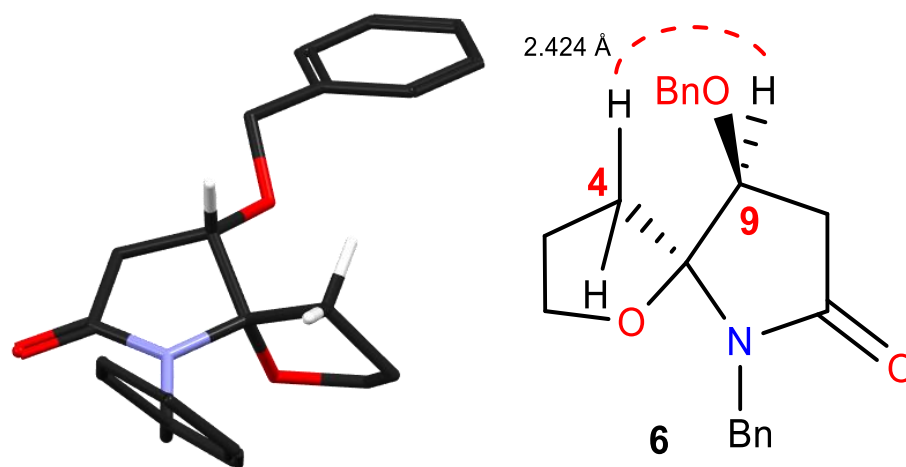
APT NMR (CDCl₃, 500 MHz)**6** Major Diastereomer

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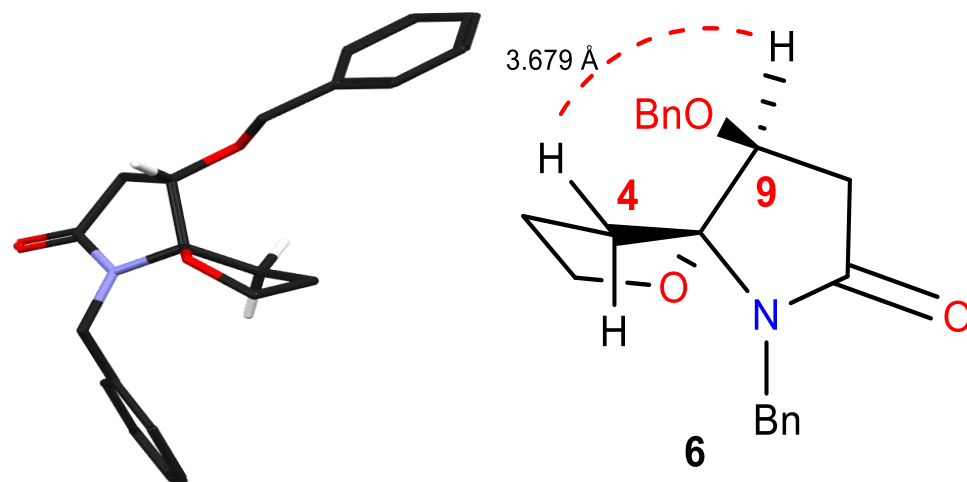
NOESY NMR (CDCl₃).

6 Major Diastereomer

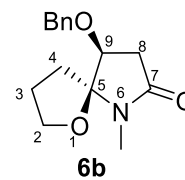




Molecular model (DFT minimised, B3LYP/6-31G(d) basis set) of *S,S* compound **6** (Cyclisation *cis* to OBn).

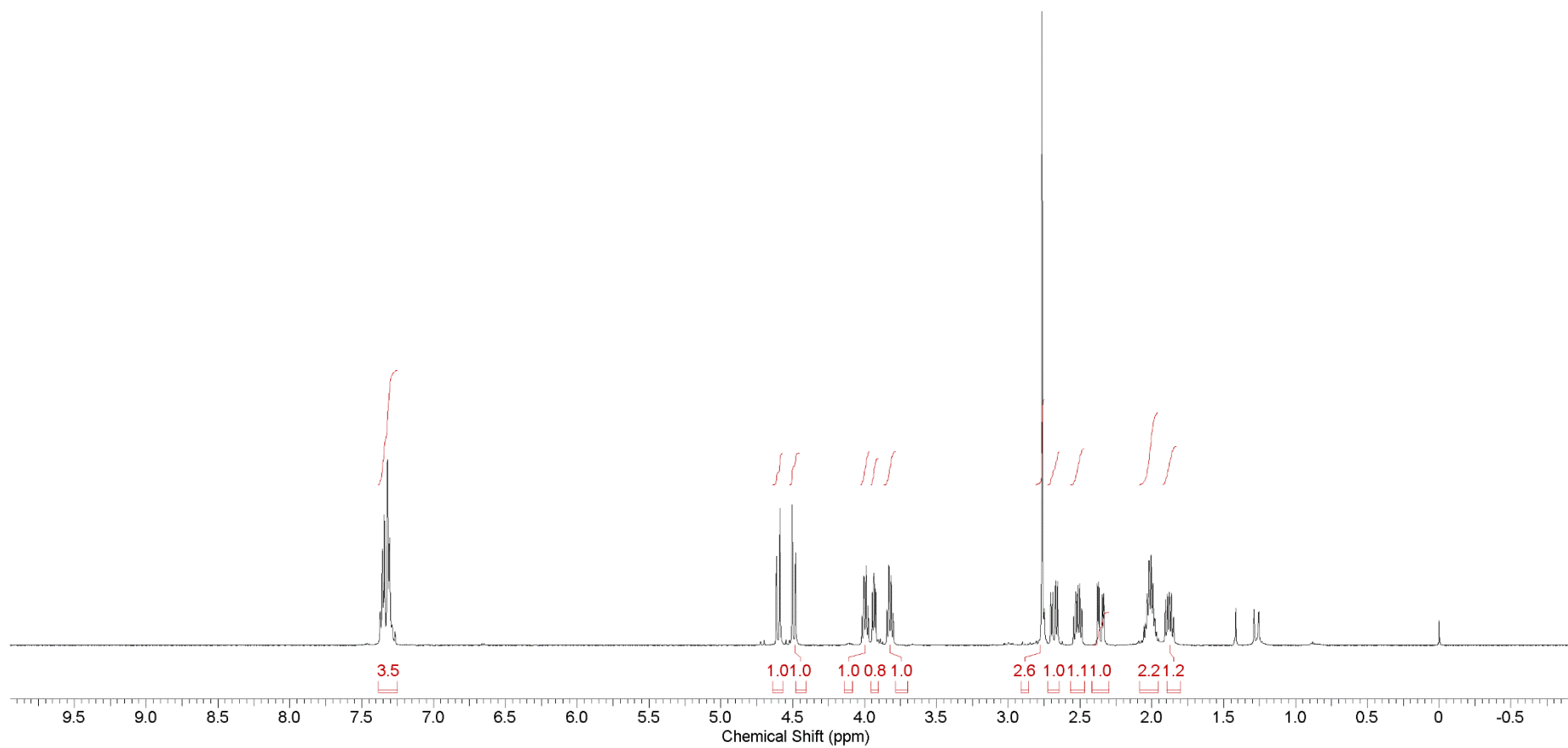


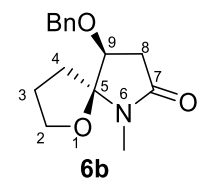
Molecular model (DFT minimised, B3LYP/6-31G(d) basis set) of *S,R* compound **6** (Cyclisation *trans* to OBn).



^1H NMR (CDCl_3 , 500 MHz).

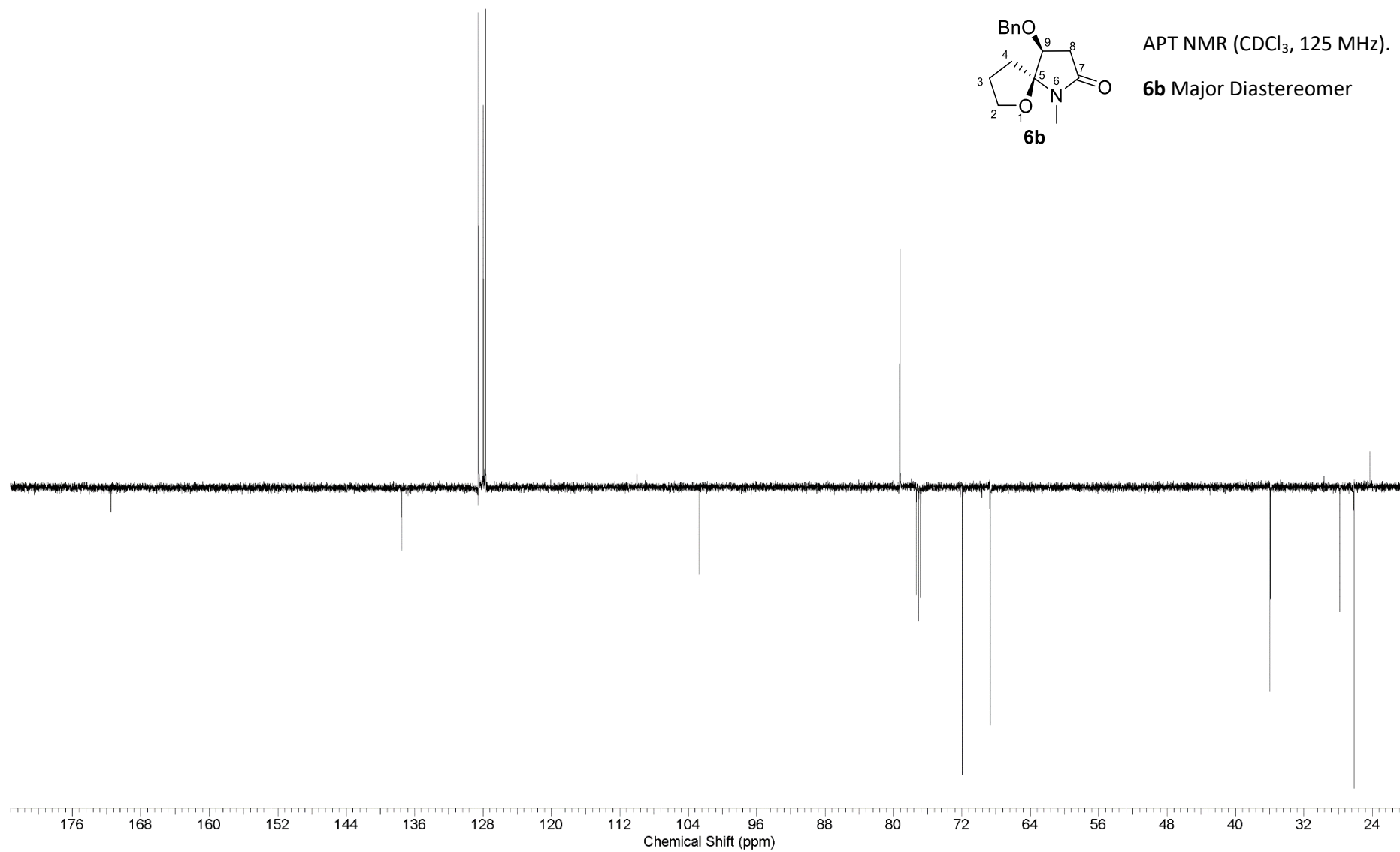
6b Major Diastereomer



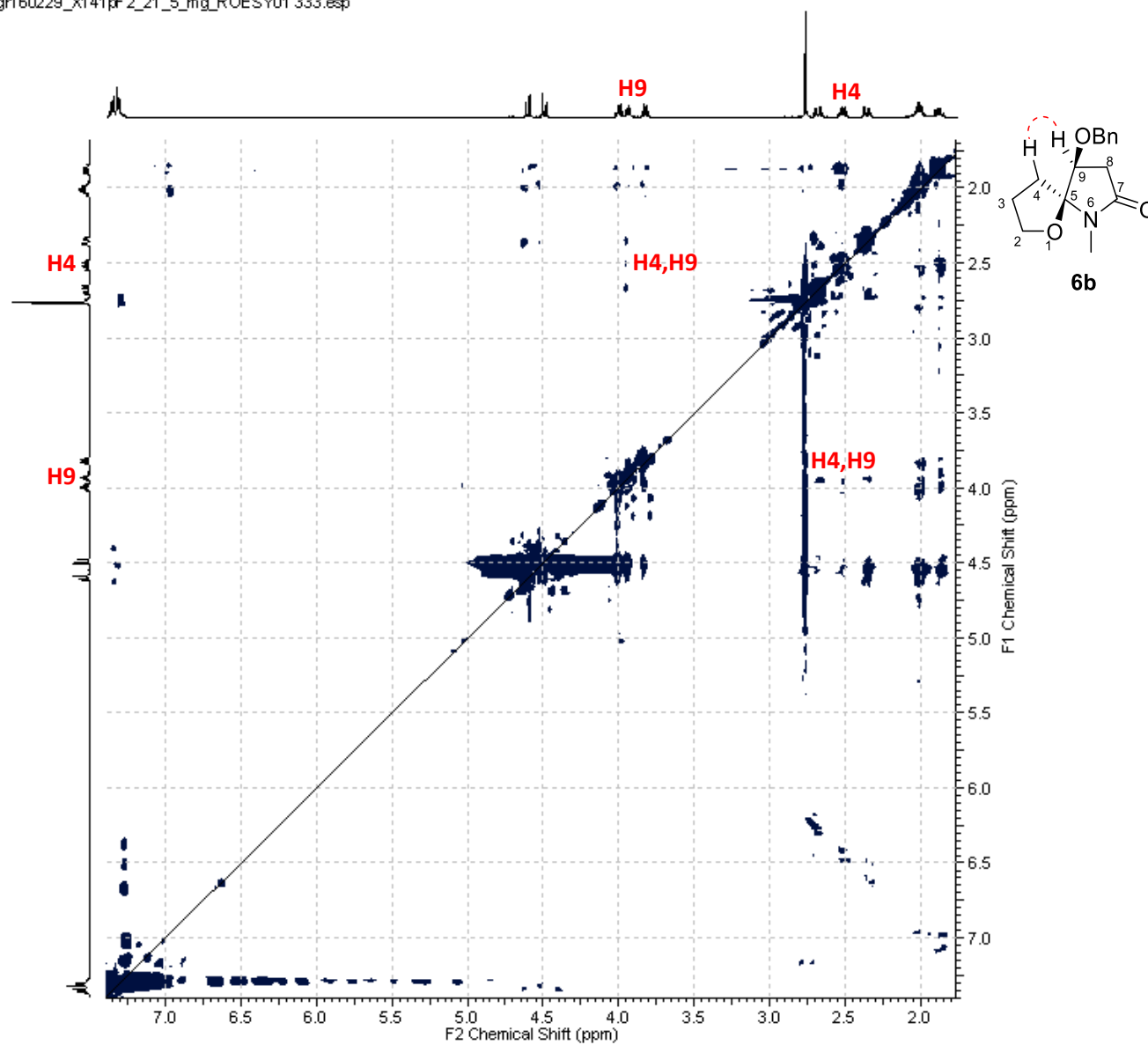


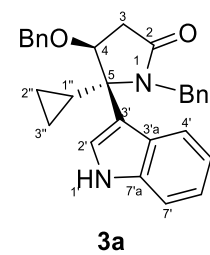
APT NMR (CDCl_3 , 125 MHz).

6b Major Diastereomer



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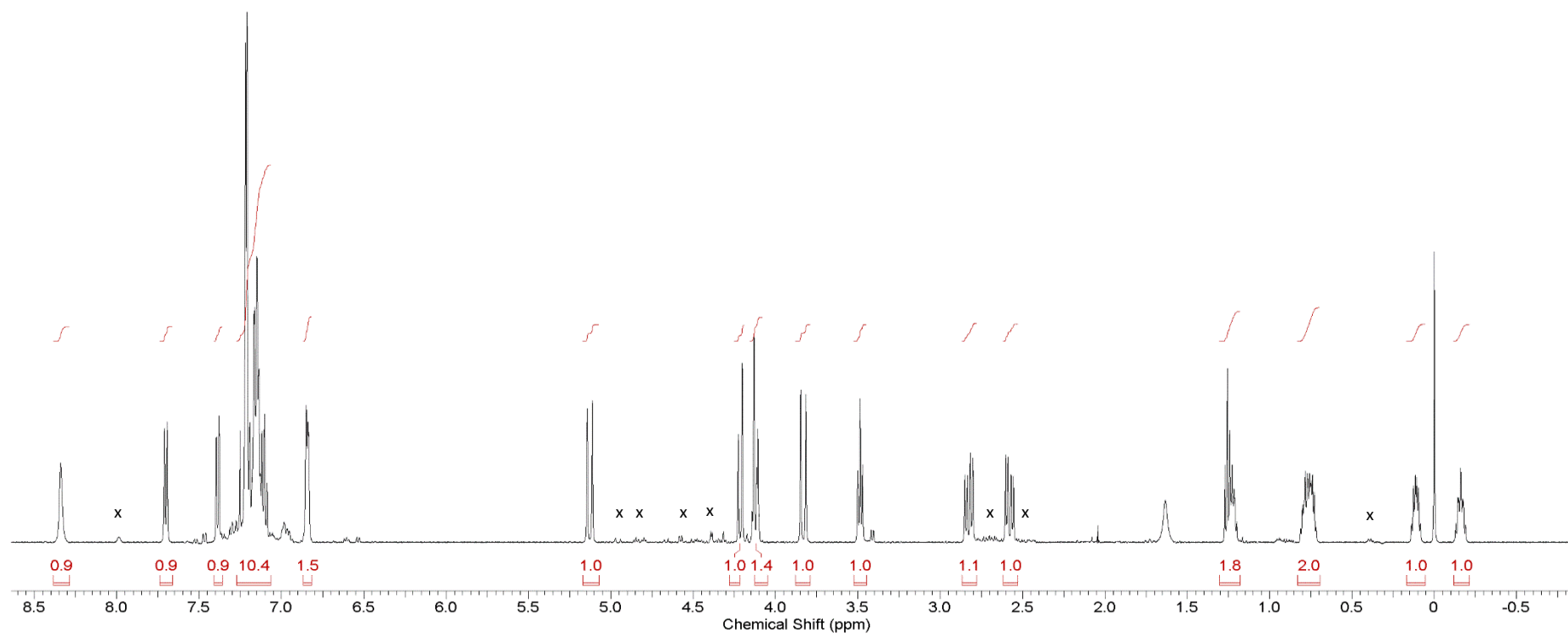


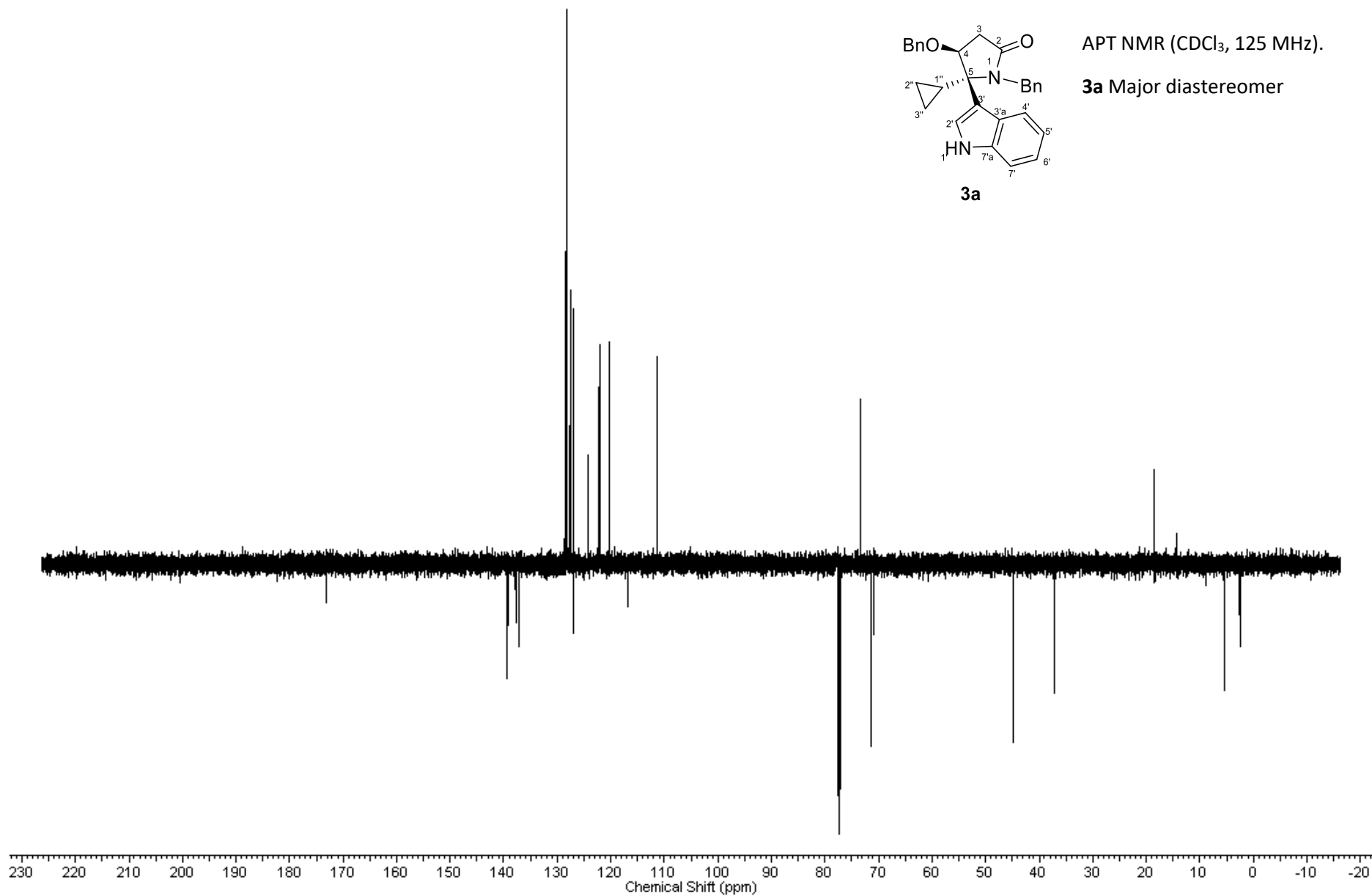


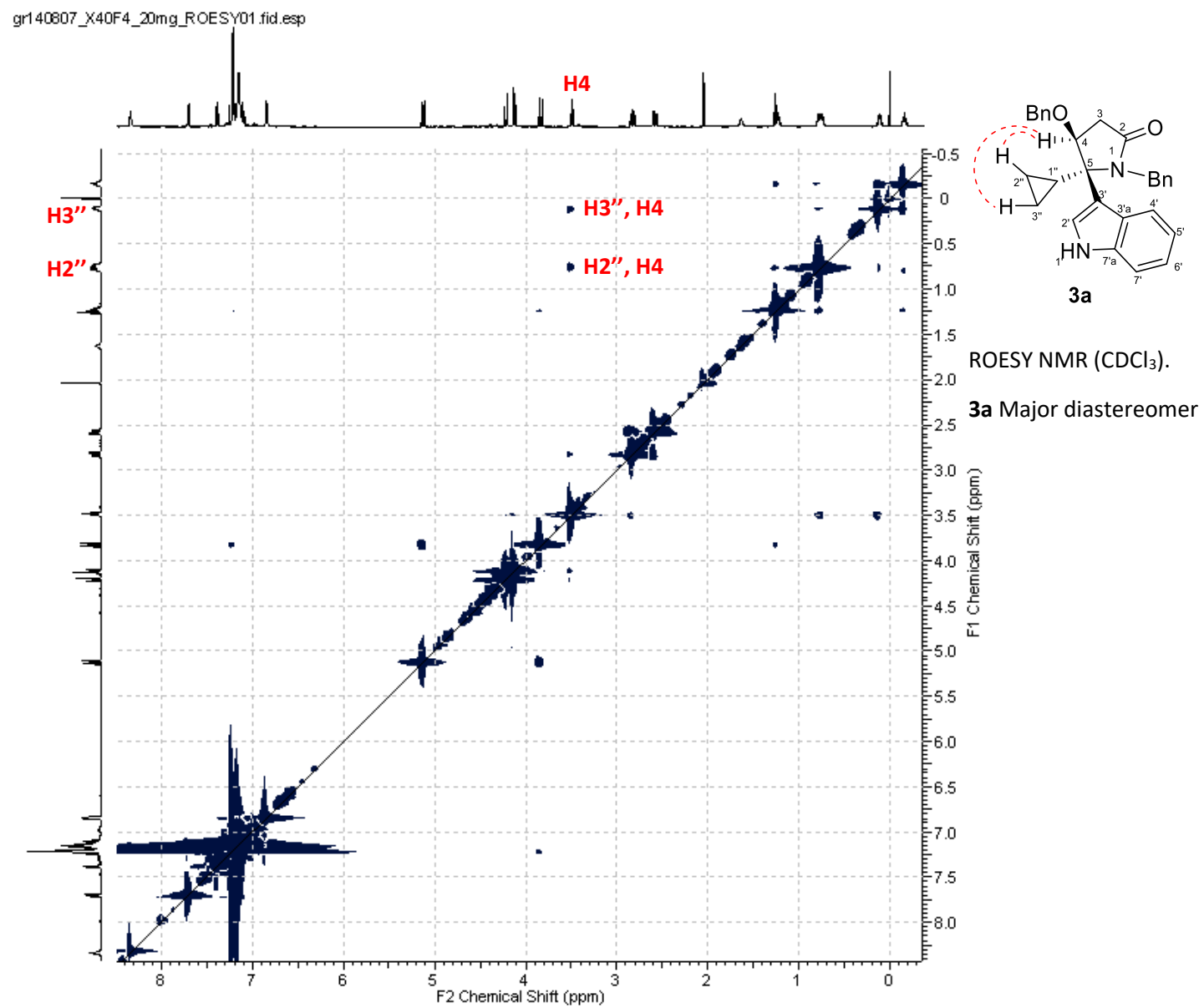
$^1\text{H-NMR}$ (CDCl_3 , 125 MHz).

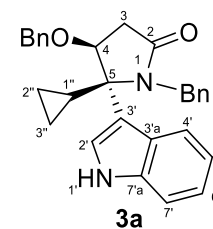
3a Major diastereomer

3a Minor diastereomer indicated with x





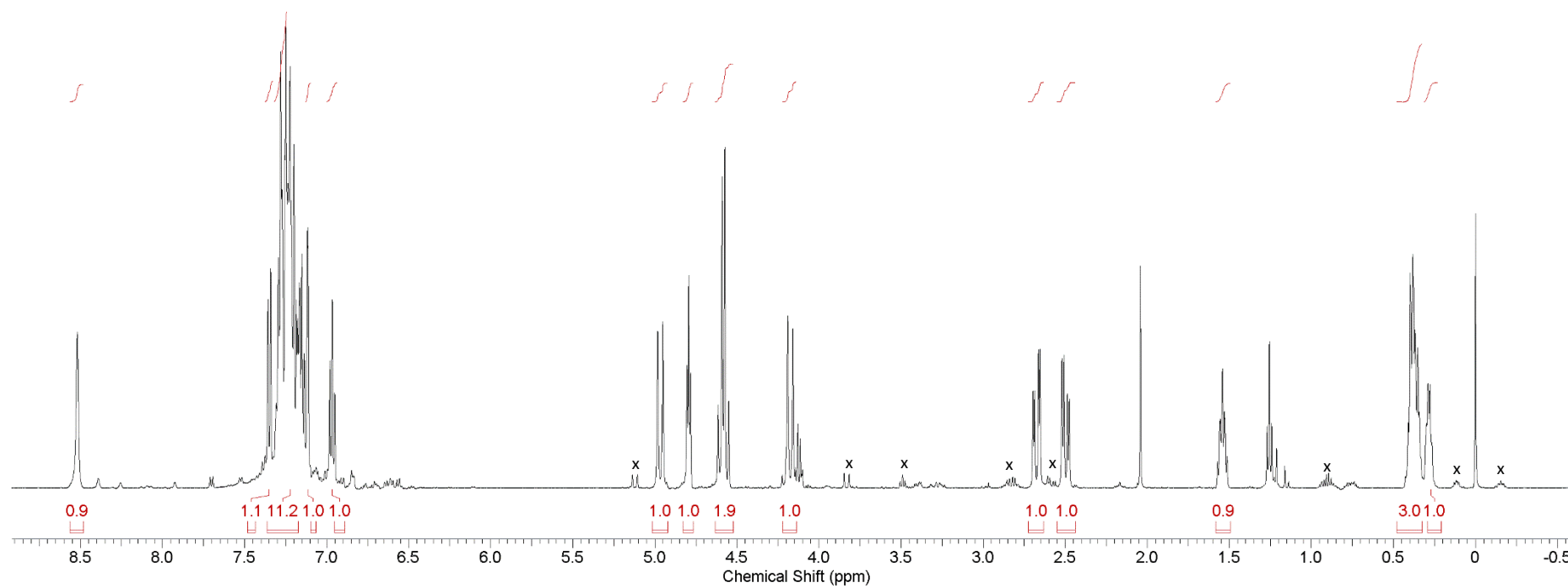


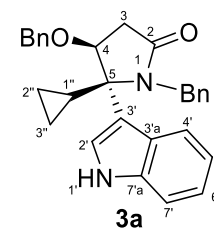


^1H NMR (CDCl_3 , 500 MHz).

3a Minor diastereomer.

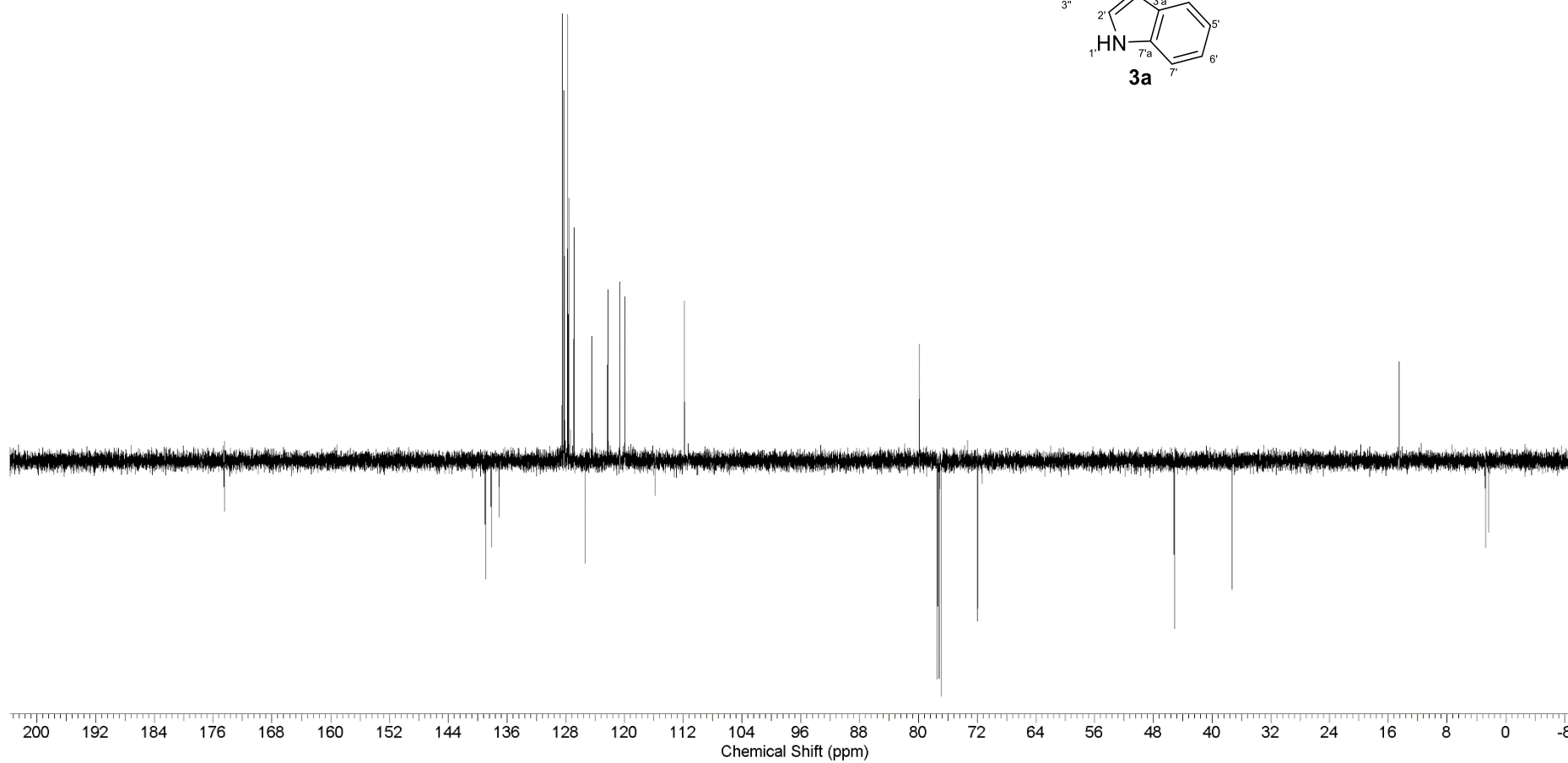
3a Major diastereomer indicated by x.



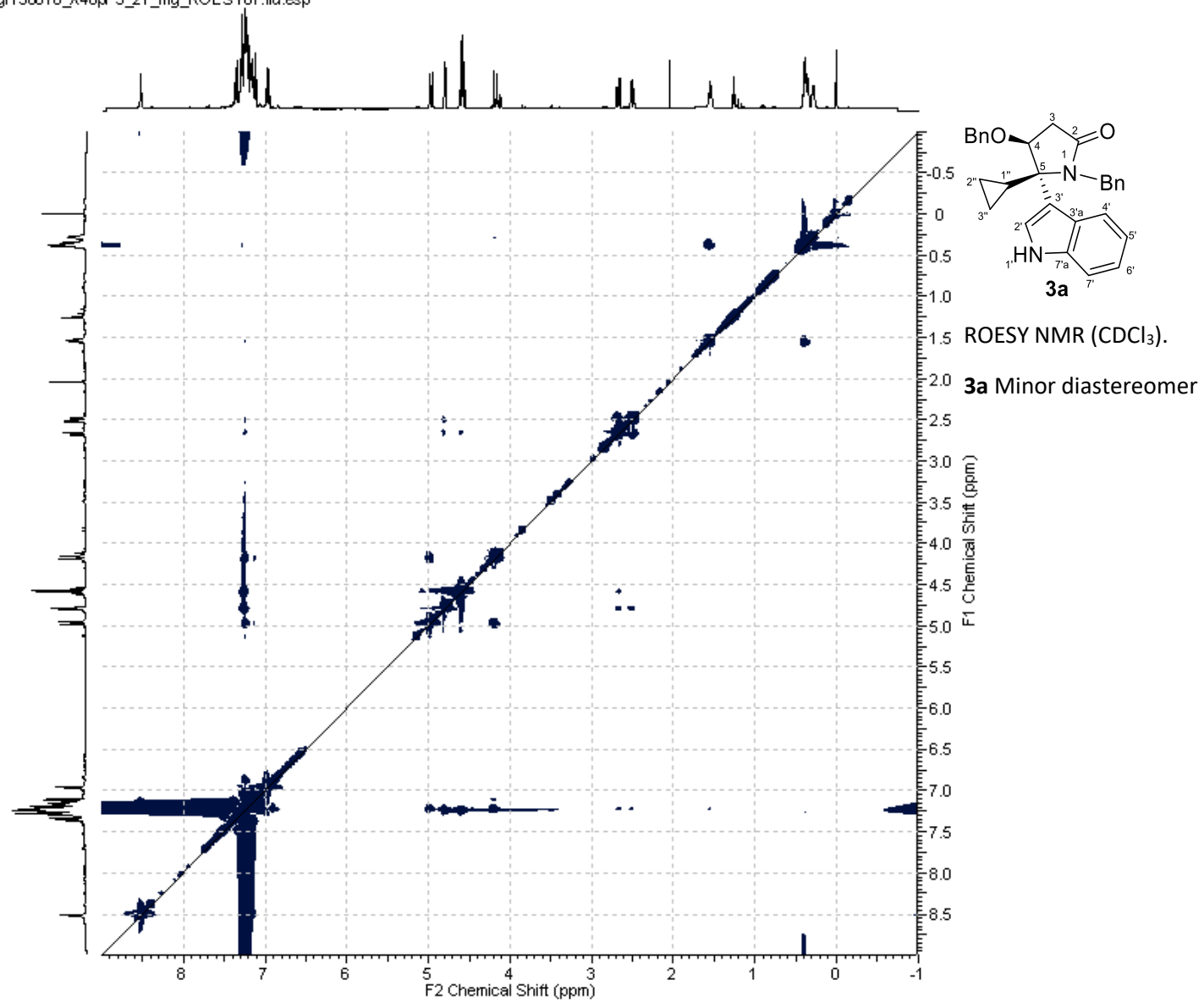


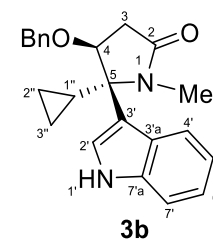
APT NMR (CDCl_3 , 125 MHz).

3a Minor diastereomer



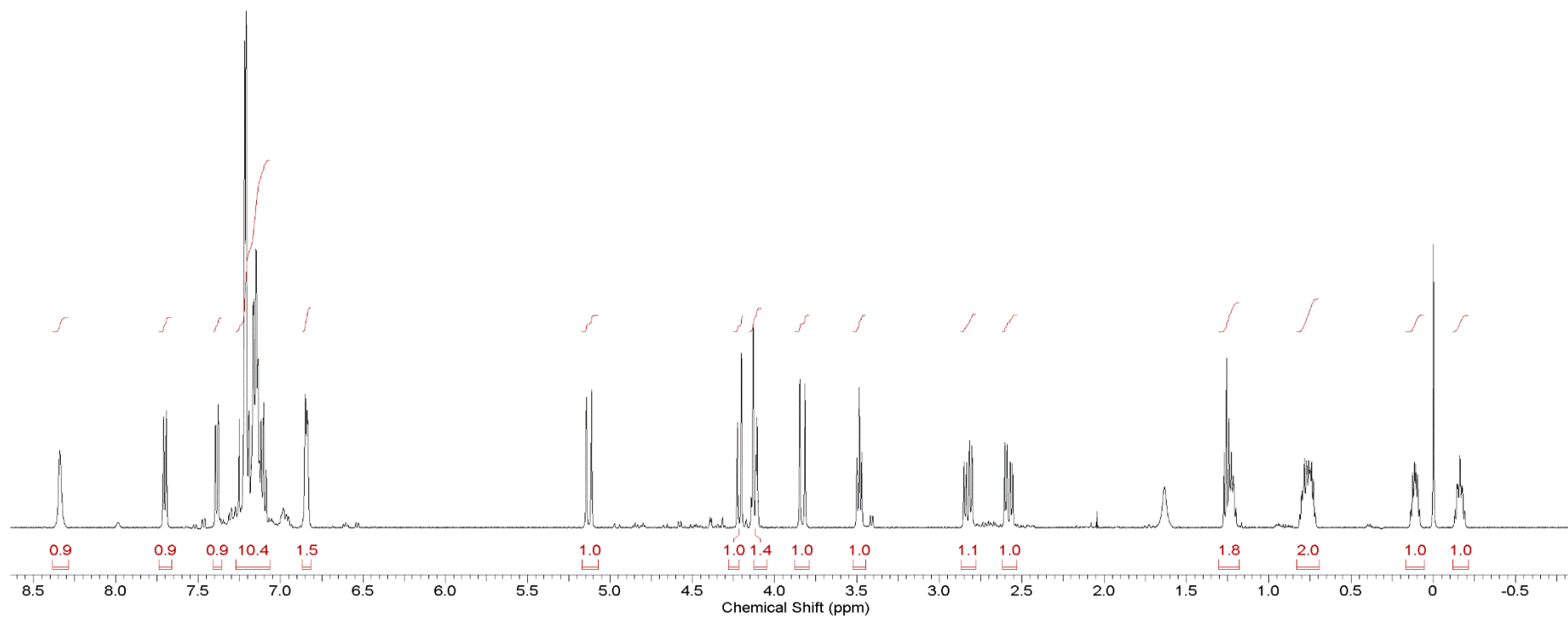
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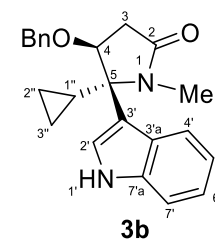




^1H NMR (CDCl_3 , 500 MHz).

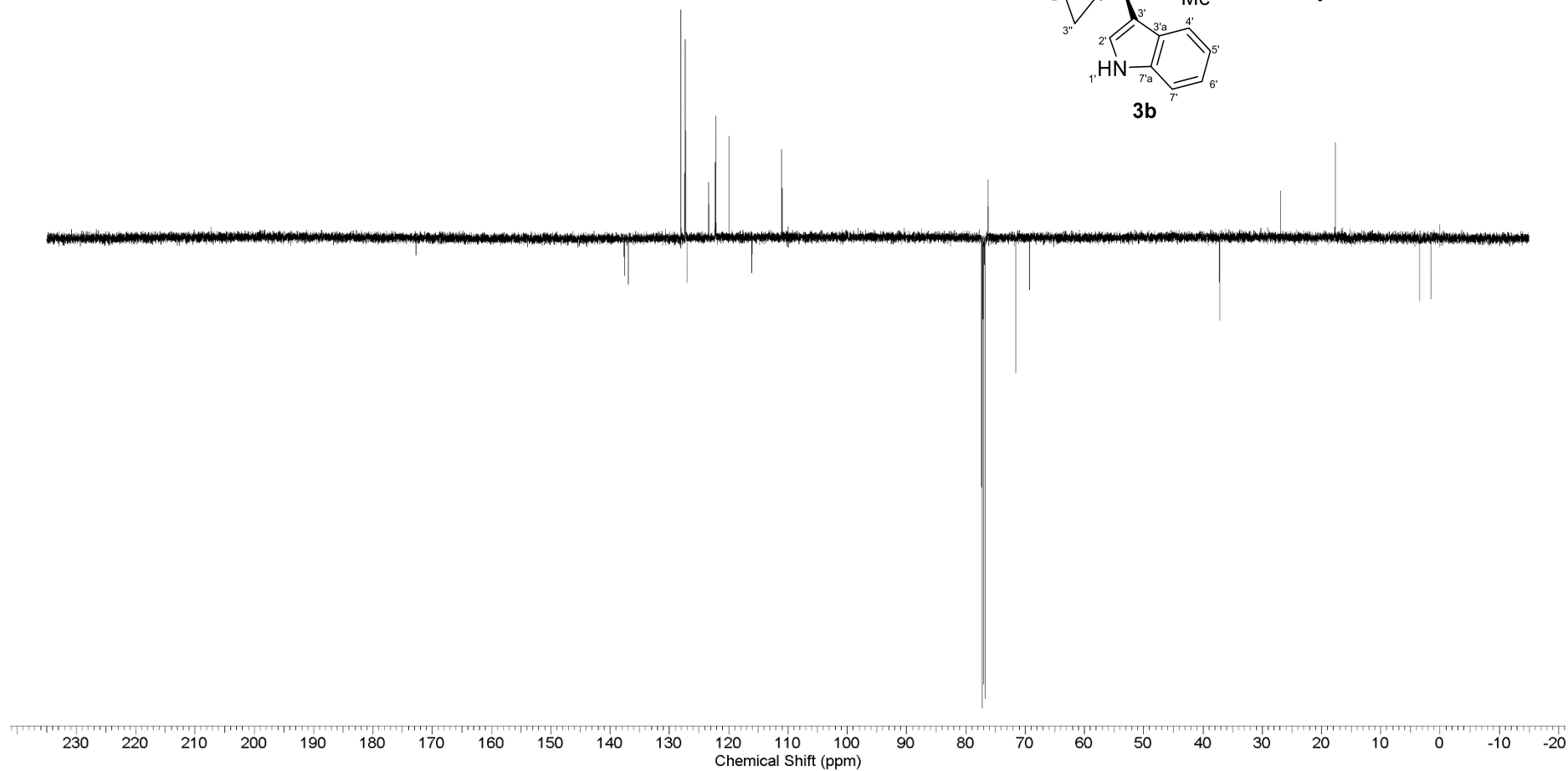
3b Major diastereomer



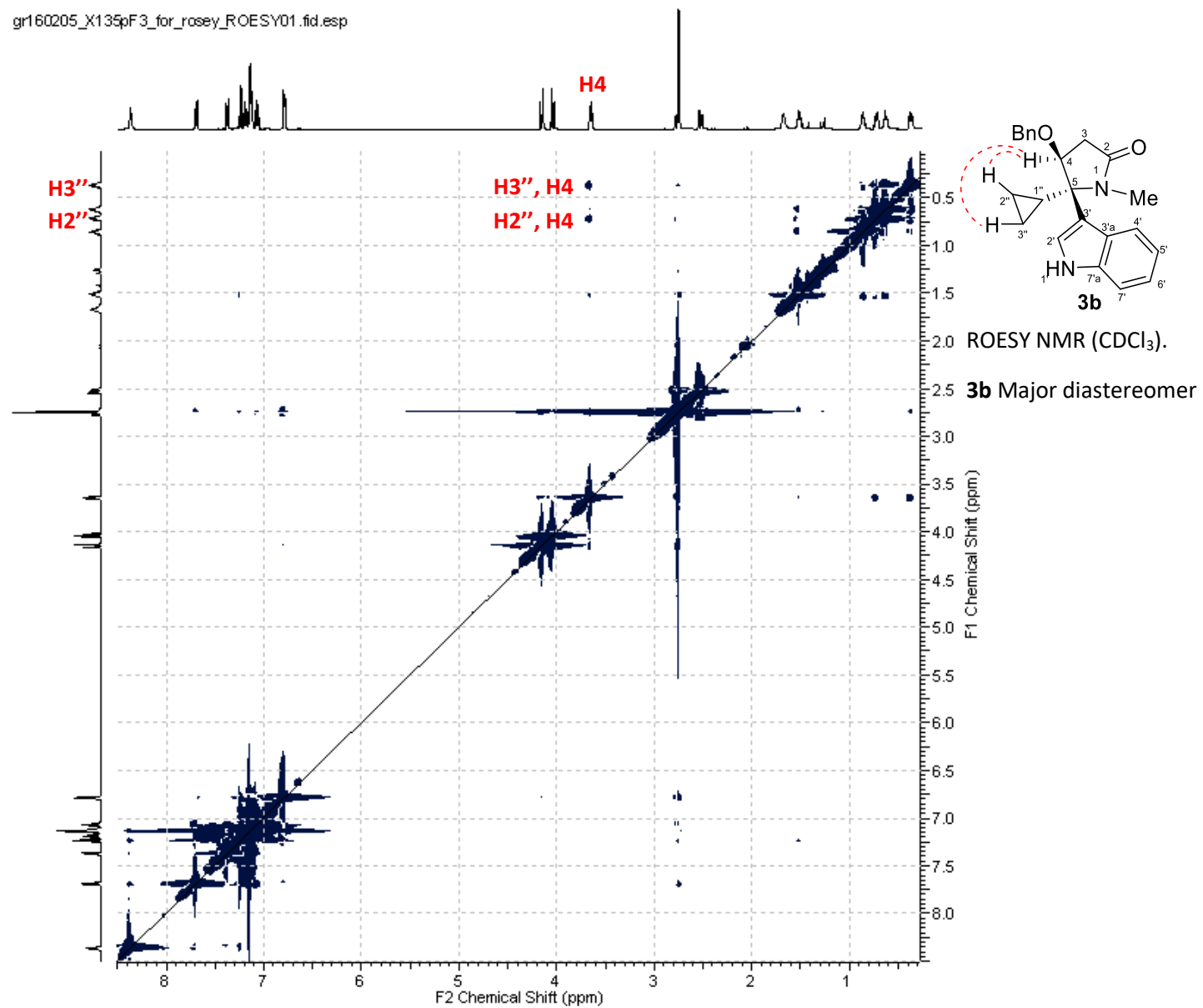


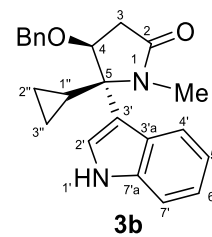
APT NMR (CDCl₃, 125 MHz).

3b Major diastereomer



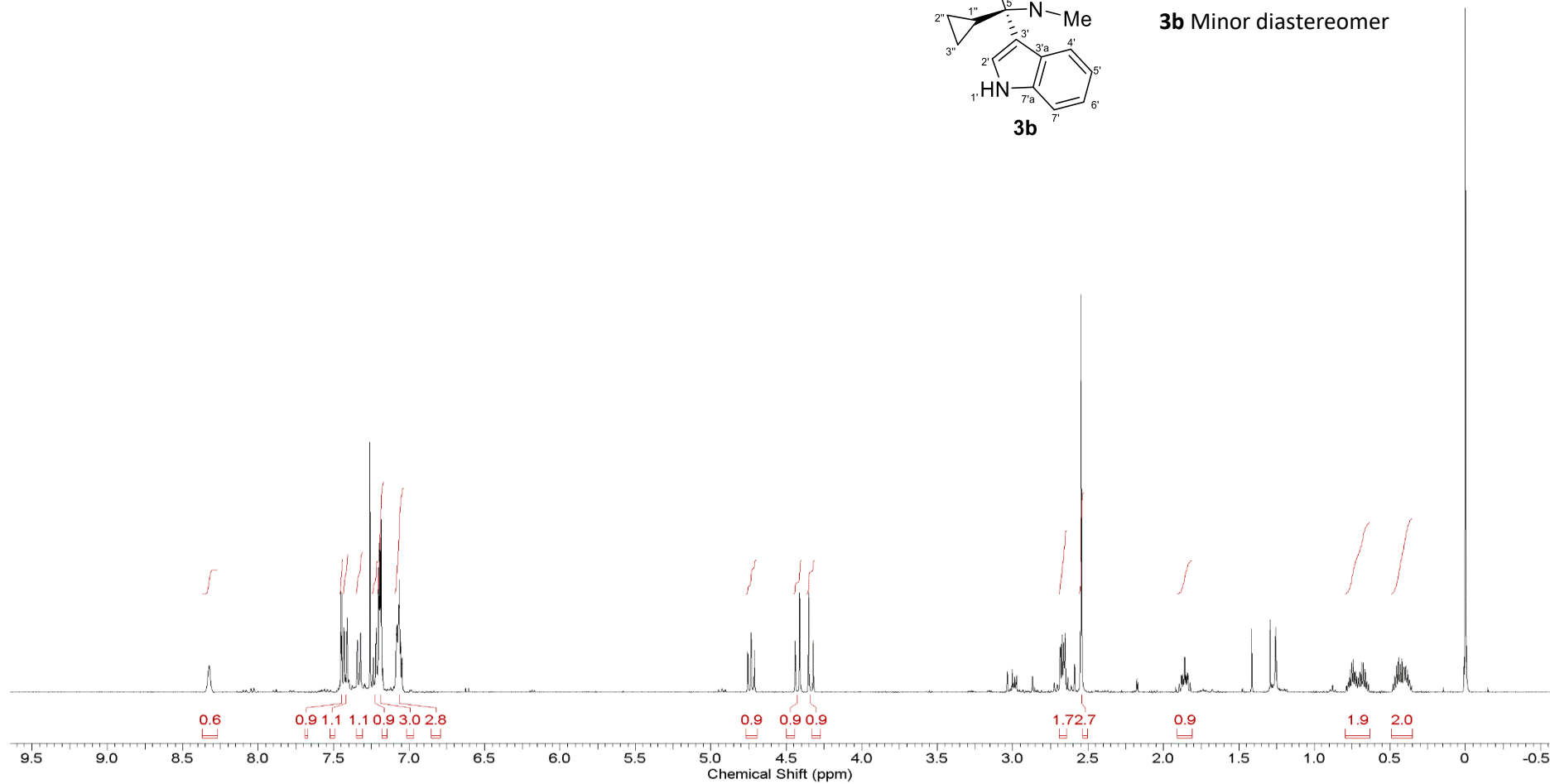
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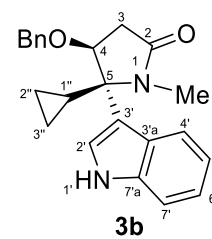




^1H NMR (CDCl_3 , 500 MHz).

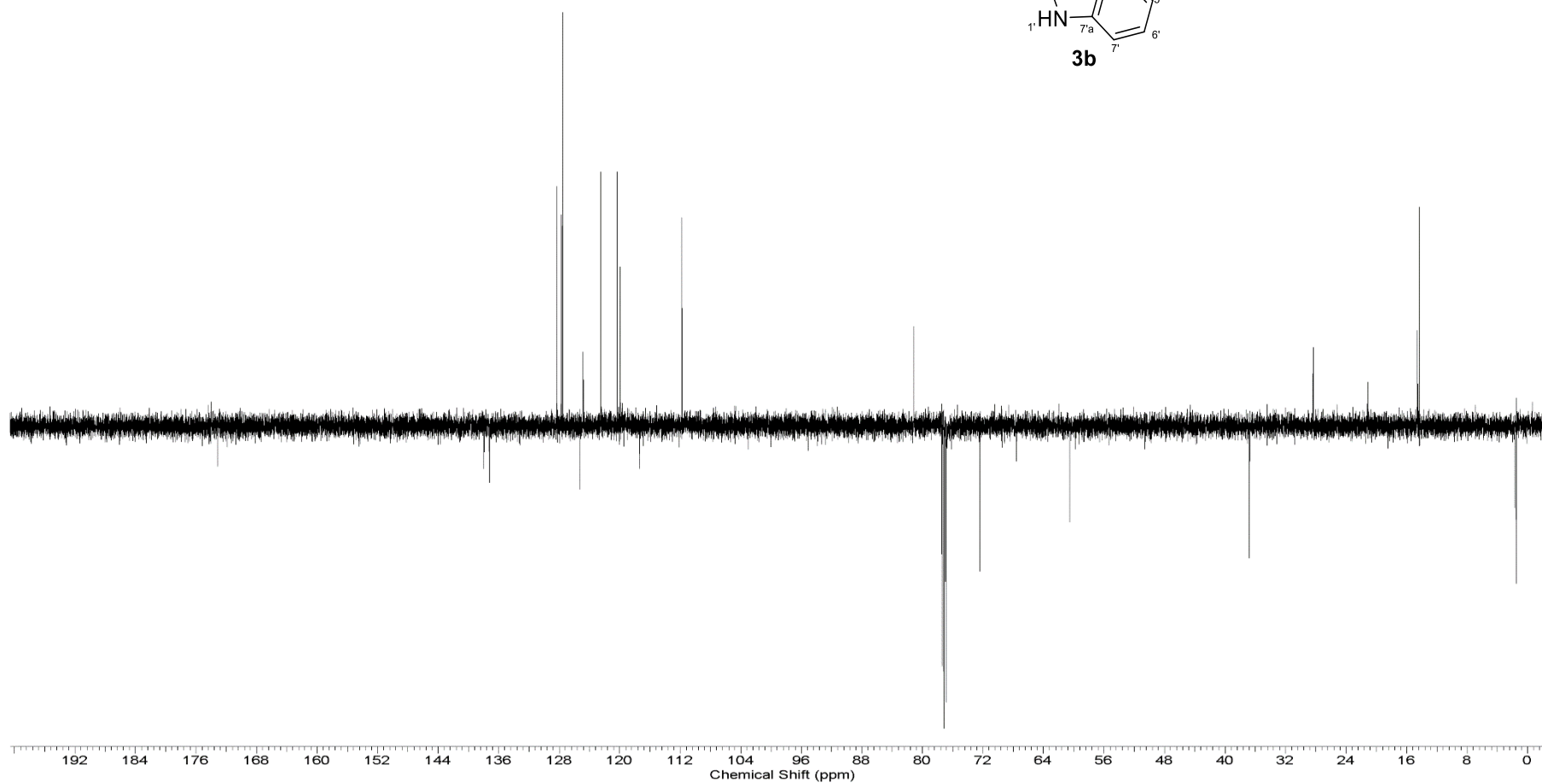
3b Minor diastereomer



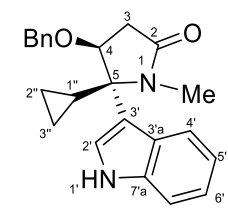
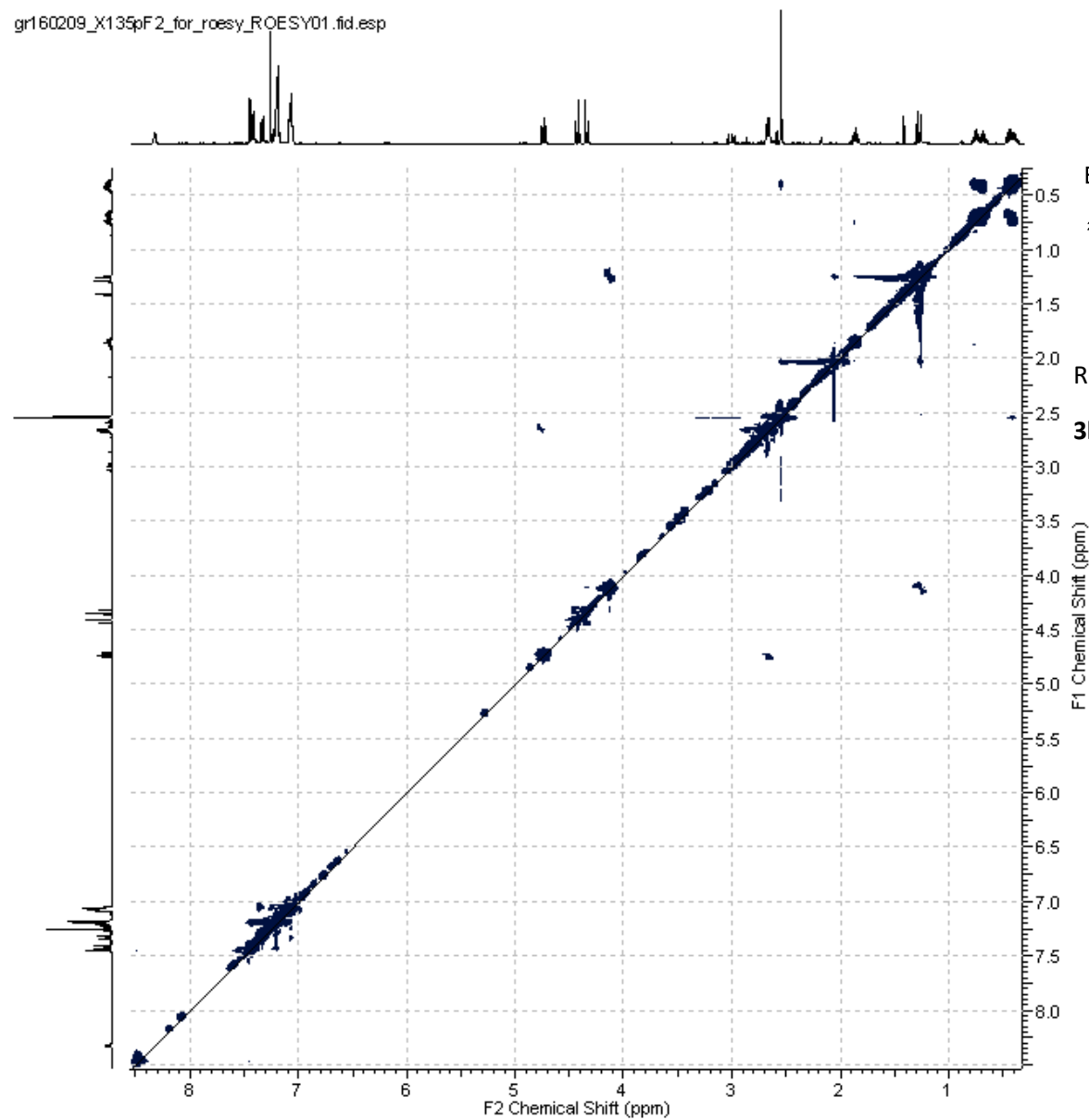


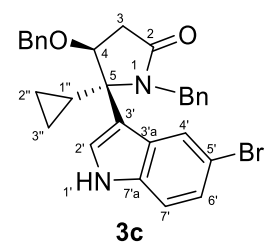
APT NMR (CDCl₃, 125 MHz).

3b Minor diastereomer



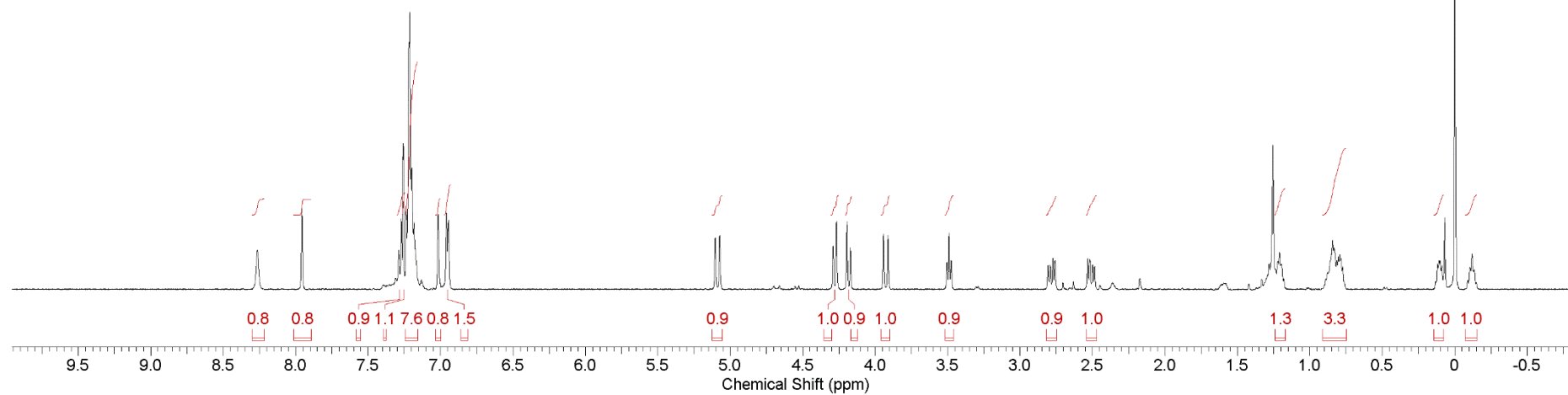
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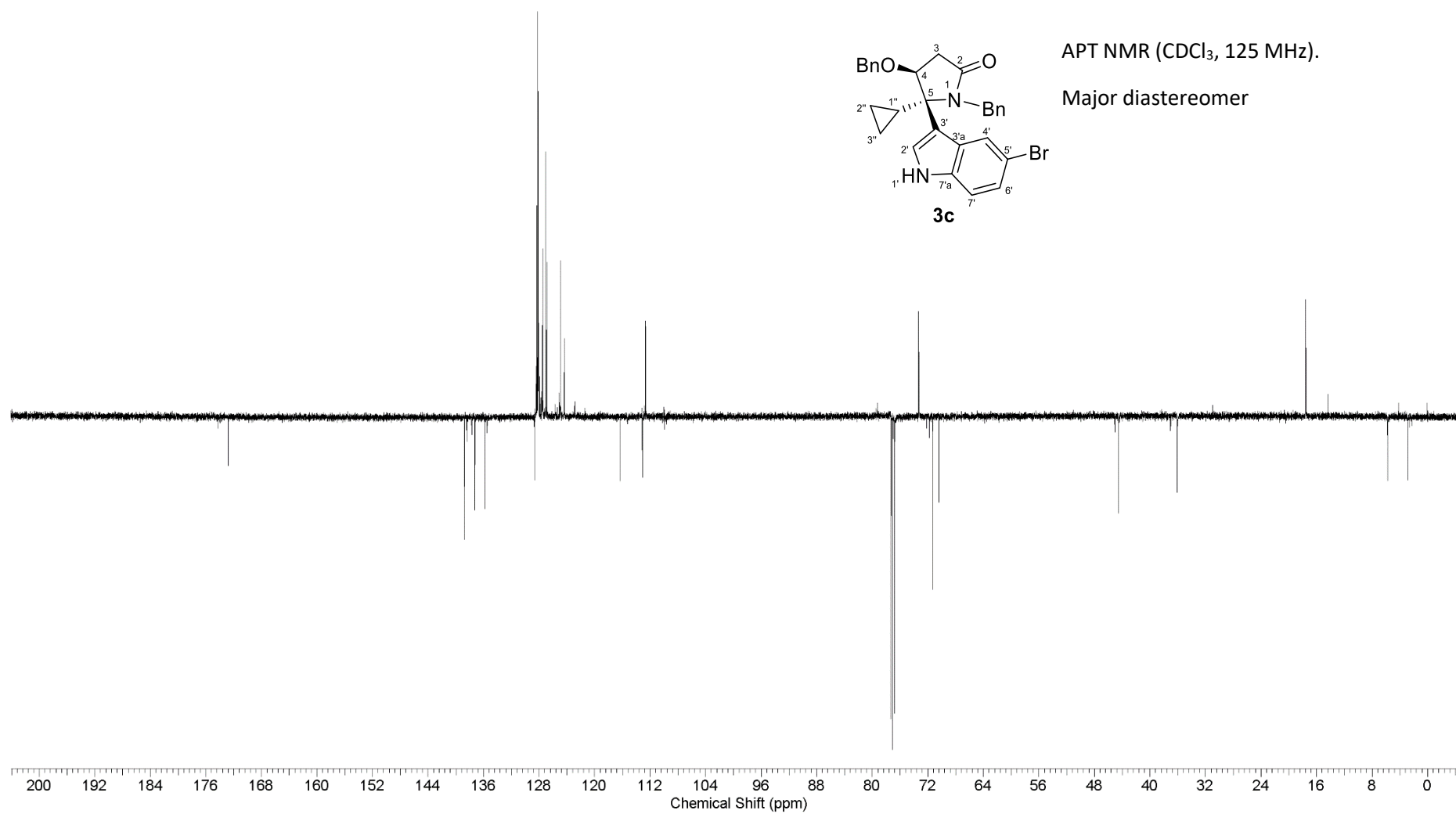
**3b**
ROESY NMR (CDCl₃).**3b** Minor diastereomer

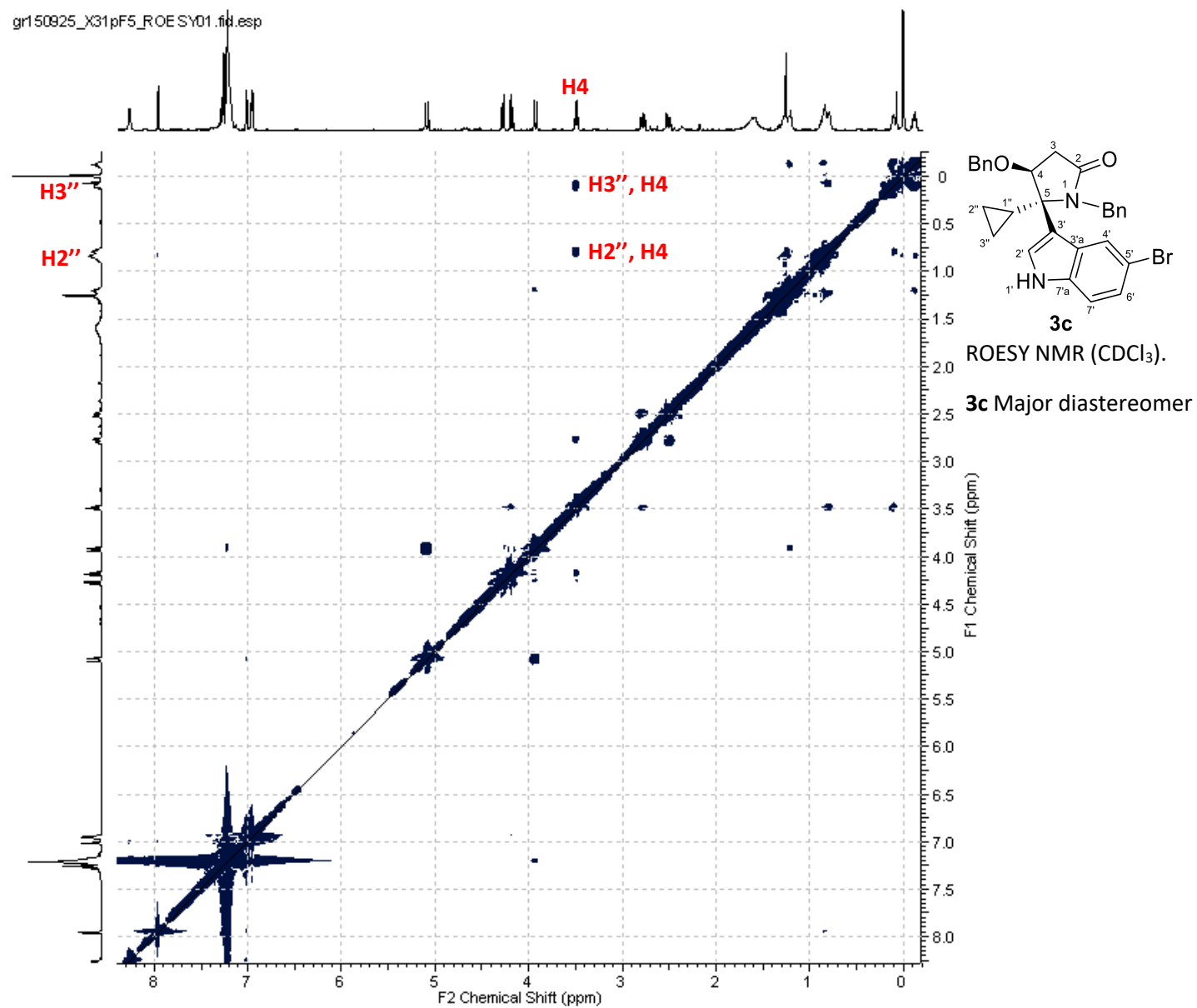


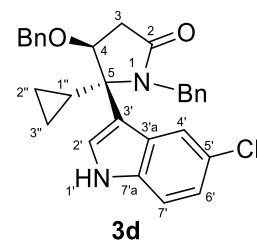
^1H NMR (CDCl_3 , 500 MHz).

Major diastereomer



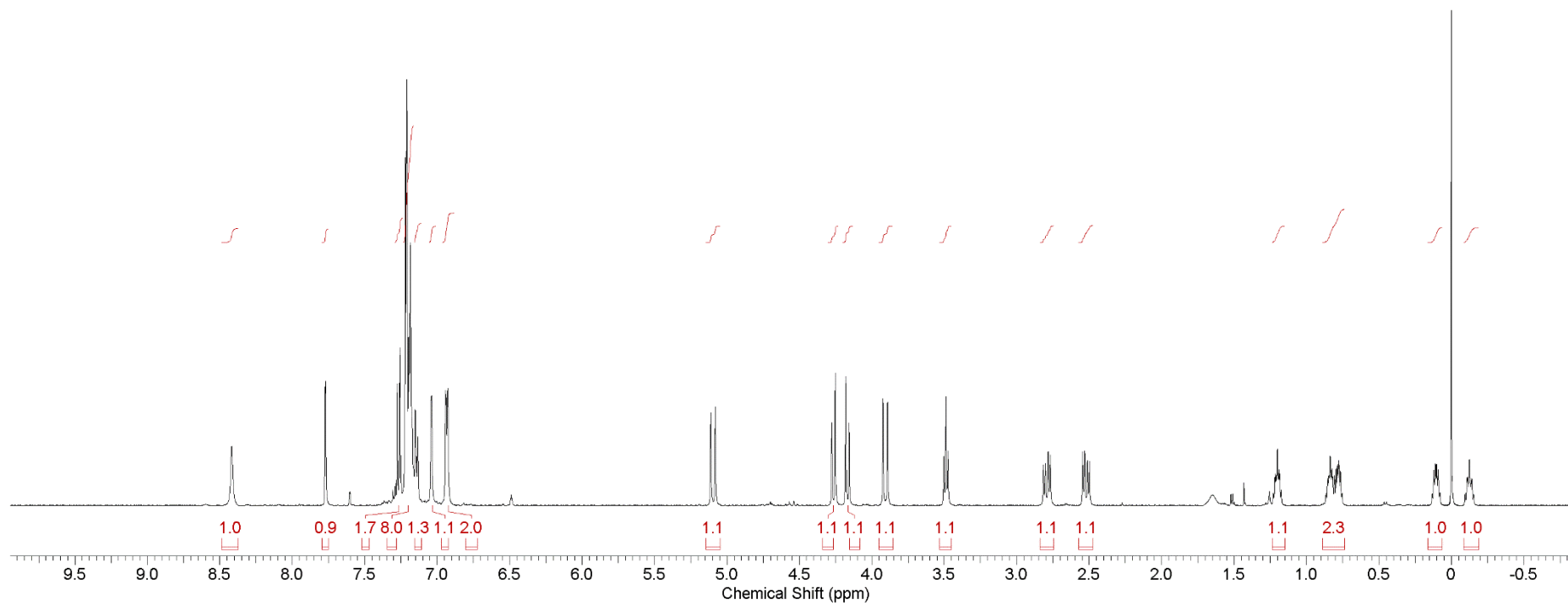


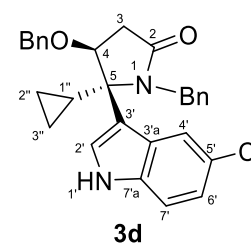




^1H NMR (CDCl_3 , 500 MHz).

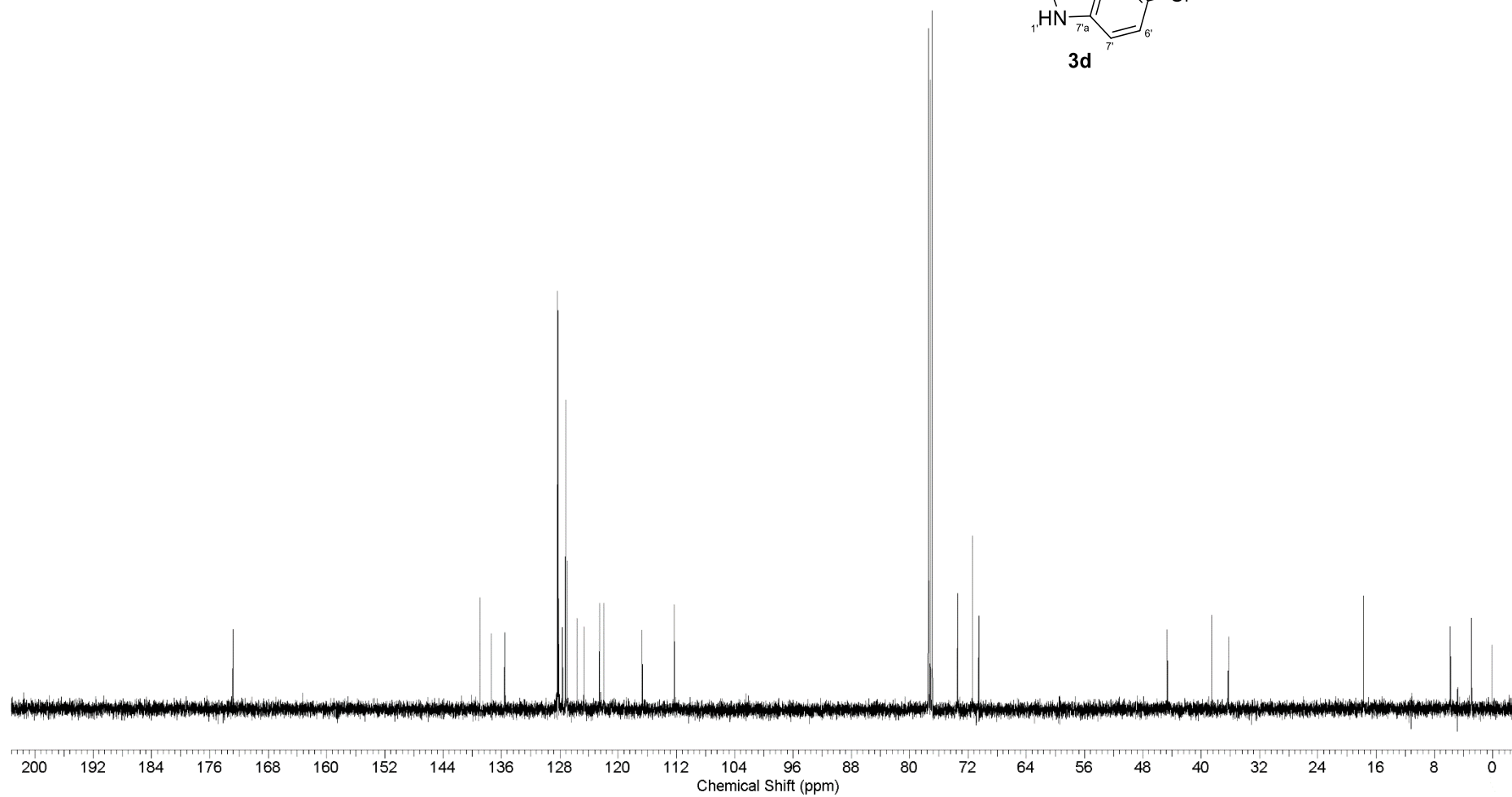
3d Major diastereomer

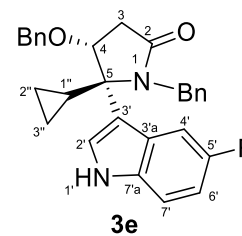




^{13}C NMR (CDCl_3 , 125 MHz).

3d Major diastereomer

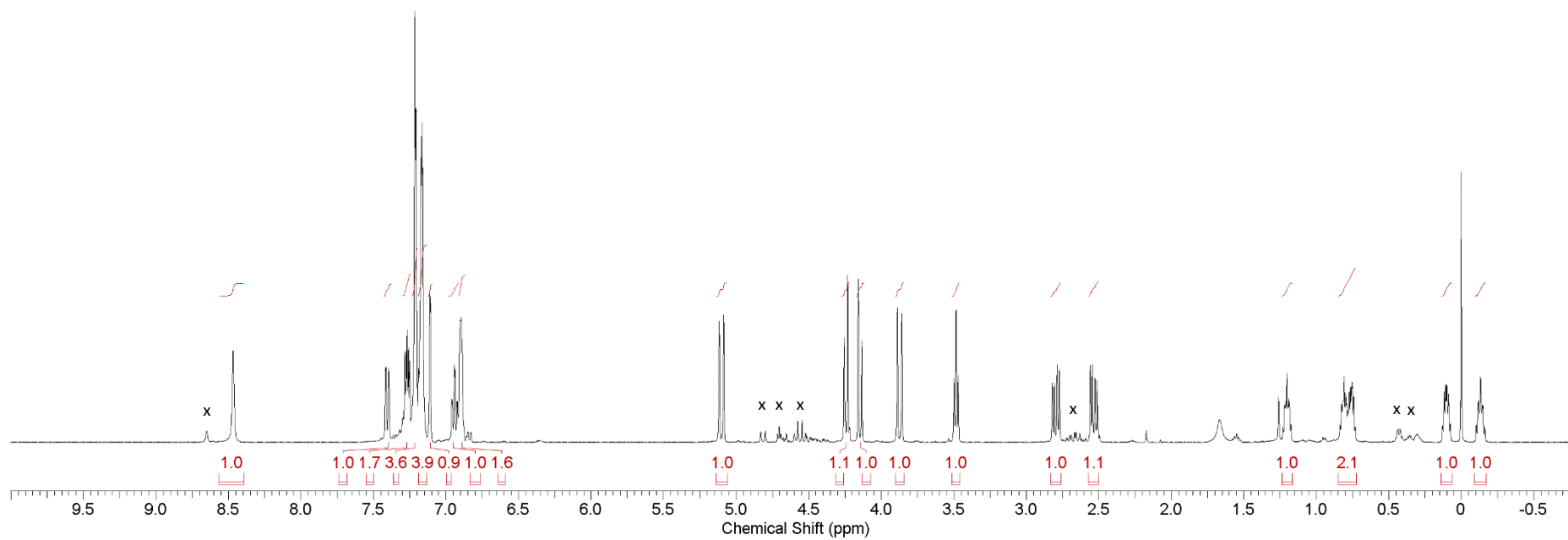


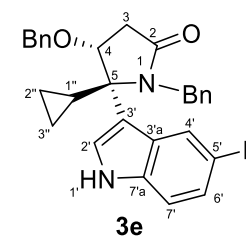


^1H NMR (CDCl_3 , 500 MHz).

3e Major diastereomer.

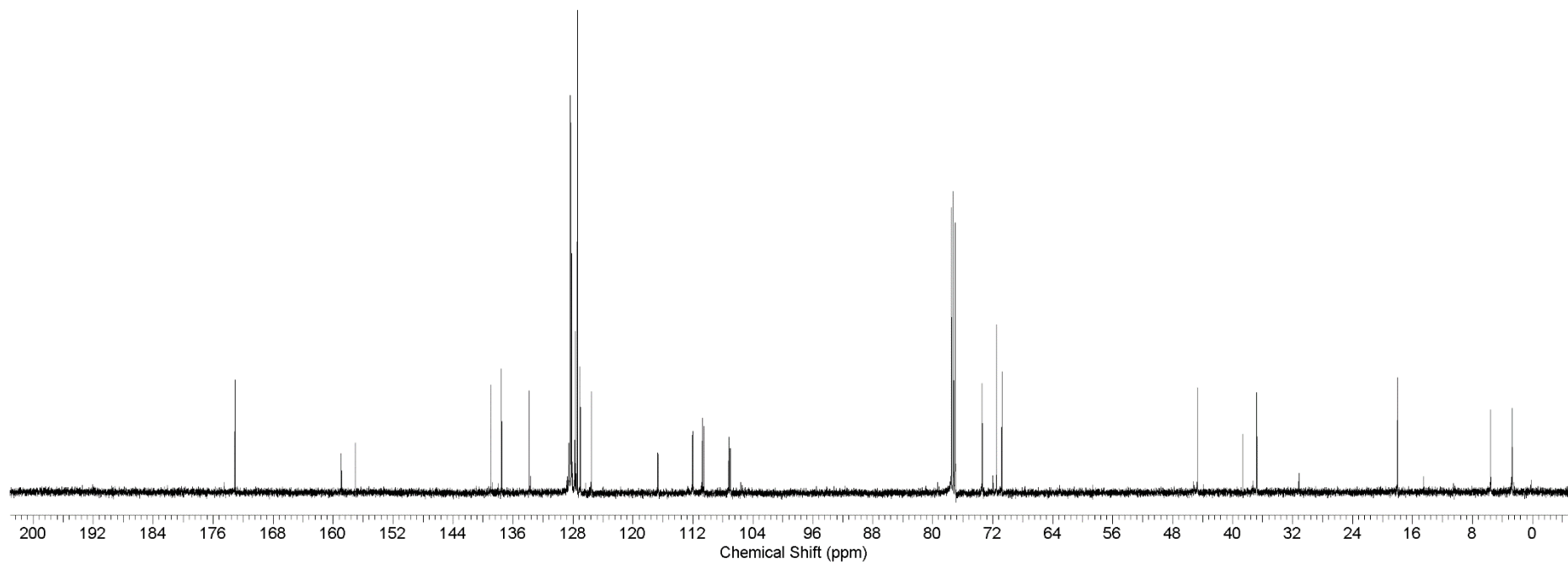
Minor diastereomer indicated by x.



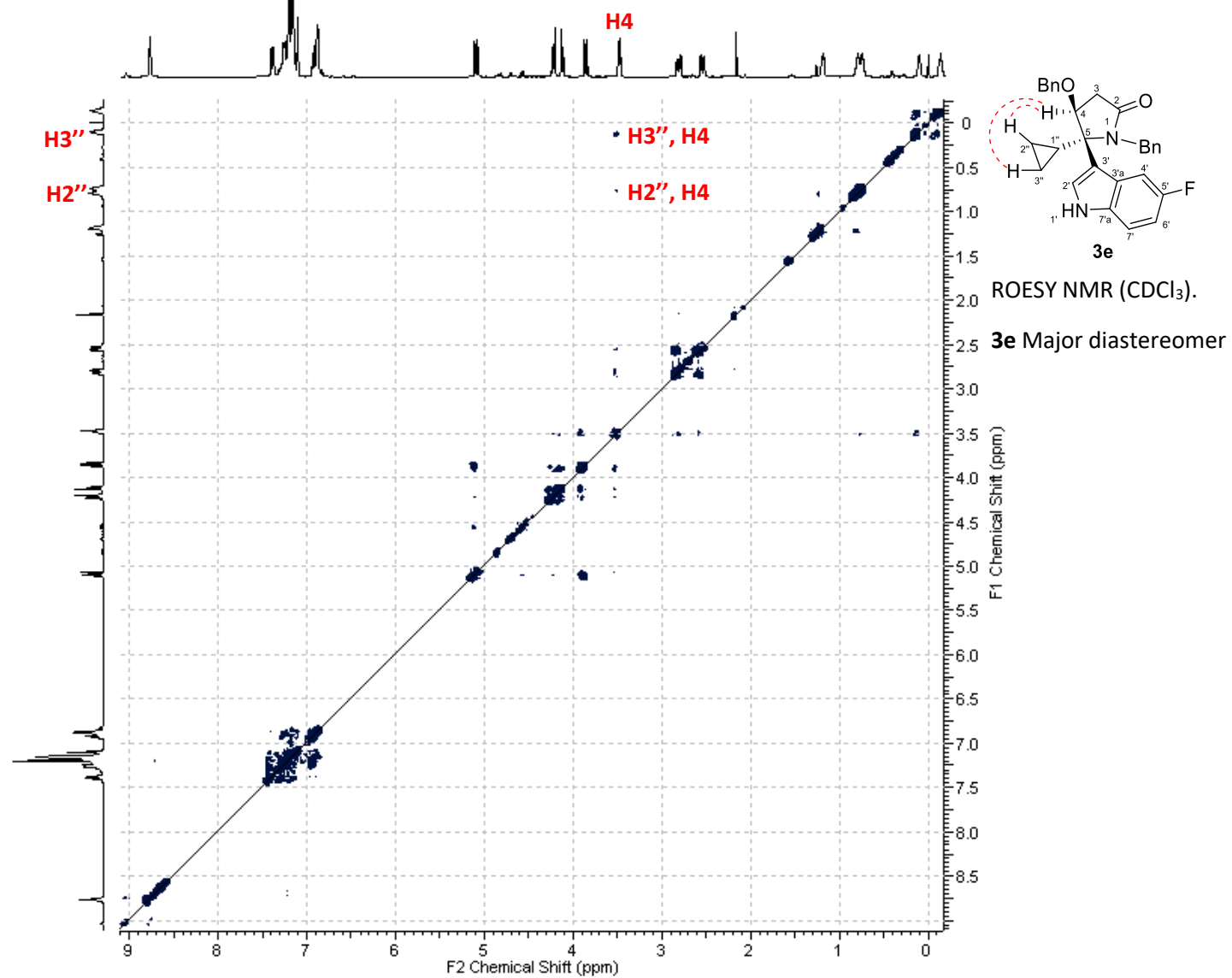


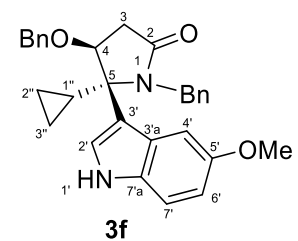
^{13}C NMR (CDCl_3 , 125 MHz).

3e Major diastereomer



GR150603_X44PF4_FOR_2D_NOESY01.FID.ESP

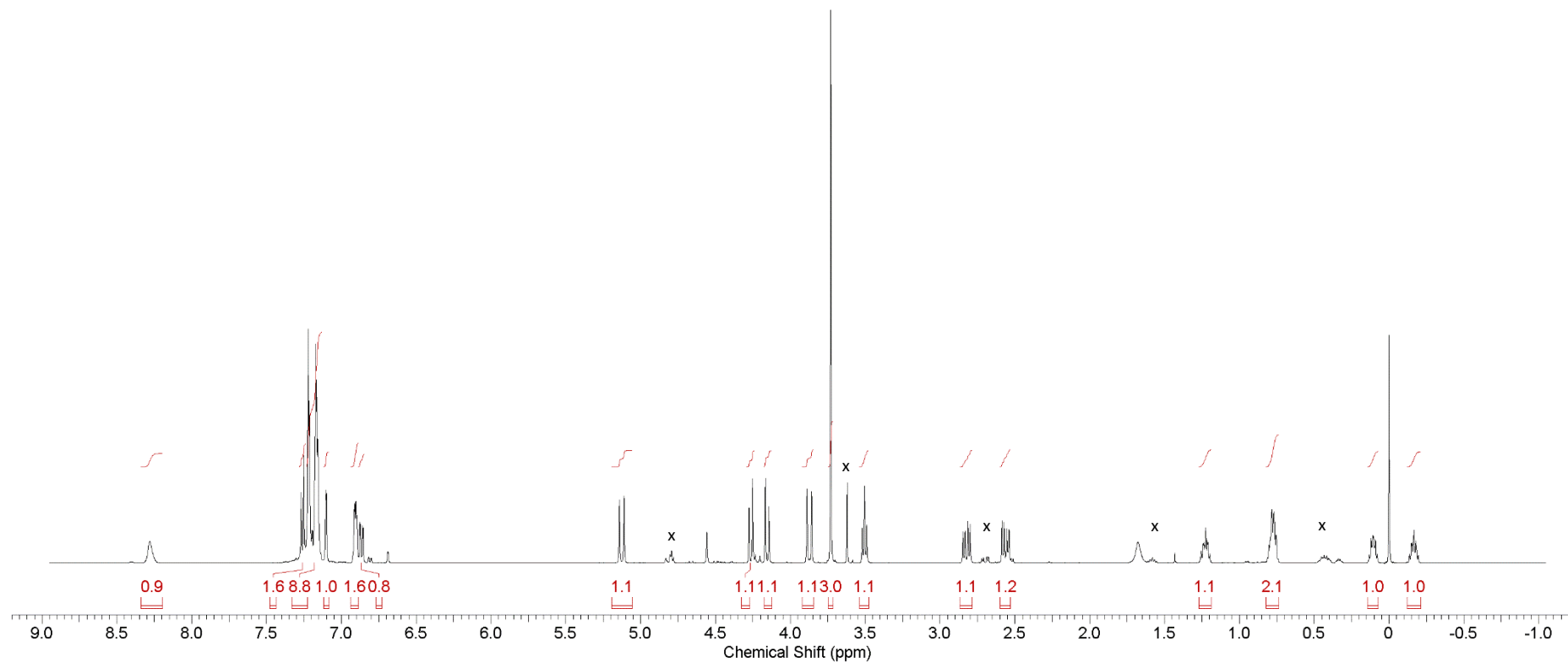


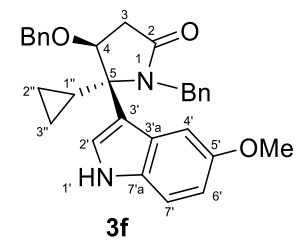


^1H NMR (CDCl_3 , 500 MHz).

3f Major diastereomer

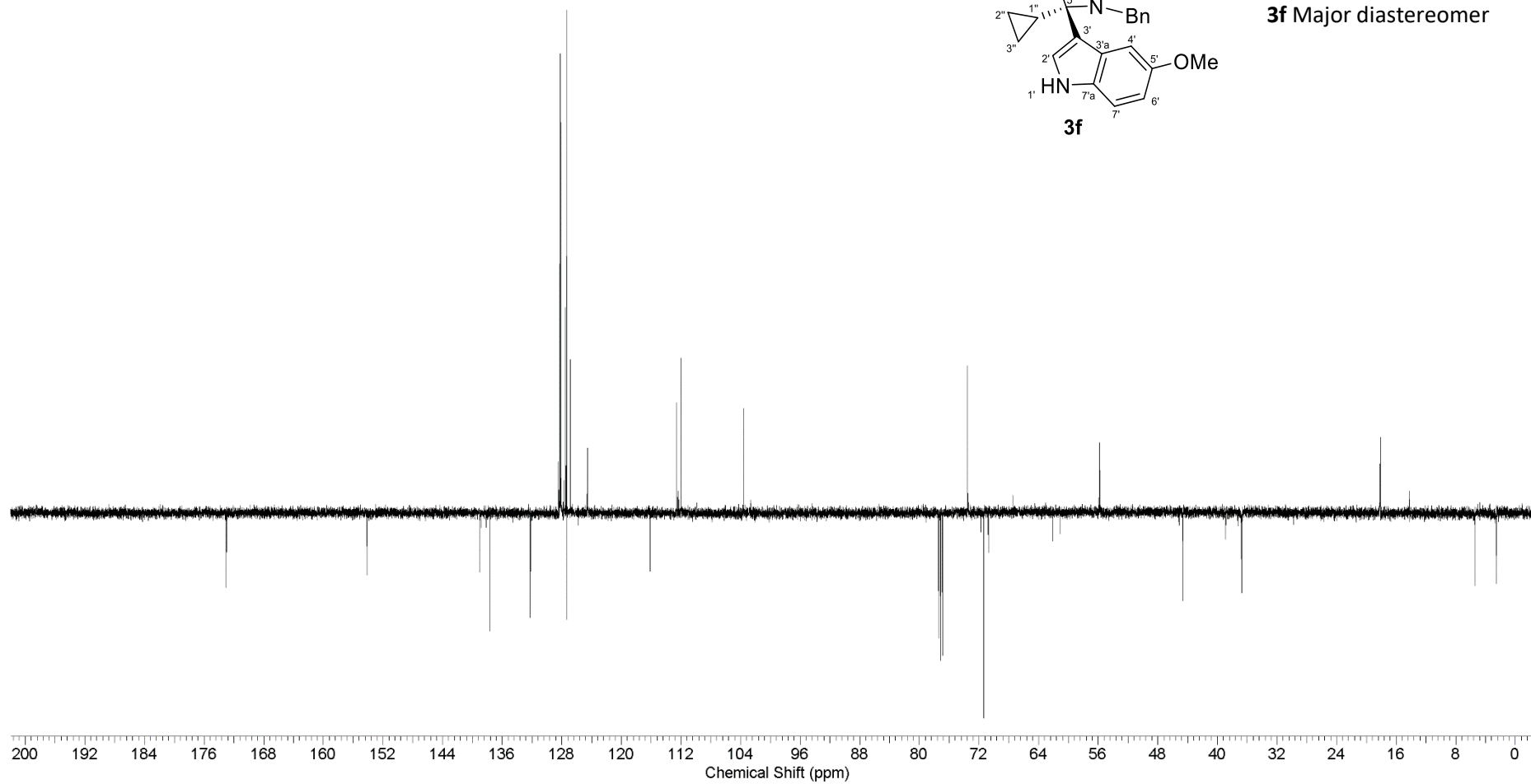
3f Minor diastereomer indicated by x.

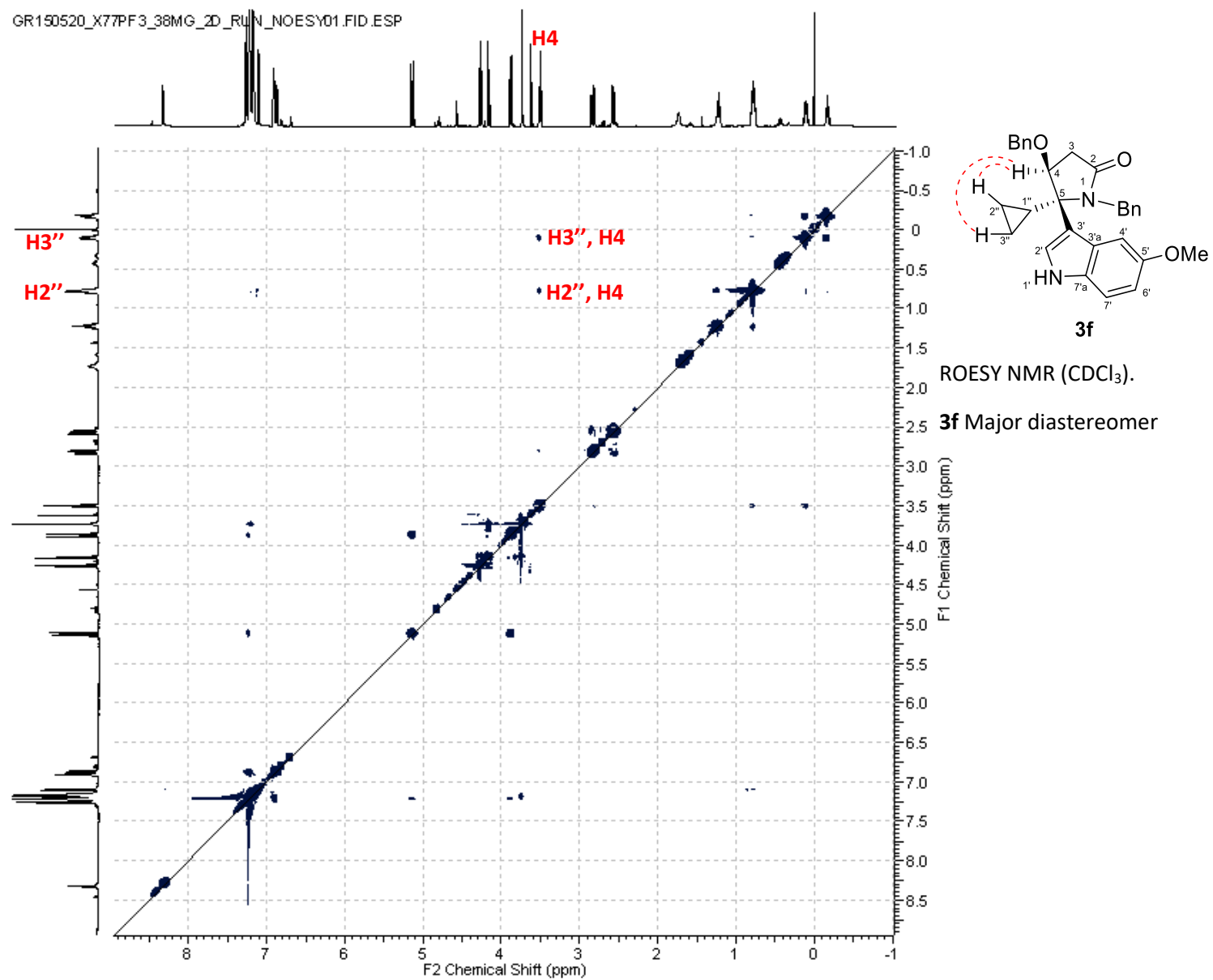


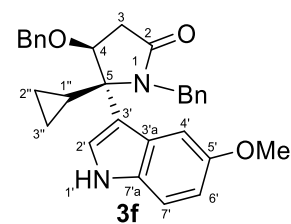


^{13}C NMR (CDCl_3 , 125 MHz).

3f Major diastereomer



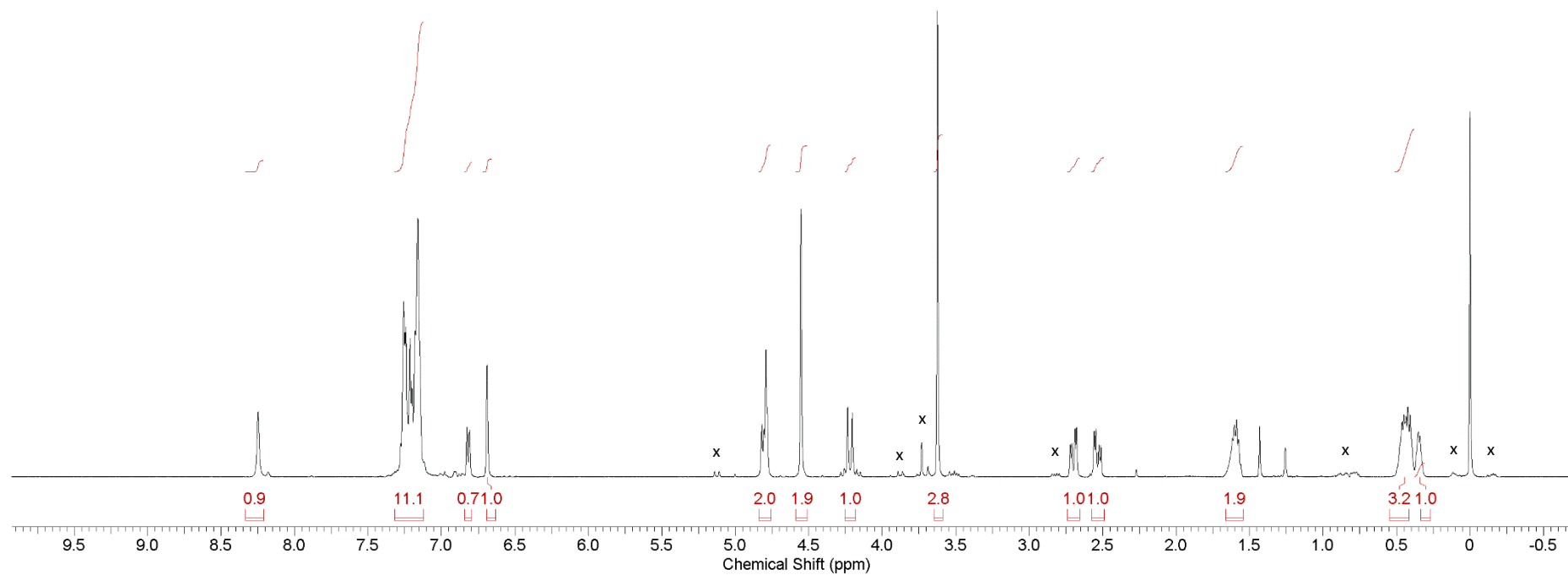


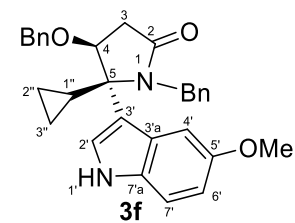


^1H NMR (CDCl_3 , 500 MHz).

3f Minor diastereomer.

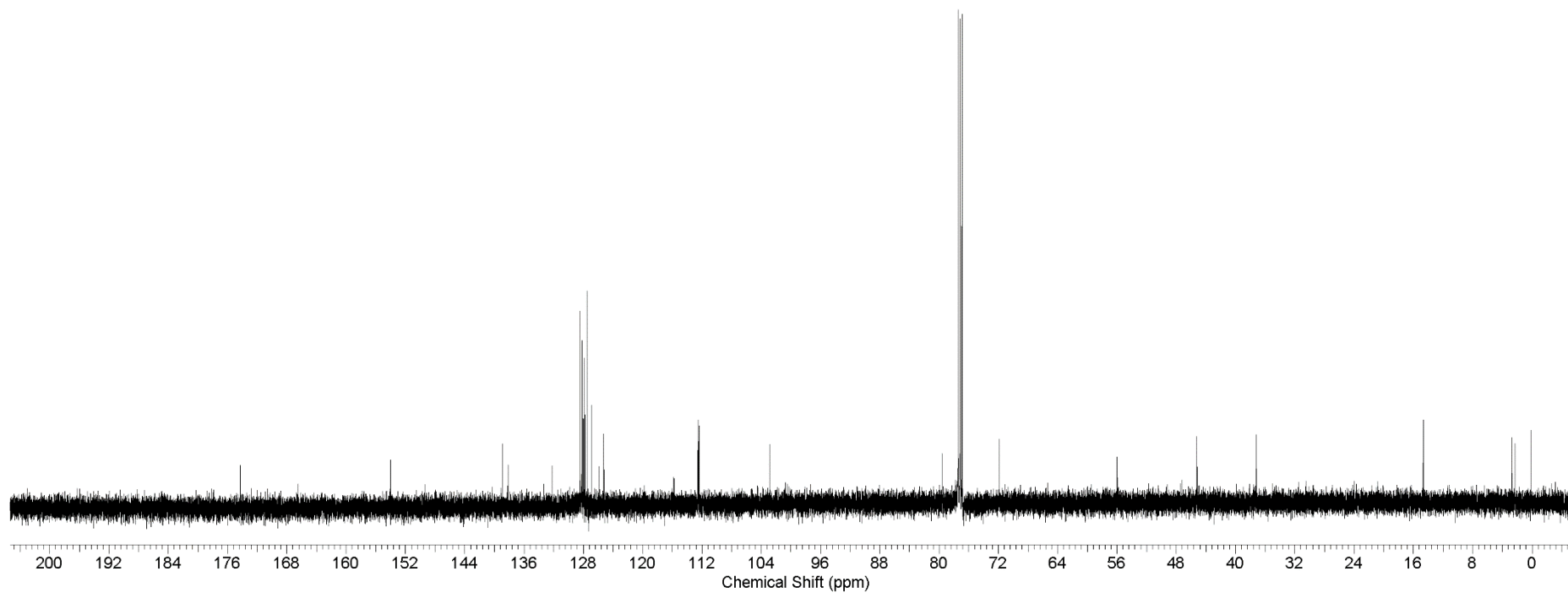
3f Major diastereomer indicated by x.

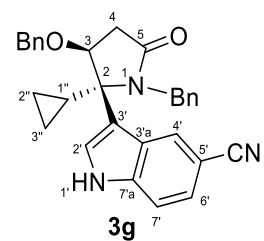




^{13}C NMR (CDCl_3 , 125 MHz).

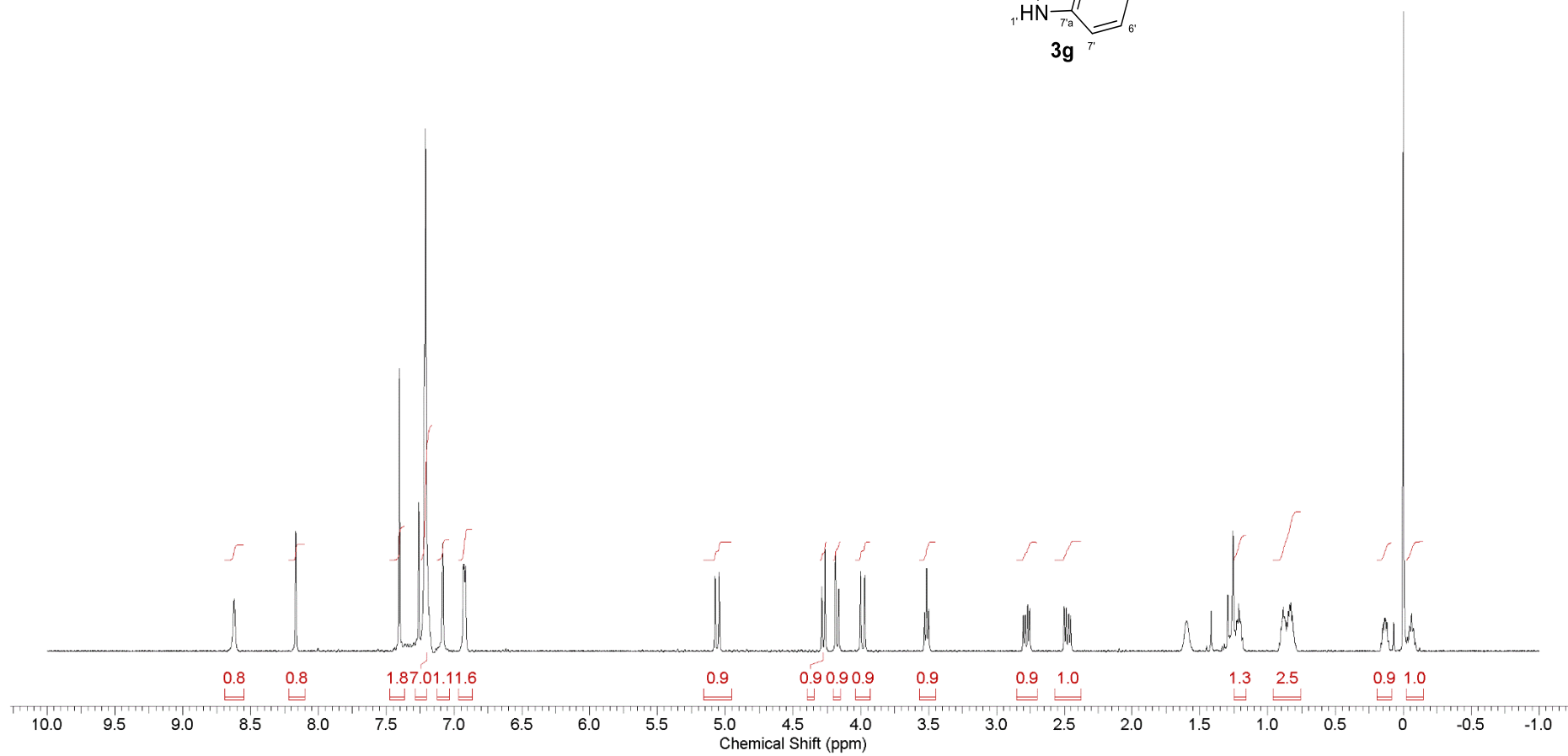
3f Minor diastereomer

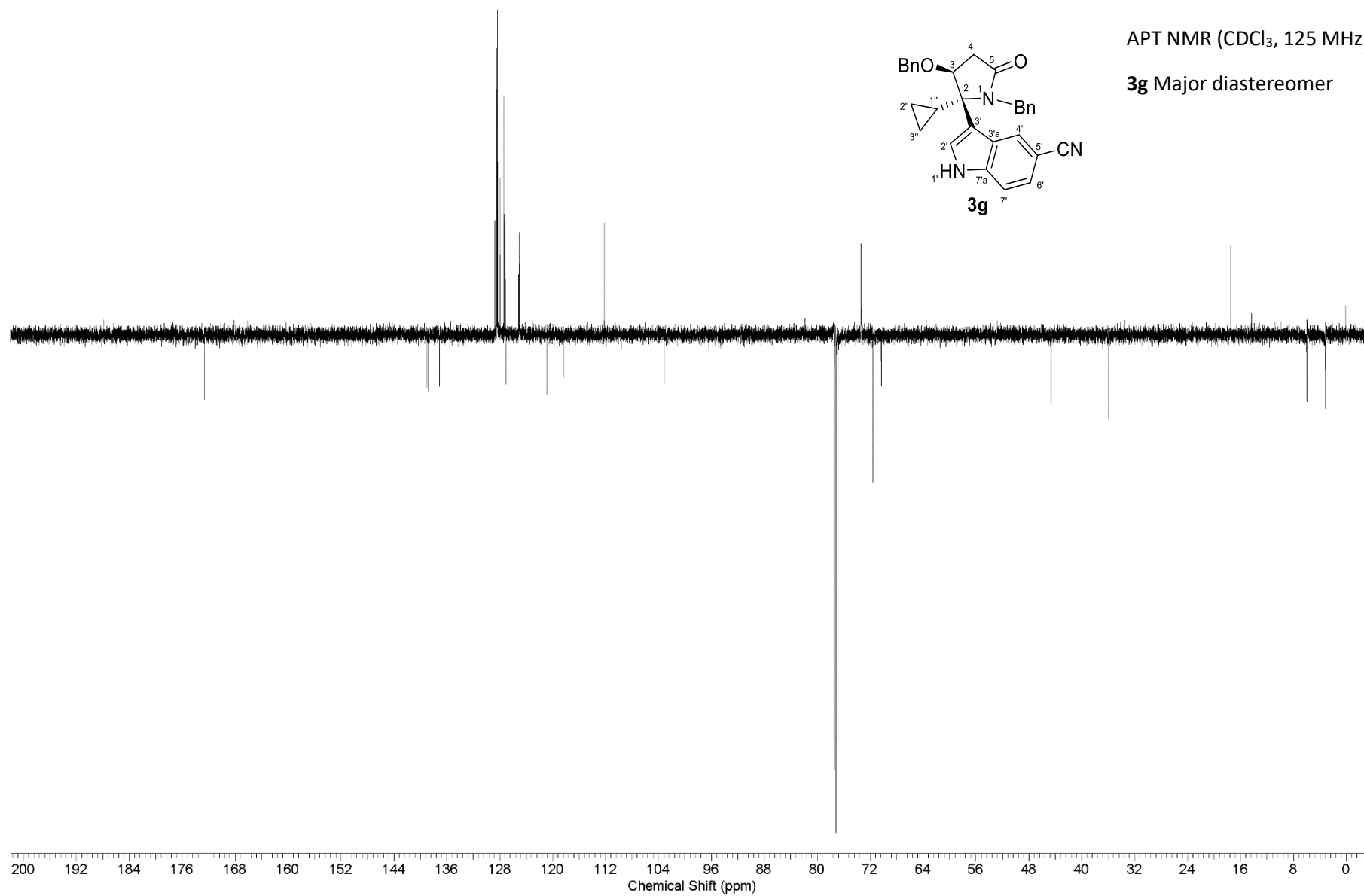
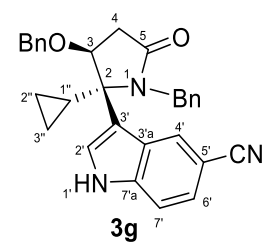


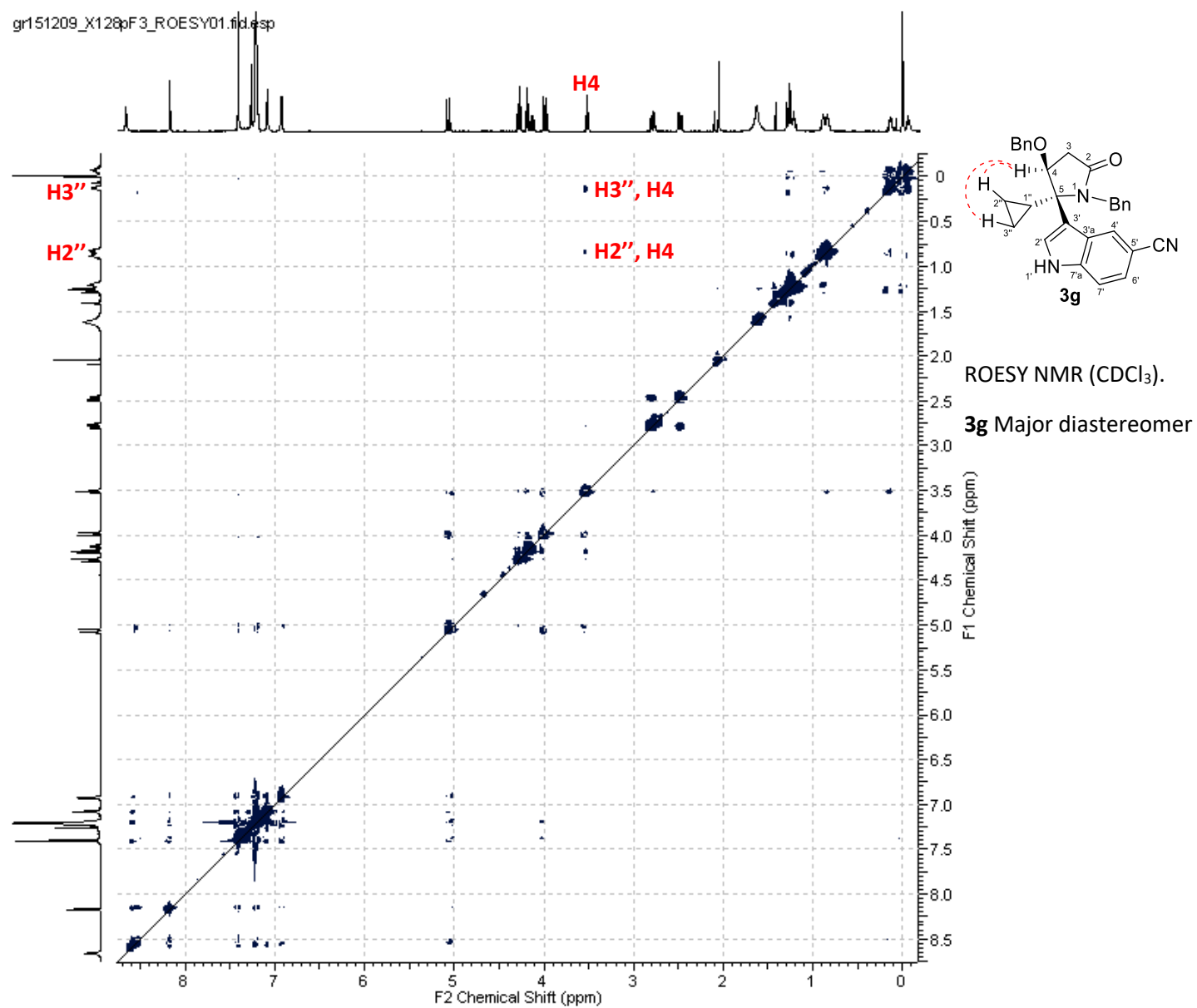


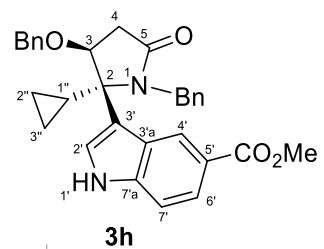
^1H NMR (CDCl_3 , 500 MHz).

3g Major diastereomer



APT NMR (CDCl₃, 125 MHz).**3g** Major diastereomer

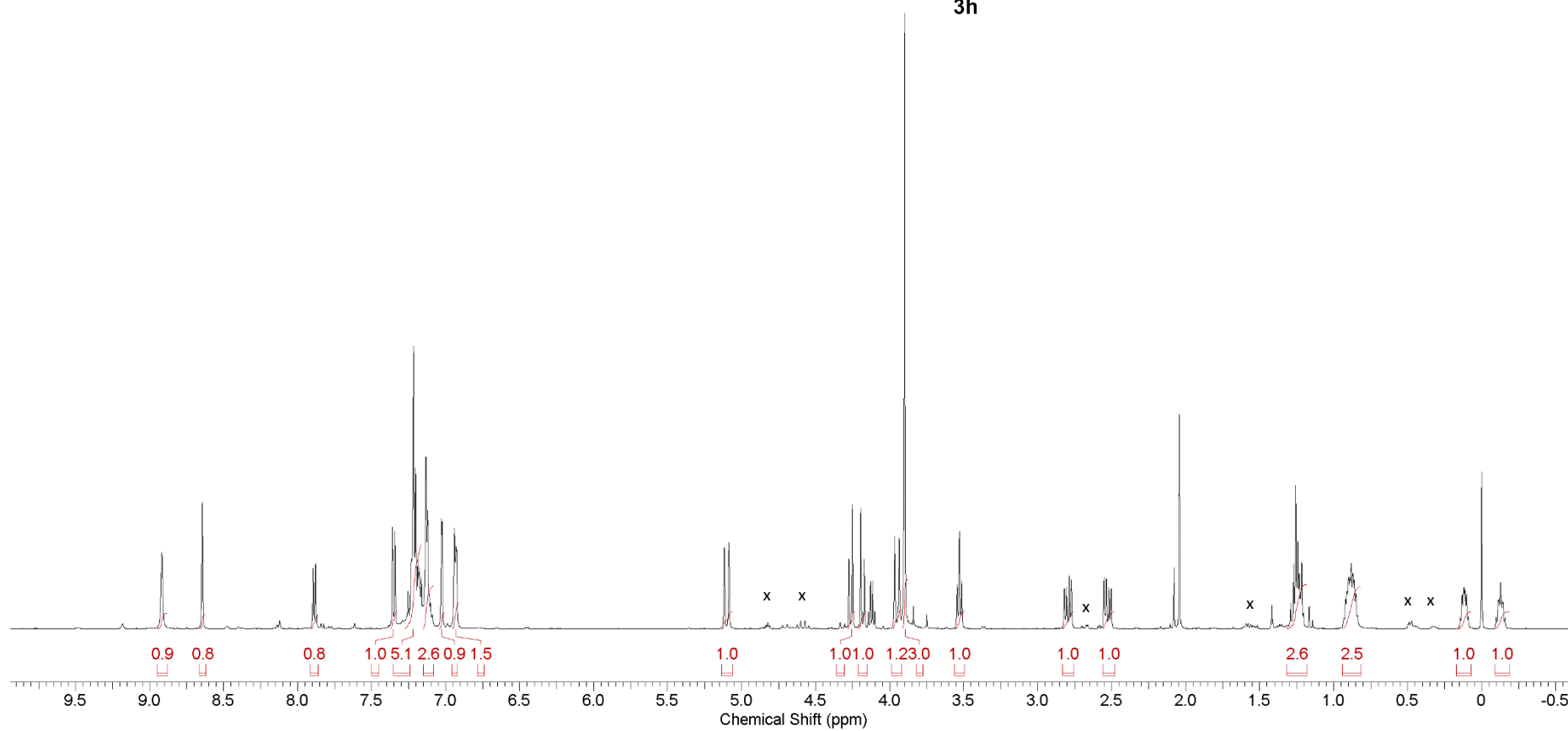


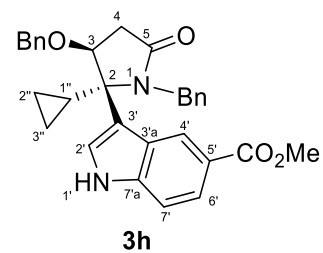


¹H NMR (CDCl₃, 500 MHz).

3h Major diastereomer.

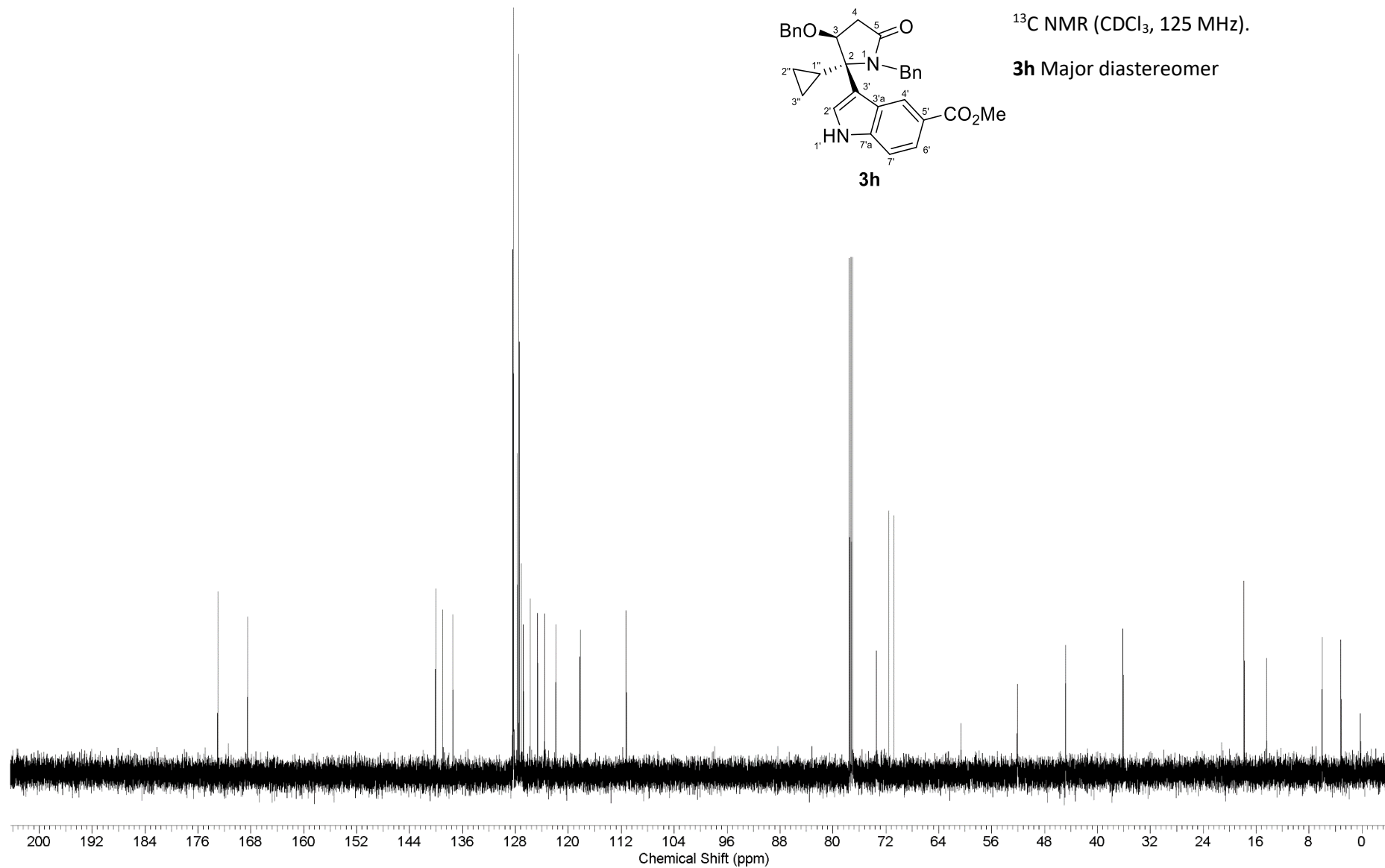
3h Minor diastereomer indicated by x.

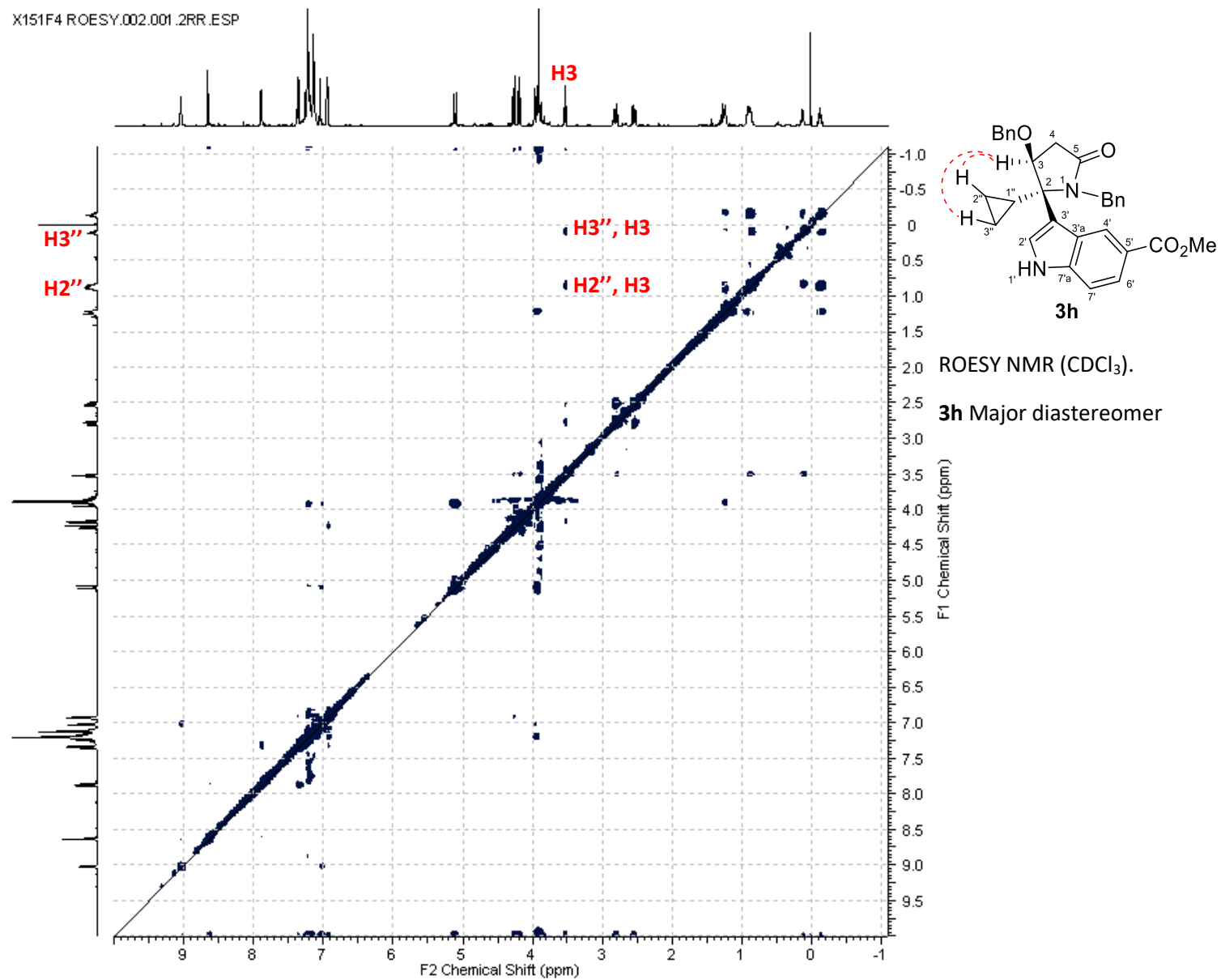


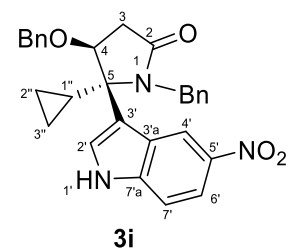


¹³C NMR (CDCl₃, 125 MHz).

3h Major diastereomer

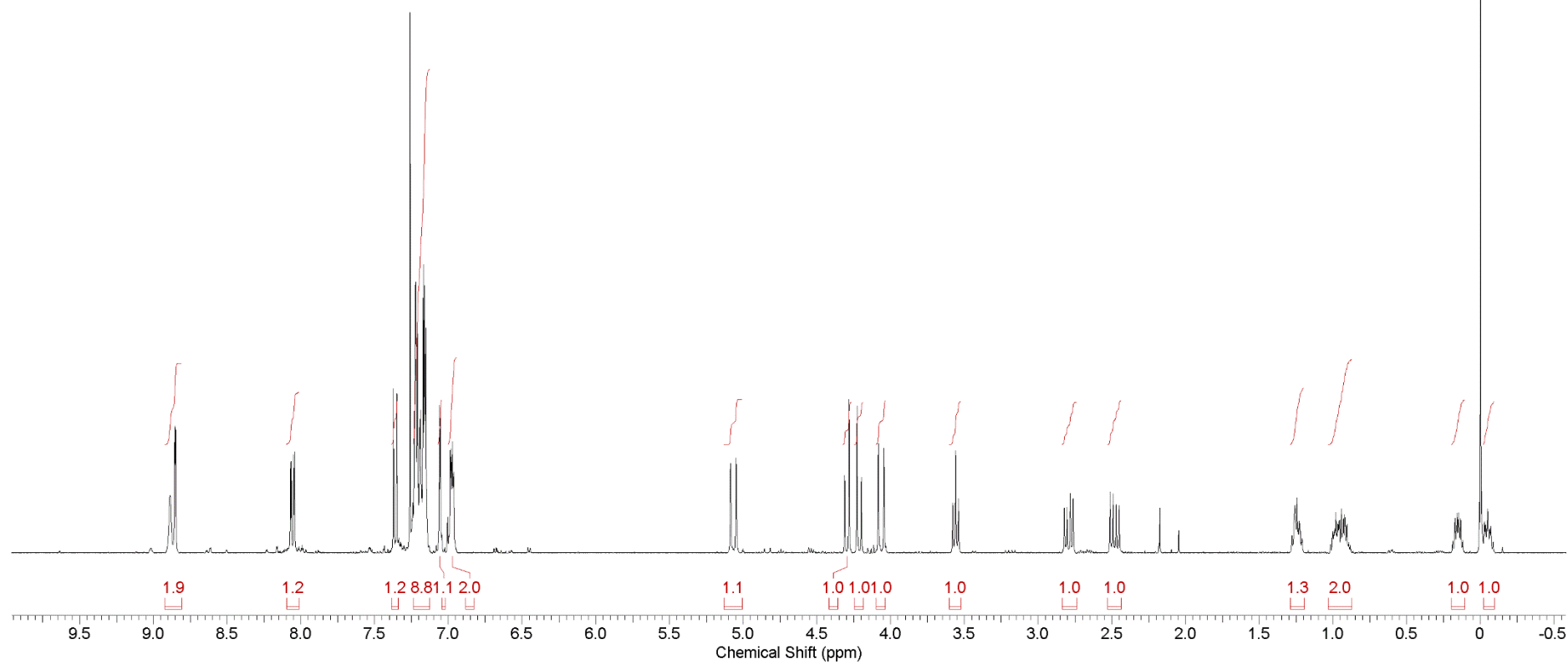


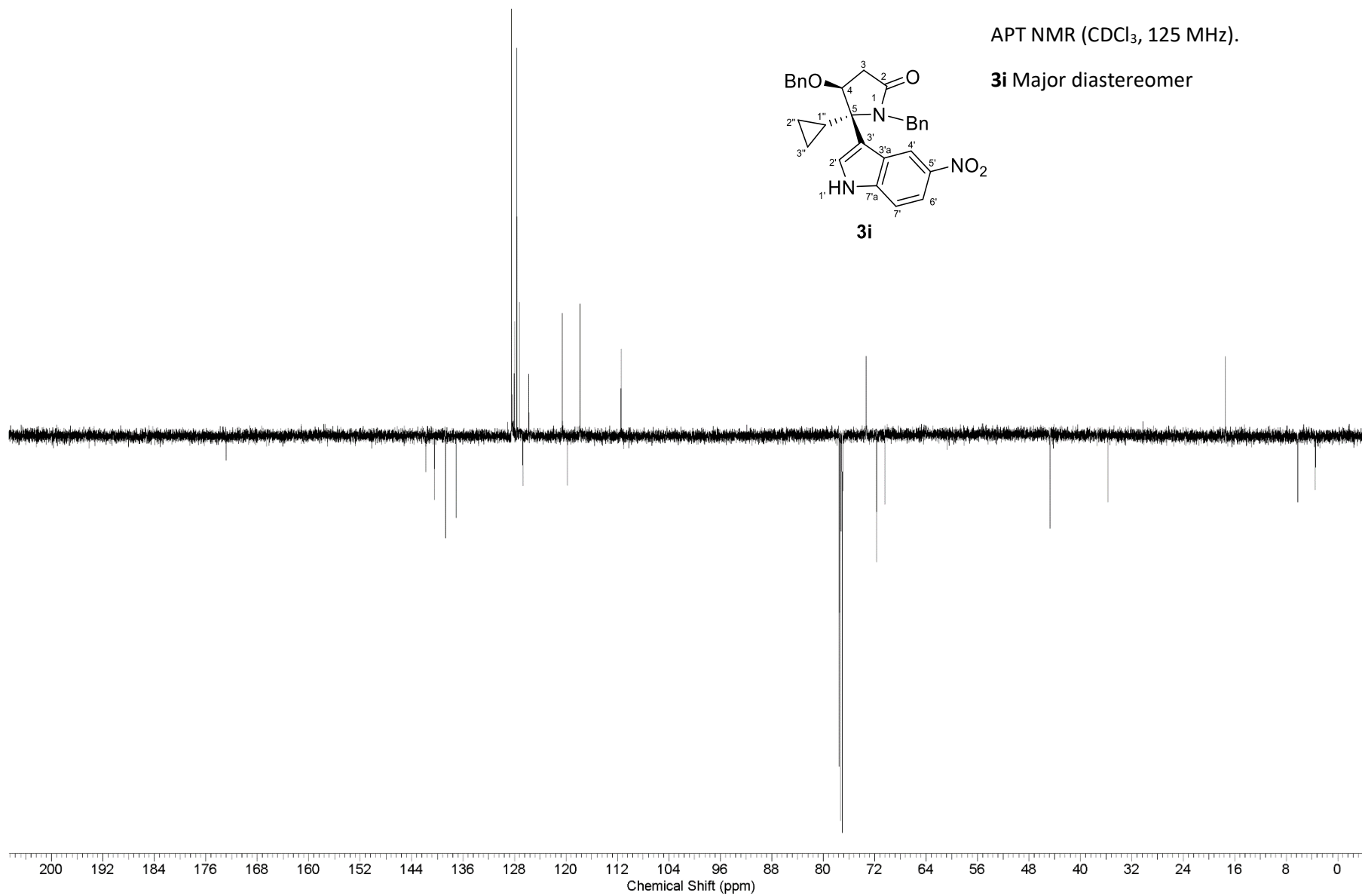
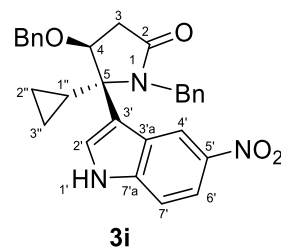


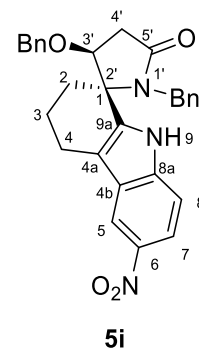


^1H NMR (CDCl_3 , 500 MHz).

3i Major diastereomer



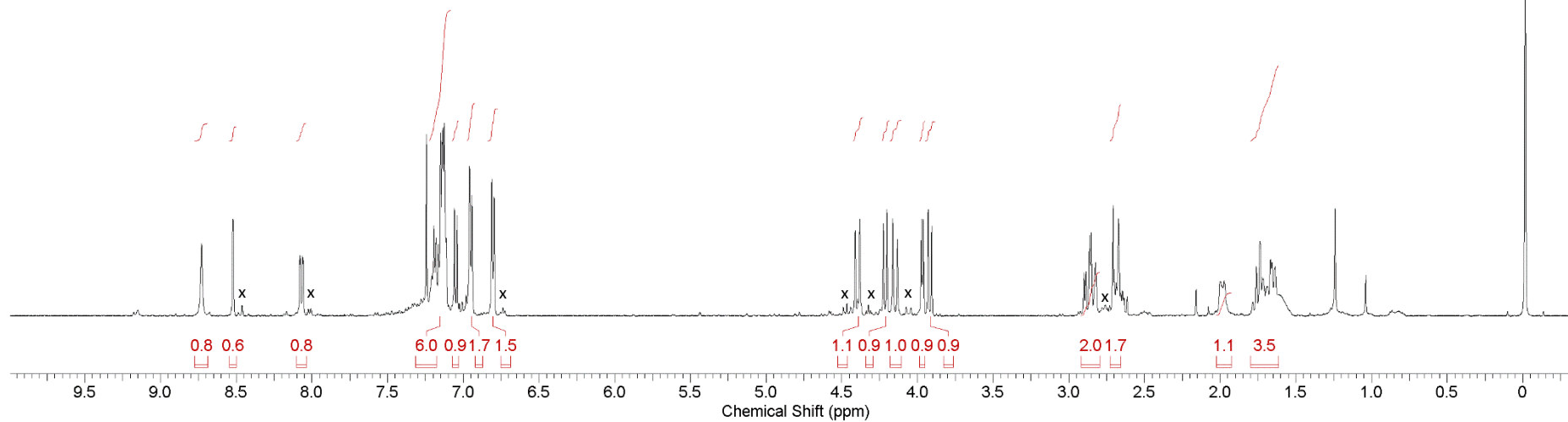
APT NMR (CDCl₃, 125 MHz).**3i** Major diastereomer

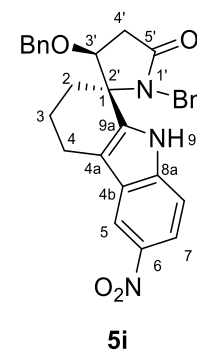


^1H NMR (CDCl_3 , 500 MHz).

5i Major diastereomer

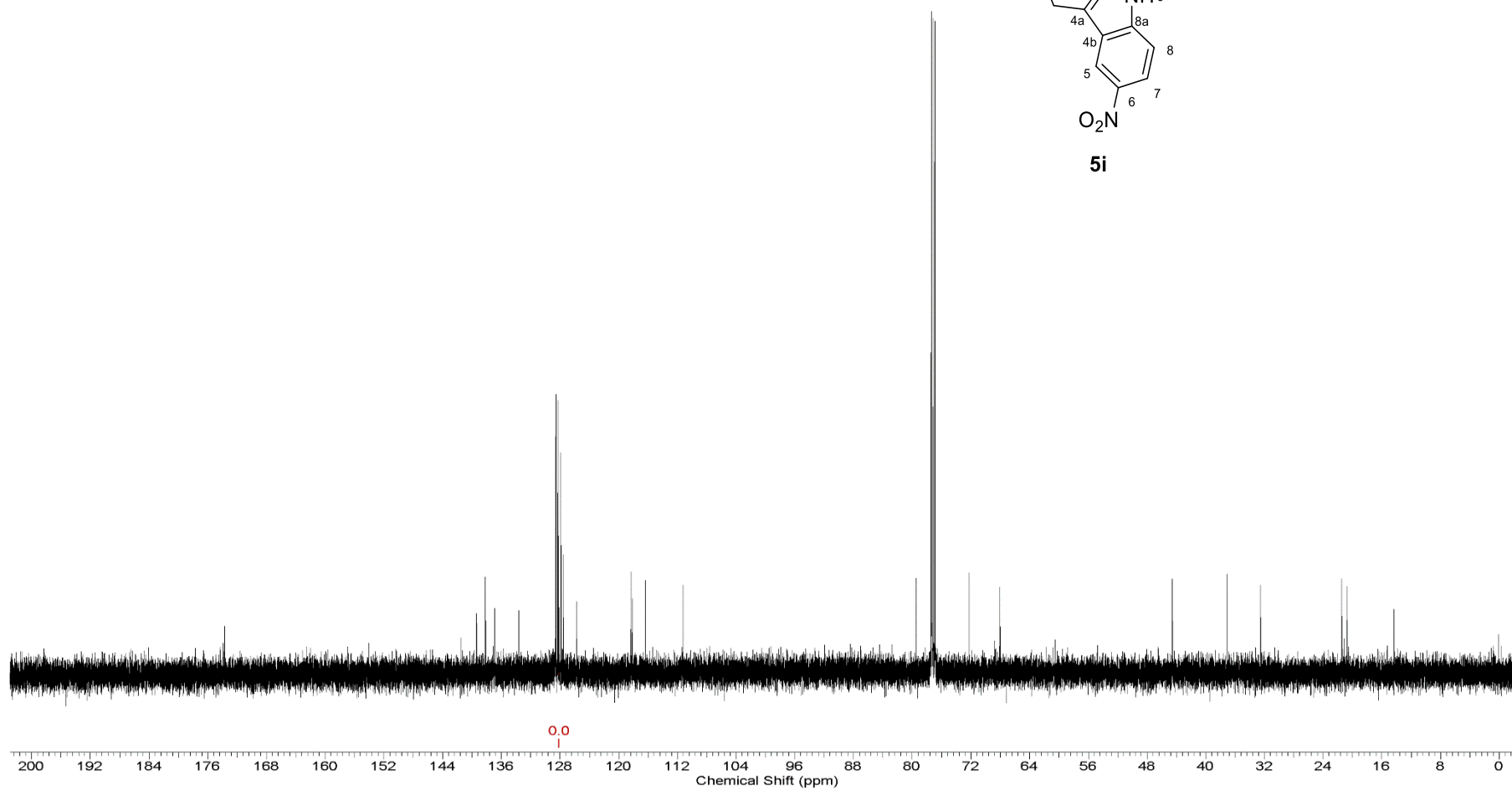
5i Minor diastereomer indicated by x.



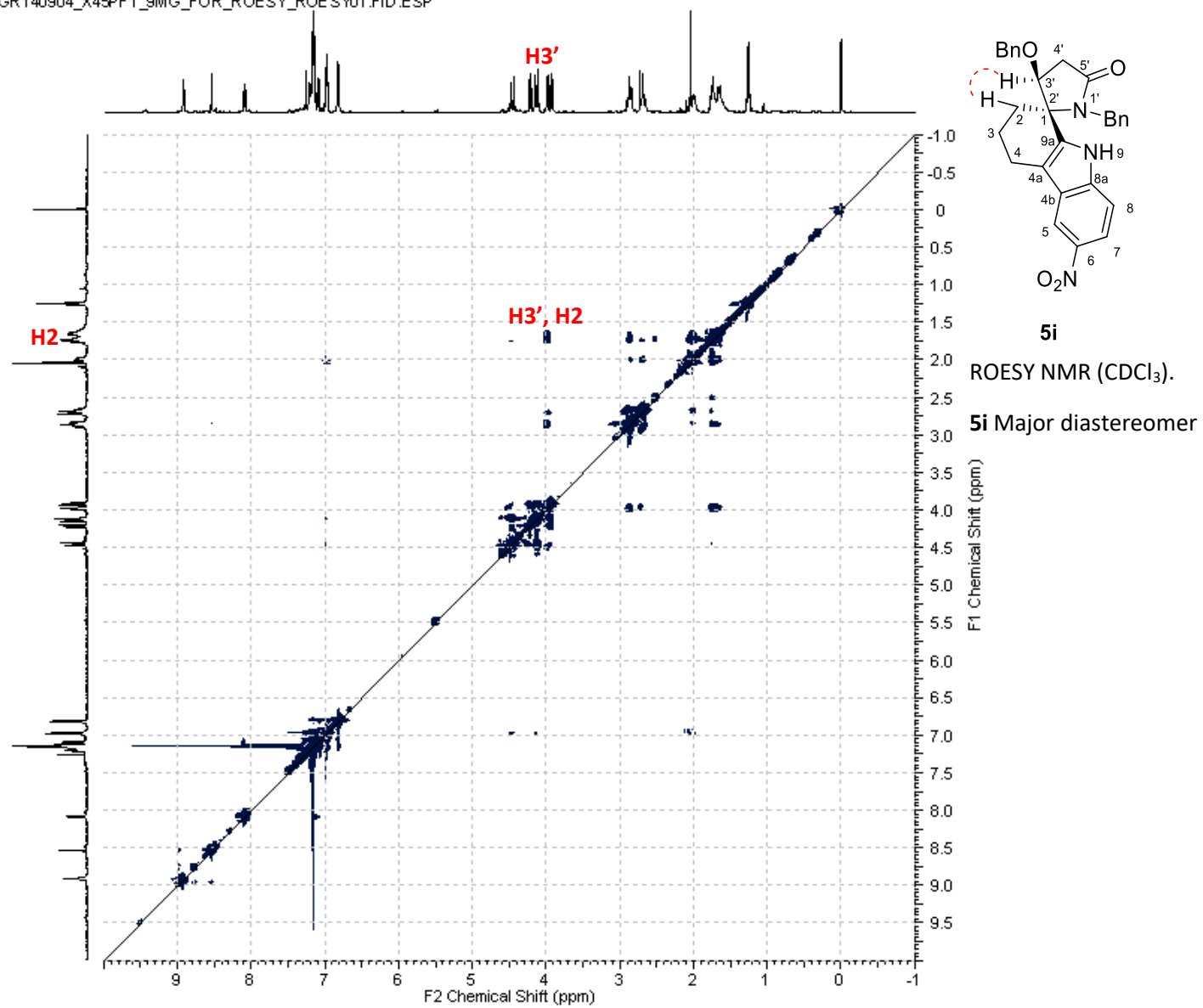


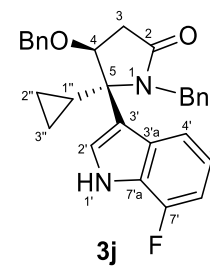
^{13}C NMR (CDCl_3 , 125 MHz).

5i Major diastereomer



GR140904_X45PF1_9MG_FOR_ROESY_ROESY01.FID.ESP

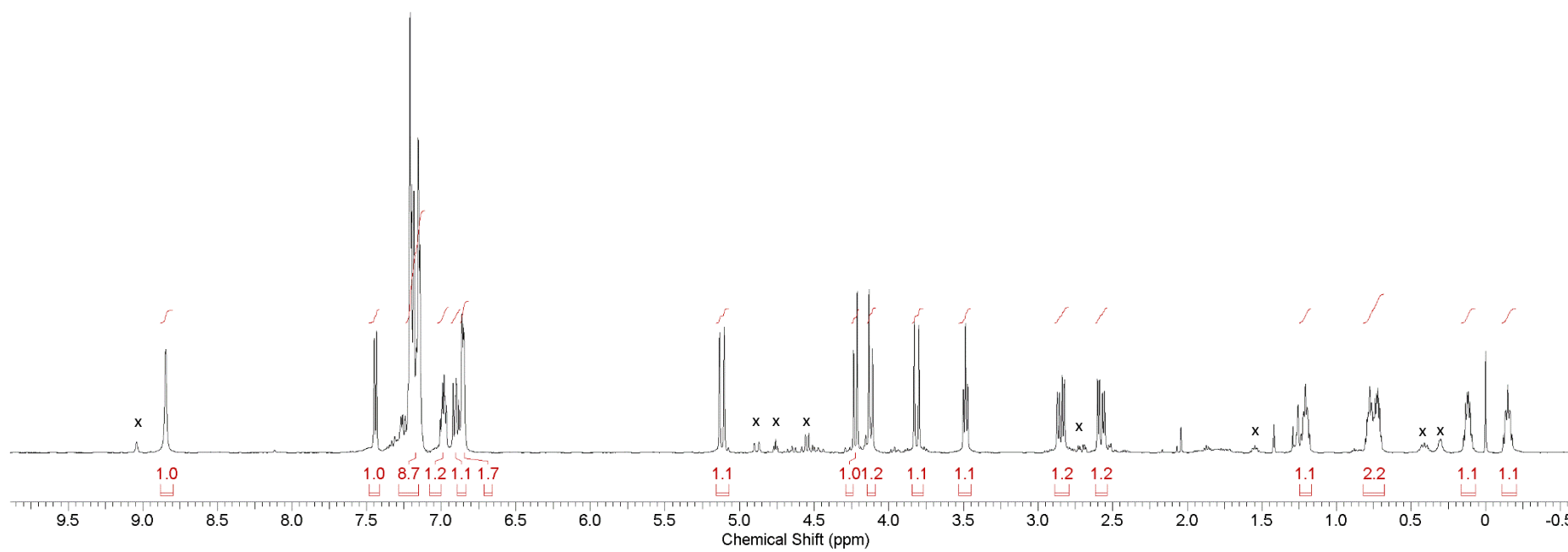


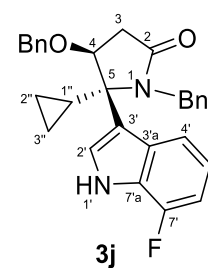


^1H NMR (CDCl_3 , 500 MHz).

3j Major diastereomer.

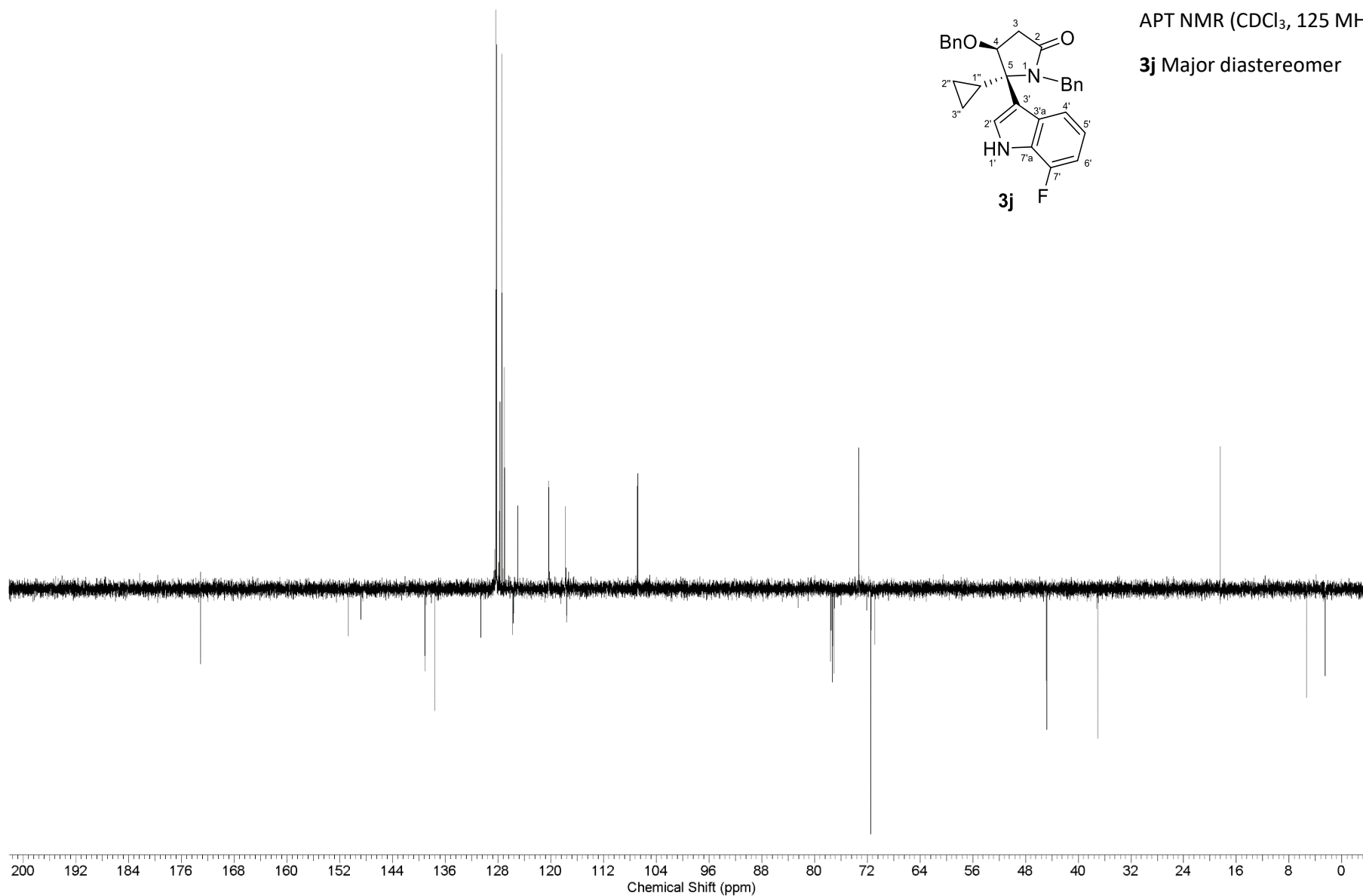
3j Minor diastereomer indicated by x.

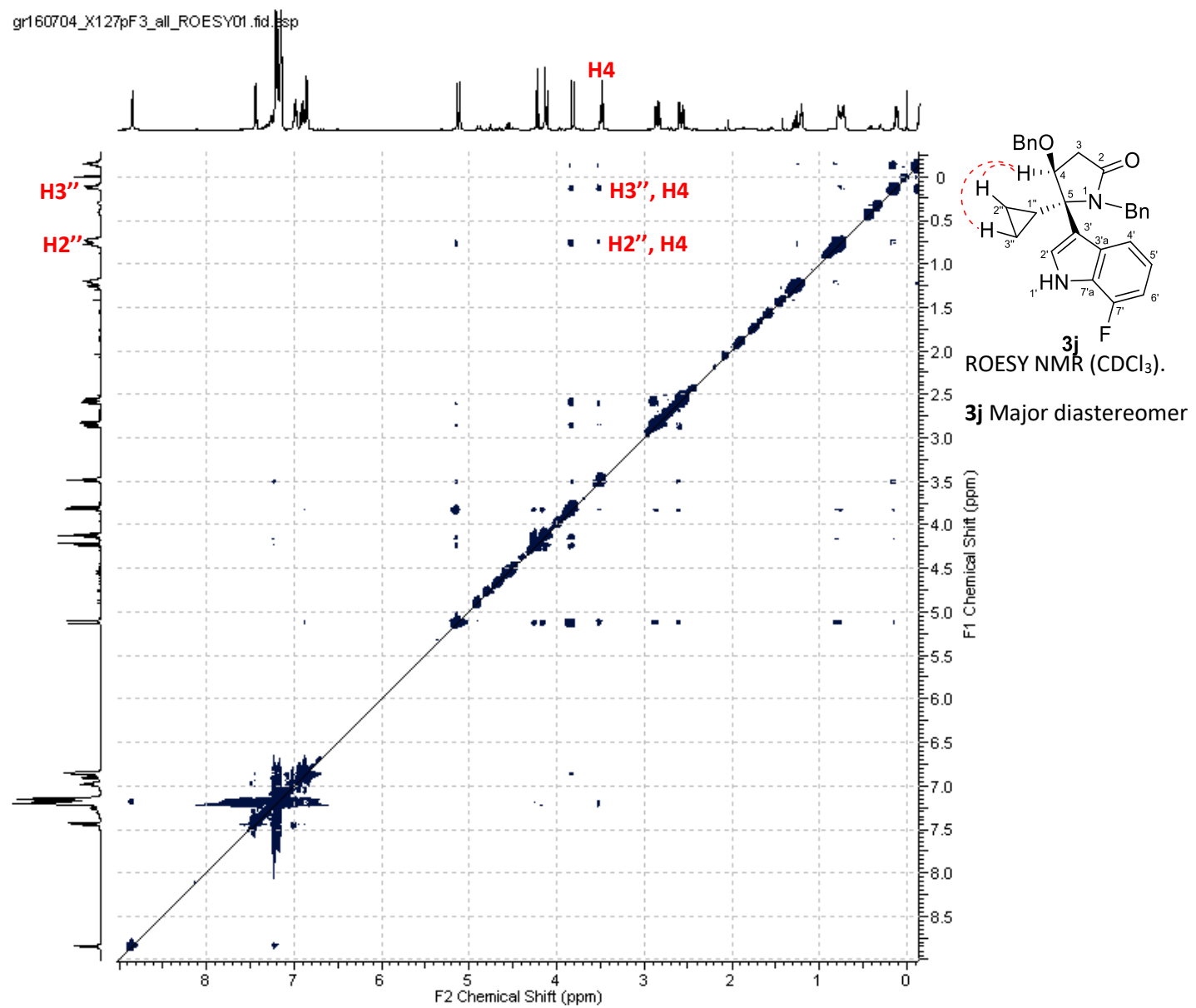


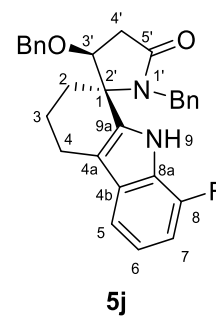


APT NMR (CDCl₃, 125 MHz).

3j Major diastereomer



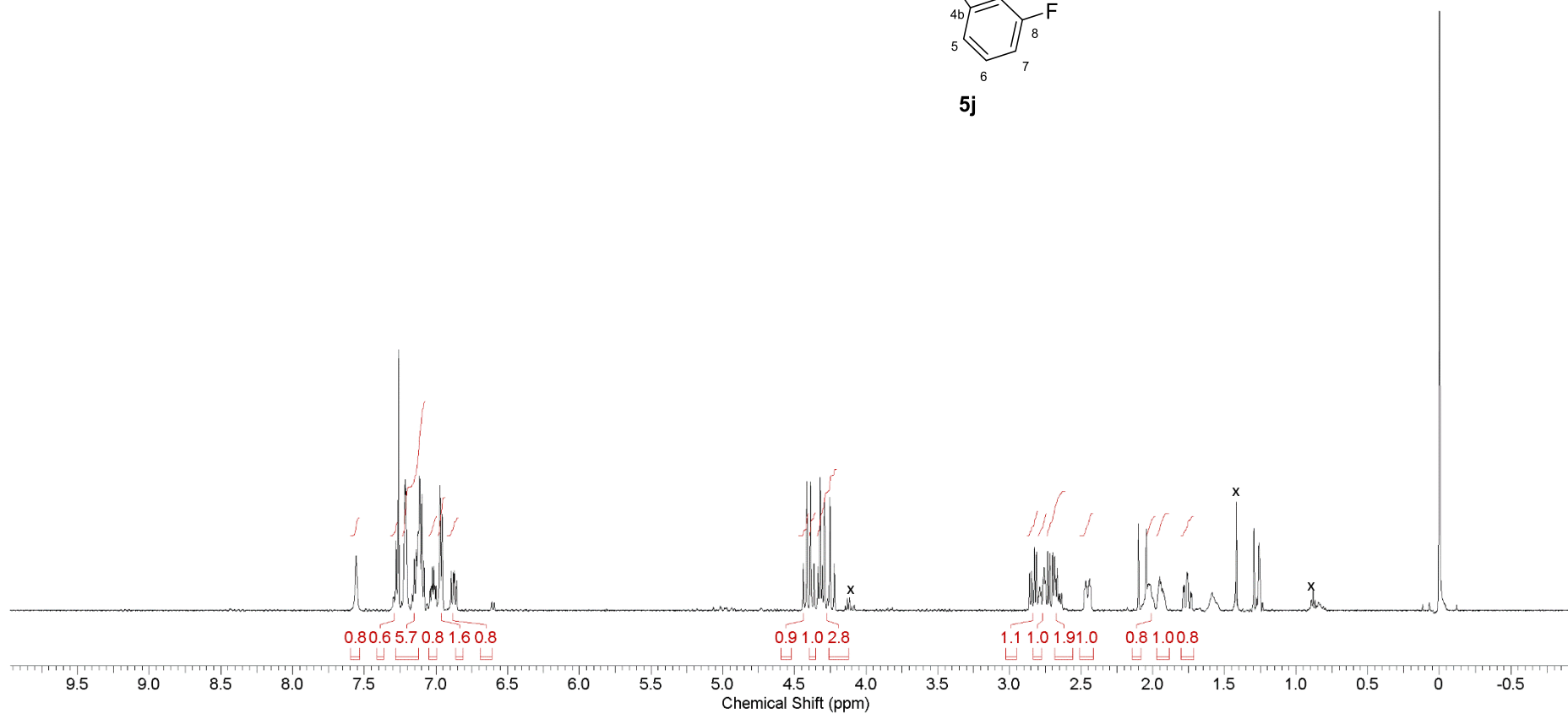


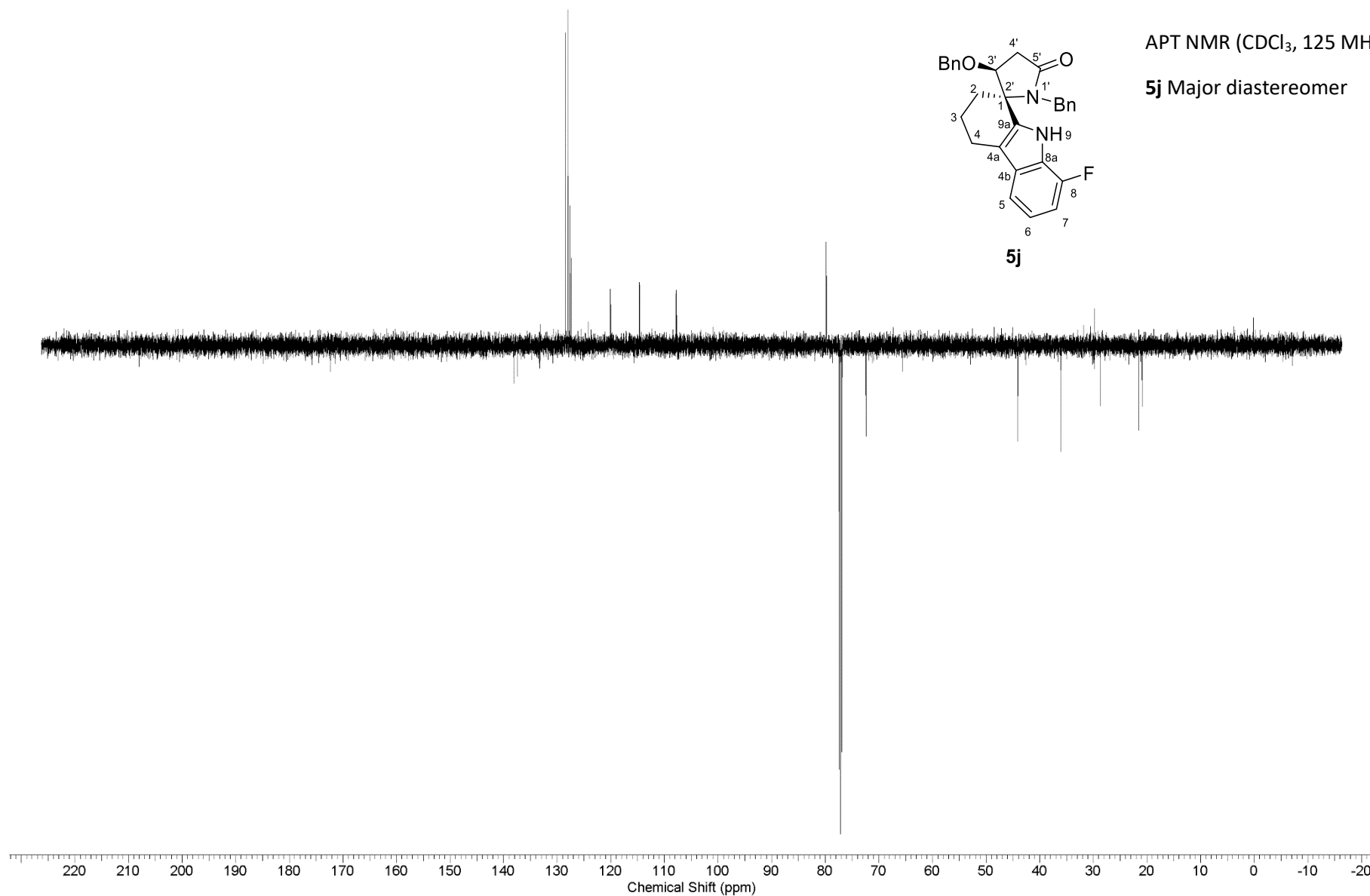
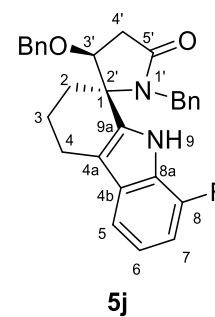


^1H NMR (CDCl_3 , 500 MHz).

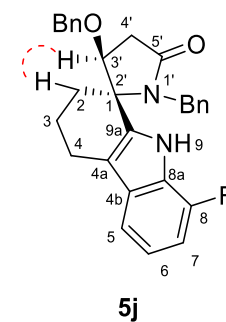
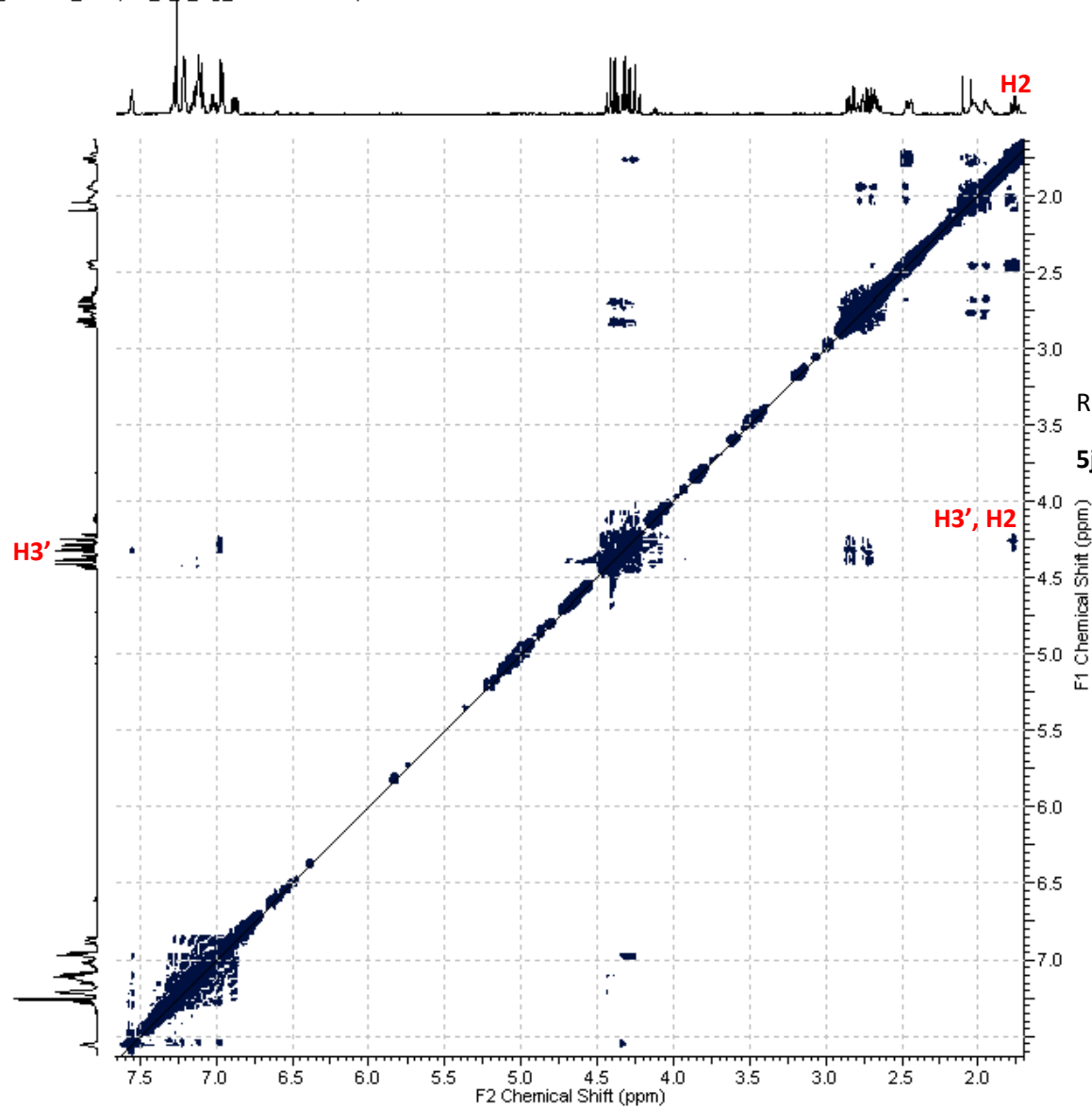
5j Major diastereomer

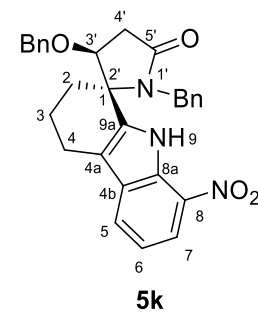
EtOAc indicated by x.



APT NMR (CDCl_3 , 125 MHz).**5j** Major diastereomer

gr151214_X127pF2_3_2_mg_ROESY01.fid.esp

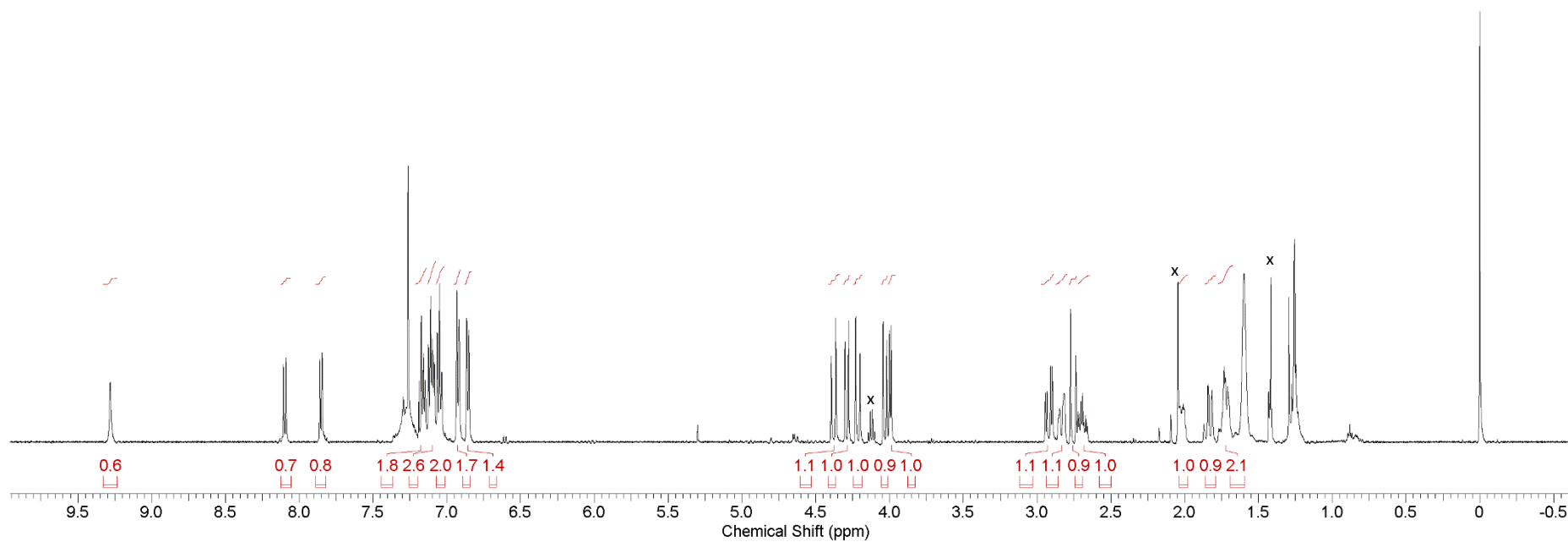
ROESY NMR (CDCl₃).**5j** Major diastereomer

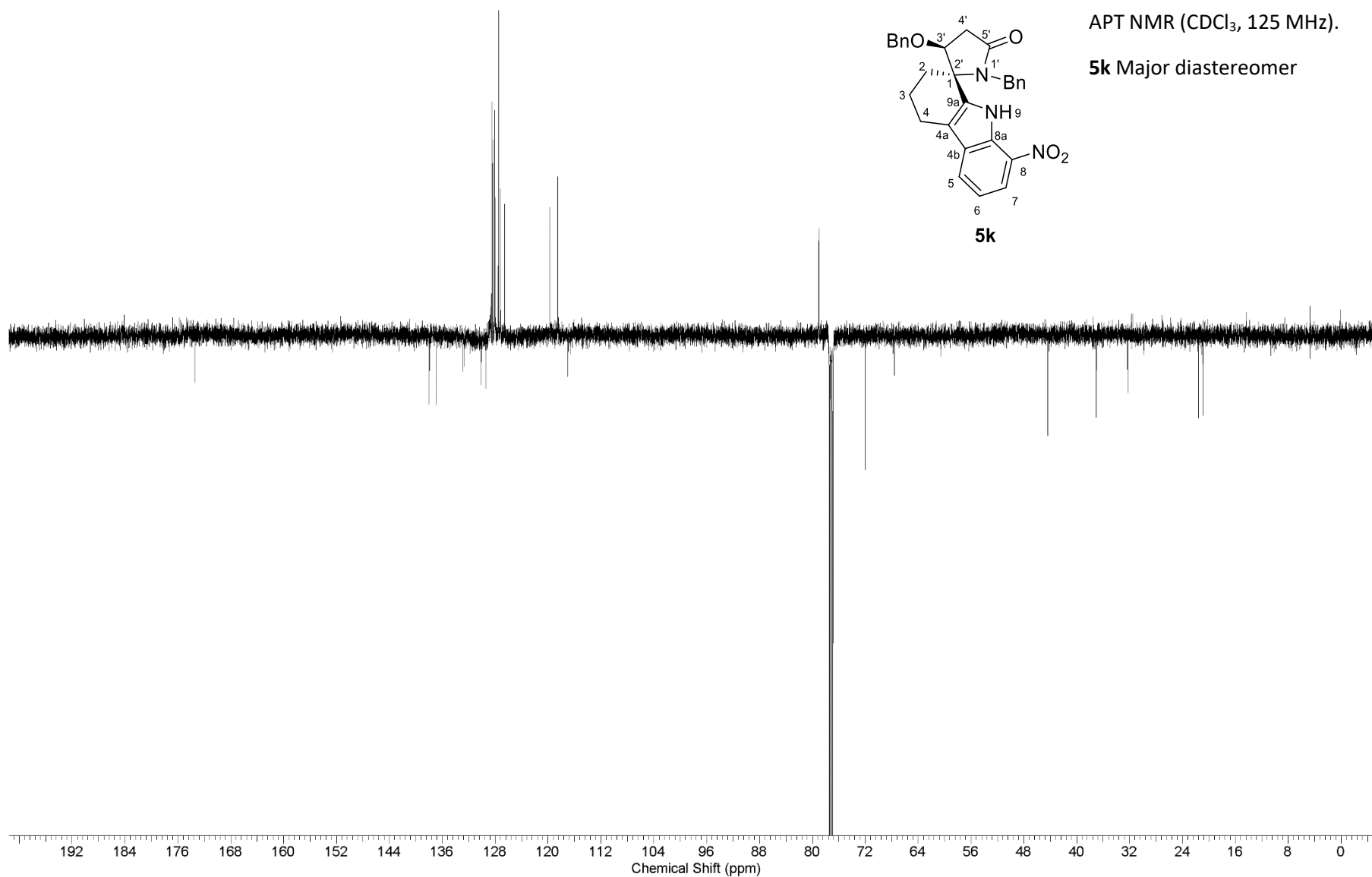
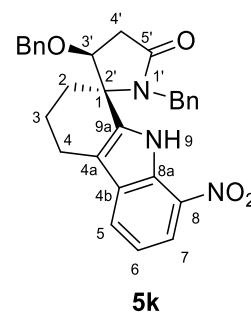


^1H NMR (CDCl_3 , 500 MHz).

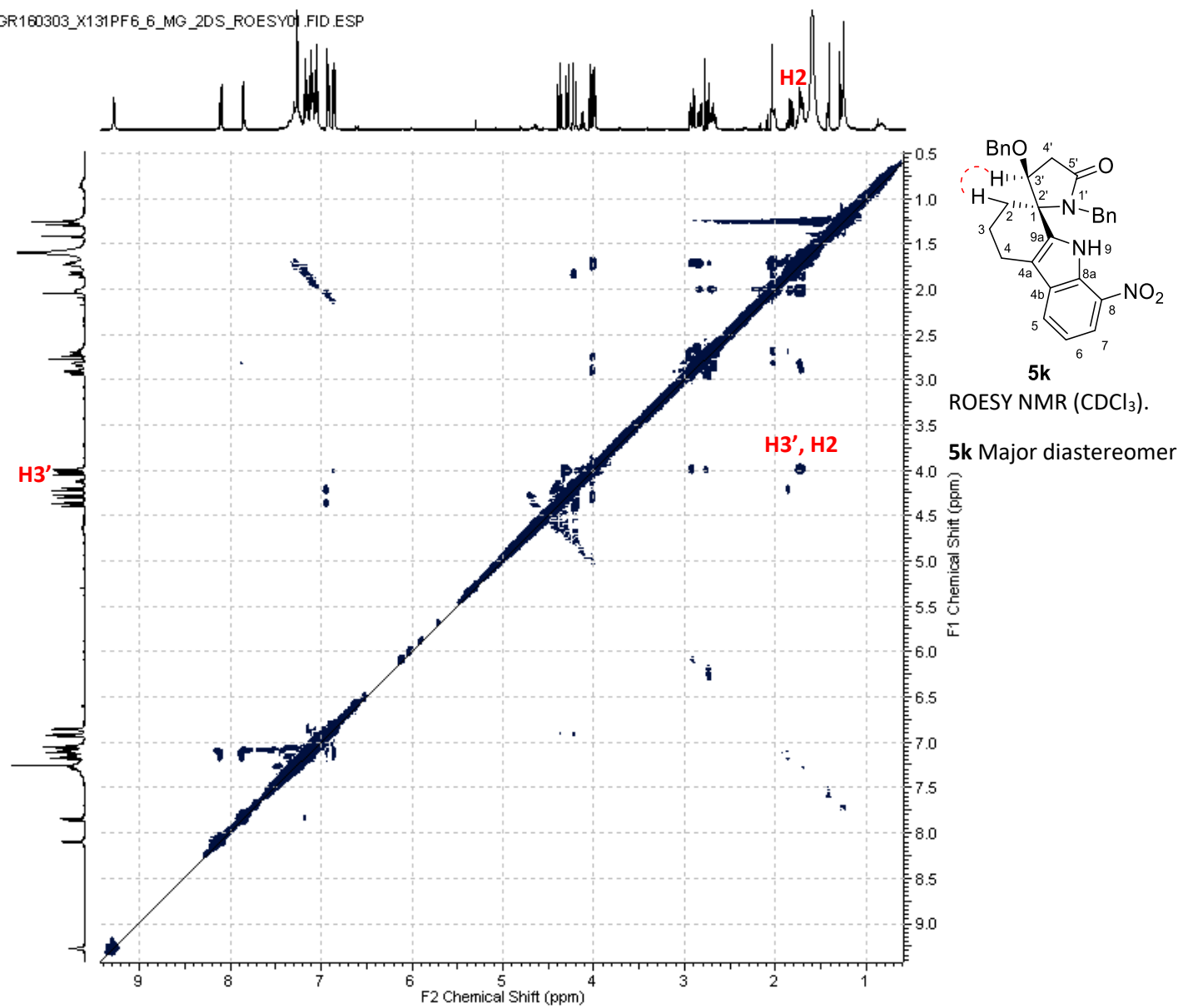
5k Major diastereomer

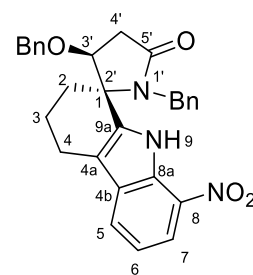
EtOAc indicated by x.



APT NMR (CDCl_3 , 125 MHz).**5k** Major diastereomer

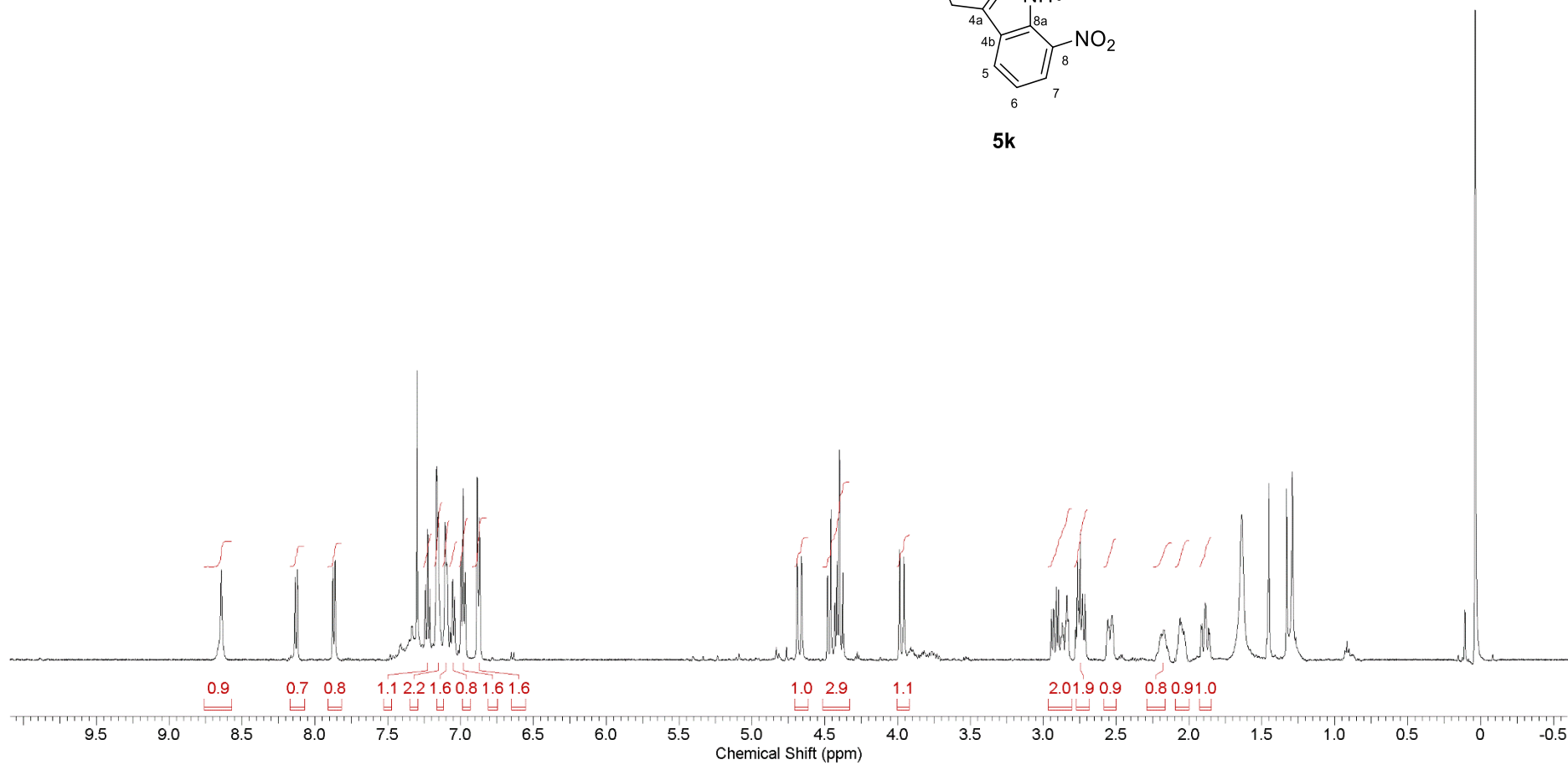
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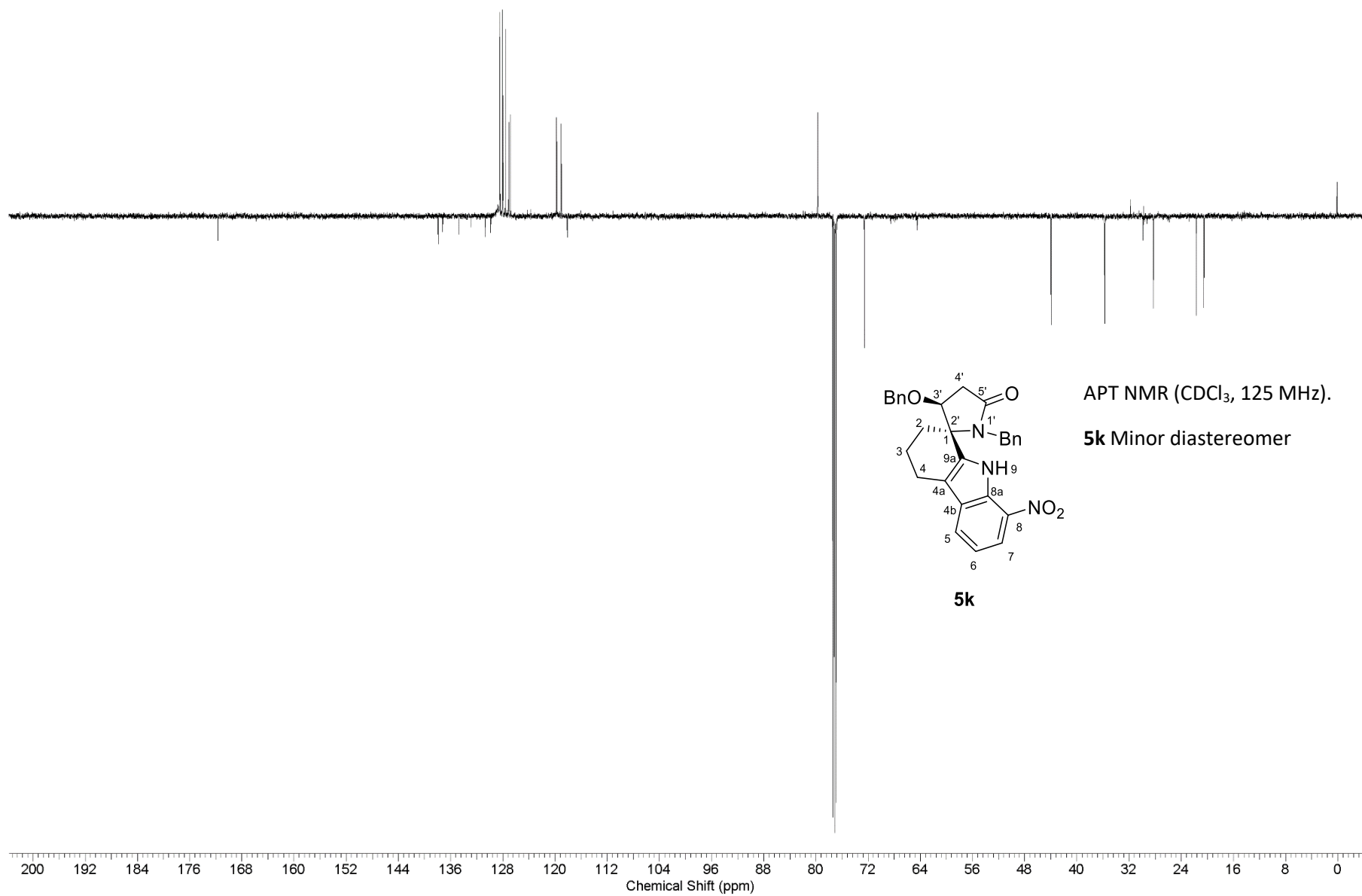


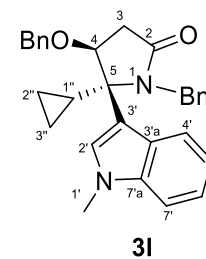


¹H NMR (CDCl₃, 500 MHz).

5k Minor diastereomer





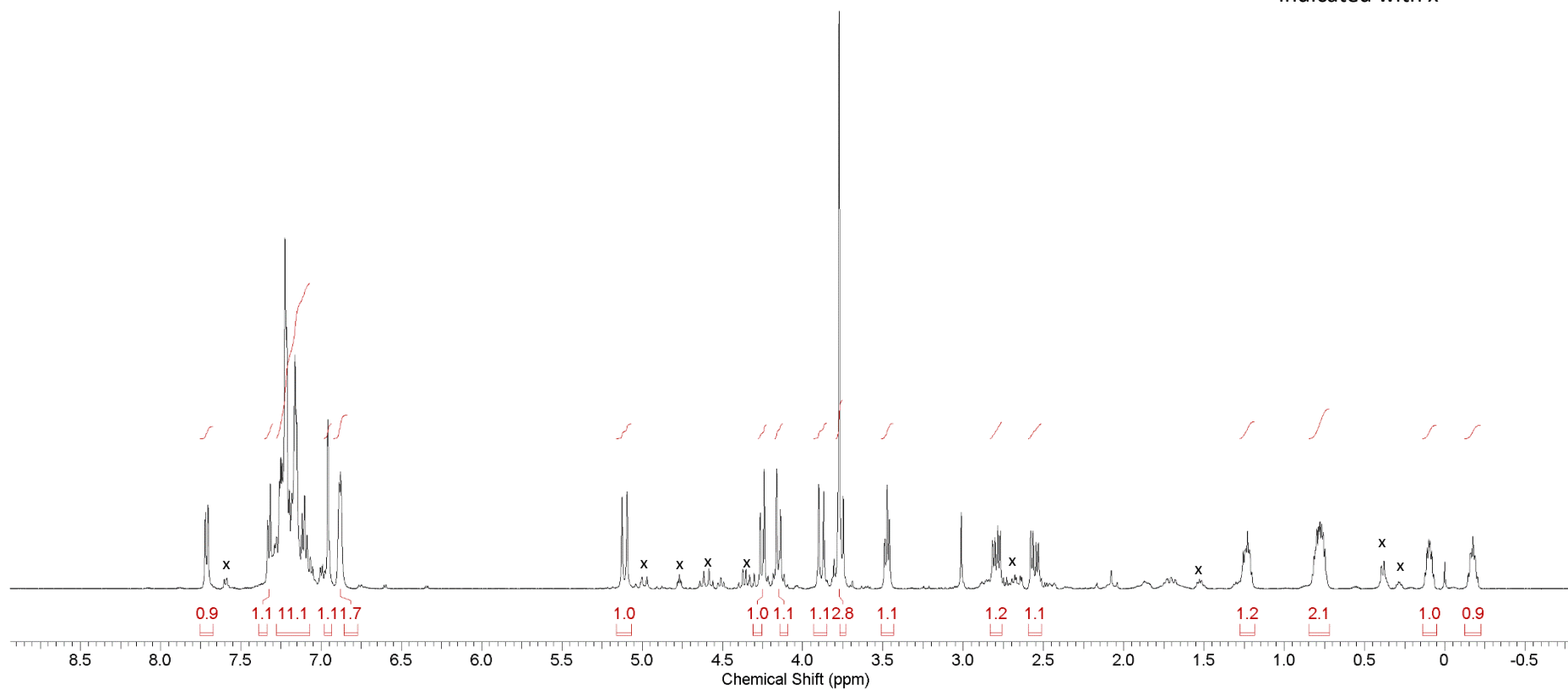


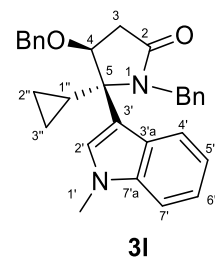
^1H NMR (CDCl_3 , 500 MHz).

3I Major diastereomer enriched

Dr = 89:11

3I Minor diastereomer indicated with x





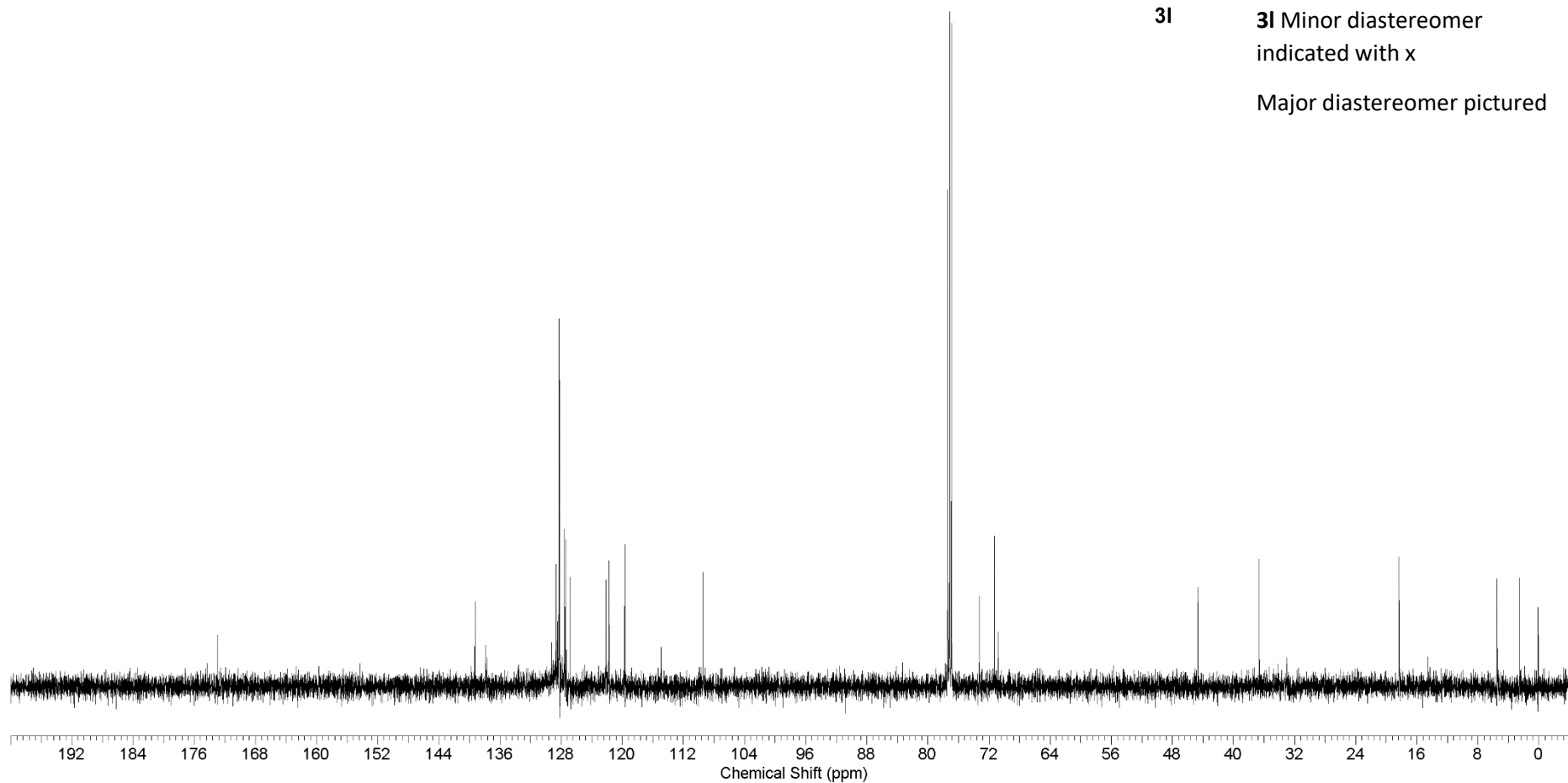
^{13}C NMR (CDCl_3 , 125 MHz).

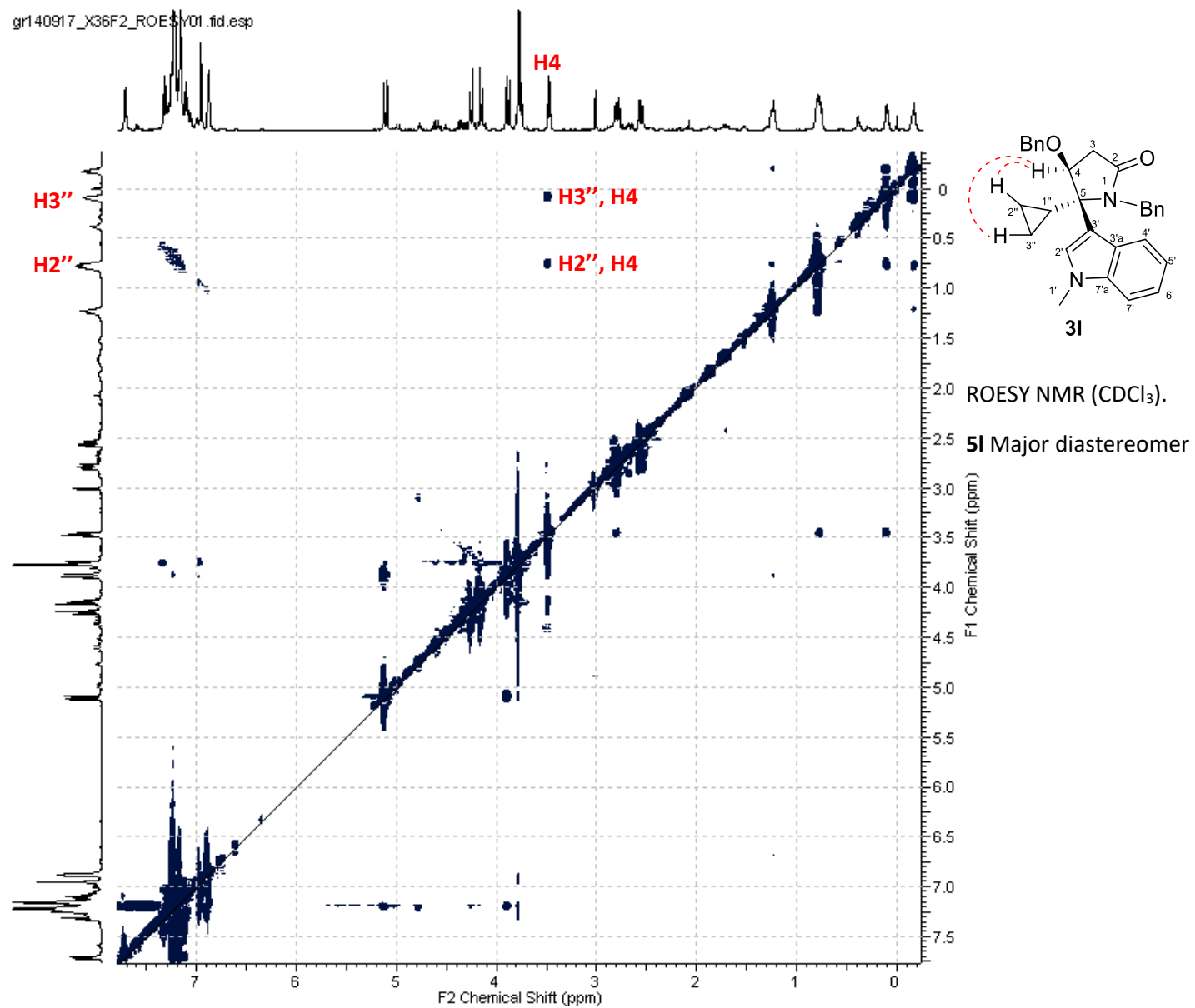
3I Major diastereomer enriched

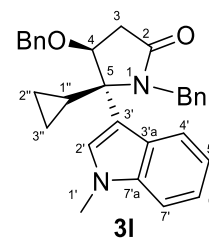
Dr = 89:11

3I Minor diastereomer indicated with x

Major diastereomer pictured

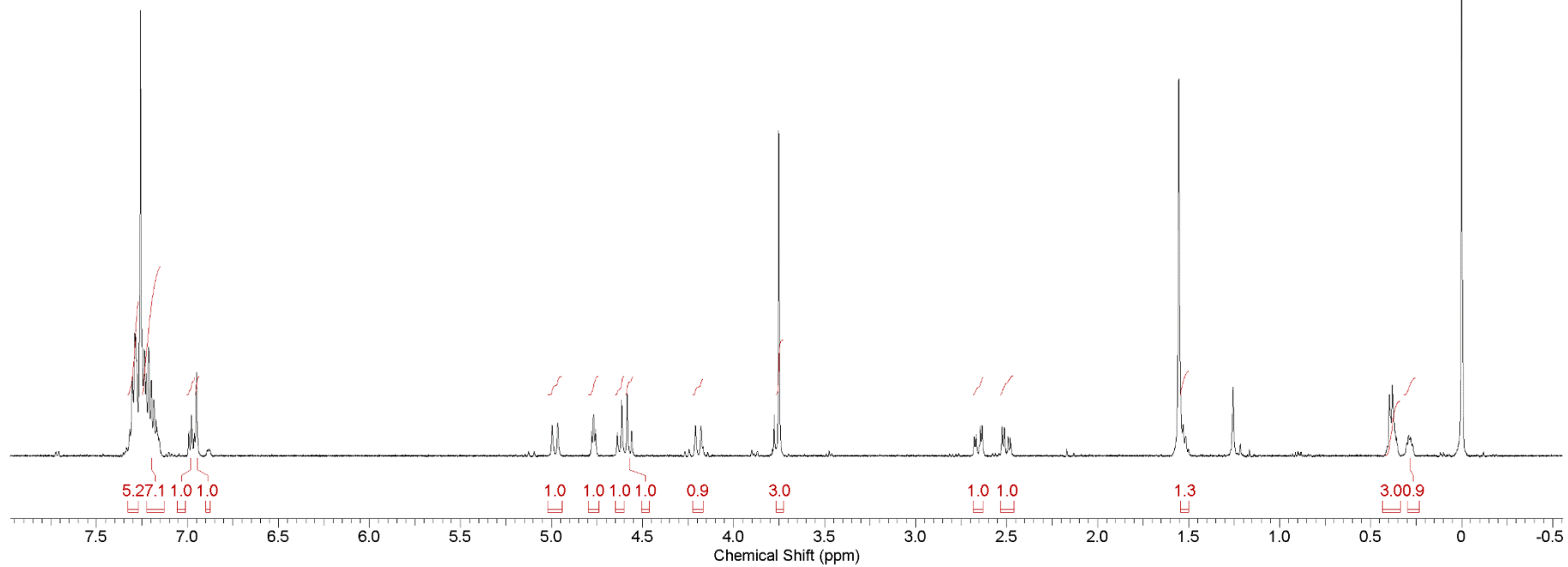


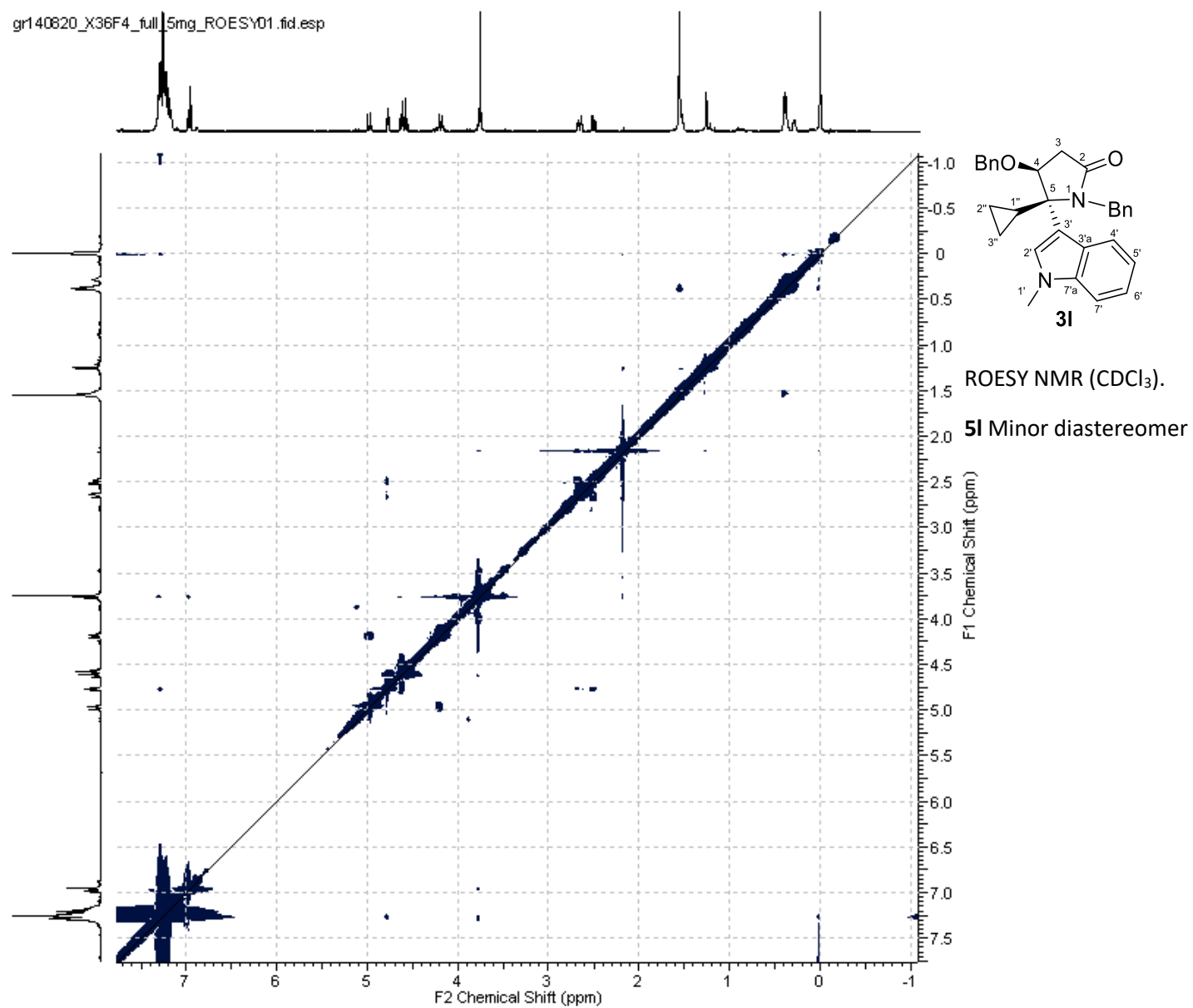


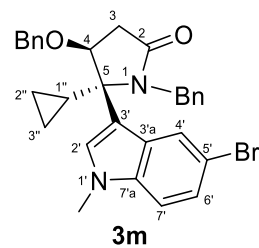


^1H NMR (CDCl_3 , 500 MHz).

3I Minor diastereomer
Crystal





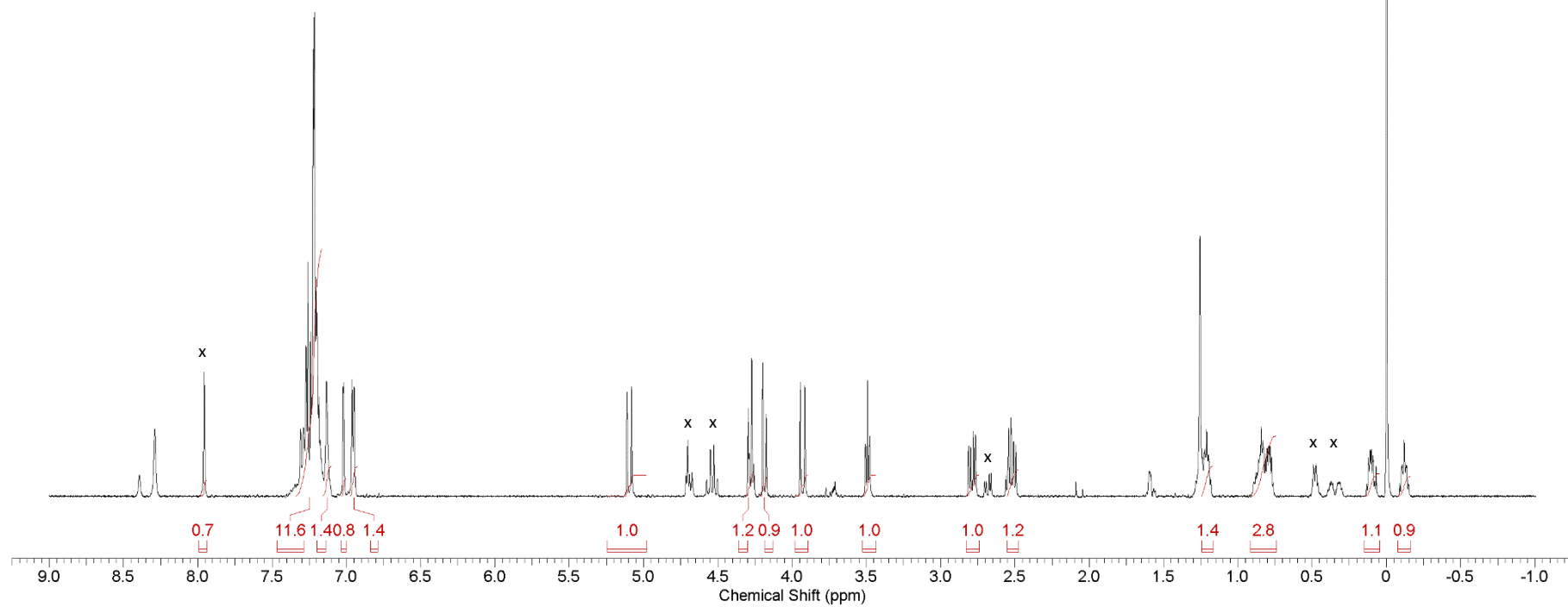


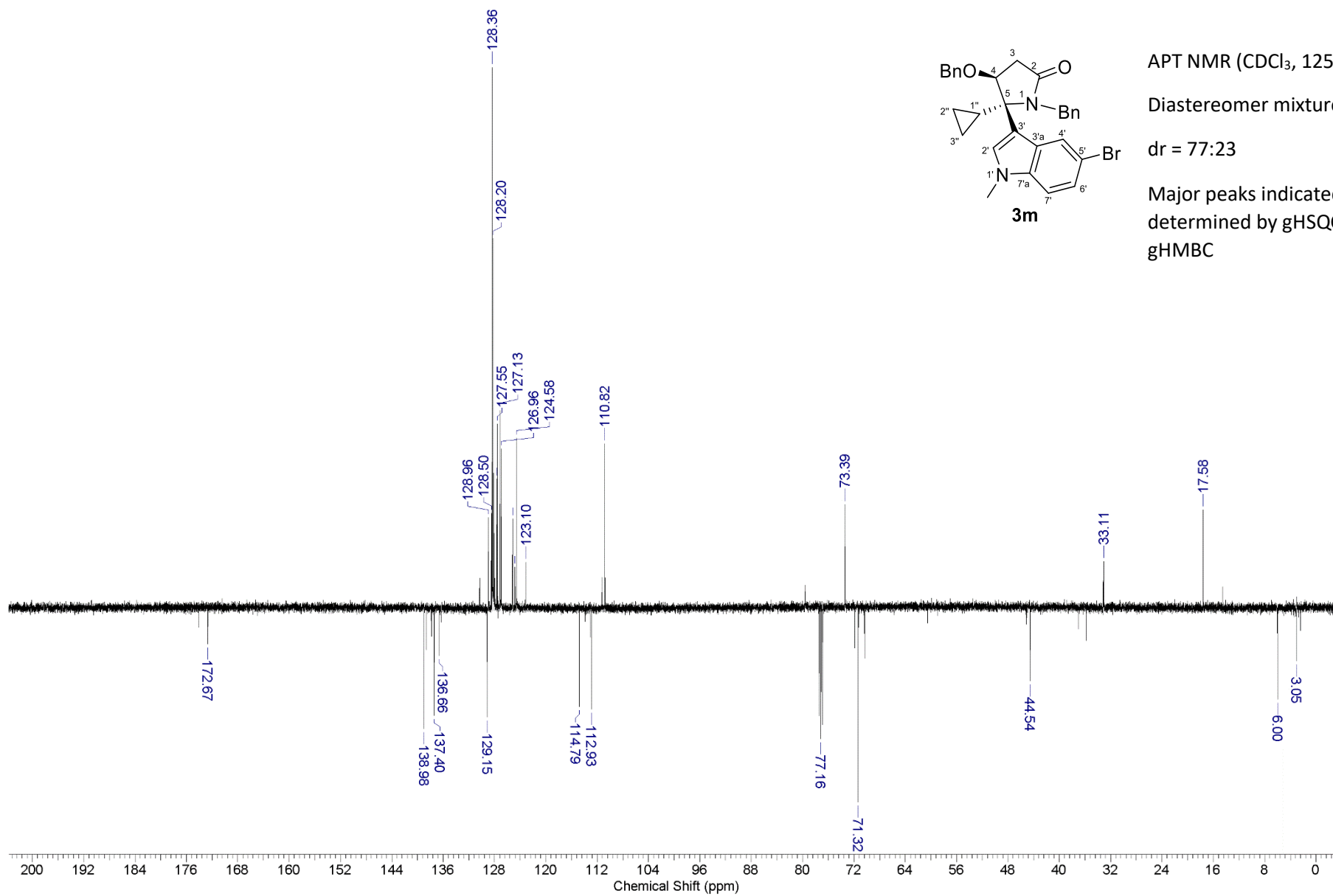
^1H NMR (CDCl_3 , 500 MHz).

3m Diastereomer mixture

dr = 77:23

3m Minor diastereomer indicated with x

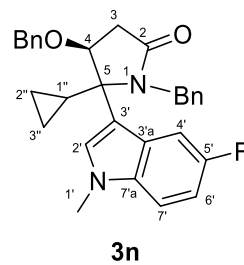


APT NMR (CDCl_3 , 125 MHz).

Diastereomer mixture

dr = 77:23

Major peaks indicated,
determined by gHSQC and
gHMBC

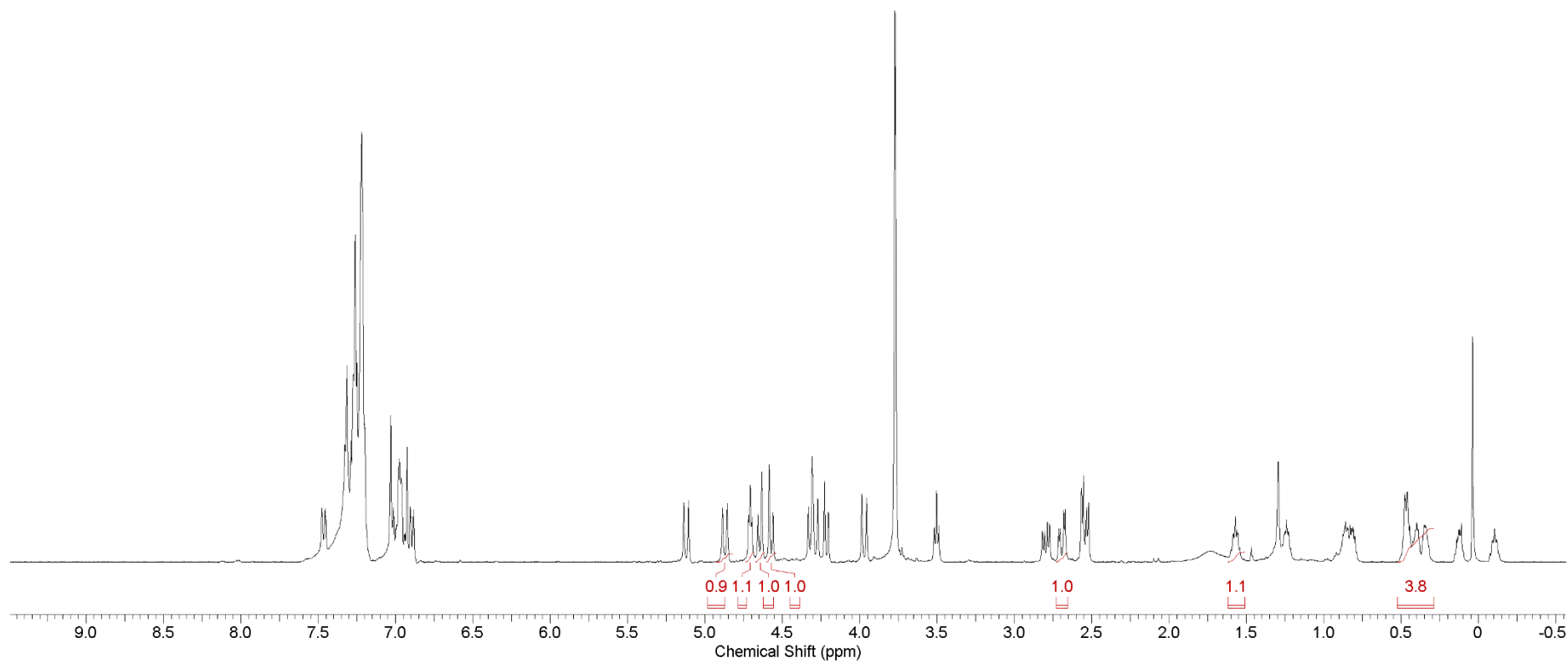


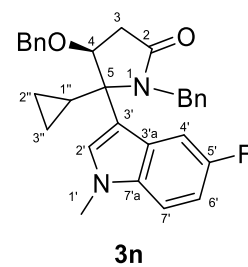
^1H NMR (CDCl_3 , 500 MHz).

3n Diastereomer mixture

3n Minor diastereomer
integrated

dr = 52:48

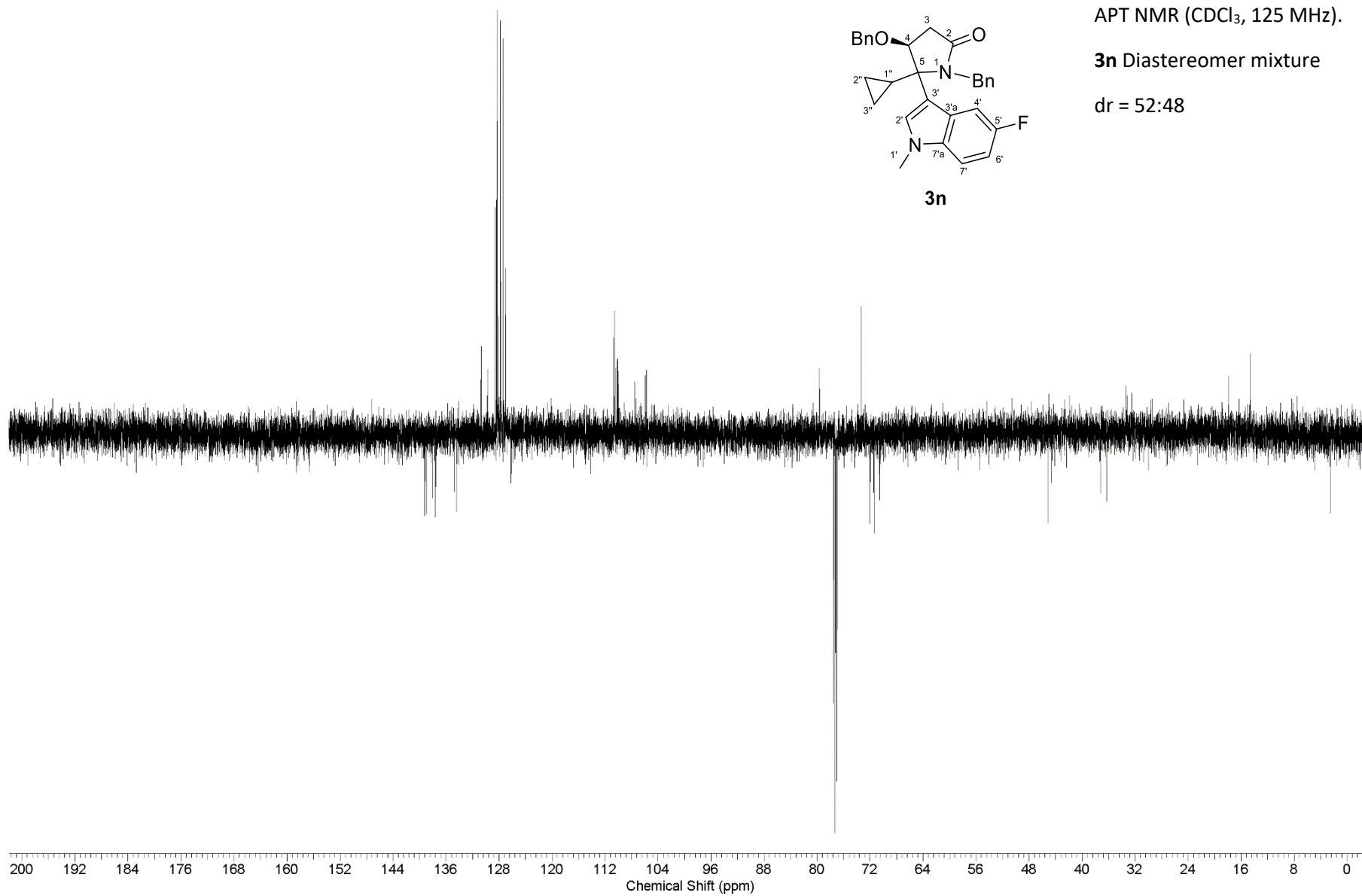


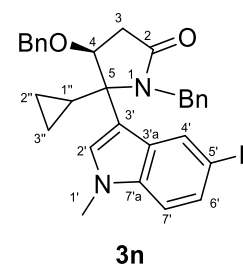


APT NMR (CDCl₃, 125 MHz).

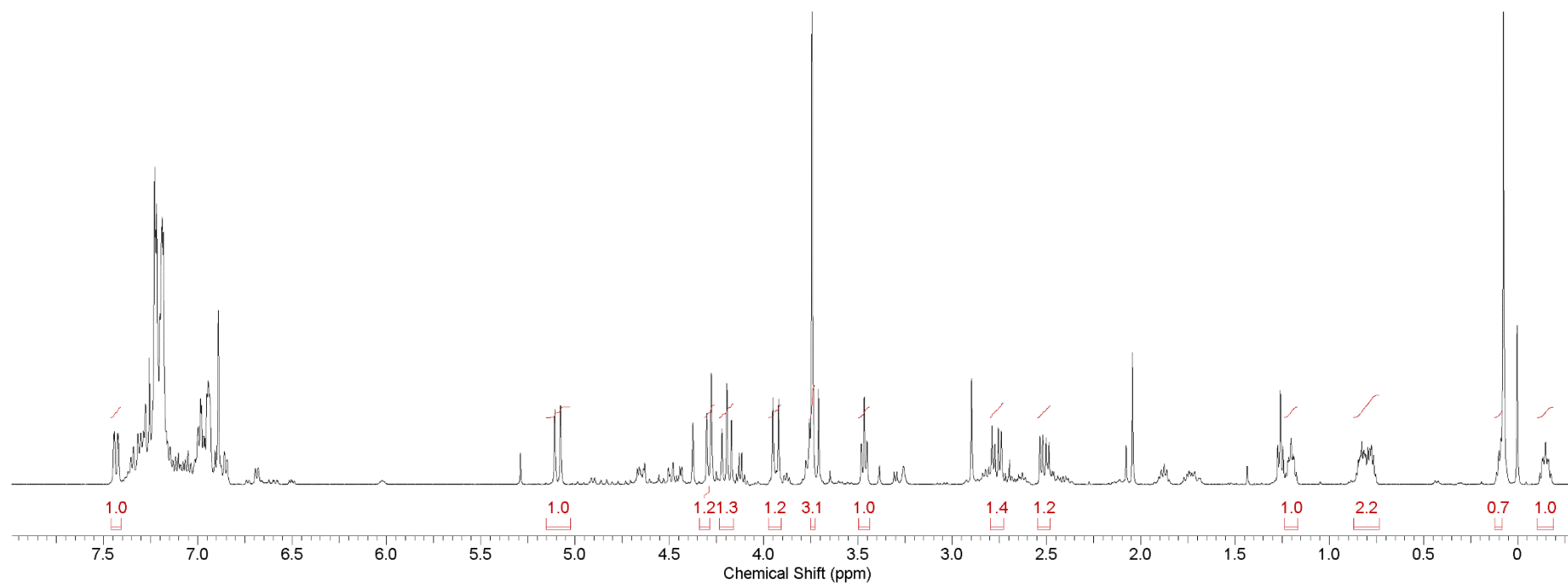
3n Diastereomer mixture

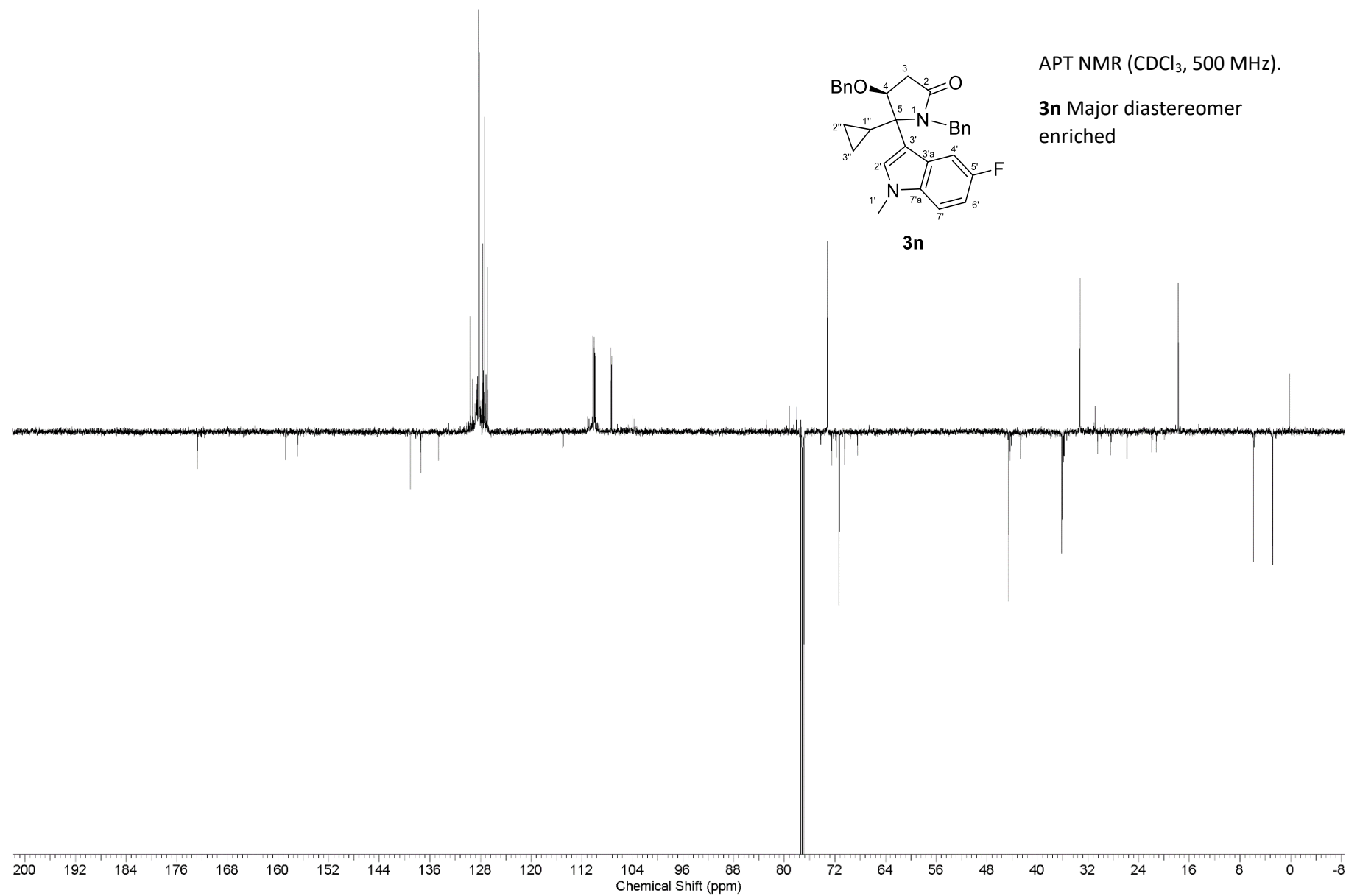
dr = 52:48

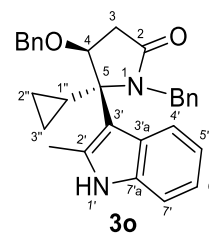


¹H NMR (CDCl₃, 500 MHz).

3n Major diastereomer enriched

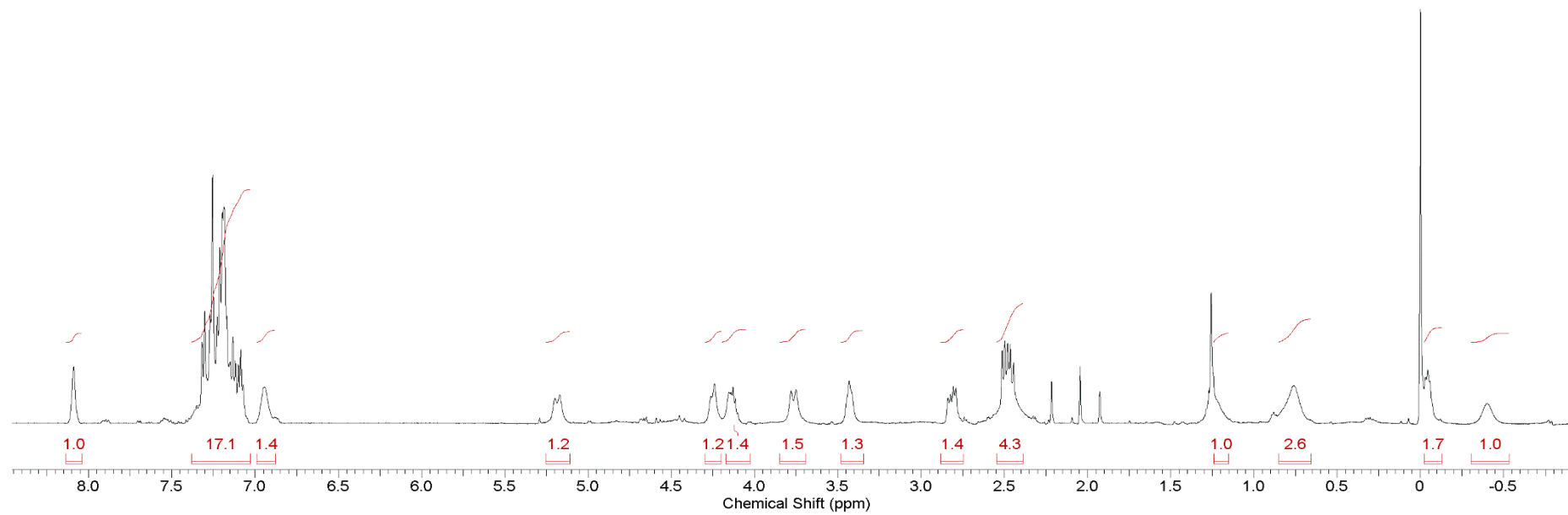


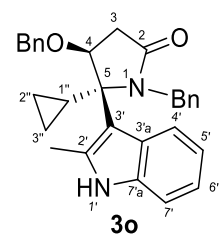




^1H NMR (CDCl_3 , 500 MHz).

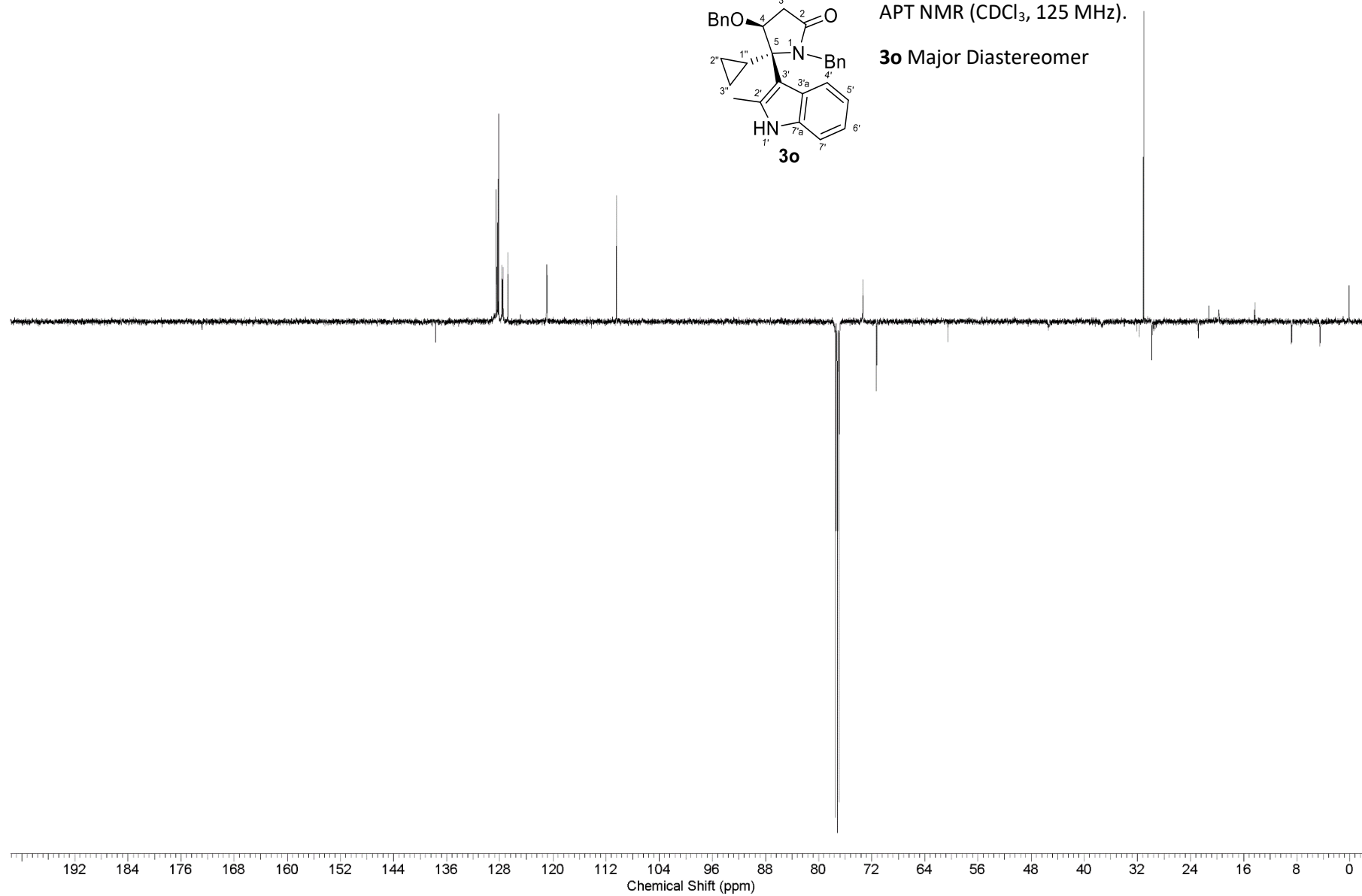
3o Major Diastereomer

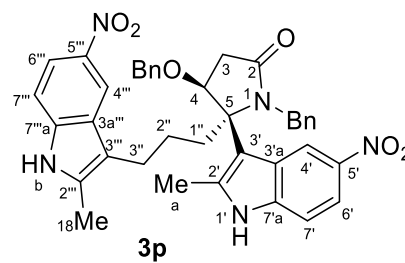




APT NMR (CDCl₃, 125 MHz).

3o Major Diastereomer

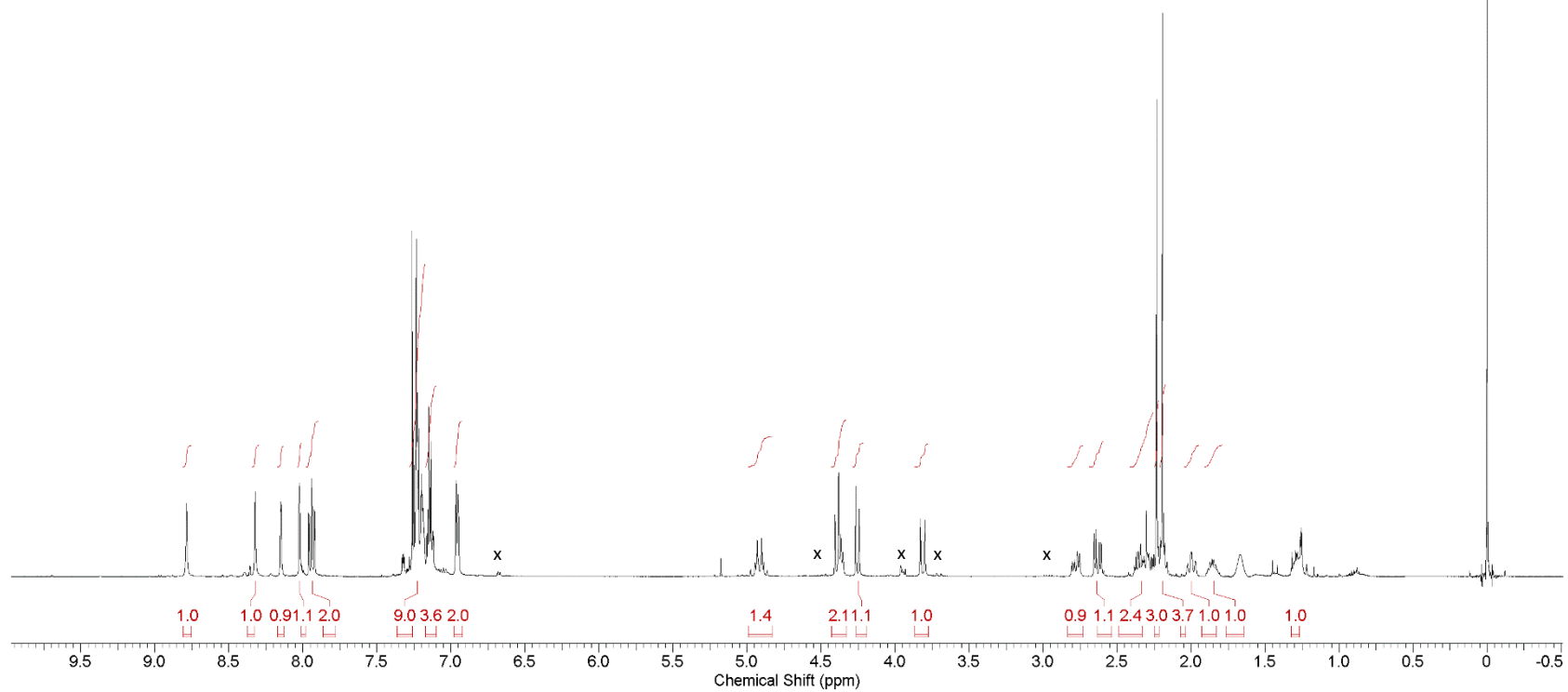


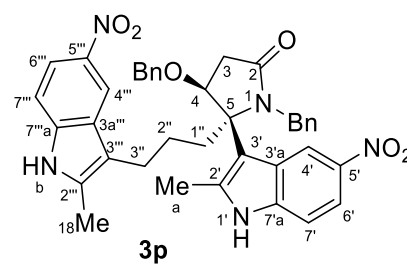


^1H NMR (CDCl_3 , 500 MHz).

3p Major Diastereomer

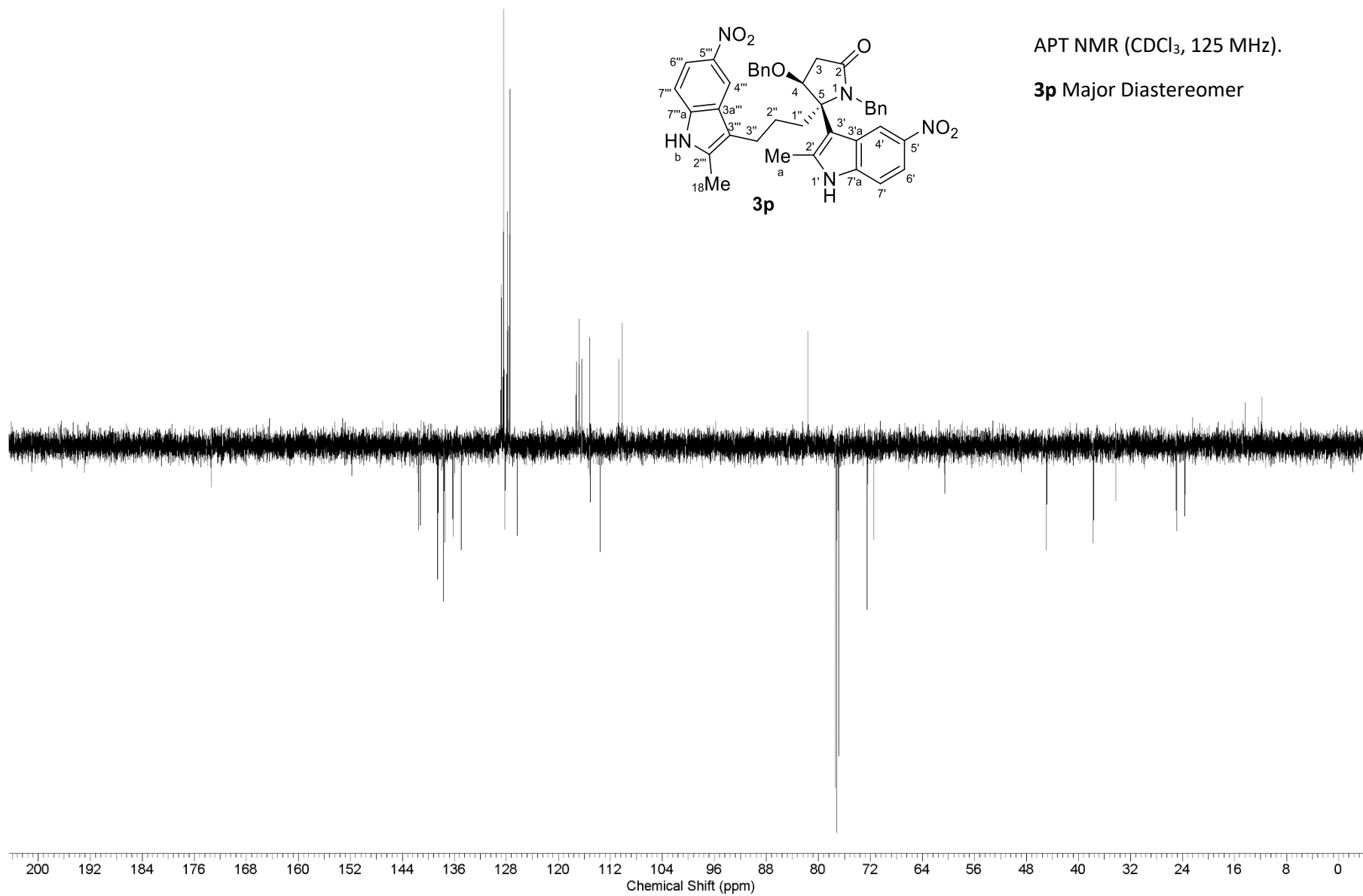
3p Minor diastereomer indicated by x.



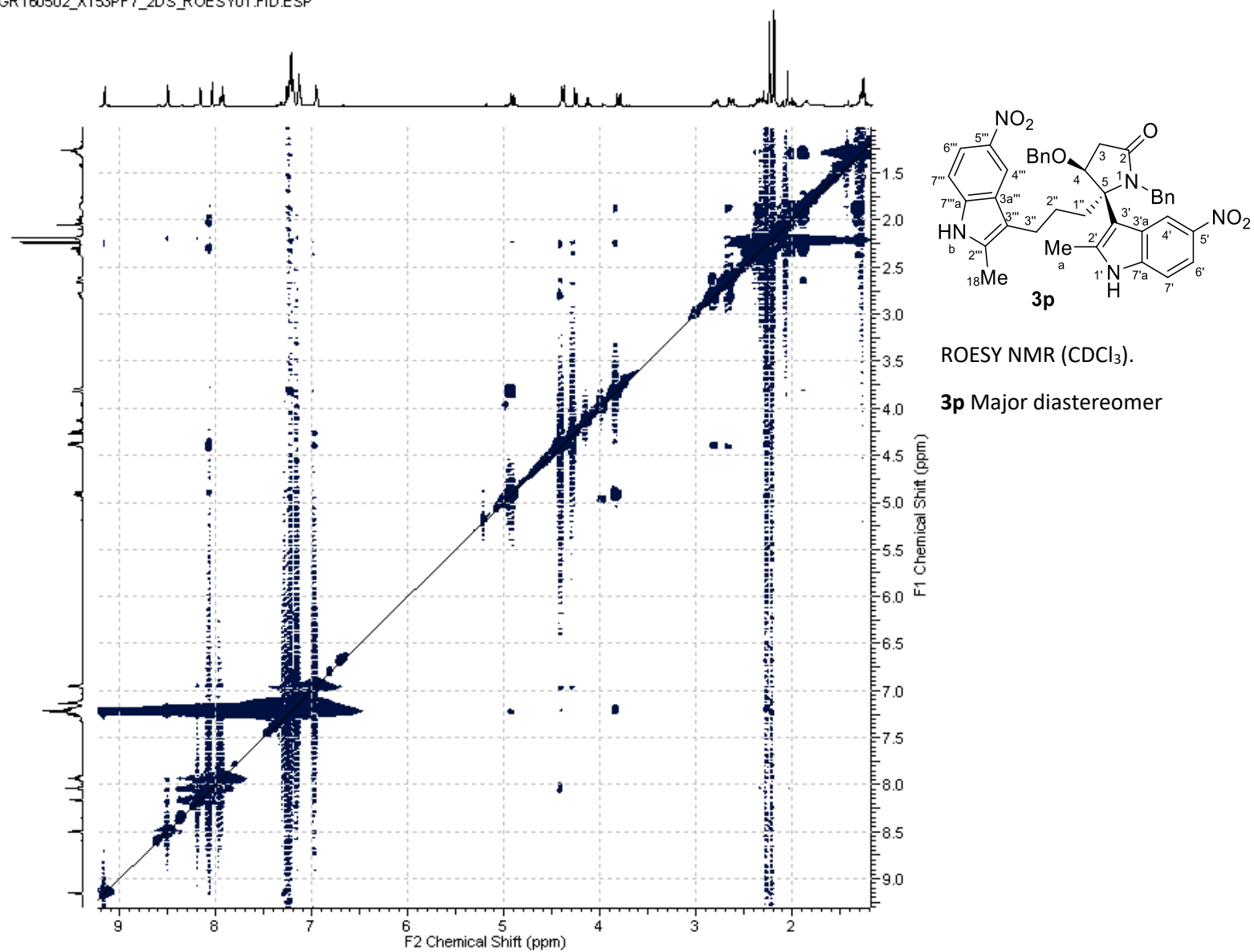


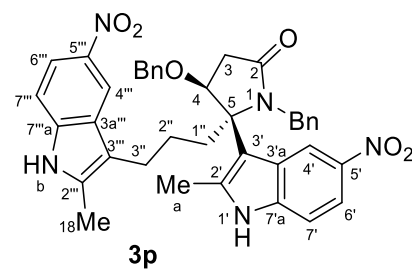
APT NMR (CDCl_3 , 125 MHz).

3p Major Diastereomer



GR160502_X153PF7_2DS_ROESY01.FID.ESP

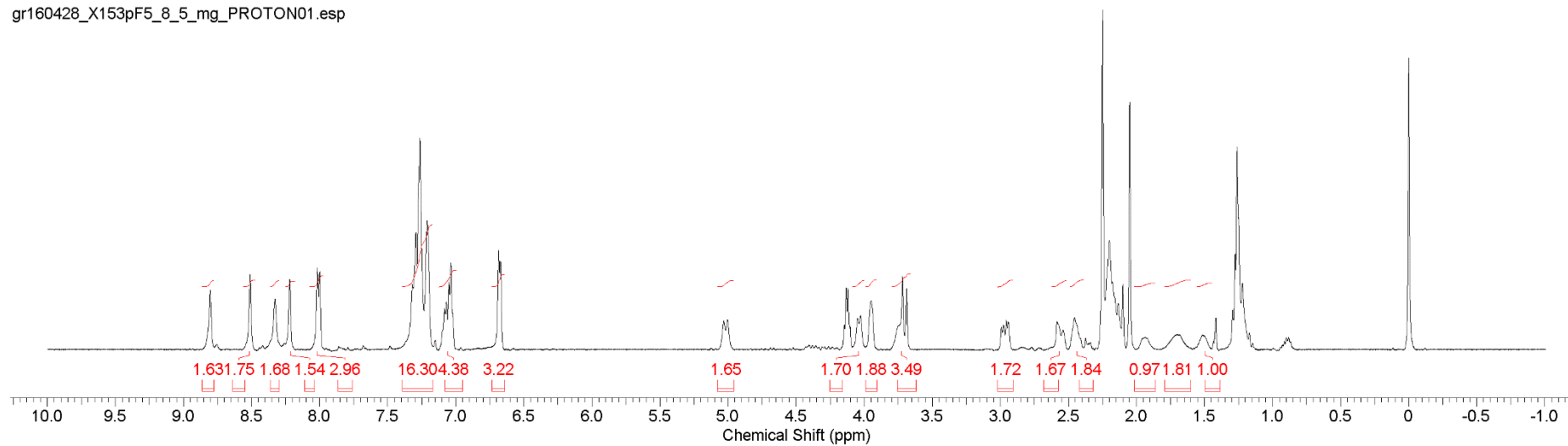


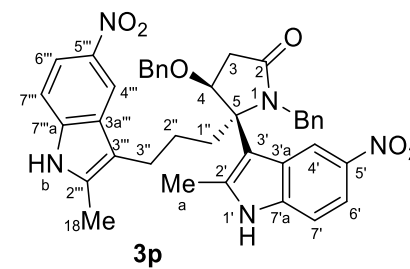


^1H NMR (CDCl_3 , 500 MHz).

3p Minor Diastereomer

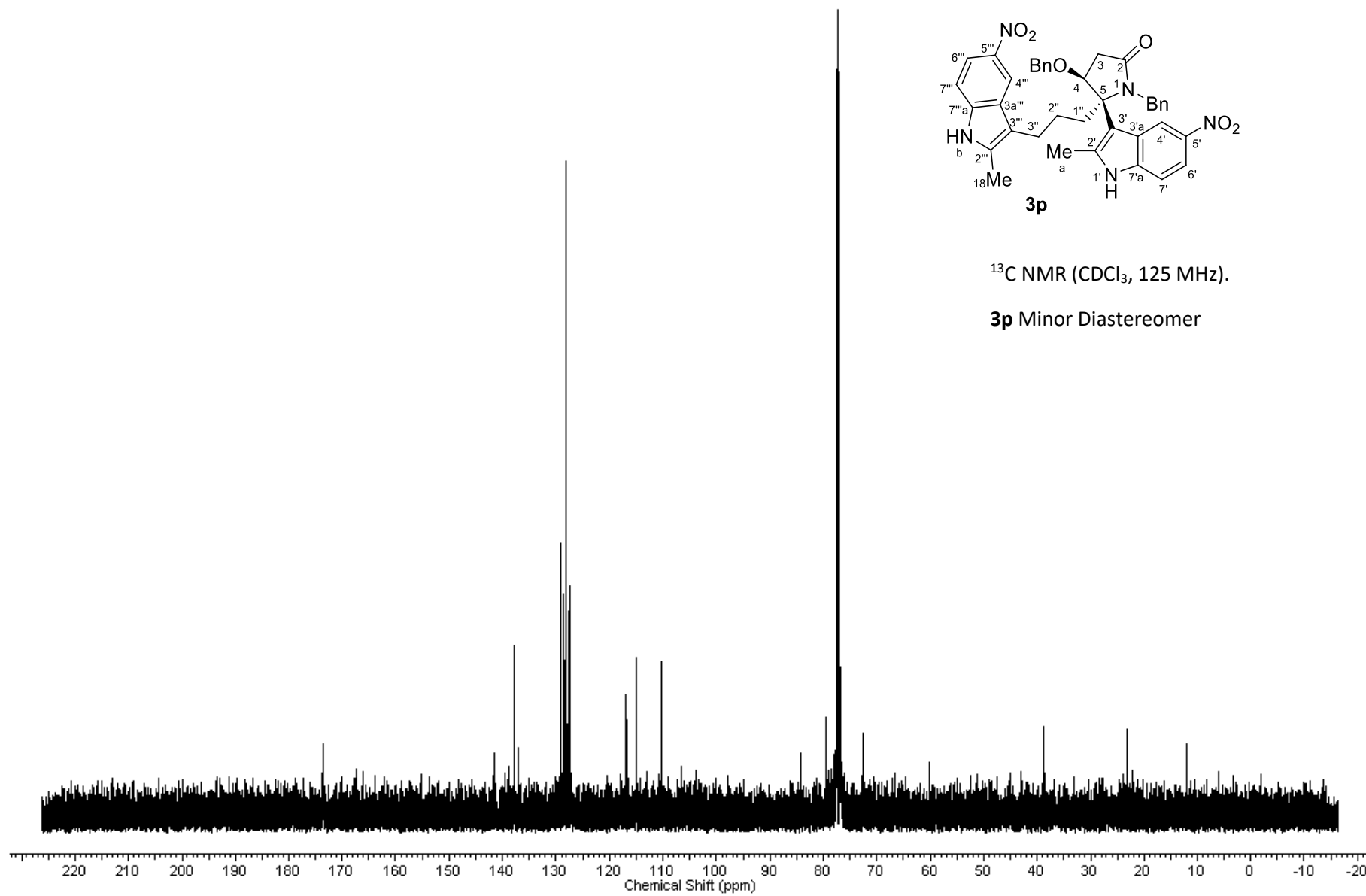
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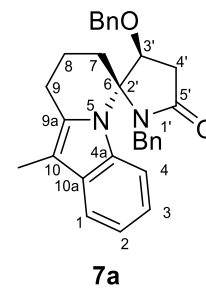




^{13}C NMR (CDCl_3 , 125 MHz).

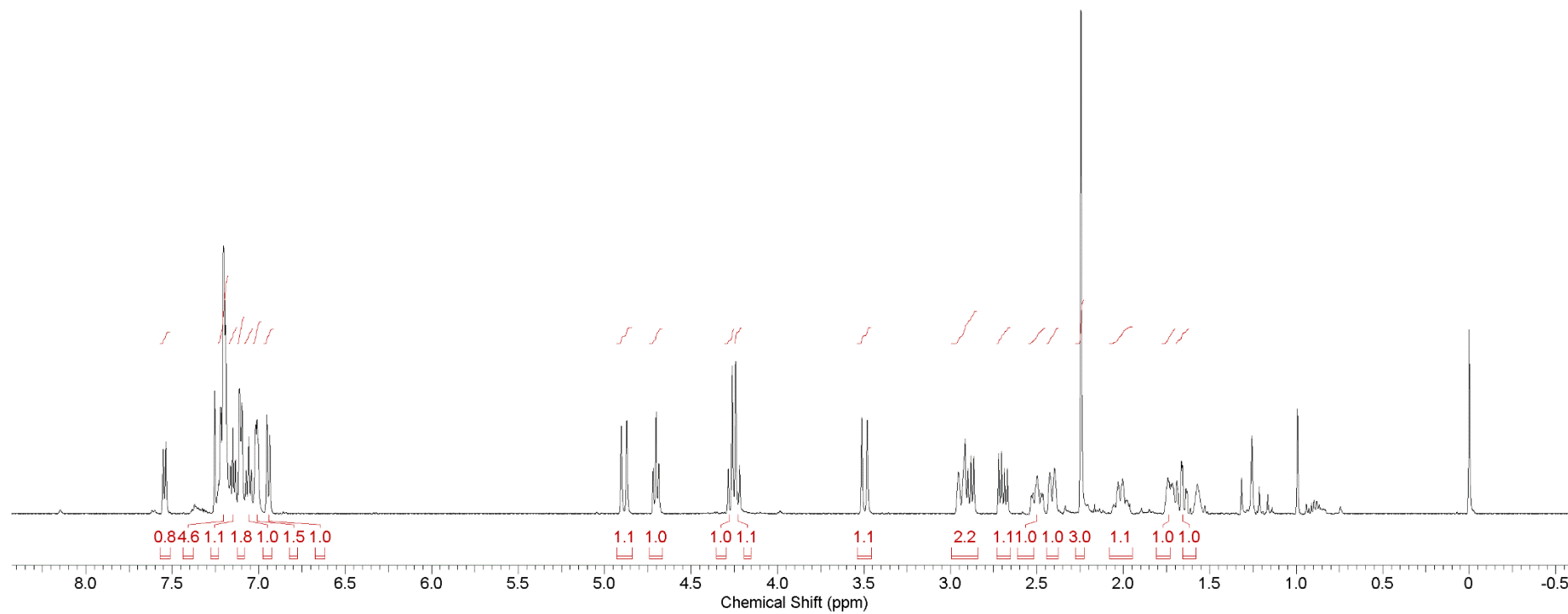
3p Minor Diastereomer

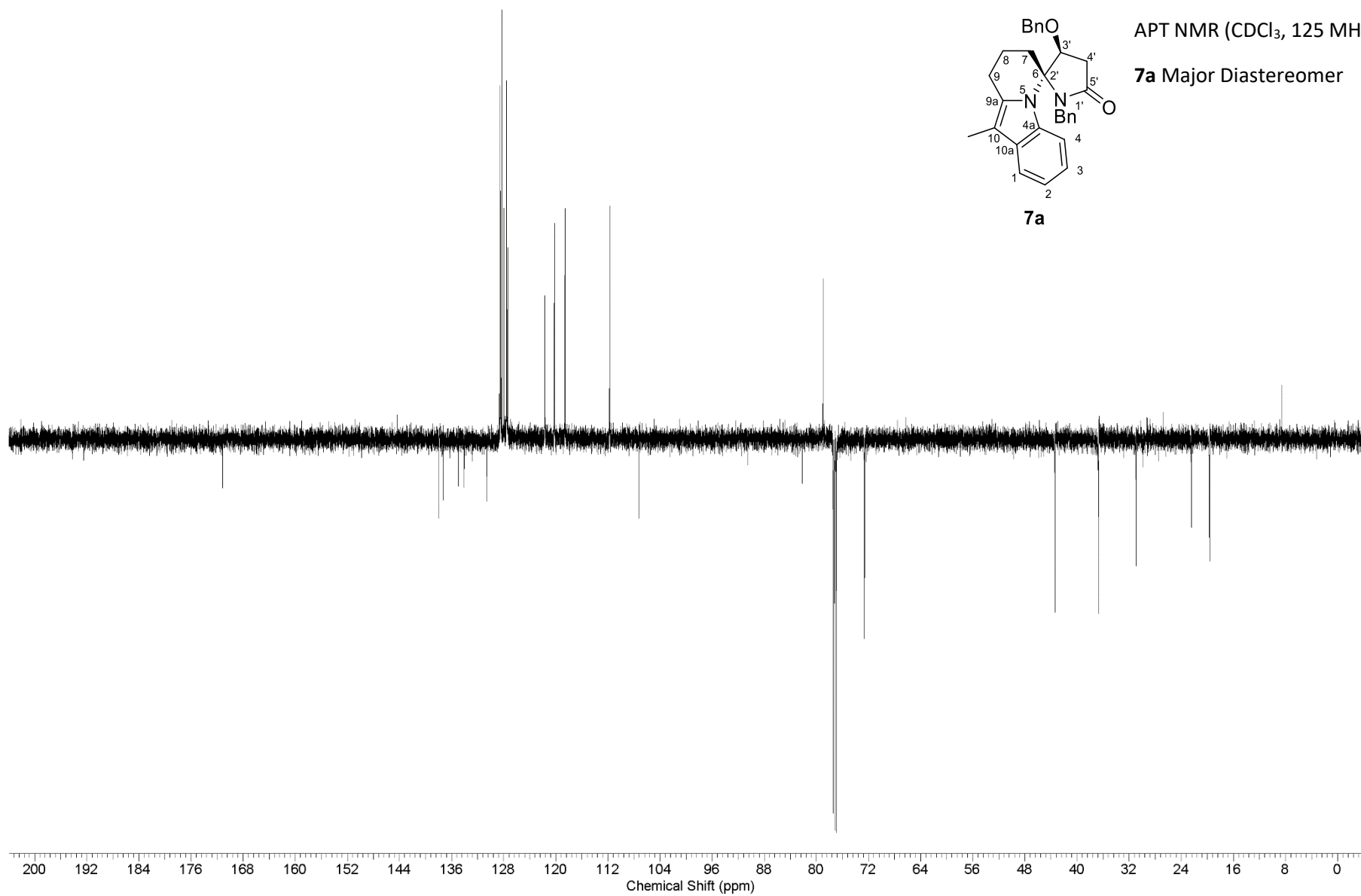
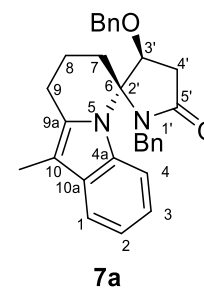




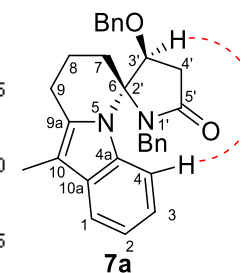
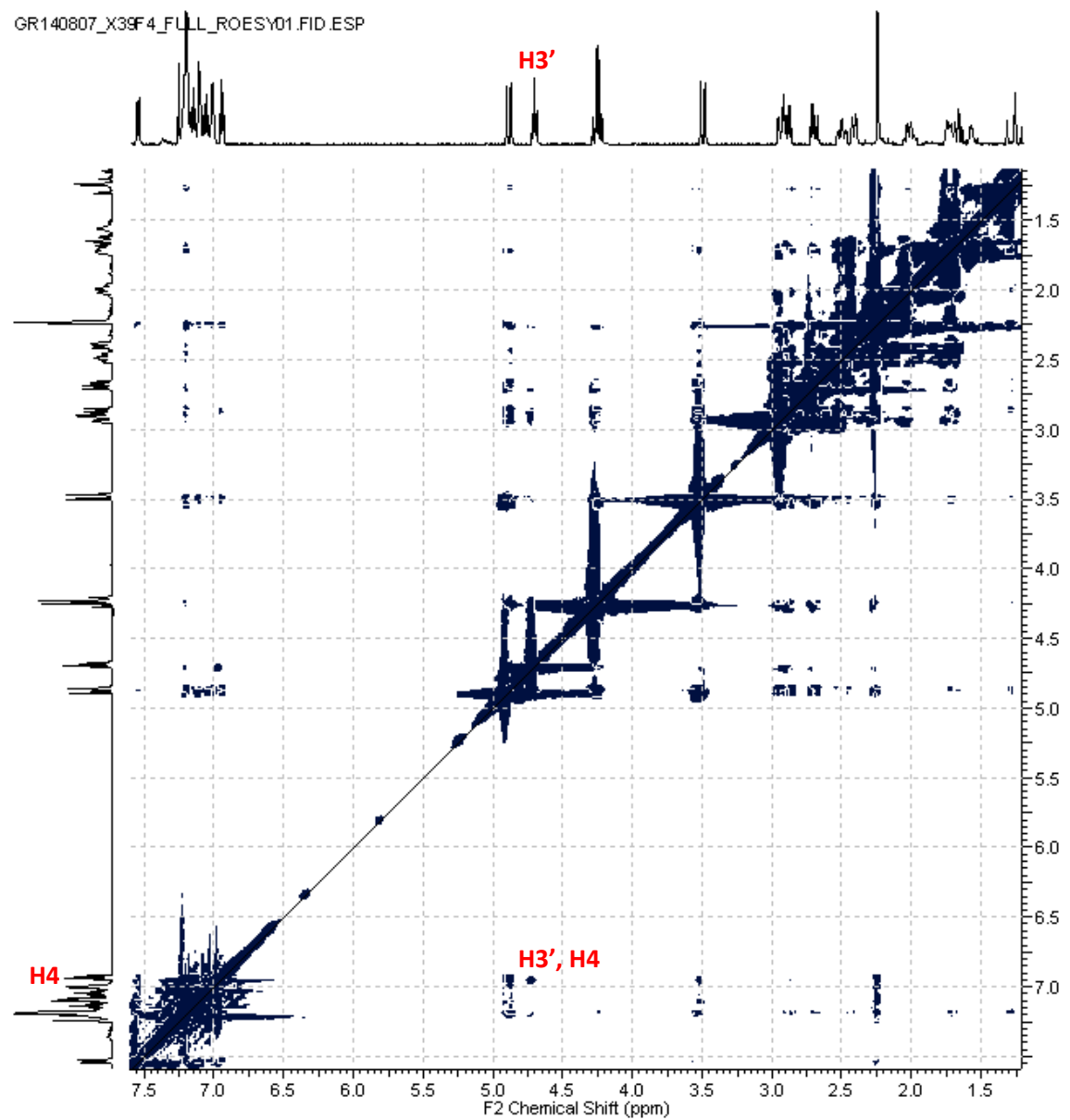
^1H NMR (CDCl_3 , 500 MHz).

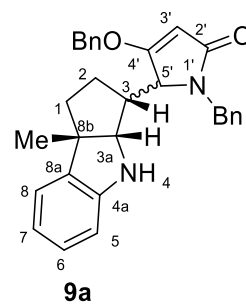
7a Major Diastereomer



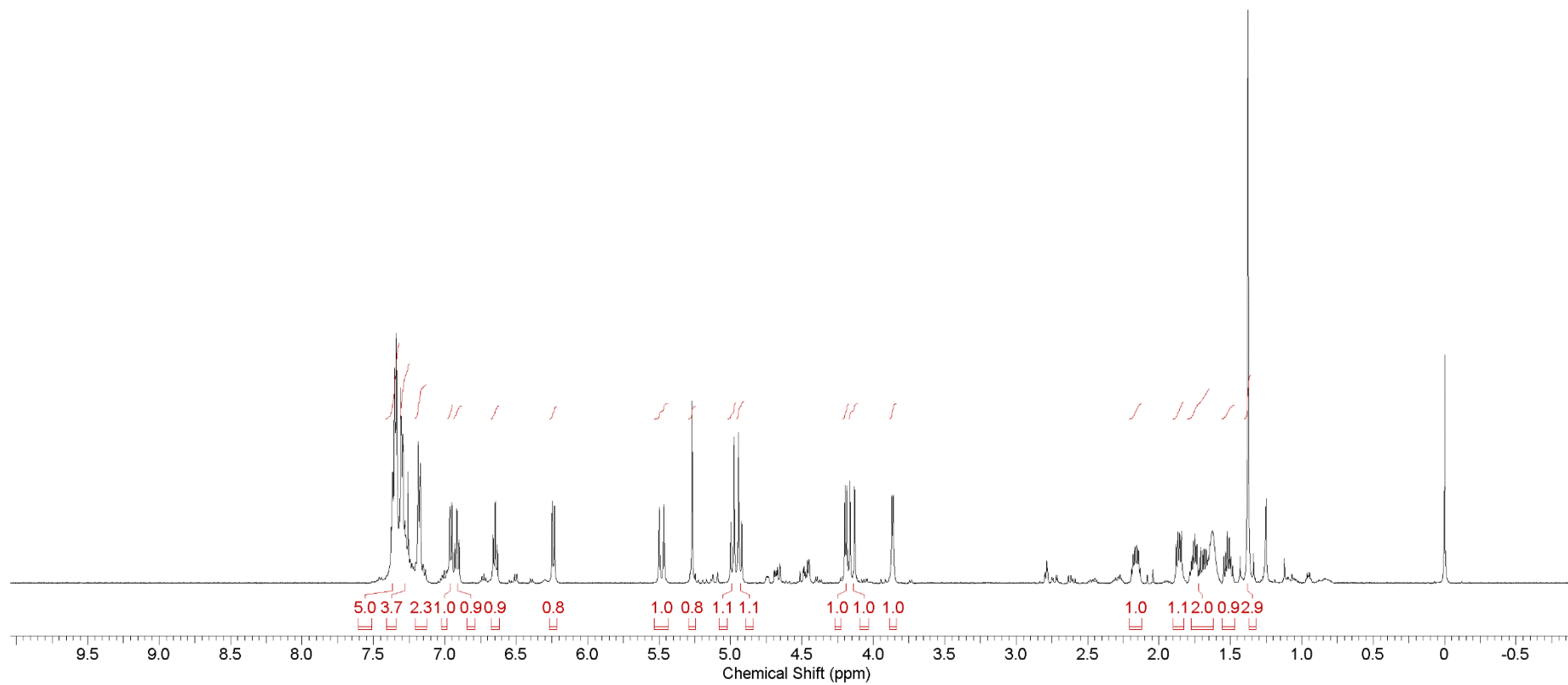
APT NMR (CDCl₃, 125 MHz).**7a** Major Diastereomer

GR140807_X39F4_FULL_ROESY01.FID.ESP

ROESY NMR (CDCl₃).**7a** Major diastereomer

¹H NMR (CDCl₃, 500 MHz).

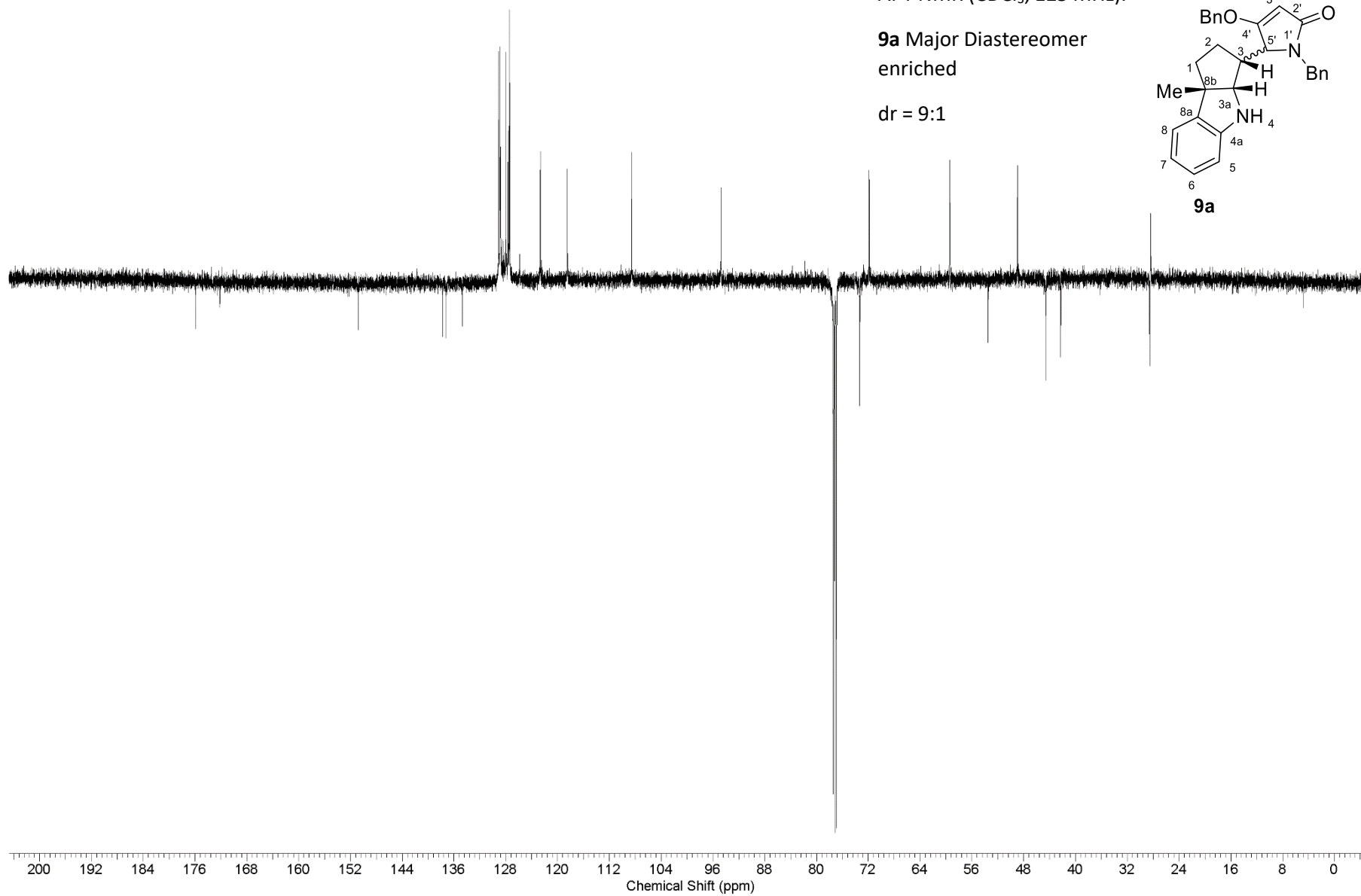
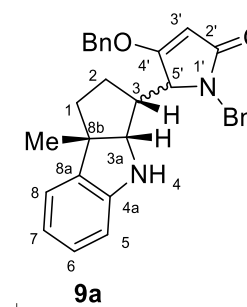
9a Major Diastereomer enriched

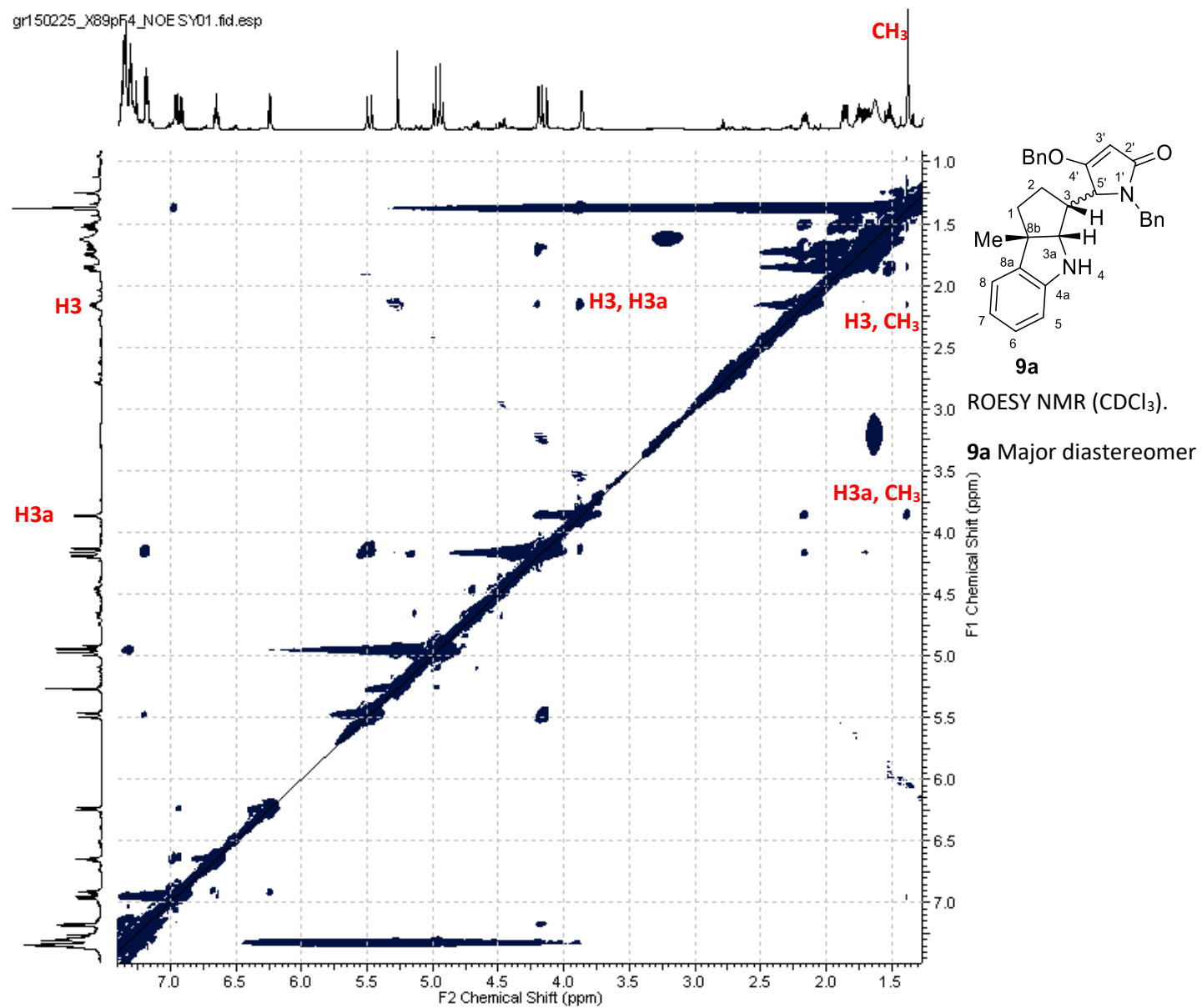
$$dr = 9:1$$


APT NMR (CDCl_3 , 125 MHz).

9a Major Diastereomer
enriched

dr = 9:1

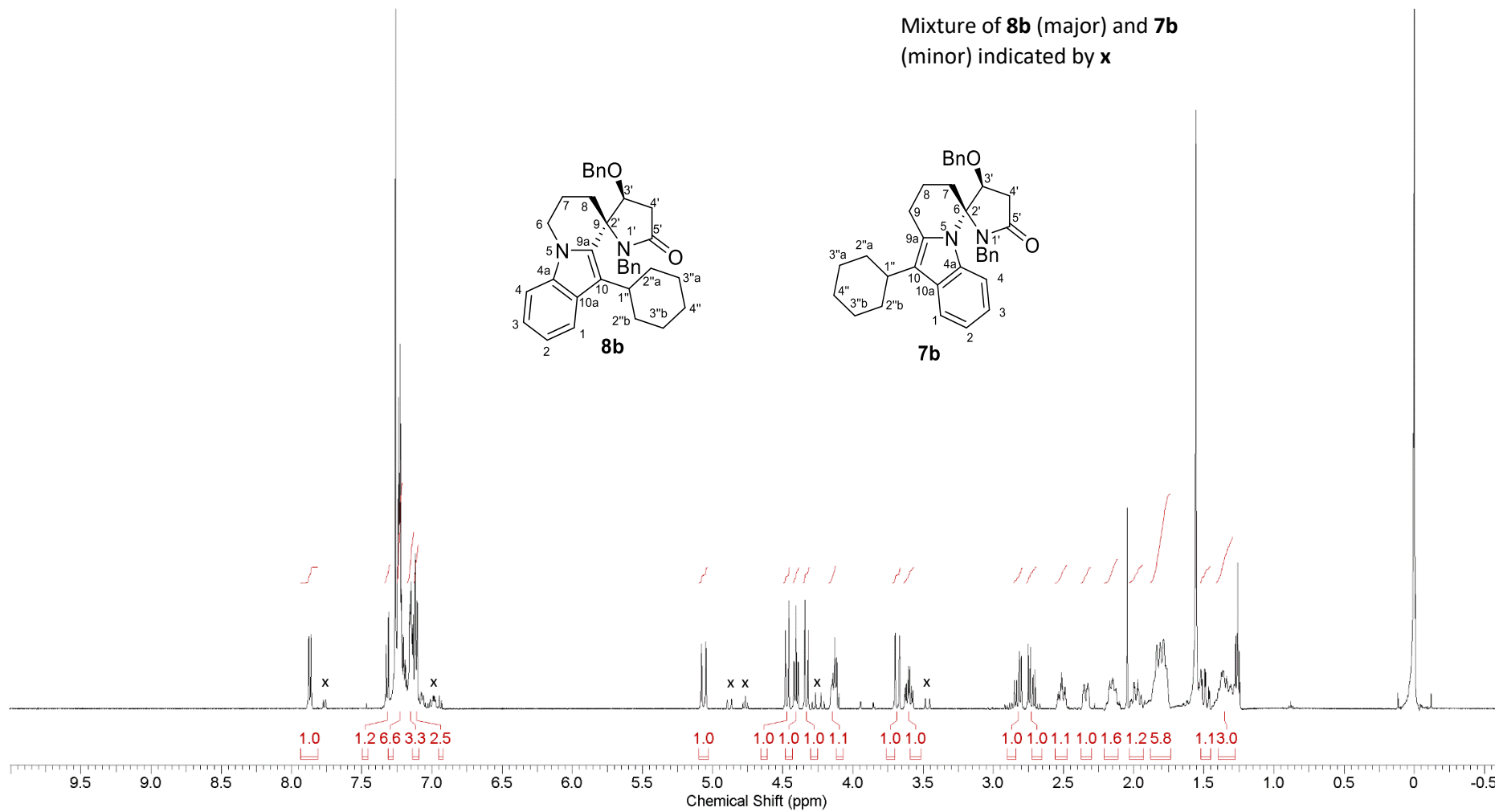
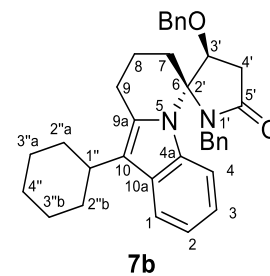
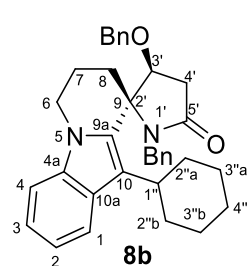


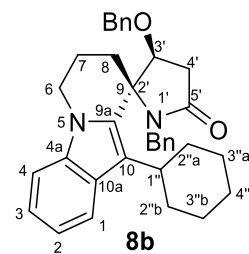


^1H NMR (CDCl_3 , 500 MHz).

8b Major Diastereomer

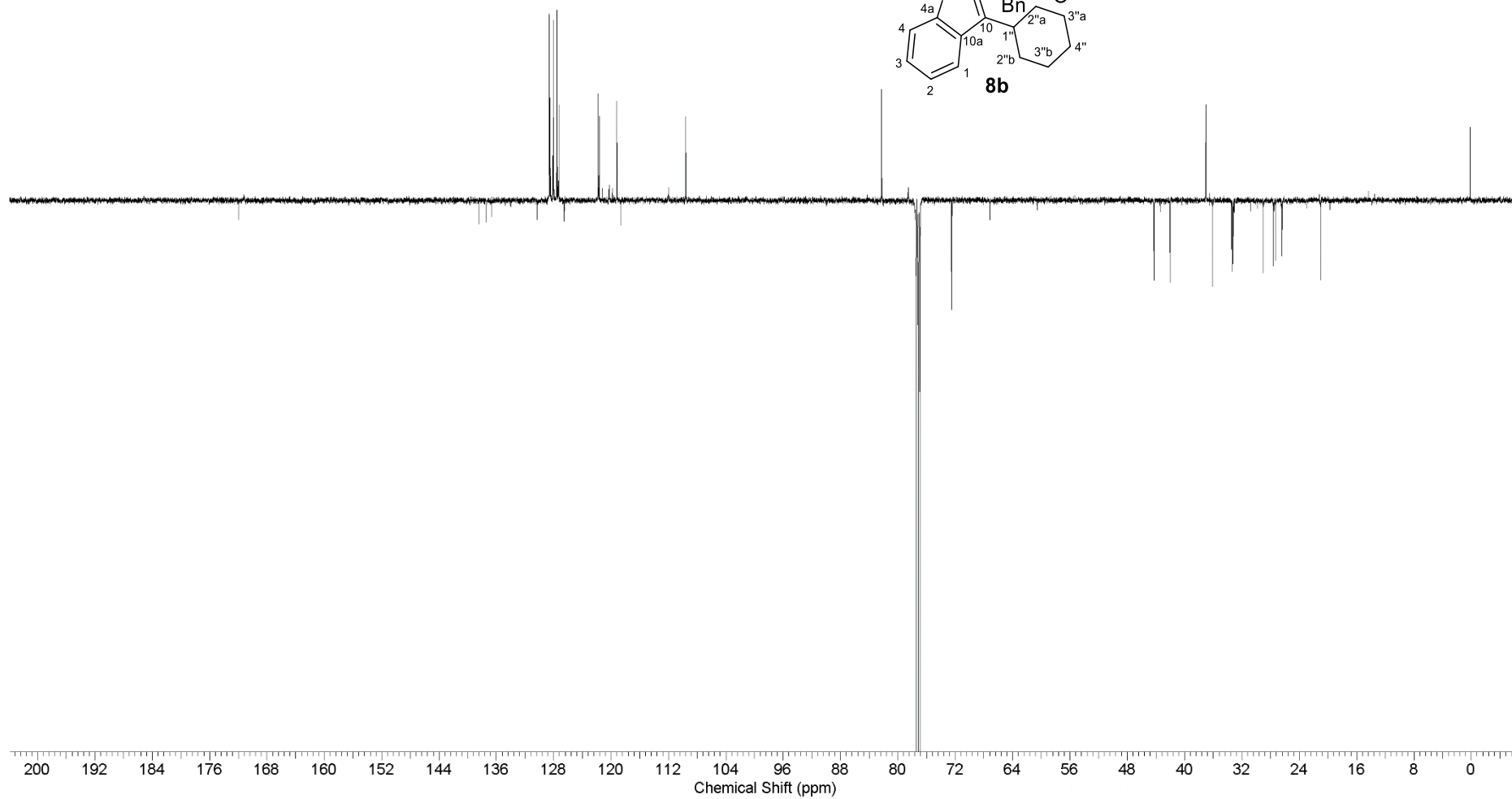
Mixture of **8b** (major) and **7b** (minor) indicated by **x**

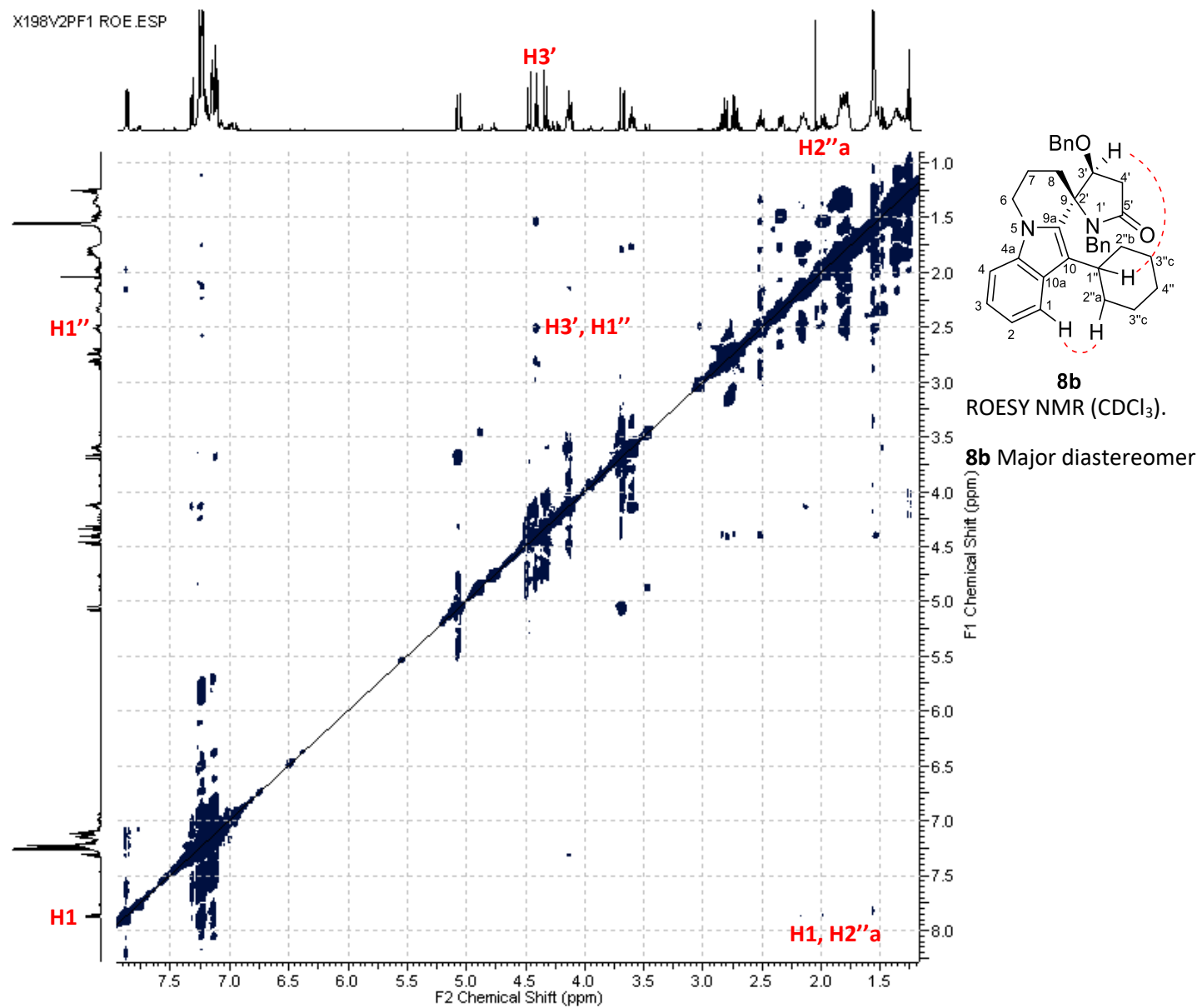




APT NMR (CDCl_3 , 125 MHz).

8b Major Diastereomer

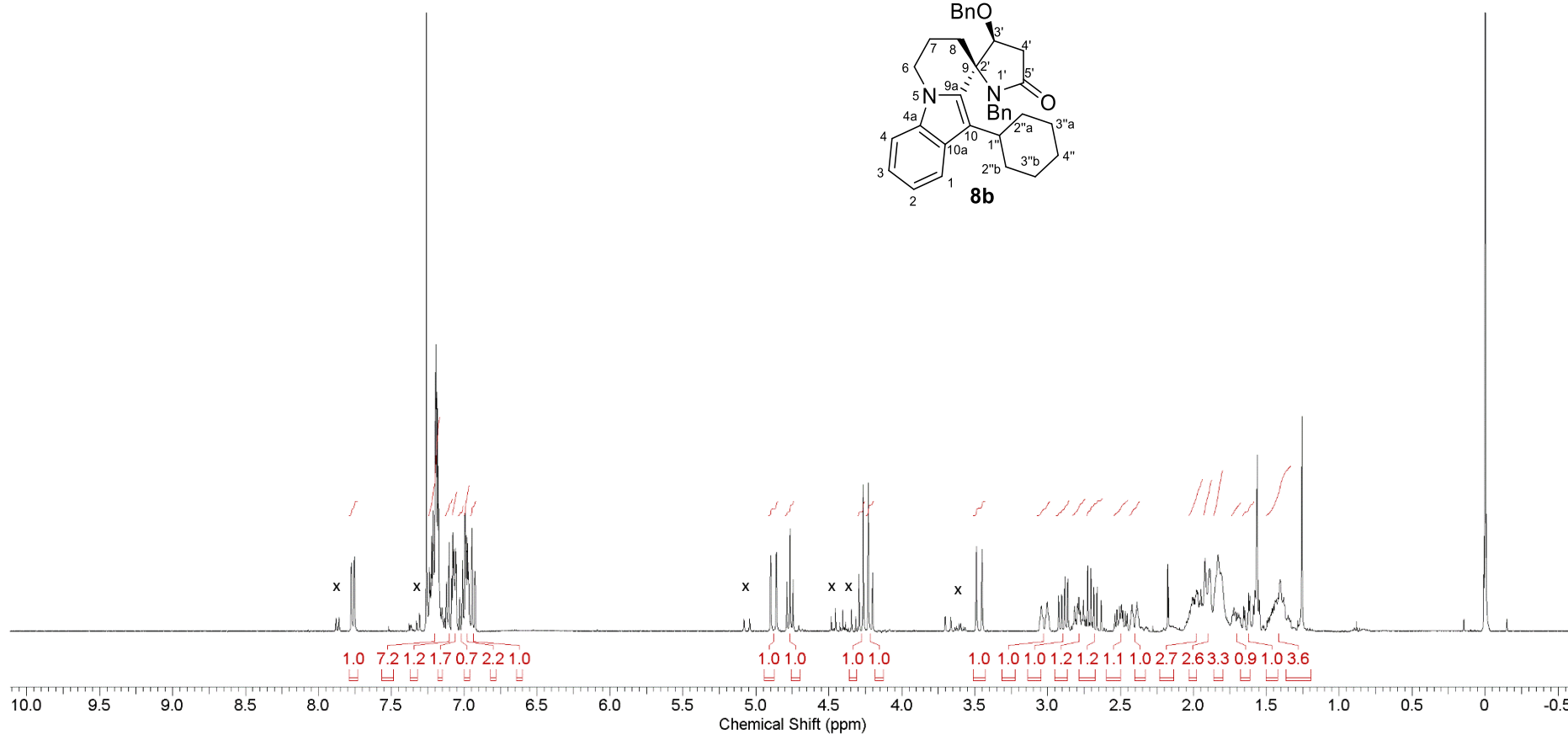
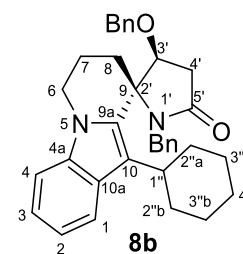
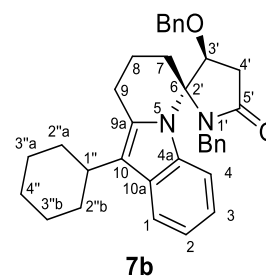


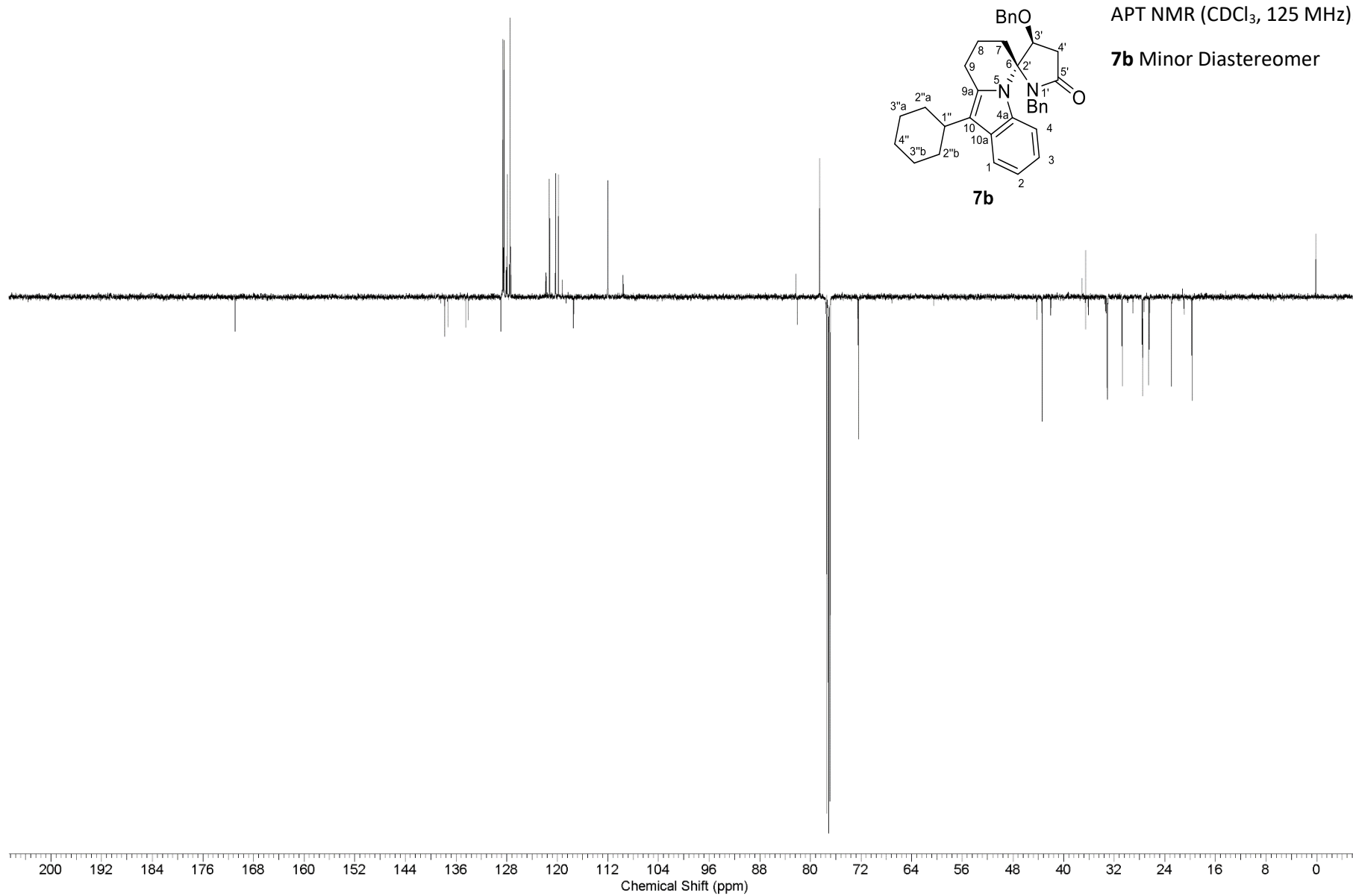


^1H NMR (CDCl_3 , 500 MHz).

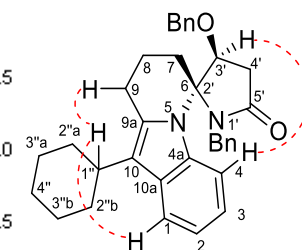
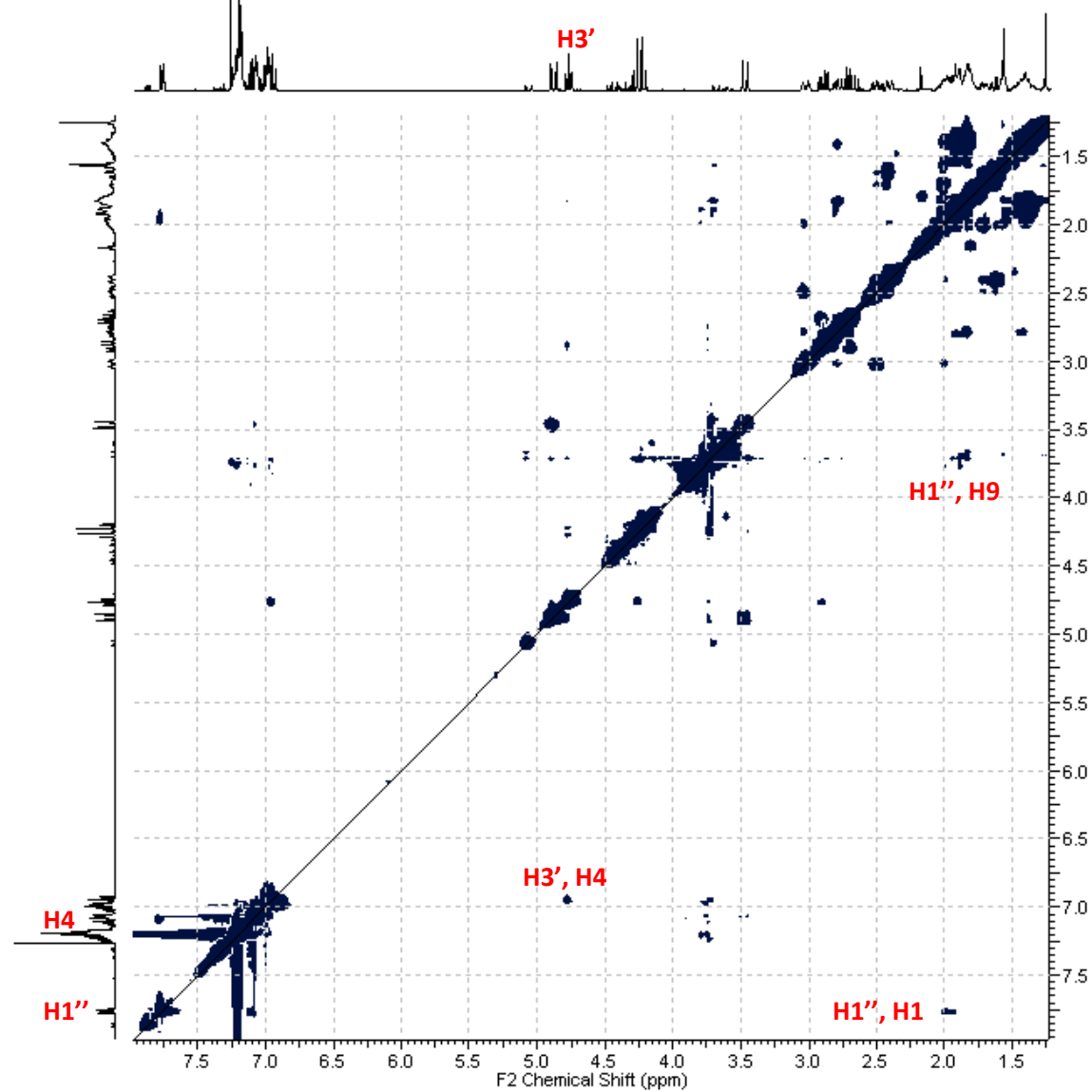
7b Minor Diastereomer

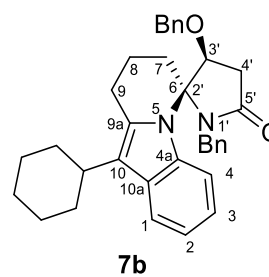
Mixture of **7b** (major) and **8b** (minor) indicated by x.





gr180416_X198V2pF3_2ds_long_ROESY02.fid.esp

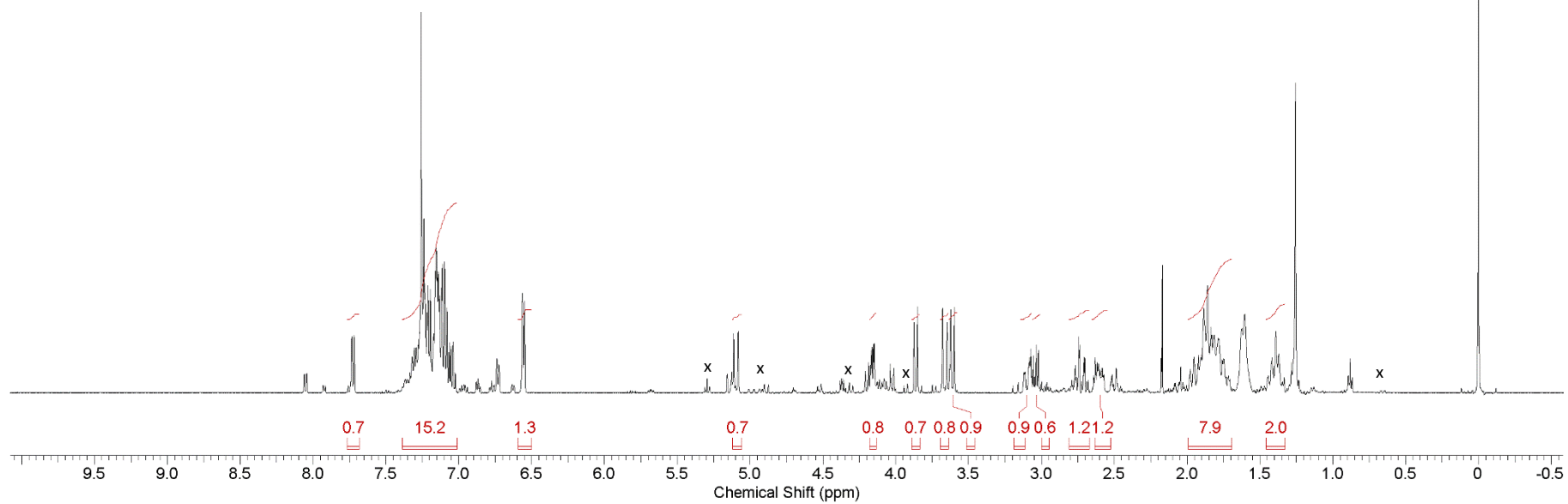
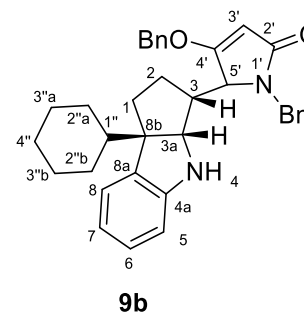
**7b**ROESY NMR (CDCl₃).**7b** Minor diastereomer

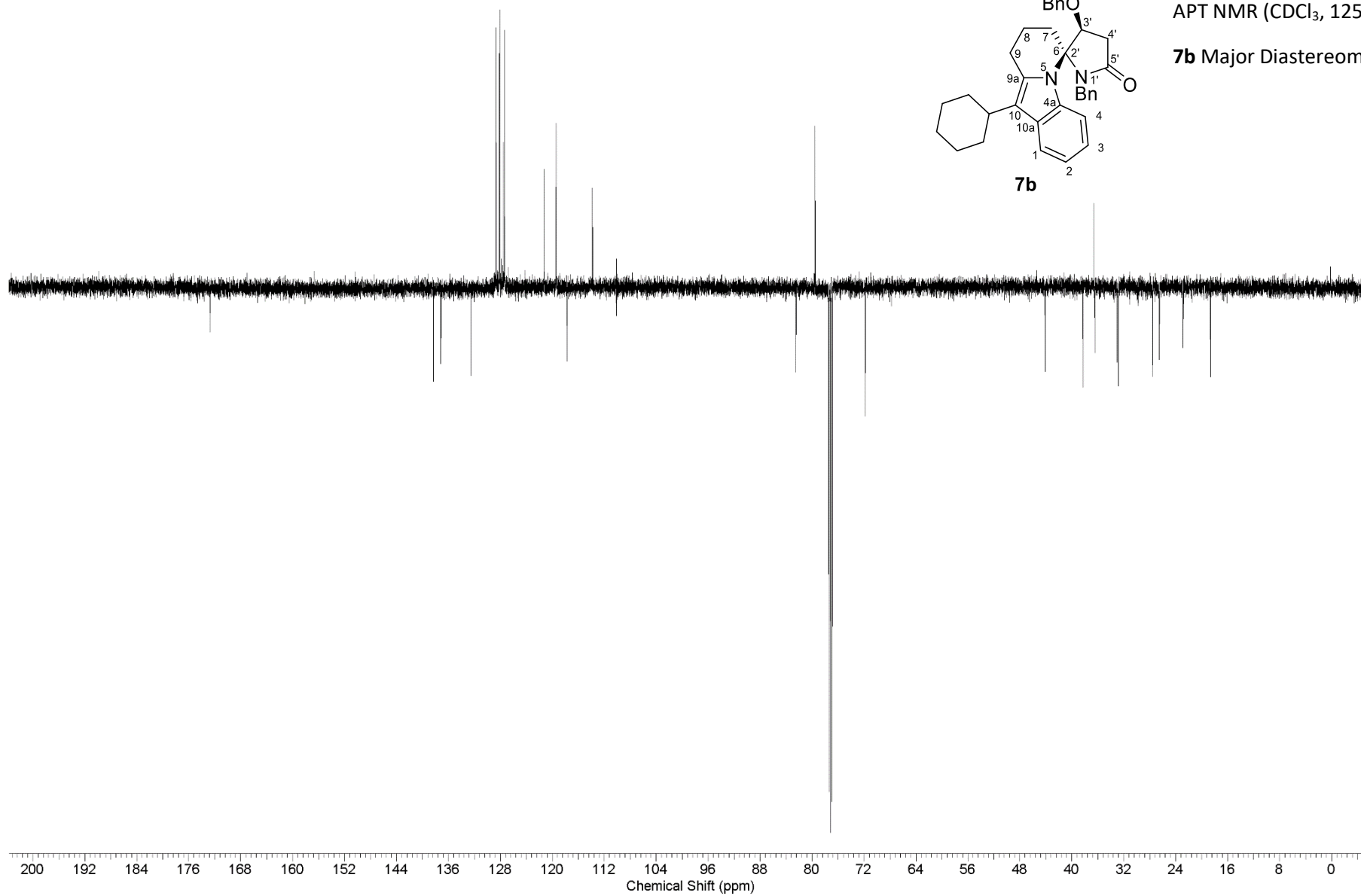
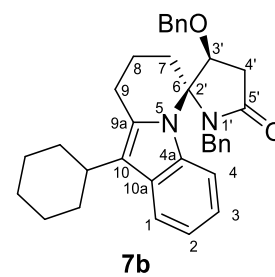


^1H NMR (CDCl_3 , 500 MHz).

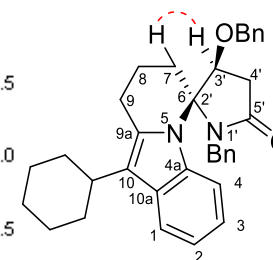
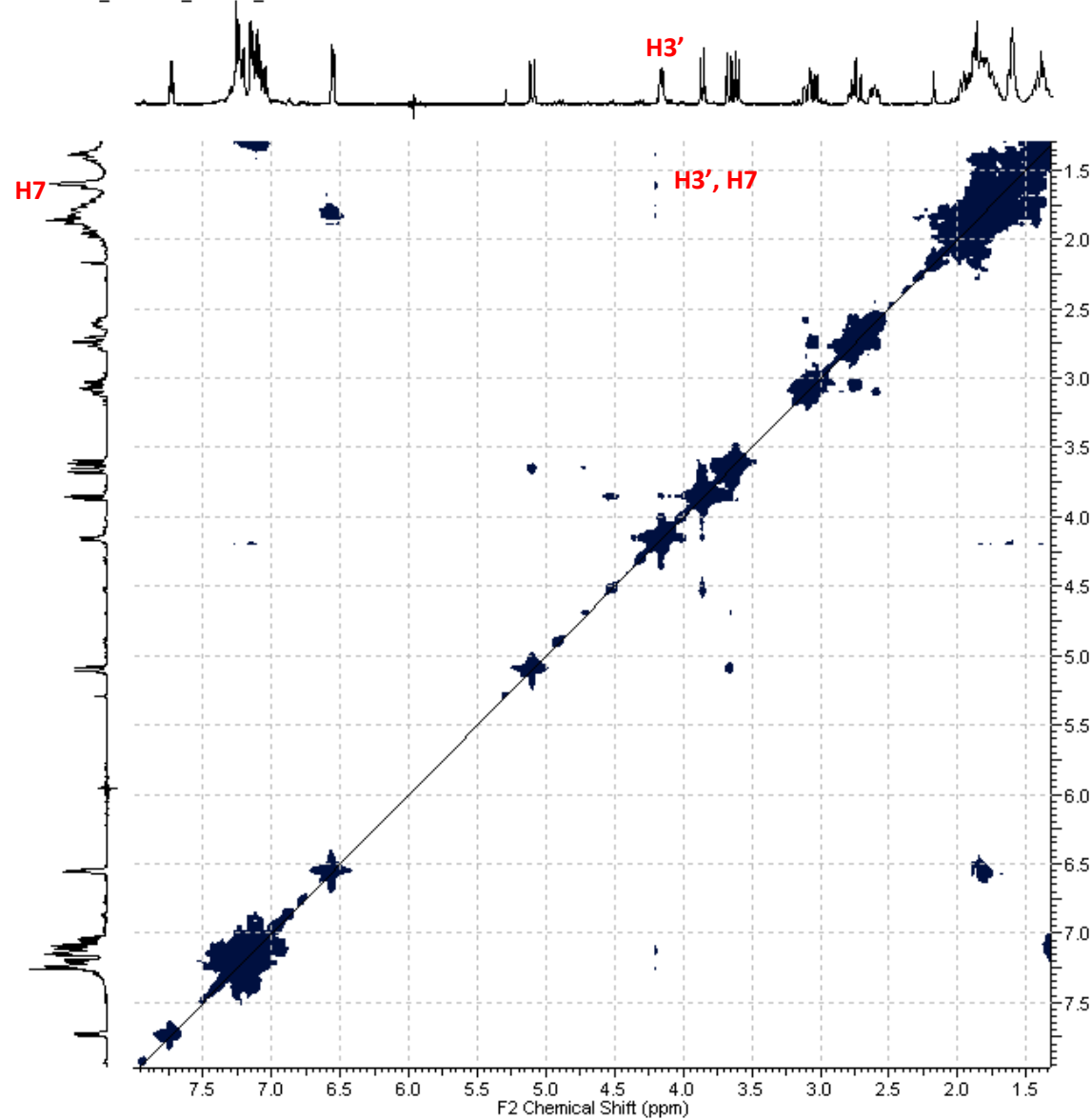
7b Major Diastereomer

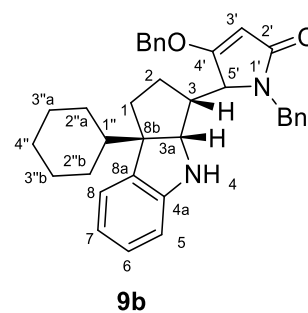
Mixture of **7b** (major) and **9b** (minor) indicated by x



APT NMR (CDCl₃, 125 MHz).**7b** Major Diastereomer

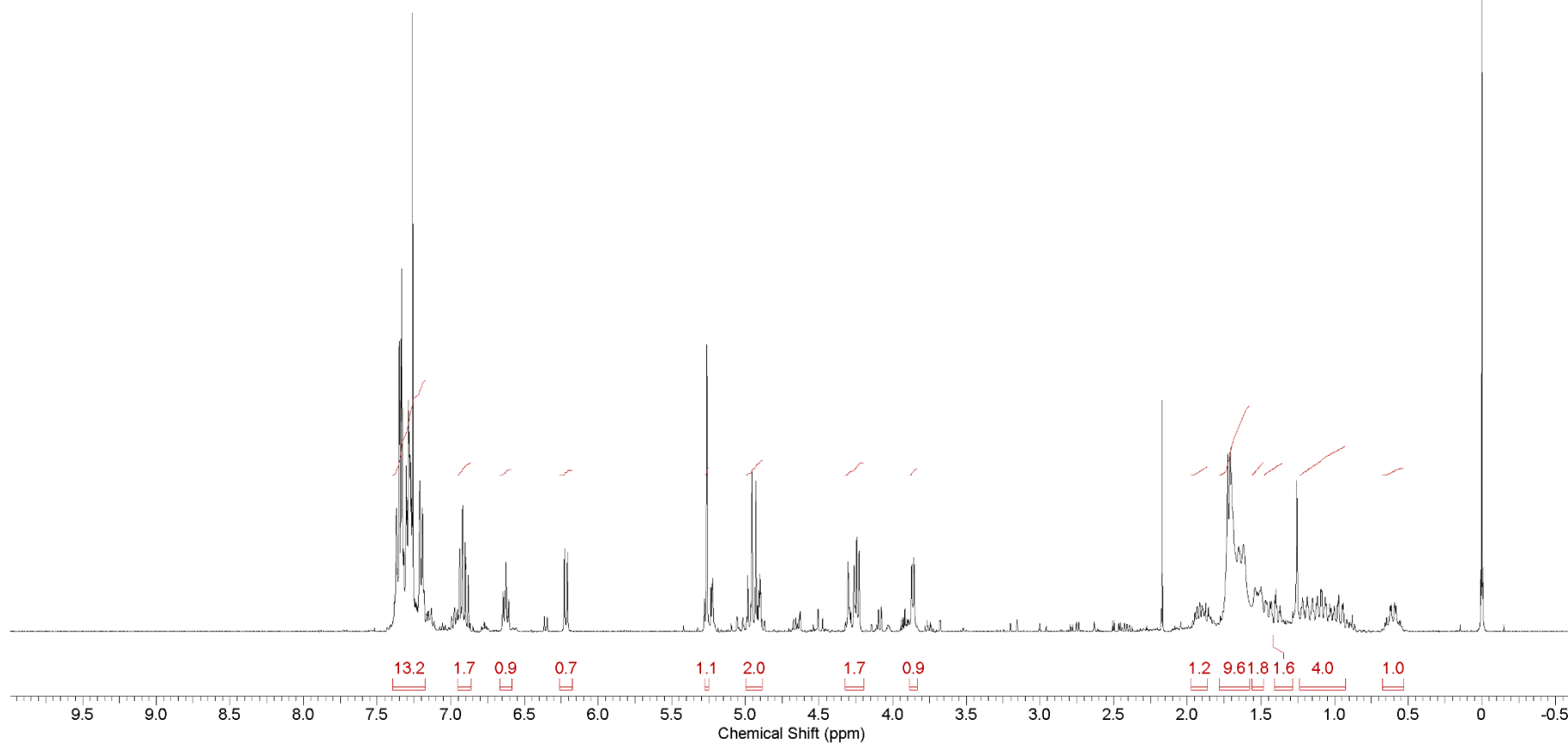
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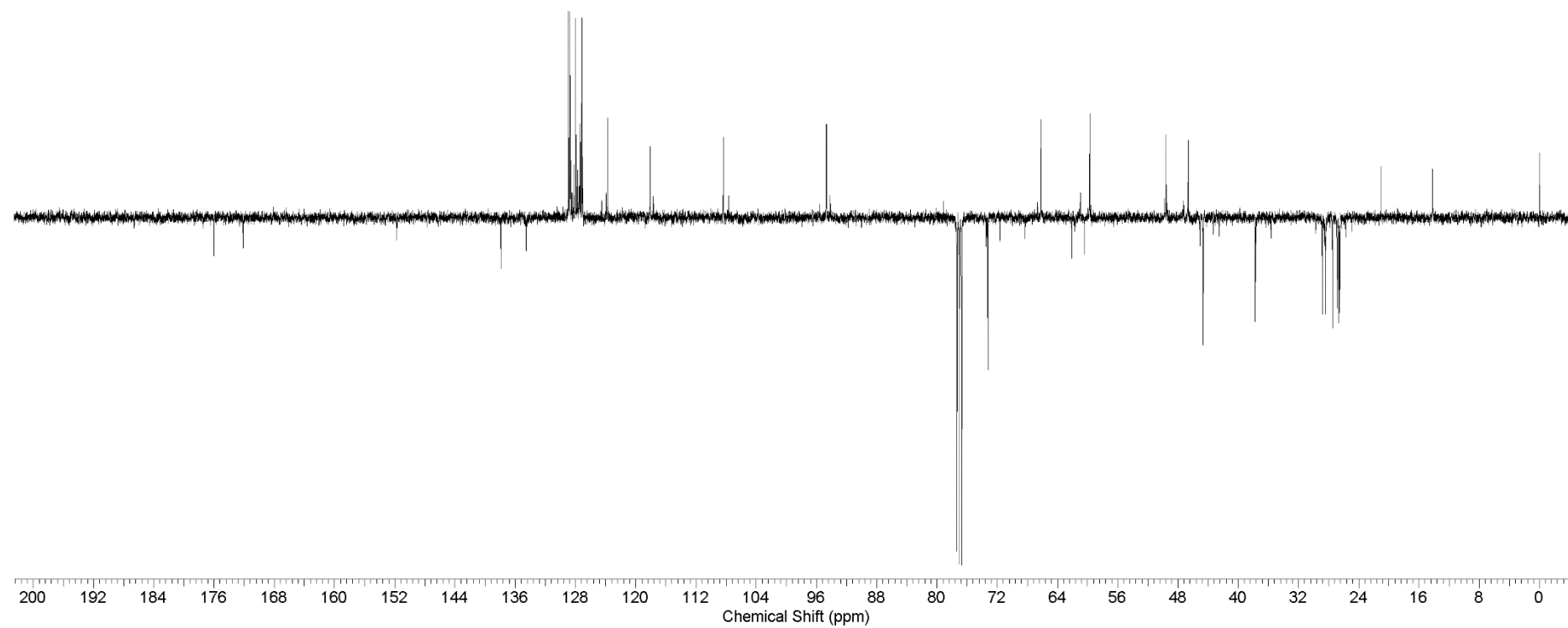
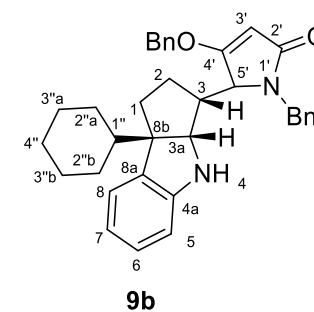
^1H NMR (CDCl_3 , 500 MHz).

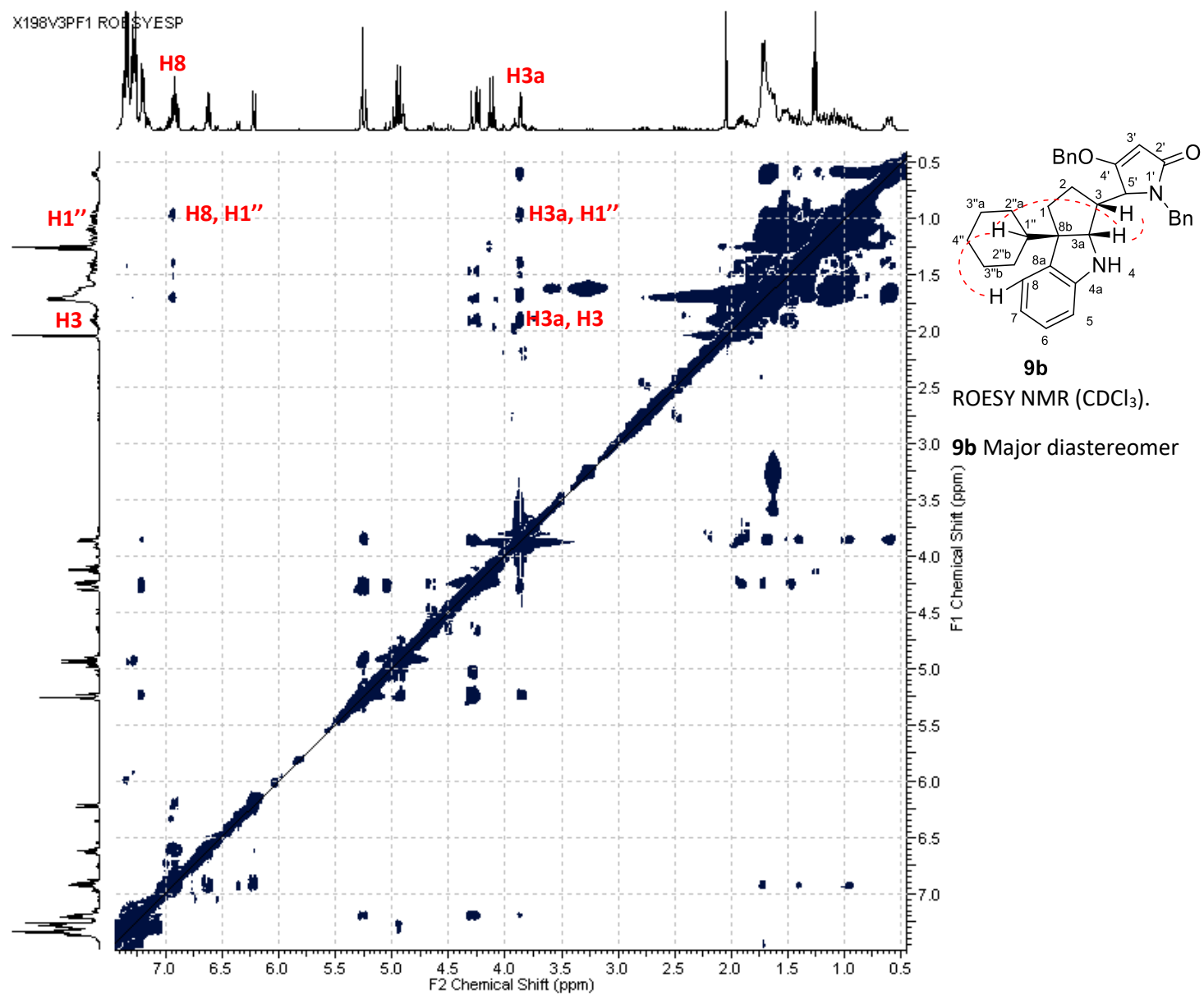
9b Major Diastereomer



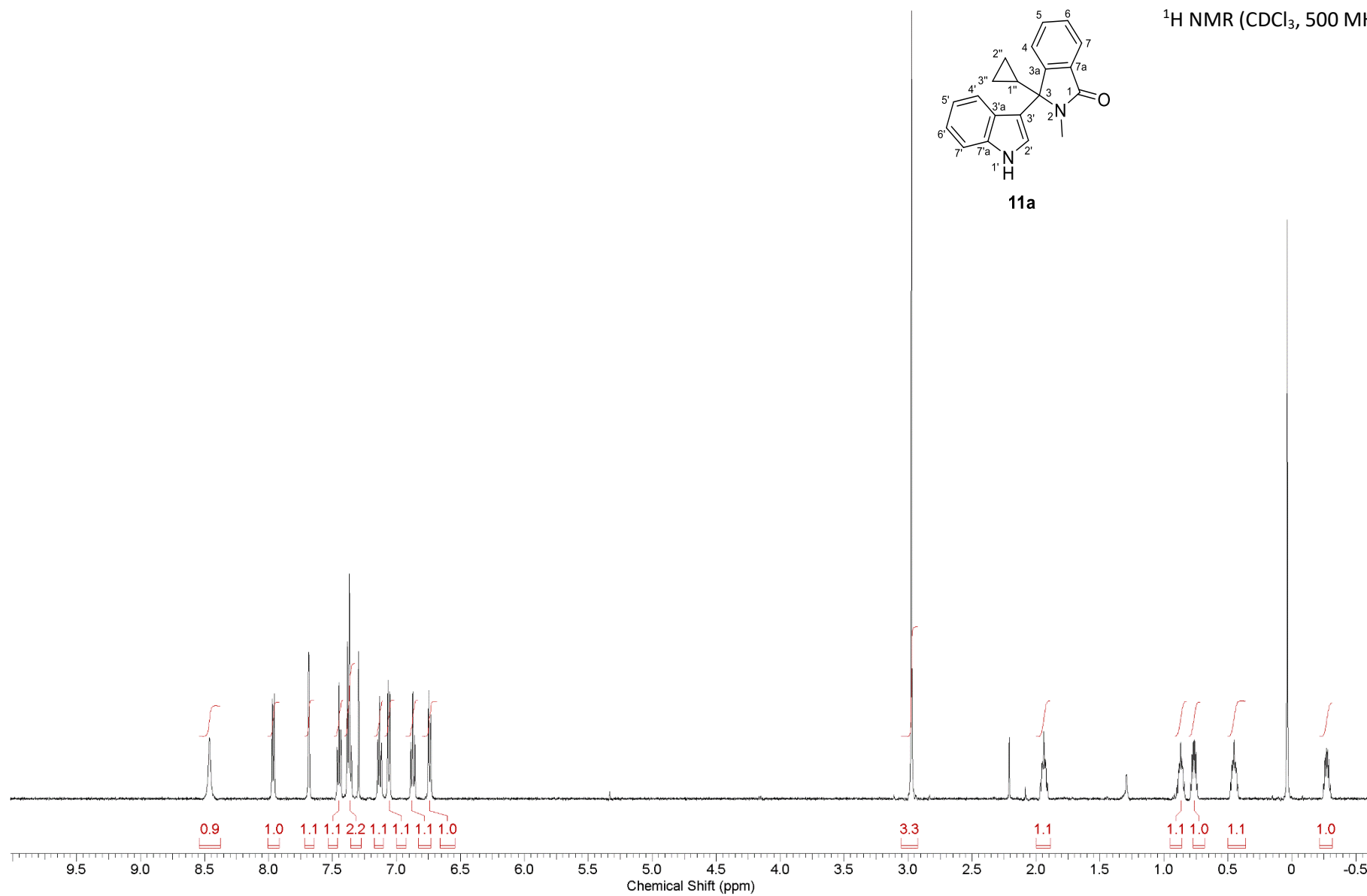
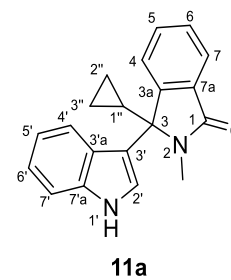
APT NMR (CDCl_3 , 125 MHz).

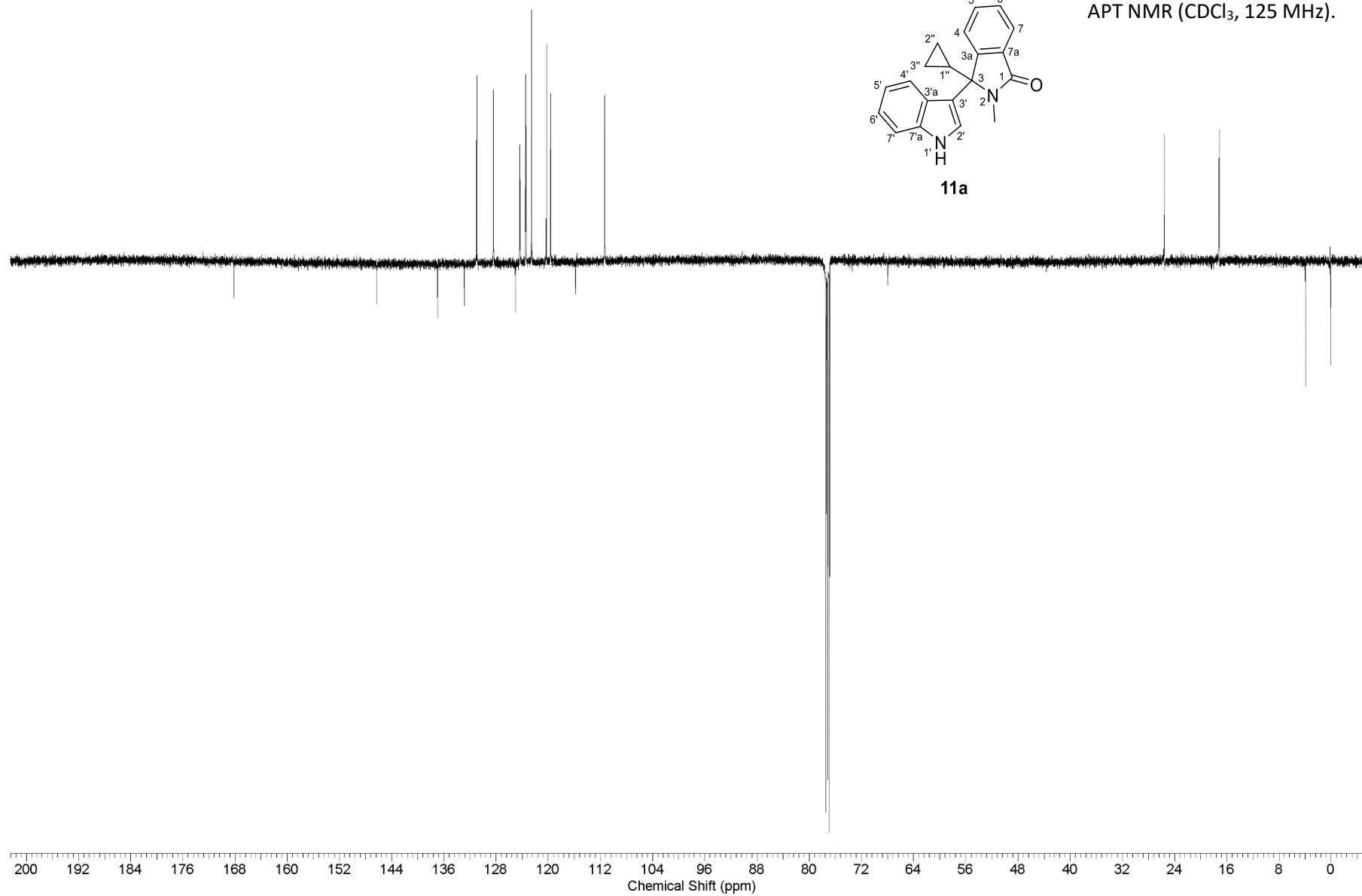
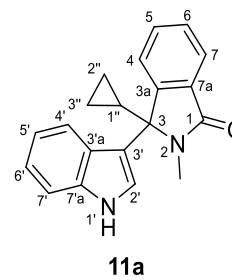
9b Major Diastereomer

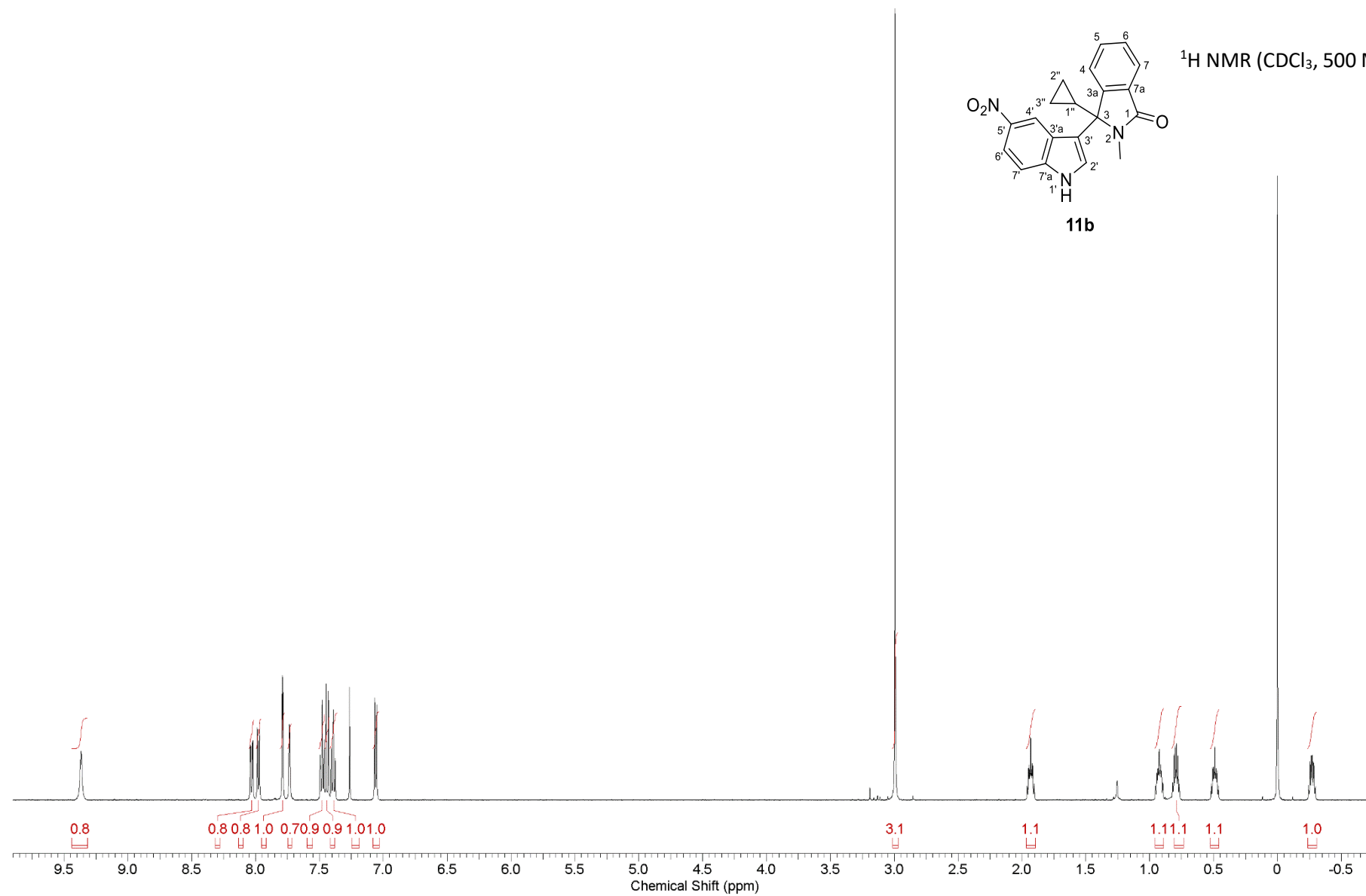
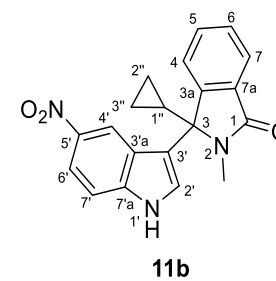


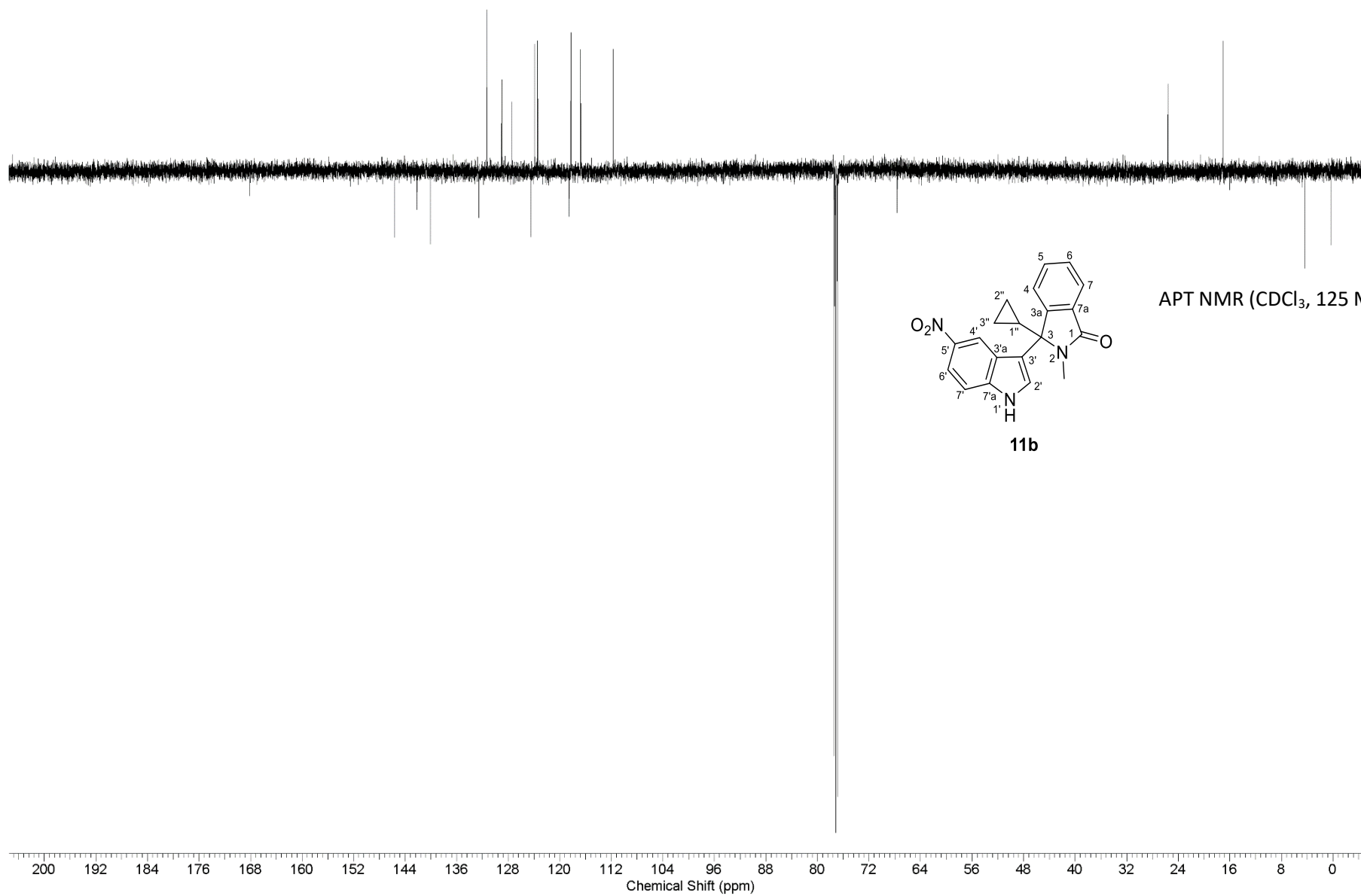


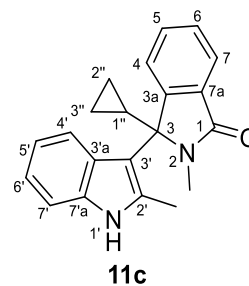
^1H NMR (CDCl_3 , 500 MHz).



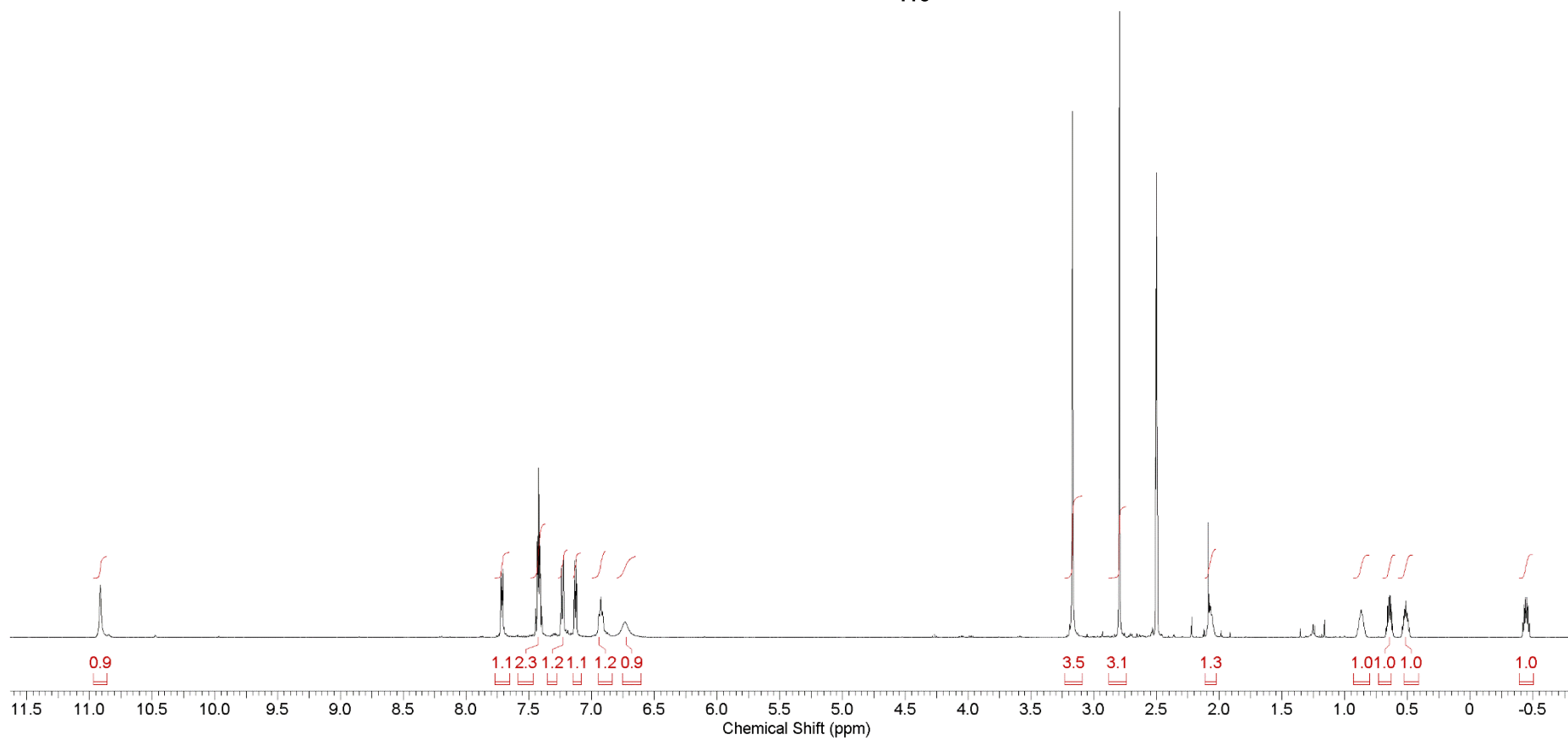
APT NMR (CDCl₃, 125 MHz).

¹H NMR (CDCl₃, 500 MHz).

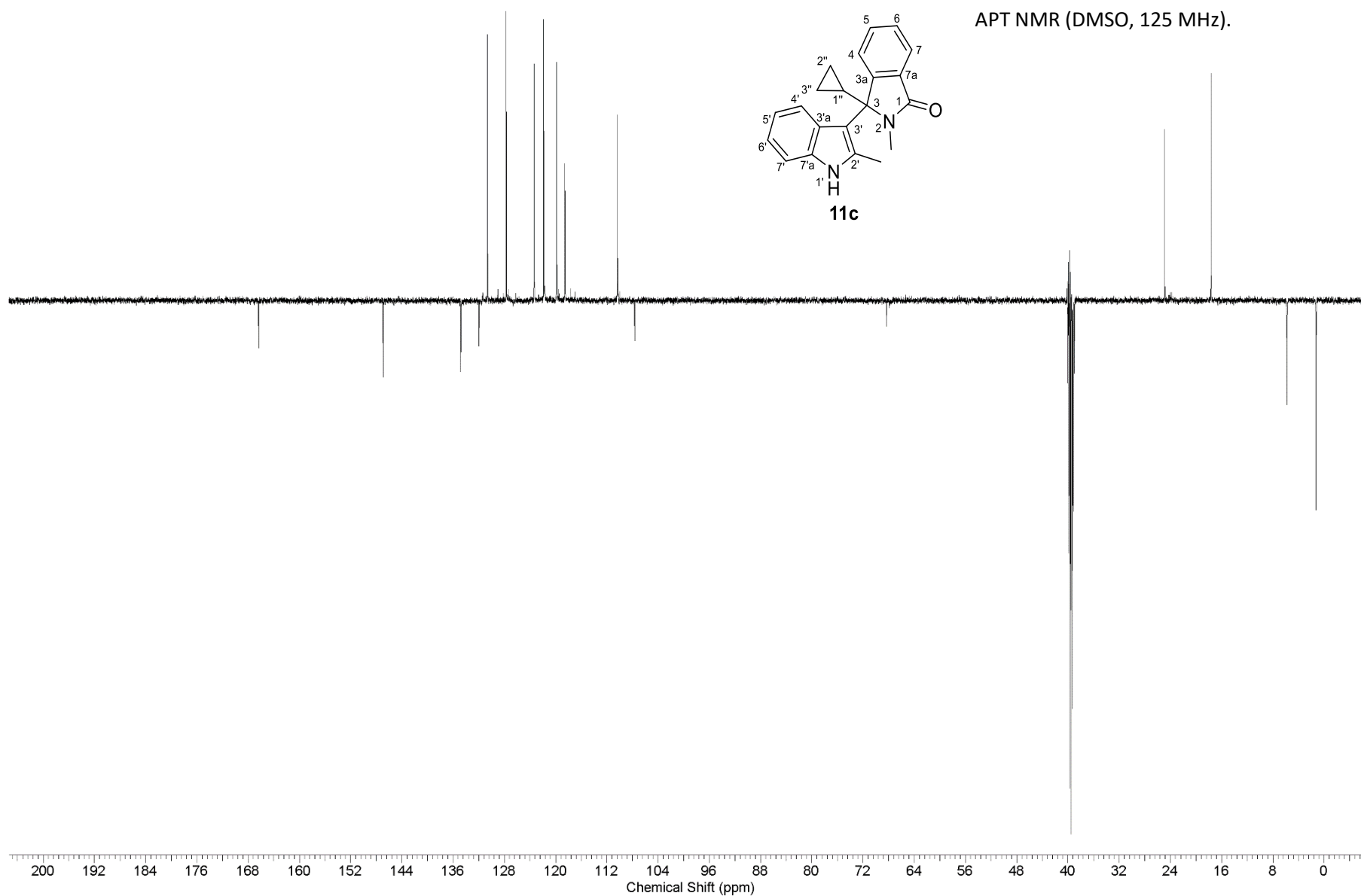
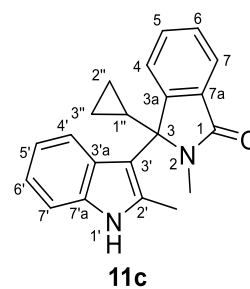


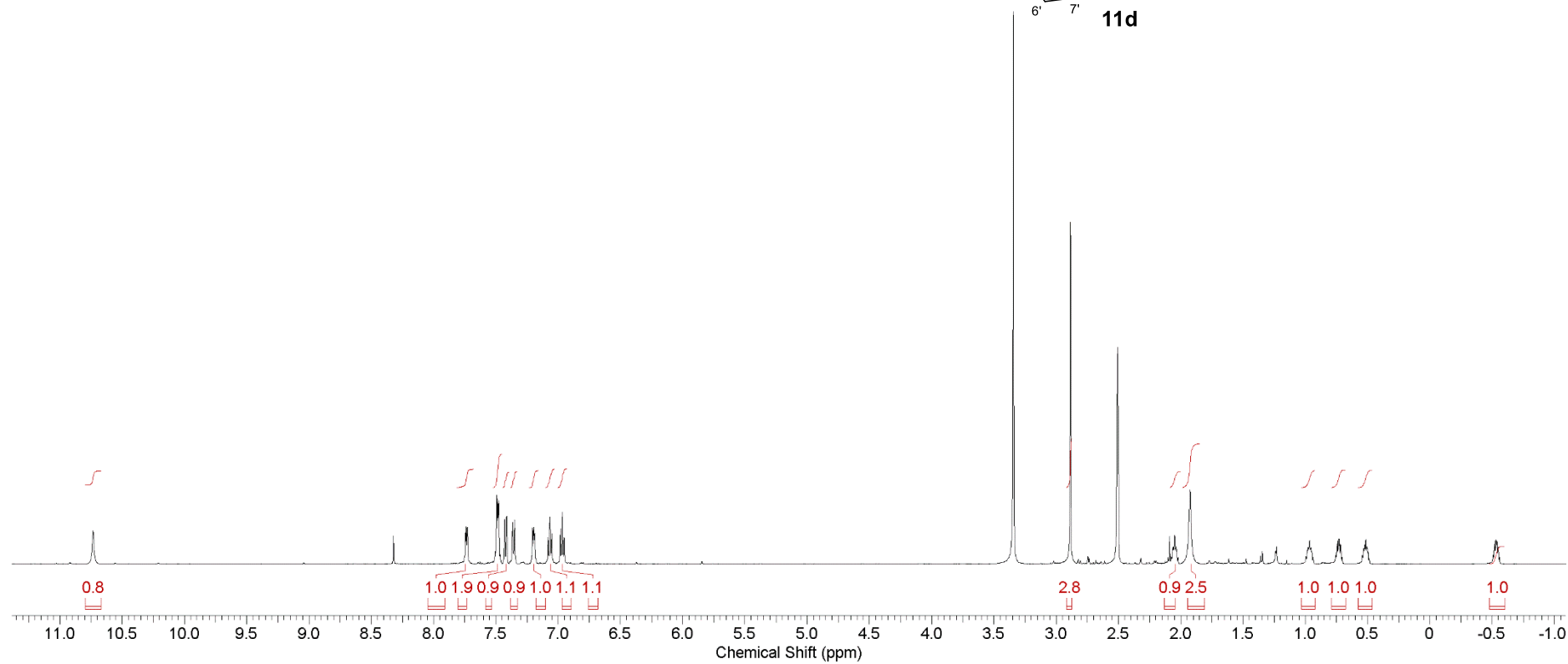
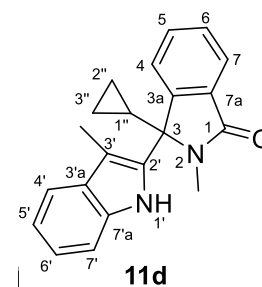


^1H NMR (DMSO, 500 MHz).

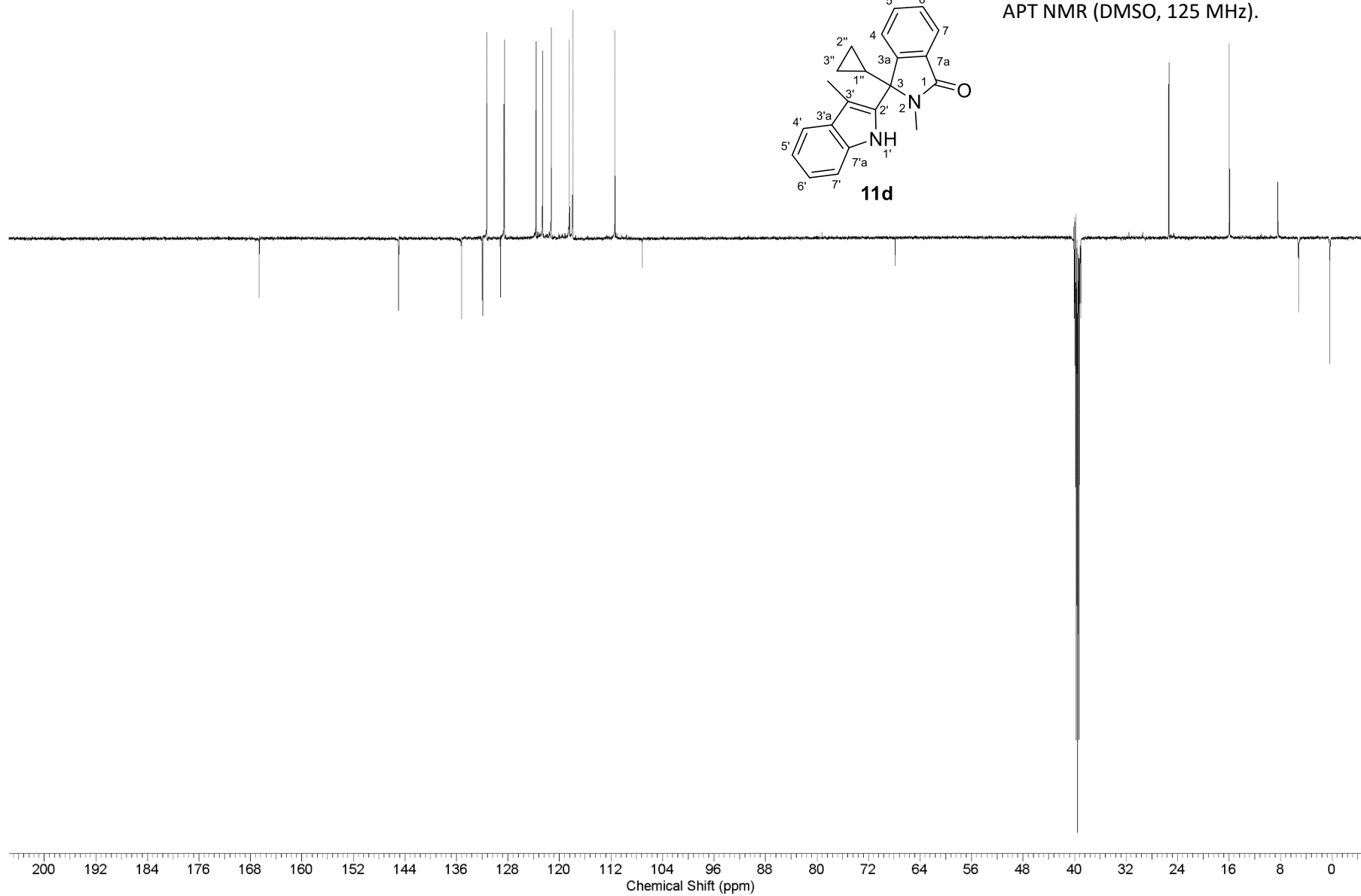
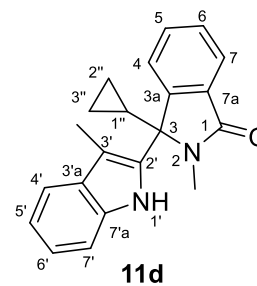


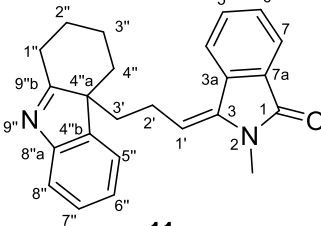
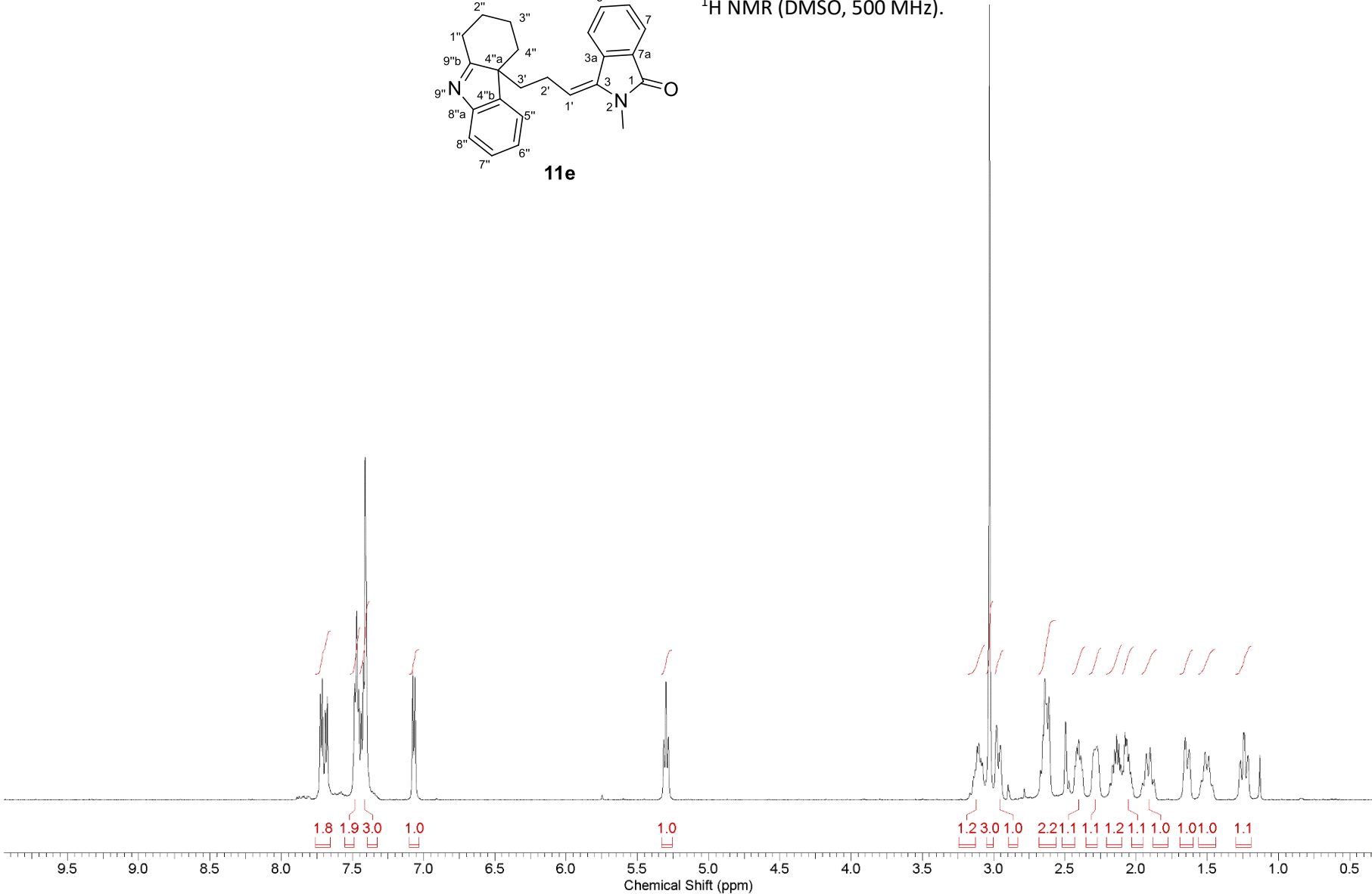
APT NMR (DMSO, 125 MHz).

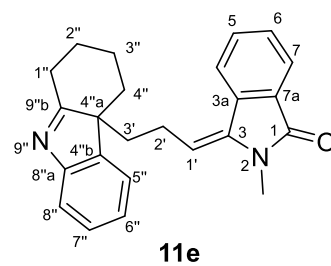


¹H NMR (DMSO, 500 MHz).

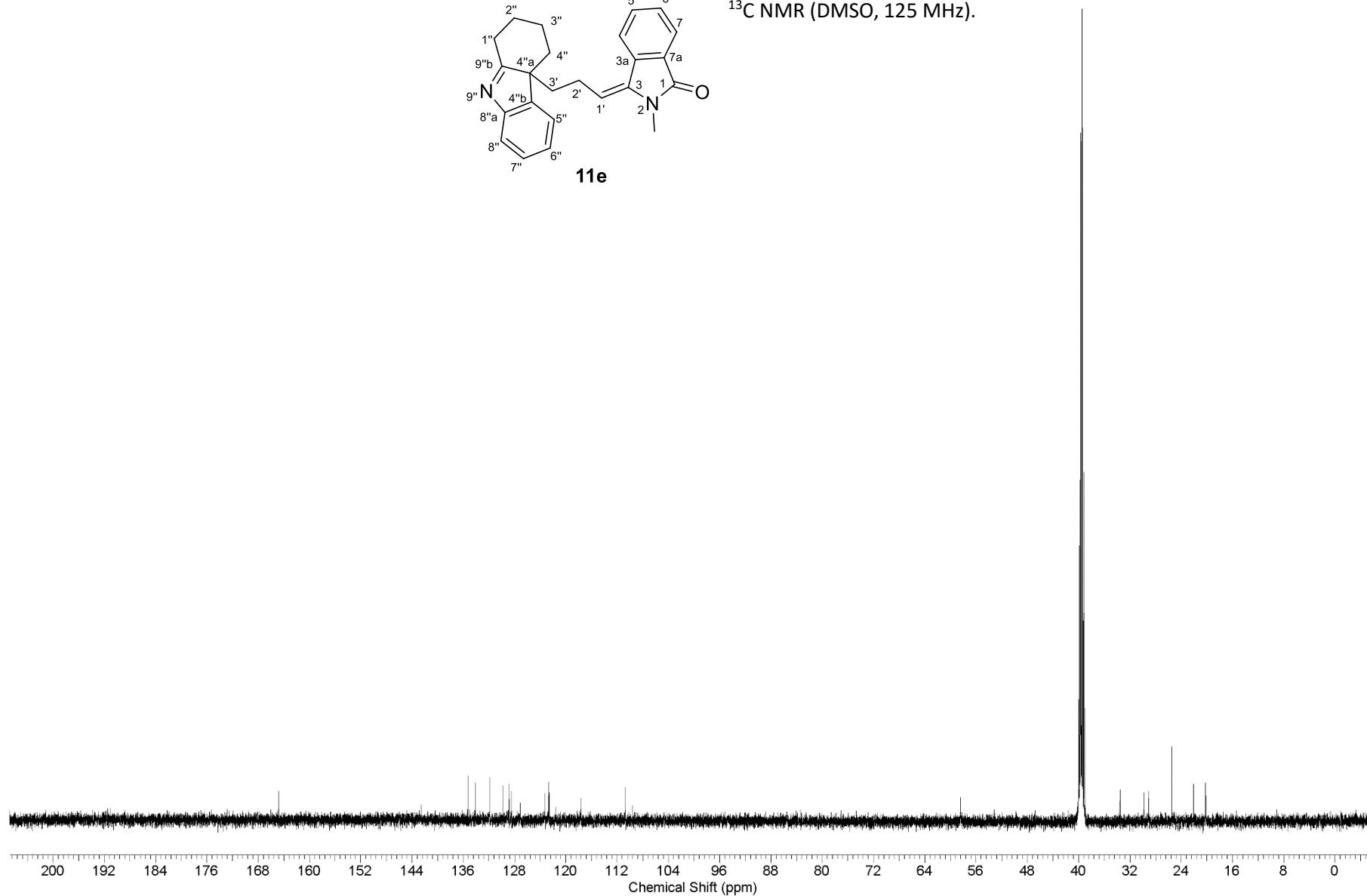
APT NMR (DMSO, 125 MHz).



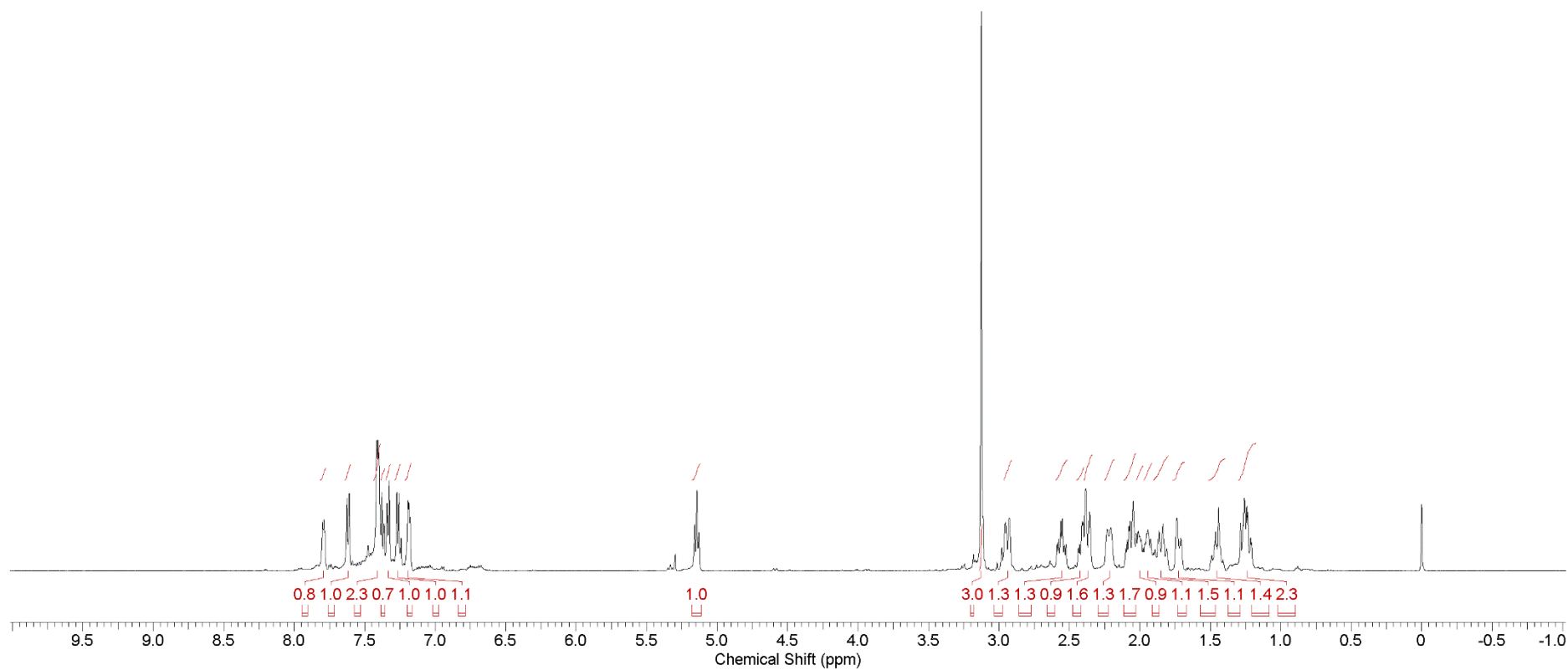
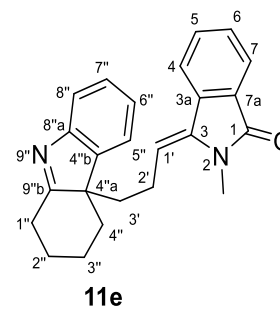
¹H NMR (DMSO, 500 MHz).

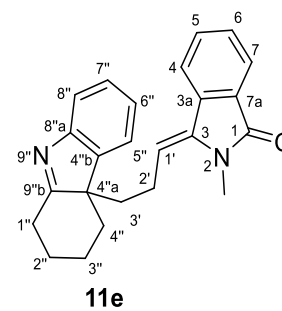
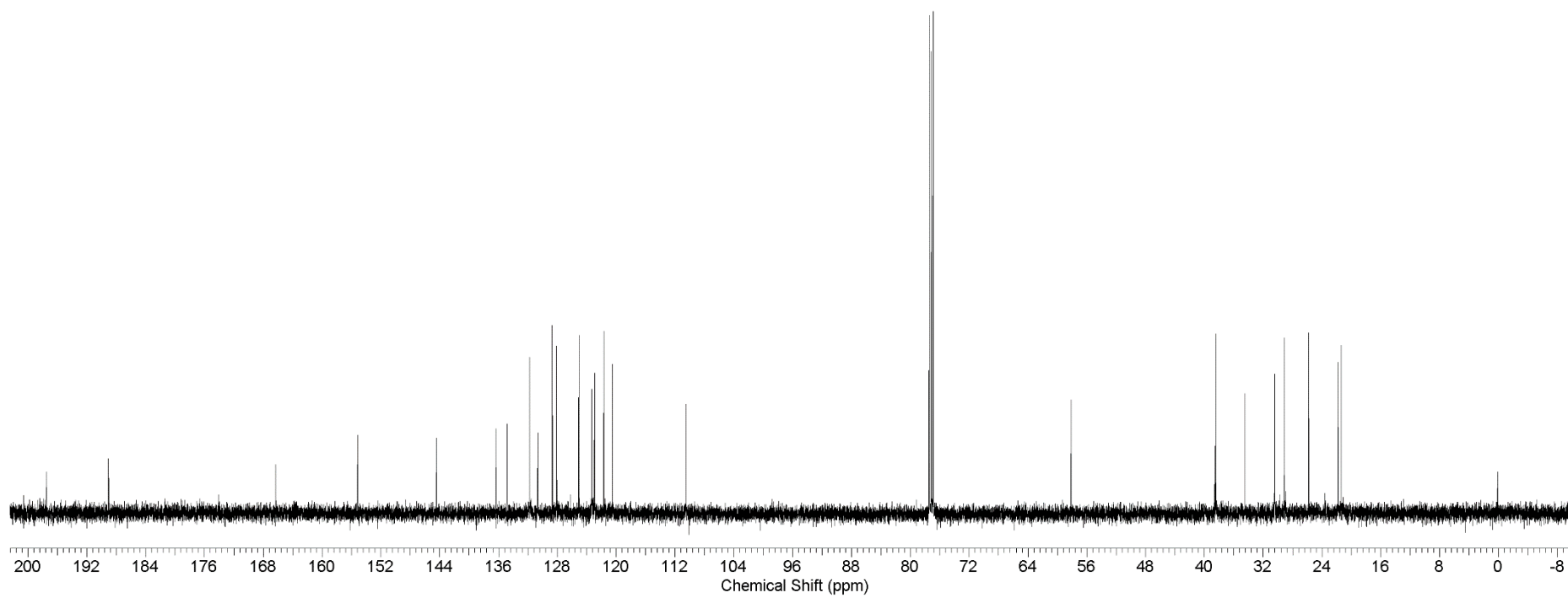


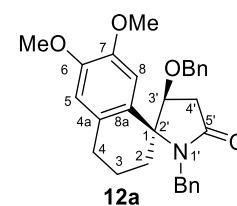
^{13}C NMR (DMSO, 125 MHz).



¹H NMR (DMSO, 500 MHz).



¹³C NMR (DMSO, 125 MHz).



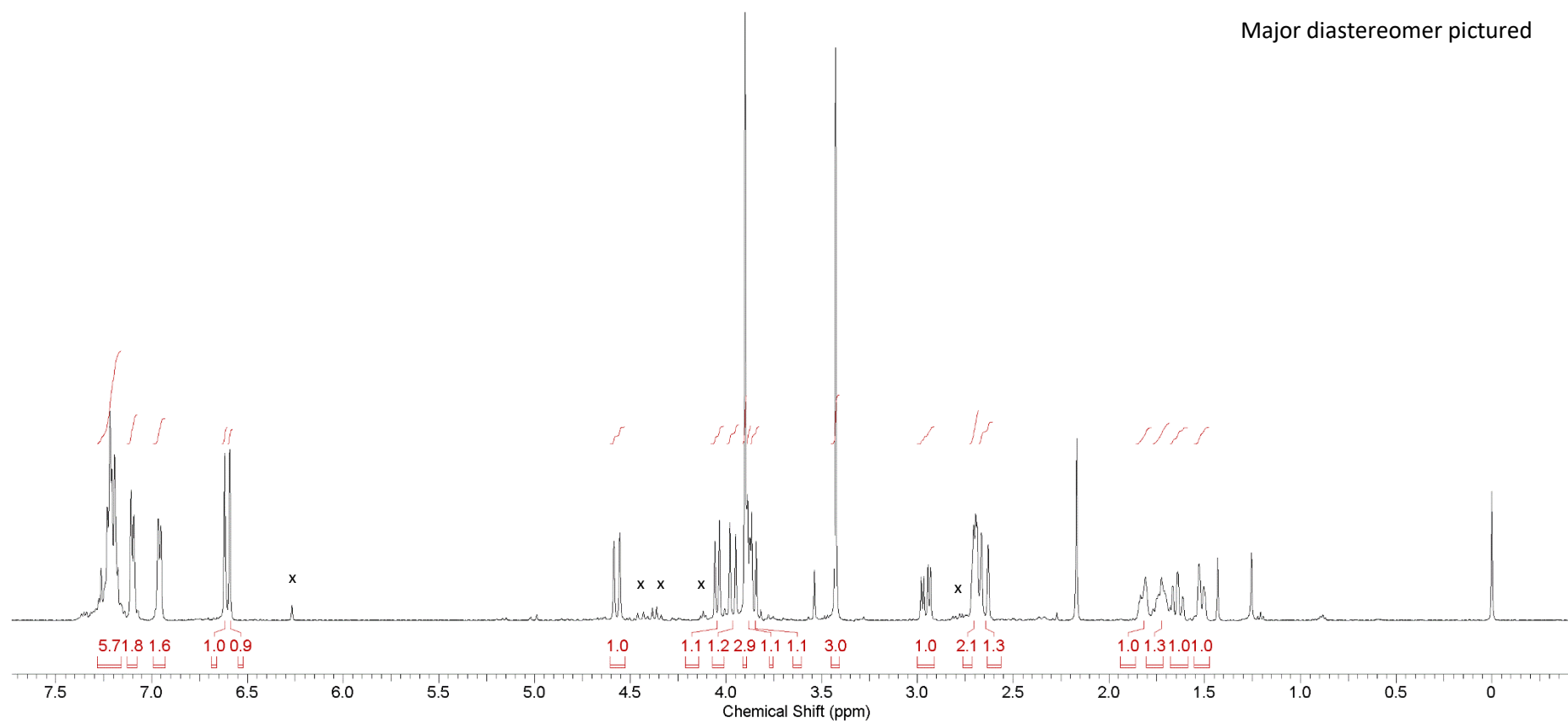
^1H NMR (CDCl_3 , 500 MHz).

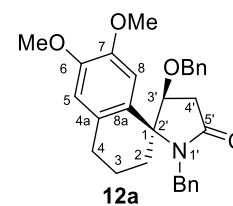
12a Diastereomer Mix

Dr = 90:10

Minor diastereomer
indicated with x

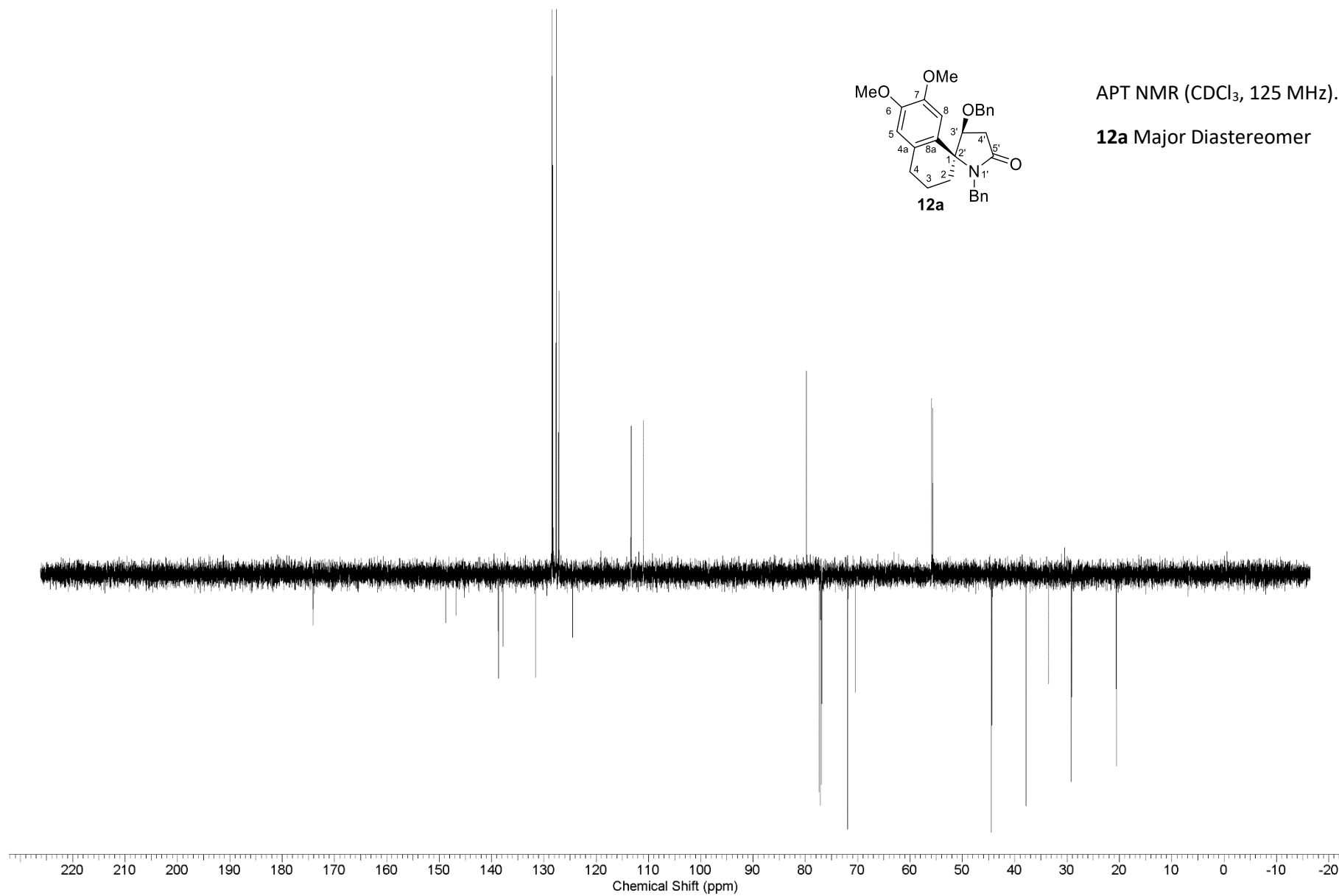
Major diastereomer pictured



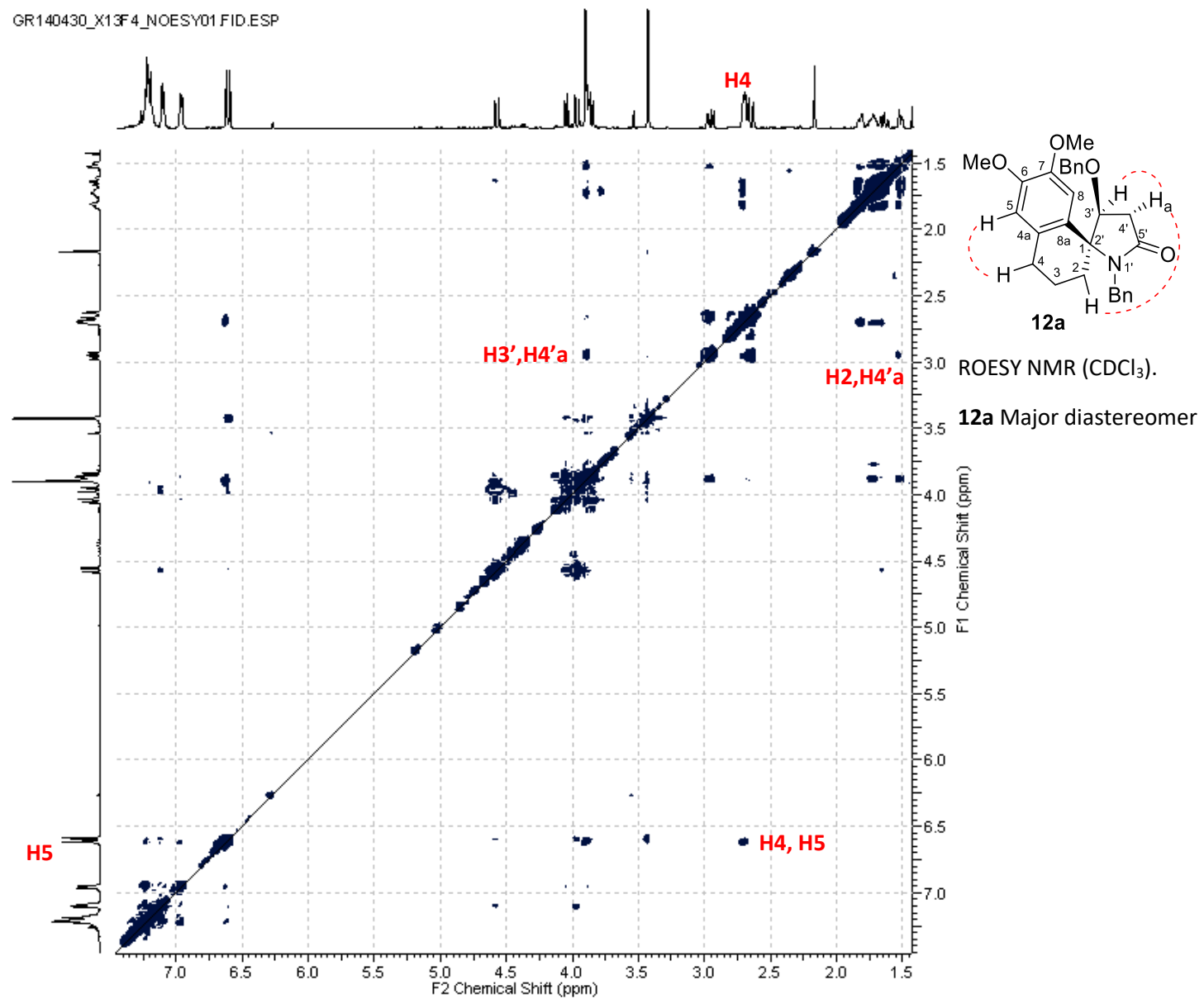


APT NMR (CDCl₃, 125 MHz).

12a Major Diastereomer



GR140430_X13F4_NOESY01.FID.ESP



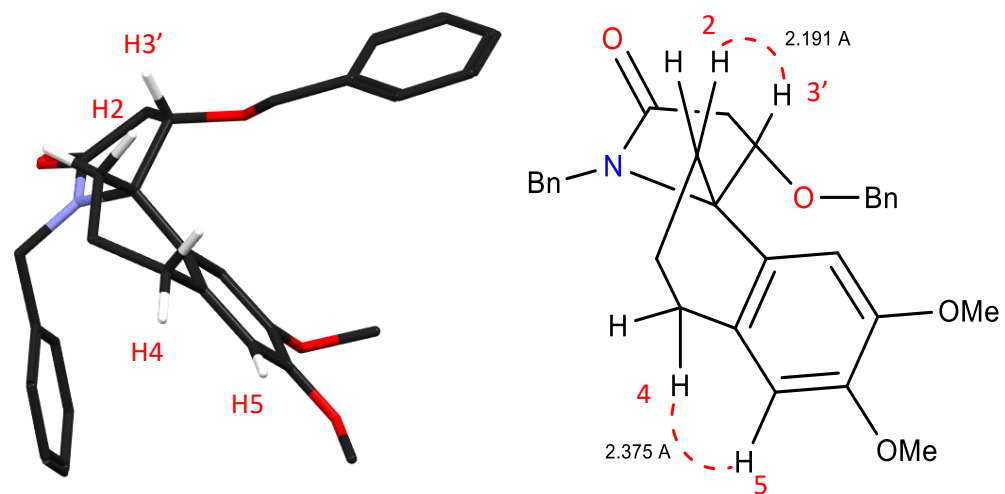
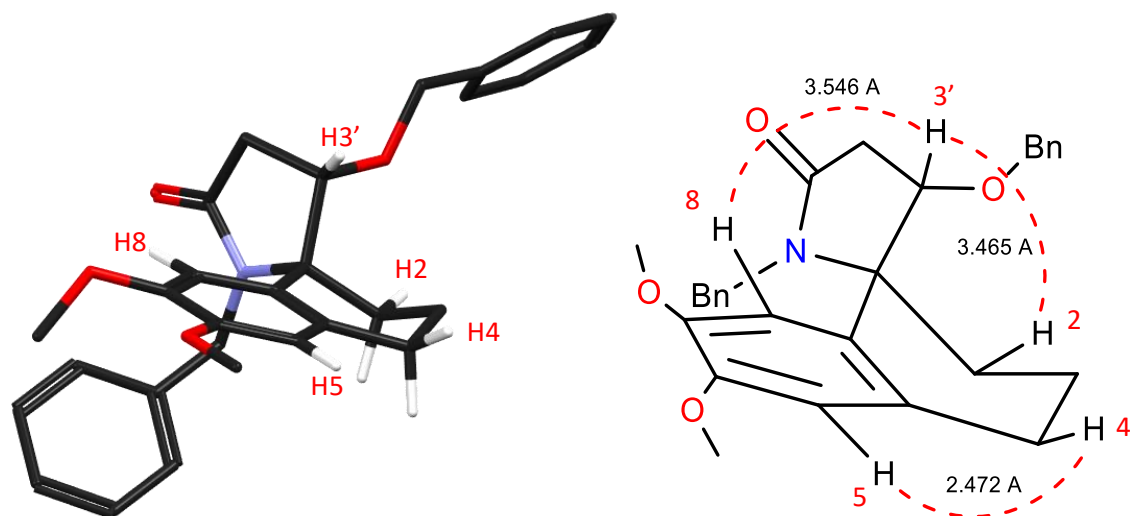
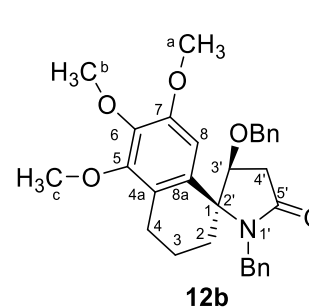


Figure 2.13. Molecular model (DFT minimised, B3LYP/6-31G(d) basis set) of *S,S* compound **218a** (Final addition *syn* to OBn).



Molecular model (DFT minimised, B3LYP/6-31G(d) basis set) of *S,R* compound **12a** (Final addition *anti* to OBn).



^1H NMR (CDCl_3 , 500 MHz).

12b Diastereomer Mix

Dr = 75:25

12b Minor diastereomer indicated with x

Major diastereomer pictured

