

Supplementary Data

Thiourea and Isothiocyanate – Two Useful Chromophores for Stereochemical Studies. A Comparison of Experiment and Computation.

Jacek Gawronski,* Marcin Kwit and Pawel Skowronek

Department of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60 780 Poznan, Poland. Fax: 00 48 61 829 1505; Tel: 00 61 829 1313; E-mail: gawronsk@amu.edu.pl

- S3. Figure A. Calculated at B3LYP/6-311++G(2D,2P) level structures of thermally accessible conformers of **1–3**, labeled according to their increasing energies.
- S4. Figure B. Calculated at B3LYP/6-311++G(2D,2P) level structures of thermally accessible conformers of **4**. Note that conformers are labeled according to their structural similarity and increasing energies
- S5. Figure C. Calculated at B3LYP/6-311++G(2D,2P) level structures of thermally accessible conformers of **5 – 10**.
- S6. Figure D. Calculated at B3LYP/6-311++G(D,P) level PES for the rotation around the C–N bonds in diequatorial (a) and diaxial (b) conformations of **4**.
- S7. Figure E. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (black lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV spectra for model compounds **1a**, **2a**, **3a** and **10'** (wavelength not corrected).
- S8. Figure F. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (black lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV spectra for individual conformers of **1b** (wavelength not corrected).
- S9. Figure G. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV (upper panels) and CD (middle panels – velocity; lower panels – length method) spectra for individual conformers of **4**. All calculated spectra were wavelength corrected to match the experimental UV spectrum of **4**.
- S10. Figure G. continued
- S11. Figure H. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (solid lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (dashed lines) UV (upper panels) CD spectra for families of structurally similar conformers of compound **4**, normalized to their relative populations (wavelength not corrected).
- S12. Figure I. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV (upper panels) and CD (middle panels – velocity; lower panels – length method) spectra for individual conformers of **5a** (wavelength not corrected).
- S13. Figure J. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV (upper panels) and CD (middle panels – velocity; lower panels – length method) spectra for individual conformers of **5b**. All calculated spectra were wavelength corrected to match the experimental UV spectrum of **5b**.
- S14. Figure K. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV (upper panels) and CD (middle panels – velocity; lower panels – length method) spectra for individual conformers of **8a** (wavelength not corrected).
- S15. Figure L. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV (upper panels) and CD (middle panels – velocity; lower panels – length method) spectra for individual conformers of **8b**. All calculated spectra were wavelength corrected to match the experimental UV spectrum of **8b**.
- S16. Figure M. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV (upper panels) and CD (middle panels –

velocity; lower panels – length method) spectra for individual conformers of **9**. All calculated spectra were wavelength corrected to match the experimental UV spectrum of **9**.

- S17. Figure N. Experimental (black lines, left panels) and calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines, right panels) CD spectra for of **5a** (upper panels) and **8a** (lower panels). All calculated spectra were wavelength corrected to match the experimental UV spectra of **5a** and **8a**.
- S18. ¹H NMR spectra of **5a**
- S19. ¹³C NMR spectra of **5a**
- S20. MS spectra of **5a**
- S21. ¹H NMR spectra of **5b**
- S22. ¹³C NMR spectra of **5b**
- S23. MS spectra of **5b**
- S24. ¹H NMR spectra of **7**
- S25. ¹³C NMR spectra of **7**
- S26. MS spectra of **7**
- S27. ¹H NMR spectra of **8a**
- S28. ¹³C NMR spectra of **8a**
- S29. MS spectra of **8a**
- S30. ¹H NMR spectra of **8b**
- S31. ¹³C NMR spectra of **8b**
- S32. MS spectra of **8b**
- S33. ¹H NMR spectra of **9**
- S34. ¹³C NMR spectra of **9**
- S35. MS spectra of **9**
- S36. ¹H NMR spectra of **10**
- S37. ¹³C NMR spectra of **10**
- S38. MS spectra of **10**

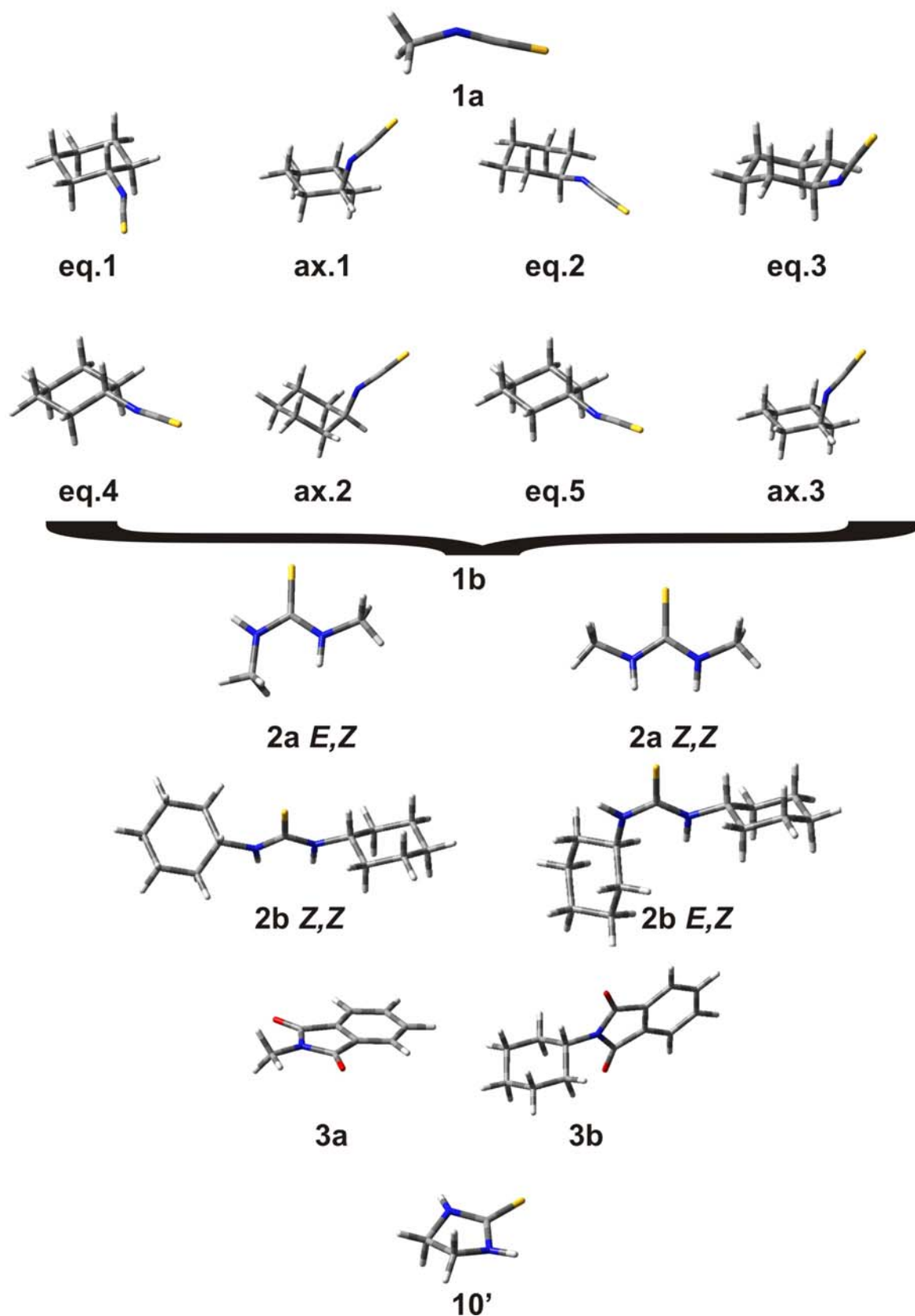


Figure A. Calculated at B3LYP/6-311++G(2D,2P) level structures of thermally accessible conformers of **1–3**, labeled according to their increasing energies

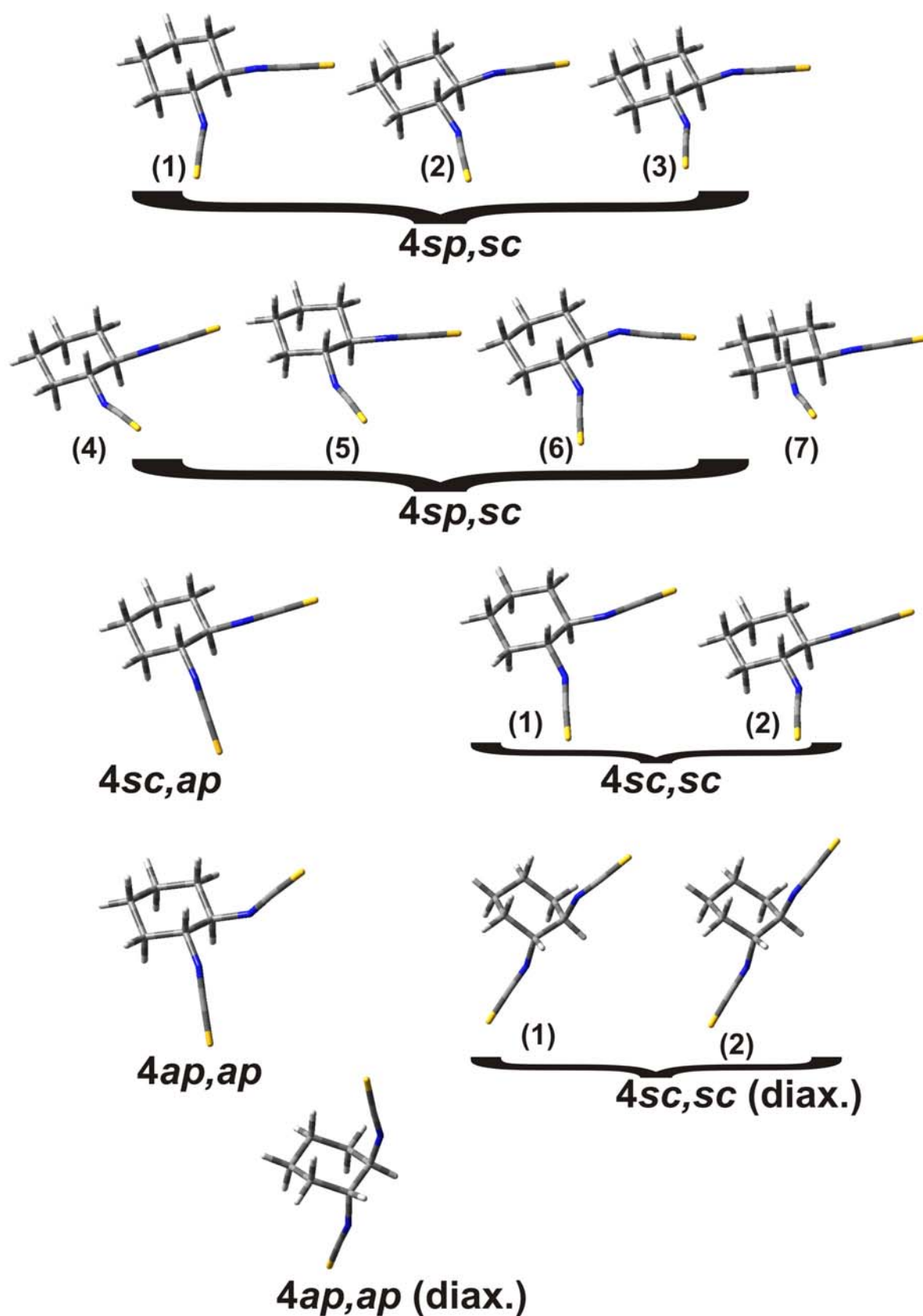


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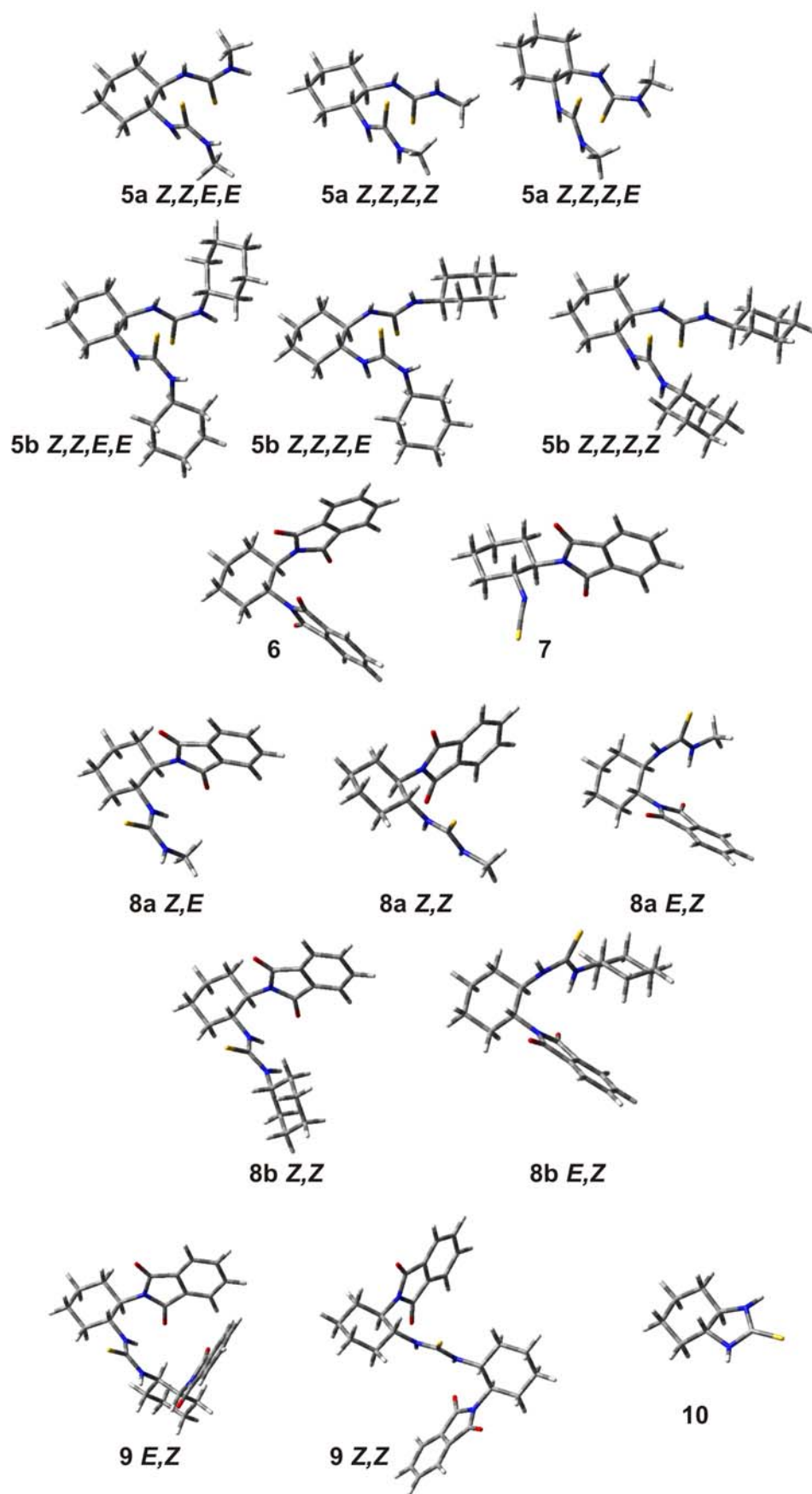
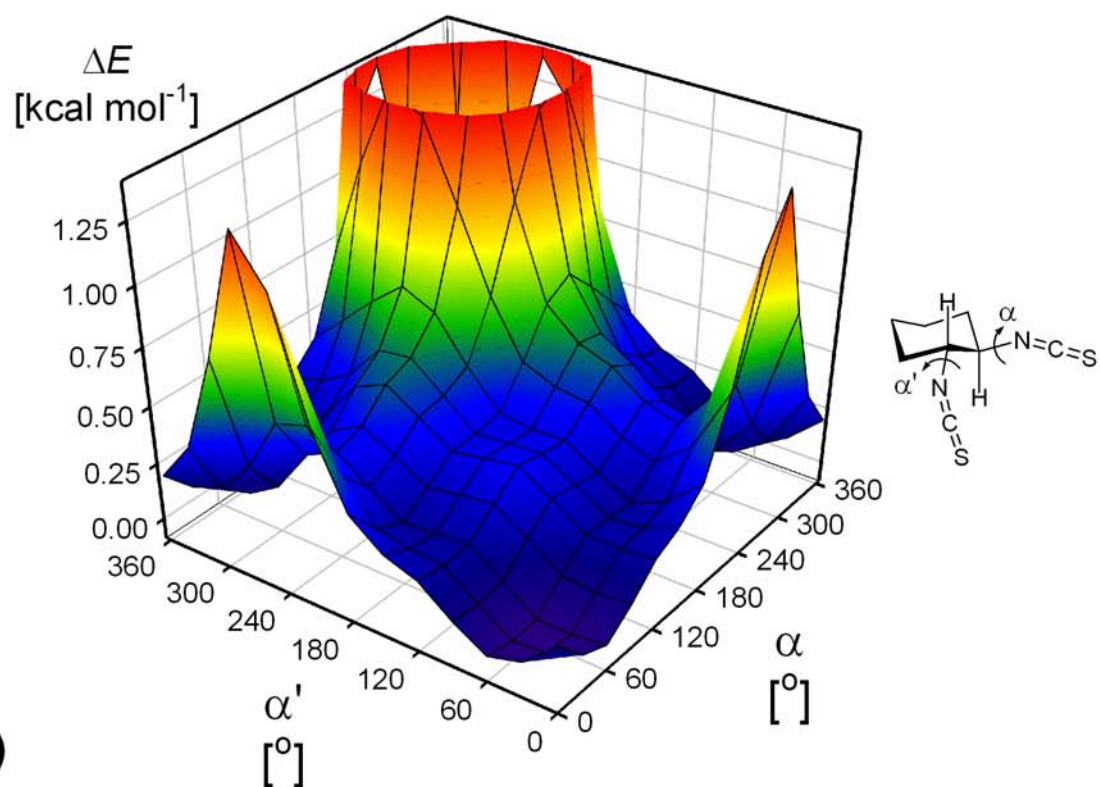


Figure C. Calculated at B3LYP/6-311++G(2D,2P) level structures of thermally accessible conformers of **5** – **10**.

(a)



(b)

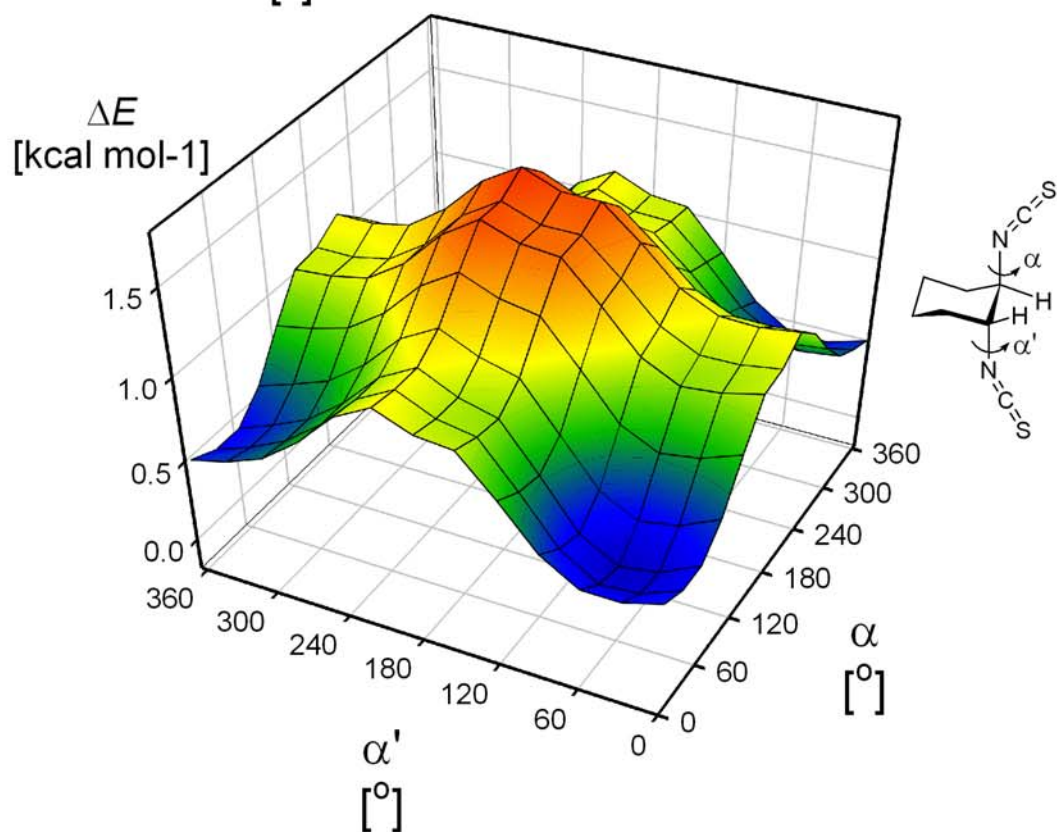


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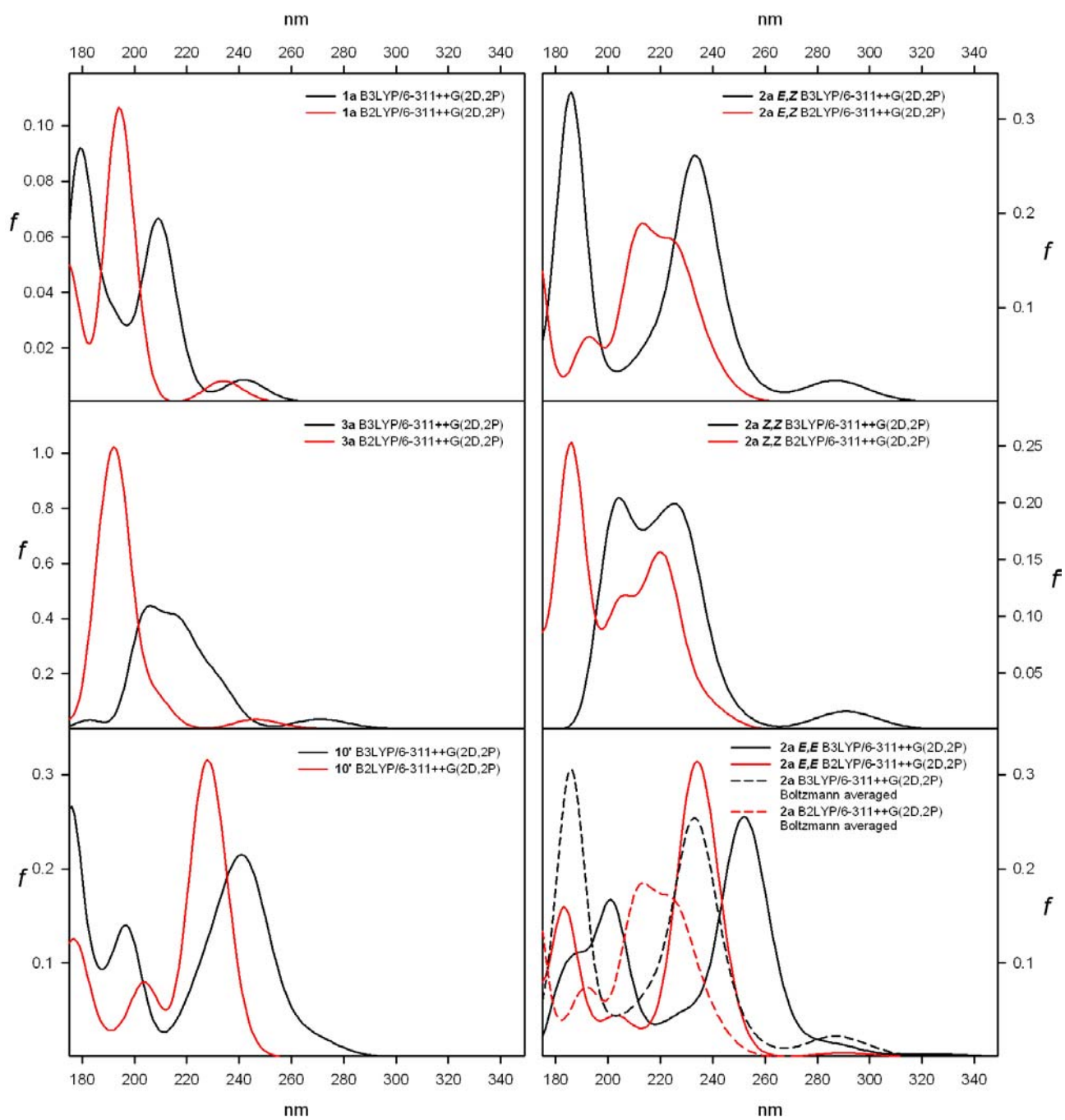


Figure E. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (black lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV spectra for model compounds **1a**, **2a**, **3a** and **10'** (wavelength not corrected).

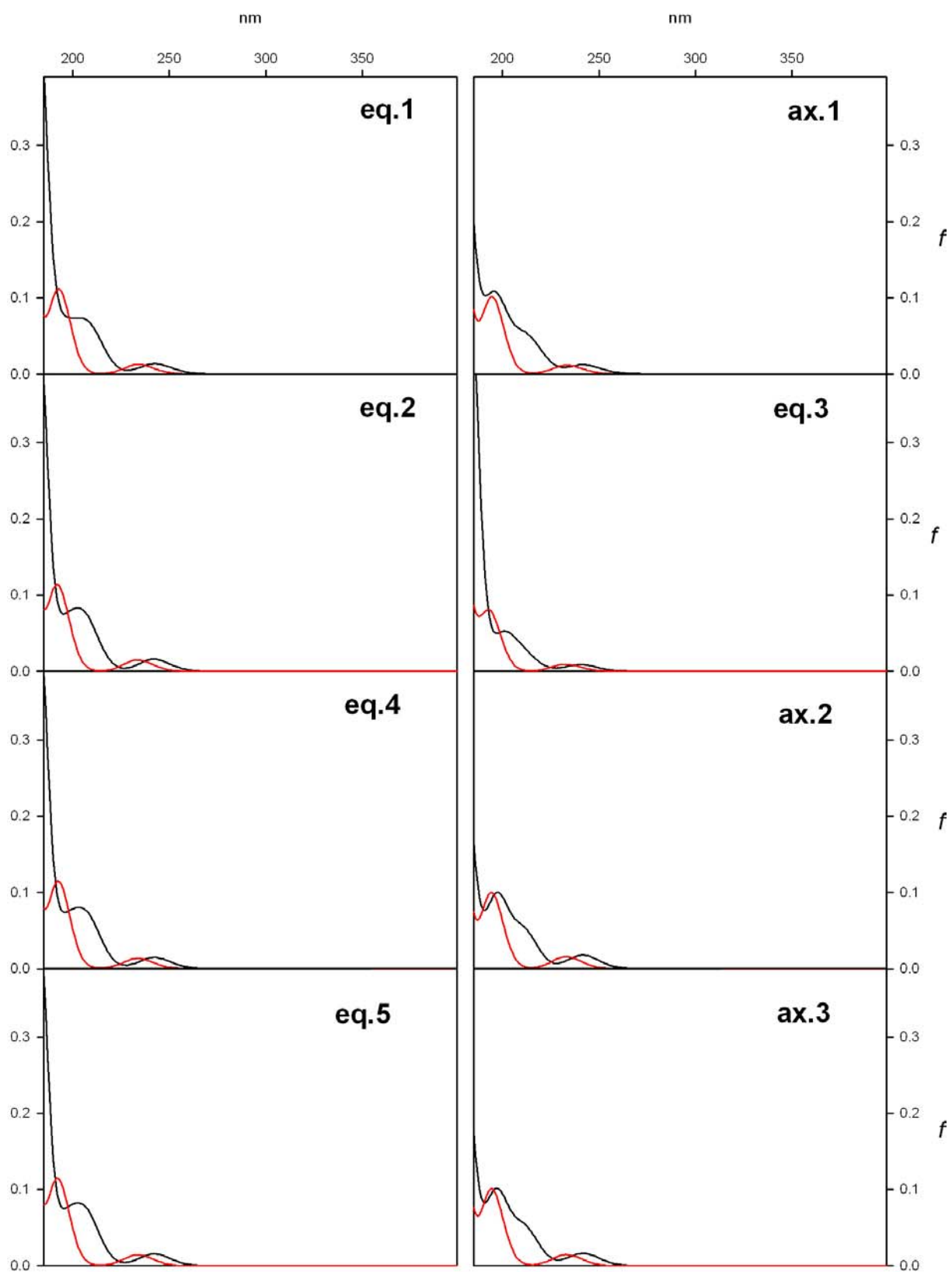
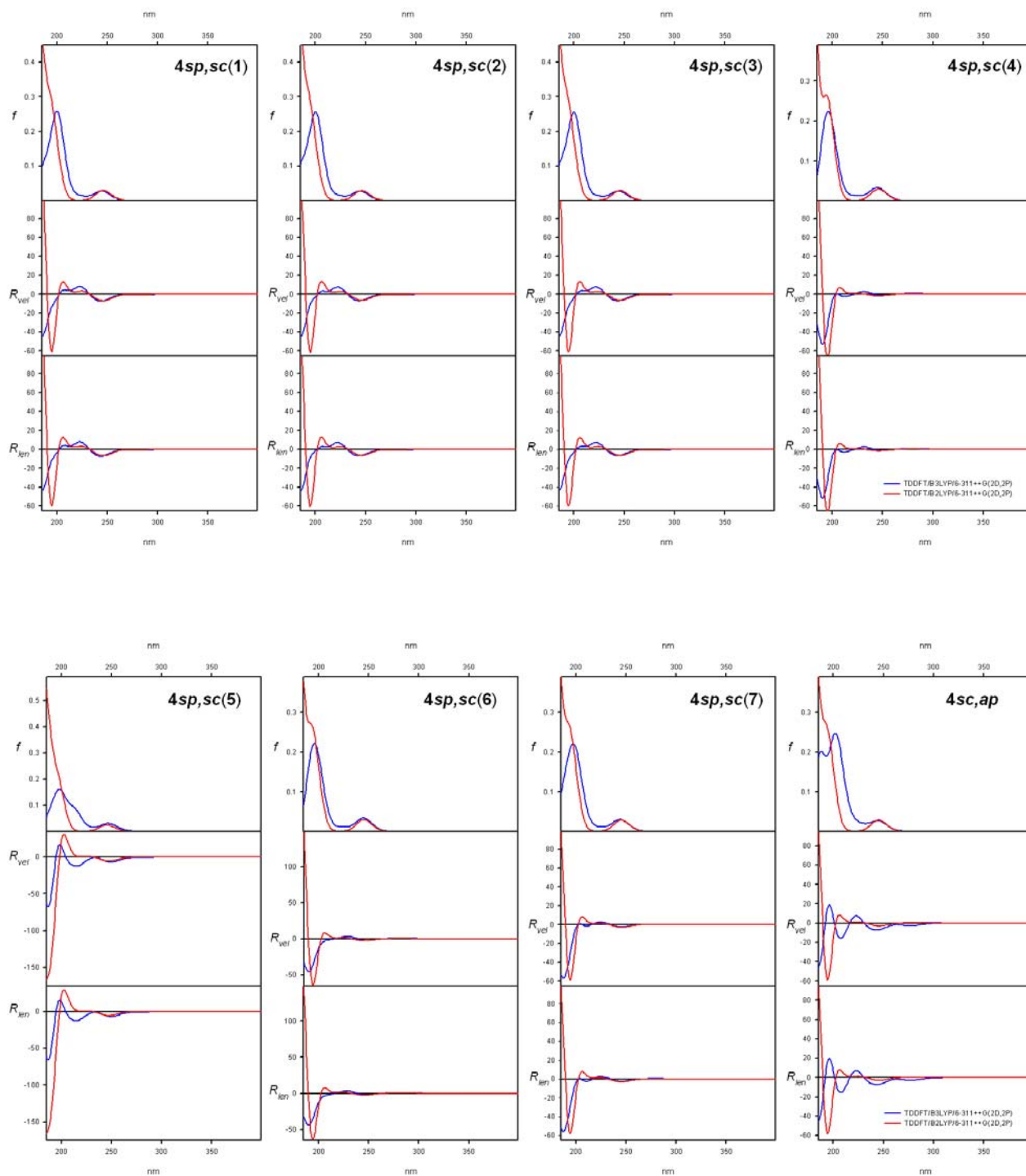
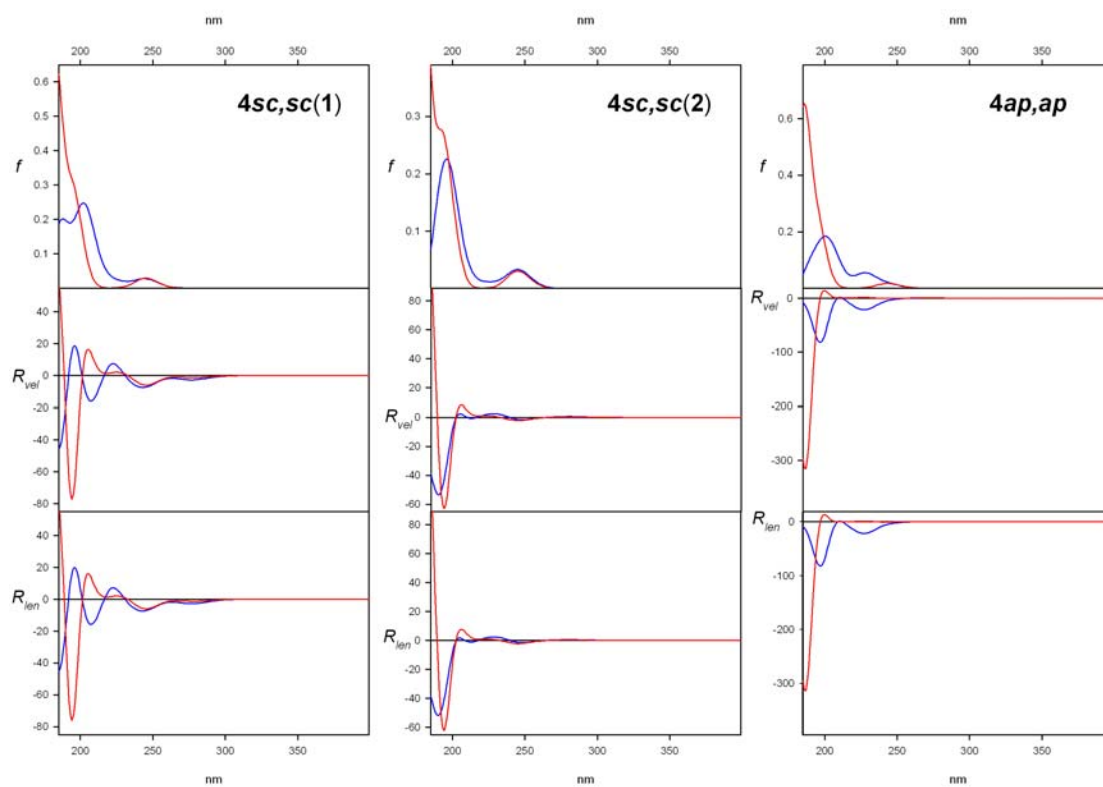


Figure F. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (black lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV spectra for individual conformers of **1b** (wavelength not corrected).

Diequatorial conformers



Continued on next page



Diaxial conformers

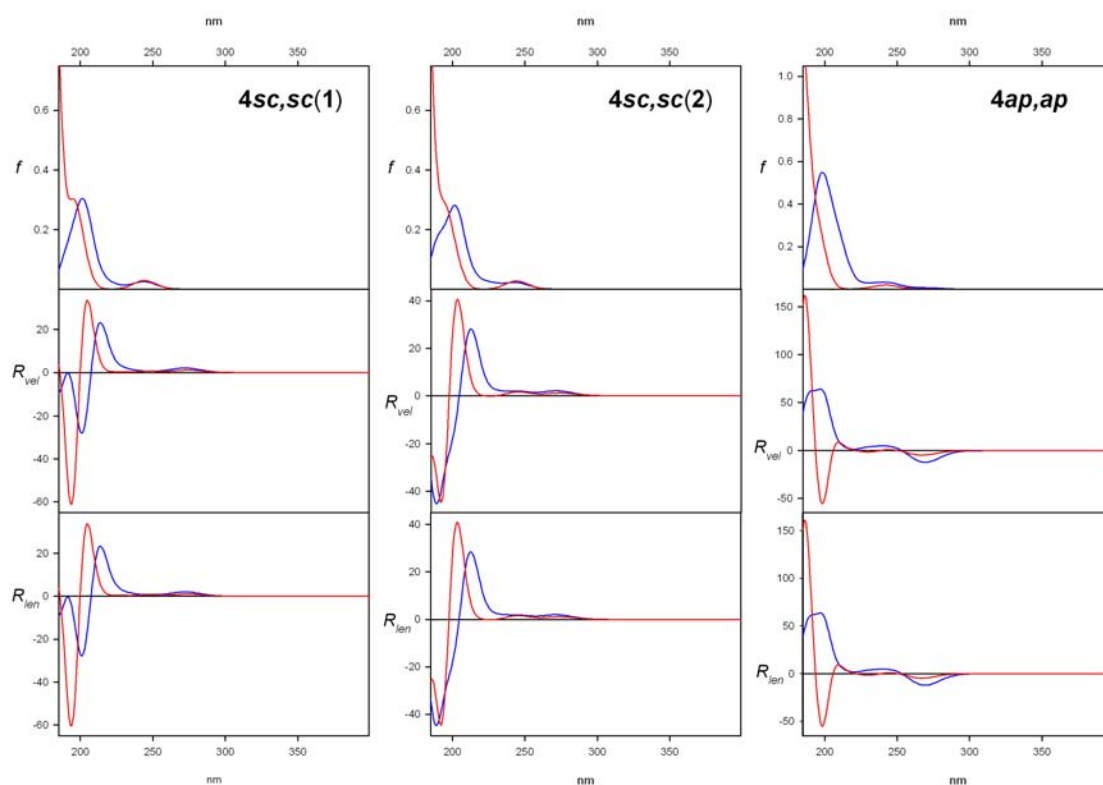


Figure G. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/BPLYP/6-311++G(2D,2P) level of theory (red lines) UV (upper panels) and CD (middle panels – velocity; lower panels – length method) spectra for individual conformers of **4**. All calculated spectra were wavelength corrected to match the experimental UV spectrum of **4**.

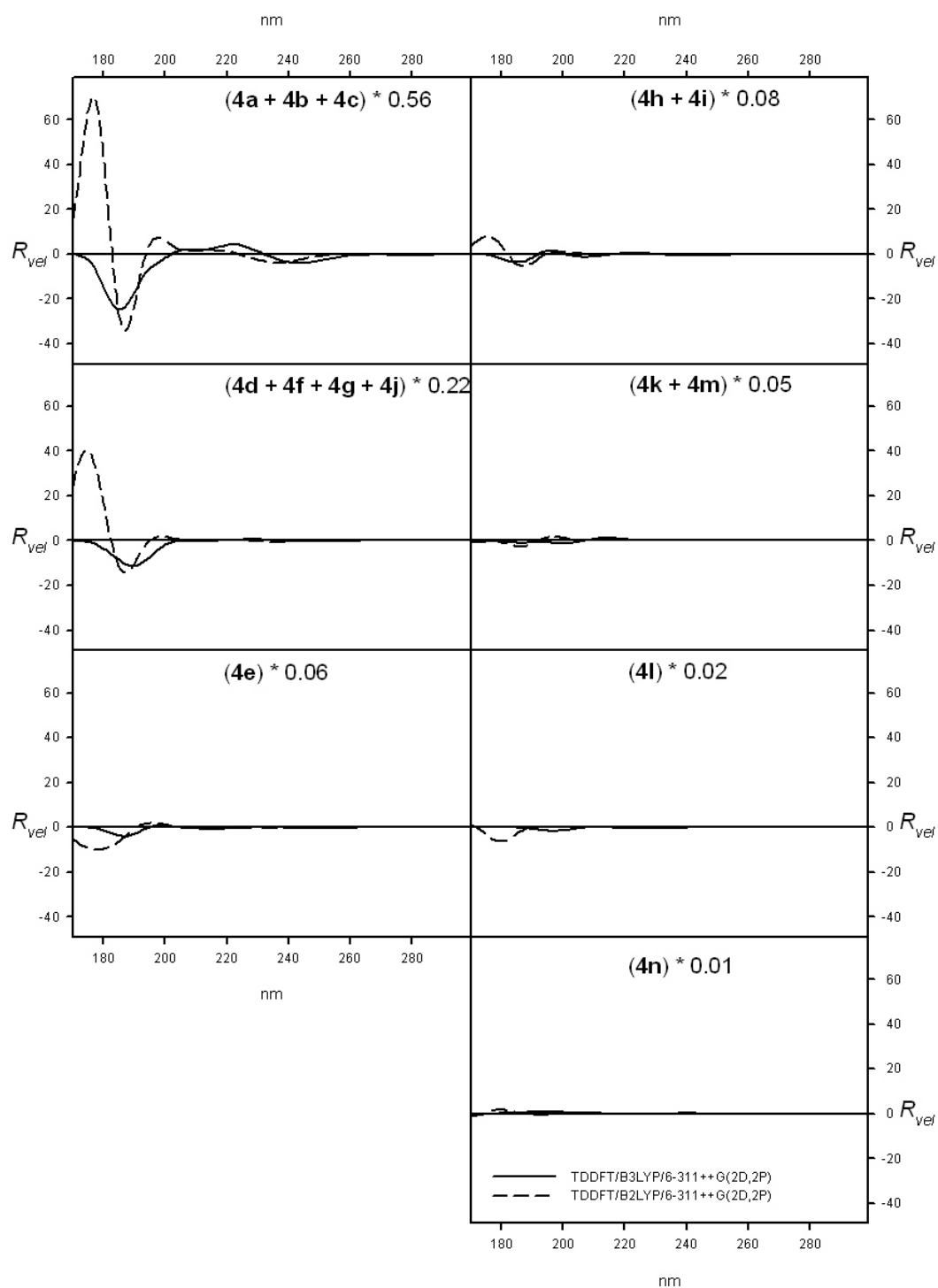


Figure H. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (solid lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (dashed lines) UV (upper panels) CD spectra for families of structurally similar conformers of compound **4**, normalized to their relative populations (wavelength not corrected).

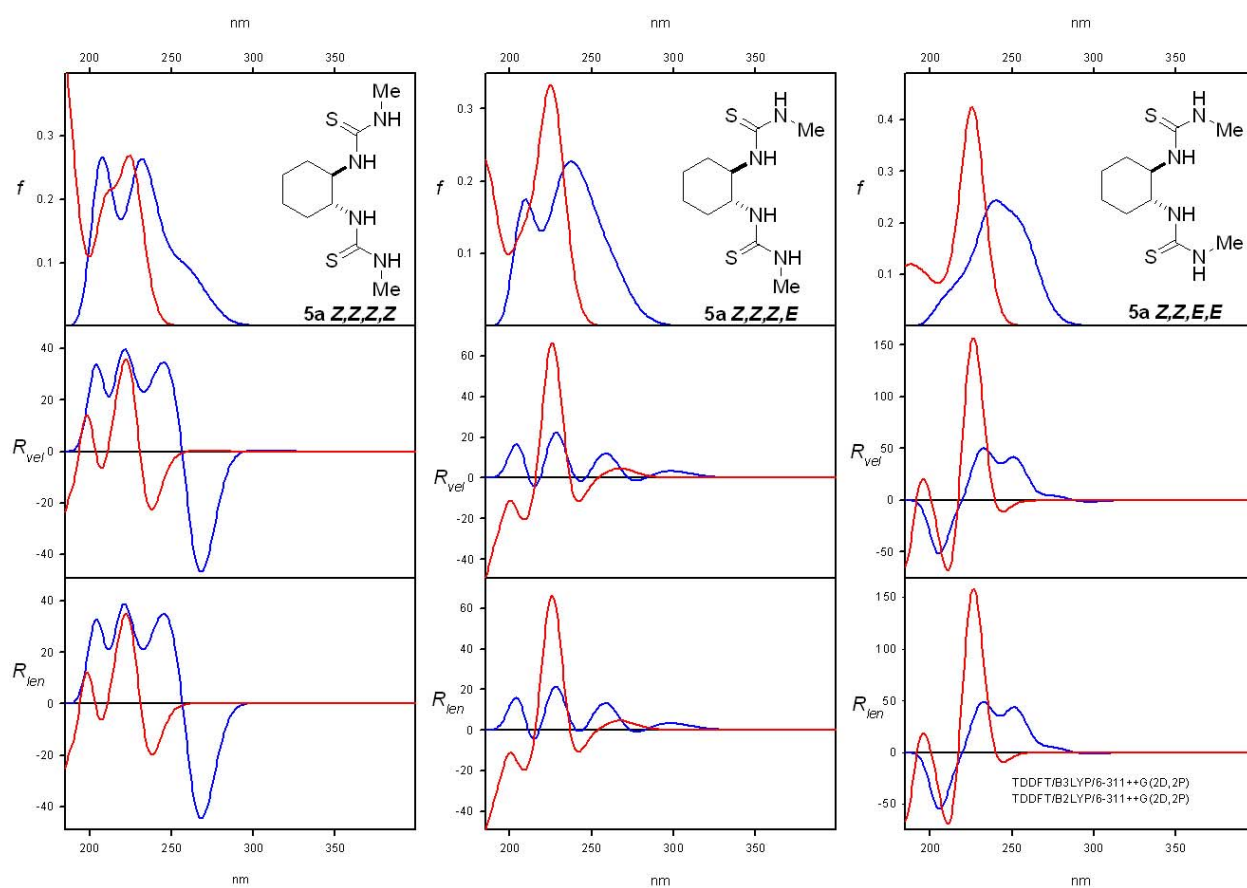


Figure I. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV (upper panels) and CD (middle panels – velocity; lower panels – length method) spectra for individual conformers of **5a** (wavelength not corrected).

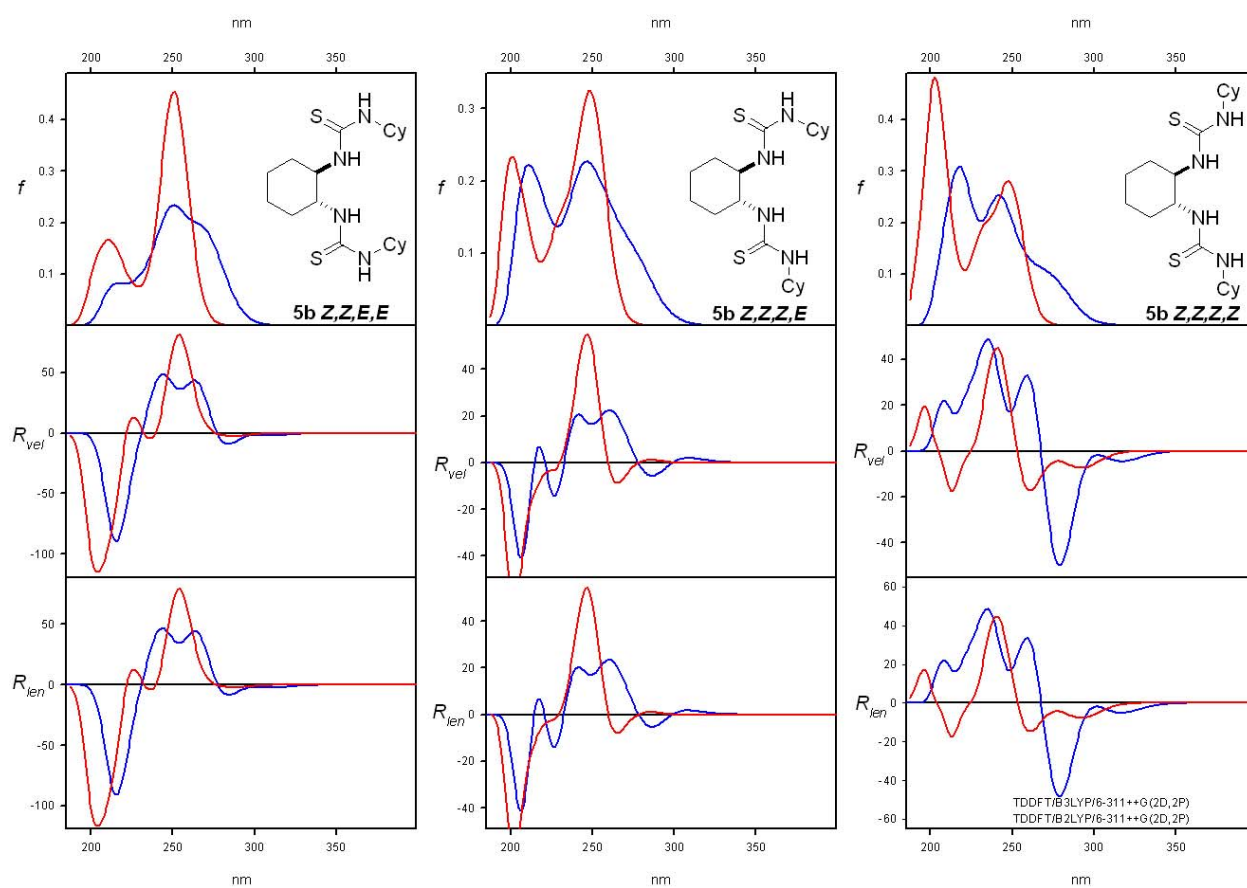


Figure J. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV (upper panels) and CD (middle panels – velocity; lower panels – length method) spectra for individual conformers of **5b**. All calculated spectra were wavelength corrected to match the experimental UV spectrum of **5b**.

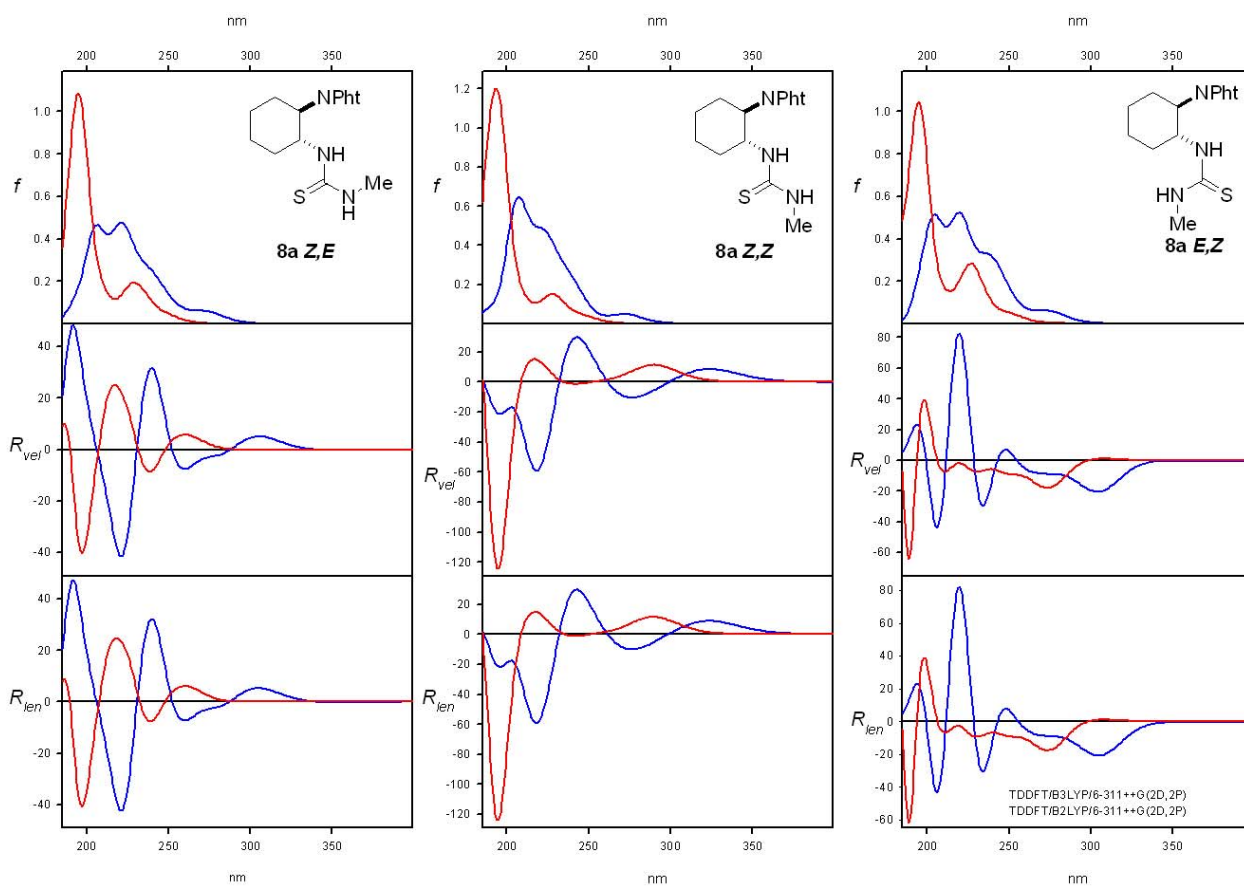


Figure K. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV (upper panels) and CD (middle panels – velocity; lower panels – length method) spectra for individual conformers of **8a** (wavelength not corrected).

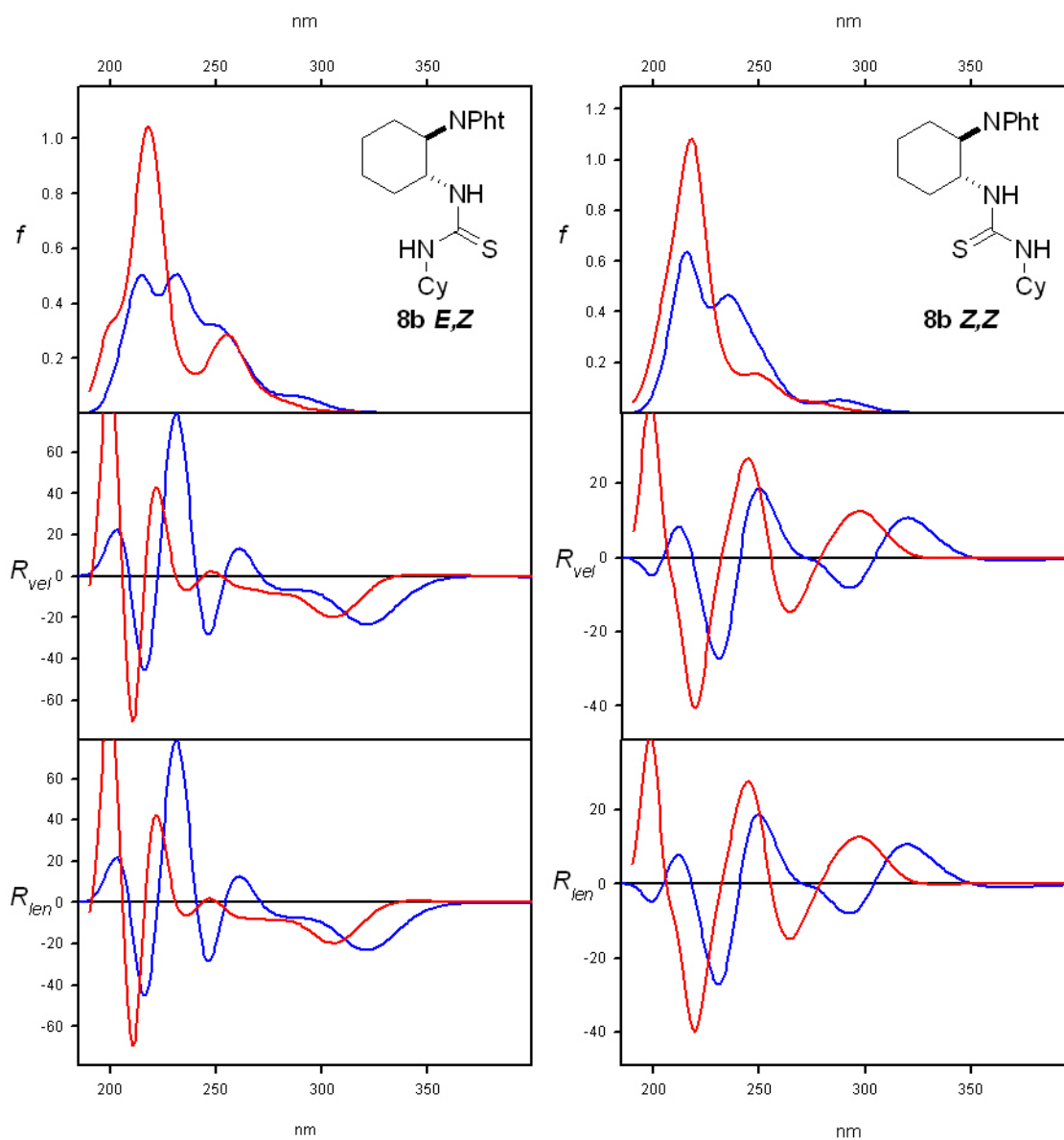


Figure L. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV (upper panels) and CD (middle panels – velocity; lower panels – length method) spectra for individual conformers of **8b**. All calculated spectra were wavelength corrected to match the experimental UV spectrum of **8b**.

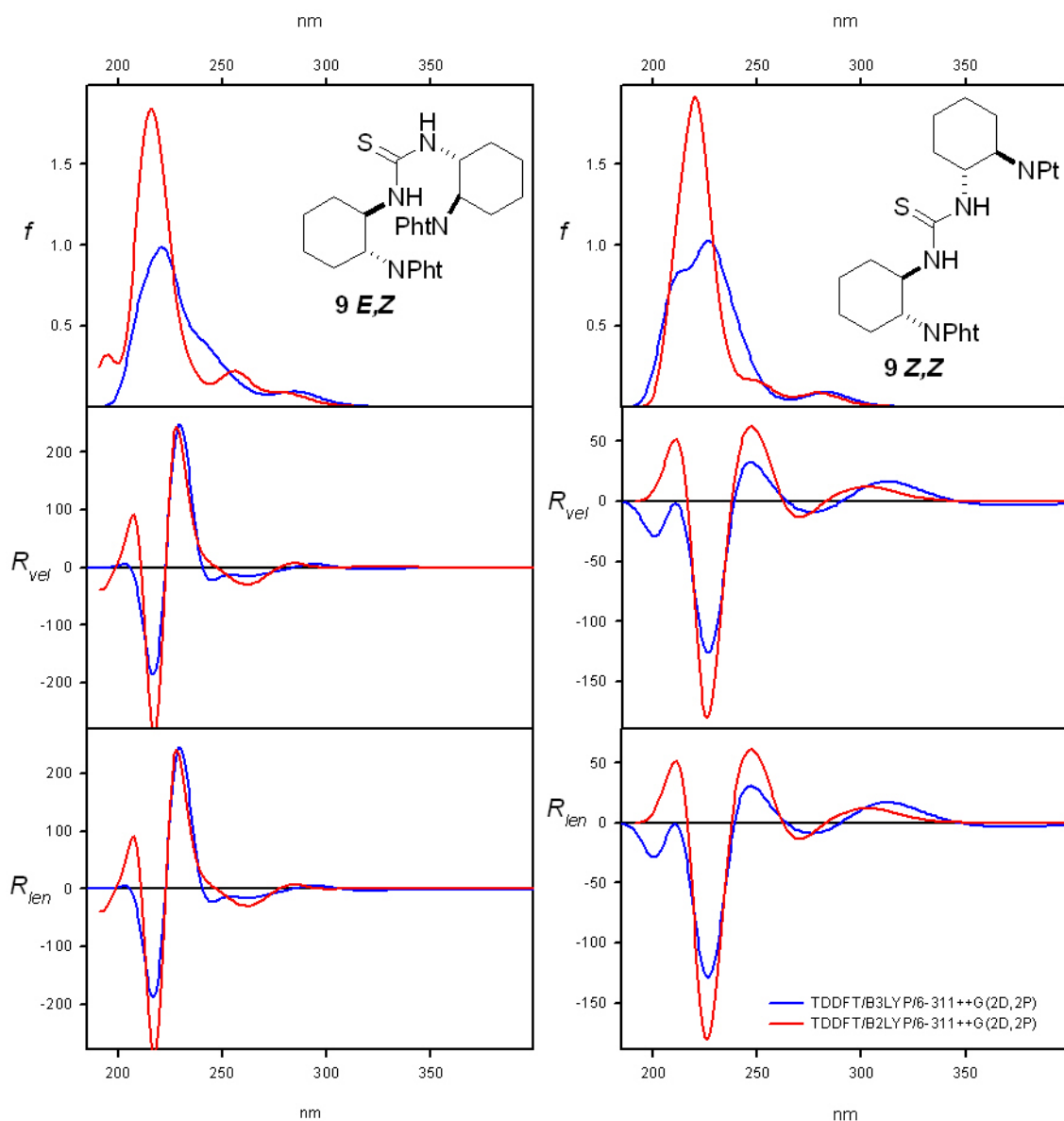


Figure M. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines) UV (upper panels) and CD (middle panels – velocity; lower panels – length method) spectra for individual conformers of **9**. All calculated spectra were wavelength corrected to match the experimental UV spectrum of **9**.

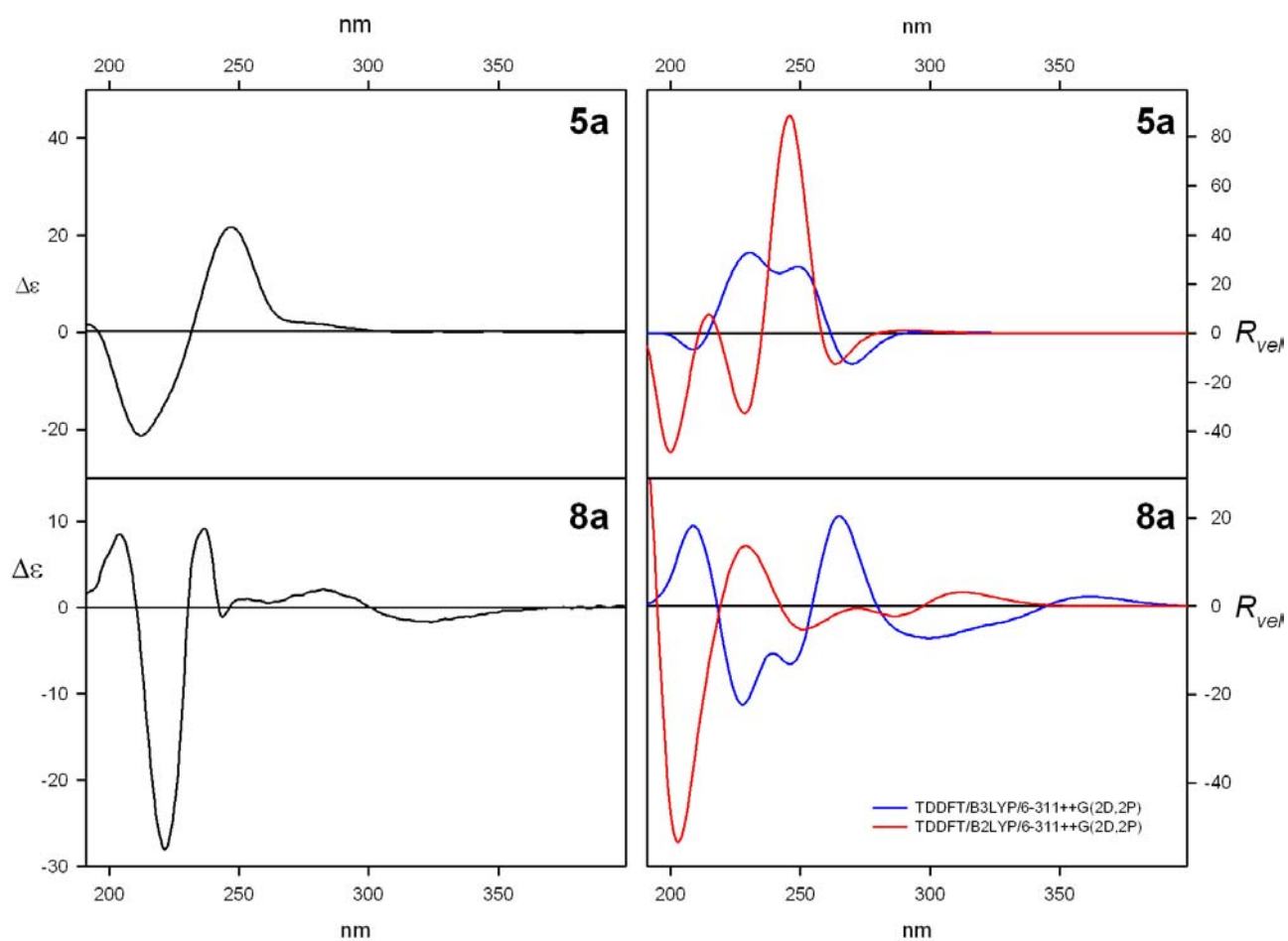
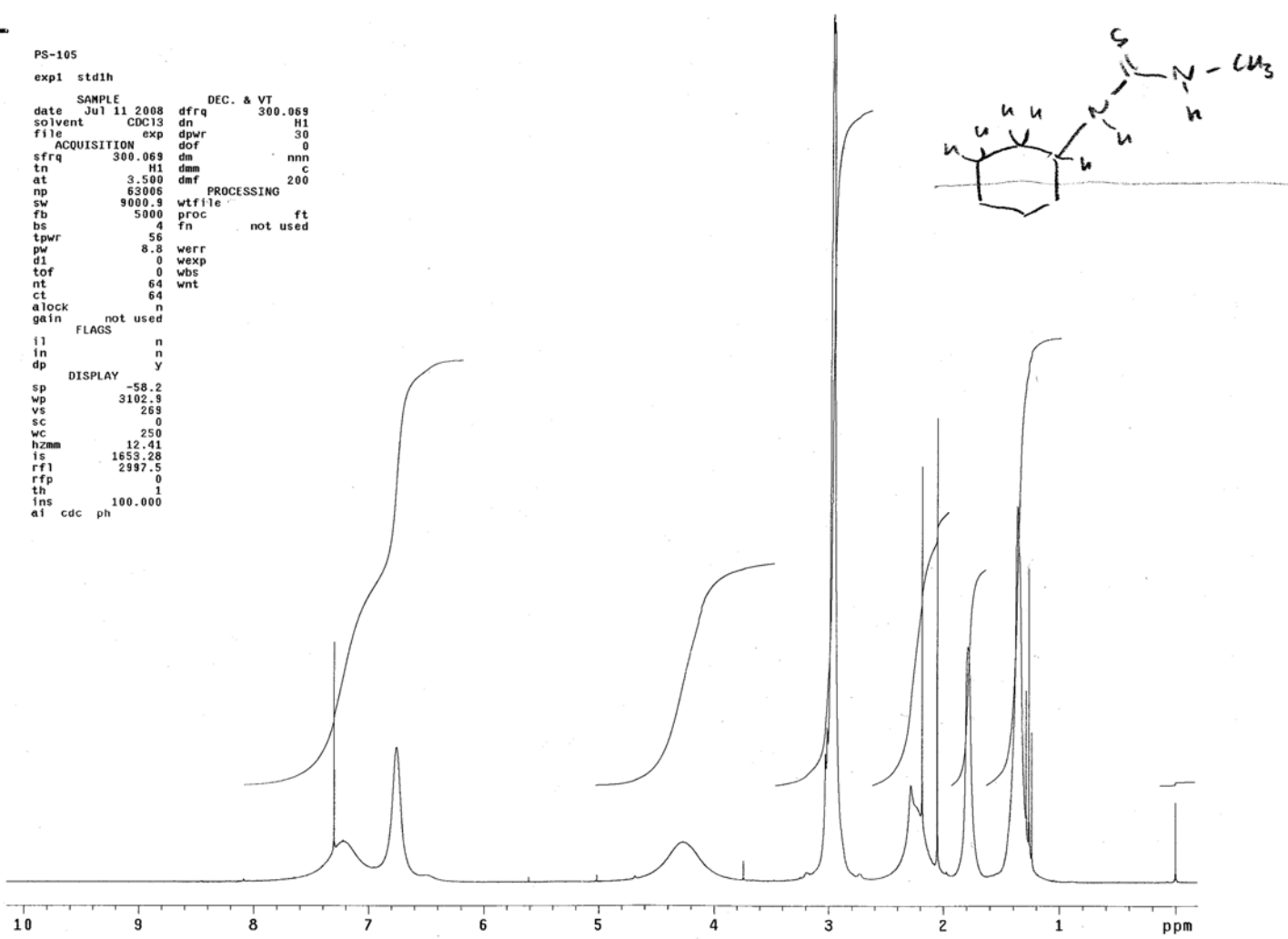


Figure N. Experimental (black lines, left panels) and calculated at TDDFT/B3LYP/6-311++G(2D,2P) level of theory (blue lines) and TDDFT/B2LYP/6-311++G(2D,2P) level of theory (red lines, right panels) CD spectra for of **5a** (upper panels) and **8a** (lower panels). All calculated spectra were wavelength corrected to match the experimental UV spectra of **5a** and **8a**.

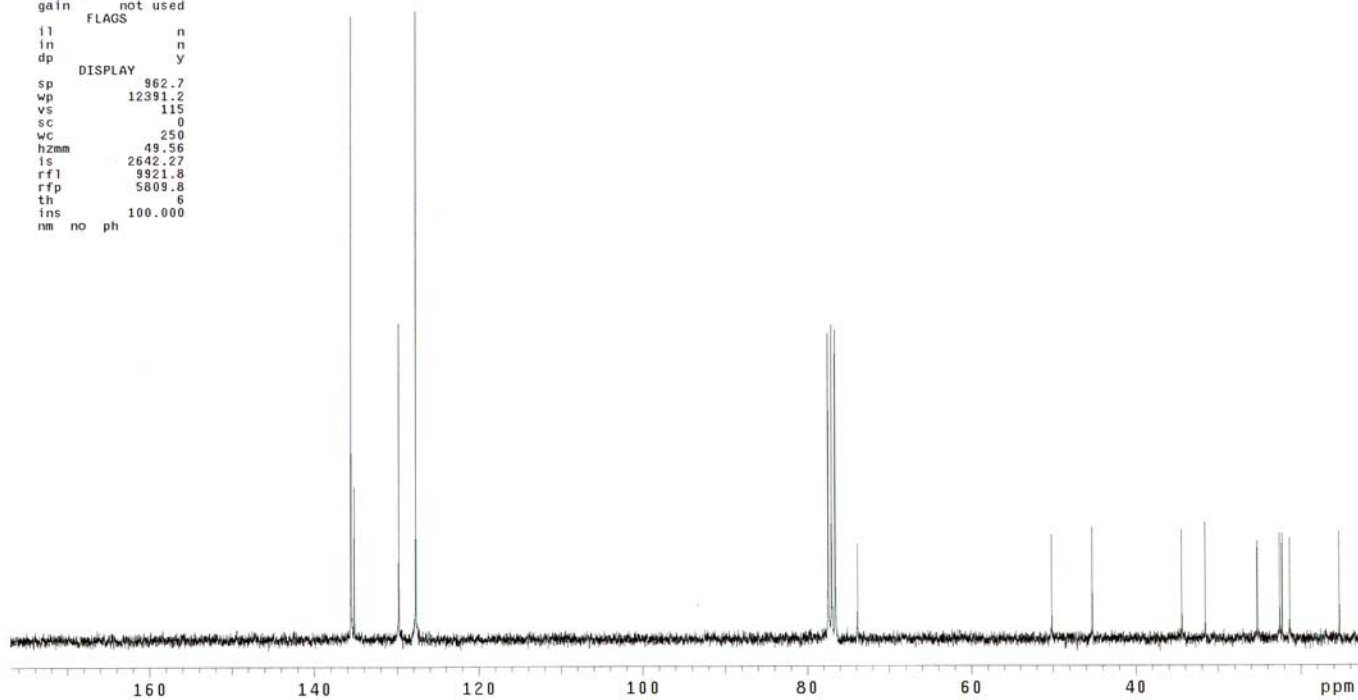
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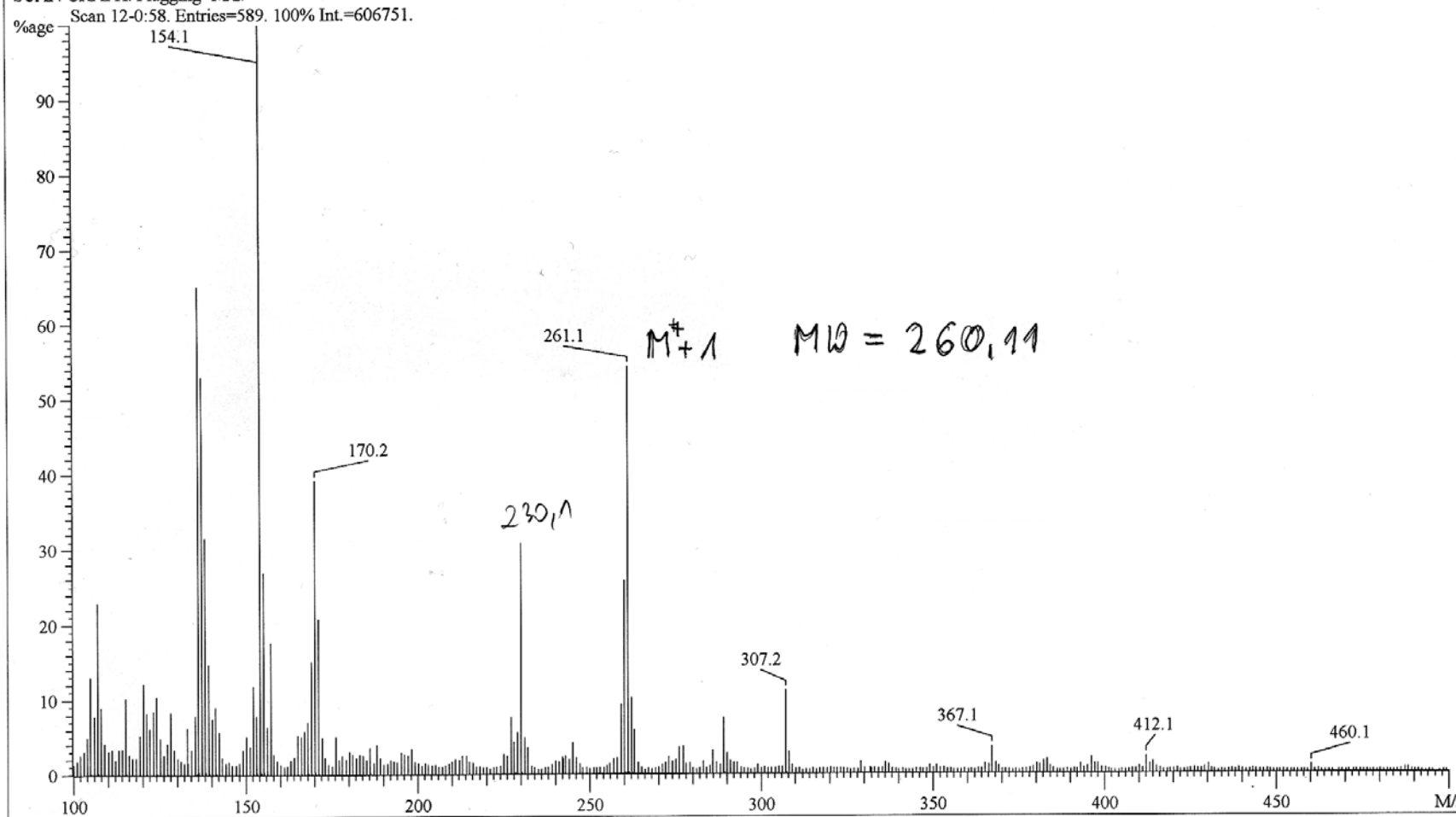
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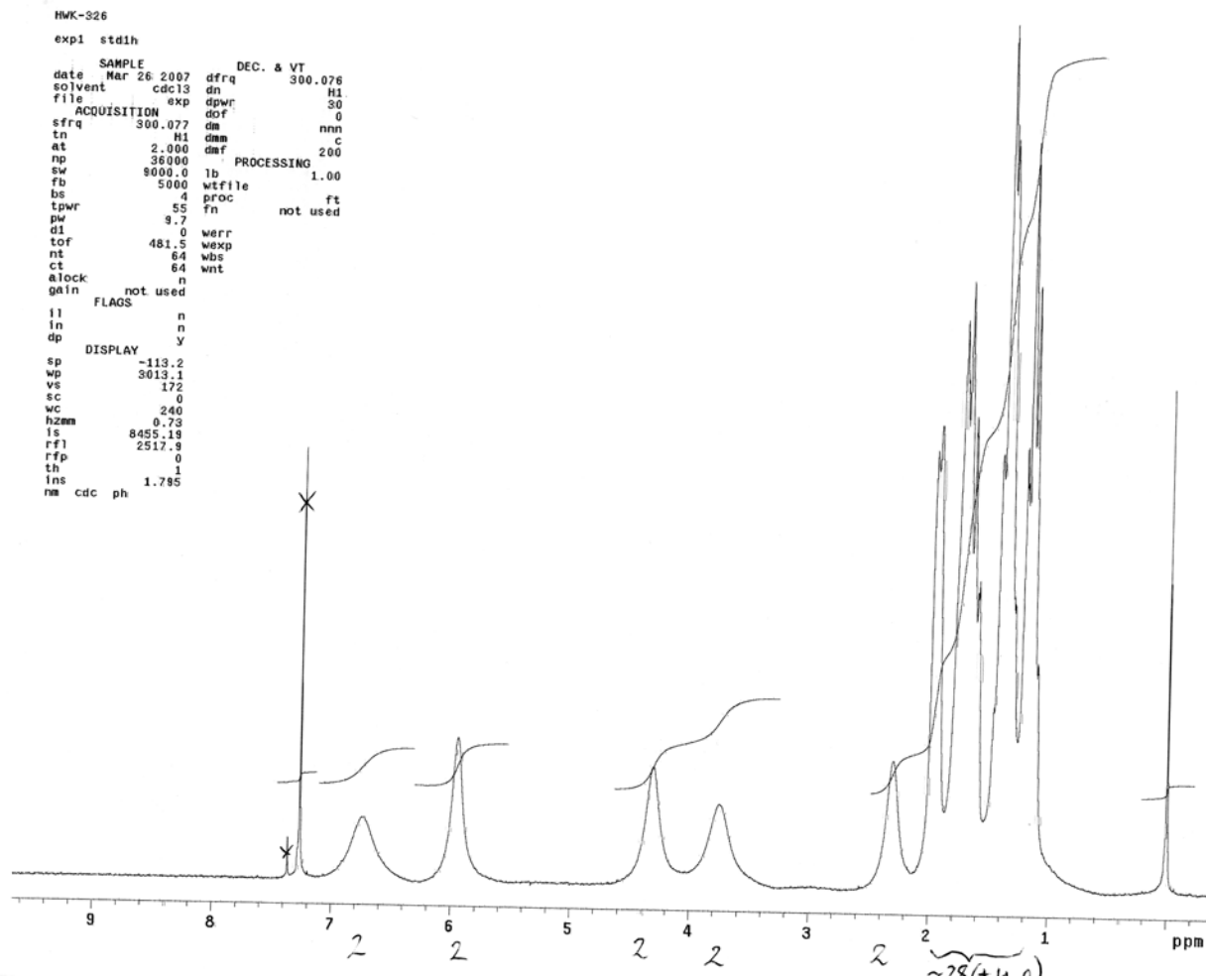


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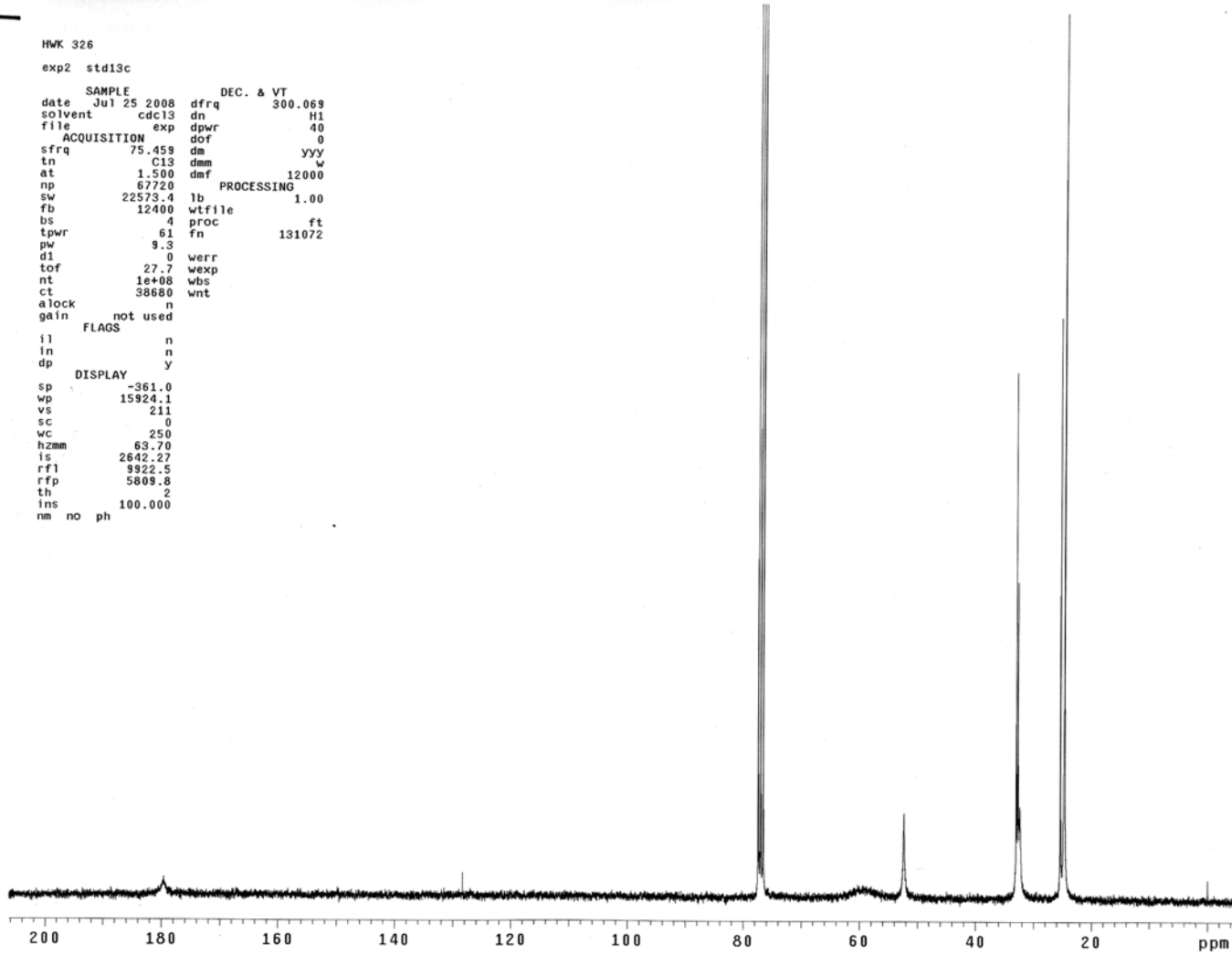
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HWK 326

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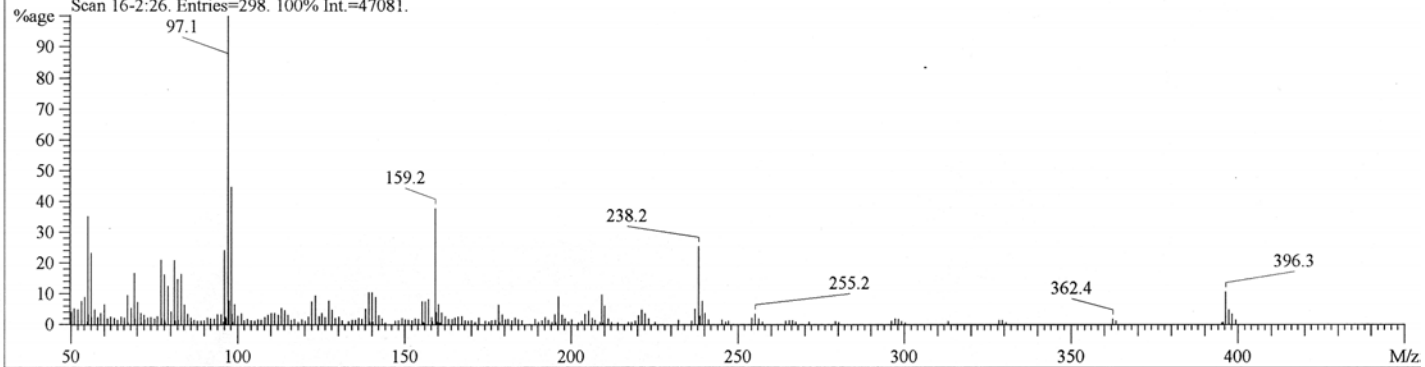
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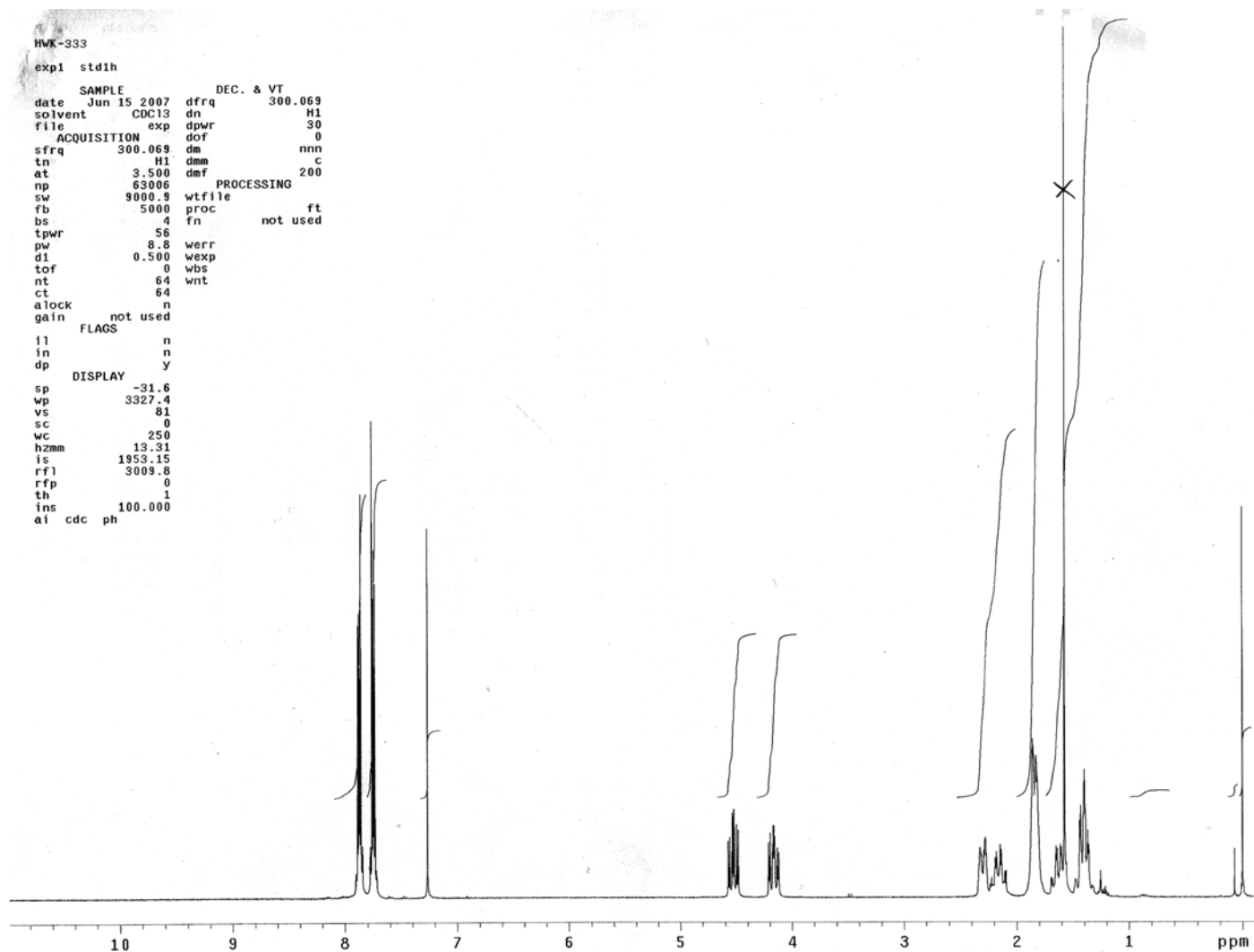
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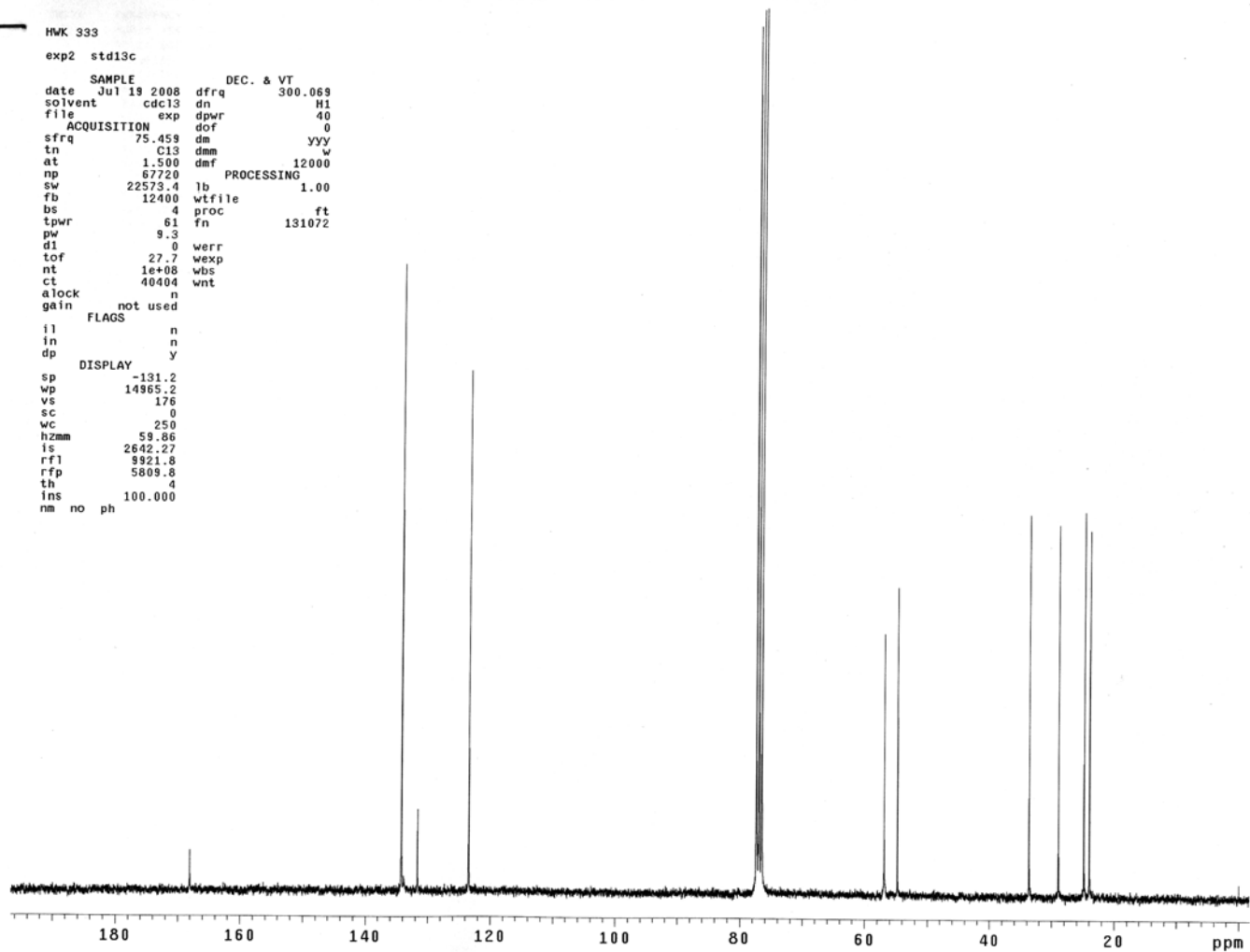
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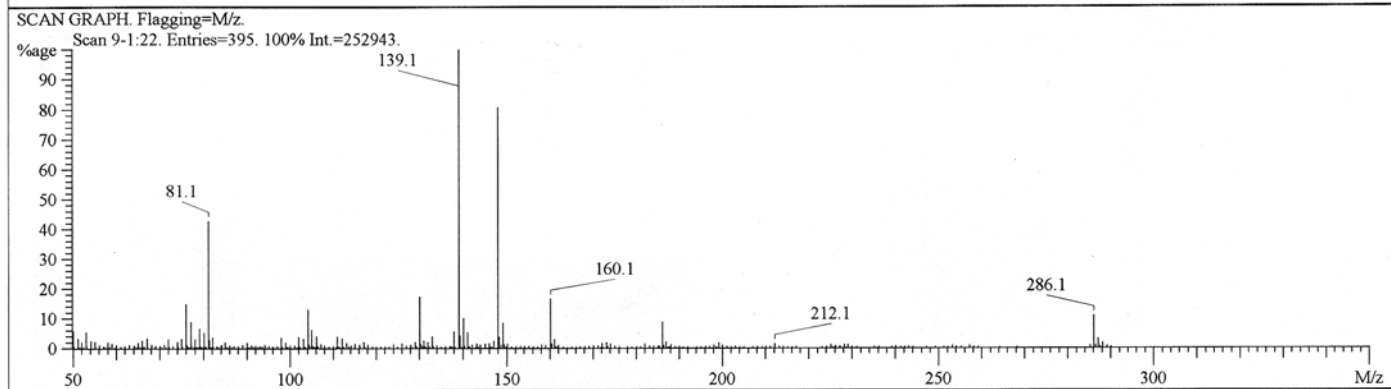
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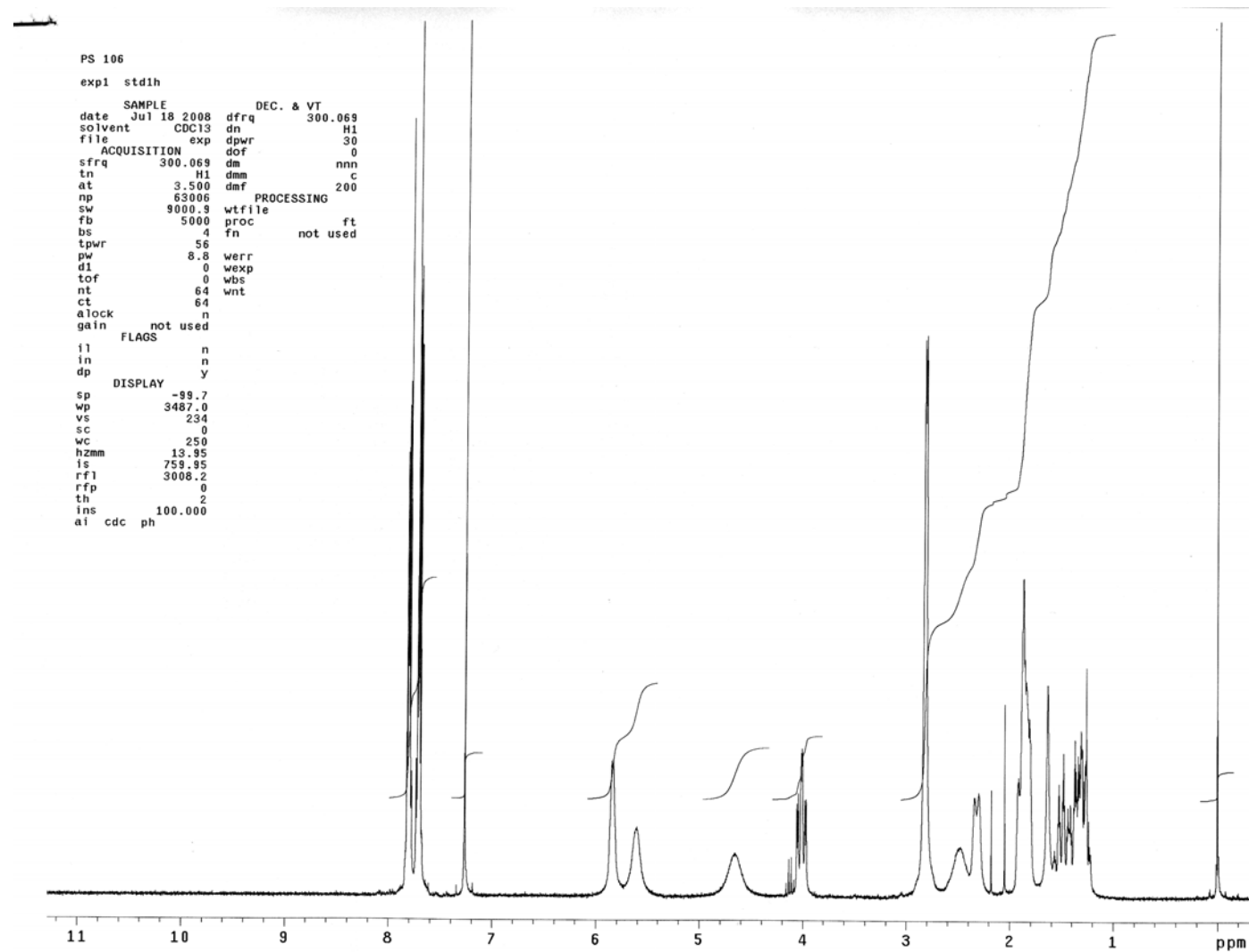
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Compound 8a

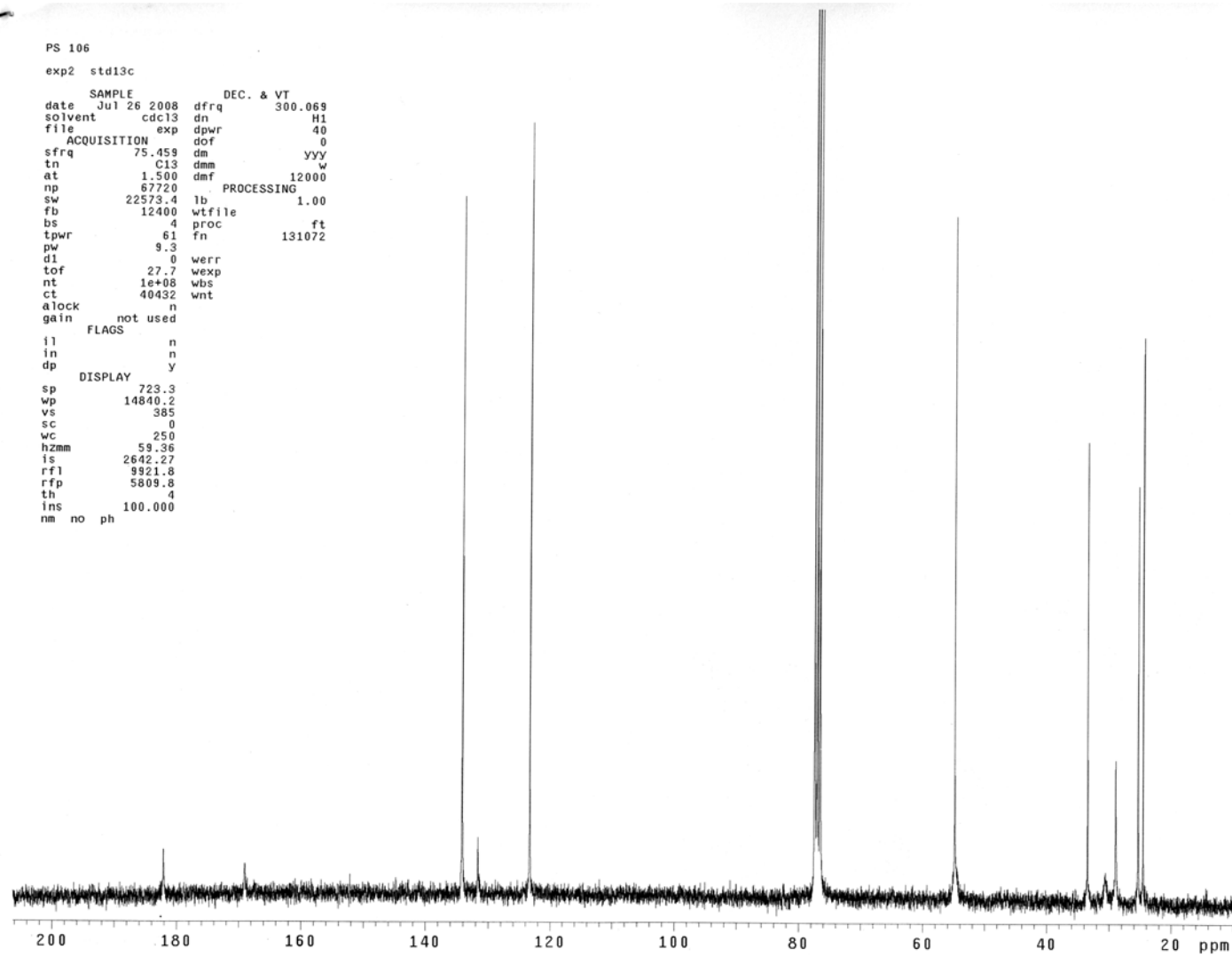


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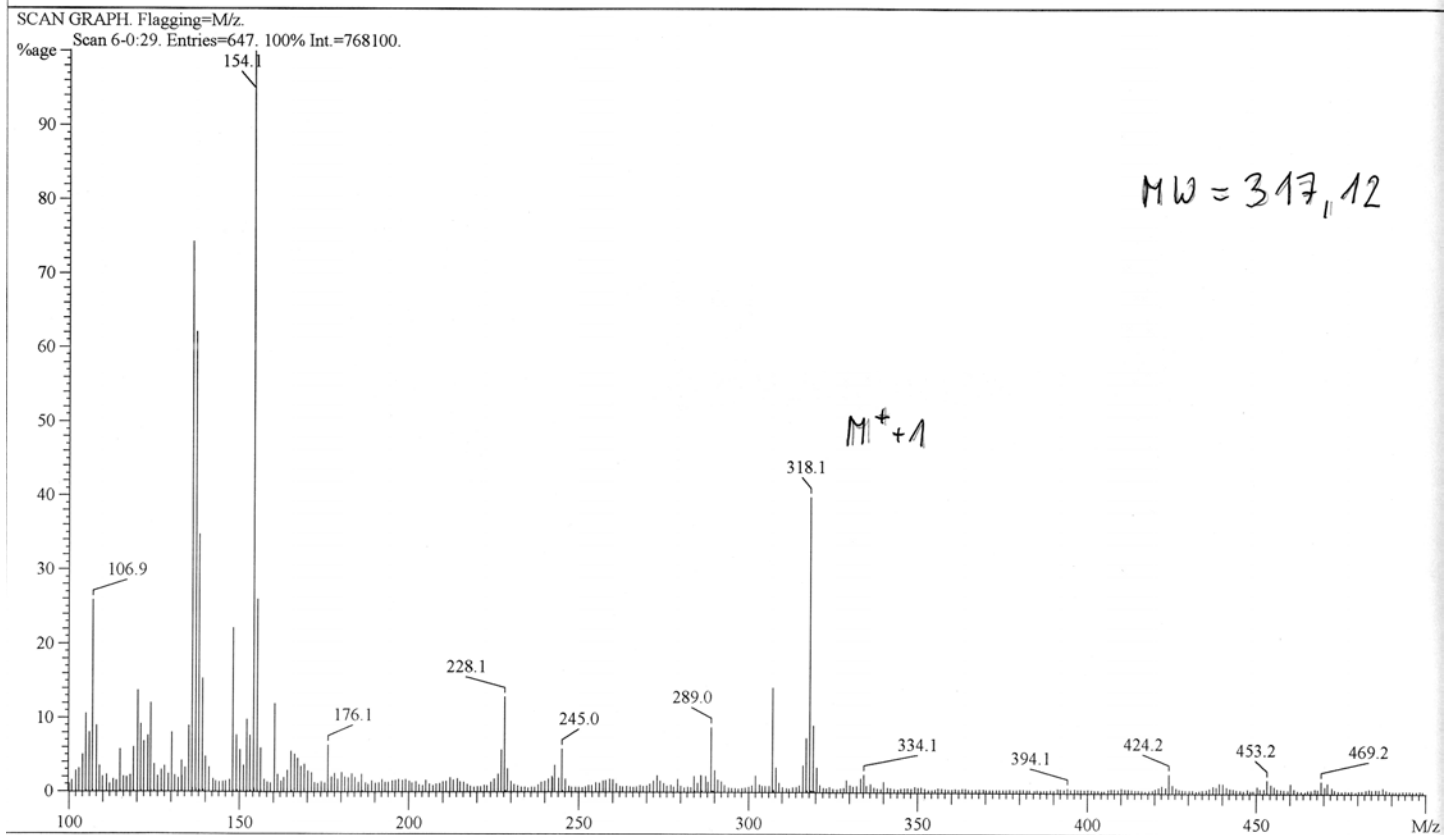
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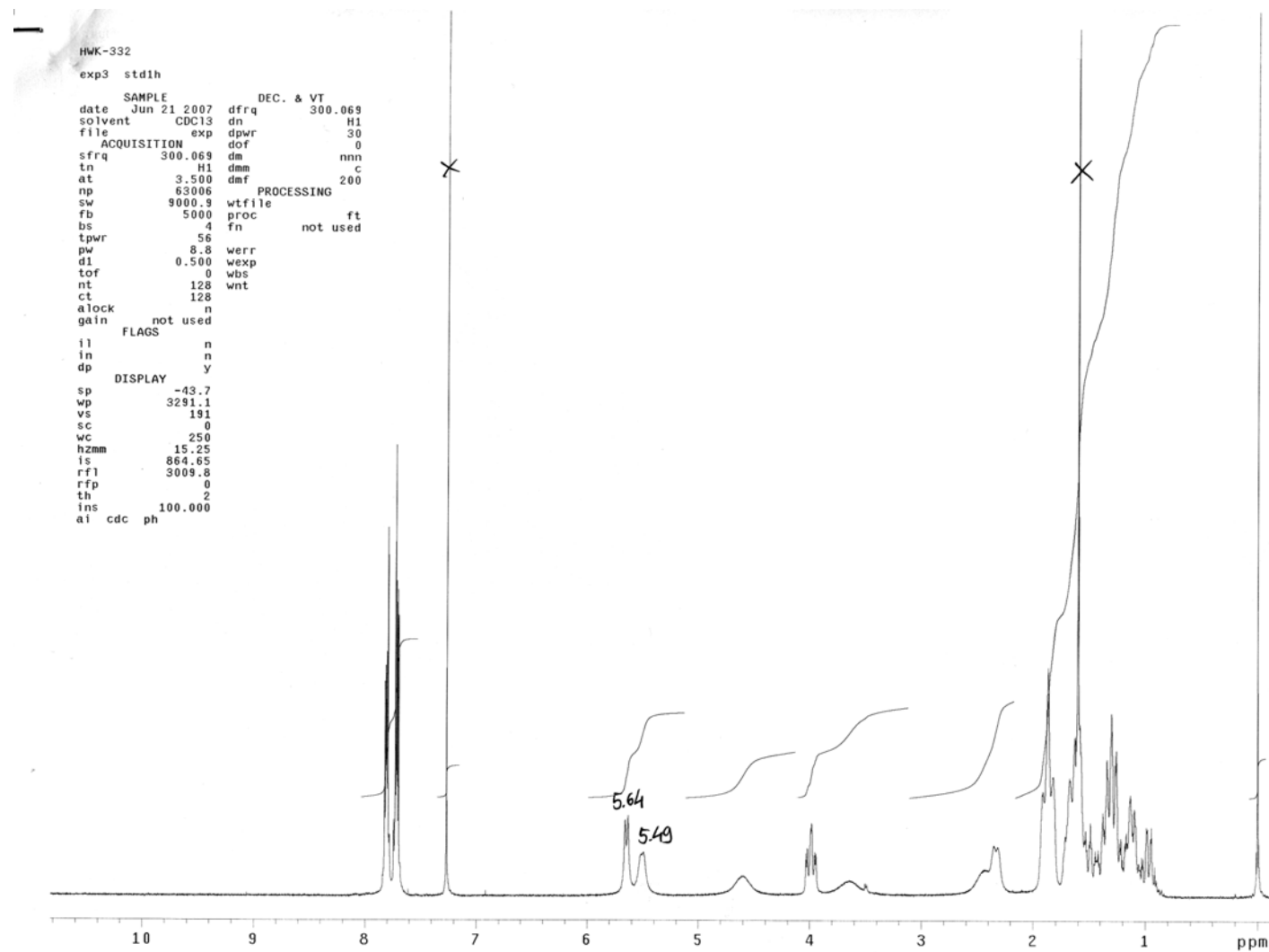
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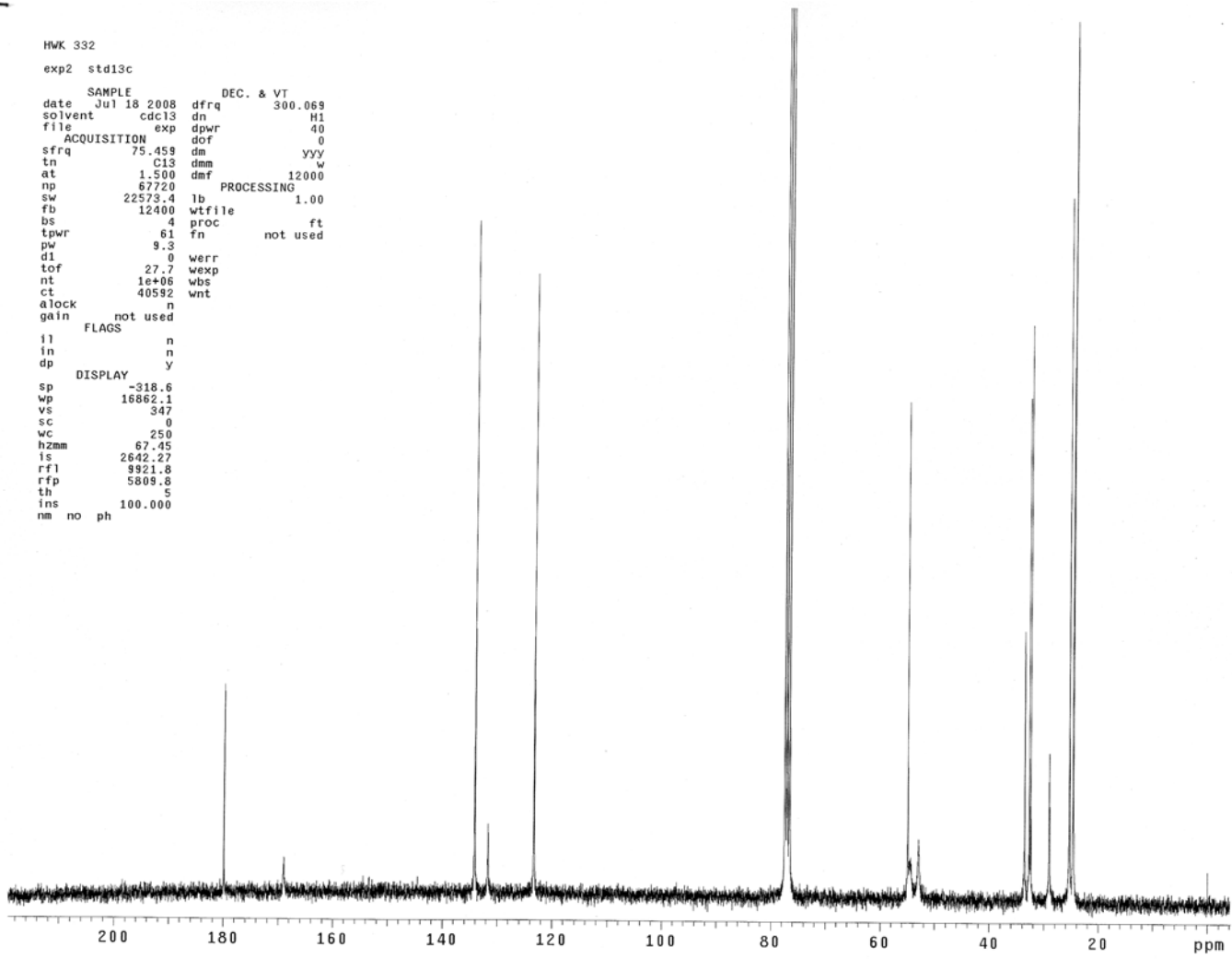
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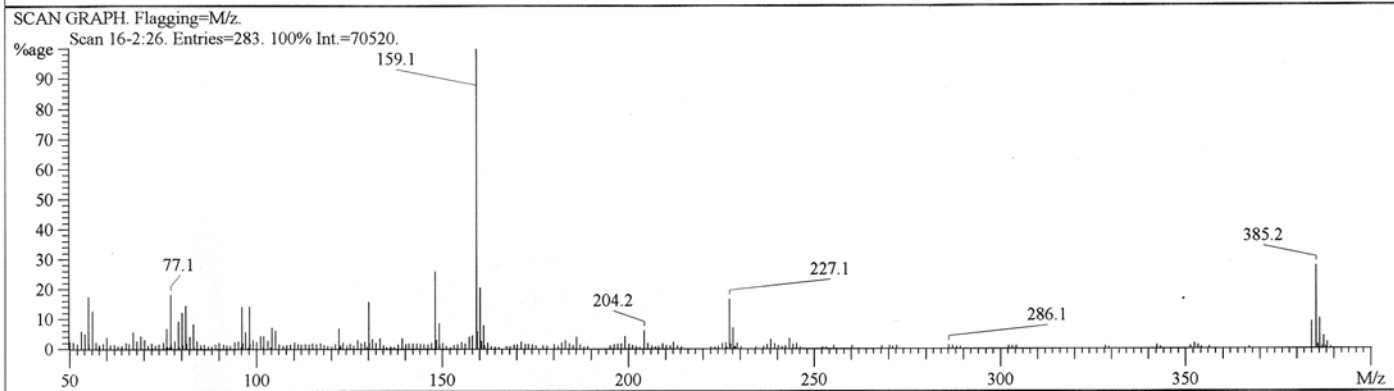
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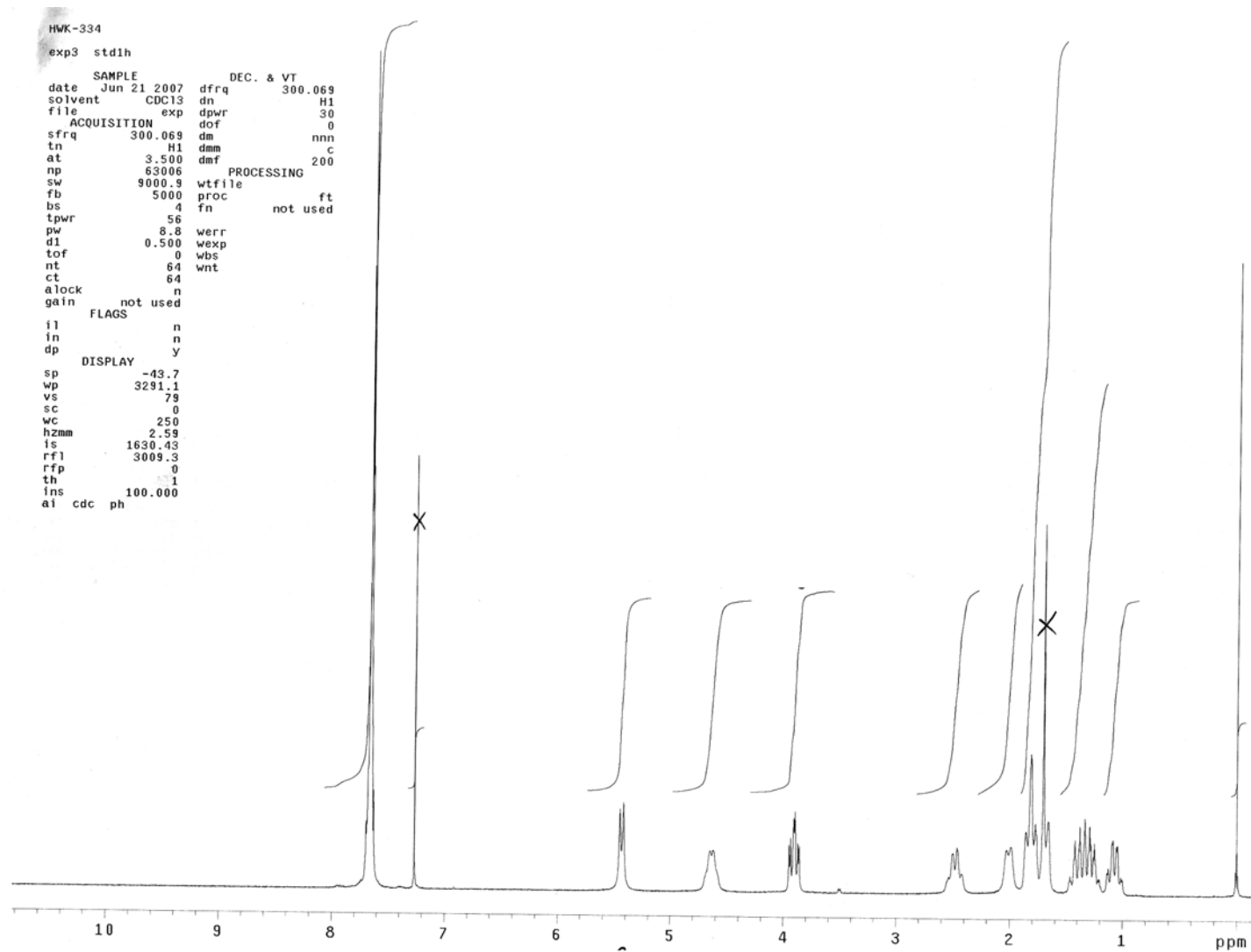
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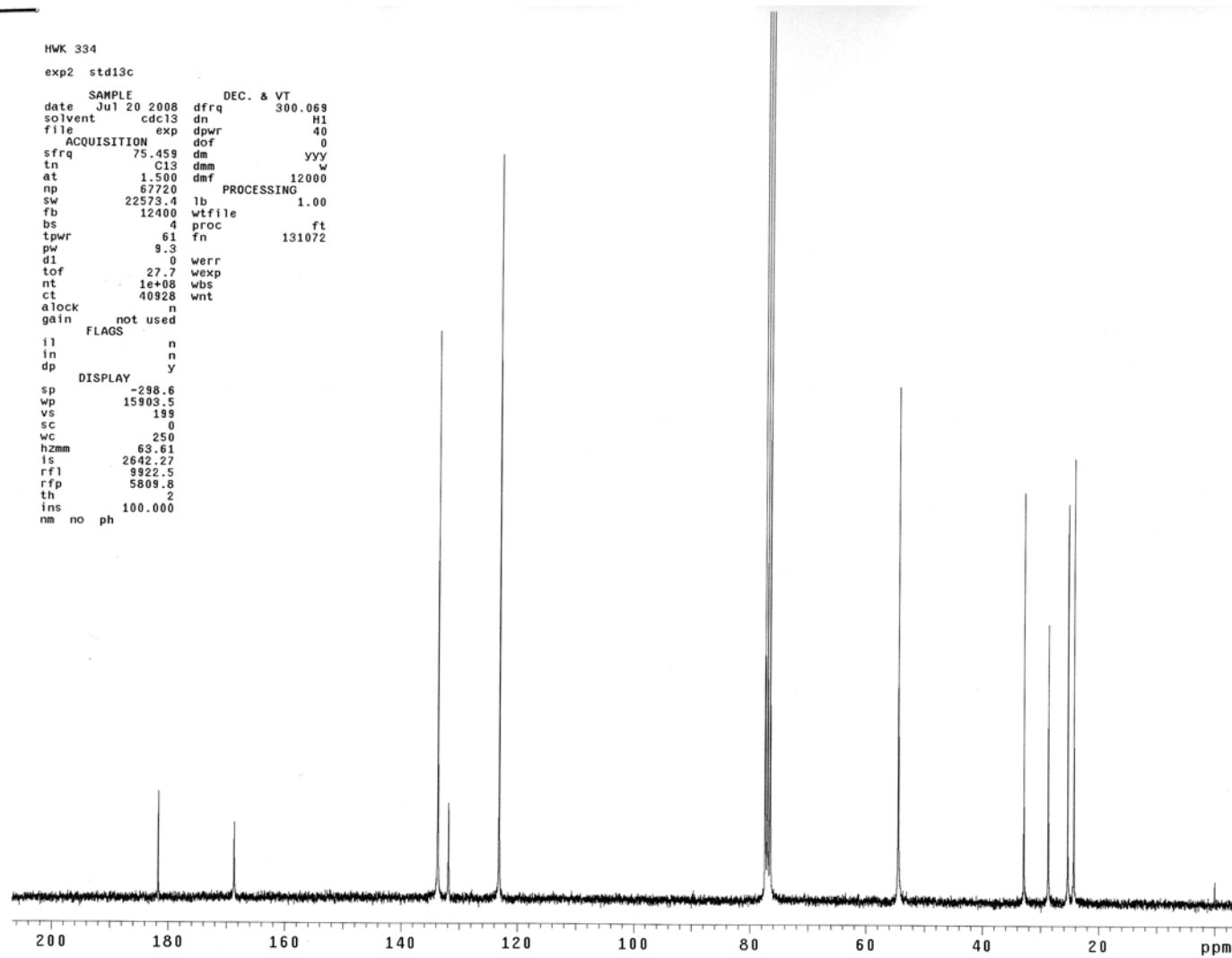
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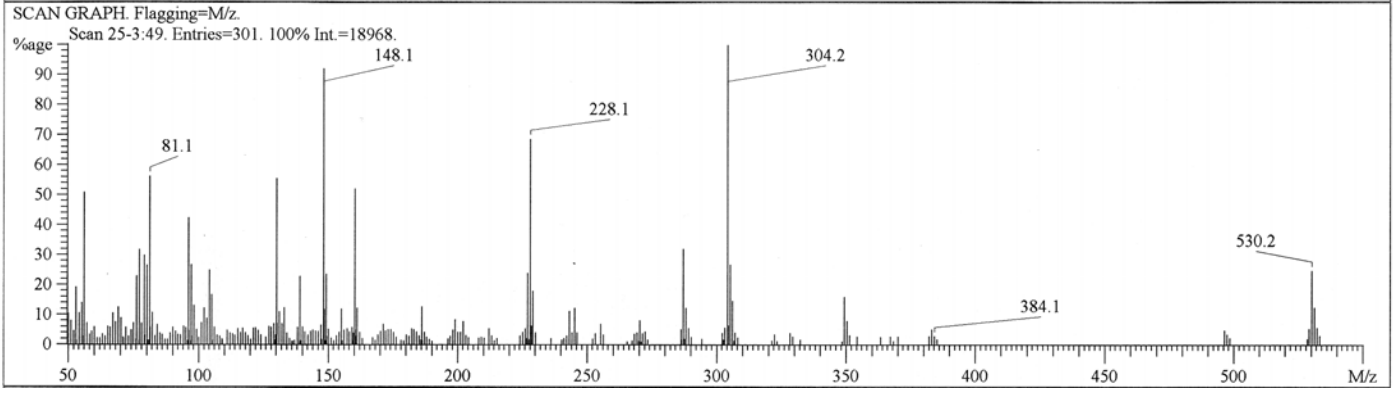
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d1 0          werr
tof 27.7      wexp
nt 1e+08     wbs
ct 40928     wnt
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -298.6
wp 15903.5
vs 199
sc 0
wc 250
hzmm 63.61
is 2642.27
rfl 9922.5
rfp 5809.8
th 2
ins 100.000
nm no ph

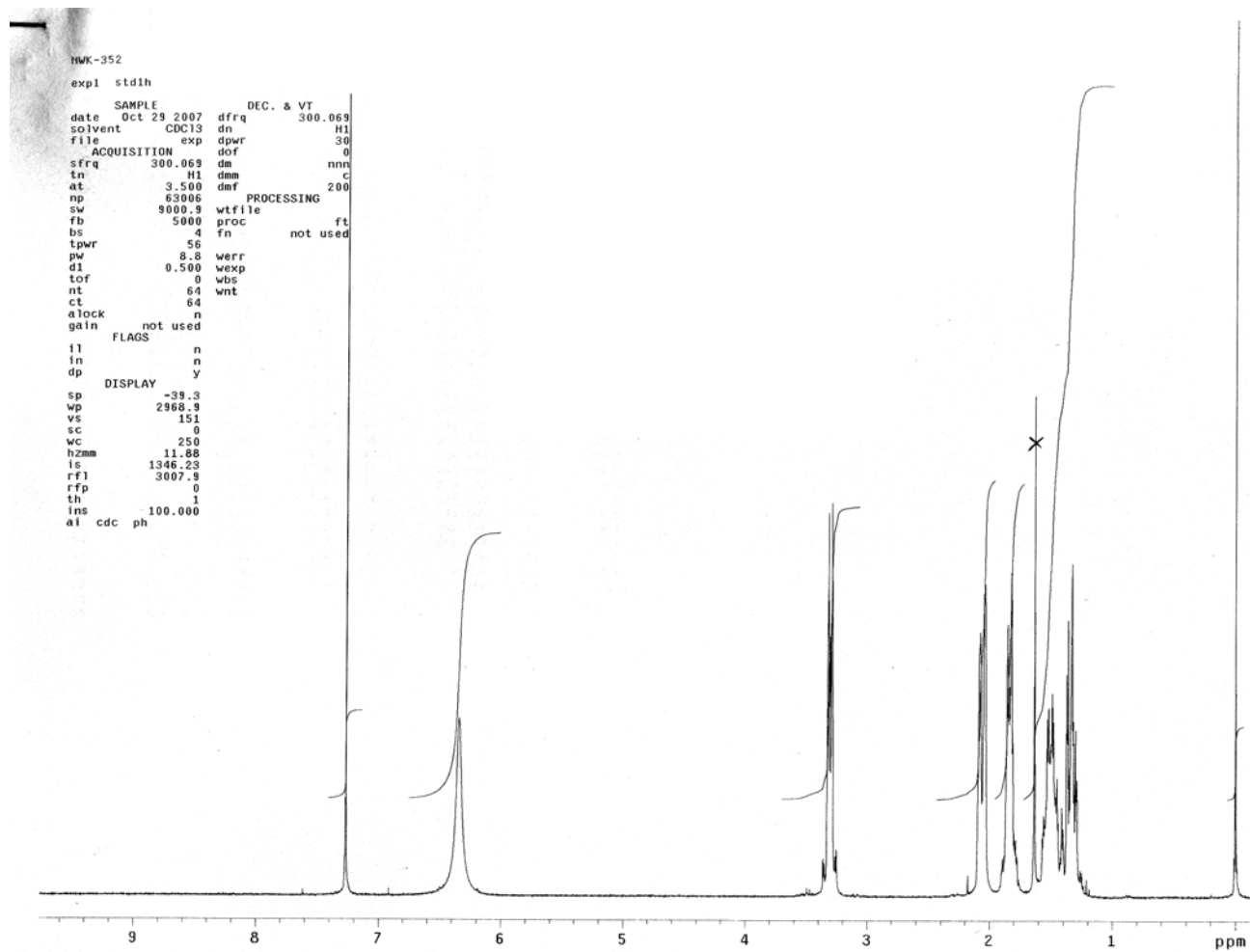
```



File Name : c:\samples\dse12959.mss
Creation Date/Time : 5-12-2007 at 12:12:49
File Type : Lo-Res Mass Data (Centroid)
File Source : Acquired on MASPEC system [msw/96A2]
File Title : 3
Operator : D.Siatkowska
Instrument : AMD 402



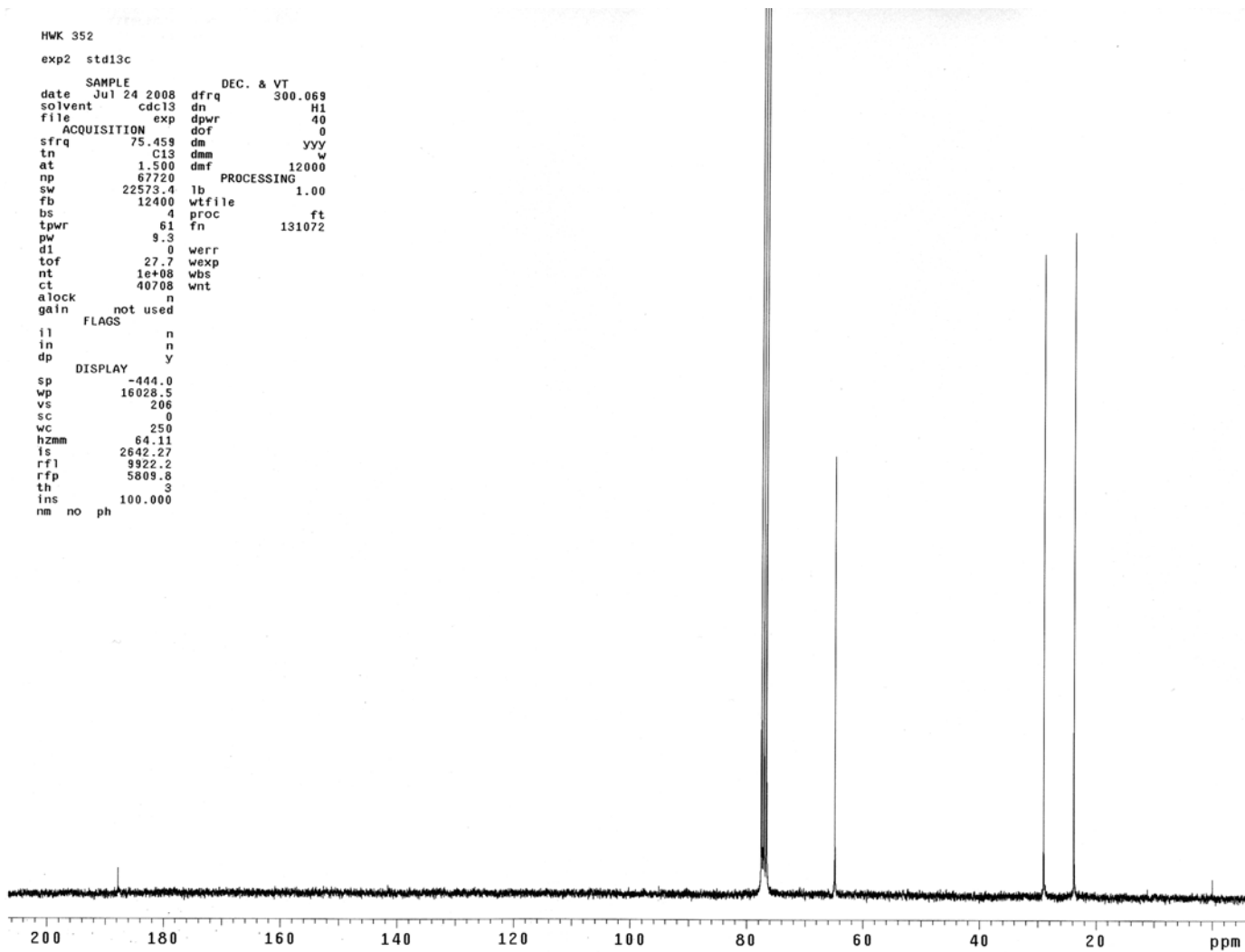
Compound 10



HWK 352

exp2 std13c

```
SAMPLE          DEC. & VT
date Jul 24 2008 dfrq 300.069
solvent cdc13   dn      H1
file    exp    dpwr   40
ACQUISITION    dof    0
sfrq 75.459   dm      yy
tn    C13     dmm     w
at    1.500   dmf     12000
np    67720
sw    22573.4 lb      1.00
fb    12400  wfile
bs    4      proc    ft
tpwr  61    fn      131072
pw    9.3
d1    0     werr
tof   27.7  wexp
nt    1e+08 wbs
ct    40708 wnt
alock n
gain  not used
FLAGS
il    n
in    n
dp    y
DISPLAY
sp    -444.0
wp    16028.5
vs    206
sc    0
wc    250
hzmm  64.11
fs    2642.27
rfl   9922.2
rff   5809.8
th    3
ins   100.000
nm no ph
```



File Name : c:\samples\dse12842.mss
Creation Date/Time : 5-11-2007 at 13:58:56
File Type : Lo-Res Mass Data (Centroid)
File Source : Acquired on MASPEC system [msw/96A2]
File Title : HWK-352
Operator : D.Siatkowska
Instrument : AMD 402

SCAN GRAPH. Flagging=M/z.
Scan 14-2.08. Entries=193. 100% Int.=101898.

