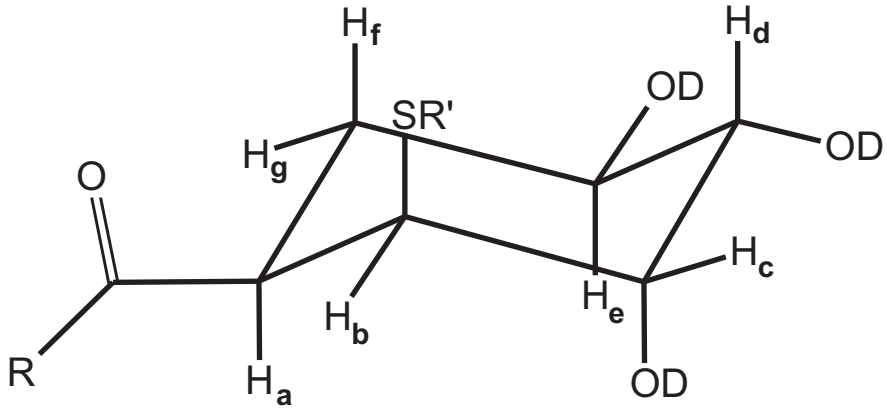
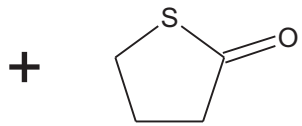
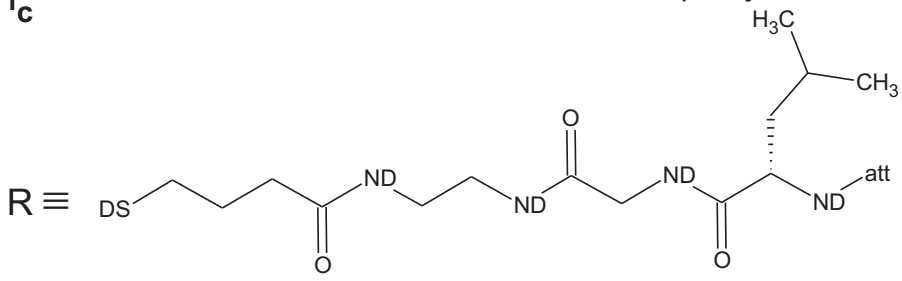




impurity



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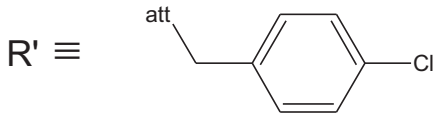
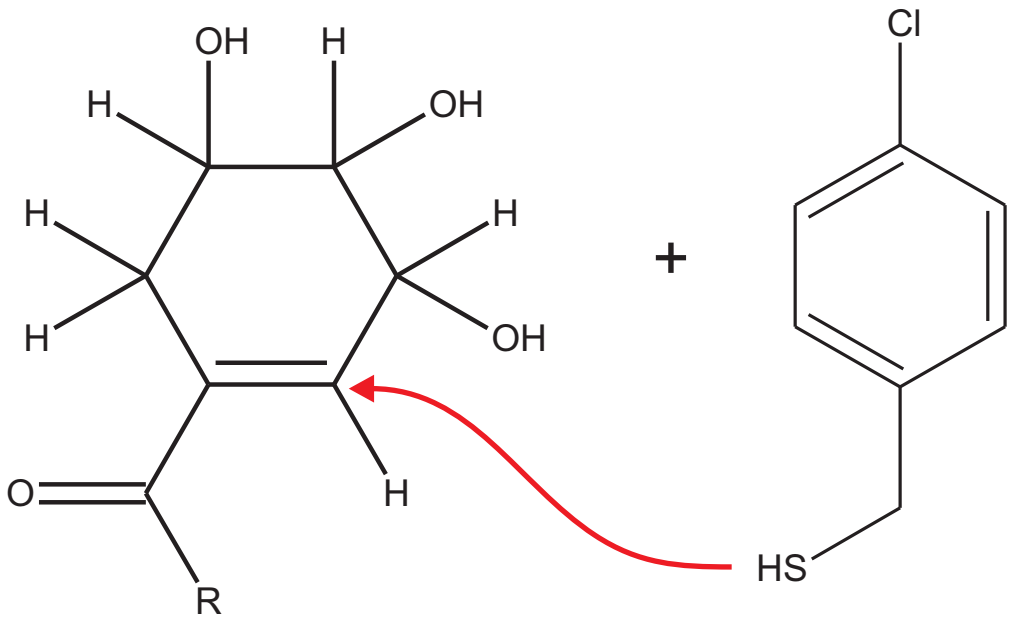
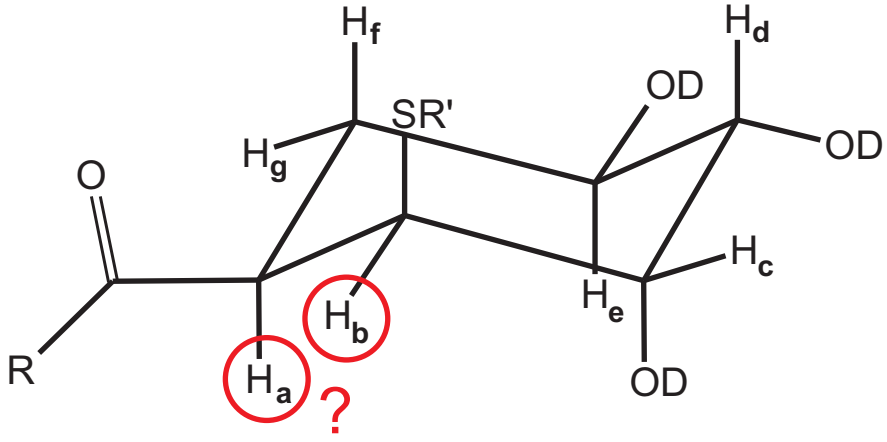
Kiessling group

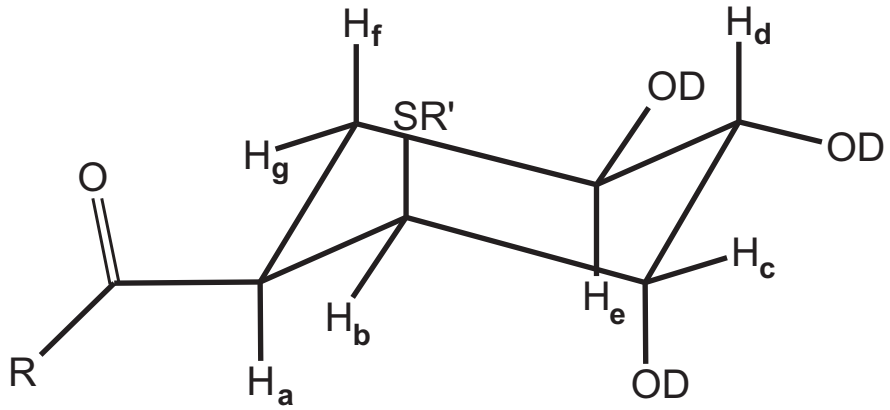






The question to be resolved is the stereochemistry following the thiol addition. This question primarily reduces to determining the axial or equatorial nature of H_a and H_b in the resulting cyclic structure.

TOCSY1D will provide definitive assignments of all the ring protons, even though some of these protons are severely overlapped by the substituent protons.



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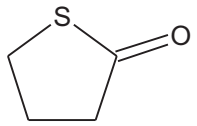
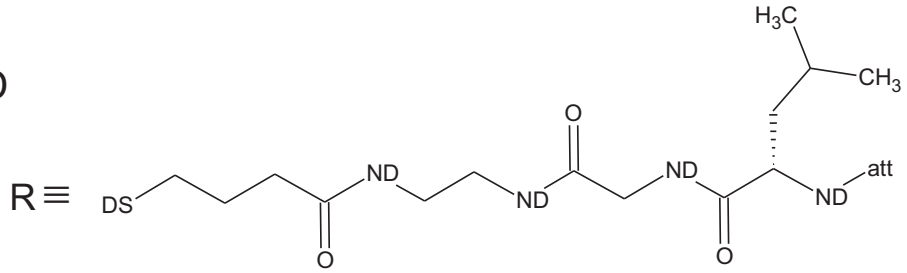
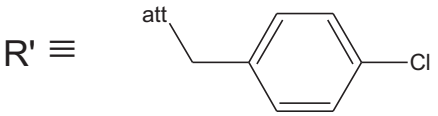
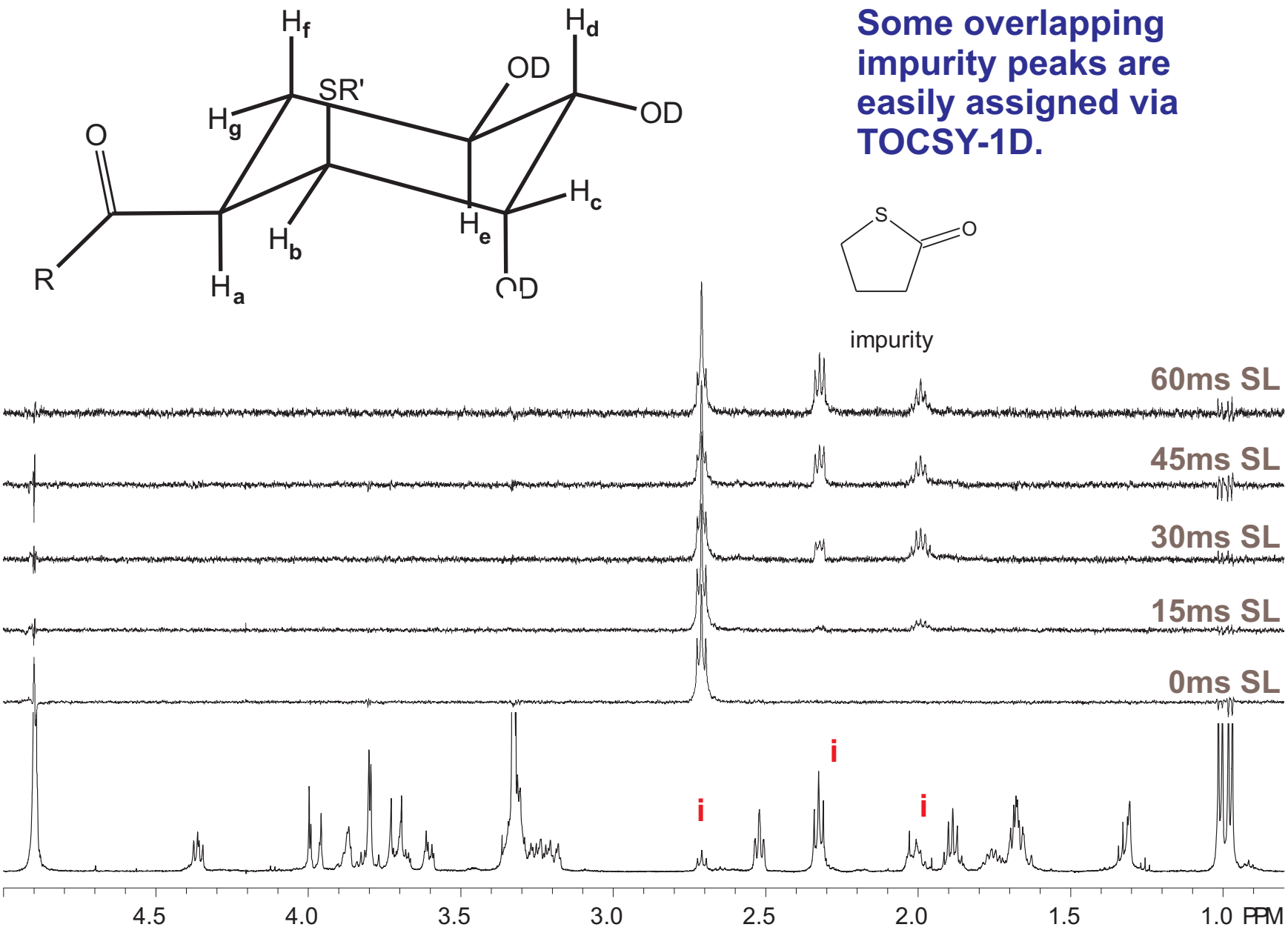


impurity

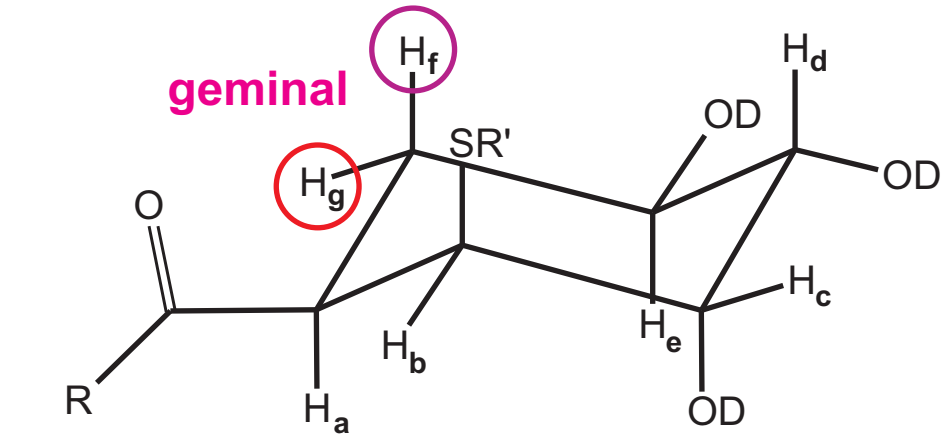




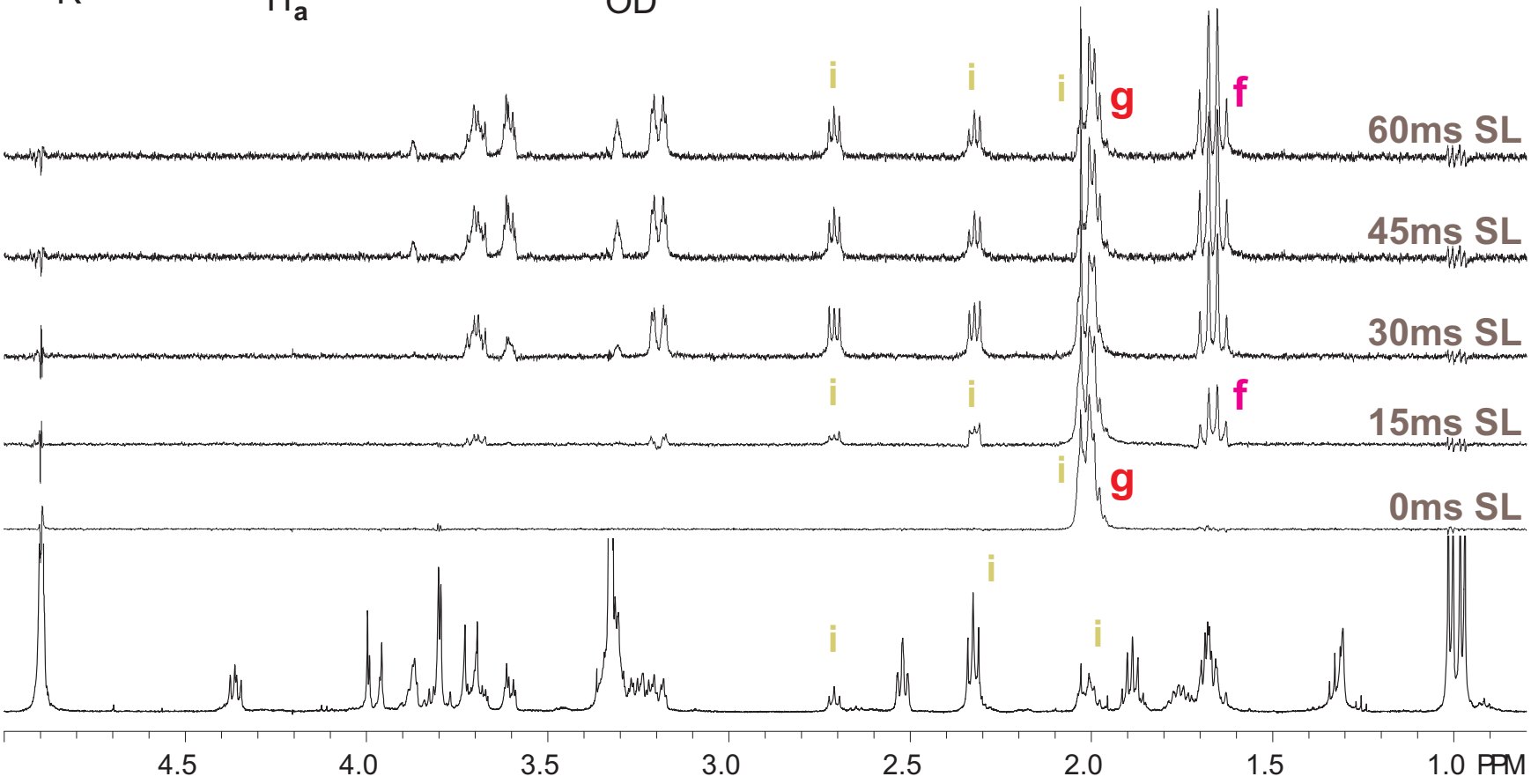
Assignments are tentative, due to lack of resolved multiplet information. Strategy is to use TOCSY1D to reobtain multiplet info for ring protons.

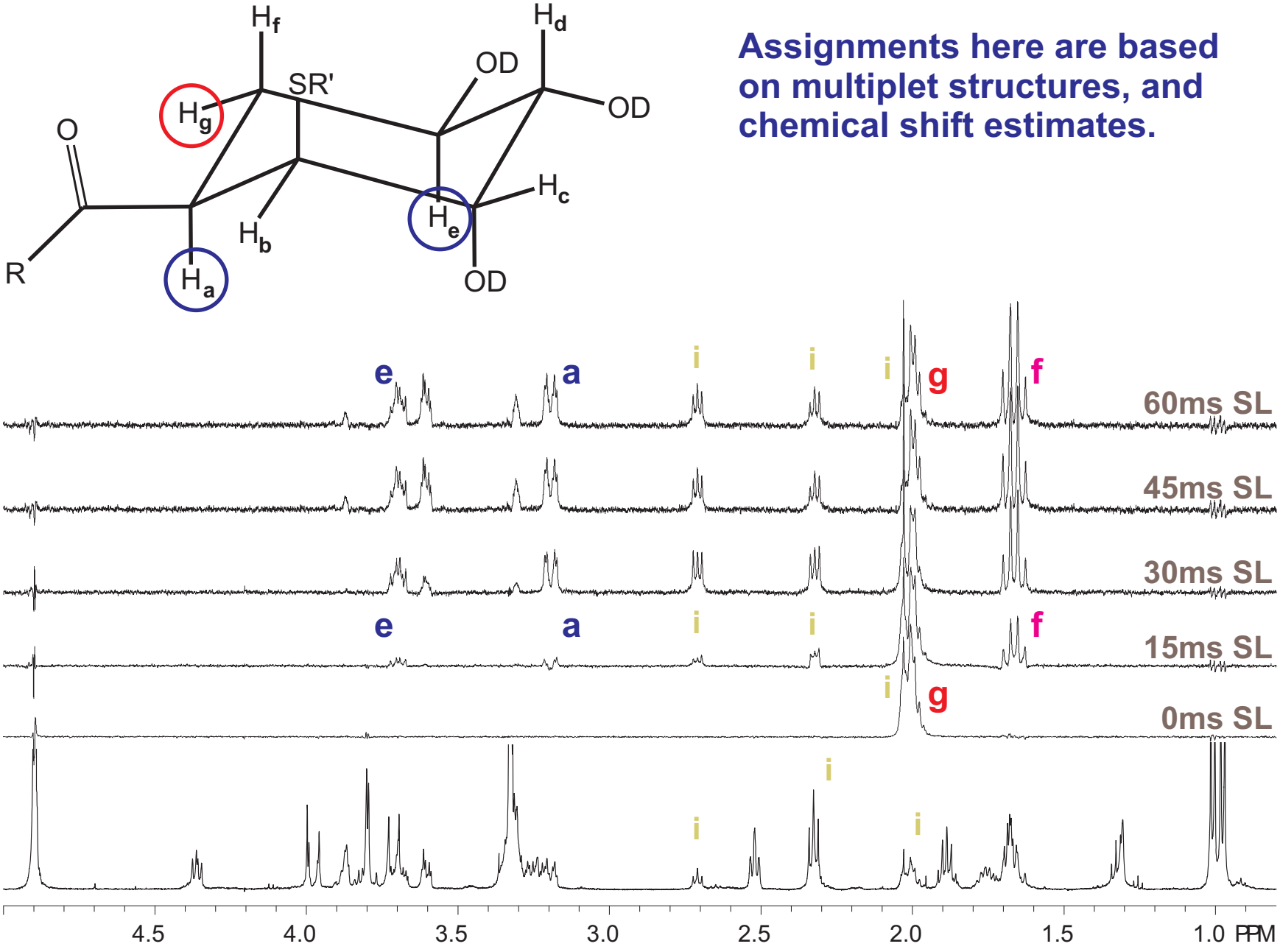


Some overlapping impurity peaks are easily assigned via TOCSY-1D.

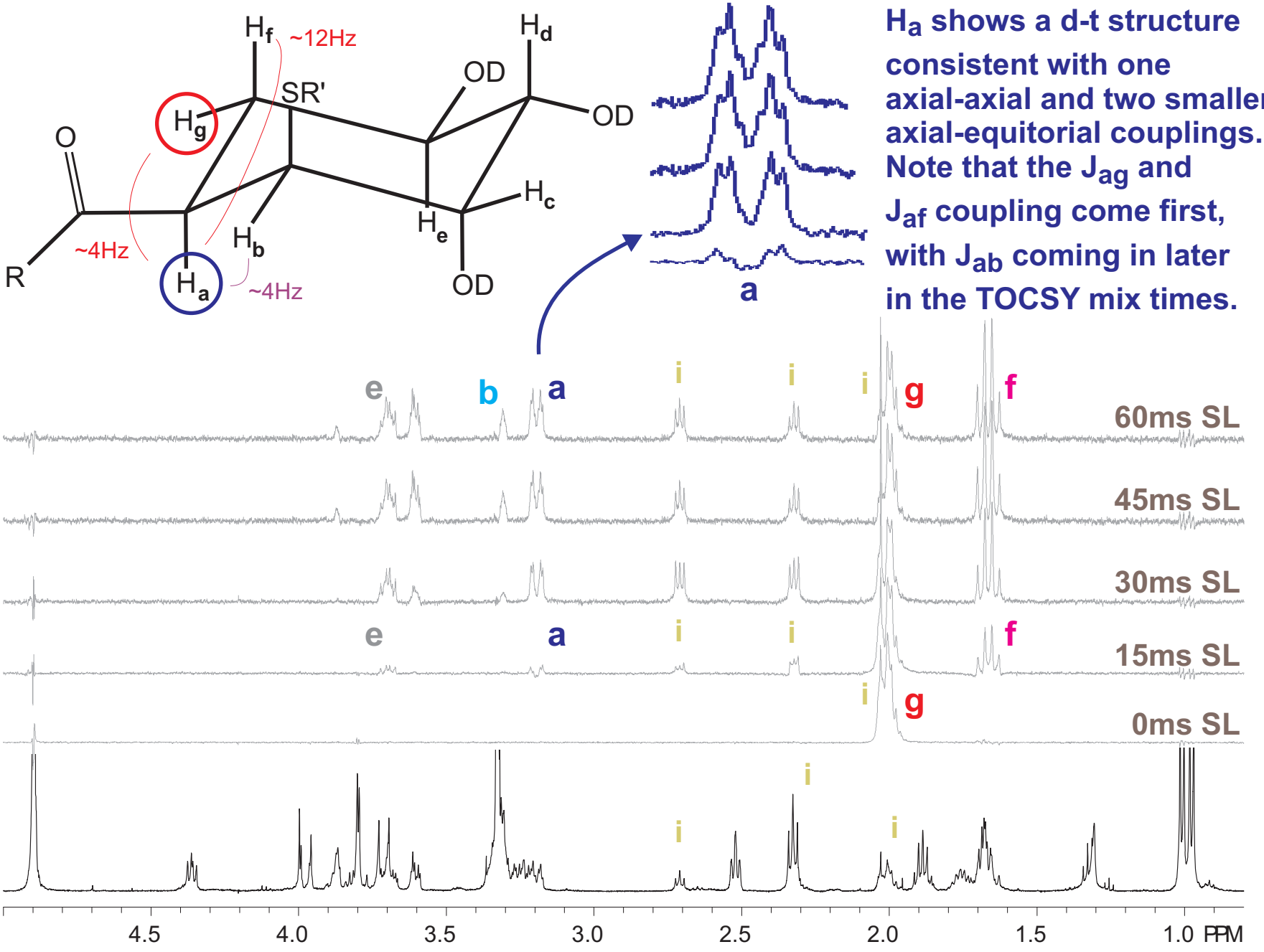


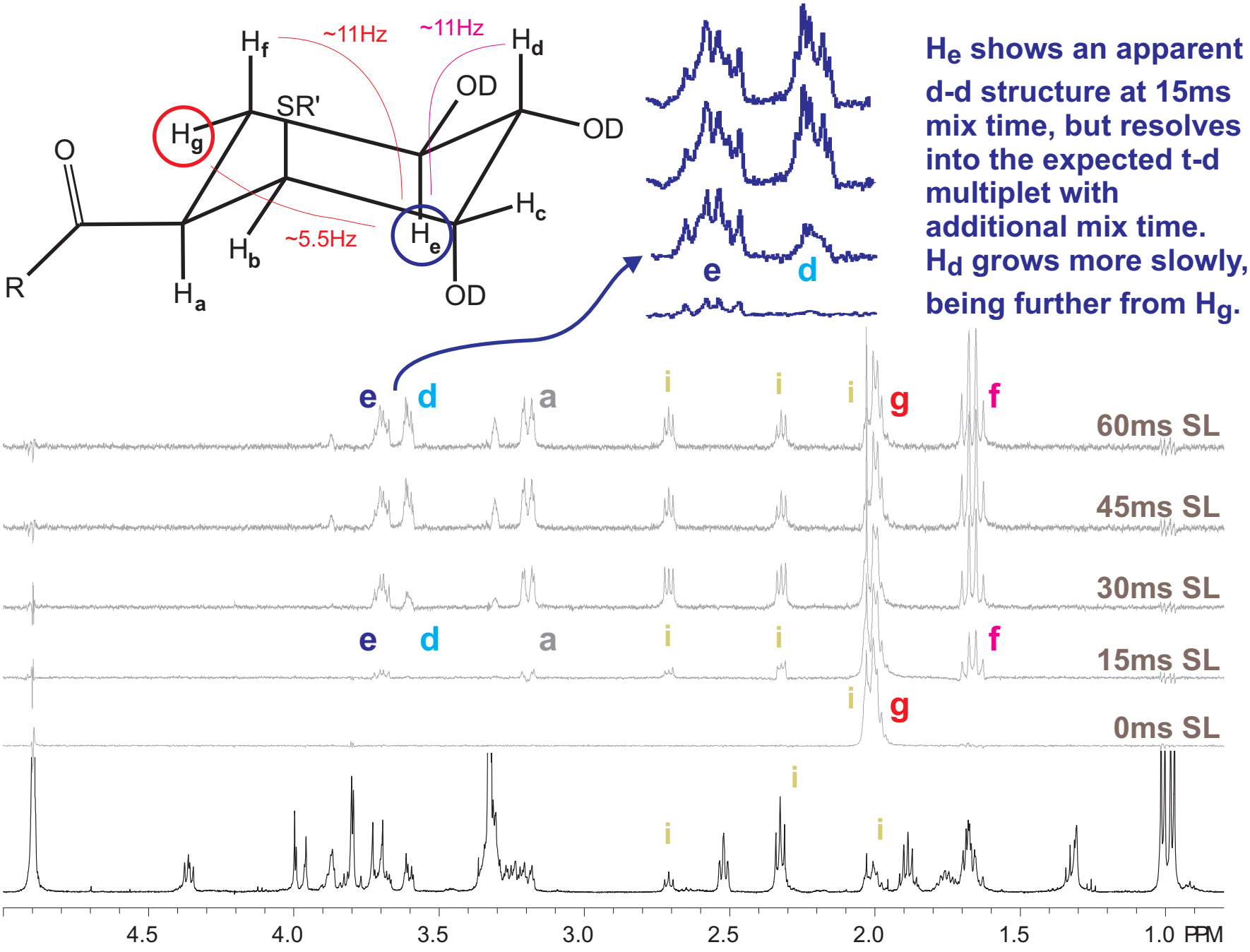
The ring assignments, as well as their stereochemistry, are then fairly easily assigned using TOCSY1D. H_f shows a quartet structure: the geminal coupling is similar in size, ~12Hz, to the two (J_{fe}, J_{fa}) axial-axial couplings.

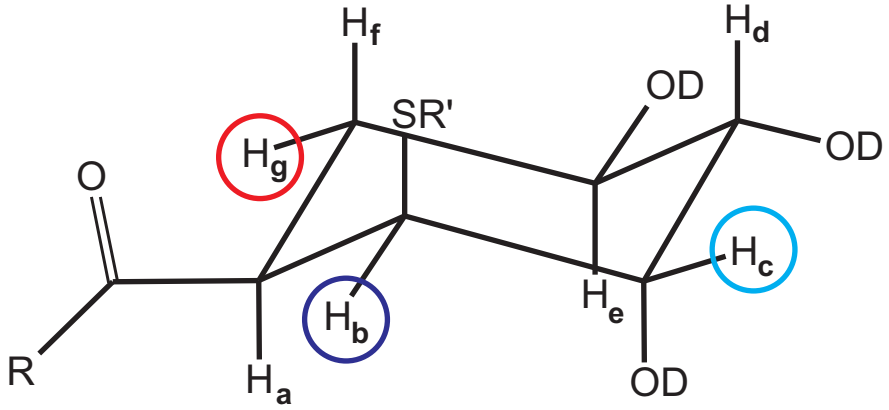




Assignments here are based on multiplet structures, and chemical shift estimates.


H_f
~12Hz
H_d
OD
SR'
H_g
OD
O
H_c
H_b
H_e
R
~4Hz
H_a
~4Hz
OD
a
H_a shows a d-t structure consistent with one axial-axial and two smaller axial-equitorial couplings. Note that the J_{ag} and J_{af} coupling come first, with J_{ab} coming in later in the TOCSY mix times.
e
b
a
i
i
i
g
f
60ms SL
45ms SL
30ms SL
e
a
i
i
f
15ms SL
i
g
0ms SL
i
i
i
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
PPM


Hf
~11Hz
~11Hz
Hd
OD
SR'
OD
Hg
O
Hc
Hb
~5.5Hz
He
R
Ha
OD
e
d
He shows an apparent d-d structure at 15ms mix time, but resolves into the expected t-d multiplet with additional mix time. Hd grows more slowly, being further from Hg.
e
d
a
i
i
i
g
f
60ms SL
45ms SL
30ms SL
e
d
a
i
i
f
15ms SL
i
g
0ms SL
i
i
i
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
PPM



Finally, H_b and H_c are assigned based on chemical shift considerations, as well as their multiplet structures (no axial-axial coupling). The lateness of their appearance in the TOCSY1D (e.g., H_c appearing last, being furthest away from H_g) confirms the assignments.