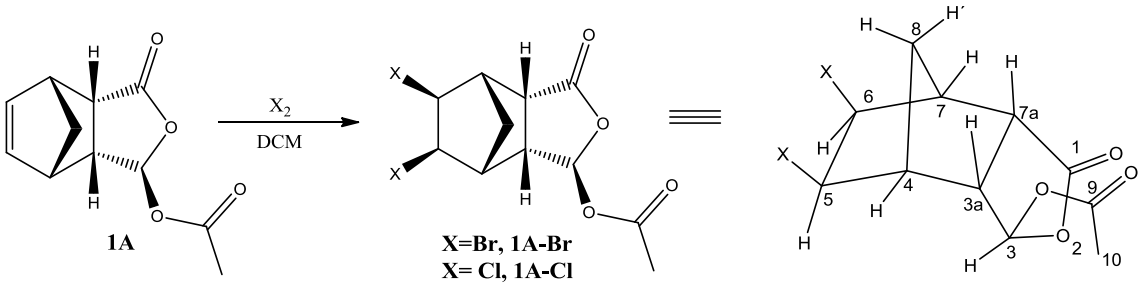
We have carried out bromination and chlorination reactions with the alkene 1A as presented in the scheme 1. Halogenation reaction usually affords the anti addition, and the product of the reaction is trans.



Scheme 1: Chlorination and bromination of the alkene 1A

THE PROBLEM IS: It looks like we have obtained the cis product.

Below is the reasoning that we have developed to reach this conclusion.

Because of the overlap of the signals of H5 and H6 in CDCl3 we have obtained the spectra in C_6D_6.

The main features that indicate formation of the dibrominated **cis** product were:

^{13}C NMR: Chemical shift changes for carbon 5 and 6 from ~ 130 ppm for 1A to ~ 50 ppm for 1A-Br

^{1}H NMR: H8 was deshielded (~ 1.66 ppm for 1A and ~ 2.48 ppm for 1A-Br). H5 and H6 were shielded (~ 6 ppm for 1A and ~ 4 ppm for 1A-Br). Changes in multiplicities of the signals were also observed.

COSY: Intense crosspeak contour for H5/H8´and H6/H8´ which indicates W coupling between these hydrogens (W coupling only occurs when H5 and H6 are downward). Intense crosspeak contour for H5/H6. This correlation was not observed for the starting **1A**.

NOESY: Absence of correlation between H5/H8 and H6/H8, which indicate that H5 and H6 are NOT UPWARD.

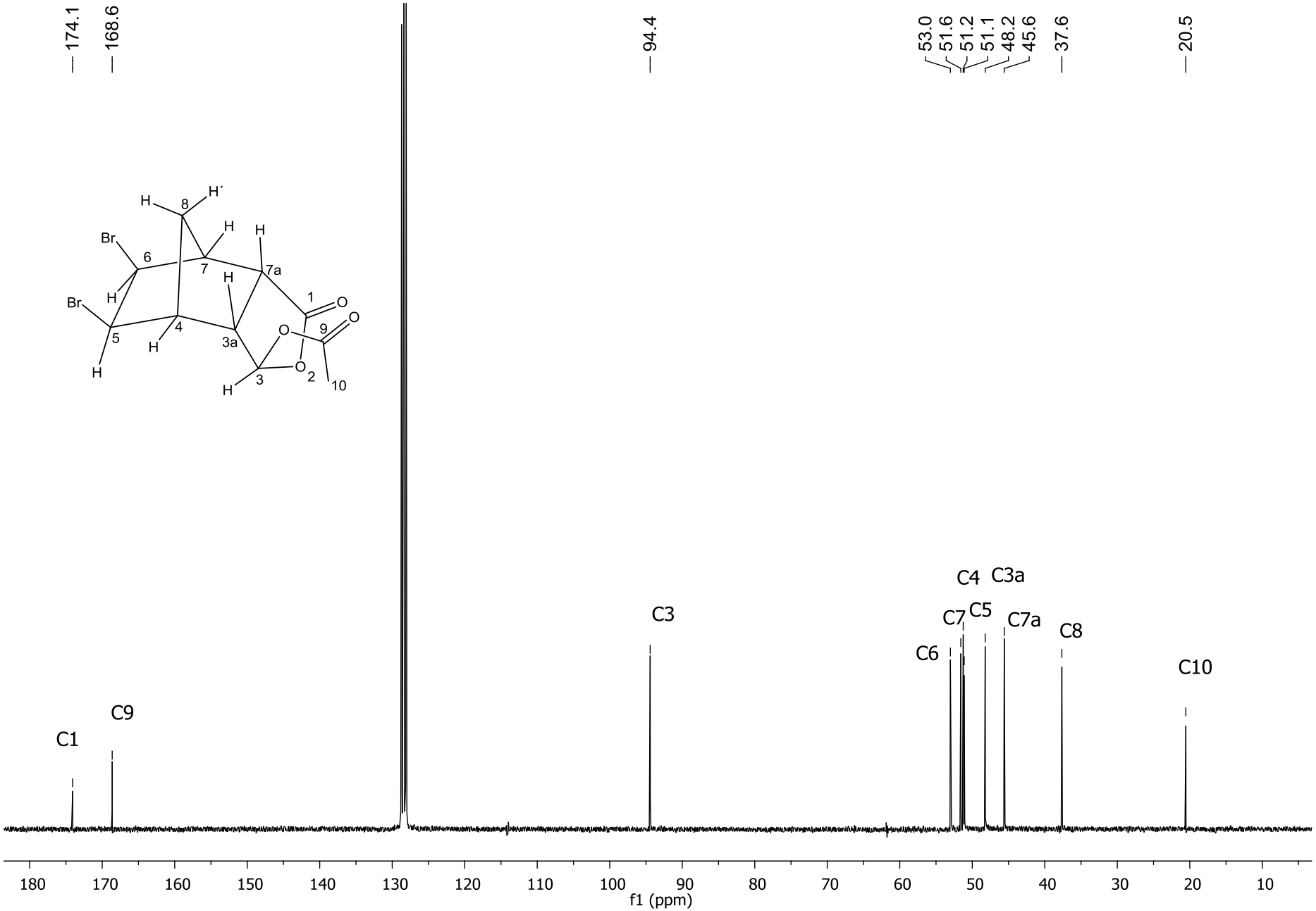


Figure 1. ^{13}C NMR (75 MHz, C_6D_6) of (3R, 3aS, 4R, 5R, 6S, 7S, 7aR)-3-acetoxi-5,6-dibromo-3a,4,6,7a-tetraidro-4,7-metanoisobenzofuran-1(*3H*)-ona

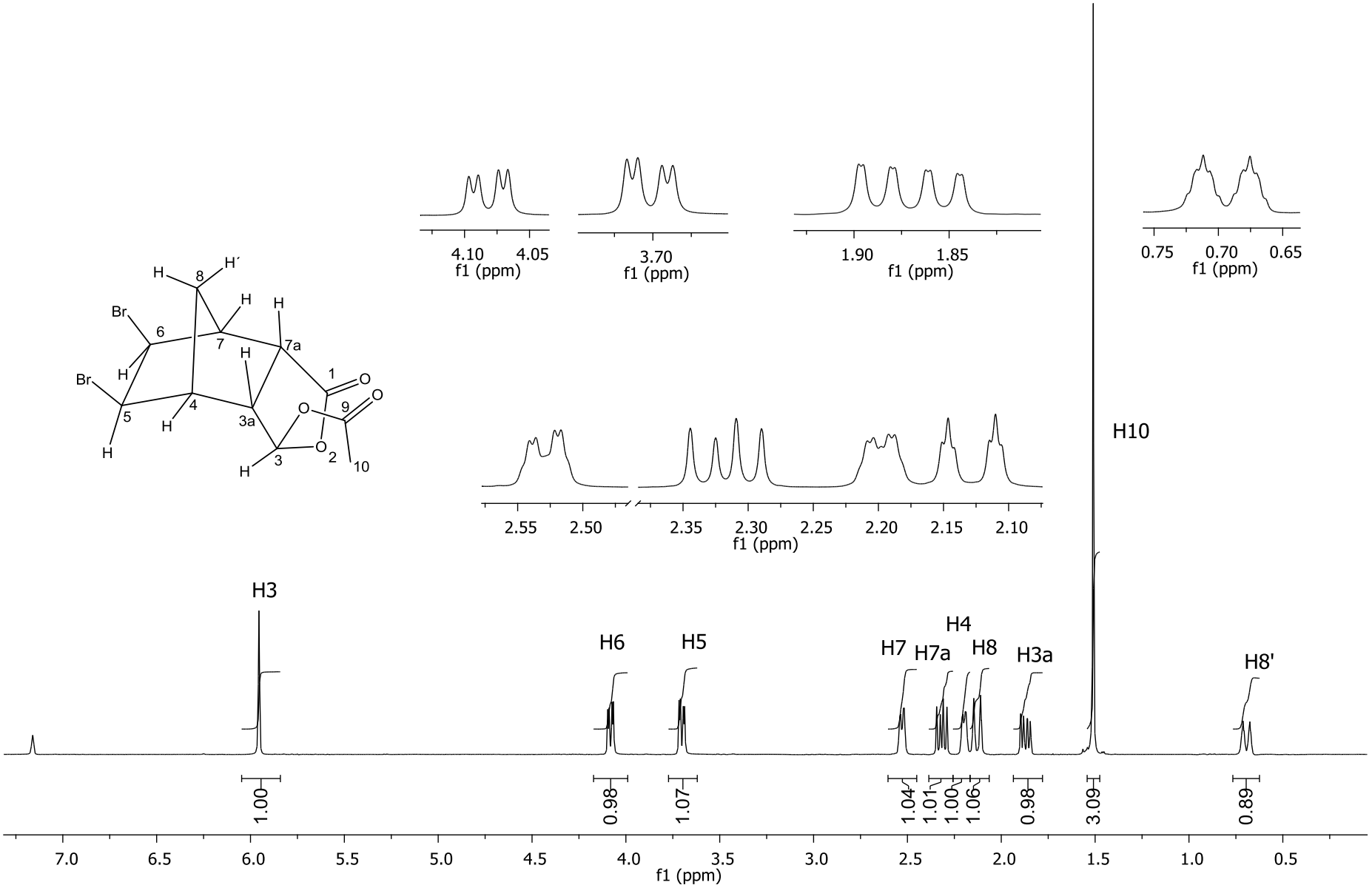


Figure 2. ^{1}H NMR (300 MHz, C_6D_6) of (3R, 3aS, 4R, 5R, 6S, 7S, 7aR)-3-acetoxi-5,6-dibromo-3a,4,6,7a-tetraidro-4,7-metanoisobenzofuran-1(*3H*)-ona.

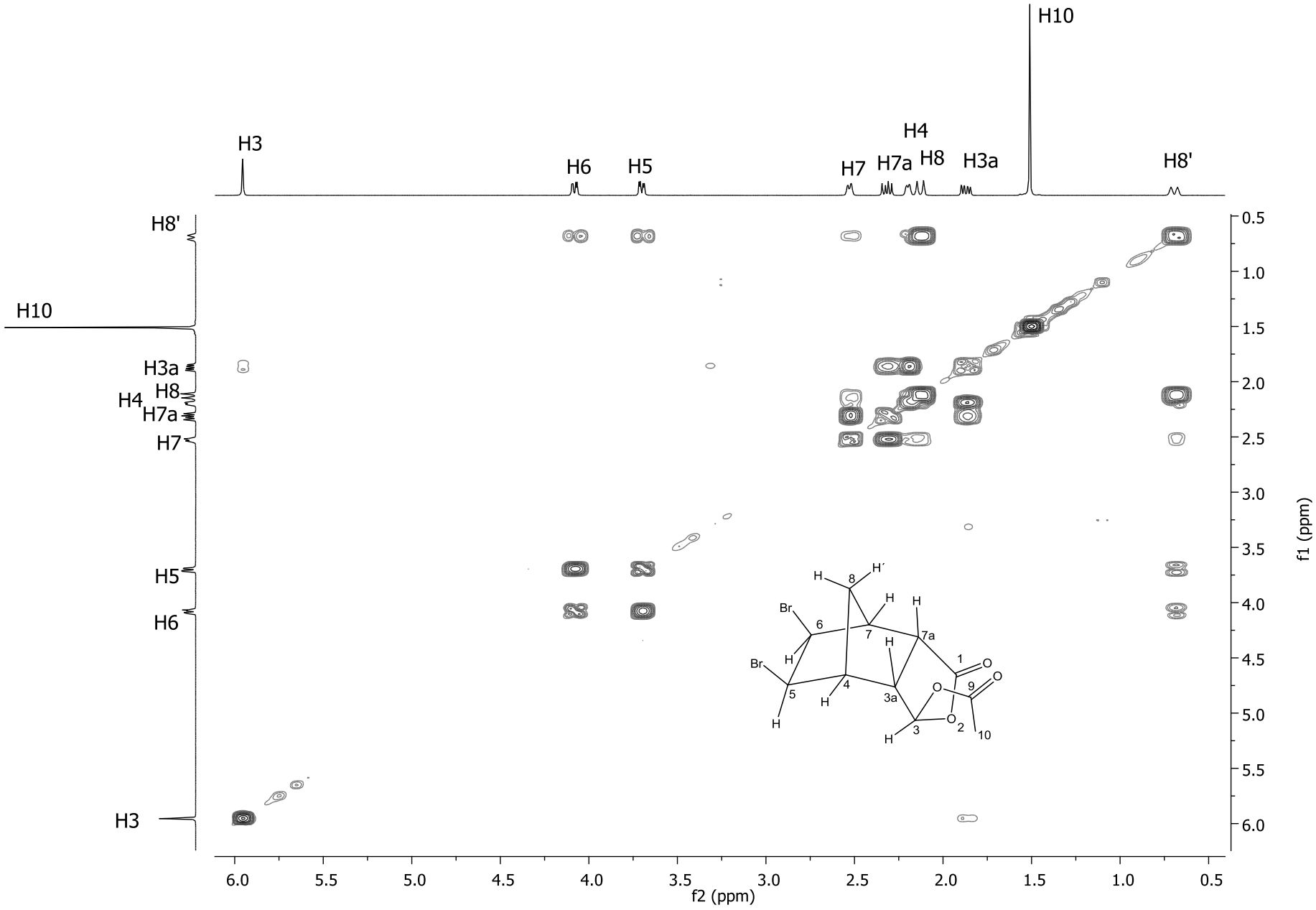


Figure 3. COSY of (3R, 3aS, 4R, 5R, 6S, 7S, 7aR)-3-acetoxi-5,6-dibromo-3a,4,6,7a-tetraidro-4,7-metanoisobenzofuran-1(*3H*)-ona.

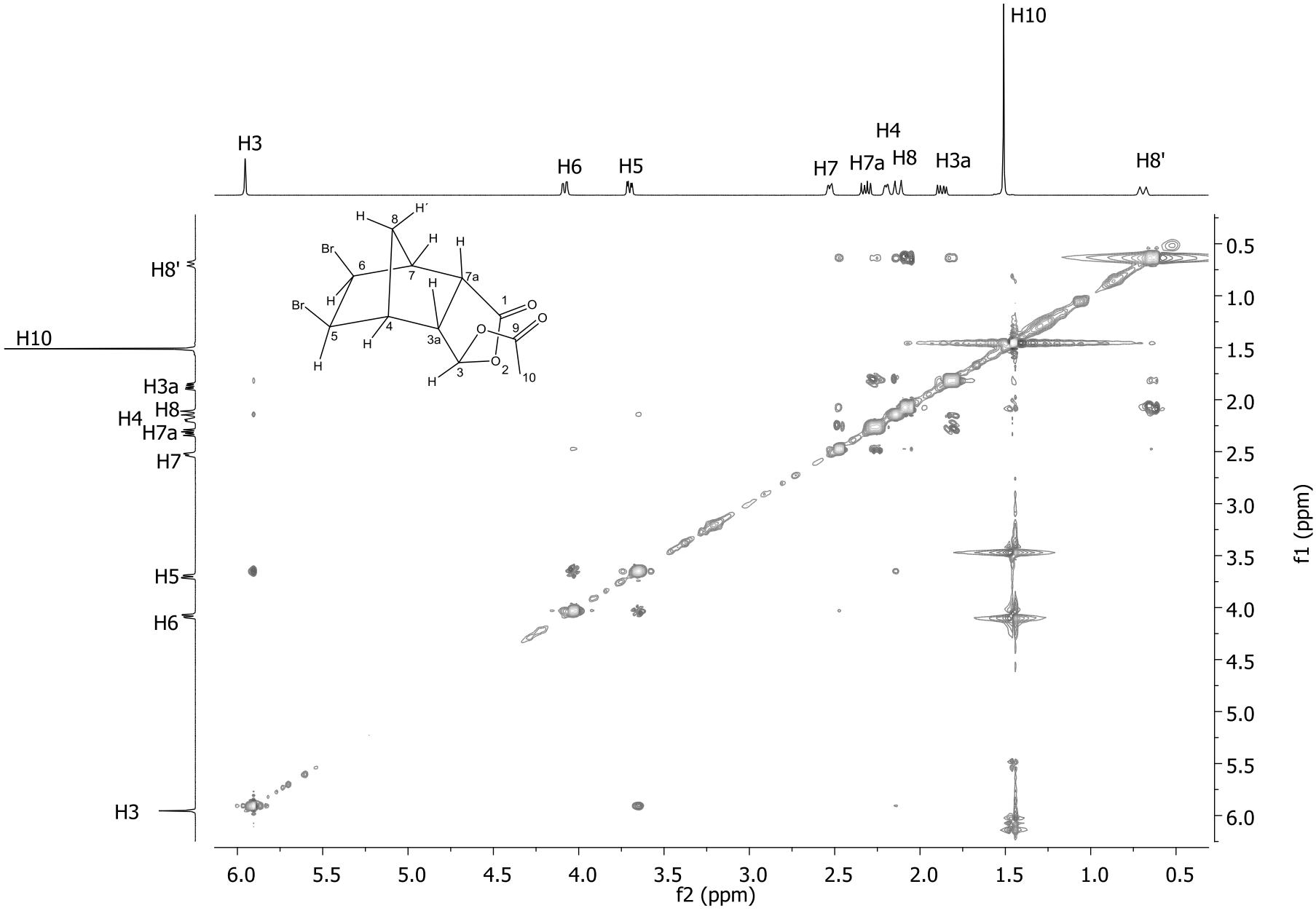


Figure 4. NOESY of (3R, 3aS, 4R, 5R, 6S, 7S, 7aR)-3-acetoxi-5,6-dibromo-3a,4,6,7a-tetraidro-4,7-metanoisobenzofuran-1(*3H*)-ona.

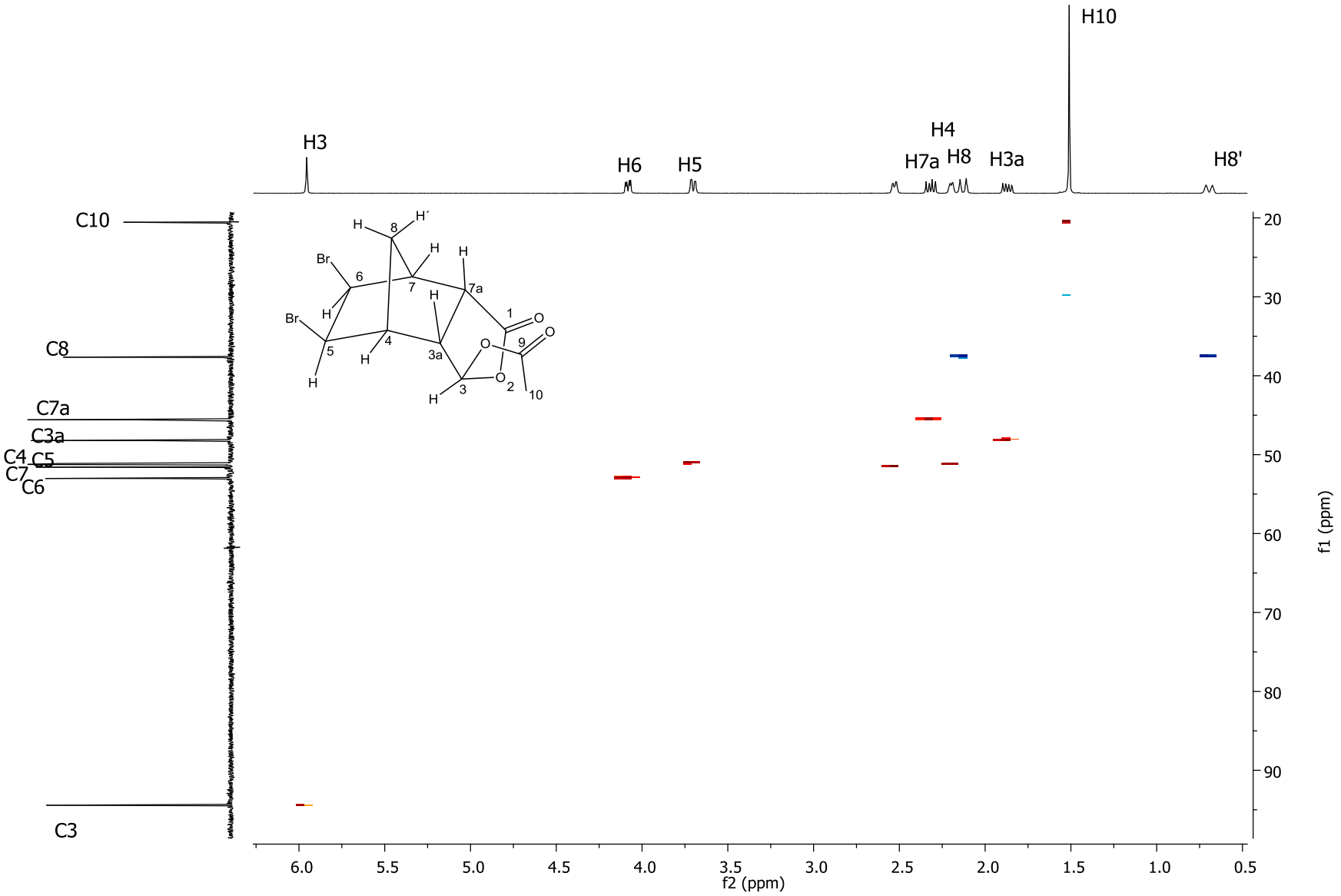


Figure 5. HSQC of (3R, 3aS, 4R, 5R, 6S, 7S, 7aR)-3-acetoxi-5,6-dibromo-3a,4,6,7a-tetraidro-4,7-metanoisobenzofuran-1(*3H*)-ona.

PLEASE EXPLAIN THIS:

The chlorinated product 1A-Cl presented very different crosspeaks from the brominated product.

The signals H8, H4 and H7 were overlapped when the spectrum was obtained in $CDCl_3$ and H7a, H7 and H8 were overlapped in C_6D_6.

The main features observed were:

^{13}C NMR: as discussed for the brominated product

^{1}H NMR: H3a is much more deshielded in 1A-Cl (~ 2.90 ppm) than in 1A-Br (~ 1.87 ppm). H3a is 4 bonds away from the chlorine. Can chlorine exert such deshielding effect on H3a?

COSY: Intense crosspeak contour for H5/H8´and H6/H8´ which indicates W coupling between these hydrogens (as discussed for 1A-Br). Intense crosspeak contour for H6/H4, H5/H4, H6/H7, H5/H7 (these correlations were not observed for the brominated 1A-Br). Correlation H5/H6 was NOT OBSERVED for 1A-Cl (Correlation H5/H6 was OBSERVED for 1A-Br).

NOESY: Correlations H5/H8 and H6/H8 were NOT OBSERVED for 1A-Cl (as observed for the 1A-Br). Crosspeaks contours for H6/H4, H5/H4, H6/H7, H5/H7 for 1A-Cl (absent in the brominated compound). Correlation H5/H6 were NOT OBSERVED for 1A-Cl (Correlation H5/H6 was present in 1A-Br)

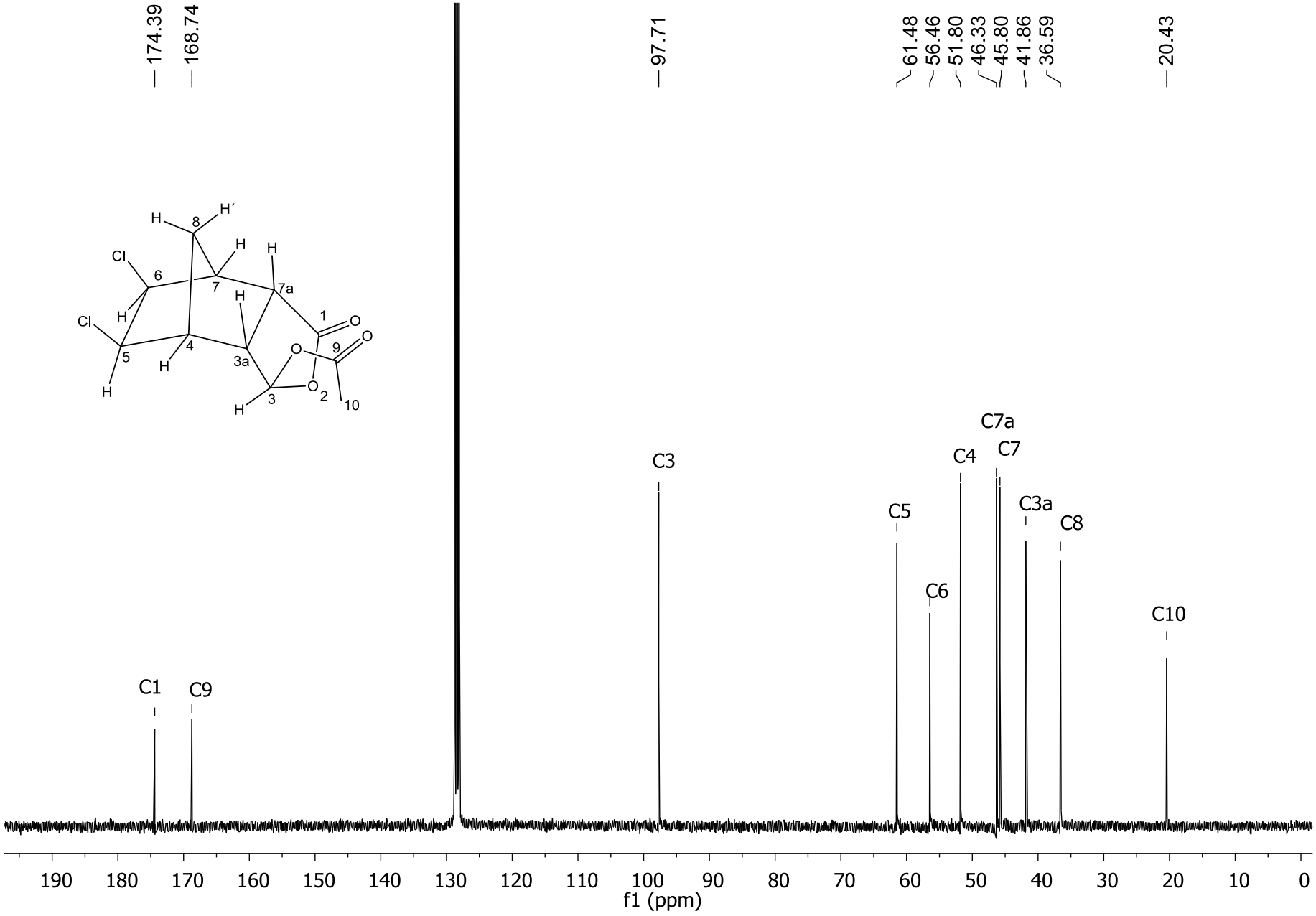


Figure 6. ^{13}C NMR (75 MHz, C_6D_6) of (3R, 3aS, 4R, 5R, 6S, 7S, 7aR)-3-acetoxi-5,6-dicloro-3a,4,6,7a-tetraidro-4,7-metanoisobenzofuran-1(*3H*)-ona.

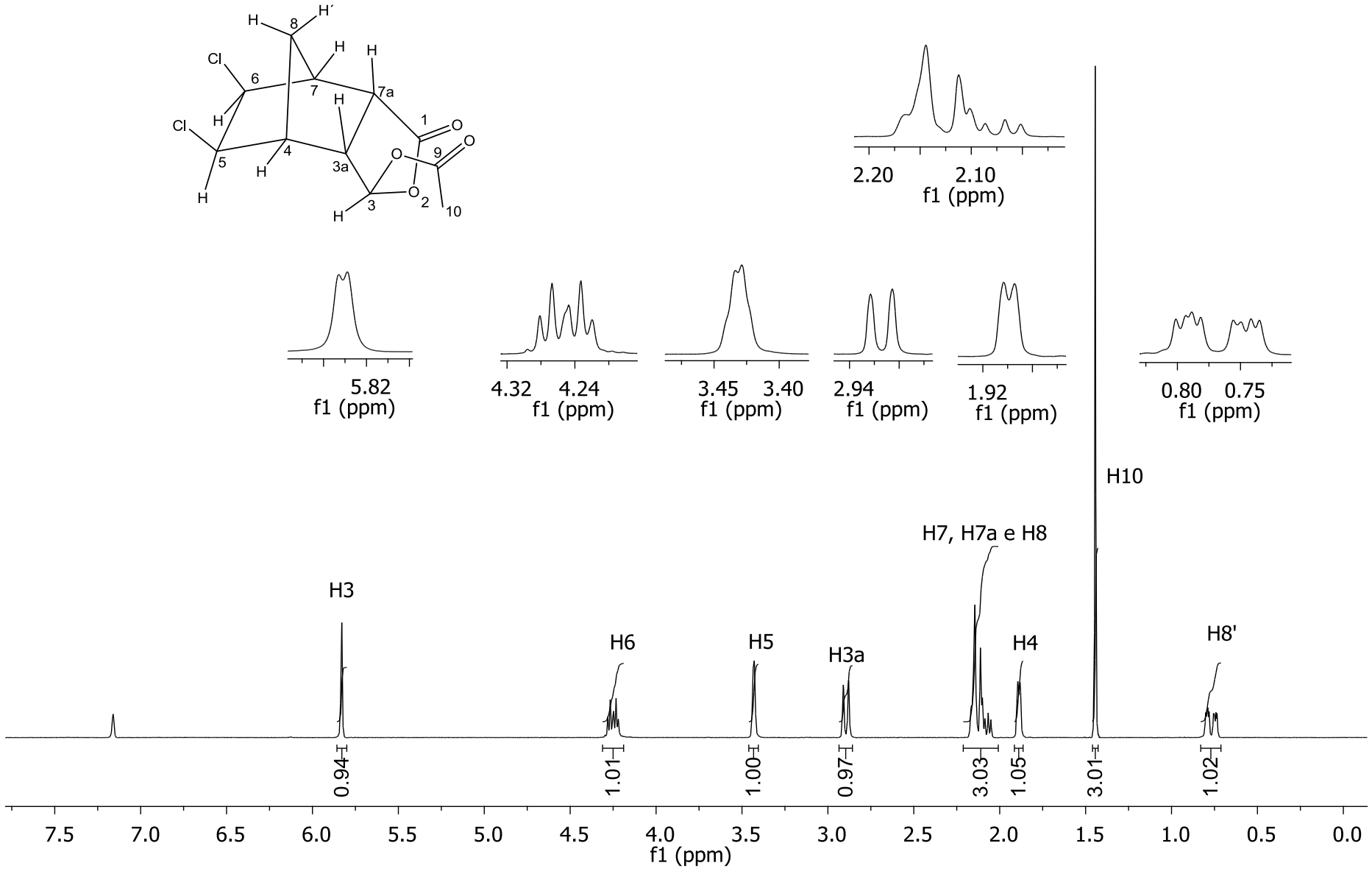


Figure 7. ^{1}H NMR of (300 MHz, C_6D_6) da (3R, 3aS, 4R, 5R, 6S, 7S, 7aR)-3-acetoxi-5,6-dicloro-3a,4,6,7a-tetraidro-4,7-metanoisobenzofuran-1(*3H*)-ona.

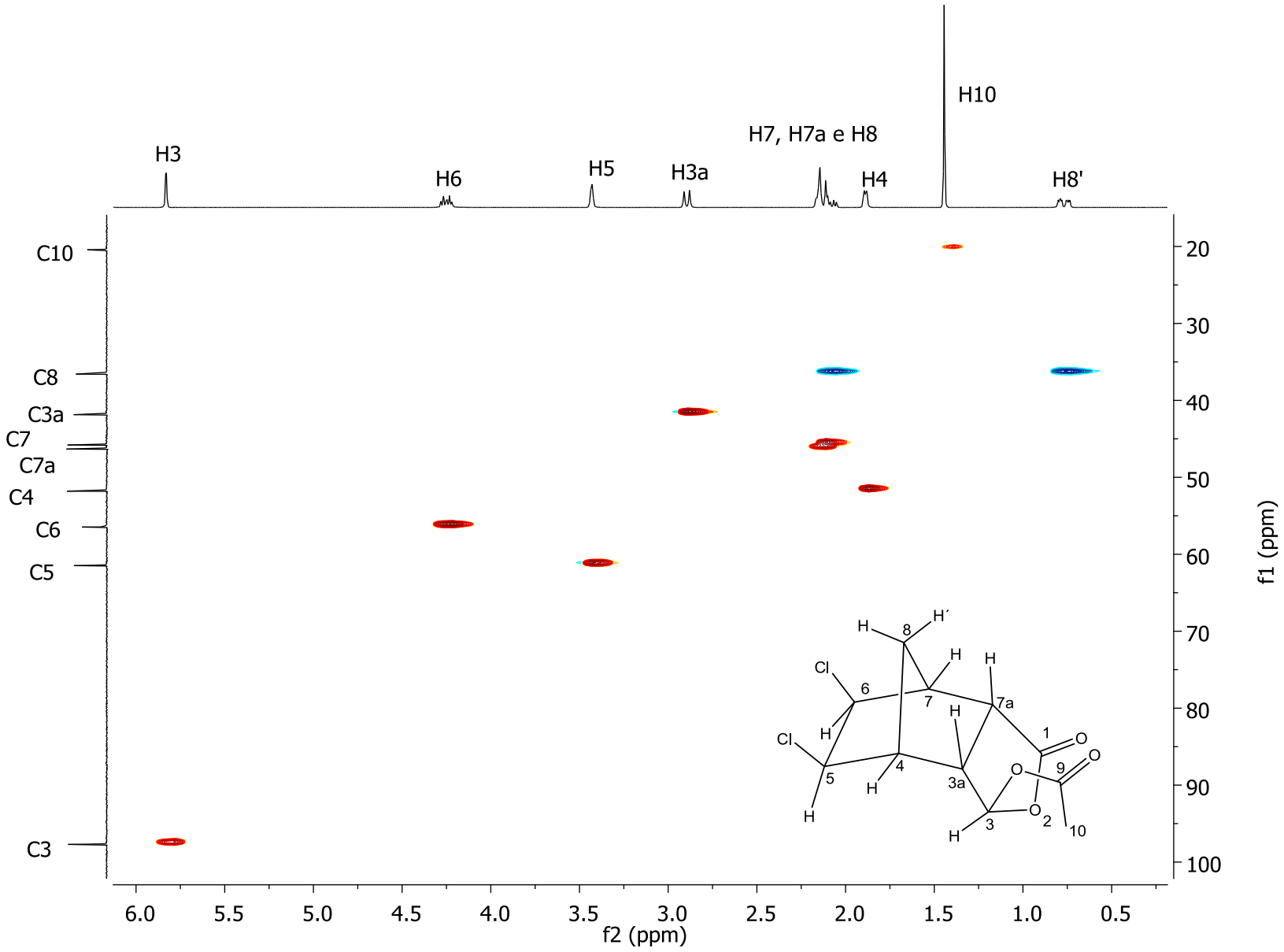


Figure 8. HSQC of (3R, 3aS, 4R, 5R, 6S, 7S, 7aR)-3-acetoxi-5,6-dicloro-3a,4,6,7a-tetraidro-4,7-metanoisobenzofuran-1(*3H*)-ona.

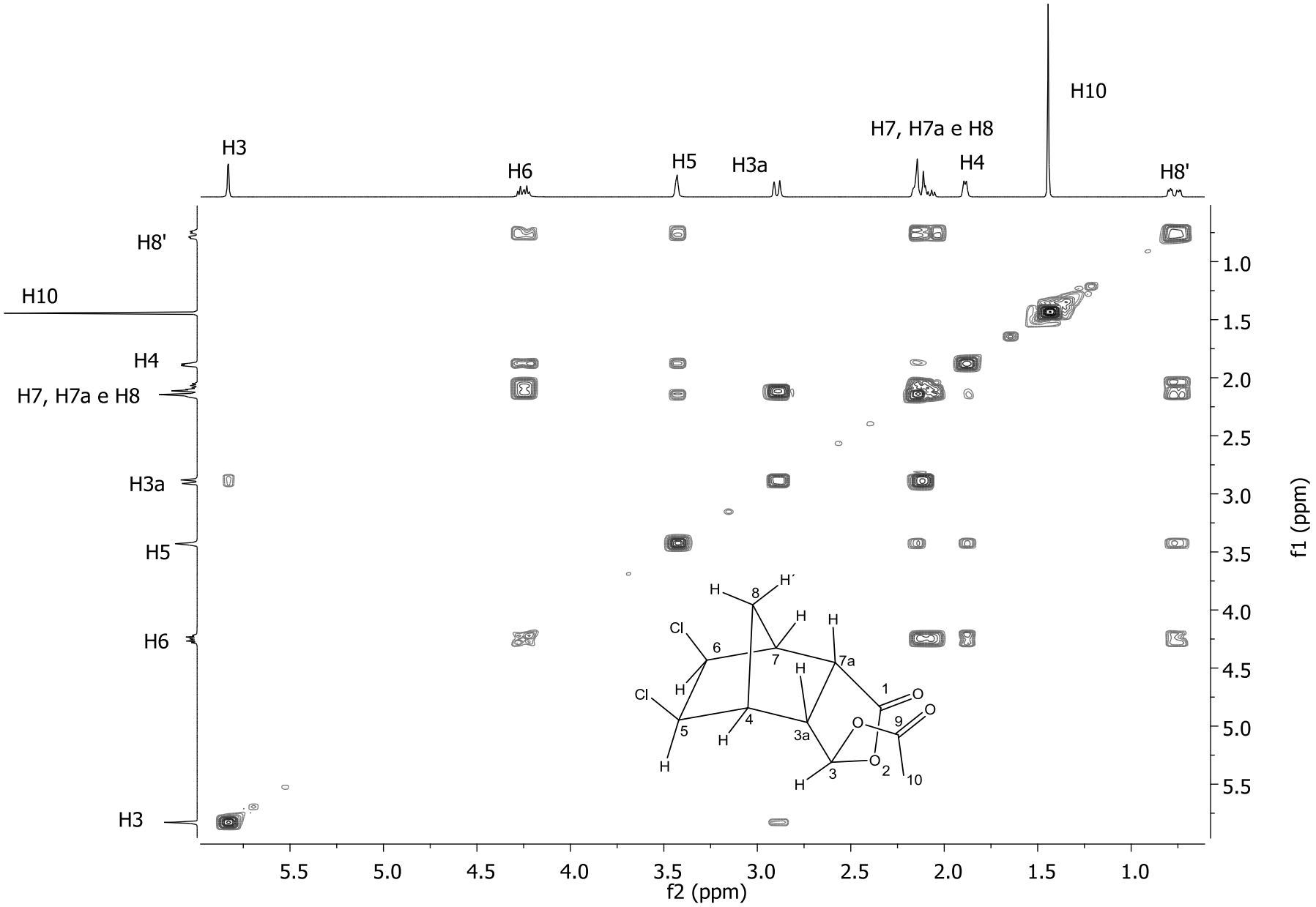


Figure 9. COSY of (3R, 3aS, 4R, 5R, 6S, 7S, 7aR)-3-acetoxi-5,6-dicloro-3a,4,6,7a-tetraidro-4,7-metanoisobenzofuran-1(*3H*)-ona.

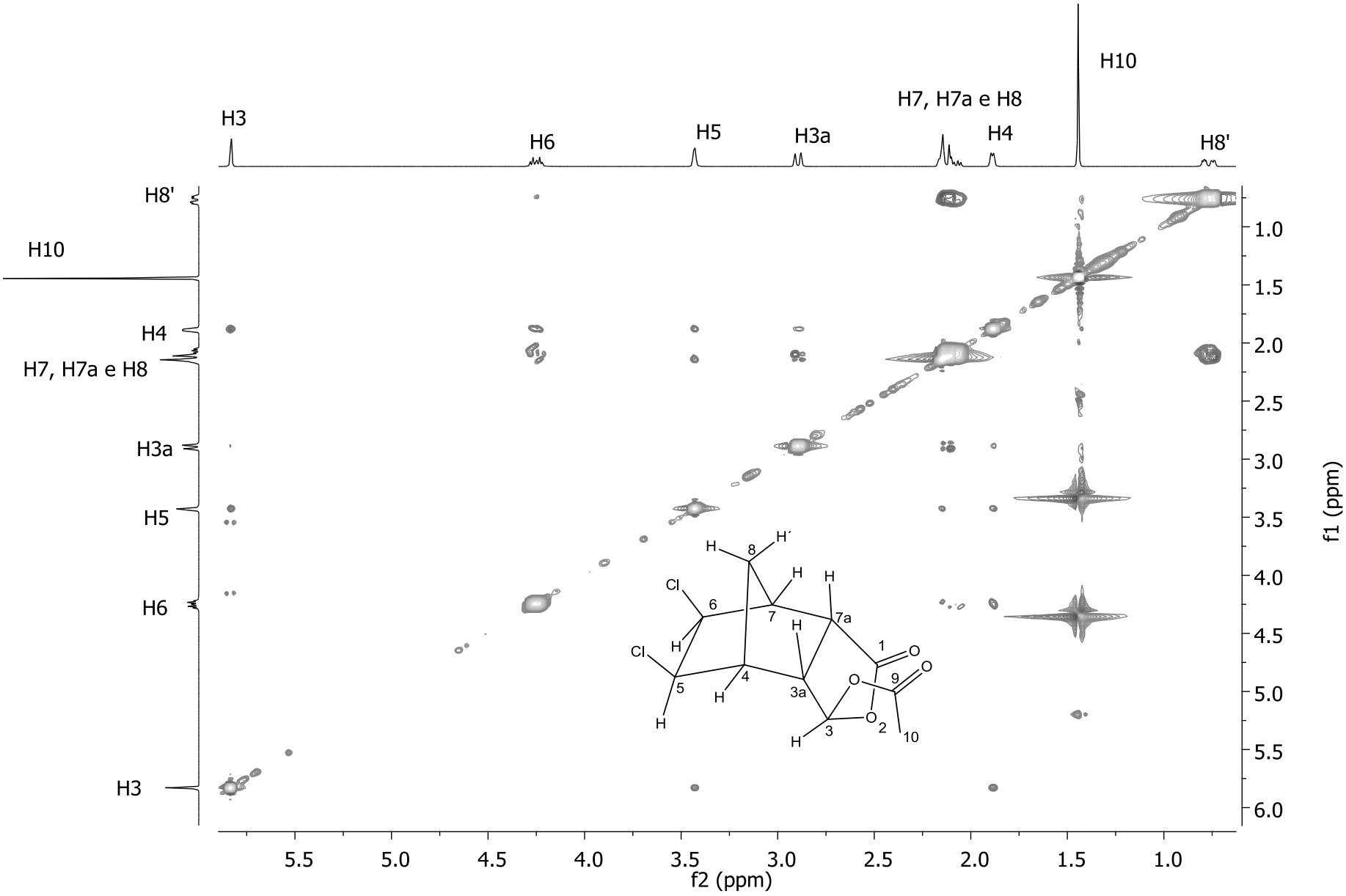


Figure 10. NOESY of (3R, 3aS, 4R, 5R, 6S, 7S, 7aR)-3-acetoxi-5,6-dicloro-3a,4,6,7a-tetraidro-4,7-metanoisobenzofuran-1(*3H*)-ona.