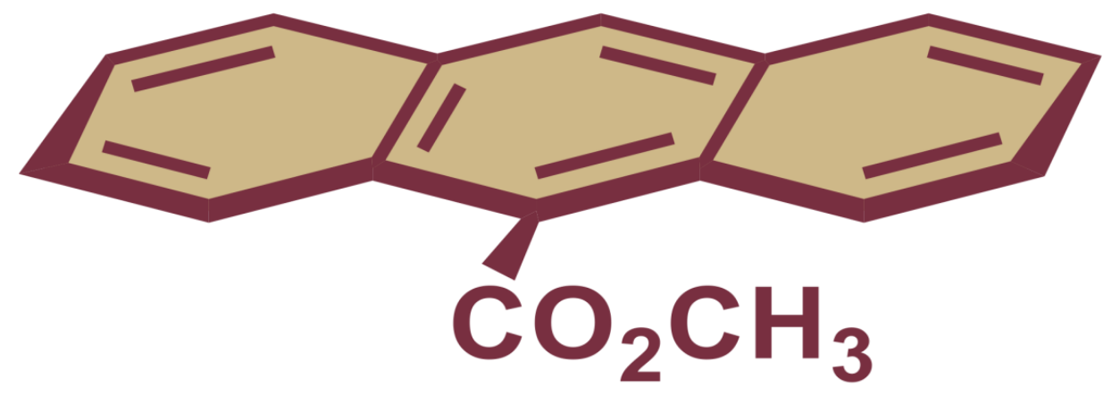
# Photodimerization of 9-Methyl Anthroate



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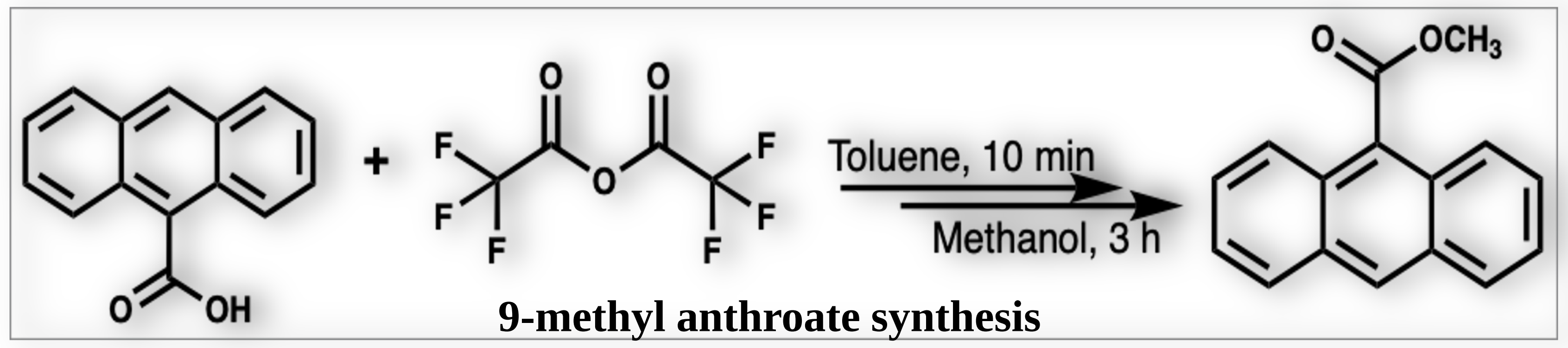
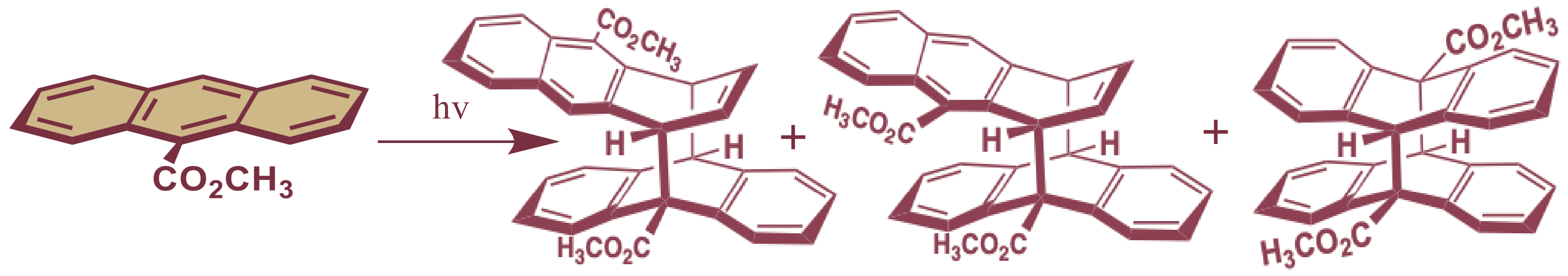
## Abstract

Anthracene ($^1A$) photodimerization occurs via the singlet excited state ($^1A^* + {}^1A$) or via triplet-triplet annihilation (TTA, $^3A^* + {}^3A^*$). To determine whether the two pathways involve common singlet excimers, we studied the photodimerization of methyl 9-anthroate (9MeA). 9MeA was selected because on direct excitation it forms three dimers: head to tail at the meso positions ($HT_m$), and head to tail and head to head ($HT_{14}$, and $HH_{14}$) involving the meso positions of one partner and the 1,4 positions of the other. Direct excitation (Uranium glass, benzene-d6, 23°C) yielded 84.2% $HT_m$, 13.1% $HT_{14}$, and 2.72% $HH_{14}$ at 59.4-93.6% conversions. Under TTA conditions (fluorenone-sensitized, 436 nm), but at lower conversions (6.3-12.3%) similar dimer distributions were obtained, except conversion to $HH_{14}$ doubled at $HT_m$'s expense. This suggests common excimer precursors with nearly complete equilibration. To assess whether photodimers can interconvert photochemically without reverting to free monomer, efforts to isolate the pure dimers are in progress. $HT_m$ (98% pure) has been obtained via column chromatography, but $HT_{14}$ and $HH_{14}$ could not be satisfactorily separated by either column chromatography or HPLC. Interestingly, pure $HT_{14}$, and $HH_{14}$ were isolated using preparative thin layer chromatography. Their photochemical interconversion will be studied in solution and in glassy media at 77 K. The classic experiments of Chandross and Ferguson at low *T* encourage us to look for excimer fluorescence from the precursor excimers and possible viscosity dependent excimer equilibration in glassy media.



9-methyl anthroate synthesis



**9MeA**

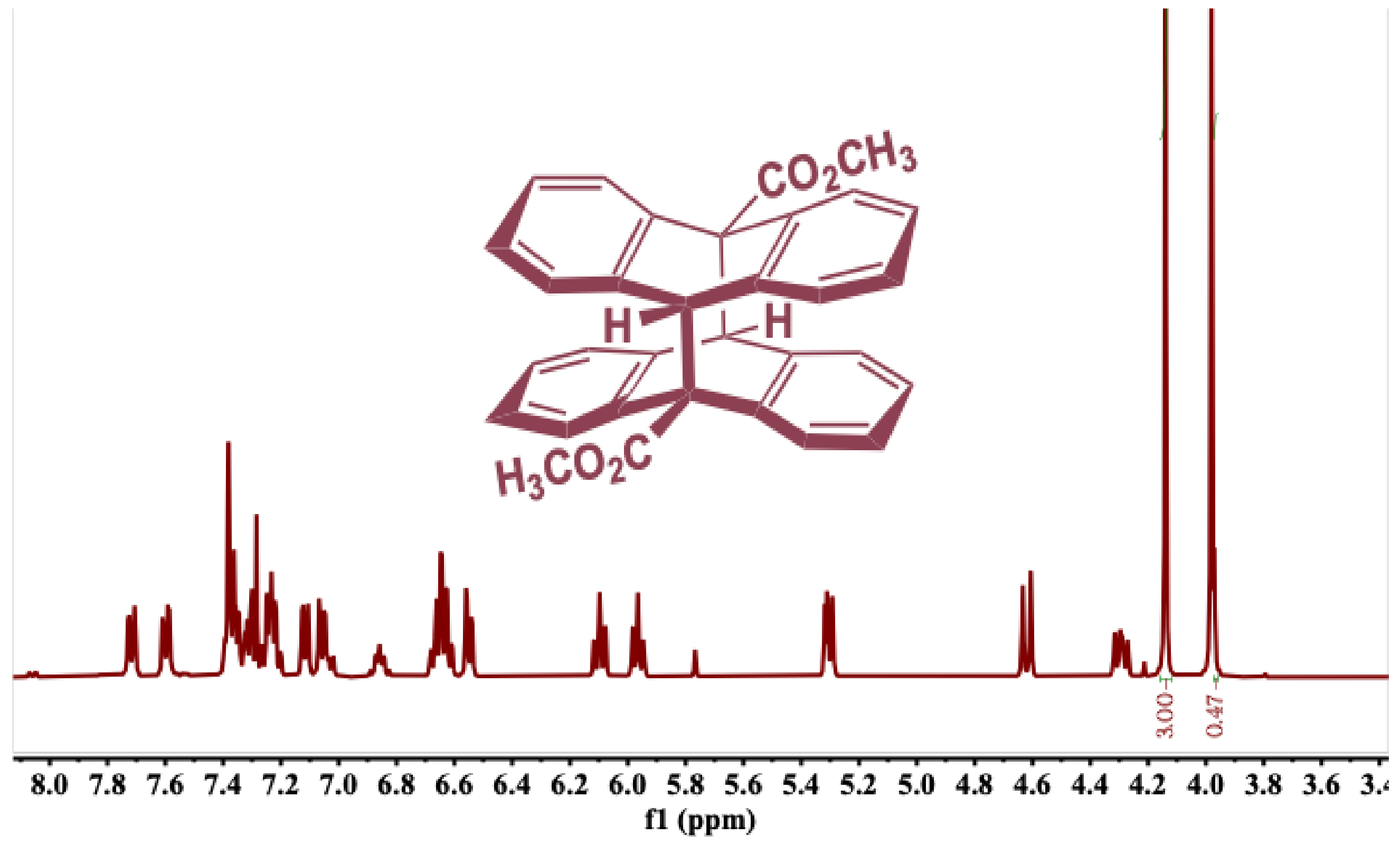
**$HT_m$**

**$HH_{14}$ Syn**

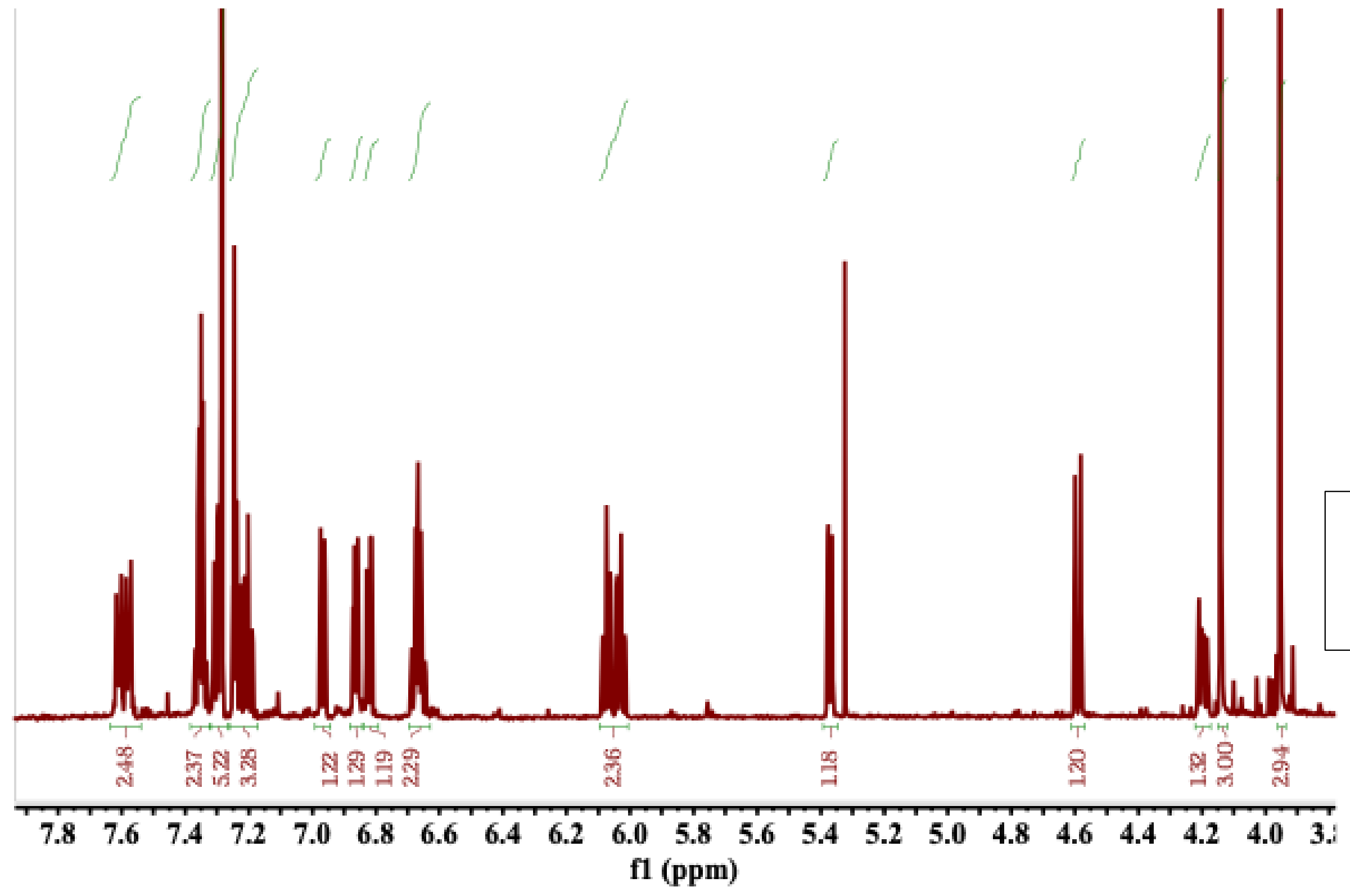
**$HT_{14}$ Anti**

## Methods

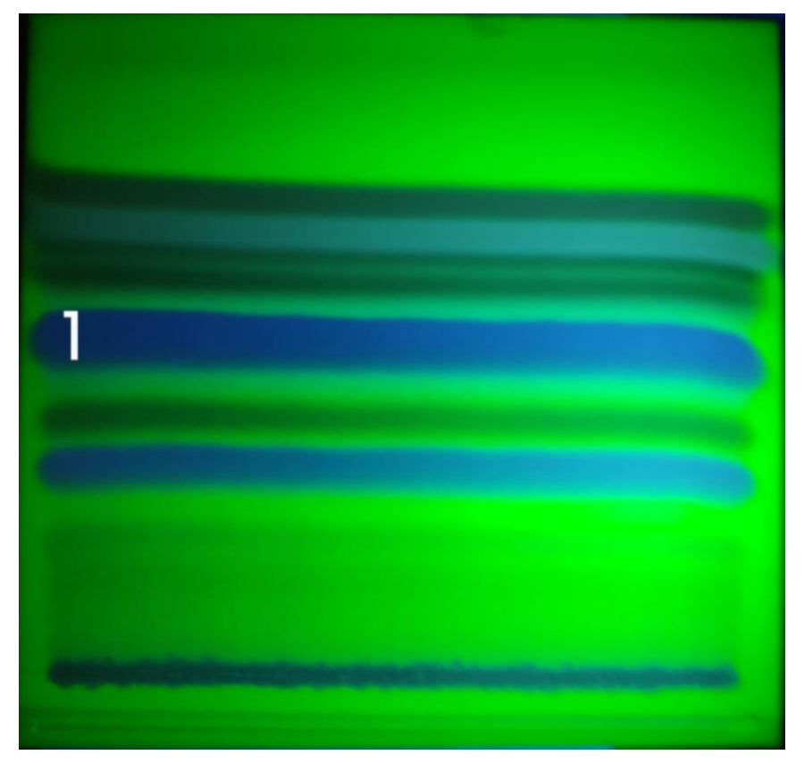
- Irradiate 9-methyl anthroate using Uranium glass as the filter.
- Separate the dimers using high performance liquid chromatography (HPLC), column chromatography, and/or thin layer chromatography (TLC)
- Use UV visible spectrophotometer to obtain absorption spectra.
- Employ fluorescence spectra to study the excimers.



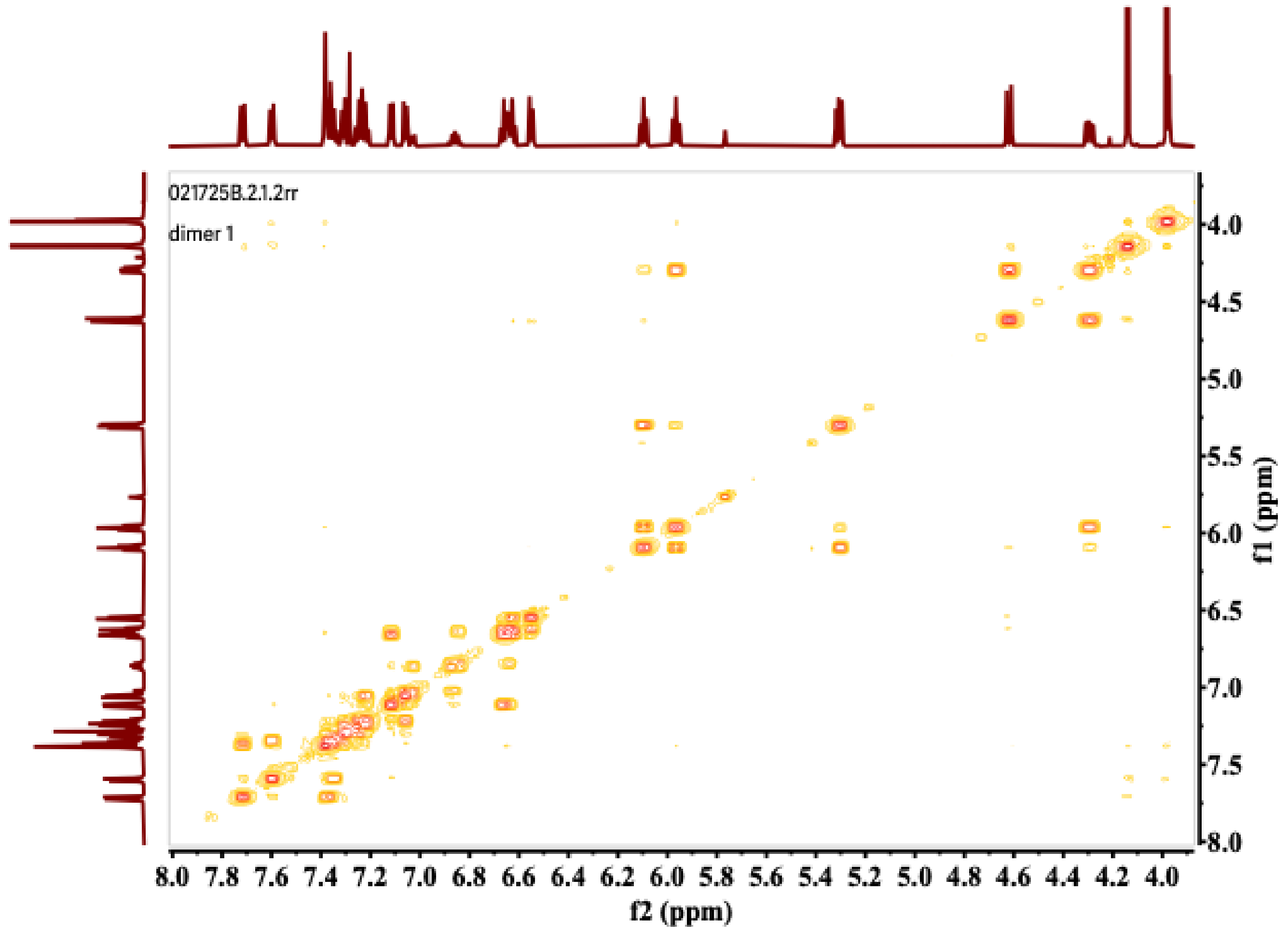
**$^1H$ NMR of $HT_m$ Dimer (Solvent: $CDCl_3$)**



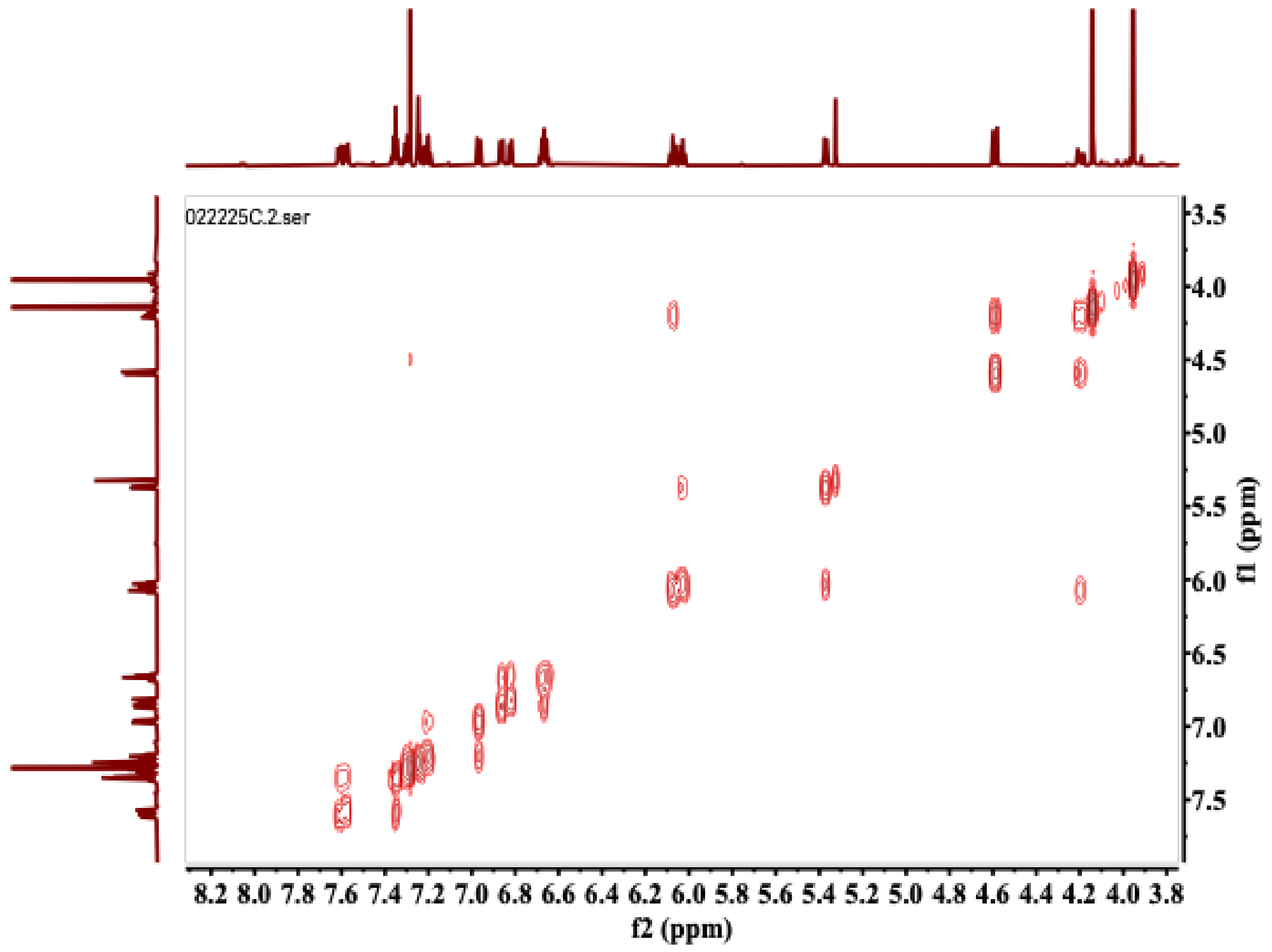
**$^1H$ NMR of $HH_{14}$ Dimer (Solvent: $CDCl_3$)**



**Preparative TLC Plate (1=Anti)**

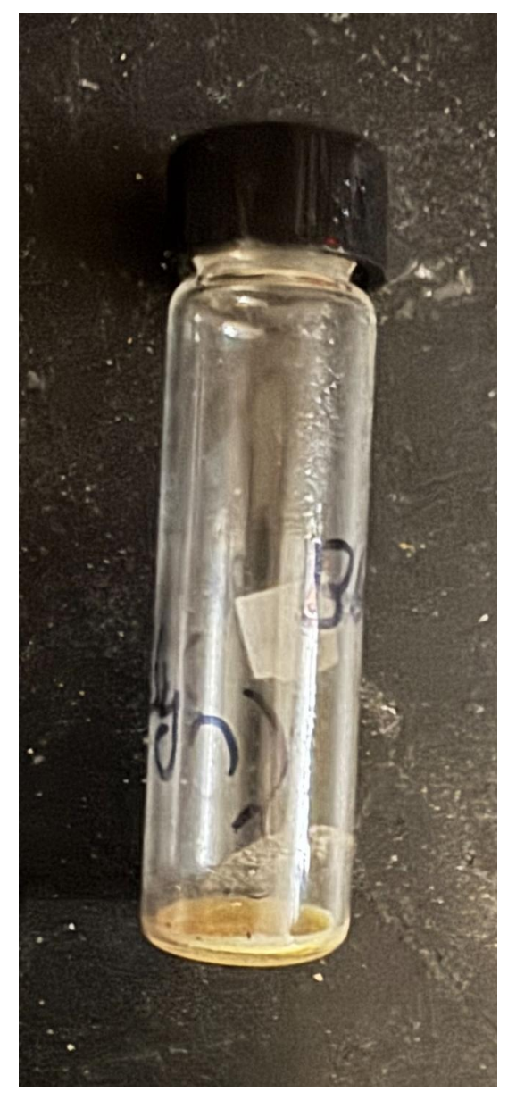


**COSY NMR of $HT_m$ Dimer (Solvent: $CDCl_3$)**

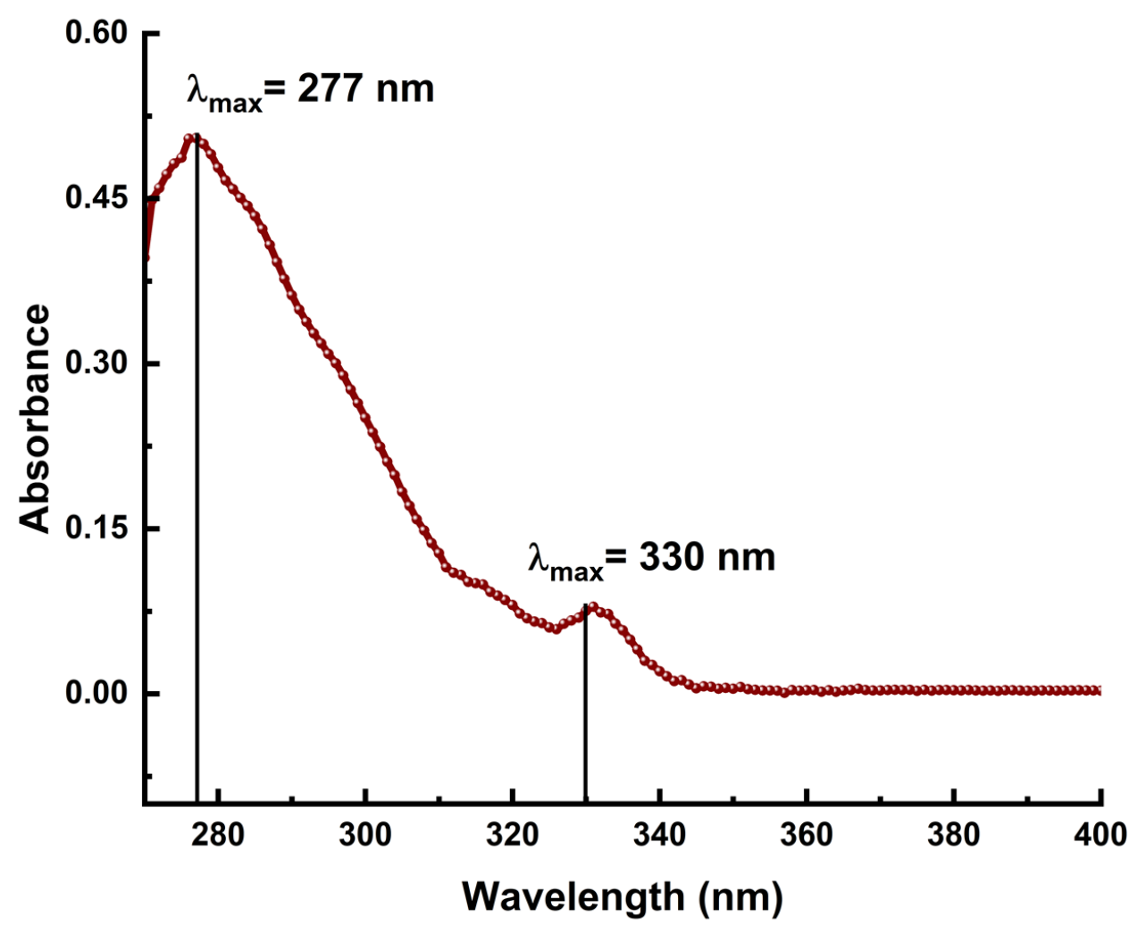


**COSY NMR of $HH_{14}$ Dimer (Solvent: $CDCl_3$)**

**Anti Dimer Crystals**



**Syn Dimer**



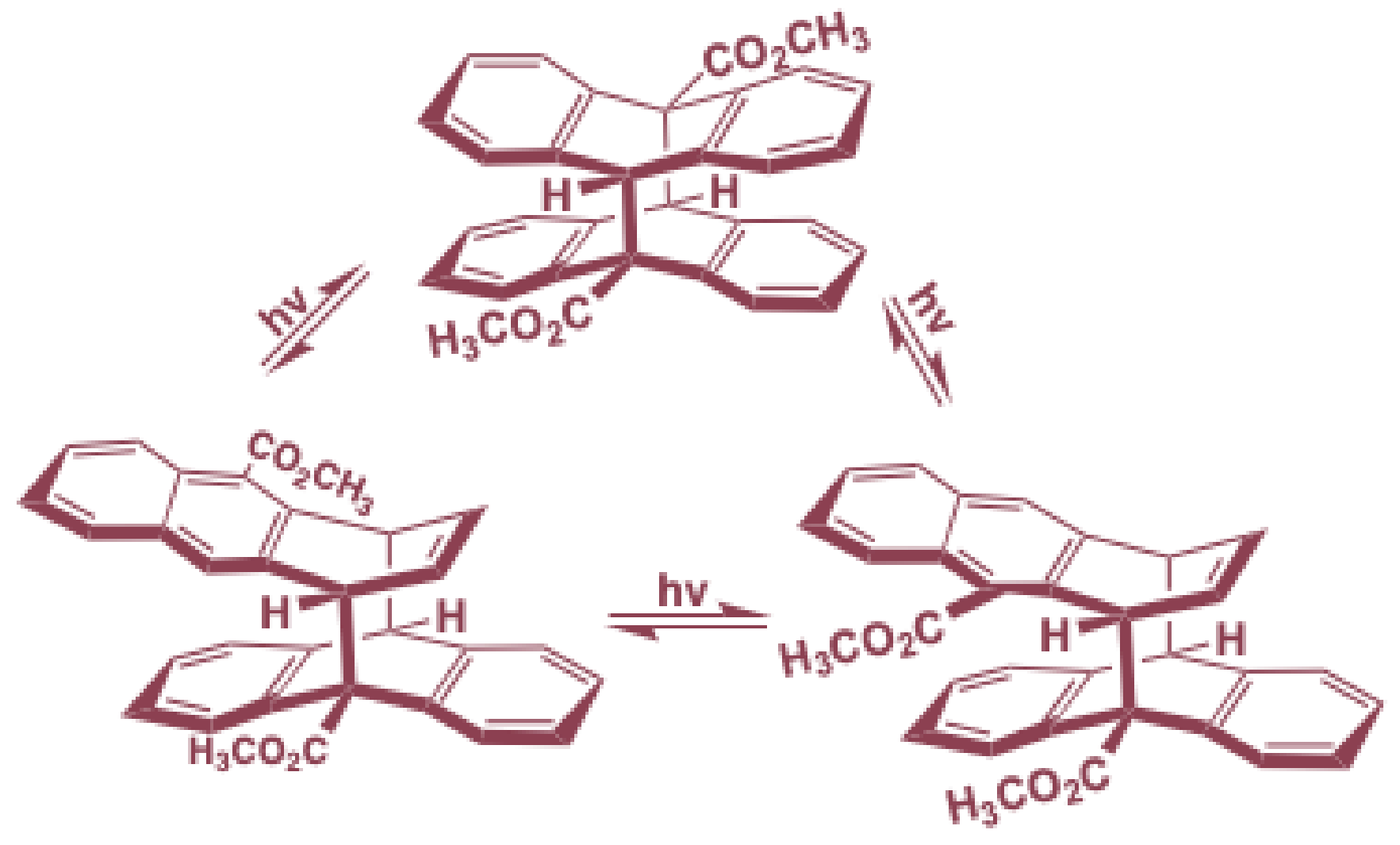
**Anti Dimer Absorption in Benzene**

## Results and Conclusion

- Obtained $^1H$ NMR and COSY NMR of syn and anti dimers.
- Separated pure $HT_{14}$ (95% pure), and $HH_{14}$ (91% pure) using preparative thin layer chromatography.
- $HT_m$ (98% pure) was isolated using column chromatography

## Future Considerations

The classic experiments of Chandross and Ferguson at low *T* encourage us to look for excimer fluorescence from the precursor excimers and possible viscosity dependent excimer equilibration in glassy media.



## References

1. Noh, T.;, Lim, H. Dissymmetrical photodimerization of methyl 9-anthroate. *Chem. Lett.* **1977**, *26*), 495-496.
2. Chandross, E. A.; Ferguson, J. Absorption and excimer fluorescence spectra of sandwich dimers of substituted anthracenes. *J. Chem. Phys.* **1966**, *45*, 3554-3564.
3. Chandross, E. A.; Ferguson, J. Absorption and fluorescence of sandwich dimers. Theory of the excimer state. *J. Chem. Phys.* **1966**, *45*, 397-398.

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