

Introduction

Photochromism refers to the electromagnetic radiation (light)-induced reversible transformation of a chemical compound between two metastable states, where they can be characterized based on their differences in absorption of light. The use of photochromic units in supramolecular complexes allows for the facile manipulation of binding motifs and therefore, complexation strengths (K_A , K_D). Incorporation of these kinds of molecules allows for the creation of materials, such as polymers, with diverse and dynamic properties (Figure 1).

The synthetic route of an AA, hydrogen bonded acceptor (HBA), containing a hemithioindigo core has been successfully established previously. Our research goal is to further optimize the synthetic route and explore the binding interactions of this HBA with various hydrogen bond donors (HBD).

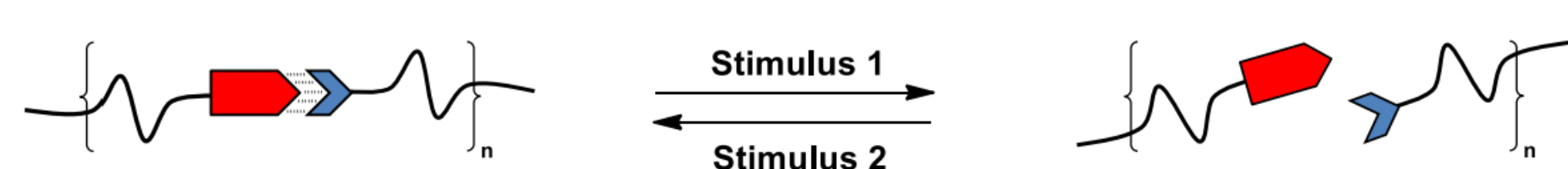
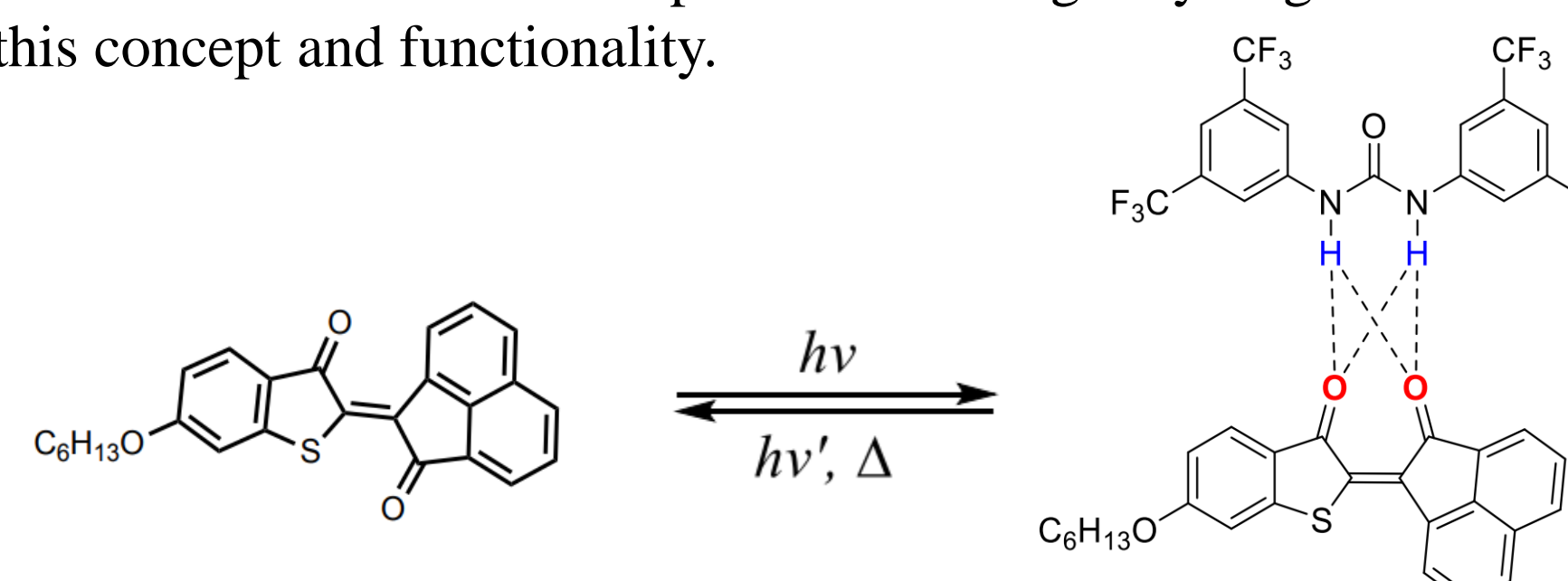


Figure 1. The reversible binding interactions of a supramolecular complex when exposed to external stimuli.

Upon exposure to light, this hemithioindigo photoswitch (PS) undergoes a reversible *E/Z* isomerization. In one isomer (*E*), hydrogen bond acceptors are spatially arranged into an AA array capable of forming strong binding interactions HBD. In the other isomer (*Z*), HBA are orientated in a manner that make it incapable of forming a hydrogen bond complex. Scheme 1 illustrates this concept and functionality.



Scheme 1. Photoisomerization of a hemithioindigo hydrogen bond array with a HBD.

Binding interactions of *E*-Isomer by ITC

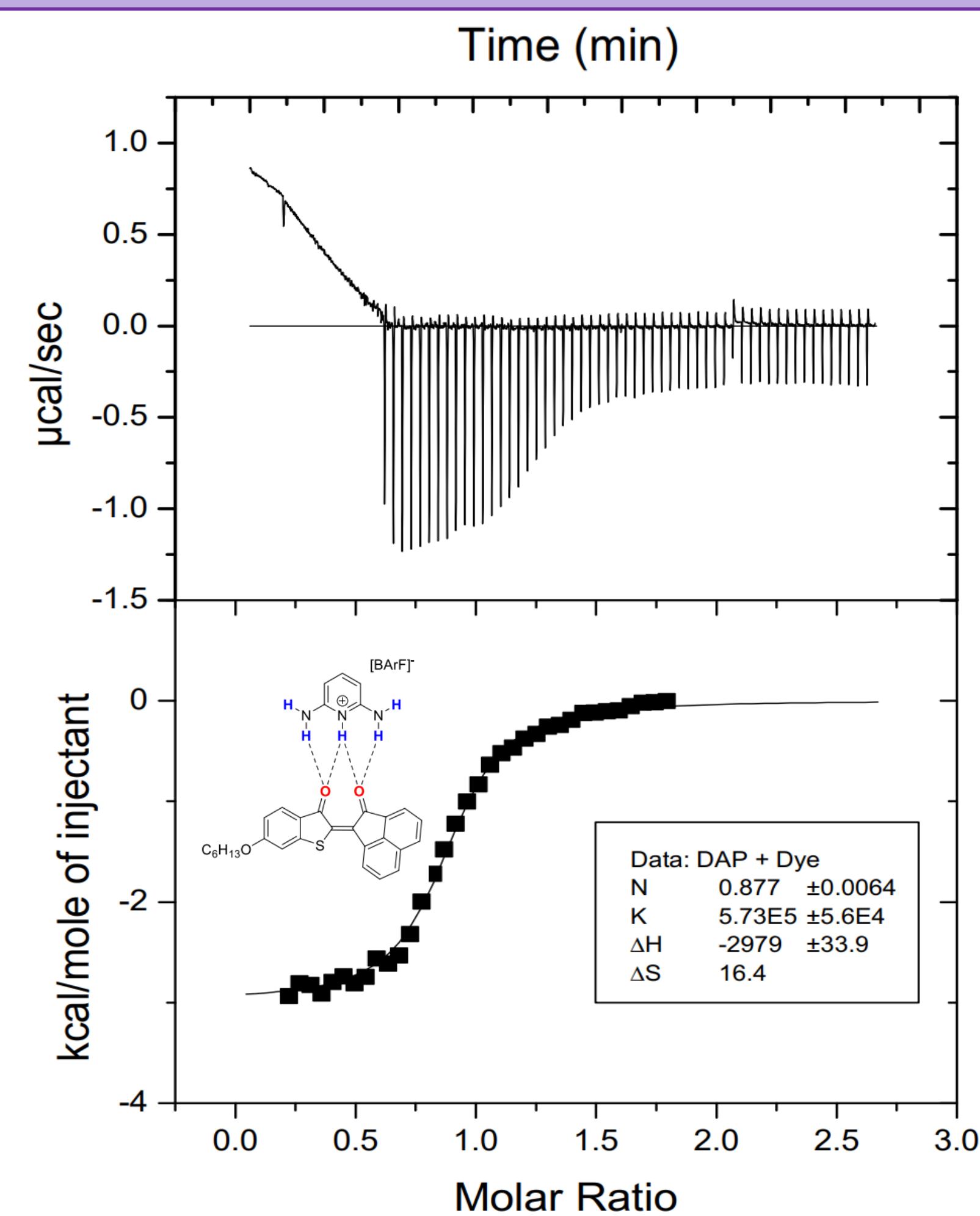


Figure 5. ITC of binding *E*-Isomer of hemithioindigo with DAP · BARf (298K, CHCl_3).

Original and Modified Synthesis of Hemithioindigo Hydrogen Bond Array

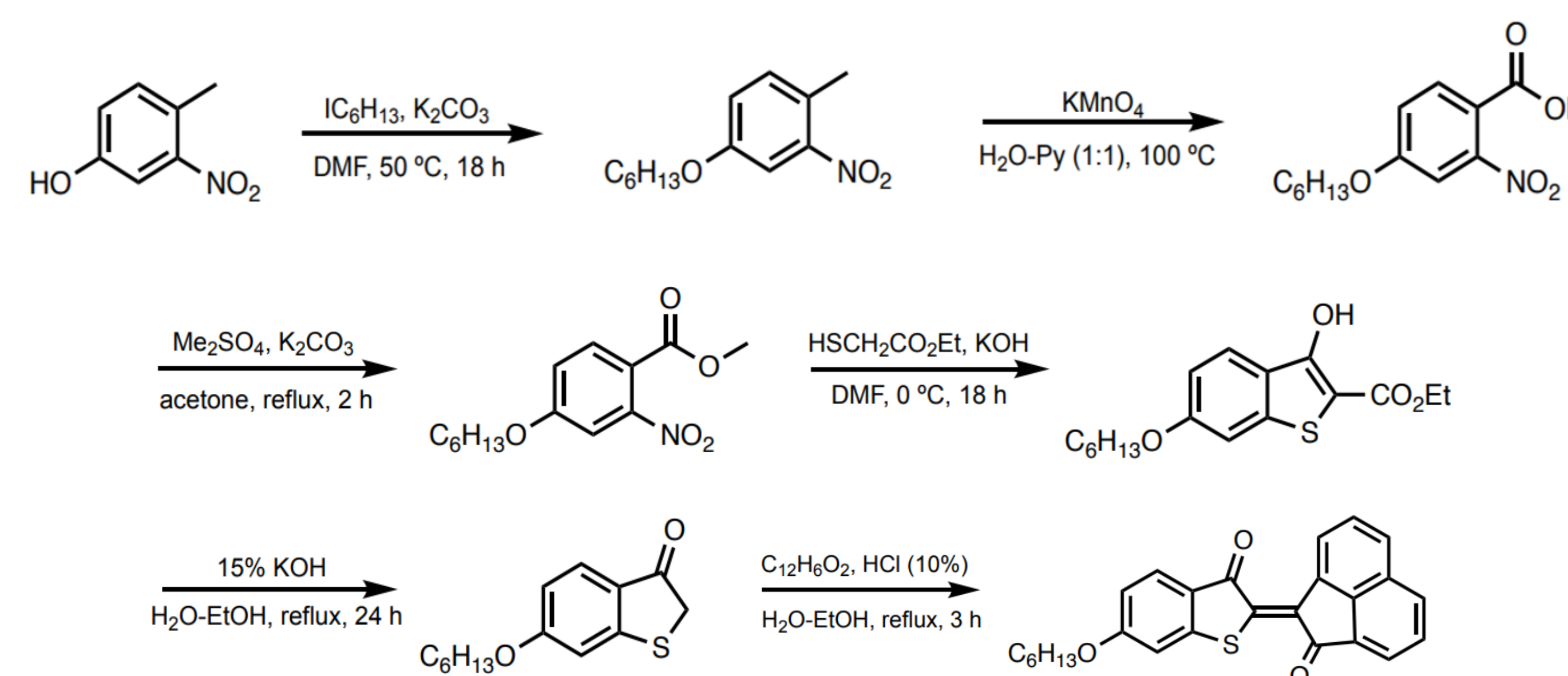


Figure 2. Original synthesis of photoswitchable hemithioindigo hydrogen bond acceptor array.

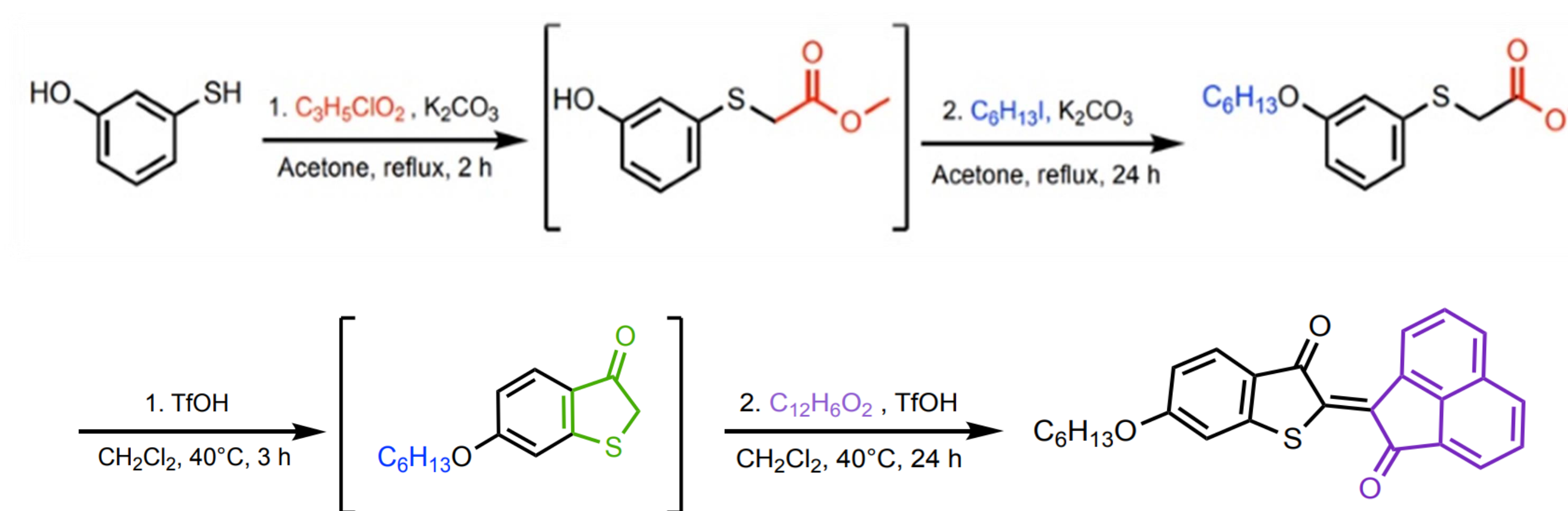


Figure 3. Modified synthesis of photoswitchable hemithioindigo hydrogen bond acceptor array.

^1H NMR of the *Z*-Isomer

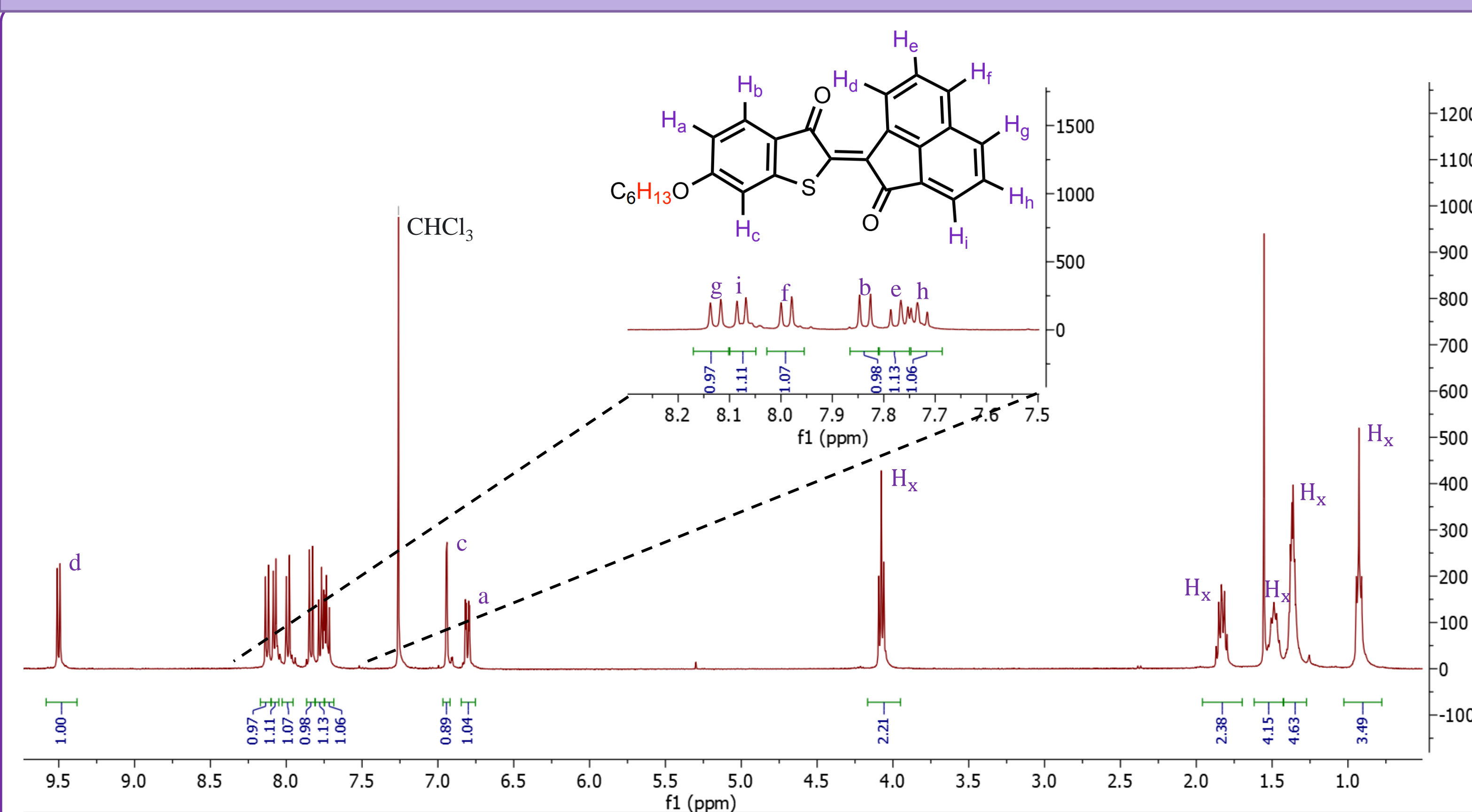


Figure 6. ^1H NMR spectrum of the *Z*-Isomer of hemithioindigo (298K, CDCl_3).

Photostationary States in Chloroform

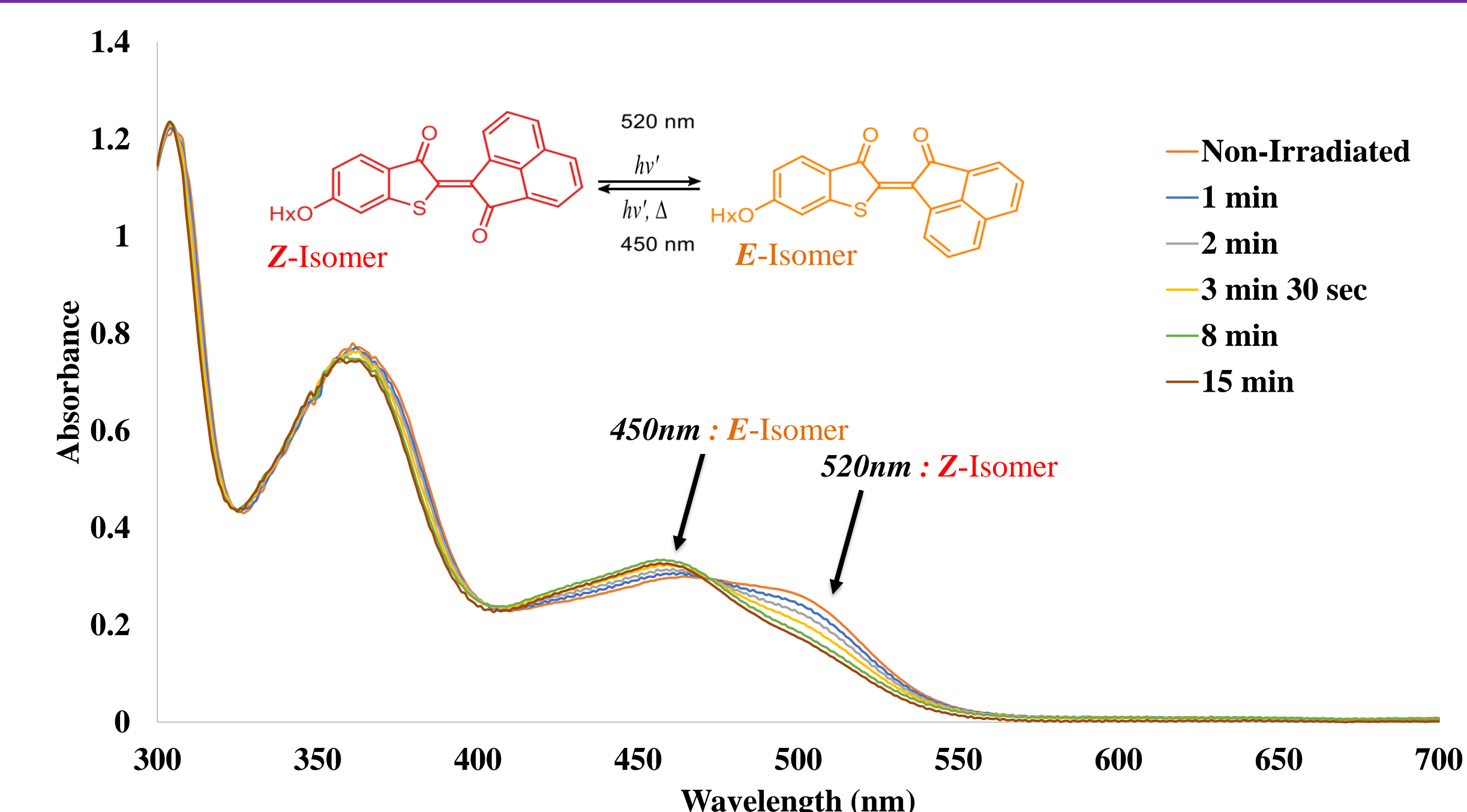


Figure 4. UV-Vis spectra of the photostationary states of hemithioindigo in CHCl_3 after irradiation at 530nm LED light at different time intervals.

Binding Interactions of *E*-Isomer by ^1H NMR

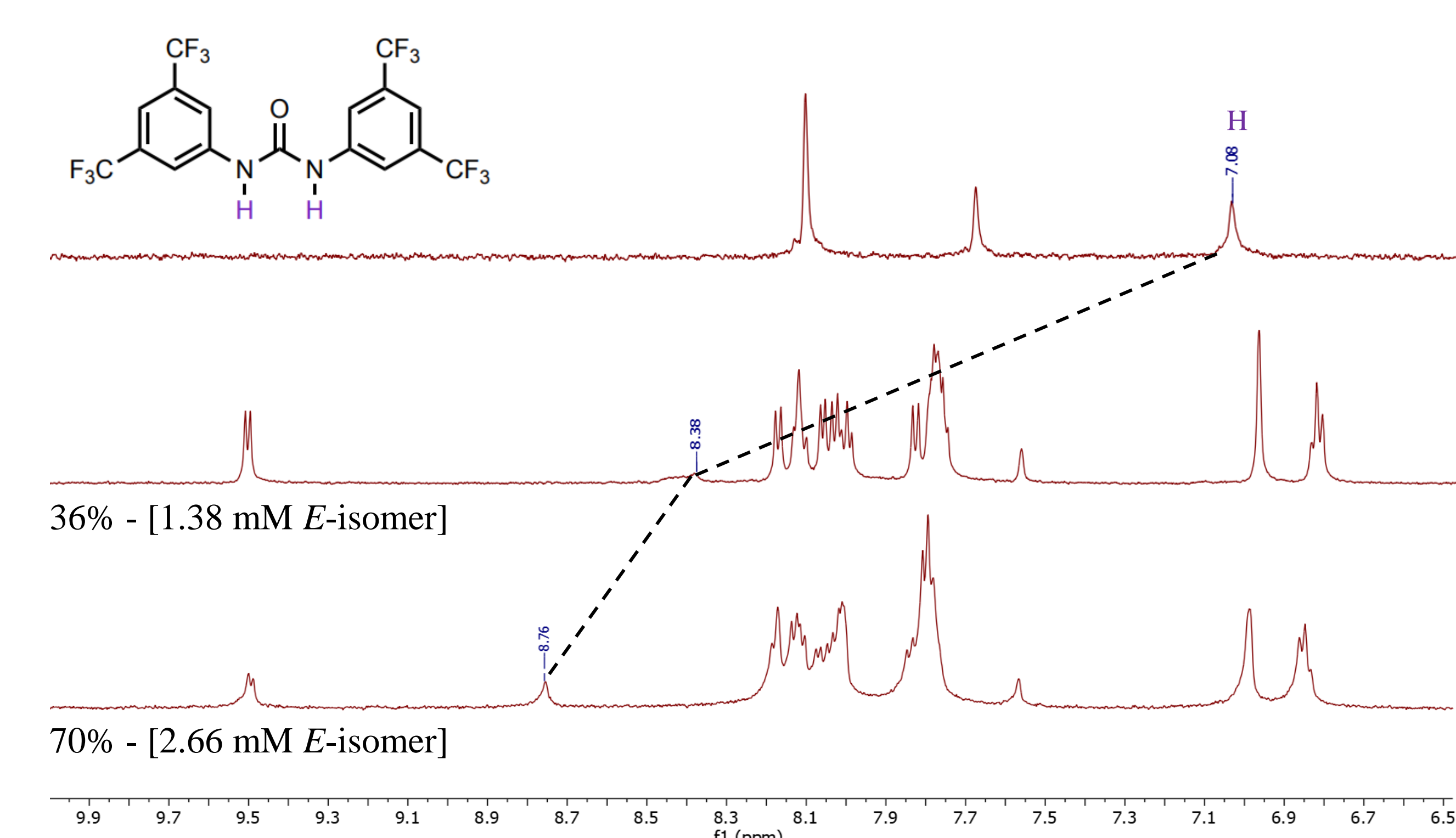


Figure 7. ^1H NMR spectra of the hemithioindigo PS as it photoisomerizes from *Z* to *E* after exposure to 530nm LED light at different time intervals.

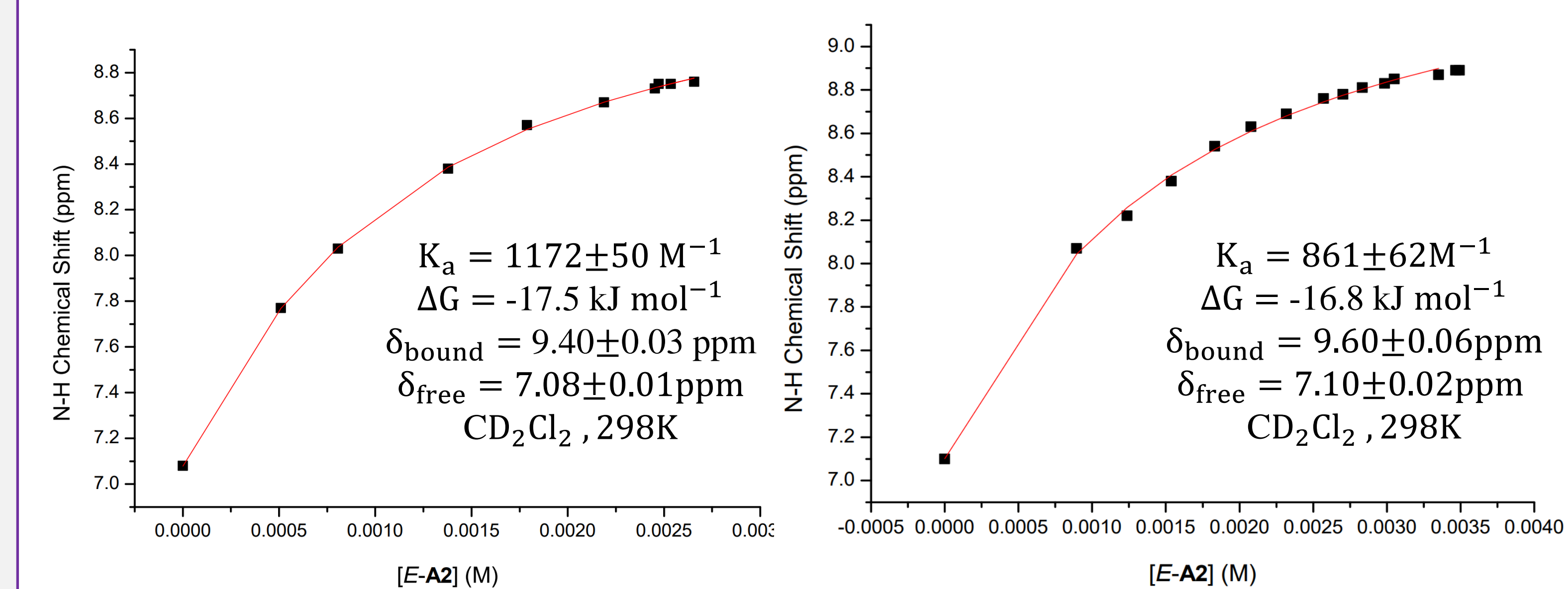


Figure 8. Calculated binding isotherm and thermodynamic parameters based on ^1H NMR titration data.