

Supporting Information

Controlling photochemical geometric isomerization of a stilbene and dimerization of a styrene using a confined reaction cavity in water

Anand Parthasarathy, Lakshmi S. Kaanumalle and V. Ramamurthy*

Department of Chemistry, University of Miami, Coral Gables, FL.

Experimental Details

1. Materials

Host OA and stilbenes **1a-1b** were synthesized and characterized following the literature procedures. Sodium tetraborate and **3** were purchased from Sigma-Aldrich.

2. General protocol for the binding studies of guests with OA and NMR characterization

Six hundred μL of a D_2O stock solution of host OA (1 mM in 10 mM $\text{Na}_2\text{B}_4\text{O}_7$) was added to a NMR tube. To this was added aliquots of guest such that 0.25 equivalents were added upon each addition (2.5 μL of a 60 mM solution in $\text{DMSO-}d_6$). The complexation was achieved by shaking the NMR tube. Spectra were recorded after ca. 2 minutes. Each sample was also examined 24 h later and no changes in the spectra were observed. Spectra were recorded at room temperature under aerated conditions on a Bruker 500 MHz NMR at 25°C. Complete complexation was observed after 0.5 equivalents of stilbene derivative was added. The addition of excess stilbene derivatives led to turbid solutions and NMR spectra demonstrated the formation of 2:1 (H:G) complex. In the case of **3**, addition of excess guest led to turbid solutions and the NMR showed appearance of unbound guest peaks besides the bound ones. Additionally 2D ^1H NMR (COSY and NOESY) were carried out to characterize the capsular complexes.

3. Fluorescence emission and lifetime studies

A stock solution (1 mM) of host OA was prepared in 10 mM sodium borate buffer. Stock solutions (1 mM) of guests (**1a** and **1b**) were prepared in hexane. A volume of solution corresponding to $2 \times 10^{-5}\text{M}$ was pipetted into a test tube. The solution was purged with air to remove the organic solvent. Two equivalents of the host **1** stock solution was added. The resulting solution was made upto 5 mL with 10 mM sodium tetraborate and stirred for 10 min. Steady state fluorescence emission was recorded for the samples by exciting at 320 nm on FS900CDT spectrophotometer (Edinburgh Instruments). Fluorescence lifetime measurements were measured using nanosecond flash lamp setup

in FL900CDT spectrophotometer (Edinburgh Instruments). All lifetime data were fitted for mono exponentials using inbuilt software provided by Edinburgh Instruments.

4. Photolysis of substrates included in OA

A solution of the host-guest complexes (2:1) prepared following the protocol detailed in binding studies section and were irradiated in a 300 nm Rayonet reactor. The irradiated reaction mixture was analyzed by ^1H NMR and also by GC after extracting the products into CDCl_3 .

5. Extraction and analysis of photoproducts from host 1

After photolysis, reactants and products were extracted from the aqueous host solution using chloroform, dried over anhydrous MgSO_4 , concentrated and analyzed on an HP-5890 series II gas chromatograph fitted with an SE-30 capillary column. Products were also identified by ^1H NMR and GC-MS.

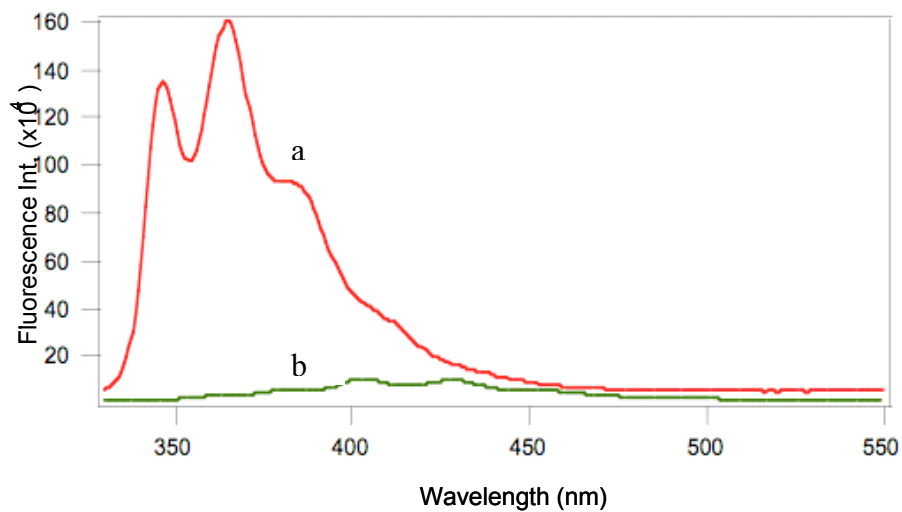


Figure S1 : a) Fluorescence emission of **1a@OA** in H₂O (10 mM borate buffer). b) in 10mM borate buffer. λ_{ex} =320 nm; [**1a**] = 2×10^{-5} M; [OA] = 4×10^{-5} M.

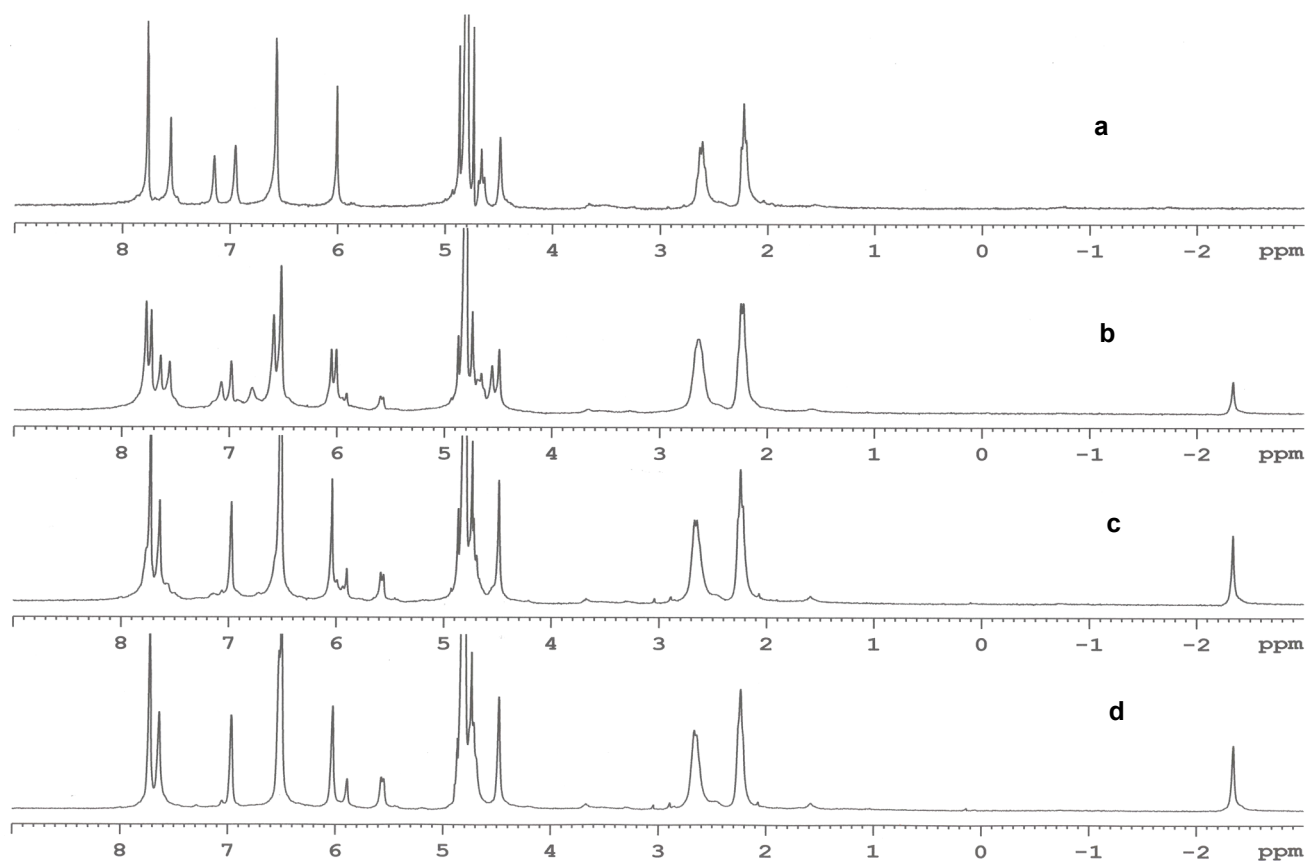


Figure S2: ^1H NMR spectra (300 MHz) showing the formation of 1:2 complex between *trans*-**1a** and OA (1 mM) in 10 mM sodium tetraborate buffer / D_2O .

- OA (2 mM).
- After addition of 0.25 equivalents of *trans*-**1a**.
- After addition of 0.5 equivalents of *trans*-**1a**.
- After addition of 1 equivalent of *trans*-**1a**.

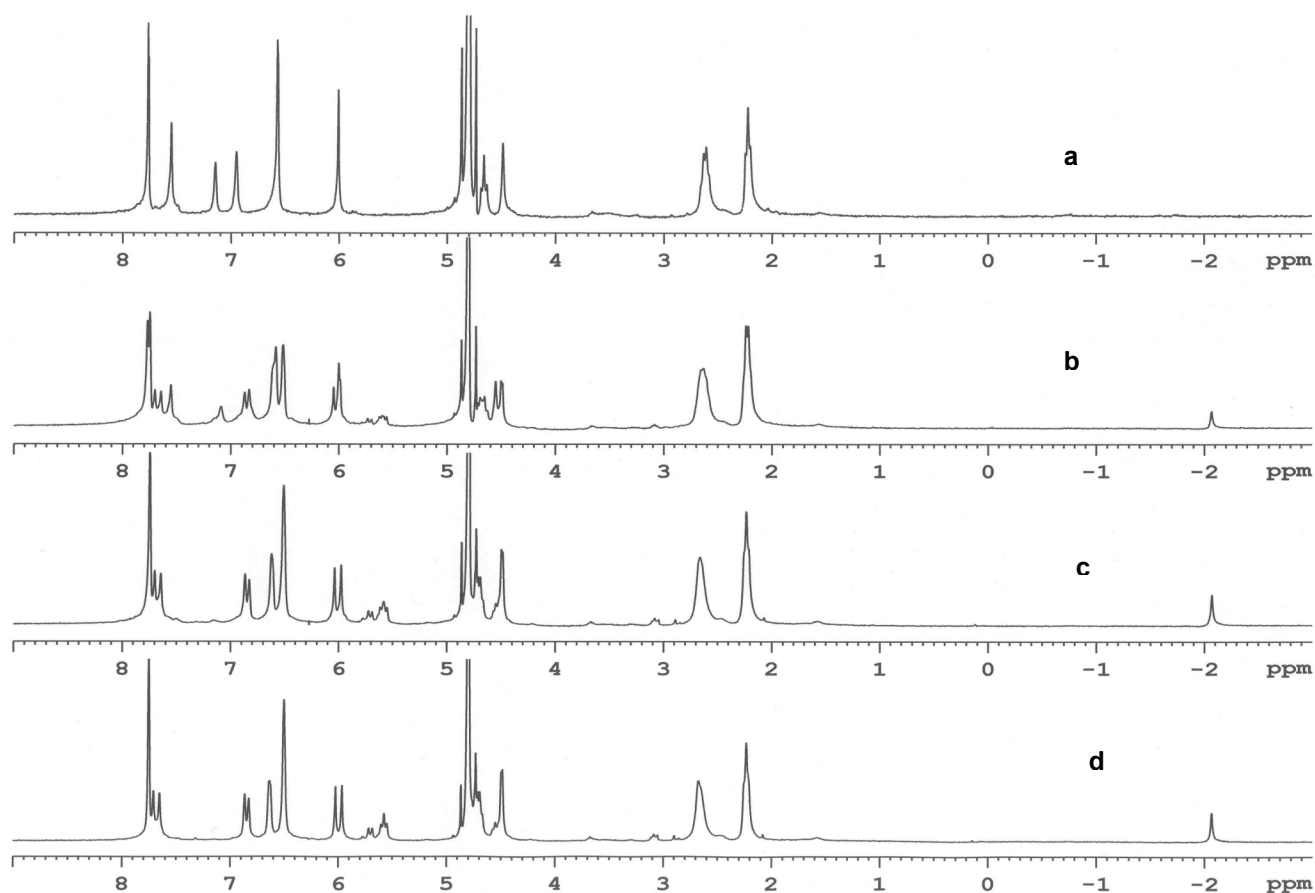


Figure S3: ^1H NMR spectra (300 MHz) showing the formation of 1:2 complex between *trans*-**1b** and OA (1 mM) in 10 mM sodium borate buffer / D_2O .

- a. OA (2 mM).
- e. After addition of 0.25 equivalents of *trans*-**1b**.
- f. After addition of 0.5 equivalents of *trans*-**1b**.
- g. After addition of 1 equivalent of *trans*-**1b**.

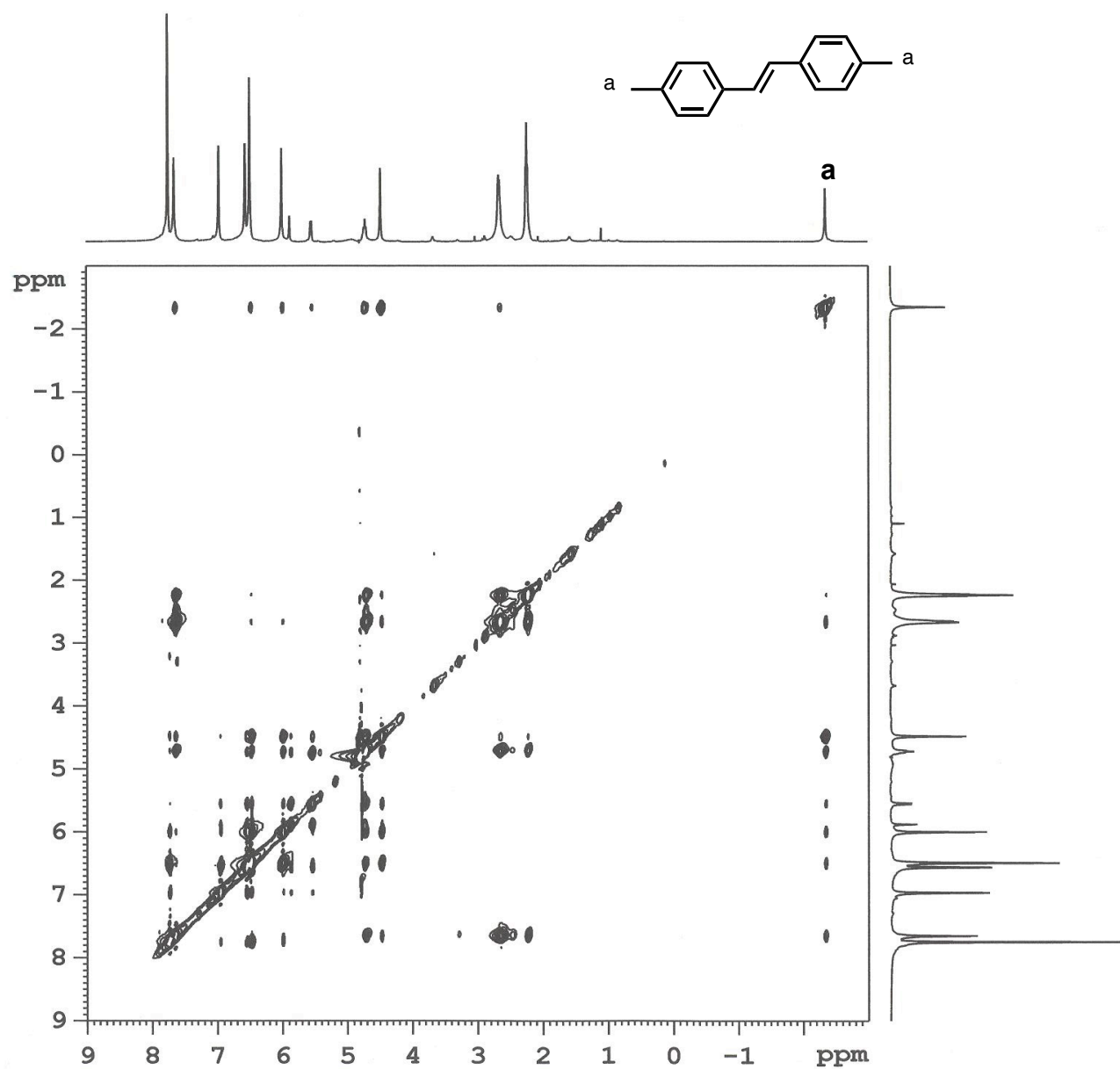


Figure S4: NOESY spectrum of *trans*-1a @ OA (5 mM) in 50mM sodium tetraborate / D₂O (500 MHz).

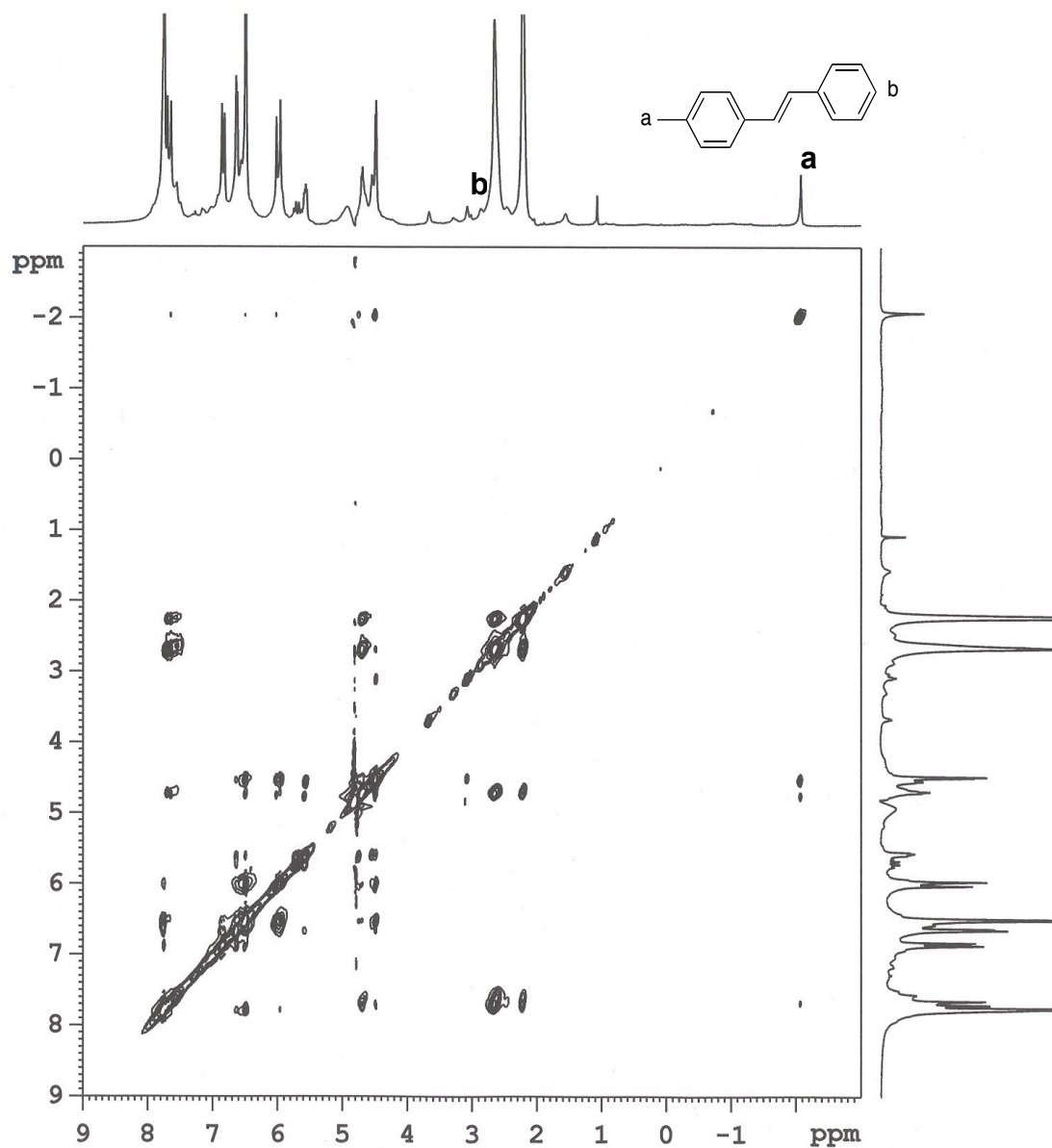


Figure S5: NOESY spectrum of *trans*-**1b** @ OA (5 mM) in 50mM sodium tetraborate / D₂O (500 MHz).

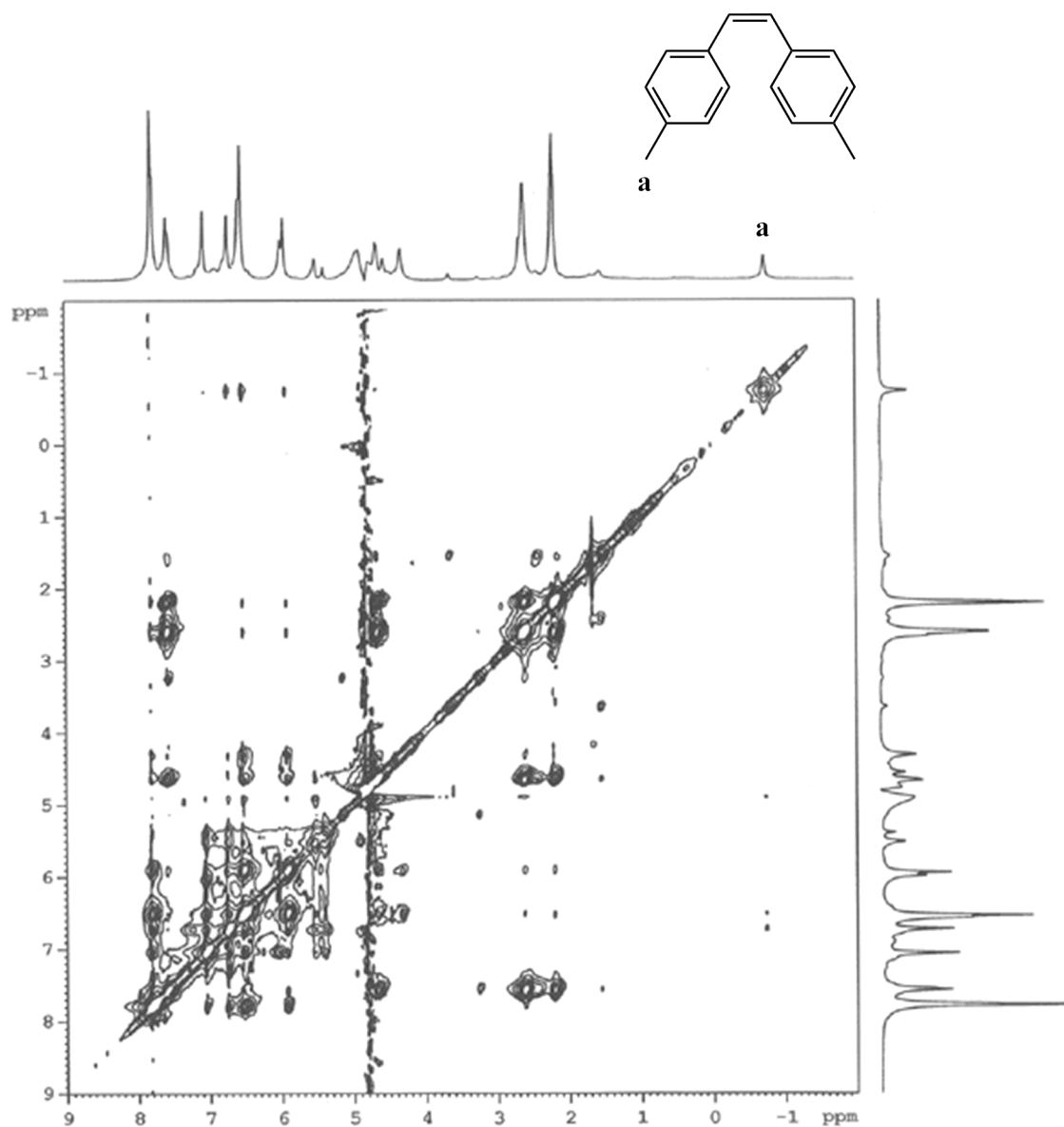


Figure S6: NOESY spectrum of *cis*-1a @ OA (5 mM) in 50mM sodium tetraborate / D₂O (500 MHz).

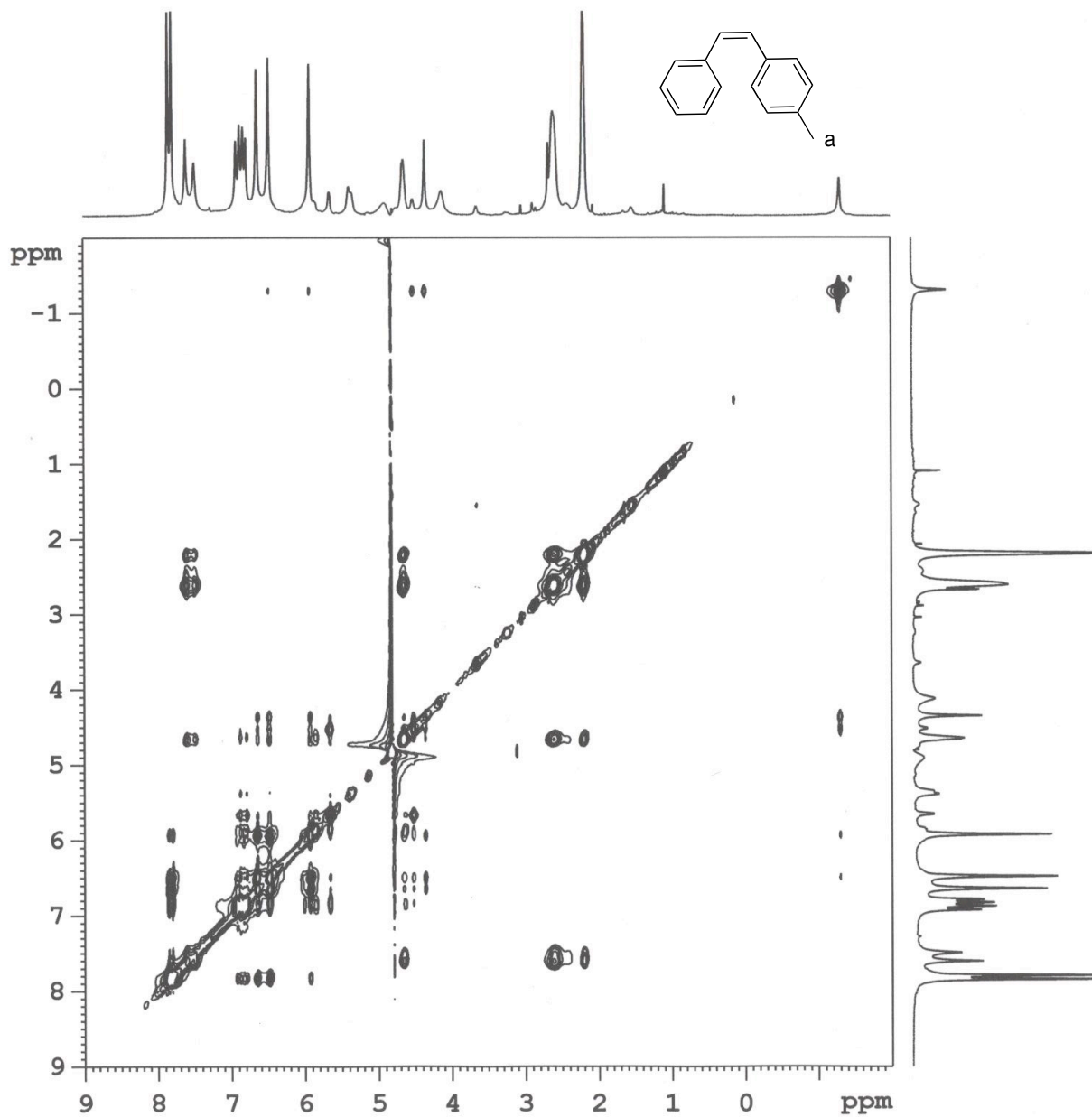


Figure S7: NOESY spectrum of *cis*-1b @ OA (5 mM) in 50mM sodium tetraborate / D₂O (500 MHz).

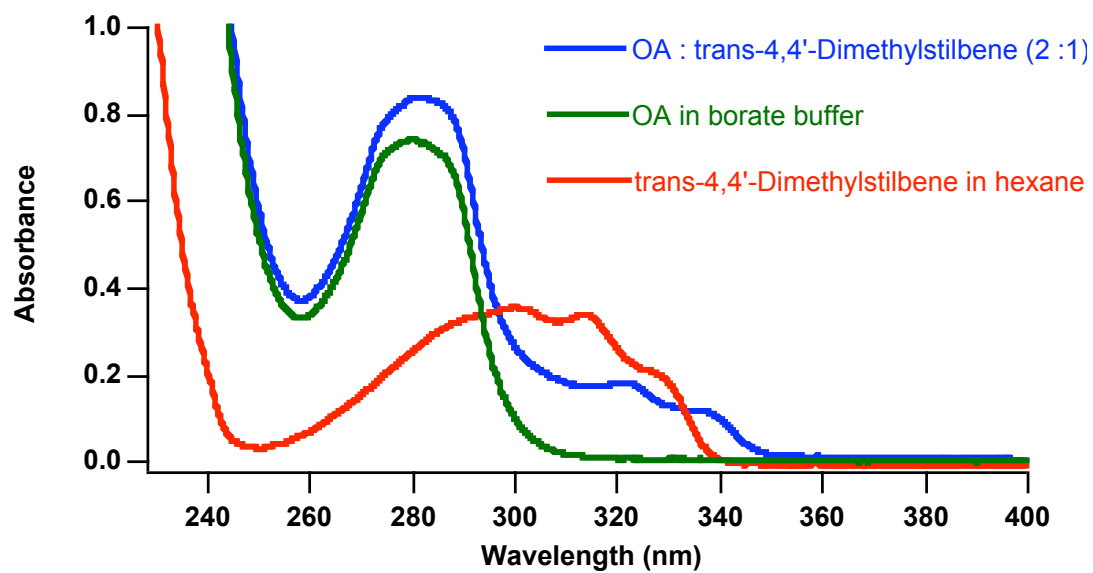
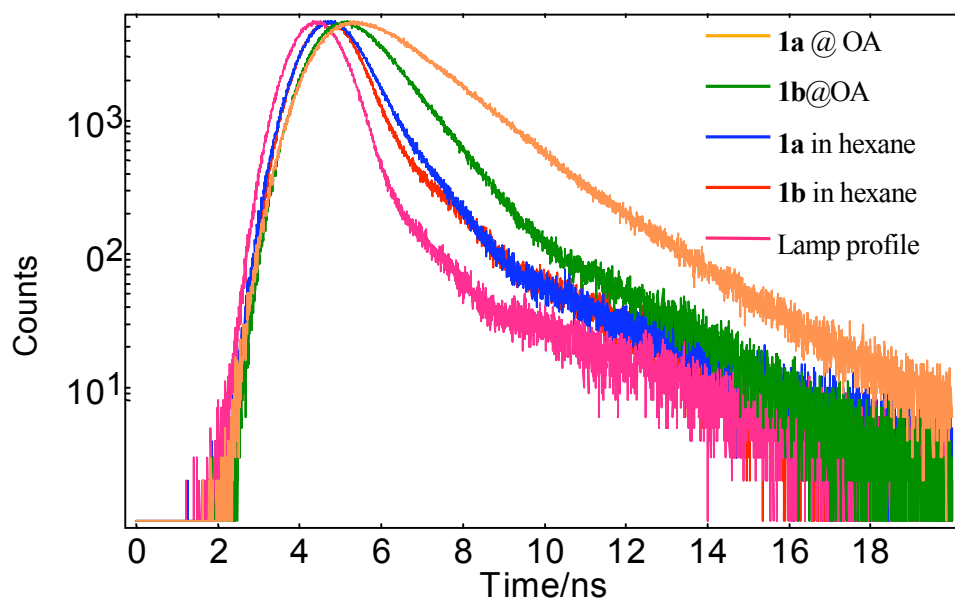


Figure S8: UV-Absorption spectra of *trans*-**1a** in hexane and OA.

[**1a**] = 1×10^{-5} M; [OA] = 2×10^{-5} M.



$\lambda_{\text{ex}}=320 \text{ nm}$; $\lambda_{\text{em}}=365 \text{ nm}$ for **1a** and $\lambda_{\text{ex}}=320 \text{ nm}$; $\lambda_{\text{em}}=360 \text{ nm}$ for **1b**
 $[\mathbf{1a}] = 2 \times 10^{-5} \text{ M}$; $[\text{OA}] = 4 \times 10^{-5} \text{ M}$.

Figure S9: Time resolved fluorescence life time spectra of *trans*-**1a** and *trans*-**1b** in OA and in hexane.

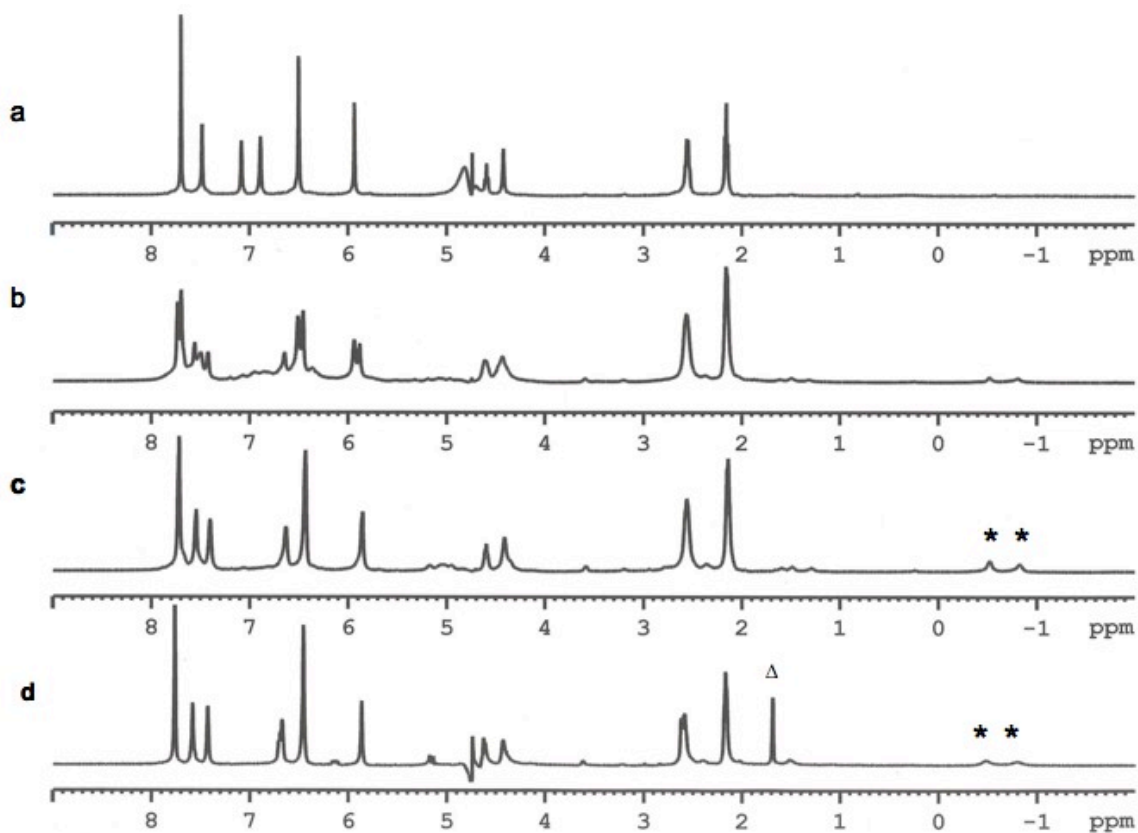


Figure S10: ^1H NMR (500 MHz) spectra showing the formation of 2:2 complex between **3** and OA (2 mM) in 20 mM sodium tetraborate / D_2O .

- OA.
- After addition of 0.5 equivalents of **3**.
- After addition of 1 equivalent of 4-methylstyrene **3**.
- After addition of 2 equivalents of 4-methylstyrene **3**. (*-bound **3**, Δ -unbound **3**)

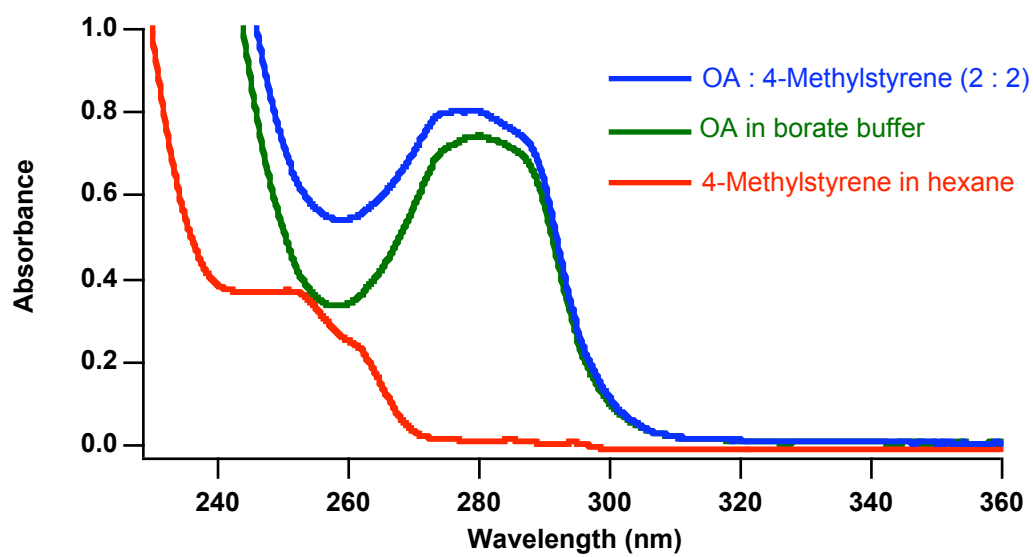


Figure S11: UV-Absorption spectra of **3** in hexane and OA.

$[3] = 1 \times 10^{-5} \text{M}$; $[\text{OA}] = 1 \times 10^{-5} \text{M}$.