Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Electronic Supporting Information

Role of free space and weak interactions on geometric isomerization of stilbenes in a confined space

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Experimental Details

Materials

Host OA and stilbenes, **1a-1h** were synthesized and characterized following the literature procedures.[1,2] Sodium tetraborate was purchased from Sigma-Aldrich.

General protocol for stilbenes binding studies and NMR characterization

Six hundred μL of a D_2O stock solution of host OA (1 mM in 10 mM $Na_2B_4O_7$) 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 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 hours 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 equivalent of stilbene derivative was added. The addition of excess guest led to turbid solutions and NMR spectra demonstrated the formation of 2:1 (H:G)complex. Additionally diffusion studies(PGSE) and 2D ^{1}HNMR (NOESY) were carried out to characterize the capsular complexes.

Direct irradiation

Two mM concentration of the host-guest complexes (2:1) prepared following the protocol detailed above and were irradiated in a 300 nm Rayonet reactor for 30 min. The irradiated reaction mixture was analyzed by ^{1}H NMR and also by GC after extracting the products into $CDCl_3$.

Direct irradiation of mixed capsules

Six hundred μL of 2 mM complexes of *trans*-**1a**@$(OA)_2$, *trans*-**1b**@$(OA)_2$ and *trans*-**1c**@$(OA)_2$ were prepared separately and were characterized by ^{1}H NMR prior to mixing. After ensuring complex formation, three hundred μL of the each of the samples were mixed in a NMR tube and ^{1}H NMR was recorded for the mixed capsules. The recorded NMR suggested the presence of three independent capsules in solution. The resulting solution was irradiated in a 300

nm Rayonet reactor for 45 min. The reaction mixture was analyzed by ^{1}H NMR and also by GC after extracting the products into $CDCl_3$.

Extraction and analysis of photoproducts from host

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 ^{1}H NMR and GC-MS.

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 (*trans*-**1a** and *trans*-**1d**) were prepared in hexane. A volume of solution corresponding to $2x10^{-5}$M was pipetted into a test tube. The solution was purged with air to remove the organic solvent. Two equivalents of the host, OA 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 S2in FL900CDT spectrophotometer (Edinburgh Instruments). All lifetime data were fitted for mono exponentials using inbuilt software provided by Edinburgh Instruments.

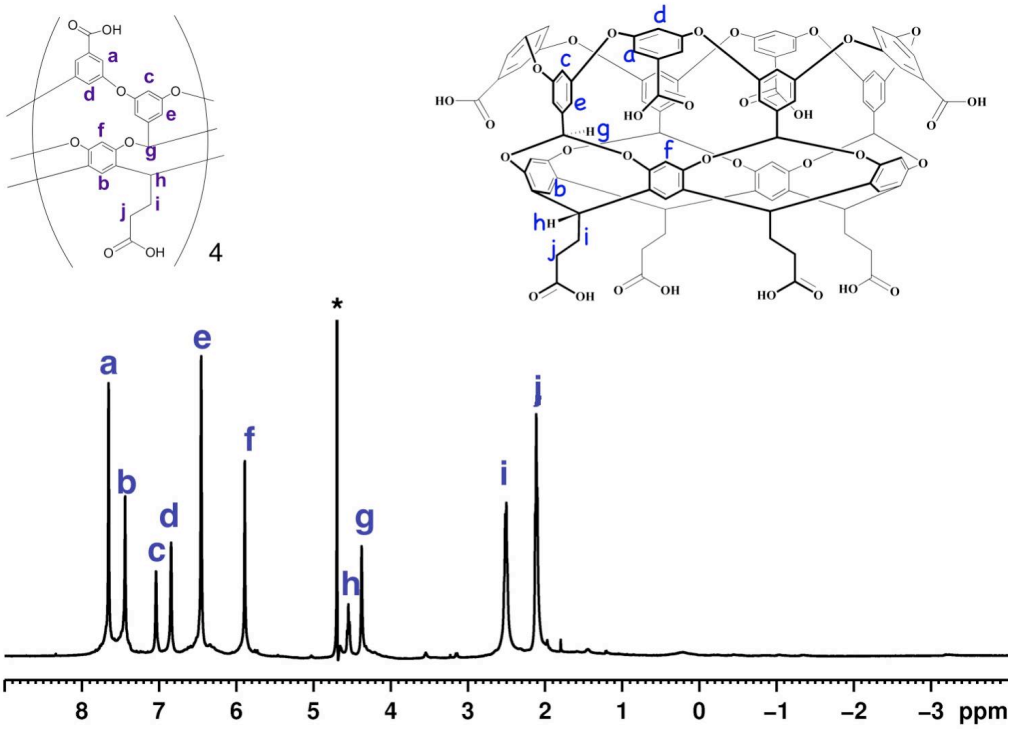

Figure S1 Two representations of the structure of OA (top) and the ^{1}H NMR spectrum (bottom) of OA (500 MHz, 10^{-3} M OA and 10^{-2} M sodium tetraborate in D_2O). OA signals are assigned as shown in the structures. Residual water signal is denoted using *.

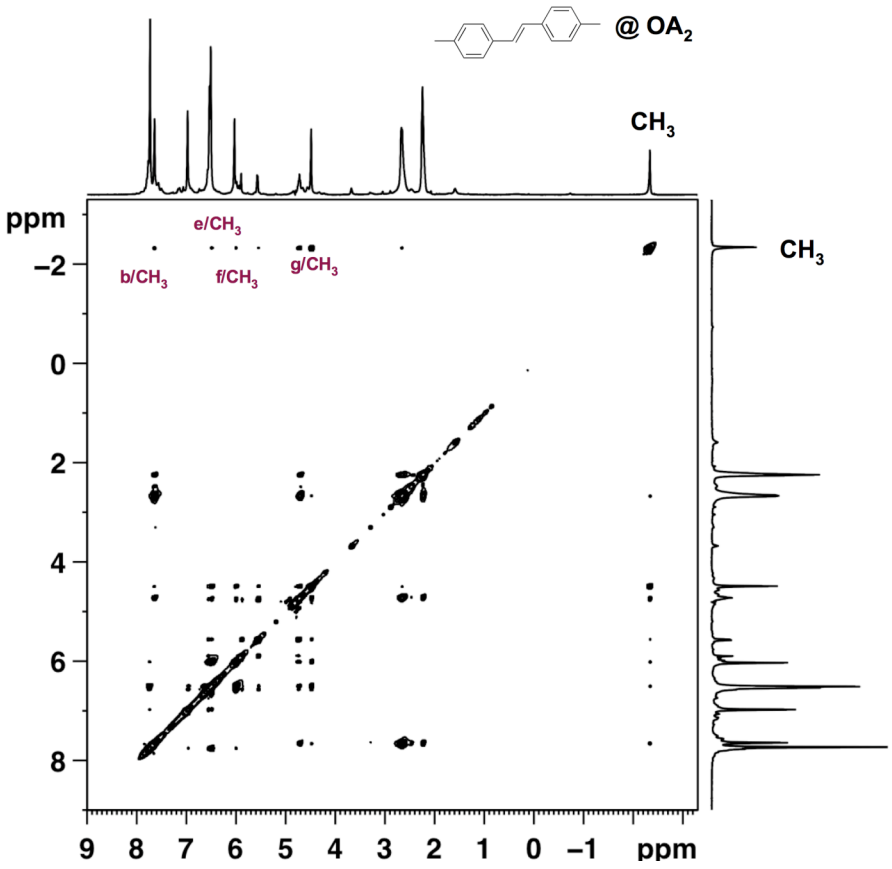

Figure S2 NOESY spectrum (500 MHz, D_2O, 5×10^{-3} M OA in 5×10^{-2} M sodium tetraborate) of **1a@**OA_2

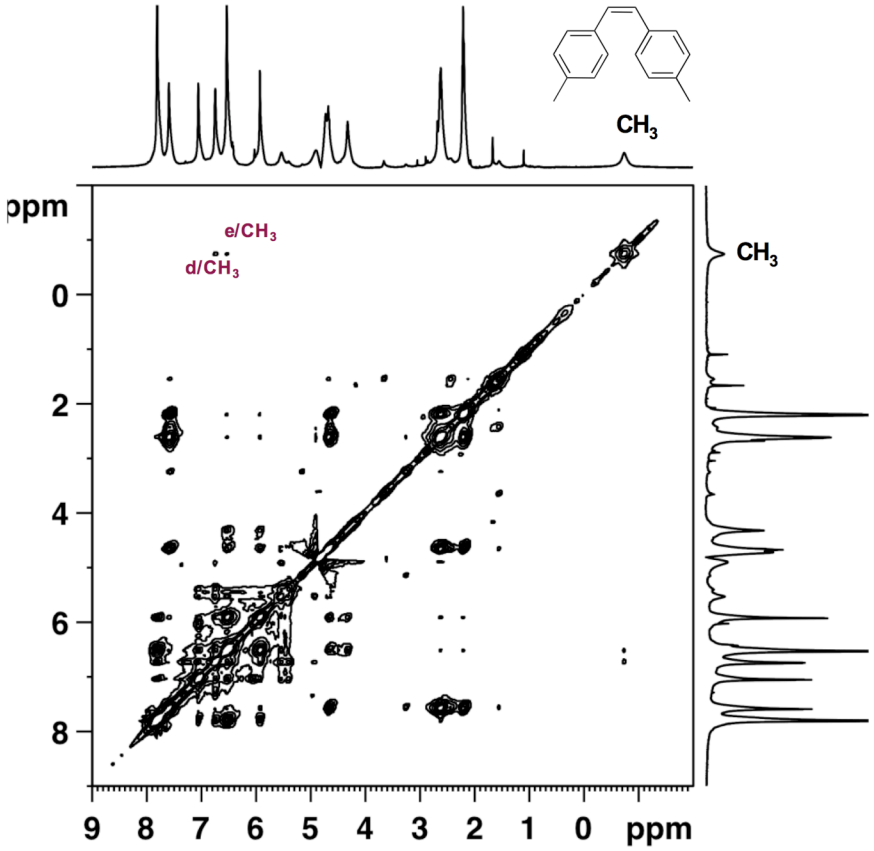

Figure S3: NOESY spectrum (500 MHz, D_2O, 5×10^{-3} M OA in 5×10^{-2} M sodium tetraborate) of **2b**@OA_2.

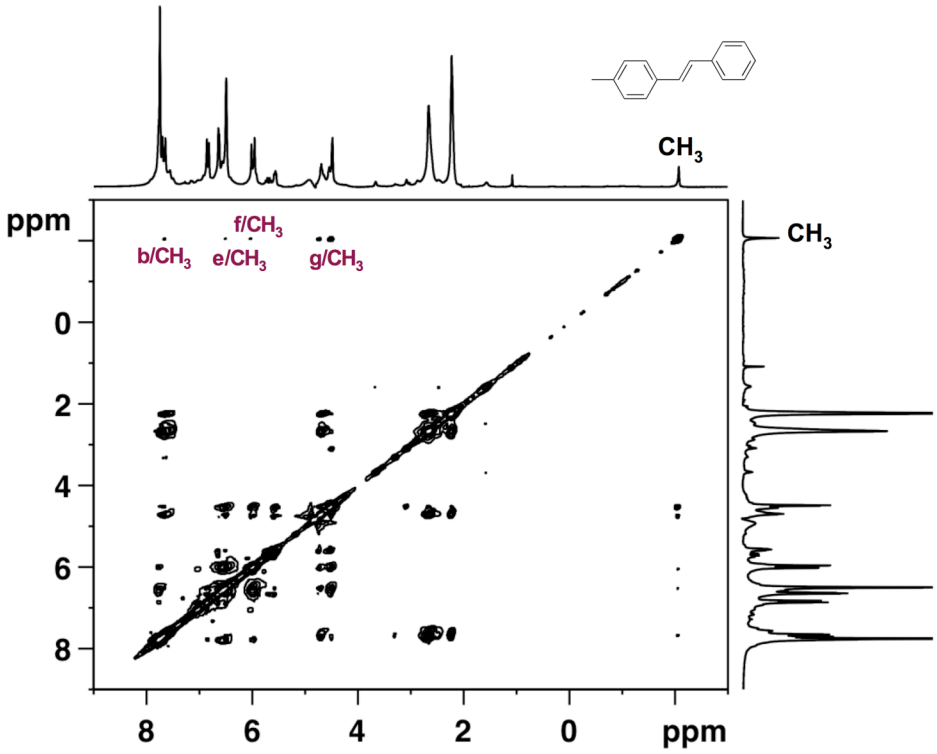

Figure S4 NOESY spectrum (500 MHz, D_2O, 5×10^{-3} M OA in 5×10^{-2} M sodium tetraborate) of **1d@**OA_2.

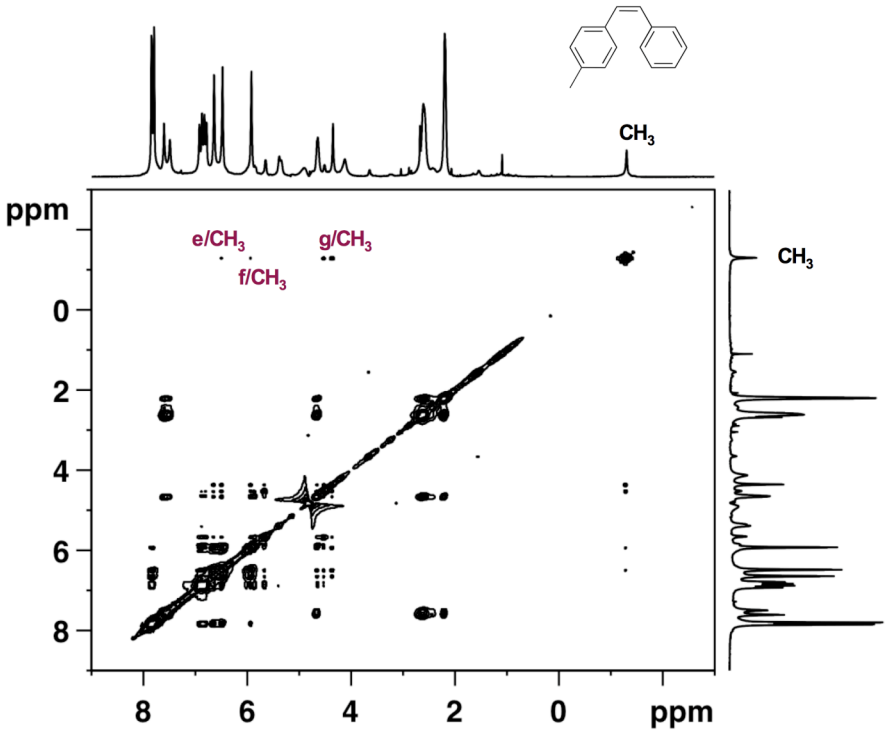

Figure S5 NOESY spectrum (500 MHz, D_2O, 5×10^{-3} M OA in 5×10^{-2} M sodium tetraborate) of **2d@OA$_2$**.

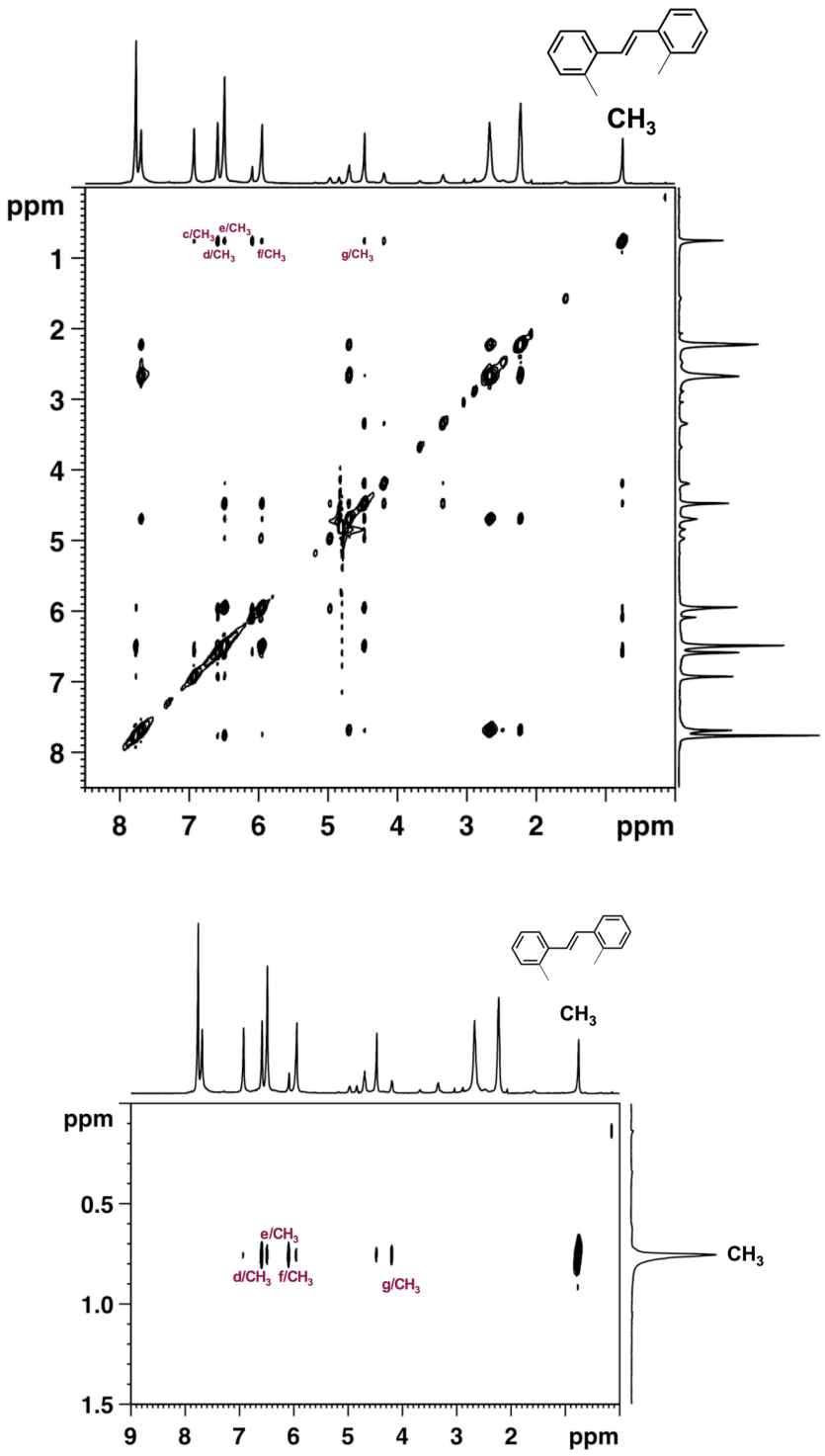

Figure S6. (**top**) NOESY spectrum (500 MHz, D_2O, 5×10^{-3} M OA in 5×10^{-2} M sodium tetraborate) of **1c@**OA_2. (**bottom**) Select region of NOESY spectrum showing correlations between 'CH_3' signal of guest with host signals.

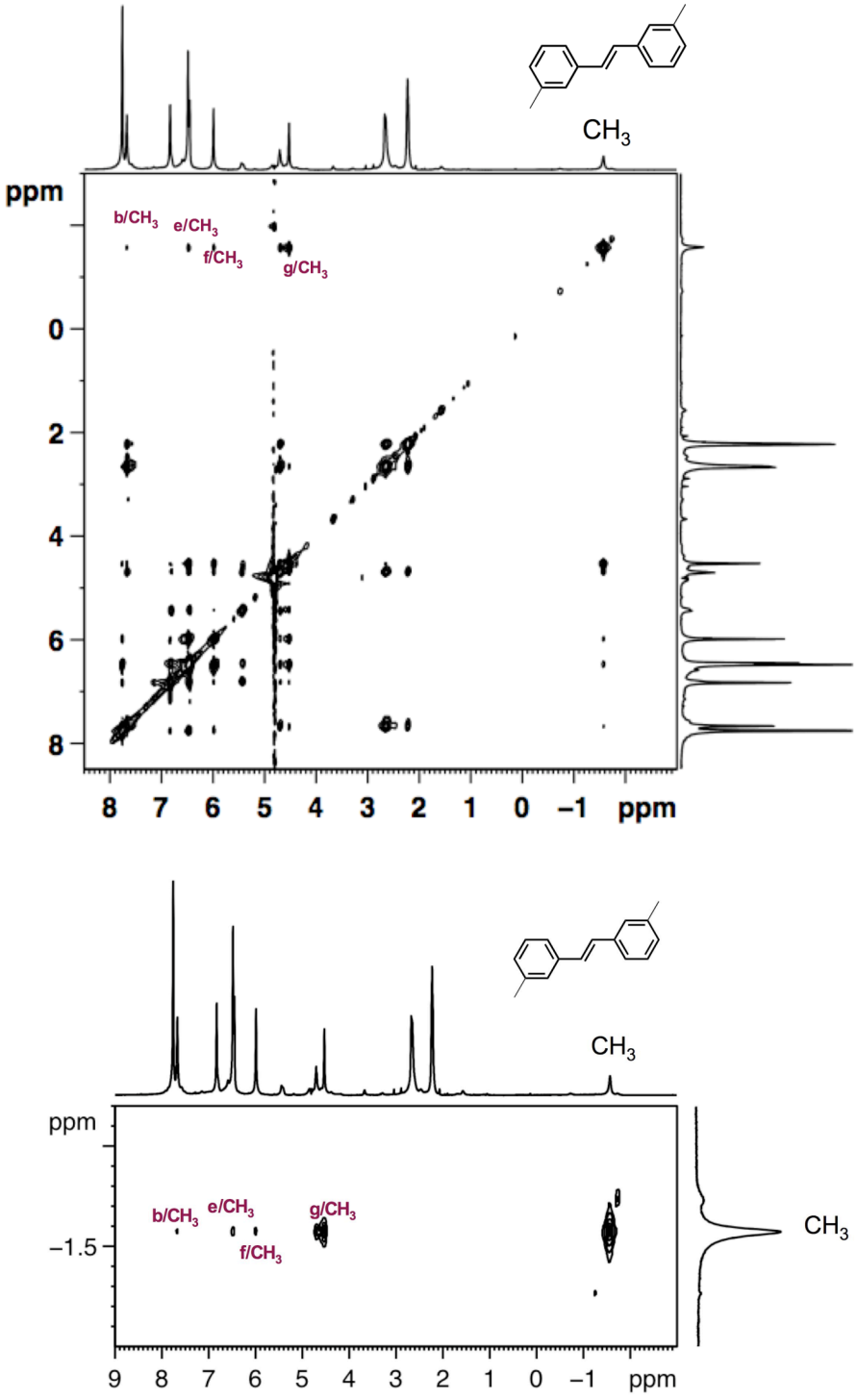

Figure S7 (**top**) NOESY spectrum (500 MHz, D_2O, 5×10^{-3} M OA in 5×10^{-2} M sodium tetraborate) of **1b@**OA_2. (**bottom**) Select region of NOESY spectrum showing correlations between 'CH_3' signal of guest with host signals.

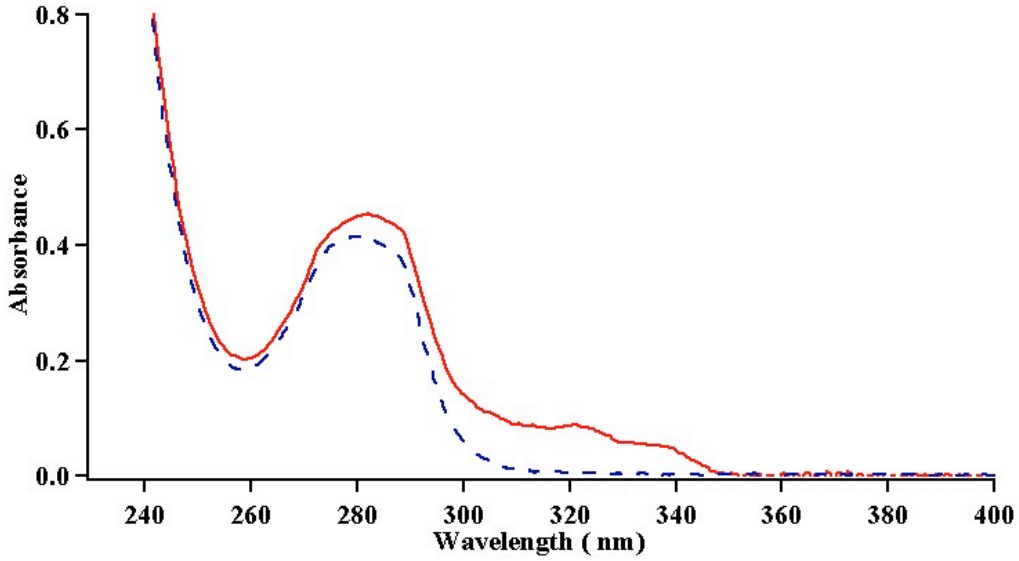

Figure S8 UV-Absorption spectra of OA (dotted line) and *trans*-**1a** **@**$(OA)_2$ (solid line). [*trans*-**1a**] = $5x10^{-6}$M; [OA] = $1x10^{-5}$M.