

Supporting Information

Photo-Fries Reaction Made Highly Selective With the Help of a Water Soluble Capsule

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Materials

Host **1** was synthesized and characterized following the literature procedure. Sodium tetraborate and acenaphthylene were purchased from Sigma-Aldrich. Naphthyl benzoate (**2a**), Naphthyl phenyl acetate (**2b**) and Dimethyl naphthyl phenyl acetate (**2c**) were prepared following literature procedures.¹²

General Protocol for Binding Studies and NMR Characterization

Six hundred mL of a D₂O stock solution of host **1** (1 mM) and sodium borate buffer (10 mM) was added to a NMR tube. The resulting NMR **1** is shown in Figure 2 (b). To this was added aliquots of guest such that 0.25 equivalents were added at each addition (5 μ L of a 30 mM solution in DMSO-*d*₆). The complexation was achieved by shaking the NMR tube. Spectra were recorded after ca. 5 minutes. Each sample was also examined 24 hours later. 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. Full complexation was observed after 0.5 equivalent of naphthyl ester was added. The addition of excess guest led to turbid solutions and NMR spectra demonstrated the presence of free guest in addition to the capsular complex.

Inclusion and Photolysis of Substrates within Host 1:

Direct Irradiation:

A 1mM stock solution of host **1** was prepared in 10m M sodium borate buffer (15.5 mg in 8.96 mL of 10 mM buffer solution, H₂O). A volume of solutions corresponding to 1 mg of the substrates 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 were added and the solution was stirred for 10 min. The clear solution was purged with dry N₂ for 20 min. and irradiated using a 450 W medium pressure Hg lamp for 2 h s in a Pyrex test tube. Relative conversion of 60-70% to product was achieved.

Extraction and Analysis of Photoproducts from Host 1:

After photolysis, reactants and products were extracted from the aqueous host solution by acidifying with 10% dil. HCl followed by extraction using an ethyl acetate and acetonitrile (6:4) solvent mixture. The extracted organic layer was dried over anhydrous MgSO₄, concentrated and analyzed on an HP-5890 series II gas chromatograph fitted with an SE-30 capillary column. Products were identified by NMR and GCMS.

Characterization of photoproducts:

Peaks in the GC traces were identified by co injecting with authentic samples which were prepared by solution irradiation. Spectral data of photoproducts from **2a-2c** prepared by solution irradiation were compared with literature reports.

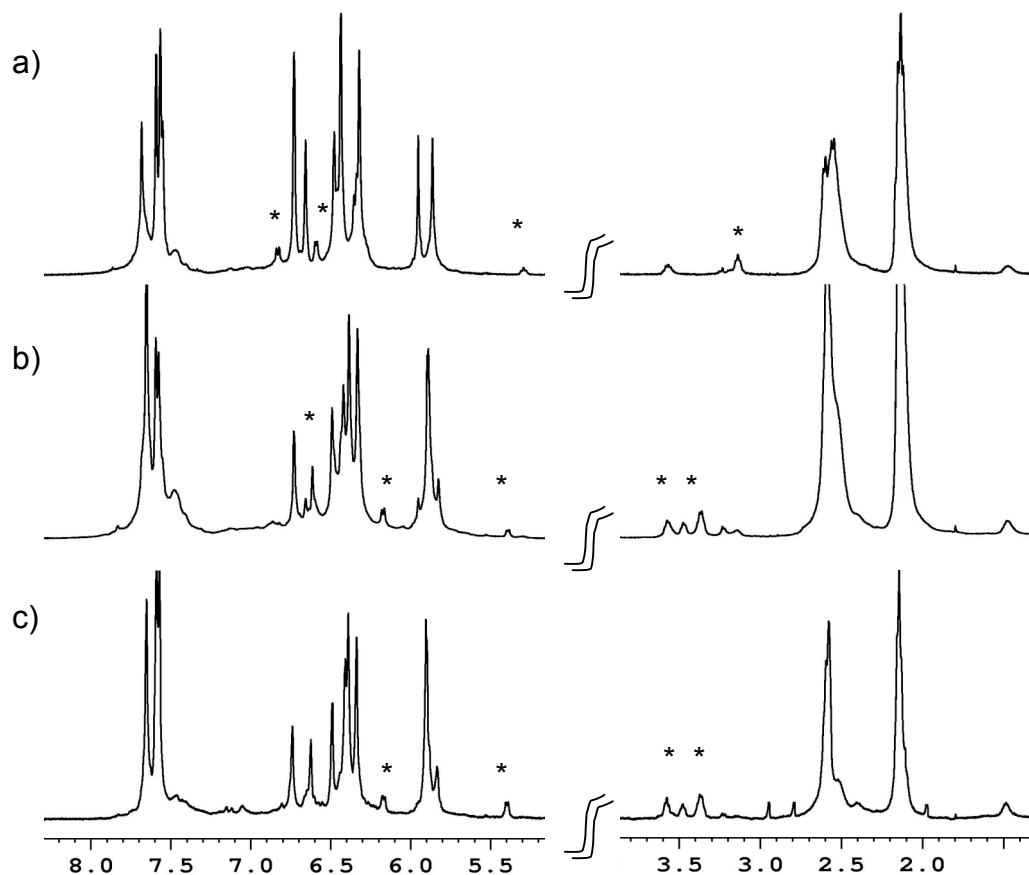


Figure S1. a) ^1H NMR of naphthyl benzoate (**2a**) in octa acid; b) Irradiated naphthyl benzoate (**2a**) in octa acid; c) encapsulated *ortho* rearrangement product of naphthyl benzoate (**3a**) in octa acid. All the spectra were recorded in D_2O (10mM borate buffer). The encapsulated guest protons are marked with * in each spectrum.

Competition Studies- encapsulation of *ortho* and *para* rearrangement products of substrate **2a in octa acid:**

ortho (**3a**) and *para* (**4a**) rearrangement products of substrate **2a** were isolated by irradiating 50 mg of **2a** in 10 ml of methanol for 16 hours in quartz test tube. Reaction mixture was concentrated and purified by column chromatography using 5% ethylacetate-hexane as eluent.

Stock solutions of 60mM **3a**, **4a** in d_6 -DMSO and 1mM octa acid in 10mM sodium borate buffer in D_2O were prepared. To 0.6 ml of octa acid stock solution, guest stock

solution **4a** was added in 2.5 μL increments. At 5 μL addition, upfield shift in guest protons was observed indicating that the guest molecule is complexed with the host (Figure S2 b). The recorded NMR of the host-guest complex was very broad, suggesting that the complex formed could be weaker. After 5 μL addition, complex solution started becoming turbid, suggesting that the stoichiometry of the complex is 1:2 (guest: host). To the same solution, 5 μL of **3a** was added and the NMR recorded showed sharp signals for both host and guest (Figure S2-c). The guest signals are highly upfield shifted, new signals between 7.5-9.00 ppm appeared. The new signals are the uncomplexed **4a** signals. This experiment clearly suggests that in presence of *ortho* product **3a**, *para* product **4a** does not complex with the host. *Ortho* is the most strongly bound guest, it is readily displacing the *para* product during competition studies.

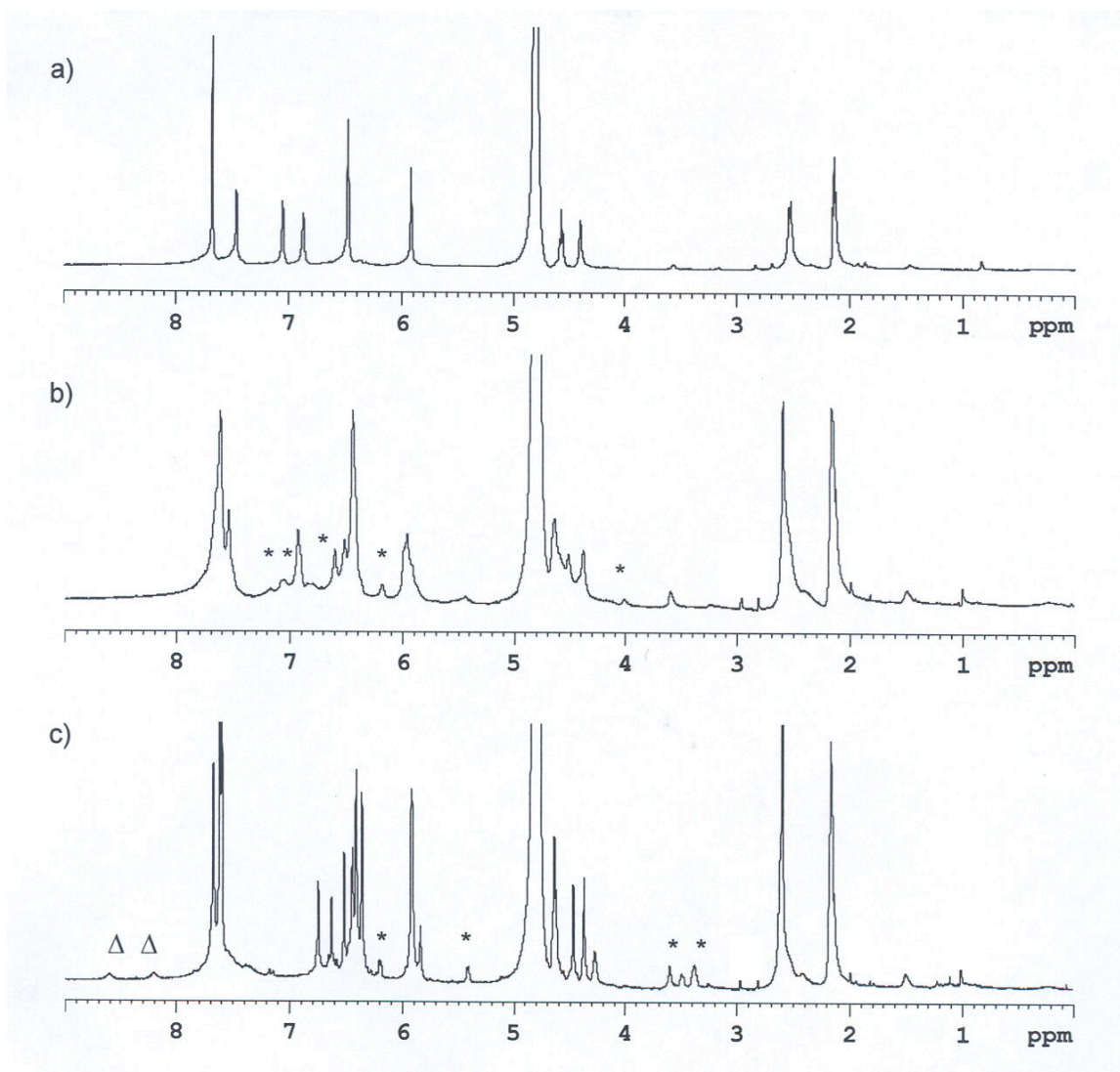


Figure S2. a) ^1H NMR of octa acid in D_2O ; b)- ^1H NMR of octa acid in D_2O and *para* rearrangement product (4a); c)- ^1H NMR of octa acid in D_2O + *para* rearrangement product (4a) + *ortho* rearrangement product (3a); **4a** is displaced by **3a**. The encapsulated guest protons are marked with * in each spectrum and the displaced guest protons are marked as Δ .