Supporting Information

Consequences of Controlling Free Space Within a Reaction Cavity With a Remote Alkyl Tether: Photochemistry of *para*-Alkyl Dibenzyl Ketones Within an Organic Capsule in Water

Arun Kumar Sundaresan and V. Ramamurthy*

Department of Chemistry

University of Miami

Coral Gables, FL 33124

U. S. A.

Table of Contents **Page No.**

General methods:

Host octa acid was synthesized using reported procedures.[1] Guests **1c**-**f** were synthesized as reported in literature.[2] Complex of octa acid and the guest were prepared using the following procedure. A stock solution of the guest was prepared in DMSO-d_6. To octa acid – sodium tetraborate solution in D_2O, guest solution was added such that the ratio of host to guest was 2 : 1. NMR spectra of the complex prepared were recorded and are presented in Figures SI 1 – SI 13. All NMR spectra were recorded using Bruker Avance Spectrometers at 298 K, unless mentioned otherwise. NOESY spectra were recorded with 0.5 s mixing time.

References:

(1) Gibb, C. L. D.; Gibb, B. C. *J. Am. Chem. Soc.* **2004**, *126*, 11408-11409.

(2) Sundaresan, A. K.; Ramamurthy, V. *Org. Lett.* **2007**, *9*, 3575-3578.

^{1}H NMR of **1c**, ^{1}H NMR and NOESY NMR spectra of **1c**@OA_2 complex.

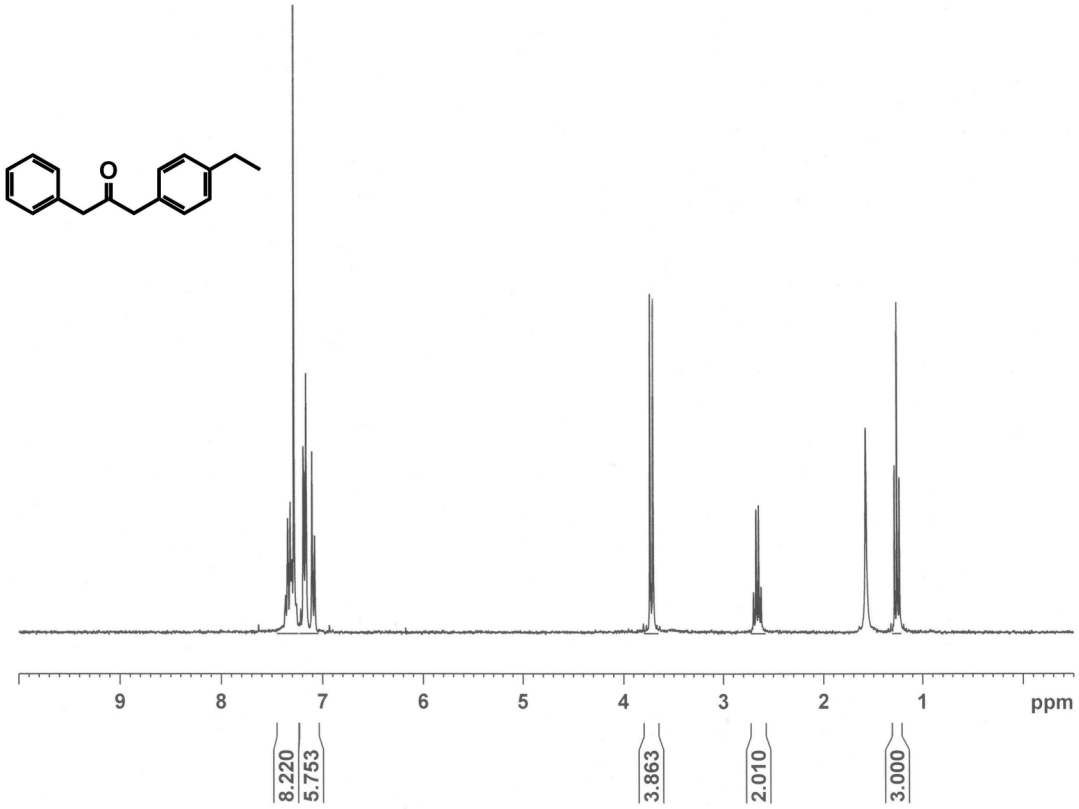

Figure SI 1: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **1c**.

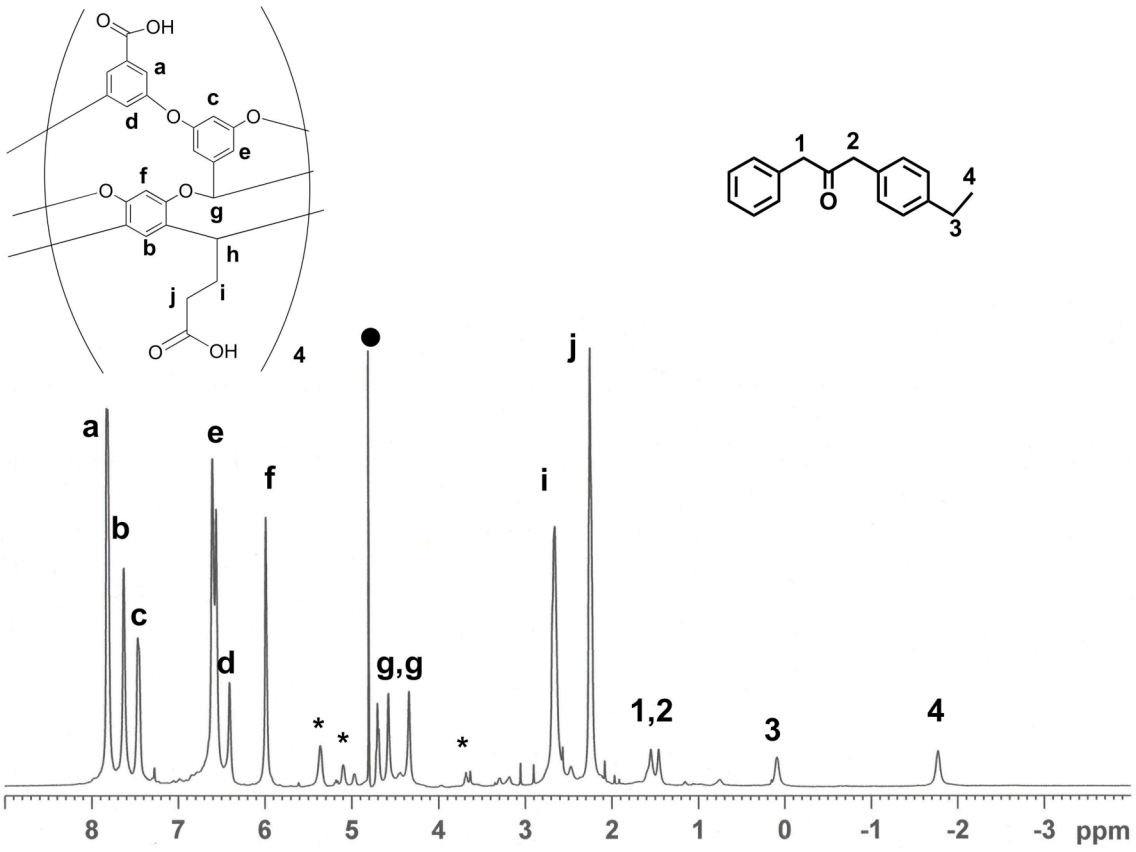

Figure SI 2: ^{1}H NMR spectrum (500 MHz, D_2O, 5 × 10^{-3} M OA, 5 × 10^{-2} M sodium tetraborate) of **1c@OA$_2$**. Aromatic signals of the guest are indicated with *. Residual water signal is denoted by '●'.

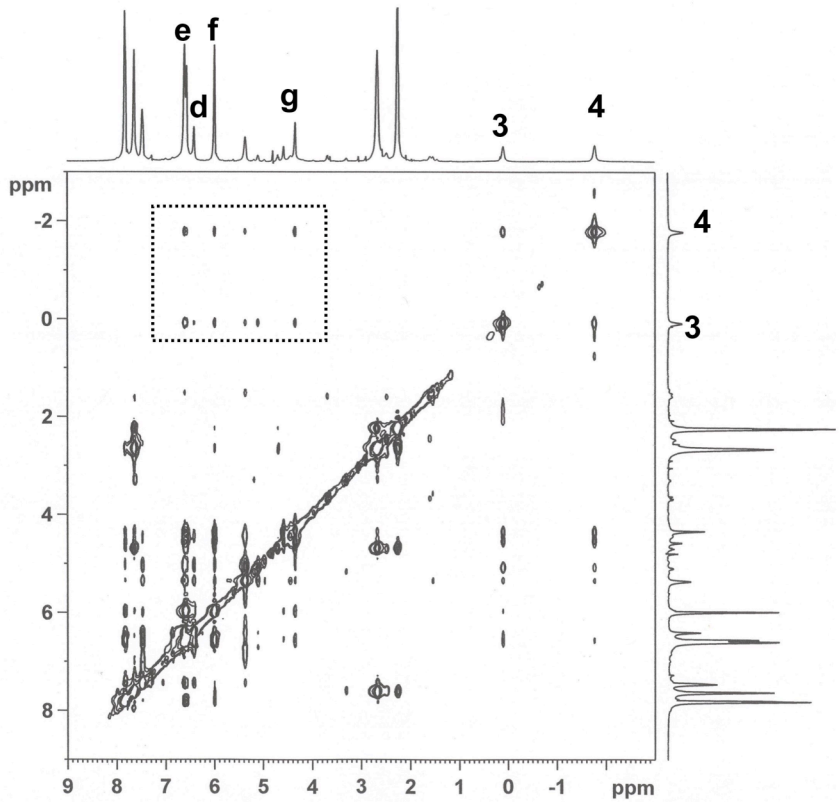

Figure SI 3: NOESY spectrum (500 MHz, D_2O, 5×10^{-3} M OA in 5×10^{-2} M sodium tetraborate) of **2.3@OA$_2$**.

^{1}H NMR of **1d**, ^{1}H NMR and NOESY NMR spectra of **1d**@OA_2 complex.

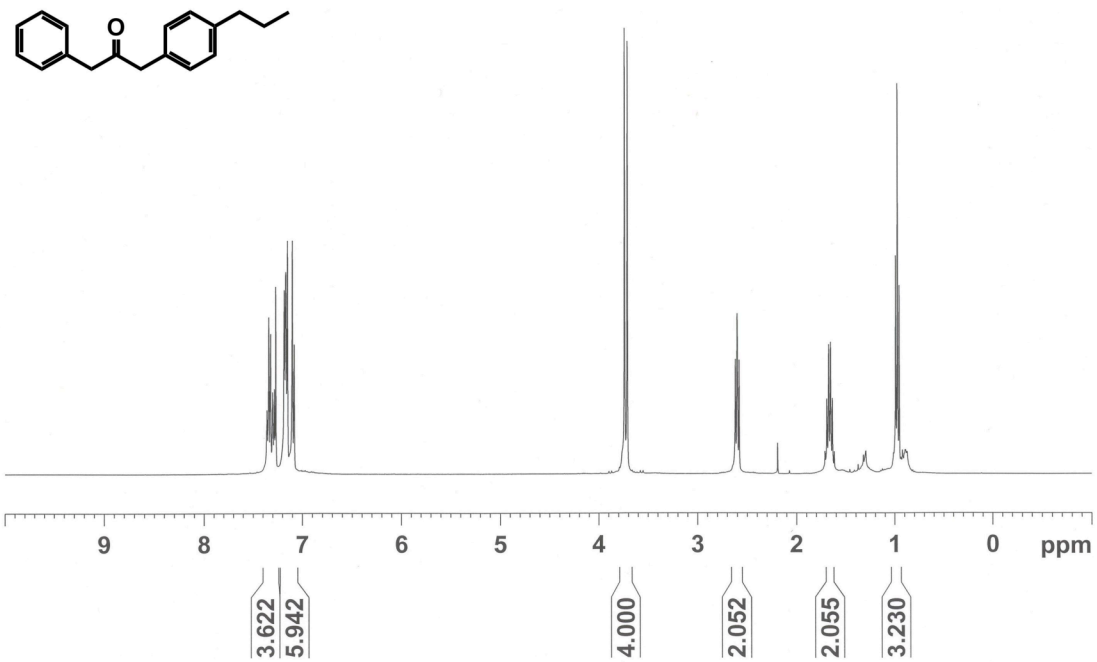

Figure SI 4: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1d**.

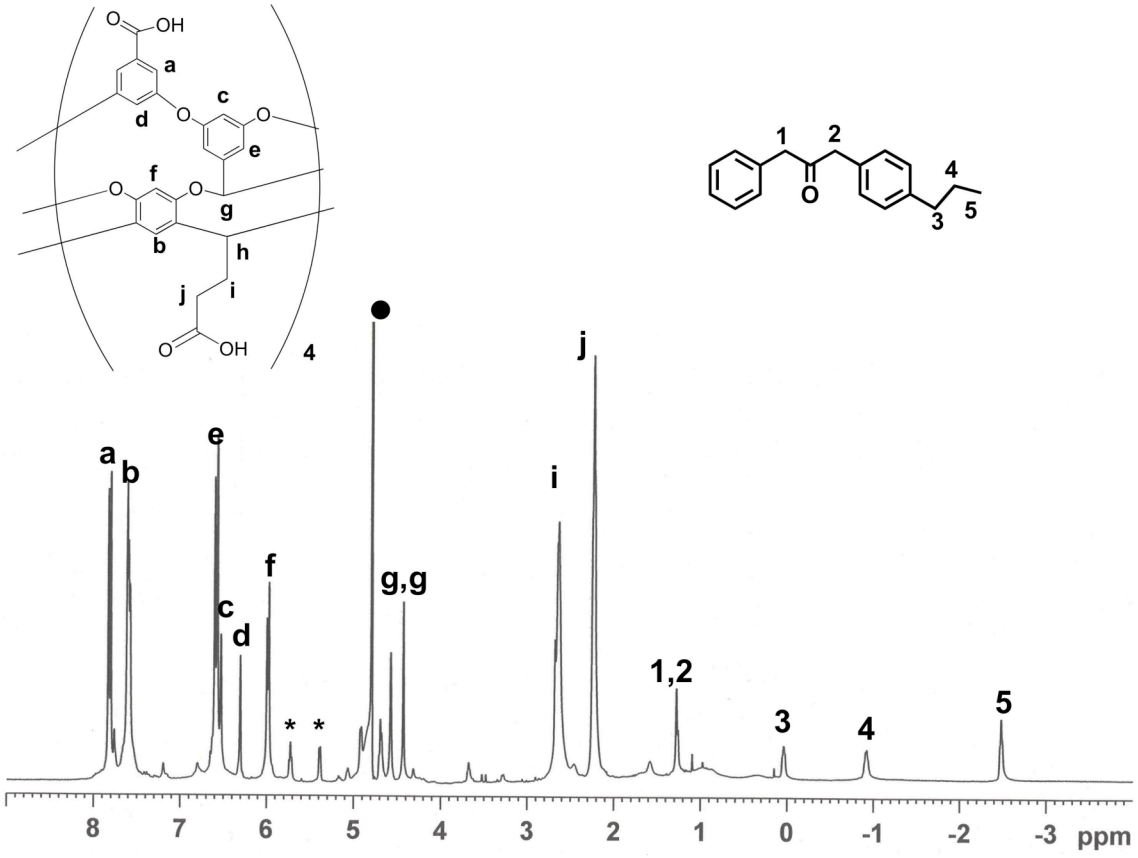

Figure SI 5: ^{1}H NMR spectrum (500 MHz, D_2O, 5 × 10^{-3} M OA, 5 × 10^{-2} M sodium tetraborate) of **1d**@OA_2. Aromatic signals of the guest are indicated with *. Residual water signal is denoted by '●'.

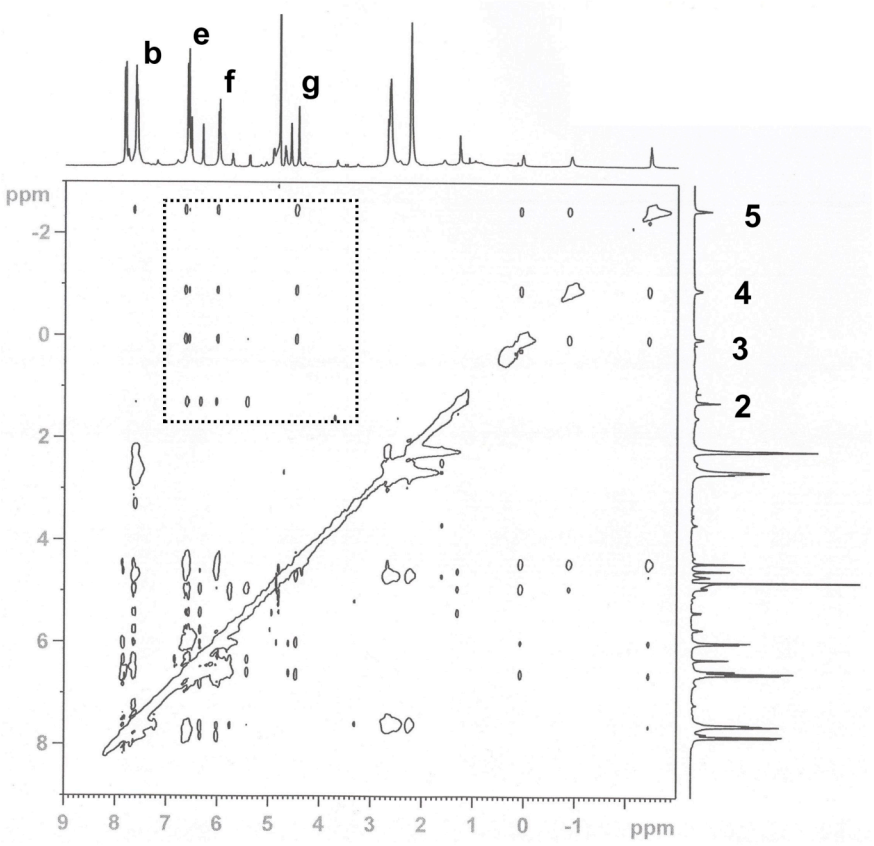

Figure SI 6: NOESY spectrum (500 MHz, D_2O, 5×10^{-3} M OA in 5×10^{-2} M sodium tetraborate) of **1d**@OA_2.

^{1}H NMR of **1e**, ^{1}H NMR and NOESY NMR spectra of **1e**@OA_2 complex.

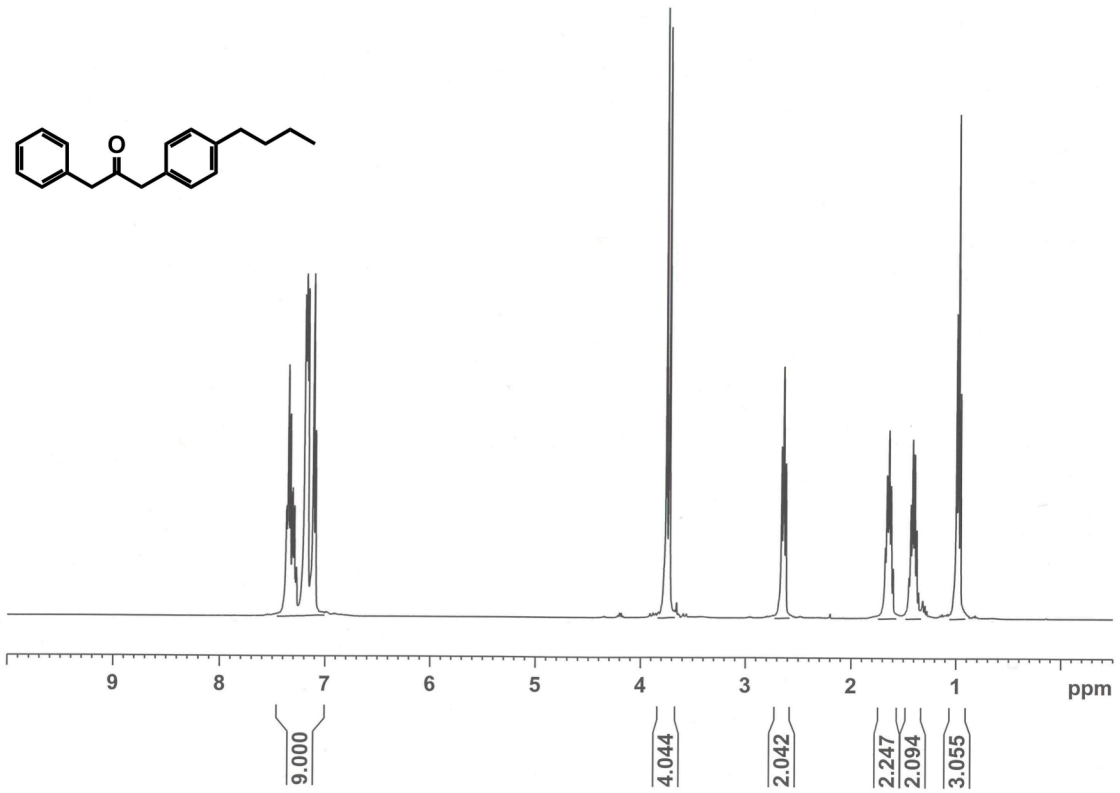

Figure SI 7: ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **1e**.

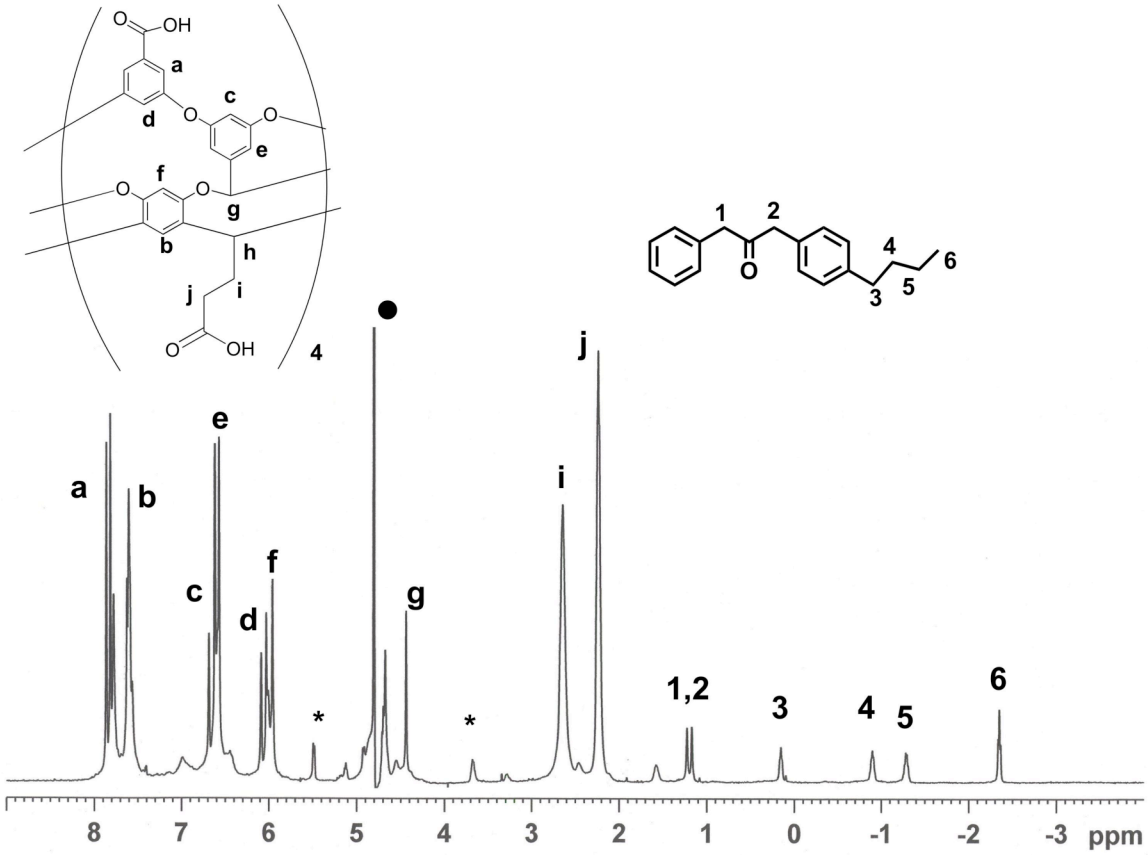

Figure SI 8: ^{1}H NMR spectrum (500 MHz, D_2O, 5 × 10^{-3} M OA, 5 × 10^{-2} M sodium tetraborate) of **1e@OA$_2$**. Aromatic signals of the guest are indicated with *. Residual water signal is denoted by '●'.

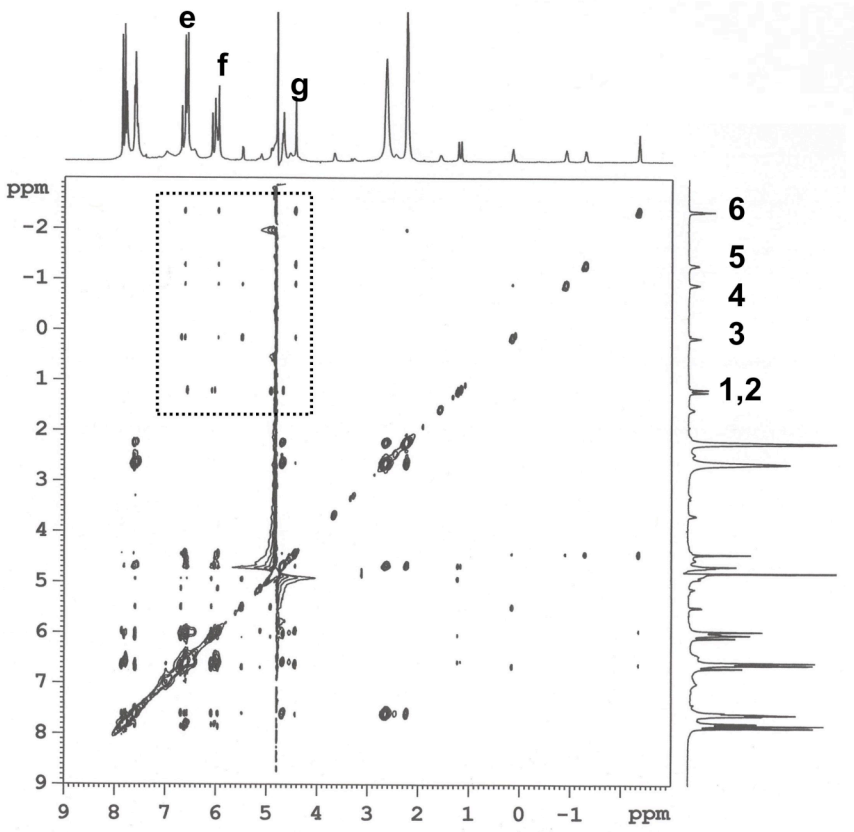

Figure SI 9: NOESY spectrum (500 MHz, D_2O, 5×10^{-3} M OA in 5×10^{-2} M sodium tetraborate) of **1e@OA$_2$**.

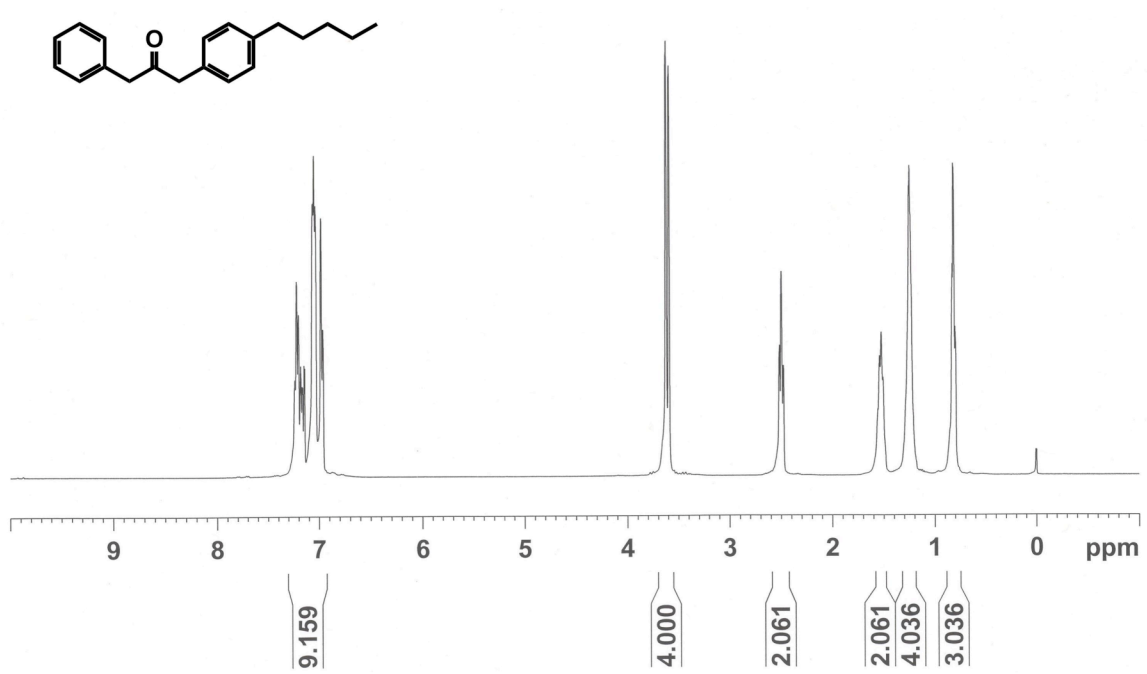

Figure SI 10: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1f**.

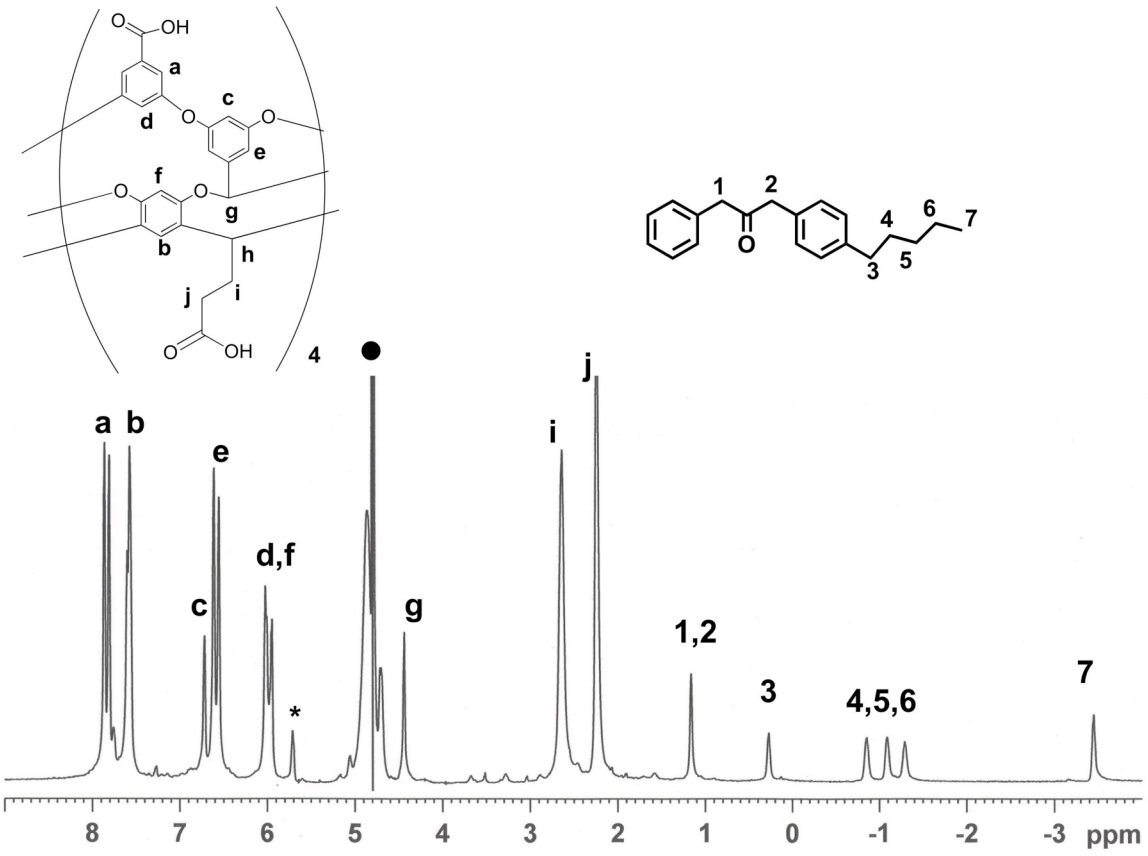

Figure SI 11: ^{1}H NMR spectrum (500 MHz, D_2O, 5×10^{-3} M OA, 5×10^{-3} M sodium tetraborate) of **2.6@OA$_2$**. Aromatic signal of the guest is denoted by *. Residual water signal is denoted by '●'.

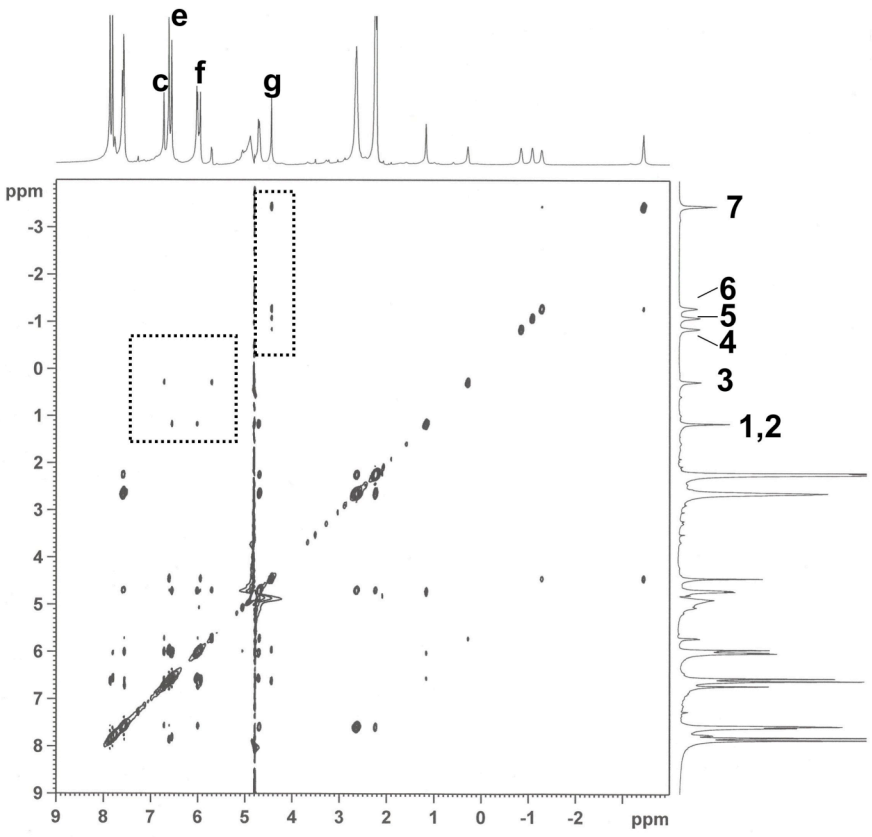

Figure SI 12: NOESY spectrum (500 MHz, D_2O, 5×10^{-3} M OA in 5×10^{-2} M sodium tetraborate) of **1f@OA$_2$**.

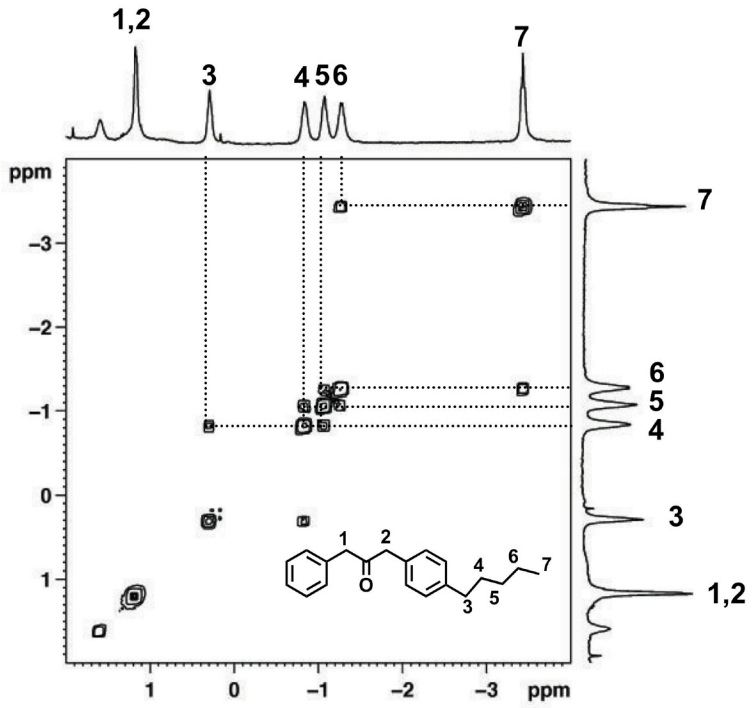

Figure SI 13: Partial COSY spectrum (300 MHz, D_2O, 5×10^{-3} M OA in 5×10^{-2} M sodium tetraborate) of **1f@OA$_2$** showing the interactions between the aliphatic methylene and methyl signals of **1f**. Sequential correlations between 3 and 4, 4 and 5, 5 and 6 and 6 and 7 can be seen in the COSY NMR spectrum.

^{1}H NMR spectra of octa acid complexes of photoproducts.

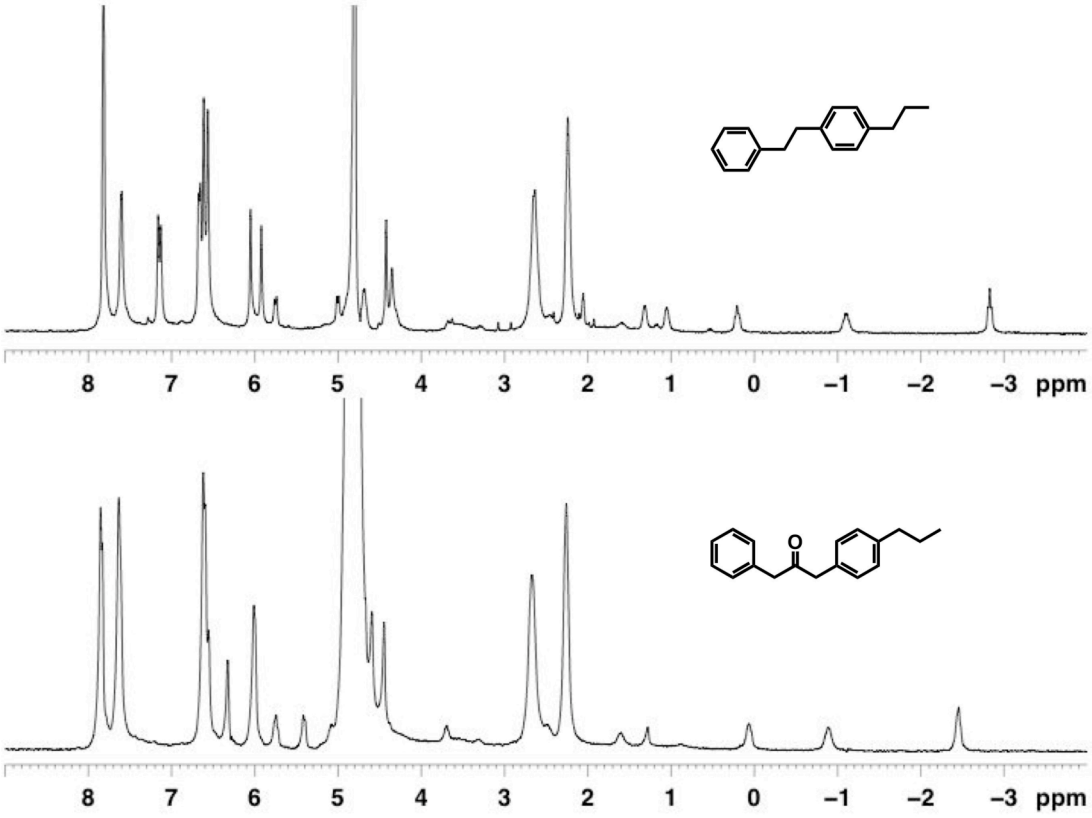

Figure SI 14: ^{1}H NMR spectra (300 MHz, D_2O) of **1c**@OA_2 (bottom) and **3c**@OA_2 (top).

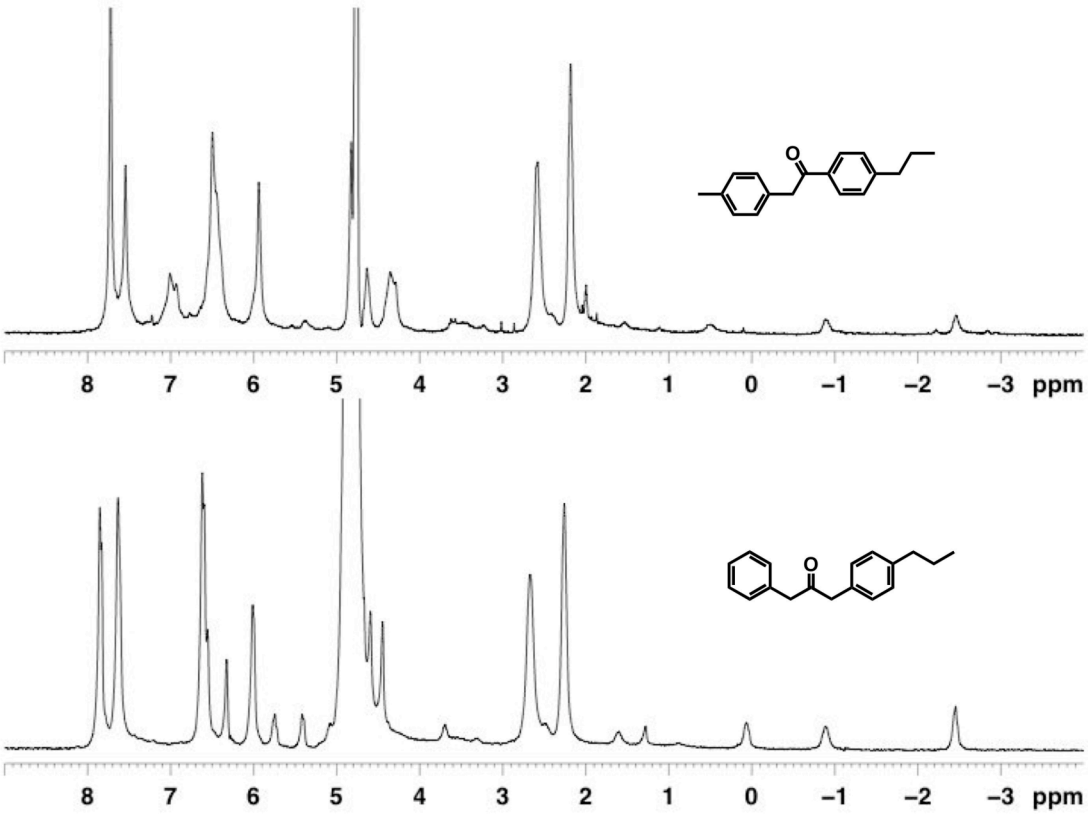

Figure SI 16: ^{1}H NMR spectra (300 MHz, D_2O) of **1c**@OA_2 (bottom) and **7c**@OA_2 (top).

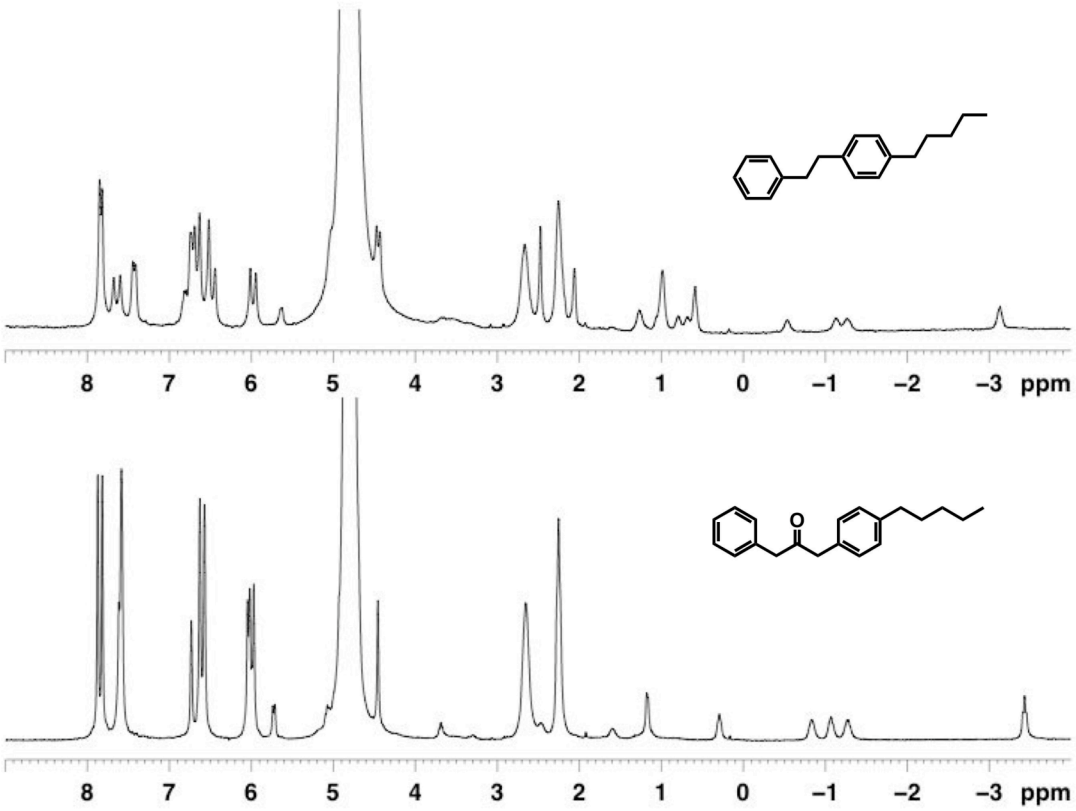

Figure SI 17: ^{1}H NMR spectra (300 MHz, D_2O) of **1f**@OA_2 (bottom) and **3f**@OA_2 (top).