A halogen-bonded supramolecular capsule transforms its guest via a mechanochemical Wittig olefination

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Abstract

Host-guest inclusion of molecular species has enabled transformations including photodimerizations,[1] Diels-Alder reactions,[2] and more,[3] which would otherwise occur with difficulty or not at all. In these systems, supramolecular hosts typically act as chemically inert containers to bring reactive species into proximity, facilitating reactivity. Here, we present an alternative strategy, where a solid-state host encapsulates a set of small carbonyl-containing molecules which it can functionalize in a Wittig olefination reaction[4] to produce 1,1-dihaloolefins in high yields.[5]

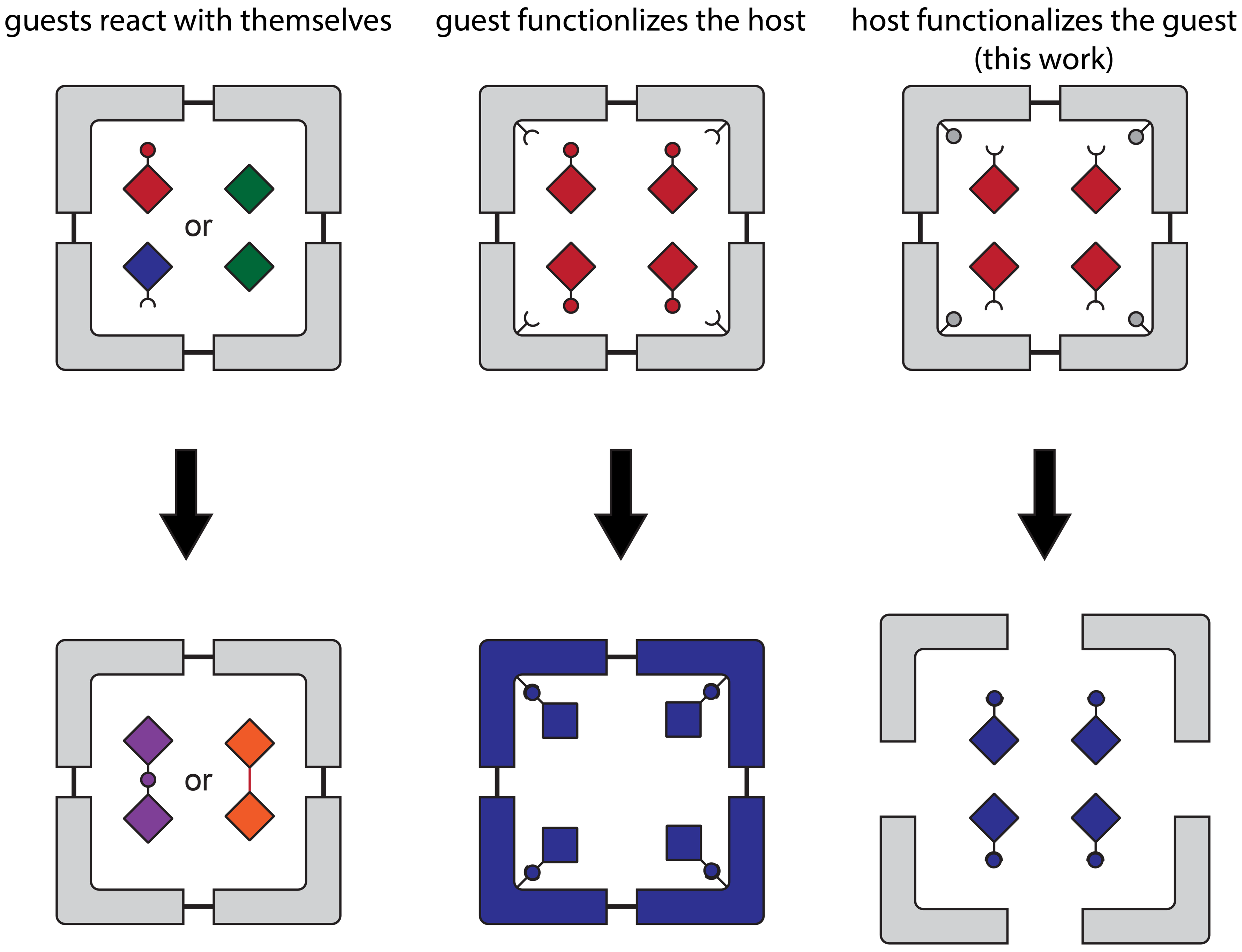

Figure 1. Comparison of the herein presented type of host-guest reactivity to other previously demonstrated ones

The salt (dibromomethyl)triphenylphosphonium bromide (1) forms hexameric halogen-bonded cages in the solid state.

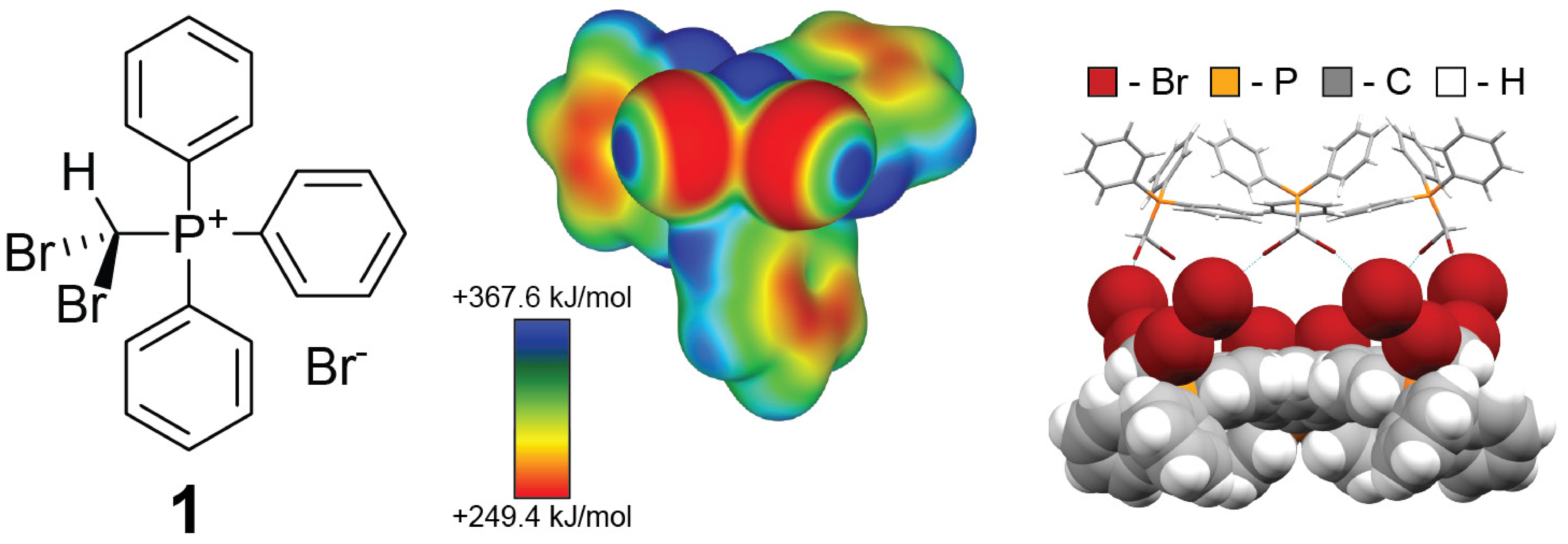

Figure 2. The salt (dibromomethy)triphenylphosphonium bromide: (**a**) chemical diagram, (**b**) electrostatic surface potential, and (**c**) crystal structure

The salt 1 can encapsulate a wide range of small, polar guests

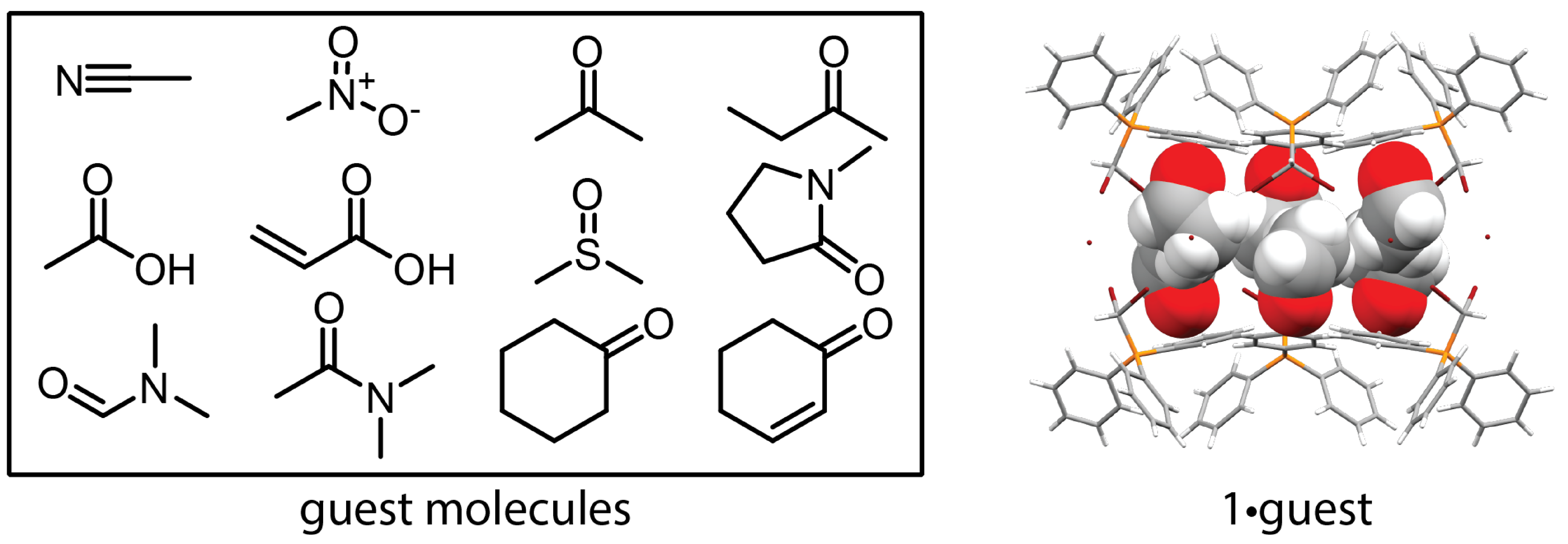

Figure 3. Encapsulated guest molecules (right) and crystal structure of **1** containing six encasulated guests

The cage based on 1 can react with carbonyl-containing guests *via* the Wittig olefination reaciton

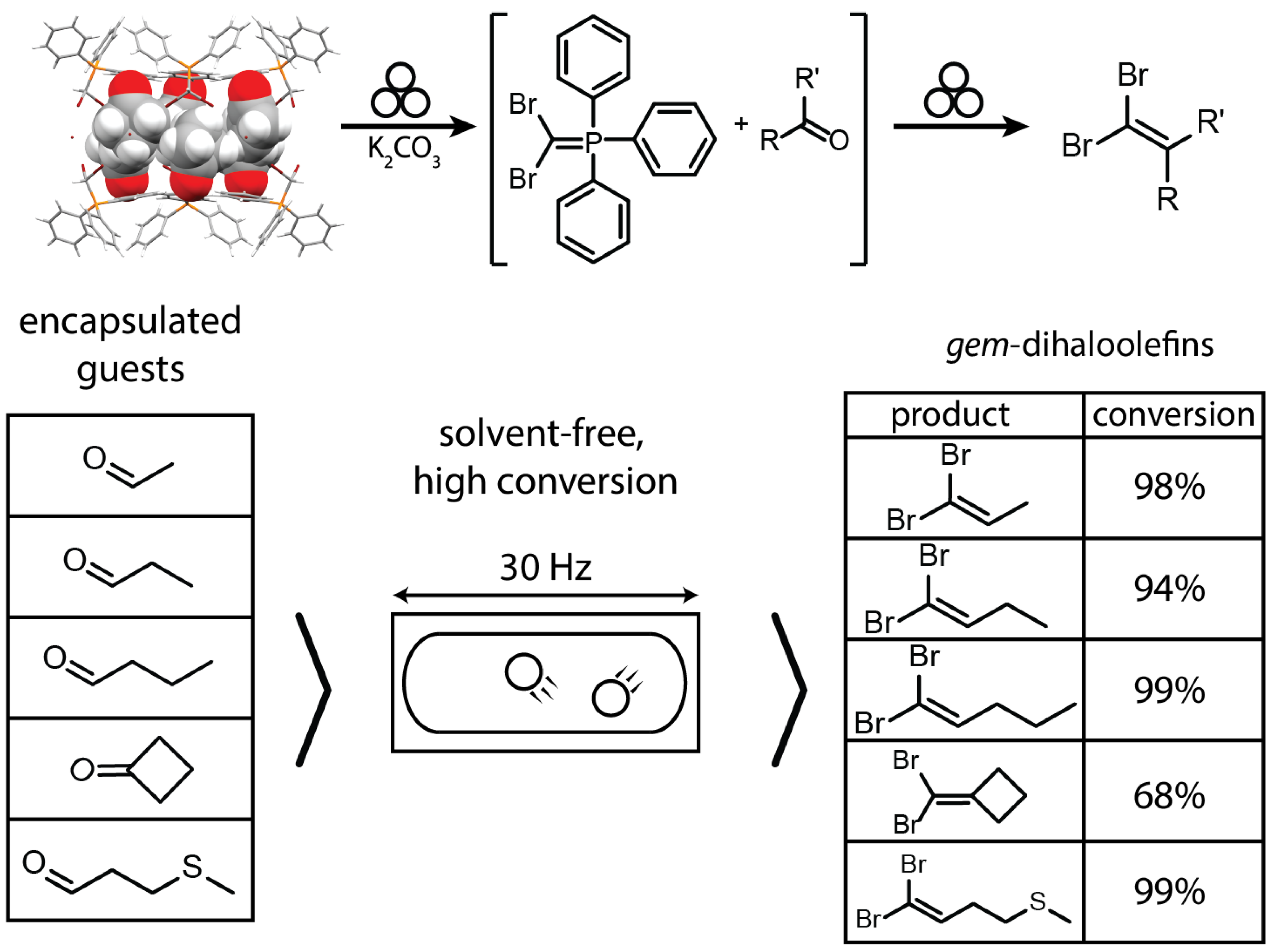

Figure 4. Reaction scheme for Wittig olefination reaction of cage and guest (top), and the carbonyl-containing guests and their corresponding Wittig olefination products (bottom)

The inclusion complexes of 1 and carbonyl-containing guest are solid-state surrogates for 1,1-dibromoolefins

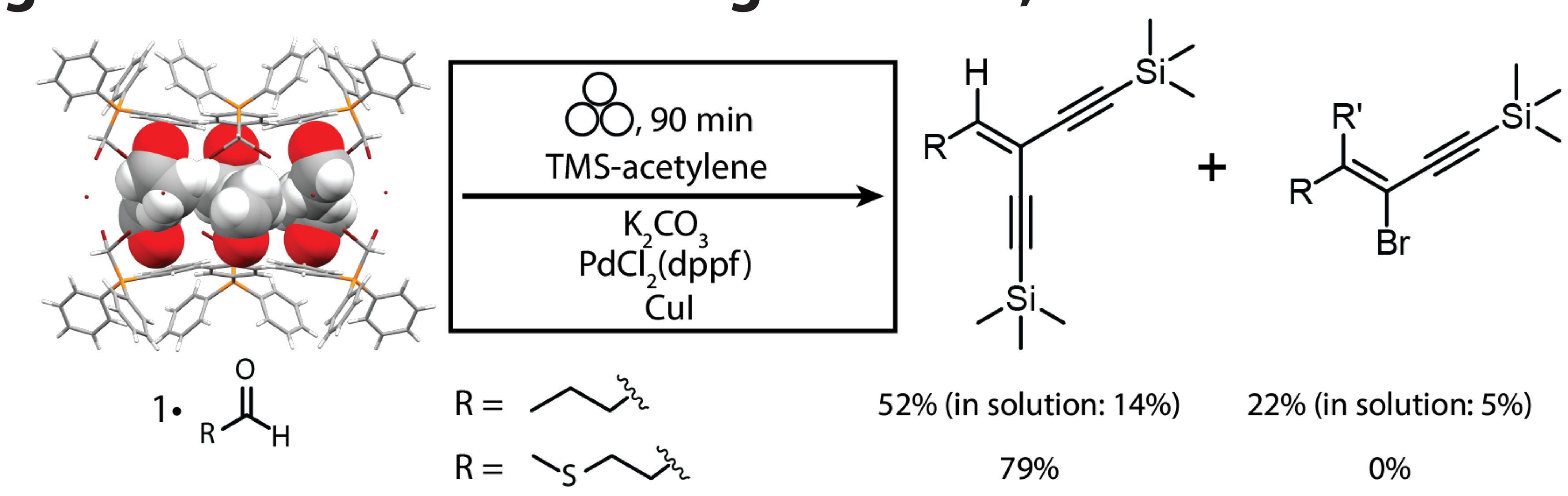

Figure 5. Reaction scheme for the one-pot Wittig olefination and Sonogashira coupling using the **1•reactive guest** complex; yields for mechanochemical reactions exceed those performed in solution

Encapsulation of volatile molecules by 1 enhances their thermal stability

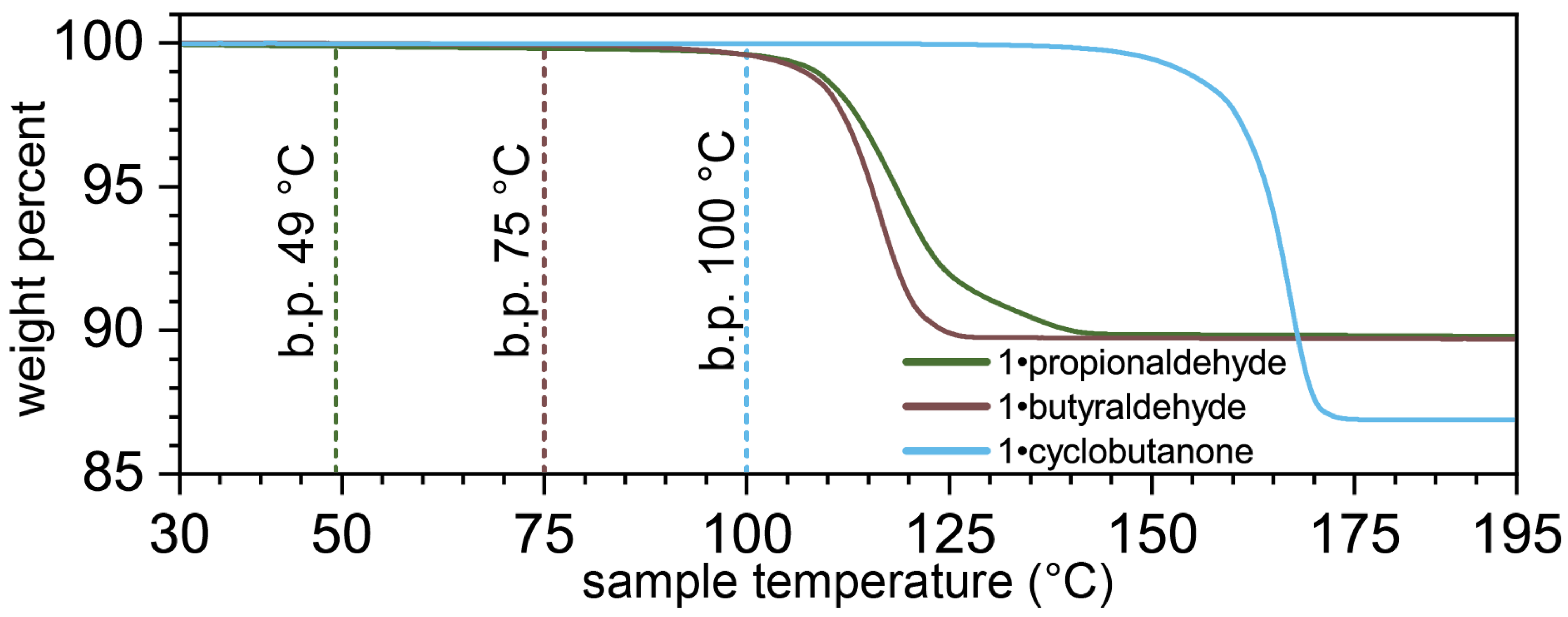

Figure 6. Thermogravimetric analysis of **1•reactive guest** complexes, showing thermal stabilities which exceed those of the **reactive guests**

Analogues to 1 based on chlorine and iodine

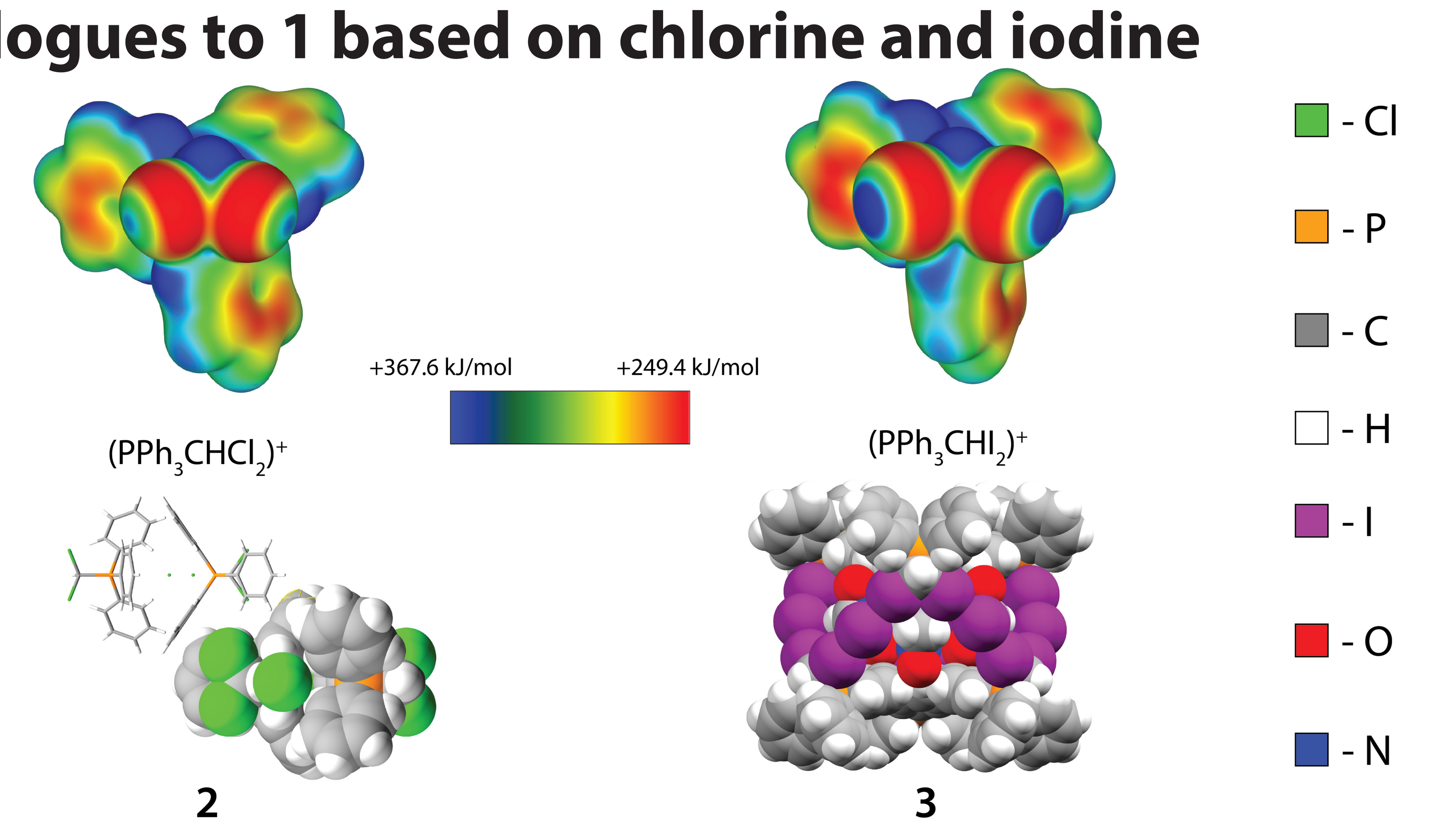

Figure 7. Chloro- and iodo-analogues of **1**: electrostatic surface potential maps of $(PPh_3CHCl_2)^+$ (**a**) and $(PPh_3CHI_2)^+$ (**b**), and crystal structures of $(PPh_3CHCl_2)^+Cl^-$ (**c**) and $(PPh_3CHI_2)^+I^-$•$MeNO_2$(**d**).

References: **1**. M. Yoshizawa, Y. Takeyama, T. Kusukawa, M. Fujita, *Angew. Chem. Int. Ed.* 2002, 41, 1347-1349. **2**. J. Kang, J. Rebek, *Nature* 1997, 385, 50-52. **3**. J. Cram, M. E. Tanner, R. Thomas, *Angew. Chem. Int. Ed.* 1991, 30, 1024-1027. **4**. V. P. Balema, J. W. Wiench, M. Pruski, V. K. Pecharsky, *J. Am. Chem. Soc.* 2002, 124, 6244-6245. **5**. J. M. Marrett, H. M. Titi, T. Friščić, *ChemRxiv* 2021.

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