



**Figure 1.** a) Structures and numbering of some of the compounds used in this project. Schematic representations of: b) Isomerization of azobenzene compound **2**. c) Stepwise formation of 1:1:1 ternary complex of CB[8] with **1** and *E*-**2** as guests. d) Isomerization of **2** in the presence of CB[8] and doubly-charged guest **1** and equilibrium after UV light irradiation of CB[8]·**1**·*E*-**2**. e) Representations of the single crystal X-ray structure of CB[8]·*Z*-**2** viewed from the side (left) and top (right). The structures of CB[8] and *Z*-**2** are represented as wire-frame and space-filling molecular models, respectively. Only the largest component of *Z*-**2** disorder is shown. Atom colors: C, gray; N, blue; O, red; H, white.