Diastereoselection in a Cylindrical Capsule
Electronic Supplementary Information

^{1}H NMR spectra were recorded on a Brüker DRX-600 spectrometer operating at 600.13 MHz. Unless otherwise indicated, all spectra were obtained at 300K. Proton spectra were acquired with a minimum of 128 scans and a sweep width of 20 ppm. Proton integrals were determined using XWINNMR software. Mesitylene-d_{12} was purchased from Cambridge Isotope Laboratories (Andover, MA). All other reagents and guests were purchased from Aldrich (St. Louis, MO) or TCI-USA (Portland, OR) and were used without further purification.

Monte Carlo Multiple Minimum (MCMM), one of Monte Carlo conformational search methods available in Maestro software package,[1] was implemented in the gas phase with the "optimized potentials for liquid simulation (OPLS)"[2] force field, which force field has been shown to fit quantum mechanics (AM1) results in geometry best for the host molecule. MCMM is known to be an efficient method for global searching. Random changes were made in torsion angles during the searching. Although there is no limit to the number of variable torsions allowed in the search, more than 10 to 15 flexible torsions greatly increase the complexity of the searching. The capsules were assembled through hydrogen bonds between eight rigid imide walls of adjacent monomers. Initial conformations were set up as the acid dimer in the gas phase. Only rotational bonds of carboxylic acid dimer were set in the conformation searching, to keep the number of variable torsions under ten. Since the host capsule is highly symmetrical and its space inside is severely constrained, guest rotation and translation were not specified (acid monomers are approximately 80–120 Å^3). For each diastereomeric dimer, several searches of 2000 to 5000 MC steps were conducted to ensure global minimum was achieved. The conformational space of each host-guest system can be divided into several clusters. Each cluster includes many similar structures with tiny rotations and translations of the guest molecules. For closely-matching host-guest systems, like **6** and **7**-homochiral dimer, the number of conformations in the cluster of global minima

---

[1] Maestro Software Package (Version 5.1.016, MMShare version 1.1.018) Schrödinger, L.L.C. 2003.

[2] Improvements to this force field have since been made (OPLS-AA): W. L. Jorgensen, D. S. Maxwell, J. Tirado-Rives. *J. Am. Chem. Soc.* 1996, **118**, 11225–11236; W. L. Jorgensen, J. P. Ulmschneider and J. Tirado-Rives *J. Phys. Chem. B* 2004, **108**, 16264–16270.

decrease significantly because of less freedom of motion. The lowest-energy conformation for each simulation was depicted in the text and ESI to show the structural features and to compute relative energies as well.

Guest dimer	**Number of lower-energy conformations found**	**Energy range (kJ mol^{-1})**	**Energy gap to the second cluster (kJ mol^{-1})**
3 (homo)	~ 250	0.4	0.2
3 (hetero)	~ 130	0.7	3
5 (homo)	~ 280	3	1.5
5 (hetero)	~ 35	0.3	1
6 (homo)	~ 50	0.2	2
6 (hetero)	~ 70	0.2	6
7 (homo)	~ 25	0.2	5.5
7 (hetero)	~ 60	0.3	1.5

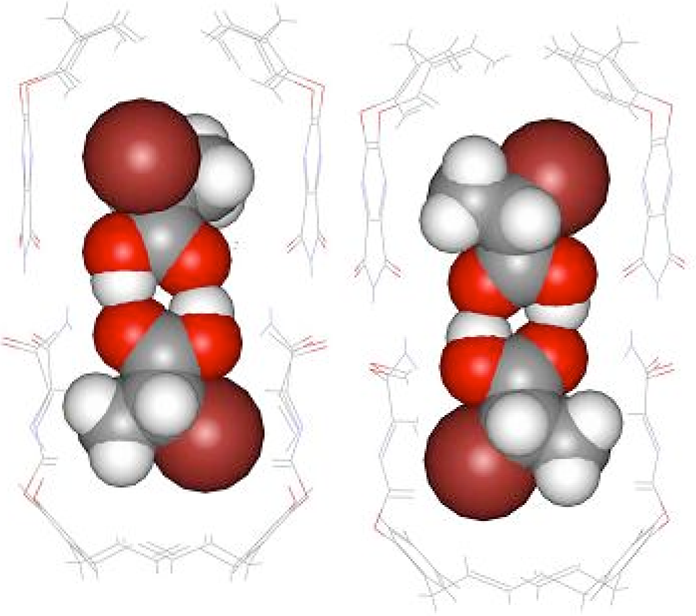

Figure S1. Calculated structures of global minima of heterochiral (left) and homochiral (right) dimers of 2-bromopropionic acid **(3)**.

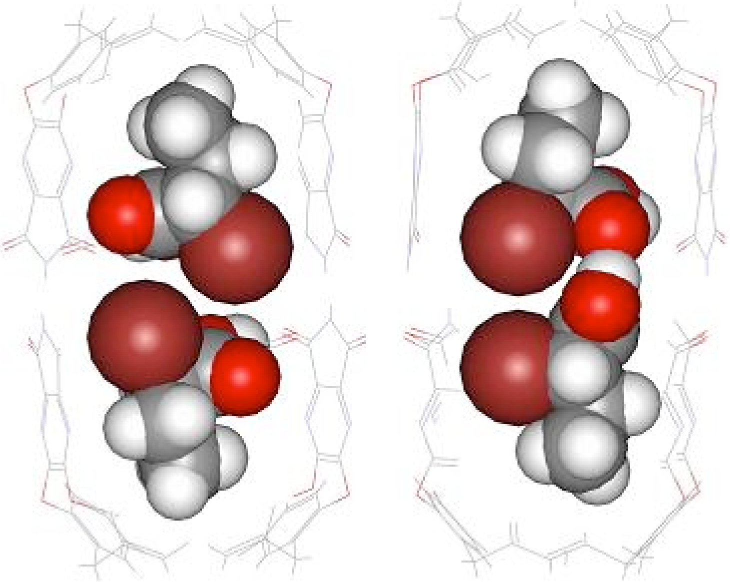

Figure S2. Calculated structures of global minima of heterochiral (left) and homochiral (right) dimers of 2-bromobutyric acid **(5)**.

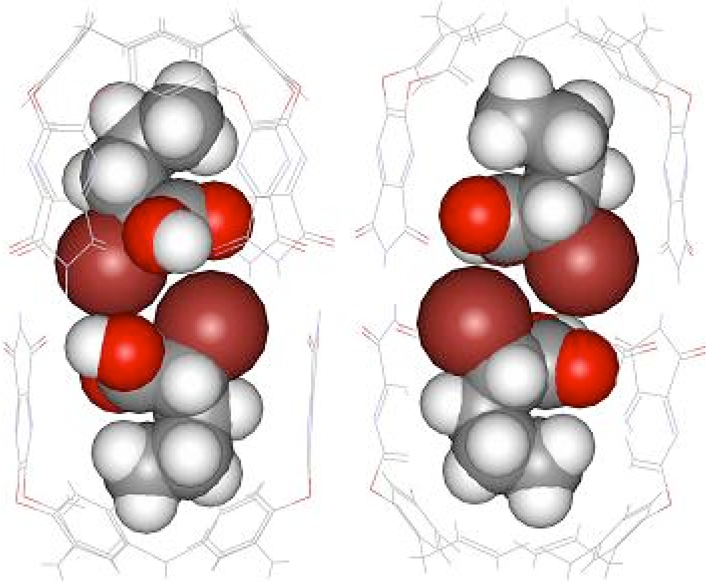

Figure S3. Calculated structures of global minima of heterochiral (left) and homochiral (right) dimers of 2-bromovaleric acid **(6)**.

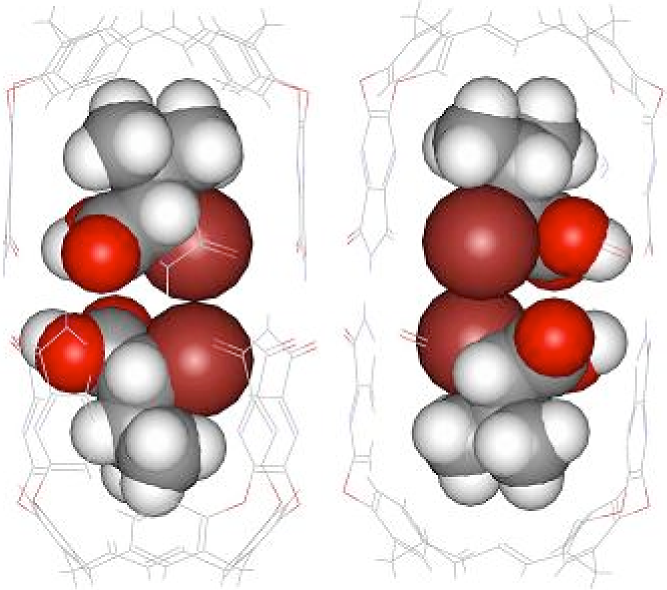

Figure S4. Calculated structures of global minima of heterochiral (left) and homochiral (right) dimers of 2-bromo-3-methylbutyric acid **(7)**.