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A 'Through-Shell' Binding Isotope Effect

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Experimental Section

^{1}H-NMR spectra were recorded on a 400 MHz Varian FT NMR spectrometer. Spectra taken in $CDCl_3$, were referenced to residual $CHCl_3$, at δ 7.26. FAB mass spectra (3-nitrobenzyl alcohol (NOBA) matrix) and ESI mass spectra (in CH_3CN) were determined at the University of Kansas Mass Spectrometry Laboratory. Gravity chromatography was performed on E. Merck silica gel (70-230 mesh). Semi-preparative HPLC column involved a Silica column (Phenomenax, 21.2*100 mm, 5μm). Thin-layer chromatography involved polyethylene-backed plates (silica gel 60, F_{254}, 0.25 mm).

Hemicarceplexes **1**⊙**8**,[1] **1**⊙**23**,[3] **1**⊙**24**,[3] **1**⊙**26**,[3] **1**⊙**33**,[3] **1**⊙**34**,[3] **1**⊙**35**,[3] **3**⊙**4**,[2] **3**⊙**37**[2] and **3**⊙**38**[2] have been prepared earlier in this laboratory.

General procedure for the synthesis of hemicarceplexes 1⊙guest (*procedure A*)

One mol equivalent of **1**⊙NMP[3] and 100-200 mol equivalents of the guest were sealed under argon in a glass ampoule and were heated for four days at 217 ˚C. After the reaction mixture had cooled to room temperature, the ampoule was opened. The reaction mixture was poured into the tenfold volume of methanol. If the free guest was solid, the content of the ampoule was dissolved in the minimum volume of $CHCl_3$, which was poured into the 10-fold volume of methanol. The precipitated crude hemicarceplex was collected on a glass sinter (pore size 10-15 μ), washed with methanol and dried at high vacuum. Purification by HPLC using a Silica column (Phenomenax, 21.2*100 mm, 5μm) with CH_2Cl_2 : Ether (100:1, v/v) as the mobile phase gave the pure hemicarceplex **1**⊙guest.

General procedure for the synthesis of hemicarceplexes 1⊙guest (*procedure B*)

One mol equivalent of **1**⊙NMP and 100 mol equivalents of diphenylether were sealed under argon in a glass ampoule and were heated for two days at 250 ˚C. After the reaction mixture had cooled to room temperature, the ampoule was opened. The reaction mixture was poured into the tenfold volume of methanol. The precipitated crude empty hemicarcerand was collected on a glass sinter (pore size 10-15 μ), washed with methanol and dried at high vacuum. Crude ^{1}H-NMR was acquired to confirm the formation of hemicarcerand **1**. The product was directly used for the synthesis without purification. One mol equivalent of hemicarcerand **1** and 100-200 mol equivalents of the guest were sealed under argon in a glass ampoule and were heated for five days at 140 ˚C. After the reaction mixture had cooled to room temperature, the ampoule was opened. The reaction mixture was poured into the tenfold volume of methanol. The precipitated crude hemicarceplex was collected on a glass sinter (pore size 10-15 μ), washed with methanol and dried at high vacuum. Purification by HPLC using a Silica column (Phenomenax, 21.2*100 mm, 5μm) with CH_2Cl_2: Ether (100:1, v/v) as the mobile phase gave the pure hemicarceplex **1**⊙guest.

Benzene hemicarceplex (1⊙4).[5] Application of *procedure B* (2 days; 130 ˚C) gave **1**⊙**4** (95 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.15-7.26 (m, 40H, C_6H_5), 6.96 (s, 8H, Ar*H* on bowl), 5.70 (d, J = 7.25 Hz, 8H OCH_2O outer), 4.85 (t, J = 8.09 Hz, 8H, C*H* methine), 4.70 (s, 6H, guest-H), 4.05 (d, J = 7.23 Hz, 8H, OCH_2O inner), 3.83 (sb, 16H, OCH_2CH_2), 2.51-2.73 (m, 32H, CH_2CH_2Ph), 1.98 (sb, 16H, OCH_2CH_2). ^{1}H NMR data obtained were in agreement with that previously reported in [5].

***p*-Difluorobenzene hemicarceplex (1⊙17)**. Application of *procedure B* (5 days; 140 ˚C; semi-preparative HPLC, Phenomenax, Si, 21.2*100 mm, 5µm) gave **1⊙17** (40 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.15-7.25 (m, 40H, C_6H_5), 6.90 (s, 8H, Ar*H* on bowl), 5.70 (d, J = 7.11 Hz, 8H OCH_2O outer), 5.40 (d, J = 5.65 Hz, 4H, guest-H), 4.83 (t, J = 7.77 Hz, 8H, C*H* methine), 4.03 (d, J = 7.06 Hz, 8H, OCH_2O inner), 3.86 (sb, 16H, OCH_2CH_2), 2.48-2.71 (m, 32H, CH_2CH_2Ph), 1.92 (sb, 16H, OCH_2CH_2). FAB-MS: *m/z* $[M + H]^+$, 2366 (100); $[M - \mathbf{17} + H]^+$, 2250.7 (75).

1,4-Dichlorobenzene hemicarceplex (1⊙18):[4] Application of *procedure A* (4 days; 217 ˚C; semi-preparative HPLC, Phenomenax, Si, 21.2*100 mm, 5µm) gave **1⊙18** (90 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.15-7.25 (m, 40H, C_6H_5), 6.85 (s, 8H, Ar*H*), 6.21 (s, 4H, guest-H), 5.68 (d, J = 6.81 Hz, 8H, OCH_2O outer), 4.85 (t, 8H, J = 7.86 Hz, C*H* methine), 4.07 (d, J = 6.79 Hz, 8H, OCH_2O inner), 3.90 (sb, 16H, OCH_2CH_2), 2.47-2.72 (m, 32H, CH_2CH_2Ph), 1.88 (sb, 16H, OCH_2CH_2). ^{1}H NMR data agreed with those reported in [4].

1-Bromo-4-chlorobenzene hemicarceplex (1⊙15):[4] Application of *procedure A* (4 days; 217 ˚C; semi-preparative HPLC, Phenomenax, Si, 21.2*100mm, 5µm) gave **1⊙15** (94 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.26 (m, 40H, C_6H_5), 6.85 (s, 4H, Ar*H* on bowl), 6.82 (s, 4H, Ar*H*), 6.46 (d, J = 8.41 Hz, 2H, guest-H), 6.16 (d, J = 8.41 Hz, 2H, guest-H), 5.68 (m, 8H OCH_2O outer), 4.86 (m, 8H, C*H* methine), 4.12 (d, J = 6.77 Hz, 4H, OCH_2O inner), 4.07 (d, J = 6.84 Hz, 4H, OCH_2O inner), 3.92 (sb, 16H, OCH_2CH_2), 2.51-2.73 (m, 32H, CH_2CH_2Ph), 1.87 (sb, 16H, OCH_2CH_2). ^{1}H-NMR data agreed with those reported in [4].

1,4-Dibromobenzene hemicarceplex (1⊙19):[5] Application of *procedure A* (4 days; 217 ˚C; semi-preparative HPLC, Phenomenax, Si, 21.2*100 mm, 5µm) gave **1⊙19** (85 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.15-7.25 (m, 40H, C_6H_5), 6.82 (s, 8H, Ar*H* on bowl), 6.43 (s, 4H, guest-H), 5.68 (d, J = 6.7 Hz, 8H, OCH_2O outer), 4.86 (t, 8H, J = 7.9 Hz, C*H* methine), 4.12 (d, J = 6.7 Hz, 8H, OCH_2O inner), 3.94 (sb, 16H, OCH_2CH_2), 2.47-2.72 (m, 32H, CH_2CH_2Ph), 1.87 (sb, 16H, OCH_2CH_2). ^{1}H NMR data agreed with those reported in [5].

1,4-Diiodobenzene hemicarceplex (1⊙20):[5] Application of *procedure B* (4 days; 160 ˚C) gave **1⊙20** (85 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.26 (m, 40H, C_6H_5), 6.77 (s, 8H, Ar*H* on bowl), 6.73 (s, 4H, guest-H), 5.70 (d, J = 6.7 Hz, 8H, OCH_2O outer), 4.89 (t, J = 7.8 Hz, 8H, C*H* methine), 4.26 (d, J = 6.7 Hz, 8H, OCH_2O inner), 3.94 (sb, 16H, OCH_2CH_2), 2.47-2.73 (m, 32H, CH_2CH_2Ph), 1.79 (sb, 16H, OCH_2CH_2). ^{1}H NMR data agreed with those reported in [5].

***p*-Xylene hemicarceplex (1⊙16)**:[4] Application of *procedure A* (4 days; 217 ˚C; semi-preparative HPLC, Phenomenax, Si, 21.2*100 mm, 5µm) gave **1⊙16** (90 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.25 (m, 40H, C_6H_5), 6.87 (s, 8H, Ar*H* on bowl), 5.89 (s, 4H, guest-H), 5.67 (d, J = 7.07 Hz, 8H, OCH_2O outer), 4.86 (t, J = 7.97 Hz, 8H, C*H* methine), 4.13 (d, J = 7.06 Hz, 8H, OCH_2O inner), 3.86 (sb, 16H, OCH_2CH_2), 2.48-2.72 (m, 32H, CH_2CH_2Ph), 1.88 (sb, 16H, OCH_2CH_2), -2.09 (s, 6H, CH_3). ^{1}H NMR data agreed with those reported in [4].

Fluorobenzene hemicarceplex (1⊙5):[4] Application of *procedure B* (5 days; 140 ˚C; semi-

preparative HPLC, Phenomenax, Si, 21.2*100 mm, 5µm) gave **1⊙5** (30 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.15-7.25 (m, 40H, C_6H_5), 6.93 (s, 8H, Ar*H* on bowl), 5.69 (d, J = 7.07 Hz, 8H, OCH_2O outer), 5.24 (m, 2H, guest-H), 5.18 (m, 2H, guest-H), 4.84 (t, J = 7.96 Hz, 8H, C*H* methine), 4.05 (d, J = 7.17Hz, 8H, OCH_2O inner), 3.84 (sb, 16H, OCH_2CH_2), 3.45 (t, J = 7.37 Hz, 1H, guest-H), 2.49-2.71 (m, 32H, CH_2CH_2Ph), 1.99 (sb, 16H, OCH_2CH_2). ^{1}H NMR data agreed with those reported in [4].

Chlorobenzene hemicarceplex (**1⊙6**):[4] Application of *procedure B* (3 days; 132 ˚C) gave **1⊙6** (90 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.26 (m, 40H, C_6H_5), 6.92 (s, 8H, Ar*H* on bowl), 6.03 (d, J = 8 Hz, 2H, guest-H_o), 5.65-5.7 (m, 10H, OCH_2O outer, guest-H_m), 4.85 (t, J = 7.8 Hz 8H, C*H* methine), 4.13 (d, J = 6.8 Hz, 8H, OCH_2O inner), 3.88 (sb, 16H, OCH_2CH_2), 3.37 (t, J = 7.3 Hz, 1H, guest-H_p), 2.51-2.73 (m, 32H, CH_2CH_2Ph), 1.92 (sb, 16H, OCH_2CH_2). ^{1}H NMR data agreed with those reported in [4].

Bromobenzene hemicarceplex (**1⊙7**):[4] Application of *procedure A* (4 days; 217 ˚C; preparative HPLC, Phenomenax, Si, 21.2*100mm, 5µm) gave **1⊙7** (94 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.26 (m, 40H, C_6H_5), 6.90 (s, 8H, Ar*H* on bowl), 6.31 (d, J = 7.66Hz, 2H, guest-H), 5.67 (d, J = 7.02 Hz, 8H OCH_2O outer), 5.63 (t, J = 7.60Hz, 2H, guest-H), 4.85 (t, J = 7.81 Hz 8H, C*H* methine), 4.16 (d, J = 6.84Hz, 8H, OCH_2O inner), 3.89 (sb, 16H, OCH_2CH_2), 3.37 (t, J = 7.33Hz, 1H, guest-H), 2.51-2.73 (m, 32H, CH_2CH_2Ph), 1.91 (sb, 16H, OCH_2CH_2). ^{1}H NMR data agreed with those reported in [4].

Benzylchloride hemicarceplex (**1⊙10**): Application of *procedure B* (26 h; 130 ˚C) gave **1⊙10** (95 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.26 (m, 40H, C_6H_5), 6.93 (s, 8H, Ar*H* on bowl), 6.21 (d, J = 7.2 Hz, 2H, guest-H_o), 5.67 (d, J = 7.2 Hz, 8H, OCH_2O outer), 5.15 (t, J = 7.4 Hz, 2H, guest-H_m), 4.87 (t, J = 7.8 Hz 8H, C*H* methine), 4.21 (d, J = 7.2 Hz, 8H, OCH_2O inner), 3.94 (sb, 16H, OCH_2CH_2), 3.20 (t, J = 7.4 Hz, 1H, guest-H_p), 2.51-2.73 (m, 32H, CH_2CH_2Ph), 1.91 (sb, 16H, OCH_2CH_2). FAB-MS: *m/z* $[M+H]^+$ 2380.0 (65); [M - **10** + H]$^+$ 2250.5 (100).

4-Fluorotoluene hemicarceplex (**1⊙11**):[5] Application of *procedure B* (5 days; 140 ˚C; semi-preparative HPLC, Phenomenax, Si, 21.2*100 mm, 5µm) gave **1⊙11** (25 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.14-7.25 (m, 40H, C_6H_5), 6.89 (s, 8H, Ar*H* on bowl), 5.79 (d, J = 7.25 Hz, 2H, guest-H), 5.68 (d, J = 7.05 Hz, 8H OCH_2O outer), 5.61 (d, J = 8.14Hz, 2H, guest-H), 4.84 (t, J = 7.97 Hz, 8H, C*H* methine), 4.09 (d, J = 6.97 Hz, 8H, OCH_2O inner), 3.86 (sb, 16H, OCH_2CH_2), 2.47-2.71 (m, 32H, CH_2CH_2Ph), 1.89 (sb, 16H, OCH_2CH_2), -1.98 (s, 3H, guest-H). ^{1}H NMR data agreed with those reported in [5].

4-Chlorotoluene hemicarceplex (**1⊙12**):[4] Application of *procedure A* (4 days; 217 ˚C; semi-preparative HPLC, Phenomenax, Si, 21.2*100 mm, 5µm) gave **1⊙12** (90 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.15-7.25 (m, 40H, C_6H_5), 6.87 (s, 4H, Ar*H* on bowl), 6.85 (s, 4H, Ar*H* on bowl), 6.12 (d, J = 7.86 Hz, 2H, guest-H), 5.98 (d, J = 7.77 Hz, 2H, guest-H), 5.69 (d, J = 7.37 Hz, 4H, OCH_2O outer), 5.67 (d, J = 6.95 Hz, 4H, OCH_2O outer), 4.86 (m, 8H, C*H* methine), 4.10 (m, 8H, OCH_2O inner), 3.89 (sb, 16H, OCH_2CH_2), 2.47-2.72 (m, 32H, CH_2CH_2Ph), 1.88 (sb, 16H, OCH_2CH_2), -2.10 (s, 3H, CH_3). ^{1}H NMR data agreed with those reported in [4].

***p*-Bromotoluene hemicarceplex (1⊙13)**:[4] Application of *procedure A* (4 days; 217 ˚C; semi-preparative HPLC, Phenomenax, Si, 21.2*100 mm, 5µm) gave **1⊙13** (95 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.26 (m, 40H, C_6H_5), 6.88 (s, 4H, Ar*H* on bowl), 6.82 (s, 4H, Ar*H* on bowl), 6.37 (d, J = 8.09 Hz, 2H, guest-H), 5.94 (d, J = 7.77 Hz, 2H, guest-H), 5.68 (m, 8H OCH_2O outer), 4.87 (m, 8H, C*H* methine), 4.18 (d, J = 6.93 Hz, 4H, OCH_2O inner), 4.10 (d, J = 6.93 Hz, 4H, OCH_2O inner), 3.90 (sb, 16H, OCH_2CH_2), 2.50-2.73 (m, 32H, CH_2CH_2Ph), 1.87 (sb, 16H, OCH_2CH_2), -2.14 (s, 3H, CH_3). ^{1}H NMR data agreed with those reported in [4].

***p*-Iodotoluene hemicarceplex (1⊙14)**. Application of *procedure A* (4 days; 217 ˚C; semi-preparative HPLC, Phenomenax, Si, 21.2*100 mm, 5µm) gave **1⊙14** (100 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.26 (m, 40H, C_6H_5), 6.88 (s, 8H, Ar*H* on bowl), 5.83 (d, J = 7.83 Hz, 2H, guest-H), 6.73 (d, J = 7.96 Hz, 2H, guest-H), 5.67 (d, J = 6.48 Hz, 8H OCH_2O outer), 4.87 (t, J = 8.00 Hz, 8H, C*H* methine), 4.10 (d, J = 7.02 Hz, 8H, OCH_2O inner), 3.92 (sb, 16H, OCH_2CH_2), 2.48-2.73 (m, 32H, CH_2CH_2Ph), 1.85 (sb, 16H, OCH_2CH_2) - 2.20 (s, 3H, guest-CH_3). FAB-MS: *m/z* $[M+H]^+$ 2472.5 (100); [M - **14** + H]$^+$ 2250.6 (65).

***p*-Chlorobenzonitrile hemicarceplex (1⊙21)**: Application of *procedure A* (4 days; 217 ˚C; semi-preparative HPLC, Phenomenax, Si, 21.2*100 mm, 5µm) gave **1⊙21** (80 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.26 (m, 40H, C_6H_5), 6.85 (s, 8H, Ar*H* on bowl), 6.62 (d, J = 8.38 Hz, 2H, guest-H), 6.41 (d, J = 8.04 Hz, 2H, guest-H), 5.70 (d, J = 6.63 Hz, 8H OCH_2O outer), 4.86 (t, J = 7.95 Hz, 8H, C*H* methine), 4.03 (d, J = 6.82 Hz, 8H, OCH_2O inner), 3.92 (sb, 16H, OCH_2CH_2), 2.48-2.75 (m, 32H, CH_2CH_2Ph), 1.87 (sb, 16H, OCH_2CH_2). FAB-MS: *m/z* $[M+H]^+$ 2388.5 (95); [M - **21** +H]$^+$, 2250.8 (84).

Methyl benzoate hemicarceplex (1⊙29): Application of *procedure B* (3 days at 210 ^{o}C) gave **1⊙29** (95 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.27 (m, 42H, 40 C_6H_5 and 2 guest-H), 6.99 (s, 4H, Ar*H* on bowl), 6.84 (s, 4H, Ar*H* on bowl), 5.74 (d, 4H, *J*=6.8 Hz, OC H_2O outer), 5.60 (d, 4H, *J*=6.8 Hz, OC H_2O outer), 5.12-5.20 (m, 2H, guest-H), 4.91 (t, 4H, *J*=7.7 Hz, C*H* methine), 4.86 (t, 4H, *J*=7.7 Hz, C*H* methine), 4.38 (d, 1H, *J*=7.6 Hz, guest-H), 4.67 (s, 1H, C*H*OCH_3 guest), 4.32 (d, 4H, *J*=6.8 Hz, OCH_2O inner), 4.16 (d, 4H, *J*=6.8 Hz, OCH_2O inner), 3.96 (t, 8H, *J*=5.6 Hz, OCH_2CH_2), 3.87 (t, 8H, *J*=4.8 Hz, OCH_2CH_2), 3.79 (t, 1H, *J*=7.4 Hz, guest-H), 2.47-2.75 (m, 32H, CH_2CH_2Ph), 1.74-1.95 (m, 16H, OCH_2CH_2). FAB-MS (NBA-matrix): m/z 2415.6 ([M + H]$^+$,100 %); 2250.8 ([M + H - **29**]$^+$, 93%) Anal. Calcd for $C_{152}H_{144}O_{26}$: C, 76.49; H, 6.09. Found: C, 76.43; H, 6.16.

Phenylisocyanate hemicarceplex (1⊙36): Application of *procedure B* (3 days; 168 ˚C) gave **1⊙36** (92 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.26 (m, 40H, C_6H_5), 6.92 (s, 8H, Ar*H* on bowl), 5.97 (d, J = 7.6 Hz, 2H, guest-H_o), 5.70 (d, J = 6.8 Hz, 8H, OCH_2O outer), 5.63 (t, J = 7.8 Hz, 2H, guest-H), 4.89 (t, J = 7.9 Hz 8H, C*H* methine), 4.21 (d, J = 6.8 Hz, 8H, OCH_2O inner), 3.90 (sb, 16H, OCH_2CH_2), 3.03 (t, J = 7.4 Hz, 1H, guest-H_p), 2.51-2.73 (m, 32H, CH_2CH_2Ph), 1.93 (sb, 16H, OCH_2CH_2). FAB-MS: *m/z* [M + H]$^+$, 2370.2 (35); [M - **36** + H]$^+$, 2250.6 (100). Anal. Calcd for $C_{151}H_{151}NO_{25}$: C, 76.21; H, 6.40; N, 0.59. Found: C, 76.47; H, 6.08; N, 0.59.

Methoxyphthalide hemicarceplex (**1⊙27**): Synthesis will be reported elsewhere. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.27 (m, 40H, C_6H_5), 6.97 (s, 4H, Ar*H* on bowl), 6.81 (s, 4H, Ar*H* on bowl), 6.58 (d, 1H, *J*=7.2 Hz, guest-H), 5.82 (d, 4H, *J*=7.2 Hz, OC H_2O outer), 5.61 (d, 1H, *J*=7.6 Hz, guest-H), 5.45 (d, 4H, *J*=7.6 Hz, OC H_2O outer), 5.26 (t, 1H, *J*=7.4 Hz, guest-H), 4.89 (t, 4H, *J*=7.8 Hz, C*H* methine), 4.85 (t, 4H, *J*=7.8 Hz, C*H* methine), 4.38 (d, 1H, *J*=7.6 Hz, guest-H), 4.67 (s, 1H, C*H*OCH_3 guest), 4.53 (d, 4H, *J*=7.2 Hz, OCH_2O inner), 3.85-4.12 (m, 20H, OC H_2C H_2, OCH_2O inner), 3.79 (t, 1H, *J*=7.4 Hz, guest-H), 2.47-2.75 (m, 32H, C H_2C H_2Ph), 1.74-1.90 (m, 16H, O CH_2C H_2) –0.68 (s, 3H, CH_3 guest). IR ($CHCl_3$) 1779.5 cm^{-1}. FAB-MS (NBA-matrix): m/z 2415.6 ($[M + H]^+$, 100 %); 2250.8 ([M + H - **27**]$^+$, 93%) Anal. Calcd for $C_{153}H_{144}O_{27}$: C, 76.10; H, 6.01. Found: C, 76.49; H, 5.98.

Coumarin hemicarceplex (**1⊙31**): Application of *procedure B* (2 days; 145 ˚C) gave **1⊙31** (25 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.26 (d, J = 9.2 Hz, 1H, guest-H_{vinyl}), 7.16-7.26 (m, 40H, C_6H_5), 6.97 (s, 8H, Ar*H* on bowl), 6.59 (d, J = 5.9 Hz, 1H, guest-H_{aryl}), 6.58 (d, J = 5.9 Hz, 1H, guest-H_{aryl}), 5.60 (d, J = 7.0 Hz, 8H, OCH_2Oouter), 4.85 (t, J = 7.8 Hz 8H, C*H* methine), 4.22 (sb, 8H, OCH_2Oinner), 3.94 (sb, 16H, OCH_2CH_2), 3.22 (t, J = 7.9 Hz, 1H, guest-H_{aryl}), 2.88 (t, J = 7.6 Hz, 1H, guest-H_{aryl}), 2.51-2.73 (m, 32H, CH_2CH_2Ph), 2.34 (d, J = 9.2 Hz, 1H, guest-H_{vinyl}), 1.86 (sb, 16H, OCH_2CH_2). FAB-MS: *m/z* $[M + H]^+$, 2397 (100); [M - **31** + H]$^+$, 2251 (80). Anal. Calcd for $C_{153}H_{152}O_{26}$: C, 76.67; H, 5.97. Found: C, 76.94; H, 6.64.

Benzonitrile hemicarceplex (1⊙9). Application of *procedure A* (4 days; 217 ˚C; semi-preparative HPLC, Phenomenax, Si, 21.2*100mm, 5µm) gave **1⊙9** (57 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.28 (m, 40H, C_6H_5), 6.91 (s, 8H, Ar*H* on bowl), 6.48 (d, J = 7.50 Hz, 2H, guest-H), 5.81 (t, J = 7.66 Hz, 2H, guest-H), 5.69 (d, J = 6.86 Hz, 8H OCH_2O outer), 4.85 (t, J = 7.89 Hz, 8H, C*H* methine), 4.08 (d, J = 6.87 Hz, 8H, OCH_2O inner), 3.90 (sb, 16H, OCH_2CH_2), 3.59 (t, J = 7.53 Hz, 1H, guest-H), 2.49-2.73 (m, 32H, CH_2CH_2Ph), 1.90 (sb, 16H, OCH_2CH_2). FAB-MS: *m/z* $[M+H]^+$ 2354.7 (100); [M - **9**+H]$^+$ 2249.7 (43).

Nitrobenzene hemicarceplex (**1⊙28**):[5] Application of *procedure B* (19 h; 180 ˚C) gave **1⊙28** (90 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.26 (m, 40H, C_6H_5), 7.04 (d, J = 7.6 Hz, 2H, guest-H_o), 6.96 (s, 8H, Ar*H*), 5.65 (d, J = 7.0 Hz, 8H, OCH_2O outer), 5.58 (t, J = 7.9 Hz, 2H, guest-H_m), 4.84 (t, J = 7.8 Hz 8H, C*H* methine), 4.06 (d, J = 7.0 Hz, 8H, OCH_2O inner), 3.92 (sb, 16H, OCH_2CH_2), 3.59 (t, J = 7.6 Hz, 1H, guest-H_p), 2.51-2.73 (m, 32H, CH_2CH_2Ph), 1.89 (sb, 16H, OCH_2CH_2). ^{1}H NMR data agreed with those reported in [5].

Benzoyl chloride hemicarceplex (**1⊙30**): Application of *procedure B* (28 h at 90 ^{o}C) gave **1⊙30** (80 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.27 (m, 40H, C_6H_5), 6.97 (s, 4H, Ar*H* on bowl), 6.96 (d, 2H, *J*=7.6 Hz, guest-H), 6.87 (s, 4H, Ar*H* on bowl), 5.60-5.78 (m, 8H, OC H_2O outer), 5.28-5.32 (m, 2H, guest-H), 4.85 (t, 8H, *J*=7.9 Hz, C*H* methine), 4.08 (sb, 4H, OCH_2O inner), 3.85-4.10 (m, 20H, OCH_2CH_2, OCH_2O inner), 3.61 (t, 1H, *J*=7.4 Hz, guest-H), 2.47-2.75 (m, 32H, CH_2CH_2Ph), 1.87 (sb, 16H, OCH_2CH_2). FAB-MS (NBA-matrix): m/z 2391 ($[M + H]^+$, 100 %); 2251 ([M + H - **30**]$^+$, 60 %) Anal. Calcd for $C_{151}H_{139}O_{25}Cl$: C, 75.78; H, 6.02. Found: C, 76.18; H, 5.68.

***p*-Tolunitrile hemicarceplex** (**1⊙22**). Application of *procedure A* (4 days; 217 ˚C; semi-

preparative HPLC, Phenomenax, Si, 21.2*100mm, 5µm) gave **1⊙22** (97 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): **7**.18-7.26 (m, 40H, C_6H_5), 6.90 (s, 8H, Ar*H* on bowl), 6.16 (d, J = 7.70 Hz, 2H, guest-H), 6.54 (d, J = 7.70 Hz, 2H, guest-H), 5.69 (d, J = 6.48 Hz, 8H OCH_2O outer), 4.87 (t, J = 8.09 Hz, 8H, C*H* methine), 4.08 (d, J = 7.45 Hz, 8H, OCH_2O inner), 3.91 (sb, 16H, OCH_2CH_2), 2.51-2.72 (m, 32H, CH_2CH_2Ph), 1.87 (sb, 16H, OCH_2CH_2), -2.03 (s, 3H, guest-CH_3). FAB-MS: *m/z* $[M+H]^+$ 2368.9 (100); [M - **22** +H]$^+$ 2250.1 (14).

DMA hemicarceplex (**1⊙25**):[5] Application of *procedure A* (4 days; 217 ˚C; preparative HPLC, Phenomenax, Si, 21.2*100mm, 5µm) gave **1⊙25** (90 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.17-7.30 (m, 40H, C_6H_5), 6.88 (s, 8H, Ar*H* on bowl), 5.83 (d, J = 7.16 Hz, 8H OCH_2O outer), 4.86 (t, J = 7.93 Hz 8H, C*H* methine), 4.32 (d, J = 7.20 Hz, 8H, OCH_2O inner), 3.95 (sb, 16H, OCH_2CH_2), , 2.51-2.73 (m, 32H, CH_2CH_2Ph), 1.95 (sb, 16H, OCH_2CH_2), 1.64 (s, 3H, guest-H), -0.38 (s, 3H, guest-H), -1.60 (s, 3H, guest-H). ^{1}H NMR data obtained were in agreement with that previously reported.[5]

Phenol hemicarceplex (**1⊙32**):[6] Application of *procedure B* (25 h; 166 ˚C) gave **1⊙32** (95 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.26 (m, 40H, C_6H_5), 6.94 (s, 8H, Ar*H* on bowl), 5.70 (d, J = 7.2 Hz, 8H, OCH_2O outer), 4.86 (t, J = 7.9 Hz 8H, C*H* methine), 4.78 (t, J = 7.8 Hz, 2H, guest-H_m), 4.55 (t, J = 7.0 Hz, 1H, guest-H_p), 4.40 (d, J = 7.8 Hz, 2H, guest-H_o), 4.18 (d, J = 7.2 Hz, 8H, OCH_2O inner), 3.88 (sb, 16H, OCH_2CH_2), 3.19 (s, 1H, guest-OH), 2.51-2.73 (m, 32H, CH_2CH_2Ph), 1.96 (sb, 16H, OCH_2CH_2).

***d*$_{10}$-*p*-Xylene hemicarceplex** (**1⊙*d*$_{10}$-16**): Application of *procedure A* (2 days; 256 ˚C; semi-preparative HPLC, Phenomenax, Si, 21.2*100mm, 5µm) gave **1⊙*d*$_{10}$-16** (93 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 7.16-7.25 (m, 40H, C_6H_5), 6.91 (s, 8H, Ar*H* on bowl), 5.69 (d, J = 7.0 Hz, 8H OCH_2O outer), 4.88 (t, J = 8.3 Hz, 8H, C*H* methine), 4.15 (d, J = 7.0 Hz, 8H, OCH_2O inner), 3.88 (sb, 16H, OCH_2CH_2), 2.48-2.72 (m, 32H, CH_2CH_2Ph), 1.90 (sb, 16H, OCH_2CH_2); ESI-MS: *m/z* $[M +23]^+$ 2387.7 (68).

***p*-Xylene hemicarceplex** (**3⊙16**): Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*100mm, 5µm) gave **3⊙16** (94 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.82 (s, 8H, Ar*H* on bowl), 5.86 (s, 4H, guest-H), 5.63 (d, J = 6.92 Hz, 8H OCH_2O outer), 4.72 (t, J = 8.13 Hz, 8H, C*H* methine), 4.09 (d, J = 7.07Hz, 8H, OCH_2O inner), 3.81 (sb, 16H, OCH_2CH_2), 2.17-2.22 (m, 16H, $CH_2(CH_2)_3CH_3$), 1.84 (sb, 16H, OCH_2CH_2), 1.28-1.34 (m, 48H, $CH_2(CH_2)_3CH_3$), 0.93 (t, J = 7.04 Hz, 24H, CH_3), -2.14 (s, 6H, guest-H). FAB-MS: *m/z* $[M + H]^+$, 2084.2 (100); [M - **16** + H]$^+$, 1979.1 (50).

Toluene hemicarceplex (**3⊙8**): Application of *procedure B* (2 days; 170 ˚C) gave **3⊙8** (95 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.88 (s, 8H, Ar*H* on bowl), 5.81 (d, J = 7.6, 2H, guest-H_o), 5.6-5.65 (m, 10H, OCH_2O outer, guest-H_m), 4.71 (t, J = 8 Hz, 8H, C*H* methine), 4.09 (d, J = 7.2Hz, 8H, OCH_2O inner), 3.82 (sb, 16H, OCH_2CH_2), 3.30 (t, J = 7.0, 1H, guest-H_p), 2.18-2.3 (m, 16H, $CH_2(CH_2)_3CH_3$), 1.88 (sb, 16H, OCH_2CH_2), 1.28-1.34 (m, 48H, $CH_2(CH_2)_3CH_3$), 0.93 (t, J = 7.2 Hz, 24H, CH_3), -1.85 (s, 3H, guest-CH_3). FAB-MS: *m/z* $[M + H]^+$, 2070.3 (100); [M - **8** + H]$^+$, 1979.5 (39).

Benzaldehyde hemicarceplex (**3⊙23**): Application of *procedure B* (2 days; 170 ˚C) gave **3⊙23**

(82 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.92 (s, 8H, Ar*H* on bowl), 6.53 (s, 1H, guest-C*H*O), 6.51 (d, J = 7.2, 2H, guest-H_o), 5.70 (d, J = 7.6, 2H, guest-H_m), 5.61 (d, J = 7.2Hz, 8H, OCH_2O outer), 4.71 (t, J = 8 Hz, 8H, C*H* methine), 4.00 (d, J = 7.2Hz, 8H, OCH_2O inner), 3.83 (sb, 16H, OCH_2CH$_2$), 3.59 (t, J = 7.2, 1H, guest-H_p), 2.18-2.3 (m, 16H, CH_2(CH$_2$)$_3$CH$_3$), 1.86 (sb, 16H, OCH$_2$CH_2), 1.28-1.34 (m, 48H, CH$_2$(CH_2)$_3$CH$_3$), 0.93 (t, J = 7.0 Hz, 24H, CH_3). FAB-MS: *m/z* [M + H]$^+$, 2084.2 (85); [M - **23** + H]$^+$, 1978.2 (100).

Phenol hemicarceplex (**3⊙32**): Application of *procedure B* (30 h; 170 ˚C) gave **3⊙32** (80 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.88 (s, 8H, Ar*H* on bowl), 5.64 (d, J = 7.2Hz, 8H, OCH_2O outer), 4.76-4.65 (m, 10H, C*H* methane, guest-H_m), 4.53 (t, J = 7.2 Hz, 1H, guest-H_p), 4.33 (d, J = 7.8 Hz, 2H, guest-H_o), 4.12 (d, J = 7.2Hz, 8H, OCH_2O inner), 3.82 (sb, 16H, OCH_2CH$_2$), 3.14 (s, 1H, guest-OH), 2.18-2.3 (m, 16H, CH_2(CH$_2$)$_3$CH$_3$), 1.91 (sb, 16H, OCH$_2$CH_2), 1.28-1.34 (m, 48H, CH$_2$(CH_2)$_3$CH$_3$), 0.93 (t, J = 7.2 Hz, 24H, CH_3). FAB-MS: *m/z* [M + H]$^+$, 2072.1 (100); [M - **32** + H]$^+$, 1978.9 (47).

Benzyl alcohol hemicarceplex (**3⊙35**): Application of *procedure B* (2 days; 170 ˚C) gave **3⊙35** (95 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.88 (s, 8H, Ar*H* on bowl), 6.05 (d, J = 7.2, 2H, guest-H_o), 5.60 (d, J = 7.2Hz, 8H, OCH_2O outer), 5.33 (t, J = 7.6, 2H, guest-H_m), 4.72 (t, J = 8 Hz, 8H, C*H* methine), 4.15 (d, J = 6.8 Hz, 8H, OCH_2O inner), 3.83 (sb, 16H, OCH_2CH$_2$), 3.20 (t, J = 7.2, 1H, guest-H_p), 2.18-2.3 (m, 16H, CH_2(CH$_2$)$_3$CH$_3$) 1.68 (d, J = 3, 2H, guest-CH_2), 1.86 (sb, 16H, OCH$_2$CH_2), 1.28-1.34 (m, 48H, CH$_2$(CH_2)$_3$CH$_3$), 0.93 (t, J = 7.0 Hz, 24H, CH_3, -2.62 (t, J = 3Hz, 1H, O*H*), FAB-MS: *m/z* [M + H]$^+$, 2086.5 (10); [M-CH$_2$O+H]$^+$, 2056.6 (100); [M - **35** + H]$^+$, 1978.6 (18).

Benzoic acid hemicarceplex (**3⊙39**): Application of *procedure B* (2 days; 170 ˚C) gave **3⊙39** (80 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.89 (s, 8H, Ar*H* on bowl), 6.82 (d, J = 7.6, 2H, guest-H_o), 5.58 (d, J = 7.2Hz, 8H, OCH_2O outer), 5.34 (d, J = 7.8, 2H, guest-H_m), 4.71 (t, J = 8 Hz, 8H, C*H* methine), 4.13 (d, J = 7.2Hz, 8H, OCH_2O inner), 3.88 (sb, 16H, OCH_2CH$_2$), 3.49 (t, J = 7.4, 1H, guest-H_p), 2.37 (s, 1H, guest-OH), 2.18-2.3 (m, 16H, CH_2(CH$_2$)$_3$CH$_3$ 1.85 (sb, 16H, OCH$_2$CH_2), 1.28-1.34 (m, 48H, CH$_2$(CH_2)$_3$CH$_3$), 0.93 (t, J = 7.0 Hz, 24H, CH_3). FAB-MS: *m/z* [M + H]$^+$, 2100.1 (82); [M - **39** + H]$^+$, 1978.4 (100).

***d_{10}*-*p*-Xylene hemicarceplex** (**3⊙*d_{10}*-16**): Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*100 mm, 5µm) gave **3⊙*d_{10}*-16** (92 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.82 (s, 8H, Ar*H* on bowl), 5.63 (d, J = 6.92 Hz, 8H OCH_2O outer), 4.72 (t, J = 8.13 Hz, 8H, C*H* methine), 4.09 (d, J = 7.07Hz, 8H, OCH_2O inner), 3.81 (sb, 16H, OCH_2CH$_2$), 2.17-2.22 (m, 16H, CH_2(CH$_2$)$_3$CH$_3$), 1.84 (sb, 16H, OCH$_2$CH_2), 1.28-1.34 (m, 48H, CH$_2$(CH_2)$_3$CH$_3$), 0.93 (t, J = 7.04 Hz, 24H, CH_3). ESI-MS: *m/z* [M + Na]$^+$, 2387.7 (70).

***d_6*-*p*-Xylene hemicarceplex** (**3⊙*d_6*-16**): Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*100 mm, 5µm) gave **3⊙** *d_6*-**16** (80 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.83 (s, 8H, Ar*H* on bowl), 5.63 (d, J = 6.92 Hz, 8H OCH_2O outer), 4.73 (t, J = 8.13 Hz, 8H, C*H* methine), 4.09 (d, J = 7.07Hz, 8H, OCH_2O inner), 3.81 (sb, 16H, OCH_2CH$_2$), 2.18-2.21 (m, 16H, CH_2(CH$_2$)$_3$CH$_3$), 1.85 (sb, 16H, OCH$_2$CH_2), 1.25-1.42 (m, 48H, CH$_2$(CH_2)$_3$CH$_3$), 0.93 (t, J = 7.04 Hz, 24H, CH_3), -2.14 (s, 6H, guest-H).

d_4-p-**Xylene hemicarceplex** (**3**⊙*d_4*-**16**): Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*100 mm, 5µm) gave **3**⊙*d_4*-**16** (80 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.83 (s, 8H, Ar*H* on bowl), 5.86 (s, 4H, guest-H), 5.63 (d, J = 6.92 Hz, 8H OCH_2O outer), 4.73 (t, J = 8.13 Hz, 8H, C*H* methine), 4.09 (d, J = 7.07Hz, 8H, OCH_2O inner), 3.82 (sb, 16H, OCH_2CH_2), 2.19-2.21 (m, 16H, CH_2(CH_2)$_3$CH_3), 1.85 (sb, 16H, OCH$_2$CH_2), 1.25-1.42 (m, 48H, CH$_2$(CH_2)$_3$CH_3), 0.93 (t, J = 7.04 Hz, 24H, CH_3).

1,4-Dibromobenzene hemicarceplex (**3**⊙**19**): Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*250mm, 5µm) gave **3**⊙**19** (77 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.76 (s, 8H, Ar*H* on bowl), 6.38 (s, 4H, guest-H), 5.63 (d, J = 6.84 Hz, 8H OCH_2O outer), 4.72 (t, J = 8.12 Hz 8H, C*H* methine), 4.07 (d, J = 7.06Hz, 8H, OCH_2O inner), 3.87 (sb, 16H, OCH_2CH_2), 2.16-2.22 (m, 16H, CH_2(CH_2)$_3$CH_3), 1.82 (sb, 16H, OCH$_2$CH_2), 1.25-1.42 (m, 48H, CH$_2$(CH_2)$_3$CH_3), 0.92 (t, J = 7.03 Hz, 24H, CH_3). ESI-MS: *m/z* [M + Na]$^+$, 2233.7 (60).

1,4-Dichlorobenzene hemicarceplex (**3**⊙**18**): Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*250mm, 5µm) gave **3**⊙**18** (79 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.79 (s, 8H, Ar*H* on bowl), 6.17 (s, 4H, guest-H), 5.64 (d, J = 6.86 Hz, 8H OCH_2O outer), 4.71 (t, J = 8.04 Hz 8H, C*H* methine), 4.02 (d, J = 6.97 Hz, 8H, OCH_2O inner), 3.87 (sb, 16H, OCH_2CH_2), 2.16-2.22 (m, 16H, CH_2(CH_2)$_3$CH_3), 1.84 (sb, 16H, OCH$_2$CH_2), 1.25-1.42 (m, 48H, CH$_2$(CH_2)$_3$CH_3) , 0.92 (t, J = 7.09 Hz, 24H, CH_3). ESI-MS: *m/z* [M + Na]$^+$, 2145.8 (100).

***p*-Fluorotoluene hemicarceplex** (**3**⊙**11**): Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*250mm, 5µm) gave **3**⊙**11** (80 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.84 (s, 8H, Ar*H* on bowl), 5.88 (t, J = 4.77 Hz, 2H, guest-H), 5.64 (d, J = 6.82 Hz, 8H OCH_2O outer), 5.58 (t, J = 7.84 Hz 2H, guest-H), 4.71 (t, J = 7.97 Hz, 8H, C*H* methine), 4.05 (d, J = 6.93 Hz, 8H, OCH_2O inner), 3.82 (sb, 16H, OCH_2CH_2), 2.16-2.22 (m, 16H, CH_2(CH_2)$_3$CH_3), 1.86 (sb, 16H, OCH$_2$CH_2), 1.25-1.42 (m, 48H, CH$_2$(CH_2)$_3$CH_3), 0.92 (t, J = 6.84 Hz, 24H, CH_3).-2.03 (s, 3H, guest-H). ESI-MS: *m/z* [M + Na]$^+$, 2110.0 (52).

1,4-Difluorobenzene hemicarceplex (**3**⊙**17**): Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*250mm, 5µm) gave **3**⊙**17** (75 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.85 (s, 8H, Ar*H* on bowl), 5.66 (d, J = 7.08 Hz, 8H OCH_2O outer), 5.36 (t, J = 5.78 Hz 4H, guest-H), 4.70 (t, J = 8.09 Hz 8H, C*H* methine), 4.00 (d, J = 7.08 Hz, 8H, OCH_2O inner), 3.83 (sb, 16H, OCH_2CH_2), 2.16-2.22 (m, 16H, CH_2(CH_2)$_3$CH_3),1.88 (sb, 16H, OCH$_2$CH_2), 1.25-1.44 (m, 48H, CH$_2$(CH_2)$_3$CH_3), 0.92 (t, J = 7.00 Hz, 24H, CH_3). ESI-MS: *m/z* [M+H]$^+$ 2091.9 (25); [M + Na]$^+$, 2113.9 (100).

Fluorobenzene hemicarceplex (**3**⊙**5**): Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*250mm, 5µm) gave **3**⊙**5** (70 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.87 (s, 8H, Ar*H* on bowl), 5.64 (d, J = 5.27 Hz, 8H OCH_2O outer), 5.14-5.20 (m, 4H, guest-H), 4.69 (t, J = 7.88 Hz 8H, C*H* methine), 4.00 (d, J = 5.72 Hz, 8H, OCH_2O inner), 3.41 (m, 1H, guest-H), 3.79 (sb, 16H, OCH_2CH_2), 2.16-2.22 (m, 16H,

CH_2(CH_2)$_3$$CH_3$),1.89 (sb, 16H, OC$H_2CH_2$), 1.25-1.42 (m, 48H, CH_2(CH_2)$_3$$CH_3$), 0.92 (t, J = 8.0 Hz, 24H, CH_3). ESI-MS: *m/z* $[M+H]^+$ 2073.9 (100); $[M + Na]^+$, 2095.9 (62).

***p*-Chlorotoluene hemicarceplex (3⊙12)**: Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*250mm, 5µm) gave **3⊙12** (80 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.82 (s, 4H, Ar*H* on bowl), 6.79 (s, 4H, Ar*H* on bowl), 6.08 (d, J = 8.12 Hz 2H, guest-H), 5.94 (d, J = 8.12 Hz 2H, guest-H), 5.65 (d, J = 7.18 Hz, 4H OCH_2O outer), 5.62 (d, J = 7.02 Hz, 4H OCH_2O outer), 4.73 (t, J = 8.11 Hz 4H, C*H* methine), 4.70 (t, J = 8.11 Hz 4H, C*H* methine), 4.07 (d, J = 6.86 Hz, 4H, OCH_2O inner),4.04 (d, J = 7.06 Hz, 4H, OCH_2O inner), 3.84 (sb, 16H, OC$H_2$$CH_2$), 2.17-2.22 (m, 16H, C$H_2$($CH_2$)$_3$$CH_3$), 1.84 (sb, 16H, OC$H_2CH_2$), 1.28-1.34 (m, 48H, CH_2(CH_2)$_3$$CH_3$), 0.92 (t, J = 7.01 Hz, 24H, CH_3), -2.14 (s, 3H, guest-H). ESI-MS: *m/z* $[M + Na]^+$, 2125.9 (85).

1-Bromo-4-chlorobenzene hemicarceplex (3⊙15): Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*250mm, 5µm) gave **3⊙15** (80 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.79 (s, 4H, Ar*H* on bowl), 6.76 (s, 4H, Ar*H* on bowl), 6.42 (d, J = 8.38 Hz 2H, guest-H), 6.12 (d, J = 8.18 Hz 2H, guest-H), 5.94 (d, J = 8.12 Hz 2H, guest-H), 5.64 (d, J = 6.84 Hz, 4H OCH_2O outer), 5.63 (d, J = 6.84 Hz, 4H OCH_2O outer), 4.73 (t, J = 5.34 Hz 4H, C*H* methine), 4.70 (t, J = 5.56 Hz 4H, C*H* methine), 4.08 (d, J = 6.87 Hz, 4H, OCH_2O inner),4.02 (d, J = 6.95 Hz, 4H, OCH_2O inner), 3.87 (sb, 16H, OC$H_2$$CH_2$), 2.16-2.22 (m, 16H, C$H_2$($CH_2$)$_3$$CH_3$), 1.83 (sb, 16H, OC$H_2CH_2$), 1.25-1.42 (m, 48H, CH_2(CH_2)$_3$$CH_3$), 0.92 (t, J = 7.11 Hz, 24H, CH_3). ESI-MS: *m/z* $[M+H]^+$ 2167.9 (45); $[M + Na]^+$, 2189.8 (95).

***p*-Iodotoluene hemicarceplex (3⊙14)**: Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*250mm, 5µm) gave **3⊙14** (82 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.82 (s, 4H, Ar*H* on bowl), 6.70 (s, 4H, Ar*H* on bowl), 6.69 (2H, guest-H), 6.12 (d, J = 8.18 Hz 2H, guest-H), 5.79 (d, J = 8.11 Hz 2H, guest-H), 5.63 (d, J = 7.03 Hz, 4H OCH_2O outer), 5.62 (d, J = 6.51 Hz, 4H OCH_2O outer), 4.73 (t, J = 8.06 Hz 8H, C*H* methine), 4.30 (d, J = 6.80 Hz, 4H, OCH_2O inner), 4.05 (d, J = 7.06 Hz, 4H, OCH_2O inner), 3.85(sb, 16H, OC$H_2$$CH_2$), 2.16-2.22 (m, 16H, C$H_2$($CH_2$)$_3$$CH_3$), 1.80 (sb, 16H, OC$H_2CH_2$), 1.25-1.42 (m, 48H, CH_2(CH_2)$_3$$CH_3$), 0.92 (t, J = 6.52 Hz, 24H, CH_3), -2.25 (s, 3H, guest-H). ESI-MS: *m/z* $[M + Na]^+$, 2217.8 (78).

***p*-Bromotoluene hemicarceplex (3⊙13)**: Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*250mm, 5µm) gave **3⊙13** (80 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.82 (s, 4H, Ar*H* on bowl), 6.76 (s, 4H, Ar*H* on bowl), 6.34 (d, J = 8.11 Hz, 2H, guest-H), 5.90 (d, J = 8.11 Hz 2H, guest-H), 5.63 (d, J = 6.87 Hz, 4H OCH_2O outer), 5.62 (d, J = 6.35 Hz, 4H OCH_2O outer), 4.73 (t, J = 7.87 Hz 4H, C*H* methine),4.71 (t, J = 7.92 Hz 4H, C*H* methine), 4.13 (d, J = 6.81 Hz, 4H, OCH_2O inner), 4.04 (d, J = 7.07 Hz, 4H, OCH_2O inner), 3.85 (sb, 16H, OC$H_2$$CH_2$), 2.16-2.22 (m, 16H, C$H_2$($CH_2$)$_3$$CH_3$), 1.83 (sb, 16H, OC$H_2CH_2$), 1.25-1.42 (m, 48H, CH_2(CH_2)$_3$$CH_3$), 0.92 (t, J = 6.33 Hz, 24H, CH_3), -2.25 (s, 3H, guest-H). ESI-MS: *m/z* $[M + Na]^+$, 2169.8(52).

Bromobenzene hemicarceplex (3⊙7): Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*250mm, 5µm) gave **3⊙7** (80 % yield) as a white powder. ^{1}H-NMR (400 MHz; $CDCl_3$; 25˚C): 6.84 (s, 8H, Ar*H* on bowl), 6.27 (d, J = 7.6 Hz 2H, guest-H),

6.12 (d, J = 8.67 Hz 2H, guest-H), 5.62 (d, J = 6.80 Hz, 8H OCH_2O outer), 5.59 (d, J = 7.6 Hz 2H, guest-H), 4.71 (t, J = 8.0 Hz 8H, C*H* methine), 4.12 (d, J = 6.80 Hz, 8H, OCH_2O inner), 3.84 (sb, 16H, OCH_2CH$_2$), 3.31 (t, J = 7.6 Hz 1H, guest-H), 2.16-2.22 (m, 48H, CH$_2$(CH_2)$_3$CH$_3$), 1.83 (sb, 16H, OCH$_2$CH_2),1.25-1.42 (m, 48H, CH$_2$(CH_2)$_3$CH$_3$), 0.93 (t, J = 6.33 Hz, 24H, CH_3). ESI-MS: *m/z* [M + Na]$^+$, 2154.9 (40).

Chlorobenzene hemicarceplex (**3⊙6**): Application of *procedure A* (4 days; 227 ˚C; preparative HPLC, Phenomenax, Si, 21.2*250mm, 5µm) gave **3⊙6** (78 % yield) as a white powder. ^{1}H-NMR (400 MHz; CDCl$_3$; 25˚C): 6.85 (s, Ar*H* on bowl), 5.98 (d, J = 7.77 Hz 2H, guest-H), 6.12 (d, J = 8.67 Hz 2H, guest-H), 5.63 (d, J = 7.05 Hz, 8H OCH_2O outer), 5.61 (2H, guest-H), 4.70 (t, J = 8.01 Hz 8H, C*H* methine), 4.08 (d, J = 7.04 Hz, 8H, OCH_2O inner), 3.83 (sb, 16H, OCH_2CH$_2$), 3.32 (t, J = 7.26 Hz 1H, guest-H), 2.16-2.22 (m, 48H, CH$_2$(CH_2)$_3$CH$_3$), 1.88 (sb, 16H, OCH$_2$CH_2), 1.25-1.42 (m, 48H, CH$_2$(CH_2)$_3$CH$_3$), 0.92 (t, J = 7.02 Hz, 24H, CH_3). ESI-MS: *m/z* [M+H]$^+$ 2089.9 (37); [M + Na]$^+$, 2111.9 (100).

d$_6$**-Benzene hemicarceplex** (**3⊙***d*$_6$-**4**): Application of *procedure B* (2 days; 130 ˚C; preparative HPLC, Phenomenax, Si, 21.2*250mm, 5µm) gave **3⊙***d*$_6$-**4** (66 % yield) as a white powder. ^{1}H-NMR (400 MHz; CDCl$_3$; 25˚C): 6.90 (s, Ar*H* on bowl), 5.65 (d, J = 7.15 Hz, 8H OCH_2O outer), 4.71 (t, J = 8.05 Hz 8H, C*H* methine), 4.00 (d, J = 7.20 Hz, 8H, OCH_2O inner), 3.78 (sb, 16H, OCH_2CH$_2$), 2.16-2.22 (m, 48H, CH$_2$(CH_2)$_3$CH$_3$), 1.94 (sb, 16H, OCH$_2$CH_2), 1.25-1.42 (m, 48H, CH$_2$(CH_2)$_3$CH$_3$), 0.93 (t, J = 7.02 Hz, 24H, CH_3).

Molecular Modeling: Stochastic molecular dynamics calculations in vacuum at 300 K were carried out using the program MAESTRO (Schroedinger, Inc. Portland, OR) with the Amber* force field as implemented in the program. The following parameters were choosen: Timestep: 1.5 fs; Equilibrium Time: 1000 ps; Simulation Time: 10000 ps and the shake all bonds option was selected. 500 snapshots (every 20 ps) were saved and *d* calculated from the coordinates of the ether oxygen.
For simulations shown in figure **S3**, C-H bonds were constrained by applying a force constant of 10000 dyn/m. The same parameters as above were applied. The total simulation time was 20 ns and 1000 snapshots were saved and the time-averaged *d* calculated as described above.

References:

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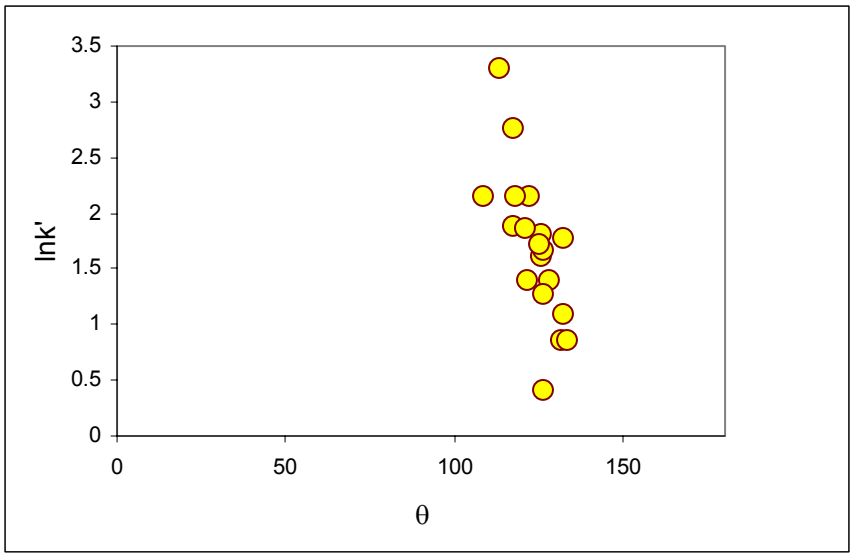

Figure S1: Plot of lnk' against dihedral angle θ for hemicarceplexes **1**⊙Guest (Guest = **4-22**)

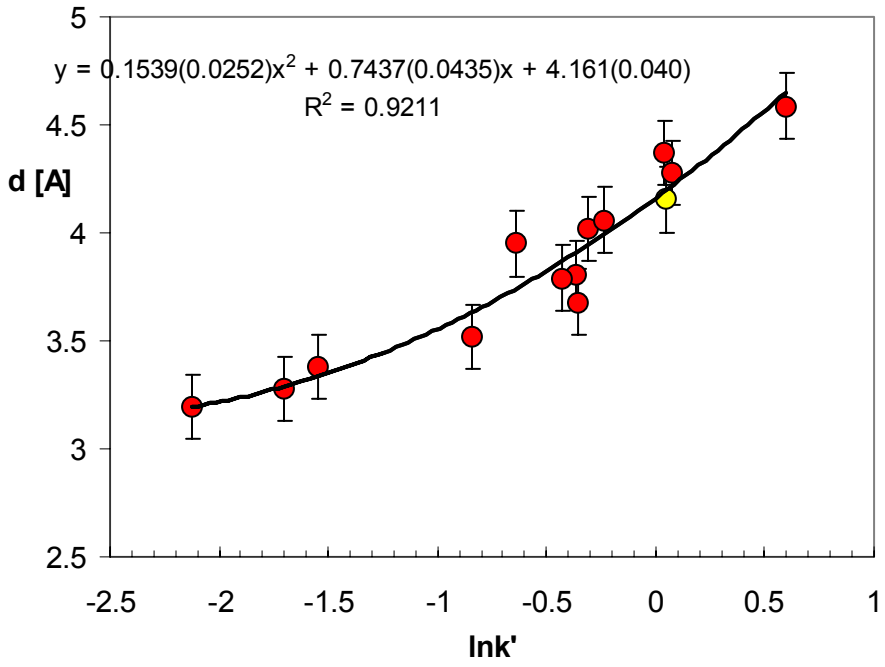

Figure S2: Semi logarithmic plot of hemicarceplex **3**⊙Guest (Guest = **4-8**; **11-19**) length *d* and retention factor k' and best fit for the correlation. The data point for hemicarceplex **3**⊙**16** is marked in yellow. Conditions: Mobile phase: A/B, 65:35, A: 2.0 v% ether in CH_2Cl_2, B: CH_2Cl_2;1 mL/min; Phenomenax, SiO_2, 25 cm x 4.6 mm, 5mm; 22°C.

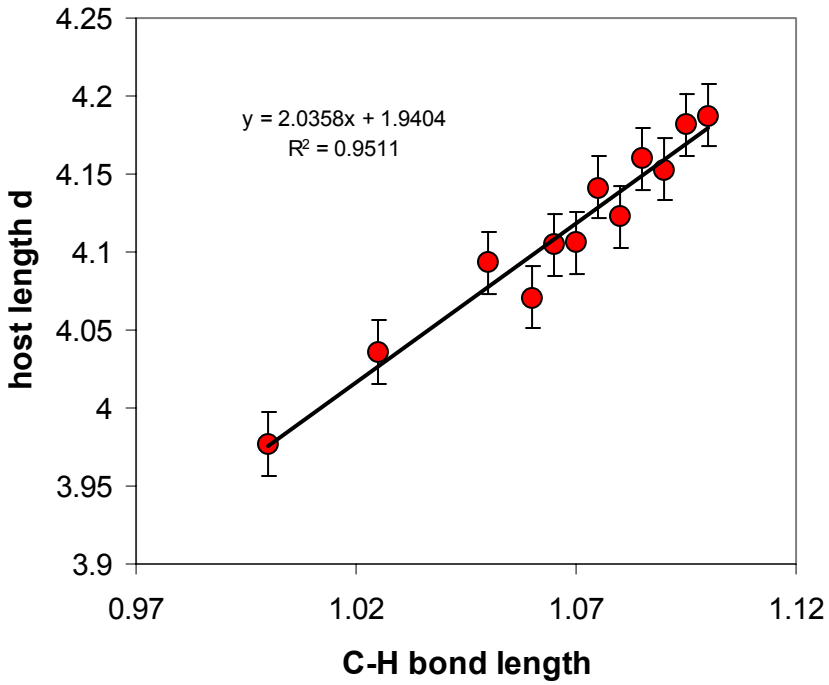

Figure S3: Computed time-averaged length *d* of hemicarceplex **1⊙16** as function of the C-H bond length of the guest's methyl groups. Each data point is the average of two MDS (20ns; Amber*, 300K).

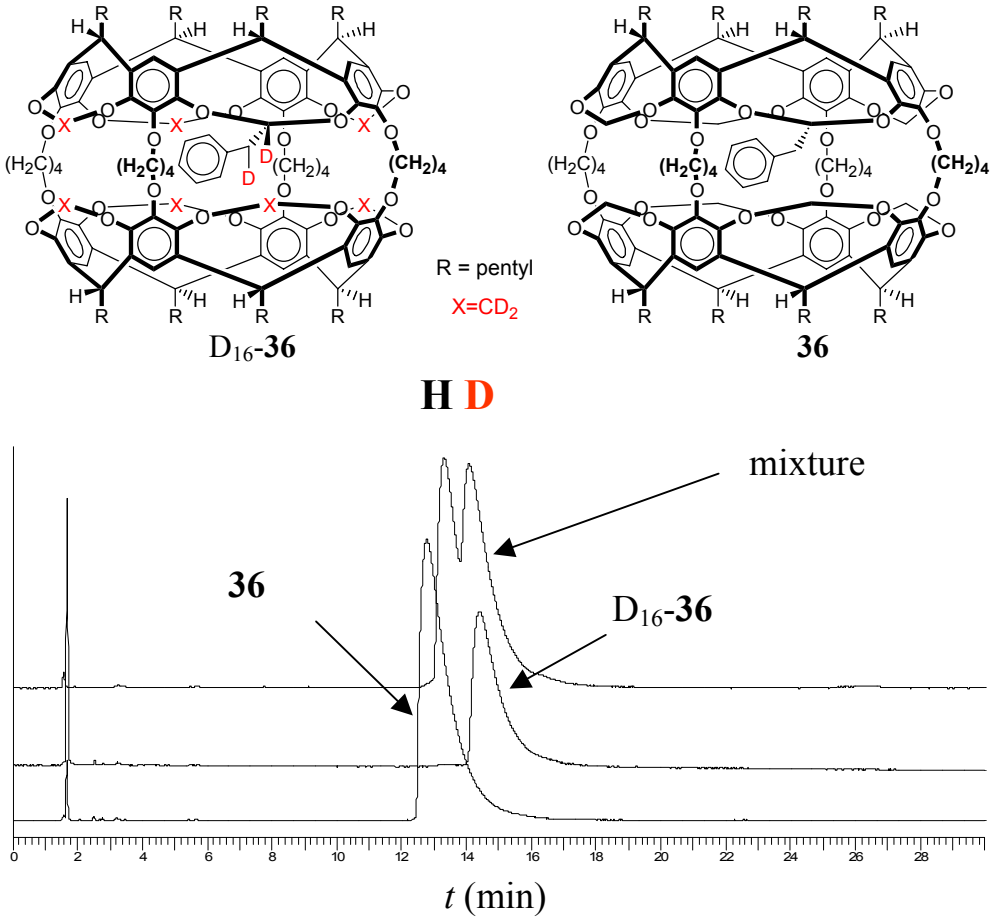

Figure S4: HPLC chromatograph of a 1:1 mixture of **36** and D_{16}-**36** and chromatograph of individual hosts. Conditions: 2.0 v% ether in CH_2Cl_2; 1 mL/min; Phenomenax, SiO_2, 25 cm x 4.6 mm, 3µm; 45°C

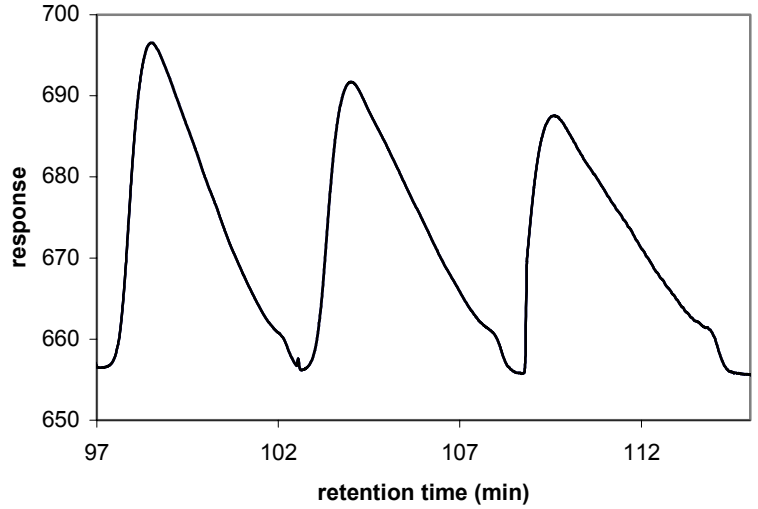

Figure S5: Recycle chromatograph of a 1:1 mixture of **3⊙16** and **3⊙**d_4**-16.** Only the 18^{th} – 20^{th} cycles are shown. Conditions: Mobile phase: 1.3 % ether in CH_2Cl_2; Si, 250 x 4.6 mm, 5mm; 22°C.

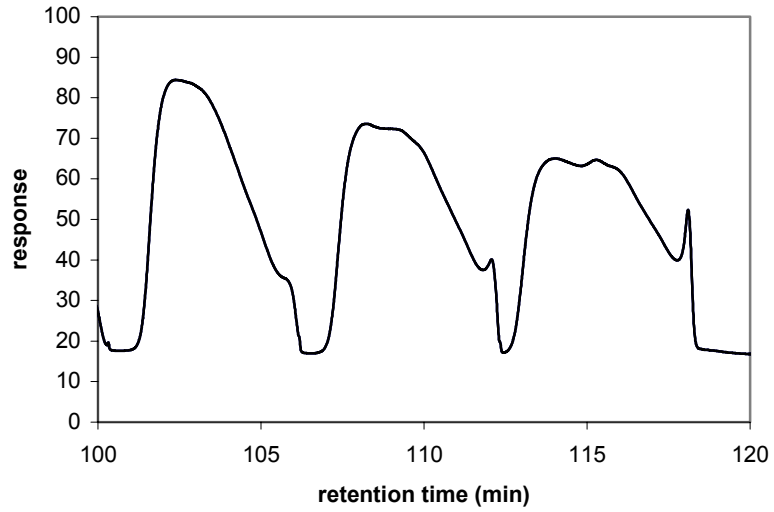

Figure S5: Recycle chromatograph of a 1:1 mixture of **3⊙16** and **3⊙**d_6**-16.** Only the 18^{th} – 20^{th} cycles are shown. Conditions: Mobile phase: 1.3 % ether in CH_2Cl_2; Si, 250 x 4.6 mm, 5mm; 22°C.

Table S1: Retention factors and time-averaged *d* for **3**⊙guest (guest = **4-8**, **11-19**,**23**, **24**, **32**, **35**, **37-39**). Conditions: Mobile phase: A/B, 65:35, A: 2.0 v% ether in CH_2Cl_2, B: CH_2Cl_2;1 mL/min; Phenomenax, SiO_2, 25 cm x 4.6 mm, 5mm; 22°C.

Guest	*Compound #*	*Distance d*	*k'*	*lnk'*
benzene	**4**	3.1923	0.11922	-2.12677
p-xylene	**16**	4.154	1.05178	0.050482
1,4-dibromobenzene	**19**	4.37	1.03622	0.035582
toluene	**8**	3.68	0.7	-0.35667
1,4-dichlorobenzene	**18**	3.95	0.52878	-0.63719
4-bromochlorobenzene	**15**	4.02	0.73056	-0.31395
1,4-difluorobenzene	**17**	3.38	0.21378	-1.54282
p-iodotoluene	**14**	4.587	1.81289	0.594922
fluorobenzene	**5**	3.278	0.18189	-1.70436
p-fluorotoluene	**11**	3.81	0.693	-0.36673
bromobenzene	**7**	3.791	0.65011	-0.43061
p-bromotoluene	**13**	4.28	1.07567	0.072941
chlorobenzene	**6**	3.52	0.43267	-0.83779
chlorotoluene	**12**	4.059	0.79189	-0.23333
cyclohepta-1,3,5-triene	**37**	3.38	0.34511	-1.06389
benzaldehyde	**23**	3.53	0.51578	-0.66208
NMP	**24**	3.766	0.77056	-0.26064
7-methoxycyclohepta-1,3,5-triene	**38**	4.29	1.35533	0.304045
benzylalcohol	**35**	3.69	1.51478	0.415269
phenol	**32**	3.13	0.41022	-0.89106
benzoic acid	**39**	4.06	1.69311	0.526568

Table S2: Retention factors and time-averaged *d* for hemicarceplexes **1**⊙guest (guest = **4-35**). Conditions: Phenomenax, SiO_2; CH_2Cl_2/0.5% ether; 1 mL/min; 150 x 4.6 mm; 22°C.

Guest	*Compound*	*Distance d*	*k'*	*lnk'*
benzene	**4**	3.1923	1.498	0.404130885
p-xylene	**16**	4.154	8.577	2.149084202
1,4-dibromobenzene	**19**	4.37	8.67	2.159868791
1,4-diiodobenzene	**20**	4.907	27.299	3.306850071
toluene	**8**	3.68	5.347	1.676535656
1,4-dichlorobenzene	**18**	3.95	5.014	1.612234
4-bromochlorobenzene	**15**	4.02	6.529	1.876253792
1,4-difluorobenzene	**17**	3.38	2.361	0.859085258
p-iodotoluene	**14**	4.587	15.804	2.760263073
fluorobenzene	**5**	3.278	2.349	0.853989706
benzonitrile	**9**	3.733	4.082	1.406587064
p-fluorotoluene	**11**	3.81	6.086	1.805991051
bromobenzene	**7**	3.791	5.601	1.722945153
p-bromotoluene	**13**	4.28	8.578	2.149200786
chlorobenzene	**6**	3.52	3.55	1.266947603
chlorotoluene	**12**	4.059	6.412	1.858171235
benzylchloride	**10**	3.907	5.961	1.785238252
p-chlorobenzonitrile	**21**	3.997	3.003	1.099611789
p-methylbenzonitrile	**22**	4.226	4.034	1.39475844
phenol	**32**	3.179	3.615	1.285091856
benzylalcohol	**35**	3.777	12.652	2.537815305
7-benzocyclobutanol	**34**	4.277	21.865	3.084887185
cis-7,8-benzocyclobutandiol	**33**	4.134	45.034	3.80741776
NMP	**24**	3.766	6.44	1.86252854
benzaldehyde	**23**	3.53	4.608	1.527793923
DMA	**25**	3.287	3.649	1.294453157
benzocyclobutanone	**26**	3.99	7.632	2.032349934
coumarin	**31**	4.29	23.351	3.15063981
methyl benzoate	**29**	4.727	47.454	3.859760821
nitrobenzene	**28**	3.92	9.065	2.204420844
benzoylchloride	**30**	4.349	22.378	3.108078333
7-methoxyphthalide	**27**	4.699	51.862	3.948586345