Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Highly selective binding of methyl orange dye by cationic water-soluble pillar[5]arenes

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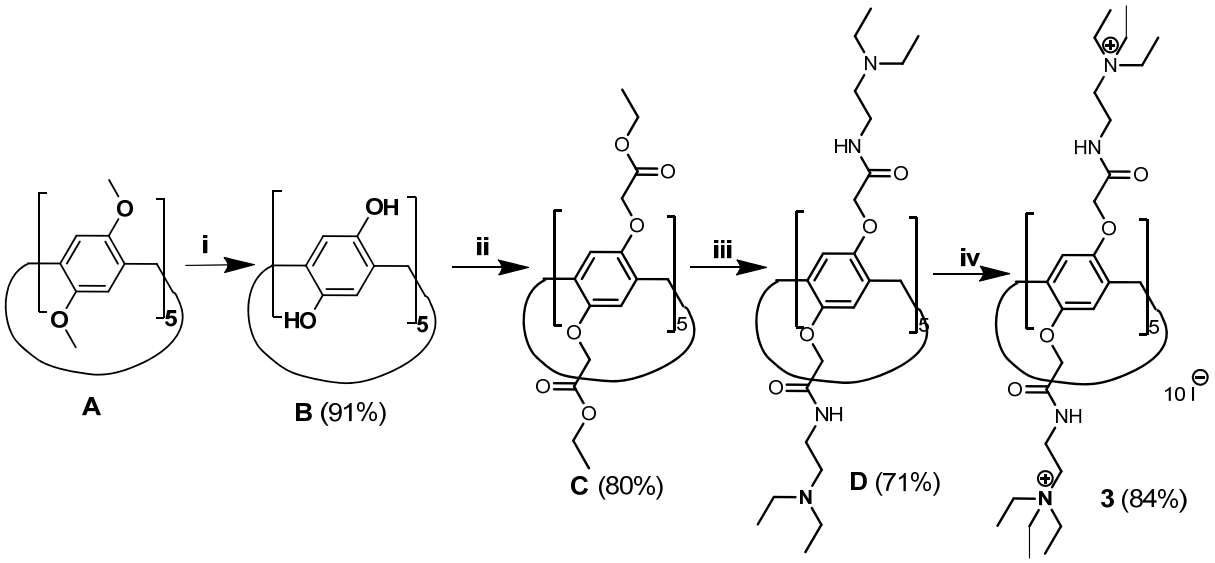
Electronic Supplementary Information (15 pages)

1. Synthetic scheme of the compounds 3



Initial 1,4-dimethoxypillar[5]arene **A** was obtained from commercially available 1,4-dimethoxybenzene by literary method.[S1] Further removal of methoxyl protections led to pillar[5]arene **B**.[S2] Pillar[5]arene with ethoxycarbonyl fragments **C** was obtained by the reaction of compound **B** with ethyl bromoacetate.

*1,4-Dimethoxypillar[5]arene (**A**).* Product yield: 80 %. Mp: 249 °C, 248.8 °C.[S1] ^{1}H NMR ($CDCl_3$) δ_H, ppm: 3.74 (s, 30H, -OCH_3), 3.76 (s, 10H, -CH_2-), 6.80 (s, 10H, ArH). MALDI-TOF MS $C_{45}H_{50}O_{10}$: calculated [M^+] m/z = 750.3, found [M+Na]$^+$ m/z = 773.4, [M+K]$^+$ m/z = 789.5.

*Pillar[5]arene (**B**).* Product yield: 91%. The decomposition was observed at 230°C without melting. ^{1}H NMR (CD_3COCD_3) δ_H, ppm: 3.66 (s, 10H, -$\underline{CH_2}$-), 6.64 (s, 10H, ArH), 7.99 (s, 10H, -$\underline{OH}$). MALDI-TOF MS $C_{35}H_{30}O_{10}$: calculated [M^+] m/z = 610.2, found [M+Na]$^+$ m/z = 633.1, [M+K]$^+$ m/z = 649.2.

*4,8,14,18,23,26,28,31,32,35-Deca-[(ethoxycarbonyl)methoxy]pillar[5]arene (**C**).* Product yield: 80%. Mp: 199 °C, 196.7 °C.[S1] ^{1}H NMR ($CDCl_3$) δ_H, ppm (*J*/Hz): 0.96 (m, 30H, -$CH_2\underline{CH_3}$), 3.86 (s, 10H, -$\underline{CH_2}$-), 4.09 (m, 20H, -$\underline{CH_2}CH_3$), 4.55 (dd, 20H, O-$\underline{CH_2}$C(O)-), 7.04 (s, 10H, ArH). MALDI-TOF MS: calculated [M^+] m/z = 1471.24, found [M+Na]$^+$ m/z = 1494.28.

*4,8,14,18,23,26,28,31,32,35-decakis-[(N-(2',2'-diethylaminoethyl)-carbamoylmethoxy]-pillar[5]arene (**D**).* In a round-bottom flask equipped with magnetic stirrer, the compound **C** (0.30 g, 0.2 mmol), 10 ml methanol and *N*,*N*-diethylethan-1,2-diamine (0.35 g, 3.1 mmol, 0.43 ml) were refluxed for 72 hrs. The residue was dissolved in minimum amount of chloroform and washed several times with distilled water. The organic layer was separated and dried (mol. sieves, 3Å), the solvent was removed under reduced pressure. The residue was dried under reduced pressure during 30 min. Light-yellow viscous oil was received. Product yield: 0.52 g (71 %). ^{1}H NMR (CD_3SOCD_3) δ_H, ppm (*J*/Hz): 0.91 (t, 60H, $^3J_{HH}$ = 7.1, -N($CH_2\underline{CH_3}$)$_2$), 2.41-2.52 (m, 60H, -$CH_2\underline{CH_2}$-N($\underline{CH_2}CH_3$)$_2$), 3.24 (m, 20H, -$\underline{CH_2}CH_2$-N(CH_2CH_3)$_2$), 3.79 (s, 10H, -$\underline{CH_2}$-), 4.32 (s, 20H, O-$\underline{CH_2}$C(O)-), 6.85 (s,10H, ArH), 7.86 (t, 10H, $^3J_{HH}$ =5.2, -C(O)NH). ^{13}C NMR (CD_3SOCD_3) δ_C ppm: 167.64, 148.95, 127.97, 114.71, 67.71, 51.37, 46.47, 36.59, 28.80, 11.75. ^{1}H-^{1}H NOESY (NOE) (the major cross-peaks): H^8/H^4; H^7/H^4; H^5/H^4; H^2/H^4; H^3/H^4; H^1/H^4; H^1/H^8; H^1/H^7; H^1/H^5; H^1/H^5; H^1/H^2; H^1/H^3; H^3/H^8; H^3/H^7; H^3/H^5; H^3/H^1; H^2/H^8; H^2/H^7; H^2/H^5; H^2/H^3; H^5/H^6; H^8/H^7. IR ν cm^{-1}: 3311.05 (N-H), 1661.33 (C=O). MALDI-TOF MS: calculated [M^+] m/z = 2172.4, found [M+H]$^+$ m/z = 2173.4,

$[M+Na]^+$ m/z = 2195.4. Found: C, 63.57; H, 8.81; N, 12.89. $C_{115}H_{190}N_{20}O_{20}$. Calculated for $C_{115}H_{190}N_{20}O_{20}$: C, 63.02; H, 8.55; N, 12.49.

*General procedure of the synthesis of the compounds **3***

Equimolar amount of ethyl iodide was added to the solution of the compound **D** (0.30 g, 0.14 mmol) in 10 ml acetonitrile. Reaction mixture was refluxed for 72 hrs and solvent was removed under reduced pressure. The powder obtained was dried under reduced pressure (P_2O_5).

4,8,14,18,23,26,28,31,32,35-decakis-[(N-(2',2',2'-triethylaminoethyl)-carbamoylmethoxy]-pillar[5]arene **3**. *Product yield: 0.52 g (84 %).* Mp: 153 °C. ^{1}H NMR (D_2O) δ_H, ppm (*J*/Hz): 1,31 (t, 90H, $^3J_{HH}$ = 7.0Hz, -N($CH_2\underline{CH_3}$)$_3$), 3.36 (m, 80H, -$CH_2\underline{CH_2}$-N($\underline{CH_2}CH_3$)$_3$), 3.63-3.85 (m, 20H, -$\underline{CH_2}CH_2$-N(CH_2CH_3)$_3$), 3.98 (s, 10H, -$\underline{CH_2}$-), 4.08 (d, 10H, AB-system, $^2J_{HH}$= 15.0, O-$\underline{CH_2}$C(O)NH-),4.37 (d, 10H, AB-system, $^2J_{HH}$= 15.0, O-$\underline{CH_2}$C(O)NH-), 6.73 (s, 10H, ArH). ^{13}C NMR (CD_3SOCD_3) δ_C ppm: 168.95, 148.30, 127.45, 114.61, 66.94, 52.94, 52.94, 52.38, 32.28, 28.56, 7.21. IR ν cm^{-1}: 3331.5 (-N^+-(CH_2CH_3)$_3$), 2975.3 (-CH_2-CH_3, -CH_2-), 1665.9 (C=O). ESI: calcd for $[M - 4\ I^-]^{4+}$ m/z = 806.2, $[M - 5\ I^-]^{5+}$ m/z = 619.6, $[M - 6\ I^-]^{6+}$ m/z = 496.8 found m/z = 806.1, 619.5, 495.2; Found: C, 57.4; H, 8.23; N, 9.65. $C_{135}H_{240}Cl_{10}N_{20}O_{20}$. Calculated for $C_{135}H_{240}Cl_{10}N_{20}O_{20}$: C, 57.54; H, 8.58; N, 9.94.

2. NMR spectra of the compound 3

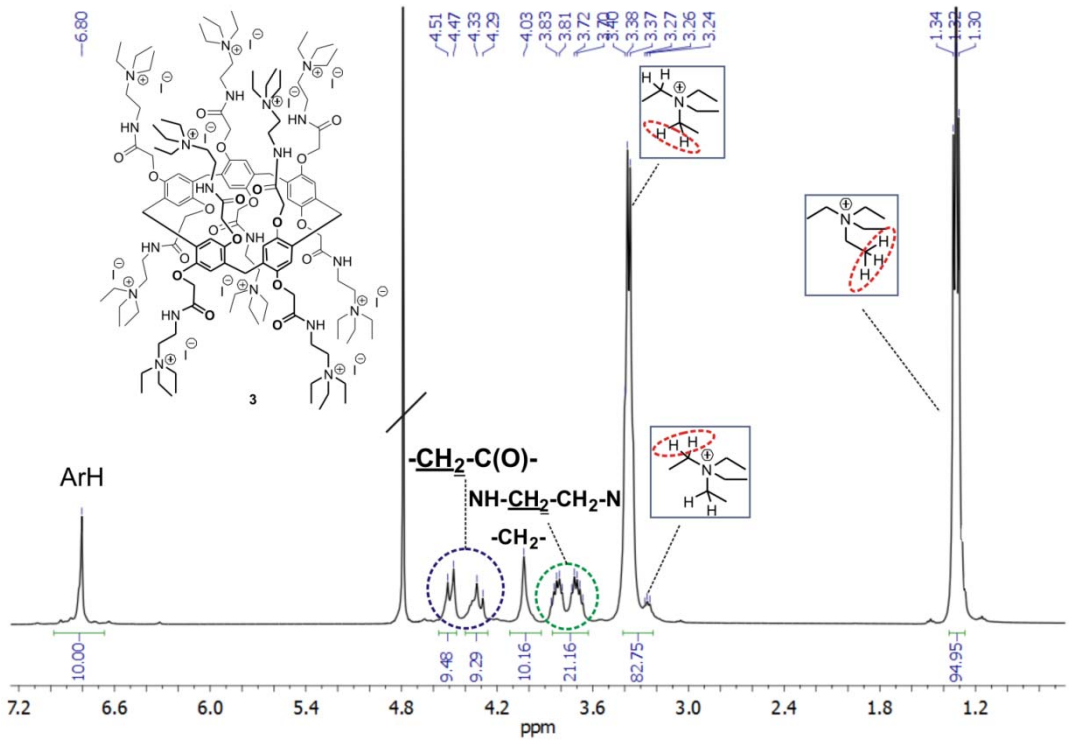


Fig. S1. ^{1}H NMR spectrum of the compound **3** (D_2O, 293K, Bruker Avance-400, 400MHz).

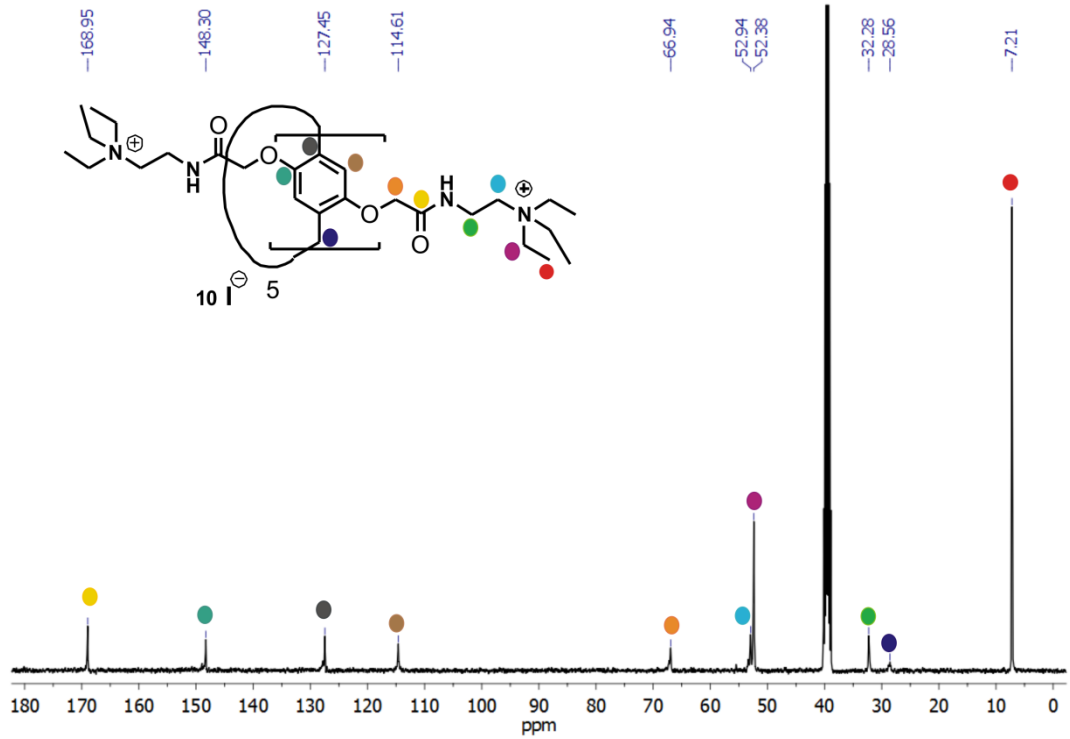


Fig. S2. ^{13}C {^{1}H} NMR spectrum of the compound **3** (D_2O, 293K, Bruker Avance-400, 125MHz).

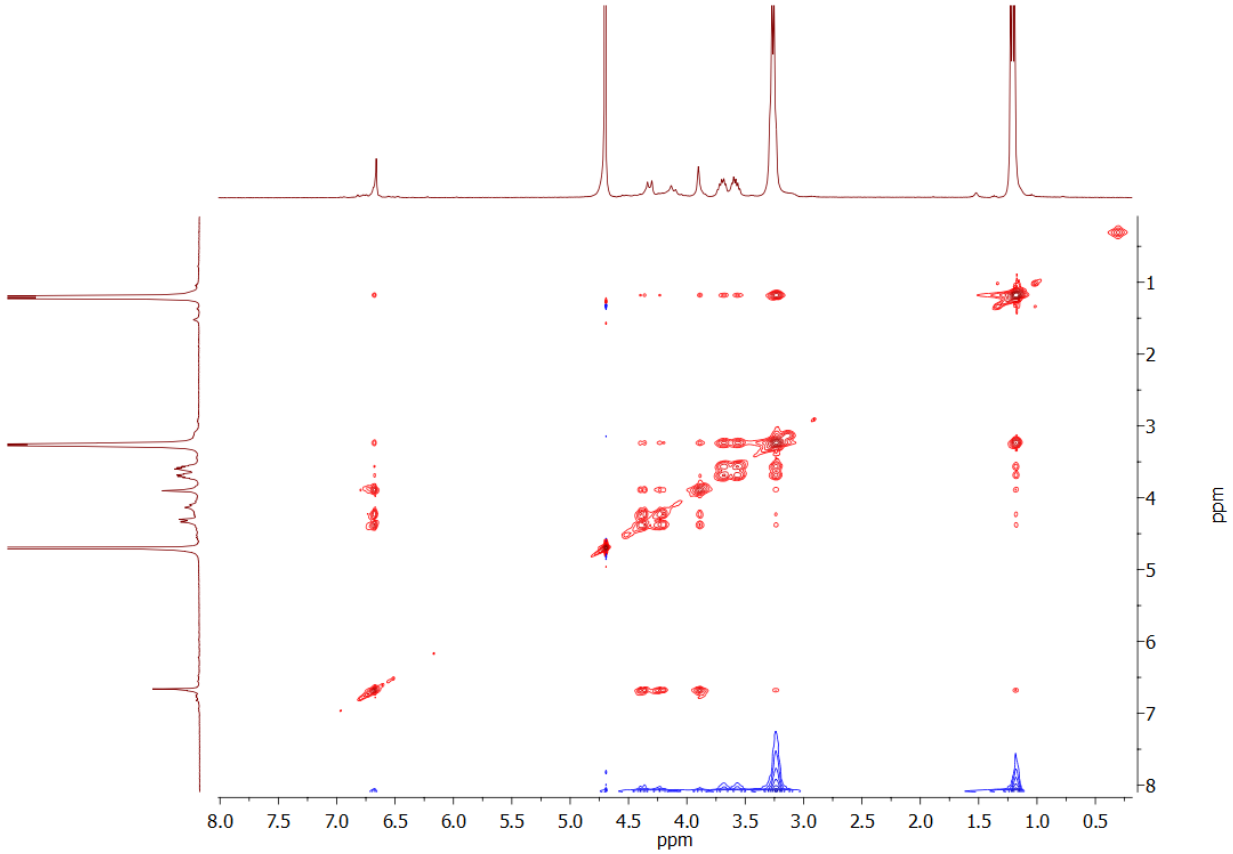


Fig. S3. 2D ^{1}H-^{1}H NOESY (500 MHz) analysis of **3** in D_2O. The host concentration is 0.0112 M.

3. Mass-spectrum (ESI) of pillar[5]arene 3

ESI Result. Institute of Organic and Physical Chemistry

Analysis Info

Method		Operator	
Sample Name		Instrument	
Comment			

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	UltraScan	Scan Begin	100 m/z	Scan End	2800 m/z
Capillary Exit	140.0 V	n/a	n/a	Trap Drive	73.0
Accumulation Time	710 µs	Averages	5 Spectra	Auto MS/MS	off

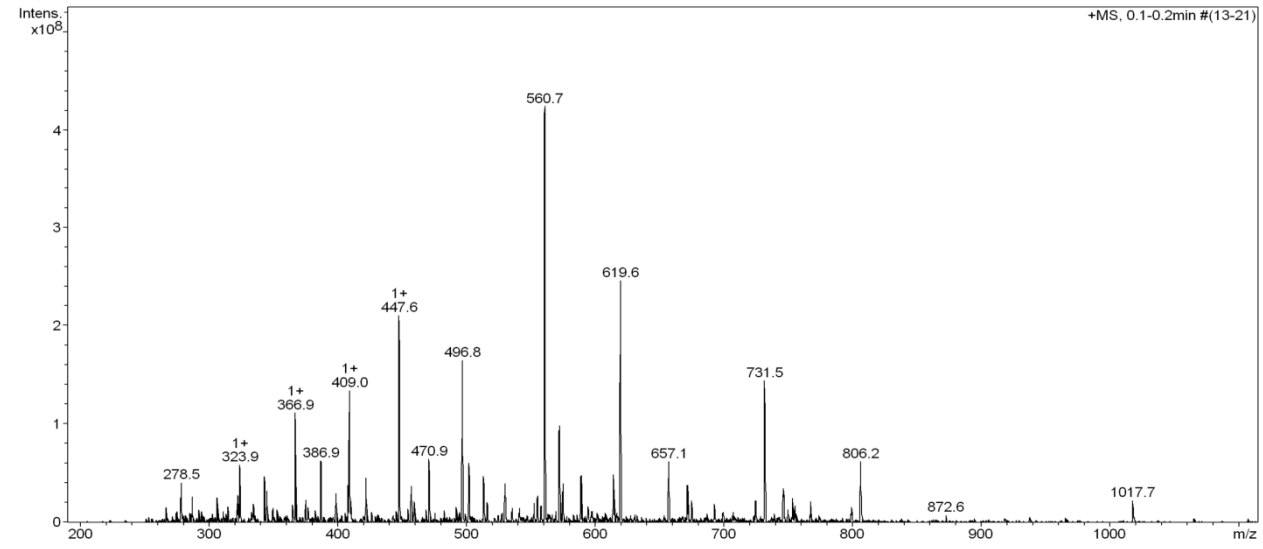


Fig. S4. Mass spectrum (ESI) of the compound **3**

4. ^{1}H NMR (DOSY) for the system 3/G8

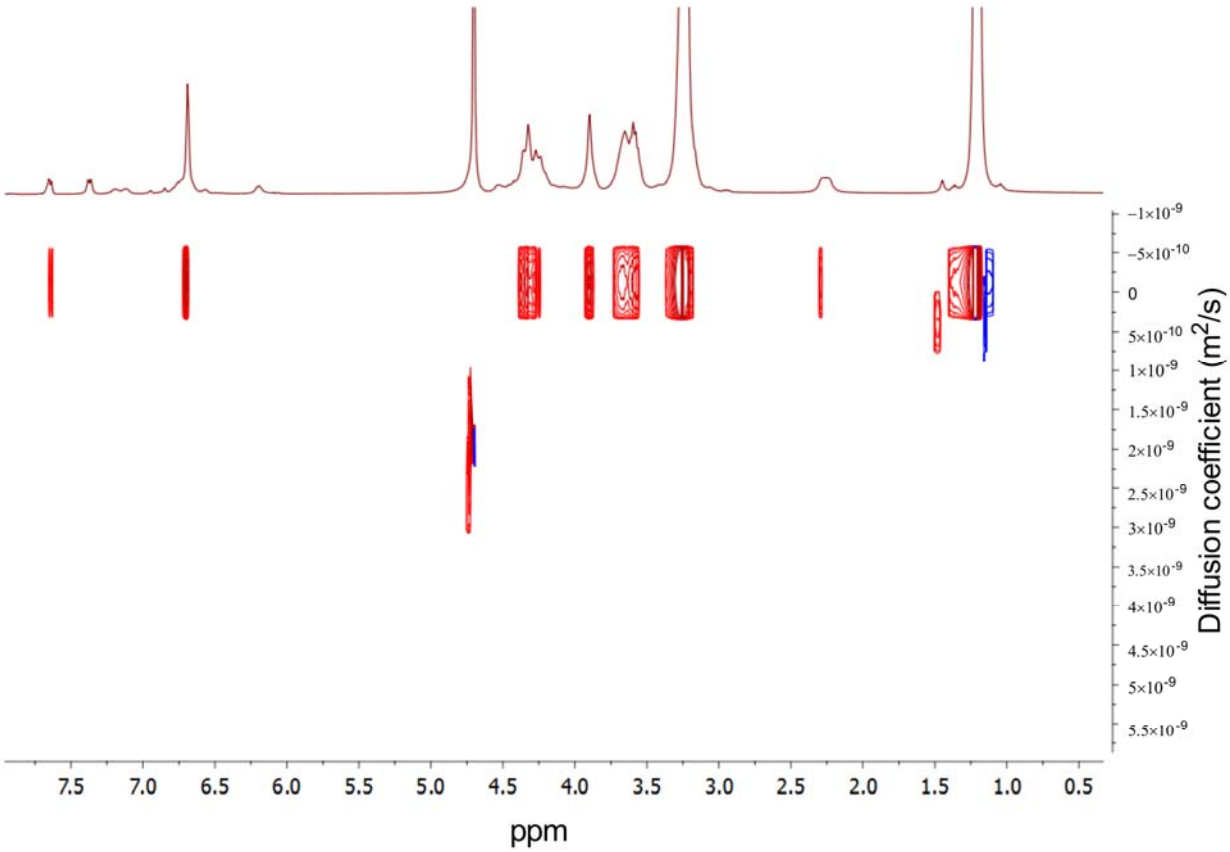


Fig. S5. ^{1}H NMR (DOSY) spectrum for the system **3**/**G8** (D_2O, 293K, Bruker Avance-400, 400 MHz).

Table S1. Diffusion coefficients of pure **3**, **G8** and **3/G8** complex in D_2O (293K, Bruker Avance-400, 400 MHz).

Compounds	**D (10^{-10} m^2 s^{-1})**
3	3.43
G8	2.21
3/G8	1.21

5. ^{1}H NMR spectra for host–guest complexation in solution

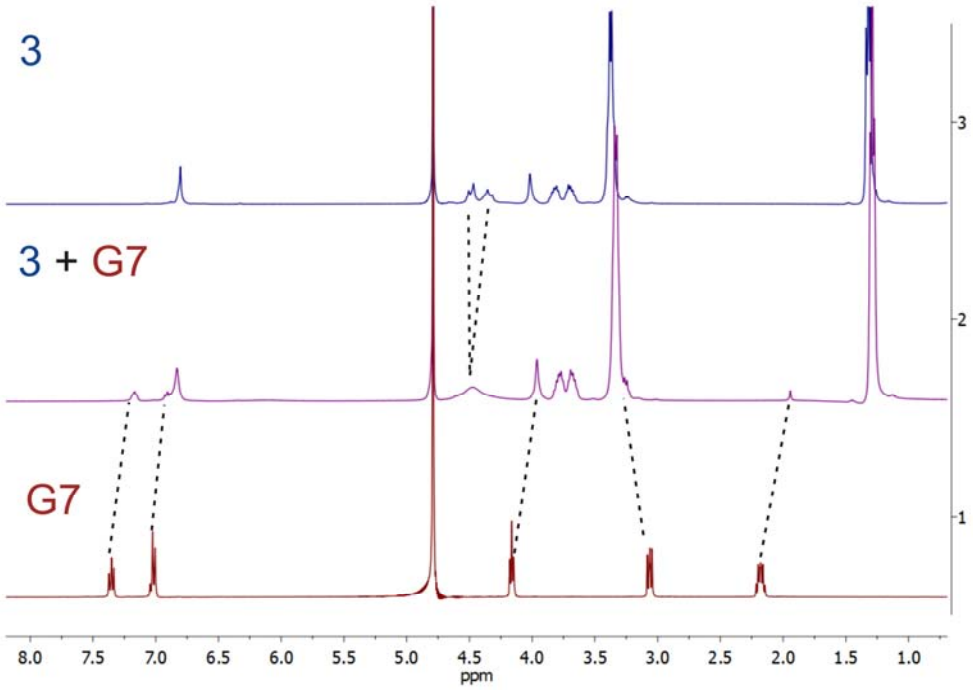


Fig.S6. ^{1}H NMR spectra (D_2O, 293K, 400MHz): **G7** (0.0112 mol/l); **G7** (0.0112 mol/l) + **3** (0.0112 mol/l); **3** (0.0112 mol/l)

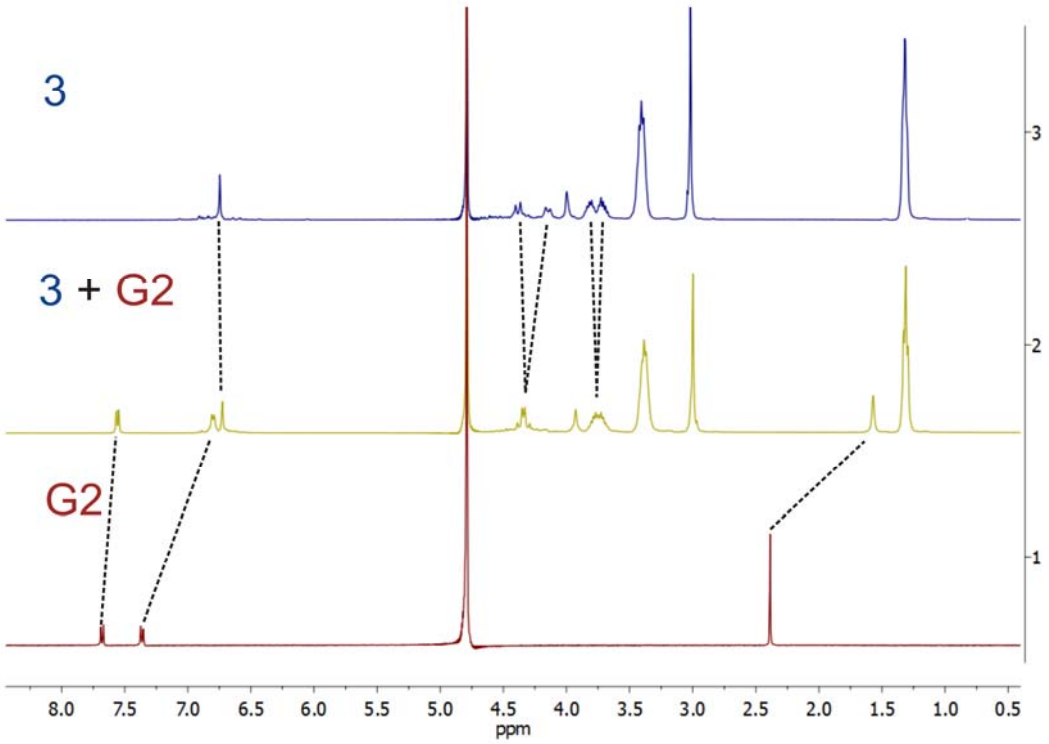


Fig.S7. ^{1}H NMR spectra (D_2O, 293K, 400MHz): **G2** (0.0112 mol/l); **G2** (0.0112 mol/l) + **3** (0.0112 mol/l); **3** (0.0112 mol/l)

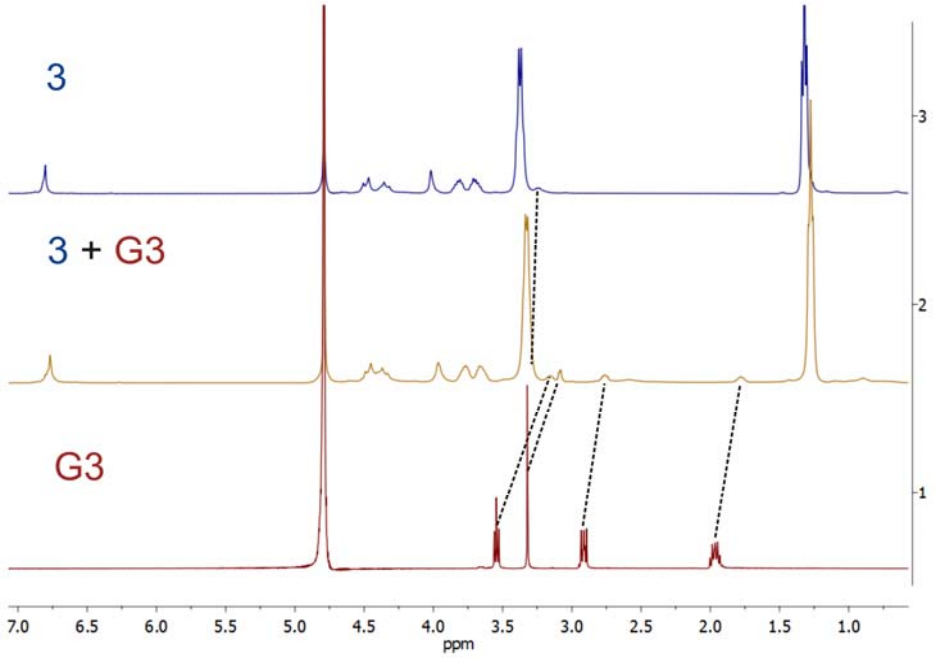


Fig.S8. ^{1}H NMR spectra (D_2O, 293K, 400MHz): **G3** (0.0112 mol/l); **G3** (0.0112 mol/l) + **3** (0.0112 mol/l); **3** (0.0112 mol/l)

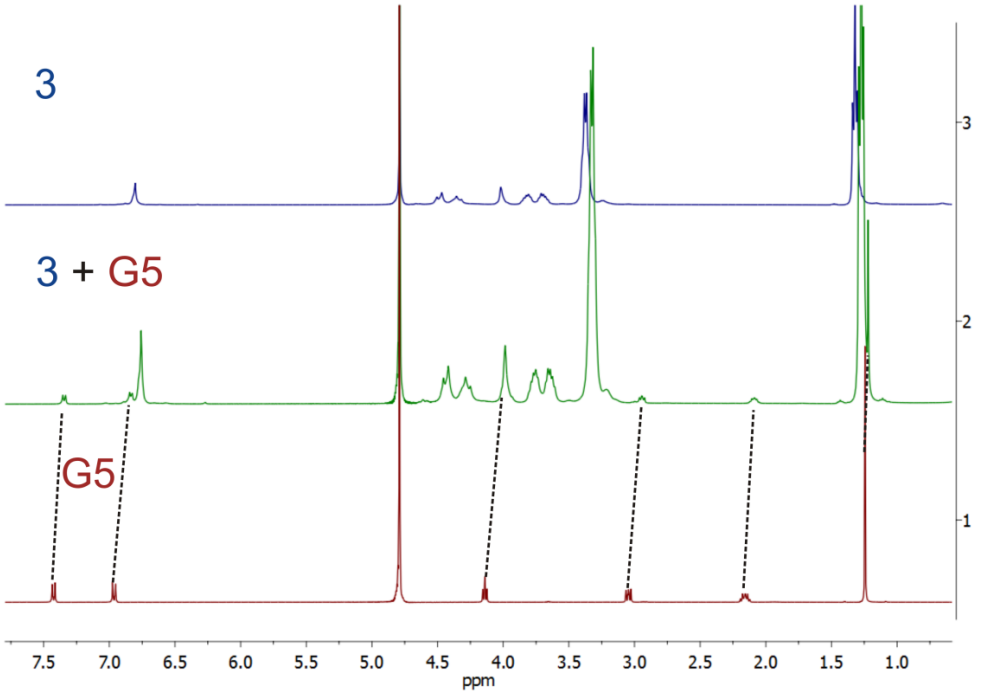


Fig.S9. ^{1}H NMR spectra (D_2O, 293K, 400MHz): **G5** (0.0112 mol/l); **G5** (0.0112 mol/l) + **3** (0.0112 mol/l); **3** (0.0112 mol/l)

6. Determination of the stability constant and stoichiometry of the complex by the UV titration

The UV measurements were performed with "Shimadzu UV-3600" instrument. The $1 \cdot 10^{-3}$ M solution of the guest (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 µl) in water was added to 0.5 ml of the solution of host ($3 \cdot 10^{-4}$ M) in water and diluted to final volume of 3 ml with water. The UV spectra of the solutions were then recorded. The stability constant and stoichiometry of complexes were calculated as described below. Three independent experiments were carried out for each series. Student's *t*-test was applied in statistical data processing.

The system equilibrium is described by Eq. (1), where H, G, G_nH denote the macrocycles **1-3**, guests **G1-G8**, , complex with guests, n – number of the guest with one macrocycle.

$$nG + H \Leftrightarrow G_nH \quad (1)$$

The association constant, K_{ass}, is defined by Eq. (2).

$$K_{ass} = [G_nH] / [G]^n [H] \quad (2)$$

To determine the stoichiometry coefficient n of the complexes forming in the water Eq. (2) was converted into Eq. (3).

$$\lg K_{ass} = \lg [G_nH] - n \lg [G] - \lg [H] \quad (3)$$

The solution absorbance A, is a sum of those related to complex, host and guest (A_{GnH}, A_H and A_G, respectevly) is equal to:

$$A = A_{GnH} + A_H + A_G \quad (4)$$

Assuming that the Beer-lambert law is obeyed for all the components considered Eq. 5, the absorbance A is expressed as:

$$A_i = c_i \varepsilon_i l \quad (5)$$

where c_i is a molar concentration of i-species, ε_i is the molar absorptivity, and l is the cell thickness. For complexation between the host and guest the absorbance mesurement is commonly conducted at the wavelength of absorbance maximum in the charge-transfer region where $A_G=0$. This gives Eq. 6.

$$A = A_{GnH} + A_H \quad (6)$$

Concentration of the complex $[G_nH]$ in the system is calculated according to equations (5) and (6).

The plot of $\lg [G_nH] - \lg [H]$ versus $\lg [G]$ (Fig. 1) presents a straight line, slope of which equals to n. Assotiation constants K_{ass} are calculated using the intercept values (b).

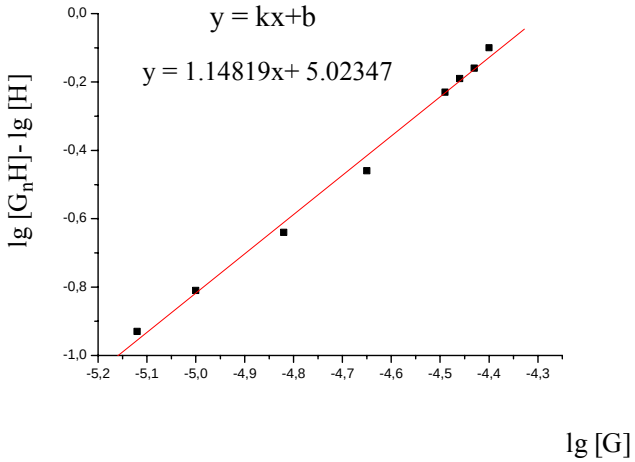


Fig. S10. Plot of lg [G_nH]- lg [H] versus lg [G] host/guest system.

$$b = \lg K_{acc} \qquad (7)$$

7. UV spectra for the systems host/guest

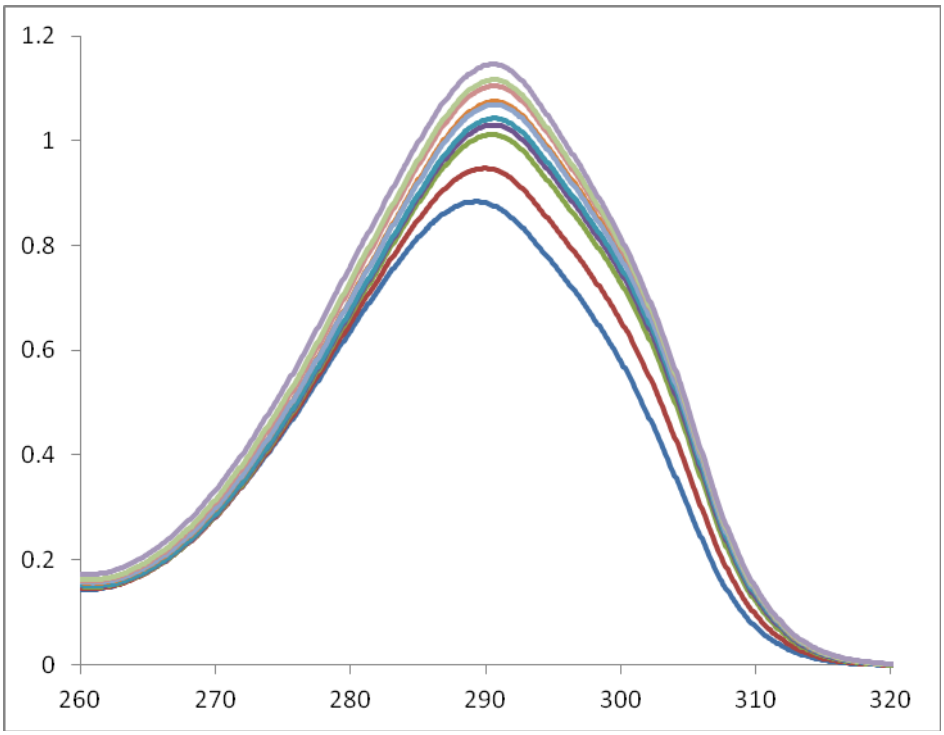


Fig.S11. The spectrophotometric titration of the systems pillar[5]arene **2** and guests **G4** in water. The molar ratio of the host and guest is changed from 0.7:1 to 6.7:1 (0.7:1, 1.3:1, 2:1, 2.7:1, 3.3:1, 4:1, 4.7:1, 5.3:1, 6:1, 6.7:1).

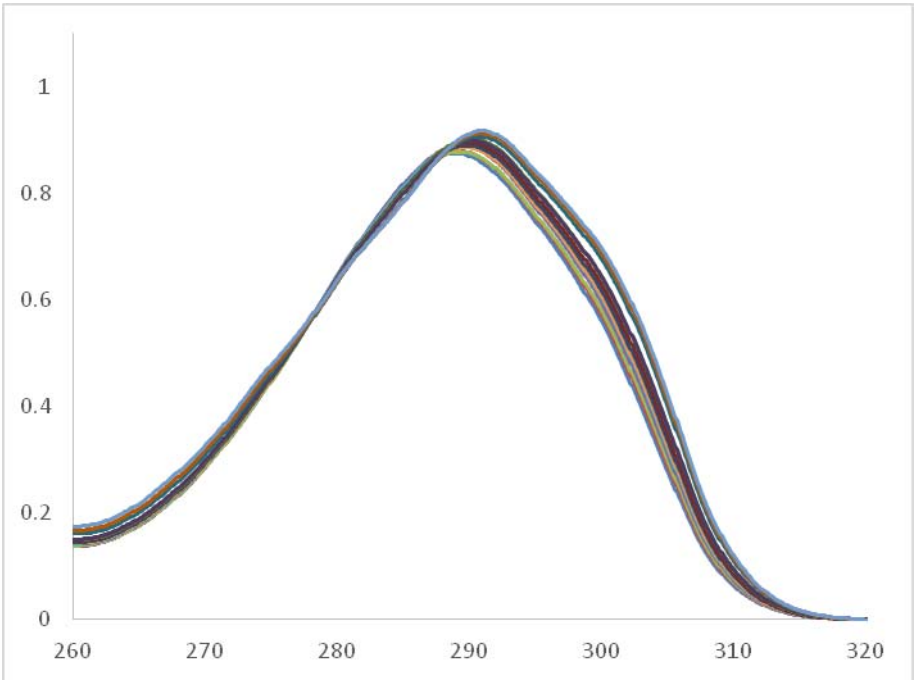


Fig.S12. The spectrophotometric titration of the systems pillar[5]arene **2** and guests **G7** in water. The molar ratio of the host and guest is changed from 0.7:1 to 6.7:1 (0.7:1, 1.3:1, 2:1, 2.7:1, 3.3:1, 4:1, 4.7:1, 5.3:1, 6:1, 6.7:1).

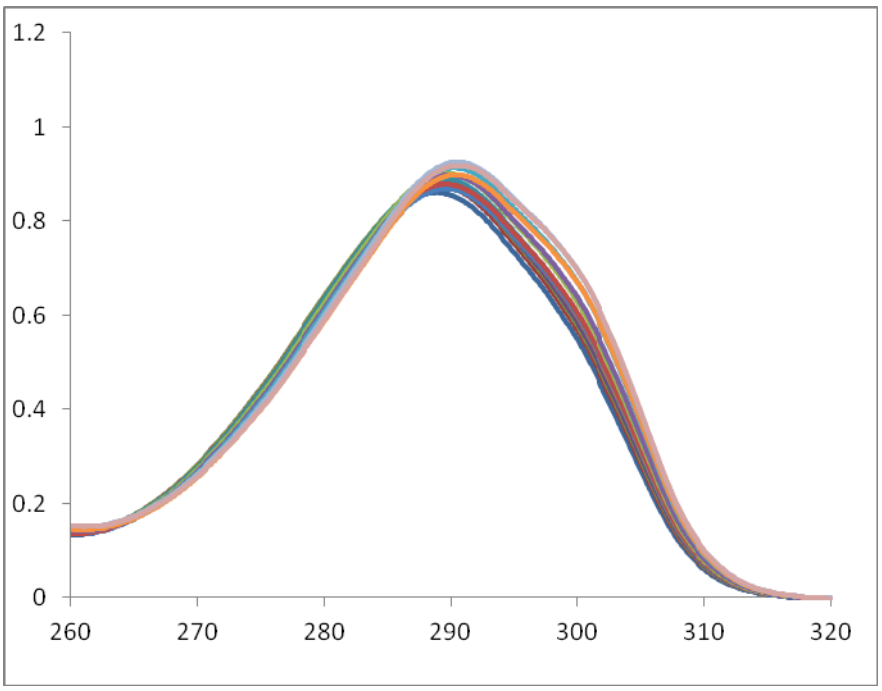


Fig.S13. The spectrophotometric titration of the systems pillar[5]arene **2** and guests **G2** in water. The molar ratio of the host and guest is changed from 0.7:1 to 6.7:1 (0.7:1, 1.3:1, 2:1, 2.7:1, 3.3:1, 4:1, 4.7:1, 5.3:1, 6:1, 6.7:1).

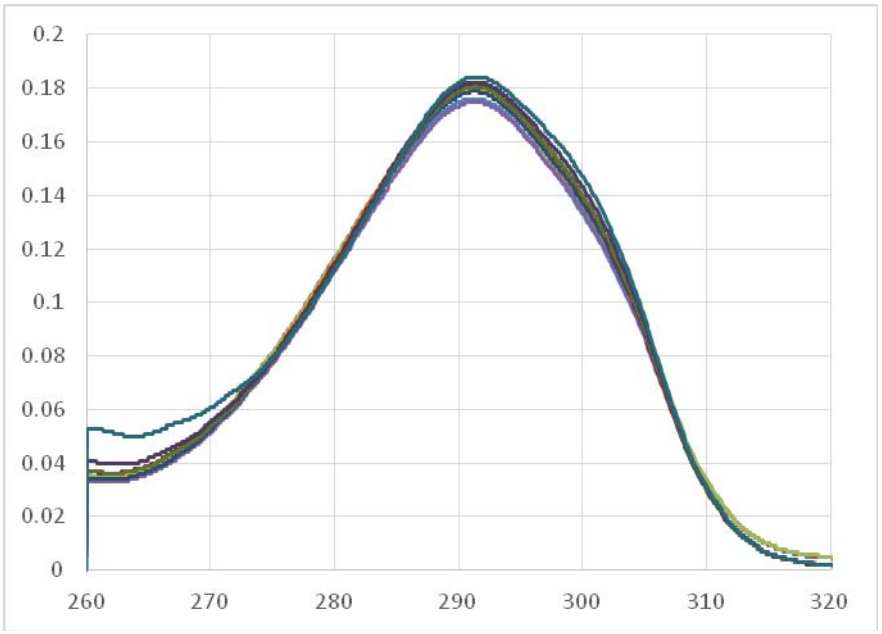


Fig.S14. The spectrophotometric titration of the systems pillar[5]arene **1** and guests **G2** in water. The molar ratio of the host and guest is changed from 0.7:1 to 6.7:1 (0.7:1, 1.3:1, 2:1, 2.7:1, 3.3:1, 4:1, 4.7:1, 5.3:1, 6:1, 6.7:1).

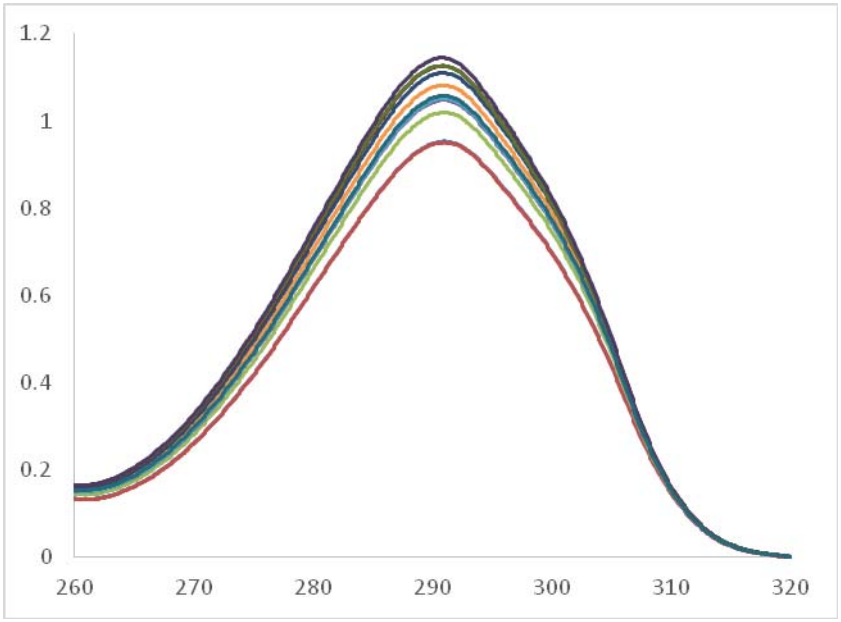


Fig.S15. The spectrophotometric titration of the systems pillar[5]arene **1** and guests **G4** in water. The molar ratio of the host and guest is changed from 0.7:1 to 6.7:1 (0.7:1, 1.3:1, 2:1, 2.7:1, 3.3:1, 4:1, 4.7:1, 5.3:1, 6:1, 6.7:1).

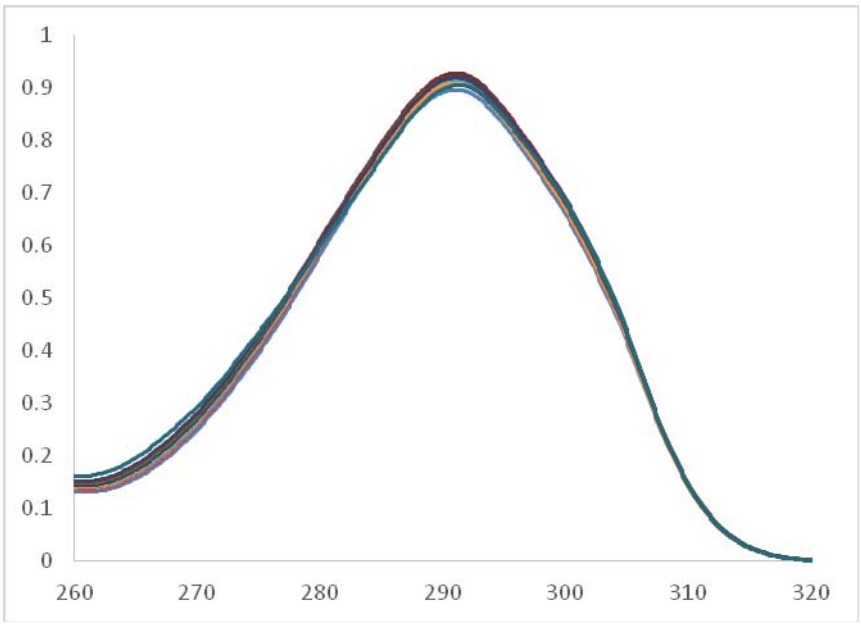


Fig.S16. The spectrophotometric titration of the systems pillar[5]arene **1** and guests **G7** in water. The molar ratio of the host and guest is changed from 0.7:1 to 6.7:1 (0.7:1, 1.3:1, 2:1, 2.7:1, 3.3:1, 4:1, 4.7:1, 5.3:1, 6:1, 6.7:1).

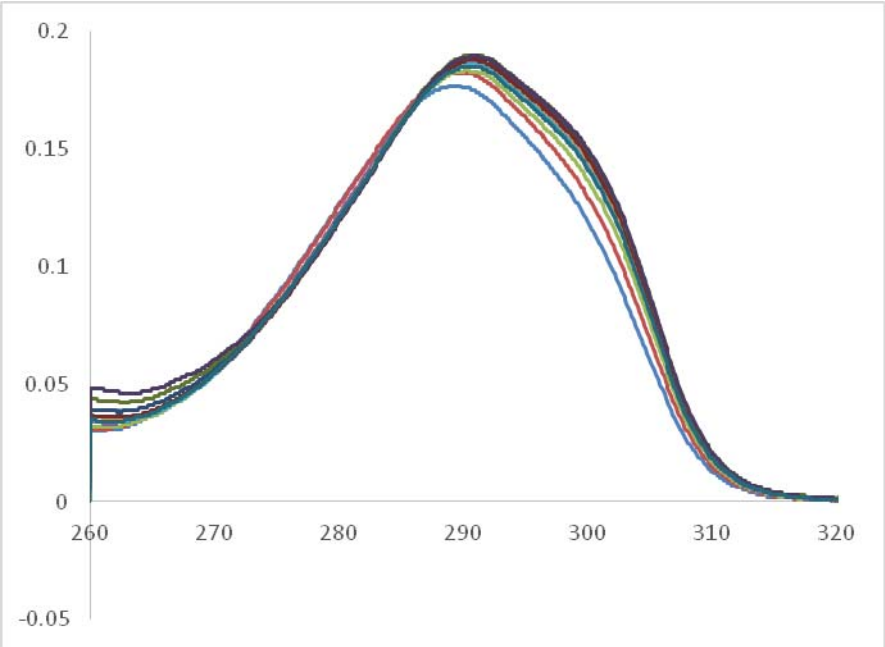


Fig.S17. The spectrophotometric titration of the systems pillar[5]arene **3** and guests **G1** in water. The molar ratio of the host and guest is changed from 0.7:1 to 6.7:1 (0.7:1, 1.3:1, 2:1, 2.7:1, 3.3:1, 4:1, 4.7:1, 5.3:1, 6:1, 6.7:1).

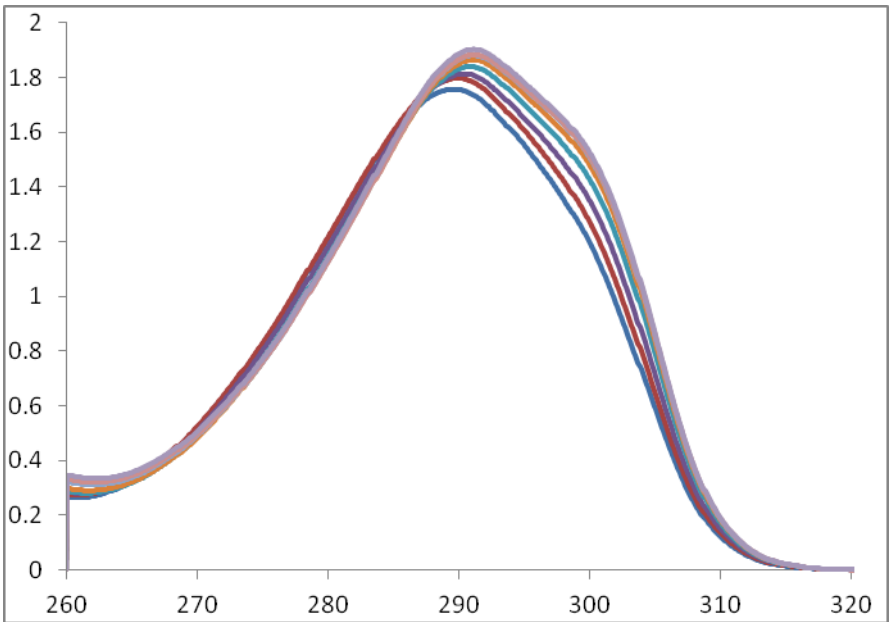


Fig.S18. The spectrophotometric titration of the systems pillar[5]arene **3** and guests **G2** in water. The molar ratio of the host and guest is changed from 0.7:1 to 6.7:1 (0.7:1, 1.3:1, 2:1, 2.7:1, 3.3:1, 4:1, 4.7:1, 5.3:1, 6:1, 6.7:1).

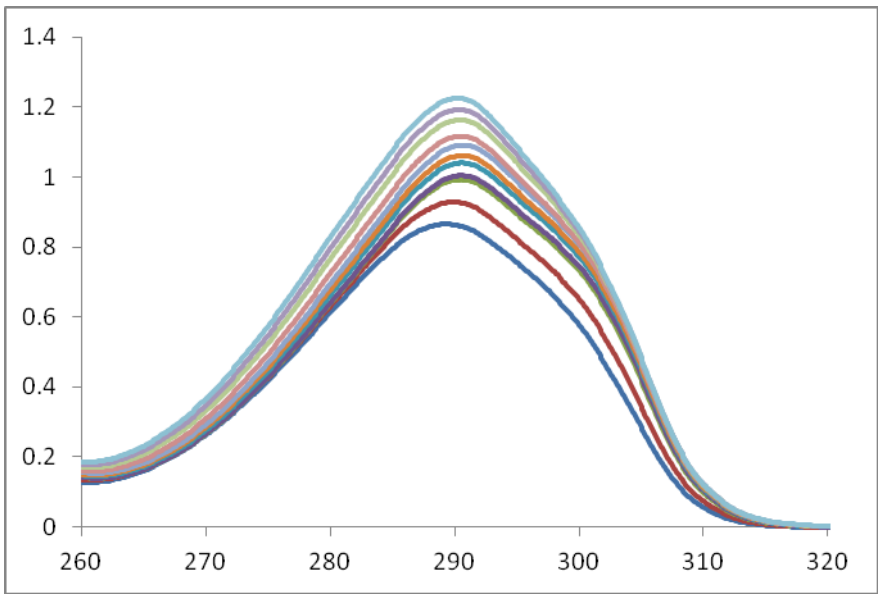


Fig.S19. The spectrophotometric titration of the systems pillar[5]arene **3** and guests **G4** in water. The molar ratio of the host and guest is changed from 0.7:1 to 6.7:1 (0.7:1, 1.3:1, 2:1, 2.7:1, 3.3:1, 4:1, 4.7:1, 5.3:1, 6:1, 6.7:1).

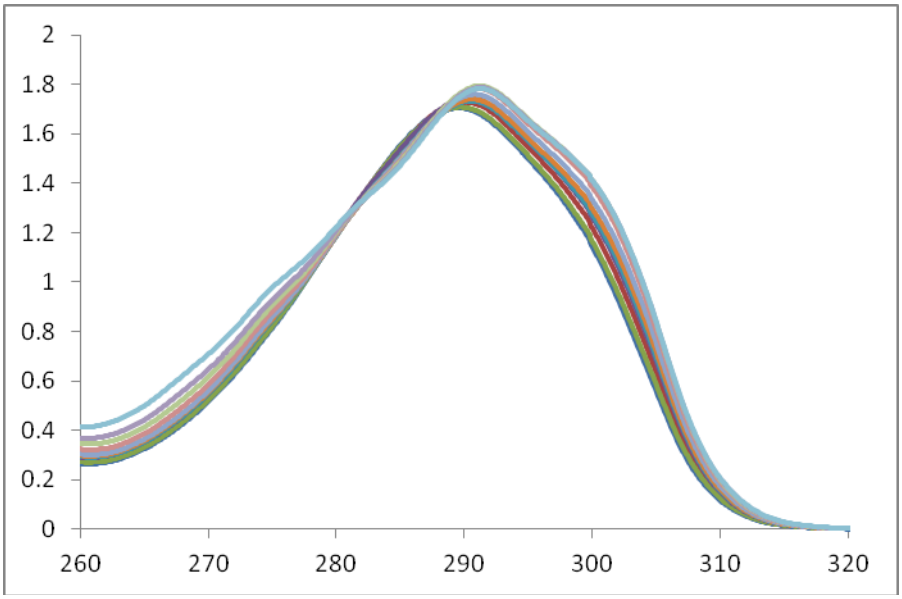


Fig.S20. The spectrophotometric titration of the systems pillar[5]arene **3** and guests **G7** in water. The molar ratio of the host and guest is changed from 0.7:1 to 6.7:1 (0.7:1, 1.3:1, 2:1, 2.7:1, 3.3:1, 4:1, 4.7:1, 5.3:1, 6:1, 6.7:1).

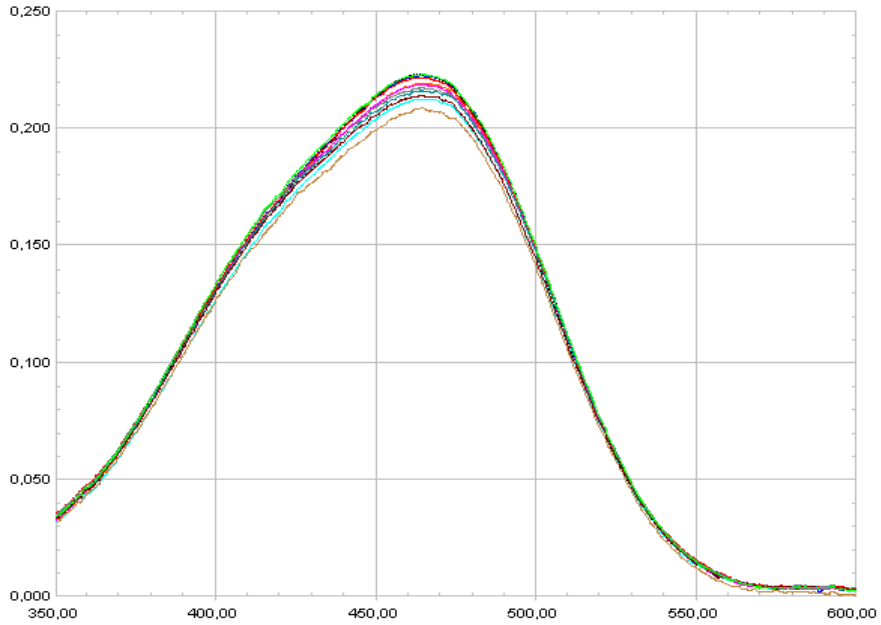


Fig.S21. The spectrophotometric titration of the systems pillar[5]arene **1** and guests **G8** in water. The molar ratio of the host and guest is changed from 0.3:1 to 2:1 (0.3:1, 0.5:1, 0.8:1, 0.9:1, 1:1, 1.1:1, 1.3:1, 1.5:1, 2:1).

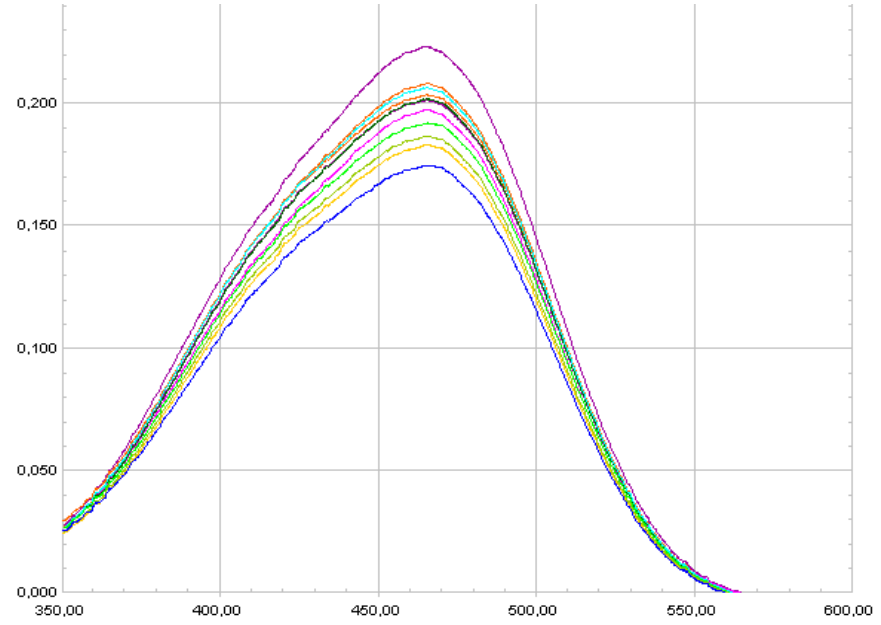


Fig.S22. The spectrophotometric titration of the systems pillar[5]arene **2** and guests **G8** in water. The molar ratio of the host and guest is changed from 0.3:1 to 2:1 (0.3:1, 0.5:1, 0.8:1, 0.9:1, 1:1, 1.1:1, 1.3:1, 1.5:1, 2:1).

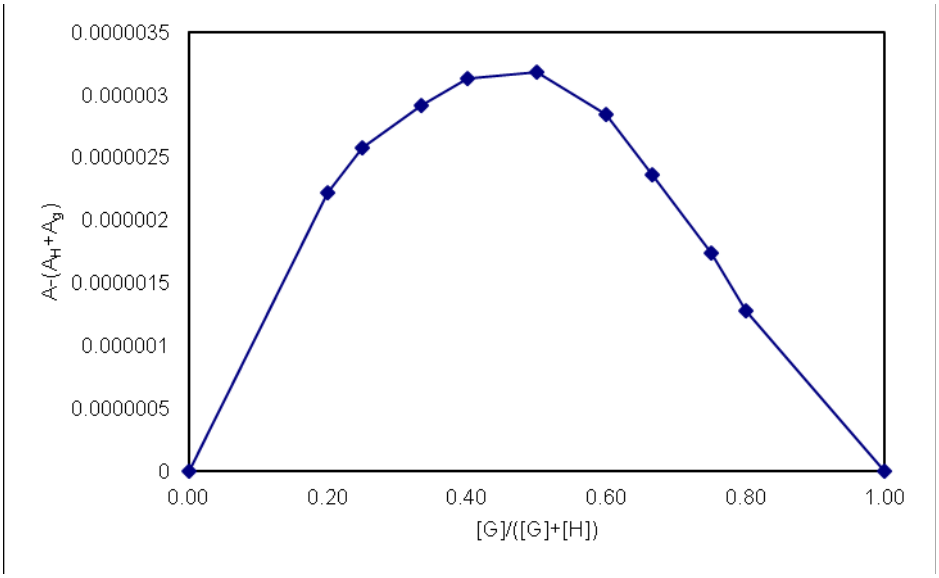


Fig.S23. The Job's plot for the determination of the stoichiometry in the complex of the systems pillar[5]arenes **3** and guest **G2** in water.

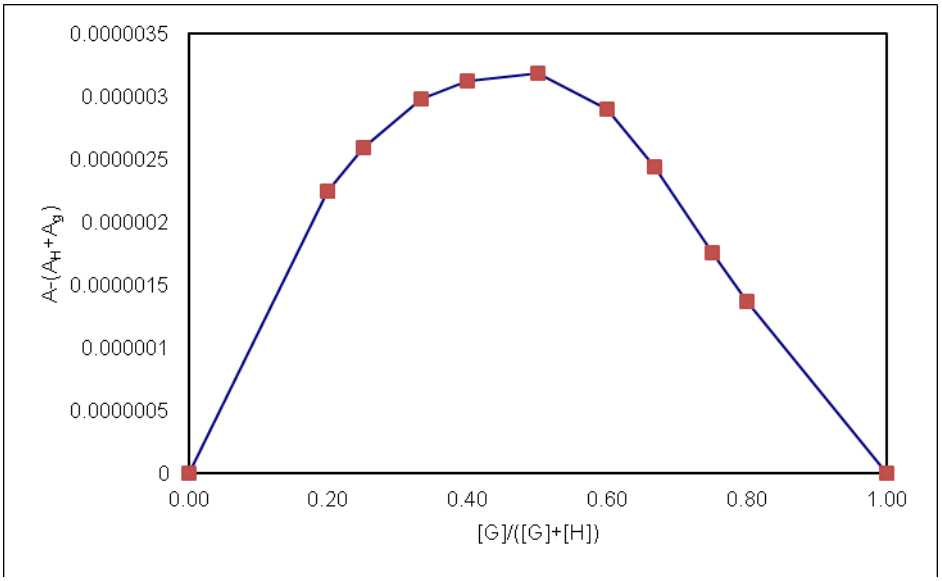


Fig.S24. The Job's plot for the determination of the stoichiometry in the complex of the systems pillar[5]arenes **2** and guests **G8** in water.

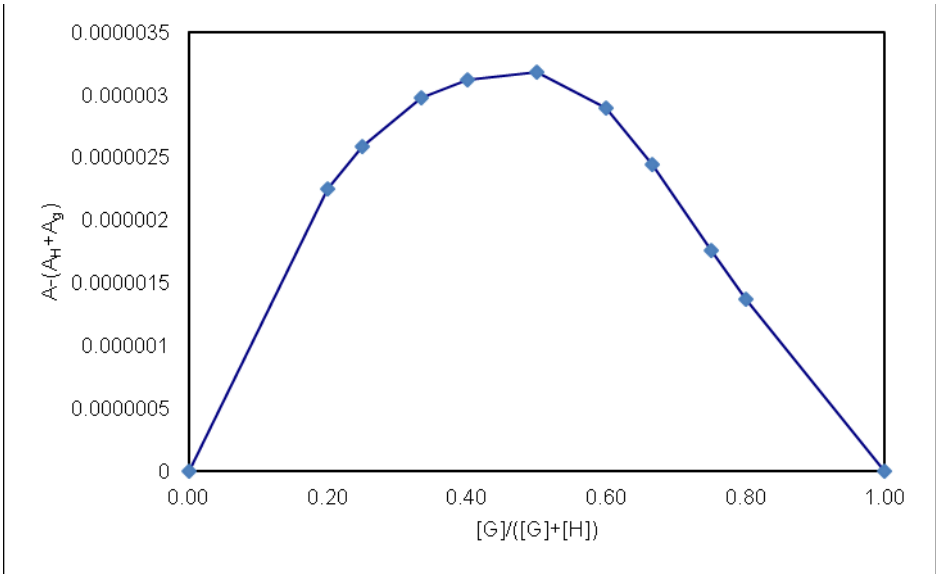


Fig.S25. The Job's plot for the determination of the stoichiometry in the complex of the systems pillar[5]arenes **1** and guests **G7** in water.

8. References

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S2. T. Ogoshi, T. Aoki, K. Kitajima, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Org. Chem.*, 2011, **76** (1), 328.