Supporting Information

Inhibition and Stabilization: Cucurbituril Induced Distinct Effects on the Schiff Base Reaction

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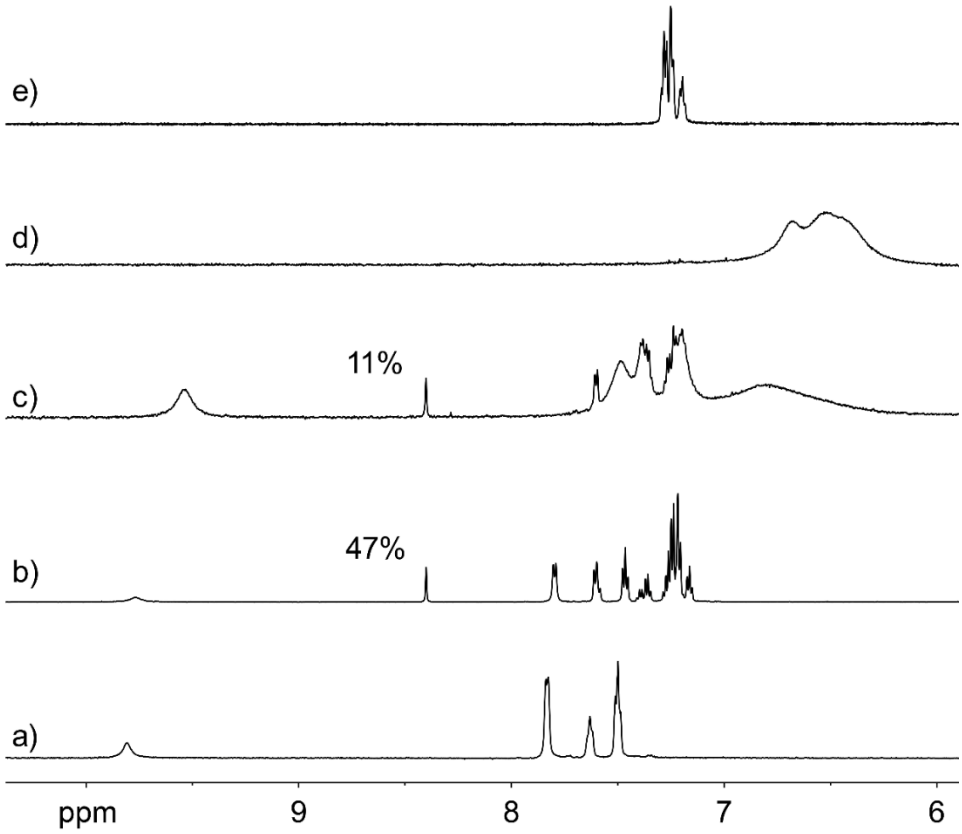


Figure S1. Partial ^{1}H NMR spectra (600 MHz, pD = 13.6) for a) **1** (2.0 mM); b) 1h after adding **1** (2.0 mM) to **2** (2.0 mM); c) 1h after adding **1** (2.0 mM) to a 1:1.1 mixture of **2** (2.0 mM) and CB[7]; d) 1:1.1 mixture of **2** (2.0 mM) and CB[7]; e) **2** (2.0 mM).

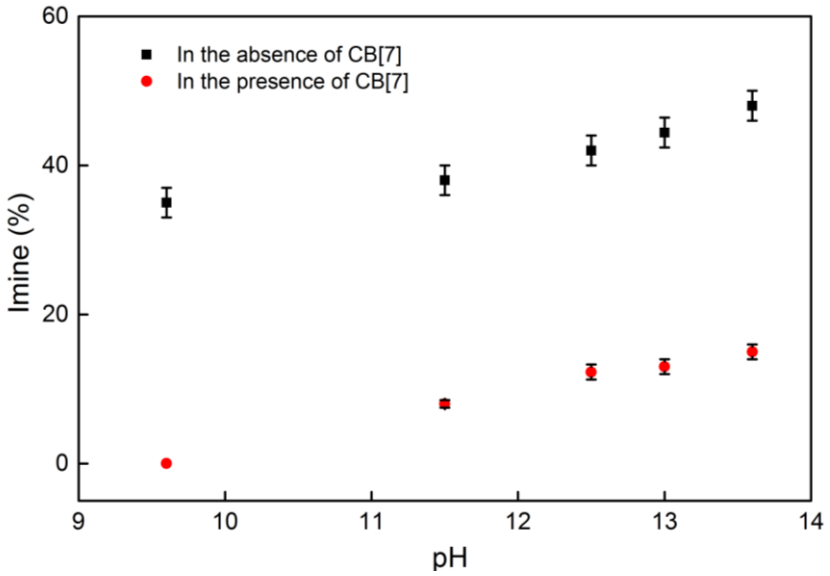


Figure S2. Plot of imine percentage at different pD for the condensation reaction of **1** and **2**.

Table S1. Values of K_a [M^{-1}] measured by UV-Vis titration for the binding of **1** and **2** with CB[7] at different pH.

Guest	pH = 9.6	pH = 13.6
1	$(6.5 \pm 0.5) \times 10^2$	$(4.3 \pm 0.3) \times 10^2$
2	$(1.7 \pm 0.3) \times 10^4$	$(1.2 \pm 0.1) \times 10^3$

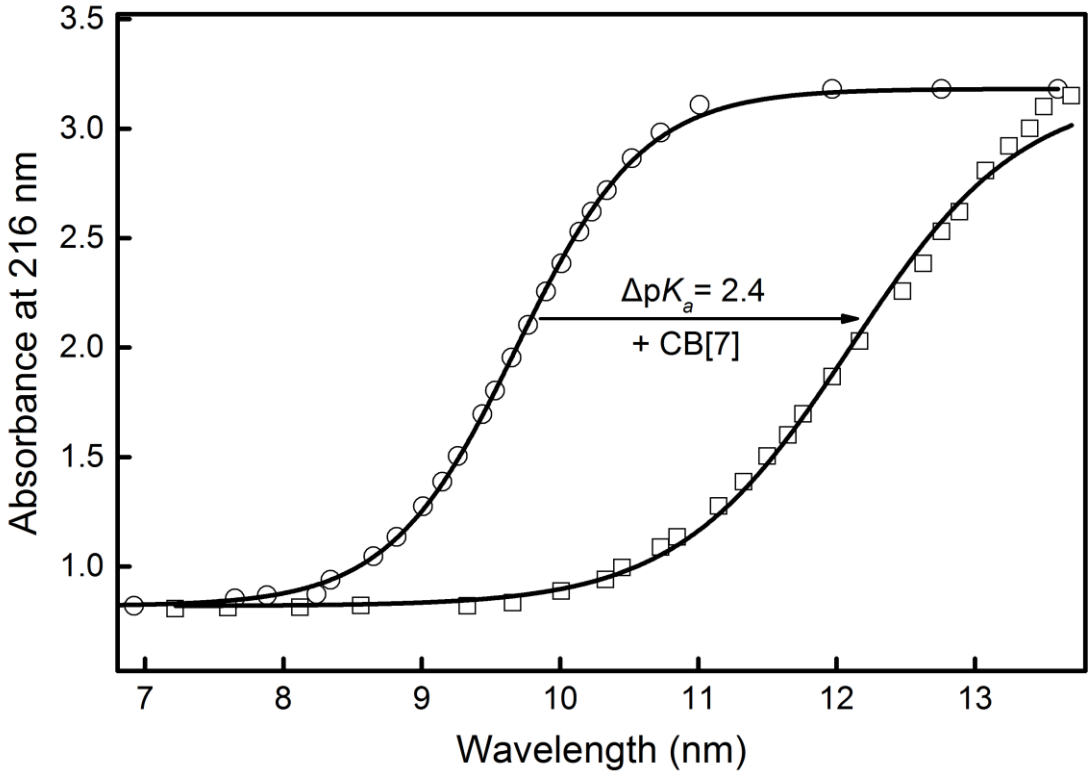


Figure S3. pH titration of **2** (1.0 mM) in the absence of CB[7] (circle) and in the presence of 5.0 mM CB[7] (square). And the pK_a values were determined according to the equation (3).

$$A=\frac{A1-A2}{1+\exp\left[\frac{pH-pK_a}{n}\right]}+A2 \qquad (3)$$

Where "n" denotes a fitting parameter, pK_a represents the negative logarithm of the equilibrium constant $K_a = [\mathbf{2}][H^+]/[\mathbf{2}H^+]$, A1 and A2 are the absorbances at low and high pH, respectively. The non-linear-squares fit of equation (3) to the experimental dates gives pK_a = 9.68 ± 0.01 for **2** in the absence of CB[7] and pK_a = 12.10 ± 0.02 for **2** in the presence of CB[7].

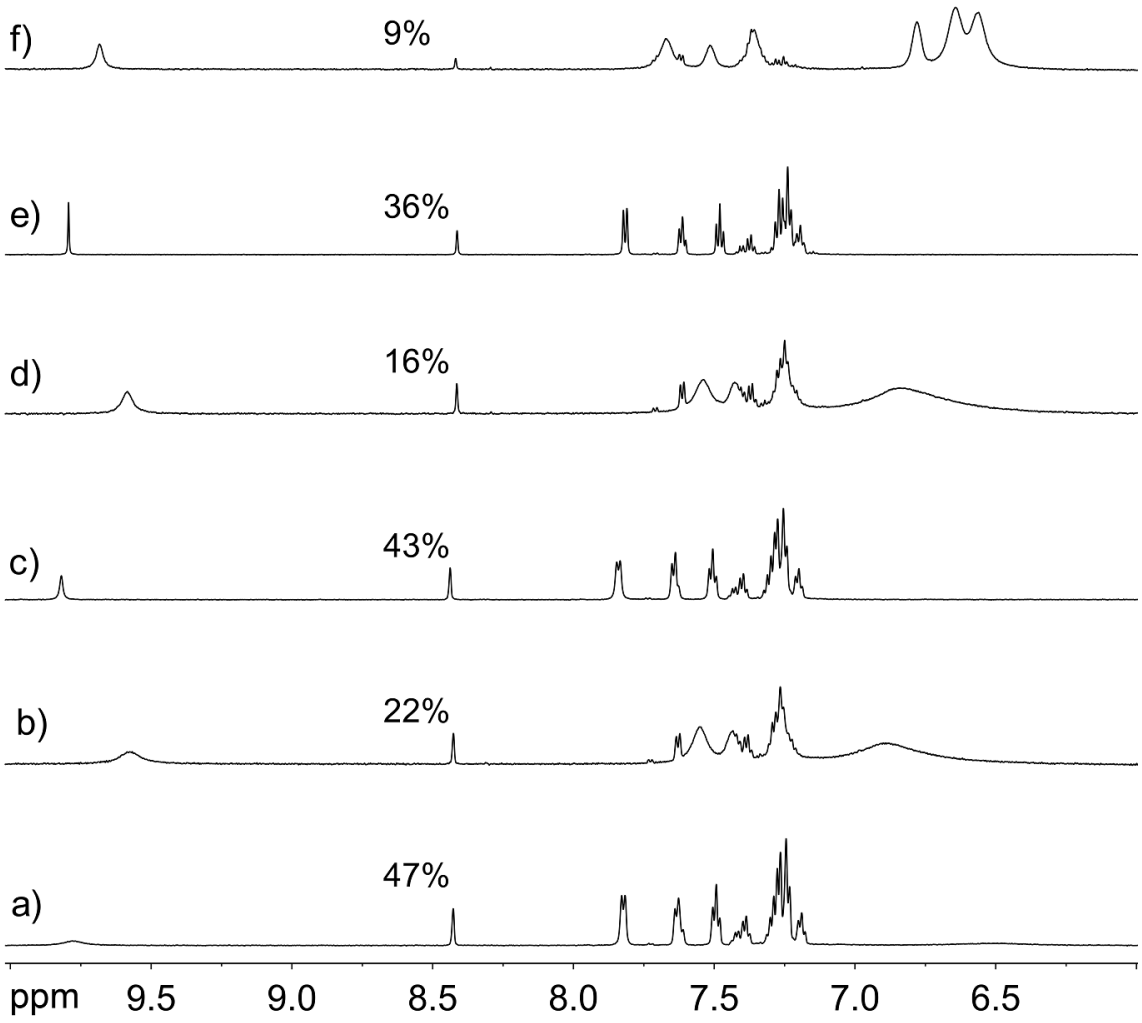
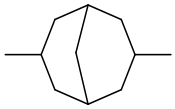


Figure S4. Partial ^{1}H NMR spectra (600 MHz, D_2O) for the hydrolysis of imine with (b, d, f) and without (a, c, e) CB[7] in pD = 13.6 (a, b), pD = 12.5 (c, d) and pD = 11.5 (e, f). Percentage of imine was calculated until there was no any change on ^{1}H NMR spectra.

Table S2. The CIS values for cations in the absence/presence of CB[7].

Guest	N–C–H (α moiety)			N=C–C–H (β moiety)		
	Free	With CB[7]	CIS	Free	With CB[7]	CIS
3	3.94	3.12	-0.82	2.17	1.96	-0.21
4	3.88	3.46	-0.42	2.82	2.14	-0.68
5	3.99	3.82	-0.17	2.79	1.87	-0.92
6	3.97	3.90	-0.07	2.91	2.06	-0.85
7	3.99	3.97	-0.02	3.23	2.44	-0.79

Table S3. Volumes of iminium cations and PCs.

	β moiety		α moiety	Volume for β moiety (Å^3)	PCs
	R_1	R_2			
3	Me	Me		62	22.22
4	—$(CH_2)_4$—			86	30.82
5	—$(CH_2)_5$—			102	36.55
6	—$(CH_2)_6$—		—$(CH_2)_4$—	118	42.29
7				147	52.68

The volumes were calculated by geometry optimization with AM1 semiempirical method for the corresponding alkane and the PCs were calculated based on the CB[7] inner cavity volume which is reported as 279 Å^3.[1]

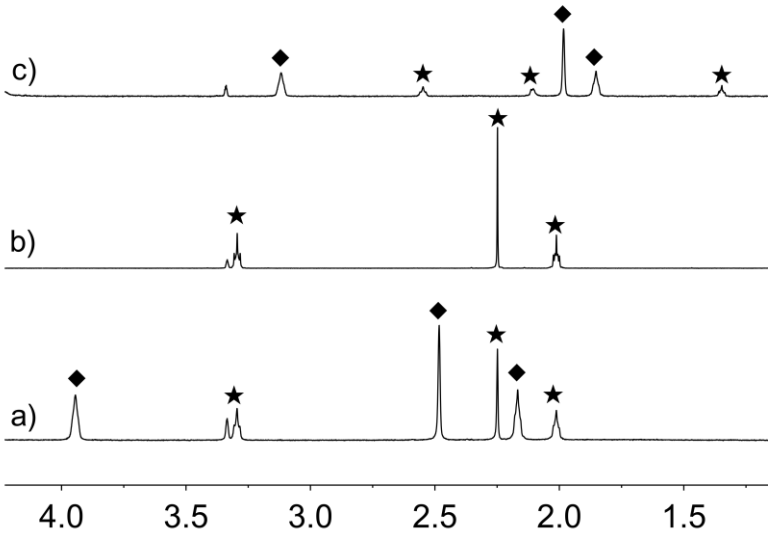


Figure S5. Partial ^{1}H NMR spectra (600 MHz, D_2O) for a) **3;** b) hydrolyzed **3**; c) **3** in the presence of CB[7] (1.0 eq). ◆ stands for **3** and ★ stands for the corresponding ketone and amine.

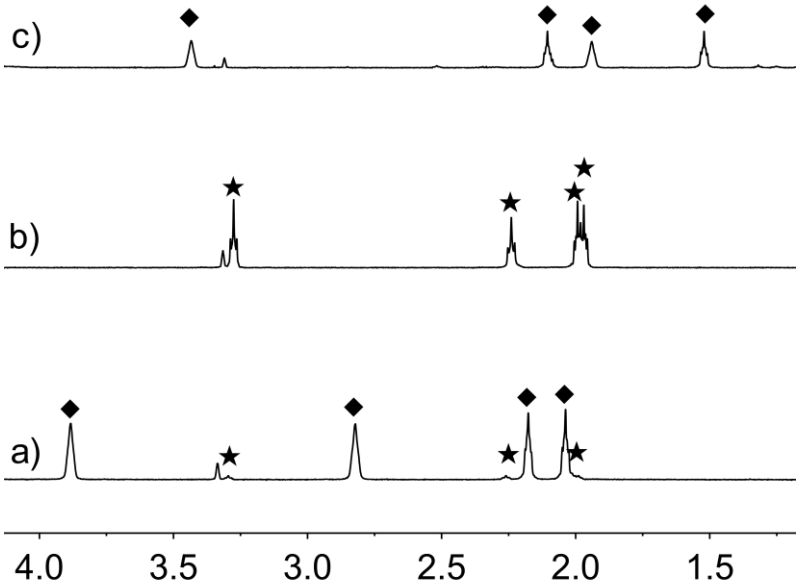


Figure S6. Partial ^{1}H NMR spectra (600 MHz, D_2O) for a) **4;** b) hydrolyzed **4**; c) **4** in the presence of CB[7] (1.0 eq). ◆ stands for **4** and ★ stands for the corresponding ketone and amine.

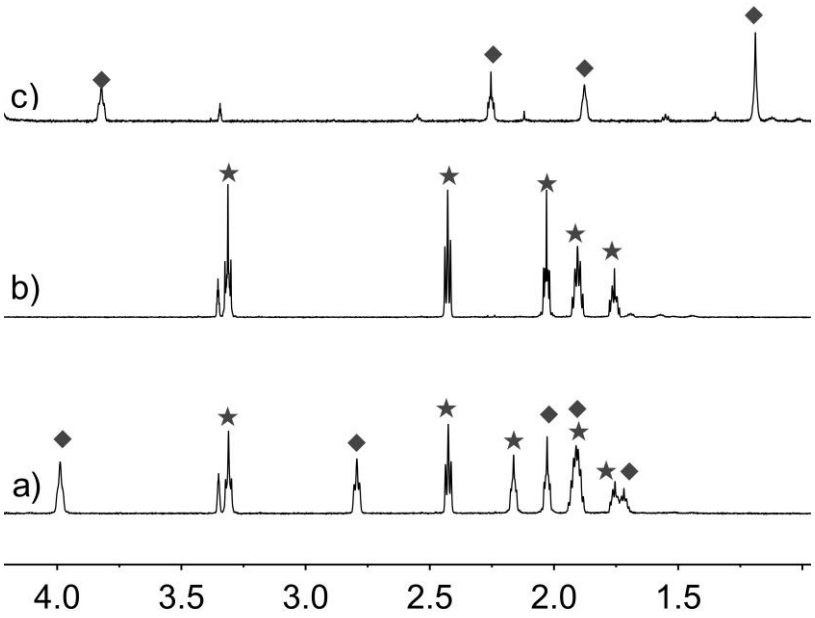


Figure S7. Partial ^{1}H NMR spectra (600 MHz, D_2O) for a) **5;** b) hydrolyzed **5**; c) **5** in the presence of CB[7] (1.0 eq). ◆ stands for **5** and ★ stands for the corresponding ketone and amine.

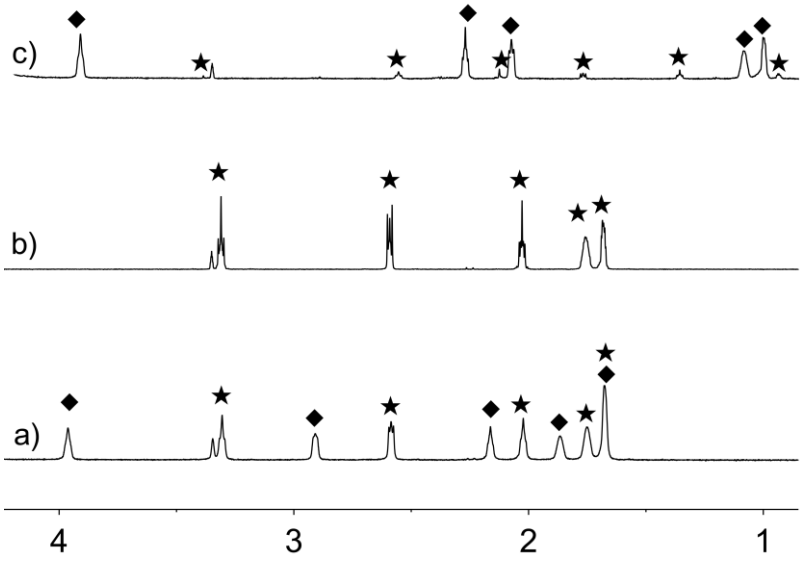


Figure S8. Partial ^{1}H NMR spectra (600 MHz, D_2O) for a) **6;** b) hydrolyzed **6**; c) **6** in the presence of CB[7] (1.0 eq). ◆ stands for **6** and ★ stands for the corresponding ketone and amine.

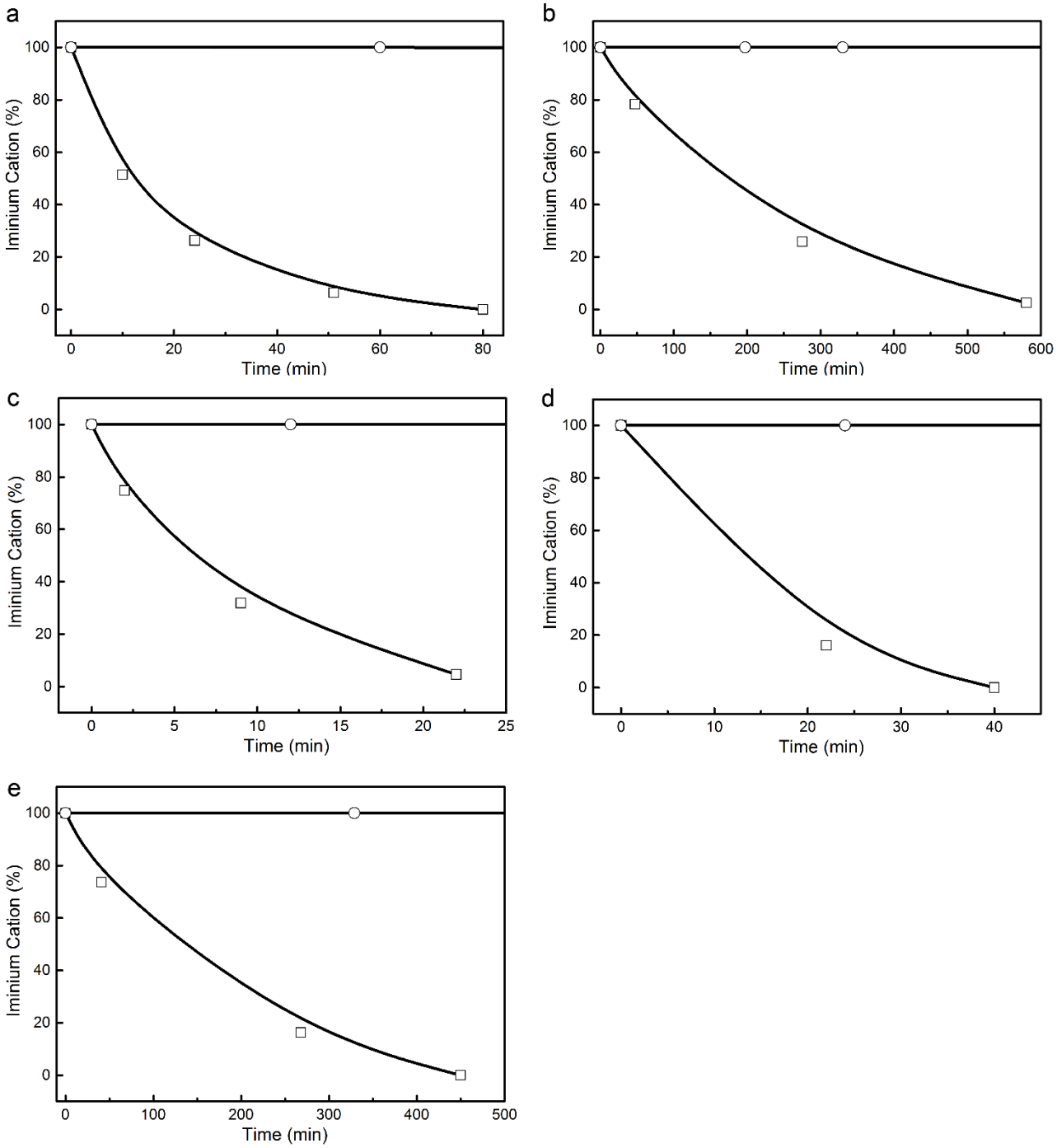


Figure S9. Lifetime of a) **3**; b) **4**; c) **5**; d) **6** and e) **7** in the absence of CB[7] (square) and in the presence of CB[7] (circle).

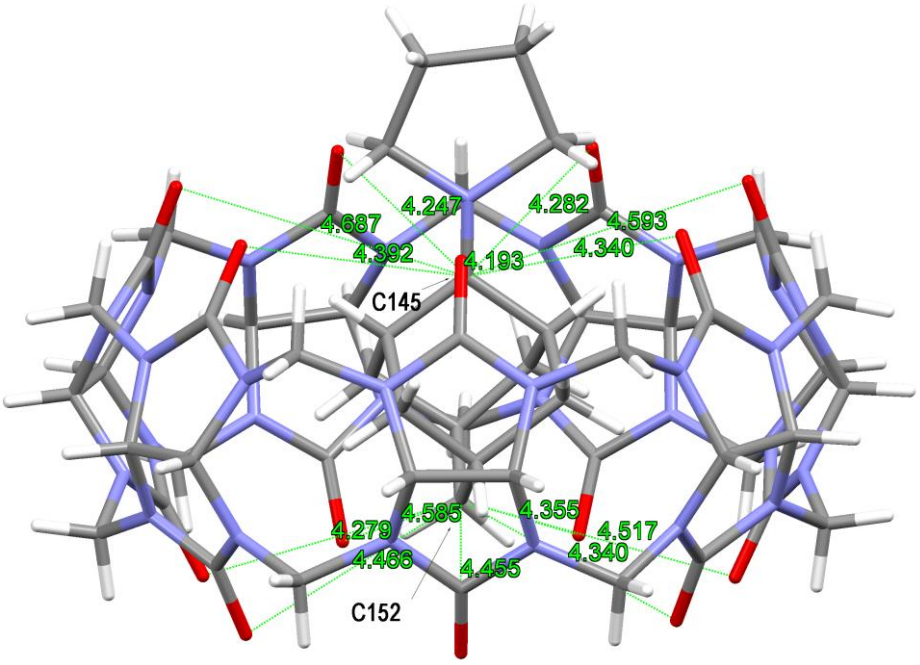


Figure S10. Side view of the crystal structure of CB[7]•**7** showing that the average distances form C145 and C152 to the adjacent oxygens on CB[7] are quite similar.

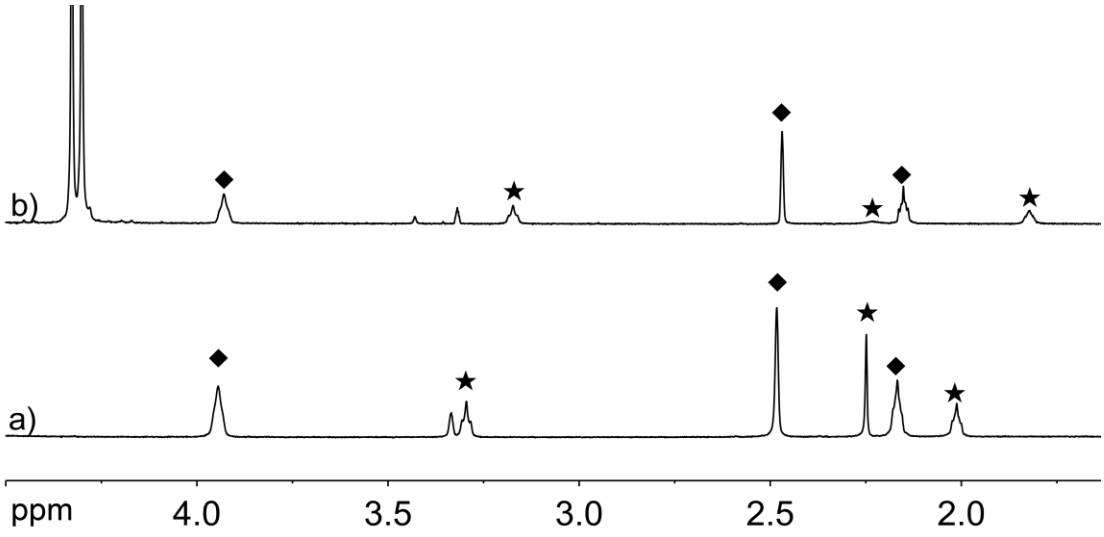


Figure S11. Partial ^{1}H NMR spectra (600 MHz, D_2O) for a) **3**; b) **3** in the presence of CB[6] (1.0 eq). ◆ stands for **3** and ★ stands for the corresponding ketone and amine.

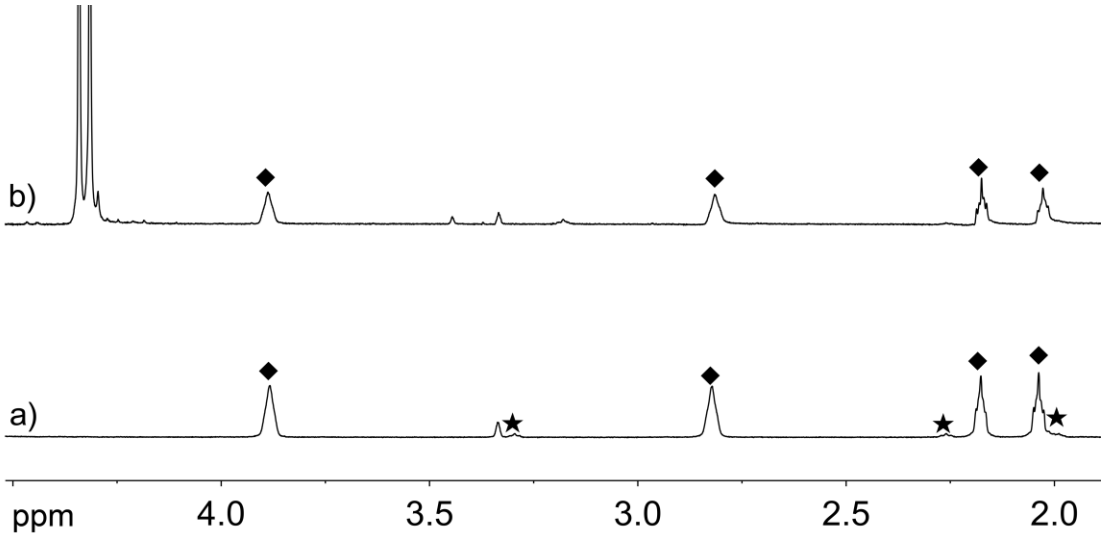


Figure S12. Partial ^{1}H NMR spectra (600 MHz, D_2O) for a) **4**; b) **4** in the presence of CB[6] (1.0 eq). ◆ stands for **4** and ★ stands for the corresponding ketone and amine.

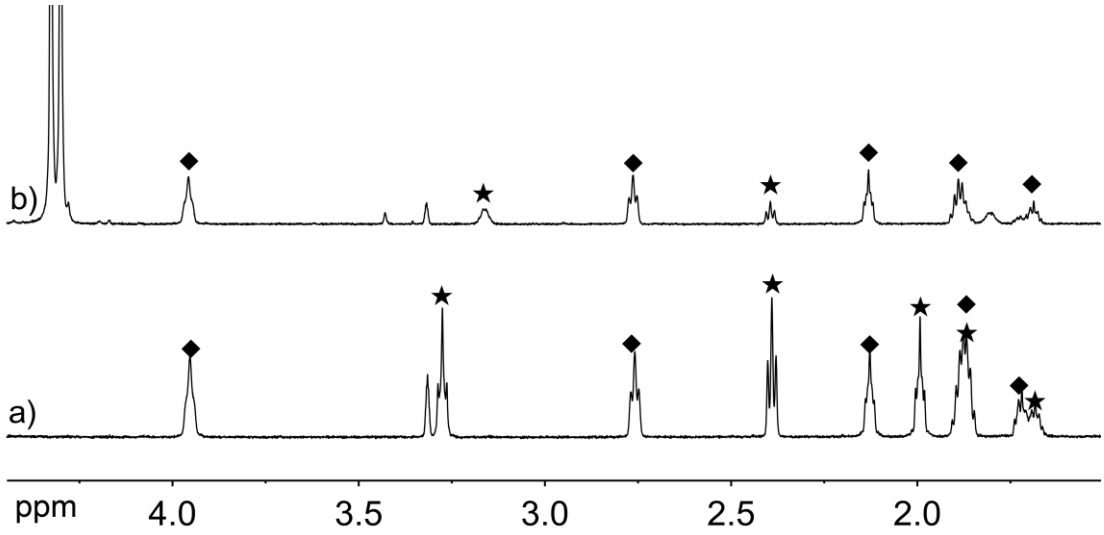


Figure S13. Partial ^{1}H NMR spectra (600 MHz, D_2O) for a) **5**; b) **5** in the presence of CB[6] (1.0 eq). ◆ stands for **5** and ★ stands for the corresponding ketone and amine.

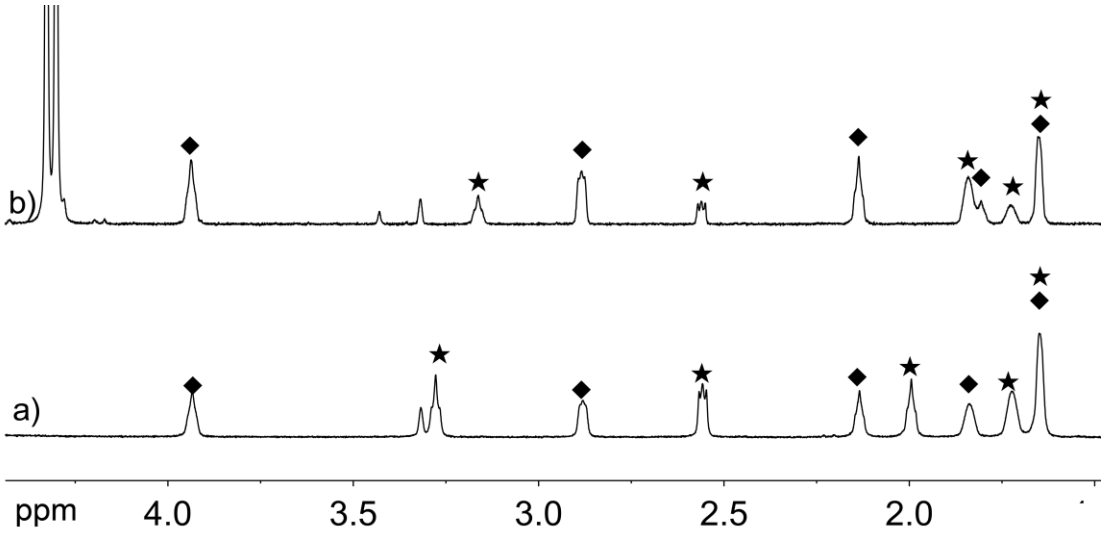


Figure S14. Partial ^{1}H NMR spectra (600 MHz, D_2O) for a) **6**; b) **6** in the presence of CB[6] (1.0 eq). ◆ stands for **6** and ★ stands for the corresponding ketone and amine.

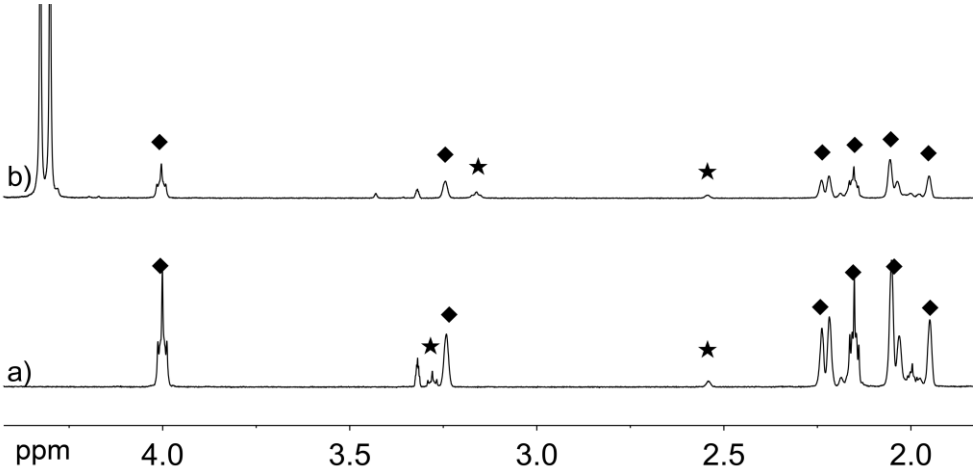


Figure S15. Partial ^{1}H NMR spectra (600 MHz, D_2O) for a) **7**; b) **7** in the presence of CB[6] (1.0 eq). ◆ stands for **7** and ★ stands for the corresponding ketone and amine.

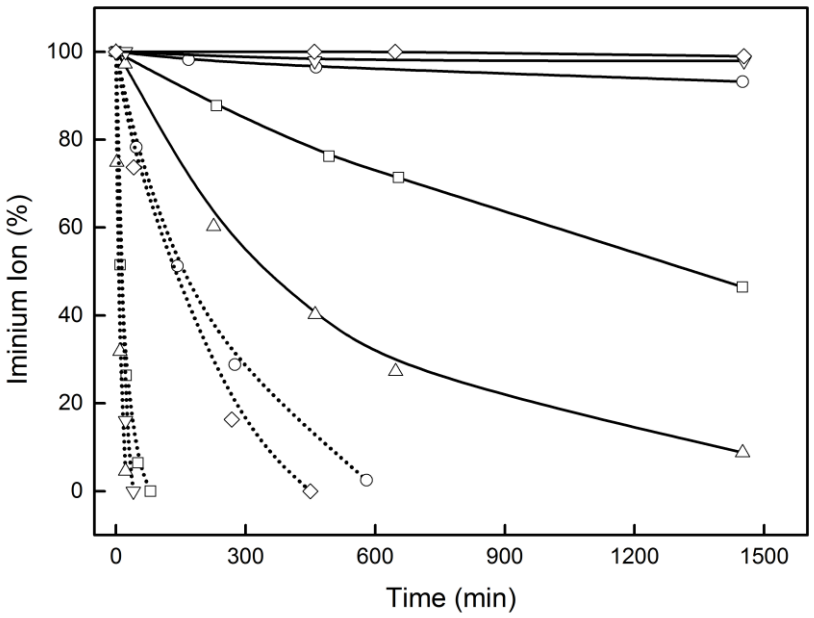


Figure S16. Lifetime of iminium cations (□ for **3**; ○ for **4**; △ for **5**; ▽ for **6**; ◇ for **7**) in the absence (dotted line) and presence (solid line) of CB[6] (1.0 eq).

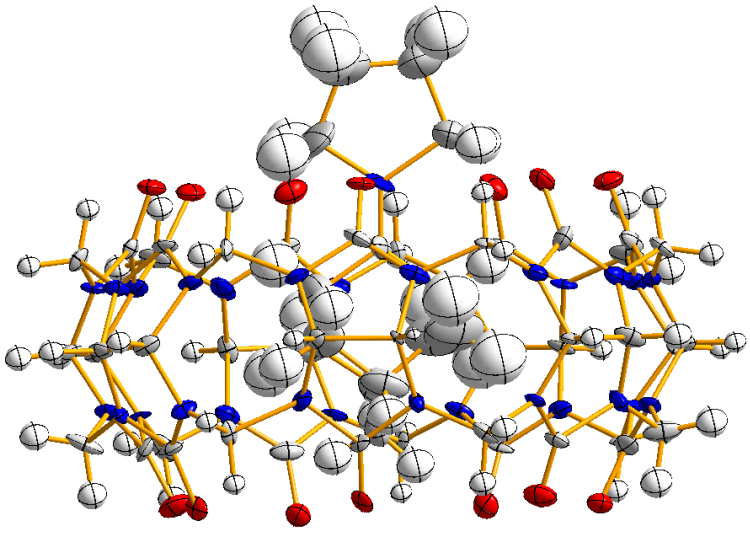


Figure S17. Crystal structure of CB[7]•**7** with thermal ellipsoid plot (50% probability ellipsoids).

(1) Nau, W. M.; Florea, M.; Assaf, K. I. *Isr. J. Chem.* **2011,** *51*, 559-577.