Electronic Supplementary Material (ESI) for RSC Advances.

An Adamantane-Based Disubstituted Binding Motif with Picomolar Dissociation Constants for Cucurbit[n]urils in Water and Related Quaternary Assemblies.

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SUPPORTING INFORMATION

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^{1}H NMR, ^{13}C NMR, and MS spectra of guests **5**–**7**

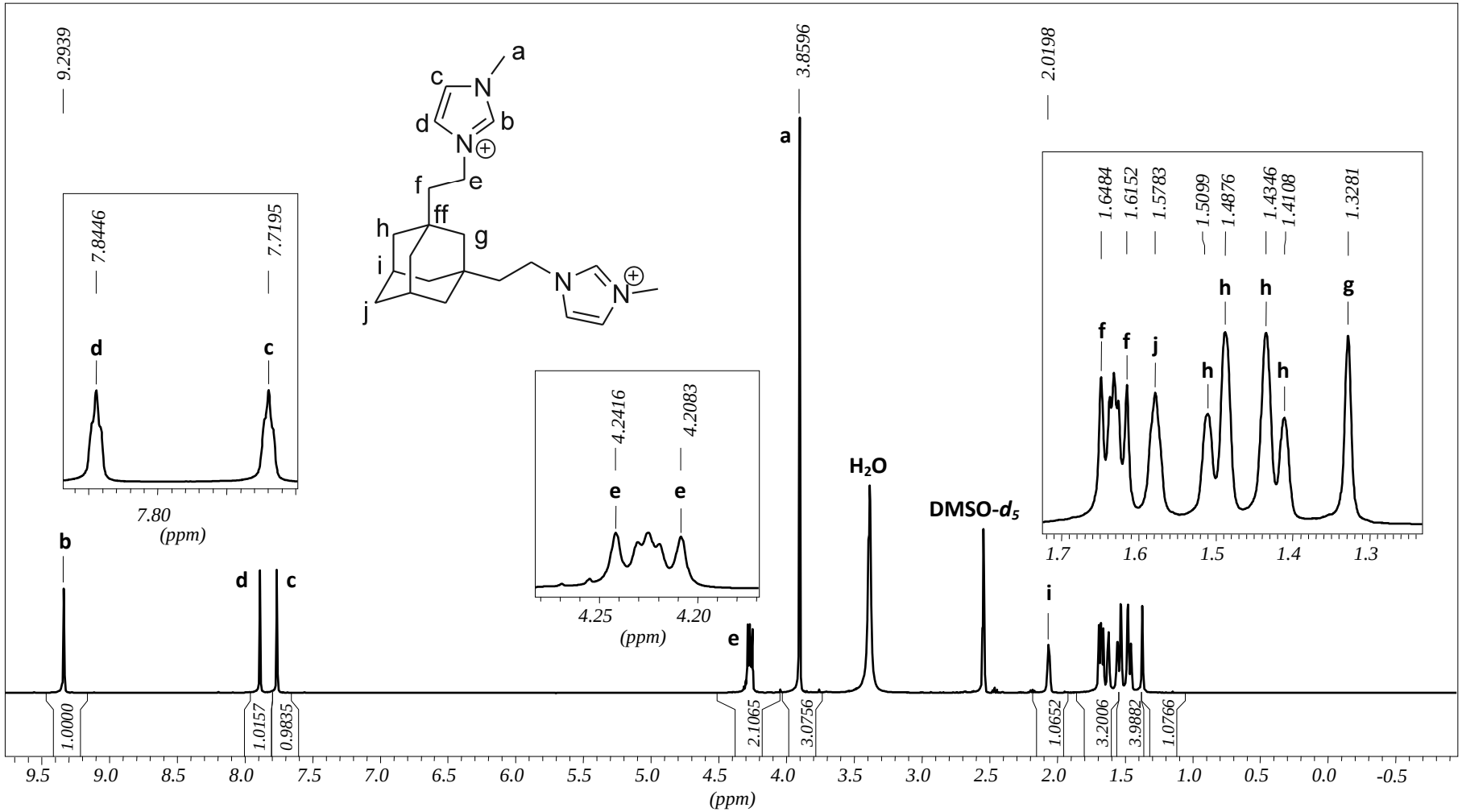


Figure S1 The ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of guest **5**.

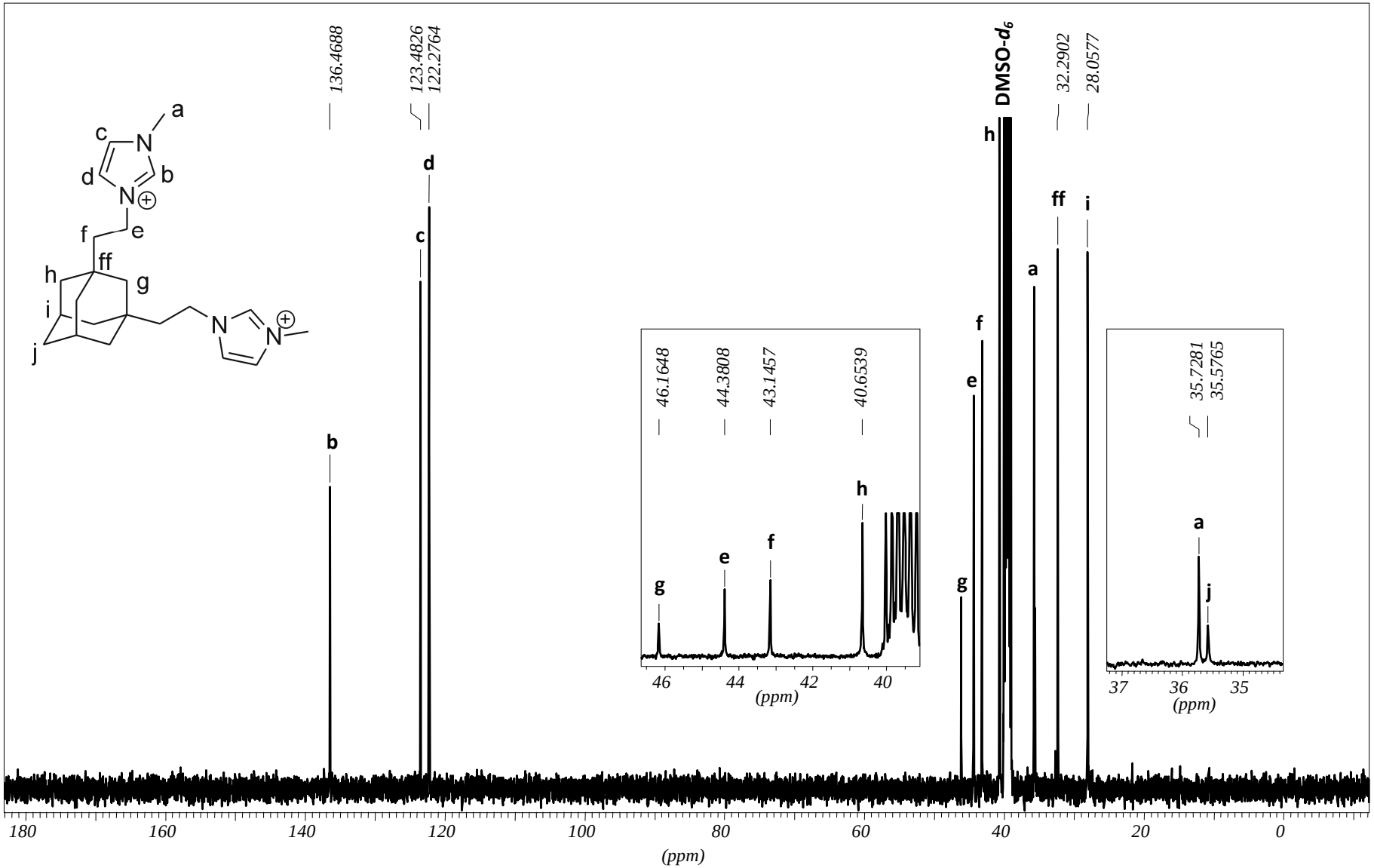


Figure S2 The $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 126 MHz) spectrum of guest **5**.

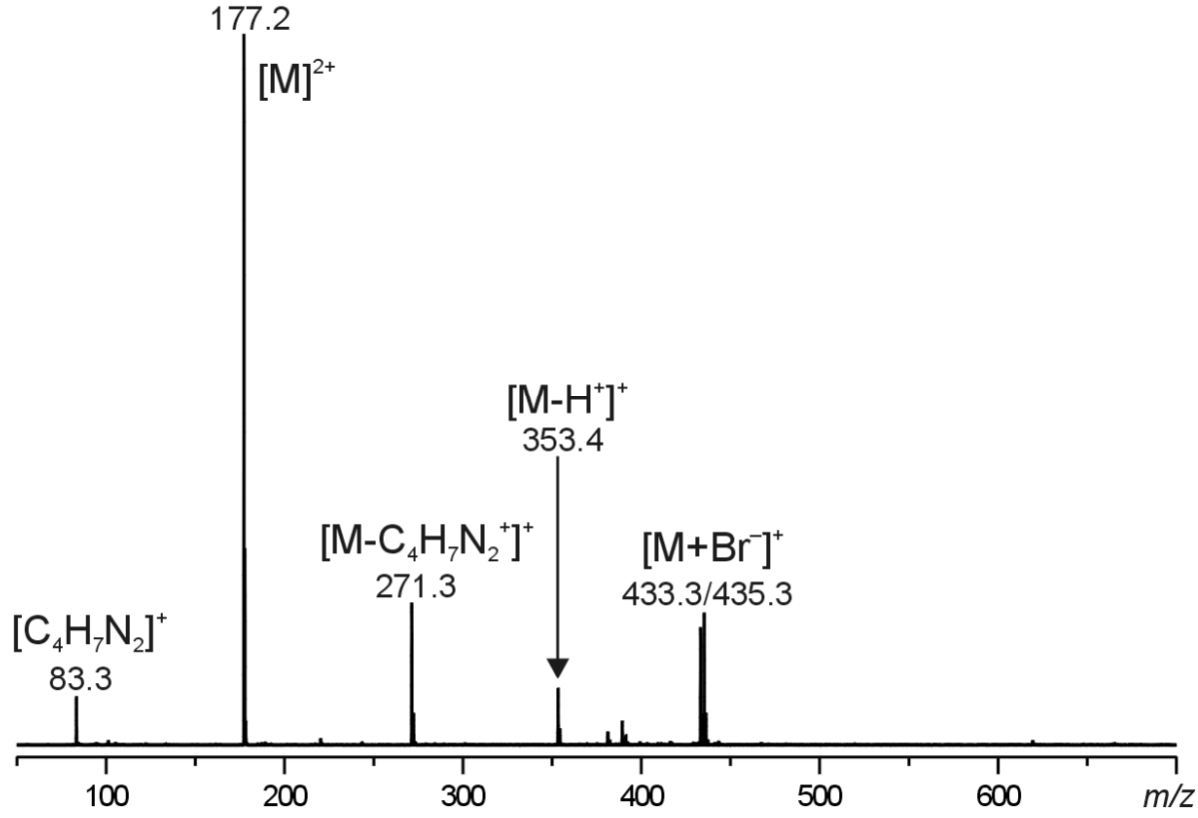


Figure S3 The positive first-order ESI mass spectrum of salt $\mathbf{5}^{2+}2Br^{-}$

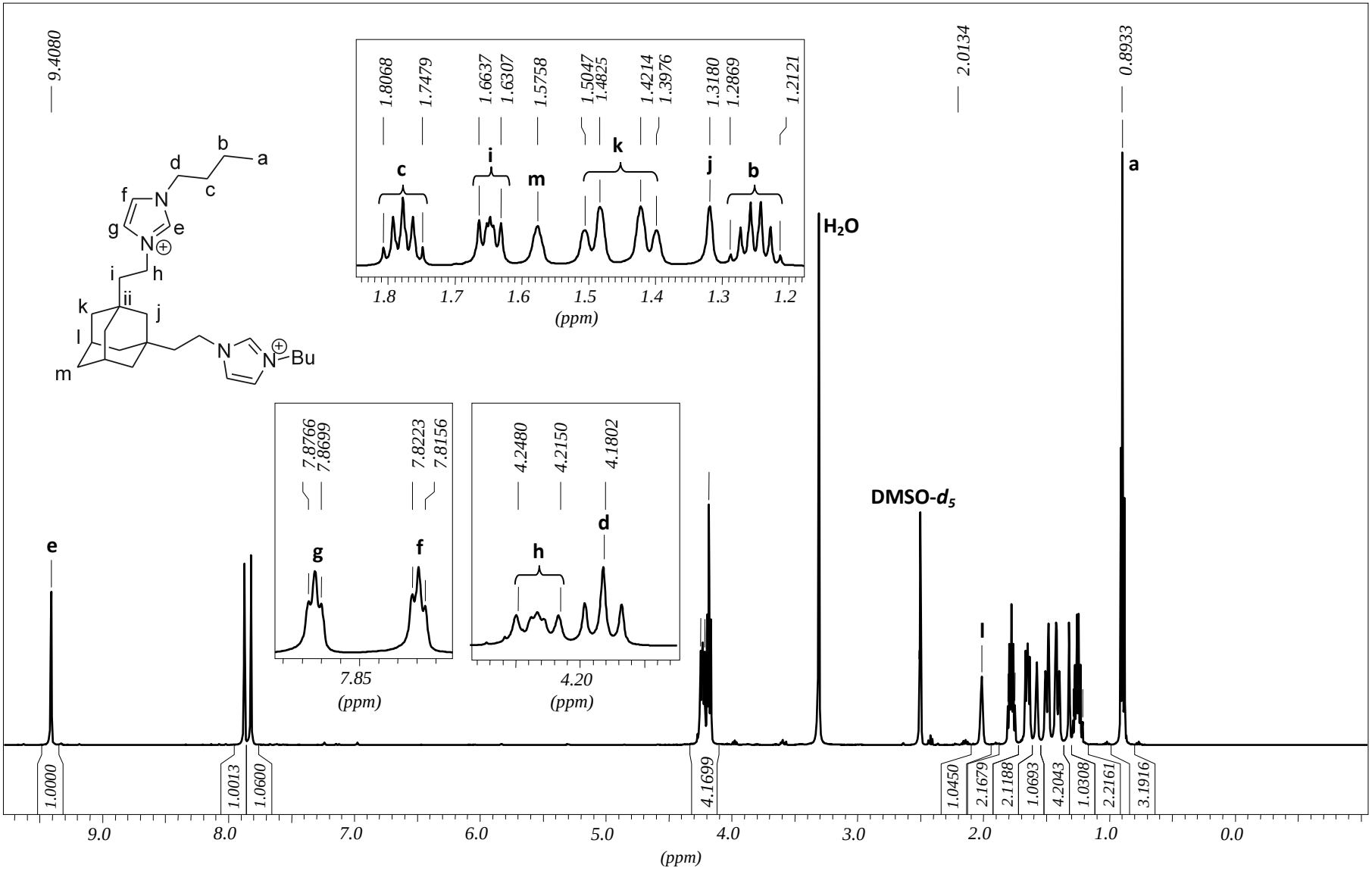


Figure S4 The ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of the guest **6**.

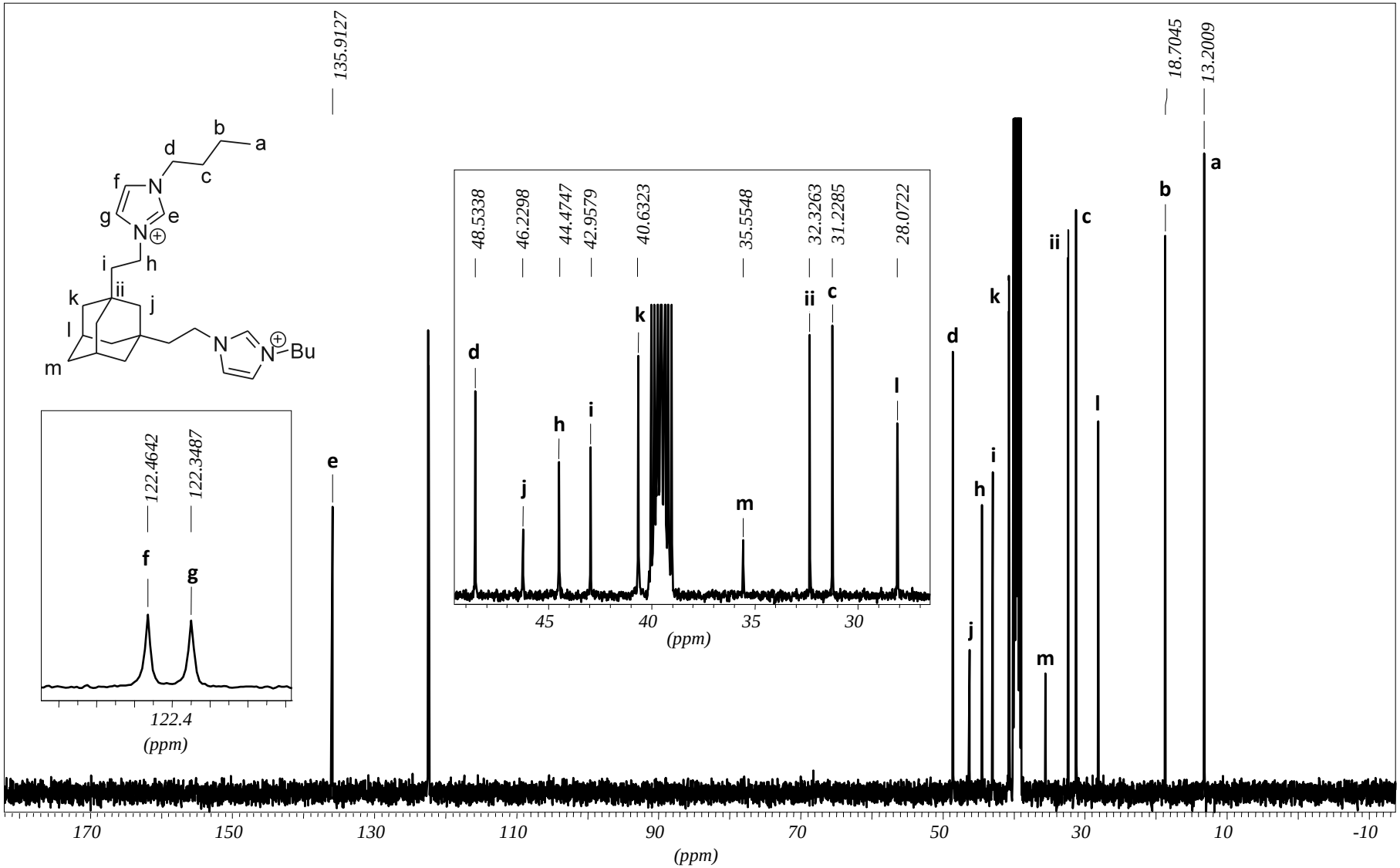


Figure S5 The $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 126 MHz) spectrum of guest **6**.

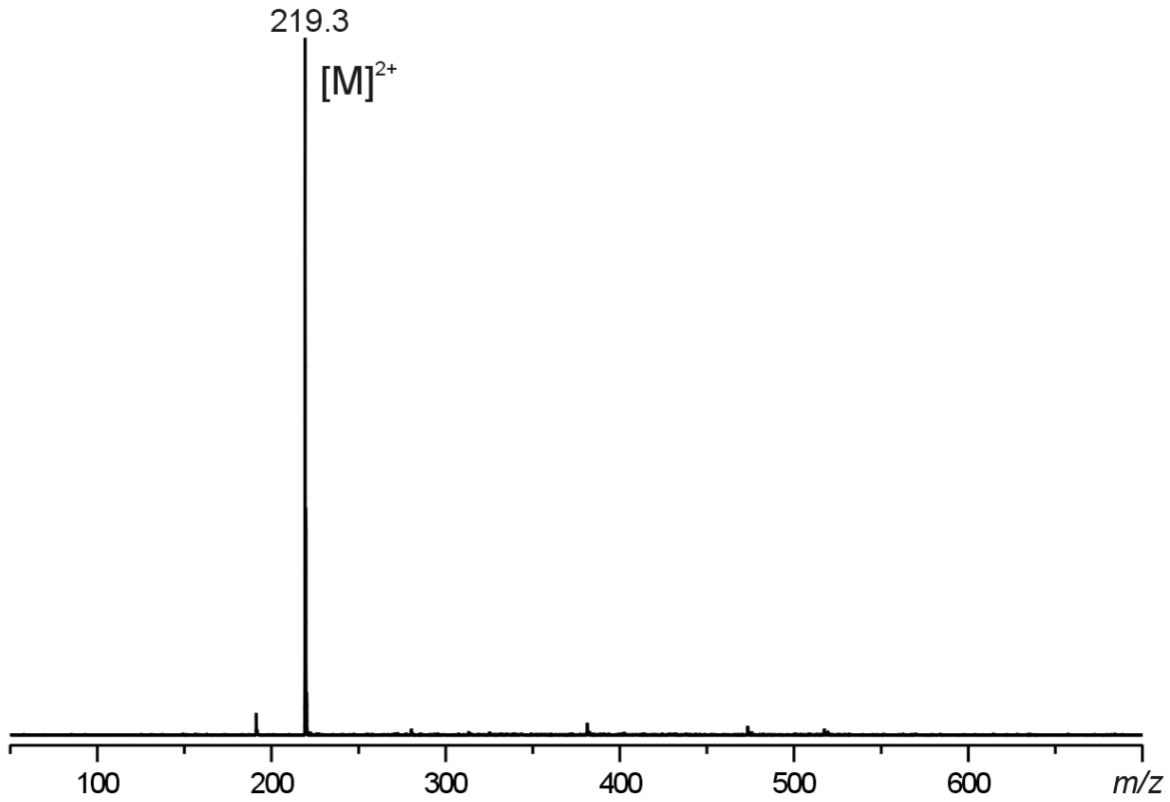


Figure S6 The positive first-order ESI mass spectrum of salt $\mathbf{6}^{2+}2Br^{-}$

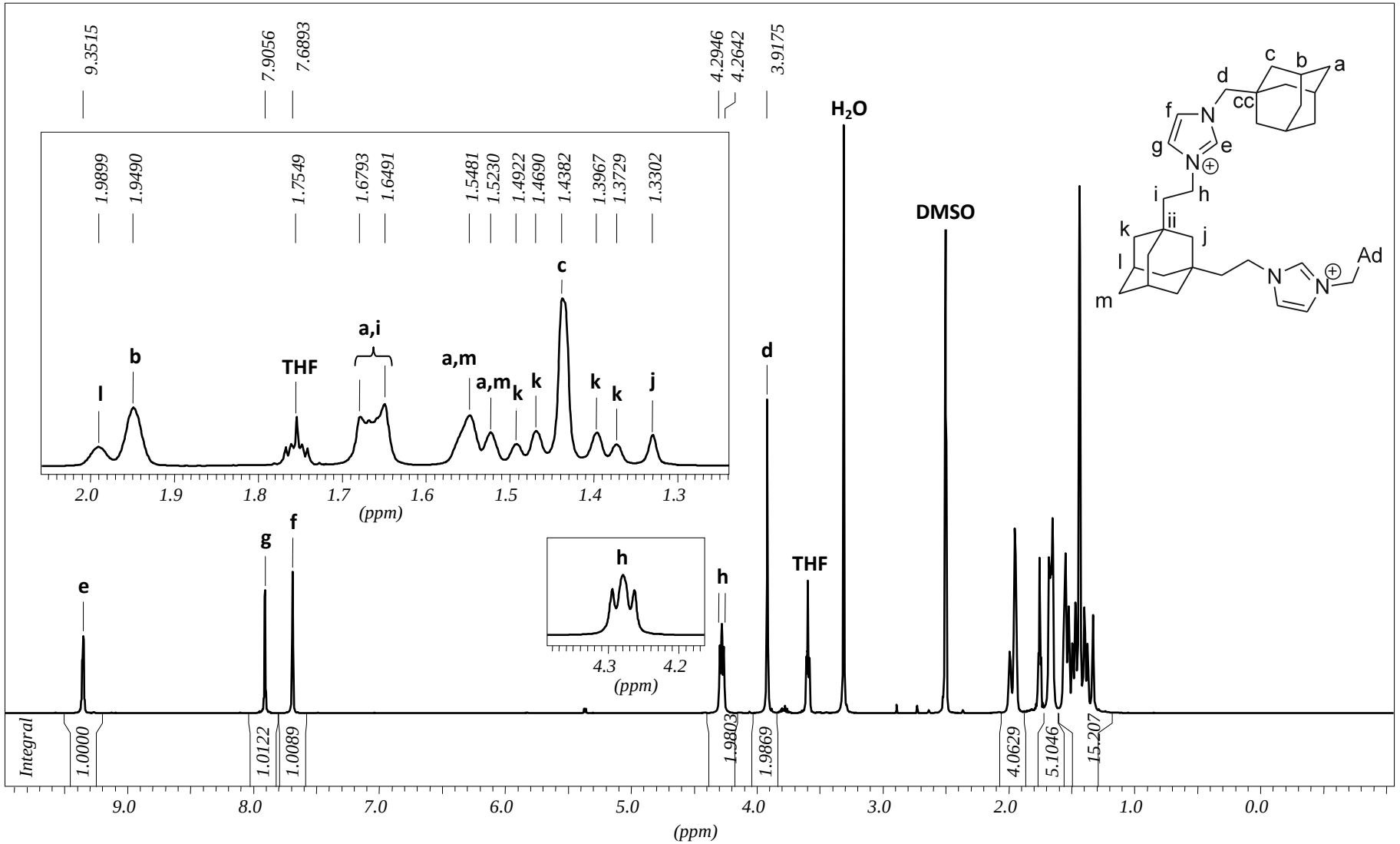


Figure S7 The ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of the guest **7**.

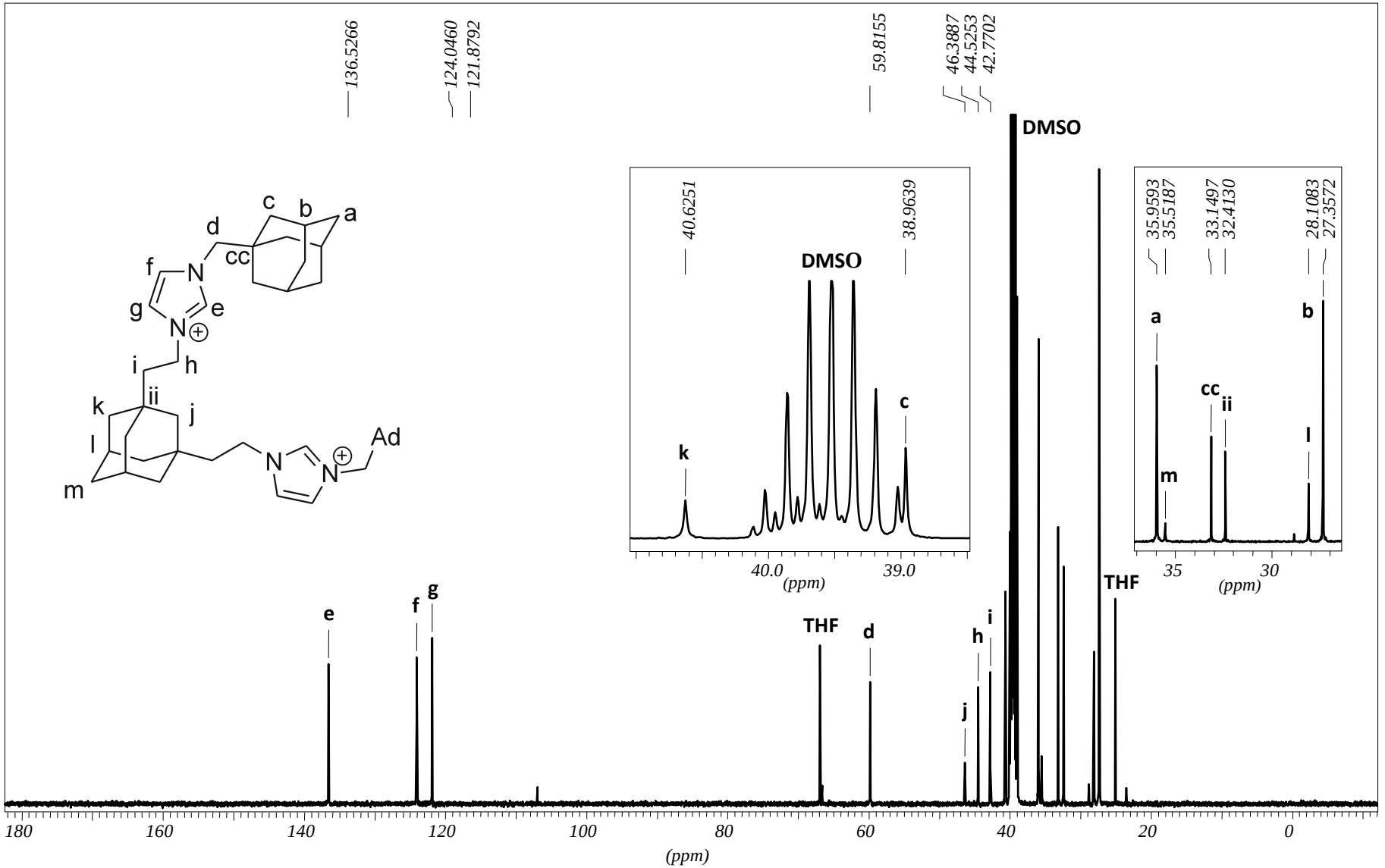


Figure S8 The $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 126 MHz) spectrum of guest **7**.

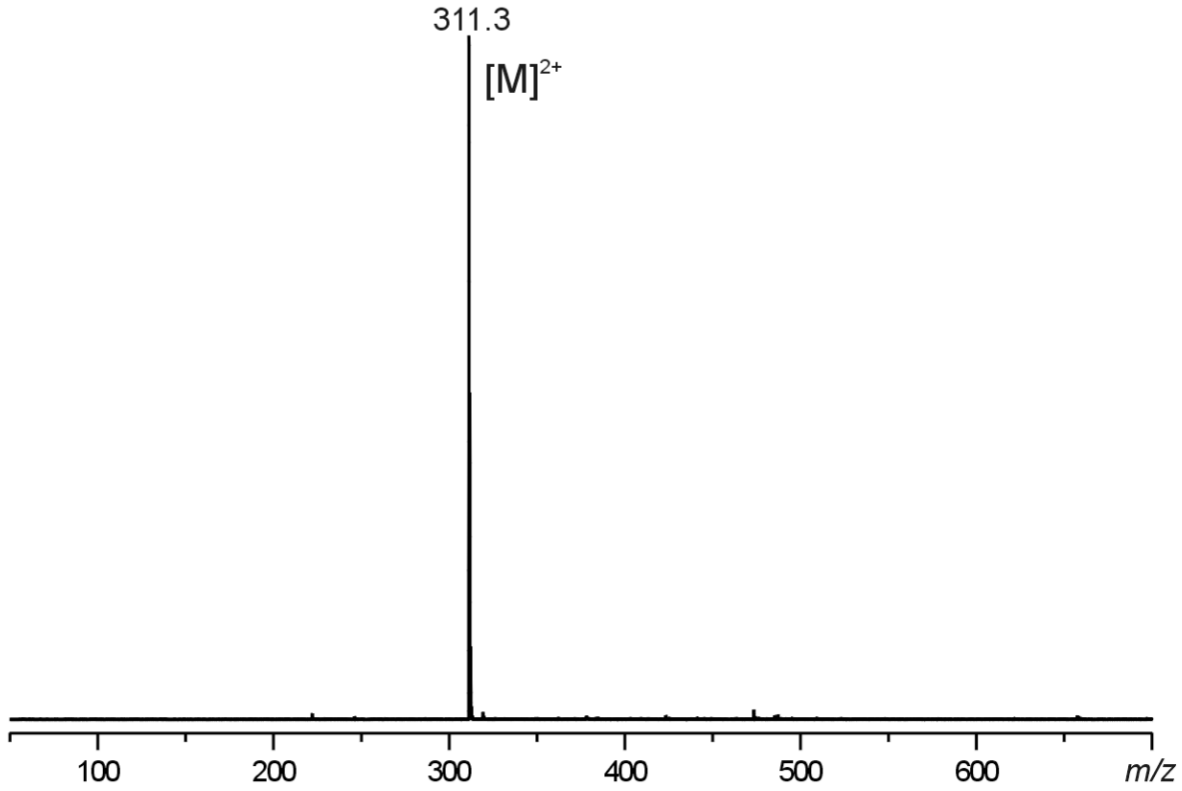


Figure S9 The positive first-order ESI mass spectrum of salt $\mathbf{7}^{2+}2Br^{-}$

NMR data for binary and ternary systems

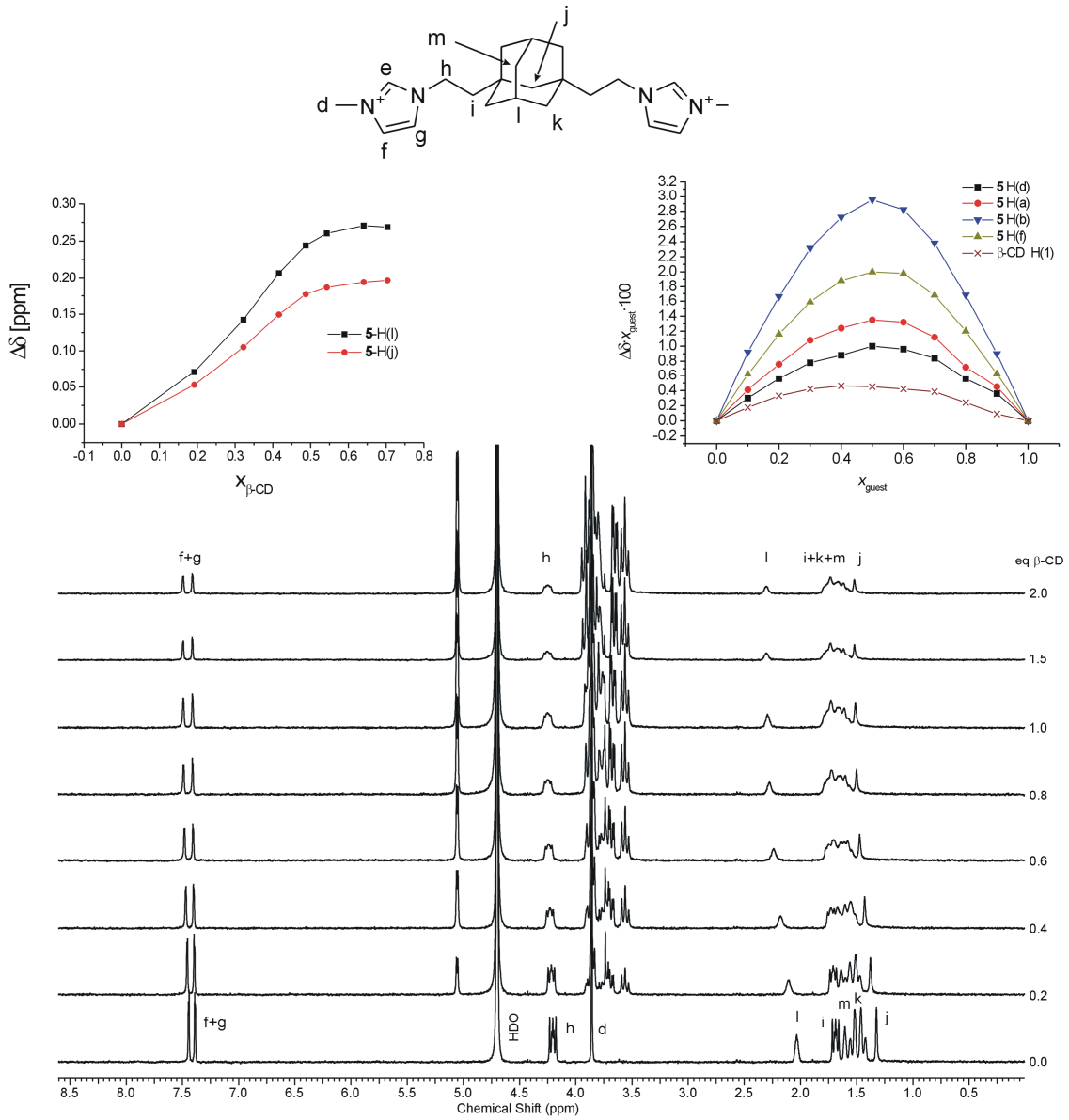


Figure S10 Stacking plot of the ^{1}H NMR spectra for the guest **5** and β-CD mixture in D_2O. Inserted graphs display plot of chemical induced shifts against host molar fraction (left) and Job plot obtained in separate experiment (right). Spectra were recorded at 303 K.

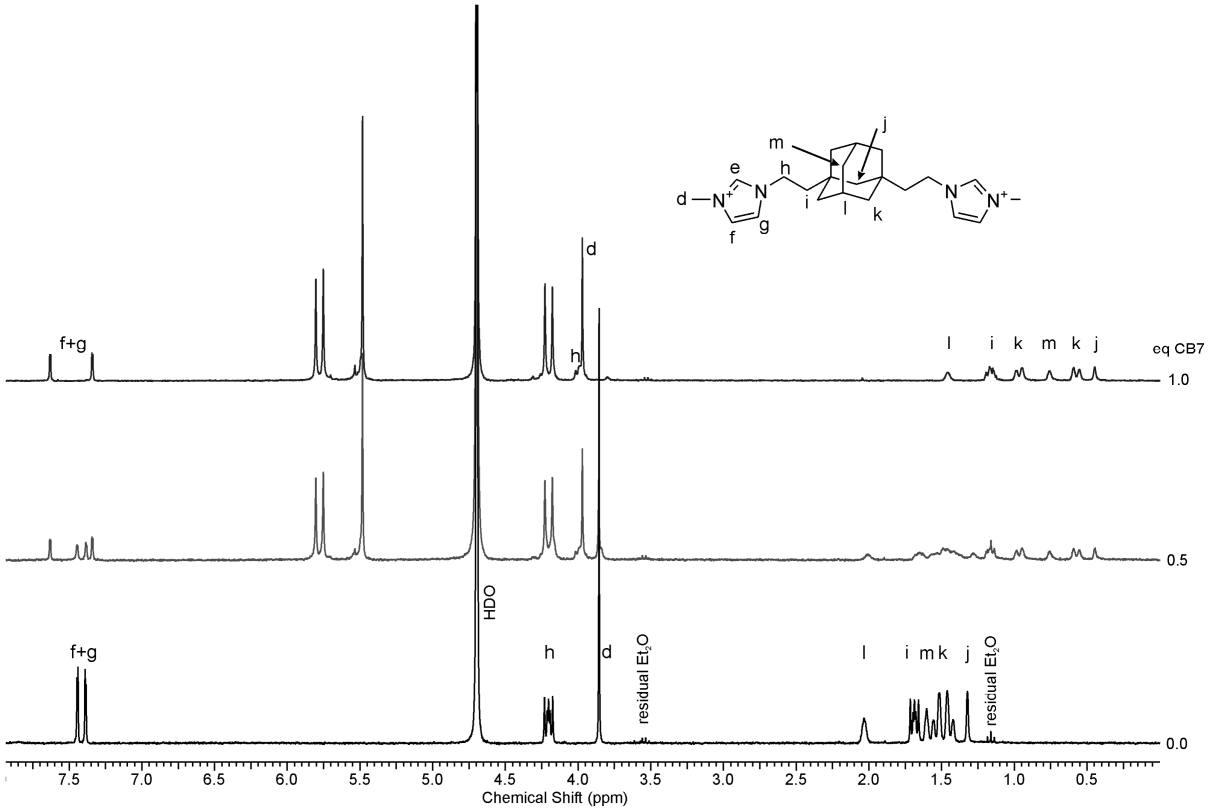


Figure S11 Stacking plot of the ^{1}H NMR spectra for the guest **5** and CB7 mixture in D_2O. Spectra were recorded at 303 K.

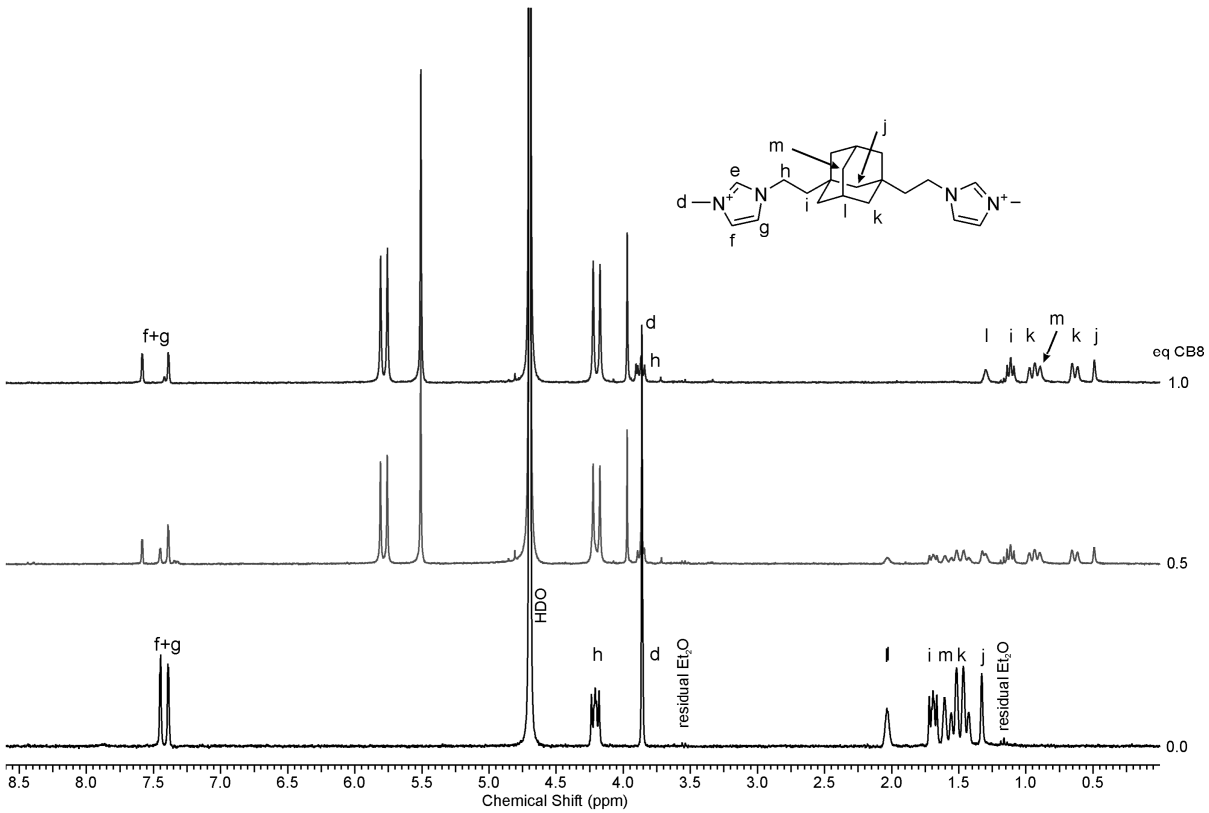


Figure S12 Stacking plot of the ^{1}H NMR spectra for the guest **5** and CB8 mixture in D_2O. Spectra were recorded at 303 K.

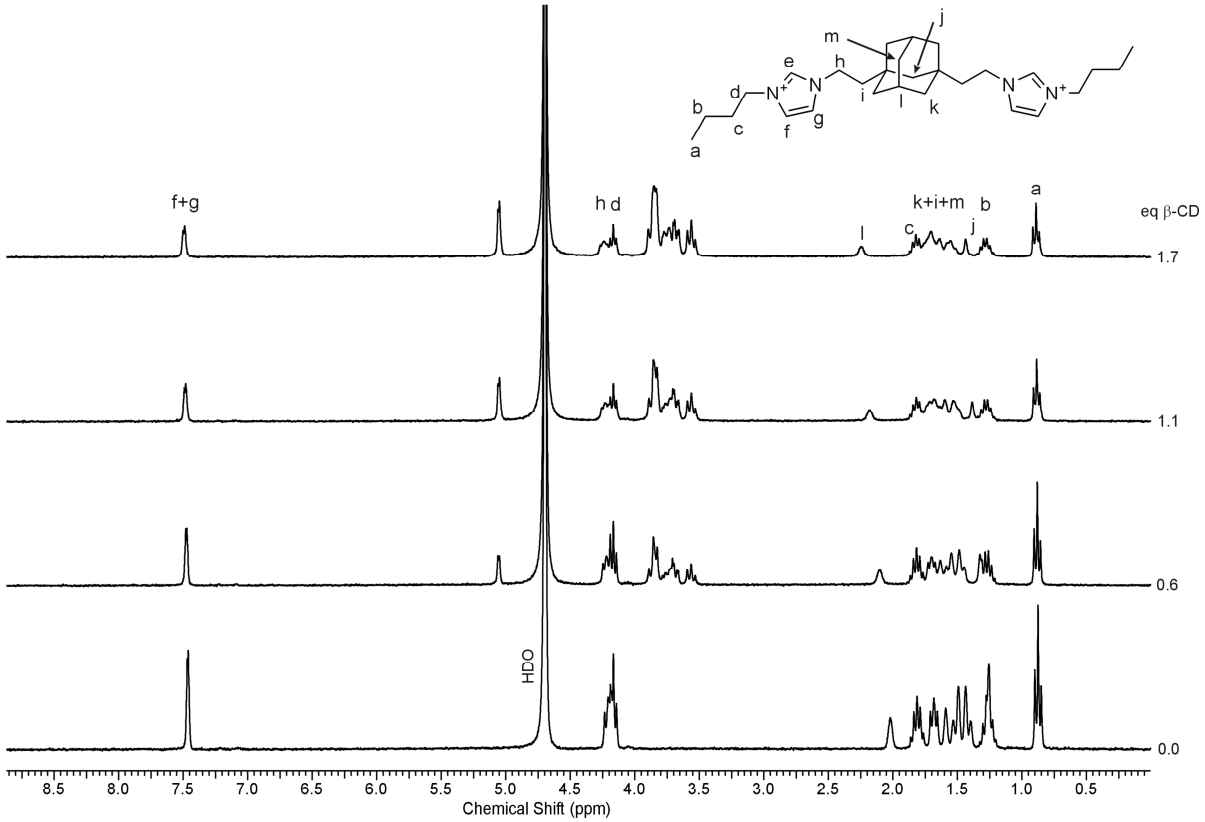


Figure S13 Stacking plot of the ^{1}H NMR spectra for the guest **6** and β-CD mixture in D_2O. Spectra were recorded at 303 K.

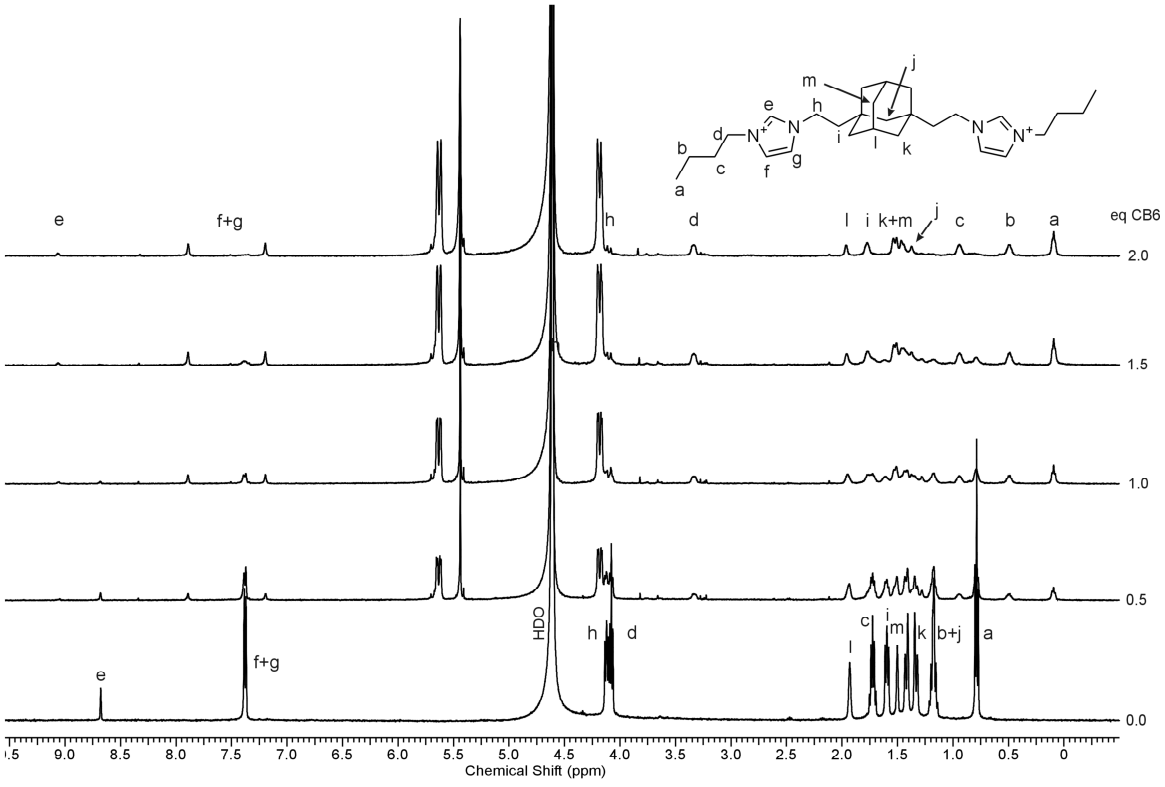


Figure S14 Stacking plot of the ^{1}H NMR spectra for the guest **6** and CB6 mixture in 50 mM NaCl solution in D_2O. Spectra were recorded at 303 K.

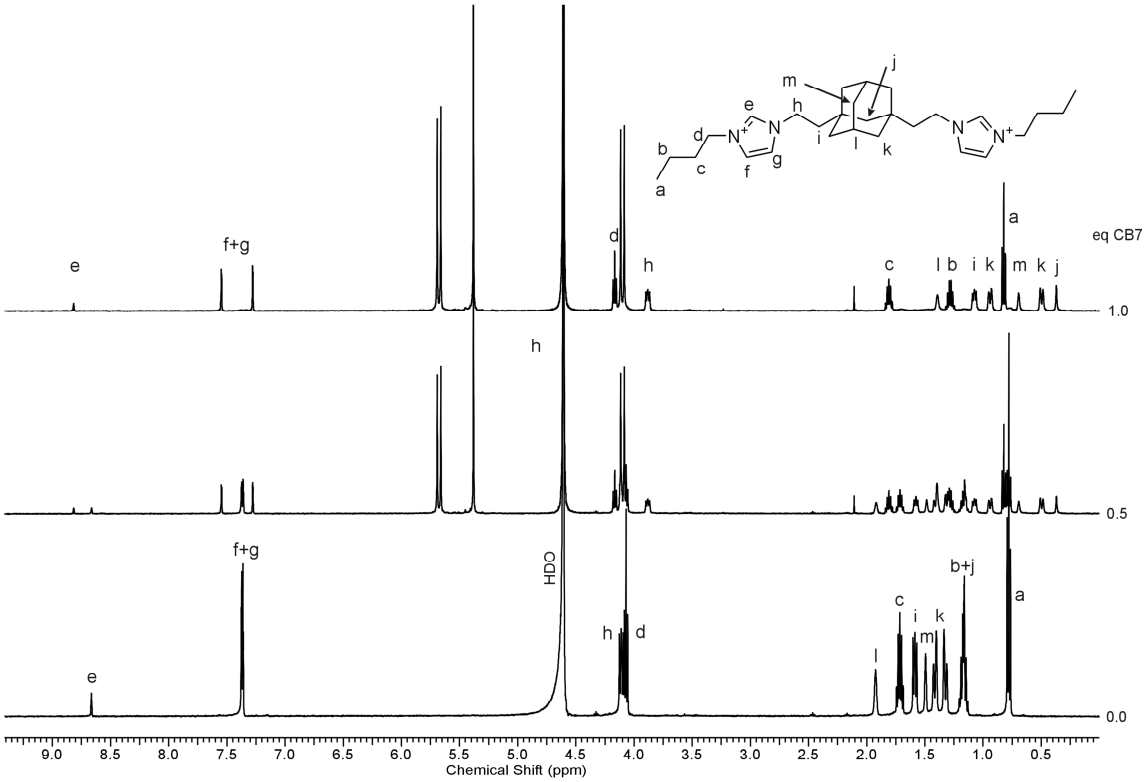


Figure S15 Stacking plot of the ^{1}H NMR spectra for the guest **6** and CB7 mixture in D_2O. Spectra were recorded at 303 K.

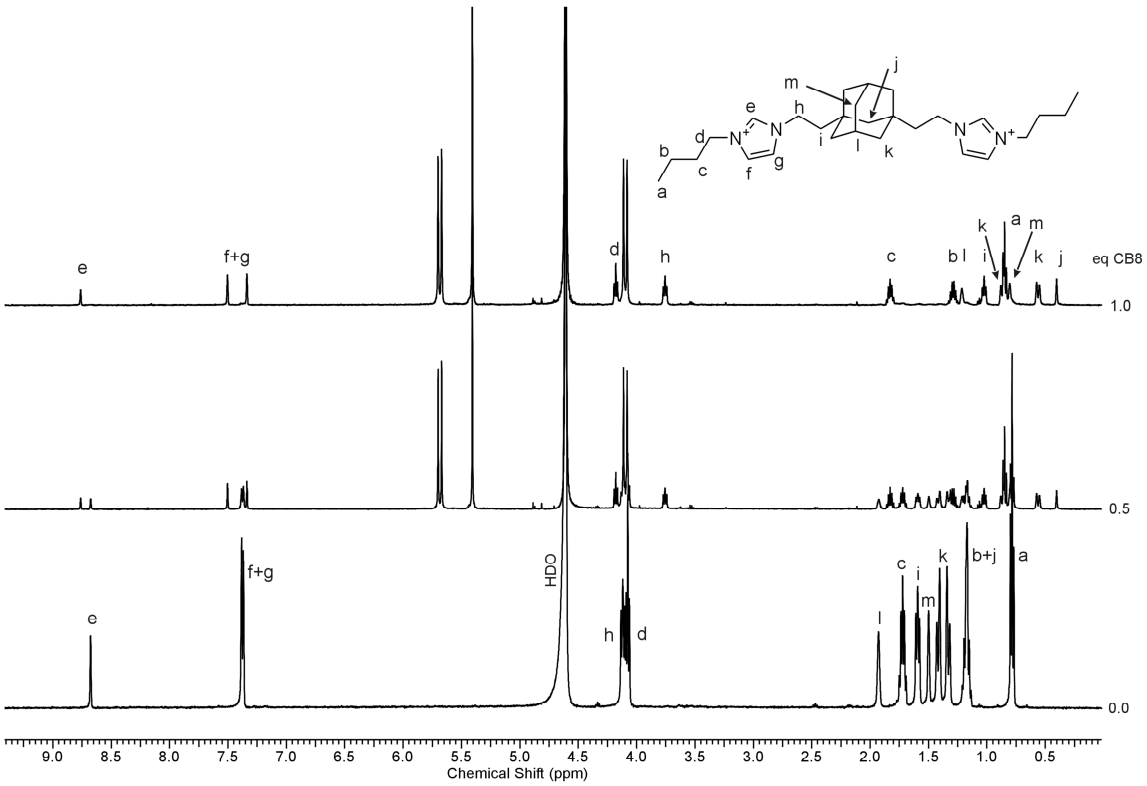


Figure S16 Stacking plot of the ^{1}H NMR spectra for the guest **6** and CB8 mixture in 50 mM NaCl solution in D_2O. Spectra were recorded at 303 K.

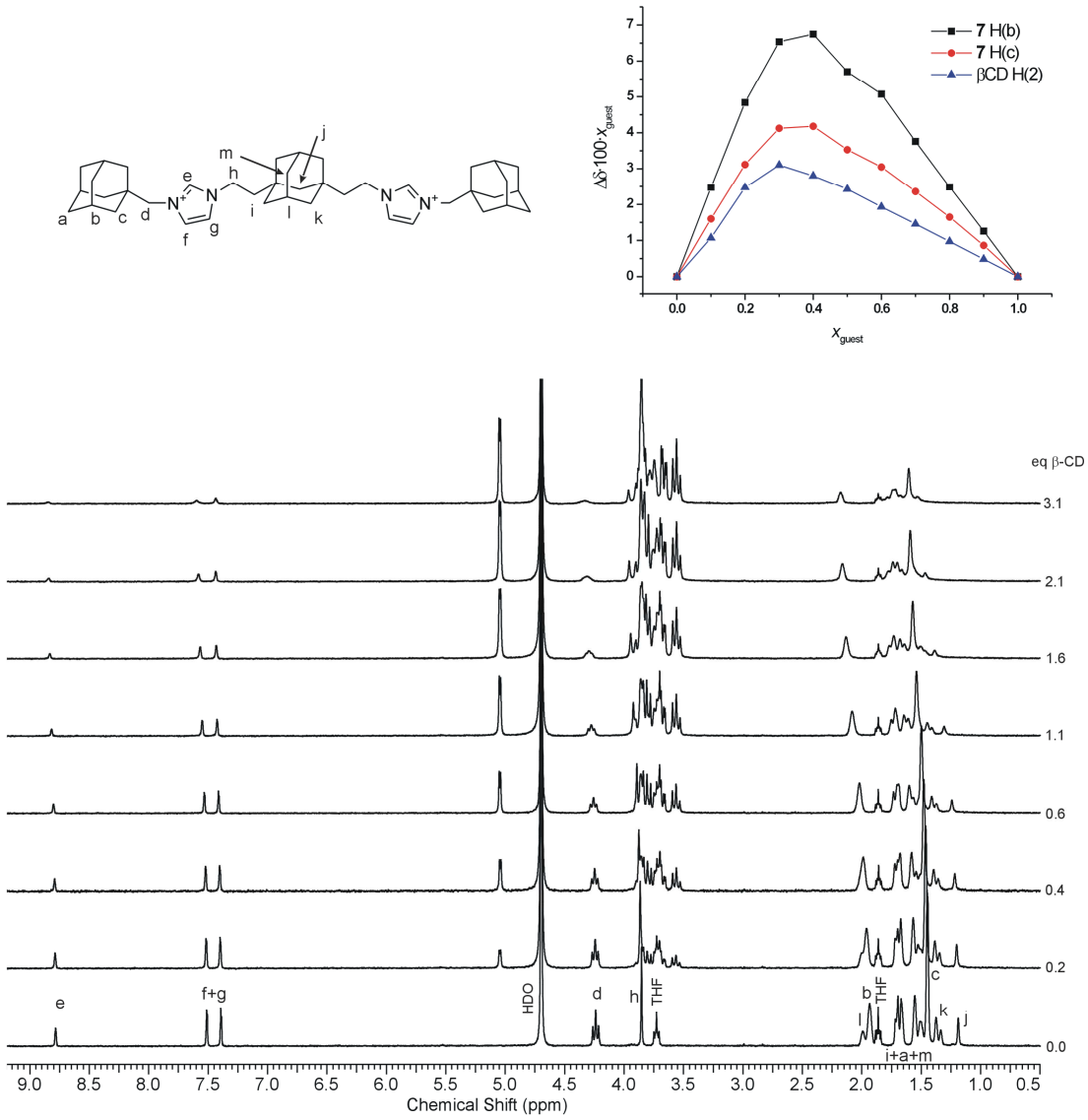


Figure S17 Stacking plot of the ^{1}H NMR spectra for the guest **7** and β-CD mixture in D_2O. Inserted graph displays Job plot obtained in separate experiment. Spectra were recorded at 303 K.

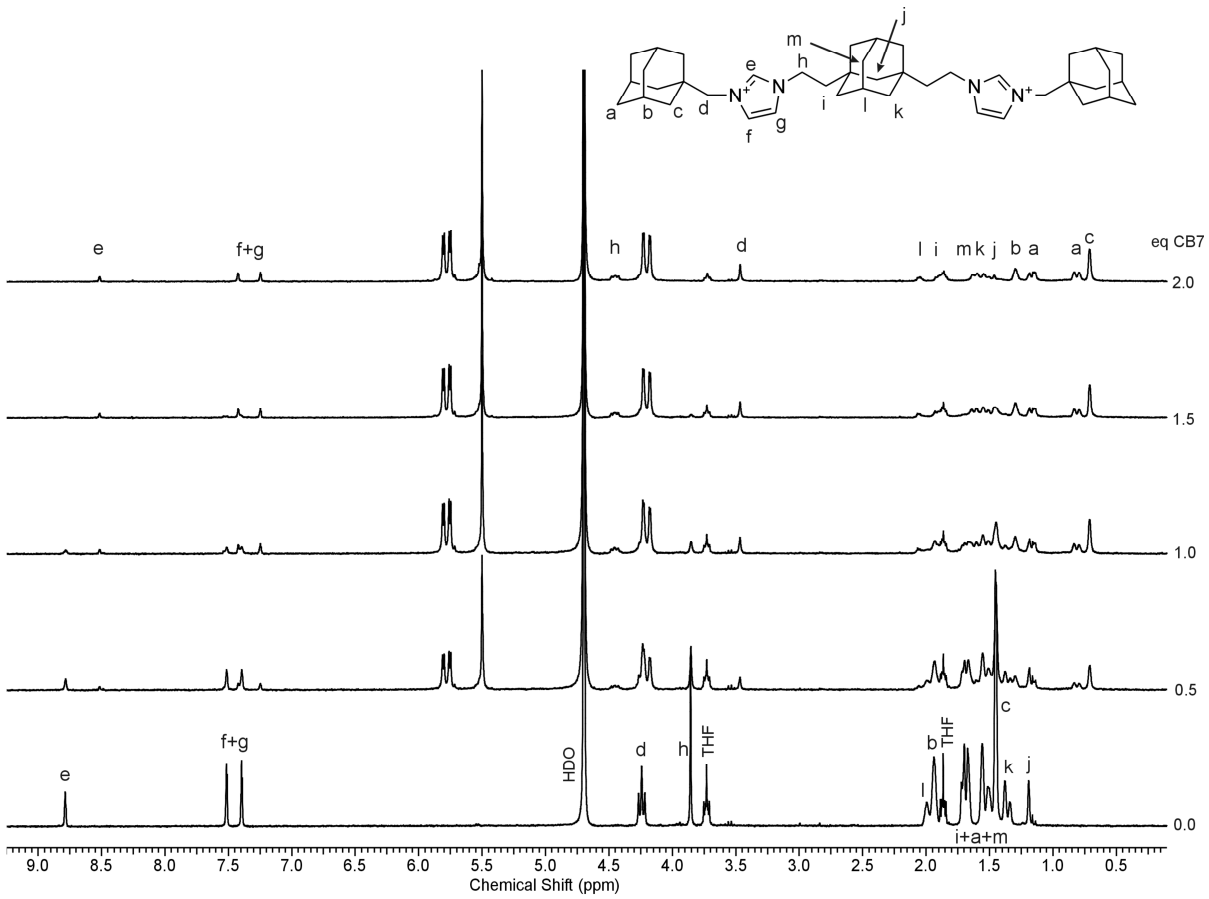


Figure S18 Stacking plot of the ^{1}H NMR spectra for the guest **7** and CB7 mixture in D_2O. Spectra were recorded at 303 K

NMR data for quaternary systems

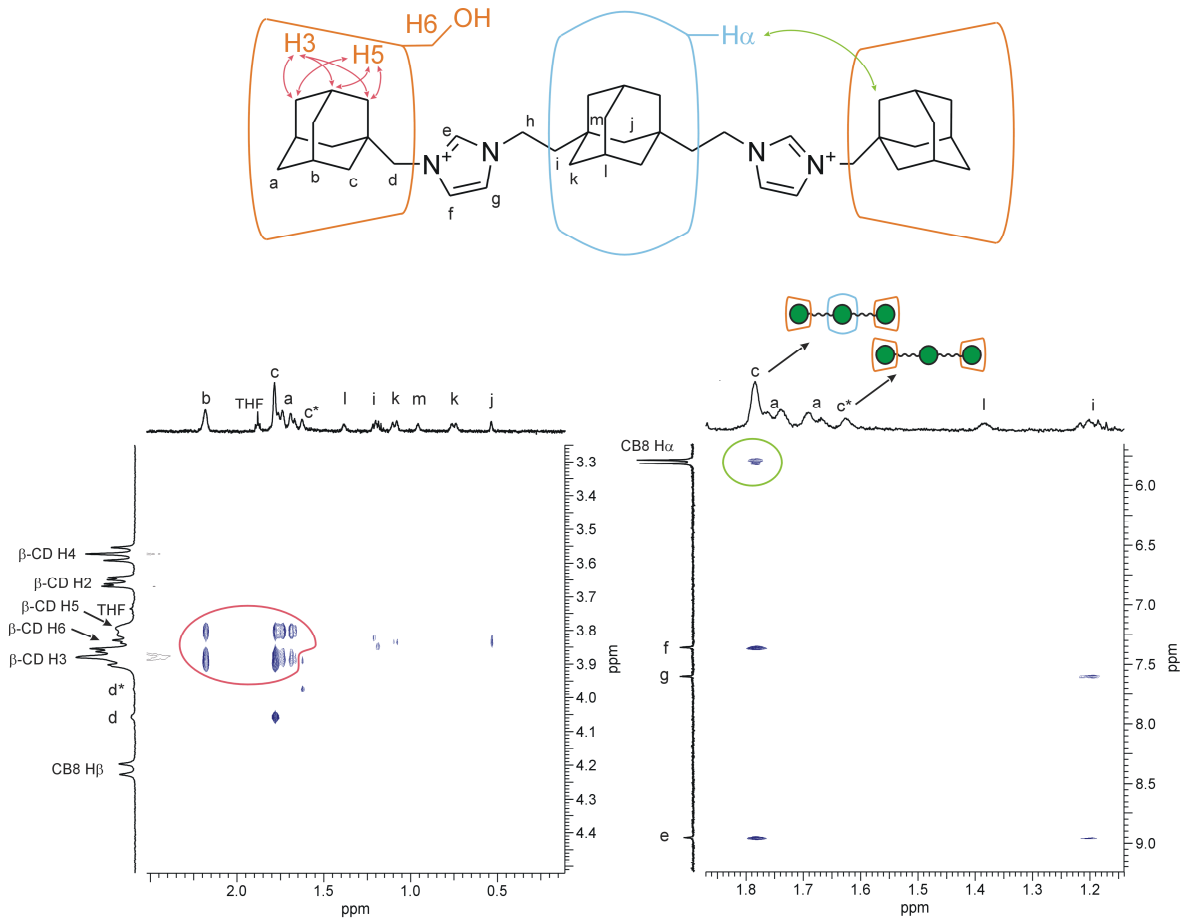


Figure S19 Portions of ROESY spectrum of mixture containing **7**, CB8, and β-CD in molar ratio 1:1:5 in 50 mM NaCl in D_2O at 303 K. The ^1H NMR of the authentic sample is depicted in Figure S20, top line.

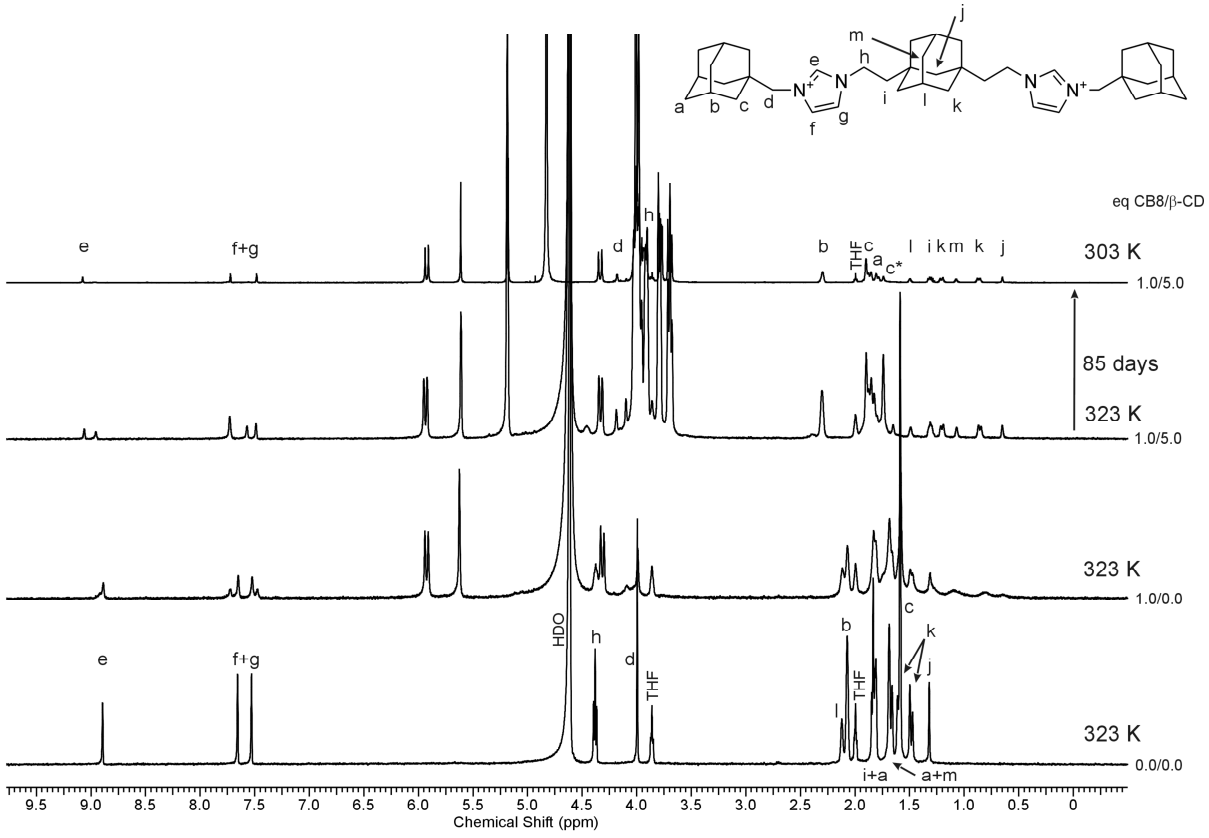


Figure S20 Stacking plot of the ^{1}H NMR spectra for the guest **7** and hosts CB8 and β-CD in D_2O.

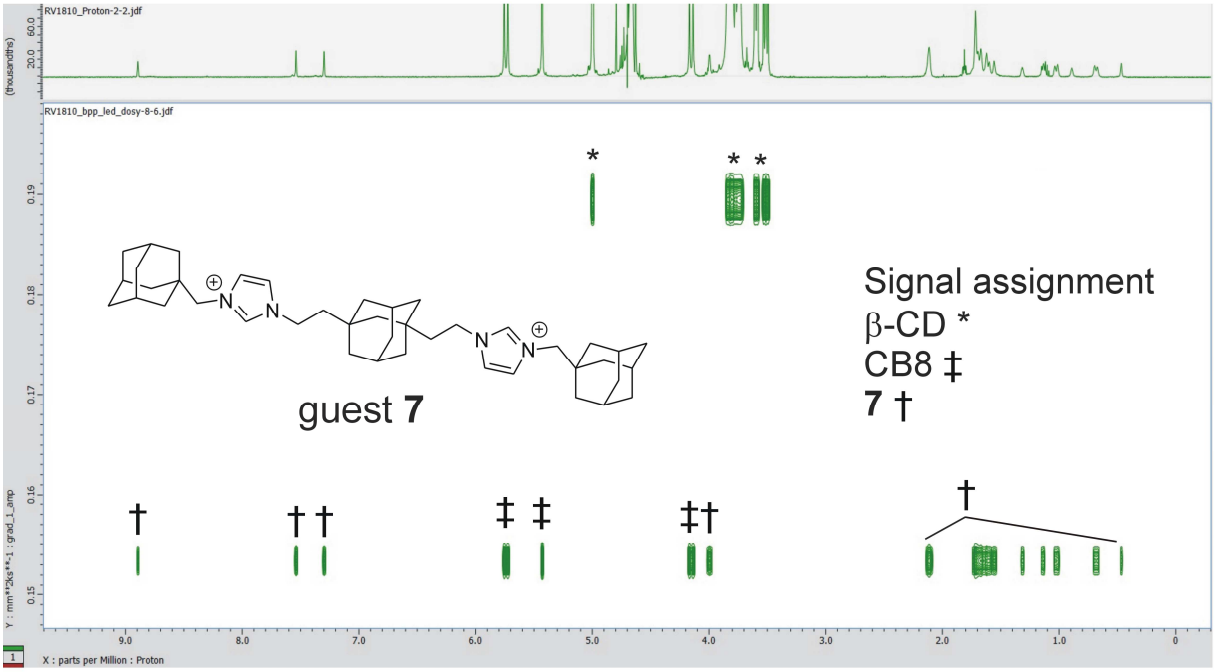


Figure S20a DOSY spectrum of mixture of **7**, CB8, and β-CD (1:1:5; top line in Figure S20).

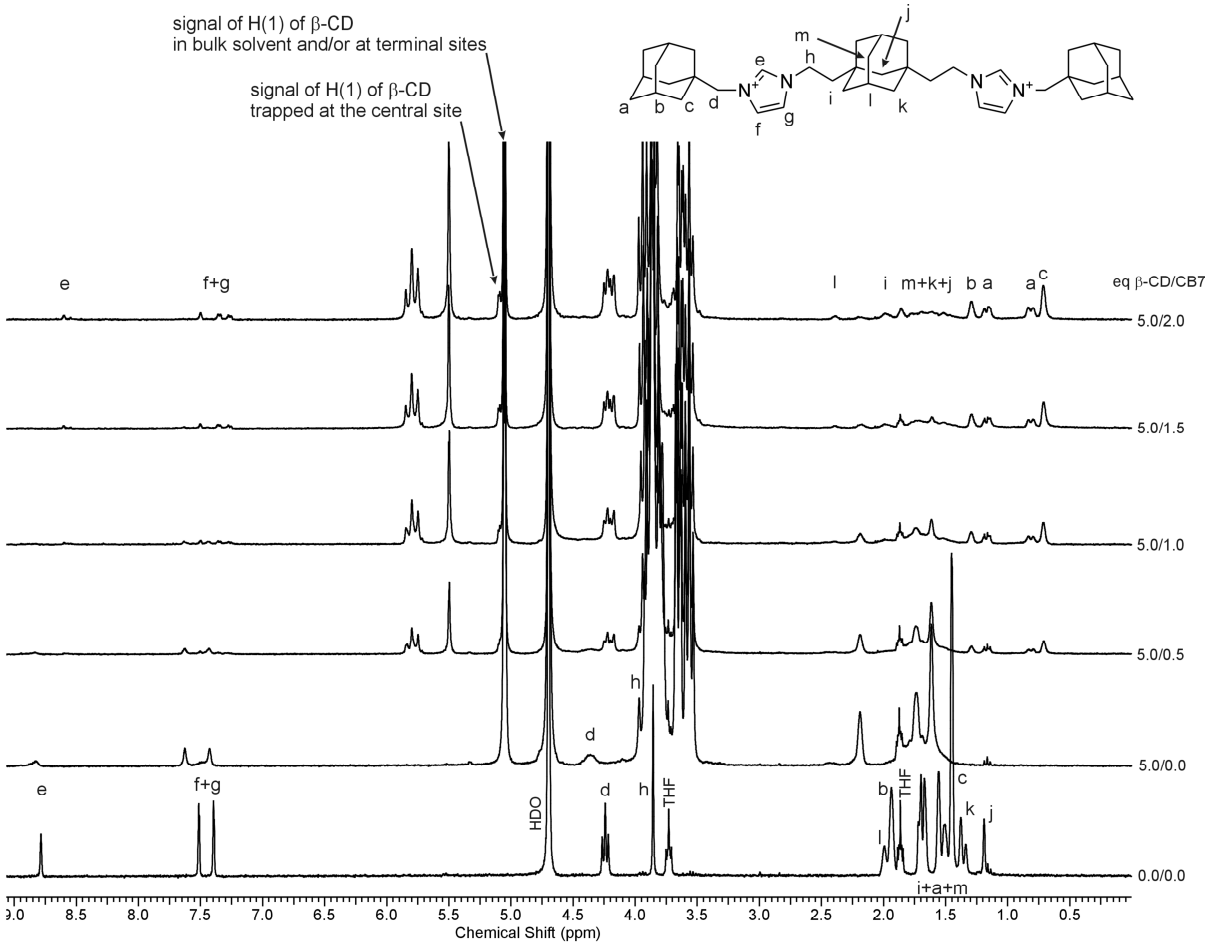


Figure S21 Stacking plot of the ^{1}H NMR spectra for the guest **7** and hosts CB7 and β-CD in D_2O. Spectra were recorded at 303 K.

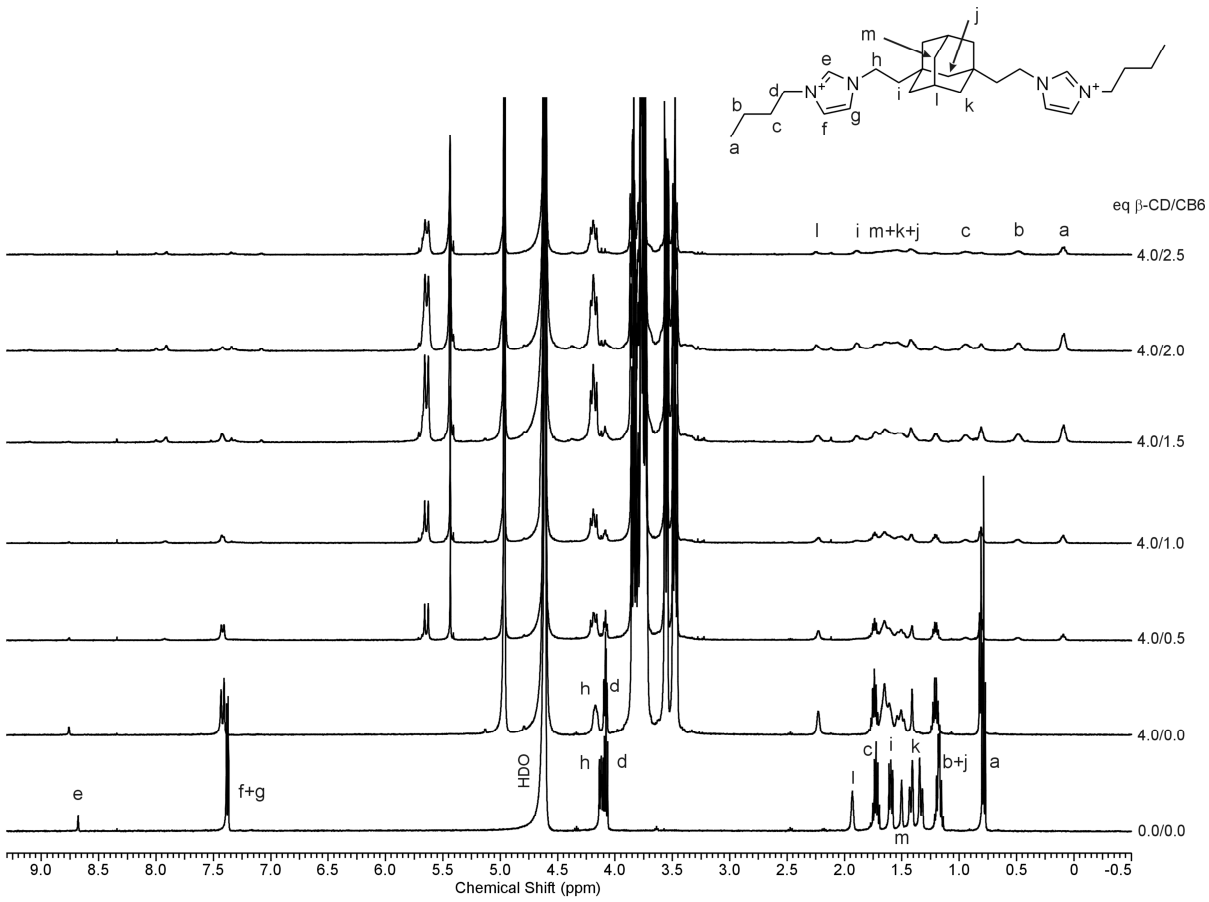


Figure S22 Stacking plot of the ^{1}H NMR spectra for the guest **6** and hosts CB6 and β-CD in 50 mM NaCl in D_2O. Spectra were recorded at 303 K.

ITC data

Table S1 Full thermodynamic data for ITC experiments on interactions of guests **5**–**7** with β-CD, CB6, CB7, and CB8 at 303 K

guest	host	model[a]	*n*	*K* [M^{-1}] [b]	$-\Delta H$ [$kJ.mol^{-1}$]	ΔS [$J.mol^{-1}\ K^{-1}$]	$-\Delta G$ [$kJ.mol^{-1}$]
5 [c]	β-CD	OSS	1.01±0.02	$1.82±0.01×10^4$	28.78±0.14	−13.46±0.23	24.70±0.07
5 [c,d]	CB7	OSS	1.04±0.01	$1.64±0.09×10^{11}$	70.19±0.88 (68.71±0.15)	−16±12	65.0±3.7
5 [c,e]	CB8	OSS	1.02±0.03	$5.3±0.3×10^{12}$	59.92±0.62 (47.76±0.02)	43±15	73.8±4.5
5 [f]	β-CD	OSS	1.02±0.03	$1.71±0.03×10^4$	29.00±0.30	−14.8±1.3	24.56±0.41
5 [d,f]	CB7	OSS	1.03±0.05	$3.5±0.3×10^{10}$	51.40±1.56 (52.01±0.54)	29±17	61.2±5.1
5 [e,f]	CB8	OSS	1.05±0.04	$3.4±0.2×10^{11}$	43.33±0.51 (37.64±0.72)	78±13	66.9±4.0
6 [c]	β-CD	OSS	0.99±0.01	$1.65±0.01·10^4$	31.24 ± 0.14	−22.29±0.50	24.49±0.07
		OSS	0.47±0.02	$1.23±0.17·10^6$	66.46±0.85	na	na
6 [g]	CB6	TSS	0.25±0.01	$1.30±0.01×10^6$	−14.63±0.14	165.24±0.63	35.47±0.01
			0.24±0.01	$1.36±0.02×10^6$	149.05±0.48	−374.77±1.67	35.57±0.03
		SEQ(2)	no reasonable result				
6 [c,d]	CB7	OSS	1.03±0.02	$1.29±0.11×10^{11}$	72.2 ± 1.0 (73.22±0.15)	−26±18	64.4±5.6
6 [c,e]	CB8	OSS	0.97±0.01	$3.29±0.15×10^{12}$	59.47±0.63 (51.5±1.1)	43±11	72.6±3.3
		OSS	0.41±0.01	$5.17±0.02×10^4$	17.16±0.13	na	na
		TSS	no reasonable result				
7 [c]	β-CD			$6.44±0.05×10^5$	25.40±0.01	27.3±0.3	33.69±0.01
		SEQ(3)	na	$6.87±0.11×10^4$	49.20±0.01	76.2±0.6	28.06±0.04
				$2.70±0.08×10^4$	−980±200	88±1	25.70±0.07
7 [c,h]	CB7	any model	no reasonable result				
7 [c,e]	CB8	any model	no reasonable result				

[a] Three models for data fitting were used: OSS=One Set of Sites, TSS=Two Sets of Sites, and SEQ(x)=Sequential binding considering x sites. [b] If the OSS model is used for multiple-site guest, the K_a are reported for single binding site. Experiments were performed in [c]water, [f]50 mM solution of AcONa, or [g]2.5 mM solution of NaCl. Competitors were used as follows: [d]1,6-hexamethylenediamine·2HCl; [e]1-adamantaneamine·HCl; [h]1-methyl-3-butylimidazolium bromide.

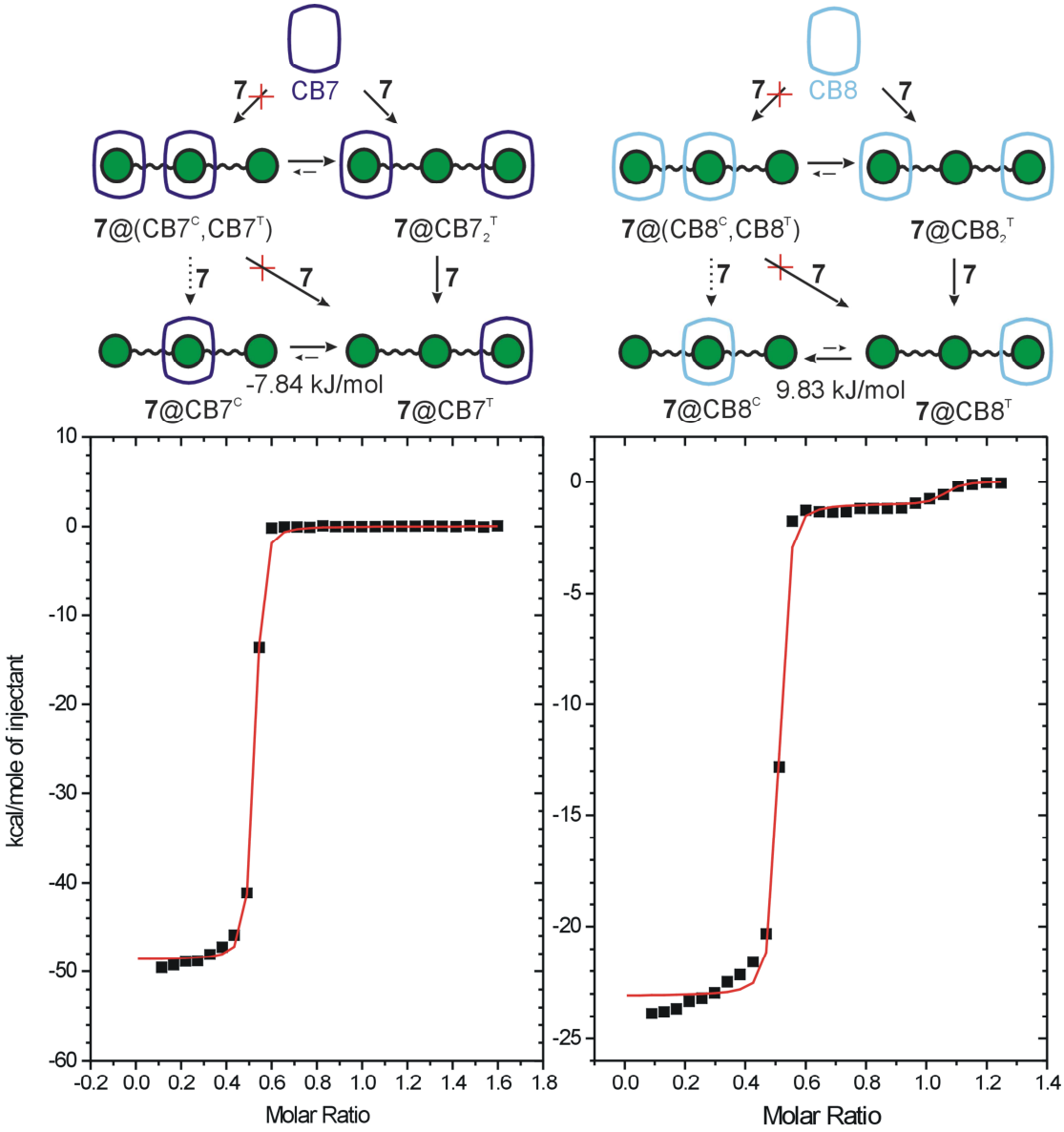


Figure S23 Assumed binding events and binding isotherms obtained by ITC for titration of the host CB7 (left) and with CB8 (right) with the guest **7** (guest in the syringe, host in the cell) in water at 303 K. Red lines denote the best fitting using OneSetSite (left) and TwoSetsSites (right) models. Unlike conversions are denoted by dotted arrows. Initial concentrations: c_{CB7}=0.0483 mM, c_7=0.4952 mM; c_{CB8}=0.0509 mM, c_7=0.2502 mM. Energy differences between the two distinct 1:1 complexes were calculated using model guests.

ESI-MS of binary and ternary systems

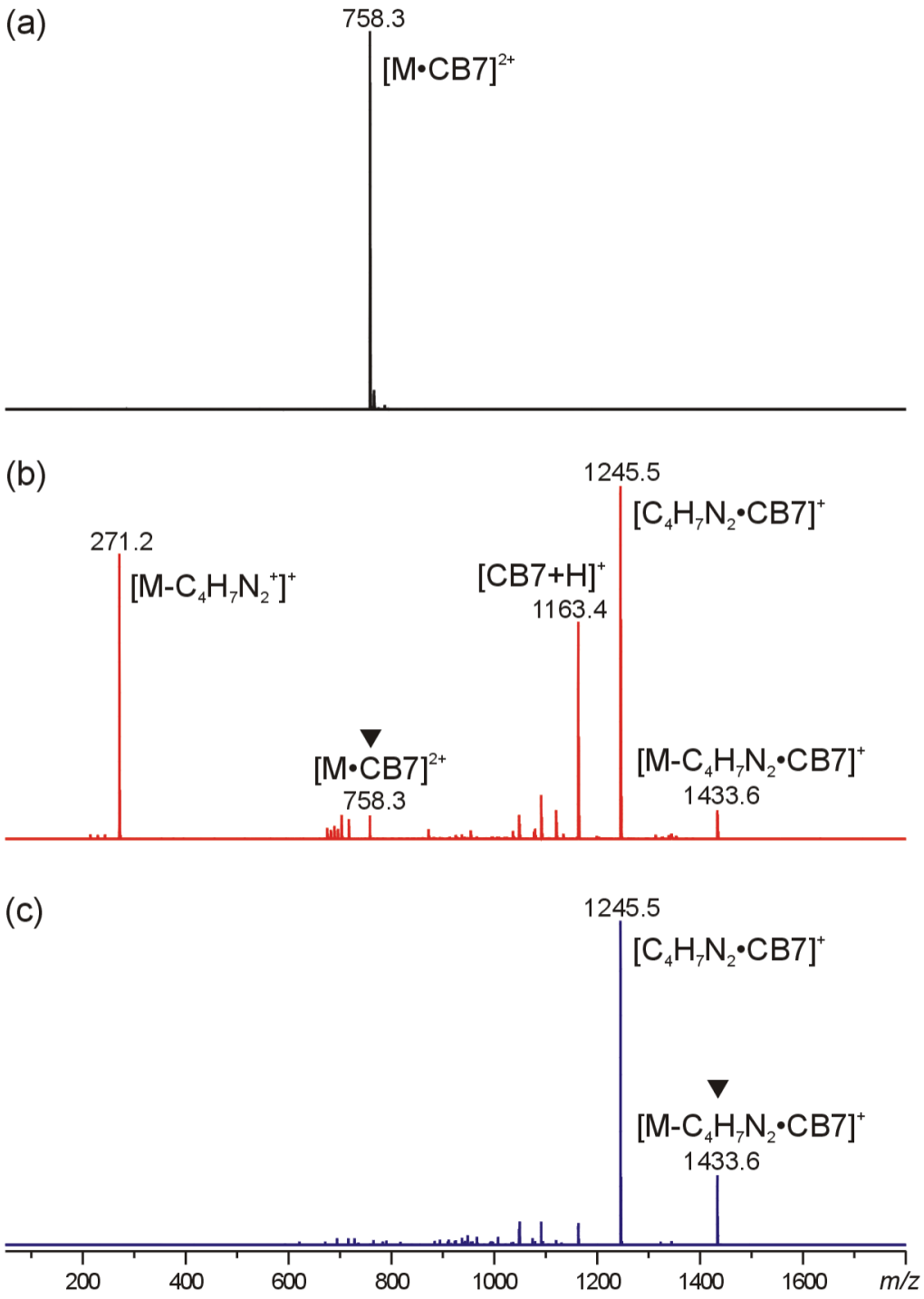


Figure S24 The positive-ion ESI mass spectra (full scan) of an aqueous solution of **5**·CB7 in molar ratio of 1:1; (a) first-order mass spectra, (b) MS^2 of *m/z* 758, (c) MS^3 of *m/z* 1433. The assignments for observed signals are shown in the brackets. The fragmented ions in tandem mass spectra are marked with triangle.

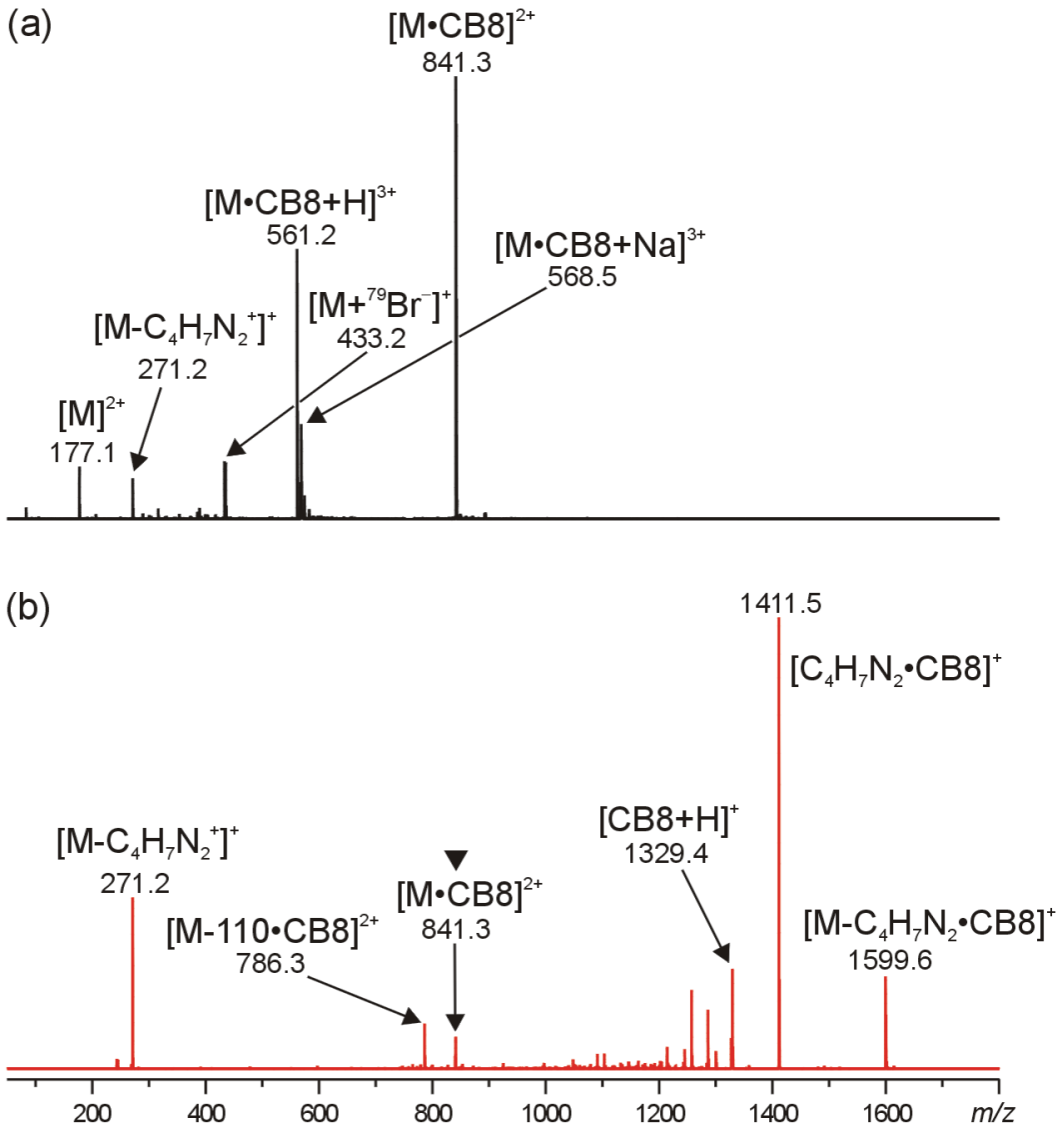


Figure S25 The positive-ion ESI mass spectra (full scan) of an aqueous solution of **5**·CB8 in molar ratio of 1:1; (a) first-order mass spectra, (b) MS^2 of *m/z* 841. The assignments for observed signals are shown in the brackets. The fragmented ion in tandem mass spectra is marked with triangle.

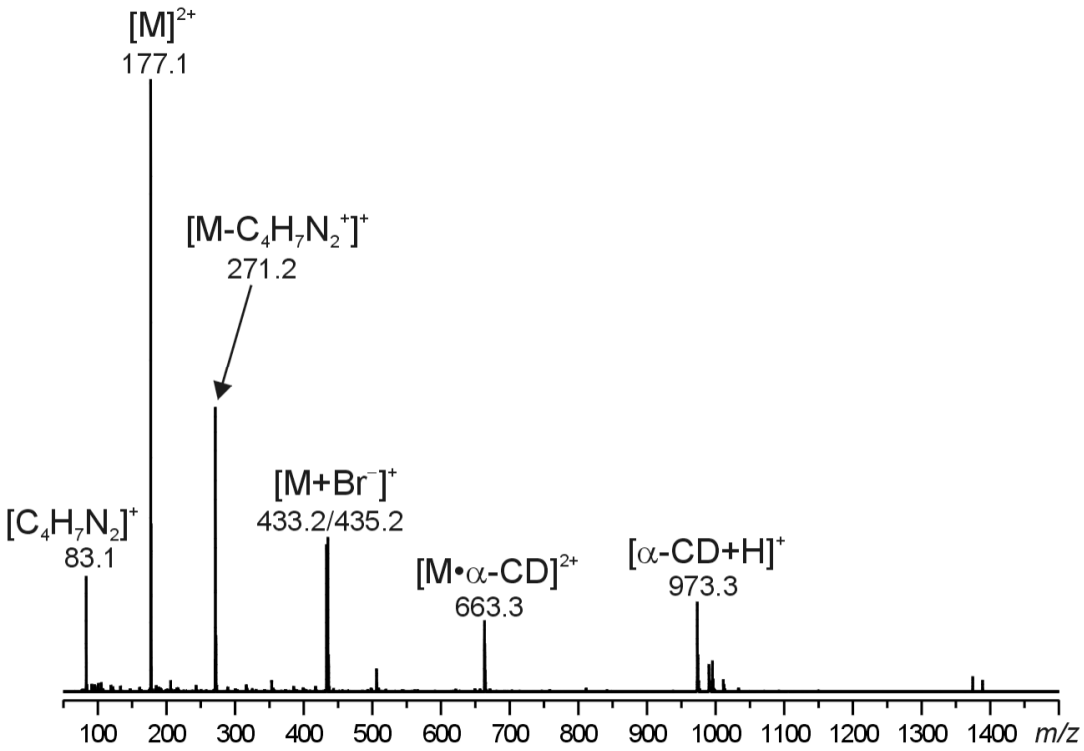


Figure S26 The positive-ion first-order ESI mass spectra (full scan) of an aqueous solution of **5**·α-CD in molar ratio of 1:1. The assignments for observed signals are shown in the brackets.

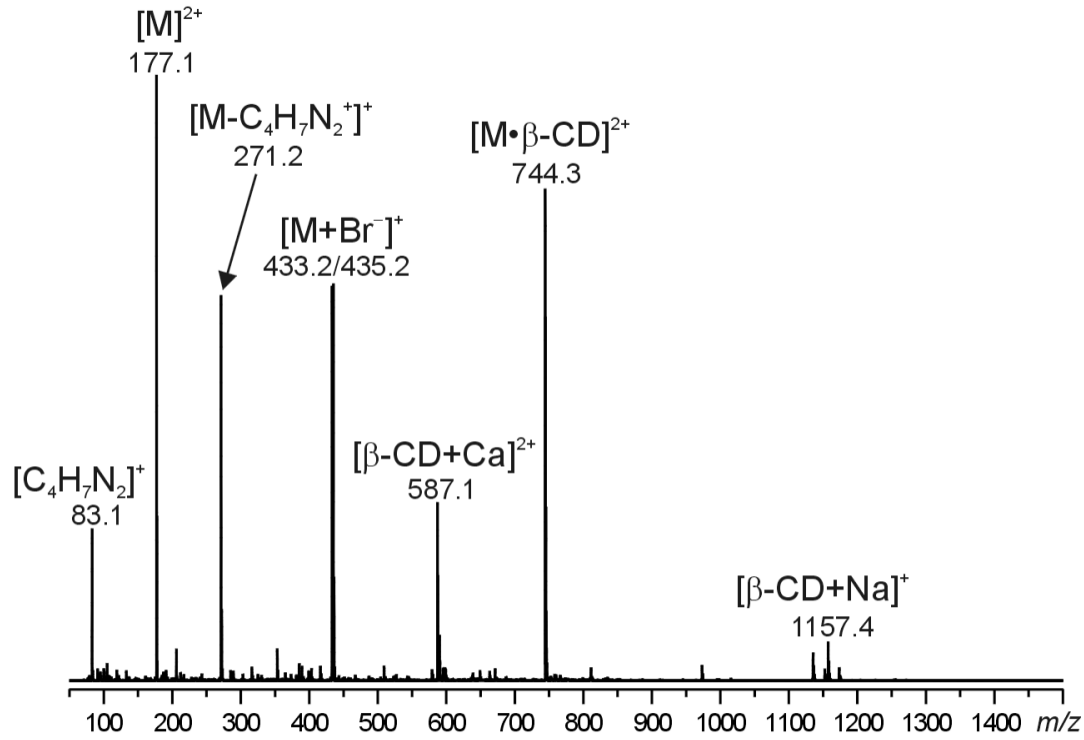


Figure S27 The positive-ion first-order ESI mass spectra (full scan) of an aqueous solution of **5**·β-CD in molar ratio of 1:1. The assignments for observed signals are shown in the brackets.

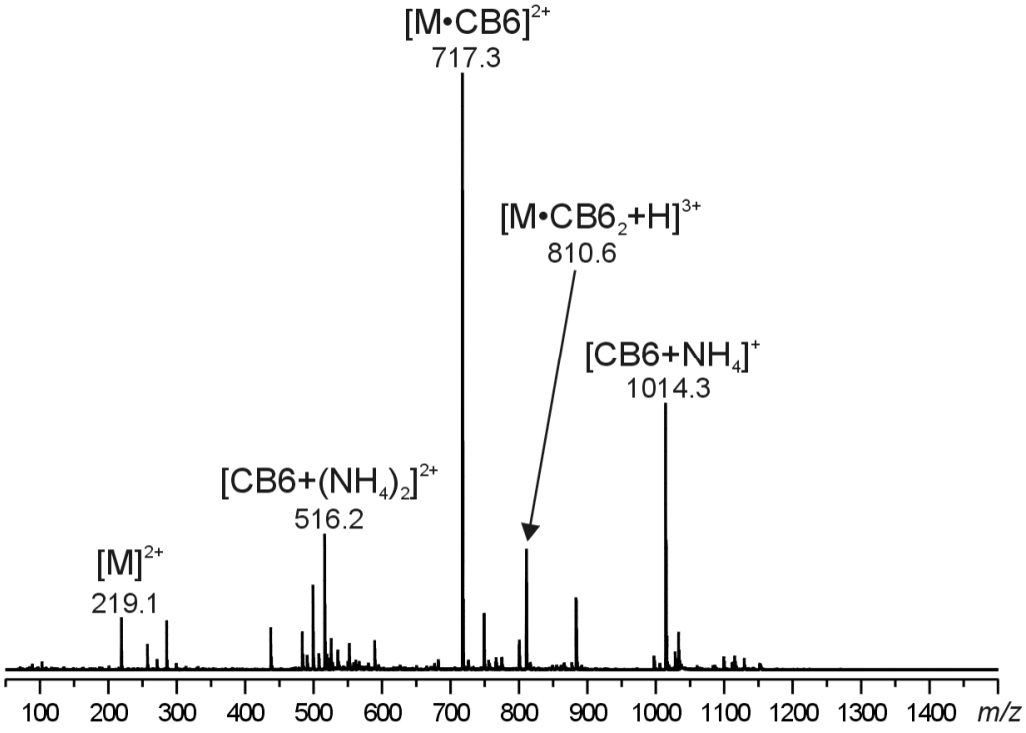
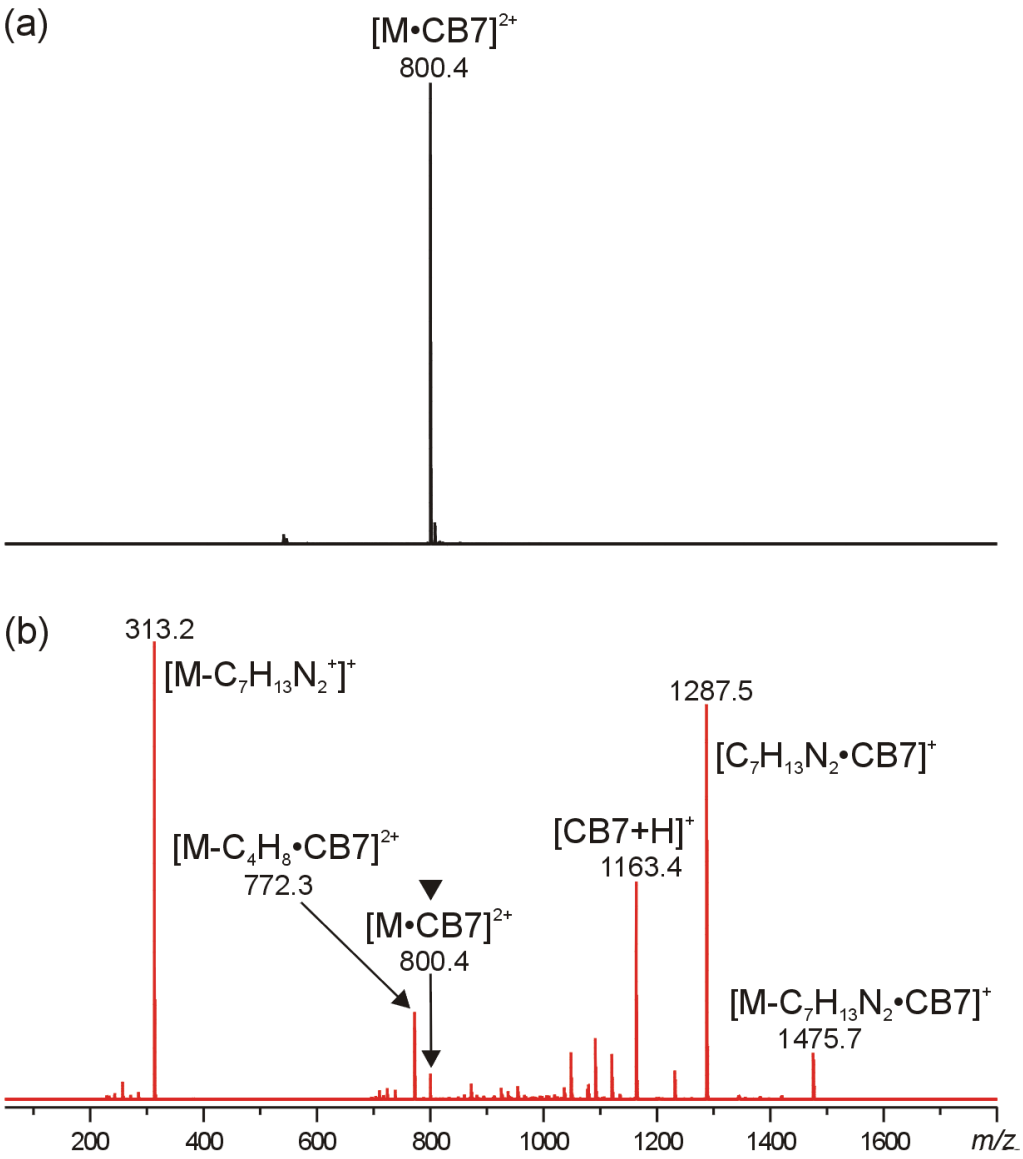


Figure S28 The positive-ion first-order ESI mass spectra (full scan) of an aqueous solution of **6**·CB6 in molar ratio of 1:5. The assignments for observed signals are shown in the brackets.



FigureS29 The positive-ion ESI mass spectra (full scan) of an aqueous solution of **6**·CB7 in molar ratio of 1:1; (a) first-order mass spectra, (b) MS^2 of *m/z* 800. The assignments for observed signals are shown in the brackets. The fragmented ion in tandem mass spectra is marked with triangle.

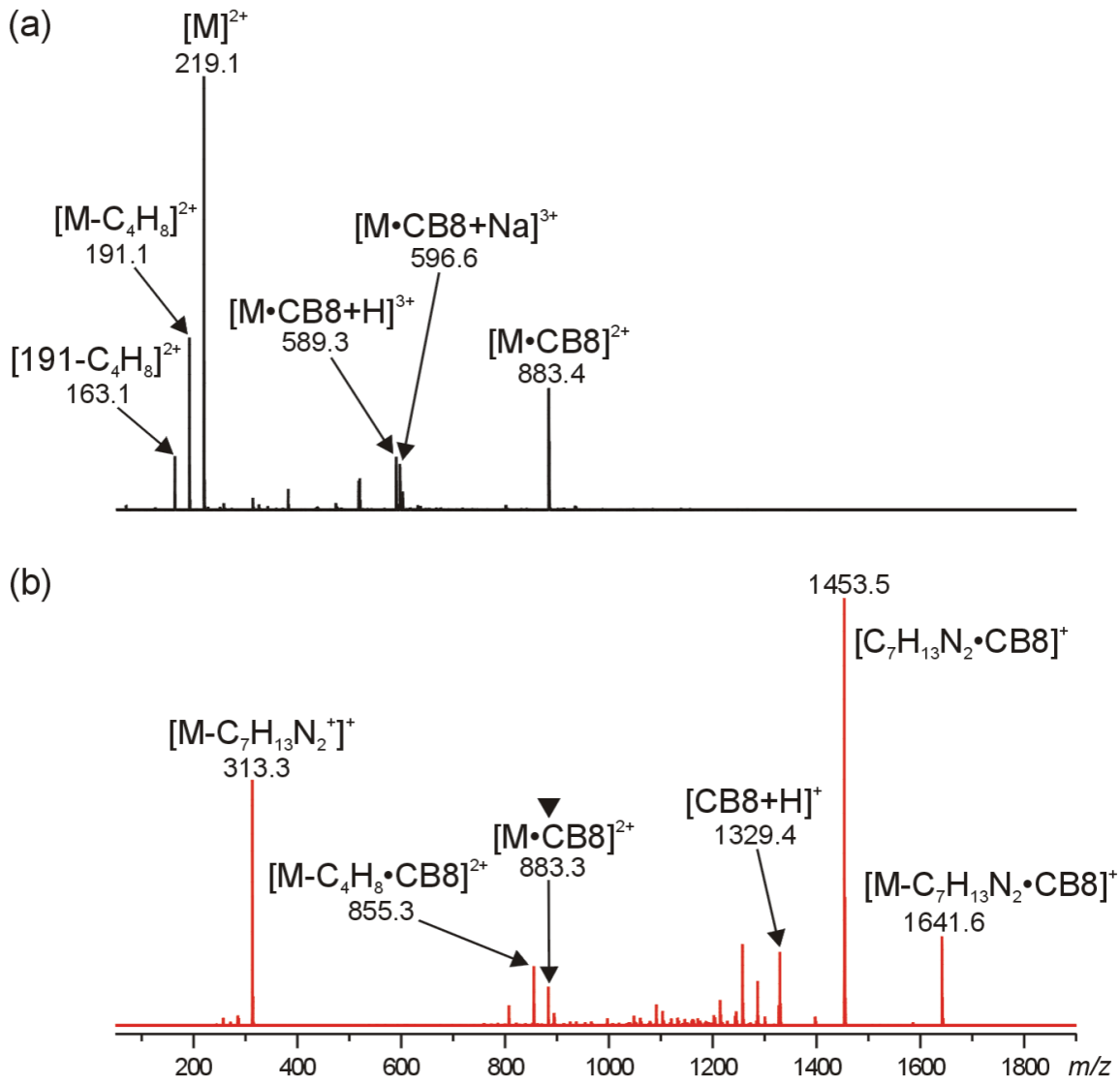


Figure S30 The positive-ion ESI mass spectra (full scan) of an aqueous solution of **6**·CB8 in molar ratio of 1:1; (a) first-order mass spectra, (b) MS^2 of *m/z* 883. The assignments for observed signals are shown in the brackets. The fragmented ion in tandem mass spectra is marked with triangle.

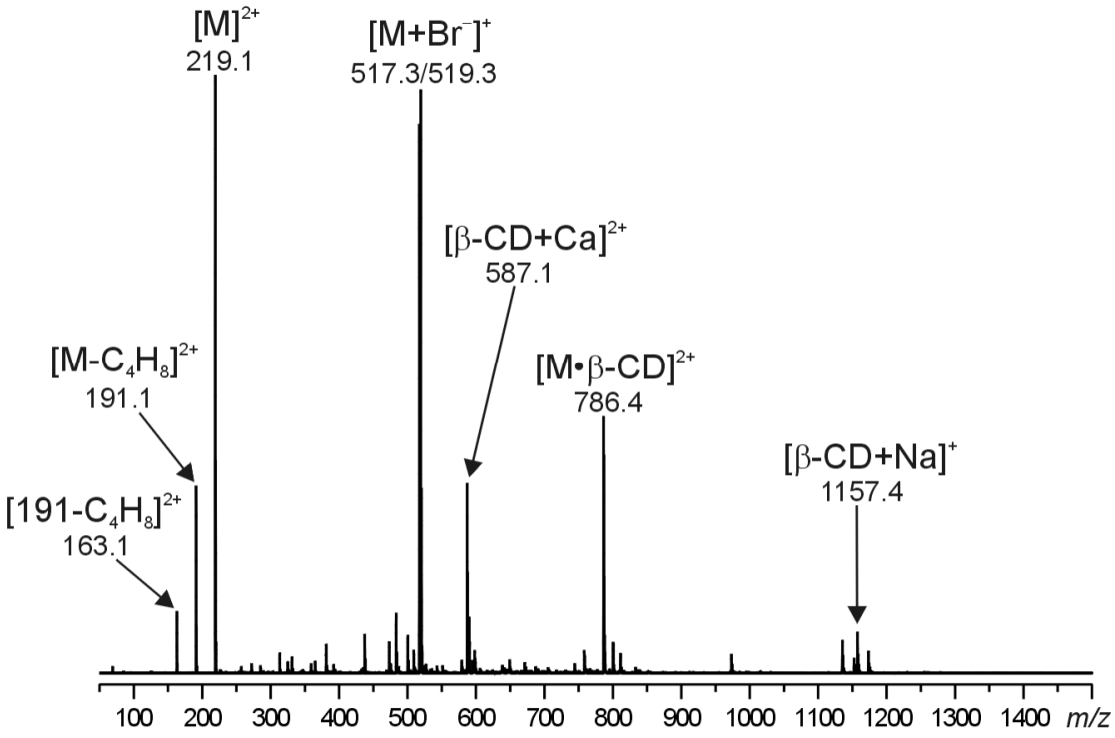


Figure S31 The positive-ion first-order ESI mass spectra (full scan) of an aqueous solution of **6**·β-CD in molar ratio of 1:1. The assignments for observed signals are shown in the brackets.

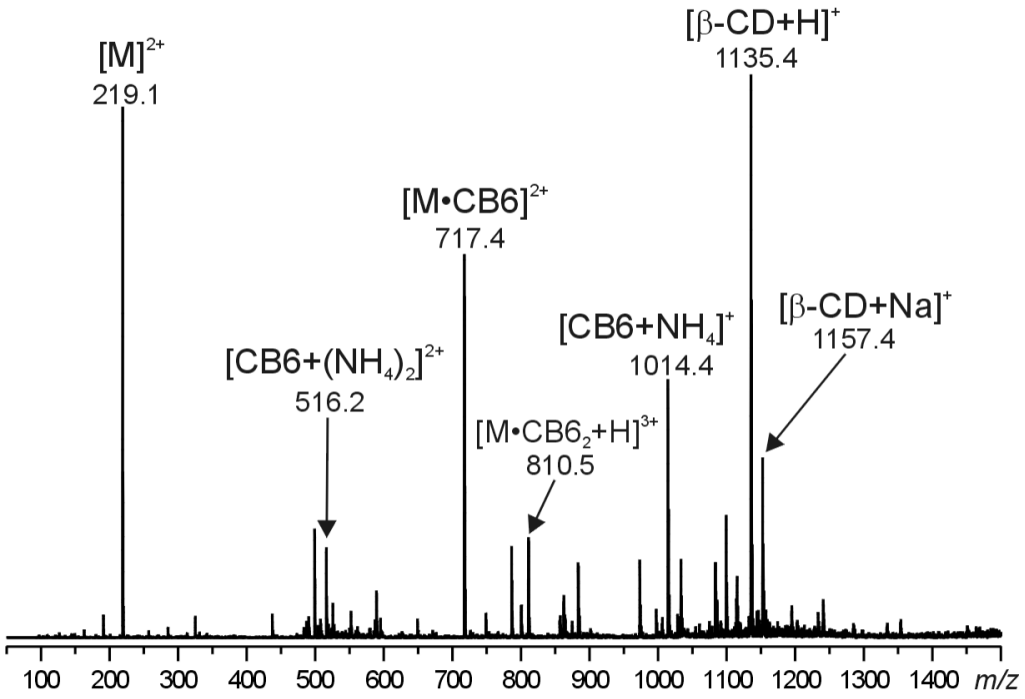


Figure S32 The positive-ion first-order ESI mass spectra (full scan) of an aqueous solution of **6**·CB6, β-CD in molar ratio of 1:2:5. The assignments for observed signals are shown in the brackets.

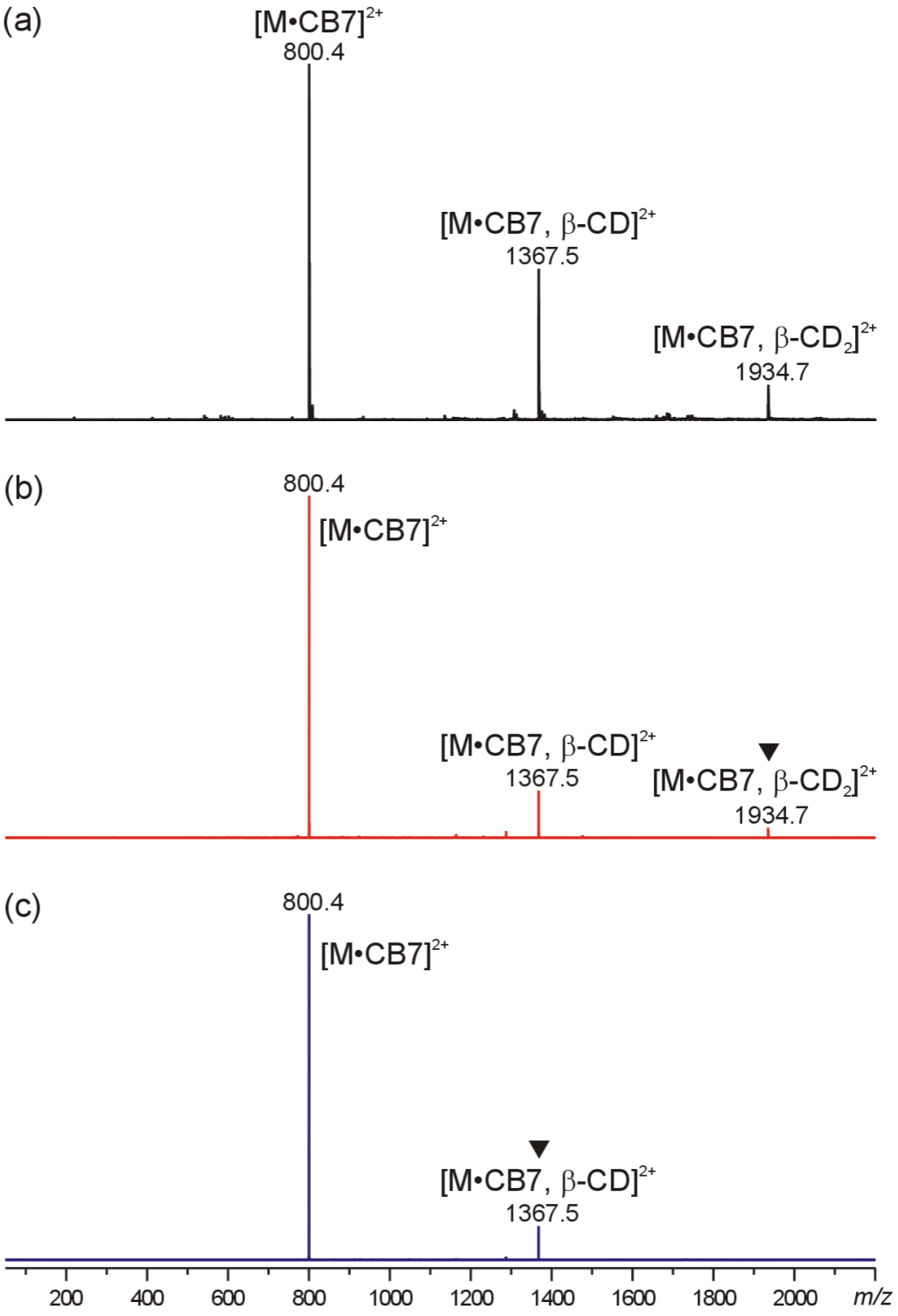


Figure S33 The positive-ion ESI mass spectra (full scan) of an aqueous solution of **6**·CB7, β-CD in molar ratio of 1:2:5; (a) first-order mass spectra, (b) MS^2 of *m/z* 1934, (c) MS^3 of *m/z* 1367. The assignments for observed signals are shown in the brackets. The fragmented ions in tandem mass spectra are marked with triangle.

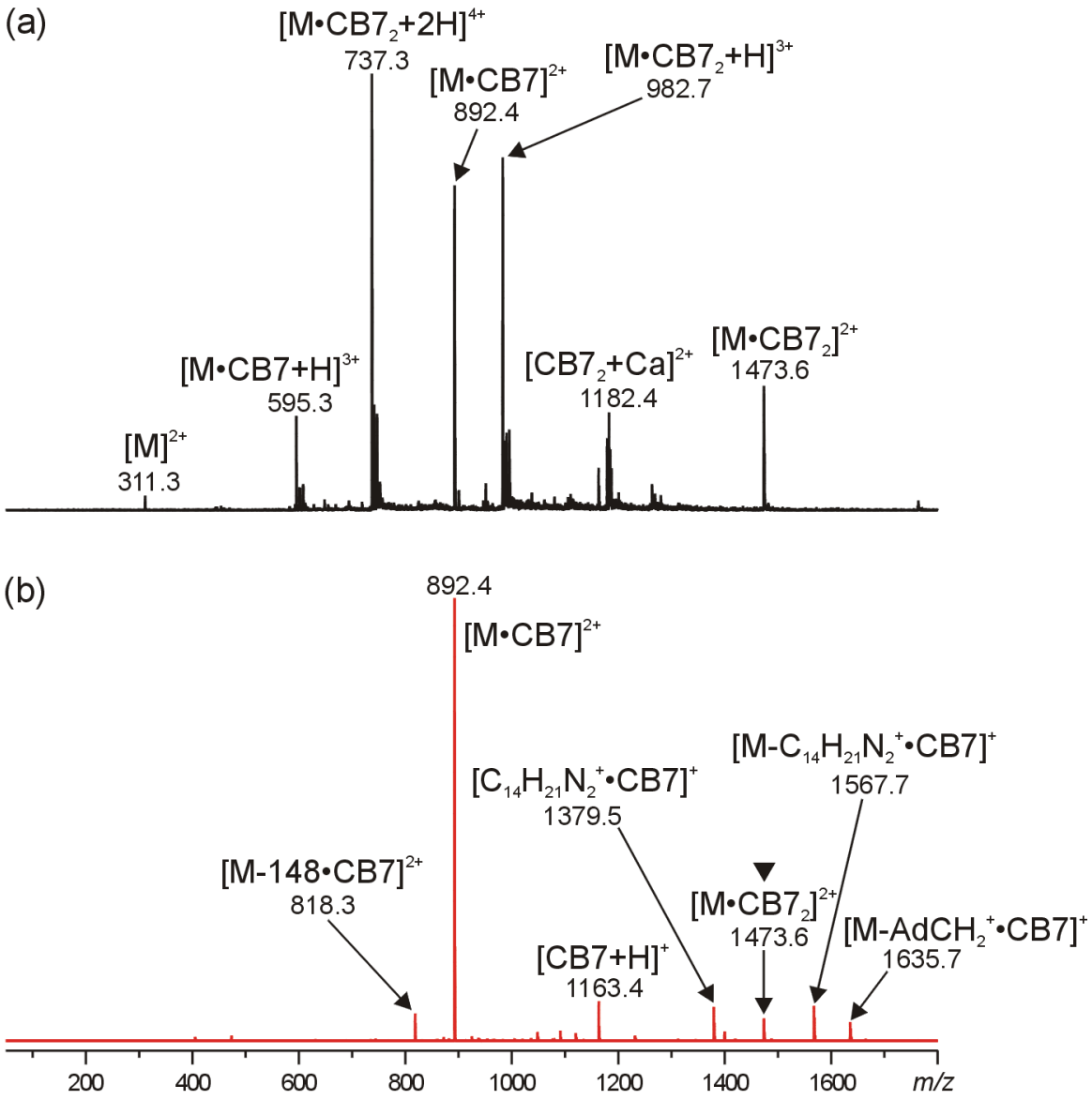


Figure S34 The positive-ion ESI mass spectra (full scan) of an aqueous solution of **7**·CB7 in molar ratio of 1:2; (a) first-order mass spectra, (b) MS^2 of *m/z* 1473. The assignments for observed signals are shown in the brackets. The fragmented ion in tandem mass spectra is marked with triangle.

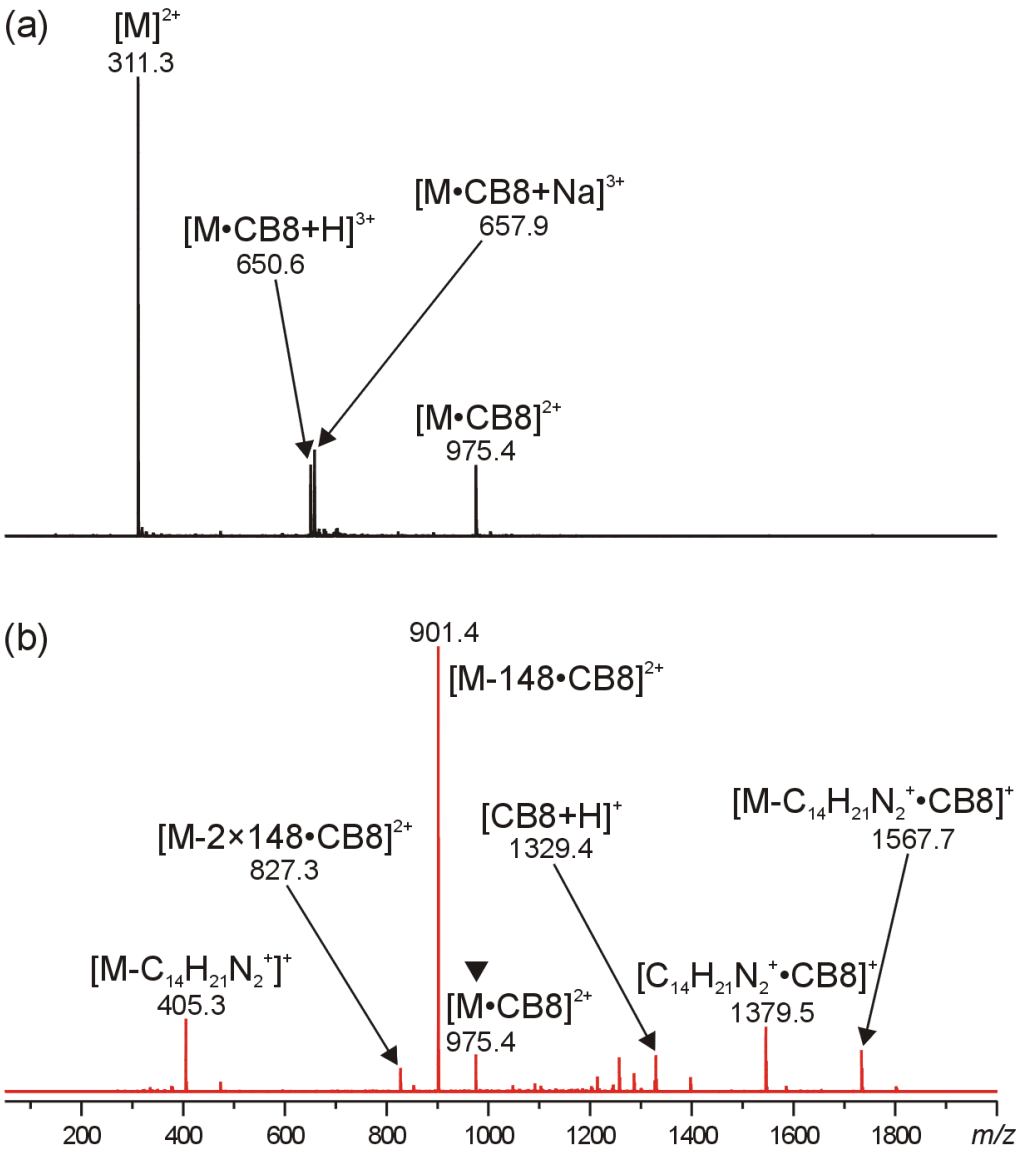


Figure S35 The positive-ion ESI mass spectra (full scan) of an aqueous solution of **7**·CB8 in molar ratio of 1:1; (a) first-order mass spectra, (b) MS^2 of *m/z* 975. The assignments for observed signals are shown in the brackets. The fragmented ion in tandem mass spectra is marked with triangle.

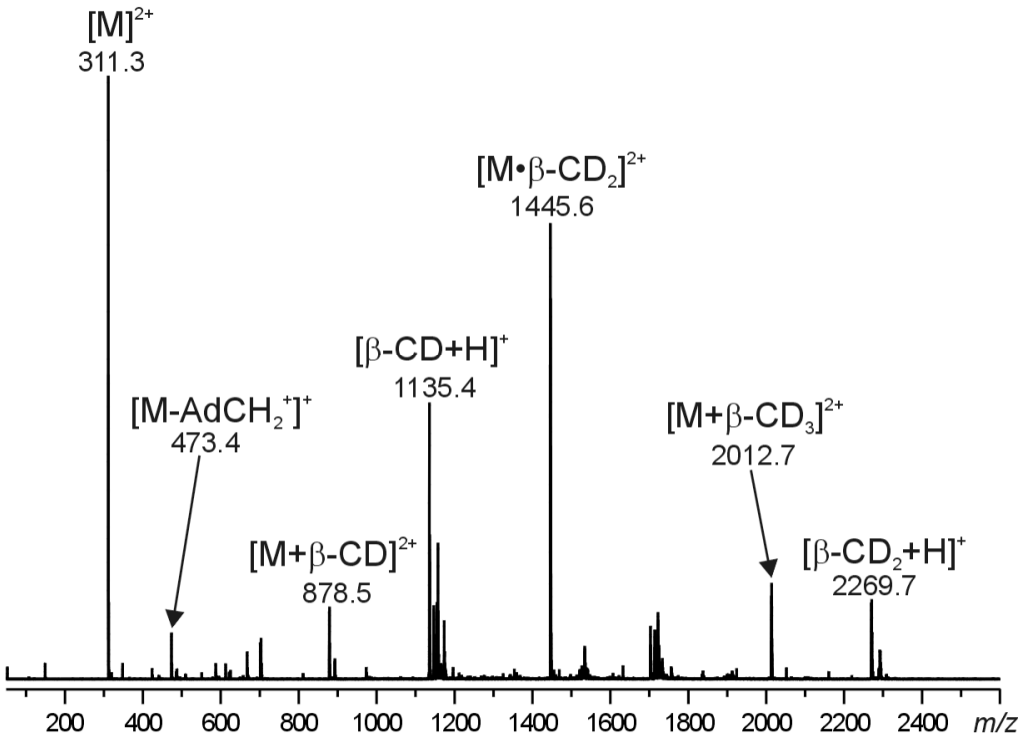


Figure S36 The positive-ion first-order ESI mass spectra (full scan) of an aqueous solution of **7**·β-CD in molar ratio of 1:5. The assignments for observed signals are shown in the brackets.

The MS data for quaternary systems

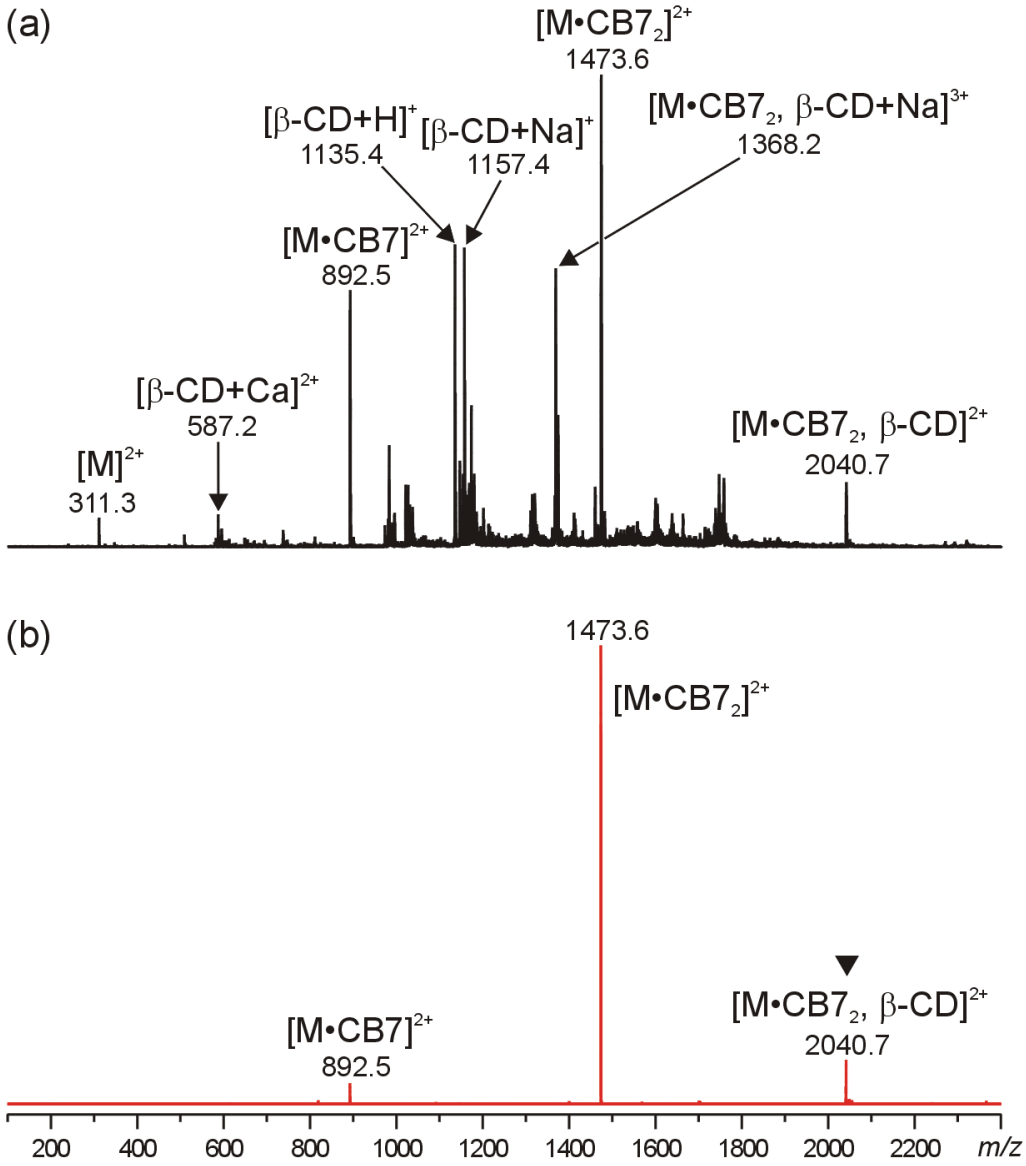


Figure S37 The positive-ion ESI mass spectra (full scan) of an aqueous solution of **7**·CB7, β-CD in molar ratio of 1:2:5; (a) first-order mass spectra, (b) MS^2 of *m/z* 2040. The assignments for observed signals are shown in the brackets. The fragmented ion in tandem mass spectra is marked with triangle.

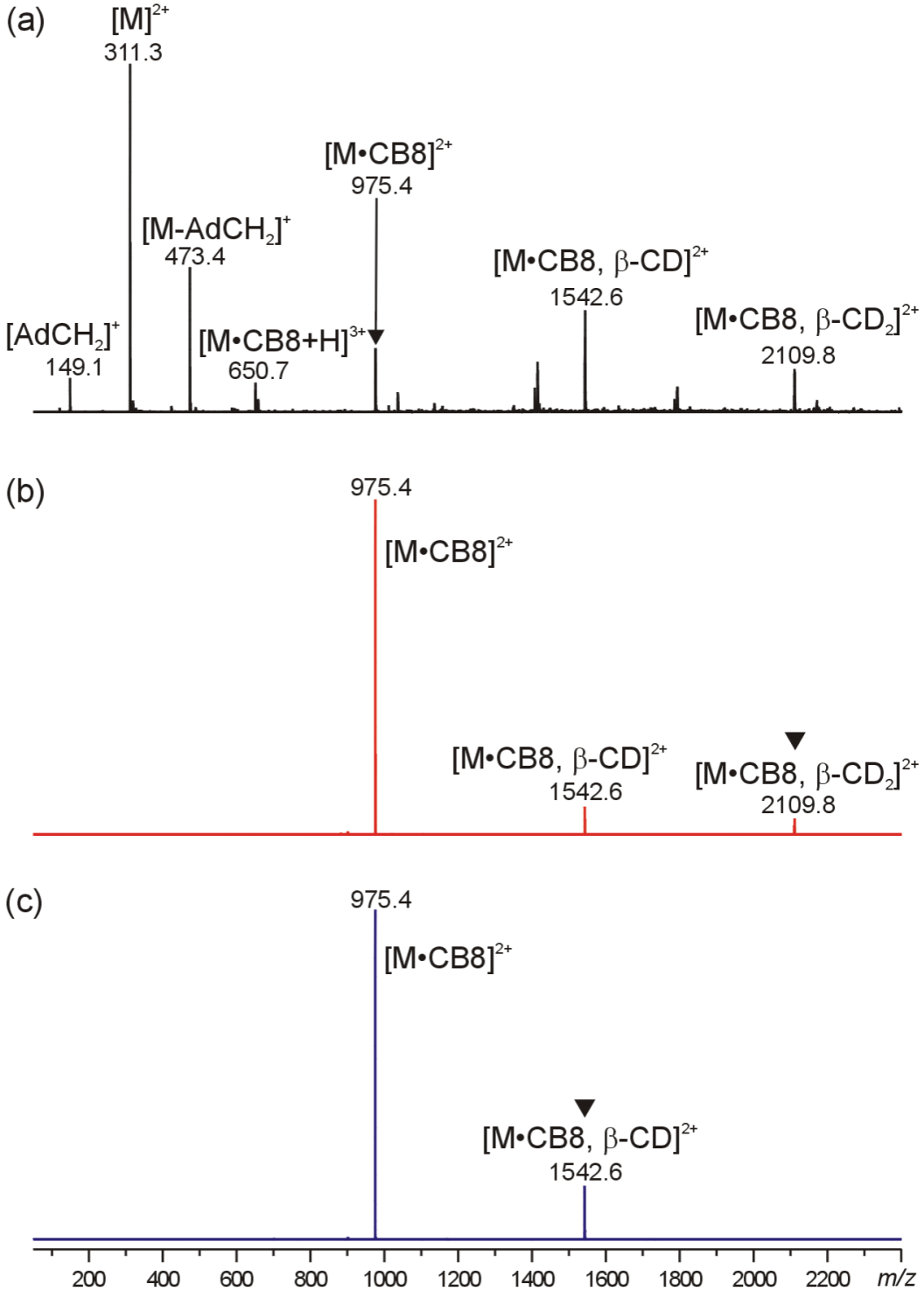


Figure S38 The positive-ion ESI mass spectra (full scan) of an aqueous solution of **7**·CB8, β-CD in molar ratio of 1:1:2; (a) first-order mass spectra, (b) MS^2 of *m/z* 2109, (c) MS^3 of *m/z* 1542. The assignments for observed signals are shown in the brackets. The fragmented ions in tandem mass spectra are marked with triangle.