Electronic Supplementary Materials

NMR studies of inclusion complexes: naphthalene and natural cyclodextrins

Sylwia Jopa,[a] Jacek Wójcik,[b] Andrzej Ejchart[b] and Michał Nowakowski*[a]

[a] Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland.

[b] Institute of Biochemistry and Biophysics, Polish Academy of Sciences, Pawińskiego 5A, 02-106 Warszawa, Poland.

* Correspondence: lyam@chem.uw.edu.pl

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Table S1. Chemical shifts of apparent signals of naphthalene (NP) upon complexation with αCD. NP concentration, c(NP) = 47 μmol/dm^3. Host to guest ratio $R = c(\alpha CD)/c(NP)$.

R	Hα(1)	Hα(2)	Hα(3)	Hα(4)	Hβ(1)	Hβ(2)	Hβ(3)	Hβ(4)
0.00	7.9080	7.9041	7.9006	7.8965	7.5204	7.5166	7.5127	7.5088
19.46	7.9093	7.9053	7.9018	7.8978	7.5211	7.5173	7.5134	7.5093
41.41	7.9109	7.9069	7.9033	7.8992	7.5221	7.5182	7.5143	7.5103
60.19	7.9132	7.9093	7.9057	7.9017	7.5236	7.5198	7.5159	7.5121
74.55	7.9147	7.9106	7.9071	7.9030	7.5245	7.5206	7.5168	7.5129
150.21	7.9246	7.9209	7.9172	7.9131	7.5309	7.5274	7.5233	7.5196
441.38	7.9677	7.9635	7.9603	7.9562	7.5595	7.5559	7.5520	7.5481
662.34	7.9940	7.9903	7.9871	7.9831	7.5772	7.5734	7.5697	7.5661
1291.54	8.0371	8.0331	8.0299	8.0259	7.6057	7.6020	7.5982	7.5946

Table S2. Chemical shifts of apparent signals of naphthalene (NP) upon complexation with βCD for three independent measurements. NP concentration, c(NP) = 53 μmol/dm^3. Host to guest ratio $R = c(\beta CD)/c(NP)$.

NP/βCD – 1st measurement

R	Hα(1)	Hα(2)	Hα(3)	Hα(4)	Hβ(1)	Hβ(2)	Hβ(3)	Hβ(4)
0.00	7.9035	7.8992	7.8956	7.8912	7.5158	7.5118	7.5076	7.5036
0.83	7.9027	7.8984	7.8947	7.8904	7.5171	7.5129	7.5089	7.5048
2.38	7.9014	7.8971	7.8934	7.8891	7.5191	7.5150	7.5109	7.5068
3.74	7.9008	7.8965	7.8929	7.8886	7.5207	7.5166	7.5125	7.5084
5.60	7.8986	7.8943	7.8907	7.8863	7.5211	7.5170	7.5130	7.5088
9.33	7.8961	7.8918	7.8881	7.8839	7.5222	7.5181	7.5140	7.5099
12.38	7.8931	7.8888	7.8851	7.8808	7.5219	7.5179	7.5138	7.5097
16.94	7.8905	7.8861	7.8826	7.8782	7.5218	7.5179	7.5137	7.5097

NP/βCD – 2nd measurement

R	Hα(1)	Hα(2)	Hα(3)	Hα(4)	Hβ(1)	Hβ(2)	Hβ(3)	Hβ(4)
0.00	7.9031	7.8991	7.8958	7.8916	7.5155	7.5117	7.5078	7.5040
0.83	7.9022	7.8981	7.8947	7.8906	7.5166	7.5127	7.5088	7.5049
2.38	7.9008	7.8967	7.8932	7.8892	7.5186	7.5146	7.5107	7.5068
3.74	7.8999	7.8958	7.8923	7.8882	7.5197	7.5158	7.5120	7.5081
5.60	7.8982	7.8942	7.8907	7.8867	7.5206	7.5168	7.5130	7.5091
9.33	7.8953	7.8915	7.8881	7.8841	7.5214	7.5176	7.5138	7.5100
12.38	7.8925	7.8890	7.8855	7.8817	7.5214	7.5178	7.5142	7.5104
16.94	7.8905	7.8867	7.8834	7.8797	7.5218	7.5181	7.5146	7.5114

NP/βCD – 3rd measurement

R	Hα(1)	Hα(2)	Hα(3)	Hα(4)	Hβ(1)	Hβ(2)	Hβ(3)	Hβ(4)
0.00	7.9031	7.8991	7.8956	7.8916	7.5155	7.5116	7.5078	7.5039
0.83	7.9023	7.8982	7.8947	7.8907	7.5167	7.5128	7.5089	7.5050
2.38	7.9008	7.8967	7.8932	7.8892	7.5186	7.5146	7.5107	7.5068
3.74	7.9001	7.8960	7.8925	7.8885	7.5199	7.5160	7.5122	7.5083
5.60	7.8984	7.8943	7.8909	7.8868	7.5208	7.5170	7.5130	7.5093
9.33	7.8957	7.8917	7.8882	7.8842	7.5215	7.5178	7.5139	7.5103
12.38	7.8923	7.8885	7.8856	7.8818	7.5211	7.5177	7.5140	7.5110
16.94	7.8904	7.8871	7.8835	7.8801	7.5217	7.5182	7.5151	7.5118

Table S3. Chemical shifts of apparent signals of naphthalene (NP) upon complexation with γCD. NP concentration, c(NP) = 53 μmol/dm^3. Host to guest ratio $R = c(\gamma CD)/c(NP)$.

R	Hα(1)	Hα(2)	Hα(3)	Hα(4)	Hβ(1)	Hβ(2)	Hβ(3)	Hβ(4)
0.00	7.9031	7.8989	7.8955	7.8913	7.5154	7.5114	7.5076	7.5037
9.23	7.9026	7.8987	7.8950	7.8908	7.5164	7.5125	7.5087	7.5047
18.98	7.9020	7.8980	7.8944	7.8903	7.5181	7.5142	7.5103	7.5064
29.73	7.9012	7.8971	7.8935	7.8893	7.5212	7.5172	7.5134	7.5095
39.70	7.9002	7.8962	7.8925	7.8883	7.5236	7.5199	7.5159	7.5122
52.37	7.8995	7.8954	7.8918	7.8878	7.5262	7.5222	7.5182	7.5144
64.51	7.8989	7.8948	7.8911	7.8873	7.5281	7.5244	7.5205	7.5166
146.24	7.8948	7.8910	7.8879	7.8839	7.5411	7.5373	7.5333	7.5299
307.91	7.8903	7.8860	7.8826	7.8786	7.5601	7.5562	7.5527	7.5488

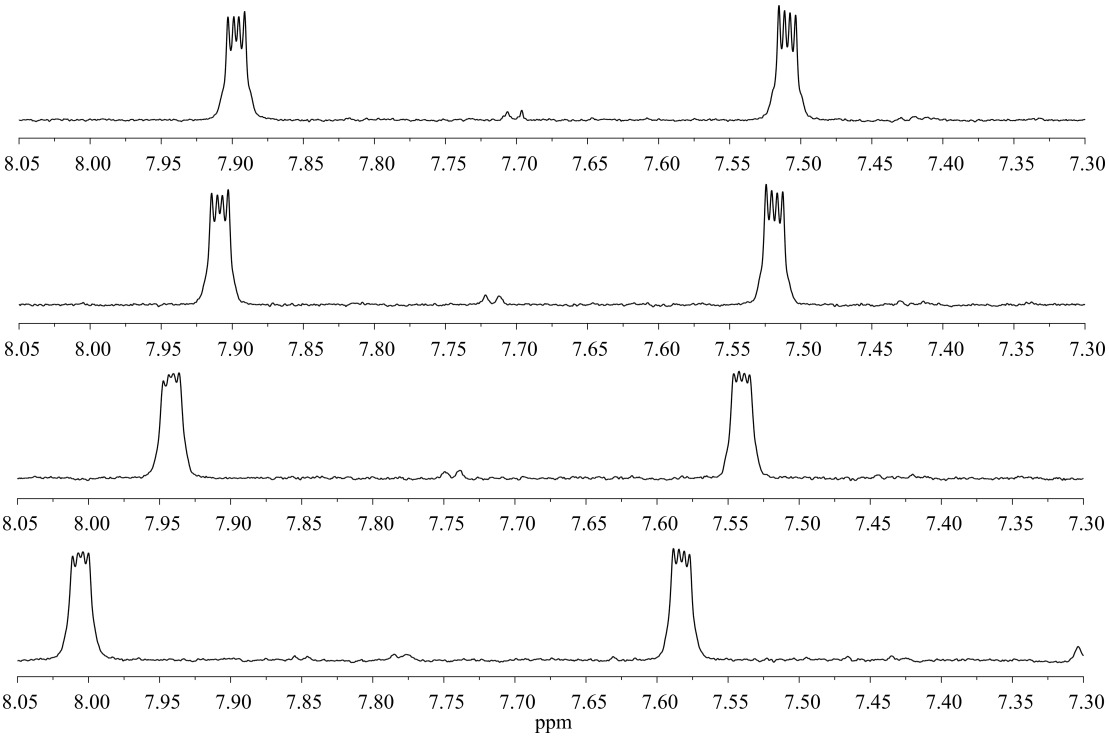

Figure S1

^{1}H NMR spectra of naphthalene titrated with αCD. Ratios R=c(αCD)/c(NP) are equal to: 0.0, 74.6, 441.4, and 1291.5 from top to bottom, respectively. NP complexation by αCD results in the deshielding of both proton groups. Signal-to-noise ratios (S/N) for Hα and Hβ protons are *ca*. 90 and fluctuate within the range ±15%. In order to determine values of integrals the following integration ranges have been used: Hα(NP) and Hβ(NP) – 0.1 ppm, H1(CD) – 0.08 ppm. Integrated signals have always been placed in the centre of a range.

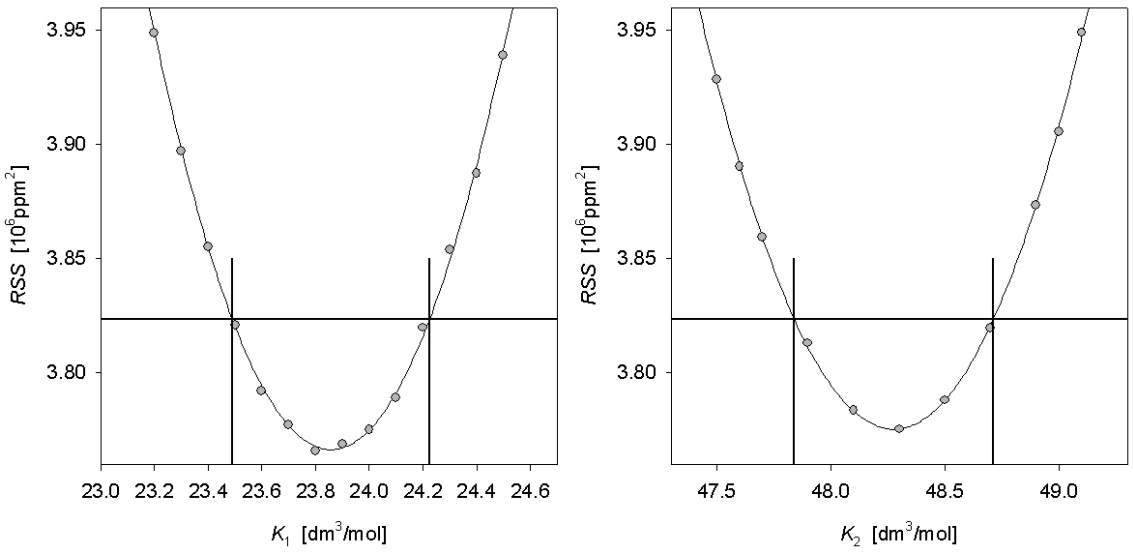

Figure S2

Determination of confidence limits of association constants estimated for NP/αCD complex by the use of an *F*-statistics. Horizontal line represent $RSS_{lim} = 3.8234$, which has been calculated by the formula: $RSS_{\lim} = RSS_{\min}\left[1 + F(1, DF, 0.3173)/DF\right]$. $RSS_{min} = 3.766$ has been found in the minimization procedure (Table 2), $DF = 66$ is the number of degrees of freedom and *F* is the value of an *F*-distribution.

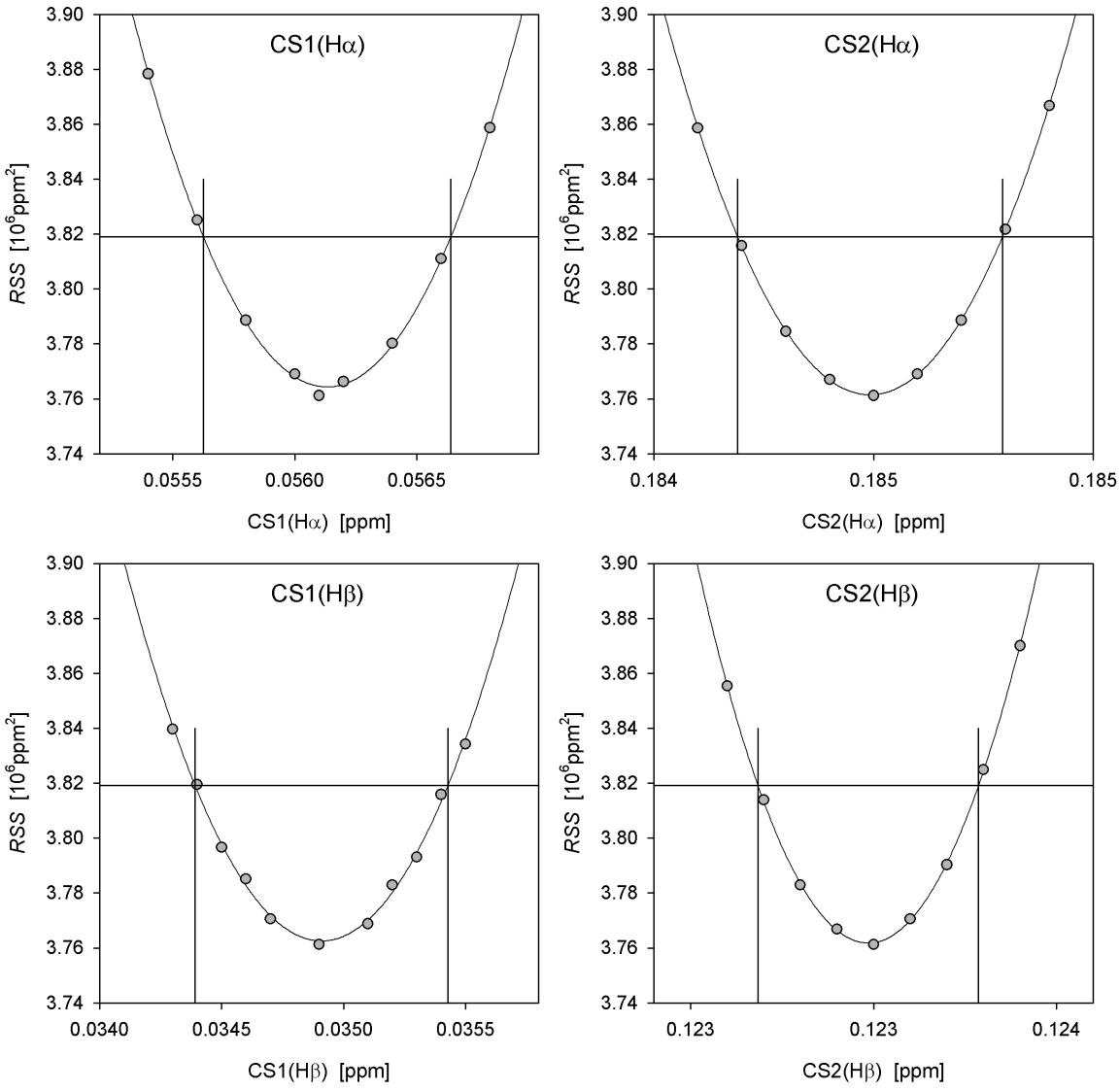

Figure S3

Determination of confidence limits of association constants estimated for NP/αCD complex by the use of an *F*-statistics. Horizontal lines represent RSS_{lim}. Calculation of RSS_{lim} is explained in the caption to Figure S2.

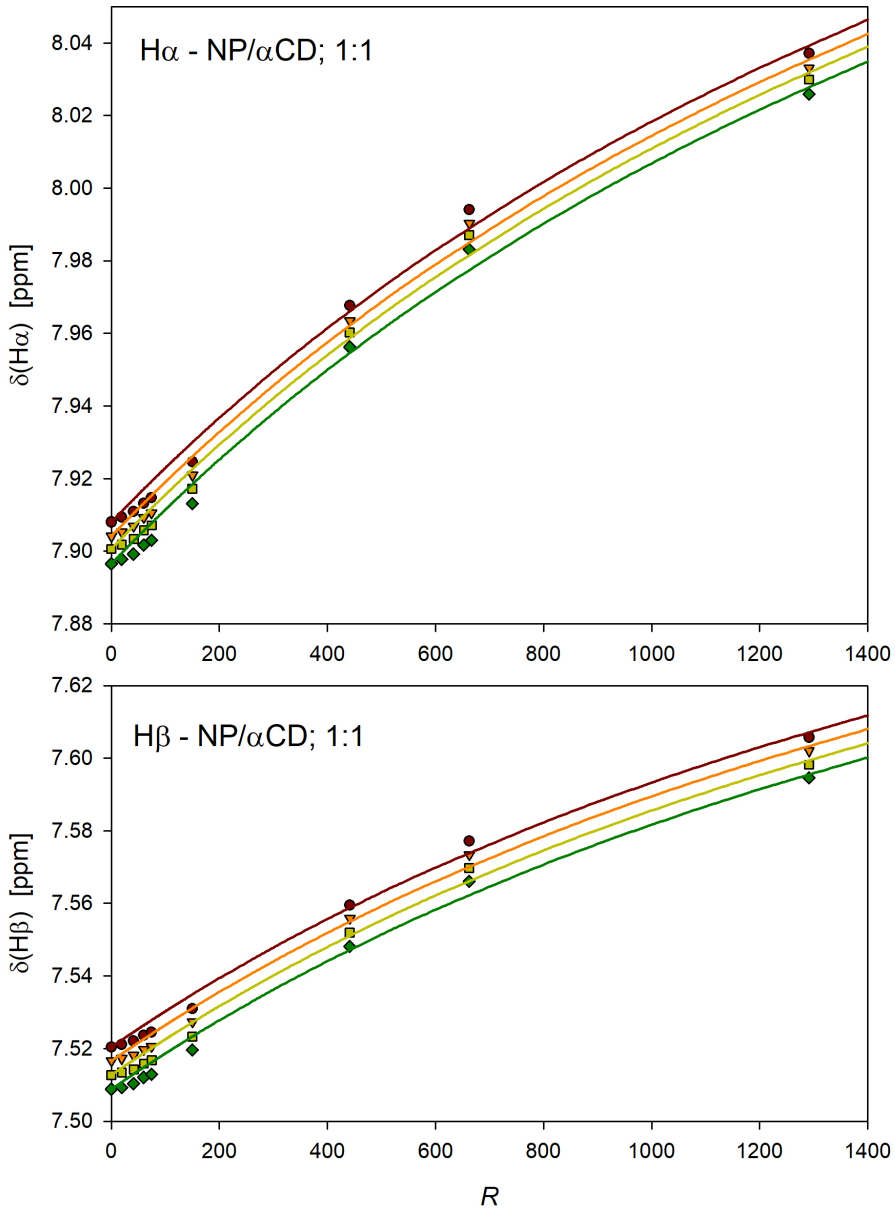

Figure S4

Symbols labeled with colors and shapes correspond to the experimental data obtained for each of 4 distinctive maxima in a symmetric multiplets of Hα (upper part) and Hβ (lower part) protons. Color coded lines represent the best fit curves for the NP/αCD complex assuming 1:1 stoichiometry (complex parameters – *cf*. Table 2).

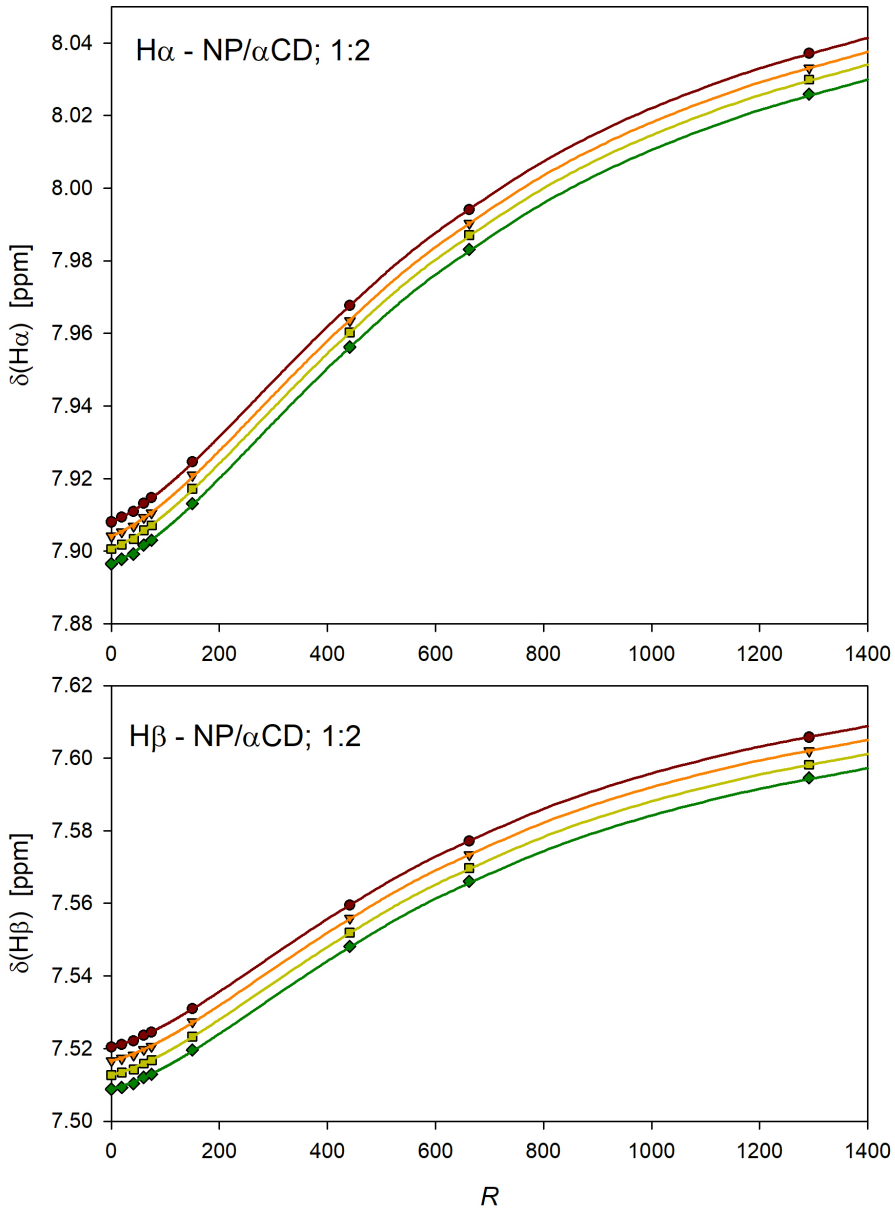

Figure S5

Symbols labeled with colors and shapes correspond to the experimental data obtained for each of 4 distinctive maxima in a symmetric multiplets of Hα (upper part) and Hβ (lower part) protons. Color coded lines represent the best fit curves for the NP/αCD complex assuming 1:2 stoichiometry (complex parameters – *cf.* Table 2). The sigmoidal shape of titration curves precisely fits to the experimental data proving a composite stoichiometry of the studied complexes.

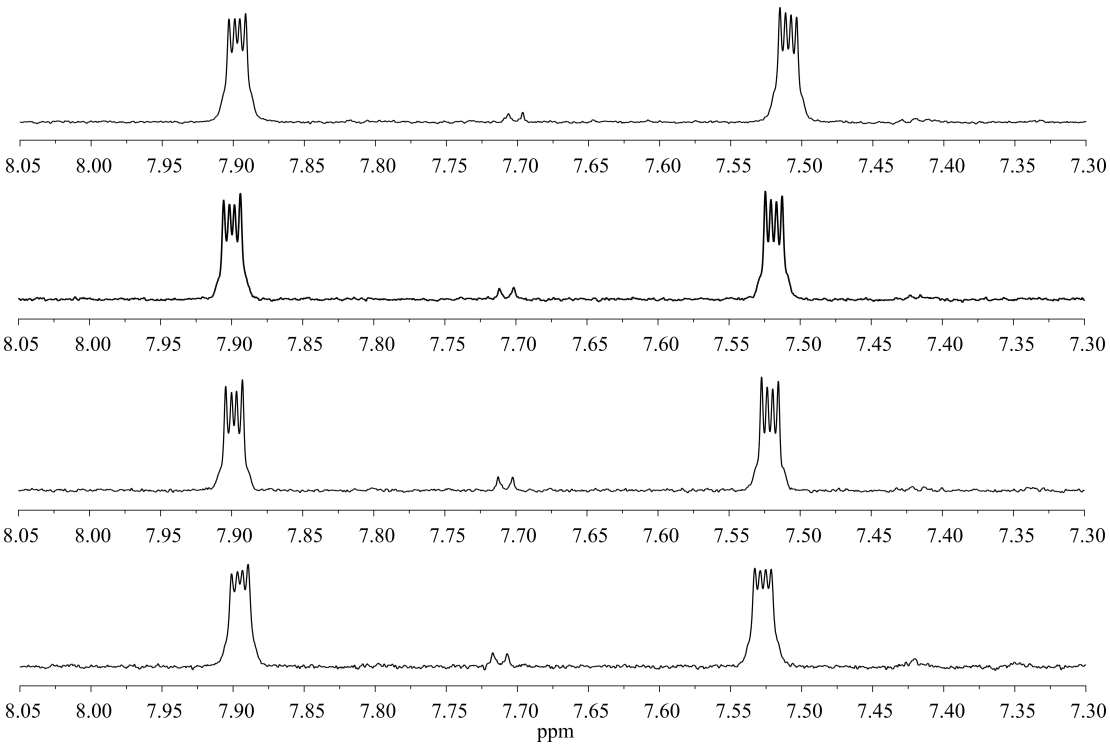

Figure S6

^{1}H NMR spectra of naphthalene titrated with βCD. Ratios R=c(βCD)/c(NP) are equal: 0.0, 5.6, 9.3, and 16.9 from top to bottom, respectively. NP complexation by βCD results in the shielding of Hα protons (left side) while Hβ protons are deshielded. Signal-to-noise ratios (S/N) for Hα and Hβ protons are *ca*. 90 and fluctuate within the range ±15%. In order to determine values of integrals the following integration ranges have been used: Hα(NP) and Hβ(NP) – 0.1 ppm, H1(CD) – 0.08 ppm. Integrated signals have always been placed in the centre of a range.

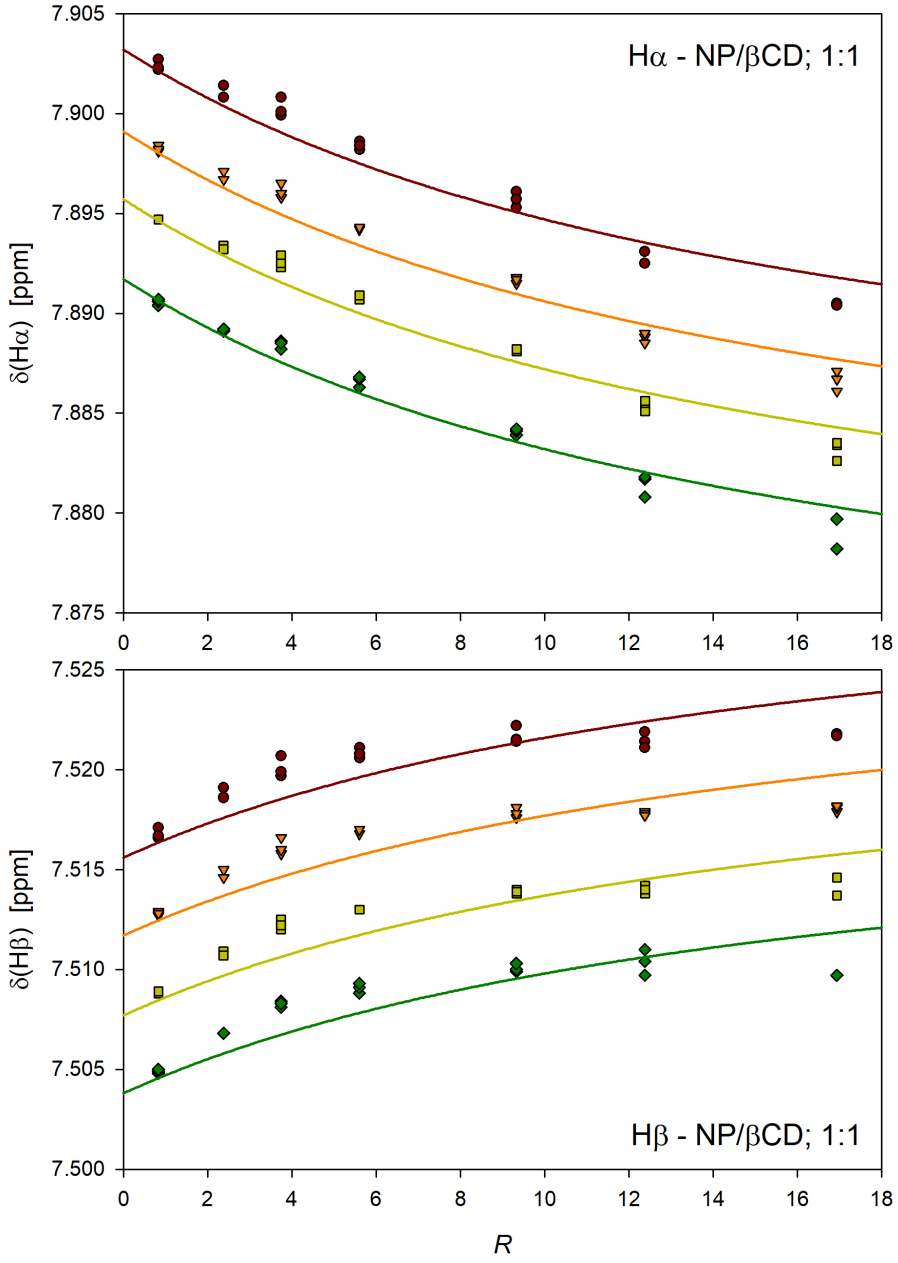

Figure S7

Symbols labeled with colors and shapes correspond to the experimental data obtained for each of 4 distinctive maxima in a symmetric multiplets of Hα (upper part) and Hβ (lower part) protons. Color coded lines represent the best fit curves for the NP/βCD complex assuming 1:1 stoichiometry (complex parameters – *cf.* Table 3).

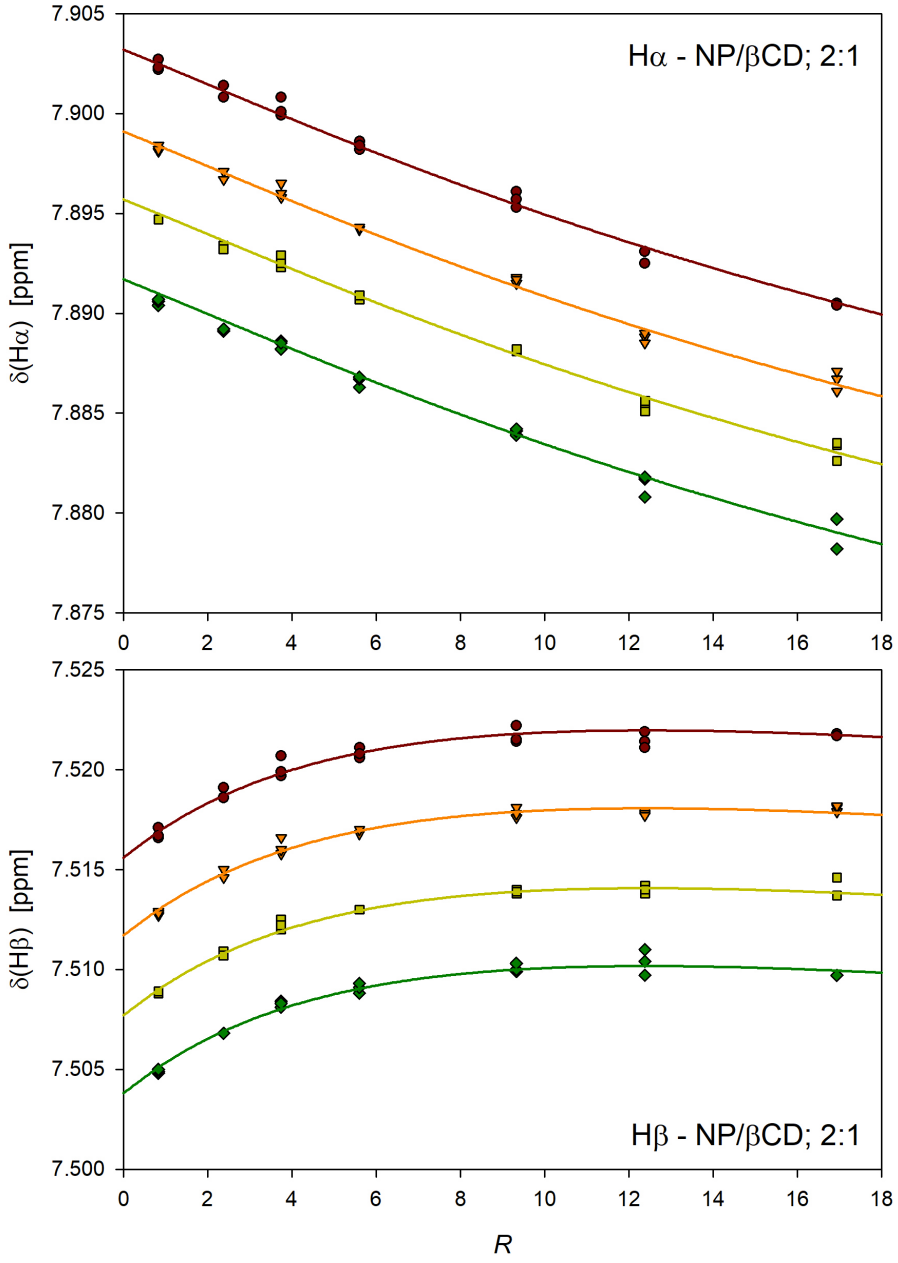

Figure S8

Symbols labeled with colors and shapes correspond to the experimental data obtained for each of 4 distinctive maxima in a symmetric multiplets of Hα (upper part) and Hβ (lower part) protons. Color coded lines represent the best fit curves for the NP/βCD complex assuming 2:1 stoichiometry (complex parameters – *cf.* Table 3).

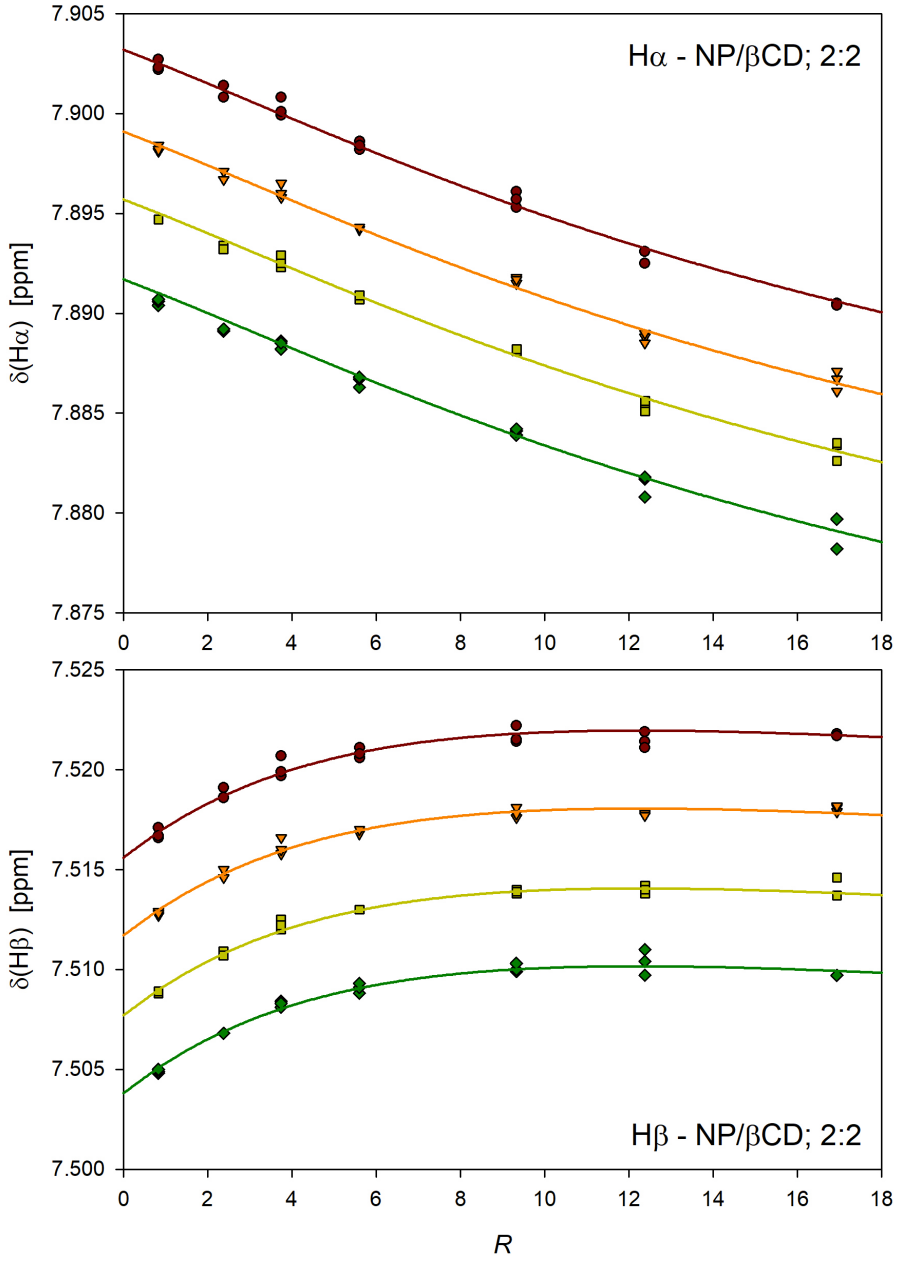

Figure S9

Symbols labeled with colors and shapes correspond to the experimental data obtained for each of 4 distinctive maxima in a symmetric multiplets of Hα (upper part) and Hβ (lower part) protons. Color coded lines represent the best fit curves for the NP/βCD complex assuming 2:2 stoichiometry (complex parameters – *cf.* Table 3).

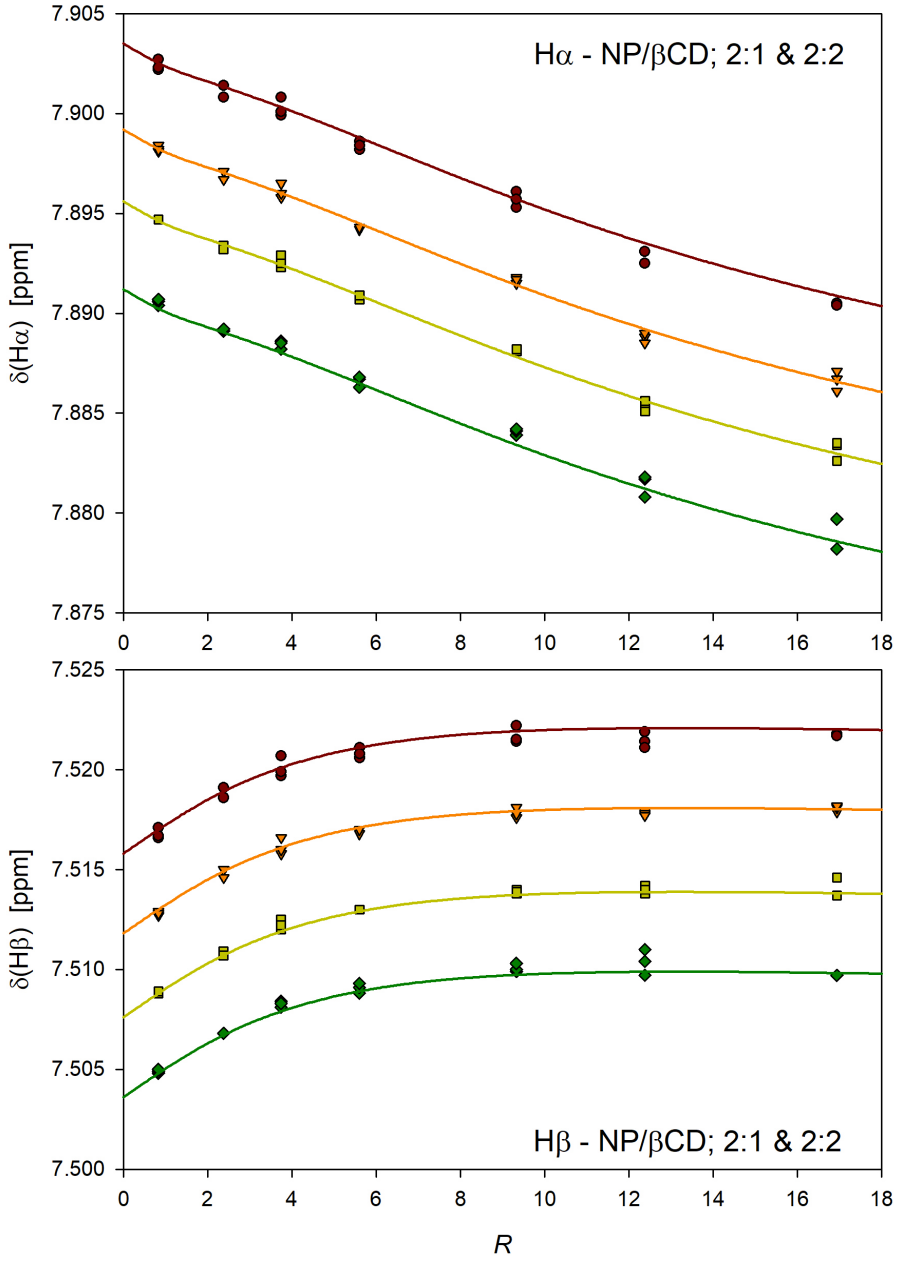

Figure S10

Symbols labeled with colors and shapes correspond to the experimental data obtained for each of 4 distinctive maxima in a symmetric multiplets of Hα (upper part) and Hβ (lower part) protons. Color coded lines represent the best fit curves for the NP/βCD complex assuming simultaneous 2:1 and 2:2 stoichiometry (complex parameters – *cf.* Table 3).

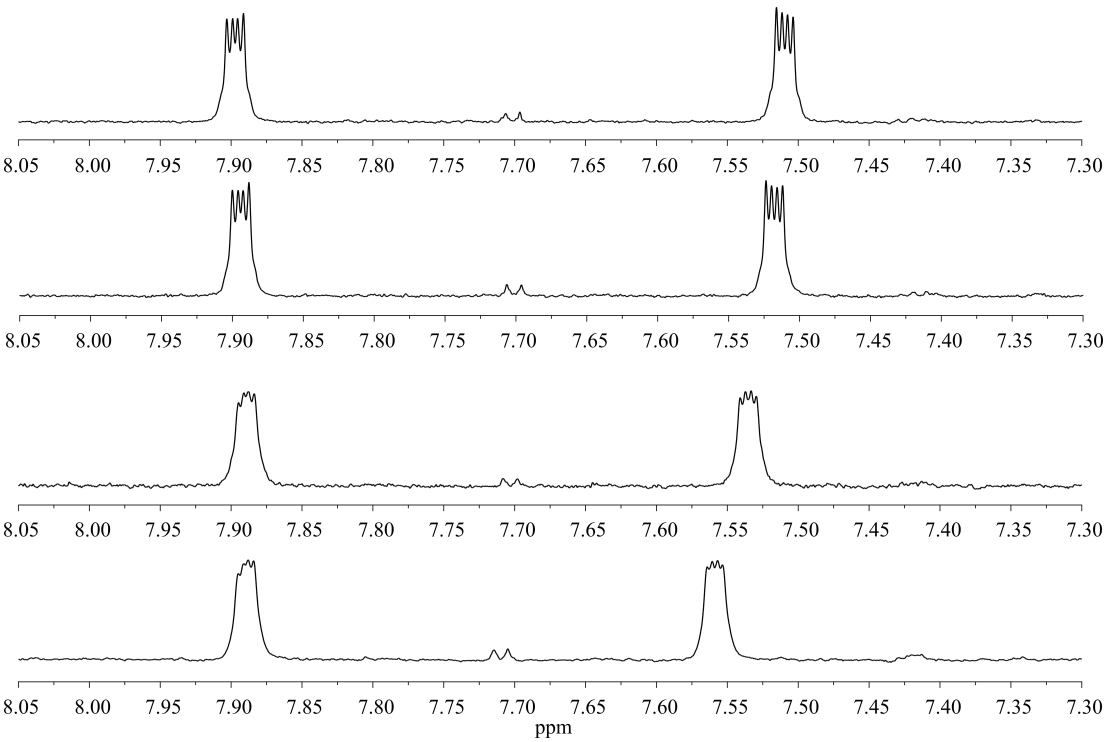

Figure S11

^{1}H NMR spectra of naphthalene titrated with γCD. Ratios $R=c(\gamma CD)/c(NP)$ are equal: 0.0, 39.7, 146.2, and 307.9 from top to bottom, respectively. NP complexation by γCD results in shielding of Hα protons (left side) while Hβ protons are deshielded like in NP/βCD complex. Signal-to-noise ratios (S/N) for Hα and Hβ protons are *ca*. 90 and fluctuate within the range ±15%. In order to determine values of integrals the following integration ranges have been used: Hα(NP) and Hβ(NP) – 0.1 ppm, H1(CD) – 0.08 ppm. Integrated signals have always been placed in the centre of a range.

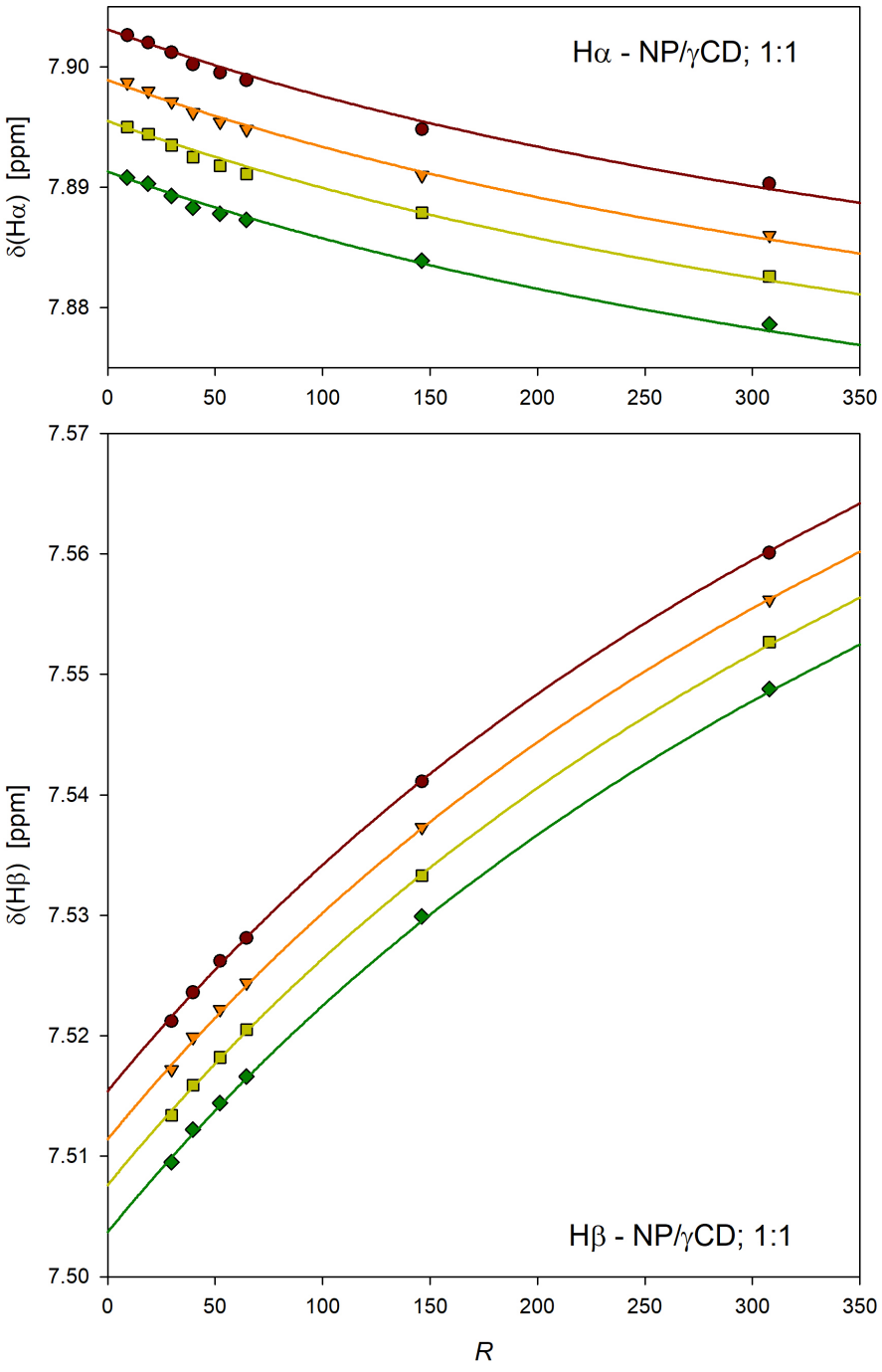

Figure S12

Symbols labeled with colors and shapes correspond to the experimental data obtained for each of 4 distinctive maxima in a symmetric multiplets of Hα (upper part) and Hβ (lower part) protons. Color coded lines represent the best fit curves for the NP/γCD complex assuming 1:1 stoichiometry (complex parameters – *cf.* Table 4).

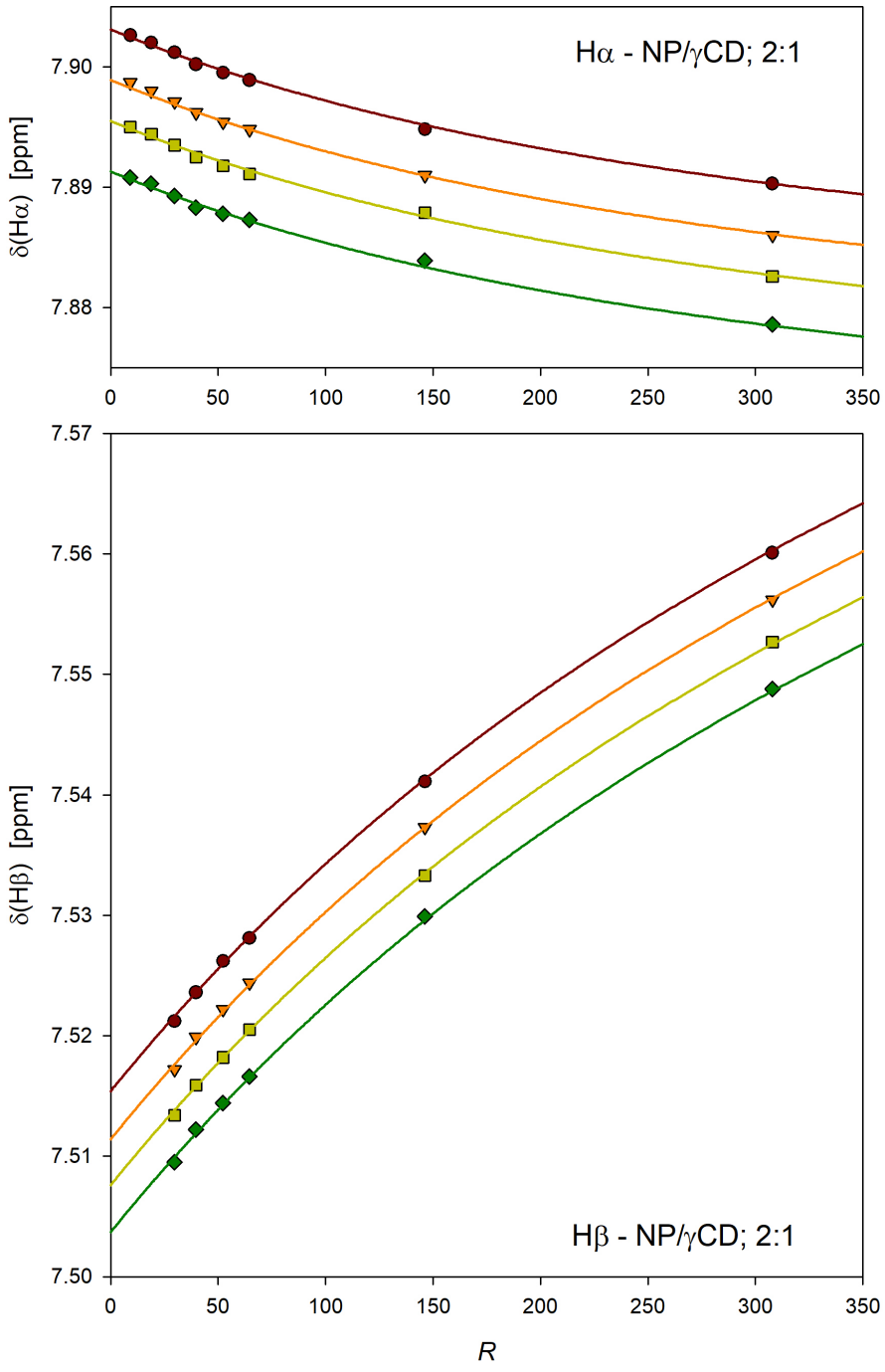

Figure S13

Symbols labeled with colors and shapes correspond to the experimental data obtained for each of 4 distinctive maxima in a symmetric multiplets of Hα (upper part) and Hβ (lower part) protons. Color coded lines represent the best fit curves for the NP/γCD complex assuming 2:1 stoichiometry (complex parameters – *cf.* Table 4).

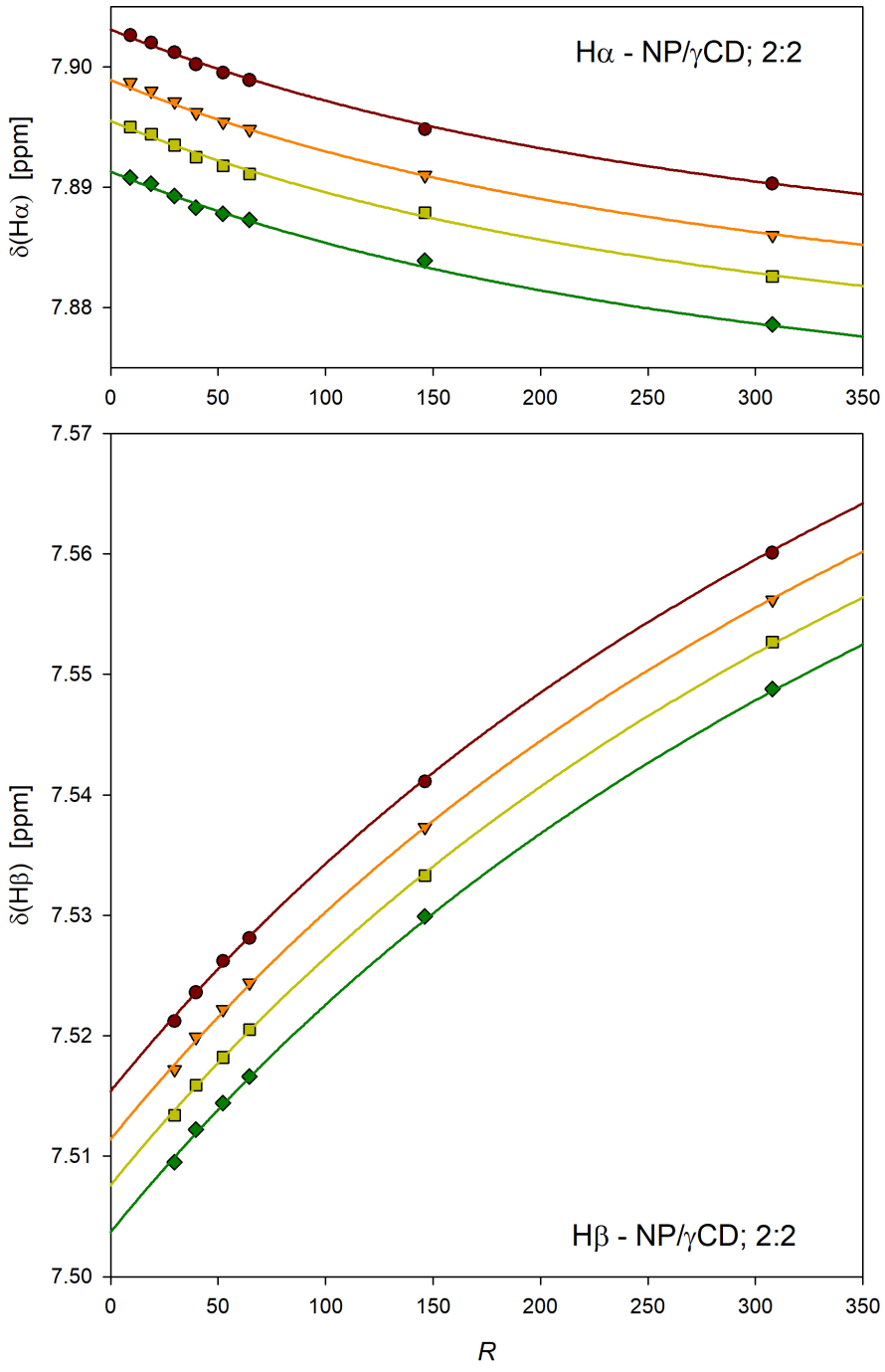

Figure S14

Symbols labeled with colors and shapes correspond to the experimental data obtained for each of 4 distinctive maxima in a symmetric multiplets of Hα (upper part) and Hβ (lower part) protons. Color coded lines represent the best fit curves for the NP/γCD complex assuming 2:2 stoichiometry (complex parameters – *cf.* Table 4).

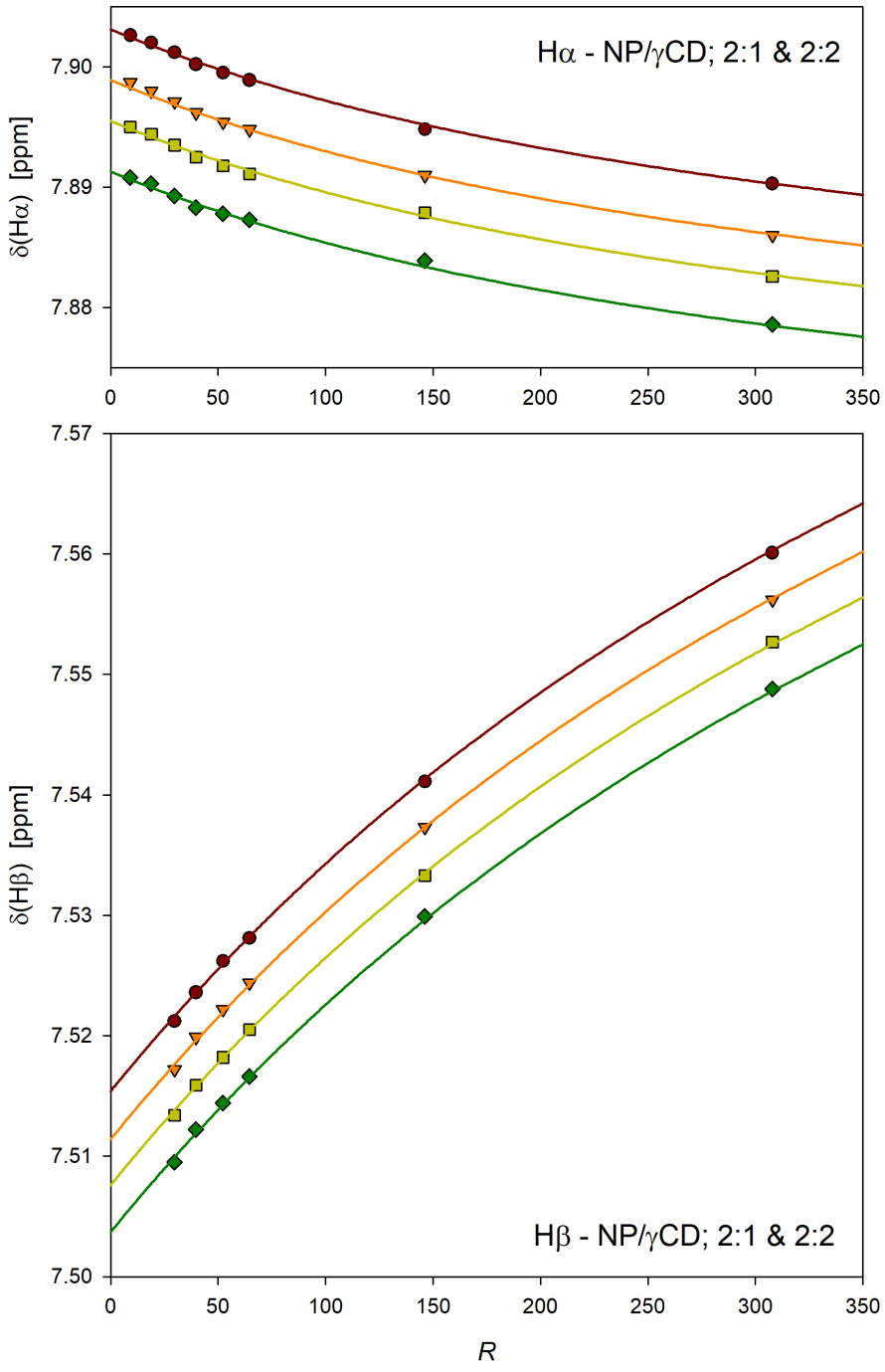

Figure S15

Symbols labeled with colors and shapes correspond to the experimental data obtained for each of 4 distinctive maxima in a symmetric multiplets of Hα (upper part) and Hβ (lower part) protons. Color coded lines represent the best fit curves for the NP/γCD complex assuming simultaneous 2:1 and 2:2 stoichiometry (complex parameters – *cf.* Table 4).