Supporting information for

Simultaneous estimation of two coupled hydrogen bond geometries from pairs of entangled NMR parameters: the test case of 4-hydroxypyridine anion

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Table S1. Geometric parameters of OHO and OHN hydrogen bonds.

R_1	R_2	R_3	R_4	R_5	R_6	r_1, Å	r_2, Å	r_3, Å	r_4, Å	∠OHO, °	∠NHO, °
H	H	H	H	H	H	1.00	1.67	1.74	1.00	169	171
H	H	CN	H	H	H	1.02	1.56	1.76	1.00	167	171
H	CN	CN	H	H	H	1.06	1.44	1.78	1.00	169	171
CN	CN	CN	H	H	H	1.49	1.04	1.81	0.99	178	169
H	H	H	CN	H	H	1.00	1.68	1.61	1.03	168	168
H	H	CN	CN	H	H	1.02	1.59	1.64	1.02	166	168
H	CN	CN	CN	H	H	1.05	1.46	1.66	1.01	168	168
CN	CN	CN	CN	H	H	1.47	1.04	1.70	1.01	177	166
H	H	H	CN	CN	H	1.00	1.70	1.48	1.07	168	170
H	H	CN	CN	CN	H	1.01	1.59	1.51	1.06	167	170
H	CN	CN	CN	CN	H	1.04	1.48	1.55	1.04	167	168
CN	CN	CN	CN	CN	H	1.44	1.05	1.61	1.03	176	167
H	H	H	CN	CN	CN	0.99	1.74	1.07	1.54	167	174
H	H	CN	CN	CN	CN	1.00	1.64	1.09	1.49	165	178
H	CN	CN	CN	CN	CN	1.02	1.53	1.09	1.50	167	172
CN	CN	CN	CN	CN	CN	1.09	1.37	1.11	1.45	171	178
H	H	NO₂	H	H	H	1.04	1.50	1.76	1.00	168	171
H	NO₂	NO₂	H	H	H	1.52	1.02	1.81	0.99	178	169
NO₂	NO₂	NO₂	H	H	H	1.68	0.99	1.82	0.99	176	168
H	H	H	NO₂	H	H	1.00	1.68	1.54	1.05	168	171
H	H	NO₂	NO₂	H	H	1.03	1.52	1.57	1.04	168	171
H	NO₂	NO₂	NO₂	H	H	1.51	1.03	1.64	1.02	177	170
NO₂	NO₂	NO₂	NO₂	H	H	1.68	1.00	1.65	1.01	176	170
H	H	H	NO₂	NO₂	H	0.99	1.73	1.05	1.66	167	166
H	H	NO₂	NO₂	NO₂	H	1.02	1.54	1.05	1.64	171	167
H	NO₂	NO₂	NO₂	NO₂	H	1.39	1.07	1.07	1.55	179	169
NO₂	NO₂	NO₂	NO₂	NO₂	H	1.65	1.00	1.45	1.08	176	175
H	H	H	NO₂	NO₂	NO₂	0.99	1.75	1.03	1.77	166	156
H	H	NO₂	NO₂	NO₂	NO₂	1.01	1.57	1.04	1.73	171	162
H	NO₂	NO₂	NO₂	NO₂	NO₂	1.08	1.38	1.04	1.68	177	164
NO₂	NO₂	NO₂	NO₂	NO₂	NO₂	1.60	1.01	1.06	1.62	167	165
H	OMe	OMe	H	OMe	OMe	1.02	1.55	1.62	1.02	171	174
H	OMe	OMe	H	H	OMe	1.03	1.53	1.74	1.00	172	168
H	OMe	OMe	H	H	H	1.03	1.52	1.76	1.00	172	171
H	OMe	OMe	OMe	OMe	OMe	1.03	1.52	1.65	1.02	172	176
H	H	OMe	H	OMe	OMe	1.00	1.69	1.68	1.02	162	163
H	H	OMe	H	H	H	1.01	1.63	1.74	1.00	170	168
H	H	OMe	H	H	H	1.01	1.60	1.75	1.00	168	171
H	H	OMe	OMe	OMe	OMe	1.00	1.66	1.13	1.40	167	175
H	H	H	H	H	OMe	1.00	1.68	1.61	1.03	168	174
H	H	H	H	H	OMe	1.00	1.67	1.65	1.02	169	172
H	H	H	OMe	OMe	OMe	0.99	1.71	1.13	1.41	167	175
OMe	OMe	OMe	H	H	OMe	1.05	1.48	1.74	1.00	170	168
OMe	OMe	OMe	OMe	OMe	OMe	1.03	1.53	1.13	1.40	170	178

OMe	OMe	OMe	H	OMe	OMe	1.04	1.49	1.62	1.02	156	172
OMe	OMe	OMe	H	H	H	1.05	1.46	1.75	1.00	170	171
H	F	F	H	H	H	1.41	1.07	1.80	0.99	179	169
H	F	F	H	H	F	1.08	1.38	1.64	1.02	177	171
H	F	F	H	H	F	1.06	1.42	1.51	1.06	176	176
H	F	F	F	F	F	1.03	1.49	1.07	1.54	175	176
H	H	F	H	H	H	1.03	1.54	1.75	1.00	171	171
H	H	F	H	H	F	1.02	1.55	1.62	1.02	171	171
H	H	F	H	F	F	1.02	1.57	1.47	1.08	171	177
H	H	F	F	F	F	1.01	1.62	1.07	1.56	170	175
F	F	F	H	H	H	1.53	1.02	1.80	0.99	175	169
F	F	F	H	H	F	1.52	1.02	1.68	1.01	175	169
F	F	F	H	F	F	1.50	1.03	1.58	1.03	175	174
F	F	F	F	F	F	1.43	1.05	1.09	1.47	176	176
H	H	H	H	H	F	1.00	1.67	1.60	1.03	168	172
H	H	H	H	F	F	1.00	1.69	1.41	1.11	168	177
H	H	H	F	F	F	0.99	1.73	1.06	1.58	167	175

Table S2. Approximation coefficients for $\Delta f(q_{1a}, q_{1b}) = a + b_1 q_{1a} + c_1 q_{1a}^2 + d_1 q_{1a}^3 + b_2 q_{1b} + c_2 q_{1b}^2 + d_2 q_{1b}^3$ (for q_{1a} and q_{1b} in Å, Δf in ppm) and R^2.

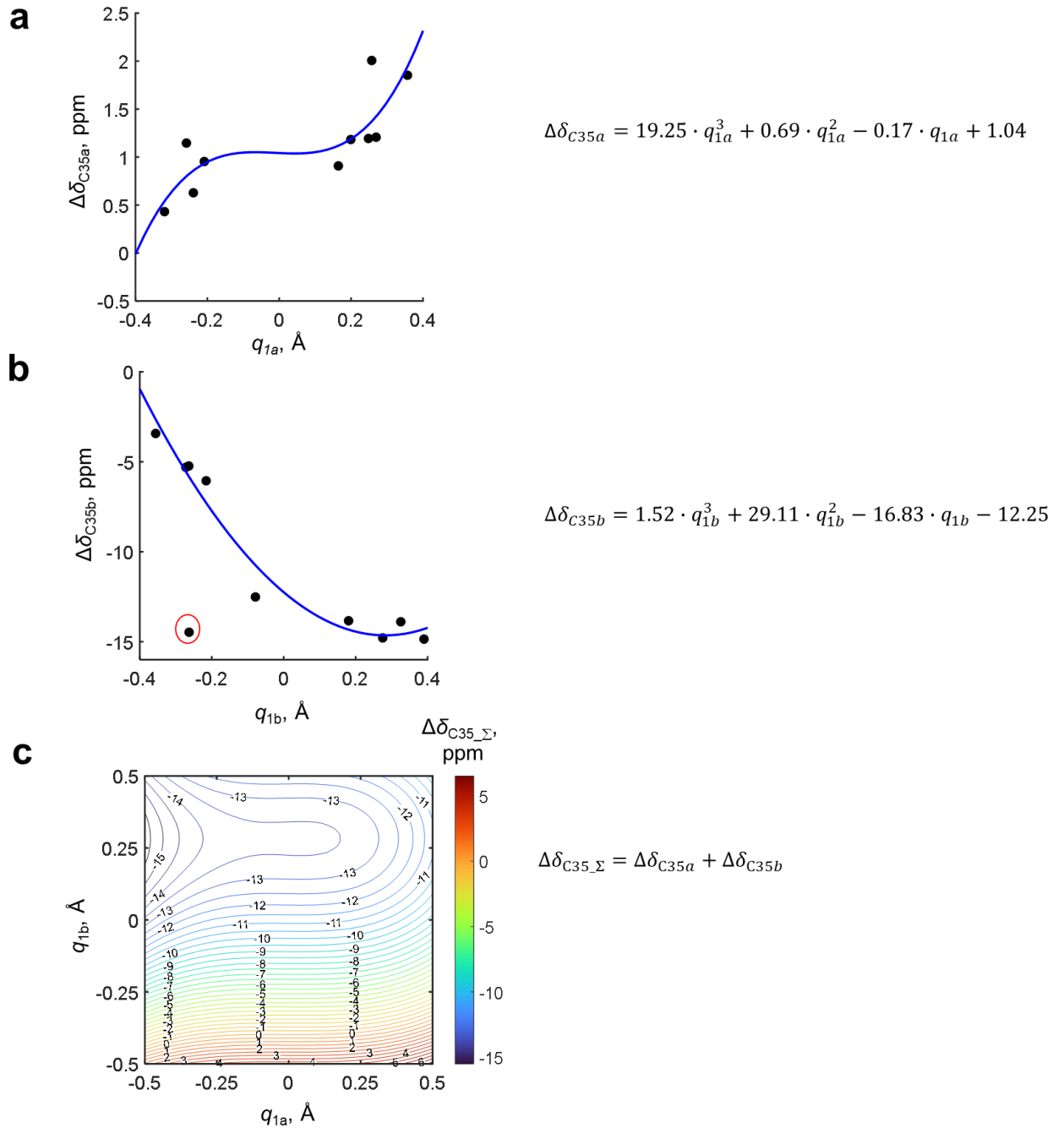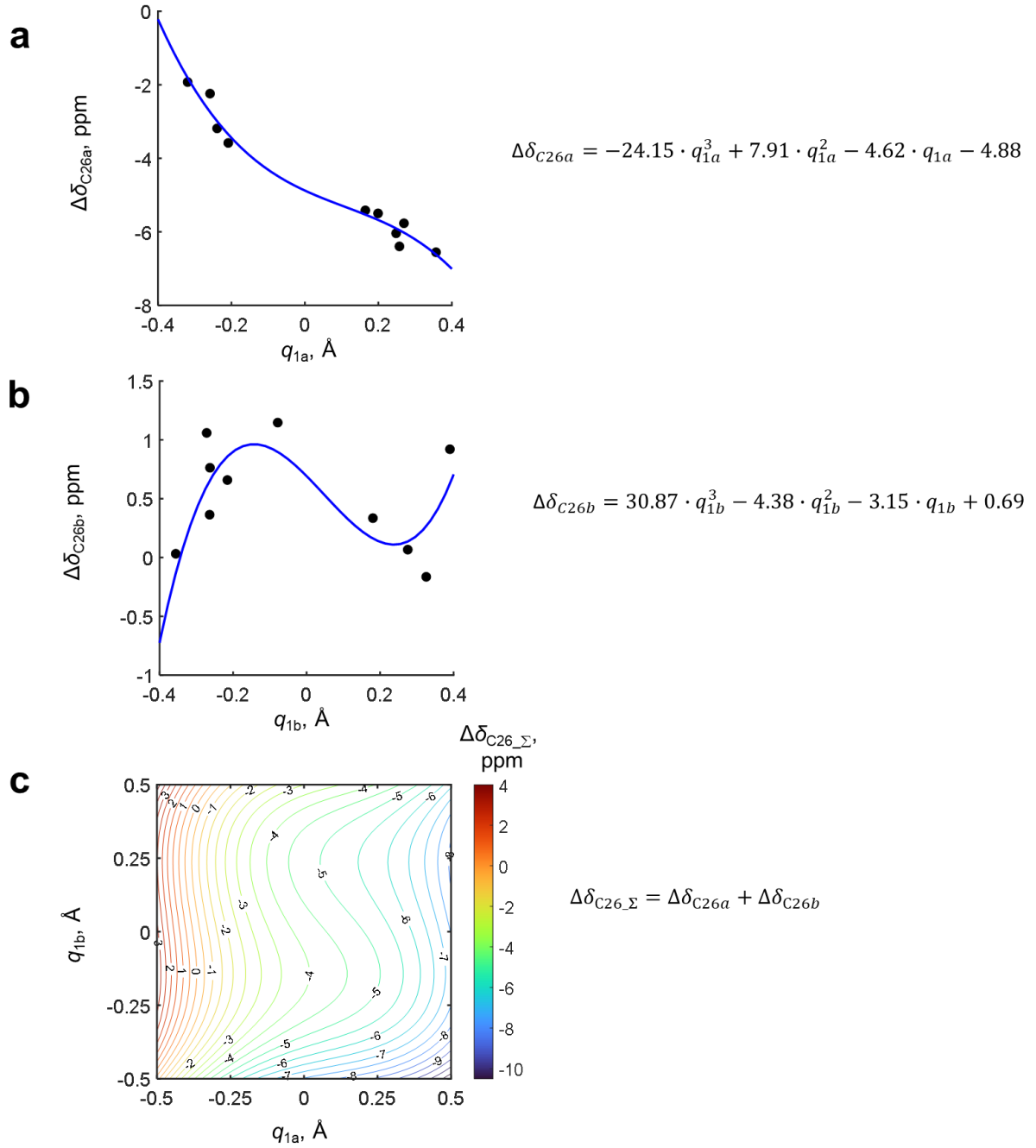| Δf	a	b_1	c_1	d_1	b_2	c_2	d_2	R^2
$\Delta\delta_{C1}$	−1.1	−15.35	−9.15	30.84	2.18	−2.33	9.91	0.97
$\Delta\delta_{N4}$	−49.4	41.45	4.37	−8.12	−106.3	14.95	−133.9	0.99
$\Delta\delta_{H1\_HB}$	17.0	4.12	−87.91	−90.03	0.21	−6.23	−16.56	0.93
$\Delta\delta_{H2\_HB}$	17.9	1.38	−2.96	−33.24	5.13	−79.22	−85.15	0.95
$\Delta\delta_{C26}$	−3.0	−4.03	0.81	−9.606	−2.07	0.67	24.56	0.82
$\Delta\delta_{C35}$	−8.1	1.10	−1.37	23.99	−16.86	13.97	30.38	0.98
$\Delta\delta_{H35}$	0.4	0.84	−0.65	−0.37	0.35	1.12	0.49	0.86

Figure S1. Distribution of the chemical shift change upon complexation $\Delta\delta_{C35}$ for complexes of hydroxypyridine with a single substituted methanol molecule (a) from the oxygen side (OHO hydrogen bond) $\Delta\delta_{C35a}$, (b) from the nitrogen site (OHN hydrogen bond) $\Delta\delta_{C35b}$. (c) Distributions of the sum of the changes upon formation of both OHO and OHN hydrogen bonds $\Delta\delta_{C35\_\Sigma} = \Delta\delta_{C35a} + \Delta\delta_{C35b}$ along q_1 coordinates for OHO (q_{1a}) and OHN (q_{1b}) hydrogen bonds. Coefficients a_1, b_1, c_1, d_1, a_2, b_2, c_2 are given near each plot. Isolines drawn with a step of 0.5 ppm.

$$\Delta\delta_{C35a} = 19.25 \cdot q_{1a}^3 + 0.69 \cdot q_{1a}^2 - 0.17 \cdot q_{1a} + 1.04$$

$$\Delta\delta_{C35b} = 1.52 \cdot q_{1b}^3 + 29.11 \cdot q_{1b}^2 - 16.83 \cdot q_{1b} - 12.25$$

$$\Delta\delta_{C35\_\Sigma} = \Delta\delta_{C35a} + \Delta\delta_{C35b}$$

Figure S2. Distribution of the chemical shift change upon complexation $\Delta\delta_{C26}$ for complexes of hydroxypyridine with a single substituted methanol molecule (a) from the oxygen side (OHO hydrogen bond) $\Delta\delta_{C26a}$, (b) from the nitrogen site (OHN hydrogen bond) $\Delta\delta_{C26b}$. (c) Distributions of the sum of the changes upon formation of both OHO and OHN hydrogen bonds $\Delta\delta_{C26\_\Sigma} = \Delta\delta_{C26a} + \Delta\delta_{C26b}$ along q_1 coordinates for OHO (q_{1a}) and OHN (q_{1b}) hydrogen bonds. Coefficients a_1, b_1, c_1, d_1, a_2, b_2, c_2 are given near each plot. Isolines drawn with a step of 0.5 ppm.

$$\Delta\delta_{C26a} = -24.15 \cdot q_{1a}^3 + 7.91 \cdot q_{1a}^2 - 4.62 \cdot q_{1a} - 4.88$$

$$\Delta\delta_{C26b} = 30.87 \cdot q_{1b}^3 - 4.38 \cdot q_{1b}^2 - 3.15 \cdot q_{1b} + 0.69$$

$$\Delta\delta_{C26\_\Sigma} = \Delta\delta_{C26a} + \Delta\delta_{C26b}$$

Non-additivity (cooperativity) of hydrogen bonds formed by hydroxypyridune anion

Figure S3. Difference (a) between carbon chemical shift changes upon formation of two hydrogen bond simultaneously $\Delta\delta_{C26}$ and of the sum of a change upon formation of OHO and OHN hydrogen bonds $\Delta\delta_{C26\_\Sigma} = \Delta\delta_{C26a} + \Delta\delta_{C26b}$, (b) between carbon chemical shift changes upon formation of two hydrogen bond simultaneously $\Delta\delta_{C35}$ and of the sum of a change upon formation of OHO and OHN hydrogen bonds $\Delta\delta_{C35\_\Sigma} = \Delta\delta_{C35a} + \Delta\delta_{C35b}$ along q_1 coordinates for OHO (q_{1a}) and OHN (q_{1b}) hydrogen bonds. Isolines drawn with a step of 0.2 ppm, and 0.5 ppm respectively.

Figure S4. Solution of inverse spectral problem for R_1=H, R_2=F, R_3=CH$_3$, R_4=H, R_5=F, R_6=CF$_3$ based on a following pairs of spectral parameters (a) $\Delta\delta_{C1}$ and $\Delta\delta_{N4}$, (b) $\Delta\delta_{C26}$ and $\Delta\delta_{C35}$, (c) $\Delta\delta_{C35}$ and $\Delta\delta_{H35}$. Green dots correspond to predicted values of q_{1a} and q_{1b}, black dots correspond to calculated ones.
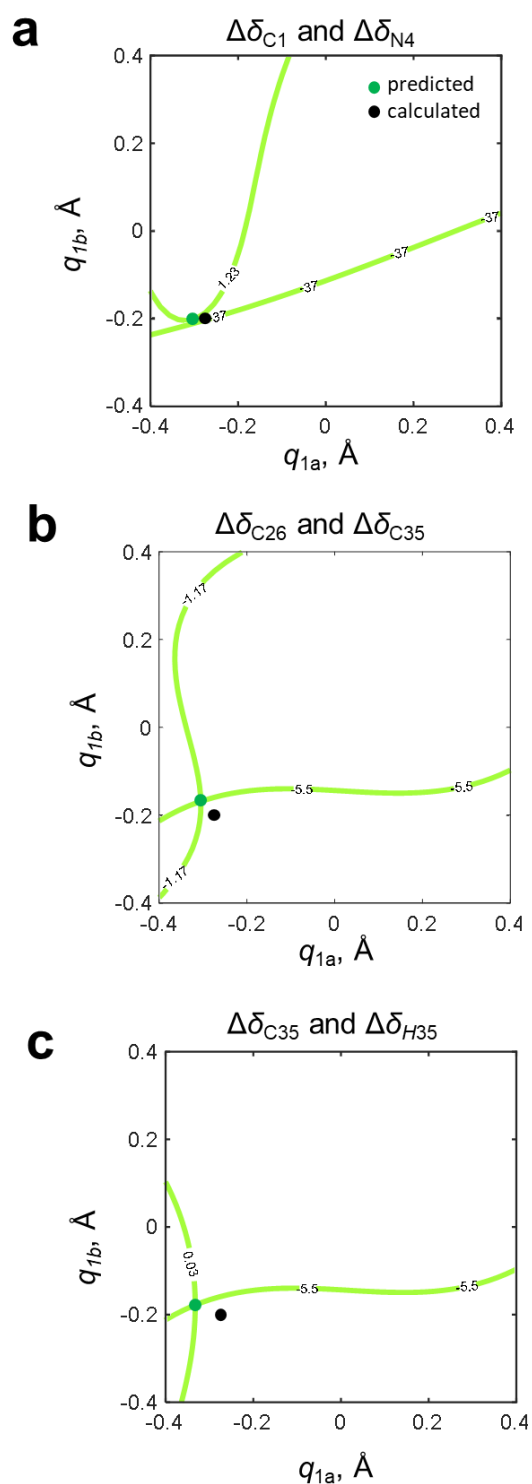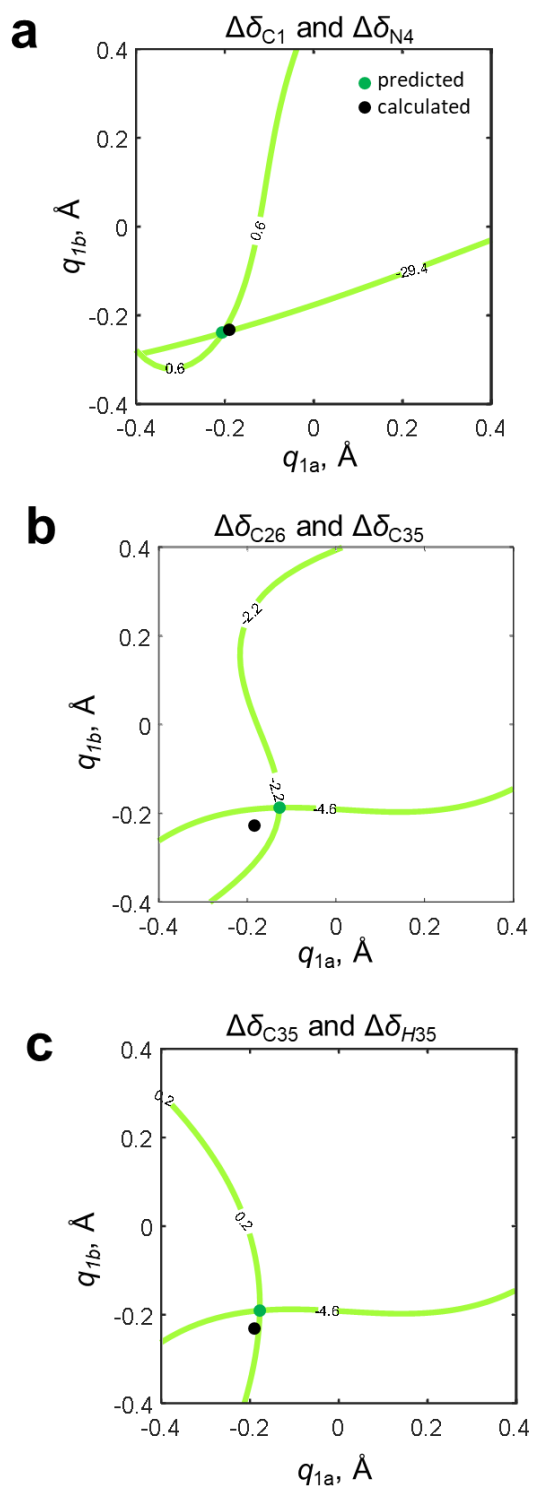
Figure S5. Solution of inverse spectral problem for R_1=H, R_2=F, R_3=CF$_3$, R_4=H, R_5=F, R_6=CF$_3$ based on a following pairs of spectral parameters (a) $\Delta\delta_{C1}$ and $\Delta\delta_{N4}$, (b) $\Delta\delta_{C26}$ and $\Delta\delta_{C35}$, (c) $\Delta\delta_{C35}$ and $\Delta\delta_{H35}$. Green dots correspond to predicted values of q_{1a} and q_{1b}, black dots correspond to calculated ones.

Figure S6. Solution of inverse spectral problem for R_1=H, R_2=F, R_3=CF$_3$, R_4=H, R_5=F, R_6=CH$_3$ based on a following pairs of spectral parameters (a) $\Delta\delta_{C1}$ and $\Delta\delta_{N4}$, (b) $\Delta\delta_{C26}$ and $\Delta\delta_{C35}$, (c) $\Delta\delta_{C35}$ and $\Delta\delta_{H35}$. Green dots correspond to predicted values of q_{1a} and q_{1b}, black dots correspond to calculated ones.
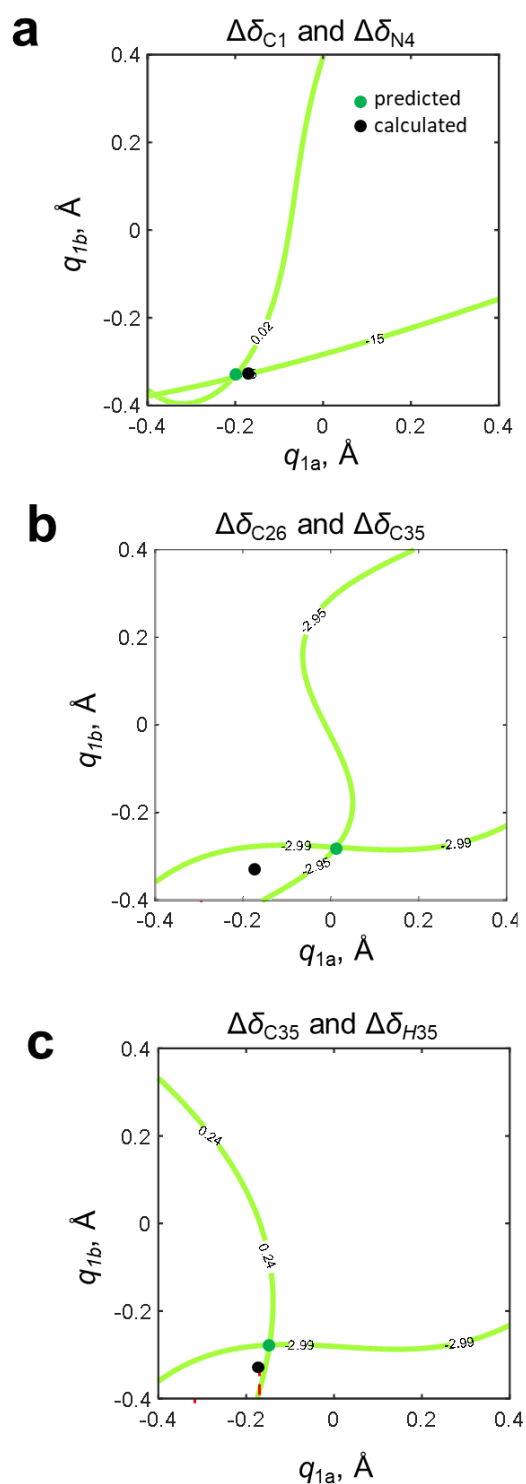
Figure S7. Optimized geometry of complex **3** with CF₃CFOH and CH₃CFHOH as hydrogen bond donors.