Supplementary Information to "A Volumetric Analysis of the ^{1}H NMR Chemical Shielding in Supramolecular Systems" by Czernek & Brus (*IJMS* **2021**)

Table S1. Experimental, δ, and theoretical, ε, chemical shifts (in ppm) plotted in Figure 1 of the main text.

HETCOR pair #	HETCOR pair designation	δ (^{13}C)	ε (^{13}C)	δ (^{1}H)	ε (^{1}H)
1	1	83.68	83.0939	4.59	4.3123
2	2	54.01	54.0977	3.21	3.1395
3	4	21.75	21.9505	2.28	2.4558
4	5	21.75	21.9505	1.76	1.8167
5	6	27.88	29.3230	2.26	2.2929
6	7	27.88	29.3230	1.97	2.0708
7	8	130.40	129.6859	5.84	6.0401
8	11	54.22	53.9077	3.01	2.9282
9	12	61.92	64.0458	2.57	2.3502
10	15	21.59	22.2478	1.79	1.8691
11	16	22.27	19.9299	1.13	1.0954
12	17	22.23	20.0244	0.92	0.9591

Table S2. The ^{13}C chemical shift, δ, and shielding, σ, of all carbon atoms of aquatolide, which are numbered as in the Supporting Materials file 'aquatolide.xyz'. This data set is plotted in Figure S1 (at page S2).

atom #	δ, in ppm	σ, in ppm
21	83.68	92.1694
23	54.01	123.5897
5	62.05	115.0800
6	21.75	158.4245
9	27.88	150.4356
12	130.40	41.6823
14	134.37	38.3085
15	211.51	–42.8888
16	54.22	123.7956
18	61.92	112.8100
20	41.19	134.4311
4	177.18	–5.1776
25	21.59	158.1023
29	22.27	160.6140
33	22.23	160.5116

Table S3. The ^{1}H chemical shift, δ, and shielding, σ, of all hydrogen atoms of aquatolide, which are numbered as in the Supporting Materials file 'aquatolide.xyz'. This data set is plotted in Figure S2 (at page S3).

atom #	δ, in ppm	σ, in ppm
22	4.59	27.2982
24	3.21	28.5215
7	2.28	29.2346
8	1.76	29.9012
10	2.26	29.4045
11	1.97	29.6362
13	5.84	25.4960
17	3.01	28.7419
19	2.57	29.3448
(26,27,28)	1.79	(30.0578+30.0500+29.4321)/3
(30,31,32)	1.13	(30.6853+30.6600+30.6156)/3
(34,35,36)	0.92	(30.7413+30.5898+31.0559)/3

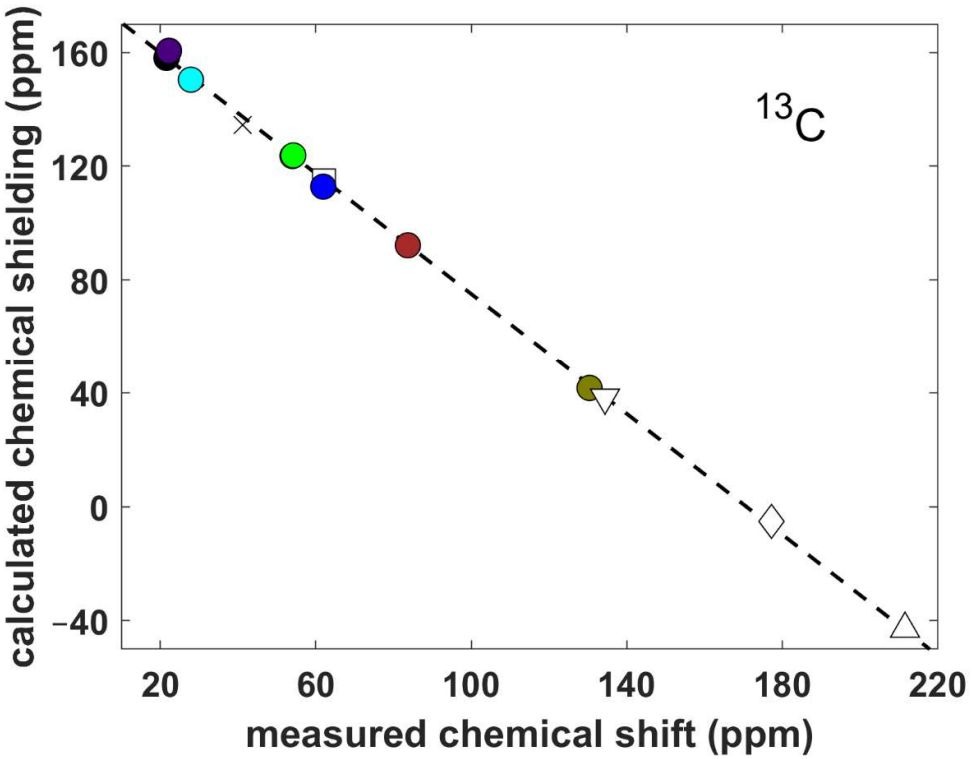

Figure S1. Comparison between theory and experiment for the ^{13}C chemical shift/shielding data of all carbons of aquatolide in DMSO. The coloring scheme follows the one used in Figure 1 of the main text, and in addition an empty square, downward-pointing triangle, upward-pointing triangle, cross, and diamond symbols are used for the C3, C7 C8, C11, and C12 atoms, respectively. The dashed line is $y = -1.0609*x + 181.11$ ppm.

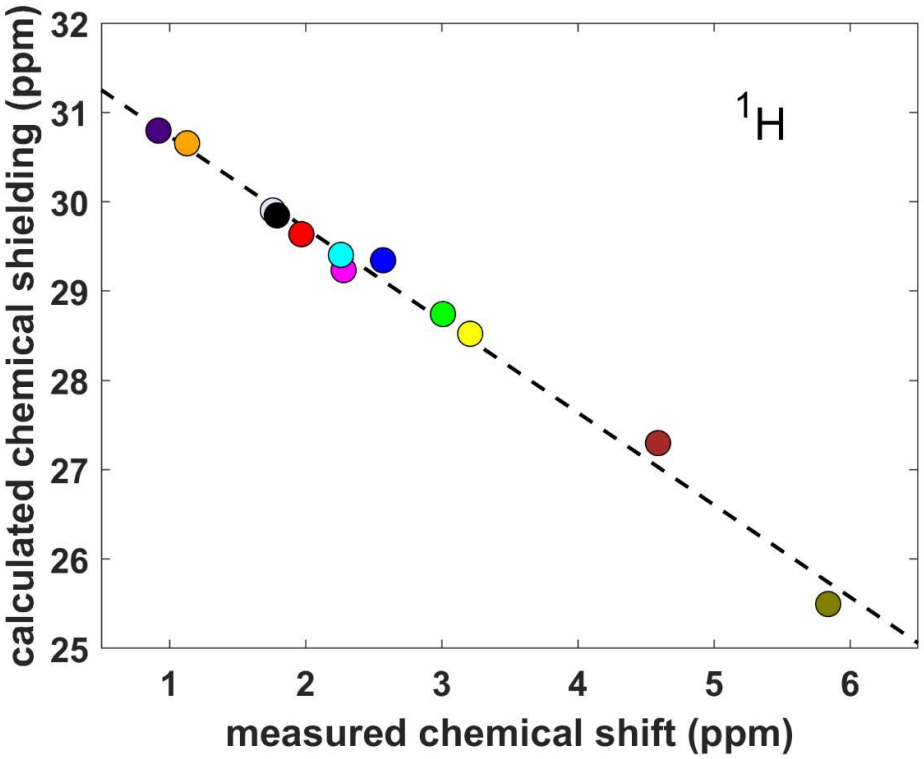

Figure S2. Comparison between theory and experiment for the ^{1}H chemical shift/shielding data of all protons of aquatolide in DMSO, which are colored accordingly to Figure 1 of the main text. The dashed line is $y = -1.0320*x + 31.767$ ppm.

Table S4. Experimental chemical shifts, δ, theoretical chemical shifts, ε, and chemical shieldings, σ, of 3,12-di(4-aminophenyl) Ni^{II} dimesitylnorcorrole used to reconstruct its HSQC spectrum in chloroform. The {^{13}C, ^{1}H} sites are designated as in reference [14], and their numbering is provided, which corresponds to the coordinates available as the Supporting Materials 'diamine.xyz' file.

site	δ (^{13}C), in ppm	ε (^{13}C), in ppm	σ (^{13}C), in ppm	averaged carbons #	δ (^{1}H), in ppm	ε (^{1}H), in ppm	σ (^{1}H), in ppm	averaged protons #
a	20.580	20.6879	161.6738	45,91	1.7305	1.6909	29.9439	64,65,66,78,79,80
e	125.823	127.2762	51.2390	13,31	1.7440	1.7505	29.8808	50,57
f	115.930	115.6563	63.2782	18,36	1.8640	1.8599	29.7649	51,58
d	113.528	112.1498	66.9113	12,30	1.9020	2.0078	29.6081	49,56
c	18.019	18.2988	164.1491	44,46,89,90	2.7230	2.6476	28.9302	61,62,63,67,68,69, 72,73,74,75,76,77
g	125.509	126.6527	51.8850	7,9,25,27	5.3005	5.3836	26.0312	53,54,93,94
h	112.340	111.1777	67.9185	6,10,24,28	5.5865	5.4728	25.9367	52,55,92,95
b	127.687	127.5166	50.9899	39,41,48,88	5.9910	6.0284	25.3480	59,60,70,71

Figure S3. Reconstructed HSQC spectrum of 3,12-di(4-aminophenyl) Ni^{II} dimesitylnorcorrole in chloroform. The experimental and theoretical chemical shifts, which are listed in Table S4 (at page S3), are plotted as circles and diamonds, respectively.

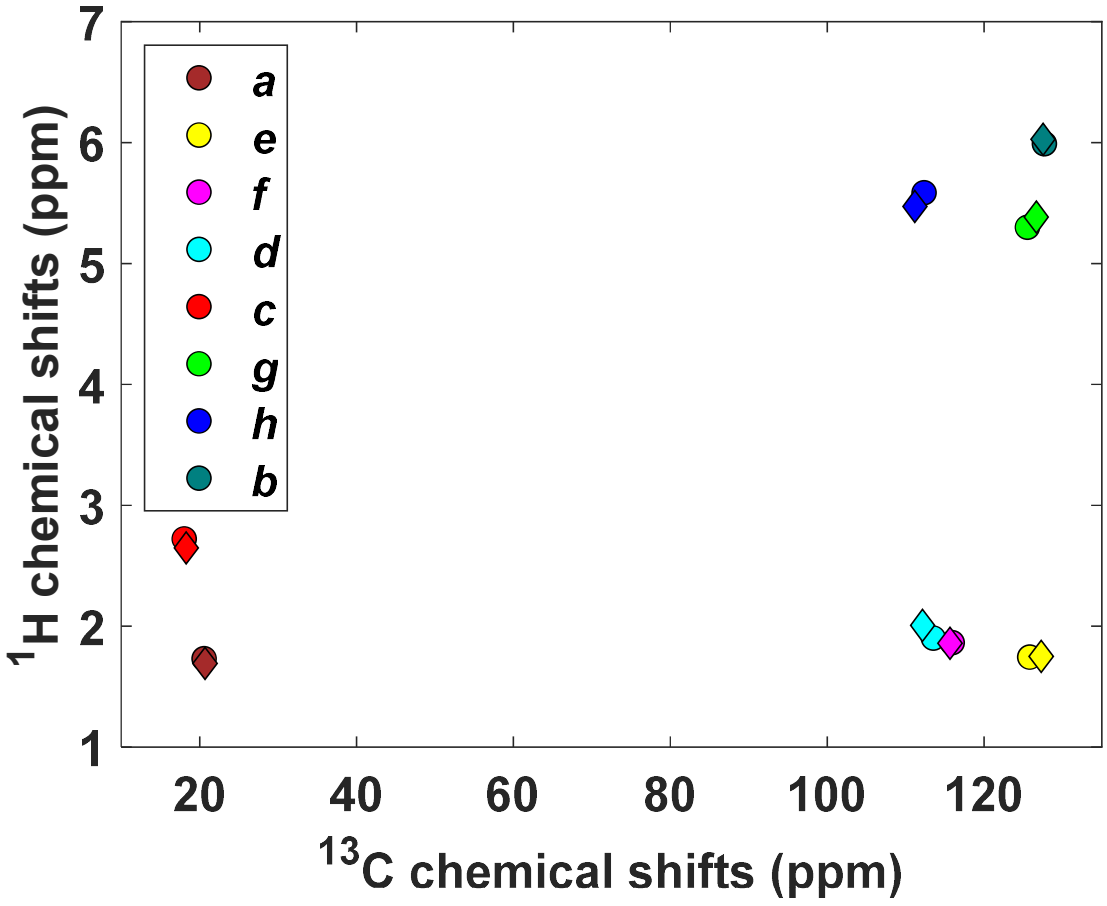

Table S5. The ^{1}H NMR parameters of three compounds presented in the main text. The assignment of respective peaks is obtainable from the corresponding author upon request together with output files from the related GIAO-B3LYP-PCM // B3LYP-PCM calculations performed using the 6-311++G(2d,2p) basis set.

compound	peak #	# of involved protons	δ, in ppm	σ, in ppm
3,12-di(4-aminophenyl) Ni^{II} dimesitylnorcorrole that is compound **2** from reference [14] of the main text	1	3	1.726	29.9041
	2	3	1.735	29.9036
	3	2	1.744	29.8862
	4	2	1.864	29.7897
	5	1	1.898	29.6346
	6	1	1.906	29.6345
	7	12	2.723	28.9218
	8	4	3.186	28.6174
	9	2	5.292	26.0480
	10	2	5.309	26.0481
	11	2	5.578	25.9134
	12	2	5.595	25.9132
	13	4	5.991	25.4019
(6,16-Dimesityl-11-oxa-20,21,22,23-tetra-azapentacyclo[15.2.1.1^{2,5}.1^{7,10}.1^{12,15}]tricosa-1(19),2,4,6,8,10(22),12(21),13,15,17-decaenato)-nickel(ii) that is compound **3** from reference [13] of the main text	1	12	1.9741	29.7121
	2	6	2.4983	29.1545
	3	4	7.1081	24.2775
	4	2	7.5604	23.8536
	5	2	7.5994	23.7793
	6	1	7.8225	23.5770
	7	1	7.8314	23.5770
	8	1	7.8383	23.5256
	9	1	7.8468	23.5256
(6,15-Dimesityl-19,20,21,22-tetra-azapentacyclo[14.2.1.1^{2,5}.1^{7,10}.1^{11,14}]docosa-1(19),2,4,6,8,10(21),11,13,15,17-decaenato)-nickel that is compound **2** from reference [13] of the main text	1	2	1.4704	30.1623
	2	2	1.4794	30.1577
	3	2	1.5692	29.9834
	4	2	1.5777	29.9517
	5	4	6.2578	25.1362
	6	6	1.8192	29.8515
	7	12	2.9003	28.7811

Table S6. Approximated ^{1}H chemical shielding (in ppm) of a proton of coronene in the model from the main text.

point #	*x* (in Å)	*y* (in Å)	*z* (in Å)	interpolated by a spline[b] on the 5 x 5 x 5 data grid[c]	interpolated by a spline[b] on the 9 x 9 x 9 data grid[d]	from the actual calculation[e]
1[a]	0.06230	0.16540	0.28300	13.9585	13.9623	13.9577
2[a]	0.02590	0.05290	0.01140	14.8506	14.8512	14.8981
3[a]	–0.24920	–0.16100	0.11880	12.9092	12.9099	12.9271

Footnotes to Table S6:

[a] randomly generated

[b] as implemented in "interp3" function of Matlab®

[c] the thinner grid with:

```
x = [-0.3 -0.2 -0.1 0.0 +0.1];
y = [-0.2 -0.1 0.0 +0.1 +0.2];
z = [-0.1 0.0 +0.1 +0.2 +0.3];
```

[d] the dense grid with:

```
x = [-0.30 -0.25 -0.20 -0.15 -0.10 -0.05 0.0 +0.05 +0.10];
y = [-0.20 -0.15 -0.10 -0.05 0.0 +0.05 +0.10 +0.15 +0.20];
z = [-0.10 -0.05 0.0 +0.05 +0.10 +0.15 +0.20 +0.25 +0.30];
```

[e] GIAO-B3LYP-SCRF(acetonitrile)/6-311++G(2d,2p)

Table S7. Values of the parameters of equation (1) of the main text (in double precision, as obtained from an application of the Levenberg–Marquardt algorithm implemented in "lsqcurvefit" function of Matlab® Optimization Toolbox).

parameter	value
a_1	–0.003076595181035
a_2	–0.008445862845137
a_3	+0.013363637157717
a_4	–0.001704440669303
a_5	–0.005758757482766
a_6	+0.018211096117826
a_7	–0.002328548611071
a_8	–0.014393382954596
a_9	+0.003682033805506
a_{10}	+8.099764744985144

Using these values, the following symmetric matrix was formed to describe the quadratic form from equation (1) of the main text:

$$A = \begin{pmatrix} a_1 & \frac{a_2}{2} & \frac{a_3}{2} & \frac{a_4}{2} \\ \frac{a_2}{2} & a_5 & \frac{a_6}{2} & \frac{a_7}{2} \\ \frac{a_3}{2} & \frac{a_6}{2} & a_8 & \frac{a_9}{2} \\ \frac{a_4}{2} & \frac{a_7}{2} & \frac{a_9}{2} & a_{10} \end{pmatrix}$$

This matrix is considered below.

Table S7: Details of the diagonalization of A using the Jacobi rotation method (credit: https://people.sc.fsu.edu/~jburkardt/m_src/jacobi_eigenvalue/jacobi_eigenvalue.html).

parameter	value
the 1st eigenvalue, λ_1	–0.023251038464845
the 2nd eigenvalue, λ_2	+0.000000692612501
the 3rd eigenvalue, λ_3	+0.000020936696243
the 4th eigenvalue, λ_4	+8.099765418522848
total number of Jacobi rotations	14

The trace of A is 8.076536009366746, while $\lambda_1 + \lambda_2 + \lambda_3 + \lambda_4$ is 8.076536009366748.

Figure S4. An approximation (shown as red crosses) of the isosurface points (provided by "isosurface" function of Matlab® and shown as black open circles; their number is 69) for y = 0.2 Å. It was obtained from equation (1) of the main text by scanning x at 100 points between –0.3 and +0.075 Å and solving a quadratic equation for the relevant value of z.

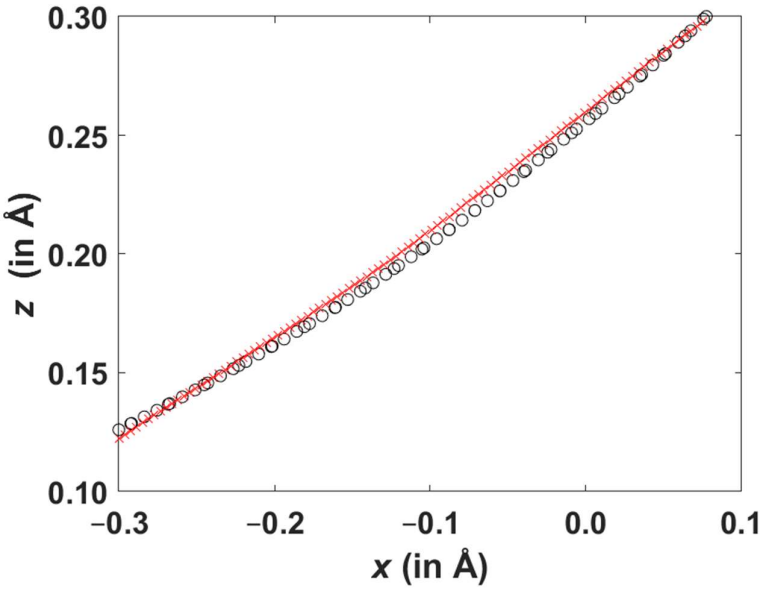

Figure S5. An approximation (shown as red crosses) of the isosurface points (provided by "isosurface" function of Matlab® and shown as black open circles; their number is 70) for x = –0.3 Å. It was obtained from equation (1) of the main text by scanning y at 100 points between –0.155 and 0.2 Å and solving a quadratic equation for the relevant value of z.