Supplementary Material (ESI) for Chemical Communications

Stereoselective Self-Assembly of Atropoisomeric Pd(II) Metallocycles Induced by an Aromatic Guest

Dolores Abella, Víctor Blanco, Elena Pía, Marcos Chas, Carlos Platas-Iglesias, Carlos Peinador* and José M. Quintela*

Departamento de Química Fundamental, Facultad de Ciencias, Universidade da Coruña. Campus A Zapateira, 15071, A Coruña, Spain

E-mail: capeveqo@udc.es (C.P.); jqqoqf@udc.es (J.M.Q.)

Supporting Information

4-Chloromethylquinoline was prepared according to published procedures.[1]

All other reagents were of analytical grade and were used as received. Milli-Q water was purified with a Millipore Gradient A10 apparatus. Merck 60 $HF_{254+366}$ foils were used for thin layer chromatography and Merck 60 (230-400 mesh) silica gel for flash chromatography. NMR spectra were obtained in a Bruker Avance 300 or a Bruker Avance 500 spectrometers equipped with a dual crioprobe for ^{1}H and ^{13}C or a BBI probe for variable temperature experiments. Mass spectrometry experiments were carried out in a Fision VG-Quattro spectrometer for low resolution FAB using 3-nitrobenzylalcohol as matrix. Elemental analysis were obtained in a ThermoQuest Flash EA 1112 analyzer.

1-(Quinolin-4-ylmethyl)-4,4´-bipyridin-1-ium hexafluorophosphate (**1**·PF_6)

To a refluxing solution of 4,4'-bipyridine (0.52 g, 3.3 mmol) in nitromethane (50 mL), a solution of 4-chloromethylquinoline (0.59 g, 3.3 mmol) in nitromethane (50 mL) was added dropwise. Heating was continued for 24 h. After the solution had cooled, the solvent was removed at reduced pressure to leave a solid residue that was purified by flash chromatography (SiO_2, acetone/MeOH/NH_4Cl 1.5M 5:1:4). The ligand-containing fractions were combined and the solvents were removed in vacuo. The residue was dissolved in water (100 mL), and a satured aqueous solution of NH_4PF_6 was added until no further precipitation was observed. The solid was filtered and washed to yield **1**·PF_6 (0.46 g, 41%). ^{1}H NMR (300 MHz, CD_3CN) δ: 6.31 (s, 2 H); 7.15 (d, J = 4.4 Hz, 1 H); 7.75 (t, J = 7.3 Hz, 1 H); 7.81 (d, J = 5.9 Hz , 2 H); 7.88 (t, J = 7.4 Hz, 1 H); 8.06 (d, J = 8.4 Hz, 1 H); 8.20 (d, J = 8.4 Hz, 1 H); 8.37 (d, J = 6.7 Hz, 2 H); 8.84-8.86 (m, 4 H); 8.94 (d, J = 4.4 Hz, 1 H). ^{13}C NMR (125 MHz, D_2O) δ: 61.6 (CH_2); 121.7 (CH); 122.8 (CH); 123.6 (CH); 126.0; 127.4 (CH); 128.9 (CH); 131.0 (CH); 131.2 (CH); 139.1; 142.0; 142.4 (CH); 149.1; 151.3 (CH); 151.9 (CH); 156.0. *Anal*. Calcd $C_{20}H_{16}F_6N_3P$: C, 54.18; H, 3.64; N, 9.48. Found C, 53.96; H, 3.89; N, 9.69.

1-(Quinolin-4-ylmethyl)-4,4´-bipyridin-1-ium nitrate (**1**·NO_3)

A mixture of **1**·PF_6 (0.46 g, 1.0 mmol) and Amberlite CG-400 (5 g) in water (50 mL) was stirred at room temperature for 4 h. The resin was removed by filtration and the filtrate evaporated in vacuo to give **1**·Cl (0.40 g, quantitative). A solution of **1**·Cl (0.40 g, 1.2 mmol) in water (10 mL) and $AgNO_3$ (0.21 g, 1.2 mmol) was stirred at room temperature for 3 h with the exclusion of light. The mixture was filtered through Celite and the filtrate evaporated to give **1**·NO_3 (0.38 g, 87 %). ^{1}H NMR (500 MHz, D_2O) δ: 6.58 (s, 2 H); 7.38 (d, J = 4.7 Hz, 1 H); 7.88 (t, J = 8.3 Hz , 1 H); 8.00-8.04 (m, 3 H); 8.19 (d, J = 8.5 Hz, 1 H); 8.25 (d, J = 8.5 Hz, 1 H); 8.56 (d, J = 6.8 Hz, 2 H); 8.86 (d, J

[1] S. R. Ramadas, M. V. Krishna *Current Science* 1981, **50**, 120-122.

= 6.3 Hz, 2 H); 8.98 (d, *J* = 4.7 Hz, 1 H); 9.14 (d, *J* = 6.9 Hz, 2 H). ^{13}C NMR (125 MHz, D_2O) *δ*: 63.6 (CH_2); 121.1 (CH); 122.8 (CH); 122.9 (CH); 125.5; 126.7 (CH); 128.1 (CH); 128.9 (CH); 131.5 (CH); 140.5; 143.0; 145.6 (CH); 146.1; 149.5 (CH); 149,7 (CH); 154.9. MS (FAB, 3-NBA) *m/z*: 298 $[M\text{-}NO_3]^+$ *Anal.* Calcd $C_{20}H_{16}N_4O_3$: C, 66.66; H, 4.48; N, 15.55. Found C, 66.47; H, 4.40; N, 15.29.

Platinum metallocycle 3b·$6PF_6$

A solution of **1**·NO_3 (27.0 mg, 0.08 mmol) and $Pt(en)(NO_3)_2$ (25.3 mg, 0.08 mmol) in water (150 mL) was heated at 100 C for 7 d. After cooling to room temperature, NH_4PF_6 (500 mg, 3.1 mmol) was added and a white solid precipitated. The precipitate was filtered and washed with water to give **3b**·$6PF_6$ (53.2 mg, 64 %). ^{1}H NMR (500 MHz, CD_3NO_2) *δ*: 3.17 (br s, 16 H); 5.09-5.21 (m, 16 H); 6.17-6.24 (m, 4 H); 6.64-6.72 (m, 4 H); 7.66 (d, *J* = 6.9 Hz, 4 H); 7.71 (d, *J* = 6.9 Hz, 4 H); 7.89 (t, *J* = 8.2 Hz, 2 H); 7.96 (d, *J* = 5.6 Hz, 2 H); 8.02 (d, *J* = 7.0 Hz, 4 H); 8.03-8.10 (m, 8 H); 8.17 (t, *J* = 7.4 Hz, 2 H); 8.21 (d, *J* = 8.4 Hz, 2 H); 8.30 (t, *J* = 7.4 Hz, 2 H); 8.44 (d, *J* = 8.3 Hz, 2 H); 8.84 (d, *J* = 7,0 Hz, 4 H); 8.87 (d, *J* = 7.0 Hz, 4 H); 8.93 (d, *J* = 6.9 Hz, 4 H); 8.97 (d, *J* = 6.9 Hz, 4 H); 9.53 (d, *J* = 5.5 Hz, 2 H); 9.67 (d, *J* = 5.5 Hz, 2 H); 9.83 (d, *J* = 8,6 Hz, 2 H); 9.92 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, CD_3NO_2*)* *δ*: 49.5 (CH_2); 49.7 (CH_2); 60.6 (CH_2); 61.2 (CH_2); 124.9 (CH); 125.2 (CH); 126.4 (CH); 126.5 (CH); 126.9 (CH); 127.5 (CH); 127.9 (CH); 128.0 (CH); 128.5 (CH); 128.9 (CH); 129.1 (CH); 132.0 (CH); 132.2 (CH); 134.8 (CH); 135.1 (CH); 143.2; 143.5; 145.8; 146.1 (CH); 153.3; 153.6; 154.4 (CH); 156.7; 156.8. MS (FAB, 3-NBA) *m/z*: 1831 $[M\text{-}PF_6]^+$; 1686 $[M\text{-}2PF_6]^+$; 1541 $[M\text{-}3PF_6]^+$; 1396 $[M\text{-}4PF_6]^+$. *Anal*. Calcd $C_{44}H_{48}F_{36}N_{10}P_6Pt_2$: C, 26.73; H, 2.45; N, 7.09. Found C, 26.58; H, 2.69; N, 7.23.

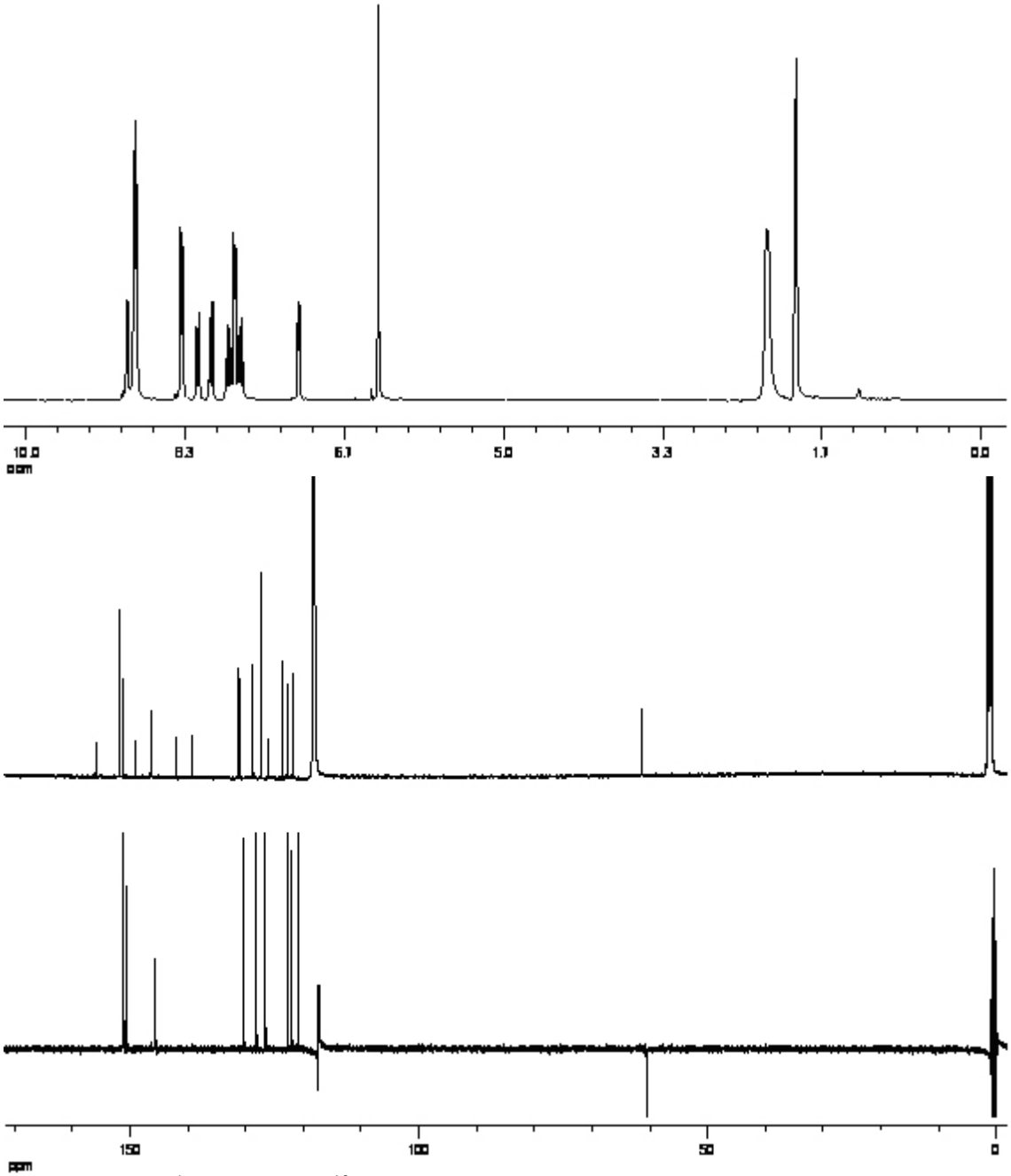


Figure S1. ^{1}H NMR and ^{13}C NMR (CD_3CN, 500 and 125 MHz) spectra of **1**·PF_6

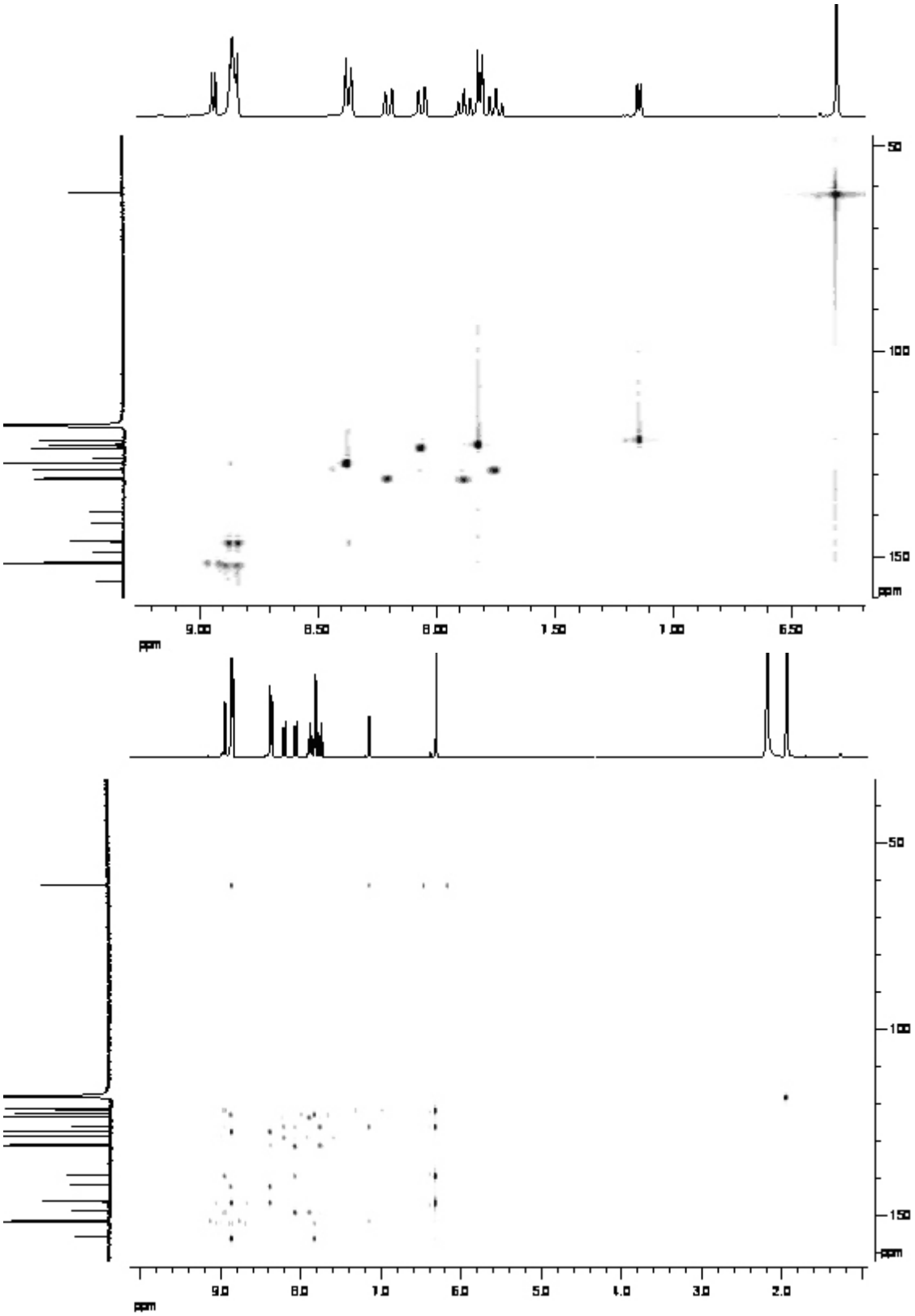


Figure S2. HSQC (top) and HMBC (bottom) (CD_3CN, 500 and 125 MHz) spectra of **1**·PF_6.

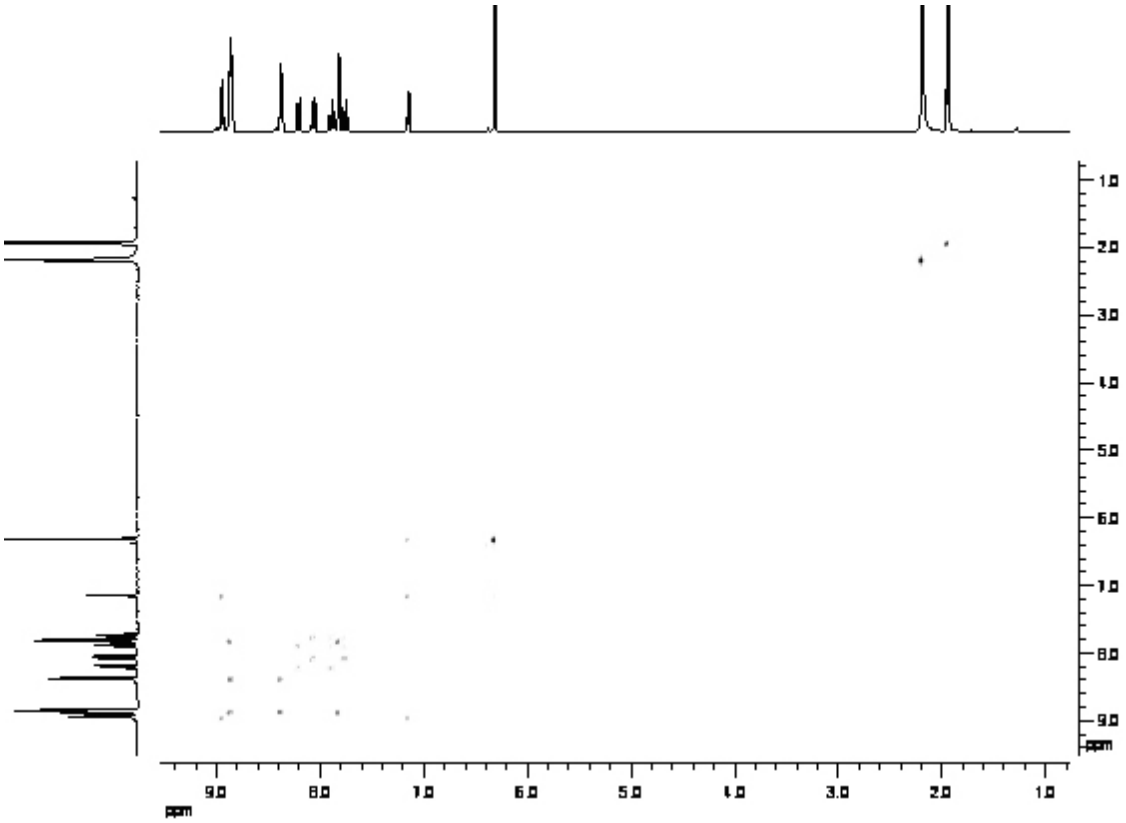


Figure S3. COSY (CD_3CN, 500 MHz) spectrum of **1**·PF_6.

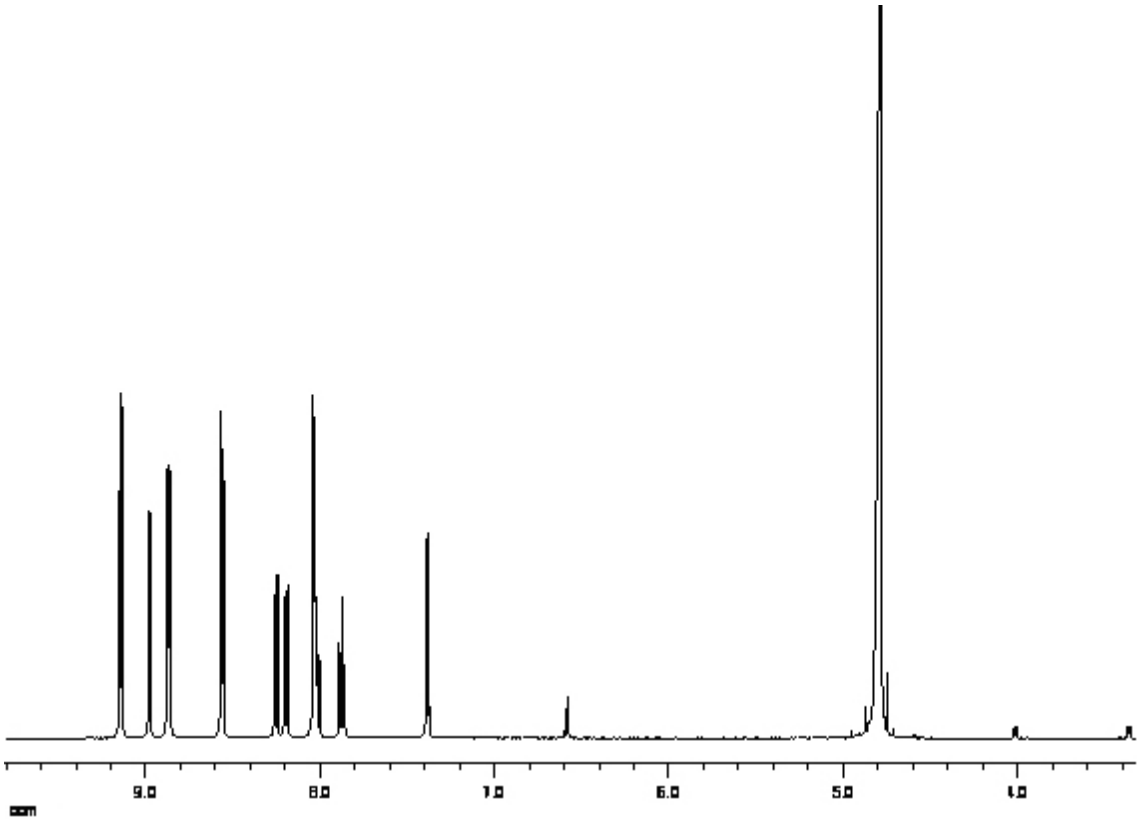


Figure S4. ^1H NMR (D_2O, 500 MHz) spectrum of **1**·NO_3

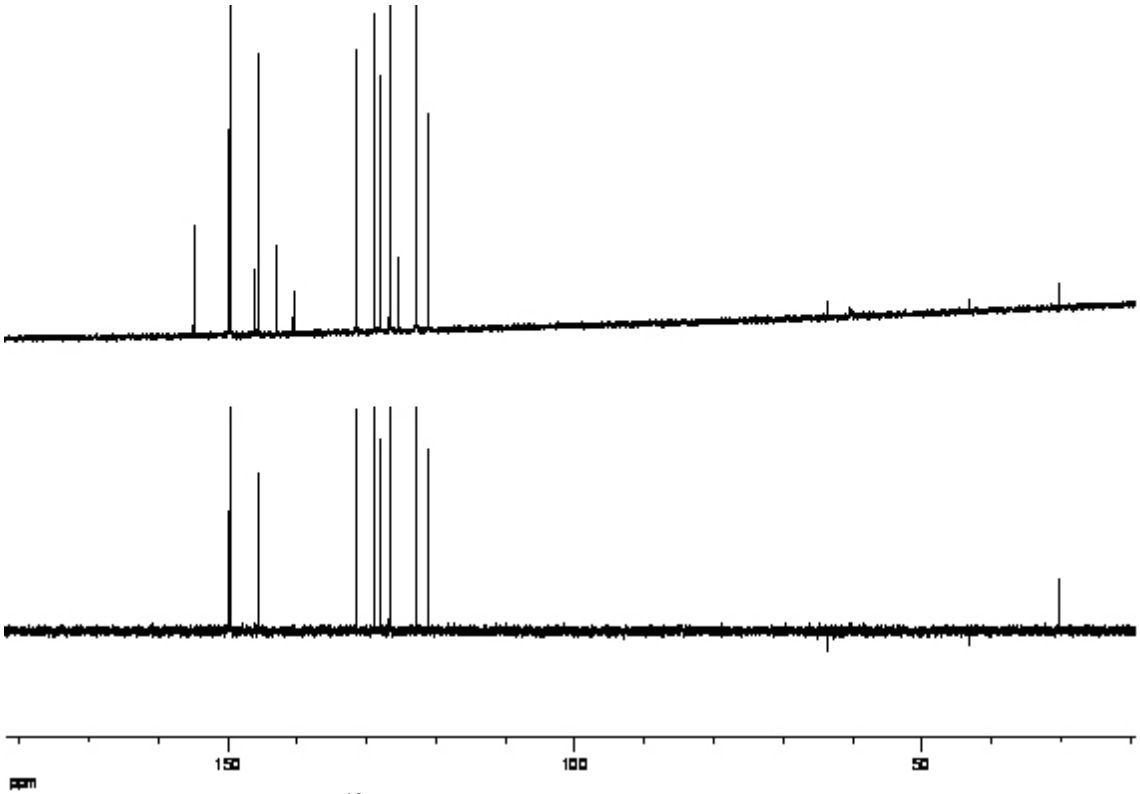


Figure S5. ^{13}C NMR (D_2O, 125 MHz) spectrum of **1**·NO_3

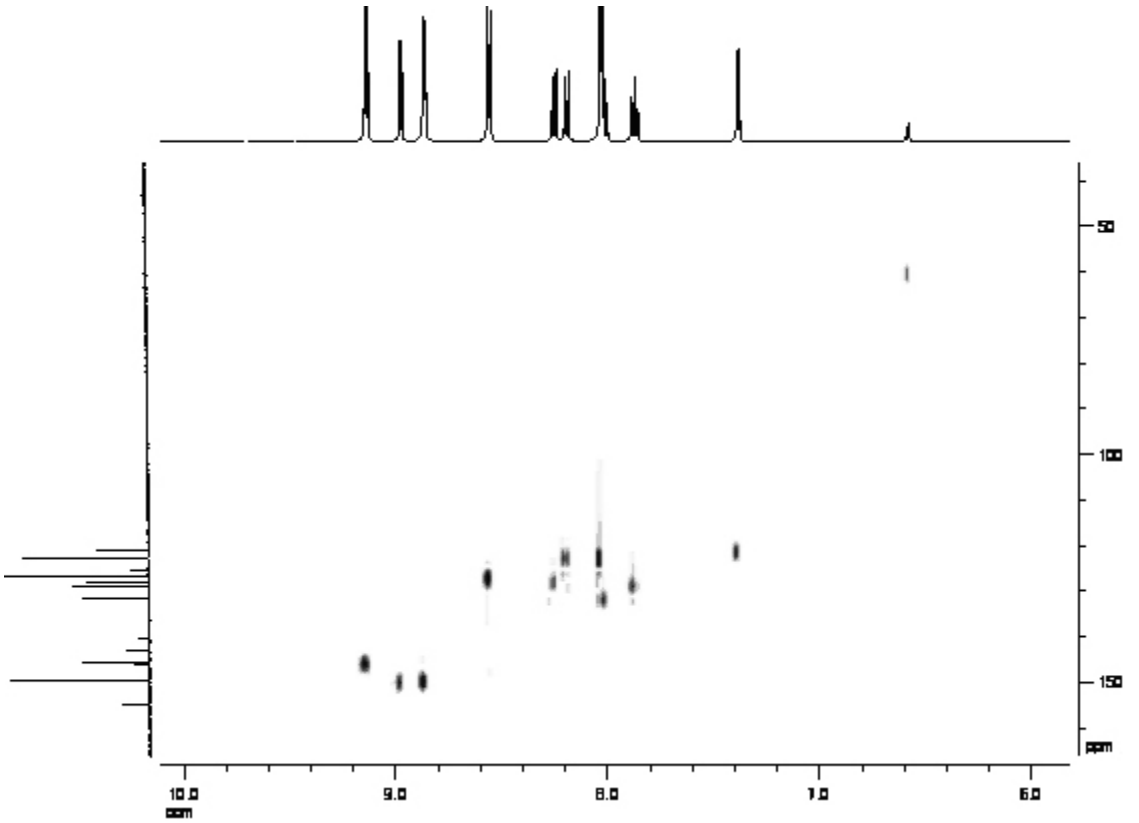


Figure S6. HSQC (D_2O, 500 and 125 MHz) spectrum of **1**·NO_3

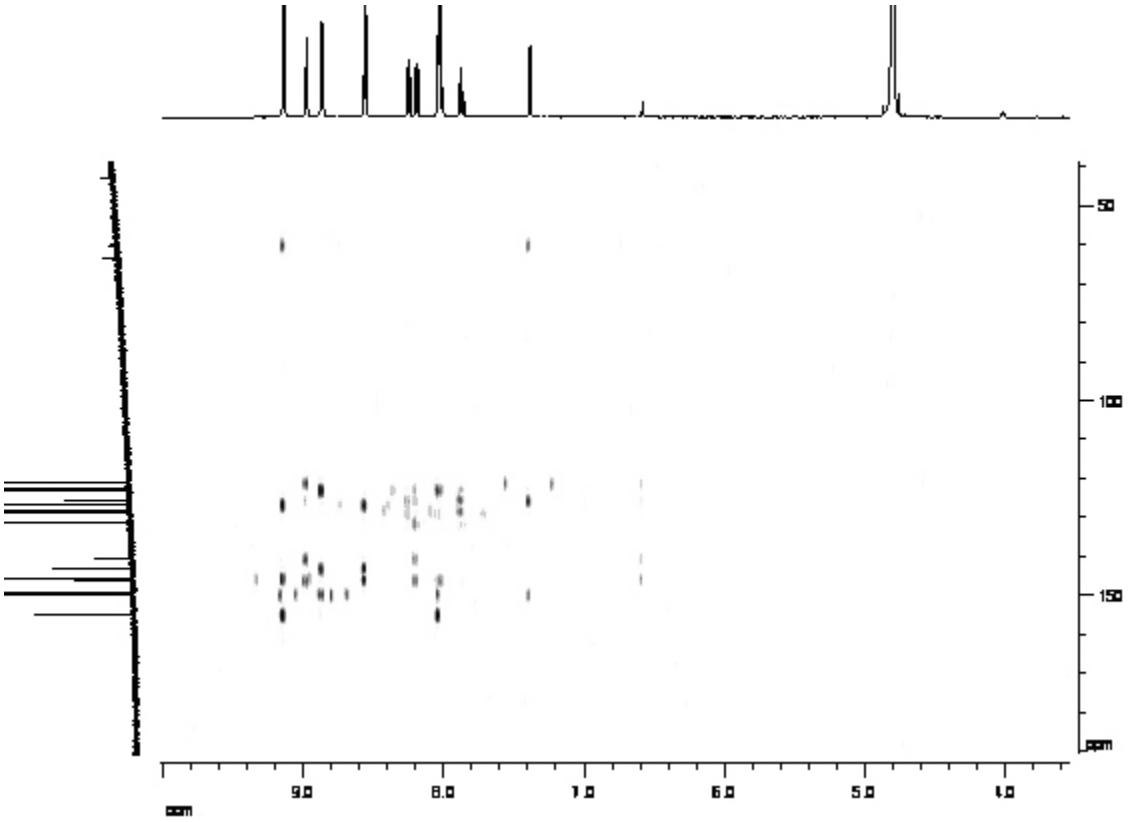


Figure S7. HMBC (D_2O, 500 and 125 MHz) spectrum of **1**·NO_3

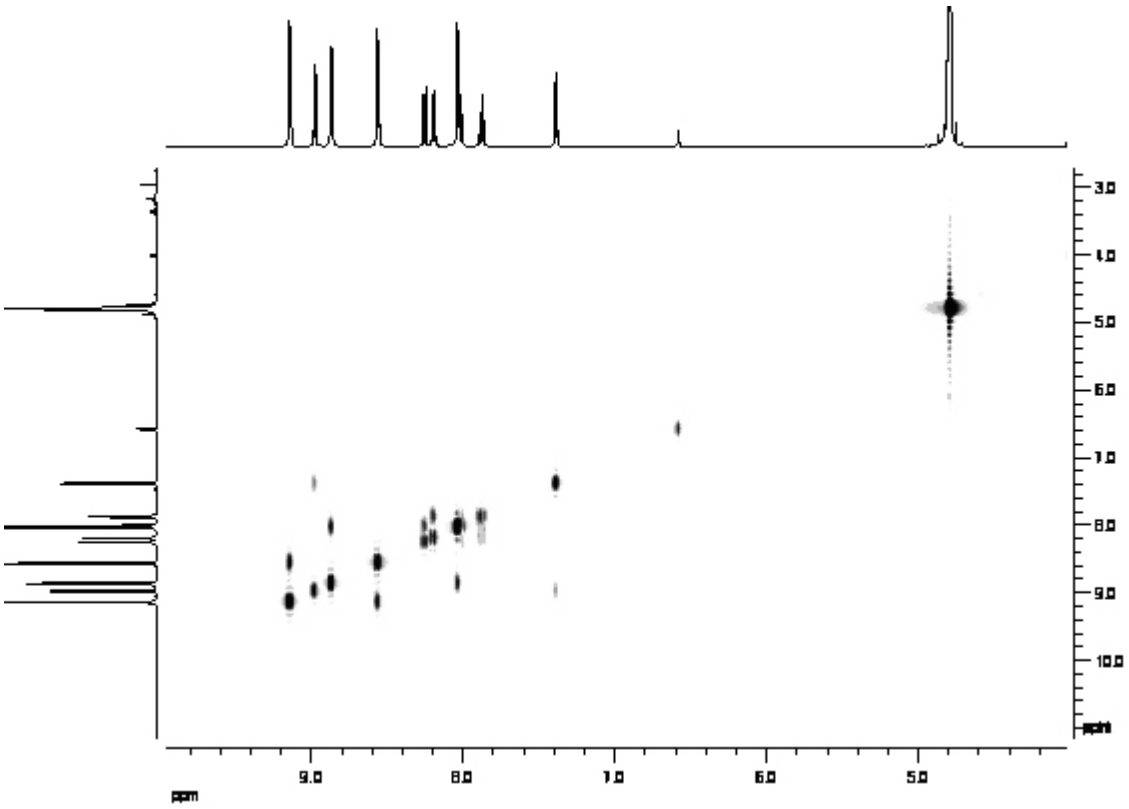


Figure S8. COSY (D_2O, 500 MHz) spectrum of **1**·NO_3

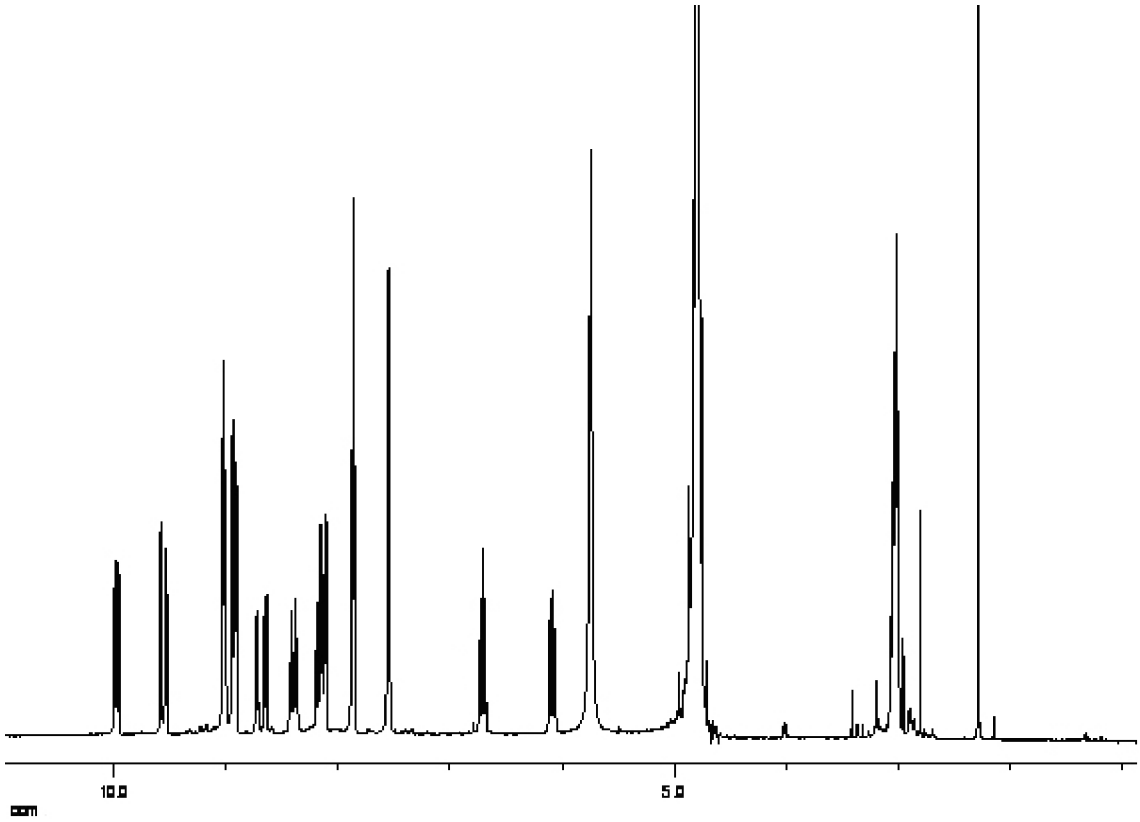


Figure S9. ^{1}H NMR (D_2O, 500 MHz) spectrum of HQ⊂**3a**·6NO_3.

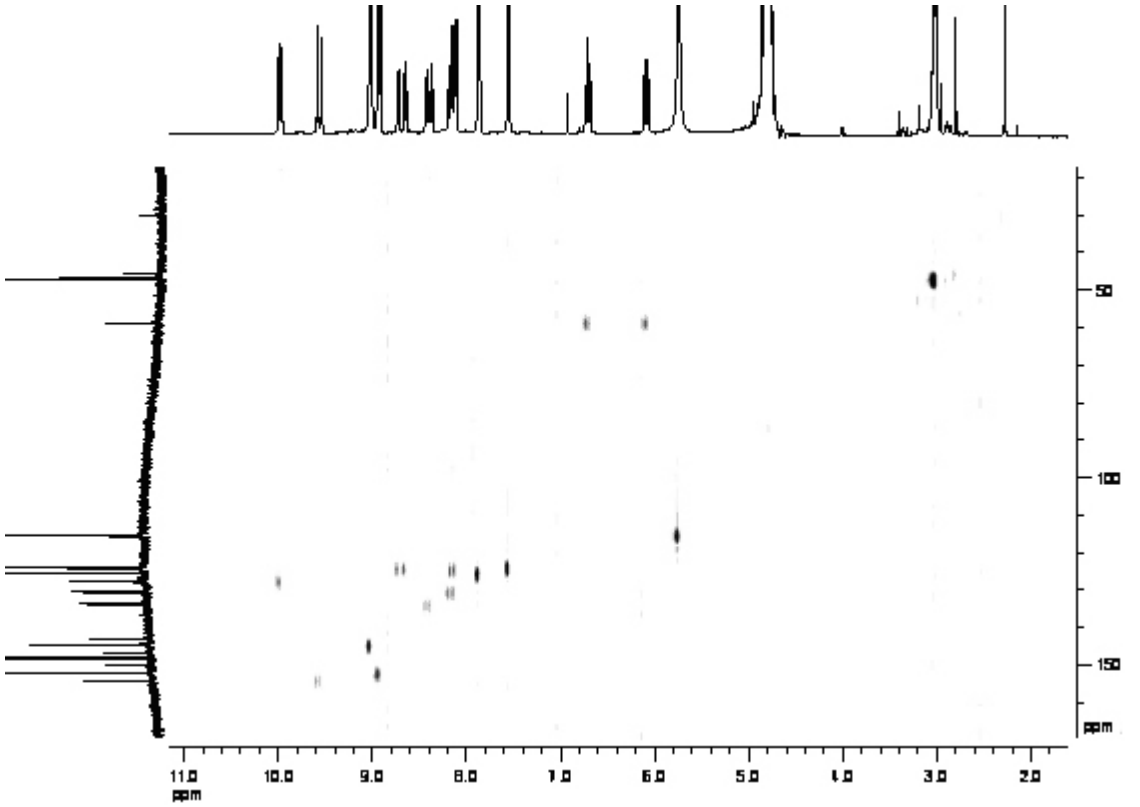


Figure S10. HSQC (D_2O, 500 and 125 MHz) spectrum of HQ⊂**3a**·6NO_3.

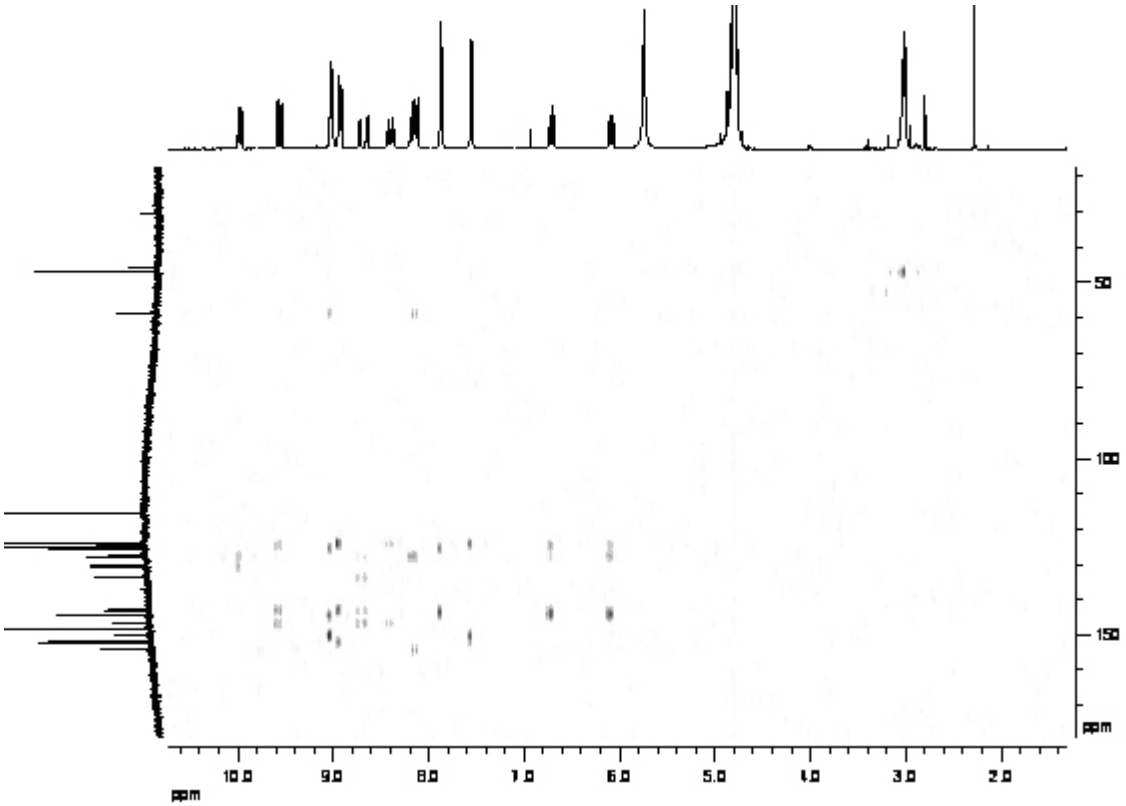


Figure S11. HMBC (D_2O, 500 and 125 MHz) spectrum of HQ⊂**3a**·6NO_3.

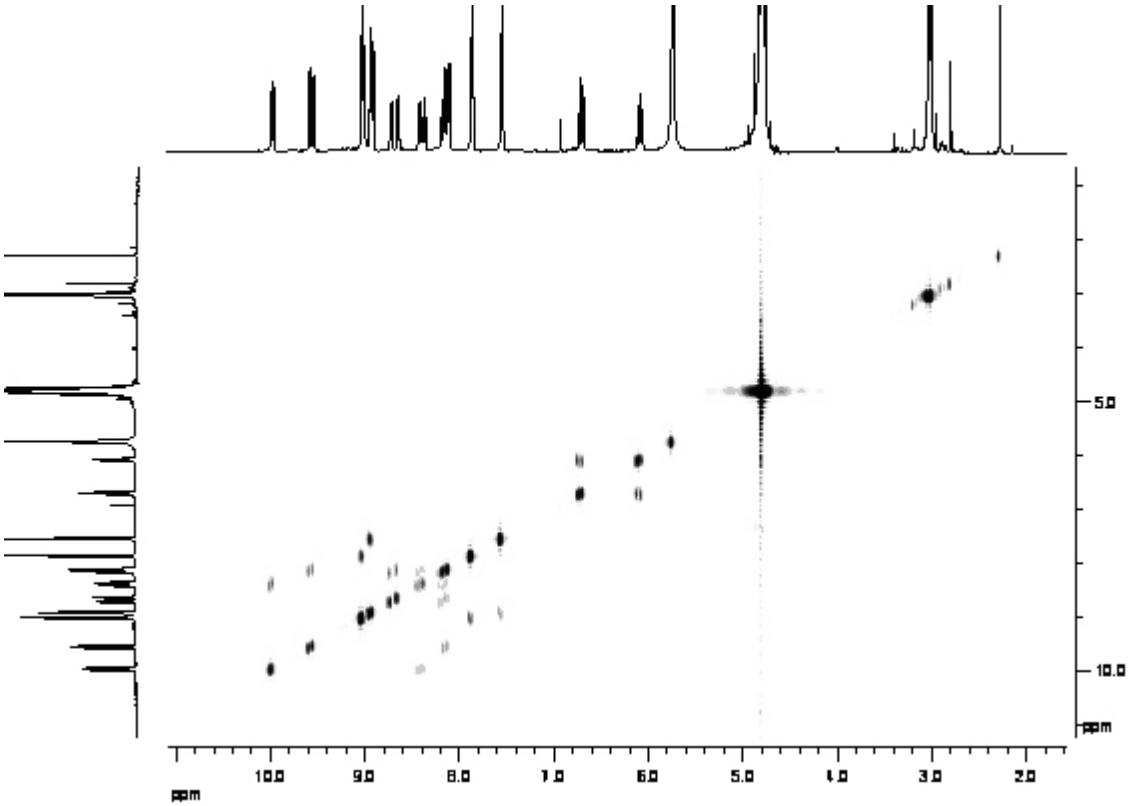


Figure S12. COSY (D_2O, 500 MHz) spectrum of HQ⊂**3a**·6NO_3.

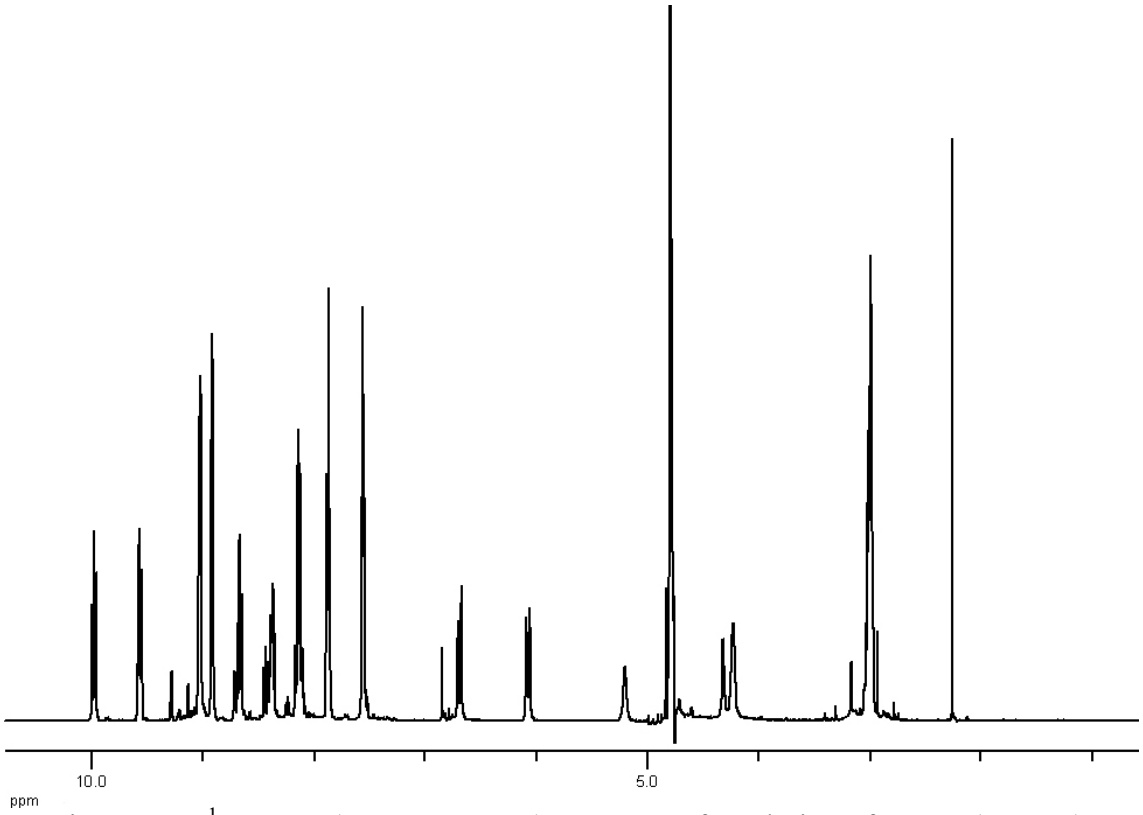


Figure S13. ^{1}H NMR (D_2O, 500 MHz) spectrum of a solution of **1**·NO_3 (10 mM), $Pd(en)(NO_3)_2$ (10 mM), and resorcinol (5 mM).

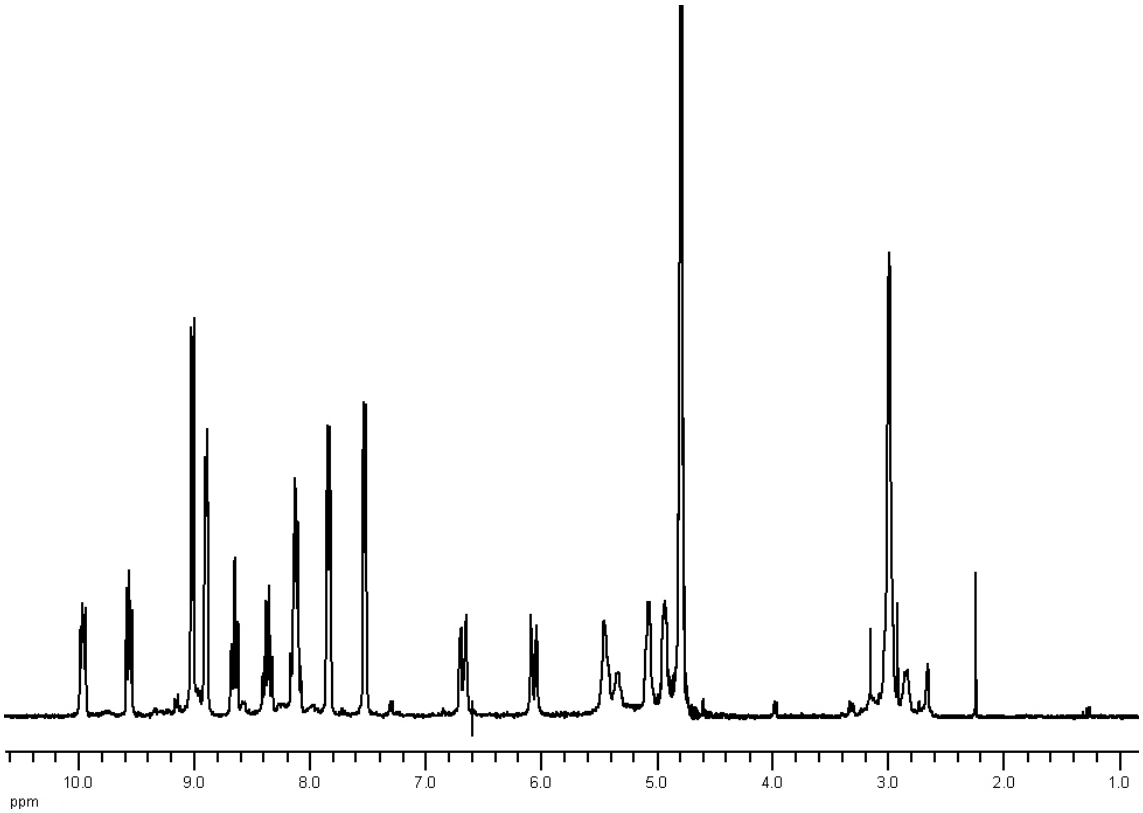


Figure S14. ^{1}H NMR (D_2O, 300 MHz) spectrum of a solution of **1**·NO_3 (10 mM), $Pd(en)(NO_3)_2$ (10 mM), and cathecol (5 mM).

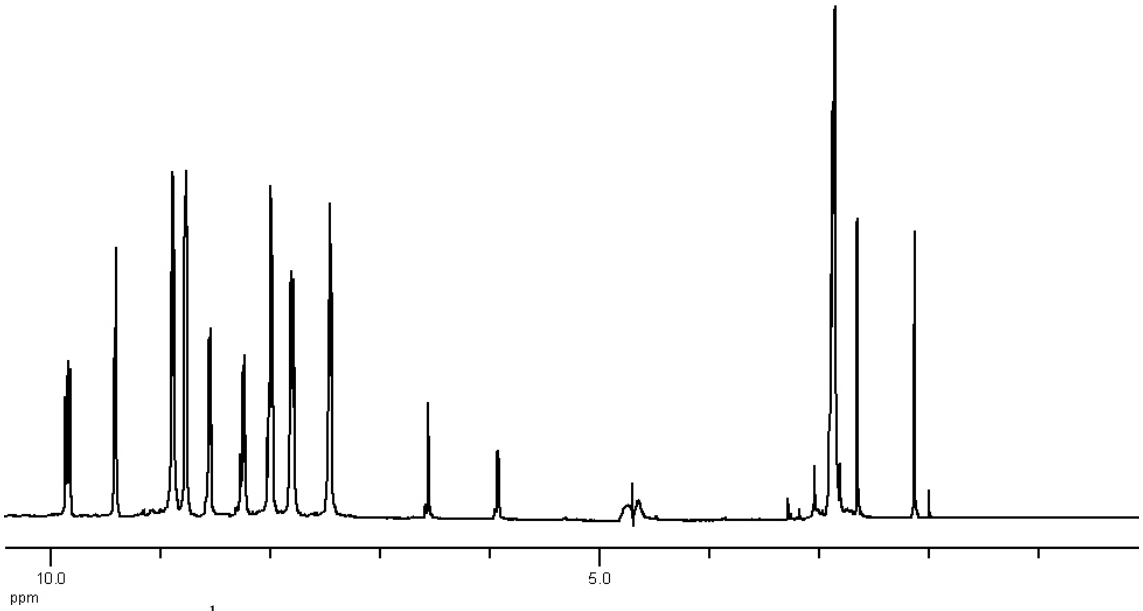


Figure S15. ^{1}H NMR (D_2O, 500 MHz) spectrum of a solution of **1**·NO_3 (10 mM), $Pd(en)(NO_3)_2$ (10 mM), and phloroglucinol (5 mM).

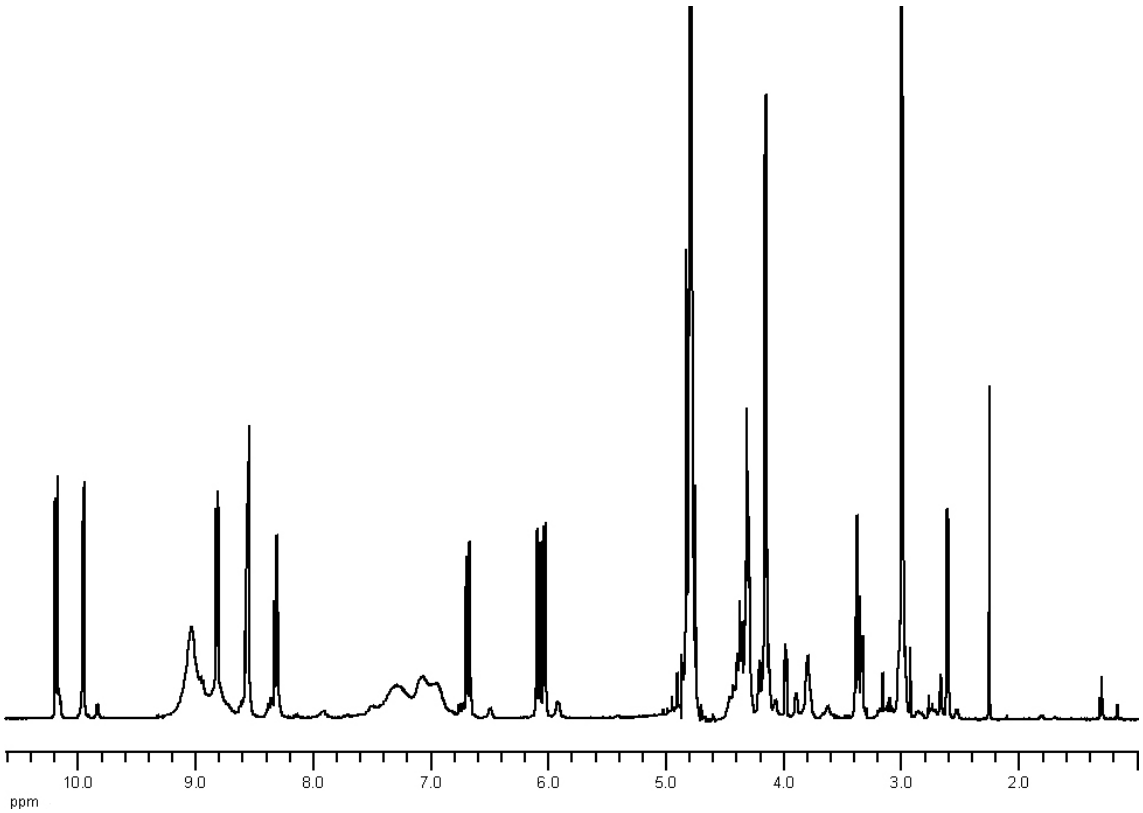


Figure S16. ^{1}H NMR (D_2O, 500 MHz) spectrum of 1,5-NPH⊂**3a**·$6NO_3$.

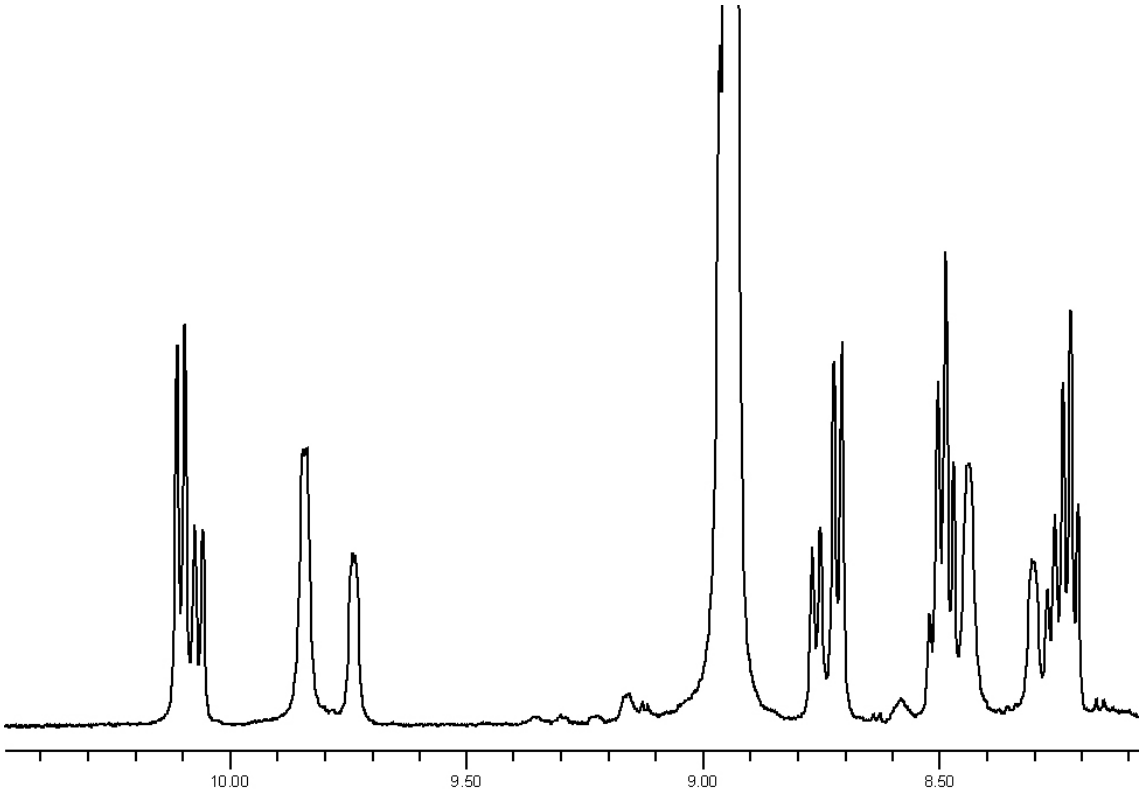


Figure S17. Partial ^{1}H NMR (D_2O, 500 MHz) spectrum of 1,3-NPH⊂**3a**·$6NO_3$.

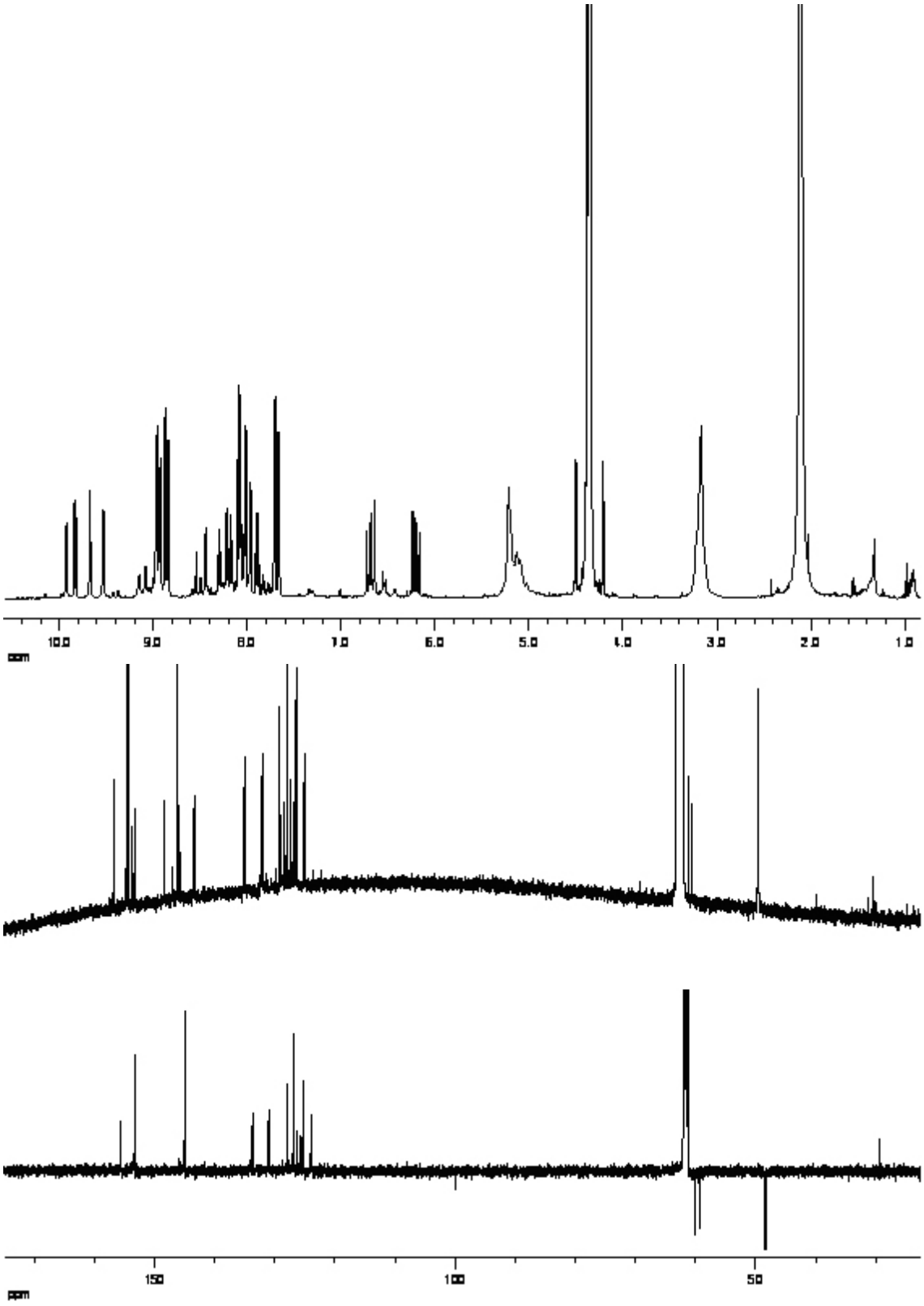


Figure S18. ^{1}H and ^{13}C NMR (CD_3CN, 500 and 125 MHz) spectra of **3b**·$6PF_6$.

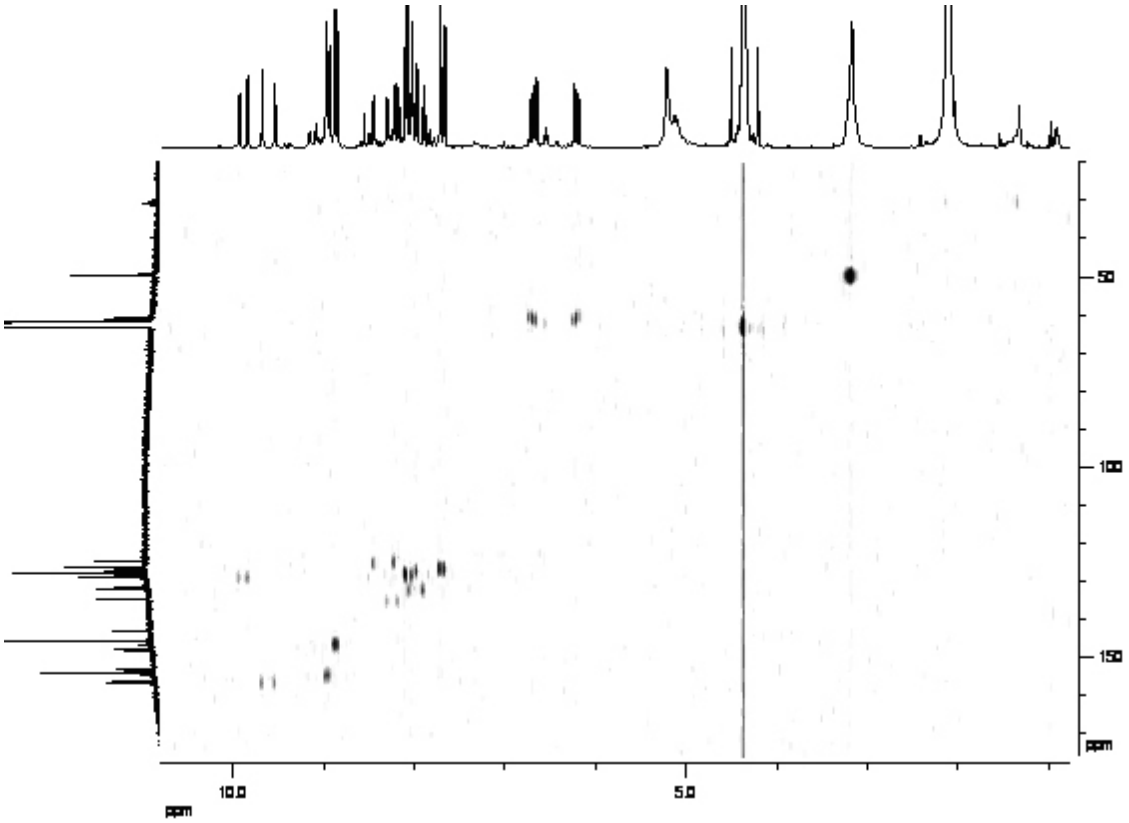


Figure S19. HSQC (CD_3CN, 500 and 125 MHz) spectrum of **3b**·$6PF_6$.

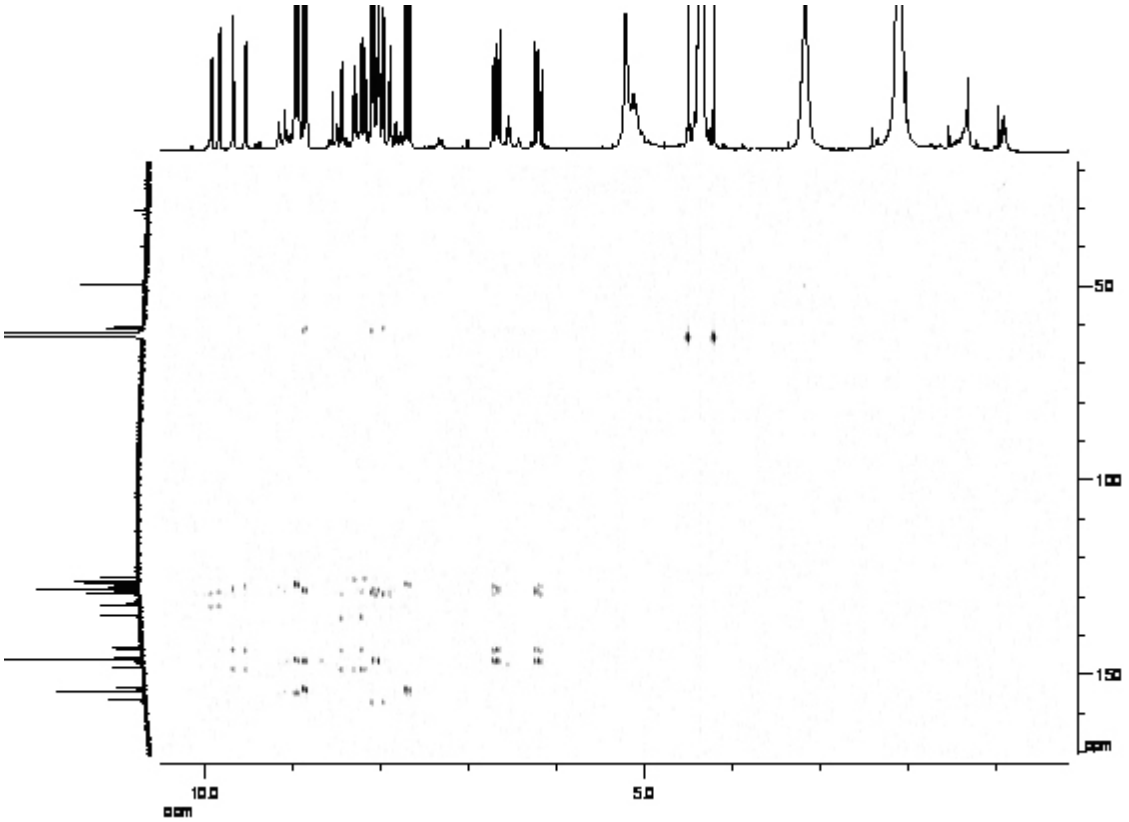


Figure S20. HMBC (CD_3CN, 500 and 125 MHz) spectrum of **3b**·$6PF_6$.

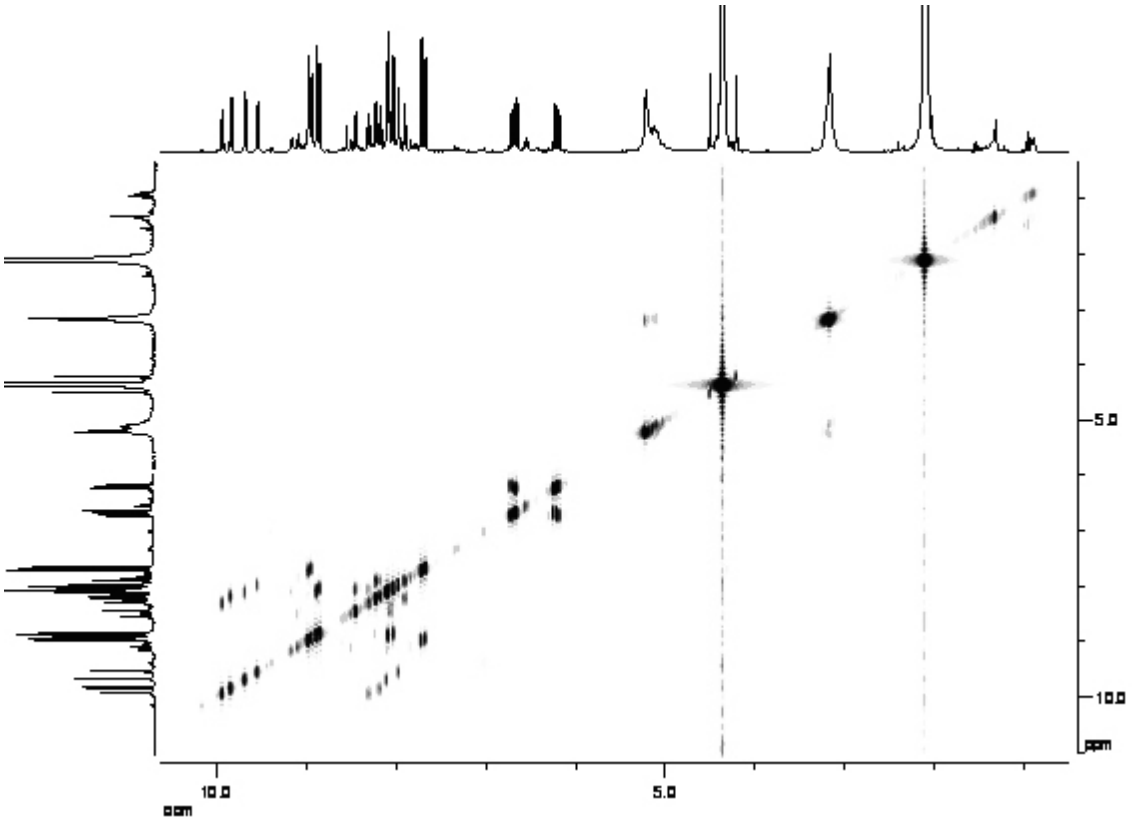


Figure S21. COSY (CD_3CN, 500) spectrum of **3b**·$6PF_6$.

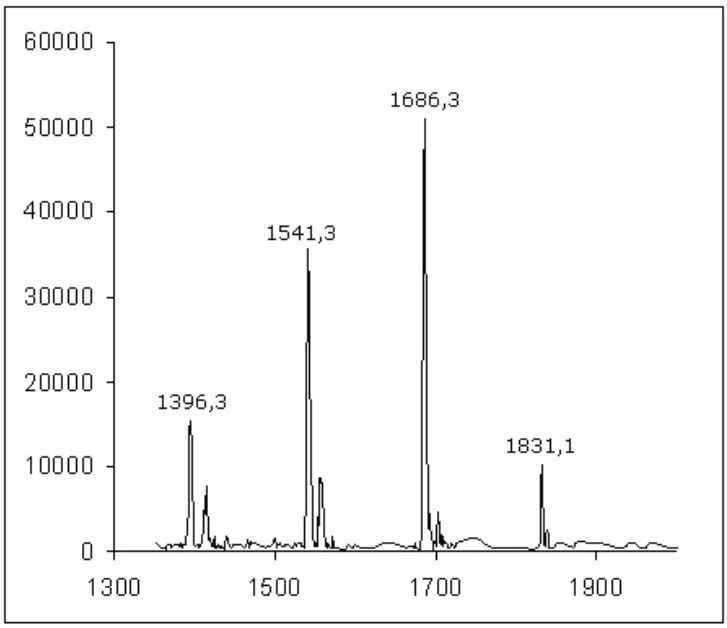


Figure S22 MS (FAB, 3-NBA) spectrum of **3b**·$6PF_6$.

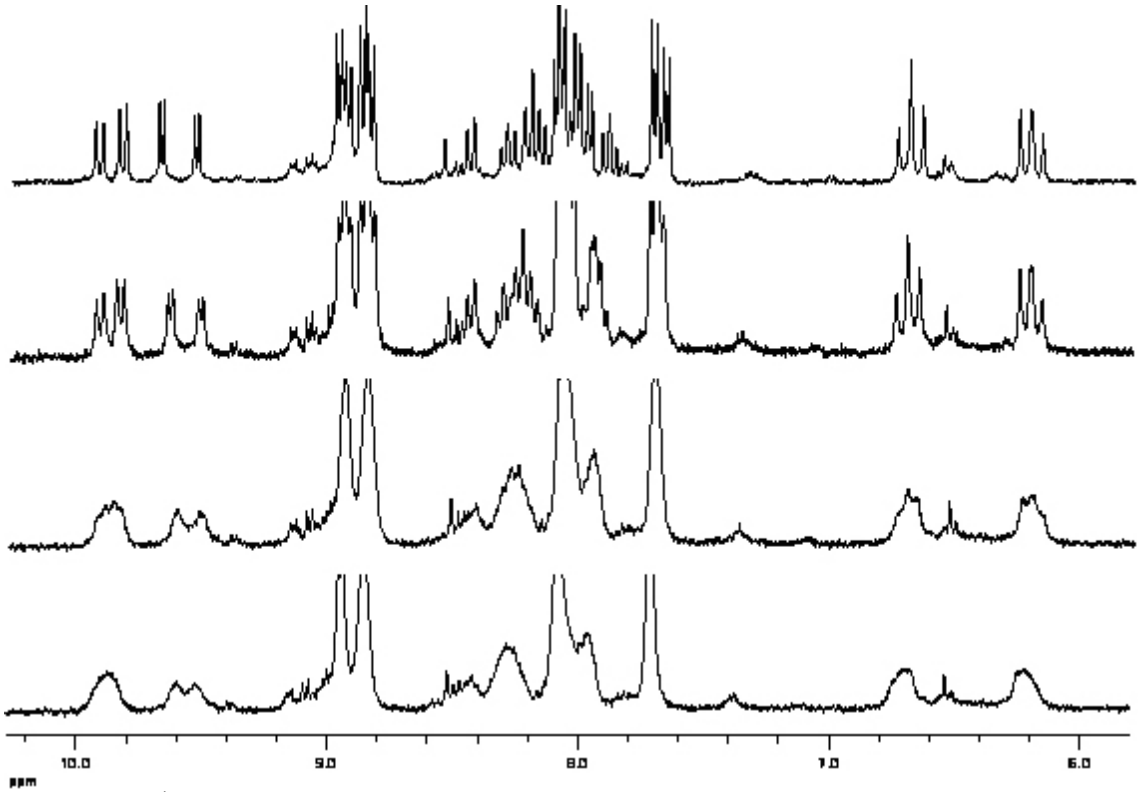
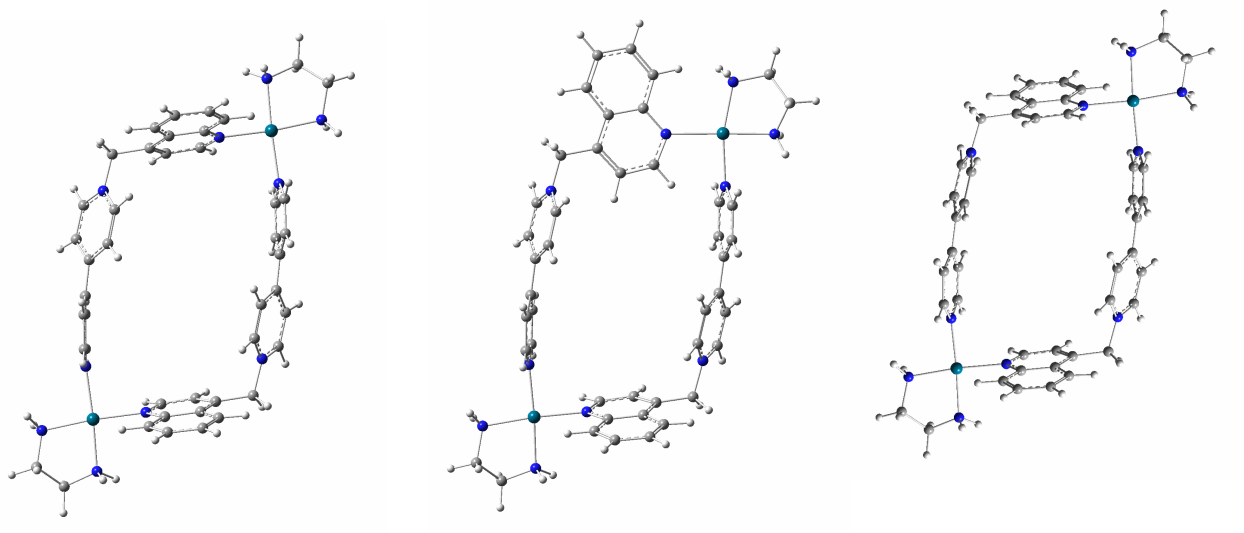


Figure S23 ^{1}H NMR (CD_3NO_2, 300 MHz) spectra of **3b**·$6PF_6$ at (from top) a) 298 K, b) 343 K, c) 353 K, d) 355 K.



syn TS *anti*

Figure S24. Optimised geometries (B3LYP) of the *syn* and *anti* atropoisomers of $[Pt_2(en)_2(\mathbf{1})_2]^{6+}$ and that of the transition state (TS) that conects these two minimum energy conformations.

Computational Methods

All calculations were performed using the Gaussian 03 (Revision C.01)[i] program package with the B3LYP[ii, iii] three parameter hybrid density functional. In vacuo geometry optimizations were carried out without constrains. Initial geometries were constructed using the GaussView program[iv] and standard bond distances and angles. In these calculations we used the standard 6-31G(d) basis set for C, H and N atoms, while for Pt the LanL2DZ valence and effective core potential functions were used.[v]

(*syn*)-$[Pt_2(en)_2(\mathbf{1})_2]^{6+}$ (0 imaginary frequencies)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6		2.528858	-3.079995	-0.201147
2	6		3.288217	-2.840268	0.957247
3	6		4.517398	-2.192609	0.863435
4	6		4.343097	-2.067277	-1.447102
5	6		3.108548	-2.709789	-1.426405
6	6		1.135876	-3.616121	-0.139389
7	6		0.290723	-3.287509	0.939829
8	6		-1.041471	-3.657731	0.930472
9	6		-0.768018	-4.748867	-1.129011
10	6		0.576023	-4.398125	-1.165667
11	1		2.952142	-3.159589	1.938555
12	1		5.105296	-1.989586	1.751299
13	1		4.791688	-1.763535	-2.386448
14	1		2.604265	-2.877165	-2.372388
15	1		0.652099	-2.715934	1.787247
16	1		-1.718779	-3.402956	1.737229
17	1		-1.222743	-5.351377	-1.908087
18	1		1.168600	-4.758285	-2.000436
19	6		-3.044354	-4.689022	-0.109980
20	1		-3.213842	-5.362162	0.730647
21	1		-3.230645	-5.259800	-1.021731
22	7		-1.570539	-4.348474	-0.110980
23	7		5.029215	-1.775483	-0.318001
24	6		3.942406	3.451376	-0.076252
25	6		4.653769	3.038764	1.093448
26	6		4.115933	2.725942	-1.243207
27	6		5.476600	1.848259	1.012951
28	6		4.945300	1.593290	-1.258114
29	1		3.648226	3.026315	-2.175791
30	7		5.589309	1.147578	-0.177363
31	1		5.096276	1.045440	-2.181877
32	6		3.044303	4.688984	-0.110102
33	1		3.230569	5.259721	-1.021884
34	1		3.213812	5.362161	0.730490
35	6		0.767898	4.748959	-1.128970
36	6		1.041494	3.657554	0.930352
37	6		-0.576146	4.398220	-1.165579
38	6		-0.290699	3.287328	0.939753
39	1		1.718859	3.402675	1.737029
40	6		-1.135926	3.616081	-0.139364
41	1		-1.168780	4.758488	-2.000260
42	1		-0.652015	2.715642	1.787120
43	1		1.222569	5.351571	-1.907998
44	7		1.570490	4.348434	-0.111046
45	6		-2.528910	3.079957	-0.201098
46	6		-3.108685	2.709917	-1.426365
47	6		-3.288186	2.840068	0.957317
48	6		-4.343232	2.067400	-1.447063
49	1		-2.604471	2.877425	-2.372361
50	6		-4.517370	2.192413	0.863504
51	1		-2.952043	3.159255	1.938645
52	7		-5.029268	1.775447	-0.317953
53	1		-4.791887	1.763782	-2.386419
54	1		-5.105203	1.989264	1.751382
55	6		-3.942453	-3.451410	-0.076158
56	6		-4.653629	-3.038636	1.093598

57	6	-4.116160	-2.726133	-1.243184
58	6	-5.476460	-1.848134	1.013072
59	6	-4.945521	-1.593477	-1.258113
60	1	-3.648600	-3.026633	-2.175801
61	1	-5.096636	-1.045747	-2.181924
62	7	-5.589352	-1.147612	-0.177318
63	7	8.082836	-2.215326	-0.705451
64	7	8.570834	0.482045	-0.539205
65	7	-8.570871	-0.482097	-0.539239
66	7	-8.082883	2.215275	-0.705483
67	6	9.672542	-0.395917	-1.097504
68	6	9.516419	-1.774939	-0.486938
69	1	10.649801	0.038497	-0.866946
70	1	9.554613	-0.419492	-2.184408
71	1	9.695360	-1.762448	0.591752
72	1	10.202887	-2.495900	-0.940796
73	1	8.843461	0.818372	0.390451
74	1	8.480290	1.322633	-1.117732
75	1	7.877362	-3.013534	-0.097472
76	1	7.982141	-2.566124	-1.664035
77	6	-9.672569	0.395857	-1.097572
78	6	-9.516469	1.774882	-0.487007
79	1	-10.649832	-0.038561	-0.867037
80	1	-9.554611	0.419427	-2.184472
81	1	-9.695440	1.762394	0.591678
82	1	-10.202929	2.495838	-0.940888
83	1	-7.877430	3.013486	-0.097499
84	1	-7.982164	2.566072	-1.664065
85	1	-8.843521	-0.818420	0.390413
86	1	-8.480308	-1.322689	-1.117759
87	6	4.624154	3.741599	2.332147
88	6	6.181697	1.414677	2.160218
89	6	5.347467	3.309721	3.422476
90	1	5.331086	3.878848	4.346947
91	6	6.125531	2.130782	3.338504
92	1	6.689312	1.797908	4.204976
93	1	4.055476	4.660576	2.425620
94	1	6.781584	0.511240	2.101367
95	6	-6.181372	-1.414392	2.160391
96	6	-4.623823	-3.741304	2.332387
97	6	-6.125027	-2.130339	3.338765
98	1	-6.688670	-1.797344	4.205281
99	6	-5.346960	-3.309273	3.422772
100	1	-5.330440	-3.878277	4.347317
101	1	-6.781263	-0.510959	2.101512
102	1	-4.055140	-4.660275	2.425893
103	78	-6.778298	0.593127	-0.407112
104	78	6.778251	-0.593169	-0.407120

HF = -2489.3531941 Hartree
Zero-point correction = 0.877978
Sum of electronic and thermal Enthalpies = -2488.425678
Sum of electronic and thermal Free Energies = -2488.560829

(*anti*)-$[Pt_2(en)_2(\mathbf{1})_2]^{6+}$ (0 imaginary frequencies)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6		2.494420	-3.036219	0.496062
2	6		3.372609	-2.730931	1.551120
3	6		4.591579	-2.109249	1.289816
4	6		4.189338	-2.147392	-0.993143
5	6		2.953991	-2.757360	-0.803005
6	6		1.109725	-3.548096	0.729920
7	6		0.431901	-3.290673	1.937690
8	6		-0.896944	-3.646434	2.092414
9	6		-0.946496	-4.571345	-0.059721
10	6		0.387694	-4.247196	-0.257189
11	1		3.139846	-2.973296	2.582685
12	1		5.263418	-1.848549	2.099725
13	1		4.547542	-1.927162	-1.992444
14	1		2.358766	-2.976563	-1.682500
15	1		0.916546	-2.795327	2.771180
16	1		-1.432452	-3.465997	3.016809
17	1		-1.521529	-5.101464	-0.809734
18	1		0.847509	-4.565857	-1.186351
19	6		-3.064360	-4.529360	1.263267
20	1		-3.202063	-4.798251	2.313095
21	1		-3.283030	-5.421124	0.677208
22	7		-1.589986	-4.239153	1.087821
23	7		4.989822	-1.789359	0.036887
24	6		3.962381	3.420623	-0.597180
25	6		4.701260	3.196749	0.606264
26	6		4.101056	2.512766	-1.633776
27	6		5.506984	1.995568	0.704435
28	6		4.919352	1.382432	-1.482355
29	1		3.613739	2.663207	-2.592183
30	7		5.582627	1.108053	-0.357128
31	1		5.045014	0.691634	-2.308941
32	6		3.066467	4.642313	-0.809612
33	1		3.219675	5.049472	-1.810875
34	1		3.266755	5.447447	-0.102616
35	6		0.771032	4.453283	-1.768728
36	6		1.088881	3.898434	0.489565
37	6		-0.570541	4.099960	-1.693680
38	6		-0.241168	3.540495	0.615093
39	1		1.782125	3.848390	1.321198
40	6		-1.106596	3.593823	-0.495970
41	1		-1.182040	4.243324	-2.578755
42	1		-0.584092	3.193797	1.583553
43	1		1.207241	4.851401	-2.678531
44	7		1.594247	4.315388	-0.699056
45	6		-2.499113	3.062163	-0.397497
46	6		-3.083917	2.362128	-1.466249
47	6		-3.252311	3.160383	0.784932
48	6		-4.319486	1.741836	-1.302110
49	1		-2.580845	2.254911	-2.421592
50	6		-4.485405	2.520836	0.877820
51	1		-2.908980	3.738786	1.636832
52	7		-5.004247	1.789170	-0.136752
53	1		-4.767697	1.177221	-2.111367
54	1		-5.070847	2.581613	1.788865
55	6		-3.962180	-3.342238	0.902083
56	6		-4.628837	-3.220935	-0.357251

57	6	-4.186655	-2.365625	1.858193
58	6	-5.445870	-2.047912	-0.593775
59	6	-5.003166	-1.259637	1.570529
60	1	-3.776870	-2.441106	2.860450
61	1	-5.185657	-0.509179	2.331945
62	7	-5.595498	-1.081226	0.388913
63	7	8.017049	-2.338713	-0.401409
64	7	8.536438	0.339052	-0.725211
65	7	-8.579593	-0.337246	0.471324
66	7	-8.069969	2.307353	-0.055376
67	6	9.602343	-0.640532	-1.172531
68	6	9.462860	-1.891370	-0.326649
69	1	10.593372	-0.189651	-1.065037
70	1	9.432322	-0.848616	-2.232496
71	1	9.691956	-1.696252	0.724607
72	1	10.121057	-2.690898	-0.679552
73	1	8.855326	0.825768	0.119293
74	1	8.424628	1.069069	-1.435127
75	1	7.835070	-3.020836	0.340601
76	1	7.866461	-2.844071	-1.281195
77	6	-9.748905	0.529100	0.051611
78	6	-9.442768	1.951743	0.478296
79	1	-10.671291	0.160787	0.510489
80	1	-9.847687	0.445649	-1.034280
81	1	-9.406236	2.047082	1.567032
82	1	-10.187677	2.655544	0.095235
83	1	-7.736083	3.155223	0.411600
84	1	-8.147214	2.555163	-1.048021
85	1	-8.661793	-0.554471	1.470724
86	1	-8.630672	-1.239985	-0.009664
87	6	4.716281	4.096928	1.710049
88	6	6.234949	1.744796	1.891194
89	6	5.462997	3.839228	2.839004
90	1	5.481377	4.555275	3.654959
91	6	6.220411	2.647686	2.934561
92	1	6.802464	2.453295	3.830568
93	1	4.165562	5.030278	1.661256
94	1	6.821294	0.834023	1.969030
95	6	-6.113195	-1.906127	-1.833651
96	6	-4.571667	-4.204724	-1.384096
97	6	-6.027591	-2.888055	-2.799590
98	1	-6.564598	-2.777267	-3.737008
99	6	-5.259185	-4.053245	-2.568290
100	1	-5.224984	-4.833155	-3.322813
101	1	-6.714569	-1.019559	-2.013144
102	1	-4.015441	-5.122172	-1.227012
103	78	-6.770161	0.665732	0.142624
104	78	6.743060	-0.667430	-0.328713

HF = -2489.3515882 Hartree
Zero-point correction = 0.878081
Sum of electronic and thermal Enthalpies = -2488.424015
Sum of electronic and thermal Free Energies = -2488.559211

(TS)-$[Pt_2(en)_2(\mathbf{1})_2]^{6+}$ (1 imaginary frequency)

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.562068	3.089379	0.098955
2	6	-3.416500	2.913369	1.201670
3	6	-4.650378	2.287678	1.037920
4	6	-4.306115	2.073099	-1.244962
5	6	-3.058510	2.680501	-1.151302
6	6	-1.165928	3.603818	0.241018
7	6	-0.453856	3.460552	1.449018
8	6	0.882944	3.813686	1.527938
9	6	0.872491	4.513436	-0.713777
10	6	-0.469818	4.187431	-0.835531
11	1	-3.153799	3.261452	2.195154
12	1	-5.305551	2.129197	1.887053
13	1	-4.693194	1.753075	-2.205689
14	1	-2.483615	2.795712	-2.063531
15	1	-0.917469	3.055624	2.341311
16	1	1.454675	3.713252	2.444024
17	1	1.432959	4.954456	-1.531022
18	1	-0.955305	4.412922	-1.778758
19	6	3.008168	4.596890	0.538097
20	1	3.178441	5.043041	1.523407
21	1	3.215384	5.373630	-0.202528
22	7	1.545327	4.295026	0.444965
23	7	-5.084309	1.840261	-0.163306
24	6	-4.117596	-3.412427	-0.307134
25	6	-4.818228	-3.062847	0.889362
26	6	-4.281976	-2.611544	-1.424854
27	6	-5.614610	-1.851707	0.890634
28	6	-5.088173	-1.463698	-1.362468
29	1	-3.824731	-2.861444	-2.377307
30	7	-5.715688	-1.072915	-0.251204
31	1	-5.233705	-0.857217	-2.249773
32	6	-3.240871	-4.659858	-0.423566
33	1	-3.415824	-5.150554	-1.382825
34	1	-3.440543	-5.396454	0.355423
35	6	-0.937314	-4.709835	-1.382596
36	6	-1.247891	-3.727452	0.725569
37	6	0.415094	-4.389083	-1.361941
38	6	0.091066	-3.389034	0.792732
39	1	-1.942832	-3.500573	1.525548
40	6	0.961285	-3.679800	-0.277365
41	1	1.022865	-4.715311	-2.199750
42	1	0.437538	-2.871392	1.680014
43	1	-1.381969	-5.256428	-2.207438
44	7	-1.760347	-4.349014	-0.366182
45	6	2.368747	-3.176704	-0.261874
46	6	3.012524	-2.768896	-1.443529
47	6	3.078180	-3.001216	0.939957
48	6	4.257166	-2.146308	-1.382717
49	1	2.549955	-2.886497	-2.418039
50	6	4.317621	-2.367929	0.931635
51	1	2.691014	-3.353681	1.890600
52	7	4.887024	-1.904784	-0.207798
53	1	4.749415	-1.795984	-2.283647
54	1	4.860310	-2.195967	1.855167
55	6	3.922127	3.390568	0.325057
56	6	5.334009	3.582060	0.289873

57	6	3.450558	2.107361	0.157520
58	6	6.199833	2.437163	0.060517
59	6	4.348138	1.040331	-0.003701
60	1	2.392222	1.872552	0.153996
61	1	3.928541	0.054813	-0.097754
62	7	5.677191	1.142580	-0.047298
63	7	-8.118125	2.382427	-0.562833
64	7	-8.675408	-0.306148	-0.593481
65	7	8.762532	-0.267118	-0.096372
66	7	7.667095	-2.737970	-0.153626
67	6	-9.746250	0.636476	-1.104294
68	6	-9.565638	1.965546	-0.396962
69	1	-10.737391	0.212449	-0.917787
70	1	-9.611310	0.732093	-2.185276
71	1	-9.762692	1.883083	0.675466
72	1	-10.226142	2.733850	-0.809840
73	1	-8.969822	-0.698166	0.307287
74	1	-8.596944	-1.107068	-1.227333
75	1	-7.904214	3.133607	0.099689
76	1	-7.991262	2.793562	-1.494025
77	6	9.709229	-1.447095	-0.223752
78	6	9.057483	-2.644844	0.427577
79	1	10.669410	-1.201962	0.238934
80	1	9.878434	-1.616465	-1.291151
81	1	8.957615	-2.522270	1.509186
82	1	9.609398	-3.568563	0.227302
83	1	7.128560	-3.441850	0.358737
84	1	7.726664	-3.081196	-1.119436
85	1	8.952067	0.227846	0.780747
86	1	8.990313	0.381444	-0.852461
87	6	-4.802840	-3.847396	2.078083
88	6	-6.307859	-1.479720	2.066350
89	6	-5.515586	-3.473548	3.196568
90	1	-5.511958	-4.104063	4.080473
91	6	-6.266689	-2.274279	3.193801
92	1	-6.822364	-1.987965	4.081855
93	1	-4.255744	-4.783806	2.107794
94	1	-6.888051	-0.561694	2.069394
95	6	7.579147	2.695032	-0.065680
96	6	5.917103	4.869114	0.447287
97	6	8.111110	3.961944	0.072512
98	1	9.180173	4.113772	-0.042262
99	6	7.276440	5.063718	0.353386
100	1	7.702437	6.054527	0.475701
101	1	8.242921	1.890513	-0.312559
102	1	5.285418	5.729408	0.641193
103	78	6.734598	-0.867410	-0.146913
104	78	-6.859238	0.710367	-0.361619

HF = -2489.3275164 Hartree
Zero-point correction = 0.878032
Sum of electronic and thermal Enthalpies = -2488.400607
Sum of electronic and thermal Free Energies = -2488.534272

[i] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A., Jr. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam,

S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[ii] A. D. Becke, *J. Chem. Phys*. **1993**, *98*, 5648-5652.

[iii] Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789.

[iv] *GaussView*, Version 2; Gaussian, Inc.: Pittsburgh, PA, 1998.

[v] P. J. Hay, W. R. Wadt, *J. Chem. Phys*. **1985**, *82*, 270-283.