Electronic Supplementary Material (ESI) for Dalton Transactions.

Amplification of a metallacyclic receptor out of a dynamic combinatorial library

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- Supporting Information -

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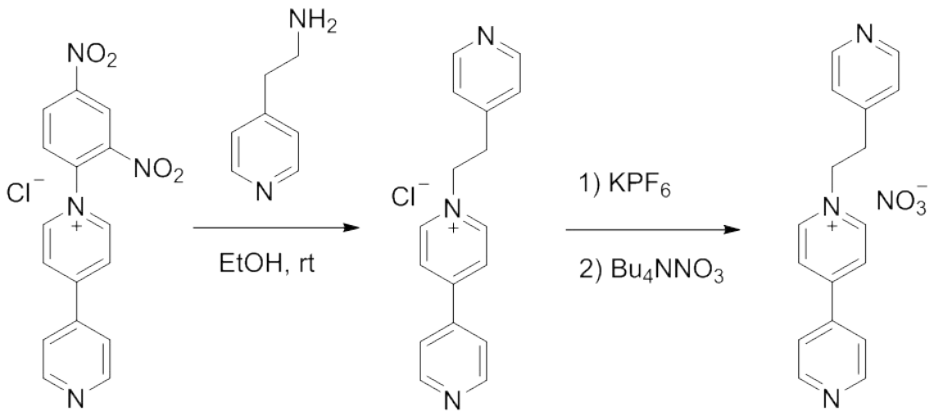
General Procedures

Compounds $(PEt_3)_2Pt(NO_3)_2$[1] and 1-(2,4-dinitrophenyl)-[4,4'-bipyridin]-1-ium[2] were prepared according to literature procedures. Starting materials were purchased from commercial suppliers and were used without further purification. Milli-Q water was purified with a Millipore Gradient A10 apparatus. Merck 60 F254 foils were used for thin layer chromatography, and Merck 60 (230-400 mesh) silica gel was used for flash chromatography. NMR spectra were recorder on a Bruker Advance 300 or 500 MHz for ^{1}H and ^{31}P, and 125 MHz for ^{13}C, equipped each other with a dual cryoprobe. The solvent for NMR experiments was deuterated water (D_2O). Mass spectrometry experiments were carried out in a LCQ-q-TOF Applied Biosystems QSTAR Elite spectrometer for low and high resolution ESI. Microanalyses for C, H, and N were performed by the elemental analyses general service of the University of A Coruña.



Ligand 1·PF_6

1-(2,4-dinitrophenyl)-[4,4'-bipyridin]-1-ium chloride (482 mg, 1.34 mmol) was dissolved in the minimum amount of ethanol and 4-(2-aminoethyl)pyridine (197 mg, 1.2 mmol) was added. The resulting solution was stirred until no bipyridinium salt was observed by TLC. The solvent was removed under reduced pressure to dryness. Residue with ligand **1·Cl** was suspended in water and washed with ethyl acetate. The aqueous layer with the ligand was concentrated to dryness under reduced pressure. The residue was dissolved in the minimum amount of water and an excess of KPF_6 was added until no further precipitation was observed. The precipitate was filtered and washed with water to yield an orange solid **1·PF_6**. *^{1}H NMR (300 MHz, CD_3NO_2) δ* 8.89 – 8.81 (m, 1H), 8.78 (d, *J* = 6.9 Hz, 1H), 8.54 – 8.45 (m, 1H), 8.39 (d, *J* = 6.6 Hz, 1H), 7.89 – 7.71 (m, 1H), 7.27 – 7.12 (m, 1H), 5.03 (t, *J* = 7.2 Hz, 1H), 3.49 (t, *J* = 7.2 Hz, 1H).

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[1] C. J. Kuehl, F. M. Tabellion, A. M. Arif and P. J. Stang, *Organometallics* 2001, **20**, 1956.
[2] D. Bongard, M. Möller, S. Nagaraja Rao, D. Corr and L. Walder, *Helv. Chim. Acta*, 2005, **88**, 3200

Ligand 1·NO_3

1·PF_6 was dissolved in the minimum amount of acetonitrile and an excess of Bu_4NNO_3 was added until no further precipitated was observed. The precipitate was filtered and washed with acetonitrile to yield a yellowish solid **1·NO_3** (342 mg, 90%). *^{1}H NMR* (*500 MHz, D_2O*) *δ* 8.81 – 8.78 (m, 2H), 8.77 (ddd, *J* = 4.5, 1.7, 0.6 Hz, 2H), 8.45 – 8.42 (m, 2H), 8.36 – 8.29 (m, 2H), 7.88 (ddd, *J* = 4.6, 1.7, 0.6 Hz, 2H), 7.27 – 7.20 (m, 2H), 5.00 (t, *J* = 6.8 Hz, 2H), 3.46 (t, *J* = 6.9 Hz, 2H). *^{13}C NMR* (*126 MHz, D_2O*) *δ* 154.25 (C), 149.95 (CH), 149.11 (CH), 146.25 (C), 144.70 (CH), 142.34 (C), 125.98 (CH), 124.67 (CH), 122.39 (CH), 61.30 (CH_2), 35.82 (CH_2). MS-ESI (*m/z*): 262.1297 $[M\text{-}NO_3]^+$ Anal. Calcd $C_{17}H_{16}N_4O_3$: C, 62.95; H, 4.97; N, 17.27; found C, 62.90; H, 4.99; N, 17.31.

Metallacycle R·6NO_3

A solution of **1**·NO_3 (0.57 mg, 1.75 μmol) and $(PEt_3)_2Pt(NO_3)_2$ (0.97 mg, 1.75 μmol) in D_2O (0.7 mL) was stirred at room temperature for 30 min. *^{1}H NMR (500 MHz, D_2O) δ* 8.97 – 8.90 (m, 4H), 8.85 (d, *J* = 6.9 Hz, 4H), 8.75 – 8.65 (m, 4H), 8.06 (d, *J* = 7.0 Hz, 4H), 7.86 (d, *J* = 6.3 Hz, 4H), 7.65 (d, *J* = 6.1 Hz, 4H), 5.19 – 5.06 (m, 4H), 3.72 – 3.58 (m, 4H), 1.70 (m, 24H), 1.13 (m, 36H). *^{13}C NMR (126 MHz, D_2O) δ* 151.07 (CH), 151.07 (C), 150.91 (C), 150.13 (CH), 145.43 (C), 144.76 (CH), 127.99(CH), 126.11 (CH), 126.11 (CH), 58.12 (CH_2), 33.15 (CH_2), 13.87 (CH_2), 7.09 (CH_3). *^{31}P{^{1}H} NMR (162 MHz, D_2O) δ* -0.02 (d, $^2J_{P\text{-}P}$ = 20.6 Hz, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 3030 Hz), -0.72 (d, $^2J_{P\text{-}P}$ = 20.7 Hz, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 3070 Hz).

Mixture of R·6NO_3, T·9NO_3 and S·12NO_3

A solution of **1**·NO_3 (4.4 mg, 8 μmol) and $(PEt_3)_2Pt(NO_3)_2$ (2.6 mg, 8 μmol) in D_2O (0.8 mL) was stirred at room temperature for 30 min. As discussed on the main text of the communication, the assignment of the ^{1}H signals corresponding to the triangle and square were deduced on the basis of the COSY and DOSY experiments for the 10 mM mixture of ligand 1 and $(PPEt_3)_2Pt(ONO_2)_2$ (vide infra).

(2,7-DHN)⊂R·6NO_3

A solution of **1**·NO_3 (5.2 mg, 16 μmol), $(PEt_3)_2Pt(NO_3)_2$ (8.9 mg, 16 μmol) and 2,7-dihydroxynaphthalene (1.3 mg, 8 μmol) in D_2O (0.8 mL) was stirred at room temperature for 30 min. *^{1}H NMR (400 MHz, D_2O) δ* 9.01 (dd, *J* = 5.7, 2.5 Hz, 4H), 8.91 (dd, *J* = 6.2, 2.3 Hz, 4H), 8.77 (d, *J* = 6.7 Hz, 4H), 7.98 (d, *J* = 6.1 Hz, 4H), 7.53 (t, *J* = 7.1 Hz, 8H), 6.33 (d, *J* = 8.6 Hz, 2H),

6.22 (s, 2H), 5.38 (s, 2H), 5.13 (t, *J* = 5.8 Hz, 4H), 3.84 – 3.74 (m, 4H), 1.70 (dp, *J* = 31.6, 7.5 Hz, 24H), 1.14 (ddt, *J* = 36.4, 18.1, 7.5 Hz, 36H). *^{13}C NMR (101 MHz, D_2O) δ* 154.08 (C) 150.82 (CH), 150.82 (C), 148.51 (C), 144.17 (CH), 129.13 (CH), 129.13 (C), 128.27 (CH), 125.27 (CH), 124.90 (CH), 124.90 (CH), 115.35 (CH), 107.57 (CH), 57.51 (CH_2), 32.87 (CH_2), 14.21 (CH_2), 7.19 (CH_3). *^{31}P NMR (162 MHz, D_2O) δ* 0.09 (d, $^2J_{P\text{-}P}$ = 20.7 Hz, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 3057 Hz), -0.64 (d, $^2J_{P\text{-}P}$ = 20.7 Hz, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 3057 Hz).

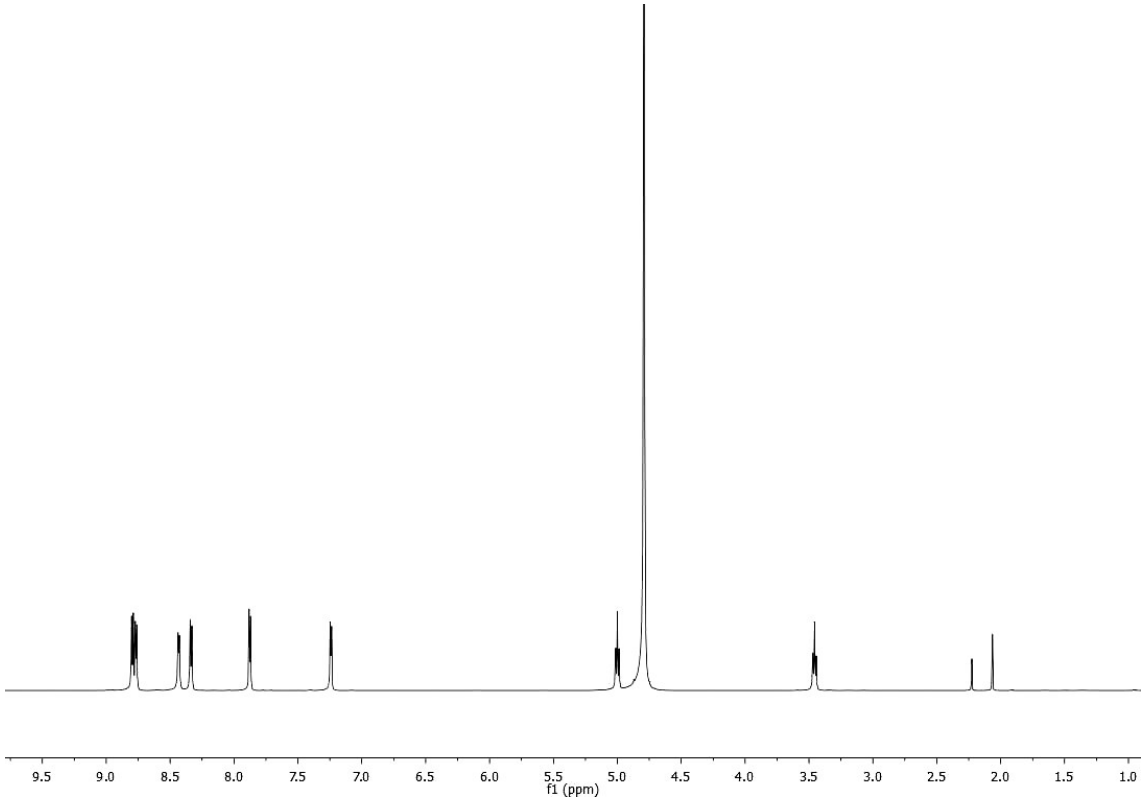


Figure S1. ^{1}H NMR (500 MHz, D_2O) spectrum of ligand **1**·NO_3.

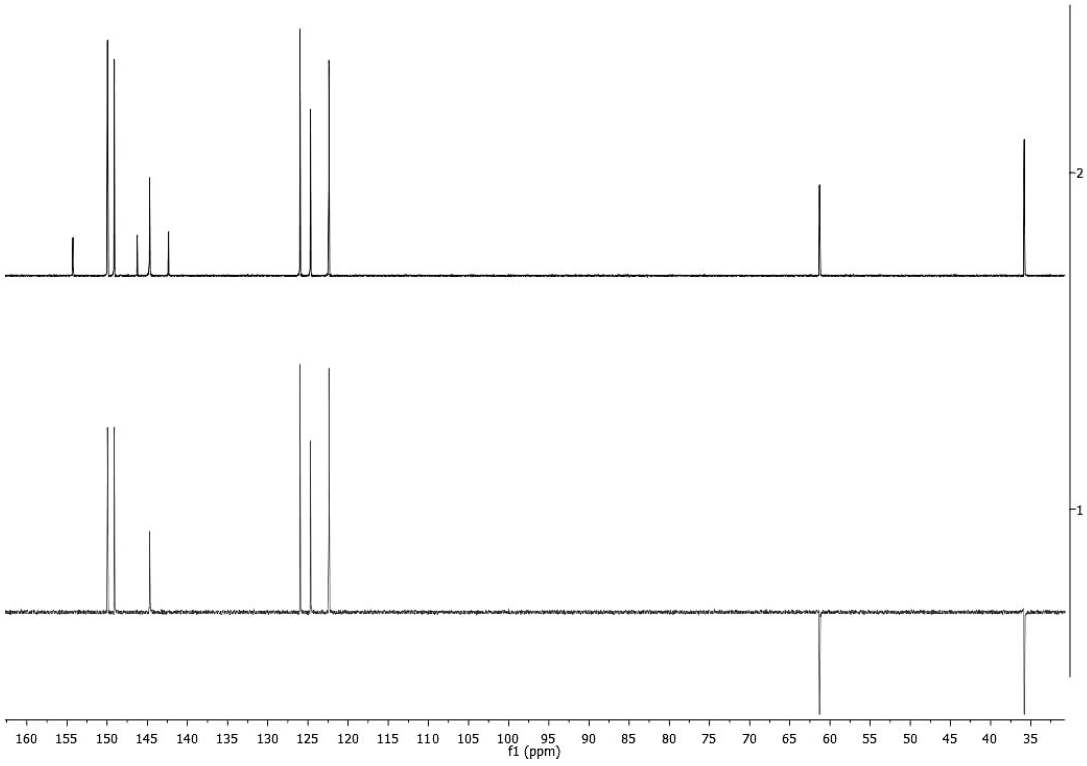


Figure S2. ^{13}C NMR and DEPT-135 (125 MHz, D_2O) spectra of ligand **1**·NO_3.

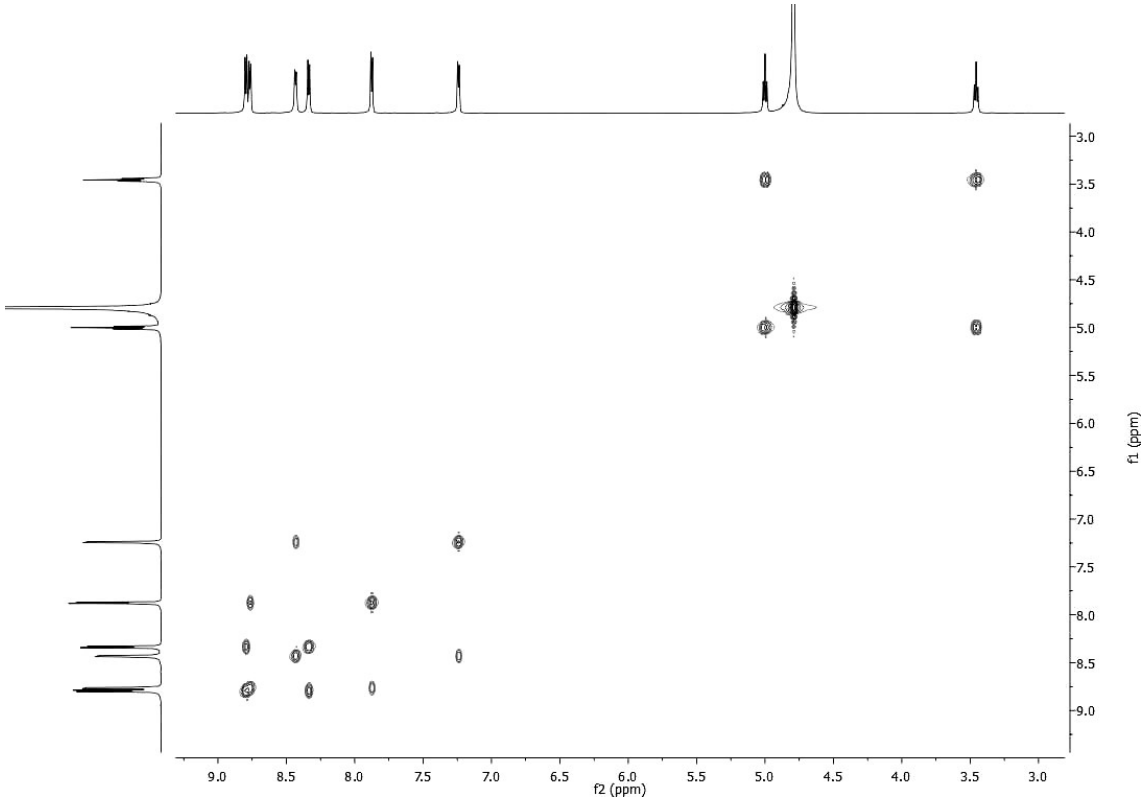


Figure S3. COSY (500 MHz, D_2O) spectrum of ligand **1**·NO_3.

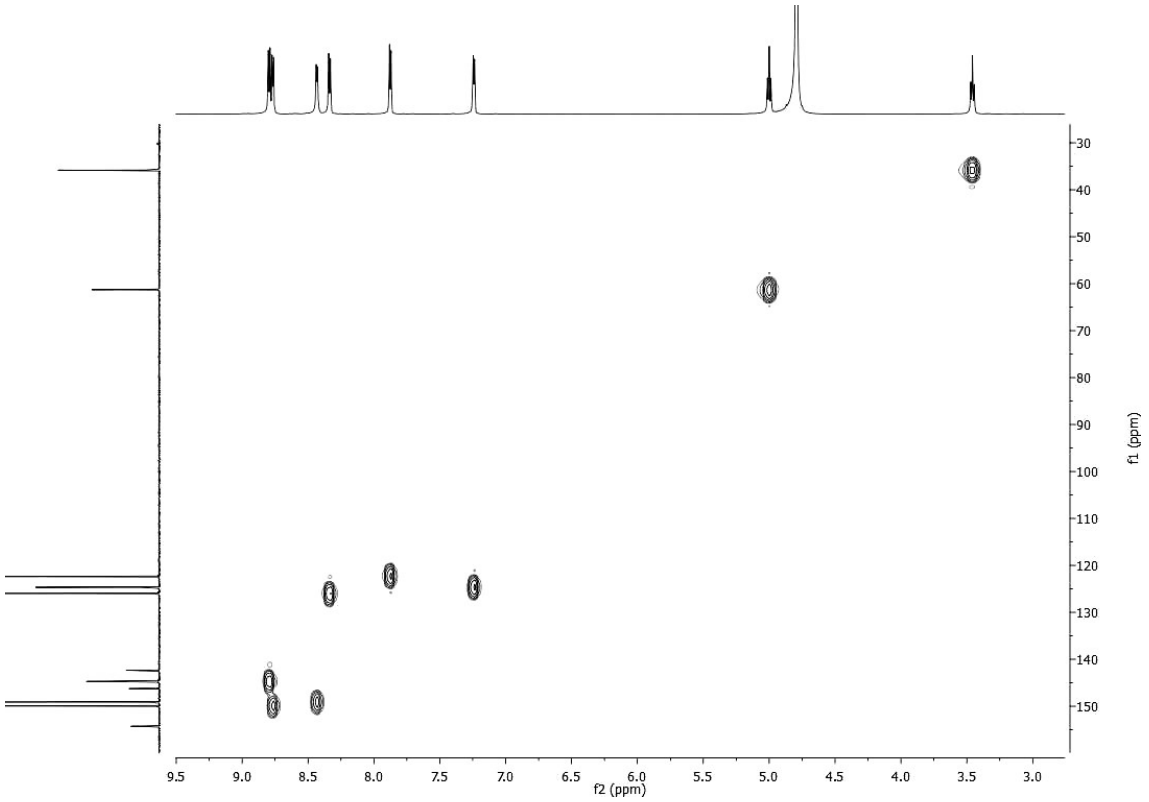


Figure S4. HSQC (500 MHz, D_2O) spectrum of ligand **1**·NO_3.

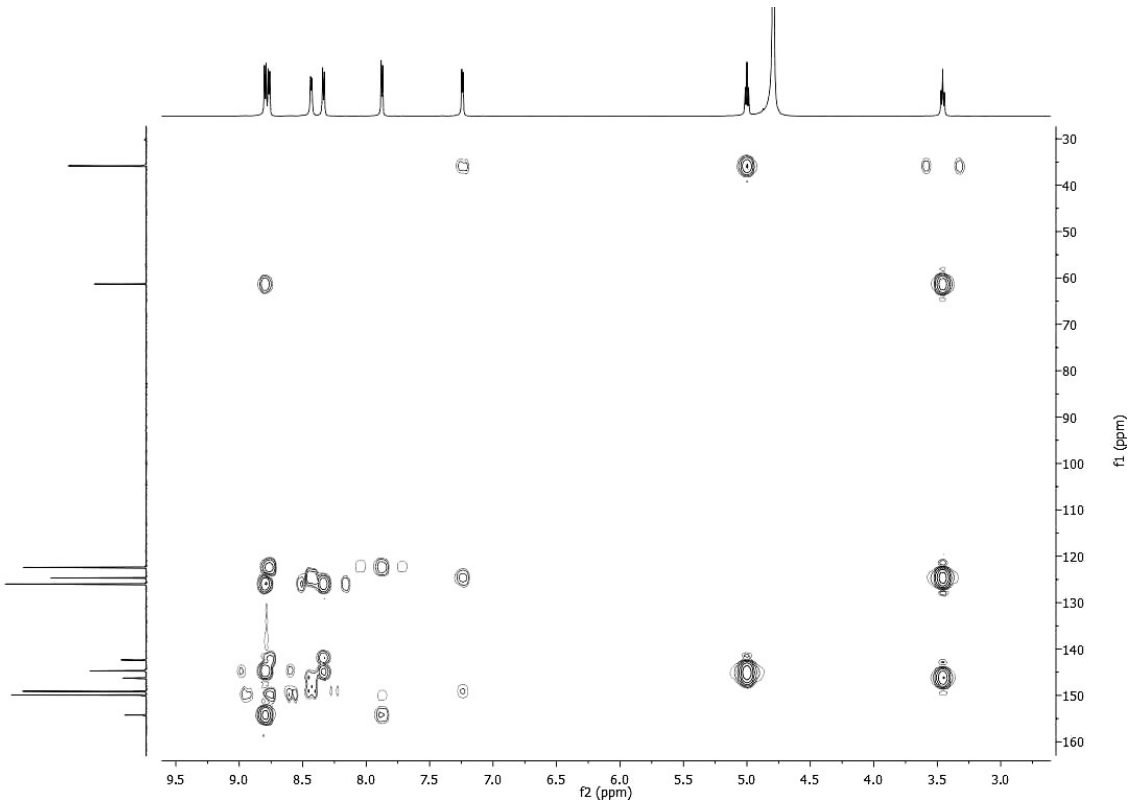


Figure S5. HMBC (500 MHz, D_2O) spectrum of ligand **1**·NO_3.

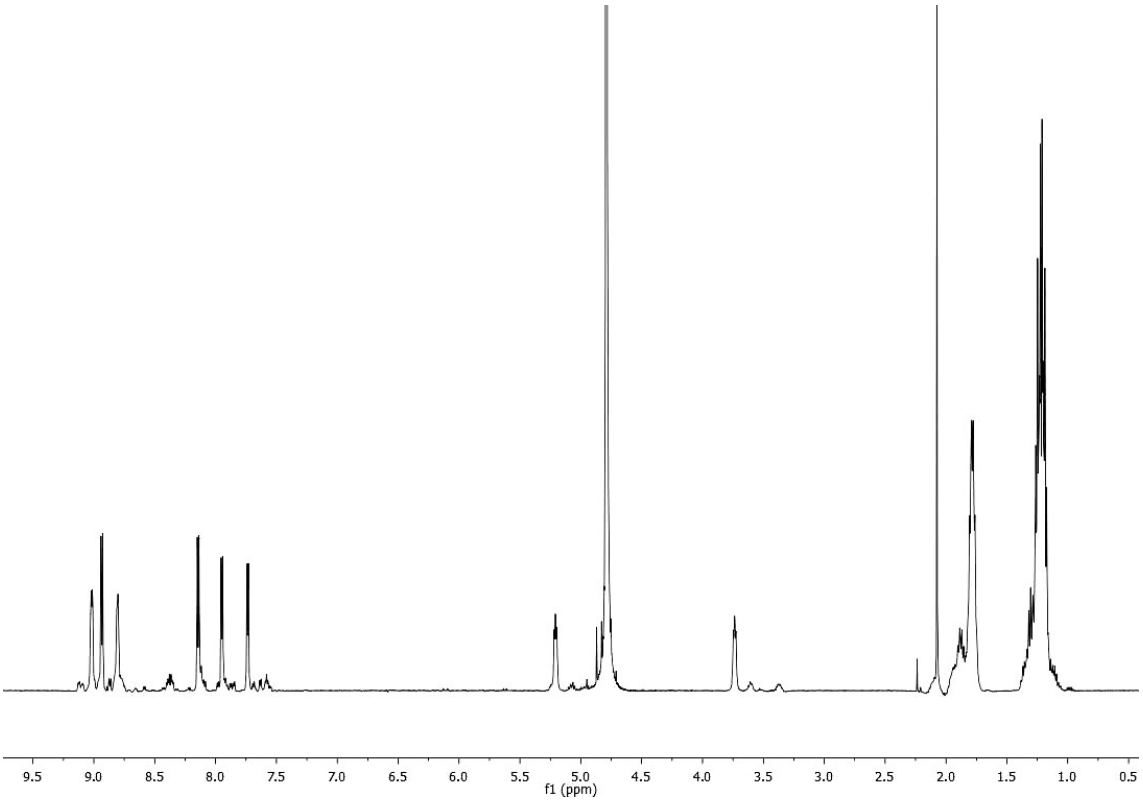


Figure S6. ^{1}H NMR (500 MHz, D_2O) spectrum of metallacycle **R**·6NO_3.

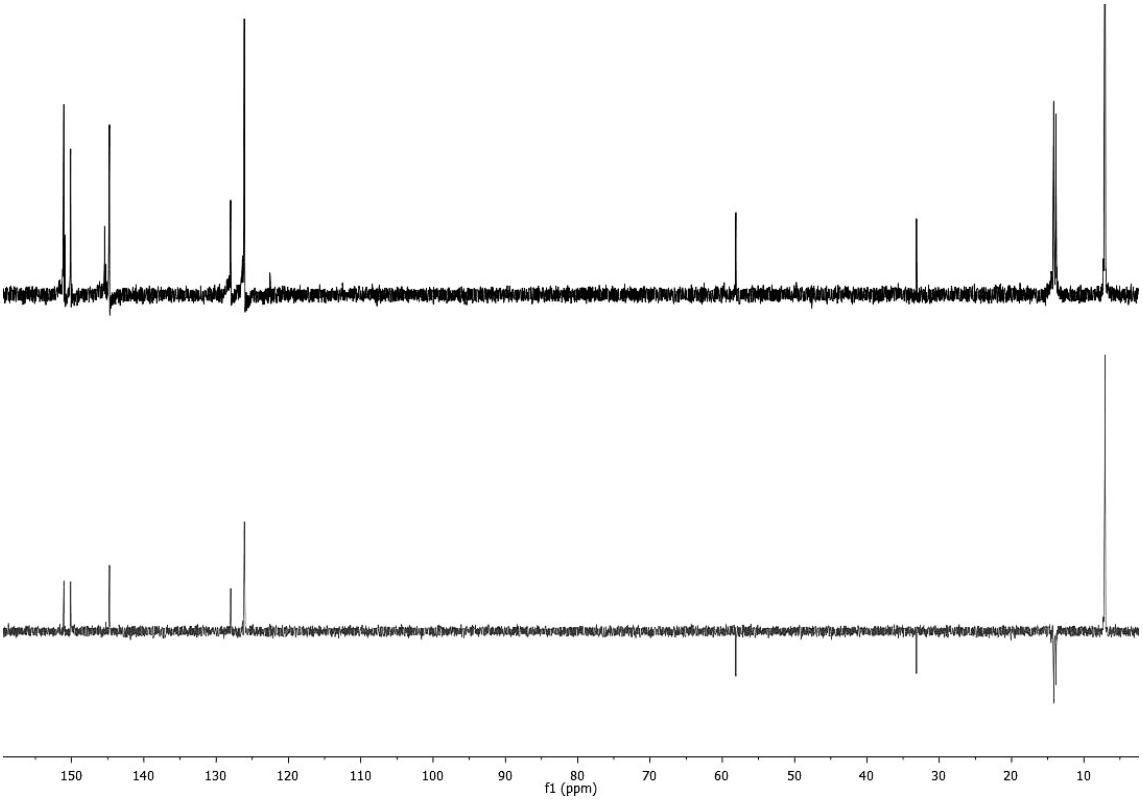


Figure S7. ^{13}C NMR and DEPT-135 (125 MHz, D_2O) spectra of **R**·6NO_3.

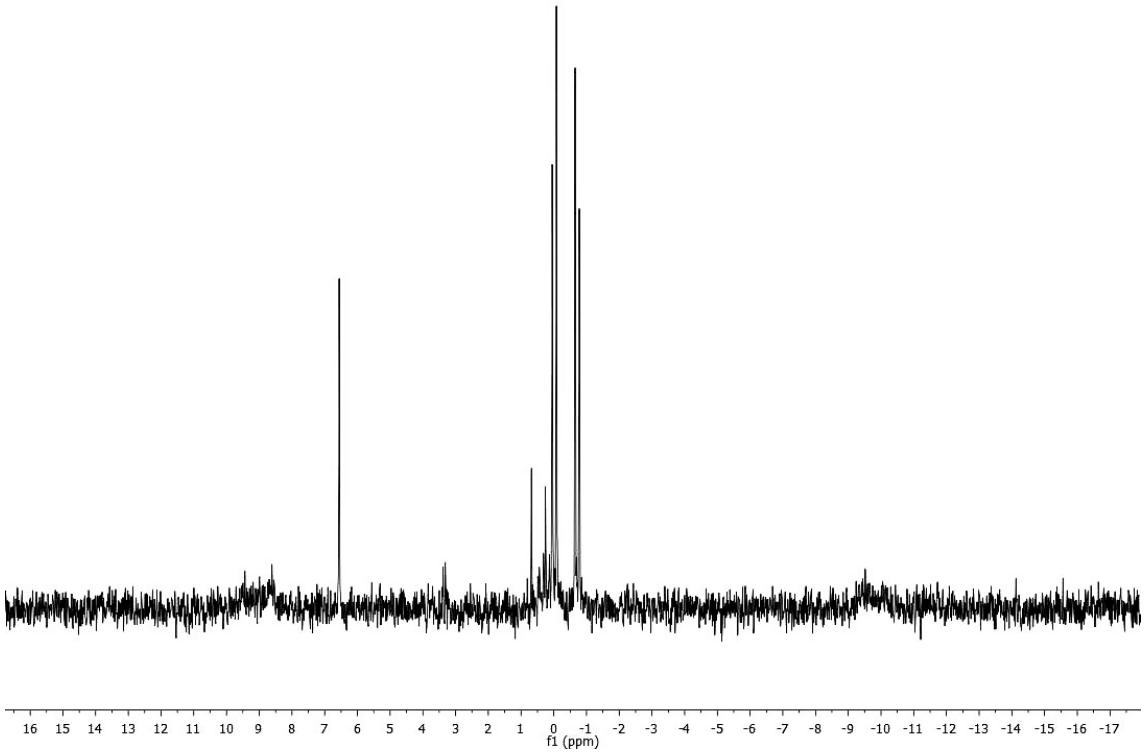


Figure S8. ^{31}P NMR (162 MHz, D_2O) spectrum of **R**·$6NO_3$.

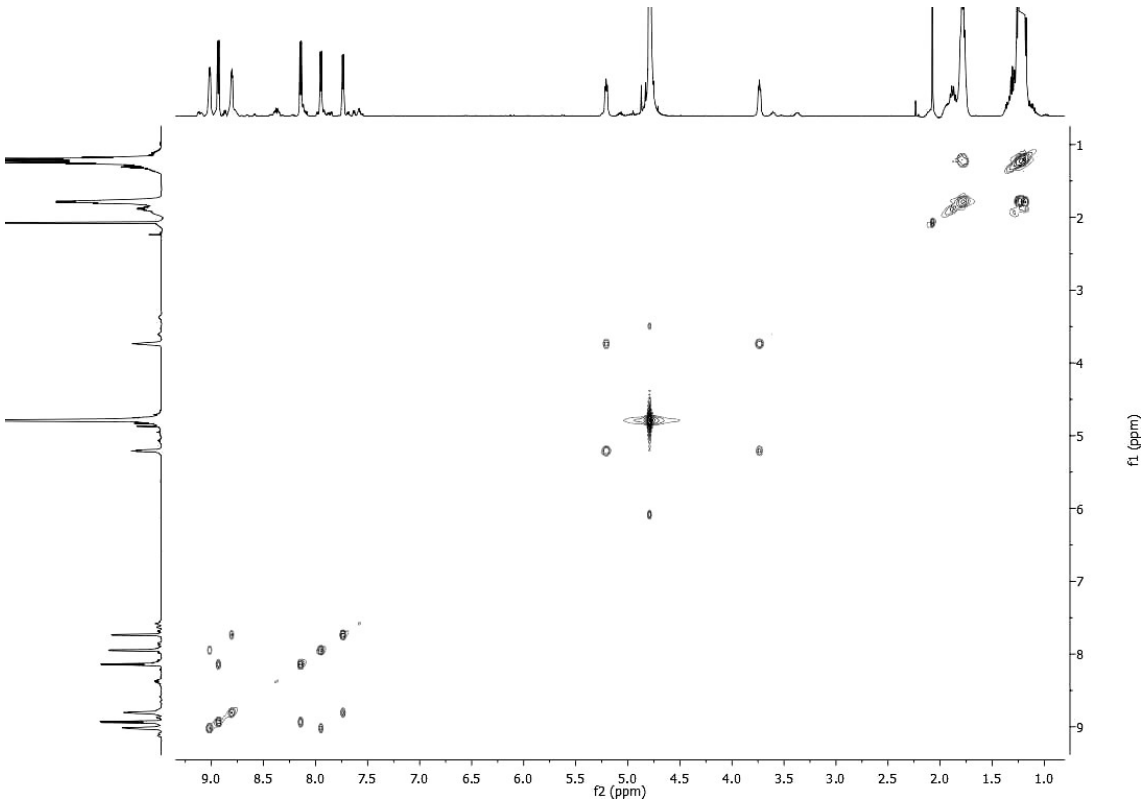


Figure S9. COSY (500 MHz, D_2O) spectrum of **R**·$6NO_3$.

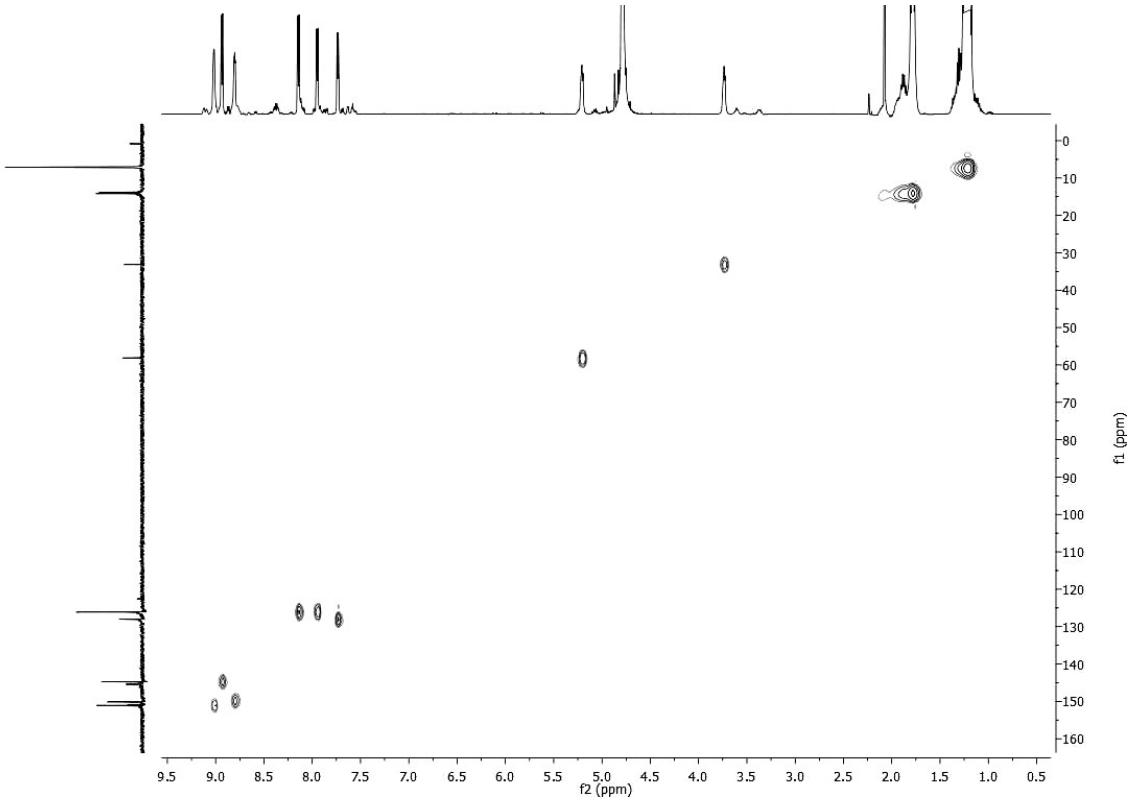


Figure S10. HSQC (500 MHz, D_2O) spectrum of **R**·6NO_3.

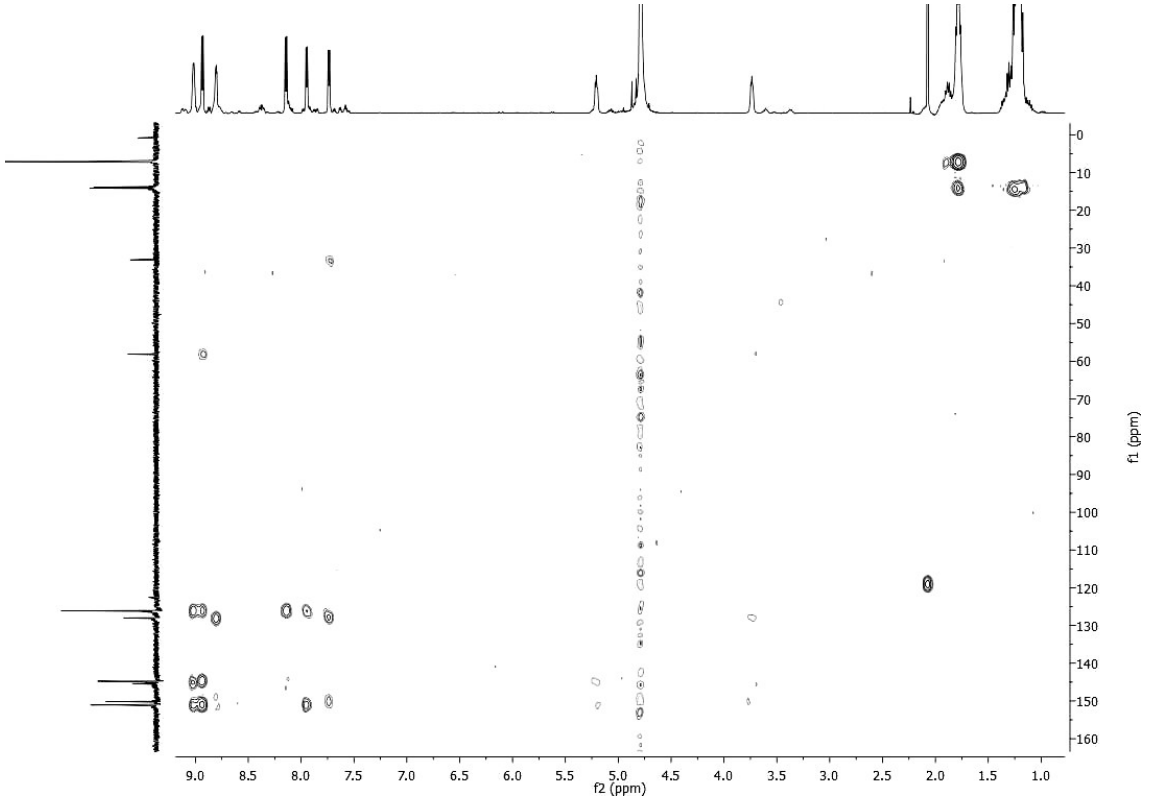


Figure S11. HMBC (500 MHz, D_2O) spectrum of **R**·6NO_3.

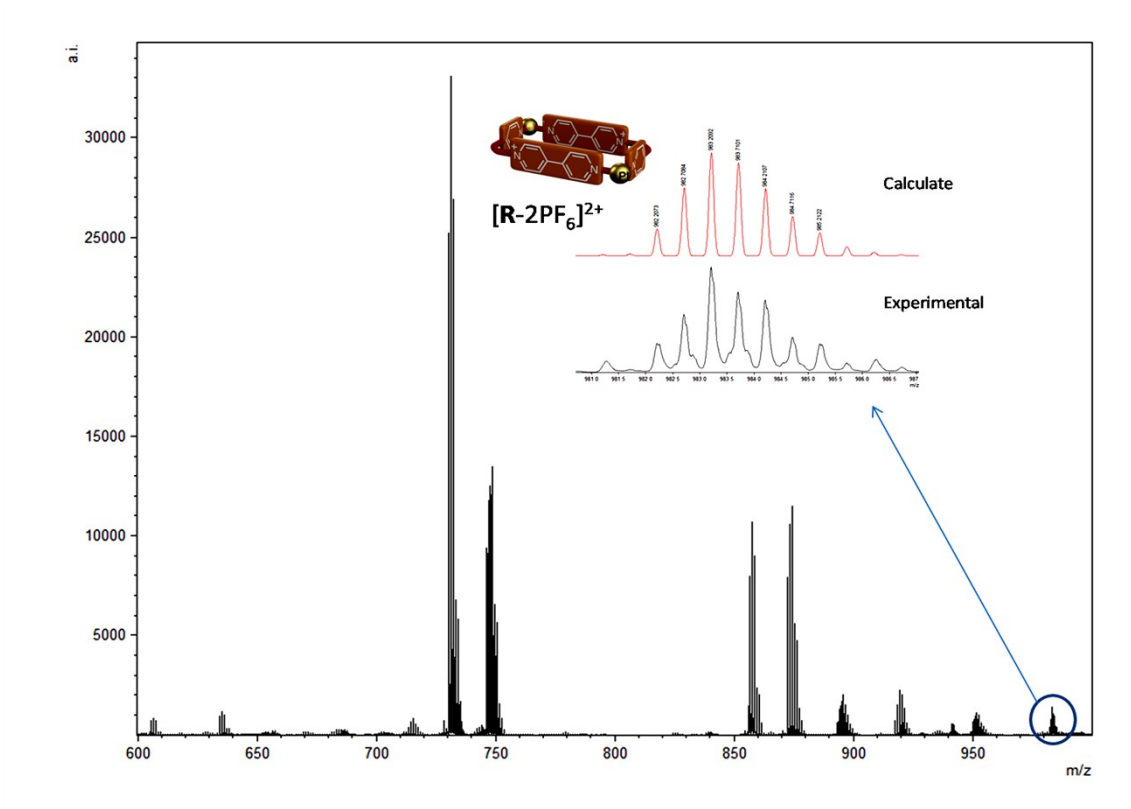


Figure S12. ESI-MS recorded for **R**·6PF_6.

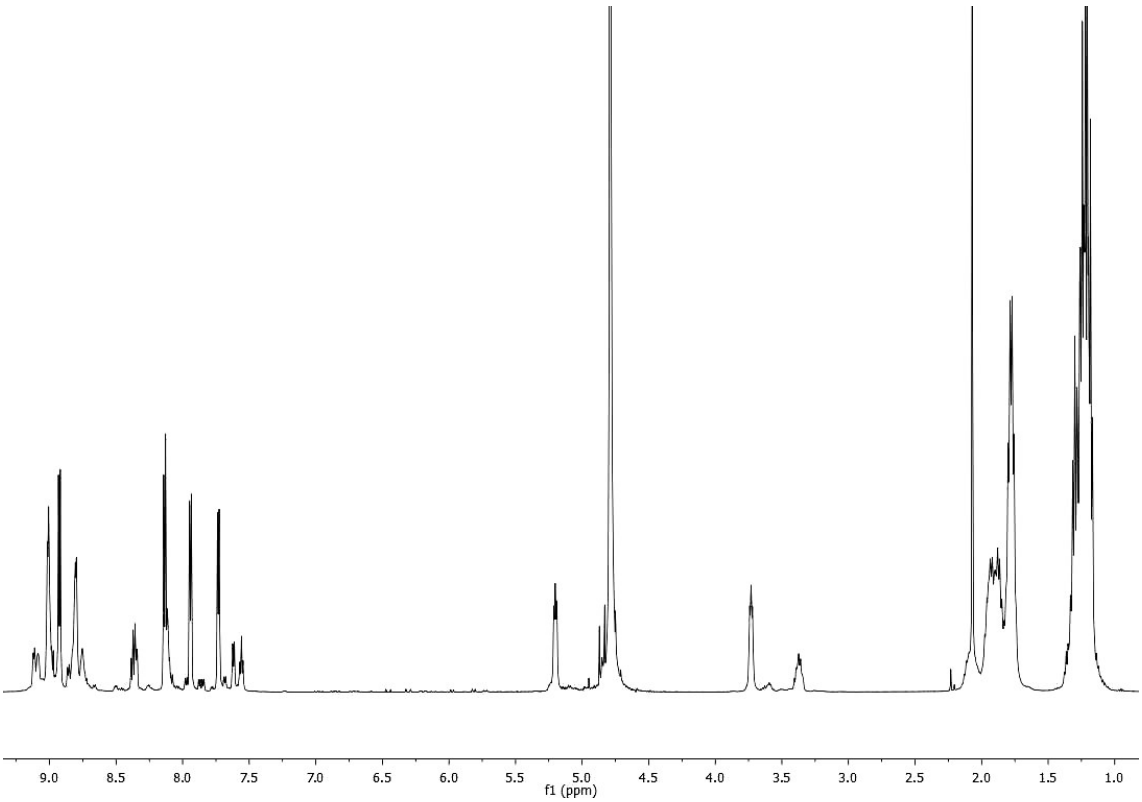


Figure S13. ^{1}H NMR (500 MHz, D_2O) spectrum of an equimolar 10 mM mixture of **1**·NO_3 and $(PEt_3)_2Pt(NO_3)_2$

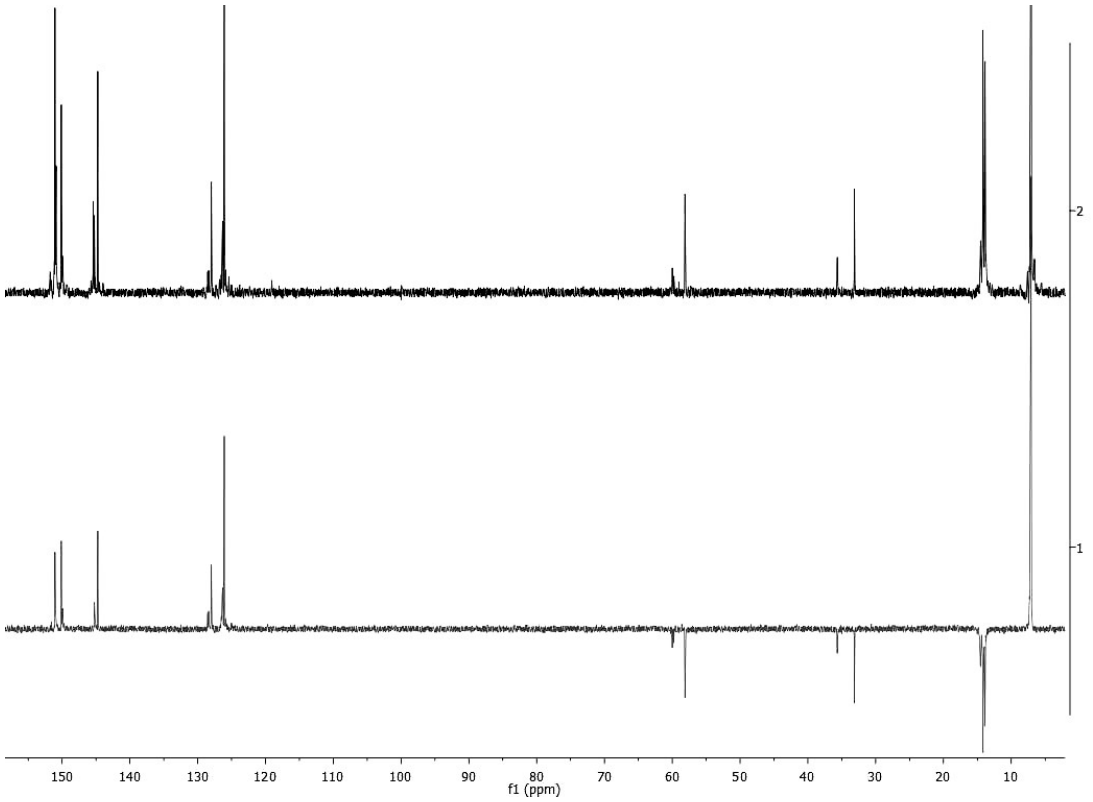


Figure S14. ^{13}C NMR and DEPT-135 (125 MHz, D_2O) spectra of an equimolar 10 mM mixture of **1**·NO_3 and $(PEt_3)_2Pt(NO_3)_2$.

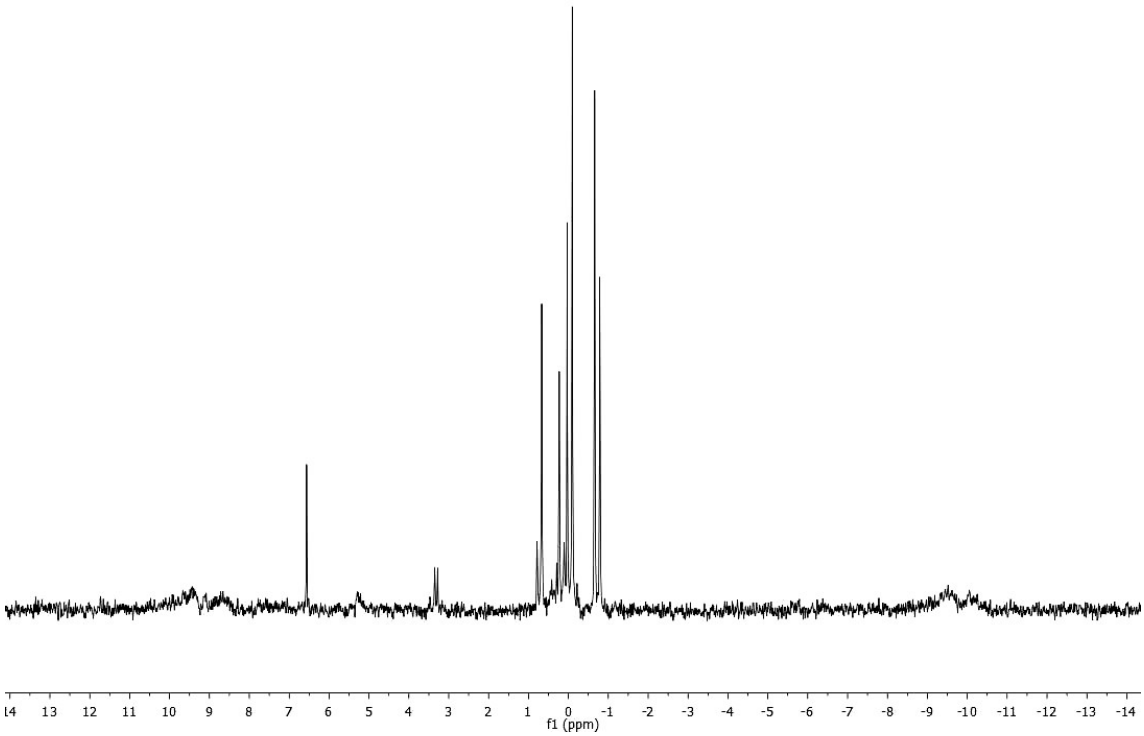


Figure S15. ^{31}P NMR (162 MHz, D_2O) spectrum of an equimolar 10 mM mixture of **1**·NO_3 and $(PEt_3)_2Pt(NO_3)_2$.

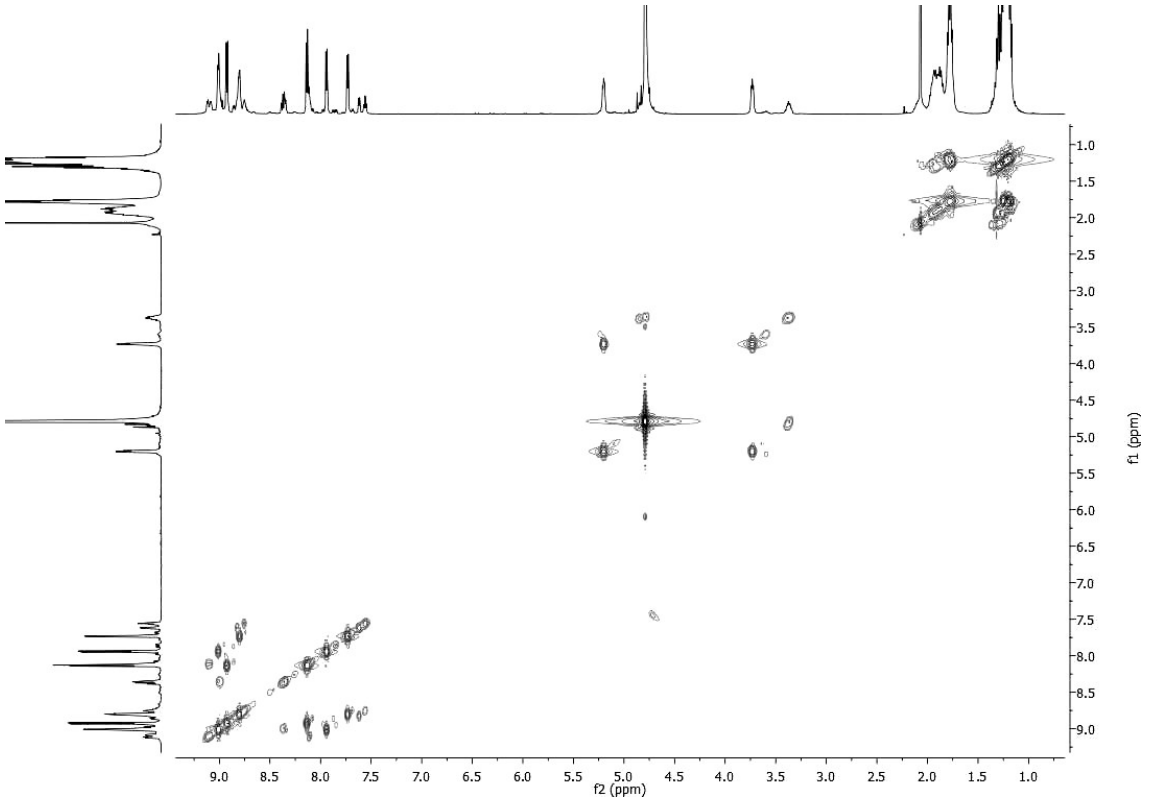


Figure S16. COSY (500 MHz, D_2O) spectrum of an equimolar 10 mM mixture of **1**·NO_3 and $(PEt_3)_2Pt(NO_3)_2$.

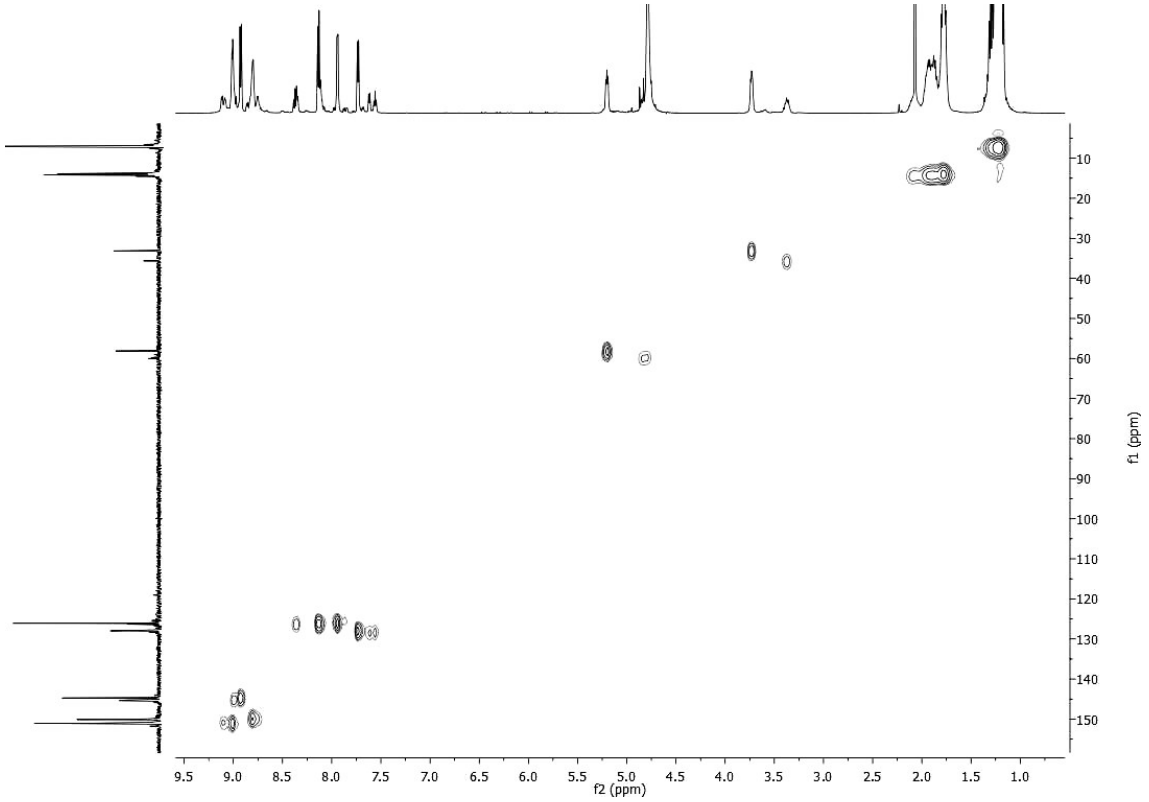


Figure S17. HSQC (500 MHz, D_2O) spectrum of an equimolar 10 mM mixture of **1**·NO_3 and $(PEt_3)_2Pt(NO_3)_2$.

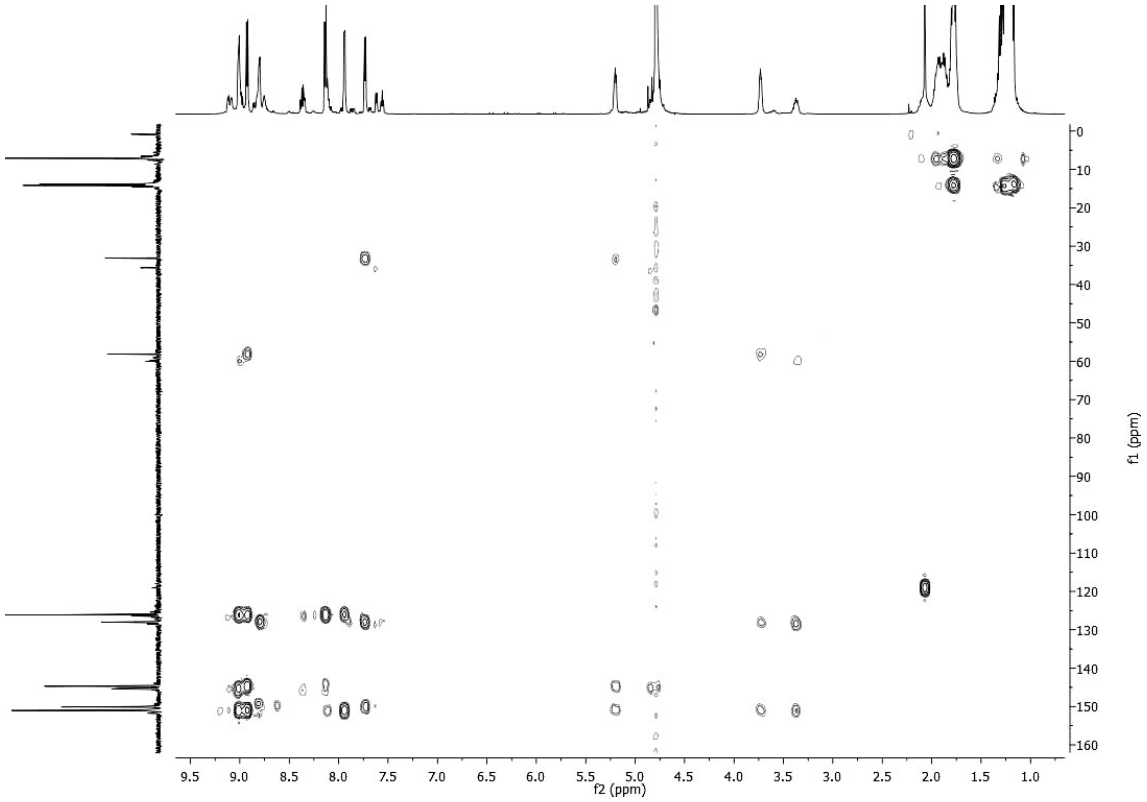


Figure S18. HMBC (500 MHz, D_2O) spectrum of **R**·6NO_3, **T**·9NO_3 and **S**·12NO_3 mixture.

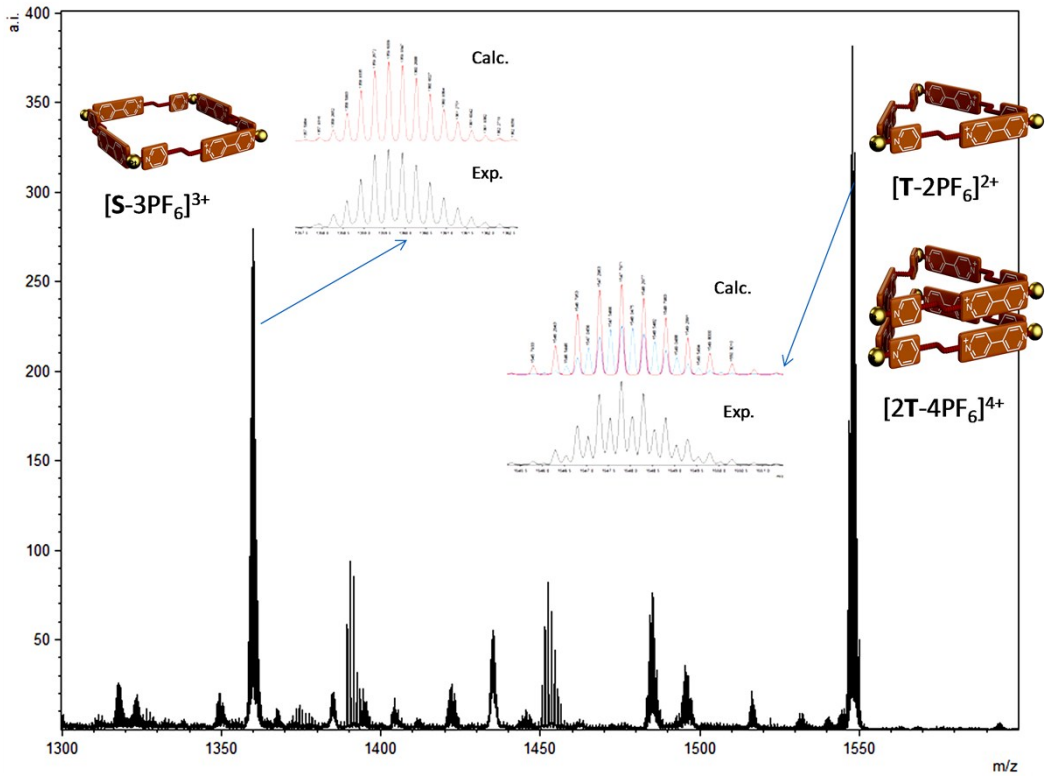


Figure S19. ESI-MS recorder for **S**·12PF_6 and **T**·9PF_6 (dimer peak for (**T**)^2·18PF_6 overlapped in the spectrum).

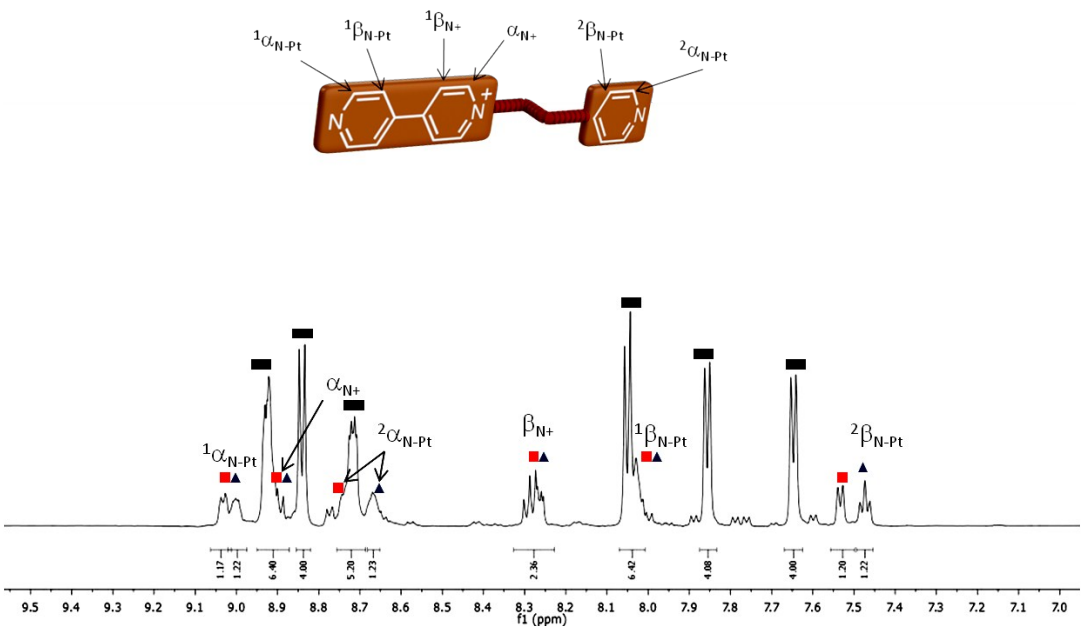


Figure S20. Partial ^{1}H NMR (500 MHz, D_2O) spectrum for the aromatic region of an equimolar 10 mM mixture of **1**·NO_3 and $(PEt_3)_2Pt(NO_3)_2$. The red squares show signals assigned to **S**·$12NO_3$ and blue triangles correspond to metallacycle **T**·$9NO_3$.

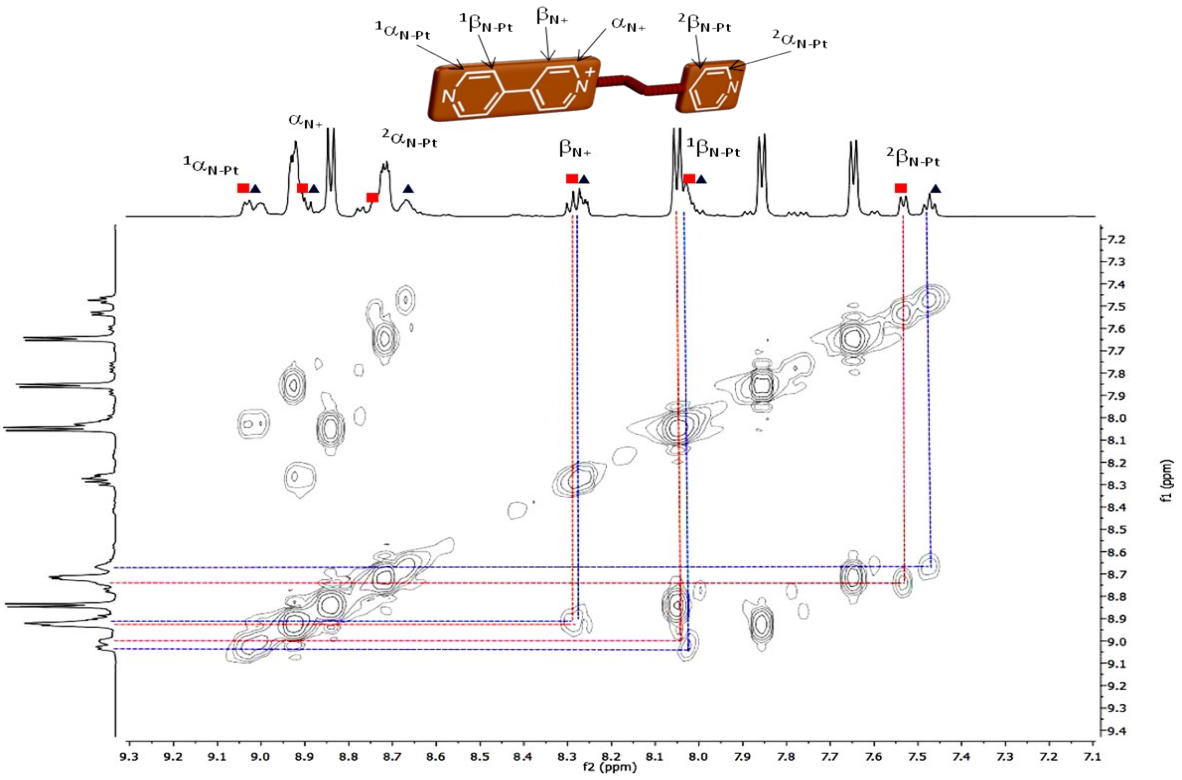


Figure S21. Partial COSY NMR (500 MHz, D_2O) spectrum for the aromatic region of an equimolar 10 mM mixture of **1**·NO_3 and $(PEt_3)_2Pt(NO_3)_2$. Blue dotted lines indicate the ^1H-^1H couplings between hydrogens of metallacycle **T**·$12NO_3$ and the red dotted lines those between hydrogens of metallacycle **S**·NO_3.

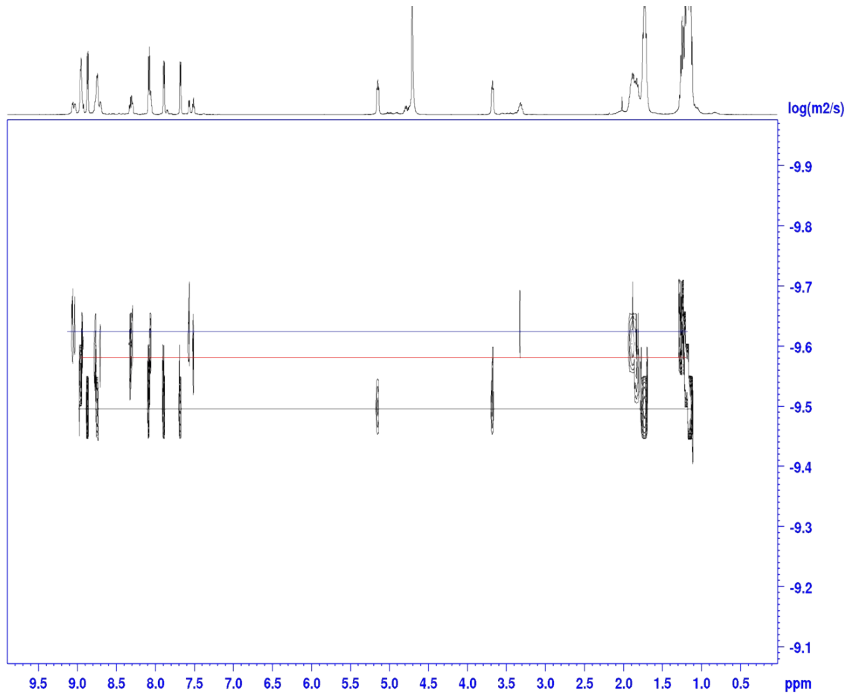


Figure S22. DOSY NMR (500 MHz, D_2O, RT) spectrum recorded for an equimolar 10 mM mixture of **1**·NO_3 and $(PEt_3)_2Pt(NO_3)_2$. Signals assigned to **R**·$6NO_3$ are marked with a black line, those correspond to **T**·$9NO_3$ with a red line and the ones assigned to **S**·$12NO_3$ with a blue line.

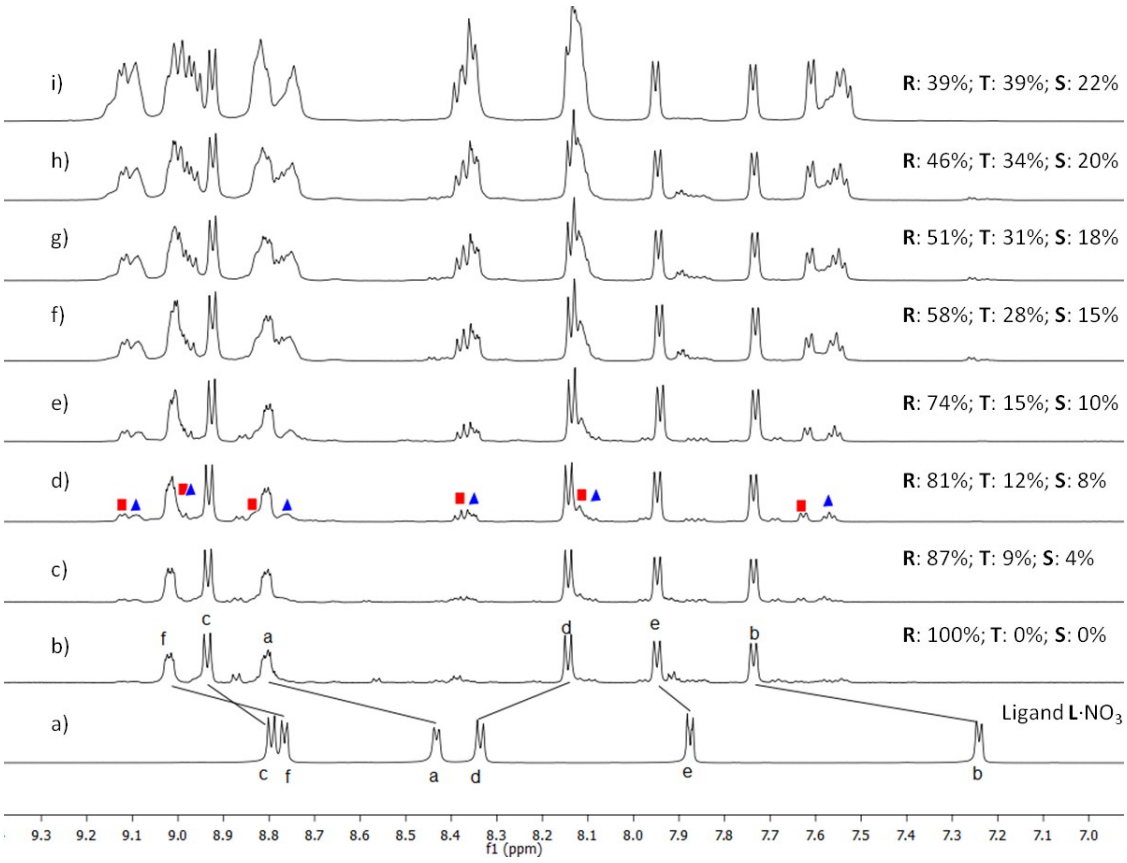


Figure S23. Partial ^{1}H NMR spectra (500 MHz, D_2O) for: a) Ligand **1**·NO_3, and equimolar mixtures of **1**·NO_3 and $(PEt_3)_2Pt(NO_3)_2$ at : b) 1.25 mM, c) 2.5 mM, d) 5 mM, e) 10 mM, f) 20 mM, g) 30 mM, h) 40 mM, i) 70 mM. Relative amounts of the species on the 70-0.75 mM range, calculated by relative integration of the signals at δ(ppm) = 7.56 (**T**$_{1\text{-}2}$), 7.62 (**S**$_{1\text{-}3}$) and 7.73 (**R**)

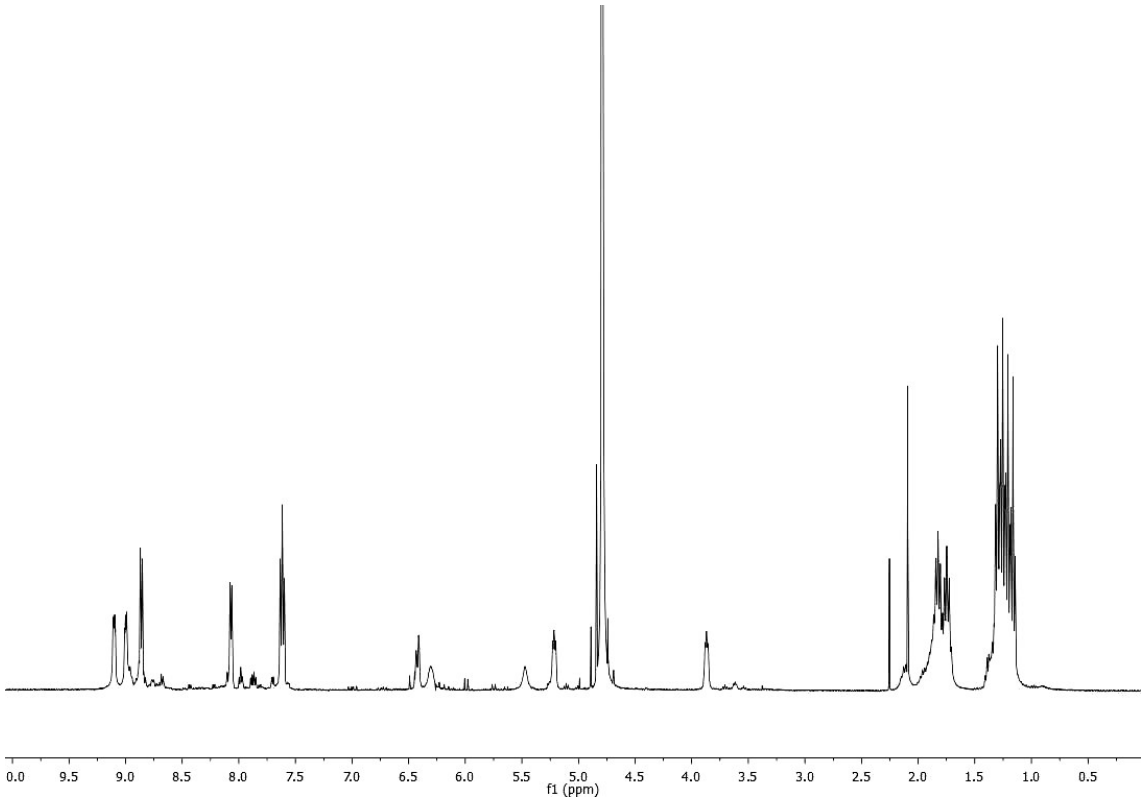


Figure S24. ^{1}H NMR (400 MHz, D_2O) spectrum of 2,7-DHN⊂**R**·6NO_3.

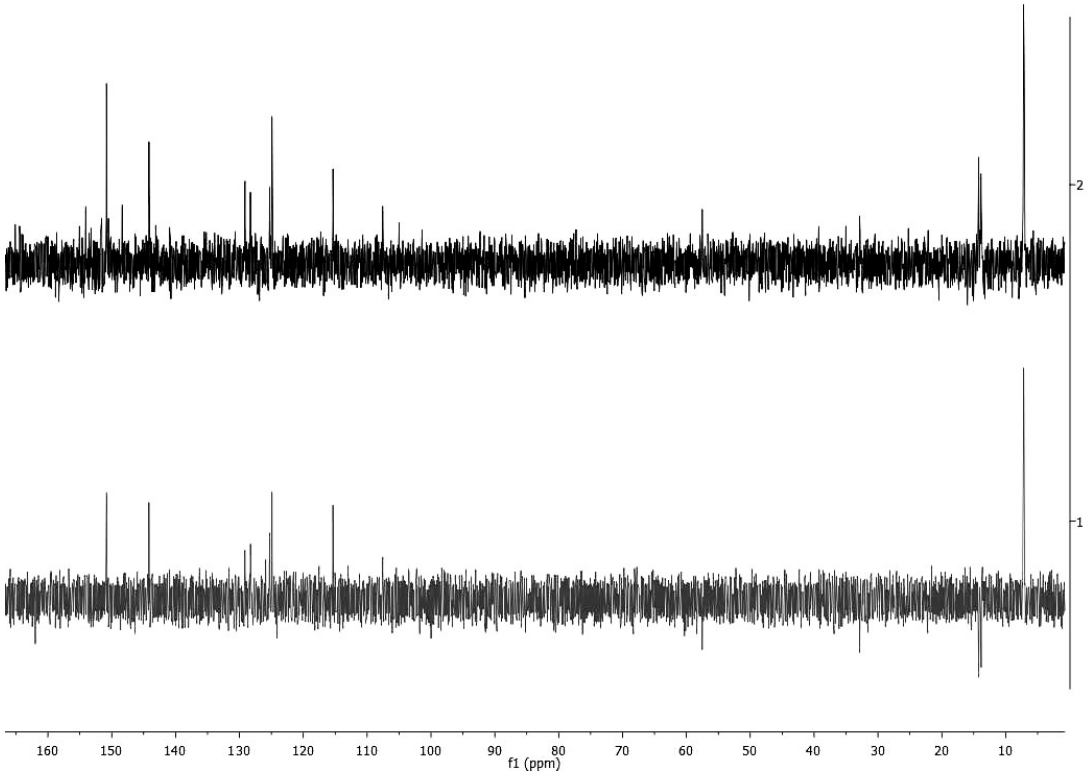


Figure S25. ^{13}C NMR and DEPT-135 (400 MHz, D_2O) spectra of 2,7-DHN⊂**R**·6NO_3.

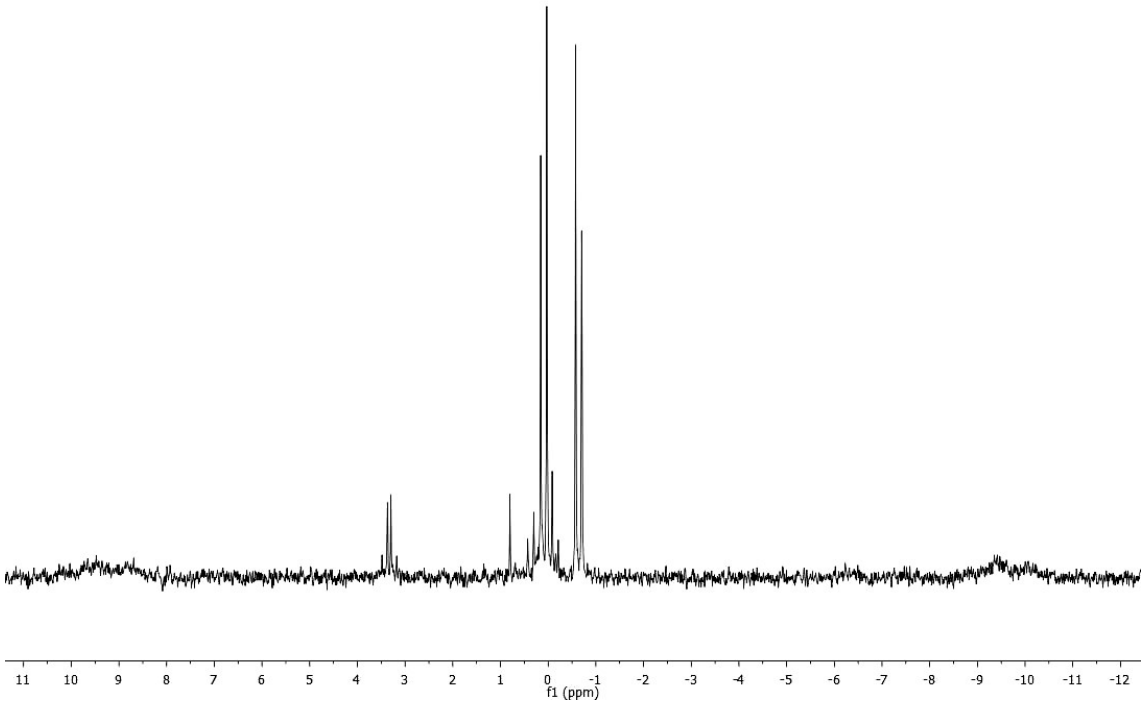


Figure S26. ^{31}P (162 MHz, D_2O) spectrum of 2,7-DHN⊂**R**·6NO_3.

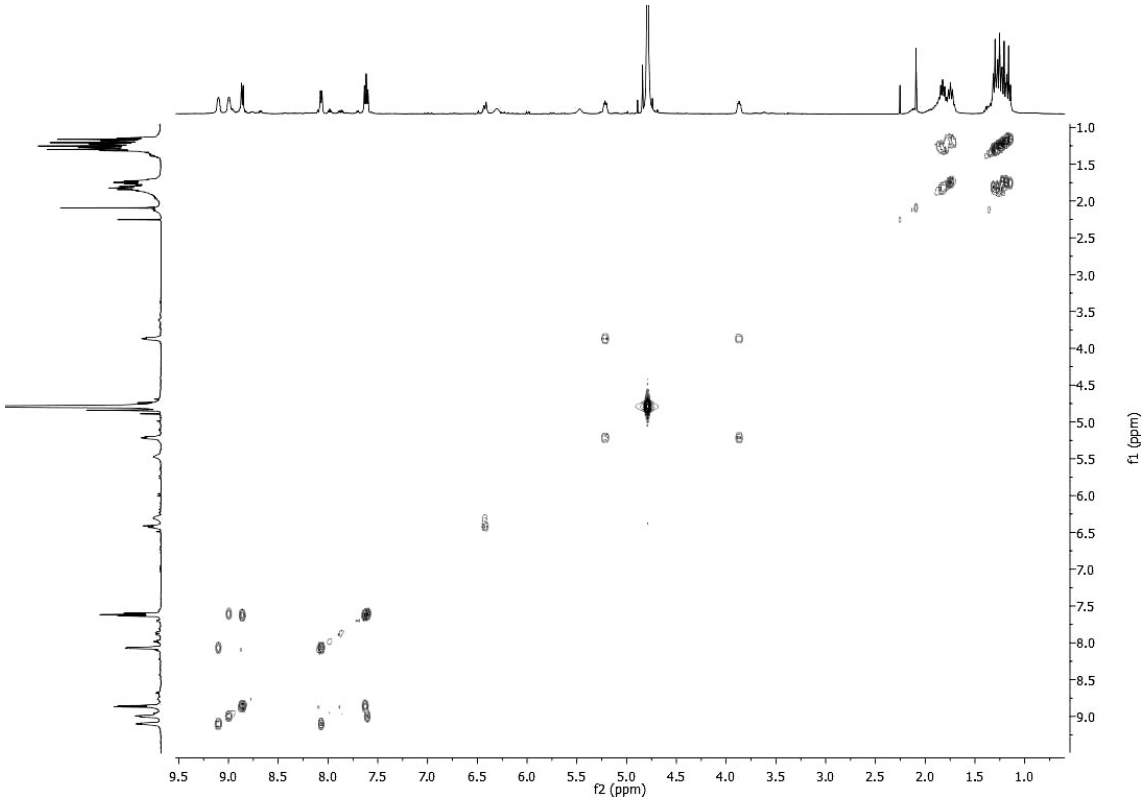


Figure S27. COSY (400 MHz, D_2O) spectrum of 2,7-DHN⊂**R**·6NO_3.

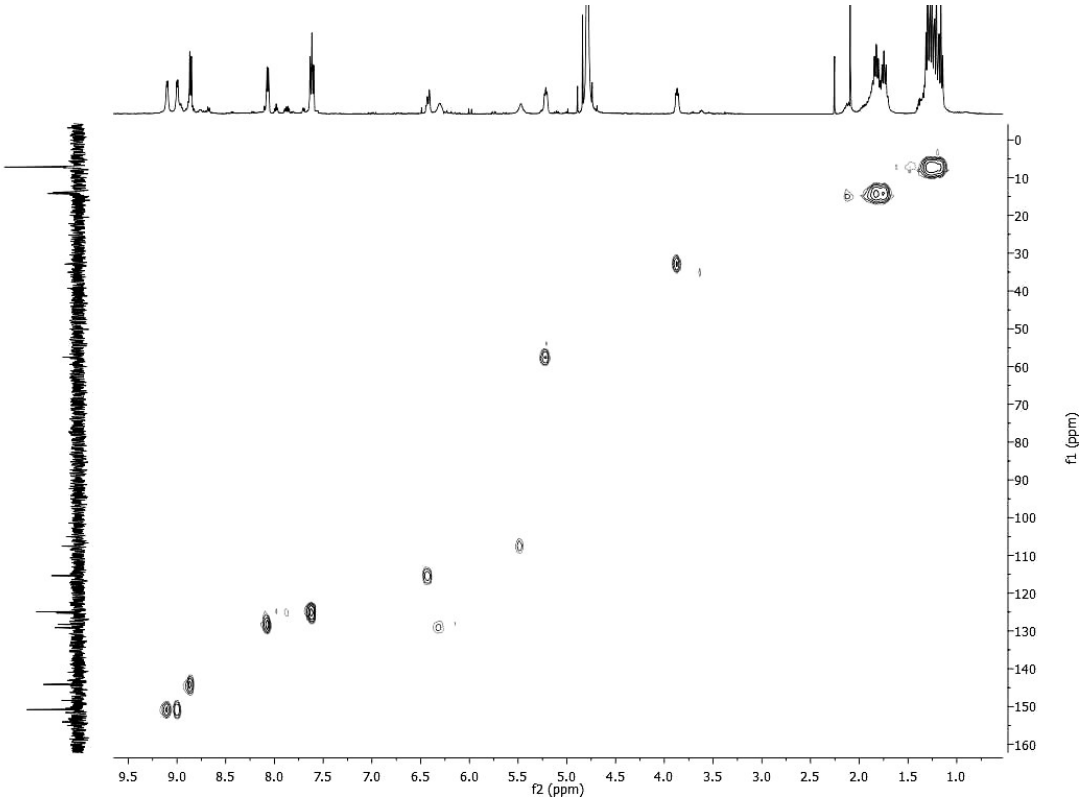


Figure S28. HSQC (400 MHz, D_2O) spectrum of 2,7-DHN⊂**R**·6NO_3.

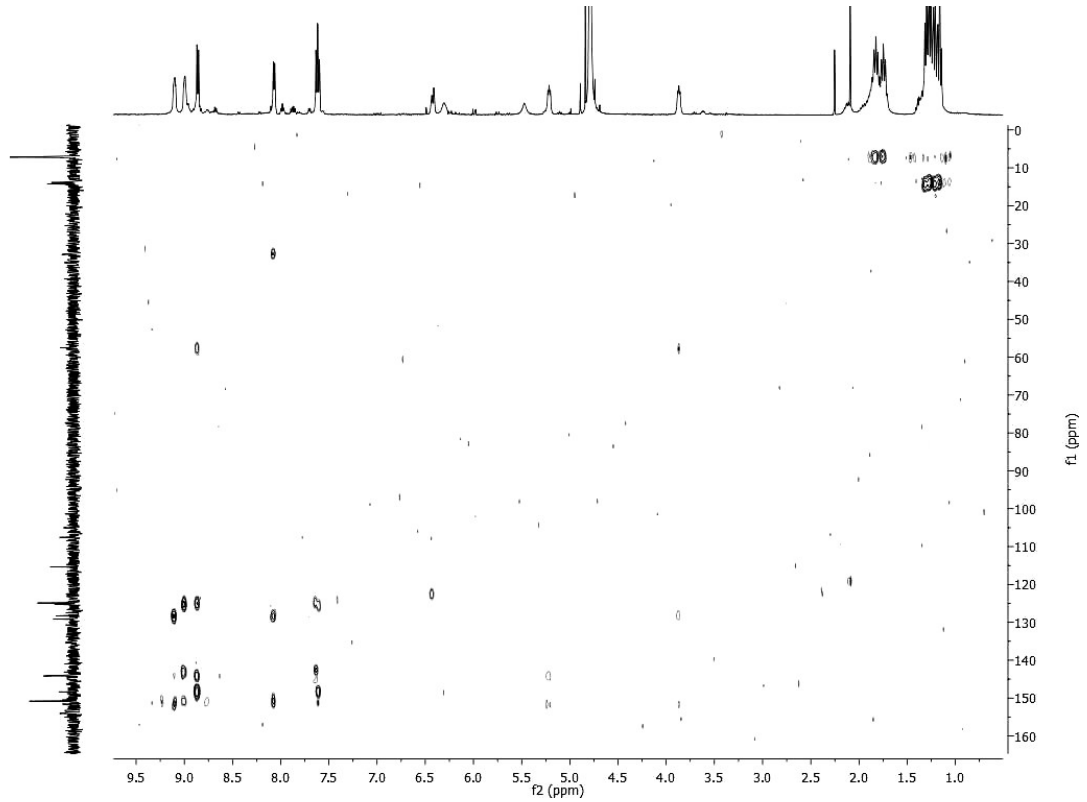


Figure S29. HMBC (400 MHz, D_2O) spectrum of 2,7-DHN⊂**R**·6NO_3.

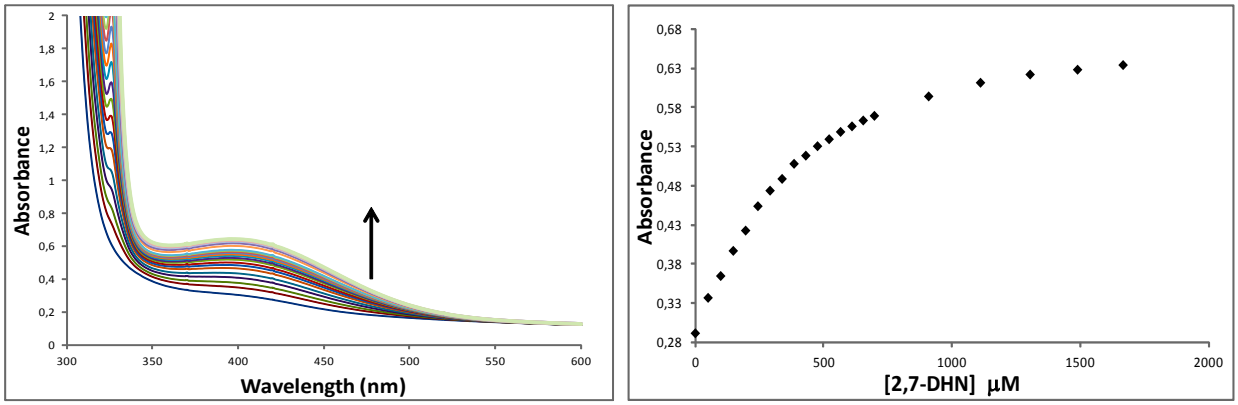


Figure S30. a) UV-Vis spectra in aqueous solution at 298 K of **R**·6NO_3 (0.50 mM) with increasing concentrations (0-1.67 mM) of 2,7-DHN. b) Plot of the absorbance at λ = 409 nm against the concentration of 2,7-DHN (0-1.67 mM).

Computational methods

DFT calculations were performed using the Gaussian 09 (Revision B.01)[3] program package. The structure optimizations were carried out with the B3LYP hybrid density functional[4] and the standard 6-31G(d,p) basis set for C, H, and N atoms and the LanL2DZ effective core potential of Wadt and Hay[5] (Los Alamos ECP) and its associated basis set for Pd and Pt. All calculations were carried out in water as solvent using the polarizable continuum model as implemented in Gaussian 09 (IEFPCM). The conformational analysis of ligand **1** was performed with an initial scan of the potential energy surface as a function of the NCCC(py) dihedral angle (every 60º) starting from the optimized *anti* geometry, followed by an optimization of the *gauche* structures. The optimization of *syn*-**1**, a maximum of the potential energy surface, was performed by using the synchronous transit-guided quasi-Newton method[6] as included in Gaussian 09 (QST2 or QST3). The Et_3P groups in **R**·$6NO_3$ were replaced by Me_3P to reduce computational cost.

[3] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[4] (a) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785.

[5] P. J. Hay and W. R. Wadt, *J. Chem. Phys*., 1985, **82**, 270.

[6] (a) C. Peng and H. B. Schlegel, *Isr. J. Chem.,* 1994, **33**, 449; (b) C. Peng, P. Y. Ayala, H. B. Schlegel and M. J. Frisch, *J. Comput. Chem.,* 1996, **17**, 49.

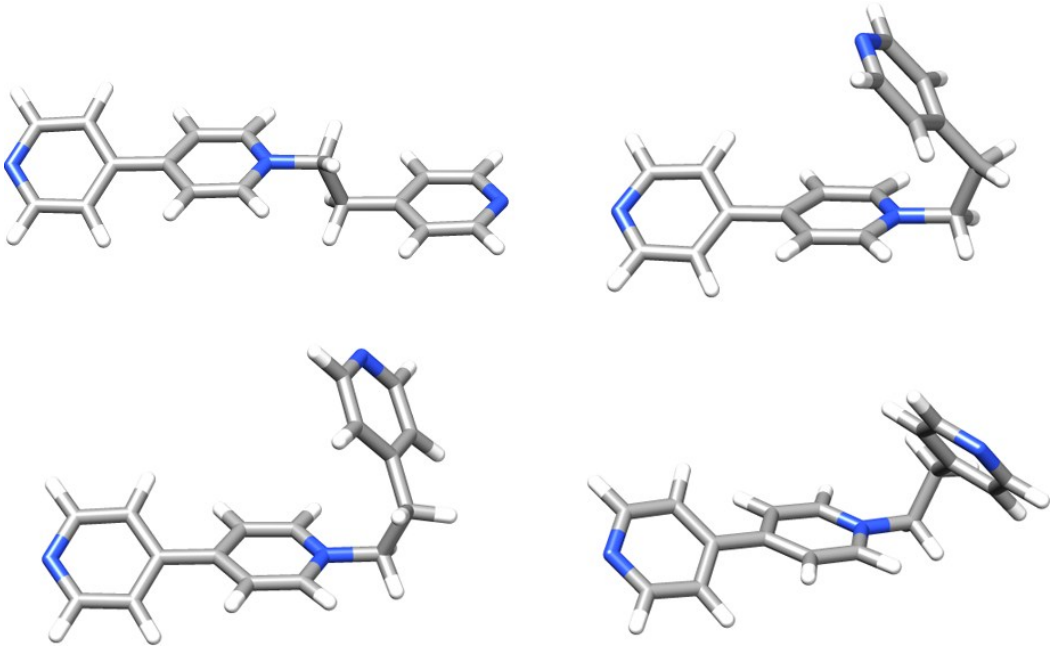


Figure S31. Optimized structures of the *anti* (top left), *syn* (top right) and staggered *gauche* (down) conformations of **1**.

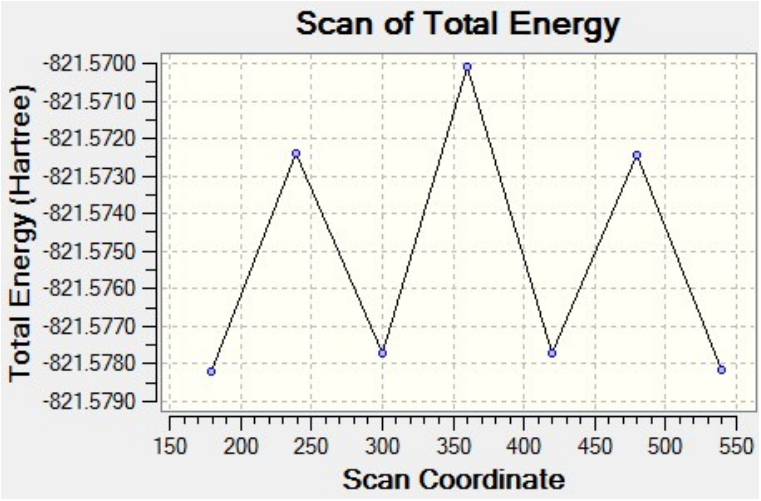


Figure S32. Scan of the potential energy surface of **1** as function of the dihedral angle NCCC(Py).

Table S1. Structural features of the different conformations of **1**.

	Anti	Gauche 1	Gauche 2	Syn
NCCC(Py) torsion angle (º)	179.7	64.1	64.4	0.8
Bipyridine torsion angle (º)	33.6	33.4	33.1	34.0
Terminal N–N distance (Å)	13.51	9.65	9.67	8.07
Pyridine-Bipyridine angle (º)[a]	0.4	76.8	77.1	51.0

[a] Calculated as the angle between the bipyridine N–N vector and the pyridine C(4)–N vector.

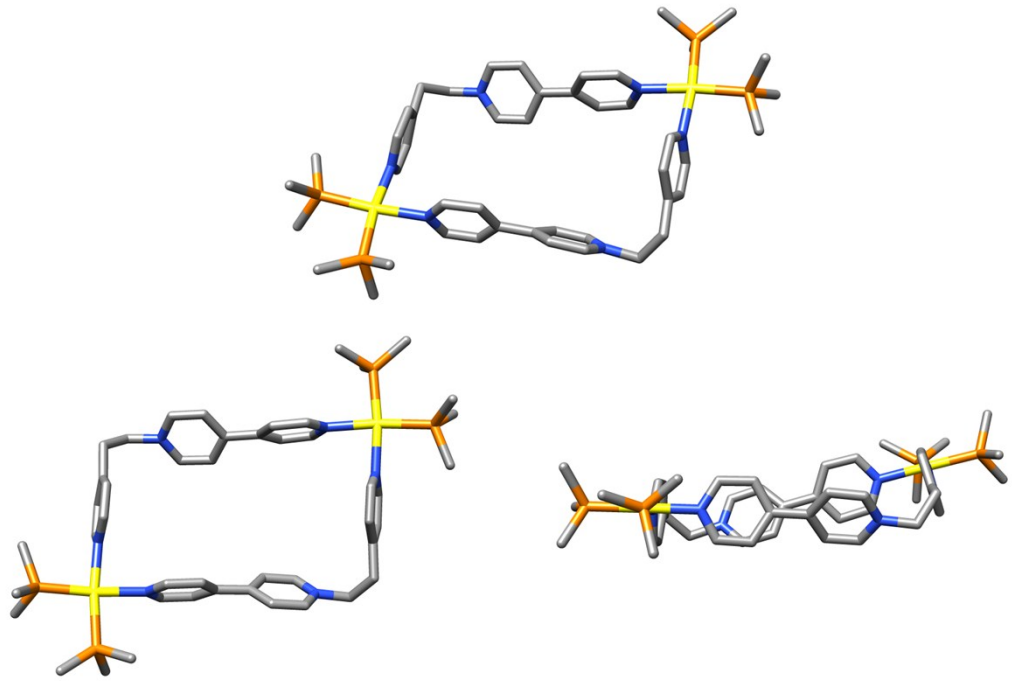
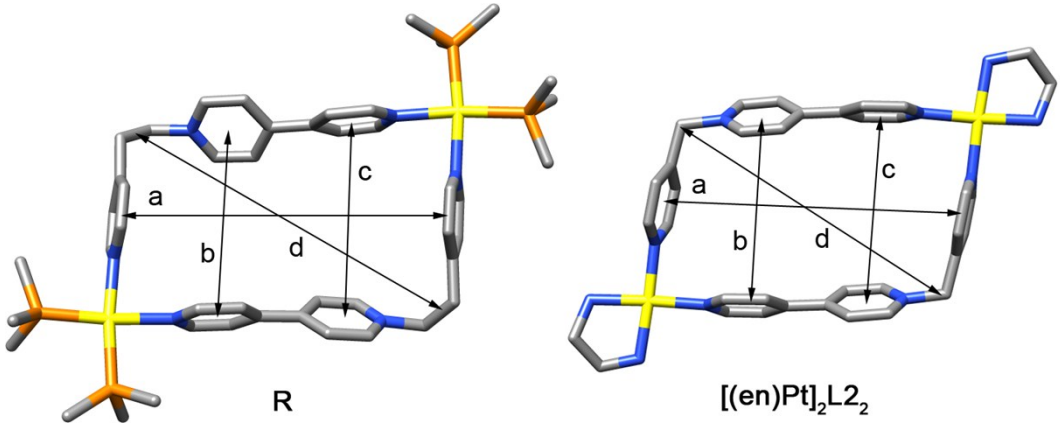


Figure S33. Different views of the optimized structure of **R**. Hydrogen atoms are omitted for clarity.

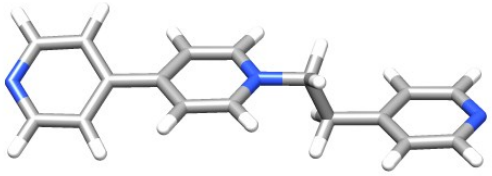
Table S2. Angles and distances in the calculated structures of **R** and **[(en)Pt]$_2$L2$_2$**



	R	**[(en)Pt]$_2$L2$_2$**
Distance a (Å)[a]	7.91	7.38
Distance b (Å)[a]	3.37	3.37
Distance c (Å)[a]	3.37	3.40
Distance d (Å)	12.10[b]	11.21
Pt–Pt distance (Å)	13.69	13.43
N-Pt-N angle (º)	84.4	88.1, 88.7
NCCC(py) torsion angle in the ligand (º)	69.0	-

[a] Distance between the centroids of the corresponding aromatic rings after subtracting two times the VdW radius of C. [b] Distance between the centroid of the C–C bond of the ethylene group. [d] C–C distance.

Table S3. Atomic coordinates of the optimized structure of *anti*-**1**



Center Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	2.528788	-0.147859	-0.588204
2	H	2.216825	0.573044	-1.349901
3	H	2.225213	-1.142770	-0.928713
4	C	1.810648	0.173493	0.735680
5	H	2.070739	1.169303	1.095797
6	H	2.071060	-0.547822	1.511172
7	C	-0.327972	-1.040074	0.714184
8	C	-0.341145	1.262115	0.247181
9	C	-1.693038	-1.112131	0.527756
10	H	0.268643	-1.901166	0.985887
11	C	-1.706965	1.241001	0.052550
12	H	0.246911	2.164994	0.146747
13	C	-2.423415	0.039870	0.188618
14	H	-2.182903	-2.066180	0.674514
15	H	-2.201722	2.163257	-0.223900
16	C	-3.888162	-0.008786	-0.013753
17	C	-4.705174	1.075921	0.335228
18	C	-4.508549	-1.140590	-0.561573
19	C	-6.079612	0.976963	0.128007
20	H	-4.293193	1.971584	0.786555
21	C	-5.891151	-1.131824	-0.735448
22	H	-3.933259	-2.004064	-0.876416
23	H	-6.728017	1.805489	0.402958
24	H	-6.386170	-1.997786	-1.168484
25	C	4.029960	-0.095484	-0.406182
26	C	4.754087	-1.222534	-0.002670
27	C	4.745838	1.089173	-0.609365
28	C	6.133106	-1.116305	0.174452

29	H	4.257436	-2.173309	0.166157
30	C	6.125267	1.093055	-0.405377
31	H	4.241744	1.996626	-0.928030
32	H	6.708486	-1.986483	0.484057
33	H	6.694156	2.007039	-0.563865
34	N	6.825317	0.016210	-0.018856
35	N	-6.678618	-0.100133	-0.399508
36	N	0.331727	0.134238	0.575359

```
Zero-point correction (Hartree/Particle)= 0.298710
Thermal correction to Energy = 0.314686
Thermal correction to Enthalpy = 0.315630
Thermal correction to Gibbs Free Energy = 0.251782
Sum of electronic and zero-point Energies = -821.279493
Sum of electronic and thermal Energies = -821.263516
Sum of electronic and thermal Enthalpies = -821.262572
Sum of electronic and thermal Free Energies = -821.326421
(0 imaginary frequencies)
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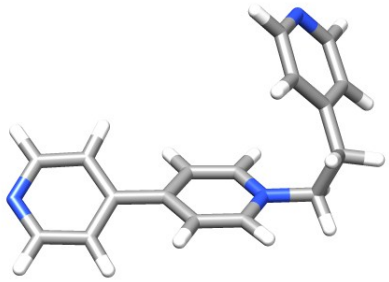
Table S4. Atomic coordinates of the optimized structure of *gauche1*-**1**

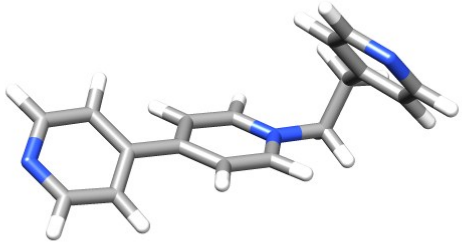


Center Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	3.166018	-1.646857	0.572252
2	H	4.099877	-2.210345	0.473674
3	H	2.771541	-1.856447	1.571093
4	C	2.210581	-2.229199	-0.485579
5	H	2.109927	-3.306966	-0.353882
6	H	2.574184	-2.042991	-1.496354
7	C	0.503793	-0.591703	-1.176838
8	C	-0.046826	-2.156776	0.485447
9	C	-0.748954	-0.018503	-1.087566
10	H	1.255722	-0.237709	-1.869118
11	C	-1.310250	-1.618447	0.611264

12	H	0.288355	-2.997595	1.078519
13	C	-1.696765	-0.524592	-0.182992
14	H	-0.984460	0.806311	-1.747911
15	H	-1.982601	-2.048039	1.342840
16	C	-3.049452	0.064510	-0.074754
17	C	-4.166026	-0.730635	0.220127
18	C	-3.260414	1.437600	-0.264609
19	C	-5.418731	-0.125990	0.304675
20	H	-4.076778	-1.802970	0.353607
21	C	-4.554252	1.941760	-0.148545
22	H	-2.436885	2.112177	-0.470557
23	H	-6.296135	-0.730250	0.522566
24	H	-4.733262	3.005788	-0.283343
25	C	3.435537	-0.167011	0.412822
26	C	2.849683	0.777960	1.261086
27	C	4.273169	0.314840	-0.601370
28	C	3.119509	2.132758	1.062254
29	H	2.197239	0.468995	2.071989
30	C	4.478552	1.688235	-0.718391
31	H	4.767519	-0.365824	-1.288283
32	H	2.670852	2.876202	1.718104
33	H	5.129604	2.074374	-1.499999
34	N	3.917783	2.599331	0.092233
35	N	-5.626779	1.186586	0.128393
36	N	0.842463	-1.647690	-0.400433

Zero-point correction (Hartree/Particle) = 0.298547
Thermal correction to Energy = 0.314459
Thermal correction to Enthalpy = 0.315404
Thermal correction to Gibbs Free Energy = 0.251601
Sum of electronic and zero-point Energies = -821.279222
Sum of electronic and thermal Energies = -821.263309
Sum of electronic and thermal Enthalpies = -821.262365
Sum of electronic and thermal Free Energies = -821.326168
(0 imaginary frequencies)

Table S5. Atomic coordinates of the optimized structure of *gauche2*-**1**



Center Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	3.181699	1.611535	0.552403
2	H	2.787305	1.834092	1.548399
3	H	4.120846	2.165621	0.450482
4	C	2.235165	2.193022	-0.514476
5	H	2.598343	1.989591	-1.522089
6	H	2.149581	3.273569	-0.396177
7	C	-0.037189	2.189864	0.425602
8	C	0.516252	0.550460	-1.162326
9	C	-1.307760	1.670305	0.558348
10	H	0.293948	3.060574	0.976421
11	C	-0.743840	-0.004918	-1.064950
12	H	1.276365	0.152815	-1.821155
13	C	-1.696345	0.546952	-0.192505
14	H	-1.997427	2.165005	1.230088
15	H	-0.966359	-0.880890	-1.660716
16	C	-3.054721	-0.026692	-0.071711
17	C	-3.695722	-0.614144	-1.171754
18	C	-3.746965	-0.002881	1.147470
19	C	-4.976622	-1.136621	-1.004061
20	H	-3.227789	-0.643207	-2.149450
21	C	-5.022071	-0.561687	1.208368
22	H	-3.300296	0.413795	2.043287
23	H	-5.490841	-1.586833	-1.849830
24	H	-5.567814	-0.559615	2.148917
25	C	3.439797	0.128162	0.408557
26	C	4.275957	-0.370166	-0.598971

27	C	2.845626	-0.803755	1.265424
28	C	4.471669	-1.746088	-0.701475
29	H	4.776592	0.299835	-1.291804
30	C	3.106351	-2.162453	1.081192
31	H	2.193606	-0.481901	2.071750
32	H	5.121373	-2.144897	-1.477819
33	H	2.651269	-2.895846	1.743878
34	N	3.903011	-2.644708	0.117566
35	N	-5.642084	-1.121109	0.159617
36	N	0.858162	1.633377	-0.425038

```
Zero-point correction (Hartree/Particle)= 0.298475
Thermal correction to Energy = 0.314397
Thermal correction to Enthalpy = 0.315342
Thermal correction to Gibbs Free Energy = 0.251257
Sum of electronic and zero-point Energies = -821.279294
Sum of electronic and thermal Energies = -821.263372
Sum of electronic and thermal Enthalpies = -821.262427
Sum of electronic and thermal Free Energies = -821.326511
(0 imaginary frequencies)
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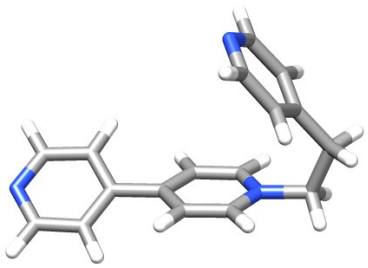
Table S6. Atomic coordinates of the optimized structure of *syn*-**1**

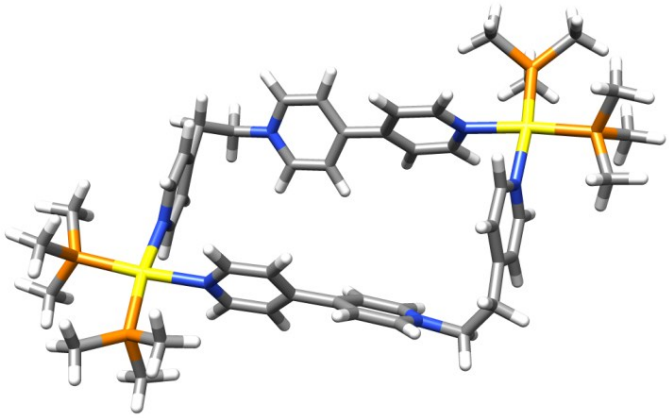


Center Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	3.721311	-1.215134	-0.109610
2	H	4.361554	-1.292687	-0.991551
3	H	4.330158	-1.493019	0.753650
4	C	2.594299	-2.296687	-0.256381
5	H	2.674013	-3.040098	0.535571
6	H	2.685841	-2.816795	-1.208522
7	C	0.576791	-1.405208	-1.342864
8	C	0.585007	-1.627214	0.994282
9	C	-0.700585	-0.884407	-1.315185
10	H	1.118817	-1.562332	-2.265844

11	C	-0.692821	-1.112136	1.073529
12	H	1.138746	-1.940242	1.869316
13	C	-1.373128	-0.721862	-0.092321
14	H	-1.173792	-0.632586	-2.255637
15	H	-1.143224	-1.002566	2.051801
16	C	-2.743359	-0.167132	-0.035741
17	C	-3.666517	-0.607985	0.923029
18	C	-3.163945	0.819748	-0.938562
19	C	-4.945040	-0.053668	0.930235
20	H	-3.414357	-1.386672	1.634147
21	C	-4.463024	1.313819	-0.837825
22	H	-2.492361	1.222670	-1.688508
23	H	-5.675915	-0.391869	1.660933
24	H	-4.801227	2.086886	-1.523711
25	C	3.273397	0.221415	0.048220
26	C	3.094390	0.793404	1.313232
27	C	3.037094	1.041999	-1.061507
28	C	2.690487	2.124948	1.409776
29	H	3.281187	0.219202	2.215576
30	C	2.634185	2.361878	-0.860243
31	H	3.178334	0.669631	-2.071631
32	H	2.553125	2.579631	2.388779
33	H	2.451257	3.008579	-1.715997
34	N	2.456578	2.912320	0.349851
35	N	-5.352101	0.893644	0.073435
36	N	1.206464	-1.769165	-0.200537

Zero-point correction = 0.298804 (Hartree/Particle)
Thermal correction to Energy = 0.313867
Thermal correction to Enthalpy = 0.314811
Thermal correction to Gibbs Free Energy = 0.254421
Sum of electronic and zero-point Energies = -821.271315
Sum of electronic and thermal Energies = -821.256252
Sum of electronic and thermal Enthalpies = -821.255307
(1 imaginary frequency)

Table S7. Atomic coordinates of the calculated structure of **R**.



Center Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-3.486957	-5.253312	0.471877
2	H	-4.223012	-6.010428	0.767611
3	H	-3.092992	-5.578155	-0.494657
4	C	-2.388718	-5.318890	1.542169
5	H	-2.056028	-6.351615	1.660151
6	H	-2.746390	-4.972425	2.510941
7	C	-0.822536	-3.466185	1.999424
8	C	-0.396447	-4.877038	0.169374
9	C	0.339969	-2.758351	1.757473
10	H	-1.484436	-3.224696	2.820299
11	C	0.769180	-4.196079	-0.119429
12	H	-0.722085	-5.733292	-0.406772
13	C	1.172937	-3.121952	0.689915
14	H	0.581099	-1.925056	2.405597
15	H	1.375701	-4.538021	-0.948704
16	C	2.459475	-2.427292	0.447178
17	C	2.908787	-2.149877	-0.851071
18	C	3.281544	-2.055440	1.519403
19	C	4.145708	-1.543540	-1.029470
20	H	2.308093	-2.385903	-1.721596
21	C	4.510273	-1.462825	1.262630
22	H	2.998388	-2.252313	2.546540
23	H	4.523068	-1.317316	-2.019388

24	H	5.175927	-1.182513	2.069999
25	C	-4.202649	-3.929146	0.314865
26	C	-4.295088	-3.308229	-0.935735
27	C	-4.860562	-3.311606	1.387425
28	C	-5.047126	-2.148996	-1.081740
29	H	-3.806279	-3.730695	-1.806699
30	C	-5.584765	-2.147128	1.175553
31	H	-4.842484	-3.734737	2.385900
32	H	-5.156473	-1.666104	-2.045557
33	H	-6.116507	-1.660721	1.984778
34	N	-5.692629	-1.581775	-0.044525
35	N	4.941970	-1.221397	0.009199
36	N	-1.173398	-4.513369	1.217994
37	Pt	-6.841170	0.218956	-0.303117
38	Pt	6.841366	-0.219013	-0.302946
39	N	-4.941877	1.221473	0.008805
40	C	-4.509688	1.461982	1.262244
41	C	-4.146095	1.544581	-1.029936
42	C	-3.280977	2.054638	1.518977
43	H	-5.174907	1.180873	2.069686
44	C	-2.909198	2.150977	-0.851565
45	H	-4.523829	1.319060	-2.019873
46	C	-2.459399	2.427467	0.446714
47	H	-2.997469	2.250753	2.546159
48	H	-2.308895	2.387750	-1.722155
49	C	-1.172894	3.122166	0.689487
50	C	-0.769402	4.196680	-0.119479
51	C	-0.339679	2.758207	1.756734
52	C	0.396204	4.877640	0.169399
53	H	-1.376106	4.538911	-0.948502
54	C	0.822769	3.466089	1.998802
55	H	-0.580574	1.924600	2.404542
56	H	0.721672	5.734155	-0.406458
57	N	1.173369	4.513639	1.217745
58	H	1.484805	3.224356	2.819496

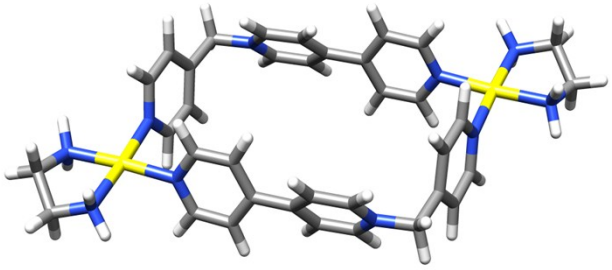
59	C	2.388671	5.319137	1.541972
60	C	3.486953	5.253514	0.471721
61	H	2.055992	6.351868	1.659915
62	H	2.746291	4.972697	2.510774
63	H	4.223016	6.010613	0.767479
64	H	3.093023	5.578357	-0.494829
65	C	4.202627	3.929331	0.314774
66	C	4.295098	3.308314	-0.935763
67	C	4.860520	3.311881	1.387407
68	C	5.047184	2.149081	-1.081654
69	H	3.806300	3.730692	-1.806777
70	C	5.584860	2.147483	1.175627
71	H	4.842346	3.735074	2.385855
72	H	5.156560	1.666148	-2.045446
73	N	5.692755	1.582022	-0.044414
74	H	6.116625	1.661167	1.984888
75	P	-8.773537	-1.044213	-0.617221
76	P	-7.861687	2.321946	-0.426031
77	P	7.861157	-2.322233	-0.426791
78	P	8.773767	1.044065	-0.617009
79	C	-10.067328	-0.795960	0.659652
80	H	-10.904350	-1.471855	0.462613
81	H	-9.643116	-1.021997	1.640689
82	H	-10.434721	0.230366	0.665109
83	C	-8.473934	-2.853402	-0.554054
84	H	-8.079667	-3.146489	0.419711
85	H	-9.426329	-3.364037	-0.720051
86	H	-7.770731	-3.148098	-1.334639
87	C	-9.581688	-0.832180	-2.250869
88	H	-10.387215	-1.565341	-2.348175
89	H	-9.999212	0.166839	-2.365581
90	H	-8.842004	-1.001529	-3.036600
91	C	-9.536100	2.538957	-1.144344
92	H	-9.515123	2.311210	-2.211826
93	H	-10.279546	1.914295	-0.649092

94	H	-9.824979	3.585846	-1.017365
95	C	-6.875606	3.531685	-1.393742
96	H	-7.415301	4.482492	-1.422552
97	H	-5.899513	3.694214	-0.936271
98	H	-6.740682	3.167574	-2.414856
99	C	-7.982049	3.033445	1.261551
100	H	-6.989219	3.083214	1.713241
101	H	-8.403029	4.041524	1.211270
102	H	-8.620053	2.402843	1.883843
103	C	9.535703	-2.539674	-1.144668
104	H	9.823664	-3.586953	-1.018826
105	H	9.515451	-2.310619	-2.211877
106	H	10.279404	-1.916260	-0.648195
107	C	7.980892	-3.034701	1.260420
108	H	6.988030	-3.084024	1.712077
109	H	8.401213	-4.043032	1.209635
110	H	8.619337	-2.404816	1.882993
111	C	6.874620	-3.530849	-1.395433
112	H	7.414143	-4.481715	-1.425404
113	H	5.898668	-3.693697	-0.937771
114	H	6.739367	-3.165667	-2.416117
115	C	10.067516	0.795238	0.659779
116	H	10.904569	1.471205	0.463122
117	H	9.643279	1.020739	1.640925
118	H	10.434820	-0.231126	0.664675
119	C	9.582048	0.832505	-2.250651
120	H	10.386442	1.566844	-2.348385
121	H	10.001172	-0.165938	-2.364620
122	H	8.842122	1.000072	-3.036528
123	C	8.474190	2.853238	-0.553172
124	H	8.080010	3.145971	0.420735
125	H	9.426579	3.363918	-0.719062
126	H	7.770936	3.148224	-1.333596

Zero-point correction (Hartree/Particle) = 1.073863
Thermal correction to Energy = 1.139771
Thermal correction to Enthalpy = 1.140715

```
Thermal correction to Gibbs Free Energy 0.971087
Sum of electronic and zero-point Energies = -3724.495892
Sum of electronic and thermal Energies = -3724.429984
Sum of electronic and thermal Enthalpies = -3724.429040
Sum of electronic and thermal Free Energies = -3724.598667
(0 imaginary frequencies)
```

Table S8. Atomic coordinates of the calculated structure of **[(en)Pt]$_2$L2$_2$**.



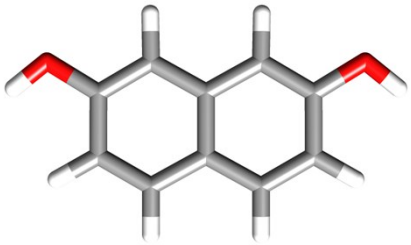
Center Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	4.200879	-1.408138	-1.165797
2	H	4.613792	-0.943299	-2.051934
3	C	2.968418	-2.045682	-1.191278
4	H	2.408052	-2.055153	-2.118400
5	C	2.458907	-2.616652	-0.016424
6	C	3.245672	-2.539120	1.141058
7	H	2.930424	-2.986654	2.075623
8	C	4.468951	-1.887661	1.096101
9	H	5.095916	-1.802597	1.974783
10	C	-0.682755	-4.448727	-1.055510
11	H	-1.117825	-4.979058	-1.892005
12	C	0.596016	-3.924445	-1.100084
13	H	1.176244	-4.067909	-2.003053
14	C	1.116899	-3.244723	0.011420
15	C	0.308114	-3.153886	1.156976
16	H	0.642018	-2.639161	2.048826
17	C	-0.960647	-3.693519	1.153041
18	H	-1.615701	-3.632087	2.011405
19	C	-2.855931	-4.826431	0.070404
20	H	-2.974305	-5.425254	0.973653
21	H	-2.971823	-5.481171	-0.792448
22	C	-3.848390	-3.679638	0.032926

23	C	-4.479988	-3.238559	1.198776
24	H	-4.325215	-3.732245	2.151483
25	C	-5.324656	-2.135796	1.146367
26	C	-4.997271	-1.925873	-1.148866
27	C	-4.139206	-3.016003	-1.163728
28	C	-4.416552	1.799884	-1.137624
29	H	-4.988846	1.621905	-2.039384
30	C	-3.190058	2.446177	-1.175309
31	H	-2.814034	2.791054	-2.130748
32	C	-2.476252	2.648820	0.014042
33	C	-3.064258	2.213071	1.209742
34	H	-2.565692	2.327429	2.164833
35	C	-4.294975	1.572550	1.175257
36	H	-4.767577	1.210537	2.079399
37	C	1.023522	3.565013	-1.049104
38	H	1.730982	3.398644	-1.850292
39	C	-0.250791	3.039645	-1.073903
40	H	-0.537173	2.432653	-1.923246
41	C	-1.126896	3.261914	0.002222
42	C	-0.664141	4.053023	1.064329
43	H	-1.295136	4.294939	1.910269
44	C	0.623042	4.558516	1.043342
45	H	1.017194	5.168922	1.844931
46	C	2.858082	4.817563	0.008332
47	H	2.962281	5.456578	0.884363
48	H	2.980762	5.434096	-0.882602
49	C	3.858310	3.678257	0.033911
50	C	4.547201	3.303897	-1.122349
51	H	4.430343	3.845701	-2.054157
52	C	5.395685	2.202941	-1.089029
53	C	4.100012	2.954724	1.206917
54	C	4.966565	1.871844	1.174768
55	C	9.648783	-0.235264	-0.302315
56	H	10.617724	0.131912	0.043437
57	H	9.661767	-0.289771	-1.392882

58	C	9.326996	-1.590334	0.304234
59	H	10.030030	-2.353027	-0.037769
60	H	9.359333	-1.546139	1.394834
61	C	-9.645651	0.195181	0.248319
62	H	-9.671384	0.288853	1.335989
63	H	-10.604670	-0.200148	-0.093776
64	C	-9.338313	1.533104	-0.402148
65	H	-9.354210	1.450518	-1.490885
66	H	-10.058625	2.295226	-0.096740
67	N	4.935194	-1.320481	-0.036896
68	N	-1.447437	-4.317326	0.053227
69	N	-5.564952	-1.480277	-0.007270
70	N	-4.953227	1.353010	0.017630
71	N	1.451464	4.301595	0.004815
72	N	5.587103	1.487479	0.037798
73	N	8.559915	0.719150	0.086776
74	H	8.596681	1.551739	-0.501299
75	H	8.702509	1.042096	1.045667
76	N	7.926997	-1.956965	-0.088793
77	H	7.585097	-2.715621	0.501037
78	H	7.912983	-2.312993	-1.046521
79	N	-8.537545	-0.755413	-0.093292
80	H	-8.665454	-1.122352	-1.038301
81	H	-8.563135	-1.561672	0.530862
82	N	-7.950355	1.936815	-0.002463
83	H	-7.956353	2.327705	0.941594
84	H	-7.609364	2.677442	-0.615386
85	Pt	6.711980	-0.256223	-0.003567
86	Pt	-6.708539	0.253538	-0.016413
87	H	-5.814533	-1.754744	2.033727
88	H	-3.709405	-3.327909	-2.108894
89	H	-5.239512	-1.384115	-2.054130
90	H	5.170808	1.284815	2.061041
91	H	3.620268	3.212489	2.144341
92	H	5.924348	1.870078	-1.973567

Zero-point correction (Hartree/Particle)= 0.787897
Thermal correction to Energy = 0.830429
Thermal correction to Enthalpy = 0.831373
Thermal correction to Gibbs Free Energy = 0.709956
Sum of electronic and zero-point Energies = -2182.714547
Sum of electronic and thermal Energies = -2182.672016
Sum of electronic and thermal Enthalpies = -2182.671072
Sum of electronic and thermal Free Energies= -2182.792489
(0 imaginary frequencies)

Table S9. Atomic coordinates of the calculated structure of **2,7-DHN**.



Center Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	2.436028	0.974353	-0.000020
2	C	1.244358	1.661214	0.000006
3	C	0.000003	0.977469	0.000003
4	C	-0.000002	-0.457905	0.000006
5	C	1.241420	-1.146819	0.000045
6	C	2.431369	-0.446595	0.000001
7	H	-1.246138	2.747850	-0.000004
8	H	3.382314	1.508648	-0.000078
9	H	1.246144	2.747853	0.000007
10	C	-1.244368	1.661208	0.000000
11	C	-1.241419	-1.146837	0.000014
12	H	1.260899	-2.232189	0.000120
13	C	-2.431359	-0.446605	0.000000
14	C	-2.436026	0.974351	-0.000005
15	H	-1.260884	-2.232203	0.000025
16	H	-3.382316	1.508637	-0.000020
17	O	-3.596521	-1.160458	-0.000023
18	O	3.596514	-1.160467	-0.000133
19	H	-4.348835	-0.552083	0.000081

20	H	4.348841	-0.552110	0.000809

Zero-point correction (Hartree/Particle)= 0.155550
Thermal correction to Energy = 0.164838
Thermal correction to Enthalpy = 0.165782
Thermal correction to Gibbs Free Energy = 0.121460
Sum of electronic and zero-point Energies = -536.200878
Sum of electronic and thermal Energies = -536.191590
Sum of electronic and thermal Enthalpies = -536.190645
Sum of electronic and thermal Free Energies = -536.234968
(0 imaginary frequencies)