Supporting Information

Activation of white phosphorus by low-valent Group 5 complexes: formation and reactivity of *cyclo*-P_4 inverted sandwich compounds

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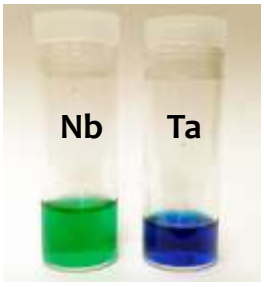
Content



*Picture of toluene solutions of compounds **1**(left) and **2** (right).*

A. NMR and IR spectroscopic data

Figure S1. ^{1}H NMR spectrum for **1** (C_6D_6, 293K, 400MHz).

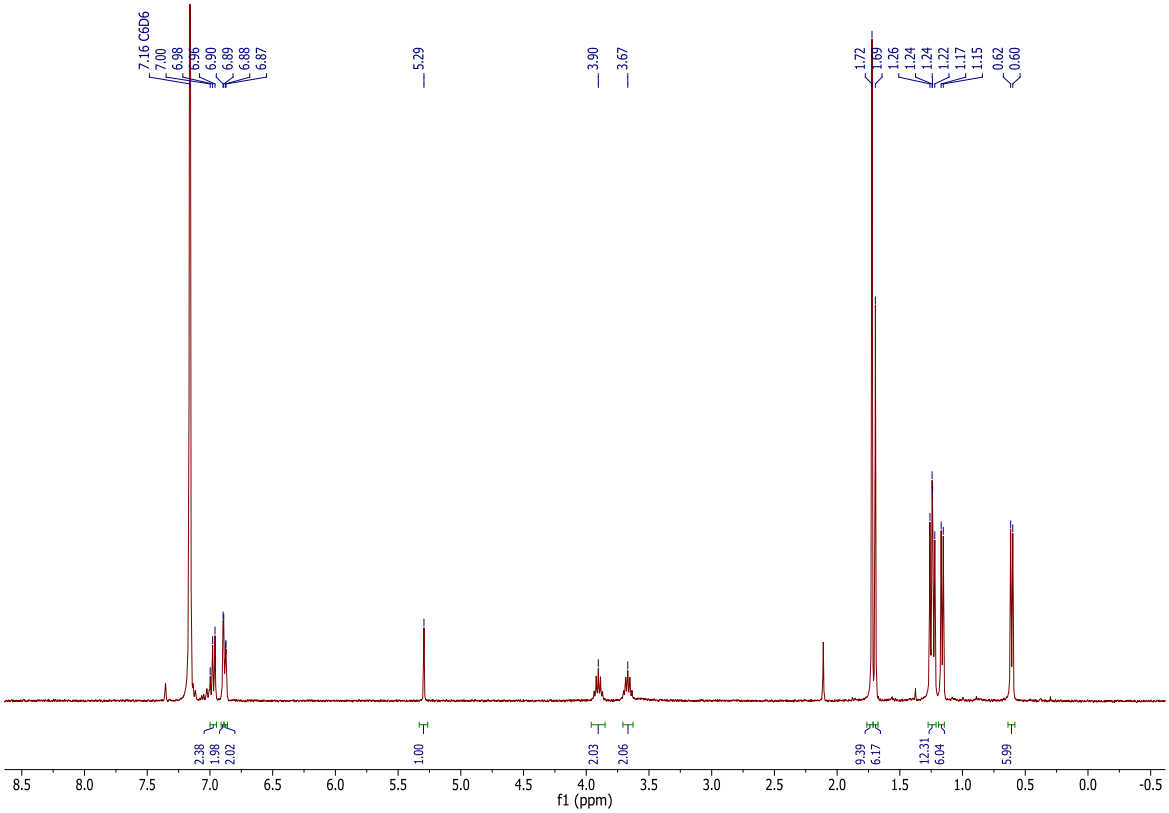


Figure S2. ^{1}H-^{1}H COSY NMR spectrum for **1** ($CDCl_3$, 293K, 400MHz).

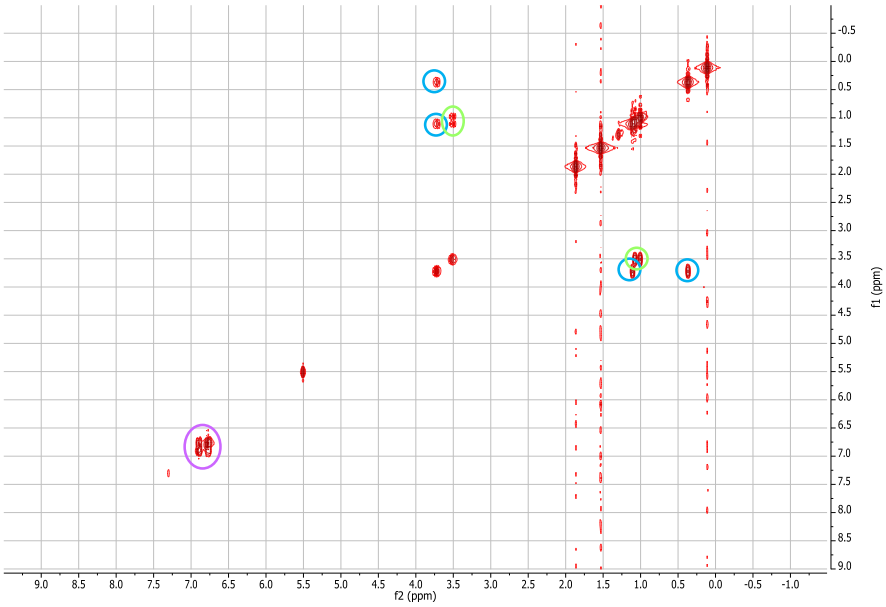


Figure S3. Solid-state ^{31}P MAS spectrum for **1** recorded at 202 MHz at 13 kHz spinning speed.

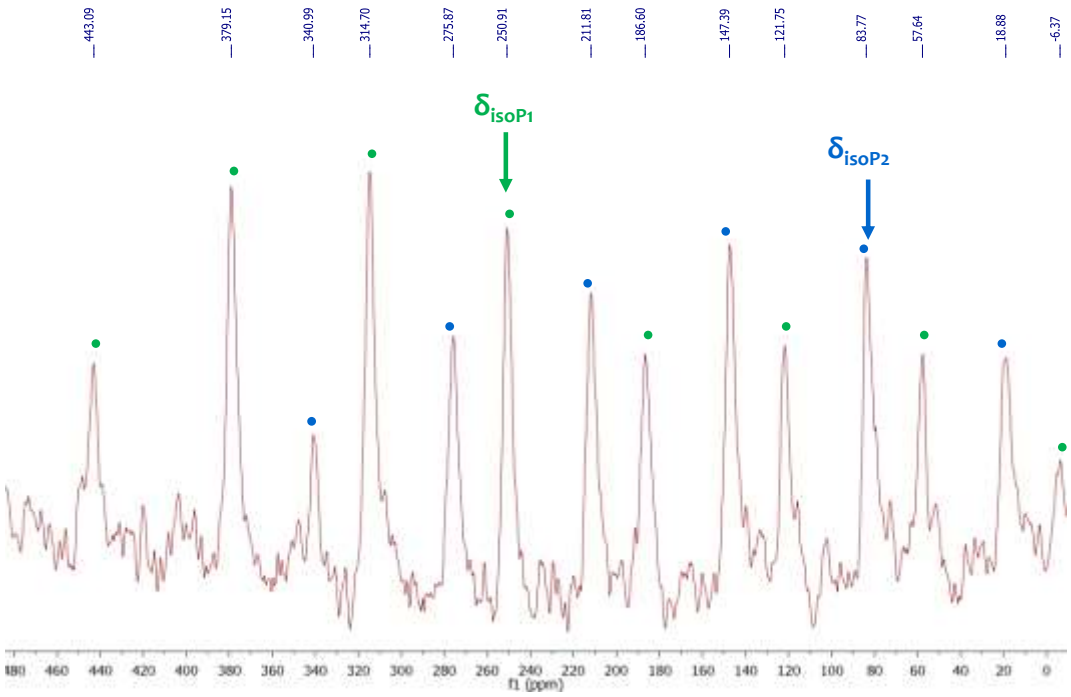


Figure S4. IR transmission spectrum for **1**.

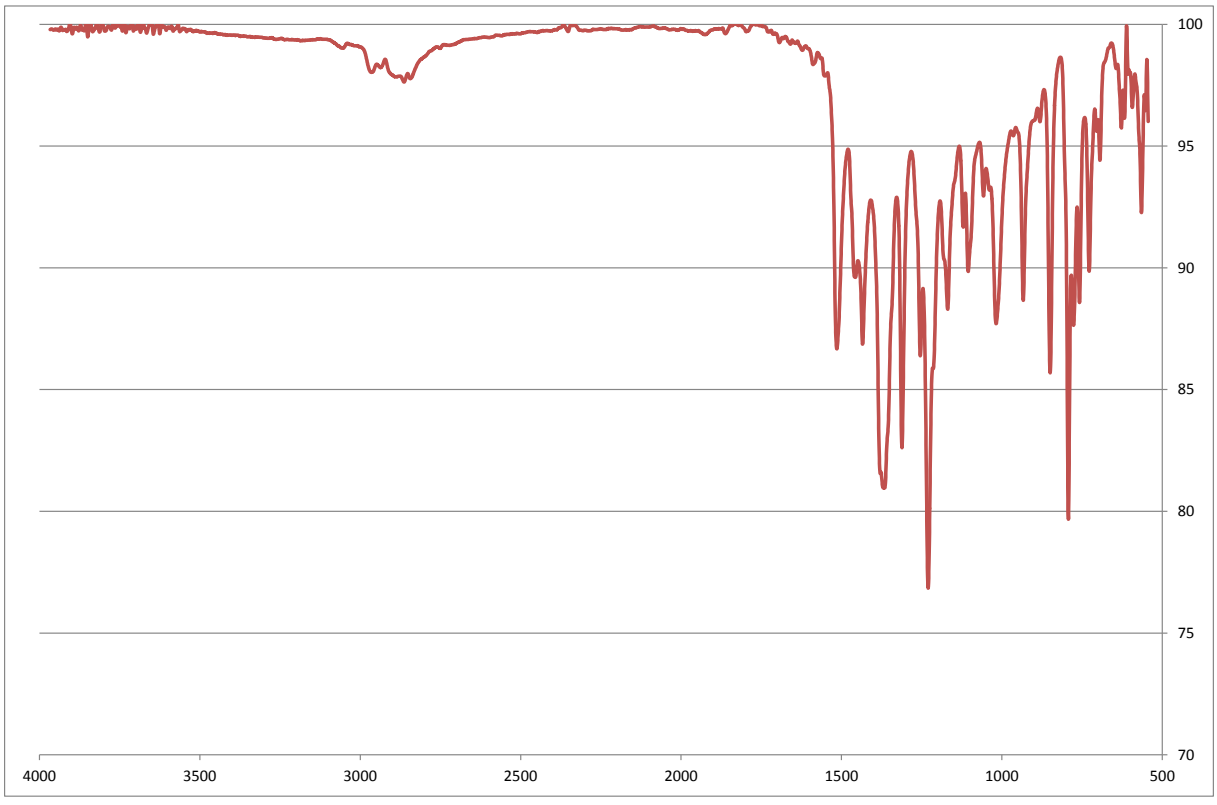


Figure S5. ^{1}H NMR spectrum for **2** (C_6D_6, 293K, 500MHz).

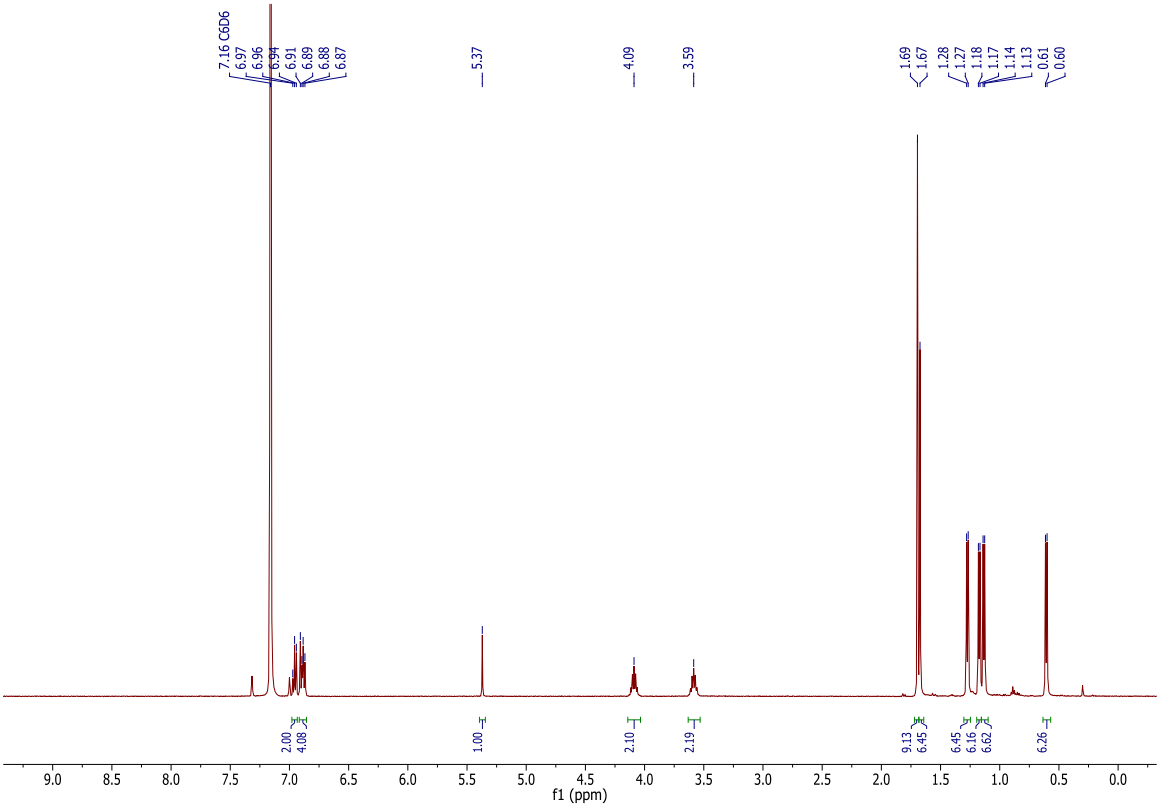


Figure S6. ^{1}H-^{1}H COSY NMR spectrum for **2** (C_6D_6, 293K, 400MHz).

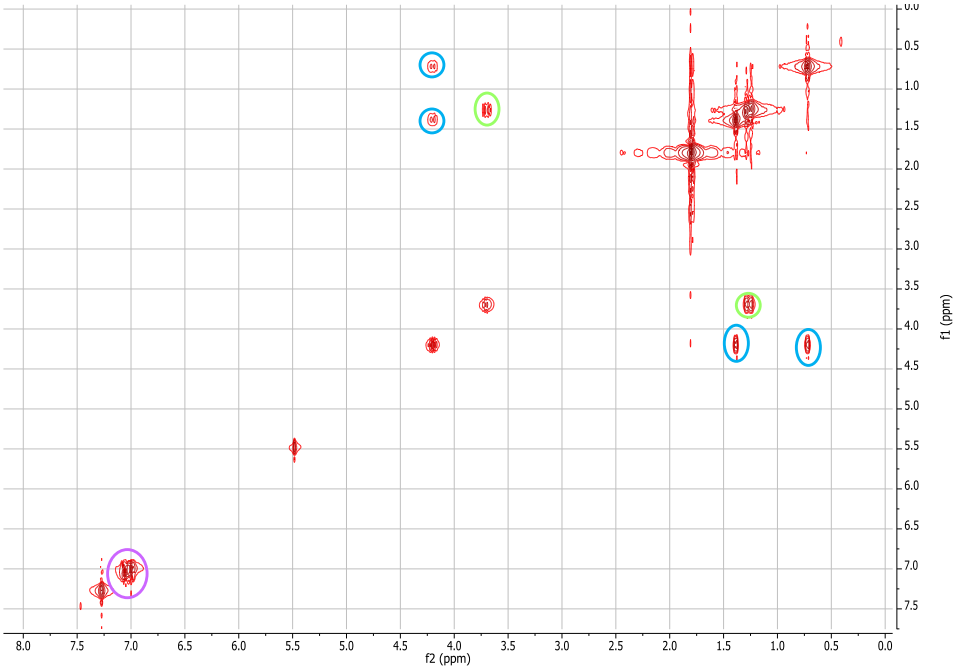


Figure S7. Solid-state ^{31}P MAS spectrum for **2** recorded at 202 MHz at 11 kHz spinning speed.

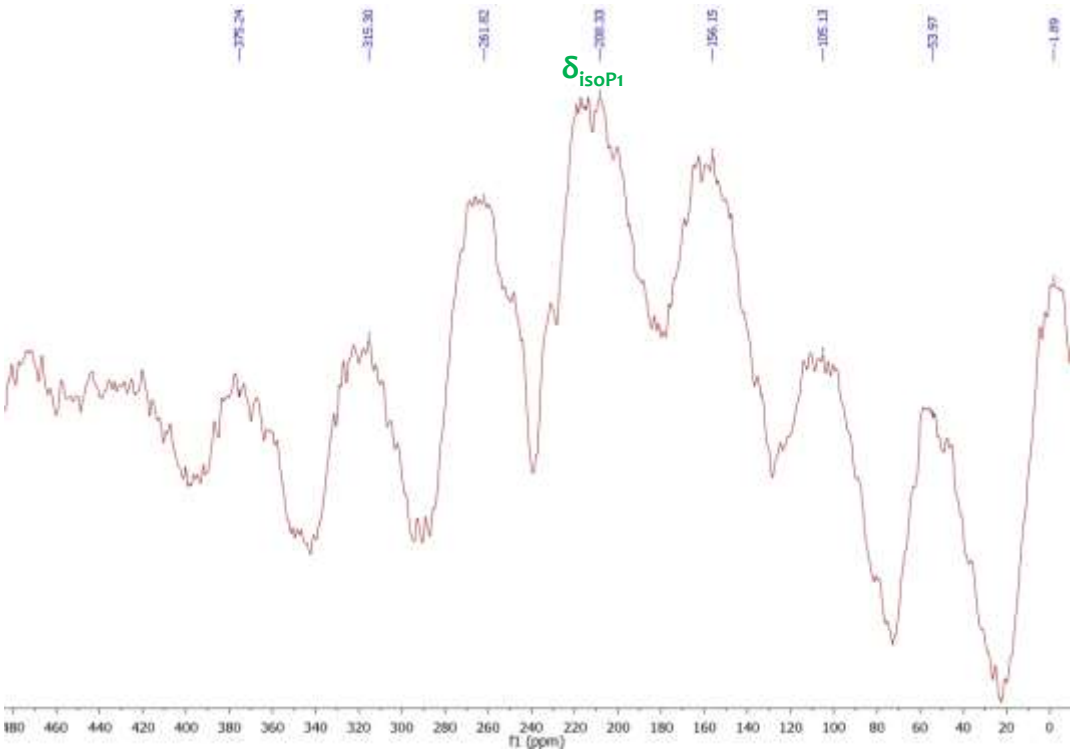


Figure S8. IR transmission spectrum for **2**.

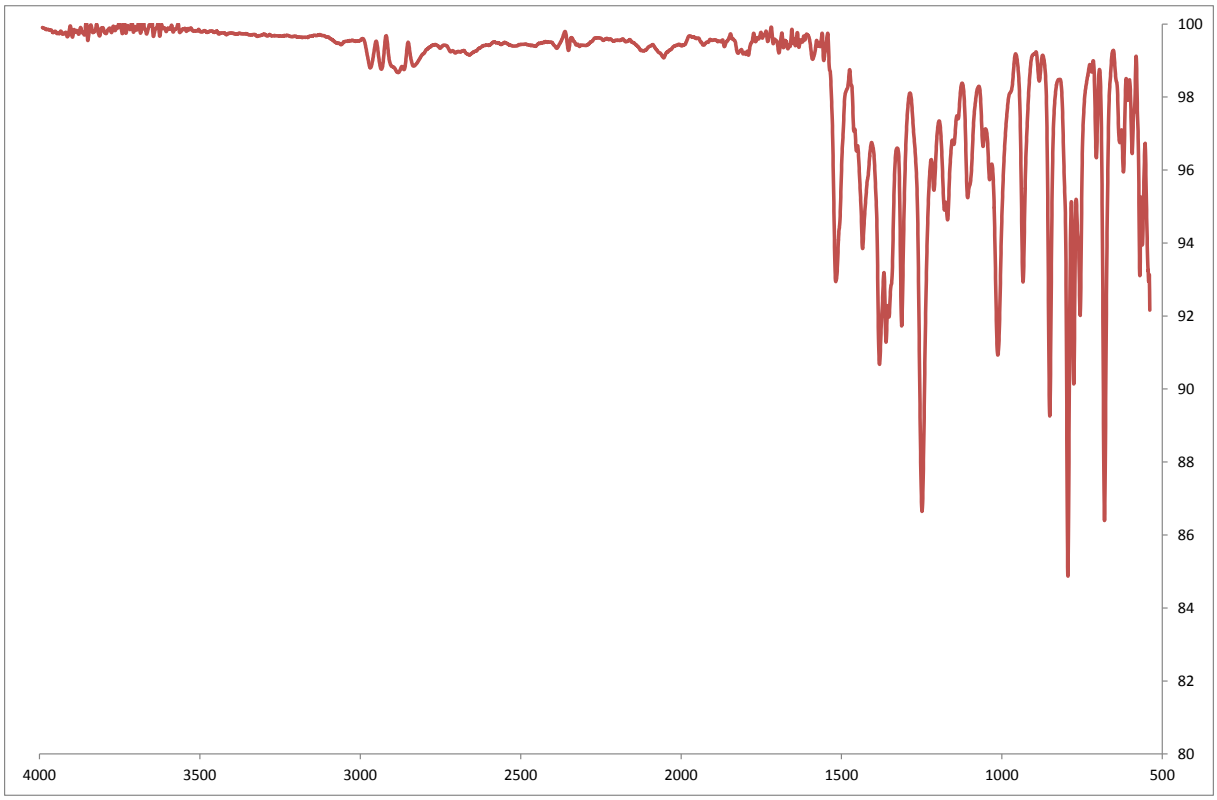


Figure S9. ^{1}H NMR spectrum of the recrystallized (hexane, -40°C) microcristalline dark green material (C_6D_6, 293K, 400MHz) from the reaction of (BDI)(NtBu)$NbMe_2$ + H_2 + P_4. The three resonances highlighted in green correspond to the *H*C(CMeN) proton of the BDI backbone in **3**. Despites several attempts, **3** could not be separated from co-crystallized impurities.

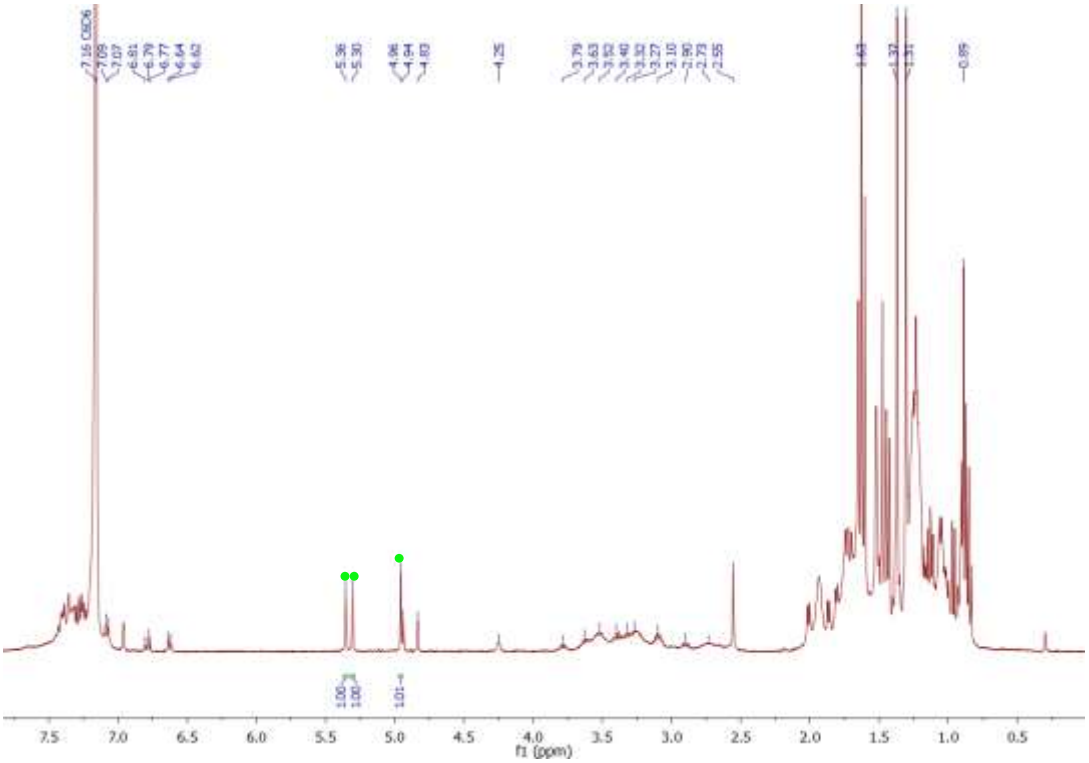


Figure S10. ^{1}H NMR spectrum for compound **4** ($C_2H_4Cl_2$:$CDCl_3$ 95:5, 293K, 400MHz).

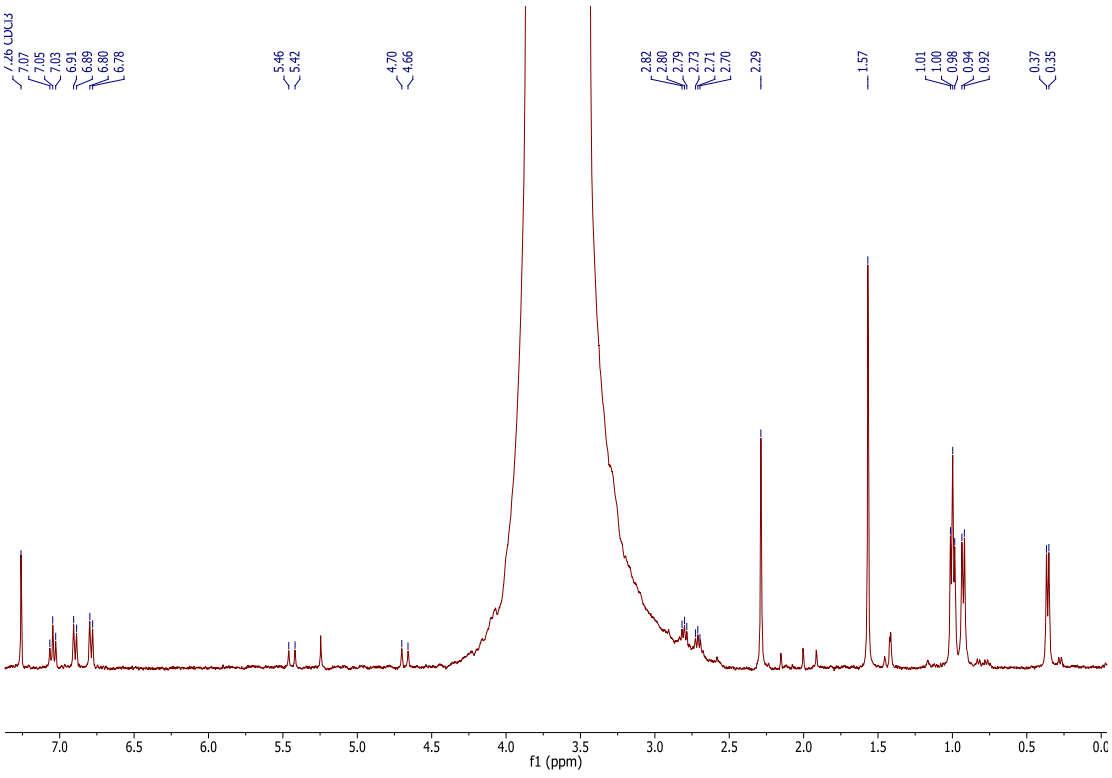


Figure S11. Detail of the ^{1}H-^{1}H COSY NMR spectrum for compound **4** ($C_2H_4Cl_2$:$CDCl_3$ 95:5, 293 K, 400 MHz).

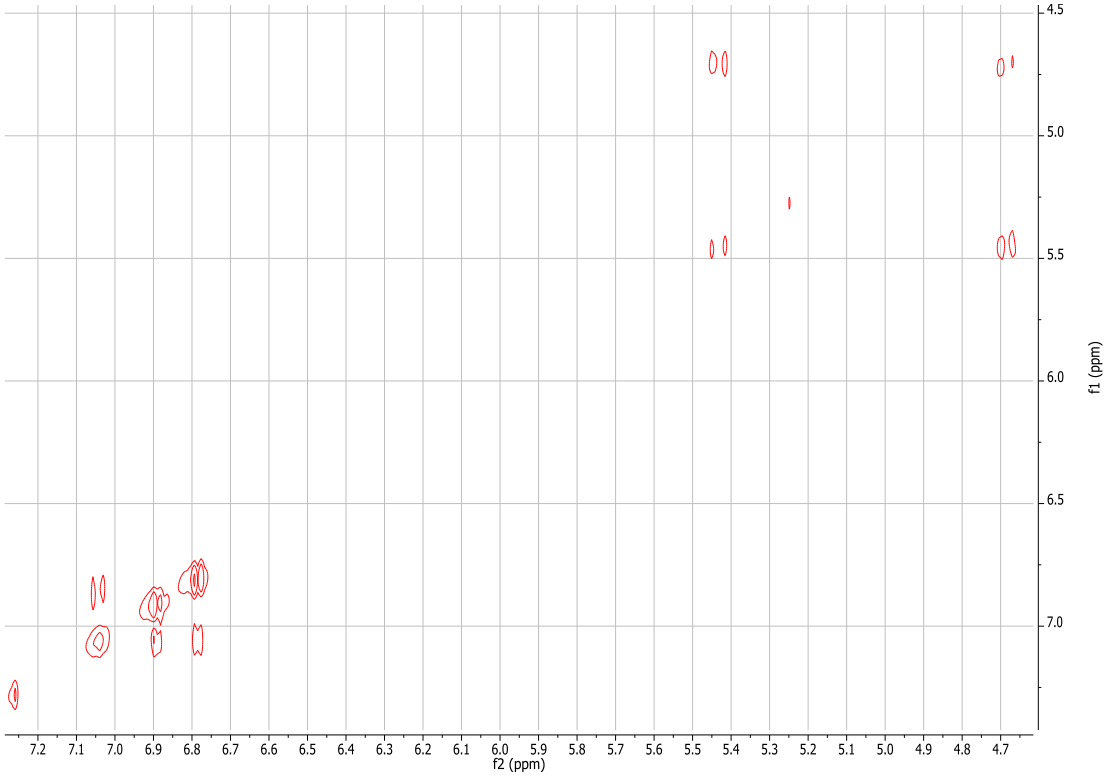


Figure S12. IR transmission spectrum for 4.

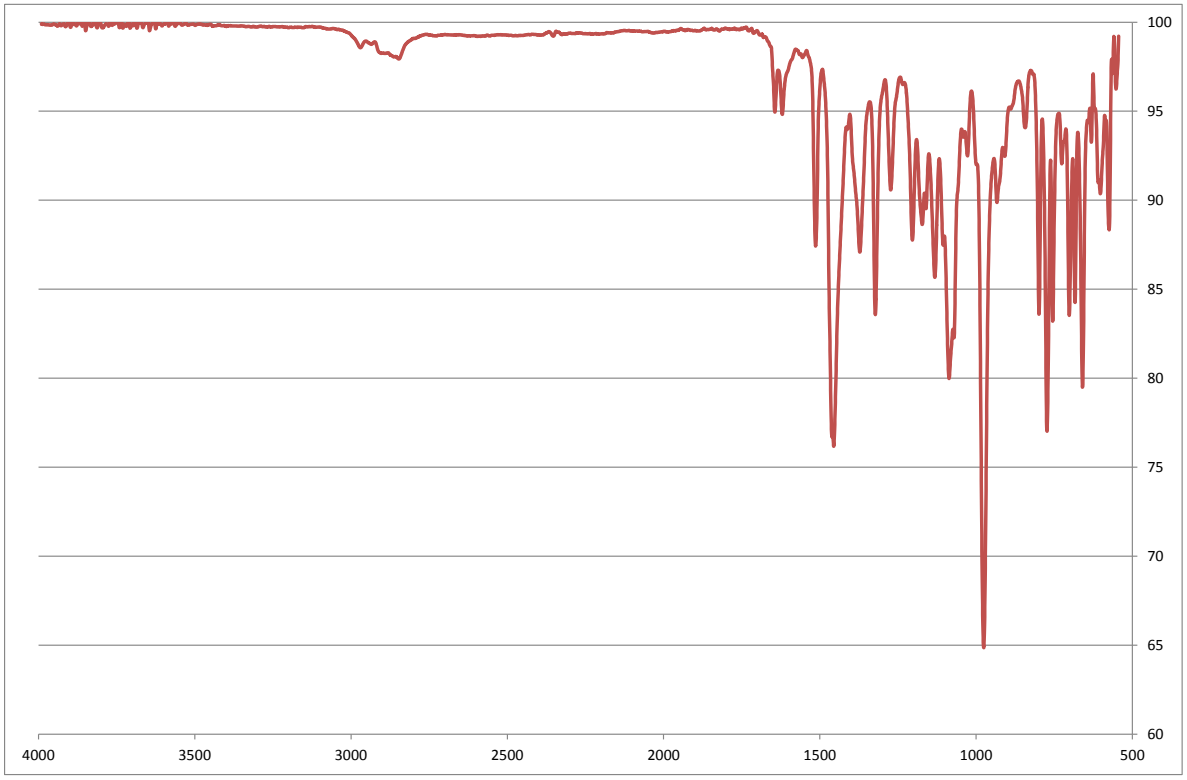


Figure S13. ^{1}H NMR spectrum of **5** ($CDCl_3$, 293K, 600MHz).

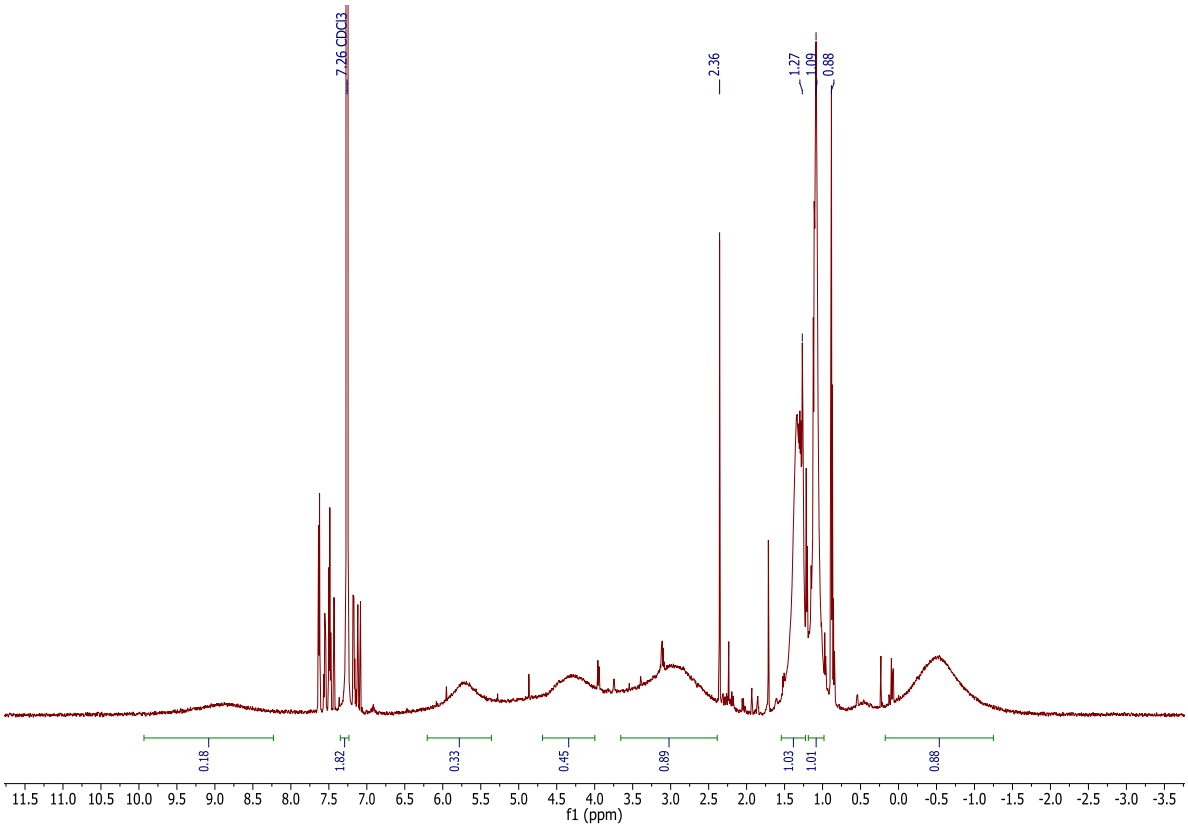


Figure S14. IR transmission spectrum for **5**.

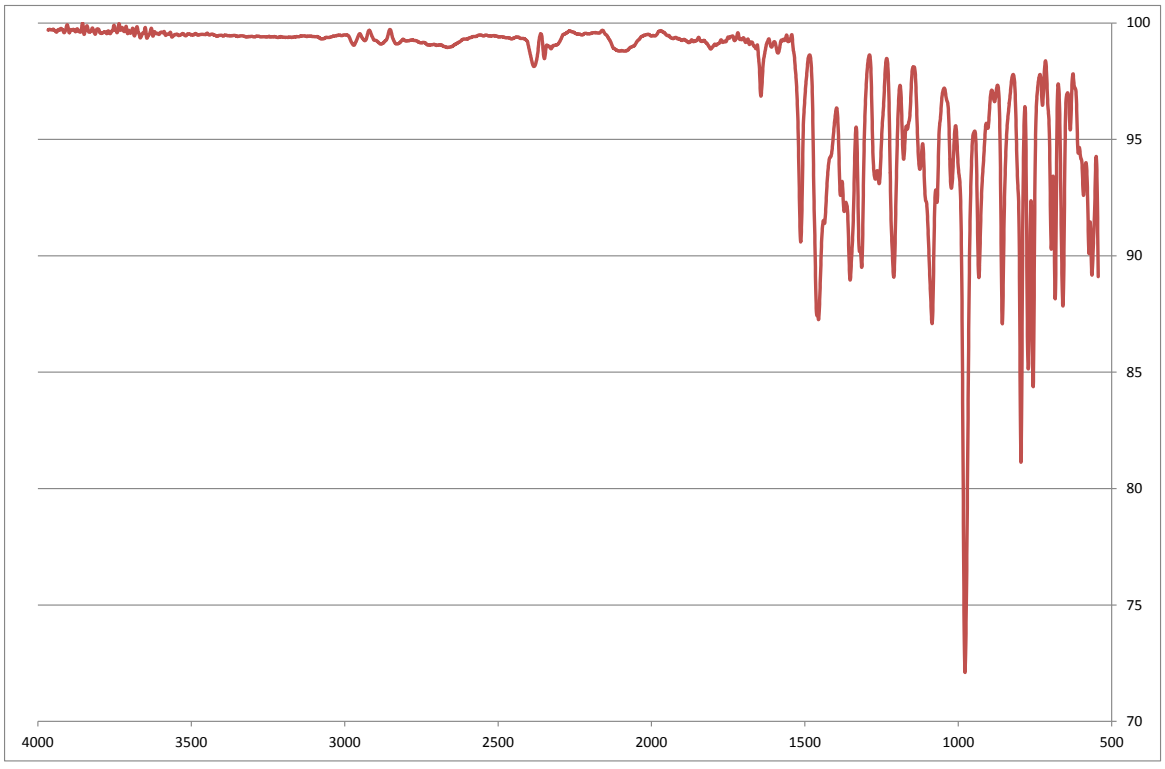


Figure S15. ^{1}H NMR spectrum of the crude reaction mixture between **5** and $Co(Cp)_2$ ($CDCl_3$, 293K, 400MHz) showing clean conversion to **1**.

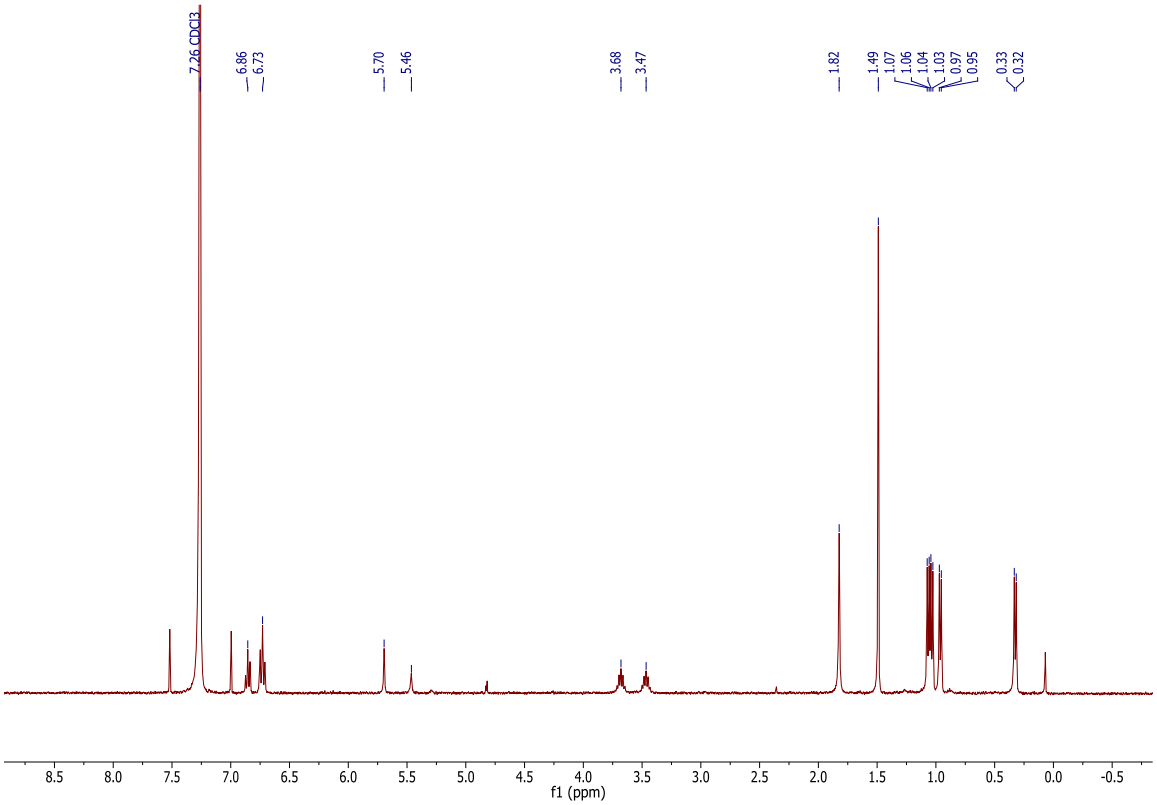


Figure S16. ^{1}H NMR spectrum for compound **6** ($CF_3C_6H_5$:C_6D_6 95:5, 293K, 600MHz).

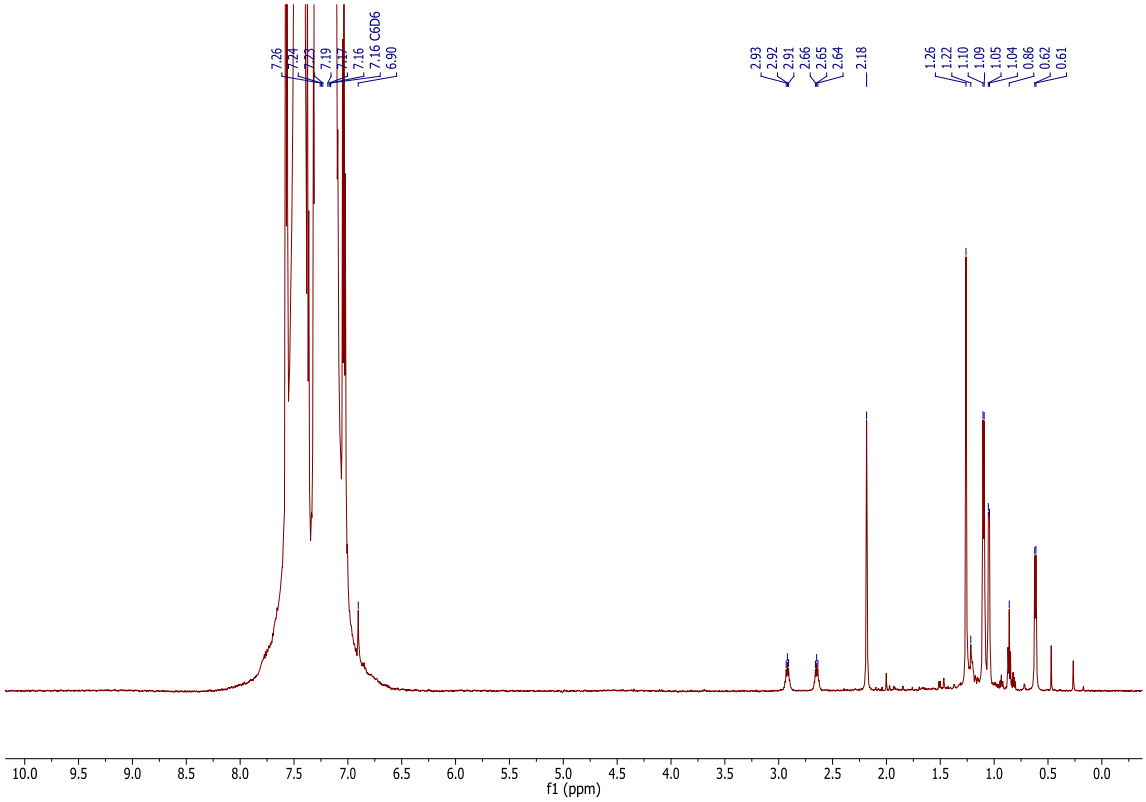


Figure S17. ^{31}P NMR spectrum for compound **6** ($CF_3C_6H_5$:C_6D_6 95:5, 293K, 243 MHz).

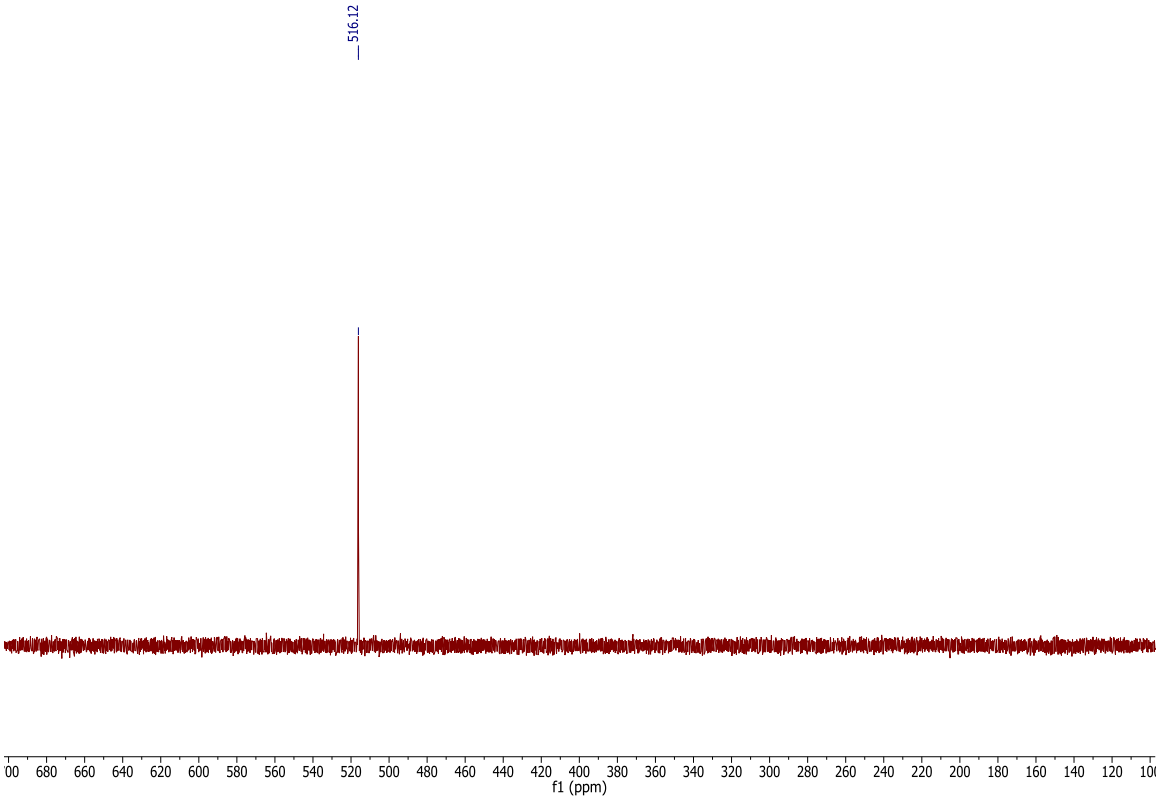


Figure S18. IR transmission spectrum for **6**.

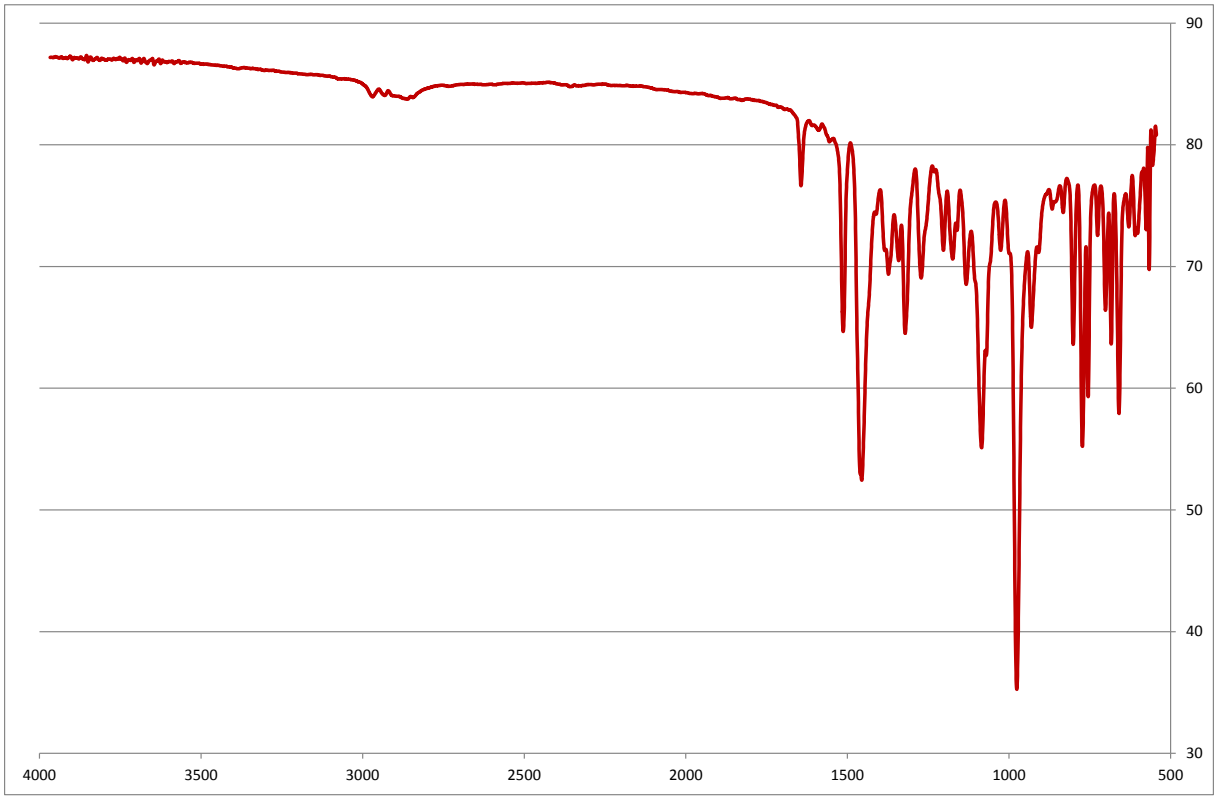
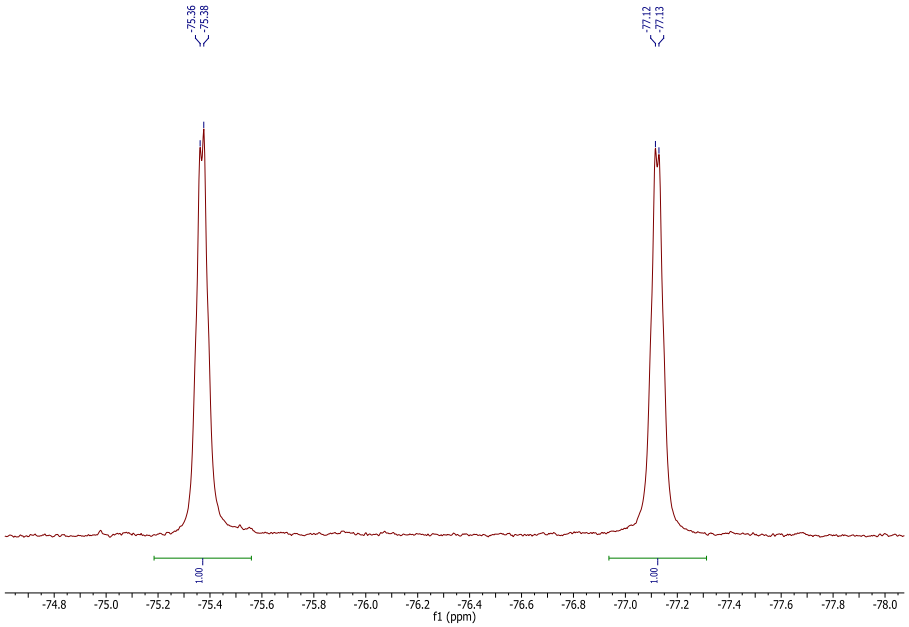


Figure S19. ^{19}F NMR spectrum for compound **7** (C_6D_6, 293K, 376MHz).



The ^{19}F NMR spectrum for (BDI)(N^{t}Bu)Nb(OTf)$_2$, **7** (376 MHz, C_6D_6, 293K) displays two quartet resonances at -75.37 and -77.12 ppm, which indicates that both triflate anions remain coordinated to the metal centre in C_6D_6 solution. (note : the ^{19}F resonances for metal-bound triflates in diamagnetic coordination compounds are generally found between -75 and -79 ppm[1] while free triflate anion resonance is observed at lower field (-80.47 ppm in $Ph_3P{=}N{=}PPh_3^+$ OTf$^-$).[2] Splitting arises from coupling between the CF_3 groups (J_{FF} = 4.9 Hz) of the two inequivalent triflate ligands, as previously observed in cis(bis-triflate) coordination compounds.[1]

Figure S20. ^{1}H NMR spectrum for **7** (C_6D_6, 293K, 500MHz).

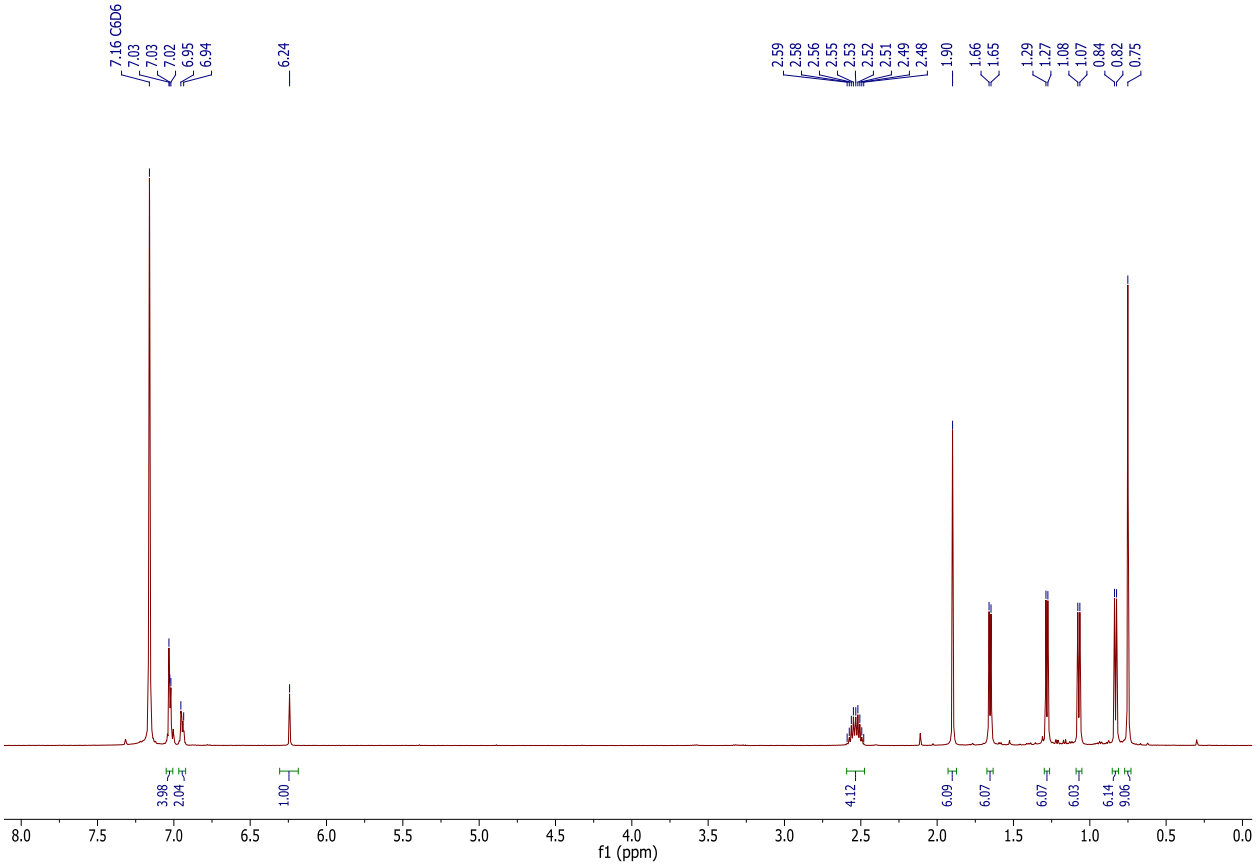
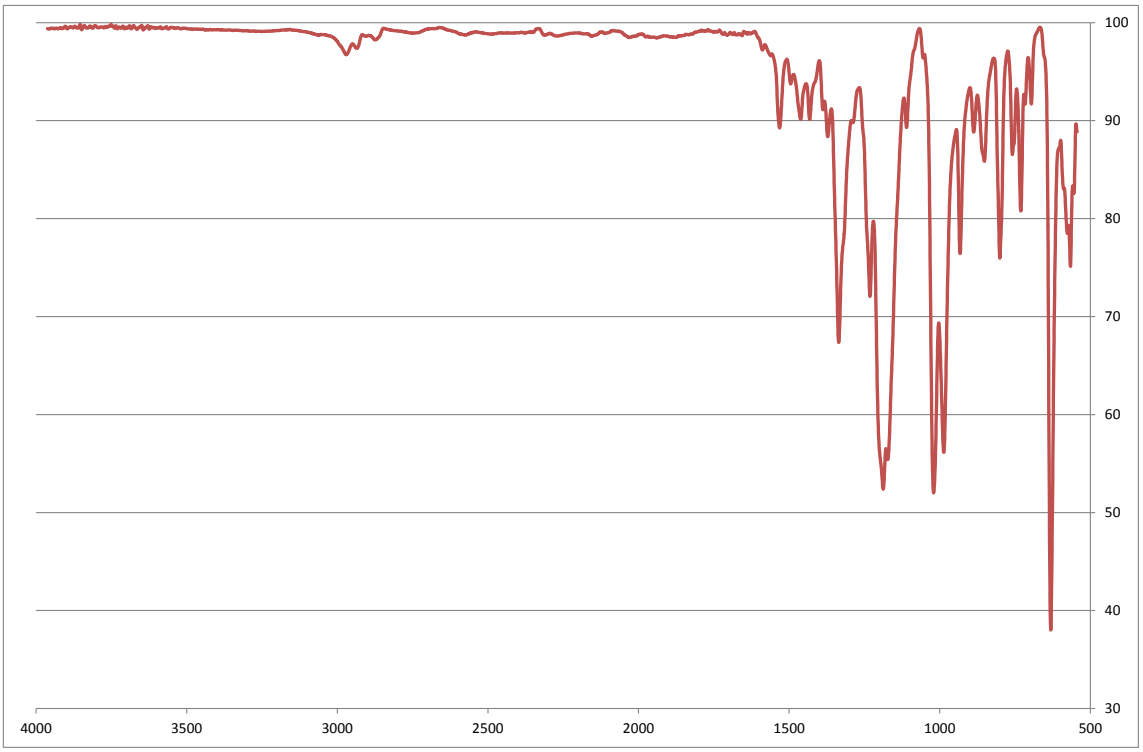


Figure S21. IR transmission spectrum for **7**.



B. ESI-MS spectrometry data

Figure S22. ESI-MS spectrum for **1.**

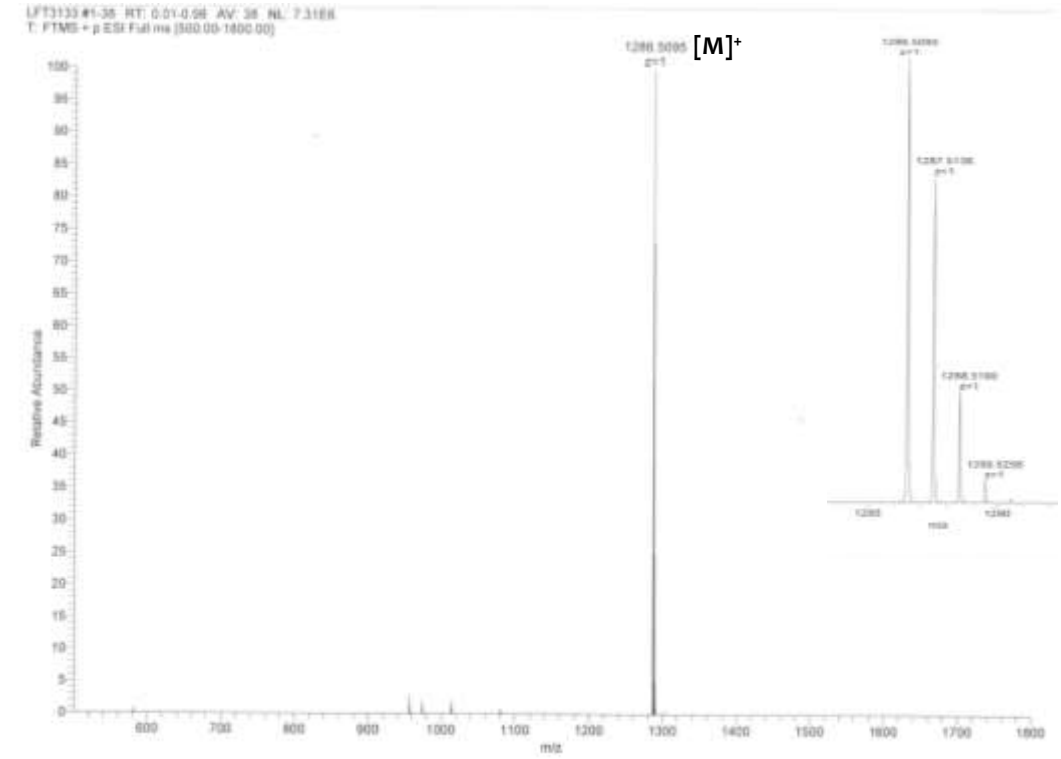


Figure S23. ESI-MS spectrum for **2**.

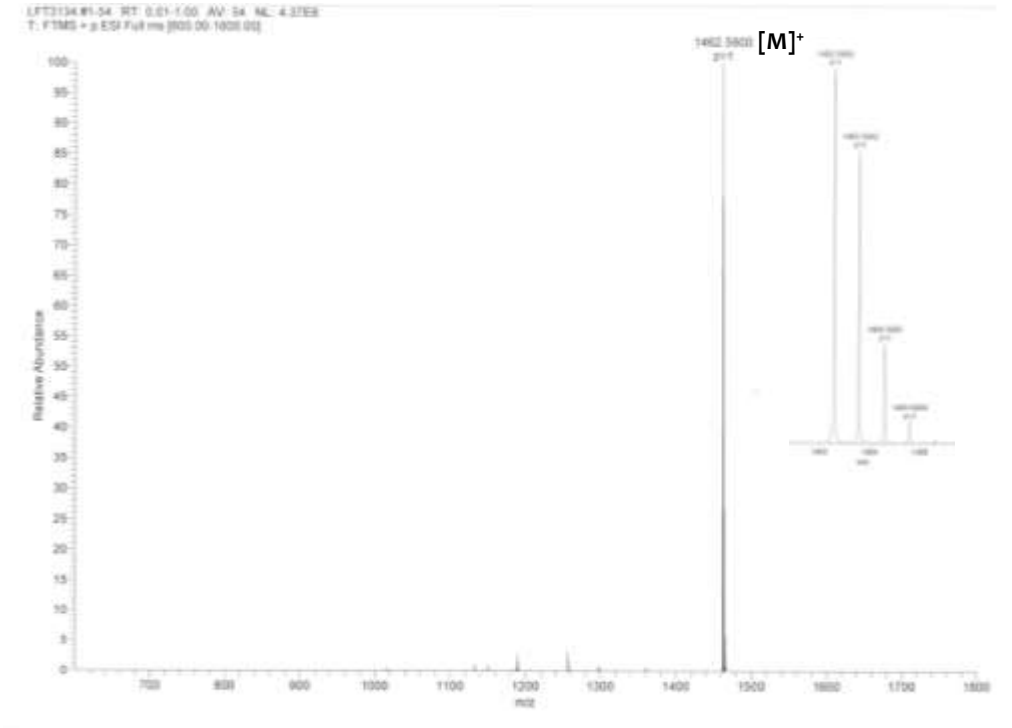


Figure S24. ESI-MS spectrum of the recrystallized (hexane, -40°C) microcristalline dark green material (C_6D_6, 293K, 400MHz) from the reaction of (BDI)(N^tBu)$NbMe_2$ + H_2 + P_4. The peak at m/z = 1698.2800 corresponds to [**3**-(BDI)]$^+$.

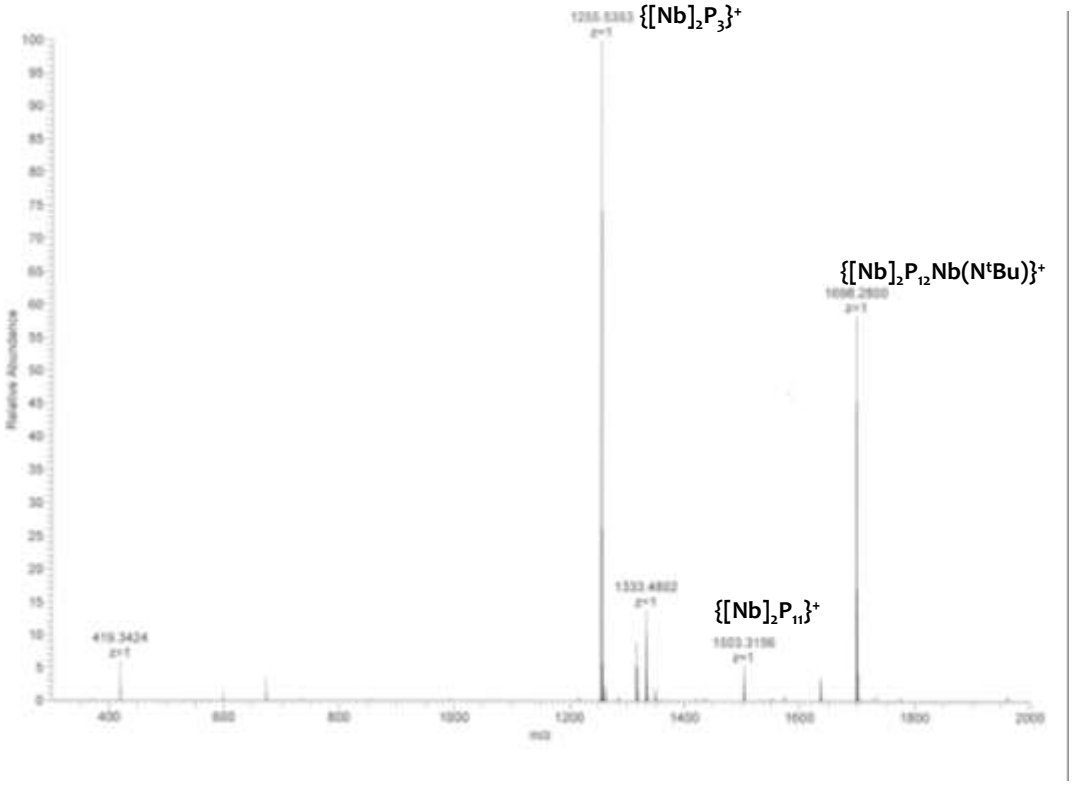
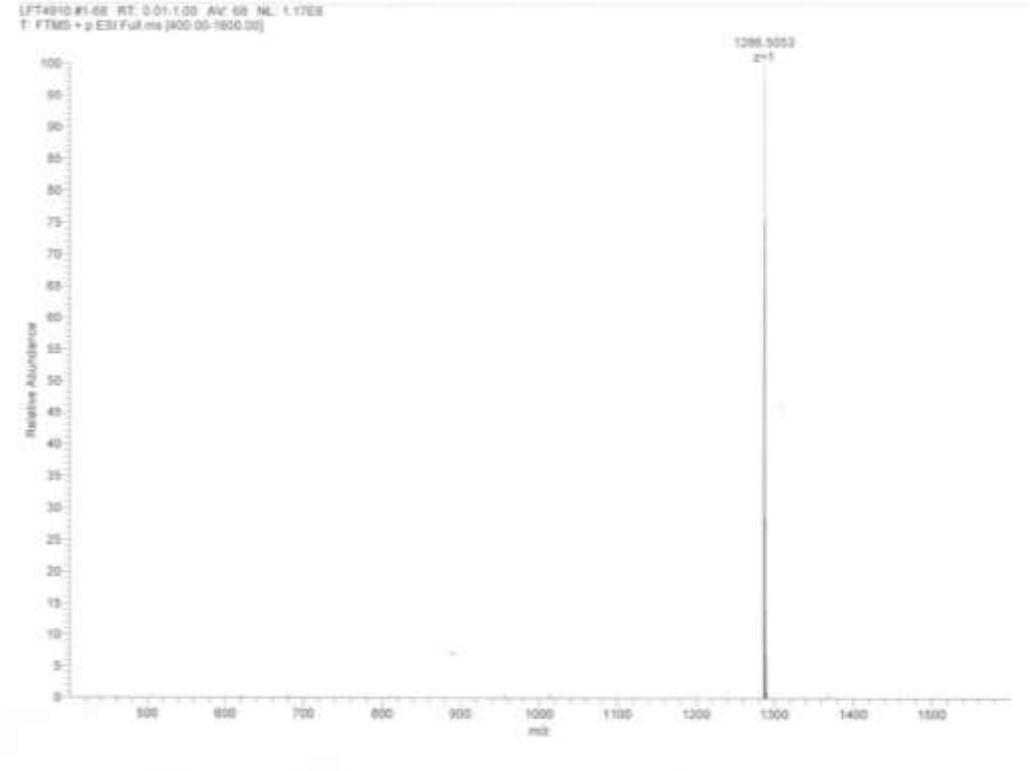


Figure S25. ES-MS spectrum of **5**.



C. X-ray crystallography

X-ray structural determinations were performed on a Bruker SMART QUAZAR diffractometer which is a 3-circle diffractometer that couple a CCD detector with a sealed-tube source of monochromated Mo Ka radiation (λ = 0.71073 Å). A crystal of appropriate size was coated in Paratone-N oil and mounted on a Kapton® loop. The loop was transferred to the diffractometer, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrices and cell constants were determined by collection of 60 10 s frames, followed by spot integration and least-squares refinement. The reported cell dimensions were calculated from all reflections with $I > 10\ \sigma$. The data were corrected for Lorentz and polarization effects; no correction for crystal decay was applied. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.[3] All software used for diffraction data processing and crystal-structure solution and refinement are contained in the APEX2 program suite (Bruker AXS, Madison, WI).[4] Thermal parameters for all non-hydrogen atoms were refined anisotropically. For all structures, $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$. Thermal ellipsoid plots were created using Mercury supplied with Cambridge Structural Database (CCDC: Cambridge, U.K., 2004-2009).

C.1 Ortep view of compound 7 and structure description

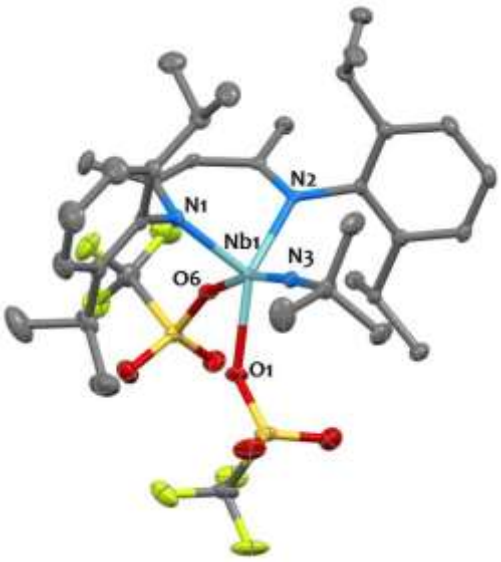


Figure S26. Solid-state molecular structure of **7**. Hydrogen atoms and interstitial solvent molecules have been removed for clarity. Niobium (light blue), fluorine (light green), nitrogen (blue), oxygen (red), sulfur (yellow) and carbon (grey) atoms are represented with 50% probability ellipsoids.

The structure of (BDI)(NtBu)Nb(OTf)$_2$ (**7**) in the solid-state, determined by single-crystal X-ray diffraction, was found to be highly distorted square pyramidal (τ = 0.35) with apical nitrogen N1 from the BDI backbone and the square base defined by N2-N3-O1-O2 (Figure S26). Both triflate anions are bound in a monodentate fashion to the metal centre. The Nb1-O6 bond distance for the triflate *trans* to the imido ligand is significantly longer than the Nb1-O1 distance for the equatorial triflate (2.218(1) Å vs 2.133(1) Å). This reflects the strong *trans* influence

of the imido group (Nb1-N3 = 1.747(1) Å), as previously observed in other Nb(V) imido species.[5,6] The Nb-N_{BDI} bond distances are roughly equivalent (Nb1-N1 = 2.033(2) Å; Nb1-N2 = 2.079(2) Å) and are slightly shorter than what is usually observed for Nb(V)(BDI) species.[5,6]

C.2 Structural parameters

Table S.1 Crystallographic parameters for complexes **1** to **4.**

Compound	**1.(toluene)**	**2.(benzene)**	**3**	**4.$(CF_3C_6H_5)_2$**
Formula	$C_{73}H_{108}N_6Nb_2P_4$	$C_{72}H_{106}N_6Ta_2P_4$	$C_{99}H_{150}N_9Nb_3P_{12}$	$C_{128}H_{112}B_2F_{46}N_6Nb_2P_4$
cryst syst	Triclinic	Monoclinic	Monoclinic	Monoclinic
space group	P-1	$P2_1/n$	$P2_1/c$	$P2_1/n$
volume (Å^3)	3575.76(16)	3516.3(3)	12410.6(4)	12664(5)
a (Å)	13.7042(4)	14.4703(7)	22.3355(4)	21.934(5)
b (Å)	14.6892(4)	13.5410(7)	18.0891(3)	18.940(5)
c (Å)	18.3018(4)	18.4709(9)	30.8800(5)	30.945(5)
α (deg)	76.230(1)	90	90	90
β (deg)	89.303(1)	103.698(2)	95.886(1)	99.913(5)
γ (deg)	87.835(1)	90	90	90
Z	2	2	4	4
formula weight (g/mol)	1379.35	1541.41	2116.66	2939.56
density (g cm^{-3})	1.281	1.456	1.133	1.542
absorption coefficient (mm^{-1})	0.454	3.245	0.468	0.352
F(000)	1460	1572	4440	5952
temp (K)	100(2)	100(2)	100(2)	100(2)
total no. reflections	81467	69860	59362	105474
unique reflections [R(int)]	81467 [0.033]	6468 [0.028]	22799 [0.054]	22101 [0.085]
Final R indices [I > 2σ(I)]	R1 = 0.0298, wR2 = 0.0745	R1 = 0.0122, wR2 = 0.0291	R1 = 0.0477, wR2 = 0.1189	R1 = 0.0751, wR2 = 0.1996
Largest diff. peak and hole (e.A^{-3})	0.345 and -0.427	0.315 and -0.346	0.764 and -0.537	1.424 and -1.468
GoF	1.032	1.082	1.026	1.040

Table S.2 Crystallographic parameters for complexes **5** to **7.**

Compound	**5.(hexane)$_{0.5}$($CF_3C_6H_5$)$_{0.5}$**	**6.($CF_3C_6H_5$)**	**7.(toluene)$_{1.5}$**
Formula	$C_{96.50}H_{109.5}B_1F_{21.5}N_6Nb_2P_4$	$C_{121}H_{105}B_2F_{43}N_6Nb_2P_4$	$C_{45.5}H_{62}F_6N_3NbO_6S_2$
cryst syst	Triclinic	Triclinic	Monoclinic
space group	P-1	P-1	$P2_1/c$
volume (Å^3)	9628.2(12)	6271.2(6)	4829.7(4)
a (Å)	14.6637(11)	17.9132(10)	12.3332(15)
b (Å)	24.0006(16)	18.2353(11)	20.583(2)
c (Å)	28.6455(19)	21.8124(11)	19.670(2)
α (deg)	81.507(3)	83.692(3)	90
β (deg)	75.240(4)	81.723(3)	104.709(5)
γ (deg)	84.921(4)	62.942(3)	90
Z	4	2	4
formula weight (g/mol)	2086.6	2794.43	1018.01
density (g cm^{-3})	1.437	1.478	1.400
absorption coefficient (mm^{-1})	0.395	0.348	0.407
F(000)	4284	2824	2124
temp (K)	100(2)	100(2)	100(2)
total no. reflections	201588	60151	80118
unique reflections [R(int)]	35332 [0.057]	23078 [0.060]	8883 [0.041]
Final R indices [I > 2σ(I)]	R1 = 0.0525, wR2 = 0.1675	R1 = 0.0983, wR2 = 0.2931	R1 = 0.0259, wR2 = 0.0683
Largest diff. peak and hole (e.A^{-3})	1.243 and -0.842	5.187 and -1.289	0.647 and -0.394
GoF	1.025	1.093	1.046

C.3 Additional structural considerations

Compound 5:

The asymmetric unit for compound **5** contains 3 independent [(BDI)(N^tBu)Nb]$_2$(μ-P_4) units, two of them lying on the inversion center of the P_{-1} space group (as well as two BArF anions, a hexane and a $CF_3C_6H_5$ molecule). In addition, a whole molecule positional disorder is found in the latter two units with 95% and 87% occupancy factors for the main position (Only Nb and P atoms of the second minor position were refined). Therefore the discussion of metrical parameters is performed on the non-centrosymmetric non-disordered [(BDI)(N^tBu)Nb]$_2$(μ-P_4) unit only.

Compound 6:

The asymmetric unit for compound **6** contains 2 independent $[(BDI)(N^tBu)Nb]_2(\mu\text{-}P_4)$ fragments lying on the inversion center of the P_{-1} space group as well as two BArF anions and a $CF_3C_6H_5$ molecule. Similarly to what found for **5**, a whole molecule positional disorder is found for both units. The high residual intensity peaks correspond to the Niobium centers in the minor disordered position which occupancies refine below 4% and was therefore not refined. Same behavior was obtained on several independently synthesized crystals. The discussion of metrical parameters is performed on an average of the two $[(BDI)(N^tBu)Nb]_2(\mu\text{-}P_4)$ units.

D. DFT Calculations

Computational Details

We used the small core Stuttgart-Dresden relativistic effective core potential in combination with its adapted basis set to treat the niobium,tantalum atoms,[7,8] while carbon, oxygen, nitrogen and hydrogen atoms were described with a 6-31G(d,p) double-ζ basis set;[9] phosphorus atoms were modeled with the Stuttgart-Dresden ECP in combination with its adapted basis set and additional *d* polarization functions.[10,11] Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91.[12,13] Geometry optimizations were performed without any symmetry restrictions and the nature of the minima was verified with analytical frequency calculations. DFT calculations were carried out with the Gaussian09 suite program.[14] The electronic density (at the DFT level) has been analyzed using the Natural Bond Orbital (NBO) technique.[15]

Cartesian coordinates of optimized structures:

1

178

SCF Done:-3043.4407507

C	11.231608	6.494756	15.979104
H	10.306430	6.881892	16.402509
H	11.365576	5.458506	16.297936
H	11.128387	6.485534	14.887515
C	12.443161	7.333702	16.337067
C	13.671683	6.673043	16.140750
C	14.971867	6.985815	16.571490
C	15.981345	5.865289	16.435083
H	16.633075	5.787574	17.306130
H	16.626439	6.062966	15.572754
H	15.485387	4.906721	16.275103
C	16.636866	8.230087	17.717413
C	17.811494	8.562482	17.001231
C	19.036318	8.549554	17.675522
H	19.939205	8.804509	17.127127
C	19.127891	8.210272	19.017430
H	20.092476	8.194108	19.517632
C	17.969499	7.893488	19.713444

H	18.036412	7.627975	20.764473
C	16.715265	7.904756	19.094173
C	15.494797	7.533783	19.923604
H	14.612532	7.875698	19.374404
C	15.486944	8.231529	21.289772
H	14.538769	8.044436	21.803040
H	15.603369	9.313582	21.186221
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H	16.032986	8.520908	13.072553
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H 11.343184 0.523411 8.646996
C 9.013673 -0.272528 11.097963
H 8.179311 -0.547417 10.446062
H 8.621849 0.208184 12.000676
H 9.511709 -1.194843 11.411839
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C 9.744361 5.804436 11.976863
C 10.240119 7.043083 12.390818
H 11.196806 7.085355 12.900906
C 9.528710 8.217047 12.180746
H 9.929837 9.168610 12.516478
C 8.289333 8.160775 11.561528
H 7.723311 9.077070 11.423891
C 7.731434 6.950199 11.130885
C 10.528568 4.547482 12.317291
H 10.180687 3.741796 11.658905
C 12.036902 4.699357 12.091759
H 12.533294 3.733425 12.225688
H 12.490685 5.387775 12.811293
H 12.262751 5.067950 11.086769
C 10.253412 4.117254 13.768581

H	10.811029	3.208144	14.017173
H	9.192360	3.921989	13.949626
H	10.566305	4.898321	14.469161
C	6.333177	7.000188	10.528446
H	6.047837	5.990033	10.212602
C	6.283305	7.905176	9.289713
H	5.269386	7.929079	8.878574
H	6.964619	7.556732	8.508679
H	6.552982	8.935880	9.538983
C	5.295361	7.487960	11.555511
H	4.286972	7.431962	11.133161
H	5.476029	8.531930	11.829865
H	5.308864	6.904952	12.479567
C	6.559612	4.414383	12.926860
H	7.060039	5.323033	13.255209
H	6.678161	3.634407	13.688404
H	5.482331	4.601084	12.847487
C	7.075452	3.899462	11.620832
C	6.518438	2.553564	11.217639
C	5.882009	2.425347	9.851661
C	4.479784	1.901398	9.879883
H	4.038131	1.791229	8.892134
H	3.856301	2.564173	10.490718
H	4.475467	0.929849	10.388996
C	5.913807	2.423257	7.497983
C	6.037376	1.132296	6.936209
C	5.338649	0.864022	5.755016
H	5.404730	-0.127671	5.318001
C	4.547950	1.824563	5.141060
H	3.998790	1.586132	4.235165
C	4.462028	3.092286	5.698205
H	3.841526	3.840661	5.216143
C	5.139664	3.427523	6.876585
C	4.965557	4.835425	7.428173
H	5.751148	5.009213	8.173420

C	5.129909	5.898164	6.332246
H	5.136809	6.898507	6.772120
H	4.306659	5.870510	5.612169
H	6.063673	5.763203	5.778060
C	3.601486	5.010206	8.116021
H	3.490419	6.029837	8.498611
H	3.464790	4.321365	8.953617
H	2.784333	4.831896	7.409487
C	6.856118	0.006579	7.552698
H	7.435594	0.417669	8.386793
C	5.953423	-1.109037	8.105304
H	6.555681	-1.891613	8.578412
H	5.374601	-1.580550	7.304656
H	5.239356	-0.737733	8.845835
C	7.855261	-0.577425	6.543104
H	8.449261	-1.369362	7.010354
H	8.536344	0.188426	6.160040
H	7.345655	-1.028760	5.686798
N	10.162270	6.942465	5.022616
N	11.518684	4.289904	4.021171
N	12.927196	6.081279	6.128962
N	9.327813	1.827692	9.889408
N	7.970166	4.480825	10.889101
N	6.562975	2.687465	8.782163
P	10.858519	3.276141	7.635748
P	10.527524	5.345516	8.524878
P	8.631147	5.493552	7.275369
P	8.961901	3.424073	6.386459
Nb	10.720099	5.477652	5.837708
Nb	8.769778	3.292034	9.073584
H	12.131518	6.928855	3.672691
H	13.693650	6.536554	2.940849
H	7.358513	1.841764	11.239032
H	5.796042	2.233752	11.970378

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C	1.888177	11.540767	7.800941
C	2.207716	10.339709	6.900050
H	2.436359	10.665484	5.881221
H	1.347027	9.662929	6.860425
H	3.066786	9.781441	7.283489
C	1.567970	11.049537	9.221506
H	1.401271	11.892227	9.899356
H	2.377232	10.432619	9.618004
H	0.657534	10.441498	9.203240
C	0.662841	12.294178	7.255742
H	0.797810	12.567016	6.207442
H	0.475712	13.203140	7.835825
H	-0.223957	11.655421	7.324093
C	3.883413	15.991140	5.905107
C	3.281698	15.516665	4.714283
C	3.539963	16.194537	3.519655
H	3.080692	15.836268	2.602169
C	4.342928	17.324927	3.483981
H	4.517179	17.846837	2.546708
C	4.901506	17.796774	4.663625
H	5.508384	18.697495	4.638758
C	4.693231	17.151307	5.887384
C	2.305560	14.352916	4.678112
H	2.259715	13.928309	5.684924
C	2.743438	13.236158	3.721875
H	2.033299	12.402222	3.761883
H	3.736812	12.851031	3.970148
H	2.778299	13.582049	2.683680
C	0.894297	14.833164	4.298588
H	0.178277	14.005177	4.345879
H	0.874019	15.225152	3.275990
H	0.537311	15.627240	4.959961
C	5.295069	17.771796	7.138347

H	5.234616	17.030842	7.942482
C	6.772132	18.145548	6.957825
H	7.169555	18.562708	7.887931
H	6.910040	18.908137	6.184484
H	7.381234	17.277629	6.688039
C	4.495987	19.010519	7.577334
H	4.903264	19.421485	8.507460
H	3.440431	18.780574	7.745833
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C	1.633349	16.735551	7.470694
H	1.918801	17.217104	6.536201
H	1.431660	17.504253	8.220432
H	0.695380	16.192775	7.303702
C	2.672736	15.756155	7.966871
C	2.527225	15.370899	9.313859
H	1.635965	15.769371	9.790153
C	3.423268	14.754172	10.209426
C	3.026528	14.857523	11.664958
H	3.849825	14.645010	12.345248
H	2.227998	14.131649	11.859917
H	2.623902	15.847853	11.889771
C	5.518114	13.787147	10.857972
C	6.515688	14.735581	11.187797
C	7.424729	14.418350	12.202469
H	8.182512	15.145573	12.476989
C	7.373640	13.206030	12.876192
H	8.088523	12.985580	13.664547
C	6.394514	12.284006	12.537803
H	6.346002	11.337137	13.069128
C	5.449643	12.549271	11.541826
C	6.619097	16.098147	10.522685
H	6.059714	16.046789	9.582037
C	8.066386	16.478845	10.182816
H	8.085420	17.415096	9.618177
H	8.555629	15.709504	9.577472

H	8.672783	16.638947	11.080291
C	5.984224	17.195464	11.393494
H	6.037188	18.166381	10.888973
H	6.512472	17.286744	12.349330
H	4.933634	16.990896	11.615351
C	4.366352	11.513103	11.294368
H	3.736174	11.878194	10.479065
C	3.475243	11.325530	12.534096
H	2.643968	10.648103	12.309455
H	3.055028	12.270970	12.888159
H	4.038618	10.887339	13.365018
C	4.945431	10.157473	10.866970
H	4.140320	9.442301	10.663172
H	5.571478	9.722639	11.652814
H	5.561475	10.242813	9.967311
C	11.125606	14.227494	5.848394
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H	11.402813	14.070650	3.683601
H	12.348664	12.904091	4.627347
H	12.839592	14.611175	4.568247
C	10.584128	15.663451	5.802405
H	10.000777	15.884203	6.701191
H	9.943138	15.811388	4.930594
H	11.413600	16.377040	5.748210
C	11.983617	14.051834	7.108644
H	11.382379	14.201633	8.010170
H	12.794038	14.788476	7.109810
H	12.432615	13.055548	7.145633
C	7.545263	11.935518	2.892859
C	6.568603	10.969633	2.549866
C	5.662407	11.271889	1.528766
H	4.922284	10.530701	1.244003
C	5.696306	12.487578	0.860619
H	4.986347	12.697300	0.064869
C	6.651066	13.428135	1.215789

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C 7.591017 13.182053 2.222343
C 8.629150 14.263130 2.490364
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H 8.991041 14.861210 0.417691
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C 10.025768 10.851871 2.074665
H 9.199329 11.063769 1.398120
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H 11.443779 9.978201 3.940624
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C 11.497036 9.045507 6.269933
H 11.242530 8.580279 7.221131
H 12.426303 9.612273 6.403064
H 11.699650 8.264090 5.533776
C 9.229032 9.715023 7.828699

C	9.813149	10.186401	9.028802
C	9.581472	9.470518	10.207106
H	10.033437	9.819337	11.131568
C	8.812981	8.315493	10.219144
H	8.658246	7.767913	11.145153
C	8.262259	7.855259	9.031327
H	7.678366	6.938992	9.037123
C	8.453241	8.531133	7.821551
C	10.745903	11.385800	9.092509
H	10.731950	11.876677	8.114019
C	10.313061	12.422021	10.137465
H	10.979355	13.290889	10.103992
H	10.363215	12.019871	11.154417
H	9.288082	12.768045	9.975098
C	12.190951	10.941659	9.378736
H	12.866718	11.803860	9.374965
H	12.556386	10.219555	8.643364
H	12.265714	10.469717	10.364682
C	7.861868	7.919460	6.560566
H	7.961608	8.649102	5.750383
C	6.369249	7.598131	6.714489
H	5.980987	7.166807	5.786775
H	5.783901	8.494094	6.942841
H	6.188418	6.864392	7.506730
C	8.628129	6.650680	6.148947
H	8.231663	6.250435	5.209533
H	8.530465	5.869049	6.910412
H	9.695698	6.840864	6.009262
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N	3.646631	15.305505	7.162894
N	4.540810	14.113338	9.832605
N	10.013154	13.298894	5.874383
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N	9.449189	10.426842	6.583846
P	6.100393	13.506965	5.483465

P	5.772440	11.518069	6.490607
P	6.965431	12.208925	8.270160
P	7.291959	14.197735	7.264283
Nb	4.496619	13.411031	7.783089
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C	7.449151	11.422777	0.291417
C	8.834645	11.371749	0.952164
H	8.907536	12.105286	1.760485
H	9.626173	11.571235	0.225845
H	9.003364	10.378390	1.379089
C	7.343151	10.368112	-0.823350
H	8.105438	10.517858	-1.591374
H	6.357525	10.400394	-1.295501
H	7.485340	9.370737	-0.396284
C	6.363218	11.160981	1.344317
H	6.412482	11.896714	2.151262
H	6.512694	10.168336	1.779580
H	5.365231	11.187387	0.899265
C	4.156453	15.467816	-0.557471
C	3.582675	16.523393	-1.303957
C	2.691785	17.381295	-0.650677
H	2.233915	18.191226	-1.210279
C	2.362021	17.209172	0.687045
H	1.657076	17.881394	1.167080
C	2.922273	16.157423	1.398287
H	2.642704	16.008940	2.436821
C	3.820916	15.265509	0.804211
C	3.840766	16.751200	-2.785600
H	4.627849	16.061166	-3.107699
C	4.330122	18.178535	-3.065539
H	4.507026	18.313314	-4.136614
H	5.261047	18.401296	-2.534169

H	3.588651	18.926346	-2.768706
C	2.583476	16.452733	-3.619866
H	2.209198	15.439215	-3.452988
H	2.798564	16.561914	-4.687496
H	1.772668	17.145999	-3.374206
C	4.311871	14.087236	1.630528
H	5.091953	13.572078	1.059604
C	4.925602	14.514343	2.969873
H	5.328955	13.643087	3.496002
H	4.182271	14.969783	3.630719
H	5.734071	15.241760	2.845137
C	3.173937	13.083089	1.881483
H	3.542130	12.217224	2.440694
H	2.727688	12.721869	0.951391
H	2.373563	13.540118	2.472301
C	3.129383	13.150353	-1.892193
H	2.529535	13.848681	-1.311499
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H	2.695777	13.053773	-2.890489
C	4.577897	13.558598	-1.976332
C	5.360535	12.838867	-2.898531
H	4.829001	12.018460	-3.372382
C	6.618461	13.108364	-3.490439
C	6.897065	12.338933	-4.757076
H	7.769551	12.705672	-5.293964
H	6.030341	12.370523	-5.422001
H	7.062326	11.286172	-4.500828
C	8.650571	14.367883	-3.786796
C	8.524007	15.454145	-4.686138
C	9.609345	15.749028	-5.517376
H	9.524771	16.564064	-6.228388
C	10.786861	15.014964	-5.468174
H	11.608687	15.254067	-6.136589
C	10.899698	13.968628	-4.565348
H	11.818646	13.391289	-4.533491

C	9.849430	13.615875	-3.710485
C	7.255498	16.282621	-4.828260
H	6.666515	16.151993	-3.912743
C	7.552405	17.781214	-4.978893
H	6.622845	18.354182	-4.940076
H	8.023636	18.010456	-5.939193
H	8.210376	18.147509	-4.184934
C	6.402235	15.800332	-6.013180
H	5.496565	16.408129	-6.106131
H	6.095965	14.756595	-5.906632
H	6.958844	15.887192	-6.952055
C	10.057316	12.407993	-2.807238
H	9.183409	12.316980	-2.153530
C	11.296993	12.564260	-1.913761
H	11.251259	13.467072	-1.298267
H	12.214257	12.619992	-2.507638
H	11.399446	11.697999	-1.252188
C	10.181825	11.109571	-3.623085
H	10.285742	10.247226	-2.956287
H	11.068861	11.133525	-4.263881
H	9.318332	10.935750	-4.269129
N	7.250665	12.739668	-0.295630
N	5.076733	14.557193	-1.220163
N	7.498517	13.983894	-2.980143
P	9.589020	15.772317	-0.742524
P	8.646065	15.266431	1.214398
Nb	7.153555	14.371627	-0.918041
P	7.001135	16.706278	0.742688
P	7.944046	17.212227	-1.214222
C	9.141873	21.055929	-0.291744
C	7.756457	21.107223	-0.952642
H	7.683512	20.373715	-1.760981
H	6.964811	20.907873	-0.226411
H	7.587969	22.100621	-1.379569
C	9.247950	22.110561	0.823053

H	8.485582	21.960931	1.591020
H	10.233534	22.078116	1.295280
H	9.105953	23.107965	0.395991
C	10.227971	21.317552	-1.344511
H	10.178662	20.581877	-2.151503
H	10.078731	22.310248	-1.779737
H	11.225906	21.290938	-0.899356
C	12.433684	17.010467	0.557947
C	13.007164	15.954889	1.304653
C	13.897926	15.096688	0.651591
H	14.355553	14.286735	1.211358
C	14.227880	15.268555	-0.686118
H	14.932719	14.596099	-1.165982
C	13.667978	16.320354	-1.397562
H	13.947721	16.468647	-2.436076
C	12.769450	17.212544	-0.803718
C	12.748939	15.727450	2.786328
H	11.961952	16.417691	3.108219
C	12.259333	14.300268	3.066606
H	12.082318	14.165808	4.137702
H	11.328419	14.077505	2.535225
H	13.000719	13.552260	2.770048
C	14.006239	16.025935	3.620584
H	14.380673	17.039357	3.453477
H	13.791090	15.917038	4.688231
H	14.816950	15.332489	3.375112
C	12.278884	18.390832	-1.630256
H	11.498854	18.906265	-1.059503
C	11.665228	17.963700	-2.969630
H	11.262219	18.834988	-3.495967
H	12.408516	17.507920	-3.630289
H	10.856513	17.236553	-2.844902
C	13.417093	19.394666	-1.881215
H	13.049162	20.260551	-2.440567
H	13.863329	19.755892	-0.951122

H	14.217419	18.937377	-2.471897
C	13.460905	19.327929	1.892552
H	14.060791	18.629257	1.312310
H	13.522476	20.314600	1.418780
H	13.894310	19.424941	2.890891
C	12.012325	18.919900	1.976561
C	11.229670	19.639864	2.898566
H	11.761251	20.460253	3.372391
C	9.971606	19.370630	3.490291
C	9.692806	20.140306	4.756731
H	8.820265	19.773627	5.293573
H	10.559444	20.108915	5.421775
H	9.527497	21.193003	4.500242
C	7.939321	18.111364	3.786451
C	8.065651	17.025287	4.686051
C	6.980115	16.730664	5.517132
H	7.064490	15.915806	6.228374
C	5.802646	17.464775	5.467507
H	4.980663	17.225859	6.135798
C	5.690045	18.510907	4.564414
H	4.771128	19.088277	4.532226
C	6.740519	18.863417	3.709710
C	9.334090	16.196753	4.828609
H	9.923372	16.327311	3.913275
C	9.037132	14.698166	4.979196
H	9.966713	14.125205	4.940743
H	8.565558	14.468951	5.939329
H	8.379464	14.331818	4.185010
C	10.187012	16.679048	6.013777
H	11.092722	16.071337	6.106909
H	10.493200	17.722824	5.907387
H	9.630181	16.592063	6.952509
C	6.532938	20.071116	2.806149
H	7.406998	20.161895	2.152614
C	5.293469	19.914771	1.912395

H	5.339261	19.011792	1.297151
H	4.376042	19.859297	2.506042
H	5.191294	20.780873	1.250571
C	6.408381	21.369727	3.621685
H	6.304740	22.231944	2.954679
H	5.521176	21.346009	4.262254
H	7.271727	21.543577	4.267918
N	9.340034	19.738990	0.295305
N	11.513456	17.921285	1.220439
N	9.091541	18.495145	2.979941
Nb	9.436717	18.107098	0.917948

Table S.3 Selected metrical parameters for complexes **1, 2, 4-6.**

Compound		P-P [Å]	P-P-P [°]	M-P [Å]	M…M [Å]	Nb=NtBu [Å]	Nb-NBDI [Å]
1	**calcd**	2.274	88.69	2.52 to 2.93	4.454	1.771	2.209
	exp	2.233(3)	88.86(3)	2.51 to 2.85	4.3605(1)	1.779(2)	2.192(6)
2	**calcd**	2.259	88.85	2.52 to 2.91	4.311	1.795	2.201
	exp	2.248(5)	88.83(2)	2.50 to 2.82	4.2993(1)	1.7912(1)	2.177(7)
4	**calcd**	2.275	91.95	2.53 to 2.84	4.364	1.766	2.312
	exp	2.235(2)	88.72(8)	2.52 to 2.79	4.298(1)	1.775(8)	2.265(6)
5	**calcd**	2.251	90.3	2.62 to 2.90	4.593	1.757	2.169
	exp	2.209(4)	89.62(6)	2.59 to 2.87	4.4929(7)	1.774(4)	2.15(2)
6	**calcd**	2.230	91.1	2.75 to 2.96	4.747	1.749	2.106
	exp	2.182(5)	88.9(2)	2.69 to 2.89	4.61(4)	1.768(6)	2.10(1)

Table S.4 Calculated and experimental values of the absorption maxima wavelengths in compounds **1, 2, 4-6.**

Compound	λ_{max} (nm) calcd	λ_{max} (nm) exp
1	604	645
2	566	603
4	707	694
5	900	921
6	543	522

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