Supporting Information for:
Molecular Titanium Nitrides: Nucleophiles Unleashed

Lauren N. Grant,[§] Balazs Pinter,[ǀ] Takashi Kurogi,[§] Maria E. Carroll,[§] Gang Wu,[‡] Brian C. Manor,[§] Patrick J. Carroll[§] and Daniel J. Mindiola[§,*]

[§]*Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia PA, 19104.*
[ǀ]*Eenheid Algemene Chemie (ALGC), Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050, Brussels (Belgium).*
[‡]*Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6.*

Corresponding author: E-mail, mindiola@sas.upenn.edu

Table of Contents

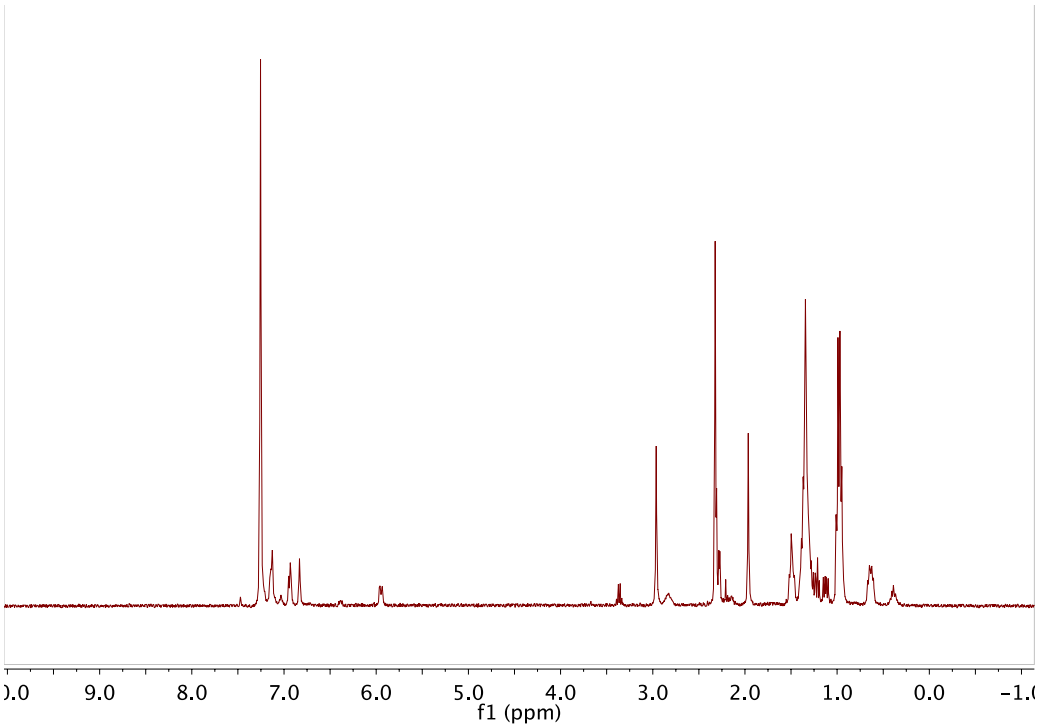

Figure S1: ^{1}H NMR Spectrum of **2** in C_6D_6, 400 MHz, 300K

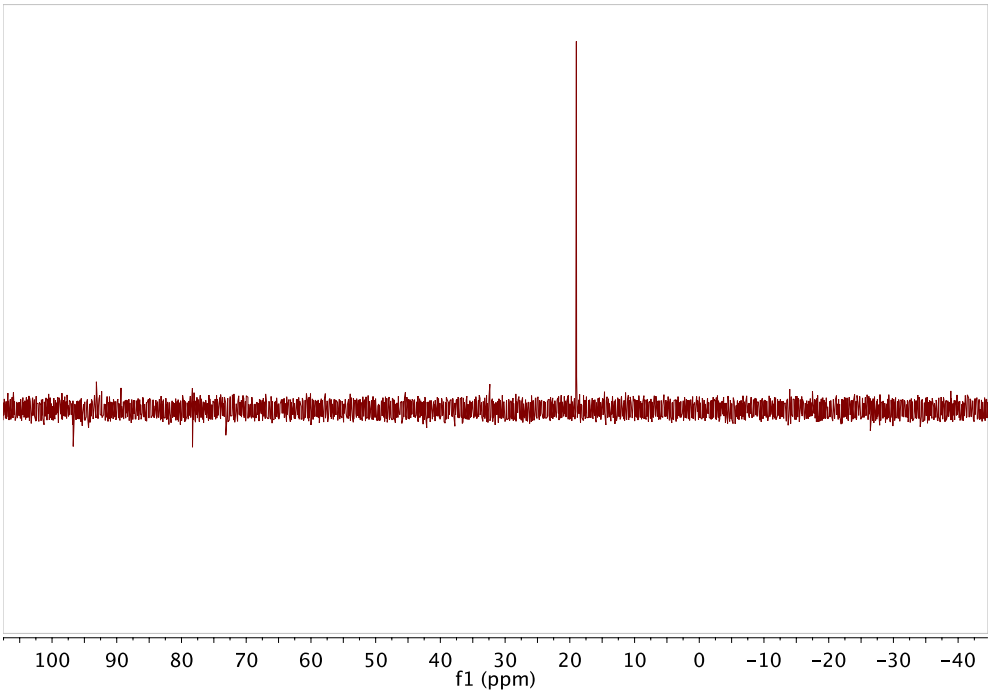

Figure S2: $^{31}P\{^{1}H\}$ NMR Spectrum of **2** in C_6D_6, 162 MHz, 300K

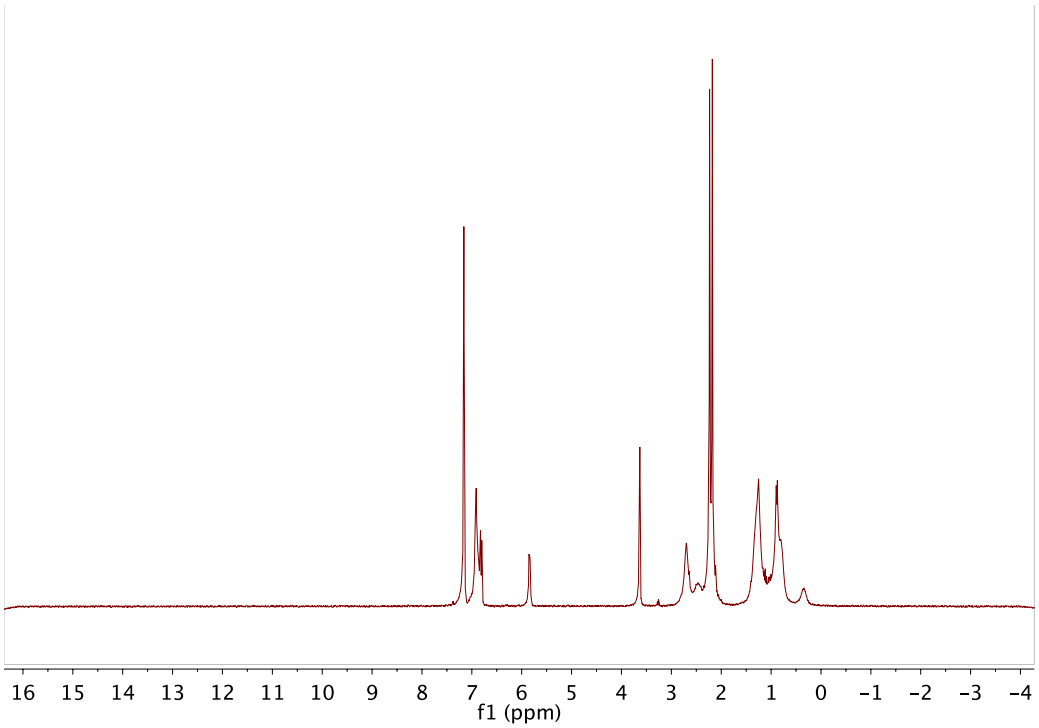

Figure S3: ^{1}H NMR Spectrum of **3** in C_6D_6, 400 MHz, 300K

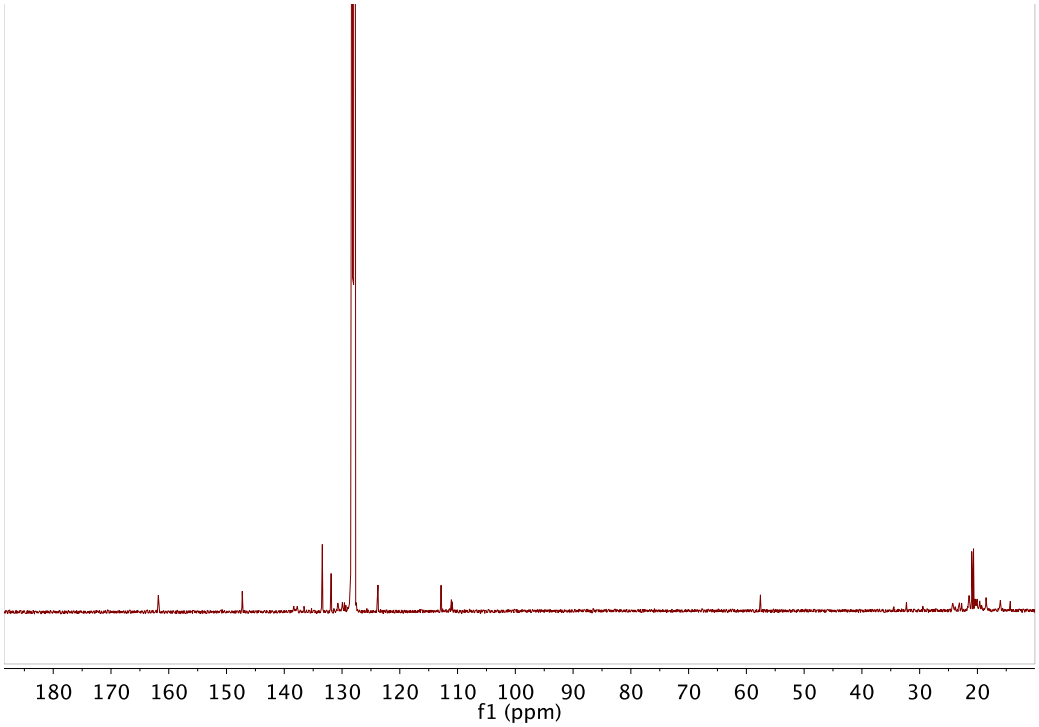

Figure S4: $^{13}C\{^{1}H\}$ NMR Spectrum of **3** in C_6D_6, 125.8 MHz, 300K

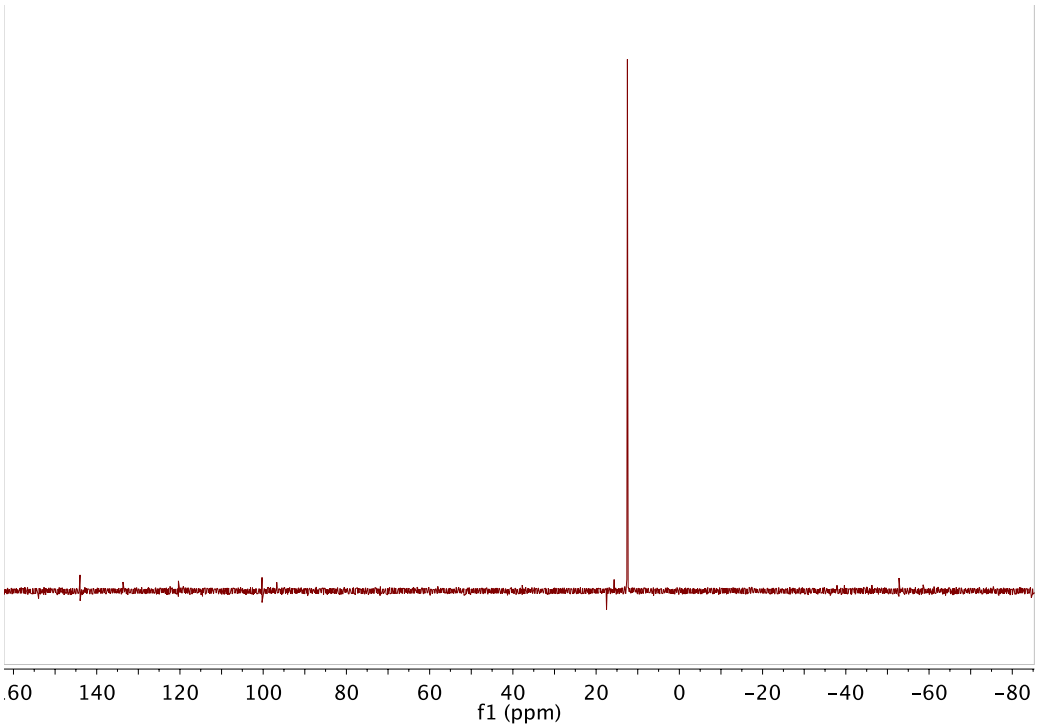

Figure S5: $^{31}P\{^{1}H\}$ NMR Spectrum of **3** in C_6D_6, 162 MHz, 300K

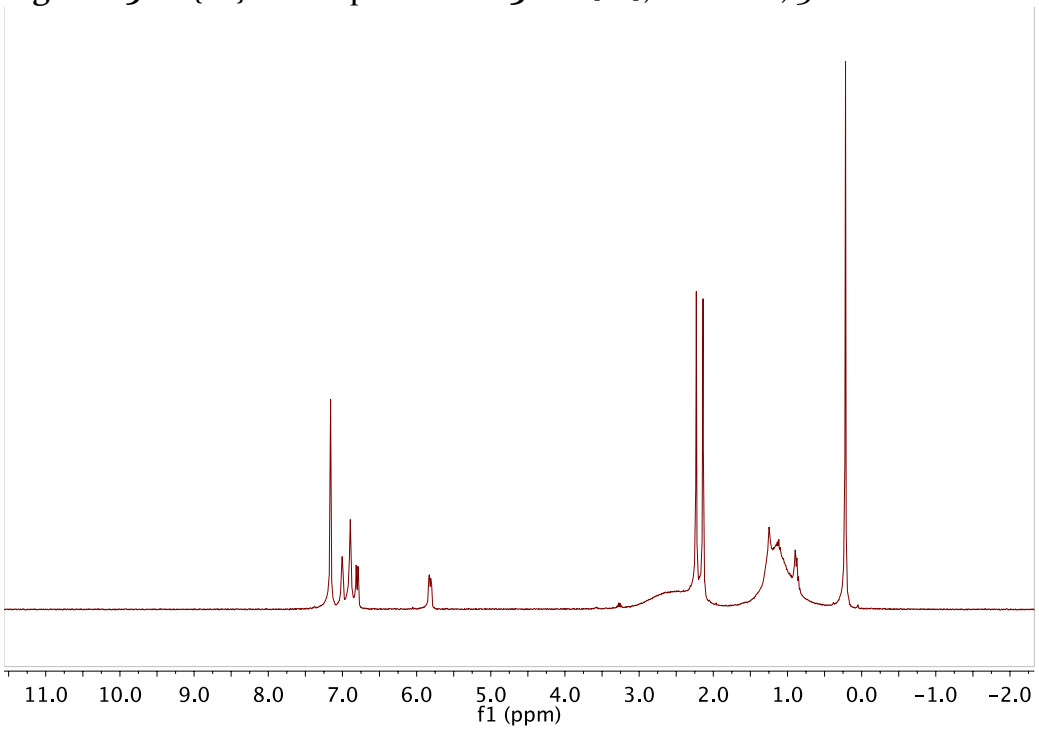

Figure S6: ^{1}H NMR Spectrum of **4** in C_6D_6, 400 MHz, 300K

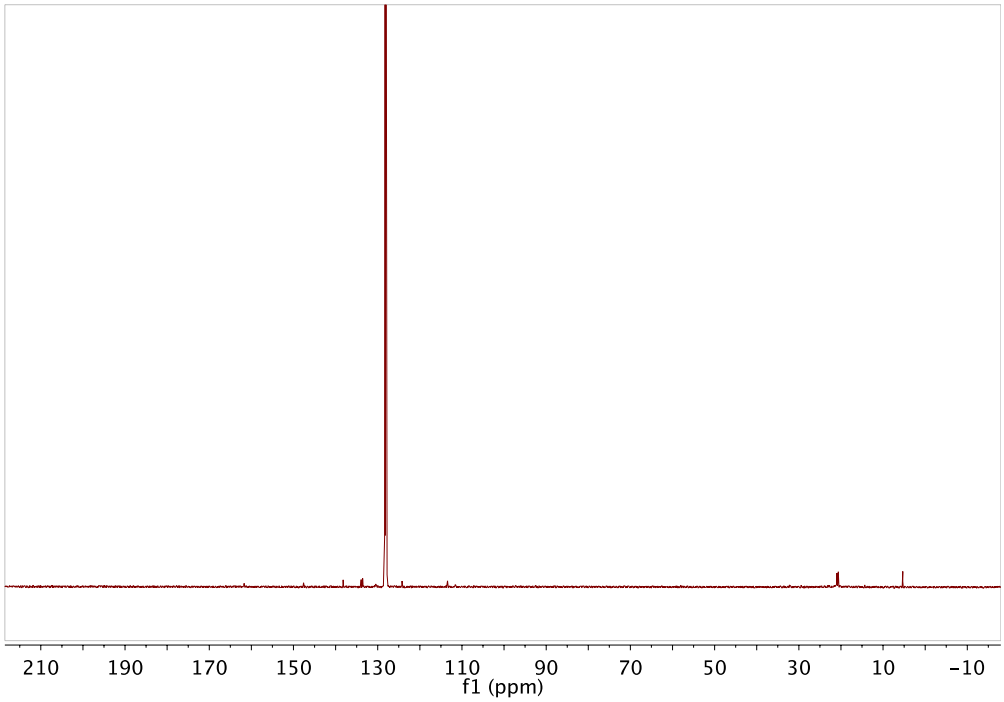

Figure S7: $^{13}C\{^{1}H\}$ NMR Spectrum of **4** in C_6D_6, 125.8 MHz, 300K

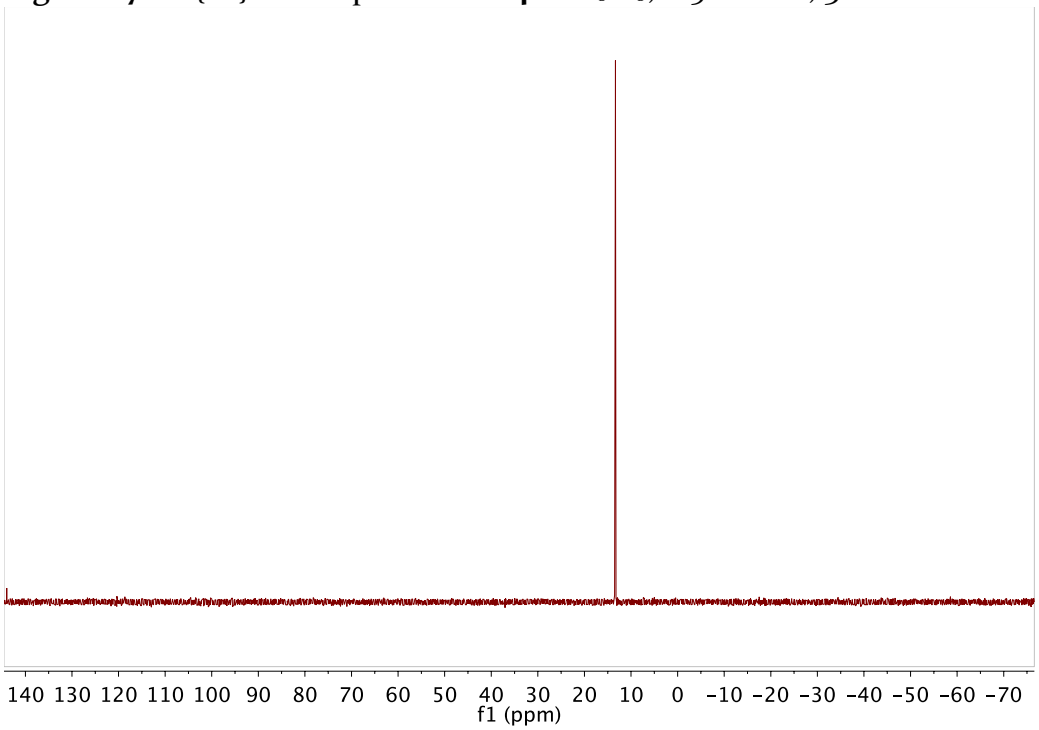

Figure S8: $^{31}P\{^{1}H\}$ NMR Spectrum of **4** in C_6D_6, 162 MHz, 300K

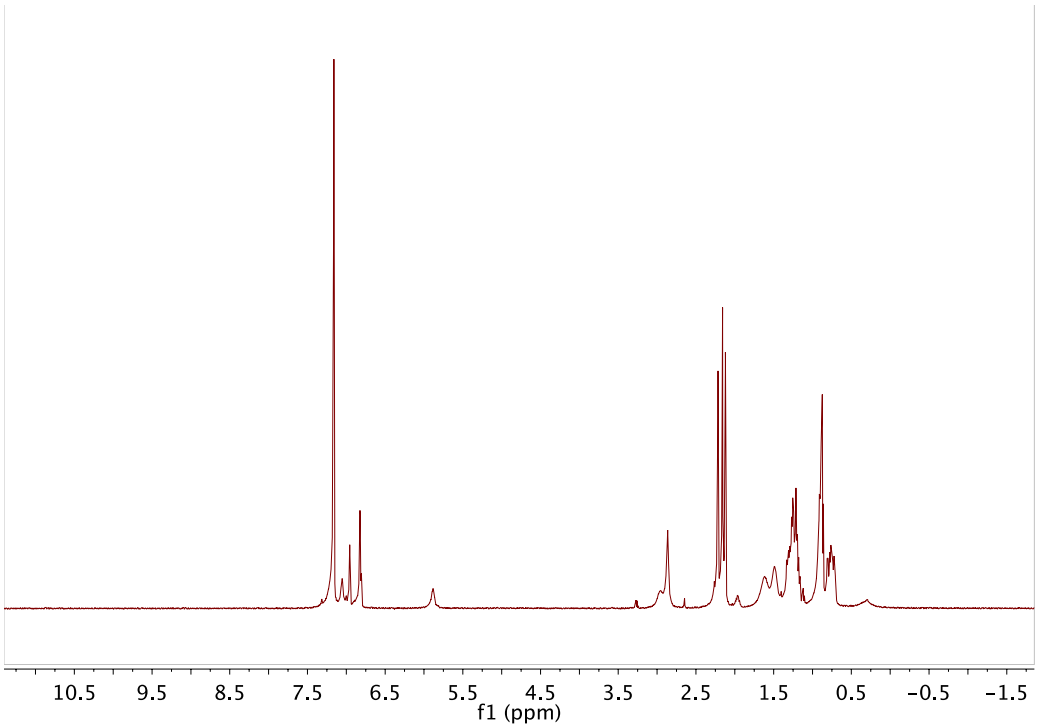

Figure S9: ^{1}H NMR Spectrum of **5** in C_6D_6, 400 MHz, 300K

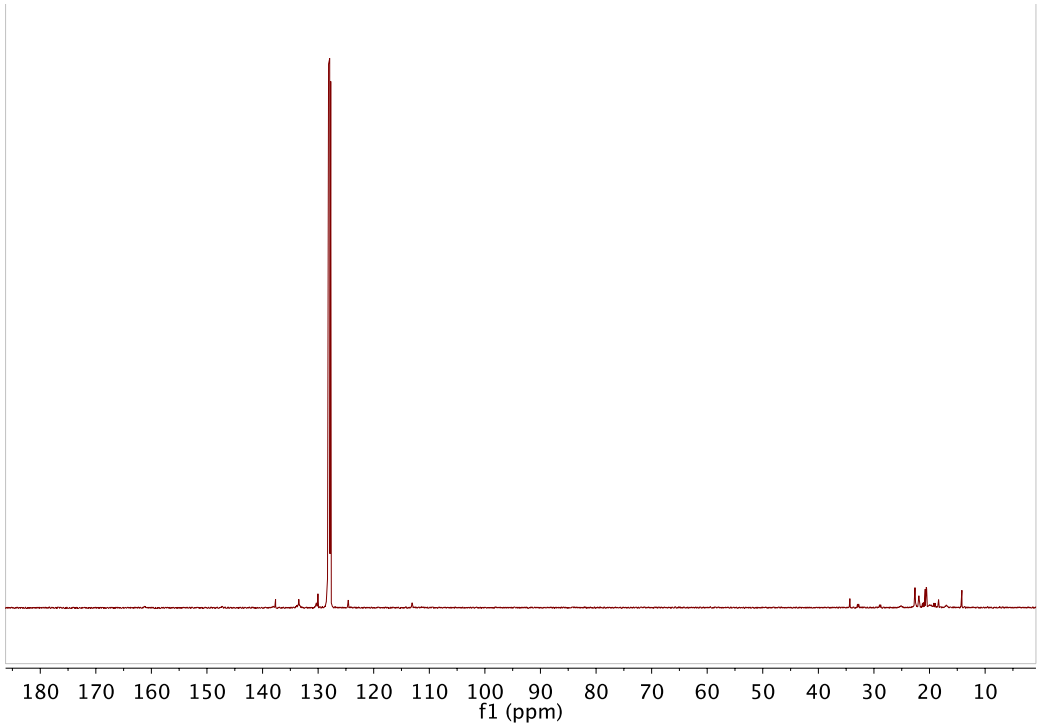

Figure S10: $^{13}C\{^{1}H\}$ NMR Spectrum of **5** in C_6D_6, 125.8 MHz, 300K

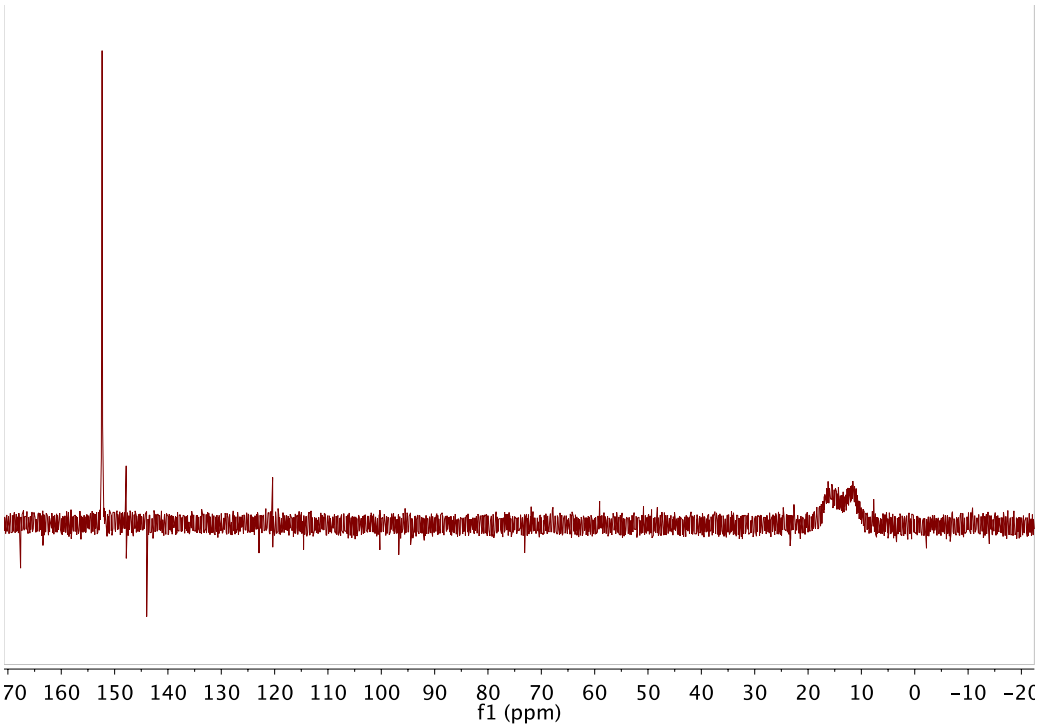

Figure S11: $^{31}P\{^{1}H\}$ NMR Spectrum of **5** in C_6D_6, 162 MHz, 300K

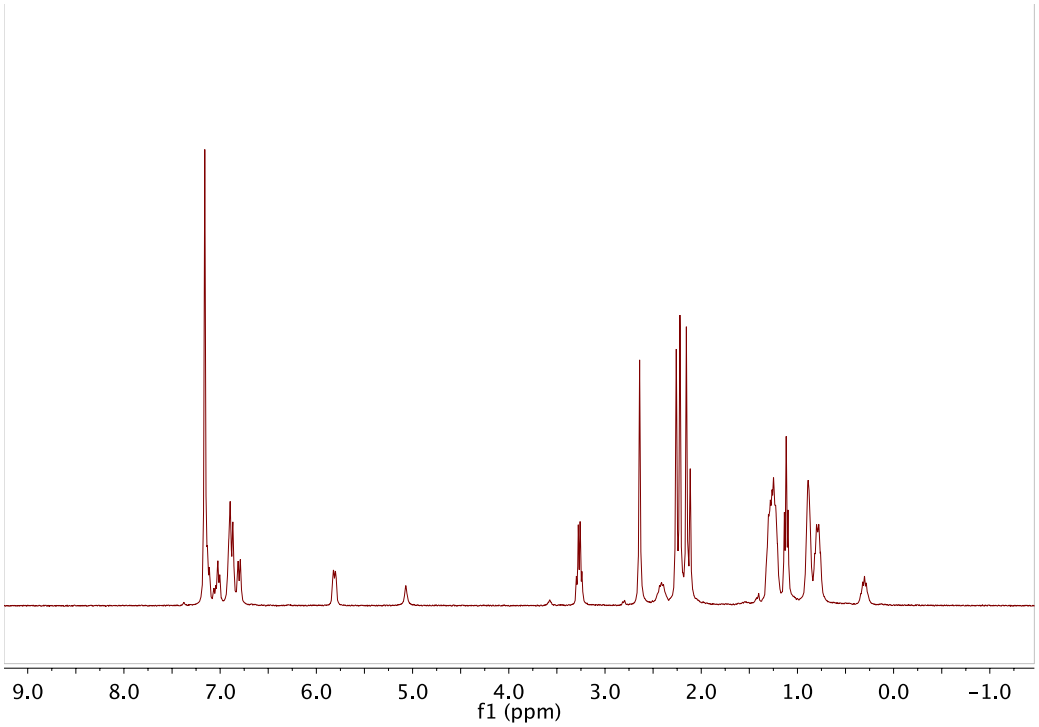

Figure S12: ^{1}H NMR Spectrum of **7** in C_6D_6, 400 MHz, 300K

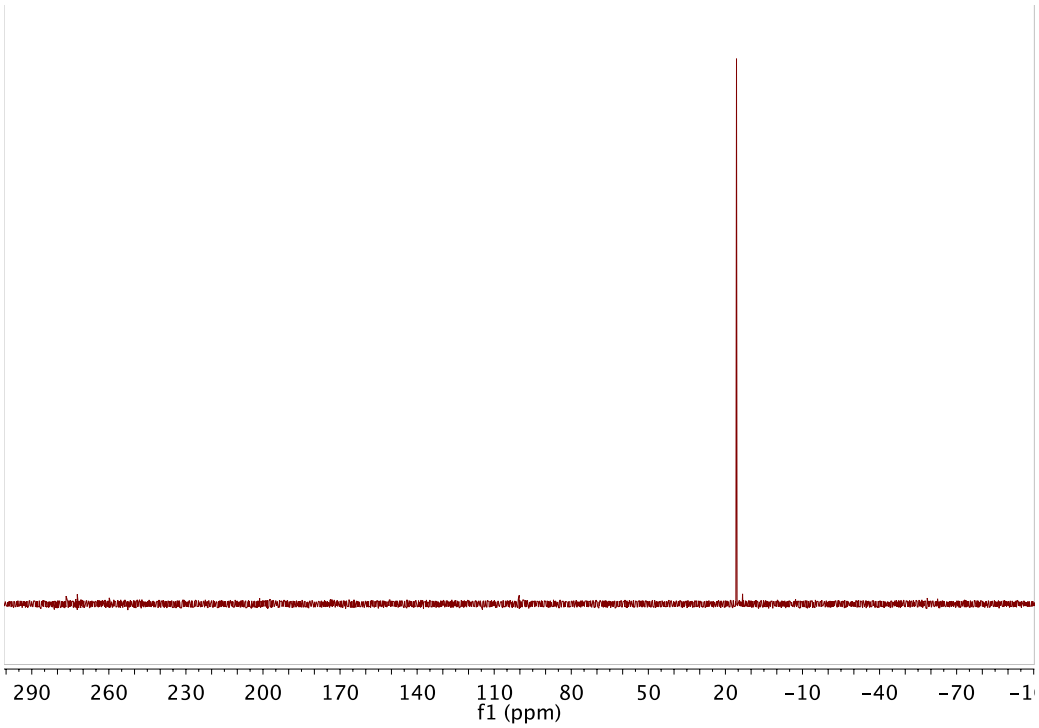

Figure S13: $^{31}P\{^{1}H\}$ NMR Spectrum of **7** in C_6D_6, 162 MHz, 300K

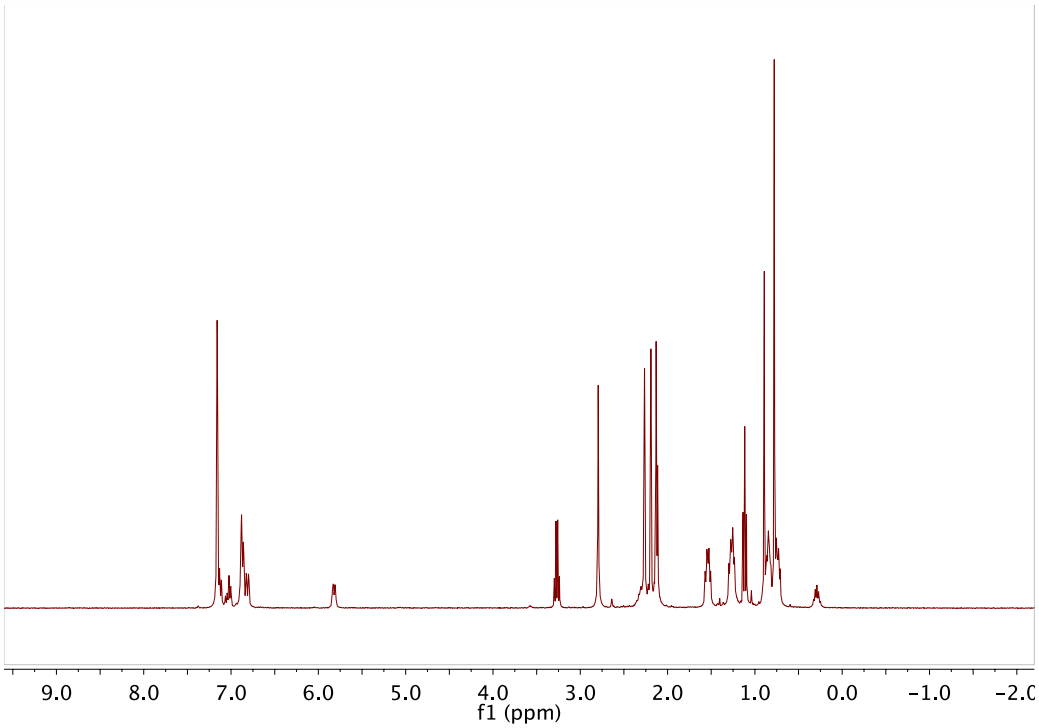

Figure S14: ^{1}H NMR Spectrum of **8** in C_6D_6, 400 MHz, 300K

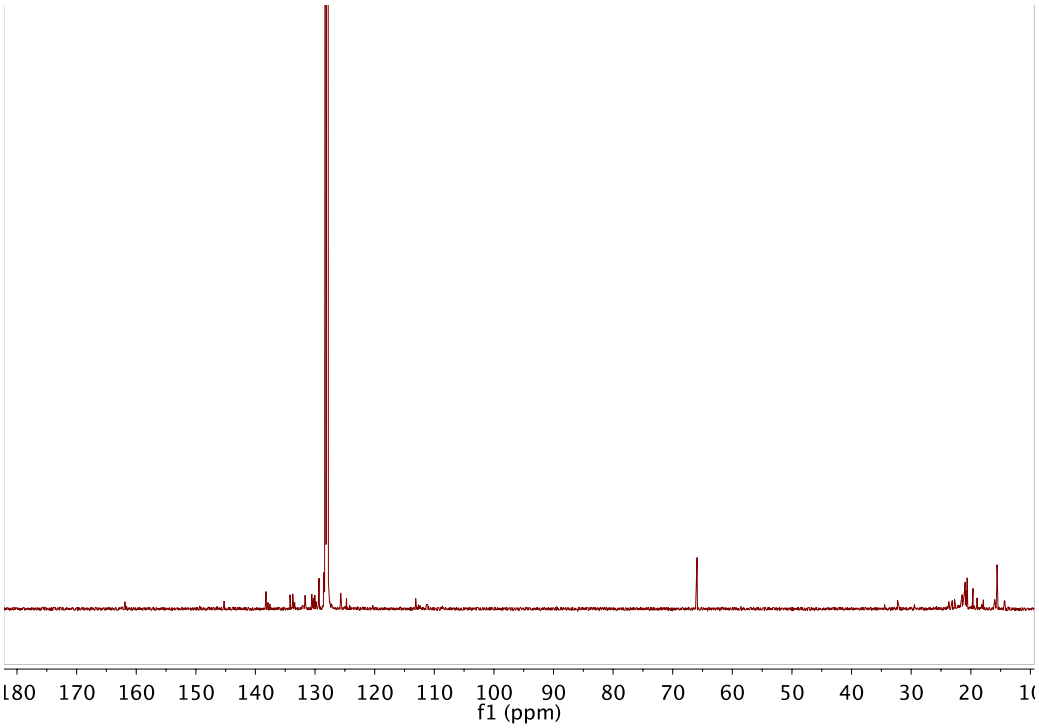

Figure S15: $^{13}C\{^{1}H\}$ NMR Spectrum of **8** in C_6D_6, 125.8 MHz, 300K

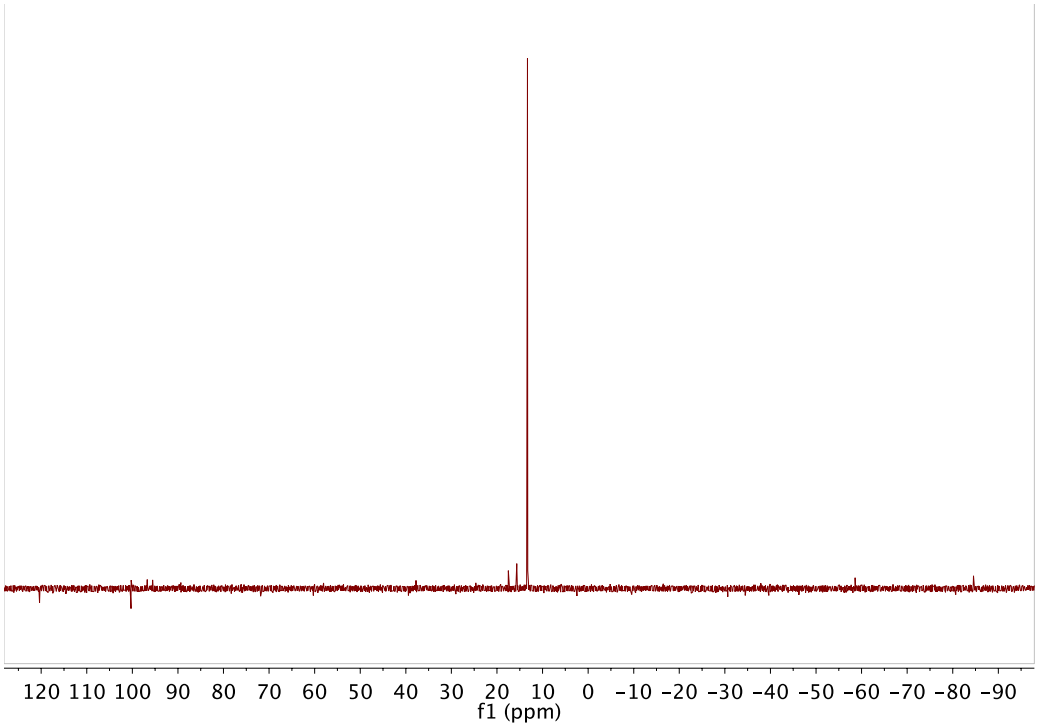

Figure S16: $^{31}P\{^{1}H\}$ NMR Spectrum of **8** in C_6D_6, 162 MHz, 300K

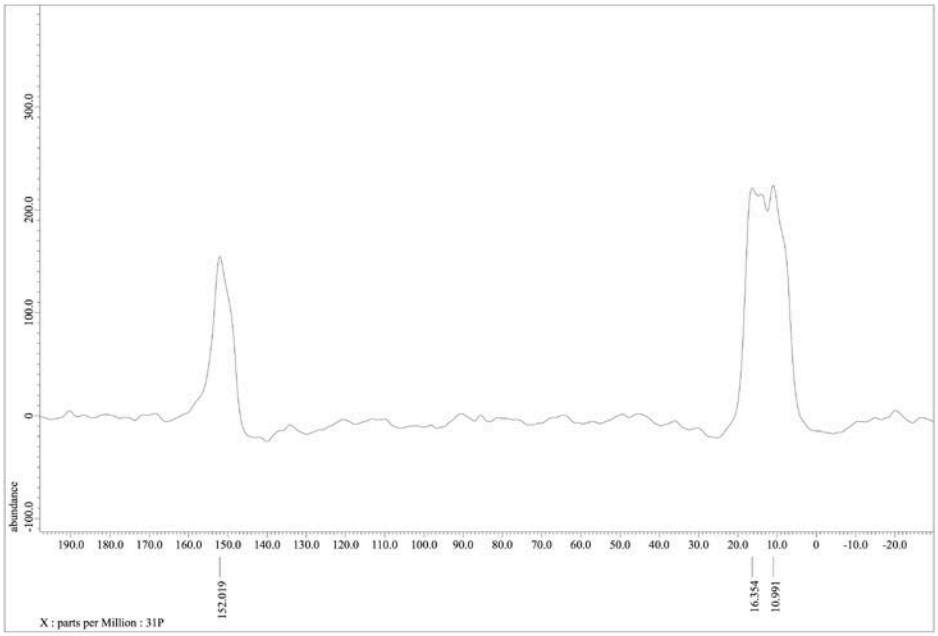

Figure S17: ^{31}P NMR Spectrum of **5** in C_7D_8, 162 MHz, 265K

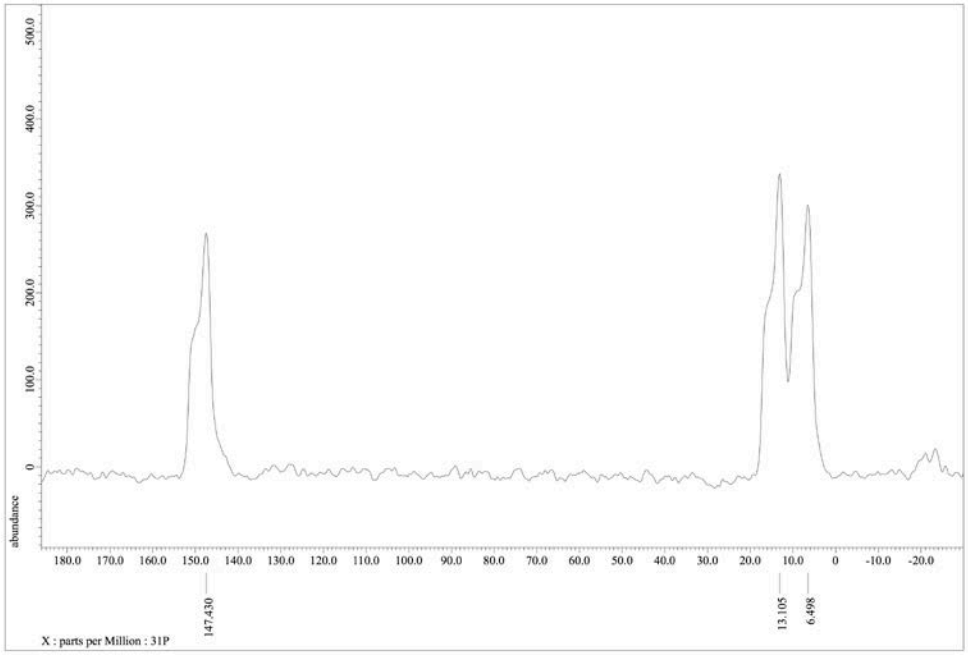

Figure S18: ^{31}P NMR Spectrum of **5** in C_7D_8, 162 MHz, 219K

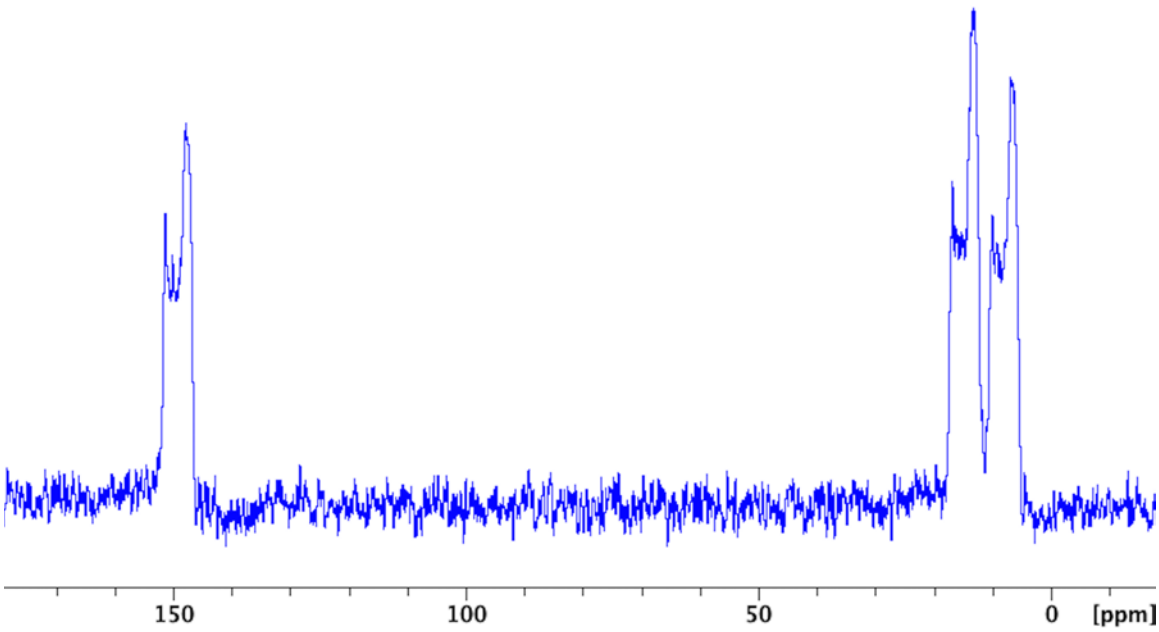

Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of **5**, taken at 219 K in C_7D_8, 162 MHz.

Computational Details. All calculations were carried out using DFT as implemented in the ORCA program package[1]. Final geometry optimizations were performed using the BLYP[2,3] functional and the all-electron def2-TZVP(-f)-ZORA[4] basis set in combination with the auxiliary basis set def2-TZV/J[5]. To accelerate geometry optimizations we used the resolution of the identity, R[6], approximation. For these optimizations a tight convergence of the wavefuntion was demanded on grid quality of Grid4 (also using SlowConv). The scalar relativistic zero'th order regular approximation (ZORA)[7] was employed to take into account relativistic effects whereas to dispersion was considered using Grimme's D3 method in all ORCA calculations. Our experience with the optimizations of the investigated extended molecules (~ 200 atoms) is that the convergence to the equilibrium structure is much faster when optimizing in Cartesian coordinates (COPT). Finally, the above-described final geometry optimizations were started from pre-optimized structures obtained via a lower level of theory (BLYP/def2-SV(P), def2-SVP/J, ZORA, RI, d3, LooseSCF, Grid3).

We used the NMR module of ADF2013[8] code to compute ^{15}N NMR chemical shifts on the equilibrium structures obtained via the protocol described above. The functional employed consisted of the local density approximation of Vosko, Wilk, and Nusair (LDA VWN)[9] augmented with the nonlocal gradient correction PW91

from Perdew and Wang[10]. This functional has been shown to provide reliable chemical shift values even for heavy atom containing transition metal complexes[11]. The full electron basis set TZVP was utilized in these calculations and relativistic corrections were applied using ZORA. The computed isotropic shielding values of complexes were referenced to that of ammonia modeled in the same way.

Cartesian coordinates of the optimized structures. Values are in Å.

$[(PN)_2Ti{\equiv}N]^-$

Ti	13.626698087600018	3.964206583517700	11.086507931125110
P	13.381576963914650	2.751979680637710	13.426121226134090
P	13.892495244806390	5.088407595794960	8.703855199718160
N	11.836423814377010	2.689458226382320	10.881183576820880
N	15.771436805382670	3.767087130183630	10.599563386975670
N	13.275186085952410	5.432064158273610	11.776954199355150
C	11.160375775141310	2.065066990780030	11.899201720707120
C	9.886545394744080	1.436400968055120	11.724042618165140
H	9.431052205334420	1.443542012427910	10.737169824900260
C	9.213615962835140	0.839188815059931	12.784348421561150
H	8.240904538662570	0.379735871540150	12.602163592124690
C	11.009440620525550	1.425320359635510	14.271000128579559
H	11.437446642586460	1.440011723975400	15.271757470541170
C	11.719662573379820	2.018512590006420	13.220669151497440
C	13.186848871852360	3.817386994076000	14.964223600666220
H	12.893962124190450	3.139212734300800	15.778943662925070
C	12.075162692320400	4.860881760582600	14.757973686916010
H	12.303712597416990	5.483011426027520	13.881659472605270
H	11.103439959722140	4.380890882707870	14.594952500602020
H	12.001160319433680	5.499177472955210	15.652326014587070
C	14.519754174452030	4.493746303277330	15.321835004752560
H	14.424010935258930	5.033854689196050	16.275647443988130
H	15.344838948638270	3.777443975700990	15.417719206754840
H	14.785543114615300	5.217059544229030	14.545517180026160
C	14.465645534851230	1.330311064464931	13.971991425424810
H	15.481965422879760	1.688765176338440	13.842640663056010
C	14.318897175905080	0.815559127600850	15.421137655611500
H	15.051782380955000	0.017855863792440	15.617938884332570
H	14.501082803652050	1.615647384216470	16.147627378860450
H	13.320675910507930	0.400533072315260	15.606362187294750
C	11.174965215149370	2.762641419825460	9.627594620199360
C	11.402501926134970	1.765468964857460	8.649504411959570
C	10.765808487770500	1.866240101367290	7.404946139178650
H	10.952787319002720	1.103313582801850	6.648400427418550
C	9.912154788271240	2.937570223160570	7.122846767232013
C	9.669320468544890	3.906284966971870	8.102916748206710
H	8.994586007820160	4.736840350358550	7.892273420178820
C	10.273280885468350	3.825105962396160	9.365840396631260
C	12.302661123486110	0.597467158901810	8.975005967059300
H	12.455784929579680	-0.037927355887970	8.094016493747470
H	13.279920431722450	0.937702706264070	9.338156725201490
H	11.874229703384500	-0.014617048997410	9.780880075683470
C	9.945720227365020	4.806511277162160	10.464233727545980
H	9.365658964277830	5.651550340013910	10.073894606568100
H	9.351881713036730	4.310653372230330	11.245888550598170
H	10.856119777557550	5.176728984178870	10.958357927816920
C	16.440122905937690	4.400176867296400	9.582232084228580
C	17.865546665582060	4.384865386116500	9.452302731757990
H	18.451911661427710	3.840133046215340	10.187752678617400
C	18.513879384115040	5.062781323612970	8.425776114981930
H	19.603081792740100	5.026416231004710	8.373035654272400
C	17.793617121380700	5.798123938318660	7.471033592547000
C	16.398208963092660	5.816980399095980	7.569944429378301
H	15.826063179291660	6.396708893905940	6.847910756651523
C	15.715477819810610	5.129285964631520	8.579984827214990
C	13.328875192344040	4.281257037709860	7.089369622082210
H	12.285804770973690	4.019706934456020	7.293361946262180
C	14.123668695212130	2.977861975769100	6.899242223322170
H	15.154782387163850	3.193866504209920	6.594574129048970
H	14.167478032190600	2.393586436328870	7.823687321754630
H	13.649895524241890	2.353414741309500	6.128899217538350
C	13.364054466114790	5.139807731113300	5.815697647137220
H	12.949055051207380	4.565122737466320	4.973259913954460
H	12.766806586783917	6.053398479031010	5.915719281122380
H	14.389207542310160	5.424081797605980	5.548843522000600
C	13.417015615426520	6.900225244105144	8.528930711418850
H	13.789738375806800	7.226547237750530	7.546909049794007
C	14.091803230733550	7.742810657401470	9.625202180903200
H	13.805505100715560	7.365080993775220	10.616536610448560
H	15.184056398988870	7.702396703702680	9.543423371937690
H	13.775167695854630	8.793027668357390	9.527378785314750
C	11.888958890342350	7.061224485756690	8.570256022947840
H	11.613995517990050	8.104942288387560	8.356418950360100
H	11.376947095488620	6.418728271105220	7.843555614610450
H	11.519236275162220	6.808550000852660	9.568339040989080
C	16.567920367956510	3.143545772086960	11.595257036996370
C	17.034167929273610	3.899531974304870	12.700171111831650
C	17.775545188710810	3.253168031580990	13.699642063913350
H	18.114787406186810	3.828737945026720	14.561696520824390
C	17.668486271905830	1.165509133566420	12.482376271102280
H	17.917122828395320	0.107284317822040	12.394527756087590
C	16.909742954936560	1.775595120291830	11.474095467958840
C	16.768753253179810	5.384352494853750	12.746342321537580
H	17.347891547570960	5.893675103526290	11.962289918484010
H	15.711474260355820	5.611309295511070	12.543292001552820
H	17.058720351190490	5.803567692243150	13.717570184082400
C	16.478013625481130	1.008814542333130	10.247038795685580
H	16.988713306008650	1.387303315950410	9.350321194072700
H	16.699114361194980	-0.060390585986200	10.352218234694460
H	15.404811538055930	1.131909620620940	10.059898277151640
C	18.090791627578150	1.893580418024230	13.599425438099900
C	14.257889703937280	0.147084938980670	12.978369428932490
H	13.285284382832470	-0.332438814589390	13.142025407635620
H	14.284000641371900	0.496202191764950	11.941419790864270
H	15.048925235997720	-0.606031169235870	13.100763031817750
C	9.757909392684110	0.830172701050140	14.078392666404990
H	18.302656067982930	6.342811237464990	6.677912793200840
H	18.660694438877470	1.403843967427070	14.388134250770790
H	9.222897491884910	0.377773967634870	14.911442639971750
H	9.440751525455330	3.018391155100320	6.144138214400060

$(PN)_2Ti{\equiv}NK(18\text{-crown-}6)$

Ti	13.553820144606790	4.207561840669830	11.084916565759120
P	13.437469350334150	2.908424947760680	13.452036314085340
P	13.797576969834990	4.965635436243260	8.512698000845770
N	11.793309302061040	2.931239264943520	10.959586433826220
N	13.691125943216900	3.963560218756300	10.622425014057490
N	13.212417111083720	5.753881866527700	11.631160882615100
C	11.122590583514670	2.346279658185600	12.012872507203100
C	9.819182730056170	1.775511169229230	11.883482031109970
H	9.333569796407257	1.789068290787400	10.911993629284250
C	9.154708022145450	1.217103198457950	12.969515312838060
H	8.158880751126720	0.798706467733750	12.822578818878960
C	11.023657672319980	1.728368824142820	14.390518893113510
H	11.486132824175430	1.711723908820380	15.375098453674500
C	11.724074505509630	2.284651380568230	13.311433251715500
C	13.387797042391410	3.784589522047080	15.114359602472620
H	13.005451457342460	3.047386623243580	15.823265382422880
C	12.404425033691350	4.959765993365250	15.033817107045310
H	12.704521356092140	5.637839659795140	14.227756804268700
H	11.385169548624700	4.614648343598660	14.829424337426680
H	12.404077977741270	5.506707863882410	15.988249093287340
C	14.769186926488815	4.251659881716290	15.595965816124740
H	14.694770585964120	4.614410846799670	16.631965775784550
H	15.521114128917780	3.455849945906170	15.569246974143520
H	15.129362604027300	5.076691131726910	14.977088230994780
C	14.464778676315820	1.358559209944990	13.765005479904290
H	15.498027346011140	1.712296109008460	13.693891200849370
C	14.274292039293440	0.669970511449900	15.124902884239400
H	14.963121166585100	-0.018487623042830	15.198888259220880
H	14.487893040949480	1.336228531509080	15.968431844495740
H	13.254780533733710	0.282915174915350	15.237219741139750
C	11.135490548227140	2.865069924312580	9.696975524108320
C	11.315216958495360	1.732081881565500	8.866156173197880
C	10.672822977442780	1.688826792033790	7.621209774235890
H	10.822969354680440	0.824221483611240	6.974616308953900
C	9.839938838685420	2.732958032464650	7.208167469202580
C	9.627971117971850	3.824693361072170	8.054488711835380
H	8.957304273351330	4.626562920066370	7.746321711435130
C	10.259803404751110	3.905638403071010	9.303611248833222
C	12.142910586447080	0.564748740287740	9.348112315574520
H	12.348406678561270	-0.136569546641450	8.533176250490150
H	13.093121883460090	0.896971187011300	9.777392673998270
H	11.621314705049510	0.022382742742280	10.149562004828740
C	9.976391406827970	5.043231440351620	10.257222031915580
H	9.319953224850440	5.788142718648270	9.790333979738520
H	9.478375476262340	4.665645989592740	11.161286410299530
H	10.902652019782540	5.525856199170310	10.602535072083870
C	16.345875738243780	4.646901035490369	9.625488512356580
C	17.771834491455860	4.753933345394420	9.562230256661720
H	18.366504307050840	4.257419814428040	10.323622646272060
C	18.410883208135960	5.471242966882880	8.558030190746810
H	19.500017506399210	5.520824281552360	8.553900242016480
C	17.676382691157070	6.139380484510890	7.566363121119316
C	16.281716886348160	6.027427612504830	7.589574564645240
H	15.707899970957580	6.522009104481260	6.808793063174020
C	15.606764696759690	5.287846643682570	8.570677256732740
C	13.598078640606010	3.771885360357670	7.061893146410910
H	12.530910672781560	3.519984528973240	7.085852414268540
C	14.401015955386430	2.498167413205670	7.355611836237320
H	15.477613816416210	2.699589920544460	7.304845146191100
H	14.178788457474240	2.106711146255280	8.349597196424570
H	14.158791495121540	1.717351520055510	6.622048473053660
C	13.951393094310630	4.321831139900043	5.671554312056720
H	13.759594937014540	3.546960282152620	4.915146163002530
H	13.355463148936900	5.199473342171860	5.397690059741460
H	15.013290605993920	4.588910928913600	5.608569491648650
C	13.124523003399470	6.570473864541020	7.801745861179990

H	13.70767777932533	6.761848939340785	6.891579365044458
C	13.35090754668825	7.721714514639744	8.780018128371o6
H	12.875339642613744	7.488178371984l2	9.739502700074l5
H	14.417139283512s3	7.897161553005zl	8.958411245714l4
H	12.914495706255o5	8.648664938578l2	8.38902367136379
C	11.644026861303l9	6.482802884894z0	7.402468604246l2
H	11.357842158366l4	7.401296133255447	6.868906250746l5
H	11.426568416704l3	5.631362924173l0	6.751393479889l8
H	11.008242026563l9	6.396430605985l4	8.286898589809ll
C	16.519692357824s2	3.266460533329l6	11.554021097939l3
C	16.962686356639l5	3.920267251180s0	12.727954060120l7
C	17.756272829039l3	3.221132156098l9	13.647843172645z2
H	18.086847190690l4	3.726365993664l6	14.555334449183s7
C	17.733165033233l7	1.270170036934l2	12.226382707370s5
H	18.040346603575l7	0.244310410238l8	12.024382303580l4
C	16.934723830207l4	1.939485243644l5	11.287826074107l6
C	16.636972448358l4	5.375889990619l1	12.930668045067s3
H	17.106280963732z2	5.990317998342z8	12.155162539688l5
H	15.555423224ll703	5.556932120005941	12.862709031253l5
H	17.004579277480l9	5.721025288512s4	13.903489156177l5
C	16.553412721570o7	1.270965449925z2	9.990742822892l5
H	16.997822221350o8	1.795042910958z3	9.134255174888l9
H	16.888677273959z9	0.227776512427l2	9.974001355253s8
H	15.470746201889s1	1.290830824736l8	9.832710127463l6
K	14.416701033485l3	8.150483703427z9	11.991965245179z3
O	11.789587673886l3	9.346787574507l8	12.768517781945l1
O	12.977532133863z2	10.320817794766l8	10.378748674609l7
O	15.702590465638l2	10.033883924189l4	10.114169274576o9
O	17.218524584854l6	8.330195970830l1	11.663731021077l8
O	16.211851107563l2	9.073476253426o7	14.212334683743l3
O	13.560440572423z3	8.200173305347l6	14.676628797234z1
C	11.073076102052l4	9.433649701765o1	11.529768882970z9
H	11.196174371568l4	8.510357628689l4	10.941831396158l9
H	9.994723868393z2	9.586676618516s0	11.715430730690s7
C	11.632900852148z7	10.630295991583s0	10.783291279124l4
H	11.627508792078s0	11.508243109276s5	11.450039440527s2
H	11.013965321703z2	10.853921461972s2	9.897250332170s0
C	13.769015258109l5	11.466413659324z0	10.051665631026l9
H	13.212593349674z5	12.157858766194l5	9.394535163828l4
H	14.043026755899ól	12.009172145349l5	10.973356801529l4
C	15.013348838566s1	11.003785707997l7	9.312650118973l7
H	15.658950416760l5	11.879263744023o7	9.122654203224l6
H	14.740913552003z3	10.553086443982z4	8.344467646830l5
C	17.011876156567s1	9.714983829219z4	9.610833584347l9
H	16.988998913371z8	9.567142099524l3	8.518532454018l5
H	17.698308902509ll	10.551563310939l9	9.827652497086l7
C	17.476493247488l4	8.408627504598s2	10.250827886665l0
H	18.548703275766l2	8.262862305378l9	10.042085314560l2
H	16.936459934115o3	7.559797952056z0	9.823396645145l7
C	17.869272993930l1	9.310795557190z6	12.482752661719z5
H	18.956636981405o7	9.315376993836l8	12.291291942838l0
H	17.468997427592ól	10.317203311396l2	12.280511058790s6
C	17.617485518249l4	8.931569557939z8	13.930562823243o3
H	18.204150111155z4	9.587711007347l3	14.597289834800ll
H	17.931859865697z4	7.889769846646l7	14.095478132570ó5
C	15.831233899034ç5	8.415389652135o8	15.434971078706l1
H	15.987325088140ç4	7.329651686727l8	15.335687929054ç3
H	16.446452119089ó6	8.781525463116ç0	16.275630481131o4
C	14.374675354232l6	8.710840668727l2	15.736606535627oo
H	14.218053885337ç9	9.798723743506z4	15.839949557848ç5
H	14.111713906934ç5	8.228692032117ó7	16.695183931467ç6
C	12.148899132379z4	8.388697379708ç4	14.907141861659o1
H	11.787154751021z7	7.653031418794ç3	15.641558281150ç1
H	11.972038178847ç3	9.403446467869ç2	15.300295114246ó4
C	11.411952685697ól	8.222405262043ç9	13.593453110380z4
H	10.324929880645ç5	8.235419043270ç2	13.784906256249ó0
H	11.681445444433ç9	7.276375022956ç9	13.092472603837ól
C	18.136230220976ól	1.897961586558ç5	13.407805642777ó2
C	14.207352269319ç2	0.372464959427ç1	12.614437043065ó6
H	13.199180989679ç3	-0.052349909672ç5	12.685497913200z1
H	14.295595702637ç3	0.860342551937ç3	11.640579007368ç3
H	14.938376000548ç7	-0.446296172236ç3	12.647723681670z2
C	9.740934647016ç8	1.194063495041ç5	14.243705161272ç3
H	18.174240288156ç0	6.706352311861ó3	6.782253905480z0
H	18.746820471442ç9	1.362206353982ç7	14.132550150183ç4
H	9.218095250496ó2	0.765238287726ç7	15.096080487154ç6
H	9.349655309857ó2	2.689554025295ç3	6.236926035401ç3

1

Ti	6.329779219977ç3	17.052368115624ç3	10.444466241531ç4
Ti	6.595559176867ó4	24.261877757623ç4	11.169200844375ç5
K	8.353220251061ç6	20.579096150899ç6	10.831673736981ç7
K	4.564877204033ç3	20.735419511827ó6	10.839414934545ç7
P	5.401938139781ç9	17.083886361703ç0	7.899577072533ç2
P	7.525725031518ç0	24.759927738537ç6	8.683087154056ç7
N	4.294807670679ç3	16.286434462062ç8	10.580854111058ç8
N	8.320063519641ç7	16.227992160984ç8	10.114278850960ç1
N	4.607108732884ç6	25.130331678291ç0	11.019483998351ç4
N	8.628146773168ç5	24.990121378768ç8	11.469289288856ç5
N	6.378824665355ç8	18.718638454806ç9	10.632240306077ç1
N	6.548033472836ç1	22.592552453926ç3	11.008719979548ç3
C	3.310866349151ç2	16.406259715636ç8	9.623239536026ç4
C	1.939820918934ç7	16.096061438702ç2	9.883378360308ç4
H	1.659949473854ç1	15.751242599751ç4	10.875192737803ç2
C	0.961481756916ç9	16.227509408665ç5	8.905451308414ç7
H	-0.070459768870ç9	15.979465170178ç5	9.154106683485ç2
C	1.279690031618ç4	16.691518784422ç4	7.620120221702ç6
C	2.613581024557ç4	16.996981894339ç7	7.338212507216ç8
H	2.865863988386ç3	17.359768558272ç0	6.344108401224ç2
C	3.628352571416ç1	16.853663626759ç9	8.296081431502ç4
C	5.383086014639ç8	18.613805301897ç1	8.801698271129ç4
H	4.614707481209ç6	18.421331503948ç0	6.041804655411ç0
C	4.957443451440ç9	19.845594026007ç2	7.609404273823ç8
H	4.874039393299ló	20.718645424636ó6	6.950849393519ó4
H	3.985381756980ç6	19.682134141184ç3	8.084420837285ç0
H	5.699861809359ç1	20.059627763912ló	8.385712392270ç9
C	6.715081843992ç8	18.854514723192ç3	6.077235179346ló
H	7.510253396319ól	19.089301265231ç6	6.787275619491ç9
H	7.035615812743ç1	17.989087297295ç5	5.490258654428ç7
H	6.612098835047ç3	19.709623099462ç1	5.394079119789ç1
C	5.773531782759ç5	15.675531528243ç7	6.701862585366ç1
H	8.857384070329ç7	15.741727646279ç8	6.559132456337ç8
C	5.456850841995ç9	14.348683221489ç2	7.409058803891ç5
H	5.863467424685ló	13.507061631665ç4	6.832982128478ç7
H	5.895424794604ç9	14.313139657504ç3	8.408435377556ç5
H	4.373924951914ç4	14.209969197307ç2	7.511952934801ç4
C	5.091071852087ç8	15.730998360668ç9	5.326819949912ç2
H	4.003099739780ç4	15.630851883297ç5	5.413150578844ç4
H	5.311988592318ól	16.653541197435ç3	4.779182834193ll
H	5.449350860845ç4	14.892289917584ç0	4.712640692095ç3
C	3.883984544950ól	15.734744864616ç3	11.833062294507ç4
C	3.811325245232ól	14.330819635578ll	12.002973288755ç4
C	4.089344076681ól	13.411119464851ç5	10.840413469280ó0
H	5.017007785871ó2	13.684924484231ç5	10.328394157495ó2
H	4.162467856527ól	12.370151031240ll	11.174118307234ç9
H	3.291247104803ç8	13.479284013089ç1	10.087259286005ç4
C	3.451361331494ç5	18.082153136544ç3	12.661584218610ç0
H	4.440421477712ç9	18.452609904451ç8	12.358068798052ç7
H	2.754298959933ç9	18.329476900990ç2	11.849909566067ç4
C	9.316035788278ç2	16.121891092046ç5	11.063805641214ç5
H	10.677669147687ól	15.850559074197ç5	10.724023499578ll
H	10.942563028367ç7	15.730918989232ç6	9.677080269747ól
C	11.664366020105ç2	15.730058011996ll	11.690623133184ç3
H	12.688176980350ç5	15.519947820801ç9	11.385902213973ó3
C	9.019063425833ól	16.275774690143ç5	12.459698130198ó6
C	7.087165048067ól	13.704157736849ç9	12.787631810118ó8
H	6.633881289231ç3	13.896337426702ló	11.812646886598ç8
H	8.163782175548ll	13.562019798201ll	12.635535068863ó8
C	8.710181159814ç6	15.935645148958ó9	8.771387397682ç1
C	9.138271463783ç1	16.979817735497ó2	7.918477816732ll
C	9.485291143929ll	16.688904654567ç4	6.592449320979ól
H	9.797232119337ç4	17.499316341022ç4	5.934310282751ç3
C	9.440703291721ç7	15.377325487804ç1	6.112398158034ç1
C	9.072466426428ç8	14.340636499085ç8	6.974045171704ll
H	9.051867359132ç9	13.313716116409ç8	6.609948466826ç3
C	8.716430636861ç2	14.599234893833ç5	8.305139881750ç8
C	9.264307611152ç9	18.377133283538ç9	8.469548715755ç7
H	9.588162431402ç2	19.082160346093ç2	7.697319400711ç9
H	8.302535729755ç2	18.702652958946ç3	8.888334314441ç1
H	9.998243823379ç3	18.406530589272ló	9.285162349118ç5
C	8.379659412978ll	13.468381831764ç3	9.243941780941ç7
H	7.460601445980ç5	13.675542948129ç5	9.800411698029ç4
H	8.257883992778ç6	12.527132423415ól	8.696452398385ç0
H	9.170741834508ól	13.334157095930ç6	9.995513758074ól
C	3.615153705122ç2	25.046795692882ll	11.975121761918ç5
C	2.256604042815ç2	25.401867663111ç1	11.708054024990ç2
H	1.991530857765ç2	25.750518116712ç3	10.713474009233ç7
H	0.251836517729ç5	25.605923246935ll	12.434388377508ç7
C	4.219493253906ç8	25.706241924217ç9	9.771084240417ç6
C	4.223198164708ç6	27.112167491287ç2	9.607267356335ç2
C	3.857894716005ól	27.657857923246ç5	8.369094203760ç7
H	3.881498751729ç7	28.739576722432ll	8.238990241707ç3
C	3.472683745494ól	26.836222576671ç0	7.306186891090ç5
C	3.423070858862ç9	25.451429163764ç7	7.487594841630ól
H	3.097377015555ç9	24.806837495939ól	6.671703689350ç3
C	3.778169138536ç2	24.875372615643ç5	8.714935139207ll
C	4.573461220322ç2	28.006891359140ç5	10.769396692002ç5
H	5.504211688955ç7	27.689856315714ç2	11.249483930931ç1
H	4.679293761526ç8	29.047448470325ç8	10.443994578519ç2
H	3.796643883903ç6	27.961057921254ç2	11.545427648852ç5
C	3.635276682973ç4	23.393393167541ç9	8.949075584461ç3
H	3.299158843240ç6	22.880282036956ç3	8.042150002707ç3
H	4.591671610514ól	22.967576858807ç9	9.280572584896ç8
H	2.899958528322ç6	23.199375509176ç7	9.741143295485ç4
C	9.615360613804ól	25.060396418024ç4	10.509776740755ól

C	10.98733309827641	25.30247182321283	10.830165835748 35
H	11.26666659726485	25.43584514977511	11.871727784923 24
C	11.96784446980782	25.36629360156839	9.847471796591 96
H	13.000777523462 36	25.55043427250732	10.143056632470 40
C	11.65039789967507	25.17742840034899	8.493974497721 52
C	10.31561655977291	24.94492200397904	8.153109682854 43
H	10.063751939548 29	24.79650782843133	7.105220019815 58
C	9.299219508799 29	24.89525688599666	9.118887526266 46
C	7.539130500156930	23.47902168404714	7.302965179894 13
H	8.311865509371 45	23.81158707988897	6.598378587732 11
C	7.947063541956 88	22.109406734157 91	7.859581834126 43
H	7.958080140256 03	21.360207499559 83	7.059034401529 34
H	8.945565226434 61	22.149643282476 27	8.306248924240 08
H	7.229536188579 03	21.796768471791 07	8.626705061017 54
C	6.207653448504 12	23.394304367907 41	6.542240909936 95
H	5.421888989642 37	22.975983332851 14	7.174600614496 85
H	5.864901309725 86	24.368665752961 58	6.181948860107 27
H	6.324816286557 72	22.731517073446 90	5.673065424182 19
C	7.160845003145 16	26.384717473021 07	7.798302505307 41
H	6.076114694720 16	26.358829591231 93	7.650341581786 51
C	7.493672248369 69	27.538302322126 46	8.757190505255 58
H	7.100957099851 38	28.483880546216 21	8.360209885690 78
H	7.053467621735 17	27.380415560901 15	9.744076576359 49
H	8.578139025454 56	27.638287413922 40	8.885582366016 16
C	7.839673964061 15	26.603095907527 71	6.437642096458 49
H	8.928981995246 01	26.669426461055 42	6.538099117392 38
H	7.604289069612 26	25.815238009337 42	5.714165579082 72
H	7.491603523898 98	27.554785747900 19	6.010984358075 27
H	10.238101539333 05	22.737616585775 70	12.293414303982 46
C	8.809175565999 22	27.745027504109 32	12.328921992778 86
H	9.602130555197 33	27.847377961105 31	11.574393555008 77
H	7.880982844916 21	27.570659658104 47	11.776367511188 26
O	11.042965968277 60	20.881305843755 96	10.442659951558 32
C	11.554566269271 35	21.910144046098 76	9.559819375875 47
H	10.762845602920 85	22.661650669758 12	9.507010327331 18
H	12.423356996689 25	22.387460536087 96	10.036083556101 68
C	11.906507561570 26	21.404822900601 28	8.162676291142 09
H	12.244390122730 50	22.252131007601 05	7.552840729811 57
H	12.708530628668 65	20.656667695296 26	8.183247419477 77
H	11.030126160378 08	20.960118644811 36	7.676139364531 54
C	12.054246772980 94	19.984790179678 57	10.955832840169 36
H	12.349496428369 20	19.261580238605 82	10.179412447586 93
H	12.944370669544 93	20.574675843605 23	11.230770736862 75
C	11.486422530651 87	19.263482768729 70	12.166173400852 43
H	12.243135221213 76	18.609541996137 42	12.611872511316 24
H	10.644415220050 41	18.619910657159 93	11.887913491079 83
O	1.889485160668 35	20.503213356455 28	10.379849855346 73
C	0.876547700941 77	21.262290890951 12	11.076207229187 76
H	0.535160712671 00	22.102783485231 58	10.451164313223 28
H	0.011495600687 13	20.605622719296 56	11.267329143055 95
C	1.467689666568 84	21.772207671632 91	12.379019069021 93
H	2.292171421966 18	22.471545582732 77	12.199064188526 78
H	1.826334038561 56	20.937213815504 89	12.993864273415 09
P	7.256249993147 36	16.477470609650 11	12.917489018005 11
P	5.676351584071 69	24.303209463755 97	13.707335359972 72
C	3.442725959065 39	13.810408554106 17	13.251288030084 52
H	3.412583817942 03	12.729639030452 95	13.386850821374 29
C	3.126241070222 53	14.655485877069 75	14.318166510302 03
C	3.145475845380 02	16.039654618499 50	14.129459114803 37
H	2.874372185364 67	16.703727176873 30	14.949470019346 65
C	3.505898465645 47	16.592652205598 67	12.892803231654 05
H	3.124298322334 30	18.607179649929 48	13.566475280482 55
C	11.363588453181 49	15.893278442305 17	13.056053215391 89
C	10.042437074149 74	16.171276245907 00	13.413873007078 13
H	9.805918500926 97	16.307522682957 79	14.466984298358 73
C	7.341330084805 59	17.723385816045 58	14.328460146637 64
H	8.084905281789 88	17.323086153255 28	15.029233150810 23
C	7.844502929417 27	19.076176750869 53	13.809486246484 36
H	7.882055611904 04	19.808861630630 02	14.624866161489 43
H	8.849308887310 97	18.981314067880 30	13.385584585620 79
H	7.162945298986 08	19.448127024903 50	13.036139258787 40
C	6.013705538583 28	17.876496239988 42	15.084552102487 02
H	5.258823661360 24	18.356297376397 91	14.457931251423 61
H	5.609081063509 04	16.918011982618 61	15.422581253290 39
H	6.167335266280 79	18.511872601078 43	15.968356191179 77
C	6.820220453353 27	14.853630453089 11	13.771521410287 56
H	5.739045553728 81	14.929189682239 03	13.929085776611 01
H	6.664266688038 79	12.768612342234 99	13.177401144101 93
C	7.495687442468 90	14.573991783220 16	15.122419685326 01
H	8.581495489500 45	14.467898989899 215	15.016152375990 39
H	7.292668207817 76	15.351134692259 97	15.866904740850 38
H	7.112178550252 06	13.625810819016 36	15.526220146656 65
C	1.272989075496 22	25.320182418977 40	12.687086837017 50
C	1.572957279800 77	24.860417472842 23	13.977618843589 82
C	2.892237855815 55	24.501049872087 98	14.262773827551 25
H	3.129691481452 96	24.138366080800 39	15.260618771505 96
C	3.913293210088 39	24.598411870789 92	13.305751422272 57
C	5.598081237193 02	22.786145751973 77	14.819551224464 74
H	4.860961273779 76	23.026893458673 41	15.596239141204 90
C	5.085096568291 96	21.572651275662 92	14.035039145906 52
H	4.982902549057 04	20.706882261951 62	14.700858802582 42
H	4.104820592143 86	21.782585254175 01	13.595459146120 26
H	5.791041873161 861	21.320446873204 16	13.236282732392 58
C	6.934917263873 09	22.481382193881 02	15.510177546639 46
H	7.692791917573 13	22.190836137648 18	14.780257075946 16
H	7.322541257089 34	23.336061331826 04	16.072609831298 76
H	6.804770786726 98	21.643746390585 25	16.209958547401 72
C	6.112253582508 55	25.702035779007 17	14.895632110952 24
H	7.193453416690 98	25.590189365819 09	15.034691167322 33
C	5.850616272447 39	27.038747979376 70	14.185244592914 60
H	6.282915298189 71	27.865368067232 48	14.764606721982 12
H	6.297896058917 38	27.057878518985 74	13.189725711509 35
H	4.774469977978 12	27.217571986480 51	14.073538982546 94
C	5.432006464624 27	25.679965403327 33	16.272682409732 43
H	4.348143194746 72	25.819769882275 31	16.187909366812 21
H	5.620459927857 27	24.752768156619 49	16.824606945599 14
H	5.822710847723 92	26.508180035389 60	16.881210488514 42
C	9.043727152132 52	25.268200647646 04	12.807715002368 04
C	9.441755706275 94	24.208858169933 23	13.656374331518 70
H	9.823549021756 40	24.490599205537 99	14.974869664428 50
H	10.114491360356 13	23.670548994326 34	15.630778954444 72
C	9.843520849195 65	25.804911051908 20	15.449492393862 359
H	9.500847138058 08	26.853574472610 65	14.591593828598 55
H	9.531753909705 02	27.882067431628 76	14.950969443238 13
C	9.110007048115 43	26.604812348177 81	13.268667046674 00
C	9.505950879991 43	22.805366171536 49	13.108569702044 18
H	9.792444820872 43	22.089934964308 09	13.887530968898 74
H	8.530863711933 67	22.522790302417 58	12.688706848249 85
H	8.725459316216 70	28.691326705808 78	12.874563391079 59
H	11.158089141021 66	19.984561071601 81	12.925286166820 14
H	0.713384992888 78	22.323466156386 61	12.949483955726 14
C	0.997579155755 79	20.443124645181 36	8.051105272502 77
H	0.685507570842 52	19.730589466085 45	7.277359365651 73
H	0.170247178092 27	21.141879279410 40	8.225816959896 4
H	1.855637755993 35	21.009916398136 48	7.669865172920 99
C	1.375459710827 87	19.669006629276 86	9.312102797556 84
H	0.518215228706 88	19.094065577783 27	9.691311705354 534
H	2.174834979604 05	18.955073395516 74	9.099232282078 67
H	10.133884675956 60	26.011488205901 14	16.477974479947 10
H	12.419834382946 23	25.213543797807 63	7.726158158732 09
H	3.203258173229 28	27.272981761817 95	6.346276989639 41
H	0.799972905062 67	24.778525396688 55	14.738416119259 40
H	0.511513173864 85	16.809379015138 71	6.859386744915 86
H	12.137826847183 25	15.814142449754 72	13.815982573269 12
H	9.698111526621 30	15.163292385623 06	5.076761726054 19
H	2.859245467565 27	14.238194526703 07	15.287378652274 40

2

H	9.784981726479 94	15.352897658681 59	2.135591567167 17
H	12.532957792300 56	15.320080910325 79	7.528057614304 83
H	9.568688629515 56	14.925655846005 10	8.726156084735 46
H	12.754477331909 73	14.912164063297 74	0.921337806417 56
C	9.393437519262 63	15.485584891236 47	6.091254550438 56
C	12.934557078730 31	15.440064733091 06	3.563350457457 87
H	9.393860604541 21	14.454654456925 47	6.468335005330 83
H	12.884341853955 307	14.413890050309 67	3.176706246804 93
Ti	11.228881424771 03	19.368280449322 01	4.840216680059 38
Ti	11.270154582566 33	24.324965895283 29	4.820993184760 92
P	9.610932369993 46	19.091269088038 77	2.759653723000 79
P	12.839360896457 49	19.049929086520 20	6.917431759638 50
P	8.671416586546 29	24.628945259512 11	5.223316740882 84
P	13.872335958097 83	24.615413168598 24	4.419583624371 22
N	9.422265646419 71	18.373300816661 22	5.644686094313 85
N	13.005588625718 12	18.323415814664 64	4.036518958300 60
N	10.521931970341 10	25.341332067057 83	2.997139059173 32
N	12.022788195378 41	25.353175248599 42	6.635144583083 68
N	11.261617819463 04	22.477148482282 34	4.831008218676 08
N	11.251127500048 32	21.215877866336 67	4.835477408905 50
C	8.169639670086 97	18.497674615735 25	5.067965989974 16
C	14.261851458331 37	18.405196151703 03	4.612697758686 21
C	6.958027889645 13	18.244852737272 85	5.778807271407 81
C	15.464157513824 32	18.107159351190 70	3.903370113865 55
H	7.017513835954 04	17.901542902638 84	6.807768119769 85
H	15.393400250266 11	17.763196789572 33	2.875362015539 03
C	5.708059590506 29	18.473997000929 355	5.205606992482 79
C	16.720957961521 52	18.288482348676 72	4.478632549821 72
H	4.811009309311 86	18.299418007697 13	5.802364979626 82
H	17.611621114702 46	18.076731249772 61	3.884275138995 98
C	5.594386662353 50	18.942289581550 20	3.891249272499 48
C	16.850387249328 99	18.752754316611 75	5.793033945326 67
C	6.770576352800 63	19.139303054590 40	3.154108820954 05
C	15.681336674973 21	18.995509706076 87	6.528043969738 45
H	6.688854056518 03	19.489005618733 54	2.126933350772 20
H	15.775053445104 13	19.340293718500 69	7.555928344529 88
C	8.038481859651 20	18.915964778854 91	3.700192294353 68

C	14.406717918421 85	18.820347586171 43	5.979786154861 94
C	9.182509537425 00	20.354835022144 48	1.424598326586 03
C	13.312432750564 58	20.303584085945 10	8.247132223177 77
H	8.257767140169 11	19.999082300656 10	0.950243629219 91
H	14.228459319713 83	19.921038905212 06	8.717676755429 25
C	8.899748612434 85	21.732863523026 07	2.031818752126 49
C	13.635341335520 42	21.667011862981 89	7.625289416981 51
H	8.795093230689 93	22.488611760048 23	1.243414860991 45
H	13.770922661186 03	22.428221945640 24	8.404447023241 69
H	7.961314741273 75	21.718506930475 06	2.582514606460 17
H	14.566954461482 33	21.612432943233 19	7.065248196675 17
H	9.685567482500 74	22.056682129183 07	2.720589752749 62
H	12.854545843598 51	22.009389614222 92	6.939557534828 12
C	12.242723876836 81	20.402057740791 94	9.344888677255 25
H	11.314191080145 72	20.816264663272 08	8.952253342580 22
H	12.013543599848 78	19.430979007094 24	9.795401127193 66
H	12.597308192447 34	21.075671396055 65	10.138970124277 34
C	9.597171441752 14	17.482570217344 18	1.728650064416 58
C	12.793595436102 76	17.440230941884 86	7.944306450173 79
H	10.564778254829 60	17.491638512462 64	1.216414052416 78
H	11.825126925509 70	17.482050281033 55	8.452714070807 35
C	9.565368841378 75	16.282943373897 20	2.680017897446 89
C	12.784300398312 90	16.244094024023 13	6.987322845243 54
H	10.303644432205 51	16.390955106641 80	3.474713863481 89
H	12.048488813092 92	16.381213930317 18	6.194675694690 37
H	8.579912764937 94	16.189542869065 58	3.151907793257 09
H	13.765048607291 56	16.118874766230 95	6.513139682933 58
C	8.478146692437 19	17.350031499550 16	0.683881600217 41
C	13.902027461052 92	17.264114088730 33	8.993535403619 93
H	7.489877640717 53	17.393033705837 13	1.159543213616 78
H	14.893405866999 90	17.268199157516 05	8.522477884607 77
H	8.523459457737 94	18.126304916135 66	-0.087980533690 67
H	13.883194634308 35	18.041933252211 38	9.765096743652 93
H	8.562949431163 58	16.375689258489 21	0.176275782426 98
H	13.776264337687 57	16.293955970525 77	9.500725694067 14
C	9.435447999424 63	17.866725854187 72	6.979405975078 72
C	12.977819647652 14	17.829473673925 38	2.697736318898 24
C	9.347682231157 79	18.757901993004 79	8.080410218766 72
C	13.103741623870 43	18.728471375307 42	1.607064162705 79
C	9.404597791696 47	18.259963825639 88	9.387327187435 60
H	9.361242728884 27	18.963664985848 51	10.219041758829 17
C	9.512171636446 49	16.886014217297 02	9.634381963944 64
C	9.520407155514 04	16.001888771889 65	8.551665834322 47
C	12.838898475164 77	15.984263308266 24	1.107191196299 18
C	9.462293318017 50	16.468487358501 49	7.231230260828 06
C	12.903345467575 11	16.435591761900 95	2.432600267662 09
C	9.126313796273 69	20.221167398206 38	7.824437361547 56
C	13.369545388761 48	20.181692922826 37	1.880821646513 53
H	9.067624912640 46	20.779388335771 95	8.764619844805 16
H	13.453447376046 99	20.746998831507 13	0.946803664326 62
H	9.913275488541 87	20.652752233105 96	7.191027448373 91
H	12.589814248036 05	20.631156380064 65	2.510902659573 86
H	8.188283784313 90	20.365708982701 45	7.280933623529 07
H	14.306801979853 18	20.292026982277 86	2.434483120893 19
H	8.487637358768 28	15.639756745197 81	5.491230817735 35
H	13.851467873072 98	15.546870227703 57	4.157195193783 53
H	10.238769503562 54	15.600888695165 46	5.405070535195 81
H	12.101204403775 57	15.587531676095 07	4.257652185651 57
C	9.212157898788 16	25.239678096609 62	2.559504538027 13
C	13.332150038187 59	25.259101822696 42	7.074645284000 17
H	8.820133244533 63	25.507934955536 67	1.213348020348 20
C	13.724671627281 54	25.550301249514 12	8.416009935661 39
H	9.574039779152 53	25.840682521493 23	0.505496242492 407
H	12.970766547283 45	25.893893000393 585	9.118646025774 67
C	7.511904254266 15	25.309505244324 46	0.775103942560 23
C	15.034593804757 24	25.366308780197 25	8.855215699761 89
H	7.269812100126 94	25.497199109525 40	-0.272497373611 56
H	15.277975942550 67	25.575333957108 74	9.898463472411 92
C	6.519768296820 53	24.856650930219 21	1.652980602846 78
C	16.027780916438 02	24.903964741491 77	7.983383978301 81
C	8.869581548800 36	24.641478162352 39	2.993540620807 56
C	15.676721336263 30	24.664004508795 76	6.647390068280 370
H	6.100707283409 96	24.301837944420 10	3.684786949626 27
H	14.446929617330 53	24.318909049149 17	5.960345155137 17
C	8.172560899230 25	24.833672047631 24	3.463717778066 56
C	14.372055844187 00	24.841992455345 85	6.176156030482 63
C	7.419550276084 19	23.385747015367 05	5.890140553887 887
C	15.134202842676 88	23.371582498532 24	3.768583053133 43
H	6.428271151767 83	23.772831804225 36	5.618104387653 12
H	16.122085768319 15	23.771148432467 69	4.035658449537 41
C	7.584996500668 53	22.011543548246 95	5.233939178481 15
C	14.979318582951 26	22.005960313273 46	4.447643882363 81
H	6.955333126499 86	21.266270542012 65	5.736058868727 02
H	15.611054028613 16	21.254869953441 90	3.955383207185 91
H	7.262362621045 43	22.048116032599 75	4.194740340250 63
H	15.303324271157 20	22.063161570251 51	5.486328554893 57
H	8.620618674552 33	21.658587788984 00	5.252172685874 94
H	13.945344039208 17	21.647365632695 74	4.436943312008 60
C	7.475523266665 02	23.305054324804 60	7.423955597298 01
C	15.079235608823 90	23.267181244744 80	2.237324366019 31
H	8.424423163641 42	22.884847700963 15	7.756317168654 27
H	14.133012047756 69	22.836171072488 31	1.911243926616 31
H	7.356214187265 64	24.282318105443 19	7.902393754285 02
H	15.193013249716 97	24.238509142844 54	1.745153014782 76
H	6.674172727816 67	22.643547848214 22	7.784831936008 76
H	15.884827395566 75	22.605434554459 30	1.886302028569 69
C	7.988624266510 37	26.240440205911 74	5.988797334111 292
C	14.542631870007 87	26.225502473275 28	3.640328403432 42
H	8.354830748072 14	26.211648186493 45	7.019628388518 47
H	14.180214394873 65	26.184235339258 29	2.608715754404 21
C	8.632665697925 76	27.434976796091 53	5.280294212764 71
C	13.883952508831 46	27.419701669982 00	4.336481621206 52
H	8.459483245975 04	28.361005061086 65	5.847442690239 14
H	14.051985184576 04	28.342699478375 55	3.763070751315 43
H	9.709618959534 68	27.297156764000 95	5.179807091101 77
H	12.807552354902 58	27.273267602778 89	4.431852401305 66
H	8.218451941835 94	27.556780485576 74	4.272199587528 60
H	14.291047199494 61	27.552764251059 05	5.345967270957 449
C	6.460554527723 57	26.400144985891 56	6.009327031498 35
H	6.068292257677 28	26.399162688733 444	3.623291200410 73
H	6.046220811999 40	26.370007586100 92	4.993258272720 93
H	16.479973673210 44	26.382833020051 579	4.640993674441 71
H	5.963823873019 62	25.629115494533 32	6.608520907985 76
H	16.574203375937 44	25.626313714764 29	3.033406752610 88
H	6.199726726260 487	27.376637562757 05	6.448212707015 72
H	16.322408359832 94	27.373465035455 99	3.175420319000 899
C	11.450026480447 87	25.846288010826 65	2.036369621461 12
C	11.091610032127 57	25.855365087534 38	7.594032895181 44
C	12.135109696520 78	24.956274756392 52	1.168532935312 53
C	10.423369902139 82	24.963230417053 91	8.472486233635 19
C	9.485484358971 88	25.456679433777 677	9.386984128020 73
H	8.965427895743 03	24.752060201755 84	10.035378178333 3
C	9.213877155504 90	26.827138183807 03	9.477130900988 07
C	12.597713477414 08	27.711069485341 53	0.956934246617 57
C	9.926102184485 02	27.713669989981 15	8.664227633812 94
H	12.757744007174 94	28.787004931878 77	0.868561718827 17
H	9.751628027752 2	28.787978937662 82	8.744415439851 72
C	11.650156742321 58	27.244613861847 90	1.878334036405 47
C	10.874663375352 67	27.252112601779 57	7.741322521494 84
H	11.795020055533 91	23.493952834423 47	1.196598820555 35
C	10.782273535966 73	23.505119996260 56	8.451696330817 84
H	12.432136523618 69	22.927843210064 96	0.509390645997 90
H	10.159703215699 03	22.936006949848 70	9.149561374184 70
H	11.881782880602 88	23.072989658336 09	2.207302618708 76
H	10.690508004627 11	23.075518670673 47	7.444882647214 04
H	10.753336817202 08	23.347316159618 29	0.896180447598 82
H	11.829123092438 06	23.373876406759 65	8.742591425142 42
C	10.826930273385 95	28.229670544004 54	2.667264810697 54
C	11.682849990315 06	28.240144466223 320	6.940601818811 01
H	11.085189386256 64	29.259521889210 10	2.388478616812 98
H	11.403804854215 46	29.269189755277 99	7.201605637640 69
H	9.754403049894 91	28.076356362718 65	2.493787381740 65
H	12.757347584280 34	28.109890931065 16	7.121472958394 94
H	10.982989672065 04	28.117705291952 49	3.745270086760 48
H	11.534867446934 39	28.107564538673 47	5.863960881790 43
C	10.261912817989 32	20.413525966521 91	0.333224833237 42
H	9.932397500168 10	21.091312851513 44	-0.467983205438 42
H	11.199190780295 72	20.803797774416 37	0.730068496166 75
H	10.466803802089 16	19.433405998444 74	-0.108817561065 05
C	13.072123979936 01	25.454671593215 21	0.255468425435 09
H	13.604802606401 83	24.751911702256 06	-0.385846856203 13
C	13.326333082021 22	26.827717254739 93	0.155397758022 78
C	13.041325626936 53	18.245247856570 37	0.294985671427 90
C	12.887701617803 96	16.878304511083 13	0.033615136611 33
H	13.116498309859 13	18.954755764594 73	-0.529464829064 20
H	9.573241583713 52	16.510687218647 83	10.655316014416 29
H	4.620955105458 329	19.145036091512 89	3.446656614746 91
H	12.822717342169 07	16.515213654122 30	-0.991516707818 92
H	17.830237194113 46	18.916436152066 54	6.239621321787 07
H	8.469310214804 85	27.198516472775 81	10.180447021816 17
H	17.048423496045 27	24.740379705042 57	8.326635890260 49
H	14.069748017424 09	27.203398278384 27	-0.546874369601 93
H	5.501210866489 38	24.679622332109 48	1.310191612770 30

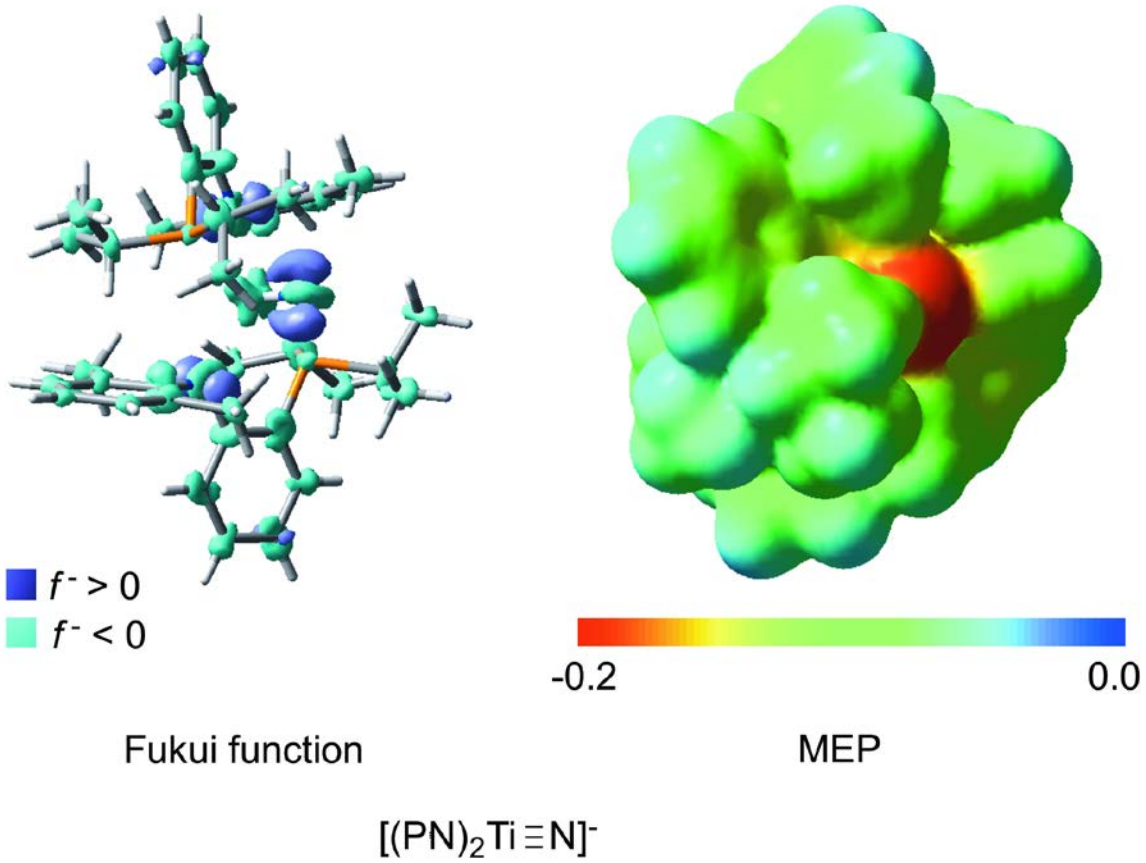

Figure S19. Nucleophilic Fukui function, f^-, and molecular electrostatic potential, MEP, for $[(PN)_2Ti{\equiv}N]^-$ characterizing soft (purple regions) and hard (red sites) electrophilic reactivity of the titanium-nitride functionality, respectively,.

Crystallography Details. Suitable single crystals for X-ray analysis of **2**-**8** were placed on the end of a Cryoloop coated in NVH oil. The X-ray intensity data collection was carried out on a Bruker APEXII CCD area detector using graphite-monochromated Mo-K radiation (λ = 0.71073 Å) at 100(1) K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. Rotation frames were integrated using SAINT,[12] producing a listing of non-averaged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL[13] program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.[14] All calculations were performed using SHELXS[15] and SHELXL.[16] The structures were solved by Patterson and Fourier transform methods. All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using riding models with exception for **7**. For **4**, two crystallographically independent, but chemically equivalent molecules are present in the asymmetric unit. For **5**, ^{i}Pr groups of NP^iPr_2 were disordered over two on the crystallographycally special position. The thermal ellipsoids were fixed by SHELXL restraint commands,

DELU and SIMU. Disordered pentane molecule was located with 0.5 occupancies and a negative PART number, and refined with a rigid group model. For **6**, one site occupied by hexane was identified in the asymmetric unit. This site was considerably disordered and was treated by SQUEEZE as a diffuse contribution.[17, 18] In the resulting void space, a contribution of 134 e^- per unit cell was found and taken to represent one hexane in the asymmetric unit, giving one pentane molecule for each Ti complex. For **7**, one site occupied by THF was identified in the asymmetric unit. This site was also treated by SQUEEZE as a diffuse contribution, resulting in a contribution of 186 e^- per unit cell to give one THF molecule for each Ti complex. This data was treated as a two-component crystal data. One component with 0.8 occupancies was refined as a terminally bound parent imide complex **7**. The hydrogen atom of the imide ligand was located from the difference map and refined isotropically. The second component was considerably an insertion product in which the imide ligand has inserted into the arm of the PN ligand. The phosphorus atom and corresponding ^{i}Pr groups were refined with 0.2 occupancies, but the hydrogen atom corresponding to the parent imide hydrogen in **7** could not be located from the difference map due to its low occupancy. These results were checked using the IUCR's CheckCIF routine. The alerts in the output are related to the disordered groups and crystal solvents.

Solid state ^{15}N NMR Details. Solid-state ^{15}N NMR spectra were recorded under the cross polarization (CP) magic-angle spinning (MAS) condition on a Bruker Avance-600 NMR spectrometer (14.1 T) operating at the ^{1}H and ^{15}N Larmor frequencies of 600.17 and 60.81 MHz, respectively. The Hartmann-Hahn matching condition was established with a solid $^{15}NH_4NO_3$ sample. High-power ^{1}H decoupling (70 kHz) was applied during data acquisition. A 4-mm Bruker MAS probe was used with sample spinning frequencies between 5.0 and 14.5 kHz. A relaxation delay of 2 s and a contact time of 2 ms for CP were used. Powder samples were packed into a ZrO_2 rotor (4-mm o.d.) in a glove box. All ^{15}N chemical shifts were referenced to that of NH_3(liq) (δ = 0 ppm) by using solid $^{15}NH_4NO_3$ as a secondary ^{15}N chemical shift reference (δ = 23.8 ppm). Spectral simulations were performed using DMFit.[19]

References

1 F. Neese, ORCA—An ab initio, Density Functional and Semiempirical Program Package Version 3.0.1 (2013)

2 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.

3 C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785.

4 D. A. Pantazis, X. Y. Chen, C. R. Landis and F. Neese, *J. Chem. Theory Comput.*, 2008, **4,** 908.

5 a) K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor. Chem. Acc.*, 1997, **97**, 119. b) K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283.

6 K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **242**, 652.

7 a) E. van Lenthe, E. J Baerends and J. G. Snijders, *J. Chem. Phys.*, 1993, **99**, 5648.; b) C. van Wullen, *J. Chem. Phys.*, 1998, **109**, 392.

8 E. J. Baerends, J. A., D. Bashford, A. Børces, F. M. Bickelhaupt, C. Bo, P. M. Boerrigter, L. Cavallo, D. P. Chong, L. Deng, R. M. Dickson, D. E. Ellis, M. van Faassen, M. Fan, T. H. Fischer, C. Fonseca Guerra, A. Ghysels, A. Giammona, S. J. A. van Gisbergen, A. W. Gotz, J. A. Groeneveld, O. V. Gritsenko, M. Grüning, F. E. Harris, P. Harris, P. van den Hoek, C. R. Jacob, H. Jacobsen, L. Jensen, G. van Kessel, F. Kootstra, M. V. Krykunov, E. van Lenthe, D. A. McCormack, A. Michalak, M. Mitoraj, J. Neugebauer, V. P. Nicu, L. Noodleman, V. P. O. Osinga, S. Patchkovskii, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, J. I. Rodriguez, P. Ros, P. R. T. Schipper, G. Schreckenbach, M. Seth, J. G. Snijders, M. Solà, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T. A. Wesolowski, E. M. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo, A. L. Yakovlev and T. Ziegler, V. U. *ADF2013.01*, Amsterdam (The Netherlands).

9 S. H. Vosko, L. Wilk, Nusair, M. *Can. J. Phys.* 1980, **58**, 1200.

10 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671.

11 M. Krykunov, T. Ziegler, E. van Lenthe, *J. Phys. Chem. A*, 2009, **113**, 11495 and references therein.

12 *SAINT*; Bruker AXS Inc.: Madison, WI, USA. 2009.

13 *SHELXTL*; Bruker AXS Inc.: Madison, WI, USA, 2009.

14 G. M. Sheldrick, *SADABS*; University of Gottingen: Germany, 2007.

15 G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112.

16 $R_1 = \Sigma||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$;where n = the number of reflections and p = the number of

parameters refined.
17 A. L. Spek, *Acta Crystallogr.* 2009, **D65**, 148.
18 P. van der Sluis and A. L. Spek, *Acta Crystallogr.* 1990, **A46**, 194.
19 D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan, G. Hoatson, Modelling one- and two-dimensional solid-state NMR spectra. *Magn. Reson. Chem.*, 2002**, 40**, 70-76.