Supporting Information for:

Pursuit of an Electron Deficient Titanium Nitride

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Experimental Details

General Procedures.

Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified dinitrogen or using high vacuum standard Schlenk techniques under an argon or dinitrogen atmosphere. Hexanes, pentane, tetrahydrofuran (THF) and toluene were purchased from Fisher Scientific and Et_2O was purchased from Sigma Aldrich. Solvents were sparged with argon for 20 minutes and dried using a two-column solvent purification system where columns designated for hexanes and toluene were packed with Q5 and alumina respectively, and columns designated for Et_2O and THF were packed with alumina. Deuterated benzene was purchased from Cambridge Isotope Laboratories (CIL) and was sparged with nitrogen for 20 minutes, then was dried over a potassium mirror, vacuum transferred to a collection flask, and degassed by freeze–pump–thaw cycles. All solvents were transferred into the dry box and were stored over 4 Å sieves. Tritylchloride and iodine (ultrapure and sublimed) were purchased from Acros Organics and used as received. *mer*-$[TiCl_3(THF)_3]$ was prepared according to literature procedures.[1] Complexes $[(PN)_2Ti{\equiv}N\{\mu_2\text{-}K(OEt_2)\}]_2$ (**1**), $(PN)_2Ti{\equiv}NH$ (**4**), $(PN)_2Ti(N_3)$ (**6**) were prepared according to published literature procedures.[2-3] NaN_3 was dried by evacuating in a Schlenk flask overnight, followed by stirring overnight in THF after bringing into the glovebox. This solution was decanted, and then suspended and stirred in toluene overnight. Finally, after decanting this solution, it was suspended in pentane, stirred overnight, and then this was taken to dryness for use. KC_8 was prepared by mixing carbon with metallic potassium and heating over a week at 150 °C in a well-sealed, high pressure flask (thick-walled), with good stirring and using a metal stir bar coated with glass. Each night, the reaction vessel was brought back into the glovebox to manually mix the two reagents to ensure good mixing without clumping of the K metal. All sieves were heated to 200 °C under vacuum overnight prior to use. Celite used for filtrations, was heated to 200 °C under vacuum overnight prior to use. Phenol-d_6 was purchased from Sigma Aldrich and dried by evacuating in a Schlenk flask overnight, followed by recrystallized from hexane and dried prior to use. ^1H NMR spectra were recorded on a Bruker AVIII 400, AVII 500 MHz, DMX 300 MHz, or a Bruker DMX 360 MHz spectrometer. ^{13}C NMR spectral data were recorded on a Bruker AVII 500 MHz spectrometer and $^{31}P\{^1H\}$ NMR spectral were recorded on a Bruker AVIII 400 spectrometer. ^1H NMR spectral data are reported with reference to residual proteo solvent resonances of C_6D_6 at δ 7.16 ppm. $^{13}C\{^1H\}$ NMR spectra were referenced to solvent resonances of benzene-d_6 at 128.06 ppm. $^{31}P\{^1H\}$ NMR spectra were referenced to external H_3PO_4 (δ 0.0 ppm). IR spectra were recorded on a JASCO FT/IR-4600LE Spectrometer using clear disks and mini KBr plates. Elemental analyses were measured by Midwest Microlab and also by Robertson Microlit Laboratories, Ledgewood, NJ, USA.

Synthesis of (NPN')(PN)Ti(I) (2) (NPN' = N-(2-NP^{i}Pr$_2$-4-methylphenyl)-2,4,6-Me$_3$C$_6$H$_2^{2-}$).

To a 10 mL orange cold (−35 ^{o}C) solution of **1** (201 mg, 0.106 mmol, 1 equiv.) in toluene in a 20 mL vial was added 5 mL solution of I_2 (53.8 mg, 0.212 mmol, 2 equiv.). The reaction was allowed to stir at room temperature overnight. The reaction is then allowed to reach completion by one of the following methods: (a) The solution can be placed into a 25 mL Schlenk flask and photolyzed for fifteen minutes, or alternatively, b) the reaction will also go if left stirring in ambient light for three days. After completion, all volatiles were removed *in vacuo*. The deep red residue was extracted into toluene and filtered over Celite. The filtrate of toluene was concentrated to a minimum (2 mL), and then carefully layered with 5 mL hexane. This vial was stored at −35 ^{o}C overnight, resulting in the deposition of red crystals suitable for XRD analysis (184 mg, 0.101 mmol, 48% yield). Due to the nature of the proposed mechanism, involving both parent imide and hydride complexes *en route* to **2**, there is inevitably always a small amount (5-10% contamination) of these species in isolated samples. Between this contamination, and the asymmetry of the resulting complex, all specific resonances are nearly impossible to assign due to overlapping peaks. Moreover, during the reaction, evolution of molecular hydrogen was detected through ^{1}H NMR spectrum at δ 4.47 ppm, which was unambiguous from proposed pathway for the formation of **2**.

^{1}H NMR (400 MHz, 298 K, benzene-d$_6$): δ 7.13-6.67 (m, unable to resolve *J* coupling value, 6H, C-*H*, Ar), 6.54 (d, *J* = 12.0 Hz, 2H, C-*H*, Ar), 6.15 (dd, *J* = 8.8, 3.6 Hz, 1H, *ortho*-Ar*H*$_{Tolyl}$ from NPN' moiety), 5.65 (dd, *J* = 8.4, 3.6 Hz, 1H, *ortho*-Ar*H*$_{Tolyl}$ from PN moiety), 2.97 (sept, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, P-C*H*Me$_2$ in PN moiety), 2.84 (s, 3H, C*H$_3$*, mesityl Ar), 2.66 (s, 3H, C*H$_3$*, mesityl Ar), 2.61 (sept, *J* = 7.2 Hz, 1H, P-C*H*Me$_2$ in NPN' moiety), 2.22-0.83 (multiple overlapping peaks from P-CH*Me$_2$* in NPN' moiety and Ar-*Me*, 43 H) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, 298 K, benzene-d$_6$): δ 163.4, 163.2, 159.9 (d, $J_{C\text{-}P}$ = 3.8 Hz), 149.4, 146.8 (d, $J_{C\text{-}P}$ = 5.0 Hz), 137.2, 136.4, 135.9, 134.4 (d, $J_{C\text{-}P}$ = 5.0 Hz), 134.1, 133.6, 132.3, (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.0, 130.3, 129.7 (d, $J_{C\text{-}P}$ = 8.8 Hz), 129.3, 128.6, 128.3, 128.2, 128.0, 118.8 (d, $J_{C\text{-}P}$ = 8.8 Hz), 116.7, 116.5, 112.8 (d, $J_{C\text{-}P}$ = 8.8 Hz), 30.2, 28.9, 28.5, 28.3, 27.8, 26.8, 26.3 (d, $J_{C\text{-}P}$ = 11.3 Hz), 24.1 (d, $J_{C\text{-}P}$ = 11.3 Hz), 21.2, 20.9, 20.7, 20.5, 20.4, 19.2 (d, $J_{C\text{-}P}$ = 6.3 Hz), 19.0 (d, $J_{C\text{-}P}$ = 6.3 Hz), 18.5, 17.8, 17.6 (d, $J_{C\text{-}P}$ = 2.5 Hz), 17.1 (d, $J_{C\text{-}P}$ = 5.0 Hz), 16.8 ppm.

^{31}P{^{1}H} NMR (162 MHz, 298 K, benzene-d$_6$): δ 34.99 (1P, N*P*N'), 14.58 (1P, *P*N) ppm. Multiple attempts to obtain satisfactory elemental analysis were unsuccessful presumably due to the thermal instability of these complexes.

Alternative Method for Synthesis of (NPN')(PN)Ti(I) (2) (NPN' = N-(2-NP*i*Pr$_2$-4-methylphenyl)-2,4,6-Me$_3$C$_6$H$_2^{2-}$) from [(PN)$_2$Ti≡N{μ$_2$-K(OEt$_2$)}]$_2$ (1).

A 0.6 mL orange solution of **1** in C_6D_6 (10 mg, 0.0053 mmol, 1 equiv.) in a J-Young NMR tube was charged with 0.4 mL C_6D_6 solution of ICH_2CH_2I (3 mg, 0.0106 mmol, 2 equiv.) at room temperature. The reaction is then performed by one of the

following methods: (a) The solution can be photolyzed for fifteen minutes, or alternatively, b) the reaction could be complete, when left the solution in ambient light for two days. The reaction was monitored by ^{31}P NMR spectroscopy. Moreover, during the reaction, formation of ethylene gas was detected by ^{1}H NMR spectrum at δ 5.25 ppm. The ^{31}P NMR spectrum of the reaction mixture at δ 34.99 and 14.58 ppm, clearly suggesting only the formation of complex **2**.

Synthesis of (NPN')(PN)Ti(Cl) (3).

To a 1 mL orange solution of **1** (10 mg, 0.005 mmol, 1 equiv.) in C_6D_6 in a 20 mL vial, was added a 0.5 mL C_6D_6 solution of $ClCPh_3$ (5.9 mg, 0.02 mmol, 4 equiv.). The reaction was allowed to stir at room temperature for overnight. Completion of the reaction was monitored through ^{31}P NMR spectrum using Triphenylphosphine (PPh_3) as an internal standard. The reaction can be driven to completion by one of the following methods: a) The solution can be photolyzed for fifteen minutes with a Xenon lamp in a J Young NMR tube, or alternatively, b) The reaction can be left stirring at room temperature in ambient light for three days. The NMR scale reaction was used to determine the best yield. This reaction however, can be scaled up to ~200-300 mg of **1**, with slightly lower yields than in the NMR scale reaction due to increased solubility of **3**.

If conducted on a larger scale, the same procedure is followed, with the exception of the use of toluene as a solvent (~20 mL). After completion, all volatiles were removed *in vacuo*. The red residue was extracted into toluene and filtered over Celite. The toluene was taken to a minimum (less than 2 mL) in a 20 mL vial and layered with 5 mL hexane. The vial was then stored at −35 ^{o}C overnight, resulting in the deposition of red crystals suitable for XRD (4 mg, 0.005 mmol, 49% yield). Due to the nature of the proposed mechanism, involving both parent imide and hydride complexes *en route* to **3**, there is inevitably always a small amount (5-10% contamination) of these species in isolated samples. Between this contamination, and the asymmetry of the resulting complex, all specific resonances are nearly impossible to assign due to overlapping peaks. In addition, *J* values cannot be determined for most resonances.

^{1}H NMR (400 MHz, 298 K, benzene-d_6): δ 7.13-7.00 (m, unable to resolve *J* coupling value, 6H, C-*H*, Ar), 6.68 (d, *J* = 8.0 Hz, 2H, C-*H*, Ar), 6.44 (dd, *J* = 8.8, 1.6 Hz, 1H, *ortho*-ArH_{Tolyl} from NPN' moiety), 5.93 (dd, *J* = 6.8, 3.6 Hz, 1H, *ortho*-ArH_{Tolyl} from PN moiety), 2.41-0.78 (multiple overlapping peaks from P-CHMe_2 and Ar-*Me*) ppm.

^{31}P{^{1}H} NMR (162 MHz, 298 K, benzene-d_6): δ 35.09 (1P, N*P*N'), 12.08 (1P, *P*N) ppm. Multiple attempts to obtain satisfactory elemental analysis were unsuccessful due to the thermal sensitivity of this complex.

Improved Synthesis of Parent Imido, $(PN)_2Ti{\equiv}NH$ (4) from 1 and Isotopic Labelling Studies.

To a 3 mL orange solution of **1** (20 mg, 0.0105 mmol, 1 equiv.) in toluene in a 20 mL vial, 1 mL toluene solution of phenol (1.98 mg, 0.0211 mmol, 2 equiv.) was added dropwise. The color of the reaction mixture was changed to magenta within few minutes and the reaction was further stirred for two days at room temperature to allow the completion of the reaction with the formation of the white color precipitate of potassium phenoxide. After completion the reaction, all volatiles were removed *in vacuo* and the deep red residue was extracted into toluene and filtered over Celite. The improved yield (94%) of the parent imido, $(PN)_2Ti{\equiv}NH$ (**4**) was realized when the same reaction was performed in C_6D_6 using PPh_3 as internal standard. The product $(PN)_2Ti{\equiv}NH$ (**4**) was identical with reported parent imide, and characterized through ^1H and ^{31}P NMR spectroscopy as well as IR spectrometry.[3]

While the same reaction was performed for the preparation of isotope of parent imido, i.e, $(PN)_2Ti{\equiv}ND$ (**4**-d_1), using 3 mL orange solution of **1** (20 mg, 0.0105 mmol, 1 equiv.) in toluene and phenol-d_6 (2.1 mg, 0.0211 mmol, 2 equiv.) at room temperature for two days, dark red color was observed along with precipitation of PhOK-d_5. The identical work up furnished the isotopic $(PN)_2Ti{\equiv}ND$ (**4**-d_1) with 91% yield.

^{1}H NMR (400 MHz, 298 K, benzene-d$_6$): δ 7.12 (d, J = 7.6 Hz, 2H, *meta*-ArH_{Tolyl}), 7.05 (d, J = 7.2 Hz, 2H, *meta*-Ar$H_{Mesityl}$), 7.01 (d, J = 8.0 Hz, 2H, *meta*-Ar$H_{Mesityl}$), 6.84 (s, 2H, *meta*-ArH_{Tolyl}) 6.29 (dd, J = 5.2, 2.8 Hz, 2H, *meta*-ArHTolyl), 2.21 (s, 6H, CH_{3Tolyl}), 2.19 (s, 6H, *ortho*-C$H_{3Mesityl}$), 2.18 (s, 6H, *ortho*-C$H_{3Mesityl}$), 2.11 (s, 6H, *para*-C$H_{3Mesityl}$), 2.06 (sept, J = 7.2 Hz, 4H, P-CHMe$_2$), 1.20, 1.18, 1.16, 1.15, 1.05, 1.03, 1.02, 1.00 (s, 3H ea, P-CHMe_2) ppm.

^{2}H{^{1}H} NMR (61.402 MHz, 298 K, benzene-d$_6$): δ 5.03 ppm.

^{31}P{^{1}H} NMR (162 MHz, 298 K, benzene-d$_6$): δ 15.55 (s, 2P, PN) ppm.

FT-IR: $\nu_{Ti=ND}$ = 2517.6 cm^{-1}.

Synthesis of (NPN')(PN)Ti(H) (5) from Complex $(PN)_2Ti(N_3)$ (6).

A 1 mL orange solution of **6** in C_6D_6 (10 mg, 0.012 mmol) was photolyzed by a Xenon lamp for 15 minutes in a J-Young NMR tube and conversion was monitored by ^{31}P NMR spectroscopy. The solution turns slightly darker upon photolysis. After completion, all volatiles were removed *in vacuo* and the reaction mixture was filtered over Celite. While stability and increased solubility of this complex prevents bulk characterization, cooling a solution of **5** in 1 mL *n*-hexane at −35 ^{o}C overnight, resulted in the deposition of some reddish brown crystals of **5** suitable for single crystal XRD. While isolated yields of **5** from crystallization was not reliable, although monitoring the solution with internal standard (PPh_3) through ^{31}P NMR spectrum yielded less than 49% conversion, as expected given the determined degradation of 50% of the ligand scaffold (4.5 mg, 0.006 mmol, ~50%), However, since bulk isolation of this complex free from starting materials

has not been possible, characterization by ^{1}H NMR spectrum has also not been possible.

^{31}P{^{1}H} NMR (162 MHz, 298 K, benzene-d$_6$): δ 22.34 (1P, N*P*N'), 7.41 (1P, *P*N) ppm.

Preparation of (NPN')(PN)Ti(H) (5) from (PN)$_2$Ti≡NH (4) and Isotopic Labelling Studies.

A 0.6 mL dark red solution of **4** in C_6D_6 (10 mg, 0.0134 mmol) was photolyzed by a Xenon lamp for 15 minutes in a J-Young NMR tube and the conversion was monitored by ^{31}P NMR spectroscopy. The solution turns darker upon photolysis. Alternatively, the conversion of **4** to **5** is sluggish at room temperature and several days required for complete conversion to **5**. After completion, all volatiles were removed *in vacuo* and the reaction mixture was filtered over Celite. However, the bulk isolation of this complex, (NPN')(PN)Ti(H) (**5**) free from other unidentifiable reaction mixture has not been possible. Similarly, isotope labeling experiment was performed using (PN)$_2$Ti≡ND (**4**-*d$_1$*) and the conversion was monitored by ^{31}P NMR spectroscopy.

^{31}P{^{1}H} NMR (162 MHz, 298 K, benzene-d$_6$): δ 22.34 (1P, N*P*N'), 7.41 (1P, *P*N) ppm.

Preparation of (NPN')(PN)Ti(Cl) (3) from (NPN')(PN)Ti(H) (5).

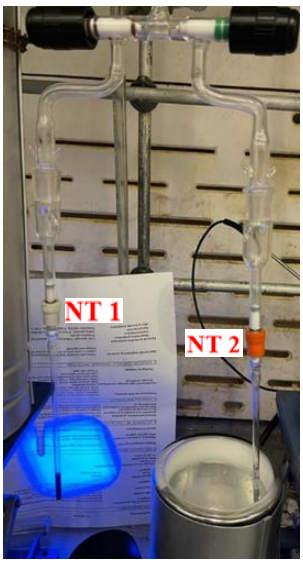
A solution of **5** (10 mg, 0.0134, 1 equiv.) in benzene-d$_6$ (0.7 mL) in a J-Young NMR tube was treated with ClCPh$_3$ (3.8 mg, 0.0134 mmol, 1 equiv.) at room temperature. After mixing the aforementioned solutions, immediately ^{1}H and ^{31}P NMR spectra were recorded, which manifests clean and quantitative formation of **3** displaying ^{31}P NMR resonances at δ 35.09 and 12.08 ppm along with formation of triphenylmethane, at δ 4.93 ppm in ^{1}H NMR spectrum.

Photolytic Conversion of (PN)$_2$Ti(N$_3$) (6) to (PN)$_2$Ti≡NH (4) and (NPN')(PN)Ti(H) (5).

A solution (1 mL) of **6** in C_6D_6 (5 mg, 0.006 mmol) was photolyzed by a Xenon lamp for 5 minutes in a J-Young NMR tube and conversion was monitored by ^{31}P NMR spectroscopy. The solution turns slightly darker and after 5 minutes all (PN)$_2$Ti(N$_3$) (**6**) was converted to mixture of (PN)$_2$Ti≡NH (**4**) and (NPN')(PN)Ti(H) (**5**) along with unidentifiable product. Moreover, we have quantified the formation of **4** using PPh$_3$ as an internal standard, furnishing 48% yield. Further photolysis of the reaction mixture for another 10 minutes afforded only **5**, displaying the resonance at δ 22.34 (1P, N*P*N'), and 7.41 (1P, *P*N) ppm in ^{31}P NMR spectrum.

Detection of Molecular Hydrogen during the Formation of (NPN')(PN)Ti(I) (2) from [(PN)$_2$Ti≡N{μ$_2$-K(OEt$_2$)}]$_2$ (1).

Inside the nitrogen filled glove box, J. young NMR tube (NT 1) was charged with dimer **1** (38 mg, 0.02 mmol), I_2 (10.2 mg, 0.04 mmol), and C_6D_6 (0.6 mL) and connected through a bridgehead connector with another J. young NMR tube (NT 2) loaded with styrene (0.1 mmol) and Pd/C (55 mg) in THF (1.0 mL). Then the NMR tube (NT 2) was degassed, kept in static vacuum, and the other NMR tube (NT 1) was charged with UV light (360 nm) for 15 minutes. The evolved hydrogen gas in NT 1 NMR tube could transfer to other NMR tube (NT 2) loaded with styrene and Pd/charcoal, while the NT 2 was dipped in liquid N_2 to allow the transfer of evolved hydrogen gas. Next, we warmed the bridgehead connector to make sure the transfer of maximum evolved hydrogen gas and after tightening of NT 2, it was warmed to room temperature and then placed in a preheated oil bath at 120 ^oC for overnight. ^1H NMR spectroscopy of the reaction mixture in $CDCl_3$ suggests 7% reduction of styrene to ethylbenzene (Fig. S16), which indicates one equivalent dimer produced roughly 0.35 equivalent of H_2; it might be complete transfer of evolved hydrogen is not possible as dissolve H_2 is also present in the reaction mixture.



Spectroscopic Characterization:

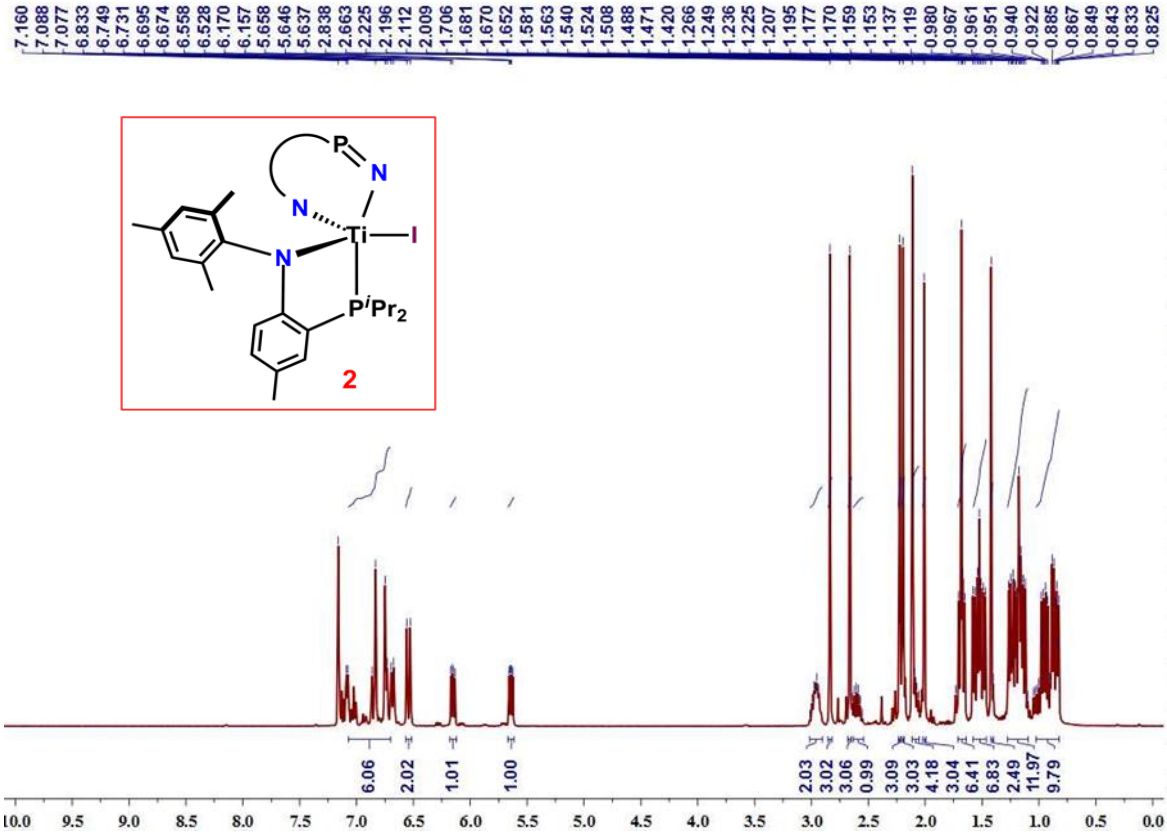


Figure S1. ^{1}H NMR (400 MHz, 298 K, benzene-d_6) spectrum of (NPN')(PN)Ti(I) (**2**). Unlabeled peaks correspond to impurities that could not be identified.

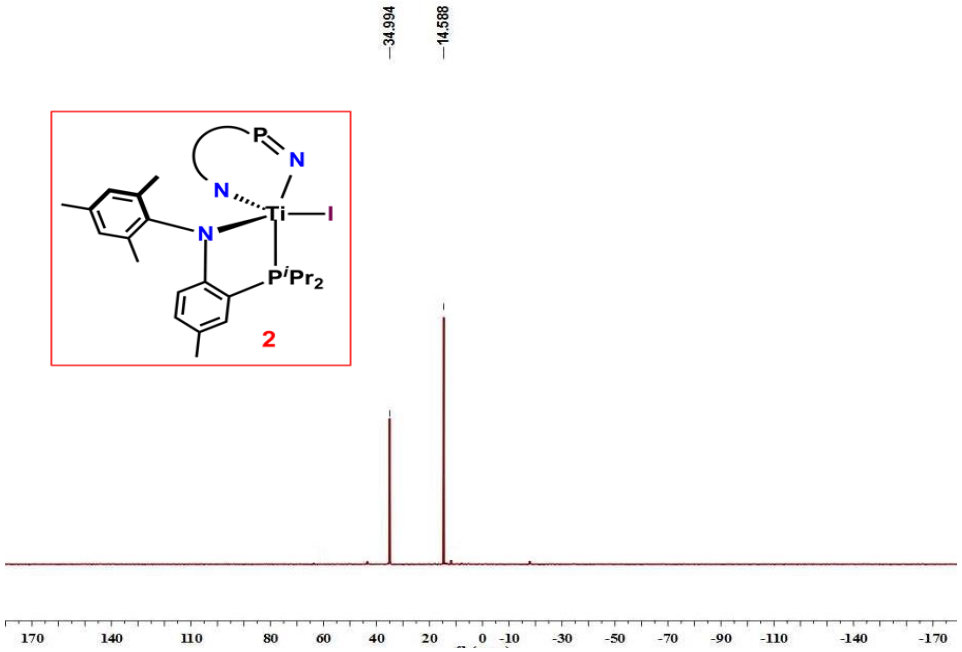


Figure S2. ^{31}P{^{1}H} NMR (162 MHz, 298 K, benzene-d_6) spectrum of (NPN')(PN)Ti(I) (**2**).

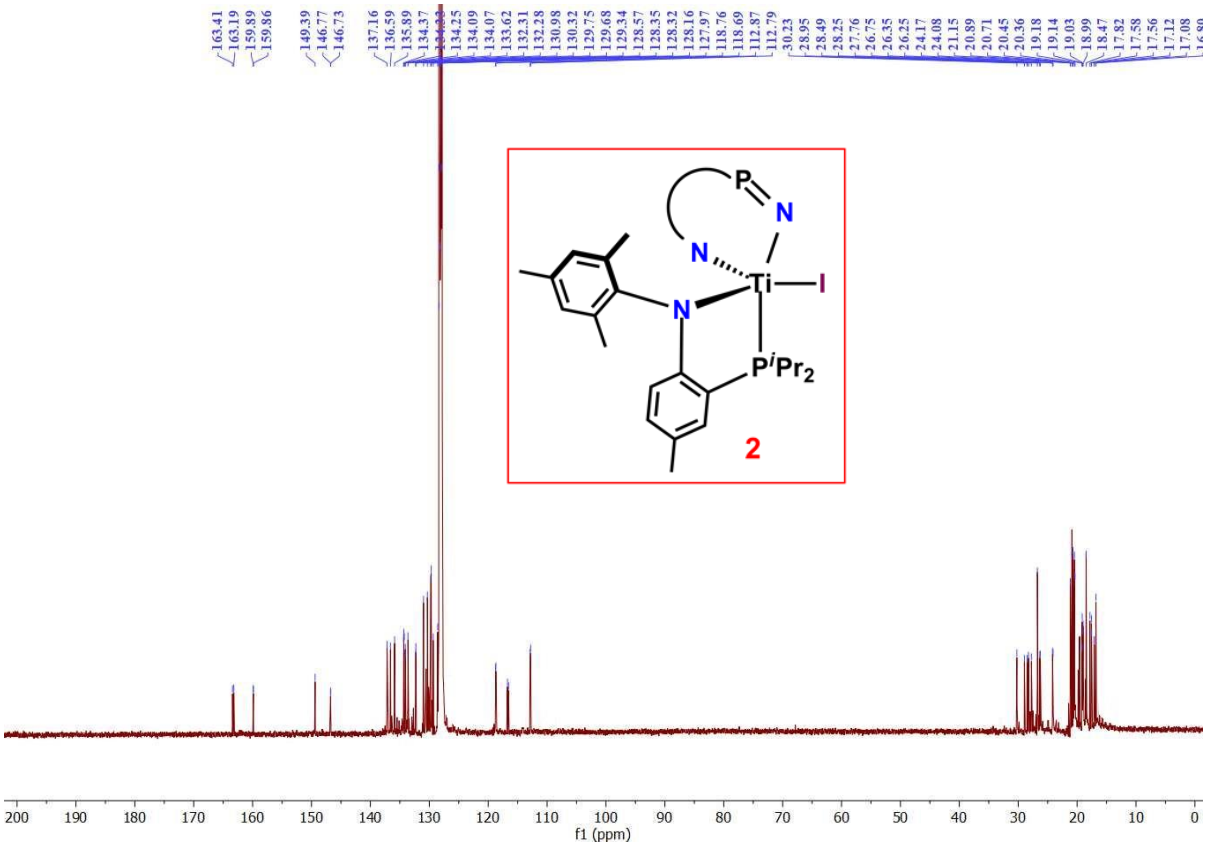


Figure S3. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, 298 K, benzene-d_6) spectrum of (NPN')(PN)Ti(I) (**2**).

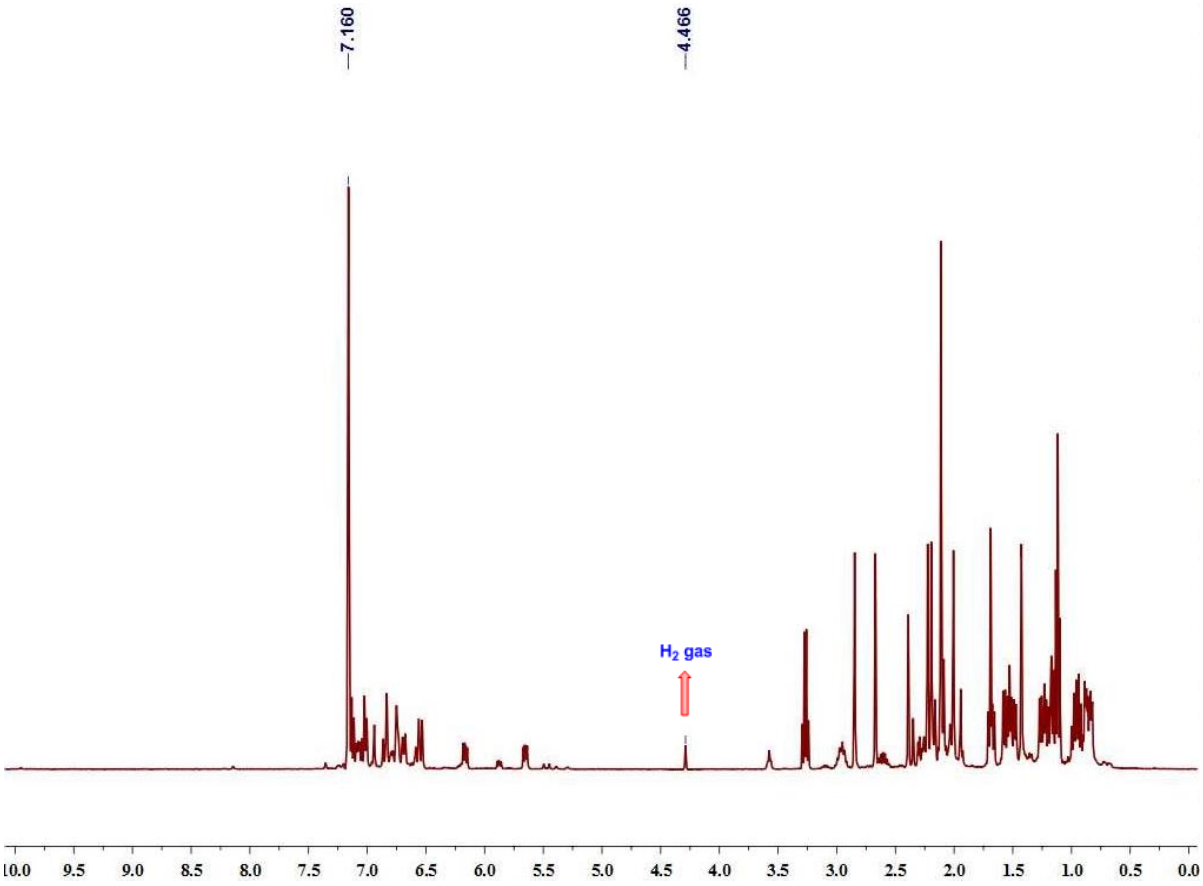


Figure S4. ^{1}H NMR (400 MHz, 298 K, benzene-d_6) spectrum of the reaction mixture containing **1** and two equiv. I_2 in a J-Young NMR tube after 2h, exhibiting a resonance at δ4.47 ppm for the formation of dihydrogen gas.

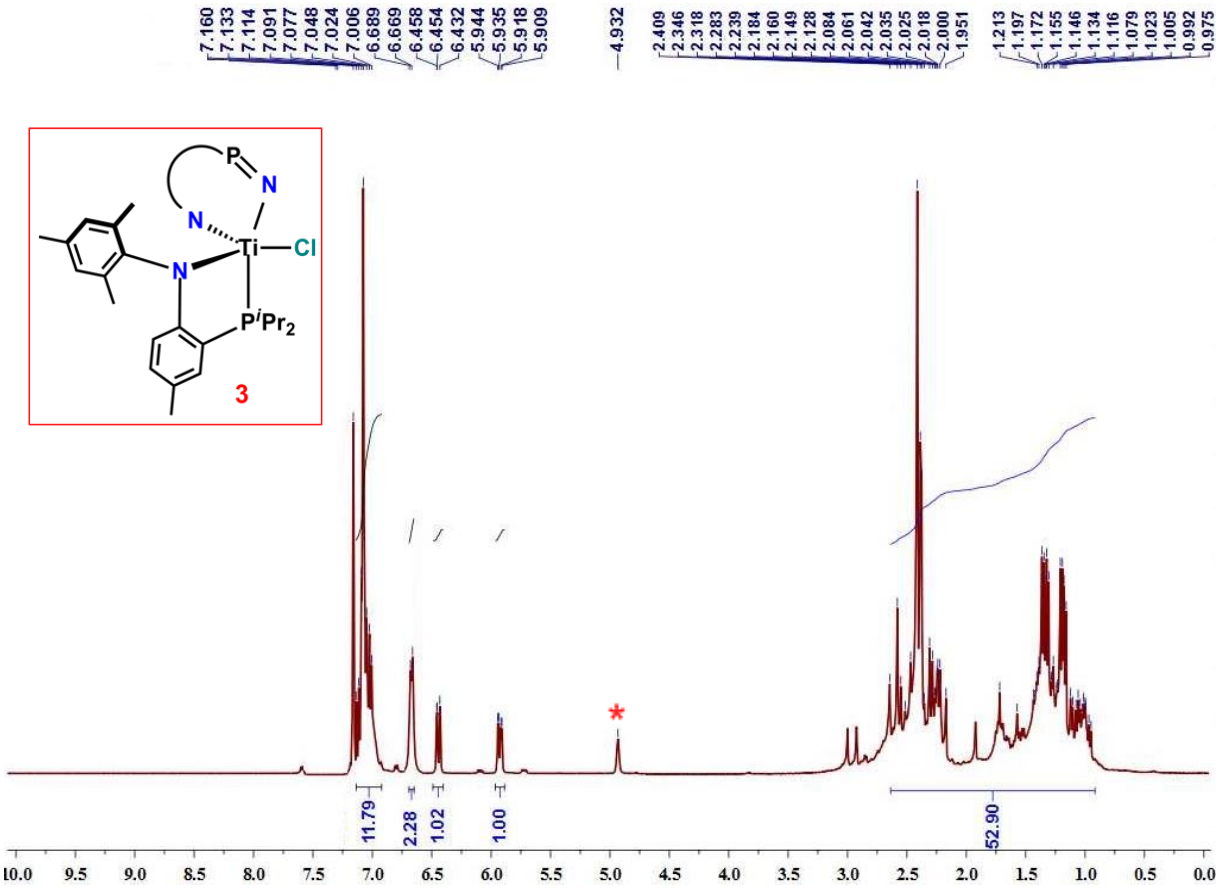


Figure S5. ^{1}H NMR (400 MHz, 298 K, benzene-d$_6$) spectrum of (NPN')(PN)Ti(Cl) (**3**). * peak at 4.93 ppm correspond to C-H proton of triphenylmethane, and other unlabeled peaks correspond to unidentified impurities.

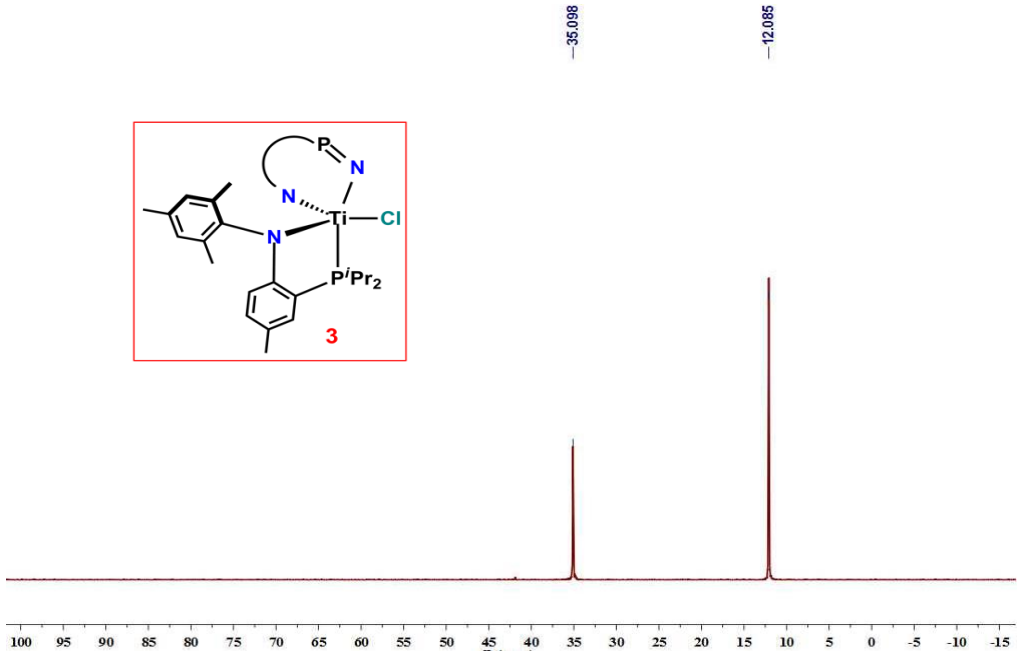


Figure S6. ^{31}P{^{1}H} NMR (162 MHz, 298 K, benzene-d$_6$) spectrum of (NPN')(PN)Ti(Cl) (**3**).

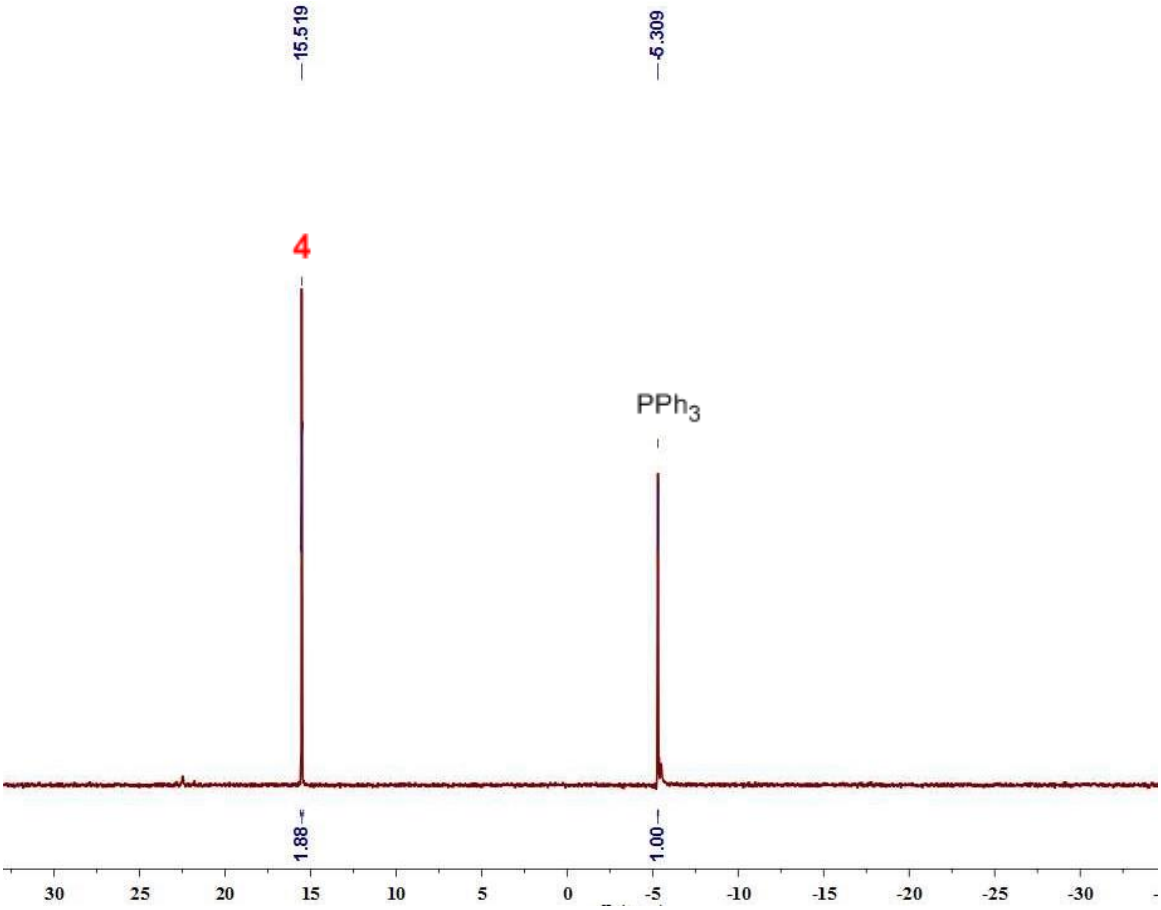


Figure S7. $^{31}P\{^{1}H\}$ NMR (162 MHz, 298 K, benzene-d_6) spectrum of improved synthesis of $(PN)_2Ti{\equiv}NH$ (**4**) from reaction of **1** and PhOH, where PPh_3 used as internal standard.

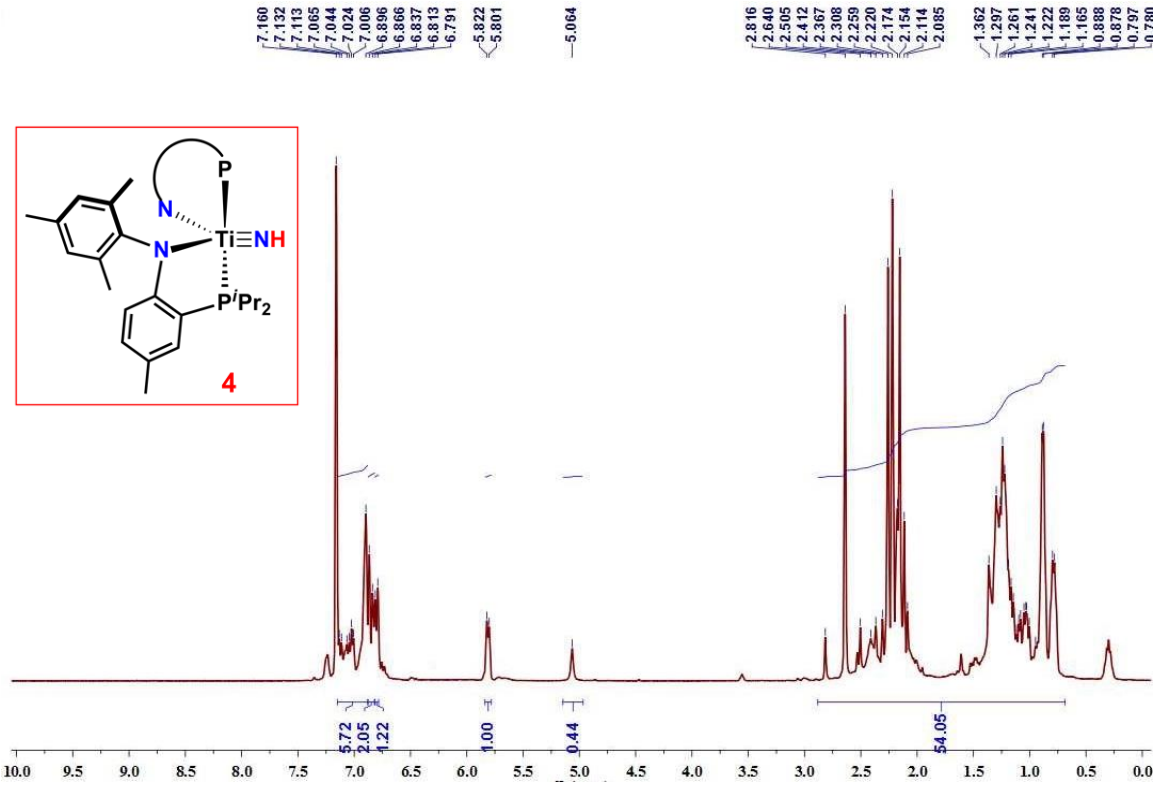


Figure S8. ^{1}H NMR (400 MHz, 298 K, benzene-d$_6$) spectrum of (PN)$_2$Ti≡NH (**4**).

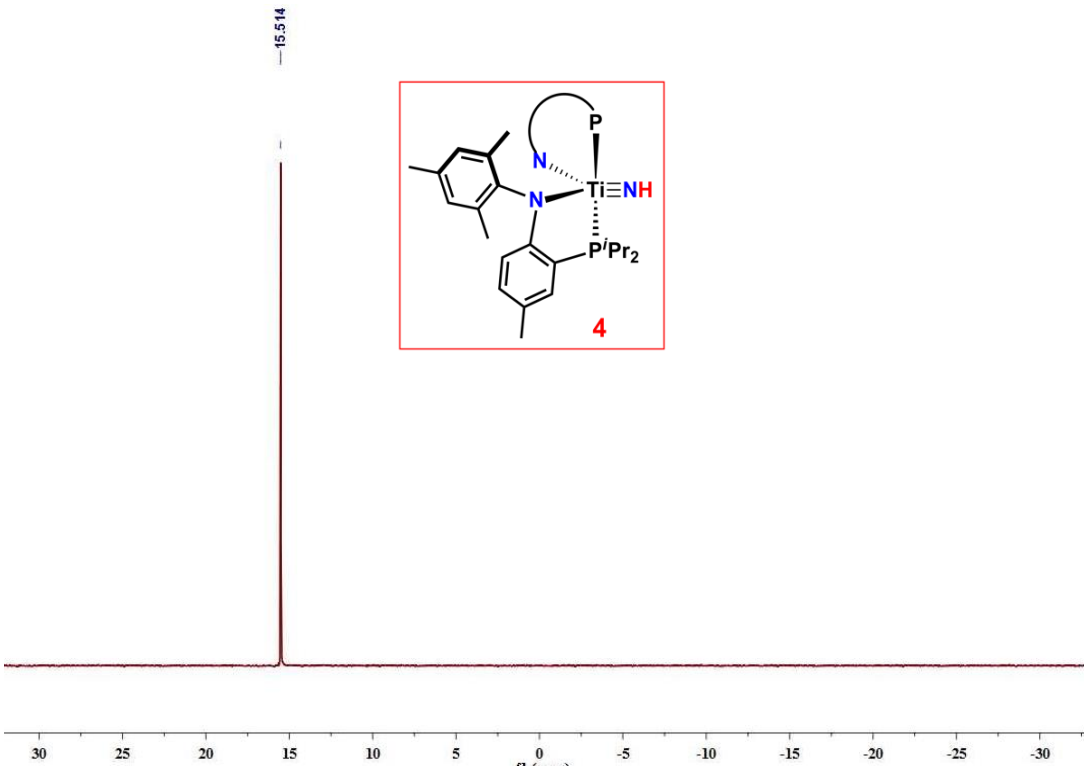


Figure S9. ^{31}P{^{1}H} NMR (162 MHz, 298 K, benzene-d$_6$) spectrum of (PN)$_2$Ti≡NH (**4**).

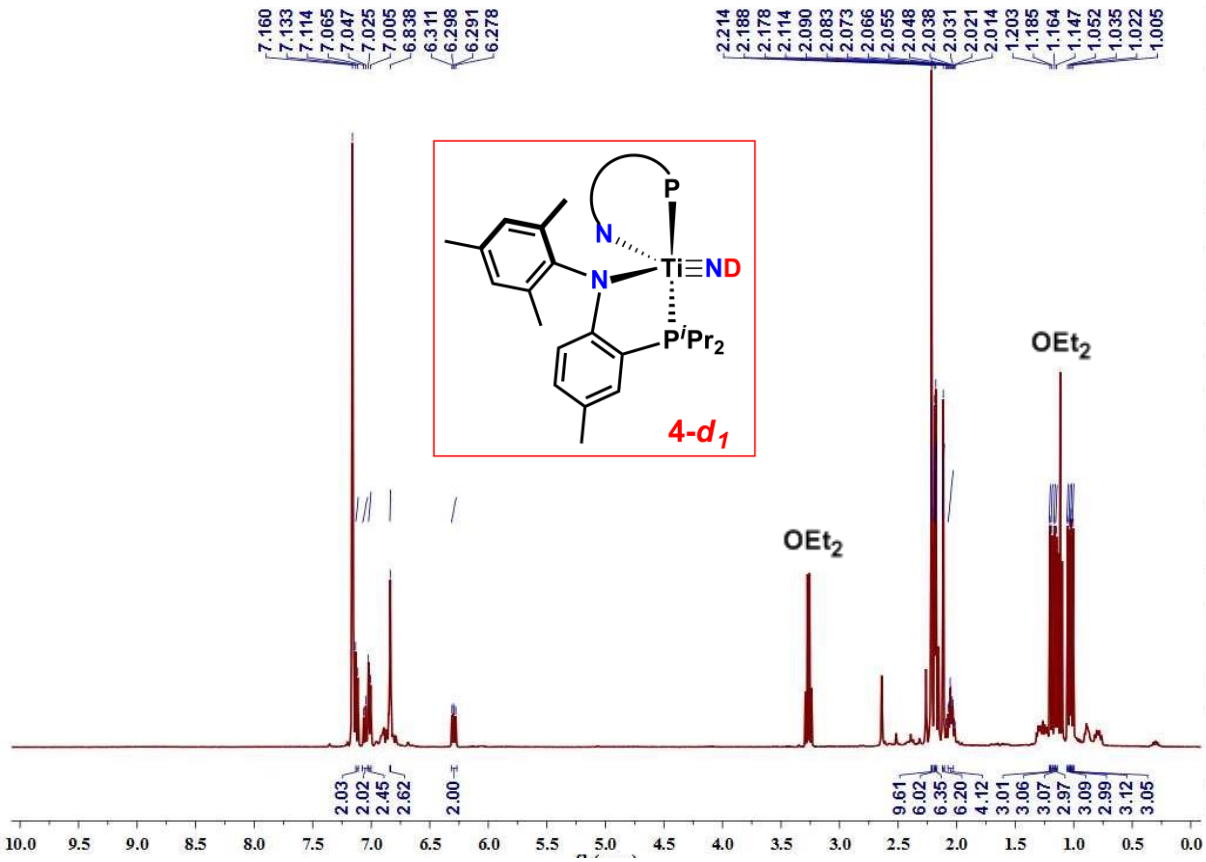


Figure S10. ^{1}H NMR (400 MHz, 298 K, benzene-d$_6$) spectrum of (PN)$_2$Ti≡ND (**4-***d*$_1$). Unlabelled peaks correspond to impurities that could not be identified.

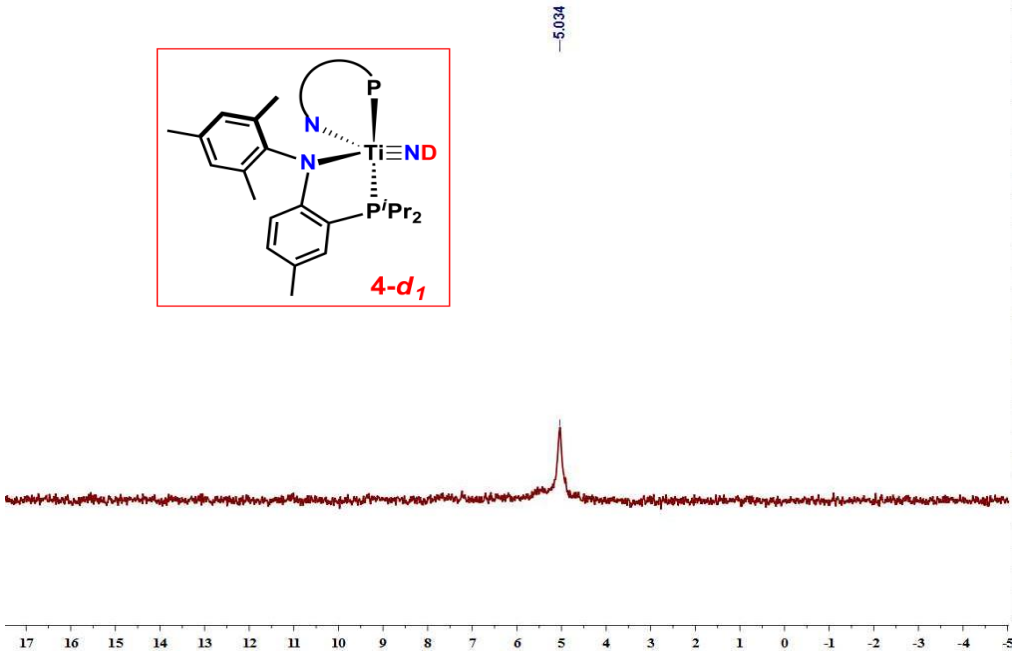


Figure S11. ^{2}H{^{1}H} NMR (61.402 MHz, 298 K, benzene-d$_6$) spectrum of (PN)$_2$Ti≡ND (**4-***d*$_1$).

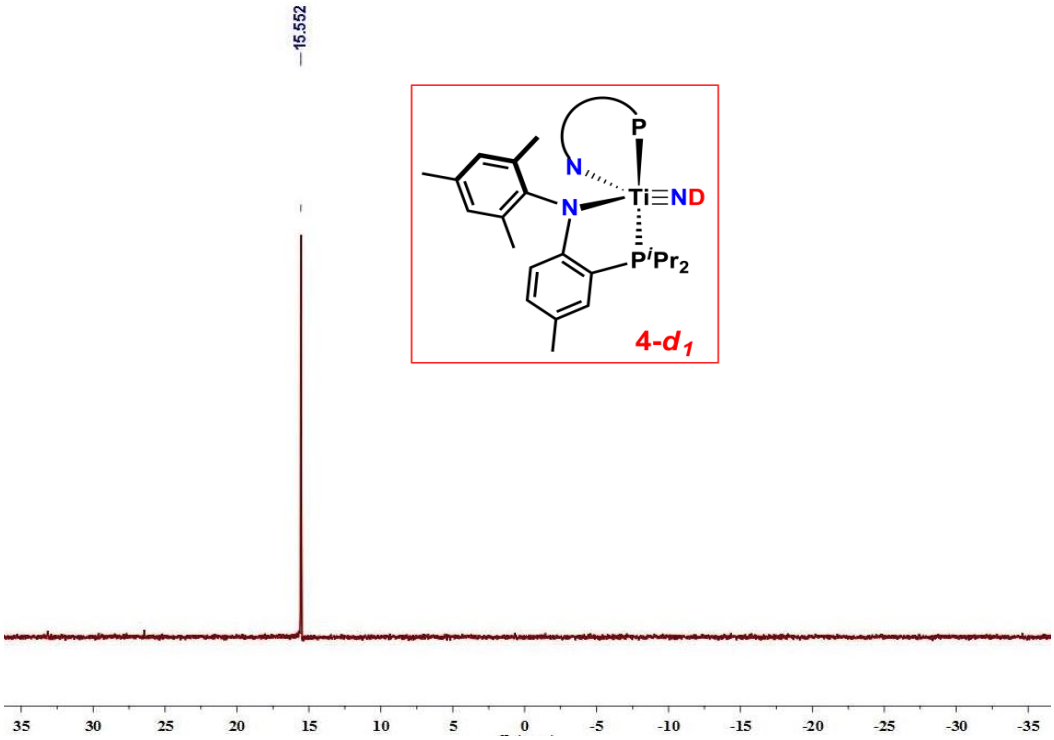


Figure S12. $^{31}P\{^1H\}$ NMR (162 MHz, 298 K, benzene-d_6) spectrum of $(PN)_2Ti{\equiv}ND$ (**4-***d*$_1$).

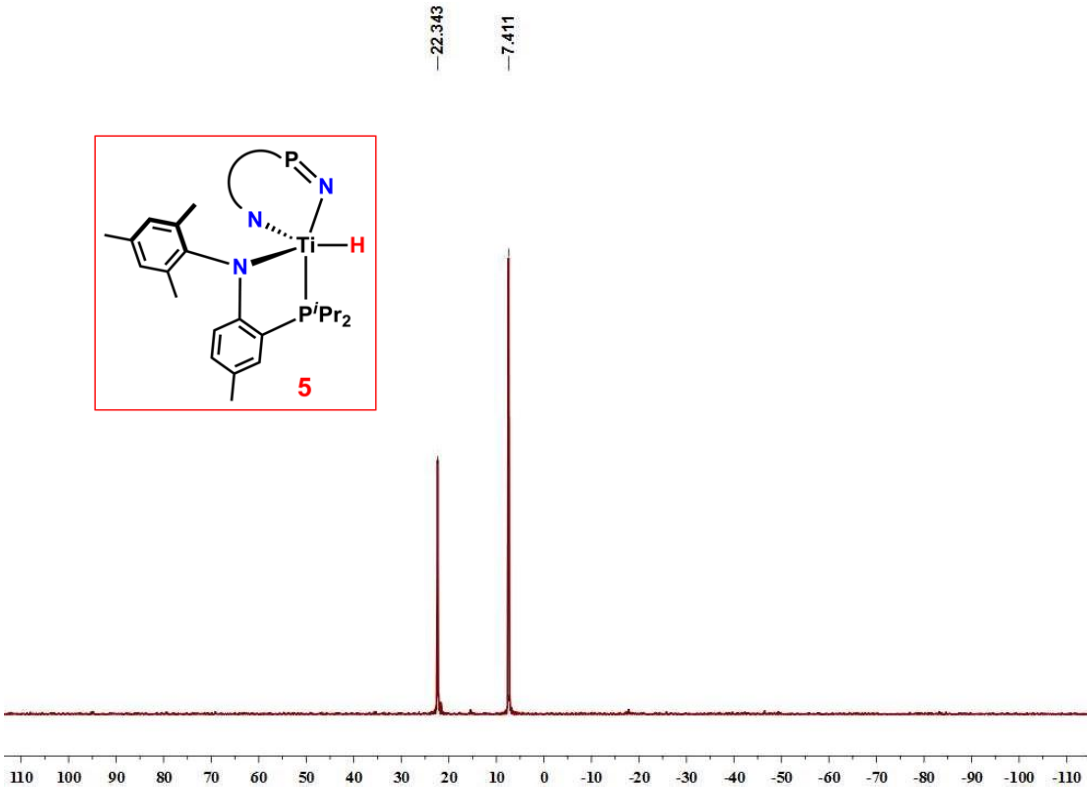


Figure S13. $^{31}P\{^1H\}$ NMR (162 MHz, 298 K, benzene-d_6) spectrum of (NPN')(PN)Ti(H) (**5**).

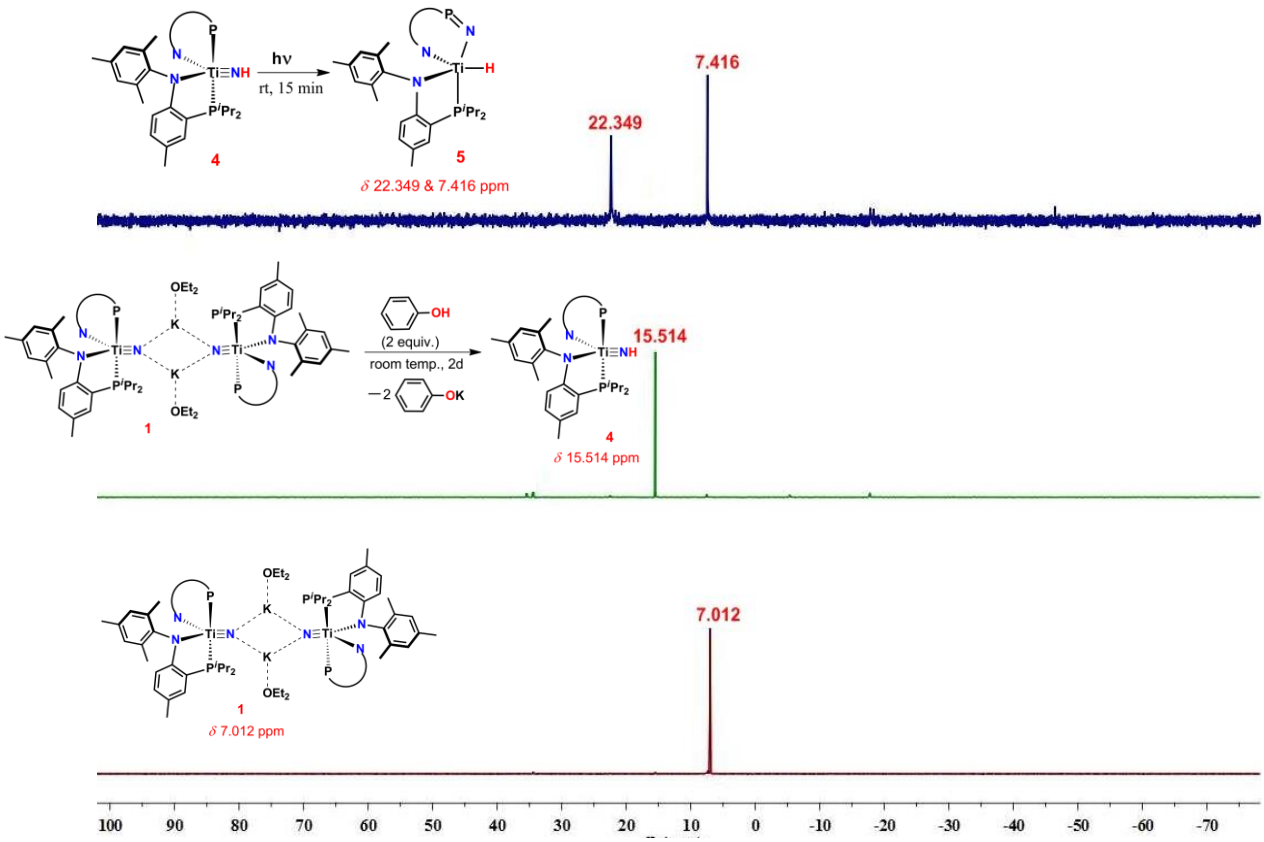


Figure S14. Stack $^{31}P\{^{1}H\}$ NMR (162 MHz, 298 K, benzene-d_6) spectra for the formation of parent imido, **4** and its conversion to **5**.

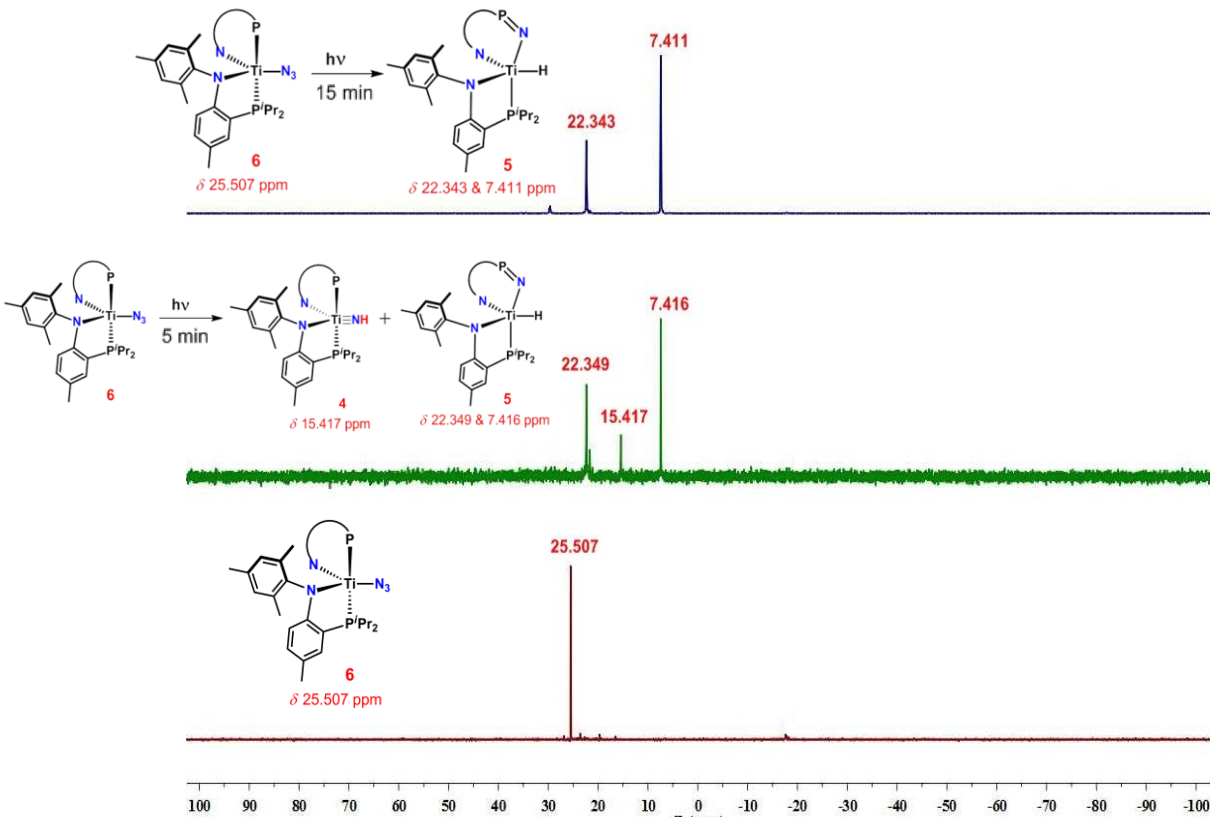


Figure S15. Stack $^{31}P\{^{1}H\}$ NMR (162 MHz, 298 K, benzene-d_6) spectra for the formation of **4** and **5** from **6** upon photolysis.

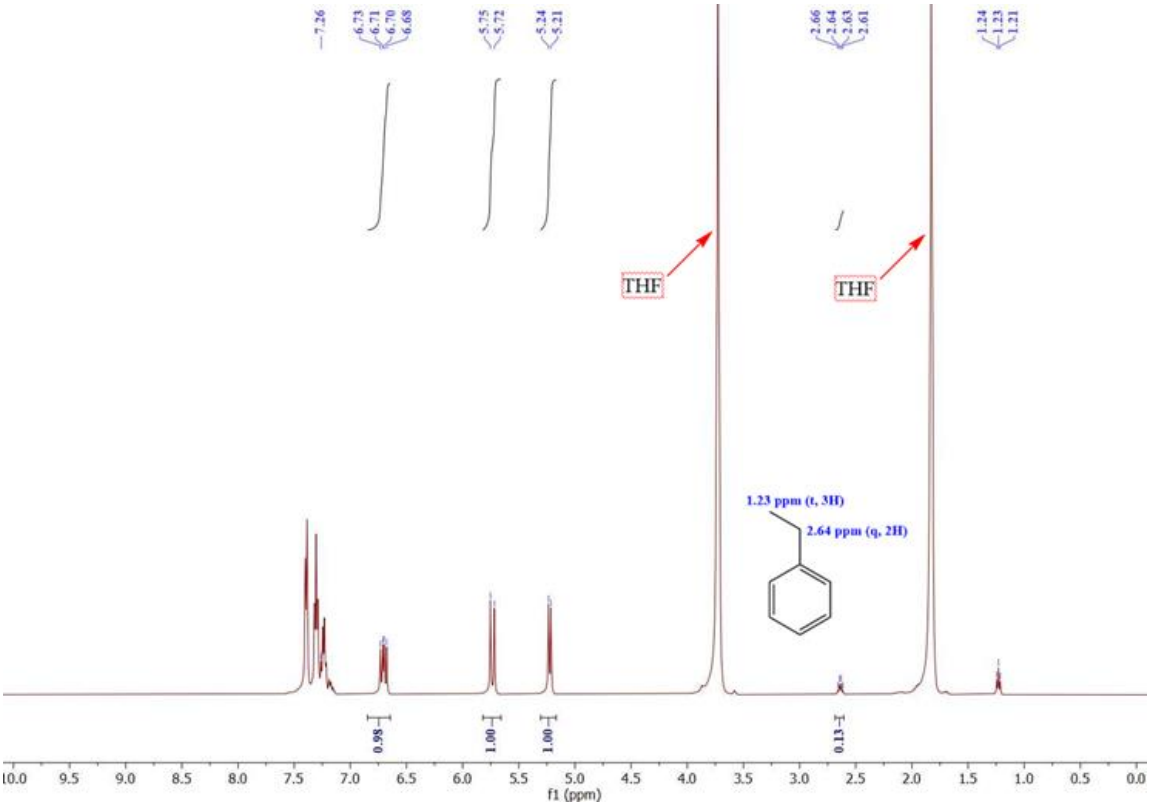


Figure S16. ^{1}H NMR (500 MHz, 298 K, Chloroform-d_3) spectrum for the reduction of styrene to ethylbenzene using in situ evolved hydrogen gas during the formation of of (NPN')(PN)Ti(I) (**2**) from $[(PN)_2Ti{\equiv}N\{\mu_2\text{-}K(OEt_2)\}]_2$ (**1**).

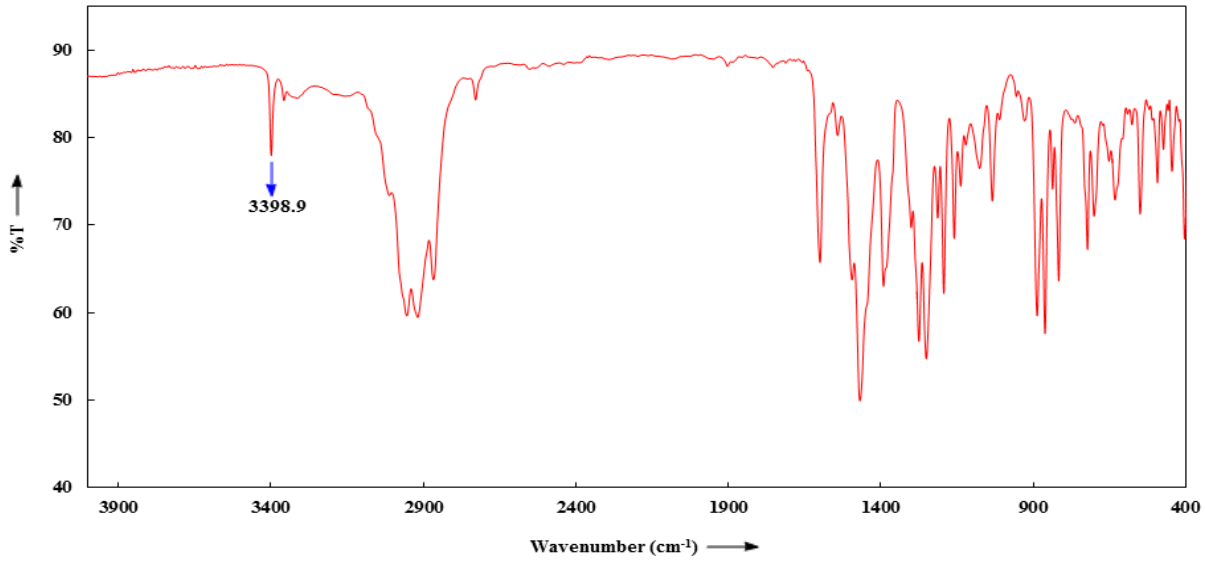


Figure S17. IR spectrum of **4**.

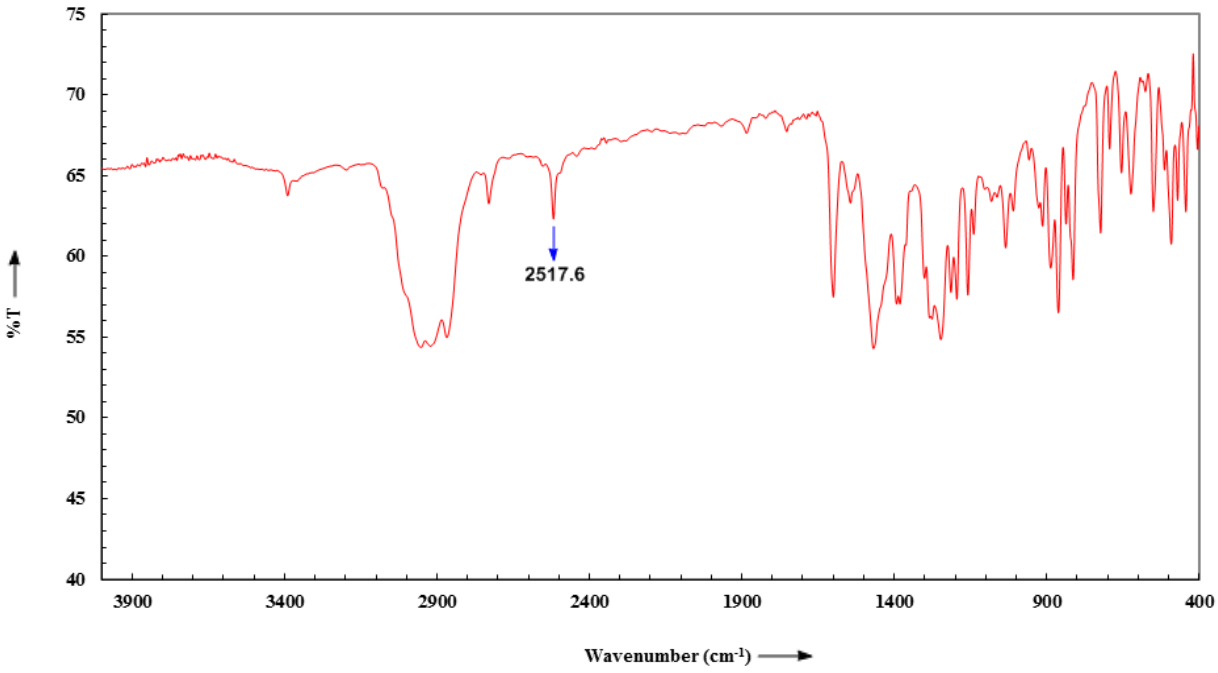


Figure S18. IR spectrum of **4-d_1**.

EPR spectroscopy.

The experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer (Bruker BioSpin Rheinstetten) equipped with a He temperature control cryostat system (Oxford Instruments). Simulations of the EPR spectra were performed by iteration of the anisotropic g-values and line widths using the EPR simulation program W95EPR developed by Professor Frank Neese.

EPR property calculations of species A and B:

The geometries of species **A** and **B** were optimized with the Turbomole program[4] coupled to the PQS Baker optimizer[5] *via* the BOpt package.[6] Geometries were fully optimized as minima or transition states using the BP86 functional,[7] the Turbomole def2-TZVP basis set[8] and a small grid size (m4). To reduce computation time, the resolution-of-identity (ri) approximation[9] was applied. Grimme's dispersion corrections (version D3, disp3, 'zero damping)' were applied to include Van der Waals interactions.[10]

The EPR parameters[11] of species **A** and **B** were calculated with the ADF[12] program system at the BP86/ZORA/TZP level, using the coordinates from the structure optimized in Turbomole as input. Separate unrestricted SCALAR ZORA and restricted SPINORBIT ZORA calculations were used to compute the HFI-tensors and g-tensors, respectively.

EPR property calculations for formation species (B) upon photolysis of 6:

Double integral before irradiation: ~4.0 x10^8

Double integral after irradiation: ~3.6x10^8

Double integral after irradiation + short warm-up: ~2.0x10^8

So, the in-cavity irradiation retains nearly 100% integral intensity, containing both **B** and **6** (and, as mentioned in the text, perhaps some unknown species leading to broadening). However, the total signal intensity is for nearly 100% retained (before warming-up).

After shortly warming-up the irradiated sample, about ~50% of the initial signal intensity remains, which consists of a 2:1 ratio of B:6 based on the simulation ratio (which are also based on relative double integrals).

This implies that the EPR photolysis experiment followed by warming-up the sample and refreezing the amount of species B formed and retained in the sample is ~33%. The amount of starting azide in this sample is ~17%. The ratio of the species **B** and **6** in Figure 3 in manuscript is 2:1 (**B**:**6**).

Crystallographic Experimental Details.

Crystallographic data are summarized in Tables 2.3-2.4. Suitable crystals for X-ray analysis of **2**, **3** and **5** were placed on the end of a Cryoloop coated in NVH oil. Data for single crystal structure determinations were taken on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 A) at a temperature of 100(1) K. Rotation frames were integrated using SAINT,[13] producing a listing of non-averaged *F*2 and s(*F*2) values The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.[14] The initial structures were solved by dual methods – SHELXT.[15] Refinement was by full-matrix least squares based on *F*2 using SHELXL.[16] All reflections were used during refinement.

Table S1. Summary of Structure Determination of Compound 2 • 0.5(C_6H_{14})

Empirical formula	$C_{93}H_{136}N_6P_4I_2Ti_2$
Formula weight	1811.56
Temperature/K	100(1) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
a	13.8717(7) Å
b	14.6574(7) Å
c	23.5957(12) Å
α	82.944(2)°
β	84.692(2)°
γ	83.895(2)°
Volume	4718.8(4) $Å^3$
Z	2
d_{calc}	1.275 Mg/m^3
Absorption coefficient (μ)	0.936 mm^{-1}
F(000)	1892
Crystal size, mm^3	0.32 x 0.20 x 0.03
2θ range for data collection	1.41-27.63°
Index ranges	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -30 ≤ l ≤ 30
Reflections collected	117385
Independent reflections	21720 [R(int) = 0.0393]
Completeness to theta = 27.63°	99.0 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.7456 and 0.6951
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	21720 / 6 / 999
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R1 = 0.0381, wR2 = 0.0880
Final R indexes [all data]	R1 = 0.0540, wR2 = 0.0933
Largest diff. peak/hole	2.752 and -1.149 e.$Å^{-3}$

Table S2. Summary of Structure Determination of Compound 3 • 0.5(C_6H_{14})

Empirical formula	$C_{44}H_{62}N_3P_2ClTi$
Formula weight	821.34
Temperature/K	100(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
a	11.3590(4) Å
b	12.5559(5) Å
c	17.5731(6) Å
α	70.559(2)°
β	82.073(2)°
γ	68.708(2)°
Volume	2201.68(14) $Å^3$
Z	2
d_{calc}	1.239 Mg/m^3
Absorption coefficient (μ)	0.363 mm^{-1}
F(000)	882
2θ range for data collection	2.83-27.54°
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -22 ≤ l ≤ 22
Reflections collected	7721
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R1 = 0.0521, wR2 = 0.1384

Table S3. Summary of Structure Determination of Compound 5

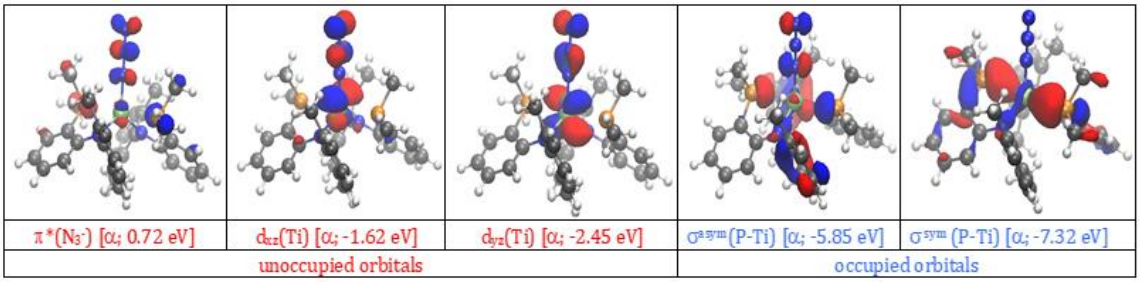
Empirical formula	$C_{44}H_{62}N_3P_2Ti$
Formula weight	742.80
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a	47.9256(11)Å
b	11.7869(3)Å
c	42.7389(10)Å
α	90°
β	120.6180(10)°
γ	90°
Volume	20777.0(9)Å^3
Z	20
d_{calc}	1.187 g/cm^3
μ	0.316 mm^{-1}
F(000)	7980.0
Crystal size, mm	0.25 × 0.12 × 0.05
2θ range for data collection	1.974 - 55.048°
Index ranges	-62 ≤ h ≤ 62, -15 ≤ k ≤ 15, -55 ≤ l ≤ 55
Reflections collected	242376
Independent reflections	23909[R(int) = 0.0735]
Data/restraints/parameters	23909/394/1209
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0939, wR_2 = 0.2489
Final R indexes [all data]	R_1 = 0.1322, wR_2 = 0.2808
Largest diff. peak/hole	2.53/-1.85 eÅ^{-3}

Computational Details.

All geometry optimization, frequency and solvent calculations were carried out using DFT as implemented in the Gaussian09 program package[17]. Final geometry optimizations were performed using the hybrid-meta-GGA TPSSh[18] functional in combination with the correlation consistent cc-pVDZ basis set[19]. Analytical vibrational frequency calculations were carried out at the same level of theory to confirm that the optimized structures correspond to either minima or first-order saddle points (transition state) of the potential energy surface. Dispersion was taken into account in all calculations, including geometry optimizations, using Grimme's D3 method[20] with the original D3 damping function and with SR6 and S8 parameters of 1.660 and 1.105, respectively, originally recommended for TPSS. The energies of the optimized structures were reevaluated using the triple-ζ basis set cc-pVTZ[21]. Solvation energies for toluene were also computed at the triple-ζ basis set (TPSSh/cc-pVTZ) using the SMD implicit solvation model[22]. We used the Solvent Accessible Surface (SAS) method to create the molecular surface of the solute-solvent boundary where the atomic radii used to generate the solute surface were the followings: H (1.150 Å), P (2.074 Å), C (1.900 Å), N (1.600 Å), and Ti (1.587 Å) while the radius of solvent (toluene) was set to be 2.70 Å. In all of these calculations an ultrafine grid has been used.

Quasi-restricted orbitals were computed at the TPSSh/def2-TZVP (TightSCF SlowConv GridX5 Grid5) level of theory using the ORCA (version 4.0.1.2) program package.[23]

Figure S19. Optimized Structure for Formation of B from 6 (without going through A) Under Photoexcitation at the TPSSh/def2-TZVP Level of Theory Using ORCA.



TD-DFT calculations on the optimized structure of the Ti(III)-azide species **6** were also performed to determine if N_2 loss from the azide could occur without proceeding through putative **A** being generated and ultimately resulting in the phosphine oxidized species **B**. Complex **6** has doublet ground state configuration and hence Gaussian cannot do open-shell TD-DFT. For this reason, ORCA was used (method: TPSSh/def2-TZVP) for this calculation. Excitations in both alpha and beta subspaces were calculated and analyzed to assess the plausibility of excitations from Ti-P interactions to the azido ligand. Orbitals above exemplify the orbitals considered as donor (Ti-P representing MOs) and acceptor orbitals (N_3 related MOs) in the alpha manifold. The following main conclusions can be drawn from these calculations;

1. The symmetric Ti-P bonding interactions (exemplified by σ^{sym} (P-Ti) have very negative energies and excitations from these orbitals were not observed.
2. Excitations from the asymmetric Ti-P bonding interactions σ^{asym} (P-Ti) are possible and in the range of 180 – 400 [nm] roughly. The σ^{asym} (P-Ti) <-> d_{yz} (Ti) excitation is computed to be at 396.5 [nm] and has a nonnegligible/notable oscillator strength.
3. The formally π* orbitals of N_3- (like π*(N_3-)) are rather high in energy and excitation from σ^{asym}(P-Ti) orbital, for example, to π*(N_3-) is at 198.1 [nm] and has a negligible oscillator strength. Most importantly, excitations to these π* orbitals of N_3- are found in the < 180 [nm] region, which is beyond the characteristic spectrum of typical Xenon lamp being used.

Based on points 1-3 it can be concluded that N_2 loss from **6** does not likely originate from an excited state in which electrons from the Ti-P interactions are promoted. The σ^{asym} (P-Ti) <-> d_{yz}(Ti) excitation plausibly can, nevertheless, generate a reactive phosphorous center and while the accepting orbital d_{yz}(Ti) has very little amplitude on the nitrogen bound to Ti (let's call it N1), the donor orbital σ^{asym} (P-Ti) actually has some contribution at N1. As a result, this excitation (σ^{asym} (P-Ti) <-> d_{yz}(Ti)) makes N1 somewhat electrophilic and the P-centers reactive that could lead to direct phosphorus attach at N1.

Cartesian coordinates.

A (507)

Ti	-0.00001600	0.00000700	0.53728600
P	-2.05725500	-1.69128300	0.50673800
N	-0.80255200	1.83387100	-0.07644200
N	0.80254100	-1.83386000	-0.07650700
N	0.00001200	0.00005400	2.24022300
C	-0.21199400	3.08926600	-0.19404700
C	-0.94088200	4.25450900	-0.55147200
H	-2.00873500	4.17309500	-0.76028400
H	-0.90613400	6.37302100	-0.90181800
C	-2.19521500	1.79876400	-0.40792400
C	-2.58878600	1.62740700	-1.75436600
C	-3.95511900	1.61325600	-2.06343200
H	-4.26025000	1.47580200	-3.10527300
C	-4.93680600	1.75990600	-1.07181900
C	-4.51722600	1.96553400	0.25136000
H	-5.26756500	2.11582300	1.03366000
C	-3.16035100	2.00870100	0.60309100
C	-1.54079400	1.51440100	-2.83252400
H	-0.77326400	0.77150400	-2.56420200
H	-1.98629000	1.22757500	-3.79572400
H	-1.01049200	2.47332800	-2.96164100
C	-2.71908000	2.36406600	1.99998200
H	-3.55982100	2.31755300	2.70679800
H	-1.90942500	1.70326200	2.34570000
H	-2.31440700	3.39135000	2.01205000
C	0.21197900	-3.08925400	-0.19409400
C	0.94085400	-4.25449400	-0.55154900

H	2.00870200	-4.17308300	-0.76038700
C	0.31429300	-5.49644300	-0.62634400
H	0.90610000	-6.37300300	-0.90191400
C	-1.05068700	-5.63542600	-0.34391200
C	-1.78264000	-4.49644100	0.00674300
H	-2.84377300	-4.59563000	0.24440700
C	-1.17894800	-3.23446300	0.06850800
C	-3.48012600	-1.55994200	-0.71616600
H	-3.78545300	-0.50812800	-0.60631500
H	2.31408100	-3.39120600	2.01203800
C	1.54090300	-1.51451800	-2.83260200
H	1.01037400	-2.47334800	-2.96148600
H	0.77354100	-0.77136500	-2.56449800
P	2.05726700	1.69128700	0.50671500
C	-0.31432200	5.49645600	-0.62627700
C	1.05067000	5.63543200	-0.34389300
C	1.78263100	4.49644700	0.00673700
H	2.84377900	4.59562500	0.24434400
C	1.17893400	3.23446900	0.06852500
C	2.82817300	2.12813900	2.16392700
H	3.52506000	2.95817100	1.94915700
C	3.48007500	1.55996700	-0.71625900
H	3.78546600	0.50817900	-0.60636800
C	2.19520800	-1.79880000	-0.40796100
C	3.16028300	-2.00868900	0.60310500
C	4.51718000	-1.96548400	0.25145700
H	5.26747400	-2.11572400	1.03381000
C	4.93683200	-1.75989300	-1.07170500
C	3.95519500	-1.61331700	-2.06338200
H	4.26037600	-1.47589800	-3.10521300
C	2.58884500	-1.62749600	-1.75439200
C	2.71890900	-2.36398600	1.99998200
H	3.55963200	-2.31758300	2.70682800
H	1.90933400	-1.70306400	2.34566400
H	1.98649200	-1.22803500	-3.79586000
H	-1.53569000	-6.61204200	-0.39201000
H	1.53567600	6.61204600	-0.39201400
C	-2.82811100	-2.12812200	2.16397600
H	-3.52511000	-2.95806000	1.94921000
C	-6.40413300	1.66145600	-1.41428700
H	-6.75140800	0.61473200	-1.34801200
H	-7.02056100	2.25615000	-0.72265400
H	-6.60266400	2.00896000	-2.43999900
C	6.40417400	-1.66141200	-1.41409600
H	6.75141400	-0.61467600	-1.34783600
H	7.02058300	-2.25606600	-0.72241000
H	6.60277000	-2.00894500	-2.43978600
C	3.60604300	0.93812600	2.73518000
H	2.90407400	0.14259400	3.02278100
H	4.32885000	0.51805200	2.01697300
H	4.16001100	1.24960300	3.63693000
C	1.75363800	2.61505100	3.14584200
H	1.24155600	3.51513600	2.77279000
H	1.00408400	1.82313600	3.30877000

H	2.22610700	2.86124500	4.11229500
C	4.71063800	2.44028600	-0.47248500
H	5.48106100	2.19579600	-1.22464200
H	4.48124400	3.51245800	-0.57763300
H	5.15588200	2.27390200	0.52003700
C	2.91611400	1.75762900	-2.13009200
H	2.69199700	2.81988000	-2.31913800
H	3.64500400	1.41077900	-2.88130400
H	1.98424300	1.18936100	-2.27565900
C	-3.60577900	-0.93803100	2.73533600
H	-2.90367700	-0.14260700	3.02291600
H	-4.32858000	-0.51782100	2.01720200
H	-4.15972300	-1.24946600	3.63711500
C	-1.75357400	-2.61523000	3.14579400
H	-1.24159800	-3.51533100	2.77263200
H	-1.00393600	-1.82340400	3.30876800
H	-2.22602400	-2.86147200	4.11224400
C	-4.71071400	-2.44018700	-0.47223800
H	-5.48120800	-2.19565600	-1.22431000
H	-4.48140500	-3.51237500	-0.57740300
H	-5.15583000	-2.27375900	0.52033400
C	-2.91627400	-1.75774000	-2.13002200
H	-2.69219100	-2.82001000	-2.31899300
H	-3.64523000	-1.41095000	-2.88120000
H	-1.98441700	-1.18948600	-2.27571700

TS$^{A/B}$ (510)

Ti	0.11492200	0.01493900	0.57398600
P	-2.13860400	-1.38013700	0.96328000
N	-0.39597400	1.74732200	-0.44288100
N	0.45617700	-1.70800900	-0.47090900
N	0.70012200	-0.09306100	2.18996900
C	0.33442400	2.90622100	-0.71991000
C	-0.18553300	3.96470000	-1.50926900
H	-1.17609300	3.85906400	-1.95380900
H	0.10250100	5.93520400	-2.31137800
C	-1.78999200	1.85485600	-0.76253900
C	-2.32730100	1.29135700	-1.94297800
C	-3.68371200	1.49245800	-2.23663400
H	-4.09377900	1.04567100	-3.14725100
C	-4.52239400	2.24388000	-1.40124800
C	-3.97283100	2.77923800	-0.22732600
H	-4.61293100	3.34841500	0.45357900
C	-2.62897500	2.58739300	0.11519000
C	-1.45397200	0.48381600	-2.86217200
H	-1.01896300	-0.37791200	-2.33117500
H	-2.02451800	0.10973100	-3.72425800
H	-0.61301700	1.09165300	-3.23178100
C	-2.07303800	3.14417100	1.39986000
H	-2.87197300	3.56701400	2.02593200
H	-1.55077300	2.35899100	1.97140500
H	-1.32851400	3.93303500	1.20270800
C	-0.46109300	-2.69875100	-0.81237800
C	-0.12590700	-3.74335000	-1.71289600

H	0.87339800	-3.75400500	-2.15158000
C	-1.03905900	-4.74180300	-2.03692200
H	-0.74093800	-5.52716700	-2.73653400
C	-2.32512500	-4.75069600	-1.48024600
C	-2.67672300	-3.73226700	-0.59311300
H	-3.67033500	-3.74345700	-0.14640000
C	-1.77841300	-2.70483400	-0.25169100
C	-3.81237500	-0.58241100	0.60729900
H	0.96383500	-4.10722400	1.01368100
C	1.81070800	-0.43238800	-2.72732000
H	0.99902600	-0.92542900	-3.28574700
H	1.34923800	0.39005900	-2.15632400
P	2.23428500	1.63890400	0.80308400
C	0.53698400	5.13974200	-1.70025500
C	1.79334300	5.31909400	-1.10702600
C	2.32950700	4.27673400	-0.34692000
H	3.29709000	4.41704700	0.13728400
C	1.64098100	3.06393200	-0.18247500
C	2.58474300	2.40370900	2.49050900
H	3.41114100	3.11754800	2.31656400
C	3.89645600	1.13663000	0.05661800
C	1.83571900	-2.00686400	-0.73252600
C	2.52585500	-2.93237300	0.09479500
C	3.84603700	-3.27316300	-0.20964200
H	4.36547300	-3.98629600	0.43807400
C	4.52603400	-2.71072000	-1.30022600
C	3.84169400	-1.77737800	-2.08520200
H	4.35342400	-1.31264300	-2.93372800
C	2.50944300	-1.41643800	-1.82506900
C	1.84324500	-3.50845800	1.30144800
H	2.52710900	-4.14791700	1.87825800
H	1.48651700	-2.68746600	1.94287600
H	2.51391200	0.00301400	-3.45275200
H	-3.03918100	-5.53807700	-1.72775900
H	2.34616600	6.25138000	-1.23588100
H	-3.51872500	0.19451600	-0.10712600
C	-2.34615700	-2.20812700	2.64691400
H	-2.56197100	-1.34838000	3.30510500
H	3.58535900	0.73942500	-0.92274300
C	4.53259500	-0.01125700	0.85226400
H	3.79215500	-0.76808900	1.15021600
H	5.29116900	-0.50746500	0.22638000
H	5.03837200	0.36664100	1.75414700
C	4.90995100	2.26446200	-0.18178000
H	5.84612600	1.82221500	-0.56542200
H	4.55684800	2.99281300	-0.92485500
H	5.16093700	2.79972500	0.74962200
C	1.34399000	3.17896700	2.95837700
H	1.03804100	3.94901600	2.23480100
H	0.50594000	2.48097100	3.11058900
H	1.56288800	3.67369700	3.91959400
C	2.99747400	1.37496700	3.55384400
H	3.96697500	0.90622500	3.33977600
H	3.07362900	1.87910900	4.53253600

H	2.23266100	0.58304300	3.61794500
C	-4.32328900	0.13170200	1.86853600
H	-5.13685900	0.81905100	1.58549000
H	-4.72120500	-0.57363200	2.61570400
H	-3.53400200	0.73363200	2.34661700
C	-4.91171200	-1.40053200	-0.07848800
H	-5.75948800	-0.72556700	-0.29003800
H	-4.56765100	-1.81076100	-1.03851500
H	-5.29225300	-2.22678900	0.54263600
C	-3.50305300	-3.21273400	2.72800900
H	-3.60839900	-3.56389100	3.76899800
H	-4.46751100	-2.78200500	2.42232900
H	-3.30135600	-4.09529100	2.10091200
C	-1.03712500	-2.84908700	3.11054200
H	-0.77159500	-3.69637400	2.45931600
H	-0.21413300	-2.11831200	3.10497700
H	-1.15941300	-3.23670500	4.13634300
C	-5.97262300	2.46802300	-1.75555600
H	-6.57605100	2.68060600	-0.85959800
H	-6.08343100	3.32678900	-2.44097100
H	-6.40238300	1.58821300	-2.25989300
C	5.95820000	-3.08862000	-1.59156900
H	6.59988400	-2.91926000	-0.71015800
H	6.04247500	-4.15740600	-1.85197400
H	6.36749200	-2.50271900	-2.42811600

B (508)

Ti	0.00776300	0.06216300	0.21230100
P	1.95529400	1.38447900	1.20035200
N	0.48884100	-1.57517800	-0.87037700
N	-0.36255100	1.93402100	-0.55050600
N	-1.23996700	-0.53910000	1.40750400
C	-0.34923000	-2.67337000	-1.07520500
C	-0.03560000	-3.61280500	-2.09367100
H	0.87804500	-3.45045600	-2.66937600
H	-0.56731500	-5.38867100	-3.17664600
C	1.87518300	-1.73411500	-1.19189200
C	2.48389500	-0.95501900	-2.20431700
C	3.86183300	-1.08529300	-2.43752000
H	4.31842200	-0.47122600	-3.21976500
C	4.66129200	-1.97317100	-1.70909200
C	4.03772300	-2.74774100	-0.71967900
H	4.63880600	-3.44296500	-0.12481700
C	2.67205000	-2.64020000	-0.44180600
C	1.67174000	0.01251300	-3.02110500
H	1.25834700	0.82372700	-2.39865500
H	2.28328100	0.47241500	-3.81090000
H	0.81507700	-0.49528600	-3.48989000
C	2.05602900	-3.42923900	0.68090400
H	2.82778600	-3.90413100	1.30417300
H	1.44563300	-2.76067400	1.30939900
H	1.37757700	-4.21433300	0.30736300
C	0.49856400	3.02811400	-0.47955300
C	0.20530900	4.25919300	-1.12271100

H	-0.72424400	4.34183800	-1.68929200
C	1.06871300	5.34651500	-1.03370200
H	0.80679200	6.27701200	-1.54445400
C	2.25857100	5.26573200	-0.29523100
C	2.56396500	4.06745000	0.35155400
H	3.46610500	4.01172500	0.96319300
C	1.71873900	2.94665400	0.26660800
C	3.67971800	0.69580100	0.85560000
H	-1.25759900	3.69153600	1.51321700
C	-1.36480500	1.46887400	-3.27473300
H	-0.41408100	2.02051300	-3.32656300
H	-1.11639300	0.41021600	-3.09346900
P	-2.09513900	-1.87866500	1.11049900
C	-0.85095200	-4.70151900	-2.37550800
C	-2.03742900	-4.90705600	-1.65738000
C	-2.36053600	-4.00954900	-0.64231800
H	-3.28876800	-4.16232800	-0.08775300
C	-1.53865200	-2.91148300	-0.31364000
C	-2.12665000	-2.91950100	2.66732700
C	-3.87616600	-1.45587400	0.73014700
C	-1.73118300	2.21944900	-0.88052200
C	-2.59522800	2.70306300	0.13558500
C	-3.94387700	2.93083100	-0.15772500
H	-4.60106200	3.29054700	0.64046600
C	-4.47415800	2.70838100	-1.43683900
C	-3.60434300	2.24919500	-2.43080400
H	-3.98932000	2.07168700	-3.43989200
C	-2.24697800	1.99733200	-2.17652300
C	-2.06460800	2.94091800	1.52393400
H	-2.85978800	3.29576800	2.19617600
H	-1.64651300	2.00567000	1.93359600
H	-1.86707100	1.53670400	-4.25098700
H	2.92794600	6.12408000	-0.21449000
H	-2.69787900	-5.74497800	-1.88651200
H	3.56175900	0.24809300	-0.14460000
C	1.96727000	1.80376200	3.05037400
H	3.03243000	1.89123800	3.32991900
H	-2.52977700	-2.18448800	3.38757800
H	-4.44771400	-2.40040100	0.73581600
C	-5.94362000	2.91606400	-1.71428000
H	-6.53543800	2.04984700	-1.36716200
H	-6.33126700	3.80533600	-1.19206600
H	-6.13725300	3.03797200	-2.79101300
C	6.14937100	-2.06919500	-1.94629900
H	6.71072400	-1.54475400	-1.15235000
H	6.49038200	-3.11702800	-1.94718900
H	6.43342500	-1.61522000	-2.90773800
C	-3.95565900	-0.81264300	-0.65961600
H	-3.33189600	0.09304900	-0.69852500
H	-3.62128700	-1.50159600	-1.44997200
H	-4.99284400	-0.51010000	-0.87710900
C	-4.41914300	-0.51469100	1.81479600
H	-5.45094100	-0.21709900	1.56531800
H	-4.43475100	-0.98697900	2.81007900

H	-3.80063000	0.39431300	1.86963400
C	-3.03098000	-4.15701700	2.65549200
H	-2.63494400	-4.93321600	1.98207400
H	-3.07277000	-4.58901900	3.66953100
H	-4.06426400	-3.92471900	2.35263100
C	-0.69479700	-3.26966500	3.08786600
H	-0.26174900	-4.01563000	2.40261500
H	-0.05408200	-2.37522700	3.08575900
H	-0.69513700	-3.69967500	4.10334000
C	3.97935300	-0.43940600	1.84584000
H	4.87316900	-0.98940100	1.51048300
H	4.18031600	-0.05202500	2.85886900
H	3.14848000	-1.15806000	1.90224200
C	4.83388900	1.70121300	0.80378500
H	5.77679200	1.15779900	0.61844100
H	4.70419600	2.43225600	-0.00633100
H	4.95014200	2.24645800	1.75651800
C	1.26302400	3.12400400	3.38108000
H	1.71893500	3.98353200	2.87024200
H	0.20130600	3.08654200	3.09690700
H	1.31511900	3.29846500	4.46947300
C	1.32681500	0.63795300	3.82452600
H	1.84293700	-0.31636700	3.64250500
H	1.35914900	0.84276900	4.90862400
H	0.27560400	0.50519000	3.51913300

2 (509)

P	2.62727300	1.10939800	0.51381100
N	0.28596400	-1.81368700	-0.00870300
N	-0.17307200	1.93201800	-0.12569200
N	-1.73163400	-0.16751800	0.75383500
C	-0.59012600	-2.91539500	-0.06136900
C	-0.09028400	-4.21532000	-0.37228600
H	0.97208800	-4.33123100	-0.58218200
H	-0.43352100	-6.30997600	-0.64814300
C	1.60792100	-2.14139000	-0.48240000
C	1.86914400	-2.13891100	-1.87131300
C	3.14453500	-2.50122800	-2.32645600
H	3.34423200	-2.48556800	-3.40220800
C	4.16481900	-2.87815800	-1.44270300
C	3.86523500	-2.92377600	-0.07264800
H	4.63260400	-3.25750300	0.63241700
C	2.59999900	-2.58107000	0.42472600
C	0.76724000	-1.82625500	-2.84913600
H	0.14315800	-0.99776800	-2.48729500
H	1.16861100	-1.56736800	-3.83941300
H	0.09509700	-2.69492700	-2.96189000
C	2.26285000	-2.77944000	1.87915100
H	3.14361700	-3.11608600	2.44449300
H	1.87015600	-1.86270100	2.34155400
H	1.47119000	-3.54118900	1.98246700
C	0.73487500	3.00666200	-0.18573300
C	0.32792600	4.31158400	-0.56634500
H	-0.71268700	4.48664300	-0.84028300

C	1.22769100	5.37619600	-0.58394100
H	0.86838000	6.36597000	-0.87709000
C	2.56744500	5.19422100	-0.22537700
C	2.98870800	3.91273200	0.13659000
H	4.03117900	3.75684200	0.42328200
C	2.10355300	2.82444600	0.15232100
C	3.65982800	0.67434400	-1.00570600
H	3.76388600	-0.41801300	-0.93110000
H	-1.14487100	3.59469400	1.92672800
C	-0.85203500	1.85837700	-2.93654200
H	-0.05516900	2.61965800	-2.98135000
H	-0.35520100	0.90612100	-2.69870100
P	-2.84952100	-1.30286200	0.50207900
C	-0.89525500	-5.34837100	-0.41055800
C	-2.26732200	-5.27429700	-0.14377200
C	-2.79714300	-4.02170400	0.14866600
H	-3.86542600	-3.93232600	0.36418500
C	-1.99978300	-2.86192200	0.18734600
C	-3.91922200	-1.45353900	2.00796700
H	-4.68302000	-2.22246500	1.79579200
C	-3.89280400	-0.85760300	-0.97020300
H	-4.06837400	0.22086500	-0.80772000
C	-1.51190700	2.28995900	-0.53482300
C	-2.44475900	2.73975400	0.42848800
C	-3.75688200	3.00689600	0.02270600
H	-4.48112100	3.33874000	0.77369100
C	-4.16577500	2.87409500	-1.31468900
C	-3.20282800	2.49884300	-2.25827900
H	-3.48464600	2.42287700	-3.31332600
C	-1.87708000	2.21500900	-1.89185200
C	-2.02272300	2.93129900	1.86178700
H	-2.83752300	3.37108600	2.45590000
H	-1.72712000	1.97348500	2.31839000
H	-1.31050500	1.77258700	-3.93253700
H	3.26956600	6.02995700	-0.22700600
H	-2.90087900	-6.16214600	-0.16061500
C	3.89707900	1.32424500	1.88987100
H	4.70238700	1.92779600	1.43565100
Ti	-0.00096600	0.08913500	0.75125000
Cl	0.36774400	0.13773200	3.02774200
C	5.55293100	-3.19317700	-1.94536900
H	6.06115200	-3.92270300	-1.29597100
H	5.52911100	-3.59844200	-2.96874500
H	6.17567900	-2.28092700	-1.96626700
C	-5.60272800	3.11656100	-1.71336300
H	-6.23655300	2.24589000	-1.46500900
H	-6.02633300	3.98595000	-1.18540800
H	-5.69591300	3.29431700	-2.79570500
C	-3.03810400	-1.03145500	-2.23213700
H	-3.53730700	-0.55470500	-3.09045400
H	-2.05634100	-0.55536000	-2.10520200
H	-2.88160600	-2.09855400	-2.45865500
C	-5.22971800	-1.60112900	-1.07095000
H	-5.79219600	-1.21971900	-1.93933700

H	-5.07834700	-2.68162800	-1.22682400
H	-5.86016200	-1.46152900	-0.17920000
C	-4.59735400	-0.09885600	2.27024100
H	-3.83816100	0.68270600	2.42484100
H	-5.24425100	0.21741800	1.43699200
H	-5.21805200	-0.16656600	3.17826900
C	-3.03794300	-1.89380500	3.18747500
H	-2.22259200	-1.17080700	3.35049400
H	-3.64782800	-1.95169000	4.10371100
H	-2.58699800	-2.88143500	3.00649600
C	5.05810400	1.29159100	-1.10382500
H	5.53905000	0.94406100	-2.03513400
H	5.01796600	2.39209100	-1.14746800
H	5.71134500	0.99585200	-0.26849800
C	2.82510400	1.00369400	-2.24978500
H	2.79731200	2.09101300	-2.42721100
H	3.25350600	0.51049800	-3.13816100
H	1.78657400	0.65966200	-2.13684400
C	4.48125800	-0.03168100	2.30517900
H	3.72235400	-0.63169800	2.82799600
H	4.84349300	-0.61468900	1.44341700
H	5.32827900	0.12053400	2.99559400
C	3.34230700	2.09270300	3.09640500
H	2.93768100	3.07349300	2.80483500
H	2.54150800	1.52618100	3.59163300
H	4.15542100	2.25823900	3.82440300

3 (511)

P	-2.62556600	-1.07894500	0.19820600
N	-0.24184100	1.83293900	-0.25915200
N	0.18353100	-1.91389000	-0.41892200
N	1.74378900	0.15565900	0.54303600
C	0.65520700	2.92219000	-0.28697400
C	0.17938900	4.23217700	-0.58987900
H	-0.87896300	4.36713200	-0.80807400
H	0.55867400	6.32338700	-0.84570200
C	-1.54001600	2.18387600	-0.78586000
C	-1.74130200	2.19691400	-2.18519400
C	-2.99142800	2.57590600	-2.69380200
H	-3.14254300	2.56910700	-3.77750300
C	-4.04558800	2.95915700	-1.85449600
C	-3.80388700	2.99632900	-0.47306100
H	-4.59593400	3.33813000	0.20008000
C	-2.56591400	2.63549000	0.07793500
C	-0.60428100	1.88183200	-3.12017300
H	0.00063700	1.04914900	-2.73744200
H	-0.96795300	1.62783100	-4.12613000
H	0.07602000	2.74735400	-3.20376500
C	-2.29793800	2.82792900	1.54602200
H	-3.19707300	3.18724900	2.06654000
H	-1.95614700	1.90169100	2.02904600
H	-1.49043400	3.56540300	1.69181500
C	-0.73827500	-2.97607000	-0.52348300
C	-0.33972800	-4.27447300	-0.93268200

H	0.70415500	-4.45565500	-1.18924500
C	-1.25203900	-5.32631600	-1.00232600
H	-0.89842500	-6.31166400	-1.31632700
C	-2.59744800	-5.13638100	-0.67112200
C	-3.00996500	-3.86137300	-0.27772700
H	-4.05724800	-3.69942300	-0.01287300
C	-2.11060000	-2.78710400	-0.20449400
C	-3.58099300	-0.58097100	-1.35783800
H	-3.65699200	0.51172700	-1.26527600
H	1.11703300	-3.60777300	1.59561200
C	0.87192400	-1.80546400	-3.23301900
H	0.07397200	-2.56403200	-3.29899700
H	0.37602000	-0.85754700	-2.97953400
P	2.88536700	1.27119500	0.29263800
C	1.00284900	5.35245700	-0.61292500
C	2.37138900	5.25303700	-0.33773500
C	2.87772300	3.98996300	-0.04889400
H	3.94265500	3.88118400	0.17437100
C	2.06059600	2.84362100	-0.02343000
C	3.98781900	1.41136300	1.77600000
H	4.79923100	2.10993200	1.50475200
C	3.91211000	0.80010300	-1.18536900
H	4.04052500	-0.28678000	-1.03764900
C	1.52148600	-2.27804900	-0.83319600
C	2.44819000	-2.76412400	0.11863100
C	3.75664300	-3.04263800	-0.29363100
H	4.47405300	-3.40326500	0.45048600
C	4.16831800	-2.89011300	-1.62738700
C	3.20969000	-2.48405000	-2.56254000
H	3.49047900	-2.39493600	-3.61679200
C	1.88897300	-2.18636300	-2.18978200
C	2.02871500	-2.99089900	1.54625300
H	2.82465500	-3.49506000	2.11396800
H	1.78820400	-2.03831200	2.04349700
H	1.33743200	-1.70043600	-4.22383600
H	-3.31079900	-5.96126000	-0.71686400
H	3.02015900	6.12995400	-0.34447600
C	-3.98025500	-1.30557400	1.49212700
H	-4.79207300	-1.81866000	0.94835300
Ti	0.01338800	-0.08175400	0.47634400
C	-5.40686300	3.29214700	-2.41510900
H	-5.93198900	4.02919100	-1.78805100
H	-5.33471300	3.69558800	-3.43690400
H	-6.04014200	2.38817300	-2.46107500
C	5.60160200	-3.14292400	-2.03206800
H	6.23509000	-2.26255200	-1.81934400
H	6.03235700	-3.99325200	-1.47988700
H	5.68484200	-3.35547900	-3.10901500
C	3.07209600	1.02797900	-2.44762700
H	3.55398600	0.54056900	-3.30972200
H	2.07043700	0.59270400	-2.33112400
H	2.96201200	2.10344400	-2.66115100
C	5.28152600	1.48371800	-1.27365400
H	5.81571500	1.10724500	-2.16186500

H	5.18182100	2.57541200	-1.38930800
H	5.91373000	1.28043300	-0.39572200
C	4.57525900	0.02235600	2.07672400
H	3.76840700	-0.68772300	2.31223400
H	5.14832400	-0.38583000	1.22942300
H	5.24838900	0.08755500	2.94664800
C	3.19059200	1.96978600	2.96339300
H	2.34046100	1.31158300	3.20319200
H	3.84477800	2.03266800	3.84835800
H	2.79632100	2.97479900	2.75006400
C	-4.99138300	-1.15241000	-1.52869300
H	-5.41009100	-0.78861300	-2.48351500
H	-4.98619200	-2.25378800	-1.57235800
H	-5.67759900	-0.83374400	-0.72910300
C	-2.70625900	-0.91076700	-2.57289400
H	-2.70222500	-1.99435300	-2.77307100
H	-3.08249300	-0.38621500	-3.46674400
H	-1.66404400	-0.60017600	-2.40967100
C	-4.49505500	0.06221600	1.95915100
H	-3.72813100	0.57304200	2.56045500
H	-4.76333700	0.71829300	1.11533800
H	-5.39099700	-0.06859300	2.58948300
C	-3.57218300	-2.18946200	2.67739100
H	-3.19465200	-3.16957400	2.35060200
H	-2.79245100	-1.70768100	3.28330900
H	-4.45508000	-2.35678000	3.31867500
I	-0.35577200	-0.16035900	3.16444300

I_2 (512)

I	0.00000000	0.00000000	1.35369900
I	0.00000000	0.00000000	-1.35369900

Cl_2 (513)

Cl	0.00000000	0.00000000	1.01822600
Cl	0.00000000	0.00000000	-1.01822600

4 (518)

Ti	-0.01527900	0.01035600	0.70945100
P	2.15896500	1.53585500	0.58591600
N	0.67444100	-1.78033000	-0.12895900
N	-0.68258600	1.77896300	-0.15889600
C	0.05117500	-3.02928700	-0.11245700
C	0.71750800	-4.23200900	-0.47088000
H	1.76320800	-4.19121400	-0.77962700
H	0.61535500	-6.36289800	-0.70280000
C	2.05114900	-1.82428400	-0.52276000
C	2.40085300	-1.73250500	-1.88870300
C	3.75506000	-1.77840300	-2.24842500
H	4.02381100	-1.69309600	-3.30590300
C	4.76933100	-1.93014700	-1.29185500
C	4.39300700	-2.08513100	0.05129100
H	5.16562900	-2.25233700	0.80818800
C	3.05041300	-2.05512900	0.45196200
C	1.32258600	-1.65874200	-2.93852500
H	0.52838800	-0.95939200	-2.64170900
H	1.72818000	-1.34825000	-3.91229000

H	0.83737100	-2.64284300	-3.05919900
C	2.64764200	-2.34995100	1.87485800
H	3.52983400	-2.46589600	2.52134600
H	1.98981500	-1.56465300	2.28208600
H	2.06568700	-3.28653900	1.91289800
C	-0.06397800	3.02775900	-0.08973800
C	-0.72415400	4.23504300	-0.44051500
H	-1.75580700	4.19427700	-0.79364200
C	-0.08426000	5.46748700	-0.32797100
H	-0.63142400	6.37361700	-0.60111400
C	1.23372700	5.55990700	0.13635900
C	1.90902600	4.37981100	0.45683300
H	2.94012700	4.43861400	0.81326800
C	1.29128900	3.12630900	0.33443100
C	3.33024000	1.44555000	-0.88385900
H	3.72015200	0.41665200	-0.83668400
H	-2.22833100	3.49193000	1.83525400
C	-1.33421000	1.51804300	-2.94639100
H	-0.72175700	2.43363600	-3.00425700
H	-0.64399100	0.70184200	-2.68861800
P	-2.15074400	-1.55862200	0.63592700
C	0.06386100	-5.46142200	-0.42285500
C	-1.27269600	-5.55963500	-0.01414300
C	-1.94729200	-4.38686000	0.33178800
H	-2.98757400	-4.44541700	0.66116600
C	-1.31294500	-3.13708800	0.27543100
C	-3.08910100	-1.91255200	2.22400300
H	-3.82208300	-2.69380200	1.95627000
C	-3.45621600	-1.40250100	-0.71083000
H	-3.74239800	-0.34137600	-0.66147300
C	-2.06168800	1.82479000	-0.54655500
C	-3.06026600	2.11331100	0.41541600
C	-4.40237200	2.13939800	0.00973100
H	-5.17384000	2.34728600	0.75785200
C	-4.77924500	1.93098500	-1.32552700
C	-3.76536100	1.72260100	-2.27200100
H	-4.03293500	1.59451600	-3.32535300
C	-2.41336300	1.67115000	-1.90644400
C	-2.66831900	2.47959400	1.82386300
H	-3.54033500	2.47698000	2.49362200
H	-1.89538100	1.79984600	2.21478100
H	-1.76121600	1.31654400	-3.93940500
H	1.72731900	6.52772300	0.24024200
H	-1.77651500	-6.52652900	0.03468900
C	3.26225100	1.88370100	2.06712100
N	-0.03091300	0.07134700	2.40823000
H	-0.05259300	0.14196300	3.42874000
C	-6.23439800	1.90375300	-1.72737000
H	-6.37187300	2.24080800	-2.76650200
H	-6.64023600	0.87856200	-1.65731600
H	-6.84574000	2.54415800	-1.07286400
C	6.22517800	-1.90277900	-1.69188800
H	6.36881700	-2.27839100	-2.71686500
H	6.62079400	-0.87165900	-1.66074000

H	6.84153400	-2.51116800	-1.01190600
C	-4.71947800	-2.25411100	-0.55079100
H	-5.39924100	-2.04894800	-1.39612700
H	-4.49296400	-3.33227100	-0.56663400
H	-5.26872400	-2.02321800	0.37493000
C	-2.77114300	-1.66596100	-2.05897400
H	-2.57144100	-2.74101100	-2.19460500
H	-3.41309800	-1.31526200	-2.88372700
H	-1.80861900	-1.13752600	-2.13030100
C	-3.84039900	-0.66785500	2.70787700
H	-3.12622300	0.09107100	3.05873600
H	-4.45536500	-0.21276400	1.91495000
H	-4.50378100	-0.93003500	3.54936900
C	-2.15525300	-2.46854100	3.30635400
H	-1.34231800	-1.75743300	3.51662000
H	-2.72607800	-2.63870700	4.23521100
H	-1.69915100	-3.42082600	2.99807900
C	2.43399200	2.21409300	3.31374500
H	1.70703000	3.01693100	3.11883900
H	1.88027900	1.32642800	3.65280800
H	3.10389400	2.53873200	4.12815400
C	2.49009800	1.59750300	-2.15882000
H	2.16762100	2.64310400	-2.29145700
H	3.07820500	1.29335100	-3.04032000
H	1.58644500	0.97270900	-2.11978900
C	4.26580600	0.75762800	2.33932600
H	3.75224400	-0.13606500	2.71919600
H	4.83078500	0.46596300	1.44108500
H	4.98818300	1.08395600	3.10673300
C	4.50636100	2.42733400	-0.88194800
H	5.16341600	2.30395000	-0.00739900
H	5.12127500	2.25381100	-1.78220800
H	4.15950500	3.47252800	-0.91681500
H	3.82588200	2.78671100	1.77339600

C (517_*S*)

P	2.46498200	1.18344900	0.69263300
N	0.31615500	-1.92964800	-0.18014600
N	-0.17855000	2.03416700	-0.16437500
C	-0.52812400	-3.02789200	-0.18735200
C	-0.07798800	-4.30667600	-0.63012500
H	0.95708600	-4.40382600	-0.96115100
H	-0.50407000	-6.37047700	-1.01544000
C	1.68285200	-2.19745800	-0.52672200
C	2.12243800	-2.03149300	-1.85943700
C	3.46878400	-2.27086000	-2.16537700
H	3.80876500	-2.13204800	-3.19610500
C	4.38752000	-2.67693600	-1.18695100
C	3.91888500	-2.87500900	0.12098600
H	4.61481100	-3.21552200	0.89365000
C	2.58011900	-2.65416700	0.46801600
C	1.13277500	-1.65822600	-2.93330100
H	0.54075800	-0.77666600	-2.64198100
H	1.63669800	-1.44455900	-3.88662600

H	0.40709200	-2.47429700	-3.09122200
C	2.06762300	-2.94934600	1.85512000
H	2.88675300	-3.23467500	2.53087100
H	1.54107200	-2.07210700	2.26909300
H	1.33575600	-3.77466800	1.82685500
C	0.65130100	3.14122500	0.01559700
C	0.24384700	4.47106800	-0.25676100
H	-0.76395700	4.65015500	-0.63626700
C	1.10885600	5.54468200	-0.04056700
H	0.76094300	6.55753000	-0.26115700
C	2.40126400	5.34437200	0.45756000
C	2.82211500	4.03466900	0.71786300
H	3.82624300	3.86736200	1.11499900
C	1.97858800	2.94043600	0.48904000
C	3.78903400	0.92448400	-0.62979700
H	3.95358200	-0.16571300	-0.60158000
H	-1.40586800	3.75151200	1.95366000
C	-0.82932000	1.99694500	-2.95448400
H	-0.01601000	2.73876600	-2.89821100
H	-0.36358000	1.01401500	-2.77280600
P	-2.63786300	-1.39584600	0.74544200
C	-0.90888800	-5.41925200	-0.66036200
C	-2.24743300	-5.33814300	-0.24732500
C	-2.71948700	-4.10681300	0.19717500
H	-3.75962600	-4.02551200	0.52405800
C	-1.89669700	-2.96322700	0.24033400
C	-3.90612300	-1.71930400	2.07294400
H	-4.70609100	-2.32972900	1.62108700
C	-3.50745800	-0.67772800	-0.73274100
H	-3.52445800	0.40405800	-0.52577000
C	-1.52358800	2.32151600	-0.55441200
C	-2.48747900	2.69154100	0.41885000
C	-3.81122100	2.90816600	0.01233700
H	-4.55571600	3.17656100	0.76927700
C	-4.20516900	2.80686800	-1.33155200
C	-3.21852300	2.51226200	-2.28457600
H	-3.49229600	2.46685800	-3.34373800
C	-1.88594500	2.27900000	-1.91999900
C	-2.07734800	2.88165700	1.85443400
H	-2.95458300	3.04489000	2.49850500
H	-1.52277800	2.00198800	2.21662100
H	-1.24897300	2.00403100	-3.97127000
H	3.07022600	6.18772200	0.63885500
H	-2.90145800	-6.21092700	-0.27113600
C	3.40697900	1.21315300	2.32470300
H	4.15740500	2.01727700	2.22743300
Ti	0.14791100	0.07111000	0.37092800
N	-1.55981000	-0.30704600	1.36093000
H	-1.09559800	-0.67283400	2.22105800
C	-5.64971800	2.98585900	-1.73490000
H	-6.17279000	3.68394900	-1.06247600
H	-5.73638700	3.37052900	-2.76322900
H	-6.19509700	2.02498200	-1.69764000
C	5.84889600	-2.85422500	-1.52213200

H	6.39769500	-1.90526000	-1.38446000
H	6.32383100	-3.60565300	-0.87262300
H	5.98768400	-3.16465700	-2.56927300
C	-4.94001600	-1.20470700	-0.90414400
H	-5.37062300	-0.75968800	-1.81580500
H	-4.95437300	-2.30010700	-1.03438400
H	-5.59996700	-0.94098500	-0.06462900
C	-2.68275400	-0.94324400	-1.99928600
H	-3.10439900	-0.36222600	-2.83332500
H	-1.63588100	-0.63120700	-1.85345700
H	-2.69324800	-2.01340300	-2.26193900
C	-3.27925900	-2.48946700	3.24499900
H	-2.46209100	-1.90913600	3.70514500
H	-4.03934700	-2.66288100	4.02422000
H	-2.87449600	-3.46268000	2.93029400
C	-4.48351700	-0.36844100	2.53083200
H	-3.69565600	0.24921600	2.98754100
H	-4.91121400	0.21126900	1.69844400
H	-5.27658300	-0.53807700	3.27697500
C	4.12966100	-0.10870900	2.60290100
H	3.40285700	-0.91576800	2.77066300
H	4.78849400	-0.41477400	1.77533500
H	4.74643500	-0.01616300	3.51334200
C	2.43606500	1.57195400	3.45634000
H	2.96919800	1.60309000	4.42217500
H	1.96451900	2.55248400	3.28604100
H	1.63266900	0.81677000	3.52048200
C	3.16678600	1.28924100	-1.98515000
H	3.03619600	2.38024500	-2.07285300
H	3.81298600	0.94419400	-2.80983900
H	2.17678400	0.82550700	-2.11370800
C	5.12980100	1.63865500	-0.43075600
H	5.82579300	1.34646800	-1.23726900
H	5.01118100	2.73277900	-0.47921200
H	5.60948600	1.38266700	0.52657900

C* (517_T)

P	2.55542700	1.10961300	0.73145900
N	0.20801800	-1.98412200	-0.18417000
N	-0.02056500	2.11584500	-0.22890300
C	-0.68537800	-3.02278500	-0.09098200
C	-0.31201600	-4.36175700	-0.42985800
H	0.70883300	-4.53476300	-0.77442400
H	-0.83917300	-6.42803100	-0.61880400
C	1.55188300	-2.34076500	-0.51637800
C	1.99755600	-2.29132600	-1.85724900
C	3.33886000	-2.58678400	-2.14084000
H	3.68213900	-2.53335900	-3.17892200
C	4.24613400	-2.95211800	-1.13685800
C	3.76830400	-3.04784600	0.18166500
H	4.45181100	-3.35911300	0.97805200
C	2.43886300	-2.76146900	0.50714700
C	1.01951600	-1.96439300	-2.95793600
H	0.51376700	-1.00185800	-2.77549200

H	1.52054600	-1.91317800	-3.93554600
H	0.22156400	-2.72432600	-3.00934700
C	1.91593000	-2.91166100	1.91177800
H	2.71406900	-3.20836200	2.60770700
H	1.46231100	-1.96737600	2.26337100
H	1.11697900	-3.67052100	1.95272800
C	0.88816200	3.15845200	-0.07997600
C	0.58325400	4.50527700	-0.40747500
H	-0.40185200	4.73751400	-0.81843600
C	1.51249400	5.52501700	-0.20582300
H	1.23806900	6.55139700	-0.46467100
C	2.78133600	5.25433400	0.32186400
C	3.10700400	3.92858900	0.62871000
H	4.09392900	3.70711500	1.04326800
C	2.19193800	2.88560900	0.43184800
C	3.77296700	0.68061000	-0.64090100
H	3.89005900	-0.41160700	-0.54437400
H	-1.14524400	4.11218900	1.85563800
C	-0.82022000	1.98414700	-2.98391200
H	0.02198700	2.69470500	-3.00302100
H	-0.37912700	0.99023300	-2.79803200
P	-2.77462400	-1.25368900	0.70206500
C	-1.19054300	-5.43078500	-0.34078600
C	-2.51320100	-5.24989100	0.09620700
C	-2.91524600	-3.96232800	0.43380100
H	-3.94152000	-3.80643900	0.77604700
C	-2.04195700	-2.85601000	0.35710800
C	-4.04683900	-1.41126200	2.05460900
H	-4.84105600	-2.08211100	1.68618300
C	-3.67488300	-0.69973200	-0.83841300
H	-3.79481100	0.38831600	-0.69057900
C	-1.35501200	2.48012800	-0.56960500
C	-2.25424700	2.92642300	0.43277800
C	-3.59942600	3.13997300	0.09760100
H	-4.29323300	3.46213600	0.88114100
C	-4.07579300	2.96429400	-1.21003800
C	-3.15333700	2.59239000	-2.20024400
H	-3.49366700	2.48529900	-3.23542000
C	-1.80536200	2.35248600	-1.90396600
C	-1.75242200	3.19103500	1.83275800
H	-2.58584300	3.30892600	2.54175300
H	-1.08724300	2.38397100	2.18366300
H	-1.29848500	1.97055900	-3.97439200
H	3.50253000	6.05611400	0.49051900
H	-3.20675700	-6.08833000	0.17178400
C	3.53624500	1.13343800	2.33059600
H	4.31032100	1.91134300	2.21032700
Ti	0.20415800	0.08903400	0.26769000
N	-1.63844100	-0.15725400	1.16554300
H	-2.12503800	0.73475000	1.32724200
C	-5.53912000	3.14172600	-1.54094600
H	-6.04931700	3.76613400	-0.79144100
H	-5.67487200	3.61185300	-2.52800000
H	-6.06080500	2.16759200	-1.57056000

C	5.70170900	-3.20020800	-1.45307100
H	6.30115200	-2.28495300	-1.29654900
H	6.12755900	-3.98343200	-0.80606900
H	5.83984000	-3.50774200	-2.50120800
C	-5.04456700	-1.35660600	-1.04962100
H	-5.48190400	-0.99336300	-1.99462200
H	-4.95309000	-2.45279700	-1.12815800
H	-5.75706500	-1.12185200	-0.24381800
C	-2.75248000	-0.93361600	-2.04201500
H	-3.13662900	-0.39199200	-2.92041000
H	-1.73248400	-0.56856100	-1.84134000
H	-2.68465900	-2.00691300	-2.28140000
C	-3.39805300	-2.00846300	3.31109100
H	-2.55151700	-1.38239400	3.63525600
H	-4.13518100	-2.05035200	4.12978500
H	-3.02002700	-3.02540900	3.12891700
C	-4.65564800	-0.02589500	2.33579300
H	-3.89421500	0.66167600	2.73865900
H	-5.08886500	0.43901400	1.43633500
H	-5.45339900	-0.11791100	3.09035600
C	4.22228300	-0.20715600	2.61548800
H	3.47891400	-0.99643200	2.79382600
H	4.86749800	-0.53530100	1.78617000
H	4.84751000	-0.12171700	3.52065600
C	2.59202700	1.54441000	3.46973200
H	3.14478100	1.60811700	4.42247900
H	2.12845400	2.52372200	3.27162800
H	1.78405800	0.80187800	3.58980900
C	3.08239700	0.98105100	-1.97983400
H	2.97659200	2.06751600	-2.13154000
H	3.66784900	0.55986700	-2.81371600
H	2.07386600	0.53920200	-2.02926900
C	5.14657400	1.35355400	-0.56930400
H	5.78406700	0.97722100	-1.38864800
H	5.06161500	2.44534100	-0.68921200
H	5.66969300	1.14740200	0.37754600

5 (514)

P	2.58225800	1.14072100	0.70119200
N	0.27669900	-1.83340700	-0.07089700
N	-0.14556800	1.93848000	-0.08401000
N	-1.65564600	-0.20656200	1.08048000
C	-0.59232400	-2.93654900	-0.11537400
C	-0.12231700	-4.21266100	-0.53670700
H	0.92017100	-4.31340200	-0.83860200
H	-0.51037200	-6.28886100	-0.89956800
C	1.62729400	-2.14323800	-0.46543300
C	2.00411200	-2.04940900	-1.82346600
C	3.31670700	-2.37680200	-2.19049300
H	3.60626300	-2.29489000	-3.24247500
C	4.26231200	-2.80264900	-1.24760100
C	3.85111800	-2.93265500	0.08785000
H	4.56325300	-3.29774300	0.83411300
C	2.54577300	-2.62758100	0.49680500

C	0.98194300	-1.67511700	-2.86432700
H	0.39783500	-0.79902500	-2.54972500
H	1.45509300	-1.45647200	-3.83217600
H	0.25686600	-2.49532900	-3.00514500
C	2.09427400	-2.89581800	1.90993200
H	2.94210800	-3.18793900	2.54594400
H	1.59424600	-2.01680000	2.34585100
H	1.35469000	-3.71512700	1.91979000
C	0.73447800	3.03185500	-0.06507300
C	0.33103200	4.34305600	-0.42996800
H	-0.69161700	4.51133500	-0.76965100
C	1.21160300	5.42081500	-0.34603200
H	0.85672800	6.41464700	-0.63150300
C	2.52603700	5.25050000	0.10379100
C	2.94629800	3.96346100	0.44919900
H	3.96760100	3.81309800	0.80747700
C	2.08303700	2.86261300	0.35592100
C	3.80102800	0.75552400	-0.68349600
H	3.89974300	-0.33986400	-0.63149100
H	-1.16911400	3.59807800	1.99682100
C	-0.80660100	1.93803700	-2.89460000
H	-0.04336700	2.73390300	-2.93312500
H	-0.26801700	1.00799300	-2.66107600
P	-2.76202700	-1.30848300	0.68728000
C	-0.93884900	-5.33899000	-0.57004400
C	-2.28275200	-5.27000900	-0.18636300
C	-2.77955800	-4.03232700	0.21648000
H	-3.82728900	-3.95307300	0.51851500
C	-1.97345400	-2.88052400	0.25249200
C	-3.92732600	-1.56929800	2.10837700
H	-4.70903700	-2.27723800	1.78274800
C	-3.72669200	-0.75944800	-0.80834500
H	-3.85992100	0.32083600	-0.62702800
C	-1.48491600	2.28465900	-0.48628600
C	-2.42518200	2.70843700	0.48375800
C	-3.73573800	2.98409000	0.07818600
H	-4.46445600	3.29688800	0.83305100
C	-4.13748200	2.88538500	-1.26473100
C	-3.16932900	2.53736200	-2.21350200
H	-3.44553500	2.49200300	-3.27183300
C	-1.84514000	2.24630900	-1.84710700
C	-2.00643200	2.88455000	1.92057000
H	-2.84170200	3.26208200	2.52919100
H	-1.66064000	1.92850200	2.34316900
H	-1.25986500	1.83943200	-3.89188500
H	3.20869600	6.09856800	0.18222400
H	-2.92431300	-6.15230300	-0.20150100
C	3.60315900	1.28041900	2.26940400
H	4.43502500	1.96848400	2.03649900
Ti	0.06529700	0.03781700	0.71738000
C	5.69106400	-3.07760200	-1.65003400
H	6.15177900	-3.84225400	-1.00569600
H	5.75718600	-3.41940000	-2.69447500
H	6.30286300	-2.16174400	-1.56355300

C	-5.57369500	3.12984600	-1.66403900
H	-6.19179300	2.23022000	-1.49050500
H	-6.02119300	3.94897200	-1.07878600
H	-5.65726300	3.38548200	-2.73159100
C	-2.83709800	-0.94919500	-2.04454800
H	-3.26040600	-0.39678500	-2.89787800
H	-1.82388000	-0.56257700	-1.86234400
H	-2.75635300	-2.01503400	-2.31260500
C	-5.08947000	-1.43990700	-0.98111100
H	-5.58254800	-1.04134900	-1.88354500
H	-4.98066800	-2.52843700	-1.11947500
H	-5.76317900	-1.26166200	-0.12887800
C	-4.56557500	-0.21458400	2.45875900
H	-3.78651400	0.50903300	2.74370400
H	-5.12939000	0.21474700	1.61570900
H	-5.25808900	-0.33751000	3.30732900
C	-3.14654600	-2.15592100	3.29403200
H	-2.31191300	-1.48999600	3.56598300
H	-3.81232800	-2.25882400	4.16664100
H	-2.73019800	-3.14623300	3.05437900
C	5.19333300	1.38387400	-0.57113300
H	5.81096000	1.05433800	-1.42524300
H	5.14545100	2.48405300	-0.60599700
H	5.71838800	1.08517300	0.34929600
C	3.13028900	1.12558800	-2.01420900
H	3.11547800	2.21848900	-2.15402700
H	3.67656700	0.66789300	-2.85570700
H	2.08873800	0.77225900	-2.05249900
C	4.18035500	-0.08278900	2.66956500
H	3.37256600	-0.76233500	2.97729500
H	4.73452600	-0.56427700	1.84789700
H	4.86942400	0.03554200	3.52309500
C	2.75674200	1.88735100	3.39708900
H	2.40086900	2.89582200	3.13642700
H	1.87810400	1.25418200	3.60125800
H	3.35934200	1.95967000	4.31874100
H	0.59894900	-0.11431600	2.34885400
H_2 (520)			
H	0.00000000	0.00000000	0.37825800
H	0.00000000	0.00000000	-0.37825800

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