Supporting Information for the Paper Entitled:
A Four Coordinate Parent Imide via a Titanium Nitridyl

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General Considerations. Unless otherwise stated, all operations were performed in an M. Braun Lab Master dry box under an atmosphere of purified nitrogen or using high vacuum standard Schlenk techniques. Anhydrous *n*-hexane, *n*- pentane, toluene, and benzene were purchased from Aldrich in sure-sealed reservoirs (18L) and dried by passage through two columns of activated alumina and a Q-5 column. Diethyl ether and CH_2Cl_2 were dried by passage through a column of activated alumina. THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored under sodium metal. Distilled THF was transferred under vacuum into sealed glass vessels before entering the dry box. C_6D_6 was purchased from Cambridge Isotope Laboratory (CIL), degassed and vacuum transferred to 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 ºC. NaN_3 were stirred in dry THF overnight under an inert atmosphere, and the suspension filtered, and the solids washed with THF and Et_2O, and then the solids dried under reduced pressure for 12-24 h. All other chemicals were used as received from Sigma-Aldrich unless otherwise stated. 98% $Na^{15}N_3$ was purchased from Cambridge Isotope Laboratories. ^1H, ^{13}C, and ^{15}N NMR spectra were recorded on Varian 400 and 500 MHz NMR spectrometer. ^1H and ^{13}C NMR spectra are reported with reference to solvent resonances of C_6D_6 at 7.16 ppm and 128.0 ppm, respectively and assignment was conducted by performing $^{13}C\{^1H\}$ NMR spectra with reference to solvent resonances of C_6D_6 at 128.0 ppm. ^{15}N NMR chemical shifts are reported with respect to a neat standard of $MeNO_2$ (380.2 ppm). X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of N_2 (g) at a range 150 to 200K. Elemental analysis was performed at Indiana University, Bloomington. Infrared spectroscopy was performed on the Thermo Nicolet 6700 FT-IR equipped with software under PC control. $HNtol_2$ and $LiN(tol)_2$ (tol = 4-Me-C_6H_4) were prepared by standard published procedures[1] using a Buchwald−Hartwig C−N cross coupling route.[2] (nacnac)$TiCl_2$(THF) ($nacnac^-$ = $[ArNC(Me)]_2CH$, Ar = 2,6-*i*$Pr_2C_6H_3$) was prepared according to published literature.[3]

Warning: NaN_3 should be handled cautiously due to its potentially explosive nature.

Synthesis of [(nacnac)TiCl(Ntol$_2$)] (1). In a 100 mL round bottom flask, to a cold solution of [(nacnac)TiCl$_2$(THF)] (2.50 g, 4.10 mol) in toluene (25 mL) at –37 °C was added solid LiN(tol$_2$) (0.877 g, 4.32 mmol). The reaction mixture immediately turned to an intensely darker green color. After stirring for 6h, all volatiles were removed under a reduced pressure. The crude product was extracted into diethyl ether and filtered through a medium porosity frit containing Celite to remove salt residues. The filtrate was removed of solvent to generate green solids. Crystalline materials were obtained from storing a concentrated diethyl ether solution in a scintillation vial at –37 °C. Yield: 60% (1.80 g, 2.58 mol). ^{1}H NMR (25 °C, 300 MHz, C_6D_6): δ 6.46 ($\Delta\nu_{1/2}$ = 100 Hz), 5.56 ($\Delta\nu_{1/2}$ = 1028 Hz), 2.99 ($\Delta\nu_{1/2}$ = 149 Hz), 2.35 ($\Delta\nu_{1/2}$ = 939 Hz), 2.10, 1.63 ($\Delta\nu_{1/2}$ = 205 Hz) 1.36 ($\Delta\nu_{1/2}$ = 275 Hz), 1.22 ($\Delta\nu_{1/2}$ = 255 Hz). Evans' Method (C_6D_6, 298 K): μ_{eff} = 1.89 μ_B. X-Band EPR (25 ºC, toluene): g_{iso} = 1.95. Anal. Calcd for $C_{43}H_{55}ClN_3Ti$: C, 74.07; H, 7.95; N, 6.03. Found: C, 73.90; H, 8.15; N, 5.85.

Synthesis of [(nacnac)Ti=NH(Ntol$_2$)] (2). At –37 °C, to a cold suspension of NaN_3 (170 mg, 2.62 mmol) in 20 mL THF in a 100 mL round bottom was added **1** (305 mg, 0.43 mmol) in THF (10 mL). The dark green solution gradually turned red over a period of 12h. All volatiles were removed under a reduced pressure. The crude product was extracted in toluene and filtered through a medium porosity frit containing Celite. The resulting filtrate was concentrated to dryness and triturated with cold *n*-pentane to yield an orange powder. Crystalline product was also obtained from storing sautrated *n*-pentane solution at –37 °C over several days. Yield = 30% (87.3 mg, 0.13 mmol). ^{1}H NMR (25 °C, 400 MHz, C_6D_6): δ 7.21-7.11 (m, 4H, Ar-*H*), 7.07-7.05 (m, 6H, Ar-*H*), 6.97 (d, *J* = 8 Hz, 2H, Ar-*H*), 6.83 (d, *J* = 8 Hz, 2H, Ar-H), 5.08 (s, 1H, γ-H), 4.22 (br s, $\Delta\nu_{1/2}$ = 84 Hz, 1H, N*H*) 3.74 (m, 2H, C*H*(Me)$_2$), 2.98 (m, 2H, C*H*(Me)$_2$), 2.17 (s, 6H, Ar-*Me*), 1.27 (s, 6H, (*Me*)CCHC(*Me*), 1.32 (d, *J* = 7 Hz, 6H, CH(*Me*)$_2$), 1.26 (d, *J* = 7 Hz, 6H, CH(*Me*)$_2$), 1.19 (d, *J* = 7 Hz, 6H, CH(*Me*)$_2$), 1.01 (d, *J* = 7 Hz, 6H, CH(*Me*)$_2$). ^{13}C NMR (25 ºC, 125 MHz, C_6D_6): δ 168.8 (ArN(CH$_3$)*C*CH*C*(CH$_3$)NAr), 144.8 (Ar), 142.9 (Ar), 142.4 (Ar), 130.1 (Ar), 130.0 (Ar), 129.5 (Ar), 126.8 (Ar), 124.5 (Ar), 124.3 (Ar), 123.5 (Ar), 118.3 (ArN(CH$_3$)C*C*HC(CH$_3$)NAr), 28.8 (*C*H(CH$_3$)$_2$), 28.6 (*C*H(CH$_3$)$_2$), 25.9 (CH(*C*H$_3$)$_2$), 24.9 (ArN(*C*H$_3$)CCHC(*C*H$_3$)NAr), 24.5 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 20.7 (Ar–*C*H$_3$). ^{15}N NMR (25 °C, 50 MHz, C_6D_6): δ 430.4 ($\Delta\nu_{1/2}$ = 8.67 Hz). The synthesis of the

^{15}N isotopomer, [(nacnac)Ti=N^{15}H(Ntol$_2$)] (**2**-^{15}N), was prepared following the same procedure to prepare **2** using Na^{15}N$_3$. The following scale was performed: compound **1** (150 mg, 0.21 mmol) and Na^{15}N$_3$ (20 mg, 0.30 mmol). FT−IR (KBr, Nujol, cm^{-1}): 3367 (N−H), 3359 (N−D).

Table S1. Summary of crystallographic data and parameters for [(nacnac)TiCl(Ntol$_2$)] (**1**) and [(nacnac)Ti=NH(Ntol$_2$)] (**2**).

	1	**2**
Molecular formula	$C_{43}H_{55}ClN_3Ti$	$C_{43}H_{56}N_4Ti$
Fw	697.25	676.82
temp (K)	150(2)	120(2)
cryst system	Monoclinic	monoclinic
space group	p$2_1/c$	p$2_1/c$
cell constants		
a (Å)	10.6177(10)	11.7466(9)
b (Å)	33.391(3)	28.974(2)
c (Å)	11.5326(11)	12.3682(9)
α (deg)	90	90
β (deg)	107.582(2)	115.276(2)
γ (deg)	90	90
Z	4	4
V (Å^3)	3897.7(6)	3806.5(5)
abs coeff, μ_{calc} (mm^{-1})	0.324	0.142
δ_{calc} (g/cm^3)	1.188	1.181
F(000)	1492	1456
cryst dimens (mm)	0.3 x 0.3 x 0.28	0.10 x 0.05 x 0.03
Radiation	Mo Kα (λ = 0.71073 Å)	Synchrotron (λ = 0.41328 Å)
h,k,l ranges colled	$-13 < h < 13, -43 < k < 42, -14 < l < 14$	$-18 < h < 17, -44 < k < 31, -19 < l < 14$
θ range (deg)	1.95-27.60	0.82-18.54
no. of reflens colled	39483	85507
no. of unique reflens	9003	14417
no. of params	478	445
data/param ratio	18.83	32.39
Refinement method	full-matrix least-squares of F^2	full-matrix least-squares of F^2
$R(F)^a$	0.0439	0.0535
$R_w(F^2)^b$	0.0985	0.1320
GOFw^c	1.034	1.040
largest diff peak and hole (e/Å^3)	0.362 and –0.329	0.953 and –1.002

[a] $R = [\sum|\Delta F| / \sum|F_o|]$. [b] $R_w = [\sum w(\Delta F)^2 / \sum wF_o^2]$. [c] Goodness of fit on F^2.

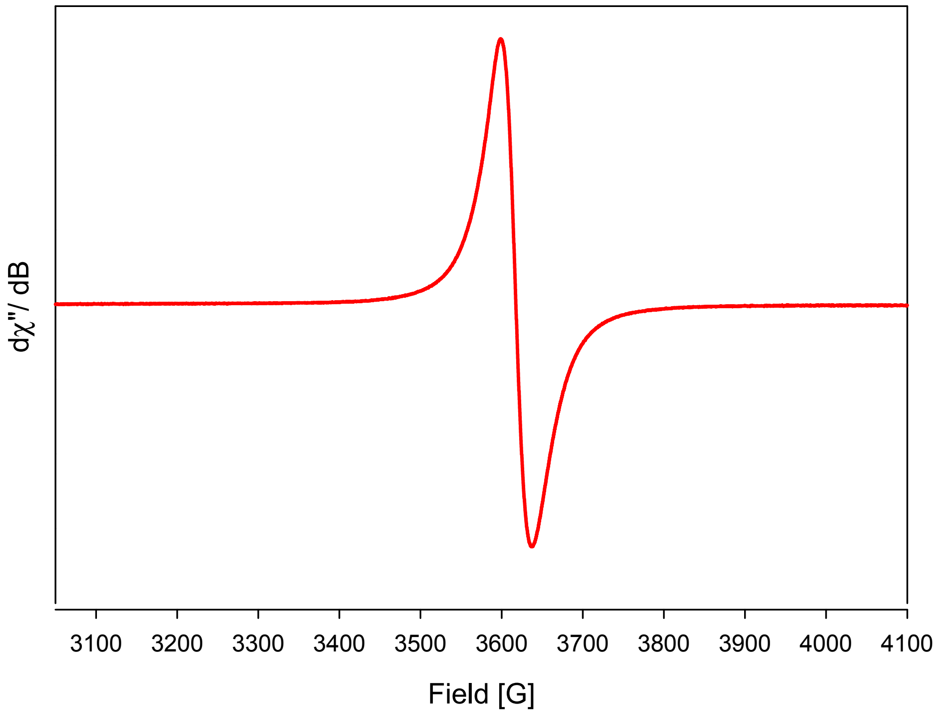

Figure S1. Room temperature X-band EPR spectrum of (nacnac)TiCl(Ntol$_2$) in toluene.

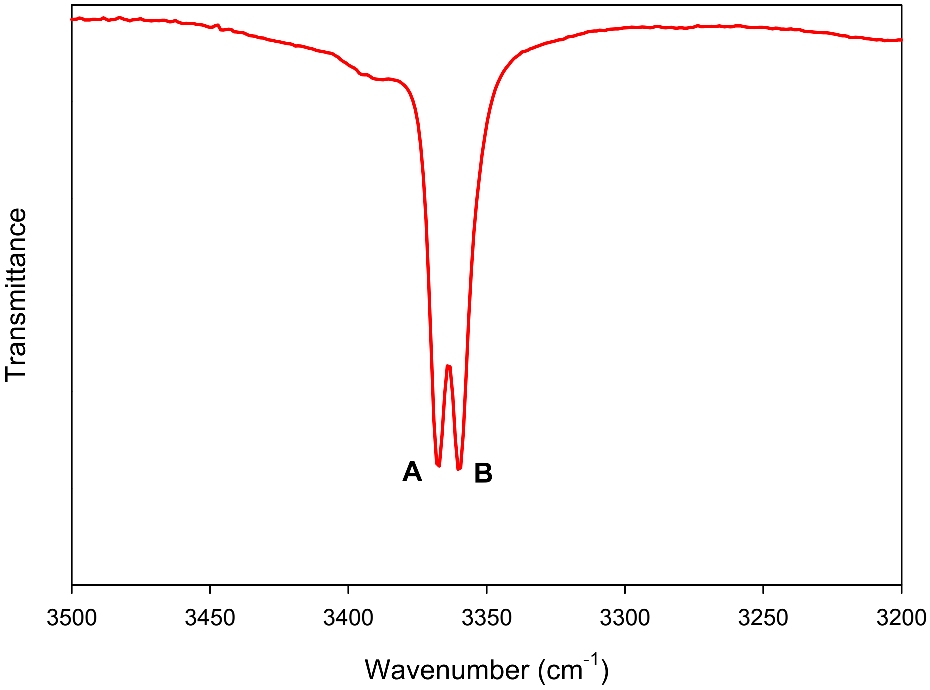

Figure S2. The FT-IR (Nujol) spectrum of (**2**)-^{15}N showing the N-H region of (nacnac)Ti=N-H(Ntol$_2$) (**A** = 3367 cm^{-1}) and (nacnac)Ti=N^{15}-H(Ntol$_2$) (**B** = 3359 cm^{-1}).

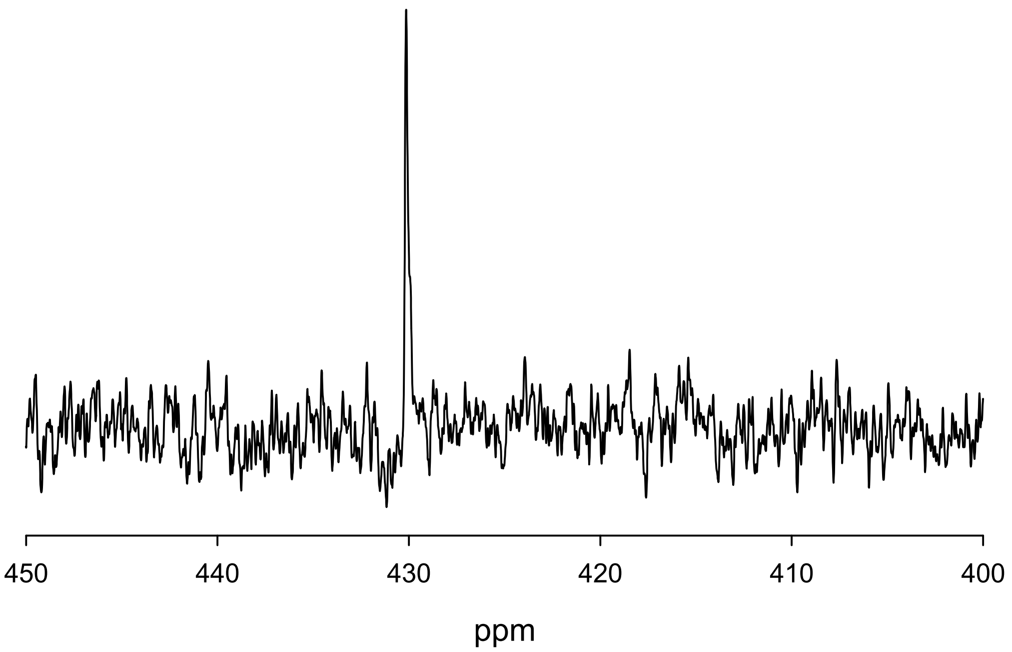

Figure S3. ^{15}N NMR spectrum of (**2**)-^{15}N shows a sharp singlet at 430.4 ppm ($\nu_{1/2}$ = 8.67 Hz) in C_6D_6.

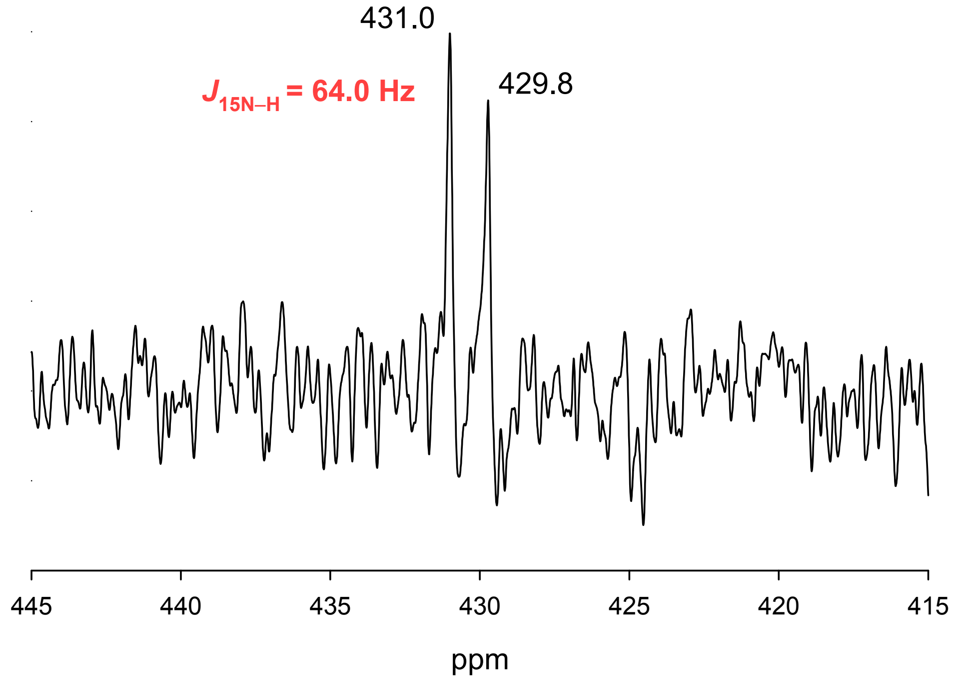

Figure S4. The ^{1}H decoupled ^{15}N NMR spectrum of **(2)**-^{15}N in C_6D_6.

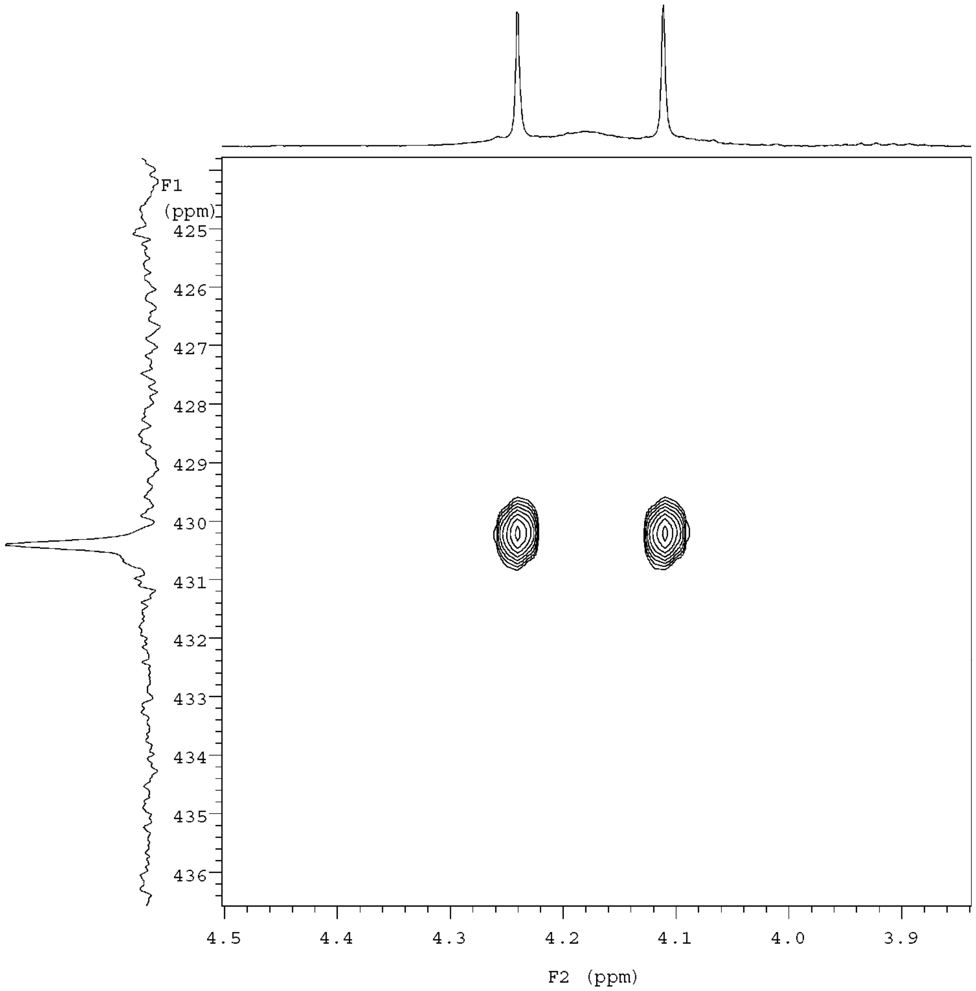

Figure S5. 2D HSQC spectroscopic experiment of **(2)**-^{15}N recorded at 25 ºC. The vertical scale (left) is the ^{15}N NMR spectrum and on the horizontal scale (top) is the ^{1}H NMR spectrum displaying the ^{15}N-H (d, J_{51N-1H} = 64.0 Hz, 1H) and broad ^{14}N-H.

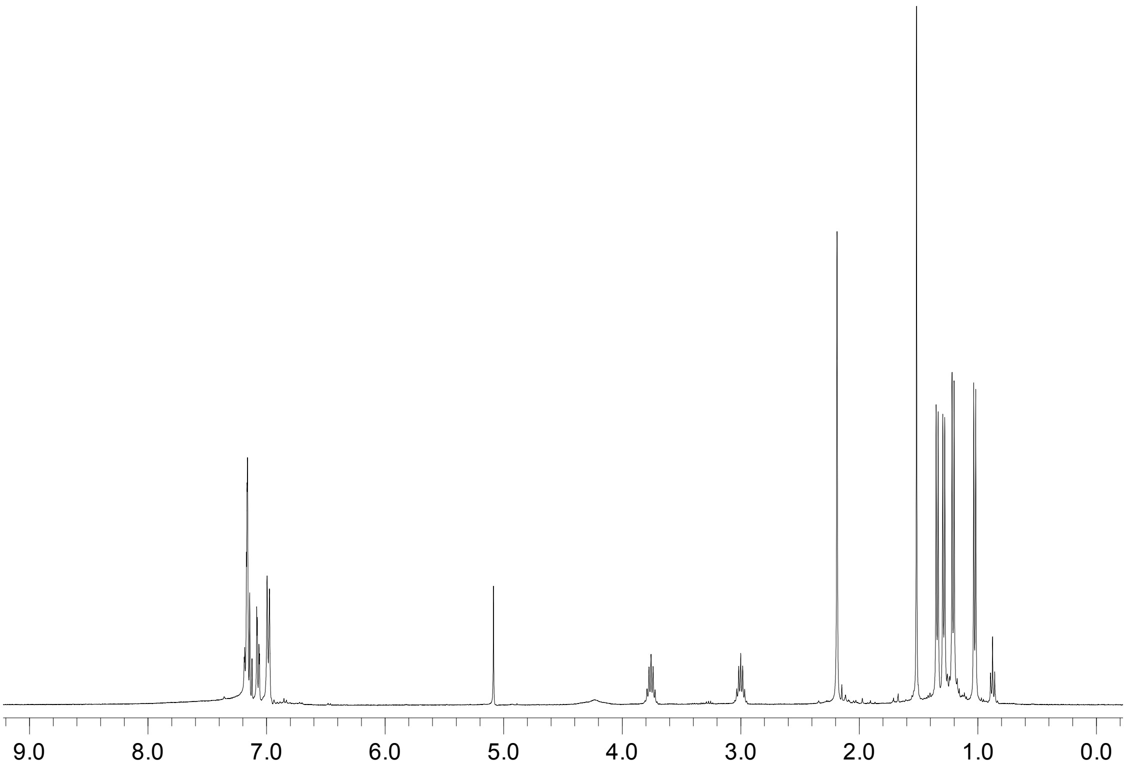

Figure S6. ^{1}H NMR (C_6D_6, 400 MHz, 25 ºC) spectrum of (nacnac)Ti=NH($Ntol_2$) (**2**).

References

1. B. L. Tran, M. Pink, X. Gao, H. Park, and D. J. Mindiola, *J. Am. Chem. Soc.*, 2010, **132**, 1458-1459.
2. (a) J. P. Wolfe, and S. L. Buchwald, *J. Org. Chem.*, 2005, **65**, 1144; J. P. Wolfe, H. Tomori, J. P. Sadighi, J. Yin, and S. L. Buchwald, *J. Org. Chem.*, 2000, **65**, 1158.
3. P. H. M. Budzelaar, A. B. v. Oort, and A. G. Orpen, *Eur. J. Inorg. Chem.*, 1998, 1485.