Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Dinitrogen Activation by Titanium Hydride Complex Supported by 2-Butene Ligand

Xianghui Shi,[a] Yongliang Zhang,[a] Mingdong Zhong,[a] Rui Feng,[a] Yuanjin Chen,[a] Lei Yu,[a] Yue Wu,[a] Junnian Wei*[a] and Zhenfeng Xi [a,b]

a. Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China.

Email: jnwei@pku.edu.cn

b. State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai, 200032, China.

Contents Page

1. General procedure for protonation

Under an atmosphere of dinitrogen, complex **5** (0.01 mmol), reductant KC_8 and proton sources ($[(Ph_2NH_2)(OTf)]$, $[H(Et_2O)_2(BAr^F{}_4)]$ or $[(HPCy_3)(BF_4)]$) were mixed in a 50 mL Schlenk flask at -78 ºC, and pre-cooled Et_2O (5 mL, -78 ºC) was added. The mixture was stirred -78 ºC for 1 h. The resultant solution was warmed slowly to room temperature. After the solution was stirred for 1 h at room temperature, HCl (100 eq. 1 M in 1,4-Dioxane) was added. The resulting solvent was removed under reduced pressure and the residue was extracted with H_2O (10.0 mL). The amounts of NH_3 and N_2H_4 were determined by the indophenol method and the *p*-(dimethylamino)benzaldehyde method, respectively. The detail results were summarized in **Table S1**.

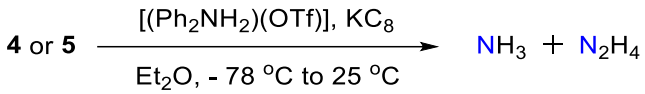


Table S1: NH_3 and N_2H_4 generation from complex **4** or **5**.[a]

Run	Complex[b]	Solvent	Reductant (eq.)	Acid (eq.)	N_2H_4 (eq.)	NH_3 (eq.)
1	**5**	Et_2O	KC_8 (0)	$[(Ph_2NH_2)(OTf)]$ (6)	0.10	0.43
2	**5**	Et_2O	KC_8 (3)	$[(Ph_2NH_2)(OTf)]$ (6)	0.07	0.87
3	**5**	Et_2O	KC_8 (6)	$[(Ph_2NH_2)(OTf)]$ (6)	0.04	0.41
4	**5**	Et_2O	KC_8 (6)	$[(Ph_2NH_2)(OTf)]$ (12)	0.22	0.72
5	**5**	Et_2O	KC_8 (18)	$[(Ph_2NH_2)(OTf)]$ (24)	0.06	0.55
6	**4**	Et_2O	KC_8 (18)	$[(Ph_2NH_2)(OTf)]$ (24)	0.21	0.70
7	**5**	Toluene	KC_8 (18)	$[(Ph_2NH_2)(OTf)]$ (24)	0.05	0.80
8	**5**	THF	KC_8 (18)	$[(Ph_2NH_2)(OTf)]$ (24)	0.33	0.88
9	**5**	Et_2O	KC_8 (18)	$[(HPCy_3)(BF_4)]$ (24)	0.08	0.23
10	**5**	Et_2O	KC_8 (18)	$[H(Et_2O)_2(BAr^F{}_4)]$ (24)	0.08	0.29
11	**5**	Et_2O	KC_8 (36)	$[(Ph_2NH_2)(OTf)]$ (42)	0.06	0.92
12	**5**	Et_2O	KC_8 (54)	$[(Ph_2NH_2)(OTf)]$ (60)	0.08	1.77
13	**4**	Et_2O	KC_8 (54)	$[(Ph_2NH_2)(OTf)]$ (60)	0.16	0.99
14	**5**	Et_2O	KC_8(72)	$[(Ph_2NH_2)(OTf)]$ (78)	0.07	1.85
15	**5**	Et_2O	KC_8 (90)	$[(Ph_2NH_2)(OTf)]$ (96)	0.08	1.87
16	**5**	Et_2O	KC_8 (108)	$[(Ph_2NH_2)(OTf)]$ (114)	0.09	1.90

[a]All reactions were performed according to the above process. [b]10 μmol complex **4** or **5** was used. [c]Yields per mol complex **4** or **5**.

2. Copies of NMR Spectra

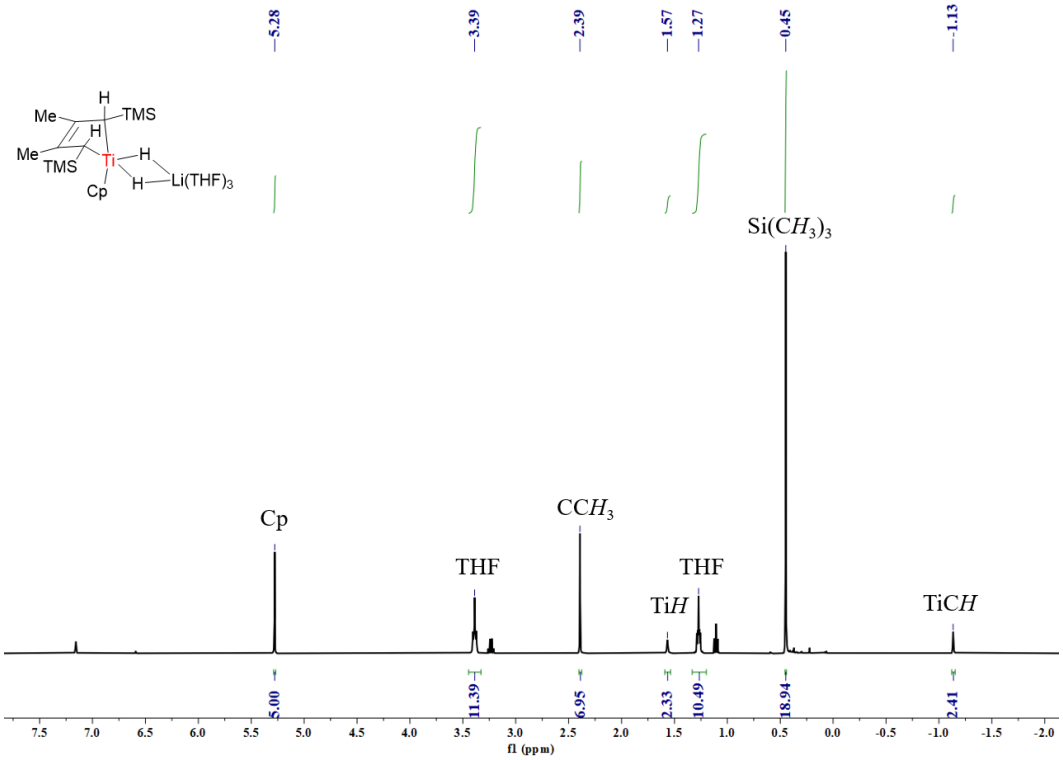


Figure S1. ^{1}H NMR spectrum (400 MHz) of **2** in C_6D_6 at 25 ^{o}C

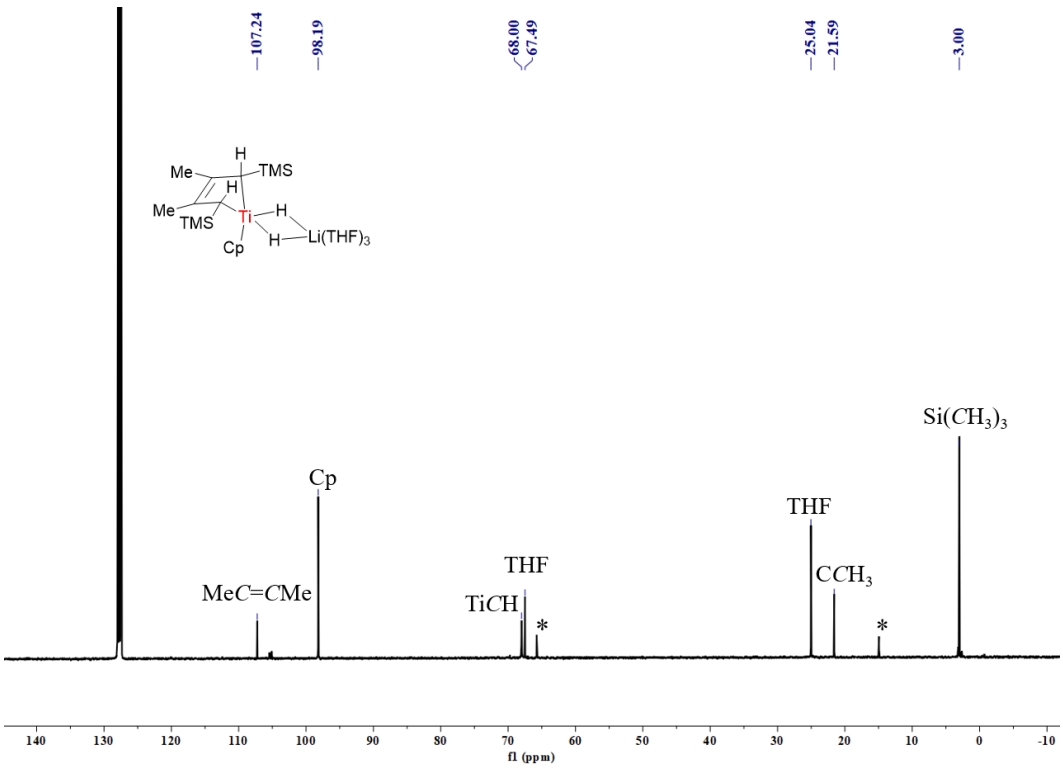


Figure S2. ^{13}C{^{1}H} NMR spectrum (101 MHz) of **2** in C_6D_6 at 25 ^{o}C (* is Et_2O)

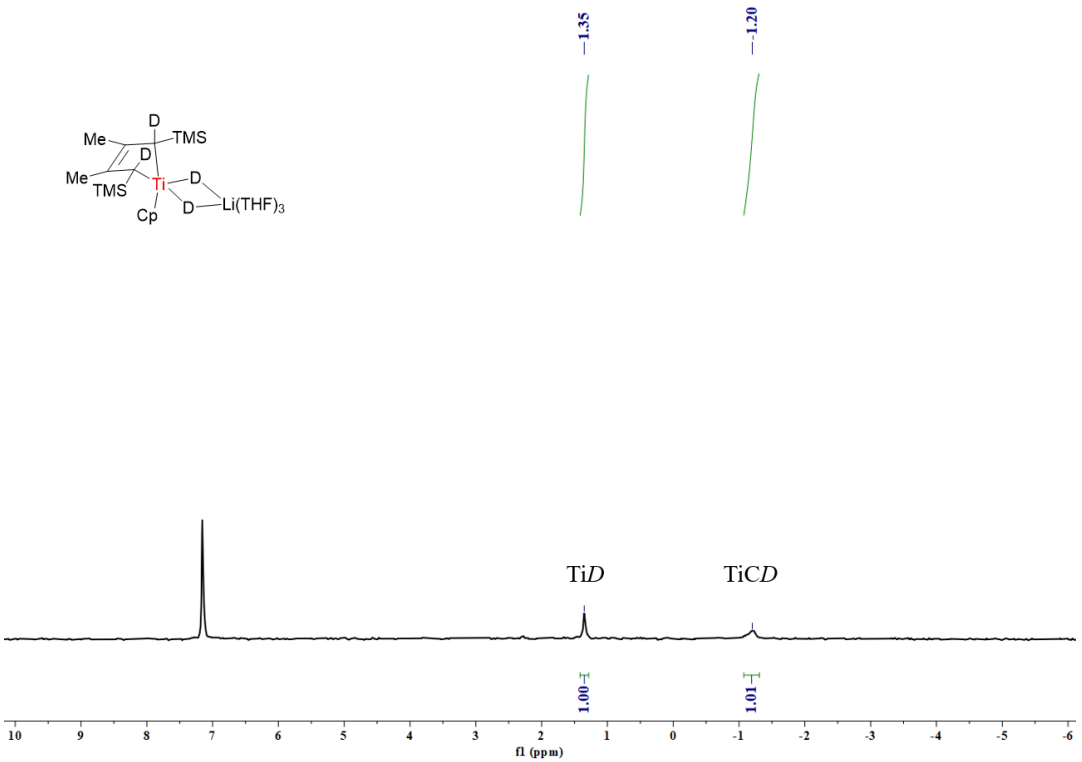


Figure S3. ^{2}H NMR spectrum (77 MHz) of **2-D** in C_6H_6 at 25 ^{o}C
(*Drops of C_6D_6 were added as internal standard*)

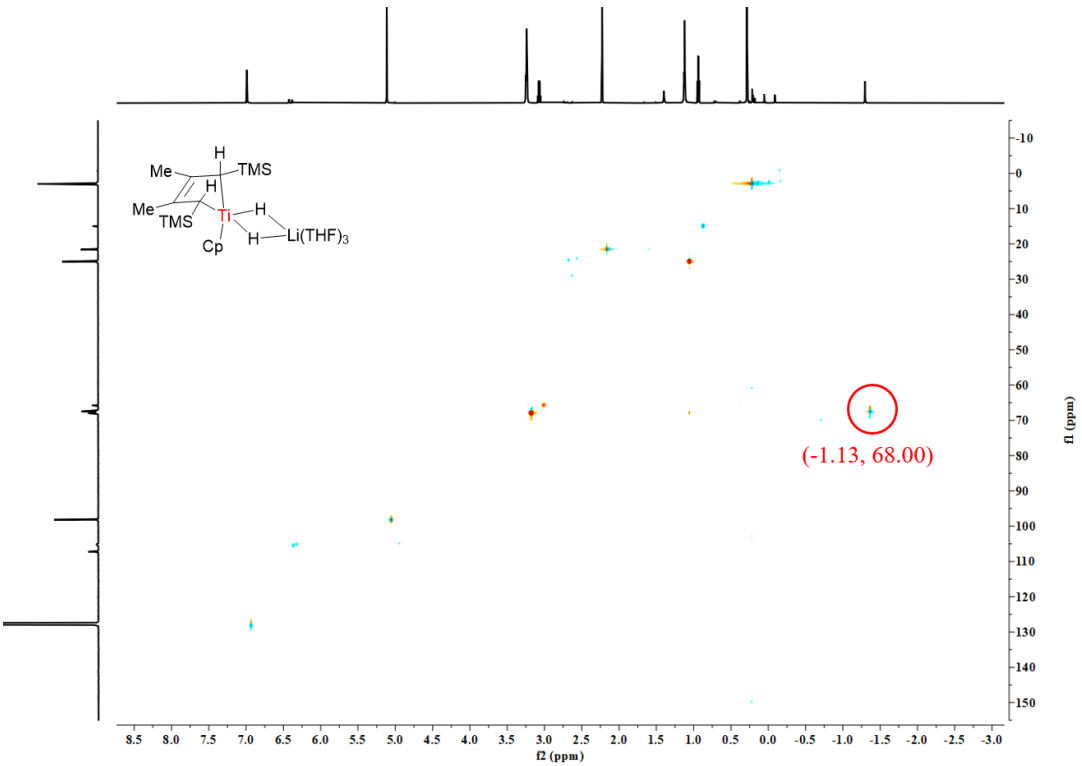


Figure S4. ^{1}H-^{13}C HSQC NMR spectrum (400 MHz) of **2** in C_6D_6 at 25 ^{o}C

(*The singlet of proton signal at -1.13 ppm is assigned to Ti-CH*)

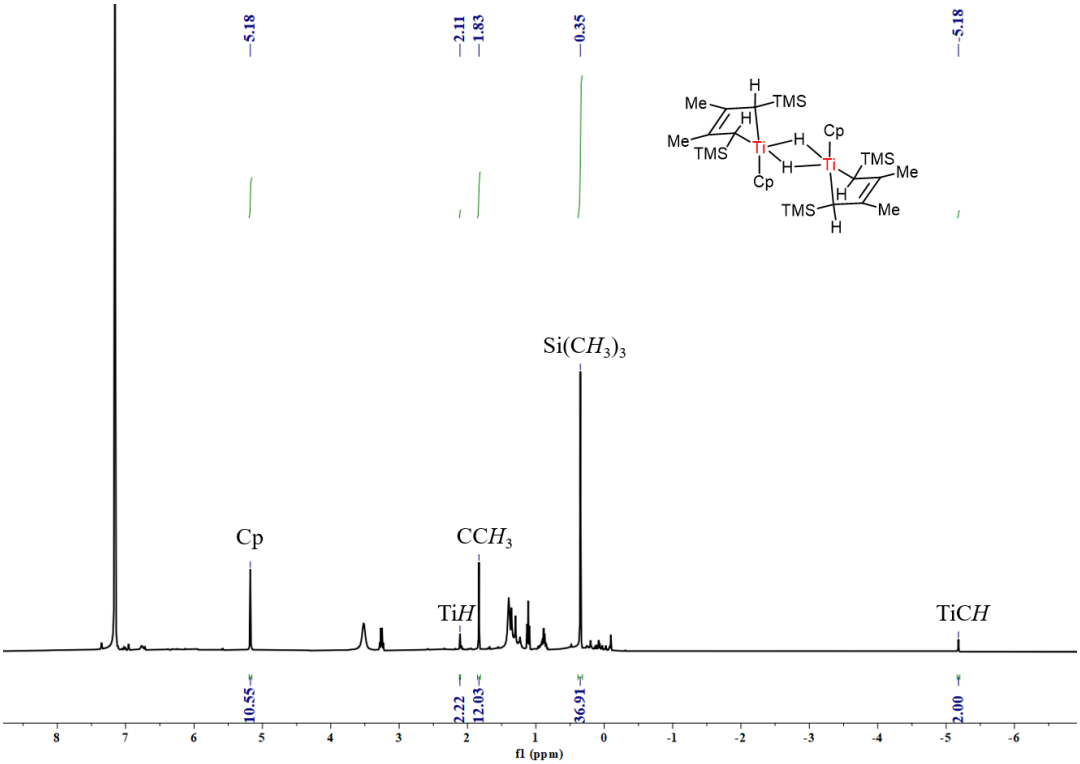


Figure S5. ^{1}H NMR spectrum (400 MHz) of **3** in C_6D_6 at 25 ^{o}C

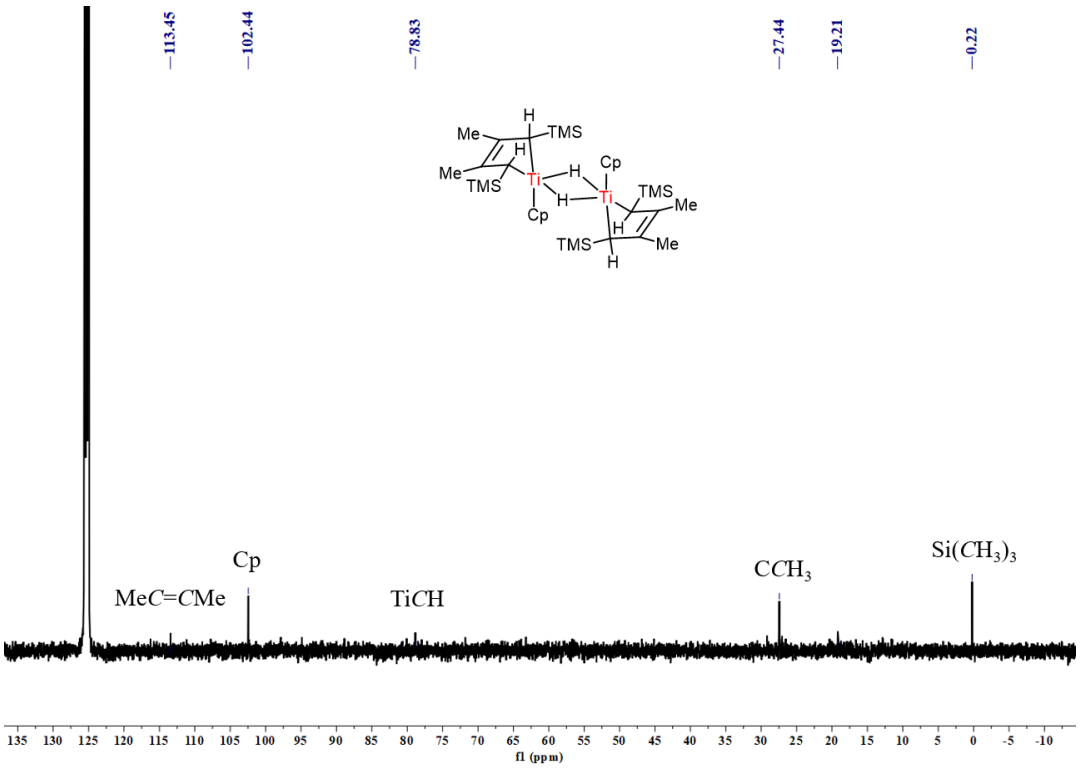


Figure S6. ^{13}C{^{1}H} NMR spectrum (101 MHz) of **3** in C_6D_6 at 25 ^{o}C

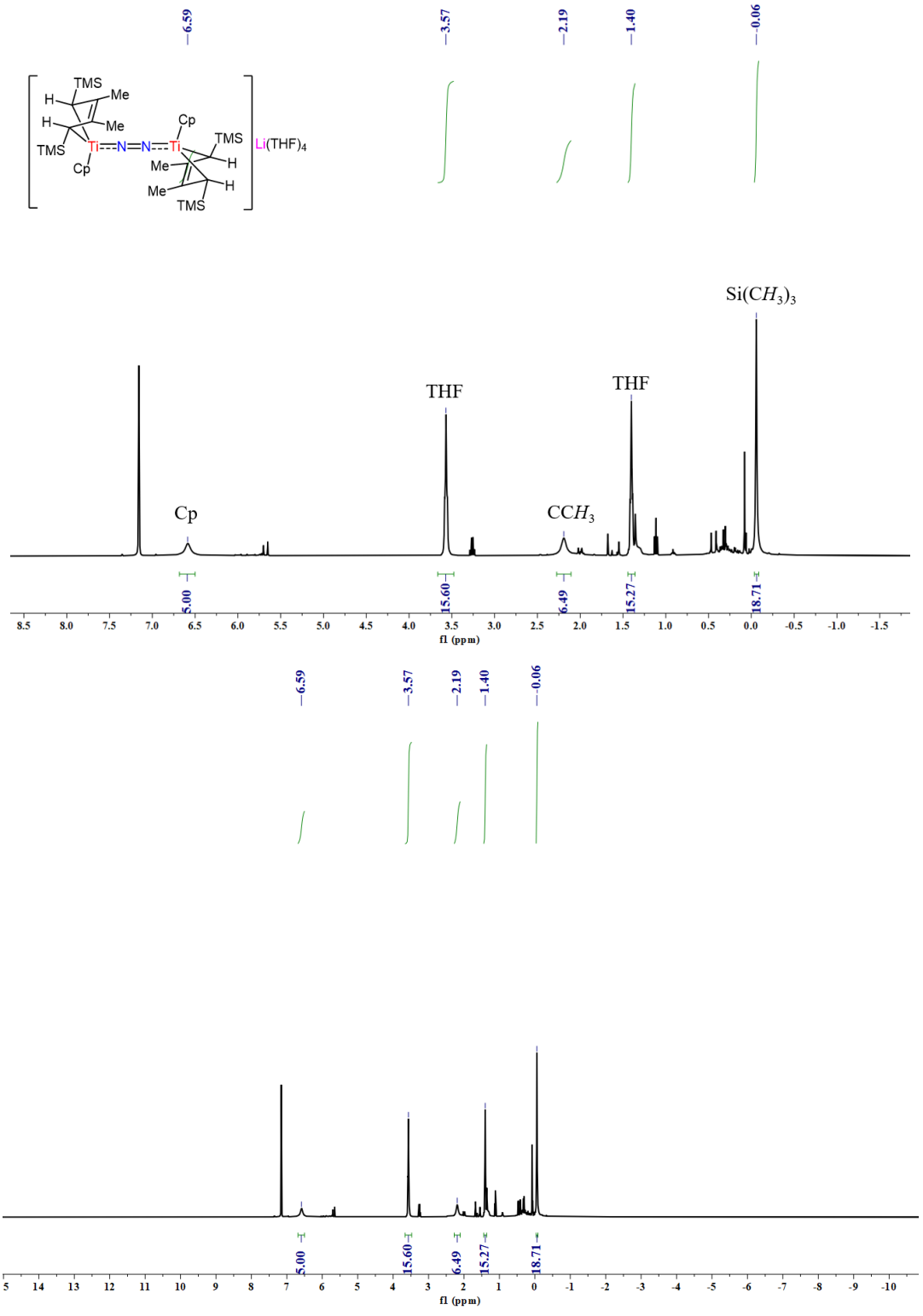


Figure S7. ^{1}H NMR spectrum (400 MHz) of **4** in C_6D_6 at 25 ^{o}C

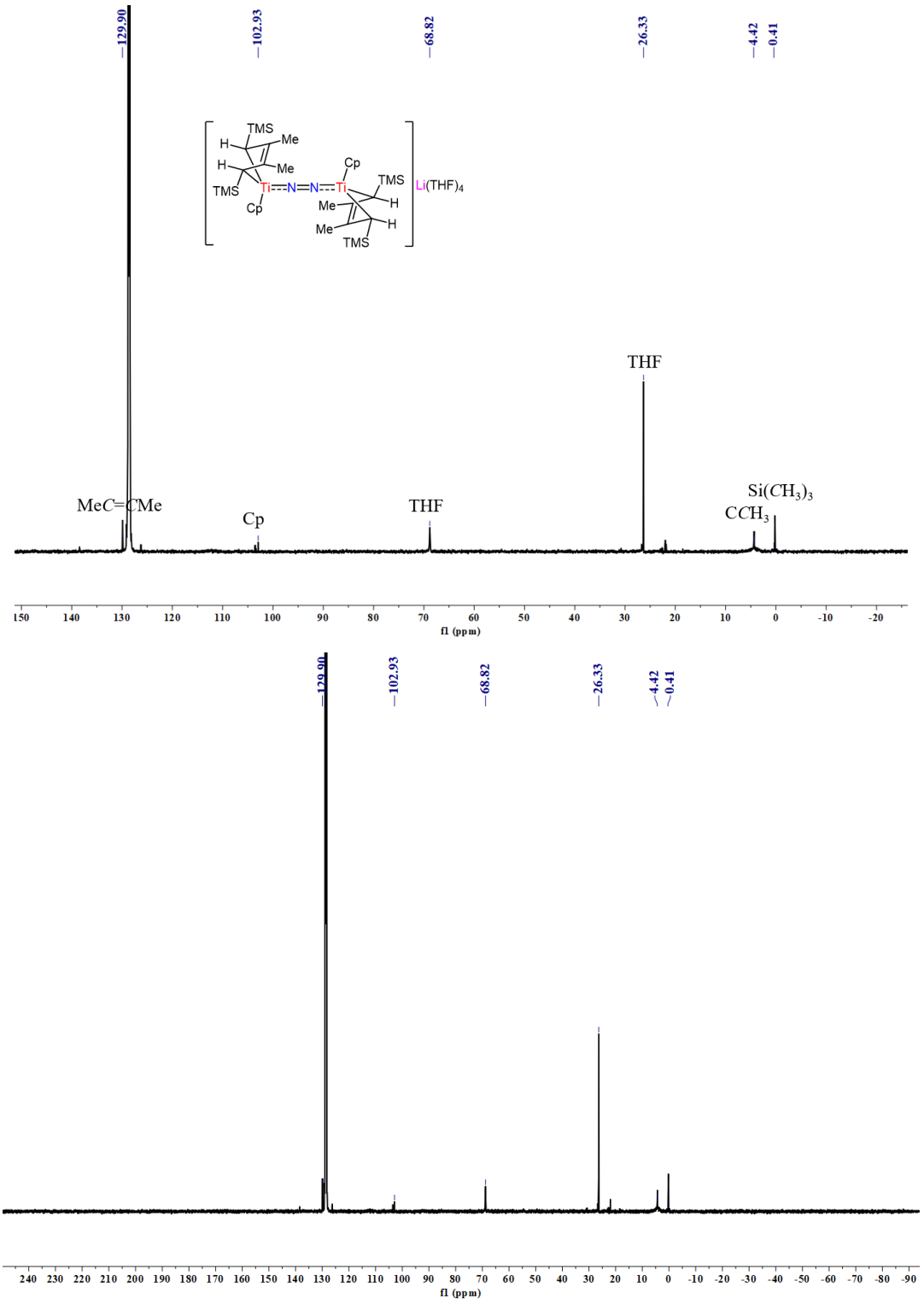


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of **4** in C_6D_6 at 25 ^{o}C

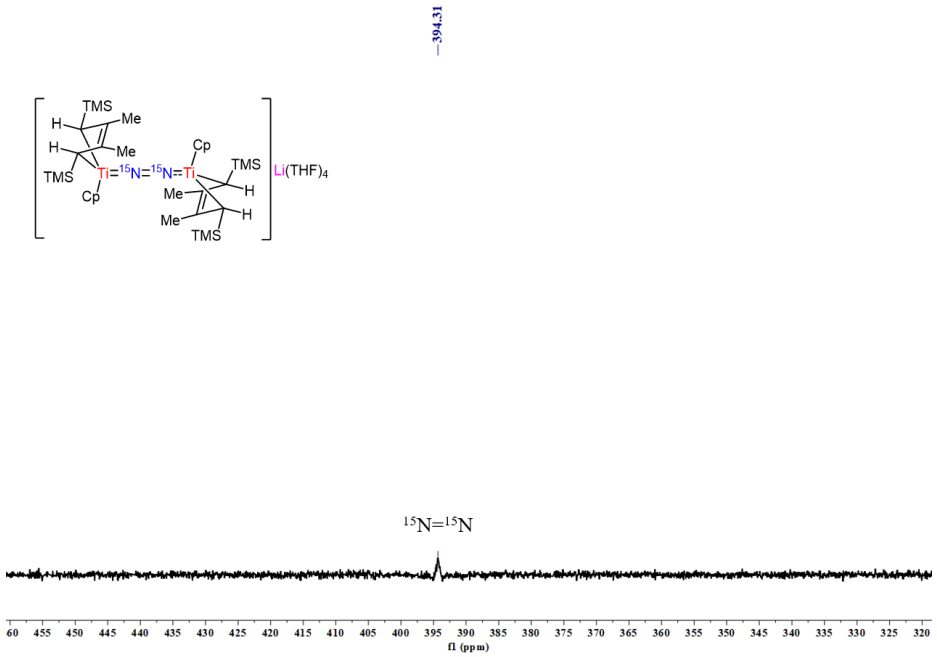


Figure S9. ^{15}N NMR spectrum (61 MHz) of **^{15}N-4** in C_6D_6 at 25 °C

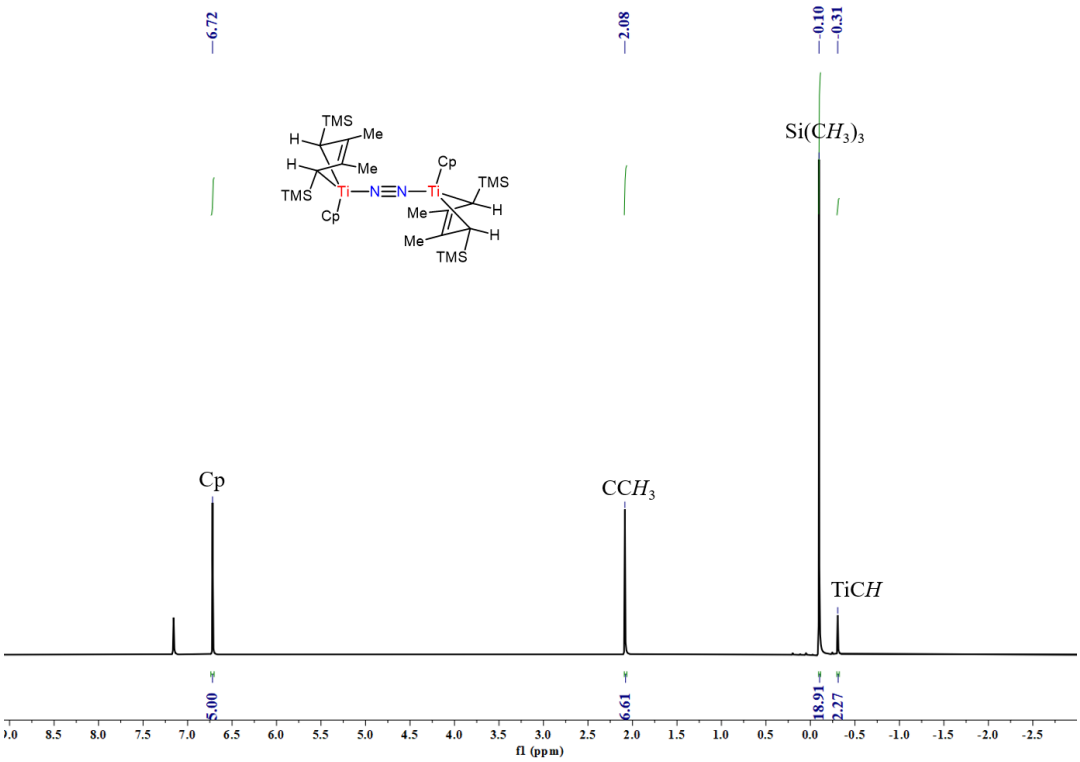


Figure S10. ^{1}H NMR spectrum (400 MHz) of **5** in C_6D_6 at 25 °C

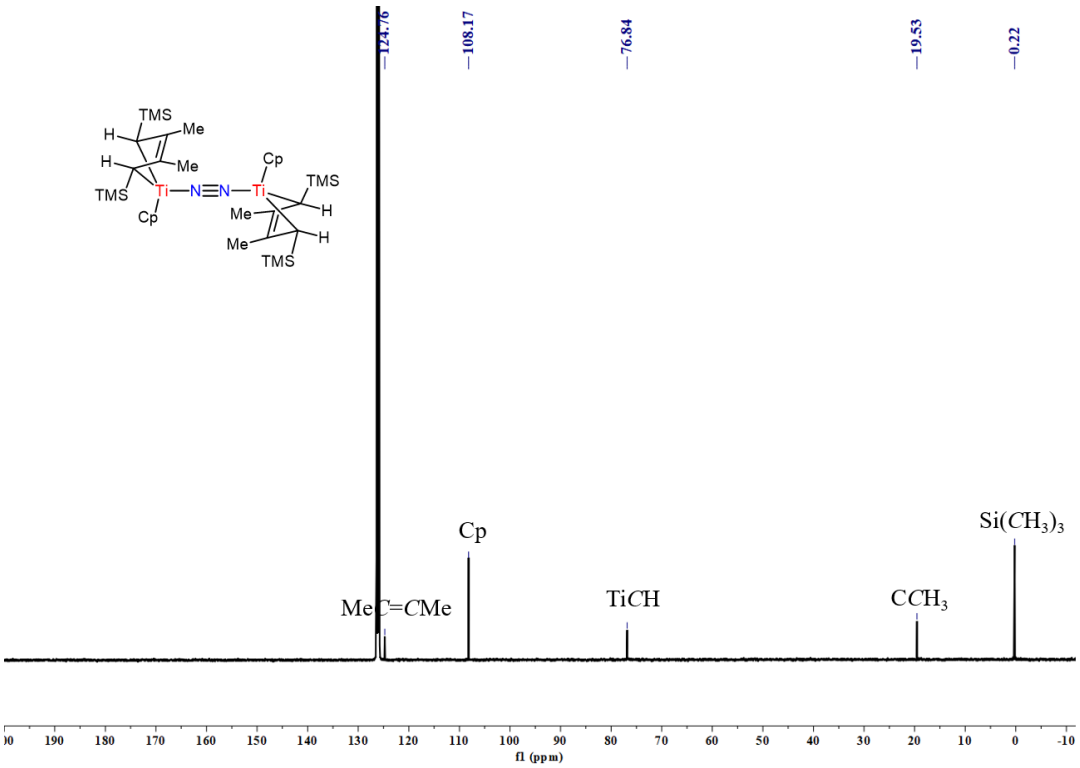


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **5** in C_6D_6 at 25 °C

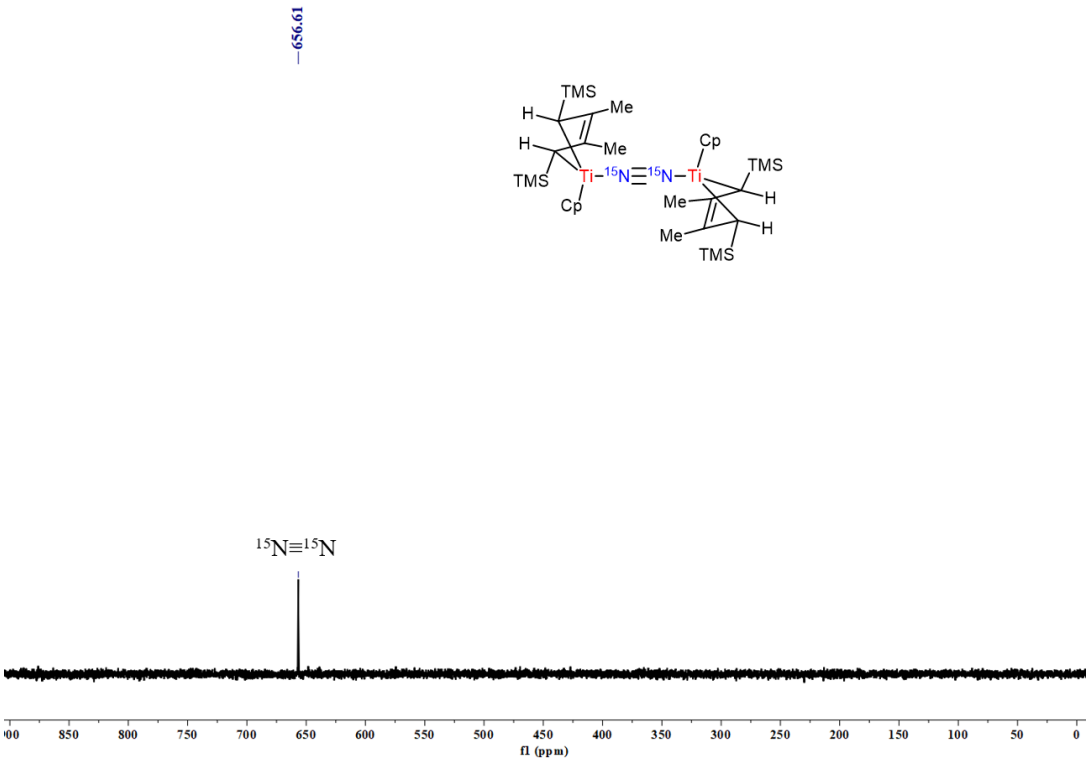


Figure S12. ^{15}N NMR spectrum (61 MHz) of **^{15}N-5** in C_6D_6 at 25 °C

Stability of complexes **2** and **3** in C_6D_6 at room temperature:

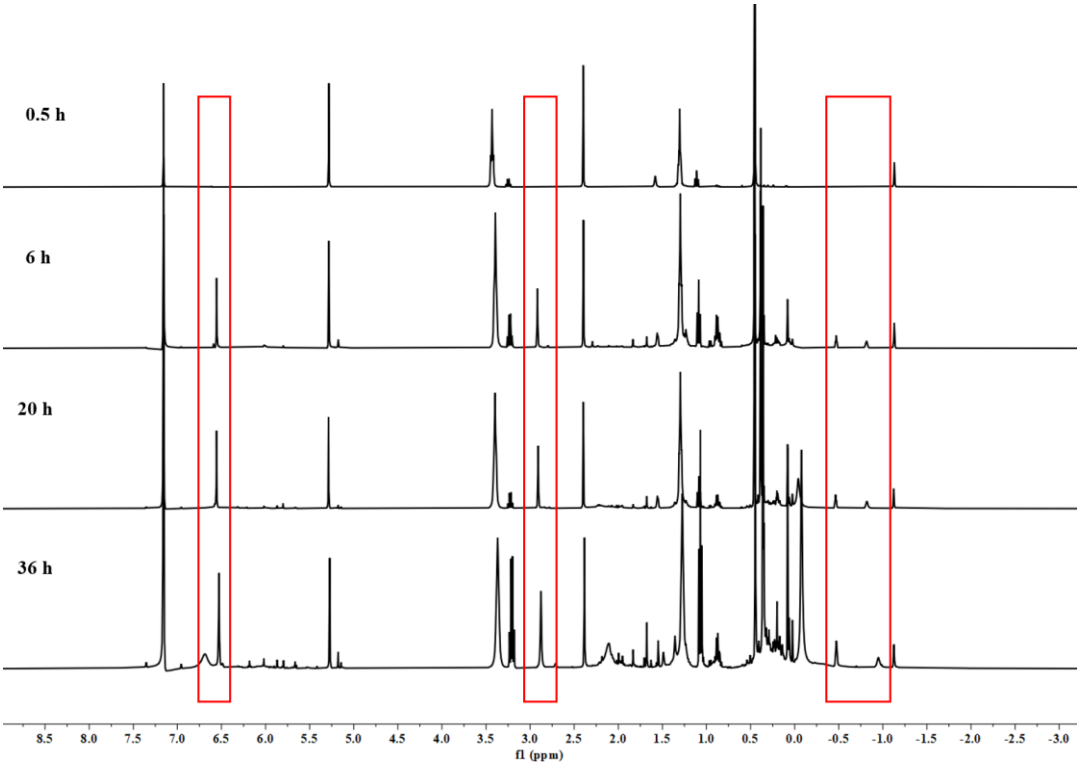


Figure S13. Stacked *in-situ* ^{1}H NMR spectra (400 MHz) of **2** in C_6D_6 at different times with the generation of uncertain by-products

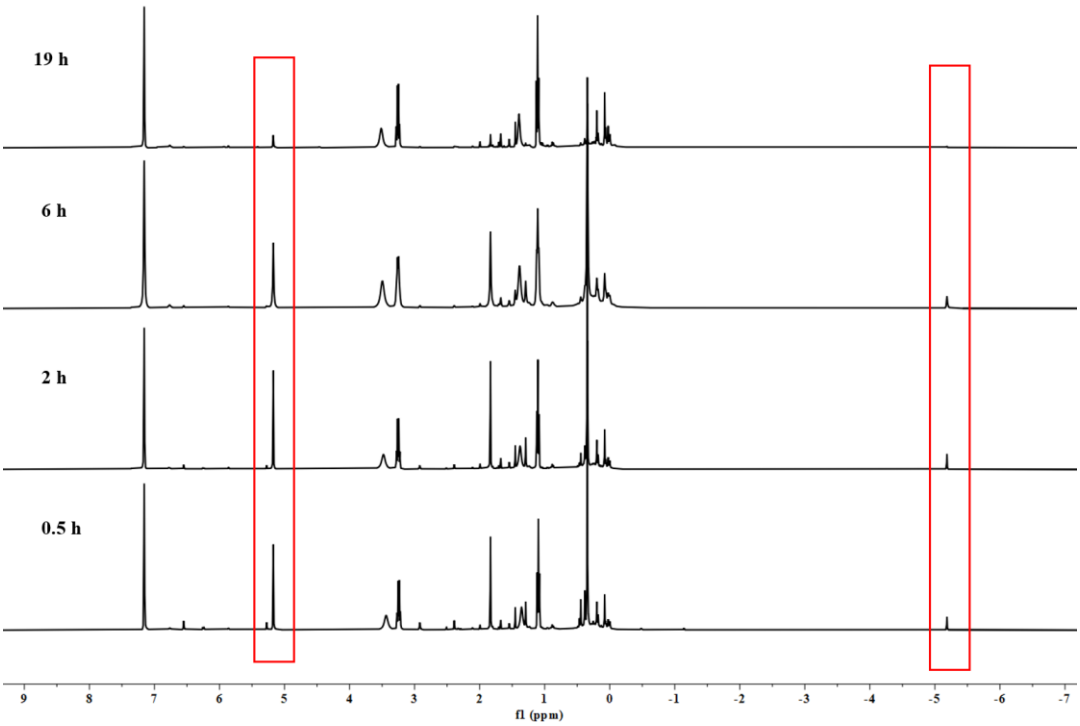


Figure S14. Stacked *in-situ* ^{1}H NMR spectra (400 MHz) of **3** in C_6D_6 at different times with the disappearance of the product

3. Copies of Raman Spectra

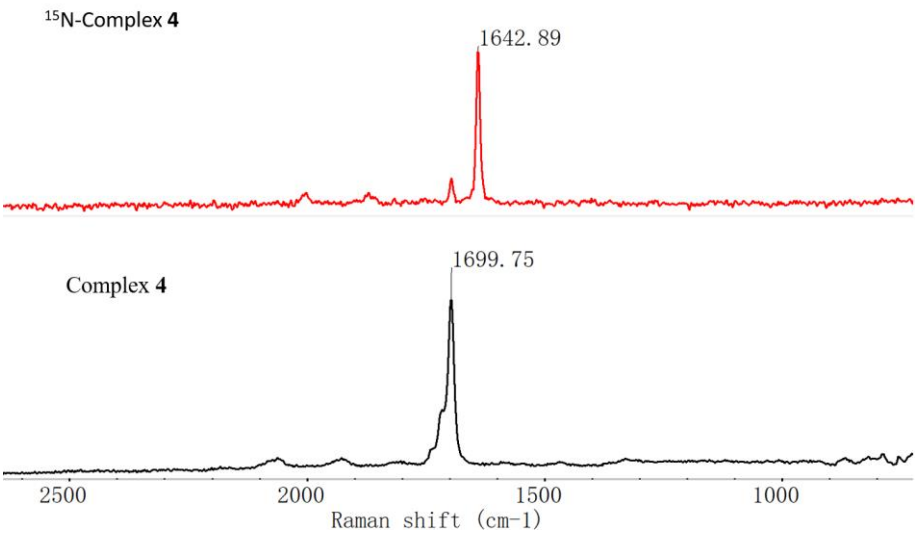


Figure S15. Select region of Raman spectra of crystal samples **4** (black line) and **^{15}N-4** (red line) at room temperature in an argon atmosphere

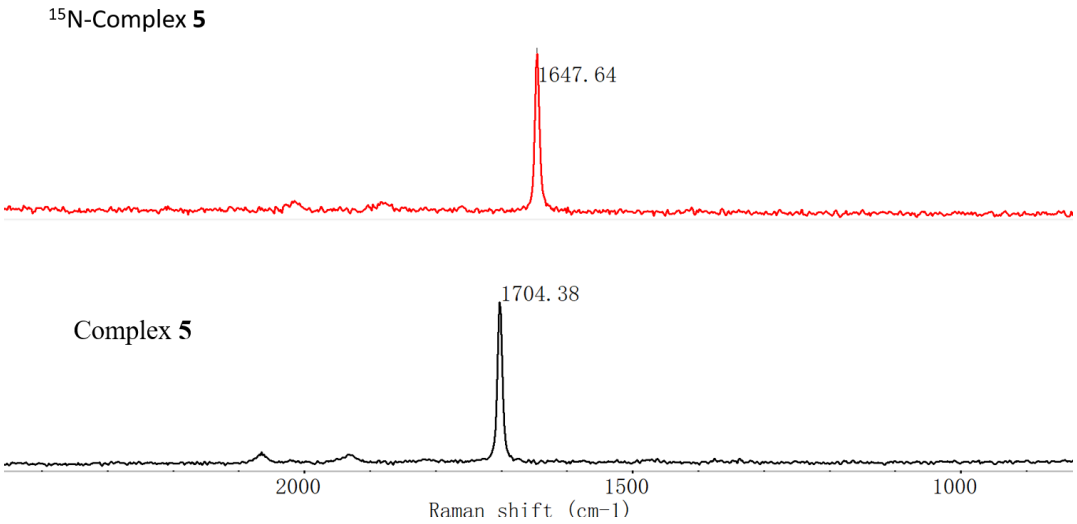


Figure S16. Select region of Raman spectra of crystal samples **5** (black line) and **^{15}N-5** (red line) at room temperature in an argon atmosphere

4. Copies of UV-vis Spectra

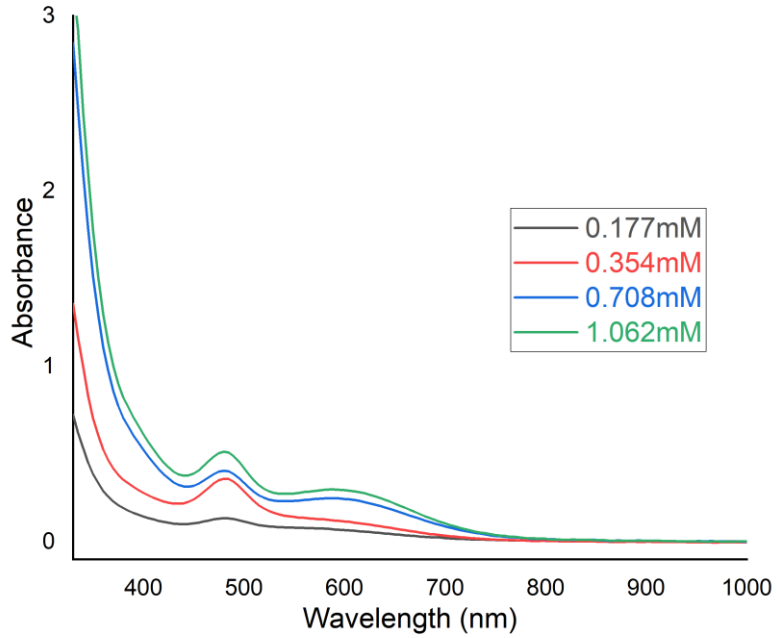


Figure S17. UV-vis spectra of **2** in 0.177-1.062 mM solutions in THF at room temperature

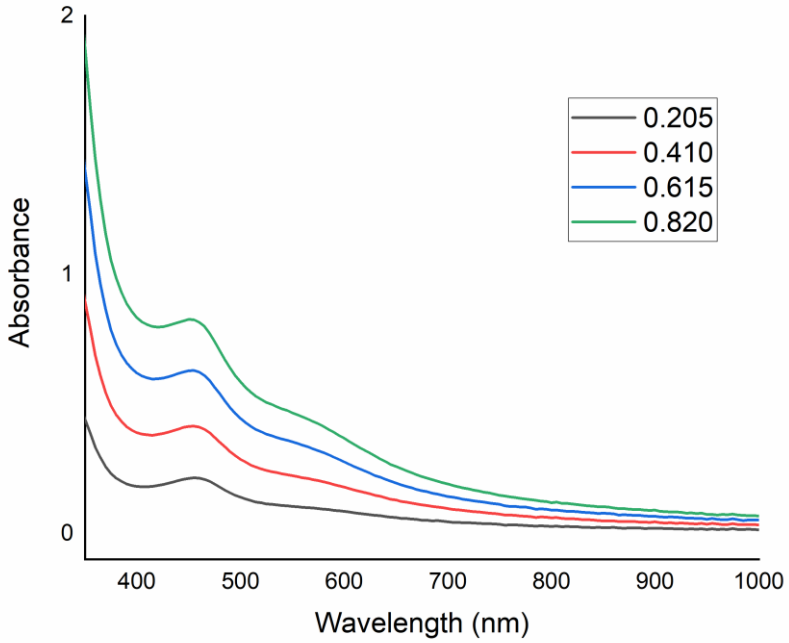


Figure S18. UV-vis spectra of **3** in 0.205-0.820 mM solutions in THF at room temperature

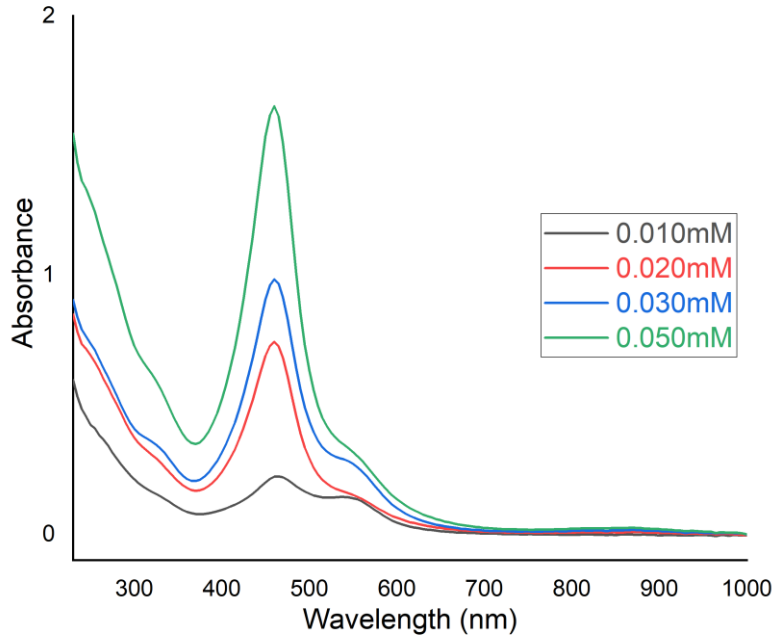


Figure S19. UV-vis spectra of **4** in 0.010-0.050 mM solutions in THF at room temperature

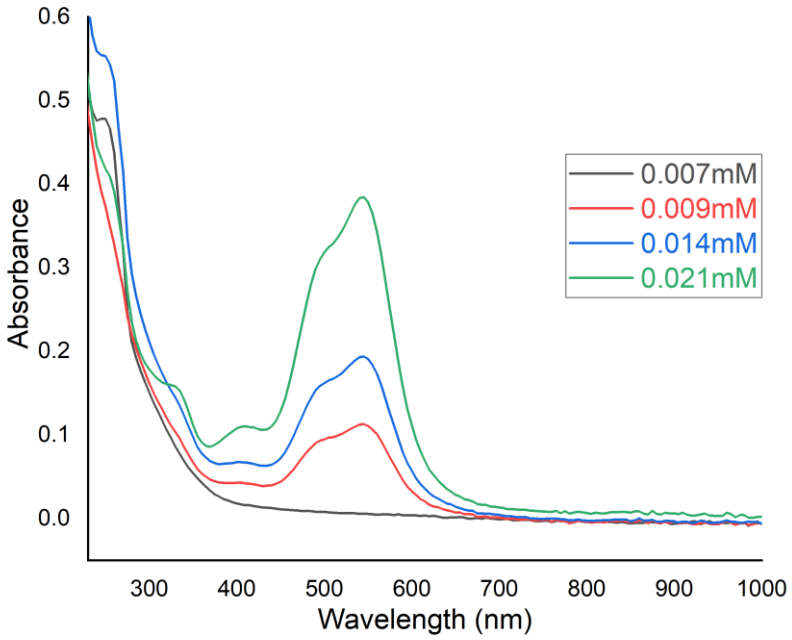


Figure S20. UV-vis spectra of **5** in 0.007-0.021 mM solutions in THF at room temperature

5. EPR Spectra

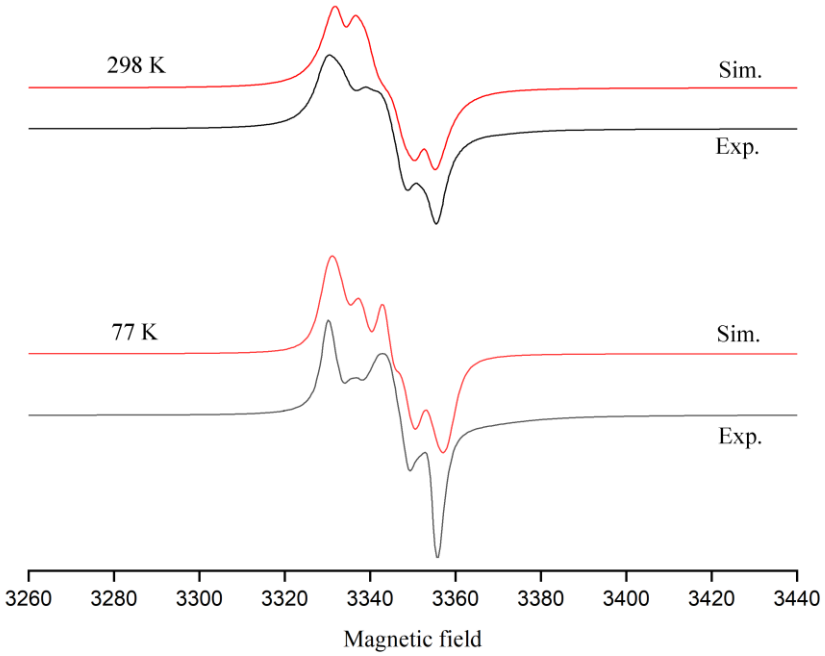


Figure S21. Experimental (black) and simulated (red) X-band EPR spectra of complex **4** recorded in toluene solution at 298 K (top) and 77 K (bottom).

EPR spectrum of **4** at 77 K is simulated by Easyspin with g = 2.006. The experimental spectrum does not show three equal-height peaks arising from the influence of a single nitrogen nucleus, indicating that two nitrogen nuclei have hyperfine interactions with unpaired electron. The spectrum also does not display five peaks with sequentially varying heights, suggesting that the strength of hyperfine interaction between the two nitrogen nuclei and electron is different. For the two nitrogen atoms, the hyperfine coupling constants are A1 = [15.21 30.39 7.32] and A2 = [8.65 6.13 18.84], respectively.

6. Cyclic Voltammetry

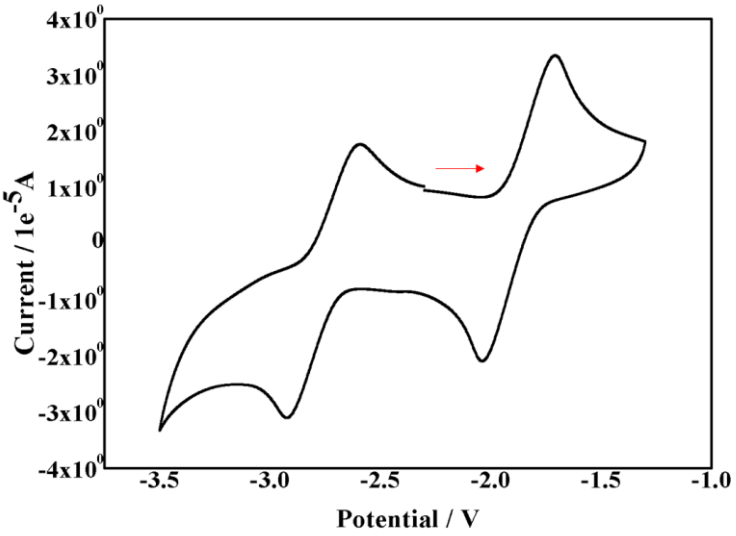


Figure S22. Cyclic voltammetry measurements of complex **4** (1 mM) at room temperature; recorded in THF under an N_2 atmosphere; [($^nBu_4NPF_6$)] (0.1 M) as the supporting electrolyte. Two reversible one-electron events at $E_{1/2}$ = -2.923 V and -1.709 V at the beginning of the experiment.

7. X-ray Crystallographic Studies

Table S2. Crystal data and structure refinement for complex **2**

CCDC number	2284338
Empirical formula	$C_{29}H_{57}O_3Si_2Li_1Ti_1$
Formula weight	564.76
Temperature/K	179.99(10)
Crystal system	Triclinic
Space group	P-1
a/Å	11.1236(6)
b/Å	12.2334(5)
c/Å	15.0490(6)
α/°	88.008(3)
β/°	68.826(4)
γ/°	64.750(4)
Volume/Å^3	1709.78(15)
Z	2
ρ_{calc}, g/cm^3	1.097
μ/mm^{-1}	0.345
F(000)	616.0
Crystal size/mm^3	0.15 x 0.06 x 0.05
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.238 to 54.97
Index ranges	$-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-19 \leq l \leq 19$
Reflections collected	30506
Independent reflections	7860 [R_{int} = 0.0244, R_{sigma} = 0.0223]
Data/restraints/parameters	7860/904/469
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0469, wR_2 = 0.1282
Final R indexes [all data]	R_1 = 0.0551, wR_2 = 0.1338
Largest diff. peak/hole / e Å^{-3}	0.76/-0.43

Table S3. Crystal data and structure refinement for complex **3**

CCDC number	2284339
Empirical formula	$C_{34}H_{64}Si_4Ti_2$
Formula weight	681.01
Temperature/K	179.99(10)
Crystal system	Triclinic
Space group	P-1
a/Å	10.1610(2)
b/Å	12.0365(2)
c/Å	15.9464(3)
α/°	90.1850(10)
β/°	98.5710(10)
γ/°	101.7520(10)
Volume/Å^3	1886.95(6)
Z	2
ρ_{calc}, g/cm^3	1.199
μ/mm^{-1}	0.571
F(000)	736.0
Crystal size/mm^3	0.18 × 0.06 × 0.06
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.818 to 54.968
Index ranges	$-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-20 \leq l \leq 20$
Reflections collected	37148
Independent reflections	8634 [R_{int} = 0.0293, R_{sigma} = 0.0236]
Data/restraints/parameters	8634/0/401
Goodness-of-fit on F^2	1.0 42
Final R indexes [I>=2σ (I)]	R_1 = 0.0269, wR_2 = 0.0698
Final R indexes [all data]	R_1 = 0.0323, wR_2 = 0.0727
Largest diff. peak/hole / e Å^{-3}	0.37/-0.36

Table S4. Crystal data and structure refinement for complex **4**

CCDC number	2284340
Empirical formula	$C_{50}H_{94}N_2O_4Si_4Li_1Ti_2$
Formula weight	1002.37
Temperature/K	179.99(10)
Crystal system	Triclinic
Space group	P-1
a/Å	10.7595(3)
b/Å	10.7982(2)
c/Å	26.3640(7)
α/°	80.790(2)
β/°	84.849(2)
γ/°	80.477(2)
Volume/Å^3	2975.59(13)
Z	2
ρ_{calc}, g/cm^3	1.119
μ/mm^{-1}	0.387
F(000)	1086.0
Crystal size/mm^3	0.12 × 0.1 × 0.04
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.606 to 54.968
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $-34 \leq l \leq 28$
Reflections collected	37625
Independent reflections	13603 [R_{int} = 0.0415, R_{sigma} = 0.0620]
Data/restraints/parameters	13603/1052/800
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0499, wR_2 = 0.1316
Final R indexes [all data]	R_1 = 0.0803, wR_2 = 0.1423
Largest diff. peak/hole / e Å^{-3}	0.53/-0.40

Table S5. Crystal data and structure refinement for complex **5**

CCDC number	2284341
Empirical formula	$C_{34}H_{62}N_2Si_4Ti_2$
Formula weight	707.01
Temperature/K	179.99(10)
Crystal system	Monoclinic
Space group	I2/a
a/Å	11.3116(4)
b/Å	18.0476(6)
c/Å	19.9174(6)
α/°	90
β/°	91.779(3)
γ/°	90
Volume/Å^3	4064.1(2)
Z	4
ρ_{calc}, g/cm^3	1.155
μ/mm^{-1}	0.534
F(000)	1520.0
Crystal size/mm^3	0.19 × 0.15 × 0.05
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.238 to 54.97
Index ranges	$-14 \leq h \leq 12$, $-23 \leq k \leq 22$, $-25 \leq l \leq 25$
Reflections collected	16160
Independent reflections	4660 [R_{int} = 0.0191, R_{sigma} = 0.0187]
Data/restraints/parameters	4660/300/265
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0301, wR_2 = 0.0878
Final R indexes [all data]	R_1 = 0.0355, wR_2 = 0.0909
Largest diff. peak/hole / e Å^{-3}	0.42/-0.38

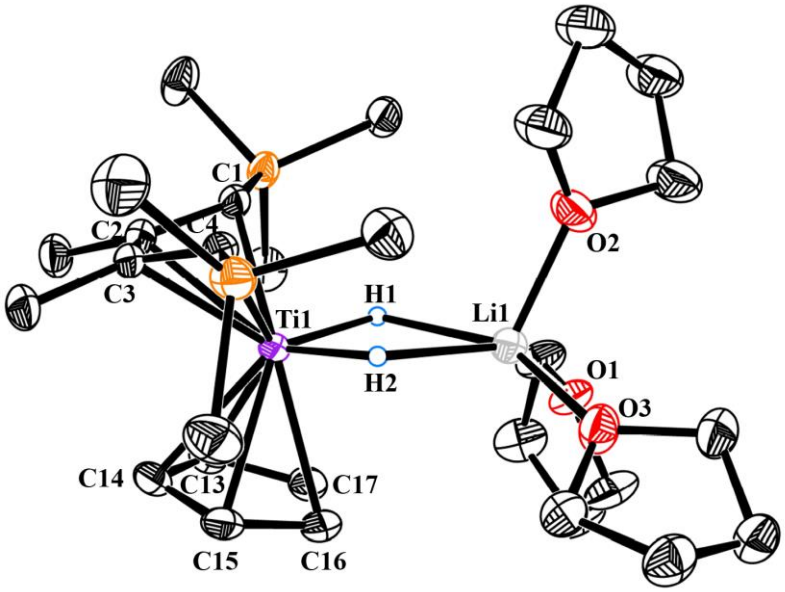


Figure S23. ORTEP plot (35% probability) of **2**. Except for the briding hydrides (H1 and H2), all the hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Ti1–H1 1.70(2), Ti1–H2 1.65(4), Li1–H1 1.99(2), Li1–H2 1.96(3), Ti1–C1 2.254(2), Ti1–C2 2.317(2), Ti1–C3 2.316(2), Ti1–C4 2.254(2), Ti1–C13 2.370(5), Ti1–C14 2.372(5), Ti1–C15 2.385(4), Ti1–C16 2.391(4), Ti1–C17 2.382(3), Ti1–Cent1 2.051, C1–C2 1.438(3), C2–C3 1.408(3), C3–C4 1.439(3), H1–Ti1–H2 73(1).

Cent1: Centre of the Cp ring (C13~C17).

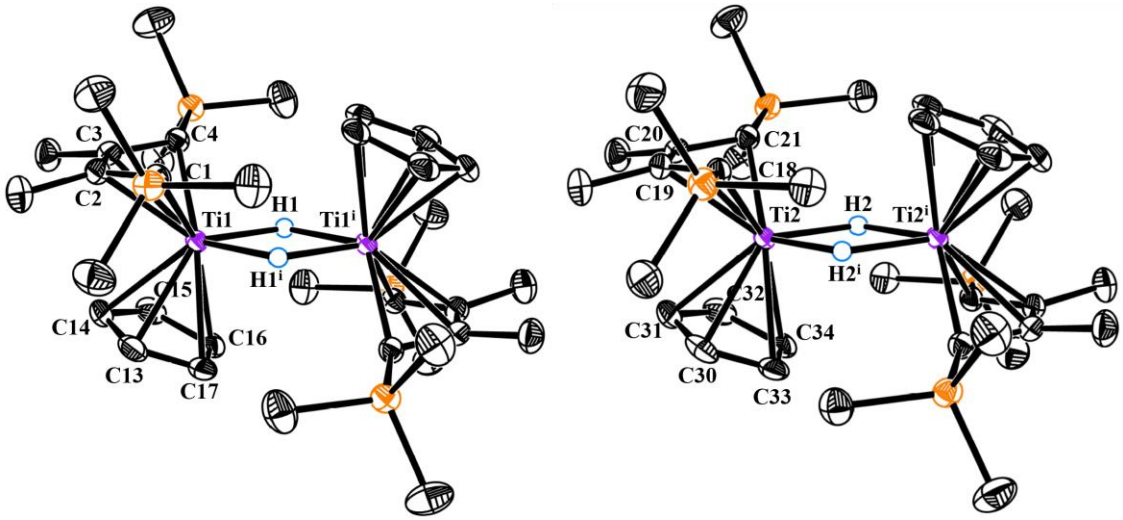


Figure S24. ORTEP plot (35% probability) of **3**. Except for the briding hydrides (H1, H2, $H1^{i}$ and $H2^{i}$), all the hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Ti1–H1 1.88(2), Ti1–$H1^{i}$ 1.87(2), Ti1–C1 2.218(1), Ti1–C2 2.376(1), Ti1–C3 2.374(1), Ti1–C4 2.223(1), Ti1–C13 2.352(2), Ti1–C14 2.351(2), Ti1–C15 2.358(2), Ti1–C16 2.393(1), Ti1–C17 2.390(1), Ti1–Cent1 2.044, C1–C2 1.444(2), C2–C3 1.412(2), C3–C4 1.439(2), H1–Ti1–$H1^{i}$ 65.3(8), Ti2–H2 1.83(2), Ti2–$H2^{i}$ 1.88(2), Ti2–C18 2.221(1), Ti2–C19 2.374(1), Ti2–C20 2.374(1), Ti2–C21 2.219(1), Ti2–C30 2.355(2), Ti2–C31 2.346(2), Ti2–C32 2.352(2), Ti2–C33 2.397(2), Ti2–C34 2.400(2), Ti2–Cent2 2.046, C18–C19 1.438(2), C19–C20 1.410(2), C20–C21 1.441(2), H2–Ti2–$H2^{i}$ 63.6(8).

Cent1: Centre of the Cp ring (C13~C17), Cent2: Centre of the Cp ring (C30~C34).

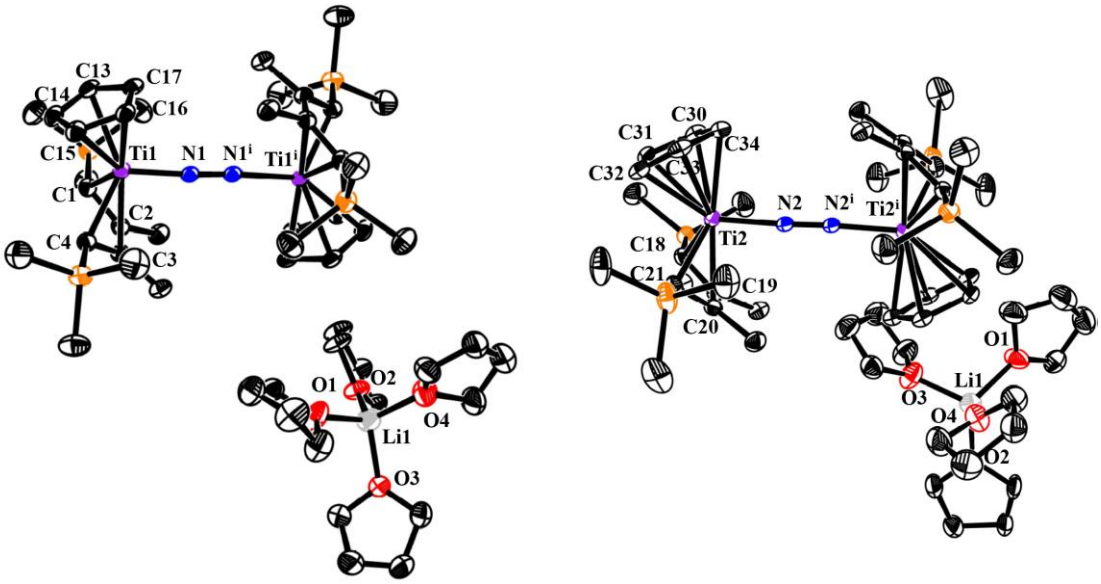


Figure S25. ORTEP plot (35% probability) of **4**. All the hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: N1–N1^{i} 1.198(2), Ti1–N1 1.903(2), Ti1–C1 2.229(2), Ti1–C2 2.314(2), Ti1–C3 2.324(2), Ti1–C4 2.237(2), Ti1–C13 2.41(2), Ti1–C14 2.42(2), Ti1–C15 2.43(2), Ti1–C16 2.39(2), Ti1–C17 2.40(2), Ti1–Cent1 2.098, C1–C2 1.448(3), C2–C3 1.403(3), C3–C4 1.443(3), Ti1–N1–N1^{i} 176.3(2), N2–N2^{i} 1.200(2), Ti2–N2 1.898(2), Ti2–C18 2.233(2), Ti2–C19 2.328(2), Ti2–C20 2.315(2), Ti2–C21 2.225(2), Ti2–C30 2.378(9), Ti2–C31 2.42(1), Ti2–C32 2.39(1), Ti2–C33 2.44(1), Ti2–C34 2.39(1), Ti2–Cent2 2.097, C18–C19 1.454(3), C19–C20 1.398(3), C20–C21 1.449(3), Ti2–N2–N2^{i} 177.0(1).

Cent1: Centre of the Cp ring (C13~C17), Cent2: Centre of the Cp ring (C30~C34).

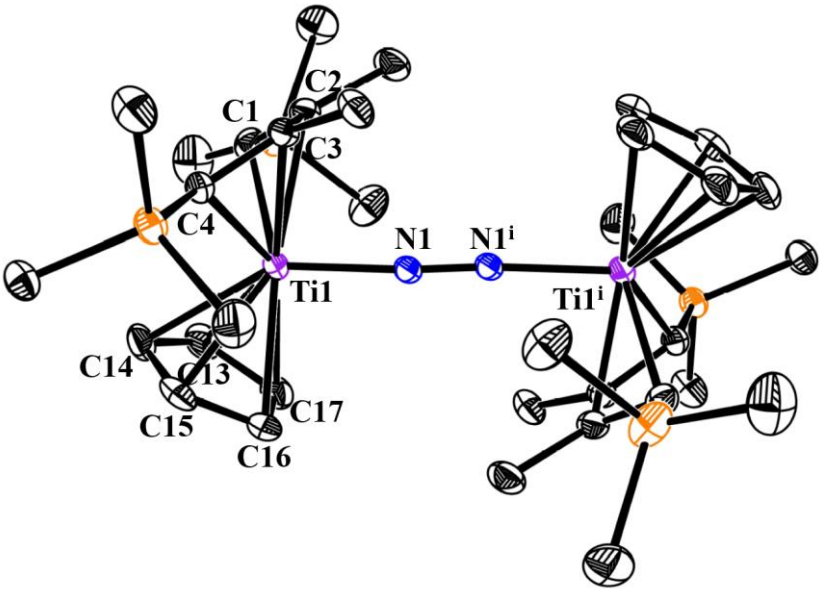


Figure S26. ORTEP plot (35% probability) of **5**. All the hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: N1–N1^{i} 1.179(2), Ti1–N1 1.945(1), Ti1–C1 2.199(1), Ti1–C2 2.296(1), Ti1–C3 2.294(1), Ti1–C4 2.196(1), Ti1–C13 2.41(1), Ti1–C14 2.38(1), Ti1–C15 2.40(2), Ti1–C16 2.37(2), Ti1–C17 2.40(1), Ti1–Cent1 2.050, C1–C2 1.448(2), C2–C3 1.414(2), C3–C4 1.441(2), Ti1–N1–N1^{i} 175.9(1).

Cent1: Centre of the Cp ring (C13~C17).

8. Computational Details

DFT calculations were performed using ORCA 5.0.3. Geometric structures were optimized employing the r2SCAN-3c level of theory. Cartesian coordinates of the optimized geometry were provided as a separate .xyz file. FBO analysis was based on the optimized structures.

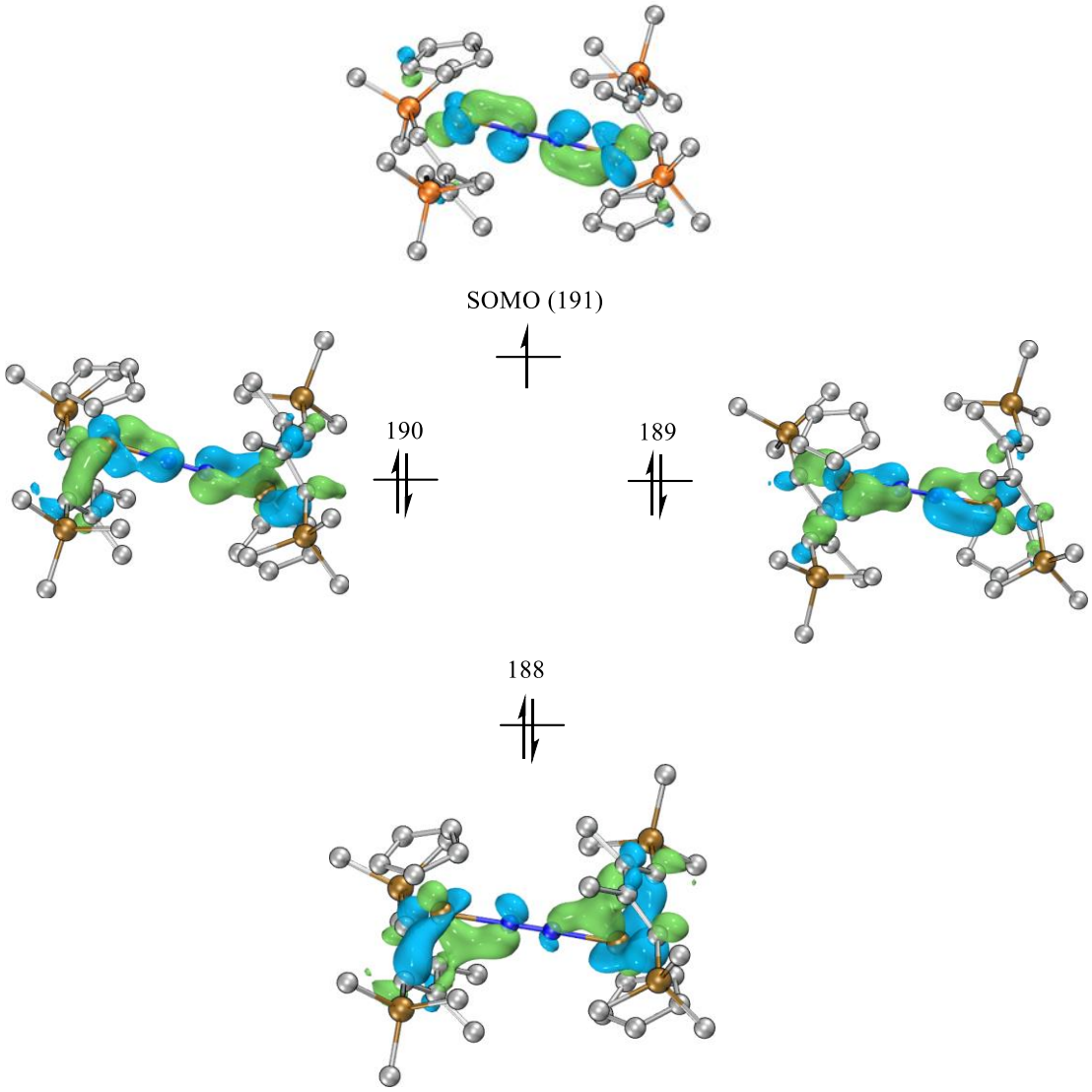
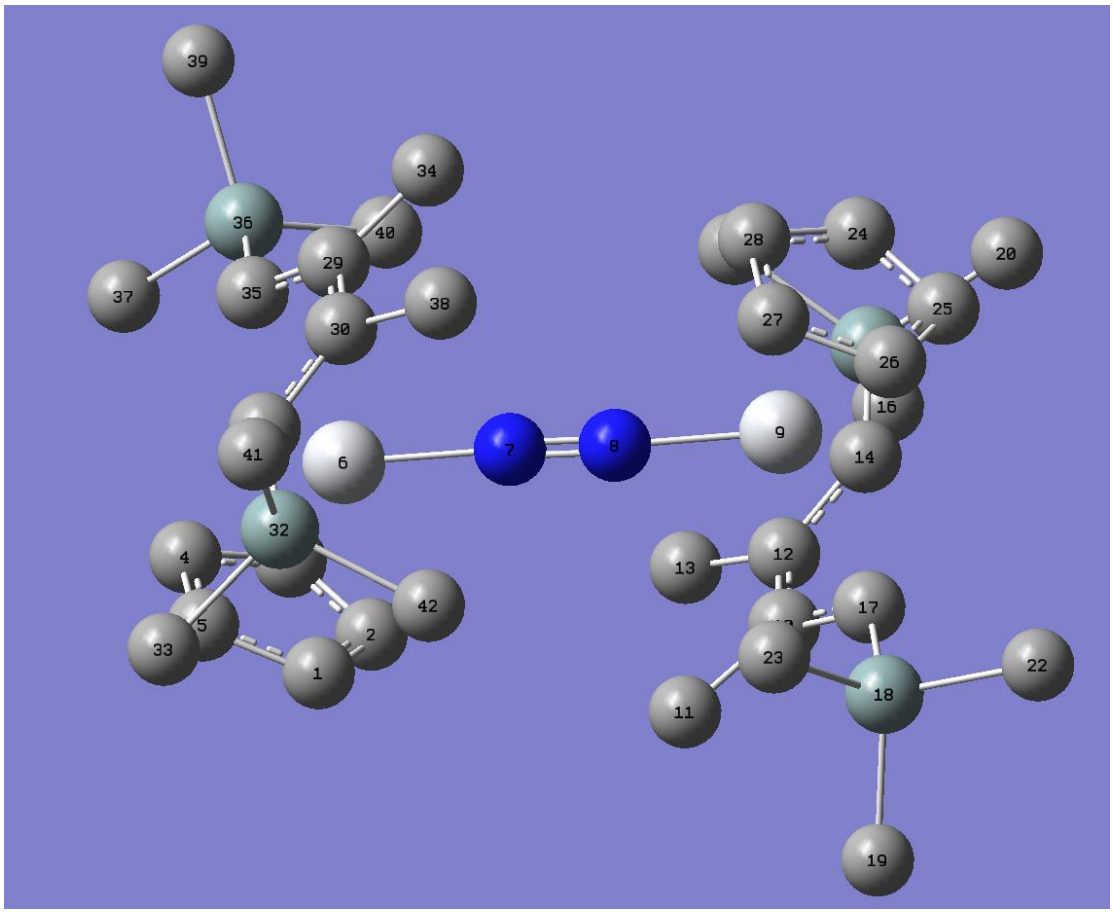


Figure S27. The selected molecular orbitals (isovalue = 0.05) of complex **4**.

Fuzzy atom bond order of complex **4**



The total bond order >= 0.050000

1: 1(C) 2(C) Alpha: 0.584879 Beta: 0.587071 Total: 1.171950

2: 1(C) 3(C) Alpha: 0.049163 Beta: 0.052355 Total: 0.101517

3: 1(C) 4(C) Alpha: 0.053131 Beta: 0.050614 Total: 0.103745

4: 1(C) 5(C) Alpha: 0.580811 Beta: 0.586574 Total: 1.167385

5: 1(C) 6(Ti) Alpha: 0.295847 Beta: 0.289156 Total: 0.585003

6: 1(C) 99(H) Alpha: 0.430664 Beta: 0.430098 Total: 0.860761

7: 2(C) 3(C) Alpha: 0.590480 Beta: 0.591598 Total: 1.182078

8: 2(C) 4(C) Alpha: 0.051063 Beta: 0.052611 Total: 0.103674

9: 2(C) 5(C) Alpha: 0.051048 Beta: 0.052320 Total: 0.103368

10: 2(C) 6(Ti) Alpha: 0.290424 Beta: 0.285957 Total: 0.576381

11: 2(C) 89(H) Alpha: 0.420626 Beta: 0.420504 Total: 0.841130

12: 3(C) 4(C) Alpha: 0.577822 Beta: 0.586113 Total: 1.163935

13: 3(C) 5(C) Alpha: 0.051764 Beta: 0.050927 Total: 0.102691

14: 3(C) 6(Ti) Alpha: 0.298418 Beta: 0.290777 Total: 0.589194

15: 3(C) 80(H) Alpha: 0.428656 Beta: 0.428188 Total: 0.856844

16: 4(C) 5(C) Alpha: 0.610246 Beta: 0.598542 Total: 1.208788

17: 4(C) 6(Ti) Alpha: 0.274645 Beta: 0.278650 Total: 0.553295

18: 4(C) 82(H) Alpha: 0.426971 Beta: 0.426479 Total: 0.853449

19: 5(C) 6(Ti) Alpha: 0.278359 Beta: 0.281043 Total: 0.559401

20: 5(C) 92(H) Alpha: 0.424015 Beta: 0.423989 Total: 0.848003

21: 6(Ti) 7(N) Alpha: 0.857907 Beta: 0.722527 Total: 1.580434

22: 6(Ti) 8(N) Alpha: 0.129441 Beta: 0.095598 Total: 0.225039

23: 6(Ti) 9(Ti) Alpha: 0.274562 Beta: 0.130589 Total: 0.405151

24: 6(Ti) 29(C) Alpha: 0.298614 Beta: 0.291001 Total: 0.589615

25: 6(Ti) 30(C) Alpha: 0.301095 Beta: 0.297011 Total: 0.598106

26: 6(Ti) 31(C) Alpha: 0.439227 Beta: 0.435270 Total: 0.874496

27: 6(Ti) 32(Si) Alpha: 0.070699 Beta: 0.069188 Total: 0.139887

28: 6(Ti) 35(C) Alpha: 0.442562 Beta: 0.433853 Total: 0.876415

29: 6(Ti) 36(Si) Alpha: 0.070294 Beta: 0.067338 Total: 0.137632

30: 6(Ti) 72(H) Alpha: 0.048387 Beta: 0.048703 Total: 0.097090

31: 6(Ti) 81(H) Alpha: 0.041466 Beta: 0.042638 Total: 0.084104

32: 7(N) 8(N) Alpha: 0.926019 Beta: 1.037228 Total: 1.963247

33: 7(N) 9(Ti) Alpha: 0.122015 Beta: 0.106072 Total: 0.228087

34: 8(N) 9(Ti) Alpha: 0.849439 Beta: 0.742265 Total: 1.591704

35: 9(Ti) 10(C) Alpha: 0.305886 Beta: 0.303769 Total: 0.609655

36: 9(Ti) 11(C) Alpha: 0.025932 Beta: 0.025448 Total: 0.051380

37: 9(Ti) 12(C) Alpha: 0.306397 Beta: 0.299834 Total: 0.606231

38: 9(Ti) 13(C) Alpha: 0.025840 Beta: 0.025429 Total: 0.051268

39: 9(Ti) 14(C) Alpha: 0.446898 Beta: 0.438770 Total: 0.885667

40: 9(Ti) 15(Si) Alpha: 0.072124 Beta: 0.069492 Total: 0.141616

41: 9(Ti) 17(C) Alpha: 0.437763 Beta: 0.432822 Total: 0.870585

42: 9(Ti) 18(Si) Alpha: 0.063838 Beta: 0.063493 Total: 0.127332

43: 9(Ti) 24(C) Alpha: 0.298728 Beta: 0.293211 Total: 0.591938

44: 9(Ti) 25(C) Alpha: 0.282184 Beta: 0.286546 Total: 0.568730

45: 9(Ti) 26(C) Alpha: 0.291792 Beta: 0.293138 Total: 0.584930

46: 9(Ti) 27(C) Alpha: 0.293451 Beta: 0.294674 Total: 0.588125

47: 9(Ti) 28(C) Alpha: 0.290140 Beta: 0.290647 Total: 0.580787

48: 9(Ti) 66(H) Alpha: 0.046814 Beta: 0.046398 Total: 0.093212

49: 9(Ti) 75(H) Alpha: 0.043853 Beta: 0.044820 Total: 0.088673

50: 10(C) 11(C) Alpha: 0.536370 Beta: 0.536535 Total: 1.072905

51: 10(C) 12(C) Alpha: 0.575772 Beta: 0.567534 Total: 1.143306

52: 10(C) 13(C) Alpha: 0.031833 Beta: 0.031540 Total: 0.063373

53: 10(C) 14(C) Alpha: 0.032520 Beta: 0.032133 Total: 0.064652

54: 10(C) 17(C) Alpha: 0.529523 Beta: 0.530340 Total: 1.059862

55: 10(C) 18(Si) Alpha: 0.037223 Beta: 0.037569 Total: 0.074792

56: 11(C) 12(C) Alpha: 0.030922 Beta: 0.030818 Total: 0.061740

57: 11(C) 13(C) Alpha: 0.027438 Beta: 0.027435 Total: 0.054872

58: 11(C) 17(C) Alpha: 0.032126 Beta: 0.032117 Total: 0.064244

59: 11(C) 18(Si) Alpha: 0.025681 Beta: 0.025740 Total: 0.051421

60: 11(C) 87(H) Alpha: 0.416954 Beta: 0.417019 Total: 0.833973

61: 11(C) 91(H) Alpha: 0.439256 Beta: 0.439605 Total: 0.878861

62: 11(C) 95(H) Alpha: 0.425491 Beta: 0.425505 Total: 0.850995

63: 12(C) 13(C) Alpha: 0.535475 Beta: 0.534576 Total: 1.070051

64: 12(C) 14(C) Alpha: 0.527667 Beta: 0.529224 Total: 1.056891

65: 12(C) 15(Si) Alpha: 0.035671 Beta: 0.036380 Total: 0.072051

66: 12(C) 17(C) Alpha: 0.033679 Beta: 0.032792 Total: 0.066471

67: 13(C) 14(C) Alpha: 0.031487 Beta: 0.031511 Total: 0.062998

68: 13(C) 73(H) Alpha: 0.430506 Beta: 0.430611 Total: 0.861117

69: 13(C) 78(H) Alpha: 0.415664 Beta: 0.415767 Total: 0.831431

70: 13(C) 79(H) Alpha: 0.434503 Beta: 0.434623 Total: 0.869126

71: 14(C) 15(Si) Alpha: 0.521752 Beta: 0.520487 Total: 1.042239

72: 14(C) 66(H) Alpha: 0.381316 Beta: 0.382932 Total: 0.764248

73: 15(Si) 16(C) Alpha: 0.554940 Beta: 0.555036 Total: 1.109976

74: 15(Si) 20(C) Alpha: 0.557728 Beta: 0.557664 Total: 1.115392

75: 15(Si) 21(C) Alpha: 0.552711 Beta: 0.552743 Total: 1.105454

76: 15(Si) 43(H) Alpha: 0.037013 Beta: 0.037010 Total: 0.074023

77: 15(Si) 45(H) Alpha: 0.032420 Beta: 0.032408 Total: 0.064828

78: 15(Si) 47(H) Alpha: 0.035364 Beta: 0.035357 Total: 0.070721

79: 15(Si) 48(H) Alpha: 0.037829 Beta: 0.037847 Total: 0.075676

80: 15(Si) 51(H) Alpha: 0.037375 Beta: 0.037494 Total: 0.074868

81: 15(Si) 54(H) Alpha: 0.032617 Beta: 0.032619 Total: 0.065236

82: 15(Si) 58(H) Alpha: 0.033242 Beta: 0.033261 Total: 0.066503

83: 15(Si) 61(H) Alpha: 0.036825 Beta: 0.036843 Total: 0.073668

84: 15(Si) 64(H) Alpha: 0.034045 Beta: 0.034050 Total: 0.068094

85: 15(Si) 66(H) Alpha: 0.026709 Beta: 0.027007 Total: 0.053716

86: 16(C) 51(H) Alpha: 0.446664 Beta: 0.446415 Total: 0.893079

87: 16(C) 61(H) Alpha: 0.447033 Beta: 0.447017 Total: 0.894050

88: 16(C) 64(H) Alpha: 0.446190 Beta: 0.446155 Total: 0.892344

89: 17(C) 18(Si) Alpha: 0.523552 Beta: 0.522361 Total: 1.045913

90: 17(C) 75(H) Alpha: 0.383092 Beta: 0.383887 Total: 0.766980

91: 18(Si) 19(C) Alpha: 0.557906 Beta: 0.557907 Total: 1.115813

92: 18(Si) 22(C) Alpha: 0.557505 Beta: 0.557397 Total: 1.114902

93: 18(Si) 23(C) Alpha: 0.553566 Beta: 0.553513 Total: 1.107079

94: 18(Si) 75(H) Alpha: 0.026883 Beta: 0.027141 Total: 0.054024

95: 18(Si) 76(H) Alpha: 0.033633 Beta: 0.033623 Total: 0.067255

96: 18(Si) 77(H) Alpha: 0.037463 Beta: 0.037464 Total: 0.074927

97: 18(Si) 84(H) Alpha: 0.036856 Beta: 0.036857 Total: 0.073713

98: 18(Si) 86(H) Alpha: 0.033872 Beta: 0.033873 Total: 0.067745

99: 18(Si) 93(H) Alpha: 0.032408 Beta: 0.032405 Total: 0.064813

100: 18(Si) 94(H) Alpha: 0.036521 Beta: 0.036496 Total: 0.073017

101: 18(Si) 96(H) Alpha: 0.037181 Beta: 0.037196 Total: 0.074377

102: 18(Si) 100(H) Alpha: 0.037435 Beta: 0.037557 Total: 0.074993

103: 18(Si) 102(H) Alpha: 0.034570 Beta: 0.034570 Total: 0.069140

104: 19(C) 96(H) Alpha: 0.445518 Beta: 0.445504 Total: 0.891022

105: 19(C) 100(H) Alpha: 0.447645 Beta: 0.447394 Total: 0.895039

106: 19(C) 102(H) Alpha: 0.443922 Beta: 0.443908 Total: 0.887831

107: 20(C) 43(H) Alpha: 0.448978 Beta: 0.448973 Total: 0.897951

108: 20(C) 45(H) Alpha: 0.440651 Beta: 0.440666 Total: 0.881316

109: 20(C) 48(H) Alpha: 0.446872 Beta: 0.446880 Total: 0.893752

110: 21(C) 47(H) Alpha: 0.447201 Beta: 0.447193 Total: 0.894394

111: 21(C) 54(H) Alpha: 0.439372 Beta: 0.439328 Total: 0.878699

112: 21(C) 58(H) Alpha: 0.434791 Beta: 0.434824 Total: 0.869615

113: 22(C) 76(H) Alpha: 0.445083 Beta: 0.445098 Total: 0.890181

114: 22(C) 77(H) Alpha: 0.447495 Beta: 0.447509 Total: 0.895004

115: 22(C) 84(H) Alpha: 0.448845 Beta: 0.448809 Total: 0.897654

116: 23(C) 86(H) Alpha: 0.440971 Beta: 0.440962 Total: 0.881933

117: 23(C) 93(H) Alpha: 0.436343 Beta: 0.436367 Total: 0.872710

118: 23(C) 94(H) Alpha: 0.448048 Beta: 0.448084 Total: 0.896132

119: 24(C) 25(C) Alpha: 0.581532 Beta: 0.588095 Total: 1.169627

120: 24(C) 26(C) Alpha: 0.050608 Beta: 0.050840 Total: 0.101448

121: 24(C) 27(C) Alpha: 0.049315 Beta: 0.051036 Total: 0.100352

122: 24(C) 28(C) Alpha: 0.591358 Beta: 0.589978 Total: 1.181335

123: 24(C) 49(H) Alpha: 0.423903 Beta: 0.423643 Total: 0.847545

124: 25(C) 26(C) Alpha: 0.594442 Beta: 0.590825 Total: 1.185267

125: 25(C) 27(C) Alpha: 0.053290 Beta: 0.050684 Total: 0.103974

126: 25(C) 28(C) Alpha: 0.051854 Beta: 0.051989 Total: 0.103843

127: 25(C) 55(H) Alpha: 0.433451 Beta: 0.432394 Total: 0.865846

128: 26(C) 27(C) Alpha: 0.586516 Beta: 0.585847 Total: 1.172363

129: 26(C) 28(C) Alpha: 0.050118 Beta: 0.050629 Total: 0.100747

130: 26(C) 65(H) Alpha: 0.424134 Beta: 0.424229 Total: 0.848364

131: 27(C) 28(C) Alpha: 0.580031 Beta: 0.580224 Total: 1.160255

132: 27(C) 69(H) Alpha: 0.429342 Beta: 0.429190 Total: 0.858533

133: 28(C) 59(H) Alpha: 0.423168 Beta: 0.423255 Total: 0.846423

134: 29(C) 30(C) Alpha: 0.582602 Beta: 0.576710 Total: 1.159312

135: 29(C) 31(C) Alpha: 0.032259 Beta: 0.032066 Total: 0.064325

136: 29(C) 34(C) Alpha: 0.534551 Beta: 0.533683 Total: 1.068234

137: 29(C) 35(C) Alpha: 0.532484 Beta: 0.533590 Total: 1.066074

138: 29(C) 36(Si) Alpha: 0.036935 Beta: 0.037556 Total: 0.074491

139: 29(C) 38(C) Alpha: 0.032117 Beta: 0.032096 Total: 0.064213

140: 30(C) 31(C) Alpha: 0.524778 Beta: 0.524452 Total: 1.049230

141: 30(C) 32(Si) Alpha: 0.039209 Beta: 0.039515 Total: 0.078723

142: 30(C) 34(C) Alpha: 0.032060 Beta: 0.031940 Total: 0.064000

143: 30(C) 35(C) Alpha: 0.033118 Beta: 0.033085 Total: 0.066204

144: 30(C) 38(C) Alpha: 0.537504 Beta: 0.537662 Total: 1.075166

145: 31(C) 32(Si) Alpha: 0.526211 Beta: 0.525928 Total: 1.052139

146: 31(C) 38(C) Alpha: 0.030357 Beta: 0.030386 Total: 0.060743

147: 31(C) 81(H) Alpha: 0.389539 Beta: 0.390169 Total: 0.779708

148: 32(Si) 33(C) Alpha: 0.559738 Beta: 0.559685 Total: 1.119424

149: 32(Si) 38(C) Alpha: 0.030806 Beta: 0.030910 Total: 0.061716

150: 32(Si) 41(C) Alpha: 0.558414 Beta: 0.558403 Total: 1.116817

151: 32(Si) 42(C) Alpha: 0.546437 Beta: 0.546406 Total: 1.092843

152: 32(Si) 81(H) Alpha: 0.027418 Beta: 0.027722 Total: 0.055140

153: 32(Si) 83(H) Alpha: 0.035605 Beta: 0.035611 Total: 0.071216

154: 32(Si) 85(H) Alpha: 0.037516 Beta: 0.037525 Total: 0.075041

155: 32(Si) 88(H) Alpha: 0.031450 Beta: 0.031481 Total: 0.062931

156: 32(Si) 90(H) Alpha: 0.036751 Beta: 0.036858 Total: 0.073609

157: 32(Si) 97(H) Alpha: 0.031405 Beta: 0.031377 Total: 0.062782

158: 32(Si) 98(H) Alpha: 0.035852 Beta: 0.035881 Total: 0.071733

159: 32(Si) 101(H) Alpha: 0.034869 Beta: 0.034834 Total: 0.069703

160: 32(Si) 103(H) Alpha: 0.034235 Beta: 0.034222 Total: 0.068457

161: 32(Si) 104(H) Alpha: 0.037970 Beta: 0.037956 Total: 0.075926

162: 33(C) 98(H) Alpha: 0.447879 Beta: 0.447873 Total: 0.895751

163: 33(C) 103(H) Alpha: 0.440246 Beta: 0.440251 Total: 0.880497

164: 33(C) 104(H) Alpha: 0.446780 Beta: 0.446797 Total: 0.893577

165: 34(C) 35(C) Alpha: 0.031558 Beta: 0.031524 Total: 0.063082

166: 34(C) 36(Si) Alpha: 0.025025 Beta: 0.025111 Total: 0.050136

167: 34(C) 38(C) Alpha: 0.030283 Beta: 0.030272 Total: 0.060555

168: 34(C) 53(H) Alpha: 0.429177 Beta: 0.429246 Total: 0.858423

169: 34(C) 57(H) Alpha: 0.434513 Beta: 0.434676 Total: 0.869189

170: 34(C) 62(H) Alpha: 0.419416 Beta: 0.419823 Total: 0.839240

171: 35(C) 36(Si) Alpha: 0.524497 Beta: 0.523459 Total: 1.047956

172: 35(C) 72(H) Alpha: 0.379877 Beta: 0.381353 Total: 0.761231

173: 36(Si) 37(C) Alpha: 0.560407 Beta: 0.560359 Total: 1.120767

174: 36(Si) 39(C) Alpha: 0.555878 Beta: 0.555937 Total: 1.111815

175: 36(Si) 40(C) Alpha: 0.555317 Beta: 0.555352 Total: 1.110669

176: 36(Si) 44(H) Alpha: 0.036904 Beta: 0.037030 Total: 0.073935

177: 36(Si) 46(H) Alpha: 0.034537 Beta: 0.034547 Total: 0.069084

178: 36(Si) 50(H) Alpha: 0.037798 Beta: 0.037814 Total: 0.075613

179: 36(Si) 52(H) Alpha: 0.036693 Beta: 0.036664 Total: 0.073357

180: 36(Si) 56(H) Alpha: 0.032557 Beta: 0.032587 Total: 0.065144

181: 36(Si) 60(H) Alpha: 0.037943 Beta: 0.037926 Total: 0.075869

182: 36(Si) 63(H) Alpha: 0.034123 Beta: 0.034107 Total: 0.068230

183: 36(Si) 67(H) Alpha: 0.036673 Beta: 0.036702 Total: 0.073374

184: 36(Si) 70(H) Alpha: 0.033381 Beta: 0.033370 Total: 0.066751

185: 36(Si) 72(H) Alpha: 0.026704 Beta: 0.027078 Total: 0.053782

186: 37(C) 60(H) Alpha: 0.447338 Beta: 0.447359 Total: 0.894697

187: 37(C) 67(H) Alpha: 0.446226 Beta: 0.446217 Total: 0.892443

188: 37(C) 70(H) Alpha: 0.437690 Beta: 0.437701 Total: 0.875390

189: 38(C) 68(H) Alpha: 0.439837 Beta: 0.440186 Total: 0.880023

190: 38(C) 71(H) Alpha: 0.414227 Beta: 0.414270 Total: 0.828496

191: 38(C) 74(H) Alpha: 0.417780 Beta: 0.417742 Total: 0.835521

192: 39(C) 44(H) Alpha: 0.448141 Beta: 0.447860 Total: 0.896001

193: 39(C) 46(H) Alpha: 0.446046 Beta: 0.446022 Total: 0.892067

194: 39(C) 50(H) Alpha: 0.446895 Beta: 0.446868 Total: 0.893763

195: 40(C) 52(H) Alpha: 0.448354 Beta: 0.448379 Total: 0.896733

196: 40(C) 56(H) Alpha: 0.436836 Beta: 0.436844 Total: 0.873680

197: 40(C) 63(H) Alpha: 0.437931 Beta: 0.437910 Total: 0.875841

198: 41(C) 83(H) Alpha: 0.443474 Beta: 0.443467 Total: 0.886941

199: 41(C) 85(H) Alpha: 0.446763 Beta: 0.446743 Total: 0.893506

200: 41(C) 90(H) Alpha: 0.448771 Beta: 0.448524 Total: 0.897294

201: 42(C) 88(H) Alpha: 0.442012 Beta: 0.441986 Total: 0.883999

202: 42(C) 97(H) Alpha: 0.431234 Beta: 0.431340 Total: 0.862574

203: 42(C) 101(H) Alpha: 0.446769 Beta: 0.446790 Total: 0.893558