

Supplementary Information

Hydrazido complexes prepared by methylation of the anionic end-on bridging dinitrogen dititanium complex

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Experimental Section

General procedure

All operations were performed under an inert atmosphere of argon using standard Schlenk techniques and in an MBraun glove box unless otherwise stated. Anhydrous hexane, pentane and toluene were purchased from Kanto Chemical Co. and dried by passage through two columns of activated alumina and a Q-5 column, while stabilizer-free DME and THF were purchased from Kishida Chemical Co. and dried by passage through two columns of activated alumina. Isotope enriched $^{15}\text{N}_2$ was purchased from Cambridge Isotope Laboratories. Benzene, benzene- d_6 and THF- d_8 were dried and degassed over a potassium mirror, vacuum transferred, and then stored in a glove box. Compound $[\text{K}(\text{THF})_6][\{(\text{O}_3\text{C})\text{Ti}\}_2(\mu\text{-N}_2)\{\text{K}_3(\text{THF})_3\}]$ (**1**) was prepared by following the literature procedures.[1] NMR spectra were recorded on a JEOL ECX-500 spectrometer. ^1H NMR are reported with reference to solvent resonances of C_6D_6 , THF- d_8 , or D_2O residual protons $\delta = 7.16$, 3.58 (alpha proton), or 4.79 ppm, respectively. ^{13}C NMR spectra are referenced to solvent peaks $\delta = 128.06$ (C_6D_6), 67.21 (THF- d_8), respectively. ^{15}N chemical shifts are referenced to 90% formamide in dimethyl sulfoxide- d_6 (112.7 ppm with respect to liq. NH_3 at 0.0 ppm) as an external standard. ^{29}Si chemical shifts are referenced to SiMe_4 as an external standard. Elemental analyses (C, H and N) were measured using Elementar vario MICRO cube.

Synthesis of $[\text{K}(\text{DME})_2][\{(\text{O}_3\text{C})\text{Ti}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2\text{Me}_2)]$ (3**).** Addition of DME (0.2 mL) to a suspension of **1** (120 mg, 55.1 μmol) in benzene (10 mL) became a dark brown solution. Methyl iodide (68.5 mg, 0.483 mmol) was added dropwise to the solution of **1** at room temperature and stirred for 1 h, during which time the color of solution was changed from dark brown to dark red to brown. After the volatiles were evaporated, the residue was extracted with benzene (5 mL). The benzene solution was layered with DME (0.5 mL) and allowed to stand for 2 d at room temperature. The resulting crystals were collected, washed with pentane, and then dried under vacuum to give **3** as dark brown crystals. Yield: 66.7 mg (55.1 μmol , 72.9%). ^1H NMR (C_6D_6 , 500.2 MHz, δ/ppm): 1.45 (s, 108H, ^iBu), 2.83 (s, 12H, DME), 2.91 (s, 8H, DME), 3.52 (s, 6H, MeN), 7.20 (d, $J = 2.3$ Hz, 6H, Ar), 7.88 (d, $J = 2.3$ Hz, 6H, Ar). ^{13}C NMR (C_6D_6 , 125.8 MHz, δ/ppm): 30.5, 32.3, 34.6, 35.1 (^iBu), 37.8 (MeN), 58.6, 71.4 (DME), 87.4 ($\text{C}_{\text{Ar}3}$), 120.3 (CH), 126.9 (CH), 132.6, 140.6, 148.6, 165.8. Anal. Calcd (%) for $\text{C}_96\text{H}_{146}\text{K}_2\text{N}_2\text{O}_{10}\text{Ti}_2 \cdot (\text{C}_6\text{H}_6)$: C 70.40, H 8.80, N 1.61. Found: C 70.43, H 8.74, N 1.79.

Preparation of $[\text{K}(\text{DME})_2][\{(\text{O}_3\text{C})\text{Ti}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}^{15}\text{N}_2\text{Me}_2)]$ (3**- ^{15}N).** The same procedure as used for **3** was followed. The reaction of **1**- ^{15}N (99.0 mg, 45.4 μmol) with MeI (228 mg, 1.61 mmol) gave **3**- ^{15}N (56.0 mg, 33.7 μmol , 74.1%). ^{15}N NMR (THF- d_8 , 50.7 MHz, δ/ppm): 164.9.

Synthesis of $[\text{K}(\text{DME})_3][\{(\text{O}_3\text{C})\text{Ti}\}_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-N}_2\text{SiMe}_3)\{\text{K}(\text{DME})\}_2]$ (4**).** A solution of trimethylsilyl triflate (17.3 mg, 77.8 μmol) in THF (2 mL) was added dropwise to a solution of **1** (169 mg, 77.6 μmol) in THF (10 mL) at room temperature and stirred for 3 h, during which time the color of solution was changed from dark brown to dark red with formation of precipitate. After the volatiles were evaporated, the residue was extracted with pentane (15 mL). The extract was mixed with DME (0.5 mL), and then reduced to 5 mL, and cooled at -37°C . The resulting dark red powder was washed with pentane, and then dried under vacuum to give **4** as a dark red powder. Yield: 78.5 mg (38.1 μmol , 49.1%). ^1H NMR (C_6D_6 , 500.2 MHz, δ/ppm): 0.09 (s, 9H, Me_3Si), 1.36 (s, 54H, ^tBu), 1.40 (s, 54H, ^tBu), 2.81 (s, 30H, DME), 2.91 (s, 20H, DME), 7.14 (d, $J = 2.0$ Hz, 6H, Ar), 7.70 (brs, 6H, Ar). ^{13}C NMR (C_6D_6 , 125.8 MHz, δ/ppm): -0.2 (Me_3Si), 31.0, 32.3, 34.5, 34.9 (^tBu), 58.6, 71.5 (DME), 119.5 (CH), 127.2 (CH), 131.6, 139.3, 147.0, 165.7. The peak for the carbon bonded to Ti was not found. ^{29}Si NMR (C_6D_6 , 99.4 MHz, δ/ppm) 16.3.

Preparation of $[\text{K}(\text{DME})_3][\{(\text{O}_3\text{C})\text{Ti}\}_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}^{15}\text{N}_2\text{SiMe}_3)\{\text{K}(\text{DME})\}_2]$ (4**- ^{15}N).** The ^{15}N -labeled analogue was prepared in a manner identical to that used for **4**, except for using the ^{15}N -labeled precursor **1**- ^{15}N . ^{15}N NMR (THF, 50.7 MHz, δ/ppm): δ 440.6 (br, NSi), 462.2 (d, $J = 15.5$ Hz).

Preparation of $[\{\text{K}(\text{DME})\}_2\{(\text{O}_3\text{C})\text{Ti}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2\text{Me}(\text{SiMe}_3))]$ (5**).** Methyl iodide (6.5 mg, 45.8 μmol) was added dropwise to the solution of **4** (13.2 mg, 6.40 μmol) in benzene (1 mL) at room temperature and stirred for 1 h, during which time the color of solution was changed from dark red to orange. After the volatiles were evaporated, the residue was dissolved in benzene- d_6 (0.5 mL) and then centrifuged to remove the insoluble solid. The supernatant was transferred into an NMR tube. ^1H NMR (C_6D_6 , 500.2 MHz, δ/ppm): -0.07 (s, 9H, Me_3Si), 1.42 (s, 54H, ^tBu), 1.44 (s, 54H, ^tBu), 2.82 (br, 12H, DME), 2.88 (br, 8H, DME), 3.62 (s, 3H, NMe), 7.23 (s, 6H, Ar), 7.88 (s, 6H, Ar). ^{13}C NMR (C_6D_6 , 125.8 MHz, δ/ppm): -0.4 (Me_3Si), 30.8, 32.3, 34.6, 35.1 (^tBu), 71.1 (DME), 120.6 (CH), 126.8 (CH), 132.7, 140.5. One peak for the carbon bonded to Ti and two peaks for the aromatic carbon were not assigned probably due to line broadening. ^{29}Si NMR (C_6D_6 , 99.4 MHz, δ/ppm) 17.2.

Preparation of $[\{\text{K}(\text{DME})\}_2\{(\text{O}_3\text{C})\text{Ti}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}^{15}\text{N}_2\text{Me}(\text{SiMe}_3))]$ (5**- ^{15}N).** The ^{15}N -labeled analogue was prepared in a manner identical to that used for **5**, except for using the ^{15}N -labeled precursor **4**- ^{15}N . ^{15}N NMR (THF, 50.7 MHz, δ/ppm): 178.4 (d, $J = 16.3$ Hz, NMe), 440.9 (br, NSi).

Reaction of **3 with methyl iodide in THF.** Methyl iodide (13.8 mg, 97.2 μmol) was added dropwise to the solution of **3**- ^{15}N (20.0 mg, 12.0 μmol) in THF (2 mL) at room temperature and stirred for 1 h, during which time

the color of solution was changed from dark brown to orange. After the volatiles were evaporated, the residue was extracted in toluene to afford an off-white precipitate. The toluene solution was evaporated to give $[(\text{O}_3\text{C})\text{Ti}(\text{THF})_2]$ as a brown powder. The off-white precipitate was suspended in D_2O (0.6 mL) and then centrifuged to remove the insoluble solid. The supernatant was transferred into an NMR tube. ^1H NMR (D_2O , 500.2 MHz, δ/ppm): 3.83 (m, 9H), 4.42 (br, 6H). ^{15}N NMR (D_2O , 50.7 MHz, δ/ppm): 45.2.

Synthesis of $[\text{K}(\text{benzo-18-crown-6})(\text{THF})_2][\{(\text{O}_3\text{C})\text{Ti}\}_2\{\mu\text{-N}_2\text{Me}_2(\text{CO}_2)_2\}]$ (6). A Teflon capped glass tube was charged with **3** (48.7 mg, 29.3 μmol) and THF (10 mL) to give a dark brown solution. Upon the headspace was evacuated and backfilled with CO_2 (1 atm), the color spontaneously changed to dark red. After 20 min stirring, the volatiles were evaporated and then dissolved in THF (4 mL). The THF solution was layered with benzene (2 mL) solution of benzo-18-crown-6 (20 mg, 64 μmol) and pentane (4 mL), and allowed to stand at room temperature. The resulting crystals were collected and dried under vacuum to give **6** as reddish-brown crystals. Yield: 40.0 mg (17.1 μmol , 58.4%). ^1H NMR ($\text{THF-}d_8$, 500.2 MHz, δ/ppm): 1.25 (s, 54H, ^tBu), 1.40 (s, 54H, ^tBu), 1.77 (m, 8H, THF), 3.20 (s, 6H, NMe), 3.45 (overlapping, 16H, CH_2), 3.50 (m, 8H, CH_2), 3.62 (m, 8H, THF), 3.69 (m, 8H, CH_2), 4.01 (m, 8H, CH_2), 6.80 (d, $J = 2.3$ Hz, 6H, Ar), 6.81–6.88 (m, 8H, CH-benzo-18-crown-6), 7.23 (d, $J = 2.3$ Hz, 6H, Ar). ^{13}C NMR ($\text{THF-}d_8$, 125.8 MHz, δ/ppm): 26.4 (THF), 30.7, 32.6, 34.8, 35.3 (^tBu), 68.2 (THF), 69.6 (CH_2), 70.78 (CH_2), 70.80 (CH_2), 70.9 (CH_2), 99.0 ($\text{C}_{\text{Ar}3}$), 112.4 (CH), 119.4 (CH), 122.0 (CH), 125.9 (CH), 132.2, 139.0, 148.1, 150.4, 165.9 (CO_2), 166.7. One peak for CH_2 carbon was not assigned due to overlapping with the solvent signal. Anal. Calcd (%) for $\text{C}_{130}\text{H}_{190}\text{K}_2\text{N}_2\text{O}_{24}\text{Ti}_2$: C 66.76, H 8.19, N 1.20. Found: C 68.05, H 8.35, N 1.46.

X-ray Crystallography

Single crystals were immersed in immersion oil on MicroLoops and transferred to a Rigaku Varimax with Saturn system or a Rigaku XtaLAB Synergy-DW system equipped a Rigaku GNNP low temperature device. Data were collected under a cold nitrogen stream at 123 K using graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å) or $\text{CuK}\alpha$ ($\lambda = 1.54184$ Å) radiation. Equivalent reflections were merged, and the images were processed with the CrysAlisPro software. Empirical absorption corrections were applied. All structures were solved by direct method using SHELXT [2] and refined by full-matrix least-squares method on F^2 for all data using SHELXL [3] with the Olex2 program [4]. All hydrogen atoms were placed at their geometrically calculated positions. Molecular graphics were performed with ORTEP-3 for Windows [5]. For **3**, one DME molecule was disordered. For **4**, two THF molecules and one benzo-18-crown were disordered. Some residual electron density was difficult to model, the program SQUEEZE [6] was used to remove the contribution of the electron density in the solvent region from the intensity

data. A void space (803 \AA^3) contains 250 electrons per unit cell, which could be attributed to two distorted benzene and four distorted THF molecules.

Table S1. Crystallographic data

Identification code	3	6
Empirical formula	C ₁₀₈ H ₁₅₈ K ₂ N ₂ O ₁₀ Ti ₂	C ₁₃₀ H ₁₉₀ K ₂ N ₂ O ₂₄ Ti ₂ , C ₆ H ₆ , 2(C ₄ H ₈ O)
Formula weight	1818.35	2561.14
Temperature/K	123	123
Crystal system	<i>Monoclinic</i>	<i>Triclinic</i>
Space group	C _c	<i>P</i> -1
<i>a</i> /Å	13.9200(1)	13.4520(4)
<i>b</i> /Å	25.4342(2)	22.8729(7)
<i>c</i> /Å	30.2821(2)	23.7434(8)
α /°	90	101.621(3)
β /°	103.153(1)	94.411(3)
γ /°	90	90.086(3)
Volume/Å ³	10439.94(14)	7133.5(4)
<i>Z</i>	4	2
$\rho_{\text{calc}}/\text{cm}^3$	1.157	1.192
μ/mm^{-1}	2.444	0.238
<i>F</i> (000)	3928	2760
Crystal size/mm ³	0.21 × 0.08 × 0.07	0.27 × 0.04 × 0.01
Radiation	Cu K α (λ = 1.54184)	Mo K α (λ = 0.71073)
2 θ range for data collection/°	5.994 to 152.99	5.186 to 55.12
Index ranges	-17 ≤ <i>h</i> ≤ 17, -28 ≤ <i>k</i> ≤ 31, -37 ≤ <i>l</i> ≤ 32	-17 ≤ <i>h</i> ≤ 17, -27 ≤ <i>k</i> ≤ 29, -30 ≤ <i>l</i> ≤ 30
Reflections collected	42396	89349
Independent reflections	14592 [<i>R</i> _{int} = 0.0315, <i>R</i> _{sigma} = 0.0366]	32875 [<i>R</i> _{int} = 0.1105, <i>R</i> _{sigma} = 0.1959]
Data/restraints/parameters	14592/108/1194	32875/102/1527
Goodness-of-fit on <i>F</i> ²	1.028	1
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0422, <i>wR</i> ₂ = 0.1134	<i>R</i> ₁ = 0.0907, <i>wR</i> ₂ = 0.1916
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0438, <i>wR</i> ₂ = 0.1148	<i>R</i> ₁ = 0.2061, <i>wR</i> ₂ = 0.2396
Largest diff. peak/hole / e Å ⁻³	0.54/-0.45	0.85/-0.50
Flack parameter	0.073(4)	

Molecular Structures

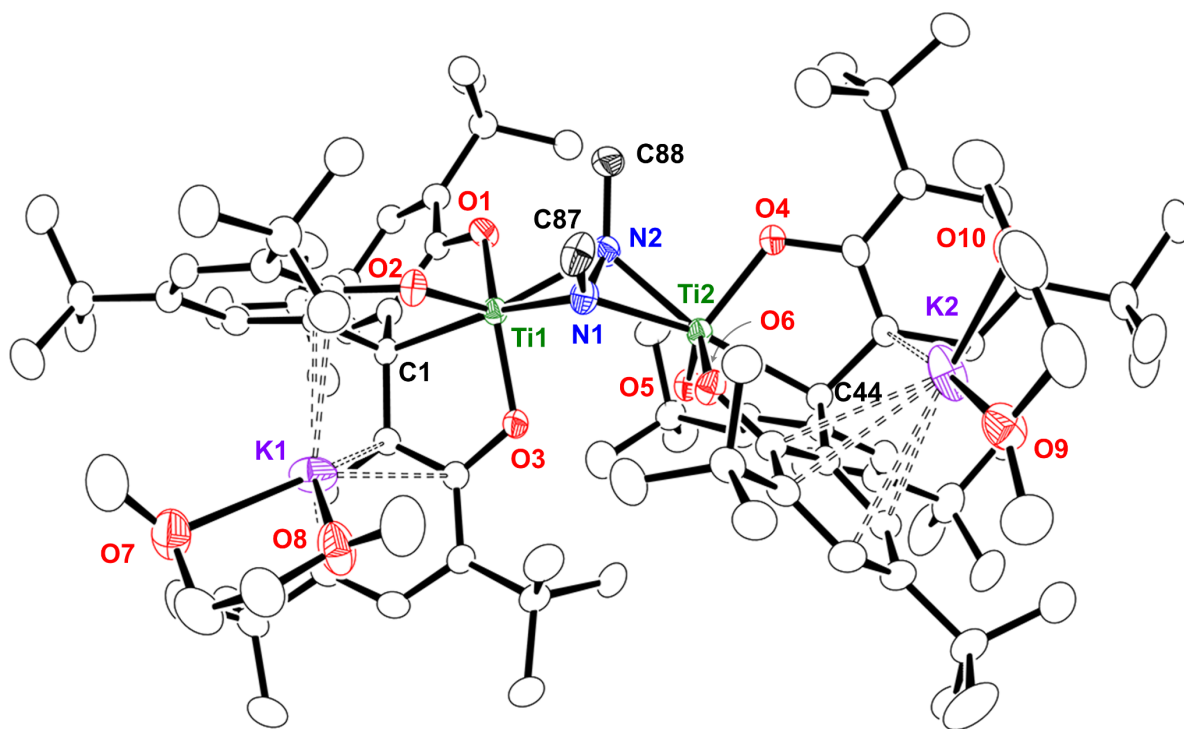


Figure S1. Molecular structure of **3** with 50% probability ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–O1 1.937(2), Ti1–O2 1.923(2), Ti1–O3 1.907(2), Ti1–N1 2.094(3), Ti1–N2 2.108(3), Ti1–C1 2.229(3), Ti2–O4 1.919(2), Ti2–O5 1.883(2), Ti2–O6 1.969(2), Ti2–N1 2.089(3), Ti2–N2 2.075(3), Ti2–C44 2.236(3), N1–N2 1.442(3), N1–C87 1.466(4), N2–C88 1.468(4), O1–Ti1–N1 120.77(10), O1–Ti1–N2 83.26(10), O1–Ti1–C1 77.59(10), O2–Ti1–O1 108.04(10), O2–Ti1–N1 86.38(10), O2–Ti1–N2 112.61(10), O2–Ti1–C1 80.53(10), O3–Ti1–O1 129.46(10), O3–Ti1–O2 111.44(10), O3–Ti1–N1 92.23(11), O3–Ti1–N2 108.43(10), O3–Ti1–C1 79.10(10), N1–Ti1–N2 40.15(9), N1–Ti1–C1 160.30(11), N2–Ti1–C1 159.55(11), N2–N1–Ti1 70.44(14), N2–N1–Ti2 69.22(14), N2–N1–C87 120.3(3), C87–N1–Ti1 128.6(2), C87–N1–Ti2 119.1(2), Ti2–N2–Ti1 111.67(12), N1–N2–Ti1 69.42(14), N1–N2–Ti2 70.24(15), Ti2–N1–N2–Ti1 123.64(9).

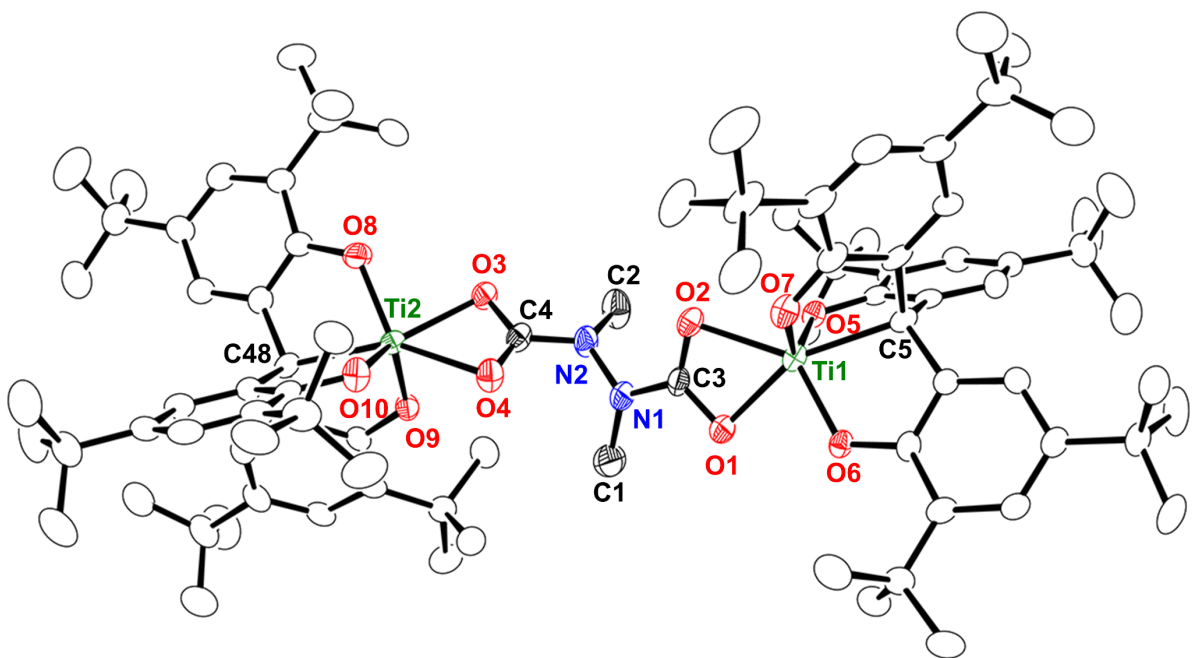


Figure S2. Molecular structure of the anion part of **6** with 50% probability ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–O1 2.114(3), Ti1–O2 2.181(3), Ti1–O5 1.871(3), Ti1–O6 1.908(3), Ti1–O7 1.914(3), Ti1–C5 2.208(4), Ti2–O3 2.152(3), Ti2–O4 2.190(3), Ti2–O8 1.881(3), Ti2–O9 1.879(3), Ti2–O10 1.867(3), Ti2–C48 2.259(4), O1–C3 1.270(5), O2–C3 1.254(5), O3–C4 1.271(5), O4–C4 1.262(5), N1–N2 1.393(5), N1–C1 1.439(6), N1–C3 1.352(5), N2–C2 1.461(6), N2–C4 1.357(5), O1–Ti1–O2 60.93(11), O1–Ti1–C5 151.84(14), O2–Ti1–C5 142.64(13), O5–Ti1–O1 123.68(13), O5–Ti1–O2 87.80(12), O5–Ti1–O6 103.93(12), O5–Ti1–O7 125.94(13), O5–Ti1–C5 79.76(14), O6–Ti1–O1 79.65(11), O6–Ti1–O2 137.96(12), O6–Ti1–O7 119.01(12), O6–Ti1–C5 79.39(13), O7–Ti1–O1 96.39(12), O7–Ti1–O2 81.64(11), O7–Ti1–C5 77.75(13), C3–O1–Ti1 90.9(3), C3–O2–Ti1 88.3(2), N2–N1–C1 117.0(4), C3–N1–N2 116.8(4), C3–N1–C1 123.7(4), O1–C3–N1 118.4(4), O2–C3–O1 119.3(4), O2–C3–N1 122.3(4), Ti1–O1–C3–O2 -7.6(4), Ti1–O1–C3–N1 171.2(4), Ti1–O2–C3–O1 7.4(4), Ti1–O2–C3–N1 -171.4(4), N2–N1–C3–O1 -163.5(4), N2–N1–C3–O2 15.4(6), C1–N1–N2–C2 -87.2(5), C1–N1–N2–C4 71.2(6), C1–N1–C3–O1 -2.0(7), C1–N1–C3–O2 176.8(5), C3–N1–N2–C2 75.5(5), C3–N1–N2–C4 -126.0(4).

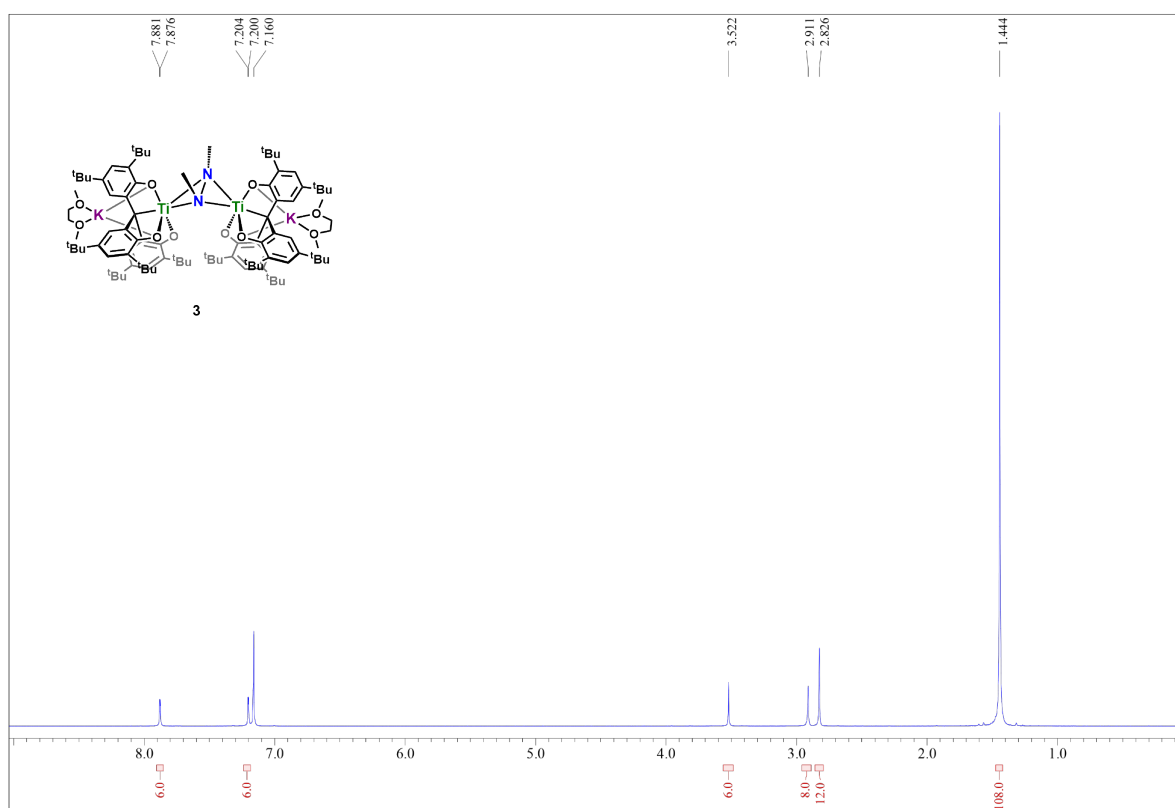


Fig. S3 ¹H NMR spectrum of **3** in C₆D₆.

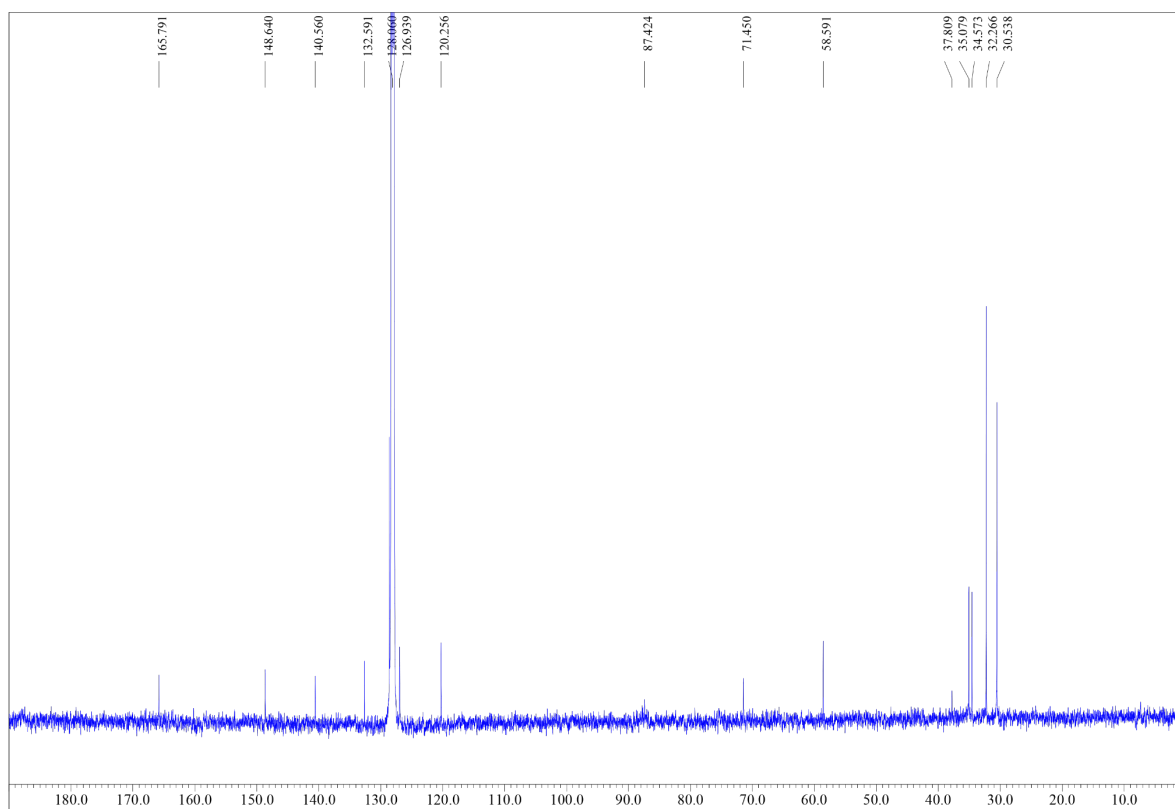


Fig. S4 ¹³C NMR spectrum of **3** in C₆D₆.

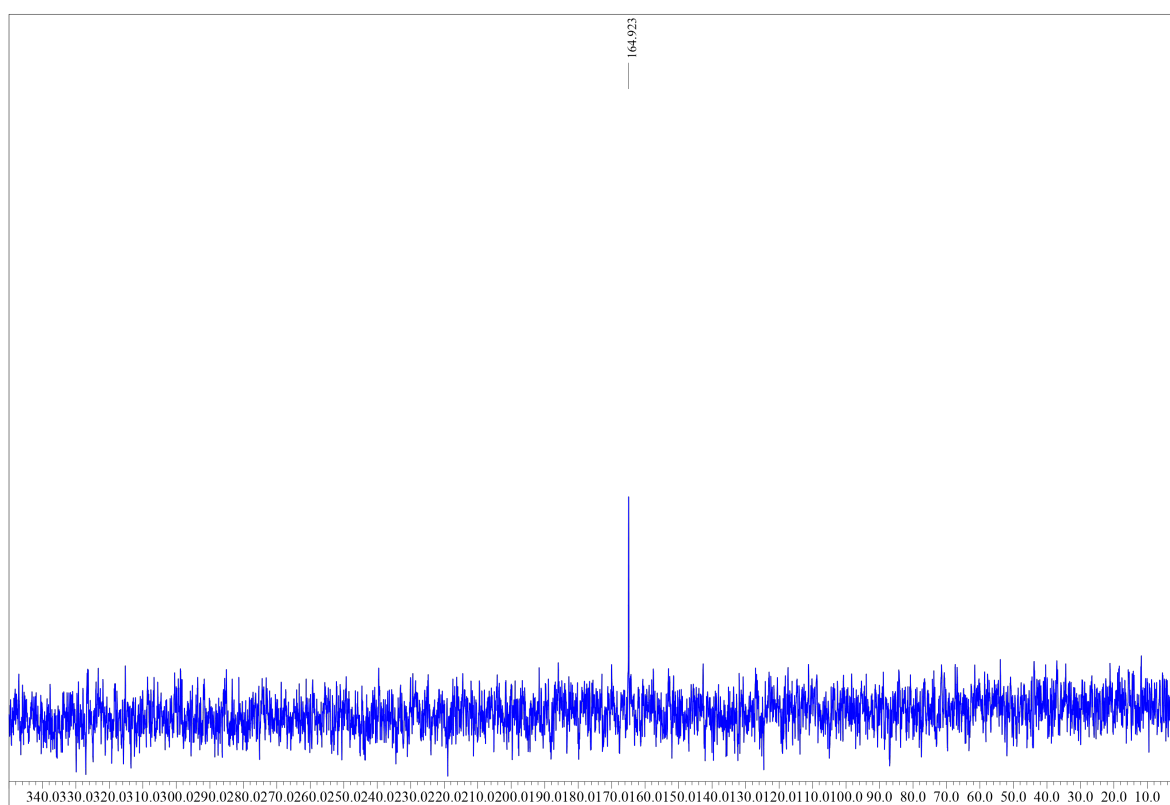


Fig. S5 ^{15}N NMR spectrum of **3**- ^{15}N in $\text{THF-}d_8$.

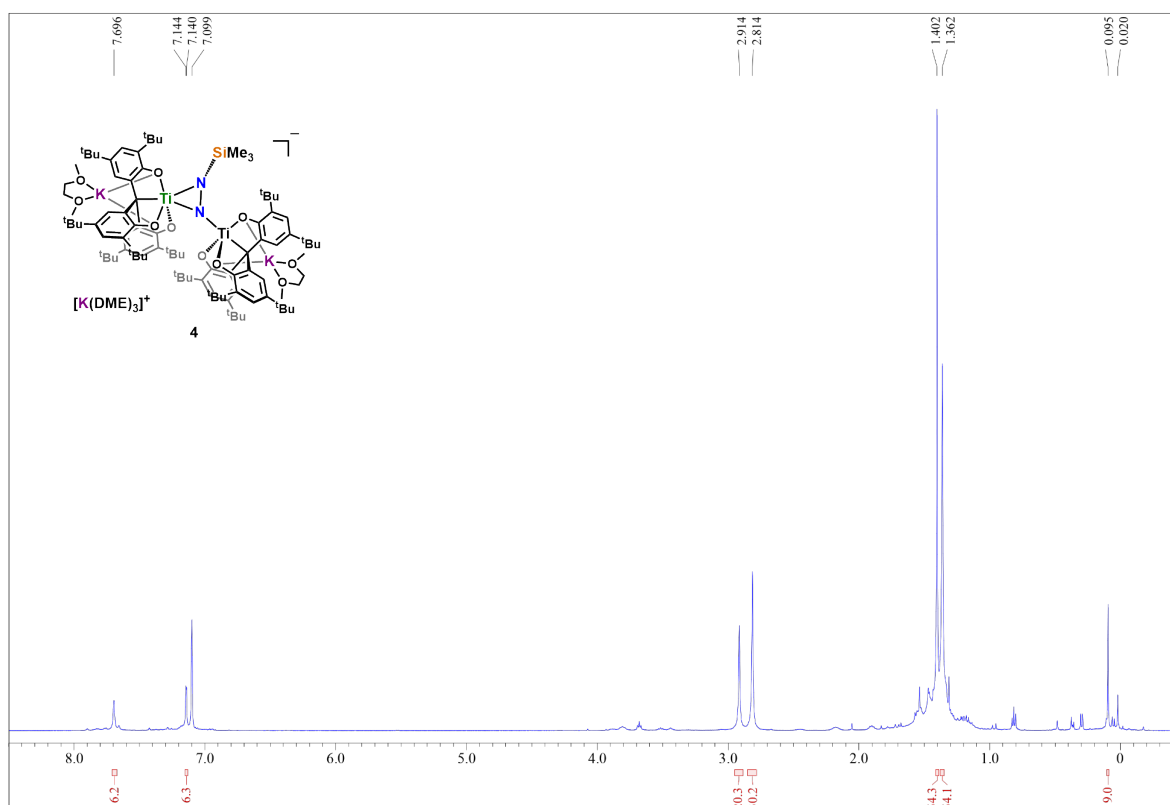


Fig. S6 ^1H NMR spectrum of **4** in C_6D_6 .

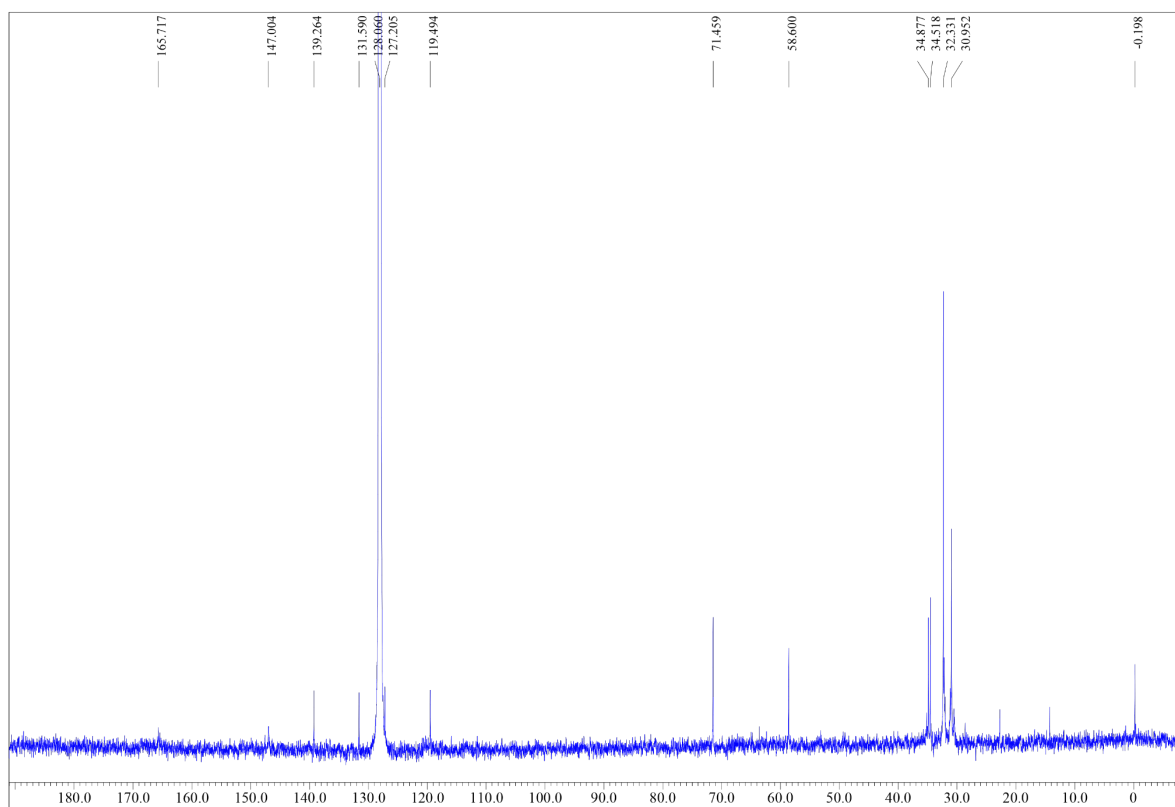


Fig. S7 ^{13}C NMR spectrum of **4** in C_6D_6 .

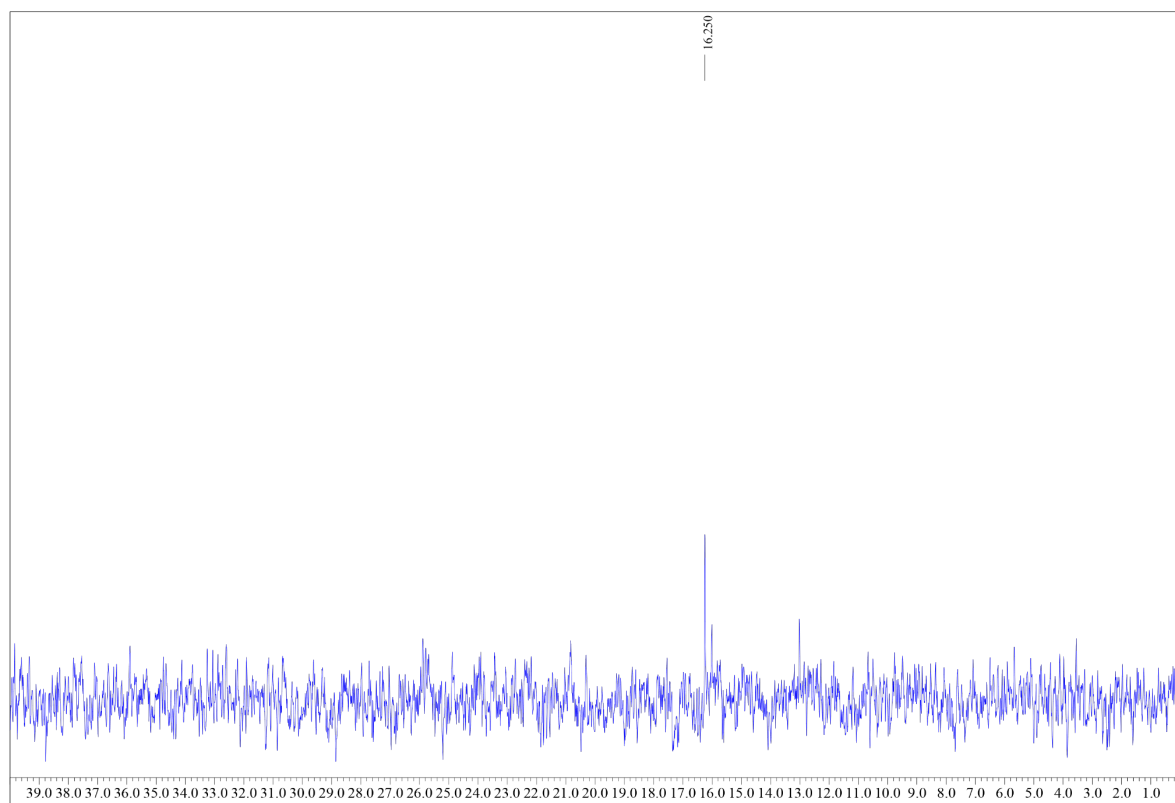


Fig. S8 ^{29}Si NMR spectrum of **4** in C_6D_6 .

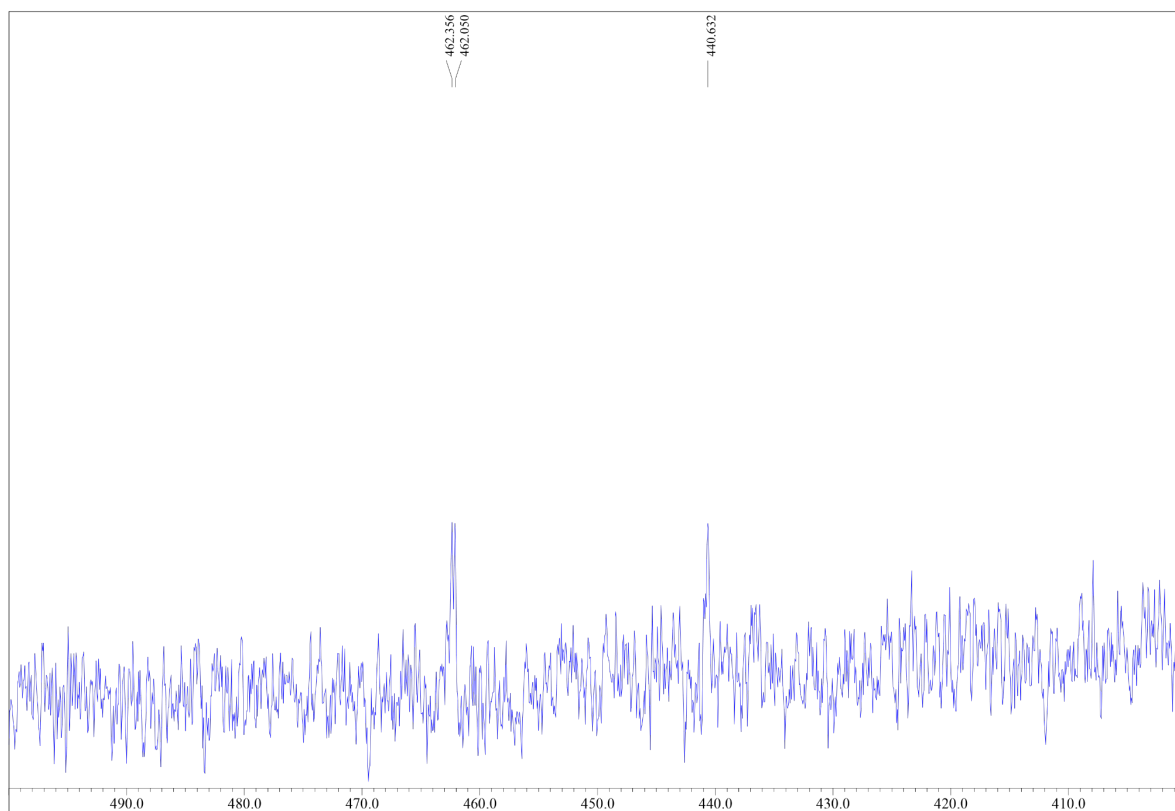


Fig. S9 ^{15}N NMR spectrum of **4**- ^{15}N in THF.

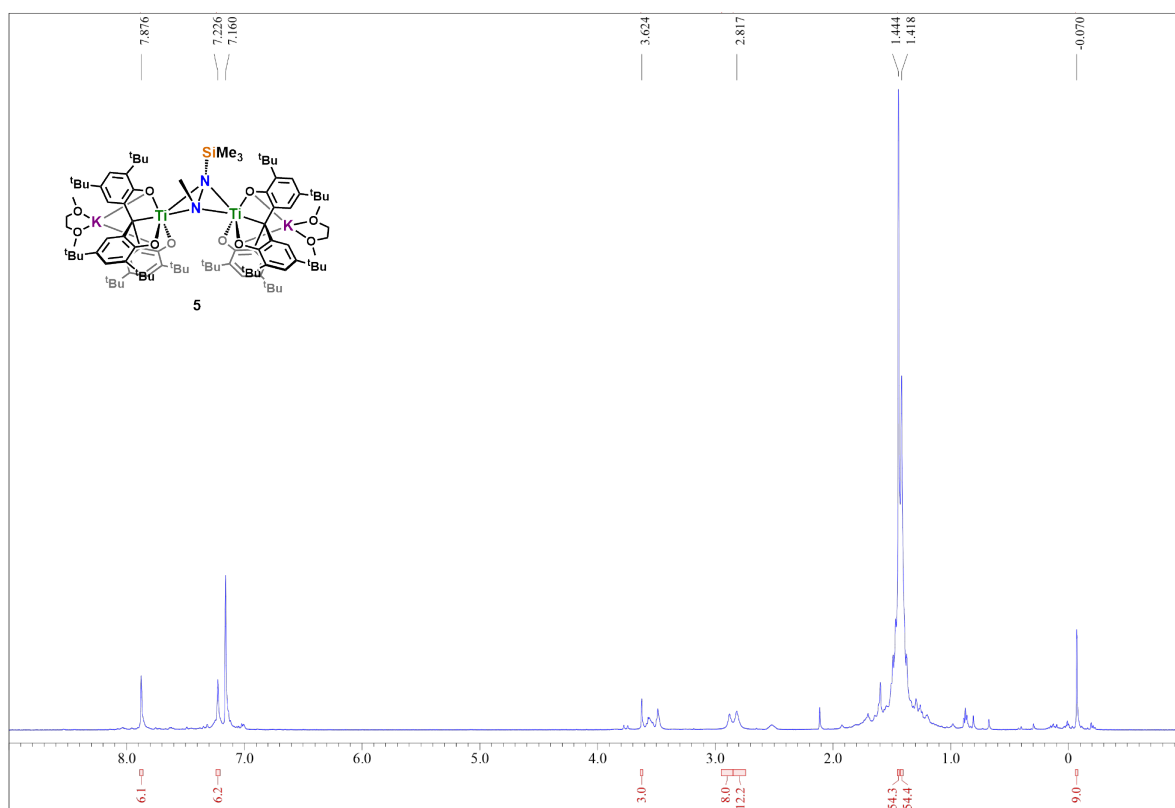


Fig. S10 ^1H NMR spectrum of **5** in C_6D_6 .

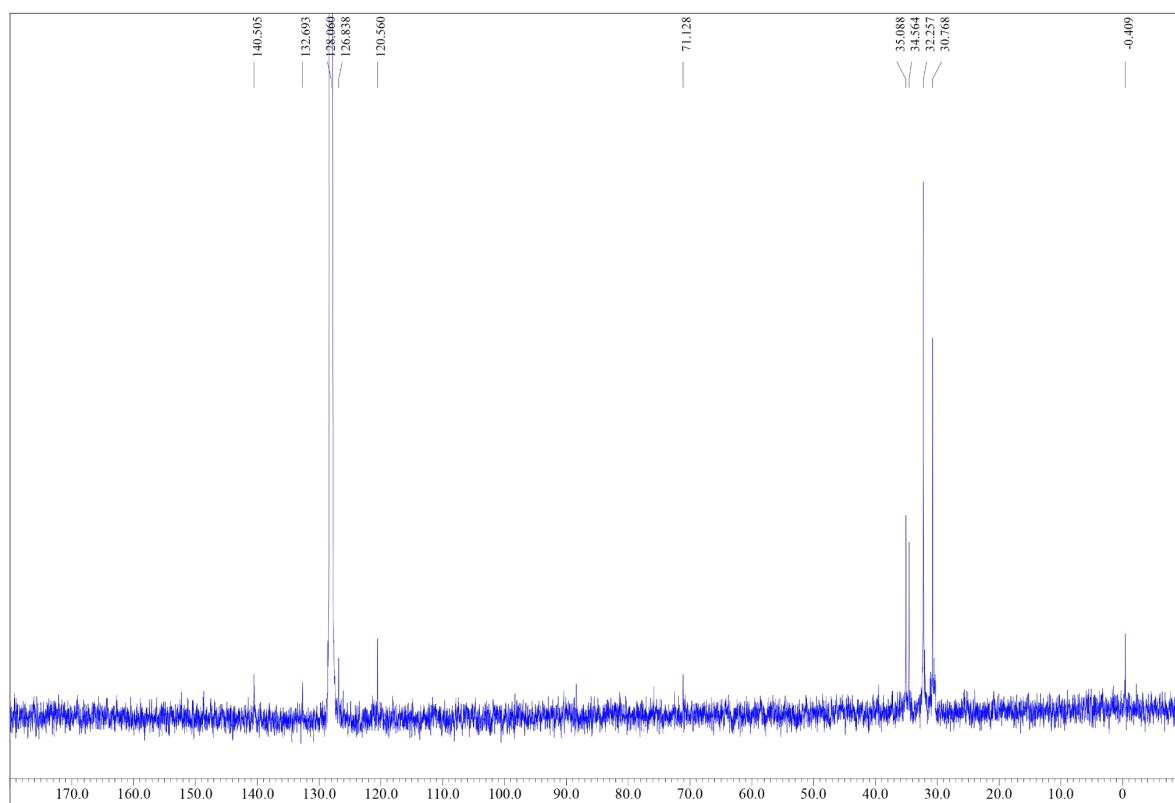


Fig. S11 ^{13}C NMR spectrum of **5** in C_6D_6 .

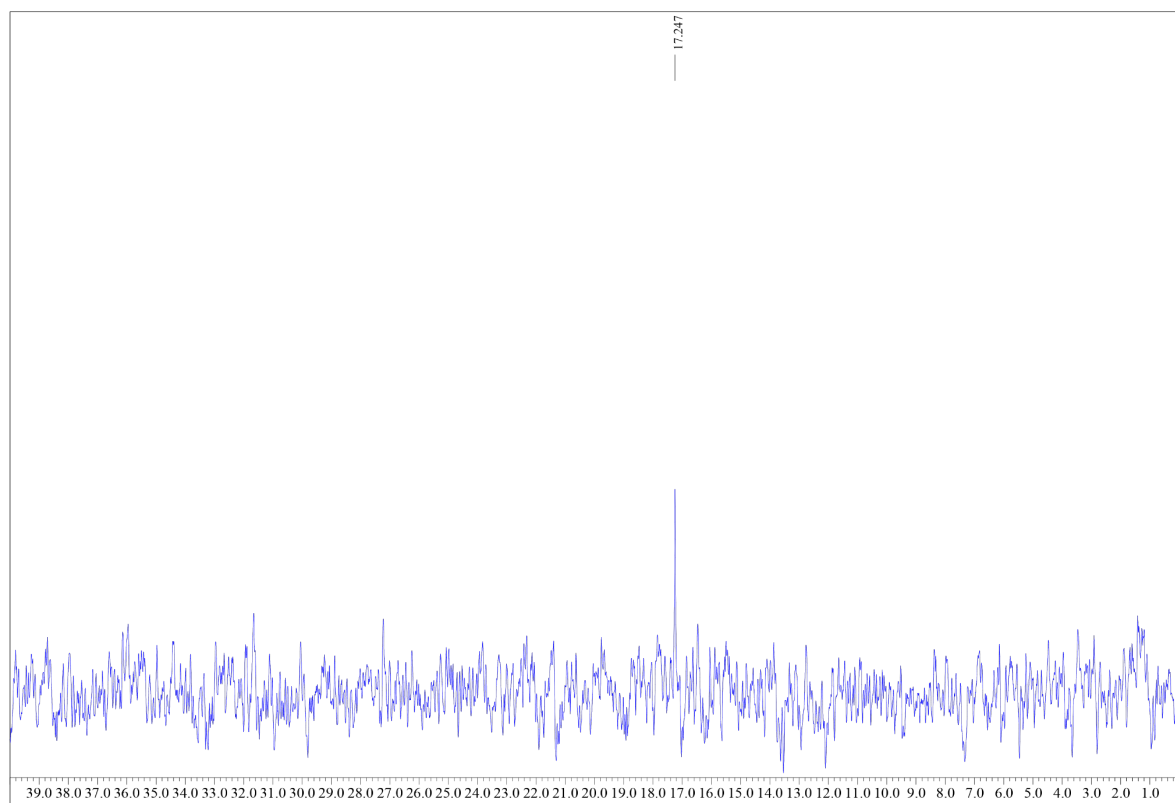


Fig. S12 ^{29}Si NMR spectrum of **5** in C_6D_6 .

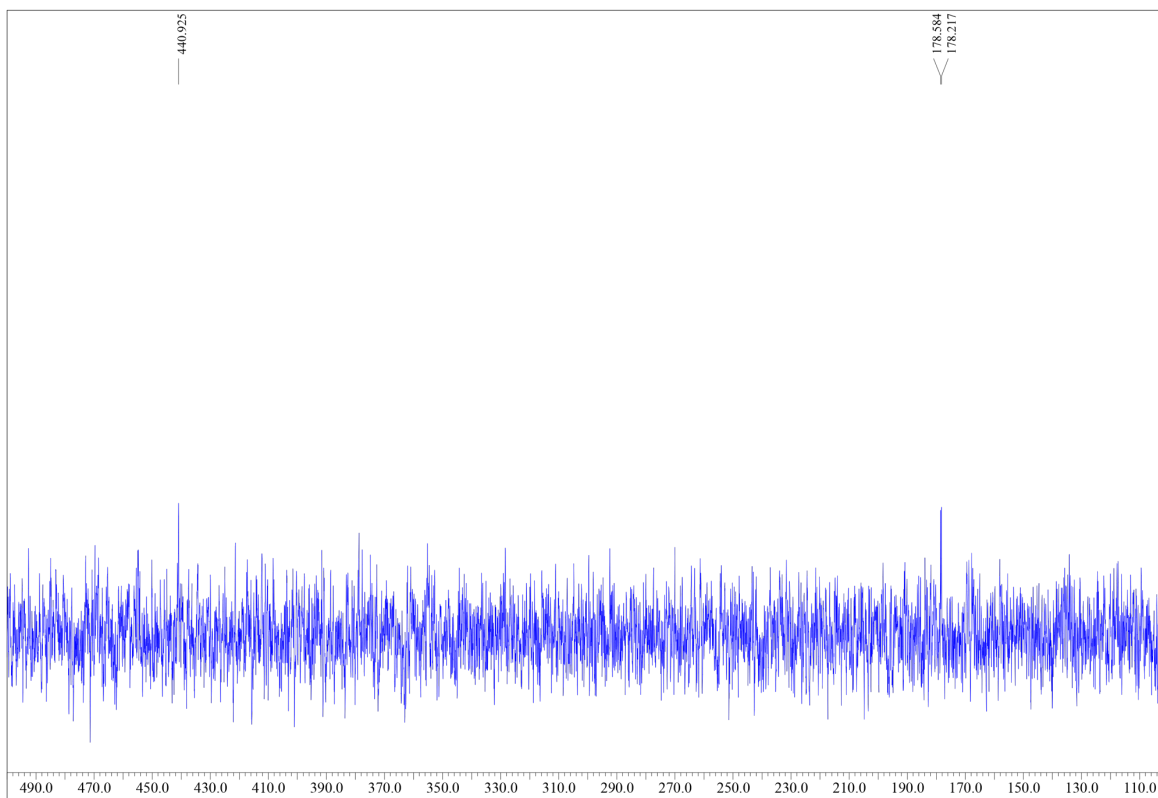


Fig. S13 ^{15}N NMR spectrum of $5\text{-}^{15}\text{N}$ in THF.

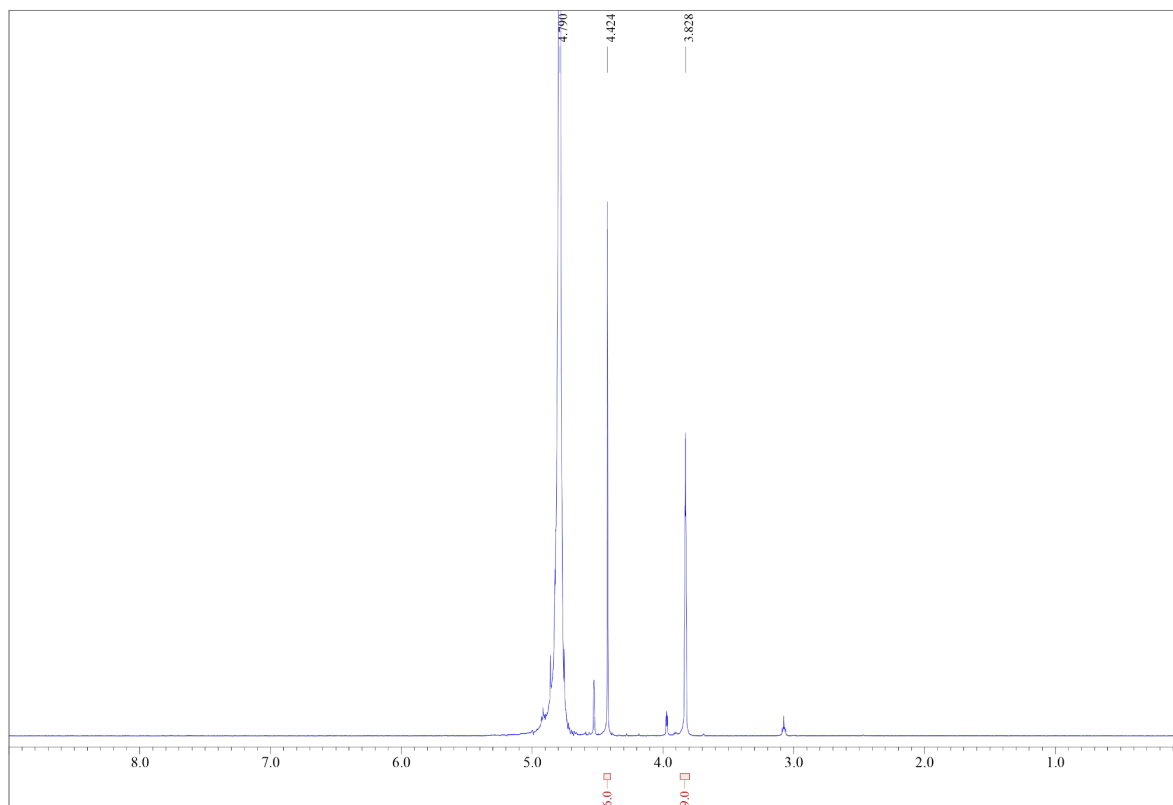


Fig. S14 ^1H NMR spectrum of $[\text{Me}_2^{15}\text{N}^{15}\text{NMe}_3]\text{I}$ in D_2O .

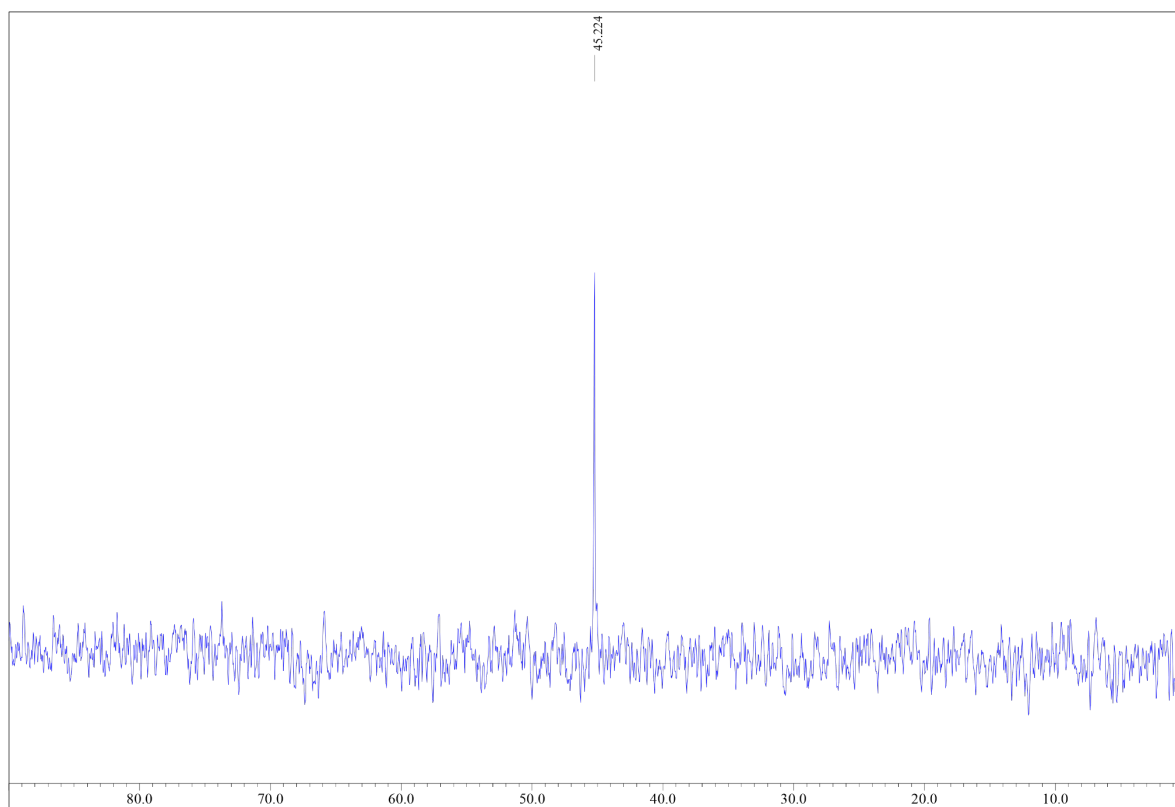


Fig. S15 ^{15}N NMR spectrum of $[\text{Me}_2^{15}\text{N}^{15}\text{NMe}_3]\text{I}$ in D_2O .

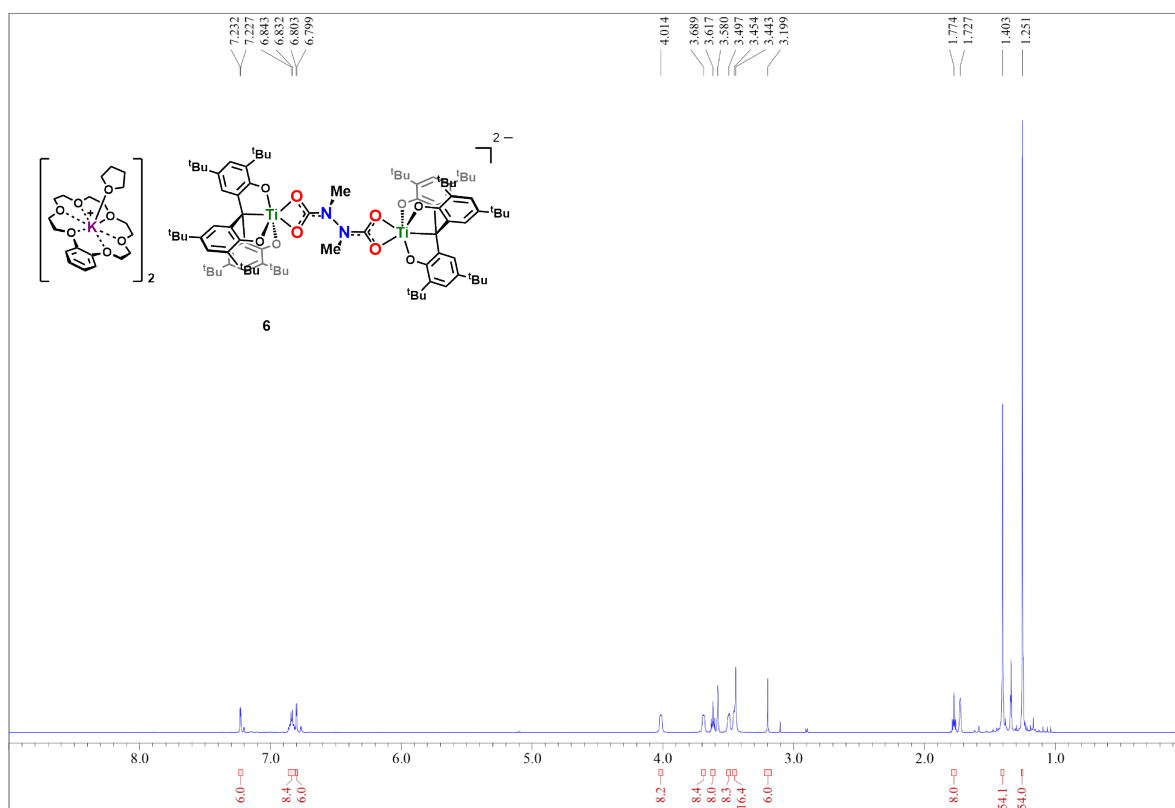


Fig. S16 ^1H NMR spectrum of **6** in C_6D_6 .

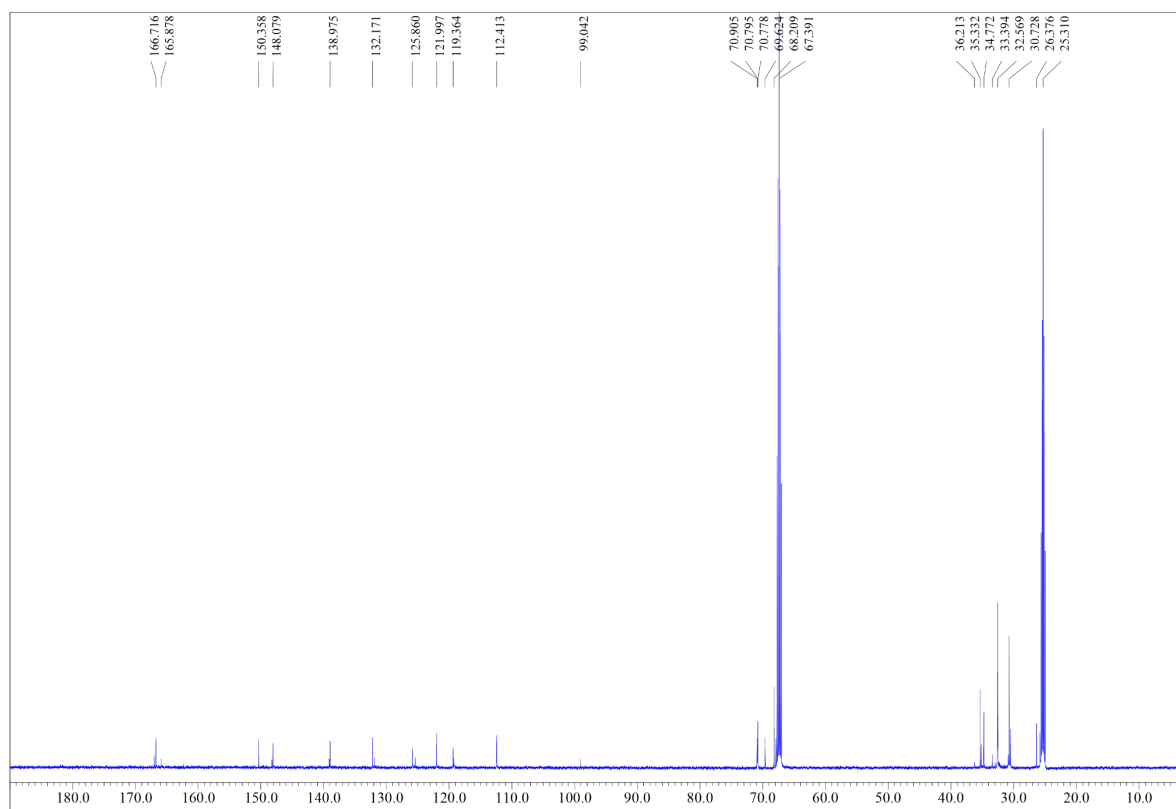


Fig. S17 ^{13}C NMR spectrum of **6** in C_6D_6 .

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