Supplementary Information (SI) for Chemical Communications.

Supporting Information for

Catalytic Dinitrogen Silylation by Tris(pyrazolyl)borate-Supported Titanium Complexes

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Content

1. Experimental Details

General Consideration

All reactions were carried out under dry and oxygen-free argon or nitrogen atmosphere by using Schlenk techniques or under an argon atmosphere in a Vigor or Mbraun glovebox. The nitrogen or argon in the glovebox was constantly circulated through a copper catalyst/activated charcoal unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O analyzer to ensure both were always below 1 ppm. Samples for NMR spectroscopic measurements were prepared in the glovebox by using of J. Young valve NMR tubes. ^{1}H and ^{13}C NMR spectrum were recorded on a JEOL JNM-ECS400 or JNM-ECS600 spectrometer. Due to their paramagnetic nature, complexes Tp*$TiCl_2$(THF), **1a-d**, **2d**, and **2e** do not yield resolvable ^{1}H NMR spectra. Their characterization and purity are instead based on elemental analysis and X-ray crystallographic data, as provided below. UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrometer. GC-MS spectra were recorded on a Shimadzu GC-2010 instrument. Elemental analyses (CHN) were performed on a VARIO EL instrument. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher Scientific photoelectron spectrometer using monochromatized Al Kα radiation. The complex was mounted to the sample holder in the glove box. Then the sample was transferred into an ultra-high vacuum chamber for XPS analysis. The binding energy calibration was conducted using carbon 1s core-level at 284.8 eV to correct charging effects. Solution magnetic susceptibilities were determined by the Evans method. Anhydrous tetrahydrofuran, hexane, benzene, and toluene were purified using an SPS-5 solvent purification system (Mbraun) and dried over fresh Na chips in the glovebox. NMR solvents were dried with activated 4 Å molecular sieves. Tp*K was prepared according to literatures.[1] Lithium 2,6-dimethylphenoxide, lithium 2,6-diisopropylphenoxide, and lithium 2,6-di-*tert*-butylphenoxide were prepared through the reactions of corresponding phenol with *n*-BuLi. Other chemicals were purchased from common commercial sources and used as received.

Synthetic Details

$Tp^*TiCl_2(THF)$. To a THF (60 mL) solution of $TiCl_3(THF)_3$ (1.970 g, 5.947 mmol), Tp*K (2.000 g, 5.947 mmol) was added at –35 °C. The mixture was allowed to slowly warm to room temperature and refluxed overnight. After removal of the solvent under vacuum, the residual purple solid was extracted with toluene and filtered. The solvent of the solution was then evaporated under reduced pressure. The resulting purple solid was re-dissolved in THF, concentrated, and cooled at –35 °C to give **$Tp^*TiCl_2(THF)$** (2.409 g, 4.936 mmol, 83%) as purple crystals. Single crystals of **$Tp^*TiCl_2(THF)$** suitable for X-ray study were obtained from a concentrated THF at –35 °C. $\mu_{eff} = 1.72$ μ_B (Evans method, 298 K).

$Tp^*Ti(OC_6H_3Me_2\text{-}2,6)Cl(THF)$ (1a). To a toluene (40 mL) solution of **$Tp^*TiCl_2(THF)$** (500 mg, 1.024 mmol), lithium 2,6-dimethylphenoxide (131 mg, 1.024 mmol) was added at –35 °C. The mixture was slowly warmed to room temperature and stirred for 8 h. The suspension was filtered and then evaporated under reduced pressure. The resulting brown solid was re-dissolved in THF, concentrated, and cooled at –35 °C to give **1a** (311 mg, 0.542 mmol, 53%) as light purple crystals. Single crystals suitable for X-ray study were obtained from a concentrated Et_2O of **1a** at –35 °C. $\mu_{eff} = 1.69$ μ_B (Evans method, 298 K). Anal. calcd. For $C_{27}H_{39}BClN_6O_2Ti$ (**1a**): C, 56.52; H, 6.85; N, 14.65. Found: C, 56.18; H, 6.80; N, 14.62.

$Tp^{Me2}Ti(OC_6H_3{}^iPr_2\text{-}2,6)Cl(THF)$ (1b). To a toluene (40 mL) solution of **$Tp^*TiCl_2(THF)$** (500 mg, 1.024 mmol), lithium 2,6-diisopropylphenoxide (262 mg, 1.024 mmol) was added at –35 °C. The mixture was slowly warmed to room temperature and stirred for 8 h. The suspension was filtered and then evaporated under reduced pressure. The resulting brown-green solid was re-dissolved in THF, concentrated, and cooled at –35 °C to give **1b** (360 mg, 0.573 mmol, 56%) as light blue crystals. Single crystals suitable for X-ray study were obtained from a concentrated THF of **1b** at –35 °C. $\mu_{eff} = 1.68$ μ_B (Evans method, 298 K). Anal. calcd. For

$C_{31}H_{47}BClN_6O_2Ti{\bullet}(C_6H_{14})_{0.15}$ (**1b**): C, 59.55; H, 7.64; N, 13.06. Found: C, 59.47; H, 7.58; N, 12.97.

Tp^{Me2}Ti(OC$_6$H$_3$^{t}Bu$_2$-2,6)Cl (1c). To a toluene (40 mL) solution of **Tp*TiCl$_2$(THF)** (500 mg, 1.024 mmol), lithium 2,6-di-tert-butylphenoxide (291 mg, 1.024 mmol) was added at –35 °C. The mixture was slowly warmed to room temperature and stirred at 50 °C for 4 h. The suspension was filtered and then evaporated under reduced pressure. The resulting pink solid was re-dissolved in THF, concentrated, and cooled at –35 °C to give **1c** (384 mg, 0.655 mmol, 64%) as pink crystals. Single crystals suitable for X-ray study were obtained from a concentrated THF of **1c** at –35 °C. $\mu_{eff} = 1.72\ \mu_B$ (Evans method, 298 K). Anal. calcd. For $C_{29}H_{43}BClN_6O_2Ti{\bullet}(C_6H_{14})_{0.4}$ (**1c**): C, 60.74; H, 7.83; N, 13.54. Found: C, 60.32; H, 7.67; N, 13.12.

Tp*Ti(O^{t}Bu)Cl$_2$(THF) (1d). To a toluene (40 mL) solution of **Tp*TiCl$_2$(THF)** (1.000 g, 2.049 mmol), lithium *tert*-butoxide (164 mg, 2.049 mmol) was added at –35 °C. The mixture was-slowly warmed to room temperature and stirred overnight. The suspension was filtered and then evaporated under reduced pressure. The resulting pink solid was re-dissolved in THF, concentrated, and cooled at –35 °C to give **1d** (678 mg, 1.291 mmol, 63%) as pink crystals. Single crystals suitable for X-ray study were obtained from a concentrated THF of **1d** at –35 °C. $\mu_{eff} = 1.69\ \mu_B$ (Evans method, 298 K). Anal. calcd. For $C_{23}H_{39}BClN_6O_2Ti$ (**1d**): C, 52.55; H, 7.48; N, 15.99. Found: C, 52.64; H, 7.48; N, 16.06.

[Tp*Ti(OC$_6$H$_3$Me$_2$-2,6)(THF)]$_2$(μ-η^1: η^1-N$_2$) (2a). To a THF (30 mL) solution of **1a** (200 mg, 0.349 mmol), KC_8 (94 mg, 0.698 mmol) was added under N_2 atmosphere at –35 °C. The mixture was slowly warmed to room temperature and stirred for 5 h. After removal of the solvent under vacuum, the residual green solid was extracted with toluene and filtered. The solvent of the solution was then evaporated under reduced pressure. The green solid was re-dissolved in THF, concentrated and cooled at –35 °C to give **2a** (121 mg, 0.110 mmol, 63%) as green crystals. Single crystals suitable for X-ray study were obtained from a concentrated THF of **2a** at –35 °C. ^{1}H NMR (600 MHz, THF-d_8, –60 °C): 0.62 (s, 3H, OCCH_3), 1.62 (s, 3H, OCCH_3), 1.70 (s, 3H, NCCH_3), 2.23 (s, 3H, NCCH_3), 2.33 (s, 3H, NCCH_3), 2.35 (s, 3H, NCCH_3), 2.44 (s, 3H, NCCH_3), 2.72 (s, 3H, NCCH_3), 5.35 (s, 1H, CCHC), 5.46 (s, 1H, CCHC), 5.71 (s, 1H, CC*H*C), 6.23 (t, J_{HH} = 7.2 Hz, 1H, CHC*H*CH), 6.50 (d, J_{HH} = 7.2 Hz, 1H, CC*H*CH), 6.84 (d, J_{HH} = 7.2 Hz, 1H, CC*H*CH). ^{13}C NMR (151 MHz, THF-d_8, –60 °C): 167.2 (s, O*C*), 153.3, 151.9, 149.8, 143.9, 143.4, 142.7 (s, N*C*), 129.0, 127.8 (s, C*C*HCH), 125.8, 124.9 (s, C*C*CH), 114.7 (s, CH*C*HCH),106.0, 105.6, 105.5, (s, C*C*HC), 20.4, 16.4, 15.6, 13.5 (s, NC*C*H$_3$), 13.2 (s, OC*C*H$_3$), 12.9, 12.7 (s, NC*C*H$_3$). Anal. calcd. For $C_{54}H_{78}B_2N_{14}O_4Ti_2$ (**2a**): C, 58.71; H, 7.12; N, 17.75. Found: C, 59.09; H, 7.04; N, 17.23. Raman (solid, cm^{-1}): 1336. **[Tp*Ti(OC$_6$H$_3$Me$_2$-2,6)(THF)]$_2$(μ-η^1: η^1-^{15}N$_2$) (2a-^{15}N)** was prepared in the same manner with ^{15}N$_2$ gas. ^{15}N NMR (41 MHz, Benzene-d_6, rt): 48.2. Raman (solid, cm^{-1}): 1307.

[Tp*Ti(OC$_6$H$_3$^{i}Pr$_2$-2,6)(THF)]$_2$(μ-η^1: η^1-N$_2$) (2b). To a THF (30 mL) solution of **1b** (200 mg, 0.318 mmol), KC$_8$ (85 mg, 0.636 mmol) was added under N$_2$ atmosphere at –35 °C. The mixture was slowly warmed to room temperature and stirred for 5 h. After removal of the solvent under vacuum, the residual green solid was extracted with toluene and filtered. The solvent of the solution was then evaporated under reduced pressure. The green solid was re-dissolved in THF, concentrated and cooled at –35 °C to give **2b** (112 mg, 0.092 mmol, 58%) as green crystals. Single crystals suitable for X-ray study were obtained from a concentrated THF of **2b** at –35 °C. Anal. calcd. For $C_{62}H_{94}B_2N_{14}O_4Ti_2$ (THF) (**2b**): C, 61.60; H, 7.83; N, 15.23. Found: C, 61.76; H, 7.89; N, 15.07. ^{1}H NMR (400 MHz, THF-d_8, rt) δ 6.89 (d, J = 8.3 Hz, 1H, CC*H*CH), 6.61 (d, J = 7.5 Hz, 1H, CC*H*CH), 6.41 (t, J = 7.4 Hz, 1H, CHC*H*CH), 5.68 (s, 1H, CCHC), 5.50 (s, 1H, CCHC), 5.25 (s, 1H, CCHC), 3.62 (s, 4H, C$_4$$H_8$O), 2.56 (s, 3H, NCC$H_3$), 2.38 (s, 3H, NCC$H_3$), 2.35 (s, 3H, NCC$H_3$), 2.20 (s, 3H, NCC$H_3$), 2.20 (m, 2H, OAr–C*H*CH$_3$), 1.78 (s, 4H, C$_4$$H_8$O), 1.66 (s, 3H, NCC$H_3$), 1.58 (s, 3H, NCC$H_3$), 1.44 (d, J =

6.9 Hz, 3H, OAr–CHC*H*$_3$), 1.32 (d, *J* = 6.8 Hz, 3H, OAr–CHC*H*$_3$), 0.53 (d, *J* = 6.7 Hz, 3H, OAr–CHC*H*$_3$), -0.19 (d, *J* = 6.7 Hz, 3H, OAr–CHC*H*$_3$). ^{13}C NMR (101 MHz, THF-*d*$_8$, rt): 164.3 (s, O*C*), 153.9, 152.0, 149.7, 143.4, 143.3, 142.6 (s, N*C*), 137.0, 135.0 (s, OAr), 123.3, 122.4 (s, OAr), 115.6 (s, OAr), 106.0, 106.0, 105.7 (s, C*C*HC), 26.4, 26.2, 23.4, 16.2 (s, NC*C*H$_3$), 13.7 (s, OAr–CH*C*H$_3$), 13.5 (s, OAr–*C*HCH$_3$), 12.7, 12.3 (s, NC*C*H$_3$).

[Tp*Ti(OC$_6$H$_3$^{t}Bu$_2$-2,6)]$_2$(μ-η^1: η^1-N$_2$) (2c). To a toluene (30 mL) solution of **1c** (200 mg, 0.341 mmol), KC$_8$ (92 mg, 0.683 mmol) was added under N$_2$ atmosphere at –35 °C. The mixture was slowly warmed to room temperature and stirred for 24 h, then filtered. The solvent of the solution was then evaporated under reduced pressure. The brown solid was re-dissolved in THF, concentrated and cooled at –35 °C to give **2c** (93 mg, 0.073 mmol, 43%) as brown-red crystals. Single crystals suitable for X-ray study were obtained from a concentrated THF of **2c** at –35 °C. ^{1}H NMR (600 MHz, Benzene-*d*$_6$, rt): 1.48 (s, 3H, NCC*H*$_3$), 1.57 (s, 9H, CCC*H*$_3$), 1.70 (s, 9H, CCC*H*$_3$), 1.91 (s, 3H, NCC*H*$_3$), 1.93 (s, 3H, NCC*H*$_3$), 2.22 (s, 3H, NCC*H*$_3$), 2.24 (s, 3H, NCC*H*$_3$), 2.25 (s, 3H, NCC*H*$_3$), 5.17 (s, 1H, CCHC), 5.61 (s, 1H, CCHC), 5.65 (s, 1H, CC*H*C), 7.01 (t, *J*$_{\mathrm{HH}}$ = 7.0 Hz, 1H, CHC*H*CH), 7.57 (d, *J*$_{\mathrm{HH}}$ = 7.0 Hz, 2H, CC*H*CH). ^{13}C NMR (151 MHz, Benzene-*d*$_6$, rt): 169.2 (s, O*C*), 152.8, 152.5, 152.4, 145.1, 144.8, 142.4 (s, N*C*), 137.1, 136.9 (s, C*C*CH), 126.0, 125.7 (s, C*C*HCH), 117.2 (s, CH*C*HCH),108.2, 1075, 107.2, (s, C*C*HC), 36.0, 35.7 (s, *C*Me$_3$), 32.5, 32.4 (s, C*Me*$_3$), 15.6, 14.6, 13.0, 12.8, 12.8, 12.5 (s, NC*C*H$_3$). Anal. calcd. For $C_{58}H_{86}B_2N_{14}O_2Ti_2$ (**2c**): C, 57.61; H, 7.36; N, 14.73. Found: C,57.37; H, 7.21; N, 14.93.

[Tp*TiO^{t}Bu(THF)]$_2$(μ-η^1: η^1-N$_2$) (2d). To a THF (30 mL) solution of **1d** (200 mg, 0.381 mmol), KC$_8$ (103 mg, 0.962 mmol) was added under N$_2$ atmosphere at –35 °C. The mixture was slowly warmed to room temperature and stirred for 5 h. After removal of the solvent under vacuum, the residual green solid was extracted with toluene and filtered. The solvent of the solution was then evaporated under reduced pressure. The green solid was re-dissolved in THF, concentrated and cooled at –35 °C to give **2d** (88 mg, 0.088 mmol, 46%) as green crystals. Single crystals suitable for X-ray study were obtained from a concentrated THF of **2d** at –35 °C. Anal. calcd. For $C_{46}H_{78}B_2N_{14}O_4Ti_2$ (THF) (**2d**): C, 55.68; H, 7.94; N, 18.17. Found: C, 54.71; H, 7.82; N, 17.20.

[Tp*TiCl(THF)]$_2$(μ-η^1: η^1-N_2) (2e). To a toluene (30 mL) solution of **Tp*TiCl$_2$(THF)** (200 mg, 0.410 mmol), potassium triethyborohydride (1 M in THF, 0.410 mL, 0.410 mmol) was added under N_2 atmosphere at –35 °C. The mixture was allowed to slowly warm to room temperature and stirred overnight. After removal of the solvent under vacuum, the residual green solid was washed with toluene, and the residue was dried under vacuum to give **2e** (55mg, 0.059 mmol, 29%) as a green powder. Single crystals suitable for X-ray study were obtained from a concentrated DCM of **2e** at –35 °C. Anal. calcd. For $C_{38}H_{60}B_2Cl_2N_{14}O_2Ti_2$ (0.95DCM) (**2e**): C, 46.23; H, 5.97; N, 19.37. Found: C, 46.75; H, 6.28; N, 18.66.

Tp*Ti(OC$_6$H$_3$Me$_2$-2,6)(NSiMe$_3$) (THF) (3a). To a toluene (15 mL) solution of **2a** (50 mg, 0.045 mmol), Me_3SiN_3 (12 mg, 0.091 mmol) was added under N_2 atmosphere at –35 °C. The mixture was slowly warmed to room temperature and stirred for 4 h. The suspension was filtered and then evaporated under reduced pressure. The resulting brown solid was re-dissolved in THF, concentrated and cooled at –35 °C to give **3a** (48 mg, 58.9%) as yellow crystals. Single crystals suitable for X-ray study were obtained from a concentrated Et_2O of **3a** at –35 °C. Anal. calcd. For $C_{28}H_{44}BN_7OSiTi$ (0.5THF) (**3a**): C, 57.06; H, 7.52; N, 16.63. Found: C, 56.77; H, 7.60; N, 16.34. ^{1}H NMR (600MHz, Benzene-d_6, rt): 0.14 (s, 9H, SiCH_3), 1.33 (s, 4H, C_4H_8O), 2.15 (s, 18H, NCCH_3), 2.40 (s, 6H, OCCH_3), 3.98 (s, 4H, C_4H_8O), 4.74 (br, 1H, B-H), 5.64 (s, 3H, CCHC), 6.85 (t, J_{HH} = 7.2 Hz, 2H, CHCHCH), 7.03 (d, J_{HH} = 7.2 Hz, 1H, CCHCH). ^{13}C NMR (600MHz, Benzene-d_6, rt): 165.1 (s, OC), 150.5, 143.3 (s, NC), 128.7, 128.6, 128.3, 126.9, 117.6 (s, OCCH + CHCHCH), 105.7 (s, NCCH), 74.1 (s, OCH$_2$), 25.6 (s, OCH$_2$$CH_2$), 15.1 (s, OC$CH_3$), 12.8 (s, NC$CH_3$), 3.5 (s, Si$CH_3$).

$Tp^*Ti(OC_6H_3Me_2\text{-}2,6)[N(SiMe_3)_2]$ (4a). To a toluene (15 mL) solution of **1a** (100 mg, 0.175 mmol), $LiN(SiMe_3)_2$ (58 mg, 0.349 mmol) was added under N_2 atmosphere at –35 °C. The mixture was allowed to slowly warm to room temperature and stirred overnight. The suspension was filtered and then evaporated under reduced pressure. The resulting orange solid was re-dissolved in Et_2O, concentrated and cooled at –35 °C to give **4a** (81 mg, 0.130 mmol, 74%) as orange crystals. Single crystals suitable for X-ray study were obtained from a concentrated Et_2O of **4a** at –35 °C. $\mu_{\mathrm{eff}} = 1.73\ \mu_{\mathrm{B}}$ (Evans method, 298 K). Anal. calcd. For $C_{29}H_{49}BN_7OSi_2Ti$ (**4a**): C, 55.59; H, 7.89; N, 15.65. Found: C, 55.62; H, 7.94; N, 15.80.

Silylation of $Tp^*Ti(OC_6H_3Me_2\text{-}2,6)[N(SiMe_3)_2]$ (4a). To a THF (10 mL) solution of **4a** (50 mg, 0.080 mmol), KC_8 (11 mg, 0.080 mmol) was added at –35 °C. The mixture was stirred for 3 h, followed by addition of Me_3SiCl (0.011 mL, 0.080 mmol) and stirred for another 3 h. The suspension was filtered and the solvent of filtrate was evaporated. The resulting green solid was extracted with toluene, concentrated and cooled at –35 °C to give **2a** (15 mg, 0.013 mmol, 33%) as crystals. In a parallel reaction, the filtrate was analyzed with GC-MS and the yield of $N(SiMe_3)_3$ (68%) was determined with cyclododecane (8.4 mg, 0.05 mmol) as internal standard.

2. NMR Spectra

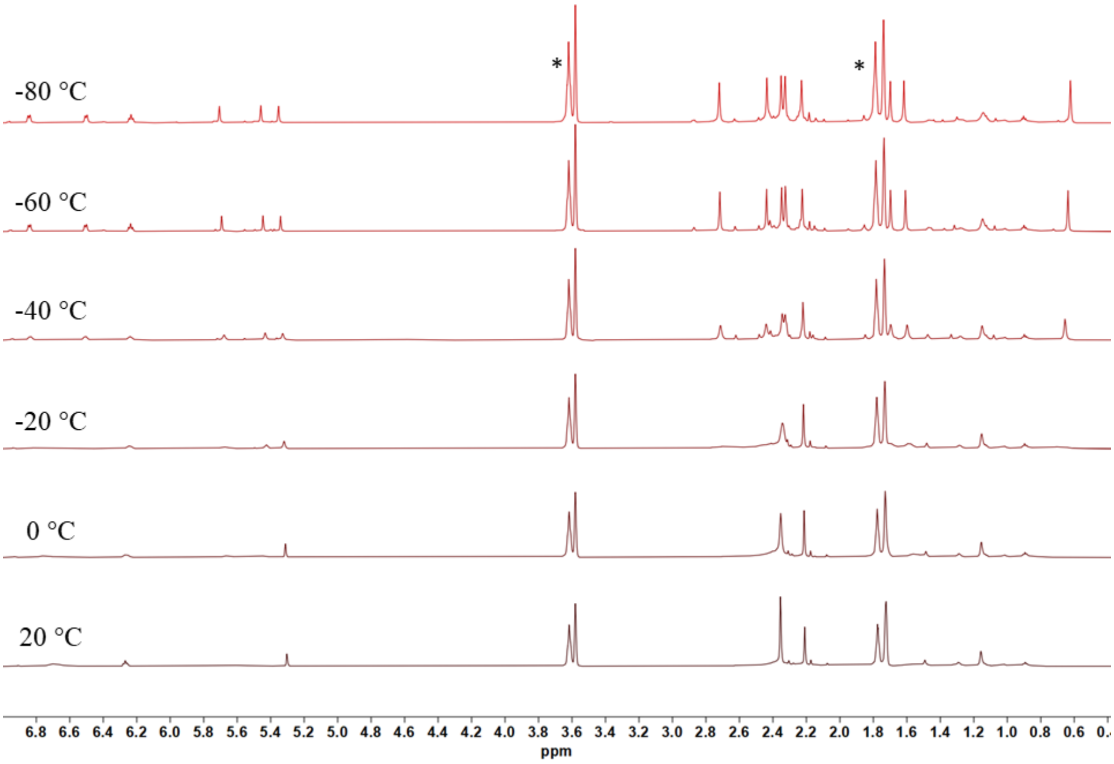


Figure S1. ^{1}H NMR spectrum (600 MHz, THF-d_8) of **2a**.

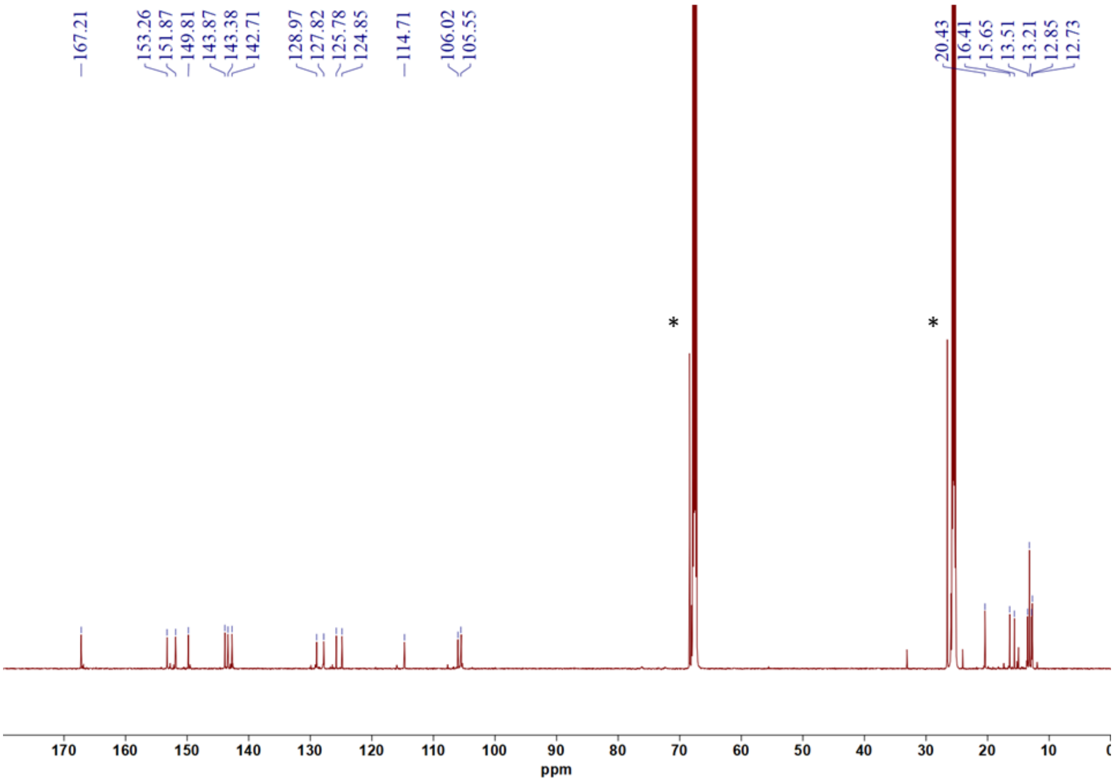


Figure S2. ^{13}C NMR spectrum (151 MHz, THF-d_8, –35 °C) of **2a**.

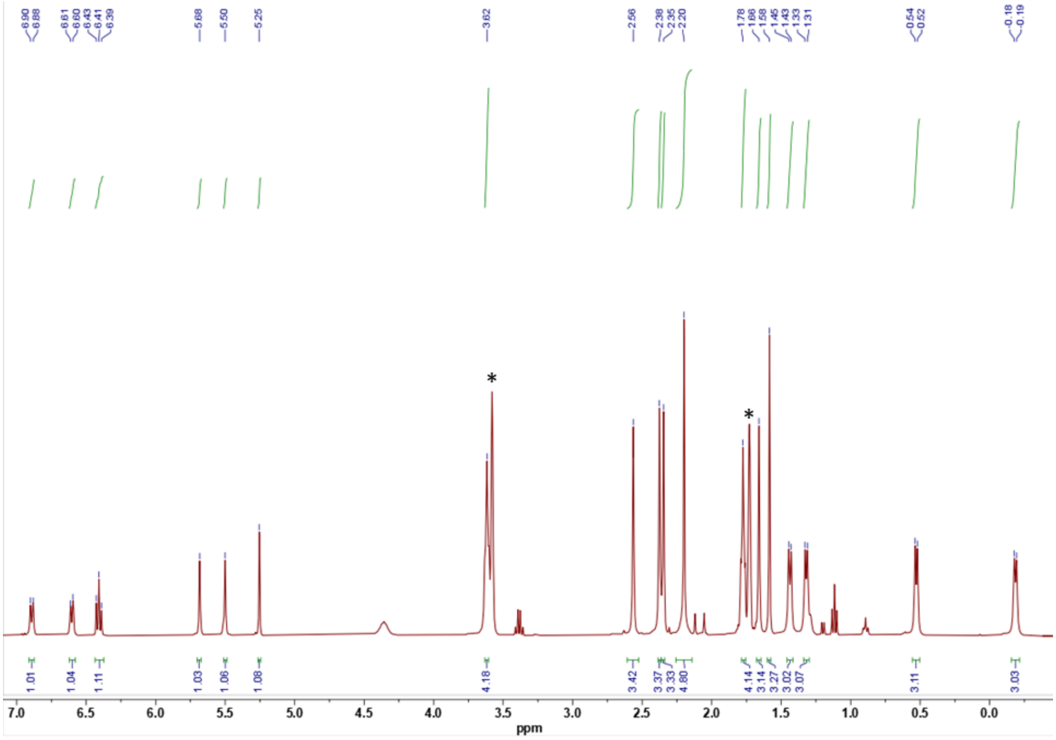


Figure S3. ^{1}H NMR spectrum (400 MHz, THF-d_8) of **2b**.

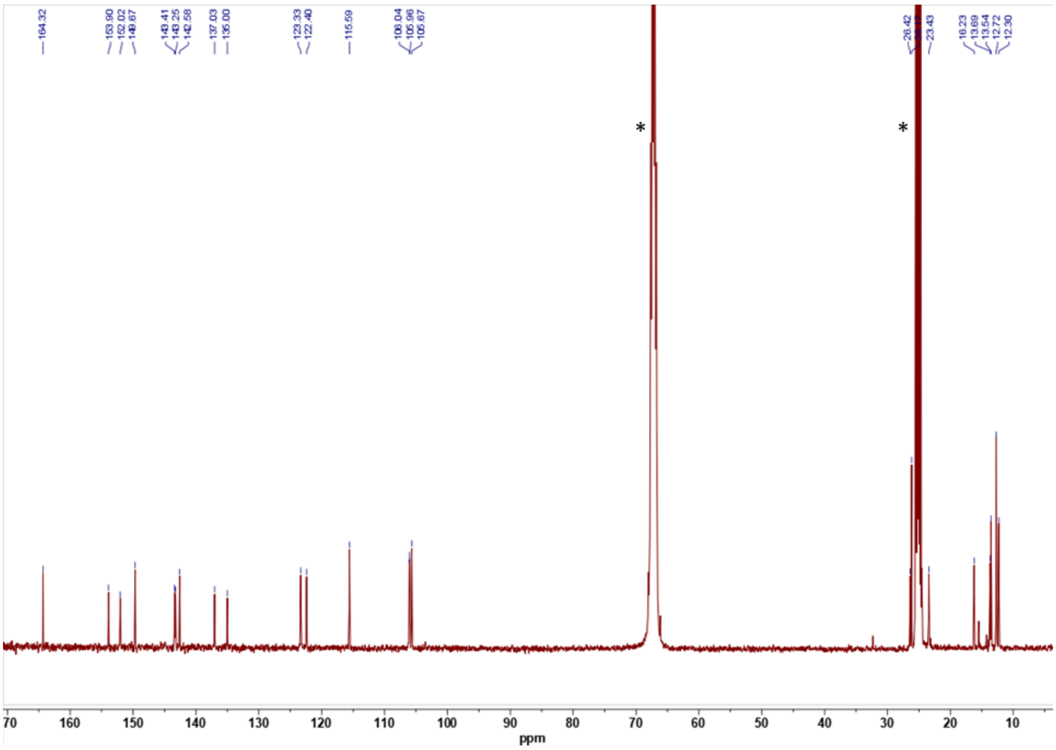


Figure S4. ^{13}C NMR spectrum (101 MHz, THF-d_8) of **2b**.

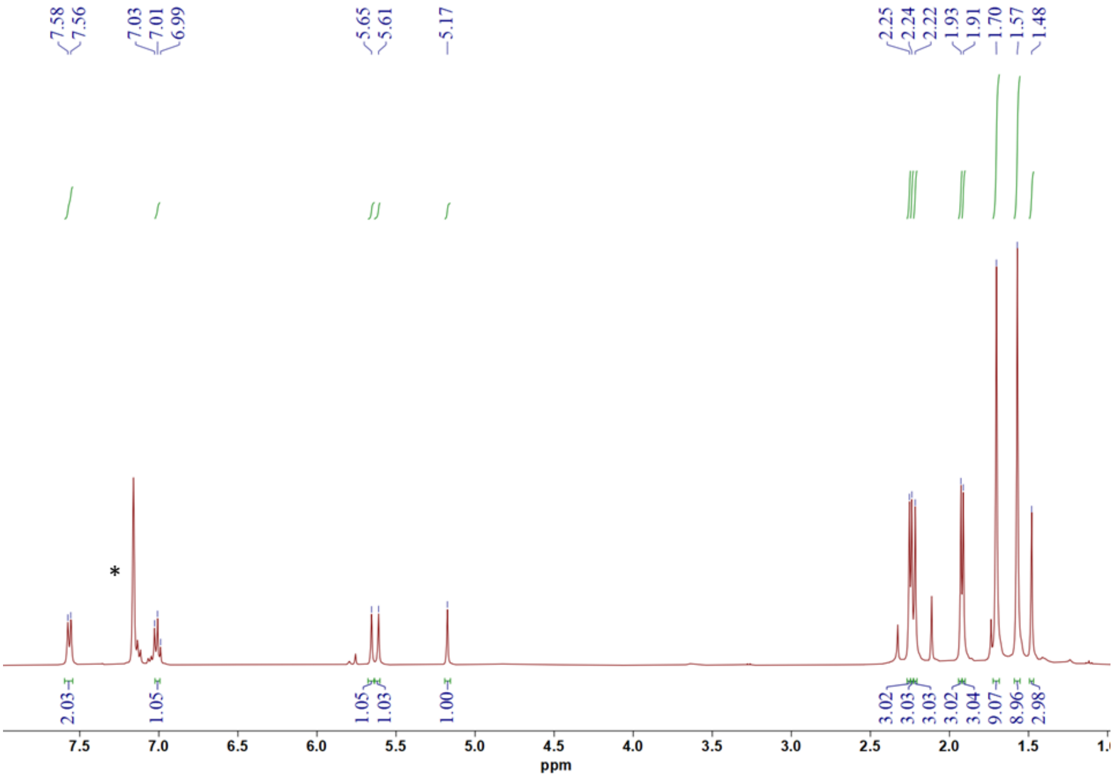


Figure S5. ^{1}H NMR spectrum (600 MHz, Benzene-d_6) of **2c**.

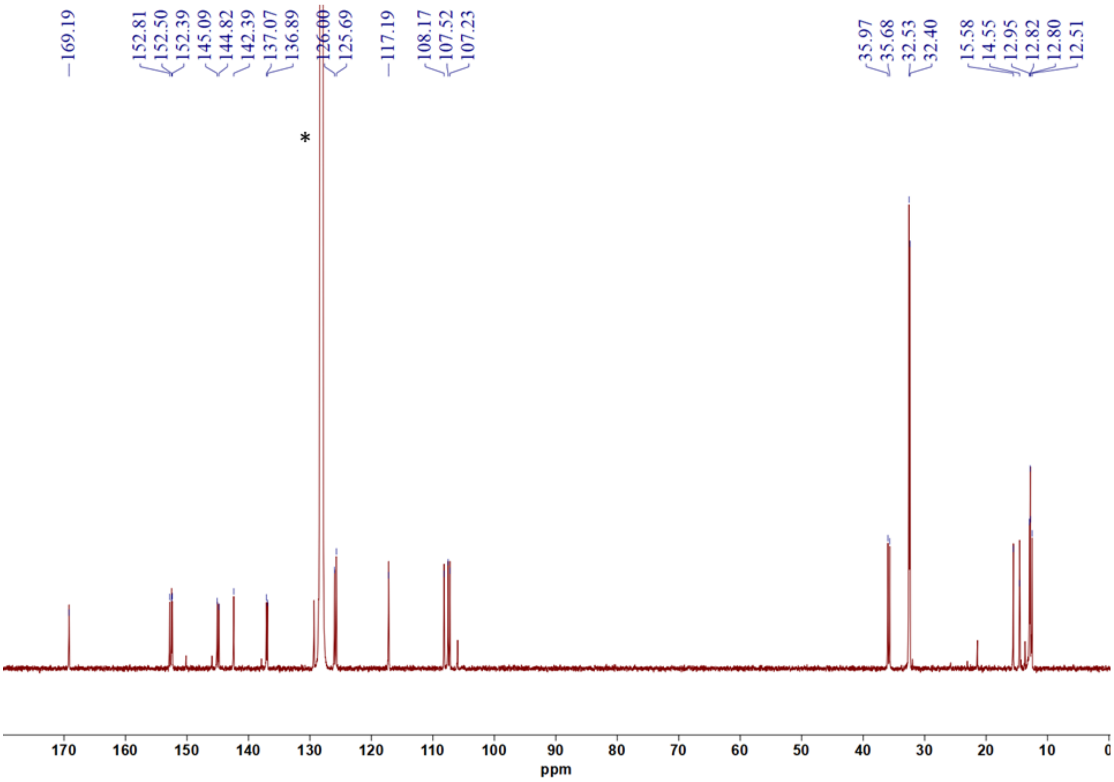


Figure S6. ^{13}C NMR spectrum (151 MHz, Benzene-d_6) of **2c**.

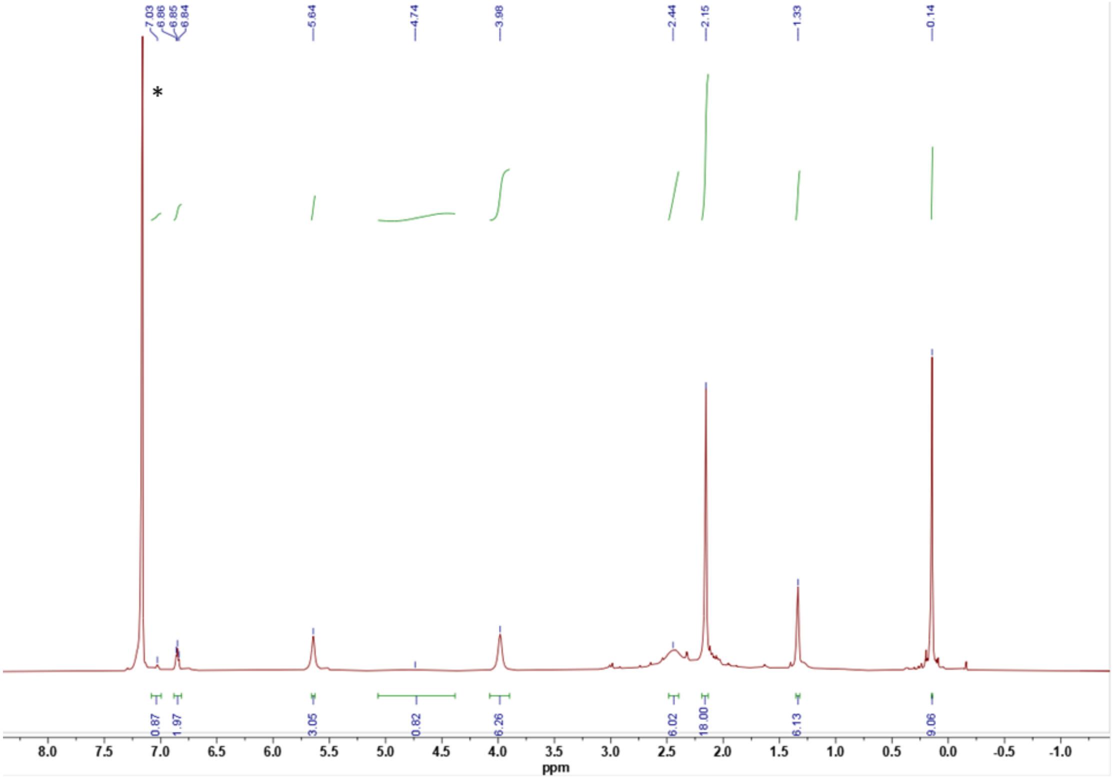


Figure S7. ^{1}H NMR spectrum (600 MHz, Benzene-d_6) of **3a**.

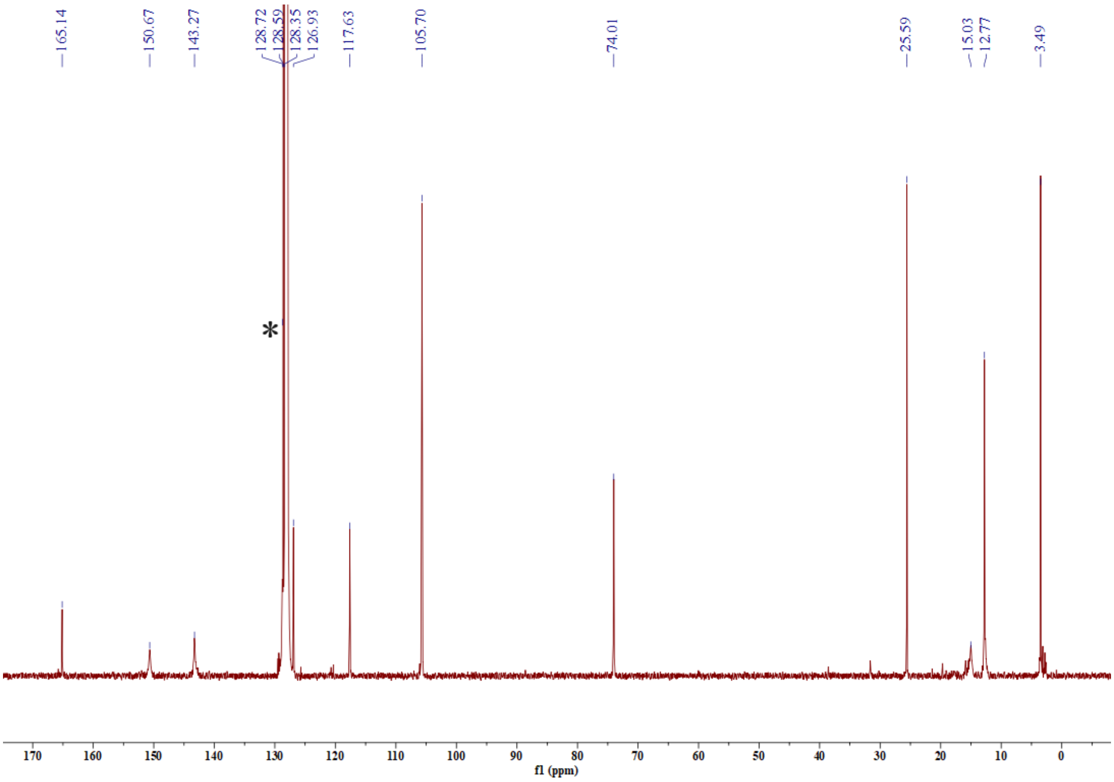


Figure S8. ^{13}C NMR spectrum (151 MHz, Benzene-d_6) of **3a**.

3. UV-vis Spectra

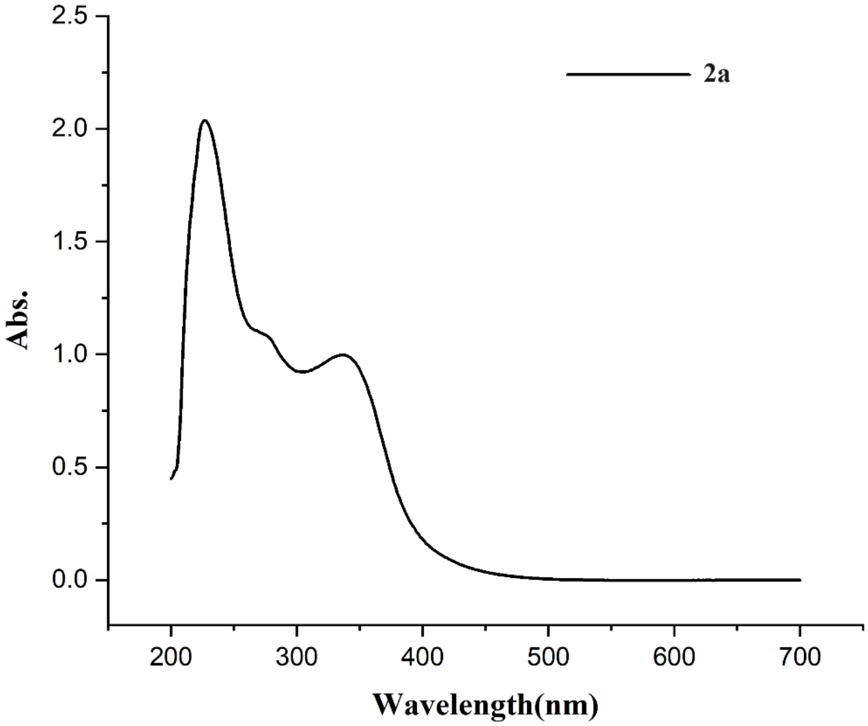


Figure S9. UV-vis spectra of titanium complexes **2a** (0.04 mM in THF) under N_2 atmosphere.

4. Raman Spectra

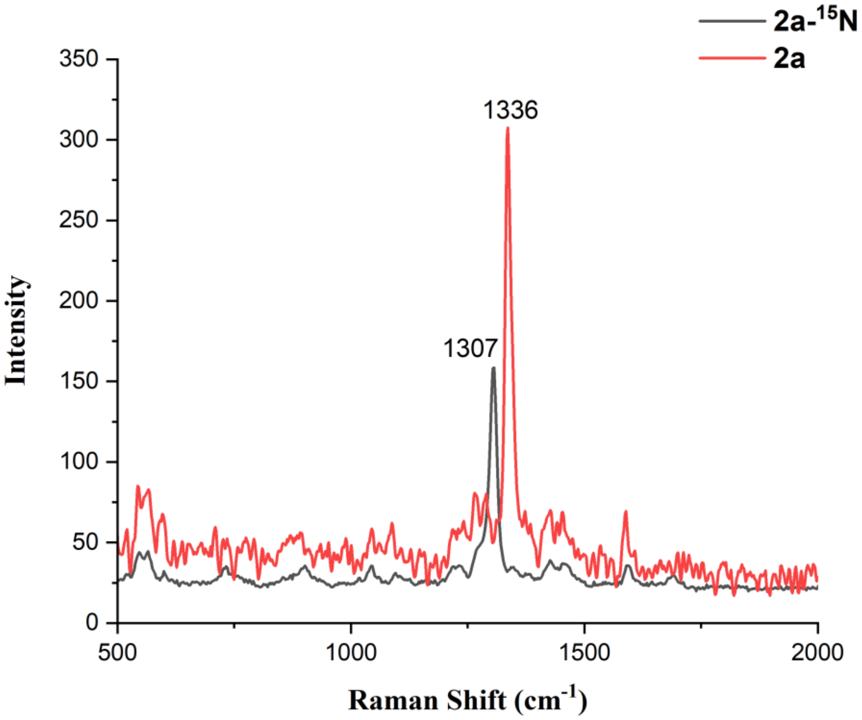


Figure S10. Raman spectra of **2a** and **2a-^{15}N**, recorded as powders.

5. Typical Procedures for Reduction of Dinitrogen to Ammonia.

Inside an N_2 glovebox, the titanium complex (0.001 mmol), $[H(Et_2O)_2][BAr^F_4]$ and KC_8, were weighed into bulb A of glass apparatus shown in Figure S1. The solvent was placed in bulb B. The apparatus was sealed and bulb B was immersed in a liquid N_2 bath (–196 °C). The apparatus was then placed under a static vacuum and solvent was vacuum transferred to bulb A. Subsequently the bulb A was refilled with N_2 (1 atm), warmed to –78 °C, sealed and allowed to stir at –78 °C for 3 h, followed by stirring at room temperature for additional 3 h. HCl (2.0 M in MeO*ᵗ*Bu, 10 mmol) was added to bulb B and frozen in liquid N_2 bath. Then the volatiles in bulb A were vacuum transferred to bulb B. The residual solid in bulb A was further treated with aqueous KOH (30%, 5 mL) under a flow of N_2 and stirred for 5 minutes before all the volatiles were again vacuum transferred to bulb B. After that, bulb B was sealed, warmed to room temperature, and stirred for approximately 10 minutes. All the solvent and excess HCl in bulb B were removed under vacuum to give white solid. NH_3 and N_2H_4 present in the apparatus were determined by the indophenol method[2] and the *p*-(dimethylamino)benzaldehyde method[3], respectively. The turnover number (TON) was calculated based on the amount of ammonia produced per Ti centre.

Figure S11 Glass apparatus used for N_2 reduction to NH_3.

Table S1. N_2 Reduction to Ammonia.

$$N_2 + [H(Et_2O)_2][BAr^F{}_4] + KC_8 \xrightarrow[\text{THF}]{\text{[Ti] (0.01 mmol)}} NH_3 \xrightarrow{H^+} NH_4^+$$

entry	[Ti]	Reductant (equiv)	Acid (equiv)	NH_3[a] (equiv.)	N_2H_4 (equiv.)	Efficiency (%)
1	**2a**	KC_8 (26)	$[H(Et_2O)_2][BAr^F{}_4]$ (20)	1.3 ± 0.1	0	39
2	**2b**	KC_8 (26)	$[H(Et_2O)_2][BAr^F{}_4]$ (20)	0.9 ± 0.1	0	27
3	**2d**	KC_8 (26)	$[H(Et_2O)_2][BAr^F{}_4]$ (20)	0.7 ± 0.1	0	21
4	**2e**	KC_8 (26)	$[H(Et_2O)_2][BAr^F{}_4]$ (20)	1.1 ± 0.1	0	33
5	**2a**	KC_8 (53)	$[H(Et_2O)_2][BAr^F{}_4]$ (40)	2.6 ± 0.1	0	39
6	**2b**	KC_8 (53)	$[H(Et_2O)_2][BAr^F{}_4]$ (40)	2.2 ± 0.1	0	33
7	**2d**	KC_8 (53)	$[H(Et_2O)_2][BAr^F{}_4]$ (40)	1.3 ± 0.1	0	20
8	**2e**	KC_8 (53)	$[H(Et_2O)_2][BAr^F{}_4]$ (40)	1.4 ± 0.1	0	21
9	**2a**	KC_8 (133)	$[H(Et_2O)_2][BAr^F{}_4]$ (100)	2.7 ± 0.1	0	16

[a] TON = equiv of ammonia/ equiv of [Ti], and represents the average of ≥2 independent runs. [b] Yield = 3 × NH_4^+/reductant. Reactions were performed at –78 °C (3 h), followed by 25 °C (3 h).

6. Typical Procedures for Catalytic Conversion of Dinitrogen to Silylamine

Catalytic process at room temperature. Inside an N_2 glovebox, a two-neck flask with a magnetic stir bar was charged with titanium catalyst (0.01 mmol) and KC_8 (1 mmol, 100 equiv), Me_3SiCl (1 mmol, 200 equiv) and THF (10 mL). The reaction flask was sealed and brought out of the glovebox. The mixture was allowed to stir at room temperature for 24 h. After filtration, the residual solid was washed with THF (2 mL×3). The combined filtrate was treated with HCl (2.0 M in MeO^tBu, 12 mmol) at –196 °C before being warmed to room temperature and stirred for 30 minutes. All the volatiles were removed under vacuum to afford white solid. The amount of ammonia was determined by the indophenol method[2]. The turnover number (TON) was calculated based on the amount of silylamine produced per Ti centre.

Catalytic process at –40 °C. Inside an N_2 glovebox, a two-neck flask with a magnetic stir bar was charged with titanium catalyst (0.01 mmol) and KC_8 (1 mmol, 100 equiv). The reaction flask was sealed and brought out of the glovebox. To the flask immersed in a liquid N_2 bath (–196 °C), a THF (10 mL) solution of Me_3SiCl (1 mmol, 100 equiv) was slowly added. The mixture was warmed to –40 °C and allowed to stir at –40 °C for 20 h, followed by stirring at 25 °C for an additional 6 h. Then it was filtered. And the residue was washed with THF (2 mL×3). The combined filtrate was treated with HCl (2.0 M in MeO^tBu, 12 mmol) at –196 °C before being warmed to room temperature and stirred for 30 minutes. All the volatiles were removed under vacuum to afford white solid. The amount of ammonia was determined by the indophenol method[2]. The turnover number (TON) was calculated based on the amount of silylamine produced per Ti centre.

Table S2. Catalytic N_2 Reduction to $N(SiMe_3)_3$.

$$N_2 + Me_3SiCl + KC_8 \xrightarrow[\text{THF}]{\text{[Ti] (0.01 mmol)}} N(SiMe_3)_3 \xrightarrow{H^+} NH_4^+$$

entry	[Ti]	Reductant (equiv)	R3SiCl (equiv)	TON [a]	Yield(%) [b]
1[c]	Tp*TiCl$_2$(THF)	KC$_8$ (100)	Me$_3$SiCl (100)	2.7 ± 0.4	8
2[c]	**1a**	KC$_8$ (100)	Me$_3$SiCl (100)	3.4 ± 0.2	10
3[c]	**1b**	KC$_8$ (100)	Me$_3$SiCl (100)	3.2 ± 0.5	10
4[c]	**1c**	KC$_8$ (100)	Me$_3$SiCl (100)	4.1 ± 0.1	12
5[c]	**1d**	KC$_8$ (100)	Me$_3$SiCl (100)	2.1 ± 0.3	6
6[c]	**2a**	KC$_8$ (100)	Me$_3$SiCl (100)	2.6 ± 0.5	16
7[c]	**2b**	KC$_8$ (100)	Me$_3$SiCl (100)	3.0 ± 0.3	18
8[c]	**2c**	KC$_8$ (100)	Me$_3$SiCl (100)	2.5 ± 0.1	15
9[c]	**2d**	KC$_8$ (100)	Me$_3$SiCl (100)	1.9 ± 0.7	11
10[c]	**2e**	KC$_8$ (100)	Me$_3$SiCl (100)	2.5 ± 0.1	15
11[d]	Tp*TiCl$_2$(THF)	KC$_8$ (100)	Me$_3$SiCl (100)	1.7 ± 0.2	5
12[d]	**1a**	KC$_8$ (100)	Me$_3$SiCl (100)	3.8 ± 0.2	12
13[d]	**1a**	KC$_8$ (200)	Me$_3$SiCl (200)	2.9 ± 0.5	5
14[d]	**1c**	KC$_8$ (100)	Me$_3$SiCl (100)	5.8 ± 0.1	18
15[d]	**2a**	KC$_8$ (100)	Me$_3$SiCl (100)	5.9 ± 0.9	35
16[d]	**2b**	KC$_8$ (100)	Me$_3$SiCl (100)	6.0 ± 0.3	36
17[d]	**2c**	KC$_8$ (100)	Me$_3$SiCl (100)	5.9 ± 0.2	35
18[d]	**2d**	KC$_8$ (100)	Me$_3$SiCl (100)	5.4 ± 1.2	32
19[d]	**2e**	KC$_8$ (100)	Me$_3$SiCl (100)	5.1 ± 0.6	31
20[d]	**2a**	KC$_8$ (200)	Me$_3$SiCl (200)	6.0 ± 0.2	18
21[e]	**2a**	KC$_8$ (100)	Me$_3$SiCl (100)	0.9 ± 0.3	6
22	/	KC$_8$ (100)	Me$_3$SiCl (100)	0.1 ± 0.0	0.2

[a] TON = equiv of [N(SiMe$_3$)$_3$]/ equiv of [Ti], and represents the average of ≥2 independent runs. [b] Yield = 3 × NH$_4^+$/reductant. [c] Reactions were performed at 25 °C (26 h). [d] Reactions were performed at –40 °C (20 h), followed by 25 °C (6 h). [e] Reactions were performed in Ar atmosphere at –40 °C (20 h), followed by 25 °C (6 h).

Table S3. Catalytic N_2 Reduction to Silyamine by 2a (Temperature Effect)

$$\mathrm{N_2 + Me_3SiCl + KC_8 \xrightarrow[\text{THF, } \textit{Temperature}]{[Ti]\ (0.01\ mmol)} silylamine \xrightarrow{H^+} NH_4^+}$$

entry	Temperature	[Ti]	Reductant (equiv)	R_3SiCl (equiv)	TON [a]	Yield(%) [b]
1	–40 °C	**2a**	KC_8 (100)	Me_3SiCl (100)	5.9 ± 0.9	35
2	–20 °C	**2a**	KC_8 (100)	Me_3SiCl (100)	5.4 ± 0.6	32
3	0 °C	**2a**	KC_8 (100)	Me_3SiCl (100)	4.3 ± 0.7	26
4	25 °C	**2a**	KC_8 (100)	Me_3SiCl (100)	2.6 ± 0.5	15

[a] equiv of $[N(SiMe_3)_3]$/ equiv of [Ti], and represents the average of ≥2 independent runs. [b] Yield = 3 × NH_4^+/reductant.

Table S4. Catalytic N_2 Reduction to Silyamine by 2a (Solvent Effect).

$$\mathrm{N_2 + Me_3SiCl + KC_8 \xrightarrow[\textit{Solvent}]{[Ti]\ (0.01\ mmol)} silylamine \xrightarrow{H^+} NH_4^+}$$

entry	[Ti]	Reductant (equiv)	R_3SiCl (equiv)	Solvent	TON [a]	Yield(%) [b]
1	**2a**	KC_8 (100)	Me_3SiCl (100)	THF	5.9 ± 0.9	35
2	**2a**	KC_8 (100)	Me_3SiCl (100)	DME	5.5 ± 1.0	33
3	**2a**	KC_8 (100)	Me_3SiCl (100)	Et_2O	4.4 ± 0.5	26
4	**2a**	KC_8 (100)	Me_3SiCl (100)	Toluene	0.3 ± 0	2

[a] equiv of $[N(SiMe_3)_3]$/ equiv of [Ti], and represents the average of ≥2 independent runs. [b] Yield = 3 × NH_4^+/reductant.

Table S5. Catalytic N_2 Reduction to Silyamine. (Silylating Reagents Effect).

$$\mathrm{N_2 + \mathit{R_3SiCl} + KC_8 \xrightarrow[THF]{[Ti]\ (0.01\ mmol)} silylamine \xrightarrow{H^+} NH_4^+}$$

entry	[Ti]	Reductant (equiv)	R_3SiCl (equiv)	TON [a]	Yield/% [b]
1	**2a**	KC_8 (100)	$^iPr_3SiCl$ (100)	4.7 ± 0.1	28
2	**2a**	KC_8 (100)	bisSi-Cl (50)	1.4 ± 0.3	8
3	**2b**	KC_8 (100)	bisSi-Cl (50)	2.1 ± 0.4	13
4	**2d**	KC_8 (100)	bisSi-Cl (50)	5.4 ± 1.2	32

[a] equiv of $[N(SiMe_3)_3]$/ equiv of [Ti], and represents the average of ≥2 independent runs. [b] Yield = 3 × NH_4^+/reductant.

Table S6. Catalytic N_2 Reduction to Silyamine by 2a (Reductant Effect).

$$N_2 + Me_3SiCl + \textbf{\textit{Reductant}} \xrightarrow[\text{THF}]{\textbf{[Ti]}\ (0.01\ \text{mmol})} \text{silylamine} \xrightarrow{H^+} NH_4^+$$

entry	[Ti]	Reductant (equiv)	R_3SiCl (equiv)	TON [a]	Yield(%) [b]
1	**2a**	KC_8 (100)	Me_3SiCl (100)	5.9 ± 0.9	35
2	**2a**	K (100)	Me_3SiCl (100)	0.5 ± 0.2	3
3[c]	**2a**	K (100)	Me_3SiCl (100)	5.8 ± 0.1	18
4	**2a**	Na (100)	Me_3SiCl (100)	0.7 ± 0.2	4
5	**2a**	Li (100)	Me_3SiCl (100)	0.6 ± 0.5	4

[a] TON = equiv of $[N(SiMe_3)_3]$/ equiv of [Ti], and represents the average of ≥2 independent runs. [b] Yield = 3 × NH_4^+/reductant. [c] Reactions were performed at 25 °C for 5 days.

Table S7. Catalytic N_2 Reduction to Silyamine by 3a and 4a.

$$N_2 + Me_3SiCl + KC_8 \xrightarrow[\text{THF}]{\textbf{[Ti]}\ (0.01\ \text{mmol})} \text{silylamine} \xrightarrow{H^+} NH_4^+$$

entry	[Ti]	Reductant (equiv)	R_3SiCl (equiv)	TON [a]	Yield(%) [b]
1	**3a**	KC_8 (50)	Me_3SiCl (50)	5.9 ± 0.6	35
2	**3a**	KC_8 (100)	Me_3SiCl (100)	7.0 ± 0.6	21
3	**4a**	KC_8 (50)	Me_3SiCl (50)	7.5 ± 0.7	45
4	**4a**	KC_8 (100)	Me_3SiCl (100)	9.8 ± 0.5	30

[a] TON = equiv of $[N(SiMe_3)_3]$/ equiv of [Ti], and represents the average of ≥2 independent runs. [b] Yield = 3 × NH_4^+/reductant.

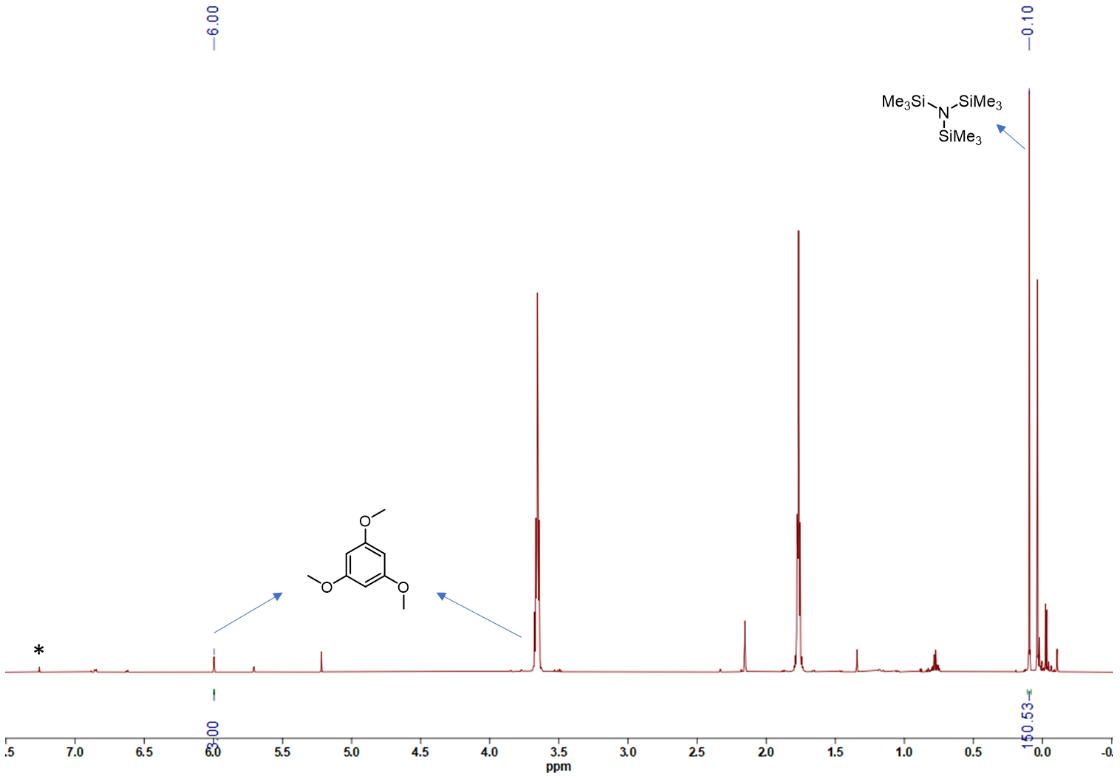


Figure S12. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of $N(SiMe_3)_3$ with 1,3,5-trimethoxybenzene (0.02 mmol) as internal standard.

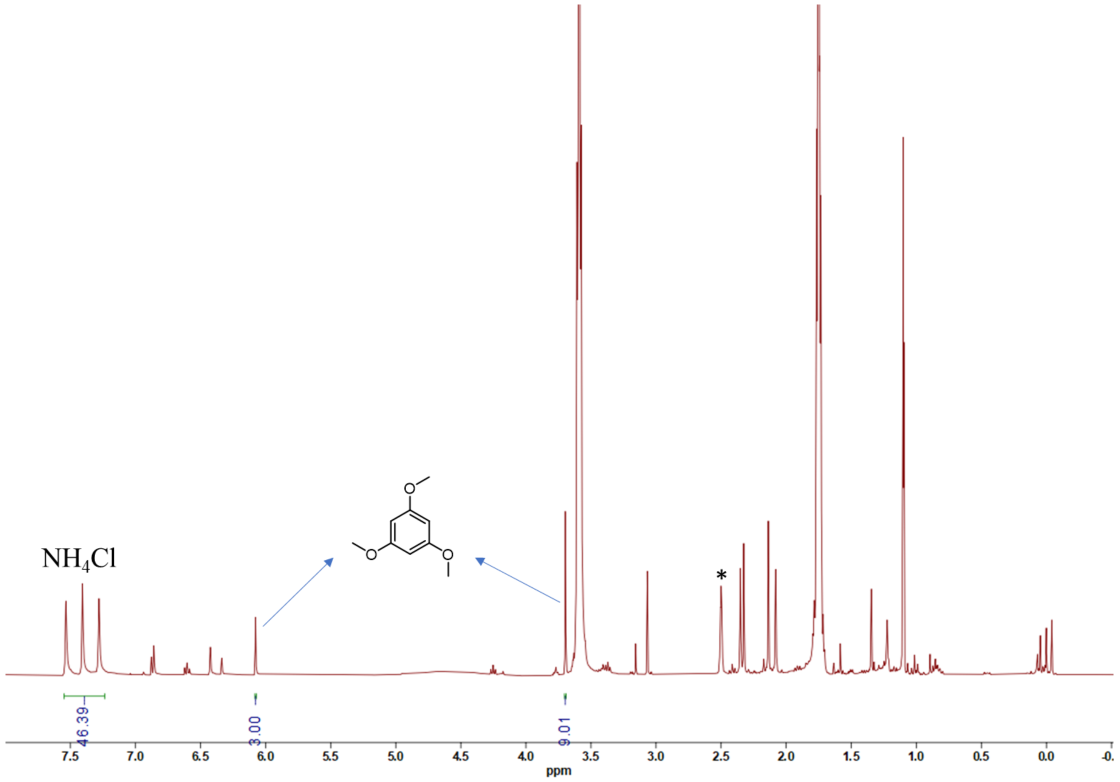


Figure S13. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of NH_4Cl with 1,3,5-trimethoxybenzene (0.01 mmol) as internal standard.

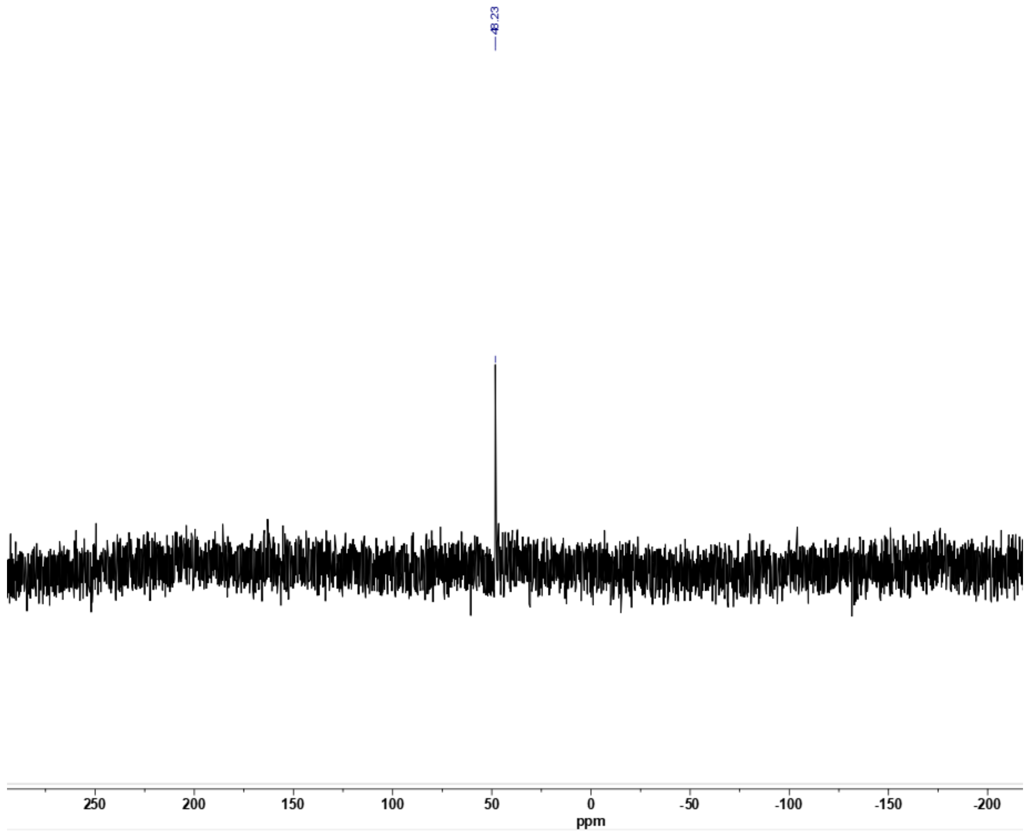


Figure S14. ^{15}N NMR spectrum (41 MHz, C_6D_6) of **2a-^{15}N**.

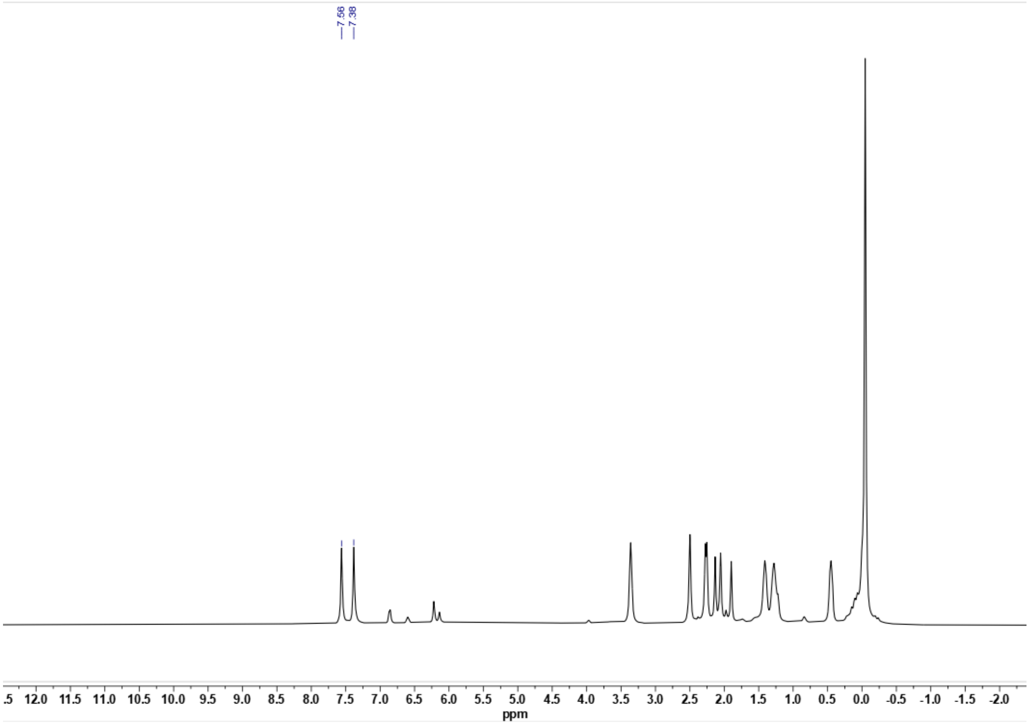
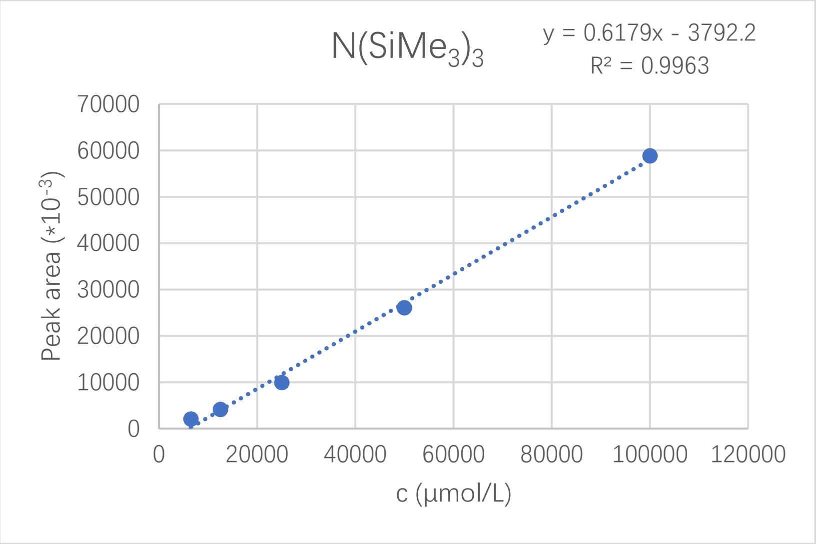


Figure S15. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of $^{15}NH_4Cl$. Catalysis was conducted with **2a-^{15}N** under a $^{15}N_2$ atmosphere (Me_3SiCl / KC_8, 100 / 100 equiv) at –40°C.

Table S8. GC-MS Analysis of By-products.

Temperature	**$Me_3SiSiMe_3$**	**$Me_3SiOC_4H_9$**	**$N(SiMe_3)_3$**
rt	13%	1%	18%
–40 °C	1%	1%	34%

Note: The yields of $N(SiMe_3)_3$ and $Me_3SiSiMe_3$ were determined by GC-MS analysis using calibration curves constructed with authentic commercial standards. Due to the commercial unavailability of $Me_3SiOC_4H_9$, its yield was estimated semi-quantitatively based on the calibration curve of $Me_3SiSiMe_3$, which has a comparable molecular weight and is expected to have a similar detector response factor.



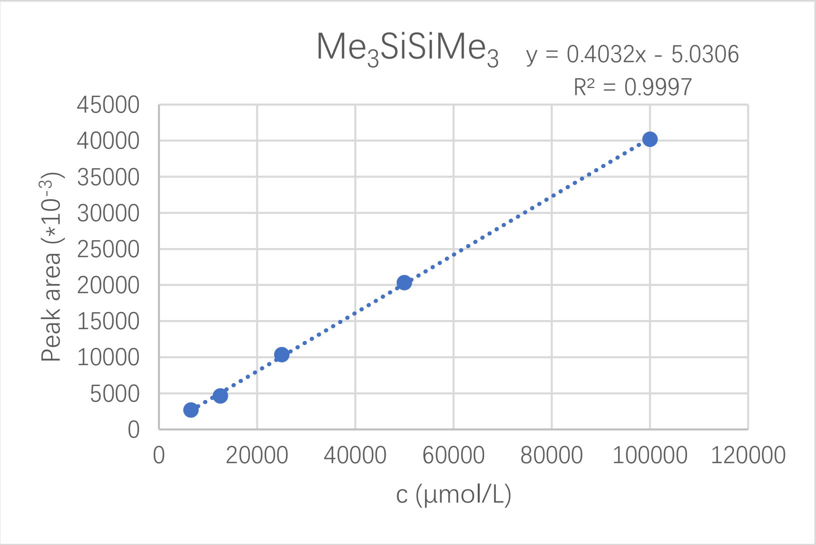


Table S9. Quantification of $N(SiMe_3)_3$ and NH_4^+.

Temperature	[Ti]	Reductant (equiv)	R_3SiCl (equiv)	$N(SiMe_3)_3$	NH_4^+ [b]
rt	**2a**	KC_8 (100)	Me_3SiCl (100)		2.6 ± 0.5
rt	**2a**	KC_8 (100)	Me_3SiCl (100)	3.0[a]	
–40 °C	**2a**	KC_8 (100)	Me_3SiCl (100)		5.9 ± 0.9
–40 °C	**2a**	KC_8 (100)	Me_3SiCl (100)	5.7[a]	
–40 °C	**2a**	KC_8 (100)	Me_3SiCl (100)	5.6[c]	

[a] $N(SiMe_3)_3$ was quantified by GC-MS. [b] NH_4^+ was obtained from acidolysis treatment of product and determined by indophenol method. [c] $N(SiMe_3)_3$ was quantified by ^1H NMR spectra (0.02 mmol 1,3,5- trimethoxybenzene as internal standard).

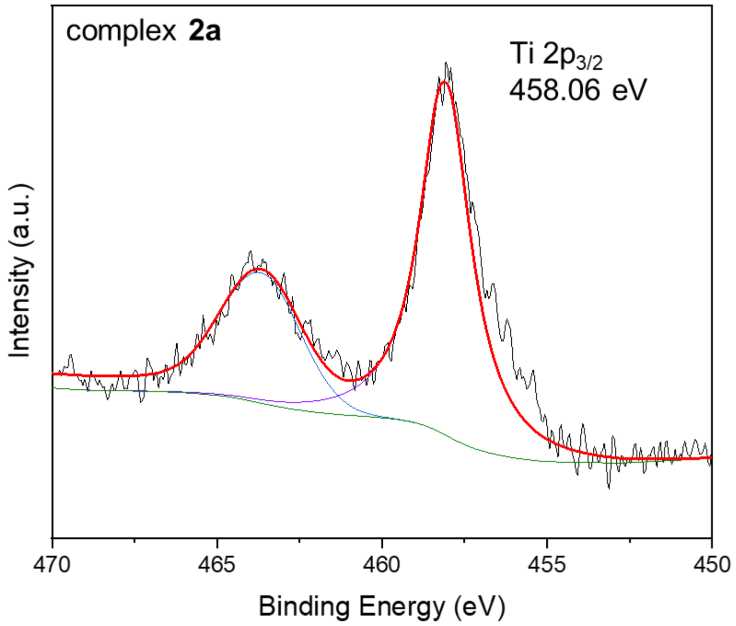
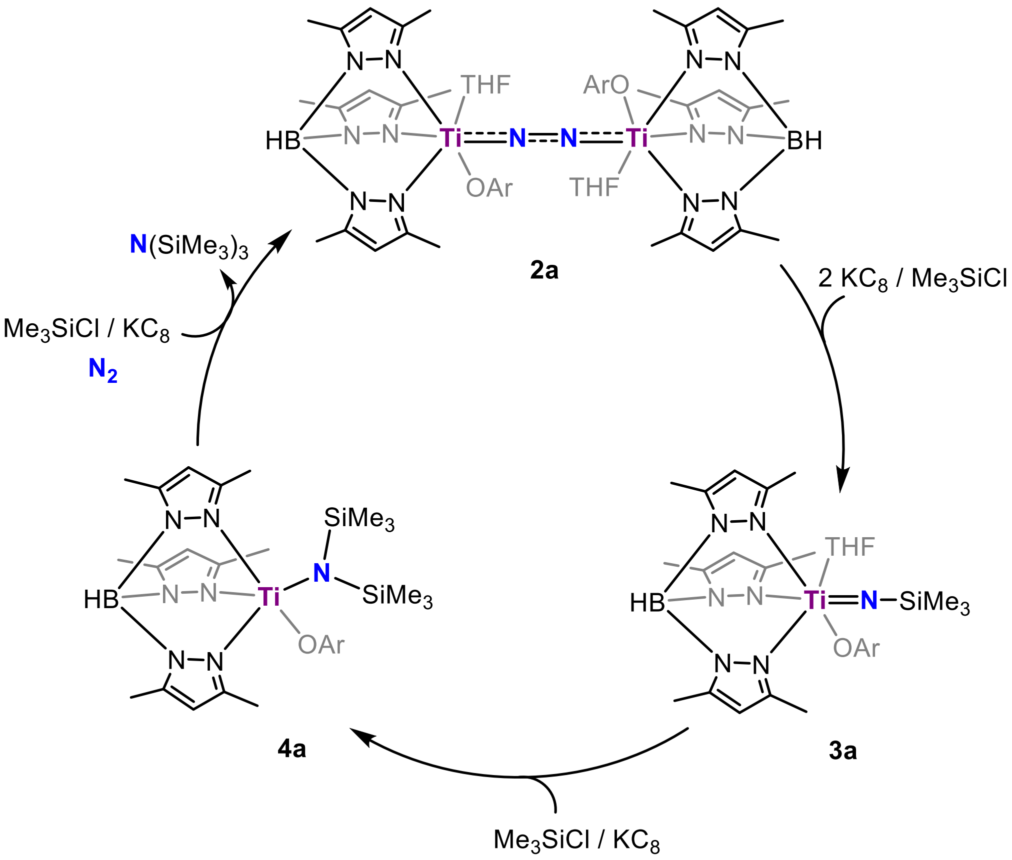


Figure S16. The titanium 2p XPS spectra of complex **2a.**



Scheme S1. Proposed reaction mechanism.

7. X-ray Crystallography

Crystals for X-ray diffraction studies were obtained as described in the preparations. The crystals were manipulated in a glovebox under a microscope and were sealed in thin-walled glass capillaries. Intensity data were collected with a Rigaku Mercury CCD area detector using Mo or Cu Ka radiation. The diffracted intensities were corrected for Lorentz–polarization effects and empirical absorption corrections. All of the structures were solved using SHELXL-2018. Structural refinement was performed using on F^2 anisotropically for all of the non-hydrogen atoms by the full matrix least-squares method. Structural refinement was performed using the SHELXL[4-6] option in the WINGX system[7], or Olex2 system[8] on F^2 anisotropically for all of the nonhydrogen atoms by the full matrix least-squares method. Analytical scattering factors for neutral atoms were used throughout the analysis. The hydrogen atoms of ligands were placed at the calculated positions, which were refined using a riding model. The analytical scattering factors for neutral atoms were used throughout the analysis. The residual electron densities were of no chemical significance.

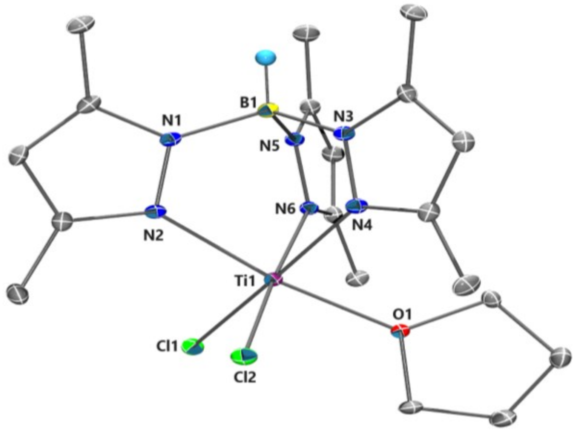


Figure S17. X-ray diffraction crystal structure of **Tp*TiCl$_2$(THF)** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

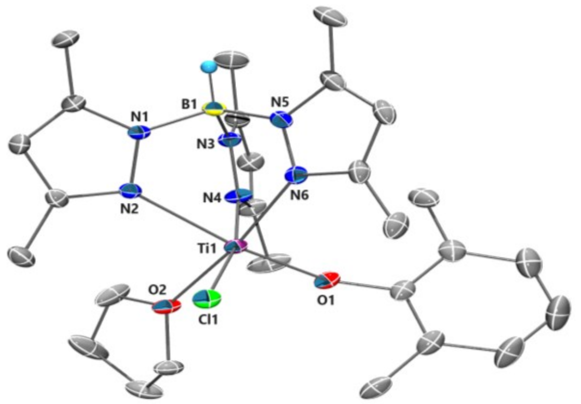


Figure S18. X-ray diffraction crystal structure of **1a** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

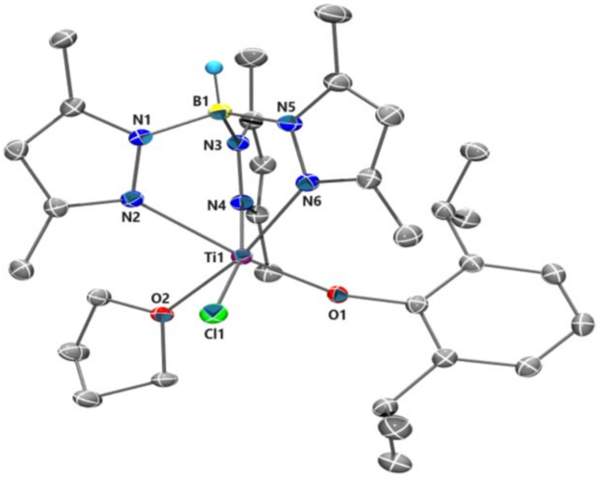


Figure S19. X-ray diffraction crystal structure of **1b** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

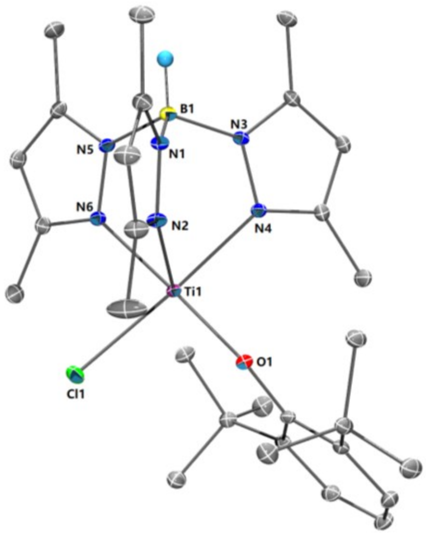


Figure S20. X-ray diffraction crystal structure of **1c** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

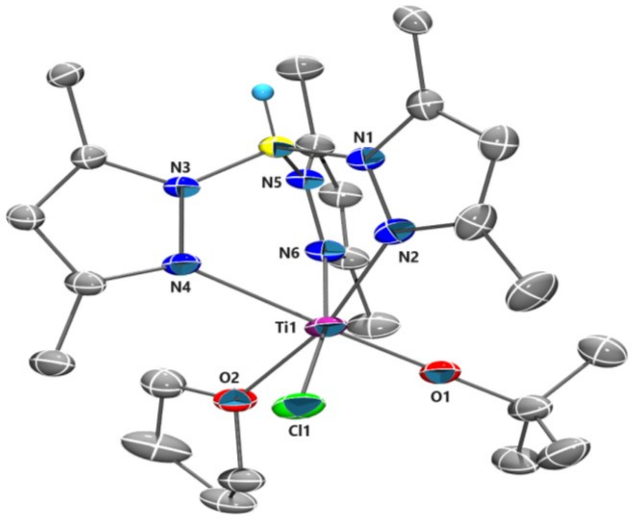


Figure S21. X-ray diffraction crystal structure of **1d** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

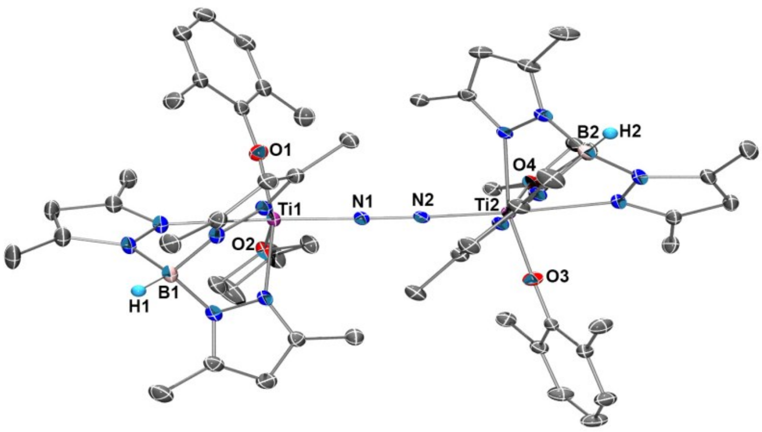


Figure S22. X-ray diffraction crystal structure of **2a** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

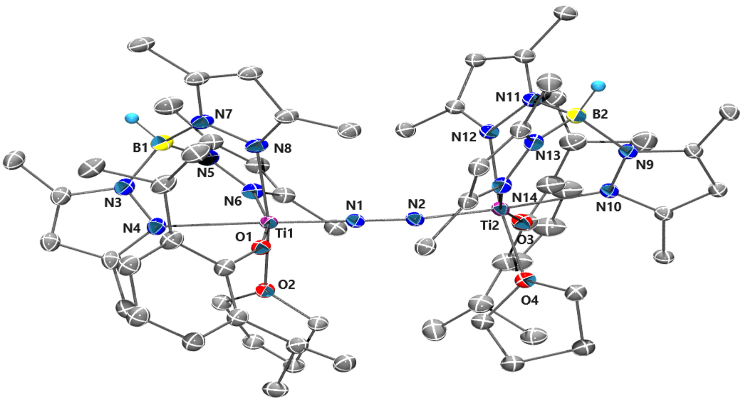


Figure S23. X-ray diffraction crystal structure of **2b** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

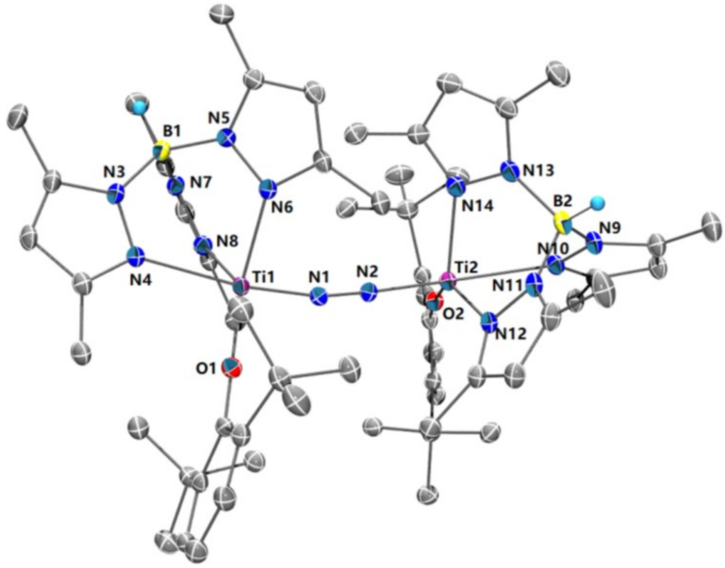


Figure S24. X-ray diffraction crystal structure of **2c** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

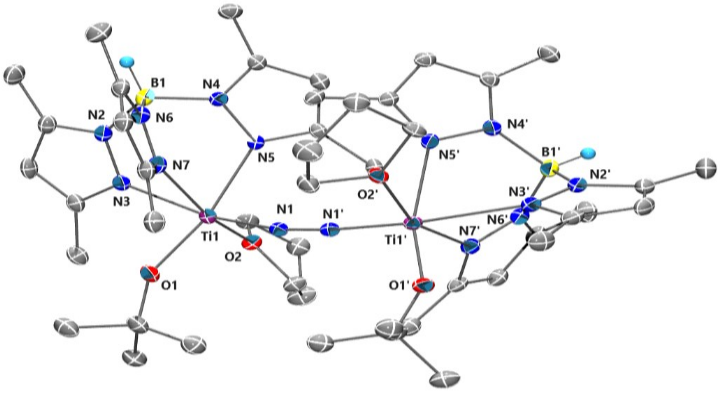


Figure S25. X-ray diffraction crystal structure of **2d** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

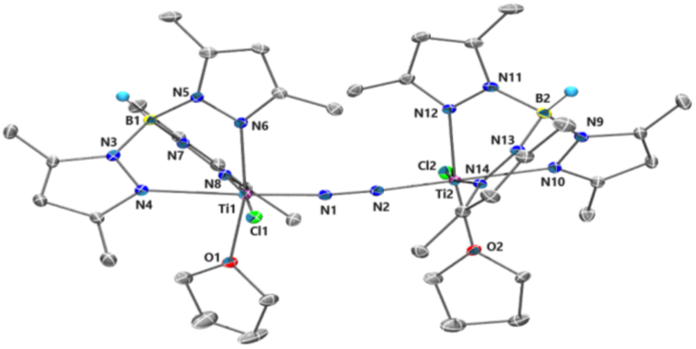


Figure S26. X-ray diffraction crystal structure of **2e** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

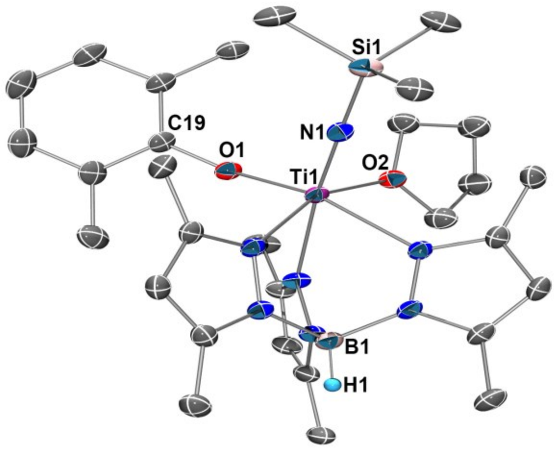


Figure S27. X-ray diffraction crystal structure of **3a** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

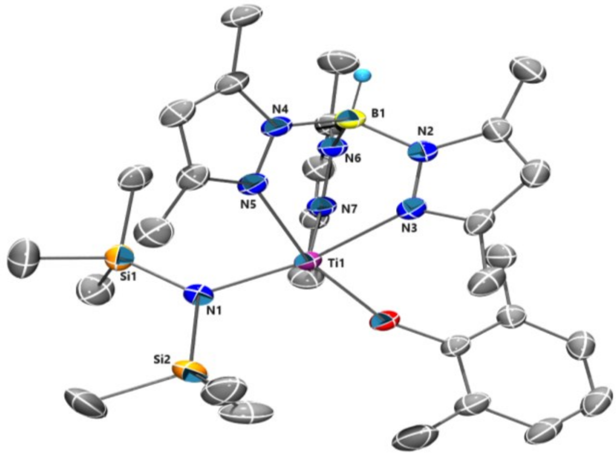


Figure S28. X-ray diffraction crystal structure of **4a** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

Table S10. X-Ray Crystallographic Data and Structure Refinement for Tp*TiCl$_2$(THF).

	Tp*TiCl$_2$(THF)
CCDC number	2311323
Empirical formula	$C_{19}H_{30}BCl_2N_6OTi$
Formula weight	488.10
Temperature [K]	100.00(10)
Crystal system	monoclinic
Space group (number)	$P2_1/n$ (14)
a [Å]	8.0509(2)
b [Å]	28.5998(9)
c [Å]	12.0209(3)
α [°]	90
β [°]	101.123(2)
γ [°]	90
Volume [Å^3]	2715.87(13)
Z	4
ρ_{calc} [gcm^{-3}]	1.194
μ [mm^{-1}]	0.532
F(000)	1020
Crystal colour	metallic violet
Crystal shape	block
Radiation	Mo K_α (λ=0.71073 Å)
2θ range [°]	6.66 to 59.42 (0.72 Å)
Index ranges	$-10 \leq h \leq 10$ $-39 \leq k \leq 38$ $-16 \leq l \leq 16$
Reflections collected	17904
Independent reflections	6561 R_{int} = 0.0405 R_{sigma} = 0.0559
Completeness to θ = 67.684°	99.8 %
Data / Restraints / Parameters	6561/0/286
Goodness-of-fit on F^2	1.023
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0461 wR_2 = 0.0996
Final R indexes [all data]	R_1 = 0.0622 wR_2 = 0.1079
Largest peak/hole [eÅ^{-3}]	0.54/-0.43

Table S11. X-Ray Crystallographic Data and Structure Refinement for 1a and 1b

	1a	**1b**
CCDC number	2331148	2331149
Empirical formula	$C_{27}H_{39}BClN_6O_2Ti$	$C_{31}H_{47}BClN_6O_2Ti$
Formula weight	573.80	629.90
Temperature [K]	100.1(5)	100.00(10)
Crystal system	monoclinic	monoclinic
Space group (number)	$P2_1/n$ (14)	$P2_1/n$ (14)
a [Å]	10.57930(10)	10.8294(2)
b [Å]	15.3351(2)	15.1747(2)
c [Å]	18.0389(2)	20.4317(3)
α [°]	90	90
β [°]	94.3620(10)	94.1780(10)
γ [°]	90	90
Volume [$Å^3$]	2918.06(6)	3348.68(9)
Z	4	4
ρ_{calc} [gcm^{-3}]	1.306	1.249
μ [mm^{-1}]	3.602	3.183
$F(000)$	1212	1340
Crystal colour	metallic pinkish pink	metallic light blue
Crystal shape	block	cube
Radiation	Cu K_α (λ=1.54184 Å)	Cu K_α (λ=1.54184 Å)
2θ range [°]	7.58 to 134.14 (0.84 Å)	7.26 to 152.49 (0.79 Å)
Index ranges	$-12 \le h \le 11$ $-18 \le k \le 17$ $-21 \le l \le 19$	$-13 \le h \le 13$ $-18 \le k \le 18$ $-25 \le l \le 20$
Reflections collected	19027	23283
Independent reflections	5204 $R_{int} = 0.0504$ $R_{sigma} = 0.0417$	6731 $R_{int} = 0.0487$ $R_{sigma} = 0.0444$
Completeness to θ = 67.684°	99.8 %	99.8 %
Data / Restraints / Parameters	5204/0/359	6731/0/389
Goodness-of-fit on F^2	1.031	1.045
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0454$ $wR_2 = 0.1189$	$R_1 = 0.0454$ $wR_2 = 0.1184$
Final R indexes [all data]	$R_1 = 0.0484$ $wR_2 = 0.1211$	$R_1 = 0.0521$ $wR_2 = 0.1223$
Largest peak/hole [$eÅ^{-3}$]	0.38/-0.27	0.47/-0.46

Table S12. X-Ray Crystallographic Data and Structure Refinement for 1c and 1d

	1c	**1d**
CCDC number	2350473	2216825
Empirical formula	$C_{29}H_{43}BClN_6OTi$	$C_{23}H_{39}BClN_6O_2Ti$
Formula weight	585.85	525.76
Temperature [K]	100.00(10)	99.99(10)
Crystal system	monoclinic	monoclinic
Space group (number)	$P2_1/n$ (14)	$C2/c$ (15)
a [Å]	8.73430(10)	21.0483(12)
b [Å]	21.1361(2)	15.4954(6)
c [Å]	16.41490(10)	22.6723(12)
α [°]	90	90
β [°]	91.3540(10)	120.388(7)
γ [°]	90	90
Volume [Å^3]	3029.49(5)	6378.7(7)
Z	4	8
ρ_{calc} [gcm^{-3}]	1.284	1.095
μ [mm^{-1}]	3.454	3.251
F(000)	1244	2232
Crystal colour	metallic pinkish violet	metallic pinkish pink
Crystal shape	cube	block
Radiation	Cu K_α (λ=1.54184 Å)	Cu K_α (λ=1.54184 Å)
2θ range [°]	6.82 to 152.96 (0.79 Å)	7.38 to 134.15 (0.84 Å)
Index ranges	$-10 \leq h \leq 10$ $-26 \leq k \leq 18$ $-20 \leq l \leq 19$	$-24 \leq h \leq 25$ $-18 \leq k \leq 16$ $-27 \leq l \leq 23$
Reflections collected	20387	19537
Independent reflections	6078 R_{int} = 0.0305 R_{sigma} = 0.0268	5635 R_{int} = 0.0370 R_{sigma} = 0.0324
Completeness to θ = 25.242°	99.9 %	98.8 %
Data / Restraints / Parameters	6078/0/365	5635/0/316
Goodness-of-fit on F^2	1.034	1.034
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0338 wR_2 = 0.0864	R_1 = 0.0770 wR_2 = 0.1928
Final R indexes [all data]	R_1 = 0.0361 wR_2 = 0.0874	R_1 = 0.0823 wR_2 = 0.1967
Largest peak/hole [eÅ^{-3}]	0.33/-0.37	1.05/-0.77

Table S13. X-Ray Crystallographic Data and Structure Refinement for 2a-2c

	2a	**2b**	**2c**
CCDC number	2310979	2311060	2350469
Empirical formula	$C_{54}H_{78}B_2N_{14}O_4Ti_2$	$C_{62}H_{94}B_2N_{14}O_4Ti_2$	$C_{58}H_{86}B_2N_{14}O_2Ti_2$
Formula weight	1104.72	1216.93	1128.82
Temperature [K]	100.00(10)	100.00(10)	100.00(10)
Crystal system	triclinic	monoclinic	monoclinic
Space group (number)	$P\bar{1}$ (2)	$P2_1/n$ (14)	$P2_1/n$ (14)
a [Å]	14.5243(3)	22.5766(2)	15.2132(2)
b [Å]	15.2715(3)	14.95160(10)	17.9147(3)
c [Å]	20.3140(3)	23.4386(2)	26.8010(5)
α [°]	102.8615(15)	90	90
β [°]	110.4311(18)	105.6860(10)	91.589(2)
γ [°]	101.9723(18)	90	90
Volume [Å^3]	3910.76(14)	7617.19(11)	7301.5(2)
Z	2	4	4
ρ_{calc} [gcm^{-3}]	0.938	1.061	1.027
μ [mm^{-1}]	2.067	2.161	2.201
F(000)	1172	2600	2408
Crystal colour	green	metallic green	reddish brown
Crystal shape	cube	block	cube
Radiation	Cu K_α (λ=1.54184 Å)	Cu K_α (λ=1.54184 Å)	Cu K_α (λ=1.54184 Å)
2θ range [°]	6.56 to 153.01 (0.79 Å)	6.36 to 152.78 (0.79 Å)	6.60 to 152.54 (0.79 Å)
Index ranges	$-17 \le h \le 18$ $-19 \le k \le 19$ $-25 \le l \le 18$	$-28 \le h \le 23$ $-18 \le k \le 18$ $-29 \le l \le 29$	$-13 \le h \le 18$ $-18 \le k \le 22$ $-33 \le l$ ≤ 33
Reflections collected	50770	54230	55802
Independent reflections	15687 R_{int} = 0.0600 R_{sigma} = 0.0557	15364 R_{int} = 0.0398 R_{sigma} = 0.0367	14393 R_{int} = 0.0513 R_{sigma} = 0.0526
Completeness to θ = 67.684°	99.2 %	99.7 %	98.7 %
Data / Restraints / Parameters	15687/0/701	15364/799/777	14393/0/727
Goodness-of-fit on F^2	1.058	1.077	1.091
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0522 wR_2 = 0.1388	R_1 = 0.0712 wR_2 = 0.1957	R_1 = 0.0549 wR_2 = 0.1269
Final R indexes [all data]	R_1 = 0.0566 wR_2 = 0.1423	R_1 = 0.0754 wR_2 = 0.2001	R_1 = 0.0756 wR_2 = 0.1381
Largest peak/hole [eÅ^{-3}]	0.47/-0.42	1.72/-1.81	0.39/-0.52

Table S14. X-Ray Crystallographic Data and Structure Refinement for 2d and 2e

	2d	**2e**
CCDC number	2311244	2312824
Empirical formula	$C_{46}H_{78}B_2N_{14}O_4Ti_2$	$C_{38}H_{60}B_2Cl_2N_{14}O_2Ti_2$
Formula weight	1008.64	933.32
Temperature [K]	99.99(10)	100.00(10)
Crystal system	tetragonal	monoclinic
Space group (number)	$P4_32_12$ (96)	$P2_1/n$ (14)
a [Å]	14.99430(10)	10.41370(10)
b [Å]	14.99430(10)	31.9745(3)
c [Å]	29.2000(4)	16.9735(2)
α [°]	90	90
β [°]	90	93.2710(10)
γ [°]	90	90
Volume [Å^3]	6565.01(13)	5642.51(10)
Z	4	4
ρ_{calc} [gcm^{-3}]	1.020	1.099
μ [mm^{-1}]	2.419	3.605
F(000)	2152	1960
Crystal colour	metallic green	metallic light green
Crystal shape	cube	block
Radiation	Cu K_α (λ=1.54184 Å)	Cu K_α (λ=1.54184 Å)
2θ range [°]	8.34 to 151.18 (0.80 Å)	8.94 to 153.00 (0.79 Å)
Index ranges	$-18 \le h \le 12$ $-18 \le k \le 17$ $-23 \le l \le 36$	$-13 \le h \le 12$ $-40 \le k \le 34$ $-21 \le l \le 20$
Reflections collected	21917	42312
Independent reflections	6491 R_{int} = 0.0423 R_{sigma} = 0.0394	11273 R_{int} = 0.0483 R_{sigma} = 0.0404
Completeness to θ = 67.684°	99.9 %	99.5 %
Data / Restraints / Parameters	6491/0/316	11273/0/553
Goodness-of-fit on F^2	1.031	1.070
Final R indexes [I≥2σ(I)]	R_1 = 0.0419 wR_2 = 0.1025	R_1 = 0.0446 wR_2 = 0.1150
Final R indexes [all data]	R_1 = 0.0442 wR_2 = 0.1041	R_1 = 0.0508 wR_2 = 0.1188
Largest peak/hole [eÅ^{-3}]	0.32/-0.28	0.91/-0.78
Flack X parameter	0.009(3)	---

Table S15. X-Ray Crystallographic Data and Structure Refinement for 3a

	3a
CCDC number	2334087
Empirical formula	$C_{30}H_{48}BN_7O_2SiTi$
Formula weight	625.55
Temperature [K]	100.01(11)
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	11.3501(2)
b [Å]	11.8716(2)
c [Å]	13.3789(2)
α [°]	85.0700(10)
β [°]	72.758(2)
γ [°]	80.766(2)
Volume [Å^3]	1697.99(5)
Z	2
ρ_{calc} [gcm^{-3}]	1.224
μ [mm^{-1}]	2.763
F(000)	668
Crystal colour	metallic light yellow
Crystal shape	block
Radiation	Cu K_α (λ=1.54184 Å)
2θ range [°]	6.92 to 153.40 (0.79 Å)
Index ranges	$-14 \le h \le 12$ $-14 \le k \le 14$ $-16 \le l \le 16$
Reflections collected	19951
Independent reflections	6727 $R_{int} = 0.0290$ $R_{sigma} = 0.0300$
Completeness to θ = 67.684°	99.3 %
Data / Restraints / Parameters	6727/18/390
Goodness-of-fit on F^2	1.098
Final *R* indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0515$ $wR_2 = 0.1391$
Final *R* indexes [all data]	$R_1 = 0.0564$ $wR_2 = 0.1423$
Largest peak/hole [eÅ^{-3}]	1.62/-1.09

Table S16. X-Ray Crystallographic Data and Structure Refinement for 4b

	4a
CCDC number	2331239
Empirical formula	$C_{29}H_{49}BN_7OSi_2Ti$
Formula weight	626.64
Temperature [K]	122(20)
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	11.9183(5)
b [Å]	12.1325(4)
c [Å]	14.2731(6)
α [°]	79.695(3)
β [°]	71.091(4)
γ [°]	65.428(4)
Volume [Å^3]	1773.34(14)
Z	2
ρ_{calc} [gcm^{-3}]	1.174
μ [mm^{-1}]	2.936
F(000)	670
Crystal colour	metallic orangish orange
Crystal shape	block
Radiation	Cu K_α (λ=1.54184 Å)
2θ range [°]	6.55 to 134.16 (0.84 Å)
Index ranges	$-14 \leq h \leq 14$ $-14 \leq k \leq 14$ $-17 \leq l \leq 16$
Reflections collected	20579
Independent reflections	6329 R_{int} = 0.0309 R_{sigma} = 0.0291
Completeness to θ = 67.079°	99.6 %
Data / Restraints / Parameters	6329/0/384
Goodness-of-fit on F^2	1.071
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0387 wR_2 = 0.1077
Final R indexes [all data]	R_1 = 0.0412 wR_2 = 0.1095
Largest peak/hole [eÅ^{-3}]	0.37/-0.41
Flack X parameter	---

8. Computational Details.

The structure of **2a** was optimized using the B3LYP/def2-SVP method for geometry optimization in the Gaussian16 package[9-11].

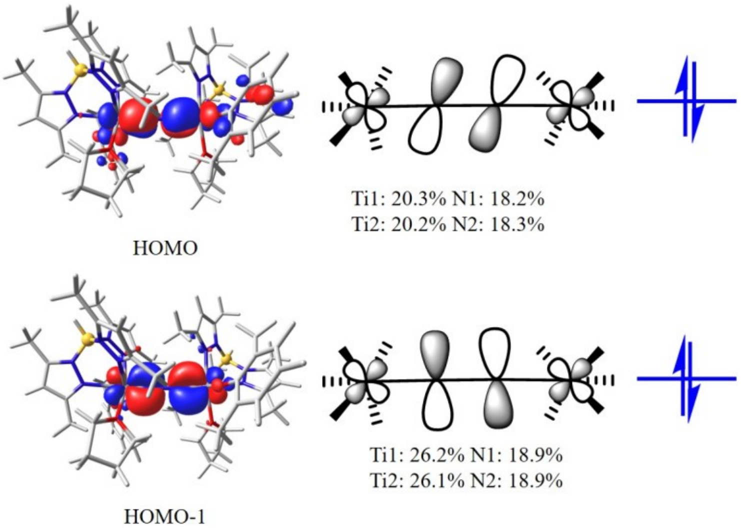


Figure S29. Frontier molecular orbitals of **2a** (Isovalue = 0.03).

Table S17. Gibbs Free Energy of 2a.

Molecule	Spin state	E [Ha]	G-E [Ha]	G [Ha]
2a	0	-4918.81286043	1.158896	-4917.653964

Table S18. Cartesian Coordinates of 2a.

Ti	**7.956829398**	**2.612047239**	**2.336177095**
Ti	8.948710714	6.868033926	0.401886992
O	8.719180558	2.967265330	4.426139710
O	9.446856691	1.557860742	1.746522787
O	11.111870677	7.038888749	0.972241617
O	8.254068523	8.070536994	1.727815604
N	6.559876551	2.082675877	0.726811833
N	8.391267356	4.196023920	1.689611345

N	9.880048067	5.994321753	-1.504290250
N	9.576732187	6.528887614	-2.720473212
N	5.985121900	3.278898781	3.292706042
N	7.223748619	7.239472010	-2.191787902
N	7.220886881	0.534233903	3.264815506
N	7.177812911	6.806990949	-0.898852104
N	5.381442316	1.444653408	0.981522756
N	5.922083502	0.168285357	3.105590607
N	9.107394196	8.938263114	-2.118828801
N	9.396422448	8.880139238	-0.792112248
N	8.657178977	5.309825478	1.180257753
N	4.888748308	2.471585112	3.225676192
C	6.654114393	2.244021210	-0.604388804
C	5.612807393	4.396564835	3.942543742
C	10.410089780	0.799988818	1.238835781
C	10.107786851	-0.295639783	0.378275024
C	7.852501892	-0.497601281	3.846790934
C	6.574013574	9.729290654	2.145818137
C	11.770698575	1.061730617	1.570911983
C	7.819144040	2.900038272	-1.271402735
H	7.743905301	2.784326041	-2.361768334
H	8.767852324	2.457985040	-0.936458074

H	7.864039861	3.973431696	-1.039326411
C	4.724667906	1.201830389	-0.179520532
C	5.512221064	1.696827455	-1.215645021
H	5.289239673	1.666338998	-2.279556098
C	5.912591015	6.433062504	-0.641373145
C	5.715719562	-1.086613627	3.581720774
C	7.644616514	8.890703203	2.574670592
C	5.131158067	6.630956644	-1.793469609
H	4.068818864	6.428545553	-1.907594583
C	10.710139577	4.958613395	-1.724854418
C	5.464306869	5.911027084	0.684964052
H	5.914063503	4.932934487	0.906305745
H	4.370895161	5.800302672	0.696592531
H	5.756189556	6.591653221	1.497008189
C	5.996049040	7.140129776	-2.758582589
C	3.828187438	3.060926592	3.832562305
C	9.803209837	10.104615439	-0.423185998
C	9.315769221	-0.496568957	4.166659784
H	9.501268231	-1.001784826	5.127650145
H	9.713544456	0.523393858	4.209231962
H	9.888182685	-1.033847051	3.393749792
C	8.073669089	8.961172573	3.931690930

C	9.330708900	10.187291341	-2.603211794
C	4.257433595	4.294917665	4.309236000
H	3.663595221	5.035266699	4.840509664
C	9.749239843	3.915779735	4.752627044
H	9.287388387	4.904334240	4.907175784
H	10.428344066	3.973231461	3.896983179
C	12.104804368	2.178033379	2.523301309
H	11.623923327	3.119801731	2.218298629
H	13.191854719	2.341309003	2.578320523
H	11.748658818	1.957478794	3.544578495
C	5.692076716	7.523714912	-4.173267303
H	5.926286545	8.581183726	-4.373225552
H	4.622682237	7.369577274	-4.374408581
H	6.264058266	6.921122363	-4.896620587
C	5.954102800	10.573111457	3.076922927
H	5.133902290	11.212218135	2.734661830
C	10.207924068	5.848174956	-3.709390453
C	6.934577542	-1.544274211	4.071216286
H	7.134414080	-2.511520648	4.527219614
C	8.112065343	2.584544632	5.675902731
H	7.565710524	1.650808879	5.509115164
H	7.394959261	3.366714793	5.975345033

C	6.524954610	5.551018171	4.208104513
H	5.960139337	6.494025205	4.202952951
H	7.314189667	5.617329954	3.450511047
H	6.998591743	5.474571426	5.201875123
C	11.637573136	6.400999760	2.159401614
H	11.646042883	5.312089298	1.999426701
H	10.965548299	6.631146143	2.992192013
C	10.948973886	4.836761004	-3.106721723
H	11.571046878	4.095053773	-3.602595308
C	11.158480239	-1.062720448	-0.142229721
H	10.913576055	-1.901619511	-0.801465990
C	10.177141721	10.466247657	0.981947537
H	9.347804765	10.987331510	1.486474032
H	11.046084790	11.143263218	0.989597736
H	10.403270537	9.575497352	1.578713924
C	12.191827302	7.608389834	0.182712422
H	12.095642193	8.702786065	0.207064694
H	12.078369159	7.269654639	-0.854774793
C	7.420511643	9.819814943	4.823919216
H	7.760073147	9.855324112	5.864130973
C	6.357444557	10.624781064	4.412400549
H	5.856752443	11.290704594	5.119538133

C	10.385076471	3.380730962	6.043636468
H	10.687339764	4.204080400	6.707457365
H	11.285646559	2.790532999	5.819516145
C	11.273432142	4.096556340	-0.641206893
H	11.481456852	3.087659690	-1.024360914
H	10.577213321	4.009741997	0.201255559
H	12.229302311	4.495710416	-0.262736205
C	9.281626017	2.484271581	6.665728458
H	9.628960130	1.445098129	6.754430048
H	8.980367208	2.818764552	7.669310677
C	6.112961969	9.725717120	0.710489022
H	6.960034936	9.675844017	0.013014946
H	5.528445956	10.631832457	0.489565095
H	5.470958468	8.859020197	0.484041950
C	4.392959196	-1.787194138	3.553008151
H	3.620064354	-1.235539832	4.111489611
H	4.492529150	-2.783613186	4.005987998
H	4.018735719	-1.918945700	2.525250972
C	9.240489418	8.129580052	4.392681876
H	10.191866819	8.498364576	3.968956566
H	9.134418431	7.082276891	4.072844469
H	9.337597200	8.155139472	5.488778512

C	8.680652539	-0.639357599	0.035175506
H	8.023990193	-0.566179026	0.912995445
H	8.614675407	-1.661189188	-0.368497001
H	8.262275427	0.040674118	-0.724518707
C	12.784848304	0.266720027	1.023996310
H	13.824969100	0.486306962	1.285788455
C	2.466756185	2.445470644	3.926418208
H	1.801628951	3.108005460	4.497859294
H	2.490010995	1.467404834	4.432238965
H	2.016676149	2.286976427	2.933523423
C	9.784391024	10.963061113	-1.541896327
H	10.060411994	12.014915780	-1.572150962
C	3.393847679	0.521627383	-0.263818646
H	2.608826010	1.083218172	0.267068401
H	3.419578319	-0.490618958	0.169543831
H	3.092929523	0.431693287	-1.316992392
C	10.078020684	6.171149347	-5.165377800
H	10.387872167	7.204220497	-5.388587902
H	9.041550099	6.058955726	-5.521201361
H	10.712666716	5.491775613	-5.751522636
C	12.493786053	-0.792248601	0.162683677
H	13.295327710	-1.405247251	-0.256773512

C	9.106177459	10.586345756	-4.028595911
H	9.715054358	9.989754501	-4.726407524
H	9.374564094	11.643643435	-4.163023072
H	8.053655023	10.463717660	-4.330041323
B	8.559405489	7.688496262	-2.839129949
H	8.373321209	7.943790576	-4.002182468
B	4.931640956	1.142227356	2.434321699
H	3.832273257	0.648676802	2.416226055
C	13.046153384	6.961867741	2.317138186
H	13.018702684	7.935448732	2.834036825
H	13.701332339	6.290287995	2.891590386
C	13.480145880	7.137164743	0.856627887
H	13.812346053	6.173839948	0.437740345
H	14.299790638	7.859263613	0.727101881

9. Reference

1. Thomas, J. R.; Sulway, S. A., In situ tracking and characterisation of scorpionate ligands via^{11}B-NMR spectroscopy. *RSC Adv.* **2021,** *11* (27), 16158-16160.

2. Weatherburn, M. W., Phenol-hypochlorite Reaction for Determination of Ammonia. *Anal. Chem.* **1967,** *39*, 971.

3. Watt, G. W.; Chrisp, J. D., A Spectrophotometric Method for Determination of Hydrazine. *Anal. Chem.* **1952,** *24* (12), 2006-2008.

4. Sheldrick, G., A Short History of SHELX. *Acta Crystallographica Section A* **2008,** *64* (1), 112-122.

5. Sheldrick, G., Crystal Structure Refinement with SHELXL. *Acta Crystallographica Section C* **2015,** *71* (1), 3-8.

6. Lubben, J.; Wandtke, C. M.; Hubschle, C. B.; Ruf, M.; Sheldrick, G. M.; Dittrich, B., Aspherical Scattering Factors for SHELXL – Model, Implementation and Application. *Acta Crystallographica Section A* **2019,** *75* (1), 50-62.

7. Farrugia, L., WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **2012,** *45* (4), 849-854.

8. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009,** *42* (2), 339-341.

9. Becke, A. D. *Phys. Rev. A.* 1988, **38**, 3098-3100.

10. Pritchard, B. P.; Altarawy, D.; Didier, B.; Gibson, T. D.; Windus, T. L. *J. Chem. Inf. Model.* 2019, **59**, 4814-4820.

11. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.;

Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J.. Gaussian 16, Revision C.01; Gaussian, Inc.: Wallingford, CT, 2016.