Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Formate Complexes of Titanium(IV) Supported by a Triamido-Amine Ligand

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Contents

General considerations

All experiments were performed using standard Schlenk and glovebox techniques under argon atmosphere. THF, *n*-pentane and diethyl ether were dried using an MBraun SPS-800 solvent purification system. THF was subsequently distilled from $LiAlH_4$. THF-d_8 and benzene-d_6 were distilled from sodium/benzophenone ketyl. Deuterated and non-deuterated 1,2-dichlorobenzene and chlorobenzene were distilled from CaH_2. Tris(2-aminoethyl)amine, Me_3SiCl, ^{n}BuLi in hexane solution, $[HNMe_2Ph][B(C_6F_5)_4]$, and NaOCHO were purchased from Sigma Aldrich and used without purification; the solids were heated at 60 °C under reduced pressure for 6 h. CS_2 was distilled from CaH_2. CO_2 was passed through a column packed with P_2O_5. [ClTi(*N$_3$N*)] (**1**),[1] [^{n}BuTi(*N$_3$N*)] (**2**),[1a] $[Ph_3C][B(3,5\text{-}Cl_2C_6H_3)_4]$,[2] and $[HNEt_3][OCHO]$[3] were prepared as reported. ^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H}, and ^{19}F NMR spectra were recorded on Bruker Avance III 400 or Bruker Avance III HD 400 spectrometers at 25 °C. NMR samples were prepared in J. Young NMR tubes sealed with Teflon screw caps. Chemical shifts for ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced internally to the residual solvent resonance and are reported in ppm relative to tetramethylsilane. If not otherwise stated, ^{13}C{^{1}H} NMR resonances are singlets. Intensity data for all structures were collected with a Bruker SMART APEX CCD detector on a D8 goniometer (Mo Kα radiation $\lambda = 0.71073$ Å, graphite monochromator). Elemental analyses were carried out using a CHN-O-Rapid VarioEL from Heraeus. The low carbon content in some samples is ascribed to metal carbide or silicide formation during combustion.[4] IR spectra were recorded on a Nicolet Avatar 360 E.S.P. spectrometer using KBr pellets.

Syntheses and spectra

1. [(OCHO)Ti(*N₃N*)] (3)

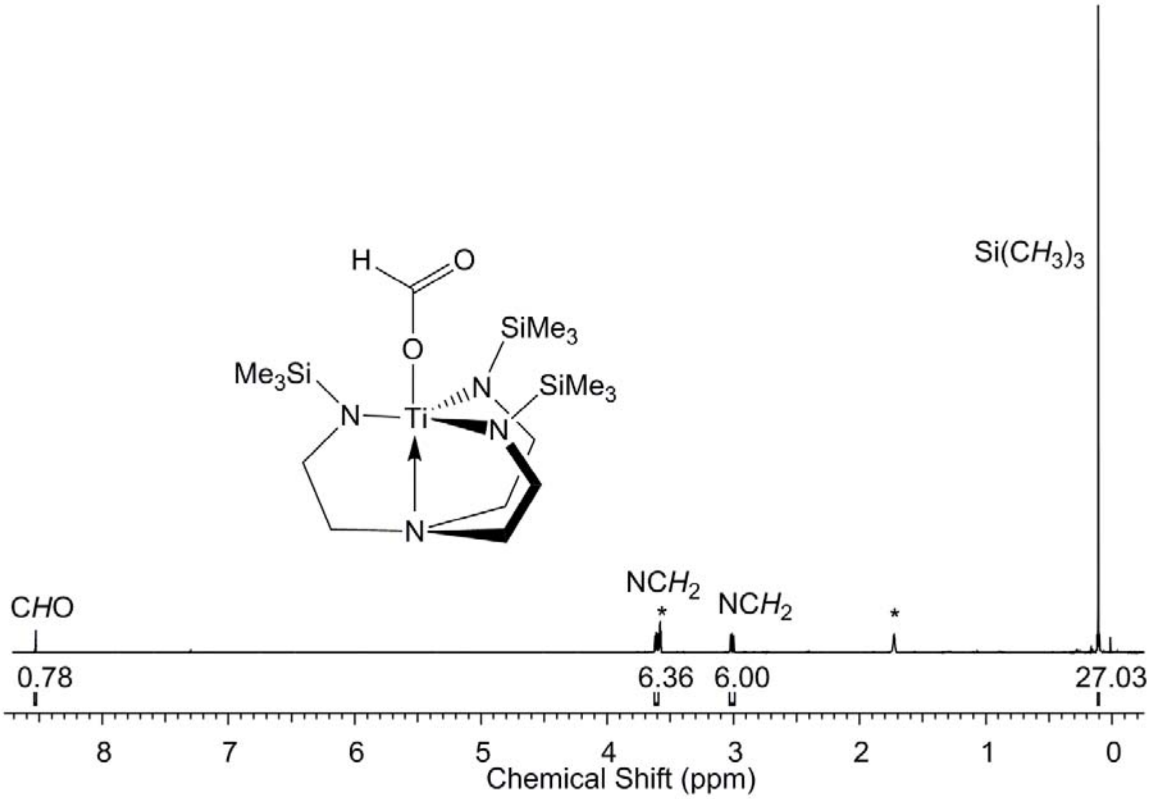

Figure S1. ^{1}H NMR spectrum of **3** in THF-d_8, $^*OC_4D_7H$.

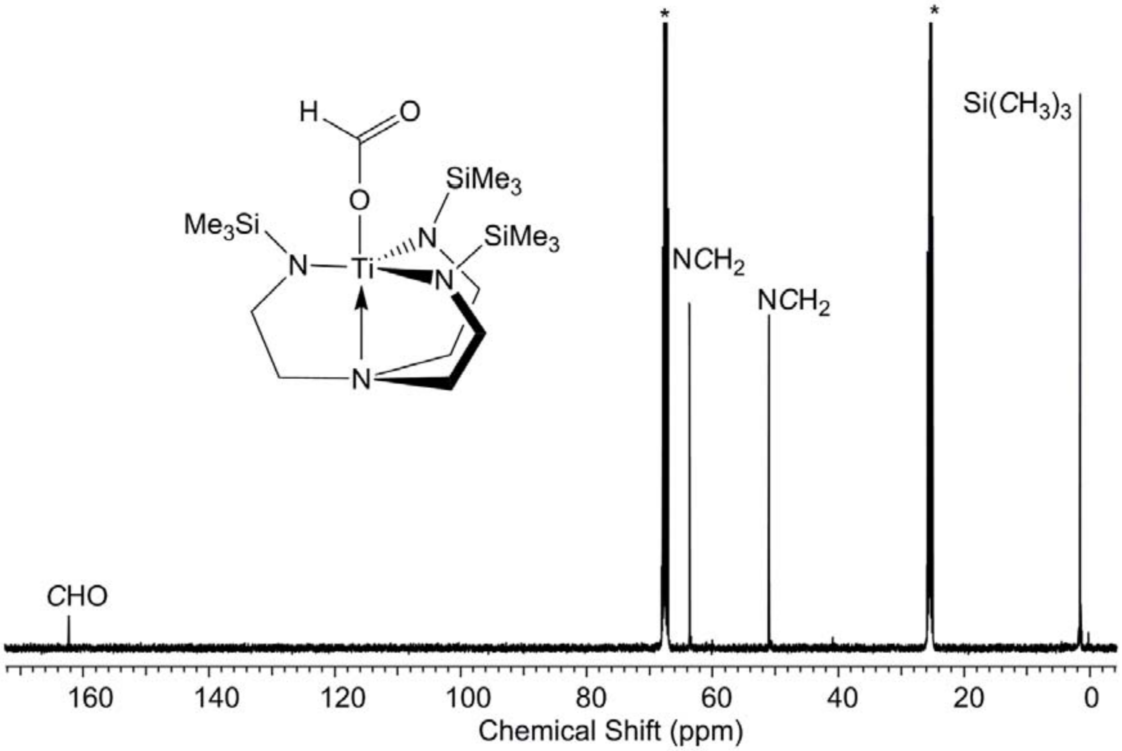

Figure S2. $^{13}C\{^1H\}$ NMR spectrum of **3** in THF-d_8, $^*OC_4D_8$.

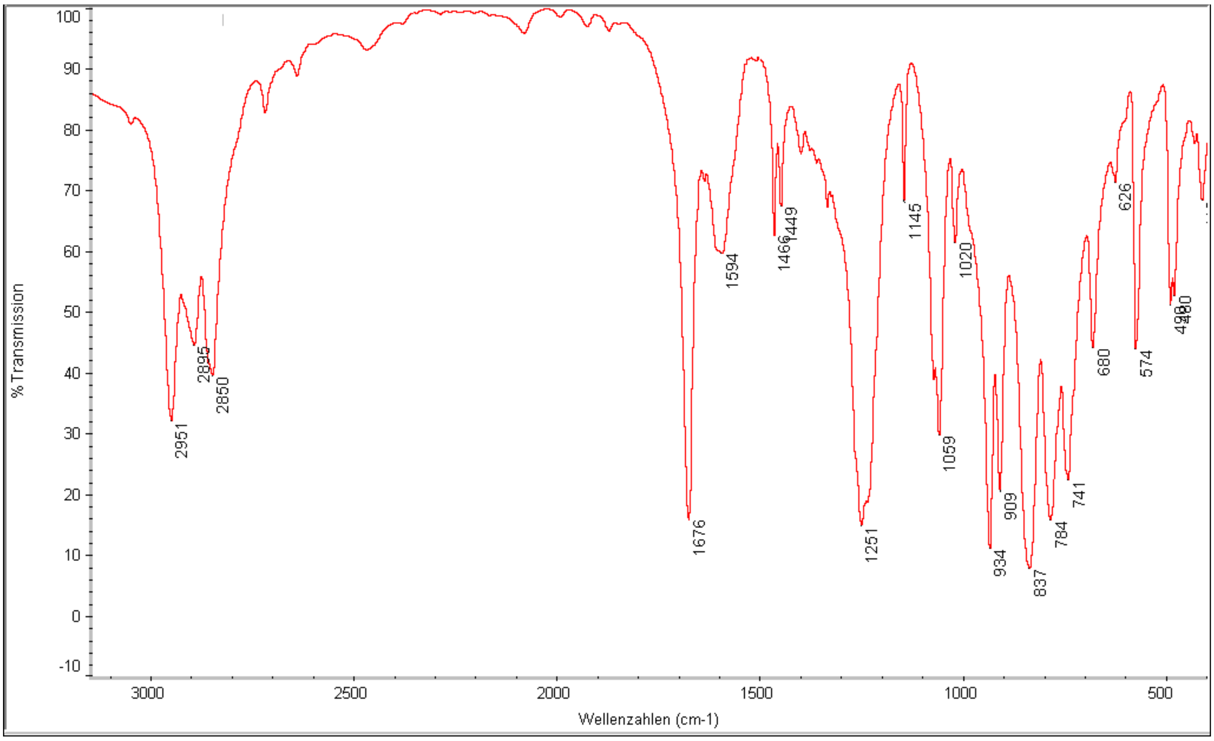

Figure S3. IR spectrum of **3** in a KBr pellet.

2. $\{K[OTi(N_3N)]\}_n$ (4)

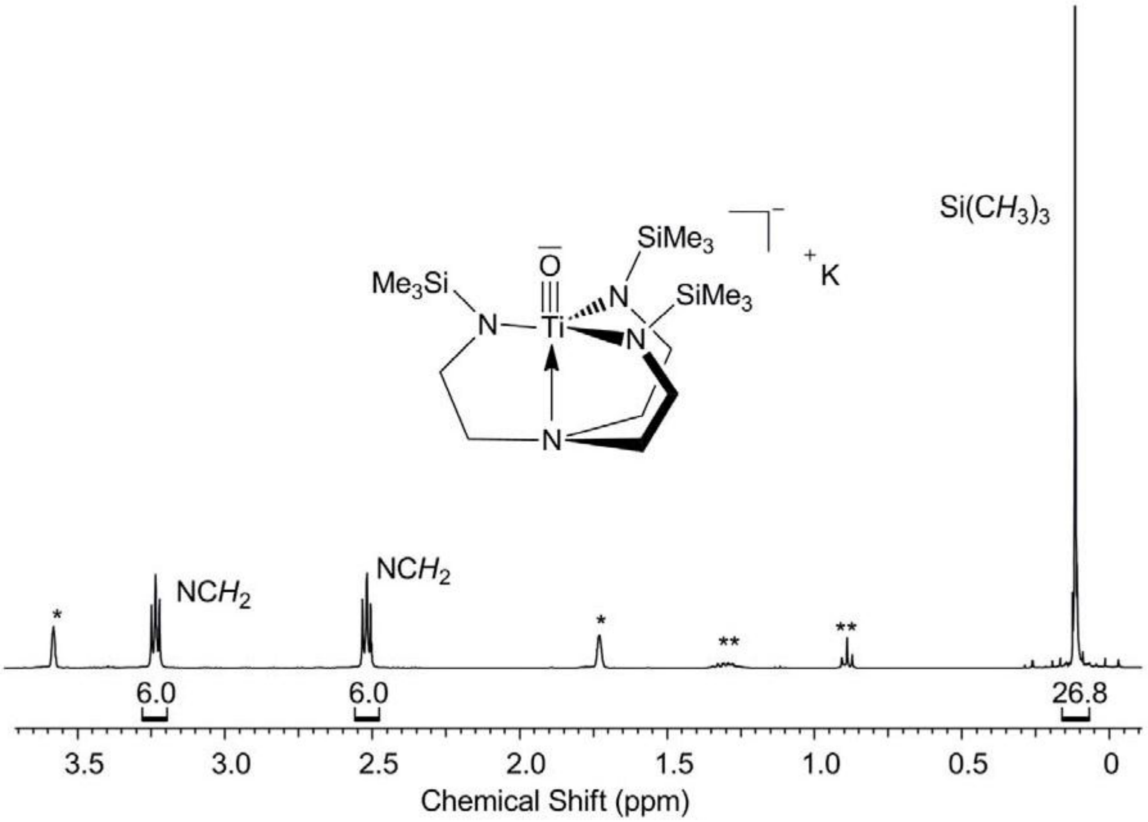

Figure S4. ^{1}H NMR spectrum of **4** in THF-d_8, *OC_4D_7H, **n-pentane.

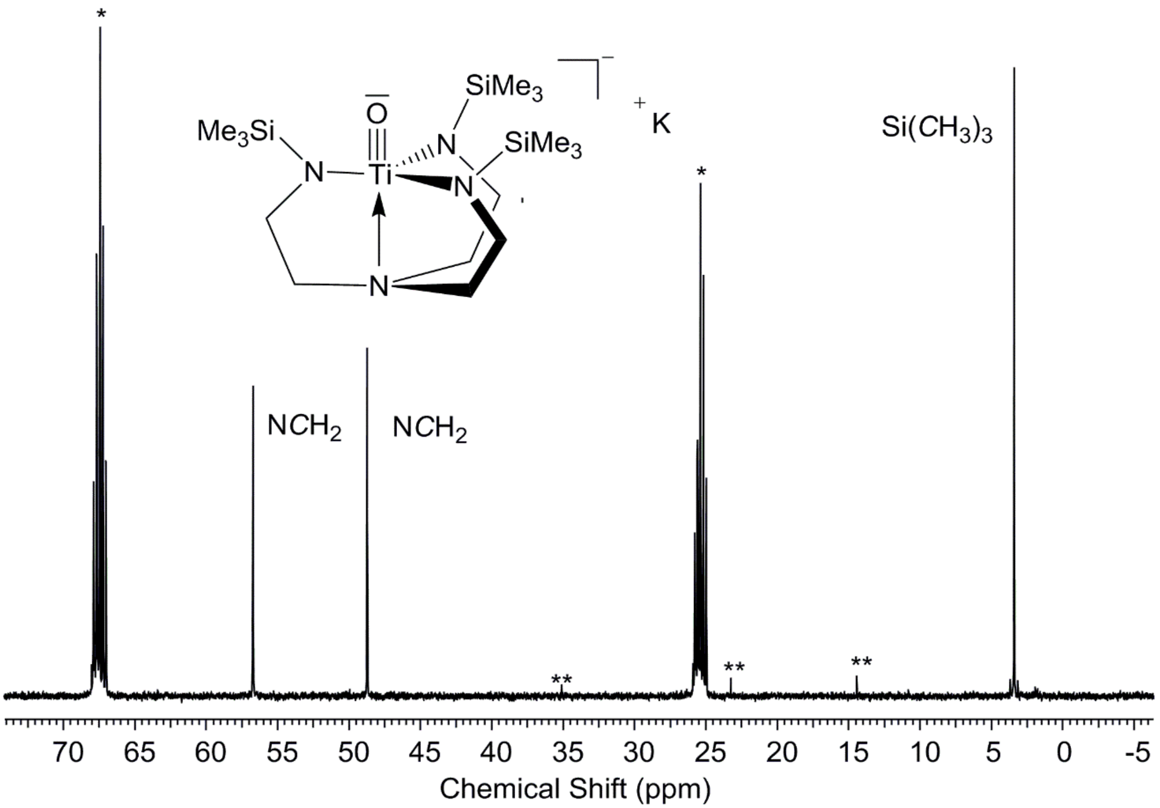

Figure S5. $^{13}C\{^1H\}$ NMR spectrum of **4** in THF-d_8, *OC_4D_8, **n-pentane.

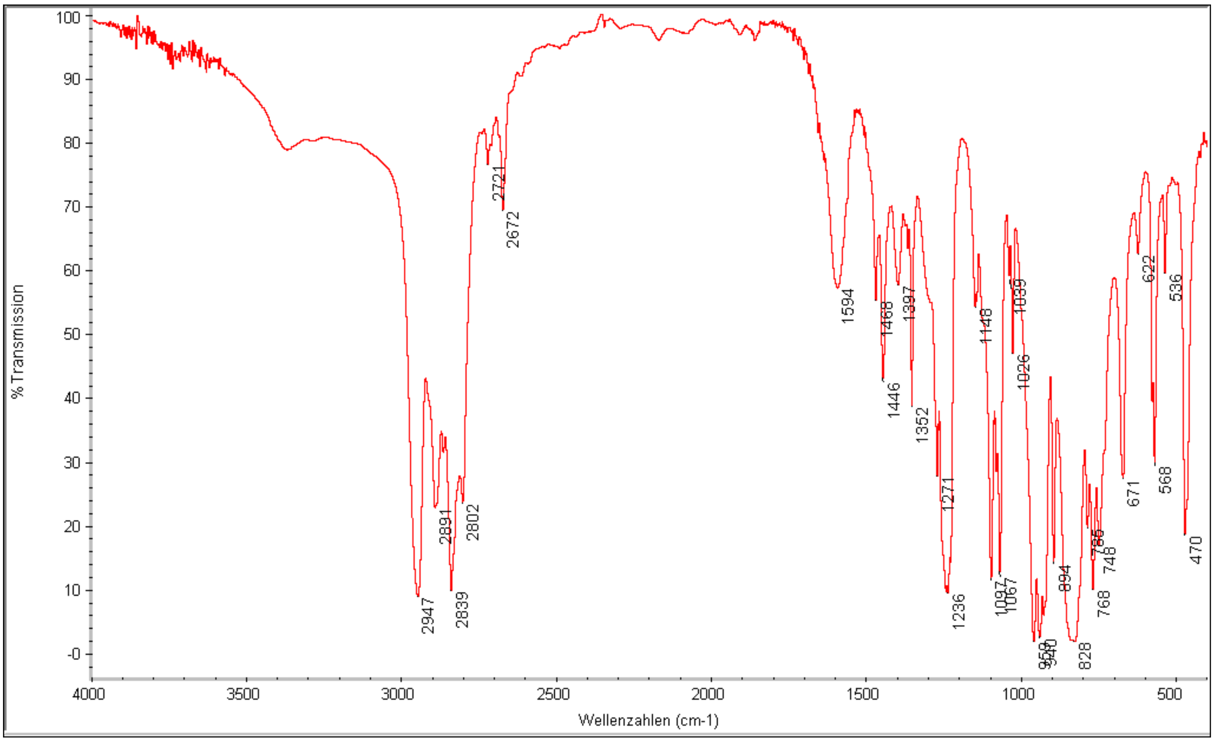

Figure S6. IR spectrum of **4** in a KBr pellet.

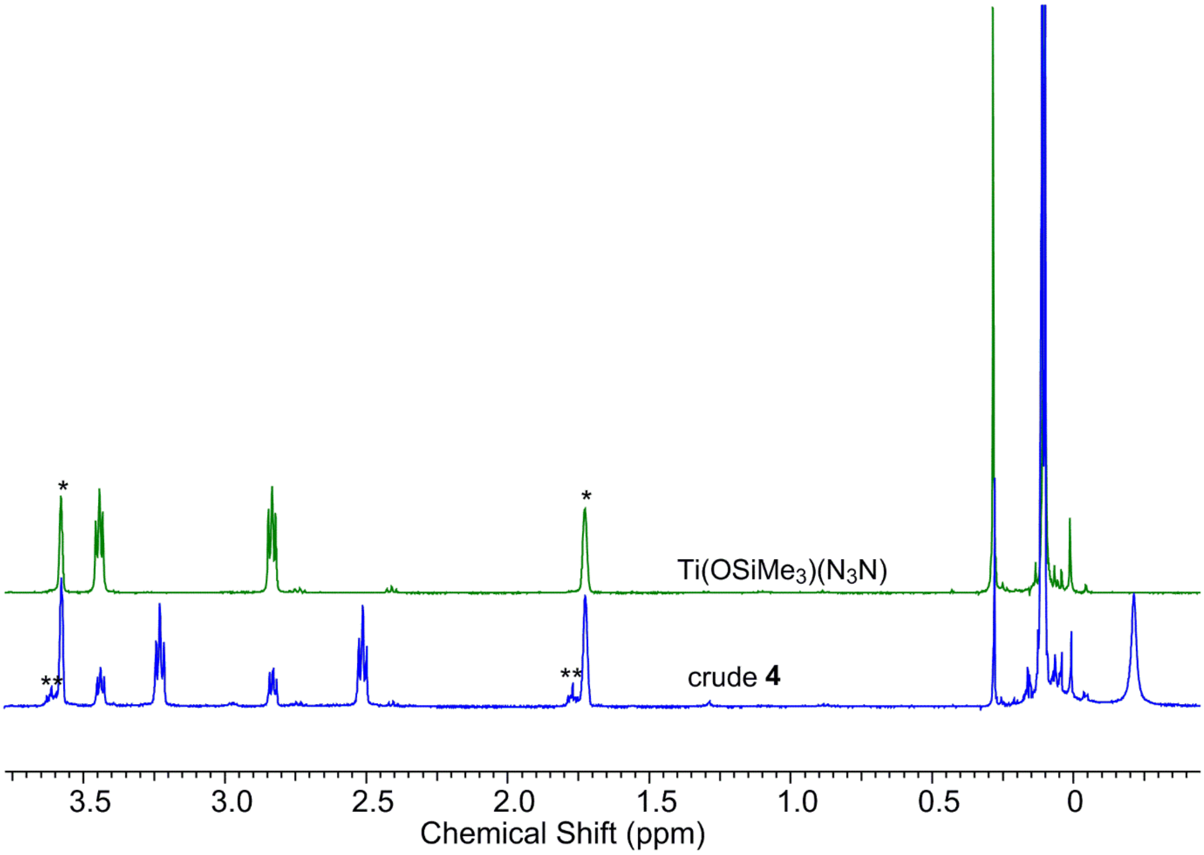

Figure S7. Comparison of the ^{1}H NMR spectra of crude **4** and [(Me$_3$SiO)Ti(*N$_3$N*)] (**5**) in THF-*d*$_8$, *OC$_4$D$_7$H, **THF.

3. [(Et$_2$O)Ti(*N$_3$N*)][B(3,5-Cl$_2$C$_6$H$_3$)$_4$] (6[B(3,5-Cl$_2$C$_6$H$_3$)$_4$]$\cdot$Et$_2$O)

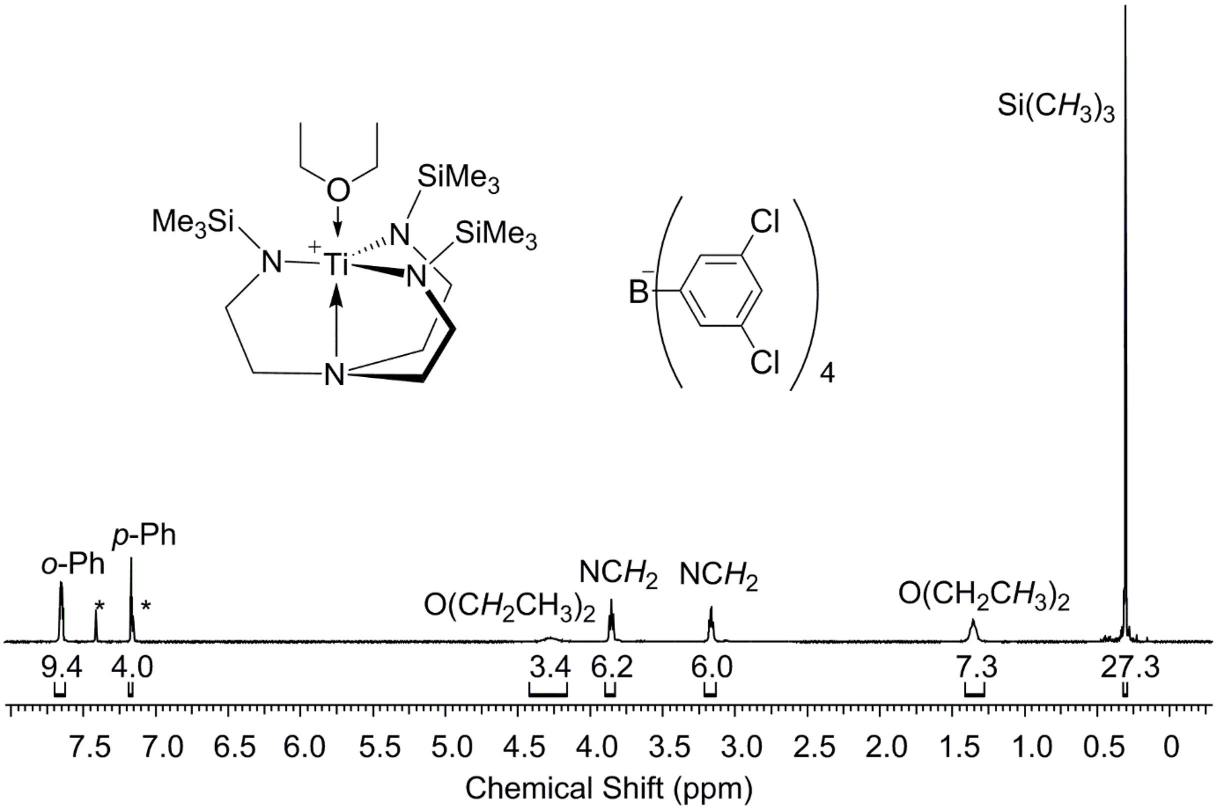

Figure S8. ^{1}H NMR spectrum of **6**[B(3,5-Cl$_2$C$_6$H$_3$)$_4$]$\cdot$Et$_2$O in 1,2-dichlorobenzene-*d*$_4$, *C$_6$Cl$_2$D$_3$H.

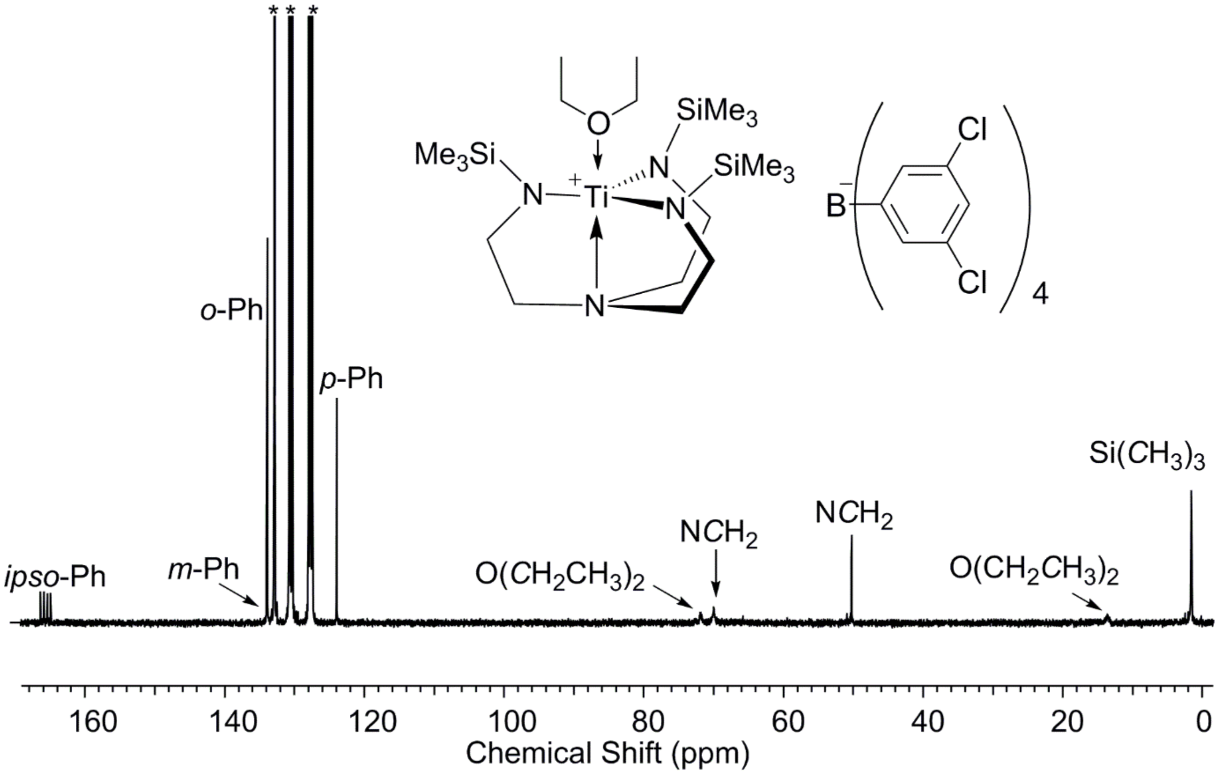

Figure S9. ^{13}C{^{1}H} NMR spectrum of **6**[B(3,5-Cl$_2$C$_6$H$_3$)$_4$]$\cdot$Et$_2$O in 1,2-dichlorobenzene-*d*$_4$, *C$_6$Cl$_2$D$_4$.

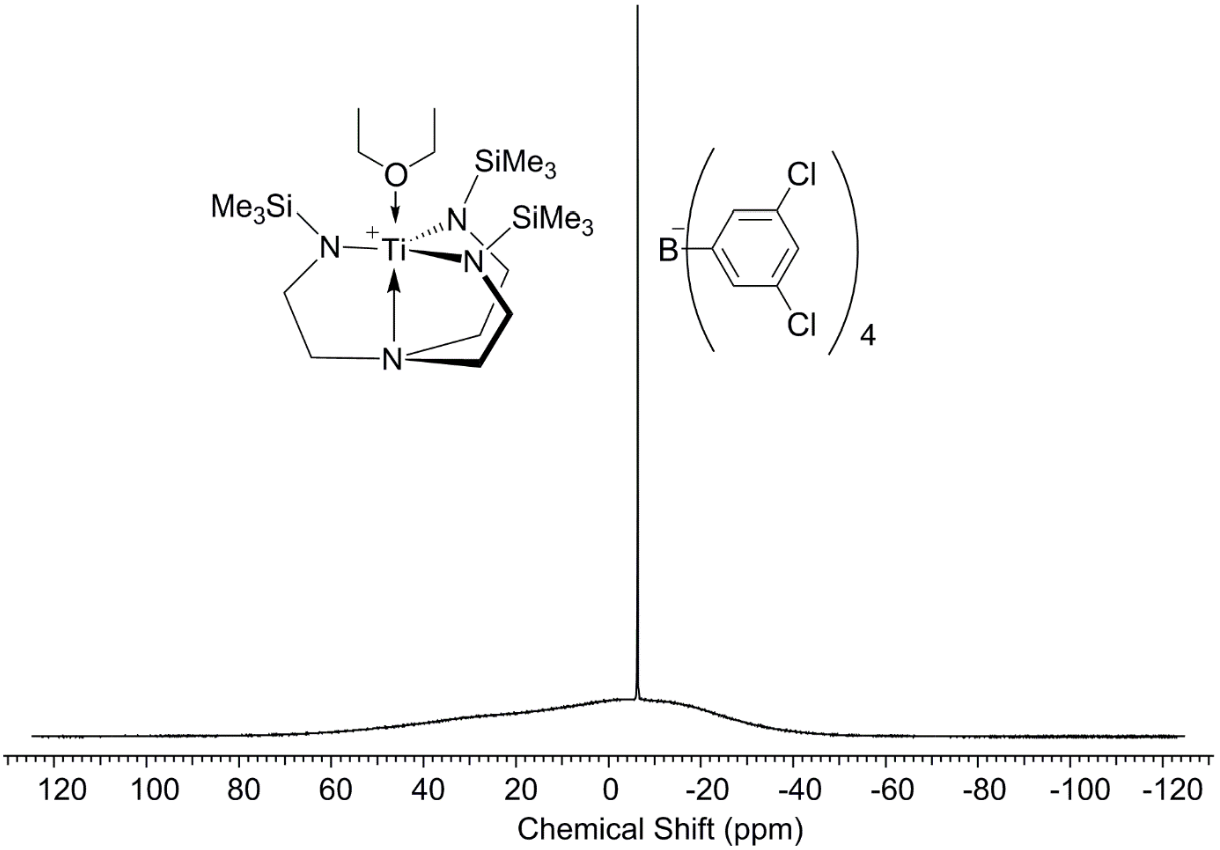

Figure S10. ^{11}B{^{1}H} NMR spectrum of **6**[B(3,5-Cl$_2$C$_6$H$_3$)$_4$]□Et$_2$O in 1,2-dichlorobenzene-*d*$_4$.

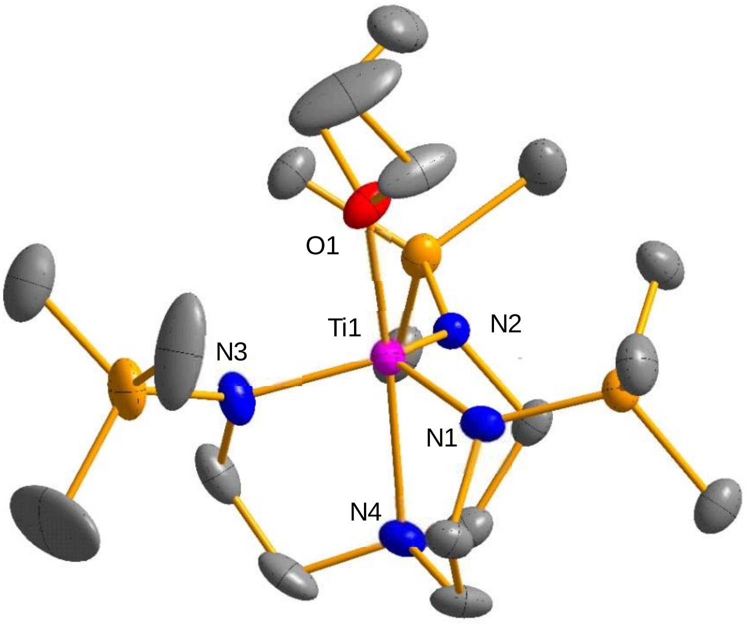

Figure S11. Molecular structure of the *Λ* enantiomer of **5** in solid state drawn at the 50% probability level. Hydrogen atoms, counter anions and the *Δ* enantiomer are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N$_{\text{amide,avg}}$ 1.908, Ti1–N4 2.330(6), Ti2–O1 2.103(5); O2-Ti2-N4 169.7(2).

4. $[(\mathrm{Et_2O})\mathrm{Ti}(N_3N)][\mathrm{B(C_6F_5)_4}]$ ($\mathbf{6}[\mathrm{B(C_6F_5)_4}]$□$\mathrm{Et_2O}$)

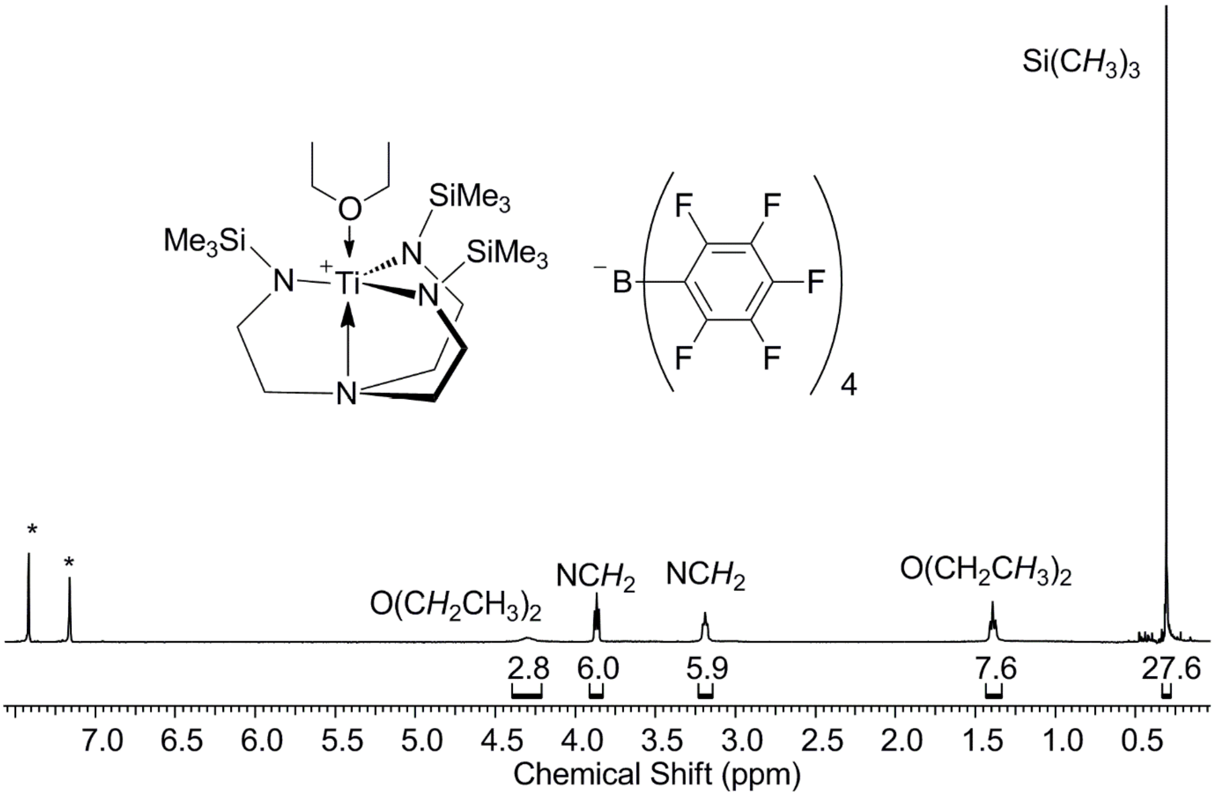

Figure S12. ^{1}H NMR spectrum of **6**[B(C$_6$F$_5$)$_4$]□Et$_2$O in 1,2-dichlorobenzene-*d*$_4$, *$\mathrm{C_6Cl_2D_3H}$.

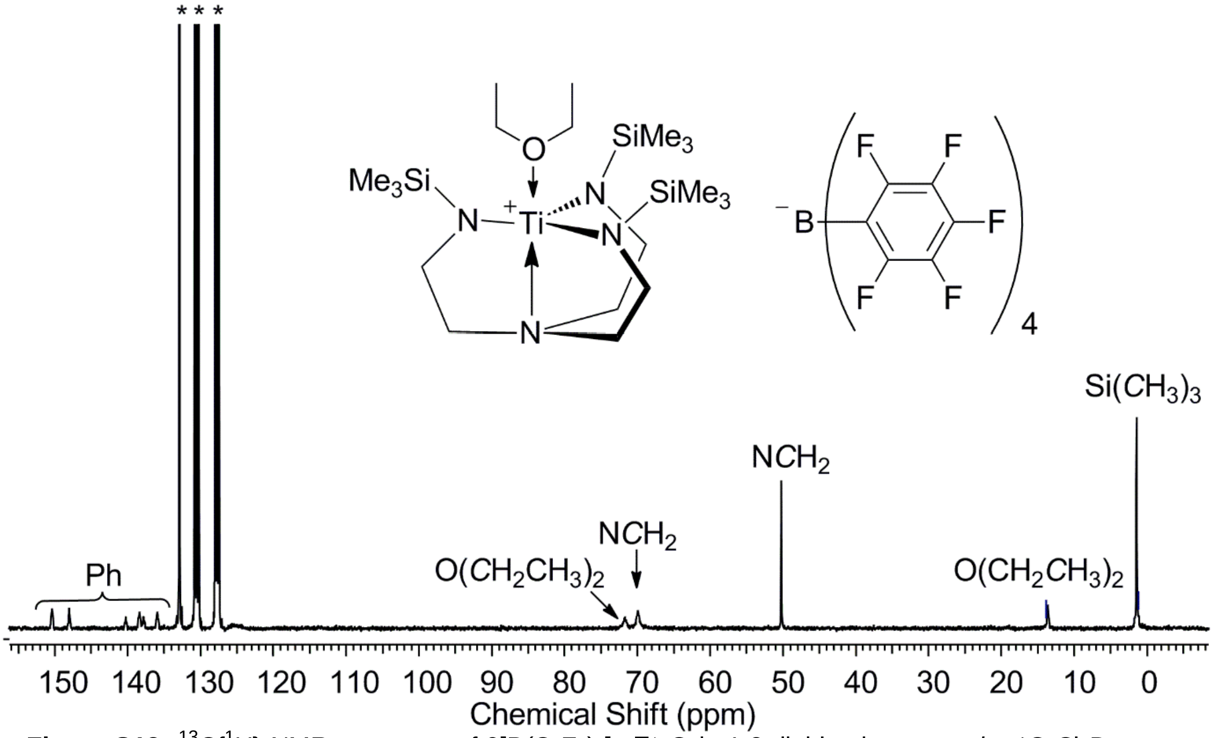

Figure S13. ^{13}C{^{1}H} NMR spectrum of **6**[B(C$_6$F$_5$)$_4$]□Et$_2$O in 1,2-dichlorobenzene-*d*$_4$, *$\mathrm{C_6Cl_2D_4}$.

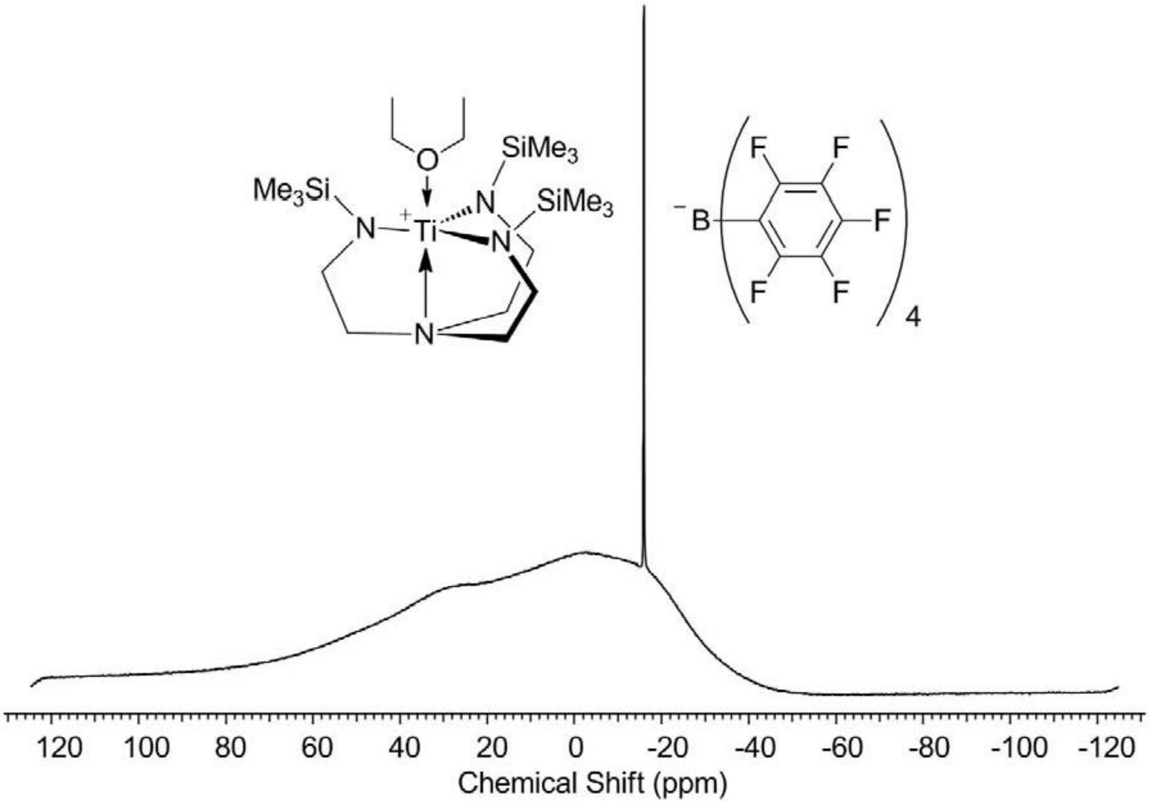

Figure S14. ^{11}B{^{1}H} NMR spectrum of **6**[B(C_6F_5)$_4$]·Et_2O in 1,2-dichlorobenzene-*d*$_4$.

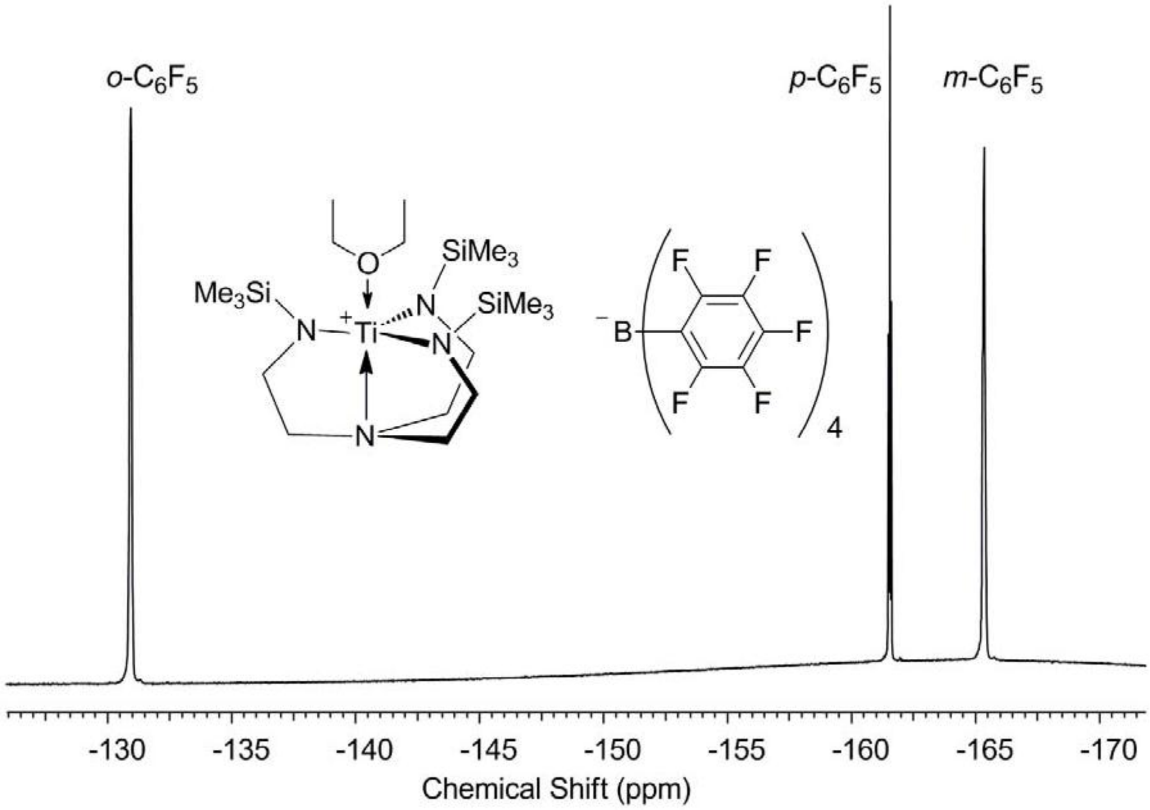

Figure S15. ^{19}F NMR spectrum of **6**[B(C_6F_5)$_4$]·Et_2O in 1,2-dichlorobenzene-*d*$_4$.

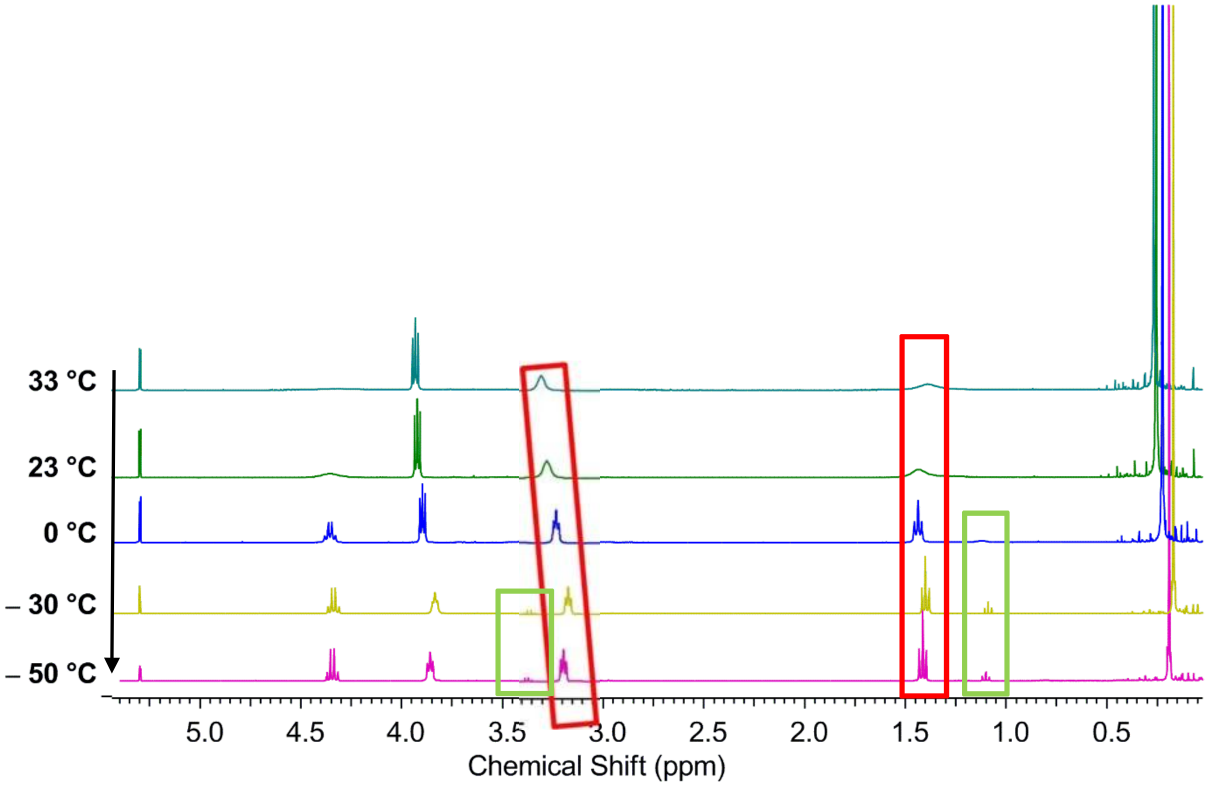

Figure S16. VT NMR of **6**[B(C_6F_5)$_4$]$\cdot$Et$_2$O in dichloromethane-*d*$_2$ from 0 to –50 °C. RED: bound Et$_2$O, GREEN: free Et$_2$O.

5. [(py)Ti(*N*$_3$*N*)][B(3,5-Cl$_2$C$_6$H$_3$)$_4$] (6[B(3,5-Cl$_2$C$_6$H$_3$)$_4$]·py)

Pyridine (8.2 µL, 102 µmol, 1.1 equiv.) was added to a solution of **6**[B(3,5-Cl$_2$C$_6$H$_3$)$_4$]·Et$_2$O (100 mg, 93 µmol) in chlorobenzene (5 mL). The reaction mixture was stirred for 1 h at room temperature. All volatiles were removed under reduced pressure and the residue was rinsed with *n*-pentane (3× 5 mL). The product was dried *in vacuo*, triturated with *n*-pentane (1 mL), and isolated as yellow powder (89 mg, 82 µmol, 88% based on **6**[B(3,5-Cl$_2$C$_6$H$_3$)$_4$]·Et$_2$O). Single crystals suitable for X-ray diffraction were grown at room temperature from a solution in 1,2-dichlorobenzene in an atmosphere of *n*-pentane. ^{1}H NMR (400 MHz, 1,2-dichlorobenzene-*d*$_4$): δ = 8.54 (d, 2H, $^3J_{HH}$ = 4.9 Hz, *o*-py), 7.75 (tt, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, *p*-py), 7.44 (m, 8H, *o*-Ph), 7.40 (m, 2H, *m*-py), 6.94 (t, $^4J_{HH}$ = 2.0 Hz, 4H, *o*-Ph), 3.76 (t, $^3J_{HH}$ = 5.4 Hz, 6H, NCH$_2$), 2.97 (t, $^3J_{HH}$ = 5.4 Hz, 6H, NCH$_2$), –0.10 (s, 27H, Si(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (101 MHz, 1,2-dichlorobenzene-*d*$_4$): δ = 165.4 (quart., $^1J_{BC'}$ = 49.3 Hz, *ipso*-Ph), 150.0 (*o*-py), 143.4 (br. s, *p*-py), 133.5 (quart., $^2J_{BC'}$ = 4.0 Hz, *m*-Ph),133.3 (*o*-Ph), 126.0 (*m*-py), 123.5 (Ph), 68.7 (N*C*H$_2$), 50.1 (N*C*H$_2$), 0.80 (Si(*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR (128 MHz, 1,2-dichlorobenzene-*d*$_4$): δ = –6.19 ppm. Anal. calcd. (found) for $C_{44}H_{56}BCl_8N_5Si_3Ti$ (1081.50 g·mol^{-1}) in %: C 48.86 (46.30), H 5.22 (5.51), N 6.48 (6.85).

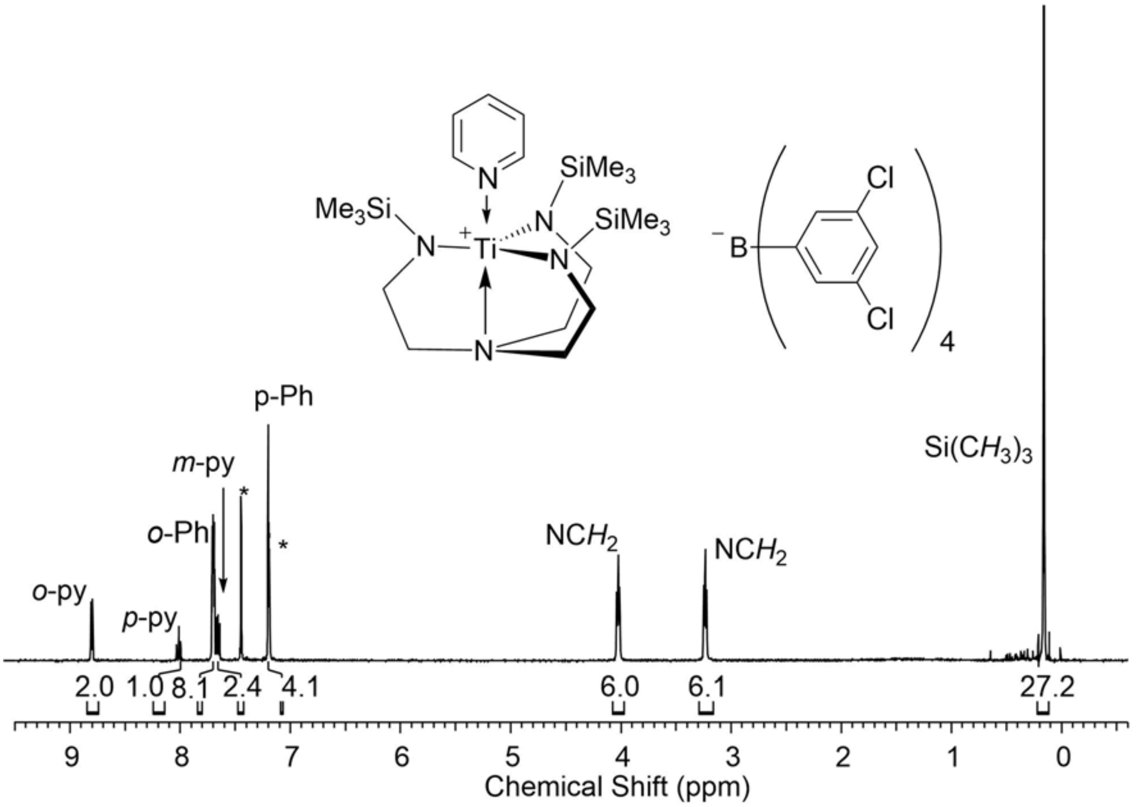

Figure S17. ^{1}H NMR spectrum of **6**[B(3,5-Cl$_2$C$_6$H$_3$)$_4$]·py in 1,2-dichlorobenzene-*d*$_4$, *$C_6Cl_2D_3H$.

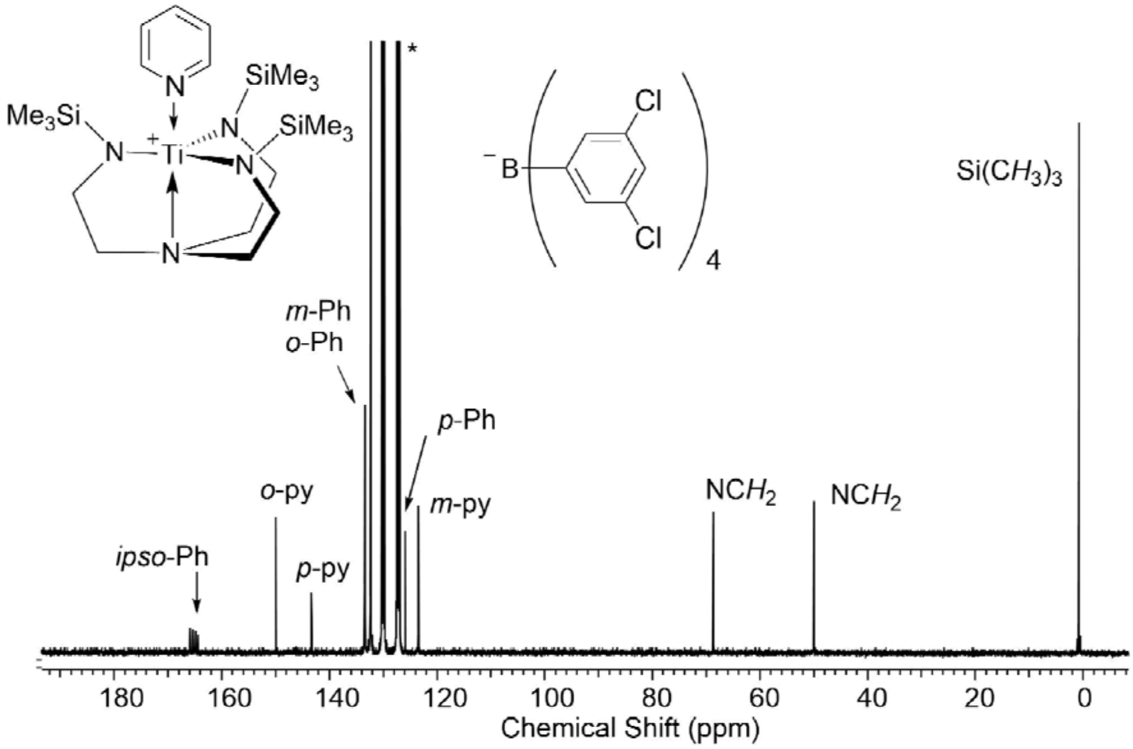

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **6**[B(3,5-$Cl_2C_6H_3)_4$]·py in 1,2-dichlorobenzene-*d*$_4$, *$C_6Cl_2D_3H_4$.

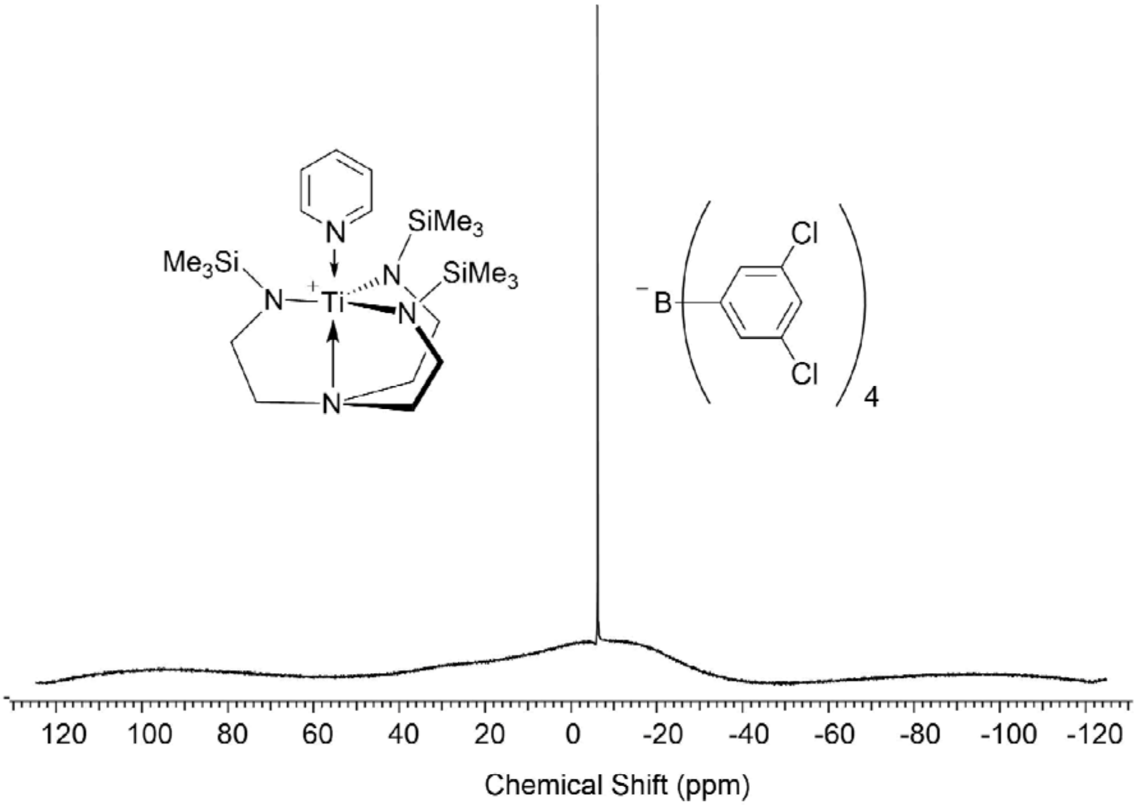

Figure S19. $^{11}B\{^{1}H\}$ NMR spectrum of **6**[B(3,5-$Cl_2C_6H_3)_4$]·py in 1,2-dichlorobenzene-*d*$_4$.

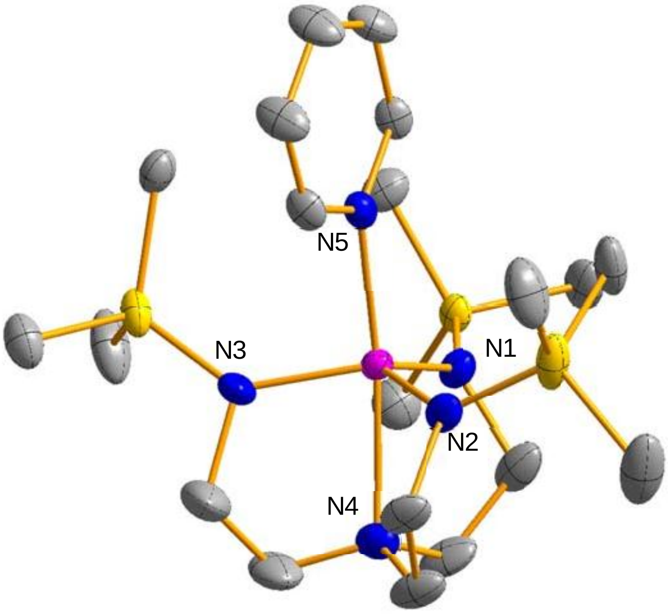

Figure S20. Molecular structure of **6**[B(3,5-Cl$_2$C$_6$H$_3$)$_4$]□py in the solid state drawn with displacement parameters at 50% probability. Hydrogen atoms and the counter anion are omitted for clarity. Selected interatomic distances (Å) and angles (°): Ti–N1 1.908(4), Ti–N2 1.906(4), Ti–N3 1.916(4), Ti–N4 2.281(4), Ti–N5 2.176(3), N4–Ti–N5 163.81.

6. $[(py)Ti(N_3N)][B(C_6F_5)_4]$ ($\mathbf{6}[B(C_6F_5)_4]\cdot py$)

Pyridine (7.6 µL, 94 µmol, 1.1 equiv.) was added to a solution of **6**$[B(C_6F_5)_4]\cdot Et_2O$ (100 mg, 86 µmol) in chlorobenzene (5 mL). The reaction mixture was stirred for 1 h at room temperature. All volatiles were removed *in vacuo*. The residue was rinsed with *n*-pentane (3× 5 mL), dried *in vacuo*, triturated with *n*-pentane (1 mL), and isolated as yellow powder (91 mg, 78 µmol, 91% based on **6**$[B(C_6F_5)_4]\cdot Et_2O$). ^{1}H NMR (400 MHz, 1,2-dichlorobenzene-*d*$_4$): δ = 8.53 (d, 2H, $^{3}J_{HH}$ = 4.9 Hz, *o*-py), 7.78 (tt, $^{3}J_{HH}$ = 4.9 Hz, $^{4}J_{HH}$ = 1.6 Hz, 1H, *p*-py), 7.04 (m, 2H, *m*-py), 3.74 (t, $^{3}J_{HH}$ = 5.3 Hz, 6H, NCH_2), 2.96 (t, $^{3}J_{HH}$ = 5.3 Hz, 6H, NCH_2), –0.13 (s, 27H, $Si(CH_3)_3$). $^{13}C\{^{1}H\}$ NMR (101 MHz, 1,2-dichlorobenzene-*d*$_4$): δ = 150.9 (*o*-py), 149.6 (d, $^{1}J_{CF}$ = 246 Hz, Ph), 144.2 (*p*-py), 139.6 (d, $^{1}J_{CF}$ = 240 Hz, Ph), 137.4 (d, $^{1}J_{CF}$ = 250 Hz, Ph) 126.8 (*m*-py), 69.5 (NCH_2), 50.8 (NCH_2), 1.53 ($Si(CH_3)_3$). $^{11}B\{^{1}H\}$ NMR (128 MHz, 1,2-dichlorobenzene-*d*$_4$): δ = –16.2 ($B(C_6F_5)_4$). ^{19}F NMR (377 MHz, 1,2-dichlorobenzene-*d*$_4$): δ = −131.68 (br. t, *o-F*), −162.35 (t, $^{3}J_{FF}$ = 20.5 Hz, *p-F*), −166.14 (br. s, *m-F*). Anal. calcd. (found) for $C_{44}H_{44}BF_{20}N_5Si_3Ti$ (1165.77 g·mol^{-1}) in %: C 45.33 (43.01), H 3.80 (4.24), N 6.01 (5.32).

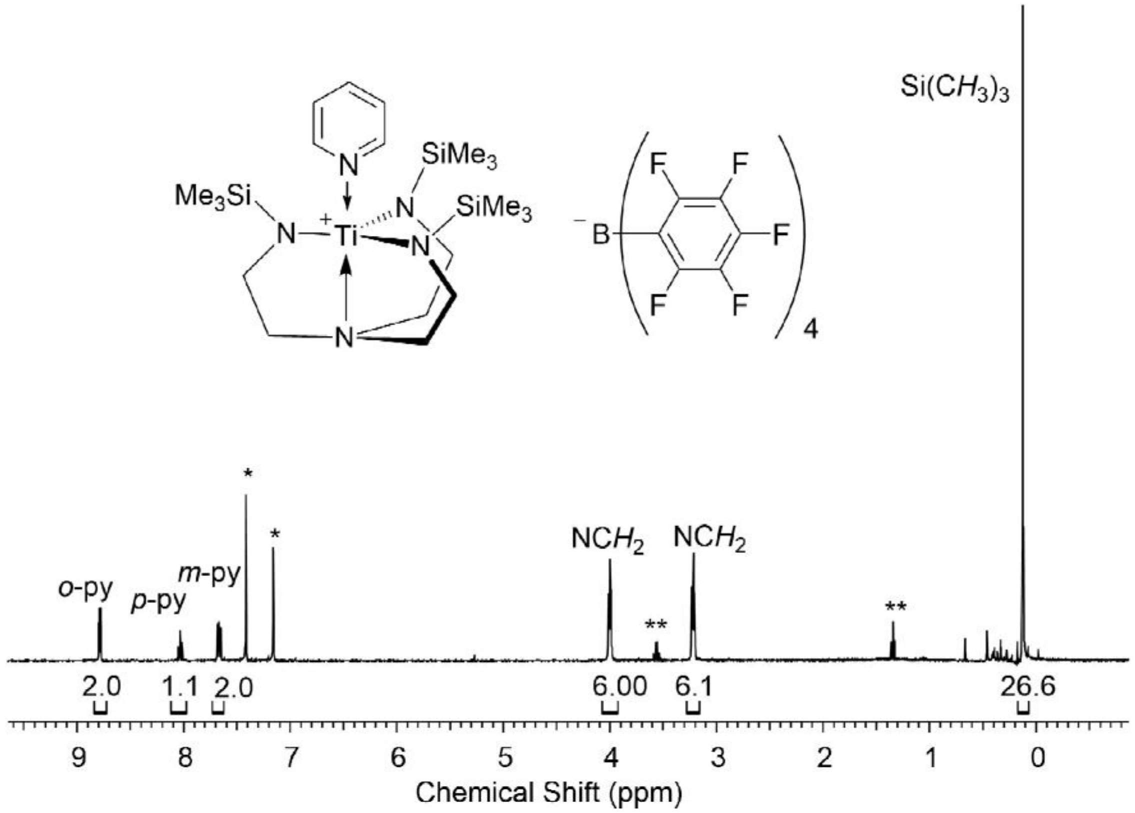

Figure S21. ^{1}H NMR spectrum of **6**$[B(C_6F_5)_4]\cdot py$ in 1,2-dichlorobenzene-*d*$_4$, $^{*}C_6Cl_2D_3H$, $^{**}Et_2O$.

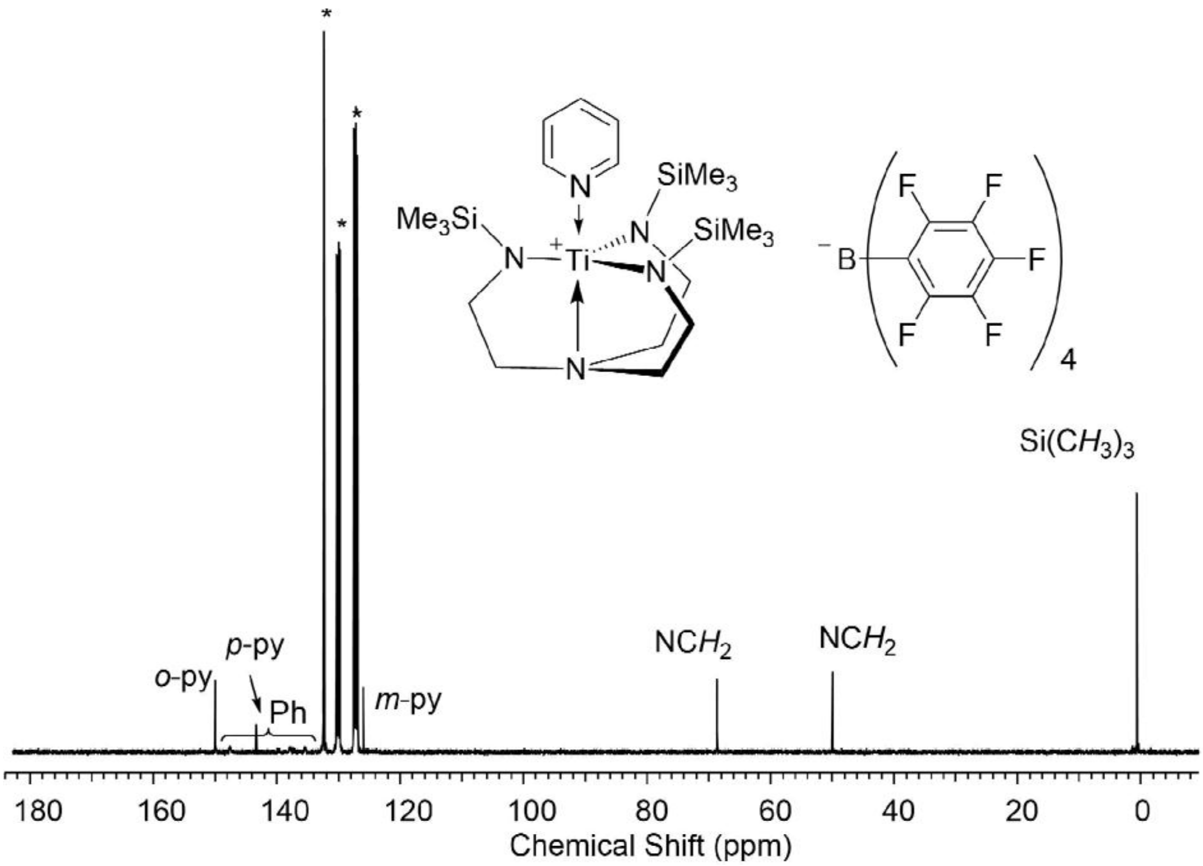

Figure S22. $^{13}C\{^1H\}$ NMR spectrum of **6**$[B(C_6F_5)_4]$□py in 1,2-dichlorobenzene-*d*$_4$, $*C_6Cl_2D_4$.

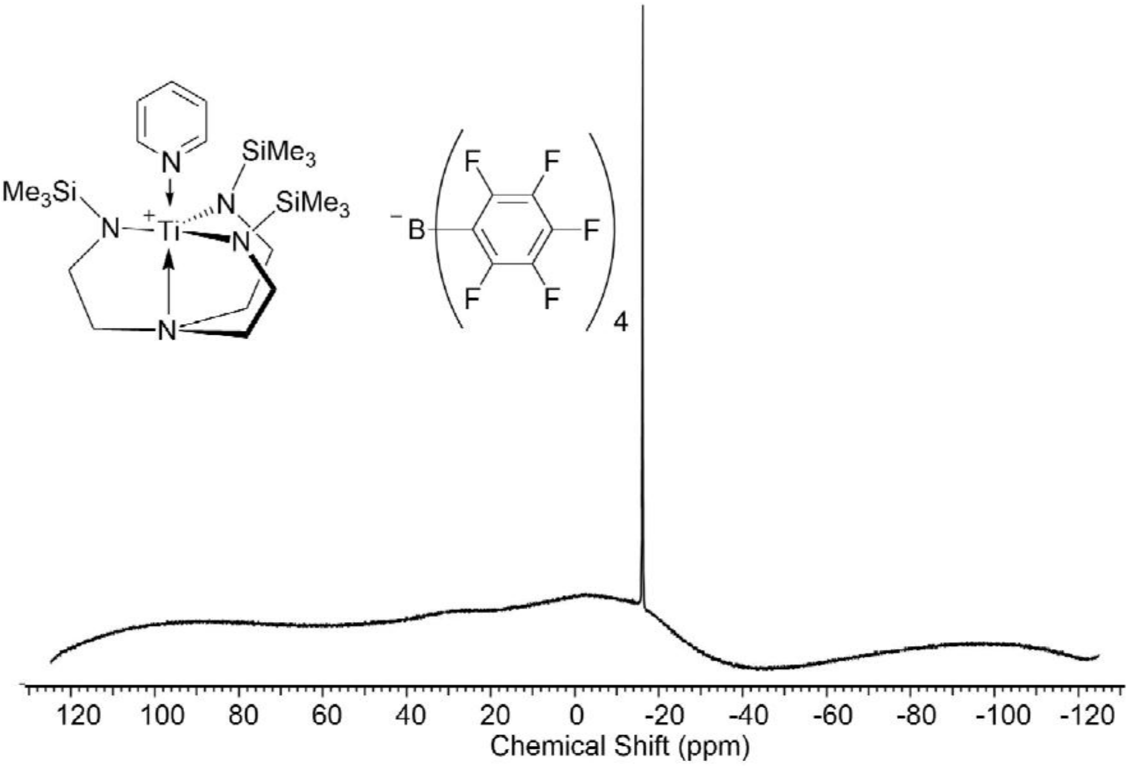

Figure S23. $^{11}B\{^1H\}$ NMR spectrum of **6**$[B(C_6F_5)_4]$□py in 1,2-dichlorobenzene-*d*$_4$.

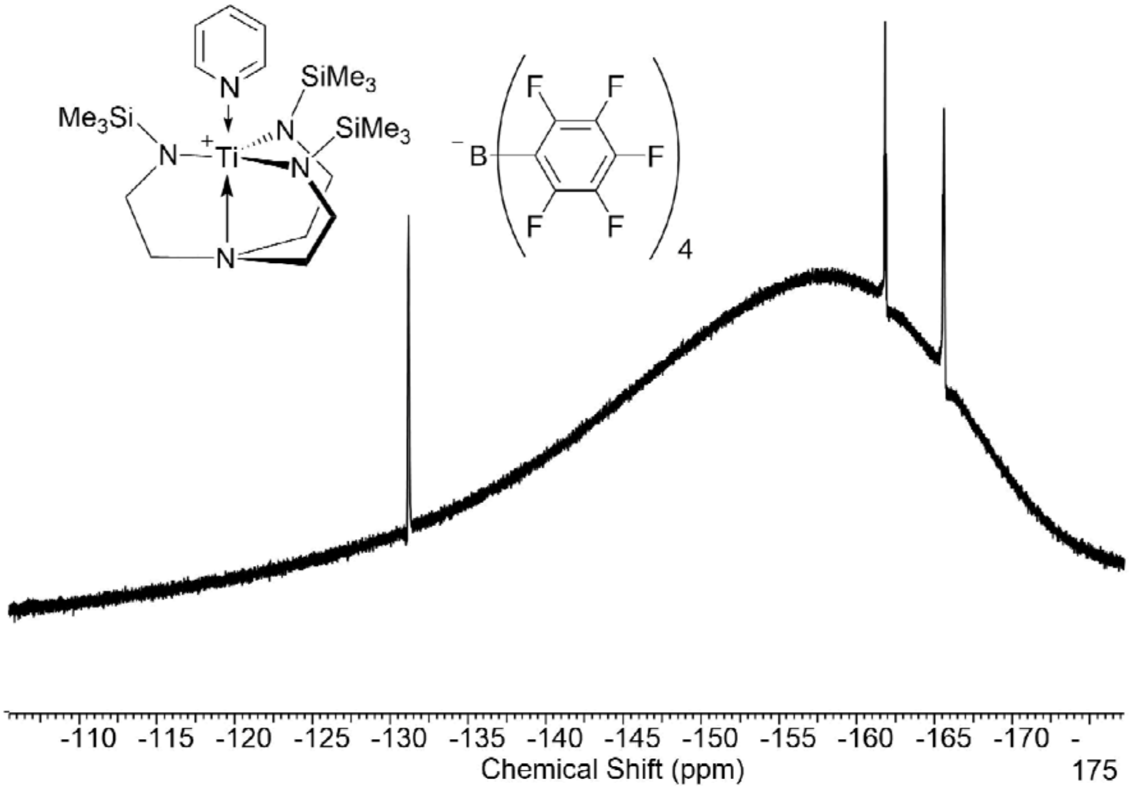

Figure S24. ^{19}F NMR spectrum of **6**[B(C$_6$F$_5$)$_4$]□py in 1,2-dichlorobenzene-d_4.

7. [(thf)Ti(N_3N)][B(3,5-$Cl_2C_6H_3$)$_4$] (6[B(3,5-$Cl_2C_6H_3$)$_4$]□thf)

Compound **6**[B(3,5-$Cl_2C_6H_3$)$_4$]□Et_2O (20 mg, 19 µmol) and THF (1.5 µL, 19 µmol) were combined in chlorobenzene (5 mL). The reaction mixture was stirred for 1 h at room temperature. All volatiles were then removed *in vacuo* and the crude product was rinsed with *n*-pentane (3× 5 mL). The product was dried *in vacuo*, triturated with *n*-pentane and isolated as yellow powder (18 mg, 17 µmol, 90% based on **6**[B(3,5-$Cl_2C_6H_3$)$_4$]□Et_2O). ^{1}H NMR (400 MHz, 1,2-dichlorobenzene-d_4): δ = 7.43 (m, 8H, *o*-Ph), 6.94 (t, $^4J_{HH}$ = 2.0 Hz, 4H, *o*-Ph), 4.18 (m, 4H, thf), 3.64 (t, $^3J_{HH}$ = 5.4 Hz, 6H, NCH_2), 2.93 (t, $^3J_{HH}$ = 5.4 Hz, 6H, NCH_2), 1.89 (m, 4H, thf), 0.06 (s, 27H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (101 MHz, 1,2-dichlorobenzene-d_4): δ = 165.4 (quart., $^1J_{BC'}$ = 49.3 Hz, *ipso-C*), 133.5 (quart., $^2J_{BC'}$ = 4.0 Hz, *m-C*),133.4 (*o-C*), 123.5 (*p-C*), 77.79 (thf), 69.3 (NCH_2), 49.7 (NCH_2), 25.6 (thf), 1.1 (Si(CH_3)$_3$). ^{11}B{^{1}H} NMR (128 MHz, 1,2-dichlorobenzene-d_4): δ = –6.28 (*B*(3,5-$Cl_2C_6H_3$)$_4$). Anal. calcd. (found) for $C_{43}H_{59}BCl_8N_4Si_3OTi$ (1074.50 g□mol^{-1}) in %: C 48.01 (45.55), H 5.53 (5.38), N 5.21 (5.27).

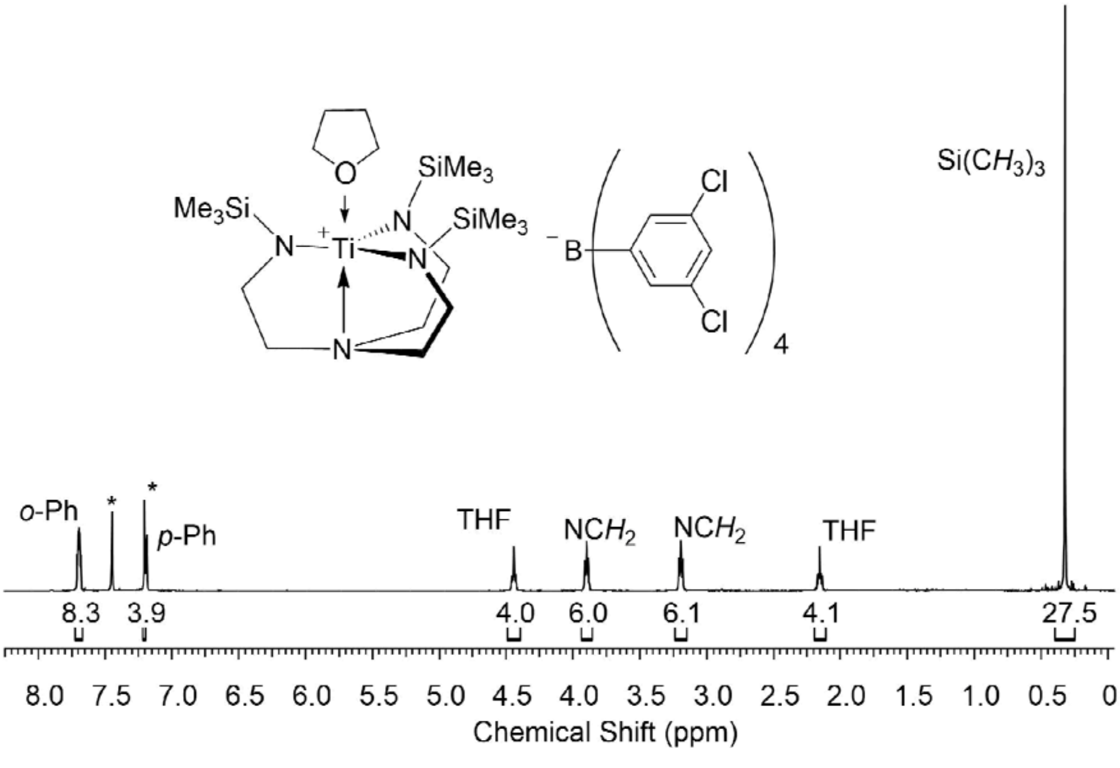

Figure S25. ^{1}H NMR spectrum of **6**[B(3,5-$Cl_2C_6H_3$)$_4$]□thf in 1,2-dichlorobenzene-d_4, *$C_6Cl_2D_3H$.

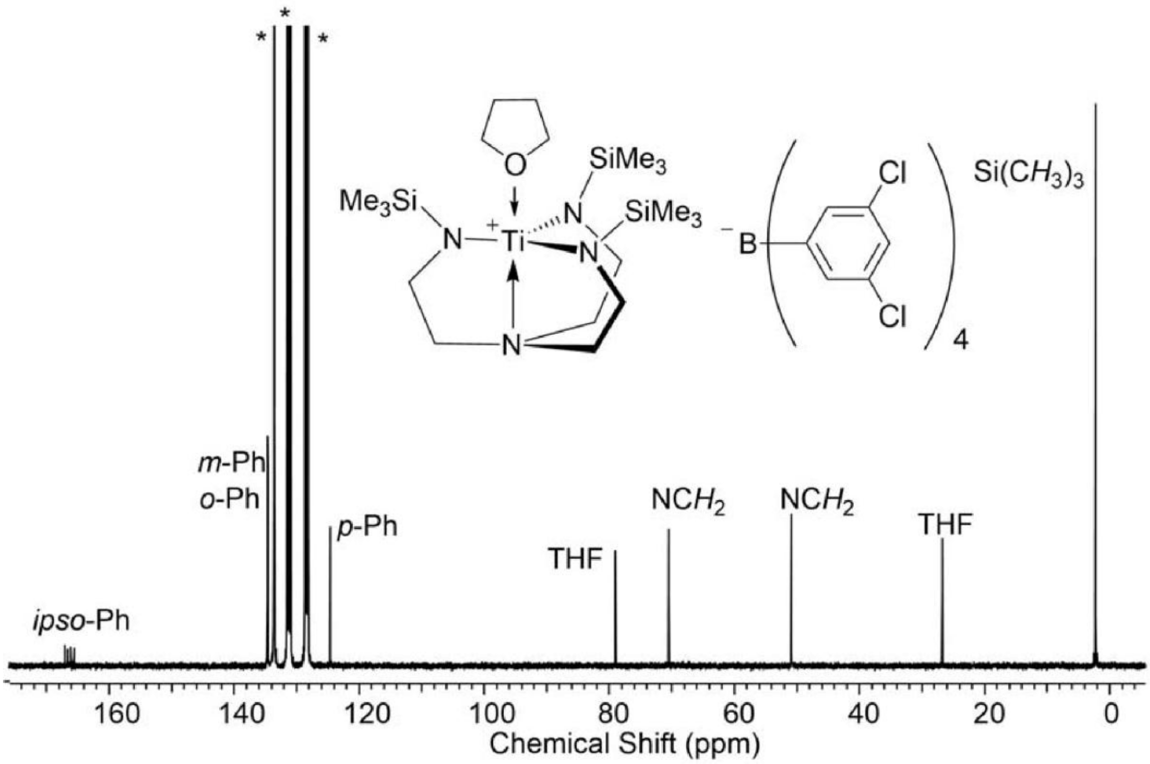

Figure S26. ^{13}C{^{1}H} NMR spectrum of [**6**[B(3,5-Cl$_2$C$_6$H$_3$)$_4$]□thf in 1,2-dichlorobenzene-*d*$_4$, *$C_6Cl_2D_4$

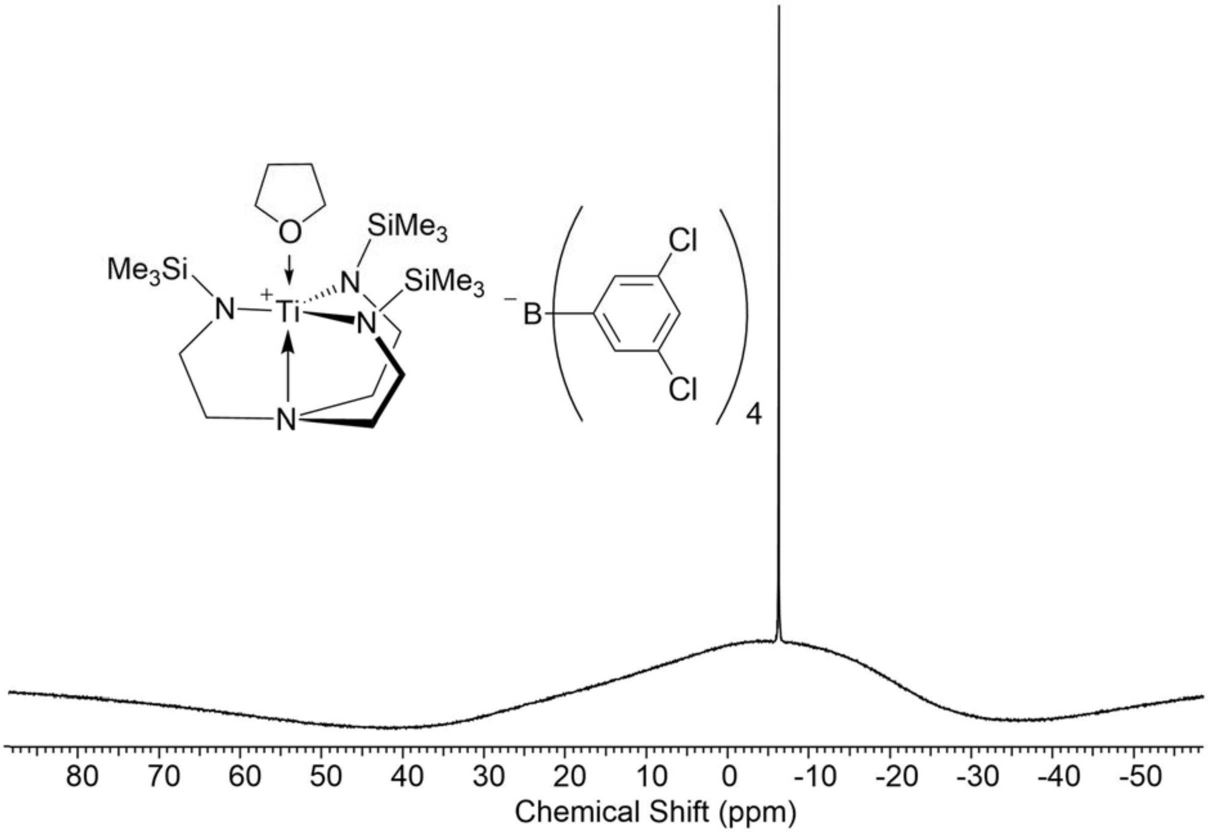

Figure S27. ^{11}B{^{1}H} NMR spectrum of **6**[B(3,5-Cl$_2$C$_6$H$_3$)$_4$]□thf in 1,2-dichlorobenzene-*d*$_4$.

8. [(thf)Ti(*N₃N*)][B(C₆F₅)₄] (6[B(C₆F₅)₄]□thf)

Compound **6**[B(C_6F_5)$_4$]□Et_2O (20 mg, 17 µmol) was dissolved in chlorobenzene (5 mL) and THF (1.4 µL, 17 µmol) was added *via* microsyringe. The reaction mixture was stirred for 1 h at room temperature. All volatiles were removed under reduced pressure and the crude product was rinsed with *n*-pentane (3× 5 mL). The product was dried *in vacuo*, triturated with *n*-pentane (1 mL), and isolated as yellow powder (18 mg, 15 µmol, 91% based on **6**[B(C_6F_5)$_4$]□Et_2O). ^{1}H NMR (400 MHz, 1,2-dichlorobenzene-*d*$_4$): δ = 4.19 (m, 4H, thf), 3.64 (t, $^3J_{HH}$ = 5.4 Hz, 6H, NC*H*$_2$), 2.95 (t, $^3J_{HH}$ = 5.3 Hz, 6H, NC*H*$_2$), 1.92 (m, 4H, thf), 0.06 (s, 27H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (101 MHz, 1,2-dichlorobenzene-*d*$_4$): δ = 149.2 (d, $^1J_{CF}$ = 242 Hz, Ph), 138.5 (d, $^1J_{CF}$ = 245 Hz, Ph), 136.8 (d, $^1J_{CF}$ = 241 Hz, Ph), 77.8 (thf), 69.3 (N*C*H$_2$), 49.7 (N*C*H$_2$), 25.5 (thf), 0.96 (Si(*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR (128 MHz, 1,2-dichlorobenzene-*d*$_4$): δ = –16.19 (*B*(C_6F_5)$_4$). ^{19}F NMR (377 MHz, 1,2-dichlorobenzene-*d*$_4$): δ = −131.4 (br. t, *o-F*), −162.1 (t, $^3J_{FF}$ = 20.7 Hz, *p-F*), −165.6 (br. s, *m-F*). Anal. calcd. (found) for $C_{43}H_{47}BF_{20}N_4OSi_3Ti$ (1158.78 g□mol^{-1}) in %: C 44.57 (42.39), H 4.09 (4.33), N 4.84 (4.92).

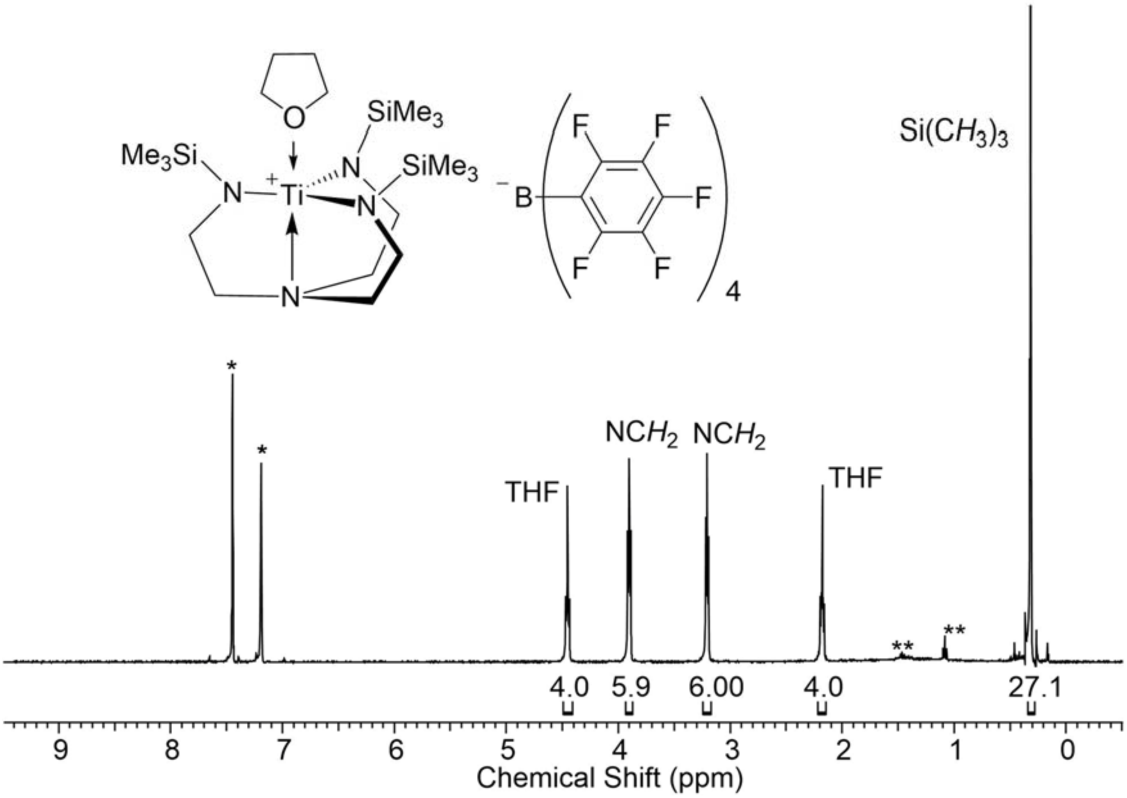

Figure S28. ^{1}H NMR spectrum of **6**[B(C_6F_5)$_4$]□thf in 1,2-dichlorobenzene-*d*$_4$, *$C_6Cl_2D_3H$, ***n*-pentane.

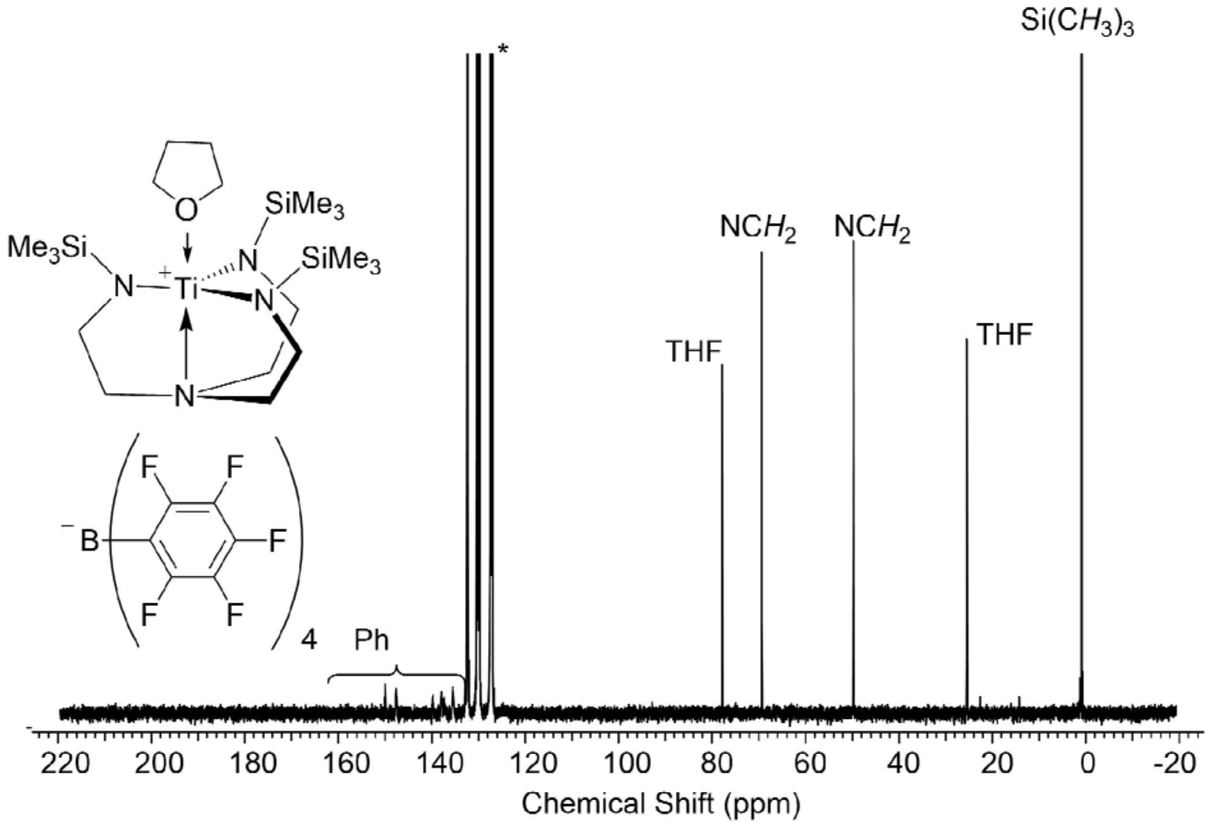

Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **6**[B(C_6F_5)$_4$]□thf in 1,2-dichlorobenzene-*d*$_4$, *$C_6Cl_2D_4$.

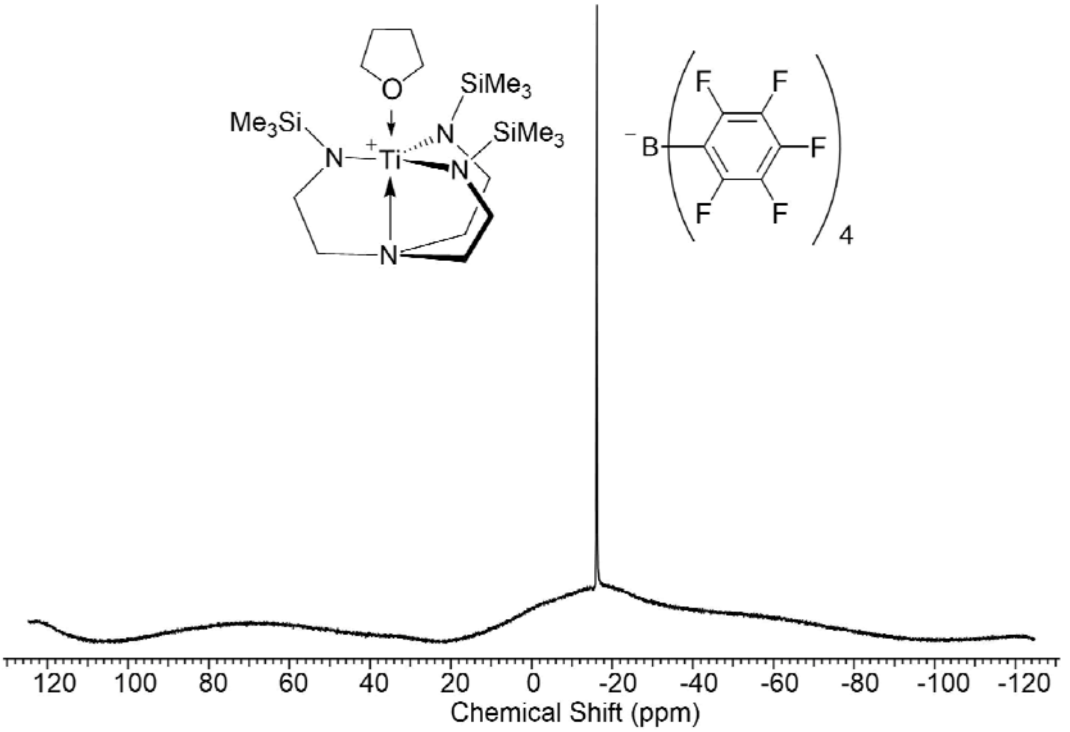

Figure S30. $^{11}B\{^{1}H\}$ NMR spectrum of **6**[B(C_6F_5)$_4$]□thf in 1,2-dichlorobenzene-*d*$_4$.

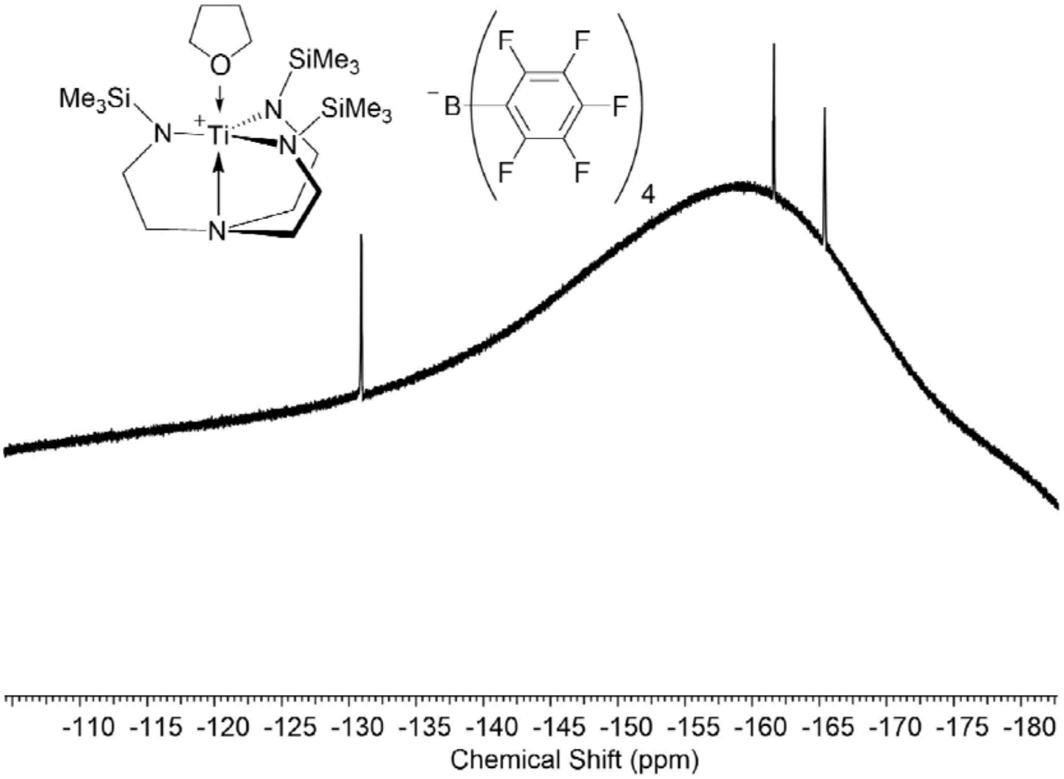

Figure S31. ^{19}F NMR spectrum of **6**[B(C_6F_5)$_4$]□thf in 1,2-dichlorobenzene-d_4.

9. [(dmap)Ti(N_3N)][B(3,5-$Cl_2C_6H_3$)$_4$] (**6**[B(3,5-$Cl_2C_6H_3$)$_4$]$\cdot$dmap)

Compound **6**[B(3,5-$Cl_2C_6H_3$)$_4$]$\cdot$$Et_2O$ (20 mg, 19 mmol) and DMAP (4.3 mg, 38 µmol, 2 equiv) were combined in chlorobenzene (5 mL). The reaction mixture was stirred for 1 h at room temperature. All volatiles were removed under reduced pressure and the crude product was rinsed with *n*-pentane (3× 5 mL). The product was dried *in vacuo*, triturated with *n*-pentane (1 mL), and isolated as yellow powder (18 mg, 16 µmol, 86% based on **6**[B(3,5-$Cl_2C_6H_3$)$_4$]$\cdot$$Et_2O$). ^{1}H NMR (400 MHz, 1,2-dichlorobenzene-d_4): δ = 8.14 (d, 2H, $^3J_{HH}$ = 7.4 Hz, *m*-dmap), 7.44 (m, 8H, *o*-Ph), 6.94 (t, $^4J_{HH}$ = 2.0 Hz, 4H, *p*-Ph), 6.39 (d, $^3J_{HH}$ = 7.5 Hz, *o*-dmap), 3.70 (t, $^3J_{HH}$ = 5.2 Hz, 6H, NCH_2), 2.91 (t, $^3J_{HH}$ = 5.2 Hz, 6H, NCH_2), 2.63 (s, 6H, N(CH_3)$_2$), 0.00 (s, 27H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (101 MHz, 1,2-dichlorobenzene-d_4): δ = 165.4 (quart., $^1J_{BC'}$ = 49.4 Hz, *ipso-C*), 155.8 (*ipso*-dmap), 148.9 (*m*-dmap), 133.5 (quart., $^2J_{BC'}$ = 4.0 Hz, *m-C*), 133.4 (*o-C*), 123.4 (*p-C*), 106.0 (*o*-dmap), 67.2 (NCH_2), 50.1 (NCH_2), 38.8 (N(CH_3)$_2$), 1.1 (Si(CH_3)$_3$). ^{11}B{^{1}H} NMR (128 MHz, dichlorobenzene-d_4): δ = –6.27 (*B*(3,5-$Cl_2C_6H_3$)$_4$). Anal. calcd. (found) for $C_{46}H_{62}BCl_8N_6Si_3Ti$ (1124.57 g$\cdot$mol^{-1}) in %: C 49.09 (48.46), H 5.55 (5.78), N 7.47 (7.37).

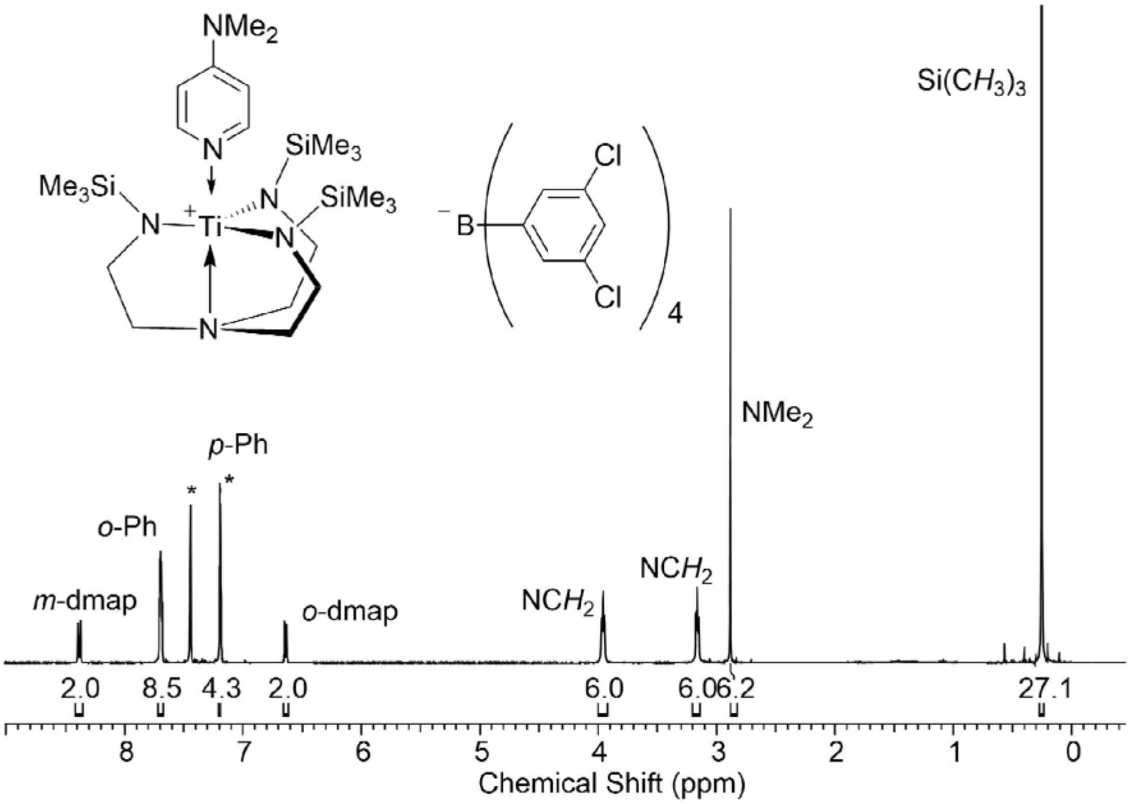

Figure S32. ^{1}H NMR spectrum of **6**[B(3,5-$Cl_2C_6H_3$)$_4$]$\cdot$dmap in 1,2-dichlorobenzene-d_4, *$C_6Cl_2D_3H$.

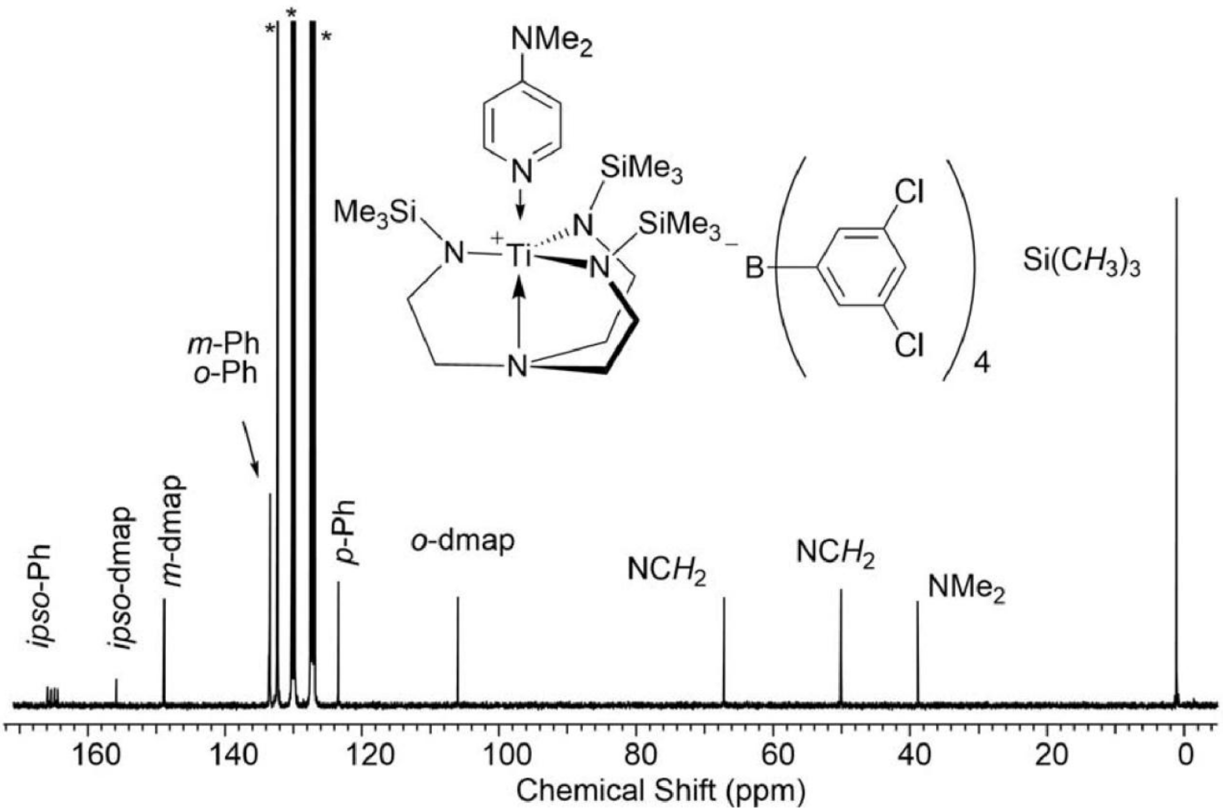

Figure S33. $^{13}C\{^1H\}$ NMR spectrum of **6**[B(3,5-$Cl_2C_6H_3)_4$]dmap in 1,2-dichlorobenzene-*d*4, *$C_6Cl_2D_4$.

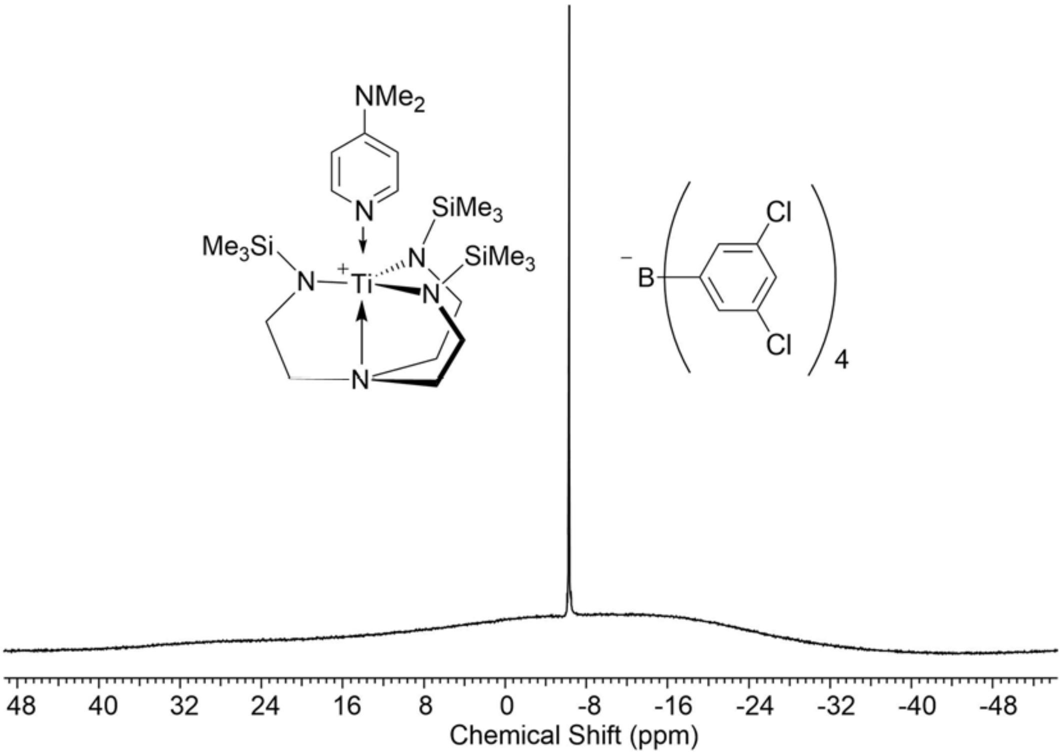

Figure S34. $^{11}B\{^1H\}$ NMR spectrum of **6**[B(3,5-$Cl_2C_6H_3)_4$]dmap in 1,2-dichlorobenzene-*d*4.

10. [(dmap)Ti(N_3N)][B(C_6F_5)$_4$] (**6**[B(C_6F_5)$_4$]□dmap)

Compound **6**[B(C_6F_5)$_4$]□Et_2O (20 mg, 17 µmol) and DMAP (4.2 mg, 34 µmol, 2 equiv.) were combined in chlorobenzene (5 mL). The reaction mixture was stirred for 1 h at room temperature. All volatiles were removed under reduced pressure and the crude product rinsed with *n*-pentane (3× 5 mL). The product was dried *in vacuo*, triturated with *n*-pentane (1 mL), and isolated as yellow powder (18 mg, 15 µmol, 86% based on **6**[B(C_6F_5)$_4$]□Et_2O). ^{1}H NMR (400 MHz, 1,2-dichlorobenzene-d_4): δ = 8.15 (d, 2H, $^3J_{HH}$ = 7.4 Hz, *m*-dmap), 6.14 (d, 2H, $^3J_{HH}$ = 7.4 Hz, *o*-dmap), 3.71 (t, $^3J_{HH}$ = 5.2 Hz, 6H, NCH_2), 2.91 (t, $^3J_{HH}$ = 5.2 Hz, 6H, NCH_2), 2.68 (s, 6H, N(CH_3)$_2$), –0.01 (s, 27H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (101 MHz, 1,2-dichlorobenzene-d_4): δ = 155.6 (*ipso*-dmap), 148.7 (*m*-dmap), 148.5 (d, $^1J_{CF}$ = 241 Hz, Ph), 138.2 (d, $^1J_{CF}$ = 247 Hz, Ph), 136.4 (d, $^1J_{CF}$ = 255 Hz, Ph), 128.3 (Ph), 105.7 (*o*-dmap), 66.9 (N*C*H$_2$), 49.8 (N*C*H$_2$), 38.6 (N(*C*H$_3$)$_2$), 0.7 (Si(*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR (128 MHz, 1,2-dichlorobenzene-d_4): δ = –16.18 (*B*(C_6F_5)$_4$). ^{19}F NMR (377 MHz, dichlorobenzene-d_4): δ = −131.7 (br. t, *o-F*), −162.4 (t, $^3J_{FF}$ = 20.5 Hz, *p-F*), −166.2 (br. s, *m-F*). Anal. calcd. (found) for $C_{46}H_{49}BF_{20}N_6Si_3Ti$ (1208.84 g□mol^{-1}) in %: C 45.71 (44.75), H 4.09 (4.77), N 6.95 (6.63).

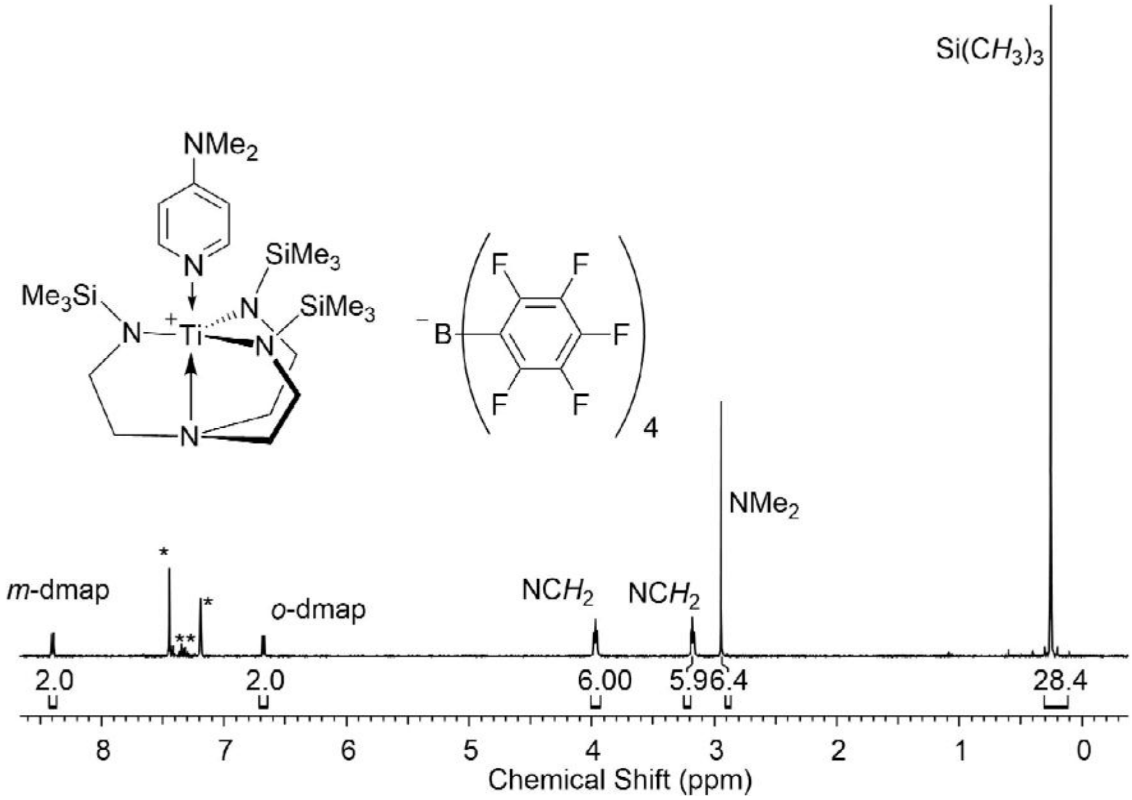

Figure S35. ^{1}H NMR spectrum of **6**[B(C_6F_5)$_4$]□dmap in 1,2-dichlorobenzene-d_4, *$C_6Cl_2D_3H$, **chlorobenzene.

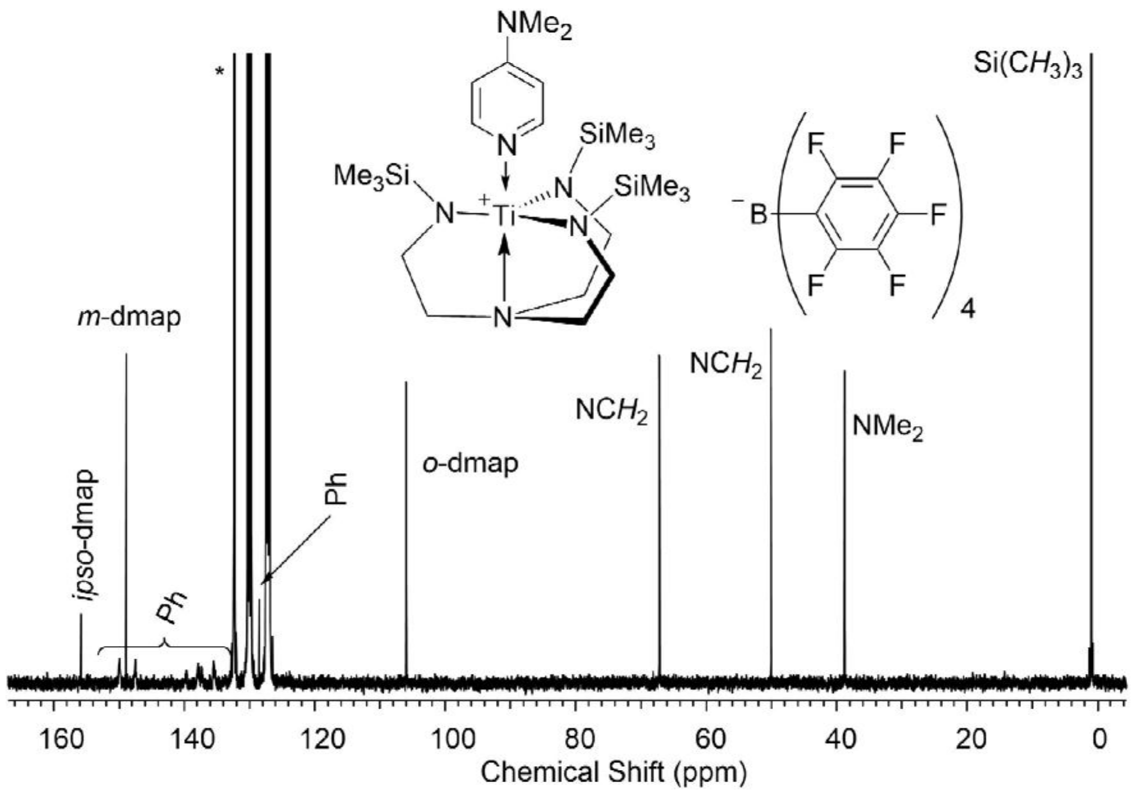

Figure S36. $^{13}C\{^1H\}$ NMR spectrum of **6**[B(C_6F_5)$_4$]□dmap in 1,2-dichlorobenzene-*d*$_4$, *$C_6Cl_2D_4$.

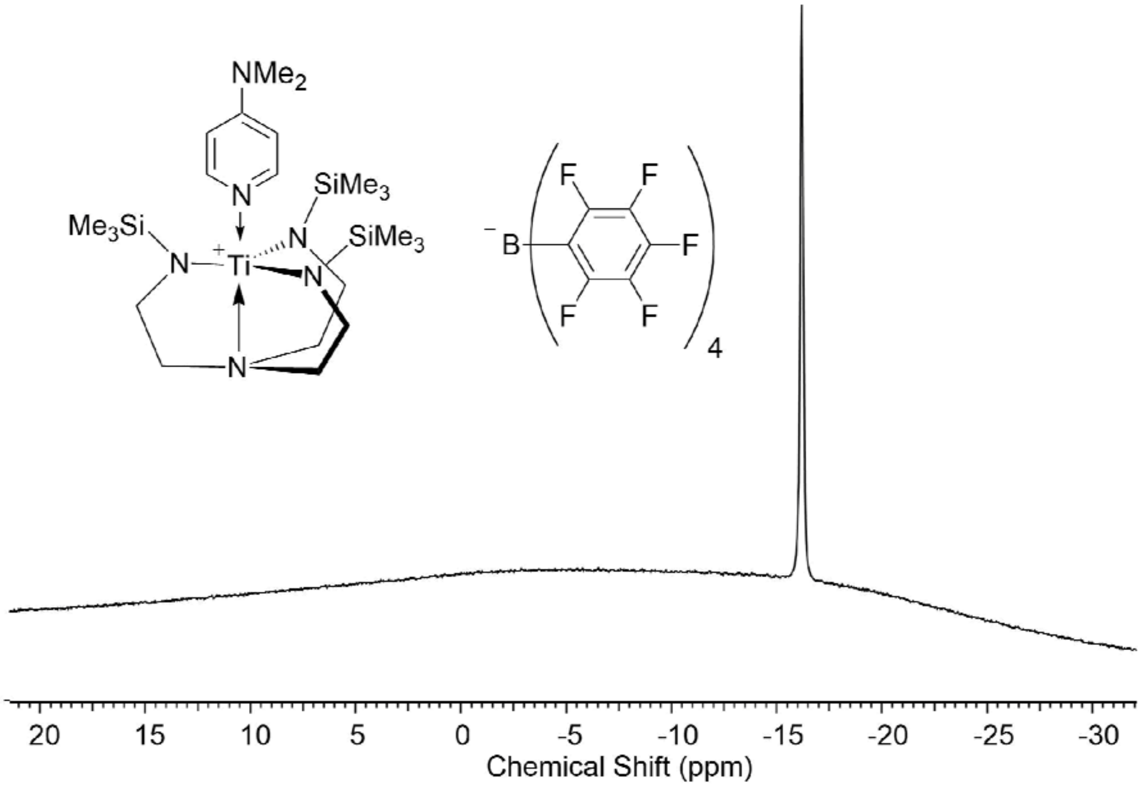

Figure S37. $^{11}B\{^1H\}$ NMR spectrum of **6**[B(C_6F_5)$_4$]□dmap in 1,2-dichlorobenzene-*d*$_4$.

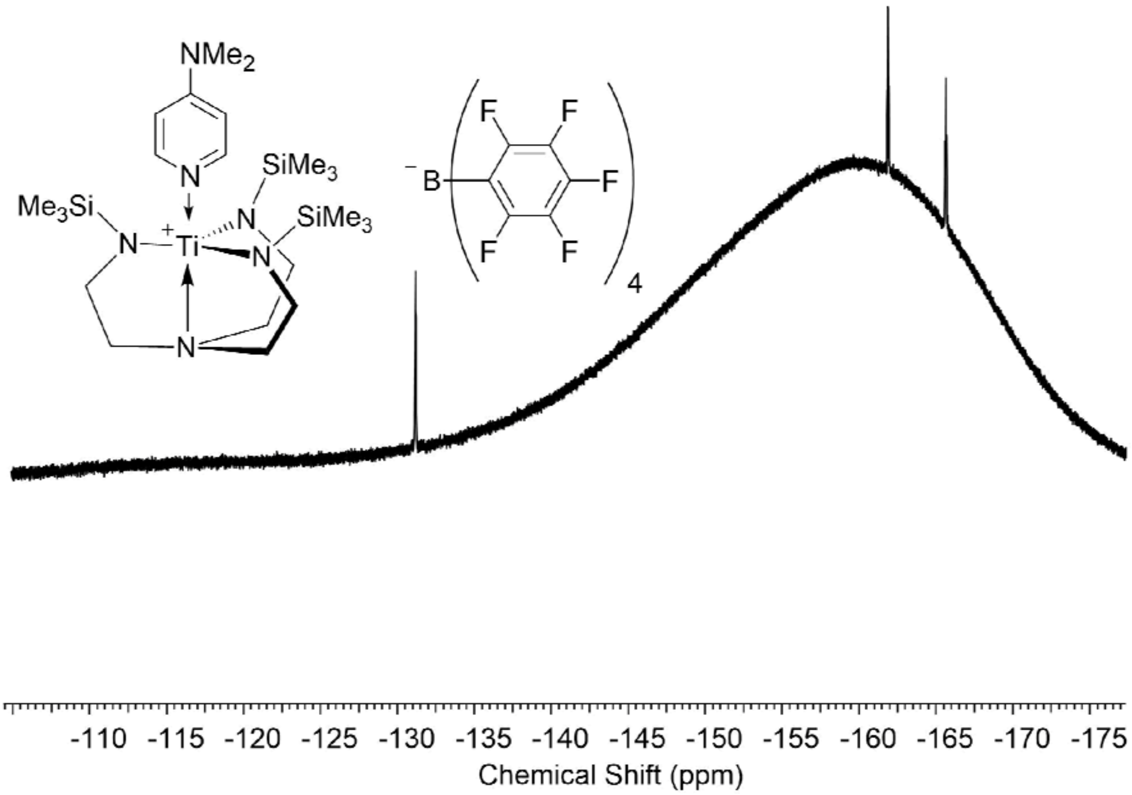

Figure S38. ^{19}F NMR spectrum **6**[B(C$_6$F$_5$)$_4$]□dmap in 1,2-dichlorobenzene-d_4.

11. $[Ti\{N(CH_2CH_2NSiMe_3)_2(CH_2CH_2NSiMe_3(\mu\text{-}CO_2\text{-}\eta O{:}\eta O'))\}]_2[B(3,5\text{-}Cl_2C_6H_3)_4]_2$ ($7[B(3,5\text{-}Cl_2C_6H_3)_4]_2$)

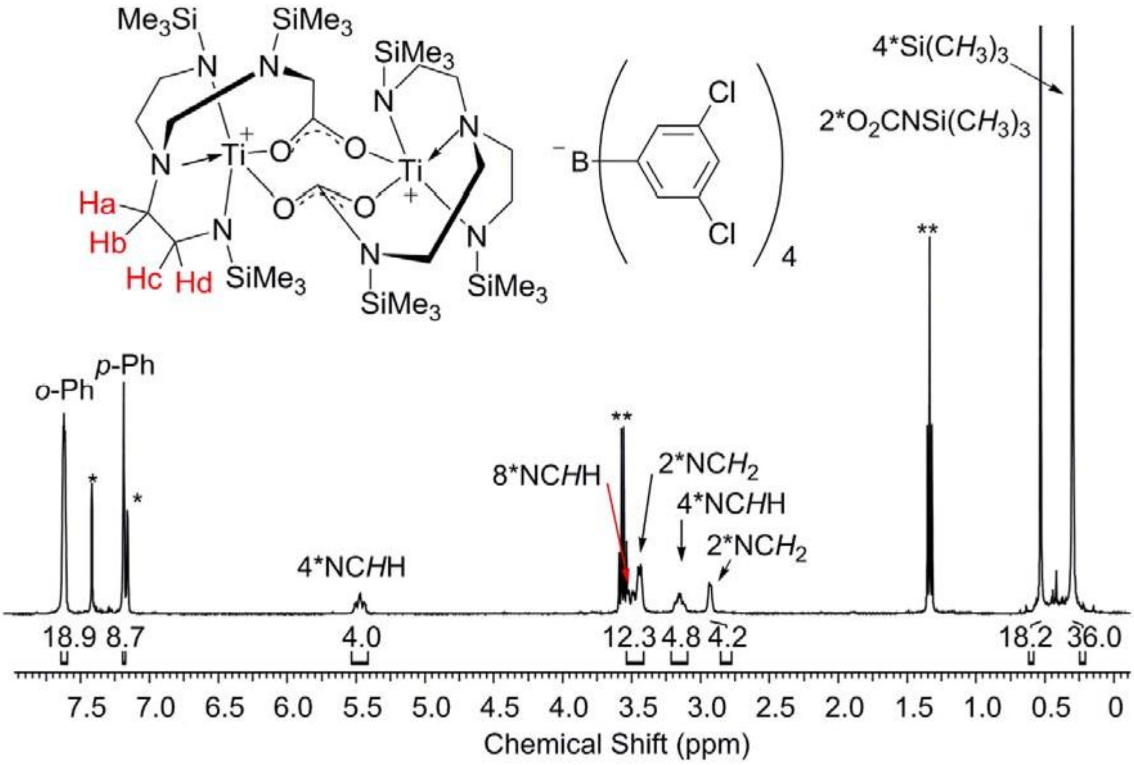

Figure S39. ^{1}H NMR spectrum of **7**$[B(3,5\text{-}Cl_2C_6H_3)_4]_2$ in 1,2-dichlorobenzene-d_4, $^*C_6Cl_2D_3H$, $^{**}Et_2O$.

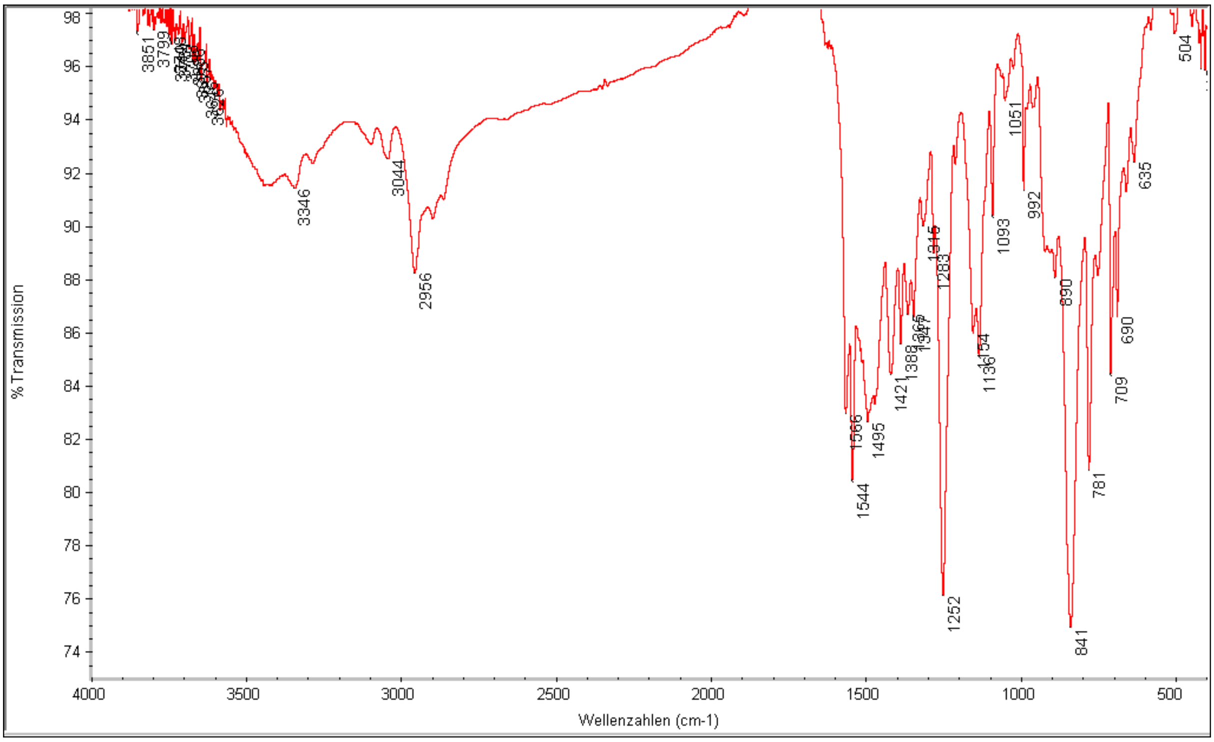

Figure S40. IR spectrum of **7**$[B(3,5\text{-}Cl_2C_6H_3)_4]_2$ in a KBr pellet.

12. $[Ti\{N(CH_2CH_2NSiMe_3)_2(CH_2CH_2NSiMe_3(\mu\text{-}CO_2\text{-}\eta O{:}\eta O'))\}]_2[B(C_6F_5)_4]_2$ $(\mathbf{7}[B(C_6F_5)_4]_2)$

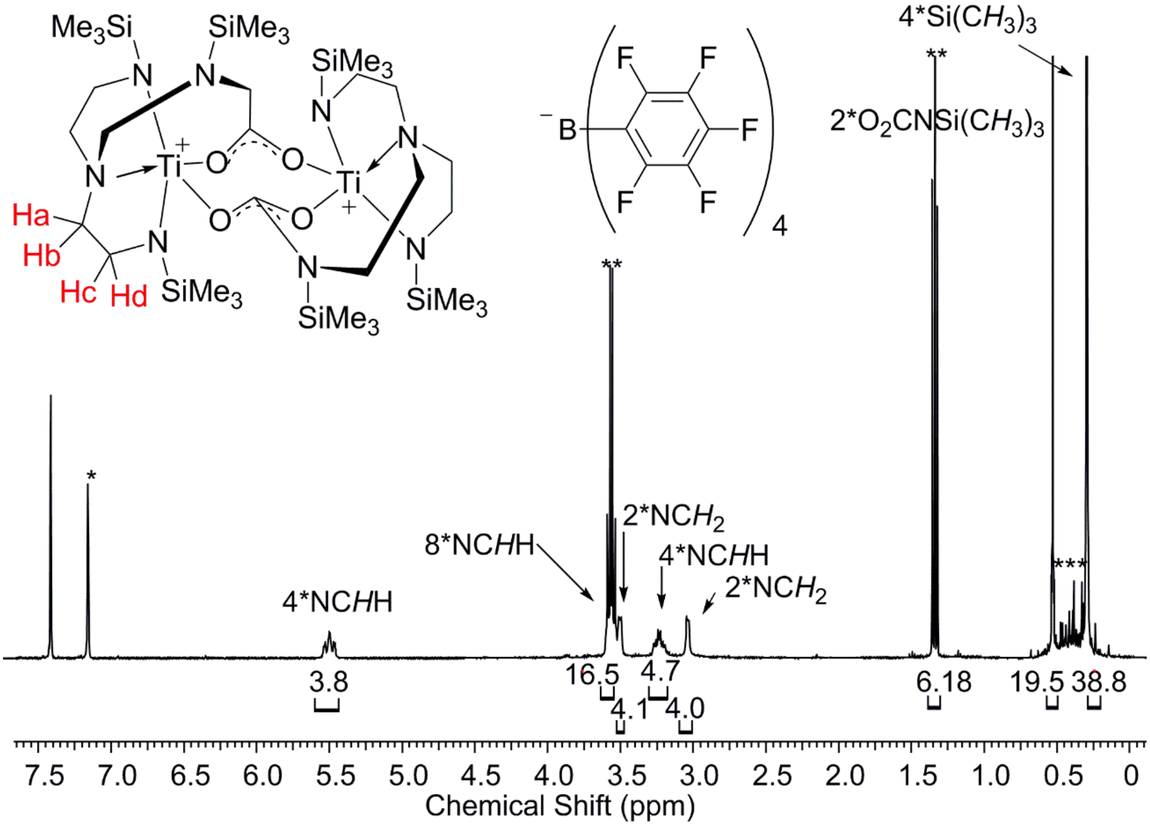

Figure S41. ^1H NMR spectrum of $\mathbf{7}[B(C_6F_5)_4]_2$ in 1,2-dichlorobenzene-d_4, $*C_6Cl_2D_3H$, $**Et_2O$, ***decomposition products.

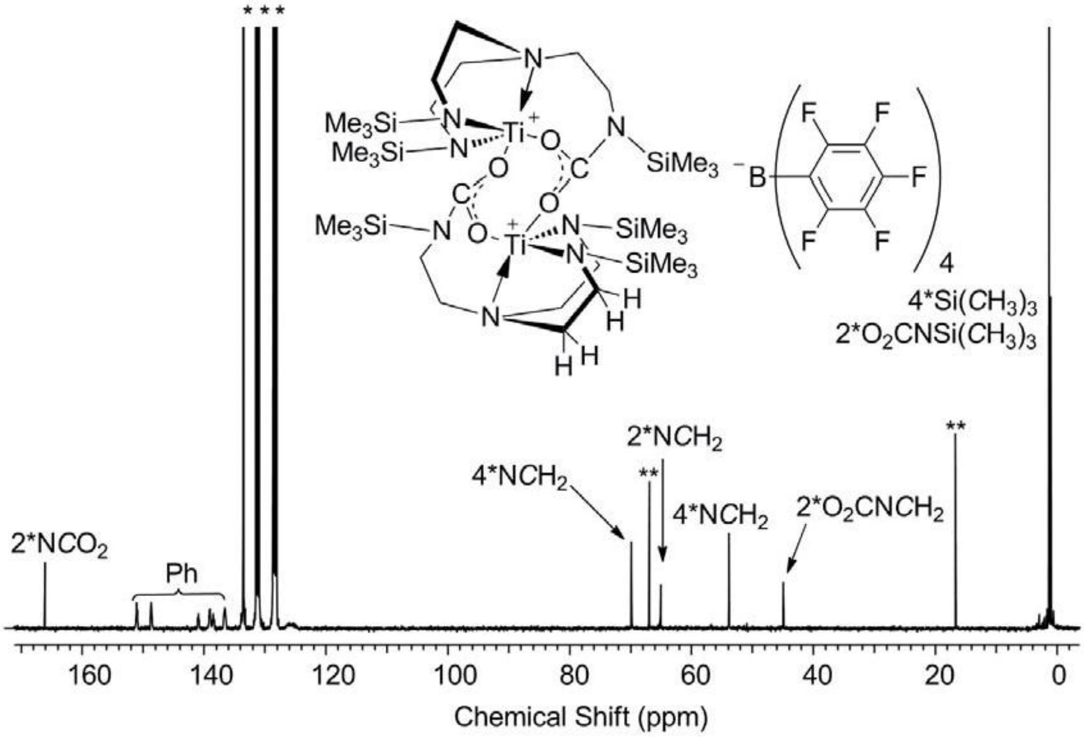

Figure S42. $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{7}[B(C_6F_5)_4]_2$ in 1,2-dichlorobenzene-d_4, $*C_6Cl_2D_4$, $**Et_2O$.

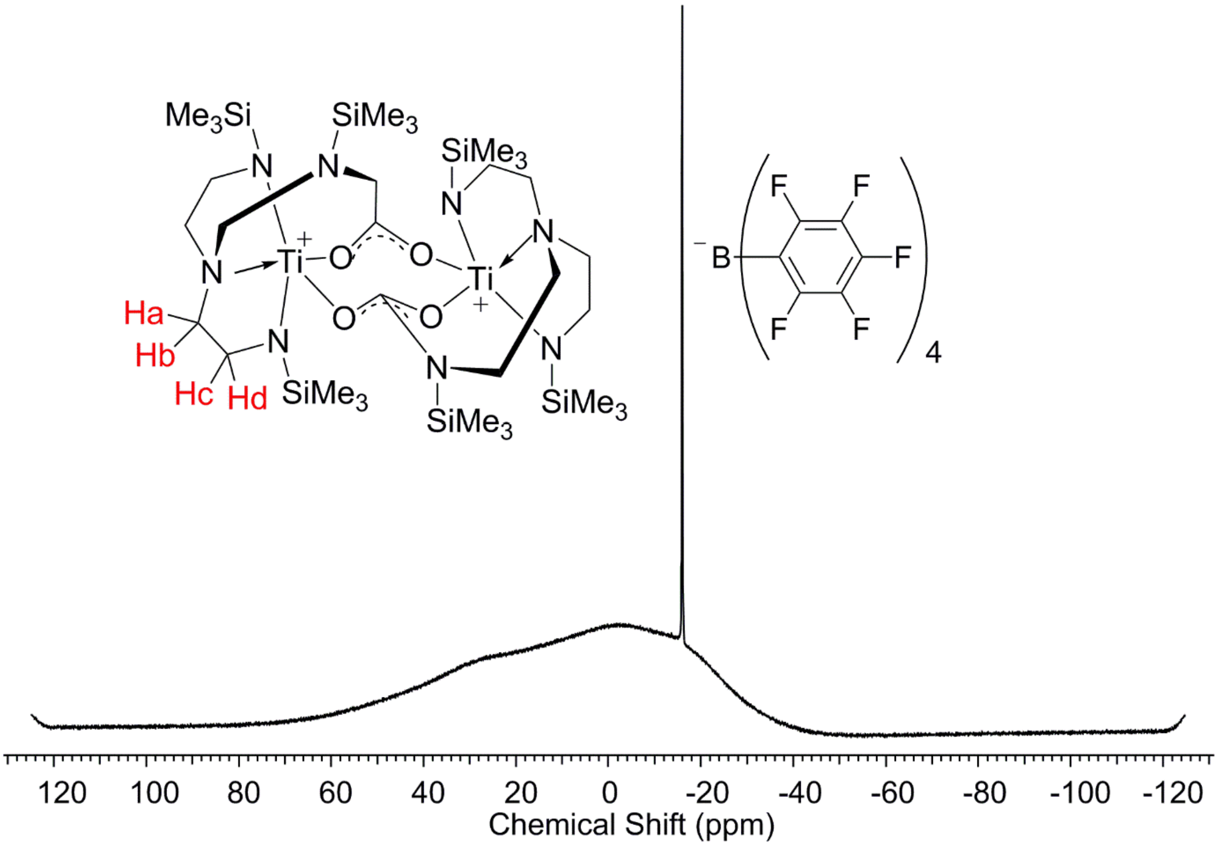

Figure S43. $^{11}B\{^{1}H\}$ NMR spectrum of **7**[B(C_6F_5)$_4$]$_2$ in 1,2-dichlorobenzene-*d*$_4$.

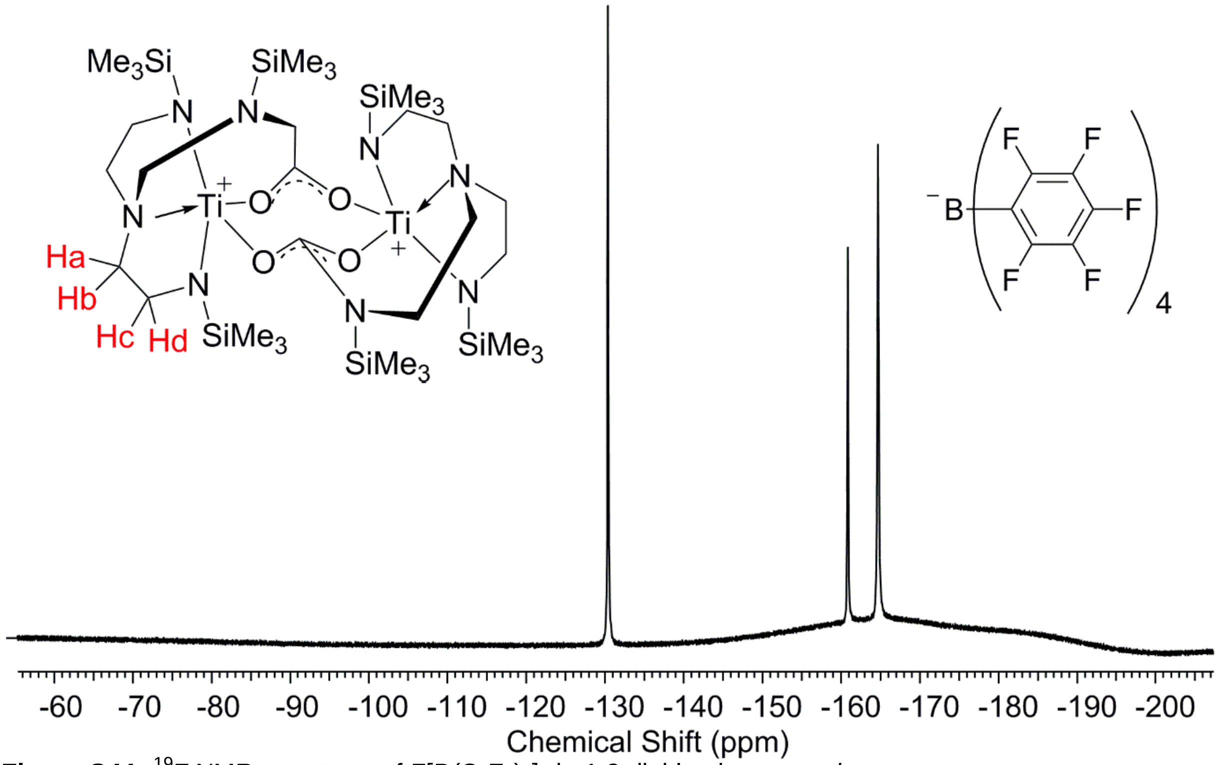

Figure S44. ^{19}F NMR spectrum of **7**[B(C_6F_5)$_4$]$_2$ in 1,2-dichlorobenzene-*d*$_4$.

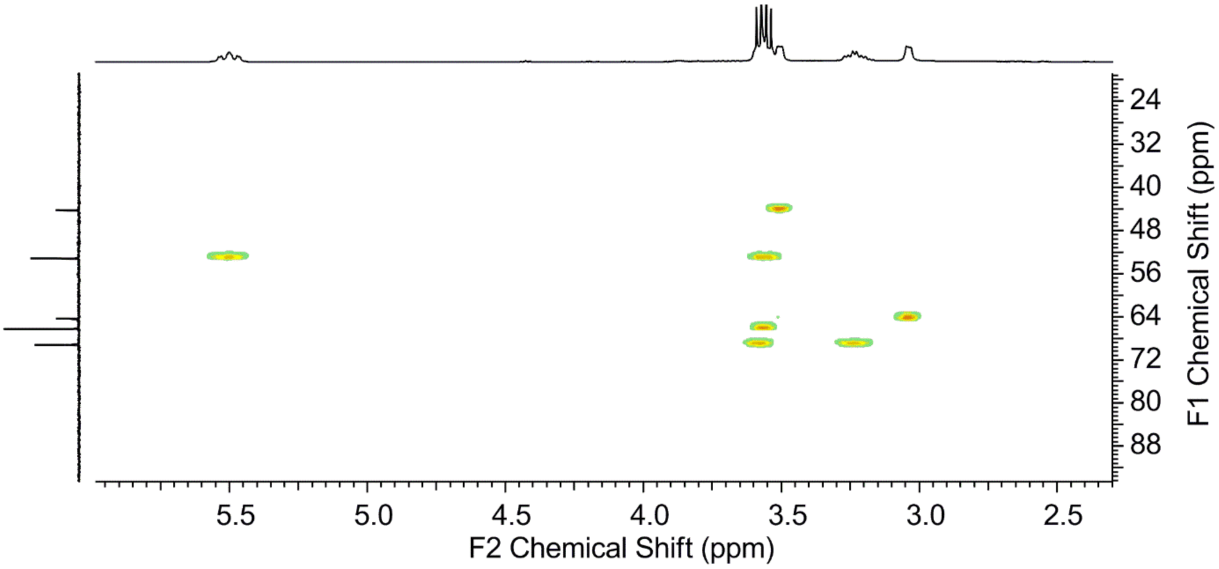

Figure S45. Extract from the HSQC spectrum of **7**[B(C_6F_5)$_4$]$_2$ in 1,2-dichlorobenzene-*d*$_4$.

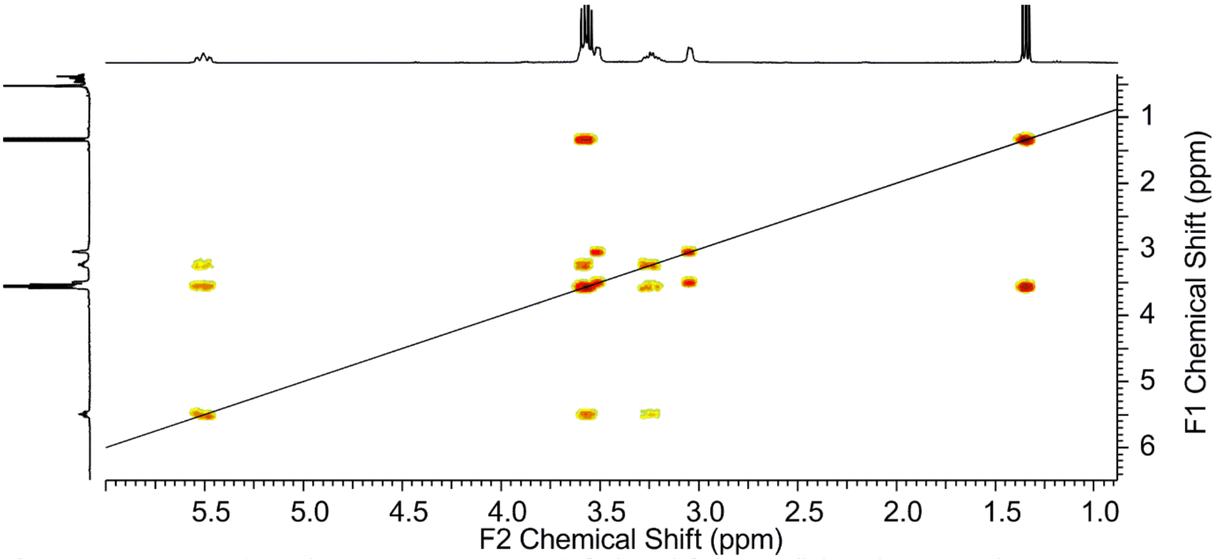

Figure S46. Extract from the COSY spectrum of **7**[B(C_6F_5)$_4$]$_2$ in 1,2-dichlorobenzene-*d*$_4$.

13. [(py)Ti{N($CH_2CH_2NSiMe_3$)$_2$($CH_2CH_2NSiMe_3$(CO_2-κ^2*O*,*O´*))}] (8[B(C_6F_5)$_4$]□py)

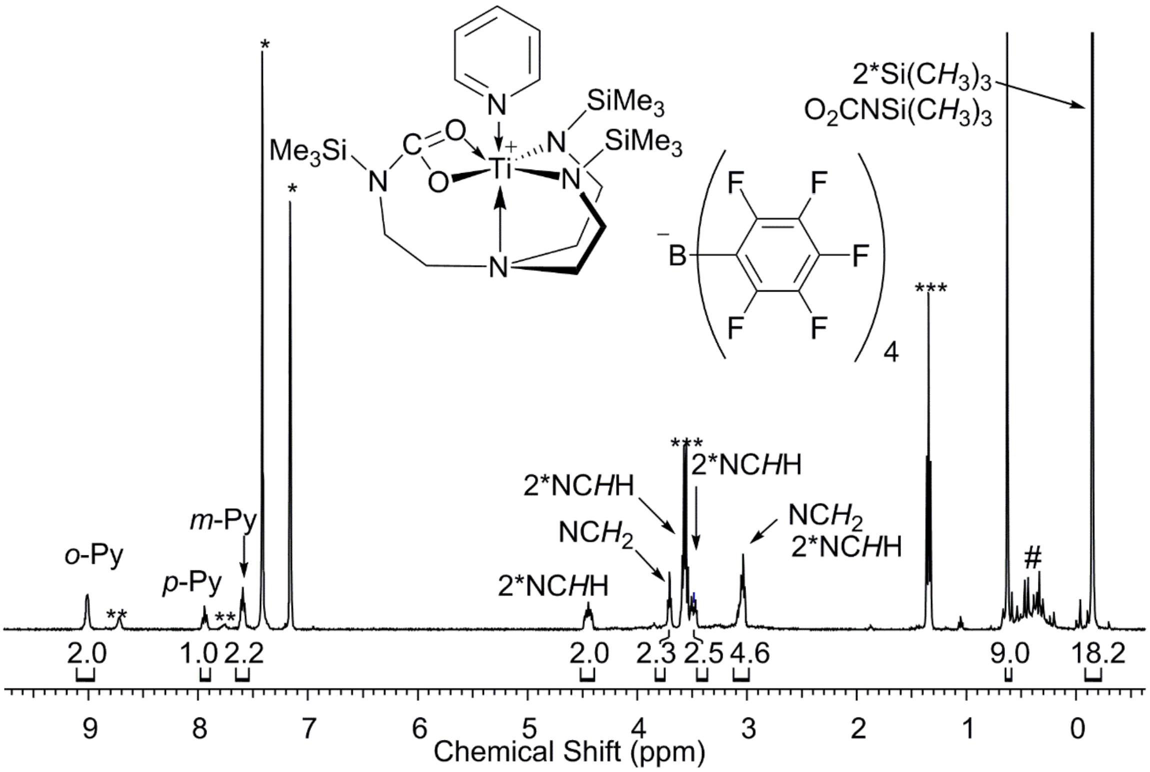

Figure S47. ^{1}H NMR spectrum of **8**[B(C_6F_5)$_4$]□py in 1,2-dichlorobenzene-*d*$_4$, *$C_6Cl_2D_3H$, **free pyridine, ***Et_2O, # unidentified impurity.

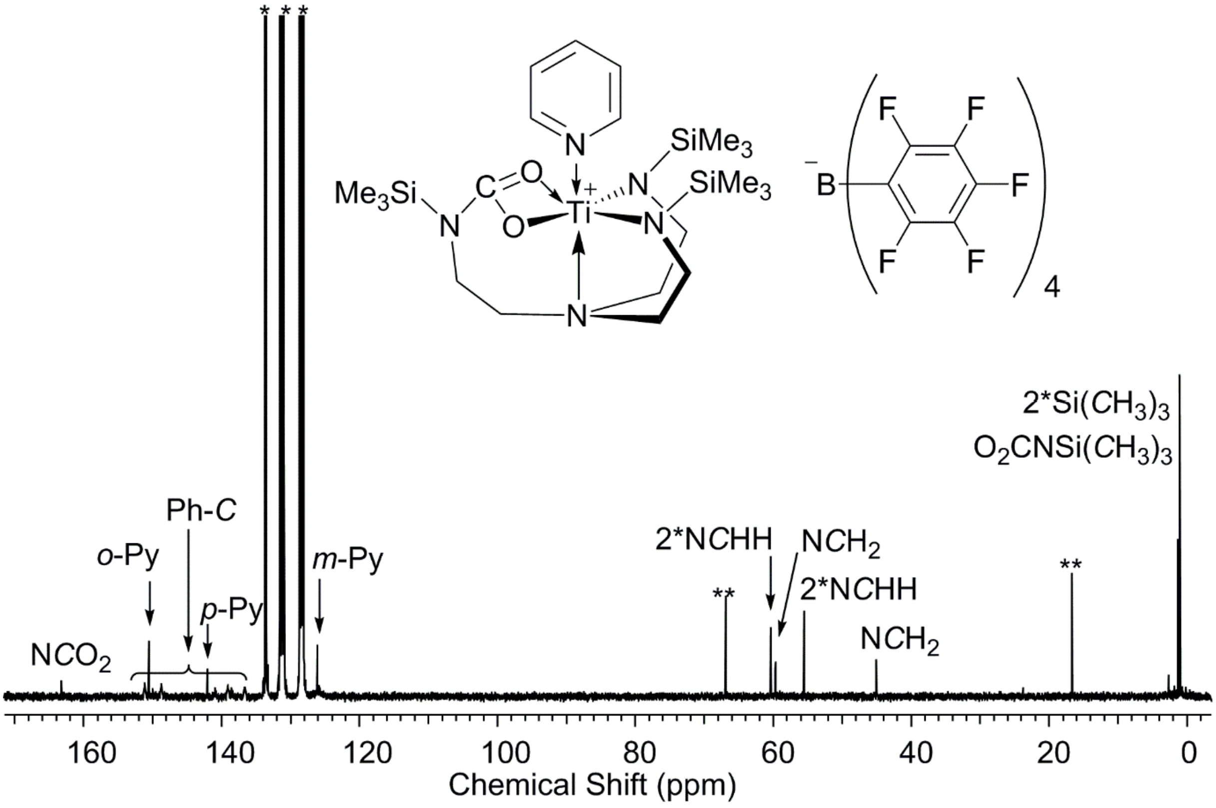

Figure S48. $^{13}C\{^1H\}$ NMR spectrum of **8**[B(C_6F_5)$_4$]□py in 1,2-dichlorobenzene-*d*$_4$, *$C_6Cl_2D_4$, **Et_2O.

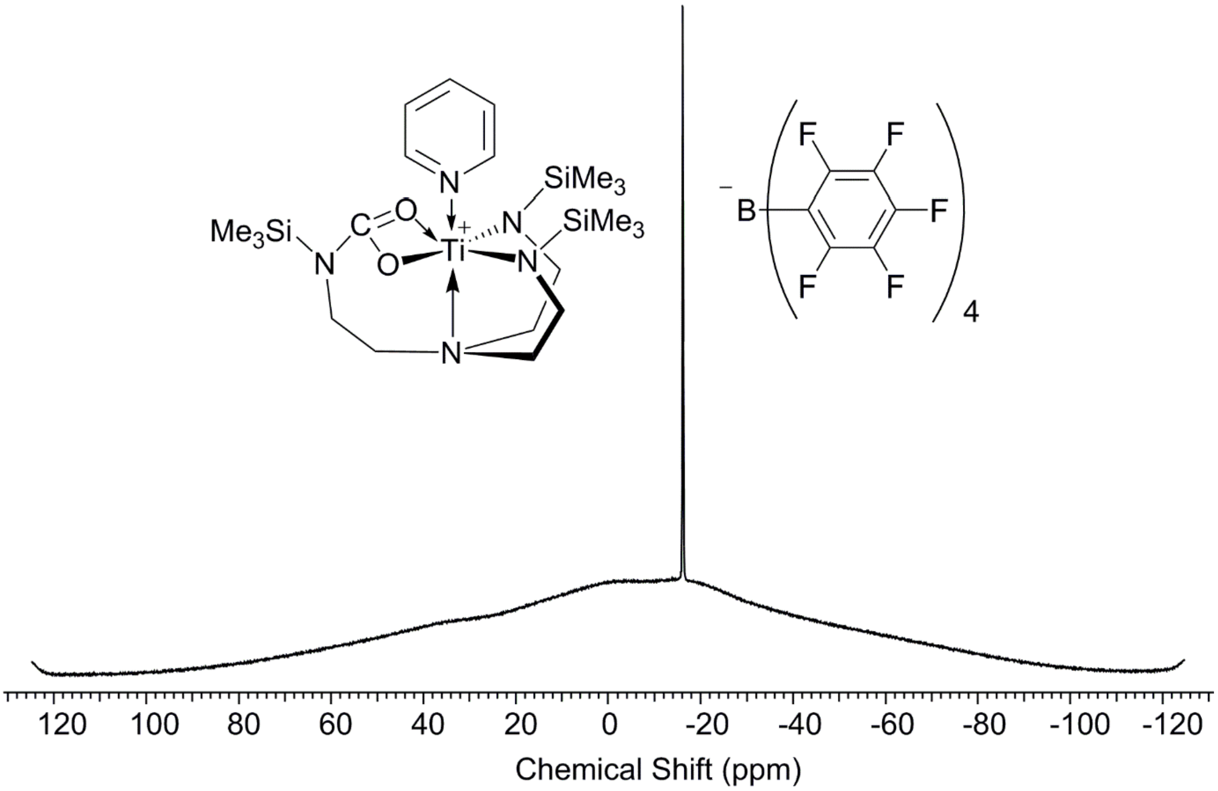

Figure S49. ^{11}B{^{1}H} NMR spectrum of **8**[B(C$_6$F$_5$)$_4$]□py in 1,2-dichlorobenzene-*d*$_4$.

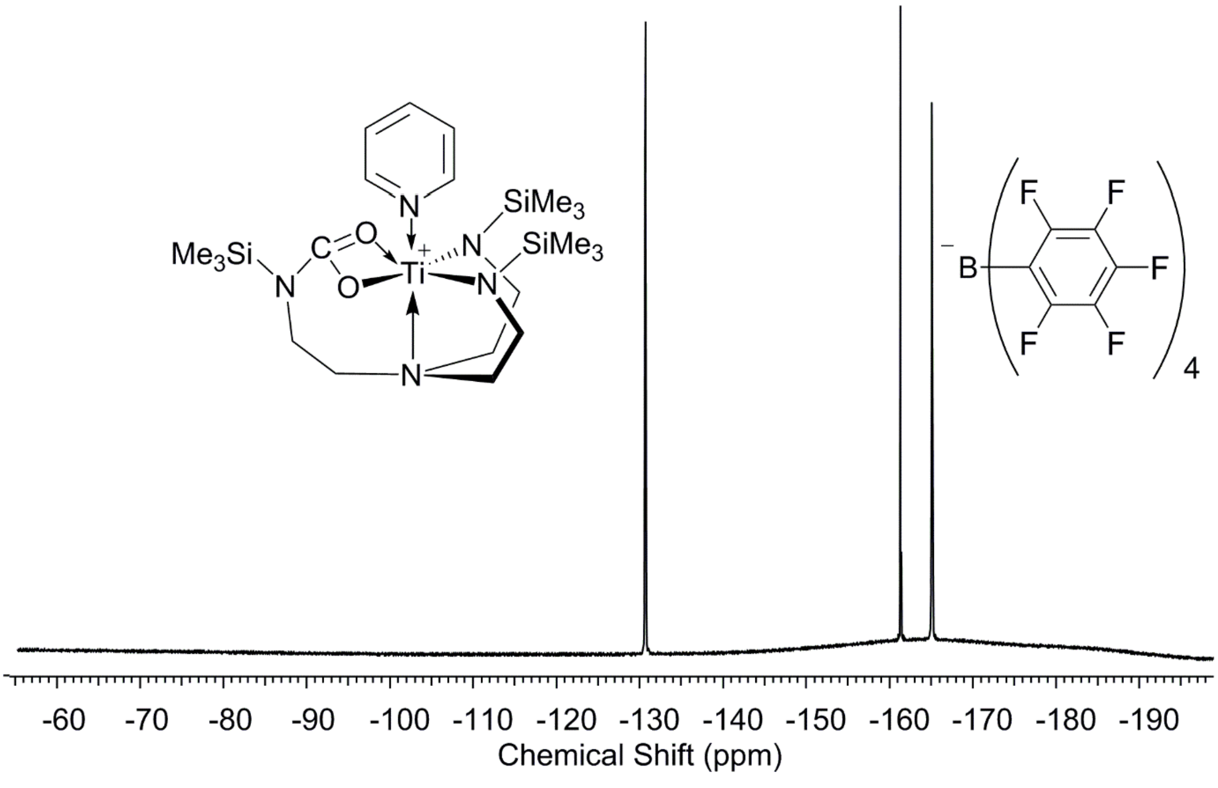

Figure S50. ^{19}F NMR spectrum of **8**[B(C$_6$F$_5$)$_4$]□py in 1,2-dichlorobenzene-*d*$_4$.

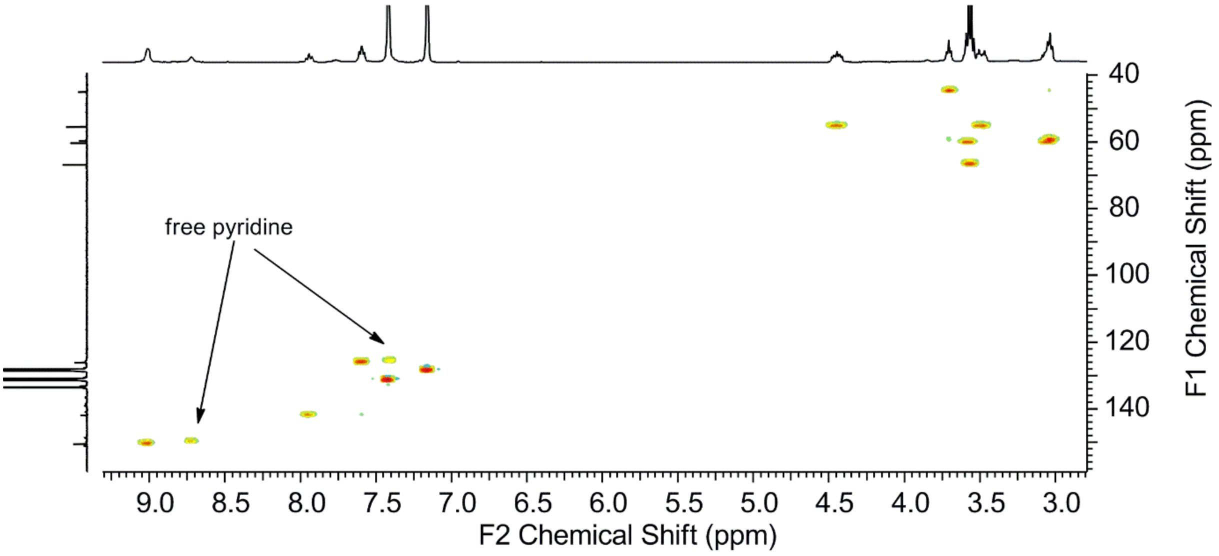

Figure S51. Extract from the HSQC spectrum of **8**[B(C_6F_5)$_4$]□py in 1,2-dichlorobenzene-*d*$_4$.

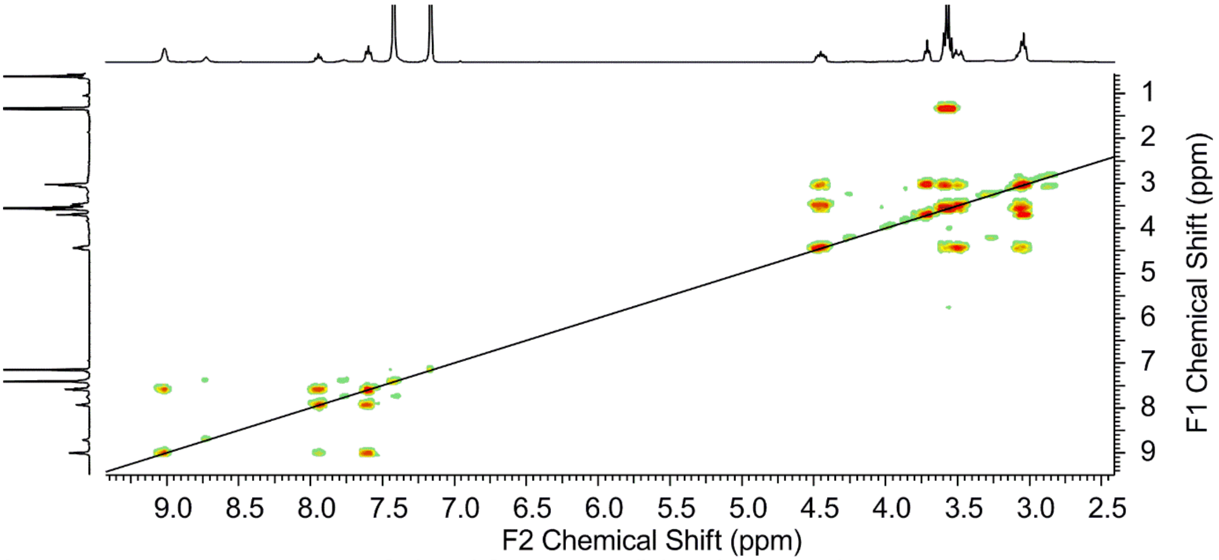

Figure S52. COSY spectrum of **8**[B(C_6F_5)$_4$]□py in 1,2-dichlorobenzene-*d*$_4$.

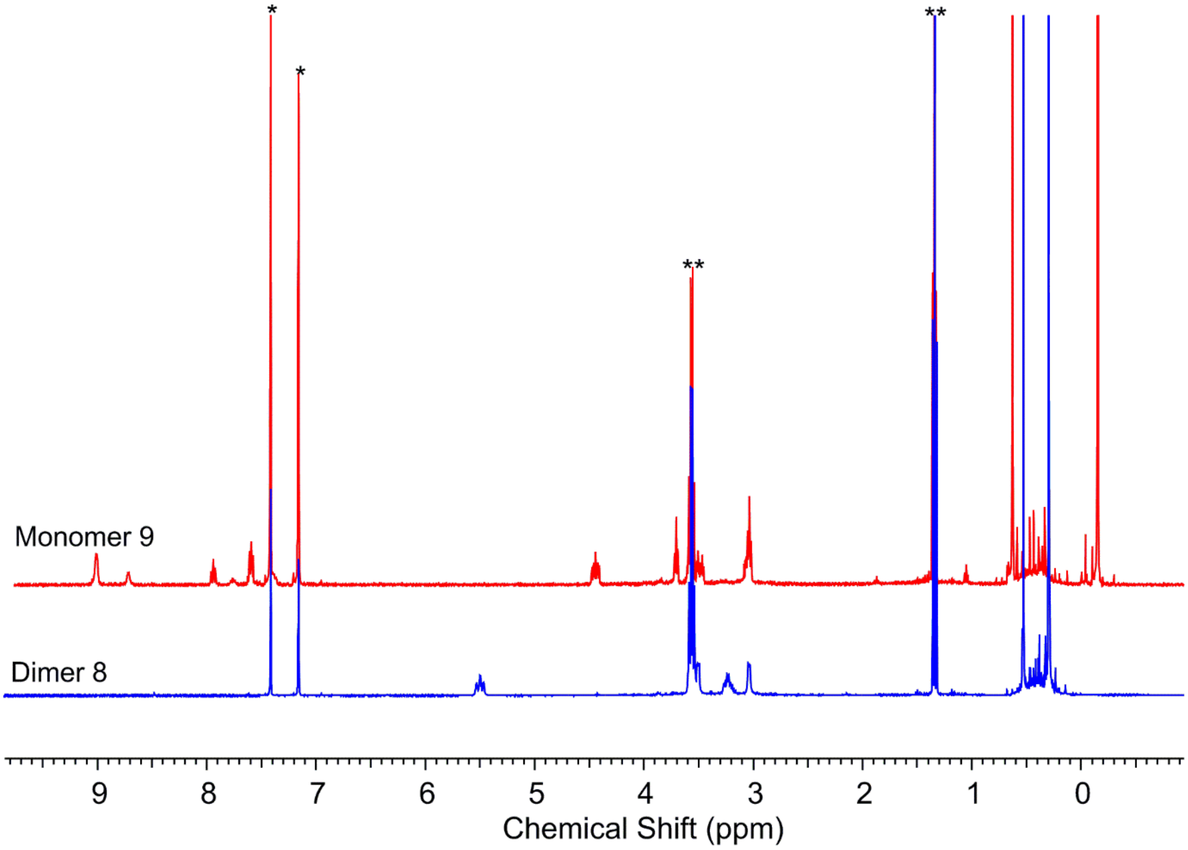

Figure S53. Comparison of the ^{1}H NMR spectra of 8[B(C_6F_5)$_4$]□py ("Monomer") and **7**[B(C_6F_5)$_4$]$_2$ ("Dimer") in 1,2-dichlorobenzene-*d*$_4$, *$C_5D_3Cl_2H$, **Et_2O.

14. $[\mathrm{Ti}\{\mathrm{N}(\mathrm{CH_2CH_2NSiMe_3})_2(\mathrm{CH_2CH_2NSiMe_3}(\mu\text{-}\mathrm{CS_2}\text{-}\eta S{:}\eta S'))\}]_2[\mathrm{B}(3,5\text{-}\mathrm{Cl_2C_6H_3})_4]_2$

($\mathbf{9}[\mathrm{B}(3,5\text{-}\mathrm{Cl_2C_6H_3})_4]_2$)

CS_2 (0.6 µL, 9 µmol) was added to a solution of **6**$[B(3,5\text{-}Cl_2C_6H_3)_4]$□$Et_2O$ (10 mg, 9 µmol) in 1,2-dichlorobenzene-d_4 (0.6 mL). The reaction mixture was allowed to stand at room temperature, which gave red crystals within 24 h. The liquor was decanted off, the crystals rinsed with *n*-pentane (1 mL), and dried under reduced pressure (8 mg, 4 µmol, 82% based on **6**$[B(3,5\text{-}Cl_2C_6H_3)_4]$□$Et_2O$). ^1H NMR (400 MHz, 1,2-dichlorobenzene-d_4): δ = 7.64 (m, 16H, *o*-Ph), 7.18 (t, $^3J_{HH}$ = 2.0 Hz, 8H, *p*-Ph), 4.08 (m, 4H, 4× NC*H*H), 3.73 (m, 8H, 4× NC*H*H and 2× NCH_2), 3.38 (t, $^3J_{HH}$ = 5.5 Hz, 4H, 2× NCH_2), 3.28 (m, 4H, 4× NC*H*H), 3.09 (m, 4H, 2× NC*H*H), 0.74 (s, 18H, 2× $S_2CNSi(CH_3)_3$), 0.41 (s, 36H, 2× $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (101 MHz, 1,2-dichlorobenzene-d_4): δ = 199.5 (NCS_2), 165.6 (quint., $^1J_{BC}$ = 49.4 Hz, *o-C*), 133.9 (t, $^2J_{BC}$ = 4.2 Hz, *m-C*), 133.8 (br. s, *o-C*), 124.0 (*p-C*), 55.7 (2× S_2CNCH_2), 53.2 (2× S_2CNCH_2), 53.1 (4× NCH_2), 51.1 (4× NCH_2) 1.0 (s, 4× $Si(CH_3)_3$), 0.4 (s, 2× $S_2CNSi(CH_3)_3$). $^{11}B\{^1H\}$ NMR (128 MHz, 1,2-dichlorobenzene-d_4): δ = −6.6 ($B(3,5\text{-}Cl_2C_6H_3)_4$). Anal. calcd. (found) for $C_{80}H_{102}N_8Si_6S_4B_2Cl_{16}Ti_2$ (2157.06 g□mol^{-1}) in %: C 44.55 (43.50), H 4.77 (4.49), N 5.19 (5.08). IR (KBr pellet): $\nu_{asym}(NCS_2)$ = 1562 cm^{-1} and 1543 cm^{-1}.

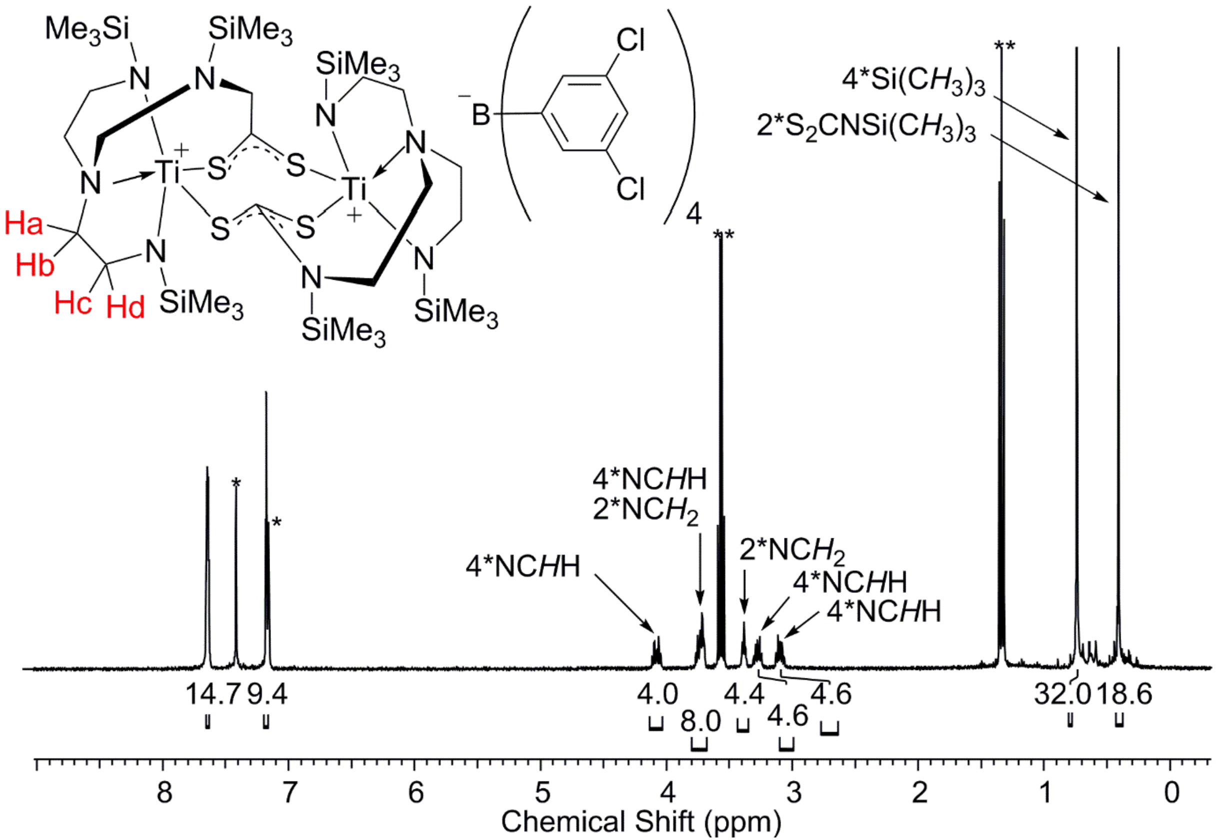

Figure S54. ^{1}H NMR spectrum of **9**[B(3,5-$Cl_2C_6H_3$)$_4$]$_2$ in 1,2-dichlorobenzene-*d*$_4$, *$C_6Cl_2D_3H$, **Et_2O.

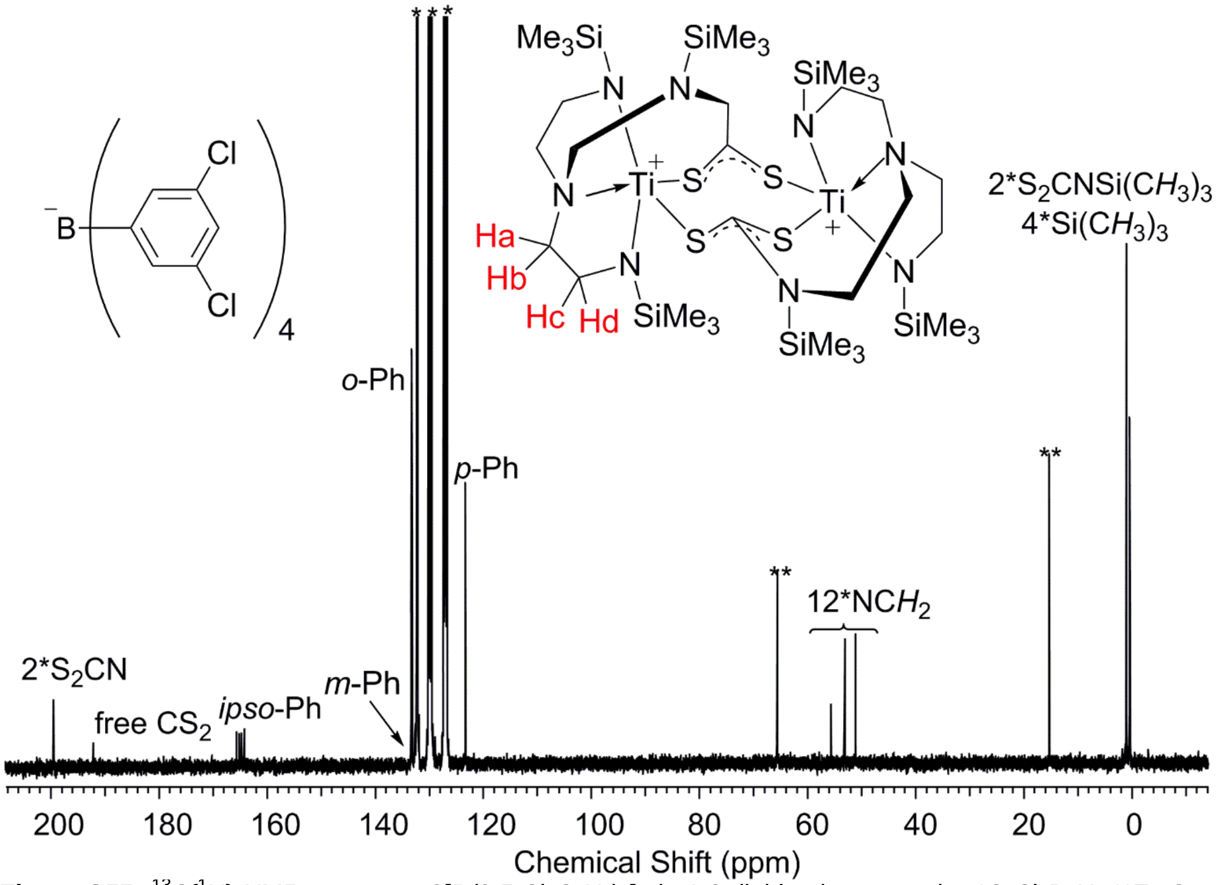

Figure S55. ^{13}C{^{1}H} NMR spectrum **9**[B(3,5-$Cl_2C_6H_3$)$_4$]$_2$ in 1,2-dichlorobenzene-*d*$_4$, *$C_6Cl_2D_3H$, **Et_2O.

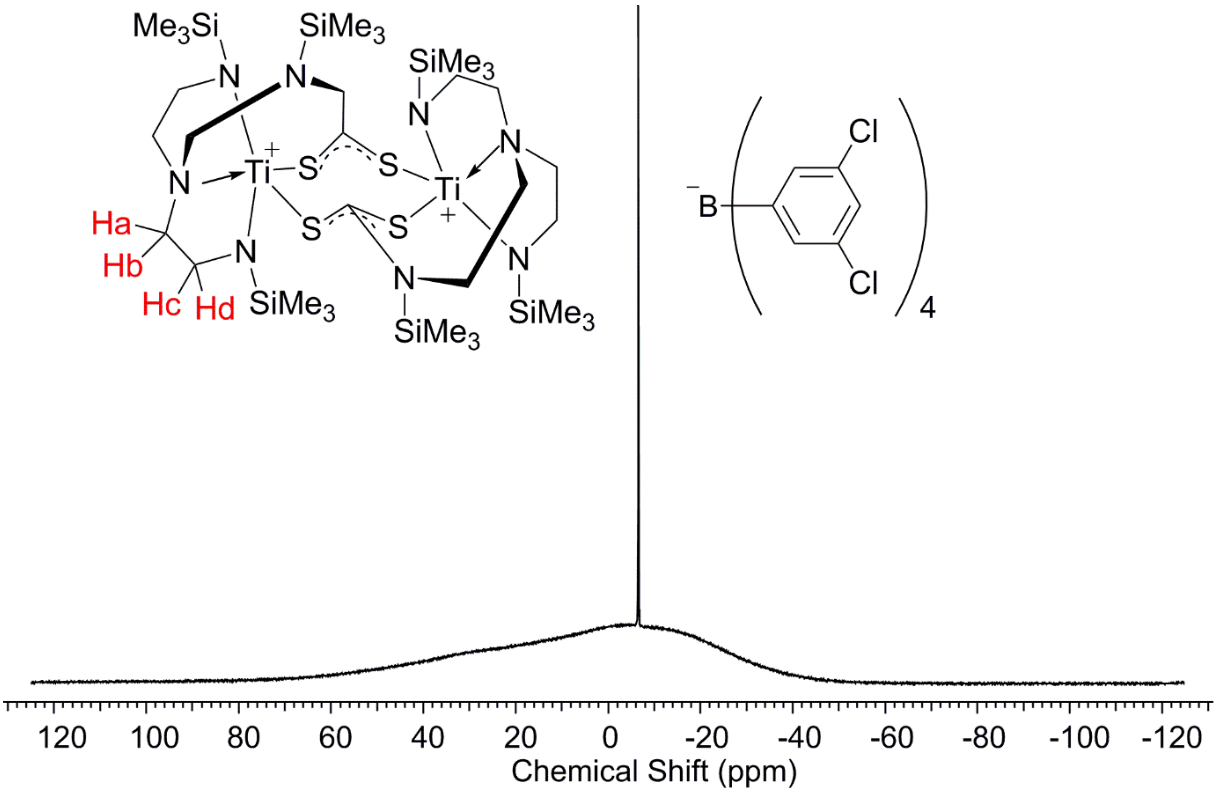

Figure S56. $^{11}B\{^{1}H\}$ NMR spectrum of **9**[B(3,5-$Cl_2C_6H_3$)$_4$]$_2$ in 1,2-dichlorobenzene-*d*$_4$.

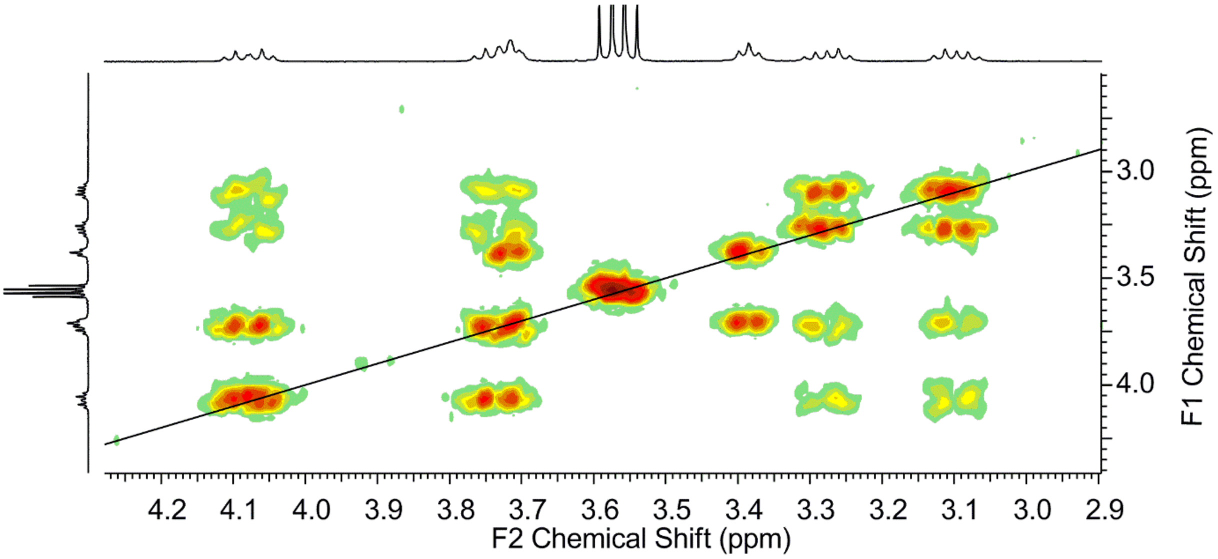

Figure S57. Extract from the COSY spectrum of **9**[B(3,5-$Cl_2C_6H_3$)$_4$]$_2$ in 1,2-dichlorobenzene-*d*$_4$.

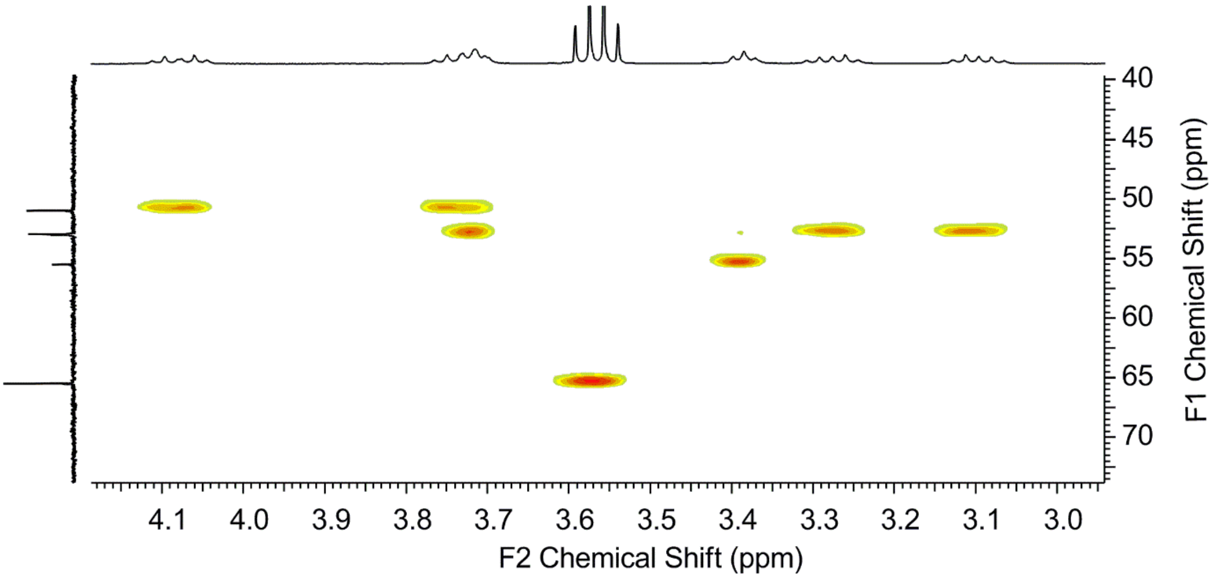

Figure S58. Extract from the HSQC spectrum of **9**[B(3,5-$Cl_2C_6H_3$)$_4$]$_2$ in 1,2-dichlorobenzene-*d*$_4$.

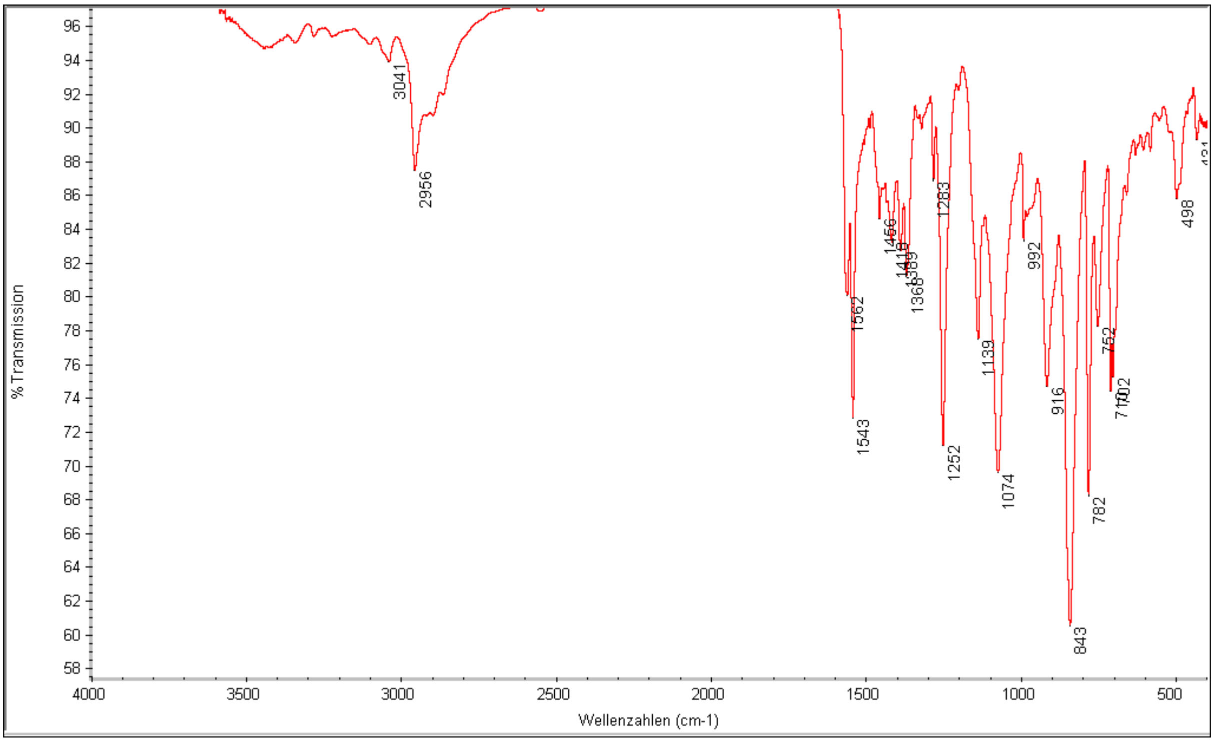

Figure S59. IR spectrum of **9**[B(3,5-$Cl_2C_6H_3$)$_4$]$_2$ in a KBr pellet.

15. $[(\mathrm{Ti}(N_3N))_2(\mu\text{-OCHO-}\eta O{:}\eta O')][\mathrm{B}(3,5\text{-}\mathrm{Cl}_2\mathrm{C}_6\mathrm{H}_3)_4]$ $(\mathbf{10}[\mathrm{B}(3,5\text{-}\mathrm{Cl}_2\mathrm{C}_6\mathrm{H}_3)_4])$

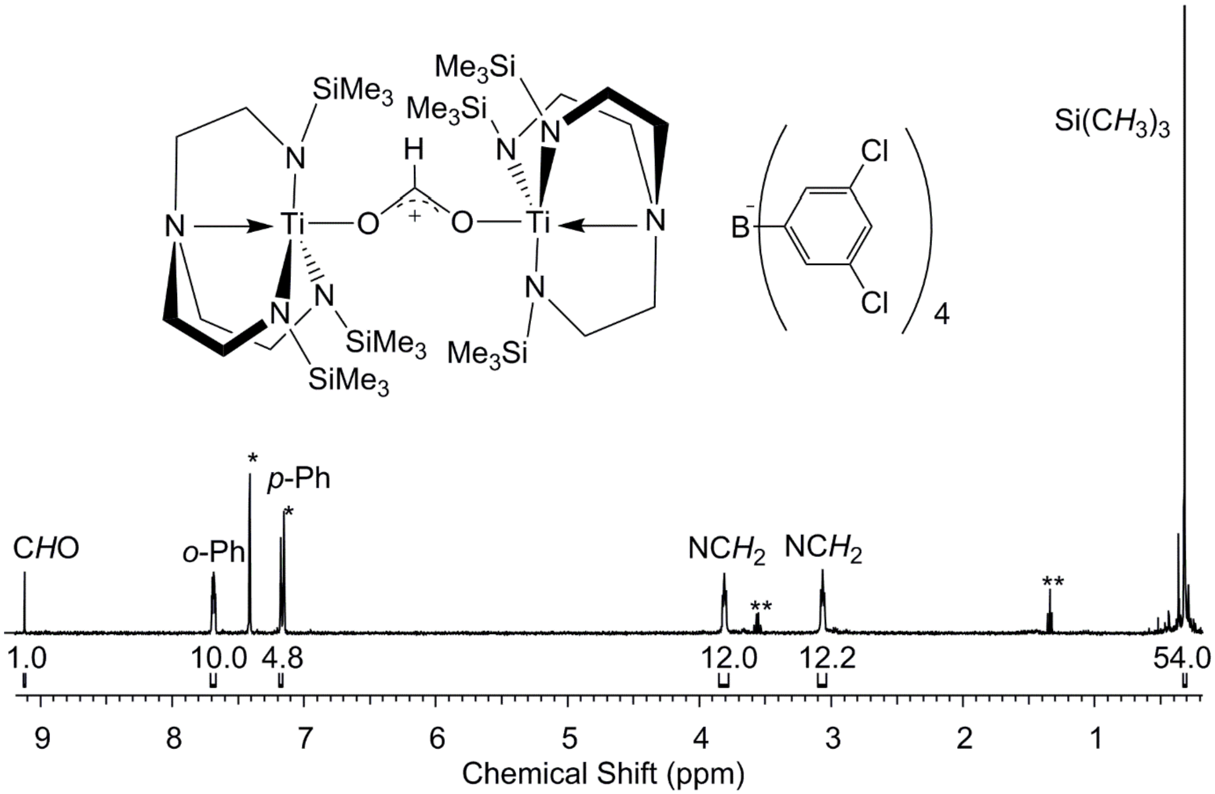

Figure S60. ^{1}H NMR spectrum of **10**[B(3,5-$\mathrm{Cl_2C_6H_3}$)$_4$] in 1,2-dichlorobenzene-d_4, *$\mathrm{C_6Cl_2D_3H}$, **$\mathrm{Et_2O}$.

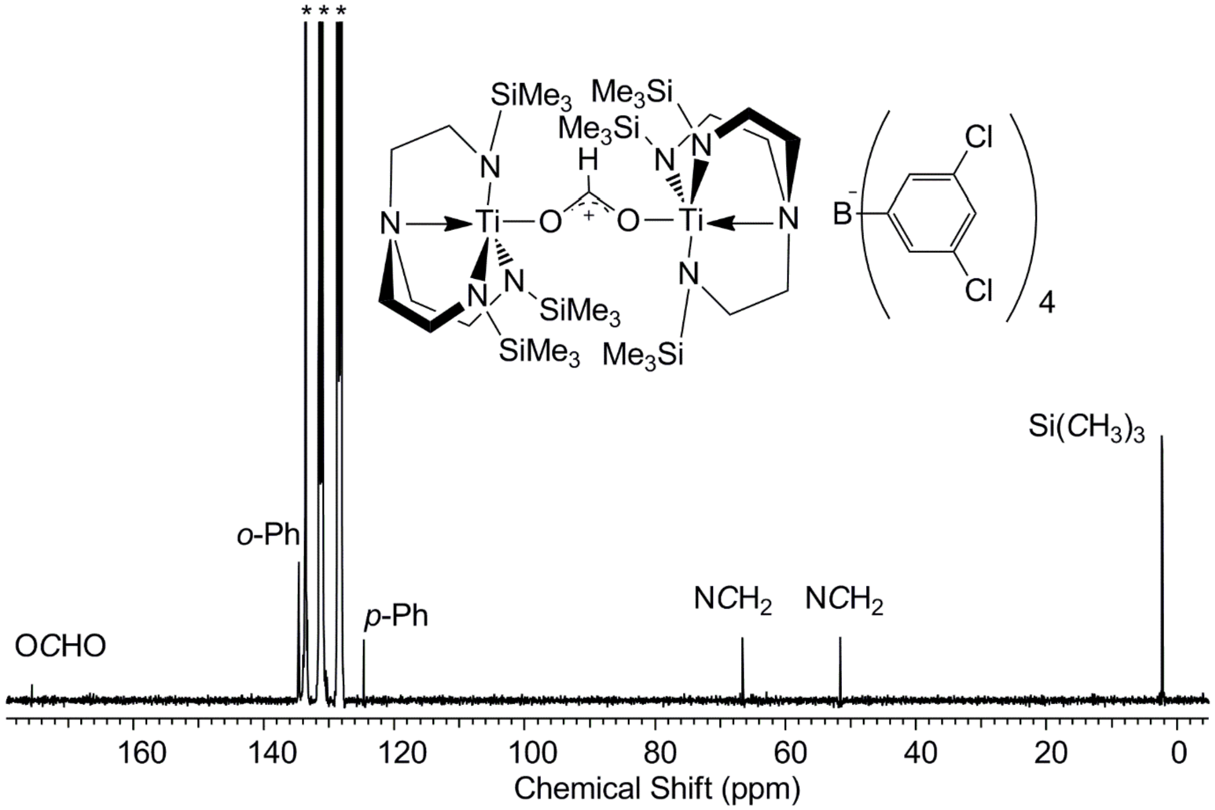

Figure S61. ^{13}C{^{1}H} NMR spectrum of **10**[B(3,5-$\mathrm{Cl_2C_6H_3}$)$_4$] in 1,2-dichlorobenzene-d_4, *$\mathrm{C_6Cl_2D_4}$.

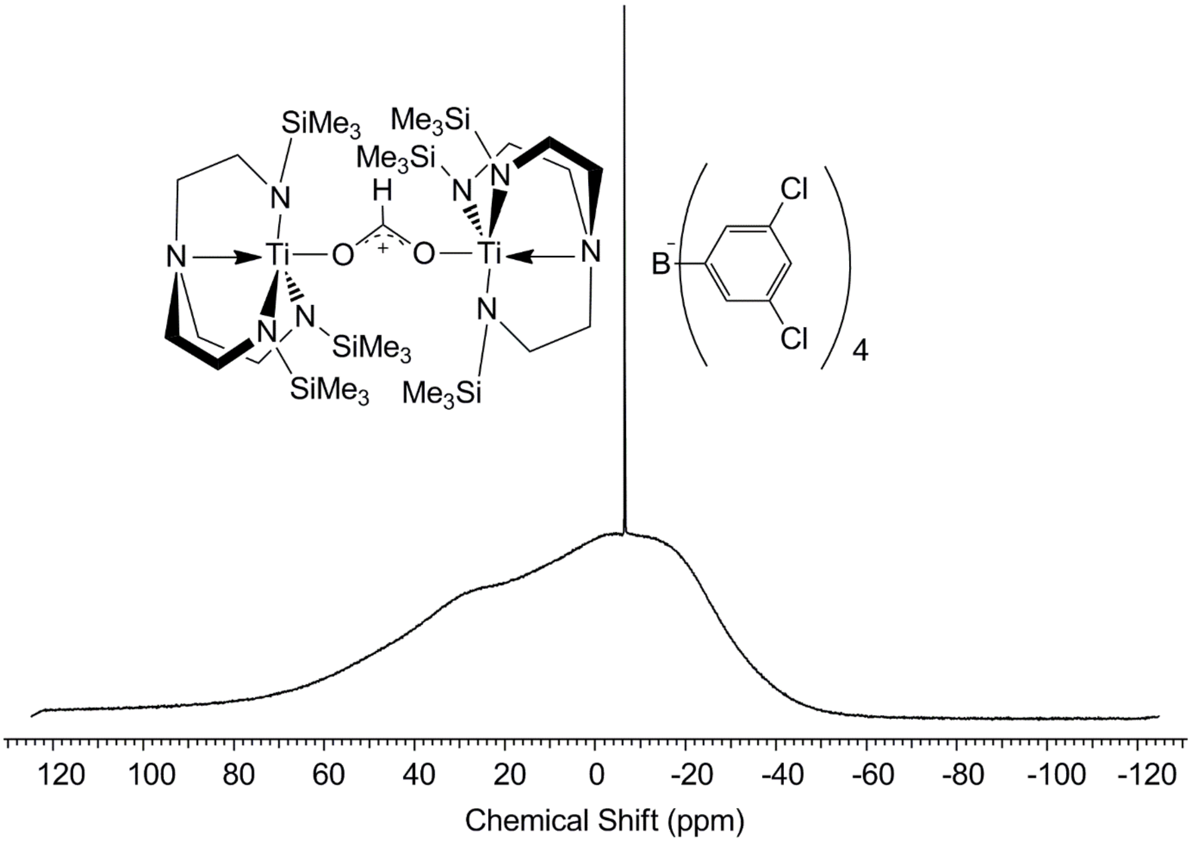

Figure S62. ^{11}B{^{1}H} NMR spectrum of **10**[B(3,5-Cl$_2$C$_6$H$_3$)$_4$] in 1,2-dichlorobenzene-*d*$_4$.

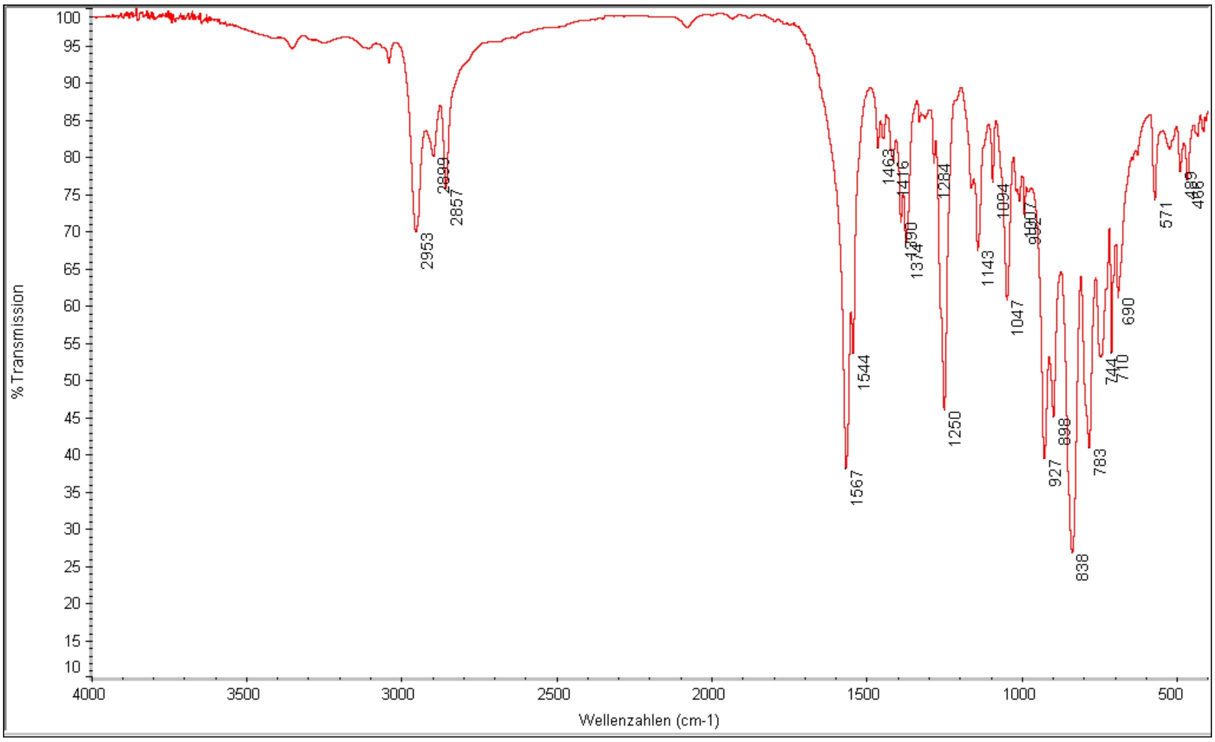

Figure S63. IR spectrum of **10**[B(3,5-Cl$_2$C$_6$H$_3$)$_4$] in a KBr pellet.

16. $[(\mathrm{Ti}(N_3N))_2(\mu\text{-OCHO-}\eta O{:}\eta O')][\mathrm{B(C_6F_5)_4}]$ ($\mathbf{10}[\mathrm{B(C_6F_5)_4}]$)

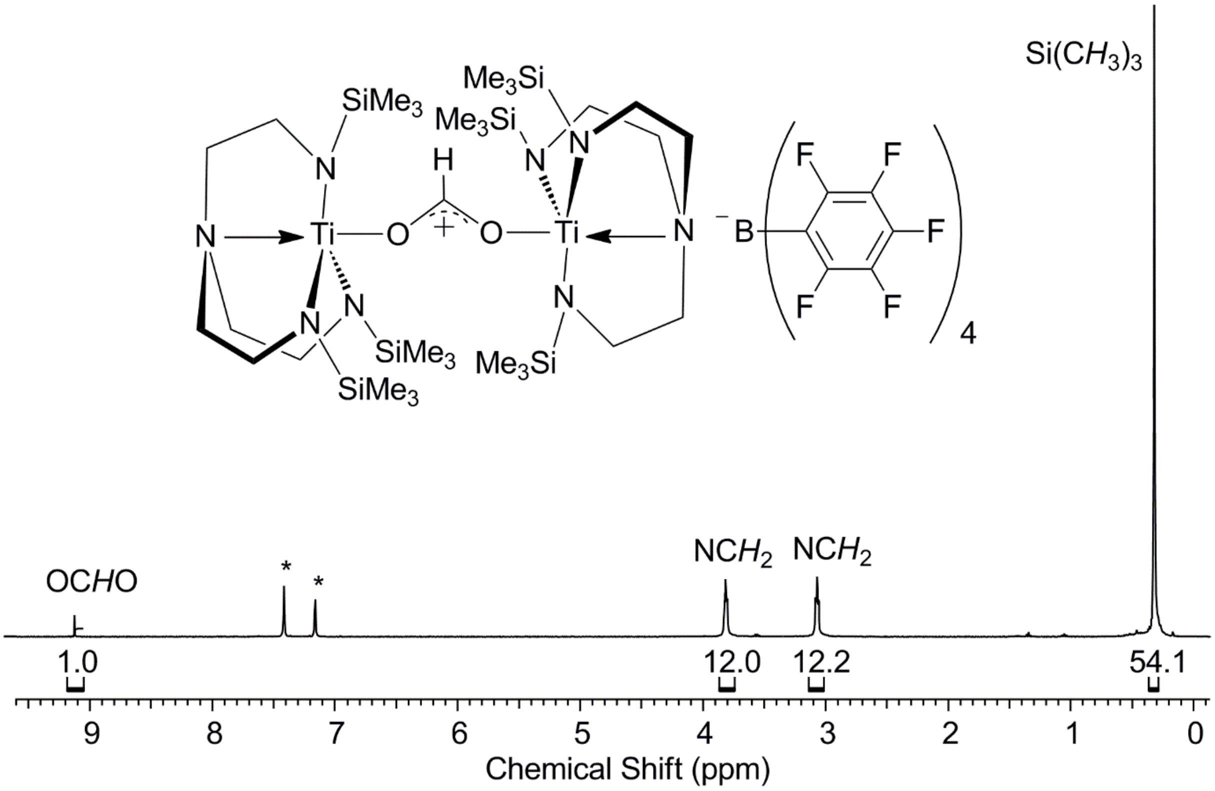

Figure S64. ^{1}H NMR spectrum of **10**[B(C_6F_5)$_4$] in 1,2-dichlorobenzene-d_4, *$C_6Cl_2D_3H$.

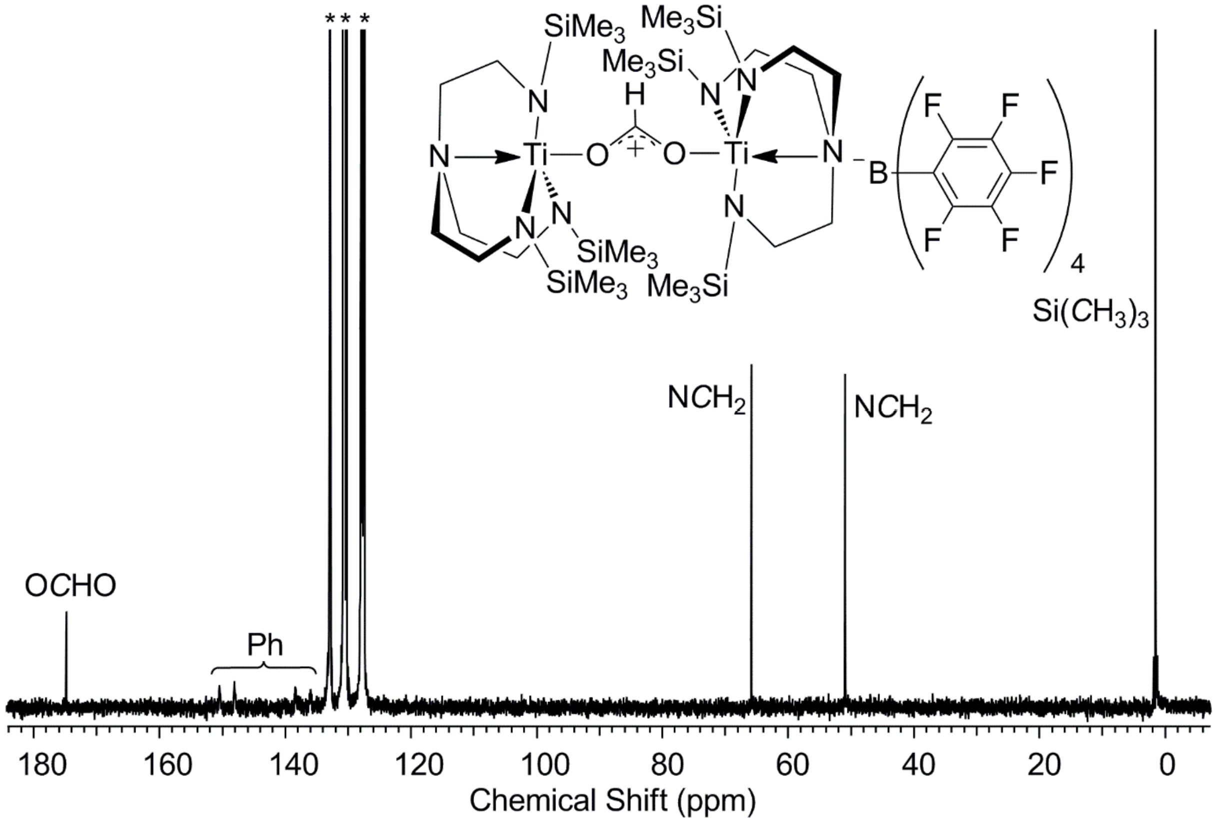

Figure S65. ^{13}C{^{1}H} NMR spectrum of **10**[B(C_6F_5)$_4$] in 1,2-dichlorobenzene-d_4, *$C_6Cl_2D_4$.

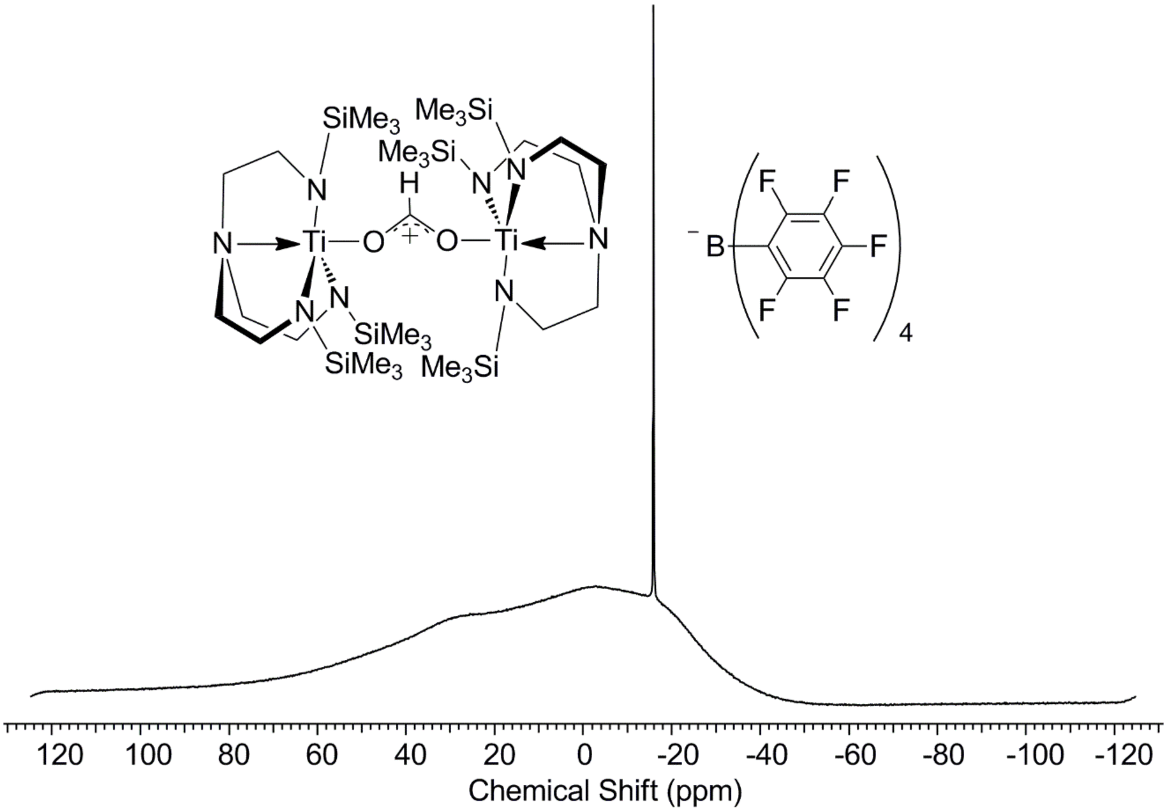

Figure S66. $^{11}B\{^{1}H\}$ NMR spectrum of **10**[B(C_6F_5)$_4$] in 1,2-dichlorobenzene-*d*$_4$.

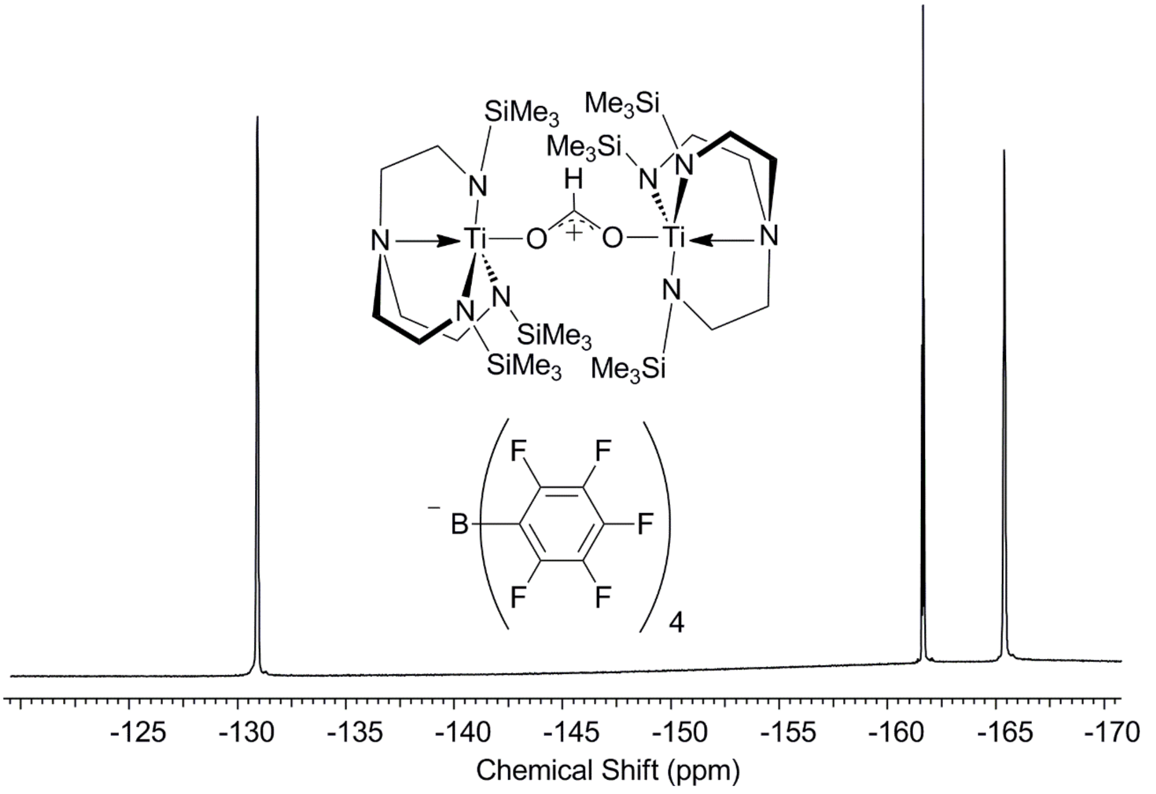

Figure S67. ^{19}F NMR spectrum of **10**[B(C_6F_5)$_4$] in 1,2-dichlorobenzene-*d*$_4$.

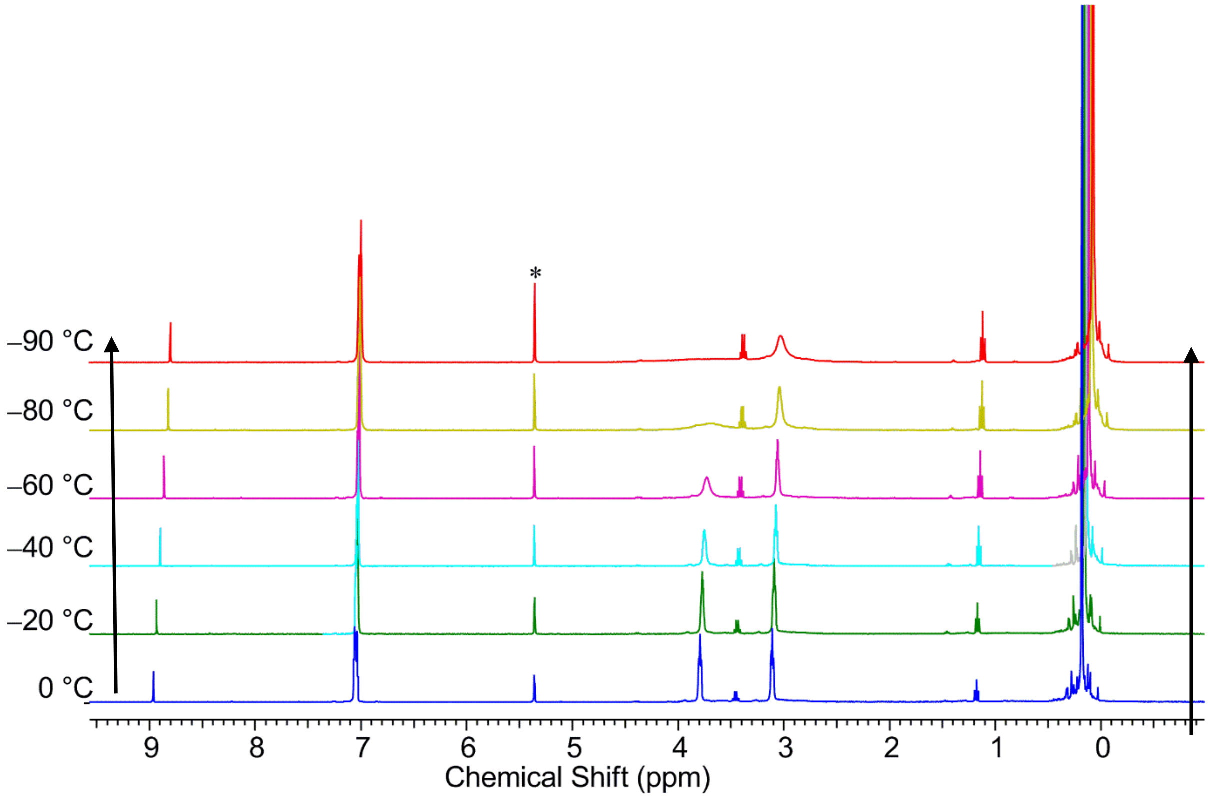

Figure S68. Stacked VT NMR spectra of **10**[B(C_6F_5)$_4$] in dichloromethane-*d*$_2$ from 0 °C to –90 °C.

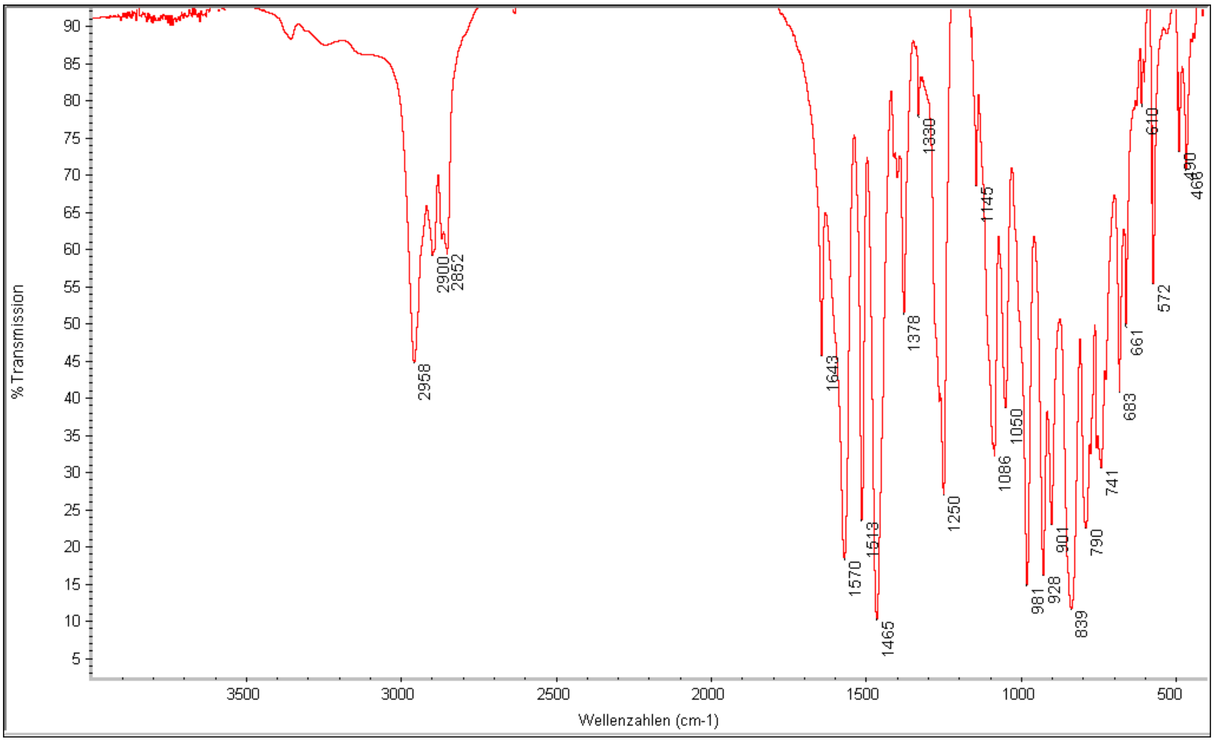

Figure S69. IR spectrum of **10**[B(C_6F_5)$_4$] in a KBr pellet.

X-ray crystallography

X-ray diffraction data of **4**, **6**[B(3,5-$Cl_2C_6H_3)_4$]·Et_2O, **6**[B(3,5-$Cl_2C_6H_3)_4$]·py, **7**, and **10** were collected at –173 °C on a Bruker D8 goniometer with an APEX CCD area-detector in ω-scan mode. Mo-Kα radiation (multilayer optics, λ = 0.71073 Å) from an Incoatec microsource was used. The SMART program package was used for the data collection and unit cell determination; processing of the raw frame data was performed using SAINT,[5] absorption corrections were applied with SADABS.[6] The structures were solved by direct methods using SIR-92.[7]

The crystal lattice of **7** shows crystallographic C_i symmetry for the molecular cation around a center of inversion (Wyckoff letter 2*e*). Each of the structures **6**[B(3,5-$Cl_2C_6H_3)_4$]·Et_2O and **6**[B(3,5-$Cl_2C_6H_3)_4$]·py was found with two crystallographically independent molecular cations as well as two molecular anions.

The refinements were carried out against F^2 with SHELXL-2013[8] as implemented in the program system WinGX.[9] In the refinement, all reflections were used except for the reflection 1 −1 1 in **6**[B(3,5-$Cl_2C_6H_3)_4$]·py and the reflection 0 0 1 in **7** that were omitted because they were most likely affected by the beam stop. The structure of **6**[B(3,5-$Cl_2C_6H_3)_4$]·Et_2O was refined as an inversion twin. In the structure of **6**[B(3,5-$Cl_2C_6H_3)_4$]·Et_2O, the methyl carbon atoms C14 and C15 as well as the atoms Si4, N7, C46, C48, and C52 of the second independent molecule were disordered. The disorder was modelled with split positions. All non-hydrogen atoms were refined with anisotropic displacement parameters. Because of the disorder in the structure of **6**[B(3,5-$Cl_2C_6H_3)_4$]·Et_2O, the atoms C14, C15, C16, N7, and C46 were refined with isotropic displacement parameters. Refinement results are given in Table S1 and in Table S2.

All hydrogen atoms were included in idealized position and treated as riding. Only the hydrogen atom H1 in **10** that belongs to the formyl unit was located in a Fourier difference map and its position was refined with an isotropic displacement parameter. Graphical representations were performed with the program DIAMOND.[10]

Table S1. Crystallographic data of compounds **4**, **6**[B(3,5-$Cl_2C_6H_3)_4]\cdot Et_2O$ and **6**[B(3,5-$Cl_2C_6H_3)_4]\cdot$py.

	4	**6**[B(3,5-$Cl_2C_6H_3)_4]\cdot Et_2O$	**6**[B(3,5-$Cl_2C_6H_3)_4]\cdot$py
formula	$C_{15}H_{39}N_4KOSi_3Ti$	$C_{24}H_{12}BCl_8$,$C_{19}H_{49}N_4OSi_3Ti$	$C_{24}H_{12}BCl_8$,$C_{20}H_{44}N_5Si_3Ti$
Fw /g·mol^{-1}	462.77	1076.53	1081.51
color, habit	colourless, block	yellow, block	orange, fragment
crystal size / mm	0.15 × 0.20 × 0.28	0.09 × 0.20 × 0.27	0.30 × 0.30 × 0.35
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$	$Pca2_1$	P-1
a / Å	10.2840(15)	24.6983(14)	16.8069(18)
b / Å	10.5727(15)	17.2605(10)	17.8453(19)
c / Å	23.865(3)	24.7312(14)	17.9679(19)
α / °			94.240(2)
β / °	100.149(3)		92.638(3)
γ / °			92.916(3)
V / Å^3	2554.2(6)	10543.0(10)	5360.6(10)
Z	4	8	4
d_{calc}/Mg·m^{-3}	1.203	1.356	1.340
μ(MoKα)/mm^{-1}	0.650	0.673	0.661
F(000)	992	4480	2240
θ range / °	2.01–25.10	1.18–30.51	1.14–26.55
index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-28 \le l \le 28$	$-35 \le h \le 35$, $-24 \le k \le 24$, $-35 \le l \le 35$	$-21 \le h \le 21$, $-22 \le k \le 22$, $-22 \le l \le 22$
refln.	27064 (0.0873)	158987 (0.1287)	66527 (0.1127)
indep. refl. (R_{int})	4549	31318	22235
observed reflns	3489	17922	13949
data/restr./param	4549 / 0 / 235	31318 / 1 / 1143	22235 / 0 / 1135
R_1, $wR2$ [$I > 2\sigma(I)$]	0.0405, 0.0882	0.0401, 0.0661	0.0612, 0.1271
R_1, $wR2$ (all data)	0.0597, 0.0972	0.0818, 0.0731	0.1107, 0.1494
GooF on F^2	1.025	0.675	1.015
largest diff. peak, hole/ e·Å^3	0.380, −0.281	0.546, −0.395	1.200, −0.957
CCDC number	1586682	1586683	1586684

Table S2. Crystallographic data of compounds **7** and **10**.

	7	**10**
formula	$C_{32}H_{78}N_8O_4Si_6Ti$, $2(C_{24}H_{12}BCl_8)$	$C_{31}H_{79}N_8O_2Si_6Ti_2$, $C_{24}BF_{20}$
Fw /g·mol^{-1}	2092.85	1539.41
color, habit	yellow, block	yellow, rod
crystal size / mm	0.13 × 0.24 × 0.30	0.16 × 0.17 × 0.30
crystal system	triclinic	monoclinic
space group	P-1	$P2_1/c$
a / Å	13.750(5)	11.2553(7)
b / Å	14.046(6)	27.0488(17)
c / Å	14.333(6)	23.3434(15)
α / °	85.429(7)	
β / °	88.237(7)	91.2981(13)
γ / °	60.975(6)	
V / Å^3	2412.7(17)	7104.9(8)
Z	1	4
d_{calc}/Mg·m^{-3}	1.440	1.439
μ(MoKα)/mm^{-1}	0.734	0.423
F(000)	1080	3176
θ range / °	2.11–26.71	1.15–25.05
index ranges	$-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-18 \leq l \leq 17$	$-13 \leq h \leq 13$, $-32 \leq k \leq 32$, $-27 \leq l \leq 27$
refln.	29139 (0.1311)	77161 (0.1193)
indep. refl. (R_{int})	10136	12551
observed reflns.	5463	8172
data/restr/param	29136 / 0 / 541	12551 / 0 / 869
R_1, $wR2$ [$I > 2\sigma(I)$]	0.0952, 0.2399	0.0388, 0.0623
R_1, $wR2$ (all data)	0.1729, 0.2853	0.0655, 0.0688
GooF on F^2	1.045	0.797
largest diff. peak, hole/ e·Å^3	1.949, −1.298	0.349, −0.364
CCDC number	1586685	1586686

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