Electronic Supporting Information

Dihydrogen cleavage by a dimetalloxycarbene-borane frustrated Lewis pair

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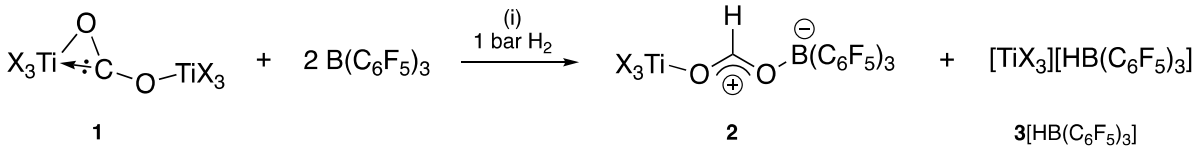
Content

1. General considerations

All manipulations were performed under argon atmosphere using standard Schlenk or glove box techniques. Prior to use, glassware was dried overnight at 130 °C and solvents were dried, distilled and degassed using standard methods. NMR measurements were performed on a Bruker DRX 400 at 24 °C unless otherwise mentioned. Deuterated solvents for NMR spectroscopy were obtained from *eurisotop*. The chemical shifts δ in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported in ppm relative to tetramethylsilane if not indicated otherwise.[1] ^{11}B and ^{19}F NMR spectra were referenced to external $BF_3.OEt_2$. Abbreviations for NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), quint. (quintet), sept. (septet), br. (broad), *J* (coupling constant). IR spectra were measured on KBr pellets using an AVATAR 360 FT-IR spectrometer, and the bands were reported in cm^{-1}. Abbreviations for IR spectra: w (weak), m (medium), s (strong), br. (broad). The ligand *N*-(*tert*-butyl)-3,5-dimethylanilide is abbreviated as "N[^{t}Bu]Ar" with Ar = 3,5-Me_2-C_6H_3 or simply "X". The starting materials $B(C_6F_5)_3$,[2] [Ti(N[^{t}Bu]Ar)$_3$],[3] [Ti(N[^{t}Bu]Ar)$_3$($O^{13}CHO$)] and [(Ti(N[^{t}Bu]Ar)$_3$)$_2$(μ-CO_2-η^2*O*,*C*:η*O*′)] (**1**)[4] were prepared according to reported procedures. The NMR-standard 1,3,5-trimethoxybenzene (99%) was purchased from *Alfa Aesar* and was dried at reduced pressure and 80 °C for 48 h. Elemental analyses were performed by the department of organic chemistry of the RWTH on Elementar varioEL and Elementar varioEL cube. High resolution mass spectra were recorded in THF solution on a Thermo Finnigan LCQ Deca XP Plus spectrometer using the Electron Spray Ionization (ESI) method. H_2 (99.9990%) was purchased from Praxair and used as obtained. D_2 was purchased from *Air Products GmbH* and used as obtained. Argon (99.998% at the Schlenk line and 99.996% at the glovebox) was purchased from *Westfalen AG*. General abbreviations: equiv. (equivalents), *t* (time) in s (seconds), *T* (temperature) in K (Kelvin), *Θ* (temperature) in °C (degree Celsius), r.t. (room temperature, 20-24 °C).

2. Experimental

2.1. Reaction of [(Ti(N[^{t}Bu]Ar)$_3$)$_2$(CO$_2$)]·B(C$_6$F$_5$)$_3$ with H$_2$



1 **2** **3**[HB(C$_6$F$_5$)$_3$]

Scheme S1. (i) benzene or toluene, −196 °C - 24 °C, 2 h.

An orange suspension of **1** (70.0 mg, 58.5 µmol) and B(C$_6$F$_5$)$_3$ (59.9 mg, 117 µmol, 2 equiv.) was prepared in toluene (4 mL). The reaction mixture was subjected to three cycles of freeze-pump-thaw. Dihydrogen (1 bar) was introduced to the still frozen suspension. The reaction mixture was then allowed to warm to room temperature. Upon thawing, vigorous stirring was pursued. A dark-red solution formed within 30 min. After stirring for another 90 min, the volatiles were removed under reduced pressure in a warm water bath (50 °C). The remaining red gelatinous material was triturated once with a mixture of *n*-hexane and diethyl ether (v:v = 10:1, 2 mL). The residue was rinsed with *n*-hexane (4 × 1 mL) until the filtrates were merely yellow. Each rinsing proceeded *via* stirring for at least 10 min before removing the liquor and combining it in a separate glass vial. The remaining red substance |**A**| and the orange filtrate |**B**| were dried or concentrated under reduced pressure, respectively.

|**A**| was recrystallized from a concentrated solution in diethyl ether at –40 °C. The red, chunky crystals were isolated by decantation and rinsing with *n*-hexane (0.5 mL). Another crop was collected likewise after concentration of the mother liquor. Drying of the combined crops under reduced pressure gave [Ti(N[^{t}Bu]Ar)$_3$][HB(C$_6$F$_5$)$_3$] (**3**[HB(C$_6$F$_5$)$_3$]) as a red-orange powder (38.1 mg, 35.0 µmol, 60 % based on **1**). Red crystals suitable for X-ray diffraction studies were grown within five days from a concentrated diethyl ether solution in an atmosphere of *n*-hexane at room temperature.

3[HB(C$_6$F$_5$)$_3$]:[5]

^{1}H NMR (chloroform-*d*$_1$, 400 MHz): δ = 7.47 (br. s, 3H, *o*-C*H*), 7.31 (s, 3H, *p*-C*H*), 3.84 (s, 3H, *o*-C*H*), 2.43 & 2.06 (2 × br. s, 18H, *m*-C*H*$_3$) 1.30 (s, 27H, C(C*H*$_3$)$_3$).

^{11}B{^{1}H} NMR (chloroform-*d*$_1$, 128 MHz): δ = −24.7 (s, H–*B*(C$_6$F$_5$)$_3$).

^{11}B NMR (chloroform-d_1, 128 MHz): δ = −24.4 (d, $^{1}J_{BH}$ = 88.0 Hz, H–*B*(C_6F_5)$_3$).

^{13}C{^{1}H} NMR (chloroform-d_1, 101 MHz): δ = 149.6 (br. s), 147.2 (br. s), 144.8 (*m*-*C*), 139.5 (*o*-*C*H), 139.2, 137.7, 136.6, 135.3, 134.8 (*p*-*C*H), 114.3 (br. s), 66.4 (s, *C*(CH_3)$_3$), 30.7 (C(*C*H_3)$_3$), 21.5 (*m*-*C*H_3).

^{19}F NMR (chloroform-d_1, 376 MHz): δ = −133 (d, $^{3}J_{FF}$ = 22 Hz, 6F, *o*-*F*), −165 (t, $^{3}J_{FF}$ = 20 Hz, 3F, *p*-*F*), −167 (td, $^{3}J_{FF}$ = 20 Hz, $^{4}J_{FF}$ = 7 Hz, 6F, *m*-*F*).

CHN Elemental Analysis for $C_{54}H_{55}N_3BF_{15}Ti$ (M = 1089.88 g·mol^{-1}) %found (calcd.): C 58.57 (59.51), H 5.27 (5.09), N 3.76 (3.85).

IR (KBr pellet): ν = 2980, 2417 br (ν_{BH}), 1640 w, 1599, 1509 s, 1464 s, 1185, 1115, 1106, 1092, 969 s, 714.

|**B**| was recrystallized at –40 °C from concentrated solutions in diethyl ether or *n*-hexane, respectively. Crystals grown from diethyl ether were subjected to X-ray diffraction studies. Good yields for the orange [(N[^{t}Bu]Ar)$_3$Ti(μ-OCHO-η*O*:η*O*′)B(C_6F_5)$_3$] (**2**) were obtained by trituration of the filtrate with benzene (0.5 mL) and drying under reduced pressure while vigorously stirring (41.1 mg, 36.2 μmol, 62 % based on **1**).

2:

^{1}H NMR (chloroform-d_1, 400 MHz): δ = 6.75 (s, 3H, *p*-C*H*), 6.53 (s, 6H, *o*-C*H*), 5.84 (s, 1H, OC*H*O), 2.21 (s, 18H, *m*-CH_3), 1.18 (s, 27H, C(CH_3)$_3$).

^{11}B NMR (chloroform-d_1, 128 MHz): δ = –1.8 (br. s, *B*(C_6F_5)$_4$).

^{13}C{^{1}H} NMR (chloroform-d_1, 101 MHz): δ = 173.1 (O*C*HO), 142.8 (*ipso*-*C*), 137.9 (*m*-*C*), 129.4 (*o*-*C*H), 128.5 (*p*-*C*H), 64.4 (*C*(CH_3)$_3$), 30.1 (C(*C*H_3)$_3$), 21.0 (*m*-*C*H_3).

^{19}F NMR (chloroform-d_1, 377 MHz): δ = –134 (dd, $^{3}J_{FF}$ = 24 Hz, $^{4}J_{FF,\,right}$ = 8 Hz, $^{4}J_{FF,\,left}$ = 10 Hz, 6F, *o*-*F*), –158 (t, $^{3}J_{FF}$ = 20 Hz, 3F, *p*-*F*), –164 (td, $^{3}J_{FF}$ = 23 Hz, $^{4}J_{FF,\,right}$ = 8 Hz, $^{4}J_{FF,\,left}$ = 10 Hz, $^{4}J_{FF,\,middle}$ = 6 Hz, 6F, *m*-*F*).

^{1}H NMR (dichloromethane-d_2, 400 MHz): δ = 6.78 (s, 3H, *p*-C*H*), 6.56 (s, 6H, *o*-C*H*), 5.87 (s, 1H, OC*H*O), 2.21 (s, 18H, *m*-CH_3), 1.18 (s, 27H, C(CH_3)$_3$).

^{11}B NMR (dichloromethane-d_2, 128 MHz): δ = –1.4 (br. s, *B*(C_6F_5)$_4$).

$^{13}C\{^{1}H\}$ NMR (dichloromethane-d_2): δ = 173.3 (O*C*HO), 143.1 (*ipso*-*C*), 138.2 (*m*-*C*), 129.7 (*o*-*C*H), 129.6 (*p*-*C*H), 64.7 (*C*$(CH_3)_3$), 30.1 (C(*C*$H_3)_3$), 21.0 (*m*-*C*H_3).

^{19}F NMR (dichloromethane-d_2, 377 MHz): δ = −134 (dd, $^3J_{FF}$ = 23 Hz, $^4J_{FF}$ = 8 Hz, 6F, *o*-*F*), −158 (t, $^3J_{FF}$ = 20 Hz, 3F, *p*-*F*), −165 (td, $^3J_{FF}$ = 20 Hz, $^4J_{FF,\ outside}$ = 8 Hz, $^4J_{FF,\ middle}$ = 6 Hz, 6F, *m*-*F*).

^{1}H NMR (benzene-d_6, 400 MHz): δ = 6.61 (s, 9H, *p*+*o*-C*H*), 6.04 (s, 1H, OC*H*O), 2.12 (s, 18H, *m*-CH_3), 1.15 (s, 27H, C(C$H_3)_3$).

^{19}F NMR (benzene-d_6, 377 MHz): δ = −133 (dd, $^3J_{FF}$ = 24 Hz, $^4J_{FF}$ = 8 Hz, 6F, *o*-*F*), −157 (t, $^3J_{FF}$ = 21 Hz, 3F, *p*-*F*), −164 (td, $^3J_{FF}$ = 21 Hz, $^4J_{FF,\ outside}$ = 8 Hz, $^4J_{FF,\ middle}$ = 6 Hz, 6F, *m*-*F*).

^{1}H NMR (toluene-d_8 locked at benzene-d_6, 400 MHz): δ = 6.58 (s, 9H, *p*+*o*-C*H*), 5.99 (s, 1H, OC*H*O), 2.12 (s, 18H, *m*-CH_3), 1.13 (s, 27H, C(C$H_3)_3$).

^{11}B NMR (toluene-d_8 locked at benzene-d_6, 128 MHz): δ = 3.9 (br. s, *B*$(C_6F_5)_4$).

^{19}F NMR (toluene-d_8 locked at benzene-d_6, 377 MHz): δ = −129 (dd, $^3J_{FF}$ = 23 Hz, $^4J_{FF}$ = 8 Hz, 6F, *o*-*F*), −158 (t, $^3J_{FF}$ = 20 Hz, 3F, *p*-*F*), −159 (td, $^3J_{FF}$ = 22 Hz, $^4J_{FF,\ outside}$ = 8 Hz, $^4J_{FF,\ middle}$ = 7 Hz, 6F, *m*-*F*).

^{1}H NMR (THF-d_8, 400 MHz): δ = 8.27 (s, OC*H*O of [Ti(N[^{t}Bu]Ar)$_3$(OCHO)]), 6.84 (s, 3H, *p*-C*H*), 6.80 (s, *p*-C*H* of [Ti(N[^{t}Bu]Ar)$_3$(OCHO)]), 6.61 (s, 6H, *o*-C*H*), 6.04 (br. s, *o*-C*H* of [Ti(N[^{t}Bu]Ar)$_3$(OCHO)]), 2.24 (s, 18H, *m*-CH_3), 2.22 (s, *m*-CH_3 of [Ti(N[^{t}Bu]Ar)$_3$(OCHO)]), 1.21 (s, 27H, C(C$H_3)_3$), 1.17 (s, C(C$H_3)_3$ of [Ti(N[^{t}Bu]Ar)$_3$(OCHO)]).

^{11}B NMR (THF-d_8, 128 MHz): δ = 2.5 (br. s, *B*$(C_6F_5)_4$).

^{19}F NMR (THF-d_8, 377 MHz): δ = −133.6 (d, $^3J_{FF}$ = 20 Hz, 2F, *o*-*F* of [(thf-d_8)B$(C_6F_5)_3$]), −134.0 (dd, $^3J_{FF}$ = 23 Hz, $^4J_{FF}$ = 8 Hz, 4F, *o*-*F*), −158 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-*F* of [(thf-d_8)B$(C_6F_5)_3$]), −159 (t, $^3J_{FF}$ = 20 Hz, 2F, *p*-*F*), −165 (td, $^3J_{FF}$ = 20 Hz, $^4J_{FF,\ outside}$ = 8 Hz, $^4J_{FF,\ middle}$ = 4 Hz, 2F, *m*-*F* of [(thf-d_8)B$(C_6F_5)_3$]), −169 (td, $^3J_{FF}$ = 20 Hz, $^4J_{FF,\ left}$ = 8 Hz, $^4J_{FF,\ middle}$ = 6 Hz, $^4J_{FF,\ right}$ = 10 Hz, 4F, *m*-*F*).

CHN elemental analysis for $C_{55}H_{55}N_3O_2BF_{15}Ti_2$ (M = 1133.88 g·mol^{-1}) %found (calcd.): C 57.89 (58.26), H 5.17 (4.89), N 3.68 (3.70).

IR (KBr pellet): ν = 2977, 1645 m (ν_{asym}(C–O)), 1617 s (ν_{asym}(C–O)), 1601 m (ν_{aryl}), 1588 m (ν_{aryl}), 1518 s, 1468 s, 1342, 1288, 1178, 1100, 980.

2.2. Kinetics on the reaction of 1 with H_2 or D_2

Standard procedure: A J. Young NMR tube with Teflon valve was equipped with **1** (3.0 mg, 2.5 μmol), a slight excess of $B(C_6F_5)_3$ (2.7 mg, 5.3 μmol, 2.1 equiv.) to achieve full conversion of **1** and the internal standard 1,3,5-trimethoxybenzene (0.5 mg, 3.0 μmol) in benzene-d_6 (0.5 mL). The tube was then set under static low pressure at room temperature. The reaction mixture was carefully cooled at 0 °C and H_2 (1 bar) or D_2 (1 bar), respectively, was introduced. According to the ideal gas law, the remaining 2 mL headspace of the tube contained approximately 82 μmol of an ideal gas at T = 295 K and $p = 10^5$ N m^{-2}, corresponding to an excess of the gas. The kinetic experiment was performed at preset 50 °C under periodic data collection by ^{1}H NMR spectroscopy. t = 0 was set to the point of time when the tube was inserted into the NMR probe. The signal intensity of the O*Me*-resonance of the standard was always set to 9.0. The decay of the signal intensity of the ^{t}Bu resonance of the substrate **1** was monitored, since it was the largest signal without any overlap with other signals. The concentration was calculated by division of the intensity of the ^{t}Bu resonance by the factor 54 (number of ^{t}Bu protons of one molecule of **1**) multiplied by the concentration of the standard (Eq. 1). Hence, the reaction constants were calculated based on the consumption of the substrate.

$$c(\text{group}) = \frac{intensity_{\text{group's-signal}}}{n_{\text{group's protons}}} \times c(standard) \quad \text{(Eq. 1)}$$

H_2, 50 °C: The reaction did not follow any standard 0th, 1st, 2nd or 3rd order reaction kinetics when considering the whole reaction profile (Figure S1).[6] Instead, the consumption of **1** proceeded virtually 1st order for up to 60 % consumption. Then another pseudo 1st order regime with a different reaction constant took over until full consumption of **1** (Figure S2). Therefore, two 1st order reaction constants are provided herein:

k^1_H(60 % conversion, ^{t}Bu) = –2.12(6)·10^{-4} s^{-1}

k^1_H(last 40 %, ^{t}Bu) = –3.9(2)·10^{-4} s^{-1}.

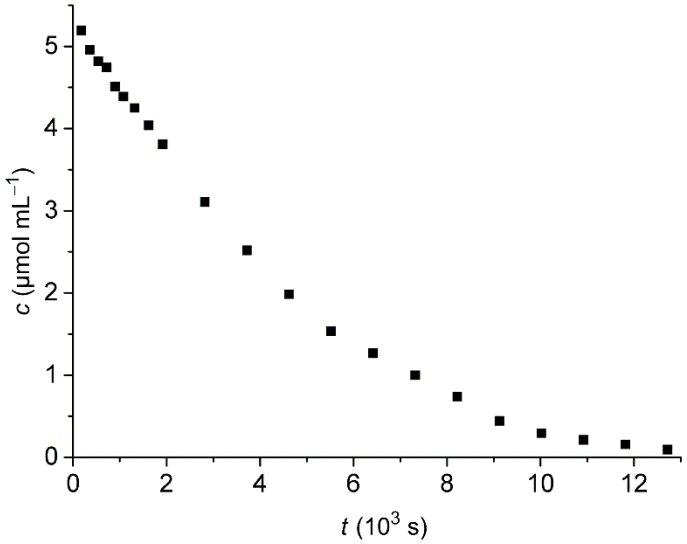


Figure S1. Concentration profile of the substrate **1** in its reaction with H_2 at 50 °C in benzene-d_6.

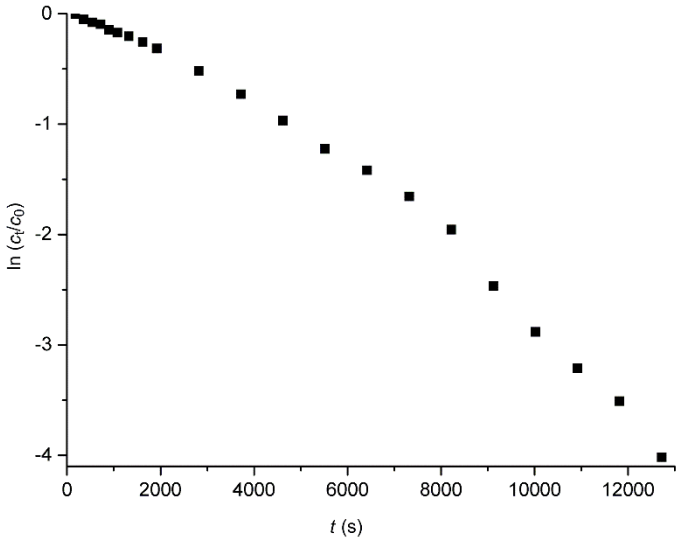


Figure S2. Kink in the plot suggesting a change in the reaction regime during the reaction.

D_2, 50 °C: This reaction also showed an initiation phase which was much shorter than in the case of H_2. No rate constant could be reliably deduced for the first part of the reaction profile. Upon reaching a conversion of 20 %, the pseudo 1st order regime started (Figure S3). The reaction constant for the second part was deduced from the logarithmic plot (Figure S4):

k^1_D(after 20 % conversion, ^{t}Bu) = –4.39(5)·10^{-4} s^{-1}.

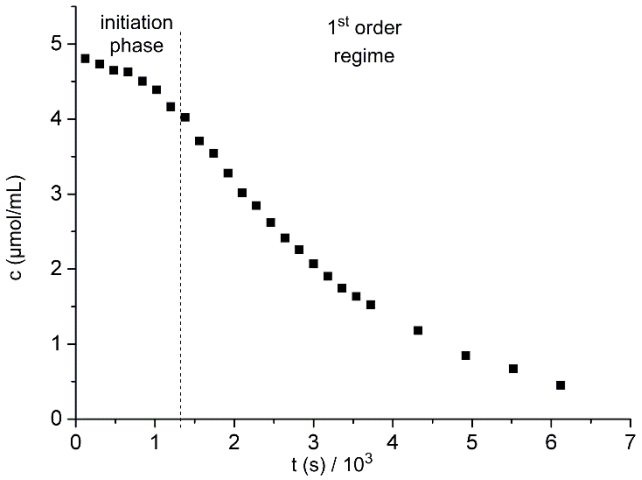


Figure S3. Concentration profile of the substrate **1** in its reaction with D_2 at 50 °C in benzene-d_6.

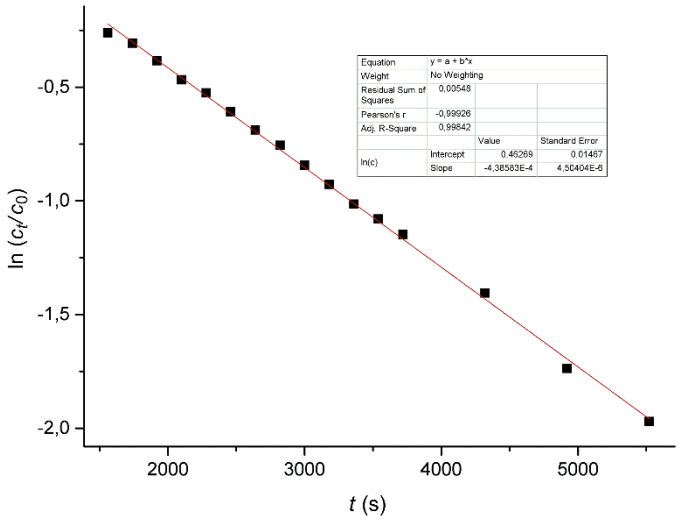
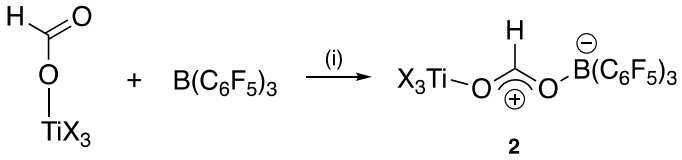


Figure S4. 1st order reaction regime for the reaction of **1** with D_2 at 50 °C.

The observed inverse kinetic isotope effect of $k^1_H/k^1_D = 0.9$ for the first order regimes after the initiation phases has to be regarded with due care.

2.3. Alternative synthesis of 2



Scheme 2. (i) benzene or toluene, 24 °C, 1 min.

An orange suspension of [Ti(N[^{t}Bu]Ar)$_3$(OCHO)] (200 mg, 322 µmol) in benzene (5 mL) was treated with $B(C_6F_5)_3$ (165 mg, 322 µmol) in benzene (1 mL). The suspension transformed within seconds into a red solution. Concentration under reduced pressure was started immediately after starting the reaction. The title compound **2** was obtained as an orange powder

after drying for 6 h under reduced pressure (350 mg, 309 µmol, 96 % based on [Ti(N[^{t}Bu]Ar)$_3$(OCHO)]). Recrystallization from diethyl ether or *n*-pentane, respectively, at -40 °C rendered crystals suitable for X-ray diffraction studies.

2.4. Synthesis of [(N[^{t}Bu]Ar)$_3$Ti(µ-O^{13}CHO-η*O*:η*O*´)B(C$_6$F$_5$)$_3$] (^{13}C-2)

An orange suspension of [Ti(N[^{t}Bu]Ar)$_3$(O^{13}CHO)] (50.0 mg, 80.3 µmol) in toluene (3 mL) was treated with solid B(C$_6$F$_5$)$_3$ (41.5 mg, 81.1 µmol, 1.01 equiv.). The reaction mixture immediately turned deep red. After 5 min, the volatiles were removed under reduced pressure. Drying was pursued for 4 h under reduced pressure at 50 °C to remove unreacted borane by sublimation (88.7 mg, 78.2 µmol, 97 % based on [Ti(N[^{t}Bu]Ar)$_3$(O^{13}CHO)]).

^{1}H NMR (benzene-d_6, 400 MHz): δ = 6.60 (s, 9H, *p*+*o*-C*H*), 6.04 (d, $^1J_{CH}$ = 219.4 Hz, 1H, O^{13}C*H*), 2.12 (s, 18H, *m*-CH_3), 1.15 (s, 27H, C(CH_3)$_3$).

^{13}C{^{1}H} NMR (benzene-d_6, 101 MHz): δ = 173.8 (s, O^{13}*C*HO), 138.2 (s, *m*-*C*), 129.7 (s, *o*-*C*H), 129.6 (s, *p*-*C*H), 64.4 (s, *C*(CH$_3$)$_3$), 30.0 (s, C(*C*H$_3$)$_3$), 20.9 (s, *m*-*C*H$_3$).

^{19}F NMR (benzene-d$_6$, 377 MHz): δ = −133 (dd, $^3J_{FF}$ = 25 Hz, $^4J_{FF}$ = 8 Hz, 6F, *o*-*F*), −157 (t, $^3J_{FF}$ = 20 Hz, 3F, *p*-*F*), −164 (td, $^3J_{FF}$ = 25 Hz, $^4J_{FF,sides}$ = 8 Hz, $^4J_{FF,middle}$ = 6 Hz, 6F, *m*-*F*).

IR (KBr pellet): ν = 2977, 1645 m (ν_{asym}(^{12}C–O) from residual ^{12}C), 1574 s (ν_{asym}(^{13}C–O)), 1518, 1469 s, 1338, 1289, 1178, 1101, 982.

3. X-ray crystallography

Single-crystal X-ray diffraction measurements of **2** and **3**[HB(C_6F_5)$_3$] were performed on a Bruker AXS diffractometer equipped with an Incoatec microsource and an APEX area detector using MoKα radiation (λ = 0.71073 Å), multilayer optics and ω-scans. Temperature control was achieved with an Oxford cryostream 700. The SMART program was used for data collection and unit cell determination, processing of the raw data frame was performed using SAINT+.[7] Multi scan absorption corrections were applied with SADABS.[8] The structures were solved by direct methods (SIR-92).[9] The crystal lattice **2** contained co-crystallized diethyl ether. The refinements were performed against F^2 with the program SHELXL-2013 using all reflections and the non-hydrogen atoms were refined anisotropically.[10] The diethyl ether molecules in the packing of **2** were disordered and split positions for C56, C57, O3, C58, C59 were used to refine these atoms with common isotropic displacement parameters. Distance restraints were used for the refinement of this ether molecule. Hydrogen atoms were included as riding on calculated positions with U_{iso}(H) = 1.2U_{eq}(C) or 1.5$U_{eq.}$(non-H), except for that bound to boron B1 in **3**[HB(C_6F_5)$_3$] and that to the carbon atom C1 of the CO_2H fragment in **2**. These were localized in difference Fourier maps and refined in their position with isotropic displacement parameters U_{iso}(H) = 1.2U_{eq}(B) or 1.2U_{eq}(C), respectively. Refinement results are given in Table S1. Graphical representations were performed with the program DIAMOND.[11] CCDC-1550958 (**3**[HB(C_6F_5)$_3$]) and 1550959 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement.

	2	**3**[$HB(C_6F_5)_3$]
chemical formula	$2(C_{55}H_{55}BF_{15}N_3O_2Ti)$, $3(C_4H_{10}O)$	$C_{36}H_{54}N_3Ti$, $C_{18}HBF_{15}$
fw ($g \cdot mol^{-1}$)	2489.81	1089.72
space group	$P\bar{1}$	$P2_1/c$
crystal size (mm)	0.56 × 0.45 × 0.13	0.33 × 0.21 × 0.09
unit cell parameters		
a (Å)	13.570(2)	17.895(3)
b (Å)	16.462(3)	14.464(2)
c (Å)	16.688(3)	19.870(3)
α (°)	64.910(3)	
β (°)	89.059(3)	96.448(4)
γ (°)	67.790(3)	
V ($Å^3$)	3079.4(10)	5110.5(14)
Z	1	4
T (K)	100(2)	100(2)
μ(Mo K_α) (mm^{-1})	0.231	0.262
reflns	33876	35080
independent reflns ($R_{int.}$)	11182 (0.0565)	7413 (0.1163)
observed reflns	8286	5399
parameters	785	685
goodness of fit on F^2	1.039	1.036
final R indices:		
*R*1, *wR*2 [$I \geq 2\sigma(I)$]	0.0703, 0.1847	0.0531, 0.1181
*R*1, *wR*2 (all data)	0.0947, 0.2020	0.0808, 0.1341

4. NMR spectra

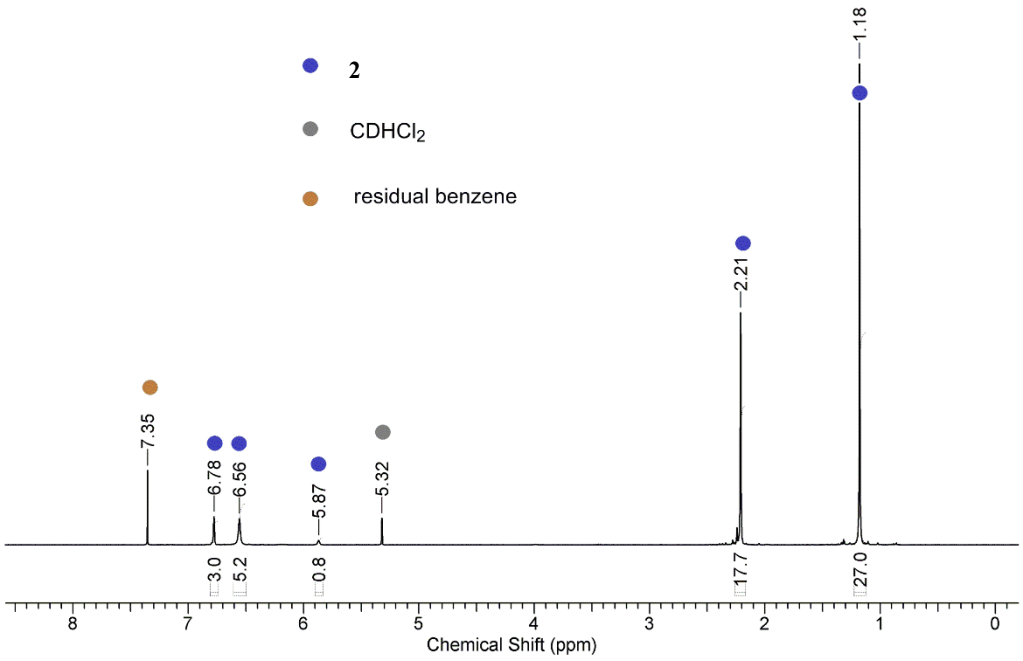


Figure S5. ^{1}H NMR spectrum of **2** (dichloromethane-d_2).

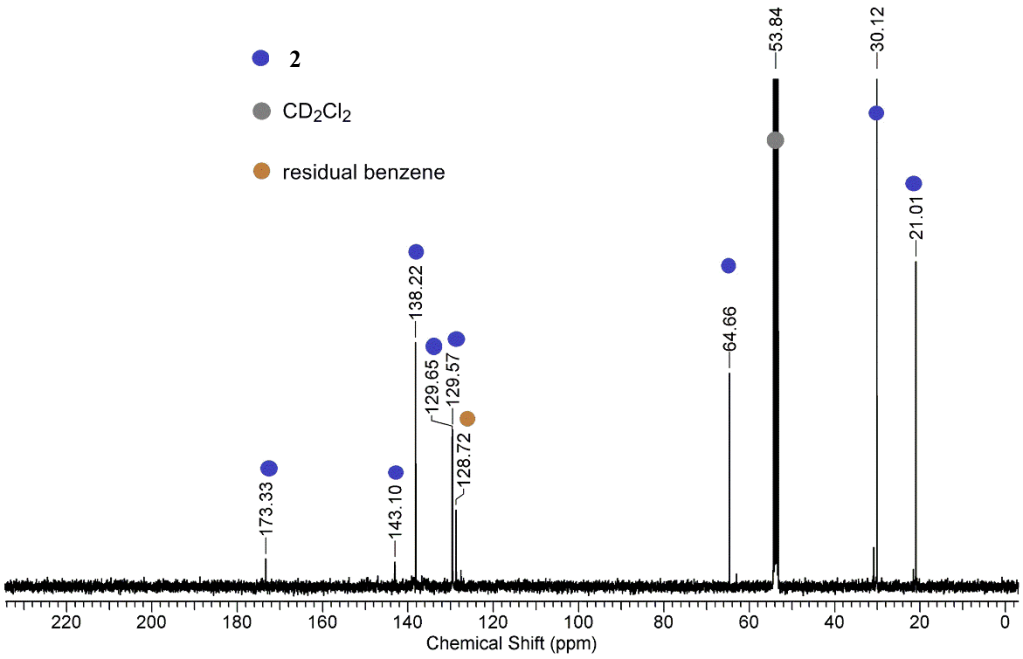


Figure S6. ^{13}C{^{1}H} NMR spectrum of **2** (dichloromethane-d_2).

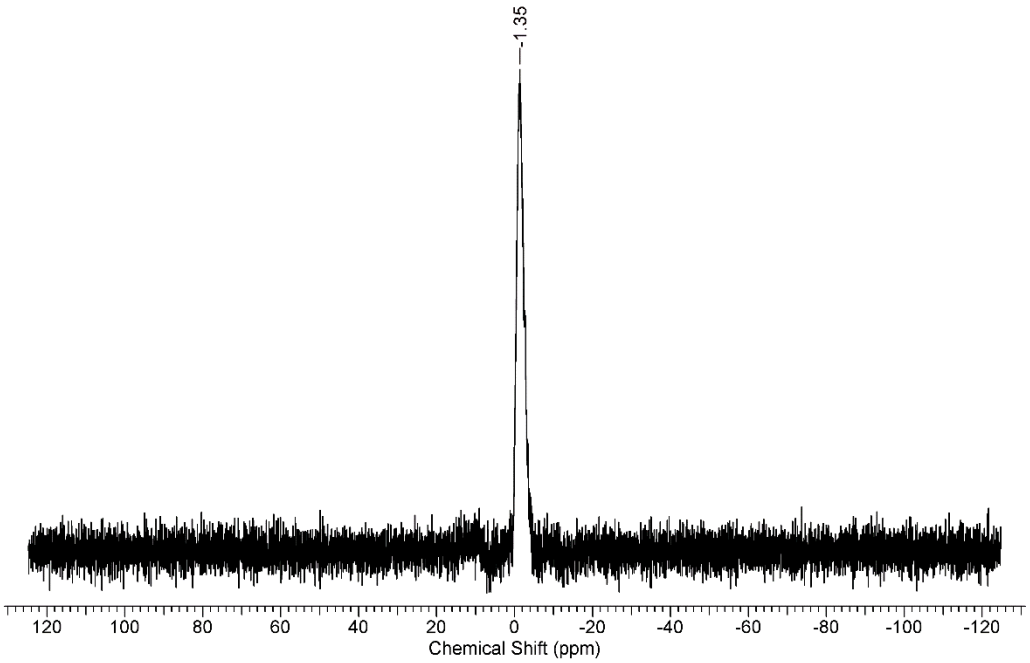


Figure S7. Baseline-corrected $^{11}B\{^{1}H\}$ NMR spectrum of **2** (dichloromethane-d_2).

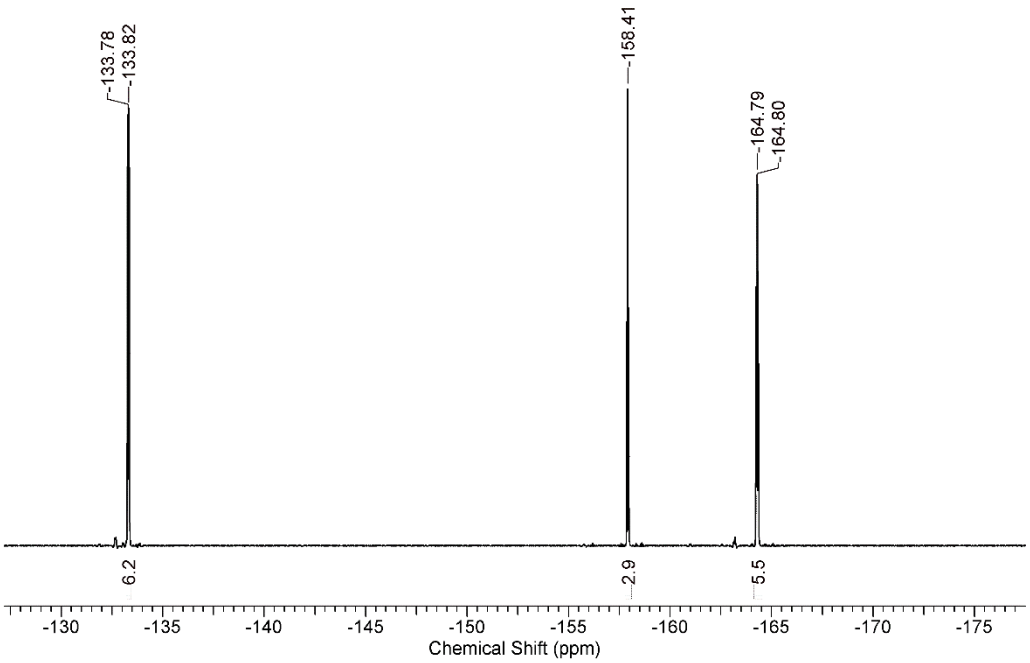


Figure S8. ^{19}F NMR spectrum of **2** (dichloromethane-d_2).

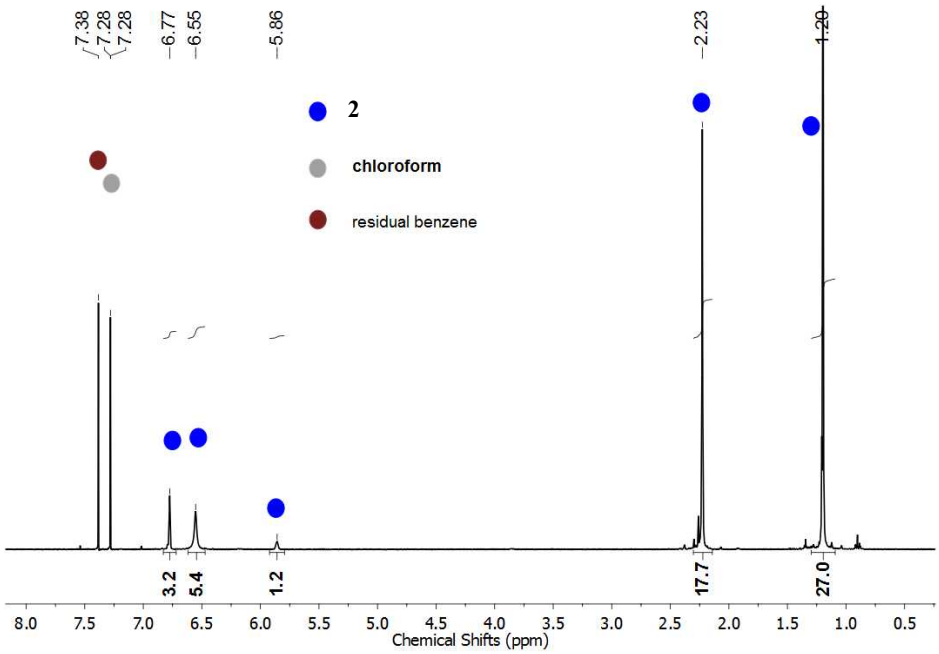


Figure S9. ^{1}H NMR spectrum of **2** (chloroform-d_1).

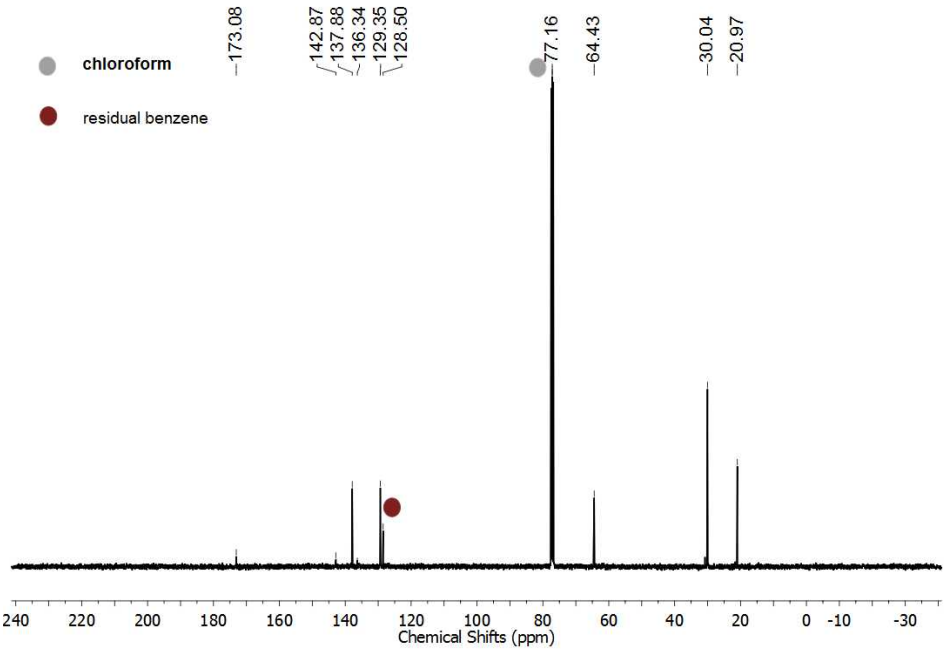


Figure S10. ^{13}C{^{1}H} NMR spectrum of **2** (chloroform-d_1).

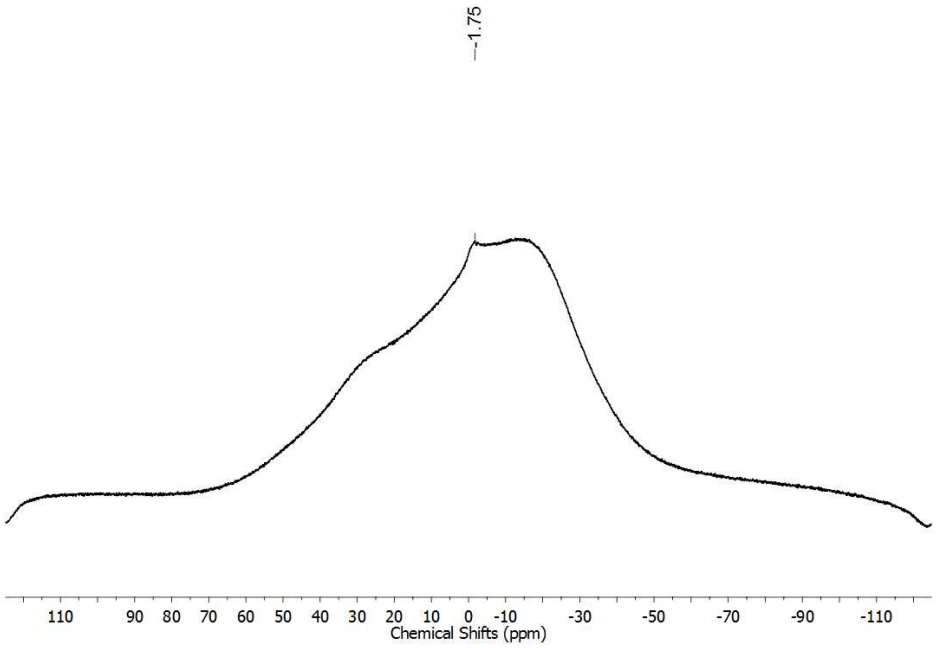


Figure S11. $^{11}B\{^{1}H\}$ NMR spectrum of **2** (chloroform-d_1).

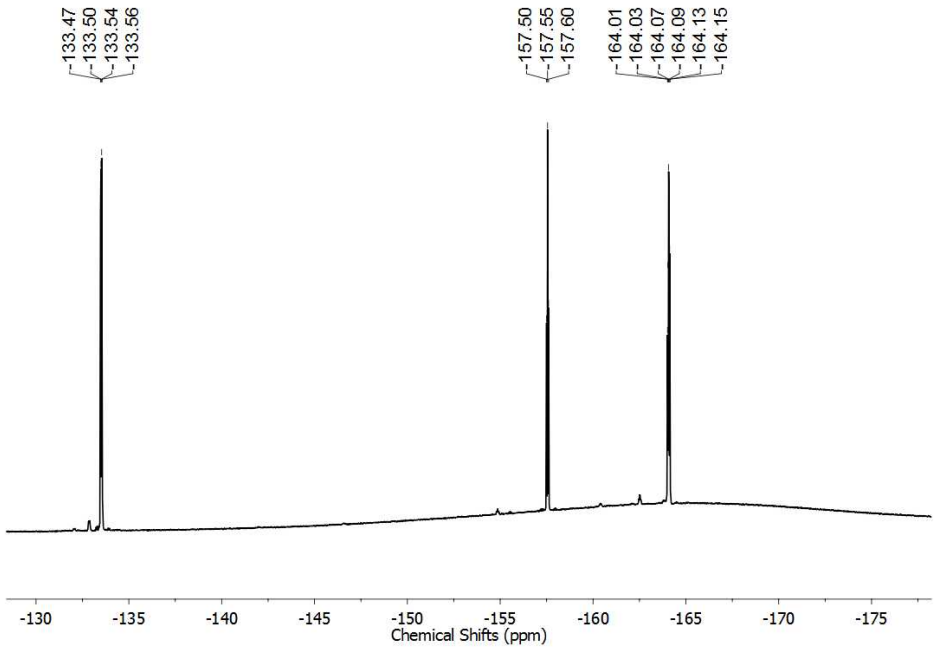


Figure S12. ^{19}F NMR spectrum of **2** (chloroform-d_1).

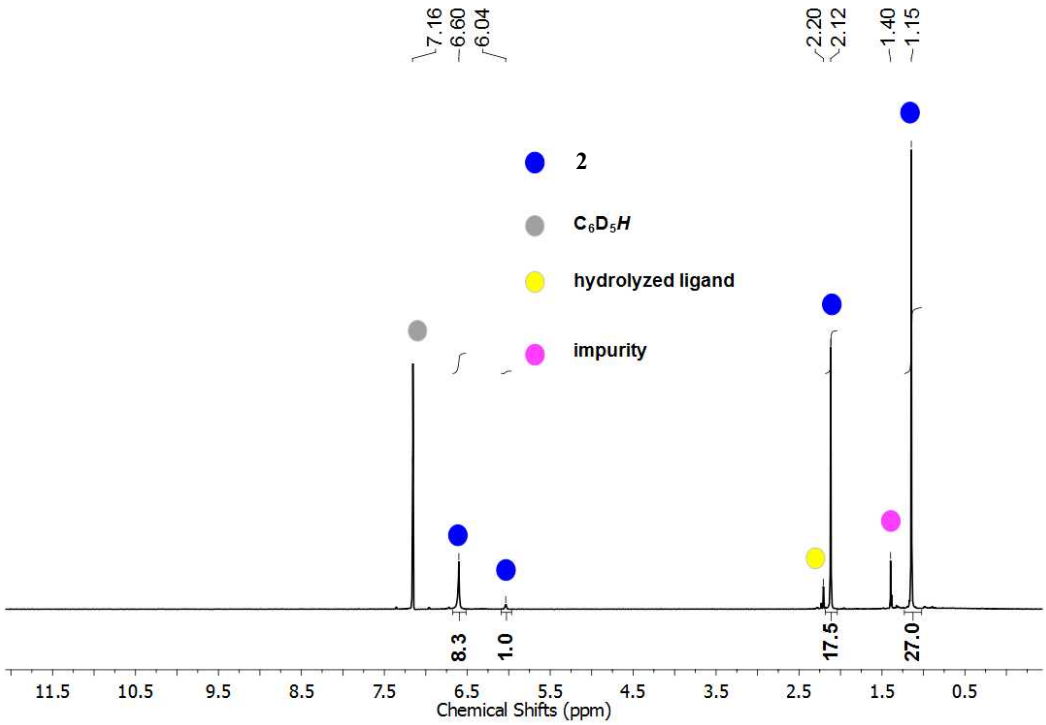


Figure S13. ^{1}H NMR spectrum of **2** (benzene-d_6).

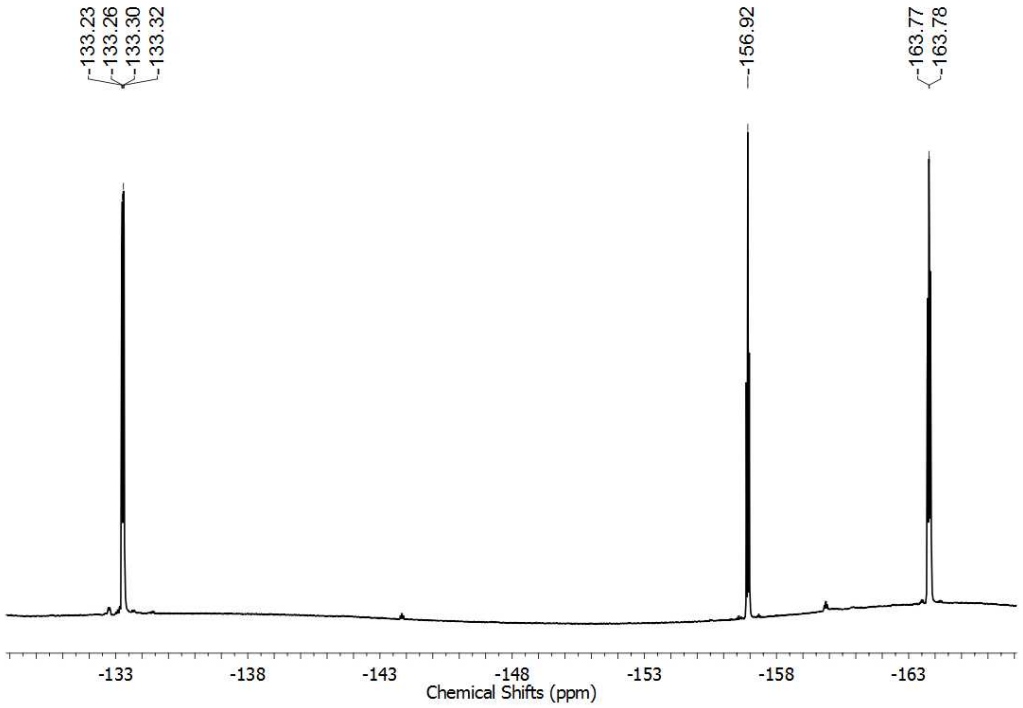


Figure S14. ^{19}F NMR spectrum of **2** (benzene-d_6).

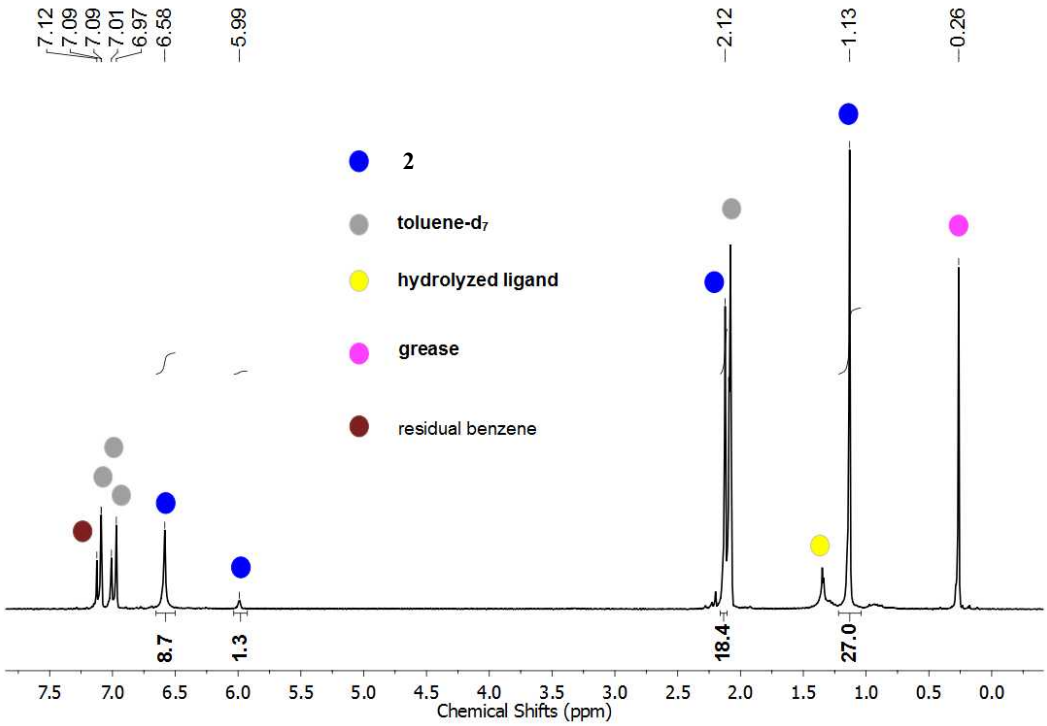


Figure S15. ^{1}H NMR spectrum of **2** (toluene-d_8).

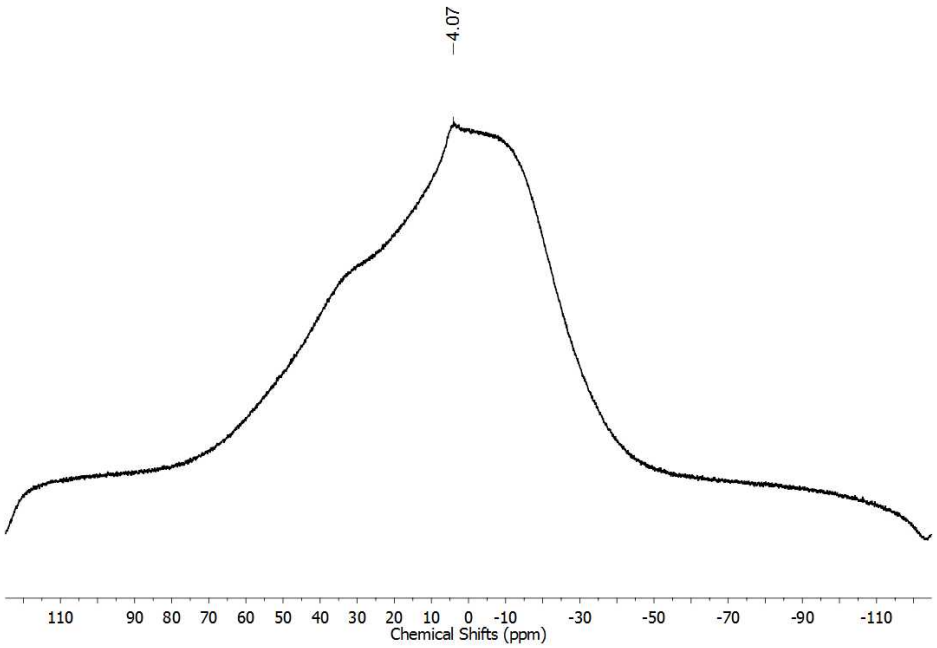


Figure S16. ^{11}B{^{1}H} NMR spectrum of **2** (toluene-d_8).

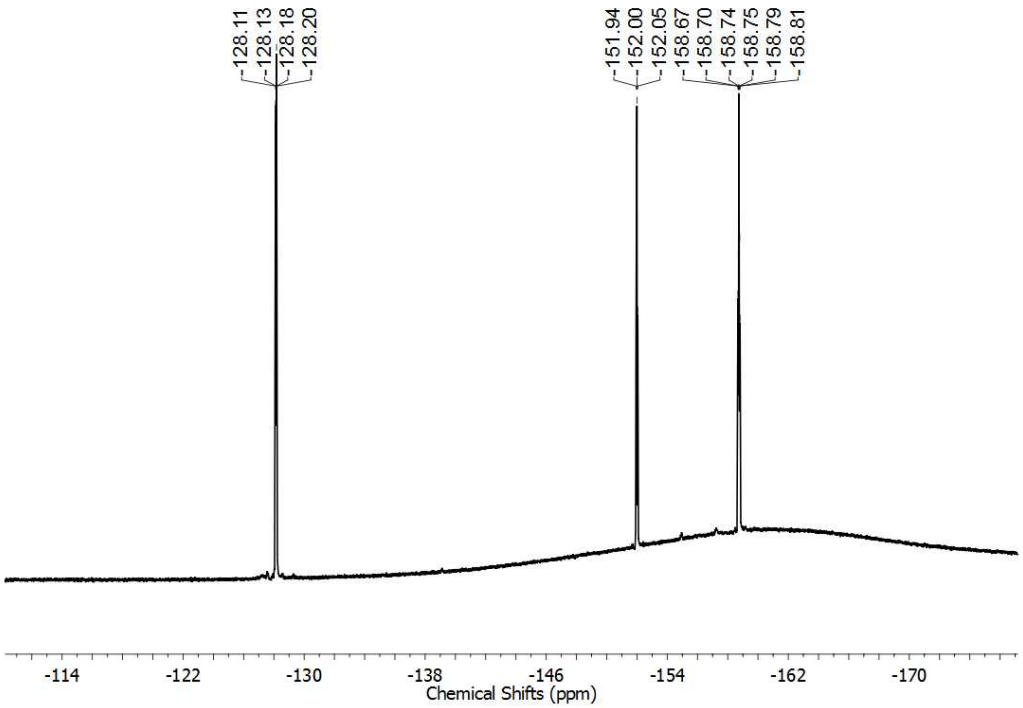


Figure S17. ^{19}F NMR spectrum of **2** (toluene-d_8).

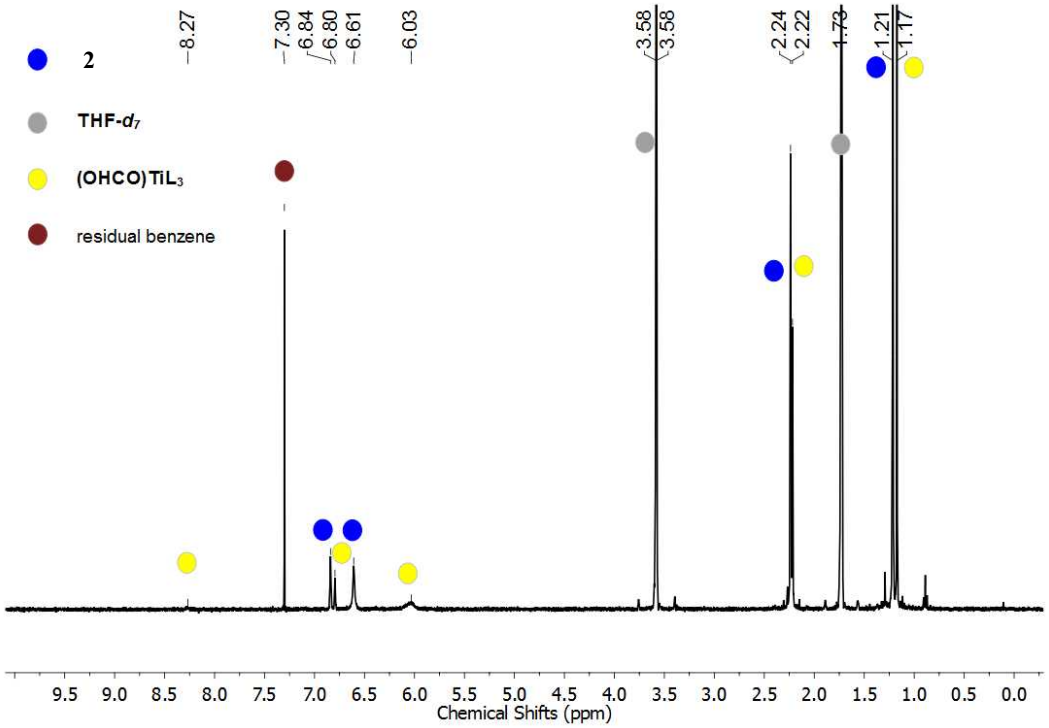


Figure S18. ^{1}H NMR spectrum of **2** (THF-d_8).

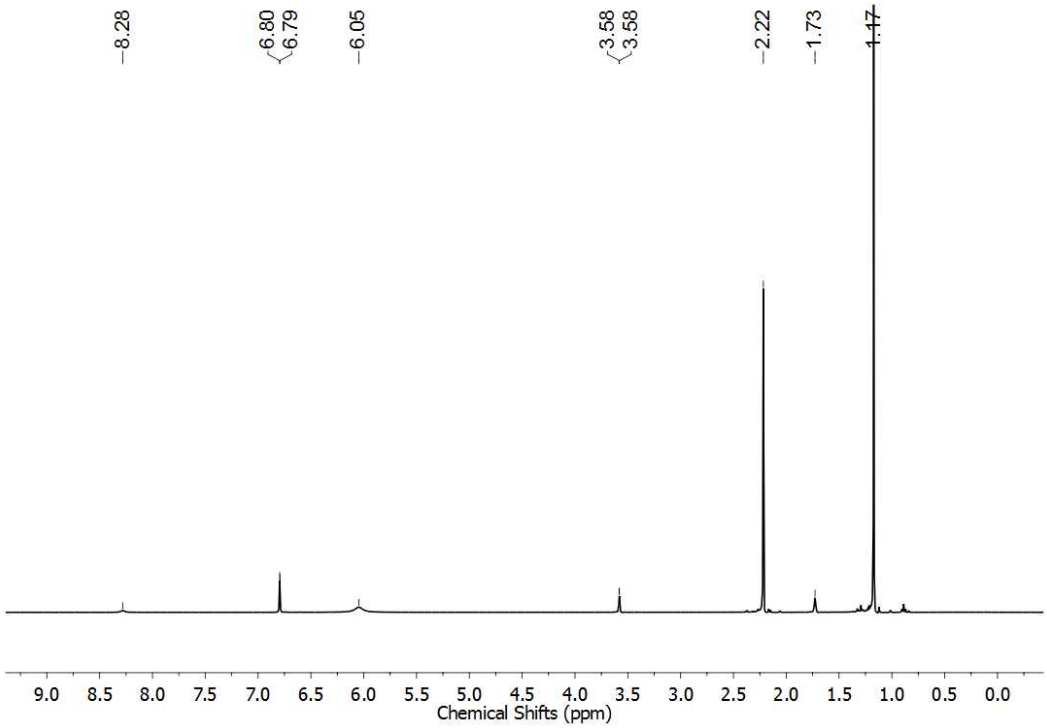


Figure S19. ^{1}H NMR spectrum of [Ti(N[^{t}Bu]Ar)$_3$(OCHO)] for comparison (THF-d_8).

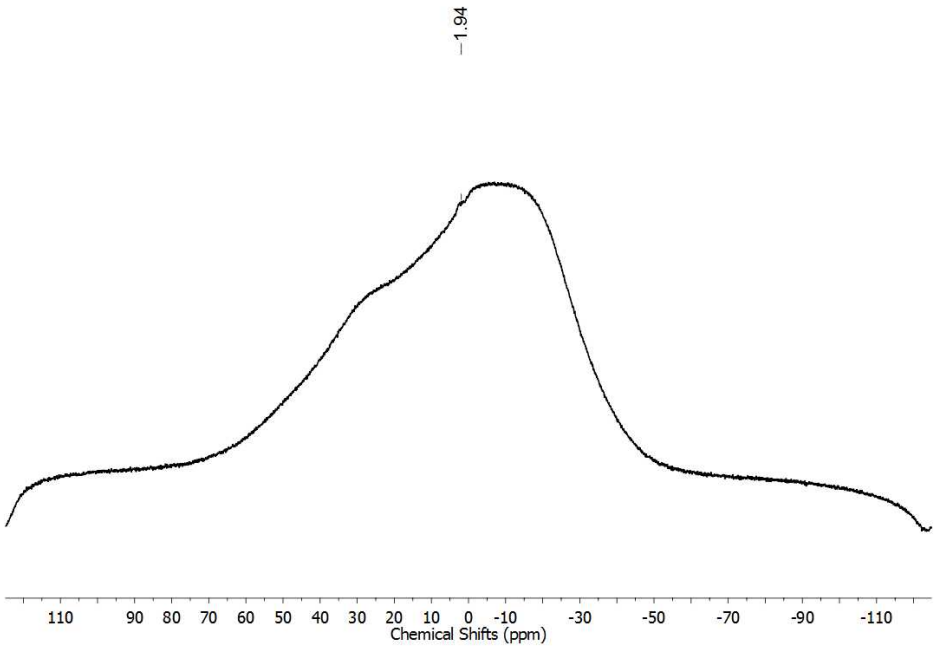


Figure S20. ^{11}B{^{1}H} NMR spectrum of **2** (THF-d_8).

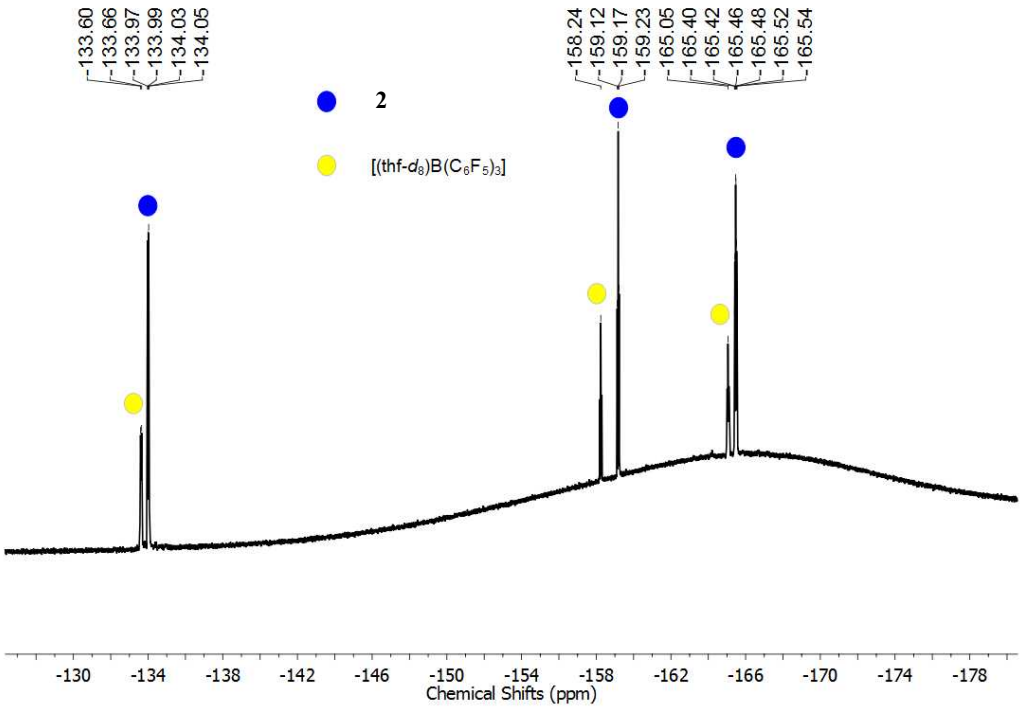


Figure S21. ^{19}F NMR spectrum of **2** (THF-d_8).

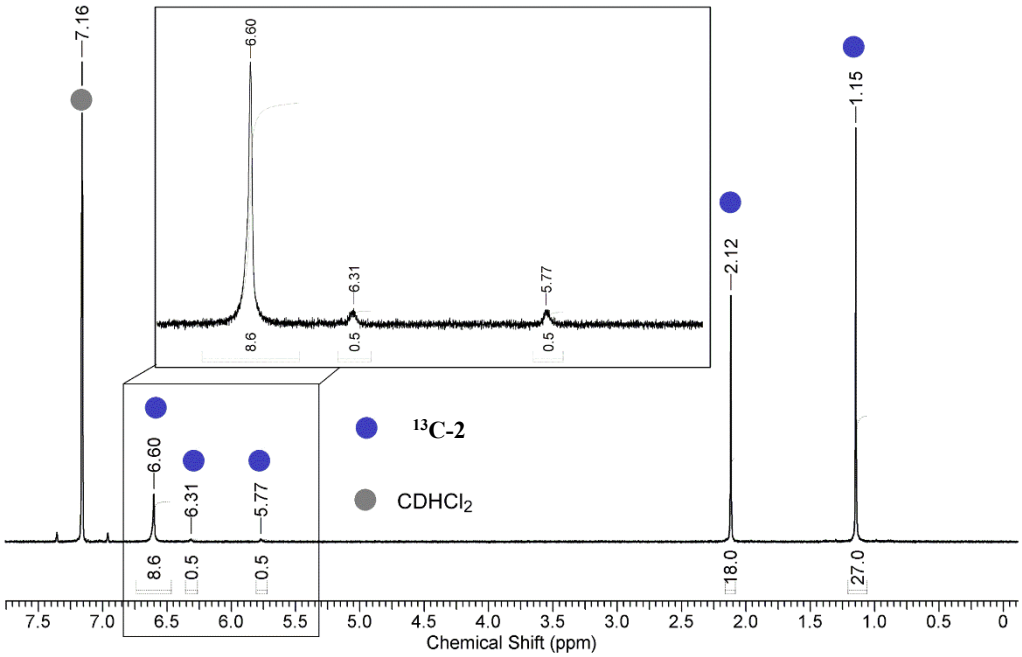


Figure S22. ^{1}H NMR spectrum of **^{13}C-2** (benzene-d_6).

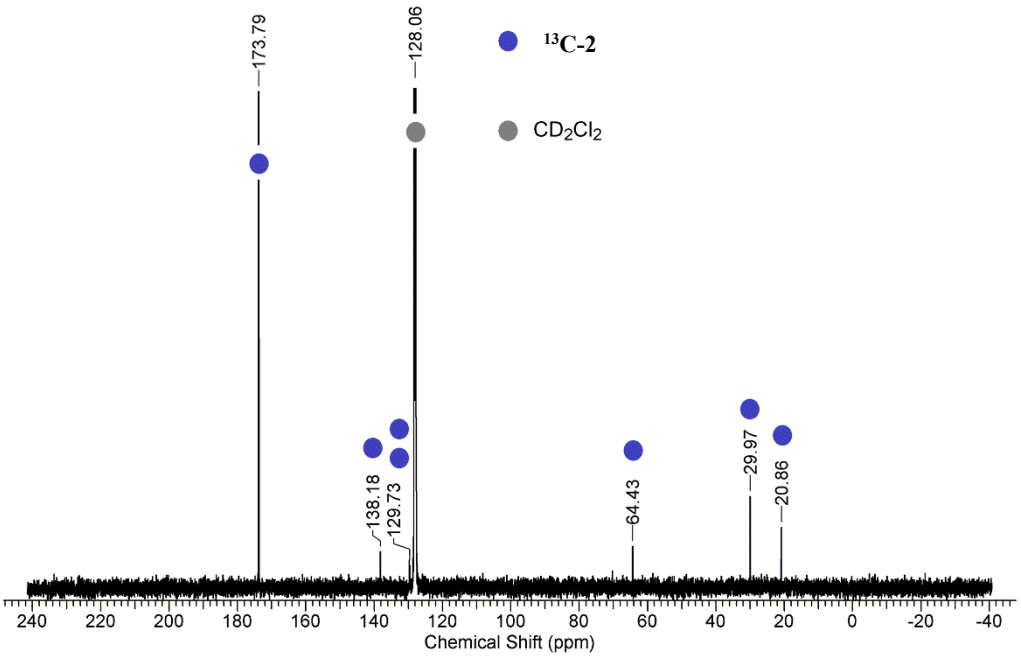


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **^{13}C-2** (benzene-d_6).

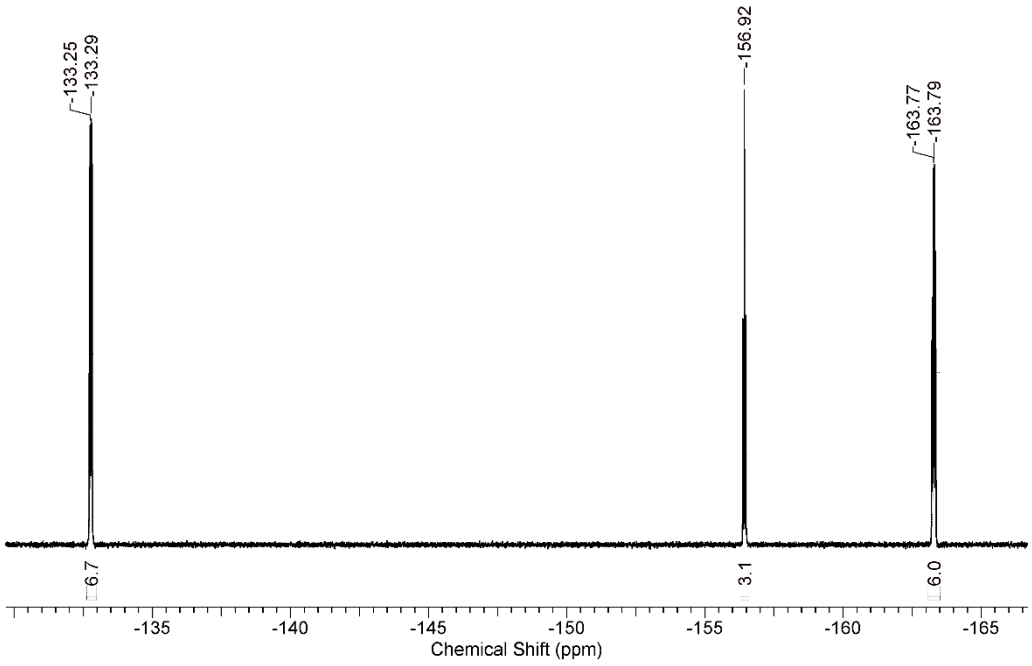


Figure S24. ^{19}F NMR spectrum of ^{13}C-**2** (benzene-d_6).

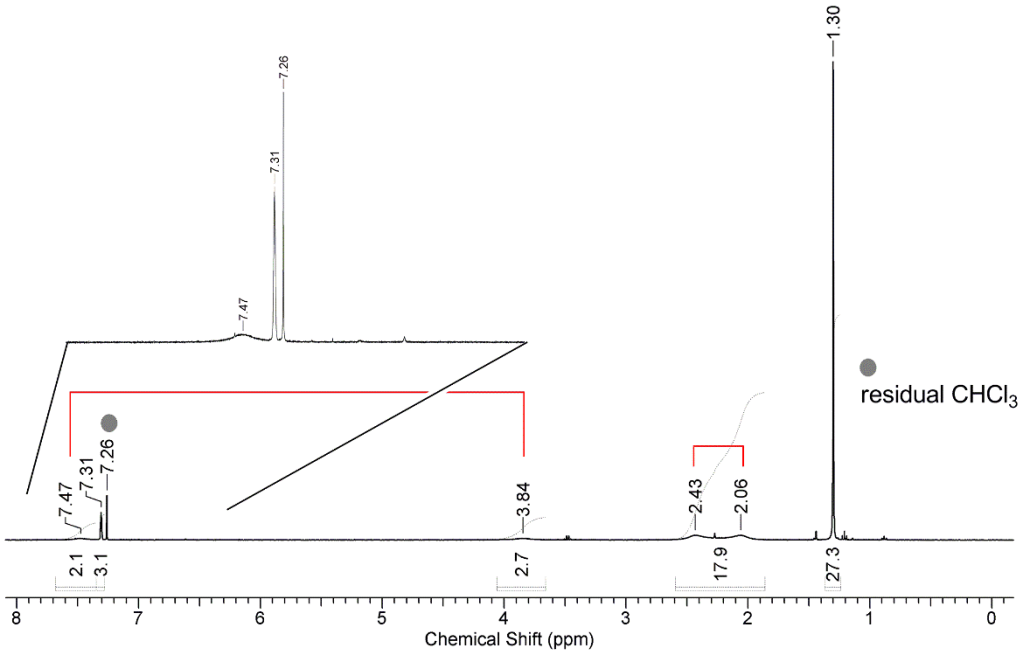


Figure S25. ^{1}H NMR spectrum of **3**[HB(C_6F_5)$_3$] (chloroform-d_1).

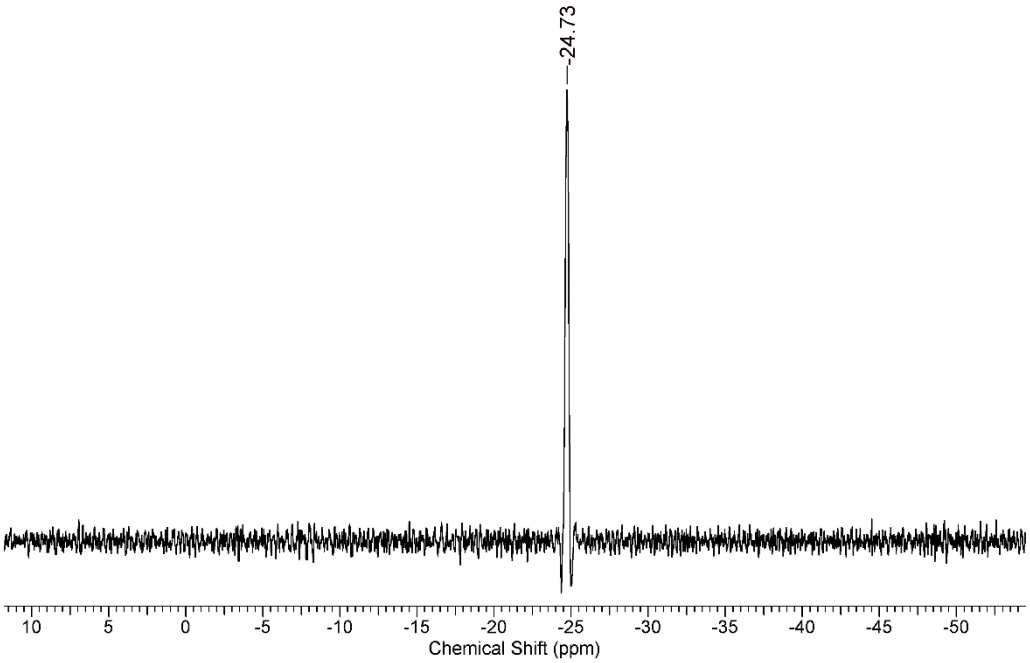


Figure S26. Baseline-corrected ^{11}B{^{1}H} NMR spectrum of **3**[HB(C_6F_5)$_3$] (chloroform-d_1).

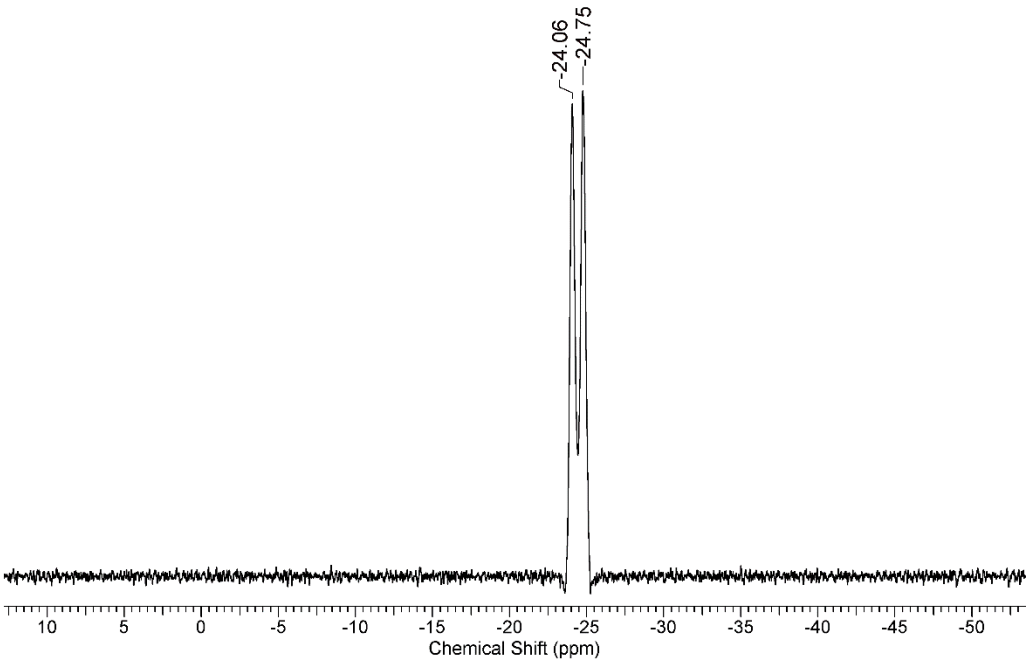


Figure S27. Baseline-corrected ^{11}B NMR spectrum of **3**[HB(C_6F_5)$_3$] (chloroform-d_1).

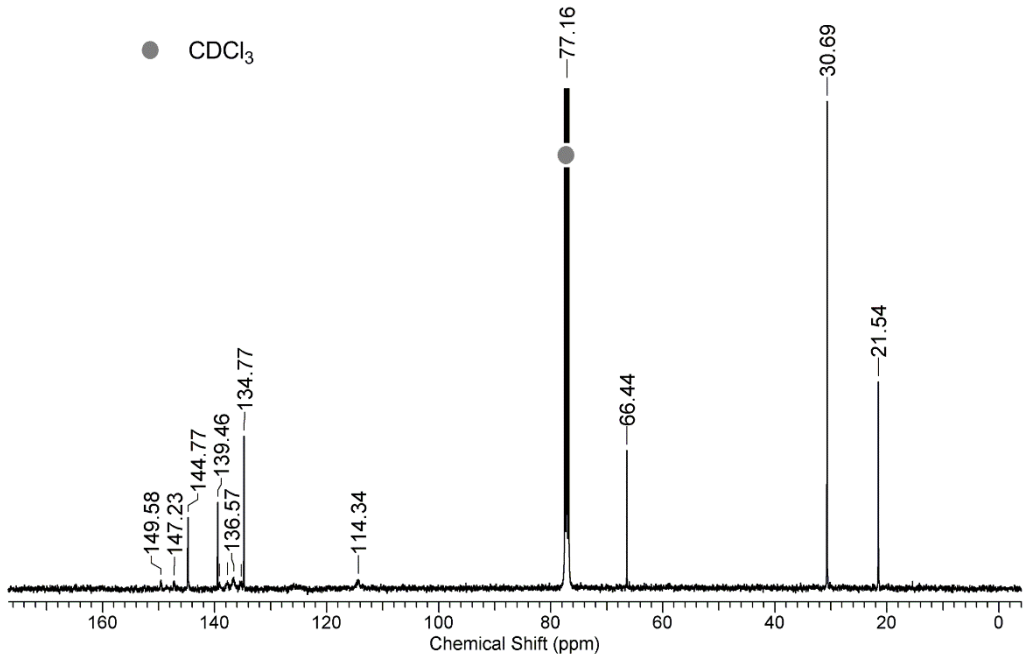


Figure S28. ^{13}C{^{1}H} NMR spectrum of **3**[HB(C_6F_5)$_3$] (chloroform-d_1).

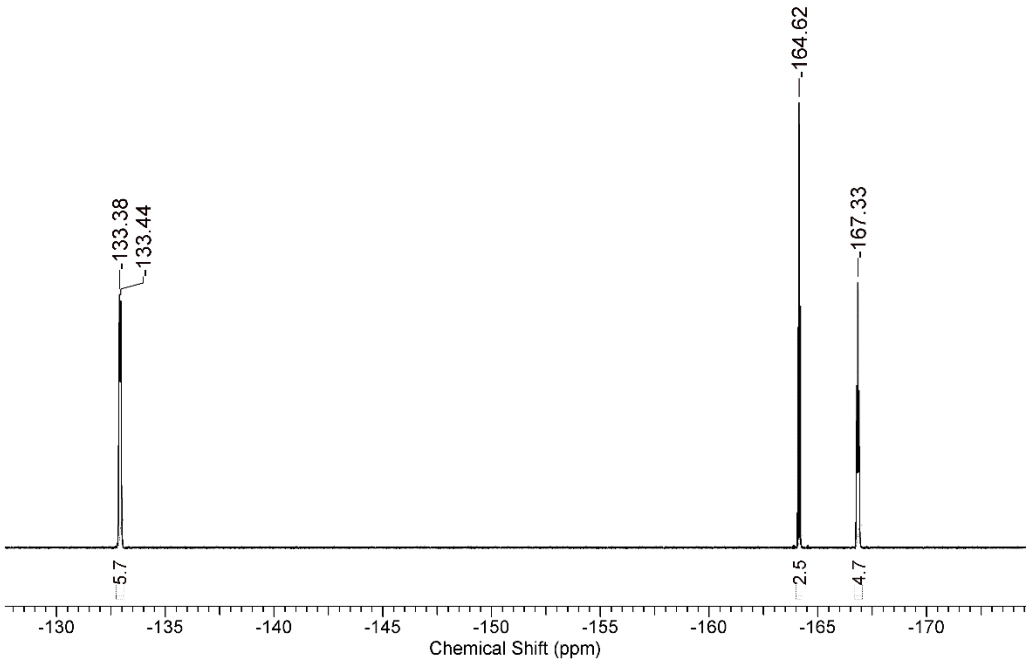


Figure S29. Baseline-corrected ^{19}F NMR spectrum of **3**[$HB(C_6F_5)_3$] (chloroform-d_1).

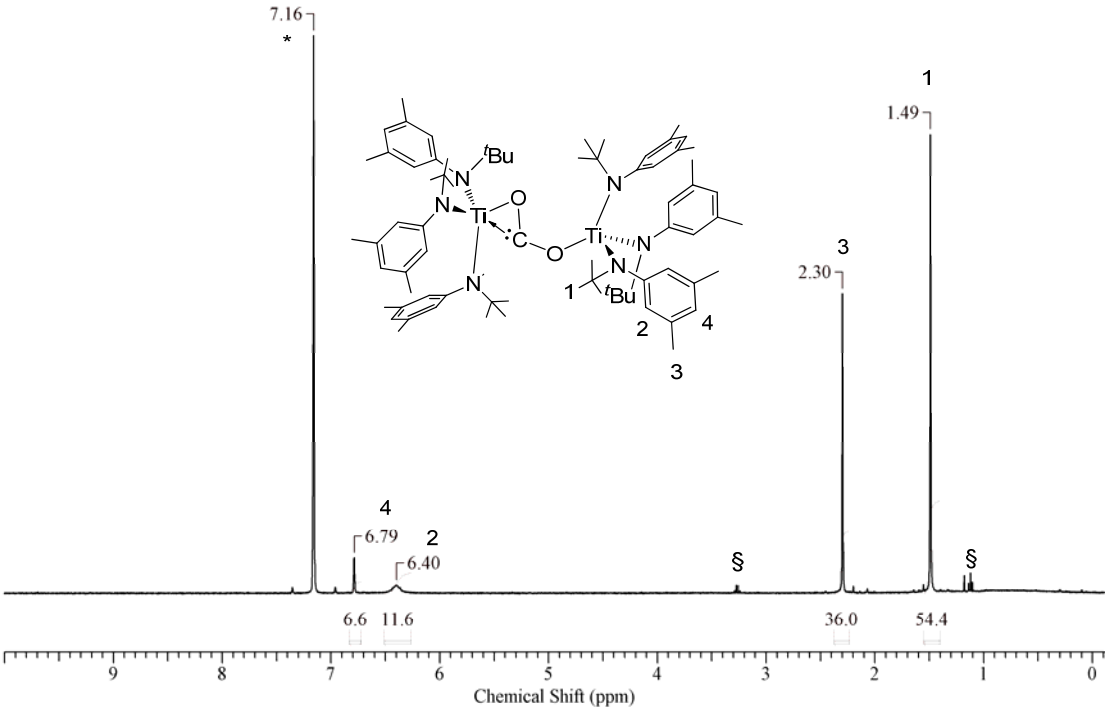


Figure S30. ^1H NMR spectrum of **1** in benzene-d_6 (*) after treatment with dihydrogen and $B(C_6F_5)_3$. § denotes diethyl ether.

5. IR spectra

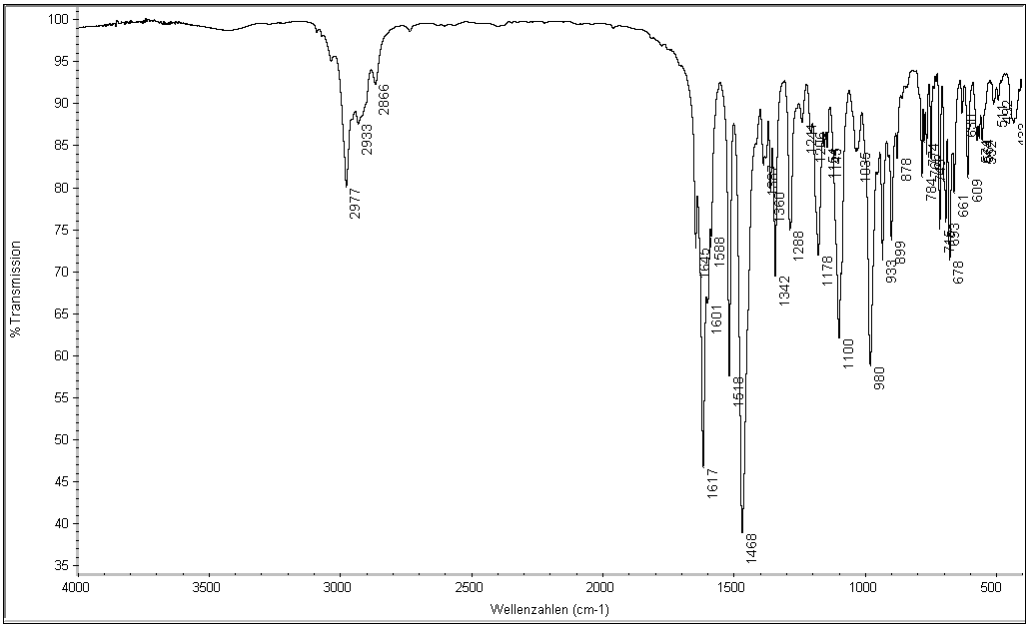


Figure S30. IR spectrum of **2** in a KBr pellet.

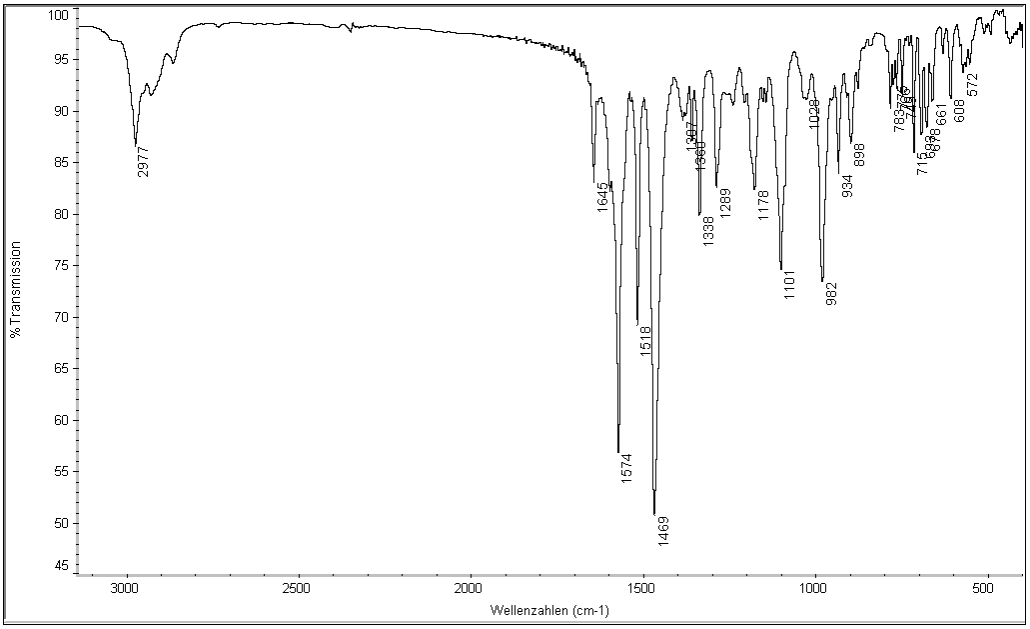


Figure S31. IR spectrum of ^{13}**C-2** in a KBr pellet.

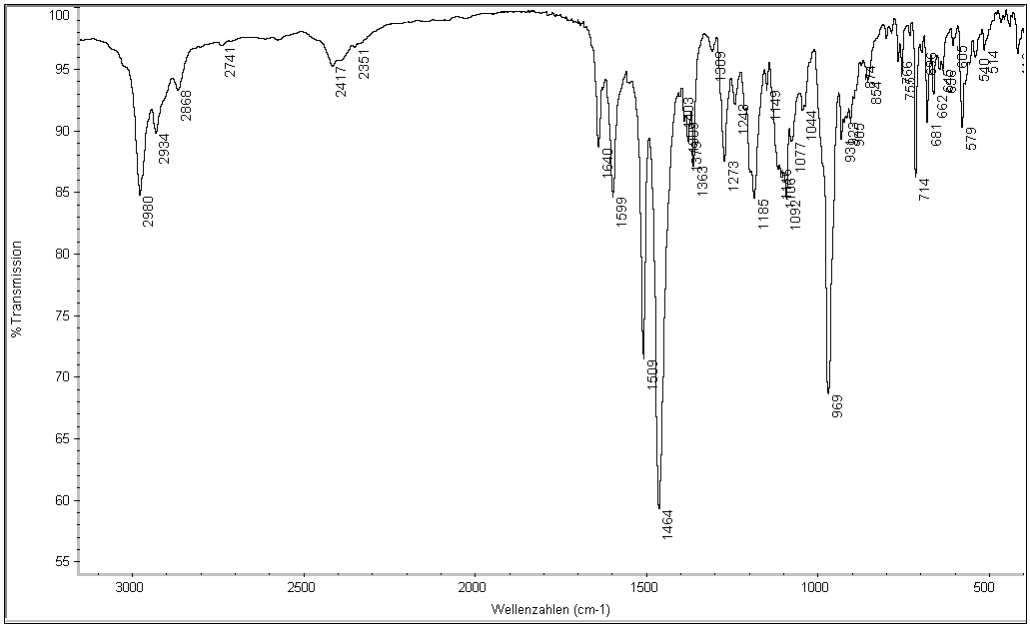


Figure S32. IR spectrum of **3**[$HB(C_6F_5)_3$] in a KBr pellet.

6. Computations

The equilibrium and transition structures were fully optimized with Becke's 3-parameter hybrid functional[12] combined with the non-local correlation functional provided by Perdew/Wang.[13] Titanium and fluorine atoms were represented by the relativistic effective core potential (denoted as SDDALL),[14] augmented by a *f/d* polarization function.[15] The 6-31G(dp) basis set was used for all the non-metal atoms.[16] The connections between the transition states and the corresponding minima were done by performing IRC calculations.[17] The natural bond order analysis (NBO) was performed using Weinhold's methodology.[18] All the above calculations have been performed using the *Gaussian-09 suite*.[19]

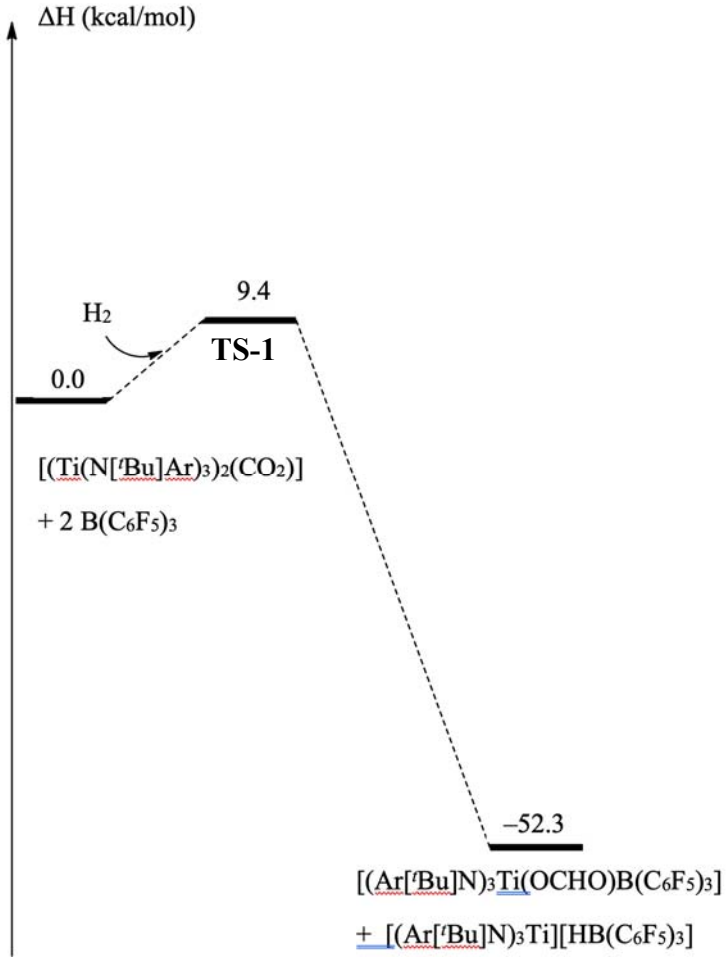


Figure S68. Computed enthalpy profile (room temperature) for the FLP-type activation of H_2.

Cartesian coordinates of all optimized structures

[(Ti(N[^{t}Bu]Ar)$_3$)$_2$(μ-CO$_2$-η^2*O*,*C*:η*O*′)]

192

Ti	-0.01758700	-0.46237600	2.90830800
Ti	0.16879900	0.07308600	-2.93734900
C	0.48636800	-1.03097800	-0.07131000
O	0.14241100	-0.43063400	1.04883700
O	0.15605500	-0.29182500	-1.10902600
N	0.64530800	1.20314900	3.62537300
N	0.99987700	-1.92686300	3.63566800
N	-1.87099800	-0.67370000	3.39120400
N	0.93276600	-1.40866600	-3.90130900
N	1.22085600	1.65342300	-3.27219800
N	-1.64371000	0.35931200	-3.53775500
C	0.63238700	2.54796800	2.94744500
C	2.04683600	2.92213800	2.47396200
H	2.44208800	2.15911300	1.79438000
H	2.73586600	3.03050400	3.31747600
H	2.02531700	3.87847600	1.93702000
C	0.12103700	3.64289700	3.89993200
H	0.77428400	3.77329500	4.76715100
H	0.08210600	4.59807500	3.36263900
H	-0.88648100	3.40938300	4.25882900
C	-0.29544600	2.52346000	1.72801900
H	-1.29958700	2.18199500	2.00002300
H	0.07886100	1.87402100	0.93549200
H	-0.38609500	3.53824800	1.32369300
C	1.27606400	1.21726200	4.91200000
C	2.66004100	1.04756700	5.05613200
H	3.26446500	0.86627700	4.17296000
C	3.27929800	1.10629700	6.30953200
C	4.76557500	0.88819000	6.43961500
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H	5.30914000	1.30770400	5.58578900
H	5.00881200	-0.18184200	6.48339400
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H	2.96416700	1.42049900	8.41418000
C	1.10802200	1.54169700	7.32755200
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H	-0.55818700	1.59288400	5.96351700
C	2.34200400	-2.41375900	3.15746900
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H	3.98218900	-1.67614300	1.96100800
H	2.90356400	-0.39308800	2.52515500
H	2.40632100	-1.46364800	1.19104500
C	2.20852300	-3.77385100	2.45112500
H	3.18263400	-4.07750900	2.04732900
H	1.87807000	-4.55715600	3.14033000
H	1.50158900	-3.70468600	1.61763400
C	3.32132500	-2.55741700	4.33485100
H	4.30235900	-2.86511600	3.95346800
H	2.98961900	-3.31254200	5.05361100

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C	0.47598000	-2.67365700	4.73991300	C	-2.42913100	0.08679600	4.46839900
C	-0.22136400	-3.87437800	4.55424800	C	-2.45449800	-0.43832600	5.76541600
H	-0.40095000	-4.23084500	3.54421900	H	-2.00320200	-1.40963900	5.94402100
C	-0.69088000	-4.62260500	5.64059700	C	-3.05474200	0.25879000	6.82194400
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H	-2.42777900	-5.71101300	4.94504300	H	-2.16492300	-0.78883900	8.49242400
H	-0.90529300	-6.57770300	4.73775100	H	-3.42285900	0.37421400	8.95198400
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C	0.25651600	-2.96421500	7.15506100	C	-3.58394900	2.07844100	5.28754200
C	0.56505100	-2.50816900	8.55868700	C	-4.17222200	3.44494800	5.04163200
H	1.39783800	-3.08379500	8.98467300	H	-3.51833800	4.23615400	5.43148900
H	-0.29324400	-2.64643400	9.22670000	H	-5.14386000	3.55766300	5.53651900
H	0.85210000	-1.45250200	8.57957800	H	-4.31478800	3.63410200	3.97271000
C	0.70046800	-2.23008200	6.05325800	C	-3.00204100	1.35049700	4.24906200
H	1.24595500	-1.30314300	6.20295300	H	-2.99621200	1.76194800	3.24408700
C	-2.86920200	-1.56895400	2.70721800	H	-4.55938800	-0.17278000	2.74431200
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H	-1.27378100	-2.90834100	2.02103300	C	2.03390900	-3.47982900	-3.02122400
H	-1.88223800	-1.81016900	0.77114200	H	2.34844000	-2.93388100	-2.12542600
H	-2.85383400	-3.19176900	1.27985700	H	2.84806400	-3.47057800	-3.75263200
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H	-4.11260100	-1.97954900	4.46764000	H	1.12866200	-3.61236100	-5.62639500
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C	-3.96169500	-0.73383800	2.01901500	H	-0.57387600	-3.24060300	-5.29679900
H	-3.51938000	-0.02714700	1.30867900	C	-0.36203400	-3.04705500	-2.54853900

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H	-0.62481800	-4.10886000	-2.47324700	H	3.39885000	3.14564000	-4.24131400
C	1.79875700	-1.16239900	-5.01474900	H	3.80865100	1.41969800	-4.19396400
C	3.19260000	-1.12404600	-4.86952000	C	0.78776600	2.60903800	-4.24693800
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C	4.03637600	-0.92948200	-5.96826700	H	-0.42243900	3.74159200	-2.87703100
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H	5.84127500	0.12608300	-5.41186800	H	-0.86122600	6.73239000	-4.54735900
C	3.46490600	-0.78441100	-7.23511600	H	-2.25902100	5.80255900	-5.08892600
H	4.11345100	-0.64473100	-8.09905400	C	0.02545500	4.52147100	-6.14664700
C	2.07865800	-0.82539500	-7.41699500	H	-0.26561000	5.26832200	-6.88442300
C	1.48117400	-0.73416800	-8.79835200	C	0.88055700	3.48502300	-6.52358200
H	0.45678000	-0.35045800	-8.76489200	C	1.43761000	3.40969300	-7.92255900
H	1.44217600	-1.72333100	-9.27439000	H	2.48086700	3.75126800	-7.94849200
H	2.07313400	-0.08532700	-9.45374600	H	0.86980900	4.03842400	-8.61661700
C	1.25824100	-1.00098000	-6.29935700	H	1.42704900	2.38296300	-8.30296800
H	0.17909500	-1.02996600	-6.41745700	C	1.24303700	2.52720000	-5.56756900
C	2.49180400	2.05041000	-2.57099800	H	1.89382900	1.70394300	-5.84544800
C	2.93739500	0.93589400	-1.61846000	C	-2.77997500	0.93358900	-2.73453500
H	3.94071500	1.16038400	-1.23915000	C	-2.25397400	1.57036900	-1.44346900
H	2.98212600	-0.03740100	-2.11903200	H	-1.46757500	2.30353900	-1.65123300
H	2.26993500	0.85159700	-0.75932700	H	-1.85025100	0.83013500	-0.75135300
C	2.27586700	3.32659600	-1.74027500	H	-3.07466400	2.09398600	-0.93953200
H	3.19153600	3.56890700	-1.18688800	C	-3.52107100	2.02513500	-3.52665100
H	2.03176400	4.18512300	-2.37365400	H	-4.30973500	2.45371400	-2.89670500
H	1.46787600	3.18627800	-1.01441600	H	-3.99351000	1.62960200	-4.43024700

H	-2.83888500	2.82964900	-3.81893800
C	-3.78187000	-0.16944700	-2.35448800
H	-3.28606600	-0.96569600	-1.78816200
H	-4.58115900	0.24705800	-1.72888100
C	-2.01882000	-0.03517300	-4.86377900
C	-1.90341400	0.87447100	-5.92597000
H	-1.50002600	1.86188300	-5.72502400
C	-2.31812300	0.54192800	-7.21843400
C	-2.25990700	1.55941600	-8.32979800
H	-1.56940100	2.37283100	-8.08842000
H	-1.94321300	1.10769000	-9.27707500
H	-3.24780700	2.00730200	-8.50286600
C	-2.83284100	-0.73752700	-7.45268200
H	-3.15676700	-1.00753900	-8.45716500
C	-2.95309800	-1.67197300	-6.42108800
C	-3.49027100	-3.05517500	-6.68982700
H	-2.67614000	-3.77253300	-6.85929000
H	-4.12914800	-3.07068800	-7.57921900
H	-4.07837200	-3.42884600	-5.84428400
C	-2.54987800	-1.30454600	-5.13287400
H	-2.65078700	-2.01775700	-4.32075400
H	-4.24942200	-0.60983900	-3.24065100

$B(C_6F_5)_3$

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B	0.360926	-0.002826	-0.127897
C	0.061771	0.144964	1.401577
C	1.836697	-0.157284	-0.626638
C	-0.817626	0.006262	-1.158349
C	-2.050033	-0.603745	-0.887932
C	-3.104295	-0.611817	-1.791300
C	-2.953335	0.029387	-3.017959
C	-1.751064	0.658722	-3.329410
C	-0.711181	0.627612	-2.409866
F	-2.242815	-1.236056	0.266660
F	-4.244854	-1.217051	-1.499326
F	-3.947697	0.040486	-3.883856
F	-1.611546	1.275163	-4.492567
F	0.413863	1.249355	-2.752906
C	2.180402	-0.997001	-1.694694
C	3.484834	-1.154701	-2.143470
C	4.506931	-0.436334	-1.528843
C	4.214727	0.419528	-0.470253
C	2.901528	0.535340	-0.034583
F	1.242610	-1.711952	-2.310857
F	3.764499	-1.974464	-3.144419
F	5.750105	-0.566406	-1.948722
F	5.185673	1.108777	0.108002
F	2.675211	1.371640	0.975149
C	-0.946534	0.988602	1.887038
C	-1.219678	1.140389	3.239850
C	-0.481121	0.412049	4.168571
C	0.524463	-0.447996	3.735386
C	0.783565	-0.557866	2.375757

F	-1.676119	1.712532	1.041927	F	1.220349	-1.146808	4.618334
F	-2.170535	1.963520	3.652800	F	1.749616	-1.398481	2.014366
F	-0.733813	0.536462	5.456766				

H_2

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C	-3.332996	1.457101	-6.992182	H	0.000000	0.000000	-0.001664
C	-3.593409	1.054496	-5.676481	H	0.000000	0.000000	0.741664
C	-4.341239	-0.114240	-5.470583	Ti	-2.452756	2.365872	2.057366
C	-4.820032	-0.872101	-6.542143	N	-4.320635	2.760357	1.857403
C	-4.548561	-0.438113	-7.842570	C	-5.326780	1.749786	1.365921
C	-3.808206	0.721425	-8.084278	C	-6.104227	2.255006	0.140651
N	-3.165216	1.870749	-4.575128	N	-0.493330	3.476028	-4.246541
C	-4.252191	2.797746	-4.084138	C	0.850569	3.858716	-3.672284
C	-5.494186	2.019494	-3.619040	C	1.884011	3.979995	-4.801378
C	-5.592095	-2.142525	-6.298079	C	-1.001994	4.427968	-5.191775
C	-3.536353	1.174417	-9.495302	C	-1.602115	5.625343	-4.783306
Ti	-1.386562	1.824051	-3.851906	C	-2.060001	6.567174	-5.713137
N	-0.448268	0.367375	-4.640801	C	-1.912047	6.293071	-7.072130
C	-0.734484	-1.090638	-4.347714	C	-1.309369	5.109196	-7.515395
C	-1.822554	-1.187166	-3.273436	C	-0.859894	4.187884	-6.567571
O	-1.574280	1.627485	-1.858083	C	-2.690551	7.851980	-5.241271
C	-1.182620	1.232779	-0.721873	C	-1.136263	4.855245	-8.990542
O	-1.705924	1.610929	0.360260	N	-1.488820.	3.979221	2.408736
				C	-1.338596	5.113982	1.423281
				C	-1.998254	4.726808	0.097955
				N	-2.258519	1.161229	3.531025
				C	-0.948671	0.501018	3.906805
				C	-0.472535	1.019250	5.272779

C	-0.863346	4.247506	3.673520
C	0.520520	4.106288	3.848923
C	1.132361	4.410871	5.068506
C	0.335254	4.865743	6.122547
C	-1.046001	5.024256	5.977550
C	-1.633433	4.710557	4.747747
C	2.615129	4.216855	5.250619
C	-1.874434	5.568915	7.112458
C	-3.323135	0.815738.	4.429348
C	-4.015150	-0.397189	4.305218
C	-5.000576	-0.772548	5.223035
C	-5.292920	0.090695	6.281657
C	-4.620276	1.306161	6.437679
C	-3.635842	1.654994	5.507305
C	-5.744350	-2.072396	5.058621
C	-4.950615	2.215812	7.592760
C	-4.900327	4.019070	2.229048
C	-5.143547	4.303434	3.581484
C	-5.731239	5.506805	3.976997
C	-6.081480	6.440256	2.994377
C	-5.864201.	6.185243	1.640669
C	-5.273040	4.970962	1.271597
C	-6.020649	5.789885	5.428210
C	-6.242271	7.194438	0.587329
C	0.083356	0.805766	2.823645
C	-1.074836	-1.025310	3.995441
C	0.586237	0.559635	-5.621876
C	1.945183	0.517563	-5.280765
C	2.940168	0.690527	-6.250086
C	2.555932	0.884814	-7.578994
C	1.210612	0.907103	-7.954264
C	0.234592	0.753052	-6.964936
C	4.399065	0.678351	-5.875898
C	0.832926	1.069834	-9.403882
C	0.510916	-1.804664	-3.806302
C	-1.195166	-1.801551	-5.629149
C	-3.736721	3.596806	-2.884483
C	-4.671138	3.762360	-5.204894
C	1.281435	2.794608	-2.658262
C	0.796893	5.199945	-2.922889
C	-4.581362	0.479675	0.939825
C	-6.341118	1.437422	2.476146
C	0.138109	5.423230	1.125936
C	-2.007095	6.378830	1.983539
F	1.827345	1.317248	0.357569
C	2.962049	0.774958	0.839206
C	3.184659	-0.597336	0.763082
C	4.422979	-1.002823	1.266213
C	5.355471	-0.135358	1.827487
C	5.069207	1.223086	1.897917
C	3.860374	1.681210	1.394121
B.	2.119699	-1.617204	0.049242
C	2.935733	-2.560693	-1.020555
C	3.052862	-3.950966	-0.996582

C	3.798160	-4.682828	-1.919154	H	-1.516259	6.709203	2.902413
C	4.483339	-4.022562	-2.928526	H	-1.925471	7.189348	1.250941
C	4.402517	-2.637869	-2.997290	H	-3.065163	6.209250	2.194537
C	3.638327	-1.952296	-2.060815	H	-3.018988	4.364673	0.235200
F	3.567746	2.985950	1.446246	H	-1.423769	3.962205	-0.427233
F	5.939883	2.072556	2.436921	H	-2.050792	5.606072	-0.551334
F	6.515905	-0.587888	2.296317	H	1.132285	3.747850	3.028052
F	4.773306	-2.289640	1.217246	H	3.045080	4.998237	5.884757
F	2.446678	-4.679421	-0.051278	H	3.143008	4.225818	4.293266
F	3.863751	-6.010131	-1.837036	H	2.827893	3.254997	5.732603
F	5.202583	-4.700790	-3.818242	H	0.801428	5.106005	7.076440
F	5.054041	-1.986330	-3.962098	H	-2.928516	5.296947	7.009070
F	3.599414	-0.613567	-2.194326	H	-1.823286	6.664124	7.145955
C	1.201419	-2.507814	1.072616	H	-1.519957	5.199595	8.079769
C	-0.034684	-2.982595	0.631890	H	-2.700377	4.849246	4.598405
C	-0.852366	-3.837512	1.362961	H	1.073063	0.478120	3.153179
C	-0.439772	-4.263046	2.619055	H	0.157977	1.873147	2.600887
C	0.772756	-3.805464	3.117023	H	-0.143896	0.266316	1.902284
C	1.550062	-2.939856	2.351400	H	-0.082550	-1.435997	4.201461
F	-0.491613	-2.639897	-0.584154	H	-1.736935	-1.344158	4.802890
F	2.688306	-2.529409	2.922566	H	-1.426407	-1.456448	3.052739
F	1.167621	-4.178073	4.333157	H	0.505612	0.582693	5.500463
F	-1.207368	-5.072291	3.343363	H	-1.161280	0.720964	6.067800
F	-2.022982	-4.251149	0.873452	H	-0.375271	2.105396	5.283742
H	0.670750	4.532929	0.777441	H	-3.771485	-1.071349	3.490662
H	0.660319	5.824999	1.996414	H	-5.139744	-2.818030	4.534427
H	0.187142	6.178724	0.334392	H	-6.034072	-2.491394	6.026706

H	-6.663926	-1.928706	4.478021	H	-0.403596	-1.805959	-6.382689
H	-6.049967	-0.196408	7.009157	H	-1.434589	-2.844079	-5.393767
H	-5.159611	1.643628	8.501951	H	-2.082994	-1.331576	-6.057366
H	-5.842276	2.819041	7.381434	H	-2.686481	-0.554412	-3.495041
H	-4.128529	2.903417	7.810532	H	-1.427198	-0.933293	-2.289264
H	-3.066200	2.571578	5.630985	H	-2.181848	-2.218042	-3.209204
H	-3.893811	0.121984	1.712118	H	2.239214	0.354264	-4.249894
H	-4.021129	0.644998	0.015593	H	4.888913	-0.235248	-6.229518
H	-5.296594	-0.327058	0.753279	H	4.538139	0.722608	-4.794085
H	-7.045139	0.674610	2.125604	H	4.926050	1.526067	-6.326676
H	-6.918145	2.329472	2.735071	H	3.323741	1.018449	-8.339279
H	-5.851292	1.066507	3.377117	H	1.089365	0.173004	-9.980170
H	-5.427163	2.568891	-0.657430	H	1.364626	1.909123	-9.865062
H	-6.725198	1.439262	-0.245441	H	-0.239979	1.240847	-9.524012
H	-4.886399	3.550954	4.320798	H	-0.818539	0.758337	-7.229579
H	-5.510505	5.080967	6.085192	H	2.332597	2.934323	-2.391743
H	-5.706441	6.800518	5.709109	H	1.189644	1.775594	-3.045474
H	-7.094880	5.717316	5.636515	H	0.706170	2.881087	-1.734416
H	-6.538190	7.382133	3.292577	H	1.759628	5.363898	-2.426964
H	-5.357999	7.564387	0.055662	H	0.622550	6.042590	-3.595650
H	-6.751280	8.057259	1.024909	H	0.019785	5.192433	-2.153415
H	-6.910313	6.756819	-0.162845	H	2.867491	4.204618	-4.374942
H	-5.097834	4.768476	0.220162	H	1.621741	4.792801	-5.484058
H	-6.768322	3.086013	0.388809	H	1.960149	3.055004	-5.374101
H	0.903630	-1.303813	-2.917247	H	-1.716142	5.832639	-3.724329
H	1.301341	-1.874034	-4.556891	H	-3.505020	7.661679	-4.533861
H	0.236728	-2.823389	-3.513851	H	-1.959276	8.487404	-4.728068

H	-3.099874	8.426602	-6.076375
H	-2.264584	7.018344	-7.803293
H	-0.635278	3.902623	-9.177449
H	-0.537780	5.644681	-9.459006
H	-2.102031	4.837752	-9.508623
H	-0.363117	3.275521	-6.884789
H	-2.800257	4.111985	-3.107362
H	-3.578366	2.955343	-2.015956
H	-4.472403	4.361359	-2.616184
H	-5.425808	4.459616	-4.823979
H	-5.112337	3.222560	-6.046654
H	-3.820534	4.341594	-5.569479
H	-5.233622	1.272768	-2.862648
H	-6.206461	2.719834	-3.169758
H	-2.781782	2.379829	-7.149892
H	-4.243449	0.726877	-10.199405
H	-3.608733	2.262317	-9.588276
H	-2.529853	0.885535	-9.820660
H	-4.929662	-1.011820	-8.685254
H	-4.918547	-3.006250	-6.240840
H	-6.304389	-2.339050	-7.104775
H	-6.148233	-2.101346	-5.356863
H	-4.560923	-0.435922	-4.457944
H	-6.001673	1.518779	-4.446293
H	-0.158064	0.355321	-0.668456
H	1.147973	-0.760594	-0.745973

[(Ar[^{t}Bu]N)$_3$Ti(OCHO)B(C$_6$F$_5$)$_3$] (2)

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Ti	14.003004	8.402243	4.643963
F	11.115940	3.626484	3.005563
F	11.653509	1.055415	2.576330
F	10.843342	-0.836629	4.362692
F	9.484613	-0.078770	6.595148
F	8.951865	2.473692	7.054082
F	11.245547	4.248066	7.639537
F	10.623847	4.888376	10.152406
F	8.324630	6.250014	10.688628
F	7.304275	6.392928	6.141764
F	6.693212	6.986473	8.641410
F	7.214859	3.634429	4.777821
F	5.494477	4.157488	2.808302
F	6.040862	6.114437	0.989962
F	8.363316	7.527395	1.204361
F	10.076539	7.030645	3.146586
O	12.698586	7.001320	5.097104
O	11.190400	5.415788	5.020703
N	14.106748	8.181518	2.750896
N	13.263920	10.116350	5.020959
N	15.690138	8.148110	5.500905
B	9.771399	4.804064	5.251536
C	11.528994	6.597839	5.312174
H	10.806858	7.280923	5.775778

C	13.791771	9.267000	1.868335
C	12.475289	9.485914	1.433417
H	11.688479	8.828884	1.790470
C	12.169050	10.519507	0.546199
C	13.205122	11.347063	0.093757
H	12.976960	12.152573	-0.601792
C	14.524157	11.154590	0.505953
C	14.803919	10.104906	1.390297
H	15.827965	9.916733	1.699397
C	10.752039	10.748324	0.087061
H	10.319202	11.636478	0.563289
H	10.110216	9.895873	0.324756
H	10.707017	10.911575	-0.994635
C	15.631383	12.053401	0.019589
H	15.299275	12.684854	-0.808842
H	16.495054	11.474114	-0.323541
H	15.984161	12.715693	0.819185
C	14.317411	6.860363	2.038578
C	15.344461	7.007055	0.904307
H	16.317621	7.343989	1.273018
H	15.006300	7.709218	0.138738
H	15.487099	6.032582	0.426116
C	12.997462	6.350887	1.438659
H	13.159559	5.363167	0.994277
H	12.627845	7.011409	0.650400
H	12.228325	6.250326	2.206480
C	14.830057	5.809887	3.028236
H	15.757342	6.133620	3.504518
H	15.034570	4.878930	2.490643
H	14.090733	5.581649	3.799360
C	11.906214	9.938463	5.463353
C	11.644328	9.677308	6.816764
H	12.482376	9.580855	7.501267
C	10.333308	9.557558	7.293930
C	9.279132	9.673741	6.383604
H	8.255332	9.580736	6.740855
C	9.506985	9.909293	5.021442
C	10.825026	10.038403	4.573551
H	11.027350	10.225495	3.524553
C	10.075878	9.343887	8.763070
H	10.338912	10.239129	9.338542
H	10.676037	8.519143	9.160888
H	9.022950	9.126616	8.959093
C	8.348703	10.052737	4.069469
H	7.570761	9.310387	4.272854
H	8.666567	9.937710	3.030512
H	7.884329	11.041458	4.167182
C	13.752553	11.530301	5.058862
C	12.980388	12.378748	4.035143
H	13.076037	11.960135	3.029936
H	13.383879	13.397305	4.025691
H	11.918963	12.446294	4.288858
C	15.233208	11.540771	4.690983
H	15.810787	10.941419	5.396909

H	15.617179	12.565711	4.708741
H	15.382033	11.143556	3.683696
C	13.582861	12.154163	6.452889
H	12.532391	12.212477	6.749166
H	13.985480	13.172378	6.446820
H	14.123186	11.582133	7.212973
C	15.264678	7.740912	6.814411
C	15.004131	6.388146	7.089529
H	15.115257	5.662392	6.289084
C	14.608932	5.964780	8.361690
C	14.457201	6.928642	9.363869
H	14.141470	6.612166	10.356507
C	14.704664	8.285986	9.129023
C	15.105186	8.678690	7.849493
H	15.314765	9.723430	7.642717
C	14.390467	4.504133	8.656334
H	15.302760	4.051798	9.064394
H	14.121399	3.948810	7.754417
H	13.594444	4.356913	9.390730
C	14.573866	9.292608	10.243055
H	15.469326	9.294787	10.876218
H	13.722168	9.064222	10.890931
H	14.445024	10.307672	9.856940
C	17.169351	8.156000	5.283764
C	17.765191	6.747258	5.456507
H	17.606933	6.368083	6.469775
H	18.845144	6.781998	5.278961
H	17.332931	6.032297	4.751665
C	17.871509	9.086093	6.289168
H	17.506500	10.113883	6.211632
H	18.947043	9.098168	6.083662
H	17.733961	8.746368	7.319213
C	17.458364	8.654896	3.868822
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H	18.534164	8.610654	3.671493
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C	9.302954	5.255704	6.752806
C	10.109178	4.921204	7.844353
C	9.806439	5.235193	9.162099
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C	8.150155	5.966655	7.083345
C	8.755633	5.267494	4.052615
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C	6.627411	4.844834	2.890851
C	6.900689	5.843835	1.962571
C	8.084164	6.558707	2.075473
C	8.972164	6.263539	3.106405

[Ti(N[^{t}Bu]Ar)$_3$][HB(C$_6$F$_5$)$_3$]
(3[HB(C$_6$F$_5$)$_3$])

129

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C	3.531431	1.113495	13.524173	H	5.594370	7.813671	16.102100
H	2.921276	1.204248	12.626474	H	3.881558	7.423842	16.244855
C	3.210220	0.151686	14.499353	C	2.712927	5.028728	15.271722
C	4.059829	0.016307	15.593897	C	1.709059	6.014759	15.212633
H	3.829473	-0.729688	16.352316	H	1.933215	6.975736	14.762620
C	5.214059	0.806112	15.749820	C	0.441548	5.773115	15.744044
C	5.505543	1.758765	14.778364	C	0.187065	4.519813	16.329080
H	6.375866	2.397918	14.884849	H	-0.798240	4.336470	16.753469
C	2.013011	-0.743478	14.322959	C	1.153883	3.520066	16.410087
H	1.712771	-1.203356	15.268035	C	2.421380	3.781030	15.862961
H	2.236465	-1.554712	13.619715	H	3.220044	3.047657	15.962810
H	1.158455	-0.192636	13.920403	C	-0.627533	6.827048	15.722459
C	6.096221	0.624538	16.955772	H	-0.457484	7.561774	14.932939
H	6.981151	1.263219	16.906555	H	-0.625737	7.374277	16.670913
H	6.433019	-0.413957	17.042848	H	-1.619870	6.385002	15.590008
H	5.558014	0.867227	17.878681	C	0.880892	2.227901	17.131816
C	5.105829	5.856254	15.332784	H	1.171155	2.313554	18.185832
C	6.333154	5.775356	14.426491	H	1.450887	1.399923	16.701905
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H	7.181871	6.272951	14.904792	C	2.454382	9.414569	18.841059
H	6.144255	6.274018	13.470722	C	2.823270	8.125921	19.218064
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H	4.531283	5.238307	17.348728	C	3.552507	8.806934	21.401087
H	6.241892	5.628856	17.161797	C	3.200565	10.112322	21.077418
H	5.616321	4.097478	16.520825	C	2.668607	10.383946	19.821207
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F 2.676656 7.094049 18.366495
F 3.700472 6.544492 20.753468
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F 3.382510 11.083558 21.970504
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F -0.889632 14.038132 17.048409
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F 4.591120 10.899211 17.662594
F 6.117914 11.690010 15.646890
F 5.214295 11.563525 13.078918
F 2.712394 10.594210 12.586085
F 1.165310 9.773528 14.594029
B 1.763344 9.725473 17.392987
H 1.365806 8.662698 16.963184

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