Supporting Information

# Synthesis, Characterization and Functionalization of Titanium κ$^1$*N* Amidinato Complexes from Carbodiimides

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## General Considerations

All reactions were performed under a dry oxygen free nitrogen or argon atmosphere with rigorous exclusion of oxygen and moisture using standard Schlenk and glovebox (< 0.5 ppm $O_2$, < 0.05 ppm $H_2O$) techniques. The glass equipment was stored in an oven at 120 °C, evacuated, and purged before use. Complexes **1a** and **1b** were prepared according to published procedures.[1,2] Carbodiimides were purchased by common suppliers and used without further purification. Solvents were dried according to standard procedures over Na/K alloy with benzophenone as an indicator and subsequently distilled and stored under a nitrogen atmosphere. NMR spectra were recorded on a Bruker AVANCE III RMN 1Bay 500 MHz spectrometer or a JEOL JNM-ECZL 500 MHz spectrometer ($^1$H 500 MHz; $^{11}$B 160 MHz; $^{13}$C 126 MHz; $^{15}$N 51 MHz). The NMR chemical shifts of $^1$H and $^{13}$C were referenced to the solvents. Absolute values of the coupling constants (δ) are provided in Hertz (Hz). Multiplicities of signals are abbreviated as single (s), double (d), triplet (t), septet (sept), multiplet (m) or broad (br). Given chemical shifts of $^{15}$N resulted out of $^1$H,$^{15}$N HMBC NMR experiments with nitromethane as external standard ($\delta$ = 378.9 ppm vs. $NH_3$). IR spectra were recorded on a Bruker Tensor 27 spectrometer using the attenuated total reflection (ATR) method. Elemental analysis was performed on a Euro EA 3000 Elemental Analyzer. Because of the high sensitivity to moisture and air, sample preparation was performed in a glovebox. For this purpose, 0.5-2.5 mg of the samples together with a small amount of vanadium pentoxide as combustion aid were weighed into tin capsules before sealing and quickly measured in triplicate. Deviations in C, N and H values are due to the sensitivity of the compounds and possible incomplete combustion of titanium carbide and nitride. UV/vis spectra were recorded on an Analytic Jena Specord 200 photometer. Melting points were determined using a Mettler Toledo MP30. The samples were prepared in a glovebox, pre-sealed with silicon grease and then fused before measurement.

## Experimental Section

### General procedure A for single insertion reactions of carbodiimides

In a glovebox, either **1a** or **1b** (1.00 equiv.) were suspended in *n*-hexane. To these suspensions were added the corresponding carbodiimide (1.00 equiv., DCC was dissolved in 1 mL of *n*-hexane) dropwise with a syringe at room temperature. The reaction mixtures turned from blue (for **1a**) and green (for **1b**) to red and green and a precipitate formed after a few hours of stirring. The suspensions were stirred for 16 h to accomplish full conversion along with full precipitation of the products. The mother liquors were then decanted, the residues washed twice with a small amount of *n*-hexane and the received solids were dried in high vacuum before transferred into a glovebox.

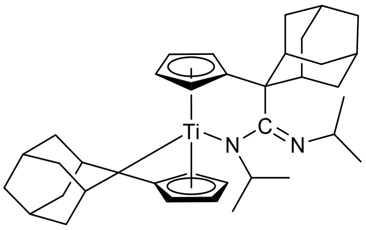
### General procedure B for double insertion reactions of carbodiimides

Inside A glovebox, **1b** (0.400 mmol) was dissolved in 5 mL of toluene. To this solution was added the corresponding carbodiimide (0.800 mmol, DCC was dissolved in 1 mL of toluene) dropwise with a syringe at room temperature, resulting in a colour change from green to yellow. The reaction mixtures were stirred for 16 h to obtain violet solutions. Afterwards, all volatile compounds were removed under reduced pressure and the residues washed with a small amount of *n*-hexane. The received violet solids were dried in high vacuum before transferred into a glovebox.

### General procedure C for reactivity studies

In a glovebox, **2a** (1.00 equiv.) was either suspended in 5 mL of *n*-hexane together with 1.00 equiv. of solid substrates, or liquid substrates were added to suspensions of **2a** in 5 mL of *n*-hexane dropwise with a syringe at room temperature. The reactions can be tracked by a colour change of the resulting suspensions. The suspensions were stirred for the time required to accomplish full conversion along with full precipitation of the products. The mother liquors were then decanted, the residues washed twice with 3 mL of *n*-hexane and the received solids were dried in high vacuum before transferred into a glovebox.

## Synthesis of 2a



Following the general procedure **A** with 4.500 mmol of each substrate in 60 mL of *n*-hexane, **2a** was obtained as a green powder (2.401 g, 4.205 mmol, 93%, mp. 171 °C (dec.)).

**$^1$H NMR** (500 MHz, $C_6D_6$, 305 K): δ = 0.95 (d, 3 H, $^3J$ = 6.6 Hz, $CH_3$), 1.08-1.10 (m, 1 H, Ad–H), 1.16-1.19 (m, 6 H, 2 x $CH_3$), 1.28 (d, 3 H, $^3J$ = 6.8 Hz, $CH_3$), 1.41-1.45 (m, 1 H, Ad–H), 1.61-2.17 (m, 21 H, Ad–H), 2.26-2.35 (m, 2 H, Ad–H), 2.67-2.72 (m, 2 H, Ad–H), 3.14 (sept, 1 H, $^3J$ = 6.0 Hz, $^i$Pr–CH), 3.29 (sept, 1 H, $^3J$ = 6.7 Hz, $^i$Pr–CH), 3.95-3.98 (m, 1 H, Cp–H), 4.22-4.26 (m, 1 H, Ad–H), 4.37-4.40 (m, 1 H, Cp–H), 4.48-4.52 (m, 1 H, Cp–H), 4.98-5.01 (m, 1 H, Cp–H), 5.35-5.37 (m, 1 H, Cp–H), 6.09-6.11 (m, 1 H, Cp–H), 6.54-6.56 (m, 1 H, Cp–H), 6.71-6.73 (m, 1 H, Cp–H) ppm.

**$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$, 305 K): δ = 24.3 ($CH_3$), 26.7 ($CH_3$), 27.7 ($CH_3$), 28.4 (Ad–CH), 28.7 (Ad–CH), 28.8 (Ad–CH), 29.7 (Ad–CH), 30.9 ($CH_3$), 32.2 (Ad–CH), 34.6 (Ad–$CH_2$), 34.9 (Ad–$CH_2$), 35.1 (Ad–$CH_2$), 36.2 (Ad–CH), 36.3 (Ad–$CH_2$), 36.6 (Ad–$CH_2$), 37.0 (Ad–CH), 37.2 (Ad–CH), 38.2 (Ad–$CH_2$), 39.7 (Ad–$CH_2$), 40.0 (Ad–$CH_2$), 44.1 (Ad–$CH_2$), 45.3 (Ad–$CH_2$), 48.5 ($^i$Pr–CH), 52.9 (Cp–$C_{exo}$), 61.4 ($^i$Pr–CH), 97.1 (Cp–CH), 105.0 (Cp–CH), 105.7 (Cp–CH), 108.2 (Cp–CH), 108.5 (Cp–CH), 109.3 (Cp–CH), 110.2 (Cp–CH), 115.7 (Cp–CH), 118.9 (Cp–$C_{exo}$), 121.9 (Cp–$C_{ipso}$),132.3 (Cp–$C_{ipso}$), 173.1 (N=C–N) ppm.

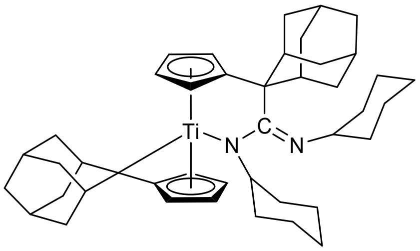
**$^1$H,$^{15}$N HMBC NMR** (51 MHz, 500 MHz, $C_6D_6$, 305 K): Could not be detected.

The assignment is difficult due to poor solubility in benzene-*d*$_6$, toluene-*d*$_8$ or THF-*d*$_8$.

**IR** (ATR): ṽ = 2901 (m), 2847 (w), 1577 (m), 1503 (m), 1448 (w), 1313 (m), 1258 (m), 1213 (w), 1188 (w), 1097 (m), 1060 (m), 1018 (m), 988 (w), 803 (s), 776 (m), 767 (m), 727 (m), 694 (m), 514 (m) cm$^{-1}$.

**EA**: calcd. for $C_{37}H_{50}N_2Ti$: C 77.87, H 8.83, N 4.91; found: C 77.91, H 8.53, N 4.93.

## Synthesis of 2b



Following the general procedure **A** with 0.562 mmol of each substrate in 5 mL of *n*-hexane, **2b** was obtained as a green powder (293 mg, 0.450 mmol, 80%, mp. 196 °C (dec.)).

**$^1$H NMR** (500 MHz, $C_6D_6$, 305 K): δ = 0.94-2.53 (m, 44 H, Ad–H, Cy–H), 2.68-2.70 (m, 2 H, Ad–H/Cy–H), 2.81-2.85 (m, 2 H, Ad–H/Cy–H), 3.00-3.04 (m, 1 H, Cy–H), 3.98-4.00 (m, 1 H, Cp–H), 4.18-4.20 (m, 1 H, Ad–H), 4.40-4.42 (m, 1 H, Cp–H), 4.53-4.55 (m, 1 H, Cp–H), 5.03-5.05 (m, 1 H, Cp–H), 5.39-5.41 (m, 1 H, Cp–H), 6.06-6.08 (m, 1 H, Cp–H), 6.58-6.60 (m, 1 H, Cp–H), 6.77-6.79 (m, 1 H, Cp–H) ppm.

**$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$, 305 K): δ = 24.7 ($CH_2$), 25.1 ($CH_2$), 26.75 ($CH_2$), 26.79 ($CH_2$), 28.33 ($CH_2$), 28.38 ($CH_2$), 28.43 (CH), 28.8 (CH), 29.7 (CH), 32.4 (CH), 34.6 ($CH_2$), 34.7 ($CH_2$), 35.0 ($CH_2$), 35.1 ($CH_2$), 36.2 (CH), 36.4 ($CH_2$), 36.6 ($CH_2$), 36.8 ($CH_2$), 36.9 ($CH_2$), 37.0 (CH), 37.4 (CH), 38.3 ($CH_2$), 39.6 ($CH_2$), 39.8 ($CH_2$), 41.7 ($CH_2$), 44.3 ($CH_2$), 45.4 ($CH_2$), 53.2 (Cp–$C_{exo}$), 56.8 (Cy–CH), 73.3 (CH), 97.3 (Cp–CH), 104.9 (Cp–CH), 105.9 (Cp–CH), 108.1 (Cp–CH), 108.7 (Cp–CH), 109.1 (Cp–CH), 110.0 (Cp–CH), 115.8 (Cp–CH), 119.0 (Cp–$C_{exo}$), 122.0 (Cp–$C_{ipso}$), 132.0 (Cp–$C_{ipso}$), 172.5 (N=C–N) ppm.

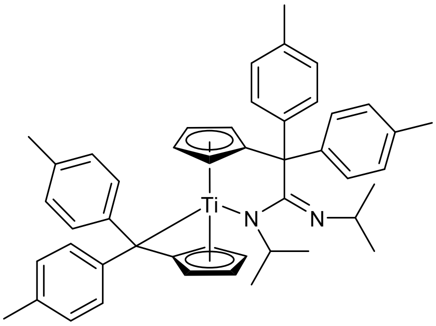
**$^1$H,$^{15}$N HMBC NMR** (51 MHz, 500 MHz, $C_6D_6$, 305 K): Could not be detected.

The assignment is difficult due to the poor solubility in benzene-*d*$_6$, toluene-*d*$_8$, or THF-*d*$_8$ and signal overlap with the sideproduct 2b'.

**IR** (ATR): ṽ = 2921 (m), 2902 (m), 2846 (m), 1624 (m), 1469 (w), 1449 (m), 1127 (m), 1093 (m), 1036 (m), 947 (m), 904 (m), 812 (s), 803 (s), 746 (m) cm$^{-1}$.

**EA**: calcd. for $C_{43}H_{58}N_2Ti$: C 79.36, H 8.98, N 4.30; found: 79.13, H 8.91, N 4.23.

## Synthesis of 3a



Following the general procedure **A** with 0.443 mmol of each substrate in 5 mL of *n*-hexane, **3a** was obtained as a red powder (245 mg, 0.355 mmol, 80%, mp. 95 °C (dec.)).

**$^1$H NMR** (500 MHz, $C_6D_6$, 305 K): δ = 0.76 (d, 3 H, $^3J$ = 5.8 Hz, $^i$Pr–CH$_3$), 0.93 (d, 3 H, $^3J$ = 5.8 Hz, $^i$Pr–CH$_3$), 1.41 (d, 3 H, $^3J$ = 6.7 Hz, $^i$Pr–CH$_3$), 1.59 (d, 3 H, $^3J$ = 6.7 Hz, $^i$Pr–CH$_3$), 2.03 (s, 3 H, *p*-Tol–CH$_3$), 2.14 (s, 3 H, *p*-Tol–CH$_3$), 2.18 (s, 3 H, *p*-Tol–CH$_3$), 2.22 (s, 3 H, *p*-Tol–CH$_3$), 3.39-3.43 (m, 1 H, Cp–H), 3.54 (sept, $^3J$ = 5.9 Hz, 1 H, $^i$Pr–CH), 3.89 (sept, $^3J$ = 6.7 Hz, 1 H, $^i$Pr–CH), 4.34-4.38 (m, 1 H, Cp–H), 4.58-4.63 (m, 1 H, Cp–H), 4.97-5.01 (m, 1 H, Cp–H), 5.61-5.65 (m, 1 H, Cp–H), 5.88-5.93 (m, 1 H, Cp–H), 6.05-6.12 (m, 2 H, Cp–H), 6.74-6.80 (m, 2 H, *p*-Tol–H), 7.05-7.09 (m, 2 H, *p*-Tol–H), 7.10-7.14 (m, 2 H, *p*-Tol–H), 7.19-7.24 (m, 2 H, *p*-Tol–H), 7.25-7.30 (m, 2 H, *p*-Tol–H), 7.40-7.46 (m, 2 H, *p*-Tol–H), 7.69-7.75 (m, 2 H, *p*-Tol–H), 7.87-7.92 (m, 2 H, *p*-Tol–H) ppm.

**$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$, 305 K): δ = 20.9 (*p*-Tol–CH$_3$), 21.0 (*p*-Tol–CH$_3$), 21.1 (2 x *p*-Tol–CH$_3$), 23.1 ($^i$Pr–CH$_3$), 23.4 ($^i$Pr–CH$_3$), 23.8 ($^i$Pr–CH$_3$), 24.3 ($^i$Pr–CH$_3$), 49.8 ($^i$Pr–CH), 61.1 ($^i$Pr–CH), 61.4 (Cp–C$_{exo}$), 105.9 (Cp–CH), 106.2 (Cp–CH), 108.4 (Cp–CH), 109.5 (Cp–CH), 109.9 (Cp–CH), 114.1 (Cp–CH), 115.4 (Cp–CH), 117.7 (Cp–C$_{exo}$), 119.3 (Cp–CH), 125.6 (Cp–C$_{ipso}$), 126.8 (*p*-Tol–CH), 128.5 (*p*-Tol–CH), 128.7 (*p*-Tol–CH), 128.7 (*p*-Tol–CH), 129.1 (*p*-Tol–CH), 130.4 (*p*-Tol–CH), 131.6 (*p*-Tol–CH), 132.6 (*p*-Tol–CH), 134.5 (*p*-Tol–CH), 136.1 (*p*-Tol–C$_q$), 136.1 (*p*-Tol–C$_q$), 136.6 (*p*-Tol–C$_q$), 136.7 (Cp–C$_{ipso}$), 140.4 (*p*-Tol–C$_q$), 141.8 (*p*-Tol–C$_q$), 141.8 (*p*-Tol–C$_q$), 142.6 (*p*-Tol–C$_q$), 175.2 (N=C–N) ppm.

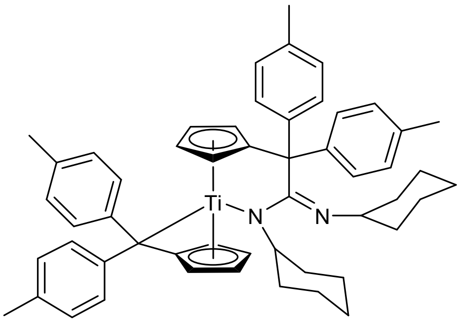
**$^1$H,$^{15}$N HMBC NMR** (51 MHz, 500 MHz, $C_6D_6$, 305 K): 276.7 (N–C=N), 278.2 (N=C–N) ppm.

**IR** (ATR): ṽ = 3090 (w), 3021 (w), 2919 (w), 1602 (m), 1508 (m), 1449 (m), 1417 (m), 1390 (m), 1431 (m), 1316 (m), 1260 (m), 1192 (m), 1094 (m), 1040 (m), 1021 (m), 808 (s), 776 (s), 763 (s), 749 (s), 723 (m), 710 (m), 674 (m), 616 (m), 575 (s) cm$^{-1}$.

**EA**: calcd. for $C_{47}H_{50}N_2Ti$: C 81.72, H 7.30, N 4.06; found: 80.513; H, 6.81; N, 3.512.*

* Slightly off, probably due to residual *n*-hexane.

## Synthesis of 3b



Following the general procedure **A** with 0.443 mmol for each substrate in 5 mL of *n*-hexane, **3b** was obtained as a green powder (176 mg, 0.288 mmol, 52%, mp. 144 °C (dec.)).

**$^1$H NMR** (500 MHz, $C_6D_6$, 305 K): δ = 0.92-1.00 (m, 2 H, Cy–$CH_2$), 1.09-1.19 (m, 2 H, Cy–$CH_2$), 1.27-1.42 (m, 8 H, Cy–$CH_2$), 1.48-1.52 (m, 1 H, Cy–$CH_2$), 1.56-1.65 (m, 3 H, Cy–$CH_2$), 1.66-1.71 (m, 1 H, Cy–$CH_2$), 1.86-1.91 (m, 1 H, Cy–$CH_2$), 2.04 (s, 3 H, *p*-Tol–$CH_3$), 2.16 (s, 3 H, *p*-Tol–$CH_3$), 2.19 (s, 3 H, *p*-Tol–$CH_3$), 2.20 (s, 3 H, *p*-Tol–$CH_3$), 3.10-3.26 (m, 3 H, Cy–CH, Cy–$CH_2$), 3.31-3.37 (m, 1 H, Cy–CH), 3.56-3.59 (m, 1 H, Cp–H), 4.39-4.42 (m, 1 H, Cp–H), 4.65-4.69 (m, 1 H, Cp–H), 5.02-5.06 (m, 1 H, Cp–H), 5.52-5.56 (m, 1 H, Cp–H), 5.93-5.96 (m, 1 H, Cp–H), 6.14-6.19 (m, 2 H, Cp–H), 6.78-6.82 (m, 2 H, *p*-Tol–H), 7.06-7.12 (m, 4 H, *p*-Tol–H), 7.17-7.20 (m, 2 H, *p*-Tol–H), 7.30-7.33 (m, 2 H, *p*-Tol–H), 7.41-7.45 (m, 2 H, *p*-Tol–H), 7.70-7.74 (m, 2 H, *p*-Tol–H) , 7.85-7.90 (m, 2 H, *p*-Tol–H) ppm.

**$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$, 305 K): δ = 20.9 (*p*-Tol–$CH_3$), 21.0 (*p*-Tol–$CH_3$), 21.0 (*p*-Tol–$CH_3$), 21.1 (*p*-Tol–$CH_3$), 25.1 (Cy–$CH_2$), 25.3 (Cy–$CH_2$), 26.8 (Cy–$CH_2$), 27.0 (Cy–$CH_2$), 27.9 (Cy–$CH_2$), 28.4 (Cy–$CH_2$), 32.3 (Cy–$CH_2$), 32.4 (Cy–$CH_2$), 34.5 (Cy–$CH_2$), 34.6 (Cy–$CH_2$), 58.0 (Cy–CH), 61.5 (Cp–$C_{exo}$), 72.2 (Cy–CH), 106.2 (Cp–CH), 106.7 (Cp–CH), 108.0 (Cp–CH), 109.6 (Cp–CH), 109.8 (Cp–CH), 114.5 (Cp–CH), 114.6 (Cp–CH), 117.5 (Cp–$C_{exo}$), 119.7 (Cp–CH), 125.7 (Cp–$C_{ipso}$), 127.1 (*p*-Tol–CH), 128.4 (*p*-Tol–CH), 128.5 (*p*-Tol–CH), 128.7 (*p*-Tol–CH), 129.2 (*p*-Tol–CH), 130.7 (*p*-Tol–CH), 131.5 (*p*-Tol–CH), 132.7 (*p*-Tol–CH), 134.5 (*p*-Tol–$C_q$), 136.0 (Cp–$C_{ipso}$), 136.1 (*p*-Tol–$C_q$), 136.2 (*p*-Tol–$C_q$), 136.4 (*p*-Tol–$C_q$), 140.9 (*p*-Tol–$C_q$), 141.7 (*p*-Tol–$C_q$), 141.8 (*p*-Tol–$C_q$), 142.9 (*p*-Tol–$C_q$), 175.1 (N=C–N) ppm.

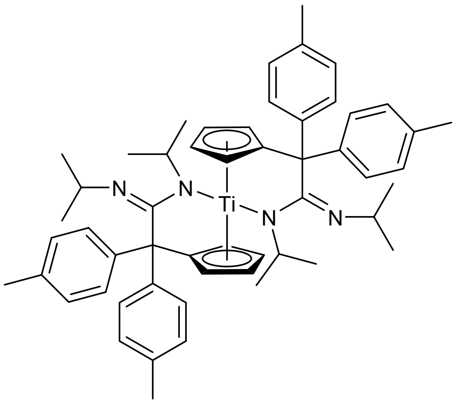
**$^1$H,$^{15}$N HMBC NMR** (51 MHz, 500 MHz, $C_6D_6$, 305 K): Could not be detected.

**IR** (ATR): ṽ = 3020 (w), 2922 (s), 2852 (m), 1582 (s), 1508 (m), 1449 (m), 1363 (w), 1348 (w), 1184 (w), 1167 (m), 1140 (w), 1052 (w), 1022 (w), 994 (w), 913 (w), 870 (w), 805 (s), 790 (s), 775 (s), 741 (s), 690 (m), 675 (m), 571 (s) $cm^{-1}$.

**EA**: calcd. for $C_{53}H_{58}N_2Ti$: C 82.57, H 7.58, N 3.63; found: C 79.513, H 6.30, N 3.51.*

* Slightly off, probably due to residual *n*-hexane.

## Synthesis of 4a



Following the general procedure **B**, **4a** was obtained as a violet crystalline solid (254 mg, 0.311 mmol, 78%, mp. 220 °C (dec.)).

**$^1$H NMR** (500 MHz, C$_6$D$_6$, 305 K): δ = 0.39 (d, $J$ = 5.8 Hz, 3 H, $^i$Pr–CH$_3$), 1.16 (d, $J$ = 5.8 Hz, 3 H, $^i$Pr–CH$_3$), 1.81 (d, $J$ = 6.3 Hz, 3 H, $^i$Pr–CH$_3$), 1.95 (d, $J$ = 6.3 Hz, 3 H, $^i$Pr–CH$_3$), 2.15 (s, 6 H, *p*-Tol–CH$_3$), 2.17 (s, 6 H, *p*-Tol–CH$_3$), 3.42 (sept, $J$ = 5.8 Hz, 1 H, $^i$Pr–CH), 4.46 (sept, $J$ = 6.3 Hz, 1 H, $^i$Pr–CH), 5.20-5.25 (m, 2 H, Cp–H), 5.37-5.43 (m, 2 H, Cp–H), 6.03-6.10 (m, 2 H, Cp–H), 6.45-6.50 (m, 2 H, Cp–H), 6.94-7.15 (m, 10 H, *p*-Tol–H), 7.56-7.87 (m, 6 H, *p*-Tol–H) ppm.

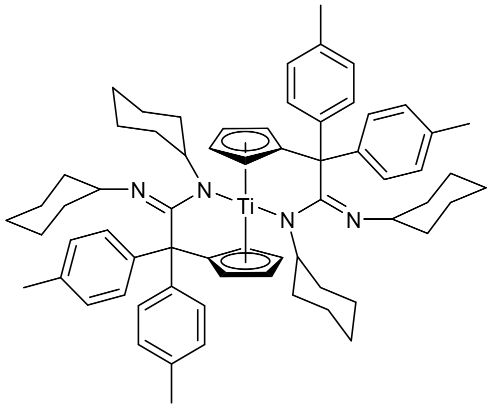
**$^{13}$C{$^1$H} NMR** (126 MHz, C$_6$D$_6$, 305 K): δ = 21.0 (*p*-Tol–CH$_3$), 21.0 (*p*-Tol–CH$_3$), 21.4 ($^i$Pr–CH$_3$), 23.0 ($^i$Pr–CH$_3$), 25.1 ($^i$Pr–CH$_3$), 25.5 ($^i$Pr–CH$_3$), 49.5 ($^i$Pr–CH), 58.2 ($^i$Pr–CH), 60.7 (Cp–C$_{exo}$), 106.0 (Cp–CH), 109.1 (Cp–CH), 113.5 (Cp–CH), 114.9 (Cp–CH), 128.8 (br, *p*-Tol–CH) 129.0 (*p*-Tol–CH), 130.7 (*p*-Tol–CH), 131.2 (br, *p*-Tol–CH), 136.2 (*p*-Tol–C$_q$), 136.5 (*p*-Tol–C$_q$), 140.0 (Cp–C$_{ipso}$), 140.4 (*p*-Tol–C$_q$), 141.3 (*p*-Tol–C$_q$), 173.8 (N=C–N) ppm.

**$^1$H,$^{15}$N HMBC NMR** (51 MHz, 500 MHz, C$_6$D$_6$, 305 K): 261.0 (N=C–N), 267.3 (N–C=N) ppm.

**IR** (ATR): ṽ = 2961 (w), 2919 (w), 2893 (w), 2861 (w), 1576 (s), 1511 (m), 1478 (m), 1372 (w), 1340 (w), 1206 (m), 1193 (w), 1185 (w), 1156 (w), 1141 (w), 1114 (w), 1007 (m), 900 (m), 880 (w), 819 (m), 806 (m), 783 (s), 672 (m), 558 (m), 549 (m), 515 (s) cm$^{-1}$.

**EA**: calcd. for C$_{54}$H$_{64}$N$_4$Ti: C 79.39, H 7.90, N 6.86; found: 79.33, H 7.80, N 7.19.

## Synthesis of 4b



Following the general procedure **B, 4b** was obtained as a violet crystalline solid (225 mg, 0.230 mmol, 58%, mp. 198 °C (dec.)).

**$^1$H NMR** (500 MHz, $C_6D_6$, 305 K): δ = 0.81-0.84 (m, 2 H, Cy–$CH_2$), 1.00-1.08 (m, 5 H, Cy–$CH_2$), 1.16-1.20 (m, 2 H, Cy–$CH_2$), 1.33-1.59 (m, 12 H, Cy–$CH_2$), 1.63-1.81 (m, 9 H, Cy–$CH_2$), 1.85-1.89 (m, 2 H, Cy–$CH_2$), 2.03-2.07 (m, 4 H, Cy–$CH_2$), 2.16 (s, 6 H, *p*-Tol–$CH_3$), 2.19 (s, 6 H, *p*-Tol–$CH_3$), 3.11-3.16 (m, 2 H, Cy–$CH_2$), 3.51-3.60 (m, 4 H, Cy–$CH_2$, Cy–CH), 3.97-4.03 (m, 2 Cy–CH), 5.20-5.25 (m, 2 H, Cp–H), 5.37-5.43 (m, 2 H, Cp–H), 6.03-6.10 (m, 2 H, Cp–H), 6.45-6.50 (m, 2 H, Cp–H), 6.94-7.15 (m, 10 H, *p*-Tol–H), 7.56-7.87 (m, 6 H, *p*-Tol–H) ppm.

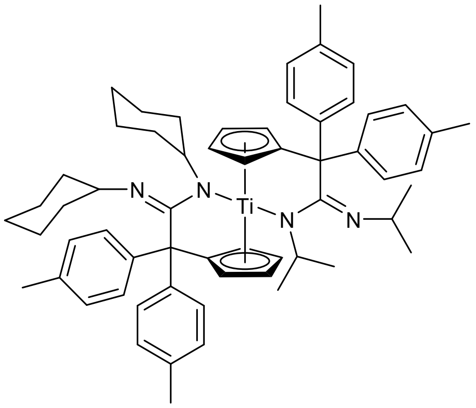
**$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$, 305 K): δ = 21.0 (*p*-Tol–$CH_3$), 21.0 (*p*-Tol–$CH_3$), 25.1 (Cy–$CH_2$), 25.3 (Cy–$CH_2$), 25.8 (Cy–$CH_2$), 26.9 (Cy–$CH_2$), 27.4 (Cy–$CH_2$), 28.3 (Cy–$CH_2$), 28.7 (Cy–$CH_2$), 30.9 (Cy–$CH_2$), 32.1 (Cy–$CH_2$), 33.6 (Cy–$CH_2$), 35.2 (Cy–$CH_2$), 35.4 (Cy–$CH_2$), 57.8 (Cy–$CH_2$), 60.9 (Cp–$C_{exo}$), 69.5 (Cy–CH), 108.1 (Cp–CH), 108.5 (Cp–CH), 110.4 (Cp–CH), 114.3 (Cp–CH), 128.9 (*p*-Tol–CH), 130.9 (*p*-Tol–CH), 136.1 (*p*-Tol–$C_q$), 136.5 (*p*-Tol–$C_q$), 140.7 (Cp–$C_{ipso}$), 140.8 (*p*-Tol–$C_q$), 141.2 (*p*-Tol–$C_q$), 175.3 (N=C–N) ppm.

**$^1$H,$^{15}$N HMBC NMR** (51 MHz, 500 MHz, $C_6D_6$, 305 K): Could not be detected.

**IR** (ATR): ṽ = 3023 (w), 2920 (m), 2850 (m), 1566 (s), 1510 (m), 1475 (m), 1467 (m), 1449 (m), 1363 (w), 1346 (w), 1252 (m), 1190 (s), 1183 (s), 1174 (s), 1143 (s), 1043 (w), 1022 (w), 994 (m), 912 (m), 889 (m), 876 (m), 839 (m), 814 (s), 802 (s), 789 (s), 770 (s), 672 (m), 550 (m), 509 (m) $cm^{-1}$.

**EA**: calcd. for $C_{66}H_{80}N_4Ti$: C 81.12, H 8.25, N 5.73; found: C 80.73, H 8.17, N 5.87.

## Synthesis of 4c



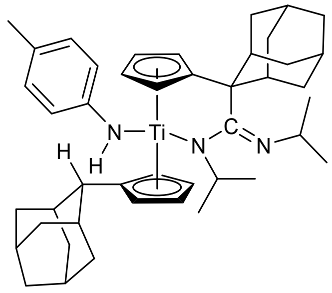
Inside a glovebox, **3a** (27.8 mg, 0.040 mmol) and di-cyclohexyl carbodiimide (8.3 mg, 0.040 mmol) were dissolved in 0.6 mL of benzene-$d_6$ at room temperature. On another way, **3b** (30.8 mg, 0.040 mmol) and di-*iso*-propyl carbodiimide (5.1 mg, 0.040 mmol) were dissolved in 0.6 mL of benzene-$d_6$. The reaction mixtures were analyzed by NMR spectroscopy over a period of 3 days and violet solutions of **4c** were obtained.

**$^{1}$H NMR** (500 MHz, $C_6D_6$, 298 K): δ = 0.51 (d, *J* = 5.8 Hz, 3 H, $^{i}$Pr–$CH_3$), 0.55-0.59 (m, 1 H, Cy–$CH_2$), 0.78-0.83 (m, 1 H, Cy–$CH_2$), 1.06 (d, *J* = 5.8 Hz, 3 H, $^{i}$Pr–$CH_3$), 1.21-1.25 (m, 2 H, Cy–$CH_2$), 1.30-1.40 (m, 4 H, Cy–$CH_2$), 1.44-1.51 (m, 2 H, Cy–$CH_2$), 1.55-1.64 (m, 3 H, Cy–$CH_2$), 1.80 (d, *J* = 6.3 Hz, 3 H, $^{i}$Pr–$CH_3$), 1.83-1.91 (m, 4 H, Cy–$CH_2$), 1.98 (d, *J* = 6.3 Hz, 3 H, $^{i}$Pr–$CH_3$), 2.14 (s, 3 H, *p*-Tol–$CH_3$), 2.17 (s, 3 H, *p*-Tol–$CH_3$), 2.18 (s, 6 H, *p*-Tol–$CH_3$), 3.07-3.17 (m, 2 H, Cy–$CH_2$, Cy–CH), 3.43 (sept, *J* = 5.8 Hz, 1 H, $^{i}$Pr–CH), 3.53-3.68 (m, 2 H, Cy–$CH_2$), 3.96-4.04 (m, 1 H, Cy–CH), 4.48 (sept, *J* = 6.3 Hz, 1 H, $^{i}$Pr–CH), 5.10-5.15 (m, 1 H, Cp–H), 5.21-5.24 (m, 1 H, Cp–H), 5.26-5.30 (m, 1 H, Cp–H), 5.38-5.42 (m, 1 H, Cp–H), 6.01-6.06 (m, 2 H, Cp–H), 6.38-6.43 (m, 2 H, Cp–H), 6.99-7.04 (m, 4 H, *p*-Tol–H), 7.09-7.15 (m, 4 H, *p*-Tol–H), 7.17-7.41 (br.m, 2 H, *p*-Tol–H), 7.66-7.89 (br.m, 6 H, *p*-Tol–H) ppm.

**$^{13}$C{$^{1}$H} NMR** (126 MHz, $C_6D_6$, 298 K): δ = 20.9 (*p*-Tol–$CH_3$), 21.0 (*p*-Tol–$CH_3$), 21.0 (*p*-Tol–$CH_3$), 21.0 (*p*-Tol–$CH_3$), 21.7 ($^{i}$Pr–$CH_3$), 23.2 ($^{i}$Pr–$CH_3$), 24.8 ($^{i}$Pr–$CH_3$), 24.9 (Cy–$CH_2$), 25.1 (Cy–$CH_2$), 25.2 (Cy–$CH_2$), 25.8 ($^{i}$Pr–$CH_3$), 25.8 ($^{i}$Pr–$CH_3$, Cy–$CH_2$), 26.9 (Cy–$CH_2$), 27.3 (Cy–$CH_2$), 28.4 (Cy–$CH_2$), 28.9 (Cy–$CH_2$), 30.5 (Cy–$CH_2$), 32.5 (Cy–$CH_2$), 33.3 (Cy–$CH_2$), 35.4 (2 x Cy–$CH_2$), 35.5 (Cy–$CH_2$), 49.6 ($^{i}$Pr–CH), 57.7 (Cy–CH), 58.6 ($^{i}$Pr–CH), 60.5 (Cp–$C_{exo}$), 61.0 (Cp–$C_{exo}$), 69.0 (Cy–CH), 107.0 (Cp–CH), 107.3 (Cp–CH), 108.6 (Cp–CH), 108.8 (Cp–CH), 111.9 (Cp–CH), 112.6 (Cp–CH), 114.0 (Cp–CH), 115.0 (Cp–CH), 128.9 (*p*-Tol–CH), 130.7 (br, *p*-Tol–CH), 130.8 (*p*-Tol–CH), 136.1 (*p*-Tol–$C_q$), 136.2 (*p*-Tol–$C_q$), 136.5 (*p*-Tol–$C_q$), 136.5 (*p*-Tol–$C_q$), 139.8 (Cp–$C_{ipso}$), 140.4 (*p*-Tol–$C_q$), 140.8 (*p*-Tol–$C_q$), 140.8 (Cp–$C_{ipso}$), 141.2 (*p*-Tol–$C_q$), 141.4 (*p*-Tol–$C_q$), 174.3 (NCN–Cy), 174.5 (NCN–$^{i}$Pr) ppm.

**$^{1}$H,$^{15}$N HMBC NMR** (51 MHz, 500 MHz, $C_6D_6$, 298 K): 266.9 ($^{i}$Pr), 273.2 ($^{i}$Pr) ppm.

## Synthesis of 5a



Following the general procedure **C** and stirring for 16 h gave **5a** as a red solid (218 mg, 0.322 mmol, 80%, mp. 178 °C (dec.)).

**$^1$H NMR** (500 MHz, $C_6D_6$, 305 K): δ = 1.24 (d, *J* = 5.8 Hz, 3 H, $^i$Pr–$CH_3$), 1.29 (d, *J* = 5.9 Hz, 3 H, $^i$Pr–$CH_3$), 1.37 (d, *J* = 5.9 Hz, 3 H, $^i$Pr–$CH_3$), 1.41 (d, *J* = 6.4 Hz, 3 H, $^i$Pr–$CH_3$), 1.44-1.53 (m, 2 H, Ad–H), 1.73-1.90 (m, 17 H, Ad–H), 2.00-2.03 (m, 1 H, Ad–H), 2.04-2.14 (m, 3 H Ad–H), 2.19 (s, 3 H, Ph–$CH_3$), 2.25-2.29 (m, 1 H, Ad–H), 2.45-2.48 (m, 1 H, Ad–H), 2.50-2.55 (m, 1 H, Ad–H), 2.59-2.64 (m, 1 H, Ad–H), 2.80 (s, 1 H, Cp–$C_{exo}$H ), 3.87 (sept, *J* = 5.9 Hz, 1 H, $^i$Pr–CH), 3.93 (sept, *J* = 6.2 Hz, 1 H, $^i$Pr–CH), 4.29-4.36 (m, 1 H, Ad–H), 5.15-5.18 (m, 1 H, Cp–H), 5.21-5.24 (m, 1 H, Cp–H), 5.40-5.45 (m, 3 H, 3 x Cp–H), 6.03-6.07 (m, 1 H, Cp–H), 6.35-6.38 (m, 1 H, Cp–H), 6.65-6.68 (m, 1 H, Cp–H), 6.69-6.73 (m, 2 H, Ph–H), 6.97-7.01 (m, 2 H, Ph–H), 8.38 (br.s, 1 H, N–H) ppm.

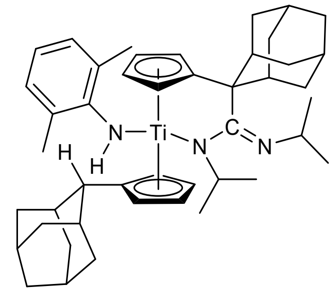
**$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$, 305 K): δ = 20.8 (Ph–$CH_3$), 22.6 ($^i$Pr–$CH_3$), 25.8 ($^i$Pr–$CH_3$), 27.3 ($^i$Pr–$CH_3$), 27.9 ($^i$Pr–$CH_3$), 28.2 (2 x Ad–CH), 28.6 (Ad–CH), 28.7 (Ad–CH), 32.2 (Ad–$CH_2$), 32.6 (Ad–$CH_2$, Ad–CH), 33.0 (Ad–CH), 33.7 (Ad–CH), 34.4 (Ad–$CH_2$), 34.7 (Ad–$CH_2$), 35.2 (Ad–$CH_2$), 36.9 (Ad–CH), 37.0 (Ad–$CH_2$), 38.2 (Ad–$CH_2$), 38.9 (Ad–$CH_2$), 39.1 (Ad–$CH_2$), 39.6 (Ad–$CH_2$), 44.8 (Cp–$C_{exo}$H), 48.4 ($^i$Pr–CH), 52.5 (Cp–$C_{exo}$), 56.7 ($^i$Pr–CH), 101.3 (Cp–CH), 106.0 (Cp–CH), 107.9 (Cp–CH), 109.3 (Cp–CH), 110.2 (Cp–CH), 114.3 (Cp–CH), 115.6 (Cp–CH), 117.4 (Cp–CH), 121.3 (2 x Ph–CH), 128.8 (Cp–$C_{ipso}$), 129.1 (2 x Ph–CH), 129.2 (Ph–$C_q$), 134.4 (Cp–$C_{ipso}$), 157.0 (Ph–$C_q$), 164.0 (N=C–N) ppm.

**$^1$H,$^{15}$N HMBC NMR** (51 MHz, 500 MHz, $C_6D_6$, 305 K): 229.7 (NH), 239.0 (N=C-N), 260.1 (N-C=N) ppm.

**IR** (ATR): ṽ = 3363 (w), 2965 (w), 2890 (m), 2850 (w), 1583 (m), 1503 (m), 1468 (w), 1447 (w), 1354 (w), 1262 (m), 1164 (w), 1146 (w), 1131 (w), 1108 (w), 1092 (m), 1061 (m), 1038 (m), 954 (w), 903 (w), 837 (m), 814 (s), 801 (s), 768 (m), 536 (w), 511 (m) $cm^{-1}$.

**EA**: calcd. for $C_{44}H_{59}N_3Ti$: C 77.97, H 8.77, N 6.20; found: C 77.81, H 8.74, N 6.26.

## Synthesis of 5b



Based on the general procedure **C** but with toluene instead of *n*-hexane with a reaction time of nine days, until the solvent was removed under reduced pressure and the residue washed with 3 mL of *n*-hexane, gave **5b** as an orange solid (205 mg, 0.286 mmol, 80%, mp. 179 °C (dec.)).

**$^1$H NMR** (500 MHz, $C_6D_6$, 305 K): δ = 1.28 (d, 3 H, *J* = 5.8 Hz, $^i$Pr–$CH_3$), 1.32 (d, 3 H, *J* = 5.8 Hz, $^i$Pr–$CH_3$), 1.39 (d, 3 H, *J* = 5.9 Hz, $^i$Pr–$CH_3$), 1.44 (d, 3 H, *J* = 6.5 Hz, $^i$Pr–$CH_3$), 1.48-1.54 (m, 2 H, Ad–H), 1.61-1.67 (m, 2 H, Ad–H), 1.69 (s, 3 H, Ph–$CH_3$), 1.70-1.93 (m, 15 H, Ad–H), 2.05-2.58 (m, 11 H, Ad–H, Ph–$CH_3$), 2.75 (s, 1 H, Cp–$C_{exo}$H), 4.06 (2 x sept, *J* = 6.0 Hz, 2 H, 2 x $^i$Pr–CH), 4.31-4.36 (m, 1 H, Ad–H), 4.88-4.91 (m, 1 H, Cp–H), 5.16-5.19 (m, 1 H, Cp–H), 5.24-5.26 (m, 1 H, Cp–H), 5.27-5.29 (m, 1 H, Cp–H), 5.52-5.54 (m, 1 H, Cp–H), 5.72-5.74 (m, 1 H, Cp–H), 5.91-5.93 (m, 1 H, Cp–H), 6.43-6.45 (m, 1 H, Cp–H), 6.91-6.95 (m, 1 H, Ph–CH), 7.04-7.08 (m, 2 H, Ph–CH), 7.87 (br.s, 1 H, N–H) ppm.

**$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$, 305 K): δ = 22.1 ($^i$Pr–$CH_3$), 26.3 ($^i$Pr–$CH_3$), 26.9 ($^i$Pr–$CH_3$), 27.9 (Ph–$CH_3$), 28.0 (Ph–$CH_3$), 28.4 ($^i$Pr–$CH_3$), 28.5 (Ad–CH), 28.7 (Ad–CH), 32.65 (Ad–CH), 32.73 (Ad–CH), 32.8 (Ad–$CH_2$), 32.9 (Ad–$CH_2$), 34.52 (Ad–$CH_2$), 34.55 (Ad–$CH_2$), 35.2 (Ad–$CH_2$), 36.9 (Ad–$CH_2$), 37.5 (Ad–CH), 38.2 (Ad–$CH_2$), 38.38 (Ad–$CH_2$), 38.41 (Ad–$CH_2$), 39.6 (Ad–$CH_2$), 44.7 (Cp–$C_{exo}$H), 48.3 ($^i$Pr–CH), 52.6 (Cp–$C_{exo}$), 55.2 ($^i$Pr–CH), 102.3 (Cp–CH), 102.7 (Cp–CH), 104.9 (Cp–CH), 109.1 (Cp–CH), 113.1 (Cp–CH), 114.3 (Cp–CH), 114.4 (Cp–CH), 117.6 (Cp–CH), 123.1 (3 x Ph–CH), 134.9 (Cp–$C_{ipso}$), 135.9 (Cp–$C_{ipso}$), 159.2 (Ph–$C_q$–N), 163.8 (N=C–N) ppm.*

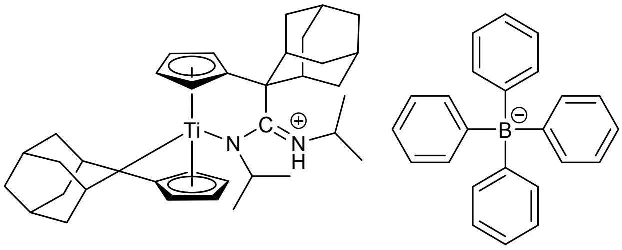
* The signal for Ph–$\underline{C_q}$–$CH_3$ could not be assigned.

**$^1$H,$^{15}$N HMBC NMR** (51 MHz, 500 MHz, $C_6D_6$, 305 K): 232.8 (N=C–N), 239.8 (NH), 257.8 (N–C=N) ppm.

**IR** (ATR): $\tilde{\nu}$ = 3325 (w), 2956 (w), 2895 (m), 2848 (m), 1592 (m), 1468 (w), 1448 (m), 1373 (w), 1355 (w), 1203 (m), 1164 (m), 1147 (m), 1111 (m), 1093 (s), 1059 (s), 1043 (m), 903 (w), 833 (s), 812 (w), 795 (s), 768 (s), 676 (w), 536 (w), 516 (m) cm$^{-1}$.

**EA**: calcd. for $C_{45}H_{61}N_3Ti$: C 77.97, H 8.77, N 6.20; found: C 77.81, H 8.74, N 6.26.

## Synthesis of 6



Based on the general procedure **C** but with toluene instead of *n*-hexane with a reaction time of three days gave **6** as a yellow solid (336 mg, 0.377 mmol, 94%, mp. 73 °C (dec.)).

**$^1$H NMR** (500 MHz, $CD_2Cl_2$, 305 K): δ = 0.37 (d, *J* = 6.3 Hz, 3 H, $^i$Pr–$CH_3$), 0.73-0.76 (m, 1 H, Ad–H), 0.95 (d, *J* = 6.3 Hz, 3 H, $^i$Pr–$CH_3$), 0.98-1.01 (m, 1 H, Ad–H), 1.10 (d, *J* = 6.3 Hz, 3 H, $^i$Pr–$CH_3$), 1.24 (d, *J* = 6.3 Hz, 3 H, $^i$Pr–$CH_3$), 1.53-1.59 (m, 1 H, Ad–H), 1.69-1.73 (m, 1 H, Ad–H), 1.77-1.81 (m, 1 H, Ad–H), 1.82-1.85 (m, 1 H, Ad–H), 1.87-2.23 (m, 16 H, Ad–H), 2.29-2.34 (m, 2 H, Ad–H), 2.45-2.49 (m, 1 H, Ad–H), 2.58-2.63 (m, 1 H, Ad–H), 2.86-2.91 (m, 1 H, Ad–H), 3.12-3.19 (dsept, *J* = 10.0 Hz, 6.3 Hz, 1 H, $^i$Pr–CH), 3.40 (sept, *J* = 6.3 Hz, 1 H, $^i$Pr–CH), 4.20-4.24 (m, 1 H, Cp–H), 4.88-4.92 (m, 1H, Cp–H), 5.04-5.08 (m, 2 H, 2 x Cp–H), 5.69-5.73 (m, 1 H, Cp–H), 6.45-6.50 (m, 1 H, Cp–H), 6.67-6.70 (m, 1 H, Cp–H), 6.73 (br.d, *J* = 10.1 Hz, 1 H, N–H), 6.87-6.90 (m, 4 H, Ph–CH), 7.01-7.05 (m, 8 H, Ph–CH), 7.31-7.34 (m, 9 H, Ph–CH, 1 x Cp–H) ppm.

**$^{13}$C{$^1$H} NMR** (126 MHz, $CD_2Cl_2$, 305 K): δ = 23.1 ($^i$Pr–$CH_3$), 23.6 ($^i$Pr–$CH_3$), 23.7 ($^i$Pr–$CH_3$), 26.9 (Ad–CH), 27.7 (Ad–CH), 27.9 (Ad–CH), 29.2 (Ad–CH), 30.3 ($^i$Pr–$CH_3$), 34.5 (Ad–CH), 34.9 (Ad–$CH_2$), 35.08 (Ad–$CH_2$), 35.12 (Ad–$CH_2$, Ad–CH), 35.8 (Ad–$CH_2$), 35.9 (Ad–CH), 37.0 (Ad–$CH_2$), 37.1 (Ad–CH), 37.5 (Ad–$CH_2$), 38.6 (Ad–$CH_2$), 38.9 (Ad–$CH_2$), 40.4 (Cp–$C_{exo}$), 45.8 (Ad–$CH_2$), 46.1 (Ad–$CH_2$), 49.4 ($^i$Pr–CH), 59.2 ($^i$Pr–CH), 102.3 (Cp–CH), 110.6 (Cp–CH), 111.2 (Cp–CH), 111.5 (Cp–CH), 112.0 (2 x Cp–CH), 113.4 (Cp–CH), 121.5 (Cp–$C_{ipso}$), 122.1 (4 x Ph–CH), 122.2 (Cp–CH), 125.7 (Cp–$C_{ipso}$), 125.98 (2 x Ph–CH), 126.00 (2 x Ph–CH), 126.03 (2 x Ph–CH), 126.05 (2 x Ph–CH), 136.4 (8 x Ph–CH), 138.6 (Cp–$C_{exo}$), 164.0 (Ph–$C_q$), 164.4 (Ph–$C_q$), 164.7 (Ph–$C_q$), 165.1 (Ph–$C_q$), 172.5 (N–C=N) ppm.

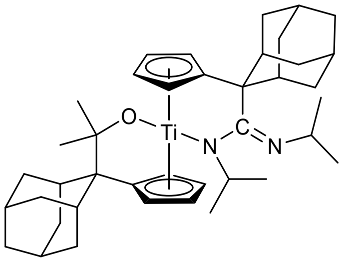
**$^{11}$B{$^1$H} NMR** ($CD_2Cl_2$, 160 MHz, 305 K): δ = -6.6 ppm.

**IR** (ATR): ṽ = 3391 (w), 3053 (w), 2982 (w), 2903 (m), 2847 (w), 1579 (w), 1542 (m), 1494 (m), 1468 (m), 1447 (m), 1424 (w), 1261 (w), 1138 (w), 1122 (m), 1098 (m), 1063 (m), 1051 (m), 1031 (m), 949 (w), 825 (m), 807 (m), 746 (m), 732 (s), 704 (s), 645 (m), 612 (m) $cm^{-1}$.

**EA**: calcd. for $C_{61}H_{71}BN_2Ti$: C 79.39, H 7.90, N 6.86; found: C 78.93, H 6.86, N 7.19.*

* Slightly off, probably due to residual toluene.

## Synthesis of 7



Following the general procedure **C** and stirring for three days gave **7** as a pale yellow solid (100 mg, 0.159 mmol, 40%, mp. 193 °C (dec.)).

**$^1$H NMR** (500 MHz, $C_6D_6$, 305 K): δ = 1.04 (d, *J* = 5.8 Hz, 3 H, $^i$Pr–$CH_3$), 1.21 (s, 3 H, $CH_3$) 1.24 (d, *J* = 6.1 Hz, 3 H, $^i$Pr–$CH_3$), 1.34 (d, *J* = 6.1 Hz, 3 H, $^i$Pr–$CH_3$), 1.38 (d, *J* = 5.8 Hz, 3 H, $^i$Pr–$CH_3$), 1.41 (s, 3 H, $CH_3$), 1.57-1.62 (m, 1 H, Ad–H), 1.63-1.90 (m, 15 H, Ad–H), 2.04-2.10 (m, 3 H, Ad–H), 2.18-2.20 (m, 1 H, Ad–H), 2.35-2.37 (m, 1 H, Ad–H), 2.44-2.56 (m, 5 H, Ad–H), 2.69-2.72 (m, 1 H, Ad–H), 3.58 (sept, *J* = 5.9 Hz, 1 H, $^i$Pr–CH), 3.80 (sept, *J* = 6.2 Hz, 1 H, $^i$Pr–CH), 3.90-4.15 (br.m, 1 H, Ad–H), 4.84-4.87 (m, 1 H, Cp–H), 5.01-5.03 (m, 1 H, Cp–H), 5.34-5.36 (m, 1 H, Cp–H), 5.52-5.54 (m, 1 H, Cp–H), 5.65-5.68 (m, 1 H, Cp–H), 5.72-5.74 (m, 1 H, Cp–H), 5.76-5.78 (m, 1 H, Cp–H), 6.22-6.25 (m, 1 H, Cp–H) ppm.

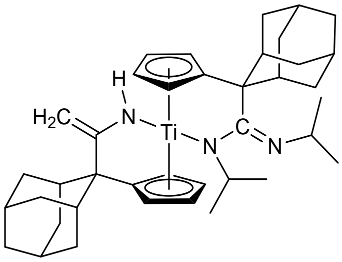
**$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$, 305 K): δ = 24.1 ($^i$Pr–$CH_3$), 25.4 ($^i$Pr–$CH_3$), 26.6 ($^i$Pr–$CH_3$), 27.7 (Ad–CH), 28.0 (Ad–CH), 28.2 ($^i$Pr–$CH_3$), 28.7 (Ad–CH), 28.8 (Ad–CH), 31.5 ($CH_3$), 33.0 (Ad–CH), 33.4 ($CH_3$), 33.6 (Ad–CH), 34.3 (Ad–CH), 34.5 (Ad–$CH_2$), 34.8 (Ad–$CH_2$), 34.9 (Ad–$CH_2$), 35.0 (Ad–$CH_2$), 35.3 (Ad–$CH_2$), 36.8 (Ad–$CH_2$, Ad–CH), 37.5 (Ad–$CH_2$), 38.7 (Ad–$CH_2$), 39.39 (Ad–$CH_2$), 39.43 (Ad–$CH_2$), 48.1 ($^i$Pr–CH), 53.3 (Cp–$C_{exo}$), 55.1 (Cp–$C_{exo}$), 56.1 ($^i$Pr–CH), 101.2 (Cp–CH), 101.4 (Cp–CH), 107.4 (Cp–CH), 107.8 (Cp–CH), 108.1 (Cp–CH), 110.0 (O–$C_q$), 110.7 (Cp–CH), 112.8 (Cp–CH), 116.6 (Cp–CH), 137.6 (Cp–$C_{ipso}$), 157.9 (Cp–$C_{ipso}$), 165.2 (N=C–N) ppm.

**$^1$H,$^{15}$N HMBC NMR** (51 MHz, 500 MHz, $C_6D_6$, 305 K): 240.6 (N–C=N), 260.9 (N=C–N) ppm.

**IR** (ATR): ṽ = 2970 (w), 2898 (m), 2850 (w), 2817 (w), 1604 (m), 1478 (w), 1470 (w), 1454 (w), 1376 (w), 1176 (m), 1149 (m), 1134 (m), 1092 (m), 1061 (m), 1049 (m), 1038 (m), 973 (m), 959 (m), 950 (m), 878 (m), 821 (s), 813 (s), 618 (m), 518 (m) $cm^{-1}$.

**EA**: calcd. for $C_{40}H_{56}N_2OTi$: C 76.41, H 8.98, N 4.46; found: C 76.15, H 8.79, N 4.52.

## Synthesis of 8



Following the general procedure **C** and stirring for 16 h gave **8** as an orange solid (189 mg, 0.309 mmol, 77%, mp. 196 °C (dec.)).

**$^1$H NMR** (500 MHz, $C_6D_6$, 305 K): δ = 0.96 (d, *J* = 5.9 Hz, 3 H, $^i$Pr–$CH_3$), 1.05 (d, *J* = 6.1 Hz, 3 H, $^i$Pr–$CH_3$), 1.14 (d, *J* = 6.0 Hz, 3 H, $^i$Pr–$CH_3$), 1.35 (d, *J* = 5.8 Hz, 3 H, $^i$Pr–$CH_3$), 1.64-1.75 (m, 6 H, Ad–H), 1.77-1.85 (m, 7 H, Ad–H), 1.89-1.96 (m, 3 H, Ad–H), 2.00-2.09 (m, 3 H, Ad–H), 2.12-2.20 (m, 1 H, Ad–H), 2.36-2.56 (m, 5 H, Ad–H), 2.79-2.85 (m, 1 H, Ad–H), 2.87-2.92 (m, 1 H, Ad–H), 3.42 (sept, *J* = 5.9 Hz, 1 H, $^i$Pr–CH), 3.61 (sept, *J* = 6.1 Hz, 1 H, $^i$Pr–CH), 3.77 (s, 1 H, C=$CH_2$), 3.90-4.11 (br.m, 1 H, Ad–H), 4.30 (s, 1 H, C=$CH_2$), 4.90-4.92 (m, 1 H, Cp–H), 4.96-4.98 (m, 1 H, Cp–H), 5.20-5.22 (m, 1 H, Cp–H), 5.25-5.27 (m, 1 H, Cp–H), 5.29-5.31 (m, 1 H, Cp–H), 5.36-5.38 (m, 1 H, Cp–H), 5.62-5.64 (m, 1 H, Cp–H), 6.23-6.25 (m, 1 H, Cp–H), 7.35 (br.s, 1 H, N–H) ppm.

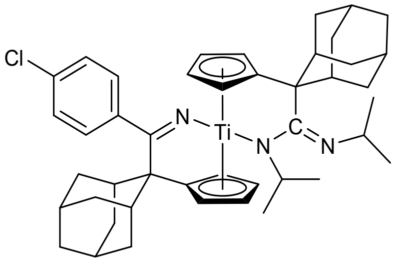
**$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$, 305 K): δ = 24.3 ($^i$Pr–$CH_3$), 25.5 ($^i$Pr–$CH_3$), 26.2 ($^i$Pr–$CH_3$), 27.4 (Ad–CH), 28.57 (Ad–CH), 28.63 (Ad–CH), 28.9 (Ad–CH), 29.6 ($^i$Pr–$CH_3$), 32.9 (Ad–CH), 33.2 (Ad–$CH_2$), 33.8 (Ad–$CH_2$), 34.2 (Ad–CH), 34.8 (Ad–$CH_2$), 35.1 (Ad–$CH_2$), 35.3 (Ad–$CH_2$), 35.5 (Ad–$CH_2$), 36.2 (Ad–CH), 36.6 (Ad–$CH_2$), 37.1 (Ad–CH), 37.3 (Ad–$CH_2$), 39.4 (Ad–$CH_2$), 40.2 (Ad–$CH_2$), 47.8 ($^i$Pr–CH), 50.7 (Cp–$C_{exo}$), 53.0 (Cp–$C_{exo}$), 56.6 ($^i$Pr–CH), 86.0 (C=$\underline{C}H_2$), 100.2 (Cp–CH), 103.3 (Cp–CH), 104.3 (Cp–CH), 107.0 (Cp–CH), 108.8 (Cp–CH), 111.5 (Cp–CH), 112.0 (Cp–CH), 114.0 (Cp–CH), 137.3 (Cp–$C_{ipso}$), 149.4 (Cp–$C_{ipso}$), 164.6 (N=C–N), 180.5 ($\underline{C}$=$CH_2$) ppm.

**$^1$H,$^{15}$N HMBC NMR** (51 MHz, 500 MHz, $C_6D_6$, 305 K): 232.8 (N=C–N), 239.8 (NH), 257.8 (N–C=N) ppm.

**IR** (ATR): ṽ = 3351 (w), 2951 (w), 2900 (m), 2851 (w), 2814 (w), 1598 (s), 1453 (w), 1235 (w), 1174 (w), 1165 (w), 1149 (w), 1126 (w), 1093 (m), 1059 (m), 1038 (m), 997 (w), 949 (w), 815 (s), 805 (s), 763 (s), 573 (w), 547 (m) $cm^{-1}$.

**EA**: calcd. for $C_{39}H_{53}N_3Ti$: C 76.57, H 8.73, N 6.87; found: C 76.19, H 8.43, N 6.82.

## Synthesis of 9



Following the general procedure **C** and stirring for 16 h gave **9** as a pink solid (228 mg, 0.322 mmol, 80%, mp. 180 °C (dec.)).

**$^1$H NMR** (500 MHz, $C_6D_6$, 305 K): δ = 0.94 (d, *J* = 6.0 Hz, 3 H, $^i$Pr–$CH_3$), 1.03 (d, *J* = 6.3 Hz, 3 H, $^i$Pr–$CH_3$), 1.10-1.26 (br.m, 6 H, $^i$Pr–$CH_3$), 1.19-2.62 (m, 27 H, Ad–H), 3.16-3.48 (br.m, 1 H, $^i$Pr–CH), 3.53-4.20 (br.m, 1 H, Ad–H), 3.83 (sept, *J* = 6.3 Hz, 1 H, $^i$Pr–CH), 4.85-4.87 (m, 1 H, Cp–H), 4.88-5.02 (br.m, 1 H, Cp–H), 5.48-5.50 (m, 1 H, Cp–H), 5.63-5.65 (m, 1 H, Cp–H), 5.87-5.89 (m, 1 H, Cp–H), 6.04-6.26 (br.m, 3 H, 3 x Cp–H), 6.61-7.01 (br.m, 2 H, Ph–H), 7.03-7.11 (m, 2 H, Ph–H) ppm.

**$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$, 305 K): δ = 24.8 ($CH_3$), 25.2 (br, $CH_3$), 27.6 (br, $CH_3$), 27.8 (Ad–CH), 28.1 (Ad–CH), 28.6 (Ad–CH), 28.8 (Ad–CH), 29.6 (br, $CH_3$), 33.1 (Ad–$CH_2$), 34.0 (Ad–$CH_2$), 34.8 (Ad–CH), 34.9 (Ad–CH), 35.00 (Ad–$CH_2$), 35.3 (Ad–$CH_2$), 35.4 (Ad–$CH_2$), 35.8 (Ad–$CH_2$), 36.3 (Ad–$CH_2$), 39.1 (Ad–$CH_2$), 39.2 (Ad–$CH_2$), 48.3 ($^i$Pr–CH), 53.4 (Cp–$C_{exo}$), 61.0 (Cp–$C_{exo}$), 100.7 (br, Cp–CH), 103.1 (br, Cp–CH), 105.3 (br, Cp–CH), 107.7 (br, Cp–CH), 108.5 (Cp–CH), 112.9 (br, Cp–CH), 119.9 (br, Cp–CH), 128.6 (Ph–CH), 132.3 (Ph–$C_q$), 135.4 (Cp–$C_{ipso}$), 145.0 (Ph–$C_q$), 149.0 (Cp–$C_{ipso}$) ppm.*

* The remaining signals of the adamantyl moieties, the isopropyl group and the signal for N=$\underline{C}$–N are missing in the spectrum / cannot be assigned due to strong broadening.

**$^1$H,$^{15}$N HMBC NMR** (51 MHz, 500 MHz, $C_6D_6$, 305 K): Could not be detected.

**IR** (ATR): ṽ = 3016 (w), 2969 (w), 2953 (m), 2933 (m), 2906 (m), 2893 (m), 2881 (m), 2859 (m), 2801 (w), 1600 (m), 1588 (s), 1483 (w), 1450 (w), 1304 (w), 1261 (w), 1169 (m), 1147 (m), 1111 (m), 1089 (s), 1060 (s), 1041 (m), 1015 (m), 987 (m), 952 (m), 830 (s), 816 (s), 799 (s), 772 (m), 736 (m), 610 (m), 510 (m) $cm^{-1}$.

**EA**: calcd. for $C_{44}H_{54}ClN_3Ti$: C 74.62, H 7.69, N 5.93; found: C 73.91, H 7.38, N 5.96.*

* Slightly off, probably due to residual *n*-hexane and silicon grease.

# NMR Spectra

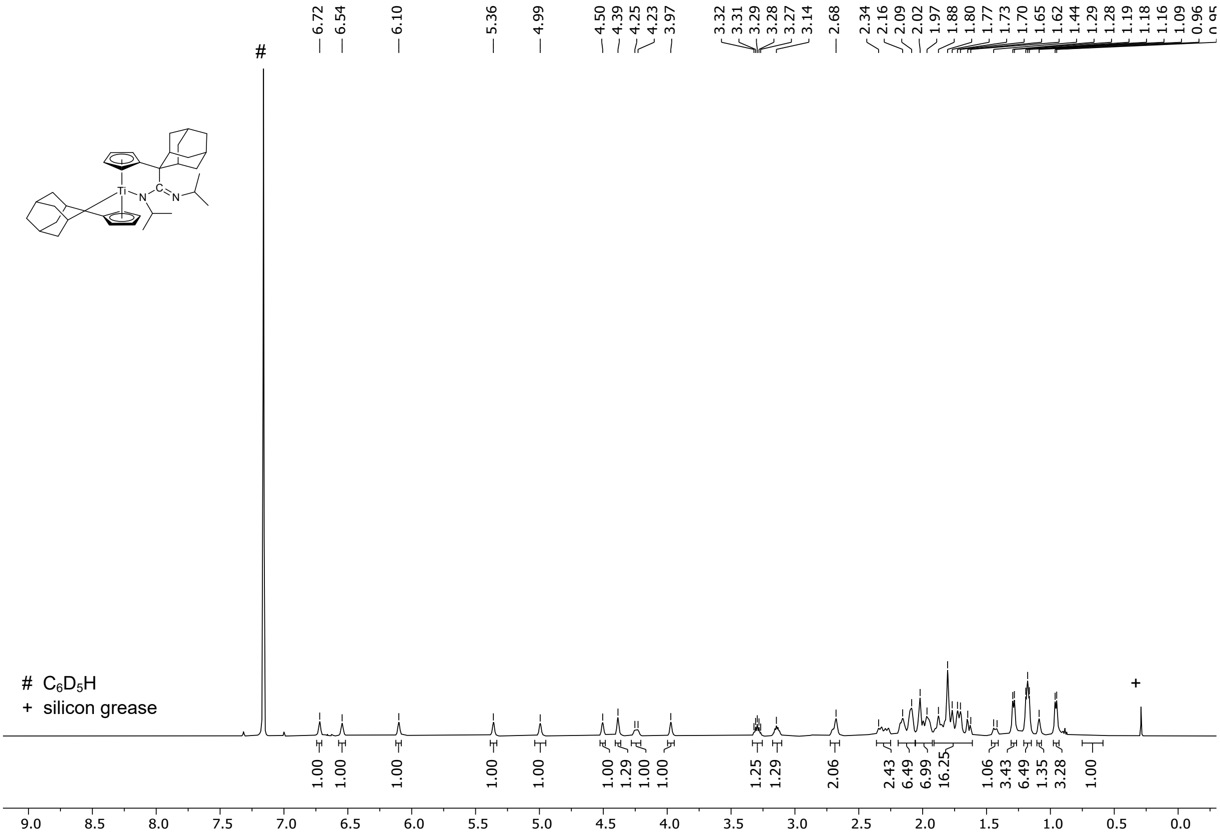


**Figure S1:** $^1H$ NMR spectrum of **2a** (500 MHz, $C_6D_6$, 305 K).

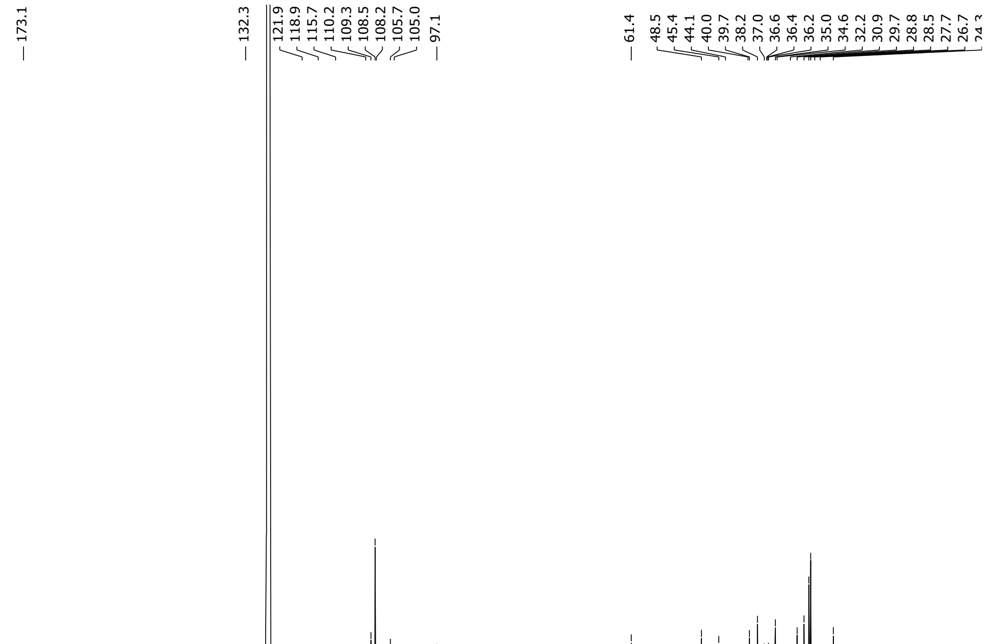


**Figure S2:** $^{13}C\{^1H\}$ NMR spectrum of **2a** (126 MHz, $C_6D_6$, 305 K).

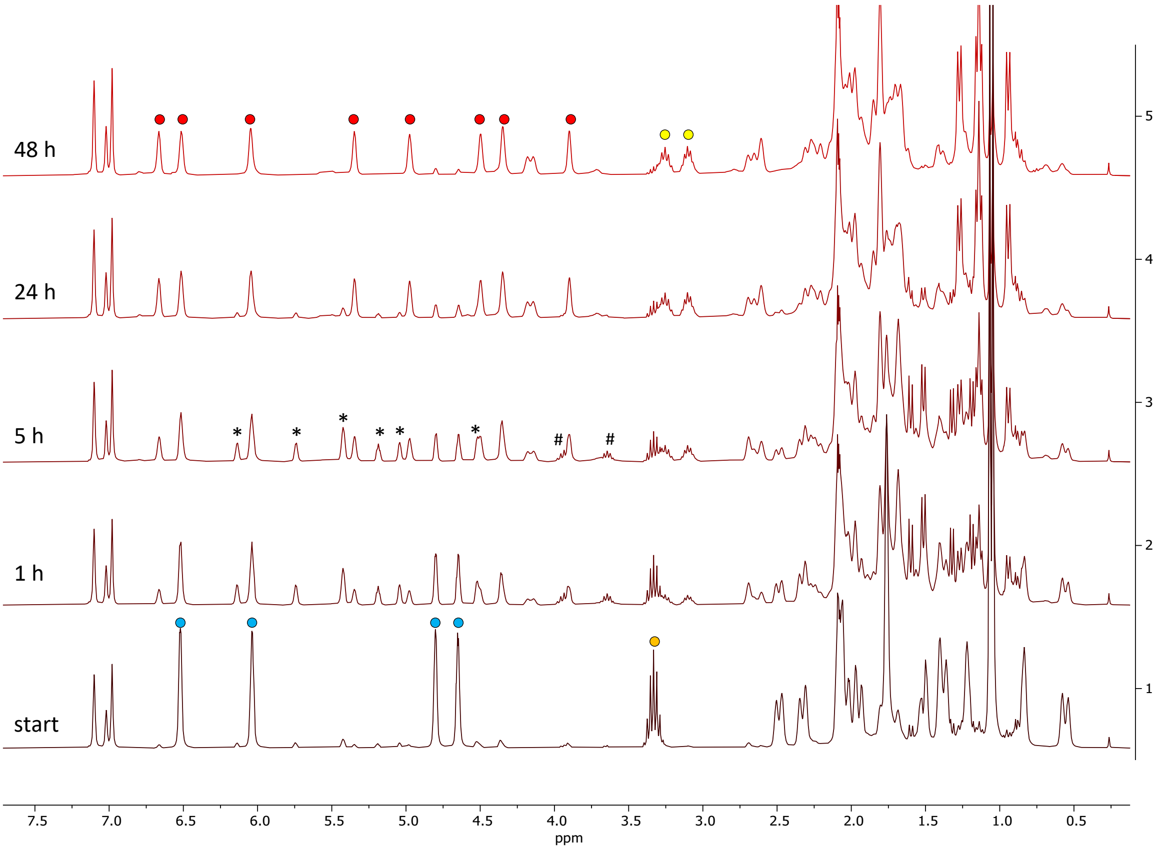


**Figure S3:** Tracking of the reaction of **1a** with *N*,*N*'-diisopropylcarbodiimide (DIC) (300 MHz, $C_7D_8$, 293 K); markings: Cp–H of **1a** (blue), $^i$Pr–H of DIC (orange), Cp–H of **2a** (red), $^i$Pr–H of **2a** (yellow), Cp–H of adduct (*), $^i$Pr–H of adduct (#).

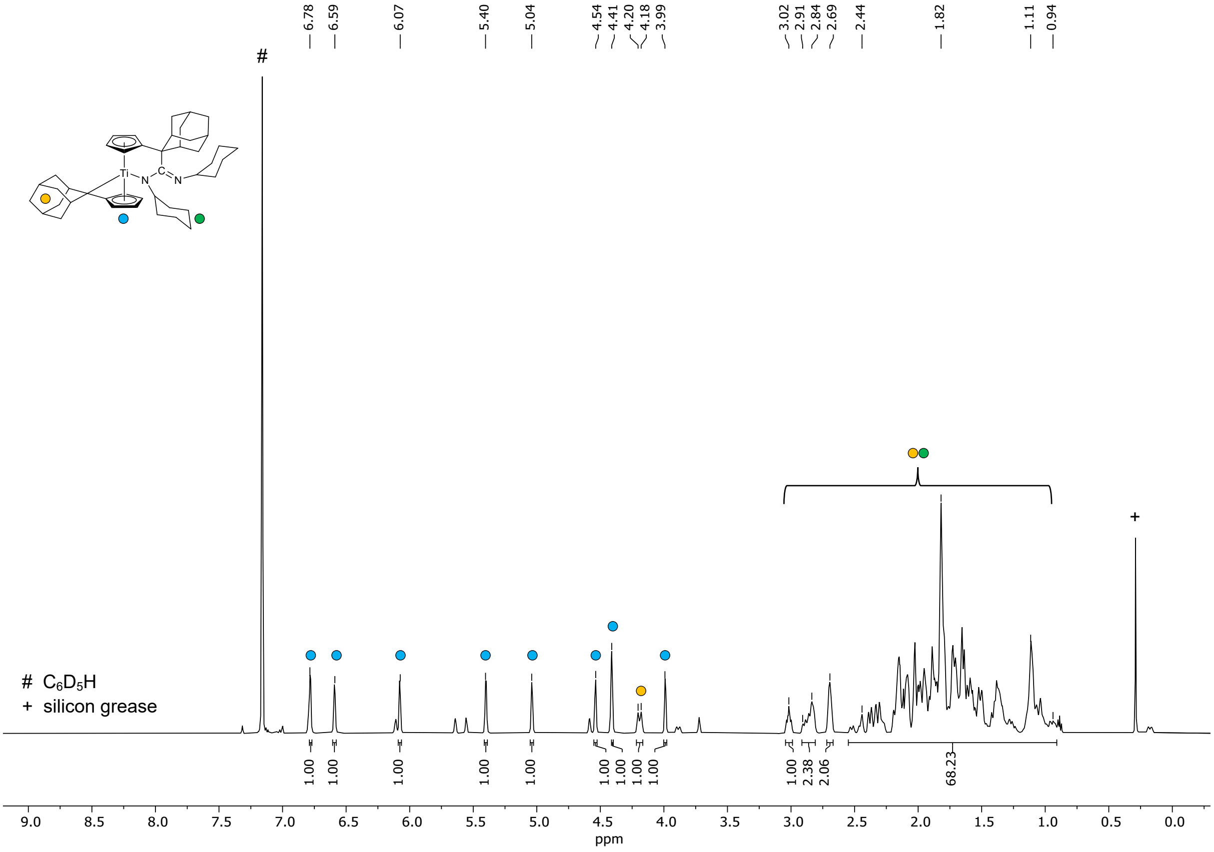


**Figure S4:** $^1$H NMR spectrum of **2b** (500 MHz, $C_6D_6$, 305 K).

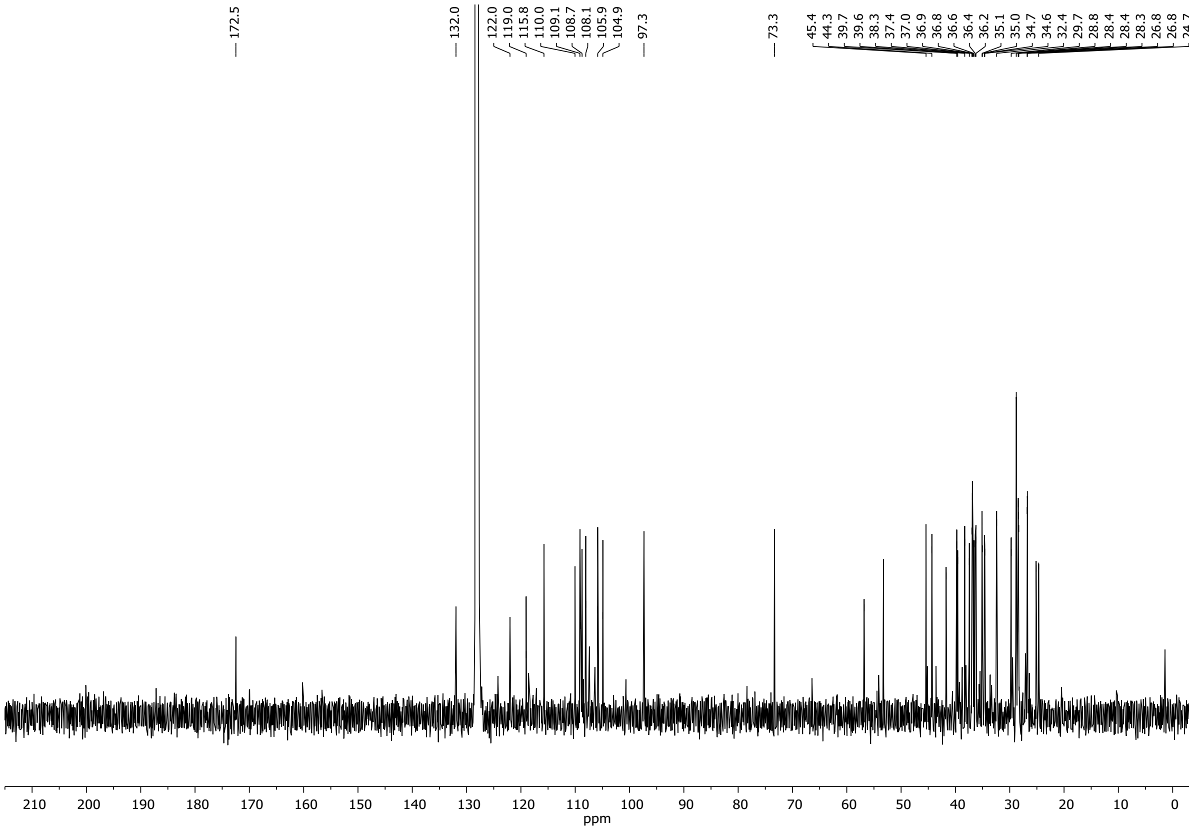


**Figure S5:** $^{13}C\{^1H\}$ NMR spectrum of **2b** (126 MHz, $C_6D_6$, 305 K).

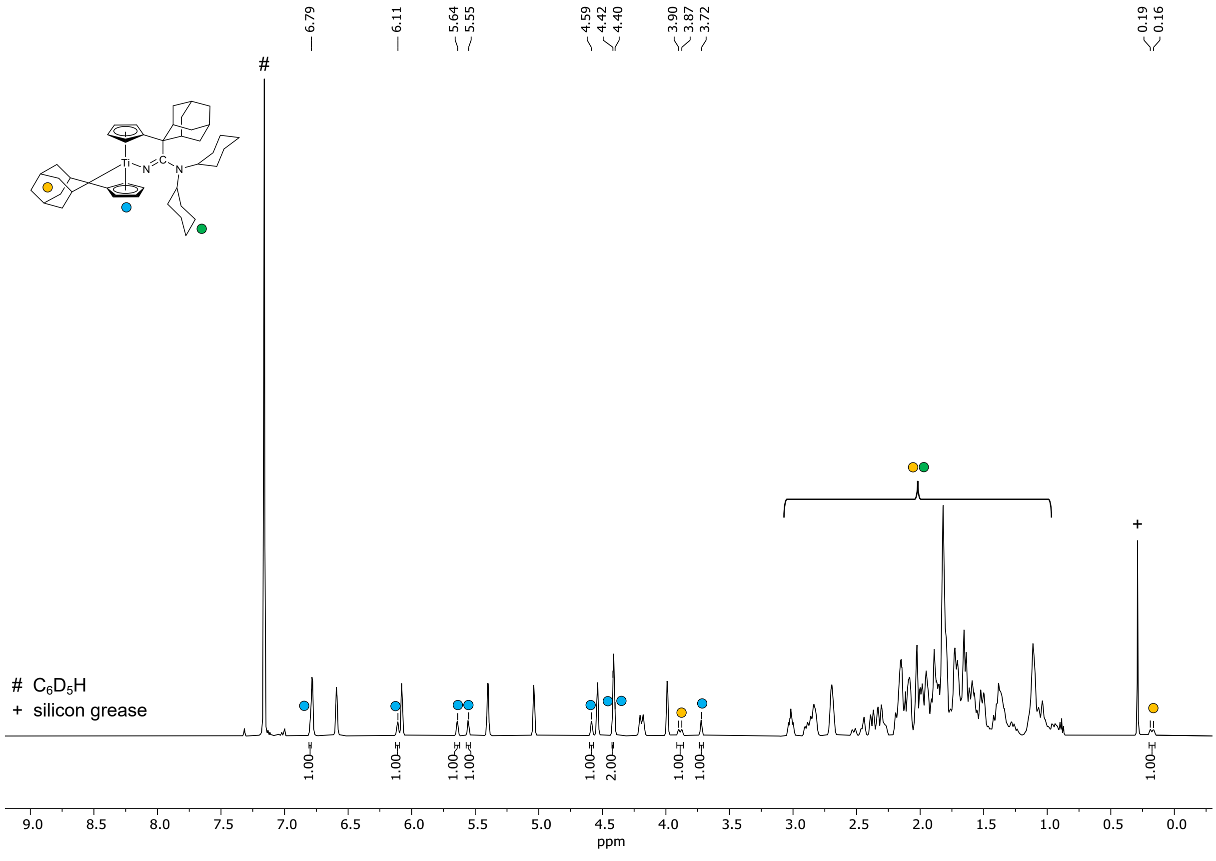


**Figure S6:** $^1H$ NMR spectrum of **2b’** (500 MHz, $C_6D_6$, 305 K).

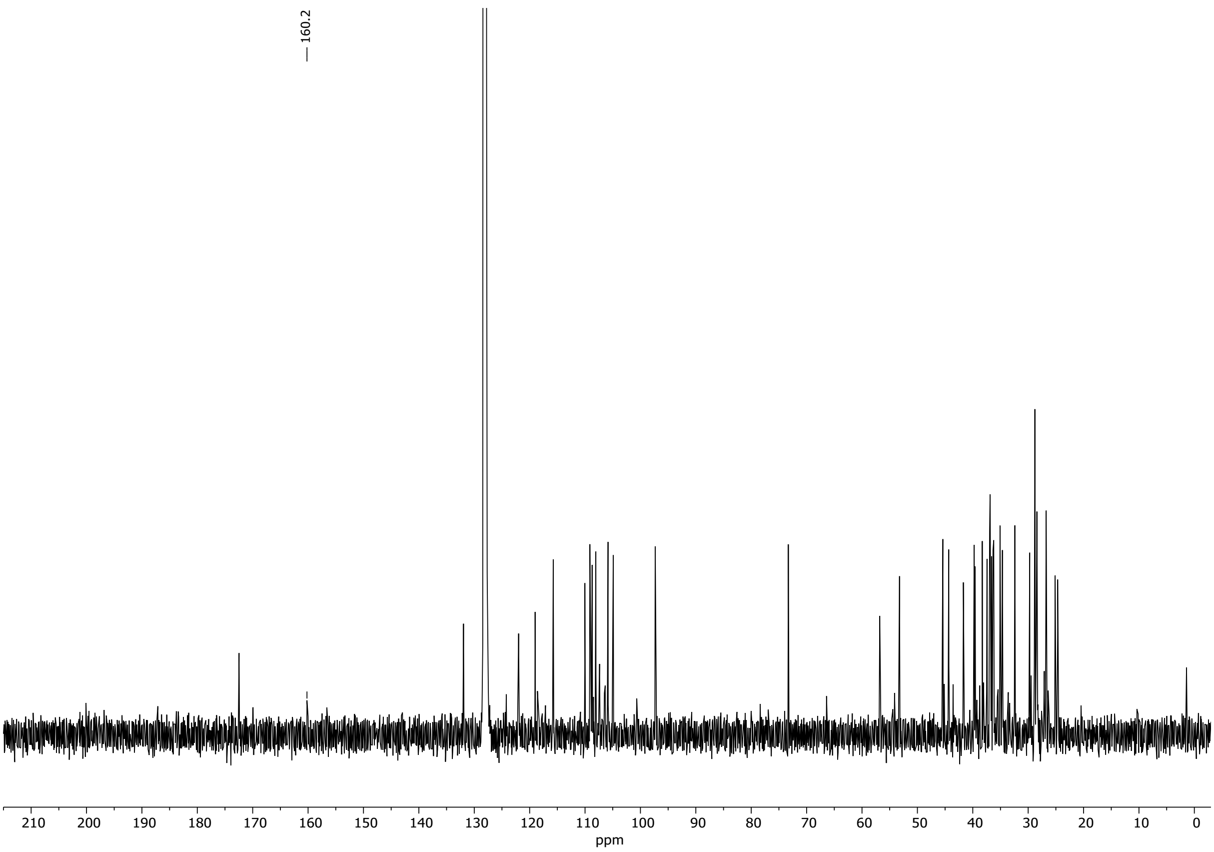


**Figure S7:** $^{13}C\{^1H\}$ NMR spectrum of **2b’** (126 MHz, $C_6D_6$, 305 K).

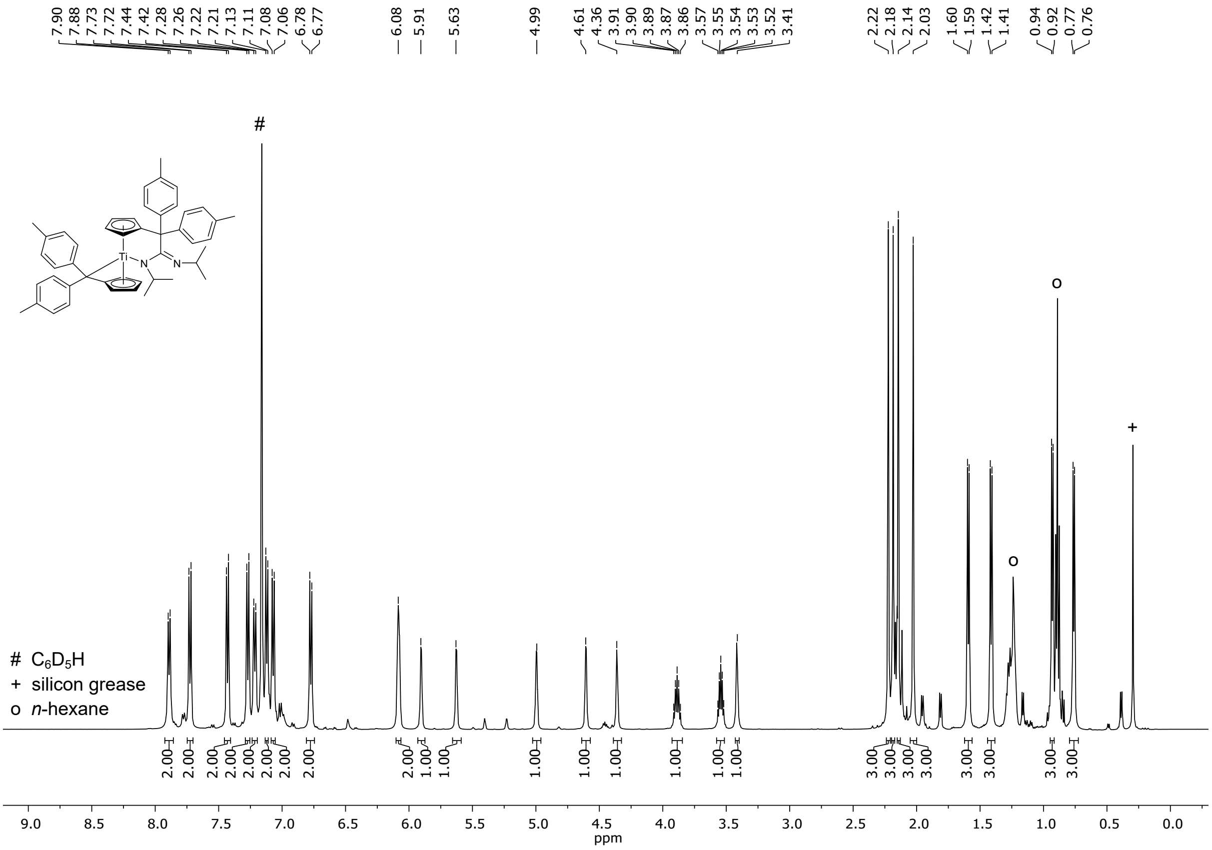


**Figure S8:** $^1H$ NMR spectrum of **3a** (500 MHz, $C_6D_6$, 305 K).

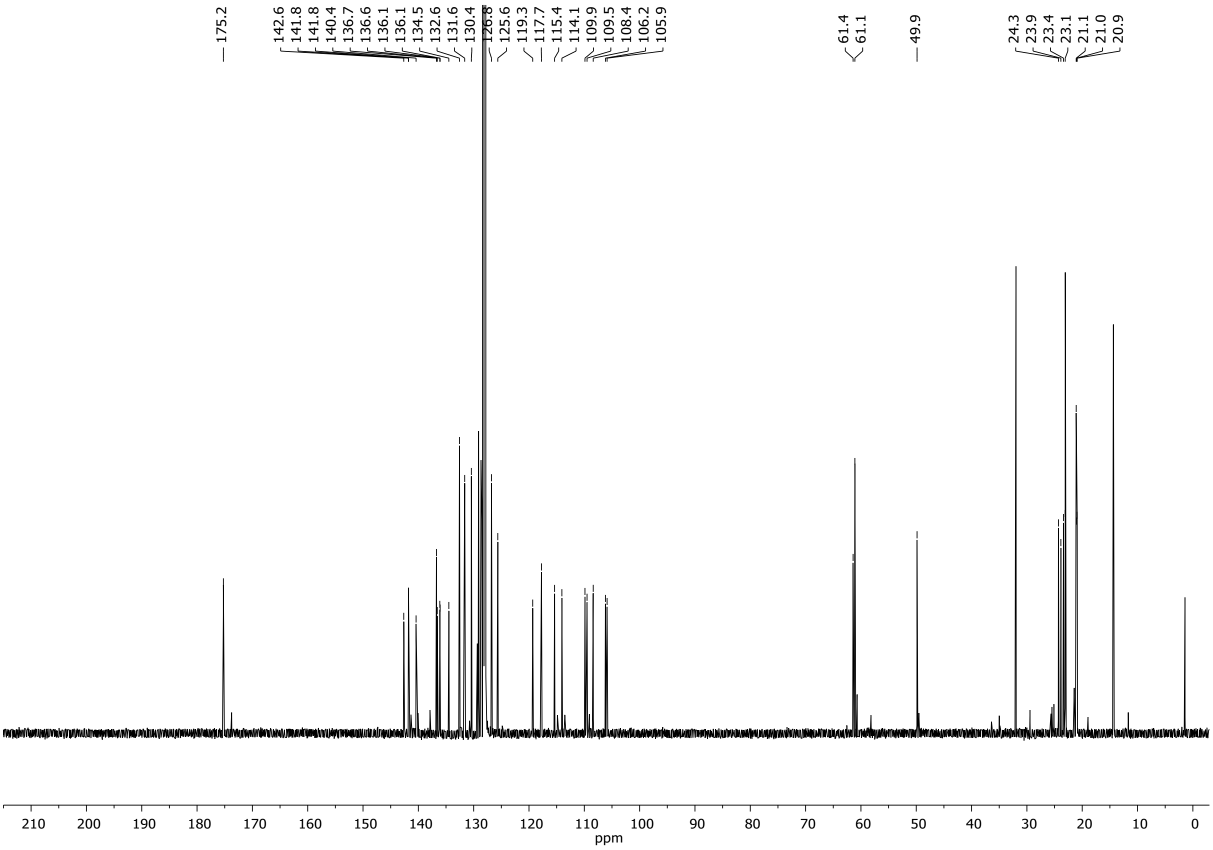


**Figure S9:** $^{13}C\{^{1}H\}$ NMR spectrum of **3a** (126 MHz, $C_6D_6$, 305 K).

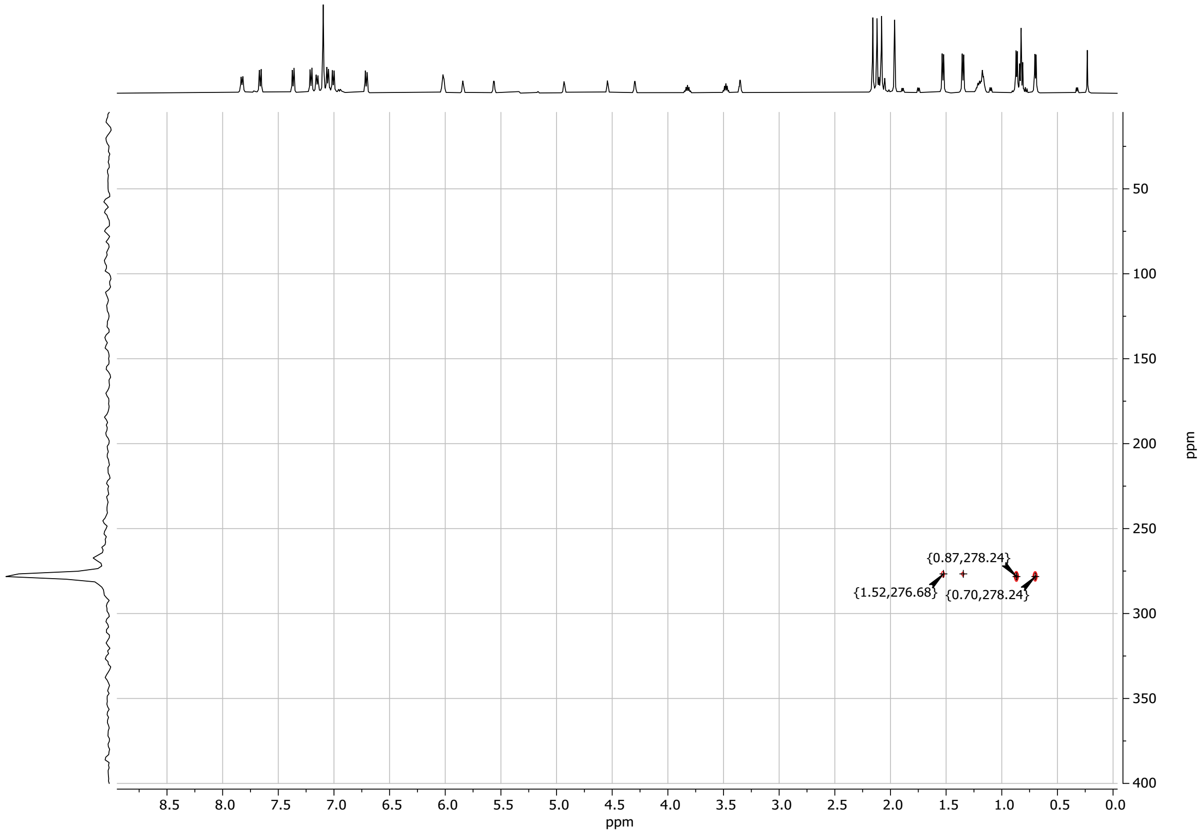


**Figure S10:** $^{1}H,^{15}N$ HMBC NMR spectrum of **3a** (500 MHz, 51 MHz, $C_6D_6$, 305 K).

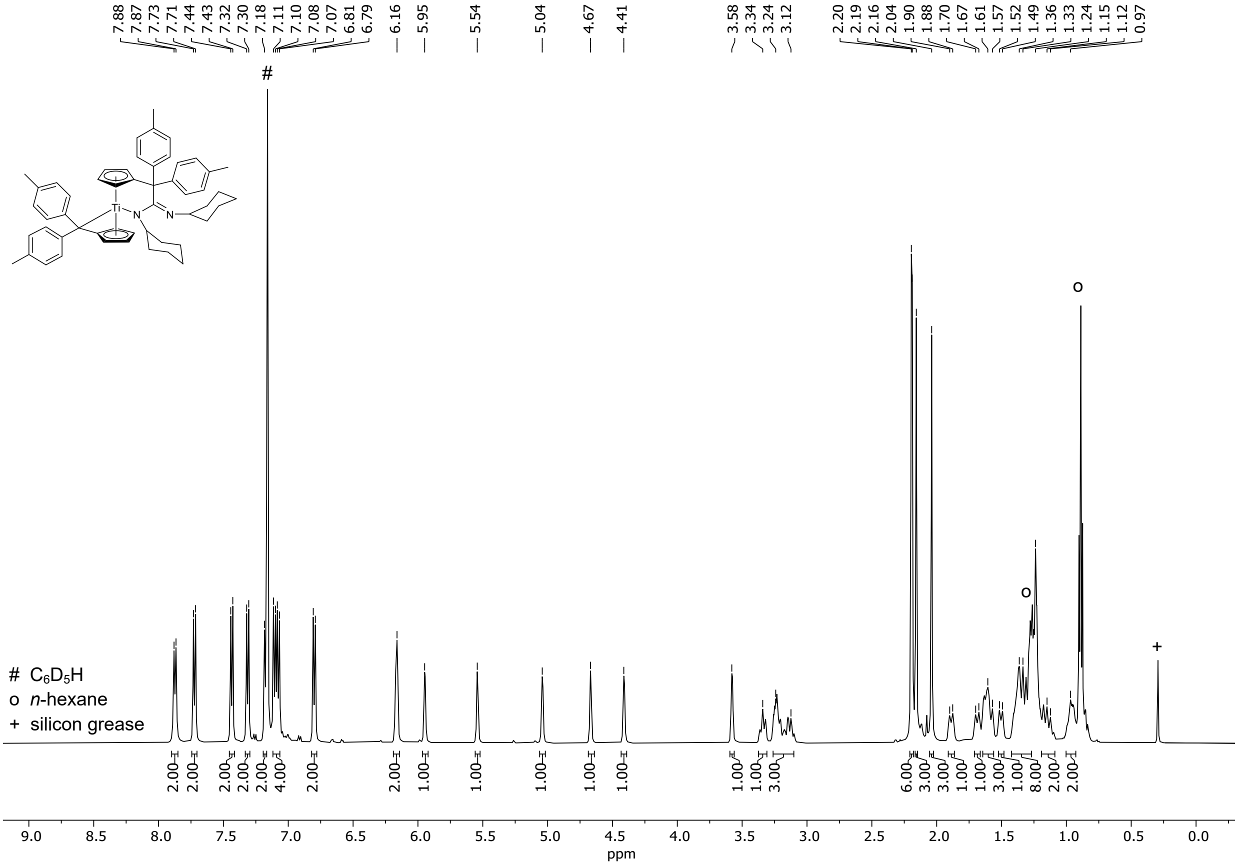


**Figure S11:** $^1$H NMR spectrum of **3b** (500 MHz, $C_6D_6$, 305 K).

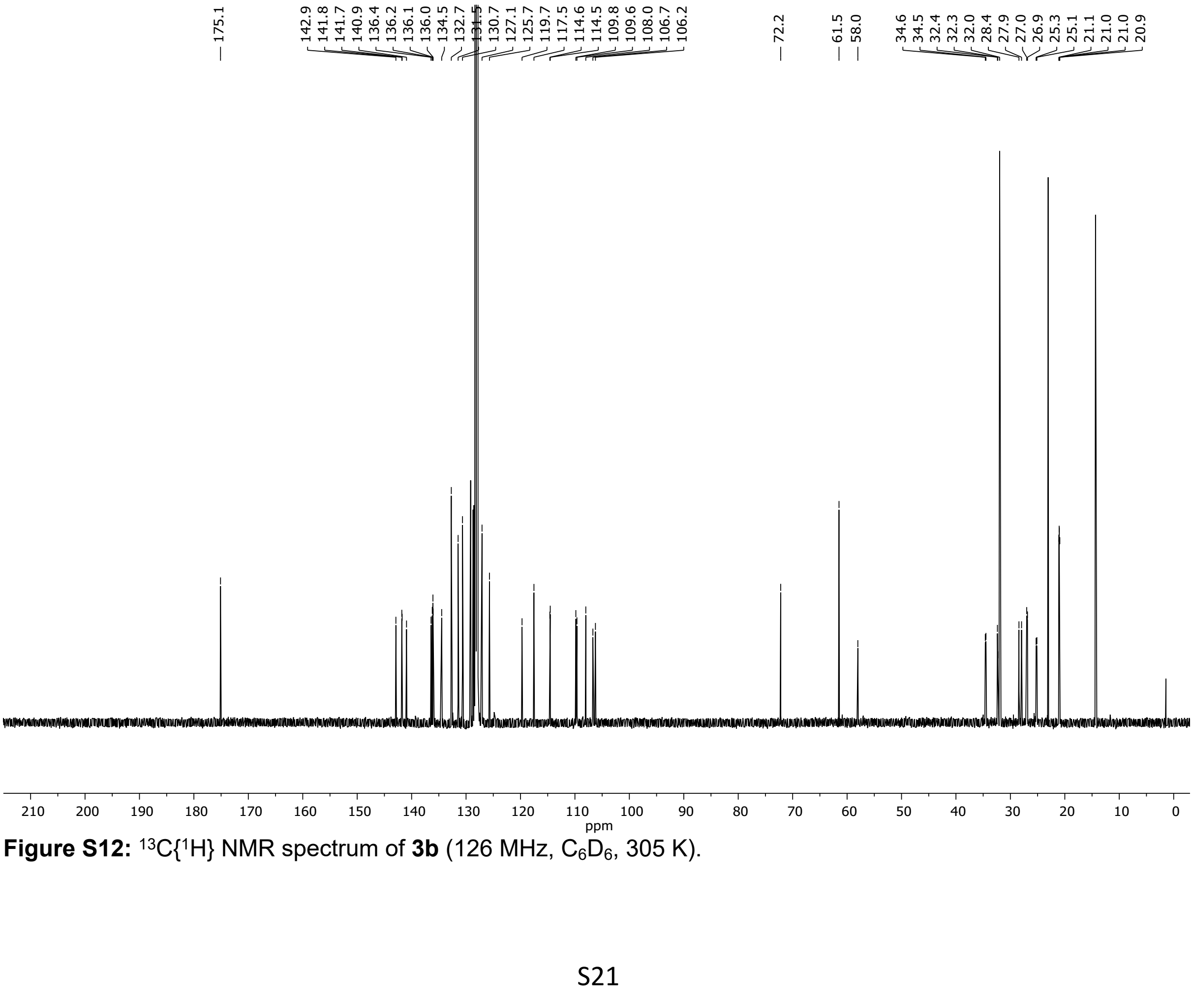


**Figure S12:** $^{13}$C{$^1$H} NMR spectrum of **3b** (126 MHz, $C_6D_6$, 305 K).

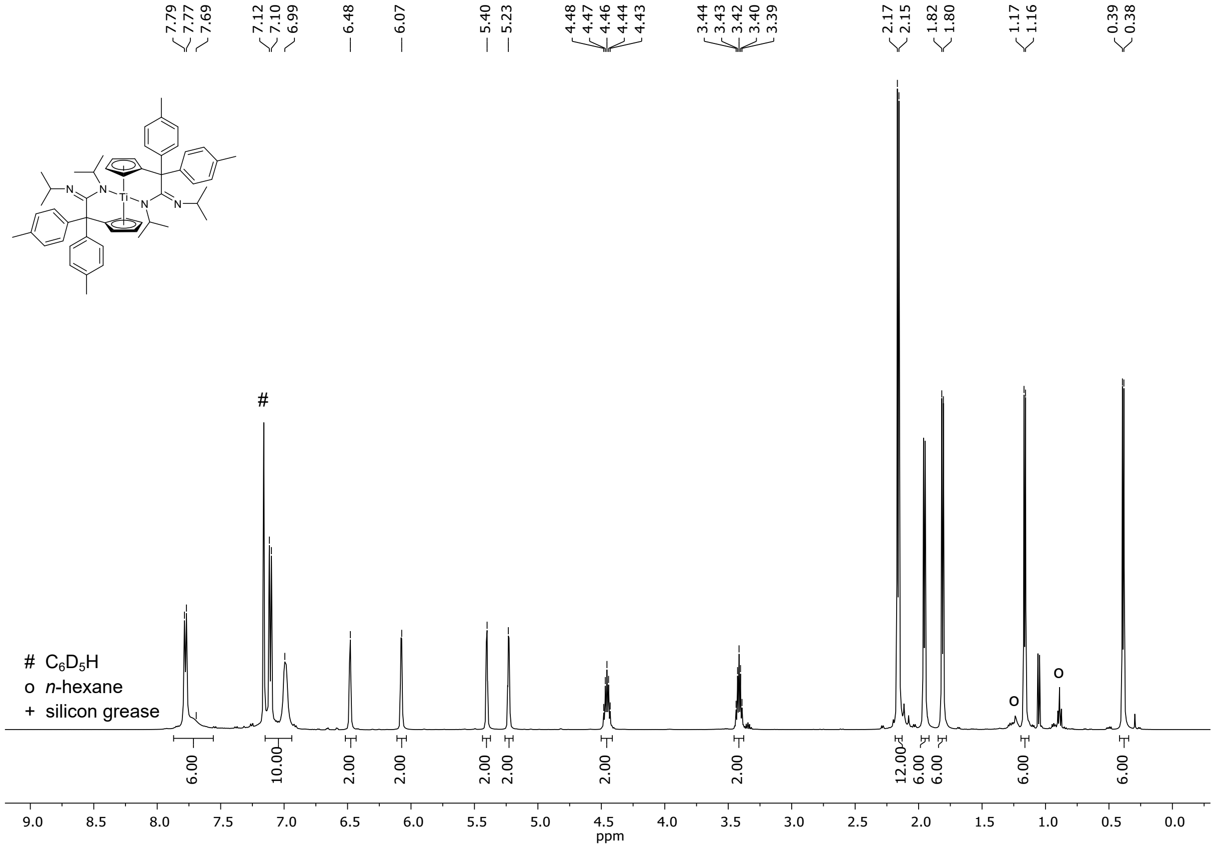


**Figure S13:** $^1$H NMR spectrum of **4a** (500 MHz, $C_6D_6$, 305 K).

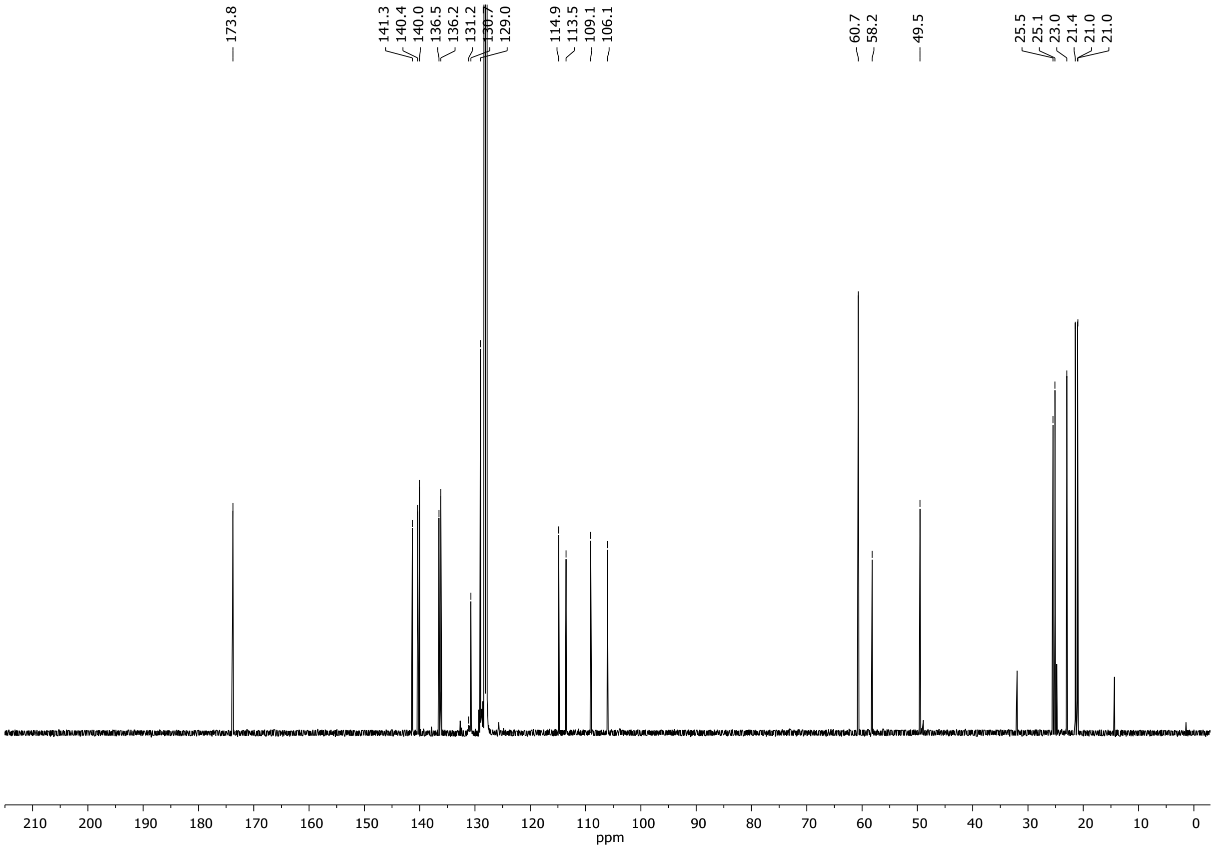


**Figure S14:** $^{13}C\{^1H\}$ NMR spectrum of **4a** (126 MHz, $C_6D_6$, 305 K).

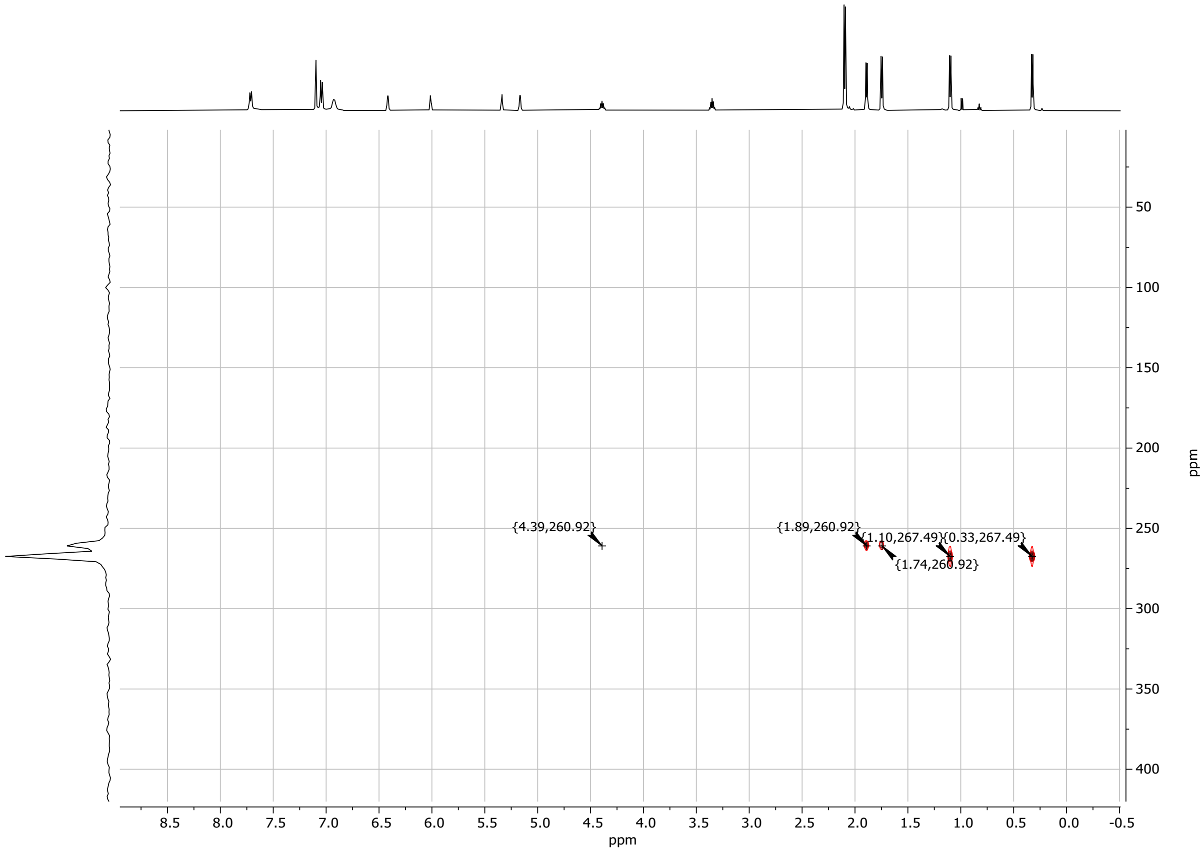


**Figure S15:** $^1$H,$^{15}$N HMBC NMR spectrum of **4a** (500 MHz, 51 MHz, $C_6D_6$, 305 K).

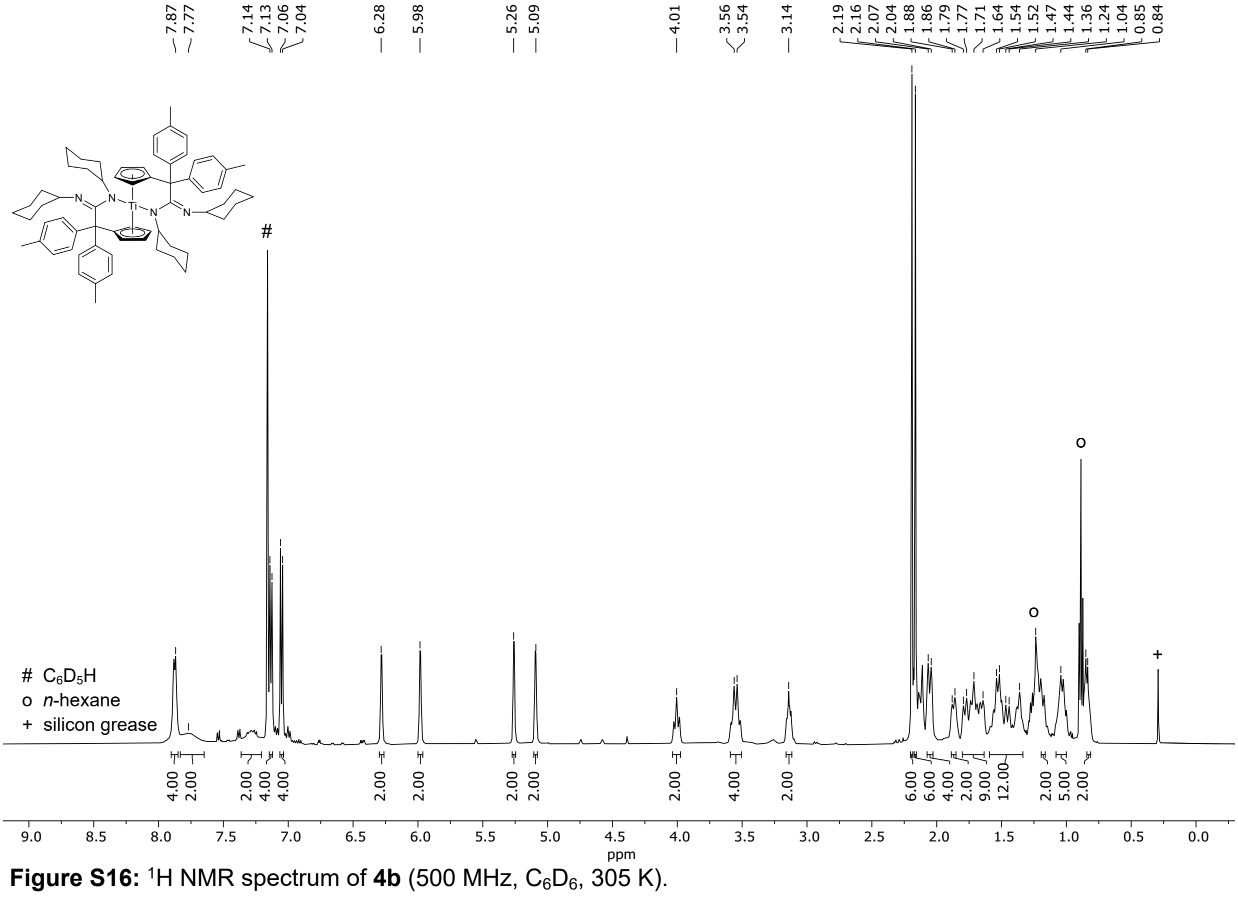


**Figure S16:** $^1$H NMR spectrum of **4b** (500 MHz, $C_6D_6$, 305 K).

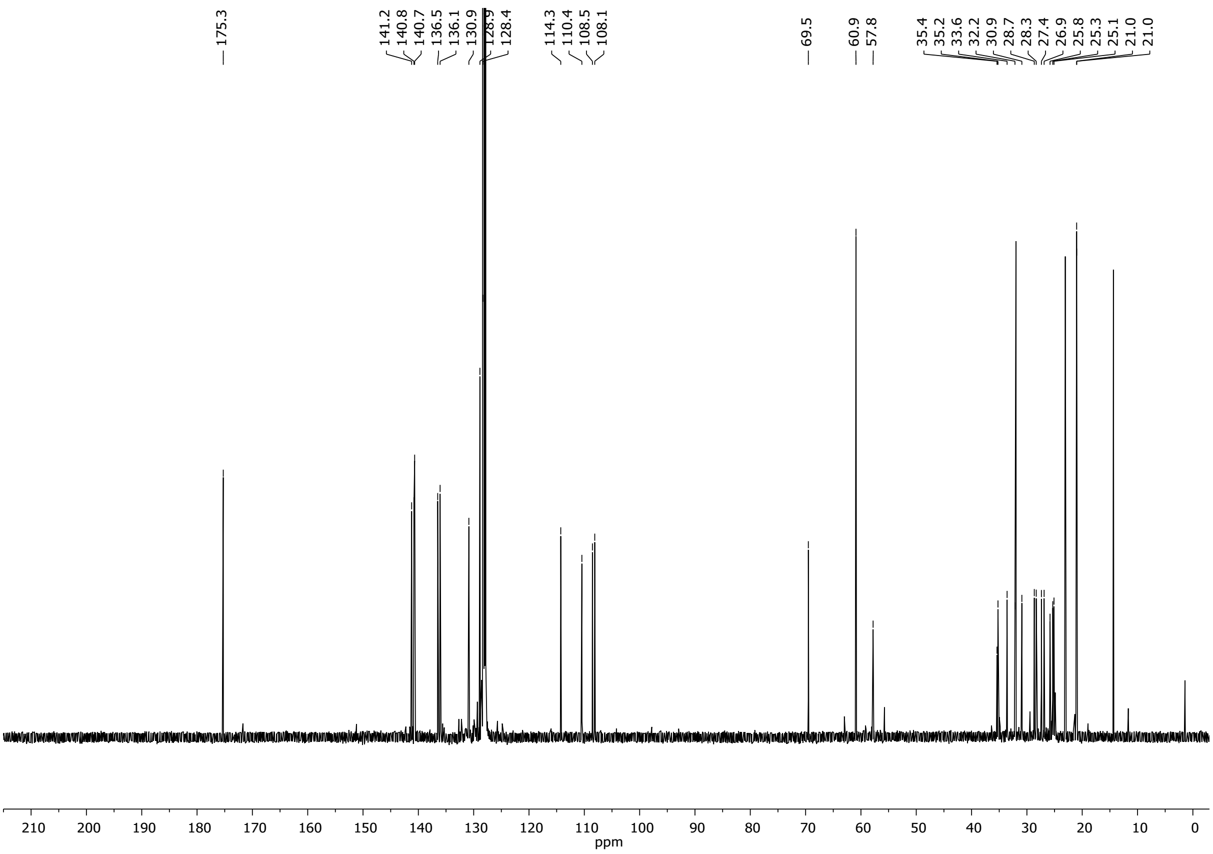


**Figure S17:** $^{13}C\{^1H\}$ NMR spectrum of **4b** (126 MHz, $C_6D_6$, 305 K).

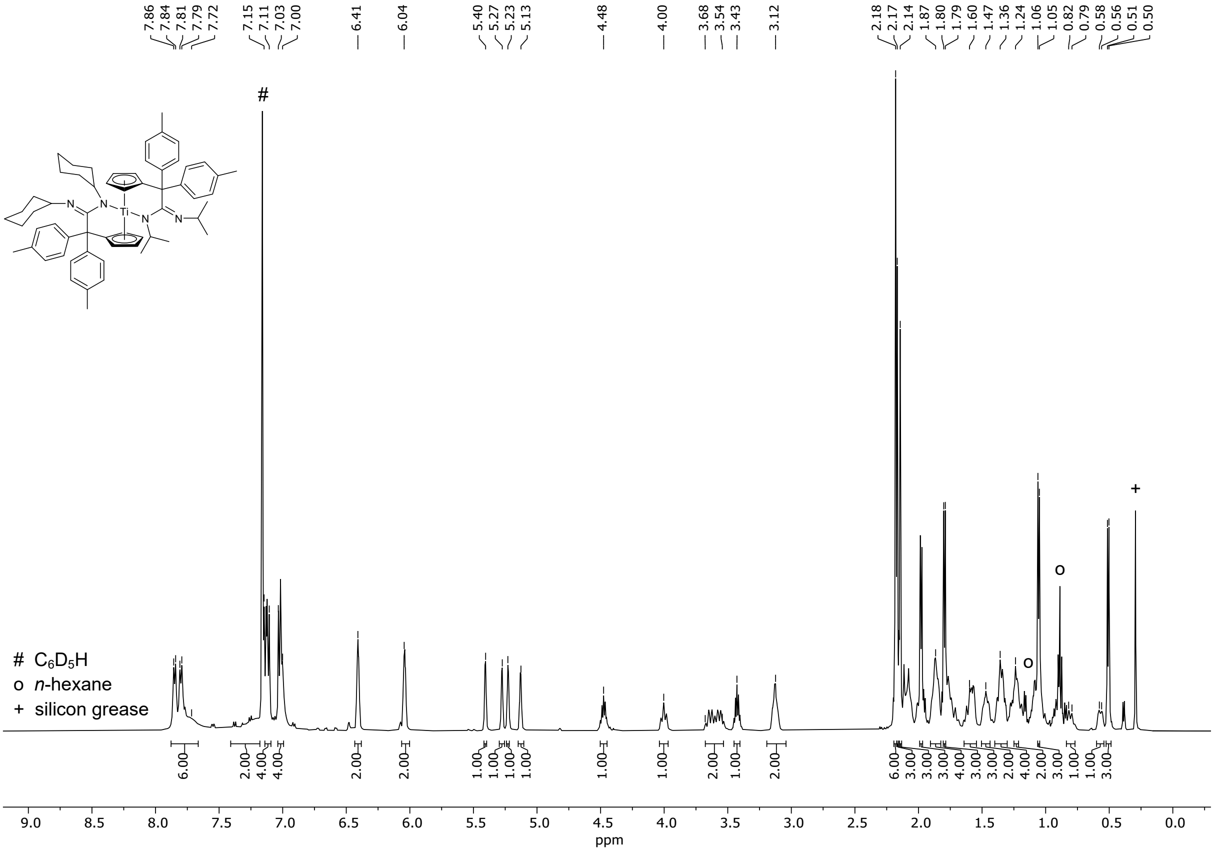


**Figure S18:** $^1H$ NMR spectrum of **4c** (500 MHz, $C_6D_6$, 298 K).

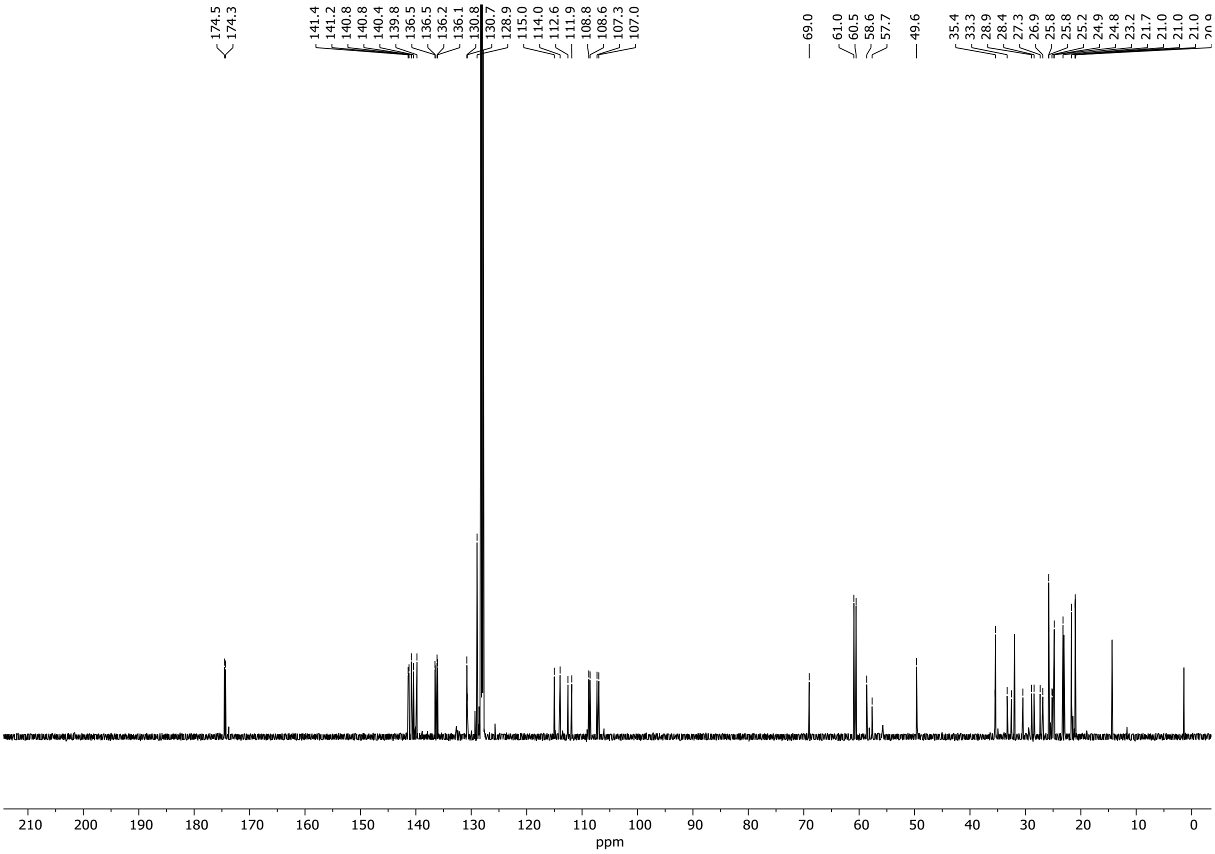


**Figure S19:** $^{13}C\{^1H\}$ NMR spectrum of **4c** (126 MHz, $C_6D_6$, 298 K).

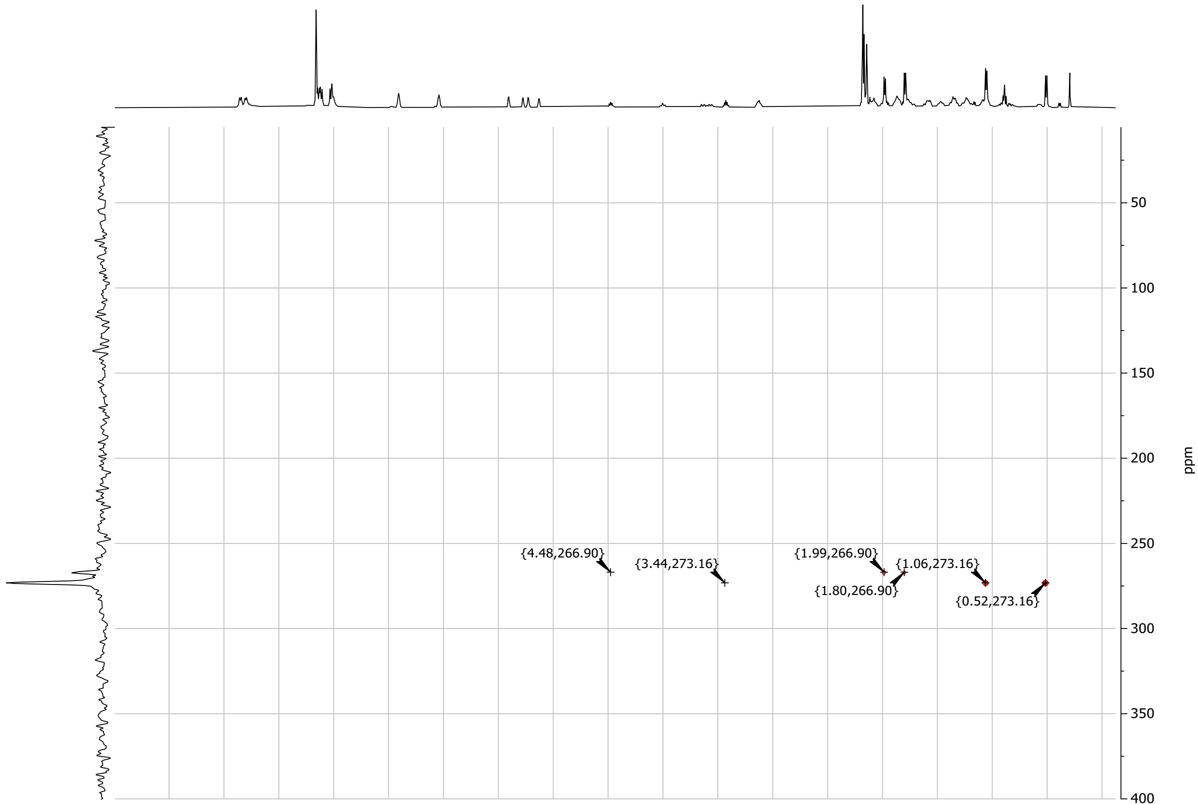


**Figure S20:** $^1H,^{15}N$ HMBC NMR spectrum of **4c** (500 MHz, 51 MHz, $C_6D_6$, 298 K).

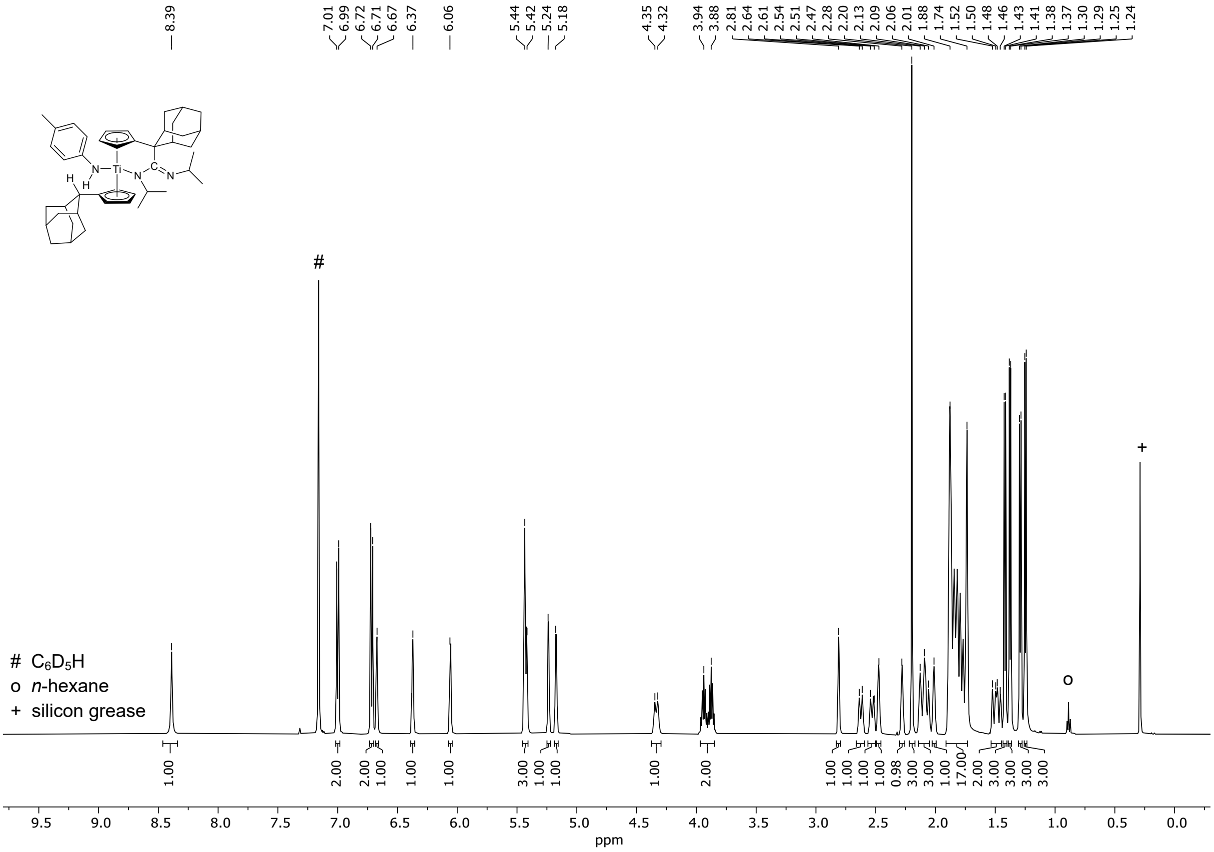


**Figure S21:** $^1$H NMR spectrum of **5a** (500 MHz, $C_6D_6$, 305 K).

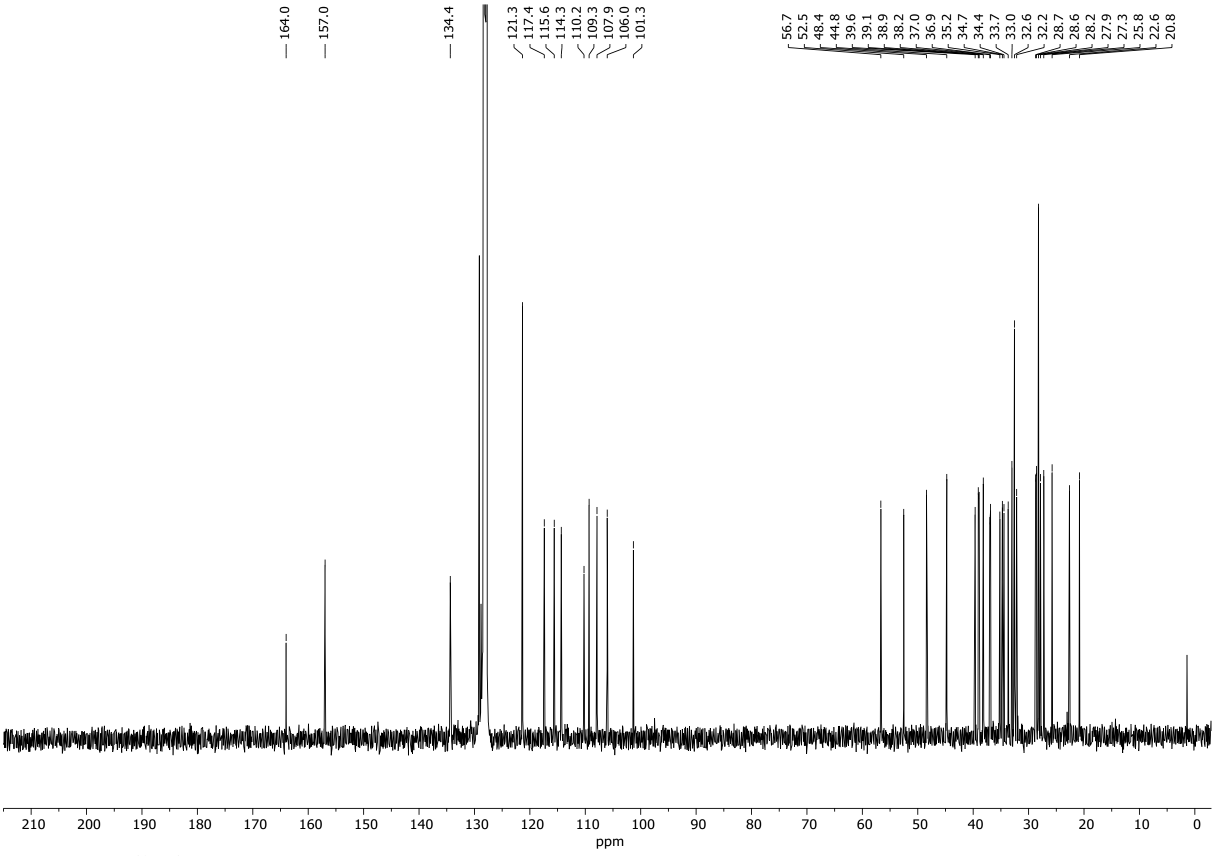


**Figure S22:** $^{13}C\{^1H\}$ NMR spectrum of **5a** (126 MHz, $C_6D_6$, 305 K).

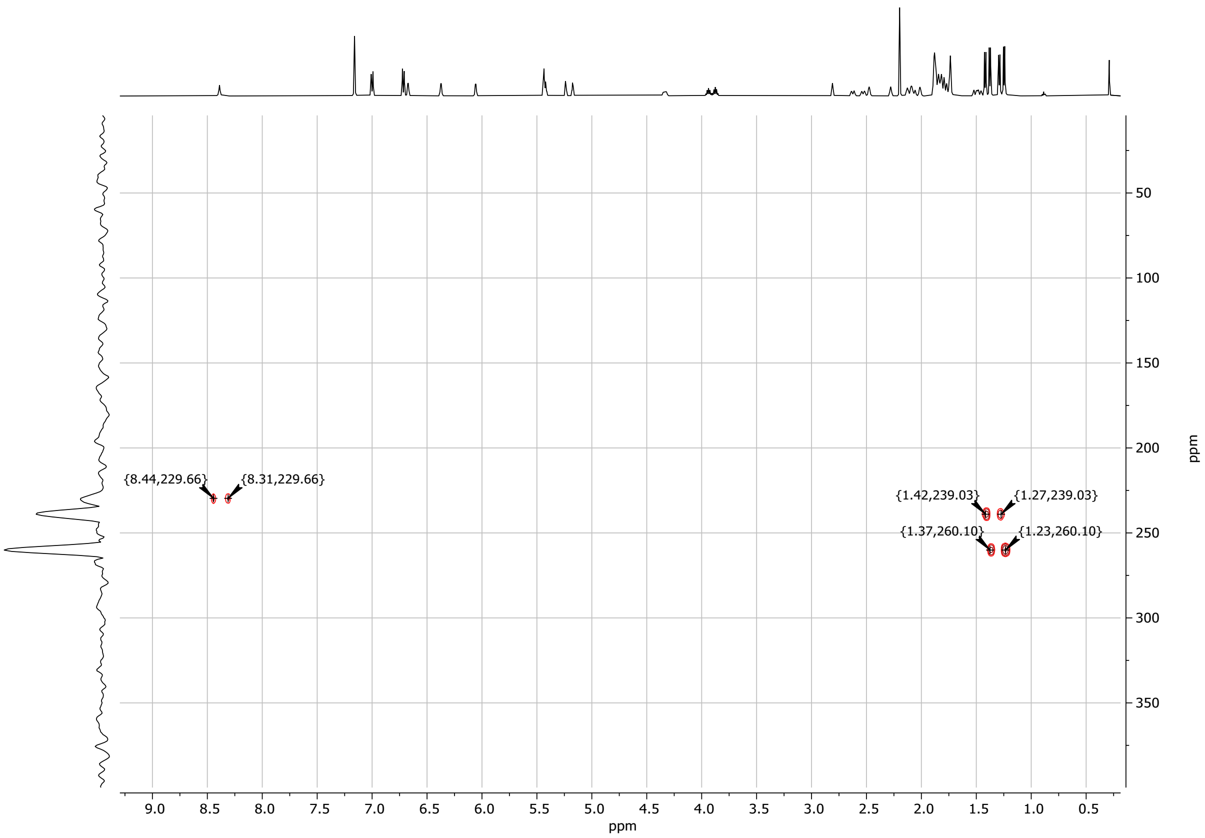


**Figure S23:** $^1H,^{15}N$ HMBC NMR spectrum of **5a** (500 MHz, 51 MHz, $C_6D_6$, 305 K).

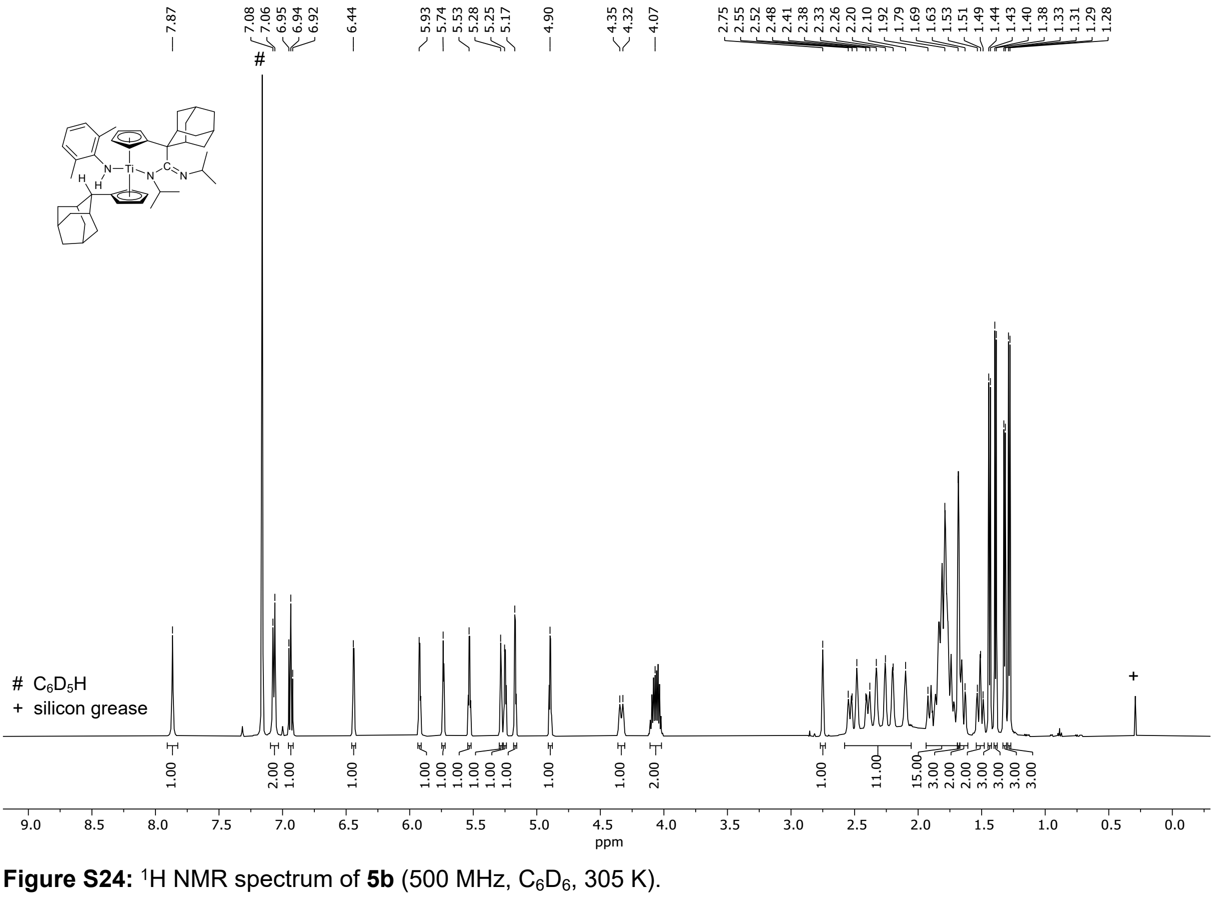


**Figure S24:** $^1H$ NMR spectrum of **5b** (500 MHz, $C_6D_6$, 305 K).

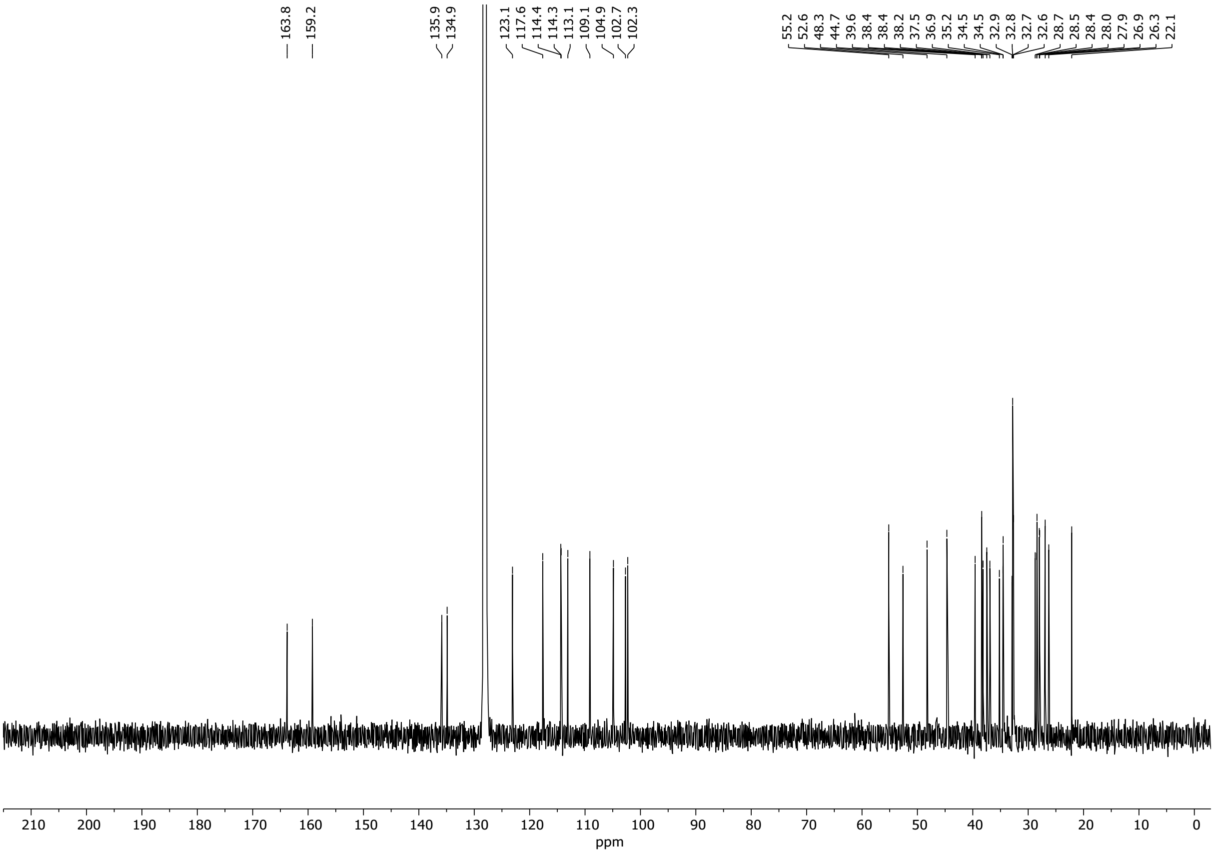


**Figure S25:** $^{13}C\{^1H\}$ NMR spectrum of **5b** (126 MHz, $C_6D_6$, 305 K).

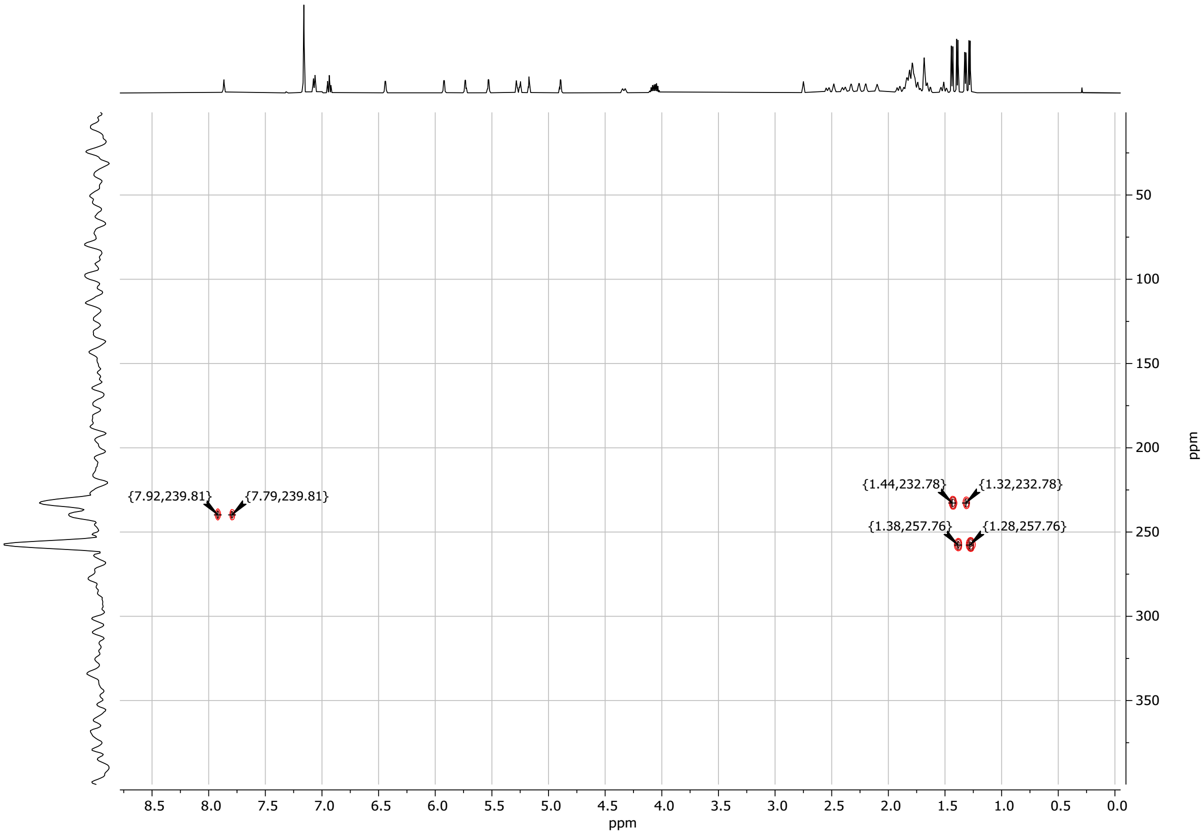


**Figure S26:** $^1H,^{15}N$ HMBC NMR spectrum of **5b** (500 MHz, 51 MHz, $C_6D_6$, 305 K).

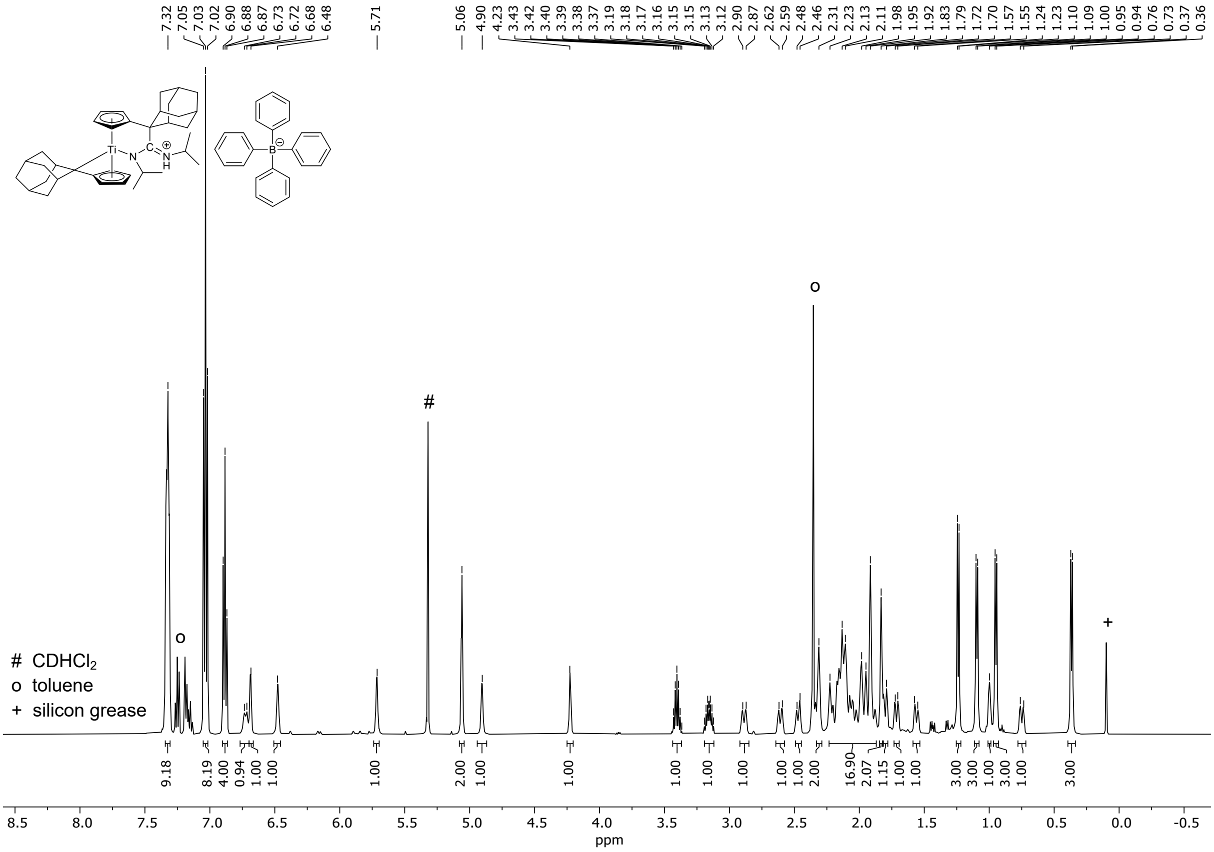


**Figure S27:** $^1$H NMR spectrum of **6** (500 MHz, $CD_2Cl_2$, 305 K).

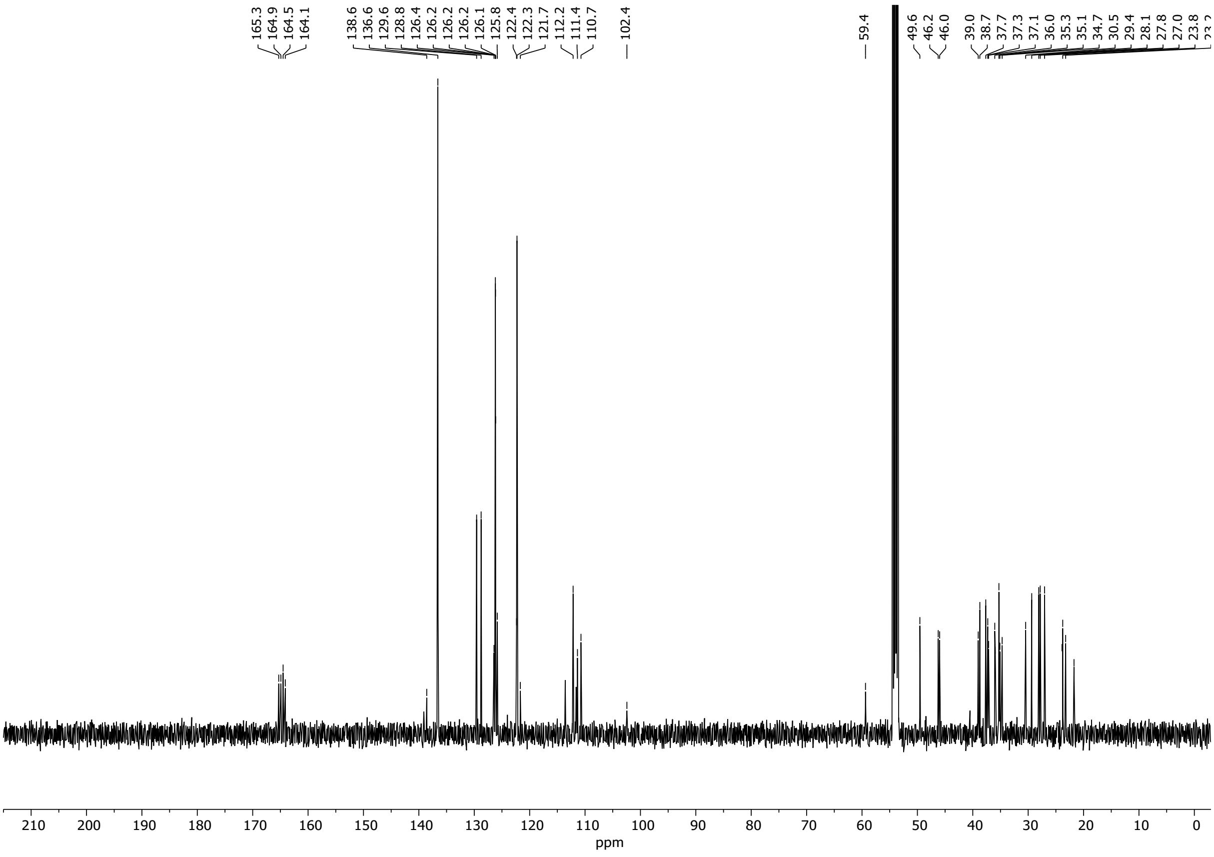


**Figure S28:** $^{13}C\{^1H\}$ NMR spectrum of **6** (126 MHz, $CD_2Cl_2$, 305 K).

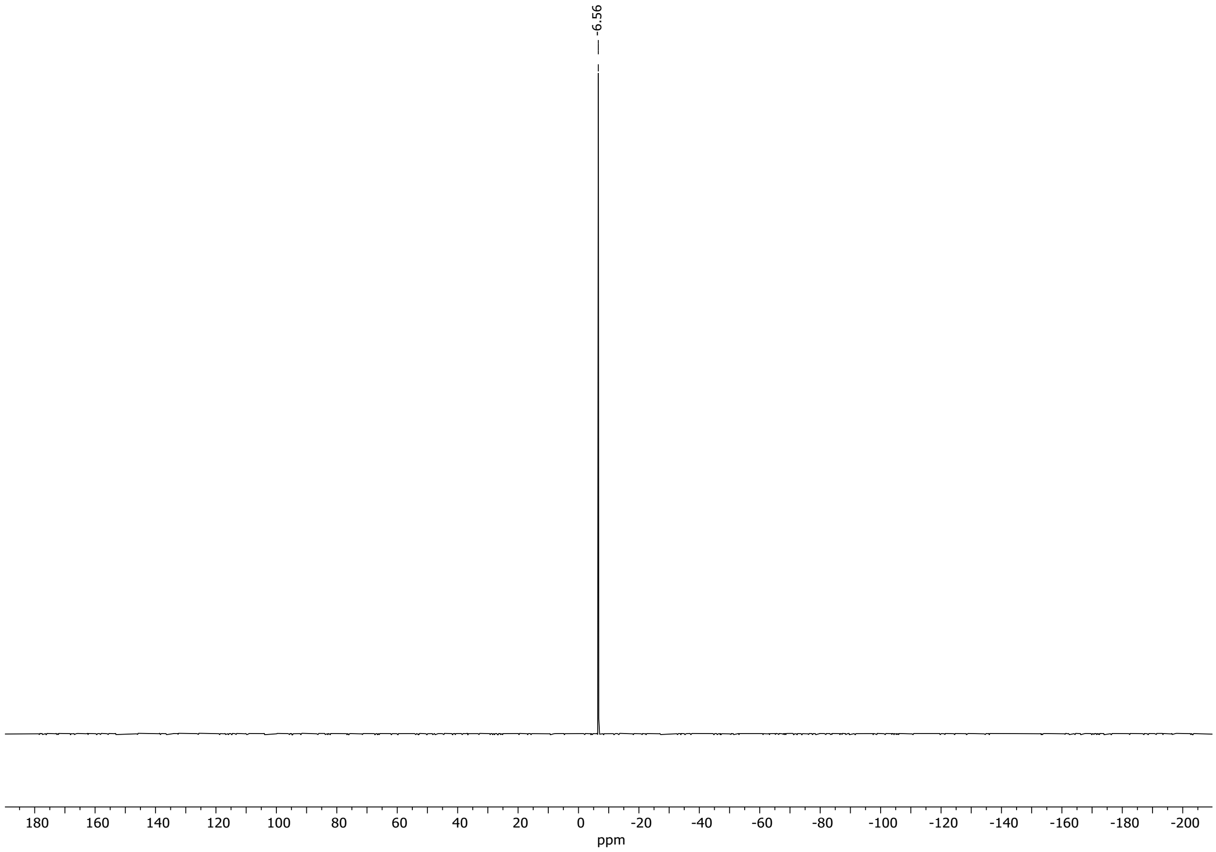


**Figure S29:** $^{11}B\{^{1}H\}$ NMR spectrum of **6** (160 MHz, $CD_2Cl_2$, 305 K).

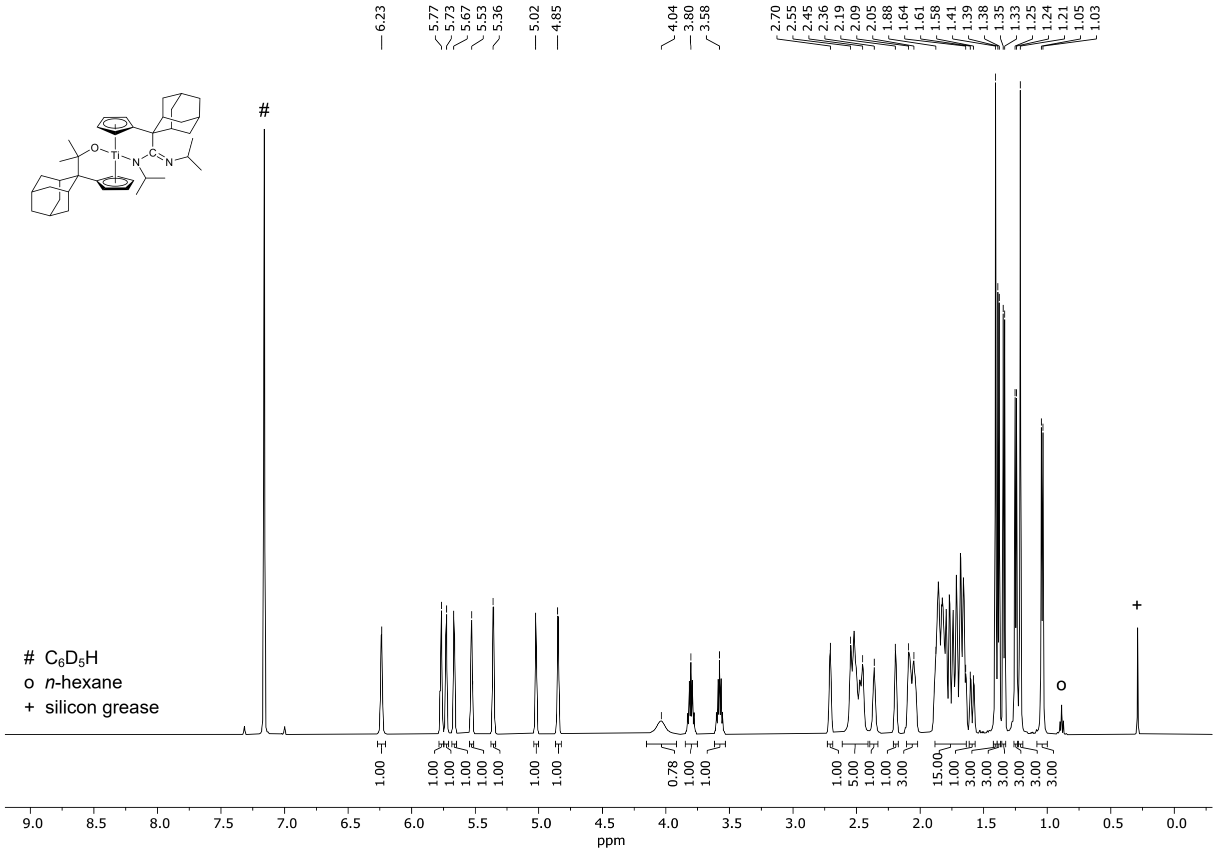


**Figure S30:** $^{1}H$ NMR spectrum of **7** (500 MHz, $C_6D_6$, 305 K).

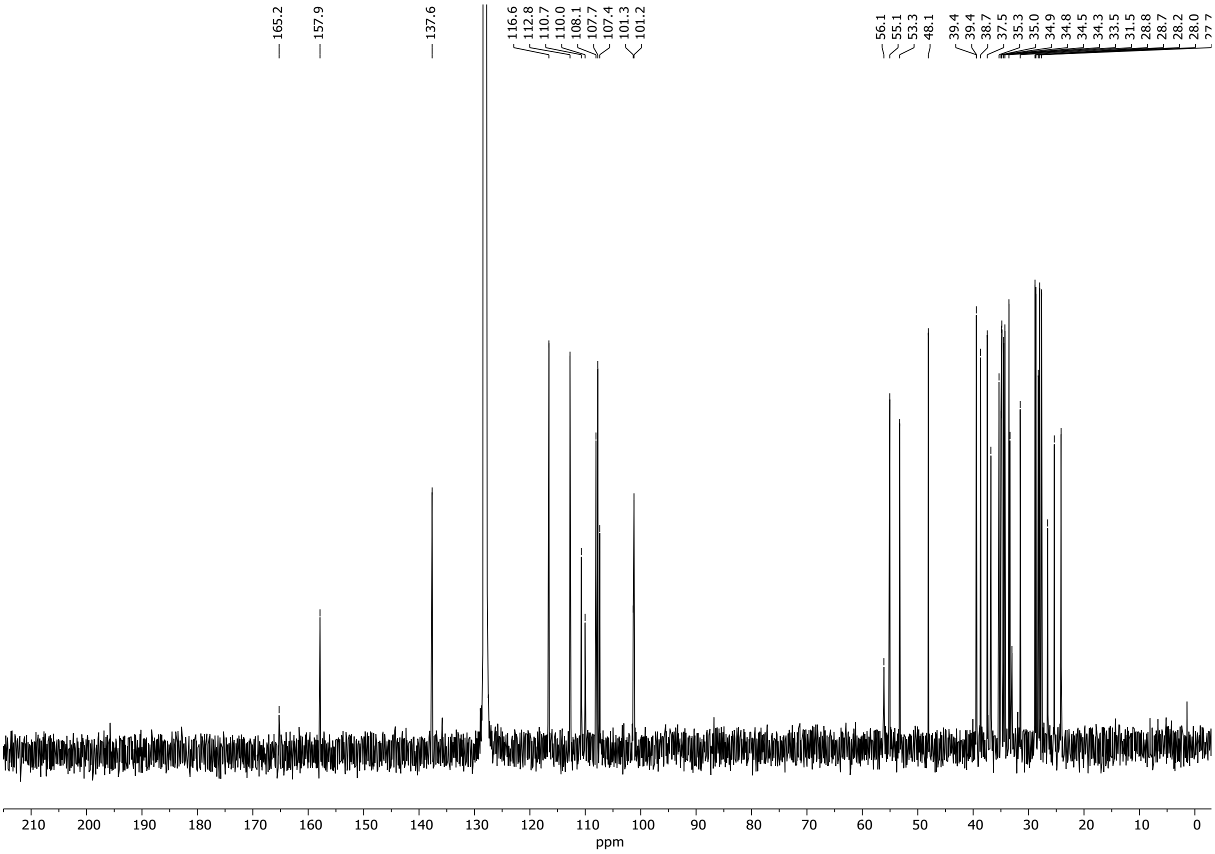


**Figure S31:** $^{13}C\{^1H\}$ NMR spectrum of **7** (126 MHz, $C_6D_6$, 305 K).

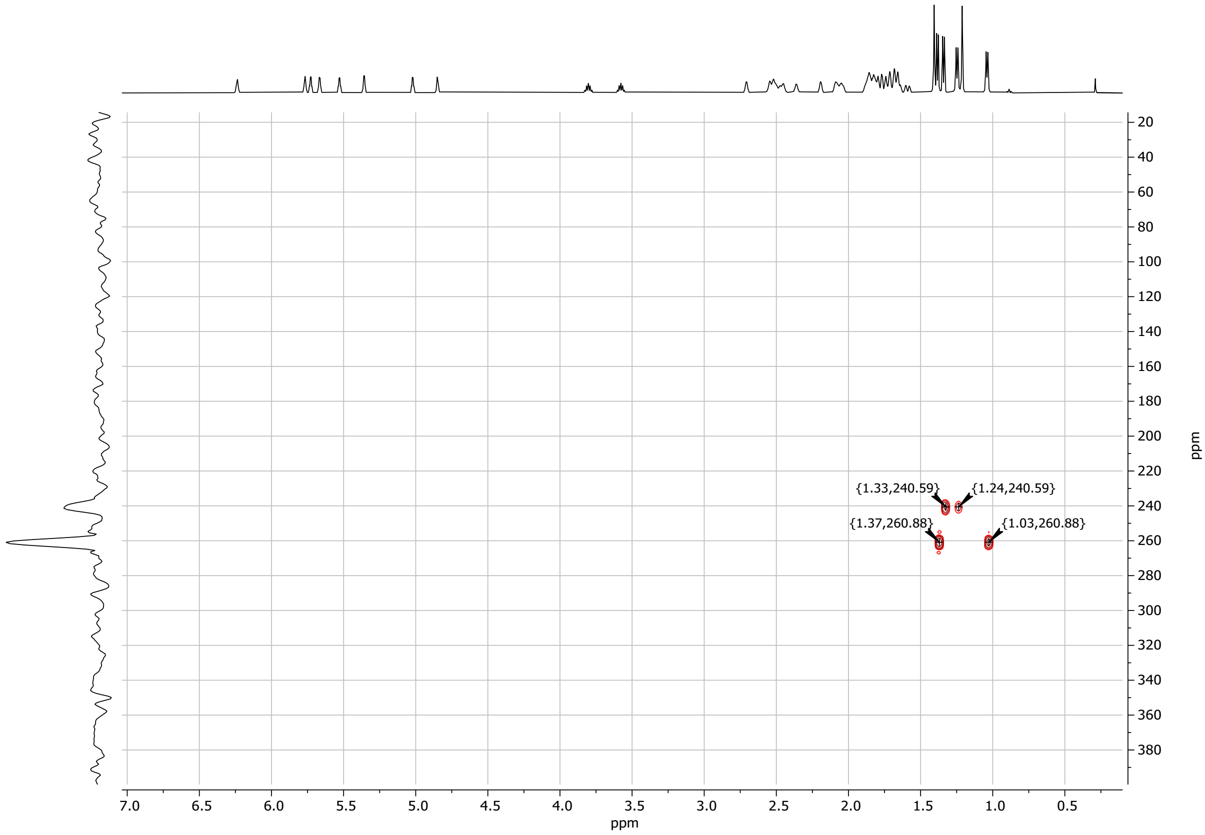


**Figure S32:** $^1H,^{15}N$ HMBC NMR spectrum of **7** (500 MHz, 51 MHz, $C_6D_6$, 305 K).

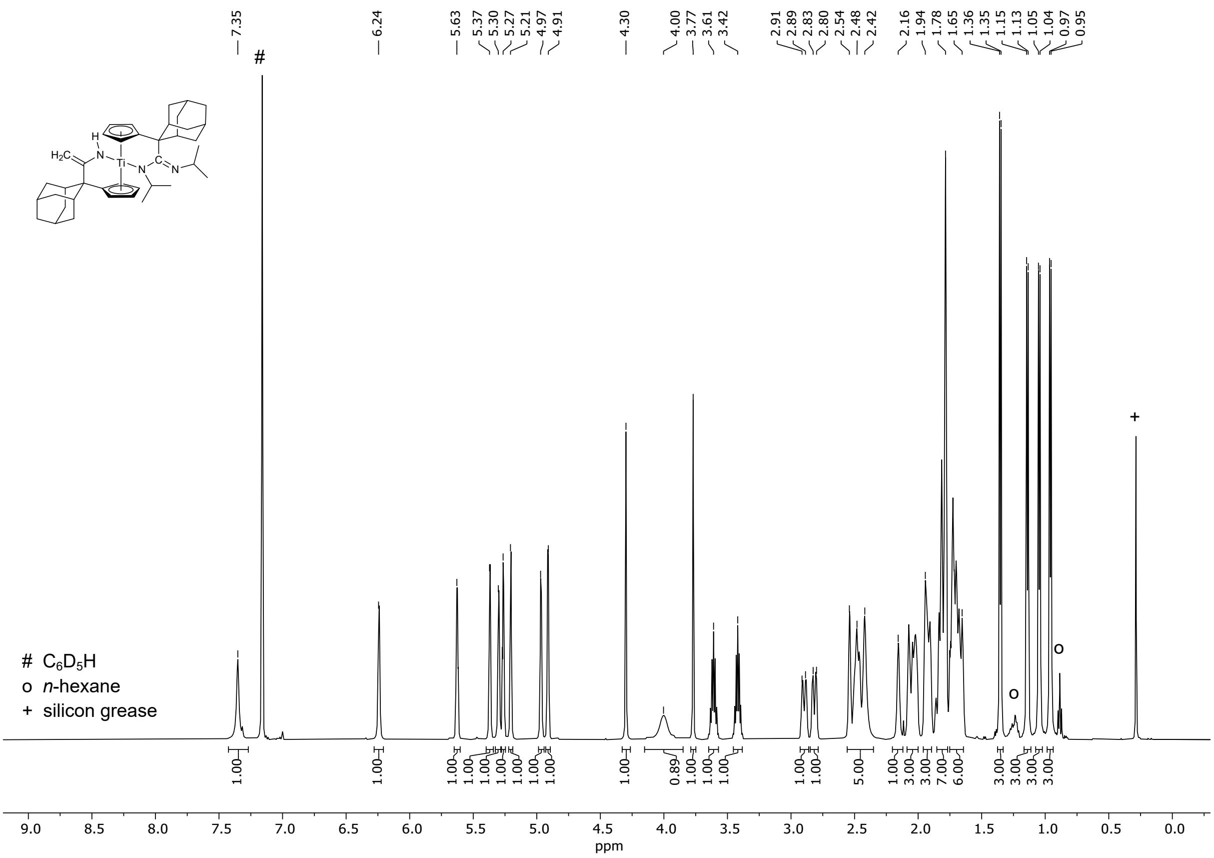


**Figure S33:** $^1$H NMR spectrum of **8** (500 MHz, $C_6D_6$, 305 K).

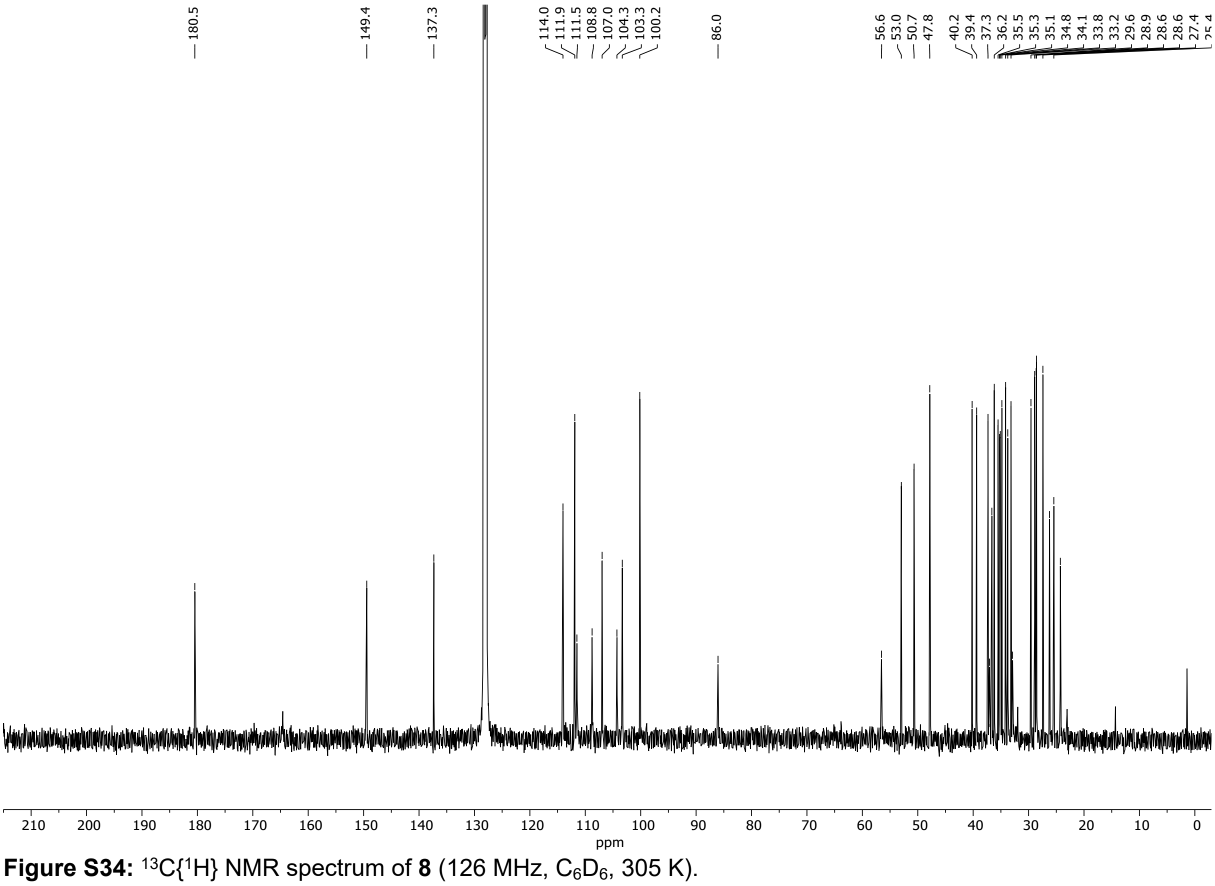


**Figure S34:** $^{13}C\{^1H\}$ NMR spectrum of **8** (126 MHz, $C_6D_6$, 305 K).

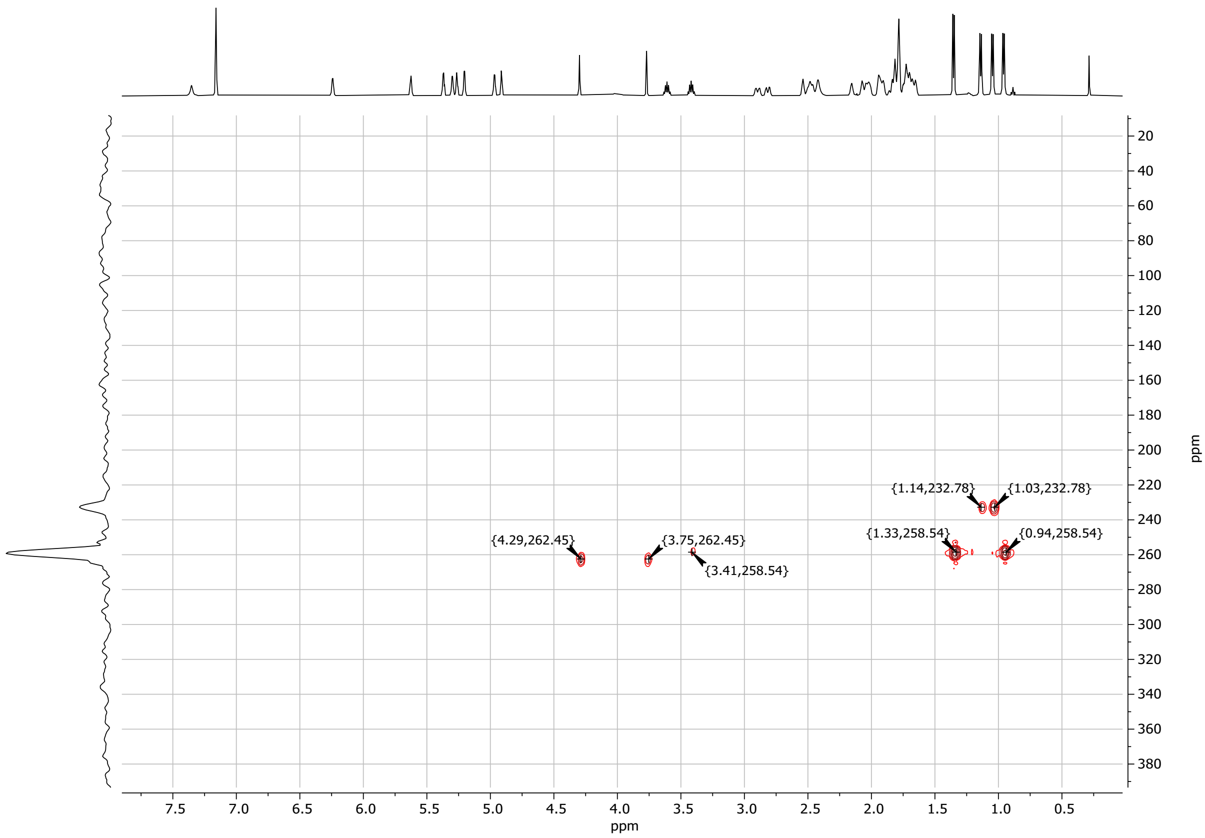


**Figure S35:** $^1$H,$^{15}$N HMBC NMR spectrum of **8** (500 MHz, 51 MHz, $C_6D_6$, 305 K).

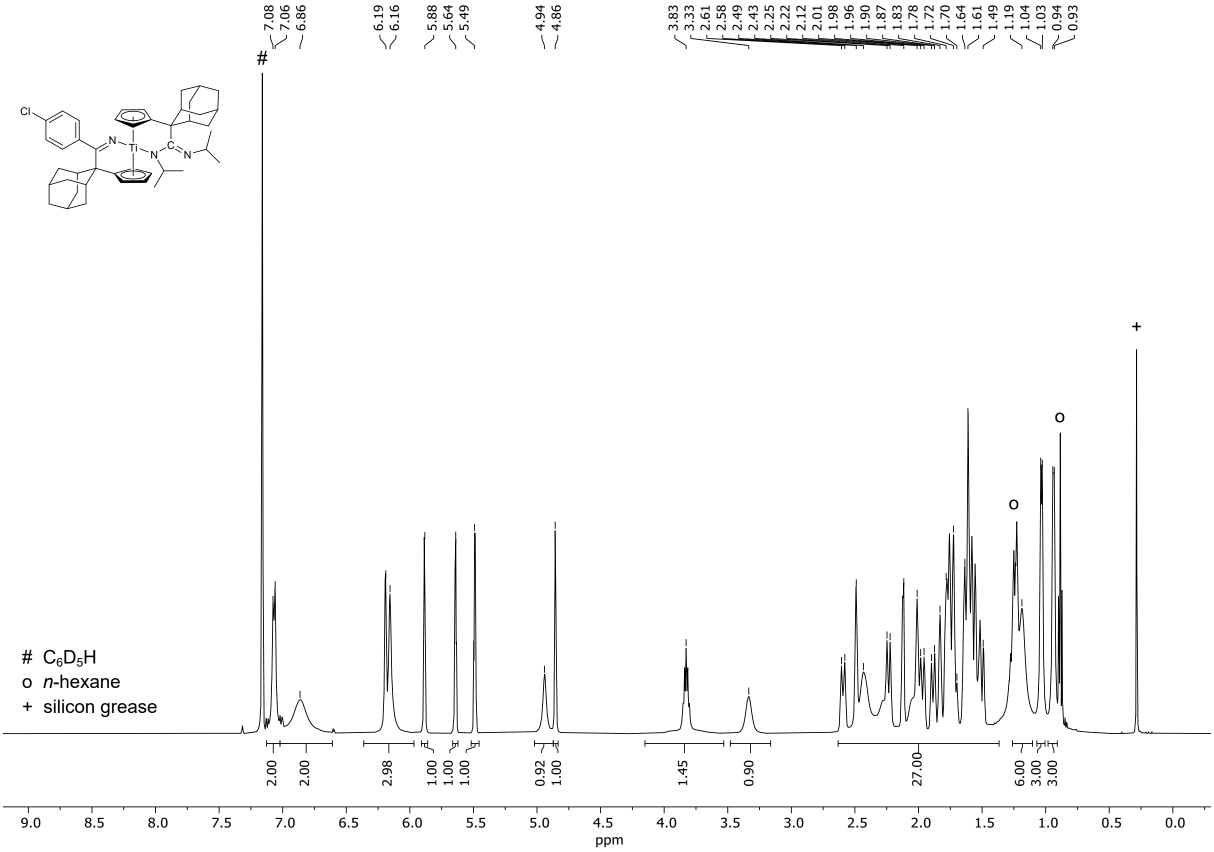


**Figure S36:** $^1$H NMR spectrum of **9** (500 MHz, $C_6D_6$, 305 K).

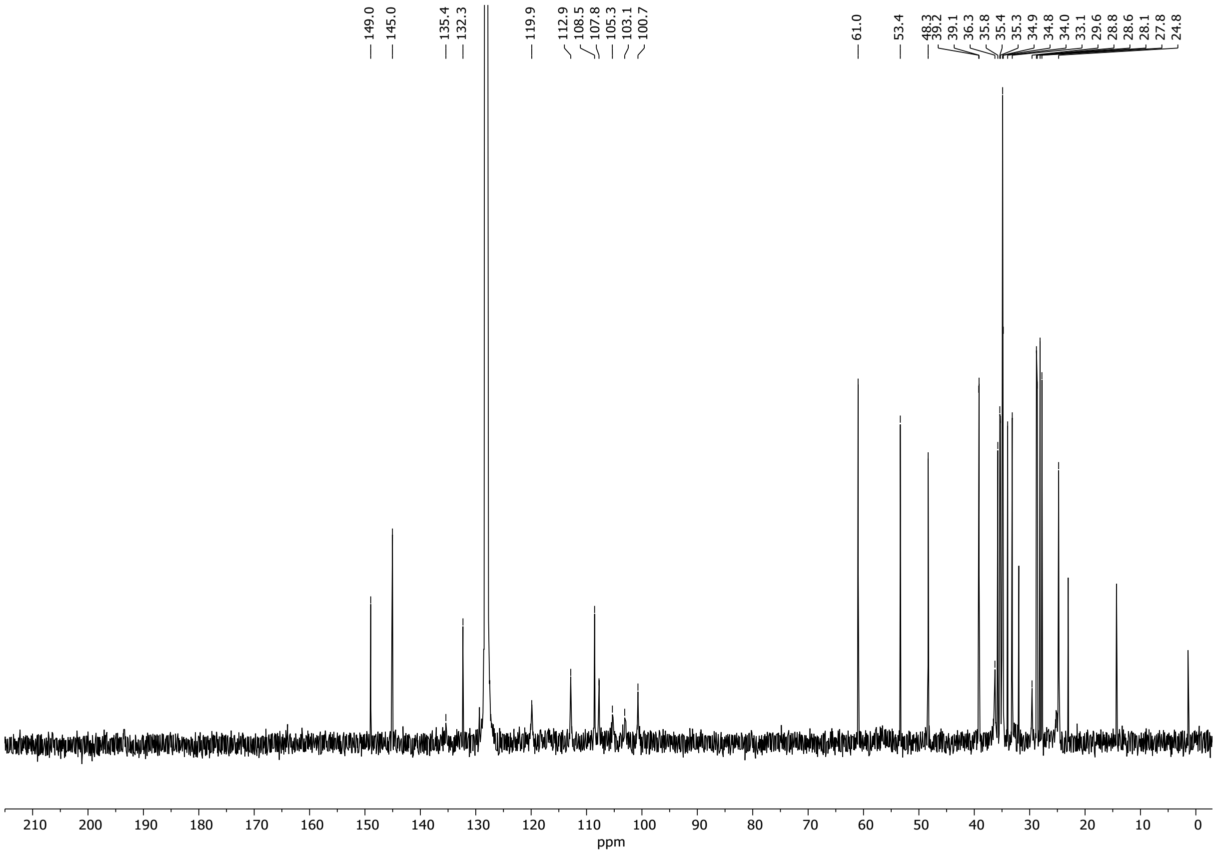


**Figure S37:** $^{13}C\{^1H\}$ NMR spectrum of **9** (126 MHz, $C_6D_6$, 305 K).

# IR spectra

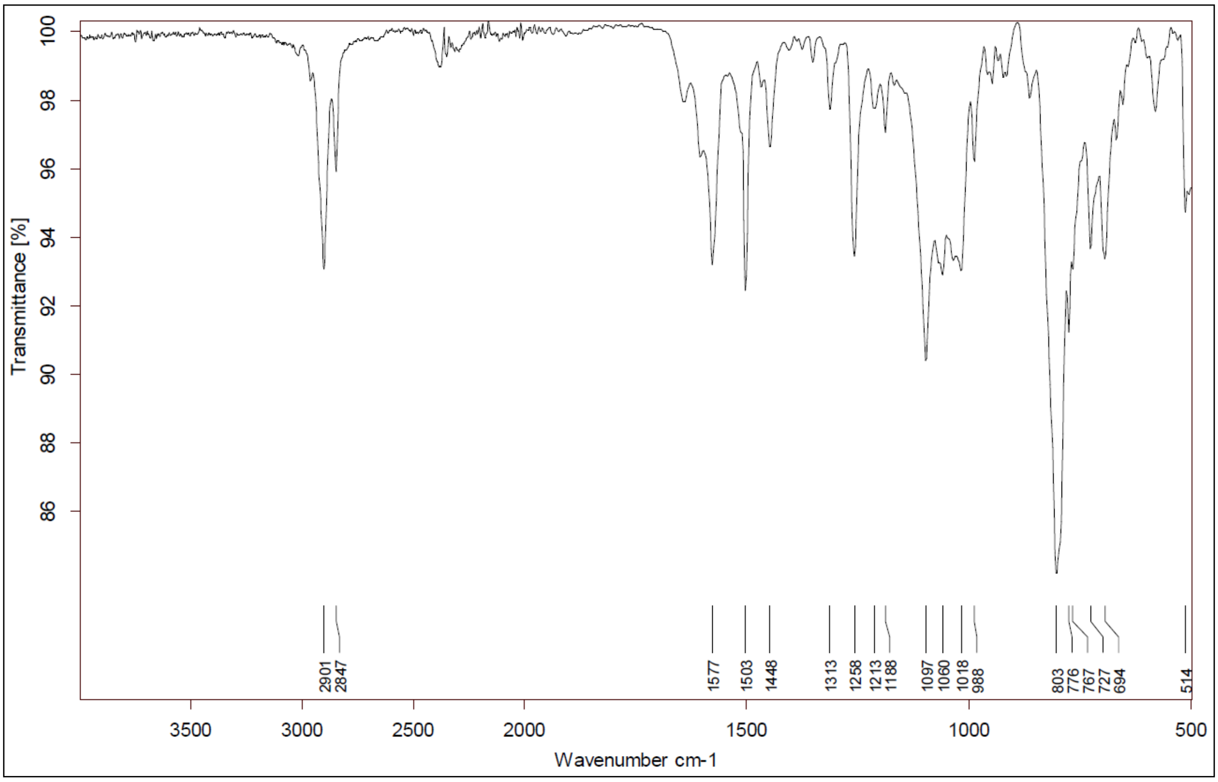


**Figure S38:** IR (ATR) spectrum of **2a**.

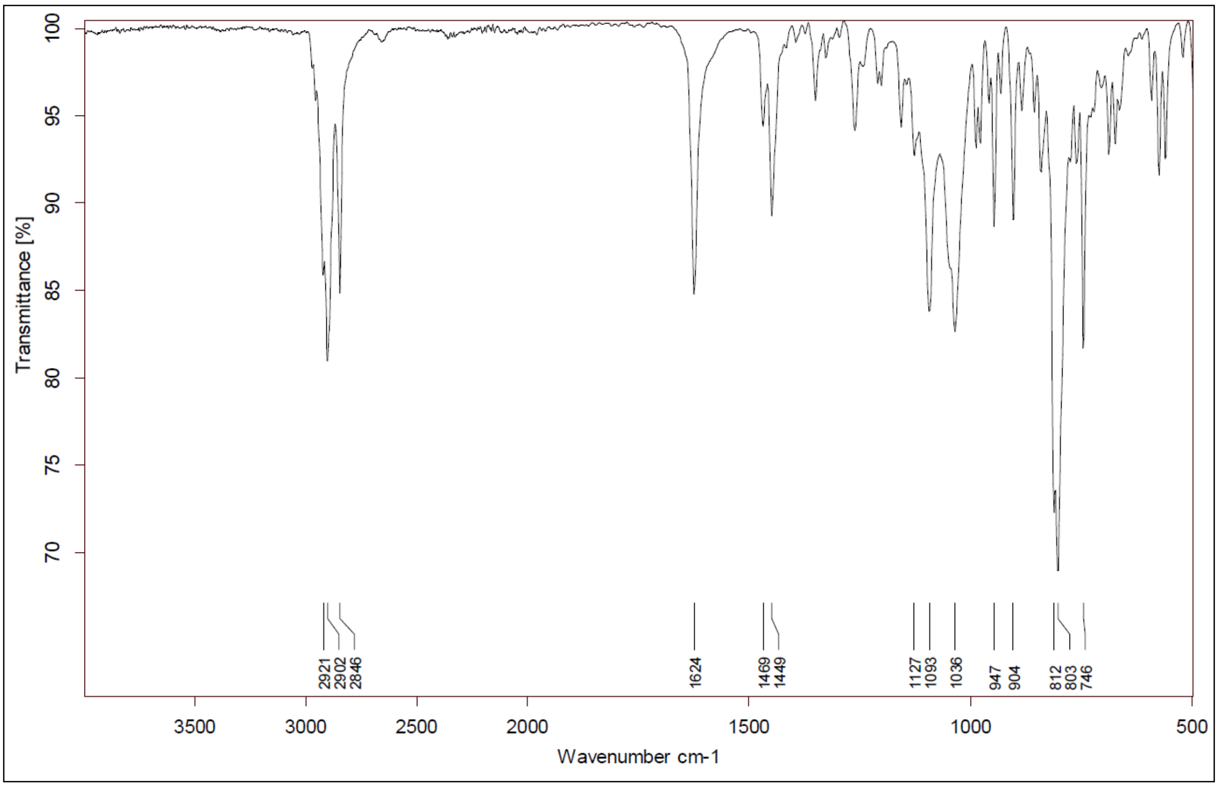


**Figure S39:** IR (ATR) spectrum of **2b**.

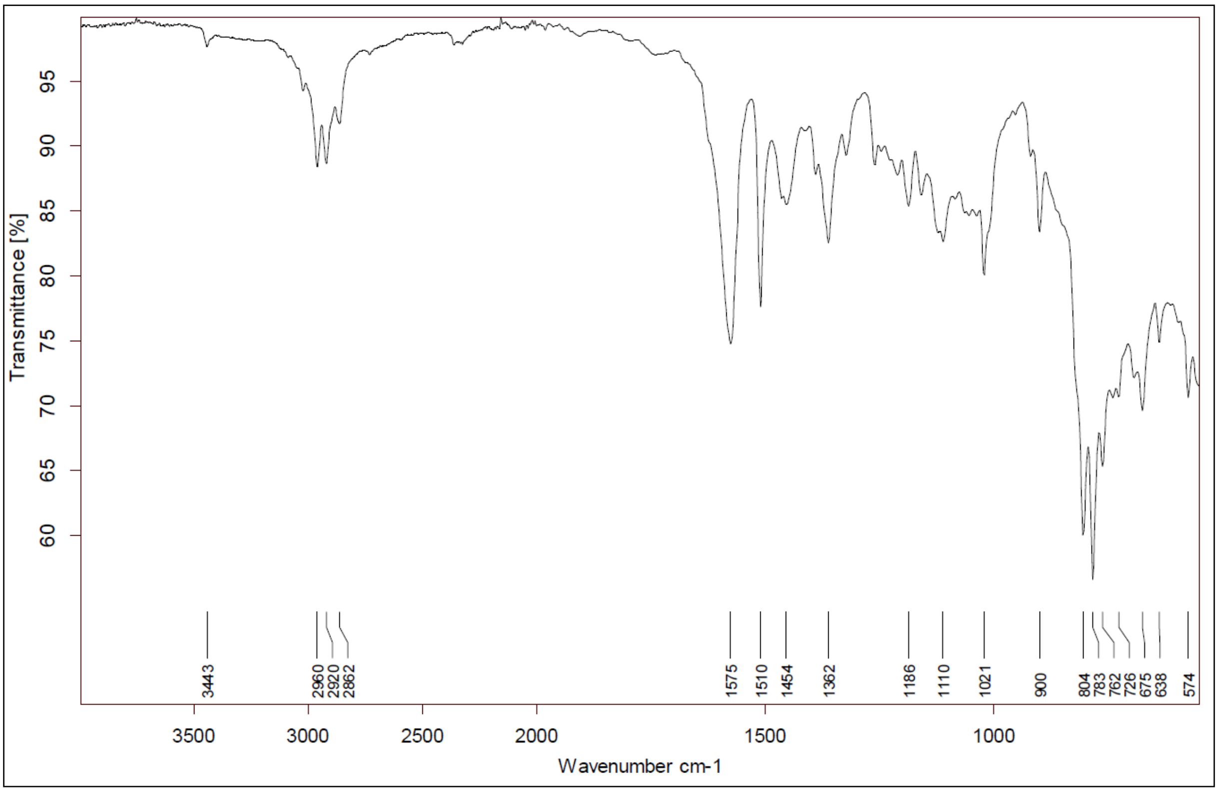


**Figure S40:** IR (ATR) spectrum of **3a**.

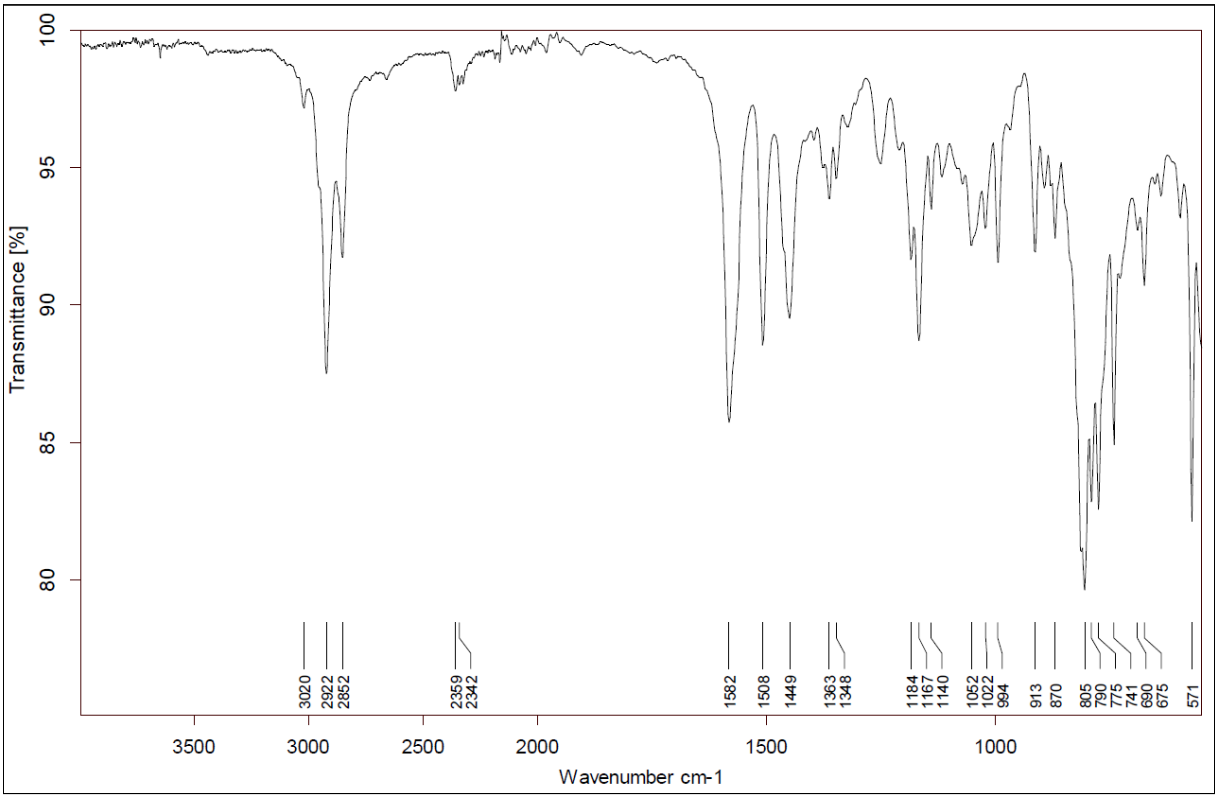


**Figure S41:** IR (ATR) spectrum of **3b**.

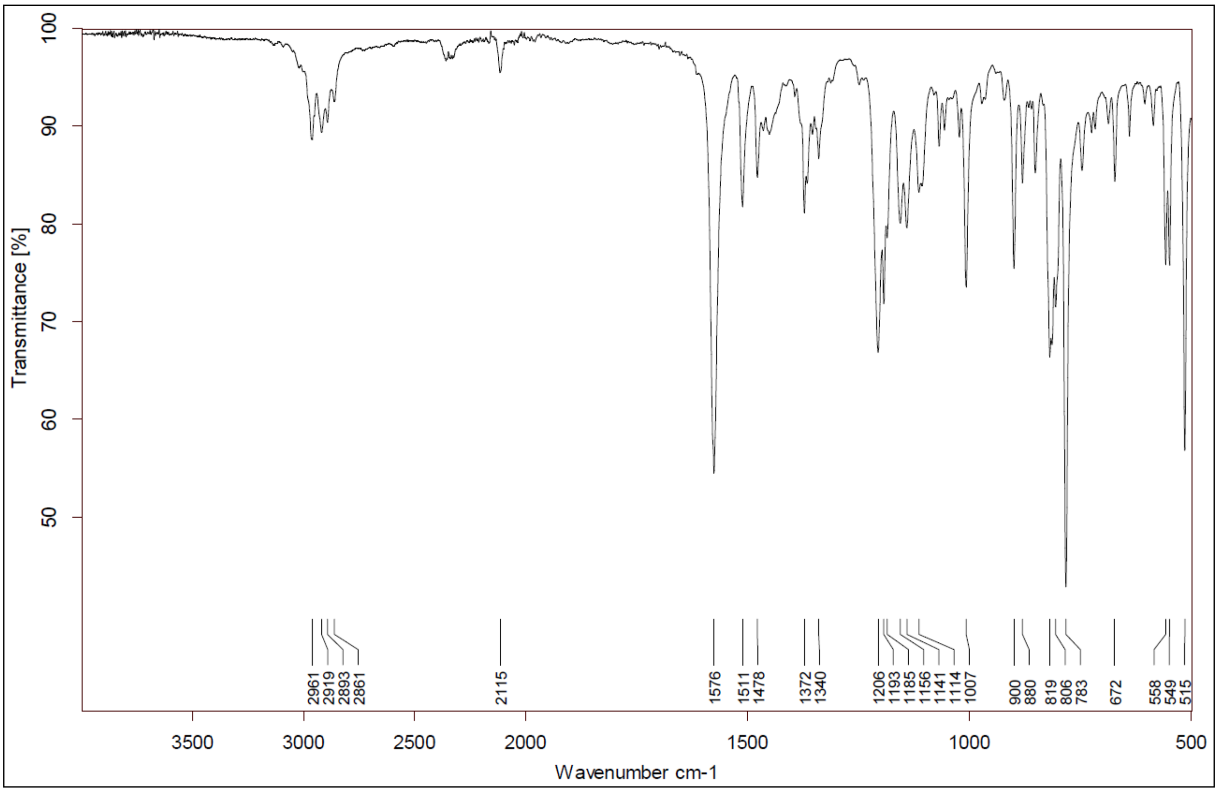


**Figure S42:** IR (ATR) spectrum of **4a**.

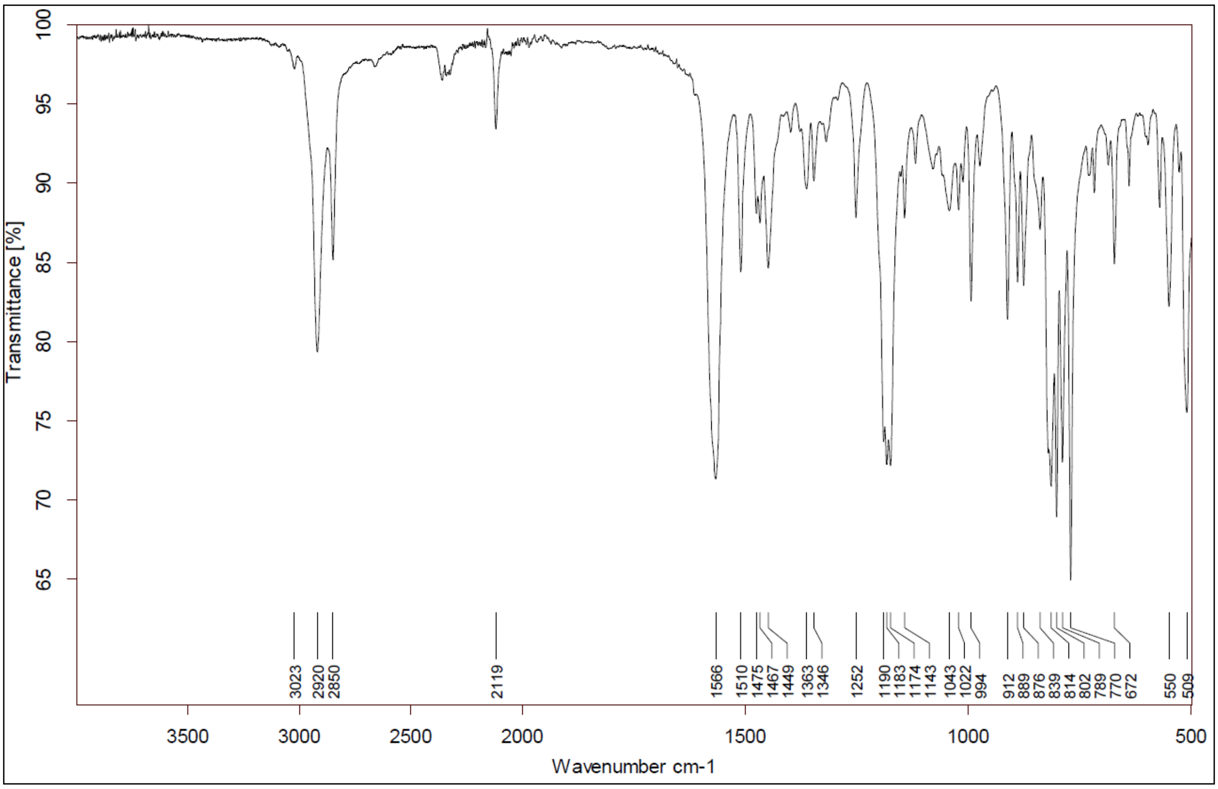


**Figure S43:** IR (ATR) spectrum of **4b**.

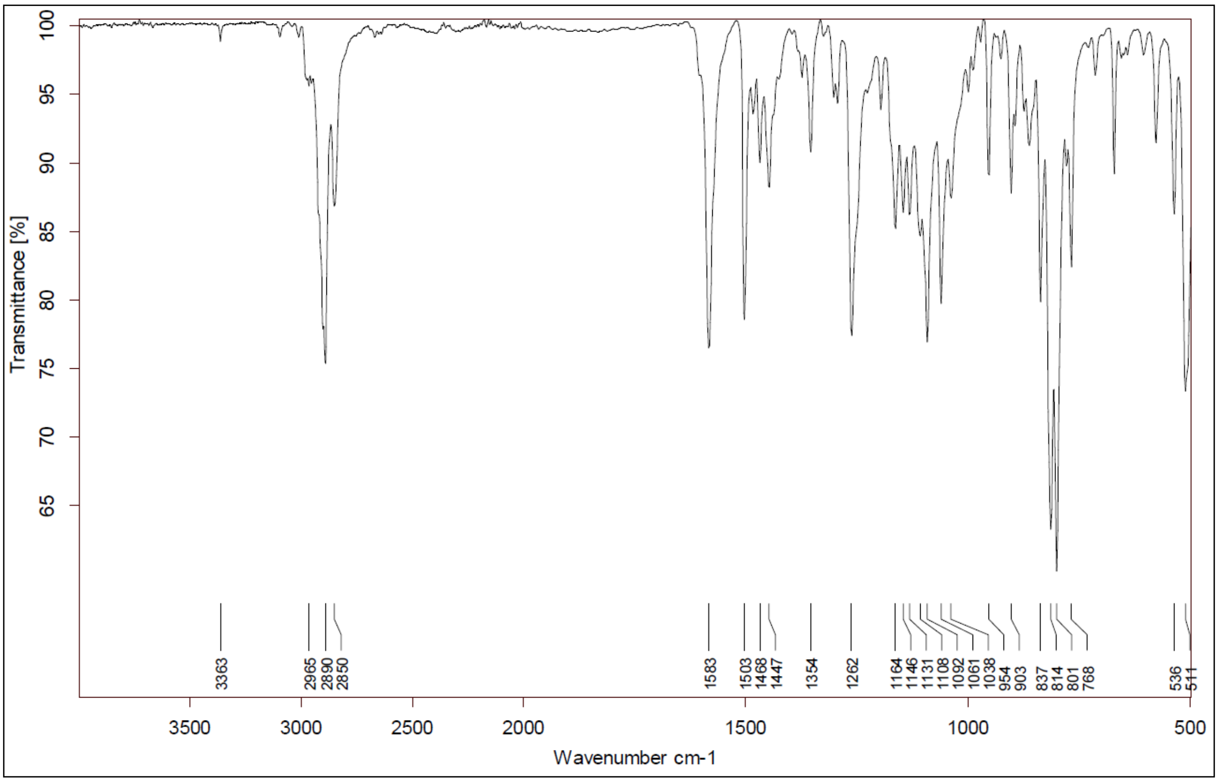


**Figure S44:** IR (ATR) spectrum of **5a**.

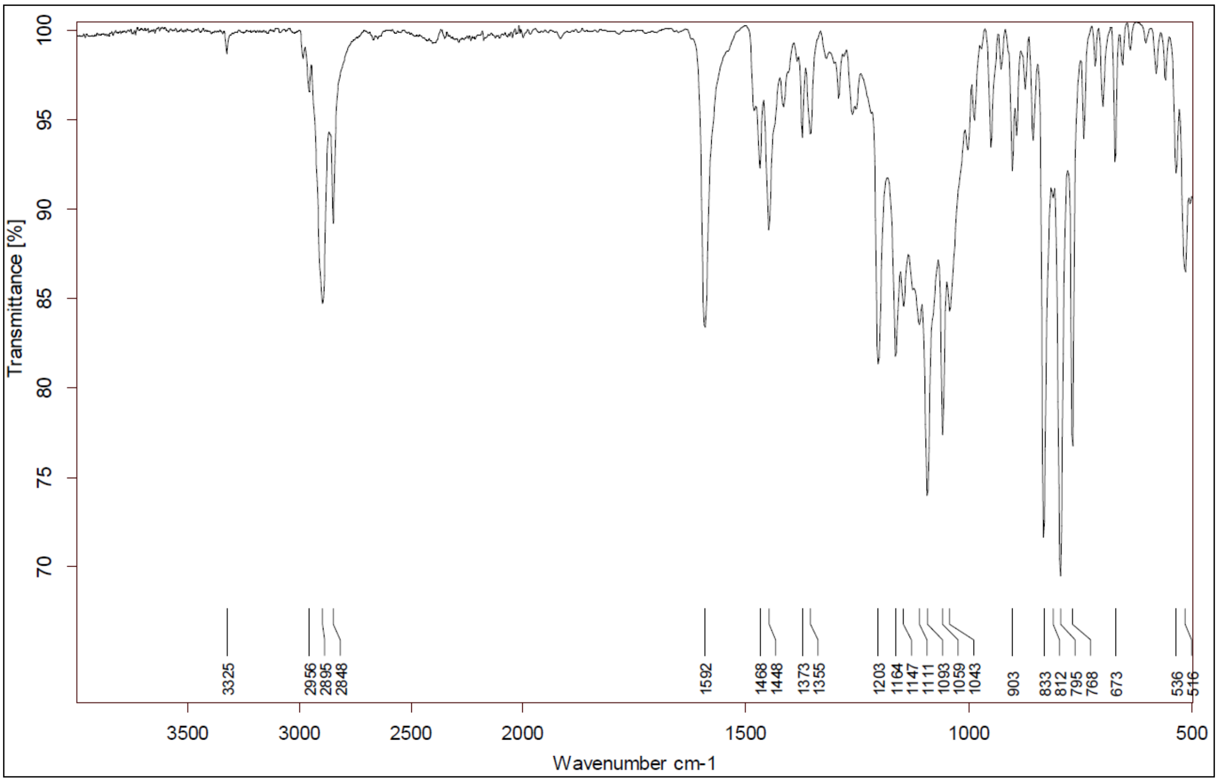


**Figure S45:** IR (ATR) spectrum of **5b**.

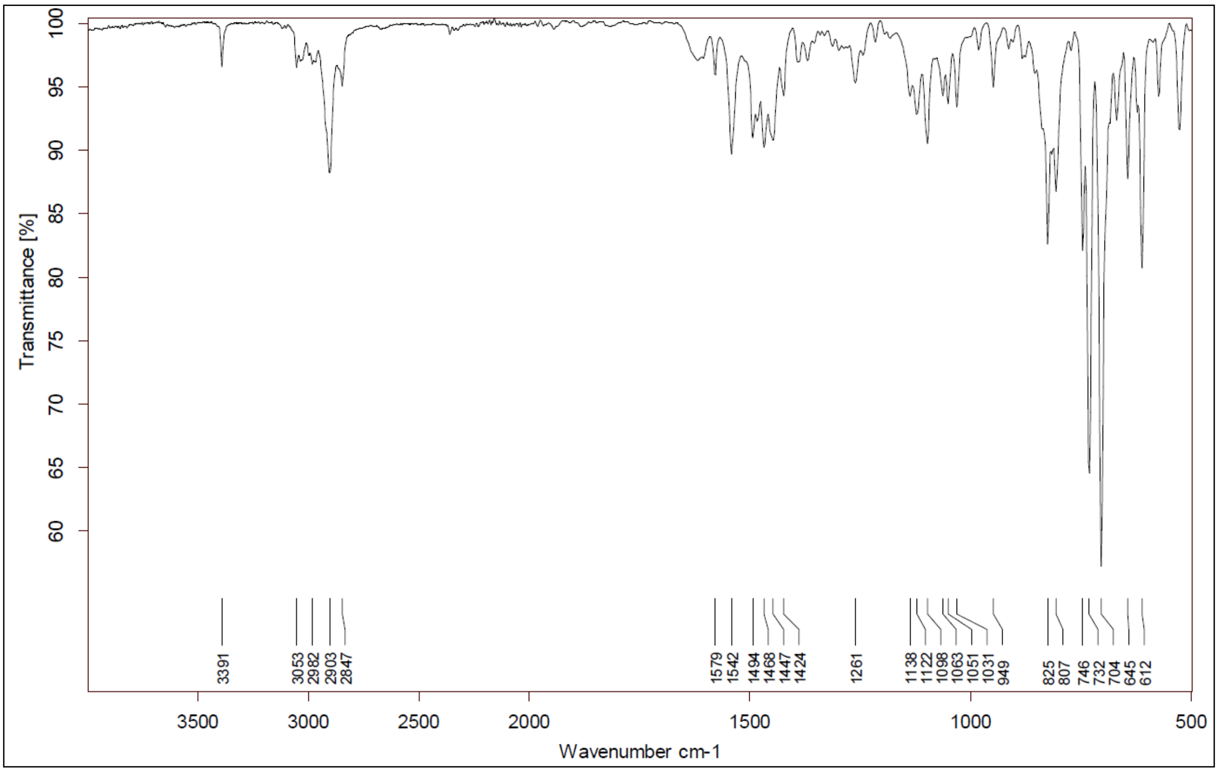


**Figure S46:** IR (ATR) spectrum of **6**.

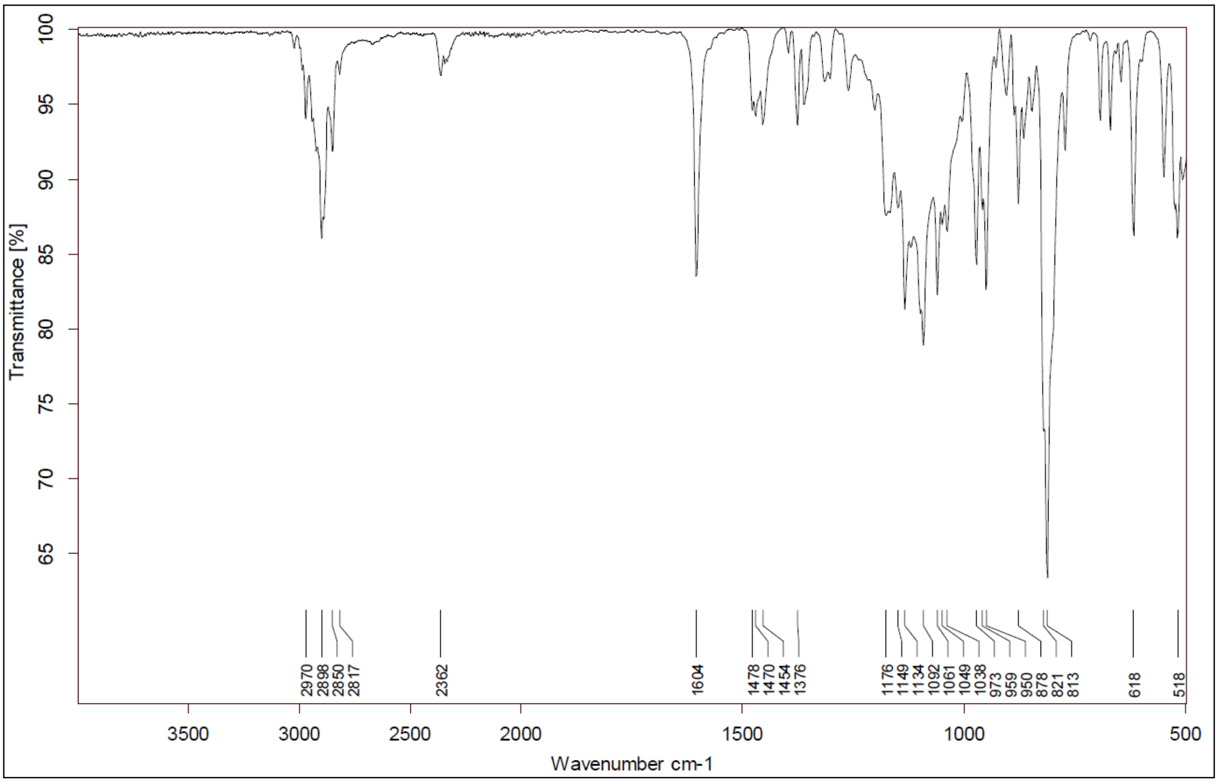


**Figure S47:** IR (ATR) spectrum of **7**.

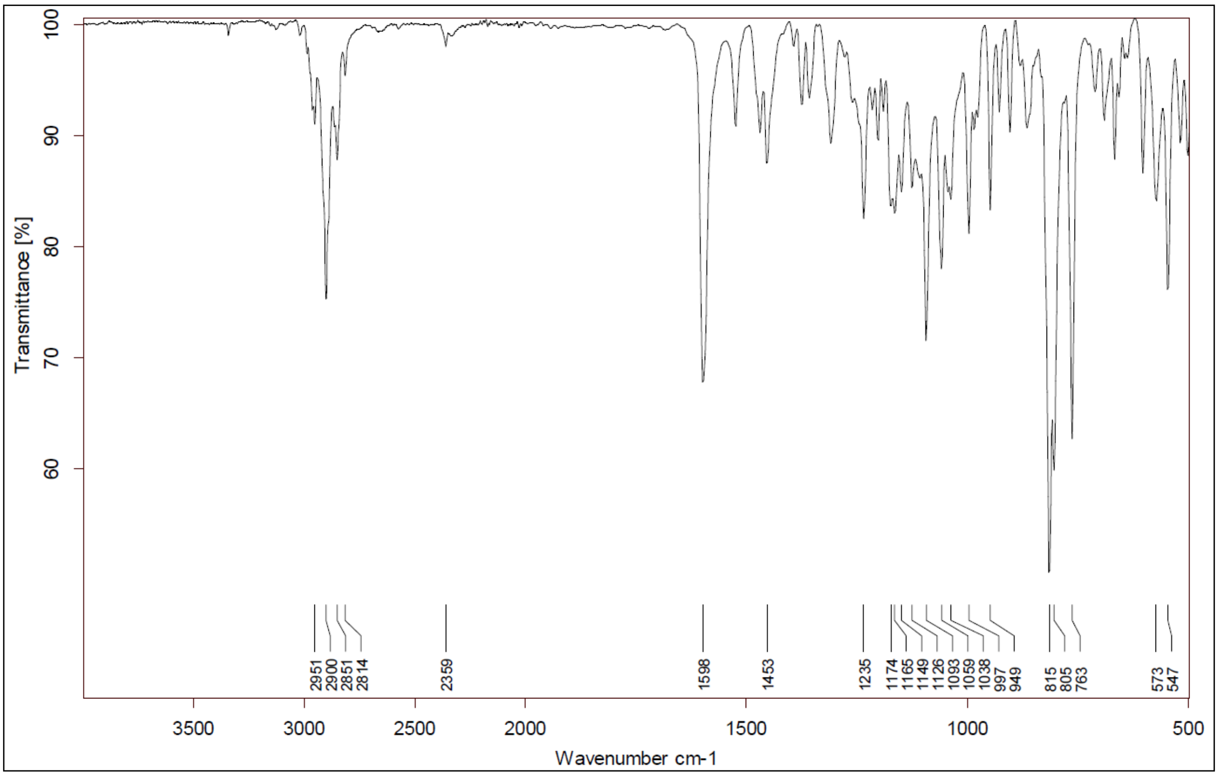


**Figure S48:** IR (ATR) spectrum of **8**.

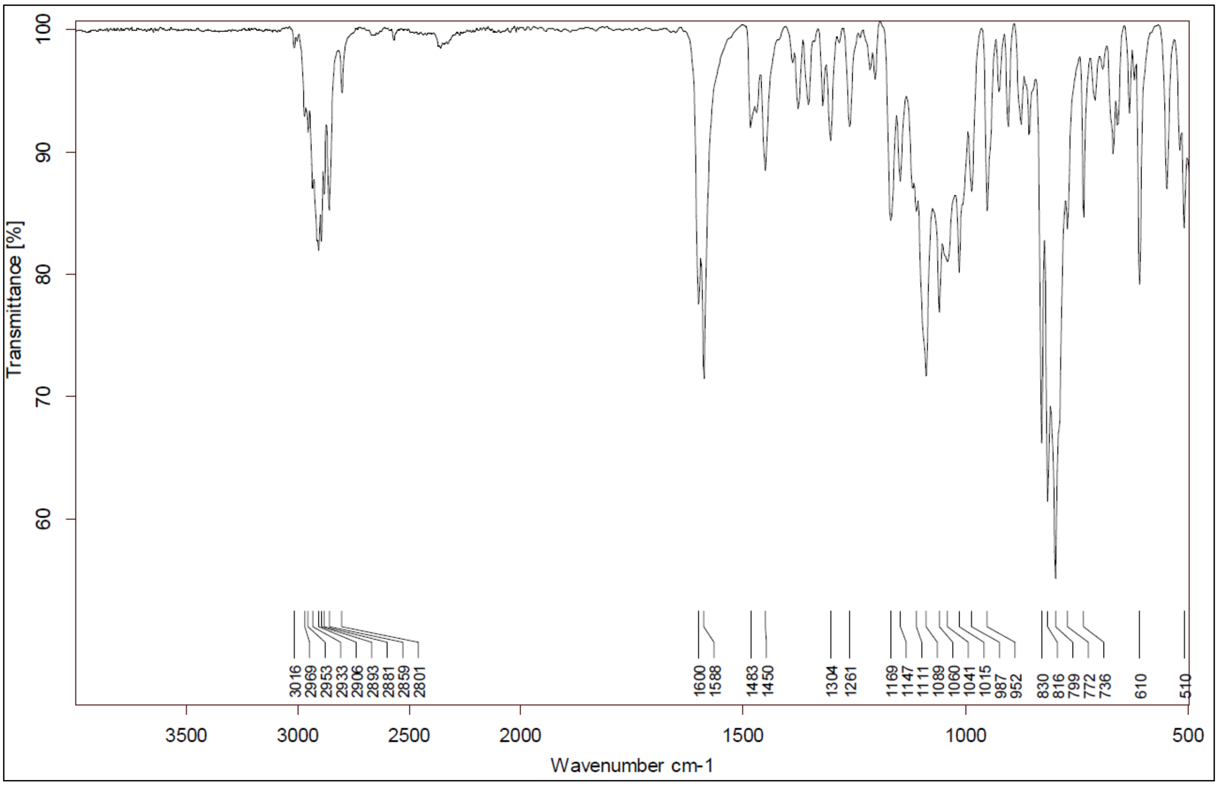


**Figure S49:** IR (ATR) spectrum of **9**.

## UV/vis spectra

UV/vis spectra were recorded with a visible amount of sample dissolved in *n*-hexane. An exact concentration was not determined.

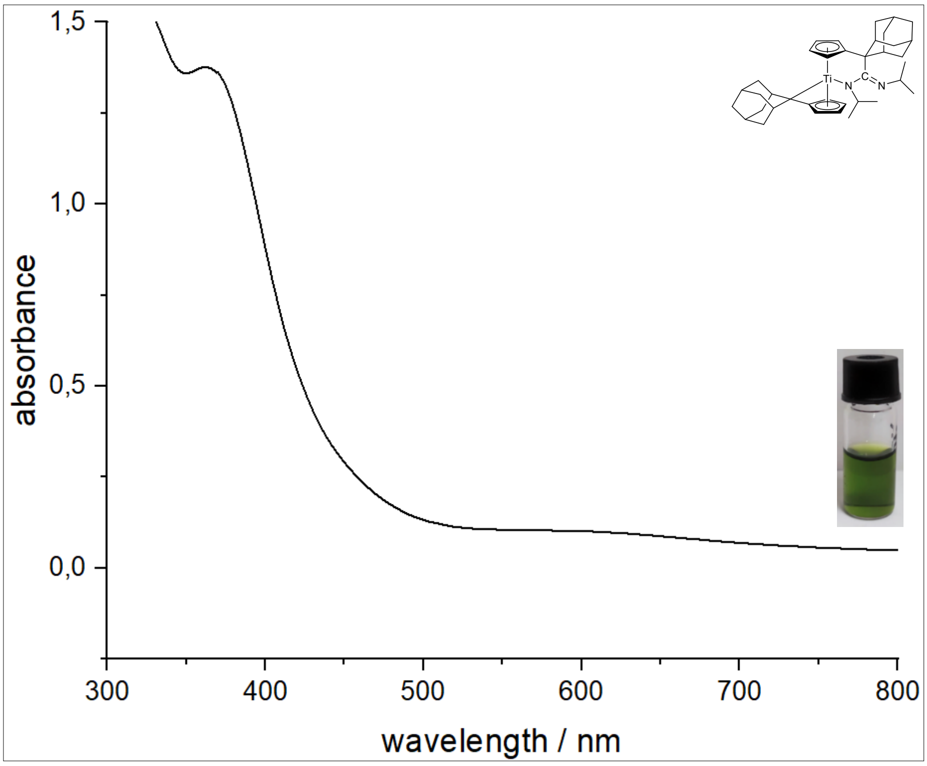


**Figure S50:** UV/vis spectrum of **2a**.

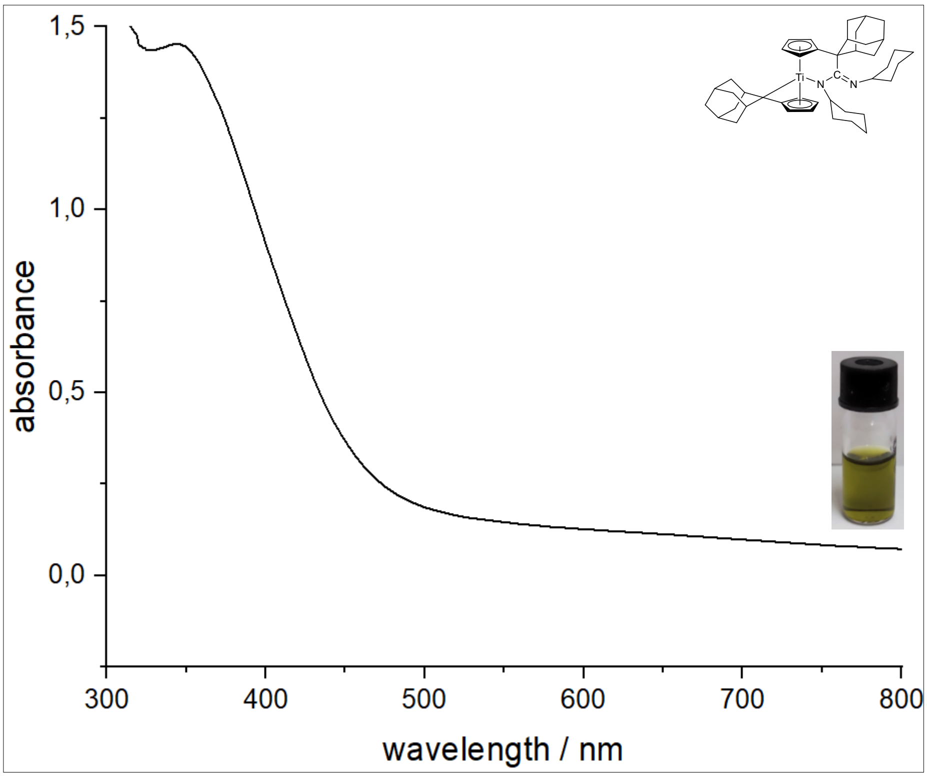


**Figure S51:** UV/vis spectrum of **2b**.

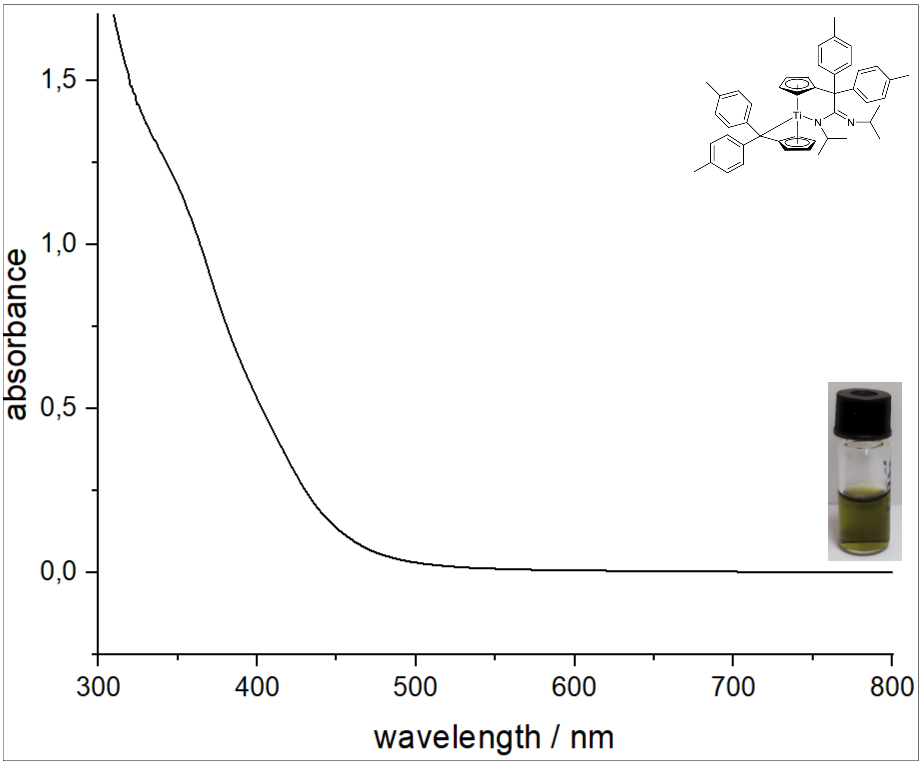


**Figure S52:** UV/vis spectrum of **3a**.

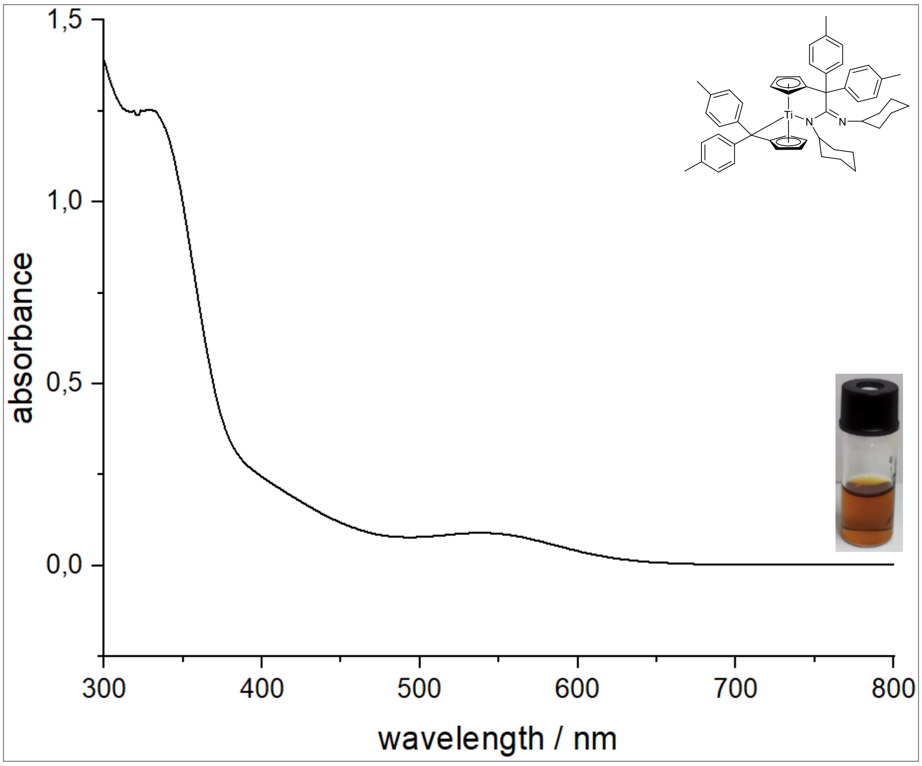


**Figure S53:** UV/vis spectrum of **3b**.

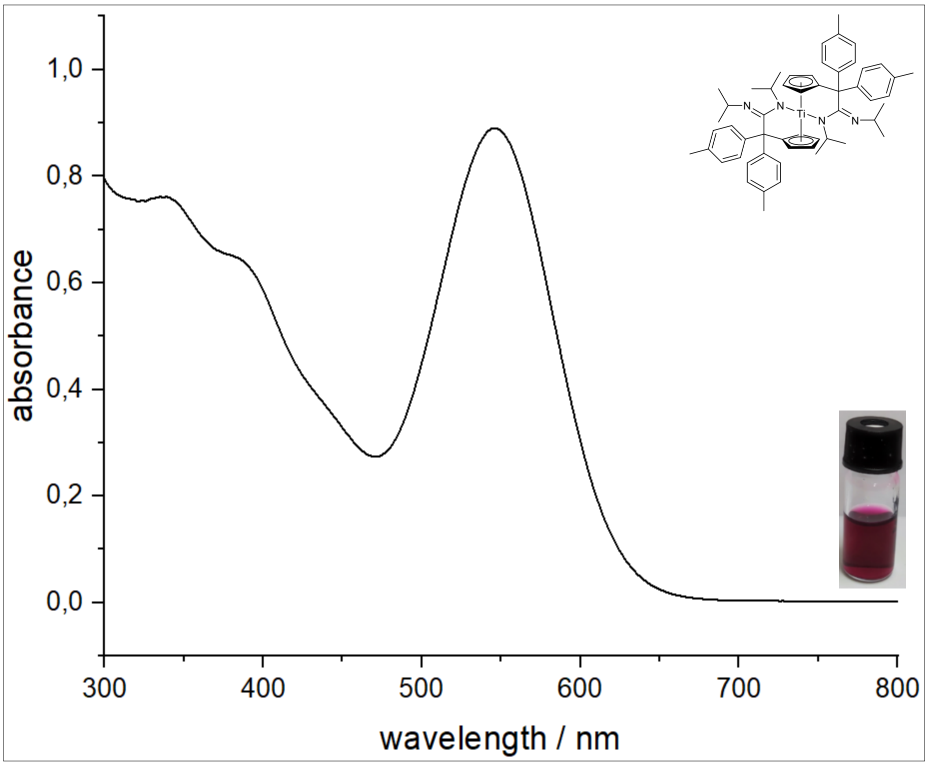


**Figure S54:** UV/vis spectrum of **4a**.

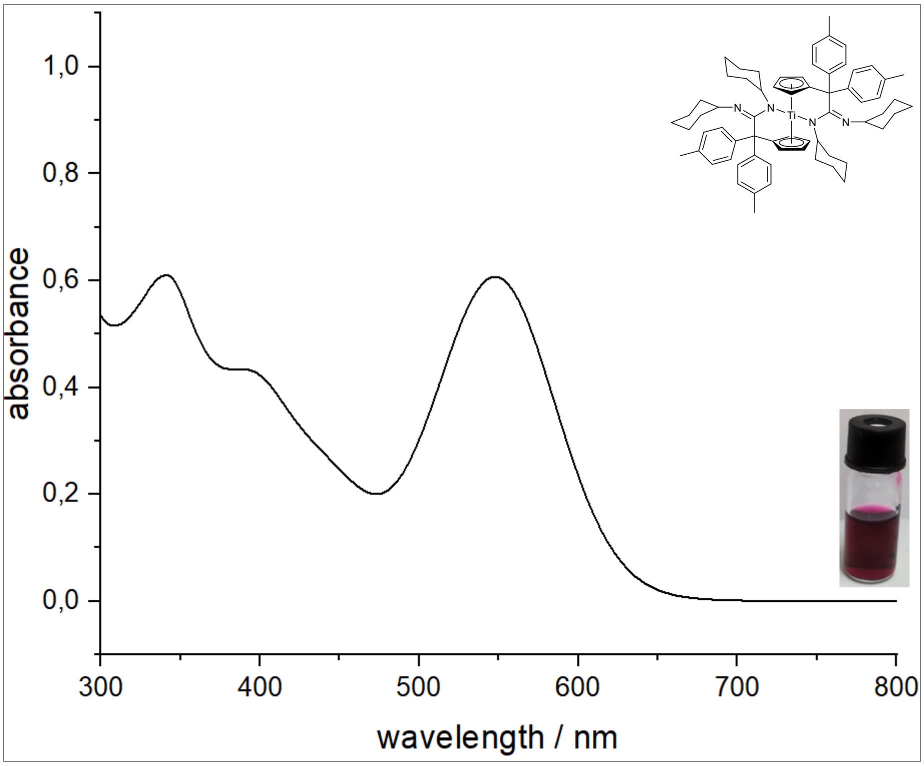


**Figure S55:** UV/vis spectrum of **4b**.

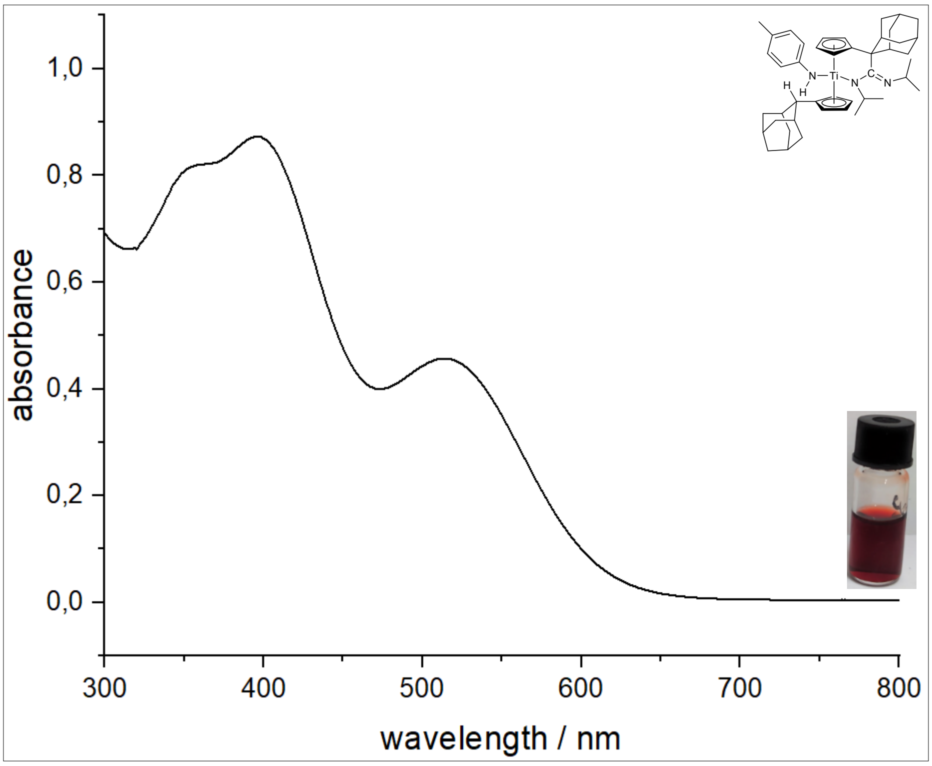


**Figure S56:** UV/vis spectrum of **5a**.

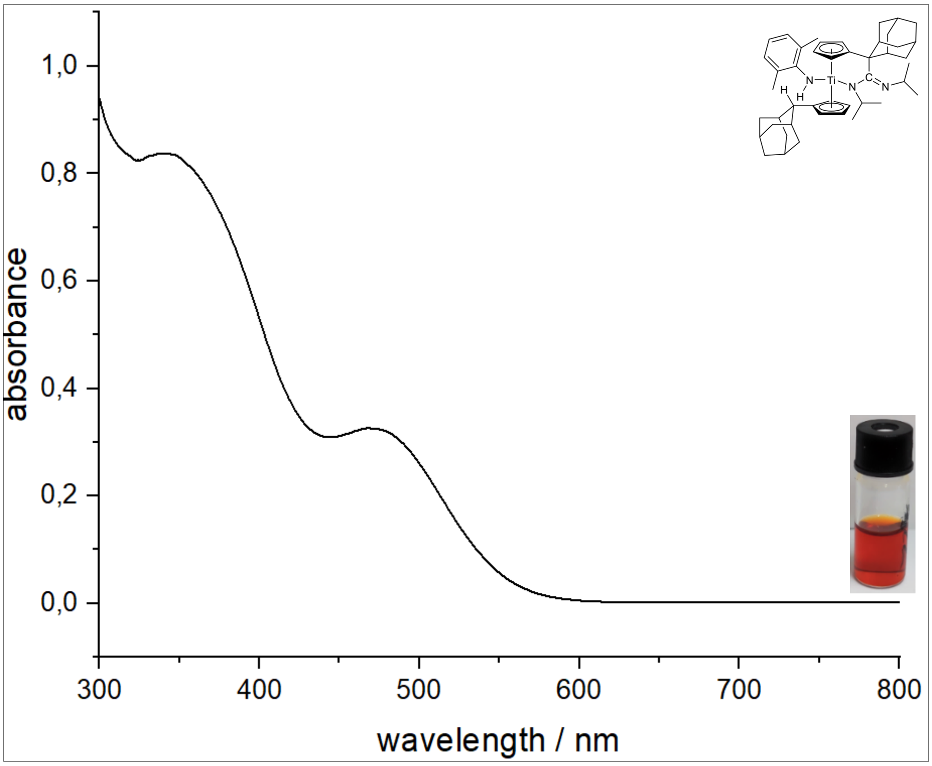


**Figure S57:** UV/vis spectrum of **5b**.

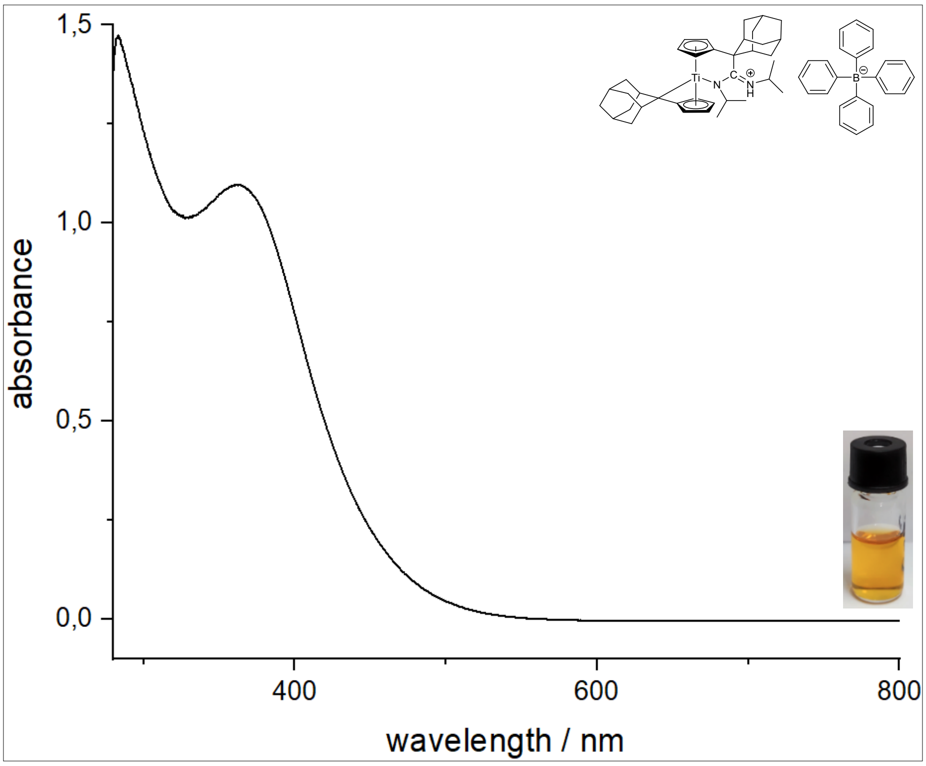


**Figure S58:** UV/vis spectrum of **6**.

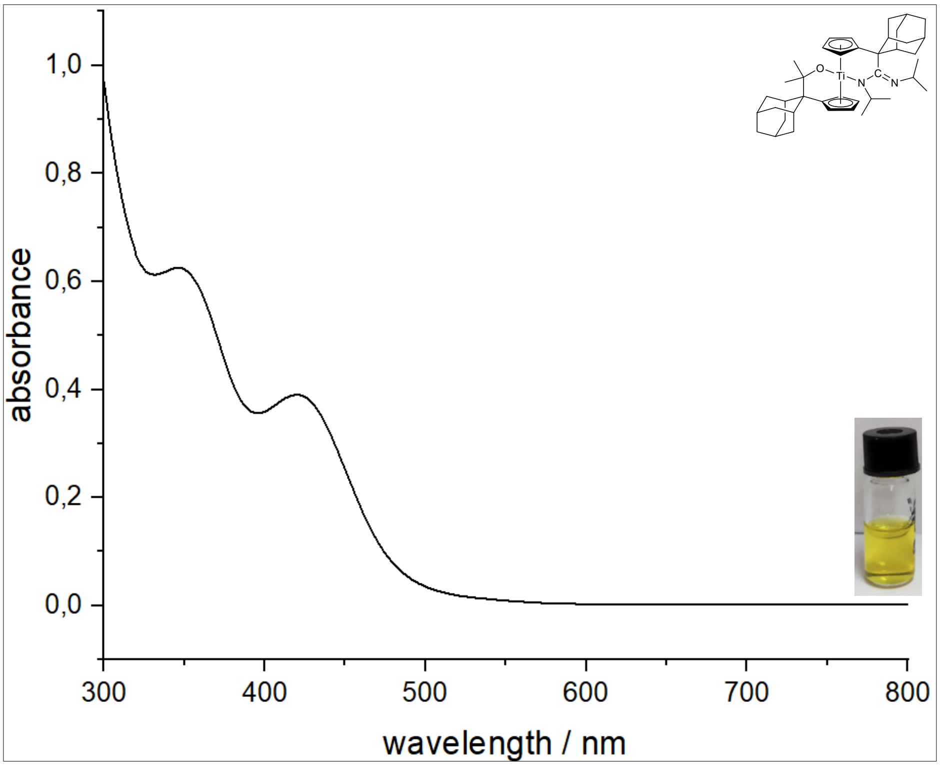


**Figure S59:** UV/vis spectrum of **7**.

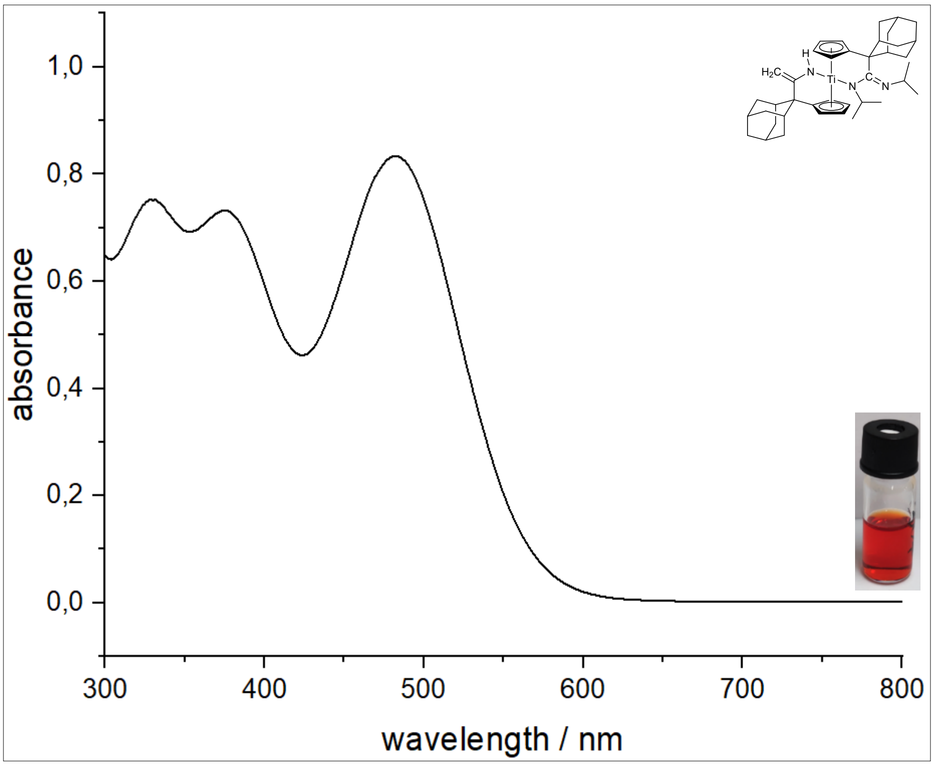


**Figure S60:** UV/vis spectrum of **8**.

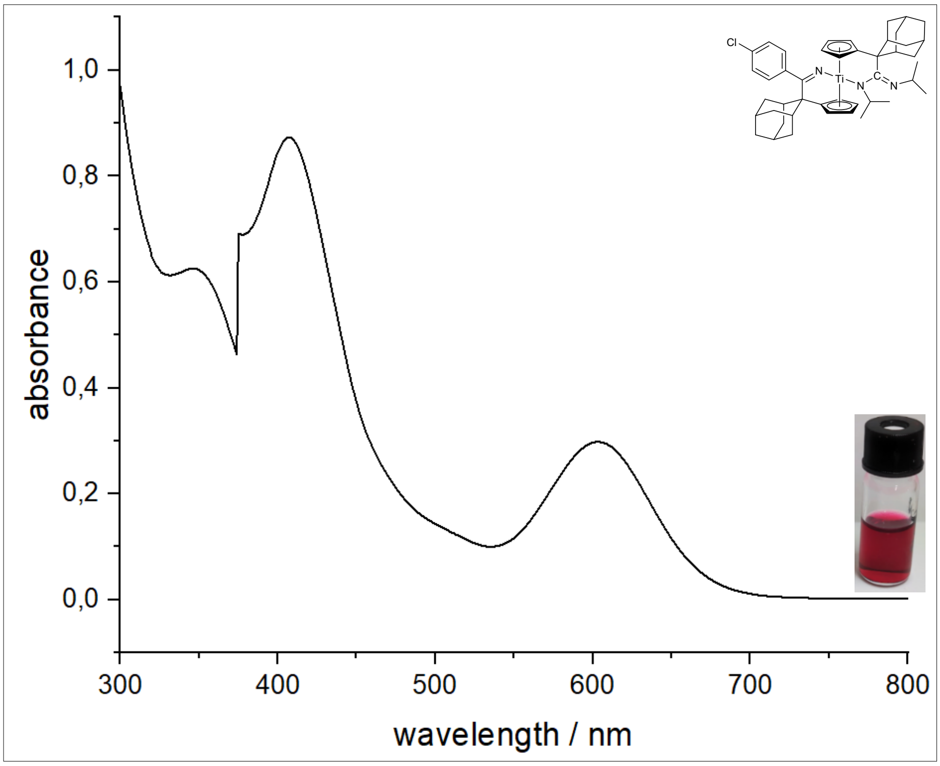


**Figure S61:** UV/vis spectrum of **9**.

## Crystallographic Data

Single crystal X-ray data for **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **4c**, **5a** and **9** were measured on a Bruker AXS D8 Venture diffractometer (multilayer optics, Mo-Kα and Cu-Kα radiation with λ = 0.71073 Å and 1.54178 Å respectively, Kappa 4-circle goniometer, Photon III C14 CPAD detector). Single crystal X-ray data for **5b**, **7**, and **8** were measured on a Bruker AXS Apex II diffractometer (graphite monochromator, Mo-Kα radiation, λ = 0.71073 Å, Kappa 4-circle goniometer, Apex II CCD detector). All crystals were measured at a temperature of 100 K except for **5b** which was measured at 180 K, because at lower temperatures the mosaicity of the crystals increased visibly. Absorption corrections using equivalent reflections were performed with the program SADABS.[3] For **5b**, **7** and **8** numerical absorption corrections were performed using the same program. All structures were solved with the program SHELXS[4] and refined with SHELXL[5] using the OLEX2[6] GUI.

All non-H atoms were refined using anisotropic atomic displacement parameters (ADPs). The minor site of the disordered *iso*-propyl group in **2a** was refined using isotropic ADPs. H atoms bonded to C were located in the difference Fourier maps and placed on idealized geometric positions with idealized ADPs using the riding model. H atoms bonded to N in were refined freely. **3b** contains sites of toluene disordered with *n*-hexane. Here, restraints on the anisotropic ADPs were applied using the RIGU instruction within SHELXL and the geometry of the toluene phenyl groups was idealized (AFIX 66).

The crystallographic data can be obtained free of charge from https://www.ccdc.cam.ac.uk/structures/ quoting the CCDC numbers 2402660-2402670 and 2404156.

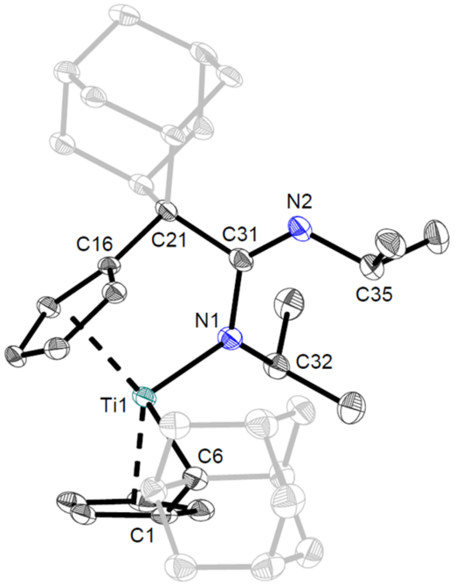


**Figure S62.** Molecular structure of complex **2a**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and disordered *iso*-propyl atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N1 2.0292(15), Ti1–C6 2.446(2), C1–C6 1.435(3), C16–C21 1.517(2), C21–C31 1.556(3), N1–C31 1.446(2), N2–C31 1.272(2), N1–C32 1.503(3), N2–C35 1.458(3); N1–Ti1–C6 110.52(7), Ti1–N1–C31 115.89(11), N1–C31–N2 129.39(17), N1–C31–C21 113.55(15), C31–N1–C32 118.0(2), C31–N2–C35 126.57(16).

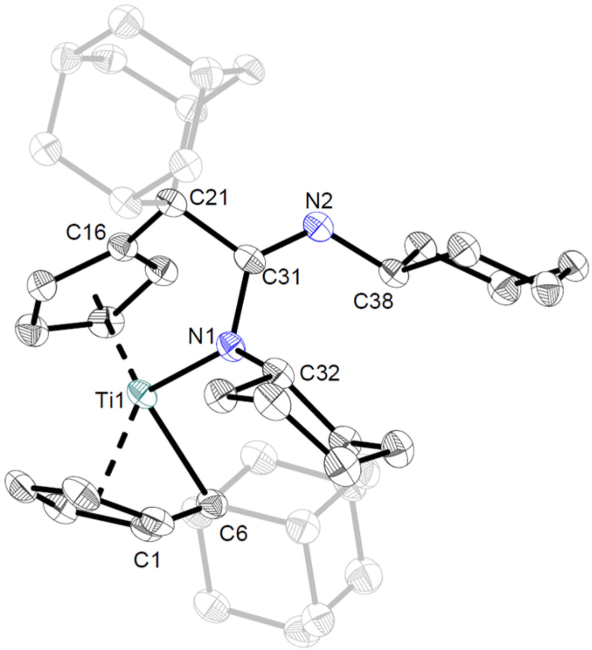


**Figure S63.** Molecular structure of complex **2b**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N1 2.0466(18), Ti1–C6 2.469(2), C1–C6 1.428(3), C16–C21 1.523(3), C21–C31 1.538(3), N1–C31 1.451(3), N2–C31 1.272(3), N1–C32 1.506(3), N2–C38 1.445(3); N1–Ti1–C6 106.78(8), Ti1–N1–C31 111.83(13), N1–C31–N2 129.2(2), N1–C31–C21 112.84(17), C31–N1–C32 109.24(16), C31–N2–C38 125.10(19).

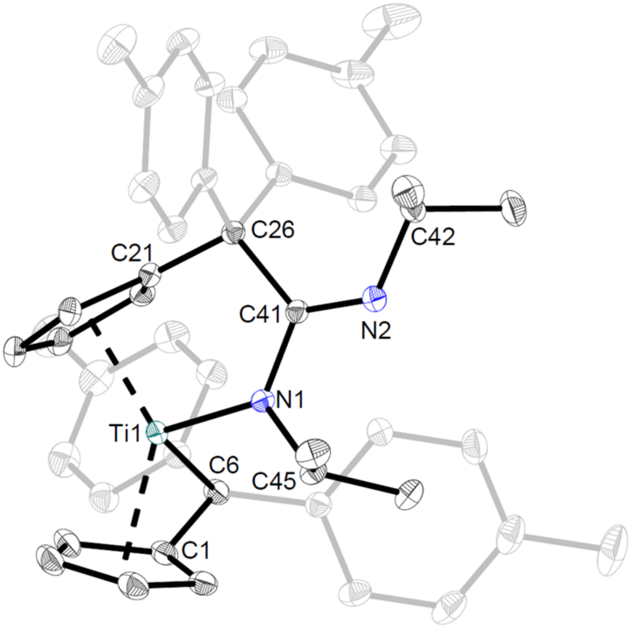


**Figure S64.** Molecular structure of complex **3a**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N1 2.0499(5), Ti1–C6 2.4634(6), C1–C6 1.4471(8), C21–C26 1.5187(8), C26–C41 1.5643(7), N1–C41 1.4092(7), N2–C41 1.2843(7), N2–C42 1.4595(8), N1–C45 1.5034(7); N1–Ti1–C6 110.099(19), Ti1–N1–C41 123.99(3), N1–C41–N2 120.53(5), N1–C41–C26 115.26(4), C41–N2–C42 124.39(5), C41–N1–C45 113.27(4).

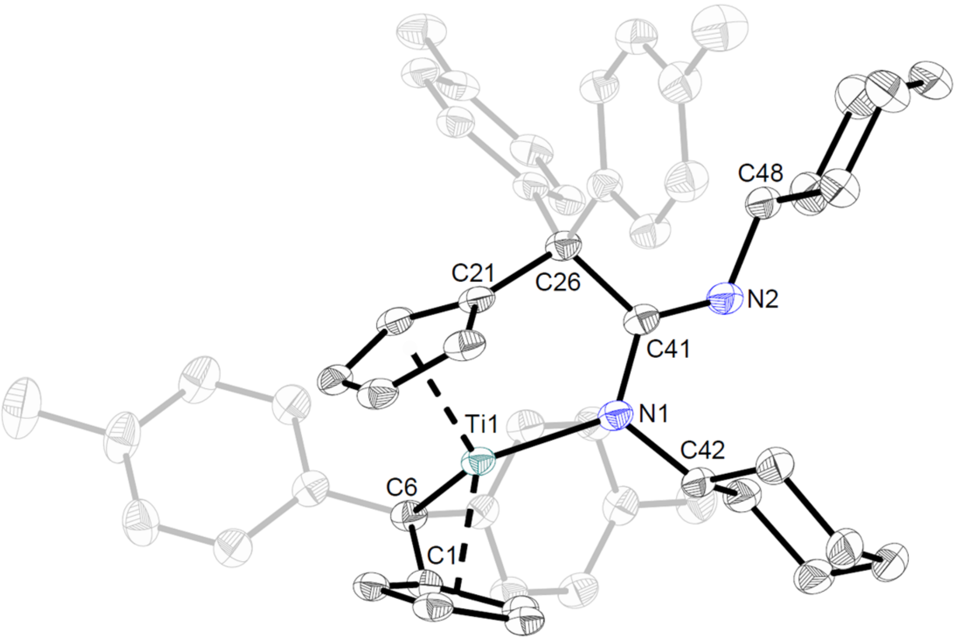


**Figure S65.** Molecular structure of complex **3b**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, solvent molecules and additional crystallographic independent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N1 2.0595(17), Ti1–C6 2.469(2), C1–C6 1.436(3), C21–C26 1.521(3), C26–C41 1.567(3), N1–C41 1.412(3), N2–C41 1.282(3), N1–C42 1.505(3), N2–C48 1.456(3); N1–Ti1–C6 109.84(7), Ti1–N1–C41 124.23(13), N1–C41–N2 120.13(18), N1–C41–C26 115.07(17), C41–N1–C42 112.97(16), C41–N2–C48 126.09(18).

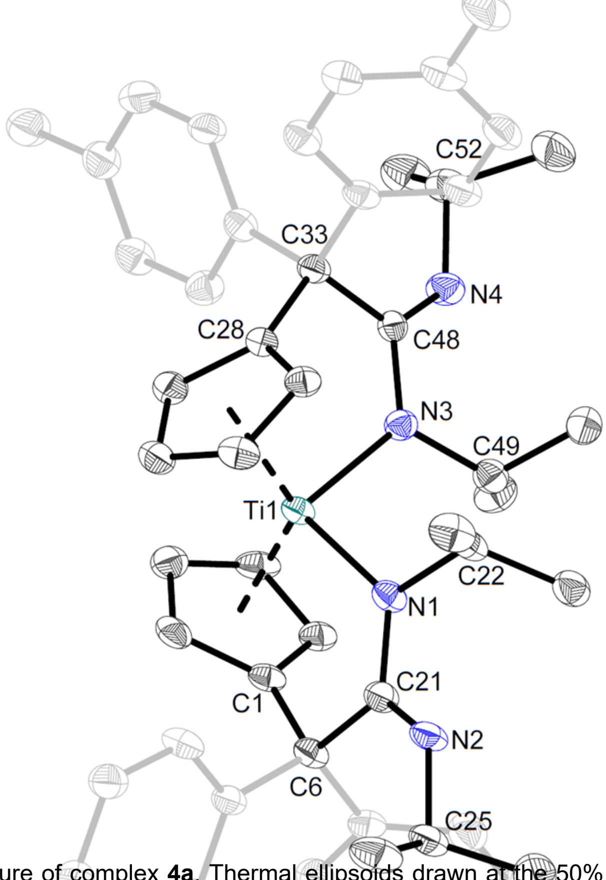


**Figure S66.** Molecular structure of complex **4a**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N1 2.055(3), Ti1–N3 2.058(3), C1–C6 1.524(5), C6–C21 1.557(4), C28–C33 1.523(4), C33–C48 1.564(4), N1–C21 1.399(4), N2–C21 1.298(4), N1–C22 1.501(4), N2–C25 1.455(4), N3–C48 1.391(4), N4–C48 1.290(4), N3–C49 1.501(4), N4–C52 1.450(4); N1–Ti1–N3 99.42(11), C1–C6–C21 10 C48–N4 120.8(3), Ti1–N1–C21 127.9(2), Ti1–N3–C48 48–N3–C49 115.6(3), C48–N4–C52 124.8(3).

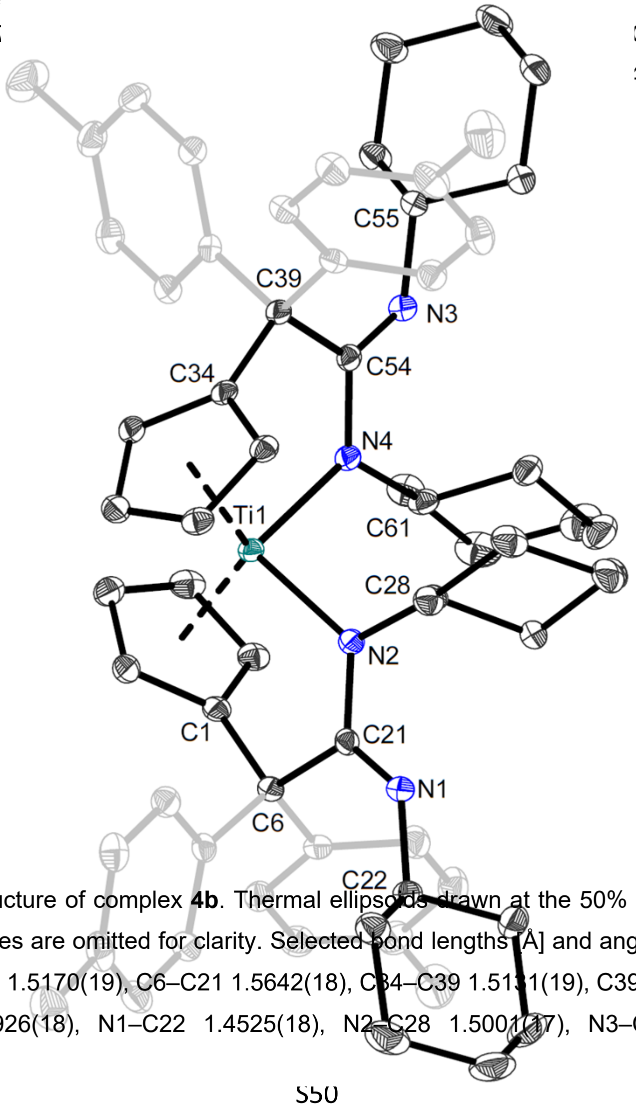


**Figure S67.** Molecular structure of complex **4b**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N2 2.0659(11), Ti1–N4 2.0742(12), C1–C6 1.5170(19), C6–C21 1.5642(18), C34–C39 1.5131(19), C39–C54 1.5655(18), N1–C21 1.2851(18), N2–C21 1.3926(18), N1–C22 1.4525(18), N2–C28 1.5001(17), N3–C54 1.2830(18), N4–C54

1.3932(17), N3–C55 1.4588(17), N4–C61 1.4995(17); N2–Ti1–N4 96.56(5), C1–C6–C21 108.11(11), C34–C39–C54 108.55(11), N1–C21–N2 121.19(12), N3–C54–N4 121.57(12), Ti1–N2–C21 127.35(9), Ti1–N4–C54 127.68(9), C21–N1–C22 125.19(12), C21–N2–C28 114.93(11), C54–N3–C55 124.15(12), C54–N4–C61 114.80(11).

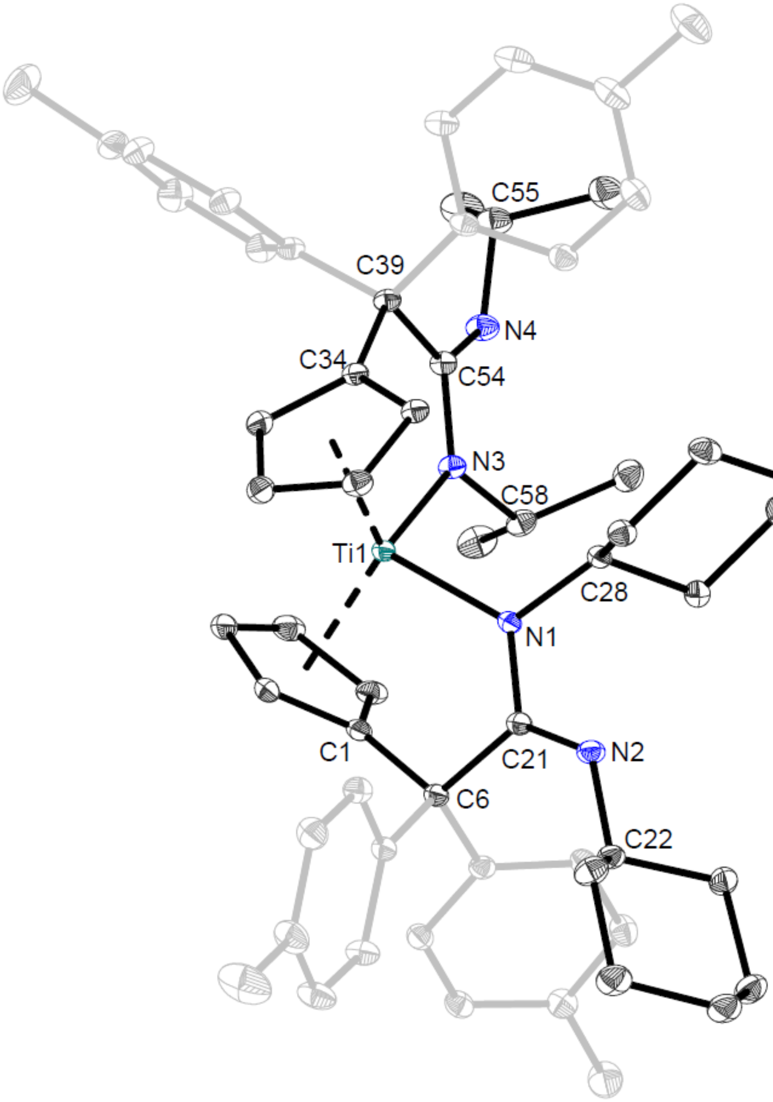


**Figure S68.** Molecular structure of complex **4c**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N1 2.0624(8), Ti1–N3 2.0565(9), C1–C6 1.5177(13), C6–C21 1.5639(13), C34–C39 1.5175(13), C39–C54 1.5660(14), N1–C21 1.3952(12), N2–C21 1.2841(13), N2–C22 1.4595(12), N1–C28 1.4925(12), N3–C54 1.3988(12), N3–C58 1.5017(13), N4–C54 1.2806(13), N4–C55 1.4583(13); N1–Ti1–N3 99.37(3), C1–C6–C21 108.18(7), C34–C39–C54 107.61(7), N1–C21–N2 121.10(9), N3–C54–N4 119.60(9), Ti1–N1–C21 128.06(6), Ti1–N3–C54 129.22(7), C21–N1–C22 121.10(9), C21–N1–C28 115.31(8), C54–N4–C55 127.47(9), C54–N3–C58 113.73(8).

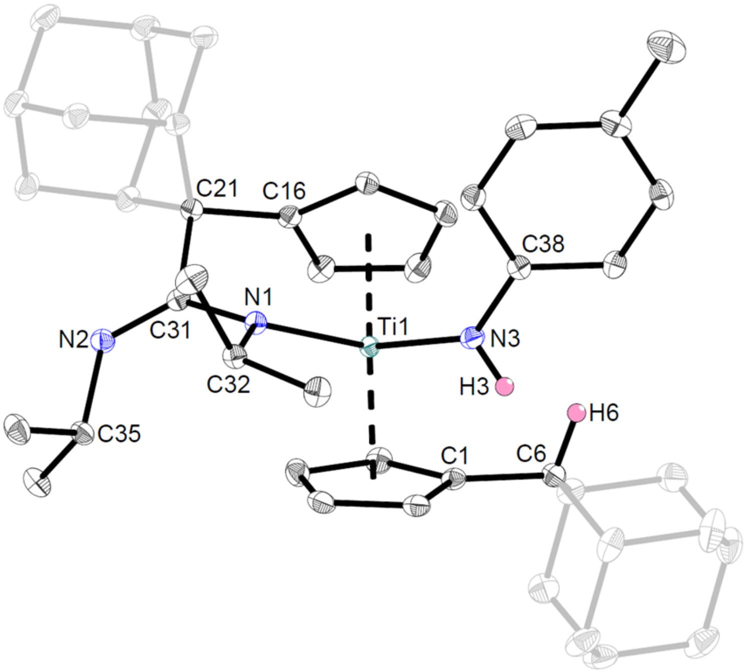


**Figure S69.** Molecular structure of complex **5a**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms (except for H3 and H6) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N1 2.0741(12), Ti1–N3 1.9872(13), C1–C6 1.5168(19), C16–C21 1.5110(19), C21–C31 1.5612(19), N1–C31 1.4112(18), N1–C32 1.4911(17), N2–C31 1.2823(18), N2–C35 1.4629(18); N1–Ti1–N3 103.74(5), Ti1–N1–C31 112.51(8), Ti1–N3–C38 136.12(10), C16–C21–C31 102.62(11), N1–C31–C21 112.79(11), N1–C31–N2 130.82(13), C31–N1–C32 114.60(11), C31–N2–C35 125.24(12).

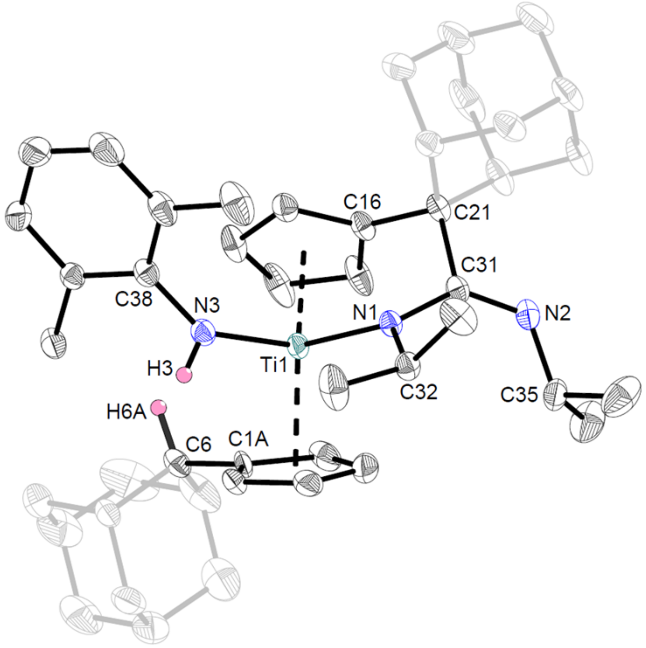


**Figure S70.** Molecular structure of complex **5b**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms (except for H3 and H6A) and disorders are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N1 2.0989(14), Ti1–N3 1.9993(16), C1A–C6 1.56(2), C16–C21 1.515(2), C21–C31 1.552(3), N1–C31 1.419(2), N1–C32 1.491(2), N2–C31 1.281(2), N2–C35 1.458(3); N1–Ti1–N3 103.06(6), Ti1–N1–C31 114.11(11), Ti1–N3–C38 136.94(13), C16–C21–C31 100.87(13), N1–C31–C21 111.80(14), N1–C31–N2 131.60(17), C31–N1–C32 114.39(14), C31–N2–C35 126.80(17).

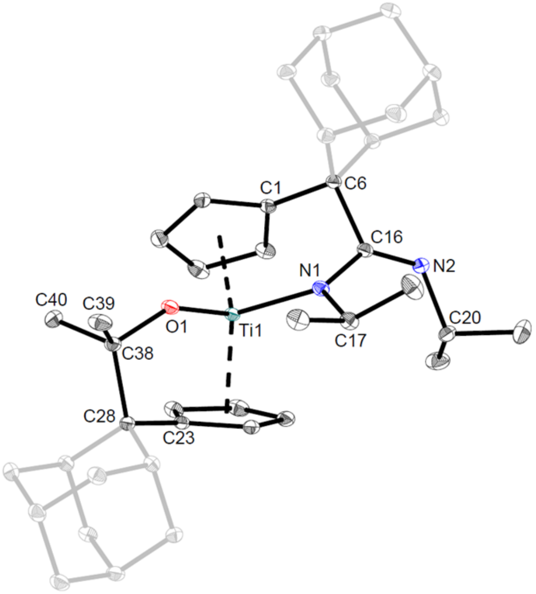


**Figure S71.** Molecular structure of complex **7**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N1 2.0528(8), Ti1–O1 1.8689(7), C1–C6 1.5133(12), C23–C28 1.5211(12), C6–C16 1.5474(12), C28–C38 1.6284(12), N1–C16 1.4236(11), N1–C17 1.4872(12), N2–C16 1.2784(11), N2–C20 1.4628(12), O1–C38 1.4229(11), C38–C39 1.5333(14), C38–C40 1.5383(14); N1–Ti1–O1 103.66(3), Ti1–N1–C16 115.45(6), Ti1–O1–C38 135.11(6), C1–C6–C16 98.88(6), C23–C28–C38 102.87(6), N1–C16–C6 110.75(7), N1–C16–N2 130.80(8), C16–N1–C17 117.41(7), C16–N2–C20 122.99(8), O1–C38–C28 108.58(6), O1–C38–C39 104.96(7), O1–C38–C40 107.11(7).

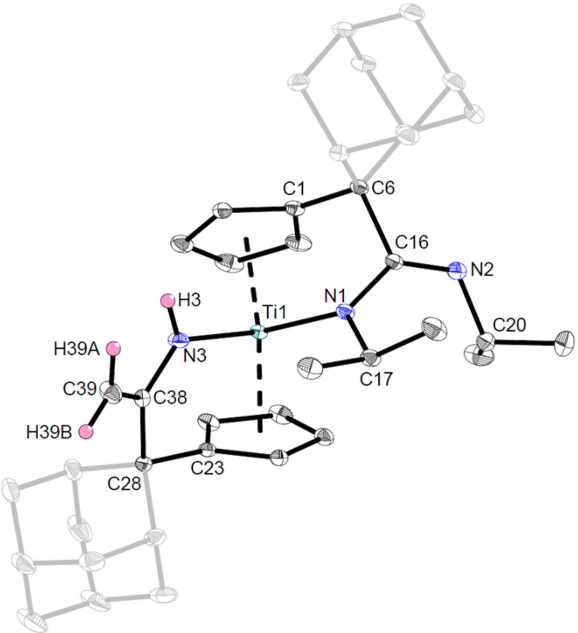


**Figure S72.** Molecular structure of complex **8**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms (except for H3, H39A and H39B) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N1 2.0562(8), Ti1–N3 1.9768(8), C1–C6 1.5150(13), C23–C28 1.5235(12), C6–C16 1.5488(12), C28–C38 1.5429(13), N1–C16 1.4191(11), N1–C17 1.4873(12), N2–C16 1.2797(12), N2–C20 1.4604(13), N3–C38 1.3926(12), C38–C39 1.3505(13); N1–Ti1–N3 104.04(3), Ti1–N1–C16 114.08(6), Ti1–N3–C38 133.17(6), C1–C6–C16 99.02(7), C23–C28–C38 103.71(7), N1–C16–C6 111.41(7), N1–C16–N2 130.04(8), C16–N1–C17 118.08(7), C16–N2–C20 122.22(8), N3–C38–C28 112.30(7), N3–C38–C39 119.83(8).

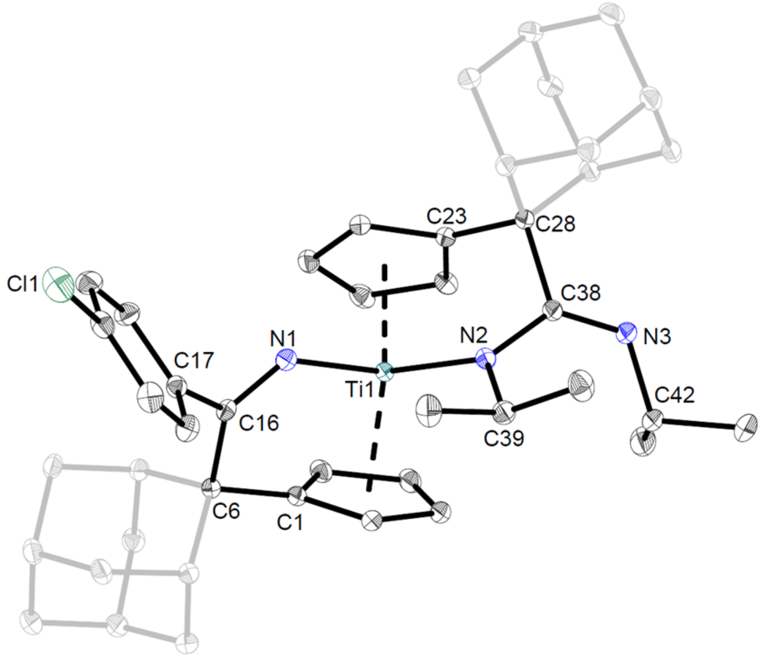


**Figure S73.** Molecular structure of complex **9**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N1 1.9861(9), Ti1–N2 2.0461(9), C1–C6 1.5245(14), C23–C28 1.5158(14), C6–C16 1.5695(14), C28–C38 1.5491(14), N1–C16 1.2709(13), N2–C38 1.4194(13), N2–C39 1.4880(14), N3–C38 1.2809(13), N3–C42 1.4566(14), C16–C17 1.5110(14); N1–Ti1–N2 103.67(4), Ti1–N1–C16 130.75(8), Ti1–N2–C38 113.88(7), C1–C6–C16 101.12(8), C23–C28–C38 100.17(8), N1–C16–C6 119.29(9), N1–C16–C17 113.84(9), N2–C38–C28 111.93(8), N2–C38–N3 130.3(1), C38–N3–C42 123.90(9).

**Table S1:** Crystal Structure Data for Compounds **2a**, **2b**, **3a** and **3b**.

| | **2a** | **2b** | **3a** | **3b** |
|---|---|---|---|---|
| CCDC | 2402660 | 2402661 | 2402669 | 2402665 |
| Lab-ID | SBF15 | MAFIP151 | MAP403 | SBF07 |
| empirical formula | $C_{37}H_{50}N_2Ti$ | $C_{43}H_{58}N_2Ti$ | $C_{50}H_{57}N_2Ti$ | $C_{59.50}H_{69}N_2Ti$ |
| Fw | 570.69 | 650.81 | 733.87 | 860.06 |
| Color | yellow green | pale green | yellow green red | green orange |
| Habit | plate | plate | block | plate |
| Wavelength, Å | 1.54178 | 1.54178 | 0.71073 | 1.54178 |
| cryst dimens, mm | 0.08 x 0.04 x 0.01 | 0.06 x 0.04 x 0.01 | 0.15 x 0.13 x 0.12 | 0.10 x 0.04 x 0.015 |
| cryst syst | monoclinic | monoclinic | triclinic | triclinic |
| space group | $P2_1/c$ | $P2_1/c$ | $P$-1 | $P$-1 |
| $a$, Å | 17.9178(6) | 10.9348(5) | 12.0635(6) | 14.2560(5) |
| $b$, Å | 18.9524(6) | 10.6136(5) | 12.2468(6) | 16.1873(6) |
| $c$, Å | 8.6109(3) | 29.6984(13) | 15.7143(8) | 22.3006(8) |
| $\alpha$, deg | 90 | 90 | 83.224(2) | 106.082(2) |
| $\beta$, deg | 91.401(2) | 100.484(3) | 81.978(2) | 91.2550(8) |
| $\gamma$, deg | 90 | 90 | 62.7942(17) | 91.973(3) |
| V, Å³ | 2923.26(17) | 3389.2(3) | 2040.70(18) | 4832.1(3) |
| Z | 4 | 4 | 2 | 4 |
| $\rho$ $_{\text{caclcd}}$, g cm$^{-3}$ | 1.297 | 1.275 | 1.194 | 1.182 |
| $\mu$, mm$^{-1}$ | 2.683 | 2.378 | 0.246 | 1.791 |
| T, K | 100(2) | 100(2) | 100(2) | 100(2) |
| $\lambda$ range, deg | 2.467 – 74.436 | 3.026 – 66.593 | 1.873 – 40.249 | 2.109 – 66.595 |
| no. of rflns collected | 37944 | 64993 | 269509 | 90603 |
| no. of indep rflns (R(int)) | 5943<br>0.0696 | 5981<br>0.1106 | 25667<br>0.0477 | 16999<br>0.0674 |
| no. of rflns with $I>2\sigma(I)$ | 4756 | 4782 | 22652 | 13622 |
| abs cor | semi-empirical | semi-empirical | semi-empirical | semi-empirical |
| max, min transmission | 1.00000, 0.8807 | 1.0000, 0.8520 | 1.0000, 0.9288 | 1.0000, 0.8251 |
| final R indices [$I>2\sigma(I)$] | R1 = 0.0393<br>wR2 = 0.0910 | R1 = 0.0451<br>wR2 = 0.1089 | R1 = 0.0365<br>wR2 = 0.1049 | R1 = 0.0453<br>wR2 = 0.1093 |
| R indices (all data) | R1 = 0.0549<br>wR2 = 0.0976 | R1 = 0.0610<br>wR2 = 0.1172 | R1 = 0.0427<br>wR2 = 0.1099 | R1 = 0.0627<br>wR2 = 0.1189 |
| GOF on $F^2$ | 1.035 | 1.046 | 1.099 | 1.021 |
| largest diff peak / hole (e.Å$^{-3}$) | 0.365 / -0.448 | 0.633 / -0.354 | 0.685 / -0.606 | 0.797 / -0.508 |

**Table S2:** Crystal Structure Data for Compounds **4a**, **4b**, **4c** and **5a**.

| | **4a** | **4b** | **4c** | **5a** |
|---|---|---|---|---|
| CCDC | 2402666 | 2402664 | 2404156 | 2402663 |
| Lab-ID | MAFIP165 | MAP413 | MAP464 | SBF16 |
| empirical formula | $C_{54}H_{64}N_4Ti$ | $C_{72}H_{80}D_6N_4Ti$ | $C_{60}H_{72}N_4Ti$ | $C_{44}H_{59}N_3Ti$ |
| fw | 816.99 | 1061.38 | 897.11 | 677.84 |
| color | purple | brown violet | red | orange |
| Habit | plate | plate | block | rod |
| Wavelength, Å | 1.54178 | 1.54178 | 0.71073 | 0.71073 |
| cryst dimens, mm | 0.09 x 0.04 x 0.01 | 0.08 x 0.05 x 0.015 | 0.09 x 0.07 x 0.05 | 0.09 x 0.04 x 0.02 |
| cryst syst | orthorhombic | triclinic | monoclinic | triclinic |
| space group | *Pbcn* | *P*-1 | $P2_1/c$ | *P*-1 |
| *a*, Å | 27.3853(7) | 10.7094(3) | 16.1533(8) | 10.0711(5) |
| *b*, Å | 9.3969(3) | 14.8769(5) | 17.6468(9) | 14.4862(9) |
| *c*, Å | 35.9247(10) | 19.1824(6) | 17.4463(9) | 14.5192(9) |
| $\alpha$, deg | 90 | 90.7480(17) | 90 | 118.955(2) |
| $\beta$, deg | 90 | 100.9596(16) | 101.351(2) | 94.269(2) |
| $\gamma$, deg | 90 | 94.3094(16) | 90 | 83.0431(13) |
| V, Å$^3$ | 9244.8(5) | 2990.80(16) | 4875.9(4) | 98.537(2) |
| Z | 8 | 2 | 4 | 2 |
| $\rho_{\text{caclcd}}$, g cm$^{-3}$ | 1.174 | 1.179 | 1.222 | 1.246 |
| $\mu$, mm$^{-1}$ | 1.860 | 1.546 | 0.219 | 0.273 |
| T, K | 100(2) | 100(2) | 100(2) | 100(2) |
| $\lambda$ range, deg | 2.460 – 66.595 | 2.347 – 74.494 | 1.658 – 32.032 | 1.626 – 30.034 |
| no. of rflns collected | 93681 | 78260 | 235881 | 89812 |
| no. of indep rflns (R(int)) | 8171<br>0.1103 | 12165<br>0.0448 | 16960<br>0.0571 | 10585<br>0.0588 |
| no. of rflns with $I>2\sigma(I)$ | 6317 | 10699 | 15014 | 9317 |
| abs cor | semi-empirical | semi-empirical | semi-empirical | semi-empirical |
| max, min transmission | 1.0000, 0.8969 | 1.0000, 0.8928 | 1.0000, 0.9203 | 1.0000, 0.9293 |
| final R indices [$I>2\sigma(I)$] | R1 = 0.0684<br>wR2 = 0.1657 | R1 = 0.0384<br>wR2 = 0.0964 | R1 = 0.0420<br>wR2 = 0.1051 | R1 = 0.0478<br>wR2 = 0.0992 |
| R indices (all data) | R1 = 0.0899<br>wR2 = 0.1775 | R1 = 0.0455<br>wR2 = 0.1012 | R1 = 0.0489<br>wR2 = 0.1089 | R1 = 0.0575<br>wR2 = 0.1030 |
| GOF on $F^2$ | 1.084 | 1.021 | 1.077 | 1.135 |
| largest diff peak / hole (e.Å$^{-3}$) | 2.156 / -0.638 | 0.405 / -0.395 | 0.536 / -0.487 | 0.427 / -0.419 |

**Table S3:** Crystal Structure Data for Compounds **5b**, **7**, **8** and **9**.

| | **5b** | **7** | **8** | **9** |
|---|---|---|---|---|
| CCDC | 2402668 | 2402662 | 2402670 | 2402667 |
| Lab-ID | SBF19 | SBF20 | SBF21 | SBF17 |
| empirical formula | $C_{45}H_{61}N_3Ti$ | $C_{40}H_{56}N_2OTi$ | $C_{39}H_{53}N_3Ti$ | $C_{44}H_{54}ClN_3Ti$ |
| fw | 691.86 | 628.76 | 611.74 | 708.25 |
| color | red | yellow | red | red |
| Habit | block | block | block | rod |
| Wavelength, Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| cryst dimens, mm | 0.40 x 0.30 x 0.25 | 0.30 x 0.25 x 0.15 | 0.40 x 0.20 x 0.20 | 0.11 x 0.05 x 0.05 |
| cryst syst | monoclinic | triclinic | tetragonal | monoclinic |
| space group | $P2_1/n$ | $P$-1 | $I4_1/a$ | $P2_1/c$ |
| $a$, Å | 18.4897(7) | 10.4084(4) | 34.7739(9) | 9.1467(8) |
| $b$, Å | 10.5066(4) | 10.5144(4) | 34.7739(9) | 18.2623(17) |
| $c$, Å | 19.5043(7) | 15.5909(6) | 10.5045(3) | 21.447(2) |
| $\alpha$, deg | 90 | 104.6063(17) | 90 | 90 |
| $\beta$, deg | 104.0950(13) | 91.7705(17) | 90 | 92.118(4) |
| $\gamma$, deg | 90 | 95.8688(17) | 90 | 90 |
| V, Å$^3$ | 3674.9(2) | 1639.59(11) | 12702.3(7) | 3580.0(6) |
| Z | 4 | 2 | 16 | 4 |
| $\rho_{\text{caclcd}}$, g cm$^{-3}$ | 1.251 | 1.274 | 1.280 | 1.314 |
| $\mu$, mm$^{-1}$ | 0.269 | 0.296 | 0.302 | 0.350 |
| T, K | 180(2) | 100(2) | 100(2) | 100(2) |
| $\lambda$ range, deg | 1.745 – 32.030 | 1.352 – 34.971 | 1.656 – 34.969 | 1.465 – 33.724 |
| no. of rflns collected | 145941 | 81719 | 209068 | 130934 |
| no. of indep rflns (R(int)) | 12799<br>0.0652 | 14397<br>0.0431 | 13938<br>0.0618 | 14286<br>0.0480 |
| no. of rflns with $I>2\sigma(I)$ | 10505 | 11300 | 11376 | 12596 |
| abs cor | semi-empirical | numerical | numerical | semi-empirical |
| max, min transmission | 0.9536, 0.8848 | 0.9751, 0.8971 | 1.0000, 0.8633 | 1.0000, 0.9538 |
| final R indices [$I>2\sigma(I)$] | R1 = 0.0629<br>wR2 = 0.1373 | R1 = 0.0360<br>wR2 = 0.0875 | R1 = 0.0405<br>wR2 = 0.0957 | R1 = 0.0420<br>wR2 = 0.0984 |
| R indices (all data) | R1 = 0.0773<br>wR2 = 0.1428 | R1 = 0.0554<br>wR2 = 0.0961 | R1 = 0.0550<br>wR2 = 0.1023 | R1 = 0.0500<br>wR2 = 0.1019 |
| GOF on $F^2$ | 1.210 | 1.031 | 1.085 | 1.118 |
| largest diff peak / hole (e.Å$^{-3}$) | 0.392 / -0.778 | 0.527 / -0.523 | 0.514 / -0.347 | 0.715 / -0.487 |

## Computational Part

The DFT (density functional theory) calculations were performed with the B3LYP/Def2-TZVP level of theory.[7] The optimized ground state geometry of **2a** and the transition state **TS** were calculated in toluene at room temperature using the SMD solvation model.[8]

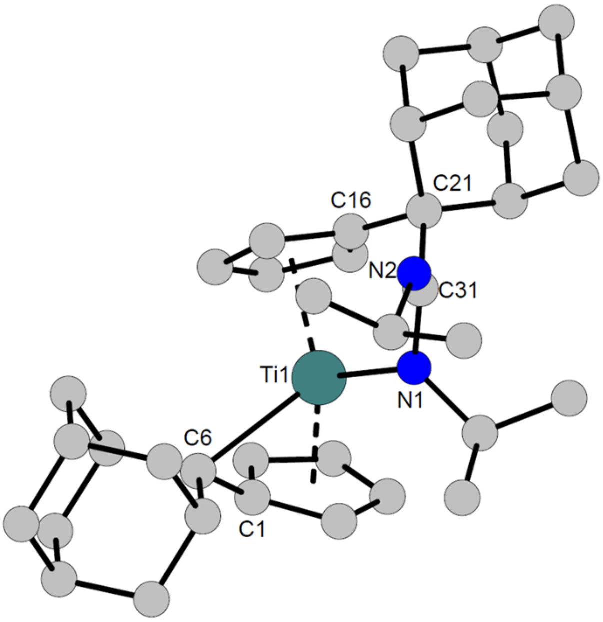


**Figure S74.** Ground state optimized geometry of complex **2a**, calculated in toluene at the B3LYP/Def2-TZVP level of theory. Selected bond lengths (Å): Ti1–N1 2.052, Ti1–C6 2.538, C1–C6 1.425, C16–C21 1.518, C21–C31 1.569, C31–N1 1.437, C31–N2 1.269.

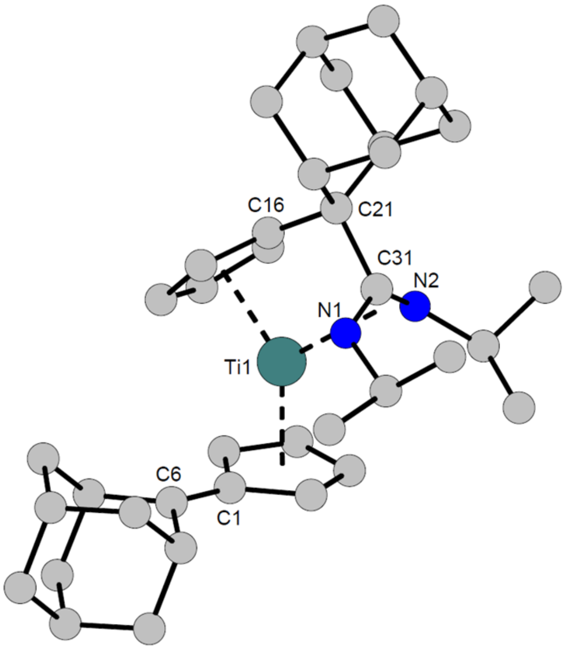


**Figure S75.** Transition state optimized geometry of complex **2a**, calculated in toluene at the B3LYP/Def2-TZVP level of theory. Selected bond lengths (Å): Ti1–N1 2.547, Ti1–C31 2.372, Ti1–N2 2.390, Ti1---C6 3.280, C1–C6 1.385, C16–C21 1.508, C21–C31 1.601, C31–N1 1.320, C31–N2 1.348.

**Table S4:** Cartesian coordinates (Å) of **2a** and **TS**:

| | | **2a** | | | | **TS** | |
|---|---|---|---|---|---|---|---|
| Ti | 5.001537 | 10.979389 | 1.130647 | Ti | 4.939183 | 10.475579 | 0.945246 |
| N | 4.970770 | 9.098714 | 0.311588 | N | 6.102584 | 8.740976 | -0.516476 |
| C | 3.549940 | 12.500216 | 0.506620 | C | 2.914882 | 11.766457 | 0.770227 |
| C | 3.880648 | 11.797474 | -0.709256 | C | 2.896932 | 10.792470 | -0.313226 |
| C | 5.206170 | 12.102801 | -1.075269 | C | 3.935558 | 11.066562 | -1.201191 |
| C | 5.721676 | 13.011937 | -0.135930 | C | 4.717708 | 12.127036 | -0.690306 |
| C | 4.717765 | 13.283505 | 0.812438 | C | 4.102793 | 12.556987 | 0.511792 |
| C | 2.688058 | 11.959752 | 1.506681 | C | 2.098868 | 11.825516 | 1.889937 |
| C | 6.489984 | 9.645273 | 2.428566 | C | 6.738814 | 9.703751 | 2.150073 |
| C | 5.434326 | 10.010663 | 3.302906 | C | 5.815622 | 10.223362 | 3.098845 |
| C | 5.459607 | 11.407583 | 3.487550 | C | 5.741446 | 11.620009 | 2.923480 |
| C | 6.530926 | 11.921769 | 2.730778 | C | 6.634931 | 11.981201 | 1.889193 |
| C | 7.148796 | 10.847921 | 2.049639 | C | 7.242076 | 10.815141 | 1.401479 |
| C | 5.312799 | 8.010995 | 1.187943 | C | 5.708376 | 8.249104 | 0.644365 |
| C | 4.714362 | 8.783227 | -1.133736 | C | 5.883237 | 8.556735 | -1.948575 |
| H | 3.228673 | 11.118137 | -1.227255 | H | 2.174304 | 10.001672 | -0.427407 |
| H | 5.738711 | 11.720153 | -1.932046 | H | 4.129656 | 10.538827 | -2.117649 |
| H | 6.716536 | 13.430243 | -0.144593 | H | 5.563336 | 12.582991 | -1.179362 |
| H | 4.831983 | 13.920232 | 1.672986 | H | 4.418518 | 13.402823 | 1.095625 |
| C | 2.372938 | 12.786791 | 2.753193 | C | 2.210714 | 12.931872 | 2.915316 |
| C | 1.446375 | 11.177854 | 1.081016 | C | 0.793575 | 11.078186 | 2.022532 |
| C | 6.682584 | 8.224623 | 1.925657 | C | 6.871159 | 8.255675 | 1.746668 |
| H | 4.720663 | 9.332345 | 3.742865 | H | 5.237377 | 9.647892 | 3.802189 |
| H | 4.789278 | 11.979079 | 4.107226 | H | 5.113821 | 12.294502 | 3.483150 |
| H | 6.825730 | 12.956238 | 2.670511 | H | 6.802259 | 12.980175 | 1.518785 |
| H | 7.986315 | 10.939877 | 1.380268 | H | 7.953355 | 10.767623 | 0.594562 |
| N | 4.611256 | 7.014776 | 1.545786 | N | 4.485748 | 8.141118 | 1.206028 |
| H | 4.982337 | 9.698495 | -1.650953 | H | 5.941533 | 9.561750 | -2.374622 |
| C | 3.262131 | 8.485416 | -1.551668 | C | 4.596194 | 7.909359 | -2.478542 |
| C | 5.629949 | 7.706293 | -1.722296 | C | 7.086575 | 7.795010 | -2.537197 |
| H | 3.255173 | 13.332217 | 3.091079 | H | 3.167689 | 13.446256 | 2.831827 |
| C | 1.858281 | 11.891444 | 3.897718 | C | 2.050520 | 12.367371 | 4.344257 |
| C | 1.260729 | 13.807207 | 2.397289 | C | 1.064365 | 13.946836 | 2.656223 |
| C | 0.936956 | 10.283294 | 2.225376 | C | 0.626147 | 10.515485 | 3.451982 |
| H | 1.658466 | 10.558568 | 0.209931 | H | 0.725167 | 10.271042 | 1.294295 |
| C | 0.330726 | 12.192194 | 0.716011 | C | -0.358633 | 12.088086 | 1.757840 |
| C | 7.938710 | 8.059085 | 1.010746 | C | 8.276137 | 7.924588 | 1.175696 |
| C | 6.914700 | 7.258961 | 3.140742 | C | 6.626844 | 7.288785 | 2.938912 |
| C | 3.212946 | 6.765041 | 1.247295 | C | 3.322094 | 7.511713 | 0.581433 |
| H | 2.986530 | 7.442052 | -1.408637 | H | 4.509250 | 6.870523 | -2.159915 |
| H | 3.152521 | 8.700612 | -2.618942 | H | 4.622342 | 7.913733 | -3.571857 |
| H | 2.542075 | 9.100353 | -1.014549 | H | 3.694510 | 8.435188 | -2.173196 |
| H | 6.682384 | 7.962360 | -1.605661 | H | 8.025610 | 8.259772 | -2.235986 |
| H | 5.428288 | 7.615722 | -2.793054 | H | 7.037950 | 7.797458 | -3.629884 |
| H | 5.457532 | 6.727260 | -1.275124 | H | 7.097124 | 6.754436 | -2.205945 |
| H | 2.626513 | 11.172631 | 4.191671 | H | 2.861033 | 11.667261 | 4.564550 |
| H | 1.641943 | 12.509270 | 4.775815 | H | 2.122767 | 13.185665 | 5.068186 |
| C | 0.592634 | 11.142943 | 3.451393 | C | 0.692650 | 11.659931 | 4.474958 |
| H | 1.035885 | 14.426934 | 3.272487 | H | 1.132617 | 14.765431 | 3.380809 |

| | | | |
|---|---|---|---|
| H | 1.609271 | 14.479610 | 1.608002 |
| C | -0.003484 | 13.059764 | 1.940871 |
| H | 1.697624 | 9.545198 | 2.488140 |
| H | 0.052508 | 9.730092 | 1.892546 |
| H | 0.657154 | 12.821619 | -0.116926 |
| H | -0.562564 | 11.652585 | 0.382385 |
| H | 7.828673 | 8.700282 | 0.133285 |
| C | 8.091836 | 6.589177 | 0.561912 |
| C | 9.238166 | 8.439943 | 1.759326 |
| C | 7.107134 | 5.791858 | 2.705941 |
| H | 6.051866 | 7.320149 | 3.806083 |
| C | 8.188872 | 7.685570 | 3.902072 |
| H | 2.753954 | 7.591547 | 0.700474 |
| C | 2.475482 | 6.613368 | 2.583505 |
| C | 3.071734 | 5.476543 | 0.432183 |
| H | 0.241035 | 10.499966 | 4.264288 |
| C | -0.503323 | 12.156843 | 3.081642 |
| H | -0.781186 | 13.783334 | 1.676664 |
| H | 7.208495 | 6.253521 | 0.019171 |
| H | 8.936775 | 6.518386 | -0.131449 |
| C | 8.319982 | 5.671215 | 1.775430 |
| H | 10.083330 | 8.311232 | 1.074332 |
| H | 9.241391 | 9.484720 | 2.062536 |
| C | 9.425756 | 7.547844 | 2.994926 |
| H | 7.263155 | 5.180855 | 3.602216 |
| H | 6.209306 | 5.430083 | 2.212863 |
| H | 8.103147 | 8.713936 | 4.262939 |
| H | 8.302708 | 7.049423 | 4.785862 |
| H | 2.882850 | 5.773425 | 3.151428 |
| H | 1.409541 | 6.435662 | 2.417808 |
| H | 2.576736 | 7.512158 | 3.193746 |
| H | 3.619192 | 5.526949 | -0.509721 |
| H | 2.021273 | 5.279243 | 0.203050 |
| H | 3.461459 | 4.626290 | 0.997650 |
| H | -0.766516 | 12.762683 | 3.955295 |
| H | -1.413166 | 11.631229 | 2.773107 |
| H | 8.419855 | 4.636700 | 1.431596 |
| C | 9.585306 | 6.091568 | 2.535941 |
| H | 10.318612 | 7.865617 | 3.542543 |
| H | 10.470144 | 5.995195 | 1.897156 |
| H | 9.738187 | 5.433601 | 3.397995 |

| | | | |
|---|---|---|---|
| H | 1.174918 | 14.386658 | 1.660840 |
| C | -0.291696 | 13.234409 | 2.779893 |
| H | 1.407213 | 9.780666 | 3.661162 |
| H | -0.334672 | 9.996111 | 3.529023 |
| H | -0.283252 | 12.479780 | 0.739490 |
| H | -1.319194 | 11.567754 | 1.834799 |
| H | 8.470094 | 8.571014 | 0.321588 |
| C | 8.347439 | 6.454937 | 0.721331 |
| C | 9.350774 | 8.151971 | 2.258424 |
| C | 6.708159 | 5.821541 | 2.481675 |
| H | 5.636014 | 7.475623 | 3.349019 |
| C | 7.700156 | 7.513507 | 4.025452 |
| H | 3.052622 | 7.969674 | -0.375844 |
| C | 2.132168 | 7.658607 | 1.524700 |
| C | 3.564115 | 6.017052 | 0.327691 |
| H | 0.587853 | 11.252972 | 5.485256 |
| C | -0.441398 | 12.662991 | 4.200886 |
| H | -1.098291 | 13.947075 | 2.581908 |
| H | 7.610228 | 6.261597 | -0.059980 |
| H | 9.331345 | 6.260903 | 0.280906 |
| C | 8.101395 | 5.517616 | 1.912219 |
| H | 10.339885 | 7.954911 | 1.831203 |
| H | 9.351607 | 9.194592 | 2.587191 |
| C | 9.099066 | 7.222716 | 3.457009 |
| H | 6.498102 | 5.168130 | 3.335399 |
| H | 5.944894 | 5.613594 | 1.730711 |
| H | 7.658669 | 8.536542 | 4.407103 |
| H | 7.495400 | 6.851072 | 4.873315 |
| H | 2.316839 | 7.115228 | 2.455043 |
| H | 1.218052 | 7.264751 | 1.071655 |
| H | 1.967547 | 8.701385 | 1.778850 |
| H | 4.447830 | 5.837682 | -0.284170 |
| H | 2.705843 | 5.579740 | -0.190784 |
| H | 3.692866 | 5.485158 | 1.272897 |
| H | -0.414110 | 13.472875 | 4.937226 |
| H | -1.412482 | 12.168449 | 4.305861 |
| H | 8.143789 | 4.476330 | 1.576656 |
| C | 9.168302 | 5.758898 | 2.992345 |
| H | 9.854467 | 7.402957 | 4.228404 |
| H | 10.164493 | 5.535083 | 2.595547 |
| H | 9.003716 | 5.086431 | 3.841237 |

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