Supporting Information

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General Considerations

All air- and moisture-sensitive reactions were carried out under an inert atmosphere of argon or nitrogen with rigorous exclusion of oxygen and moisture using standard glovebox and Schlenk techniques. The glass equipment was stored in an oven at 120 °C and evacuated prior to use. Solvents and liquid educts were dried according to standard procedures and/or freeze-pump-thaw degassed three times prior to use. Solvents were distilled over Na/K alloy and benzophenone or CaH_2 under nitrogen atmosphere. Solid materials were stored and weighed in a glovebox or dried under high vacuum before use. The methyl lithium was used as a 1.6 M solution in diethyl ether. The pentafulvene complex **1** was synthesized according to a literature procedure.[1]

Methyl vinyl ketone, diethylamine, and dibenzylamine were purchased from commercial sources, distilled over $CaCl_2$, and freeze-pump-thaw degassed three times prior to use, and stored under nitrogen.

High-resolution mass spectra were measured on a Finnigan-MAT95 spectrometer using ESI (solvent: dichloromethane or toluene and some drops of bromobenzene for **4a,b**).

Infrared spectra were performed on a Bruker Tensor 27 spectrometer with a MKII Reflection Golden Gate Single Diamond ATR system.

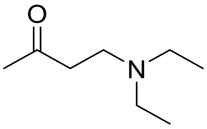
NMR spectra were recorded on Bruker Avance 300, Bruker Avance 500, and Bruker Avance III 500 spectrometers. ^1H NMR spectra were referenced to the residual solvent resonance as internal standard (benzene-d_6 (C_6D_6): $\delta^1H(C_6D_5H)$ = 7.16 ppm, dichloromethane-d_2 (CD_2Cl_2): $\delta^1H(CDHCl_2)$ = 5.32 ppm) and $^{13}C\{^1H\}$ spectra were referenced by using the central line of the solvent signal (benzene-d_6 (C_6D_6): $\delta^{13}C\{^1H\}(C_6D_6)$ = 128.06 ppm, dichloromethane-d_2 (CD_2Cl_2): $\delta^{13}C\{^1H\}(CD_2Cl_2)$ = 53.84 ppm). $^{11}B\{^1H\}$ NMR, and $^{19}F\{^1H\}$ NMR spectra were referenced against external standards ($BF_3{\bullet}OEt_2$ ($\delta^{11}B\{^1H\}(BF_3{\bullet}OEt_2)$ = 0.0 ppm; $CFCl_3$ ($\delta^{19}F\{^1H\}(CFCl_3)$ = 0.0 ppm)). The given chemical shifts of ^{15}N result out of $^{15}N,^1H$ HMBC NMR experiments with nitromethane as external standard (δ = 378.9 vs. NH_3).

Elemental analyses were carried out on a EuroEA 3000 Elemental Analyzer. The carbon and nitrogen values in the elemental analysis are often lowered by titanium carbide and titanium nitride formation, although vanadium pentoxide as combustion aid was used. Although in some cases satisfactory elemental analysis could not be obtained, the data is included to demonstrate the best results to date. Unsatisfactory combustion analyses can also be attributed to the high air-sensitivity of the compounds. The combustion analysis of group 4 organometallics is known to be difficult (and in this case also attributed to the high reactivity of the complexes).[5,6]

Melting points were determined using a “Mel-Temp” apparatus by Laboratory Devices, Cambridge, U.K..

Synthesis and characterization of the compounds:

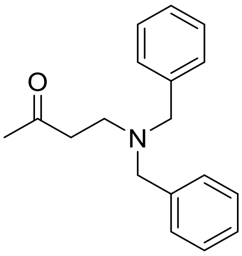
Synthesis of L1a:



Freshly condensed diethylamine (6.1 mL, 59.21 mmol) was slowly added slowly to freshly condensed methyl vinyl ketone (5 mL, 59.21 mmol) at 0 °C (exothermic reaction). The solution was stirred for five minutes at room temperature to yield **L1a** as a slightly yellow oil. No further purification steps are required.

Yield: 8.372 g (58.45 mmol, 99%).
IR (ATR): $\tilde{\nu}$ = 2970, 2935, 2875, 2805, 1713 (C=O), 1449, 1420, 1356, 1294, 1230, 1201, 1161, 1122, 1069, 991, 944, 904, 896, 843, 822, 802, 758, 744, 692, 658 cm^{-1}.
^{1}H NMR (500 MHz, C_6D_6, 299 K): δ = 0.88 (t, $^{3}J_{H,H}$ = 7.1 Hz, 6H, 2×$CH_2C\mathit{H}_3$), 1.70 (s, 3H, O=C_qCH_3), 2.14 (t, $^{3}J_{H,H}$ = 7.0 Hz, N$C\mathit{H}_2CH_2$), 2.29 (q, $^{3}J_{H,H}$ = 7.1 Hz, 2×$C\mathit{H}_2CH_3$), 2.58 (t, $^{3}J_{H,H}$ = 7.0 Hz, N$CH_2C\mathit{H}_2$) ppm.
^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 299 K): δ = 12.3 (2×$CH_2\underline{C}H_3$), 29.7 ($OC_q\underline{C}H_3$), 41.9 (N$\underline{C}H_2CH_2$), 47.2 (2×$\underline{C}H_2CH_3$), 48.2 (N$CH_2\underline{C}H_2$), 206.0 (O=$\underline{C}_qCH_3$) ppm.
^{15}N-NMR (202 MHz, C_6D_6, 299 K): δ = 44.4 ppm.
HR/MS calculated: m/z = 144.1388 [M+H^{+}]; measured (ESI): m/z = 144.1383.

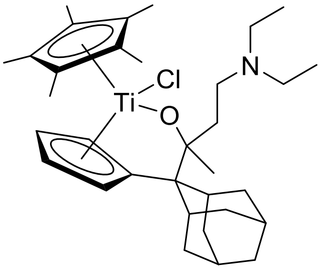
Synthesis of L1b:



Freshly condensed dibenzylamine (4.5 mL, 23.68 mmol) was slowly added to freshly condensed methyl vinyl ketone (2 mL, 23.68 mmol) at room temperature. The solution was stirred for 36 h at room temperature. The slight excess of methyl vinyl ketone was carefully removed under reduced pressure to yield **L1b** as a colorless solid.

Yield: 60.71 g (22.71 mmol, 96%).
Melting point: 49-51 °C.
IR (ATR): $\tilde{\nu}$ = 3061, 3033, 2968, 2936, 2917, 2890, 1698 (C=O), 1602, 1494, 1453, 1427, 1363, 1316, 1251, 1224, 1187, 1111, 1042, 1030, 1003, 968, 949, 876, 797, 737, 620 $\mathrm{cm^{-1}}$.
^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 1.55 (s, 3H, CH_3), 2.15 (t, $^{3}J_{\mathrm{H,H}}$ = 7.1 Hz, 2H, $\mathrm{NCH_2C}H_2$), 2.63 (t, $^{3}J_{\mathrm{H,H}}$ = 7.1 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH_2}$), 3.36 (s, 4H, CH_2Ph), 7.07-7.10 (m, 2H, 2×p-$\mathrm{C}H_{\mathrm{Ph}}\mathrm{CH_2}$), 7.16-7.19 (4×$o$-$\mathrm{C}H_{\mathrm{Ph}}\mathrm{CH_2}$)*, 7.29-7.31 (m, 4H, 4×$o$-$\mathrm{C}H_{\mathrm{Ph}}\mathrm{CH_2}$) ppm.
^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 28.9 ($\mathrm{O{=}C_q\underline{C}H_3}$), 41.7 ($\mathrm{NCH_2\underline{C}H_2}$), 48.7 ($\mathrm{N\underline{C}H_2CH_2}$), 58.5 (2×$\mathrm{\underline{C}H_2Ph}$), 127.2 (2×$p$-$\mathrm{\underline{C}H_{Ph}CH_2}$), 128.4 (4×$m$-$\mathrm{\underline{C}H_{Ph}CH_2}$), 129.1 (4×$o$-$\mathrm{\underline{C}H_{Ph}CH_2}$), 139.7 (2×$\mathrm{C_{q,Ph}}$), 205.4 ($\mathrm{O{=}\underline{C}_qCH_3}$) ppm.
* = overlap with C_6D_6 signal
^{15}N-NMR (202 MHz, C_6D_6, 305 K): δ = 47.8 ppm.
HR/MS calculated: m/z = 268.1701 [M+H^{+}]; measured (ESI): m/z = 268.1695.

Synthesis of 2a:



In a glove box compound **L1a** (0.168 g, 1.173 mmol) in toluene (3×2 mL) was added to a solution of complex **1** (0.489 g, 1.173 mmol) in 12 mL of toluene. The reaction mixture was stirred for 16 h at room temperature. All volatiles were removed under vacuum to give **2a** as an orange solid as a mixture of both diastereosiomers (ratio: approximately 4:1). NMR data is given for the clearly assignable signals of the main diastereoisomer.

Yield: 0.524 g (0.936 mmol, 80%).

Melting point: 74-76 °C (dec.).

IR (ATR): $\tilde{\nu}$ = 2964, 2902, 2854, 1712, 1481, 1450, 1373, 1205, 1171, 1147, 1119, 1097, 1064, 1043, 1022, 979, 960, 943, 875, 851, 811, 792, 732, 691, 659, 635 cm^{-1}.

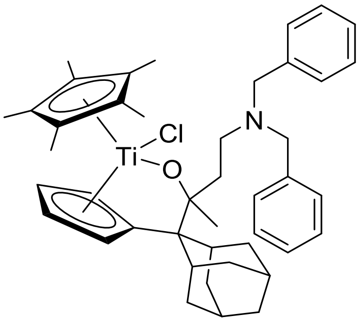
^{1}H NMR (500 MHz, C_6D_6, 299 K): δ = 1.18 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, 2×CH_2CH_3), 1.47 (s, 3H, OC_qCH_3), 1.78 (s, 15H, C_5Me_5), 5.04-5.06 (m, 1H, C_5H_4), 5.42-5.44 (m, 2H, 2×C_5H_4), 6.46-6.47 (m, 1H, C_5H_4) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 299 K): δ = 12.6 ($C_5\underline{Me}_5$), 12.7 (2×$CH_2\underline{C}H_3$) 27.6 (CH_{Ad}), 28.0 (CH_{Ad}), 31.4 ($OC_q\underline{C}H_3$), 32.96 (CH_{Ad}), 33.0 (CH_{Ad}), 33.8 ($CH_{2,Ad}$), 34.9 ($CH_{2,Ad}$), 37.2 ($CH_{2,Ad}$), 37.4 ($CH_{2,Ad}$), 39.4 ($CH_{2,Ad}$), 48.8 (2×$\underline{C}H_2CH_3$), 54.8 ($C_{q,exo}$), 104.3 (C_5H_4), 112.0 (C_5H_4), 112.4 ($O\underline{C}_qCH_3$), 112.5 (C_5H_4), 119.7 (C_5H_4), 123.5 ($\underline{C}_5Me_5$), 157.0 ($C_{q,ipso}$) ppm.

^{15}N NMR (202 MHz, C_6D_6, 299 K): δ = 45.0 ppm.

EA: Anal. calcd. for $C_{33}H_{50}ClNOTi$: C, 70.77; H, 9.00; N, 2.50; Found: C, 69.88; H, 8.62; N, 2.03.

Synthesis of 2c:



Compound **L1b** (0.356 g, 1.331 mmol) and complex **1** (0.555 g, 1.331 mmol) were dissolved in 12 mL of *n*-hexane. The reaction mixture was stirred for 16 h at room temperature, resulting in a yellow suspension. The supernatant was decanted and the residue was dried under vacuum to yield diastereomerically pure **2b** as a yellow solid.

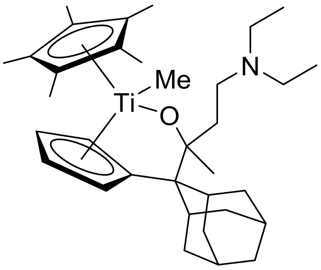
Yield: 0.701 g (1.025 mmol, 77%).
Melting point: 150-152 °C.
IR (ATR): $\tilde{\nu}$ = 3007, 2953, 2935, 2891, 2853, 2837, 2792, 1494, 1479, 1449, 1371, 1354, 1331, 1261, 1163, 1151, 1116, 1103, 1093, 1075, 1061, 1025, 1003, 979, 961, 947, 905, 884, 867, 850, 825, 815, 742, 732, 701, 685, 628, 618 cm^{-1}.
^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 1.29 (s, 3H, OC_qCH_3), 1.43-1.65 (m, 8H, $CH_{Ad}/CH_{2,Ad}/NCH_2CH_2$), 1.76 (s, 15H, C_5Me_5), 1.78-1.88 (m, 3H, $CH_{Ad}/CH_{2,Ad}/NCH_2CH_2$), 2.08-2.09 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.31-2.32 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.40-2.47 (m, 2H, $CH_{Ad}/CH_{2,Ad}/NCH_2CH_2$), 2.68-2.78 (m, 3H, $CH_{Ad}/CH_{2,Ad}/NCH_2CH_2$), 3.63 (d, $^2J_{H,H}$ = 13.9 Hz, 2H, CH_2Ph), 3.98 (d, $^2J_{H,H}$ = 14.0 Hz, 2H, CH_2Ph), 5.02-5.03 (m, 1H, C_5H_4), 5.42-5.46 (m, 2H, 2×C_5H_4), 6.43-6.44 (m, 1H, C_5H_4), 7.10-7.13 (m, 2H, 2×p-$CH_{Ph}CH_2$), 7.22-7.25 (m, 4H, 2×m-$CH_{Ph}CH_2$), 7.56-7.58 (m, 4H, 2×o-$CH_{Ph}CH_2$) ppm.
^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 12.6 ($C_5\underline{Me}_5$), 27.6 (CH_{Ad}), 28.1 (CH_{Ad}), 31.2 ($OC_q\underline{C}H_3$), 32.9 (2×CH_{Ad}), 33.8 (CH_2), 34.9 (CH_2), 37.2 (CH_2), 37.4 (CH_2), 37.5 (CH_2), 39.4 (CH_2), 50.5 (CH_2), 54.8 ($C_{q,exo}$), 60.1 (2×$\underline{C}H_2Ph$), 104.3 (C_5H_4), 111.9 (C_5H_4), 112.1 ($O\underline{C}_qCH_3$), 112.6 (C_5H_4), 119.8 (C_5H_4), 123.6 ($\underline{C}_5Me_5$), 126.9 (2×p-$\underline{C}H_{Ph}CH_2$), 128.4 (4×m-$\underline{C}H_{Ph}CH_2$), 129.4 (4×o-$\underline{C}H_{Ph}CH_2$), 141.6 (2×$C_{q,Ph}$), 156.9 ($C_{q,ipso}$) ppm.
^{15}N NMR (202 MHz, C_6D_6, 305 K): δ = 48.4 ppm.

EA: Anal. calcd. for $C_{43}H_{54}ClNOTi$: C, 75.48; H, 7.96; N, 2.05; Found: C, 75.44; H, 8.32; N, 2.07.

One pot procedure:

Complexes **3a,b** can also be prepared in a one-pot procedure: Complex 1 (1.0 equiv.) was dissolved in THF (2 mL per 0.100 g of **1**), followed by addition of the respective ligand precursor (1.0 equiv.). The reaction mixture was stirred for 16 h at room temperature. A methyl lithium solution (1.0 equiv.; 1.6 M in diethyl ether) was added slowly to the solution and the reaction mixture was stirred for another 16 h at room temperature. All volatiles were removed under vacuum, the residue was dissolved in toluene (5 mL per 0.100 g of **1**), filtered, and washed with toluene (2×5 mL per 0.100 g of **1**). The solvent was removed under vacuum to give the complexes **3a,b**.

Synthesis of 3a:



To a solution of complex **2a** (0.500 g, 0.893 mmol) in 12 mL of tetrahydrofurane was added a methyllithium solution (0.6 mL, 0.893 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed, and the residue was dissolved in 15 mL of toluene. The solution was filtered, and the residue was washed with toluene (2×10 mL). All volatiles were removed under vacuum to give complex **3a** as a pale orange solid as a mixture of both diastereosiomers (ratio: approximately 10:1). NMR data is given for the clearly assignable signals of the main diastereoisomer.

Yield: 0.373 g (0.691 mmol, 77%).

Melting point: 130-132 °C (dec.).

IR (ATR): $\tilde{\nu}$ = 2968, 2902, 2853, 2800, 1449, 1373, 1260, 1206, 1171, 1148, 1100, 1087, 1063, 1041, 1023, 981, 961, 949, 919, 876, 849, 811, 690, 635 cm^{-1}.

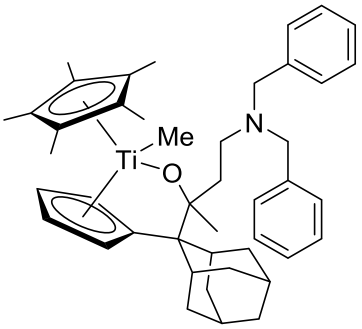
^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 0.23 (s, 3H, $TiCH_3$), 1.11 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, 2×CH_2CH_3), 1.39 (s, 3H, OC_qCH_3), 1.72 (s, 15H, C_5Me_5), 4.85-4.87 (m, 1H, C_5H_4), 512-5.14 (m, 1H, 2×C_5H_4), 5.31-5.32 (m, 1H, C_5H_4), 6.20-6.22 (m, 1H, C_5H_4) ppm.

$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 300 K): δ = 11.9 ($C_5\underline{Me}_5$), 12.7 ($2\times CH_2\underline{C}H_3$), 27.9 ($CH_{Ad}$), 28.2 ($CH_{Ad}$), 31.3 ($OC_q\underline{C}H_3$), 32.9 ($CH_{Ad}$), 33.3 ($CH_{Ad}$), 34.1 ($CH_2$), 34.5 ($TiCH_3$), 35.1 ($CH_2$), 37.4 ($2\times CH_2$), 38.0 ($CH_2$), 39.7 ($CH_2$), 47.8 ($2\times \underline{C}H_2CH_3$), 49.0 ($CH_2$), 55.1 ($C_{q,exo}$), 103.3 ($C_5H_4$), 107.9 ($O\underline{C}_qCH_3$), 108.2 ($C_5H_4$), 108.4 ($C_5H_4$), 116.1 ($C_5H_4$), 118.4 ($\underline{C}_5Me_5$), 151.7 ($C_{q,ipso}$) ppm.

^{15}N NMR (202 MHz, C_6D_6, 300 K): δ = 44.9 ppm.

EA: Anal. calcd. for $C_{34}H_{53}NOTi$: C, 75.67; H, 9.90; N, 2.60; Found: C, 72.31; H, 10.45; N, 1.90.

Synthesis of 3b:



To a solution of complex **2b** (0.700 g, 1.023 mmol) in 15 mL of tetrahydrofurane was added a methyllithium solution (0.6 mL, 1.190 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed, and the residue was dissolved in 20 mL of toluene. The solution was filtered, and the residue was washed with toluene (2×15 mL). All volatiles were removed under vacuum to give complex **3b** as a pale yellow solid as a mixture of both diastereosiomers (ratio: approximately 4:1). NMR data is given for the clearly assignable signals of the main diastereoisomer.

Yield: 0.539 g (0.812 mmol, 79%).

Melting point: 66-68 °C (dec.).

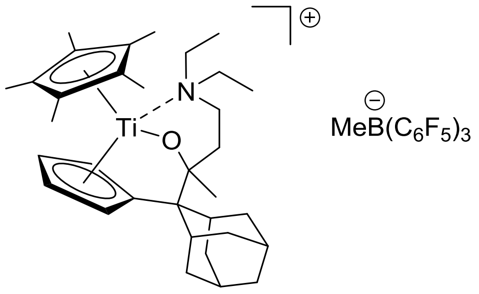
IR (ATR): $\tilde{\nu}$ = 2900, 2854, 1494, 1480, 1452, 1373, 1322, 1244, 1205, 1149, 1120, 1098, 1062, 1042, 1027, 980, 962, 877, 848, 808, 733, 696, 660, 635 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 0.10 (s, 3H, $TiCH_3$), 1.24 (s, 3H, OC_qCH_3), 1.66 (s, 15H, C_5Me_5), 3.57 (d, $^2J_{H,H}$ = 13.7 Hz, 2H, CH_2Ph), 3.69 (d, $^2J_{H,H}$ = 13.7 Hz, 2H, CH_2Ph), 4.84-4.86 (m, 1H, C_5H_4), 5.12-5.14 (m, 1H, C_5H_4), 5.27-5.28 (m, 1H, C_5H_4), 6.18-6.19 (m, 1H, C_5H_4), 7.11-7.14 (m, 2H, 2×*p*-$CH_{Ph}CH_2$), 7.23-7.26 (m, 4H, 4×*m*-$CH_{Ph}CH_2$), 7.49-7.51 (m, 4H, 4×*o*-$CH_{Ph}CH_2$) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 11.9 ($C_5\underline{Me}_5$), 27.8 (CH_{Ad}), 28.2 (CH_{Ad}), 31.1 ($OC_q\underline{C}H_3$), 32.9 (CH_{Ad}), 33.2 (CH_{Ad}), 34.1 (CH_2), 34.8 ($TiCH_3$), 35.1 (CH_2), 37.4 (CH_2), 37.5 (CH_2), 38.5 (CH_2), 39.7 (CH_2), 51.1 (CH_2), 55.0 ($C_{q,exo}$), 60.2 (2×$\underline{C}H_2Ph$), 103.2 (C_5H_4), 107.6 ($O\underline{C}_qCH_3$), 108.0 (C_5H_4), 108.5 (C_5H_4), 116.2 (C_5H_4), 118.5 ($\underline{C}_5Me_5$), 127.0 (2×*p*-$\underline{C}H_{Ph}CH_2$), 128.5 (4×*m*-$\underline{C}H_{Ph}CH_2$), 129.3 (4×*o*-$\underline{C}H_{Ph}CH_2$), 141.1 (2×$C_{q,Ph}$), 151.5 ($C_{q,ipso}$) ppm.

EA: Anal. calcd. for $C_{44}H_{57}NOTi$: C, 79.61; H, 8.66; N, 2.11; Found: C, 77.45; H, 9.21; N, 2.07.

Synthesis of 4a:



A mixture of complex **3a** (0.140 g, 0.259 mmol) and $B(C_6F_5)_3$ (0.133 g, 0.259 mmol) was stirred in 8 mL of toluene. By stopping the stirring process after a few minutes, the development of two phases can be observed due to the formation of **4a**. The solvent was decanted, and the residue was washed with *n*-hexane (3×6 mL) and dried under vacuum to give complex **4a** as a pale orange solid.

4a is nearly unsoluble in aliphatic and aromatic solvents like *n*-hexane and toluene, and reacts with dichloromethane and dichloromethane-d_2 to the corresponding complexes **5a** and **5a-*d*₂** respectively. **4a** is also only merely soluble in tetrahydrofuran and bromobenzene, so that THF-d_8 and C_6D_5Br solutions of **4a** were not adequate for NMR spectroscopy. To verify the poor solubility, the ^{1}H NMR of **4a** (0.100 g) in THF-d_8 is shown in below.

Yield: 0.212 g (0.202 mmol, 78%).

Melting point: 78-80 °C (dec.).

IR (ATR): $\tilde{\nu}$ = 2914, 2860, 1640, 1509, 1451, 1378, 1266, 1081, 977, 963, 951, 880, 803, 758, 735, 693, 660, 635 cm^{-1}.

HR/MS calculated: m/z = 547.3348 [M+Na$^+$]; measured (ESI): m/z = 547.3364.

EA: Anal. calcd. for $C_{52}H_{53}BF_{15}NOTi$: C, 59.39; H, 5.08; N, 1.33; Found: C, 58.97; H, 4.88; N, 0.91.

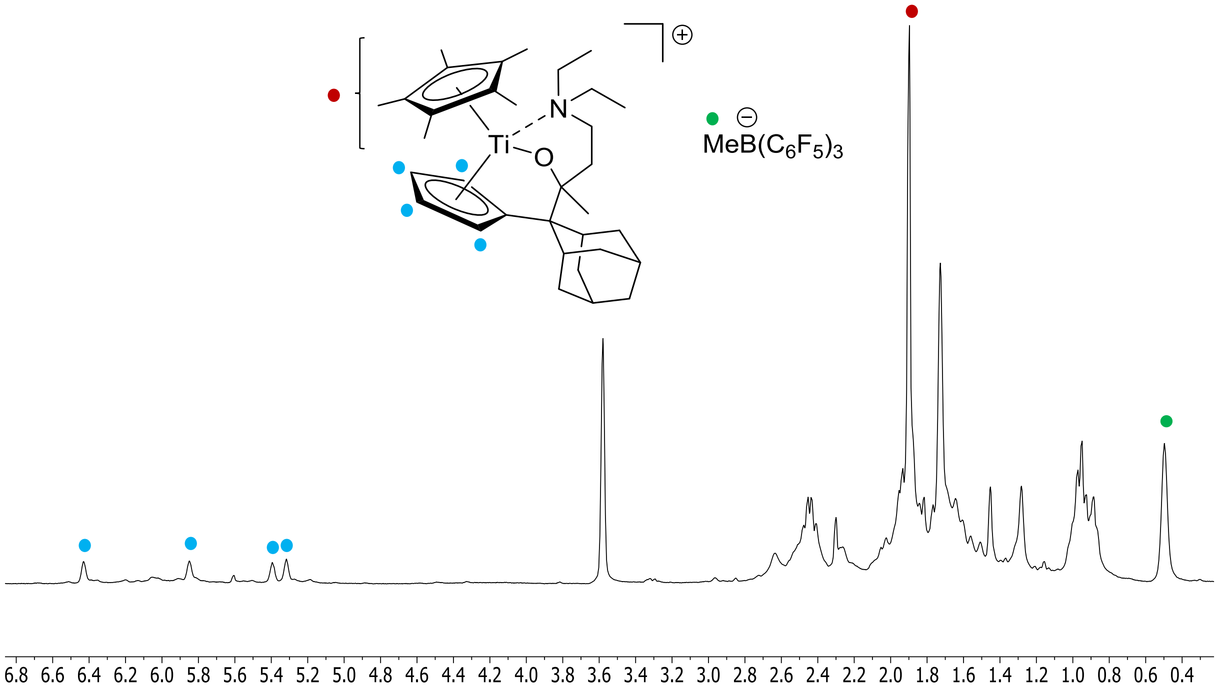
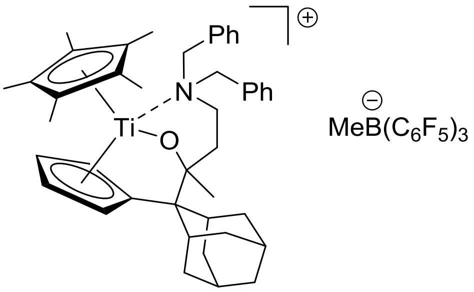


Figure S0: ^{1}H NMR spectrum of **4a** (500 MHz, THF-d_8, rt).

Synthesis of 4b:



A mixture of complex **3b** (0.100 g, 0.151 mmol) and $B(C_6F_5)_3$ (0.077 g, 0.151 mmol) was stirred in 8 mL of toluene. By stopping the stirring process after a few minutes, the development of two phases can be observed due to the formation of **4b**. The solvent was decanted, and the residue was washed with *n*-hexane (3×5 mL) and dried under vacuum to give complex **4b** as a pale orange solid.

4b is nearly unsoluble in aliphatic and aromatic solvents like *n*-hexane and toluene, and reacts with dichloromethane and dichloromethane-d_2 to the corresponding complexes **5b** and **5b-d_2** respectively. **4b** is also only merely soluble in tetrahydrofuran and bromobenzene, so that THF-d_8 and C_6D_5Br solutions of **4b** were not adequate for NMR spectroscopy.

Yield: 0.142 g (0.121 mmol, 80%).

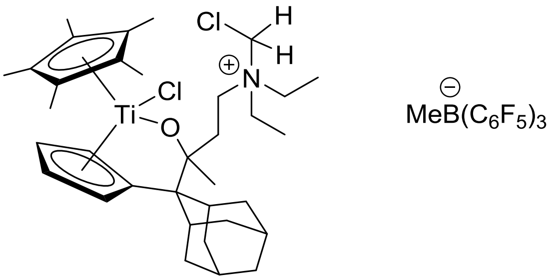
Melting point: 56-58 °C (dec.).

IR (ATR): $\tilde{\nu}$ = 2914, 2858, 1640, 1509, 1453, 1378, 1267, 1081, 964, 950, 935, 883, 828, 804, 738, 698, 659, 642, 604 cm^{-1}.

HR/MS calculated: m/z = 648.3685 [M^+]; measured (ESI): m/z = 648.3660.

EA: Anal. calcd. for $C_{62}H_{57}BF_{15}NOTi$: C, 63.33; H, 4.89; N, 1.19; Found: C, 63.21; H, 5.53; N, 1.15.

Synthesis of 5a:



Complex **3a** (0.150 g, 0.277 mmol) and $B(C_6F_5)_3$ (0.142 g, 0.277 mmol) were stirred in 10 mL of dichloromethane. By stopping the stirring process after a few minutes, the development of two phases can be observed due to the formation of **5a**. The solvent was decanted, and the residue was washed with *n*-hexane (3×8 mL) and dried under vacuum to give complex **5a** as a pale yellow solid.

Yield: 0.224 g (0.197 mmol, 71%).
Melting point: 75-77 °C.
IR (ATR): $\tilde{\nu}$ = 2961, 2912, 2861, 1682, 1640, 1509, 1448, 1378, 1263, 1145, 1080, 1027, 994, 979, 965, 950, 934, 879, 803, 765, 757, 736, 692, 668, 659, 642, 635, 605 cm^{-1}.
^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 0.49 (s, 3H, BCH_3), 1.40 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_2CH_3), 1.43 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_2CH_3), 1.52 (s, 3H, OC_qCH_3), 1.59-2.53 (m, 15H, NCH_2CH_2, $CH_{Ad}/CH_{2,Ad}$), 1.91 (s, 15H, C_5Me_5), 2.72-2.78 (m, 1H, NCH_2CH_2), 3.13-3.19 (m, 1H, NCH_2CH_2), 3.29-3.38 (m, 2H, CH_2CH_3), 3.48-3.57 (m, 2H, CH_2CH_3), 3.58-3.67 (m, 1H, NCH_2CH_2), 4.80 (d, $^2J_{H,H}$ = 10.6 Hz, 1H, NCH_2Cl), 5.00 (d, $^2J_{H,H}$ = 10.6 Hz, 1H, NCH_2Cl), 5.36-5.37 (m, 1H, C_5H_4), 5.43-5.45 (m, 1H, C_5H_4), 5.99-6.01 (m, 1H, C_5H_4), 6.46-6.48 (m, 1H, C_5H_4) ppm.
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 300 K): δ = 10.0 (BCH_3)*, 7.9 ($CH_2\underline{C}H_3$), 8.2 ($CH_2\underline{C}H_3$), 12.8 (C_5Me_5), 27.4 (CH_{Ad}), 27.8 (CH_{Ad}), 31.1 ($OC_q\underline{C}H_3$), 32.8 (CH_{Ad}), 33.5 (CH_{Ad}), 34.1 ($CH_{2,Ad}$), 34.7 ($CH_{2,Ad}$), 36.9 ($CH_{2,Ad}$), 37.2 ($CH_{2,Ad}$), 39.0 ($CH_{2,Ad}$), 55.2 ($C_{q,exo}$), 55.4 (NCH_2CH_2), 55.5 (NCH_2CH_2), 56.5 (NCH_2Cl), 106.9 (C_5H_4), 109.6 ($O\underline{C}_qCH_3$), 112.7 (C_5H_4), 114.5 (C_5H_4), 119.9 (C_5H_4), 125.7 ($\underline{C}_5Me_5$), 128.8 ($C_{q,Ar}B$)*, 136.8 (dm, $^1J_{C,F}$ = 239.9 Hz, $C_{q,Ar}F$), 137.9 (dm, $^1J_{C,F}$ = 232.1 Hz, $C_{q,Ar}F$), 148.7 (dm, $^1J_{C,F}$ = 235.4 Hz, $C_{q,Ar}F$), 157.0 ($C_{q,ipso}$) ppm.
* = assignment by $^1H/^{13}C$-HMQC/HMBC spectra

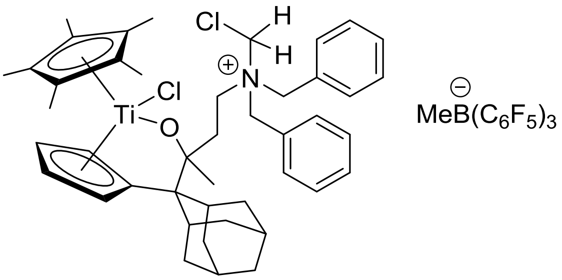
^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 300 K): δ = -15.0 ppm.

^{19}F{^{1}H} NMR (470 MHz, CD_2Cl_2, 300 K): δ = -167.8 (m, 6F, *m*-F_{Ar}B), -165.1 (t, $^{3}J_{F,F}$ = 20.4 Hz, 3F, *p*-F_{Ar}B), -133.3 (m, 6F, *o*-F_{Ar}B) ppm.

^{15}N NMR (202 MHz, C_6D_6, 300 K): δ = 69.6 ppm.

HR/MS calculated: m/z = 608.2900 [M^+]; measured (ESI): m/z = 608.2891.

Synthesis of 5b:



Complex **3b** (0.100 g, 0.151 mmol) and $B(C_6F_5)_3$ (0.077 g, 0.151 mmol) were stirred in 6 mL of toluene. Five drops of dichloromethane were added to the reaction mixture, resulting in a slight observable color change. By stopping the stirring process after a few minutes, the development of two phases can be observed due to the formation of **5c**. The solvent was decanted, and the residue was washed with *n*-hexane (3×5 mL) and dried under vacuum to give complex **5b** as a pale orange solid.

Yield: 0.122 g (0.097 mmol, 64%).
Melting point: 62-64 °C (dec.).
IR (ATR): $\tilde{\nu}$ = 2913, 2857, 1639, 1509, 1451, 1377, 1266, 1143, 1080, 1028, 976, 964, 949, 877, 827, 766, 742, 698, 659, 634, 604 cm^{-1}.
^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 0.49 (s(br), 3H, BCH_3), 1.41 (s, 3H, OC_qCH_3), 1.59-1.76 (m, 10H, $CH_{Ad}/CH_{2,Ad}$), 1.84 (s, 15H, C_5Me_5), 1.96-2.00 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.15-2.20 (m, 2H, $CH_{Ad}/CH_{2,Ad}$, NCH_2CH_2), 2.45-2.46 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.51-2.54 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.82-2.87 (m, 1H, NCH_2CH_2), 3.15-3.21 (m, 1H, NCH_2CH_2), 3.58-3.64 (m, 1H, NCH_2CH_2), 4.49 (d, $^2J_{H,H}$ = 13.4 Hz, 1H, NCH_2Ph), 4.54-4.55 (m, 2H, NCH_2Ph), 4.81 (d, $^2J_{H,H}$ = 10.3 Hz, 1H, NCH_2Cl), 4.90 (d, $^2J_{H,H}$ = 10.3 Hz, 1H, NCH_2Cl), 5.00 (d, $^2J_{H,H}$ = 13.4 Hz, 1H, NCH_2Ph), 5.36-5.37 (m, 1H, C_5H_4), 5.44-5.46 (m, 1H, C_5H_4), 5.97-5.98 (m, 1H, C_5H_4), 6.38-6.39 (m, 1H, C_5H_4), 7.40-7.41 (m, 2H, 2×CH_{Ph}), 7.54-7.66 (m, 8H, 8×CH_{Ph}) ppm.
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 300 K): δ = 10.0 (BCH_3)*, 12.8 ($C_5\underline{Me}_5$), 27.4 (CH_{Ad}), 27.8 (CH_{Ad}), 31.2 ($OC_q\underline{C}H_3$), 31.6 ($CH_{2,Ad}$), 32.7 (CH_{Ad}), 33.6 (CH_{Ad}), 34.2 ($CH_{2,Ad}$), 34.7 ($CH_{2,Ad}$), 36.9 ($CH_{2,Ad}$), 37.2 ($CH_{2,Ad}$), 38.9 (NCH_2CH_2), 55.3 ($C_{q,exo}$), 57.8 (NCH_2CH_2), 63.2 (NCH_2Ph), 64.0 (NCH_2Ph), 66.2 (NCH_2Cl), 106.8 (C_5H_4), 109.6 ($O\underline{C}_qCH_3$), 113.1 (C_5H_4), 114.3 (C_5H_4), 119.5 (C_5H_4), 125.2 ($C_{q,Ph}$), 125.6 ($\underline{C}_5Me_5$), 126.5 ($C_{q,Ph}$), 128.9 ($C_{q,ArB}$)*, 130.59 (2×CH_{Ph}), 130.61 (2×CH_{Ph}), 132.42 (*p*-$\underline{C}H_{Ph}CH_2$),

132.44 (p-$\underline{C}H_{Ph}CH_2$), 132.88 ($2\times CH_{Ph}$), 132.97 ($2\times CH_{Ph}$), 136.3 (dm, $^1J_{C,F}$ = 245.8 Hz, $C_{q,Ar}F$), 137.8 (dm, $^1J_{C,F}$ = 234.3 Hz, $C_{q,Ar}F$), 148.6 (dm, $^1J_{C,F}$ = 235.9 Hz, $C_{q,Ar}F$), 156.8 ($C_{q,ipso}$) ppm.

* = assignment by $^1H/^{13}C$-HMQC/HMBC spectra

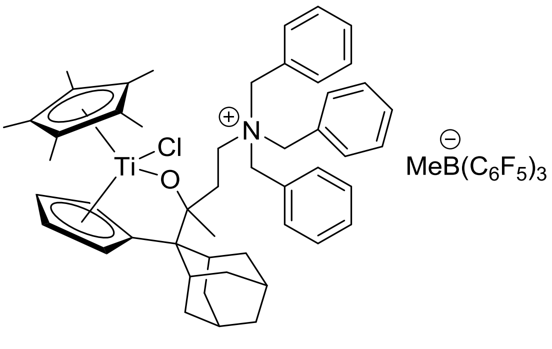
$^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 300 K): δ = -14.9 ppm.

$^{19}F\{^1H\}$ NMR (470 MHz, CD_2Cl_2, 300 K): δ = -167.8 (m, 6F, m-$F_{Ar}B$), -165.2 (t, $^3J_{F,F}$ = 20.4 Hz, 3F, p-$F_{Ar}B$), -133.1 (m, 6F, o-$F_{Ar}B$) ppm.

HR/MS calculated: m/z = 732.3218 [M^+]; measured (ESI): m/z = 732.3223.

EA: Anal. calcd. for $C_{63}H_{59}BCl_2F_{15}NOTi$: C, 60.02; H, 4.72; N, 1.11; Found: C, 61.03; H, 5.50; N, 1.09.

Synthesis of 6:



Complex **3b** (0.071 g, 0.106 mmol) and $B(C_6F_5)_3$ (0.054 g, 0.106 mmol) were stirred in 8 mL of toluene for the *in-situ* preparation of cationic complex **4b**. Excess benzyl chloride (0.1 mL, 0.869 mmol) was added after 5 minutes to the solution, resulting in a slight color change of the reaction mixture. All volatiles were removed under vacuum, and the residue was washed with *n*-hexane (3×5 mL) and dried again under vacuum to give complex **6** as a pale yellow solid. Only the clearly assignable NMR signals are listed.

Yield: 0.101 g (0.078 mmol, 74%).
Melting point: 66-68 °C (dec.).
IR (ATR): $\tilde{\nu}$ = 2912, 2858, 1641, 1509, 1454, 1377, 1265, 1205, 1081, 1045, 1025, 964, 950, 884, 824, 803, 745, 698, 659, 642, 603 cm^{-1}.
^{1}H NMR (500 MHz, CD_2Cl_2, 305 K): δ = 0.52 (s(br), 3H, BCH_3), 1.31 (s, 3H, OC_qCH_3), 1.95 (s, 15H, C_5Me_5), 4.08-4.13 (m, 2H, NCH_2Ph), 4.37 (d, $^2J_{H,H}$ = 13.8 Hz, 1H, NCH_2Ph), 4.37 (d, $^2J_{H,H}$ = 13.3 Hz, 1H, NCH_2Ph), 4.47 (d, $^2J_{H,H}$ = 13.4 Hz, 1H, NCH_2Ph), 4.61 (d, $^2J_{H,H}$ = 9.4 Hz, 1H, NCH_2Ph), 5.27-5.29 (m, 1H, C_5H_4), 5.34-5.35 (m, 1H, C_5H_4), 5.95-5.97 (m, 1H, C_5H_4), 6.12-6.13 (m, 1H, C_5H_4), 7.27-7.42 (m, 6H, 6×CH_{Aryl}), 7.51-7.63 (m, 9H, 9×CH_{Aryl}) ppm.
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 305 K): δ = 10.2 (BCH_3)*, 12.9 ($C_5\underline{Me}_5$), 27.4 (CH_{Ad}), 27.9 (CH_{Ad}), 30.9 ($OC_q\underline{C}H_3$), 32.2 (CH_{Ad}), 33.1 (CH_{Ad}), 33.3 (CH_2), 34.4 (CH_2), 36.7 (CH_2), 37.0 (CH_2), 37.1 (CH_2), 39.1 (CH_2), 54.4 ($C_{q,exo}$), 55.1 (CH_2), 57.2 (NCH_2Ph), 62.2 (NCH_2Ph), 64.4 (NCH_2Ph), 107.8 (C_5H_4), 109.0 ($O\underline{C}_qCH_3$), 111.8 (C_5H_4), 115.8 (C_5H_4), 120.4 (C_5H_4), 126.5 ($\underline{C}_5Me_5$), 129.0 ($C_{q,Ar}B$)*, 136.9 (dm, $^1J_{C,F}$ = 239.7 Hz, $C_{q,Ar}F$), 138.0 (dm, $^1J_{C,F}$ = 243.1 Hz, $C_{q,Ar}F$), 148.8 (dm, $^1J_{C,F}$ = 235.1 Hz, $C_{q,Ar}F$), 157.3 ($C_{q,ipso}$) ppm.

* = assignment by $^{1}H/^{13}C$-HMQC/HMBC spectra

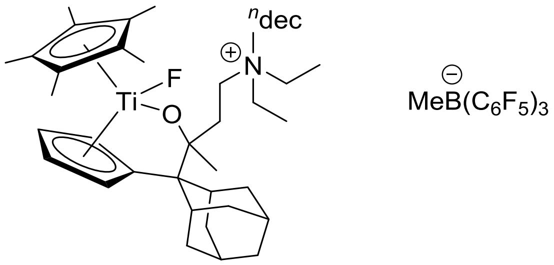
$^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 305 K): δ = -14.9 ppm.

$^{19}F\{^{1}H\}$ NMR (470 MHz, CD_2Cl_2, 305 K): δ = -167.8 (m, 6F, *m*-$F_{Ar}B$), -165.2 (t, $^{3}J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), -133.0 (m, 6F, *o*-$F_{Ar}B$) ppm.

^{15}N NMR (202 MHz, C_6D_6, 300 K): δ = 64.2 ppm.

HR/MS calculated: m/z = 774.3921 [M^+]; measured (ESI): m/z = 774.3914.

Synthesis of 7a:



Complex **3a** (0.100 g, 0.185 mmol) and $B(C_6F_5)_3$ (0.095 g, 0.185 mmol) were stirred in 8 mL of toluene for the *in-situ* preparation of cationic complex **4a**. Excess *n*-fluorodecane (0.1 mL, 0.505 mmol) was added after 5 minutes to the solution, resulting in a slight color change of the reaction mixture. All volatiles were removed under vacuum, and the residue was washed with *n*-hexane (3×5 mL) and dried again under vacuum to give complex **7a** as a yellow solid. Only the clearly assignable NMR signals are listed.

Yield: 0.157 g (0.130 mmol, 70%).

Melting point: 54-56 °C (dec.).

IR (ATR): $\tilde{\nu}$ = 2919, 2857, 1640, 1509, 1449, 1377, 1266, 1145, 1081, 980, 964, 950, 935, 877, 825, 803, 758, 691, 659, 635 cm^{-1}.

^{1}H NMR (500 MHz, CD_2Cl_2, 305 K): δ = 0.50 (s(br), 3H, BCH_3), 1.55 (s, 3H, OC_qCH_3), 1.89 (s, 15H, C_5Me_5), 5.18-5.19 (m, 1H, C_5H_4), 5.47-5.48 (m, 1H, C_5H_4), 6.05-6.06 (m, 1H, C_5H_4), 6.27-6.28 (m, 1H, C_5H_4) ppm.

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 305 K): δ = 10.0 (BCH_3)*, 12.1 ($C_5\underline{Me}_5$), 32.0 ($OC_q\underline{C}H_3$), 55.2 ($C_{q,exo}$), 106.3 (C_5H_4), 106.7 ($O\underline{C}_qCH_3$), 111.0 (C_5H_4), 115.1 (C_5H_4), 119.2 (C_5H_4), 124.6 ($\underline{C}_5Me_5$), 129.3 ($C_{q,Ar}B$)*, 136.8 (dm, $^1J_{C,F}$ = 245.1 Hz, $C_{q,Ar}F$), 138.0 (dm, $^1J_{C,F}$ = 243.0 Hz, $C_{q,Ar}F$), 148.7 (dm, $^1J_{C,F}$ = 236.4 Hz, $C_{q,Ar}F$), 156.2 ($C_{q,ipso}$) ppm.

* = assignment by ^{1}H/^{13}C-HMQC/HMBC spectra

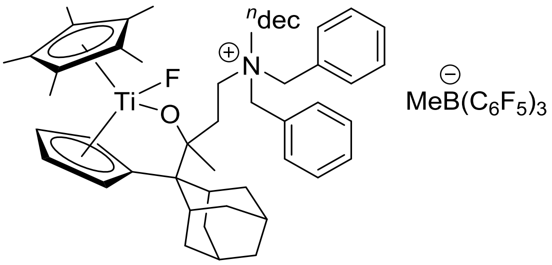
^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 305 K): δ = -14.9 ppm.

^{19}F{^{1}H} NMR (470 MHz, CD_2Cl_2, 305 K): δ = -167.9 (m, 6F, *m*-$F_{Ar}B$), -165.3 (t, $^3J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), -133.1 (m, 6F, *o*-$F_{Ar}B$) ppm.

^{15}N NMR (202 MHz, CD_2Cl_2, 300 K): δ = 64.2 ppm.

HR/MS calculated: m/z = 684.4999 [M^+]; measured (ESI): m/z = 684.4995.

Synthesis of 7b:



Complex **3b** (0.100 g, 0.151 mmol) and $B(C_6F_5)_3$ (0.077 g, 0.151 mmol) were stirred in 8 mL of toluene for the *in-situ* preparation of cationic complex **4b**. Excess *n*-fluorodecane (0.1 mL, 0.505 mmol) was added after 5 minutes to the solution, resulting in a slight color change of the reaction mixture. All volatiles were removed under vacuum, and the residue was washed with *n*-hexane (3×5 mL) and dried again under vacuum to give complex **7b** as a yellow solid. Only the clearly assignable NMR signals are listed.

Yield: 0.164 g (0.123 mmol, 81%).
Melting point: 50-52 °C (dec.).
IR (ATR): $\tilde{\nu}$ = 2921, 2857, 1640, 1509, 1453, 1377, 1265, 1208, 1143, 1081, 979, 964, 950, 935, 876, 826, 804, 745, 725, 701, 659, 642, 603 cm^{-1}.
^{1}H NMR (500 MHz, CD_2Cl_2, 305 K): δ = 0.50 (s(br), 3H, BCH_3)*, 1.49 (s, 3H, OC_qCH_3), 1.86 (s, 15H, C_5Me_5), 4.30 (d, $^{2}J_{H,H}$ = 13.4 Hz, NCH_2Ph), 4.37-4.40 (m, 2H, NCH_2Ph)**, 4.47-4.51 (m, 1H, NCH_2Ph)**, 4.73 (d, $^{2}J_{H,H}$ = 13.6 Hz, NCH_2Ph), 5.20-5.21 (m, 1H, C_5H_4), 5.48-5.49 (m, 1H, C_5H_4), 6.14-6.15 (m, 1H, C_5H_4), 6.29-6.30 (m, 1H, C_5H_4), 7.35-7.36 (m, 2H, 2×CH_{Ph}), 7.46-7.48 (m, 2H, 2×CH_{Ph}), 7.52-7.63 (m, 6H, 6×CH_{Ph}) ppm.
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 305 K): δ = 10.3 (BCH_3)*, 12.2 ($C_5\underline{Me}_5$), 30.8 ($OC_q\underline{C}H_3$), 59.4 ($N\underline{C}H_2Ph$), 64.1 ($N\underline{C}H_2Ph$), 106.4 (C_5H_4), 106.7 ($O\underline{C_q}CH_3$), 111.5 (C_5H_4), 115.1 (C_5H_4), 118.9 (C_5H_4), 124.6 ($\underline{C}_5Me_5$), 126.7 ($C_{q,Ph}$), 127.1 ($C_{q,Ph}$), 128.9 ($C_{q,Ar}B$)*, 130.3 (2×CH_{Ph}), 130.4 (2×CH_{Ph}), 131.9 (2×CH_{Ph}), 132.9 (2×CH_{Ph}), 133.0 (2×CH_{Ph}), 136.9 (dm, $^{1}J_{C,F}$ = 249.5 Hz, $C_{q,Ar}F$), 137.9 (dm, $^{1}J_{C,F}$ = 240.2 Hz, $C_{q,Ar}F$), 148.7 (dm, $^{1}J_{C,F}$ = 231.0 Hz, $C_{q,Ar}F$), 156.2 ($C_{q,ipso}$) ppm.
* = assignment by ^{1}H/^{13}C-HMQC/HMBC spectra
** = overlap with the signal of *n*-fluorodecane
^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 305 K): δ = -14.9 ppm.

^{19}F{^{1}H} NMR (470 MHz, CD_2Cl_2, 305 K): δ = -167.9 (m, 6F, *m*-$F_{Ar}B$), -165.3 (t, $^{3}J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), -133.1 (m, 6F, *o*-$F_{Ar}B$) ppm.

HR/MS calculated: m/z = 808.5312 [M^+]; measured (ESI): m/z = 808.5316.

Crystallographic Data:

Single crystals were measured on a 'Bruker APEX-II diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 100 K. Using Olex2,[2] the structures were solved with SHELXS[3] using direct methods and refined with the SHELXL[4] using Least Squares minimisation. Regarding the crystal packing (Figures S2,4,6,8,10,12), no particular supramolecular features are observed for **2a,b**, **3a,b**, **5b**, and **L1b** between the complex molecules or between the complex molecules and the solvent molecules (in the case of **5b** the solvent molecules are located in the voids resulting from the packing arrangements of the complex molecules). Thus, the intermolecular forces appear to be dominated by van der Waals interactions.

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

	2a	**3a**	**2b**	**3b**
CCDC	1871464	1871466	1871469	1871470
empirical formula	$C_{33}H_{50}ClNOTi$	$C_{34}H_{53}NOTi$	$C_{43}H_{54}ClNOTi$	$C_{44}H_{57}NOTi$
fw	560.09	539.67	684.22	663.80
colour	yellow	pale yellow	yellow	colorless
Habit	block	block	plate	block
cryst dimens, mm	0.45 x 0.35 x 0.30	0.36 x 0.32 x 0.12	0.40 x 0.36 x 0.06	0.40 x 0.16 x 0.06
cryst syst	orthorhombic	orthorhombic	triclinic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	P-1	$P2_1/c$
a, Å	11.5799(3)	11.5804(3)	10.0365(4)	23.4500(8)
b, Å	13.4100(3)	13.5510(4)	12.8104(5)	40.0669(13)
c, Å	18.5438(5)	18.5297(5)	14.1398(5)	15.0655(5)
α, deg	90	90	93.3822(13)	90
β, deg	90	90	92.2358(14)	90.1527(18)
γ, deg	90	90	107.6715(13)	90
V, Å^3	2879.60(13)	2907.79(14)	1726.07(11)	14155.0(8)
Z	4	4	2	16
D $_{\text{caclcd}}$, g cm^{-3}	1.292	1.233	1.316	1.246
μ, mm^{-1}	0.417	0.321	0.361	0.277
T, K	100(2)	100(2)	100(2)	100(2)
θ range, deg	1.874 – 36.319	1.862 – 36.311	1.445 – 40.249	1.337 – 28.699
no. of rflns collected	141913	150848	143098	246338
no. of indep rflns (R(int))	13980 (0.0388)	14105 0.0384	21711 (0.0318)	36597 (0.1043)
no. of rflns with I>2σ(I)	13476	13243	18207	23400
abs cor	numerical	numerical	numerical	numerical
max, min transmission	0.8892 and 0.8490	0.9676 and 0.8987	0.9797 and 0.8946	1.0000 and 0.8714
final R indices [I>2σ(I)]	R1 = 0.0275 wR2 = 0.0725	R1 = 0.0255 wR2 = 0.0643	R1 = 0.0298 wR2 = 0.0786	R1 = 0.0542 wR2 = 0.1113
R indices (all data)	R1 = 0.0290 wR2 = 0.0733	R1 = 0.0293 wR2 = 0.0664	R1 = 0.0399 wR2 = 0.0841	R1 = 0.1076 wR2 = 0.1341
GOF on F^2	1.093	1.058	1.028	1.044
largest diff peak / hole (e.Å^{-3})	1.300 / -0.225	0.358 / -0.175	0.663 / -0.276	0.633 / -0.670

Table S2: Crystal Structure Data for Compounds **5b** and **L1b**.

	5b	**L1b**
CCDC	1871467	1871463
empirical formula	$C_{63}H_{59}BClF_{15}NOTi$ + 0.5 C_6H_5Br	$C_{18}H_{21}NO$
fw	1339.22	267.36
colour	yellow	colorless
Habit	block	rods
cryst dimens, mm	0.28 x 0.24 x 0.14	0.35 x 0.20 x 0.10
cryst syst	triclinic	orthorhombic
space group	*P*-1	$P2_12_12_1$
a, Å	11.9091(9)	7.3597(2)
b, Å	14.5982(11)	10.2273(2)
c, Å	18.1227(13)	20.1564(5)
α, deg	71.5865(18)	90
β, deg	78.1350(19)	90
γ, deg	80.585(2)	90
V, Å^3	2908.9(4)	1517.17(6)
Z	2	4
D $_{\text{caclcd}}$, g cm^{-3}	1.529	1.170
μ, mm^{-1}	0.677	0.072
T, K	100(2)	100(2)
θ range, deg	1.479 – 32.032	2.021 – 36.316
no. of rflns collected	125582	47789
no. of indep rflns (R(int))	20249 0.0365	7348 (0.0416)
no. of rflns with I>2σ(I)	16019	6508
abs cor	numerical	semi-empirical
max, min transmission	0.9260 and 0.8559	1.0000 and 0.9490
final R indices [I>2σ(I)]	R1 = 0.0389 wR2 = 0.0968	R1 = 0.0401 wR2 = 0.0997
R indices (all data)	R1 = 0.0553 wR2 = 0.1046	R1 = 0.0491 wR2 = 0.1055
GOF on F^2	1.053	1.043
largest diff peak / hole (e.Å^{-3})	0.589 / -0.617	0.381 / -0.188

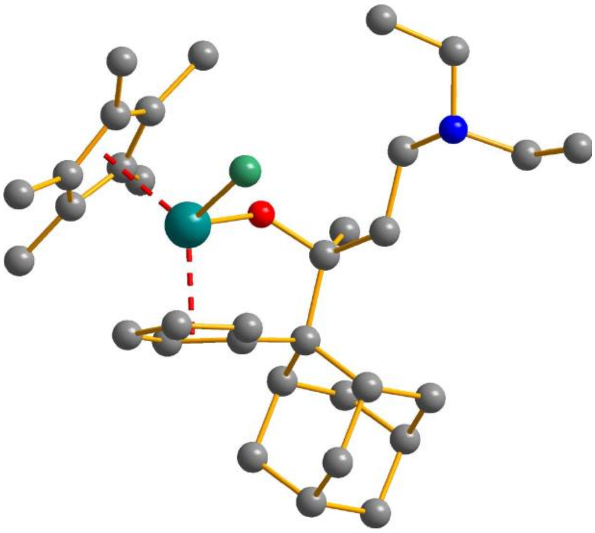


Figure S1: Molecular structure of **2a**.

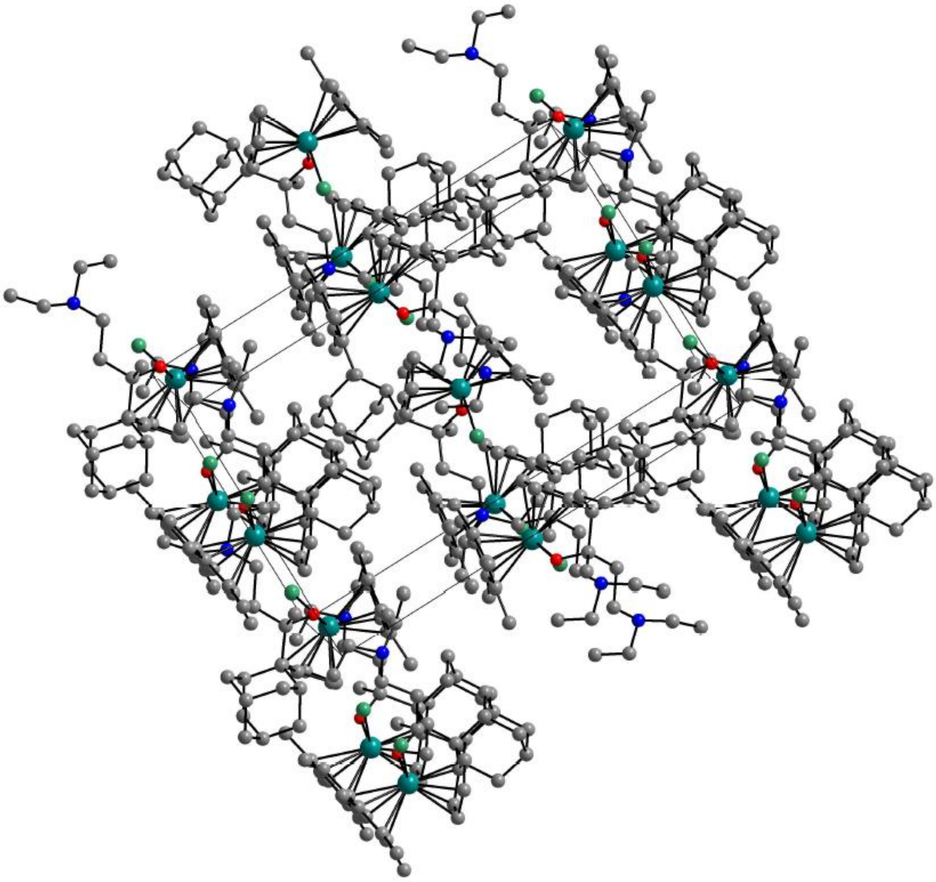


Figure S2: View along the *b* axis showing the packing of molecules in the crystal structure of complex **2a**. Hydrogen atoms have been omitted for clarity.

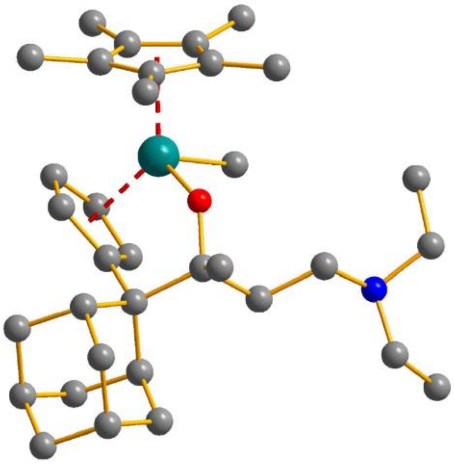


Figure S3: Molecular structure of **3a**.

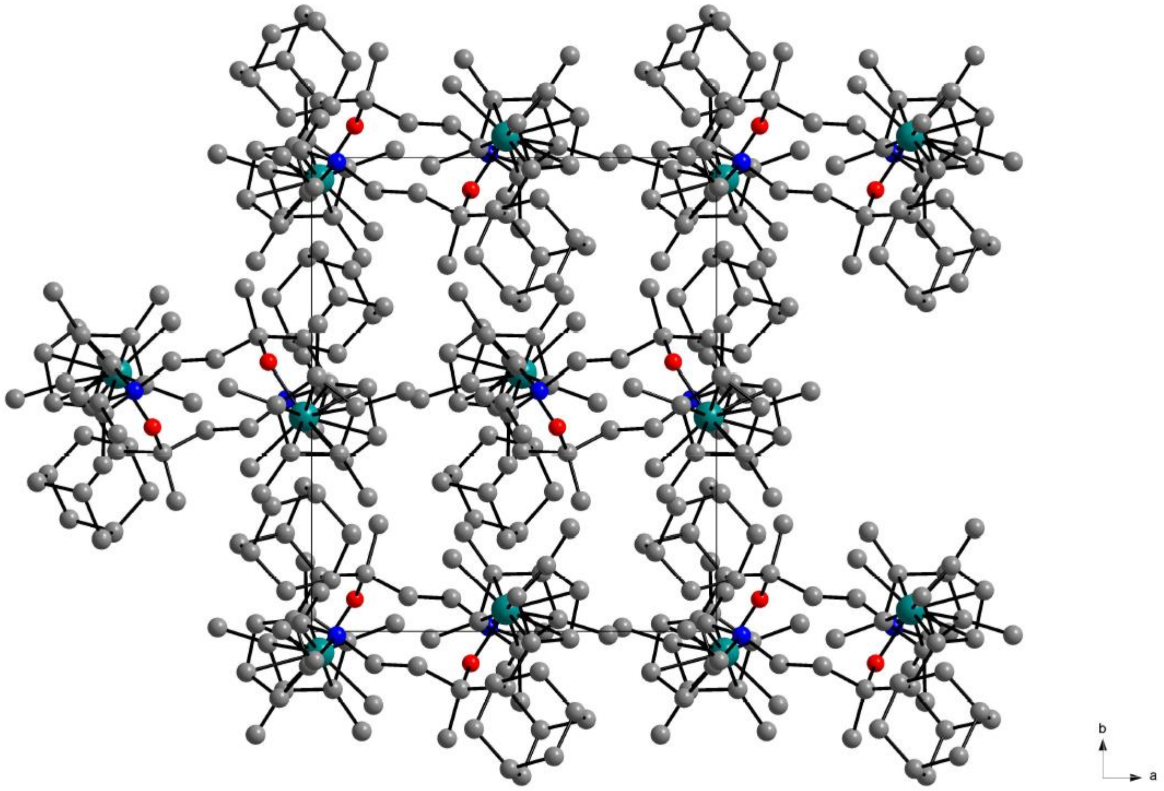


Figure S4: View along the *c* axis showing the packing of molecules in the crystal structure of complex **3a.** Hydrogen atoms have been omitted for clarity.

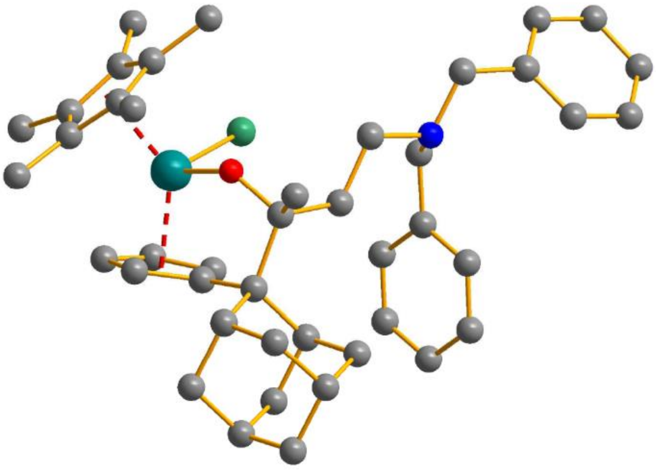


Figure S5: Molecular structure of **2b**.

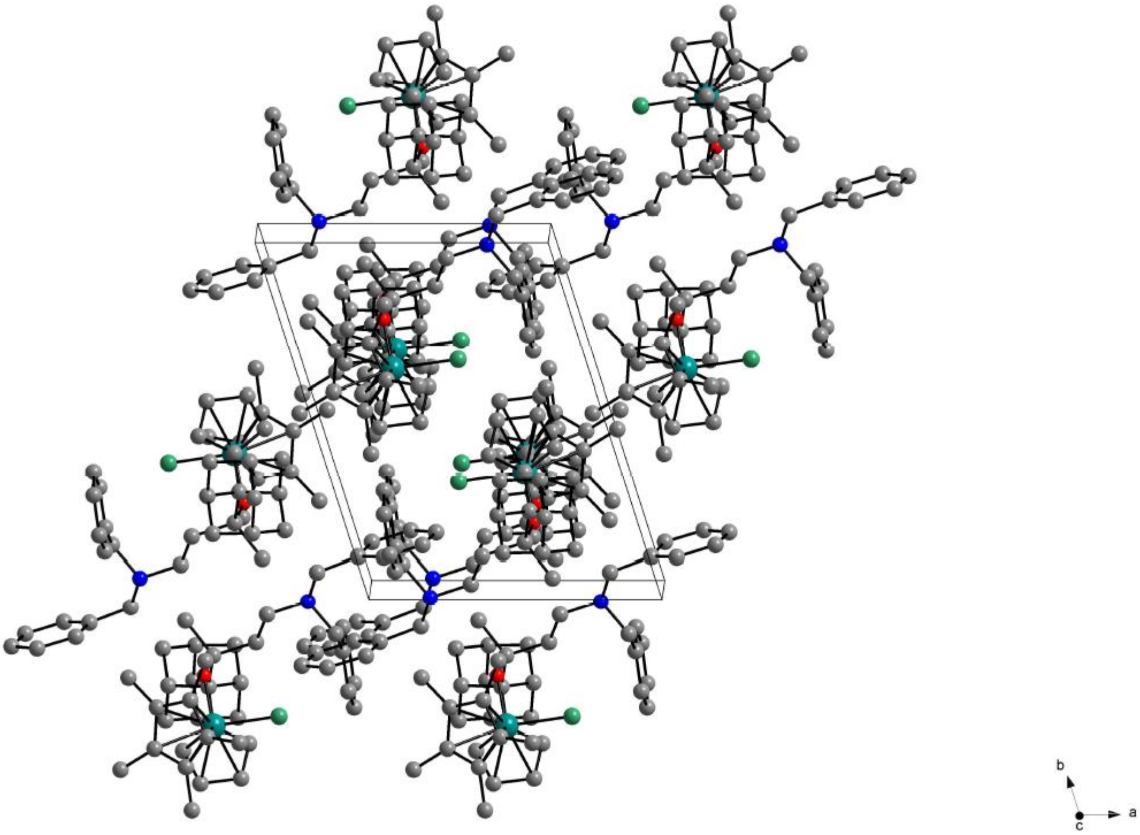


Figure S6: View along the *c* axis showing the packing of molecules in the crystal structure of complex **2b**. Hydrogen atoms have been omitted for clarity.

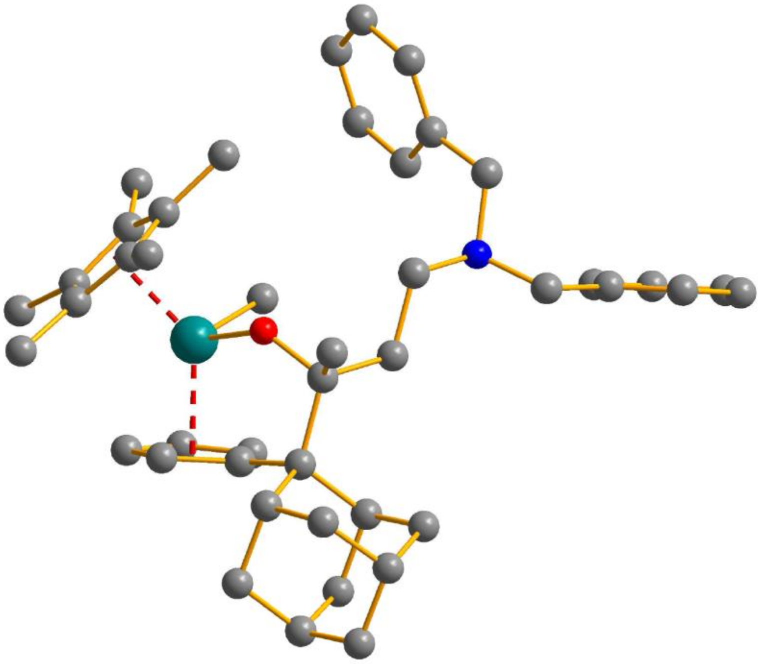


Figure S7: Molecular structure of **3b**.

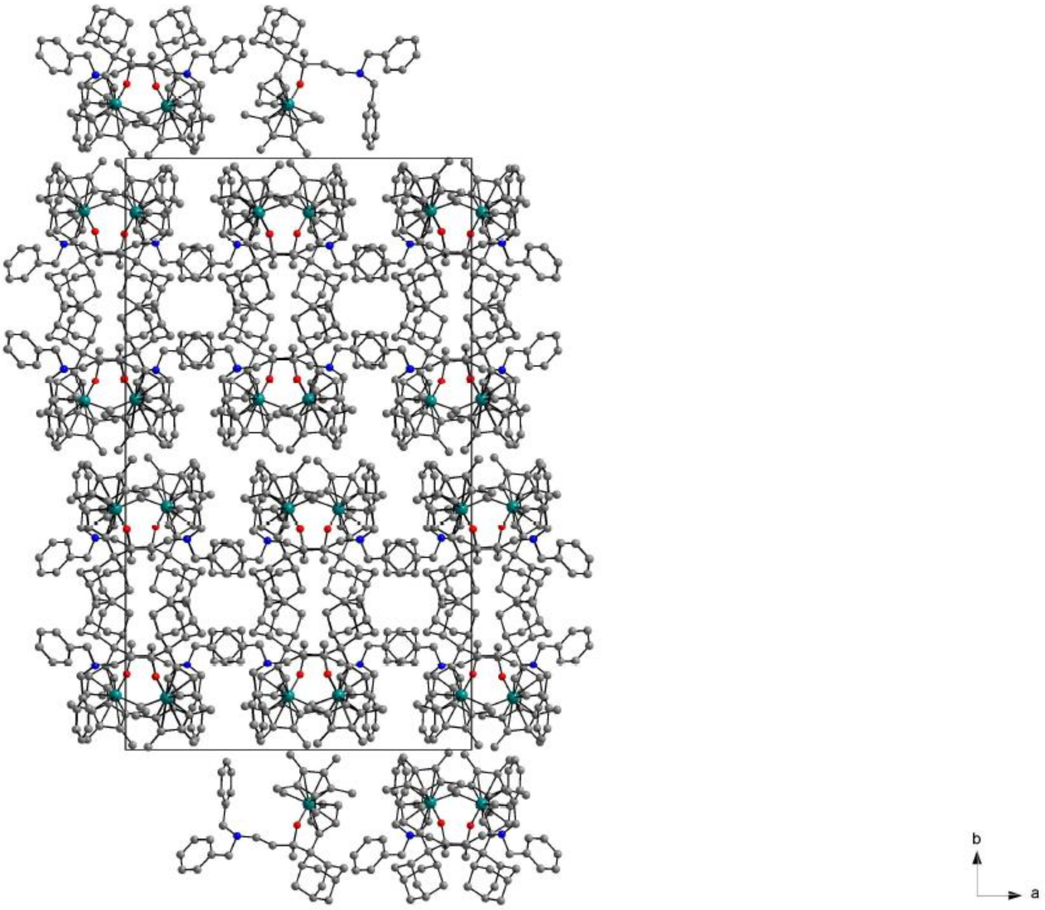


Figure S8: View along the *c* axis showing the packing of molecules in the crystal structure of complex **3b**. Hydrogen atoms have been omitted for clarity.

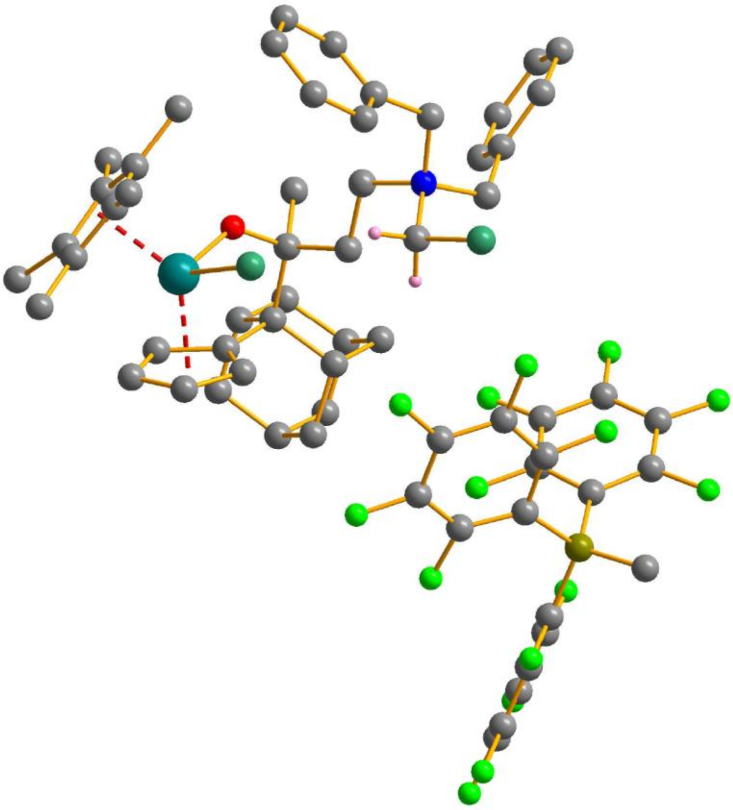


Figure S9: Molecular structure of **5b**.

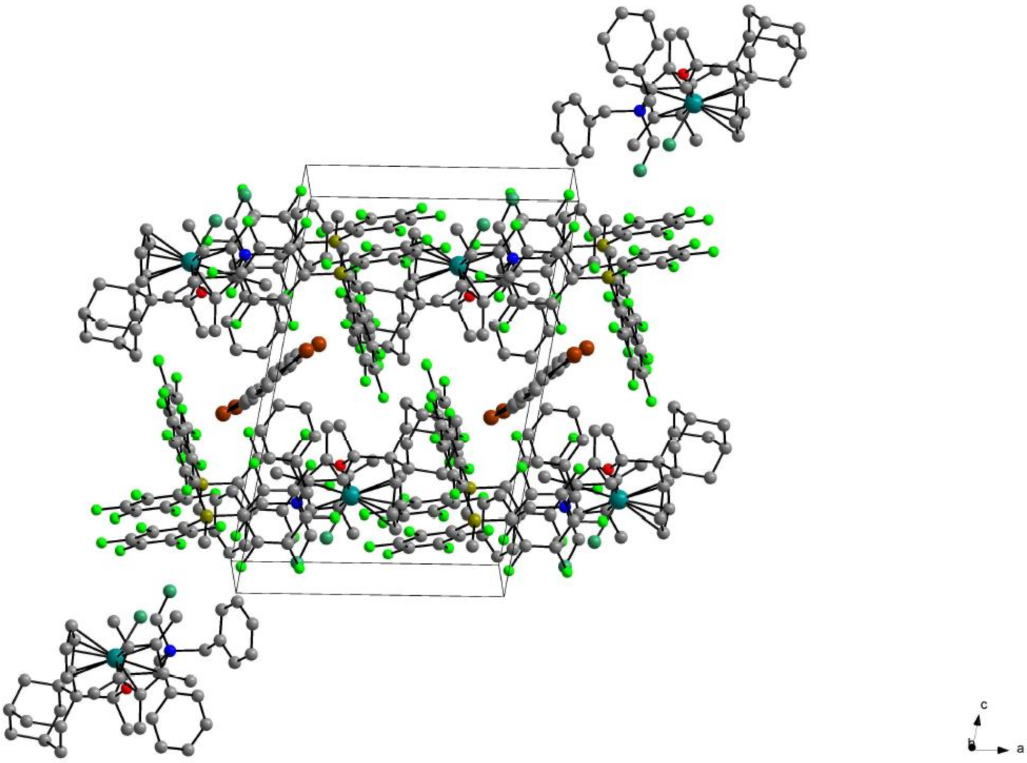


Figure S10: View along the *b* axis showing the packing of molecules in the crystal structure of complex **5b**. Hydrogen atoms have been omitted for clarity.

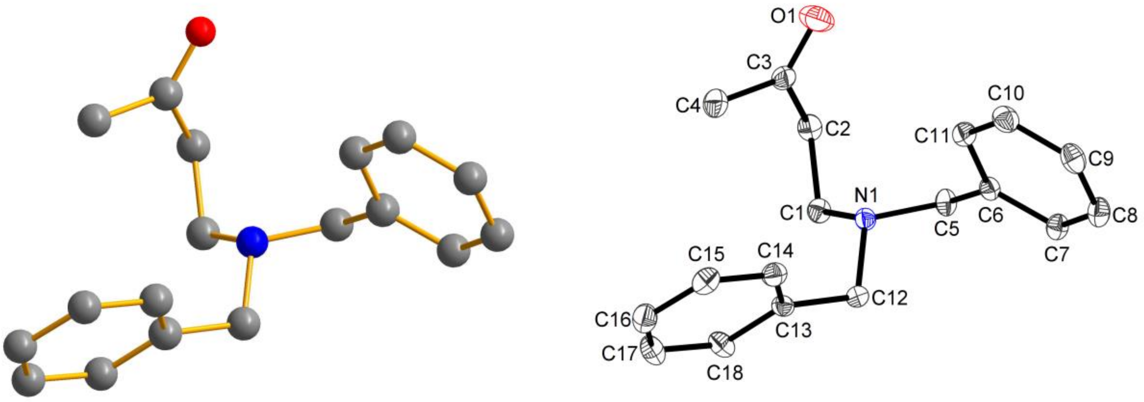


Figure S11: Molecular structure of **L1b** and ORTEP presentation.

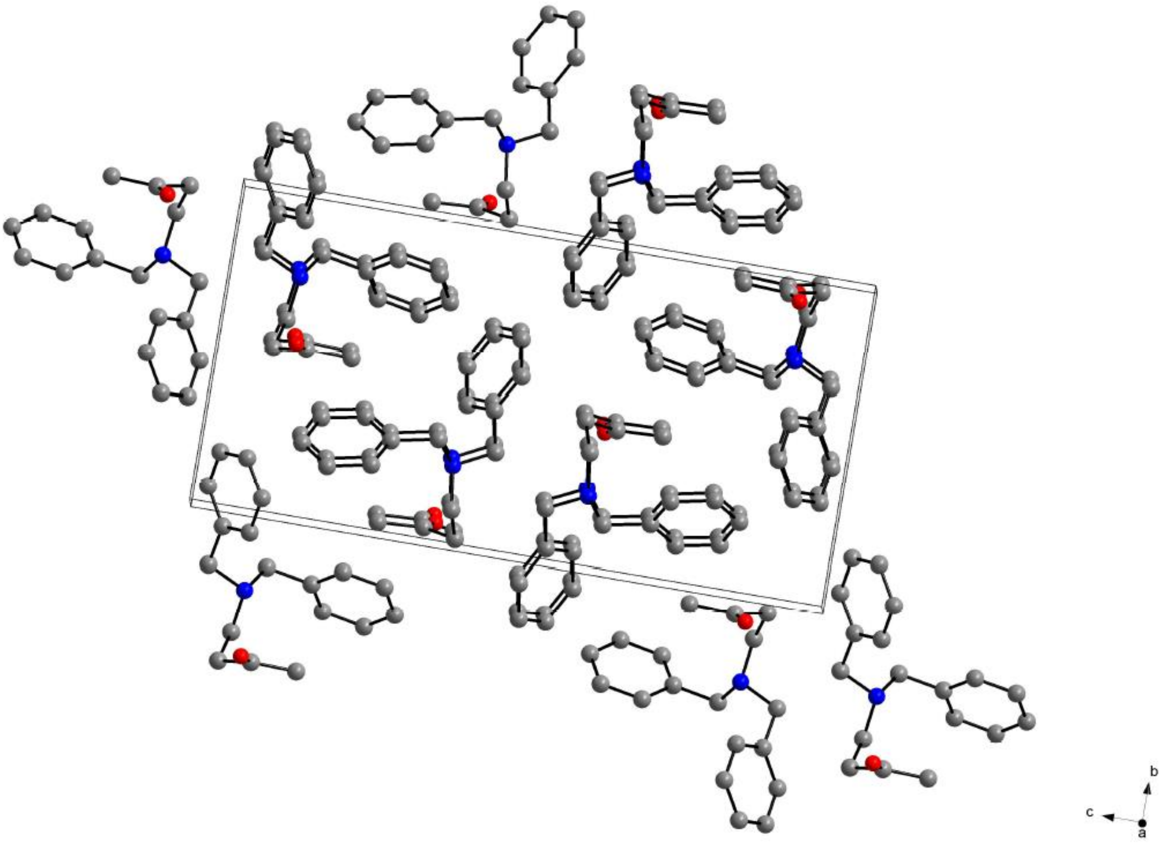


Figure S12: View along the *a* axis showing the packing of molecules in the crystal structure of complex **L1b**. Hydrogen atoms have been omitted for clarity.

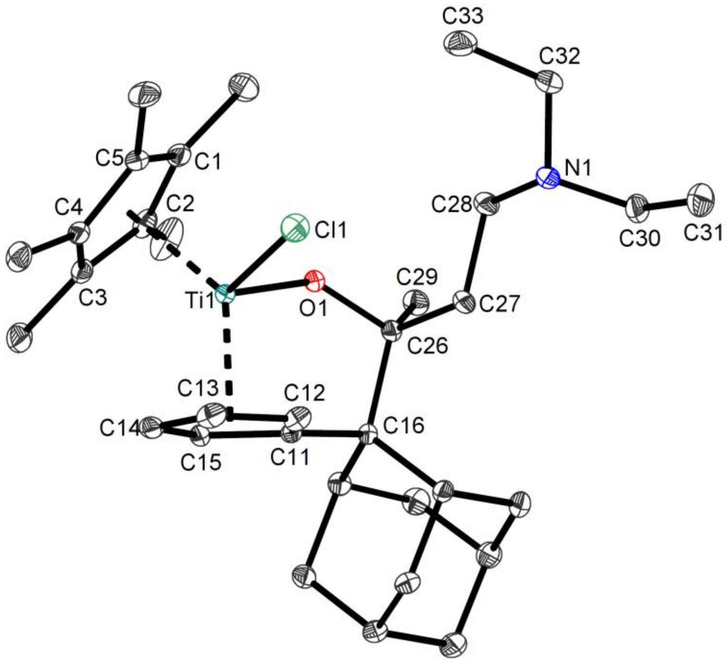


Figure S13. Molecular structure of **2a** in the crystal. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1–Cl1 2.3766(3), Ti1–O1 1.8713(8), O1–C26 1.4326(13), N1–C28 1.4673(15), C11–C16 1.5235(15), C16–C26 1.6250(15), C26–C27 1.5446(15), C26–C29 1.5359(15), C26–C27 1.5446(15), C27–C28 1.5331(16), Cl1–Ti1–O1 99.40(3), Ct1–Ti1–Ct2 133.6, Σ∠C26 321.4 (O1–C26–C27 + O1–C26–C29 + C27–C26–C29), Σ∠N1 331.5 (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

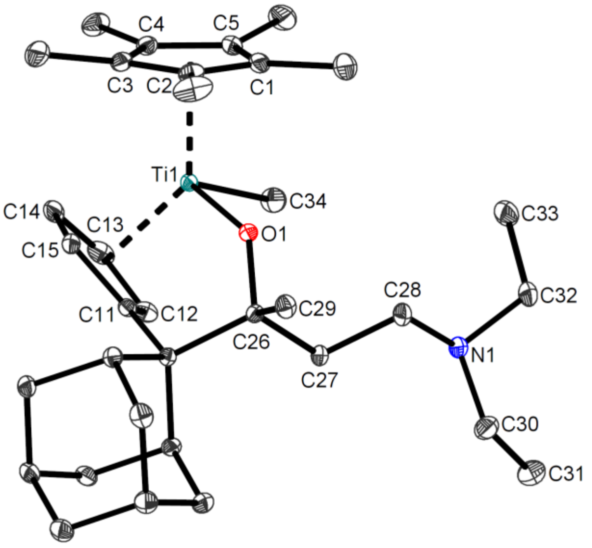


Figure S14. Molecular structures of **3a** in the crystal. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1–C34 2.1846(11), Ti1–O1 1.8654(7), O1–C26 1.4272(11), N1–C28 1.4673(13), C11–C16 1.5234(13), C16–C26 1.6312(13), C26–C27 1.5459(13), C26–C29 1.5377(14), C26–C27 1.5459(13), C27–C28 1.5297(14), C34–Ti1–O1 98.09(4), Ct1–Ti1–Ct2 134.4, Σ∠C26 321.3 (O1–C26–C27 + O1–C26–C29 + C27–C26–C29), Σ∠N1 330.7 (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

NMR-Spectra of Compounds:

Figure S15: ^{1}H NMR spectrum of **L1a** (500 MHz, C_6D_6, rt).

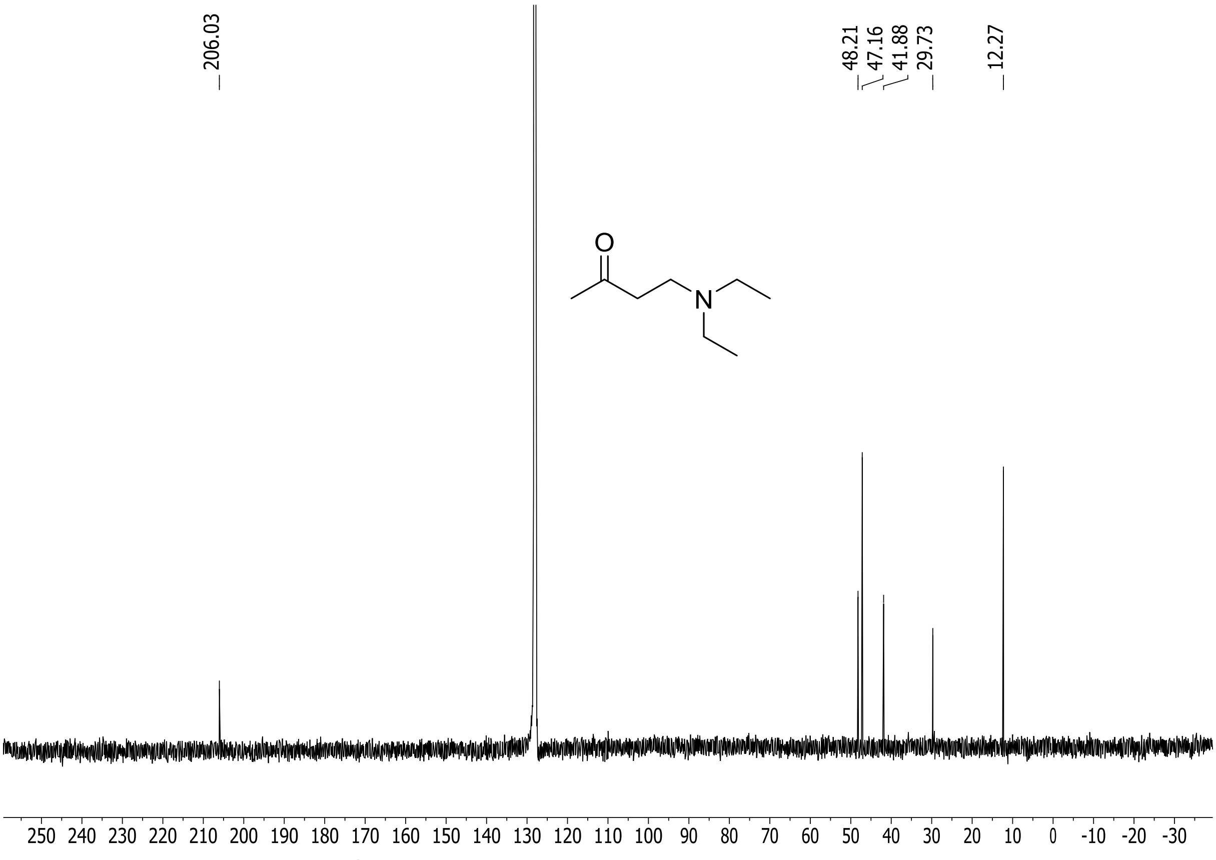


Figure S16: ^{13}C{^{1}H} NMR spectrum of **L1a** (126 MHz, C_6D_6, rt).

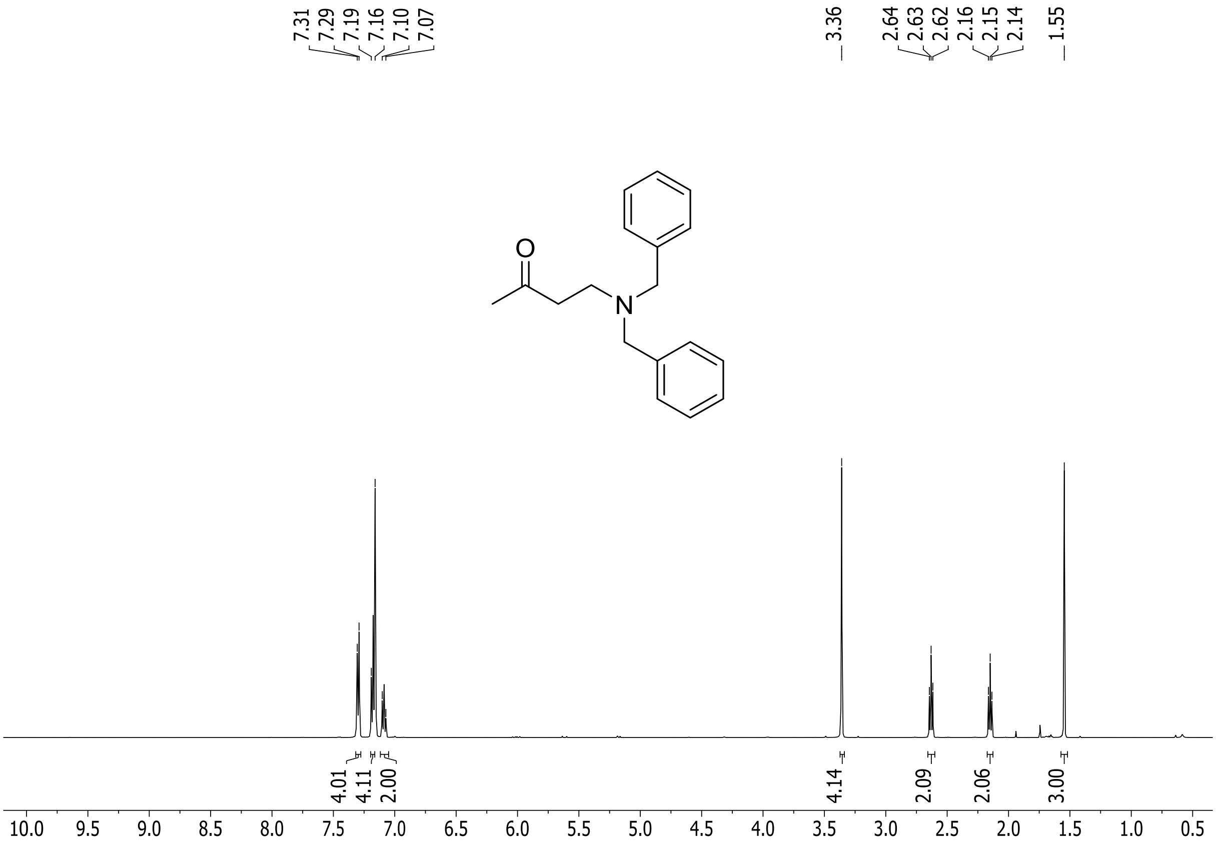


Figure S17: ^{1}H NMR spectrum of **L1b** (500 MHz, C_6D_6, rt).

Figure S18: $^{13}C\{^1H\}$ NMR spectrum of **L1b** (126 MHz, C_6D_6, rt).

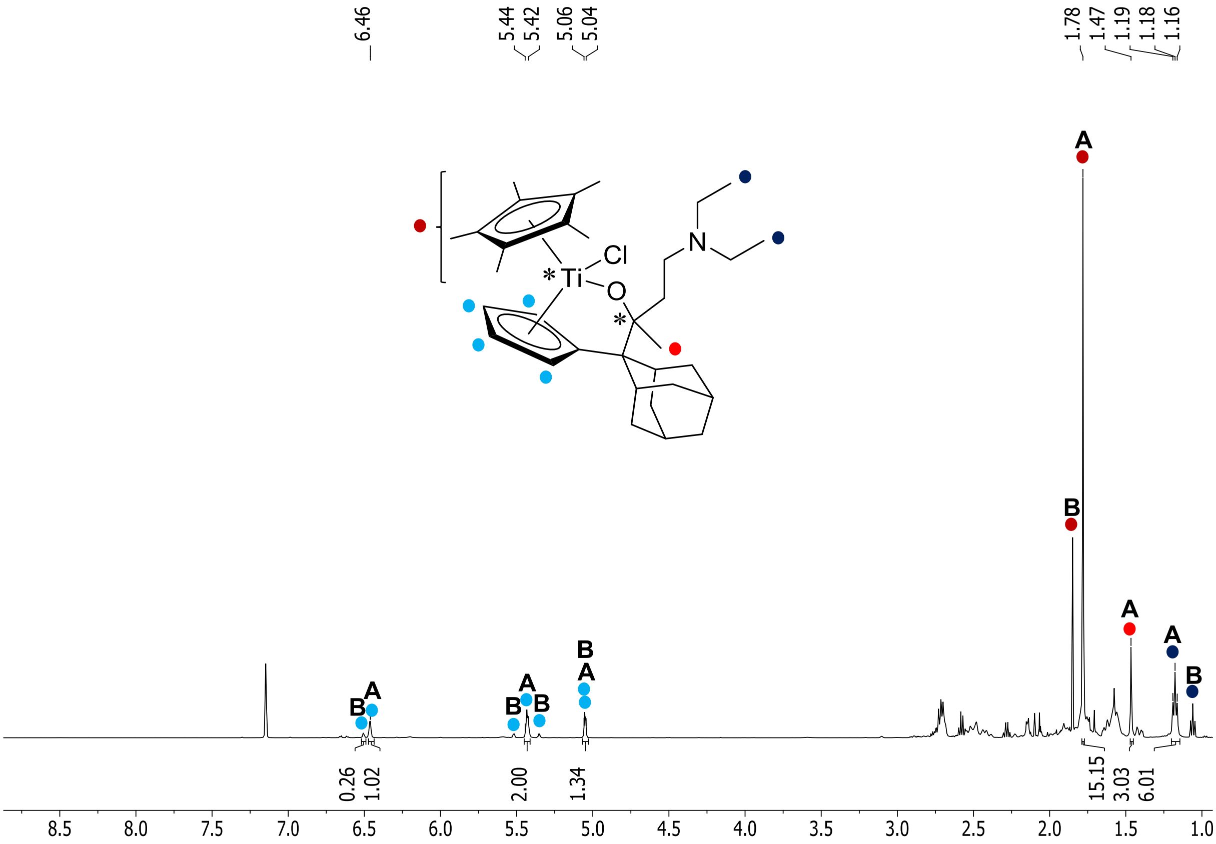


Figure S19: ^{1}H NMR spectrum of **2a** (500 MHz, C_6D_6, rt); diastereoisomer **A** and diastereoisomer **B**.

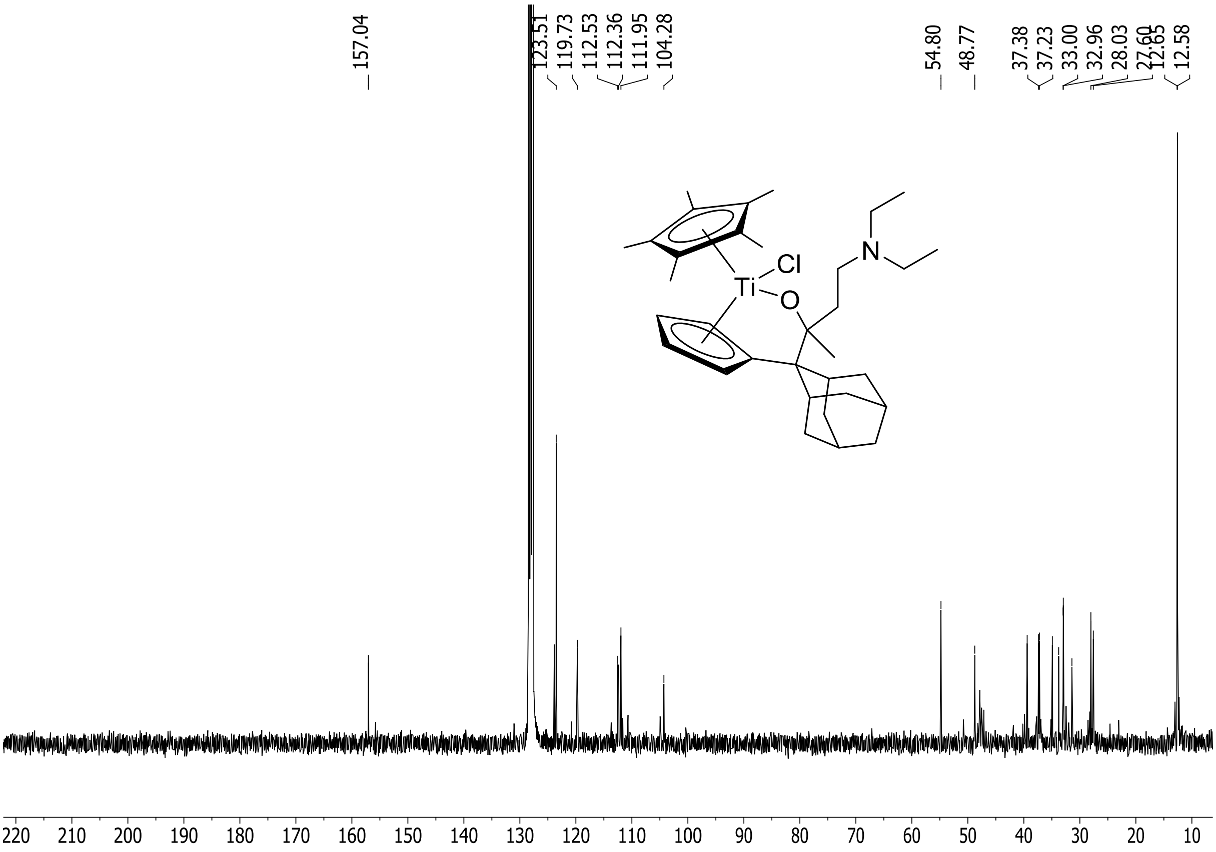


Figure S20: ^{13}C{^{1}H} NMR spectrum of **2a** (126 MHz, C_6D_6, rt); only clearly assignable signals of the main diastereoisomer are picked.

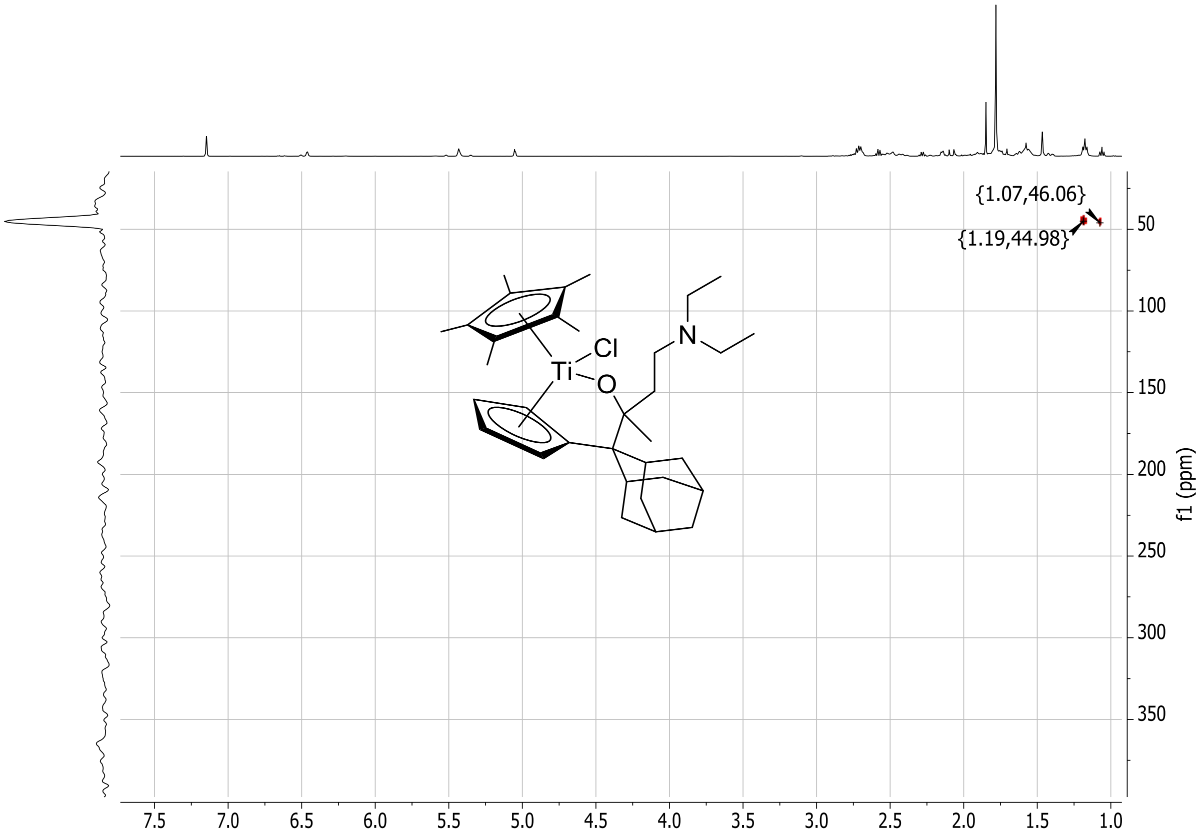


Figure S21: $^{15}N/^{1}H$ HMBC NMR spectrum of **2a** (51 MHz, C_6D_6, rt).

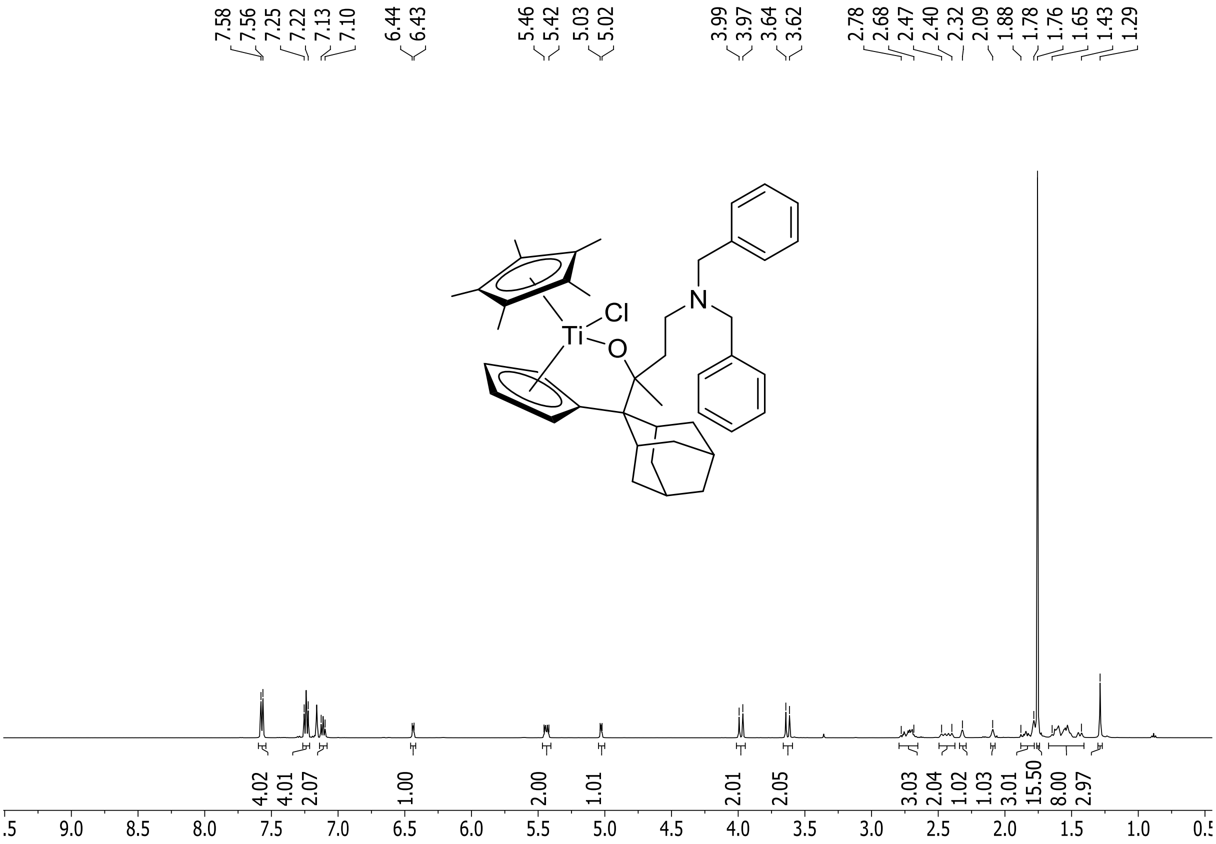


Figure S22: ^{1}H NMR spectrum of **2b** (500 MHz, C_6D_6, rt).

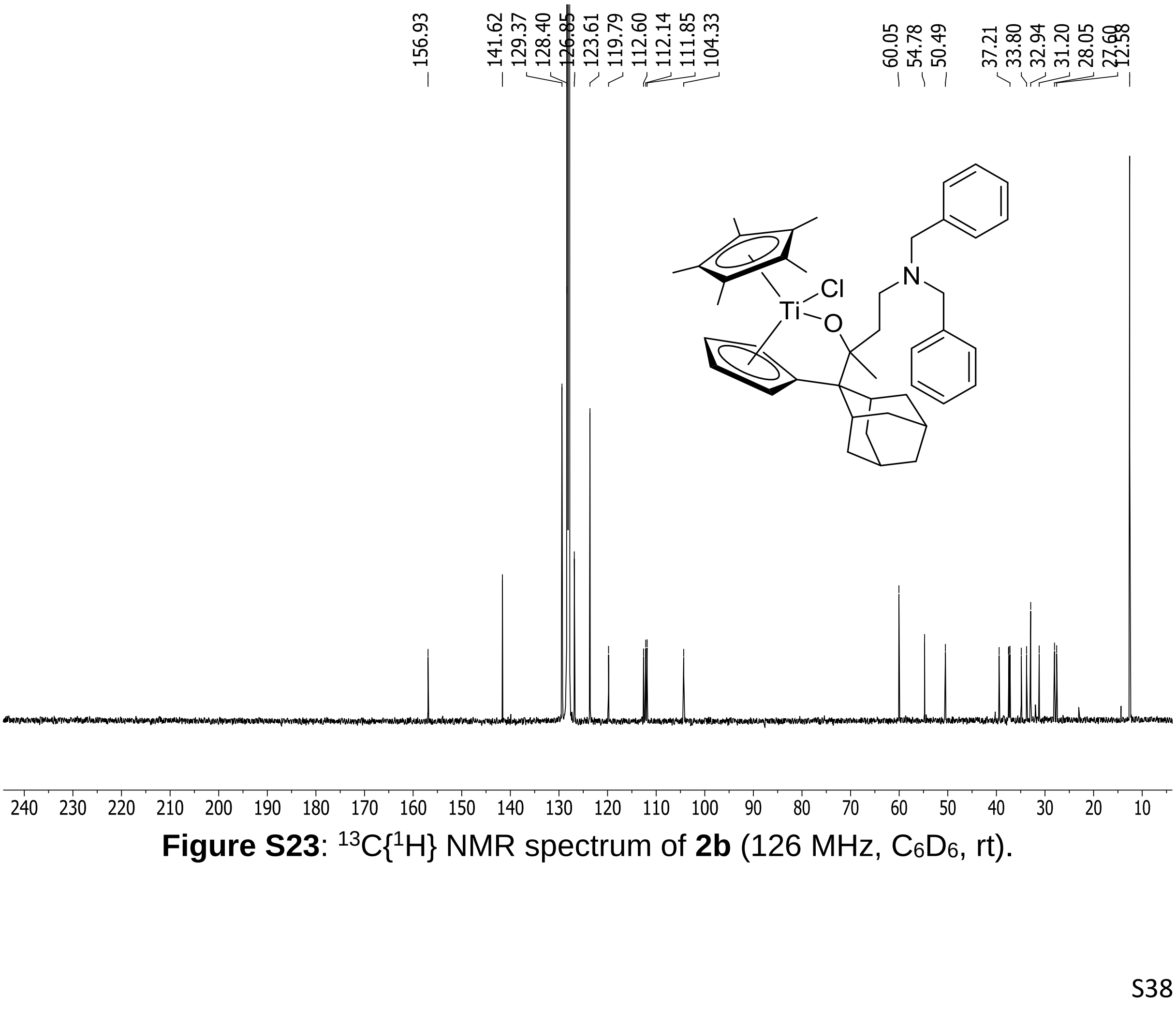


Figure S23: ^{13}C{^{1}H} NMR spectrum of **2b** (126 MHz, C_6D_6, rt).

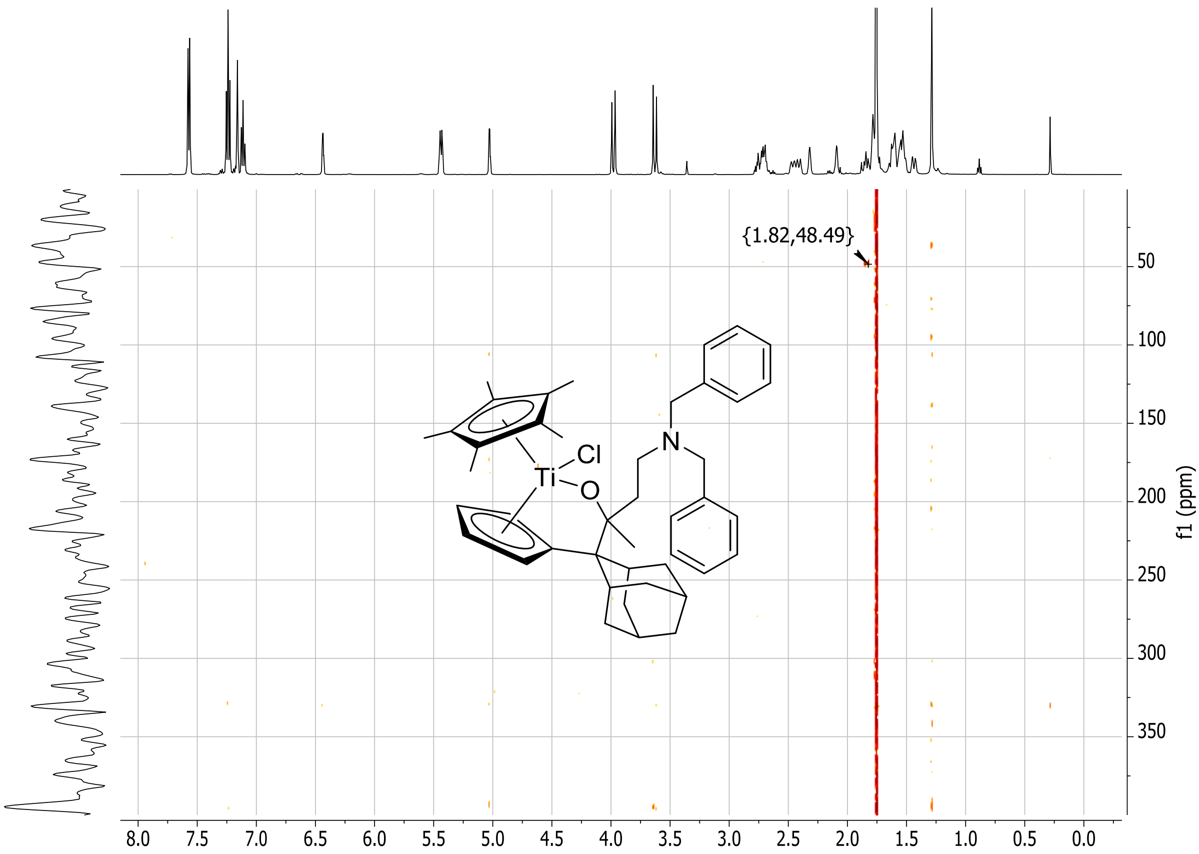


Figure S24: ^{15}N/^{1}H HMBC NMR spectrum of **2b** (51 MHz, C_6D_6, rt).

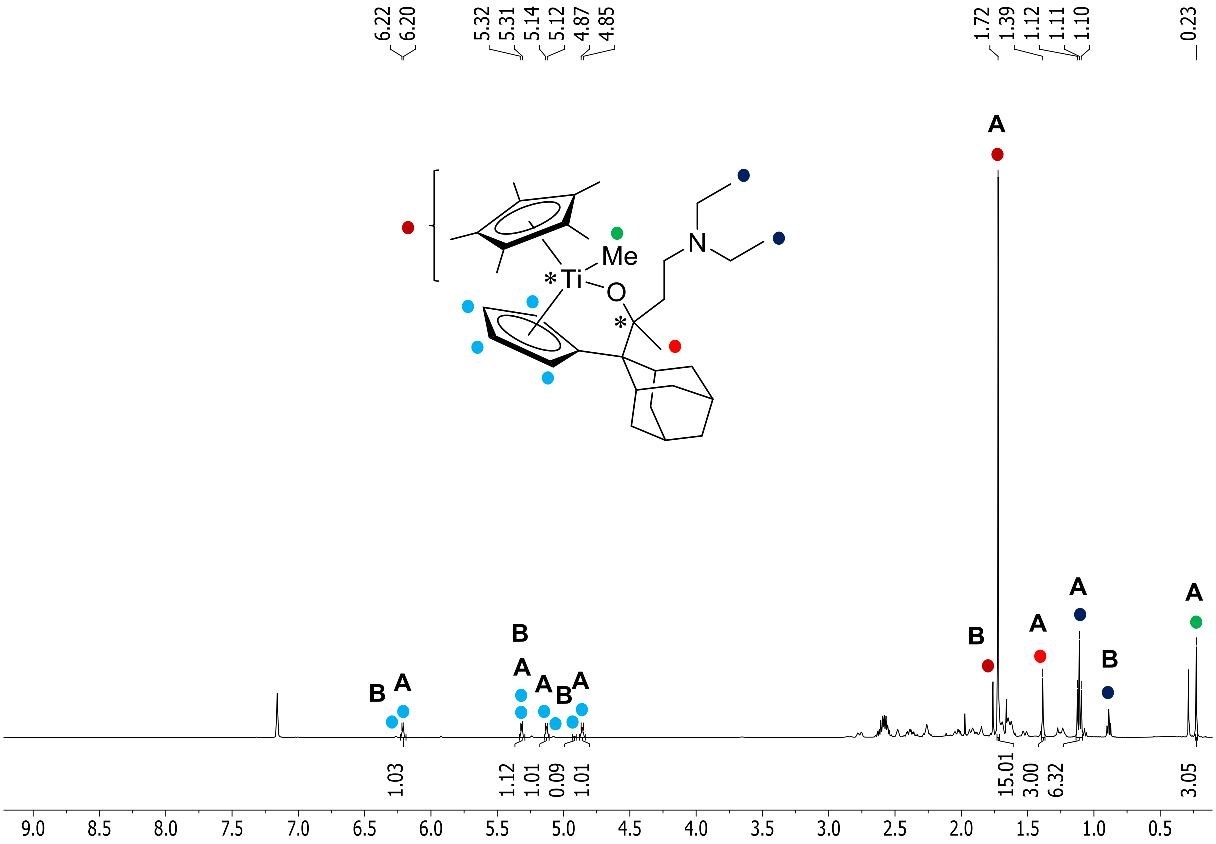


Figure S25: ^{1}H NMR spectrum of **3a** (500 MHz, C_6D_6, rt); diastereoisomer **A** and diastereoisomer **B**; 0.29 ppm: silicon grease.

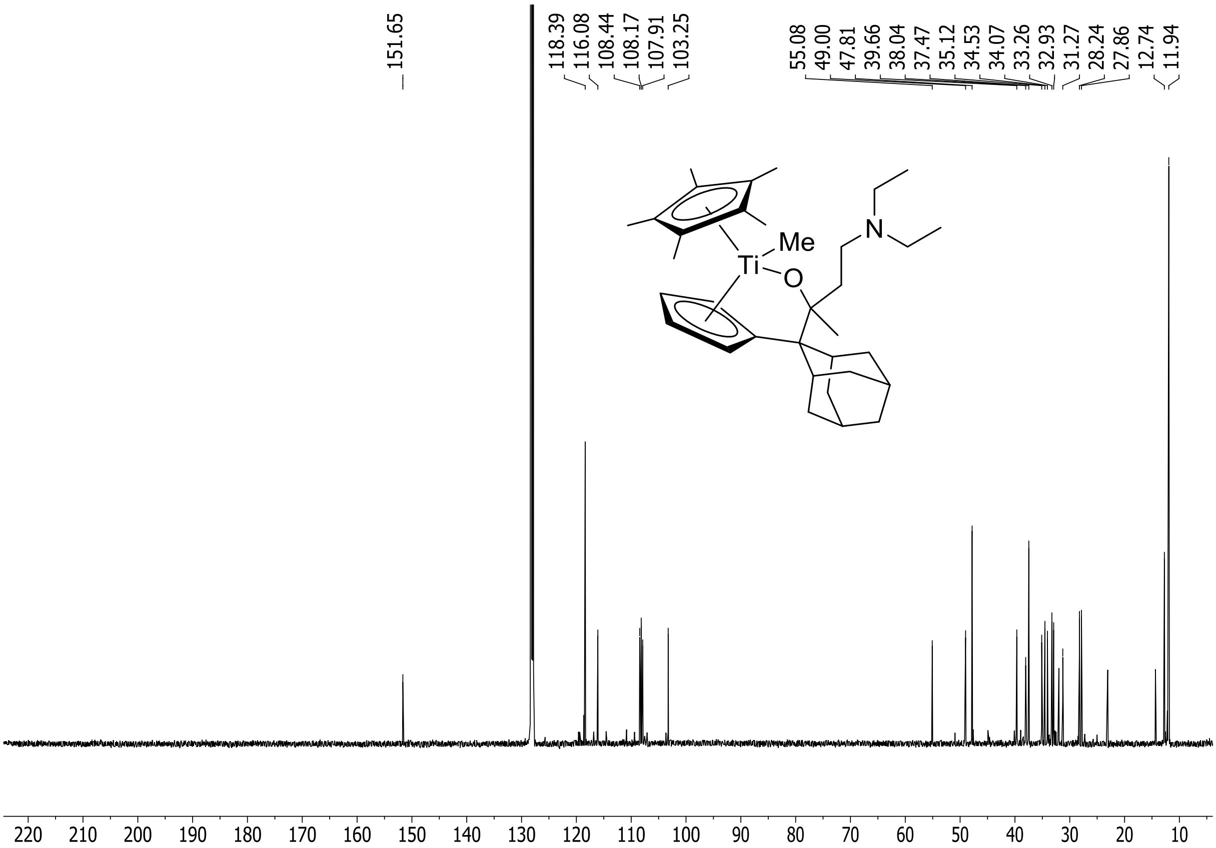


Figure S26: $^{13}C\{^{1}H\}$ NMR spectrum of **3a** (126 MHz, C_6D_6, rt); only clearly assignable signals of the main diastereoisomer are picked.

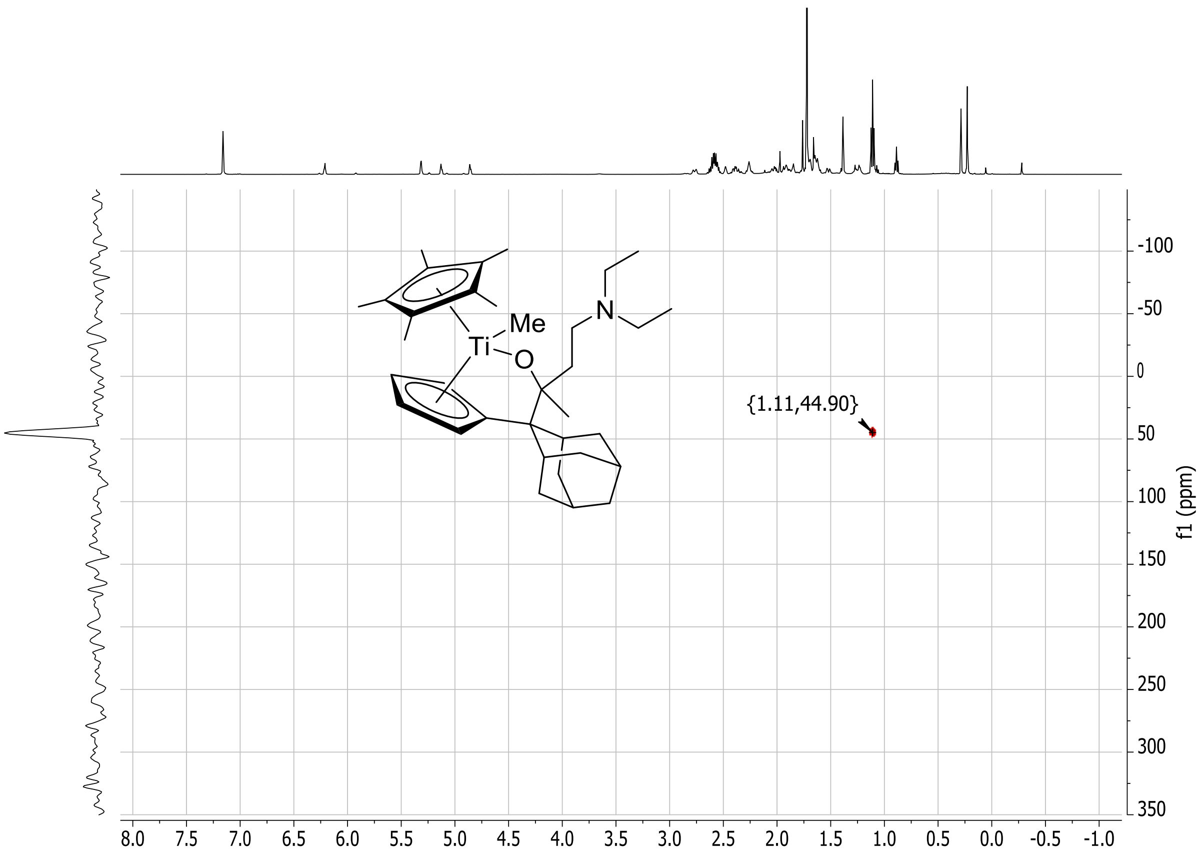


Figure S27: ^{15}N/^{1}H HMBC NMR spectrum of **3a** (51 MHz, C_6D_6, rt).

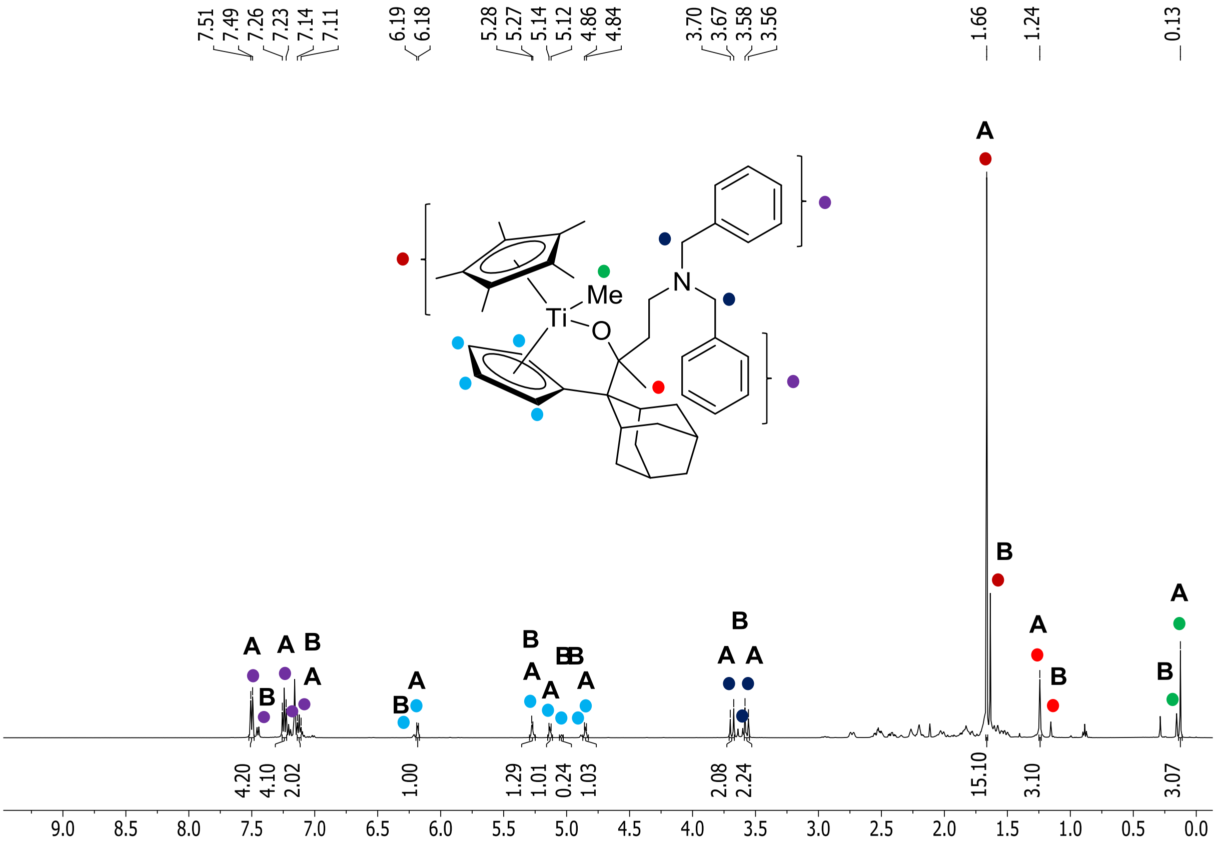


Figure S28: ^{1}H NMR spectrum of **3b** (500 MHz, C_6D_6, rt); diastereoisomer **A** and diastereoisomer **B**.

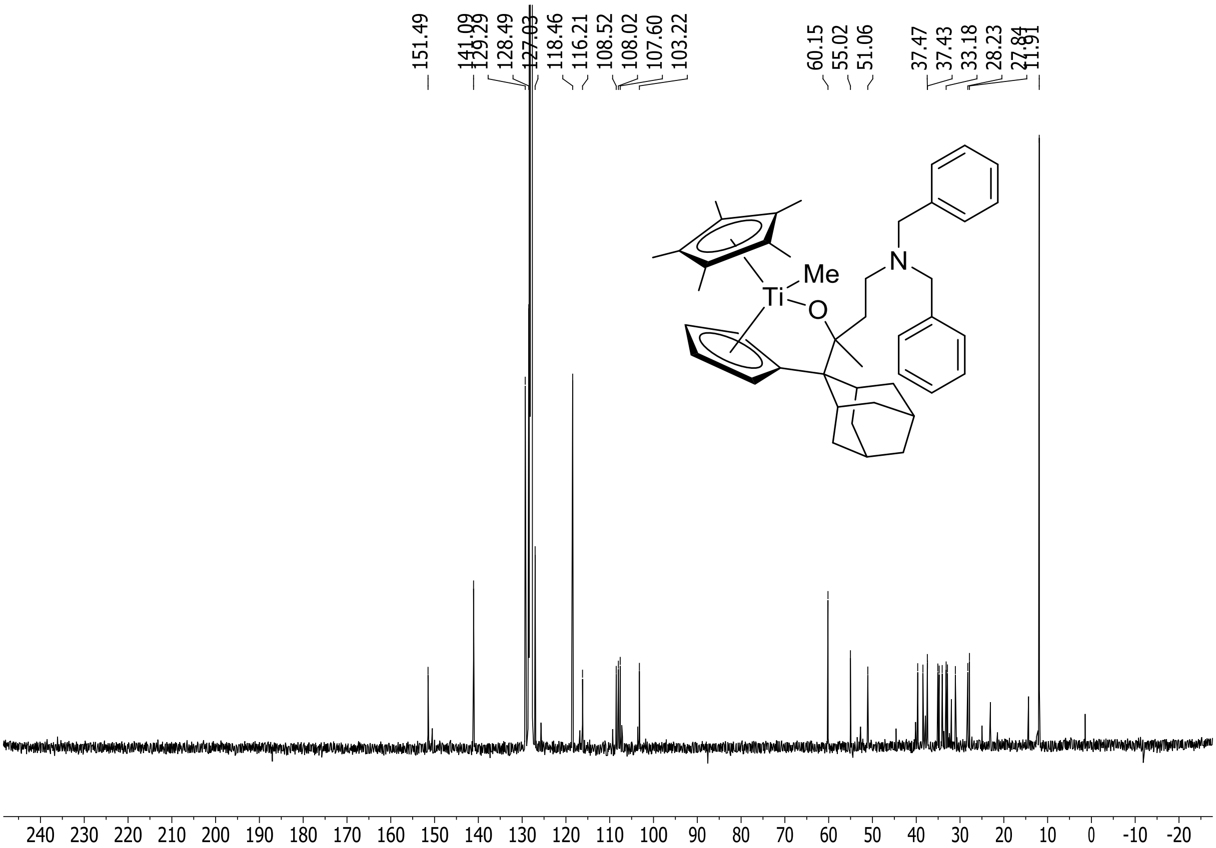


Figure S29: $^{13}C\{^{1}H\}$ NMR spectrum of **3b** (126 MHz, C_6D_6, rt); only clearly assignable signals of the main diastereoisomer are picked.

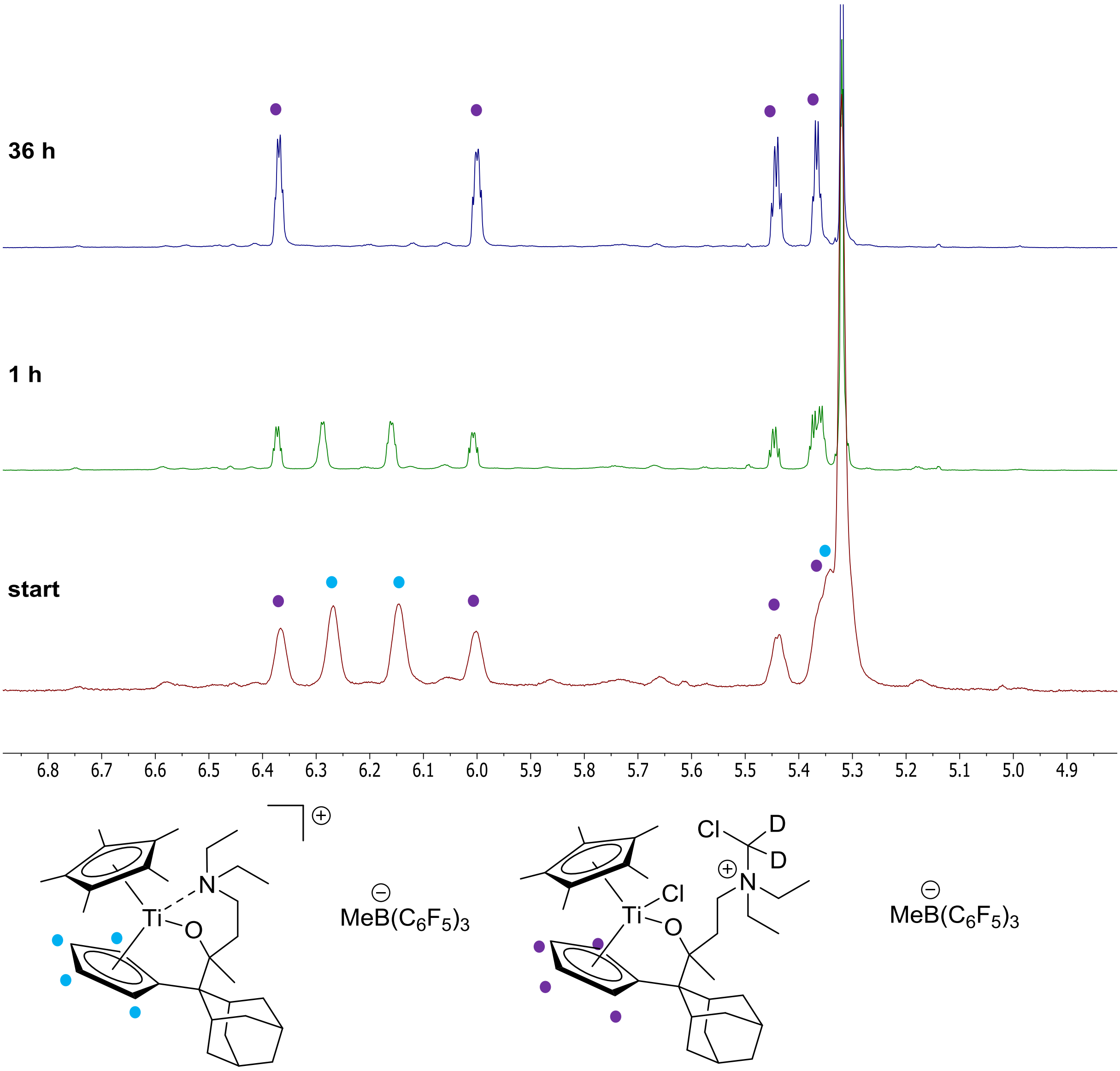


Figure S30: Excerpt of the ^{1}H NMR spectra of the reaction of **4a** with dichloromethane-*d*$_2$ (bottom: 300 MHz, CD_2Cl_2, rt; middle, top: 500 MHz, CD_2Cl_2, rt).

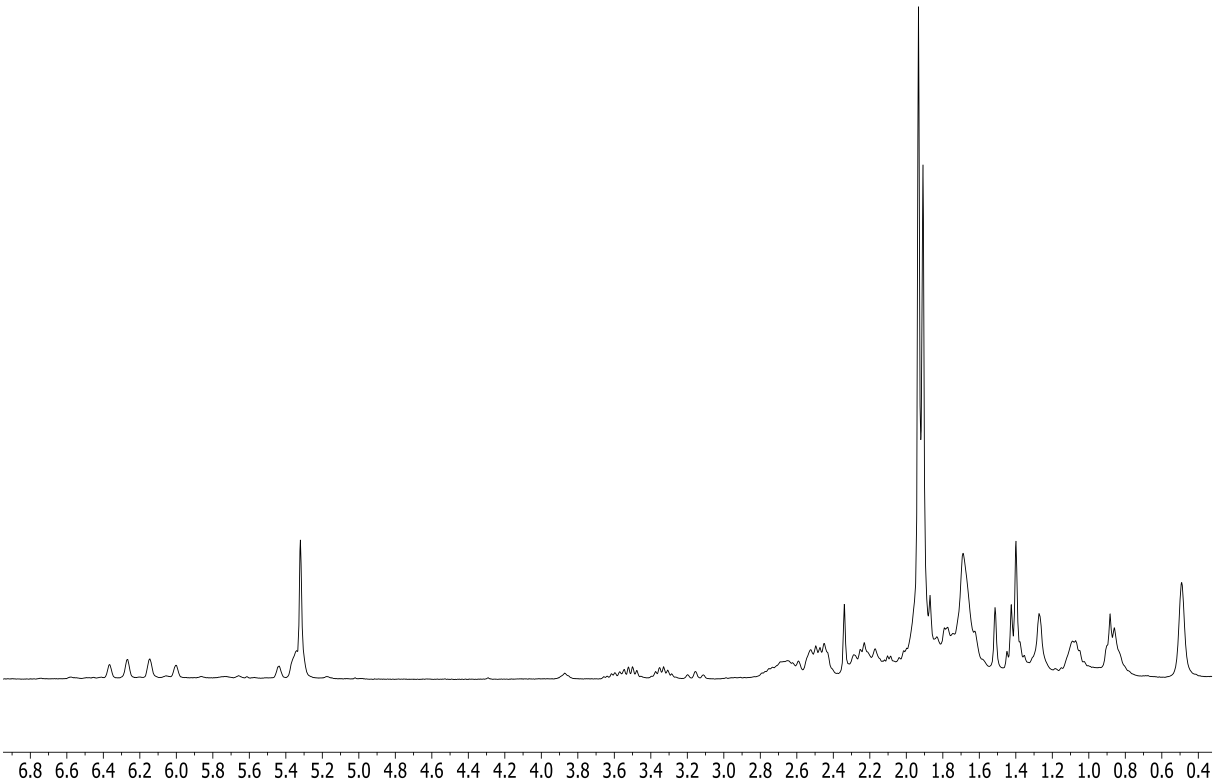


Figure S31: ^{1}H NMR spectrum after 5 minutes of the reaction of **4a** with dichloromethane-d_2 (300 MHz, CD_2Cl_2, rt).

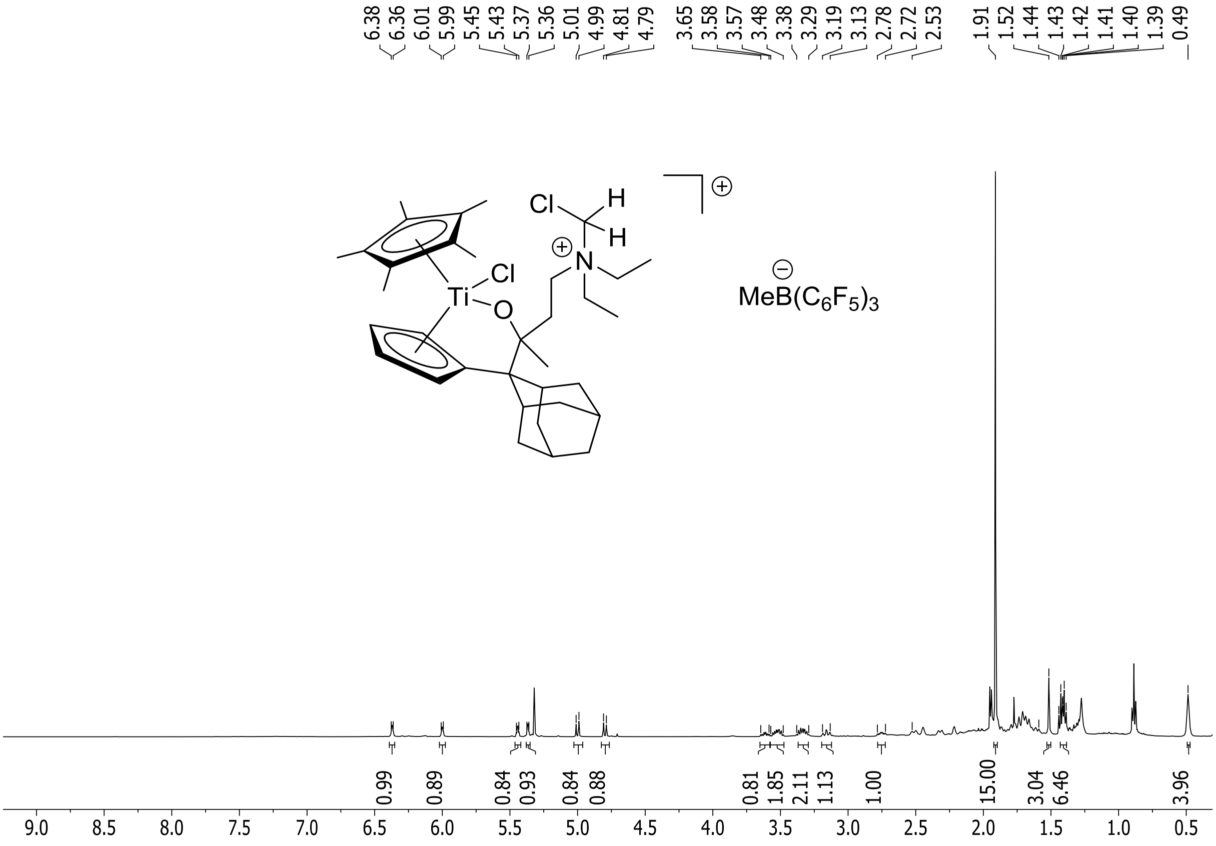


Figure S32: ^{1}H NMR spectrum of **5a** (500 MHz, CD_2Cl_2, rt); 0.89, 1.27 ppm: *n*-hexane.

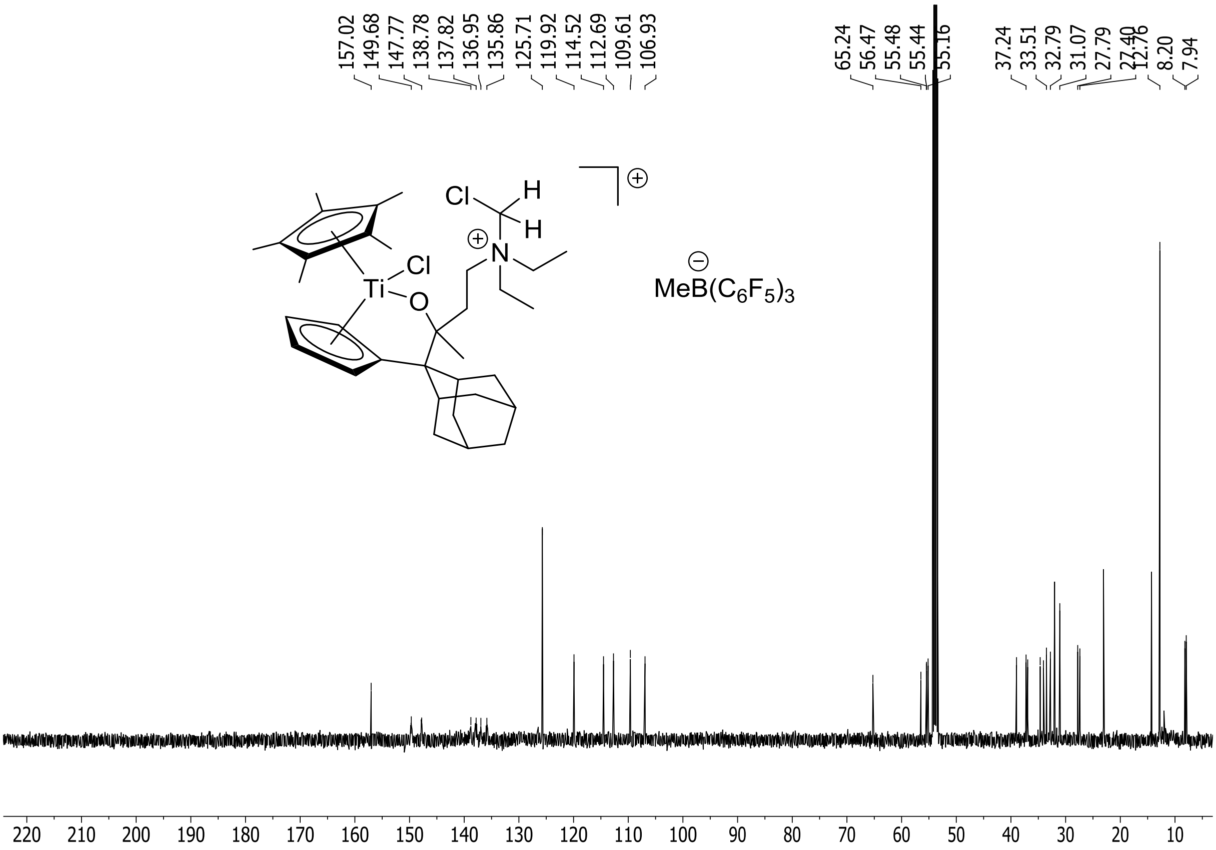


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum of **5a** (126 MHz, CD_2Cl_2, rt); 14.3, 23.1, 32.0 ppm: *n*-hexane.

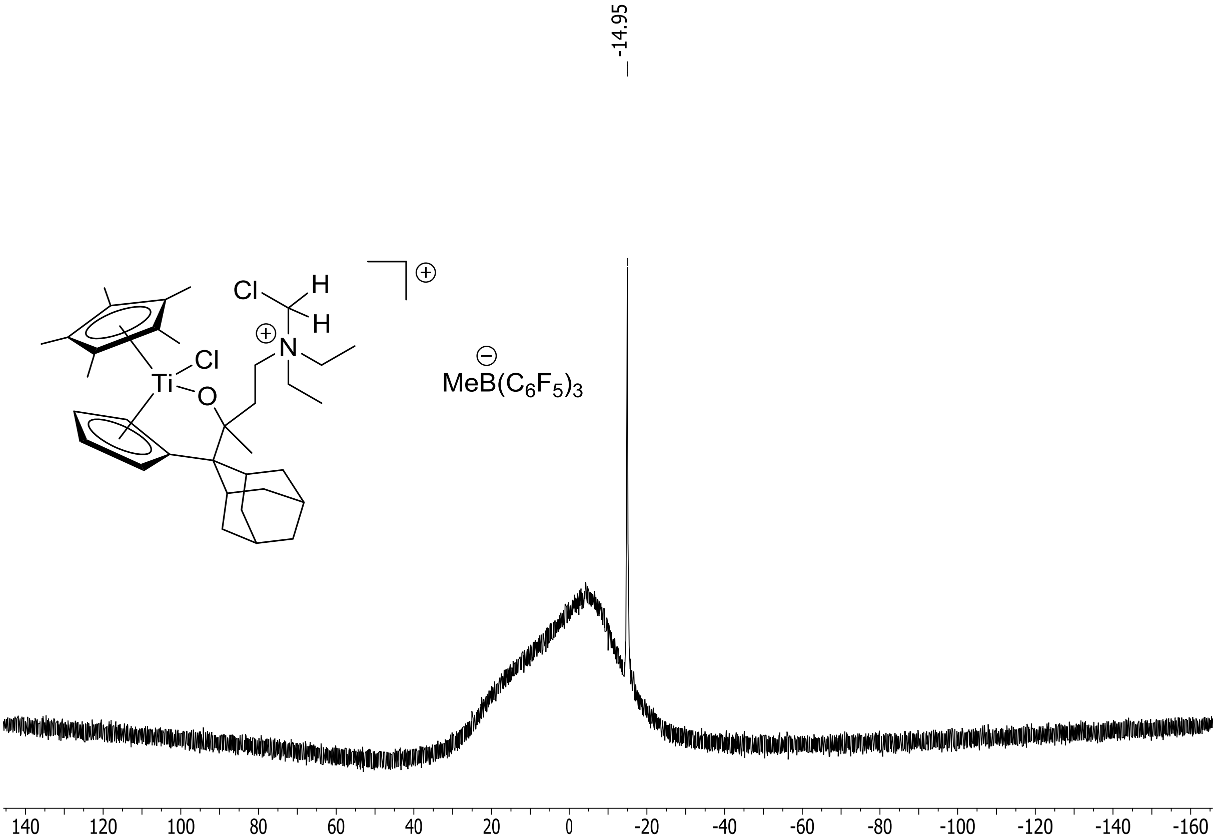


Figure S34: $^{11}B\{^{1}H\}$ NMR spectrum of **5a** (160 MHz, CD_2Cl_2, rt).

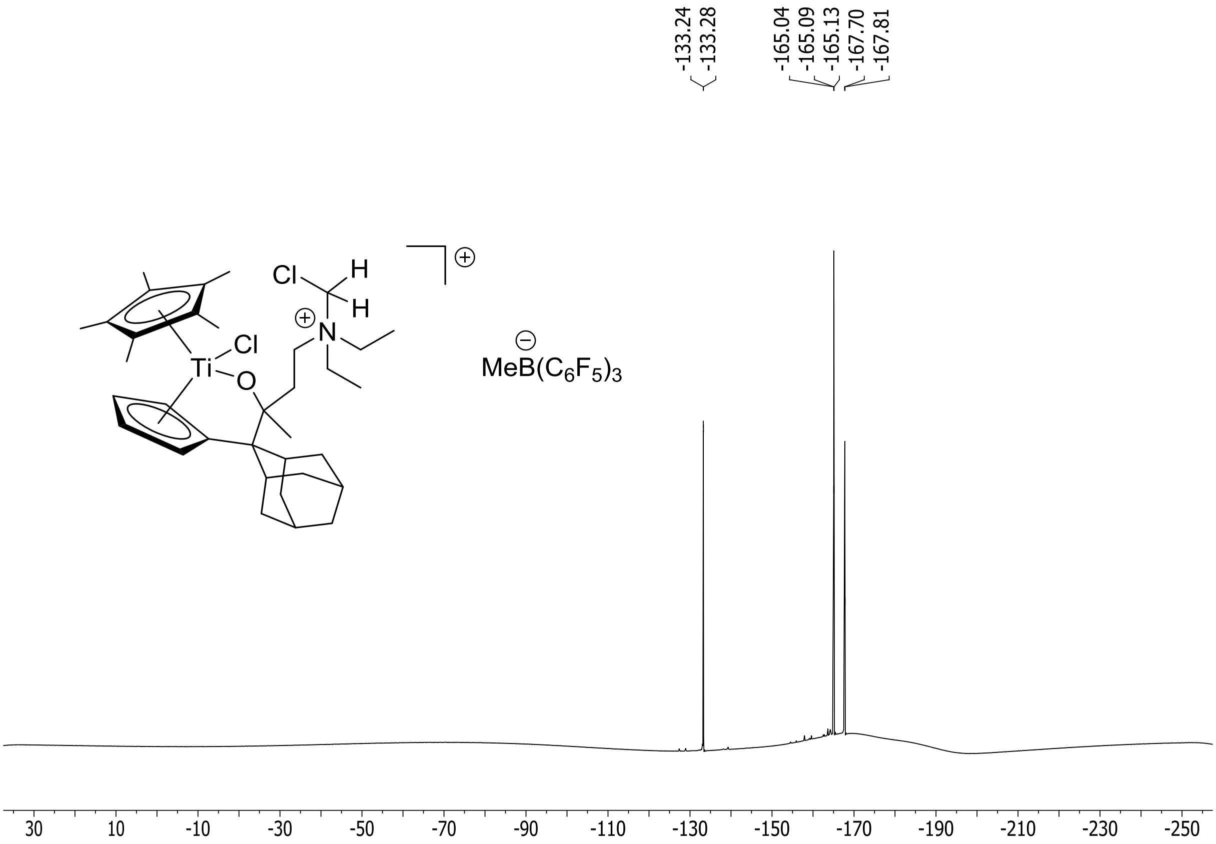


Figure S35: $^{19}F\{^1H\}$ NMR spectrum of **5a** (470 MHz, CD_2Cl_2, rt).

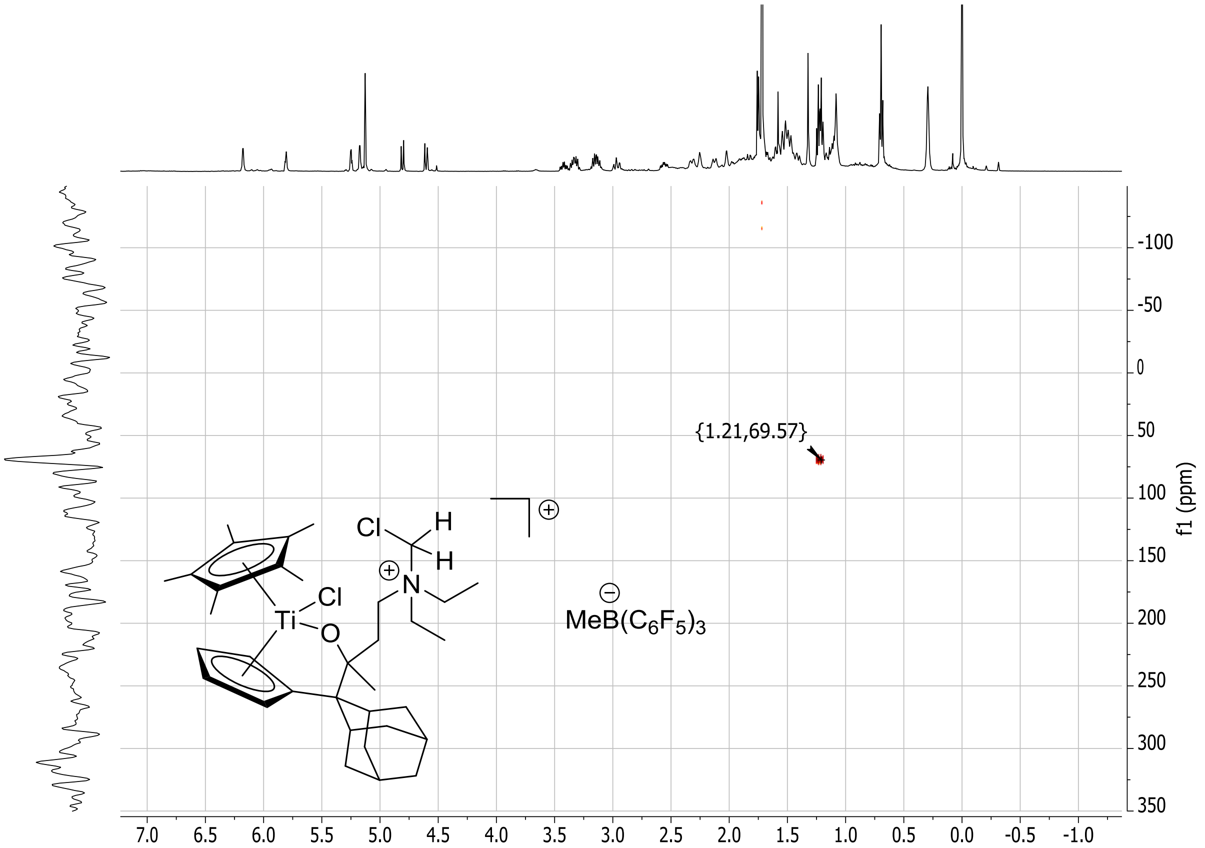


Figure S36: $^{15}N/^{1}H$ HMBC NMR spectrum of **5a** (51 MHz, CD_2Cl_2, rt).

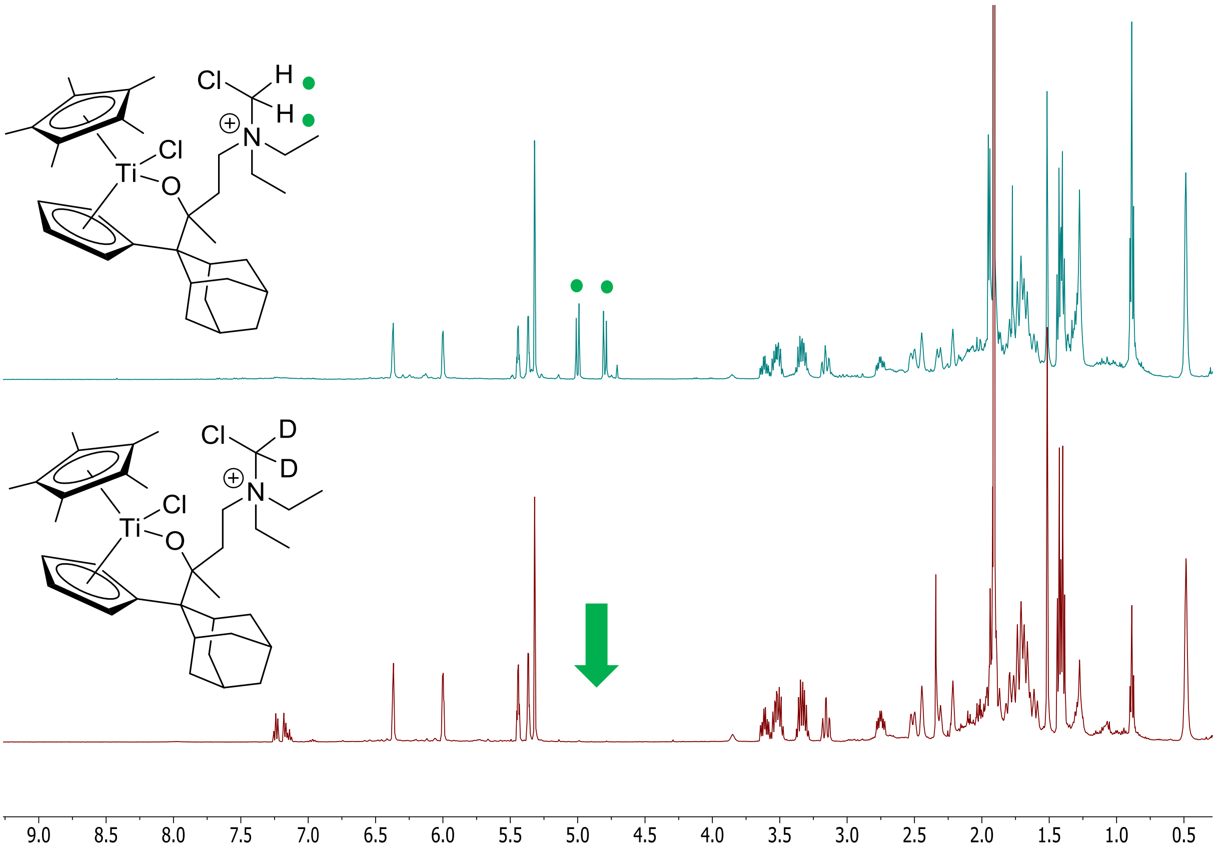


Figure S37: ^{1}H NMR spectra of **5a** (top) and **5a-*d*$_2$** (bottom) (500 MHz, CD$_2$Cl$_2$, rt); 0.89, 1.27 ppm: *n*-hexane; 2.34, 7.15-7.24 ppm: toluene (bottom).

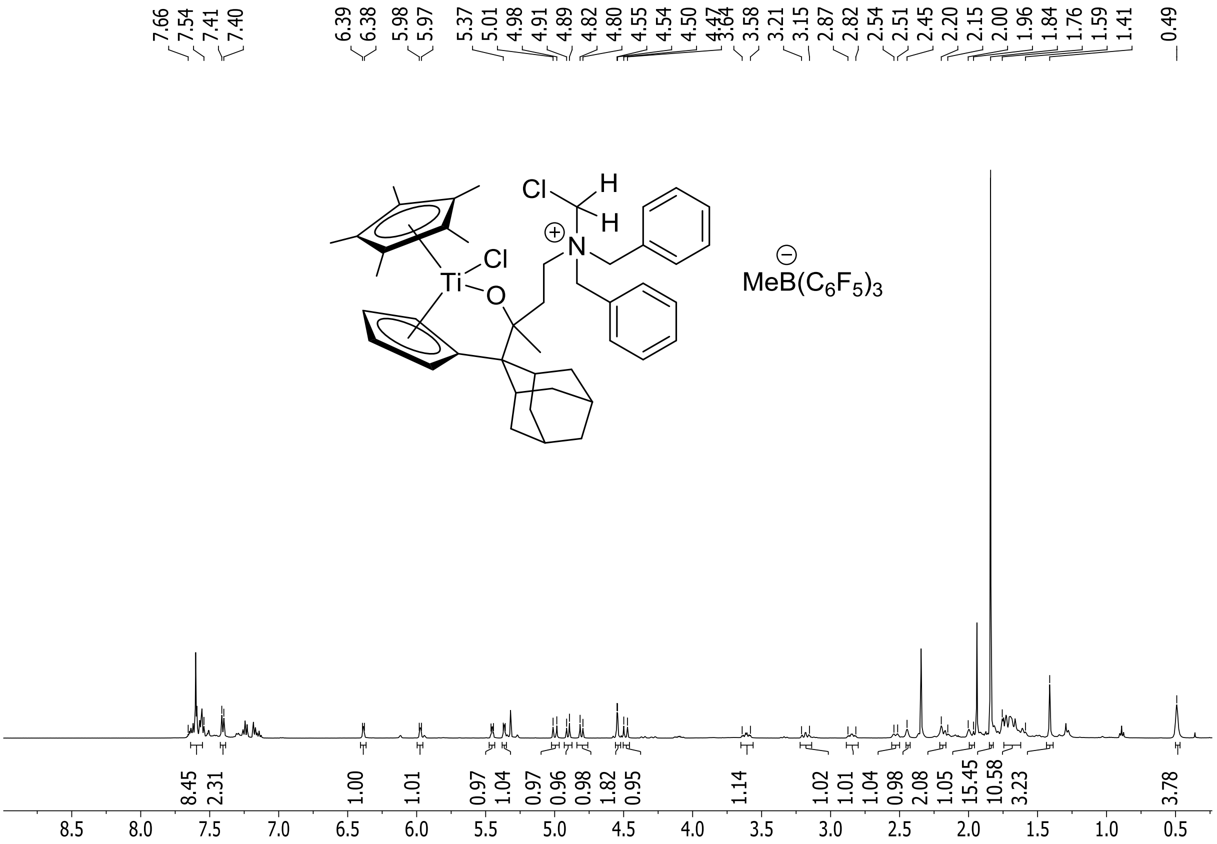


Figure S38: ^{1}H NMR spectrum of **5b** (500 MHz, CD_2Cl_2, rt); 2.34, 7.15-7.24 ppm: toluene.

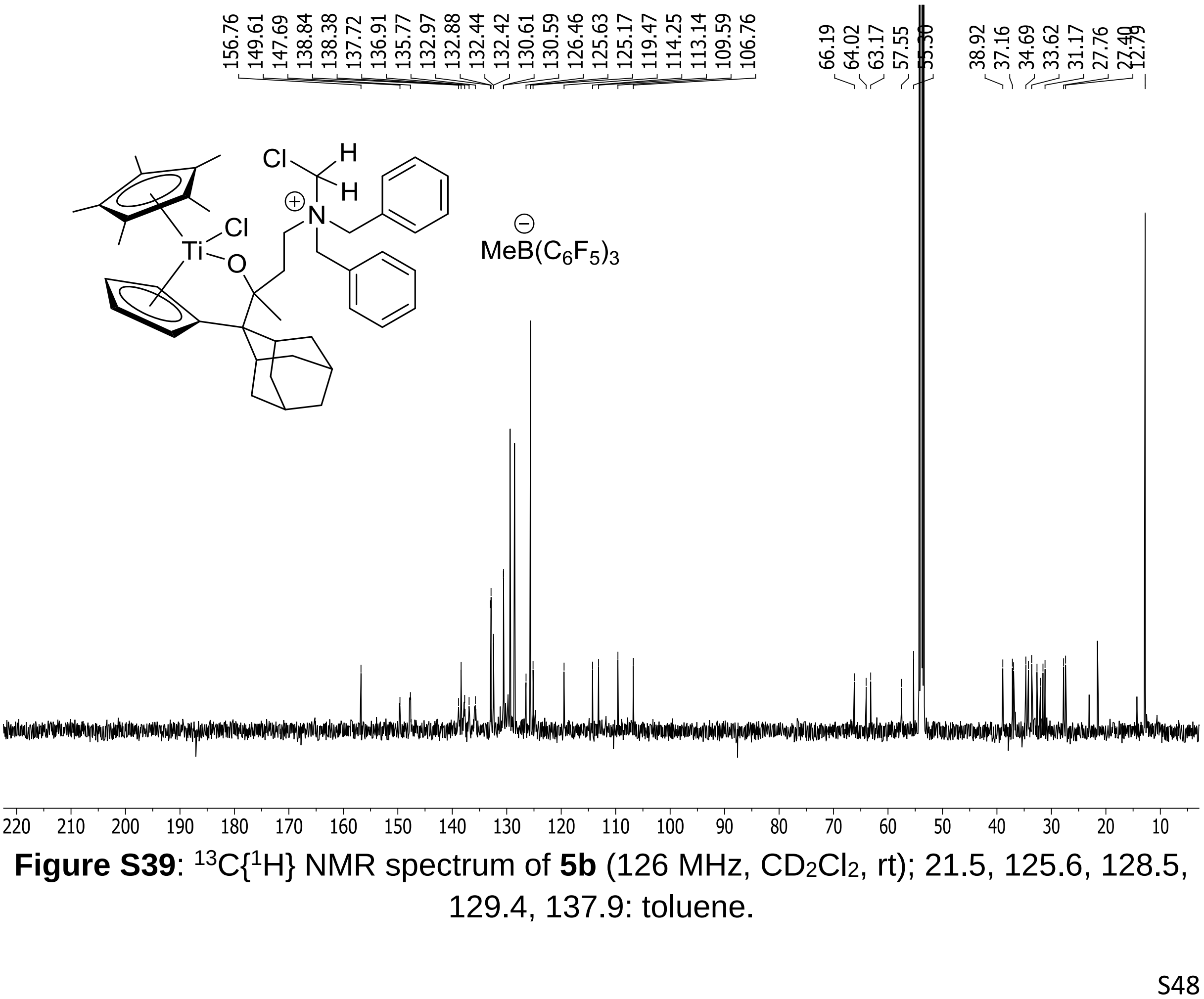


Figure S39: $^{13}C\{^1H\}$ NMR spectrum of **5b** (126 MHz, CD_2Cl_2, rt); 21.5, 125.6, 128.5, 129.4, 137.9: toluene.

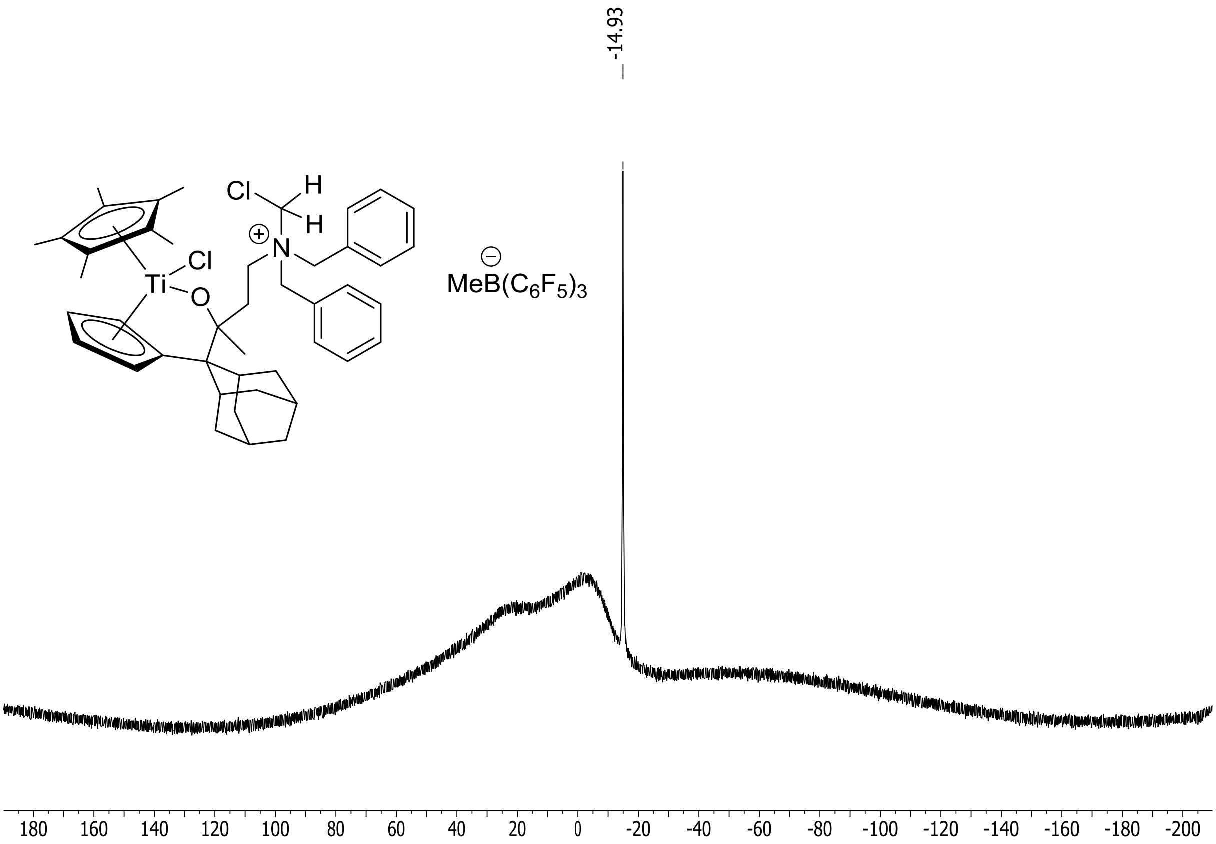


Figure S40: $^{11}B\{^1H\}$ NMR spectrum of **5b** (160 MHz, CD_2Cl_2, rt).

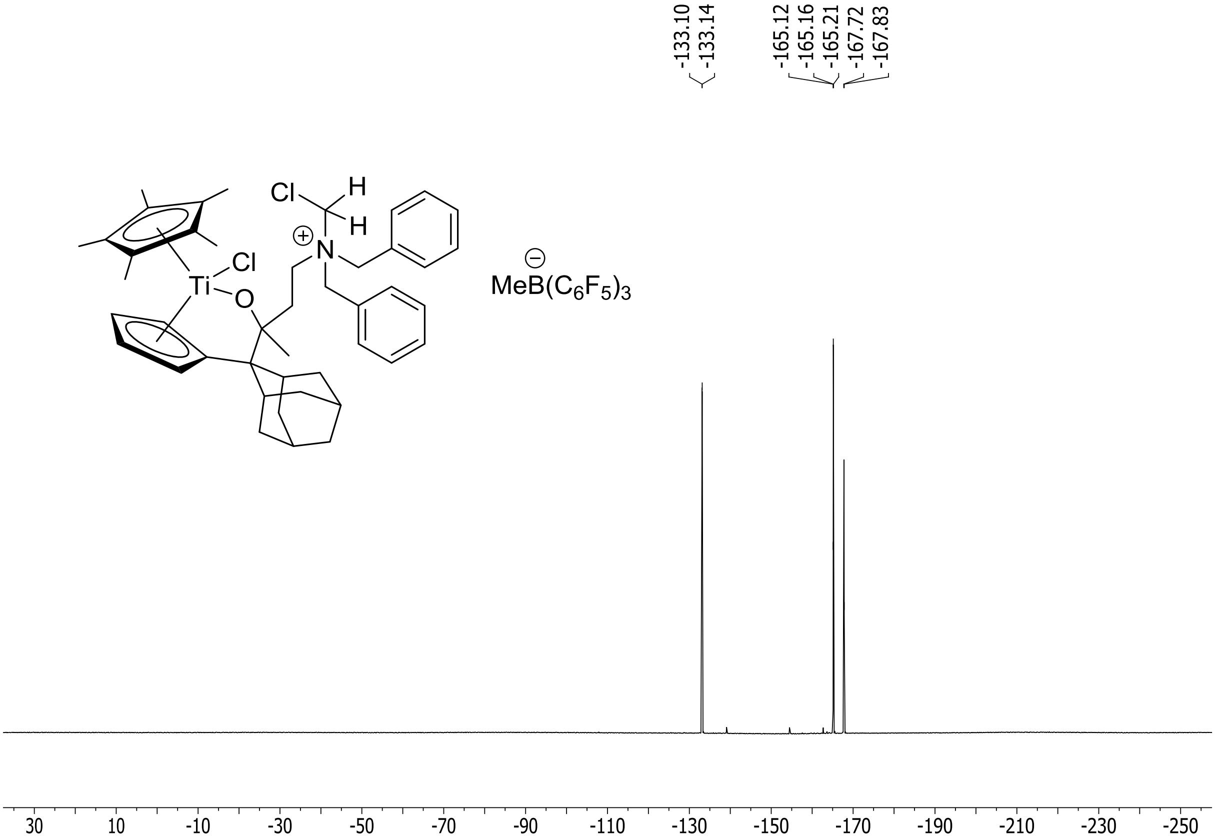


Figure S41: $^{19}F\{^1H\}$ NMR spectrum of **5b** (470 MHz, CD_2Cl_2, rt).

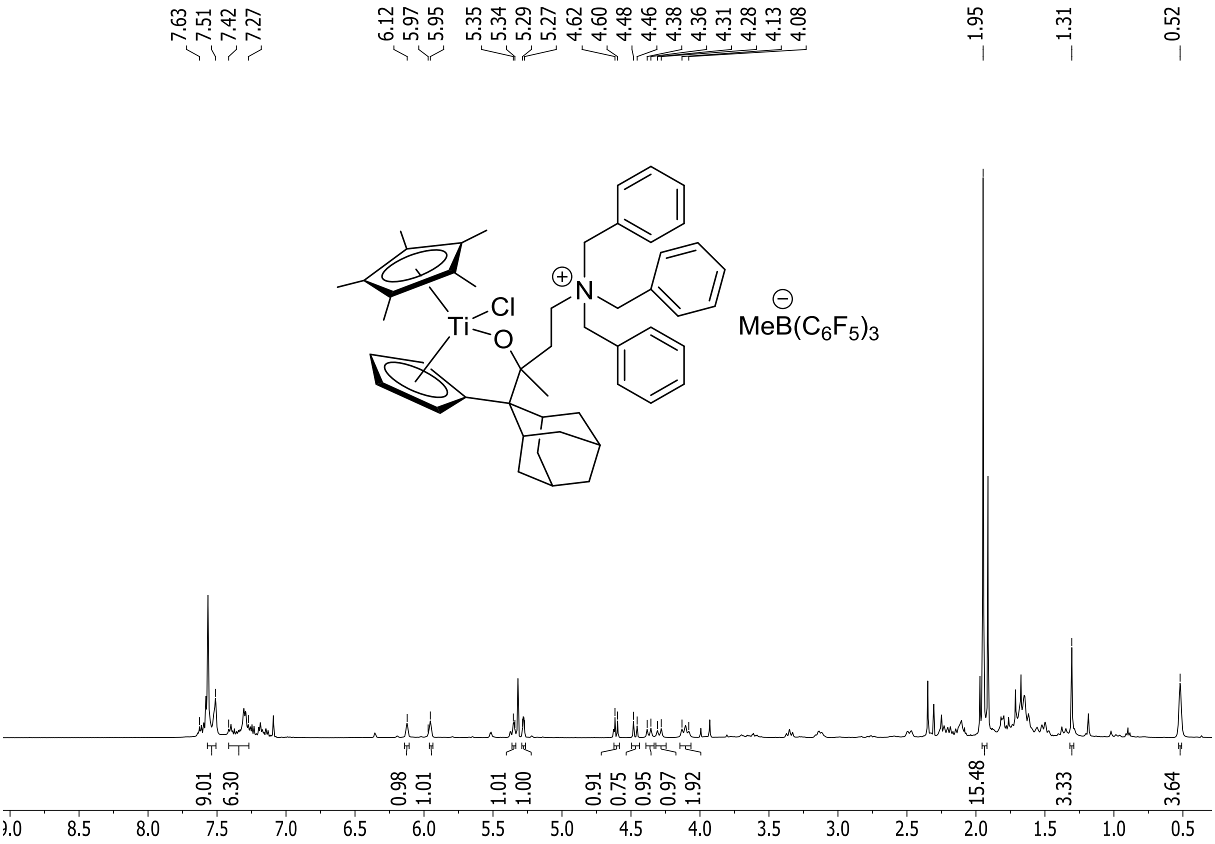


Figure S42: ^{1}H NMR spectrum of **6** (500 MHz, CD_2Cl_2, rt); 2.34, 7.15-7.24 ppm: toluene.

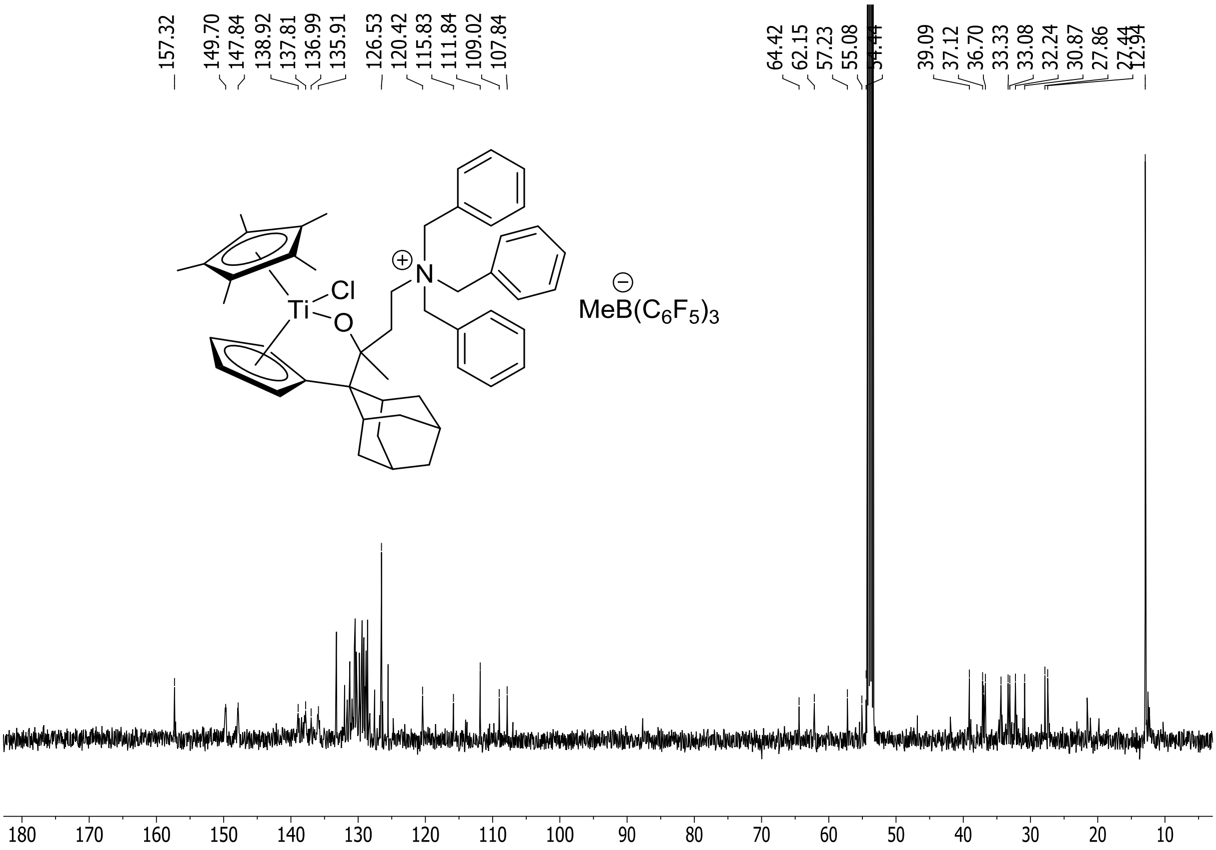


Figure S43: $^{13}C\{^{1}H\}$ NMR spectrum of **6** (126 MHz, CD_2Cl_2, rt); 21.5, 125.6, 128.5, 129.4, 137.9: toluene.

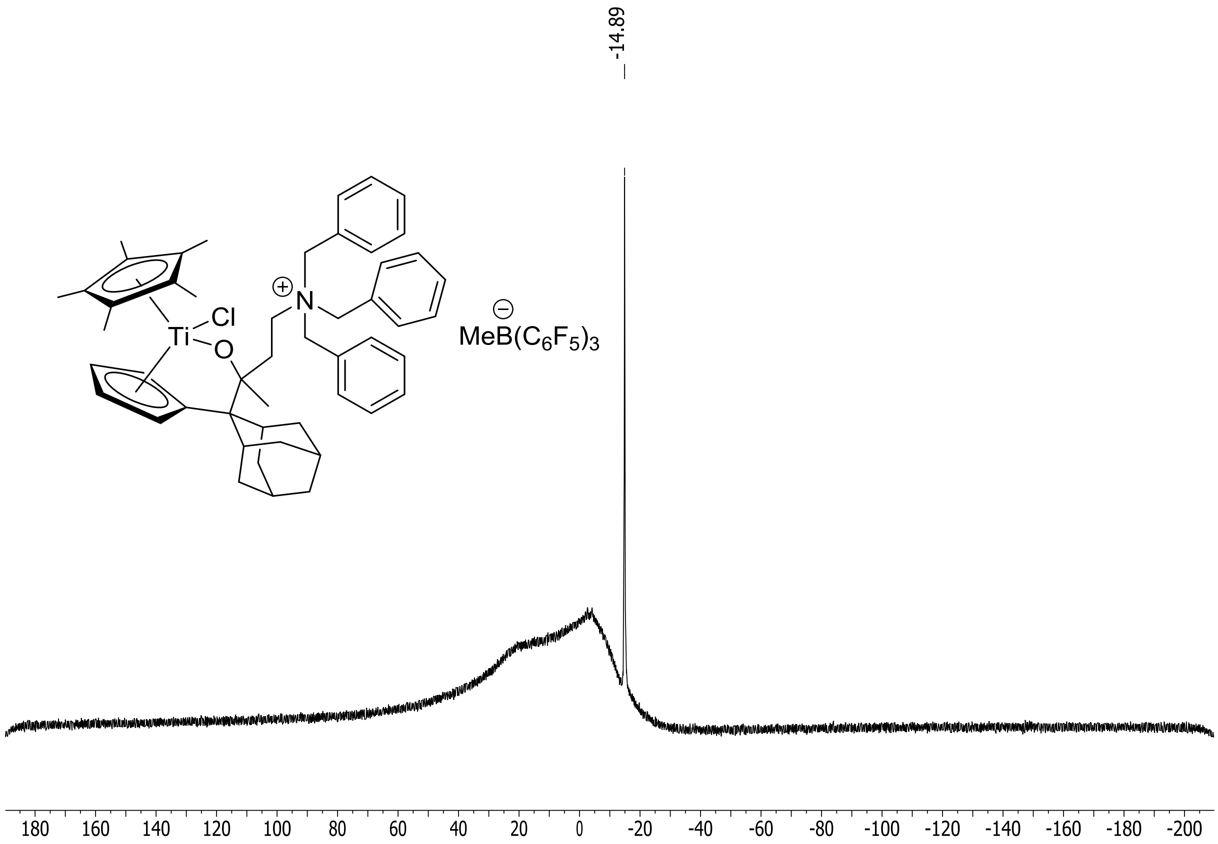


Figure S44: $^{11}B\{^1H\}$ NMR spectrum of **6** (160 MHz, CD_2Cl_2, rt).

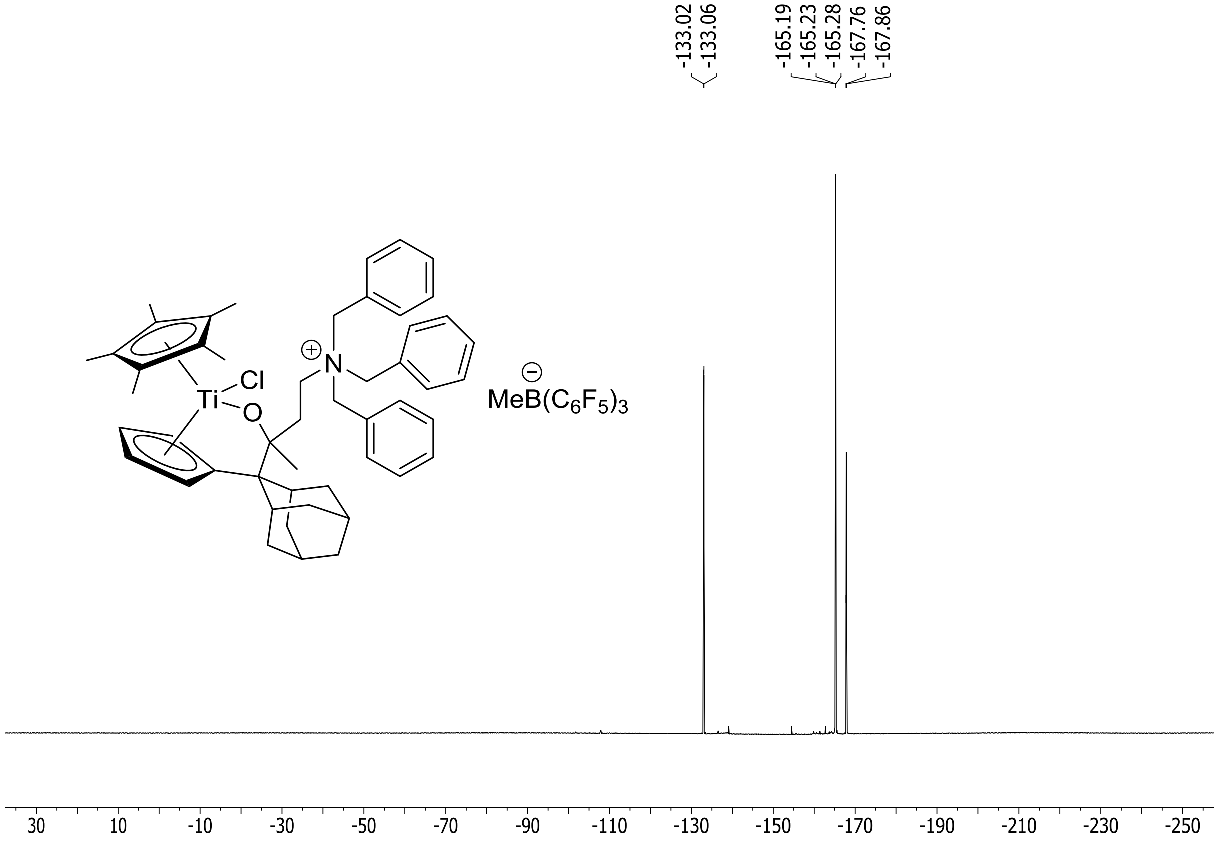


Figure S45: $^{19}F\{^1H\}$ NMR spectrum of **6** (470 MHz, CD_2Cl_2, rt).

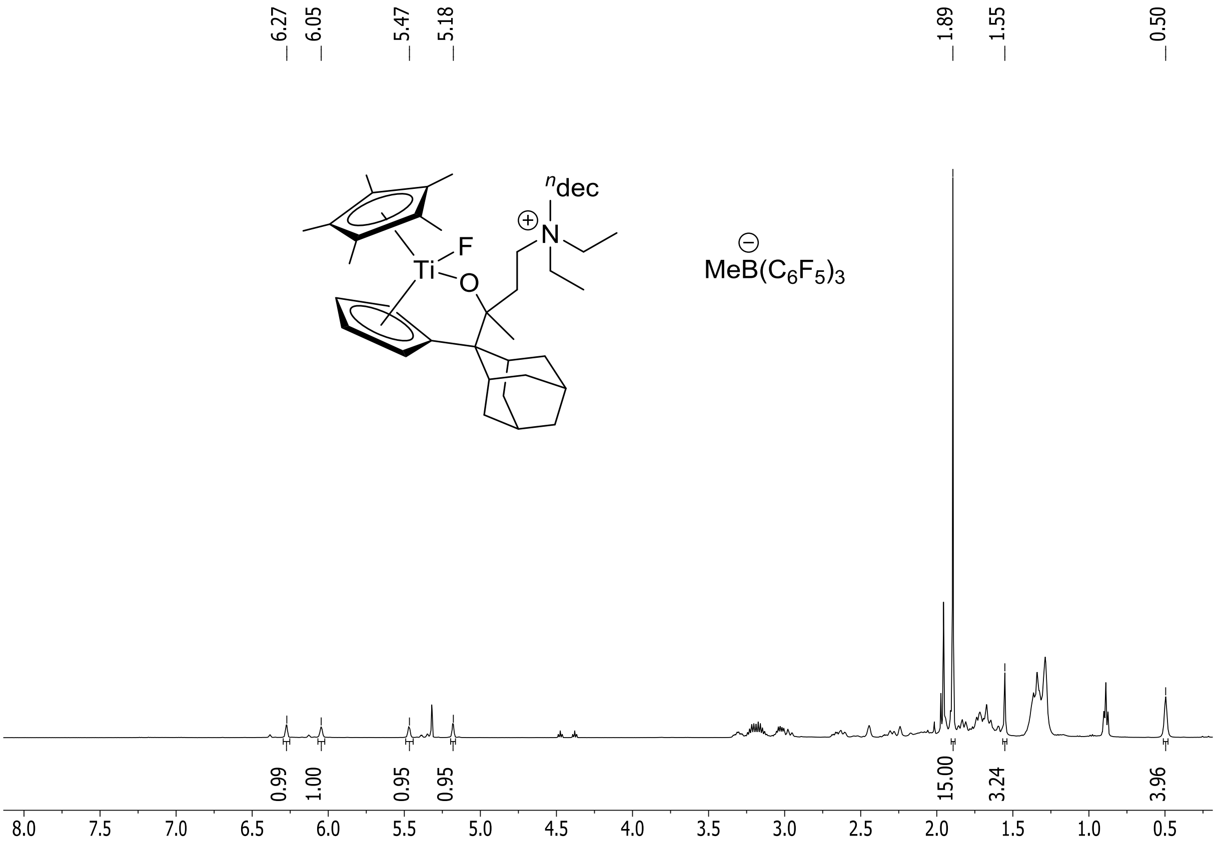


Figure S46: ^{1}H NMR spectrum of **7a** (500 MHz, CD$_2$Cl$_2$, rt); 0.89, 1.27 ppm: *n*-hexane, e.g. 4.38, 4.48 ppm: residue of *n*-fluorodecane.

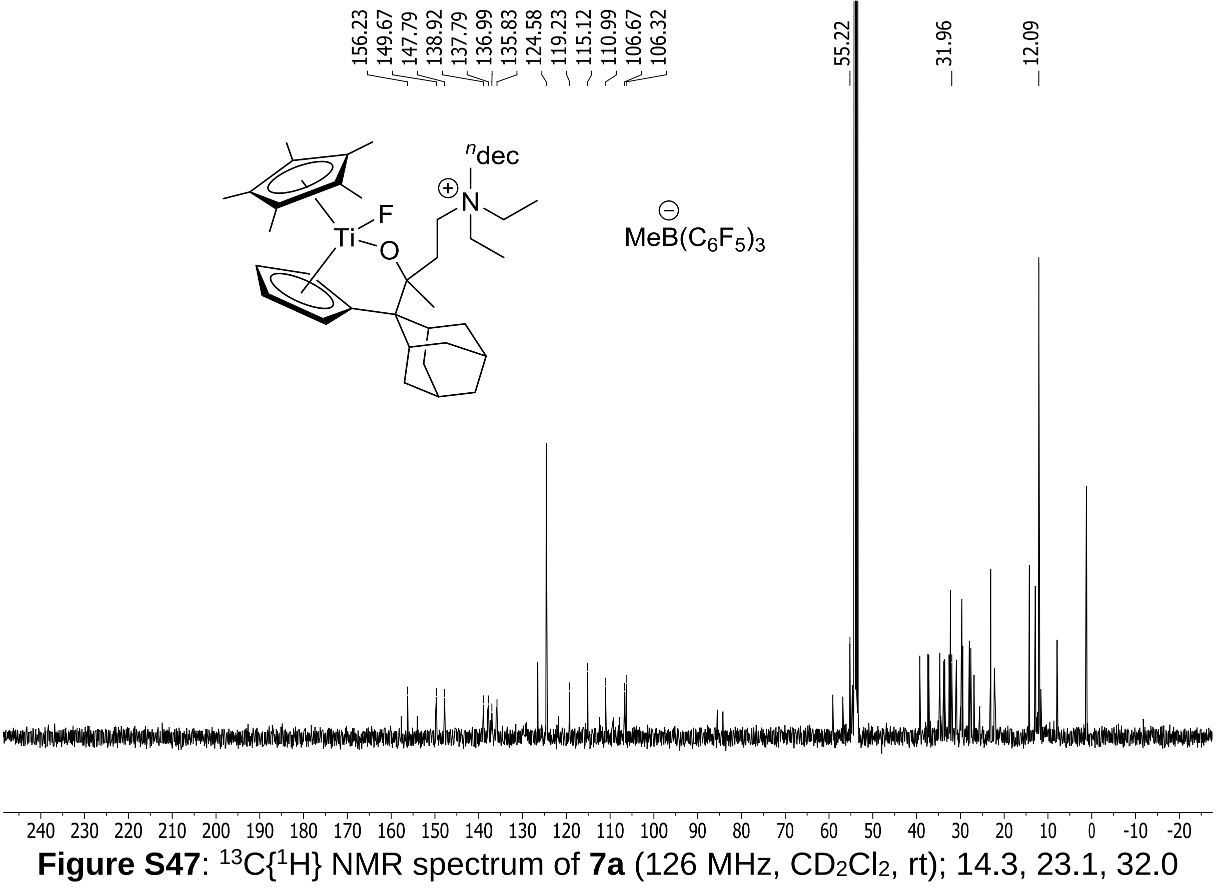


Figure S47: ^{13}C{^{1}H} NMR spectrum of **7a** (126 MHz, CD$_2$Cl$_2$, rt); 14.3, 23.1, 32.0 ppm: *n*-hexane.

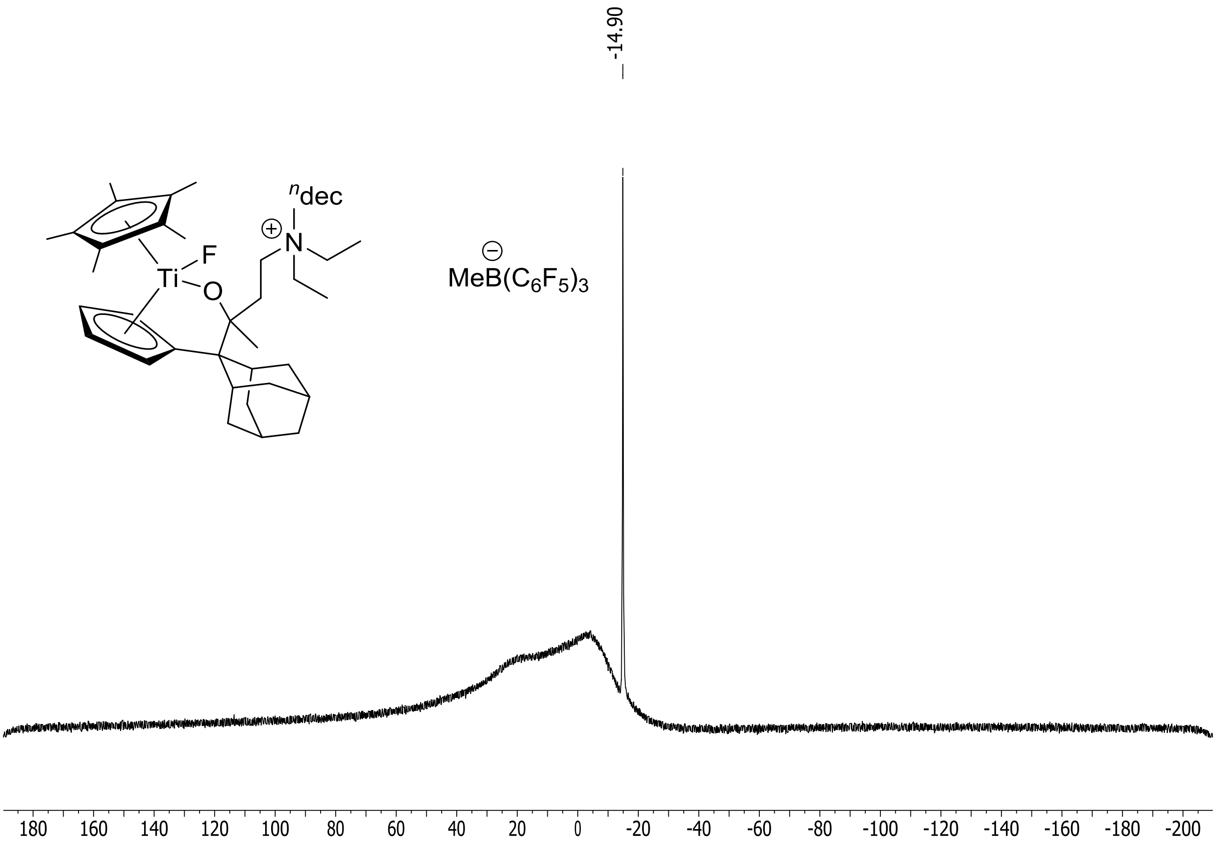


Figure S48: ^{11}B{^{1}H} NMR spectrum of **7a** (160 MHz, CD$_2$Cl$_2$, rt).

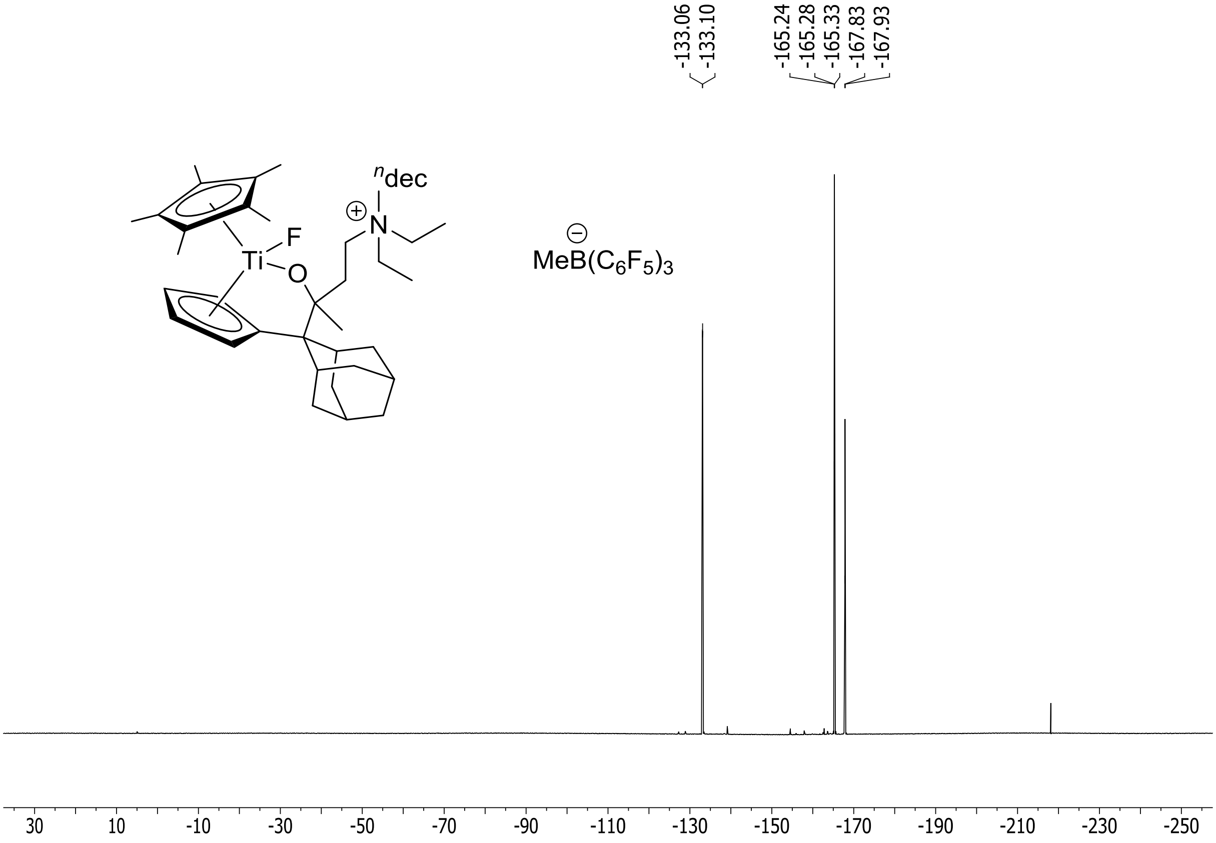


Figure S49: ^{19}F{^{1}H} NMR spectrum of **7a** (470 MHz, CD$_2$Cl$_2$, rt); -218.1 ppm: *n*-fluorodecane.

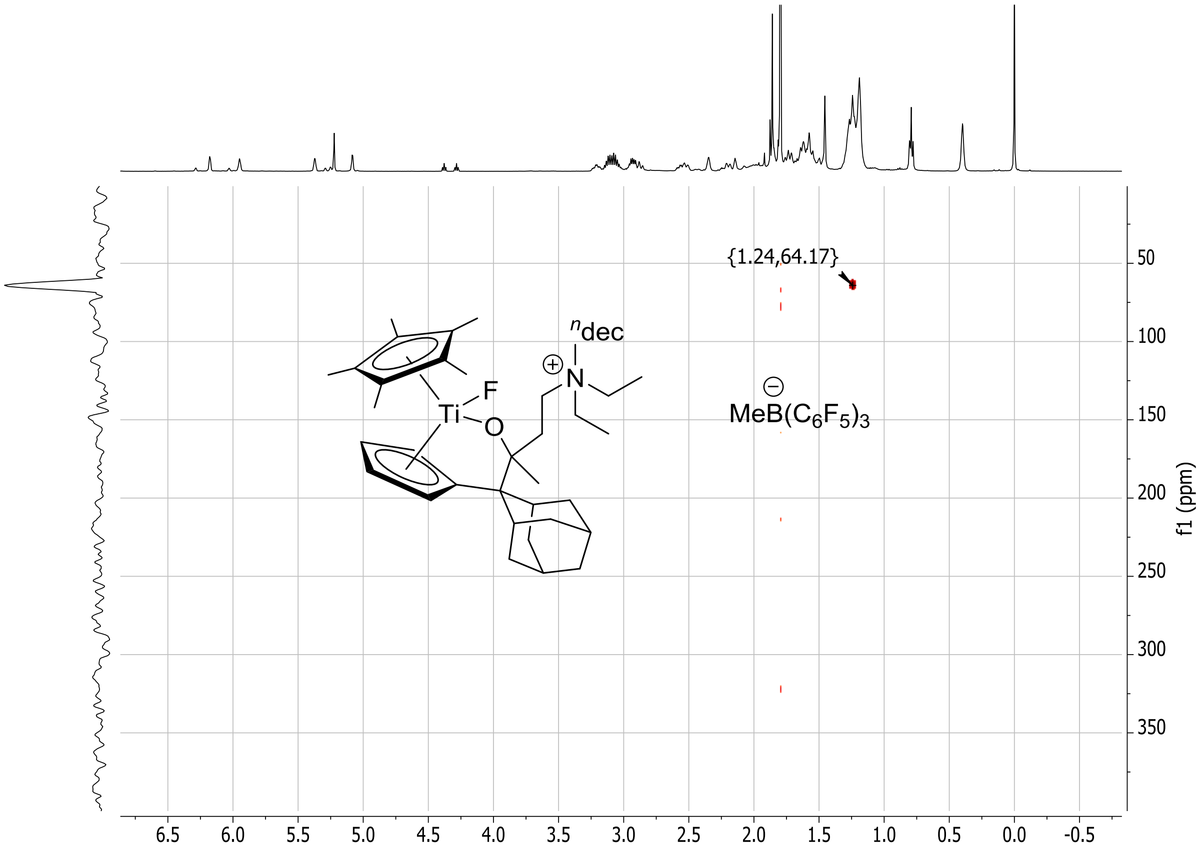


Figure S50: $^{15}N/^{1}H$ HMBC NMR spectrum of **7a** (51 MHz, CD_2Cl_2, rt).

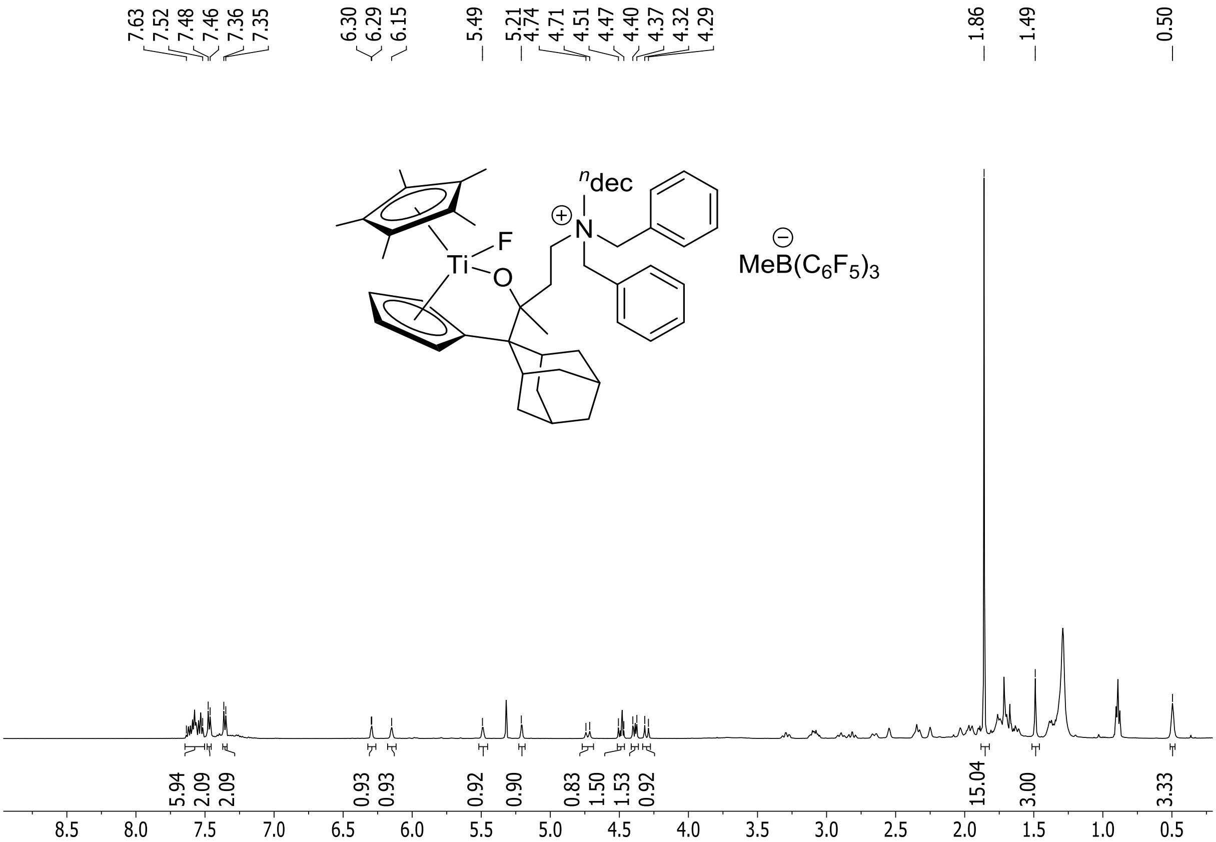


Figure S51: ^{1}H NMR spectrum of **7b** (500 MHz, CD_2Cl_2, rt); 0.89, 1.27 ppm: *n*-hexane, e.g. 4.38, 4.48 ppm: residue of *n*-fluorodecane.

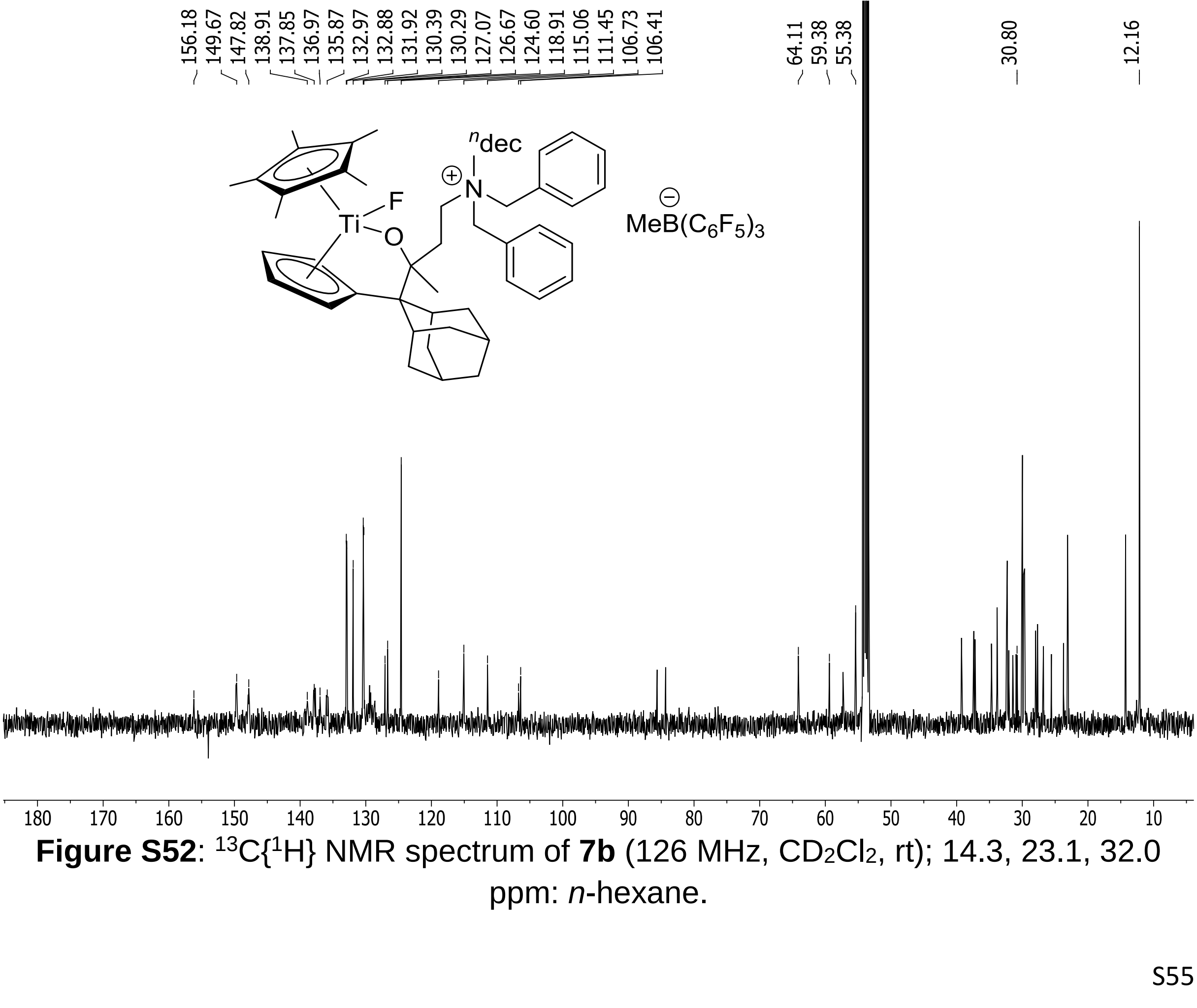


Figure S52: $^{13}C\{^{1}H\}$ NMR spectrum of **7b** (126 MHz, CD_2Cl_2, rt); 14.3, 23.1, 32.0 ppm: *n*-hexane.

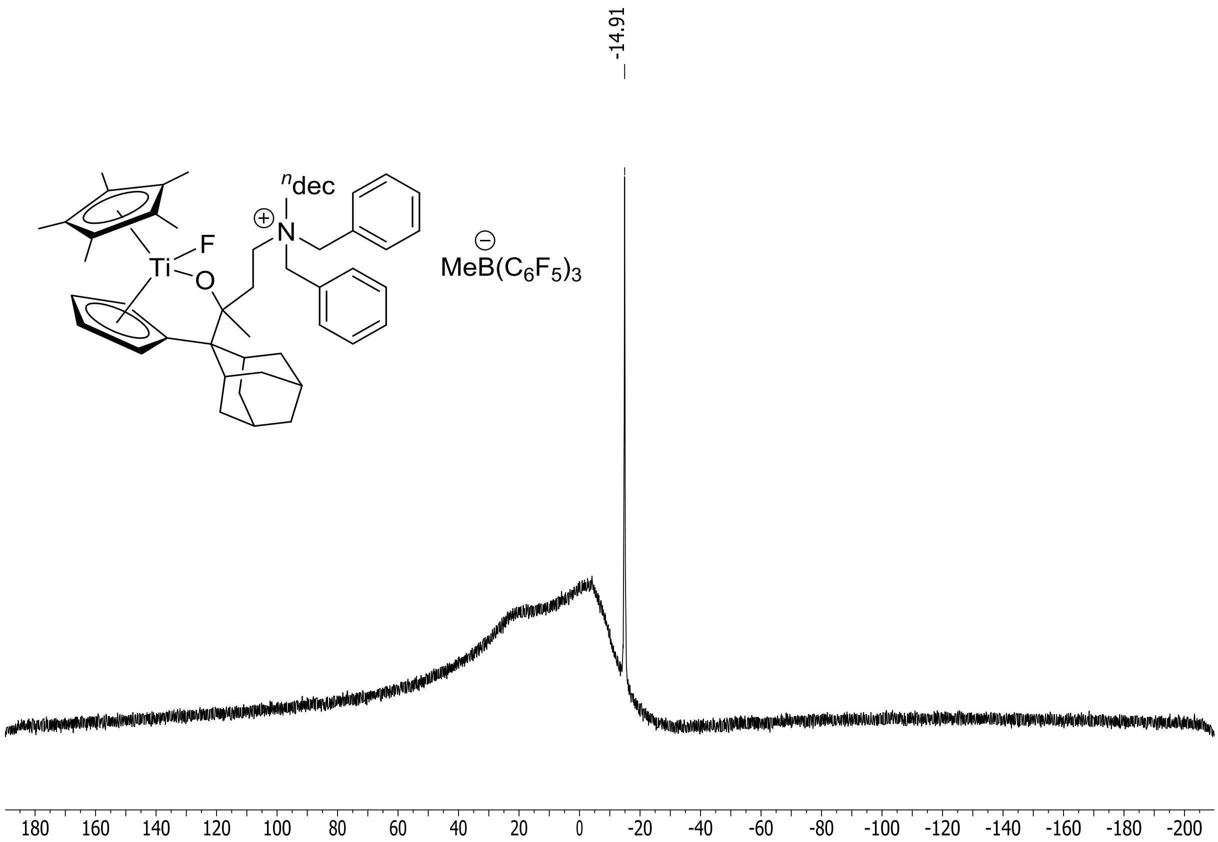


Figure S53: ^{11}B{^{1}H} NMR spectrum of **7b** (160 MHz, CD_2Cl_2, rt).

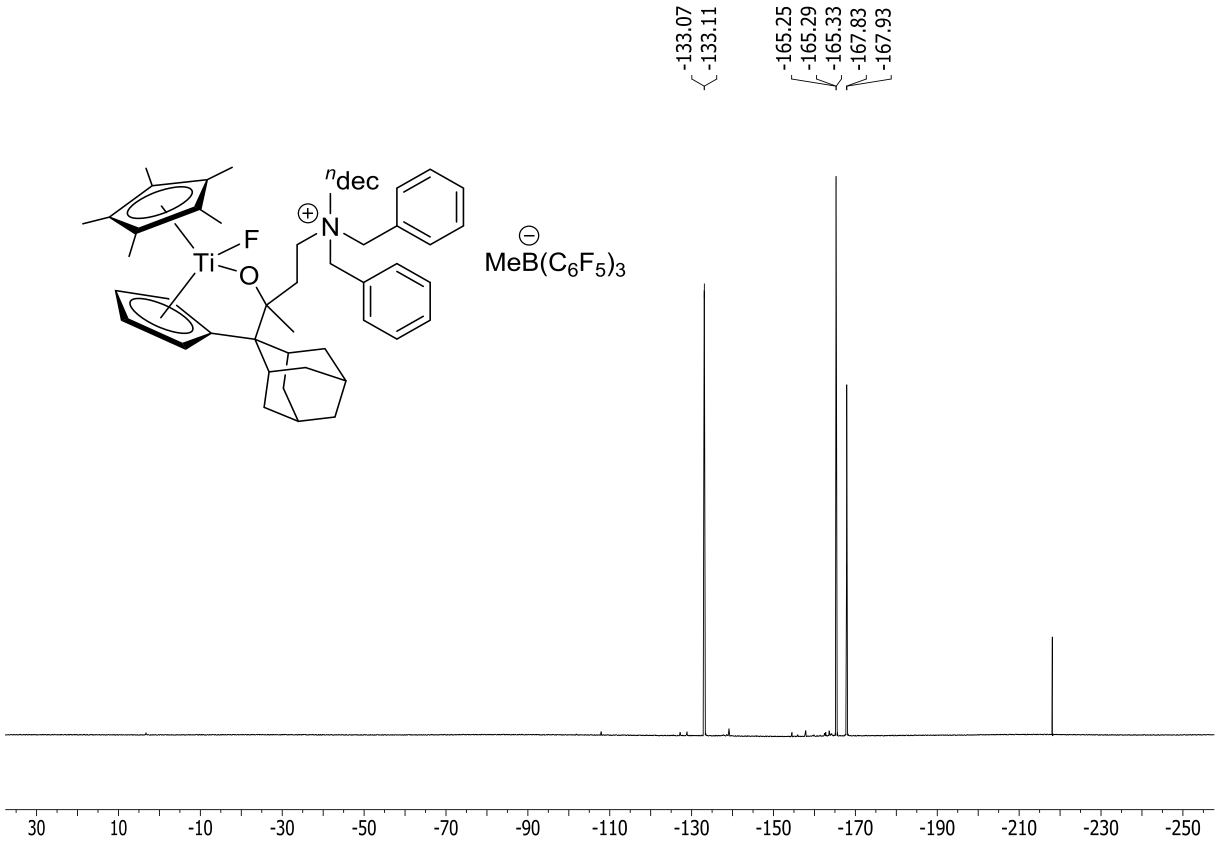


Figure S54: ^{19}F{^{1}H} NMR spectrum of **7b** (470 MHz, CD_2Cl_2, rt); -218.1 ppm: *n*-fluorodecane.

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