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 CaH₂ 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 CaCl₂, 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-d₆ (C₆D₆): δ¹H(C₆D₆H) = 7.16 ppm, dichloromethane-d₂ (CD₂Cl₂): δ¹H(CDHC₁₈) = 5.32 ppm) and ¹³C(¹H) spectra were referenced by using the central line of the solvent signal (benzene-d₆ (C₆D₆): δ¹³C(¹H)(C₆D₆) = 128.06 ppm, dichloromethane-d₂ (CD₂Cl₂): δ¹³C(¹H)(CD₂Cl₈) = 53.84 ppm). ¹¹B(¹H) NMR, and ¹⁹F(¹H) NMR spectra were referenced against external standards (BF₃•OEt₂ (δ¹¹B(¹H)(BF₃•OEt₂) = 0.0 ppm; CFC₁₈ (δ¹⁹F(¹H)(CFC₁₈) = 0.0 ppm)). The given chemical shifts of ¹⁵N result out of ¹⁵N, ¹H HMBC NMR experiments with nitromethane as external standard (δ = 378.9 vs. NH₃).

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:

![Chemical structure 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$_6$D$_6$, 299 K): $\delta = 0.88$ (t, $^3J_{H,H} = 7.1$ Hz, 6H, 2×CH$_2$CH$_3$), 1.70 (s, 3H, O=CH$_3$), 2.14 (t, $^3J_{H,H} = 7.0$ Hz, NCH$_2$CH$_2$), 2.29 (q, $^3J_{H,H} = 7.1$ Hz, 2×CH$_2$CH$_3$), 2.58 (t, $^3J_{H,H} = 7.0$ Hz, NCH$_2$CH$_2$) ppm.

$^{13}$C{$^1$H} NMR (126 MHz, C$_6$D$_6$, 299 K): $\delta = 12.3$ (2×CH$_2$CH$_3$), 29.7 (OC$_2$CH$_3$), 41.9 (NCH$_2$CH$_2$), 47.2 (2×CH$_2$CH$_3$), 48.2 (NCH$_2$CH$_2$), 206.0 (O=CH$_3$) ppm.

$^{15}$N-NMR (202 MHz, C$_6$D$_6$, 299 K): $\delta = 44.4$ 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 cm$^{-1}$.

**$^1$H NMR** (500 MHz, C$_6$D$_6$, 305 K): $\delta$ = 1.55 (s, 3H, CH$_3$), 2.15 (t, $^3\tilde{J}_{H,H} = 7.1$ Hz, 2H, NCH$_2$CH$_2$), 2.63 (t, $^3\tilde{J}_{H,H} = 7.1$ Hz, 2H, NCH$_2$CH$_2$), 3.36 (s, 4H, CH$_2$Ph), 7.07-7.10 (m, 2H, 2×p-CH$_{Ph}$CH$_2$), 7.16-7.19 (4×o-CH$_{Ph}$CH$_2$)*, 7.29-7.31 (m, 4H, 4×o-CH$_{Ph}$CH$_2$) ppm.

**$^{13}$C{$^1$H} NMR** (126 MHz, C$_6$D$_6$, 305 K): $\delta$ = 28.9 (O=C$_q$CH$_3$), 41.7 (NCH$_2$CH$_2$), 48.7 (NCH$_2$CH$_2$), 58.5 (2×CH$_2$Ph), 127.2 (2×p-CH$_{Ph}$CH$_2$), 128.4 (4×m-CH$_{Ph}$CH$_2$), 129.1 (4×o-CH$_{Ph}$CH$_2$), 139.7 (2×C$_q$Ph), 205.4 (O=C$_q$CH$_3$) ppm.

* = overlap with C$_6$D$_6$ signal

**$^{15}$N-NMR** (202 MHz, C$_6$D$_6$, 305 K): $\delta$ = 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 diastereoisomers (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): $\tilde{\nu} = 2964, 2902, 2854, 1712, 1481, 1450, 1373, 1205, 1171, 1147, 1119, 1097, 1064, 1043, 1022, 979, 960, 943, 875, 851, 811, 792, 732, 691, 659, 635 \text{ cm}^{-1}$.  

$^1$H NMR (500 MHz, C$_6$D$_6$, 299 K): $\delta = 1.18$ (t, $^3J_{H,H} = 7.1$ Hz, 6H, 2×CH$_2$C$_6$H$_3$), 1.47 (s, 3H, OC$_q$CH$_3$), 1.78 (s, 15H, C$_5$Me$_5$), 5.04-5.06 (m, 1H, C$_5$H$_4$), 5.42-5.44 (m, 2H, 2×C$_5$H$_4$), 6.46-6.47 (m, 1H, C$_5$H$_4$) ppm.  

$^{13}$C($^1$H) NMR (126 MHz, C$_6$D$_6$, 299 K): $\delta = 12.6$ (C$_5$Me$_5$), 12.7 (2×CH$_2$C$_6$H$_3$) 27.6 (C$_{Ad}$), 28.0 (CH$_{Ad}$), 31.4 (OC$_q$C$_6$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×CH$_2$C$_6$H$_3$), 54.8 (C$_{q,exo}$), 104.3 (C$_5$H$_4$), 112.0 (C$_5$H$_4$), 112.4 (OC$_q$C$_6$H$_3$), 112.5 (C$_5$H$_4$), 119.7 (C$_5$H$_4$), 123.5 (C$_5$Me$_5$), 157.0 (C$_{q,ipso}$) ppm.  

$^{15}$N NMR (202 MHz, C$_6$D$_6$, 299 K): $\delta = 45.0$ ppm.  

EA: Anal. calcd. for C$_{33}$H$_{50}$ClNO Ti: 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, 1103, 1093, 1075, 1061, 1025, 979, 961, 947, 905, 884, 867, 850, 825, 815, 742, 732, 701, 685, 628, 618 \text{ cm}^{-1}.

\(^1\text{H} \text{NMR} \ (500 \text{ MHz}, \text{C}_6\text{D}_6, \ 305 \text{ K}) \): \( \delta = 1.29 \) (s, 3H, OC\(_\text{q}\)CH\(_3\)), 1.43-1.65 (m, 8H, CH\(_\text{Ad/CH}_2\text{Ad/NCH}_2\text{CH}_2\)), 1.76 (s, 15H, C\(_5\)Me\(_5\)), 1.78-1.88 (m, 3H, CH\(_\text{Ad/CH}_2\text{Ad/NCH}_2\text{CH}_2\)), 2.08-2.09 (m, 1H, CH\(_\text{Ad/CH}_2\text{Ad}\)), 2.31-2.32 (m, 1H, CH\(_\text{Ad/CH}_2\text{Ad}\)), 2.40-2.47 (m, 2H, CH\(_\text{Ad/CH}_2\text{Ad/NCH}_2\text{CH}_2\)), 2.68-2.78 (m, 3H, CH\(_\text{Ad/CH}_2\text{Ad/NCH}_2\text{CH}_2\)), 3.63 (d, \( ^2J_{H,H} = 13.9 \text{ Hz} \)), 3.98 (d, \( ^2J_{H,H} = 14.0 \text{ Hz} \)), 5.02-5.03 (m, 1H, C\(_5\)H\(_4\)), 5.42-5.46 (m, 2H, 2×C\(_5\)H\(_4\)), 6.43-6.44 (m, 1H, C\(_5\)H\(_4\)), 7.10-7.13 (m, 2H, 2×p-CH\(_\text{Ph/CH}_2\)), 7.22-7.25 (m, 4H, 2×m-CH\(_\text{Ph/CH}_2\)), 7.56-7.58 (m, 4H, 2×o-CH\(_\text{Ph/CH}_2\)) ppm.

\(^{13}\text{C}\{\text{H}\} \text{NMR} \ (126 \text{ MHz}, \text{C}_6\text{D}_6, \ 305 \text{ K}) \): \( \delta = 12.6 \) (C\(_5\)Me\(_5\)), 27.6 (CH\(_\text{Ad}\)), 28.1 (CH\(_\text{Ad}\)), 31.2 (OC\(_\text{q}\)CH\(_3\)), 32.9 (2×CH\(_\text{Ad}\)), 33.8 (CH\(_2\)), 34.9 (CH\(_2\)), 37.2 (CH\(_2\)), 37.4 (CH\(_2\)), 37.5 (CH\(_2\)), 50.5 (CH\(_2\)), 54.8 (C\(_\text{q,exo}\)), 60.1 (2×CH\(_2\text{Ph}\)), 104.3 (C\(_5\)H\(_4\)), 111.9 (C\(_5\)H\(_4\)), 112.1 (OC\(_\text{q}\)CH\(_3\)), 112.6 (C\(_5\)H\(_4\)), 119.8 (C\(_5\)H\(_4\)), 123.6 (C\(_5\)Me\(_5\)), 126.9 (2×p-CH\(_\text{Ph/CH}_2\)), 128.4 (4×m-CH\(_\text{Ph/CH}_2\)), 129.4 (4×o-CH\(_\text{Ph/CH}_2\)), 141.6 (2×C\(_\text{q,Ph}\)), 156.9 (C\(_\text{q,ipso}\)) ppm.

\(^{15}\text{N} \text{NMR} \ (202 \text{ MHz}, \text{C}_6\text{D}_6, \ 305 \text{ K}) \): \( \delta = 48.4 \text{ ppm} \).
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 diastereoisomers (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$_6$D$_6$, 300 K): $\delta = 0.23$ (s, 3H, TiCH$_3$), 1.11 (t, $^3$J$_{H,H} = 7.1$ Hz, 6H, 2×CH$_2$CH$_3$), 1.39 (s, 3H, OC$_9$CH$_3$), 1.72 (s, 15H, C$_5$Me$_5$), 4.85-4.87 (m, 1H, C$_5$H$_4$), 512-5.14 (m, 1H, 2×C$_5$H$_4$), 5.31-5.32 (m, 1H, CsH$_4$), 6.20-6.22 (m, 1H, CsH$_4$) ppm.
$^{13}$C{H} NMR (126 MHz, C$_6$D$_6$, 300 K): $\delta = 11.9$ (C$_5$Me$_5$), 12.7 (2×CH$_2$CH$_3$), 27.9 (CH$_{Ad}$), 28.2 (CH$_{Ad}$), 31.3 (OC$_q$CH$_3$), 32.9 (CH$_{Ad}$), 33.3 (CH$_{Ad}$), 34.1 (CH$_2$), 34.5 (TiCH$_3$), 35.1 (CH$_2$), 37.4 (2×CH$_2$), 38.0 (CH$_2$), 39.7 (CH$_2$), 47.8 (2×CH$_2$CH$_3$), 49.0 (CH$_2$), 55.1 (C$_{q,exo}$), 103.3 (C$_5$H$_4$), 107.9 (OC$_q$CH$_3$), 108.2 (C$_5$H$_4$), 108.4 (C$_5$H$_4$), 116.1 (C$_5$H$_4$), 118.4 (C$_5$Me$_5$), 151.7 (C$_{q,ipso}$) ppm.

$^{15}$N NMR (202 MHz, C$_6$D$_6$, 300 K): $\delta = 44.9$ 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 diastereoisomers (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, 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$_6$D$_6$, 305 K): $\delta = 0.10$ (s, 3H, TiCH$_3$), 1.24 (s, 3H, OC$_q$CH$_3$), 1.66 (s, 15H, C$_5$Me$_5$), 3.57 (d, $^2J_{H,H} = 13.7$ Hz, 2H, CH$_2$Ph), 3.69 (d, $^2J_{H,H} = 13.7$ Hz, 2H, CH$_2$Ph), 4.84-4.86 (m, 1H, C$_5$H$_4$), 5.12-5.14 (m, 1H, C$_5$H$_4$), 5.27-5.28 (m, 1H, C$_5$H$_4$), 6.18-6.19 (m, 1H, C$_5$H$_4$), 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$_6$D$_6$, 305 K): $\delta = 11.9$ (C$_5$Me$_5$), 27.8 (CH$_{Ad}$), 28.2 (CH$_{Ad}$), 31.1 (OC$_q$CH$_3$), 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×CH$_2$Ph), 103.2 (C$_5$H$_4$), 107.6 (OC$_q$CH$_3$), 108.0 (C$_5$H$_4$), 108.5 (C$_5$H$_4$), 116.2 (C$_5$H$_4$), 118.5 (C$_5$Me$_5$), 127.0 (2×p-CH$_{Ph}$CH$_2$), 128.5 (4×m-CH$_{Ph}$CH$_2$), 129.3 (4×o-CH$_{Ph}$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(C₆F₅)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-d₂ to the corresponding complexes 5a and 5a-d₂ respectively. 4a is also only merely soluble in tetrahydrofuran and bromobenzene, so that THF-d₈ and C₆D₅Br solutions of 4a were not adequate for NMR spectroscopy. To verify the poor solubility, the ¹H NMR of 4a (0.100 g) in THF-d₈ is shown in below.

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

**Melting point:** 78-80 °C (dec.).

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

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

**EA:** Anal. calcd. for C₅₂H₅₃BF₁₅NOr: 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(C₆F₅)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-d₂ to the corresponding complexes 5b and 5b-d₂ respectively. 4b is also only merely soluble in tetrahydrofuran and bromobenzene, so that THF-d₈ and C₆D₅Br 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 C₆₂H₅₇BF₁₅NOTi: 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(C₆F₅)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.

**¹H NMR** (500 MHz, CD₂Cl₂, 300 K): $\delta = 0.49$ (s, 3H, BCH₃), 1.40 (t, $^3J_{H,H} = 7.2$ Hz, 3H, CH₂CH₃), 1.43 (t, $^3J_{H,H} = 7.3$ Hz, 3H, CH₂CH₃), 1.52 (s, 3H, OC₆CH₃), 1.59-2.53 (m, 15H, NCH₂CH₂, CH₂CH₃), 1.91 (s, 15H, C₅Me₅), 2.72-2.78 (m, 1H, NCH₂CH₂), 3.13-3.19 (m, 1H, NCH₂CH₂), 3.29-3.38 (m, 2H, CH₂CH₃), 3.48-3.57 (m, 2H, CH₂CH₃), 3.58-3.67 (m, 1H, NCH₂CH₂), 4.80 (d, $^2J_{H,H} = 10.6$ Hz, 1H, NCH₂Cl), 5.00 (d, $^2J_{H,H} = 10.6$ Hz, 1H, NCH₂Cl), 5.36-5.37 (m, 1H, C₅H₄), 5.43-5.45 (m, 1H, C₅H₄), 5.99-6.01 (m, 1H, C₅H₄), 6.46-6.48 (m, 1H, C₅H₄) ppm.

**¹³C{¹H} NMR** (126 MHz, CD₂Cl₂, 300 K): $\delta = 10.0$ (BCH₃)*, 7.9 (CH₂CH₃), 8.2 (CH₂CH₃), 12.8 (C₅Me₅), 27.4 (CH₂), 27.8 (CH₅), 31.1 (OC₆CH₃), 32.8 (CH₂), 33.5 (CH₂), 34.1 (CH₂), 34.7 (CH₂), 36.9 (CH₂), 37.2 (CH₂), 39.0 (CH₂), 55.2 (C₅exo), 55.4 (NCH₂CH₂), 55.5 (NCH₂CH₂), 56.5 (NCH₂Cl), 106.9 (C₅H₄), 109.6 (OC₆CH₃), 112.7 (C₅H₄), 114.5 (C₅H₄), 119.9 (C₅H₄), 125.7 (C₅Me₅), 128.8 (C₅Ar)*, 136.8 (dm, $^1J_{C,F} = 239.9$ Hz, C₅Ar), 137.9 (dm, $^1J_{C,F} = 232.1$ Hz, C₅Ar), 148.7 (dm, $^1J_{C,F} = 235.4$ Hz, C₅Ar), 157.0 (C₅ipso) ppm.

* = assignment by $¹H/¹³C$-HMBC spectra
$^{11}$B{$^1$H} NMR (160 MHz, CD$_2$Cl$_2$, 300 K): $\delta = -15.0$ ppm.

$^{19}$F{$^1$H} NMR (470 MHz, CD$_2$Cl$_2$, 300 K): $\delta = -167.8$ (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$_6$D$_6$, 300 K): $\delta = 69.6$ 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$_6$F$_5$)$_3$ (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 cm$^{-1}$.

$^1$H NMR (500 MHz, CD$_2$Cl$_2$, 300 K): $\delta$ = 0.49 (s(br), 3H, BCH$_3$), 1.41 (s, 3H, OC$_6$H$_3$), 1.59-1.76 (m, 10H, CH$_{Ad}$/CH$_{2,Ad}$), 1.84 (s, 15H, C$_5$Me$_5$), 1.96-2.00 (m, 1H, CH$_{Ad}$/CH$_{2,Ad}$), 2.15-2.20 (m, 2H, CH$_{Ad}$/CH$_{2,Ad}$, NCH$_2$CH$_2$), 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$_2$CH$_2$), 3.15-3.21 (m, 1H, NCH$_2$CH$_2$), 3.58-3.64 (m, 1H, NCH$_2$CH$_2$), 4.49 (d, $^2$$J_{H,H}$ = 13.4 Hz, 1H, NCH$_2$Ph), 4.54-4.55 (m, 2H, NCH$_2$Ph), 4.81 (d, $^2$$J_{H,H}$ = 10.3 Hz, 1H, NCH$_2$Cl), 4.90 (d, $^2$$J_{H,H}$ = 10.3 Hz, 1H, NCH$_2$Cl), 5.00 (d, $^2$$J_{H,H}$ = 13.4 Hz, 1H, NCH$_2$Ph), 5.36-5.37 (m, 1H, C$_5$H$_4$), 5.44-5.46 (m, 1H, C$_5$H$_4$), 5.97-5.98 (m, 1H, C$_5$H$_4$), 6.38-6.39 (m, 1H, C$_5$H$_4$), 7.40-7.41 (m, 2H, 2×CH$_{Ph}$), 7.54-7.66 (m, 8H, 8×CH$_{Ph}$) ppm.

$^{13}$C($^1$H) NMR (126 MHz, CD$_2$Cl$_2$, 300 K): $\delta$ = 10.0 (BCH$_3$)*, 12.8 (C$_5$Me$_5$), 27.4 (CH$_{Ad}$), 27.8 (CH$_{Ad}$), 31.2 (OC$_6$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$_2$CH$_2$), 55.3 (C$_3$exo), 57.8 (NCH$_2$CH$_2$), 63.2 (NCH$_2$Ph), 64.0 (NCH$_2$Ph), 66.2 (NCH$_2$Cl), 106.8 (C$_5$H$_4$), 109.6 (OC$_6$H$_3$), 113.1 (C$_5$H$_4$), 114.3 (C$_5$H$_4$), 119.5 (C$_5$H$_4$), 125.2 (C$_q$ph), 125.6 (C$_5$Me$_5$), 126.5 (C$_q$Ph), 128.9 (C$_q$ArB)*, 130.59 (2×CH$_{Ph}$), 130.61 (2×CH$_{Ph}$), 132.42 (p-CH$_{Ph}$CH$_2$),
132.44 (p-\text{CH}_2\text{Ph}CH_2), 132.88 (2\times\text{CH}_2\text{Ph}), 132.97 (2\times\text{CH}_2\text{Ph}), 136.3 (\text{dm}, J_{\text{C,F}} = 245.8 \text{ Hz}, \text{C}_{\text{q,Ar}}\text{F}), 137.8 (\text{dm}, J_{\text{C,F}} = 234.3 \text{ Hz}, \text{C}_{\text{q,Ar}}\text{F}), 148.6 (\text{dm}, J_{\text{C,F}} = 235.9 \text{ Hz}, \text{C}_{\text{q,Ar}}\text{F}), 156.8 (\text{C}_{\text{q,ipso}}) \text{ ppm.}

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

\textsuperscript{11}B\{\textsuperscript{1}H\} NMR (160 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 300 K): \text{\delta} = -14.9 \text{ ppm.}

\textsuperscript{19}F\{\textsuperscript{1}H\} NMR (470 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 300 K): \text{\delta} = -167.8 (m, 6F, m-F\textsubscript{Ar}B), -165.2 (t, J_{F,F} = 20.4 \text{ Hz}, 3F, p-F\textsubscript{Ar}B), -133.1 (m, 6F, o-F\textsubscript{Ar}B) \text{ ppm.}

\textbf{HR/MS} calculated: m/z = 732.3218 [M\textsuperscript{+}]; measured (ESI): m/z = 732.3223.

\textbf{EA}: Anal. calcd. for C\textsubscript{63}H\textsubscript{59}BCl\textsubscript{2}F\textsubscript{15}NO\textsubscript{Ti}: 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$_6$F$_5$)$_3$ (0.054 g, 0.106 mmol) were stirred in 8 mL of toluene for the \textit{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 \textit{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.

\textbf{Yield}: 0.101 g (0.078 mmol, 74\%).

\textbf{Melting point}: 66-68 °C (dec.).

\textbf{IR} (ATR): $\tilde{\nu}$ = 2912, 2858, 1641, 1509, 1454, 1377, 1265, 1205, 1081, 1045, 1025, 964, 950, 884, 824, 803, 754, 698, 659, 642, 603 cm$^{-1}$.

\textbf{1H NMR} (500 MHz, CD$_2$Cl$_2$, 305 K): $\delta$ = 0.52 (s(br), 3H, BCH$_3$), 1.31 (s, 3H, OC$_q$CH$_3$), 1.95 (s, 15H, C$_5$Me$_5$), 4.08-4.13 (m, 2H, NCH$_2$Ph), 4.37 (d, $^2$$J_{H,H}$ = 13.8 Hz, 1H, NCH$_2$Ph), 4.37 (d, $^2$$J_{H,H}$ = 13.4 Hz, 1H, NCH$_2$Ph), 4.47 (d, $^2$$J_{H,H}$ = 13.4 Hz, 1H, NCH$_2$Ph), 4.61 (d, $^2$$J_{H,H}$ = 9.4 Hz, 1H, NCH$_2$Ph), 5.27-5.29 (m, 1H, C$_5$H$_4$), 5.34-5.35 (m, 1H, C$_5$H$_4$), 5.95-5.97 (m, 1H, C$_5$H$_4$), 6.12-6.13 (m, 1H, C$_5$H$_4$), 7.27-7.42 (m, 6H, 6×CH$_{Aryl}$), 7.51-7.63 (m, 9H, 9×CH$_{Aryl}$) ppm.

\textbf{13C\{1H\} NMR} (126 MHz, CD$_2$Cl$_2$, 305 K): $\delta$ = 10.2 (BCH$_3$)*, 12.9 (C$_5$Mes), 27.4 (CH$_{Ad}$), 27.9 (CH$_{Ad}$), 30.9 (OC$_q$CH$_3$), 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$_2$Ph), 62.2 (NCH$_2$Ph), 64.4 (NCH$_2$Ph), 107.8 (C$_5$H$_4$), 109.0 (OC$_q$CH$_3$), 111.8 (C$_5$H$_4$), 115.8 (C$_5$H$_4$), 120.4 (C$_5$H$_4$), 126.5 (C$_5$Mes), 129.0 (C$_q$,Ar)*, 136.9 (dm, $^{1}$$J_{C,F}$ = 239.7 Hz, C$_q$,Ar,F), 138.0 (dm, $^{1}$$J_{C,F}$ = 243.1 Hz, C$_q$,Ar,F), 148.8 (dm, $^{1}$$J_{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$_2$Cl$_2$, 305 K): $\delta$ = -14.9 ppm.

$^{19}$F{$^1$H} NMR (470 MHz, CD$_2$Cl$_2$, 305 K): $\delta$ = -167.8 (m, 6F, $m$-F$_A$B), -165.2 (t, $^3J_{F,F}$ = 20.3 Hz, 3F, $p$-F$_A$B), -133.0 (m, 6F, $o$-F$_A$B) ppm.

$^{15}$N NMR (202 MHz, C$_6$D$_6$, 300 K): $\delta$ = 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(C₆F₅)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, CD₂Cl₂, 305 K): $\delta$ = 0.50 (s(br), 3H, BCH₃), 1.55 (s, 3H, OC₃C₅H₃), 1.89 (s, 15H, C₅Me₅), 5.18-5.19 (m, 1H, C₅H₄), 5.47-5.48 (m, 1H, C₅H₄), 6.05-6.06 (m, 1H, C₅H₄), 6.27-6.28 (m, 1H, C₅H₄) ppm.

$^{13}$C{¹H} NMR (126 MHz, CD₂Cl₂, 305 K): $\delta$ = 10.0 (BCH₃)*, 12.1 (C₅Mes), 32.0 (OC₃C₅H₃), 55.2 (C₅exo), 106.3 (C₅H₄), 106.7 (OC₃C₅H₃), 111.0 (C₅H₄), 115.1 (C₅H₄), 119.2 (C₅H₄), 124.6 (C₅Mes), 129.3 (C₅ArB)*, 136.8 (dm, $^1$J₃F = 245.1 Hz, C₅ArF), 138.0 (dm, $^1$J₃F = 243.0 Hz, C₅ArF), 148.7 (dm, $^1$J₃F = 236.4 Hz, C₅ArF), 156.2 (C₅ipso) ppm.

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

$^{11}$B{¹H} NMR (160 MHz, CD₂Cl₂, 305 K): $\delta$ = -14.9 ppm.

$^{19}$F{¹H} NMR (470 MHz, CD₂Cl₂, 305 K): $\delta$ = -167.9 (m, 6F, m-FₐB), -165.3 (t, $^3$J₃F = 20.3 Hz, 3F, p-FₐB), -133.1 (m, 6F, o-FₐB) ppm.

$^{15}$N NMR (202 MHz, CD₂Cl₂, 300 K): $\delta$ = 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$_6$F$_5$)$_3$ (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$_2$Cl$_2$, 305 K):** $\delta =$ 0.50 (s(br), 3H, BCH$_3$)*, 1.49 (s, 3H, OC$_q$CH$_3$), 1.86 (s, 15H, C$_5$Me$_5$), 4.30 (d, $^2$J$_{H,H}$ = 13.4 Hz, NCH$_2$Ph), 4.37-4.40 (m, 2H, NCH$_2$Ph)**, 4.47-4.51 (m, 1H, NCH$_2$Ph)**, 4.73 (d, $^2$J$_{H,H}$ = 13.6 Hz, NCH$_2$Ph), 5.20-5.21 (m, 1H, C$_5$H$_4$), 5.48-5.49 (m, 1H, C$_5$H$_4$), 6.14-6.15 (m, 1H, C$_5$H$_4$), 6.29-6.30 (m, 1H, C$_5$H$_4$), 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$_2$Cl$_2$, 305 K):** $\delta =$ 10.3 (BCH$_3$)*, 12.2 (C$_5$Me$_5$), 30.8 (OC$_q$CH$_3$), 59.4 (NCH$_2$Ph), 64.1 (NCH$_2$Ph), 106.4 (C$_5$H$_4$), 106.7 (OC$_q$CH$_3$), 111.5 (C$_5$H$_4$), 115.1 (C$_5$H$_4$), 118.9 (C$_5$H$_4$), 124.6 (C$_5$Me$_5$), 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$_2$Cl$_2$, 305 K):** $\delta =$ -14.9 ppm.
$^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CD$_2$Cl$_2$, 305 K): $\delta = -167.9$ (m, 6F, $m$-F$_{ArB}$), -165.3 (t, $^3J_{F,F} = 20.3$ Hz, 3F, $p$-F$_{ArB}$), -133.1 (m, 6F, $o$-F$_{ArB}$) 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.
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<td>( R1 = 0.0553 ) wR2 = 0.1046</td>
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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, ΣC26 321.4 (O1–C26–C27 + O1–C26–C29 + C27–C26–C29), ΣN1 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$_6$D$_6$, rt).

Figure S16: $^{13}$C[$^1$H] NMR spectrum of L1a (126 MHz, C$_6$D$_6$, rt).
Figure S17: $^1$H NMR spectrum of L1b (500 MHz, C$_6$D$_6$, rt).

Figure S18: $^{13}$C($^1$H) NMR spectrum of L1b (126 MHz, C$_6$D$_6$, rt).
Figure S19: $^1$H NMR spectrum of 2a (500 MHz, C$_6$D$_6$, rt); diastereoisomer A and diastereoisomer B.

Figure S20: $^{13}$C($^1$H) NMR spectrum of 2a (126 MHz, C$_6$D$_6$, 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$_6$D$_6$, rt).
Figure S22: $^1$H NMR spectrum of 2b (500 MHz, C$_6$D$_6$, rt).

Figure S23: $^{13}$C($^1$H) NMR spectrum of 2b (126 MHz, C$_6$D$_6$, rt).
Figure S24: $^{15}$N/$^1$H HMBC NMR spectrum of 2b (51 MHz, C$_6$D$_6$, rt).
**Figure S25**: $^1$H NMR spectrum of 3a (500 MHz, C$_6$D$_6$, rt); diastereoisomer A and diastereoisomer B; 0.29 ppm: silicon grease.

**Figure S26**: $^{13}$C($^1$H) NMR spectrum of 3a (126 MHz, C$_6$D$_6$, 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$_6$D$_6$, rt).
Figure S28: $^1$H NMR spectrum of 3b (500 MHz, C$_6$D$_6$, rt); diastereoisomer A and diastereoisomer B.

Figure S29: $^{13}$C($^1$H) NMR spectrum of 3b (126 MHz, C$_6$D$_6$, 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$_2$Cl$_2$, rt; middle, top: 500 MHz, CD$_2$Cl$_2$, rt).
Figure S31: $^1$H NMR spectrum after 5 minutes of the reaction of 4a with dichloromethane-$d_2$ (300 MHz, CD$_2$Cl$_2$, rt).

Figure S32: $^1$H NMR spectrum of 5a (500 MHz, CD$_2$Cl$_2$, rt); 0.89, 1.27 ppm: $n$-hexane.
Figure S33: $^{13}$C($^1$H) NMR spectrum of 5a (126 MHz, CD$_2$Cl$_2$, rt); 14.3, 23.1, 32.0 ppm: $n$-hexane.

Figure S34: $^{11}$B($^1$H) NMR spectrum of 5a (160 MHz, CD$_2$Cl$_2$, rt).
Figure S35: $^{19}$F($^1$H) NMR spectrum of 5a (470 MHz, CD$_2$Cl$_2$, rt).

Figure S36: $^{15}$N/$^1$H HMBC NMR spectrum of 5a (51 MHz, CD$_2$Cl$_2$, 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$_2$Cl$_2$, rt); 2.34, 7.15-7.24 ppm: toluene.

Figure S39: $^{13}$C($^1$H) NMR spectrum of 5b (126 MHz, CD$_2$Cl$_2$, rt); 21.5, 125.6, 128.5, 129.4, 137.9: toluene.
Figure S40: $^{11}\text{B}^{(1}\text{H})$ NMR spectrum of 5b (160 MHz, CD$_2$Cl$_2$, rt).

Figure S41: $^{19}\text{F}^{(1}\text{H})$ NMR spectrum of 5b (470 MHz, CD$_2$Cl$_2$, rt).
Figure S42: $^1$H NMR spectrum of 6 (500 MHz, CD$_2$Cl$_2$, rt); 2.34, 7.15-7.24 ppm: toluene.

Figure S43: $^{13}$C($^1$H) NMR spectrum of 6 (126 MHz, CD$_2$Cl$_2$, rt); 21.5, 125.6, 128.5, 129.4, 137.9: toluene.
**Figure S44**: $^{11}$B{$^1$H} NMR spectrum of 6 (160 MHz, CD$_2$Cl$_2$, rt).

**Figure S45**: $^{19}$F{$^1$H} NMR spectrum of 6 (470 MHz, CD$_2$Cl$_2$, 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{¹H} NMR spectrum of 7a (160 MHz, CD$_2$Cl$_2$, rt).

Figure S49: $^{19}$F{¹H} NMR spectrum of 7a (470 MHz, CD$_2$Cl$_2$, rt); -218.1 ppm: $n$-fluorodecane.
Figure S50: $^{15}\text{N}/^1\text{H}$ HMBC NMR spectrum of 7a (51 MHz, CD$_2$Cl$_2$, rt).
**Figure S51**: $^1$H NMR spectrum of 7b (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 S52**: $^{13}$C($^1$H) NMR spectrum of 7b (126 MHz, CD$_2$Cl$_2$, rt); 14.3, 23.1, 32.0 ppm: $n$-hexane.
**Figure S53**: $^{11}$B{$^{1}$H} NMR spectrum of 7b (160 MHz, CD$_2$Cl$_2$, rt).

**Figure S54**: $^{19}$F{$^{1}$H} NMR spectrum of 7b (470 MHz, CD$_2$Cl$_2$, rt); -218.1 ppm: $n$-fluorodecane.


**References:**

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