

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 if not stated otherwise. The glass equipment was stored in an oven at 120 °C and evacuated prior to use. Solvents were dried according to standard procedures prior to use. Cp*Ti(Cl)AdFv (**1**) was synthesized according to a literature procedure.^[1] Ethylmagnesium bromide was used as a 3.0 M solution in diethyl ether. 2-Butyne, 3-hexyne, 1-phenyl-1-propyne, and bis(trimethylsilyl)acetylene (btmsa) were purchased from commercial sources, distilled from CaCl₂, freeze-pump-thaw degassed three times, and stored under inert atmosphere prior to use.

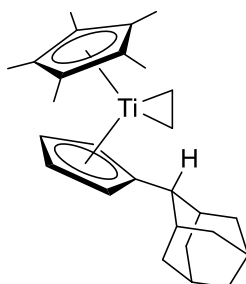
Infrared spectra were performed on a Bruker Tensor 27 spectrometer with a MKII Reflection Golden Gate Single Diamond ATR system.

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 (C₆D₆): δ¹H(C₆D₅H) = 7.16 ppm, and toluene-*d*₈ (C₇D₈): δ¹H(C₇D₇H) = 2.08 ppm) and ¹³C{¹H} spectra were referenced by using the central line of the solvent signal (benzene-*d*₆ (C₆D₆): δ¹³C{¹H}(C₆D₆) = 128.06 ppm, and toluene-*d*₈ (C₇D₈): δ¹³C{¹H}(C₇D₈) = 20.43 ppm). The ²⁹Si{¹H} INEPT spectra were recorded with the combination D3 = 0.0086 s and D4 = 0.0313 s.

Elemental analyses were carried out on a EuroEA 3000 Elemental Analyzer.

Synthesis and Characterization of the Compounds

Synthesis of 2:



To a solution of **1** (0.500 g, 1.199 mmol) in 10 mL of *n*-hexane was added ethylmagnesium bromide (0.4 mL, 1.199 mmol; 3.0 M in diethyl ether) at room temperature. A direct color change from the orange-brown solution to a yellow suspension was observed. The suspension was stirred for 15 minutes at room temperature. All volatile components were removed under vacuum, the residue was suspended in 8 mL of *n*-hexane, filtered, and washed with *n*-hexane (2×8 mL). All volatile components were removed under vacuum to yield **2** as a yellowish solid.

Crystals suitable for single-crystal X-ray diffraction were obtained from an *n*-hexane solution of **2** at -4 °C.

Yield: 0.352 g (0.858 mmol, 83%).

Melting point: 70-72 °C.

IR (ATR): $\tilde{\nu}$ = 2901, 2848, 1488, 1466, 1448, 1376, 1351, 1328, 1261, 1214, 1098, 1060, 1022, 949, 934, 874, 789, 770, 751, 724, 685, 626, 604 cm⁻¹.

¹H NMR (500 MHz, C₆D₆, 305 K): δ = 0.74 (s, 1H, CH_{exo}), 1.40-1.42 (m, 2H, CH_{Ad}/CH_{2,Ad}), 1.58 (s, 15H, C₅Me₅), 1.63-1.64 (m, 2H, C₂H₄), 1.70-1.77 (m, 6H, CH_{Ad}/CH_{2,Ad}), 1.99-2.04 (m, 4H, CH_{Ad}/CH_{2,Ad}), 2.78-2.79 (m, 4H, CH_{Ad}/CH_{2,Ad}, C₂H₄), 5.65-5.66 (m, 2H, C₅H₄), 6.58-6.59 (m, 2H, C₅H₄) ppm.

¹³C{¹H} NMR (126 MHz, C₆D₆, 305 K): δ = 12.1 (C₅Me₅), 28.3 (CH_{Ad}), 28.6 (CH_{Ad}), 32.5 (2×CH_{Ad}), 33.0 (2×CH_{2,Ad}), 38.4 (CH_{2,Ad}), 38.9 (2×CH_{2,Ad}), 44.9 (CH_{exo}), 98.7 (C₂H₄), 113.6 (2×C₅H₄), 116.1 (2×C₅H₄), 120.3 (C₅Me₅), 135.0 (C_{q,ipso}) ppm.

EA: Anal. calcd. for C₂₇H₃₈Ti: C, 79.01; H, 9.33; Found: C, 79.82; H, 9.95.

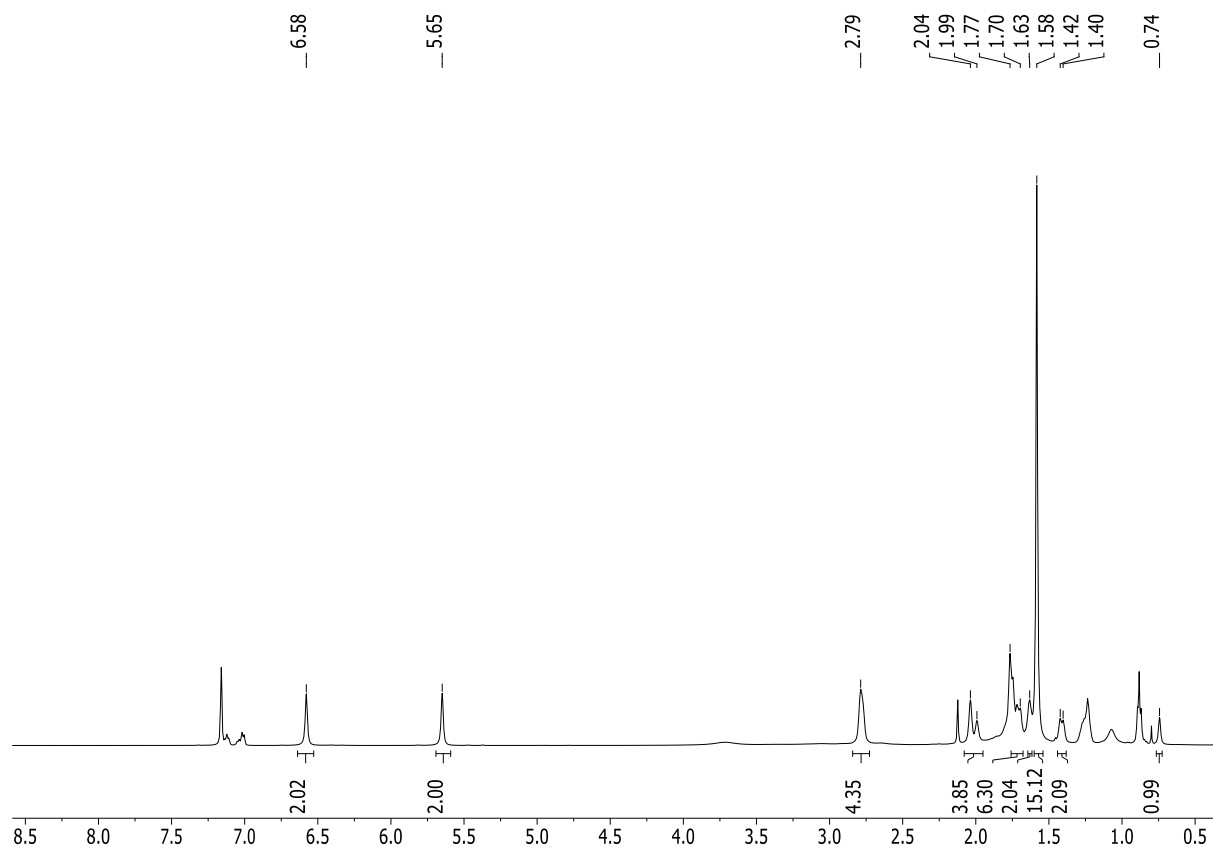


Figure S1: ^1H NMR spectrum of **2** (500 MHz, C_6D_6 , rt); 0.89, 1.24 ppm: *n*-hexane.

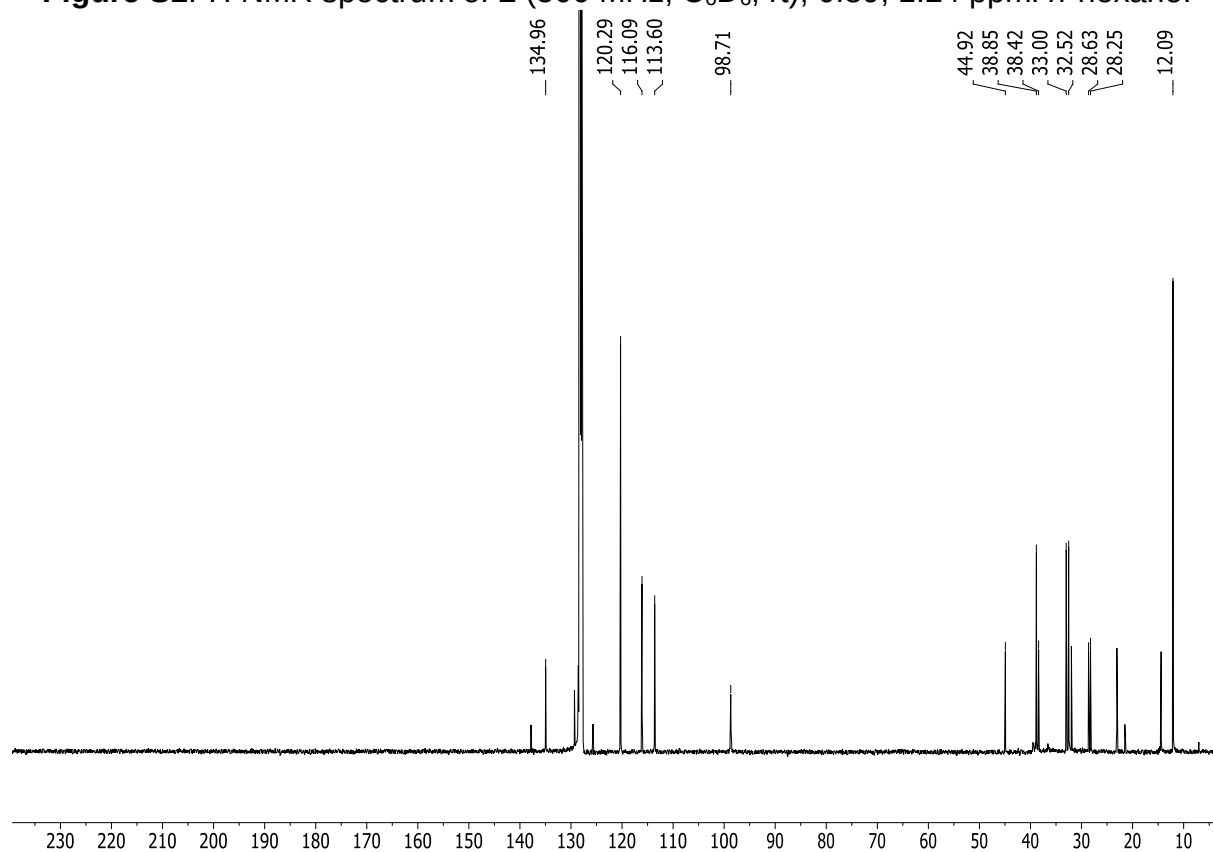


Figure S2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** (126 MHz, C_6D_6 , rt); 14.3, 23.0, 32.0 ppm: *n*-hexane.

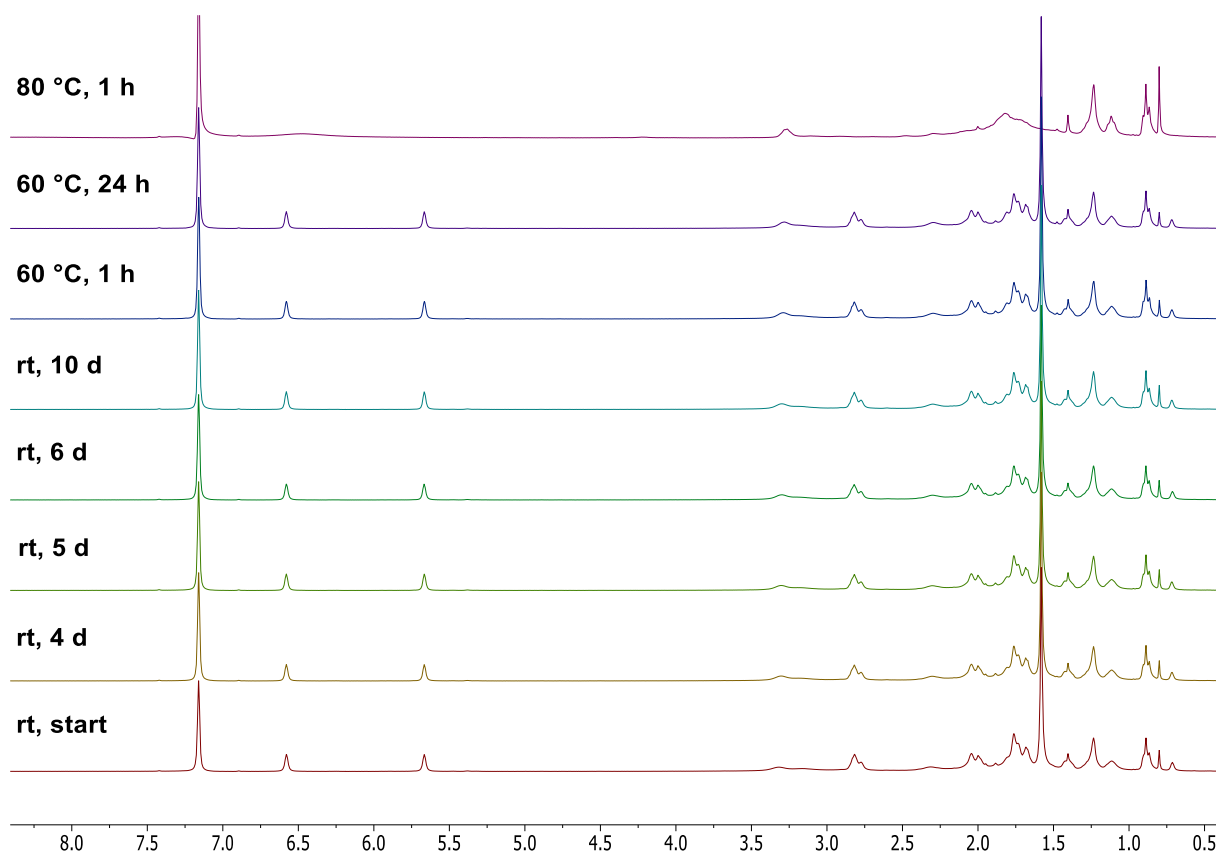


Figure S3: Stability test: ^1H NMR spectrum of **2** (500 MHz, C_6D_6 , rt - 80 °C); 0.89, 1.24 ppm: *n*-hexane.

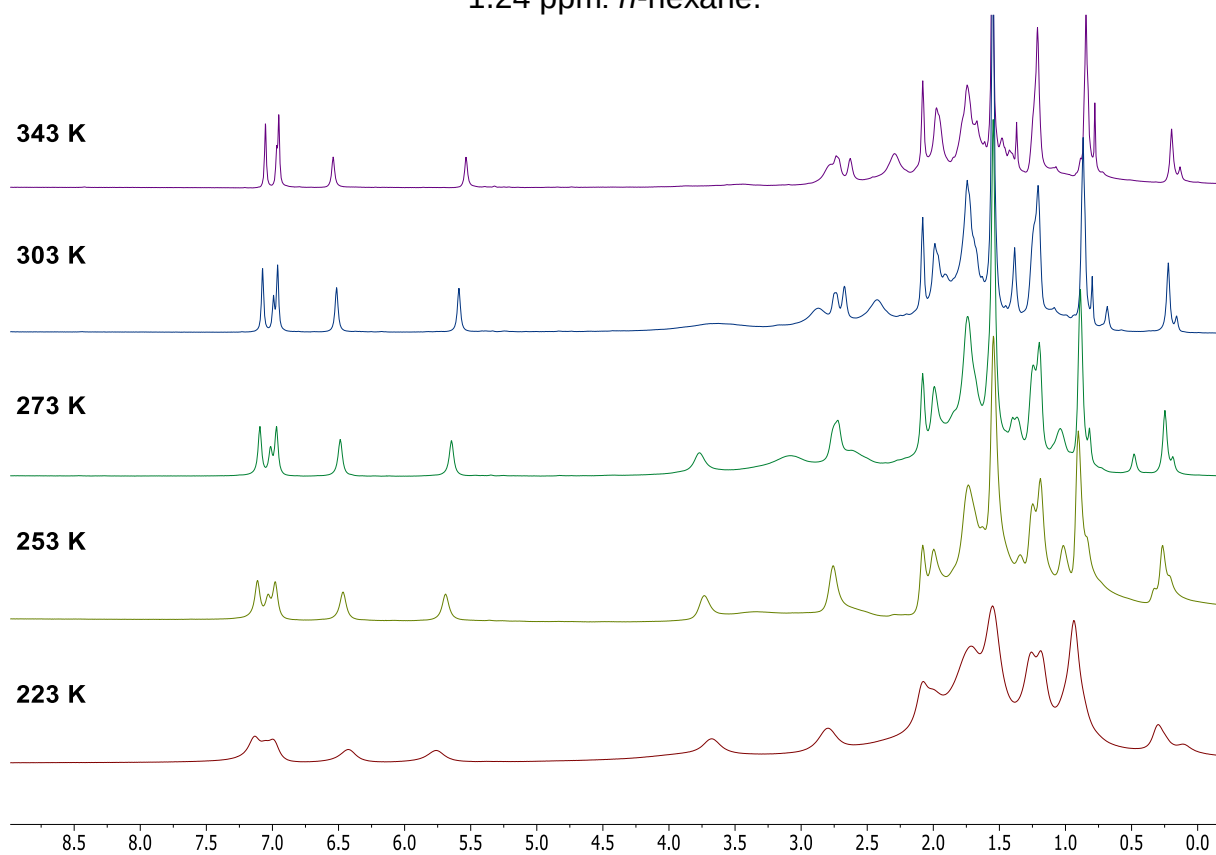
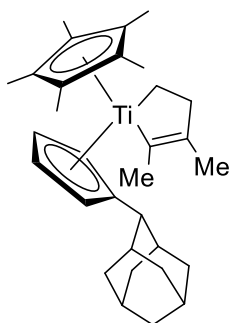


Figure S4: Excerpt of the ^1H NMR spectra of the variable temperature experiment of **2** (500 MHz, $\text{toluene-}d_8$, 213 K - 353 K).

Synthesis of **3a**:



To a solution of complex **1** (0.050 g, 0.120 mmol) in 5 mL of *n*-hexane was added ethylmagnesium bromide (0.04 mL, 0.120 mmol; 3.0 M in diethyl ether) and the reaction mixture was stirred for 15 minutes at room temperature. 2-Butyne (0.01 mL, 0.120 mmol) was added and the reaction mixture was stirred for 16 h at room temperature, which was accompanied by a color change to orange-red. All volatile components were removed under vacuum. 5 mL of *n*-hexane were added, the suspension was filtered, and washed with *n*-hexane (2×5 mL). All volatile components were removed under vacuum to yield **3a** as an orange-red solid. The sample was completely transferred to an NMR tube.

¹H NMR (500 MHz, C₆D₆, 305 K): δ = 0.04-0.08 (m, 1H, TiCH₂), 1.15 (s, 3H, TiC_qCH₃), 1.47 (s, 3H, TiC_qCH₃C_qCH₃), 1.70 (s, 15H, C₅Me₅), 1.77-1.83 (m, 4H, CH_{Ad}/CH_{2,Ad}), 1.90-2.00 (m, 6H, CH_{Ad}/CH_{2,Ad}), 2.08-2.12 (m, 1H, TiCH₂CH₂), 2.24-2.40 (m, 4H, CH_{Ad}/CH_{2,Ad}, TiCH₂CH₂), 2.45-2.46 (m, 1H, CH_{Ad}/CH_{2,Ad}), 2.52-2.53 (m, 1H, CH_{Ad}/CH_{2,Ad}), 3.01 (s, 1H, CH_{exo}), 4.94-4.95 (m, 1H, C₅H₄), 5.27-5.29 (m, 1H, C₅H₄), 5.75-5.77 (m, 1H, C₅H₄), 6.34-6.35 (m, 1H, C₅H₄) ppm.

¹³C{¹H} NMR (126 MHz, C₆D₆, 305 K): δ = 12.1 (C₅Me₅), 19.0 (TiC_qCH₃C_qCH₃), 22.1 (TiC_qCH₃), 28.6 (CH_{Ad}), 28.7 (CH_{Ad}), 32.5 (CH_{Ad}), 32.9 (TiCH₂CH₂), 33.1 (CH_{2,Ad}), 33.4 (CH_{Ad}), 37.7 (CH_{2,Ad}), 38.6 (CH_{2,Ad}), 39.4 (2×CH_{2,Ad}), 45.4 (CH_{exo}), 52.6 (TiCH₂), 108.8 (C₅H₄), 109.0 (C₅H₄), 115.4 (C₅H₄), 116.5 (C₅H₄), 120.7 (C₅Me₅), 130.8 (TiC_qCH₃C_qCH₃), 134.3 (C_{q,ipso}), 192.5 (TiC_qCH₃) ppm.

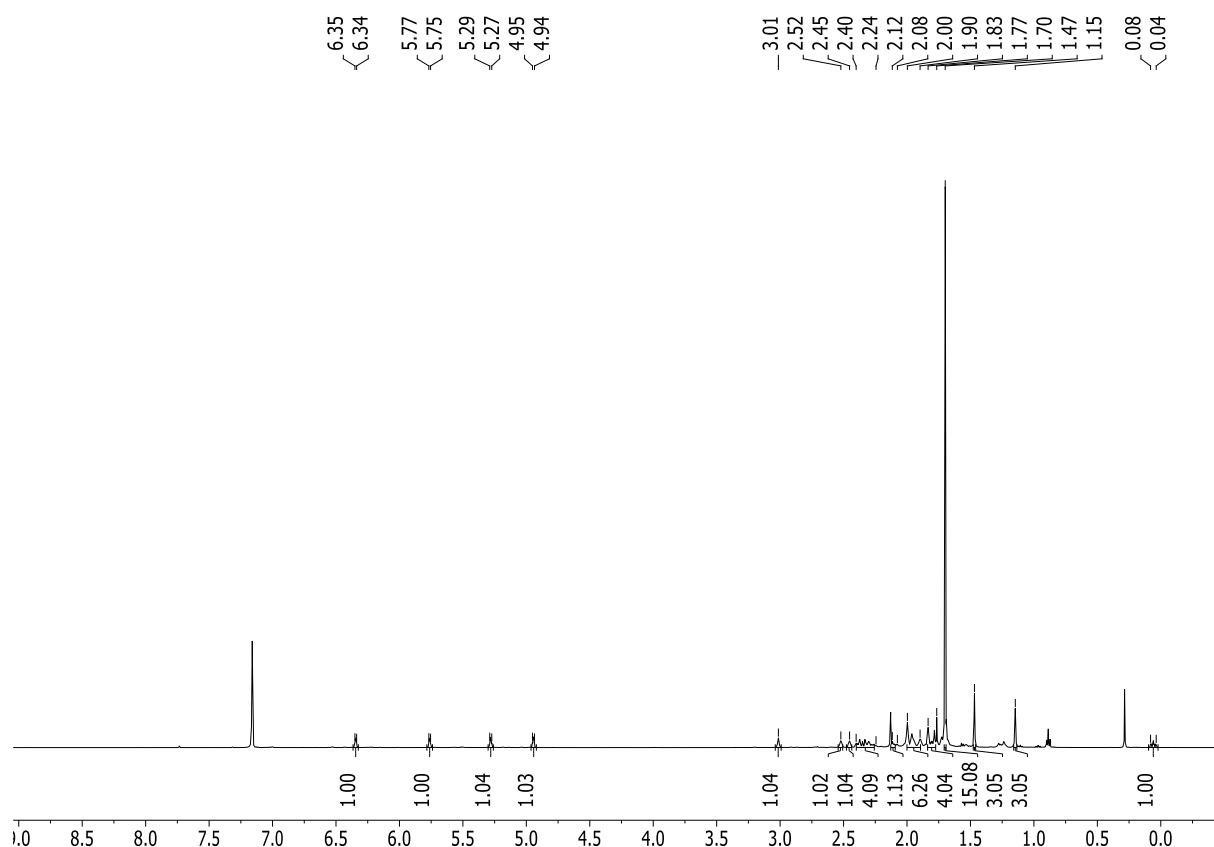


Figure S5: ^1H NMR spectrum of **3a** (500 MHz, C_6D_6 , rt); 0.29: silicon grease, 0.89, 1.24 ppm: *n*-hexane.

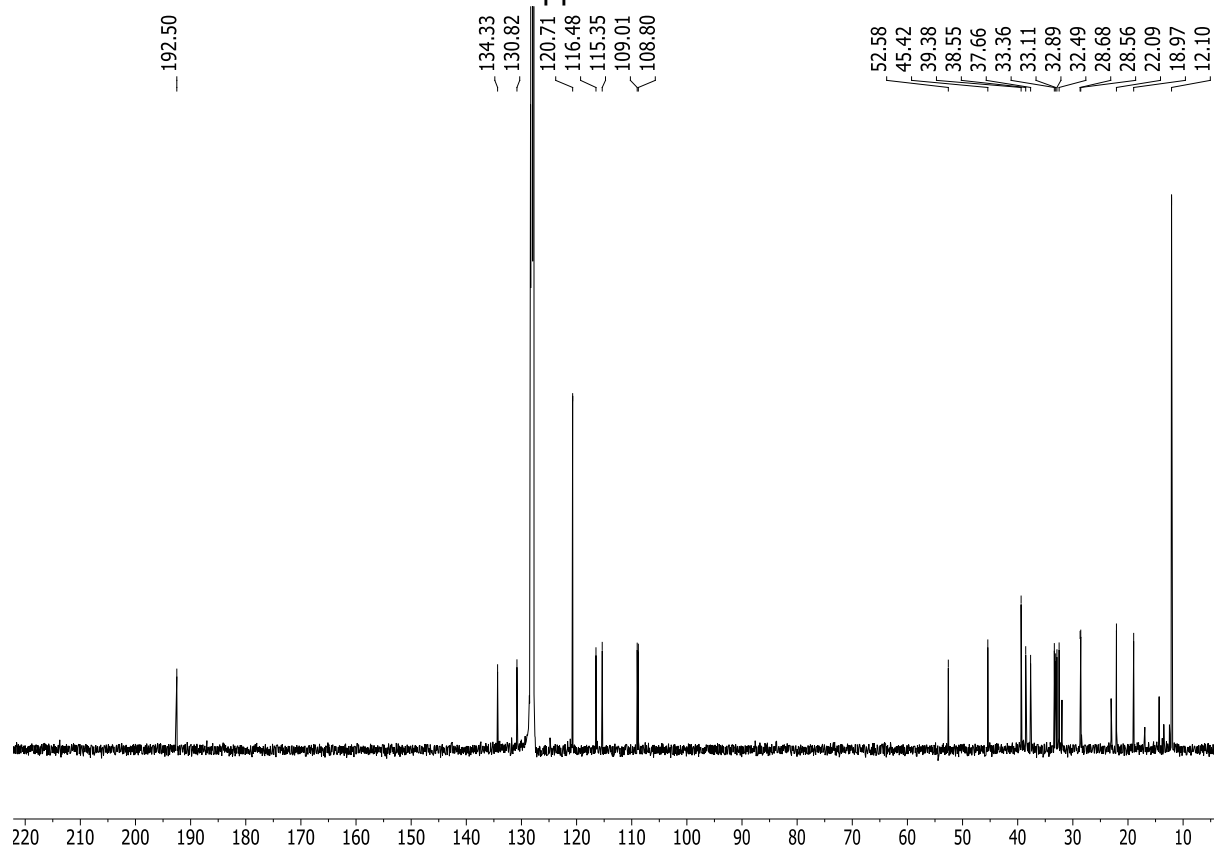
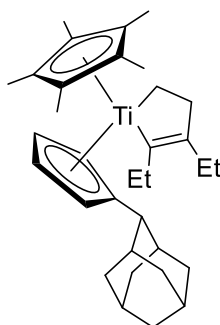


Figure S6: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3a** (126 MHz, C_6D_6 , rt); 14.3, 23.0, 32.0 ppm: *n*-hexane.

Synthesis of **3b**:



To a solution of complex **1** (0.050 g, 0.120 mmol) in 5 mL of *n*-hexane was added ethylmagnesium bromide (0.04 mL, 0.120 mmol; 3.0 M in diethyl ether) and the reaction mixture was stirred for 15 minutes at room temperature. 3-Hexyne (0.01 mL, 0.120 mmol) was added and the reaction mixture was stirred for 16 h at room temperature, which was accompanied by a color change to orange-red. All volatile components were removed under vacuum. 5 mL of *n*-hexane were added, the suspension was filtered, and washed with *n*-hexane (2×5 mL). All volatile components were removed under vacuum to yield **3b** as an orange-red solid. The sample was completely transferred to an NMR tube.

¹H NMR (500 MHz, C₆D₆, 305 K): δ = -0.26-(-0.22) (m, 1H, CH_{aliphatic}), 0.95-1.02 (m, 4H, CH₂CH₃, CH_{aliphatic}), 1.06-1.07 (t, ³J_{H,H} = Hz, 3H, CH₂CH₃), 1.11-1.15 (m, 1H, CH_{aliphatic}), 1.70 (s, 15H, C₅Me₅), 1.77-1.89 (m, 6H, CH_{aliphatic}), 1.98-2.06 (m, 6H, CH_{aliphatic}), 2.13-2.15 (m, 2H, CH_{aliphatic}), 2.28-2.31 (m, 1H, CH_{aliphatic}), 2.38-2.42 (m, 2H, CH_{aliphatic}), 2.48-2.49 (m, 1H, CH_{aliphatic}), 2.64-2.65 (m, 1H, CH_{aliphatic}), 2.99 (s, 1H, CH_{exo}), 4.94-4.95 (m, 1H, C₅H₄), 5.46-5.47 (m, 1H, C₅H₄), 5.54-5.55 (m, 1H, C₅H₄), 6.63-6.64 (m, 1H, C₅H₄) ppm.

¹³C{¹H} NMR (126 MHz, C₆D₆, 305 K): δ = 12.3 (C₅Me₅), 14.0 (CH₂CH₃), 15.4 (CH₂CH₃), 27.3 (CH₂), 27.6 (CH₂), 28.5 (CH_{Ad}), 28.6 (CH_{Ad}), 32.6 (CH_{Ad}), 32.8 (CH₂), 32.2 (CH₂), 34.41 (CH_{Ad}), 34.44 (CH₂), 38.5 (CH₂), 38.9 (CH₂), 39.3 (CH₂), 44.7 (CH_{exo}), 54.5 (CH₂), 109.09 (C₅H₄), 109.14 (C₅H₄), 113.8 (C₅H₄), 116.2 (C₅H₄), 120.7 (C₅Me₅), 134.4 (C_{q,ipso}), 138.9 (TiC_q(CH₂CH₃)C_q), 198.8 (TiC_qCH₂CH₃)

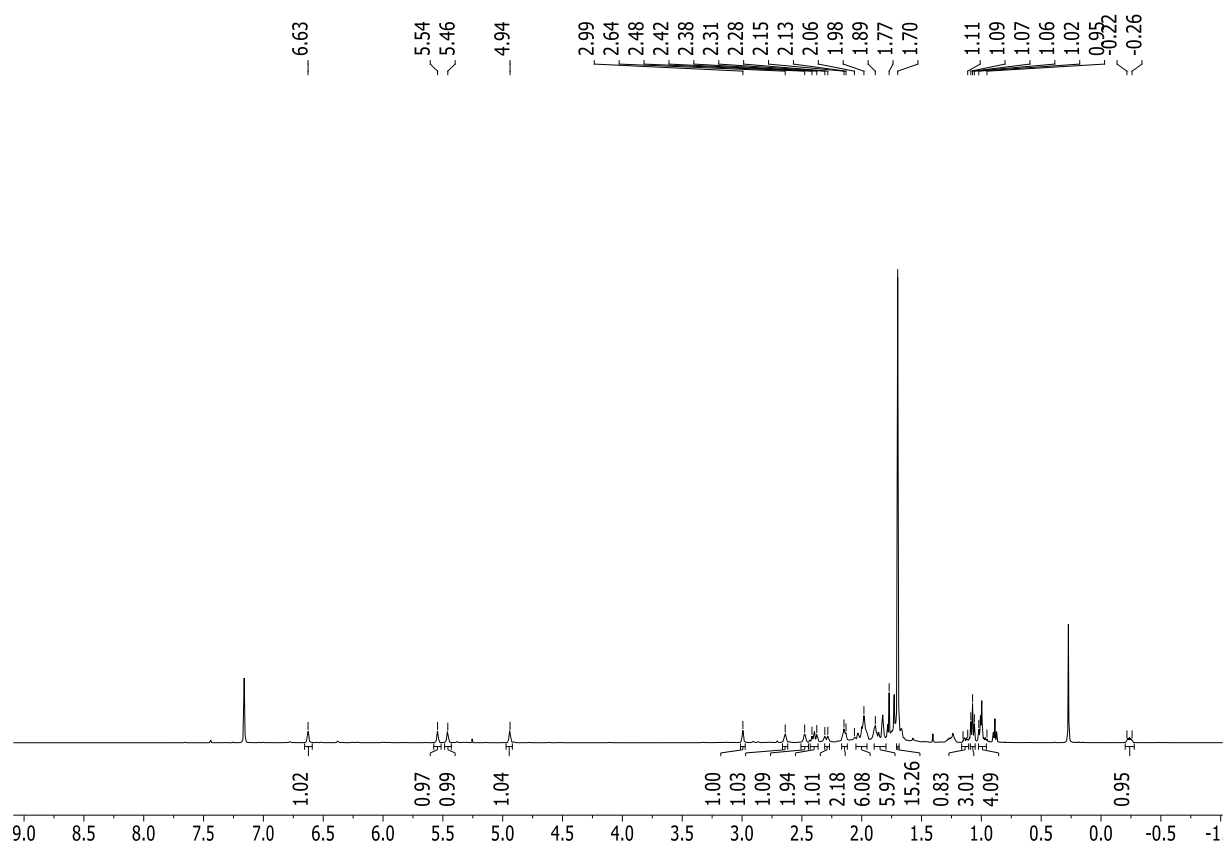


Figure S7: ^1H NMR spectrum of **3b** (500 MHz, C_6D_6 , rt); 0.29: silicon grease, 0.89, 1.24 ppm: *n*-hexane.

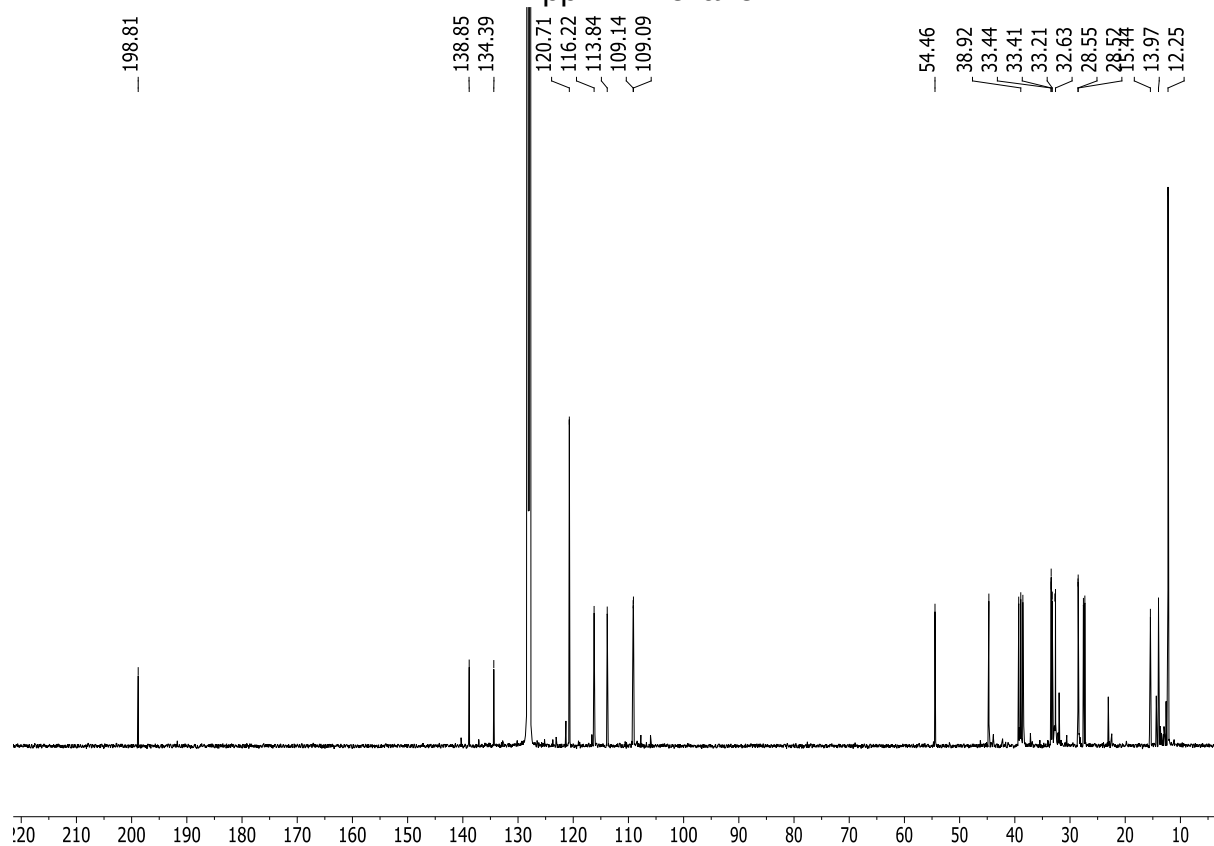
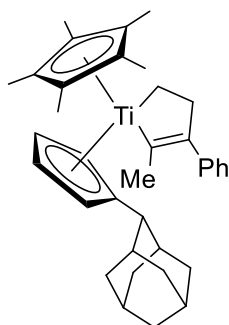


Figure S8: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3b** (126 MHz, C_6D_6 , rt); 14.3, 23.0, 32.0 ppm: *n*-hexane.

Synthesis of 3c:



To a solution of complex **1** (0.200 g, 0.480 mmol) in 8 mL of *n*-hexane was added ethylmagnesium bromide (0.16 mL, 0.480 mmol; 3.0 M in diethyl ether) and the reaction mixture was stirred for 15 minutes at room temperature. A solution of 1-phenylprop-1-yne (0.06 mL, 0.480 mmol) was added and the reaction was stirred for another 16 h at room temperature. A slowly occurring color change to red could be observed. All volatile components were removed under vacuum. 10 mL of *n*-hexane were added, the suspension was filtered, and washed with *n*-hexane (2×8 mL). All volatile components were removed under vacuum to yield **3c** as an orange solid.

Yield: 0.152 g (0.289 mmol, 60%).

Melting point: 78-80 °C.

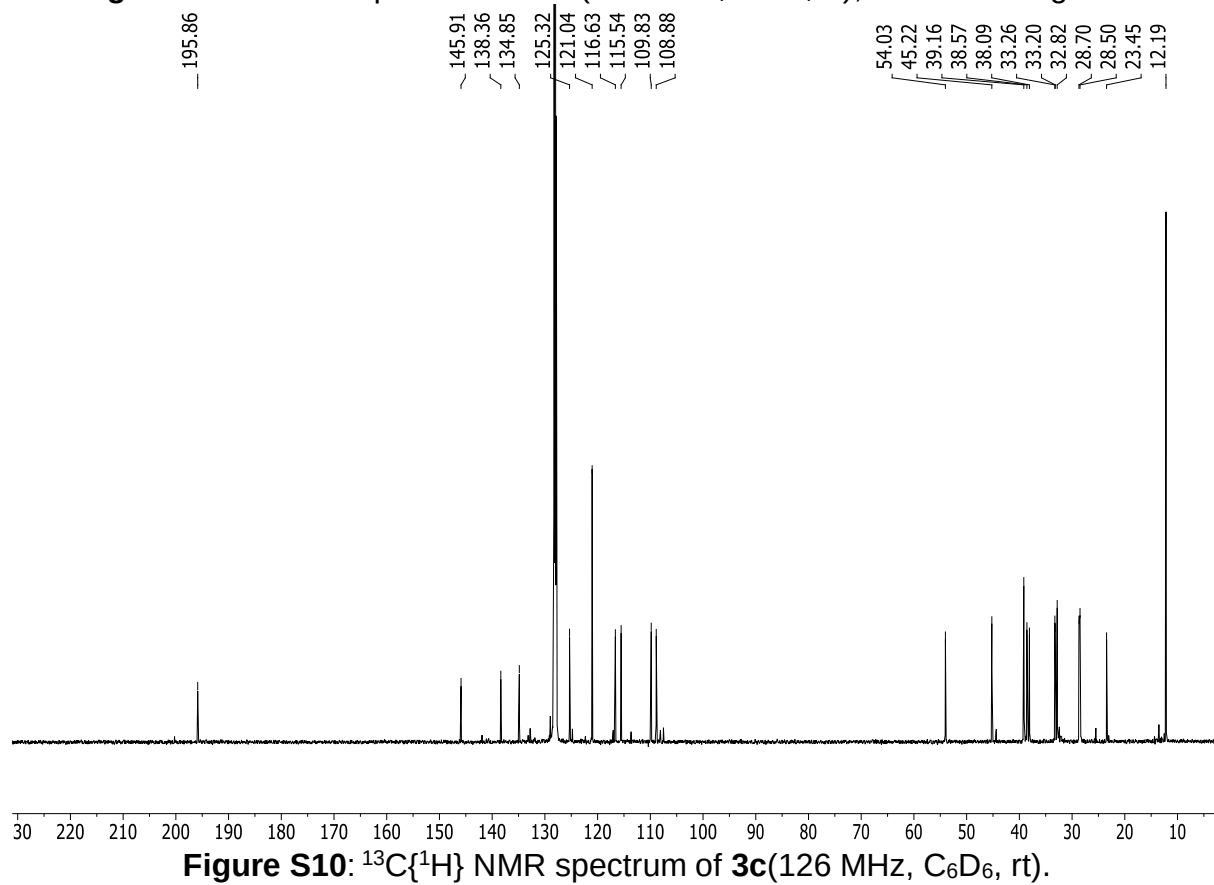
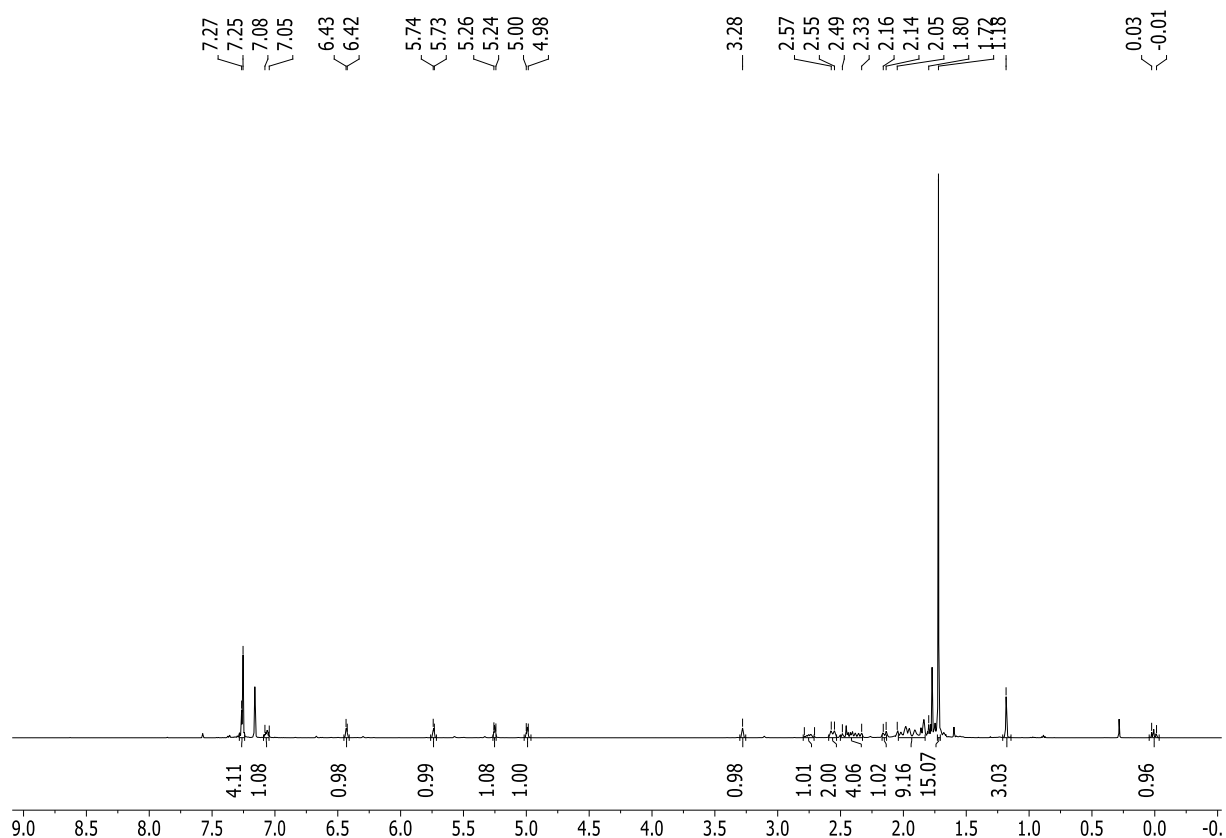
IR (ATR): $\tilde{\nu}$ = 2959, 2902, 2847, 1593, 1487, 1467, 1449, 1375, 1354, 1261, 1099, 1062, 1021, 955, 872, 799, 762, 699, 643, 589 cm⁻¹.

¹H NMR (500 MHz, C₆D₆, 305 K): δ = -0.01-0.03 (m, 1H, CH₂), 1.18 (s, 3H, TiC_qCH₃), 1.72 (s, 15H, C₅Me₅), 1.90-2.05 (m, 9H, CH/CH₂), 2.14-2.16 (m, 1H, CH/CH₂), 2.33-2.49 (m, 4H, CH/CH₂), 2.55-2.57 (m, 2H, CH/CH₂), 2.71-2.79 (m, 1H, CH/CH₂), 3.28 (s, 1H, CH_{exo}), 4.98-5.00 (m, 1H, C₅H₄), 5.24-5.26 (m, 1H, C₅H₄), 5.73-5.74 (m, 1H, C₅H₄), 6.42-6.43 (m, 1H, C₅H₄), 7.05-7.08 (m, 1H, CH_{Ph}), 7.25-7.27 (m, 4H, 4×CH_{Ph}) ppm.

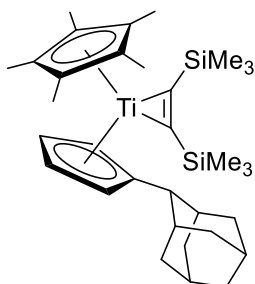
¹³C{¹H} NMR (126 MHz, C₆D₆, 305 K): δ = 12.2 (C₅Me₅), 23.5 (TiC_qCH₃), 28.5 (CH_{Ad}), 28.7 (CH_{Ad}), 32.82 (CH₂), 32.85 (CH_{Ad}), 33.20 (CH₂), 33.3 (CH_{Ad}), 38.1 (CH₂), 38.6 (CH₂), 39.2 (2×CH₂), 45.2 (CH_{exo}), 54.0 (CH₂), 108.9 (C₅H₄), 109.8 (C₅H₄), 115.5 (C₅H₄), 116.6 (C₅H₄), 121.0 (C₅Me₅), 125.3 (CH_{Ph}), 128.07 (2×CH_{Ph})*, 128.09 (2×CH_{Ph})*, 134.9 (C_{q,ipso}), 138.4 (TiC_q(CH₃)C_q), 145.9 (C_{q,Ph}), 195.8 (TiC_qCH₃) ppm.

* = overlap with the C₆D₅H signal

EA: Anal. calcd. for C₃₆H₄₆Ti: C, 82.11; H, 8.80; Found: C, 81.89; H, 8.73.



Synthesis of 4:



To a solution of complex **1** (0.200 g, 0.480 mmol) in 8 mL of *n*-hexane was added ethylmagnesium bromide (0.16 mL, 0.480 mmol; 3.0 M in diethyl ether) and the reaction mixture was stirred for 15 minutes at room temperature. A solution of BTMSA (0.1 mL, 0.480 mmol) in 5 mL of *n*-hexane was added and the reaction was stirred for another 16 h at room temperature. All volatile components were removed under vacuum. 10 mL of *n*-hexane were added, the suspension was filtered, and washed with *n*-hexane (2×8 mL). All volatile components were removed under vacuum to yield **4** as a yellow solid.

Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated *n*-hexane solution of **4** at room temperature.

Yield: 0.189 g (0.342 mmol, 71%).

Melting point: 160-162 °C (dec.).

IR (ATR): $\tilde{\nu}$ = 2903, 2850, 1614, 1487, 1468, 1449, 1375, 1355, 1248, 1099, 1061, 1019, 955, 933, 845, 826, 801, 786, 746, 681, 653, 618 cm⁻¹.

¹H NMR (500 MHz, C₆D₆, 305 K): δ = -0.07 (s, 18H, 2×SiMe₃), 1.22 (s, 1H, CH_{exo}), 1.59 (s, 15H, C₅Me₅), 1.59-1.61 (m, 2H, CH_{Ad}/CH_{2,Ad}), 1.67-1.69 (m, 2H, CH_{Ad}/CH_{2,Ad}), 1.74-1.75 (m, 2H, CH_{Ad}/CH_{2,Ad}), 1.80-1.82 (m, 3H, CH_{Ad}/CH_{2,Ad}), 1.91-1.92 (m, 1H, CH_{Ad}/CH_{2,Ad}), 2.19-2.20 (m, 2H, CH_{Ad}/CH_{2,Ad}), 2.63-2.66 (m, 2H, CH_{Ad}/CH_{2,Ad}), 5.93-5.94 (m, 2H, 2×C₅H₄), 6.54-6.55 (m, 2H, 2×C₅H₄) ppm.

¹³C{¹H} NMR (126 MHz, C₆D₆, 305 K): δ = 2.4 (2×SiMe₃), 12.6 (C₅Me₅), 28.2 (CH_{Ad}), 28.4 (CH_{Ad}), 32.5 (2×CH_{Ad}), 32.9 (2×CH_{2,Ad}), 38.3 (CH_{2,Ad}), 38.5 (2×CH_{2,Ad}), 43.8 (CH_{exo}), 113.5 (2×C₅H₄), 115.3 (2×C₅H₄), 122.1 (C₅Me₅), 136.2 (C_{q,ipso}), 244.2 (2×C_qSiMe₃) ppm.

²⁹Si{¹H} INEPT NMR (99 MHz, C₆D₆, 305 K): δ = -16.6 ppm.

EA: Anal. calcd. for C₃₃H₅₂Si₂Ti: C, 71.70; H, 9.48; Found: C, 70.76; H, 8.99.

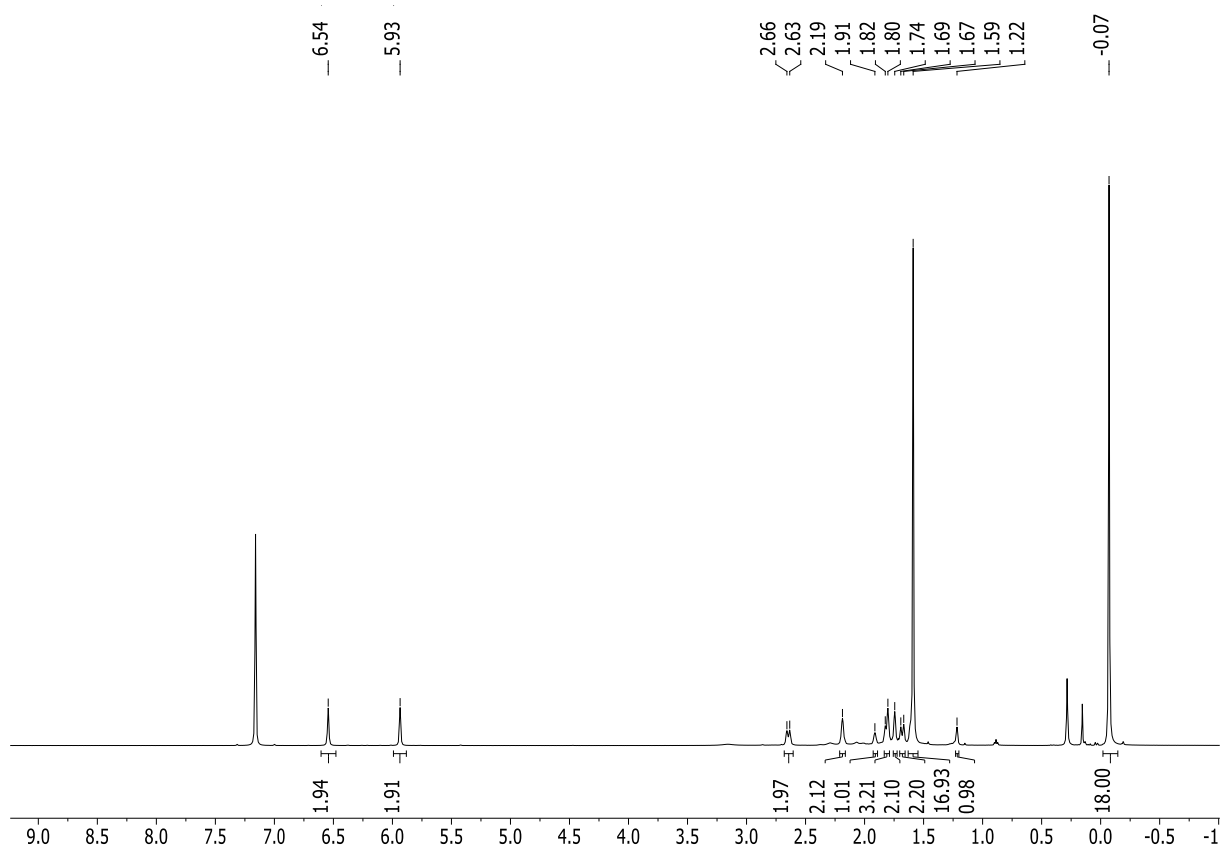


Figure S11: ^1H NMR spectrum of **4** (500 MHz, C_6D_6 , rt); 0.29 ppm: silicon grease, 0.16 ppm: BTMSA.

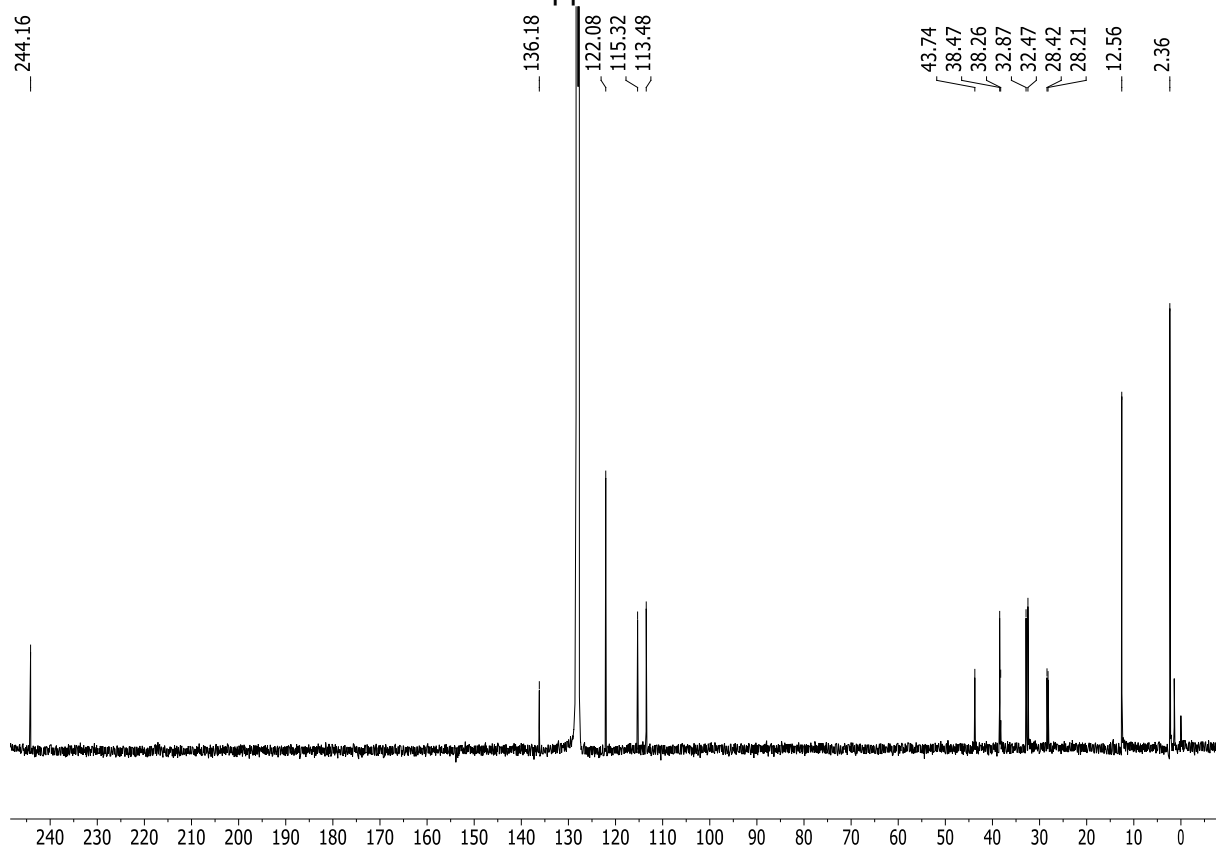


Figure S12: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** (126 MHz, C_6D_6 , rt); 1.4 ppm: silicon grease, 0.0 ppm: BTMSA.

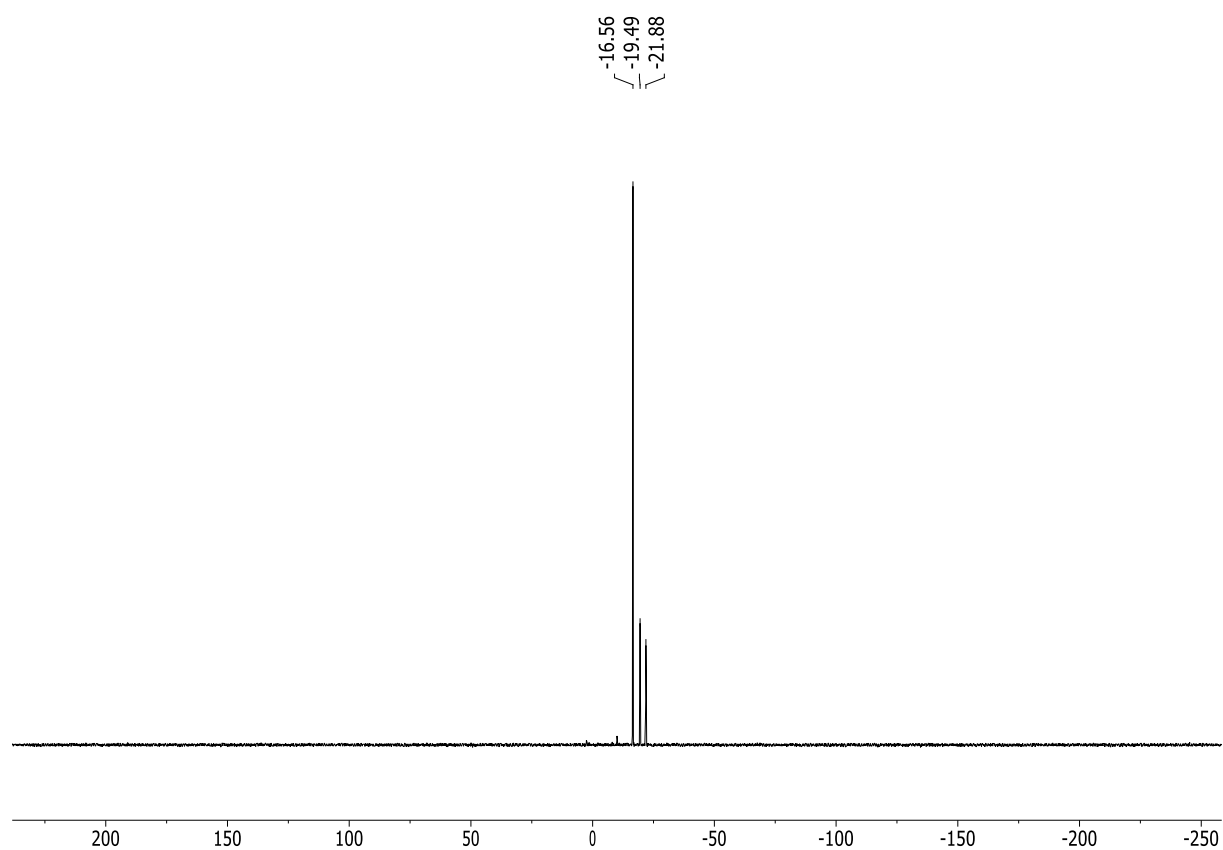
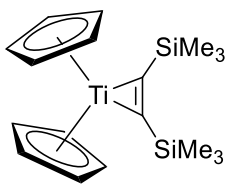


Figure S13: $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR spectrum of **4** (99 MHz, C_6D_6 , rt); -21.9 ppm: silicon grease, -19.5 ppm: BTMSA.

Synthesis of 6:



Cp_2TiCl_2 (1.500 g, 6.025 mmol) was suspended in 30 mL of *n*-hexane. Ethylmagnesium bromide (4.0 mL, 12.05 mmol; 3.0 M in diethyl ether) was added dropwise at room temperature, which is accompanied by a direct color change of the reaction mixture and by the evolution of ethylene as evident by the gas development. The reaction mixture was stirred for 1 h followed by the addition of BTMSA (1.4 mL, 6.025 mmol). The reaction was stirred for another 16 h at room temperature. All volatile components were removed under vacuum. 15 mL of toluene were added, the suspension was filtered over celite, washed with toluene (2×10 mL), and all volatile components were removed under vacuum to yield **5** as a yellow-brown solid.

Yield: 1.462 g (4.196 mmol, 70%).

^1H NMR (500 MHz, C_6D_6 , 305 K): δ = -0.32 (s, 18H, $\text{Me}_3\text{SiC}_2\text{SiMe}_3$), 6.42 (s, 10H, C_5H_5) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 305 K): δ = 0.7 ($\text{Me}_3\text{SiC}_2\text{SiMe}_3$), 117.9 (C_5H_5), 244.8 ($\text{Me}_3\text{SiC}_2\text{SiMe}_3$) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (99 MHz, C_6D_6 , 305 K): δ = -14.8 ppm.

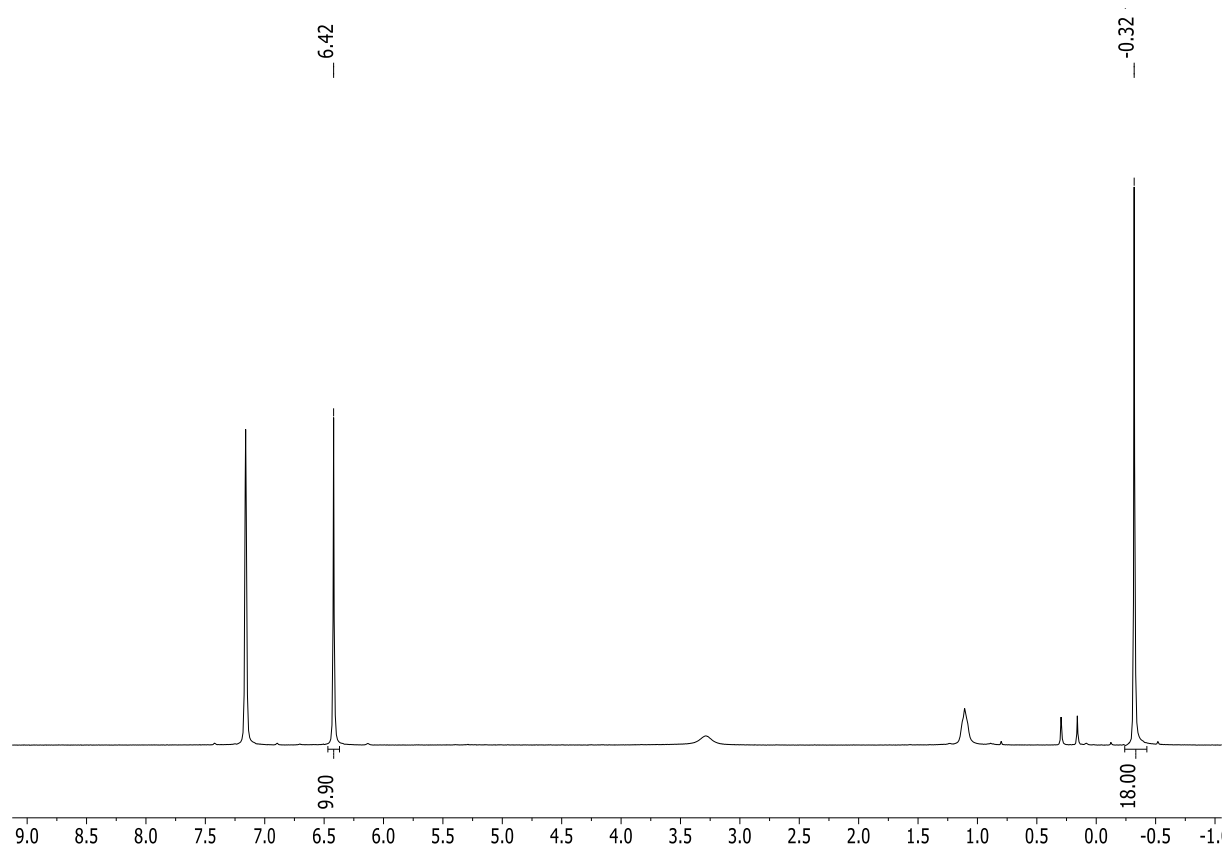


Figure S14: ^1H NMR spectrum of the crude product before filtration (300 MHz, C_6D_6 , rt); 0.29 ppm: silicon grease, 0.16 ppm: BTMSA, 1.11, 3.30 ppm: diethyl ether adducts.

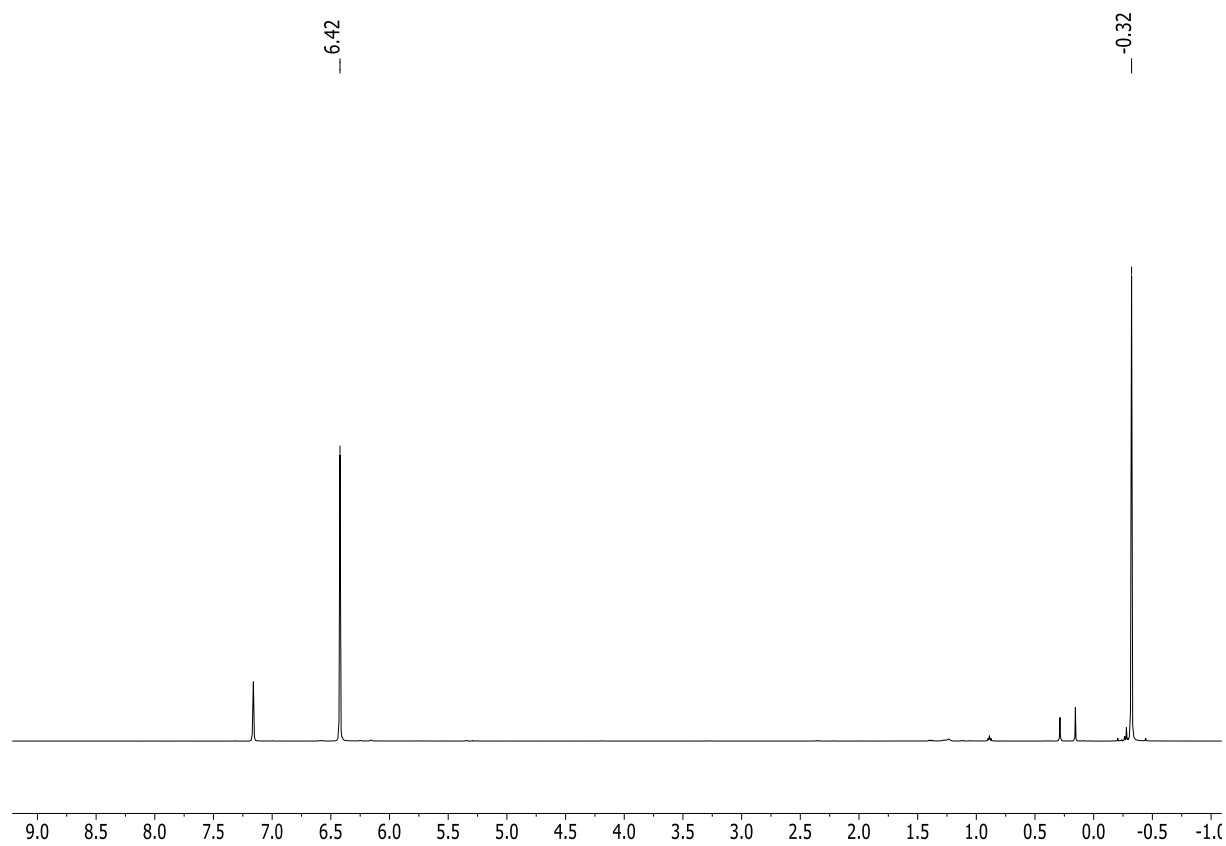


Figure S15: ^1H NMR spectrum of **5** (500 MHz, C_6D_6 , rt); 0.29 ppm: silicon grease, 0.16 ppm: BTMSA.

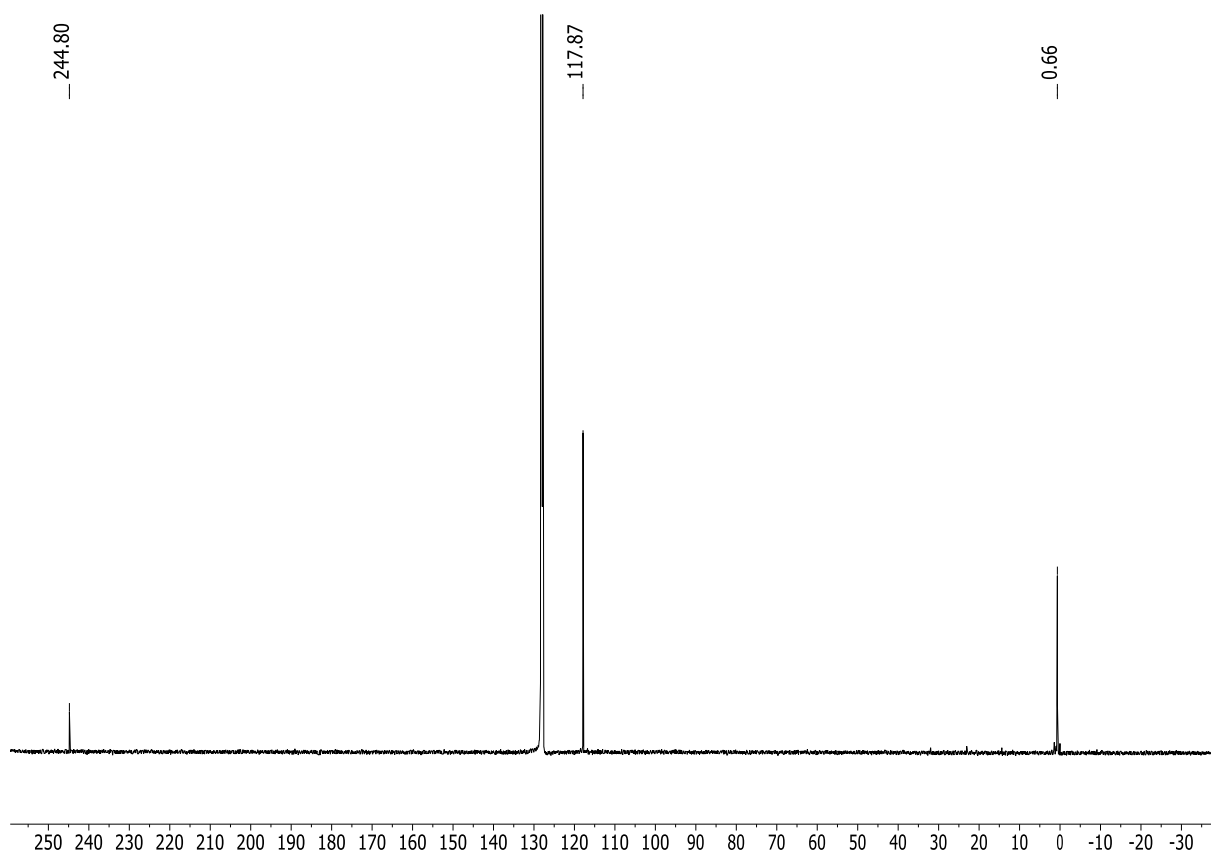


Figure S16: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** (126 MHz, C_6D_6 , rt).

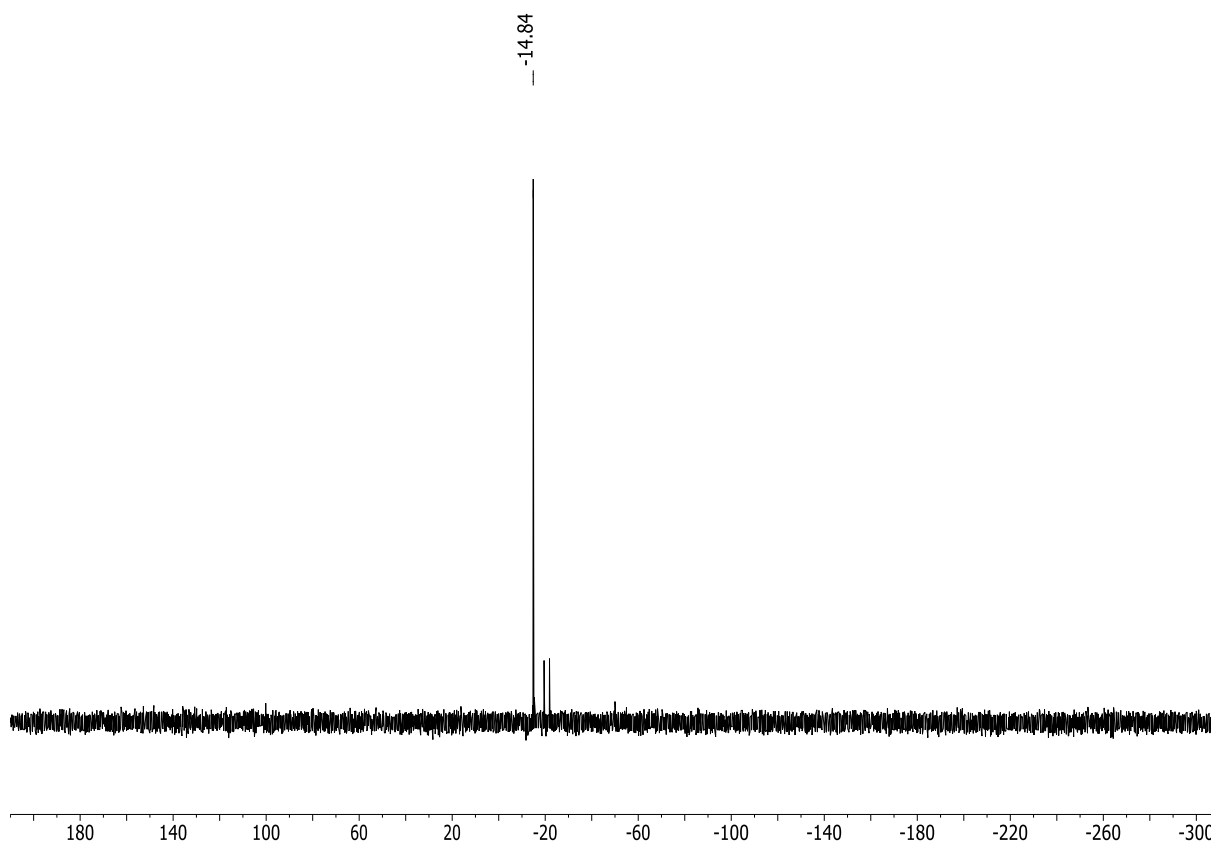


Figure S17: $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR spectrum of **4** (99 MHz, C_6D_6 , rt); -21.9 ppm: silicon grease, -19.5 ppm: BTMSA.

Crystallographic Data:

Suitable crystals were selected and measured on a 'Bruker APEX-II CCD' diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal was kept at 100.15 K during data collection. Using Olex2,^[2] the structure was solved with the ShelXS^[3] structure solution program using Direct Methods and refined with the ShelXL^[4] refinement package using Least Squares minimisation.

Table S1: Crystal Structure Data for Compounds **2** and **4**.

	2	4		
CCDC	1968512	1968513		
empirical formula	C ₂₇ H ₃₈ Ti	C ₃₃ H ₅₂ Si ₂ Ti		
fw	410.47	552.82		
colour	yellow-green	yellow		
Habit	rod	block		
cryst dimens, mm	0.30 x 0.08 x 0.06	0.50 x 0.35 x 0.30		
cryst syst	orthorhombic	orthorhombic		
space group	<i>Pnma</i>	<i>P2₁2₁2₁</i>		
a, Å	9.1810(3)	11.3854(3)		
b, Å	11.4645(4)	12.8121(3)		
c, Å	20.7463(7)	21.3362(5)		
α , deg	90	90		
β , deg	90	90		
γ , deg	90	90		
V, Å ³	2183.6(13)	3112.33(13)		
Z	4	4		
D _{calcd} , g cm ⁻³	1.249	1.180		
μ , mm ⁻¹	0.402	0.372		
T, K	100(2)	100(2)		
θ range, deg	1.963 – 33.726	1.854 – 36.316		
no. of rflns collected	76093	188971		
no. of indep rflns	4547	15106		
(R(int))	0.0643	0.0271		
no. of rflns with $I > 2\sigma(I)$	3511	14681		
abs cor	numerical	numerical		
max, min transmission	0.9823 and 0.9131	0.9261 and 0.8596		
final R indices	R1 = 0.0438	R1 = 0.0193		
[$I > 2\sigma(I)$]	wR2 = 0.1112	wR2 = 0.0542		
R indices (all data)	R1 = 0.0626	R1 = 0.0205		
	wR2 = 0.1238	wR2 = 0.0550		
GOF on F ²	1.039	1.064		
largest diff peak / hole (e.Å ⁻³)	0.605 / -0.377	0.424 / -0.152		

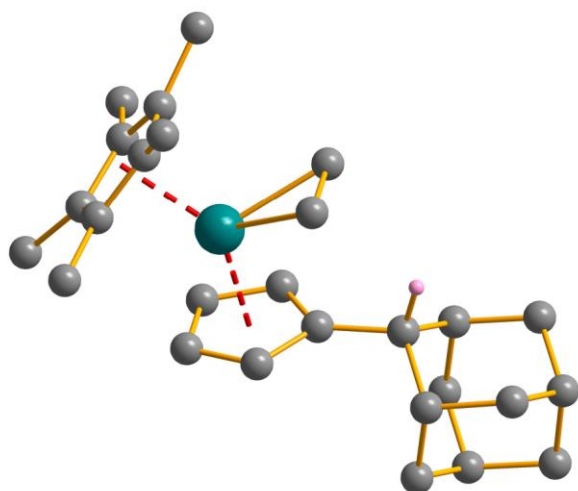


Figure S18: Molecular structure of **2**.

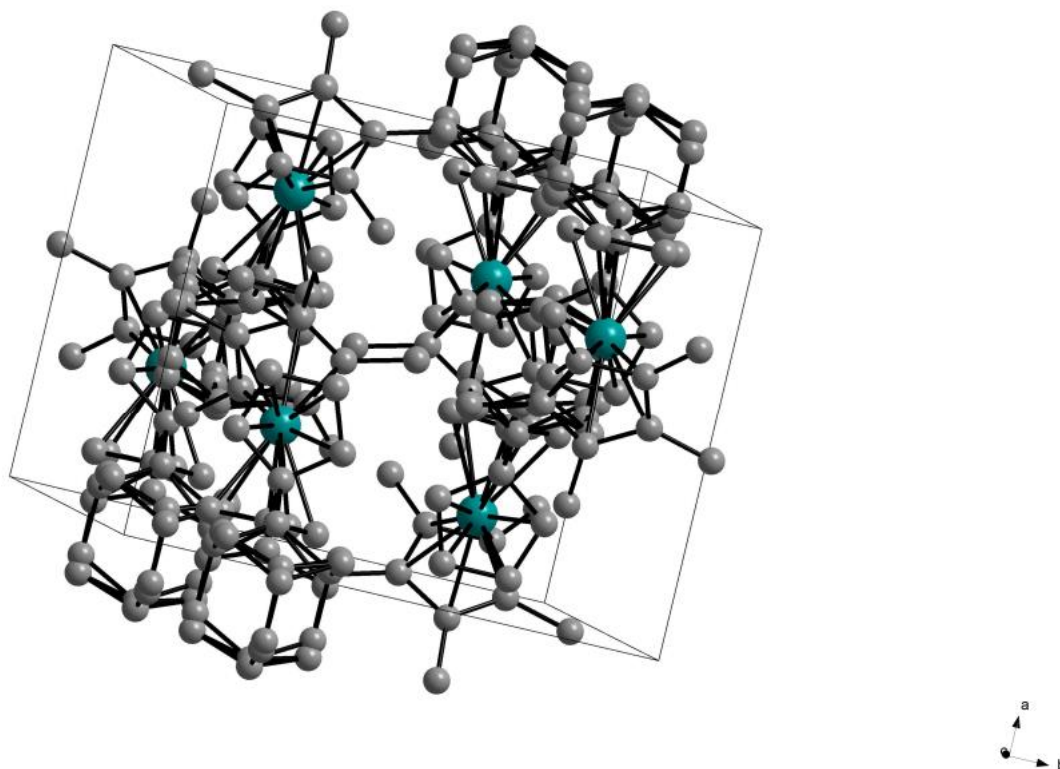


Figure S19: View along the *c* axis showing the packing of molecules in the crystal structure of complex **2**. Hydrogen atoms have been omitted for clarity.

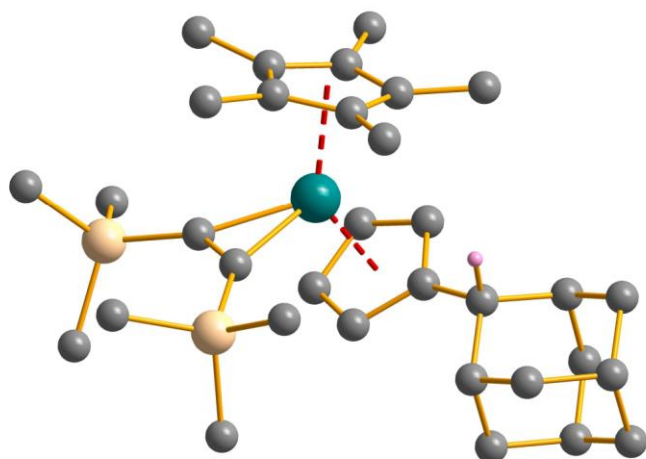


Figure S20: Molecular structure of **4**.

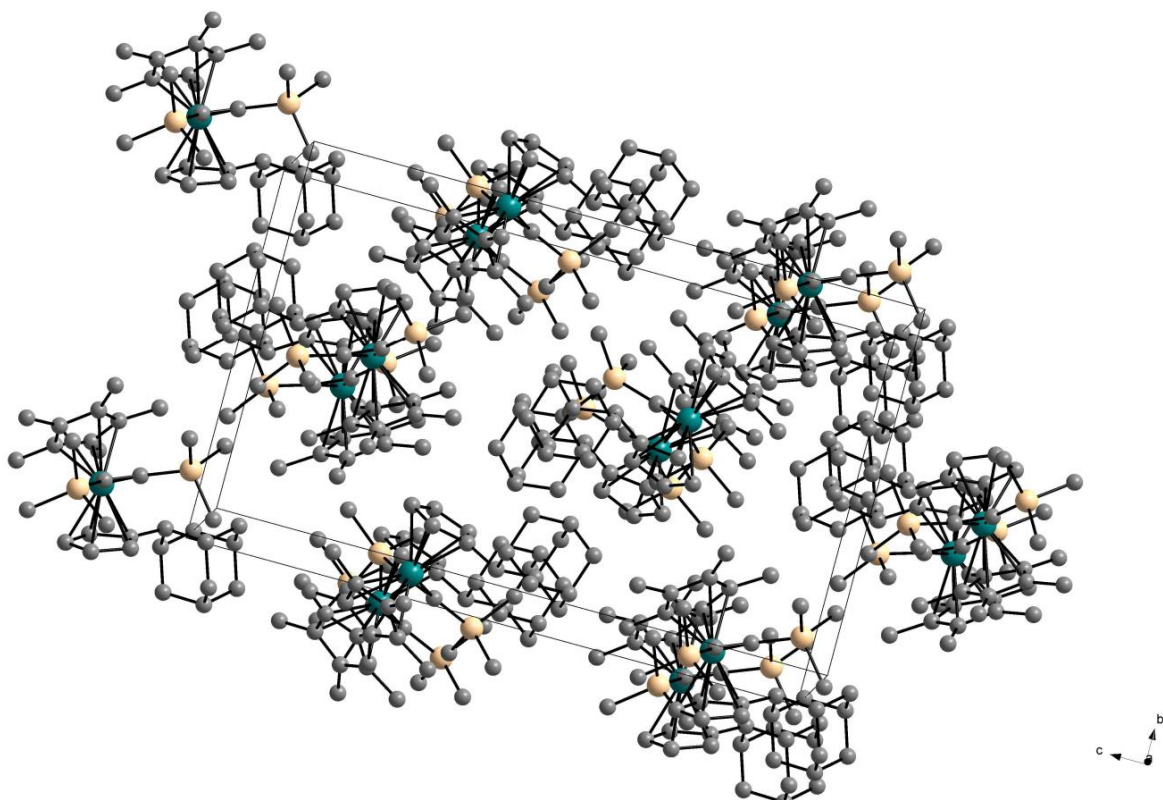


Figure S21: View along the *c* axis showing the packing of molecules in the crystal structure of complex **4**. Hydrogen atoms have been omitted for clarity.

References

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