

Electronic Supporting Information

Formate Complexes of Tri- and Tetravalent Titanium Supported by a Tris(phenolato)amine Ligand

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1. General considerations

All manipulations were performed under argon atmosphere using standard Schlenk or glovebox techniques unless otherwise noted. Prior to use, glassware was dried overnight at 150 °C. The solvents used for NMR spectroscopy were dried, distilled and degassed by standard methods and stored over 4 Å molecular sieves. Tetrahydrofuran (THF), toluene, *n*-pentane and diethyl ether (Et₂O) were dried with a MBraun SPS and stored over 4 Å molecular sieves. All other solvents were dried and degassed by standard methods. Unless otherwise stated, the reactions were performed at room temperature (21–24 °C) in Schlenk flasks, Schlenk tubes or snap cap vials of suitable size equipped with a PTFE magnetic stir bar. NMR measurements were performed on a Bruker Avance II or Avance III spectrometer operating at 400 MHz for ¹H nuclei and 101 MHz for ¹³C nuclei. The chemical shifts (δ in ppm) of the ¹H and ¹³C{¹H} NMR spectra were referenced to the residual proton signals of the deuterated solvents and reported relative to tetramethylsilane. Standard abbreviations indicating multiplicities were used as follows: s (singlet), d (doublet), t (triplet) and m (multiplet). Solid-state IR spectra were measured on KBr pellets using an AVATAR 360 FT-IR spectrometer or in powder form using Shimadzu IRSpirit spectrometer fitted with a Single Reflection ATR accessory. Solution IR spectra were measured using a stainless steel cell with NaCl windows using the AVATAR 360 FT-IR spectrometer. Abbreviations for IR spectra were used as follows: vw (very weak), w (weak), m (medium), s (strong), vs (very strong), br (broad), sh (shoulder). UV-Vis spectra were recorded on a Shimadzu UV-2600 spectrophotometer using 10 mm quartz glass cuvettes. EPR spectra were obtained at 77 K on a Miniscope MS 400 from Magnettech with a microwave frequency of 9.4 GHz. Solutions in toluene with a concentration of ca. 2 mM of the titanium(III) complex were measured as glass at 77 K. The *B*₀ field was adjusted to 345 mT with a range of 60 mT (315 – 375 mT) and a sweep time of 60 s. Other parameters were adjusted as follows: modulation amplitude = 0.5 mT, microwave attenuation = 10.0 dB, smooth = 0.1000 s, NOPs = 4096, gain mantissa = 9, and gain exponent = 0. Elemental analyses were carried out using a CHN-O-Rapid VarioEL from Heraeus. The starting materials ([[(O₃N)TiCl] (**1-Cl**; (H₃(O₃N) = tris(4,6-di-*tert*-butyl-2-hydroxybenzyl)amine)^[S 1] and [[(O₃N)TiOCHO] (**2**)^[S2] were prepared according to the reported procedure. All other chemicals were purchased from commercial sources and used as received without further purification.

2. Syntheses, spectroscopic data and selected spectra of 3-Na –7

2.1. [Na₂{(O₃N)Ti}₄(OCHO)₆] (3-Na)

A solid mixture of **2** (76 mg, 0.1 mmol) and sodium formate (10 mg, 0.15 mmol) was treated with THF (2 mL) and the resulting solution was stirred overnight at room temperature. After completion of the reaction, as confirmed by ¹H NMR spectroscopy, the solution was filtered and the residue was extracted with *n*-pentane (2 mL). The combined extract was dried to obtain compound **3-Na** as an orange powder. Yield: 80 mg (0.025 mmol, quantitative).

Elemental analysis calculated for C₁₈₆H₂₇₀N₄Na₂O₂₄Ti₄: C: 70.77, H: 8.55, N: 1.76%; found: C: 70.28, H: 8.65, N: 2.01%.

¹H NMR (400 MHz, THF-*d*₈, 298 K): δ 9.10 (br s, OCHO), 7.60 (br s, OCHO), 7.14 (br s, H_{aryl}), 6.96 (br s, H_{aryl}), 3.97 (br s, NCH₂), 3.67 (br s, NCH₂), 1.33 (br s, 108H, C(CH₃)₃), 1.25 (s, 108H, C(CH₃)₃).

¹³C{¹H} NMR (101 MHz, THF-*d*₈, 298 K): δ 168.3 (br s, OCHO), 167.5 (br s, OCHO), 159.4 (br s, C_{aryl}), 141.4 (s, C_{aryl}), 135.3 (s, C_{aryl}), 125.8 (s, C_{aryl}), 124.6 (s, C_{aryl}), 123.5 (s, C_{aryl}), 62.8 (br, NCH₂; two signals overlap with each other), 35.6 (s, C(CH₃)₃), 34.8 (s, C(CH₃)₃), 32.1 (s, C(CH₃)₃), 30.6 (s, C(CH₃)₃).

IR (powder): ν = 2952 (vs), 2903 (s), 2867 (s), 1641 (vs, sh), 1474(s), 1444 (s), 1412 (w), 1389 (w), 1361 (m), 1258 (vs), 1238 (vs), 1202 (m), 1169 (m), 1127 (m), 914 (m), 873 (m), 840 (s), 810 (w), 755 (m), 604 (m) cm⁻¹.

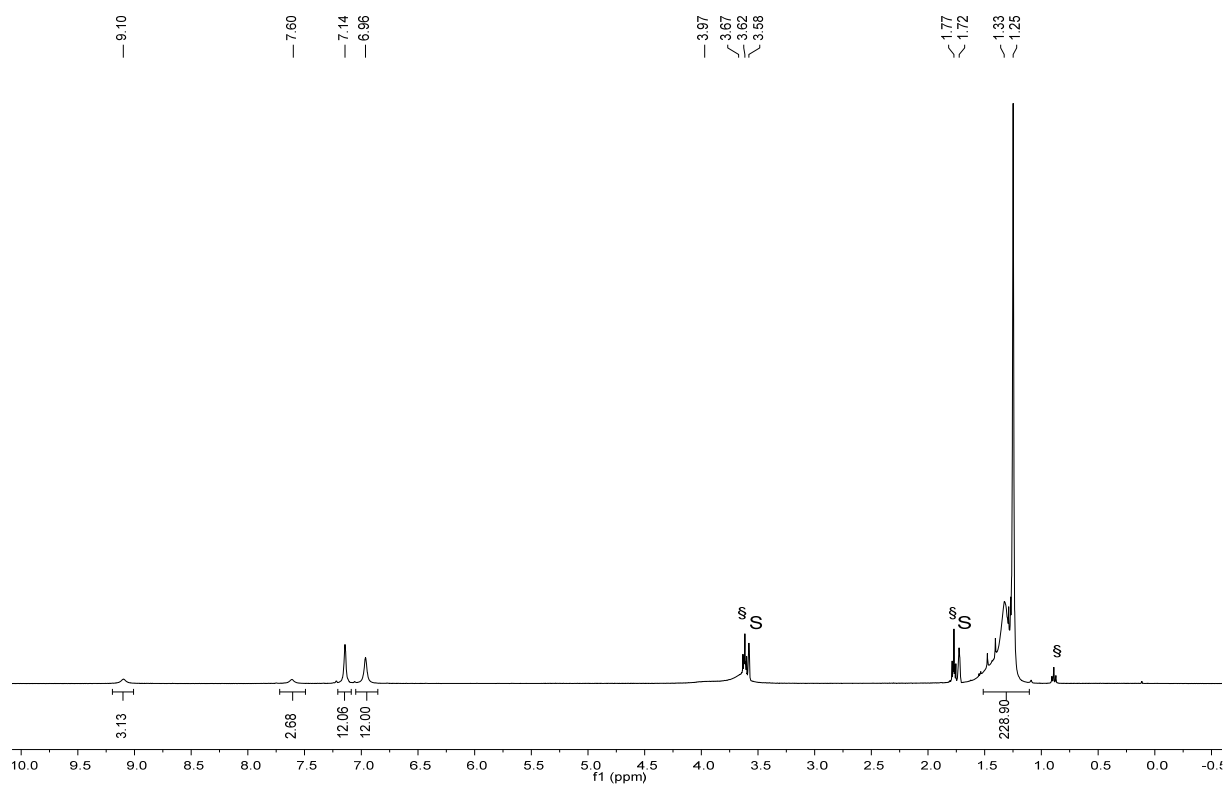


Figure S1. ^1H NMR spectrum of **3-Na** in $\text{THF-}d_8$ at 298 K; S denotes the residual proton signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane and THF present in the sample.

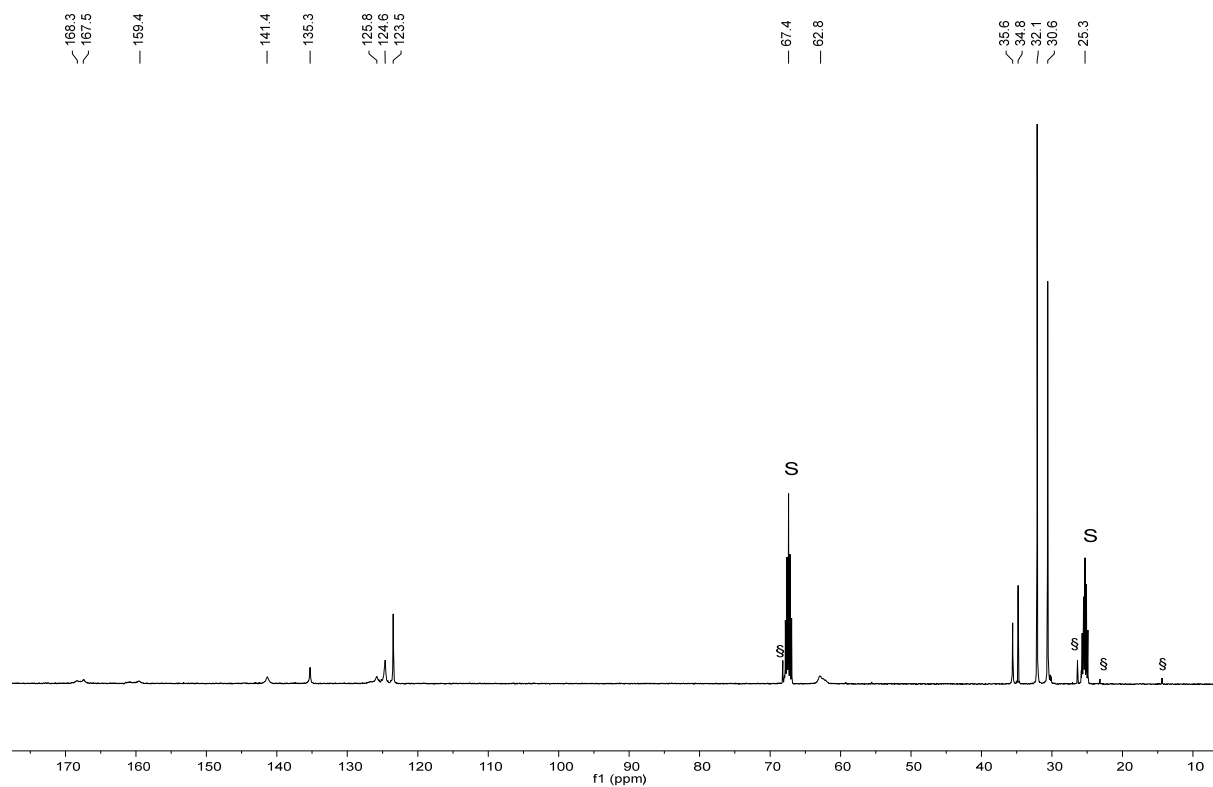


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3-Na** in $\text{THF-}d_8$ at 298 K; S denotes the ^{13}C NMR signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane and THF present in the sample.

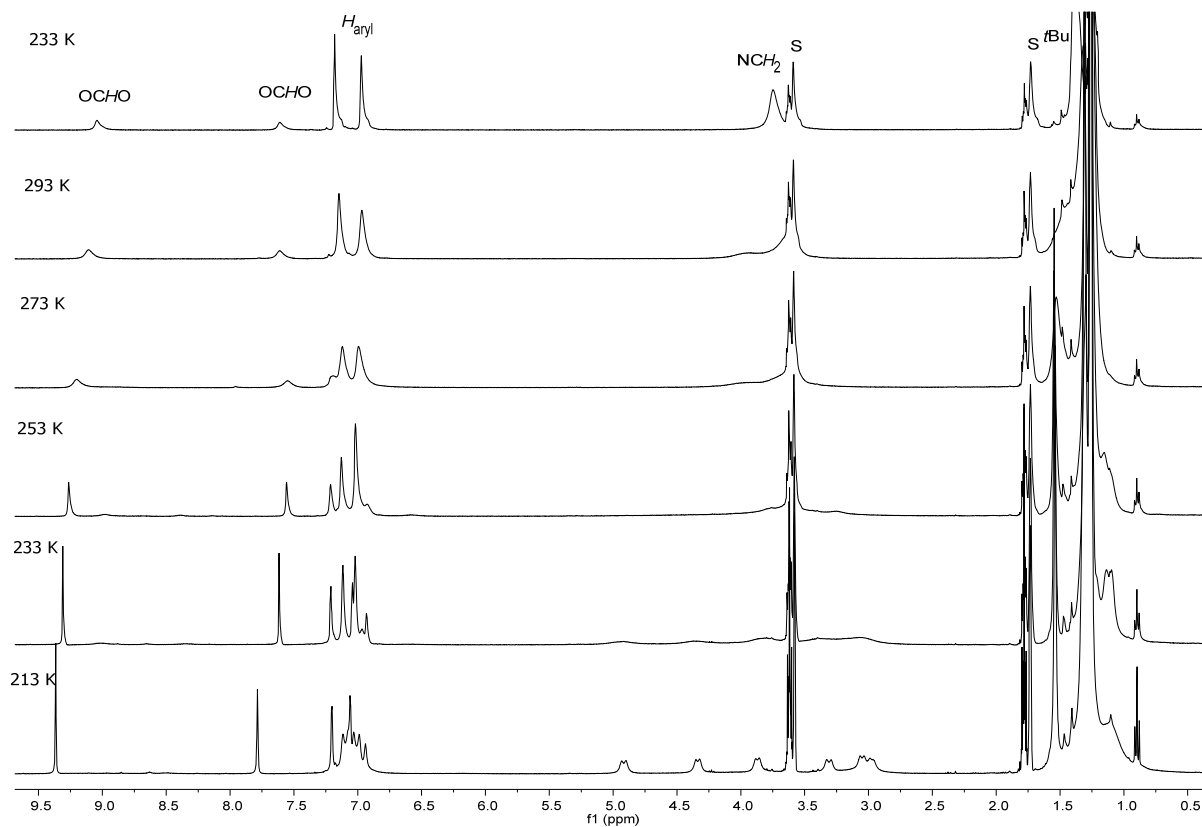


Figure S3. Variable temperature ^1H NMR spectrum of **3-Na** in THF-d_8 (213–333 K); S denotes the residual proton signal of the deuterated solvent.

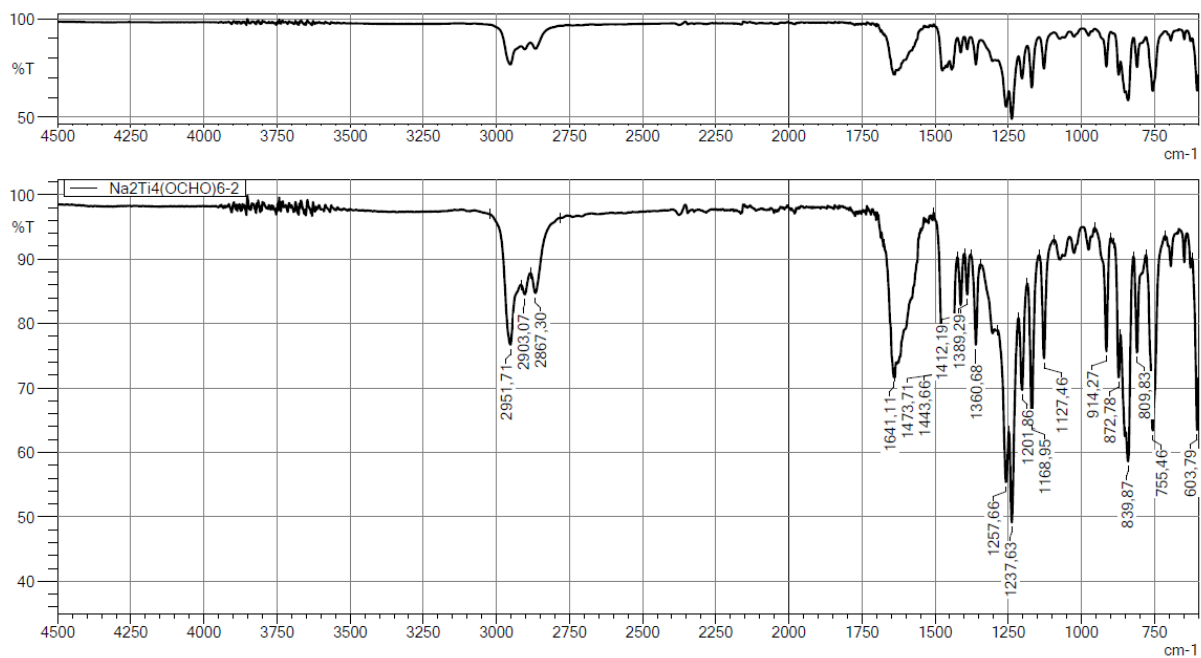


Figure S4. IR spectrum of **3-Na** in powder form at 298 K.

2.2. $[K_3\{(O_3N)Ti\}_4(OCHO)_7]$ (**3-K**)

Method A: A solid mixture of **1-CI** (753 mg, 1.0 mmol) and potassium formate (168 mg, 2.0 mmol) was treated with THF (10 mL) and the resulting solution was stirred overnight at room temperature. After completion of the reaction, as confirmed by 1H NMR spectroscopy, the solvent was removed under reduced pressure. The resulting residue was extracted with *n*-pentane (10 mL). The combined extract was evaporated to dryness and the residue was crystallized by slow evaporation from a small amount of toluene at room temperature under argon atmosphere to obtain orange crystals. The crystals were isolated by decantation of the supernatant solution and washed with a small amount of *n*-pentane to give compound **3-K** as an orange powder. Yield: 218 mg (0.066 mmol, 24%).

Method B: A solid mixture of **2** (76 mg, 0.1 mmol) and potassium formate (25 mg, 0.3 mmol) was treated with toluene (5 mL) and the resulting solution was stirred overnight at room temperature. After completion of the reaction, as confirmed by 1H NMR spectroscopy, the solvent was removed under reduced pressure. The resulting residue was extracted with *n*-pentane (10 mL) and the extract was evaporated to dryness to provide compound **3-K** as an orange powder. Yield: 67 mg (0.081 mmol, 81%).

Elemental analysis calculated for $C_{187}H_{271}K_3N_4O_{26}Ti_4$: C: 68.06, H: 8.28, N: 1.70%; found: C: 67.78, H: 8.09, N: 1.84%.

1H NMR (400 MHz, benzene- d_6 , 298 K): δ 9.78 (br s, H_{aryl}), 8.59 (br s, H_{aryl}), 6.58-7.72 (br m, H_{aryl}), 6.28 (br s, H_{aryl}), 2.23-5.71 (br m, NCH_2), 0.49-2.07 (br m, $C(CH_3)_3$).

1H NMR (400 MHz, toluene- d_8 , 253 K): δ 9.83, 8.67 and 8.55 (each s, 2H each, $OCHO$), 7.62, 7.49, 7.46, 7.34, 7.22, 7.21, 7.18, 6.905, 6.900, 6.87, 6.81 and 6.20 (each s, 2H each, H_{aryl}), 5.80 (s, 1H, $OCHO$), 5.06, 4.68, 4.25, 4.19, 4.10, 4.07, 3.37, 3.16, 2.91, 2.44, 2.32 and 2.28 (each d, $^2J_{H,H} = \sim 12$ Hz, 2H each, NCH_2), 1.92 (br s, 18H, $C(CH_3)_3$), 1.64 (s, 18H, $C(CH_3)_3$), 1.61 (s, 18H, $C(CH_3)_3$), 1.58 (s, 18H, $C(CH_3)_3$), 1.57 (s, 18H, $C(CH_3)_3$), 1.53 (s, 18H, $C(CH_3)_3$), 1.45 (s, 36H, $C(CH_3)_3$, two signals overlap with each other), 1.25 (s, 18H, $C(CH_3)_3$), 1.24 (s, 18H, $C(CH_3)_3$), 1.15 (s, 18H, $C(CH_3)_3$), 0.88 (br s, 18H, $C(CH_3)_3$).

1H NMR (400 MHz, toluene- d_8 , 333 K): δ 9.10 (br s, $OCHO$), 7.86 (br s, $OCHO$), 7.29 (br s, 12H, H_{aryl}), 6.87 (s, 12H, H_{aryl}), 3.56 (br s, 24H, NCH_2), 1.45 (br s, 108H, $C(CH_3)_3$), 1.33 (br s, 108H, $C(CH_3)_3$).

$^{13}C\{^1H\}$ NMR (101 MHz, toluene- d_8 , 213 K): δ 28.8, 29.9, 30.2, 30.80, 30.84, 31.1, 31.7, 32.0, 32.1, 32.3, 32.5, 32.8 (each s, 6C each, $C(CH_3)_3$), 34.2, 34.45, 34.49, 34.67, 34.69, 34.8, 34.96, 35.01, 35.12, 35.14, 35.2, 35.7 (each s, 2C each, $C(CH_3)_3$), 58.7, 60.2, 63.4, 64.4, 66.5 (br s, NCH_2 ; all the expected signals are not visible due to the broadening as well as overlap

with each other), 125.8, 126.0, 126.2, 131.5, 133.2, 134.2, 134.6, 135.3, 135.4, 140.0, 140.17, 140.19, 140.6, 141.6, 142.1, 158.4, 158.7, 160.6, 160.8, 162.3, 162.0 (each s, C_{aryl}; all the expected signals are not visible due to the overlap with the deuterated solvent signals), 166.2, 168.7, 171.6 (each s, OCHO).

¹³C{¹H} NMR (101 MHz, toluene-*d*₈, 333 K): δ 169.8 and 167.2 (br s each, OCHO), 160.4 (C_{aryl}), 142.1 (C_{aryl}), 135.3 (C_{aryl}), 62.6 (NCH₂), 35.4 (C(CH₃)₃), 34.6 (C(CH₃)₃), 32.1 (C(CH₃)₃), 30.6 (C(CH₃)₃).

IR (KBr pellet): ν = 2955 (vs), 2899 (s), 2867 (s), 1639 (vs, sh), 1477 (s), 1451 (s), 1413 (w), 1391 (w), 1361 (m), 1260 (vs), 1239 (vs), 1203 (m), 1170 (m), 1128 (m), 915 (m), 873 (m), 842 (s), 809 (w), 756 (m), 605 (m), 568 (s), 477 (m) cm⁻¹.

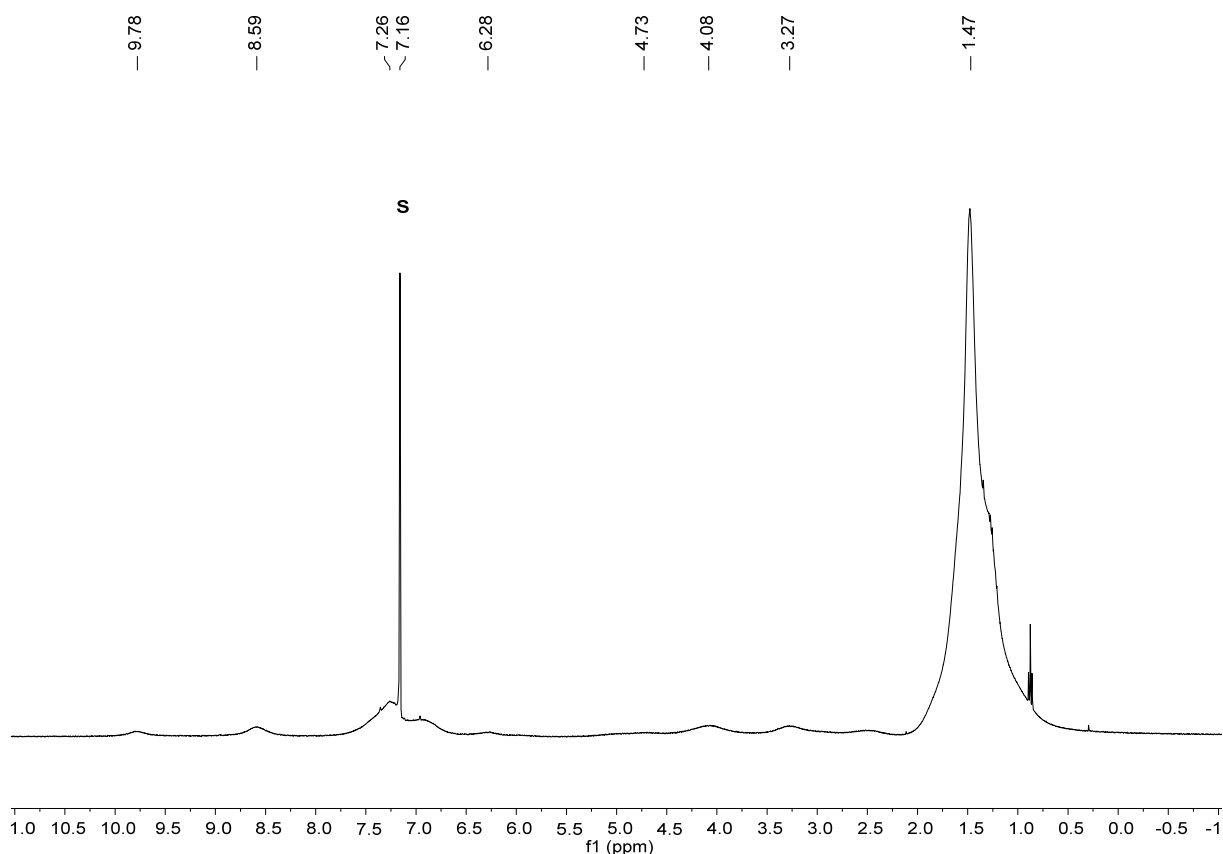


Figure S5. ¹H NMR spectrum of **3-K** in benzene-*d*₆ at 298 K; S denotes the residual proton signal of the deuterated solvent.

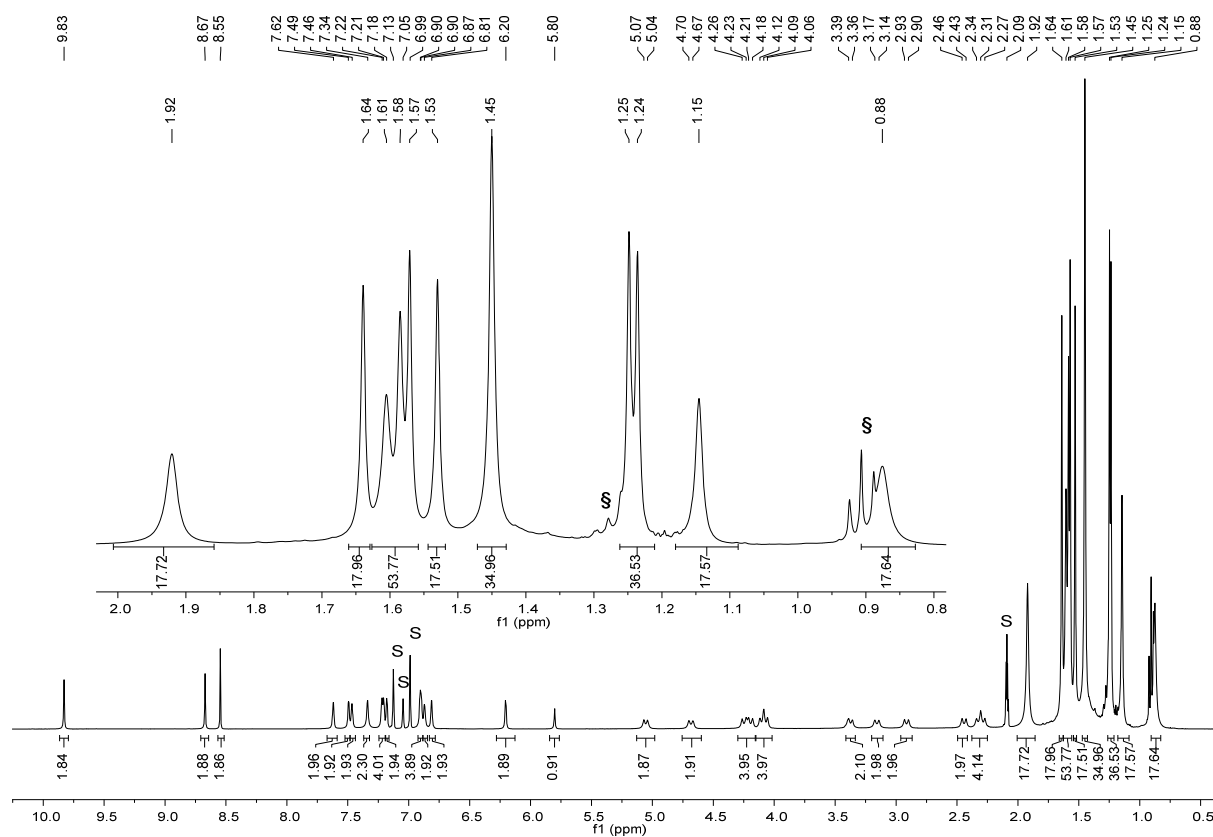


Figure S6. ^1H NMR spectrum of **3-K** in $\text{toluene-}d_8$ at 253 K; S denotes the residual proton signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

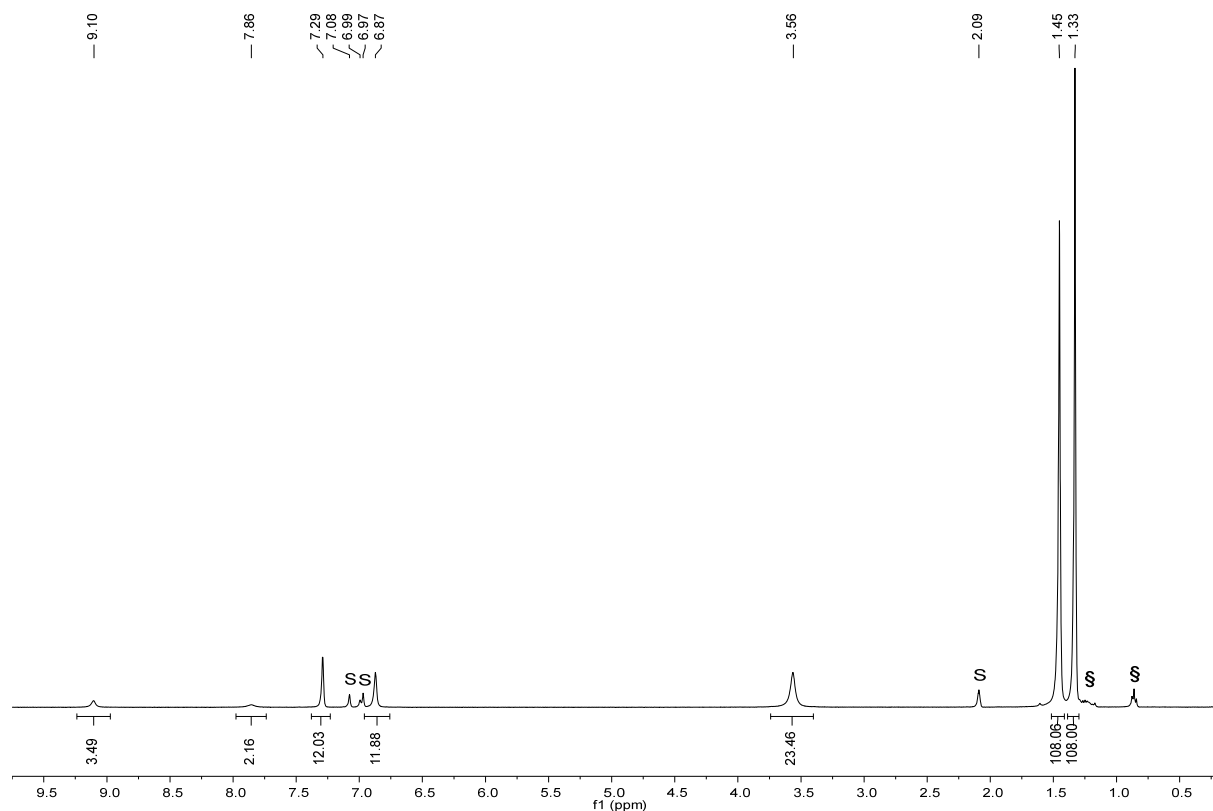


Figure S7. ^1H NMR spectrum of **3-K** in $\text{toluene-}d_8$ at 333 K; S denotes the residual proton signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

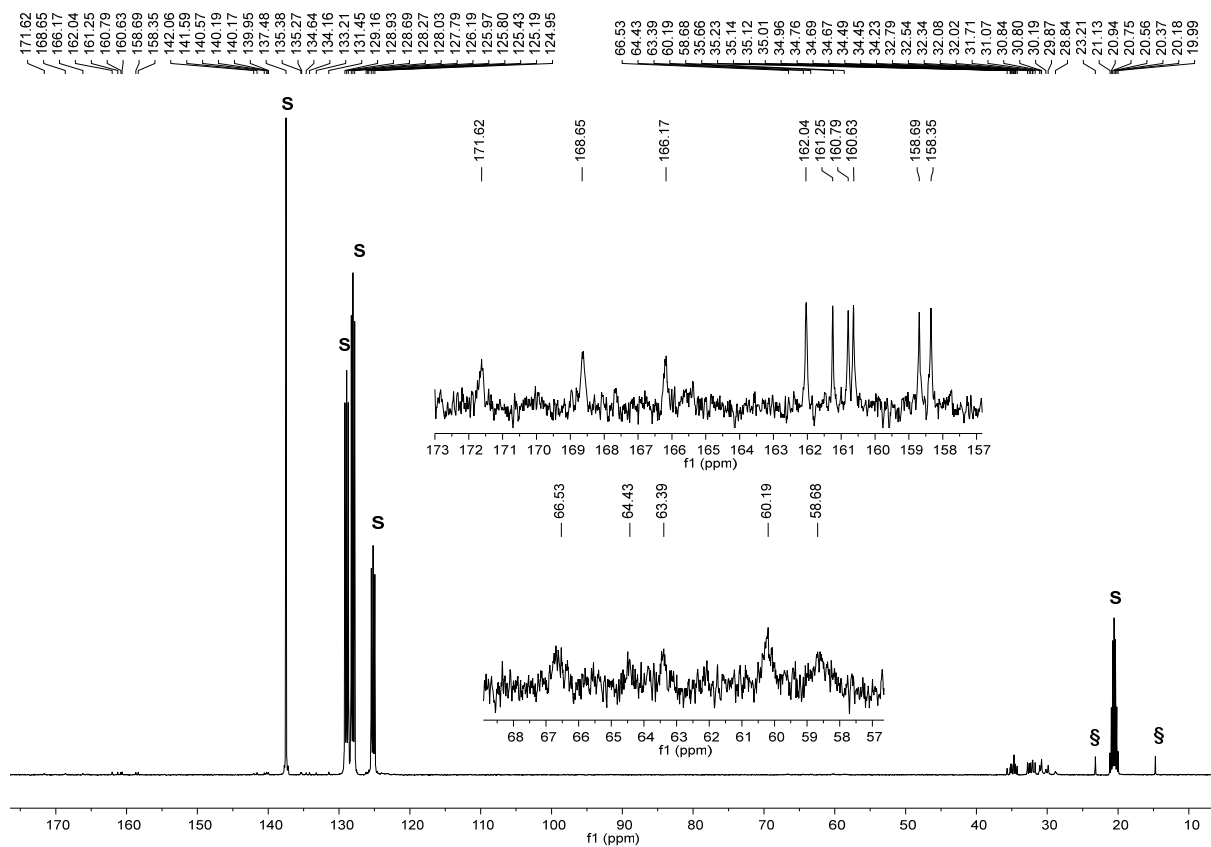


Figure S8. ^{13}C NMR spectrum of **3-K** in toluene- d_8 at 213 K; S denotes the ^{13}C NMR signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

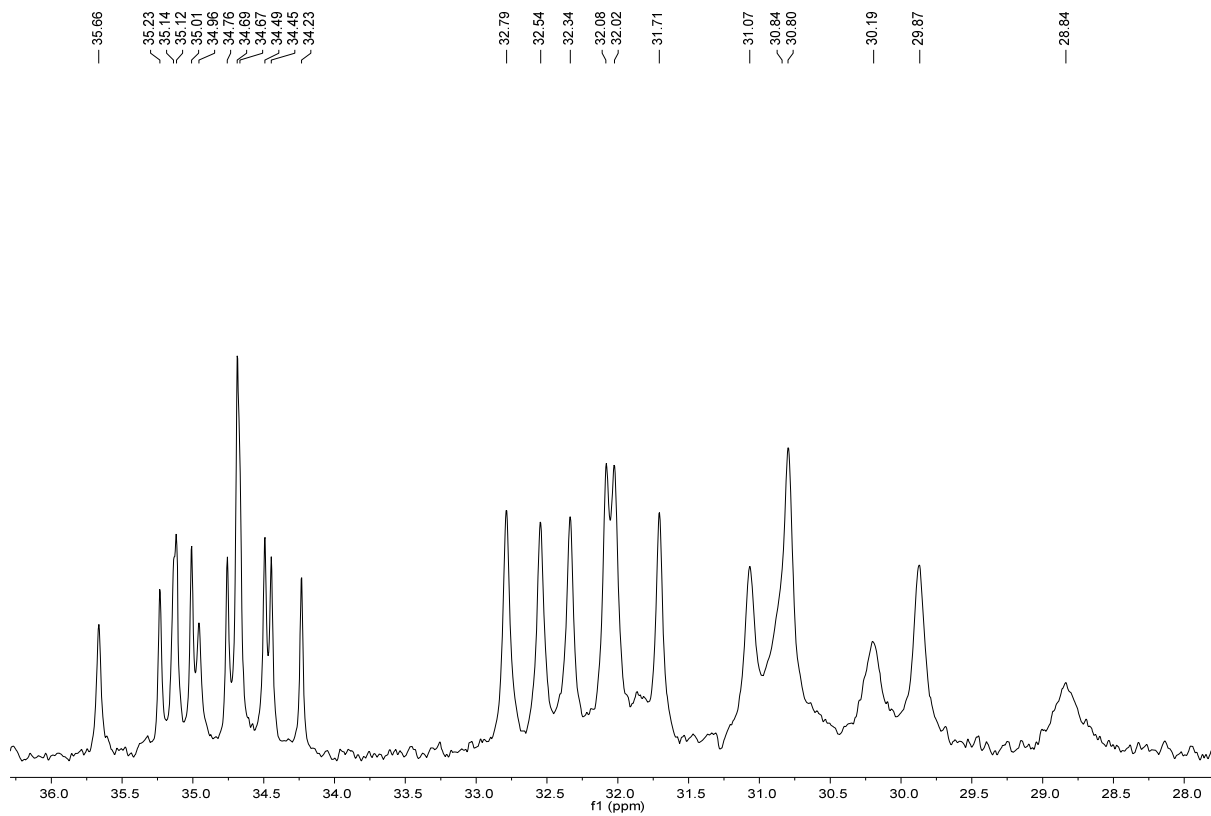


Figure S9. Excerpt of the *Figure S8* in the range of 28.0–36.0 ppm.

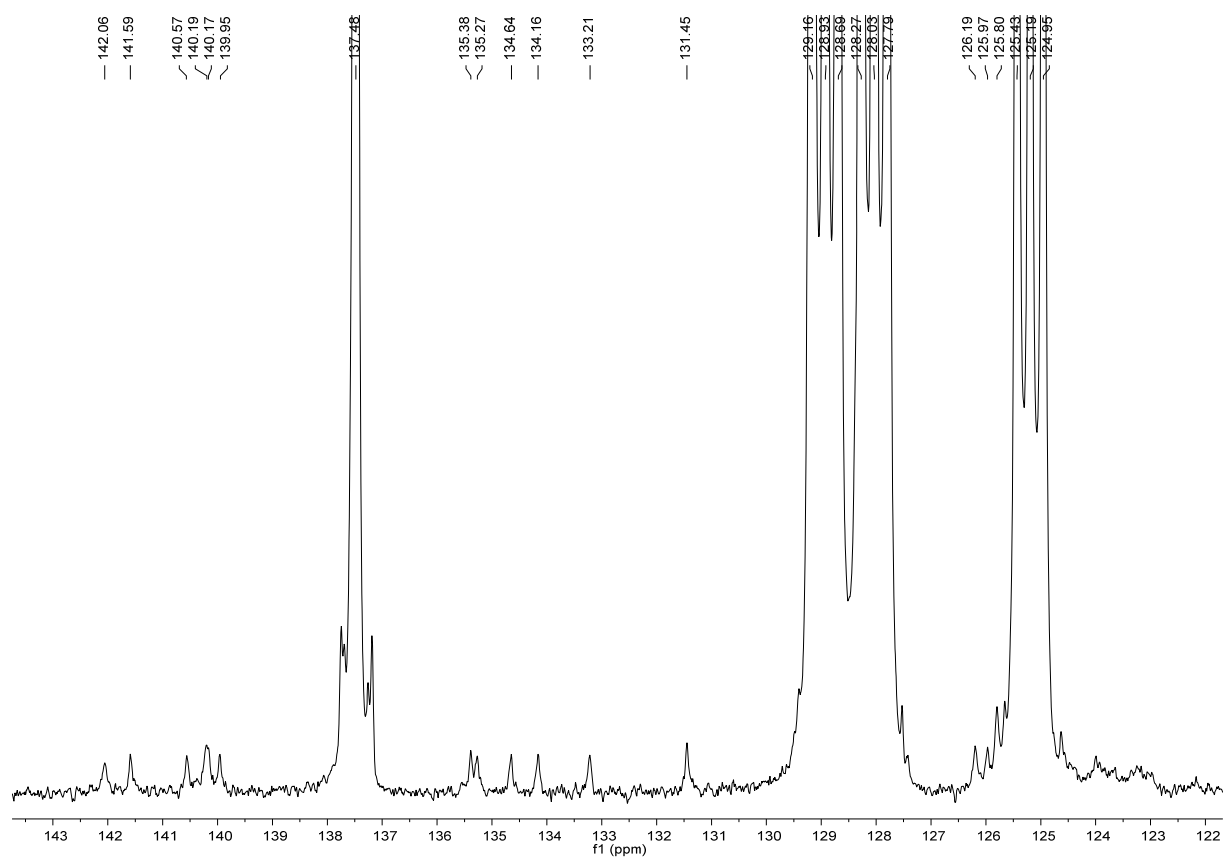


Figure S10. Excerpt of Figure S4 in the range of δ 122.0–143.0 ppm.

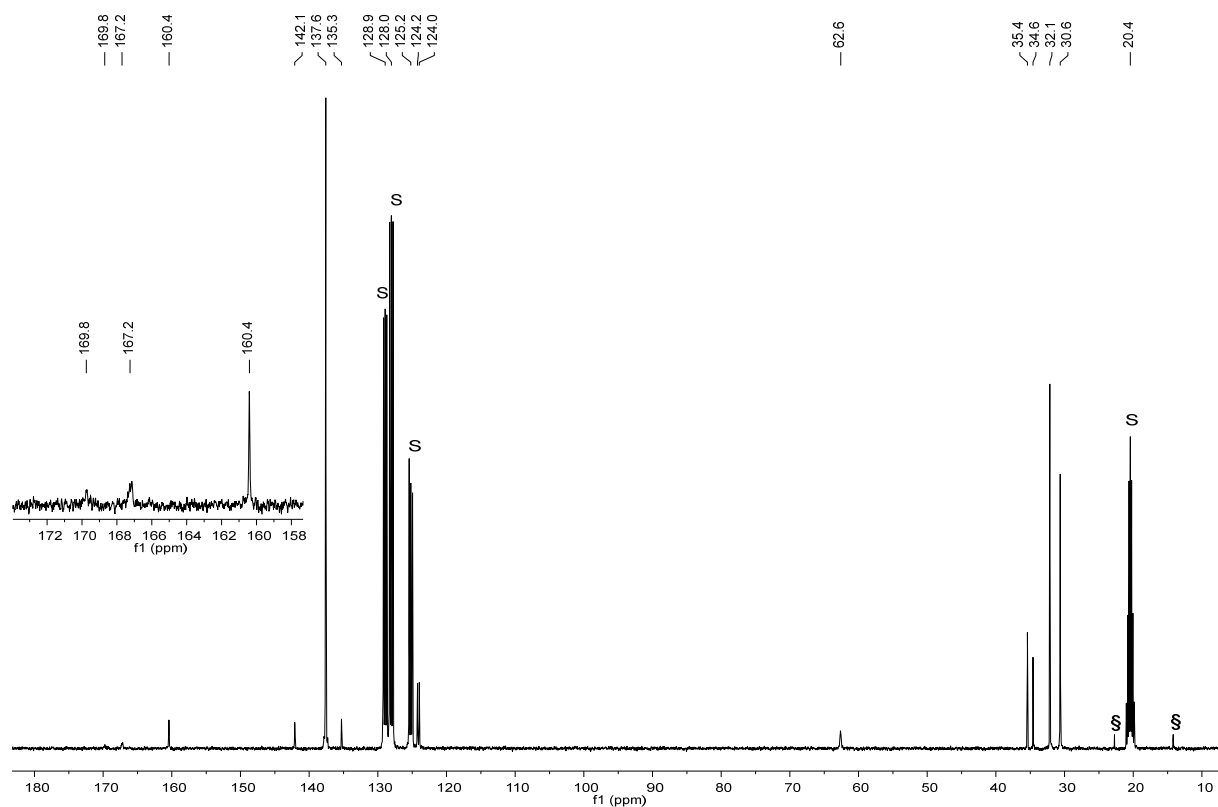


Figure S11. ^{13}C NMR spectrum of **3-K** in toluene- d_8 at 333 K; S denotes the ^{13}C NMR signal of the deuterate solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

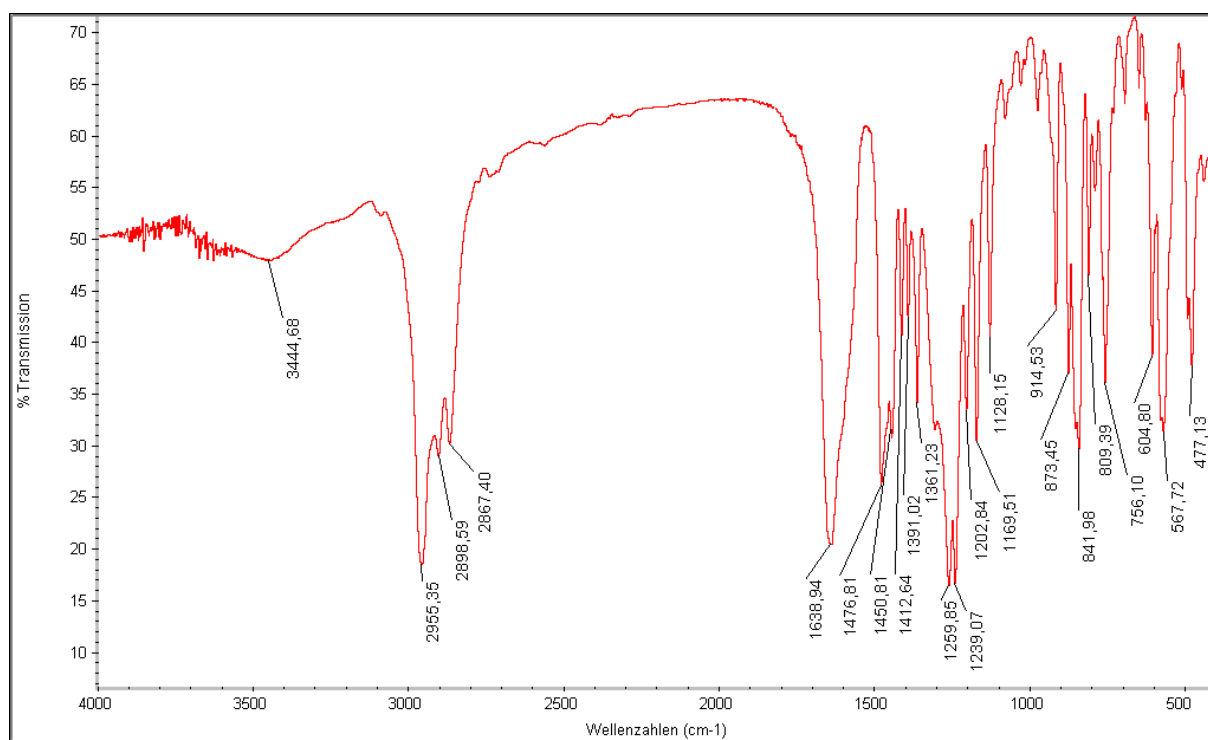


Figure S12. IR spectrum of **3-K** in KBr at 298 K.

2.3. [(O₃N)Ti(THF)] (**4-THF**)

A solution of **1-Cl** (75 mg, 0.10 mmol) in THF (1 mL) was treated with Mg sand (10 mg, 0.40 mmol) at room temperature and stirred for 6 h. Upon stirring the color of the suspension changed from orange to light purple. The complete and selective conversion of the starting materials into the product were confirmed by an aliquot ¹H NMR spectrum. After completion, the reaction mixture was filtered through a pad of celite and the residue was extracted with THF (3 × 3 mL). The combined filtrate was dried under reduced pressure to give the titanium(III) complex **4-THF** as a light blue powder. Yield: 74 mg (0.094 mmol, 94%).

¹H NMR (400 MHz, benzene-*d*₆, 298 K): δ 43.27 (br s), 7.40 (br s, 3H, *H*_{aryl}), 5.28 (br, 3H), 4.87 (br, 3H), 4.64 (br s, 3H, *H*_{aryl}), 1.58 (br s, 27H, C(CH₃)₃), 1.35 ppm (s, 27H, C(CH₃)₃).

¹³C{¹H} NMR (101 MHz, benzene-*d*₆, 298 K): δ 182.1 (br s, *C*_{aryl}), 127.0 (s, *C*_{aryl}), 126.0 (s, *C*_{aryl}), 112.8 (br s, *C*_{aryl}), 61.3 (br s, NCH₂), 40.2 (s, C(CH₃)₃), 37.7 (s, C(CH₃)₃), 35.7 (s, C(CH₃)₃), 30.3 (br s), 28.6 (s, C(CH₃)₃).

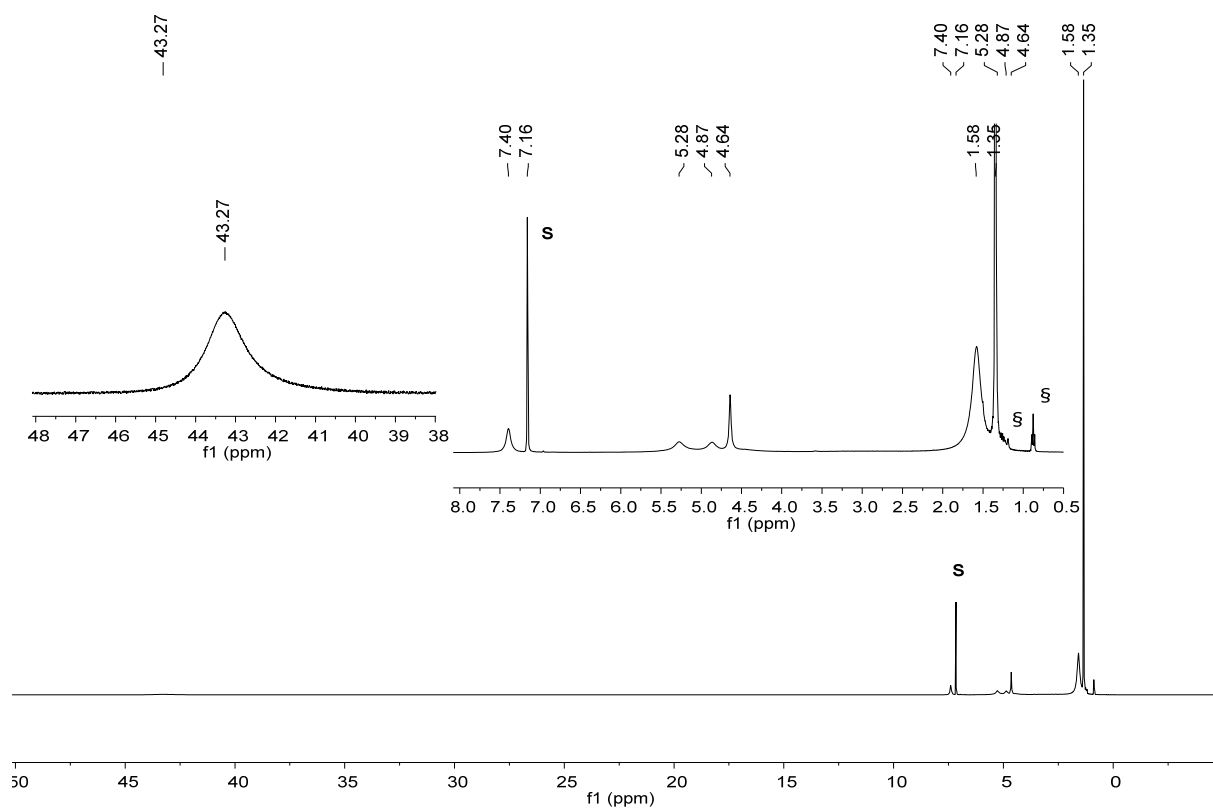


Figure S13. ^1H NMR spectrum of **4-THF** in benzene- d_6 at 298 K; S denotes the residual proton signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

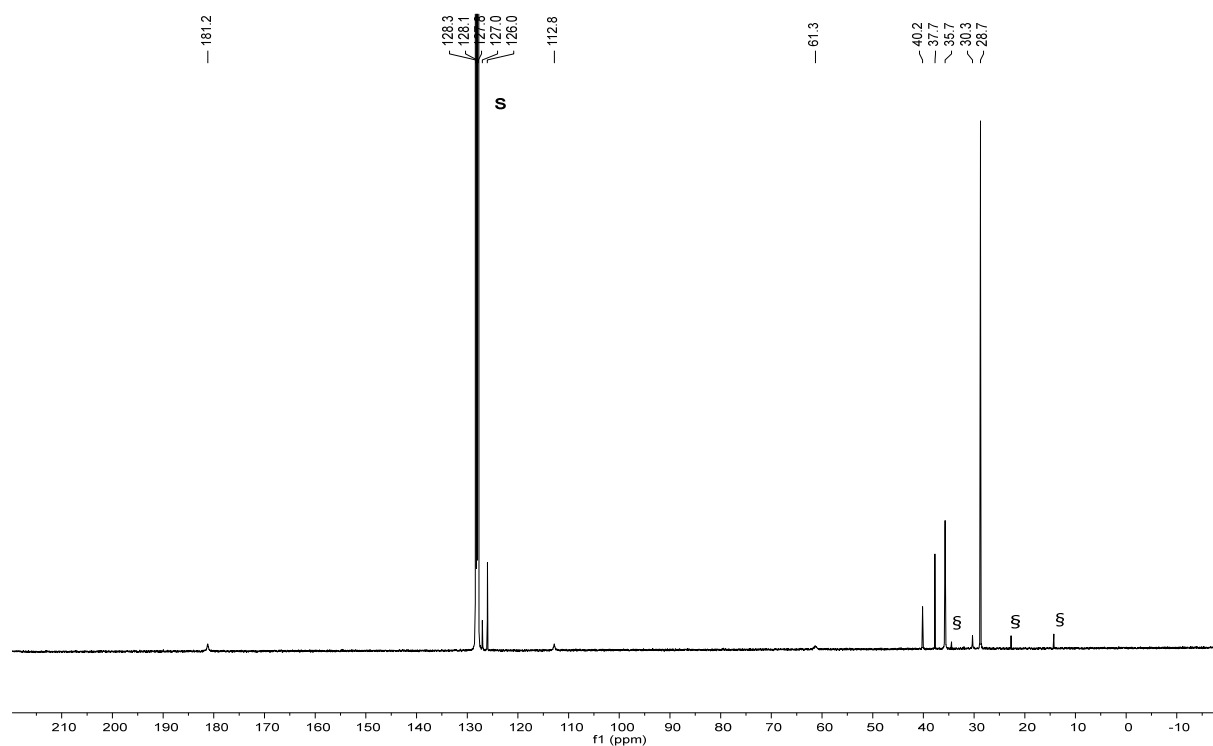


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4-THF** in benzene- d_6 at 298 K; S denotes the ^{13}C NMR signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

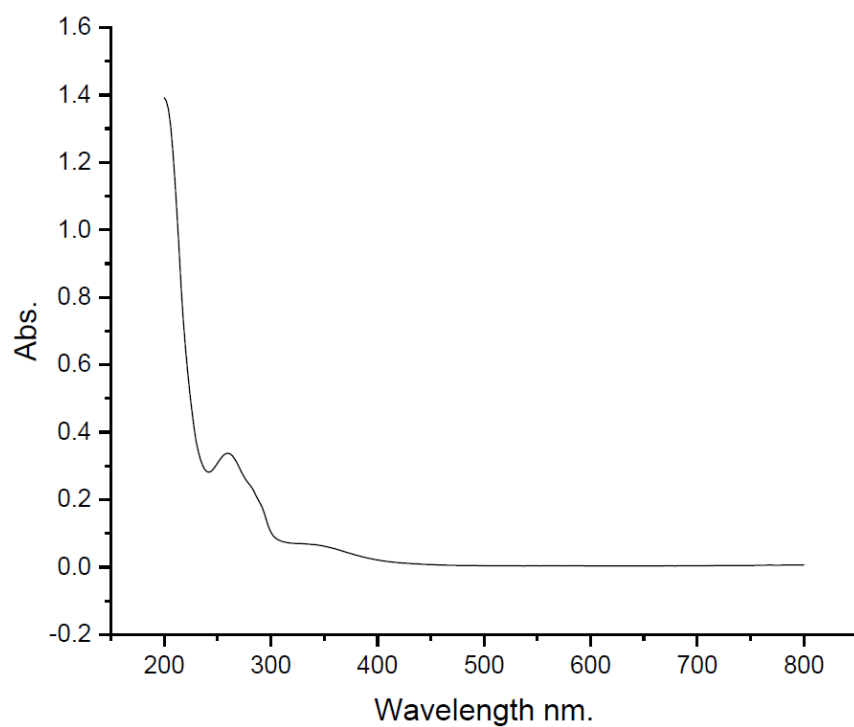


Figure S15. UV-Vis spectrum of **4-THF** in *n*-pentane (200 nm – 800 nm).

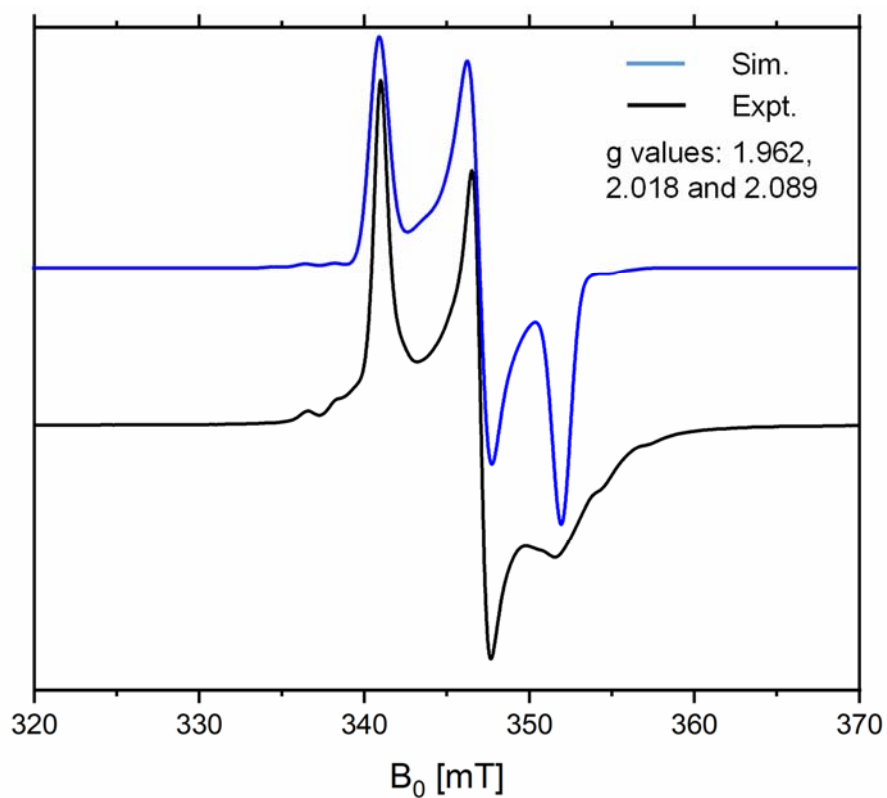


Figure S16. EPR spectrum of **4-THF** as toluene glass at 77 K.

2.4. [(O₃N)Ti(THP)] (4-THP)

A solution of **4-THF** (75 mg, 0.095 mmol) in THP (5 mL) was stored overnight at room temperature to selectively form the titanium(III) THP complex **4-THP**, which was isolated as a light blue powder after removal of all the volatiles. Yield: 76 mg (0.095 mmol, quantitative). Elemental analysis calculated for C₅₀H₇₆NO₄Ti: C: 74.79, H: 9.54, N: 1.74%; found: C: 69.33, H: 9.37, N: 1.71%. Multiple attempts to obtain acceptable carbon value in elemental analysis consistently gave lower values than expected, probably due to the formation of titanium carbide, which is known for group 4 metal complexes.

¹H NMR (400 MHz, benzene-*d*₆, 298 K): δ 43.14 (br s), 7.39 (br s, 3H), 4.62 (br s, 3H), 4.47 (br s, 3H), 1.97 (br s, 3H), 1.60 (br s, 27H, C(CH₃)₃), 1.34 (s, 27H, C(CH₃)₃).

¹³C{¹H} NMR (101 MHz, benzene-*d*₆, 298 K): δ 181.5 (C_{aryl}), 127.0 (C_{aryl}), 125.9 (C_{aryl}), 114.7 (C_{aryl}), 61.4 (NCH₂), 57.9 (NCH₂), 40.1 (C(CH₃)₃), 37.7 (C(CH₃)₃), 36.2 (C(CH₃)₃), 28.7 (C(CH₃)₃), 24.2 (CH₂).

Magnetic moment: μ_{eff}(Evans' Method, benzene-*d*₆, 298 K) = 1.59 μ_B

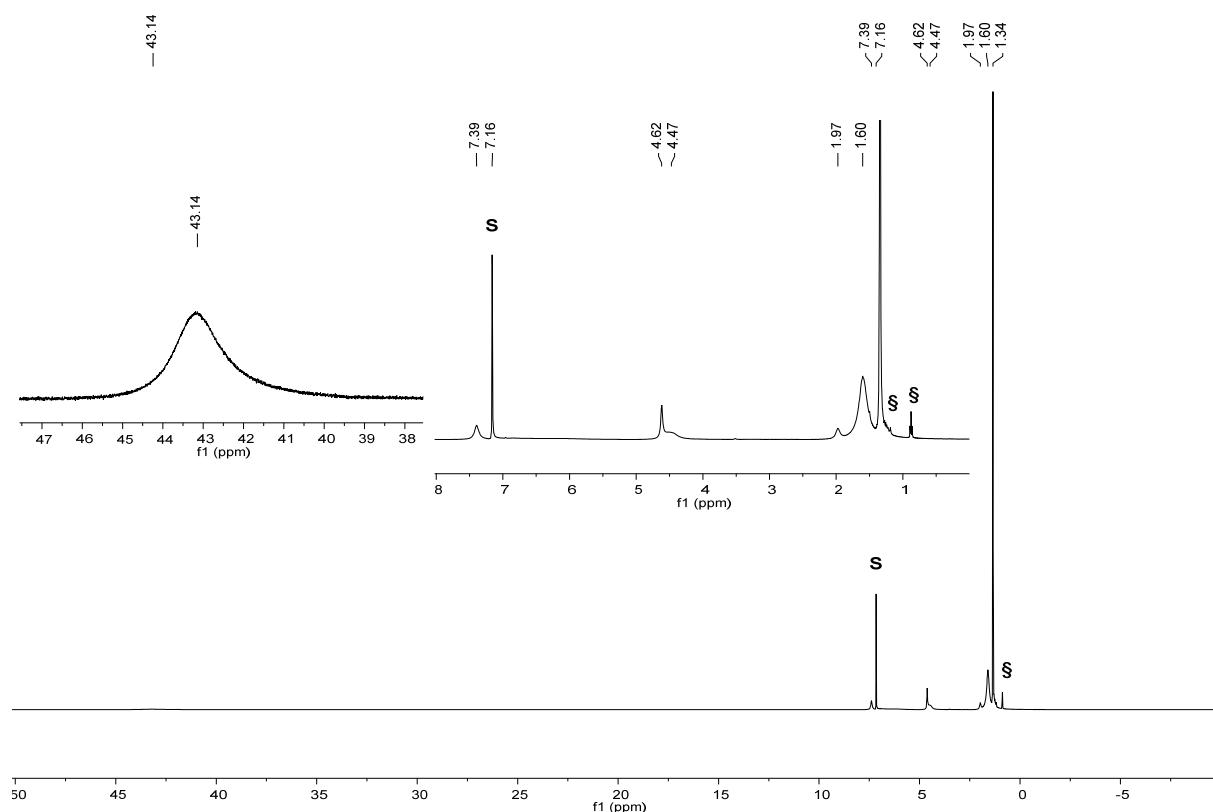


Figure S17. ¹H NMR spectrum of **4-THP** in benzene-*d*₆ at 298 K; S denotes the residual proton signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

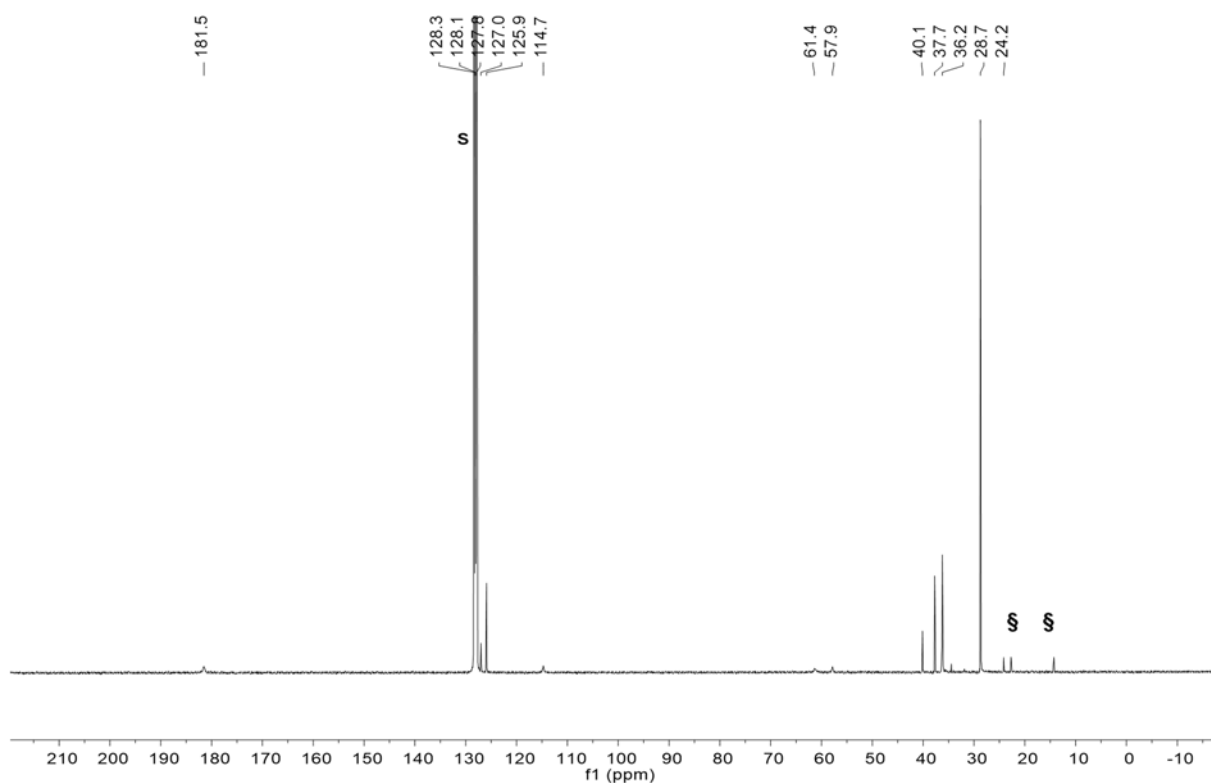


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4-THP** in benzene- d_6 at 298 K; S denotes the ^{13}C NMR signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

2.5. $[(\text{O}_3\text{N})\text{Ti}(\text{Et}_2\text{O})]$ (**4-Et₂O**)

A solution of **1-Cl** (750 mg, 1.0 mmol) in Et_2O (5 mL) was treated with sodium sand (92 mg, 4.0 mmol) at room temperature and was stirred for 30 min, leading to a color change from orange to purple. The reaction mixture was filtered over celite and the residue was extracted with Et_2O (3 × 3 mL). The combined extracts were evaporated to dryness and the residue was washed with *n*-pentane (3 × 3 mL). The resulting residue was dried under reduced pressure to give **4-Et₂O** as a blue green powder. The combined *n*-pentane washings were concentrated and recrystallized to give another batch of the product. Combined yield: 505 g (0.67 mmol, 67%). Elemental analysis calculated for $\text{C}_{49}\text{H}_{76}\text{NO}_4\text{Ti}$: C: 74.40, H: 9.68, N: 1.77%; found: C: 71.27, H: 9.02, N: 2.08%. Multiple attempts to obtain acceptable carbon value in elemental analysis consistently gave lower values than expected, probably due to the formation of titanium carbide, which is known for group 4 metal complexes.

^1H NMR (400 MHz, benzene- d_6 , 298 K): δ 43.9 (br s), 10.6 (br s), 9.5 (br s), 7.39 (br s, 3H, H_{aryl}), 4.61 (br s, 3H, H_{aryl}), 2.44 (br s, 6H), 1.55 (br s, 27H, $\text{C}(\text{CH}_3)_3$), 1.34 (s, 27H, $\text{C}(\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, benzene- d_6 , 298 K): δ 181.1 (C_{aryl}), 128.3 (C_{aryl}), 127.3 (C_{aryl}), 125.7 (C_{aryl}), 118.0 (C_{aryl}), 60.7 (NCH_2), 40.1 ($\text{C}(\text{CH}_3)_3$), 37.7 ($\text{C}(\text{CH}_3)_3$), 35.9 ($\text{C}(\text{CH}_3)_3$), 28.7 ($\text{C}(\text{CH}_3)_3$).

Magnetic moment: μ_{eff} (Evans' Method, benzene- d_6 , 298 K) = 1.70 μ_{B} .

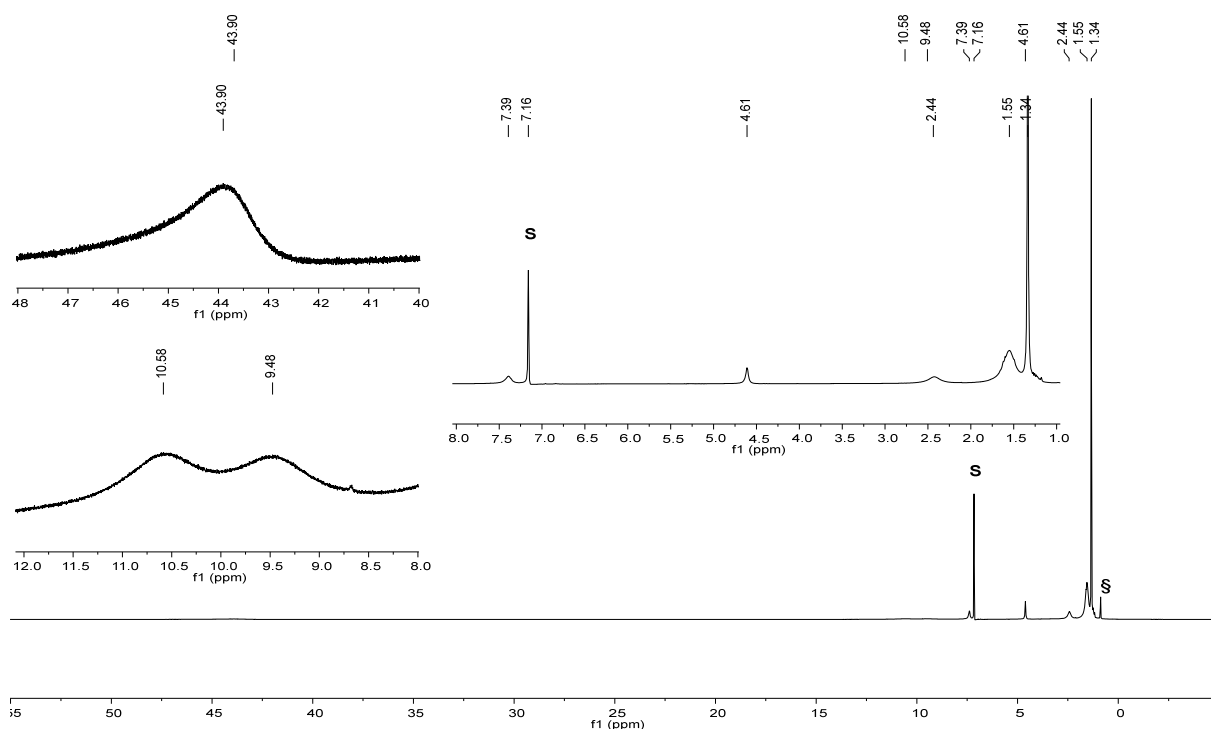


Figure S19. ^1H NMR spectrum of **4-Et₂O** in benzene-*d*₆ at 298 K; S denotes the residual proton signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

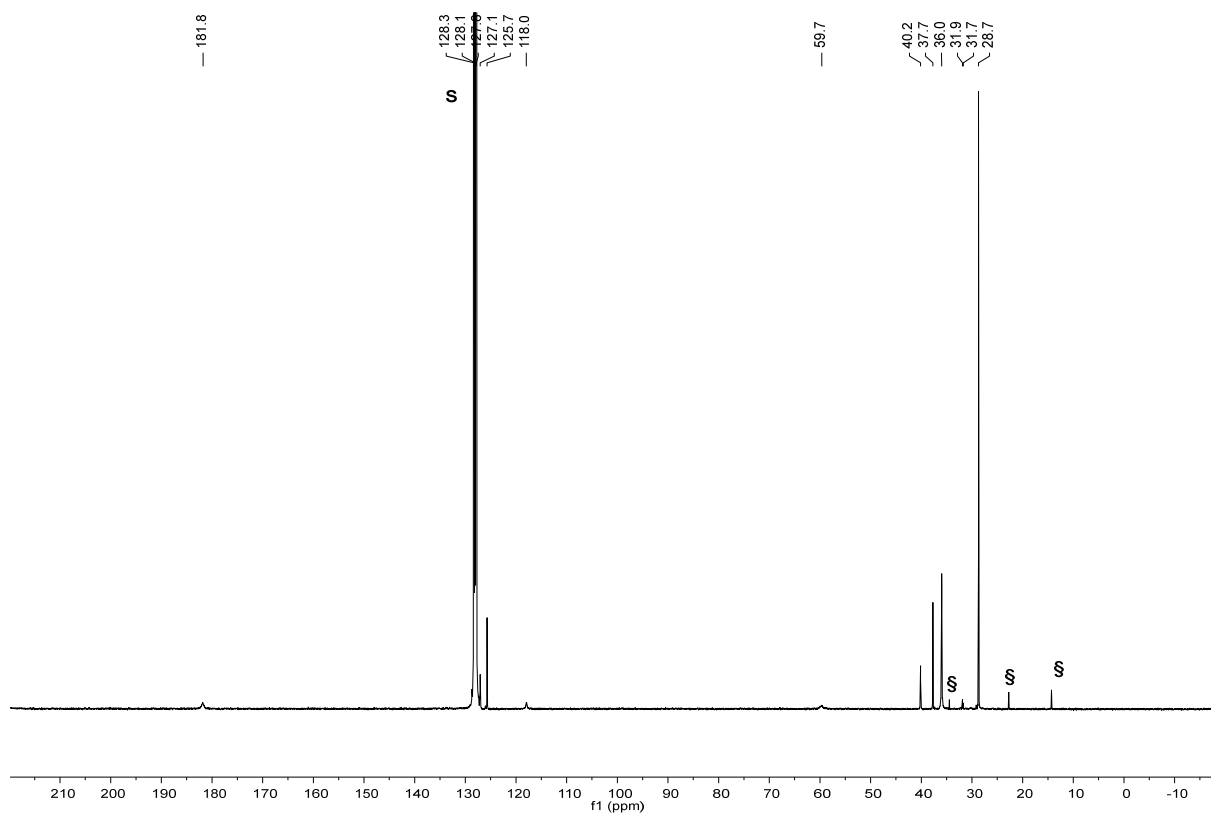


Figure S20. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4-Et₂O** in benzene-*d*₆ at 298 K; S denotes the ^{13}C NMR signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

2.6. [(O₃N)Ti]₂ (**5**)

A solution of **1-Cl** (753 mg, 1.0 mmol) in *n*-pentane (5 mL) was treated with Na sand (46 mg, 2.0 mmol) at room temperature and was stirred for 30 min, leading to a color change from orange to brown. The resulting reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was dissolved in toluene (10 mL) and filtered. The resulting solution was cooled to -30 °C. The brown precipitate that formed upon cooling was isolated by decantation of the supernatant solution and dried under reduced pressure to obtain **5** as an analytically pure solid. The supernatant solution was concentrated to ca. 1 mL and cooled to -30 °C to obtain another batch of the product. Combined yield: 438 mg (0.31 mmol, 62%). Elemental Analysis calculated for C₉₀H₁₃₂N₂O₆Ti₂: C: 75.39, H: 9.28, N: 1.95%; found: C: 75.57, H: 9.27, N: 2.18%.

¹H NMR (400 MHz, benzene-*d*₆, 298 K): δ 47.9 (br s), 8.68 (br s), 6.82 (br s), 6.59 (br s), 6.13 (br s), 5.53 (br s), 4.39 (br s), 4.35 (br s), 0.94-1.48 (br m), 1.34 (s, C(CH₃)₃), 1.32 (br s, C(CH₃)₃), 1.24 (s, C(CH₃)₃), 1.18 (s, C(CH₃)₃), -4.49 (br s), -6.43 (br s).

¹³C{¹H} NMR (101 MHz, benzene-*d*₆, 298 K): δ 225.0, 159.3, 152.0, 146.1, 138.7, 135.9, 128.7, 127.2, 124.3, 124.1, 110.0, 102.5, 92.4, 79.6, 67.6, 61.9, 41.5, 39.6, 38.5, 37.2, 33.4, 32.7, 32.6, 32.3, 29.4, 28.7, 27.9.

Magnetic moment: μ_{eff}(Evans' Method, benzene-*d*₆, 298 K) = 2.22 μ_B.

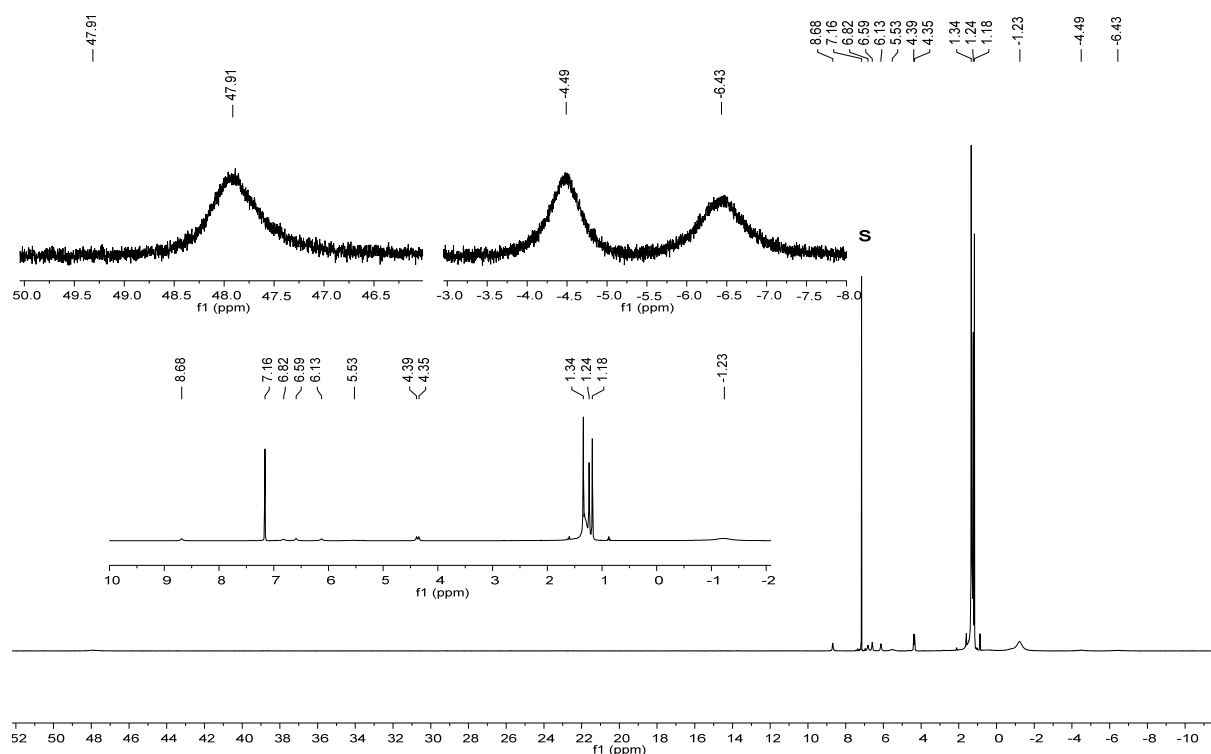


Figure S21. ¹H NMR spectrum of **5** in benzene-*d*₆ at 298 K; S denotes the residual proton signal of the deuterated solvent.

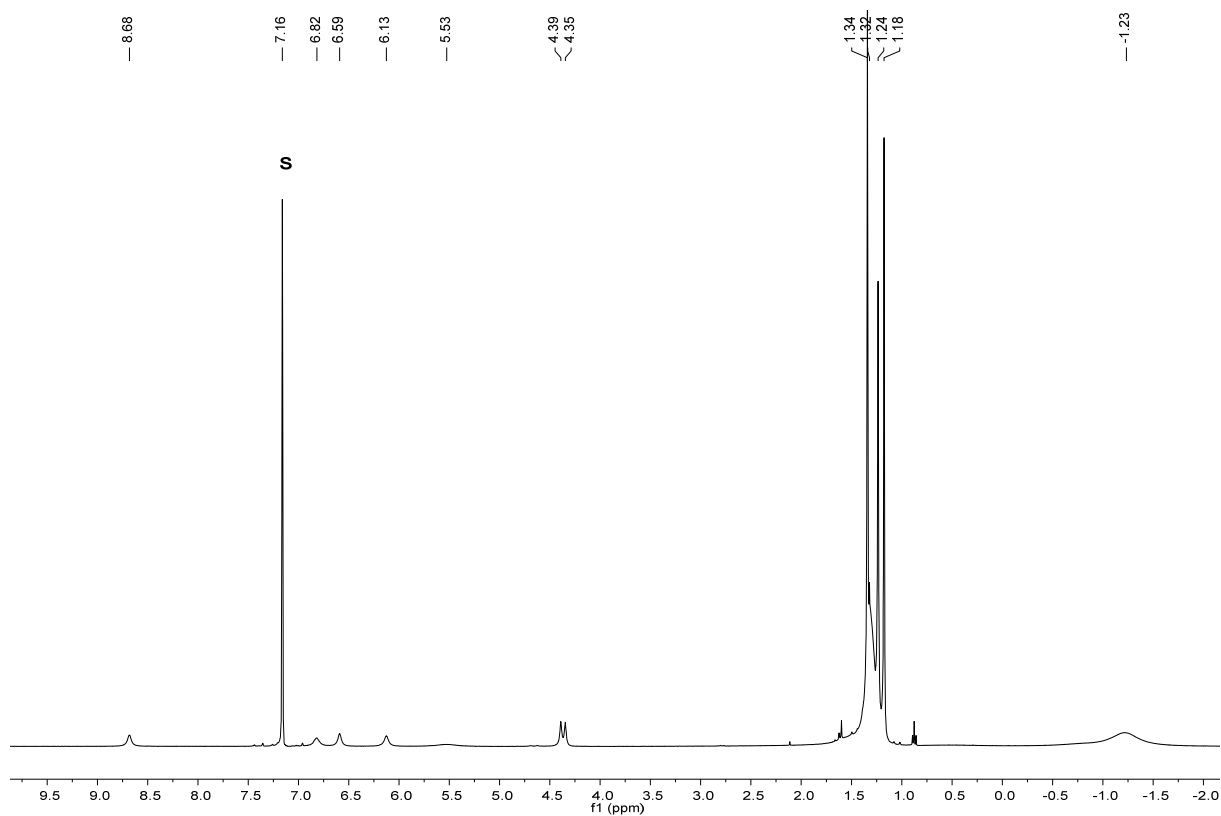


Figure S22. ^1H NMR spectrum of **5** in benzene- d_6 at 298 K; S denotes the residual proton signal of the deuterated solvent.

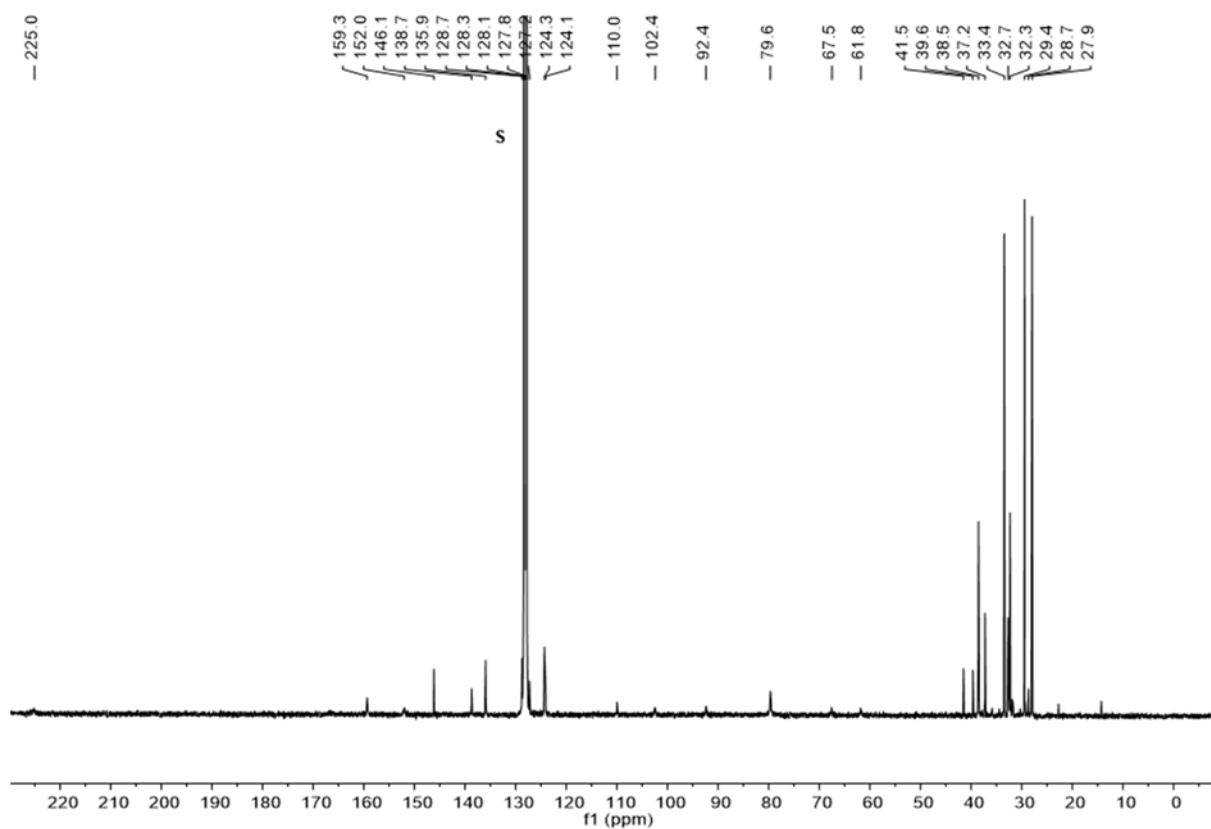


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** in benzene- d_6 at 298 K; S denotes the ^{13}C NMR signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

2.7. [(O₃N)Ti(^tBuOCHO)] (6)

Method A: To a solution of **5** (45 mg, 0.031 mmol) in *n*-pentane (2 mL) was added *tert*-butyl formate (10 mg, 0.1 mmol) dropwise at room temperature. After stirring for few minutes all the volatiles were removed under reduced pressure to obtain **6** as a brown powder. Yield: 51 mg (0.62 mmol, quantitative).

Method B: To a solution of **4-Et₂O** (79 mg, 0.10 mmol) in *n*-pentane (5 mL) *tert*-butyl formate (20 mg, 0.2 mmol) was added dropwise at room temperature. Upon addition the color of the solution changed from light blue to brown. After stirring for few minutes all the volatiles were removed under reduced pressure to obtain **6** as a brown powder. Yield: 82 mg (0.10 mmol, quantitative).

Elemental analysis calculated for C₅₀H₇₆NO₅Ti: C: 73.32, H: 9.35, N: 1.71%; found: C: 72.36, H: 9.37, N: 1.87%.

¹H NMR (400 MHz, benzene-*d*₆, 298 K): δ 41.65 (br s), 4.84 (br s, *H*_{aryl}), 1.63 (br s, 27H, C(CH₃)₃), 1.36 (s, 27H, C(CH₃)₃), -23.01 (br s).

¹³C{¹H} NMR (101 MHz, benzene-*d*₆, 298 K): δ 178.7 (C_{aryl}), 125.9 (C_{aryl}), 98.6 (C_{aryl}), 64.6 (NCH₂), 41.9 (C(CH₃)₃), 39.5 (C(CH₃)₃), 37.4 (C(CH₃)₃), 34.7 (C(CH₃)₃), 29.1 (C(CH₃)₃); all the expected signals are not visible due to the broadening at room temperature.

Magnetic moment: μ_{eff} (Evans' Method, benzene-*d*₆, 298 K) = 1.70 μ_B.

IR (*n*-pentane, 298 K): ν = 1663 cm⁻¹.

IR (KBr pellet): ν = 2959 (vs), 2903 (s), 2868 (s), 1661 (m), 1603 (vw), 1478 (s), 1445 (s), 1413 (m), 1392 (w), 1362 (m), 1306 (w), 1258 (vs), 1239 (vs), 1204 (m), 1171 (s), 1129 (m), 1024 (m), 916 (m), 875 (m), 858 (s), 812 (w), 761 (m), 692 (w), 605 (m), 583(m), 570 (m), 491 (m) cm⁻¹.

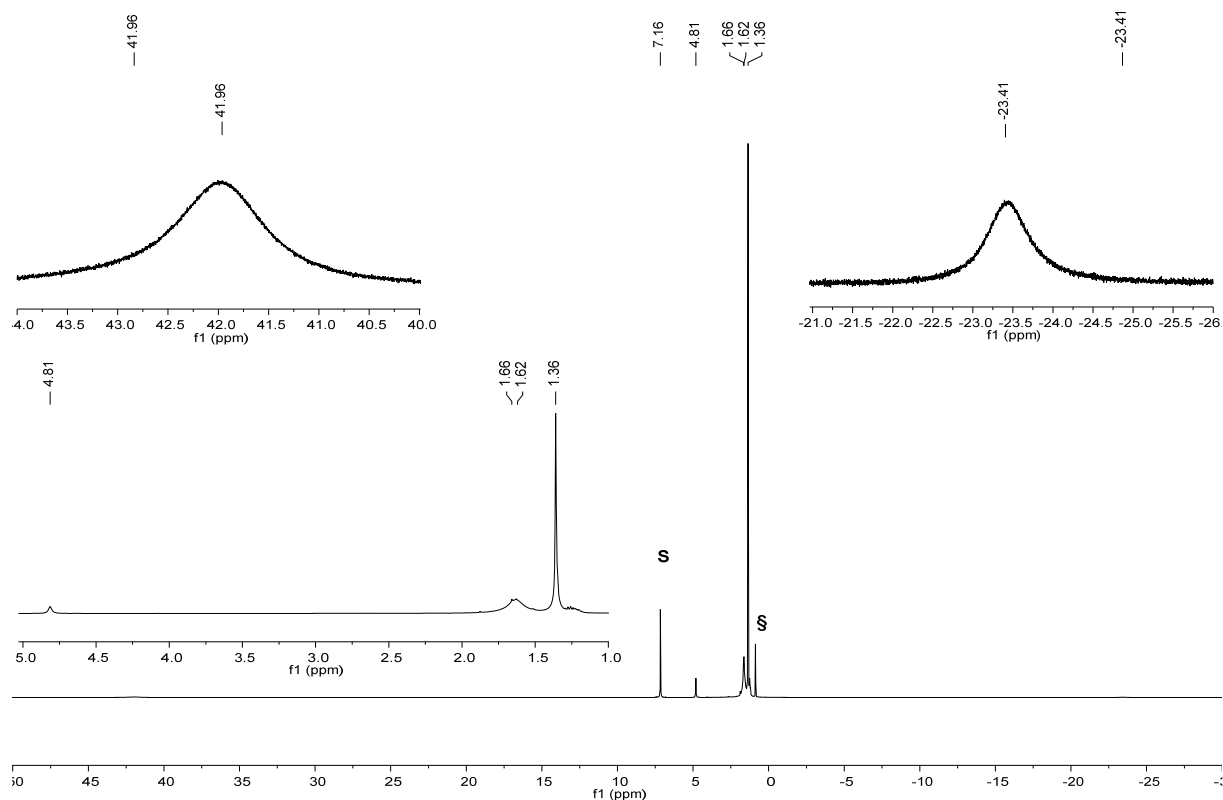


Figure S24. ^1H NMR spectrum of **6** in benzene- d_6 at 298 K; S denotes the residual proton signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

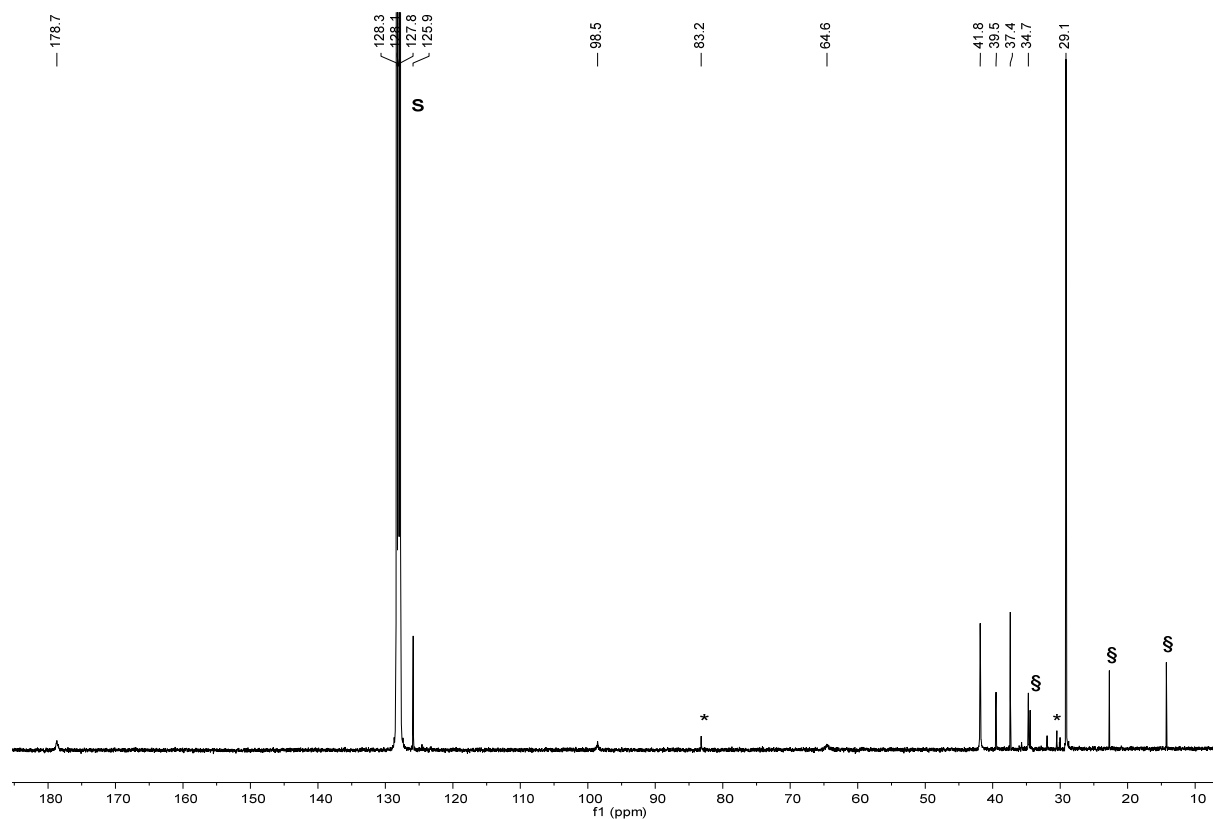


Figure S25. ^{13}C NMR spectrum of **6** in benzene- d_6 at 298 K; S denotes the ^{13}C NMR signal of the deuterated solvent; the symbols § and * correspond to a small amount of *n*-pentane and some unknown impurities, respectively, present in the sample.

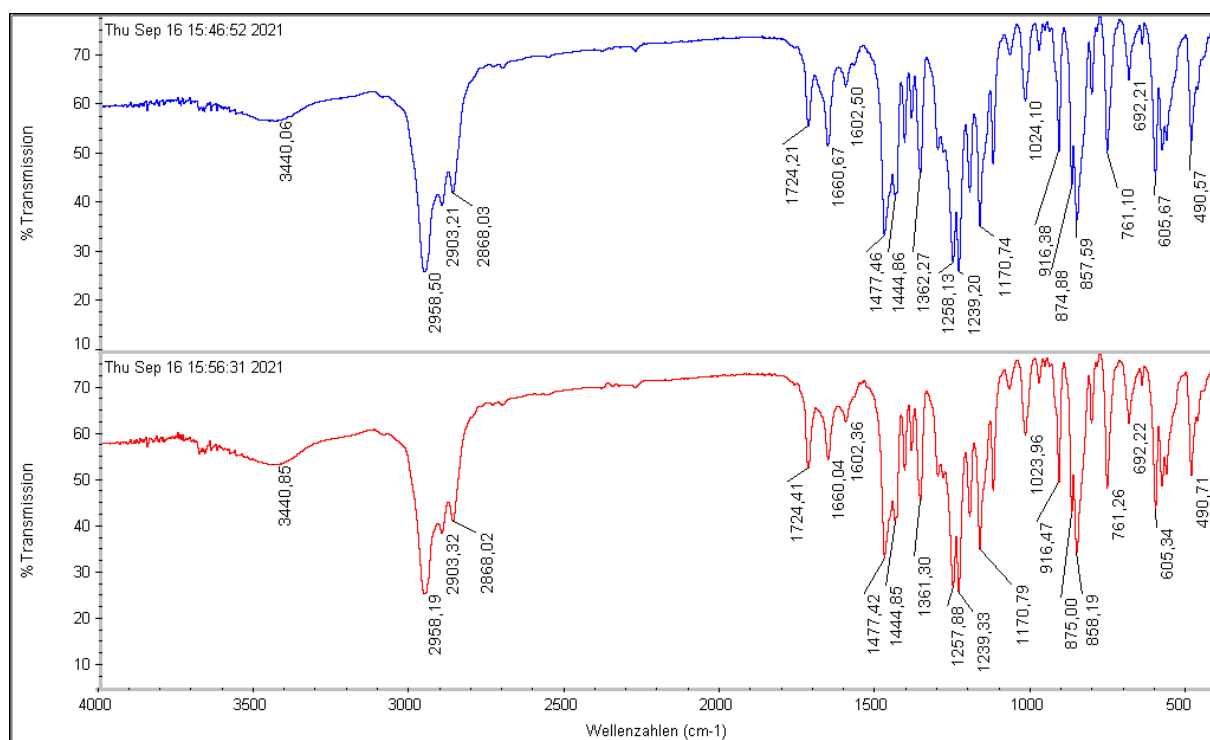


Figure S26. Upper: IR spectrum of **6** in KBr. Partially decomposed by air. The peak at 1724 cm⁻¹ is assigned to tert-butyl formate. Lower: IR spectrum of **6** in KBr after 10 minutes.

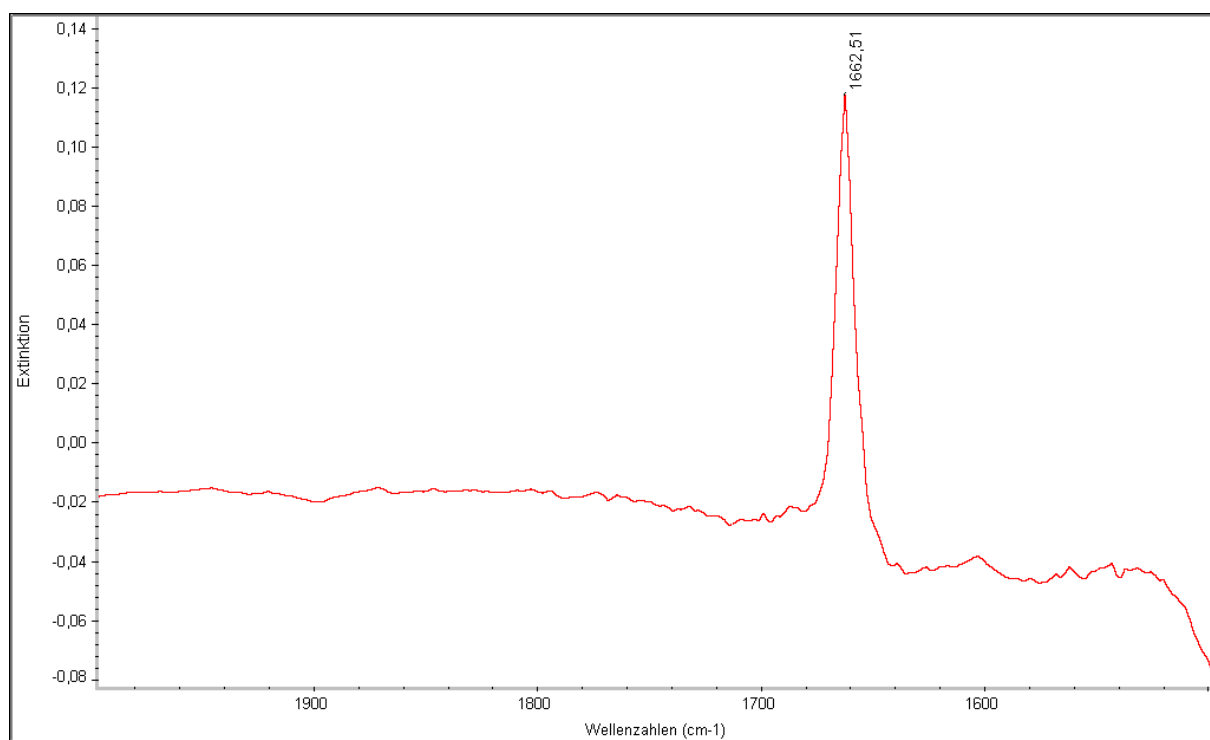


Figure S27. IR spectrum of **6** in *n*-pentane in a NaCl cell.

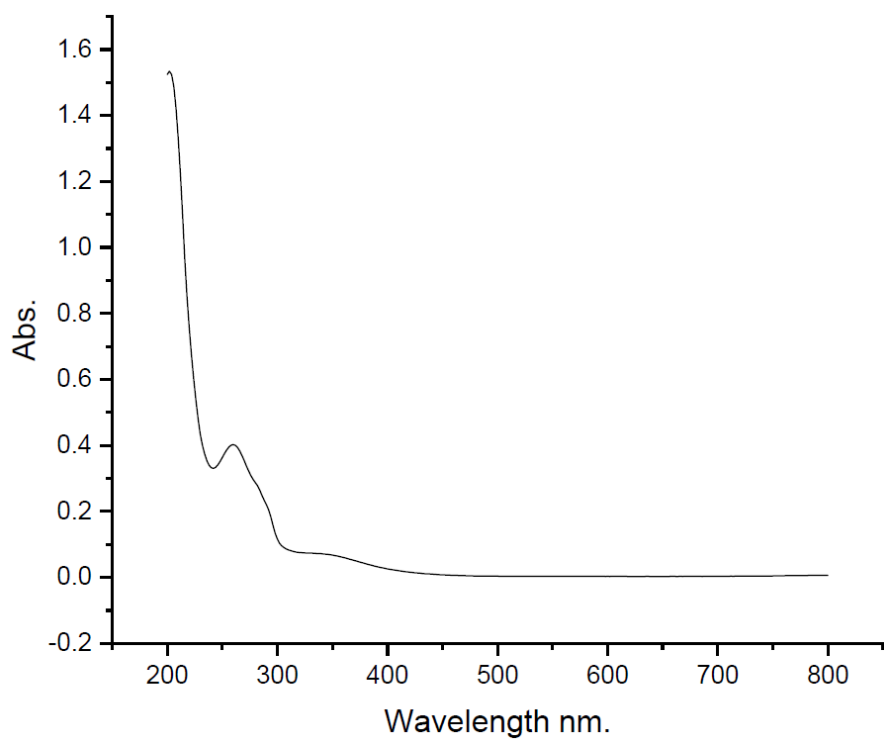


Figure S28. UV-Vis spectrum of **6** in *n*-pentane (200 nm – 800 nm).

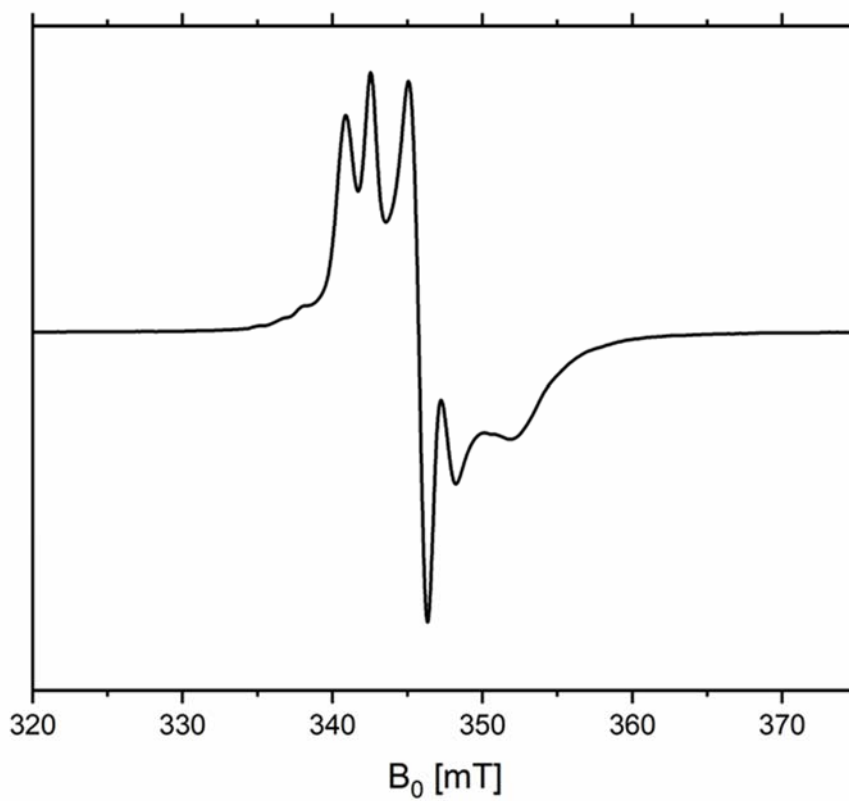


Figure S29. EPR spectrum of **6** as toluene glass at 77 K. The spectrum could not be simulated due to its complicated nature.

2.8 $[(\text{O}_3\text{N})\text{Ti}]_2(\mu\text{-OCHO}-\eta\text{O}:\eta\text{O}')$ (**7**)

To a solid mixture of $[(\text{O}_3\text{N})\text{Ti}(\text{OCHO})]$ (229 mg, 0.3 mmol) and the titanium(III) dimer **5** (216 mg, 0.15 mmol) in a centrifuge vial *n*-pentane (10 mL) was added at room temperature and the resulting orange suspension was stirred for 3 h. Upon stirring the colour of the suspension changed to dark green. After completion of the reaction, as confirmed by ^1H NMR spectroscopy, the suspension was centrifuged and the supernatant solution was decanted. Resulting residue was washed with *n*-pentane (4 x 10 mL) and dried under reduced pressure to yield the formate bridge complex **7** as a dark green powder. Yield: 338 mg (0.23 mmol, 76%). Elemental analysis calculated for $\text{C}_{91}\text{H}_{133}\text{N}_2\text{O}_8\text{Ti}_2$: C: 73.91, H: 9.07, N: 1.89%; found: C: 71.51, H: 9.08, N: 1.86%. Multiple attempts to obtain acceptable carbon value in elemental analysis consistently gave lower values than expected, probably due to the formation of titanium carbide, which is known for group 4 metal complexes.

^1H NMR (400 MHz, benzene- d_6 , 298 K): δ 21.53 (br s), 7.11 (br s), 6.12 (br s), 1.76 (br s, 54H, $\text{C}(\text{CH}_3)_3$), 1.63 (br s; this signal overlaps with the signal at 1.75 ppm), 1.36 (s, 54H, $\text{C}(\text{CH}_3)_3$), -37.06 (br s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, benzene- d_6 , 298 K): δ 152.5 (C_{aryl}), 136.0 (C_{aryl}), 124.6 (C_{aryl}), 116.2 (C_{aryl}), 37.6 ($\text{C}(\text{CH}_3)_3$), 36.1 ($\text{C}(\text{CH}_3)_3$), 35.8 ($\text{C}(\text{CH}_3)_3$), 31.9 ($\text{C}(\text{CH}_3)_3$), 30.4 ($\text{C}(\text{CH}_3)_3$), 28.7 ($\text{C}(\text{CH}_3)_3$); all the expected signals are not visible due to the broadening at room temperature.

Magnetic moment: μ_{eff} (Evans' Method, benzene- d_6 , 298 K) = 1.92 μ_{B} .

IR (KBr): ν = 2952 (s), 2903 (m), 2867 (m), 1648 (w), 1578 (m), 1475 (s), 1412 (w), 1392 (w), 1361 (m), 1255 (s), 1238 (vs), 1202 (m), 1170 (m), 1127 (m), 980 (vw), 917 (s), 874 (s), 860 (vs), 814 (m), 761 (s), 728 (m), 694 (m), 640 (w), 607 (vs) cm^{-1} .

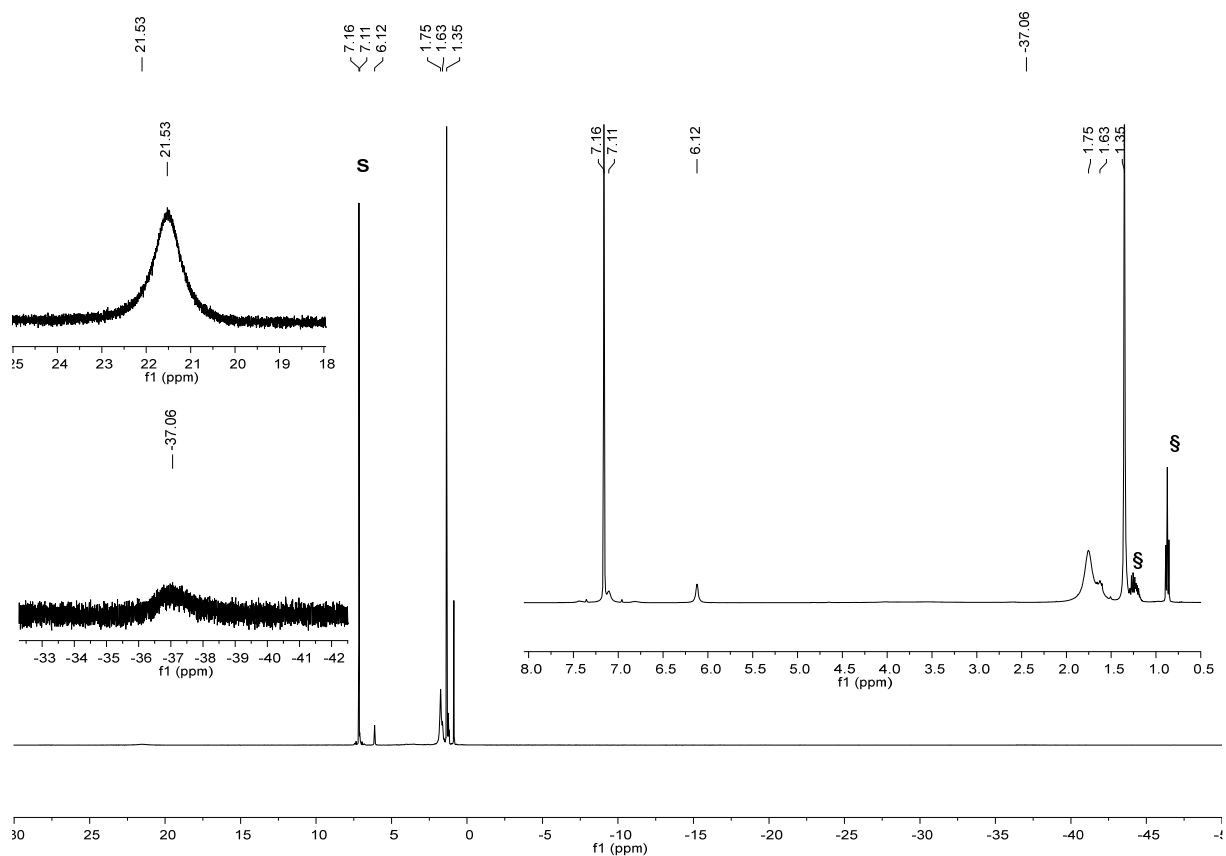


Figure S30. ^1H NMR spectrum of **7** in benzene- d_6 at 298 K; S denotes the residual proton signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

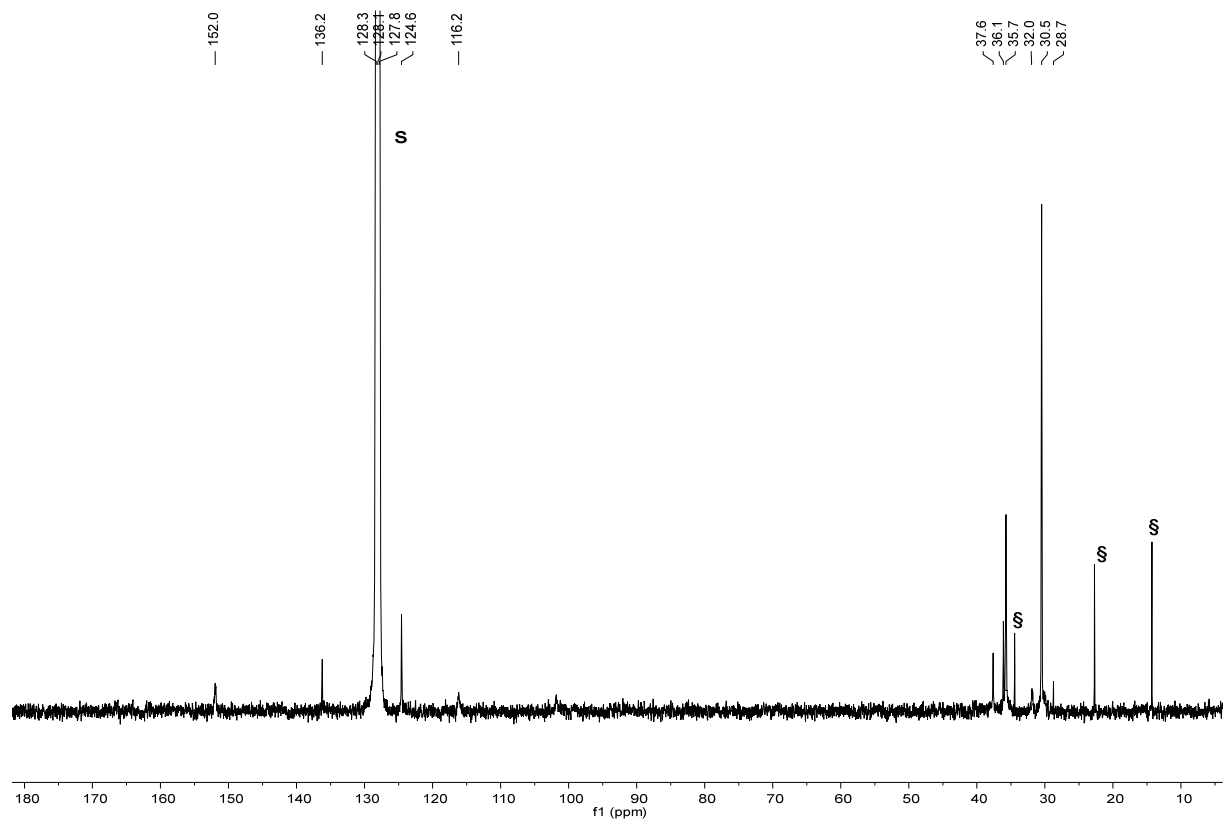


Figure S31. ^{13}C NMR spectrum of **7** in benzene- d_6 at 298 K; S denotes the ^{13}C NMR signal of the deuterated solvent; the symbol § corresponds to a small amount of *n*-pentane present in the sample.

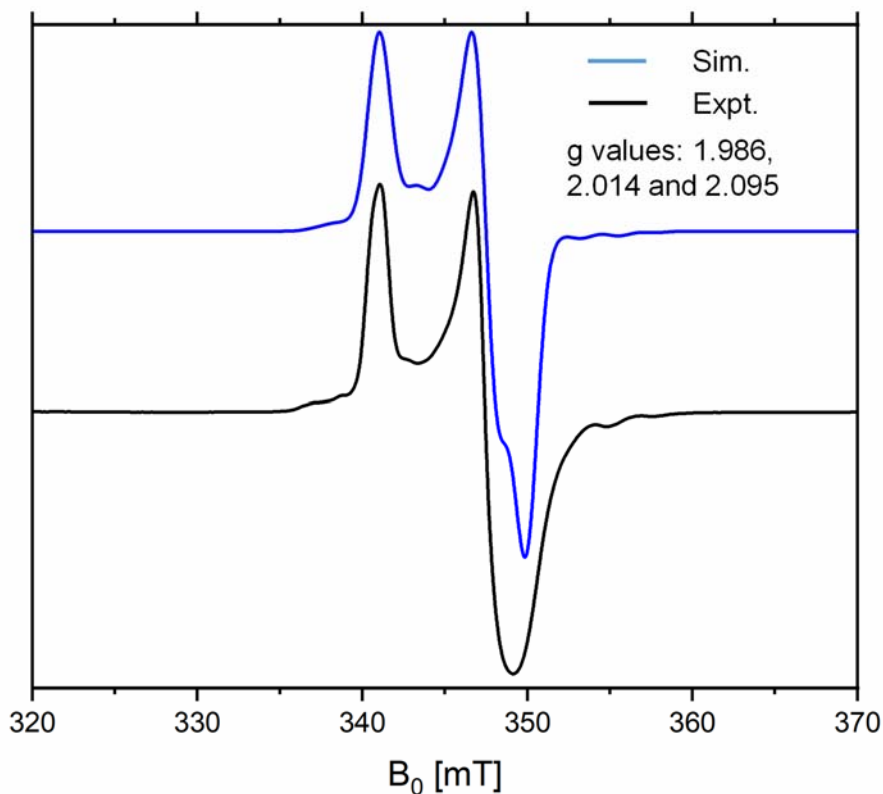


Figure S32. EPR spectrum of **7** as toluene glass at 77 K.

3. Decomposition study of **6**

3.1. Decomposition in a J. Young NMR tube

A benzene- d_6 solution of **6** in a J. Young NMR tube was stored at room temperature. The reaction was monitored by ^1H NMR spectroscopy. After 1 day, the formation of **7** was observed. After 2 weeks, the formation of $[(\text{O}_3\text{N})\text{Ti}-\text{O}-\text{Ti}(\text{O}_3\text{N})]$, **2** and $^t\text{BuOCHO}$ was confirmed. After 2 months, signals of **7** became smaller and after 3 months, **7** was completely consumed.

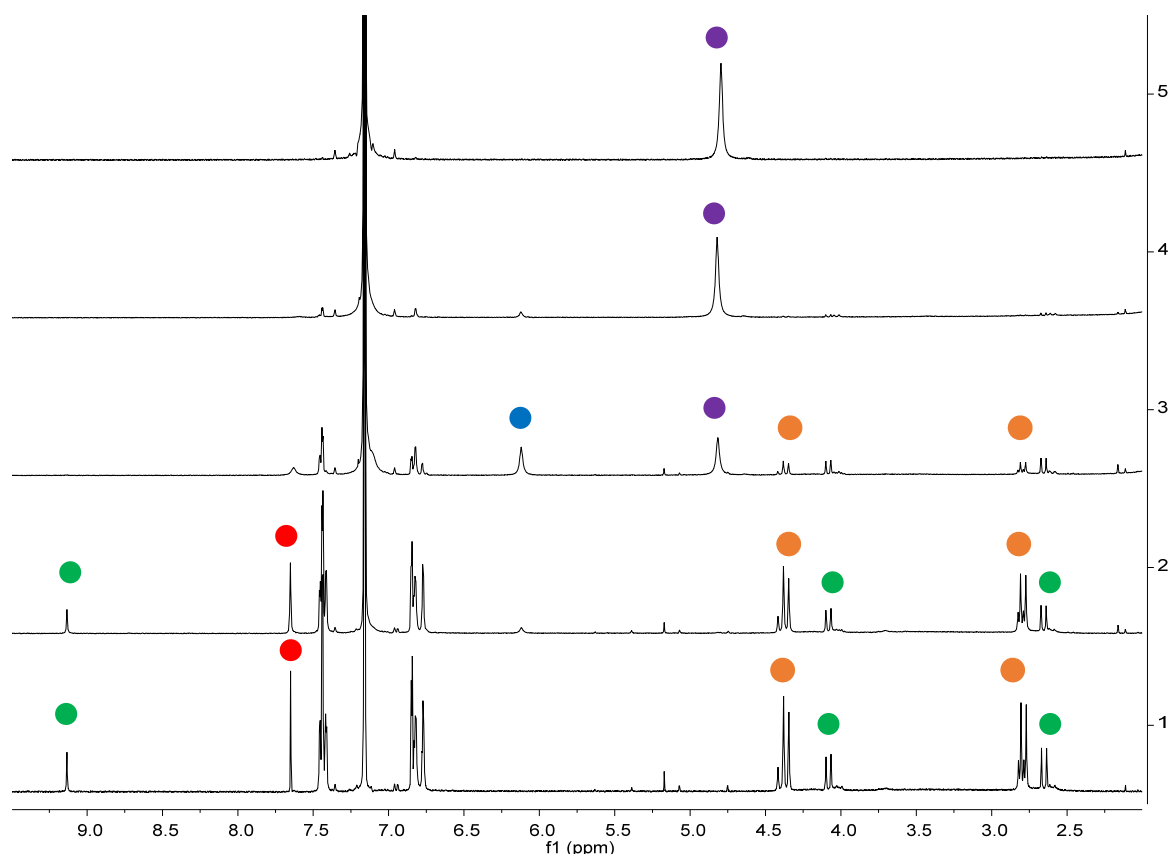


Figure S33. ^1H NMR spectrum of the reaction mixture in benzene- d_6 at 298 K; 1st row: compound **6** in benzene- d_6 . 2nd row: after 1 day. 3rd row: after 2 weeks. 4th row: after 2 months. 5th row: after 3 months. Green: **2**, purple: **6**, blue: **7**, red: $t\text{BuOCHO}$, orange: $[(\text{O}_3\text{N})\text{Ti}-\text{O}-\text{Ti}(\text{O}_3\text{N})]$.

3.2. Decomposition on a synthetic scale

A solution of **6** (82 mg, 0.1 mmol) in *n*-pentane (10 mL) was filtered to a push-in cap glass vial. The solution was stored at room temperature under argon atmosphere and the conversion of **6** to **7** was followed by ^1H NMR spectroscopy. After one month, formation of yellowish green crystals was observed. The crystals were isolated after decantation of the supernatant solution, washed with *n*-pentane (3 \times 1 mL) and dried under reduced pressure to obtain **7** as a green powder. Yield: 23 mg (0.016 mmol, 32%).

4. Crystal structure determination of compounds **3-Na**, **3-K**, **4-Et₂O**, **4-THP**, **5**, **6** and **7**

X-ray diffraction data were collected at 100 K on an Eulerian 4-circle diffractometer STOE STADIVARI in ω -scan mode with Cu-K α radiation. The structures were solved by direct methods using SHELXT.^[S3] All refinements were carried out against F^2 with ShelXL^[S4] as implemented in the program system Olex2.^[S5] The compounds **3-Na**, **3-K**, **4-THP**, **5**, **6** and **7** were found as solvates with co-crystallized acetonitrile (**3-Na**), toluene (**3-K**), hexane (**5**) and benzene (**6** and **7**). In the crystal structure of **3-Na**, CH_3 units of $t\text{Bu}$ groups (involving C45 and

C46, as well as C119 – C121) are disordered. In **3-K**, ^tBu groups are also disordered (involving atoms C45 – C50 as well as C66 – C73, C127 – C132 and C190 – C195). In addition, a toluene molecule is disordered (involving positions C215 – C228). One methyl unit which is part of a ^tBu group in **4-Et₂O** (involving atom C15) was treated as disordered as well as one coordinated hexane molecule in **5**. In **4-THP**, disorder involves most of the tris(phenolato)amine ligand, as well as the THP ligand and the non-coordinated pentane molecule in **4-THP**. In **7**, the carbon atom C1 of the bridging formyl OCHO group as well those of several non-coordinated benzene molecules (C122 – C169 and C176 – C187) are disordered. Each disorder could be resolved with split positions for the involved atom positions. Distance restraints were used in the refinement of **3-K**, but only involving a toluene molecule, in the refinement of **5**, but only involving the non coordinated hexane molecule, as well as in the refinement of **7**, but only involving non-coordinated benzene molecules. When **6** was refined with split positions of the tris(phenolato)amine ligand and of the ^tBuOCO ligand, the refinement values were improved with $R1 = 0.0510$ and $wR2 = 0.0780$ (for $I > 2\sigma(I)$), but the disordered fraction only showed an occupancy of 10% and the refinement needed 846 restraints with an additional 213 parameters. Hydrogen atoms were included in calculated positions. Refinement results are given in Table S1. Graphical representations were performed with the program DIAMOND.^[S9] CCDC-2176437, CCDC-2176438, CCDC-2176439, CCDC-2176440, CCDC-2176441, CCDC-2176442 and CCDC-2176443 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1: Crystallographic data of **3-Na**, **3-K**, **4-Et₂O**, **4-THP**, **5**, **6** and **7**

	3-Na	3-K	4-Et₂O	4-THP	5	6	7
formula	C ₁₉₀ H ₂₇₆ N ₆ Na ₂ O ₂₄ Ti ₄ , 6(C ₂ H ₃ N)	C ₁₈₇ H ₂₇₁ K ₃ N ₄ O ₂₆ Ti ₄ , 3(C ₇ H ₈)	C ₄₉ H ₇₆ NO ₄ Ti	C ₅₀ H ₇₆ NO ₄ Ti, C ₅ H ₁₂	C ₉₀ H ₁₃₂ N ₂ O ₆ Ti ₂ , 4(C ₆ H ₁₄)	C ₅₀ H ₇₆ NO ₅ Ti, 0.5(C ₆ H ₆)	C ₉₁ H ₁₃₃ N ₂ O ₈ Ti ₂ , 11(C ₆ D ₆)
<i>F</i> _w /g mol ⁻¹	3512.05	3576.36	791.00	875.16	1778.45	858.07	2404.38
cryst. color, habit	dark orange block	orange plate	pale blue block	blue block	orange rod	orange block	dark yellow block
crystal size / mm	0.42 × 0.55 × 0.66	0.08 × 0.23 × 0.44	0.32 × 0.40 × 0.42	0.31 × 0.46 × 0.58	0.05 × 0.21 × 0.48	0.13 × 0.17 × 0.22	0.24 × 0.33 × 0.39
crystal system	monoclinic	triclinic	monoclinic	tetragonal	monoclinic	Monoclinic	trigonal
space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> $\bar{1}$ (no. 2)	<i>Cc</i> (no. 9)	<i>P</i> 4 ₁ (no. 76)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)	<i>P</i> 3 ₁ (no. 144)
<i>a</i> / Å	24.1034(3)	19.351(4)	21.251(4)	14.476(2)	19.488(4)	29.2227(4)	17.598(3)
<i>b</i> / Å	34.4125(3)	22.616(5)	18.683(4)		23.772(5)	15.9396(3)	
<i>c</i> / Å	24.7529(3)	30.581(6)	12.230(2)	25.385(5)	25.128(5)	23.4470(3)	39.046(8)
α / °		69.99(3)					
β / °	93.3425(8)	88.96(3)	108.06(3)		107.21(3)	111.5672(11)	
γ / °		66.13(3)					
<i>V</i> / Å ³	20496.6(4)	11387(5)	4616.3(18)	5320.0(18)	11119(4)	10156.9(3)	10472(4)
<i>Z</i>	4	2	4	4	4	8	3
<i>d</i> _{calc} /Mg m ⁻³	1.138	1.043	1.138	1.093	1.062	1.122	1.144
μ (CuK α)/mm ⁻¹	1.827	2.095	1.884		1.595	1.765	1.399
μ (MoK α)/mm ⁻¹				0.203			
<i>F</i> (000)	7568	3848	1724	1916	3912	3728	3789
θ range / °	2.57 – 72.68	2.25 – 77.20	3.22 – 72.16	2.13 – 27.48	2.54 – 72.12	3.21 – 72.09	2.90 – 70.93
index ranges	-29 ≤ <i>h</i> ≤ 28, -42 ≤ <i>k</i> ≤ 39, -11 ≤ <i>l</i> ≤ 29	-23 ≤ <i>h</i> ≤ 21, -27 ≤ <i>k</i> ≤ 27, -38 ≤ <i>l</i> ≤ 31	-23 ≤ <i>h</i> ≤ 26, -13 ≤ <i>k</i> ≤ 22, -15 ≤ <i>l</i> ≤ 13	-18 ≤ <i>h</i> ≤ 15, -18 ≤ <i>k</i> ≤ 18, -31 ≤ <i>l</i> ≤ 32	-23 ≤ <i>h</i> ≤ 17, -28 ≤ <i>k</i> ≤ 26, -30 ≤ <i>l</i> ≤ 26	-25 ≤ <i>h</i> ≤ 35, -18 ≤ <i>k</i> ≤ 19, -26 ≤ <i>l</i> ≤ 28	-21 ≤ <i>h</i> ≤ 17, -21 ≤ <i>k</i> ≤ 20, -47 ≤ <i>l</i> ≤ 43
refln.	273898	307544	26594	41253	69768	98976	187957
independ. reflns (<i>R</i> _{int})	40090 (0.0650)	44350 (0.1026)	8038 (0.0356)	11956 (0.0494)	20847 (0.0578)	9828 (0.0709)	25795 (0.0429)
observed reflns	28559	24221	7780	8852	14251	6496	22483
data/restr./param.	40090 / 0 / 2331	44350 / 1969 / 2475	8038 / 362 / 526	11956 / 1333 / 929	20847 / 885 / 1218	9828 / 0 / 544	25795 / 626 / 1844
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0845, 0.2397	0.0627, 0.1521	0.0692, 0.1735	0.0589, 0.1473	0.0731, 0.1669	0.0706, 0.2077	0.0419, 0.1054
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1055, 0.2674	0.0997, 0.1642	0.0748, 0.1988	0.0885, 0.1628	0.1174, 0.1986	0.1000, 0.2279	0.0485, 0.1080
Goof on <i>F</i> ²	1.091	0.860	1.056	1.034	1.063	1.060	0.990
largest diff. peak, hole/ e Å ³	0.899, -0.651	0.736, -0.608	1.262, -0.793	0.673, -0.350	0.391, -0.399	0.843, -0.274	0.413, -0.315
CCDC number	2176437	2176438	2176439	2176440	2176441	2176442	2176443

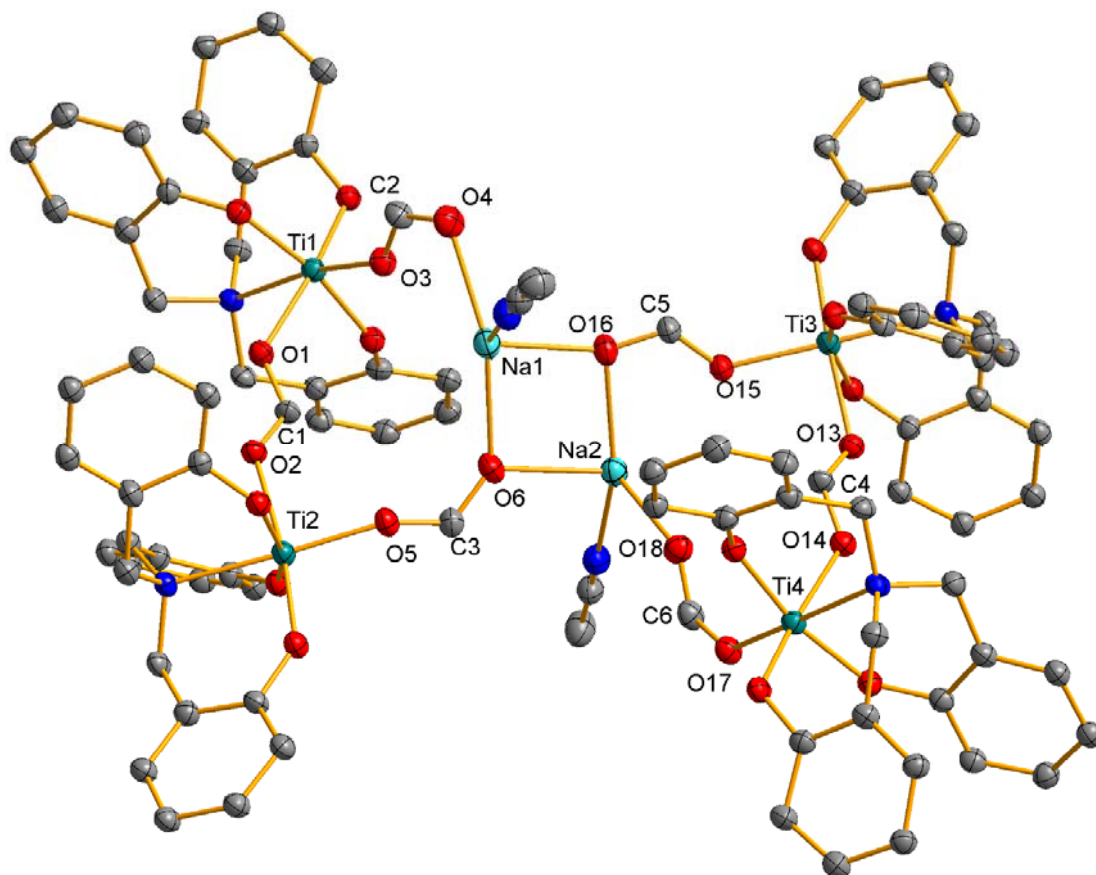


Figure S34. Molecular structure of **3-Na** in the solid state with displacement parameters at 30% probability level. H atoms, ^tBu groups and non-coordinated acetonitrile molecules are omitted for clarity. Selected interatomic distances (Å) and angles (°): Na1-O6 2.411(3), Na1-O16 2.275(3), Na2-O6 2.379(3), Na2-O16 2.391(3), Na1-O4 2.337(3), Na2-O18 2.244(3), Na2-O15 2.767(3), Ti1-O3 1.975(2), Ti2-O5 1.968(2), Ti3-O15 2.010(2), Ti4-O17 1.974(2), C2-O3 1.268(4), C2-O4 1.224(4), C3-O5 1.256(4), C3-O6 1.236(4), C5-O15 1.276(4), C5-O16 1.217(4), C6-O17 1.282(4), C6-O18 1.220(4); Na1-O6-Na2 98.85(10), O6-Na1-O16 80.11(10), O6-Na2-O16 78.50(9), Na1-O16-Na2 102.45(11), O1-C1-O2 123.0(3), O3-C2-O4 124.6(4), O5-C3-O6 124.7(4), O13-C4-O14 122.0(3), O15-C5-O16 123.1(3), O17-C6-O18 126.5(3).

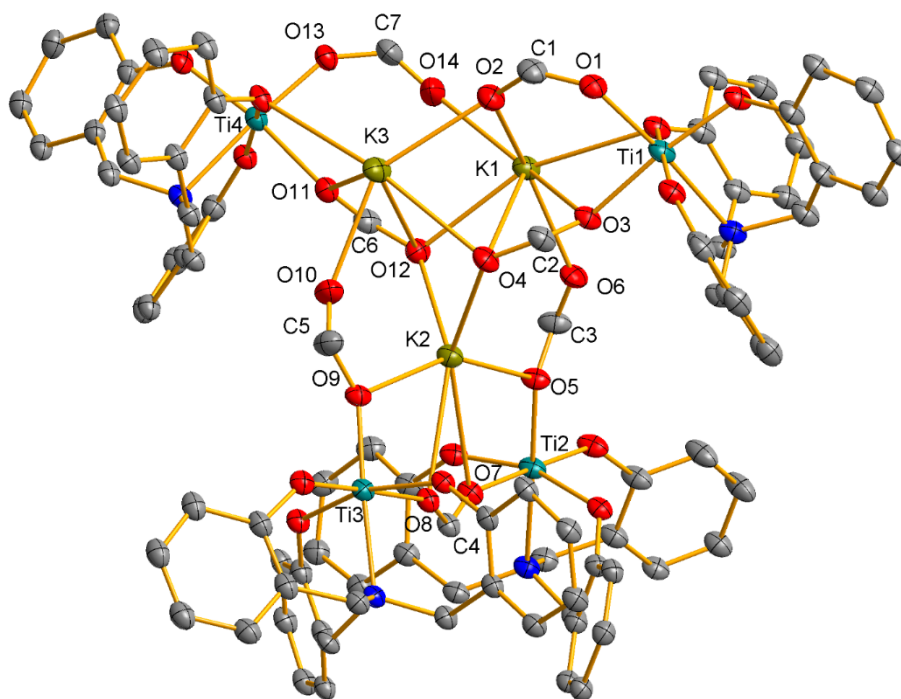


Figure S35. Molecular structure of **3-K** in the solid state with displacement parameters at 30% probability level. H atoms, ^tBu groups and non-coordinated toluene molecules are omitted for clarity. Selected interatomic distances (Å) and angles (°): Ti1-O1 1.981(3), Ti1-O3 2.045(2), Ti2-O5 1.940(2), Ti2-O7 2.068(2), Ti3-O8 2.103(2), Ti3-O9 1.970(2), Ti4-O11 2.070(2), Ti4-O13 1.944(3), K1-O2 2.745(3), K1-O3 2.735(2), K1-O4 3.330(3), K2-O4 2.632(2), K2-O5 2.731(3), K2-O7 3.049(2), K2-O8 3.033(2), K2-O9 2.756(3), K2-O12 2.665(3), K3-O2 2.721(3), K3-O4 2.855(3), K3-O11 2.638(2), K3-O12 3.337(2), K1---K2 4.2190(14), K1---K3 3.813(2), K2---K3 4.2372(16), O1-C1-O2 130.4(4), O3-C2-O4 128.0(3), O5-C3-O6 126.8(3), O7-C4-O8 124.5(3), O9-C5-O10 126.5(4), O11-C6-O12 126.6(3), O13-C7-O14 128.9(4), O1-Ti1-O3 88.80(11), O5-Ti2-O7 87.82(9), O8-Ti3-O9 85.49(10), O11-Ti4-O13 90.37(10).

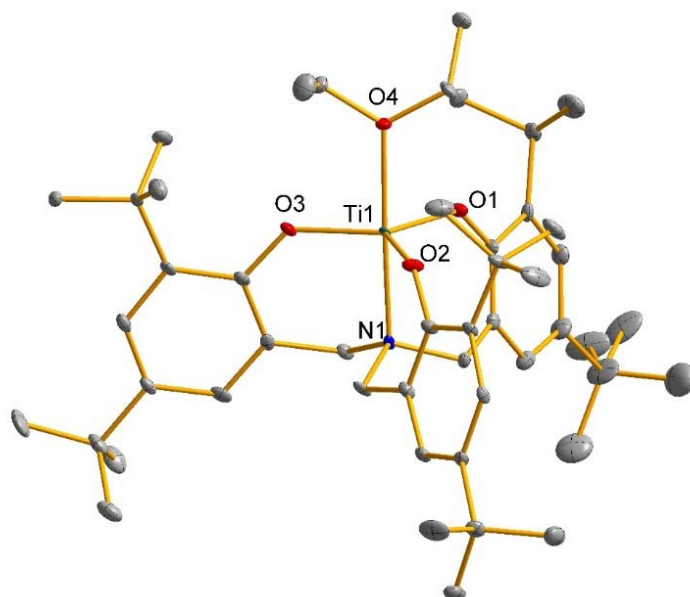


Figure S36. Molecular structure of **4-Et₂O** in the solid state with displacement parameters at 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Ti1-N1 2.181(5), Ti1-O1 1.931(4), Ti1-O2 1.877(3), Ti1-O3 1.938(3), Ti1-O4 2.149(4); N1-Ti1-O1 89.42(16), N1-Ti1-O2 86.29(15), N1-Ti1-O3 88.28(14), N1-Ti1-O4 178.23(18).

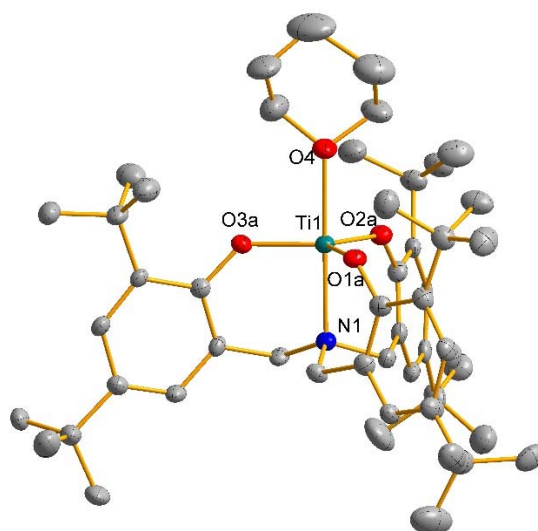


Figure S37. Molecular structure of **4-THP** in the solid state with displacement parameters at 50% probability level. Hydrogen atoms and non-coordinated pentane molecules are omitted for clarity. Atoms refined with split positions are only shown with one position. Selected interatomic distances (Å) and angles (°): Ti1-N1 2.188(3), Ti1-O1a 1.925(5), Ti1-O2a 1.912(5), Ti1-O3a 1.892(5), Ti1-O4 2.147(3); N1-Ti1-O1a 88.84(16), N1-Ti1-O2a 88.83(16), N1-Ti1-O3a 89.22(16), N1-Ti1-O4 177.56(15).

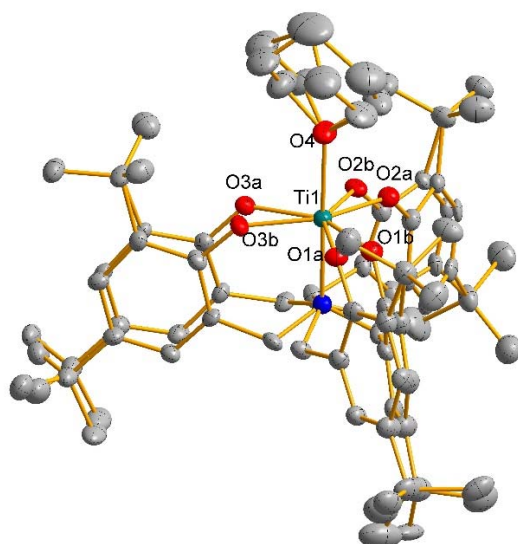


Figure S38. Molecular structure of **4-THP** in the solid state showing the disorder.

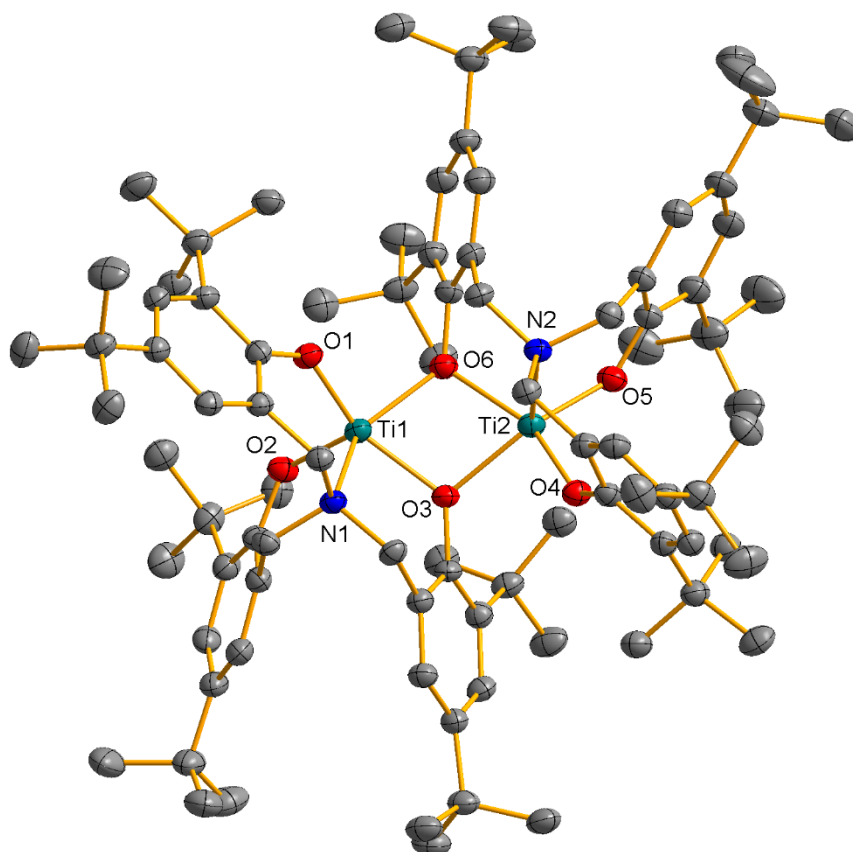


Figure S39. Molecular structure of **5** in the solid state with displacement parameters at 50% probability level. H atoms and the non-coordinated hexane molecules are omitted for clarity. Selected interatomic distances (Å) and angles (°): Ti1---Ti2 3.2142(15), Ti1-N1 2.216(3), Ti1-O1 1.904(2), Ti1-O2 1.885(3), Ti1-O3 2.046(2), Ti1-O6 2.062(3); N1-Ti1-O1 87.72(10), N1-Ti1-O2 92.83(11), N1-Ti1-O3 85.50(10), N1-Ti1-O6 135.74(11), Ti1-O3-Ti2 101.51(10), .

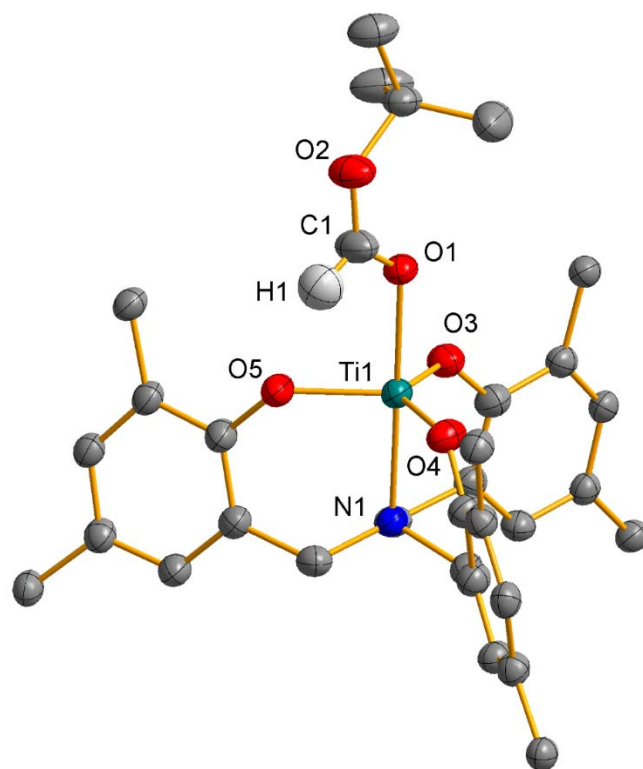


Figure S40. Molecular structure of **6** in the solid state with displacement parameters at 30% probability level. Hydrogen atoms, methyl groups of the tris(phenolato)amine ligand and non-coordinated benzene molecules are omitted for clarity. Selected interatomic distances (Å) and angles (°): Ti1-N1 2.197(2), Ti1-O1 2.139(2), Ti1-O3 1.871(3), Ti1-O4 1.887(3), Ti1-O5 1.915(2), C1-O1 1.186(5), C1-O2 1.310(5); N1-Ti1-O1 179.06(10), O1-C1-O2 127.9(4).

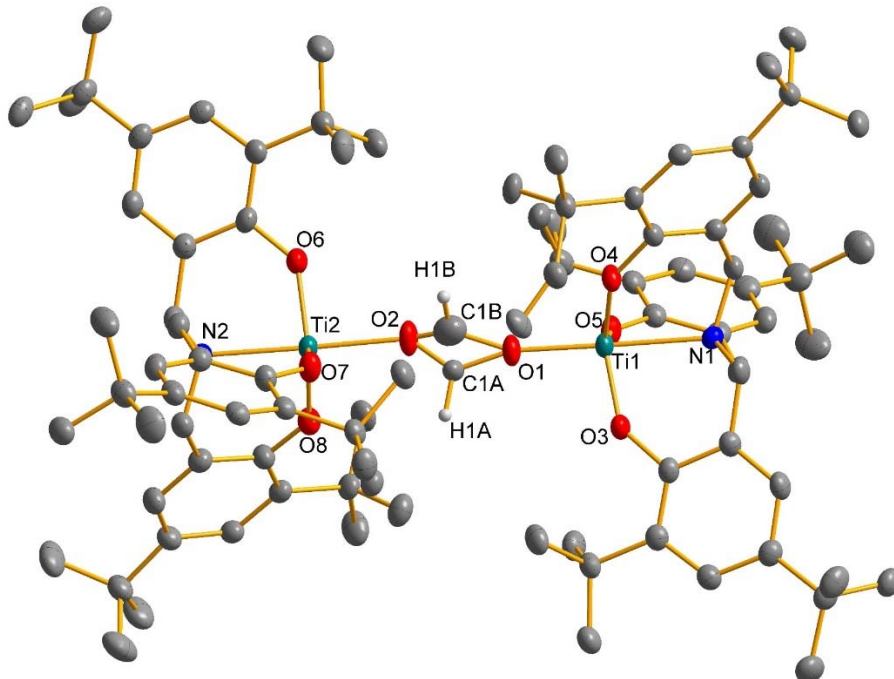


Figure S41. Molecular structure of **7** in the solid state with displacement parameters at 30% probability level. H atoms except for the formate proton as well as the non-coordinated benzene molecules are omitted for clarity. Selected interatomic distances (Å) and angles (°): Ti1-N1 2.222(3), Ti1-O1 1.911(2), Ti1-O3 1.807(2), Ti1-O4 1.806(2), Ti1-O5 1.799(2), Ti2-N2 2.189(3), Ti2-O2 2.073(3), Ti2-O6 1.869(2), Ti2-O7 1.904(2), Ti2-O8 1.887(2), C1A-O1 1.274(5), C1A-O2 1.185(7), C1B-O1 1.33(2), C1B-O2 0.98(2); N1-Ti1-O1 179.16(11), N1-Ti1-O3 83.86(9), N1-Ti1-O4 83.33(9), N1-Ti1-O5 83.55(9), N2-Ti2-O2 177.81(10), N2-Ti2-O6 87.62(9), N2-Ti2-O7 88.18(9), N2-Ti2-O8 88.80(9), Ti1-O1-C1A 161.9(4), Ti1-O1-C1B 158.6(14), Ti2-O2-C1A 135.9(4), Ti2-O2-C1B 150.5(12), O1-C1A-O2 125.8(7), O1-C1B-O2 143(3).

5. Cyclovoltammetry

The cyclic voltammogram was recorded with a Metrohm Autolab PGSTAT101 using a Pt-disk working electrode, a Pt-wire counter electrode and a Ag-wire quasi-reference electrode. The voltammogram was referenced to the Fc/Fc⁺ couple.

5.1. Cyclic voltammogram of 1-Cl

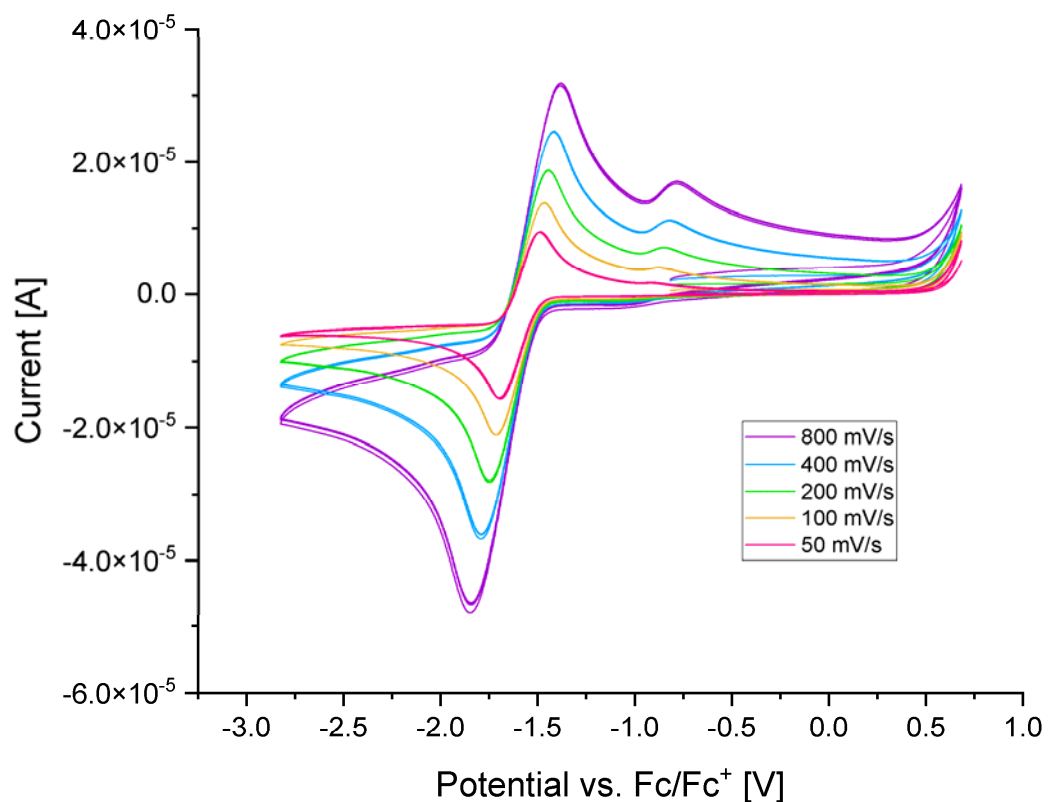


Figure S42. Cyclic voltammogram of **1-Cl** (2 mM in THF, scan rate 50 mV/s – 800 mV/s, 100 mM [ⁿBu₄N][PF₆]). $E_{1/2} = -1.60$ V.

6. References

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