

Electronic Supplementary Information for

**Coordination-Induced Reductive Elimination from a Titanium(IV)-
Complex**

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1. Methods and materials

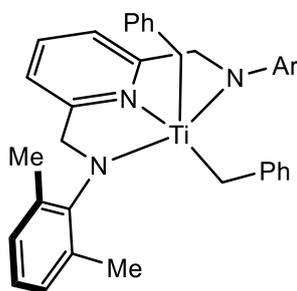
All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Both deuterated and non-deuterated solvents were stored under argon over activated 4 Å molecular sieves. NMR spectra were acquired either on a Bruker Avance 500 (operating at 500 MHz for ^1H and 125 MHz for ^{13}C) or a Bruker Avance 400 NMR (operating at 400 MHz for ^1H , 56 MHz for ^9Be and 100 MHz for ^{13}C). Chemical shifts (δ) are given in ppm and internally referenced to the carbon nuclei ($^{13}\text{C}\{^1\text{H}\}$) or residual protons (^1H) of the solvent. Microanalyses (C, H, N) were performed on an Elementar vario MICRO cube elemental analyzer.

$\text{Ti}(\text{CH}_2\text{Ph})_2$ ^[1] and $^{\text{R}}\text{PDA-H}_2$ (R = Me, Et, iPr)^[2] were prepared following literature procedures. Bis(trimethylsilyl)acetylene, 3-hexyne and 2-butyne were degassed, dried over calcium hydride and distilled under reduced pressure prior to use.

2. Synthetic procedures for novel compounds

MePDA-Ti(CH₂Ph)₂

MePDA-H₂ (487 mg, 1.41 mmol, 1.00 equiv.) and Ti(CH₂Ph)₄ (583 mg, 1.41 mmol, 1.00 equiv.) were dissolved in *n*-pentane (20 mL). The reaction mixture was stirred for 16 h at room temperature, after which an orange solid precipitated. The solution was filtered off and the resulting solid was washed with *n*-pentane (3 x 2.5 mL). After drying *in vacuo*, MePDA-Ti(CH₂Ph)₂ was obtained as an orange powder (690 mg, 1.20 mmol, 85%). Single crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a saturated thf solution.



C₃₇H₃₉N₃Ti, MW = 573.61 g/mol

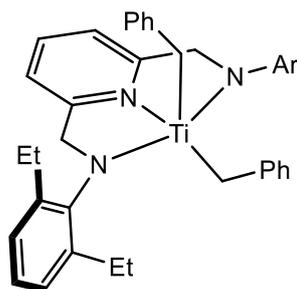
¹H NMR (500 MHz, 300 K, benzene-*d*₆): δ = 2.47 (s, 12H, CH₃), 2.64 (s, 4H, CH₂Ph), 4.60 (s, 4H, CH₂), 6.27 (d, 2H, ³J = 7.7 Hz, *m*-CH_{PyR}), 6.62 (d, 4H, ³J = 7.6 Hz, CH_{Ph}), 6.68 (t, 2H, ³J = 7.6 Hz, *p*-CH_{Ph}), 6.77 (t, 1H, ³J = 7.7 Hz, *p*-CH_{PyR}), 6.89 (t, 4H, ³J = 7.6 Hz, CH_{Ph}), 7.04-7.06 (m, 2H, CH_{Xyl}), 7.17-7.19 (m, 2H, CH_{Xyl}) ppm.

¹³C{¹H} NMR (125.8 MHz, 300 K benzene-*d*₆): δ = 19.9 (CH₃), 65.5 (CH₂, NCH₂), 83.0 (v. br, CH₂, TiCH₂), 116.8 (CH, *m*-CH_{PyR}), 122.3 (CH, CH_{Ph}), 125.47 (CH, CH_{Xyl}), 128.1 (overlapping with solvent signal assigned via HSQC and HMBC, CH, CH_{Ph}), 129.2 (CH, CH_{Xyl}), 134.4 (C_q, C(CH₃)), 137.8 (CH, *p*-CH_{PyR}), 145.8 (br. C_q, C_{Ph}), 156.9 (C_q, C_{Xyl}), 161.8 (C_q, NC_{PyR}) ppm.

Elemental analysis (%) calc. for C₃₇H₃₉N₃Ti [573.61 g mol⁻¹]: C 77.48, H 6.85, N 7.33; found: C 76.98, H 7.01, N 7.33.

$\text{Et}^t\text{PDA-Ti}(\text{CH}_2\text{Ph})_2$

$\text{Et}^t\text{PDA-H}_2$ (510 mg, 1.27 mmol, 1.00 equiv.) and $\text{Ti}(\text{CH}_2\text{Ph})_4$ (526 mg, 1.27 mmol, 1.00 equiv.) were dissolved in *n*-pentane (20 mL). The reaction mixture was stirred for 24 h, after which an orange solid precipitated. The solution was filtered off and the resulting solid was washed with *n*-pentane (3 x 2.5 mL). After drying *in vacuo* $\text{Et}^t\text{PDA-Ti}(\text{CH}_2\text{Ph})_4$ was obtained as an orange powder (362 mg, 575 μmol , 45%).



$\text{C}_{41}\text{H}_{47}\text{N}_3\text{Ti}$, MW = 629.71 g/mol

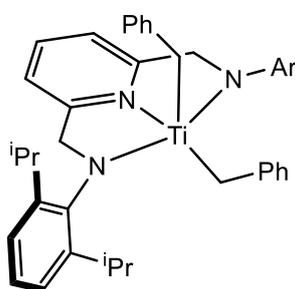
$^1\text{H NMR}$ (500 MHz, 300 K, benzene- d_6): δ = 1.30 (t, 12H, 3J = 7.5 Hz CH_3), 2.63 (s, 4H, CH_2Ph), 2.98-3.05 (m, 8H, CH_2CH_3), 4.71 (s, 4H, CH_2), 6.27 (d, 2H, 3J = 7.8 Hz, *m*- CH_{Pyr}), 6.62 (d, 4H, 3J = 7.2 Hz, CH_{Ph}), 6.69 (br. t, 2H, 3J = 7.2 Hz, *p*- CH_{Ph}), 6.76 (t, 1H, 3J = 7.7 Hz, *p*- CH_{Pyr}), 6.91 (t, 4H, 3J = 7.7 Hz, CH_{Ph}), 7.20-7.23 (m, 2H, CH_{Dep}), 7.26-7.28 (m, 2H, CH_{Dep}) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, 300 K, benzene- d_6): δ = 15.1 (CH_3), 24.7 (CH_2 , CH_2CH_3), 66.9 (CH_2 , NCH_2), 116.8 (CH, *m*- CH_{Pyr}), 122.3 (br., CH, CH_{Ph}), 125.8 (CH, CH_{Dep}), 126.4 (CH, CH_{Dep}), 128.3 (overlapping with solvent signal assigned via HSQC and HMBC, CH, CH_{Ph}), 137.9 (CH, *p*- CH_{Pyr}), 139.6 (C_q , C_{Dep}), 146.0 (br. C_q , C_{Ph}), 156.0 (C_q , C_{Dep}), 161.8 (C_q , NC_{Pyr}) ppm. The ^{13}C resonance of $\text{Ti}(\text{CH}_2\text{Ph})_2$ was not detected.

Elemental analysis (%) calc. for $\text{C}_{41}\text{H}_{47}\text{N}_3\text{Ti}$ [629.71 g mol $^{-1}$]: C 78.20, H 7.52, N 6.67; found: C 78.44, H 7.48, N 6.84.

ⁱPrPDA-Ti(CH₂Ph)₂

ⁱPrPDA-H₂ (726 mg, 1.59 mmol, 1.00 equiv.) and Ti(CH₂Ph)₄ (690 mg, 1.67 mmol, 1.05 equiv.) were suspended in *n*-pentane (15 mL). After stirring the reaction mixture for 16 hours at room temperature, the formation of an orange precipitate was observed. The supernatant solution was filtered off and the resulting solid was washed with *n*-pentane (3 x 5 mL). After drying *in vacuo* ⁱPrPDA-Ti(CH₂Ph)₂ was obtained as an orange powder (840 mg, 1.22 mmol, 77%). Single crystals suitable for X-ray analysis were grown by slow diffusion of *n*-hexane into a saturated benzene solution of ⁱPrPDA-Ti(CH₂Ph)₂.



C₄₅H₅₅N₃Ti, MW = 685.82 g/mol

¹H NMR (500 MHz, 233 K, thf-*d*₈): δ = 1.06 (d, 6H, ³J = 6.7 Hz, CH(CH₃)₂), 1.13 (d, 6H, ³J = 6.8 Hz, CH(CH₃)₂), 1.32 (d, 6H, ³J = 6.7 Hz, CH(CH₃)₂), 1.35 (d, 6H, ³J = 6.8 Hz, CH(CH₃)₂), 1.95 (s, 2H, CH₂Ph), 2.84 (s, 2H, CH₂Ph), 3.29 (sept., 2H, ³J = 6.7 Hz, CH(CH₃)₂), 4.39 (sept., 2H, ³J = 6.8 Hz, CH(CH₃)₂), 4.79 (d, ²J = 21 Hz, 2H, CH₂), 5.18 (d, ²J = 21 Hz, 2H, CH₂), 5.69 (d, 2H, ³J = 7.6 Hz, CH_{Ph}), 6.29 (t, 1H, ³J = 7.3 Hz, CH_{Ar}), 6.43-6.44 (m, 2H, CH_{Ph}), 6.54-6.58 (m, 3H, CH_{Ar}), 6.68 (t, 2H, ³J = 7.6 Hz, CH_{Ar}), 7.19-7.22 (m, 4H, CH_{Ar}), 7.23 (*overlapping with resonance at 7.19-7.22*, 2H; ³J = 7.6 Hz, CH_{Pyr}), 7.29-7.31 (m, 2H, CH_{Ar}), 7.76 (t, 1H, ³J = 7.6 Hz, *p*-CH_{Pyr}) ppm.

¹³C{¹H} NMR (125.8 MHz, 233 K, thf-*d*₈): δ = 23.5 (CH₃, CH(CH₃)₂), 24.2 (CH₃, CH(CH₃)₂), 27.5 (CH₃, CH(CH₃)₂), 27.8 (CH₃, CH(CH₃)₂), 28.2 (CH, CH(CH₃)₂), 28.9 (CH, CH(CH₃)₂), 68.3 (CH₂, NCH₂), 76.7 (CH₂, TiCH₂), 93.2 (CH₂, TiCH₂), 118.2 (CH, *m*-CH_{Pyr}), 121.2 (CH, CH_{Ar}), 122.2 (CH, CH_{Ar}), 124.4 (CH, CH_{Ar}), 125.0 (CH, CH_{Ar}), 125.5 (CH, CH_{Ph}), 126.3 (CH, CH_{Ar}), 127.4 (CH, CH_{Ar}), 128.1 (CH, CH_{Ar}), 128.5 (CH, CH_{Ph}), 139.7 (CH, *p*-CH_{Pyr}), 144.3 (C_q, C_{Ph}), 145.5 (C_q, C_{Dipp}), 145.7 (C_q, C_{Dipp}), 147.7 (C_q, C_{Ph}), 154.2 (C_q, C_{Dipp}), 161.9 (C_q, NC_{Pyr}) ppm.

Elemental analysis (%) calc. for $C_{45}H_{55}N_3Ti$ [685.82 g mol⁻¹]: C 78.81, H 8.08, N 6.13; found: C 78.84, H 8.37, N 6.22.

Ti(CD₂Ph-d₅)₄

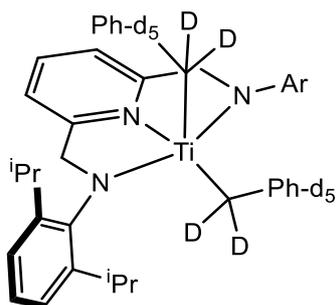
The synthesis of **Ti(CD₂Ph-d₅)₄** was based on the literature synthesis of TiBn₄.^[1] Magnesium chips (184 mg, 7.41 mmol, 4.10 equiv.) and Et₂O (20 mL) were combined in a 50 mL Schlenk tube. A solution of benzylchloride-d₇ (1.00 g, 7.57 mmol, 4.05 equiv.) in Et₂O (5 mL) was slowly added. After ca. ½ of the benzylchloride-d₇ solution was added, the reaction mixture was heated to reflux and the remaining benzylchloride-d₇ solution was added. Subsequently, the reaction mixture was stirred for one hour and the solution was decanted from the remaining magnesium. The obtained solution was cooled to -20 °C and a solution of TiCl₄ (351 mg, 1.85 mmol, 1.00 equiv.) in *n*-pentane (10 mL) was added dropwise. After stirring the reaction mixture for three hours at -20 °C, the resulting solid was filtered off over Celite and washed with Et₂O (2 x 10 mL). The solvent was removed *in vacuo* and the remaining dark brown residue was extracted with *n*-pentane (2 x 10 mL). The obtained filtrate was concentrated (ca. 1/2) *in vacuo* and stored at -30 °C overnight. Dark red needles of **Ti(CD₂Ph-d₅)₄** (391 mg, 888 μmol, 48%) were isolated by decanting the supernatant solution and dried *in vacuo*.

²D NMR (76.8 MHz, 300 K, C₆D₆): δ = 2.70 (CD₂), 6.58 (CD_{Ph}) ppm.

¹³C{¹H} NMR (125.8 MHz, 300 K, C₆D₆): δ = 96.9 (quint, ¹J_{CD} = 20.4 Hz, CD₂), 124.3 (t, ¹J_{CD} = 24.2 Hz, *p*-CD_{Ph}), 129.4 (two overlapping triplets, ¹J_{CD} = 24.2 Hz, ¹J = 23.7 Hz, CD, *o/m*-CD_{Ph}), 142.1 (s, C_q) ppm.

ⁱPrPDATi(CD₂Ph-*d*₅)

ⁱPrPDA-H₂ (102 mg, 223 μmol, 1.00 equiv.) and Ti(CD₂Ph-*d*₅)₄ (99.5 mg, 223 μmol, 1.00 equiv.) were suspended in 10 mL *n*-pentane. The reaction mixture was stirred for 18 h at room temperature and a red solid precipitated. The solution was filtered off and the resulting solid was washed with *n*-pentane (2 x 1.5 mL). After drying *in vacuo* ⁱPrPDATi(CD₂Ph-*d*₅) was obtained as an orange powder (80.8 mg, 115 μmol, 51%).

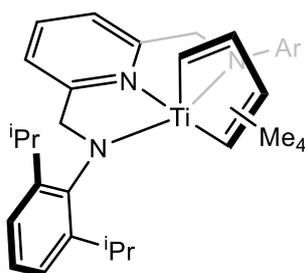


C₄₅H₄₁D₁₄N₃Ti, MW = 699.92 g/mol

¹H NMR (500 MHz, 233 K, benzene-*d*₆): δ = 1.38 (brs, 24H, CH(CH₃)₂), 3.50 (brs, 2H, CH(CH₃)₂ or CH₂), 4.71 (brs, 4H, CH(CH₃)₂ or CH₂), 5.20 (brs, 2H, CH(CH₃)₂ or CH₂), 6.25 (d, 2H, ³J_{HH} = 7.6 Hz, *m*-CH_{Pyr}), 6.75 (t, 1H, ³J_{HH} = 7.6 Hz, *p*-CH_{Pyr}), 7.30 (brs, 6H, CH_{D_{ipp}}) ppm. See Figure S31.

ⁱPrPDATi(C₄Me₄)

ⁱPrPDA-Ti(CH₂Ph)₂ (40.0 mg, 58.3 μmol, 1.00 eq) was suspended in benzene-*d*₆ (0.5 mL) in a J.Young NMR tube and 2-butyne (63.1 mg, 1.17 μmol, 20.0 eq) was added. The red suspension was agitated at ambient temperature and monitored *via* NMR-spectroscopy. After 7 days, the reaction was completed, and the solvent was removed *in vacuo*. The residue was washed with *n*-pentane (2 x 0.3 mL) to afford ⁱPrPDATi(C₄Me₄) as red solid (33.1 mg, 53.9 μmol, 92%). Single crystals suitable for X-ray analysis were grown from concentrated solutions of ⁱPrPDATi(C₄Me₄) in *n*-hexane at ambient temperature.



$C_{39}H_{53}N_3Ti$, MW = 611.74 g/mol

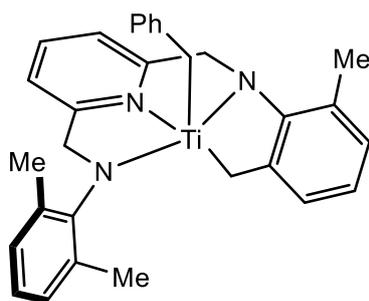
1H NMR (500 MHz, 300 K, benzene- d_6): δ = 1.24 (d, 12H, 3J = 6.8 Hz, $CH(CH_3)_2$), 1.30 (d, 12H, 3J = 6.8 Hz, $CH(CH_3)_2$), 1.56 (s, 6H, CH_3), 1.65 (s, 6H, CH_3), 3.65 (sept, 4H, $CH(CH_3)_2$), 4.97 (s, 4H, CH_2), 6.44 (d, 2H, 3J = 7.7 Hz, $m-CH_{Pyr}$), 6.87 (t, 1H, 3J = 7.7 Hz, $p-CH_{Pyr}$), 7.09-7.13 (m, 4H, CH_{Dipp}), 7.17-7.18 (m, 2H, CH_{Dipp}) ppm.

$^{13}C\{^1H\}$ NMR (125.8 MHz, 300 K, benzene- d_6): δ = 14.7 (CH_3), 20.4 (CH_3), 24.4 ($CH(CH_3)_2$), 26.6 ($CH(CH_3)_2$), 28.7 ($CH(CH_3)_2$), 68.1 (NCH_2), 116.8 (CH , $m-CH_{Pyr}$), 123.0 (CH , CH_{Dipp}), 125.5 (CH , CH_{Dipp}), 136.4 (C_q , $C(CH_3)$), 137.7 (CH , $p-CH_{Pyr}$), 143.8 (C_q , C_{Dipp}), 152.5 (C_q , C_{Dipp}), 162.1 (C_q , C_{Pyr}), 221.6 (C_q , $TiC(CH_3)$) ppm.

Elemental analysis (%) calc. for $C_{39}H_{53}N_3Ti$ [$611.74 \text{ g mol}^{-1}$]: C 76.57, H 8.73, N 6.87; found: C 76.85, H 8.62, N 6.31.

($^{Me}PDA^H$)Ti(CH_2Ph)

$^{Me}PDA-Ti(CH_2Ph)_2$ (96.0 mg, 0.17 mmol, 1.00 equiv.) was dissolved in benzene (3 mL) in a Schlenk tube and heated to 80 °C for 24 hours. Subsequently, the solvent was removed *in vacuo* and the remaining solid was washed with *n*-pentane (2 mL). The residue was extracted with benzene and the solvent removed *in vacuo* to afford ($^{Me}PDA^H$)Ti(CH_2Ph) (63 mg, 0.13 mmol, 77%) as an orange powder. Single crystals suitable for X-ray analysis were grown from concentrated solutions of ($^{Me}PDA^H$)Ti(CH_2Ph) in *n*-hexane at ambient temperature.



$C_{30}H_{31}N_3Ti$, MW = 481.47 g/mol

1H NMR (500 MHz, 300 K, benzene- d_6): δ = 0.46 (d, 1H, 2J = 11.7 Hz, CH_2 -Xyl-H-Ti), 1.36 (d, 1H, 2J = 9.8 Hz, $PhCH_2$ -Ti), 2.12 (d, 1H, 2J = 9.9 Hz, $PhCH_2$ -Ti), 2.37 (s, 3H, CH_{3-Xyl}), 2.44 (s, 3H, $CH_{3-Xyl-H}$), 2.46 (s, 3H, CH_{3-Xyl}), 3.18 (d, 1H, 2J = 11.9 Hz, CH_2 -Xyl-H-Ti), 4.61 (d, 1H, 2J = 20.1 Hz, N- CH_2), 4.74 (d, 1H, 3J = 21.0 Hz, N- CH_2), 4.92 (d, 1H, 3J = 21.0 Hz, N- CH_2), 5.57 (d, 1H, 2J = 20.2 Hz, N- CH_2), 6.28-6.33 (m, 3H, $m-CH_{Pyr}$ + CH_{Ph}), 6.43-6.47 (m, 1H, $m-CH_{Pyr}$), 6.69-6.74 (m, 1H, CH_{Ph}), 6.83 (t, 1H, 3J = 7.7 Hz, $p-CH_{Pyr}$), 6.86-6.90 (m, 2H, CH_{Ph}), 6.97-7.00 (m, 1H, CH_{Ph}), 7.19 (m, 3H, CH_{Xyl} + CH_{Xyl-H}), 7.22-7.25 (m, 1H, CH_{Xyl}), 7.29-7.33 (m, 1H, CH_{Xyl}) ppm.

$^{13}C\{^1H\}$ NMR (125.8 MHz, 300 K, benzene- d_6): δ = 18.9 (CH_{3-Xyl}), 19.1(CH_{3-Xyl}), 21.5 ($CH_{3-Xyl-H}$), 63.4 (N- CH_2), 65.6 (N- CH_2), 77.3 ($PhCH_2$ -Ti), 83.6 (Xyl-H- CH_2 -Ti), 117.25 (CH, $m-CH_{Pyr}$), 117.29 (CH, $m-CH_{Pyr}$), 120.6 (CH, CH_{Ph}), 124.5 (CH, CH_{Xyl}), 125.3 (CH, CH_{Ph}), 125.6 (C_q , C_{Xyl-H}), 126.0 (CH, CH_{Xyl-H}), 127.5 (CH, CH_{Ph}), 128.13 (CH, CH_{Xyl-H} , overlap with benzene- d_6 signal), 129.0 (CH, CH_{Xyl}), 129.1 (CH, CH_{Xyl-H}), 129.5 (CH, CH_{Xyl}), 133.4 (C_q , C_{Xyl-H}), 135.4 (C_q , C_{Xyl}), 136.3 (C_q , C_{Xyl}), 137.3 (CH, $p-CH_{Pyr}$), 147.4 (C_q , $C_{Xyl-H-N}$), 147.9 (C_q , C_{Ph}), 149.6 (C_q , C_{Xyl}), 163.0 (C_q , C_{Pyr}), 165.4 (C_q , C_{Pyr}) ppm.

Elemental analysis (%) calc. for $C_{30}H_{31}N_3Ti$ [481.47 g mol $^{-1}$]: C 74.84, H 6.49, N 8.73; found: C 75.06, H 6.48, N 8.89.

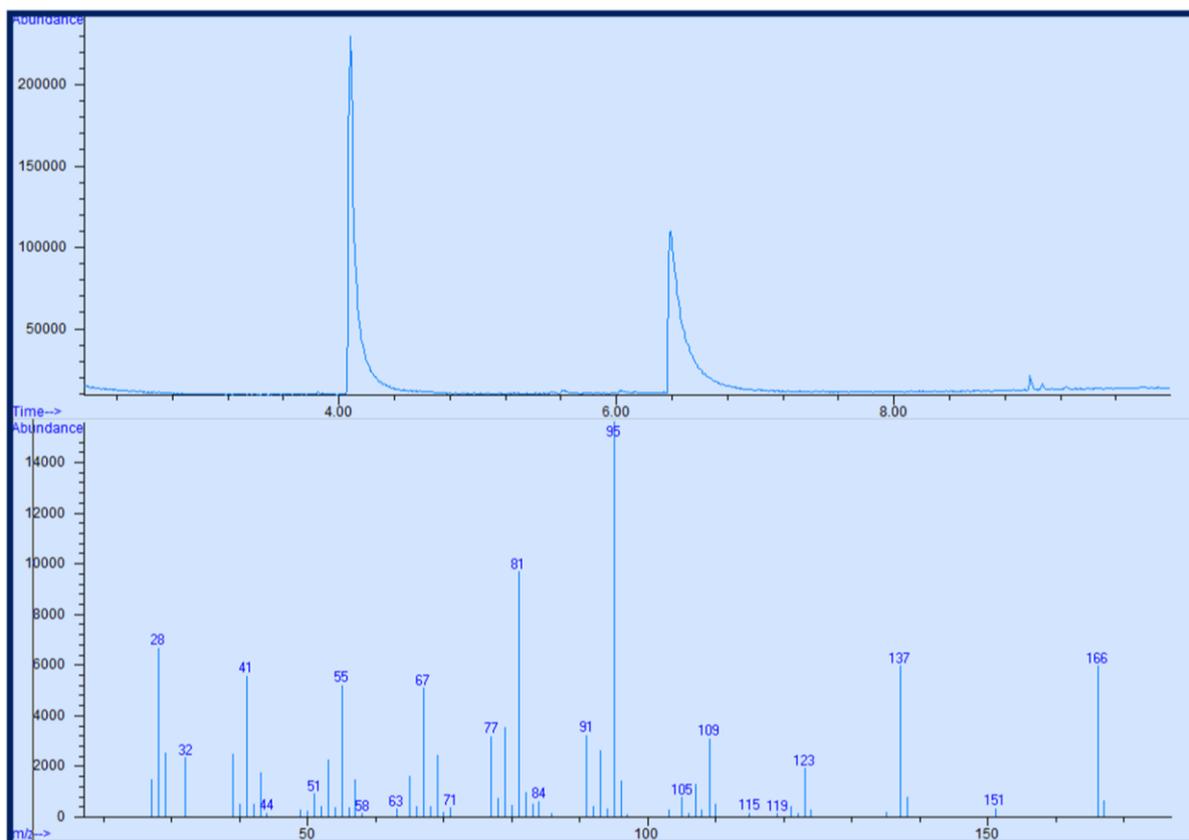


Figure S1. GC-MS data of the reaction of $i\text{PrPDA Ti}(\text{CH}_2\text{Ph})_2$ with 3-hexyne after aqueous work-up. The upper part shows the GC chromatogram, the lower part shows the mass spectrum at a retention time of 4.1 min, representing 4,5-diethylocta-3,5-diene.

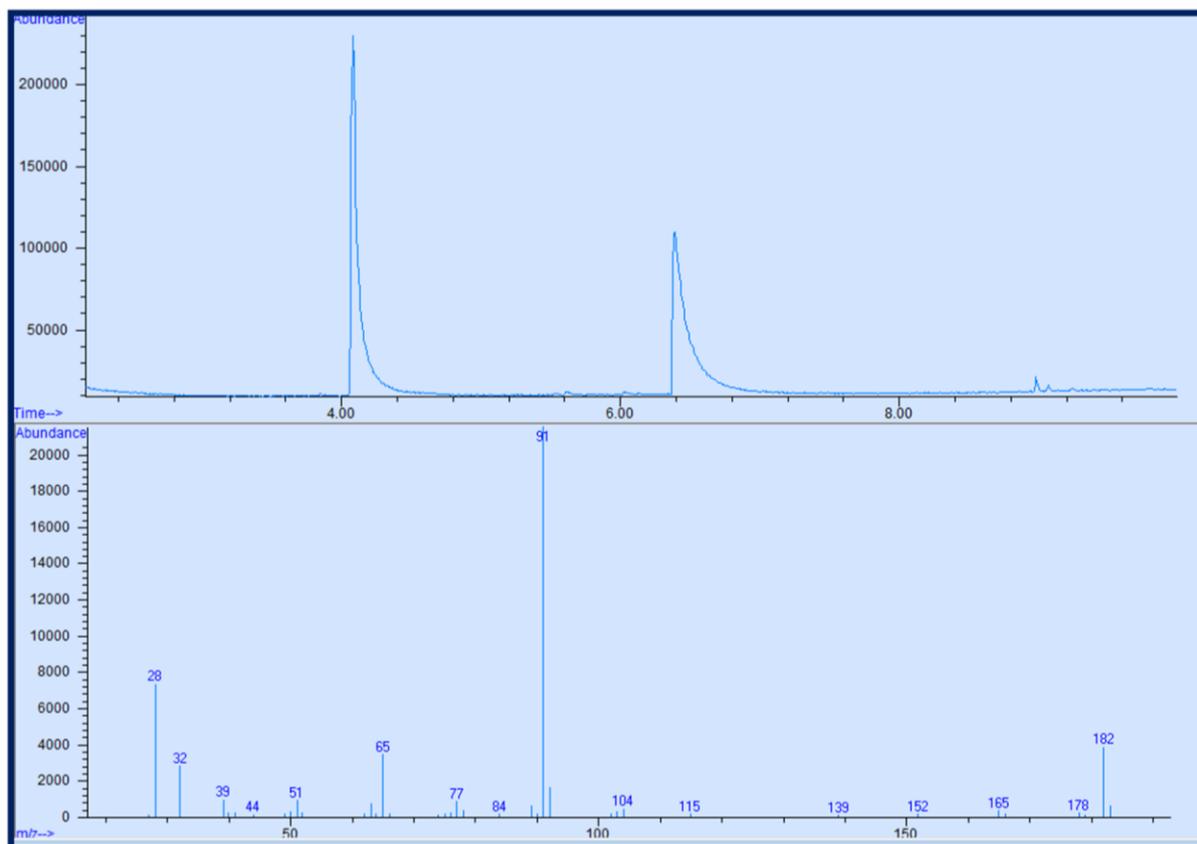


Figure S2. GC-MS data of the reaction of $i\text{PrPDATi}(\text{CH}_2\text{Ph})_2$ with 3-hexyne after aqueous work-up. The upper part shows the GC chromatogram, the lower part shows the mass spectrum at a retention time of 6.7 min, assigned to bibenzyl.

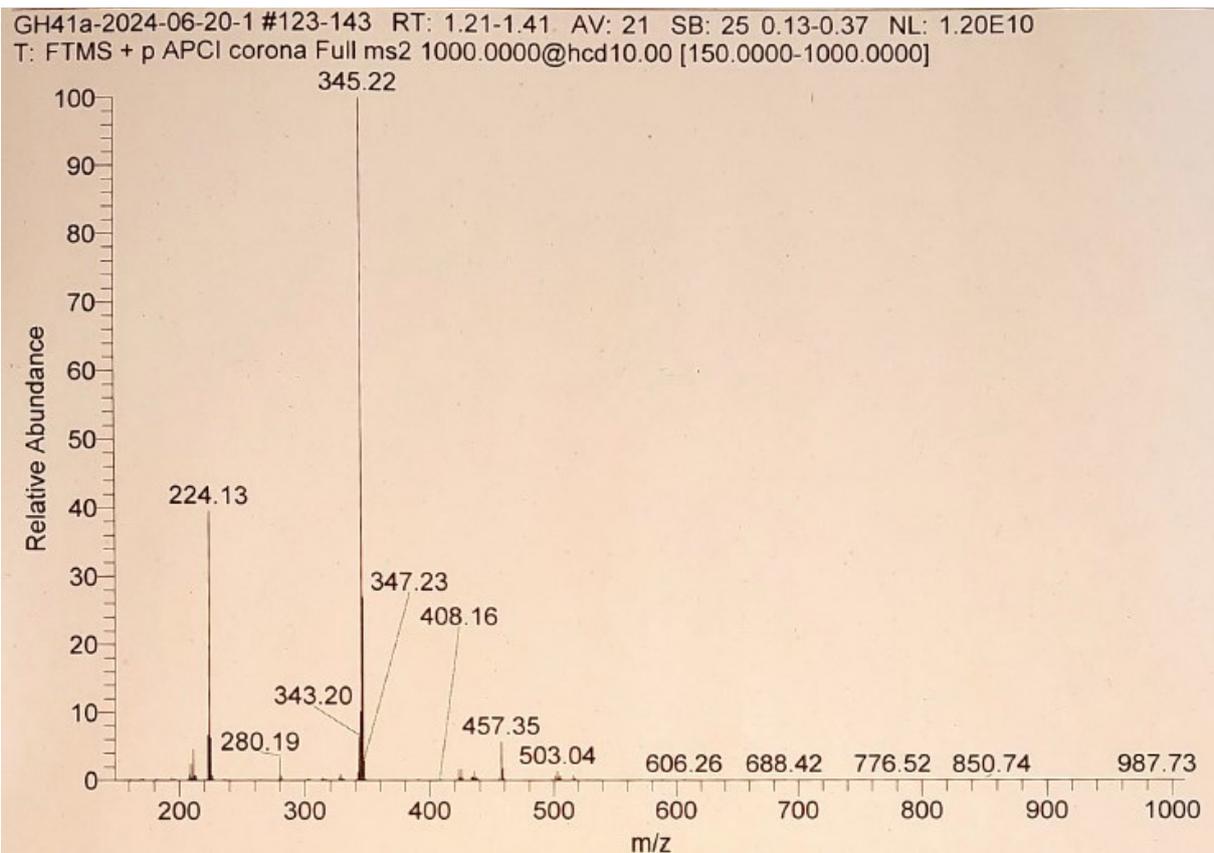


Figure S3. LIFDI-MS data for **1-(CH₂Ph)** showing mainly ^{Me}PDA-H₂ (protonated ligand) with m/z = 345.22.

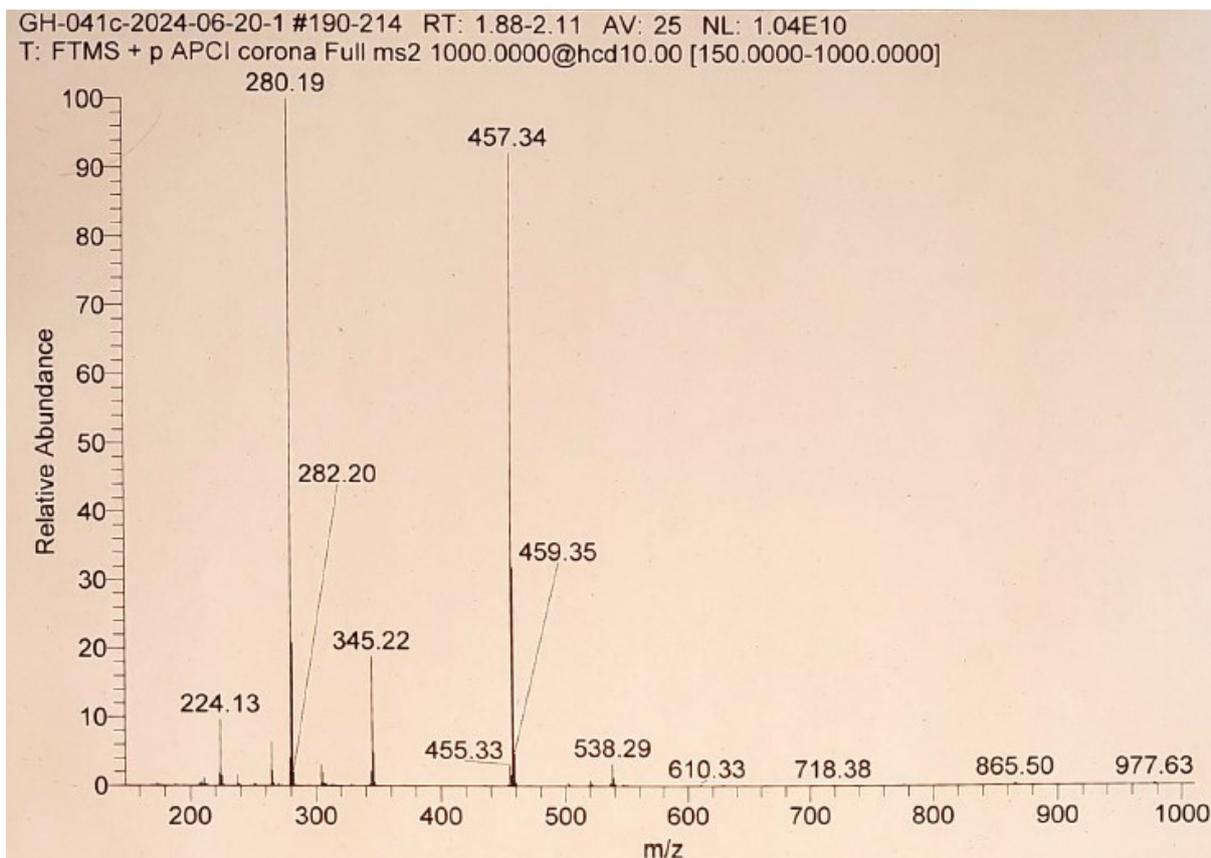


Figure S4. LIFDI-MS data for **3-(CH₂Ph)** showing mainly ⁱPrPDA-H₂ (protonated ligand) with m/z = 457.35.

3. Synthetic procedures for reactivity & mechanistic studies

Reductive Elimination from ⁱPrPDATi(CH₂Ph)₅

ⁱPrPDATi(CH₂Ph)₂ (10.0 mg, 14.6 μmol, 1.00 equiv.) and alkyne (2-butyne or 3-hexyne, 10.0 equiv.) were suspended in benzene-*d*₆ (0.5 mL). The reaction mixture was agitated and monitored for two days at ambient temperature showing the formation of ⁱPrPDATi(C₄R₄) (R = Me, Et) and bibenzyl (see Figure S32). Single scan ¹H NMR confirmed quantitative formation of both products.

Upon scaling up the reaction to 40 mg ⁱPrPDATi(CH₂Ph)₂ in the same amount of solvent (0.5 mL benzene-*d*₆), reaction times are significantly elongated up to 7 days.

Exchange between ${}^{\text{iPr}}\text{PDATi}(\text{CD}_2\text{Ph-}d_5)$ and ${}^{\text{Et}}\text{PDATi}(\text{CH}_2\text{Ph})_2$

${}^{\text{iPr}}\text{PDATi}(\text{CD}_2\text{Ph-}d_5)$ (10.0 mg, 14.2 μmol , 1.00 equiv.) and ${}^{\text{Et}}\text{PDATi}(\text{CH}_2\text{Ph})_2$ (9.00 mg, 14.2 μmol , 1.00 equiv.) were suspended in benzene- d_6 (0.5 mL). The reaction mixture was monitored for three days at ambient temperature and no exchange reaction was observed. After heating to 60 $^\circ\text{C}$ for 3 hours, decomposition of ${}^{\text{Et}}\text{PDATi}(\text{CH}_2\text{Ph})_2$ was observed.

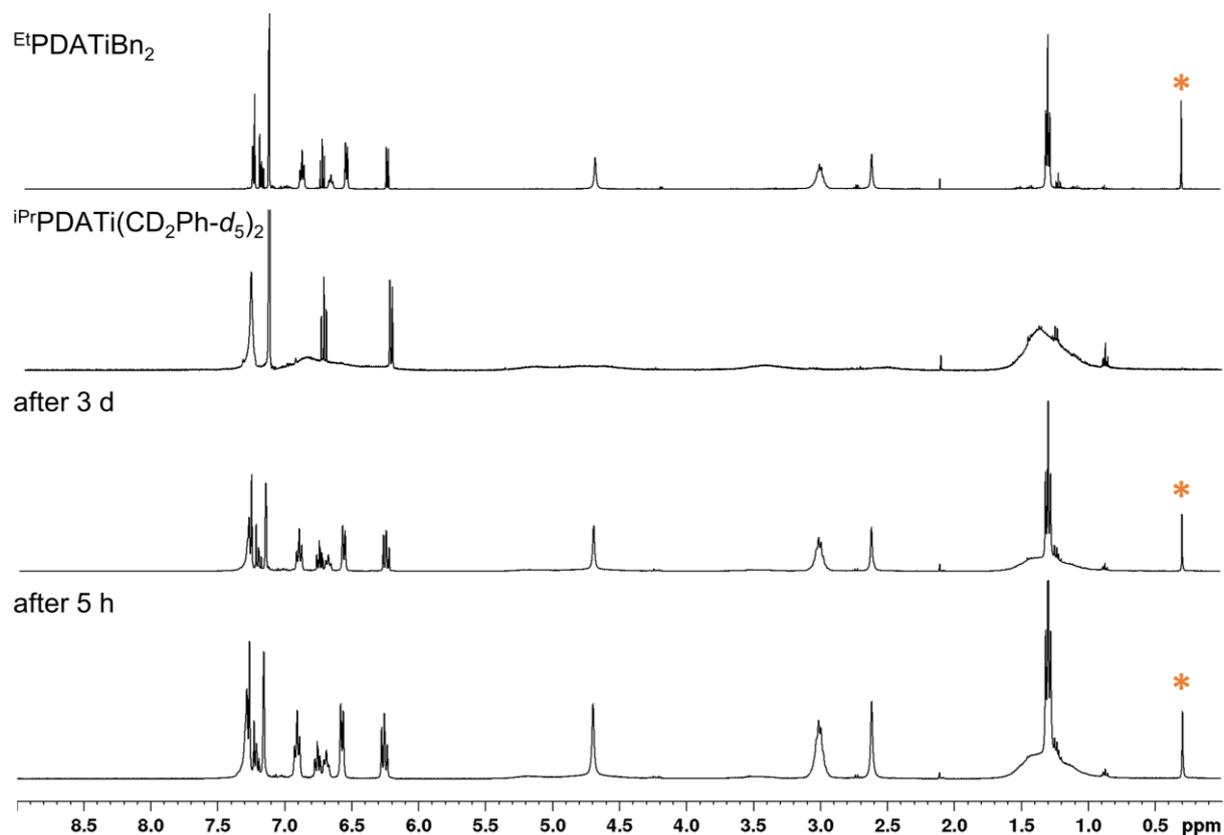


Figure S5. ${}^1\text{H}$ NMR spectrum of the reaction between ${}^{\text{iPr}}\text{PDATi}(\text{CD}_2\text{Ph-}d_5)$ and ${}^{\text{Et}}\text{PDATi}(\text{CH}_2\text{Ph})_2$ in benzene- d_6 over a period of three days, illustrating the absence of an exchange reaction compared to the two spectra of the starting material. The resonances marked with * belong to silicon grease.

Crossover experiment: ${}^{\text{iPr}}\text{PDATi}(\text{CD}_2\text{Ph-}d_5) + {}^{\text{iPr}}\text{PDATi}(\text{CH}_2\text{Ph})_2 + 3\text{-hexyne}$

${}^{\text{iPr}}\text{PDATi}(\text{CD}_2\text{Ph-}d_5)$ (15.3 mg, 21.9 μmol , 1.01 equiv.), ${}^{\text{iPr}}\text{PDATi}(\text{CH}_2\text{Ph})_2$ (14.9 mg, 21.7 μmol , 1.00 equiv.) and 3-hexyne (40.4 mg, 492 μmol , 23.0 equiv.) were suspended in benzene- d_6 (1 mL) and stirred at ambient temperature for two days. Subsequently, an aliquot of the orange solution was transferred to a J. Young NMR tube and analysed by NMR spectroscopy. The remaining solution was subjected to

GC-MS analysis, and the formation of three different bibenzyl products $C_{14}H_{14}$ (m/z: 182), $C_{14}D_{14}$ (m/z: 196), and $C_{14}H_7D_7$ (m/z: 189) was confirmed.

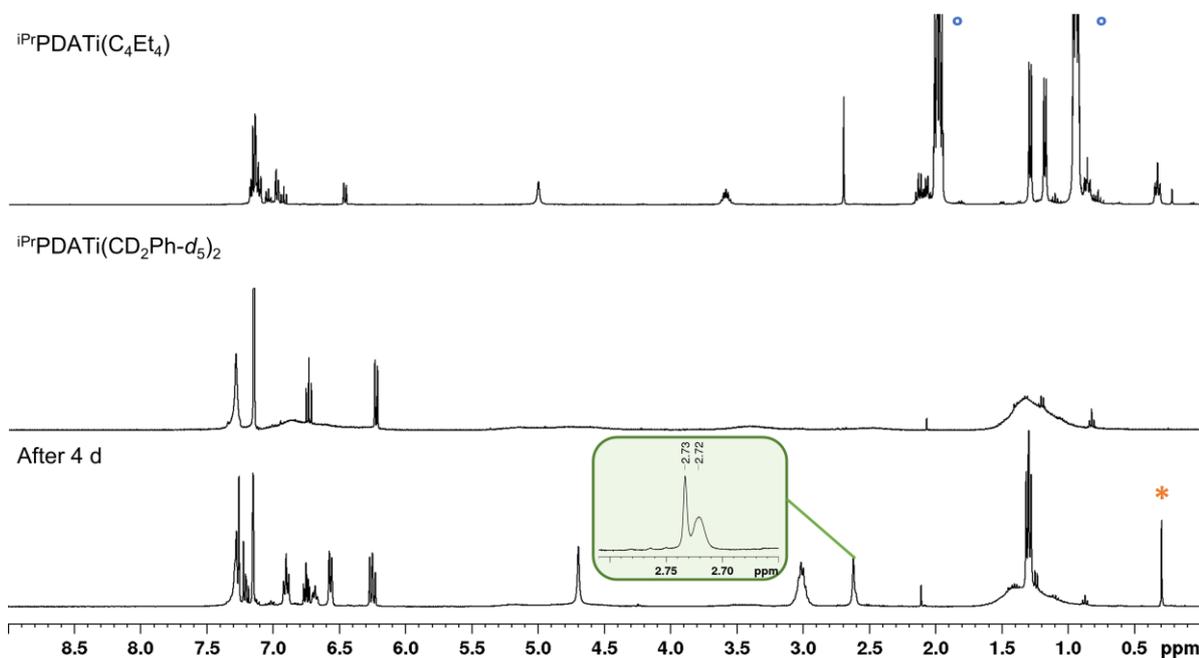


Figure S6. 1H NMR spectrum of the reaction between $iPrPDATi(CD_2Ph-d_5)$, $iPrPDATi(CH_2Ph)_2$ and 3-hexyne in benzene- d_6 over a period of four days. The resonances marked with a * belong to silicon-grease. The resonances marked with a ° belong to 3-hexyne.

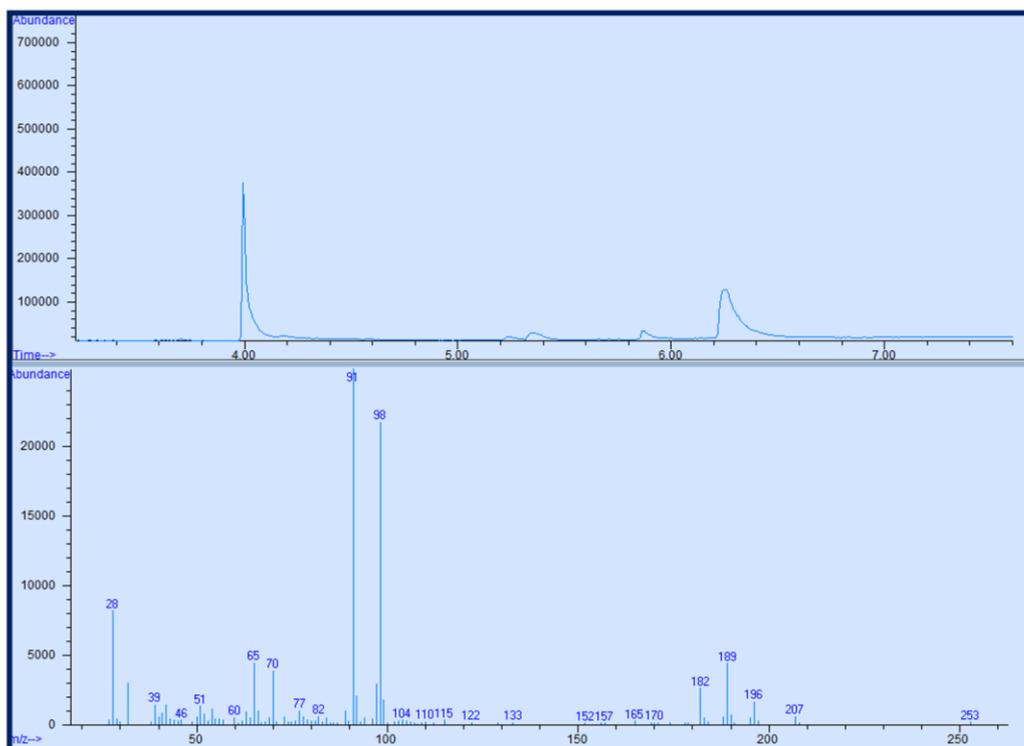


Figure S7. GC-MS data of the reaction of $iPrPDATi(CH_2Ph)_2$ and $iPrPDATi(CD_2Ph-d_5)_2$ with 3-hexyne after aqueous work-up. The upper part shows the GC chromatogram, the lower part shows the mass spectrum at a retention time of 4.1 min, representing bibenzyl-isotopomers.

Reaction of $i\text{PrPDATi}(\text{CH}_2\text{Ph})_2$ with 3-hexyne and 9,10-dihydroanthracene

$i\text{PrPDATiBn}_2$ (10.1 mg, 15.0 μmol , 1.00 equiv.), 9,10-dihydroanthracene (13.5 mg, 74.9 μmol , 5.00 equiv.) and 3-hexyne (13.6 mg, 165 μmol , 11.0 equiv.) were dissolved in benzene- d_6 (0.5 mL). The reaction mixture was monitored by NMR spectroscopy for three days. The formation of $i\text{PrPDATi}(\text{C}_4\text{Et}_4)$ and bibenzyl was observed and no formation of toluene or dimerization of 9,10-dihydroanthracenyl was detected.

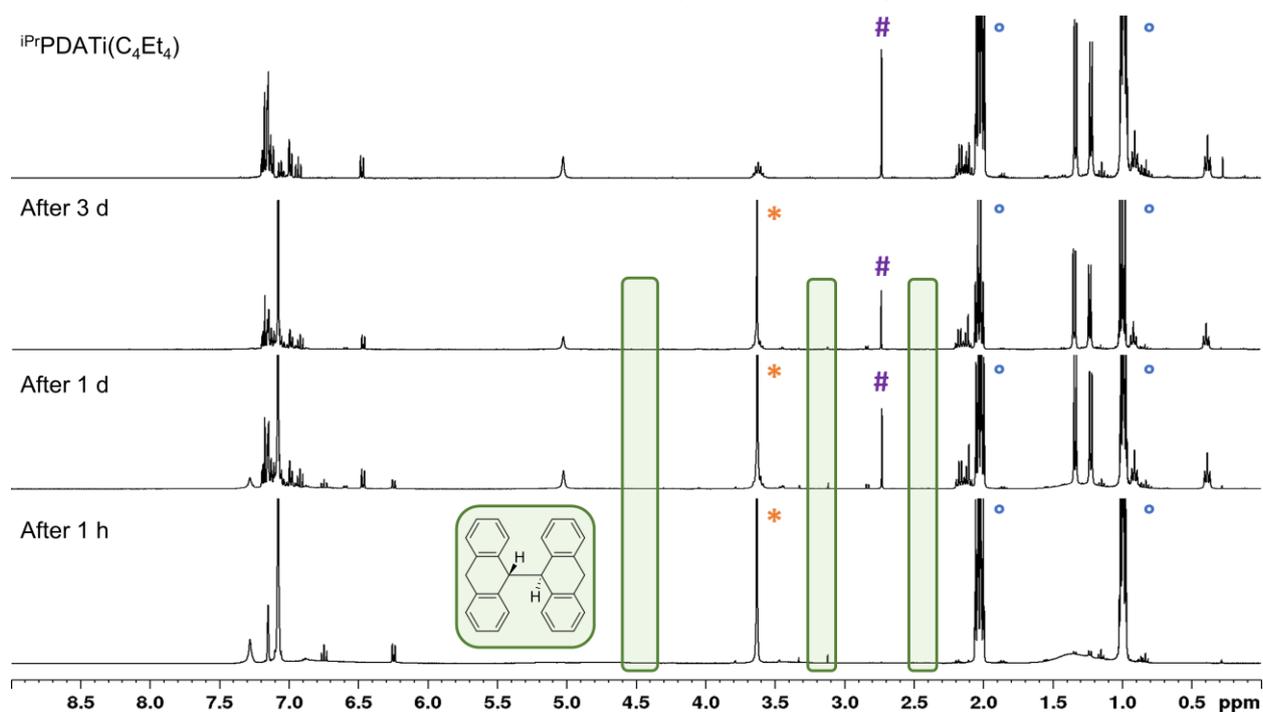


Figure S8. ^1H NMR spectrum of the reaction between $i\text{PrPDATi}(\text{CH}_2\text{Ph})_2$, 3-hexyne and 9,10-dihydroanthracene in benzene- d_6 over a period of three days, illustrating the formation of $i\text{PrPDATi}(\text{C}_4\text{Et}_4)$ and bibenzyl. No formation of toluene or dimerization of 9,10-dihydroanthracenyl (marked with green boxes) were detected. The resonances marked with a * belong to 9,10-dihydroanthracene. The resonances marked with a ° belong to 3-hexyne. The resonances marked with a # belong to bibenzyl.

Reaction of $i\text{PrPDATi}(\text{CH}_2\text{Ph})_2$ with 3-hexyne and 1,4-cyclohexadiene

$i\text{PrPDATi}(\text{CH}_2\text{Ph})_2$ (10.3 mg, 15.0 μmol , 1.00 equiv.), cyclohexa-1,4-diene (6.00 mg, 74.8 μmol , 4.98 equiv.) and 3-hexyne (12.0 mg, 146 μmol , 10.0 equiv.) were dissolved in benzene- d_6 (0.5 mL). The reaction mixture was monitored for three days. The formation of $i\text{PrPDATi}(\text{C}_4\text{Et}_4)$ and bibenzyl was observed and no formation of toluene or benzene was detected.

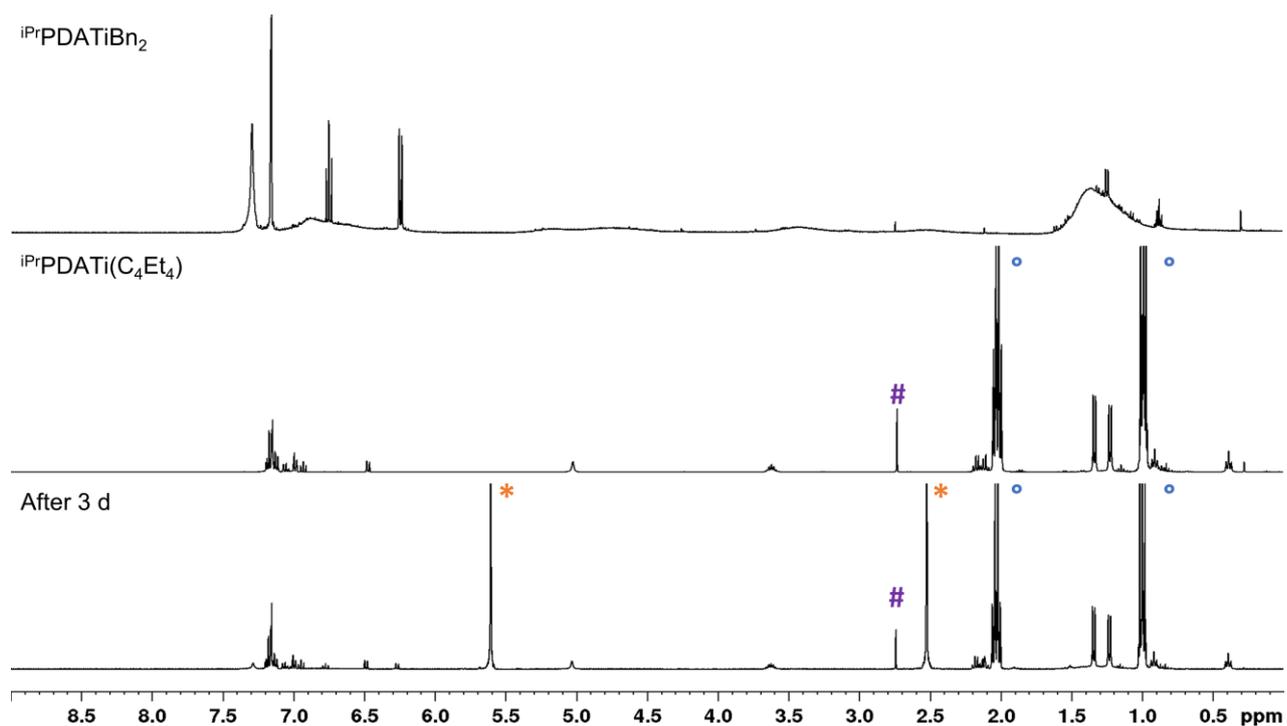


Figure S9. ¹H NMR spectrum of the reaction between *i*PrPDATi(CH₂Ph)₂, 3-hexyne and cyclohexa-1,4-diene in benzene-*d*₆ after three days compared to the spectra of *i*PrPDATiBn₂ and *i*PrPDATi(C₄Et₄), illustrating the formation of *i*PrPDATi(C₄Et₄) and bibenzyl. No formation of benzene was detected. The resonances marked with a * belong to 1,4-cyclohexadiene. The resonances marked with a ° belong to 3-hexyne. The resonances marked with a # belong to bibenzyl.

General procedure for thermolysis reactions of PDATi(CH₂Ph)₂

PDATiBn₂ (15.0 μmol, 1.00 equiv.) was dissolved in benzene-*d*₆ (0.5 mL). The reaction mixture was heated in a metal heating block (60 or 80 °C) and monitored by NMR spectroscopy (see Figure S10, Figure S11 and Figure S12).

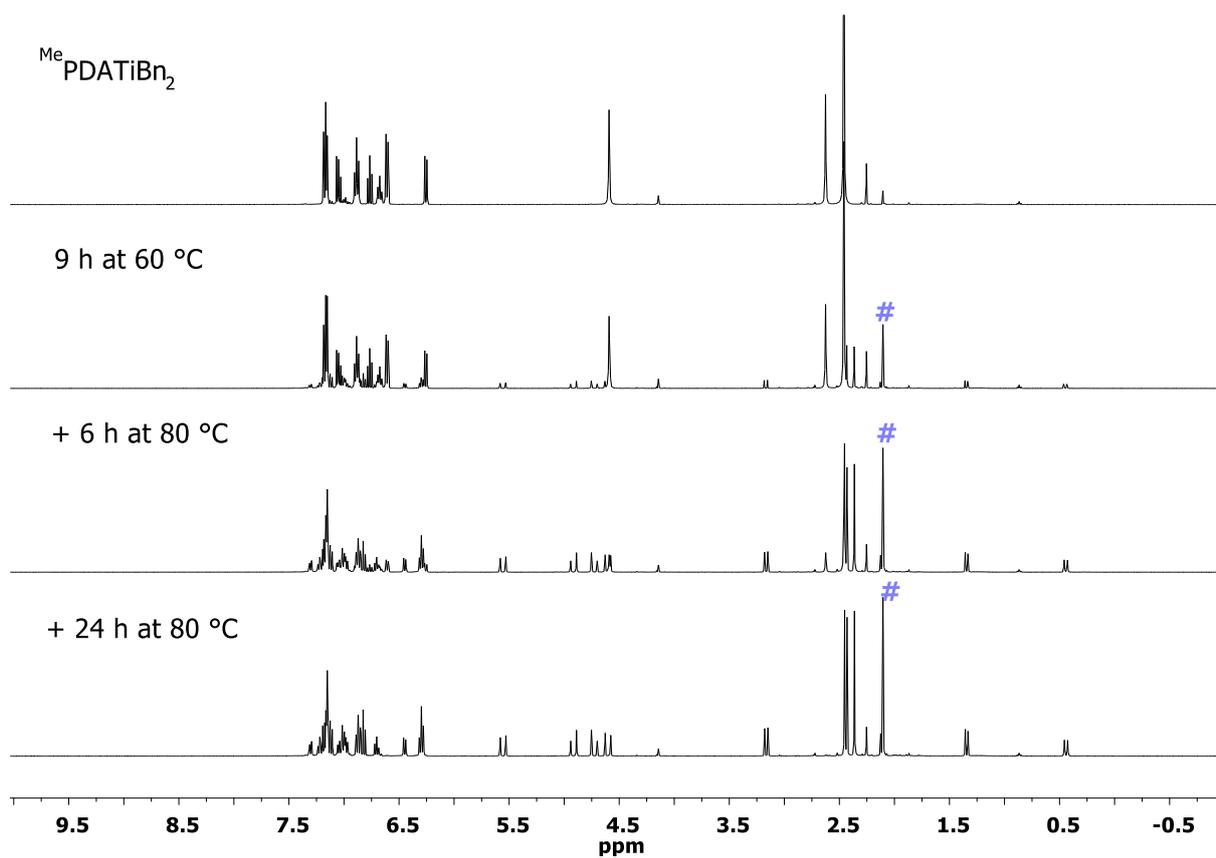


Figure S10. ^1H NMR spectrum of the thermolysis reaction of $^{\text{Me}}\text{PDA Ti(CH}_2\text{Ph)}_2$ in benzene- d_6 . The resonances marked with a # belong to toluene. No bibenzyl was detected.

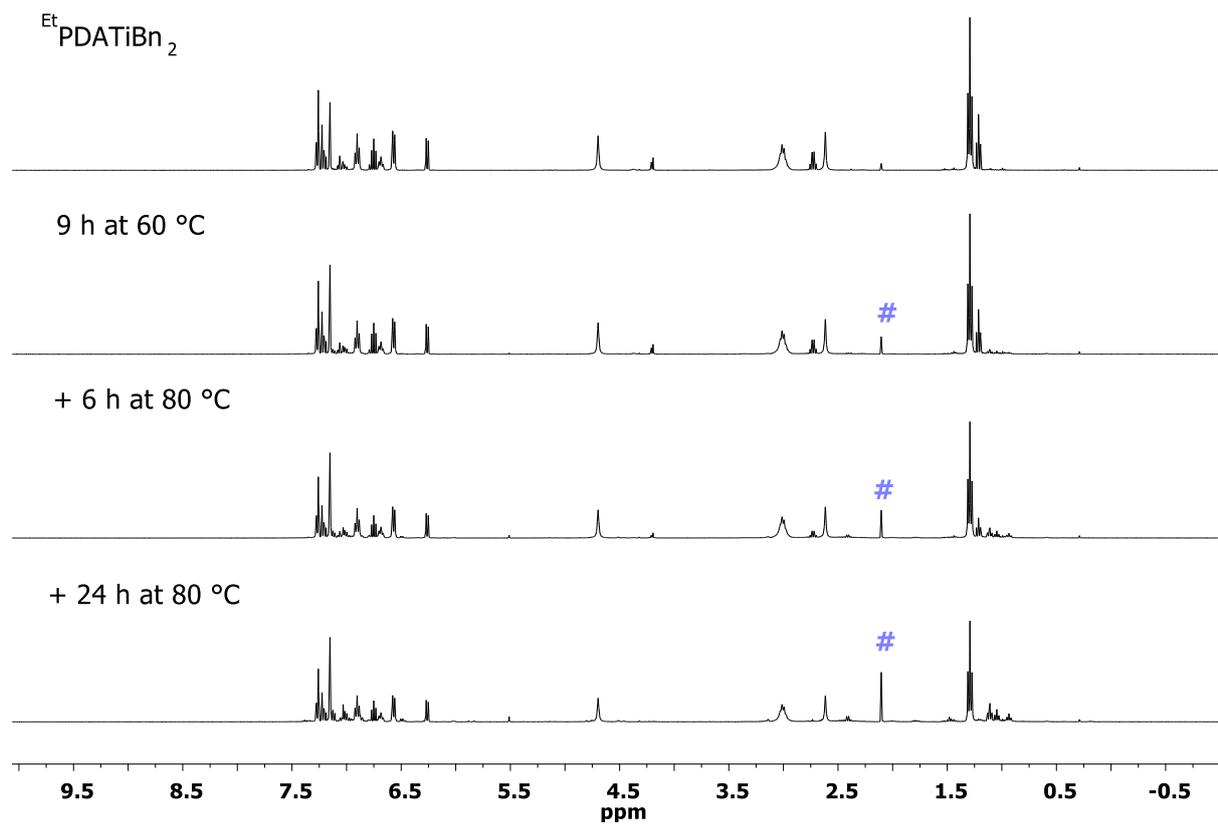


Figure S11. ^1H NMR spectrum of the thermolysis reaction of $\text{EtPDATi}(\text{CH}_2\text{Ph})_2$ in benzene- d_6 . The resonances marked with a # belong to toluene. No bibenzyl was detected.

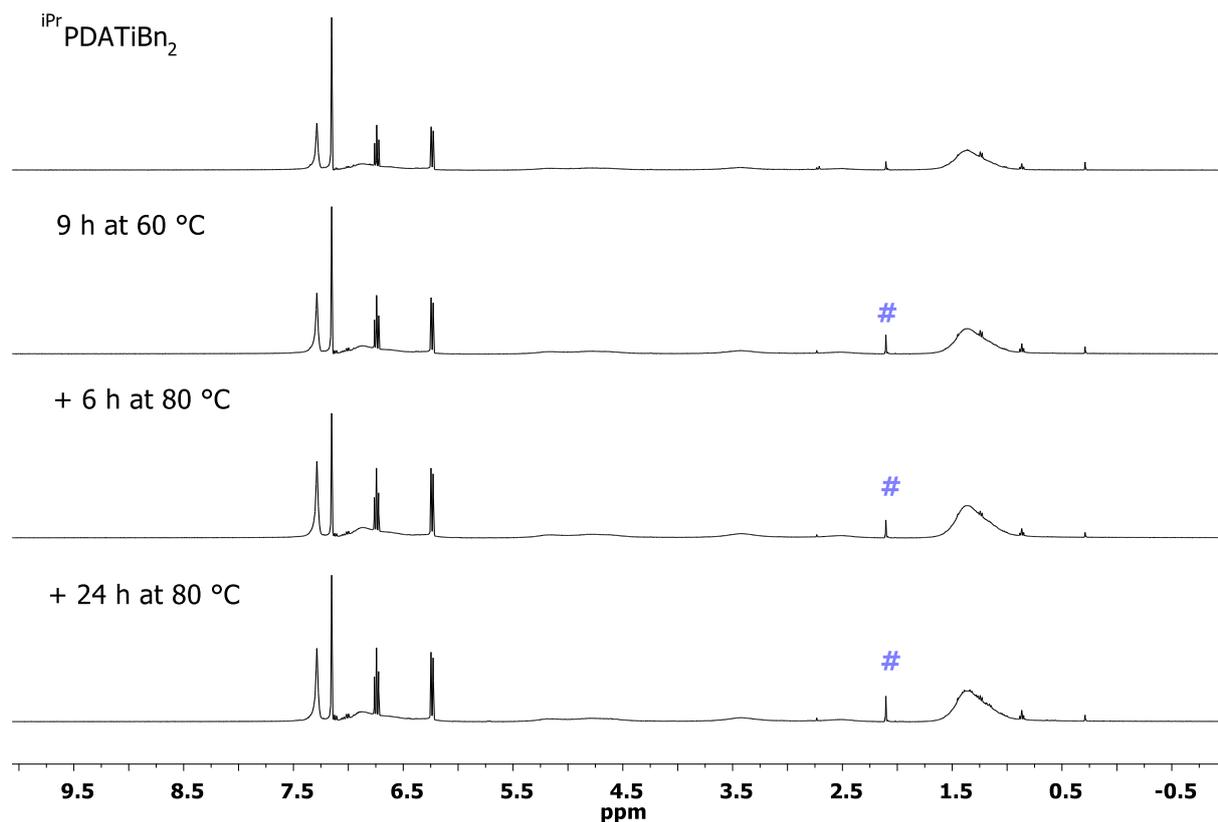


Figure S12. ¹H NMR spectrum of the thermolysis reaction of ⁱPrPDATi(CH₂Ph)₂ in benzene-*d*₆. The resonances marked with a # belong to toluene. No bibenzyl was detected.

General procedure for rate comparison in reductive elimination reactions of PDATi(CH₂Ph)₂

PDATiBn₂ (10.0 μmol, 1.00 equiv.) was dissolved in a stock solution of 3-hexyne and HMDSO in benzene-*d*₆ (0.7 mL, *c*^{HMDSO} = 1.11 mmol·L⁻¹, *c*^{hexyne} = 0.03 mol·L⁻¹). The reaction mixture was monitored by quantitative ¹H NMR spectroscopy (see Figure S13,

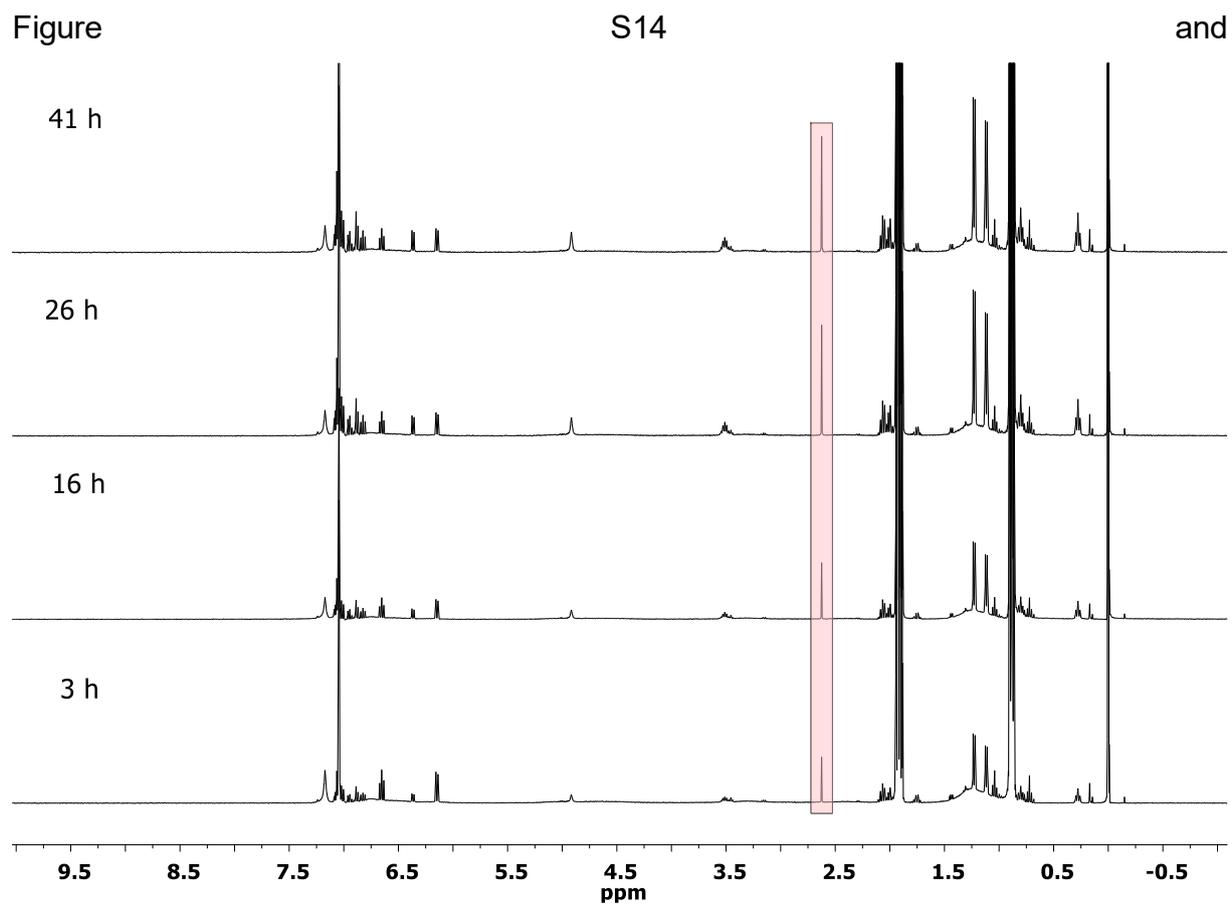


Figure S15).

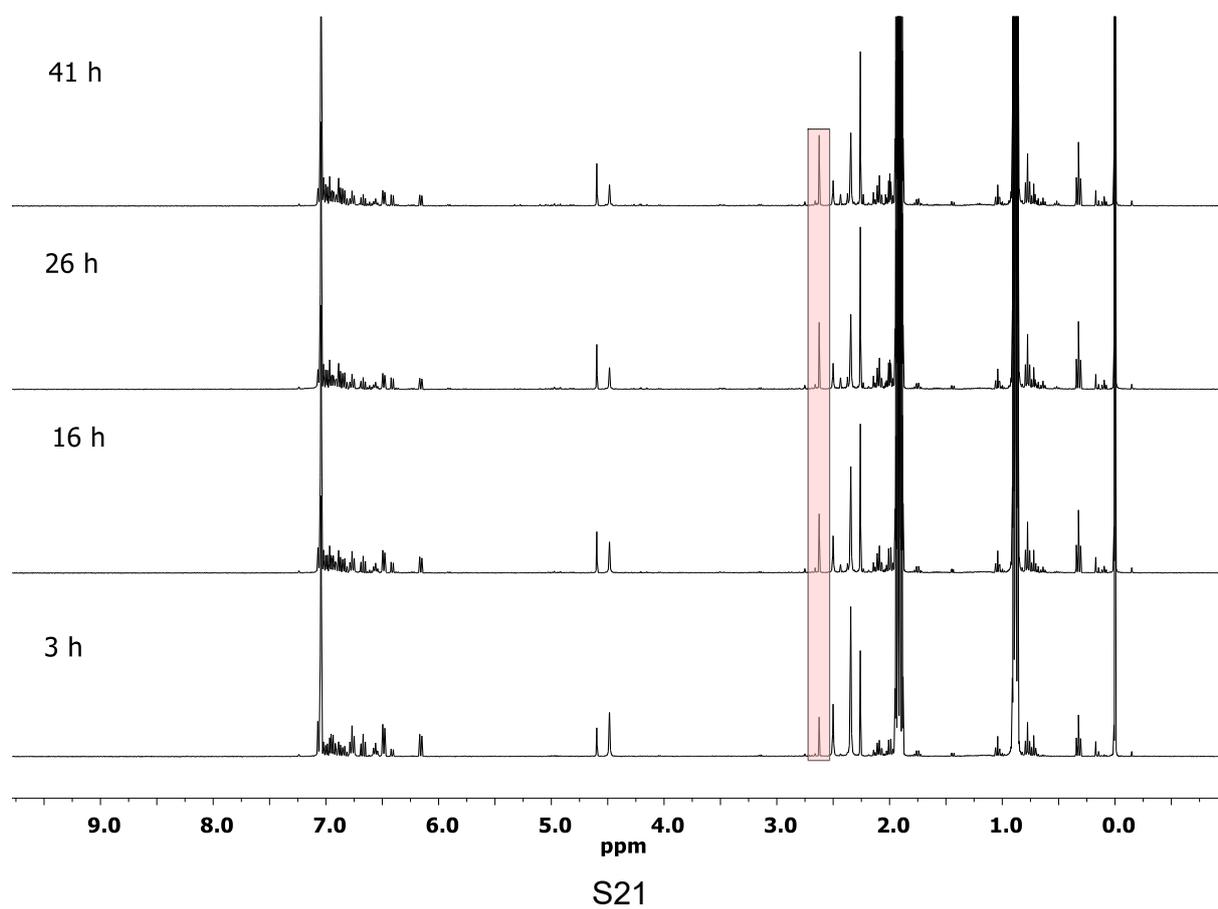


Figure S13. ^1H NMR spectrum of the reaction of $^{\text{Me}}\text{PDATi}(\text{CH}_2\text{Ph})_2$ with 3-hexyne (20 equiv.) with HMDSO as internal standard in benzene- d_6 . The resonances marked belong to bibenzyl.

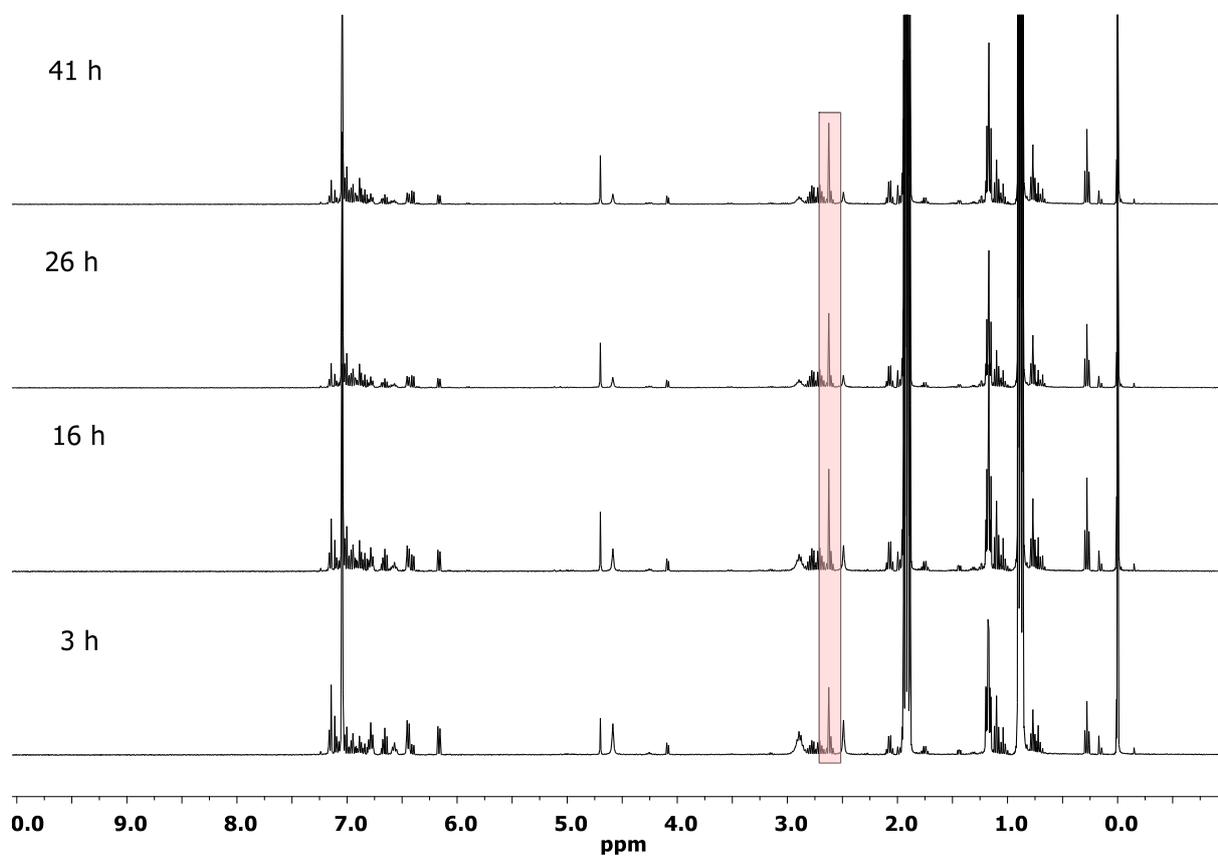


Figure S14. ^1H NMR spectrum of the reaction of $^{\text{Et}}\text{PDATi}(\text{CH}_2\text{Ph})_2$ with 3-hexyne (20 equiv.) with HMDSO as internal standard in benzene- d_6 . The resonances marked belong to bibenzyl.

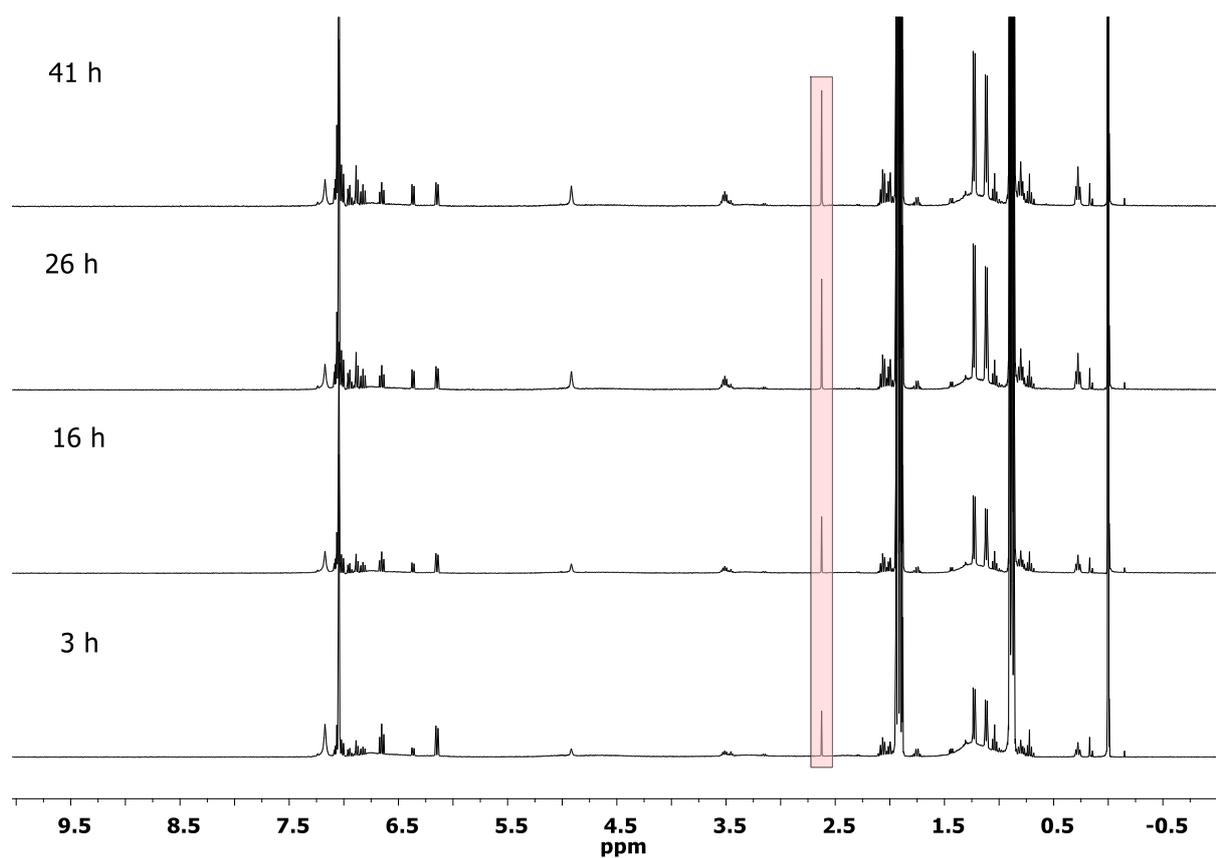


Figure S15. ¹H NMR spectrum of the reaction of $i^{\text{Pr}}\text{PDATi}(\text{CH}_2\text{Ph})_2$ with 3-hexyne (20 equiv.) with HMDSO as internal standard in benzene- d_6 . The resonances marked belong to bibenzyl.

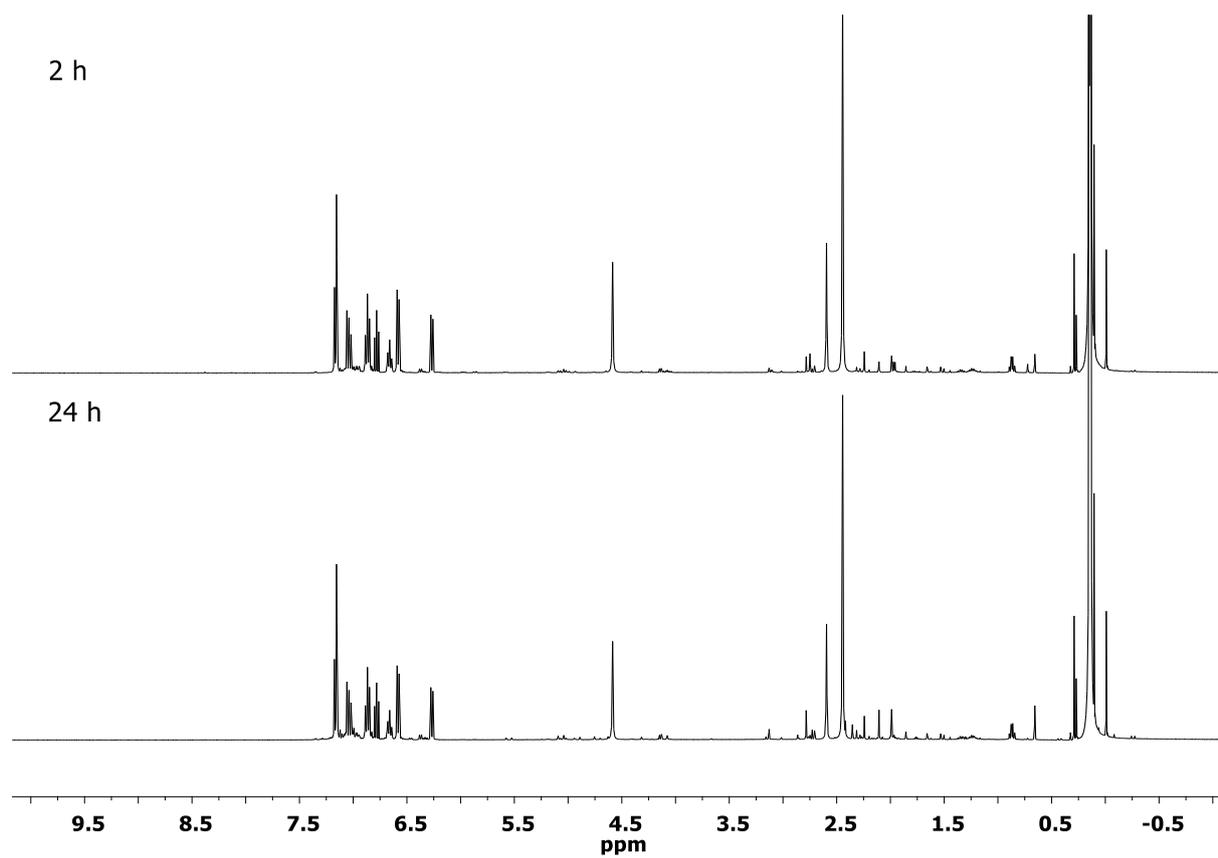
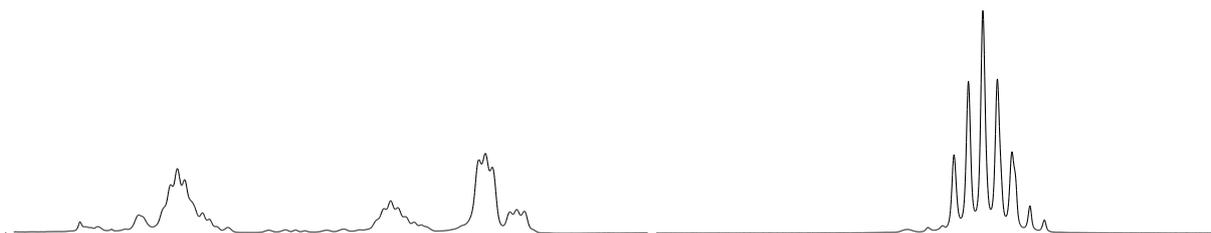


Figure S16. ^1H NMR spectrum of the reaction of $^{\text{Me}}\text{PDATi}(\text{CH}_2\text{Ph})_2$ with bis(trimethylsilyl)acetylene (20 equiv.).

reaction with toluene- d_8 capillary



reaction without capillary

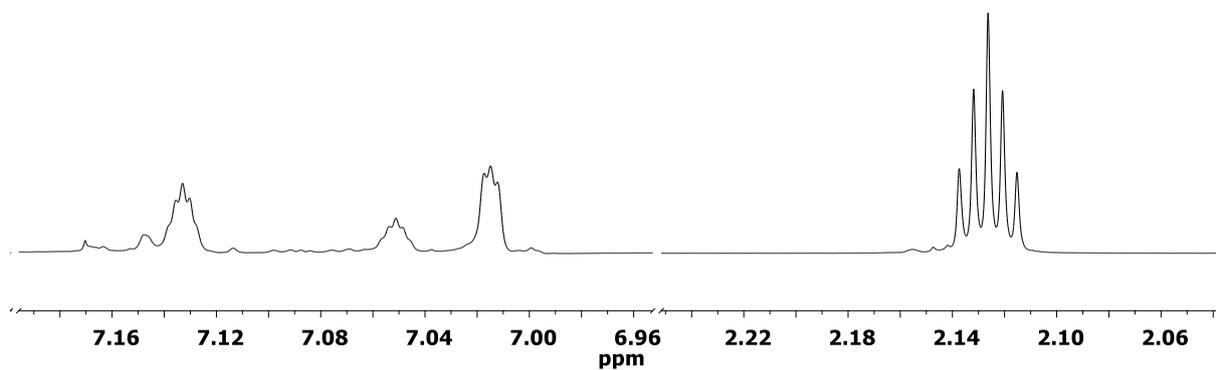


Figure S17. ^1H NMR spectrum of the reaction of $^i\text{PrPDATi}(\text{CH}_2\text{Ph})_2$ with 2-butyne (20 equiv.) in toluene- d_6 with and without an additional toluene- d_8 capillary. Only the solvent resonances are shown.

4. NMR spectra of isolated compounds

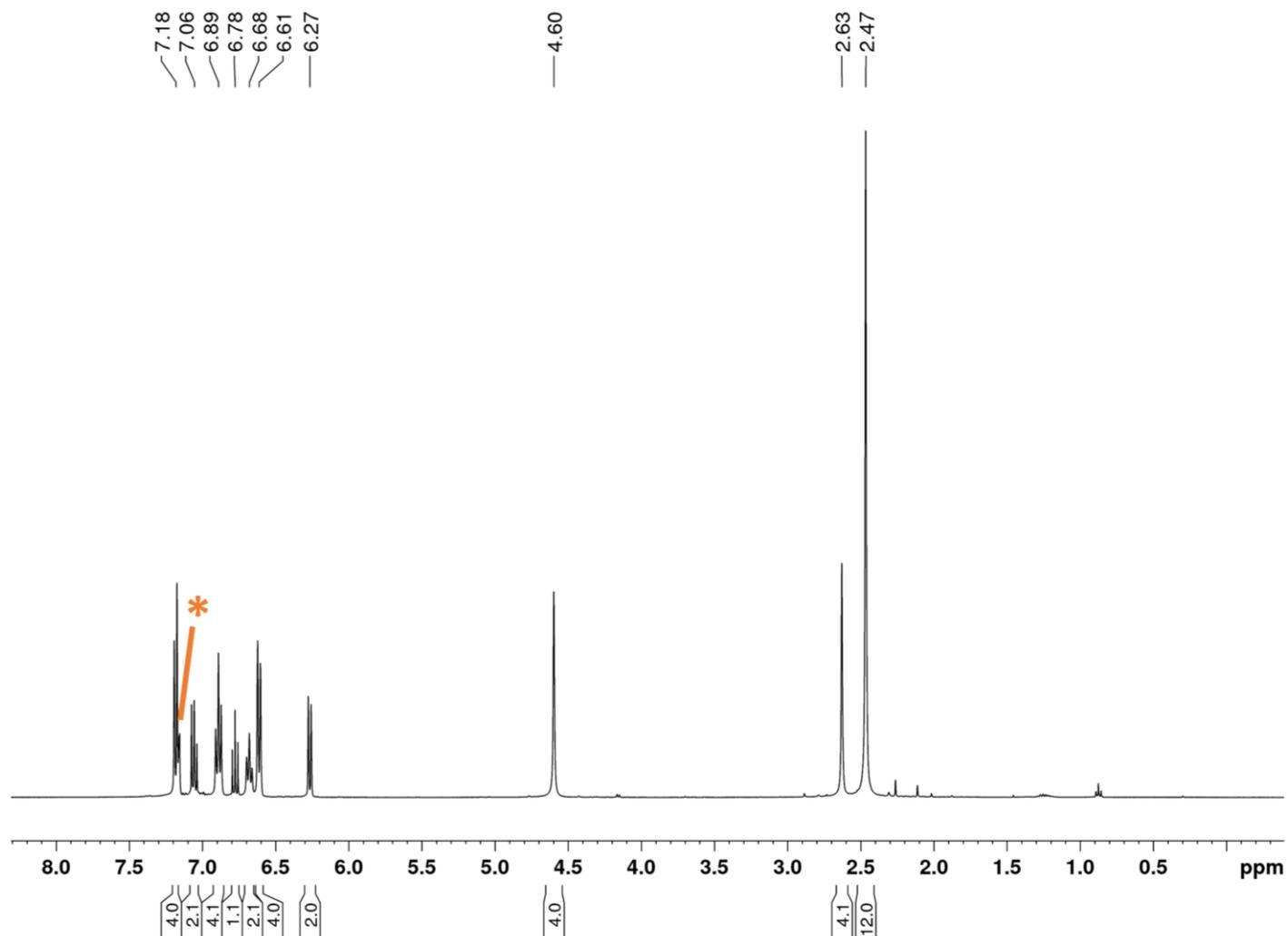


Figure S18. ^1H NMR spectrum of $\text{MePDATi}(\text{CH}_2\text{Ph})_2$ in benzene- d_6 at 300 K. The resonance marked with a * belongs to benzene- d_6 .

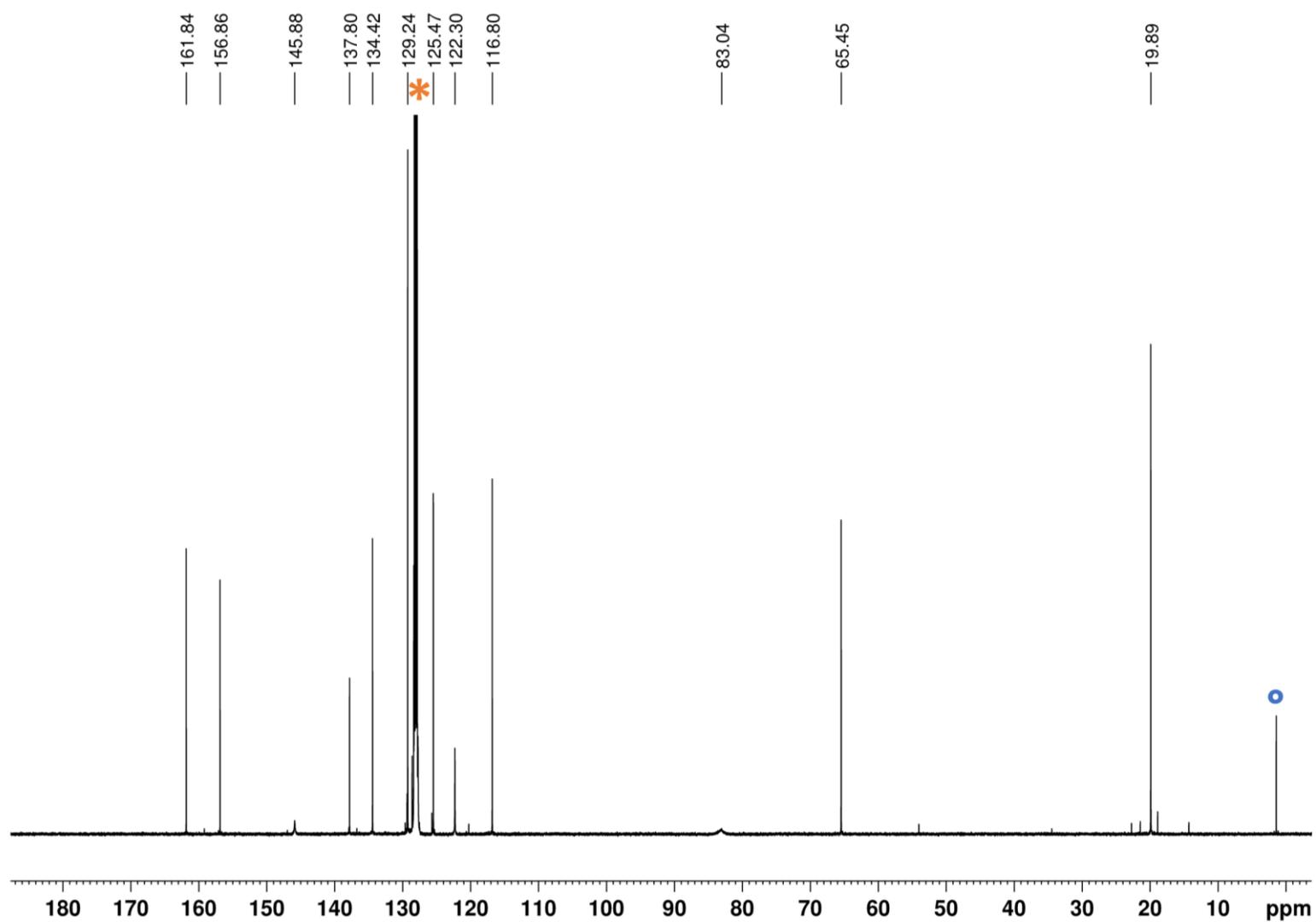


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{MePDATi}(\text{CH}_2\text{Ph})_2$ in benzene- d_6 at 300 K. The resonance marked with a * belongs to benzene- d_6 . The resonance marked with a ° belongs to silicon grease.

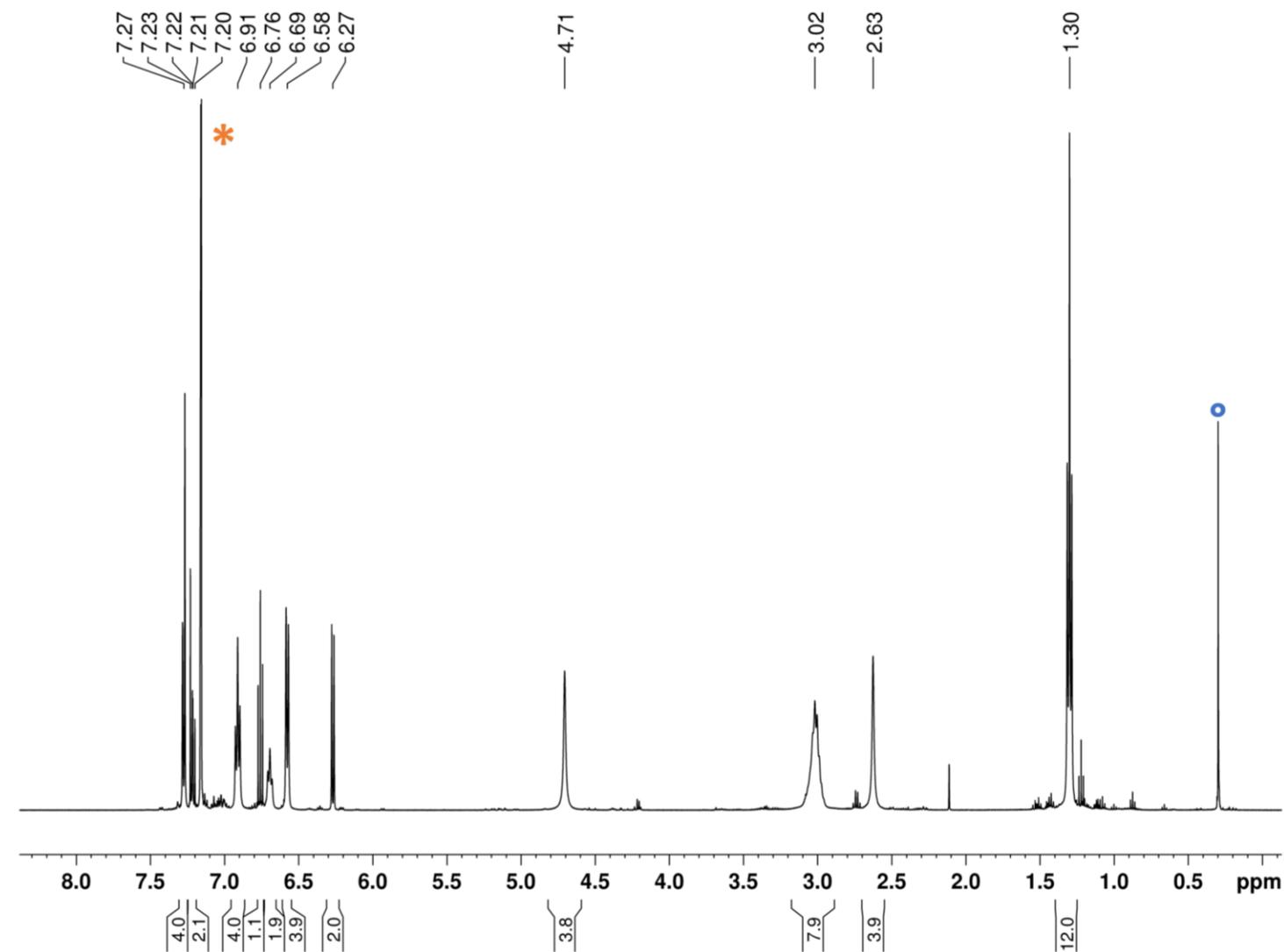


Figure S20. ^1H NMR spectrum of $\text{EtPDATi}(\text{CH}_2\text{Ph})_2$ in benzene- d_6 at 300 K. The resonance marked with a * belongs to benzene- d_6 . The resonance marked with a \circ belongs to silicon grease.

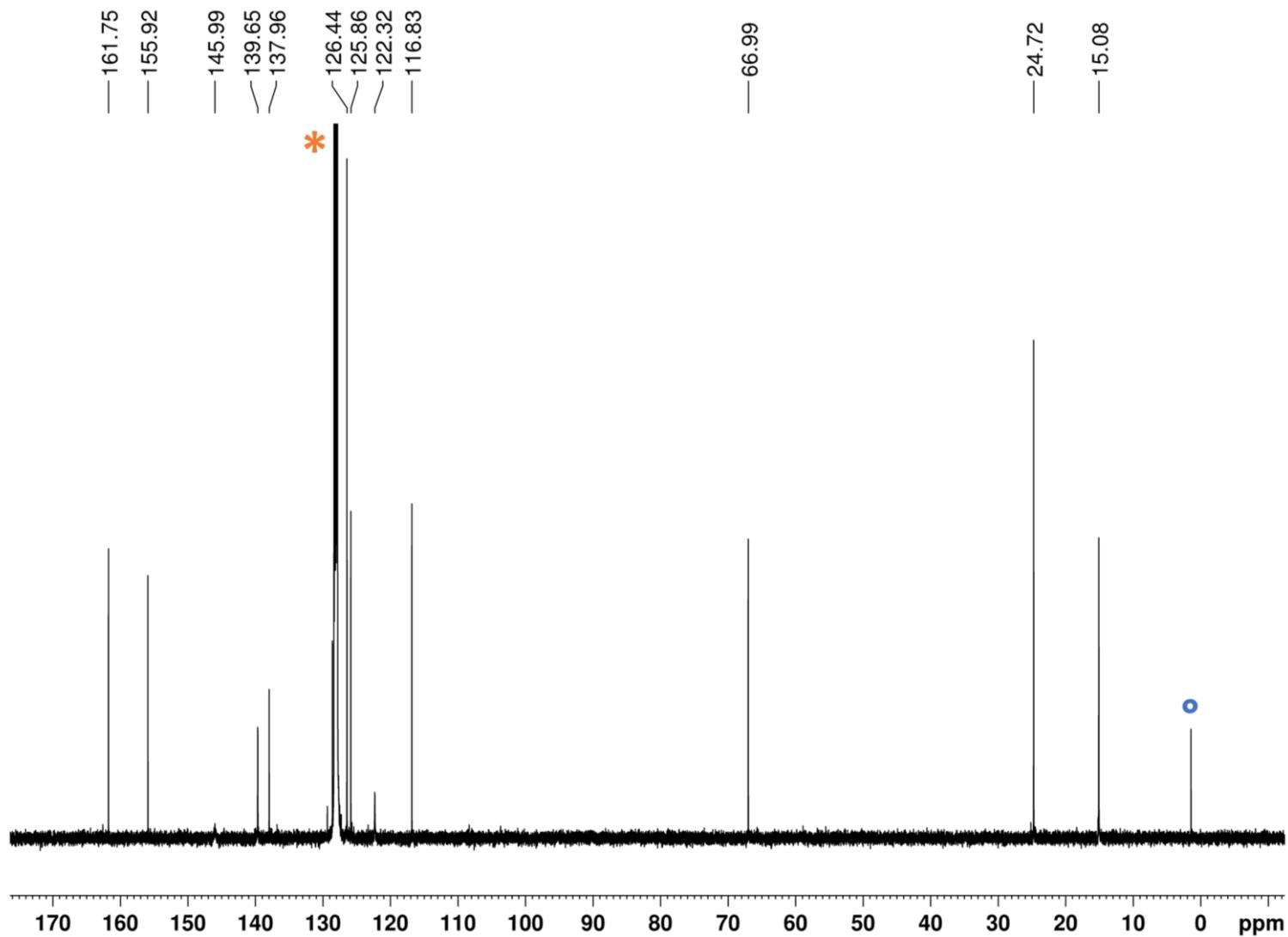


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{EtPDATi}(\text{CH}_2\text{Ph})_2$ in benzene- d_6 at 300 K. The resonance marked with a * belongs to benzene- d_6 . The resonance marked with a \circ belongs to silicon grease.

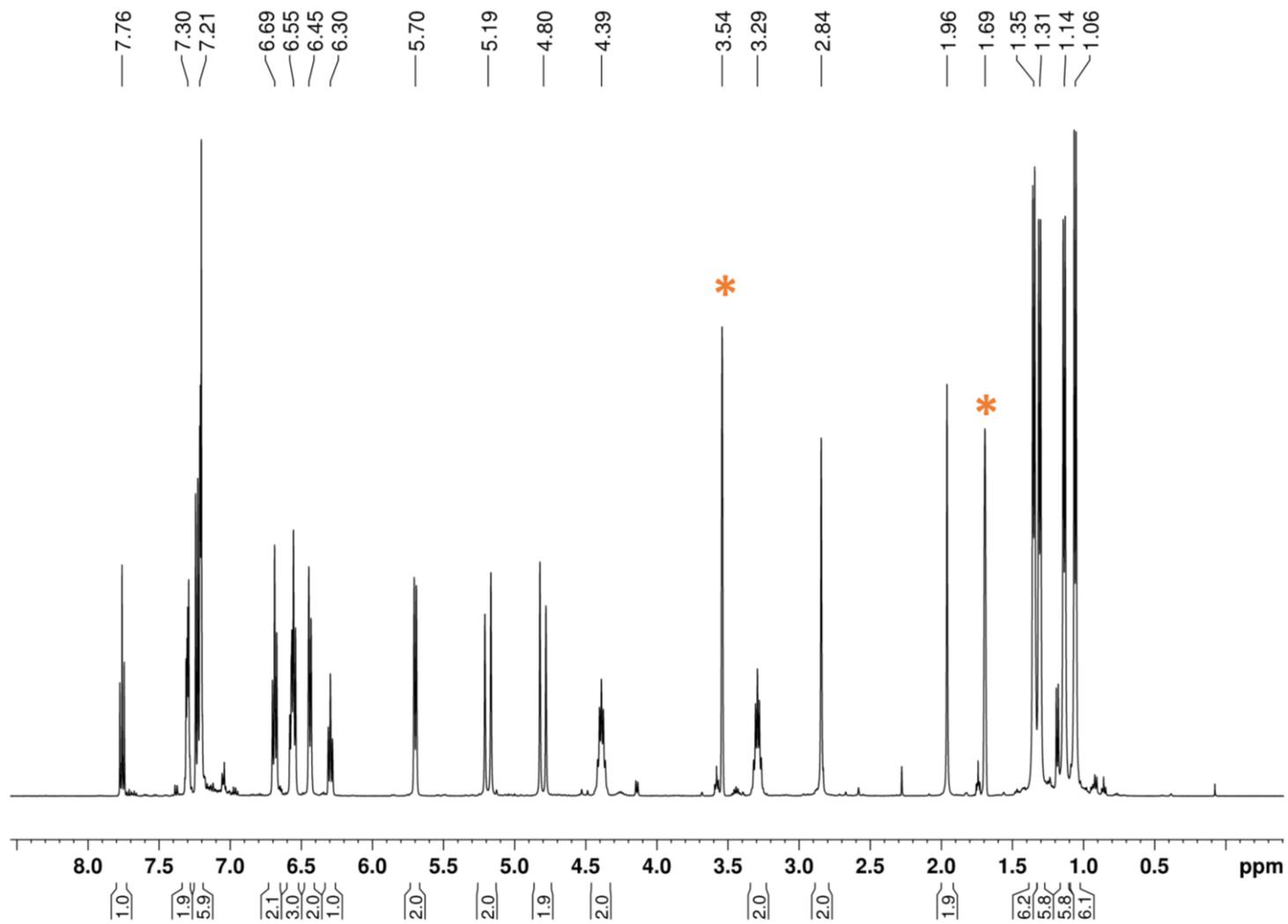


Figure S22. ^1H NMR spectrum of $i\text{PrPDATi}(\text{CH}_2\text{Ph})_2$ in $\text{thf-}d_8$ at 233 K. The resonances marked with a * belong to $\text{thf-}d_8$.

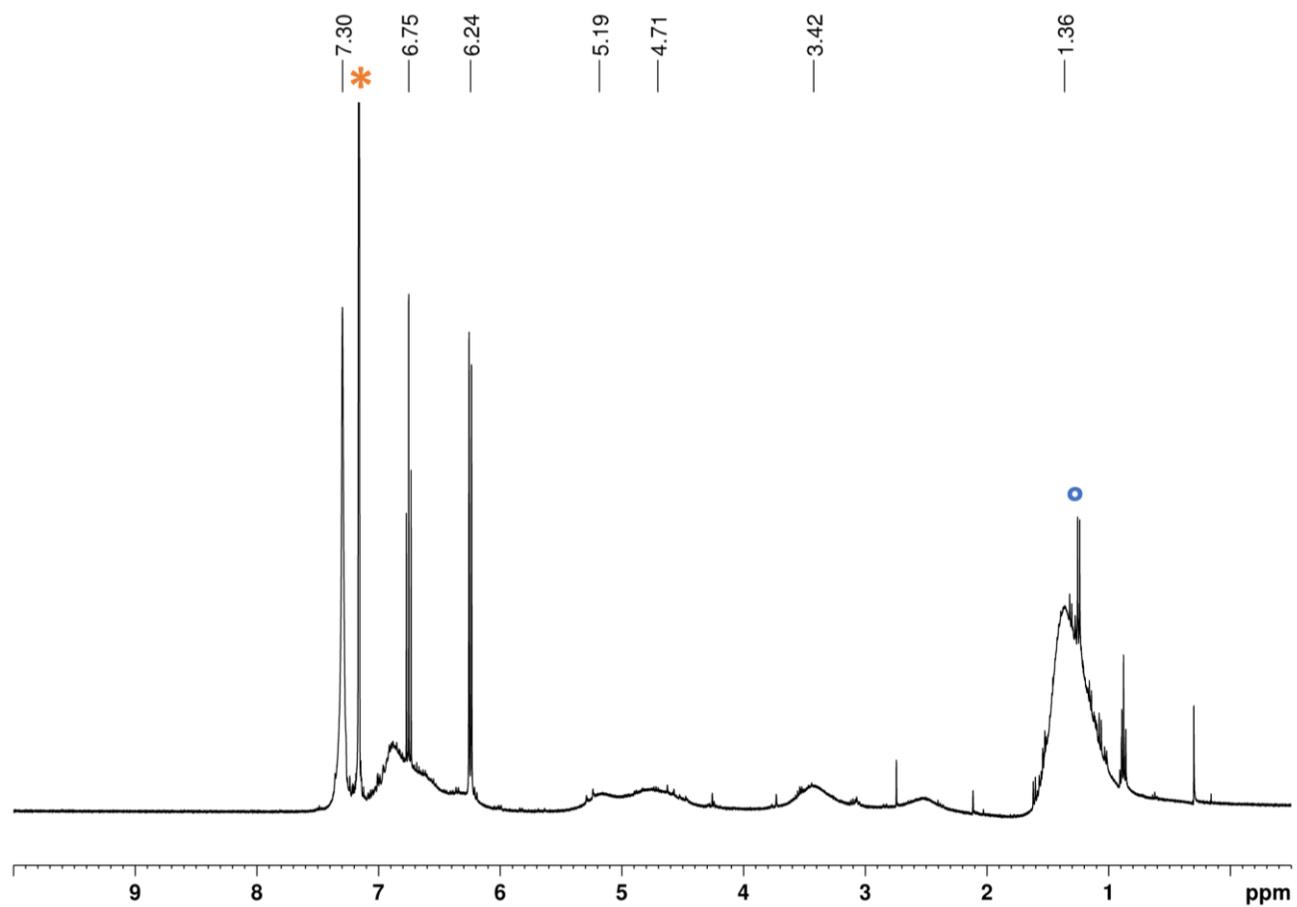


Figure S23. ^1H NMR spectrum of $i\text{PrPDATi}(\text{CH}_2\text{Ph})_2$ in benzene- d_6 at 300 K. The resonance marked with a * belongs to benzene- d_6 . The resonance marked with a \circ belong to free $i\text{PrPDA-H}_2$.

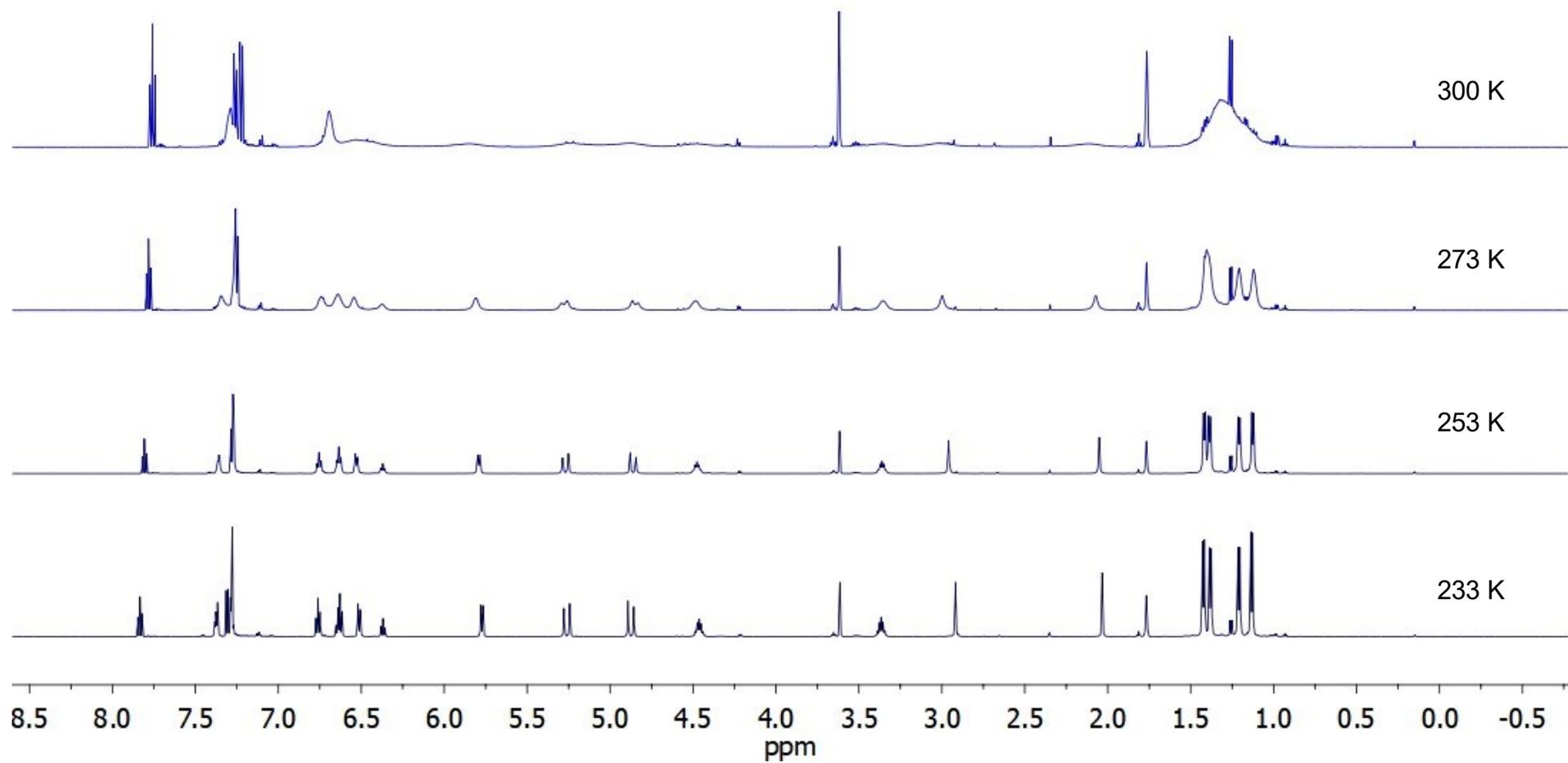


Figure S24. ^1H NMR spectra of $i\text{PrPDATi}(\text{CH}_2\text{Ph})_2$ in $\text{thf-}d_8$ at variable temperatures.

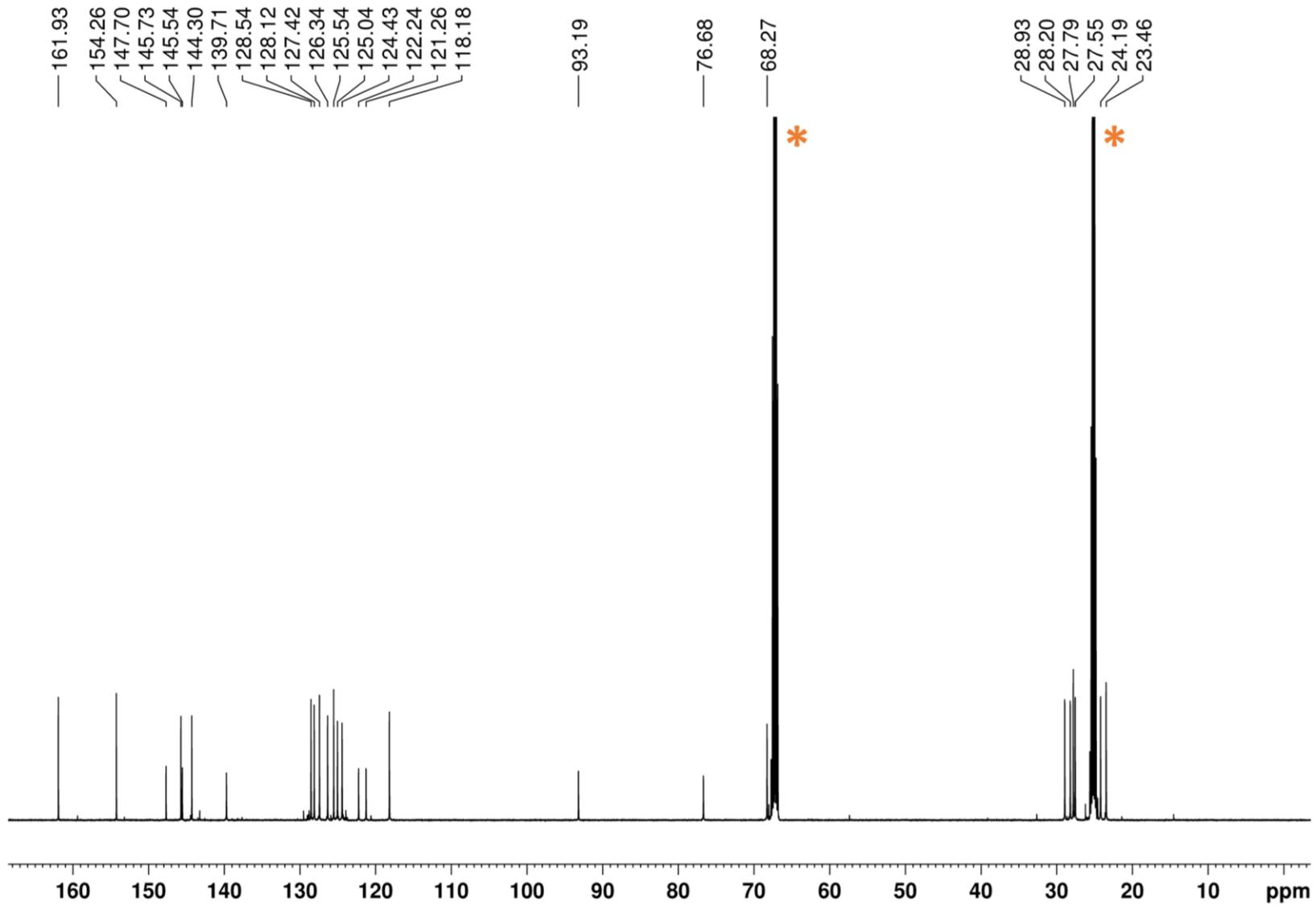


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $i\text{PrPDATi}(\text{CH}_2\text{Ph})_2$ in $\text{thf-}d_8$ at 233 K. The resonances marked with a * belong to $\text{thf-}d_8$.

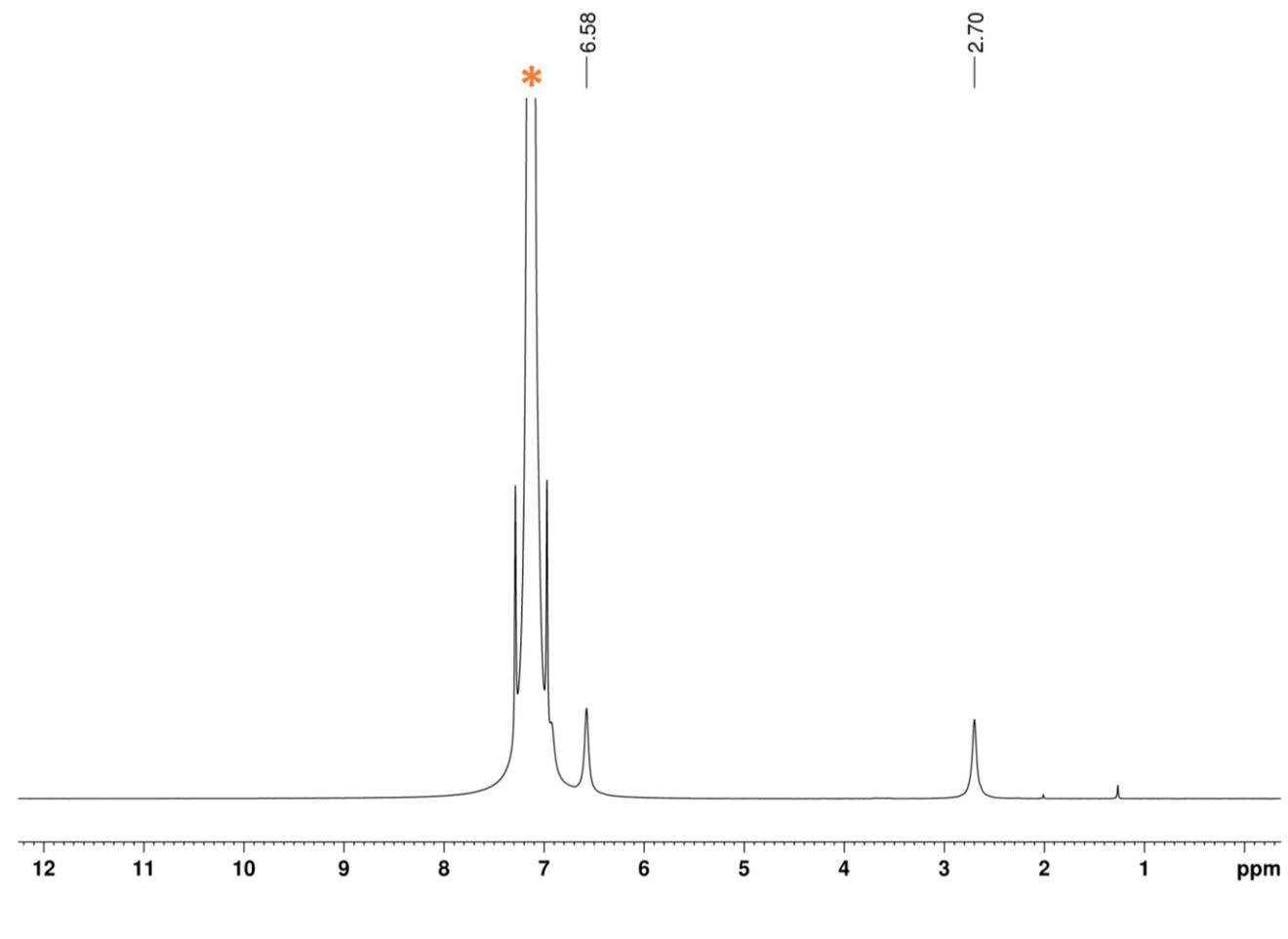


Figure S26. ^1H NMR spectrum of $\text{Ti}(\text{CD}_2\text{Ph-}d_5)_4$ in benzene- d_6 at 300 K. The resonance marked with a * belongs to benzene- d_6 .

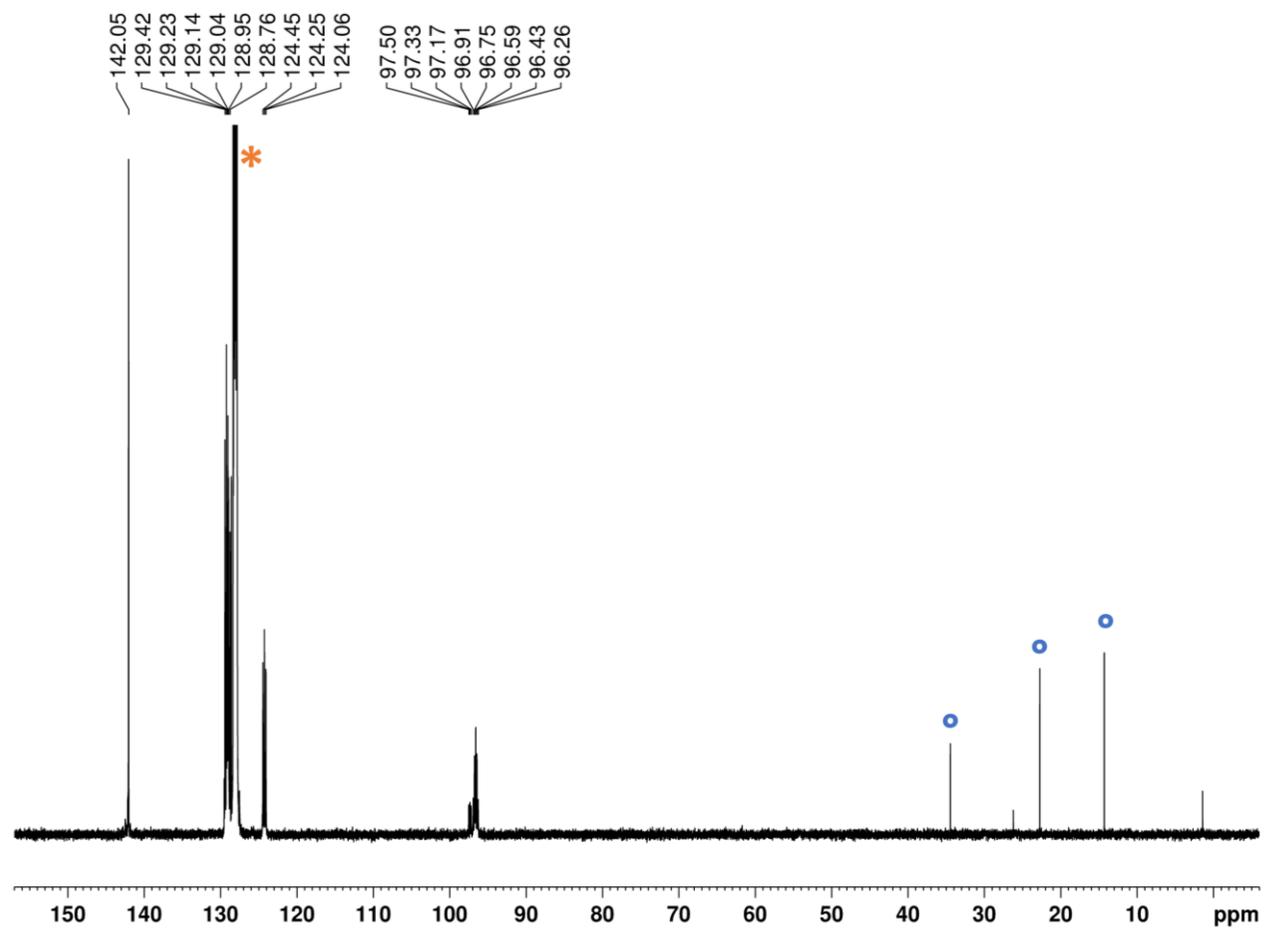


Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ti}(\text{CD}_2\text{Ph-}d_5)_4$ in benzene- d_6 at 300 K. The resonance marked with a * belongs to benzene- d_6 . The resonances marked with a ° belong to *n*-pentane.

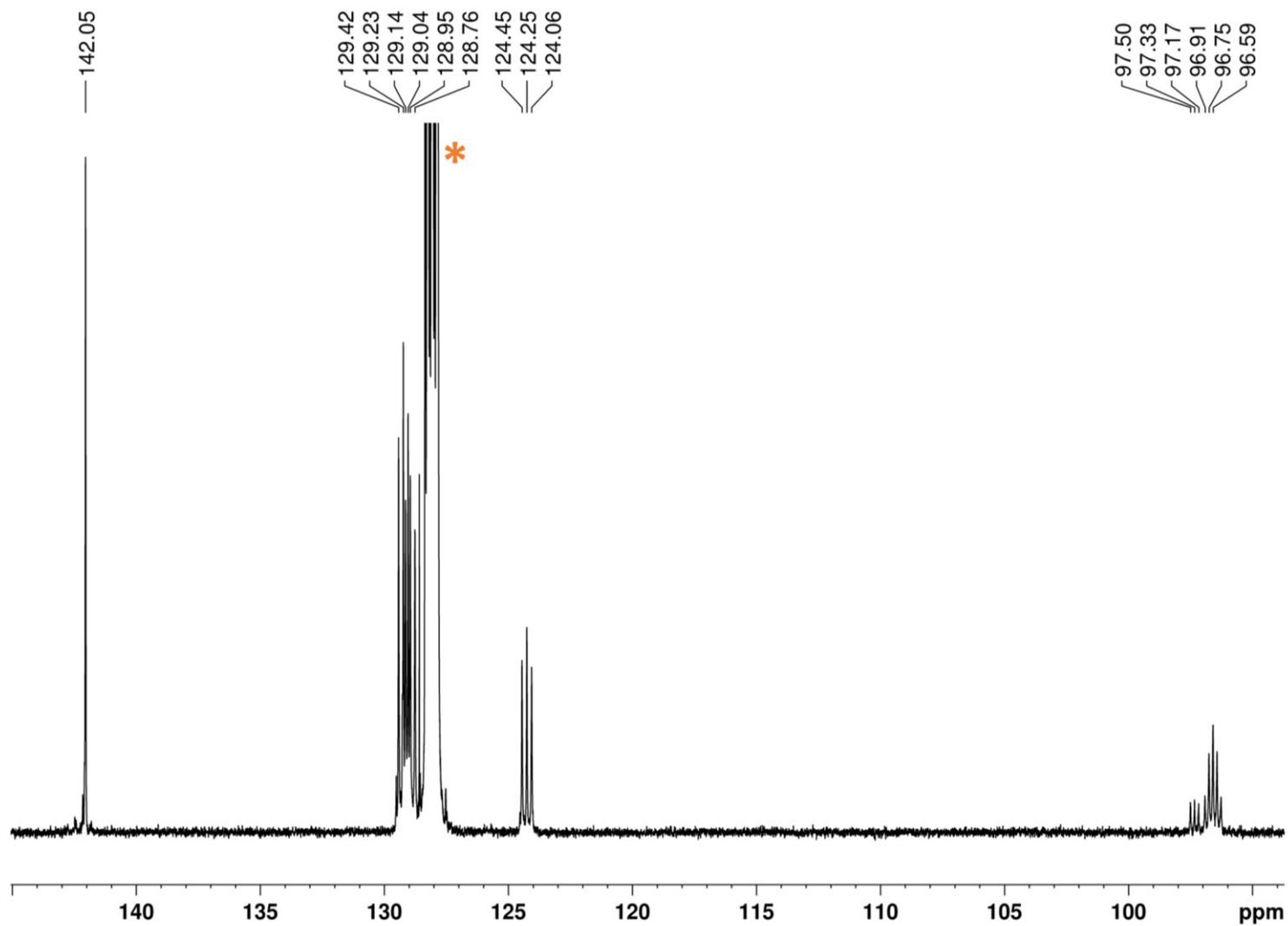


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ti}(\text{CD}_2\text{Ph-}d_5)_4$ in benzene- d_6 at 300 K. Relevant area (150-90 ppm) enlarged. The resonance marked with a * belongs to benzene- d_6 .

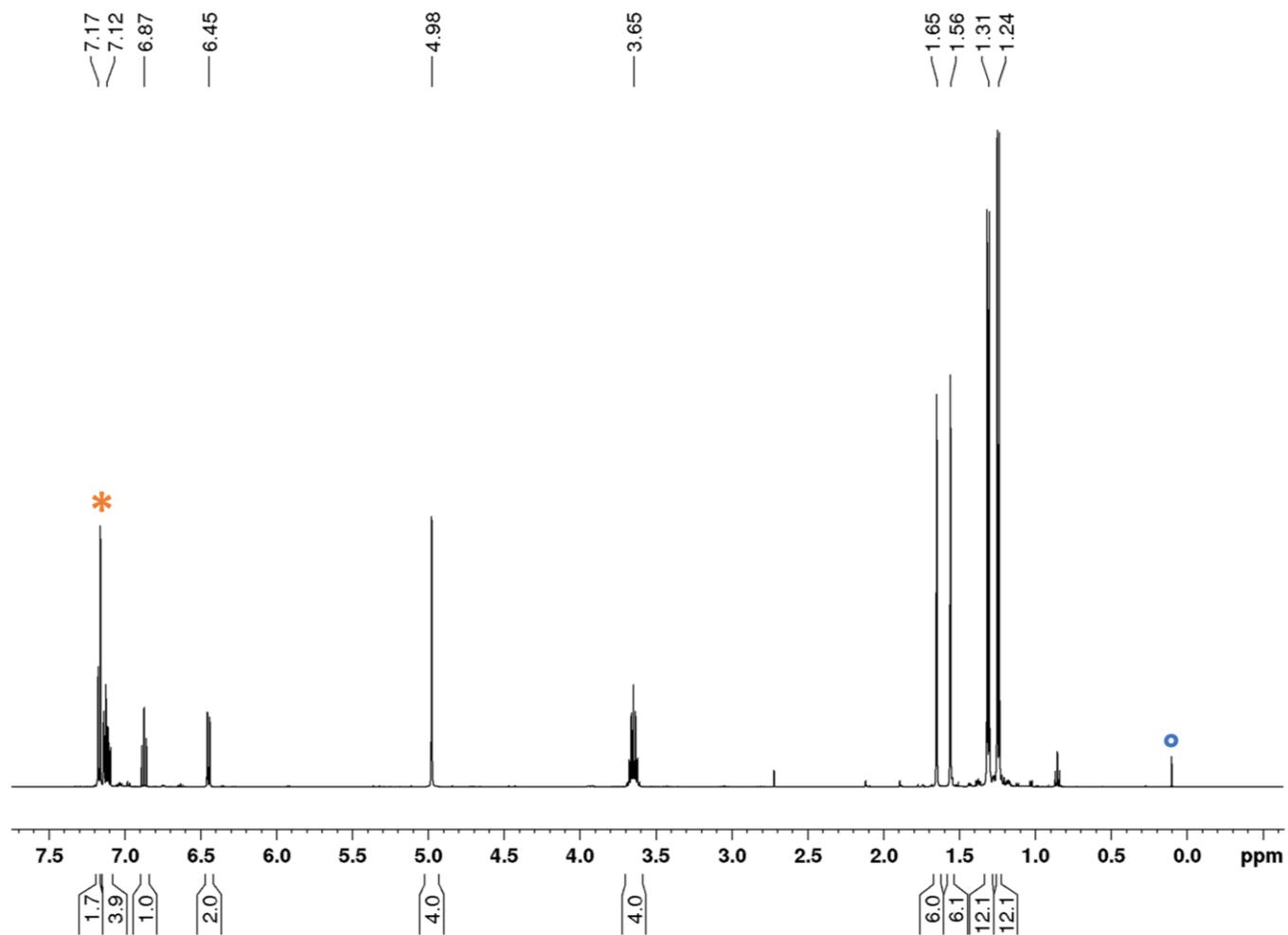


Figure S29. ^1H NMR spectrum of $i\text{PrPDATi}(\text{C}_4\text{Me}_4)$ in benzene- d_6 at 300 K. The resonance marked with a * belongs to benzene- d_6 . The resonance marked with a \circ belongs to silicon grease.

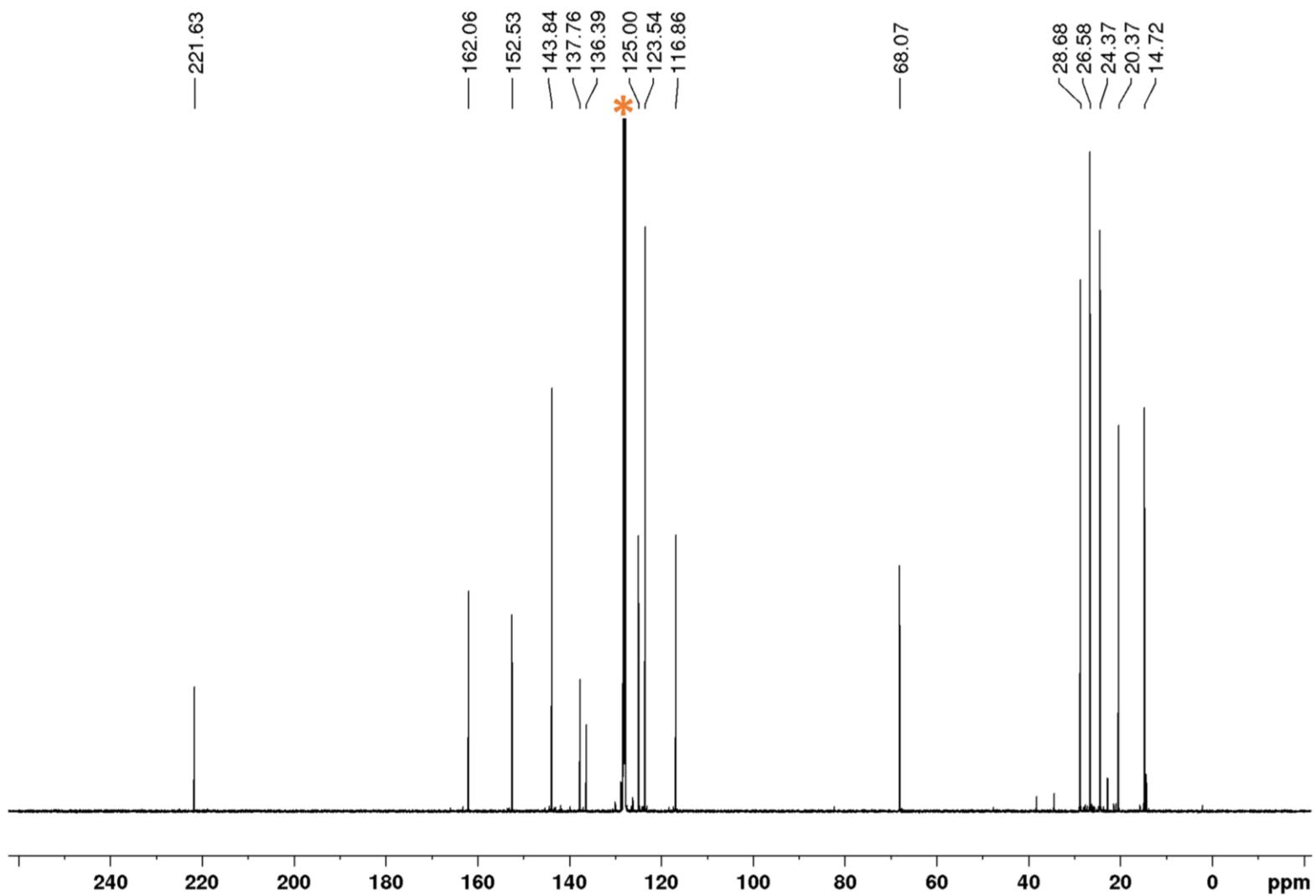


Figure S30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $i\text{PrPDATi}(\text{C}_4\text{Me}_4)$ in benzene- d_6 . The resonance marked with a * belongs to benzene- d_6 .

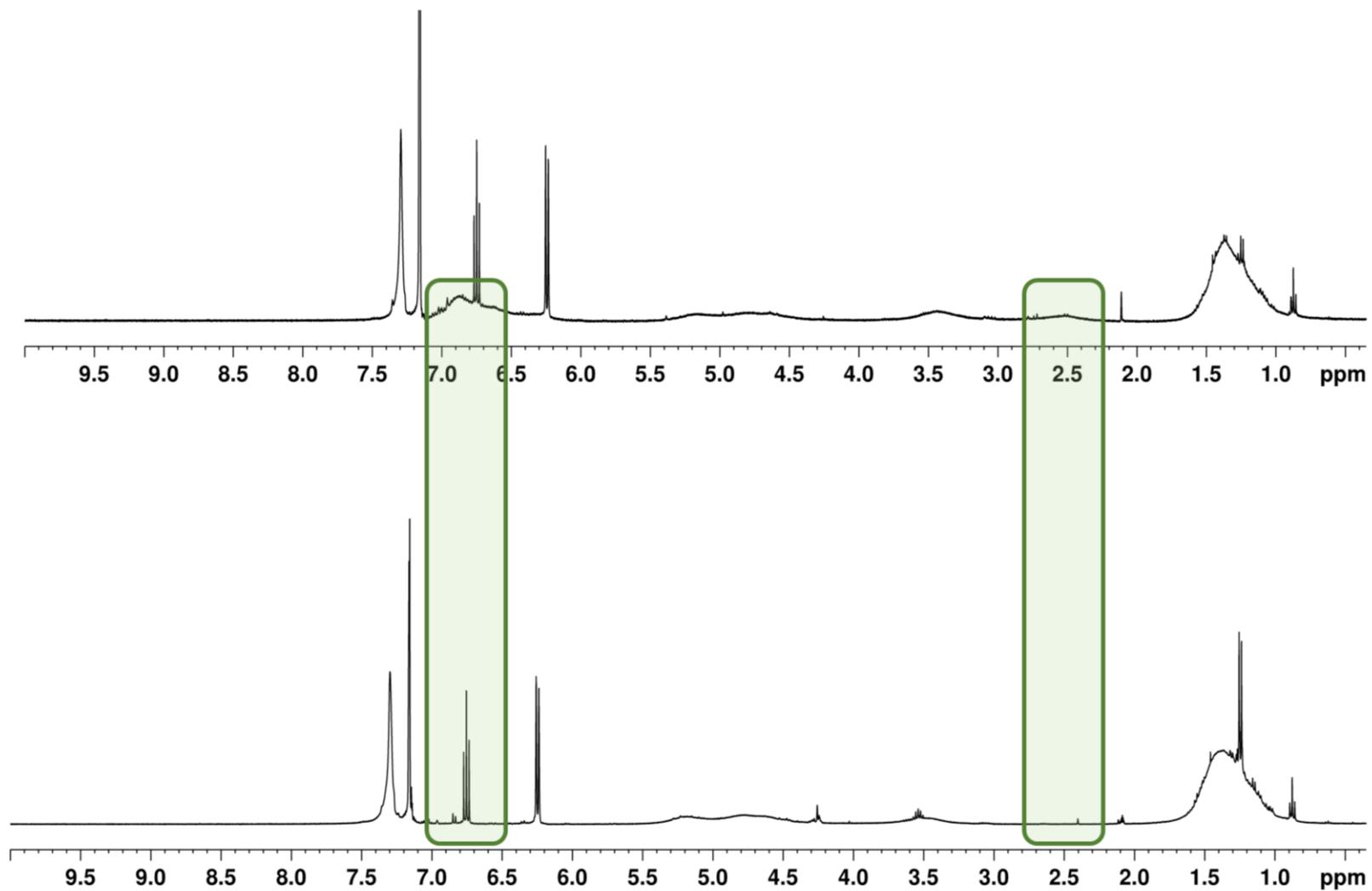


Figure S31. ^1H NMR spectra of $i\text{PrPDA-TiBn}_2$ (top) and $i\text{PrPDA-Ti}(\text{CD}_2\text{Ph-}d_5)_2$ (bottom) in benzene- d_6 . The green boxes illustrate the absence of benzylic protons in $i\text{PrPDA-Ti}(\text{CD}_2\text{Ph-}d_5)_2$ compared to $i\text{PrPDA-TiBn}_2$.

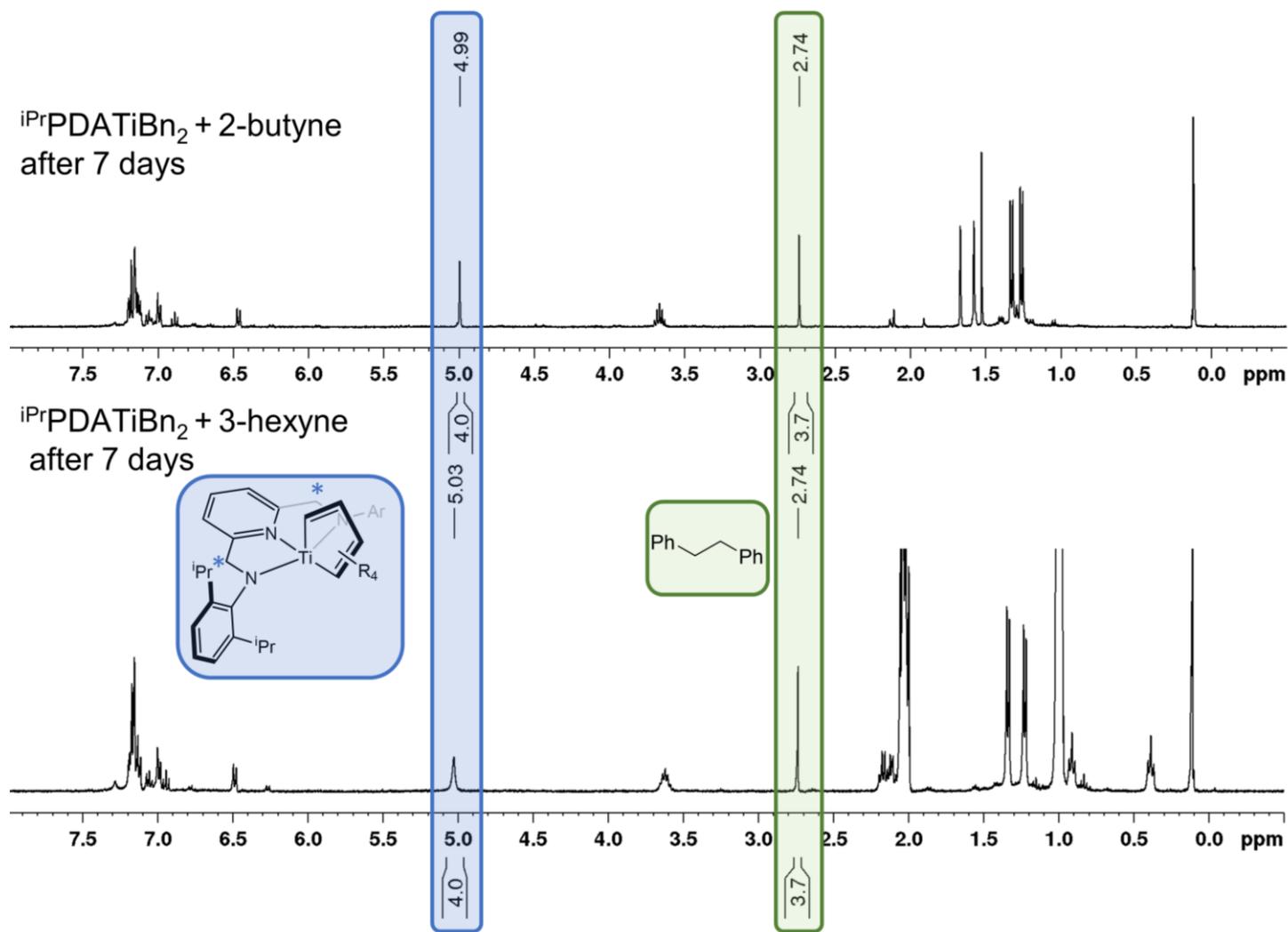


Figure S32. ^1H NMR spectra (single scan) of the reactions of $i\text{PrPDA-Ti}(\text{CH}_2\text{Ph})_2$ with 2-butyne (top) and 3-hexyne (bottom) in benzene- d_6 after 7 days. The green box shows the formation of bibenzyl in nearly stoichiometric amounts compared to the distinct signals of the products $i\text{PrPDA-Ti}(\text{C}_4\text{R}_4)$ (R = Me, Et, blue box).

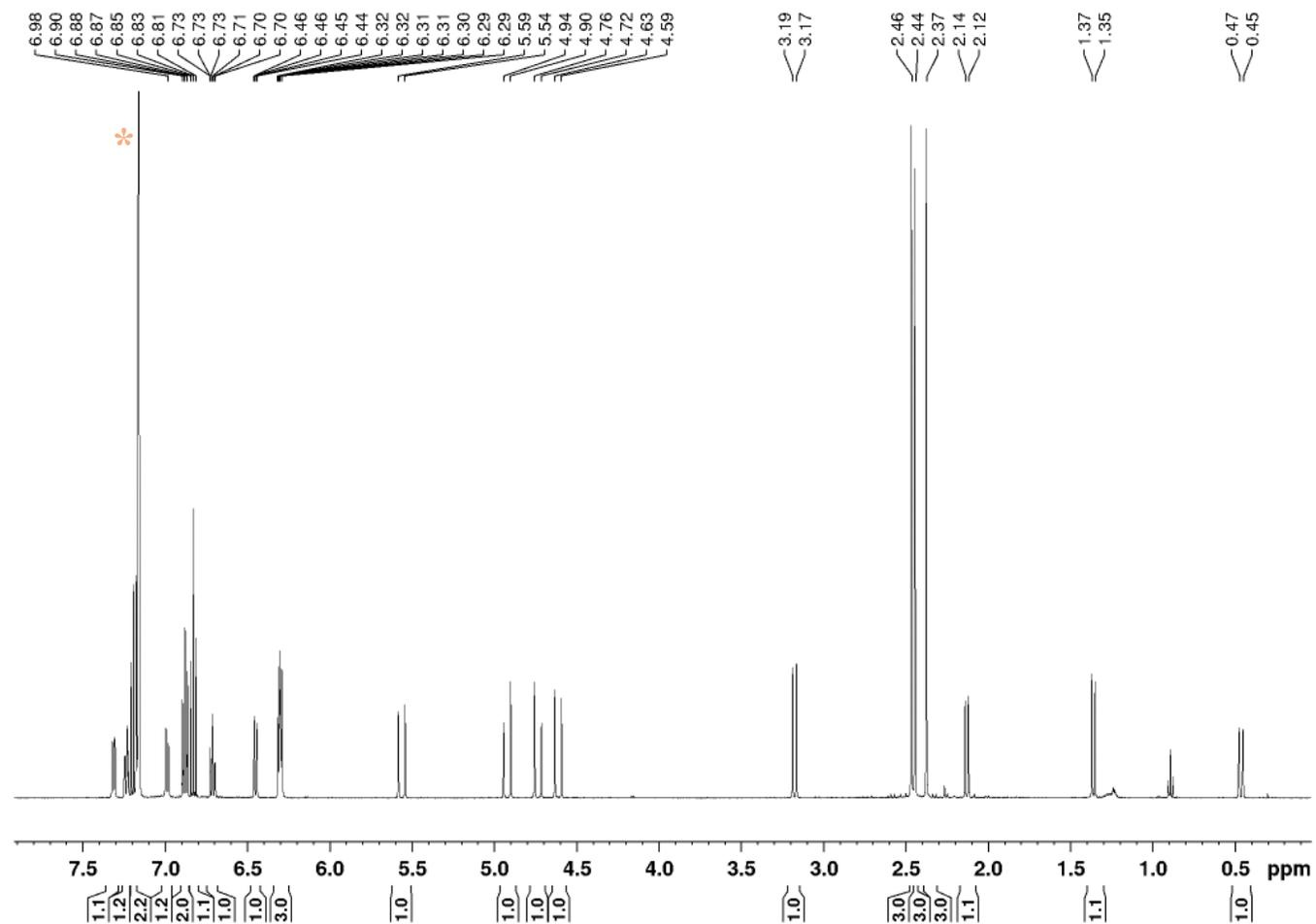


Figure S33. ¹H NMR spectrum of MePDA-HTi(CH₂Ph) in benzene-*d*₆ at 300 K. The resonance marked with a * belongs to benzene-*d*₆.

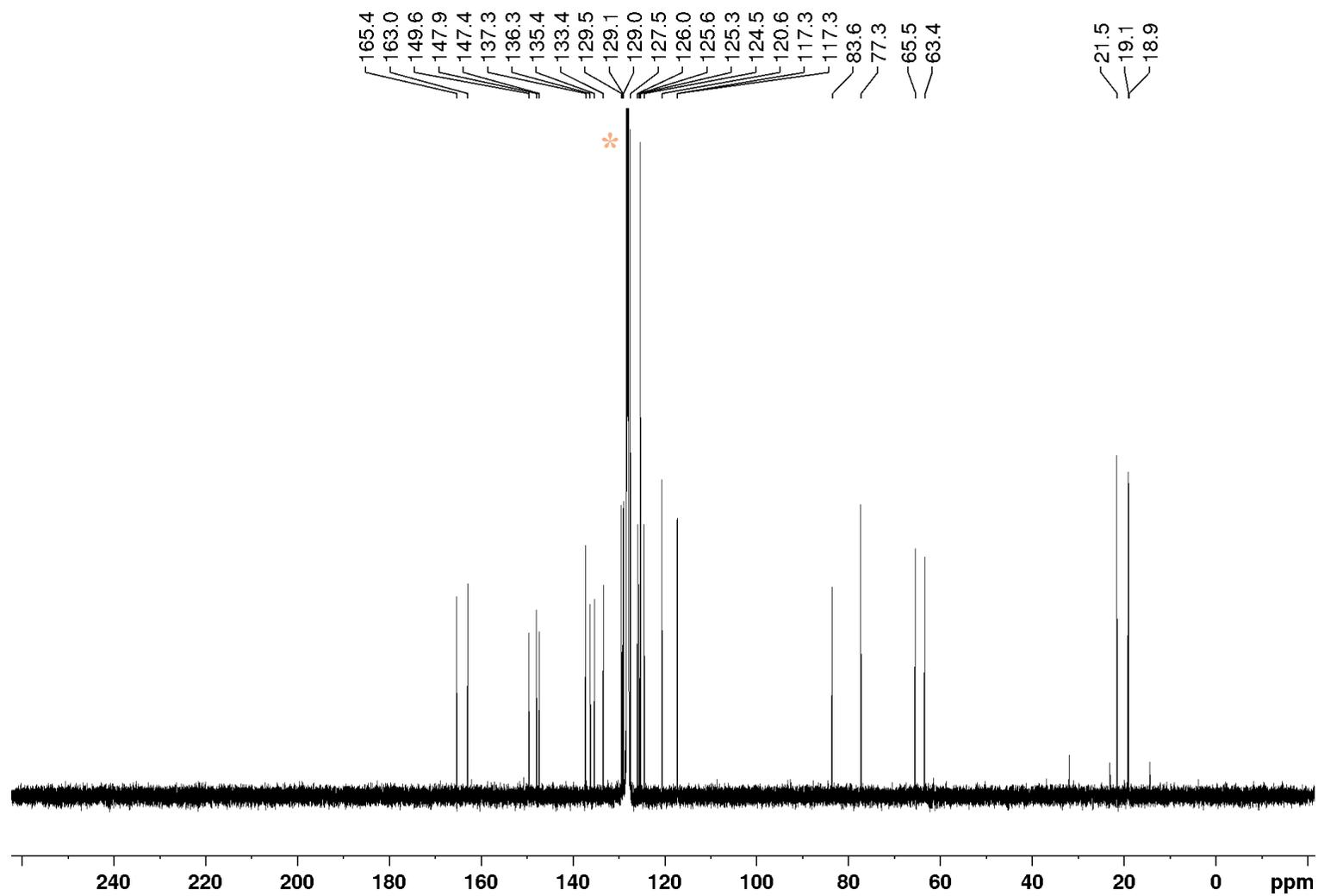


Figure S34. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{MePDA-}^{\text{HTi}}(\text{CH}_2\text{Ph})$ in benzene- d_6 at 300 K. The resonance marked with a * belongs to benzene- d_6 .

5. X-ray crystallographic details

The crystal data of all compounds was collected on a RIGAKU XTALAB SYNERGY-R diffractometer with a HPA area detector and multi-layer mirror monochromated Cu- $K\alpha$ radiation. Multi-scan absorption correction was applied to the data.^[3,4] The structures were solved with SHELXT,^[5] refined with the SHELXL^[6] using full matrix least squares minimization on F^2 ^[7] using Olex2 as the graphical interface.^[8] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in idealized positions and refined isotropically with a riding model.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

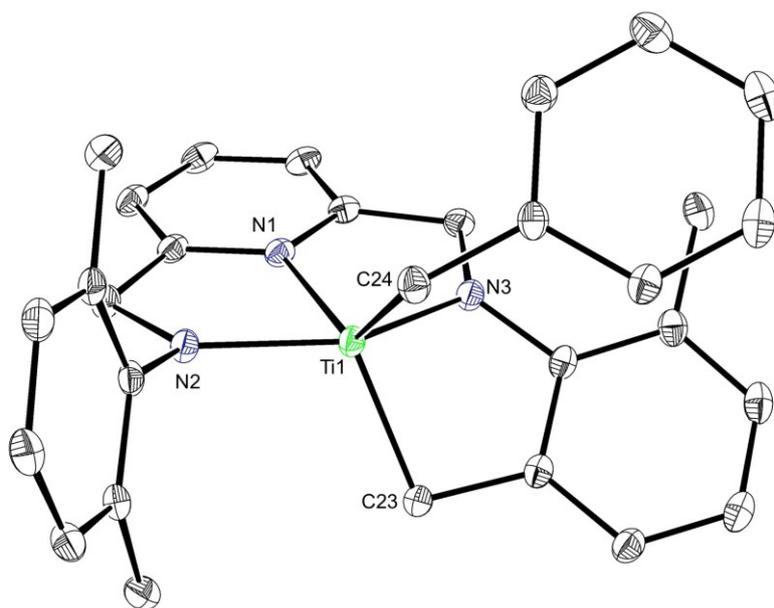


Figure S35. Molecular structure of $(\text{MePDA-H})\text{Ti}(\text{CH}_2\text{Ph})$ in the solid state with 30% probability ellipsoids and H atoms omitted for clarity.

Table S1. Crystallographic data and structure refinement for $\text{Me}^{\text{e}}\text{PDATi}(\text{CH}_2\text{Ph})_2$, ${}^{\text{iPr}}\text{PDATi}(\text{CH}_2\text{Ph})_2$, ${}^{\text{iPr}}\text{PDATi}(\text{C}_4\text{Me}_4)$ and $\text{Me}^{\text{e}}\text{PDA-}^{\text{H}}\text{Ti}(\text{CH}_2\text{Ph})$.

| | $\text{Me}^{\text{e}}\text{PDATi}(\text{CH}_2\text{Ph})_2$ | ${}^{\text{iPr}}\text{PDATi}(\text{CH}_2\text{Ph})_2$ | ${}^{\text{iPr}}\text{PDATi}(\text{C}_4\text{Me}_4)$ | $\text{Me}^{\text{e}}\text{PDA-}^{\text{H}}\text{Ti}(\text{CH}_2\text{Ph})$ |
|--|--|---|--|---|
| CCDC | 2356666 | 2356668 | 2356667 | 2368342 |
| Empirical formula | $\text{C}_{37}\text{H}_{39}\text{N}_3\text{Ti}$ | $\text{C}_{45}\text{H}_{55}\text{N}_3\text{Ti}$ | $\text{C}_{39}\text{H}_{53}\text{N}_3\text{Ti}$ | $\text{C}_{30}\text{H}_{31}\text{N}_3\text{Ti}$ |
| Formula weight | 573.61 | 685.82 | 611.74 | 481.48 |
| Temperature/K | 100.01(10) | 99.98(10) | 100.01(11) | 100.4(9) |
| Crystal system | orthorhombic | triclinic | triclinic | monoclinic |
| Space group | $Pbca$ | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ |
| a/Å | 16.6089(2) | 10.13950(10) | 11.0602(2) | 11.5575(2) |
| b/Å | 14.6227(2) | 12.81710(10) | 12.0620(2) | 17.8865(3) |
| c/Å | 24.9167(3) | 16.65920(10) | 14.3315(3) | 11.9883(2) |
| $\alpha/^\circ$ | 90 | 71.4210(10) | 77.339(2) | 90 |
| $\beta/^\circ$ | 90 | 85.3130(10) | 77.207(2) | 103.6090(10) |
| $\gamma/^\circ$ | 90 | 66.8060(10) | 70.6190(10) | 90 |
| Volume/Å ³ | 6051.44(13) | 1883.94(3) | 1736.62(6) | 2408.68(7) |
| Z | 8 | 2 | 2 | 4 |
| $\rho_{\text{calc}}/\text{cm}^3$ | 1.259 | 1.209 | 1.170 | 1.328 |
| μ/mm^{-1} | 2.614 | 2.176 | 2.299 | 3.178 |
| F(000) | 2432.0 | 736.0 | 660.0 | 1016.0 |
| Crystal size/mm ³ | 0.159 × 0.104 × 0.031 | 0.152 × 0.087 × 0.033 | 0.229 × 0.139 × 0.091 | 0.175 × 0.057 × 0.018 |
| Radiation | Cu K α ($\lambda = 1.54184$) | Cu K α ($\lambda = 1.54184$) | Cu K α ($\lambda = 1.54184$) | Cu K α ($\lambda = 1.54184$) |
| 2 θ range for data collection/ $^\circ$ | 7.096 to 150.154 | 5.604 to 149.162 | 6.406 to 149.942 | 7.87 to 148.34 |
| Index ranges | -20 ≤ h ≤ 20, -17 ≤ k ≤ 17, -31 ≤ l ≤ 26 | -12 ≤ h ≤ 11, -15 ≤ k ≤ 15, -20 ≤ l ≤ 19 | -13 ≤ h ≤ 13, -13 ≤ k ≤ 14, -17 ≤ l ≤ 17 | -14 ≤ h ≤ 12, -22 ≤ k ≤ 22, -13 ≤ l ≤ 14 |
| Reflections collected | 30986 | 34556 | 41332 | 25101 |
| Independent reflections | 5919 0.0280, [R _{int} = 0.0227] | 7378 0.0317, [R _{int} = 0.0192] | 6859 0.0252, [R _{int} = 0.0128] | 4851 [R _{int} = 0.0332, R _{sigma} = 0.0278] |
| Data/restraints/parameters | 5919/0/374 | 7378/0/450 | 6859/0/400 | 4851/0/310 |
| Goodness-of-fit on F ² | 1.085 | 1.094 | 1.097 | 1.135 |
| Final R indexes [I >= 2 σ (I)] | R ₁ = 0.0386, wR ₂ = 0.1062 | R ₁ = 0.0343, wR ₂ = 0.0940 | R ₁ = 0.0287, wR ₂ = 0.0803 | R ₁ = 0.0419, wR ₂ = 0.1184 |
| Final R indexes [all data] | R ₁ = 0.0458, wR ₂ = 0.1103 | R ₁ = 0.0358, wR ₂ = 0.0949 | R ₁ = 0.0290, wR ₂ = 0.0805 | R ₁ = 0.0468, wR ₂ = 0.1208 |
| Largest diff. peak/hole / e Å ⁻³ | 0.37/-0.45 | 0.36/-0.39 | 0.32/-0.32 | 0.37/-0.59 |

6. EPR spectroscopy

EPR measurements at X-band (9.39 GHz) were carried out using a Bruker ELEXSYS E580 CW EPR spectrometer.

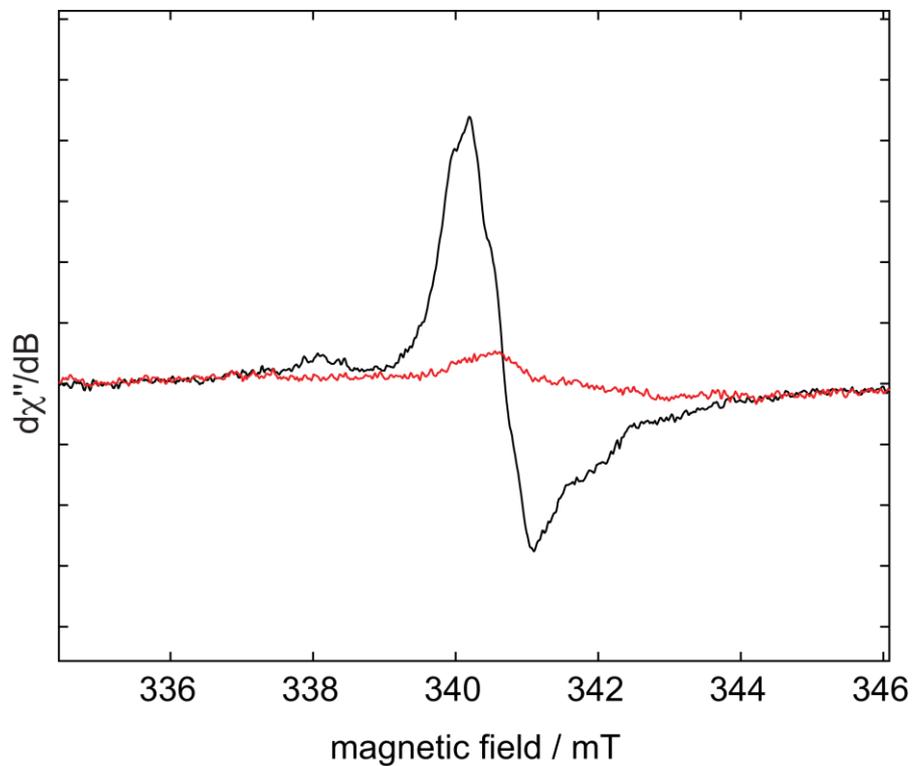


Figure S36. Experimental X-band EPR spectra of the reaction of the reaction of $i\text{PrPDATi}(\text{CH}_2\text{Ph})_2$ with 2-butyne (20 equiv.) (black) in toluene and the starting material $i\text{PrPDATi}(\text{CH}_2\text{Ph})_2$ (red) in toluene solution at room temperature. The black signal is centered around an isotropic g -factor of 1.968.

7. References

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